An easy one-step procedure for the synthesis of novel β-functionalised tellurides

CrossMark

Damiano Tanini [a, *], Anna Grechi [a, b], Silvia Dei [b], Elisabetta Teodori [b], Antonella Capperucci [a, *]

[a] Dipartimento di Chimica "Ugo Schiff", Università di Firenze, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy
[b] NEUROFARBA - Dipartimento di Neuroscienze, Psicologia, Area del Farmaco e Salute del Bambino, Sezione Scienze Farmaceutiche e Nutraceutiche, Università di Firenze, Via U. Schiff 6, 50019 Sesto Fiorentino, FI, Italy

ABSTRACT

Novel β-hydroxy-,β-amino- and β-mercapto- dialkyl- and phenyl-alkyl tellurides have been achieved through regioselective ring opening reactions of oxiranes, aziridines and thiiranes with different Te-nucleophiles, including tellurosilanes. Tellurium-125 NMR chemical shifts of selected compounds have been measured.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Organotellurium compounds,[1] are able to generate nucleophilic, electrophilic or radicophilic species that often react in a chemo-, regio- and stereo-selective manner. For these properties, they have been employed in different functional group conversions,[2] in the formation of new carbon-carbon bonds,[3] in the synthesis of natural products[4] and in materials science.[5] Furthermore, several tellurium-containing organic molecules have been studied for their biological properties as thioredoxin reductase modulators, glutathione peroxidase mimics and cancer cell growth inhibitors.[6]

A number of differently functionalised organotellurium compounds, including suitable amino- and hydroxy-substituted systems, have been reported as useful synthetic intermediates in organic transformations.[7]

Several methods for the synthesis of diaryl tellurides and ditellurides have emerged over recent years,[8] nonetheless the corresponding symmetric dialkyl analogues have received less

attention. They are commonly synthesised through the reaction of tellurolates or silyl tellurides[9] with haloalkanes[1,10] or alkyl tosylates.[11] Other methods involve the reactivity of elemental tellurium with organolithium compounds[1,12] or Grignard reagents.[1] β-Halo tellurides or ditellurides can be synthesised from alkenes or alkynes and $TeCl_4$ or $TeBr_4$.[13] Unsymmetrical β-amino tellurides can be accessed through reaction of alkyl- or aryl- tellurolates with mesylates,[14] 2-haloamines or by ring opening of 2-oxazolines and 2-oxazolidinones.[15] A few examples of ring opening reactions of epoxides and aziridines with organic tellurolates (RTe^-) towards unsymmetrical β-hydroxy- and β-amino- tellurides are also reported.[7d,10,16]

During our studies towards the synthesis of novel sulfur- and selenium- containing molecules,[17] we explored the reactivity of three membered heterocycles with chalcogen-containing silyl-nucleophiles disclosing convenient procedures for the synthesis of sulfides and selenides through a ring opening-based protocol. Indeed, thiosilanes and selenosilanes such as HMDST and HMDSS ($Me_3Si-S-SiMe_3$ and $Me_3Si-Se-SiMe_3$, respectively) were efficiently reacted with epoxides, thiiranes and aziridines leading to a straightforward formation of β-functionalised thiols, selenides and diselenides.[18] These bidentate molecules can find application in

---

* Corresponding authors.
  E-mail addresses: damiano.tanini@unifi.it (D. Tanini), antonella.capperucci@unifi.it (A. Capperucci).

organic synthesis, as ligands, catalysts or intermediates, and in biology. We recently reported our preliminary findings on the GPx-like catalytic activity of selected organoselenium compounds.[19]

As an extension of our interest in the synthesis of chalcogen-containing molecules, we evaluated whether new β-functionalised tellurides could be achieved through ring opening reactions of three membered heterocycles with a suitable tellurium nucleophile. To the best of our knowledge, only a few reports dealing with the synthesis of β-functionalised symmetric tellurides through nucleophilic reactions on tosylates, halides, and β-lactones are available in the literature.[11,20] We report herein an easy and versatile procedure for the preparation of novel tellurium-containing β-substituted organic small molecules *via* ring opening of oxiranes, aziridines and thiiranes.

2. Results and discussion

Aiming to access β-functionalised dialkyl tellurides, on the basis of our previous findings in silicon-mediated reactions, we initially considered the possibility to synthesise these chalcogen-containing compounds exploiting the reactivity of strained heterocycles with a suitable tellurosilane such as $(Me_3Si)_2Te$. We began our studies with the synthesis of bis(trimethylsilyl)telluride, the tellurium containing analogue of HMDST and HMDSS, from Li_2Te (or Na_2Te) and Me_3SiCl following literature reported procedures.[21,22] This tellurosilane proved to be rather unstable and, as already observed by other authors,[21b] a partial decomposition was observed over 24 h, even though it was stored in the dark under inert atmosphere at low temperature (-20 °C). Nevertheless, the reactivity of bis(-trimethylsilyl)telluride with epoxides was investigated under conditions used for the ring opening of oxiranes with HMDST and HMDSS towards thiols,[18a] selenides and diselenides[18b] (room temperature or 0 °C, 20% TBAF). Unfortunately, only traces of desired β-hydroxydialkyl tellurides were detected, most likely due to a rapid decomposition of the tellurosilane. The reaction was also performed under milder conditions; however, neither lower temperatures nor the use of a minor amount of TBAF led to the formation of the desired tellurides in useful yields.

The difficulties encountered in handling $(Me_3Si)_2Te$, coupled with the volatility and the pungent odour of the decomposition products, prompted us to explore the reactivity of a different Te nucleophilic species. Thus, the ring opening reaction of epoxides was carried out in the presence of Li_2Te, generated *in situ* by the reaction of elemental tellurium with $LiBEt_3H$. Pleasingly, under these conditions, treatment of 2-methyloxirane **1a** led to 1,1′-tellurobis(propan-2-ol) **2a** as a mixture of diastereoisomers, arising from a clean regioselective attack of the tellurium nucleophile on the less hindered side of the oxirane (Scheme 1).

In order to evaluate the generality of this procedure, a series of substituted epoxides was reacted under the same conditions as reported in Table 1 (entries 1–5). The reactivity proved general, leading to the regioselective formation of differently substituted β-hydroxy tellurides. The methodology can also be applied to useful

but labile compounds such as glycidol derivatives. Glycidyl benzyl- and allyl- ethers **1b-c** were opened affording tellurides **2b-c** without cleavage of the protecting group. β-Hydroxy tellurides were isolated in rather good yields, even though partial decomposition on silica gel was evidenced during purification. Nevertheless, it is worthwhile to remember that these compounds are the result of three different consecutive reactions. In fact, the *in situ* generated dianion Te^{2-} reacts with the epoxide, then a subsequent S_N2 type reaction of the [AlkTe$^-$] intermediate on a second equivalent of the electrophile leads to the β-dialkyl tellurides **2**. When the non racemic epoxide (*R*)-**1b** was employed, the ring opening took place with complete retention of stereochemistry, and the corresponding diastereoenriched telluride (2*S*,2′*S*)-**2b** was achieved. Furthermore, the di-substituted oxirane **1d**, limonene oxide, which arises from a natural product, gave the corresponding β-hydroxy tellurides **2d**, albeit in lower yields with respect to the mono-substituted ones.

In order to evaluate whether the yield of the process could be increased by using different reducing agents, Na/naphthalene and Na/DMF were reacted with elemental tellurium to generate Te^{2-} but, upon *in situ* treatment with epoxides, β-hydroxy tellurides were formed in lower yields with respect to $LiEt_3BH$ conditions.

With the aim to explore the scope and the limitations of the procedure, *N*-protected aziridines synthesised from natural amino acids were reacted with Li_2Te under the same conditions. This investigation led to an easy and direct access to enantioenriched *N*-Tosyl or *N*-Boc β-amino tellurides **4a-c** and **4d** following a regio-selective and stereospecific ring opening pathway. Examples of such reactivity are listed in Table 1 (entries 6–9).

Having evaluated the reactivity of oxiranes and aziridines with Li_2Te, we sought to apply this methodology to thiiranes, aiming to synthesise sulfur-containing organotellurium compounds.

To the best of our knowledge, no example dealing with the ring opening of episulfides with Te-nucleophiles has been reported to date. Thus, thiiranes **5a** and **5b** were reacted under the described conditions leading to 3,7-disubstituted 1,2,5-dithiatellurepanes **6a,b**, together with a minor amount of β-mercapto tellurides **7a,b** (Scheme 2).

In analogy with what was observed in the reaction of silyl chalcogenides (HMDST and HMDSS) with episulfides,[18c] the formation of dithiatellurepanes **6** occurred through the oxidation of the thiol groups of tellurides **7**. However, it was observed that dithiatellurepanes **6**, as well as β-functionalised tellurides **2** and **4** were labile on exposure to air and partially decomposed during purification on silica gel.

Aiming to extend this study to different tellurium nucleophiles, we evaluated the reactivity of thiiranes with PhTe$^-$, *in situ* generated through the reduction of diphenyl ditelluride with $NaBH_4$, as reported in Scheme 3. The ring opening reactions were conducted under two sets of conditions: i) conditions **A**: addition of the thiirane to PhTe$^-$ at 0 °C, followed by warming to room temperature for 3 h; ii) conditions **B**: addition of the thiirane to PhTe$^-$ at 0 °C, followed after 30 min by addition of citric acid (50%, H_2O
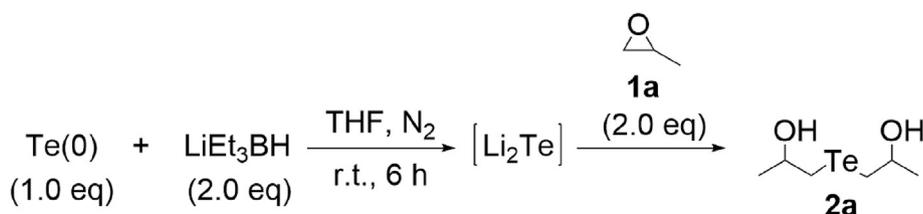
Scheme 1. Synthesis of β-hydroxy tellurides from epoxides.

Table 1
Synthesis of β-dialkyl tellurides: exploration of substrate scope.

$$\text{Te(0)} \quad + \quad \text{LiEt}_3\text{BH} \xrightarrow[\text{r.t., 6 h}]{\text{THF, N}_2} \left[\text{Li}_2\text{Te}\right] \xrightarrow{\text{(2.0 eq)}}$$
(1.0 eq)   (2.0 eq)

1: X = O
3: X = NPg

2: X = O
4: X = NPg

| Entry	Electrophile	Product	Yield (%)[a]
1	**1a**	**2a**	38[b,c]
2	**1b**	**2b**	52[b,c]
3	(*R*)-**1b**	(*2S,2'S*)-**2b**	50
4	**1c**	**2c**	56[b,c]
5	**1d**	**2d**	31[b]
6	**3a**	**4a**	37
7	**3b**	**4b**	39
8	**3c**	**4c**	41
9	**3d**	**4d**	36

[a] Isolated yield is given
[b] Mixture of two diastereoisomers, see experimental
[c] Racemic

solution), yet prior to warming to room temperature. In the first case, a direct access to α-substituted β-phenyltelluro disulfides **8a,b** was found, whereas under conditions **B**, β-mercaptophenyl telluride **9b** was formed through a regioselective ring opening route.

For the characterization of tellurium compounds, [125]Te NMR measurements were a very useful technique.[23] The dependence of [125]Te chemical shifts on variations in molecular structure are evidenced by the considerable differences of resonance frequency,
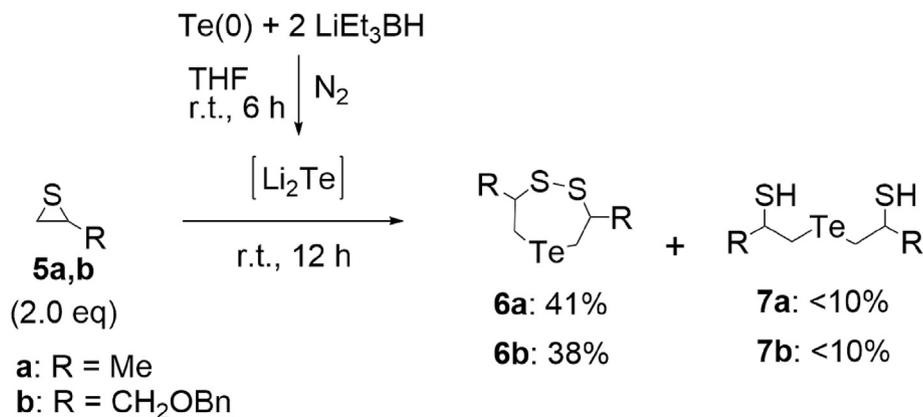
Scheme 2. Synthesis of sulfurated tellurides.
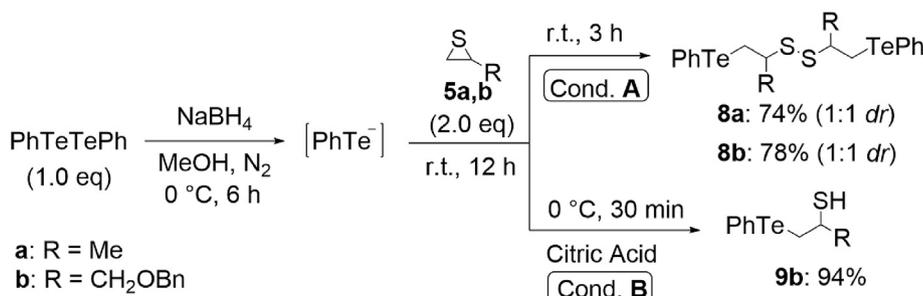
Scheme 3. β-Aryltelluro-thiols and -disulfides.

which can be due to various effects, including the effects of substitution on different positions (α, β and γ) with respect to tellurium. Thus, [125]Te NMR spectra of a selected set of the new β-functionalised dilakyl tellurides **2a**, **2c**, **6a** and phenyl-alkyl tellurides **8a**, **8b**, **9a** were performed (see experimental). The chemical shifts for β-hydroxy tellurides **2a** and **2c** are respectively 29.7/36.5 ppm and 94.1/91.0 ppm for each diastereoisomer. Te-125 resonance is strongly deshielded in the sulfurated series. In fact the chemical shifts of dithiatellurepane **6a** was found at ca. 290 ppm, while the acyclic phenyltelluro alkyl derivatives bearing a disulfide moiety (**8a**, **8b**) or a mercapto group (**9b**) on the β-position show very large downfield shifts, the resonance frequencies ranging between 477 ppm and 473 ppm for **8a,b** to 445 ppm for **9b**. These data confirm the significant effect of groups as well as the nature of the heteroatom in the β-position on [125]Te chemical shifts, which could suggest an interaction between the lone pairs on oxygen (and sulfur) and the chalcogen d-orbitals in compounds in which the substituent is three bonds away from the chalcogen.[23c]

Furthermore, on the basis of our previous findings on the chemical behaviour of silyl chalcogenides with strained heterocycles,[24] we evaluated whether the phenyltelluro moiety could be transferred onto thiiranes by using the corresponding silyl derivative phenyltellurotrimethylsilane, which can behave as an efficient reagent for organotelluration.[25] In fact, the high nucleophilic character of the PhTe group, coupled with the weakness of the Si-Te bond, allows the functionalization of silyl tellurides under mild conditions. Thus, when episulfide **5b** was treated with PhTeSiMe₃ at 0 °C in the presence of a catalytic amount of TBAF, a clean regioselective ring opening occurred, leading to the isolation of β-phenyltelluro thiol **9b** (Scheme 4). Such a procedure may represent an interesting alternative to access β-mercapto tellurides through

the F⁻ mediated functionalization of the tellurosilane. To the best of our knowledge, the reaction described herein represents the first example of thiirane ring opening with a tellurosilane.

Having developed a synthetic method to access alkyl disubstituted β-hydroxy- and β-amino- tellurides and having evaluated the reactivity of thiiranes with different Te-containing nucleophiles, we turned our attention to the synthesis of β-functionalised ditellurides. We proposed that access to β-hydroxy ditellurides might be possible through the ring opening of epoxides with Li₂Te₂, generated *in situ* from elemental tellurium and LiEt₃BH by using an equimolar ratio of the reagents (Scheme 5).

Intriguingly, when 2-methyloxirane **1a** was reacted with Li₂Te₂ the expected ditelluride **10a** was formed only in poor yield, whereas the β-hydroxy ethyltelluride **11a** was isolated as the major product. This reactivity was extended to differently substituted epoxides **1b** and **1c**, allowing direct access to ethyl tellurides **11b** and **11c** through an unexpected pathway, together with minor amounts of the corresponding hydroxy-ditellurides **10b** and **10c**. Further laboratory experiments are under investigation to elucidate the reaction mechanism.

3. Conclusions

In summary, we have developed an easy and practical synthetic procedure to access novel cyclic and open-chain β-functionalised organotellurium compounds through the ring-opening reaction of strained heterocycles such as epoxides, thiiranes and aziridines with different Te-containing nucleophiles. Further investigations concerning the synthesis and the reactivity of new tellurium containing molecules, as well as the evaluation of their antioxidant properties, are currently ongoing in our laboratories.
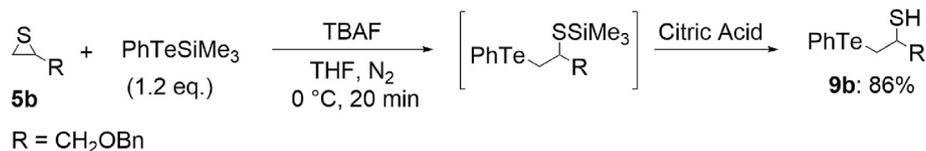
Scheme 4. Silyl-telluride induced ring opening of thiiranes.
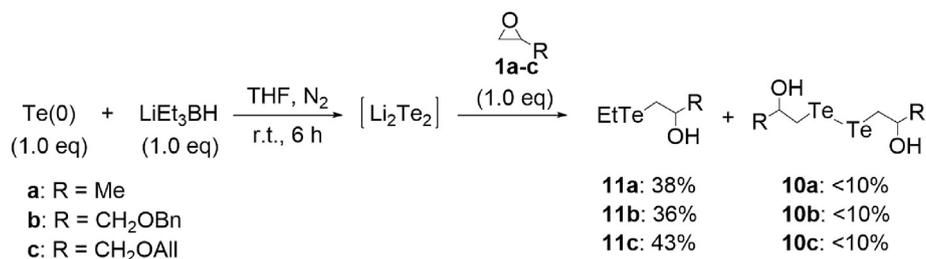
Scheme 5. Synthesis of β-hydroxy ethyl tellurides.

4. Experimental part

4.1. General

^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ with a Varian Mercury Plus instrument or with a Varian INOVA instrument at 400 and 100 MHz, respectively, or with a Varian INOVA instrument at 400 and 100 MHz, respectively. The corresponding residual non-deuterated solvent was used as a reference (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C). ^{125}Te NMR spectra were recorded in CDCl$_3$ at 126 MHz with a Bruker Ultrashield 400 Plus instrument. (PhTe)$_2$ was used as an external reference (δ = 420 ppm). ^{1}H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet, etc.), coupling constant (J) or line separation (ls), and assignment. Mass spectra (MS) were determined by ESI. All the reactions were performed under a positive pressure of nitrogen and were monitored by TLC using commercially available precoated plates (silica gel 60 F 254) and compounds were visualised by fluorescence quenching or by staining the plates with acidic *p*-anisaldehyde solution. Silica gel 60, 230–400 mesh, was used for flash column chromatography. Dry solvents were obtained using a Pure Solv™ Micro system. Commercially available reagents were used as obtained from freshly opened containers without further purification. PhTe-SiMe$_3$,[25] thiiranes[26] and aziridines[27] were synthesised according to literature procedures.

4.2. Synthesis of β-functionalised tellurides 2, 4 and dithiatellurepanes 6

4.2.1. General procedure

Li$_2$Te was generated according to literature[21b] from 1 mL of a 1 M THF solution of LiEt$_3$BH (1.0 mmol, 2.0 eq.) and elemental tellurium powder (63 mg, 0.5 mmol, 1.0 eq.), stirred at ambient temperature under inert atmosphere (N$_2$) for 6 h. The chalky-white suspension of Li$_2$Te in THF was *in situ* treated with the electrophile (epoxide, aziridine or thiirane - 1.0 mmol, 2.0 eq.) and the reaction was stirred for 12 h at ambient temperature. Afterwards, the mixture was diluted with Et$_2$O (10 mL), filtered through a short pad of celite, washed with sat. aq. NH$_4$Cl and then with H$_2$O (2 × 5 mL). The organic phase was dried over Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The crude residue was then purified by flash chromatography to yield β-functionalised tellurides.

4.2.1.1. 1,1′-Tellurobis(propan-2-ol) (2a).
Following the general procedure, 2-methyloxirane **1a** (69.9 μL, 1.0 mmol), LiEt$_3$BH (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (EtOAc/petroleum ether 3:1, R_f = 0.68) **2a** as a colourless oil (46 mg, 38%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 1.28 (6H, d, J = 6.6 Hz), 1.30 (6H, d, J = 6.7 H), 2.67–2.97 (8H, m, **CH$_2$**Te), 3.81–3.89 (4H, m, **CH**OH). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 16.1 (CH$_2$Te), 24.1 (CH$_3$), 67.7 (CH), 67.8 (CH). ^{125}Te NMR (126 MHz, CDCl$_3$): δ (ppm) 29.7, 36.5 (Two diastereoisomers). MS (ESI positive) *m/z* (%): 269 [M+Na]$^+$, (100). Elemental analysis: C$_6$H$_{14}$O$_2$Te Calcd. C 29.32%, H 5.74%. Found: C 29.27%, H 5.77%.

4.2.1.2. 3,3′-Tellurobis(1-(benzyloxy)propan-2-ol) (2b).
Following the general procedure, 2-((benzyloxy)methyl)oxirane **1b** (152 μL, 1.0 mmol), LiEt$_3$BH (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et$_2$O/petroleum ether 5:3, R_f = 0.48) **2b** as a colourless oil (118 mg, 52%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 2.76–2.87 (8H, m, **CH$_2$**Te), 3.05 (4H, bs, OH), 3.47 (4H, dd, J = 6.6, 9.4 Hz, **CH$_a$**H$_b$O), 3.52 (4H, dd, J = 4.2, 9.4 Hz, CH$_a$**H$_b$**O), 3.91–4.01 (4H, m, **CH**OH), 4.54 (8H, ap s, CH$_2$Ph), 7.27–7.38 (20H, m). ^{13}C NMR (50 MHz, CDCl$_3$): δ (ppm) 8.8 (CH$_2$Te), 70.8 (CH), 73.4 (CH$_2$), 74.4 (CH$_2$), 127.7 (CH), 128.4 (CH), 137.8 (C). MS (ESI positive) *m/z* (%): 483 [M+Na]$^+$, (100). Elemental analysis: C$_{20}$H$_{26}$O$_4$Te Calcd. C 52.45%, H 5.72%. Found: C 52.39%, H 5.75%.

4.2.1.3. 3,3′-Tellurobis(1-(allyloxy)propan-2-ol) (2c).
Following the general procedure, 2-((allyloxy)methyl)oxirane **1c** (119 μL, 1.0 mmol), LiEt$_3$BH (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et$_2$O/petroleum ether 5:3, R_f = 0.51) **2c** as a colourless oil (99 mg, 56%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 2.76–2.91 (8H, m, **CH$_2$**Te), 3.01 (4H, bs, OH), 3.41–3.46 (4H, m, **CH$_a$**H$_b$O), 3.50 (4H, dd, J = 4.1, 9.4 Hz, CH$_a$**H$_b$**O), 3.89–3.98 (4H, m, **CH**OH), 4.01 (8H, ap d, ls = 5.6 Hz), 5.18–5.29 (8H, m, CH=**CH$_2$**), 5.84–5.96 (4H, m, **CH**=CH$_2$). ^{13}C NMR (50 MHz, CDCl$_3$): δ (ppm) 8.8 (CH$_2$Te), 70.8 (CH), 72.3 (CH$_2$), 74.3 (CH$_2$), 117.4 (CH$_2$), 134.3 (CH). ^{125}Te NMR (126 MHz, CDCl$_3$): δ (ppm) 94.1, 91.0 (Two diastereoisomers). GC-MS (CI) *m/z* (%): 359 [M+H]$^+$ (8), 245 (95), 81 (100). Elemental analysis: C$_{12}$H$_{22}$O$_4$Te Calcd. C 40.27%, H 6.20%. Found: C 40.33%, H 6.18%.

4.2.1.4. (1R,1′R,3S,3′S)-6,6′-Tellurobis(1-methyl-3-(prop-1-en-2-yl) cyclohexan-1-ol) (2d). Following the general procedure, limonene oxide **1d** (164 μL, 1.0 mmol), LiEt$_3$BH (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (petroleum ether/EtOAc 2:1, R_f = 0.36) **2d** as a colourless oil (67 mg, 31%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) 1.51 (6H, s, C(OH)**CH$_3$**), 1.57−1.66 (8H, m, CH$_2$CH$_2$, C(OH)CH$_a$**H$_b$**, OH), 1.73 (6H, s, CH$_2$=C(CH)**CH$_3$**), 1.75−1.81 (2H, m, C(OH)CH$_a$H$_b$), 2.03−2.17 (4H, m, CH$_2$CHCH$_2$ and CHTeCH$_a$H$_b$), 2.45−2.54 (2H, m, CHTeCH$_a$**H$_b$**), 3.27−3.35 (2H, m, CHTe), 4.75 (4H, ap d, J = 6.1 Hz, C=CH$_2$). **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) 21.4 (CH$_2$=C(CH)**CH$_3$**), 26.4 (**CH$_2$**CH$_2$C), 31.5 (CH(OH)**CH$_3$**), 35.7 (**CH$_2$**CH(OH)), 36.6 (CHTe**CH$_2$**), 39.6 (CHTe), 42.3 (CH$_2$=C(CH$_3$)**CH**), 73.1 (**C**(OH)), 109.4 (C=**CH$_2$**), 148.7 (**C**=CH$_2$). MS (ESI positive) *m/z* (%): 459 [M+Na]$^+$, (100). Elemental analysis: C$_{20}$H$_{34}$O$_2$Te Calcd. C 55.34%, H 7.89%. Found: C 55.40%, H 7.86%.

4.2.1.5. N,N′-((2S,2′S)-Tellurobis(propane-1,2-diyl))bis(4-methylbenzenesulfonamide) (4a). Following the general procedure, (S)-2-methyl-1-tosylaziridine **3a** (106 mg, 0.5 mmol), LiEt$_3$BH (0.5 mL, 0.5 mmol) and elemental tellurium (32 mg, 0.25 mmol) gave after flash chromatography (petroleum ether/Et$_2$O 1:1, R_f = 0.48) **4a** as a yellowish oil (51 mg, 37%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) 1.04 (6H, d, J = 6.5 Hz, CH$_3$), 2.43 (6H, s, CH$_3$), 2.66−2.78 (4H, m, CH$_2$Te), 3.39−3.51 (2H, m, **CH**NH), 4.86 (2H, bs, CHN**H**), 7.31 (4H, ap d, ls = 8.0 Hz), 7.77 (4H, ap d, ls = 8.0 Hz). **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) 15.0, 21.5, 22.7, 50.1, 127.1, 129.8, 138.0, 143.5. HRMS (ESI) calcd for C$_{20}$H$_{29}$N$_2$O$_4$S$_2$Te: 555.0631; found: 555.0613.

4.2.1.6. N,N′-((2S,2′S)-Tellurobis(3-methylbutane-1,2-diyl))bis(4-methylbenzenesulfonamide) (4b). Following the general procedure, (S)-2-isopropyl-1-tosylaziridine **3b** (120 mg, 0.5 mmol), LiEt$_3$BH (0.5 mL, 0.5 mmol) and elemental tellurium (32 mg, 0.25 mmol) gave after flash chromatography (petroleum ether/Et$_2$O 1:1, R_f = 0.55) **4b** as a yellowish oil (59 mg, 39%). **^{1}H NMR** (200 MHz, CDCl$_3$): δ (ppm) 0.71 (6H, d, J = 6.8 Hz, CH$_3$), 0.72 (6H, d, J = 6.6 Hz, CH$_3$), 1.57−1.78 (2H, m, **CH**(CH$_3$)$_2$), 2.41 (6H, s, CH$_3$), 2.68−2.83 (4H, m, CH$_2$Te), 3.02−3.12 (2H, m, C**H**NH), 5.41 (2H, bd, J = 8.2 Hz, NH), 7.28 (4H, ap d, ls = 8.0 Hz), 7.76 (4H, ap d, ls = 8.0 Hz). **^{13}C NMR** (50 MHz, CDCl$_3$): δ (ppm) 15.1, 21.9, 22.6, 25.1, 49.3, 127.4, 130.1, 138.2, 143.5. MS (ESI positive) *m/z* (%): 633 [M+Na]$^+$, (100). Elemental analysis: C$_{24}$H$_{36}$N$_2$O$_4$S$_2$Te Calcd. C 47.39%, H 5.97%, N 4.61%. Found: C 47.31%, H 6.01%, N 4.67%.

4.2.1.7. 4-Methyl-N-((2S,3S)-3-methyl-1-(((2S,3R)-3-methyl-2-((4-methylphenyl)sulfonamido)pentyl)tellanyl)pentan-2-yl)benzenesulfonamide (4c). Following the general procedure, (S)-2-((R)-*sec*-butyl)-1-tosylaziridine **3c** (127 mg, 0.5 mmol), LiEt$_3$BH (0.5 mL, 0.5 mmol) and elemental tellurium (32 mg, 0.25 mmol) gave after flash chromatography (petroleum ether/Et$_2$O 1:1, R_f = 0.57) **4c** as a yellowish oil (65 mg, 41%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) 0.69−0.76 (12H, m), 0.81−0.95 (4H, m), 1.19−1.34 (2H, m), 2.42 (6H, s), 2.75 (4H, ap d, J = 5.5 Hz, CH$_2$Te), 3.14−3.24 (2H, m, **CH**NH), 5.38 (2H, bd, J = 8.8 Hz, CHN**H**), 7.29 (4H, ap d, ls = 8.3 Hz), 7.76 (4H, ap d, ls = 8.3 Hz). **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) 11.9, 14.8, 15.2, 21.8, 32.4, 37.9, 50.9, 127.6, 129.8, 137.7, 143.6. HRMS (ESI) calcd for C$_{26}$H$_{41}$N$_2$O$_4$S$_2$Te: 639.1570; found: 639.1547.

4.2.1.8. Di-tert-butyl ((2S,2′S)-tellurobis(3-phenylpropane-1,2-diyl)) dicarbamate (4d). Following the general procedure, *tert*-butyl (S)-2-benzylaziridine-1-carboxylate **3d** (58 mg, 0.25 mmol), LiEt$_3$BH (0.25 mL, 0.25 mmol) and elemental tellurium (16 mg, 0.13 mmol) gave after flash chromatography (petroleum ether/Et$_2$O 6:1, R_f = 0.32) **4d** as a colourless oil (27 mg, 36%). **^{1}H NMR** (200 MHz,

CDCl$_3$): δ (ppm) 1.43 (18H, s), 2.75−3.05 (4H, m), 3.28−3.59 (4H, m), 4.51−4.74 (2H, m), 4.84 (2H, d, J = 8.3 Hz), 7.13−7.38 (10H, m). **^{13}C NMR** (50 MHz, CDCl$_3$): δ (ppm) 9.8, 28.3, 43.2, 52.6, 79.5, 126.6, 128.5, 129.2, 137.5, 155.2. HRMS (ESI)calcd for C$_{28}$H$_{41}$N$_2$O$_4$Te: 599.2129; found: 599.2101.

4.2.1.9. 3,7-Dimethyl-1,2,5-dithiatellurepane (6a). Following the general procedure, 2-methylthiirane **5a** (74 mg, 1.0 mmol), LiEt$_3$BH (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (petroleum ether/Et$_2$O 6:1, R_f = 0.65) **6a** as an equimolar mixture of two diastereoisomers. Yellowish oil (56 mg, 41%). **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) 1.32−1.38 (12H, m, CH$_3$), 2.59−2.64 (4H, m), 2.83−3.10 (8H, m). **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) 9.6 (CH$_2$Te), 20.7 (CH$_3$), 38.3 (CHS), 41.1 (CHS). **^{125}Te NMR** (126 MHz, CDCl$_3$): δ (ppm) 288.5, 291.4. MS (ESI positive) *m/z* (%): 300 [M+Na]$^+$, (100). Elemental analysis C$_6$H$_{12}$S$_2$Te: Calcd. C 26.12%, H 4.38%. Found: C26.07%, H 4.41%.

4.2.1.10. 3,7-Bis((benzyloxy)methyl)-1,2,5-dithiatellurepane (6b). Following the general procedure, 2-((benzyloxy)methyl)thiirane **5b** (180 mg, 1.0 mmol), LiEt$_3$BH (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (petroleum ether/EtOAc 4:1, R_f = 0.78) **6b** as an equimolar mixture of two diastereoisomers. Yellowish oil (93 mg, 38%). **^{1}H NMR** (200 MHz, CDCl$_3$): δ (ppm) 2.85−3.18 (8H, m, CH$_2$Te), 3.32−3.78 (12H, m), 4.54 (8H, ap s, CH$_2$Ph), 7.30−7.38 (20H, m). **^{13}C NMR** (50 MHz, CDCl$_3$): δ (ppm) 9.8 (CH$_2$Te), 49.7 (CHS), 50.2 (CHS), 70.6, 73.2, 127.7, 128.6, 129.7, 137.9. Elemental analysis: C$_{20}$H$_{24}$O$_2$S$_2$Te Calcd. C 49.21%, H 4.96%. Found: C 49.30%, H 4.94%.

4.3. Synthesis of β-phenyltellurodisulfides **8**

4.3.1. General procedure

NaBH$_4$ (28 mg, 0.75 mmol, 3.0 eq.) was portionwise added to a solution of diphenyl ditelluride (102 mg, 0.25 mmol, 1.0 eq.) in EtOH (2 mL) at 0 °C under inert atmosphere (N$_2$). After 30 min, the thiirane (90 mg, 0.5 mmol, 2.0 eq.) was slowly added at 0 °C and the reaction mixture was allowed to warm to ambient temperature before leaving to react 14 h at the same temperature. Afterwards, 2 mL of H$_2$O were added and the organic phase was extracted with Et$_2$O (2 × 5 mL), washed with brine (1 × 5 mL), dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield β-phenyltellurodisulfides **8**.

4.3.1.1. 1,2-Bis(1-(phenyltellanyl)propan-2-yl)disulfane (8a). Following the general procedure, 2-methylthiirane **5a** (37 mg, 0.5 mmol) gave after flash chromatography (petroleum ether/Et$_2$O 6:1, R_f = 0.59) **8a** as an equimolar mixture of diastereoisomers. Yellowish oil (103 mg, 74%). **^{1}H NMR** (200 MHz, CDCl$_3$): δ (ppm) 1.42 (12H, d, J = 6.5 Hz), 2.96 (4H, dd, J = 9.5, 11.4 Hz, CH$_2$Te), 3.06−3.23 (4H, m, CHS), 3.39 (4H, dd, J = 3.9, 11.4 Hz, CH$_2$Te), 7.18−7.28 (12H, m), 7.66−7.75 (8H, m). **^{13}C NMR** (50 MHz, CDCl$_3$): δ (ppm) 10.2 (CH$_2$Te), 10.5 (CH$_2$Te), 21.1 (CH$_3$), 21.3 (CH$_3$), 44.6 (CHS), 112.1, 127.7, 129.3, 138.3. **^{125}Te NMR** (126 MHz, CDCl$_3$): δ (ppm) 477.1, 477.5 (Two diastereoisomers). MS (ESI positive) *m/z* (%): 581 [M+Na]$^+$, (100). Elemental analysis: C$_{18}$H$_{22}$S$_2$Te$_2$ Calcd. C 38.77%, H 3.98%. Found: C 38.71%, H 4.01%.

4.3.1.2. 1,2-Bis(1-(benzyloxy)-3-(phenyltellanyl)propan-2-yl)disulfane (8b). Following the general procedure, 2-((benzyloxy)methyl) thiirane **5b** (90 mg, 0.5 mmol) gave after flash chromatography (petroleum ether/Et$_2$O 30:1, R_f = 0.28) **8b** as an equimolar mixture of diastereoisomers. Yellowish oil (150 mg, 78%). **^{1}H NMR** (200 MHz, CDCl$_3$): δ (ppm)3.20−3.34 (12H, m, CH$_2$Te overlapped

with CHS), 3.60–3.65(4H, m, CH$_2$O), 3.70–3.77 (4H, m, CH$_2$O), 4.38-4-52 (8H, m, CH$_2$Ph), 7.16–7.21 (8H, m), 7.25–7.38 (24H, m), 7.71–7.74 (8H, m). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm)10.7 (CH$_2$Te), 10.8 (CH$_2$Te), 53.2 (CHS), 53.3 (CHS), 72.0, 73.1, 112.7, 127.7, 128.4, 129.3, 137.8, 138.2. ^{125}Te NMR (126 MHz, CDCl$_3$): δ (ppm) 472.8, 473.4 (Two diastereoisomers). MS (ESI positive) m/z (%): 803 [M+Na]$^+$, (100). Elemental analysis: C$_{32}$H$_{34}$O$_2$S$_2$Te$_2$ Calcd. C 49.92%, H 4.45%. Found: C 49.99%, H 4.39%.

4.4. Synthesis of β-phenyltelluro thiols 9

4.4.1. General procedure

Method A. NaBH$_4$ (28 mg, 0.75 mmol, 3.0 eq.) was portionwise added to a solution of diphenyl ditelluride (102 mg, 0.25 mmol, 1.0 eq.) in EtOH (2 mL) at 0 °C under inert atmosphere (N$_2$). After 30 min, the thiirane **5** (0.5 mmol, 2.0 eq.) was slowly added and the reaction mixture was stirred at 0 °C and the reaction progress was monitored by TLC. When the starting thiirane had completely reacted (monitored by TLC), 2 mL of a 50% aqueous solution of citric acid were added and the organic phase was extracted with Et$_2$O (2 × 5 mL), washed with brine (1 × 5 mL), dried over Na$_2$SO$_4$, filtered and concentrated under vacuum. The crude material was purified by flash chromatography to yield β-phenyltelluro thiols **9**.

Method B. A solution of thiirane **5** (0.2 mmol) and PhTeSiMe$_3$ (0.24 mmol) in dry THF (1 mL) was cooled under inert atmosphere (N$_2$) at 0 °C, and treated with TBAF (72 μL of 1 M THF solution, 0.072 mmol). The reaction was stirred for 20 min and then 1 mL of a 50% aqueous solution of citric acid was added. The solution was diluted with diethyl ether (5 mL), washed with water (1 × 5 mL), and dried over Na$_2$SO$_4$. The solvent was evaporated under vacuum and the crude product was purified by flash chromatography to give β-phenyltelluro thiols **9**.

4.4.1.1. 1-(Benzyloxy)-3-(phenyltellanyl)propane-2-thiol (9b).
Following the general procedure, 2-((benzyloxy)methyl)thiirane **5b** (90 mg, 0.5 mmol) and diphenyl ditelluride (Method A, 102 mg, 0.25 mmol) or PhTeSiMe$_3$ (Method B, 166 mg, 0.6 mmol) gave after flash chromatography (petroleum ether/Et$_2$O 3:1, R_f = 0.47) **9b** as a yellowish oil (181 mg, 94%). ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 2.09 (1H, d, J = 7.5 Hz, SH), 3.23–3.36 (3H, m, CH$_2$Te and CHS overlapped), 3.55 (1H, dd, J = 5.8, 9.5 Hz, CH$_a$H$_b$O), 3.68 (1H, dd, J = 4.7, 9.5 Hz, CH$_a$**H$_b$**O), 4.45 (2H, ap s, CH$_2$Ph), 7.15–7.21 (2H, m), 7.25–7.37 (6H, m), 7.75 (2H, ap d, ls = 7.0 Hz). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 16.4 (CH$_2$Te), 41.0 (CHS), 73.0 (CH$_2$), 75.1 (CH$_2$), 112.4 (C), 127.7 (CH), 127.8 (CH), 128.4 (CH), 129.2 (CH), 137.8 (C) 138.4 (CH). ^{125}Te NMR (126 MHz, CDCl$_3$): δ (ppm) 445.4. MS (ESI positive) m/z (%): 409 [M+Na]$^+$, (100). Elemental analysis: C$_{16}$H$_{18}$OSTe Calcd. C 49.79%, H 4.70%. Found: C 49.86%, H 4.65%.

4.5. Synthesis of β-hydroxyethyltellurides 11

4.5.1. General procedure

Li$_2$Te$_2$ was generated from 0.5 mL of a 1 M THF solution of LiEt$_3$BH (0.5 mmol, 2.0 eq.) and 63 mg of elemental tellurium powder (0.5 mmol, 1.0 eq.), stirred at ambient temperature under inert atmosphere (N$_2$) for 6 h.

The dark red suspension of Li$_2$Te$_2$ in THF was *in situ* treated with the epoxide (0.5 mmol, 1.0 eq.) and the reaction was stirred for 12 h at ambient temperature. Afterwards, the mixture was diluted with Et$_2$O (5 mL), filtered through a short pad of celite, washed with NH$_4$Cl (sat. aq. solution), and then with H$_2$O (2 × 3 mL). The organic phase was dried over Na$_2$SO$_4$, filtered and evaporated under reduced pressure. The crude residue was then purified by flash chromatography to yield β-hydroxyethyl tellurides **11**, together with a minor amount of corresponding ditellurides **10**.

4.5.1.1. 1-(Ethyltellanyl)propan-2-ol (11a).
According to the general procedure, 2-methyloxirane **1a** (35 μL, 0.5 mmol), LiEt$_3$BH (0.5 mL, 0.5 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et$_2$O/petroleum ether 1:1, R_f = 0.67) **11a** as a colourless oil (21 mg, 38%). ^{1}H NMR (200 MHz, CDCl$_3$): δ (ppm) 1.30 (3H, d, J = 6.1 Hz, CH$_3$), 1.61 (3H, t, J = 7.6 Hz, CH$_3$CH$_2$), 2.21 (1H, d, J = 4.4 Hz, OH), 2.63 (2H, qd, J = 3.1, 7.6 Hz, CH$_3$CH$_2$), 2.71 (1H, dd, J = 12.2, 7.5 Hz, CH$_a$H$_b$Te), 2.89 (1H, dd, J = 4.5, 12.2 Hz, CH$_a$**H$_b$**Te), 3.78–4.02 (1H, m, CHOH). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) −4.7 (CH$_3$**CH$_2$**Te), 16.0, 17.7, 23.7, 67.3. ^{125}Te NMR (126 MHz, CDCl$_3$): δ (ppm) 179.4. MS (ESI positive) m/z (%): 238 [M+Na]$^+$, (100). Elemental analysis: C$_5$H$_{12}$OTe Calcd. C 27.83%, H 5.61%. Found: C 27.86%, H 5.57%.

4.5.1.2. 1-(Benzyloxy)-3-(ethyltellanyl)propan-2-ol (11b).
According to the general procedure, 2-((benzyloxy)methyl)oxirane **1b** (76 μL, 0.5 mmol), LiEt$_3$BH (0.5 mL, 0.5 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et$_2$O/petroleum ether 1:1, R_f = 0.65) **11b** as a colourless oil (29 mg, 36%). ^{1}H NMR (200 MHz, CDCl$_3$): δ (ppm) 1.60 (3H, t, J = 7.6 Hz, CH$_3$), 2.63 (2H, ap q, J = 7.6 Hz, CH$_3$**CH$_2$**Te), 2.63 (1H, bs, OH), 2.74–2.90 (2H, m, CH$_2$Te), 3.45 (1H, m, CH$_a$H$_b$O), 3.59 (1H, dd, J = 4.0, 9.5 Hz, CH$_a$**H$_b$**O), 3.44–3.99 (1H, m, CHOH), 4.56 (2H, ap s, CH$_2$Ph), 7.27–7.41 (5H, m). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) −4.5(CH$_3$**CH$_2$**Te), 7.7 (CH$_2$Te), 17.6, 70.7, 73.4, 74.2, 127.8, 127.9, 128.5, 137.9. ^{125}Te NMR (126 MHz, CDCl$_3$): δ (ppm) 213.3. HRMS (ESI) calcd for C$_{12}$H$_{19}$O$_2$Te: 325.0447; found: 325.0457.

4.5.1.3. 1-(Allyloxy)-3-(ethyltellanyl)propan-2-ol (11c).
According to the general procedure, 2-((allyloxy)methyl)oxirane **1c** (60 μL, 0.5 mmol), LiEt$_3$BH (0.5 mL, 0.5 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et$_2$O/petroleum ether 1:1, R_f = 0.73) **11c** as a colourless oil (30 mg, 43%). ^{1}H NMR (200 MHz, CDCl$_3$): δ (ppm) 1.61 (3H, t, J = 7.7 Hz, CH$_3$), 2.59 (1H, d, J = 4.4 Hz, OH), 2.65 (2H, ap q, J = 7.7 Hz, CH$_3$**CH$_2$**Te), 2.82 (2H, ap dd, J = 1.3, 6.3 Hz, CH$_2$Te), 3.45 (1H, dd, J = 6.5, 9.5 Hz, CH$_a$H$_b$O), 3.56 (1H, dd, J = 4.0, 9.5 Hz, CH$_a$**H$_b$**O), 3.84–3.97 (1H, m, CHOH), 4.00–4.05 (2H, m, OCH$_2$All), 5.16–5.34 (2H, m, CH=CH$_2$), 5.81–6.01 (1H, m, CH=CH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) −4.6 (CH$_3$**CH$_2$**Te), 7.6 (CH$_2$Te), 17.5 (CH$_3$), 70.6 (CH), 72.2 (CH$_2$),74.1 (CH$_2$) 117.3 (CH$_2$), 134.4 (CH). HRMS (ESI) calcd for C$_8$H$_{17}$O$_2$Te: 275.0291; found: 275.0283.

4.5.1.4. 1,1'-Ditellanediylbis(propan-2-ol) (10a).
^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 1.32 (12H, d, J = 6.1 Hz), 2.10 (4H, bs, OH), 3.26–3.32 (4H, m, CH$_2$Te), 3.46 (4H, dd, J = 4.1, 12.0 Hz, CH$_2$Te), 3.88–3.96 (4H, m, CHOH). ^{13}C NMR (100 MHz, CDCl$_3$): δ (ppm) 17.2 (CH$_2$Te), 17.3 (CH$_2$Te), 23.5 (CH$_3$), 68.9 (CHOH), 69.0 (CHOH). ^{125}Te NMR (126 MHz, CDCl$_3$): δ (ppm) 49.3, 52.0. MS (ESI positive) m/z (%): 396 [M+Na]$^+$, (100). Elemental analysis: C$_6$H$_{14}$O$_2$Te$_2$. Calcd. C 19.30%, H 3.78%. Found: C 19.35%, H 3.76%.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2017.07.061.

References

1. Petragnani N, Stefani HA. *Tellurium in Organic Synthesis.* second ed. Amsterdam: Elsevier; 2007.
2. (a) Petragnani N, Stefani HA. *Tetrahedron.* 2005;61:1613;
   (b) Comasseto JV, Barrientos-Astigarraga RE. *Aldrichim Acta.* 2000;33:66.
3. (a) Stefani HA, Pena JM, Manarin F, et al. *Tetrahedron Lett.* 2011;52:4398;
   (b) Stefani HA, Pena JM, Gueogjian K, et al. *Tetrahedron Lett.* 2009;50:5589;
   (c) Tucci FC, Chieffi A, Comasseto JV, et al. *J Org Chem.* 1996;61:4975.

4. (a) Wendler EP, Dos Santos AA. *Synlett*. 2009;7:1034;
   (b) Marino JP, Mc Clure MS, Holub DP, et al. *J Am Chem Soc*. 2002;8:1664.
5. Yu F, Li P, Wang B, et al. *J Am Chem Soc*. 2013;135:7674.
6. (a) Jamier V, Ba LA, Jacob C. *Chem Eur J*. 2010;16:10920. and ref. cited therein;
   (b) Lin T, Ding Z, Li N, et al. *Carcinogenesis*. 2010;32:154;
   (c) Engman L, Al-Maharik N, McNaughton M, et al. *Anti-Cancer Drugs*. 2003;14:153;
   (d) Rooseboom M, Vermeulen NPE, Durgut F, et al. *Chem Res Toxicol*. 2002;15:1610;
   (e) Tiano L, Fedeli D, Santroni AM, et al. *Mutat Res*. 2000;464:269. For a review see: Nogueira CW, Zeni G, Rocha JBT. Chem. Rev. 2004; 104: 6255.
7. (a) Nagatomo M, Nishiyama H, Fujino H, et al. *Angew Chem Int Ed*. 2015;54:1537;
   (b) Princival JL, Dos Santos AA, Comasseto J. *J Braz Chem Soc*. 2010;21:2042;
   (c) Comasseto JV, Gariani RA. *Tetrahedron*. 2009;65:8447;
   (d) Ericsson C, Engman L. *J Org Chem*. 2004;69:5143;
   (e) Berlin S, Ericsson C, Engman L. *J Org Chem*. 2003;68:8386.
8. (a) Kumar A, Kumar S. *Tetrahedron*. 2014;70:1763;
   (b) Prasad CD, Balkrishna SJ, Kumar A, et al. *J Org Chem*. 2013;78:1434;
   (c) Kassaee MZ, Motamedi E, Movassagh B, et al. *Synthesis*. 2013;45:2337–2342;
   (d) Singh D, Deobald AM, Camargo LRS, et al. *Org Lett*. 2010;12:3288.
9. Yamago S, Iida K, Yoshida J. *Tetrahedron Lett*. 2001;42:5061.
10. Sasaki K, Mori T, Doi Y, et al. *Chem Lett*. 1991;415.
11. Borges EL, Peglow TJ, Silva MS, et al. *New J Chem*. 2016;40:2321.
12. (a) Oliveira JMR, Freitas JC, Comasseto JV, et al. *Tetrahedron*. 2011;67:3003.
13. (a) Musalova MV, Udalova SI, Musalov MV, et al. *Russ J Org Chem*. 2016;52:1509;
    (b) Musalova MV, Musalov MV, Udalova SI, et al. *Russ J Org Chem*. 2015;51:1666;
    (c) Musalova MV, Musalov MV, Potapov VA, et al. *Russ J Gen Chem*. 2014;84:2460.
14. Revanna RH, Kumar RP, Hosamani A, et al. *J Organomet Chem*. 2015;799–800:61.
15. (a) Braga AL, Galetto FZ, Taube PS, et al. *J Organomet Chem*. 2008;693:3563;

16. (b) Sehnem JA, Vargas F, Milani P, et al. *Synthesis*. 2008;8:1262.
16. (a) Sui D, Wu F, Xu Q, et al. *J Chem Res*. 2011;288;
    (b) Vargas F, Comasseto JV. *J Organomet Chem*. 2009;694:122;
    (c) Dos Santos AA, Da Costa CE, Princival JL, et al. *Tetrahedron Asymmetry*. 2006;17:2252;
    (d) Silva PC, Borges EL, Lima DB, et al. *Arkivoc*. 2016;5:376;
    (e) Dowsland J, McKerlie F, Procter DJ. *Tetrahedron Lett*. 2000;41:4923.
17. (a) Menichetti S, Capperucci A, Tanini D, et al. *Eur J Org Chem*. 2016:3097;
    (b) Tanini D, Panzella L, Amorati R, et al. *Org Biol Chem*. 2015;13:5757;
    (c) Degl'Innocenti A, Capperucci A, Cerreti A, et al. *Synlett*. 2005:3063;
    (d) Degl'Innocenti A, Capperucci A, Castagnoli G, et al. *Synlett*. 2005:1965;
    (e) Angeli A, Tanini D, Viglianisi C, et al. *Bioorg Med Chem*. 2017;25:2518.
18. (a) Degl'Innocenti A, Pollicino S, Capperucci A. *Chem Commun*. 2006:4881–4893;
    (b) Tanini D, Capperucci A, Degl'Innocenti A. *Eur J Org Chem*. 2015;357;
    (c) Capperucci A, Tanini D, Borgogni C, et al. *Heteroat Chem*. 2014;25:678.
19. Tanini D, D'Esopo V, Chen D, et al. *Phosphorus Sulfur Silicon Relat Elem*. 2017;192:166.
20. (a) Schneider A, Rodrigues OED, Paixao MW, et al. *Tetrahedron Lett*. 2006;47:1019;
    (b) Milton MD, Khan S, Singh JD, et al. *Tetrahedron Lett*. 2005;46:755.
21. (a) Lange H, Herzog U. *J Organomet Chem*. 2002;660:36;
    (b) Detty MR, Seidler MD. *J Org Chem*. 1982;47:1354.
22. Finger LH, Scheibe B, Sundermeyer J. *Inorg Chem*. 2015;54:9568.
23. (a) Elder PJW, Vargas-Baca I. *Phys Chem Chem Phys*. 2016;18:30740;
    (b) Duddeck H, Biallaβ A. *Magn Reson Chem*. 1994;32:303;
    (c) Baiwir M, Llabres G, Christiaens L, et al. *Magn Reson Chem*. 1986;24:362;
    (d) O'Brien DH, Dereu N, Huang CK, et al. *Organometallics*. 1983;2:305.
24. Capperucci A, Tiberi C, Pollicino S, et al. *Tetrahedron Lett*. 2009;50:2808.
25. (a) Yamago S, Iida K, Ji Yoshida. *Tetrahedron Lett*. 2001;42:5061;
    (b) Sasaki K, Aso Y, Otsubo T, et al. *Tetrahedron Lett*. 1985;26:453.
26. Pederson RL, Liu KKC, Rutan JF, et al. *J Org Chem*. 1990;55:4897.
27. (a) Bieber MB, de Araujo MCF. *Molecules*. 2002;7:902;
    (b) Berry MB, Craig D. *Synlett*. 1992;41;
    (c) Osborn HMI, Sweeney J. *Tetrahedron Asymmetry*. 1997;8:1693.