A simple and non-conventional method for the synthesis of selected β-arylalkylchalcogeno substituted alcohols, amines and carboxylic acids

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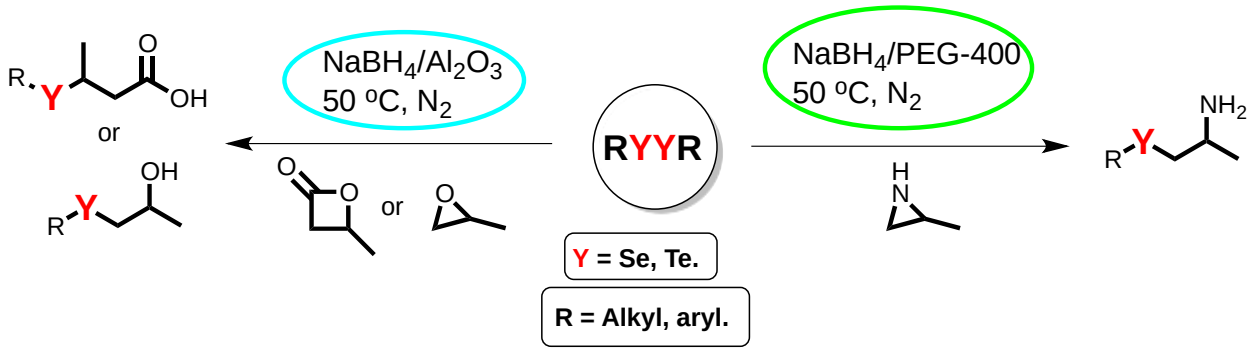
Abstract

A simple and mild procedure for the reaction of nucleophilic chalcogenium species (Se and Te) with lactones, epoxides or aziridines to prepare chalcogen-containing acids, alcohols and amines in non-conventional media is described. The chalcogenolate nucleophiles were generated *in situ* from the respective diorganyl dichalcogenide using $NaBH_4/Al_2O_3$ under solvent-free conditions (to prepare the chalcogen-containing acids and alcohols) or a $NaBH_4$/PEG-400 system (for the synthesis of chalcogen-containing amines) at 50 °C. The functionalized organochalcogenides were prepared in short reaction times and good yields.



Keywords: organochalcogen compounds; lactone; epoxide; aziridine; ring opening reaction.

Introduction

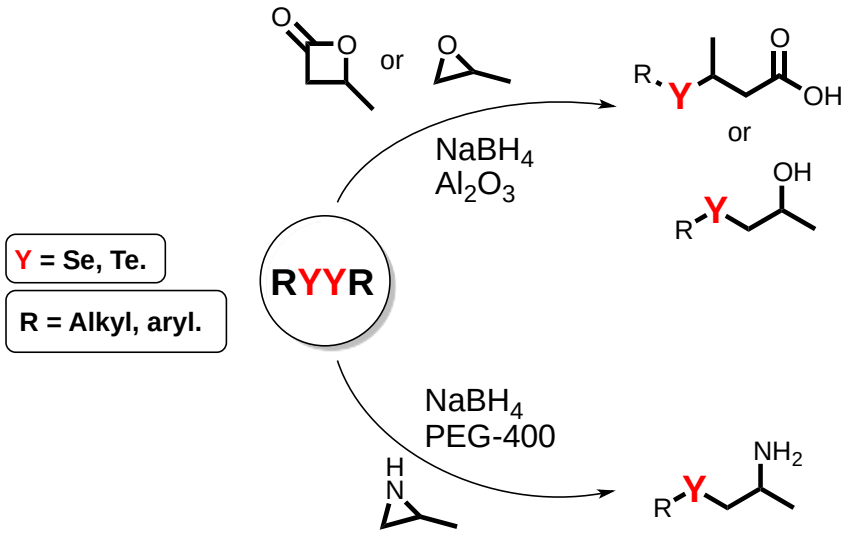
The development and applications of organoselenium and organotellurium compounds are well known.[1-3] Organochalcogen compounds, when associated with other functionalities, are versatile

reagents in organic synthesis.[4] Additionally, recently they have been applied in materials science,[5] biological and pharmacological studies[6] and organic synthesis. In view of these features, the search for greener reaction conditions and efficient methodologies to reduce wastes in the synthesis of new organochalcogen compounds has received much attention.[7-11]

On the other hand, the ring opening reaction by nucleophilic selenium and tellurium species is a very useful method to incorporate these elements into organic molecules, due to their soft nucleophilicity and low basicity. The use of cleaner procedures for producing nucleophilic species of organochalcogen has been an efficient strategy. Among the alternative methods employed for generation in situ of chalcogenolate anions for ring opening reactions of epoxides, aziridines and lactones are: Zn/HCl/biphasic,[12] Zn/THF/reflux,[13] Zn/HCl/[bmim][BF_4],[14] KOH/CuO/[bmim][BF_4][15] and Zn/$AlCl_3$/CH_3CN/70 ºC.[16] In most cases, these methods employ strong base or acid, high temperatures and volatile organic compounds (VOCs), limiting their use to a few functional groups.

Recently, we developed a new method to the *in situ* generation of chalcogenolate anions by using the $(RY)_2$/$NaBH_4$/PEG-400 system. This protocol was successfully used to prepare vinyl chalcogenides,[17] bis-chalcogen alkenes[18] and β-chalcogen esters, ketones and carboxylic acids.[19,20] By this procedure, the use of odoriferoous, unstable compounds and drastic reaction conditions are avoided, enabling us to explore the soft nucleophilicity of organochalcogen (Se and Te) compounds under mild conditions.

In this work, we describe the ring-opening reaction of lactones, epoxides and non-activated aziridines by chalcogenolate anions using solvent-free $NaBH_4$/Al_2O_3 or $NaBH_4$/PEG-400 systems at 50 ºC to prepare chalcogen-functionalized carboxylic acids, alcohols and amines (Scheme 1).



Scheme 1. Synthesis of chalcogen-containing acids, alcohols and amines under mild conditions.

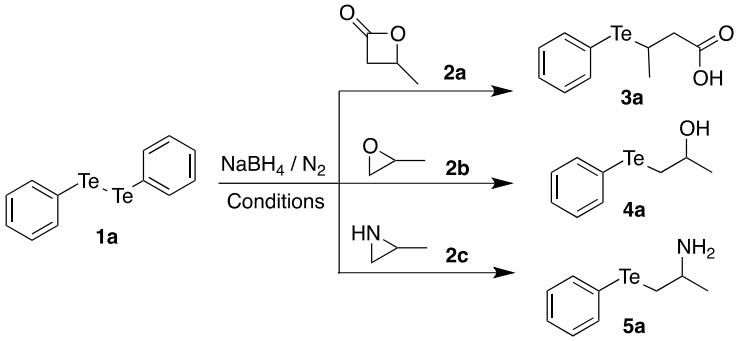
Discussion

In the initial experiments, we chose diphenyl ditelluride **1a** as the chalcogen source and β-methyl-β-propiolactone **2a**, propylene oxide **2b** and 2-methylaziridine **2c** as the electrophiles to evaluate the best conditions for the nucleophilic ring-opening reaction (Table 1). In the optimization study, we examined the influence of the amount of electrophile, the temperature and the use of solvent or solid-supported reducing agent. It was observed that the presence of solid support or solvent is essential for the success of the ring-opening of the three electrophiles (Table 1, entries 1, 17 and 22). As can be seen in Table 1, the use of 50.0 mg of solid support or 50 μL of solvent and an excess of electrophile (1.5 mmol) provided the best results (entries 5, 13 and 20). The reactions were monitored by thin layer chromatography (TLC) and gas chromatography (GC).

Among the conditions that were tested for the ring-opening of lactone **2a** to obtain the tellurium-containing acid **3a**, the most effective approach was that using $NaBH_4/Al_2O_3$ at 50 ºC, which afforded the product in 76% yield (Table 1, entry 3). A decrease in the yield of **3a** was observed when the reaction was performed either at room temperature or at 80 ºC (Table 1, entries 2 and 4), while 83% of the product was obtained using an excess of **2a** (1.5 equiv) with respect to the ditelluride **1a** (Table 1, entry 5). We also tested alternative solvents in the reaction, such as PEG-400, glycerol and ethanol. A satisfactory yield of **3a** was obtained only when $NaBH_4$/PEG-400 was used (Table 1, entries 9-10). Ethanol delivered **3a** in only 34% yield, while using glycerol caused the formation of a solid in the reaction vessel, thus preventing mixing of reagents (Table 1, entries 11-12). When propylene oxide **2b** was used as the electrophile, the profile of the reaction remained the same, with the $NaBH_4/Al_2O_3$ system, affording the desired tellurium-containing alcohol **4a** in 88% yield after 2 h at 50 ºC (Table 1, entry 13). The $NaBH_4$/PEG-400 system afforded the alcohol **4a** in 80% yield (Table 1, entry 15). We observed that SiO_2 is not as good as Al_2O_3 as the solid support and the ring-opening was less efficient for both lactone **2a** and epoxide **2b** (Table 1, entries 8 and 14). Ethanol was not a good solvent to prepare **4a**, which was obtained in only 41% yield after 2 h (Table 1, entry 16). A longer reaction time did not improve the yield.

In striking contrast to these results, $NaBH_4$/PEG-400 system gave the best result in the ring-opening of 2-methylaziridine **2c**, affording the tellurium-containing amine **5a** in 76% yield (Table 1, entry 20). Clearly, to produce chalcogen amines the presence of a hydrogen source is essential for success. These results are corroborated by those using conventional methodologies.[21,22] However, when the reaction was carried out in ethanol, the yield of **5a** decreased to 57% (Table 1, entry 21). The use of additional ethanol (2.0, 5.0 and 10.0 mL) did not change the outcome. Neither increasing the temperature (80 and 100 ºC) nor using a larger excess of aziridine **2c** (2.0, 3.0 and 5.0 equiv) improved the yield of **5a** using the $NaBH_4$/PEG-400 system.

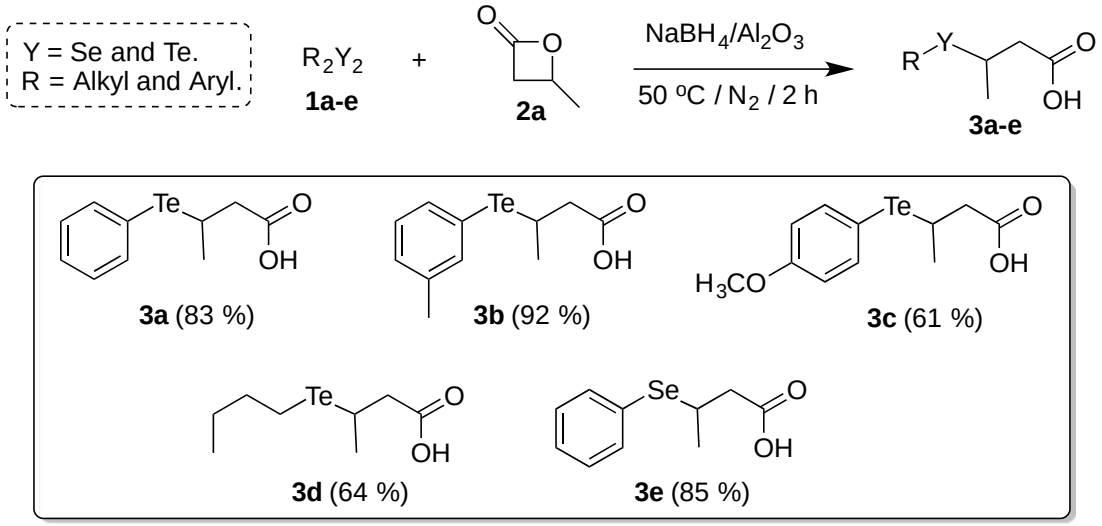
Table 1. Optimization of the ring-opening reactions of lactone, epoxide and aziridine by phenyltellurolate anion[a]



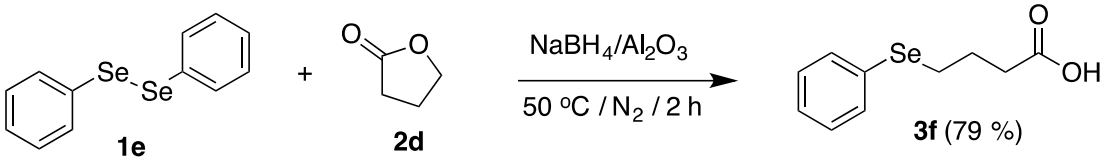
Entry	Conditions (mg or □L)	Electrophile (mmol)	Temp. (°C)	Yield (%)[b]
1	----	 (1.0)	25	22
2	Al_2O_3 (50)	**2a** (1.0)	25	53
3	Al_2O_3 (50)	**2a** (1.0)	50	76
4	Al_2O_3 (50)	**2a** (1.0)	80	55
5	Al_2O_3 (50)	2a (1.5)	50	83
6	Al_2O_3 (100)	**2a** (1.5)	50	73
7	Al_2O_3 (50)	**2a** (2.0)	50	80
8	SiO_2 (50)	**2a** (1.5)	50	63
9	PEG-400 (50)	**2a** (1.5)	50	78
10	PEG-400 (100)	**2a** (1.5)	50	67
11	ethanol (50)	**2a** (1.5)	50	34
12	glycerol (50)	**2a** (1.5)	50	----
13	Al_2O_3 (50)	 **(1.5)**	50	88
14	SiO_2 (50)	**2b** (1.5)	50	71
15	PEG-400 (50)	**2b** (1.5)	50	80
16	ethanol (50)	**2b** (1.5)	50	41
17	----	**2b** (1.5)	50	32
18	Al_2O_3 (50)	 (1.5)	50	48
19	SiO_2 (50)	**2c** (1.5)	50	25
20	PEG-400 (50)	2c (1.5)	50	76
21	ethanol (50)	**2c** (1.5)	50	57
22	----	**2c** (1.5)	50	18

[a] Reaction performed in the presence of 0.5 mmol of diphenyl ditelluride **1a** and 1 mmol of $NaBH_4$ for 2 h. [b] Yields are given for isolated products **3a**, **4a** or **5a**.

With the standard reaction conditions defined, we next investigated the scope of our methodology by employing a variety of chalcogenolate anions and electrophiles. To establish the generality for the lactone **2a** ring-opening reaction, various diorganyl dichalcogenides **1** were used in the presence of $NaBH_4/Al_2O_3$ system at 50 °C. The reactions proceeded with good yields employing diaryl and dialkyl dichalcogenides and they are not sensitive to electronic effects in the aromatic ring of the diaryl ditellurides (Scheme 2). This approach was successfully extended to diphenyl diselenide **1e** and the respective β-phenylselanyl carboxylic acid **3e** was obtained in 85% yield (Scheme 2). A good result was obtained when γ-butyrolactone **2d** was reacted with diphenyl diselenide **1e** in the presence of $NaBH_4/Al_2O_3$, yielding the γ-phenylselanyl acid **3f** in 79% yield (Scheme 3).



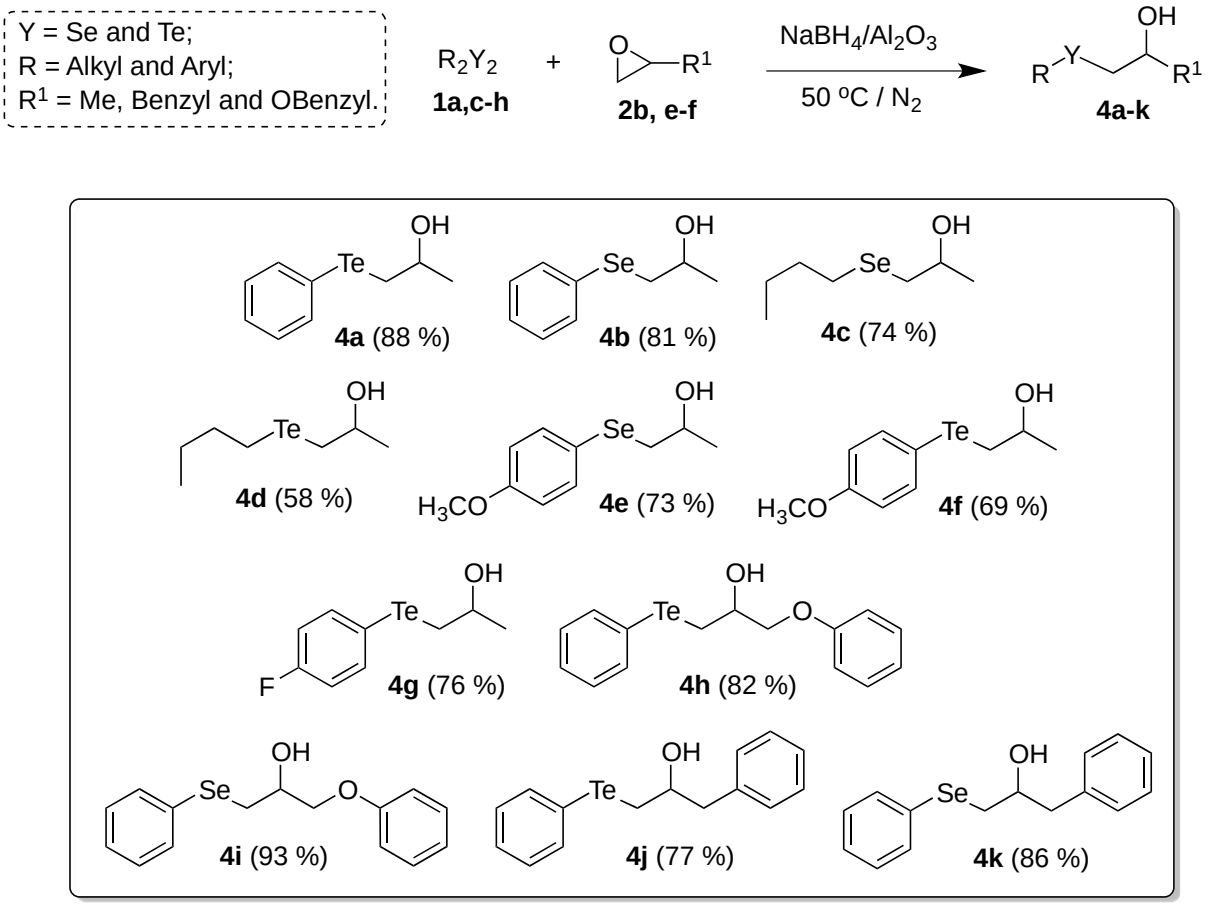
Scheme 2. Synthesis of β-organylchalcogenyl acids **3a–e** by the ring-opening reaction of β-methyl-β-propiolactone **2a**.



Scheme 3. Synthesis of the γ-phenylselanyl acid **3f** by the ring opening reaction of γ-butyrolactone **2d**.

Excellent results were obtained in the reaction of the chalcogenolate anions generated *in situ* with epoxides (Scheme 4). As can be seen in Scheme 4, β-chalcogen alcohols **4a-k** were obtained in good to excellent yields from different epoxides and a variety of ditellurides and diselenides. For instance, 2-benzyloxirane **2e** reacted with diphenyl ditelluride **1a** and diphenyl diselenide **1e** in the presence of $NaBH_4/Al_2O_3$ to afford, after 2 h, the respective phenyltelluro alcohol **4j** and

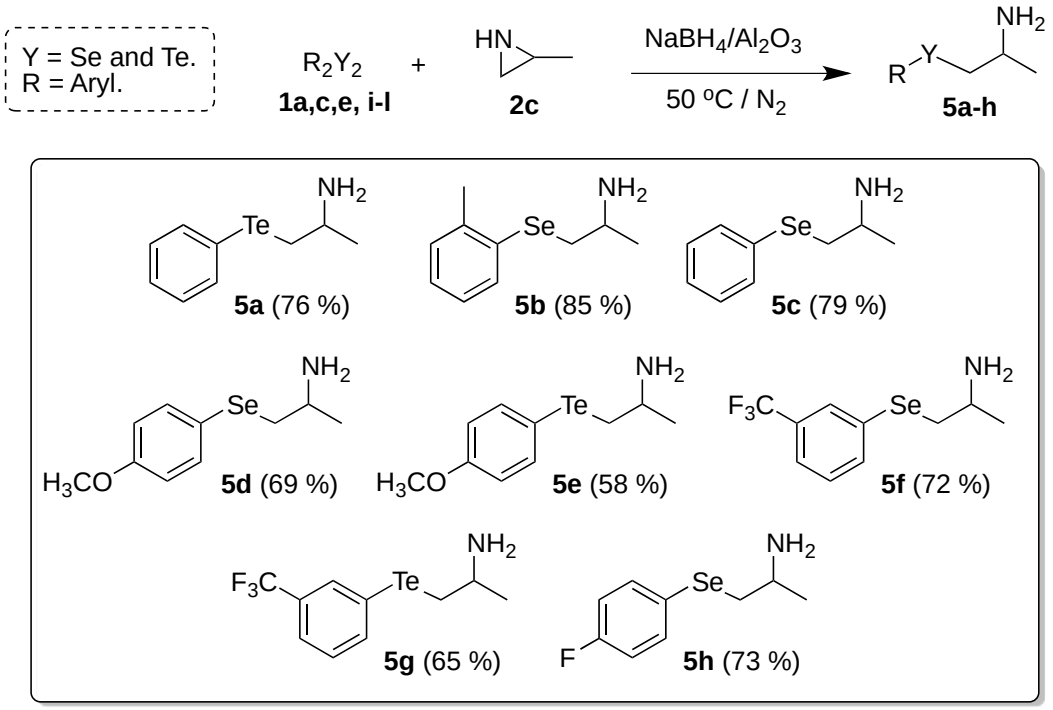
phenylseleno alcohol **4k** in 77 and 86% yields respectively (Scheme 4). An excellent result was obtained with 2-(phenoxymethyl)oxirane **2f**, which afforded the respective phenyltelluteluro and phenylseleno alcohols in 82 and 93% yields (Scheme 4, **4h** and **4i**). In the reaction of propylene oxide **2b** with dibutyl dichalcogenides **1d** and **1g**, it was necessary 3.0 equiv of the dichalcogenide to obtain satisfactory yields of the respective alcohols in 2 h (Scheme 4, **4d** and **4c**).



Scheme 4. Synthesis of chalcogen-containing alcohols **4a–k** by ring opening reactions of epoxides.

Next, we explored our protocol using $NaBH_4$/PEG-400 in the ring-opening of 2-methylaziridine **2c**, aiming to prepare β-chalcogen-containing amines **5a-h** (Scheme 5). We found that the ring-opening of aziridine **2c** is more efficient when nucleophilic selenium is used, producing the respective selenium-containing amines in better yields that the telluro-products. As in the ring-opening of lactone and epoxides (Schemes 2 and 4), the presence of electron-withdrawing or electron-releasing groups in the aromatic ring of the ditelluride and diselenide did not influence the yields of products in a predictable way. The yields of tellurium-containing aziridines ranged from 58 to 76%, while the selenium-containing aziridines were obtained with yields from 69 to 85% (Scheme 5). Because of the basicity of the chalcogen-containing amines, in these reactions aqueous NaCl was used instead NH_4Cl in the work up, to avoid product loss.

Regarding the stability of the obtained chalcogen compounds, we have observed the following order: chalcogen-containing amines > chalcogen-containing alcohols > chalcogen-containing acids. In the presence of solvent, light or at high temperatures, the chalcogen-containing acids are decomposed. Thus, work-up and purification steps must be performed rapidly. The same care should be taken when working with the chalcogen-containing alcohols, but the degradation rate is lower. In contrast, the chalcogen-containing amines are very stable and do not require the same attention.



Scheme 5. Synthesis of chalcogen-containing amines **5a–h** by ring opening reactions of 2-methylaziridine.

Conclusions

In conclusion, we have shown that the use of $NaBH_4$/PEG-400 and $NaBH_4/Al_2O_3$ as reducing systems to prepare chalcogenolate anions can be successfully applied in the synthesis of tellurium- and selenium-functionalized acids, alcohols and amines. This atom-economic strategy involves the ring-opening of lactones, epoxides and aziridines and is general for dialkyl and diaryl ditellurides and diselenides. Moreover, this simple procedure does not involve harsh reaction conditions and is not time consuming, with good-to-excellent yields of products being obtained in only a two-hour reaction.

Experimental Section

Analytical thin-layer chromatography (TLC) was performed by using aluminum-backed silica plates coated with a 0.25 mm thickness of silica gel 60 F254 (Merck), visualized with an ultraviolet light (λ = 254 nm). Either 300 MHz or 500 MHz acquired the NMR spectra. The ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) peak (δ0.0 ppm). The data are reported in chemical shift (δ), multiplicity, coupling constant (*J*) in Hertz and integrated intensity. The ^{13}C NMR chemical shifts were reported at either 75 or 125 MHz in ppm relative to $CDCl_3$ signal (δ77.0 ppm). The ^{77}Se NMR chemical shifts are reported in ppm relative to internal standard $C_6H_5SeSeC_6H_5$ (δ 467 ppm). The ^{125}Te NMR chemical shifts are reported in ppm relative to internal standard $C_6H_5TeTeC_6H_5$ (δ422 ppm). High-resolution mass spectra (HRMS) were acquired using a Bruker Daltonics MicroTOF instrument, operating electrospray ionization (ESI) mode with ion mass/charge (*m/z*) ratios as values in atomic mass units.

General procedure: To a 5 mL vial equipped with magnetic stirrer and a rubber septum under nitrogen, was added dialkyl or diaryl dichalcogenide (0.5 mmol) and the electrophile (1.5 mmol) followed by the catalyst system. To synthesize the chalcogen-containing acids and alcohols a $NaBH_4/Al_2O_3$ (1 mmol/50 mg) system was employed and to prepare chalcogen-containing amines a $NaBH_4$/PEG-400 (1 mmol/50 μL) system was used. The mixture was then stirred for 120 min at 50 ºC. The reaction progress was monitored by thin layer chromatography (TLC) and gas chromatography (GC). After 1 h at rt the reaction medium was diluted with AcOEt (20 mL) and washed with saturated aq solution of NH_4Cl (15 mL) for acids and alcohols and NaCl (15 mL) for amines. The phases were separated and the aq phase was extracted with AcOEt (2 × 20 mL). The organic phase was dried over $MgSO_4$ and the solvents were evaporated under reduced pressure. The product was purified by flash column chromatography eluting first with hexane to remove alkyl or aryl chalcogen byproducts and then with hexane/AcOEt (8:2) to remove the acids or alcohols and AcOEt only to remove the amine.

3-(phenyltellanyl)butanoic acid (3a). Red oil, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.82-7.84 (m, 2H); 7.32-7.36 (m, 1H); 7.22-7.26 (m, 2H); 3.65 (sex, *J* 7.1 Hz, 1H); 2.86 (dd, *J* 6.7 Hz and 16.4 Hz, 1H); 2.82 (dd, *J* 7.7 Hz and 16.4 Hz, 1H); 1.64 (d, *J* 7.15 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 178.0, 140.8, 129.2, 128.4, 111.2, 44.5, 24.2, 14.2. ^{125}Te NMR (94.74 MHz, $CDCl_3$, 25 ºC, $C_6H_5TeTeH_5C_6$ standard δ ppm 422): 709.4. IR *v* (cm^{-1}): 3064, 1708, 1573, 1433, 1297, 1222, 734, 693, 455. HR-MS: Calculated value $[M + 1]^+$ 294.9899; Found value $[M + H]^+$ 294.9912.

3-(m-tolyltellanyl)butanoic acid (3b). Red oil, 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.81 (d, *J* 7.4 Hz, 1H); 7.20-7.29 (m, 2H); 7.02 (dt, *J* 1.4 Hz, and 7.4 Hz, 1H); 3.70 (sex, *J* 7.14 Hz, 1H); 2.85 (m, 1H); 2.83 (d, *J* 1.8 Hz, 1H); 2.51 (s, 3H); 1.64 (d, *J* 7.11 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 178.3, 143.8, 140.6, 129.0, 128.9, 126.6, 116.3, 44.5, 27.6, 24.0, 14.0. IR *v* (cm^{-1}): 3053, 2862, 2731, 2627, 1565, 1341, 1075, 1049, 989, 931, 909,

796, 705, 648, 603, 539, 477, 403. HR-MS: Calculated value $[M + 1]^+$ 309.0086; Found value $[M + H]^+$ 309.011.

3-((4-methoxyphenyl)tellanyl)butanoic acid (3c). Red crystals, 61% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.74 (dd, *J* 2.0 Hz and 6.6 Hz, 2H); 6.78 (dd, *J* 2.0 Hz and 6.6 Hz, 2H); 3.80 (s, 3H); 3.56 (sex, *J* 7.1 Hz, 1H); 2.80 (d, *J* 0.6 Hz and 1.4 Hz, 2H); 1.59 (d, *J* 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 178.1, 160.2, 143.0, 115.1, 100.3, 55.1, 44.5, 24.1, 13.9. IR (cm^{-1}): 3433, 3016, 2857, 2732, 2066, 1967, 1835, 1563, 1461, 1397, 1340, 1133, 1102, 1064, 997, 911, 886, 789, 622, 588, 496, 418. HR-MS: Calculated value $[M + 1]^+$ 325.0005; Found value $[M + H]^+$ 324.9996

3-(butyltellanyl)butanoic acid (3d). Red oil, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 3.48 (sex, *J* 7.1 Hz, 1H); 2.86 (t, *J* 6.6 Hz, 2H); 2.73 (dt, *J* 7.4 and 3.1 Hz, 2H); 1.78 (qt, *J* 7.4 Hz, 2H); 1.68 (d, *J* 7.2 Hz, 3H); 1.38 (sex, *J* 7.4 Hz, 2H); 0.92 (t, *J* 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 178.3, 45.4, 34.4, 25.3, 24.9, 13.4, 8.5, 3.5. IR (cm^{-1}): 2926, 2730, 1164, 1105, 1074, 990, 889, 769, 604, 496. HR-MS: Calculated value $[M + 1]^+$ 275.0212; Found value $[M + H]^+$ 275.0194.

3-(phenylselanyl)butanoic acid (3e). Yellow oil, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.57-7.59 (m, 2H); 7.25-7.31 (m, 3H); 3.62 (sex, *J* 6.8 Hz, 1H); 2.73 (dd, *J* 6.3 Hz and 16.1 Hz, 1H); 2.61 (dd, *J* 4.0 Hz and 16.1 Hz, 1H); 1.46 (d, *J* 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 177.5, 135.7, 129.1, 128.1, 127.8, 42.4, 33.2, 21.8. IR (cm^{-1}): 3071, 2731, 1952, 1880, 1605, 1595, 1499, 1377, 1110, 931, 813, 671, 471. HR-MS: Calculated value $[M + 1]^+$ 245.0002; Found value $[M + H]^+$ 244.9987.

4-(phenylselanyl)butanoic acid (3f). Yellow oil, 79% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 1.99 (quin,(*J* 7.2 Hz, 2H), 2.51 (t, *J* 7.2 Hz, 2H), 2.94 (t, *J* 7.3 Hz, 2H), 7.24 (d, *J*8.5 Hz, 2H), 7.43 (d, *J* 8.5 Hz , 2H), 11.50 (br s, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 24.8, 27.1, 33.5, 127.7, 129.3, 133.3, 134.2, 179.3 ppm.

1-(phenyltellanyl)propan-2-ol (4a). Red oil, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.73-7.75 (m, 2H), 7.25-7.29 (m, 1H), 7.18-7.21 (m, 2H), 3.91 (sex, *J* 5.8 Hz, 1H), 3.13 (dd, *J* 4.5 and 12.3 Hz, 1H), 2.96 (dd, *J* 7.6 and 12.3 Hz, 1H), 1.29 (d, *J* 6.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 138.4, 129.3, 127.8, 111.1, 67.3, 23.7, 21.6. ^{125}Te NMR (94.7 MHz, $CDCl_3$, 25 ºC, $C_6H_5TeTeC_6H_5$, δ ppm): 365.8. HR-MS: Calculated value $[M + 23]^+$ 288.9950; Found value $[M + Na]^+$ 288.9937.

1-(phenylselanyl)propan-2-ol (4b). Yellow oil, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.50-753 (m, 2H), 7.24-7.26 (m, 3H), 3.85 (sex, *J* 3.48 Hz, 1H), 3.09 (dd, *J* 4.0 and 12.7 Hz, 1H), 2.87 (dd, *J* 8.2 and 12.7 Hz, 1H), 1.26 (d, *J* 6.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 132.9, 129.2, 129.1, 127.2, 66.0, 38.3, 22.3. ^{77}Se NMR (57 MHz, $CDCl_3$, 25 ºC, $C_6H_5SeSeC_6H_5$, δ ppm): 239.9 HR-MS: Calculated value $[M + 1]^+$ 217.0053; Found value [$[M + H]^+$ 217.0062.

1-(butylselanyl)propan-2-ol (4c). Yellow oil, 74 % yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 3.84 (sex, *J* 6.1 Hz, 1H), 2.77 (dd, *J* 3.9 and 12.7 Hz, 1H), 2.64 (br s, 1H), 2.58 (dt, *J* 3.4 and 7.2 Hz, 2H), 2.53 (dd, *J* 8.4 and 12.7 Hz, 1H), 1.64 (qt, *J* 7.2 Hz, 2H), 1.40 (sex, *J* 7.45

Hz, 2H), 1.27 (d, *J* 6.2 Hz, 3H), 0.92 (t, *J* 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 65.9, 34.6, 32.7, 24.2, 22.9, 22.4, 13.5. HR-MS: Calculated value $[M + 1]^+$ 197.0366; Found value $[M + H]^+$ 197.0372.

1-(butyltellanyl)propan-2-ol (4d). Red oil, 58 % yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 3.62 (sex, *J* 6.0 Hz, 1H), 2.58 (dd, *J* 4.9 and 12.0 Hz, 1H), 2.46 (dd, *J* 7.1 and 12.0 Hz, 1H), 2.37 (dt, *J* 3.8 and 6.8 Hz, 2H), 1.53 (qt, *J* 7.4 Hz, 2H), 1.20 (sex, *J* 7.4 Hz, 2H), 1.12 (d, *J* 6.1 Hz, 3H), 0.79 (t, *J* 7.35 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 68.0, 35.0, 25.6, 24.3, 16.4, 13.9, 3.32. HR-MS: Calculated value $[M + 23]^+$ 269.0263; Found value $[M + Na]^+$ 269.0262.

1-((4-methoxyphenyl)selanyl)propan-2-ol (4e). Yellow oil, 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.47 (d, *J* 8.8 Hz, 2H), 6.81 (d, *J* 8.7 Hz, 2H), 3.73-3.84 (m, 1H), 3.78 (s, 3H), 2.99 (dd, *J* 3.9 and 12.6 Hz, 1H), 2.77 (dd, *J* 8.4 and 12.6 Hz, 1H), 2.59 (br s, 1H), 1.24 (d, *J* 6.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 159.4, 135.8, 118.6, 114.8, 65.8, 55.2, 39.4, 22.2. ^{77}Se NMR (57 MHz, $CDCl_3$, 25 ºC, $C_6H_5SeSeC_6H_5$, δ ppm): 227.8. CG-MS - m/z^+ (relative intensity): 246 (88); 229 (30); 186 (100); 107 (28); 59 (17). HR-MS: Calculated value $[M + 1]^+$ 247.0159; Found value $[M + H]^+$ 247.0102.

1-((4-methoxyphenyl)tellanyl)propan-2-ol (4f). Yellow oil, 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.68 (d, *J* 7.2 Hz, 2H), 6.75 (d, *J* 7.4 Hz, 2H), 3.86-3.91 (m, 1H), 3.77 (s, 3H), 3.04 (dd, *J* 4.5 and 12.1 Hz, 1H), 2.87 (dd, *J* 7.6 and 12.1 Hz, 1H), 2.39 (br s, 1H), 1.27 (d, *J* 6.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 159.7; 140.9; 115.2; 99.9; 67.2; 55.0; 23.5; 21.7. ^{125}Te NMR (94.7 MHz, $CDCl_3$, 25 ºC, $C_6H_5TeTeC_6H_5$, δ ppm): 350.3. CG-MS - m/z^+ (relative intensity): 296 (94); 237 (48); 108 (100); 78 (15); 59 (11). HR-MS: Calculated value $[M + 1]^+$ 297.0056; Found value $[M + H]^+$ 297.0089.

1-((4-fluorophenyl)tellanyl)propan-2-ol (4g). Yellow oil, 76% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.23 (dd, *J* 4.3 Hz and 6.6 Hz, 2H), 6.90 (t, *J* 6.69 Hz, 2H), 3.88-3.93 (m, 1H), 3.09 (dd, *J* 4.6 and 12.2 Hz, 1H), 2.93 (dd, *J* 7.5 and 12.2 Hz, 1H), 2.31 (br s, 1H), 1.29 (d, *J* 6.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 162 (d, $J_{C\text{-}F}$ 246.6 Hz); 140.8 (d, $J_{C\text{-}F}$ 7.5 Hz); 116.6 (d, $J_{C\text{-}F}$ 20.8 Hz); 104.6 (d, $J_{C\text{-}F}$ 3.7 Hz); 67.3; 23.7; 21.9. ^{125}Te NMR (94.7 MHz, $CDCl_3$, 25 ºC, $C_6H_5TeTeC_6H_5$, δ ppm): 369.6 (d, $J_{Te\text{-}F}$ 9.5 Hz). CG-MS - m/z^+ (relative intensity): 283 (100); 242 (55); 95 (53); 59 (28). HR-MS: Calculated value $[M + 1]^+$ 284.9856; Found value $[M + H]^+$ 284.9832.

1-phenoxy-3-(phenyltellanyl)propan-2-ol (4h). Yellow oil, 82% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.72-7.75 (m, 2H), 7.22-7.27 (m, 3H); 7.14-7.19 (m, 2H); 6.91-6.96 (m, 1H); 6.82-6.85 (m, 2H); 4.11-4.18 (m, 1H); 4.02 (dd, *J* 7.2 and 9.3 Hz, 1H); 3.96 (dd, *J* 9.0 and 9.3 Hz, 1H); 3.16 (d, *J* 6.2 Hz, 2H); 2.78 (br d, *J* 4.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 158.2; 138.3; 129.4; 129.2; 127.8; 121.1; 114.4; 111.4; 71.4; 70.0; 13.6. ^{125}Te NMR (94.7 MHz, $CDCl_3$, 25 ºC, $C_6H_5TeTeC_6H_5$, δ ppm): 389.3. CG-MS - *m/z* (relative intensity): 356 (100); 207 (46); 133 (71); 107 (48); 91 (25); 77 (63). HR-MS: Calculated value $[M + 1]^+$ 359.0213; Found value $[M + H]^+$ 359.0191.

1-phenoxy-3-(phenylselanyl)propan-2-ol (4i). Yellow oil, 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.51-7.55 (m, 2H); 7.21-7.28 (m, 5H); 6.91-6.97 (m, 1H); 6.83-6.86 (m, 2H); 4.05-4.14 (m, 1H); 4.03 (dd, *J* 4.1 and 9.3 Hz, 1H); 3.99 (dd, *J* 5.8 and 9.3 Hz, 1H); 3.21 (dd, *J* 5.6 and 12.8 Hz, 1H); 3.12 (dd, *J* 6.8 and 12.8 Hz, 1H); 2.78 (br d, *J* 4.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 158.2; 132.8; 129.4; 129.2; 129.1; 127.2; 121.1; 114.4; 70.3; 69.0; 31.7. ^{77}Se NMR (94.7 MHz, $CDCl_3$, 25 ºC, $C_6H_5SeSeC_6H_5$, δ ppm): 242.5. CG-MS - *m/z* (relative intensity): 307 (96); 215 (100); 183 (28); 134 (59); 91 (30); 77 (42). HR-MS: Calculated value $[M + 1]^+$ 309.0316; Found value $[M + H]^+$ 309.0351.

1-phenyl-3-(phenyltellanyl)propan-2-ol (4j). Yellow oil, 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.65-7.68 (m, 2H); 7.11-7.27 (m, 8H); 3.92-3.97 (m, 1H); 3.08 (dd, *J* 4.5 and 12.1 Hz, 1H); 2.97 (dd, *J* 7.4 and 12.1 Hz, 1H); 2.86 (dd, *J* 5.4 and 13.5 Hz, 1H); 2.78 (dd, *J* 7.2 and 13.5 Hz, 1H); 2.37 (br d, *J* 3.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 138.1; 137.8; 129.2; 129.1; 128.4; 127.6; 126.4; 111.4; 72.2; 44.0; 18.4. ^{125}Te NMR (94.7 MHz, $CDCl_3$, 25 ºC, $C_6H_5TeTeC_6H_5$, δ ppm): 377.4. CG-MS - *m/z* (relative intensity): 340 (55); 207 (43); 91 (100); 77 (25). HR-MS: Calculated value $[M + H]^+$ 343.0263; Found value $[M^+ + 1]$: 343.0211.

1-phenyl-3-(phenylselanyl)propan-2-ol (4k). Yellow oil, 86% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.42-7.46 (m, 2H); 7.12-7.27 (m, 8H); 3.86-3.94 (m, 1H); 3.07 (dd, *J* 4.2 and 12.6 Hz, 1H); 2.90 (dd, *J* 7.9 and 12.6 Hz, 1H); 2.85 (dd, *J* 5.8 and 7.7 Hz, 1H); 2.75 (dd, *J* 6.9 and 7.7 Hz, 1H); 2.49 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 137.7; 132.6; 129.4; 129.3; 129.0; 128.4; 127.0; 126.4; 71.0; 42.7; 35.6. ^{77}Se NMR (94.7 MHz, $CDCl_3$, 25 ºC, $C_6H_5SeSeC_6H_5$, δ ppm): 240.7. CG-MS - *m/z* (relative intensity): 291 (31); 200 (61); 183 (74); 157 (56); 115 (95); 91 (100); 77 (18). HR-MS: Calculated value $[M + 1]^+$ 293.0366; Found value $[M + H]^+$ 293.0315.

1-(phenyltellanyl)propan-2-amine (5a). Red oil, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.74 (dd, *J* 1.0 and 11.4 Hz, 2H), 7.25-7.28 (m, 1H), 7.19 (t, *J* 7.55 Hz, 2H), 3.21 (sex, *J* 6.3 Hz, 1H), 3.07 (dd, *J* 6.0 and 12.1 Hz, 1H), 3.01 (dd, *J* 6.7 and 12.1 Hz, 1H), 1.26 (d, *J* 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 138.4, 129.3, 127.8, 111.4, 48.2, 23.4, 19.6. IR ν (cm^{-1}): 3314; 3104; 2934; 2870; 1556; 1445; 1088; 698. CG-MS - m/z^+ (relative intensity %): 265 (1); 222 (16); 57 (13); 44 (100). HR-MS: Calculated value $[M + 1]^+$ 266.0110; Found value $[M + H]^+$ 266.0118.

1-(o-tolylselanyl)propan-2-amine (5b). Yellow oil, 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.43 (d, *J* 7.5 Hz, 2H), 7.16 (d, *J* 7.1 Hz, 1H), 7.14 (t, *J* 6.4 Hz, 1H), 7.09 (t, *J* 6.4 Hz, 1H), 3.09 (sex, *J* 6.3 Hz, 1H), 2.99 (dd, *J* 4.7 and 12.1 Hz, 1H), 2.77 (dd, *J* 8.2 and 12.1 Hz, 1H), 2.42 (s, 1H), 1.18 (d, *J* 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 139.3, 131.7, 131.0, 129.9, 126.7, 126.4, 46.9, 37.9, 23.5, 22.4. IR (KBr) ν (cm^{-1}): 3351; 3058; 2964; 2868; 1590; 1466; 1036; 749. CG-MS - *m/z* (relative intensity %): 229 (3); 186 (18); 91 (20); 44 (100). HR-MS: Calculated value $[M + 1]^+$ 230.0369; Found value $[M + H]^+$ 230.0358.

1-(phenylselanyl)propan-2-amine (5c). Yellow oil, 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.51-752 (m, 2H), 7.23-7.26 (m, 3H), 3.09 (sex, *J* 4.9 Hz, 1H), 3.03 (dd, *J* 4.9

and 12.2 Hz, 1H), 2.81 (dd, *J* 7.8 and 12.2 Hz, 1H), 1.18 (d, *J* 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 132.7, 129.9, 129.0, 126.9, 46.6, 38.8, 23.2. IR (KBr) *v* (cm^{-1}): 3367; 3049; 2941; 2870; 1604; 1420; 1012; 776. CG-MS - m/z^+ (relative intensity %): 215 (2); 172 (22); 57 (9); 44 (100). HR-MS: Calculated value $[M + 1]^+$ 216.0213; Found value $[M + H]^+$ 216.0221.

1-((4-methoxyphenyl)selanyl)propan-2-amine (5d). Yellow oil, 69% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.48 (d, *J* 8.7 Hz, 2H), 6.81 (d, *J* 8.8 Hz, 2H), 3.78 (s, 3H), 3.02 (sex, *J* 4.6 Hz, 1H) 2.93 (dd, *J* 4.5 and 12.2 Hz, 1H), 2.69 (dd, *J* 8.8 and 12.2 Hz, 1H), 1.14 (d, *J* 6.27 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 159.3, 135.6, 119.7, 114.7, 55.2, 46.5, 40.1, 23.2. IR (KBr) *v* (cm^{-1}): 3351; 3282; 2961; 2836; 1590; 1491; 1348; 1029; 825; 519. CG-MS - m/z^+ (relative intensity %): 245 (12); 202 (32); 187 (17); 58 (17); 44 (100). HR-MS: Calculated value $[M + 1]^+$ 246.0318; Found value $[M + H]^+$ 246.0284.

1-((4-methoxyphenyl)tellanyl)propan-2-amine (5e). Yellow oil, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.68 (d, *J* 8.7 Hz, 2H), 6.74 (d, *J* 6.7 Hz, 2H), 3.77 (s, 3H), 3.08 (sex, *J* 6.2 Hz, 1H) 2.99 (dd, *J* 5.1 and 11.9 Hz, 1H), 2.81 (dd, *J* 7.2 and 11.90 Hz, 1H), 2.28 (br s, 2H), 1.17 (d, *J* 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 159.6, 140.8, 115.1, 100.3, 55.0, 47.5, 24.2, 22.2. IR (KBr) *v* (cm^{-1}): 3354; 3275; 2943; 2835; 1597; 1456; 1332; 1029; 811; 533. CG-MS - m/z^+ (relative intensity %): 295 (5); 252 (44); 237 (11); 58 (10); 44 (100). HR-MS: Calculated value $[M + 23]^+$ 318.0215; Found value $[M + Na]^+$ 318.0180.

1-((3-(trifluoromethyl)phenyl)selanyl)propan-2-amine (5f). Yellow oil, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.75 (s, 1H); 7.68 (d, *J* 7.8 Hz, 1H), 7.47 (d, *J* 7.8 Hz, 1H), 7.36 (t, *J* 7.75 Hz, 1H), 3.13 (sex, *J* 4.9 Hz, 1H) 3.07 (dd, *J* 4.7 and 12.1 Hz, 1H), 2.87 (dd, *J* 7.6 and 12.1 Hz, 1H), 1.56 (br s, 2H), 1.18 (d, *J* 6.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 135.5 ($J_{C\text{-}F3}$ 1.2 Hz), 131.5, 131.2 ($J_{C\text{-}F3}$ 32.5 Hz), 129.2, 128.8 ($J_{C\text{-}F3}$ 3.7 Hz), 123.6 ($J_{C\text{-}F3}$ 271.3 Hz), 123.5 ($J_{C\text{-}F3}$ 3.7 Hz). IR (KBr) *v* (cm^{-1}): 3352; 3284; 2966; 2872; 1579; 1328; 1166; 959; 795; 695. CG-MS - *m/z* (relative intensity %): 283 (1); 240 (20); 57 (8); 44 (100). HR-MS: Calculated value $[M + 1]^+$ 284.0087; Found value $[M + H]^+$ 284.0112.

1-((3-(trifluoromethyl)phenyl)tellanyl)propan-2-amine (5g). Yellow oil, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.96 (s, 1H); 7.88 (d, *J* 7.6 Hz, 1H), 7.4 (d, *J* 7.8 Hz, 1H), 7.29 (t, *J* 7.7 Hz, 1H), 3.12-3.18 (m, 2H), 2.96 (dd, *J* 5.1 and 13.3 Hz, 1H), 1.43 (br s, 2H), 1.19 (d, *J* 6.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 141.2, 134.6 ($J_{C\text{-}F3}$ 3.7 Hz), 131.0 ($J_{C\text{-}F3}$ 31.2 Hz), 129.2, 124.2 ($J_{C\text{-}F3}$ 3.7 Hz), 123.5 ($J_{C\text{-}F3}$ 271.2 Hz), 112.7. IR (KBr) *v* (cm^{-1}): 3351; 3279; 2953; 2881; 1591; 1302; 1196; 949; 778; 667. CG-MS - m/z^+ (relative intensity %): 332 (1); 290 (25); 57 (16); 44 (100). HR-MS: Calculated value $[M + 23]^+$ 355.9984; Found value $[M + Na]^+$ 355.9923.

1-((4-fluorophenyl)selanyl)propan-2-amine (5h). Yellow oil, 73% yield. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 7.50 (dd, *J* 8.7 and 5.4 Hz, 2H); 6.96 (t, *J* 8.7 Hz, 2H), 3.05 (sex, *J* 6.3 Hz, 1H), 2.98 (dd, *J* 12.0 and 4.6 Hz, 1H), 2.76 (dd, *J* 7.8 and 12.0 Hz, 1H), 1.80 (br s, 2H), 1.15 (d, *J* 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC, TMS, δ ppm): 162.7 ($J_{C\text{-}F}$ 981.5 Hz), 135.2 ($J_{C\text{-}F}$ 31.5 Hz), 124.2 ($J_{C\text{-}F}$ 13.7 Hz), 116.1 ($J_{C\text{-}F}$ 85.3 Hz), 46.5, 39.8, 23.2. IR (KBr) *v* (cm^{-1}): 3351; 3281; 2964; 2870; 1584; 1487; 1226; 1157; 826; 591. CG-MS - m/z^+ (relative intensity

%): 233 (1); 190 (25); 109 (7); 44 (100). HR-MS: Calculated value $[M + 23]^+$ 256.0119; Found value $[M + Na]^+$ 256.0095.

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