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Hydrochalcogenation of activated olefines. Synthesis of functionalized dialkylchalcogenides

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ABSTRACT

Alkanethiols, selenols and tellurols are generated *in situ* by reaction of elemental sulfur, selenium and tellurium with commercial alkyllithiums, followed by reaction with deoxygenated water. The alkanechalcogenols react *in situ* with activated olefins in a Michael-type addition reaction.

1. Introduction

Organic compounds of sulfur [1], selenium [2] and tellurium [3] present useful synthetic applications. Notwithstanding their synthetic potential, the organic compounds of these elements, specially those containing selenium and tellurium, are avoided by the synthetic organic chemists. The bad reputation of these elements many times arises from comments found in the literature concerning the bad smell of the organic chalcogen compounds. A long time concern of our laboratory is the development of experimental protocols which avoid the manipulation of bad smelling organochalcogen compounds [4]. We could conclude that some of the comments on the bad smell of such compounds are effectively true, but only for the low molecular weight representatives of specific classes of the organochalcogen compounds. Once incorporated into a more complex structure, the bad smell of the organochalcogen compound varnishes or disappears, giving rise to products which present smell not more unpleasant than most of the chemicals found in an organic synthesis laboratory. Among the very bad smelling organochalcogen compounds of large synthetic use are the alkanethiols and selenols and low weight non-functionalized dialkylditellurides, precursors of metal alkanetellurolates and alkanetellurols. In the last years our laboratory has been devoted to develop friendly conditions to generate and use these reagents *in situ*, so avoiding their manipulation in the laboratory atmosphere. We found that most of the products resulting from the interaction of alkanethiols, –selenols and –tellurols (tellurolates) with organic substrates are easily isolated as non-bad smelling synthetic intermediates. In this paper we give a full account of the scope and limitations of the *in situ* generation and use of low molecular weight alkanethiols, –selenols and –tellurols in Michael-type addition reactions to electron-deficient olefins.

2. Results and discussion

The reaction of elemental sulfur with alkyllithiums is a long known method to prepare thiols [5]. However, nowadays this reaction is rarely used to prepare this class of organosulfur compounds. In this work we observed that elemental sulfur suspended in THF reacts rapidly with ^{n}butyllithium giving initially an orange solution, which becomes limpid and colorless after reaction with stoichiometric amount of ^{n}butyllithium. The initially observed orange color is probably due to the initial formation of lithium alkylpolysulfides [6], which are transformed into the desired colorless lithium alkanethiolate by addition of the stoichiometric amount of ^{n}butyllithium. Addition of 2-cyclohexen-1-one (**1**) to this solution leads to the formation of 3-(butylthio)cyclohexanone (**2**) in 50% isolated yield. However, if deoxygenated water, obtained by bubbling deoxygenated nitrogen under sonication, is added to

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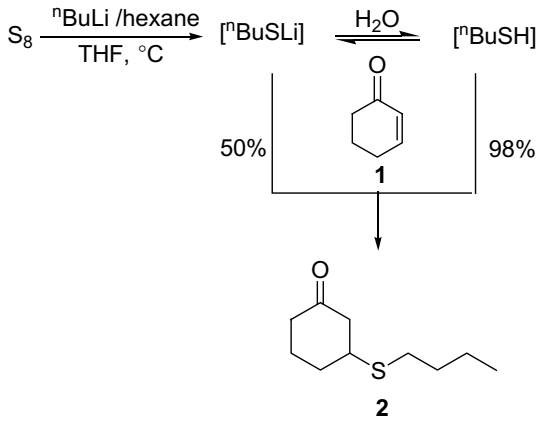
the lithium ^{n}butanethiolate solution prior to the addition of **1**, the yield of **2** rises to 98% isolated yield. We can presume that in the presence of water an equilibrium is established leading to an alkanethiol in the reaction medium, which reacts with the enone to give a Michael-type addition reaction to the α,β-unsaturated system (Scheme 1).

In this way, it was demonstrated that the presence of water in the reaction medium is mandatory for the success of the 1,4-addition reaction. To determine the scope and limitations of the methodology, other α,β-unsaturated compounds were allowed to react with the ^{n}BuSLi/ H_2O system. The results are summarized in Table 1.

As can be observed, unhindered enones give excellent yields of the Michael adducts (Table 1, entries 4, 21 and 24). Enones with some degree of steric hindrance give less satisfactory yields (Table 1, entries 26 and 27). The yields are however, still comparable with those obtained for similar compounds prepared by Michael-type reactions of alkanethiols using other sulfenilation methods [7]. Unsaturated nitrile (Table 1, entry 7) and ester (Table 1, entry 12) also gave good yields of the Michael adduct. Unsaturated aldehydes (Table 1, entries 1 and 3) also reacted, but the product had to be reduced *in situ* with sodium borohydride in view of the instability of the resulting 3-butylthioaldehyde. The resulting alcohols were isolated in 50% yield. Finally, the sulfenilation of ethyl propiolate (Table 1, entry 28) gave the corresponding *Z*-vinylic sulfide in 80% yield.

It is worth mentioning that during all the operations described above, the peculiar bad smell of ^{n}butanethiol was not detected. Another fact to be mentioned is that no additive was necessary to promote this Michael-type addition. In recent years a number of papers were published on the addition of alkanethiols to electron-deficient olefins [7]. In all cases, the alkanethiols were used in combination with other agents, which in some cases are expensive or present acidic or basic character. In all papers published on this subject, the isolated alkanethiol was used as the nucleophilic starting material. As far as we know, there is just one recent paper on the *in situ* generation of the lithium butanethiolate from butyllithium and sulfur in a subsequent step [5b,8].

Contrary to the scarcity of synthetic methods involving the reaction of an alkyllithium and sulfur, the reaction of alkyllithiums with selenium is widely used to generate lithium alkaneselenolates which are used in further reactions [9]. However, when alkaneselenols are needed, the isolated compounds are used, which are indeed very unpleasant compounds to work with [10]. In this work we employed the same reaction sequence shown in Scheme 1 to generate alkaneselenols *in situ*, which reacted with activated olefins leading to the Michael-type addition products in good yields (Scheme 2 and Table 1).



Scheme 1. Hydrosulfenylation of activated olefins.

When the ^{n}butyllithium solution is added to a suspension of gray elemental selenium in tetrahydrofuran the reaction mixture becomes red. After the addition of the stoichiometric amount of the ^{n}butyllithium the red color fades giving rise to a pale yellow solution. The initially observed red color probably is due to the formation of alkanepolyselenide anions [11] and the final pale yellow color corresponds to the lithium alkaneselenolate. Addition of deoxygenated water to the lithium alkaneselenolate leads to an equilibration responsible for the presence of the alkaneselenol in the reaction mixture (Scheme 2).

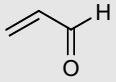
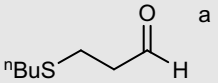
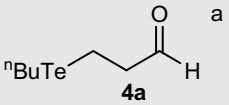
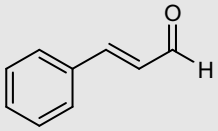
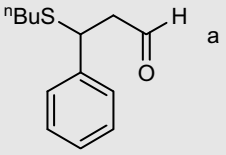
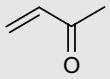
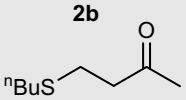
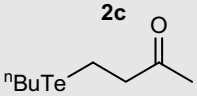
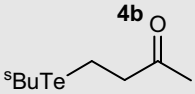
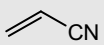
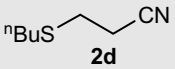
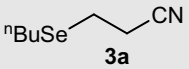
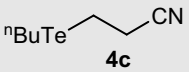
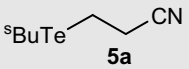
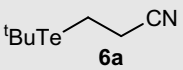
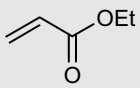
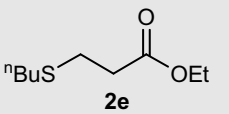
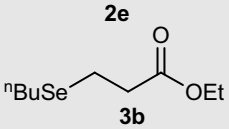
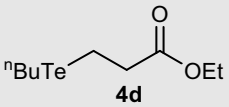
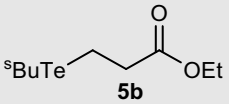
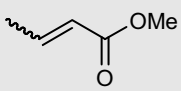
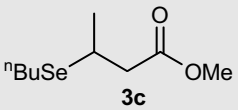
By using the present method, the 1,4-addition products were obtained in good yields (Table 1) with no need to manipulate the bad smelling alkaneselenol and, as in the case of the ^{n}butanethiol 1,4-addition described before, no bad smell was detected during the addition reaction of the ^{n}butaneselenol to the α,β-unsaturated system.

Organotellurols are too unstable to be isolated [12]. It is presumed that these compounds are formed *in situ* by reduction of diorganoditellurides with sodium borohydride. However, no evidences for the formation of such species were presented to date [12]. Some time ago, the reaction of alkyllithiums with elemental tellurium to generate alkanetellurolates has been synthetically explored [3b,13]. We applied this procedure to perform the hydrotelluration of alkynes under non-reducing conditions [14]. This method avoids the use of the bad smelling dibutylditelluride as starting material. In this work, a number of activated olefins were submitted to the hydrotelluration reaction giving functionalized alkanetellurides in good yields. ^{n}Butyl, ^{s}butyl and ^{t}butyllithium were used to generate the lithium alkanetellurolates (Scheme 3). We found that both deoxygenated water or ethanol can be used as the proton source in these 1,4-addition reactions. As in the preceding cases the chalcogen is rapidly consumed by addition of the alkyllithium to the suspension of elemental tellurium in THF at 0 °C. Initially a purple solution is formed. The purple color probably arises from the lithium alkanepolytellurides [11] initially present, which equilibrate with the alkyllithium leading to the lithium alkanetellurolate. The color fades as the stoichiometric amount of the added alkyllithium is reached. Addition of the proton source followed by the activated olefin gives the 1,4-addition product in good yield (Table 1). It is worth to mention that the water or ethanol used as the proton source must be carefully deoxygenated by sonication while a stream of deoxygenated nitrogen is bubbled into the vial containing the solvent. The optimal amount of water was found to be 2.5 times the amount of the lithium alkylchalcogenate employed. Larger amounts lead to a decrease in the reaction yield. As in the preceding cases, no bad smell associated with low molecular weight dialkylditellurides was detected during the reaction or the work-up.

The obtained products constitute a scarcely studied class of organic tellurium compounds, in view of the comments on the bad smell, and the light and air instability of dialkyltellurides found in the literature. In view of this, a more complete study on the 1,4-addition of alkanetellurolates to enones was performed as a method to prepare functionalized dialkyltellurides (Scheme 3 and Table 1).

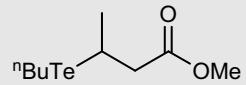
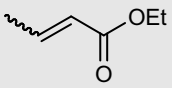
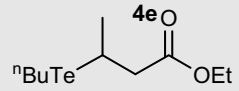
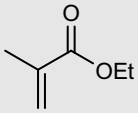
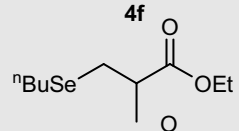
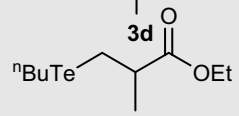
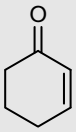
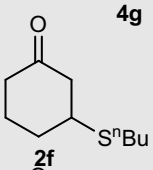
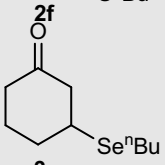
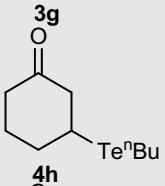
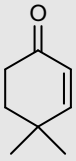
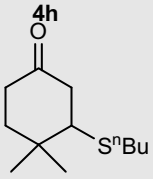
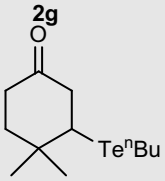
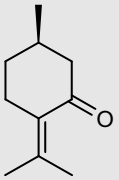
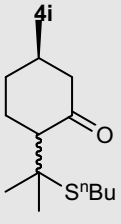
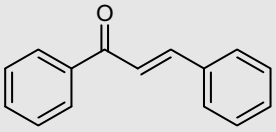
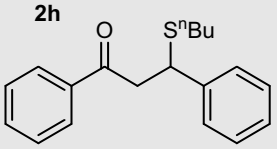
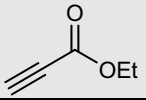
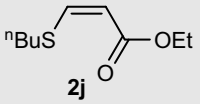
As in the case of the sulfides, surprisingly we observed that none of the prepared tellurides presented bad smell when in the pure form. When some of the prepared functionalized tellurides, specially those bearing a ^{s}Bu or ^{t}Bu group, were stored for some time, a bad smell resembling that of the corresponding dibutylditellurides was detected. We concluded that the reported bad smelling character of the samples of functionalized tellurides does not arise from the original by prepared tellurides, but rather from small amounts of dialkylditellurides resulting from the slow

Table 1
Dialkylchalcogenides prepared

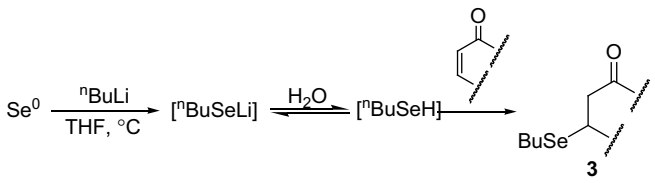
Entry	Electrophile	Product	Yield (%)
1		 **2a**	50
2		 **4a**	85
3		 **2b**	50
4		 **2c**	93
5		 **4b**	86
6		 **5a**	85
7		 **2d**	90
8		 **3a**	97
9		 **4c**	98
10		 **5a**	83
11		 **6a**	83
12		 **2e**	78
13		 **3b**	79
14		 **4d**	96
15		 **5b**	95
16		 **3c**	82

(*continued on next page*)

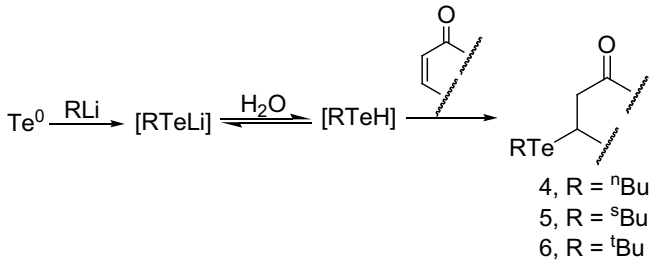
Table 1 (*continued*)

Entry	Electrophile	Product	Yield (%)
17		 **4e**	82
18		 **4f**	82
19		 **3d**	81
20		 **4g**	90
21		 **2f**	97
22		 **3g**	82
23		 **4h**	89
24		 **2g**	96
25		 **4i**	62
26		 **2h**	66
27		 **2i**	64
28		 **2j**	80

[a] **2a**, **2b** and **4a** were reduced in situ and the yields refer to the isolated alcohols **7a**, **7b** and **8**.



Scheme 2. Hydroselenation of activated olefins.



Scheme 3. Hydrotelluration of activated olefins.

decomposition of the functionalized dialkyltellurides. In this way, it is advisable to prepare the functionalized dialkyltellurides and use them immediately for further synthetic transformations.

β-Tellurocarbonyl compounds constitute a rather unexplored class of organotellurium compounds [15,16]. In view of this fact, we undertook a systematic investigation on their reactivity and found that β-telluroketones can be converted to the corresponding ketals [16,17] and telluroaldehydes, ketones and esters can be reduced to corresponding hydroxytellurides [18], which were resolved into enantiomers by enzymatic kinetic resolution [19]. All these tellurium containing compounds can be transformed into reactive organometallics, by Te/Li exchange [20], followed by transmetallation [18,21]. The resulting reactive organometallics were employed in the construction of useful carbon frameworks [17] and in the synthesis of insect pheromones [22,23].

3. Conclusion

β-Thio- [7] and β-selenocarbonyl [24] compounds are long known synthetic intermediates which are prepared by Michael-type addition reactions on α,β-unsaturated compounds with organothio- or organoselenium nucleophiles. β-Tellurocarbonyl compounds were only recently described [16] and synthetically explored, showing promising synthetic applications. The method described in this paper to prepare these classes of compounds is advantageous over the existing methods in view of its practicability and friendly experimental conditions employed.

4. Experimental

4.1. General considerations

The ^{1}H and ^{13}C spectra were recorded on either a Bruker DPX-300, Bruker DRX-500 or a Bruker AC-200 spectrometers using as internal standard tetramethylsilane and the central peak of $CDCl_3$ (77 ppm), respectively. The ^{125}Te NMR spectra were obtained in a Bruker DRX-500 spectrometer operating at 157.79 MHz using $CDCl_3$ as the solvent. The ^{125}Te chemical shifts refer to diphenylditelluride (δ = 420 ppm, 25 °C if dimethyltelluride is considered, δ = 0.0 ppm, 25 °C) as external standard. The ^{77}Se NMR spectra were obtained in a Bruker DRX-500 spectrometer operating at 95.338 MHz using $CDCl_3$ as the solvent. The ^{77}Se chemical shifts refer to diphenyldiselenide (δ = 463 ppm, 25 °C if dimethylselenide is considered, δ = 0.0 ppm, 25 °C) as external standard. Infrared spectra were recorded on a Bomem MB-100 spectrophotometer. Low resolution mass spectra were obtained on a Finnigan 4021 spectrometer or on a GC–MS Hewlett Packard 5988-8/5890 spectrometer, both operating at 70 eV. Elemental analyses were performed in a Perkin–Elmer CHNO analyzer and high resolution mass spectra were obtained on a Bruker Daltonics Micro TOF with time of flight analyzer. Column chromatography was carried out with Merck silica gel (230–400 mesh). Thin layer chromatographies (TLC) were performed on silica gel F-254 on aluminum. All solvents used were previously dried and distilled according to the usual methods. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone under N_2, immediately before use. Elemental sulfur, selenium and tellurium (200 mesh) were purchased from Aldrich. The remaining chemicals were obtained from commercial sources. All operations were carried out in dried glassware, under an inert atmosphere of dry and deoxygenated N_2. The IUPAC names were obtained using the ACD/Lab web service, version 3.5, at http://www.acdlabs.com/ilab and ChemDraw 9.0.

4.2. General procedures for the hydrochalcogenations reactions

4.2.1. General procedure for the hydrosulfenylation reaction [25]

A 50-mL, two-necked, round-bottomed flask was equipped with a magnetic stir bar, rubber septa and a glass adapter for a nitrogen inlet. This reaction flask was flame-dried twice under a positive nitrogen stream and cooled down to room temperature. Elemental sulfur (Aldrich, 0.20 g, 6.0 mmol) was added to the reaction flask followed by freshly distilled THF (10 mL). ^{n}Butyllithium (5.47 mL of a 1.17 mol/L solution in hexanes, 6.4 mmol) was added dropwise to the vigorously stirred S_8/THF mixture at 0 °C under nitrogen atmosphere. After the addition of the first drops of ^{n}butyllithium, the mixture turned into orange and by the end of the addition of the stoichiometric amount of ^{n}butyllithium, the powder was completely consumed and a pale yellow solution had been formed. Deoxygenated water (0.27 mL, 15.0 mmol) was then slowly added into the lithium butanethiolate solution. The resulting colorless solution was stirred for 10 min and the appropriate activated olefin or alkyne (6.0 mmol) was added in a portion and the solution was stirred for additional 30 min. After the reaction was complete, the mixture was quenched with 3 mL of water. The product was extracted 3 times with ethyl acetate. The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Column chromatography (20:1 hexane/ethyl acetate) of the crude oil on silica gel afforded a colorless oil.

4.2.2. General procedure for the hydroselenation of olefins [26]

In a two-necked 50 mL equipped as described above, was placed elemental selenium (0.315 g, 4 mmol) in dry THF (5 mL). To this suspension at room temperature was added *n*-butyllithium (3.08 mL of a 1.3 mol/L solution in hexane, 4 mmol). A deep red solution was formed as the initial drops of ^{n}butyllithium were added. By the end of the addition the reaction mixture became pale yellow. To this solution it was added water (0.18 mL, 10 mmol) previously deoxygenated under a N_2 flow and sonication. Then the appropriate olefin (4 mmol) was added at room temperature. The mixture was maintained under stirring for 1 h. The organic phase was washed with NH_4Cl solution (3 × 15 mL) and brine (3 × 15 mL) and then dried with magnesium sulfate. The solution was filtered and the solvent was evaporated. The residue was purified by silica gel column chromatography eluting first with hexane, and then with hexane/ethyl acetate (10:1).

4.2.3. General procedure for the hydrotelluration of olefins [26]

In a two-necked 50 mL flask equipped as described in this section. It was placed elemental tellurium (0.511 g, 4.0 mmol) in dry

THF (5 mL). To this suspension at room temperature it was added *n*, *s* or *t*-butyllithium (4.0 mmol, 1.0 equiv.). A deep purple solution was formed as the initial drops of the alkyllithium were added. By the end of the addition of the alkyllithium the reaction mixture became pale yellow. To this solution it was added water (0.18 mL, 10 mmol) previously deoxygenated under a N_2 flow and sonication. Then the appropriate olefin or alkyne (4.0 mmol) was added at room temperature. The mixture was maintained under stirring at room temperature for 1 h. The organic phase was washed with NH_4Cl solution (3 × 15 mL) and brine (3 × 15 mL) and then dried with $MgSO_4$. The solution was filtered and the solvent was evaporated. The residue was purified by silica gel column chromatography eluting first with hexane and then with hexane/ethyl acetate (10:1).

4-(Butylthio)butan-2-one (**2c**): (Registry Number: 69688-97-7), Yield, 0.89 g (93%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 0.91 (t, 7.5 Hz, 3H), 1.41 (sx, J = 7.5 Hz, 2H), 1.56 (qt, J = 7.5 Hz, 2H), 2.17 (s, 3H), 2.52 (t, J = 7.5 Hz, 2H), 2.73 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 206.9, 43.7, 32.1, 31.6, 30.0, 25.8, 21.9, 13.6.

4-(Butyltellanyl)butan-2-one (**4b**): (Registry Number: 444144-98-3), Yield, 0.88 g (86%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.4 Hz, 3H), 1.38 (sext, J = 7.4 Hz, 2H), 1.73 (q, J = 7.4 Hz, 2H), 2.15 (s, 3H), 2,69 (m, 4H), 3.03 (t, J = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 207.8, 46.4, 34.3, 29.8, 25.0, 13.3, 3.4, −7,0. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 279.6. LRMS: *m*/*z* (70 eV, relative intensity, %): 258 (7, M^+), 71 (40), 57 (24), 55 (26), 43 (100). IR (ZnSe, cm^{-1}): 2955, 2925, 2865, 1715. Anal. Calc.: C, 37.56; H, 6.30. Found: C, 37.32; H, 6.02%.

4-(sec-Butyltellanyl)butan-2-one (**5a**): Yield, 0.87 g (85%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.97 (t, J = 7.2 Hz, 3H), 1.63 (d, J = 7.2 Hz, 3H), 1.67 (quint, J = 7.2 Hz, 2H), 2.15 (s, 3H), 2,73 (t_{ap}, J = 7.2 Hz, 2H), 3.03 (t, J = 7.2 Hz, 2H), 3.20 (sext, J = 7.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 207.9, 46.5, 33.0, 29.8, 24.3, 21.0, 13.9, 7.3. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 432.8. LRMS: *m*/*z* (70 eV, relative intensity, %): 258 (10, M^+), 71 (42), 57 (36), 55 (21), 43 (100). IR (ZnSe, cm^{-1}): 2960, 2926, 2913, 2870, 1718, 1452, 1375, 1180, 1138, 1127, 996. Anal. Calc.: C, 37.55; H, 6.25. Found: C, 37.28; H, 6.41%.

3-(Butylthio)propanenitrile (**2d**): (Registry Number: 26901-99-5), Yield, 0.77 g (90%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 4.3 Hz, 3H), 1.42 (sx, J = 4.3 Hz, 2H), 1.58 (qt, J = 4.23 Hz, 2H), 2.58–2.61 (m, 2H), 2.64 (t, J = 4.3 Hz, 2H), 2.78–2.81 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 118.4, 31.9, 31.5, 27.6, 21.8, 18.9, 13.6. IR (cm^{-1}) 2959, 2930, 2869, 2249, 1461, 1423.

3-(Butylselanyl)propionitrile (**3a**): (Registry Number: 1017904-13-0), Yield, 0.74 g (97%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 0.93 (t, J = 7.3 Hz, 3H), 1.41 (sext, J = 7.3 Hz, 2H), 1.66 (quint, J = 7.3 Hz, 2H), 2.68 (t, J = 7.3 Hz, 2H), 2.71–2.74 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 118.8, 32.4, 24.5, 22.8, 19.7, 17.1, 13.5. ^{77}Se RMN (95 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 19.7. LRMS: *m*/*z* (70 eV, relative intensity, %): 191 (26, M^+), 189 (13), 57 (79), 41 (100). IR (ZnSe, cm^{-1}): 2959, 2930, 2868, 2249, 1461, 1421, 1263, 1200. Anal. Calc.: C, 44.22; H, 6.89; N, 7.37. Found: C, 44.35; H, 6.72; N, 7.38%.

3-(Butyltellanyl)propanenitrile (**4c**): (Registry Number: 444145-02-2), Yield, 0.93 g (98%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 0.93 (t, J = 7.4 Hz, 3H), 1.39 (sext, J = 7.4 Hz, 2H), 1.76 (quint, J = 7.4 Hz, 2H), 2.79 (t, J = 7.4 Hz, 2H), 2.80 (t, J = 7.2 Hz, 2H), 2.90 (t, J = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 120.0, 34.1, 24.9, 21.4, 13.3, 4.2, −6.8. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhTe)_2$) δ 317.2. LRMS: *m*/*z* (70 eV, relative intensity, %): 241 (5, M^+), 239 (4), 149 (15), 57 (33), 32 (100). IR (ZnSe, cm^{-1}): 2957, 2927, 2870, 2247, 1461, 1421, 1248, 1160. Anal. Calc.: C, 32.21; H, 5.49; N, 5.87. Found: C, 35.39; H, 5.37; N, 5.74%.

3-(sec-Butyltellanyl)propanenitrile (**5a**): Yield, 0.79 g (83%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.97 (t, J = 7.3 Hz, 3H), 1.64 (d, J = 7.3 Hz, 3H), 1.68–1.76 (dqt, J = 7.3 Hz, J = 6.9 Hz, 2H), 2.77–2.82 (m, 2H), 2.86–2.92 (m, 2H), 3.32 (sx, J = 6.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 120.0, 32.9, 24.2, 22.2, 21.5, 13.8, −7.1. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhTe)_2$) δ 465.9. LRMS: *m*/*z* (70 eV, relative intensity, %): 241 (5, M^+), 185 (11), 183 (10), 156 (9), 57 (65), 41 (100). IR (ZnSe, cm^{-1}): 2960, 2923, 2870, 2247, 1455, 1420, 1376, 1250, 1186, 1164, 1133. Anal. Calc.: C, 35.21; H, 5.49; N, 5.87. Found: C, 35.28; H, 5.35; N, 5.84%.

3-(*tert*-Butyltellanyl)propanenitrile (**6a**): Yield, 0.79 g (83%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 1.66 (s, 9H), 2.89 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 120.0, 67.8, 35.7, 21.1, −5.4. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhTe)_2$) δ 684.7. LRMS: *m*/*z* (70 eV, relative intensity, %): 241 (2, M^+), 239 (2), 58 (5), 57 (100), 41 (48). IR (ZnSe, cm^{-1}): 2949, 2857, 2247, 1461, 1420, 1365, 1146, 1018, 907, 879. Anal. Calc.: C, 35.21; H, 5.49; N, 5.87. Found: C, 35.20; H, 5.17; N, 5.77%.

Ethyl 3-(butylthio)propanoate (**2e**): (Registry Number: 68298-26-0), Yield, 0.89 g (78%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 0.91 (t, 7.5 Hz, 3H), 1.27 (t, 7.5 Hz, 3H), 1.40 (sx, J = 7.5 Hz, 2H), 1.57 (qt, J = 7.5 Hz, 2H), 2.53 (t, 7.5 Hz, 2H), 2.59 (t, 7.5 Hz, 2H), 2.78 (t, 7.5 Hz, 2H), 4.15 (q, J = 7.5 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 171.7, 60.3, 34.7, 31.6, 31.4, 26.8, 21.7, 14.0, 13.4.

Ethyl 3-(butylselanyl)propanoate (**3b**): (Registry Number: 444145-05-5), Yield, 0.75 g (79%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.3 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.40 (sext, J = 7.3 Hz, 2H), 1.65 (quint, J = 7.3 Hz, 2H), 2.59 (t, J = 7.4 Hz, 2H), 2.72 (A2B2, $\Delta\nu/J$ 1,5 Hz, J = 1.2 Hz, 4H), 4.14 (q, J = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 171.7, 60.1, 35.4, 32.2, 23.5, 22.5, 16.9, 13.8, 13.1. ^{77}Se RMN (95 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 180.1. LRMS: *m*/*z* (70 eV, relative intensity, %): 238 (27, M^+), 236 (13), 182 (30), 180 (15), 165 (11), 137 (11), 135 (60), 55 (100). IR (ZnSe, cm^{-1}): 2959, 2930, 2870, 1736, 1372, 1341, 1222, 1163, 1134, 1038. Anal. Calc.: C, 45.53; H, 7.58. Found: C, 45.38; H, 7.39%.

Ethyl 3-(butyltellanyl)propanoate (**4d**): (Registry Number: 444144-91-6), Yield, 1.10 g (96%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.4 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.38 (sext, J = 7.4 Hz, 2H), 1.74 (quint, J = 7.4 Hz, 2H), 2.68 (t, J = 7.4 Hz, 2H), 2.83 (A2B2, $\Delta\nu/J$ 1,1 Hz, 4H), 4.15 (q, J = 7.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 173.1, 60.6, 37.5, 34.3, 25.1, 14.3, 13.4, 3.3, −5.8. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhTe)_2$) δ 279.2. LRMS: *m*/*z* (70 eV, relative intensity, %): 288 (35), 286 (30, M^+), 231 (28), 229 (26), 186 (29), 184 (28), 57 (94), 55 (100). IR (ZnSe, cm^{-1}): 2958, 2928, 2870, 1735. Anal. Calc.: C, 37.82; H, 6.35. Found: C, 37.69; H, 6.35%.

Ethyl 3-(sec-butyltellanyl)propanoate (**5b**): (Registry Number: 444144-04-4), Yield, 1.08 g (95%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.98 (t, J = 7.3 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.64 (d, J = 7.3 Hz, 3H), 1.68 (quint, J = 7.3 Hz, 2H), 2.77–2.90 (m, 4H), 3.20 (sext, J = 7.3 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 173.0, 60.5, 37.5, 32.9, 24.3, 20.8, 14.1, 13.8, −6.1. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhTe)_2$) δ 433.3. LRMS: *m*/*z* (70 eV, relative intensity, %): 288 (16, M^+), 286 (15), 232 (17), 230 (16), 186 (33), 184 (31), 158 (26), 156 (24), 57 (96), 55 (60), 41 (100). IR (ZnSe, cm^{-1}): 2961, 1735, 1454, 1372, 1200, 1133, 1038. Anal. Calc.: C, 37.82; H, 6.35. Found: C, 38.09; H, 6.27%.

Methyl 3-(butylselanyl)butanoate (**3c**): Yield, 0.78 g (82%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.89 (t, J = 7.2 Hz, 3H), 1.38 (sext, J = 7.2 Hz, 2H), 1.44 (d, J = 7.2 Hz, 3H), 1.63 (quint, J = 7.2 Hz, 2H), 2.53–2.73 (abx, J_{ax} = 6.6 Hz, J_{bx} = 8.2 Hz, J_{ab} = 15.4 Hz, 4H), 3.30 (sext, J = 7.2 Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 172.3, 51.8, 43.5, 32.9, 29.3, 23.3, 23.2, 22.8, 13.8. ^{77}Se RMN (95 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 285.3. LRMS: *m*/*z* (70 eV, relative intensity, %): 238 (15, M^+), 236 (8), 101 (31), 69 (19), 59 (100), 57 (20), 55 (25). IR (ZnSe, cm^{-1}): 2957, 2928, 2868, 1740, 1210, 774. Anal. Calc.: C, 45.57; H, 7.65; Found: C, 45.58; H, 7.51%.

Methyl 3-(butyltellanyl)butanoate (**4e**): (Registry Number: 444144-94-9), Yield, 0.94 g (82%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.4 Hz, 3H), 1.39 (sext, J = 7.4 Hz, 2H), 1.66 (d, J = 7.2 Hz, 3H), 1.76 (q, J = 7.5 Hz, 2H), 2.71 (dt, J = 7.8 Hz, J = 15 Hz, 2H), 2.80 (abx, J_{ax} = 6.8 Hz, J_{bx} = 7.8 Hz, J_{ab} = 15.0 Hz, 2H), 3.49 (sext, J = 7.2 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 172.6, 51.6, 45.4, 34.4, 25.2, 24.9, 13.4, 9.2, 3.2. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhTe)_2$) δ 456.3. LRMS: m/z (70 eV, relative intensity, %): 288 (7, M^+), 286 (7), 101 (23), 69 (14), 59 (100), 57 (37), 55 (15). IR (ZnSe, cm^{-1}): 2956, 2926, 2870, 1738, 1203, 722. Anal. Calc.: C, 37.82; H, 6.35. Found: C, 37.73; H, 6.39%.

Ethyl 3-(butyltellanyl)butanoate (**4f**): (Registry Number: 444145-03-3), Yield, 0.98 g (82%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.4 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.39 (sext, J = 7.3 Hz, 2H), 1.66 (d, J = 7.2 Hz, 3H), 1.76 (q, J = 7.4 Hz, 2H), 2.71 (dt, J = 7.5 Hz, J = 2.7 Hz, 2H), 2.78 (abx, J_{ax} = 7.0 Hz, J_{bx} = 8.0 Hz, J_{ab} = 16.0 Hz, 2H), 3.49 (sext, J = 7.1 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 172.1, 60.5, 45.6, 34.4, 25.2, 24.9, 14.2, 13.4, 9.3, 3.1. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhTe)_2$) δ 455.6. LRMS: m/z (70 eV, relative intensity, %): 302 (11, M^+), 166 (11), 148 (67), 114 (16), 87 (43), 83 (18), 73 (56), 57 (100). IR (ZnSe, cm^{-1}): 2957, 2926, 2870, 1735, 1461, 1196, 1030. Anal. Calc.: C, 40.05; H, 6.72. Found: C, 40.12; H, 6.50%.

Ethyl 3-(butylselanyl)-2-methylpropanoate (**3d**): Yield, 0.81 g (81%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.91 (t, J = 7.3 Hz, 3H), 1.25 (d, J = 6.7 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.39 (sext, J = 7.3 Hz, 2H), 1.64 (quint, J = 7.4 Hz, 2H), 2.60 (m, 3H), 2.70 (sext, J = 6.7 Hz, 1H), 2.84 (dd, J = 6.7 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 175.2, 60.4, 40.9, 32.6, 26.7, 24.4, 22.9, 17.6, 14.1, 13.5. ^{77}Se RMN (95 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 153.3. LRMS: m/z (70 eV, relative intensity, %): 252 (18, M^+), 250 (9), 196 (8), 168 (11), 150 (21), 148 (11), 122 (24), 115 (23), 87 (33), 41 (100). IR (ZnSe, cm^{-1}): 2964, 2930, 2870, 1734. Anal. Calc.: C, 47.76; H, 7.96. Found: C, 47.97; H, 7.94%.

Ethyl 3-(butyltellanyl)-2-methylpropanoate (**4g**): (Registry Number: 444145-03-3), Yield, 1.08 g (90%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.3 Hz, 3H), 1.26 (dt, J = 7.2 Hz, 6H), 1.37 (sext, J = 7.2 Hz, 2H), 1.72 (quint, J = 7.4 Hz, 2H), 2.70 (m, 4H), 2.89 (m, 1H), 4.15 (q, J = 7.2 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 175.3, 60.4, 41.8, 34.1, 24.9, 19.2, 14.1, 13.3, 5.4, 3.5. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 221.1. LRMS: m/z (70 eV, relative intensity, %): 302 (19, M^+), 245 (20), 172 (19), 168 (11), 115 (16), 87 (33), 57 (70), 55 (47), 43 (22), 41 (100). IR (ZnSe, cm^{-1}): 2963, 2928, 1732, 1456, 1374, 1252, 1192, 1152, 1045, 1023. Anal. Calc.: C, 40.05; H, 6.67. Found: C, 39.89; H, 6.46%.

3-(Butylthio)cyclohexanone (**2f**): (Registry Number: 505062-31-7), Yield, 1.08 g (97%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 0.91 (t, J = 7.0 Hz, 3H), 1.40 (sext, J = 7.5 Hz, 2H), 1.56 (qt, J = 7.5 Hz, 2H), 1.69–1.75 (m, 2H), 2.10–2.17 (m, 2H), 2.28–2.40 (m, 3H), 2.55 (t, J = 7.5 Hz, 2H), 2.68–2.73 (m, 1H), 3.03–3.08 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 208.8, 48.1, 42.6, 40.8, 31.6, 31.5, 30.1, 24.1, 21.9, 13.5.

3-(Butylselanyl)cyclohexanone (**3g**): (Registry Number: 444145-06-6), Yield, 0.76g (82%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.91 (t, J = 7.2 Hz, 3H), 1.39 (sext, J = 7.2 Hz, 2H), 1.64 (quint, J = 7.2 Hz, 2H), 1.71–1.88 (m, 2H), 2.07–2.26 (m, 2H), 2.32–2.40 (m, 2H), 2.49 (ddd, J = 1.1 Hz, J = 10.7 Hz, J = 14.3 Hz, 1H), 2.61 (m, 2H), 2.79 (ddt, J = 1.3 Hz, J = 4.6 Hz, J = 14.3 Hz, 1H), 3.16–3.38 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 208.8, 49.3, 40.9, 35.7, 32.7, 32.5, 25.4, 23.1, 23.0, 13.5. ^{77}Se RMN (95 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 276.5. LRMS: m/z (70 eV, relative intensity, %): 234 (12, M^+), 97 (58), 96 (6), 69 (100), 68 (13), 57 (10), 55 (65), 41 (99). IR (ZnSe, cm^{-1}): 2957, 2931, 2868, 1713, 1448, 1421, 1312, 1276, 1220. Anal. Calc.: C, 51.50; H, 7.78. Found: C, 51.32; H, 7.60%.

3-(Butyltellanyl)cyclohexanone (**4h**): (Registry Number: 444144-99-4), Yield, 1.00 g (89%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.3 Hz, 3H), 1.38 (sext, J = 7.3 Hz, 2H), 1.77 (quint, J = 7.4 Hz, 2H), 1.77 (m, 1H), 1.93 (m, 1H), 2.07 (m, 1H), 2.29 (m, 1H), 2.39 (m, 1H), 2.63 (dd, J = 1.6 Hz, J = 2.6 Hz, 1H), 2.71 (t, J = 7.4 Hz, 2H), 2.90 (dt, J = 1.6 Hz, 1H), 3.46 (tt, J = 3.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 208.9, 51.3, 41.0, 34.7, 34.3, 27.7, 25.1, 16.1, 13.3, 3.3. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 441.7. LRMS: m/z (70 eV, relative intensity, %): 284 (1, M^+), 97 (13), 96 (16), 69 (33), 68 (72), 57 (52), 55 (36), 41 (100). IR (ZnSe, cm^{-1}): 2955, 2926, 2869, 2258, 1710. Anal. Calc.: C, 42.61; H, 6.44. Found: C, 42.32; H, 6.51%.

3-(Butylthio)-4,4-dimethylcyclohexanone (**2g**): (Registry Number: 50987-48-9), Yield, 1.23 g (96%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 0.90 (t, J = 7.0 Hz, 3H), 1.12 (s, 3H), 1.20 (s, 3H), 1.40 (dsx, J = 7.0 Hz, 3.0 Hz, 2H), 1.51–1.64 (m, 3H), 1.86 (ddd, J = 14 Hz, 6 Hz, 4 Hz, 1H), 2.27–2.32 (m, 1H) 2.40–2.47 (m, 1H) 2.50–2.56 (m, 3H), 2.67–2.71 (m, 2H). ^{13}C NMR: (125 MHz, $CDCl_3$, ppm) δ 208.8, 53.2, 45.6, 38.4, 37.5, 34.2, 31.6, 31.5, 28.6, 21.6, 20.3, 13.3.

3-(Butyltellanyl)-4,4-dimethylcyclohexanone (**4i**): (Registry Number: 444145-00-0), Yield, 0.77 g (62%). ^{1}H NMR: (300 MHz, $CDCl_3$, ppm) δ 0.91 (t, J = 7.3 Hz, 3H), 1.17 (s, 2H), 1.20 (s, 3H), 1.37 (sext, J = 7.3 Hz, 2H), 1.72 (quint, J = 7.3 Hz, 2H), 1.77 (m, 1H), 1.97–2.05 (m, 1H), 2.30–2.39 (m, 1H), 2.43–2.56 (m, 1H), 2.66 (td, J = 1.7 Hz, J = 7.3 Hz, 2H), 2.80–2.97 (m, 2H), 3.23 (dd, J = 5.2 Hz, J = 12.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 209.8, 49.2, 38.2, 38.0, 35.2, 34.5, 34.1, 31.7, 25.4, 23.5, 13.6, 4.2. ^{125}Te RMN (157 MHz, $CDCl_3$, ppm, $(PhSe)_2$) δ 361.3. LRMS: m/z (70 eV, relative intensity, %): 312 (6, M^+), 125 (34), 96 (11), 83 (39), 69 (44), 57 (25), 55 (100), 41 (61). IR (ZnSe, cm^{-1}): 2956, 2924, 2864, 1713. Anal. Calc.: C, 46.51; H, 7.16. Found: C, 46.49; H, 7.21%.

(5R)-2-(2-(Butylthio)propan-2-yl)-5-methylcyclohexanone (**2h**): (Registry Number: 1017904-05-0), Yield, 0.96 g (66%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.86–0.96 (m, 3H), 0.98–1.02 (m, 3H), 1.32–1.59 (m, 10H), 1.77–2.08 (m, 5H), 2.26–2.32 (m, 1H), 2.40–2.60 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 210.4, 57.8, 52.2, 46.6, 36.5, 34.5, 31.3, 29.4, 27.7, 27.1, 23.7, 22.1, 22.0, 13.5. IR (cm^{-1}) 1121, 1456, 1711, 2871, 2928, 2957. HRMS calc. for $[C_{14}H_{26}OS+Na]^+$: 247.1132. Found: 247.1128%.

3-(Butylthio)-1,3-diphenylpronan-1-one (**2i**): (Registry Number: 21205-11-8), Yield, 1.14 g (64%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 0.81 (t, J = 7.2 Hz, 3H), 1.25–1.35 (m, 2H), 1.42–1.52 (m, 2H), 2.24–2.41 (m, 2H), 3.52 (d, J = 7.2Hz, 2H), 4.55 (t, J = 7.2 Hz, 1H), 7.15–7.52 (m, 8H), 7.87–7.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 196.7, 142.0, 136.7, 132.9, 128.4, 128.3, 127.9, 127.7, 127.0, 45.3, 44.2, 31.1, 31.0, 21.7, 13.4. IR (cm^{-1}) 2952, 2922, 1961, 1890, 1815, 1769, 1678, 1229.

(*Z*)-ethyl-3-(butylthio)acrylate (**2j**):(Registry Number: 875822-74-5), Yield, 0.90 g (80%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 0.93 (t, J = 7.5 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 1.44 (sx, J = 7.5 Hz, 2H), 1.66 (quint, J = 7.5 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H), 4.19 (qt, J = 7.5 Hz, 2H), 5.83 (d, J = 10 Hz, 1H), 7.10 (d, J = 10 Hz, 1H). ^{13}C NMR (125 M Hz, $CDCl_3$, ppm) δ 166.4, 150.2, 112.6, 59.7, 35.5, 32.1, 21.3, 14.1, 13.3. IR (cm^{-1}) 2959, 2931, 2873, 1698, 1569, 1373, 1211, 1105, 1034, 799.

4.3. Hydrochalcogenation followed by reduction

4.3.1. Hydrosulfenilation followed by reduction

The lithium ^{n}butanethiolate solution was prepared from elemental sulfur (0.20 g, 6.0 mmol) as described in Section 4.2.1. Deoxygenated water (0.27 mL, 15.0 mmol) was slowly added to the lithium ^{n}butanethiolate solution. The resulting colorless solution was stirred for 10 min and then the α,β-unsaturated aldehyde (6.0 mmol) was added in one portion and the solution was stirred

for additional 30 min. After the reaction was complete, the aldehyde was reduced *in situ* with excess of sodium borohydride in ethanol. The product was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. Column chromatography (4:1 hexane/ethyl acetate) of the crude oil on silica gel afforded a colorless oil.

3-(Butylthio)propan-1-ol (**7a**): (Registry Number: 26901-99-5), Yield, 0.44 g (50%). ^{1}H NMR (200 MHz, $CDCl_3$, ppm) δ 0.92 (t, J = 7.0 Hz, 3H), 1.31–1.65 (m, 4H), 1.84 (qt, J = 7.0 Hz, 2H), 2.53 (t, J = 7.0 Hz, 2H), 2.63 (t, J = 7.0 Hz, 2H), 3.01 (s, 1H), 3.75 (t, J = 7.0 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm) δ 61.6, 31.7, 31.6, 31.5, 28.6, 21.9, 13.5. IR (cm^{-1}) 3362, 2956, 2930, 28721741, 1721, 1650, 1462, 1059.

3-(Butylthio)-3-phenylpropan-1-ol (**7b**): (Registry Number: 1017904-13-0), Yield: 0.63 g (50%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 0.82 (t, 7.2 Hz, 3H), 1.22–1.50 (m, 4H), 1.99–2.15 (m, 2H), 2.22–2.36 (m, 2H), 3.51–3.74 (m,2H), 3.95 (t, 7.5 Hz, 1H), 7.18–7.33 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 142.5, 128.3, 127.6, 126.9, 60.4, 46.3, 39.0, 31.2, 30.5, 21.8, 13.4.

4.4. Hydrotelluration followed by reduction

4.4.1. Hydrotelluration of acrolein followed by reduction of 3-(butyltellanyl)propanal (4a)

A solution of lithium ^{n}butyltellurolate was prepared from 1.28 g (10 mmol) of elemental tellurium as described in Section 4.2.3. To the yellow solution it was added deoxygenated water (0.43 mL, 24 mmol). The mixture was stirred for 5 min and then acrolein (0.67 mL, 10 mmol) was added in one portion. The resulting red mixture was stirred for 30 min and then $NaBH_4$ (0.38 g, 10 mmol) was added in one portion followed by addition of LiCl (42 mg, 1 mmol). The progress of the reaction was monitored by TLC and then it was quenched with water (20 mL) and a mixture of ethyl acetate/hexane (1:1, 50 mL). The phases were separated and the aqueous phase was washed with a mixture of ethyl acetate/hexane (1:1.2, 50 mL). The organic phases were combined, dried with magnesium sulfate, filtered and the solvents were removed under reduced pressure. The residue was purified by silica gel chromatography eluting with a mixture of hexane/ethyl acetate (4:1). Yield of **8**: 2.09 g (85%).

4.4.2. Hydrotelluration of ethyl acrylate followed by reduction of 3-butyltelanylpropionic acid ethyl ester (4d)

A solution of lithium ^{n}butyltellurolate was prepared from 0.64 g (5 mmol) of elemental tellurium as described in Section 4.2.3. To the yellow solution it was added deoxygenated water (0.22 mL, 12 mmol). The mixture was stirred for 5 min and then ethyl acrylate (0.54 mL, 5 mmol) was added in one portion. The resulting red mixture was stirred for 30 min and then $LiAlH_4$ (0.57 g, 15 mmol) was added in three portions. The progress of reaction was monitored by TLC and then it was quenched with water (20 mL) and a mixture of ethyl acetate/hexane (1:1, 50 mL). The phases were separated and the aqueous phase was washed with a mixture of ethyl acetate/hexane (1:1.2, 50 mL). The organic phases were combined, dried with magnesium sulfate, filtered and the solvents were removed under reduced pressure. The residue was purified by silica gel chromatography eluting with a mixture of hexane/ethyl acetate (4:1). Yield of **8**: 1.92 g (78%).

3-(Butyltellanyl)propan-1-ol (**8**): ^{1}H RMN: (Registry Number: 943643-06-9), (300 MHz, $CDCl_3$, ppm) δ 0.89 (*t*, J^3 = 7.2 Hz, 3H), 1.36 (sext, J^3 = 7.2 Hz, 2H), 1.70 (quint, J^3 = 7.5 Hz, 2H), 1.91–2.00 (m, 3H), 2.63 (t, J^3 = 7.5 Hz), 2.66 (t, J^3 = 7.5 Hz), 3.66 (t, J^3 = 6.3 Hz). ^{13}C RMN (75 MHz, $CDCl_3$, ppm) δ 2.1, 2.8, 13.3, 25.0, 34.2, 34.6, 63.9. ^{125}Te NMR (157.79 MHz, $CDCl_3$, 25°C Ph_2Te_2, ppm) δ 244.45. LRMS: m/z (70 eV, relative intensity, %): 246 (M^{+2}, 26%), 244 (M^+, 24%), 242 (15%), 240 (3%), 188 (6%), 186 (7%), 172 (23%), 170 (23%), 168 (13%), 144 (4%), 142 (2%), 130 (6%), 126 (4%), 57 (100%), 41 (86%).

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References

[1] S.O. Ohno, S. Oae, Organic Chemistry of Sulfur, Plenum Press, New York, 1977.
[2] (a) T. Wirth, in: R.H. Crabtree, D.M.P. Mingos (Eds.), Selenium in Comprehensive Organometallic Chemistry III, vol. 7, Elsevier, Oxford, 2007, p. 457;
(b) T.G. Back, Organoselenium Chemistry: A Practical Approach, Oxford University Press, New York, 1999.
[3] (a) N. Petragnani, H.A. Stefani, Tellurium in Organic Synthesis, Second, Updated and Enlarged Edition, Elsevier, Amsterdam, 2007;
(b) J.V. Comasseto, R.L.O.R. Cunha, G.C. Clososki, in: R.H. Crabtree, D.M.P. Mingos (Eds.), Tellurium in Comprehensive Organometallic Chemistry III, vol. 7, Elsevier, Oxford, 2007, p. 587;
(c) J.V. Comasseto, R.E. Barrientos-Astigarraga, Aldrichim. Acta 33 (2000) 66.
[4] (a) J.T.B. Ferreira, J.V. Comasseto, A.L. Braga, Synth. Commun. 12 (1982) 595;
(b) J.V. Comasseto, J.T.B. Ferreira, C.A. Brandt, J. Chem. Res. (1982) 212;
(c) J.V. Comasseto, E.S. Lang, J.T.B. Ferreira, F. Simoneli, V.R. Correia, J. Organomet. Chem. 334 (1987) 329.
[5] (a) J.V. Comasseto, A.S. Guarezemini, Product class 6: acyclic alkanethiolates of group 1, 2, and 13–15 metals, in: Science of Synthesis, Houben-Weyl, Methods of Molecular Transformations, Thieme, Stuttgart, 2008, p. 413;
(b) J.V. Comasseto, A.S. Guarezemini, Product class 5: alkanethiols, in: Science of Synthesis, Houben-Weyl, Methods of Molecular Transformations, Thieme, Stuttgart, 2008, p. 391.
[6] J.F. Boscato, J.M. Catala, E. Franta, J. Brossas, Tetrahedron Lett. 21 (1980) 1519.
[7] (a) A.T. Khan, S. Ghosh, L.H. Choudhury, Eur. J. Org. Chem. (2006) 2226;
(b) See for example: B.C. Ranu, T. Mandal, Can. J. Chem. 84 (2006) 762;
(c) F.M. Moghaddam, G.R. Bardajee, R.O.C. Veranlou, Synth. Commun. 35 (2005) 2427;
(d) B.C. Ranu, S.S. Dey, Tetrahedron 60 (2004) 4183;
(e) B.C. Ranu, S.S. Dey, A. Hajra, Tetrahedron 59 (2003) 2417;
(f) N. Srivastava, B.K. Banik, J. Org. Chem. 68 (2003) 2109.
[8] X. Huang, Z.C. Xiong, Tetrahedron Lett. 44 (2003) 5913.
[9] J.V. Comasseto, A.S. Guarezemini, Product class 19: acyclic alkaneselenolates of group 1, 2, and 13–15 metals, in: Science of Synthesis, Houben-Weyl, Methods of Molecular Transformations, Thieme, Stuttgart, 2008, p. 947.
[10] J.V. Comasseto, A.S. Guarezemini, Product class 18: alkaneselenols, in: Science of Synthesis, Houben-Weyl, Methods of Molecular Transformations, Thieme, Stuttgart, 2008, p. 941.
[11] C. Köllemann, D. Obendorf, F. Sladky, Phosphorus Sulfur 38 (1988) 69.
[12] J.V. Comasseto, A.S. Guarezemini, Product class 31: alkanetellurols, in: Science of Synthesis, Houben-Weyl, Methods of Molecular Transformations, Thieme, Stuttgart, 2008, p. 1137.
[13] J.V. Comasseto, A.S. Guarezemini, Product class 32: acyclic alkanetellurolates of group 1, 2, and 13–15 metals, in: Science of Synthesis, Houben-Weyl, Methods of Molecular Transformations, Thieme, Stuttgart, 2008, p. 1139.
[14] (a) M.L. Vieira, F.K. Zinn, J.V. Comasseto, J. Braz. Chem. Soc. 12 (2001) 586;
(b) G. Zeni, H.B. Formiga, J.V. Comasseto, Tetrahedron Lett. 41 (2000) 1311.
[15] K. Ohe, H. Takahashi, S. Uemura, N. Sugita, Nippon Kagaku Kaishi (1987) 1469.
[16] F.K. Zinn, V.E. Righi, S.C. Luque, H.B. Formiga, J.V. Comasseto, Tetrahedron Lett. 43 (2002) 1625.
[17] J.V. Comasseto, A.A. Dos Santos, Phosphorus Sulfur Silicon 183 (2008) 939.
[18] A.A. Dos Santos, J.L. Princival, J.V. Comasseto, S.M.G. de Barros, J.E. Brainer Neto, Tetrahedron 63 (2007) 5167.
[19] A.A. Dos Santos, C.E. Da Costa, J.L. Princival, J.V. Comasseto, Tetrahedron: Asymm. 17 (2006) 2252.
[20] J.L. Princival, S.M.G. Barros, J.V. Comasseto, A.A. Dos Santos, Tetrahedron Lett. 46 (2005) 4423.
[21] A.A. Dos Santos, J.L. Princival, J.V. Comasseto, unpublished results.
[22] A.A. Dos Santos, R.S. Ferrarini, J.L. Princival, J.V. Comasseto, Tetrahedron Lett. 47 (2006) 8933.
[23] A.A. Dos Santos, R.S. Ferrarini, J.L. Princival, J.V. Comasseto, J. Braz. Chem. Soc. 000 (2008).
[24] (a) See for example: P.A. Grieco, M. Miyashita, Tetrahedron Lett. (1974) 1869;
(b) K.B. Sharpless, M.W. Young, R.F. Lauer, Tetrahedron Lett. (1973) 1979.
[25] For a preliminary communication see: R.A. Gariani, A.A. Dos Santos, J.V. Comasseto, Synth. Commun. 38 (2008) 789.
[26] For a preliminary communication see Ref. [16].