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Enantioselective ring-opening of epoxides by HF-reagents Asymmetric synthesis of fluoro lactones

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Abstract

The asymmetric ring opening of *meso*- and racemic-epoxides with different HF-reagents mediated by enantiopure (salen)chromium chloride provides optically active fluorohydrins with maximum 90% e.e. This reaction as well as lipase-catalyzed deracemization of a fluorohydrin is applied to synthesize a building block for the preparation of both enantiomers of a fluorinated analogue of the prostaglandin biosynthesis inhibitor lasiodiplodin using a cyclizing olefin metathesis reaction as a key-step.

Keywords: Fluorinating reagents; Epoxides; Fluorohydrins; Asymmetric synthesis; Lipase-catalyzed racemate cleavage; Fluorinated lactones; Olefin metathesis

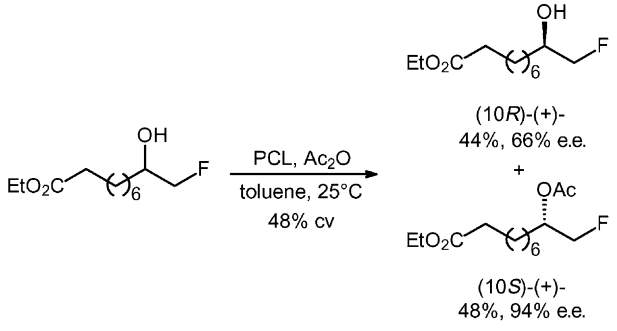
1. Introduction

There is a fast growing demand of optically active fluorinated compounds for many different applications, e.g. in medicinal chemistry, biochemistry or material sciences. Consequently, there is a great interest in synthetic methods for such compounds. Besides syntheses starting from already optically active building blocks, there are in principle two methodologies to obtain optically active fluorinated compounds: (i) the classical or enzyme-catalyzed racemate cleavage and (ii) the asymmetric introduction of fluorine into prochiral substrates [1]. Many different examples of enzyme-catalyzed deracemizations of fluorinated amino acids, fluorinated carboxylic acids, or fluorinated alcohols have been described. For example, ethyl 10-fluoro-9-hydroxy-decanoate was deracemized by acetylation with acetic anhydride in toluene using *Pseudomonas cepacia* lipase as a biocatalyst [2] (Scheme 1).

Asymmetric fluorinations of prochiral substrates can be carried out following two different protocols [3]. The first option is the enantioselective electrophilic α-fluorination of carbonyl enolates, a method which has been discovered by Differding and Lang [4] and which got much attention in recent years [5] and most recently by Davis and co-workers [6,7], Takeuchi and co-workers [8,9] and Cahard et al. [10]. Two recent examples, described by two research groups [9,10] simultaneously, are shown in Scheme 2 proceeding with 61 or 42% e.e., respectively.

Even a catalytic asymmetric electrophilic fluorination using titanium TADDOLAT complexes of the Seebach type and F-TEDA (Selectfluor) showing maximum of 90% e.e. has been published by Hintermann and Togni recently [11].

The second alternative is the nucleophilic fluorination. Until recently, there was only one example of such an enantioselective introduction of fluoride, namely the desoxyfluorination of ethyl 2-(trimethylsilyloxy)propanoate using an (*S*)-proline-based enantiopure DAST analogue. However, a maximum of 16% e.e. was the best result reported [12] (Scheme 3).



Scheme 1.

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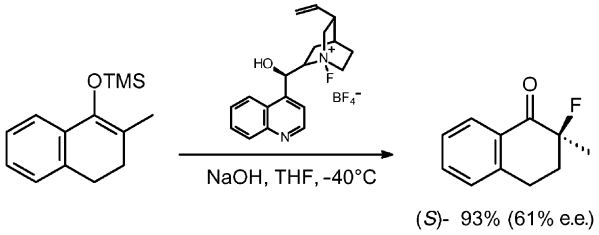
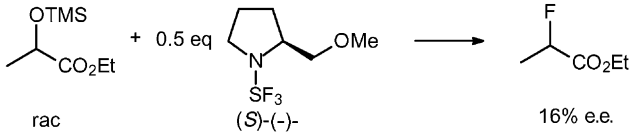


Scheme 2.



Scheme 3.

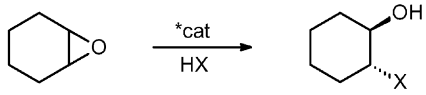
We present here our results of the asymmetric ring opening of *meso*- and racemic epoxides by hydrofluorinating reagents mediated by enantiopure (salen)chromium chloride [13] and the application of an enantiopure fluorohydrin for synthesis of a fluorinated analogue of lasiodiplodin [14].

2. Results and discussion

2.1. Asymmetric ring opening of meso- and racemic epoxides

Asymmetric ring opening of epoxides by nucleophiles using enantiopure catalysts or mediators is one of the most powerful methods in asymmetric syntheses of 1,2-disubstituted compounds [15,16].

This type of reaction, exemplified in Scheme 4, has been successfully accomplished with many different nucleophiles such as carbon nucleophiles, thiols, phenols, carboxylic acids, aromatic amines, azide, cyanide, chloride, bromide and iodide mediated or catalyzed by different Lewis acidic



Scheme 4.

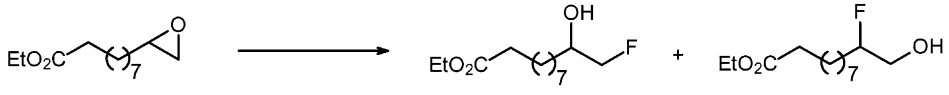
complexes. No results on the application of fluoride has been known before we published our first results [13].

On the other hand, there are many papers on the diastereo- and regioselective ring opening of epoxides with hydrofluorinating reagents [17,18]. Reactions of terminal epoxides with Olah's reagent (Py·9HF) which form fluorohydrins bearing a secondary fluorine proceed via an S_N1-like process, though there is no evidence for the formation of a free carbocation as an intermediate [19]. This method has also been used by Umezawa et al. in synthesis of optically active fluorohydrins from enantiopure epoxides, although with poor yield [20].

In contrast, applying more nucleophilic reagents such as trialkylamine hydrogen-fluorides or potassium hydrogendifluoride, products with fluorine attached to the primary position are formed in S_N2-like reactions. For these reactions, relatively high temperature is necessary leading sometimes to rearrangements or oligomerization as competitive processes. An example for the dependence of the regioselectivity of ring opening of a terminal epoxide from the hydrofluorinating agent is shown in Scheme 5 [21].

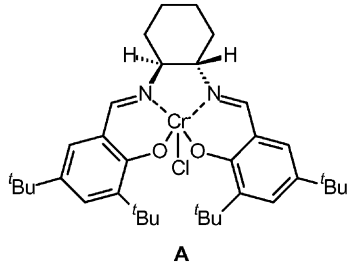
During our investigations of ring opening of α-alkylstyrene oxides, which are very sensitive to acidic conditions or high temperatures, we obtained that ring opening with triethylamine tris(hydrogenfluoride) ($Et_3N{\cdot}3HF$) can be catalysed by $BF_3{\cdot}OEt_2$ [22]. In this way from cyclohexene oxide *trans*-2-fluorocyclohexanol was obtained in 80% yield after 24 h at room temperature. Thus, if Lewis acids can catalyze this type of ring opening, than chiral metal complexes should steer the ring opening asymmetrically. However, D-Eu(hfc)$_3$ or the polymeric zinc (*R*,*R*)-tartrate gave (*S*,*S*)-(+)-2-fluorocyclohexanol with maximum of 10% e.e. [13]. The first efficient asymmetric ring opening we observed in the reaction of cyclohexene oxide with $Et_3N{\cdot}3HF$ in the presence of 100 mol% of Jacobsen's (salen)-chromium chloride **A** [23] as the mediator [24]. Earlier, this complex was shown to be a very efficient catalyst for ring opening of epoxides with azide [25,26] (Fig. 1).

However, the conversion to (*R*,*R*)-(−)-2-fluorocyclohexanol of cyclohexene oxide with $Et_3N{\cdot}3HF$ was very slow



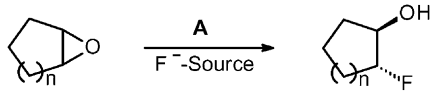
Py·9HF, CH_2Cl_2, rt, 6 h [83%]	8	:	92
$Et_3N{\cdot}3HF$, toluene, 100°C, 36 h [77%]	55	:	45
KHF_2, 18-crown-6, DMF, 153°C, 36 h [88%]	74	:	26

Scheme 5.



A

Fig. 1.



Scheme 6.

and the e.e. was only moderate. After 50 h at 0°C 20% conversion and 43% e.e. was determined (Scheme 6, Table 1, entry 1). Better results were observed with KHF_2 in DMF in the presence of 18-crown-6 at 60°C. However, using this hydrofluorinating reagent *trans*-2-chlorocyclohexanol was formed as a by-product [13] (Table 1, entry 2). Thus, a partial liberation of chloride from the catalyst seems to occur. Since chloride is more nucleophilic than the fluoride it can compete successfully in the ring opening.

Consequently, we changed again the fluoride source and used silver fluoride for the first time in ring opening of epoxides [24]. From cyclohexene oxide in the presence of equimolar amount of the (salen)complex **A** (*R*,*R*)-(−)-2-fluorocyclohexanol was formed exclusively with 72% e.e. Applying 50 mol% of **A** the e.e. dropped only slightly. Analogously, cyclopentene oxide and cycloheptene oxide were asymmetrically opened (Table 1, entries 3–6).

There are at least two mechanistic alternatives for the enantioselective ring opening, the S_N1-like and the S_N2-like mechanism. In the first case, the optically active Lewis acid complexes the epoxide. Subsequently, a not necessarily free carbocationic center is formed which is attacked by the hydrofluorinating reagent under liberation of the catalyst and the fluorohydrin. In this case, the asymmetric induction will be quite small, since the chiral auxiliary is remote from the reaction center (Scheme 7).

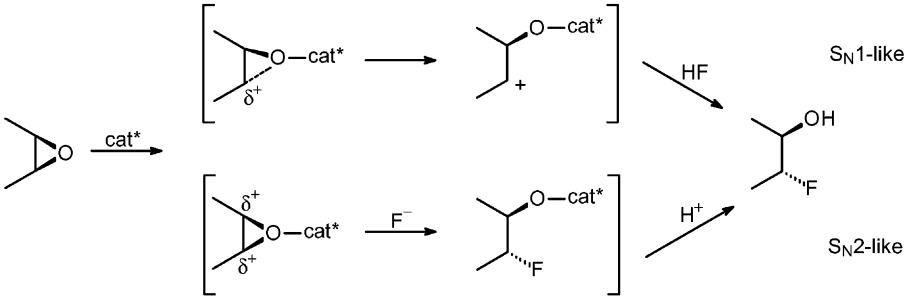
Alternatively, an S_N2-like mechanism can operate. In this case, the chiral metal complex is closer to the reaction center and can steer the attack of the fluoride equivalent more effectively. In principle, there is a third alternative, the intermediary formation of a fluorinated chromium(salen)-complex from which the fluoride could be transferred directly to the epoxide. We cannot differentiate between the alternatives yet, because silver chloride did not precipitate in the reactions with silver fluoride and also in the reactions with $Et_3N{\cdot}3HF$ or KHF_2, respectively, only small amounts of chlorohydrins were formed.

Subsequently, we studied the ring opening of racemic epoxides. With styrene oxide, 50 mol% of the (salen)complex and KHF_2 (*R*)-(−)-2-fluoro-1-phenylethanol was formed in 70% yield (based on 42% conversion) with 90% e.e. Two by-products, 2-fluoro-2-phenyl-ethanol (7%, GC) and 2-chloro-1-phenylethanol (14%, GC), were also found. The part of a

Table 1
Results of ring opening of *meso*-epoxides in the presence of (salen)chromium chloride **A**

Entry	*n*	Fluorinating reagent	**A** (mol%)	Solvent	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)[a]	e.e. (%)
1	2	$Et_3N{\cdot}3HF$	100	CH_2Cl_2	0	50	20	N.D.	43
2	2	KHF_2	100	DMF	60	80	92	64	55[b]
3	1	AgF	50	CH_3CN	70	50	85	75	44
4	2	AgF	100	CH_3CN	50	50	100	90	72
5	2	AgF	50	CH_3CN	70	20	100	85	66
6	3	AgF	50	CH_3CN	60	20	50	82	65

[a] Based on conversion.
[b] Additionally 20% (GC) of *trans*-2-chlorocyclohexanol was formed.



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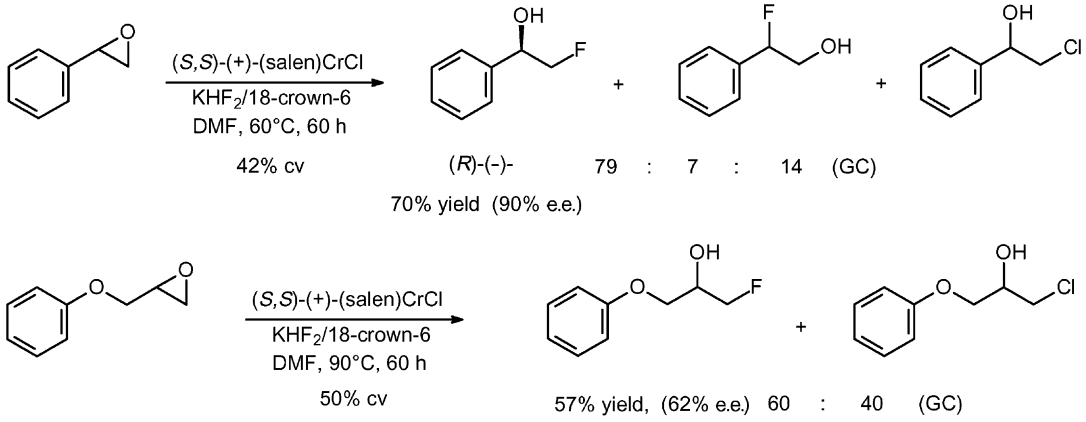


Scheme 8.

chlorohydrin was even 40% (GC) in the reaction of phenylglycidyl ether under the conditions shown in Scheme 8. The enantiomeric excess of the fluorohydrin was determined to be 62% e.e. (Scheme 8).

2.2. Synthesis of both enantiomers of fluoro lasiodiplodin

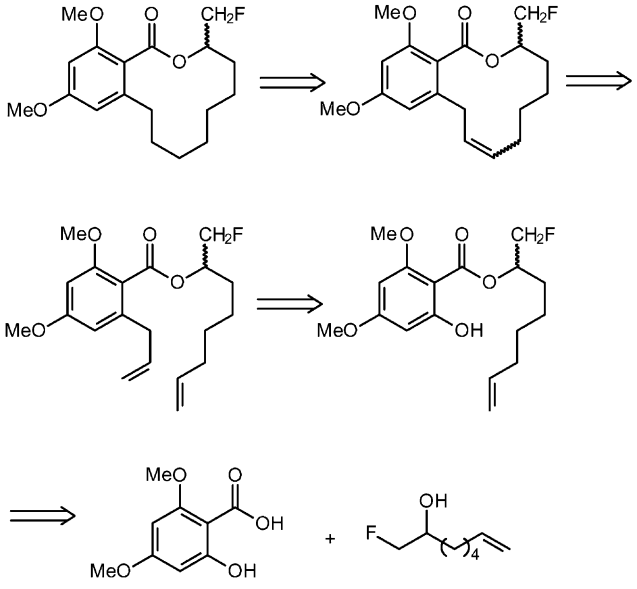
Now we became interested to apply this asymmetric ring opening as one key-step in a synthesis of a fluorinated analogue of lasiodiplodin, which is a prostaglandin biosynthesis inhibitor showing anti-cancer activity [27,28] (Fig. 2).

We planned a synthetic pathway, which involves an olefin metathesis as one key-step [14] (Scheme 9).

In order to explore whether such a cyclizing metathesis can be employed to fluorinated dienes, we first investigated a model reaction of this type. For this reason, 1-fluorooct-7-en-2-ol [29] was synthesized in 83% yield from 7,8-epoxyoctene by ring opening with KHF_2 in the presence of 18-crown-6 in DMF and subsequent chromatographic separation from its regioisomer (Scheme 10).

Subsequently (1-fluorooct-7-en)-2-yl pent-4-enoate was synthesized in 82% yield from 1-fluorooct-7-en-2-ol and pent-4-enoic acid using the method by Hasser and Alexanian with dicyclohexyl carbodiimide (DCC) and a catalytic amount of dimethylaminopyridine (DMAP) [30]. The cyclizing olefin metathesis of this ester occurred at room temperature in high dilution in methylene chloride using Grubbs catalyst [31] to yield a 64:36 mixture of the (*E*,*Z*)-isomeric unsaturated macrolides (Scheme 11) contaminated with 15% (GC) of diolides which were separated by bulb to bulb distillation under reduced pressure. The identity of the unsaturated lactones was proved spectroscopically (cf. Section 4) and by hydrogenation to the known saturated macrolide [32].

Having shown that fluorine substituents do not disturb olefin metathesis, we synthesized both enantiomers of fluoro lasiodiplodin following the pathway (Scheme 9) which is similar to the one used in total synthesis of lasiodiplodin itself reported by Fürstner and Langemann [33]. The fluoro-



Scheme 9.

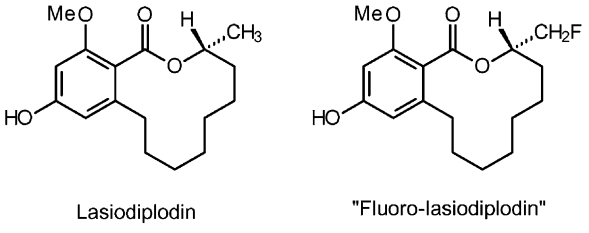
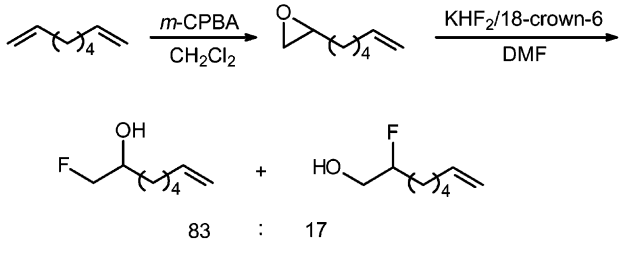
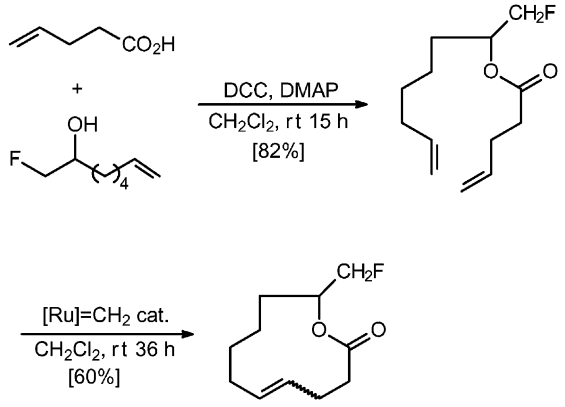


Fig. 2.



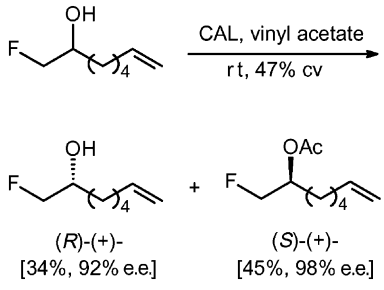
Scheme 10.



Scheme 11.

hydrin was available in optically active form by asymmetric ring opening from 7,8-epoxyoctene. However, the reaction proceeded with low enantioselectivity, 50% e.e. was found under the yet most selective conditions [24]. Consequently, racemic 1-fluorooct-7-en-2-ol (Scheme 10) was deracemized by enzyme-catalyzed acetylation with vinyl acetate in an organic solvent using *Candida antarctica* lipase as a biocatalyst [14] (Scheme 12).

The unreacted (*R*)-fluorohydrin was isolated in 34% yield with 92% e.e., while the (*S*)-(+)-acetate was isolated in 49% yield with 98% e.e. After conventional hydrolysis of the acetate, the (*S*)-alcohol was obtained in excellent yield having 98% e.e. The absolute configuration of (+)-7-acetoxy-8-fluorooct-1-ene (98% e.e.) has been determined by CD spectroscopy [34]. An UV and subsequently a CD spectrum was measured from a 1.48×10^{-3} M solution in cyclohexane ($d = 1$ cm). λ_{max} has been determined as 205 nm and the CD is positive over the complete range of wave lengths between 200 and 245 nm. From the carboxylate-sector rules [35] relevant for the acetate-chromophore, an (*S*)-configuration for the stereogenic center is predicted based on the following assumptions: The $(CH_2)_n$-backbone in long-chain alkanes prefers a *trans-anti*-orientation (zig–zag), the OAc group is smaller than the alkenyl rest, one H atom at C_8 and the C=O double bond both point in the same direction, and the influence of the alkenyl function (C_1) can be neglected due to its far distance from the stereogenic center. This assignment agrees with the known stereopreference of the enzyme [36]. For the enantiomeric acetate, prepared by acetylation with Ac_2O from the (*R*)-(+)-fluorohydrin, the CD is negative over the whole range of wave lengths proving the (*R*)-configuration for this enantiomer.



Scheme 12.

Having both enantiomers of the fluorohydrin in hands, we synthesized both antipodes of the desired fluorinated analogue of the natural lasiodiplodin on the pathway shown in Scheme 9 as a retrosynthesis [14]. Esterification of the salicylic acid using Yamaguchi and co-worker's method [37] gave the enantiomers of the ester in 62 or 67% yields, respectively. After activation of the phenolic OH-group, the Stille coupling gave the dienes in 62 or 73% yields, respectively. The Grubbs metathesis proceeded with 60 or 66% yields, respectively, to give 86:14 mixtures of the (*E*,*Z*)-isomeric 12-membered rings in both cases. Finally, the catalytic hydrogenation gave the desired products in 80 or 85% yields [14].

3. Conclusion

Asymmetric epoxide ring opening has been presented as the first efficient method for the enantioselective introduction of fluoride into organic molecules. For the total synthesis of a fluorinated analogue of the natural biosynthesis inhibitor lasiodiplodin, however, the ring opening of 7,8-epoxyoct-1-ene with KHF_2 to racemic 1-fluorooct-7-en-2-ol and subsequent lipase-catalyzed cleavage was shown to proceed with higher enantioselectivity than the asymmetric ring opening. Consequently, this way was used for the synthesis of the enantiomers of 1-fluorooct-7-en-2-ol. Subsequently, it has been shown that ring closing metathesis of a fluorinated α,ω-unsaturated ester was successful in case of synthesis of the model lactone, 11-fluoroundec-4-en-10-olide, from (1-fluorooct-7-en)-2-yl pentenoate. This method was than used as a key-step in the synthesis of both enantiomers of fluoro lasiodiplodin.

4. Experimental

4.1. General remarks

General remarks on the used reagents, separation techniques, the spectrometers (cf. [13,14]). The asymmetric ring opening of *meso*- and racemic epoxides using KHF_2 and the Jacobsen complex **A** have been described [13] and also the enantioselective synthesis of both enantiomers of the fluorinated analogue of lasiodiplodin has been published recently [14].

4.2. Ring opening of epoxides with AgF in the presence of (salen)chromium chloride A

4.2.1. General procedure

Under an argon atmosphere a mixture of the epoxide (1 mmol) and the chromium complex **A** (632 mg, 1 mmol,

or 316 mg, 0.5 mmol, respectively) in dry DMF (5 ml) was stirred for 15 min at room temperature, treated with AgF (252 mg, 1.5 mmol) and heated with stirring at the temperature and for the time given in Table 1. In order to monitor the progress of the reaction samples of the reaction mixture were taken and worked up. After cooling to room temperature, the mixture was poured into water (25 ml) and extracted with CH_2Cl_2 (5 × 10 ml). The combined organic layer was washed with water (2 × 10 ml) and dried with $MgSO_4$. The solvent was evaporated and the crude product was filtered (column with 3 cm of silica gel, cyclohexane/ethyl acetate 5:1) in order to remove traces of the metal complex, silver salts, and oligomeric material. After removing the solvent, the residue was analyzed by GC (HP1, 40–280°C, heating rate 10°C/min) and chiral GC (Beta-Dex® 120, isothermic, temperature between 80 and 110°C depending on the products). Pure fluorohydrins were obtained by column chromatography (silica gel 70–260 mesh, cyclohexane/ethyl acetate 5:1). Yields and enantiomeric excesses are given in Table 1. Spectroscopic data of the optically active fluorohydrins agree with those published for the racemic compounds [13,38,39].

4.3. Synthesis of 11-fluoroundec-4-en-10-olide

4.3.1. Esterification of 1-fluorooct-7-en-2-ol with pentenoic acid

Under argon a solution of pentenoic acid (525 mg, 5 mmol), DCC (1.14 g, 5.5 mmol), 1-fluorooct-7-en-2-ol (813 mg, 5.5 mmol) [14] and DMAP (61 mg, 0.55 mmol) in dry CH_2Cl_2 (30 ml) was stirred at room temperature for 15 h. The precipitated *N,N*-dicyclohexylurea was filtered-off and the solution was washed successively with water (3 × 50 ml), 5% diluted aqueous HOAc (3 × 50 ml), and with water again (3 × 50 ml). The organic layer was dried over $MgSO_4$, the solvent was removed and the residue was chromatographed through a 5 cm column with silica gel using CH_2Cl_2 as the eluent to give 93 mg (82%) pure (1-fluorooct-7-en)-2-yl pentenoate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29–1.47 (m, 4H, H_2-4′ and H_2-5′); 1.58–1.69 (m, 2H, H_2-3′); 2.01–2.09 (m, 2H, H_2-6′); 2.34–2.47 (m, 4H, H_2-3 and H_2-2); 4.36 (ddd, $^2J_{H,F} = 47.2$ Hz, $^2J_{H,H} = 10.1$ Hz, $^3J_{H,H} = 4.8$ Hz, 1H, H-1′); 4.47 (ddd, $^2J_{H,F} = 47.5$ Hz, $^2J_{H,H} = 10.3$ Hz, $^3J_{H,H} = 3.3$ Hz, 1H, H-1′); 4.92–5.13 (m, 5H, H_2-5, H_2-8′ and H-2′); 5.71–5.89 (m, 2H, H-4 and H-7′). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.5 (t, C-5′); 28.6 (t, C-4′); 28.9 (t, C-2); 29.4 (dt, $^3J_{C,F} = 5.1$ Hz, C-3′); 33.4 and 33.6 (2t, C-3 and C-6′); 72.2 (dd, $^2J_{C,F} = 19.1$ Hz, C-2′); 83.5 (dt, $^1J_{C,F} = 174.2$ Hz, C-1′); 114.6 and 115.5 (2t, C-5 and C-8′); 136.5 and 138.4 (2d, C-4 and C-7′); 172.5 (s, C-1). ^{19}F NMR (282 MHz, $CDCl_3$): δ −231.4 (dt, $^2J_{F,H} = 47.7$ Hz, $^3J_{F,H} = 21.0$ Hz, F-1′). MS (GC/MS, 70 eV), *m/z* (%): 228 (<1) $[M]^+$, 128 (14) $[M–C_4H_7COOH]^+$, 100 (44) $[C_4H_7COOH]^+$, 95 (31) $[128-CH_2F]^+$, 83 (64) $[M–C_8H_{14}O_2F;\ C_6H_{11}]^+$, 55 (100) $[C_4H_7]^+$. Anal. Calcd. for $C_{13}H_{21}O_2F$ (228.3): C, 68.39; H, 9.27. Found C, 68.70; H, 9.37.

4.3.2. Ring closing metathesis of (1-fluorooct-7-en)-2-yl pentenoate

Under an argon atmosphere solutions of (1-fluorooct-7-en)-2-yl pentenoate (114 mg, 0.5 mmol) in dry CH_2Cl_2 (30 ml) and of benzylidenebis(tricyclohexylphosphine)dichloro-ruthenium (14 mg, 0.017 mmol, 3.4 mol%) [33] in dry CH_2Cl_2 (30 ml) were dropped simultaneously to refluxing dry CH_2Cl_2 over a period of 12 h. After stirring for another 24 h at that temperature, the solvent was removed in vacuo, and the residue was purified by flash chromatography (silica gel, cyclohexane/ethyl acetate 3:1) to give 70 mg of crude diastereomeric mixture of the lactone containing 15% of diolides. Bulb to bulb distillation (142°C at 18 mbar) gave 60 mg (60%) of a 64:36 mixture of the (*E*/*Z*)-isomeric 11-fluoroundec-4-en-10-olides. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95–1.90 (m, 8H, H_2-7 to H_2-9, H_2-2); 2.20–2.44 (m, 4H, H_2-3 and H_2-6); 4.24–4.55 (dm, $^2J_{H,F} = 47.5$ Hz, 2H, H_2-11); 4.96–5.15 (m, 1H, H-10); 5.23–5.49 (m, 2H, H-4 and H-5). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.1 and 24.9 (2t, C-8 and C-7); 29.3 (dt, $^3J_{C,F} = 5.1$ Hz, C-9); 30.4, 32.7 and 35.5 (3t, C-2, C-3 and C-6); 71.6 (dd, $^1J_{C,F} = 17.8$ Hz, C-10); 83.6 (dt, $^1J_{C,F} = 172.9$ Hz, C-11); 129.3 and 131.6 (2d, C-4 and C-5); 173.6 (s, C-1). ^{19}F NMR (282 MHz, $CDCl_3$): δ −230.2 (dt, $^2J_{F,H} = 47.7$ Hz, $^3J_{F,H} = 21.0$ Hz, F-11). MS: GC/MS, 70 eV), *m/z* (%): 201 (2) $[MH]^+$, 200 (24) $[M]^+$, 182 (18) $[M–H_2O]^+$, 167 (5) $[M–CH_2F]^+$, 162 (8) $[182\text{-}HF]^+$, 140 (14) $[182\text{-}C_3H_6]^+$, 120 (20), 108 (23), 95 (52), 80 (80), 67 (100) $[C_6H_7]^+$. Anal. Calcd. for $C_{11}H_{17}O_2F$ (200.3): C, 65.98; H, 8.56. Found C, 66.04; H, 8.98.

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