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Tellurium in organic synthesis: a general approach to buteno- and butanolides

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ABSTRACT

The naturally occurring butanolides (−)-blastmycinolactol, (+)-blastmycinone, (−)-NFX-2, (+)-antimycinone as well as the four stereoisomers of the butenolide Acaterin were prepared in high enantiomeric purity using hydroxy-vinyl tellurides as starting materials.

1. Introduction

The organic chemistry of Te(II) compounds is well developed and documented in books[1] and review articles.[2] There are many synthetic transformations promoted by tellurium reagents.[1,2] More recently, some of these transformations, coupled to the enzymatic kinetic resolution of tellurides bearing a secondary alcohol in their structures, allowed the preparation of enantiomerically enriched chiral building blocks.[3] Despite the great development of the organic chemistry of tellurium, the application of its chemistry in the synthesis of bioactive molecules is very scarce.[4] The reluctance of the synthetic organic chemists to employ tellurium compounds for synthetic purposes is probably due to old literature comments regarding the bad smell, instability, and the toxicity of organic tellurium compounds. Presently, it is known that most organic tellurium compounds are not bad smelling and can be manipulated in the presence of light and air with no need for special precautions. Concerning the biological activity of the organic tellurium compounds, it must be said that to our knowledge there is no report in the literature on the poisoning of humans by these compounds, neither any illness is associated to them. As a matter of fact, some groups have been underscoring the biological potential of tellurium organic compounds as therapeutic agents.[5] Consequently, we see no impediment in the use of organic compounds of tellurium in total synthesis.

In this paper we present a full account of our efforts to use tellurium based methodologies in the synthesis of optically active buteno- and butanolides, which present biological activity. The methodology developed in our group constitutes a new approach to the construction of these important structural unities present in many biologically active compounds.[6] Our methodology takes advantage of the hydrotelluration of acetylenes stereoselectivity, which gives only the *Z*-alkene,[2a,c,7] and of the stereospecific transformation of *Z*-vinylic tellurides into *Z*-vinyl-lithiums.[2a,c,4,7–9] The target molecules chosen were (−)-Blastmycinolactol (**1**), (+)-Blastmycinone (**2**), (−)-NFX-2 (**3**), (+)-Antimycinone (**4**) and the four stereoisomers of Acaterin (**5**). Compounds **1**–**4** are hydrolysis products of Antimycin A_3 (**6**) and Antimycin A_1 (**7**), which were isolated from *Streptomyces* sp. and present antifungal and antitumor activities.[10] The polyketide metabolites **1**–**4** present a biological activity similar to that of the Antimycins.[10] (−)-Acaterin (**5**) is a metabolite of the bacteria *Pseudomonas* sp. *A92*, acting as acyl-coenzyme A: cholesterol acyltransferase (ACAT) inhibitor, and is considered a promising therapeutic agent against atherosclerosis.[11] The structures of the target molecules **1**–**5** are shown in Scheme 1.

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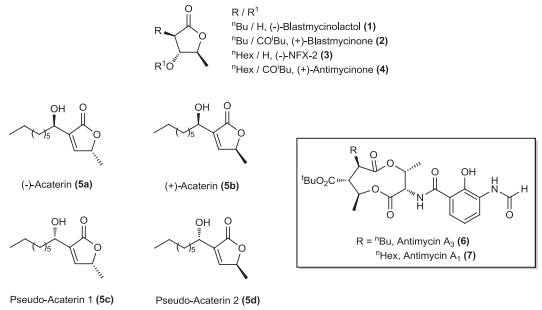
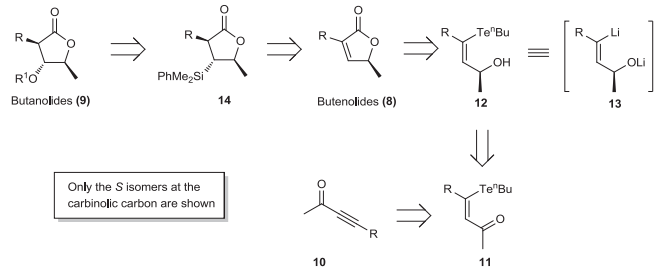


Scheme 1. Structure of the target molecules **1**–**5**.

From compounds **1**–**4**, (−)-Blastmycinolactol (**1**) and (+)-Blastmycinone (**2**) received more attention from the synthetic point of view. In general, the synthetic strategies employed to prepare these compounds in enantiomerically enriched form were based in chiral natural products transformations,[12] enzymatic resolutions,[13] oxidative heterocyclizations,[14] Sharpless oxidations,[15] use of chiral auxiliaries,[16] enolates chemistry,[17] and the use of elaborate organometallics.[18] Some of the problems found in the enantioselective synthesis of these compounds are the formation of diastereoisomeric mixtures,[19] the great number of synthetic steps,[20] low global yields and the use of elaborate and expensive starting materials. Concerning the butenolide Acaterin (**5**), few synthetic studies aiming its preparation in its enantiomerically enriched form are available.[21,22] It is important to note the existence of biosynthetic assays aiming the elucidation of the biosynthetic mechanisms for its formation.[23]

Scheme 2 shows the retrosynthesis of buteno- and butanolides via tellurium reagents. As can be observed, the butenolides **8** can be precursors of the butanolides **9**.

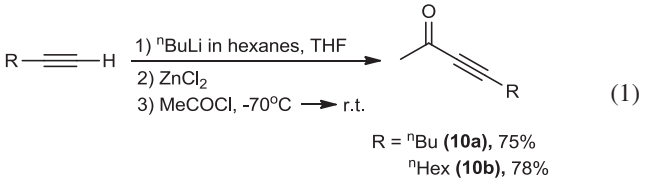


Scheme 2. Retrosynthetic analysis for **1**–**5**.

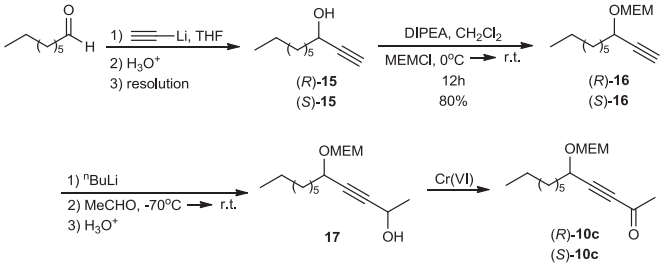
The starting material is an alkynone **10**, commercially available or easily prepared. The use of alkynones instead of propargyl alcohols as the starting material is due to the high regioselectivity of the hydrotelluration of these compounds, in contrast to the low regioselectivity of the hydrotelluration of propargyl alcohols.[24] In addition, the hydrotelluration of disubstituted non-activated alkynes does not occur.[7] The alkyltelluro alcohol **12** should be obtained by reduction of the telluroenone **11**. The tellurium–lithium exchange reaction in vinylic tellurides is well established, being one of the most studied reactions of organotellurium compounds.[2,4,9,25] Carbonation of the vinyl-lithium **13** should give the butenolide **8**. The stereochemistry of the carbinolic carbon of **12** could be established by an enzymatic kinetic resolution of the racemic **12**, leading to chiral building blocks (*R*)-**13** and (*S*)-**13**. This versatility of the methodology is important when the influence of the configuration in the biological activity of the buteno- or butanolides is being investigated, since it allows to access both stereoisomers of the target compound. Molecules **8** can constitute the target compounds, as is the case in the synthesis of Acaterin (**5**), or could be a chiral intermediate in the synthesis of a butanolide **9** as in the synthesis of **1**–**4**. In this last hypothesis, the absolute configuration of the carbinolic carbon should define the configuration of carbons **2** and **3**, since the conjugate addition to 2-furanones leads predominantly to *trans*,*trans* systems.[26] In the present case, this goal should be met by the conjugate addition of a lithium silyl cyanocuprate to the butenolide **8**, followed by a Fleming–Tamao oxidation, which occurs with retention of configuration,[27] to yield compounds **1** and **3**. Compounds **1** and **3** on acylation should give compounds **2** and **4**.

2. Results and discussion

The starting alkynones **10a** and **10b** were prepared by acylation of the corresponding alkyne, as shown in Eq. 1.

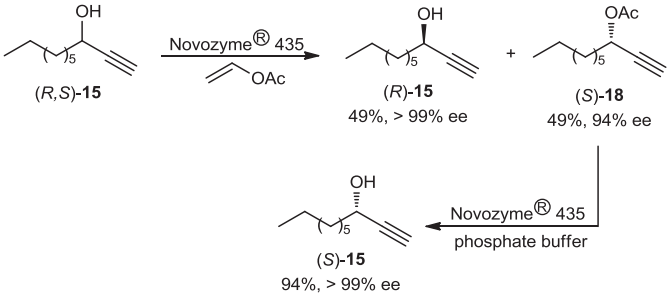


In the case of alkynone **10c**, this procedure led to the product in lower yield (34%). Alternatively, the protected propargyl alcohol **16**, prepared by addition of lithium acetylide to 1-octanal, followed by protection with 2-methoxyethoxymethyl chloride (MEM-Cl), was deprotonated with ^{n}BuLi, the resulting lithium acetylide was added to acetaldehyde and the resulting alcohol was oxidized with Cr(VI) (Scheme 3).



Scheme 3. Preparation of alkynones **10c**.

The reaction sequence shown in Scheme 3 was performed with the enantiomerically pure protected alcohols **16**. The enantiomerically pure alcohols (*R*)-**15** and (*S*)-**15** were obtained by enzymatic kinetic resolution of racemic **15** using Novozyme® 435 as the catalyst and vinyl acetate as the acetyl donor in hexane at 32 °C (Scheme 4). The reaction conditions were optimized as shown in Table 1.[28]



Scheme 4. Enantiomerically pure (*R*)-**15** and (*S*)-**15** from (*R*,*S*)-**15**.

Table 1
Enzymatic kinetic resolution of (*R*,*S*)-**15**[a]

Entry	Time (h)	Conv. (%)	ee (*R*)-**15**[b] (%)	ee (*S*)-**18**[b] (%)	*E*
1	0.5	24	32.2	>99	>200
2	1	37	56.6	98.2	176
3	1.5	44	75.5	98.6	>200
4	2	47	87.6	98	>200
5	2.5	49	93	96	167
6	3	51	97.8	95.9	>200
7[c]	**3.5**	**49**	**>99**	**94.3**	**>200**
8	4	49	>99	94	>200
9	4.5	51	98.8	94	148

[a] Reaction conditions: (*R*,*S*)-**15**, Novozyme® 435, CH_2=CHOAc, hexane, 32 °C, argon.
[b] The enantiomeric excesses were determined by chiral gas chromatography.
[c] Conditions of choice.

The best results were obtained at 3.5 h reaction time and at 49% conversion (entry 7, Table 1). Under the optimal conditions (*R*)-**15** was obtained in >99% ee and the acetate (*S*)-**18** was obtained with 94.5% ee. After the separation of (*R*)-**15** and (*S*)-**18** by silica gel column flash chromatography, the acetate (*S*)-**18** was hydrolyzed using the Novozyme® 435 recovered from the enzymatic kinetic resolution of **15** shown in Scheme 4. The reaction conditions for the hydrolysis reaction and the obtained results are shown in Table 2.

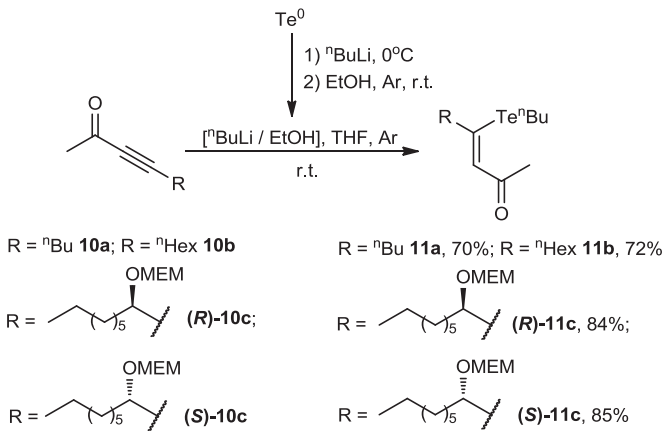
Table 2
Hydrolysis of (*S*)-**18**[a]

Entry	Time (h)	ee (*S*)-**15**[b]
1	2	98.9
2	2.5	98.2
3	3	99.8
4[c]	**3.5**	**99.9**

[a] Conditions: (*R*)-**18**, Na_2HPO_4/KH_2PO_4, 10 mM, pH=7, Novozyme® 435, acetone, 32 °C.
[b] The enantiomeric excesses were determined by chiral gas chromatography.
[c] Conditions of choice.

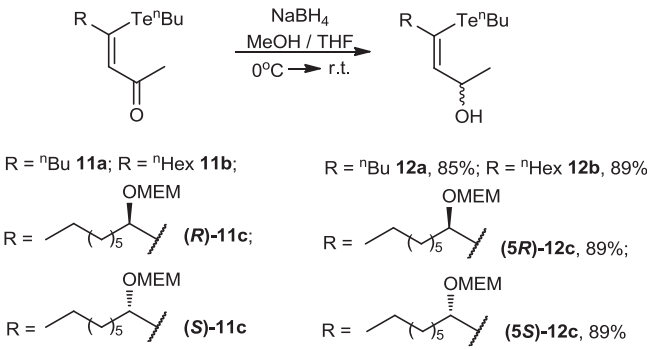
The best result was obtained at 3.5 h reaction time, and the alcohol (*S*)-**15** was obtained in >99% ee. In Scheme 4 is presented a summary of the whole process.

With the alkynones **10a**, **10b**, (*R*)-**10c** and (*S*)-**10c** in hands, the hydrotelluration reaction was performed by reacting them with a hydrotellurating mixture prepared by treating a suspension of elemental tellurium in THF with ^{n}BuLi in hexane at 0 °C followed by addition of deoxygenated ethanol at room temperature, under argon, as shown in Scheme 5. As expected[2a,7–9] only the *Z* isomer was formed.



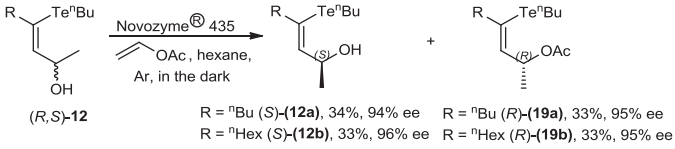
Scheme 5. Hydrotelluration of alkynones **10a**–**c**.

The next step was the reduction of **11a**–**c** to the corresponding alcohol **12**. Attempts to reduce the carbonyl group of **11c** in a stereoselective way using *N*-Me-ephedrine,[29] (*S*)-CBS-oxazoborolidine,[30] (*S*)-Binol,[31] and (*R*)-Alpineborane[32] failed, leading to decomposition or recovery of the starting material. In view of this failure the telluroenones **11** were reduced with sodium borohydride in a mixture of methanol/tetrahydrofuran (Scheme 6).



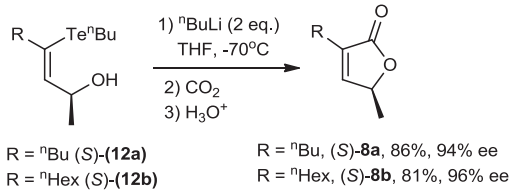
Scheme 6. Reduction of the telluroenones **11**.

In order to obtain the enantiomerically enriched allyl alcohols **12a** and **12b**, an enzymatic kinetic resolution of (*R*,*S*)-**12a** and (*R*,*S*)-**12b** was performed, using Novozyme® 435 in hexane under argon and in the dark, as shown in Scheme 7. The alcohols (*S*)-**12a** and (*S*)-**12b** were separated from the acetate (*R*)-**19a** and (*R*)-**19b** by silica gel column flash chromatography.



Scheme 7. Enzymatic kinetic resolution of **12a** and **12b**.

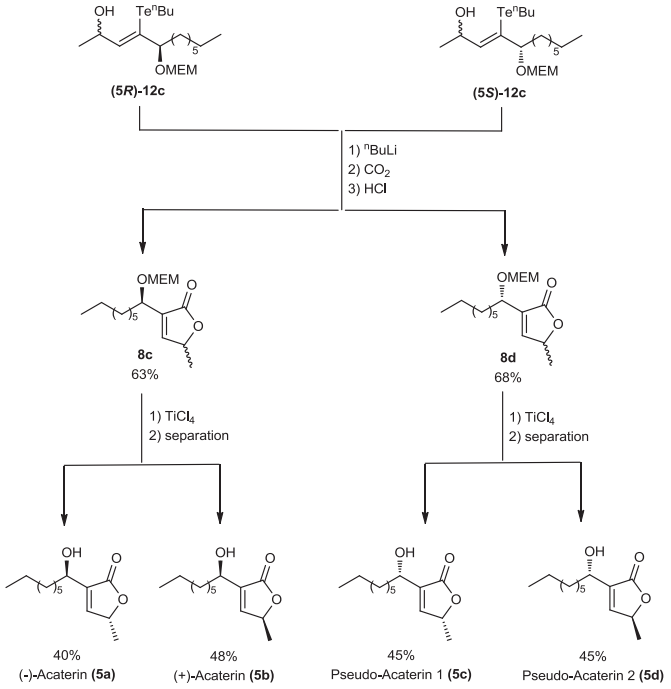
The allyl alcohols (*R*)-**12a** and (*R*)-**12b** were obtained by hydrolysis of the acetates (*R*)-**19a** and (*R*)-**19b**. With both enantiomers of the telluro alcohols **12a** and **12b** in hands, the tellurium/lithium exchange reaction was performed by treating them with 2 equiv of ^{n}BuLi. The obtained dianion was treated with ultra-dry carbon monoxide and after acidification of the reaction medium, the butenolides **8a** and **8b** were obtained with the yields and enantiomeric excesses shown in Scheme 8.



Scheme 8. Preparation of the butenolides **8a** and **8b**.

In the case of alcohols **12c** the lactonization step was performed with the two pairs of diastereomers following the same protocol shown in Scheme 8, leading to the two pairs of diastereomeric lactones **8c** and **8d**, which after deprotection with $TiCl_4$ and separation by silica gel column flash chromatography gave the four pure stereoisomers of Acaterin in high enantiomeric purity as shown in Scheme 9 and in Chart 1.

The chiral lactones (*S*)-**8a** and (*S*)-**8b** were employed as advanced precursors in the enantioselective synthesis of the target



Scheme 9. Preparation of the four stereoisomers of Acaterin (**5**).

Table 3
1,4-Addition of silylcuprates to angelicalactone (**20**)

Entry	Silylchloride	Lithium	Copper salt	Yield in **21**[a] (%)
1	$Me_2PhSiCl$	Slices	CuCN	20
2[c]	**$Me_2PhSiCl$**	**Suspension**[b]	**CuCN**	**80**
3	$^tBuPh_2SiCl$	Suspension[b]	CuCN	59
4	$^iPr_3SiCl$	Suspension[b]	CuCN	Traces
5	$Me_2PhSiCl$	Suspension[b]	CuI	50

[a] Isolated yields.
[b] Suspension in mineral oil (30% m/m) doped with sodium.
[c] Conditions of choice.

used in the 1,4-addition to enones (*S*)-**8a** and (*S*)-**8b**. The addition occurred in an *anti* fashion and the methyl group at the carbinol carbon of the butenolides (*S*)-**8a** and (*S*)-**8b** defined the stereochemistry at C_3 of the resulting enolate, which was trapped by a proton source to give the *anti*,*anti* three contiguous substituted butyrolactones **23a** and **23b** (Scheme 11). The optical rotation of **23a** and **23b** agree with those found in the literature for the same compounds.[26a]

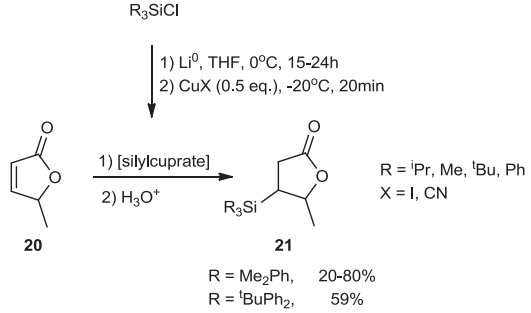
A similar reaction sequence was used by Bruckner[26a] to prepare **23a** and **23b** from **8** (R=H). The capture of the intermediate enolate by an alkylating agent gave the products **23** in moderate yields. As the alkyl groups are already present in **8a** and **8b** (R=^{n}Bu and ^{n}Hex), by our method the capture of the enolate by a proton source resulted in improved yields of **23a** and **23b**.

Stereoisomer	Absolute configuration	$[\alpha]_D$ Literature[21a]	$[\alpha]_D$ This work	Overall Yield[a,b] (%)
5a	(*R*,*R*)	-19.7 (c 0.61; $CHCl_3$)	-19.0 (c 1.0; $CHCl_3$)	15%
5b	(*R*,*S*)	+62.6 (c 1.06; $CHCl_3$)	+60.1 (c 1.0; $CHCl_3$)	13%
5c	(*S*,*R*)	-63.7 (c 0.53; $CHCl_3$)	-59.7 (c 1.0; $CHCl_3$)	14%
5d	(*S*,*S*)	+19.6 (c 1.04; $CHCl_3$)	+20.2 (c 1.0; $CHCl_3$)	13%

[a]The yields were calculated considering the alcohols (***R*)-15** and (***S*)-15** as starting materials.
[b]In the last step the maximal yield is 50%, since a pair of diastereoisomers was separated.

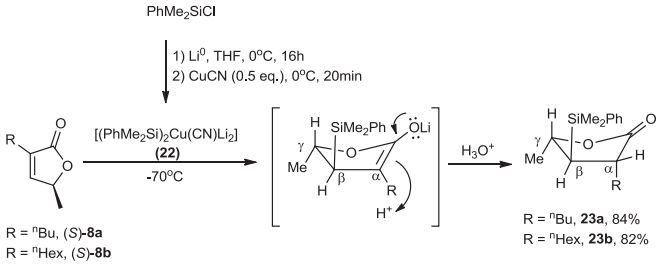
Chart 1. Optical rotations of the four stereoisomers of Acaterin (**5**).

molecules **1**–**4**. For this and, a 1,4-addition of a silylcuprate to the enones (*S*)-**8a** and (*S*)-**8b** was planed. An exploratory study to determine the optimal conditions for this reaction was performed using Angelicalactone (**20**) as a model compound. As shown in Scheme 10, different silylcuprates were employed. The results are given in Table 3.



Scheme 10. 1,4-Addition of silylcuprates to Angelicalactone (**20**).

The chosen conditions were those shown in entry 2 of Table 3. In this way, dilithium dimethyl(phenyl)silylcyanocuprate (**22**) was



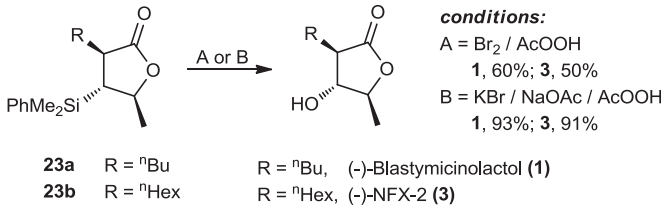
Scheme 11. Silylcuprate **22** addition to butenolides (*S*)-**8a** and (*S*)-**8b**.

The silyl lactones **23a** and **23b** were submitted to the Fleming–Tamao oxidation[27] using the conditions shown in Scheme 12.

The best results were obtained by using protocol B, in view of the milder reaction conditions.

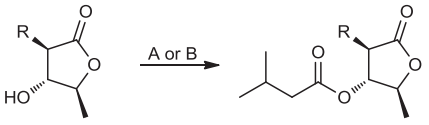
The absolute configurations of compounds **1** and **3** were confirmed by comparing the $[\alpha]_D$ values of the literature[26a] with those found by us.

By the sequence described above, (−)-Blastimycinolactol (**1**) and (−)-NFX-2 (**3**) were synthesized in four steps in 23% and 20% yield, respectively, if we consider the enantiomerically enriched



Scheme 12. Fleming–Tamao oxidation of **23a** and **23b**.

hydroxytellurides (*S*)-**12a** and (*S*)-**12b** as the starting materials, or in 9% and 11%, respectively, if we consider the alkynones **10** as the starting materials. The preparation of Blastmycinone (**2**) and Antimycinone (**4**) was accomplished by acylation of **1** and **3**, as shown in Scheme 13.[33] The enantiomeric excess of **2** and **4** were determined by chiral gas chromatography, using racemic samples of the same compounds for comparison, which were prepared by the same route described above, starting from racemic hydroxytellurides **12a** and **12b**. The optical rotation of the products obtained here agree with those found in the literature.[15b,34]



route A = tBuCOCl / DMAP / Et_3N
2, 80%, >97% ee; **4**, 84%, >97% ee
route B = tBuCOCl / py
2, 96%, >97% ee; **4**, 96%, > 97% ee

Scheme 13. Preparation of **2** and **4**.

3. Conclusion

In conclusion, a general method of synthesis of enantiomerically enriched buteno- and butanolides was developed. This method allows the synthesis of the different enantiomers of biologically active buteno- and butanolides, starting from a common telluride. The versatility of this approach allowed the preparation of compounds **1**–**5** in their enantiomerically enriched forms. Similarly, a number of naturally occurring buteno- and butanolides could be synthesized by the methodology described above.

4. Experimental section

4.1. General

The reagents and solvents were dried and purified according the literature procedures.[35] The THF was distilled from sodium/benzophenone under nitrogen immediately before use. ^{n}BuLi was titrated with isopropanol, using 1,10-phenanthroline as indicator.[36] The nitrogen or argon were deoxygenated and dried. Elemental tellurium (200 mesh), copper(I) cyanide (99%) and elemental lithium (30% m/m, dispersed in mineral oil and dropped with sodium) were purchased from Aldrich Chemical Co. The ^{n}BuLi employed was purchased from Merck KGaA, Chemetall GmbH or Acros Organics. The ultra-pure anhydrous carbon dioxide was purchased from Air Products®.

The column chromatographic separations were performed with Acros Organics (230–400 mesh) flash silica gel. Kieselgel 60 PF_{254} from Merck was used in the preparative thin layer chromatographic separations. The thin layer chromatographic analysis (TLC) were performed using commercially available plates from Merck (E. Merck, 5544, 0.2 mm), which were developed under ultraviolet light (ν=254 nm) or iodine. Alternatively the plates were developed by vanillin in a mixture of sulfuric acid/ethanol (6% vanillin m/v, 4% sulfuric acid and 10% water in ethanol v/v), by a solution of p-anisaldehyde m/v, (4% sulfuric acid, 1% acetic acid in ethanol v/v) or by an aqueous basic solution of potassium permanganate (1% $KMnO_4$, 2% NaOH in water m/v). The gas chromatographic analysis (GC) were performed with Shimadzu GC-2010 and Shimadzu GC-2014 equipments, with flame ionization detector (FID). The carrier gas was nitrogen, or hydrogen when chiral columns were employed. The columns employed were: J&B Scientific® DB-35 (30 m×0.25 mm×0.15 μm); Supelco® Gamma DEX 120 (30 m×0.25 mm×0.25 μm); Supelco® Beta DEX 110 (30 m×0.25 mm×0.25 μm). The nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were registered with Bruker DPX-300 (300 MHz, ^{1}H; 75 MHz, ^{13}C), Bruker DPX-500 (500 MHz, ^{1}H; 125 MHz, ^{13}C), Varian-Inova (300 MHz, ^{1}H; 75 MHz, ^{13}C); and Bruker AvanceIII-200 (200 MHz, ^{1}H; 50 MHz, ^{13}C). In all cases tetramethylsilane (TMS) was used as internal standard and $CDCl_3$ as solvent. The ^{125}Te NMR spectra were obtained with a Bruker DPX-500 (157.9 MHz, ^{125}Te) and a Bruker AvanceII-200 (63.2 MHz, ^{125}Te), using $CDCl_3$ as solvent and Ph_2Te_2 as internal reference. The optical rotation values were obtained with a Perkin Elmer 343 polarimeter using 5 mm or 1 cm optical pass cuvettes. The melting points were measured with a Buchi Melting Point B-545. The low resolution mass spectra were obtained with a Shimadzu GC–MS-17A/QP5050A apparatus. The high resolution mass spectra were obtained with a Bruker Daltonics MicroTOF equipment. The infrared spectra were obtained with a Bomem MB-100 spectrometer. The IUPAC names of all compounds were obtained using a ChemDraw, version 11.0.1 software. The NMR spectra were processed using a MestreNova software.

4.2. Enzymatic kinetic resolution of the propargyl alcohol 15

4.2.1. Typical procedure. In four 250 mL erlenmeyer flasks was placed the propargyl alcohol **15** (20 mmol; 3.08 g in each flask) and previously dried and deoxygenated hexane (100 mL in each flask). Then the lipase Novozyme® 435 was added (0.84 g, 10,000 PLU g^{-1} in each flask). The resulting solutions were purged with argon and then vinyl acetate (62.5 mmol, 5.0 mL in each flask) was added. The flasks were shacked in an orbital shaker (180 rpm) at 32 °C for 3.5 h. Then the enzyme was removed by filtration and the combined filtrates were concentrated under vacuum. The residue was purified by flash silica gel column chromatography eluting with a mixture (9:1) of hexane/ethyl acetate.

*4.2.1.1. (S)-Dec-1-yn-3-ol [(R)-**15**].* Colorless liquid (6.04 g, 49%); δ_H(500 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.0 Hz), 1.23–1.35 (8H, m), 1.41–1.48 (2H, m), 1.65–1.77 (2H, m), 2.33–2.39 (1H, m), 2.45 (1H, d, *J* 5.0 Hz), 4.36 (1H, dt, *J* 5.0, 2.5 Hz); δ_C (125 MHz, $CDCl_3$) 13.9, 22.5, 24.9, 29.12, 29.14, 31.7, 37.5, 62.2, 72.7, 85.0; ν_{max} (liquid film) 3311, 2926, 2857, 1466, 1046, 1022, 654, 627 cm^{-1}; $[\alpha]_D^{20}$ +4.0 (*c* 3.0, $CHCl_3$, ee >99%); chiral GC-FID [Supelco® Beta DEX 110 column, carrier gas: H_2, injector temperature: 275 °C, detector temperature: 275 °C, pressure: 100 kPa, method, isotermic: 100 °C; t_R: (*R*)-**15** 17.92 min; (*S*)-**15** 17.36 min; (*S*)-**18** 22.62 min and (*R*)-**18** 21.35 min; CAS [74867-41-7].

*4.2.1.2. (R)-Dec-1-yn-3-yl acetate [(S)-**18**].* Colorless liquid (7.68 g, 49%); δ_H (500 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.0 Hz), 1.27–1.31 (8H, m), 1.43 (2H, quint, *J* 7.5 Hz), 1.74–1.79 (2H, m), 2.07 (3H, s), 2.44 (1H, d, *J* 2.0 Hz), 5.33 (1H, dt, *J* 7.0, 2.0 Hz); δ_C (125 MHz, $CDCl_3$) 14.0, 20.9, 22.6, 24.8, 29.0, 29.1, 31.7, 34.5, 63.8, 73.3, 81.3, 169.9; ν_{max} (liquid film) 3312, 2928, 2123, 1744, 1372, 1233, 1022; HRMS

(ESI): *m*/*z* ([M+Na]$^+$) found 219.1359. $C_{12}H_{20}NaO_2$ requires 219.1361; $[\alpha]_D^{20}$ −54.1 (*c* 3.0, $CHCl_3$, ee 94%).

4.3. Enzymatic hydrolysis of the propargyl acetate (*S*)-18

In four 250 mL erlenmeyer flasks was added the propargyl acetate (*S*)-**18** (10 mmol, 1.96 g in each flask) and acetone (10 mL in each flask). Then Novozyme® 435 (1 g, 10,000 PLU g^{-1}) recovered from the preceding reaction was added to each flask. To the resulting mixture it was added Na_2HPO_4/KH_2PO_4 (10 mM, pH=7; 100 mL in each flask). The flasks were shacked for 3.5 h at 32 °C in an orbital shaker (180 rpm). Then the enzyme was removed by filtration. The combined filtrates were extracted with ethyl acetate (3×70 mL), the organic phases were washed with brine (50 mL) and dried with magnesium sulfate. The solvent was removed under vacuum and the residue was purified by silica gel flash column chromatography.

*4.3.1. (S)-Dec-1-yn-3-ol [(S)-**15**].* Colorless liquid (5.79 g, 94%); the same spectral data as those described for (*R*)-**15**; $[\alpha]_D^{20}$ −4.9 (*c* 3.0, $CHCl_3$, ee >99%); CAS [74867-42-8].

4.4. Protection of alcohols (*R*)-15 and (*S*)-15 with MEM-Cl

4.4.1. Typical procedure. To a 150 mL round bottomed flask under magnetic stirring, previously flame-dried and under argon, were added the propargyl alcohol (*R*)-**15** (39 mmol; 6.0 g), CH_2Cl_2 (80 mL) and diisopropylamine (57.2 mmol; 9.8 mL). The solution was cooled to 0 °C and then MEM-Cl (57.2 mmol; 6.6 mL) was added. After 10 min the mixture was heated to room temperature and stirred overnight. The reaction was extracted with a 5% aqueous solution of HCl (20 mL), the organic phase was extracted with CH_2Cl_2 (3×40 mL), and the combined extracts were washed with brine (50 mL) and the dried with magnesium sulfate. The solvent was evaporated under vacuum and the residue was purified by silica gel flash column chromatography eluting with a mixture (4:1) of hexane/ethyl acetate.

*4.4.1.1. (R)-3-((2-Methoxyethoxy)methoxy)dec-1-yne [(R)-**16**].* Colorless liquid (7.56 g, 80%); δ_H (300 MHz, $CDCl_3$) 0.88 (3H, t, *J* 6.6 Hz), 1.26–1.33 (8H, m), 1.44–1.51 (2H, m), 1.69–1.77 (2H, m), 2.39 (1H, d, *J* 2.1 Hz), 3.39 (3H, s), 3.54–3.56 (2H, m), 3.62–3.67 (1H, m), 3.74–3.80 (1H, m), 4.35 (1H, dt, *J* 6.6, 2.1 Hz), 4.71 (1H, d, *J* 7.0 Hz), 5.00 (1H, d, *J* 7.0 Hz); δ_C (75 MHz, $CDCl_3$) 14.1, 22.7, 25.2, 29.2, 29.3, 31.8, 35.6, 59.0, 65.6, 67.2, 71.7, 73.4, 82.7, 93.2; ν_{max} (liquid film) 3310, 2927, 2111, 1466, 1100, 1036 cm^{-1}; HRMS (ESI): *m*/*z* ([M+Na]$^+$) found 265.1769. $C_{14}H_{26}NaO_3$ requires 265.1779; $[\alpha]_D^{20}$ +106.1 (*c* 1.0, $CHCl_3$).

*4.4.1.2. (S)-3-((2-Methoxyethoxy)methoxy)dec-1-yne [(S)-**16**].* Colorless liquid (7.28 g, 77%); same spectral data as for (*R*)-**16**. $[\alpha]_D^{20}$ −108.4 (*c* 1.0, $CHCl_3$).

4.5. Preparation of alkynols (5*R*)-10c and (5*S*)-10c

*4.5.1. Preparation of alcohols **17***

4.5.1.1. Typical procedure. To a 250 mL two necks round bottomed flask, under magnetic stirring, previously flame-dried under argon, was added the MEM-ether (*R*)-**16** or (*S*)-**16** (21.8 mmol; 5.28 g) and THF (80 mL). The solution was cooled to −78 °C and ^{n}BuLi (22 mmol; 18.6 mL of a 1.18 mol L^{-1} in hexane) was added, then the mixture was allowed to reach the room temperature and stirred for 20 min. After this, the mixture was cooled again to −78 °C and acetaldehyde (79.7 mmol; 4.5 mL) was added. After the addition the reaction mixture was allowed to reach the room temperature and stirred for 10 min at this temperature. The reaction was quenched with 5% aqueous solution of HCl (20 mL), the aqueous phase was extracted with ethyl acetate (3×40 mL) and the combined extracts were washed with brine (50 mL) and dried with magnesium sulfate. The solvent was removed under vacuum and the residue was purified by silica gel flash column chromatography eluting with a mixture (3:1) of hexane/ethyl acetate.

*4.5.1.2. (5R)-5-((2-Methoxyethoxy)methoxy)dodec-3-yn-2-ol (**17a**).* Diastereoisomeric mixture (1:1) (4.75 g, 92%) as colorless liquid; δ_H (500 MHz, $CDCl_3$) 0,88 (3H, t, *J* 7.2 Hz), 1.24–1.29 (16H, m), 1.39–1.50 [(10H, m), 1.43 (3H, t, *J* 6.6 Hz), 1.44 (3H, t, *J* 6.6 Hz)], 1.67–1.78 (4H, m), 3.39 (3H, s), 3.40 (3H, s), 3.57–3.59 (4H, m), 3.68–3.80 (4H, m), 4.32–4.37 (2H, m), 4.51–4.57 (2H, m), 4.74 (1H, d, *J* 2.5 Hz), 4.75 (1H, d, *J* 2.5 Hz), 4.97 (1H, d, *J* 1.0 Hz), 4.98 (1H, d, *J* 1.0 Hz); δ_C (125 MHz, $CDCl_3$) 14.1, 22.6, 24.27, 24.34, 25.3, 29.2, 31.8, 35.69, 35.72, 58.20, 58.22, 59.0, 66.4, 66.5, 67.3, 71.89, 71.91, 82.91, 82.94, 87.43, 87.47, 93.8, 93.9; ν_{max} (liquid film) 3463, 2928, 2209, 1731, 1682, 1459, 1223, 1032 cm^{-1}; HRMS (ESI): *m*/*z* ([M+Na]$^+$) found 309.2030. $C_{16}H_{30}NaO_4$ requires 309.2042; $[\alpha]_D^{20}$ +96.0 (*c* 1.0, $CHCl_3$).

*4.5.1.3. (5S)-5-((2-Methoxyethoxy)methoxy)dodec-3-yn-2-ol (**17b**).* Diastereoisomeric mixture (1:1) (4.67 g, 90%) as colorless liquid; same spectral data as for **17a**. $[\alpha]_D^{20}$ −99.8 (*c* 1.0, $CHCl_3$).

*4.5.2. Jones oxidation of alcohols **17***

4.5.2.1. Typical procedure. To a two necked 250 mL round bottomed flask equipped with magnetic stirring and a dropping funnel, the alcohol **17** (18.2 mmol; 5.19 g) and diethyl ether (40 mL) were added. The solution was cooled to 0 °C and then it was slowly added via dropping funnel the chromic acid solution prepared from potassium dichromate (25 mmol; 7.35 g in 20 mL of water) and sulfuric acid (89 mmol; 4.9 mL in 30 mL of water). After the addition, the reaction mixture was allowed to reach the room temperature and stirred for 5 h. The mixture was then diluted with diethyl ether (100 mL) and extracted with water (40 mL). The resulting aqueous phase was extracted with diethyl ether (3×40 mL) and the combined organic phases were washed with saturated solution of $NaHCO_3$ (50 mL) and then dried with magnesium sulfate. The solvent was removed under vacuum and the residue was purified by silica gel flash chromatography eluting with a mixture (4:1) of hexane/ethyl acetate.

*4.5.2.2. (R)-5-((2-Methoxyethoxy)methoxy)dodec-3-yn-2-one [(R)-(**10c**)].* Colorless liquid (4.70 g, 91%); δ_H (500 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.2 Hz), 1.28–1.32 (8H, m), 1.45–1.48 (2H, m), 1.72–1.83 (2H, m), 2.34 (3H, s), 3.39 (3H, s), 3.55–3.57 (2H, m), 3.66–3.70 (1H, m), 3.74–3.78 (1H, m), 4.99 (1H, t, *J* 6.7 Hz), 4.72 (1H, d, *J* 7.2 Hz), 4.95 (1H, d, *J* 7.2 Hz); δ_C (125 MHz, $CDCl_3$) 14.1, 22.6, 25.2, 29.1, 29.2, 31.8, 32.7, 34.9, 59.0, 65.6, 67.4, 71.7, 84.7, 90.4, 93.6, 184.1; ν_{max} (liquid film) 2928, 2210, 1717, 1459, 1224, 1031 cm^{-1}; HRMS (ESI): *m*/*z* ([M+Na]$^+$) found 307.1876. $C_{16}H_{28}NaO_4$ requires 307.1886; $[\alpha]_D^{20}$ +138.9 (*c* 1.0, $CHCl_3$).

*4.5.2.3. (S)-5-((2-Methoxyethoxy)methoxy)dodec-3-yn-2-one [(S)-(**10c**)].* Colorless liquid (4.59 g, 89%); same spectral data as for [(*R*)-(**10c**)]. $[\alpha]_D^{20}$ −145.7 (*c* 1.0, $CHCl_3$).

4.6. Hydrotelluration of alkynones 10a and 10b

4.6.1. Typical procedure. In a 250 mL two necked flask equipped with magnetic stirring, previously flame-dried and under argon, was added elemental tellurium (30 mmol; 4.08 g) and THF (70 mL).

The suspension was cooled to 0 °C and then ^{n}BuLi (32 mmol; 26.7 mL of a 1.2 mol L^{-1} solution in hexane) was added leading to a pale yellow solution. After 5 min the mixture was allowed to reach the room temperature and then ethanol (72 mmol; 4.2 mL) was added. In the following the alkynone **10a** (30 mmol; 3.72 g) or **10b** (30 mmol; 4.57 g) was added net. After 30 min of stirring at room temperature, the reaction mixture was diluted with ethyl acetate (70 mL), washed with water (20 mL) and brine (20 mL) and the organic phase was separated and dried with magnesium sulfate. The solvents were evaporated in a rotatory evaporator and the residue was purified by flash silica gel column chromatography eluting with a mixture (20:1) of hexane/ethyl acetate.

*4.6.1.1. (Z)-4-(Butyltellanyl)oct-3-en-2-one (**11a**).* Yellow oil (6.51 g, 70%); δ_H (300 MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.3 Hz), 0.94 (3H, t, *J* 7.3 Hz), 1.41 (4H, hept, *J* 7.3 Hz), 1.52–1.60 (2H, m), 1.70 (2H, quint, *J* 7.6 Hz), 2.18 (3H, s), 2.55 (2H, t, *J* 7.6 Hz), 2.63 (2H, t, *J* 7.8 Hz), 7.18 (1H, s); δ_C (75 MHz, $CDCl_3$) 5.9, 13.5, 13.9, 22.2, 25.4, 29.9, 32.9, 33.4, 39.5, 127.6, 159.1, 196.2; δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 627.0; ν_{max} (liquid film) 2958, 2928, 2869, 1644, 1522, 1208 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 335.0692. $C_{12}H_{22}OTeNa$ requires 335.0630.

*4.6.1.2. (Z)-4-(Butyltellanyl)dec-3-en-2-one (**11b**).* Yellow oil (7.29 g, 72%); δ_H (300 MHz, $CDCl_3$) 0.88–0.96 (6H, m), 1.32–1.49 (8H, m), 1.51–1.61 (2H, m), 1.70 (2H, quint, *J* 7.9 Hz), 2.18 (3H, s), 2.55 (2H, t, *J* 7.9 Hz), 2.62 (2H, t, *J* 7.9 Hz), 7.18 (1H, s); δ_C (75 MHz, $CDCl_3$) 6.0, 13.5, 14.0, 22.6, 25.4, 28.8, 29.9, 31.4, 31.6, 32.9, 39.8, 127.7, 159.3, 196.3; δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 626.9; ν_{max} (liquid film) 2957, 2928, 2857, 1644, 1521, 1359, 1202 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 363.0938. $C_{14}H_{26}OTeNa$ requires 363.0943.

4.7. Hydrotelluration of alkynones (*S*)-10c and (*R*)-10c

4.7.1. Typical procedure. To a two necked 250 mL round bottomed flask equipped with magnetic stirring and previously flame-dried under argon, it was added elemental tellurium (14.6 mmol; 1.86 g) and THF (60 mL). The suspension was cooled to 0 °C and then ^{n}BuLi (14.6 mmol; 12.4 mL of a 1.18 mol M^{-1} solution in hexane) was added, leading to a pale yellow solution. After 5 min, the mixture was allowed to reach the room temperature and then ethanol (37.9 mmol; 2.2 mL) was added. In the following the alkynone **10c** (11.2 mmol; 3.19 g) was added. After 30 min stirring at room temperature, the reaction mixture was diluted with ethyl acetate (70 mL) and washed with water (20 mL), brine (20 mL) and dried with magnesium sulfate. The solvents were removed under vacuum and the residue was purified by silica gel flash column chromatography eluting with a mixture (4:1) of hexane/ethyl acetate.

*4.7.1.1. (R,Z)-4-(Butyltellanyl)-5-((2-methoxyethoxy)methoxy)dodec-3-en-2-one [(R)-(**11c**)].* Yellow oil (4.47 g, 84%); δ_H (500 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.5 Hz), 0.94 (3H, t, *J* 7.5 Hz), 1.27–1.46 (12H, m), 1.56–1.72 (6H, m), 2.22 (3H, s); 2.53–2.58 (1H, m), 2.65–2.71 (1H, m), 3.39 (3H, s), 3.54 (2H, t, *J* 5.0 Hz), 3.61–3.65 (1H, m), 3.79–3.84 (1H, m), 4.59 (1H, dd, *J* 9.0, 3.5 Hz), 7.47 (1H, s); δ_C (125 MHz, $CDCl_3$) 6.2, 13.5, 14.0, 22.6, 25.3, 26.0, 29.2, 29.4, 30.8, 31.8, 32.7, 37.5, 59.0, 67.4, 71.7, 79.2, 93.7, 125.8, 158.2, 196.7; δ_{Te} (157.9 MHz $CDCl_3$, Ph_2Te_2) 615.5; ν_{max} (liquid film) 2955, 2856.7, 1644.2, 1524.1, 1463.2, 1359.7, 1194.5, 1107.9, 1023 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 495.1725. $C_{20}H_{38}O_4TeNa$ requires 495.1730; $[\alpha]_D^{20}$ +167.1 (*c* 1.0, $CHCl_3$).

*4.7.1.2. (S,Z)-4-(Butyltellanyl)-5-((2-methoxyethoxy)methoxy)dodec-3-en-2-one [(S)-(**11c**)].* Yield (4.52 g, 85%) same spectral data as for [(*R*)-(**11c**)]. δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 617.2; $[\alpha]_D^{20}$ −173.7 (*c* 1.0, $CHCl_3$).

4.8. Reduction of the enones [(*R*)-(11c)] and [(*S*)-(11c)] to the allyl alcohols [(5*R*)-(12c)] and [(5*S*)-(12c)]

4.8.1. Typical procedure. To a 100 mL round bottomed flask equipped with magnetic stirring, the enone **11c** (9 mmol; 4.32 g) and THF (30 mL) were added. The solution was cooled to 0 °C and then $NaBH_4$ (10 mmol; 0.39 g) in methanol (10 mL) was added. The progress of the reaction was monitored by TLC and after the consumption of the starting material the mixture was diluted with ethyl acetate (30 mL) and washed with water (30 mL). The organic phase was extracted with ethyl acetate (2×30 mL) and the combined organic phases were washed with brine (30 mL) and then dried with magnesium sulfate. The solvents were removed in vacuum and the residue was purified by silica gel flash column chromatography using a mixture (4:1) of hexane/ethyl acetate.

*4.8.1.1. (5R,Z)-4-(Butyltellanyl)-5-((2-methoxyethoxy)methoxy)dodec-3-en-2-ol [(5R)-(**12c**)].* Diastereomeric mixture (1:1) (3.78 g, 89%) as yellow liquid; δ_H (500 MHz, $CDCl_3$) 0.80–0.85 (12H, m), 1.14–1.34 (30H, m), 1.56–1.68 (10H, m), 2.60–2.73 (4H, m); 3.32 (6H, s), 3.47–3.49 (4H, m), 3.56–3.71 (4H, m), 3.84 (1H, t, *J* 6.5 Hz), 3.91 (1H, dd, *J* 7.0, 5.5 Hz), 4.55–4.62 (4H, m), 4.68–4.69 (2H, m), 5.87 (1H, d, *J* 8.0 Hz), 5.90 (1H, d, *J* 8.0 Hz); δ_C (125 MHz, $CDCl_3$) 7.08, 7.11, 13.4, 14.1, 22.6, 22.9, 23.0, 25.0, 25.5, 25.6, 29.2, 29.4, 29.42, 31.79, 31.80, 34.1, 35.8, 36.0, 59.0, 67.15, 67.18, 71.5, 71.79, 71.84, 71.9, 83.4, 84.0, 93.16, 93.25, 122.7, 123.3, 144.2, 144.9; δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 190.5, 207.3; ν_{max} (liquid film) 3438, 2926, 1621, 1457, 1260, 1104, 1032, 799 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 497.1883.$C_{20}H_{40}O_4TeNa$ requires 497.1887; $[\alpha]_D^{20}$ −23.9 (*c* 1.0, $CHCl_3$).

*4.8.1.2. (5S,Z)-4-(Butyltellanyl)-5-((2-methoxyethoxy)methoxy)dodec-3-en-2-ol [(5S)-(**12c**)].* Diastereomeric mixture (1:1) (3.78 g, 89%) as orange oil; same spectral data as for [(5*R*)-(**12c**)]; δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 191.2, 207.3; $[\alpha]_D^{20}$ +20.0 (*c* 1.0, $CHCl_3$).

4.9. Reduction of enones 11a and 11b to the corresponding alcohols 12a and 12b

4.9.1. Typical procedures. In a 100 mL round bottomed flask equipped with magnetic stirring was added the telluroenone **11a** (20 mmol, 6.19 g) and THF (35 mL). The solution was cooled to 0 °C and then a solution of $NaBH_4$ (80 mmol; 3.12 g) in methanol (10 mL) was slowly added. The progress of the reaction was monitored by TLC and after the consumption of all of the starting material, the mixture was diluted with ethyl acetate and washed with water (30 mL). The aqueous phase was extracted with ethyl acetate (2×30 mL) and the combined organic phases were washed with brine (30 mL) and then dried with magnesium sulfate. The solvents were removed in a rotary evaporator and the residue was purified by flash silica gel column chromatography eluting with a mixture (4:1) of hexane/ethyl acetate.

*4.9.2. (R,S)-(Z)-4-(Butyltellanyl)oct-3-en-2-ol (**12a**).* Orange oil (5.30 g, 80%); δ_H (300 MHz, $CDCl_3$) 0.91 (6H, t, *J* 7.2 Hz), 1.25 (3H, d, *J* 6.3 Hz), 1.28–1.40 (4H, m), 1.48 (2H, quint, *J* 7.2 Hz), 1.72 (2H, quint, *J* 7.2 Hz), 1.85 (1H, d, *J* 3.0 Hz), 2.32 (2H, t, *J* 7.2 Hz), 2.68 (2H, dt, *J* 7.7, 3.9 Hz), 4.56 (1H, quint, *J* 6.3 Hz), 5.70 (1H, d, *J* 7.7 Hz); δ_C (75 MHz, $CDCl_3$) 5.3, 13.4, 13.9, 21.8, 23.0, 25.1, 31.9, 34.2, 41.5, 71.7, 121.5, 140.5; δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 265.8; ν_{max} (liquid film) 3339, 2959, 2927, 2871, 1460, 1054 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 337.0782. $C_{12}H_{24}OTeNa$ requires 337.0787.

*4.9.2.1. (R,S)-(Z)-4-(Butyltellanyl)dec-3-en-2-ol (**12b**).* Orange oil (6.05 g, 85%); δ_H (300 MHz, $CDCl_3$) 0.89 (3H, t, *J* 6.6 Hz), 0.92 (3H, t, *J* 7.4 Hz), 1.26 (3H, d, *J* 6.3 Hz), 1.28–1.32 (6H, m), 1.39 (2H, quint, *J*

7.5 Hz), 1.67–1.77 (4H, m), 2.32 (2H, t, J 7.5 Hz), 2.68 (2H, dt, *J* 7.4, 4.5 Hz), 4.56 (1H, quint, *J* 6.4 Hz), 5.69 (1H, d, *J* 7.7 Hz); δ_C (75 MHz, $CDCl_3$) 5.3, 13.4, 14.1, 22.6, 23.1, 25.2, 28.5, 29.8, 31.7, 34.3, 41.9, 71.8, 121.9, 140.4; δ_{Te}(157.9 MHz, $CDCl_3$, Ph_2Te_2) 265.8; ν_{max} (liquid film) 3320, 2958, 2926, 2855, 1461, 1056 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 365.1092. $C_{14}H_{28}OTeNa$ requires 365.1100.

4.10. Enzymatic kinetic resolution of the alcohols 12a and 12b

4.10.1. Typical procedures. In a 250 mL erlenmeyer involved in an aluminum foil it was added the alcohol **12a** (10 mmol; 3.12 g) and previously dried and deoxygenated hexane (100 mL). Then the lipase Novozyme® 435 (1 g, 10,000 PLU g^{-1}) was added to the solution, which was purged with argon. To the resulting suspension it was added vinyl acetate (130 mmol; 12.0 mL) and the septum stoppered flask was kept in an orbital shaker (180 rpm) at 34 °C for 27 h. Then the enzyme was removed by filtration and the solvent was removed in vacuum. The residue was then chromatographed in a silica gel column eluting with a mixture (9:1) of hexane/ethyl acetate.

*4.10.1.1. (S,Z)-4-(Butyltellanyl)oct-3-en-2-ol [(S)-(**12a**)].* Orange oil (1.06 g, 34%); same spectral data as for [(*R*,*S*)-(**12a**)]; $[\alpha]_D^{20}$ +6.1 (*c* 1.0, $CHCl_3$,, 94% ee).

*4.10.1.2. (R,Z)-4-(Butyltellanyl)oct-3-en-2-yl acetate [(R)-(**19a**)].* Orange oil (1.17 g, 33%); δ_H (500 MHz, $CDCl_3$) 0.90 (3H, t, *J* 7.3 Hz), 0.91 (3H, t, *J* 7.3 Hz), 1.28 (3H, d, *J* 6.3 Hz), 1.32–1.42 (4H, m), 1.44–1.57 (2H, m), 1.72 (2H, quint, *J* 7.6 Hz), 2.01 (3H, s), 2.34 (2H, t, *J* 7.4 Hz), 2.69 (2H, t, *J* 7.7 Hz), 5.33–5.60 (1H, m), 5.67 (1H, d, *J* 8.0 Hz); δ_C (125 MHz, $CDCl_3$) 5.3, 13.4, 13.9, 20.6, 21.3, 21.8, 25.1, 31.9, 34.2, 41.7, 75.2, 123.6, 136.4, 170.1; δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 279.5; ν_{max} (liquid film) 2959, 2929, 2871, 1739, 1369, 1239, 1044 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 379.0882. $C_{14}H_{26}O_2TeNa$ requires 379.0892; $[\alpha]_D^{20}$ +13.5 (*c* 1.0, $CHCl_3$, 96% ee).

*4.10.1.3. (S,Z)-4-(Butyltellanyl)dec-3-en-2-ol [(S)-(**12b**)].* Orange oil (1.12 g, 33%); same spectral data as for [(*R*,*S*)-(**12b**)]; $[\alpha]_D^{20}$ +9.9 (*c* 1.0, $CHCl_3$, 96% ee).

*4.10.1.4. (R,Z)-4-(Butyltellanyl)dec-3-en-2-yl acetate [(R)-(**19b**)].* Orange oil (1.26 g, 33%); δ_H (300 MHz, $CDCl_3$) 0.86–0.93 (6H, m), 1.27–1.29 (9H, m), 1.35 (2H, sext, *J* 7.2 Hz), 1.50–1.54 (2H, m), 1.72 (2H, quint, *J* 7.6 Hz), 2.01 (3H, s), 2.32 (2H, t, *J* 6.4 Hz), 2.68 (2H, t, *J* 7.6 Hz), 5.33–5.60 (1H, m); 5.67 (1H, d, *J* 8.0 Hz); δ_C (125 MHz, $CDCl_3$) 5.3, 13.4, 14.0, 20.6, 21.3, 22.6, 25.1, 28.4, 29.7, 31.6, 34.1, 41.9, 75.2, 123.6, 136.3, 170.0; δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 281.7; ν_{max} (liquid film) 2928, 2856, 1739, 1370, 1239, 1044 ppm; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 407.1205. $C_{16}H_{30}O_2TeNa$ requires 407.1205; $[\alpha]_D^{20}$ +16.0 (*c* 1.0, $CHCl_3$, 96% ee).

4.11. Tellurium/lithium exchange of alcohols (*S*)-12a and (*S*)-12b and capture of the vinyl anions with carbon dioxide, followed by acidification

4.11.1. Typical procedure. In a 50 mL two necked round bottomed flask under magnetic stirring and previously flame-dried under argon the alcohol (*S*)-**12a** (3 mmol; 0.94 g) in THF (15 mL) was added. The solution was cooled to −70 °C and then ^{n}BuLi (6 mmol; 4.8 mL of a 1.25 mol L^{-1} solution in hexane) was added. The Te/Li exchange reaction was monitored by TLC. After the consumption of the starting material dry CO_2 was bubbled for 20 min. The reaction mixture was heated to room temperature and then an aqueous solution of HCl (25 mL) was added. After 20 min the reaction mixture was extracted and the aqueous phase was washed with ethyl acetate (4×20 mL). The combined organic phases were washed with saturated solutions of $NaHCO_3$ (30 mL) and NaCl (30 mL) and dried with magnesium sulfate. The solvents were removed in vacuum and the residue was purified by flash silica gel column chromatography eluting with a mixture (4:1) of hexane/ethyl acetate.

*4.11.1.1. (S)-3-Butyl-5-methylfuran-2(5H)-one (S)-**8a**.* Colorless liquid (0.39 g, 86%); δ_H (500 MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.0 Hz), 1.37 (2H, sext, *J* 7.5 Hz), 1.41 (3H, d, *J* 7.0 Hz), 1.55 (2H, quint, *J* 8.0 Hz), 2.26–2.29 (2H, m), 5.04 (1H, dq, *J* 7.0, 1.5 Hz), 7.02 (1H, d, *J* 1.5 Hz); δ_C (125 MHz, $CDCl_3$) 13.8, 19.2, 22.3, 24.9, 29.5, 77.5, 134.2, 149.1, 174.0; δ_{Te} (157.9 MHz, $CDCl_3$, Ph_2Te_2) 2960, 2933, 1754, 1320, 1085, 1028; $[\alpha]_D^{20}$ +46.1 (*c* 1.0, $CHCl_3$, 94% ee); chiral GC-FID [Supelco® Gamma DEX 120 column, carrier gas: H_2, injector temperature: 275 °C, detector temperature: 275 °C, pressure: 100 kPa, method, initial temperature: 90 °C (20 min)–1 °C/min; final temperature: 120 °C (50 min)]; t_R: (*S*)-**8a** 32.54 min and (*R*)-**8a** 34.54 min; CAS [98587-10-1].

*4.11.1.2. (S)-3-Hexyl-5-methylfuran-2(5H)-one (S)-**8b**.* Colorless liquid (0.44 g, 81%); δ_H (300 MHz, $CDCl_3$) 0.89 (3H, t, *J* 6.9 Hz), 1.27–1.37 (6H, m), 1.41 (3H, d, *J* 6.9 Hz), 1.55 (2H, quint, *J* 7.5 Hz), 2.23–2.29 (2H, m), 4.99 (1H, dq, *J* 6.9, 1.5 Hz), 7.01 (1H, d, *J* 1.5 Hz); δ_C (75 MHz, $CDCl_3$) 14.0, 19.2, 22.5, 35.2, 27.4, 28.9, 31.5, 77.5, 134.3, 149.0, 173.9; ν_{max} (liquid film) 2930, 2859, 1755, 1462, 1319, 1118, 1074, 1027 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 183.1381. $C_{11}H_{19}O_2$ requires 183.1385; $[\alpha]_D^{20}$ +42.4 (*c* 1.0, $CHCl_3$, 96% ee); chiral GC [Supelco® Gamma DEX 120 column, carrier gas: H_2, injector temperature: 275 °C, detector temperature: 275 °C, pressure: 100 kPa, method, initial temperature: 90 °C (20 min)–1 °C/min; final time: 120 °C (50 min)]; t_R: (*S*)-**8b** 62.49 min and (*R*)-**8b** 64.19 min.

4.12. Tellurium/lithium exchange reaction of alcohols 12c and 12d, followed by capture with CO_2 and acidification

4.12.1. Typical procedure. To a two necked 50 mL round bottomed flask, equipped with magnetic stirring and previously flame-dried under argon, the alcohol **12c** or **12d** (3 mmol; l.42 g) and THF (15 mL) were added. The solution was cooled to −78 °C and then ^{n}BuLi (6 mmol; 4.8 mL of a 1.25 mol L^{-1} solution in hexane) was slowly added. The Te/Li exchange reaction was monitored by TLC. After the consumption of the starting material, dry CO_2 was bubbled into the solution for 20 min. The mixture was allowed to reach the room temperature and then an aqueous solution of HCl (25 mL) was added. After 20 min of stirring the reaction mixture was extracted with ethyl acetate (4×20 mL), the combined phases were washed with saturated solution of $NaHCO_3$ (30 mL) and brine (30 mL) and then dried with magnesium sulfate. The solvents were evaporated under vacuum and the residue was purified by silica gel flash column chromatography eluting with a mixture (2:1) of hexane/ethyl acetate.

*4.12.1.1. 3-((R)-1-((2-Methoxyethoxy)methoxy)octyl)-5-methylfuran-2(5H)-one (**8c**).* Diastereoisomeric mixture (1:1) (1.19 g, 63%) as colorless liquid; δ_H (500 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.0 Hz), 1.27–1.45 [(13H, m), 1.43 (3H, d, *J* 7.0 Hz)], 1.74–1.77 (2H, m), 3.38 (3H, s), 3.54 (2H, m), 3.64–3.77 (2H, m), 4.48 (1H, t, *J* 6.5 Hz), 4.71–4.77 (2H, m), 5.03–5.05 (1H, m), 7.23 (1H, s); δ_C (125 MHz, $CDCl_3$) 14.0, 19.1, 22.6, 25.0, 29.1, 31.7, 33.9, 59.0, 67.4, 71.5, 71.7, 77.5, 94.2, 134.9, 150.7, 171.8; ν_{max} (liquid film) 2928, 1755, 1456, 1319, 1200, 1025 cm^{-1}; HRMS (ESI): *m*/*z* ($[M+Na]^+$) found 337.1997. $C_{17}H_{30}O_5Na$ requires 337.1991; $[\alpha]_D^{20}$ −96.8 (*c* 1.0, $CHCl_3$).

*4.12.1.2. 3-((S)-1-((2-Methoxyethoxy)methoxy)octyl)-5-methylfuran-2(5H)-one (**8d**).* Diastereoisomeric mixture (1:1)

(1.28 g, 68%) as colorless liquid; same spectral data as for (**8c**); $[\alpha]_D^{20}$ +102.8 (*c* 1.0, $CHCl_3$).

4.13. Deprotection of butenolides 8c and 8d

4.13.1. Typical procedure. To a two necked 25 mL round bottomed flask equipped with magnetic stirring and previously flame-dried under argon, the butenolide **8c** (1 mmol; 0.31 g) and CH_2Cl_2 (7 mL) was added. The solution was cooled to −78 °C and $TiCl_4$ (10 mmol; 10 mL of a 1.0 mol L^{-1} in CH_2Cl_2) was slowly added. The mixture was allowed to reach the room temperature and then stirred for 10 h. The mixture was treated with aqueous saturated solution of ammonium chloride (10 mL), the aqueous phase was extracted with CH_2Cl_2 (2×10 mL) and the combined organic phases were dried with magnesium sulfate. The solvent was removed under vacuum and the residue was chromatographed on flash silica gel column eluting with a mixture (1:1) of hexane/ethyl acetate to give two fractions, consisting in (−)-Acaterin (**5a**) and (+)-Acaterin (**5b**).

*4.13.1.1. (R)-3-((R)-1-Hydroxyoctyl)-5-methylfuran-2(5H)-one; (−)-acaterin (**5a**).* Colorless liquid (0.109 g, 48%); δ_H (500 MHz, $CDCl_3$) 0.88 (3H, t, *J* 6.9 Hz), 1.24–1.41 (10H, m), 1.43 (3H, d, *J* 6.8 Hz), 1.66–1.70 (1H, m), 1.71–1.76 (1H, m), 4.48 (1H, dt, *J* 6.4, 1.5 Hz), 5.01–5.05 (1H, m), 7.14 (1H, s); δ_C (125 MHz, $CDCl_3$) 14.0, 18.9, 22.6, 25.3, 29.2, 29.4, 31.8, 35.7, 67.2, 77.8, 136.6, 149.0, 172.5; ν_{max} (liquid film) 3464, 2928, 1741, 1465 cm^{-1}; $[\alpha]_D^{20}$ −19.0 (*c* 1.0, $CHCl_3$), lit.[21a] $[\alpha]_D^{20}$ −19.7 (*c* 0.61, $CHCl_3$); CAS [144398-20-9].

*4.13.1.2. (S)-3-((R)-1-Hydroxyoctyl)-5-methylfuran-2(5H)-one; (+)-Acaterin (**5b**).* Colorless liquid (0.091 g, 40%); same spectral data as for (**5a**); $[\alpha]_D^{20}$ +60.1 (*c* 1.0, $CHCl_3$), lit.[21a] $[\alpha]_D^{20}$ +62.6 (*c* 1.06, $CHCl_3$); CAS [165880-42-2].

The same procedure was repeated for the butenolide **8d**, leading to (−)-pseudo-Acaterin 1 (**5c**) and (+)-pseudo-Acaterin 2 (**5d**).

*4.13.1.3. (R)-3-((S)-1-Hydroxyoctyl)-5-methylfuran-2(5H)-one; pseudo-Acaterin 1 (**5c**).* Colorless liquid (0.102 g, 45%); same spectral data as for (**5a**); $[\alpha]_D^{20}$ −59.7 (*c* 1.0, $CHCl_3$), lit.[21a] $[\alpha]_D^{20}$ −63.7 (*c* 0.53, $CHCl_3$); CAS [165880-41-1].

*4.13.1.4. (S)-3-((S)-1-Hydroxyoctyl)-5-methylfuran-2(5H)-one; pseudo-Acaterin 2 (**5d**).* Colorless liquid (0.093 g, 41%); same spectral data as for (**5a**); $[\alpha]_D^{20}$ +20.2 (*c* 1.0, $CHCl_3$), lit.[21a] $[\alpha]_D^{19}$ +19.6 (*c* 1.04, $CHCl_3$); CAS [165880-39-7].

4.14. 1,4-*trans* Selective addition of $(Me_2PhSi_2)_2Cu(CN)Li_2$ (22) to α-alkyl-γ-butenolides (*S*)-8a and (*S*)-8b

4.14.1. Typical procedure. In a 50 mL two necked round bottomed flask equipped with magnetic stirring, previously flame-dried under argon, it was placed elemental lithium doped with 0.5% sodium (40.4 mmol; 1 g of a 30% m/m dispersion in mineral oil), which was then washed with dry hexane (25 mL). The resulting solid was suspended in THF (16 mL) and the suspension was cooled to 0 °C. To the suspension it was slowly added $PhMe_2SiCl$ (9.12 mmol; 1.52 mL) and the mixture was stirred at this temperature for 16 h. In a second 100 mL round bottomed flask equipped with magnetic stirring and previously flame-dried under argon, was added CuCN (4.2 mmol; 0.40 g) and THF (16 mL) and then the mixture was cooled to −70 °C. The mixture of the first flask was then transferred via cannula to the second flask containing the CuCN suspension. After the addition was complete the mixture was heated to 0 °C and stirred at this temperature for 20 min. In the following, the mixture was cooled to -70 °C and the butenolide (*S*)-**8a** (2 mmol; 0.31 g) was added in THF (5 mL). After 20 min stirring at −70 °C the reaction mixture was allowed to reach the room temperature and then an aqueous saturated NH_4Cl solution (10 mL) was added. The phases were separated and the aqueous phase was washed with diethyl ether (4×20 mL). The combined organic phases were washed with brine (30 mL) and dried with magnesium sulfate. The solvents were removed in vacuum and the residue was purified by silica gel flash column chromatography eluting with a mixture (9:1) of hexane/ethyl acetate.

*4.14.1.1. (3S,4R,5S)-3-Butyl-4-(dimethyl(phenyl)silyl)-5-methyldihydrofuran-2(3H)-one (**23a**).* Colorless liquid (0.48 g, 84%); δ_H (500 MHz, $CDCl_3$) 0.39 (6H, s), 0.83 (3H, t, *J* 7.0 Hz), 1.15–1.28 [(7H, m), 1.24 (3H, d, *J* 6.0 Hz)], 1.35–1.45 [(3H, m), 1.37 (1H, dd, *J* 12.0, 10.0 Hz)], 2.49 (1H, ddd, *J* 12.0, 6.5, 4.0 Hz), 4.35 (1H, dq, *J* 10.0, 6.5 Hz), 7.34–7.42 (3H, m), 7.44–7.52 (2H, m); δ_C (125 MHz, $CDCl_3$) −4.5, −4.4, 13.8, 22.2, 22.7, 28.0, 29.9, 35.5, 43.3, 77.4,128.2, 129.8, 133.7, 135.7, 179.4; ν_{max} (liquid film) 2958, 2932, 2867, 1767, 1255, 1187, 1113, 1051, 839, 702 cm^{-1}; $[\alpha]_D^{21}$ −9.7 (*c* 1.5, $CHCl_3$), lit.[26a] $[\alpha]_D^{25}$ −9.48 (*c* 3.13, $CHCl_3$); CAS [214210-35-2].

*4.14.1.2. (3S,4R,5S)-4-(Dimethyl(phenyl)silyl)-3-hexyl-5-methyldihydrofuran-2(3H)-one (**23b**).* Colorless liquid (0.52 g, 82%); δ_H (500 MHz, $CDCl_3$) 0.39 (6H, s), 0.86 (3H, t, *J* 7.0 Hz), 1.13–1.55 [(14H, m), 1.25 (3H, d, *J* 6.0 Hz), 1.36 (1H, dd, *J* 12.0, 10.0 Hz)], 2.49 (1H, ddd, *J* 12.0, 6.5, 4.0 Hz), 4.36 (1H, dq, *J* 10.0, 6.5 Hz), 7.36–7.42 (3H, m), 7.45–7.49 (2H, m); δ_C (125 MHz, $CDCl_3$) 4.2, 4.1, 14.0, 22.2, 22.6, 25.8, 29.2, 30.3, 31.6, 35.6, 43.4, 77.4, 128.2, 129.9, 133.7, 135.7, 179.4; ν_{max} (liquid film) 2956, 2929, 2857, 1767, 1255, 1186, 1113, 1050, 839, 702 cm^{-1}; $[\alpha]_D^{22}$ −10.2 (*c* 2.0, $CHCl_3$), lit.[26a] $[\alpha]_D^{22}$ −10.9 (*c* 3.04, $CHCl_3$); CAS [214210-36-3].

4.15. Fleming–Tamao oxidation of the lactones 23a and 23b

4.15.1. Typical procedure. To a 25 mL round bottomed flask equipped with magnetic stirring were added the lactone **23a** (0.76 mmol; 0.22 g), acetic acid (2 mL), potassium bromide (1.8 mmol; 0.21 g) and anhydrous sodium acetate (2.36 mmol; 0.19 g). The resulting mixture was cooled to 0 °C and then peracetic acid (2 mL of a 30% v/v solution in acetic acid) was slowly added. The resulting mixture was stirred at room temperature for 2 h and then diluted with ethyl acetate (10 mL). The mixture was treated with saturated aqueous solution of NaI (15 mL) and with saturated solution of $Na_2S_2O_3$ (20 mL), and then the aqueous phase was extracted with ethyl acetate (4×10 mL). The combined organic phases were washed with saturated aqueous solution of $NaHCO_3$ (15 mL) and dried with magnesium sulfate. The solvents were removed under vacuum and the residue was purified by flash silica gel columns chromatography, eluting with a mixture (2:1) of hexane/ethyl acetate.

*4.15.1.1. (3R,4R,5S)-3-Butyl-4-hydroxy-5-methyldihydrofuran-2(3H)-one; (−)-blastmycinolactol (**1**).* White solid (0.12 g, 93%); mp 46.3–46.6 °C, lit.[26a] 43–44 °C; δ_H (300 MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.2 Hz), 1.43–1.61 [(8H, m), 1.53 (3H, d, *J* 6.3 Hz)], 1.83–1.92 (2H, m), 2.56 (1H, ddd, *J* 8.7, 6.6, 6.0 Hz), 3.83 (1H, dd, *J* 8.7, 7.2 Hz), 4.20 (1H, quint, *J* 6.6 Hz); δ_C (75 MHz, $CDCl_3$) 13.8, 18.3, 22.7, 28.2, 28.9, 48.7, 78.9, 80.3, 176.6; ν_{max} (KBr) 3493, 2953, 2864, 1734, 1469, 1285, 1053, 854, 652 cm^{-1}; $[\alpha]_D^{22}$ −16.0 (*c* 1.0, $CHCl_3$), lit.[26a] $[\alpha]_D^{25}$ −17.1 (*c* 1.47, $CHCl_3$); CAS [34867-17-9].

*4.15.1.2. (3R,4R,5S)-3-Hexyl-4-hydroxy-5-methyldihydrofuran-2(3H)-one; (−)-NFX-2 (**3**).* White solid (0.14 g, 91%); mp 56.2–56.6 °C; δ_H (300 MHz, $CDCl_3$) 0.89 (3H, t, *J* 6.6 Hz), 1.27–1.66 [(12H, m), 1.45 (3H, d, *J* 6.3 Hz)], 1.81–1.92 (1H, m), 2.03 (1H, sl); 2.55 (1H, ddd, *J* 8.4, 7.2, 5.4 Hz), 3.84 (1H, dd, *J* 8.4, 7.2 Hz), 4.20 (1H, quint, *J* 6.2 Hz); δ_C (75 MHz, $CDCl_3$) 14.0; 18.3; 22.6; 26.7; 28.5; 29.2; 31.6; 48.7; 79.1; 79.9; 176.0; ν_{max} (liquid film) 3439, 2951,

2849, 1734, 1467, 1274, 1187, 1059, 969, 856, 653 cm^{-1}; $[\alpha]_D^{22}$ −14.8 (*c* 2.0, $CHCl_3$), lit.[26a] $[\alpha]_D^{25}$ −13.2 (*c* 2.08, $CHCl_3$); CAS [137171-29-0].

4.16. Esterification of 1 and 3 with isovaleroyl chloride

4.16.1. Typical procedure. To a 15 mL round bottomed flask under magnetic stirring previously flame-dried over argon, it was added (−)-blastimicinolactol (**1**) (0.47 mmol; 0.08 g) and pyridine (10 mL). The mixture was cooled to 0 °C and then isovaleroyl chloride (2.43 mmol; 0.3 mL) was added. The resulting mixture was stirred at room temperature for 6 h and then diluted with ethyl acetate (10 mL), washed with saturated aqueous solution of $CuSO_4$ (2×20 mL) and brine (10 mL). The organic phase was dried with magnesium sulfate and the solvents were removed under vacuum. The residue was purified by flash silica gel column chromatography eluting with a mixture (9:1) of hexane/ethyl acetate.

*4.16.1.1. (2S,3R,4R)-4-Butyl-2-methyl-5-oxotetrahydrofuran-3-yl 3-methylbutanoate; (+)-blastmycinone (**2**).* Colorless liquid (0.12 g, 96%); δ_H (300 MHz, $CDCl_3$) 0.92 (3H, t, *J* 7.2 Hz), 0.98 (6H, d, *J* 6.6 Hz), 1.32–1.49 [(7H, m), 1.47 (3H, d, *J* 6.6 Hz)], 1.61–1.68 (1H, m), 1.84–1.88 (1H, m), 2.07–2.16 (1H, m), 2.23 (2H, d, *J* 6.9 Hz), 2.69 (1H, dt, *J* 8.1, 6.0 Hz), 4.37 (1H, dq, *J* 6.6, 4.8 Hz), 4.95 (1H, dd, *J* 6.0, 4.8 Hz); δ_C (75 MHz, $CDCl_3$) 13.8, 19.5, 22.3, 22.4, 25.7, 28.9, 29.0, 43.2, 46.5, 78.5, 79.4, 172.4, 175.9; ν_{max} (liquid film) 2960, 2874, 1785, 1468, 1181, 1040 cm^{-1}; $[\alpha]_D^{22}$ +11.8 (*c* 1.2, $CHCl_3$, ee >97%), lit.[15b] $[\alpha]_D^{20}$ +11.0 (*c* 1.2, $CHCl_3$); chiral GC-FID [Supelco® Beta DEX 110 column (30 m×0.25 mm×0.25 μm), carrier gas: H_2, injector temperature: 275 °C, detector temperature: 275 °C, pressure: 100 kPa, method: Ti 90 °C (20 min)–1 °C/min–Tf 120 °C (100 min)] t_R: *ent*-(**1**) 111.404 min and (**2**) 113.182 min; CAS [27981-25-5].

*4.16.1.2. (2S,3R,4R)-4-Hexyl-2-methyl-5-oxotetrahydrofuran-3-yl 3-methylbutanoate; (+)-Antimycinone (**4**).* Colorless liquid (0.13 g, 96%); δ_H (500 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.0 Hz), 0.98 (6H, d, *J* 7.0 Hz), 1.26–1.45 (8H, m), 1.47 (3H, d, *J* 6.5 Hz), 1.59–1.67 (1H, m), 1.84–1.89 (1H, m), 2.11–2.15 (1H, m), 2.23 (2H, d, *J* 7.0 Hz), 2.69 (1H, dt, *J* 8.5, 5.5 Hz), 4.36 (1H, dq, *J* 7.0, 5.0 Hz), 4.94 (1H, dd, *J* 5.5, 5.0 Hz); δ_C (125 MHz, $CDCl_3$) 13.9, 19.3, 22.2, 22.4, 25.6, 26.7, 28.8, 29.2, 31.4, 43.0, 46.4, 78.3, 79.3, 172.3, 175.8; ν_{max} (liquid film) 2959, 2872, 1786, 1743, 1467, 1182, 1120, 1040 cm^{-1}; $[\alpha]_D^{20}$ +10.1 (*c* 1.5, $CHCl_3$, ee >97%), lit.[26a] $[\alpha]_D^{20}$ +7.8 (*c* 1.75, $CHCl_3$); chiral GC-FID [Supelco® Beta DEX 110 column (30 m×0.25 mm×0.25 μm), carrier gas: H_2, injector temperature: 275 °C, detector temperature: 275 °C, pressure: 100 kPa, method: Ti 90 °C (20 min)–1 °C/min–Tf 120 °C (100 min)] t_R: *ent*-(**3**) 261.365 min and (**3**) 263.599 min; CAS [132864-91-6].

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Supplementary data

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