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

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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 shift of representative compounds have been measured.

Keywords: Organotellurium, Tellurides, Epoxides/Thiiranes/Aziridines, Ring opening.

Introduction

Organotellurium compounds,[1] are able to generate nucleophilic, electrophilic or radicophilic species that often react in 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 cells 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.[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 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 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.

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 $(Me_3Si)_2Te$.

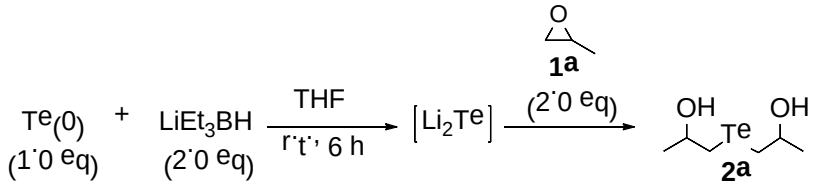
We began our studies with the synthesis of bis(trimethylsilyl)telluride, the tellurium containing analogue of HMDST and HMDSS, from Li_2Te (or Na_2Te) and Me_3SiCl following literature reported procedures.[21,22]

This tellurosilane proved to be rather unstable and, as already observed by other authors,[21b] a partial decomposition was observed over 24h, 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-hydroxy dialkyl 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.

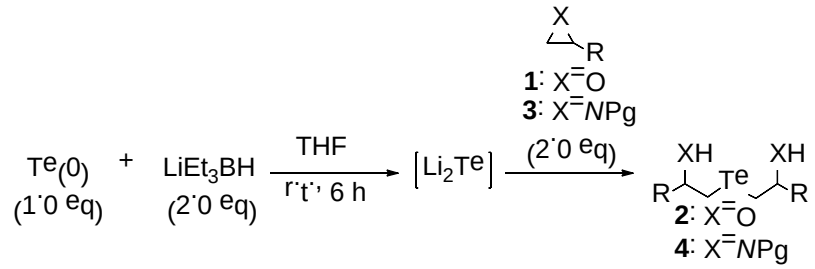
The difficulties encountered in handling $(Me_3Si)_2Te$, coupled with the volatility and the pungent odour of the decomposition products, prompted us to explore the reactivity of a different Te nucleophilic species.

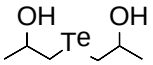
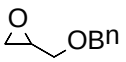
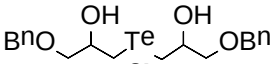
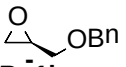
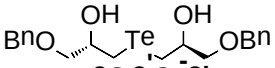
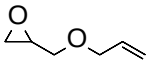
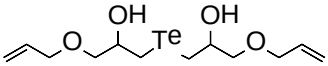
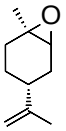
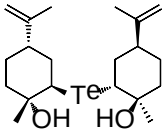
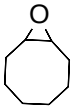
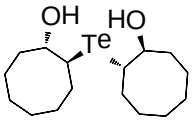
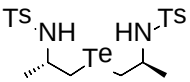
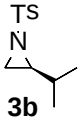
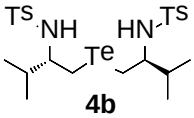
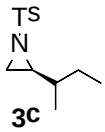
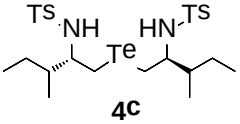
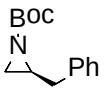
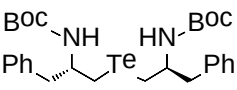
Thus, the ring opening reaction of epoxides was carried out in the presence of Li_2Te, generated *in situ* by the reaction of elemental tellurium with $LiBEt_3H$. Pleasingly, under these conditions, treatment of 2-methyloxirane **1a** led to disclose a straightforward access to 1,1'-tellurobis(propan-2-ol) **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).



Scheme 1

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



Entry	Electrophile	Product	Yield (%)[a]
1	 **1a**	 **2a**	38[b]
2	 **1b**	 **2b**	52[b]
3	 **(*R*)-1b**	 **(2*S*,2′*S*)-2b**	50
4	 **1c**	 **2c**	56[b]
5	 **1d**	 **2d**	38[b]
6	 **1e**	 **2e**	34[b,c]
7	 **3a**	 **4a**	37
8	 **3b**	 **4b**	39
9	 **3c**	 **4c**	41
10	 **3d**	 **4d**	36

[a] Isolated yield is given

[b] Mixture of two diastereoisomers

[c] Racemic

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 1-6). 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 chiral, nonracemic epoxide (*R*)-**2b** was employed, the ring opening took place with complete stereoconservativity, and the corresponding diastereoenriched telluride (2*S*,2'*S*)-**2b** was achieved.

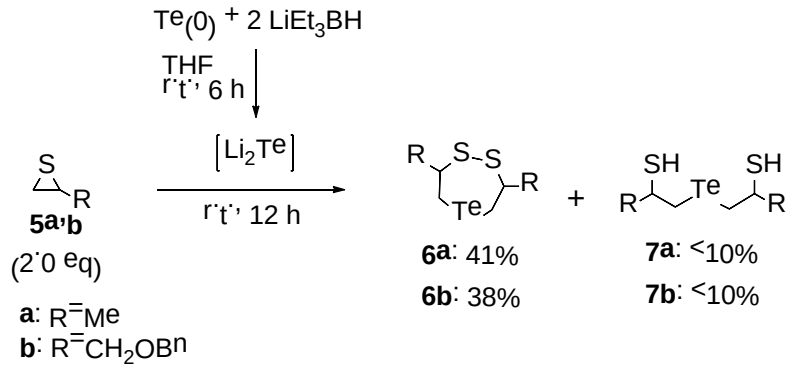
Di-substituted oxiranes, such as limonene oxide **1d** which arises from a natural product, and cyclooctene oxide **1e** gave the corresponding β-hydroxy tellurides **2d** and **2e**, despite in lower yields with respect to the mono-substituted ones.

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 deeply explore the scope and the limitations of such procedure, *N*-protected aziridines synthesised from natural aminoacids were reacted with Li_2Te under the same conditions. This investigation led to the disclosure of an easy and direct access to chiral *N*-Tosyl or *N*-Boc β-amino tellurides **4a-c** and **4d** following a regioselective and stereoconservative ring opening pathway. Examples of such reactivity are listed in Table 1 (entries 7-10).

Having evaluated the reactivity of oxiranes and aziridines with Li_2Te, we sought to apply this methodology to thiiranes, aimed to synthesise sulfurated organotellurium compounds.

To the best of our knowledge, no example dealing with ring opening of episulfides with Te-nucleophiles is to date reported. 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).

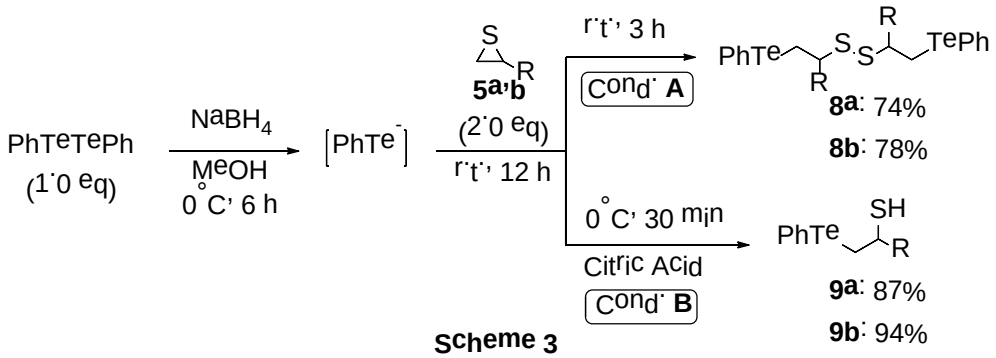


Scheme 2

In analogy with what already observed in the reaction of silyl chalcogenides (HMDST and HMDSS) with episulfides,[19c] 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 reduction of diphenyl ditelluride with $NaBH_4$, as reported in the 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 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-mercapto phenyltellurides **9a,b** were smoothly formed through a regioselective ring opening route.

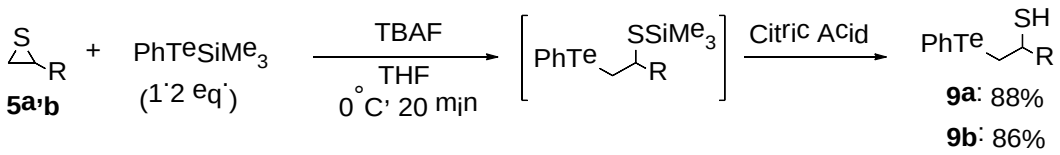


Scheme 3

For the characterization of tellurium compounds, ^{125}Te NMR measurements were demonstrated a very useful tecnique.[23] The dependence of ^{125}Te chemical shifts on variations in molecular structure are evidenced by the considerable differences of resonance frequency, 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-functionalized dilalkyl tellurides **2a**, **2c**, **6a** and phenyl-alkyl

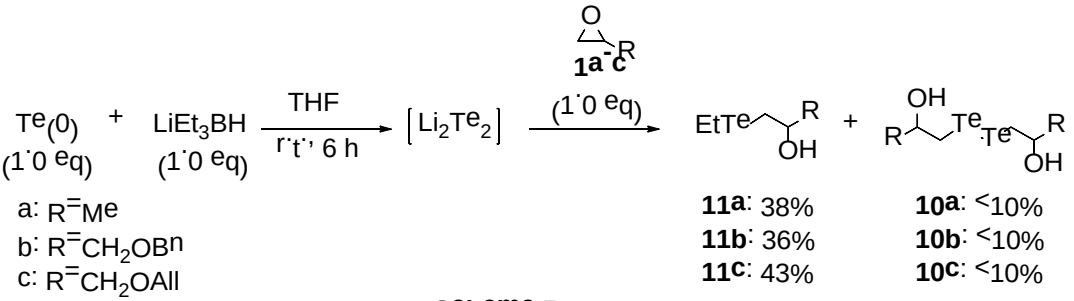
tellurides **8a**, **8b**, **9a** were performed (see experimental). The chemical shifts of β-hydroxy tellurides **2a** and **2c** are respectively 29.7/36.5 ppm and 94.1/91 ppm for each diastereoisomer. Te-125 resonance is strongly deshielded in the sulfurated series. The chemical shift of dithiatellurepane **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 β-position show very large downfield shifts, the resonance frequecies 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 β-position on ^{125}Te chemical shifts, which could suggest an interaction between the lone pairs on oxygen (and sulfur) and the tellurium *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 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 episulfides **5a,b** were treated with $PhTeSiMe_3$ at 0°C in the presence of a catalytic amount of TBAF, a clean regioselective ring opening smoothly occurred, leading to the isolation of β-phenyltelluro thiols **9a,b** (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 reactions described herein represent the first example of thiiranes ring opening with a tellurosilane.



Scheme 4

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 reasoned to access β-hydroxy ditellurides through the ring opening of epoxides with Li_2Te_2, generated *in situ* from elemental tellurium and $LiEt_3BH$ by using an equimolar ratio of the reagents (Scheme 5).



Scheme 5

Intriguingly, when 2-methyloxirane **1a** was reacted with Li_2Te_2 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 to directly access 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.

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.

Experimental part

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). Mass spectra (MS) were obtained by ESI. Reactions 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. $PhTeSiMe_3$,[25] thiiranes[26] and aziridines[27] were synthesised according to a literature procedure.

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

General procedure. Li_2Te was generated according to literature[21b] from 1 mL of a 1M THF solution of $LiEt_3BH$ (1.0 mmol, 2.0 eq.) and 63 mg of elemental tellurium powder (0.5 mmol, 1.0 eq.), stirred at ambient temperature under inert atmosphere for 6h.

The chalky-white suspension of Li_2Te 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_2O (10 mL), filtered through a short pad of celite, washed with NH_4Cl and then with H_2O (2 x 5 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude residue was then purified by flash chromatography to yield β-functionalised tellurides.

β-Hydroxy tellurides

*1,1'-Tellurobis(propan-2-ol) (**2a**).* Following the general procedure, 2-methyloxirane **1a** (69.9 µL, 1.0 mmol), $LiEt_3BH$ (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (EtOAc/petroleum ether 3:1) **2a** as a colourless oil (46 mg, 38%). Equimolar mixture of two diastereoisomers. ^{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, C$\underline{H_2}$Te), 3.81-3.89 (4H, m, C$\underline{H}$OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 8.0 (CH_2Te), 8.1 (CH_2Te), 23.7 (CH_3), 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).

*3,3'-Tellurobis(1-(benzyloxy)propan-2-ol) (**2b**).* Following the general procedure, 2-((benzyloxy)methyl)oxirane **1b** (152 µL, 1.0 mmol), $LiEt_3BH$ (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et_2O/petroleum ether 5:3) **2b** as a colourless oil (118 mg, 52%). Equimolar mixture of two diastereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.76-2.87 (8H, m, C$\underline{H_2}$Te), 3.05 (4H, bs, OH), 3.47 (4H, dd, *J*=6.6, 9.4 Hz, C$\underline{H_a}H_b$O), 3.52 (4H, dd, *J*=4.2, 9.4 Hz, $CH_a\underline{H_b}$O), 3.91-4.01 (4H, m, C$\underline{H}$OH), 4.54 (8H, ap s, CH_2Ph), 7.27-7.38 (20H, m,). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 8.8 (CH_2Te), 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: $C_{20}H_{26}O_4Te$ Calcd. C 52.45%, H 5.72%. Found: C 52.39%, H 5.75%.

*3,3'-Tellurobis(1-(allyloxy)propan-2-ol) (**2c**).* Following the general procedure, 2-((allyloxy)methyl)oxirane **1c** (119 µL, 1.0 mmol), $LiEt_3BH$ (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et_2O/petroleum ether 5:3) **2c** as a colourless oil (99 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.76-2.91 (8H, m, C$\underline{H_2}$Te), 3.01 (4H, bs, OH), 3.41-3.46 (4H, m, C$\underline{H_a}H_b$O), 3.50 (4H, dd, *J*=4.1, 9.4 Hz, $CH_a\underline{H_b}$O), 3.89-3.98 (4H, m, C$\underline{H}$OH), 4.01 (8H, ap d, ls=5.6 Hz), 5.18-5.29 (8H, m, CH=C$\underline{H_2}$), 5.84-5.96 (4H, m, C$\underline{H}$=CH_2). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 8.8 (CH_2Te), 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 (Equimolar mixture of two diastereoisomers). MS (ESI positive) *m/z* (%): 382 $[M+Na]^+$, (100). Elemental analysis: $C_{12}H_{22}O_4Te$ Calcd. C 40.27%, H 6.20%. Found: C 40.33%, H 6.18%.

(1S,1'S,2S,2'S,4R,4'R)-2,2'-Tellurobis(1-methyl-4-(prop-1-en-2-yl)cyclohexanol) ***(2d)****.* Following the general procedure, limonene oxide **1d** (164 µL, 1.0 mmol), $LiEt_3BH$ (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (petroleum ether/EtOAc 2:1) **2d** as a colourless oil (82 mg, 38%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.51 (6H, s, C(OH)C$\underline{H}_3$), 1.57-1.66 (8H, m), 1.73 (6H, s, CH_2=C(CH)C$\underline{H}_3$), 1.75-1.81 (2H, m), 2.03-2.17 (4H, m, $CH_2C\underline{H}CH_2$ and CH(Te)C$\underline{H}_a$H$_b$), 2.45-2.54 (2H, m, CH(Te)CH$_a\underline{H}_b$), 3.27-3.35 (2H, m, CHTe), 4.74-4.76 (4H, m, C=CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 21.4 (CH_2=C(CH)$\underline{C}H_3$), 26.4 ($\underline{C}H_2CH_2C$), 31.5 (CH(OH)$\underline{C}H_3$), 35.7 ($\underline{C}H_2$CH(OH)), 36.6 (CHTe$\underline{C}H_2$), 39.6 (CHTe), 42.3 (CH_2=C(CH_3)$\underline{C}$H), 73.1 (C(OH)), 109.4 (C=$\underline{C}H_2$), 148.7 ($\underline{C}$=CH_2). MS (ESI positive) *m/z* (%): 459 $[M+Na]^+$, (100).

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), $LiEt_3BH$ (0.5 mL, 0.5 mmol) and elemental tellurium (32 mg, 0.25 mmol) gave after flash chromatography (petroleum ether/Et_2O 1:1) **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_2Te), 3.39-3.51 (2H, m, C$\underline{H}$NH), 4.86 (2H, bs, CHN$\underline{H}$), 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. MS (ESI positive) *m/z* (%)*:* 577 $[M+Na]^+$, (100).

N,N'-((2*S*,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), $LiEt_3BH$ (0.5 mL, 0.5 mmol) and elemental tellurium (32 mg, 0.25 mmol) gave after flash chromatography (petroleum ether/Et_2O 1:1) **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, C$\underline{H}$(CH_3)$_2$), 2.41 (6H, s, CH_3), 2.68-2.83 (4H, m, CH_2Te), 3.02-3.12 (2H, m, C$\underline{H}$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, 143.5. MS (ESI positive) *m/z* (%): 633 $[M+Na]^+$, (100). Elemental analysis: $C_{24}H_{36}N_2O_4S_2Te$ Calcd. C 47.39%, H 5.97%, N 4.61%. Found: C 47.31%, H 6.01%, N 4.67%.

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), $LiEt_3BH$ (0.5 mL, 0.5 mmol) and elemental tellurium (32 mg, 0.25 mmol) gave after flash chromatography (petroleum ether/Et_2O 1:1) **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_2Te), 3.14-3.24 (2H, m, C$\underline{H}$NH), 5.38 (2H, bd, *J*=8.8 Hz, CHN$\underline{H}$), 7.29 (4H, ap d, ls=8.3 Hz), 7.76 (4H, ap d, ls=8.3 Hz).

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), $LiEt_3BH$ (0.25 mL, 0.25 mmol) and elemental tellurium (16 mg, 0.13 mmol) gave after flash chromatography (petroleum ether/Et_2O 6:1) **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).

3,7-Dimethyl-1,2,5-dithiatellurepane ***(6a).*** Following the general procedure, 2-methylthiirane **5a** (74 mg, 1.0 mmol), $LiEt_3BH$ (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (petroleum ether/Et_2O 6:1) **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_2Te), 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).

3,7-Bis((benzyloxy)methyl)-1,2,5-dithiatellurepane ***(6b)***. Following the general procedure, 2-((benzyloxy)methyl)thiirane **5b** (180 mg, 1.0 mmol), $LiEt_3BH$ (1.0 mL, 1.0 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (petroleum ether/EtOAc 4:1) **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_2Te), 3.32-3.78 (12H, m), 4.52 (8H, ap s, CH_2Ph), 7.30-7.38 (20H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 9.8 (CH_2Te), 49.7 (CHS), 50.2 (CHS), 70.6, 73.2, 127.7, 128.6, 129.7, 137.9.

Synthesis of β-phenyltelluro disulfides 8.

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. 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 overnight at the same temperature. Afterwards 2 mL of H_2O were added and the organic phase was extracted with Et_2O, washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude material was purified by flash chromatography to yield β-phenyltelluro disulfides **8**.

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_2O 6:1) **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_2Te), 3.06-3.23 (4H, m, CHS), 3.39 (4H, dd, *J*=3.9, 11.4 Hz, CH_2Te), 7.18-7.28 (12H, m), 7.66-7.75 (8H, m). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 10.2 (CH_2Te), 10.5 (CH_2Te), 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. MS (ESI positive) *m/z* (%): 581 $[M+Na]^+$, (100).

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_2O

30:1) **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_2Te overlapped with CHS), 3.60-3.65(4H, m, CH_2O), 3.70-3.77 (4H, m, CH_2O), 4.38-4-52 (8H, m, CH_2Ph), 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_2Te), 10.8 (CH_2Te), 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. MS (ESI positive) *m/z* (%): 803 $[M+Na]^+$, (100). Elemental analysis: $C_{32}H_{34}O_2S_2Te_2$ Calcd. C 49.92%, H 4.45%. Found: C 49.99%, H 4.39%.

Synthesis of β-phenyltelluro thiols 9.

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. 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_2O, washed with brine, dried over Na_2SO_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 at 0°C, and treated with TBAF (72 μL of 1M 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, washed with water, and dried over Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purifiede by flash chromatography to give β-phenyltelluro thiols **9**.

*1-(Phenyltellanyl)propane-2-thiol **(9a)**.* Following the general procedure, 2-methylthiirane **5a** (37 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_2O 2:1) **9a** as a yellowish oil (121 mg, 87%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.43 (3H, d, *J*=6.6 Hz, CH_3), 1.97 (1H, d, *J*=7.4 Hz, SH), 2.84-3.36 (3H, m, CH_2Te and CHS), 7.17-7.31 (3H, m), 7.68-7.84 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 15.1 (CH_2Te), 22.6 (CH_3), 38.2 (CHS), 112.4, 127.7, 129.2, 137.9, 138.4. MS (ESI positive) *m/z* (%): 304 $[M+Na]^+$, (100).

*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_2O 3:1) **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_2Te and CHS overlapped), 3.55 (1H, dd, *J*=5.8, 9.5 Hz, $C\underline{H_a}H_bO$), 3.68 (1H, dd, *J*=4.7, 9.5 Hz, $CH_a\underline{H_b}O$), 4.45 (2H, ap s, CH_2Ph), 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_2Te), 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%.

Synthesis of β-hydroxy ethyltellurides 11.

General procedure. Li_2Te_2 was generated from 0.5 mL of a 1M THF solution of $LiEt_3BH$ (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 for 6h.

The dark red suspension of Li_2Te_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_2O, filtered through a short pad of celite, washed with NH_4Cl (sat. aq. solution) and then with H_2O (2x). The organic phase was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude residue was then purified by flash chromatography to yield β-hydroxy ethyltellurides **11**, together with a minor amount of corresponding ditellurides **10**.

*1-(Ethyltellanyl)propan-2-ol (**11a**).* According to the general procedure, 2-methyloxirane **1a** (35 µL, 0.5 mmol), $LiEt_3BH$ (0.5 mL, 0.5 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et_2O/petroleum ether 1:1) **11a** as a colourless oil (21 mg, 38%). ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.29 (3H, d, *J*=6.2 Hz, CH_3), 1.61 (3H, t, *J*=7.6 Hz, $C\underline{H_3}CH_2$), 2.20 (1H, d, *J*=4.4 Hz, OH), 2.67 (2H, q, J=7.6 Hz, $CH_3C\underline{H_2}$), 2.71 (1H, dd, *J*=2.2, 7.5 Hz, $C\underline{H_a}H_bTe$), 2.89 (1H, dd, *J*=4.0, 7.5 Hz, $CH_a\underline{H_b}Te$), 3.78-4.02 (1H, m, C<u>H</u>OH).

*1-(Benzyloxy)-3-(ethyltellanyl)propan-2-ol (**11b**).* According to the general procedure, 2-((benzyloxy)methyl)oxirane **1b** (76 µL, 0.5 mmol), $LiEt_3BH$ (0.5 mL, 0.5 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et_2O/petroleum ether 1:1) **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, $CH_3C\underline{H_2}Te$), 2.63 (1H, bs, OH), 2.74-2.90 (2H, m, $C\underline{H_2}Te$), 3.45 (1H, m, $C\underline{H_a}H_bO$), 3.59 (1H, dd, *J*=4.0, 9.5 Hz, $CH_a\underline{H_b}O$), 3.44-3.99 (1H, m, C<u>H</u>OH), 4.56 (2H, ap s, $C\underline{H_2}Ph$), 7.27-7.41 (5H, m). MS (ESI positive) *m/z* (%):345 $[M+Na]^+$, (100).

*1-(Allyloxy)-3-(ethyltellanyl)propan-2-ol (**11c**).* According to the general procedure, 2-((allyloxy)methyl)oxirane **1c** (60 µL, 0.5 mmol), $LiEt_3BH$ (0.5 mL, 0.5 mmol) and elemental tellurium (63 mg, 0.5 mmol) gave after flash chromatography (Et_2O/petroleum ether 1:1) **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, $CH_3C\underline{H_2}Te$), 2.82 (2H, ap dd, *J*=1.3, 6.3 Hz, $C\underline{H_2}Te$), 3.45 (1H, dd, *J*=6.5, 9.5 Hz, $C\underline{H_a}H_bO$), 3.56 (1H, dd, *J*=4.0, 9.5 Hz, $CH_a\underline{H_b}O$), 3.84-3.97 (1H, m, C<u>H</u>OH), 4.00-4.05 (2H, m, $OC\underline{H_2}All$), 5.16-5.34 (2H, m, $CH=C\underline{H_2}$), 5.81-6.01 (1H, m, $C\underline{H}=CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) -4.6 ($CH_3\mathbf{C}H_2Te$), 7.6 (CH_2Te), 17.5 (CH_3), 70.6 (CH), 72.2 (CH_2),74.1 (CH_2) 117.3 (CH_2), 134.4 (CH). MS (ESI positive) *m/z* (%): 295 $[M+Na]^+$, (100).

*1,1'-Ditellanediylbis(propan-2-ol) (**10a**).* Equimolar mixture of two diastereoisomers. ^{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, C$\underline{H_2}$Te), 3.46 (4H, dd, *J*=4.1, 12.0 Hz, C$\underline{H_2}$Te), 3.88-3.96 (4H, m, C$\underline{H}$OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 17.2 (CH_2Te), 17.3 (CH_2Te), 23.5 (CH_3), 68.9 (CHOH), 69.0 (CHOH). MS (ESI positive) *m/z* (%): 396 $[M+Na]^+$, (100).

References and Notes

1. (a) Petragnani N, Stefani HA. *Tellurium in Organic Synthesis*, second ed.; Elsevier: Amsterdam, **2007**. (b) Chivers T, Laitinen RS. *Chem. Soc. Rev.* **2015**, *44*, 1725-1739.
2. (a) Petragnani N, Stefani HA. *Tetrahedron* **2005**, *61*, 1613-1679. (b) Comasseto, J V, Barrientos-Astigarraga, RE. *Aldrichim. Acta* **2000**, *33*, 66-78.
3. (a) Stefani HA, Pena JM, Manarin F, Ando RA, Leal M, Petragnani N. *Tetrahedron Lett.* **2011**, *52*, 4398-4401. (b) Stefani HA, Pena JM, Gueogjian K, Petragnani N, Vaz, BG, Eberlin M. *Tetrahedron Lett.* **2009**, *50*, 5589-5595. (c) Tucci FC, Chieffi A, Comasseto JV, Marino JP. *J. Org. Chem.* **1996**, *61*, 4975-4989.
4. (a) Wendler EP, Dos Santos AA. *Synlett*, **2009**, *7*, 1034-1040. (b) Marino JP, McClure MS, Holub DP, Comasseto JV, Tucci FC. *J. Am. Chem. Soc*. **2002**, *8*, 1664-1668.
5. Yu F, Li P, Wang B, Han K. *J. Am. Chem. Soc*. **2013**, *135*, 7674-7680.
6. For a review see: Nogueira CW, Zeni G, Rocha JBT. *Chem. Rev*. **2004**, *104*, 6255-6286. (a) Jamier V, Ba LA, Jacob C. *Chem. Eur. J*. **2010**, *16*, 10920-10928 and references cited therein. (b) Lin T, Ding Z, Li N, Xu J, Luo G, Liu J, Shen J. *Carcinogenesis*, **2010**, *32*, 154-167. (c) Engman L, Al-Maharik N, McNaughton M, Birmingham A, Powis G. *Anti-Cancer Drugs* **2003**, *14*, 153-161. (d) Rooseboom M, Vermeulen NPE, Durgut F, Commandeur JNM. *Chem. Res. Toxicol*. **2002**, *15*, 1610-1618. (e) Tiano L, Fedeli D, Santroni A M, Villarini M, Engman L, Falcioni G. *Mutat Res*, **2000**, *464*, 269-277.
7. (a) Nagatomo M, Nishiyama H, Fujino H, Inoue M. *Angew. Chem. Int. Ed*. **2015**, *54*, 1537-1541. (b) Princival JL, Dos Santos AA, Comasseto JV. *J. Braz. Chem. Soc*. **2010**, *21*, 2042-2054. (c) Comasseto JV, Gariani RA. *Tetrahedron*, **2009**, *65*, 8447-8459. (d) Berlin S, Ericsson C, Engman L. *J. Org. Chem.* **2003**, *68*, 8386-8396.
8. (a) Kumar A, Kumar S. *Tetrahedron*, **2014**, *70*, 1763-1772. (b) Prasad CD, Balkrishna S J, Kumar A, Bhakuni BS, Shrimali K, Biswas S, Kumar S. *J. Org. Chem*. **2013**, *78*, 1434-1443. (c) Kassaee MZ, Motamedi E, Movassagh B, Poursadeghi S. *Synthesis* **2013**, *45*, 2337-2342. (d) Singh D, Deobald AM, Camargo LRS, Tabarelli G, Rodrigues OED, Braga AL. *Org. Lett*. **2010**, *12*, 3288-3291.
9. Yamago S, Iida K, Yoshida J. *Tetrahedron Lett.* **2001**, *42*, 5061-5064.
10. Sasaki K, Mori T, Doi Y, Kawachi A, Aso Y, Otsubo T, Ogura F. *Chem. Lett.* **1991**, 415-418.
11. Borges EL, Peglow TJ, Silva MS, Jacoby CG, Schneider PH, Lenardão EJ, Jacob RG, Perin G. *New Journal of Chemistry* **2016**, *40*, 2321-2326.

12. Oliveira JM, Freitas JCR, Comasseto JV, Menezes PH. *Tetrahedron* **2011**, *67*, 3003-3009.
13. (a) Musalova MV, Udalova SI, Musalov MV, Potapov VA, Amosova SV. *Russ. J. Org. Chem.*, **2016**, *52*, 1509-1510. (b) Musalova MV, Musalov MV, Udalova SI, Potapov VA, Amosova SV. *Russ. J. Org. Chem.*, **2015**, *51*, 1666-1667.
14. Revanna RH, Kumar RP, Hosamani A, Siddagangaiah PB. *J. Organomet. Chem*. **2015**, *799-800*, 61-69.
15. (a) Braga AL, Galetto FZ, Taube PS, Paixão MW, Silveira CC, Singh D, Vargas FJ. *J. Organomet. Chem*. **2008**, *693*, 3563-3566. (b) Sehnem JA, Vargas F, Milani P, Nascimento V, Braga AL. *Synthesis* **2008**, *8*, 1262.
16. (a) Sui D, Wu F, Xu Q, Yu X. *J. Chem. Res*. **2011**, 288-290. (b) VargasF, Comasseto JV. *J. Organomet. Chem*. **2009**, *694*, 122-126. (c) Dos Santos AA, Da Costa CE, Princival JL, Comasseto JV. *Tetrahedron: Asymmetry* **2006**, *17*, 2252-2259.
17. (a) Menichetti S, Capperucci A, Tanini D, Braga AL, Botteselle GV, Viglianisi C. *Eur. J. Org. Chem*., **2016**, 3097-3102. (b) Tanini D, Panzella L, Amorati R, Capperucci A, Pizzo E, Napolitano A, MenichettiS, d'Ischia M. *Org. Biol. Chem.* **2015**, 13, 5757-5764. (c) Degl'Innocenti A, Capperucci A, Cerreti A, Pollicino S, Scapecchi S, Malesci I, Castagnoli G. *Synlett* **2005**, 3063-3066. (d) Degl'Innocenti A, Capperucci A, Castagnoli G, Malesci I. *Synlett* **2005**, 1965-1983.
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**, 357-369. (c) Capperucci A, Tanini D, Borgogni C, Degl'Innocenti A. *Heteroat. Chem.*, **2014**, 25, 678-683.
19. Tanini D, D'Esopo V, Chen D, Barchielli G, Capperucci A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2017**, *192*, 166-168.
20. (a) Schneider A, Rodrigues OED, Paixão MW, Appelt HR, Braga AL, Wessjohann LA. *Tetrahedron Lett*. **2006**, *47*, 1019-1021. (b) Milton MD, Khan S, Singh JD, Mishra V, Khandelwal BL. *Tetrahedron Lett.* **2005**, *46*, 755-758.
21. (a) Lange H, Herzog U. *J. Organomet. Chem.* **2002**, *660*, 36-42. (b) Detty, M.R.; Seidler, M. D. *J. Org. Chem*. **1982**, *47*, 1354-1356.
22. Finger LH, Scheibe B, Sundermeyer J. *Inorg.Chem*., **2015**, *54*, 9568-9575.
23. (a) Elder PJW, Vargas-Baca I. *Phys. Chem. Chem. Phys.* **2016**, *18*, 30740-30747. (b) Duddeck H, Biallaβ A. *Magn. Reson. Chem.* **1994**, *32*, 303-311. (c) Baiwir M, Llabres G, Christiaens L, Luxen A, Piette J-L. *Magn. Reson. Chem.* **1986**, *24*, 362-363. (d) O'Brien DH, Dereu N, Huang C-K, Irgolic KJ, Knapp FF Jr. *Organometallics*, **1983**, *2*, 305-307.
24. Capperucci A, Tiberi C, Pollicino S, Degl'Innocenti A. *Tetrahedron Lett.* **2009**, *50*, 2808-2810.
25. (a) Yamago S, Iida K, Yoshida J-i. *Tetrahedron Lett.*,**2001**, *42*, 5061-5064. (b) SasakiK, Aso Y, Otsubo T, Ogura F. *Tetrahedron Lett.*,**1985**, *26*, 453-456
26. Pederson RL, Liu KKC, Rutan JF, Chen L, Wong CH. *J. Org. Chem.* **1990**, *55*, 4897-4901.

27. (a) Bieber MB, de Araujo MCF. *Molecules* **2002**, *7*, 902-906. (b) Berry MB, Craig, D. *Synlett* **1992**, 41-44. (c) Osborn HMI, Sweeney J. *Tetrahedron: Asymmetry* **1997**, *8*, 1693-1715.