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First synthesis and stereochemistry of enantiomerically pure spiroselenurane and spirotellurane using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand

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Abstract

The first synthesis of enantiomerically pure spiroselenuranes **8a**–**d** and spirotelluranes **12a**,**b**, using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand, has been developed and proceeds in good yield and with excellent diastereoselectivity. The X-ray analysis of spirotellurane **12a** indicated that the spirochalcogenuranes have a trigonal bipyramidal (TBP) structure around the chalcogenium atom. A comparison of the spectroscopic properties of spirochalcogenuranes is also discussed.

1. Introduction

Chalcogenuranes have been regarded as intermediates in many organic reactions involving the chalcogenonium(IV) compounds, such as Swern oxidation and Pummerer rearrangement.[1] Much attention has been centred on the study of the synthesis and isolation of achiral spirochalcogenuranes.[2] Since the first synthesis of stable spirosulfurane by Kapovits et al., some spirosulfuranes have been synthesized or separated, and the structure as well as the hydrolysis of these compounds has been reported.[3] A recent study on spiroselenuranes and spirotelluranes has indicated that they are more stable than their sulfur analogues.[4] On the other hand, much attention has been devoted to the discovery of chalcogenonium compounds that mimic the properties of the selenium-containing enzyme (GSH-Px) and other enzymes which play important roles in the human body.[5] The formation of chalcogenonium(IV) species, chalcogenuranes, has been proposed as the key process in some of the reactions. Additionally, recent research has shown that some organotellurium(IV) compounds with the spirocyclic structure

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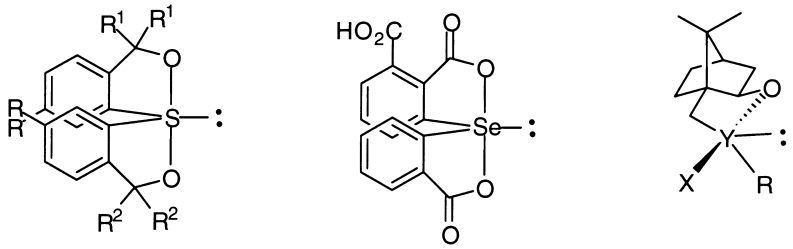
possess different levels of immunomodulating activity and could act as a potent immunomodulator with a variety of potential therapeutic applications.[5k] Therefore, the synthesis and isolation of chiral spirochalcogenuranes is important in order to investigate the stereochemical features of the reactions as well as their role in the biomimic reactions.

Although there have been several examples of the synthesis and isolation of the optically active spirosulfuranes **1a–d** (Scheme 1),[6] there is only one report on the isolation of the optically active spiroselenurane **2** via the resolution,[7] however, the stereochemistry and the enantiopurity of **2** were not clear. To the best of our knowledge, there is no report on the synthesis or the isolation of the chiral spirotelluranes; and consequently, very little is known on the systematic comparison of the properties of spirochalcogenuranes.



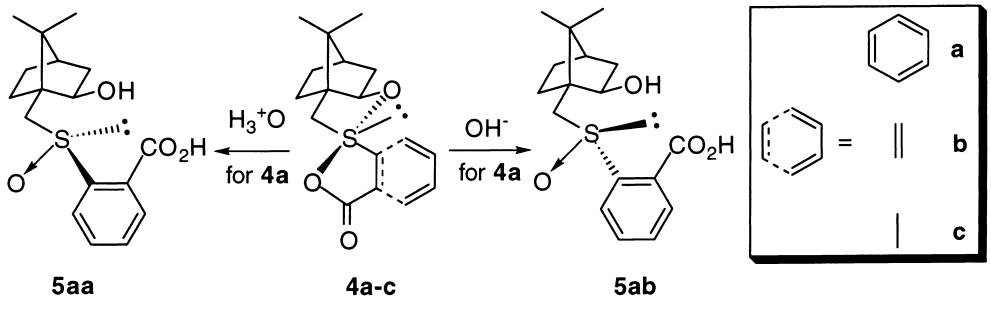
1a: R = H, R^1 = H, R^2, R^2 = O
1b: R = H, R^1,R^1 = R^2,R^2 = O
1c: R = H, R^1 = R^2 = Me
1d: R = *t*-Bu, R^1 = R^2 = CF_3

2

3a: Y = S
3b: Y = Se
3c: Y = Te
X = halogen

Scheme 1.

Due to our interest regarding the mechanism and stereochemistry of the reaction of hypervalent chalcogenium compounds, we have reported the synthesis and reaction of the halooxachalcogenuranes **3a–c**[8] (Scheme 1) and spirosulfurane **4**[9] (Scheme 2) by using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand.



5aa **4a-c** **5ab**

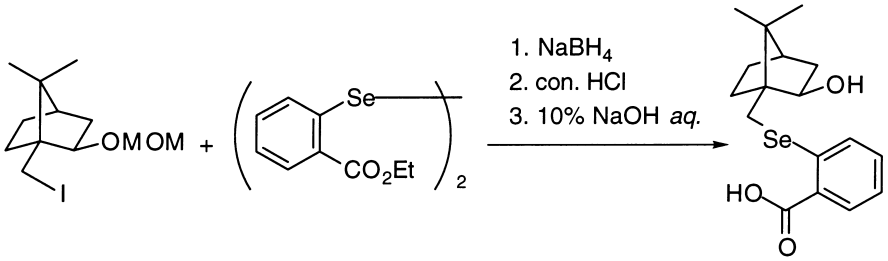
Scheme 2.

Nucleophilic reactions of halooxachalcogenuranes **3a–c** provided an excellent method for the asymmetric synthesis of enantiomerically pure chalcogenonium(IV) compounds, especially the chiral selenonium(IV) and telluronium(IV) compounds, such as selenoxides,[8a,g] selenonium ylides[8b] and telluronium salts.[8h,j] Hydrolysis of enantiomerically pure alkoxyacyloxyspirosulfurane **4a** under different conditions gave, diastereospecifically, corresponding sulfoxides **5aa** and **5ab** with the opposite absolute configuration at the sulfur atom (Scheme 2). The different reactivity of the two apical S–O bonds under various conditions has been considered as the most important reason to account for the high diastereoselectivity of the hydrolysis.[9] Herein, we report our recent result on the asymmetric synthesis and the structure

determination of the title compounds and a comparison of the stability and spectral characteristics of spirochalcogenuranes.

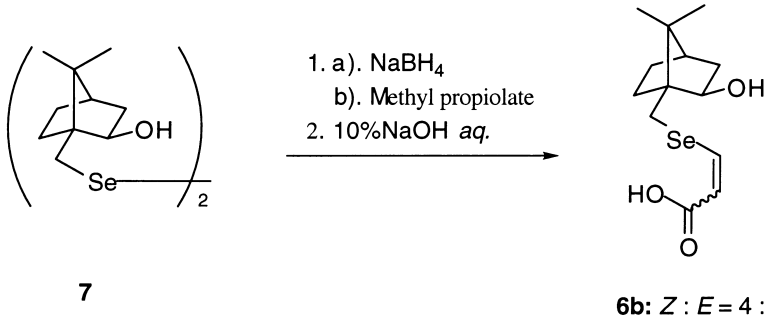
2. Results and discussion

The spiroselenuranes **8a–d** were prepared as shown in Scheme 3. Reaction of (1*S*)-10-iodo-2-*exo*-methoxymethoxy-borneol with 2,2′-diselenobisethylbenzoate in abs. EtOH in the presence of $NaBH_4$ followed by deprotection with conc. HCl in MeOH and alkaline hydrolysis of the ester gave selenide **6a** as a white solid (Eq. 1). Selenide **6b** was prepared by the 1,4-addition of methyl propiolate with the selenolate anion, which was generated in situ from di-(2-*exo*-hydroxy-10-bornyl) diselenide and sodium borohydride, followed by alkaline hydrolysis (Eq. 2). Selenide **6c** was also prepared from di-(2-*exo*-hydroxy-10-bornyl) diselenide **7** (Eq. 3), and selenide **6d** was obtained by the reaction of di-(3-hydroxy)propyl diselenide with (1*S*)-10-iodo-2-*exo*-borneol (Eq. 4). Treatment of the selenides **6a–d** with *t*-BuOCl in a CH_2Cl_2 solution followed by reaction with NEt_3 afforded the corresponding enantiomerically pure spiroselenuranes **8a–d** in high yields as single diastereoisomers, respectively, and no other epimeric compound could be detected.[10] The reactions were believed to proceed through the diastereoselective generation of the intermediates of chloroselenuranes similar in structure to **3b** followed by intramolecular cyclization under the basic conditions.



(1)

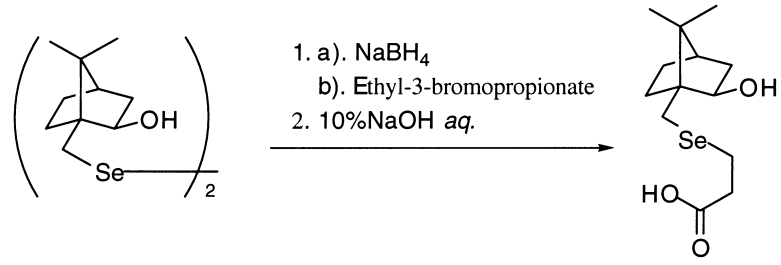
6a



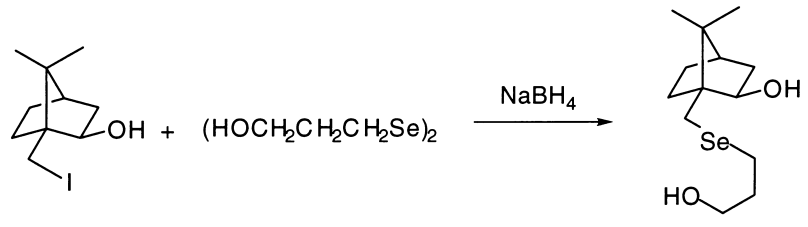
(2)

7

6b: $Z : E = 4 : 1$

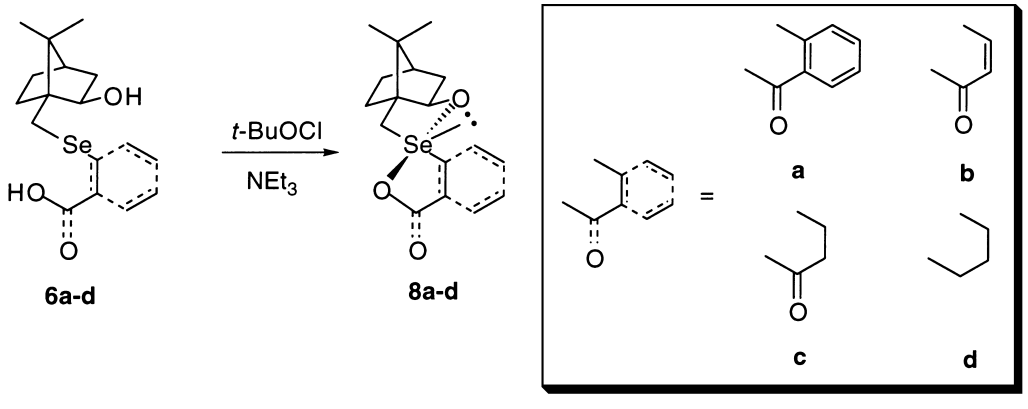


7 6c (3)



6d (4)

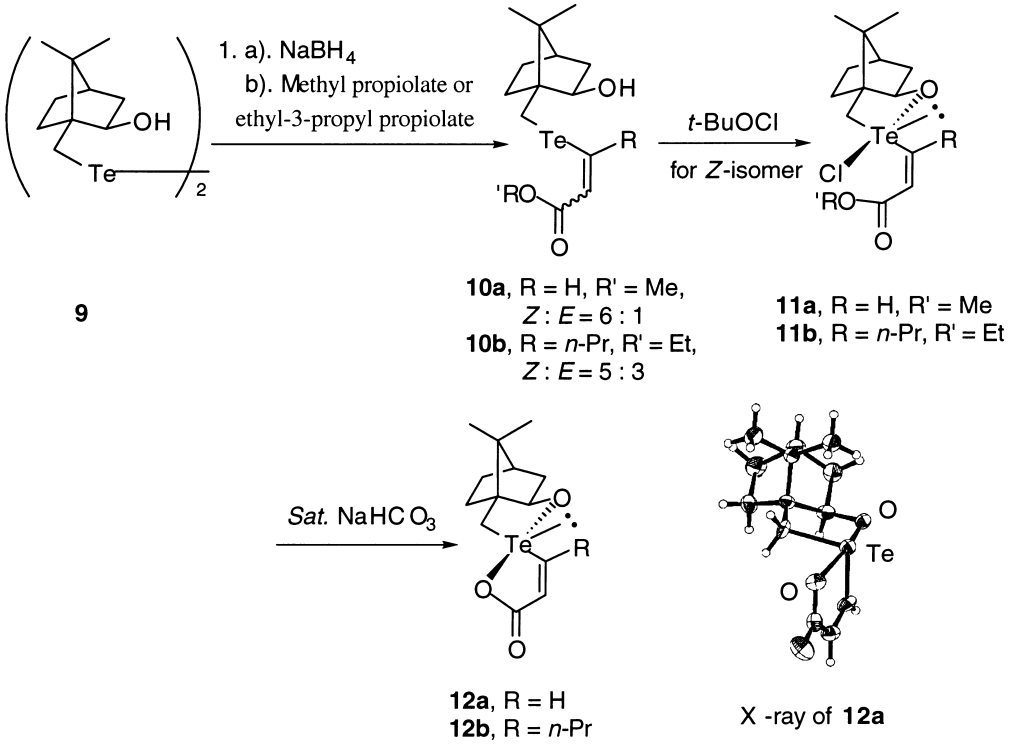
The formation of the five-membered spiroselenurane structure was confirmed by spectroscopic techniques. In the ^{1}H NMR spectra of spiroselenuranes, the chemical shift of protons (Ha, Hb) on the methylene bound to the selenium atom is shifted considerably downfield compared with that of their selenide analogues. In the ^{13}C NMR spectra, the chemical shift of the carbon (C1) bound to the alkoxy oxygen at the bornyl group of spiroselenuranes **8a–d** is at about 90 ppm whereas the shift of the corresponding carbon atom of selenides is 77 ppm. In the ^{77}Se NMR spectra, the chemical shift of selenurane is between 844 and 949 ppm, while that of selenides are smaller than 200 ppm. These spectral features could be considered characteristic of compounds with a trigonal bipyramidal (TBP) structure.[8]



Scheme 3.

Spiroselenuranes **8a–d** obtained here are considerably more stable than their sulfur analogues. For example, **8c** or **8d** could be obtained by extraction of the reaction mixture from water, while the spirosulfurane **4c** with the same structure of **8c** was sensitive to moisture and was readily hydrolyzed to give the sulfoxide. Thus, the structure of **4c** could only be detected by the ^{1}H NMR of the crude product. Attempts to synthesize the spirosulfurane with the same structure as **8d** only led to the formation of the sulfoxide.

The synthesis of chiral spirotelluranes were carried out as illustrated in Scheme 4. (1*S*)-10-Iodo-2-*exo*-hydroxy-borneol was converted to the corresponding di-(2-*exo*-hydroxy-10-bornyl) ditelluride **9** in 42% yield.[11] Addition of tellurolate anion, which was prepared in situ from ditelluride **9** and sodium borohydride, to methyl propiolate or ethyl-3-propyl propiolate produced the corresponding tellurides **10a** and **10b** as red oil. Separation of the *E*- and *Z*-isomers of **10a**,**b** followed by treatment with *t*-BuOCl in CH_2Cl_2 solution afforded the enantiomerically pure chlorotelluranes **11a** and **11b**, respectively, in high yields as the sole product. Hydrolysis of the *Z*-isomers of the chlorotelluranes **11a** and **11b** under basic conditions gave the corresponding spirotelluranes **12a** and **12b** as colorless crystals in good yields as a single diastereoisomer.[10]

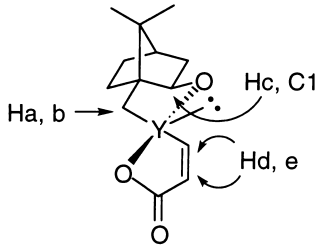


Scheme 4.

The structure of **12a** and **12b** was determined by the spectroscopy as well as an X-ray analysis of **12a** (Scheme 4). As with that of spiroselenuranes and selenides, a similar tendency of the downfield shift of the protons (Ha, Hb, Hc) and the carbon (C1) were observed in the ^{1}H and ^{13}C NMR of the spirotelluranes **12a**,**b** compared with that of the corresponding tellurides. The ^{125}Te NMR chemical shift of **12a** appears at 1894 ppm, which is consistent with the value of halooxatelluranes but lower than that of 1,1′spirobi(3*H*-2,1-benzoxatellurole)-3-one reported by Furukawa et al.[4d]

The X-ray analysis of **12a** indicated that the spirotellurane **12a** has a slightly distorted trigonal bipyramidal (TBP) geometry around the central tellurium atom as shown in Scheme 4. As expected, the two electronegative oxygen atoms bound to the tellurium atom occupy apical positions, while two carbon atoms and the lone electron pair occupy equatorial positions. The O–Te–O moiety with the angle of 177.1° in **12a** is almost linear. Similar to the alkoxyacyloxyspirosulfuranes,[9,12] the length of Te–O(acyloxy) [2.20(7) Å] is longer than that of the Te–O(alkoxy) [2.02(7) Å] in this alkoxy-acyloxyspirotellurane which reflects the polarized nature of the hypervalent O–Te–O bond resulting from the difference in the electronegativities of the apical ligands. The formation of the spirotellurane

Table 1



4b, Y = S
8b, Y = Se
12a, Y = Te

Compound	^{1}H NMR			^{13}C NMR
(X =)	Ha, Hb	Hc	Hd, He	C1
4b (S)	3.19, 4.40	4.33	6.80, 6.84	95.7
8b (Se)	3.06, 4.18	4.26	7.02, 7.24	94.9
12a (Te)	2.60, 3.55	4.06	7.43, 7.45	93.7

was considered through the following reactions: successive hydrolysis of the ester followed by the dissociation of the Te–Cl bond and the attack of the carboxylate anion at the resulting telluronium cation. The geometry of the double bond was found to play an important role in this reaction, only the *Z*-isomers of **11a**,**b** could be converted to the corresponding spirotelluranes **12a**,**b**, the similar hydrolysis of the *E*-chlorotelluranes (*E*-**11a**,**b**) gave only the decomposition of the starting materials.

The chemical shift of the quaternary carbon in the alkoxy ligands of spirosulfuranes of type **1** was found to be very responsive to the change of the nature of *trans* apical substitutes. In the ^{13}C NMR spectrum, the chemical shift of this carbon moved to a markedly lower field, which indicated the higher polarization of the hypervalent O–S–O bond, with increasing electronegativities of the *trans* apical ligands.

With the spirochalcogenuranes in hand, we then compared the spectroscopic characteristics of these compounds having the same structure but with a different chalcogenium atom at the centre of the spiro ring (Table 1). In the ^{1}H NMR spectra, the methylene protons (Ha, Hb) as well as the proton (Hc) of the alkoxy ligand in the bornyl group are shifted upfield when the chalcogenium changes from S to Se, or Se to Te. The same properties were obtained for the carbon (C1) in the ^{13}C NMR spectrum of these compounds. In contrast, the alkene protons (Hd, He) are shifted downfield when the chalcogenium changes from S to Se, or Se to Te. Although reasons to account for these results are not clear at present, the changing of the central chalcogenium atom would result in a different extent of polarization of the O–Y–O bonds and distribution of electrons which might finally appear as a variance of the chemical shift in the NMR spectra.

In conclusion, the enantiomerically pure spiroselenuranes **8a**–**d** and spirotellurane **12a**,**b** have been synthesized in good yields and with excellent diastereoselectivity, by using the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand. The structure and the stereochemistry of the spirochalcogenuranes have been studied by spectroscopy and X-ray analysis. The comparison of the spectroscopic characteristics of these compounds clearly indicated that the central chalcogenium atom plays an important role in the properties of these compounds.

3. Experimental

3.1. General methods

Melting points were recorded with a Yanaco micro melting point apparatus and are uncorrected. Microanalyses were performed by the Microanalysis Center of Toyama Medical and Pharmaceutical University.

Spectroscopic measurements were carried out with the following instruments: optical rotations, JASCO DIP-1000 digital polarimeter; IR, Perkin–Elmer 1600 Series FTIR; mass (MS) and high resolution mass spectra (HRMS), JMS-AX 505H; ^{1}H NMR, Varian Gemini-300 (300 MHz) for solutions in $CDCl_3$ (or other solvent as mentioned) with Me_4Si (0 ppm) as an internal standard, *J* values in hertz; ^{13}C NMR, Varian Gemini-300 (75 MHz) for solutions in $CDCl_3$ (or other solvent as mentioned) with $CDCl_3$ (77 ppm) as an internal standard; ^{77}Se NMR, Varian Unity 500 (95.4 MHz) for solutions in $CDCl_3$ with Me_2Se (281 ppm) as an external standard; ^{125}Te NMR, Varian Unity 500 (157.9 MHz) for solutions in $CDCl_3$ with Ph_2Te_2 (0.5 M in CH_2Cl_2, 422 ppm) as an external standard. The crystallographic data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a rotating anode generator, and the structure was solved by direct methods; all data reduction and structural refinements were performed with the teXsan crystal structure analysis package provided by Molecular Structure Corporation. All reactions were carried out in dried glassware under N_2 atmosphere. Dry CH_2Cl_2 was distilled from P_2O_5 and stored over 4 Å molecular sieves. Anhydrous EtOH was distilled from CaH_2 and stored over 4 Å molecular sieves. Column chromatography and TLC were performed on Kiesel gel 60 (Merck, 230–400 mesh) or Kiesel gel 60 (Merck, Art. 7734 and Art. 5715, respectively).

*3.2. Ethyl-2-({(1*S*,2*R*,4*R*)-2-methoxymethoxy-7,7-dimethylbicyclo[2.2.1]-heptan-1-yl}methylseleno)-benzoate*

To a solution of 2,2′-diselenobisethylbenzoate (37.5 mg, 0.082 mmol) and (1*S*)-10-iodo-2-*exo*-methoxymethoxy-borneol (53 mg, 0.16 mmol) in abs. EtOH (3 ml) was added $NaBH_4$ (38 mg, 1 mmol) under an N_2 atmosphere at 0°C, the mixture was stirred until the yellow color of the diselenide disappeared (ca. 10 min). The whole solution was heated at reflux for 5 h and cooled to rt. The reaction was quenched with NH_4Cl (5 ml) and the mixture was extracted with CH_2Cl_2 (3×15 ml). The organic layer was washed with H_2O (2×5 ml), followed by brine (5 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography (hexane:EtOAc=20:1) to give the title product (17 mg, 25%) as a yellow oil. $[\alpha]_D^{26}$ −4.37 (*c* 1.27, $CHCl_3$); IR (neat) 2952, 1707, 1456, 1388, 1045, 1009, 739 cm^{-1}; ^{1}H NMR δ: 0.93 (s, 3H), 1.11 (s, 3H), 1.3–1.47 (m, 2H), 1.4 (t, *J*=7.1, 3H), 1.6–1.93 (m, 5H), 2.81 (d, *J*=9.9, 1H), 3.17 (d, *J*=9.9, 1H), 3.33 (s, 3H), 3.74 (dd, *J*=3.8, 7.7, 1H), 4.38 (q, *J*=7.1, 2H), 4.59 (d, *J*=6.6, 1H), 4.67 (d, *J*=6.6, 1H), 7.18 (t, *J*=7.7, 1H), 7.4 (t, *J*=7.1, 1H), 7.52 (d, *J*=7.1, 1H), 7.99 (d, *J*=7.7, 1H); ^{13}C NMR δ: 14.7, 20.6, 20.9, 25.3, 27.4, 33.2, 39.6, 45.5, 48.7, 52.5, 56.0, 61.4, 83.1, 97.0, 124.2, 128.4, 129.1, 131.4, 132.3, 138.7, 166.9; *m/z*: 426 (M^+, ^{80}Se), 424 (M^+, ^{78}Se), 274, 272, 229, 227, 201, 199, 184, 182, 93. HRMS calcd for $C_{21}H_{30}O_4Se$: 426.1309 (M^+, ^{80}Se). Found: 426.1311.

*3.3. Ethyl-2-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-benzoate*

To a solution of ethyl-2-({(1*S*,2*R*,4*R*)-2-methoxymethoxy-7,7-dimethylbicyclo[2.2.1]-heptan-1-yl}methylseleno)-benzoate (59 mg, 0.14 mmol) in MeOH (3 ml) was added conc. HCl (2 drops) under an N_2 atmosphere at rt. The whole solution was heated at reflux for 3 h and cooled to rt. Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography (hexane:EtOAc=30:1–5:1) to give the desired product (45 mg, 85%) as a yellow oil. $[\alpha]_D^{26}$ −36.93 (*c* 2.90, $CHCl_3$); IR (neat) 3512, 2952, 1704, 1457, 1250, 1034, 738 cm^{-1}; ^{1}H NMR δ: 0.93 (s, 3H), 1.13 (s, 3H), 1.0–1.2 (m, 1H), 1.22–1.38 (m, 1H), 1.41(t, *J*=7.1, 3H), 1.59–1.83 (m, 5H), 2.35–2.43 (br d, 1H), 2.86 (d, *J*=9.3, 1H), 3.11 (d, *J*=9.3, 1H), 4.0 (dd, *J*=3.8, 7.7, 1H), 4.39 (q, *J*=7.1, 2H), 7.23 (t, *J*=7.7, 1H), 7.44 (t, *J*=7.7, 1H), 7.51 (d, *J*=8.2, 1H), 8.03 (d, *J*=7.7, 1H); ^{13}C NMR δ: 14.6, 20.2, 21.0,

25.7, 27.6, 31.7, 39.6, 45.2, 48.5, 52.1, 61.4, 77.1, 124.8, 128.5, 129.1, 131.4, 132.6, 137.5, 166.9; ^{77}Se NMR δ: 266; *m/z*: 382 (M^+, ^{80}Se), 380 (M^+, ^{78}Se), 364, 362, 230, 228, 184, 135, 93. HRMS calcd for $C_{19}H_{26}O_3Se$: 382.1046 (M^+, ^{80}Se). Found: 382.1046.

3.4. 2-({(1S,2R,4R)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-benzoic acid ***6a***

To a solution of ethyl-2-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-benzoate (282 mg, 0.74 mmol) in THF:H_2O:EtOH (1:1:1, 9 ml) was added a solution of 1N aqueous NaOH (3 ml, 3 mmol), and the reaction mixture was stirred under an N_2 atmosphere at rt overnight. After acidification with 1N HCl, the reaction mixture was extracted with CH_2Cl_2 (3×50 ml). The combined organic layer was then washed with H_2O (2×10 ml), followed by brine (10 ml) and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the product **6a** (261 mg) in quantative yield as a white solid. Mp 219–220°C; $[\alpha]_D^{26}$ −42.57 (*c* 0.65, $CHCl_3$); IR (KBr) 3433, 2951, 1674, 1462, 1257, 1036, 740 cm^{-1}; ^{1}H NMR δ: 0.94 (s, 3H), 1.14 (s, 3H), 1.02–1.21 (m, 1H), 1.3–1.41 (m, 1H), 1.59–1.92 (m, 7H), 2.88 (d, *J*=9.3, 1H), 3.13 (d, *J*=9.3, 1H), 4.03 (dd, *J*=3.3, 7.7, 1H), 7.24 (t, *J*=7.7, 1H), 7.42–7.59 (m, 2H), 8.14 (d, *J*=7.7, 1H); ^{13}C NMR δ: 20.3, 21.0, 25.8, 27.6, 31.8, 39.7, 45.2, 48.6, 52.1, 77.2, 124.9, 127.9, 128.8, 132.6, 133.3, 138.5, 171.1; *m/z*: 354 (M^+, ^{80}Se), 352 (M^+, ^{78}Se), 336, 334, 321, 318, 202, 200, 184, 182, 153, 135, 93. HRMS calcd for $C_{17}H_{22}O_3Se$: 354.0733 (M^+, ^{80}Se), 352.0742 (M^+, ^{78}Se). Found: 354.0706, 352.0741.

3.5. Methyl-3-({(1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-acrylate

To a solution of di-(2-*exo*-hydroxy-10-bornyl) diselenide **7** (188 mg, 0.41 mmol) and methyl propiolate (0.09 ml, 1 mmol) in abs. EtOH (6 ml) was added $NaBH_4$ (38 mg, 1 mmol) under an N_2 atmosphere at 0°C, and the mixture was stirred for 40 min at 0°C. The reaction was quenched with NH_4Cl (5 ml) and the mixture was extracted with EtOAc (2×50 ml). The organic layer was washed with H_2O (2×5 ml), followed by brine (5 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the product (270 mg, 100%) as a yellow oil. (*Z*:*E*=ca. 4:1). ^{1}H NMR for *Z*-isomer, δ: 0.87 (s, 3H), 1.0–1.27 (m, 1H), 1.08 (s, 3H), 1.2–1.8 (m, 8H), 2.79 (d, *J*=11.5, 1H), 3.08 (d, *J*=11.5, 1H), 3.76 (s, 3H), 3.91 (dd, *J*=3.7, 7.7, 1H), 6.32 (d, *J*=9.9, 1H), 7.8 (d, *J*=9.9, 1H); for *E*-isomer, δ: 0.89 (s, 3H), 1.0–1.27 (m, 1H), 1.09 (s, 3H), 1.2–1.8 (m, 8H), 2.87 (d, *J*=11.0, 1H), 3.17 (d, *J*=11.0, 1H), 3.73 (s, 3H), 3.81 (dd, *J*=3.7, 7.7, 1H), 6.08 (d, *J*=15.4, 1H), 8.16 (d, *J*=15.4, 1H).

3.6. 3-({(1S,2R,4R)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-acrylic acid ***6b***

The hydrolysis procedure described in the preparation of **6a** was followed to prepare **6b** (248 mg, 100%) from methyl-3-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-acrylate (*Z*:*E*=ca. 4:1) (270 mg, 0.82 mmol) as a yellow oil. (*Z*:*E*=ca. 4:1). ^{1}H NMR for *Z*-**6b**, δ: 0.87 (s, 3H), 1.0–1.25 (m, 1H), 1.08 (s, 3H), 1.2–1.9 (m, 8H), 2.78 (d, *J*=11.5, 1H), 3.11 (d, *J*=11.5, 1H), 3.91 (dd, *J*=3.8, 7.1, 1H), 6.33 (d, *J*=9.9, 1H), 7.96 (d, *J*=9.9, 1H); for *E*-**6b**, δ: 0.9 (s, 3H), 1.0–1.25 (m, 1H), 1.09 (s, 3H), 1.2–1.9 (m, 8H), 2.89 (d, *J*=11.0, 1H), 3.2 (d, *J*=11.0, 1H), 3.8 (dd, *J*=3.7, 7.7, 1H), 6.08 (d, *J*=15.9, 1H), 8.34 (d, *J*=15.9, 1H).

3.7. Ethyl-3-({(1S,2R,4R)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-propionate

To a solution of di-(2-*exo*-hydroxy-10-bornyl) diselenide **7** (340 mg, 0.73 mmol) and ethyl-3-bromopropionate (0.28 ml, 2.2 mmol) in abs. EtOH (20 ml) was added $NaBH_4$ (84 mg, 2.2 mmol) under an N_2 atmosphere at 0°C, and the mixture was stirred until the yellow color of the diselenide disappeared (ca. 10 min). The whole solution was stirred at rt for 4 h, then quenched with NH_4Cl (10 ml) and the mixture was extracted with EtOAc (3×50 ml). The organic layer was washed with H_2O (2×10 ml), followed by brine (10 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography (hexane:EtOAc=15:1) to give product (485 mg, 100%) as a yellow oil. $[\alpha]_D^{26}$ −34.12 (*c* 1.88, $CHCl_3$); IR (neat) 2951, 1735, 1228 cm^{-1}; ^1H NMR δ: 0.81 (s, 3H), 1.03 (s, 3H), 0.98–1.18 (m, 2H), 1.25 (t, *J*=7.1, 3H), 1.42–1.57 (m, 1H), 1.61–1.81 (m, 4H), 2.6–2.83 (m, 7H), 3.81 (dd, *J*=3.4, 7.7, 1H), 4.14 (q, *J*=7.1, 2H); ^{13}C NMR δ: 14.5, 18.9, 20.2, 20.9, 24.9, 27.3, 31.8, 35.7, 39.5, 45.4, 47.9, 52.6, 60.9, 77.2, 172.4; ^{77}Se NMR δ: 119; *m/z*: 334 (M^+, ^{80}Se), 332 (M^+, ^{78}Se), 289, 287, 182, 180, 153, 135, 109, 93. HRMS calcd for $C_{15}H_{26}O_3Se$: 334.1047 (M^+, ^{80}Se), 332.1056 (M^+, ^{78}Se). Found: 334.1045, 332.1039.

3.8. 3-({(1S,2R,4R)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-propionic acid **6c**

The hydrolysis procedure described in the preparation of **6a** was followed to prepare **6c** (249 mg, 97%) from ethyl-3-({(1*S*,2*R*,4*R*)-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-propionate (281 mg, 0.84 mmol) as a yellow oil. $[\alpha]_D^{26}$ −15.78 (*c* 1.28, $CHCl_3$); IR (neat) 2952, 1711, 1070, 756 cm^{-1}; ^1H NMR δ: 0.82 (s, 3H), 1.03 (s, 3H), 0.96–1.28 (m, 2H), 1.42–1.58 (m, 1H), 1.61–1.82 (m, 5H), 2.68–2.82 (m, 7H), 3.86 (dd, *J*=3.8, 8.2, 1H); ^{13}C NMR δ: 18.6, 20.2, 20.9, 25.1, 27.3, 31.9, 35.5, 39.3, 45.4, 48.1, 52.7, 77.4, 177.3; ^{77}Se NMR δ: 120; *m/z*: 306 (M^+, ^{80}Se), 304 (M^+, ^{78}Se), 182, 180, 153, 135, 109, 93. HRMS calcd for $C_{13}H_{22}O_3Se$: 306.0734 (M^+, ^{80}Se), 304.0743 (M^+, ^{78}Se). Found: 306.0771, 304.0800.

3.9. 3-({(1S,2R,4R)-2-Hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methylseleno)-propanol **6d**

To a solution of di-(3-hydroxy)propyl diselenide (295 mg, 1.07 mmol) and (1*S*)-10-iodo-2-*exo*-borneol (600 mg, 2.13 mmol) in abs. EtOH (15 ml) was added $NaBH_4$ (125 mg, 3.29 mmol) under an N_2 atmosphere at 0°C. The whole solution was heated at reflux for 3 h and cooled to rt. The reaction was quenched with NH_4Cl (10 ml) and the mixture was extracted with EtOAc (3×50 ml). The organic layer was washed with H_2O (2×10 ml), followed by brine (10 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography (hexane:EtOAc=5:1) to give **6d** (545 mg, 88%) as a yellow oil. $[\alpha]_D^{26}$ −23.14 (*c* 1.56, $CHCl_3$); IR (neat) 2951, 1454, 1070, 756 cm^{-1}; ^1H NMR δ: 0.83 (s, 3H), 1.05 (s, 3H), 0.98–1.21 (m, 3H), 1.43–1.59 (m, 1H), 1.62–2.0 (m, 6H), 2.58–2.78 (m, 3H), 2.66 (d, *J*=11.0, 1H), 2.8 (d, *J*=11.0, 1H), 3.76–3.86 (m, 3H); ^{13}C NMR δ: 20.1, 20.8, 21.6, 24.5, 27.2, 31.9, 32.9, 39.6, 45.3, 47.8, 52.6, 62.1, 77.2; ^{77}Se NMR δ: 97; *m/z*: 292 (M^+, ^{80}Se), 290 (M^+, ^{78}Se), 275, 273, 204, 160, 91. HRMS calcd for $C_{13}H_{24}O_2Se$: 292.0942 (M^+, ^{80}Se), 290.0951 (M^+, ^{78}Se). Found: 292.0957, 290.0969.

3.10. General procedure for preparation of spiroselenuranes **8a–d**

To a solution of selenide **6a–d** (1.10 mmol) in CH_2Cl_2 (25 ml) was added *t*-BuOCl (0.14 ml, 1.16 mmol) dropwise at 0°C under an N_2 atmosphere. The mixture was stirred at 0°C for 30 min followed by

dropwise addition of Et_3N (0.17 ml, 1.21 mmol), then the reaction was stirred for 1.5 h at 0°C to rt. The reaction mixture was worked up by removal of the solvent and excess reagents followed by diluting with H_2O (5 ml), the aqueous layer was extracted with EtOAc (3×50 ml), and the combined organic layer was washed with H_2O (3×10 ml) followed by brine (10 ml) and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product which was purified by recrystallization from hexane and CH_2Cl_2 to give the product **8a**–**d** as colorless crystals.

*3.10.1. Spiro[4*H*-3a,6-methano-3*H*-1,2-benzoxasulfole-2,2′ λ⁴-[5*H*-1,2]benzoxaselenol]-5′-one,5,6,7, 7a-tetrahydro-8,8-dimethyl-[2*R*-(2α,3aα,6α,7aβ)]-**8a***

From **6a** (177 mg, 0.5 mmol), *t*-BuOCl (0.063 ml, 0.53 mmol) and Et_3N (0.77 ml, 0.55 mmol) was obtained spiroselenurane **8a** (175 mg, 100%) as colorless crystals. Mp 168–169°C; $[\alpha]_D^{26}$ +81.0 (*c* 1.00, $CHCl_3$); IR (KBr) 2958, 1668, 1319, 1292, 1050, 763 cm^{-1}; ^1H NMR δ: 0.93 (s, 3H), 1.21 (s, 3H), 1.0–1.08 (m, 1H), 1.12–1.24 (m, 1H), 1.7–1.95 (m, 4H), 2.1–2.21 (m, 1H), 3.14 (d, *J*=13.2, 1H), 4.16 (d, *J*=13.2, 1H), 4.37 (dd, *J*=2.8, 7.1, 1H), 7.66–7.79 (m, 2H), 7.81–7.87 (m, 1H), 8.21–8.24 (m, 1H); ^{13}C NMR δ: 20.6, 20.7, 27.0, 29.4, 39.8, 45.5, 46.6, 55.1, 56.3, 93.3, 126.3, 131.1, 132.6, 132.7, 133.5, 137.4, 169.2; ^{77}Se NMR δ: 887; *m/z*: 354 (M^++2, ^{80}Se), 352 (M^++2, ^{78}Se and/or M^+, ^{80}Se), 350 (M^+, ^{78}Se), 308, 306, 200, 198, 151, 109, 107, 93. Anal. calcd for $C_{17}H_{20}O_3Se$: C, 58.12; H, 5.74. Found: C, 58.28; H, 5.56.

*3.10.2. Spiro[4*H*-3a,6-methano-3*H*-1,2-benzoxasulfole-2,2′ λ⁴-[5*H*-1,2]oxaselenol]-5′-one,5,6,7,7a-tetrahydro-8,8-dimethyl-[2*R*-(2α,3aα,6α,7aβ)]* ***8b***

From **6b** (*Z*:*E*=ca. 4:1, 267 mg, 0.88 mmol), *t*-BuOCl (0.11 ml, 0.92 mmol) and Et_3N (0.14 ml, 0.1 mmol) was obtained spiroselenurane **8b** (212 mg, 79%) as colorless crystals. Mp 126–127°C; $[\alpha]_D^{26}$ −189.41 (*c* 0.95, $CHCl_3$); IR (KBr) 2957, 2875, 1674, 1592, 1323, 104.8 cm^{-1}; ^1H NMR δ: 0.92 (s, 3H), 1.07 (s, 3H), 1.18–1.3 (m, 2H), 1.73–2.08 (m, 5H), 3.06 (d, *J*=12.7, 1H), 4.18 (d, *J*=13.2, 1H), 4.26 (dd, *J*=3.3, 7.1, 1H), 7.02 (d, *J*=6.0, 1H) 7.24 (d, *J*=6.0, 1H); ^{13}C NMR δ: 20.3, 20.6, 26.9, 29.8, 39.7, 45.8, 46.5, 55.6, 55.7, 94.9, 111.5, 136.8, 144.1; ^{77}Se NMR δ: 919; *m/z*: 302 (M^+, ^{80}Se), 300 (M^+, ^{78}Se), 258, 256, 178, 138, 136, 91, 65. Anal. calcd for $C_{13}H_{18}O_3Se$: C, 51.83; H, 6.02. Found: C, 51.65; H, 5.99.

*3.10.3. Spiro[4*H*-3a,6-methano-3*H*-1,2-benzoxasulfole-2,2′ λ⁴-3′,4′-dihydro-[5*H*-1,2]oxaselenol]-5′-one,5,6,7,7a-tetrahydro-8,8-dimethyl-[2*R*-(2α,3aα,6α,7aβ)]* ***8c***

From **6c** (116 mg, 0.38 mmol), *t*-BuOCl (0.05 ml, 0.42 mmol) and Et_3N (0.06 ml, 0.46 mmol) was obtained spiroselenurane **8c** (110 mg, 95%) as colorless crystals. Mp 137–139°C; $[\alpha]_D^{26}$ +85.74 (*c* 0.96, $CHCl_3$); IR (KBr) 2954, 1674, 1355, 629 cm^{-1}; ^1H NMR δ: 0.91 (s, 3H), 1.05 (s, 3H), 1.0–1.32 (m, 2H), 1.63–2.04 (m, 5H), 2.85–3.19 (m, 2H), 3.4 (d, *J*=13.2, 1H), 3.42–3.61 (m, 2H), 3.85 (d, *J*=13.2, 1H), 4.27 (dd, *J*=3.3, 7.1, 1H); ^{13}C NMR δ: 20.3, 20.5, 27.0, 29.9, 31.3, 39.6, 43.5, 45.6, 46.6, 49.6, 56.5, 93.6, 175.3; ^{77}Se NMR δ: 913; *m/z*: 306 (M^++2, ^{80}Se), 304 (M^++2, ^{78}Se or M^+, ^{80}Se), 302 (M^+, ^{78}Se), 260, 258, 232, 230, 189, 187, 152, 150, 135, 108, 93, 79. HRMS calcd for $C_{13}H_{20}O_3Se$: 304.0578 (M^+, ^{80}Se), 302.0587 (M^+, ^{78}Se). Found: 304.0624, 302.0595.

*3.10.4. Spiro[4*H*-3a,6-methano-3*H*-1,2-benzoxasulfole-2,2′ λ⁴-3′,4′-dihydro-[5*H*-1,2]oxaselenol]-5,6, 7,7a-tetrahydro-8,8-dimethyl-[2*R*-(2α,3aα,6α,7aβ)]* ***8d***

From **6d** (46 mg, 0.16 mmol), *t*-BuOCl (0.022 ml, 0.18 mmol) and Et_3N (0.027 ml, 0.19 mmol) was obtained spiroselenurane **8d** (34 mg, 74%) as colorless crystals. Mp 80–82°C; $[\alpha]_D^{26}$ +76.45 (*c* 0.74, $CHCl_3$); IR (KBr) 2948, 1385, 1012 cm^{-1}; ^1H NMR δ: 0.88 (s, 3H), 1.07 (s, 3H), 1.02–1.22 (m, 2H),

1.69–2.18 (m, 7H), 3.18 (d, *J*=13.2, 1H), 3.25 (d, *J*=13.2, 1H), 3.23–3.4 (m, 2H), 3.82–3.96 (m, 1H), 3.99–4.06 (m, 2H); ^{13}C NMR δ: 20.6, 20.9, 27.5, 28.1, 30.9, 40.7, 43.7, 45.4, 46.1, 46.5, 55.1, 66.2, 87.2; ^{77}Se NMR δ: 844; *m/z*: 290 (M^+, ^{80}Se), 288 (M^+, ^{78}Se), 274, 272, 232, 230, 189, 187, 138, 136, 108, 93, 79. HRMS calcd for $C_{13}H_{22}O_2Se$: 290.0785 (M^+, ^{80}Se), 288.0794 (M^+, ^{78}Se). Found: 290.0865, 288.0813.

3.11. *Di-(2*-exo-*hydroxy-10-bornyl) ditelluride* ***9***

The ditelluride was synthesized according to the procedure reported in the literature.[11] From tellurium powder (461 mg, 3.6 mmol), thioureadioxide (390 mg, 3.6 mmol), CTAB (10 mg) and (1*S*)-10-iodo-2-*exo*-borneol (100 mg, 0.36 mmol) was obtained ditelluride **9** (43 mg, 42%) as a red oil. $[\alpha]_D^{26}$ +101.6 (*c* 1.12, $CHCl_3$); IR (neat) 3454, 2949, 2876, 1453, 1168, 1069, 757 cm^{-1}; ^{1}H NMR δ: 0.85 (s, 6H), 1.07 (s, 6H), 1.08–1.92 (m, 14H), 2.55 (brs, 2H), 3.41 (d, *J*=11.5, 2H), 3.60 (d, *J*=11.5, 2H), 3.87 (dd, *J*=3.8, 7.1, 2H); ^{13}C NMR δ: 8.5, 20.3, 20.9, 27.0, 33.4, 39.5, 46.4, 47.2, 53.9, 77.9; ^{125}Te NMR δ: 660; *m*/*z*: 566 (M^+, ^{130}Te), 564 (M^+, ^{128}Te), 562 (M^+, ^{126}Te). HRMS calcd for $C_{16}H_{22}OTe$: 360.0739 (M^+, ^{130}Te), 356.0710 (M^+, ^{126}Te). Found: 360.0738, 356.0710.

3.12. *General procedure for the synthesis of tellurides* ***10a,b***

To a solution of di-(2-*exo*-hydroxy-10-bornyl) ditelluride **9** (498 mg, 0.89 mmol) in abs. EtOH (20 ml) was added $NaBH_4$ (101 mg, 2.66 mmol) under an N_2 atmosphere at 0°C and the mixture was stirred until the red color of the ditelluride disappeared (ca. 10 min). Methyl propiolate (0.24 ml, 2.66 mmol) was added and the whole solution was stirred at 0°C for 15 min. Removal of the solvent under reduced pressure was followed by addition of saturated NH_4Cl solution (15 ml). The mixture was extracted with CH_2Cl_2 (3×50 ml) and the organic layer was washed with H_2O (10 ml), followed by brine (10 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product which was purified by column chromatography (hexane:EtOAc=10:1) to give *Z*-**10a** (561 mg, 67%) and *E*-**10a** (94 mg, 11%) as yellow prisms and an oil, respectively.

3.12.1. Z-*Methyl-3-({(1*S,*2*R,*4*R*)*-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methyltelluro)-acrylic acid* Z-***10a***

Yellow prisms; mp 75–77°C; $[\alpha]_D^{25}$ −8.82 (*c* 1.06, $CHCl_3$); IR (KBr) 3520, 2953, 2879, 1686, 1552, 1340, 1211, 1180 cm^{-1}; ^{1}H NMR δ: 0.87 (s, 3H), 1.01–1.30 (m, 2H), 1.07 (s, 3H), 1.46–1.90 (m, 6H), 2.69 (d, *J*=11.3, 1H), 2.85 (d, *J*=11.3, 1H), 3.79 (s, 3H), 3.86 (ddd, *J*=3.8, 3.8, 7.7, 1H), 6.92 (d, *J*=9.9, 1H), 8.59 (d, *J*=9.9, 1H); ^{13}C NMR δ: 10.5, 20.2, 20.7, 27.0, 33.4, 40.4, 45.8, 47.7, 52.0, 52.9, 78.3, 122.9, 137.6, 169.4; *m/z*: 368 (M^+, ^{130}Te), 366 (M^+, ^{128}Te), 364 (M^+, ^{126}Te). Anal. calcd for $C_{14}H_{22}O_3Te$: C, 45.95; H, 5.78. Found: C, 46.03; H, 5.94.

3.12.2. E-*Methyl-3-({(1*S,*2*R,*4*R*)*-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methyltelluro)-acrylic acid* E-***10a***

Yellow oil; $[\alpha]_D^{26}$ −17.6 (*c* 2.11, $CHCl_3$); IR (neat) 3482, 2950, 2878, 1716, 1570, 1259, 1150 cm^{-1}; ^{1}H NMR δ: 0.90 (s, 3H), 0.85–1.30 (m, 2H), 1.09 (s, 3H), 1.51–1.91 (m, 6H), 2.92 (d, *J*=10.7, 1H), 3.09 (d, *J*=10.7, 1H), 3.73 (s, 3H), 3.78 (ddd, *J*=3.6, 3.6, 7.2, 1H), 6.40 (d, *J*=16.5, 1H), 8.64 (d, *J*=16.5, 1H); ^{13}C NMR δ: 9.2, 20.3, 20.8, 27.0, 33.7, 40.5, 46.0, 47.9, 51.8, 52.8, 78.5, 127.8, 128.0, 165.0; *m/z*: 368 (M^+, ^{130}Te), 366 (M^+, ^{128}Te), 364 (M^+, ^{126}Te). HRMS calcd for $C_{14}H_{22}O_3Te$: 368.0638 (M^+, ^{130}Te), 366.0624 (M^+, ^{128}Te), 364.0608 (M^+, ^{126}Te). Found: 368.0627, 366.0590, 364.0590.

3.12.3. Z-*Ethyl-3-({(1*S,*2*R,*4*R*)*-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methyltelluro)-3-propyl-acrylic acid* Z-***10b***

The procedure described in the preparation of **10a** was followed to prepare *Z*-**10b** (374 mg, 52%) and *E*-**10b** (223 mg, 31%) from di-(2-*exo*-hydroxy-10-bornyl) ditelluride **9** (498 mg, 0.86 mmol) and ethyl-3-propyl propiolate (360 mg, 2.57 mmol) as a red oil. $[\alpha]_D^{26}$ −28.55 (*c* 1.67, $CHCl_3$); IR (neat) 3520, 2954, 1676, 1570, 1325, 1188 cm^{-1}; ^1H NMR δ: 0.87 (s, 3H), 0.99 (t, *J*=7.7, 3H), 1.01–1.22 (m, 2H), 1.07 (s, 3H), 1.3 (t, *J*=7.1, 3H), 1.52–1.82 (m, 9H), 2.11 (m, 1H), 2.54 (dt, *J*=1.1, 8.0, 2H), 3.86 (dd, *J*=3.8, 7.7, 1H), 4.21 (q, *J*=7.1, 2H), 6.57 (d, *J*=1.1, 1H); ^{13}C NMR δ: 5.6, 13.5, 14.5, 20.0, 20.7, 23.8, 27.3, 33.0, 39.9, 41.8, 45.1, 48.1, 52.6, 60.6, 77.9, 120.2, 153.1, 168.5; *m*/*z*: 424 (M^+, ^{130}Te), 422 (M^+, ^{128}Te), 420 (M^+, ^{126}Te), 272, 270, 268, 226, 224, 222, 135, 93, 79. HRMS calcd for $C_{18}H_{30}O_3Te$: 424.1264 (M^+, ^{130}Te), 422.1250 (M^+, ^{128}Te), 420.1234 (M^+, ^{126}Te). Found: 424.1280, 422.1277, 420.1201.

3.12.4. E-*Ethyl-3-({(1*S,*2*R,*4*R*)*-2-hydroxy-7,7-dimethylbicyclo[2.2.1]heptan-1-yl}methyltelluro)-3-propyl-acrylic acid* E-***10b***

Red oil; $[\alpha]_D^{26}$ −19.62 (*c* 1.16, $CHCl_3$); IR (neat) 3521, 2955, 1712, 1588, 1367, 1177 cm^{-1}; ^1H NMR δ: 0.90 (s, 3H), 0.99 (t, *J*=7.1, 3H), 1.0–1.18 (m, 2H), 1.09 (s, 3H), 1.29 (t, *J*=7.1, 3H), 1.6–1.9 (m, 8H), 2.01 (d, *J*=3.8, 1H), 2.89 (dt, *J*=1.1, 7.1, 1H), 2.9 (d, *J*=10.4, 1H), 3.0 (d, *J*=10.4, 1H), 3.75 (dd, *J*=3.8, 7.6, 1H), 4.15 (q, *J*=7.1, 2H), 6.08 (s, 1H).

3.12.5. General procedure for synthesis of chlorotelluranes ***11a,b***

To a solution of telluride **10** (1 mmol) in dry CH_2Cl_2 (8 ml) was added *t*-BuOCl (0.13 ml, 1.05 mmol) under an N_2 atmosphere at 0°C. Then, the whole mixture was stirred at 0°C for 20 min. Removal of the solvent under reduced pressure gave the crude product as a white solid. Purification of the residue by recrystallization from hexane and CH_2Cl_2 afforded the desired product as colorless crystals.

3.12.6. Z-*5-Chloro-10,10-dimethyl-5-(2-methoxycarbonylethenyl)-5*λ^4*-tellura-4-oxatricyclo[5.2.1.0*^{3,7}*] decane* Z-***11a***

Yield 86%; colorless prisms; mp 163–165°C; $[\alpha]_D^{27}$ +129.6 (*c* 1.03, $CHCl_3$); IR (KBr) 2954, 2883, 1706, 1427, 1352, 1340, 1227, 1177, 1046, 987, 819 cm^{-1}; ^1H NMR δ: 0.92 (s, 3H), 1.08–1.23 (m, 2H), 1.06 (s, 3H), 1.60–1.96 (m, 5H), 3.32 (d, *J*=13.7, 1H), 3.46 (d, *J*=13.7, 1H), 3.91 (s, 3H), 4.02 (dd, *J*=4.4, 4.4, 1H), 6.71 (d, *J*=9.3, 1H), 7.96 (d, *J*=9.3, 1H); ^{13}C NMR δ: 20.4, 20.5, 26.9, 31.8, 40.0, 42.2, 45.5, 46.7, 53.4, 55.9, 94.2, 127.3, 143.9, 167.1; *m*/*z*: 402 (M^+, ^{130}Te, ^{35}Cl/^{128}Te, ^{37}Cl), 400 (M^+, ^{128}Te, ^{35}Cl/^{126}Te, ^{37}Cl), 398 (M^+, ^{126}Te, ^{35}Cl). Anal. calcd for $C_{14}H_{21}O_3ClTe$: C, 42.00; H, 5.29. Found: C, 41.95; H, 5.19.

3.12.7. E-*5-Chloro-10,10-dimethyl-5-(2-methoxycarbonylethenyl)-5*λ^4*-tellura-4-oxatricyclo[5.2.1.0*^{3,7}*] decane* E-***11a***

Yield 97%; colorless prisms; mp 120–122°C; $[\alpha]_D^{25}$ +82.8 (*c* 1.16, $CHCl_3$); IR (KBr) 2950, 2881, 2848, 1728, 1604, 1303, 1218, 1140, 1045, 988, 975, 867, 596 cm^{-1}; ^1H NMR δ: 0.91 (s, 3H), 0.86–1.28 (m, 2H), 1.07 (s, 3H), 1.60–1.94 (m, 5H), 3.50 (s, 2H), 3.83 (s, 3H), 4.15 (dd, *J*=5.1, 5.1, 1H), 6.93 (d, *J*=16.1, 1H), 7.94 (d, *J*=16.1, 1H); ^{13}C NMR δ: 20.2, 20.5, 26.6, 31.1, 41.6, 42.7, 45.3, 46.5, 52.5, 55.3, 93.4, 136.0, 141.4, 163.6; *m*/*z*: 404 (M^+, ^{130}Te, ^{37}Cl), 402 (M^+, ^{130}Te, ^{35}Cl/^{128}Te, ^{37}Cl), 400 (M^+, ^{128}Te, ^{35}Cl/^{126}Te, ^{37}Cl), 398 (M^+, ^{126}Te, ^{35}Cl). Anal. calcd for $C_{14}H_{21}O_3ClTe$: C, 42.00; H, 5.29. Found: C, 41.93; H, 5.31.

3.12.8. Z-5-Chloro-10,10-dimethyl-5-(2-ethoxycarbonyl-1-propylethenyl)-5λ⁴-tellura-4-oxatricyclo [5.2.1.0^{3,7}]decane Z-***11b***

Yield 90%; ^{1}H NMR δ: 0.92 (s, 3H), 1.07 (t, *J*=7.1, 3H), 1.0–1.24 (m, 2H), 1.09 (s, 3H), 1.33 (t, *J*=7.1, 3H), 1.6–2.0 (m, 7H), 2.59–2.7 (m, 1H), 3.18–3.23 (m, 1H), 3.16 (d, *J*=14.3, 1H), 3.49 (d, *J*=14.3, 1H), 3.99 (dd, *J*=4.9, 7.1, 1H), 4.33 (q, *J*=7.1, 2H), 6.38 (s, 1H).

3.12.9. E-5-Chloro-10,10-dimethyl-5-(2-ethoxycarbonyl-1-propylethenyl)-5λ⁴-tellura-4-oxatricyclo [5.2.1.0^{3,7}]decane E-***11b***

Yield 90%; ^{1}H NMR δ: 0.91 (s, 3H), 1.03 (t, *J*=7.1, 3H), 1.0–1.2 (m, 2H), 1.06 (s, 3H), 1.33 (t, *J*=7.1, 3H), 1.6–2.0 (m, 7H), 2.8–2.9 (m, 1H), 3.32 (d, *J*=13.2, 1H), 3.4–3.53 (m, 1H), 3.58 (d, *J*=13.2, 1H), 3.93 (dd, *J*=4.9, 5.5, 1H), 4.22 (q, *J*=7.2, 2H), 6.84 (s, 1H).

*3.13. Spiro[4*H*-3a,6-methano-3*H*-1,2-benzoxasulfole-2,2′ λ⁴-[5*H*-1,2]oxatellurol]-5′-one,5,6,7,7a-tetrahydro-8,8-dimethyl-[2*R*-(2α,3aα,6α,7aβ)]* ***12a***

A solution of chlorotellurane *Z*-**11a** (50 mg, 0.13 mmol) and saturated $NaHCO_3$ (0.13 ml, 1.05 mmol) in CH_2Cl_2 (15 ml) was placed in a separatory funnel. The whole mixture was then shaken for ca. 3 min at rt. The organic layer was separated, washed with water and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the crude product (46.8 mg) which was purified by column chromatography ($CHCl_3$:MeOH=20:1) to afford the product (26.9 mg, 62%) as colorless prisms. Mp 146–147°C; $[\alpha]_D^{26}$ −263.6 (*c* 1.10, $CHCl_3$); IR (KBr) 3500, 2958, 1665, 1642, 1629, 1573, 1323, 1046, 921 cm^{-1}; ^{1}H NMR δ: 0.91 (s, 3H), 1.04–1.27 (m, 2H), 1.02 (s, 3H), 1.59–1.97 (m, 5H), 2.60 (d, *J*=13.2, 1H), 3.55 (d, *J*=13.2, 1H), 4.06 (dd, *J*=3.3, 6.6, 1H), 7.43 (d, *J*=7.1, 1H), 7.50 (d, *J*=7.1, 1H); ^{13}C NMR δ: 20.2, 20.4, 26.7, 31.2, 38.9, 41.4, 45.4, 46.3, 54.8, 93.7, 138.7, 140.6, 170.4; ^{125}Te NMR δ: 1894; *m*/*z*: 352 (M$^+$, ^{130}Te), 350 (M$^+$, ^{128}Te), 348 (M$^+$, ^{126}Te). Anal. calcd for $C_{13}H_{18}O_3Te$: C, 44.63; H, 5.19. Found: C, 44.62; H, 5.10.

Recrystallization of **12a** from hexane and CH_2Cl_2 gave a crystal which was suitable for X-ray analysis. Crystallographic data for **12a**: orthorhombic, space group, $P2_12_12_1$ (#19) with *a*=11.8(1) Å, *b*=32.9(1), *c*=7.2(1) Å, *V*=2781(42) Å^3, and *Z*=8 (d_{calcd}=1.671 g cm^{-3}), μ (MoKα)=21.34 cm^{-1} absorption collected by ω scans; 3647 unique reflections; 2618 with $I>3.00\sigma(I)$ were used in refinement; R=6.2%, R_w=7.5%. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the full journal citation.

*3.14. Spiro[4*H*-3a,6-methano-3*H*-1,2-benzoxasulfole-2,2′ λ⁴-3′-propyl-[5*H*-1,2]oxatellurol]-5′-one,5,6,7,7a-tetrahydro-8,8-dimethyl-[2*R*-(2α,3aα,6α,7aβ)]* ***12b***

The procedure described in the preparation of **12a** was generally followed to prepare **12b** (59%) from *Z*-**11b** as colorless prisms; mp 104–105°C; $[\alpha]_D^{26}$ −161.17 (*c* 1.37, $CHCl_3$); IR (KBr) 2956, 1660, 1614, 1313, 1289, 1015, 870 cm^{-1}; ^{1}H NMR δ: 0.92 (s, 3H), 1.03 (t, *J*=7.1, 3H), 1.06 (s, 3H), 1.08–1.31 (m, 2H), 1.6–2.0 (m, 7H), 2.51 (dt, *J*=1.8, 8.1, 2H), 2.66 (d, *J*=13.4, 1H), 3.48 (d, *J*=13.4, 1H), 3.93 (dd, *J*=3.7, 6.4, 1H), 7.08 (s, 1H); ^{13}C NMR δ: 13.7, 20.5, 20.6, 22.8, 26.9, 31.2, 32.8, 37.7, 41.6, 45.2, 46.3, 54.6, 92.7, 132.4, 156.0, 170.0; *m*/*z*: 394 (M$^+$, ^{130}Te), 392 (M$^+$, ^{128}Te), 390 (M$^+$, ^{126}Te), 282, 280, 278, 242, 240, 238, 155, 123, 99. Anal. calcd for $C_{16}H_{24}O_3Te$: C, 49.03; H, 6.17. Found: C, 48.92; H, 6.08.

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