Reaction of Internal Fluoroolefin Oxides with Camphor Thiosemicarbazone^{*}

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Abstract—Epoxy derivatives of internal fluoroolefins (both *cis* and *trans* isomers) react in a stereospecific manner with (1*S*)- or *rac*-camphor thiosemicarbazone in a polar aprotic medium to give the corresponding 5-fluoro-4-hydroxy-4,5-bis(polyfluoroalkyl)thiazol-2-ylhydrazones. From unsymmetrical 2,3-epoxydodeca-fluorohexane a mixture of regioisomeric hydrazones is formed. According to the ¹H and ¹⁹F NMR data, the resulting *trans*-hydrazones in (CD₃)₂SO and CDCl₃ exist as mixtures of diastereoisomers occurring in a dynamic equilibrium.

We previously showed [1–3] that 2,3-epoxypolyfluoroalkanes react with ethylenediamine, 2-aminoethanol, thiourea, and thiosemicarbazide to give fluorinated heterocyclic compounds such as diazines, oxazines, and 2-amino- and 2-hydrazinodihydrothiazoles. We have found no published data on reactions of fluorinated epoxyalkanes with thiosemicarbazones.

In the present work we studied reactions of polyfluorooxiranes I-III [4] with thiosemicarbazones derived from (1*S*)- and *rac*-camphor [5] with the goal of obtaining potential biologically active compounds [6]. The reactions were carried in a polar aprotic solvent (dioxane, acetonitrile), and the corresponding 5-fluoro-4-hydroxy-4,5-bis(polyfluoroalkyl)thiazol-2-ylhydrazones **IV–VII** were selectively formed in high yields (Tables 1–3).

2,3-Epoxyoctafluorobutane (I) (*trans*: *cis* ~9:1) and 3,4-epoxydodecafluorohexane *trans*-(II) reacted with (1*S*)-camphor thiosemicarbazone [(1*S*)-CTSC] to give only one regioisomer, camphor 5-fluoro-4-hy-droxy-4,5-bis[trifluoromethyl(or pentafluoroethyl)]-thiazol-2-ylhydrazone IV or V. Using ¹⁹F NMR





 $\mathbf{I}, \ \mathbf{IV}, \ \mathbf{R}_{\mathrm{F}} \ = \ \mathbf{CF}_3; \ \mathbf{II}, \ \mathbf{V}, \ \mathbf{R}_{\mathrm{F}} \ = \ \mathbf{CF}_3\mathbf{CF}_2.$

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Scheme 2.



spectroscopy we have found [3] that the formation of the thiazole ring is stereospecific (as in reactions of internal epoxypolyfluoroalkanes with thiourea in a polar aprotic solvent [3]): the ratio of isomers with *trans* and *cis* arrangement of the fluoroalkyl substituents in the dihydrothiazole ring of **IV** is approximately the same as in initial oxirane, and from compound **II** the *trans* isomer of **V** is exclusively formed (Scheme 1).

Opening of the oxirane ring in unsymmetrical 2,3-epoxydodecafluorohexane (III) (*trans*: *cis* ~9:1) by the action of (1S)-CTSC under analogous conditions takes both possible pathways (*a* and *b* in Scheme 2), yielding regioisomeric (1S)-camphor thiazolylhydrazones VI and VII at a ratio of ~44:56; each regioisomer being a mixture of *trans* and *cis* stereoisomers with approximately the same ratio as in initial oxirane III.

Hydrazones (1*S*)-**IV** and (1*S*)-**V** and regioisomeric mixture (1*S*)-**VI**/(1*S*)-**VII** with *trans* orientation of the fluoroalkyl groups were isolated by crystallization. Their structure was confirmed by the IR, ¹H and ¹⁹F NMR, and mass spectra and analytical data; compound **IV** [(1*S*,4'*RS*,5'*RS*)-**IV**] was also examined by 13 C NMR spectroscopy (Tables 1–3). In the ¹⁹F NMR

spectra of (1S,4'RS,5'RS)-IV recorded in CDCl₃ and $(CD_3)_2SO$ we observed a double set of signals from the fluoroalkyl groups. Presumably, this compound is a mixture of two diastereoisomers, (1S,4'S,5'S) and (1S,4'R,5'R). Its ¹H and ¹³C NMR spectra also contained double sets of signals from most protons and carbon nuclei. The signal intensity ratios for diastereomers were different in different solvents: ~1:1 in $CDCl_3$ and $\sim 2:1$ in $(CD_3)_2SO$. On the other hand, the ¹⁹F and ¹H signals of the diastereoisomers in $(CD_3)_2SO$ coalesce at 80°C. These data suggest that compound (1S, 4'RS, 5'RS)-IV in CDCl₃ and $(CD_3)_2SO$ gives rise to a dynamic equilibrium between different stereoisomers, which shifts to one or another side depending on the conditions. A possible mechanism of diastereoisomer interconversion, including successive elimination-addition of HF and H_2O molecules, is shown in Scheme 3. The spectral parameters of trans-hydrazones V-VII indicate that they also exist in $CDCl_3$ and $(CD_3)_2SO$ solutions as mixtures of two diastereoisomers.

The reaction of racemic camphor thiosemicarbazone (*rac*-CTSC) with oxirane I (*cis-trans* ratio ~1:9) resulted in stereospecific formation of *rac*-IV; the corresponding *trans* isomer of (1*RS*,4'1RS,5'*RS*)-IV was





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Table 1. Yields, melting points, and IR spectra of the (1S,4'RS,5'RS) isomers of compounds IV, V, VI/VII, and VIII \cdot H₂O and of the (1RS,4'RS,5'RS) isomer of IV

Compound no.	Isomer	Yield, %	00	IR spectrum, v, cm ⁻¹ (mineral oil)			
		(solvent)	mp, ⁻ C	C=N	NH	OH, NH	
IV	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i>	43 (dioxane) ^a 25 (MeOH, H ₂ O) ^b	152–153 ^c 152–153 ^d	1645 sh, 1635, 1620 sh, 1608	3320	3070 br	
IV	1 <i>RS</i> ,4' <i>RS</i> ,5' <i>RS</i>	50 (dioxane)	149–150 ^c	1640, 1610	3320	3100 br	
V	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i>	55 (dioxane),48 (acetonitrile)	156–157 ^c	1650 sh, 1625	3320	3540, 3200 br	
VI/VII (~39:61)	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i>	70 (dioxane)	129–158 ^c	1675 sh, 1650, 1630	3350	3160 br	
VIII · H ₂ O	1 <i>S</i> ,4′ <i>RS</i> ,5′ <i>RS</i>	15 (MeOH)	162–163	1680, 1630, 1515	2800–2400 (NH ⁺)	3140 br	

^a Method *a*.

^b Method b.

^c From benzene.

^d From benzene–hexane, 1:1.

Table 2. Elemental analyses of the (1S,4'RS,5'RS) isomers of compounds **IV**, **V**, **VI/VII**, and **VIII** \cdot H₂O and of the (1RS,4'RS,5'RS) isomer of **IV**

Compound no.	Isomer	Found, %				Formula	Calculated, %					
		С	Н	F	N	S	ronnuta	С	Η	F	N	S
IV IV V	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i> 1 <i>RS</i> ,4' <i>RS</i> ,5' <i>RS</i> 1 <i>S</i> ,4' <i>PS</i> ,5' <i>PS</i>	42.89 42.71 20.10	4.31 4.18	31.68 31.48	10.03 9.95 8 10	7.71 7.53	$C_{15}H_{18}F_7N_3OS$ $C_{15}H_{18}F_7N_3OS$ $C_{15}H_{18}F_7N_3OS$	42.76 42.76	4.28 4.28	31.59 31.59 40.12	9.98 9.98 8.06	7.60 7.60
v VI/VII (~39:61) VIII · H ₂ O	15,4 /RS,5 /RS 1 <i>S</i> ,4 / <i>RS</i> ,5 / <i>RS</i>	39.19 39.21 36.41	3.48 3.43 3.42	40.08 40.88	7.98 7.44	6.08 5.69	$C_{17}H_{18}F_{11}N_{3}OS$ $C_{17}H_{18}F_{11}N_{3}OS$ $C_{17}H_{21}F_{12}N_{3}O_{2}S$	39.16 39.16 36.49	3.453.453.76	40.12 40.12 40.78	8.06 8.06 7.51	6.146.145.72

isolated in the pure state by crystallization. As in the above cases, the ¹H, ¹⁹F, and ¹³C signals of the product are doubled due to the presence of two diastereoisomers, each being a mixture of two enantiomers, 1S,4'R,5'R/1R,4'S,5'S and 1S,4'S,5'S/1R,4'R,5'R.

The geometry of the =N-NH- fragment in hydrazones **IV**-**VII** was determined by comparing the ¹³C NMR spectra of (1*S*,4'*RS*,5'*RS*)-**IV** and camphor; specifically, the chemical shifts of C³ and C¹⁰ were considered ($\delta_{\rm C}$ 42.8 and 8.83 ppm, respectively for camphor [7]). A considerable upfield shift of the C³ signal ($\delta_{\rm C}$ 33.83 and 33.72 ppm; $\Delta \sim 9$ ppm) in the spectrum of (1*S*,4'*RS*,5'*RS*)-**IV** is likely to result from steric and compression effects of the amino group, which suggests the *anti* configuration of hydrazone (1*S*,4'*RS*,5'*RS*)-**IV**, i.e., the substituent at the *sp*²- hybridized nitrogen atom is oriented opposite to the methyl group on C¹⁰. Deshielding of the latter in (1S, 4'RS, 5'RS)-**IV** ($\delta_{\rm C}$ 10.75 and 10.71 ppm; $\Delta \sim 1.90$ ppm) indicates that the methyl group interacts with the lone electron pair on the nitrogen atom, which is possible only in the *anti* isomer.

It should be noted that the reactions of oxiranes **I–III** with both (1*S*)-CTSC and *rac*-CTSC in protic solvent (MeOH) led to formation of complex mixtures of products. In these cases, the corresponding thiazolylhydrazones were isolated as hydrofluorides in low yields. In the reaction of **III** (*cis–trans* ratio ~1:9) with (1*S*)-CTSC we obtained only one regioisomeric thiazolylhydrazone, namely (1*S*,4'*RS*,5'*RS*)-**VII** which gives poorly soluble hydrofluoride (1*S*,4'*RS*,5'*RS*)-**VIII**. The latter was isolated as monohydrate

Table 3. NMR spectra of compounds IV-VIII^a

Comp. no.	Isomer	Chemical shifts $\delta_{\rm F}$, $\delta_{\rm C}$, ppm	Coupling constants <i>J</i> , Hz
IV	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i>	¹ H: 7.18 br.s (2H, OH, NH), 2.36 d.t (1H), 2.04 m (1H), 1.95–1.71 m (3H), 1.40 m (1H), 1.23 m (1H) (camphor), 1.19 s and 0.98 s (3H, CH ₃), 0.95 s (3H, CH ₃), 0.76 s (3H, CH ₃) 13 C: 171.26 and 170.81 (C ²), 165.83 and 165.68 (C ²), 122.09 q (C ^{1'''}), 121.29 q.d and 121.28 q.d (C ^{1''}), 110.86 d.q and 110.72 d.q (C ^{5'}), 100.55 d.q and 100.19 d.q (C ^{4'}), 53.25 and 53.22 (C ¹), 48.25 and 48.19 (C ⁷), 44.05 and 44.03 (C ⁴), 33.83 and 33.72 (C ³), 32.39 and 32.36 (C ⁶), 27.11 (C ⁵), 19.45 and 19.34 (C ⁹), 18.49 and 18.48 (C ⁸), 10.75 and 10.71 (C ¹⁰) 19 F: 90.30 d.q and 90.26 d.q (1"-F ₃), 83.69 d.q and 83.66 d.q (1"'-F ₃), 14.49 q.q and 14.29 q.q (5'-F)	${}^{4}J_{F,F} = 20.8,$ ${}^{3}J_{F,F} = 10.0,$ ${}^{5}J_{F,F} = 4.8,$ ${}^{1}J(C^{1'''},F) = 284.2,$ ${}^{1}J(C^{5'},F) = 243.6,$ ${}^{2}J(5',F,C^{1''}) = 33.9,$ ${}^{2}J(C^{5'},1'',F) = 32.5,$ ${}^{2}J(C^{4'},1''',F) = 32.0,$ ${}^{2}J(C^{4'},5',F) = 24.6$
IV	1 <i>RS</i> ,4' <i>RS</i> ,5'SR	$^{19}{\rm F:}$ 88.83 d.q and 88.81 d.q (1"-F), 82.72 q.d and 82.68 q.d (1"'-F_3), 19.53 m (5'-F)	${}^{3}J_{\mathrm{F,F}} = {}^{5}J_{\mathrm{F,F}} = 10.7,$ ${}^{4}J_{\mathrm{F,F}} = 3.7$
V	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i>	¹ H: 3.63 br.s (2H, OH, NH), 2.55–1.92 m (7H, camphor), 1.00 s (3H, CH ₃), 0.96 s (3H, CH ₃), 0.77 s (3H, CH ₃) ¹⁹ F: 83.60 d and 83.44 d (~1:1) (2"-F ₃), 82.00 d (2""-F ₃), 53.39 m (1"-F _A), 44.12 m (1"'-F _A), 40.35 m (1"'-F _B), 39.82 m (1"-F _B), 17.22 m (5'-F)	$J(1''-F_A, 1''-F_B) = J(1'''-F_A, 1'''-F_B) = 292$
VI	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i>	¹ H: 6.70 br.s (2H, OH, NH), 2.35 d (1H), 2.05 m (1H), 1.97– 1.70 m (3H), 1.40 m (1H), 1.22 m (1H, camphor), 0.985 s and 0.981 s (3H, CH ₃), 0.95 s (3H, CH ₃), 0.773 s and 0.762 s (3H, CH ₃) ¹⁹ F: 90.24 t and 90.22 t (5'-CF ₃), 80.88 t and 80.66 t (3"-F ₃), 46.11 m (1"-F _A), 43.99 m (1"-F _B), 40.49 t (2"-F _A), 37.99 t (2"-F _B), 13.92 m (5'-F)	$ \begin{array}{l} J(1^{\prime\prime}\text{-}\mathrm{F}_{A},1^{\prime\prime}\text{-}\mathrm{F}_{B}) = 288.5,\\ J(2^{\prime\prime}\text{-}\mathrm{F}_{A},2^{\prime\prime}\text{-}\mathrm{F}_{B}) = 286.6,\\ {}^{4}J(1^{\prime\prime\prime}\text{-}\mathrm{F},3^{\prime\prime\prime}\text{-}\mathrm{F}) = 11.0,\\ {}^{3}J(5^{\prime}\text{-}\mathrm{CF}_{3},5^{\prime}\text{-}\mathrm{F}) = 9.5 \end{array} $
VI	1 <i>S</i> ,4' <i>RS</i> ,5' <i>SR</i>	$^{19}{\rm F:}$ 92.12 m (5'-CF ₃), 80.67 t (3"-F ₃), 41.82 (1"-F ₂), 40.43 m (2"-F ₂), 24.63 m (5'-F)	
VШ	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i>	¹ H: 6.70 br.s (2H, OH, NH), 2.35 d (1H), 2.05 m (1H), 1.97–1.70 m (3H), 1.40 m (1H), 1.22 m (1H, camphor), 0.994 s and 0.985 s (3H, CH ₃), 0.95 s (3H, CH ₃), 0.768 s and 0.762 s (3H, CH ₃) ¹⁹ F: 84.35 t and 84.33 t (4'-CF ₃), 81.20 d.d (3"-F ₃), 54.17 t.q (1"-F _A), 43.13 m (1"-F _B), 40.23 m (2"-F _A), 37.69 m (2"-F _B), 15.38 m and 15.12 m (5'-F)	$ \begin{array}{l} J(2''\text{-}F_A,2''\text{-}F_B) = 290.5,\\ J(1''\text{-}F_A,1''\text{-}F_B) = 289.0,\\ {}^4J(5'\text{-}F,4'\text{-}CF_3) = \\ {}^5J(1''\text{-}F_B,4'\text{-}CF_3) = 20.9\\ {}^4J(3''\text{-}F,1''\text{-}F_A) = 13.4,\\ {}^4J(3''\text{-}F,1''\text{-}F_B) = 8.3 \end{array} $
VII	1 <i>S</i> ,4' <i>RS</i> ,5' <i>SR</i>	$^{19}{\rm F:}$ 85.00 t (4'-CF ₃), 81.24 m (3"-F ₃), 50.17 m (1"-F _A), 41.58 m (1"-F _B), 39.63 m (2'-F ₂), 24.61 m (5'-F)	
VIII · H ₂ O	1 <i>S</i> ,4' <i>RS</i> ,5' <i>RS</i>	¹ H: 7.52 br.s (5H, OH, NH, HF, H ₂ O), 2.36–1.14 m (7H, camphor), 0.91 s (6H, 2CH ₃), 0.72 s and 0.69 s (~1:1, 3H, CH ₃) ¹⁹ F: 86.71 t (4'-CF ₃), 82.54 t (3"-F ₃), 56.07 t.q (1"-F _A), 43.97 m (1"-F _B), 41.39 d.d (2"-F _A), 38.91 t (2"-F _B), 23.17 br.s (HF), 17.60 m (5'-F)	$ \begin{array}{l} J(1''\text{-}F_A,1''\text{-}F_B) = 288.1,\\ J(2''\text{-}F_A,2''\text{-}F_B) = 285.6,\\ {}^4J(5'\text{-}F,4'\text{-}CF_3) = \\ {}^5J(1''\text{-}F_B,4'\text{-}CF_3) = 21.4,\\ {}^4J(3''\text{-}F,1''\text{-}F) = 11,\\ {}^4J(2''\text{-}F_A,5'\text{-}F) = 25.0 \end{array} $

^a The ¹H and ¹⁹F NMR spectra of (1S,4'RS,5'RS)-**IV**, (1S,4'RS,5'RS)-**V**, (1S,4'RS,5'RS)-**VI**, (1S,4'RS,5'RS)-**VII**, and (1RS,4'RS,5'RS)-**IV** were recorded in CDCl₃, and of (1S,4'RS,5'RS)-**VIII** · H₂O, (1S,4'RS,5'RS)-**VI**, and (1S,4'RS,5'RS)-**VII**, in DMSO-*d*₆; the ¹³C NMR spectrum of (1S,4'RS,5'RS)-**IV** was recorded in CDCl₃

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(1S,4'RS,5'RS)-VIII · H₂O. Presumably, compound VII is protonated at the thiazole nitrogen atom, but the structure of salt VIII is analogous to those derived from nonfluorinated thiazolylhydrazones having an electron-acceptor substituent in position 4 [8] (Scheme 4).

Scheme 4.



An alternative way of synthesizing hydrazones **IV–VII** may be reaction of camphor with 5-fluoro-2-hydrazino-4-hydroxy-4,5-bis(polyfluoroalkyl)-4,5-dihydrothiazoles [3]. For example, by reaction of (1*S*)-camphor with 5-fluoro-2-hydrazino-4-hydroxy-*trans*-4,5-bis(trifluoromethyl)-4,5-dihydrothiazole (**IX**) in the presence of a catalytic amount of HCl we obtained hydrazone (1S,4'RS,5'RS)-**IV** (Scheme 5). However, this procedure is less advantageous than that described above because of formation of by-products and low yields in the synthesis of initial thiazolylhydrazines.

Scheme 5.



EXPERIMENTAL

The ¹H NMR spectra were recorded on Bruker DRX-400 and Tesla BS-567A spectrometers (400 and 100 MHz, respectively); the ¹³C and ¹⁹F NMR spectra were obtained on a Bruker DRX-400 instrument relative to TMS and C_6F_6 as internal references; CDCl₃ and DMSO- d_6 were used as solvents. The mass spectra (70 eV) were run on a Varian MAT-311 mass spectrometer. The IR spectra were measured on a Specord 75IR instrument in mineral oil. Oxiranes I–III were synthesized by the procedures reported in [5]. The product ratios were determined from

the corresponding signal intensities in the ¹⁹F NMR spectra.

(1*S*)-Camphor (4*RS*,5*RS*)-5-fluoro-4-hydroxy-4,5-bis(trifluoromethyl)-4,5-dihydrothiazol-2-ylhydrazone (1*S*,4'*RS*,5'*RS*)-(IV). *a*. A mixture of 3 g (13.9 mmol) of oxirane I (*trans–cis* ratio ~9:1), 0.5 g (2.2 mmol) of (1*S*)-CTSC, and 10 ml of dioxane was heated in a sealed ampule on a boiling water bath for 2 h with occasional shaking. After cooling to -70° C, the ampule was opened, excess oxirane I was recondensed into a trap cooled to -70° C, the residue was poured into 150 ml of water, and the resulting mixture was left to stand for 12 h for crystallization. The precipitate was filtered off, washed with water, dried at 50–60°C, and recrystallized first from hexane– benzene (~5:1) and then from benzene. The product was isolated as colorless crystals.

b. To a solution of 0.6 g (2 mmol) of hydrazine **IX** in 6 ml of H_2O and 10 ml of MeOH we added dropwise with stirring 0.5 ml of 10% hydrochloric acid and then a solution of 0.4 g (2 mmol) of (1*S*)-(–)-camphor in 4 ml of MeOH. The mixture was refluxed for 0.5 h, cooled, and left to stand for partial evaporation of the solvent and crystallization. The precipitate was filtered off, dried at ~40°C, and recrystallized from hexane–benzene (1:1).

rac-Camphor (4*RS*,5*RS*)-5-fluoro-4-hydroxy-4,5-bis(trifluoromethyl)-4,5-dihydrothiazol-2-ylhydrazone (1*RS*,4*'RS*,5*'RS*)-(IV) was synthesized as described above in *a* from oxirane I and *rac*-CTSC. The product was isolated as colorless crystals.

(1S)-Camphor (4RS,5RS)-5-fluoro-4-heptafluoropropyl-4-hydroxy-5-trifluoromethyl-4,5-dihydrothiazol-2-ylhydrazone (1S,4'RS,5'RS)-(VI) and (1S)-camphor (4RS,5RS)-5-fluoro-5-heptafluoropropyl-4-hydroxy-4-trifluoromethyl-4,5-dihydrothiazol-2-ylhydrazone (1S,4'RS,5'RS)-(VII). The reaction of 2.5 g (7.9 mmol) of 2,3-epoxydodecafluorohexane (III) (*cis-trans* ratio $\sim 1:9$) with 1 g (4.4 mmol) of (1S)-CTSC in 15 ml of dioxane was carried out as describe above for compound I (method a, reaction time 4.5 h). The ampule was cooled and opened, and the mixture was poured into 100 ml of water. The bottom layer was separated, washed with water, and left under a layer of water for crystallization. The crystals were filtered off, dried at 50–60°C, and recrystallized from benzene. A mixture of compounds VI and VII (~39:61) was isolated as colorless crystals.

(S)-Camphor (4RS,5RS)-5-fluoro-4-hydroxy-4,5bis(pentafluoroethyl)-4,5-dihydrothiazol-2-ylhydrazone (1S,4'RS,5'RS)-(V) was synthesized in a similar way from *trans*-3,4-epoxydodecafluorohexane *trans*-II and (1*S*)-CTSC. Colorless crystals. Mass spectrum, m/z (I_{rel} , %): 522 (17.6) $[M+1]^+$, 520 (1.1) $[M-1]^+$.

(S)-Camphor (4RS,5RS)-5-fluoro-4-hydroxy-5heptafluoropropyl-4-trifluoromethyl-4,5-dihydrothiazol-2-ylhydrazone hydrate (1S,4'RS,5'RS)-(VIII) \cdot H₂O. The reaction of 2.5 g (7.9 mmol) of oxirane III (*cis-trans* ratio ~1:9) with 1 g (4.4 mmol) of (1S)-CTSC in 35 ml of MeOH was carried out as described above (reaction time 4 h). After cooling, the ampule was opened, and the solvent was distilled off under reduced pressure. The solid residue was washed with hot chloroform and dried (~80°C). The product was isolated as a colorless powder. Mass spectrum, m/z (I_{rel} , %): 523 (11.88) [M-OH-F]⁺, 521 (50.04) [M-H₂O-HF]⁺.

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