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Fluoroalkyl derivatives of protected glycerol by nucleophilic substitution. Fluorine-containing amphiphilic mono- and bis-methacrylates

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Abstract

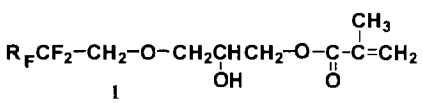
The tosylate of protected glycerol (solketal, 4-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane) was fluoroalkylated by a nucleophilic substitution reaction with sodium polyfluoroalkoxides. On deprotection, 3-O-fluoroalkylated glycerol was obtained which was converted to mono- and bis-methacrylates; analogous methacrylate derivatives were prepared from 3,3,4,5,5,5-hexafluoro-pentane-1,2-diol. © 1997 Elsevier Science S.A.

Keywords: 4-[(Polyfluoroalkoxy)methyl)]-2,2-dimethyl-1,3-dioxolanes; Polyfluoroalkoxides; Tosylates of fluoroalkanols; 3-(Polyfluoroalkoxy)propane-1,2-diols; Amphiphilic fluoroalkyl methacrylates; 2-Hydroxy-3-(polyfluoroalkoxy)propyl methacrylates; 3-(Polyfluoroalkoxy)-propane-1,2-diyl bis-methacrylates

1. Introduction

The aim to develop special monomers for polymeric materials that combine a good oxygen permeability with biocompatibility [1,2] led us to the synthesis of new amphiphilic methacrylates. These properties can be adjusted by a polyfluorinated chain and hydrophilic hydroxy unit, for example of a general structure **1** (Scheme 1). Typical applications of such materials are contact lenses [3,4], and also vein- and body-tissue prosthetics [5–7]. Some methacrylic monomers with fluoroalkyl amphiphilic ester groups are reported in the patent literature (see, for example, Refs. [8–17]), but we have not found any report in an original paper about the preparation of these compounds.

Our synthesis has been based on 2,3-protected glycerol (solketal, **2**) and the formation of an ether linkage on the unprotected hydroxyl (Schemes 2–4). There are several known general methodologies for the transformation of hydroxy compounds to the corresponding fluoroalkylethers; the most general are the following: Williamson synthesis [18–20], nucleophilic addition of alkoxides onto fluoro-olefins [21,22] and the Mitsunobu reaction [23]. We have chosen a modified Williamson synthesis in which the tosylate of the starting solketal (**3**) was used (Scheme 4). Etherification by the Mitsunobu protocol is limited to acidic alcohols [23] and hence it is also applicable to fluoroalkanols [24]



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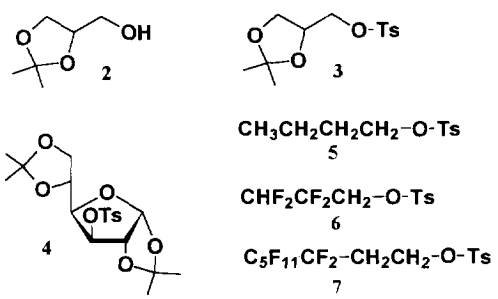
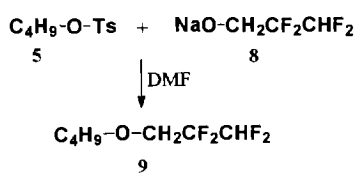
R_F = perfluoroalkyl, polyfluoroalkyl

Scheme 1. General structure of potential amphiphilic methacrylate monomers.



Scheme 2. Tosylates of hydroxy compounds.



Scheme 3. Model synthesis of fluoroalkylethers.

used in this study, but the reaction has some practical limitations in the separation of byproducts. Nucleophilic addition of protected glycerol (**2**) to perfluorolefins have not been

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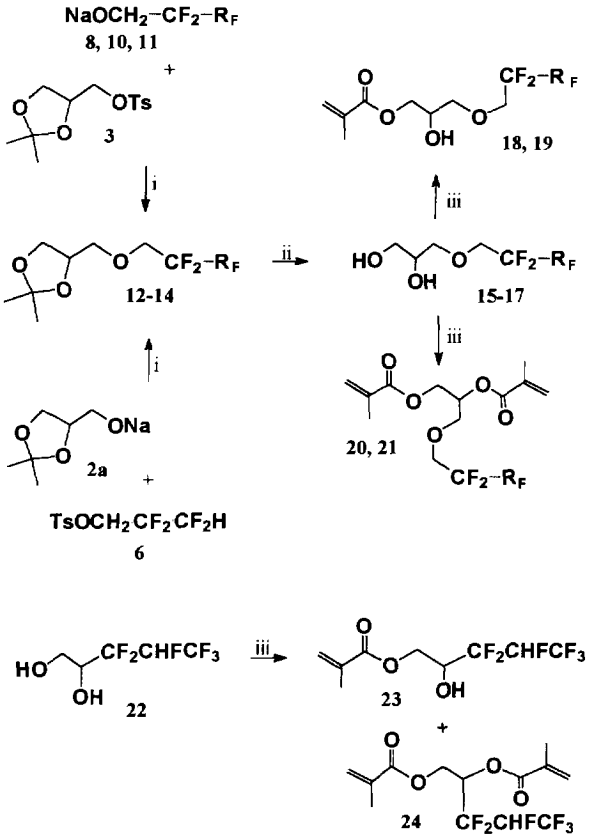


i DMF **8, 12, 15, 18, 20** $R_F = CHF_2$
ii HCl, MeOH **10, 13, 16, 19, 21** $R_F = F$
iii Py, MA-Cl **11, 14, 17** $R_F = CF_2CF_2CHF_2$

Scheme 4. Mono- and bis-methacrylates of fluoroalkylated diols.

used by us because the resulting ethers of the type R–O–CF_2–CHF–R_F contain reactive C–F bonds in the α-position and appeared to be rather unstable when applied in vivo [25].

2. Results and discussion

2.1. Syntheses of fluoroalkyl ethers

In a modified Williamson synthesis of ethers [26], we used the tosylate of solketal (**3**) (Scheme 2) and fluoroalkoxides **8**, **10**, **11** as the respective nucleophilic agents in the main reactions [27] (Scheme 4). It is also possible to arrange the reaction partners the other way round, i.e. to react non-fluorinated alkoxides with tosylates of fluoroalkanols; however, theoretical calculations for tosylates of (polyfluoroalkyl)methanols, have predicted very high activation energy for the cleavage of the leaving tosyloxy group [28]. Contrary to this theoretical prediction, some nucleophilic reactions of tosylates of fluoroalkanols have been reported [29,30]. To verify this synthetic possibility, we prepared tosylates of fluoroalkanols **6** and **7** (Scheme 2), but the attempts to realise the synthesis with these reaction partners failed (vide infra).

Tosylates of solketal (**3**, yield 79%) [26,31], 1,2:5,6-bis-o-(1-methylethylidene)-α-d-gluco-furanose (**4**, yield 52%) [32], butan-1-ol (**5**, yield 64%) [33], 2,2,3,3-tetrafluoropropan-1-ol (**6**, yield 74%) [26], and of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol (**7**, yield 51%) [26] were prepared according to the literature. In the preparation of tosylates of fluoroalkanols (**5**, **6**), the Schotten–Baumann method [26] afforded better results in our hands than the usual pyridine approach [34]. Sodium fluoroalkoxides **8**, **10**, **11** were prepared by the reaction of fluoroalkanols with sodium [35] instead of sodium hydride [36] and their solutions were used directly for alkoxylations (Schemes 2 and 3). We were not successful in the preparation of $C_5F_{11}CF_2$–CH_2CH_2–ONa in agreement with Ref. [35]; most probably, side elimination reactions take place as described for 2-(perfluoroalkyl)ethan-1-ols [37,38] and 3-(perfluoroalkyl)propan-1-ols [39,40]. This supposition was supported by the ^{1}H NMR spectrum of the raw product, in which the signals of a CH= bond as a doublet of triplets (t 5.71 ppm, t 6.21 ppm, $J = 8$ Hz) were present.

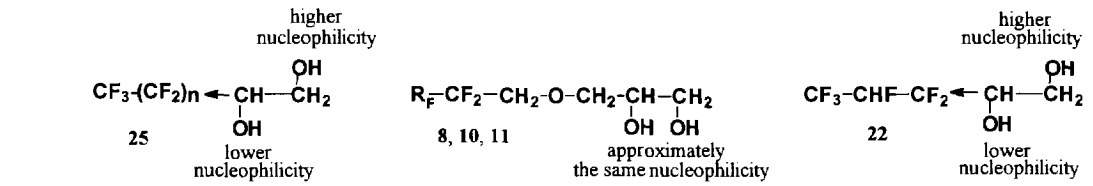
Conditions for the Williamson synthesis of solketal derivatives **12–14** (Scheme 4) were developed on a model reaction of butyl tosylate (**5**) with sodium 2,2,3,3-tetrafluoropropoxide (**8**) (Scheme 3); dimethylformamide appeared to be the solvent of choice and the resulting ether **9** was obtained in a moderate yield of 47%.

Yields of fluoroalkoxylated solketals **12–14** were strongly dependent on the fluoroalkoxide used (Scheme 4, Table 3): the highest yield of 57% (product **12**, 2,2-dimethyl-4-[(2,2,3,3-tetrafluoropropoxy)methyl]-1,3-dioxolane) was obtained in the reaction of tosylate solketal (**3**) with sodium 2,2,3,3-tetrafluoropropoxide (**8**); the reaction with sodium 2,2,2-trifluoroethoxide (**10**) (product **13**, 31%) and with sodium 2,2,3,3,4,4,5,5-octafluoropentoxide (**11**) (product **14**, 21%) afforded only low yields. No product was obtained in the reaction of the tosylate of the protected glucofuranose (**4**) with 2,2,2-trifluoroethoxide (**10**); this was probably caused by a generally low reactivity of tosylate **4** in nucleophilic substitutions [41,42] and by a lower nucleophilic reactivity of the fluoroalkoxide **10**.

Tosylates of fluoroalkanols **6** and **7** displayed very low reactivity. Attempts to carry out the reaction of tosylate **6** with sodium butoxide and the reaction of tosylate **7** with sodium salt of solketal (**2a**) were negative. Only a very low yield (ca. 2%) of the product **12** was obtained in the reaction of sodium salt **2a** with tosylate **6** (Scheme 4).

2.2. Methacrylates of fluorinated 1,2-diols

For the deprotection of ethers **12–14** to obtain fluoroalkylated diols **15–17**, a variety of methods are available, e.g. deprotection with mineral acids without solvents [43], or in organic solvents [44,45], with organic acids [47–49], on ionexes [50], with boron trifluoride etherate [51] and with aluminium iodide [52]. We used two methods: first, deacetalisation with hydrochloric acid in 1,4-dioxane [44] that



(a Refluxing diethyl ether. b 0 °C.)

Scheme 5. Estimation of nucleophilicity of hydroxyl groups in fluoroalkylated 1,2-diols.

afforded the diol **15** in a yield of 42%; second, reacetalisation with methanol in the presence of hydrochloric acid [46] that enabled better treatment of the reaction mixture and gave fluoroalkoxylated diols **15–17** in yields of 62–90%.

Mono-methacrylates and bis-methacrylates of the diols **15** and **16** were prepared by acylation with methacryloyl chloride (Scheme 4). This procedure has been successfully employed formerly for fluorinated alkanols [53,54]. Moreover, completely selective monoacylation of 2-(perfluoroalkyl)ethane-1,2-diols (**25**, Scheme 5) with methacryloyl chloride affording monomethacrylates in yields of ca. 70% has been reported [55]. In our hands, diols **15** and **16** gave mixtures of monomethacrylates and bis-methacrylates, **18** and **20**, or **19** and **21** (Scheme 4) in an approximate ratio 2:1. This disagreement with the literature [55] was most probably caused by the different structure of diols **15** and **16** when compared with the diols **25**, in which the perfluoroalkylated chain was directly attached to the C2 carbon bearing a secondary hydroxy group. The nucleophilicity of this hydroxyl has to be strongly reduced by an electron-withdrawing effect of the perfluoroalkyl groups attached to C2 in comparison with the other hydroxy group attached to the terminal C1 carbon (Scheme 5). Therefore it can be expected that in acylation reactions with methacryloyl chloride the reactivity of the secondary hydroxyl in diol **25** is strongly decreased. In the case of our diols, **8**, **10**, **11**, fluoroalkyls are four links remote from C2, therefore their electron-withdrawing effects on both hydroxy groups need not be significant (Scheme 5). The acylation of diols **8**, **10**, **11** is thus controlled only by a general reactivity of the primary and secondary hydroxy groups.

To study further the acylation selectivity, we employed 3,3,4,5,5,5-hexafluoropentane-1,2-diol (**22**, Scheme 4) which had a structure close to the diols **25** used formerly [55]. We varied the reaction temperature with the aim of optimising the formation of monomethacrylate **23**. The results in Table 1 show that the selectivity was increased up to 10:1 at room temperature and that the relative amount of mono-methacrylate **23** was slightly increasing with decreased temperature. Thus, the selectivity of monomethacrylate **23** formation was substantially better in comparison with the acylation of diols **15** and **16**. On the other hand, the results also showed the formation of bis-methacrylate **24** even at −80 °C (ratio 16:1, Table 1). We can conclude that the completely selective monoacylation of the diol **22** with methacryloyl chloride did not occur. The reason can be a slightly different structure of the diol **22** when compared with compound **25** used formerly [55].

Table 1
Reaction of diol **22** with methacryloyl chloride [a]: temperature dependence of the chemoselectivity (Scheme 4)

Temperature (°C)	Conversion [b] (%)	Composition of reaction mixture [c] (% rel.) **22:23:24**
25	77	23 70 7
0	80	25 69 6
−10	80	27 68 5
−80	33	67 31 2

[a] 1:1 mol mixture of the reactants.
[b] Reaction time 15 min; see Section 4.
[c] GC analysis.

Structures of the compounds prepared were elucidated on the basis of NMR spectra and elemental analyses. In the case of mono- and bis-methacrylates **18–21**, elemental analyses showed C, H and F contents with an above usual error limit despite the fact that the samples were apparently pure (above 97%, GC) and could be prepared repeatedly. Contrary to this result, elemental analyses of the precursors of compounds **18–21**, i.e. of diols **15–17**, were within acceptable error limits. Therefore we used mass spectra for the structure confirmation of the products **18–21**, **23** and **24**; in this case, however, the mass spectra did not contain molecular ions even when different kinds of chemical ionisation were applied [56]. Similar observations for polyfluoroalkane-1,2-diols have been reported [57].

3. Conclusions

The tosylate of protected glycerol (solketal, i.e. 4-(hydroxymethyl)-2,2-dimethyl-1,3-dioxolane) was reacted with sodium polyfluoroalkoxides in a modified Williamson synthesis to afford the corresponding ethers in moderate yields. The reaction of reversibly modified reaction partners, i.e. the reactions of the sodium salt of solketal with tosylates

of fluoroalkanols were not successful. By deprotection of fluoroalkylated solketals, 3-O-fluoroalkylated glycerols were obtained in yields of 62–90%. The attempts to convert these diols to monomethacrylates were not successful and mixtures of mono- and bis-methacrylates in an approximate ratio of 2:1 were obtained. Apparently, more selective monoacylation (10:1) was achieved with 3,3,4,5,5,5-hexafluoro-pentane-1,2-diol (**22**). The non-selectivity of the monoacylation with methacryloyl chloride was discussed on the basis of the hydroxyl group nucleophilicity.

4. Experimental details

4.1. General comments

Temperature data are uncorrected. GC analyses were performed on a Chrom 5 instrument (Laboratorní pøístroje, Prague; FID, 0.3 cm diameter packed column, carrier Chromaton N-AW-DMCS (Lachema, Brno), nitrogen; conditions used: GCa, silicon elastomer E 301, 380 cm, 200 °C, 135 kPa; GCb, E 301, 120 cm, 200 °C, 80 kPa; GCc, OV 210, 220 cm, 200 °C, 50 kPa.

NMR spectra were recorded on various apparatus (for their codes and working frequencies see Table 2); internal standards: TMS for ^{1}H NMR and ^{13}C NMR, $CFCl_3$ for ^{19}F NMR; chemical shifts in ppm (s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quadruplet; qi, quintuplet; sex, sextuplet; m, multiplet), marking 'D_2O' stands for signal vanishing on treating a sample with deuterium oxide, marking 'temp' stands for signal shift with temperature; coupling constants: if not otherwise stated, homointeraction constants; in ^{13}C-NMR spectra heterointeraction constants of carbon and fluorine nucleus.

Mass spectra were scanned (1) on a GC-Mass Spectrometer tandem JEOL DX-303 (JMA 5000, single focus, 70 eV, helium; GC inlet via a 1 m capillary column coated with silicone elastomer and 2) on a ion trap MAGNUM GC-MS benchtop system (Finnigan MAT, USA) utilized Varian 1093 injector (held at 250 °C) and DB-5 ms capillary column (JW Scientific, USA; 30 m × 0.25 mm with a 0.25 μm film thickness); the carrier gas (He 99,996%) velocity was 33.1 cm s^{-1} (at 60 °C); the GC oven maintained at 50 °C for 0.1 min, increased to 6 °C min^{-1} to maximum of 250 °C; ion trap parameters setting for CI operation using methane (99.9995% Linde-Technoplyn, Prague) and acetonitrile (Lichrosolv, Merck) were published [56]; ion–mass (m/z) scan ranges were 40–400 (EI), 45–400 (methane) and 68–400 (acetonitrile).

Table 2
NMR spectrometers and working frequencies used

Apparatus	Working frequency (MHz)	Code
Bruker AM 400	400.1	^{1}H NMRa
Bruker AM 400	376.5	^{19}F NMRb
Bruker AM 400	100.1	^{13}C NMRc
Varian Germini 300 HC	300.1	^{1}H NMRd
Varian Gemnini 300 HC	75.5	^{13}C NMRe
Bruker WP 80 SY	80.1	^{1}H NMRf
Bruker WP 80 SY	75.4	^{19}F NMRg

Chemicals used were as follows. Polyfluoroalkanols $H(CF_2)_nCH_nOH$ were prepared from tetrafluoroethylene [58,59], solketal (**2**) was prepared from glycerol [60], 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-ol was obtained from Elf Atochem SA; 1,2:5,6-bis-O-(1-methylethylidene)-α-d-glucofuranose (**4**) was prepared according to the standard procedure (m.p. 106–107.5 °C) [61]. Tosylates of solketal (**3**) [26,31] and of 1-butanol (**5**) [33] were prepared according to the literature; tosylates of fluoroalkanols **6** and **7** were prepared according to Ref. [26], the tosylate of 1,2:5,6-di-O-isopropylidene-α-d-glucofuranose (**4**) was prepared as reported in Ref. [33]. 3,3,4,5,5,5-Hexafluoro-pentane-1,2-diol was prepared according to a novel synthesis [62]. Glycerol (Lachema, Brno), 1-butanol (Lachema, Brno), dimethyl formamide (Fluka) were purified and dried according to Ref. [63]. Silica (L100/160; Lachema, Brno) was used in column chromatography.

*4.2. General procedure for the preparation of ethers **9**, **12–14***

*4.2.1. Sodium alkoxides **8**, **10**, **11***

A double-necked round-bottom flask (100 ml) equipped with a Claisen adapter, Dimroth reflux condenser fitted with drying tube, and magnetic spinbar, was charged with 2,2,3,3-tetrafluoropropanol (0.77 g; 74 mmol) and diethyl ether (50 ml) and the whole apparatus was flushed with dry argon. Sodium (1.93 g; 84 mmol) was then added in pieces to the fluoroalkanol solution (10 min) while cooled in an ice bath. The mixture was then stirred for 4 h under cooling and for additional 10 h at r.t. Dimethylformamide (20 ml) was added and ether was removed on a rotary evaporator (40 °C). The solution of sodium salt **8** was used directly for the further reaction. Sodium salts **10** and **11** (Table 3) were prepared analogously.

*4.2.2. Ethers **9**, **12–14***

Solutions (DMF, 10–15 ml) of tosylates **3** or **5** (see Table 3) were added dropwise to the solutions prepared by the procedure in Section 4.2.1, (in the same apparatus), at 0 °C while stirring for 1 h and the mixture was then stirred at 60 °C for 10 h. The mixture was cooled to r.t., diluted with diethyl ether (100 ml) and treated with a conc. water solution of sodium chloride (200 ml); the ether layer was washed with water (3 × 25 ml) and dried with magnesium sulfate. After filtering off the drier, ether was evaporated and the residue was distilled in vacuo to give the products **9**, **10–12**, purity (GCa) 95–97%. For amounts of reactants, yields, boiling points and elemental analyses of products see Table 3.

Table 3
Preparation of ethers **9**, **12–14**

Starting compounds					Fluoroalkyl ethers							
Alkoxide			Tosylate		Yield		B.p. °C kPa (Torr)	Purity dist [a] chrom [b]	Elemental analyses			
No.	ROH (g mmol^{-1})	Na (g mmol^{-1})	No.	g mmol	No.	g %			Formula M.w.	Calculated/Found %C	%H	%F
8	0.96	0.19	**5**	1.54	**9**	0.59	100–102	95%	$C_7H_{12}F_4O$	44.68	6.43	40.39
	7.23	8.26		6.73		46.5	101.3 (760)	99.5%	188.17	44.65	6.59	43.22
8	9.77	1.93	**3**	17.8	**12**	8.24	105–108	97%	$C_9H_{14}F_4O_3$	43.91	5.73	30.87
	74.0	83.9		62.1		56.6	4.7 (35)	99.5%	246.20	43.69	5.68	30.52
10	3.64	0.95	**3**	11.38	**13**	2.44	82–84	97%	$C_8H_{13}F_3O_3$	44.86	6.12	26.61
	36.4	41.3		39.7		31.3	4.3 (32)	99%	214.18	45.05	6.30	27.47
11	5.00	0.52	**3**	6.77	**14**	1.54	66–69	96%	$C_{11}H_{14}F_8O_3$	38.16	4.08	43.90
	21.5	22.6		23.7		20.7	0.1 (1)	96%	346.22	37.59	3.99	51.45

[a] Purity (GCa) achieved by distillation.
[b] Purity (GCa) achieved by the subsequent short-column chromatography.

For analytical purposes, the products **9**, **12–14** were further purified (in ca. 2–4 ml of diethyl ether) by a short-column chromatograph (load 150–300 mg, ca. 2 g of silica, eluent diethyl ether) achieving purity (GCa) above 99% with the exception of **14**, (Table 3).

The reaction of 2,2,3,3-tetrafluoropropanol tosylate (**6**, 4.55 g, 15.9 mmol) with sodium salt of solketal (**2a**, 2.34 g, 15.1 mmol) afforded, under an identical arrangement, the ether **9** in a yield of 74 mg (2%).

*4.2.2.1. 1-(2,2,3,3-Tetrafluoropropoxy)butane (**9**)*

^{1}H NMRa δ: 0.92 (t, 3H, J=7.4 Hz); 1.37 (sex, 2H, J=7.4 Hz); 1.57 (qi, 2H, J=7.0 Hz); 3.55 (t, 2H, J=6.5 Hz); 3.78 (tt, 2H, J_{HF}=12.6 and 1.7 Hz); 5.91 (tt, 1H, J_{HF}=53.3 and 5.3 Hz) ppm. ^{13}C NMRc: 13.8; 19.14; 31.3; 68.0 (t, J=28.4 Hz); 72.64; 109.3 (tt, J=249.1 and 26.4 Hz); 115.3 Hz (tt, J=249.7 and 33.9 Hz) ppm. ^{19}F NMRb: −126.2 to −126.3 (m, 2F, dec. s); −140.9 (d, 2F, J_{FH}=53.4 Hz) ppm.

*4.2.2.2. 2,2-Dimethyl-4-[(2,2,3,3-tetrafluoropropoxy)-methyl]-1,3-dioxolane (**12**)*

^{1}H NMRa δ: 1.36 (s, 3H); 1.42 (s, 3H); 3.63 (d, 2H, J=5.1 Hz); 3.75 (dd, 1H, J=8.3 and 6.2 Hz); 3.91 (tt, 2H, J_{HF}=12.6 and 1.4 Hz); 4.05 (dd, 1H, J=8.3 and 6.6 Hz); 4.26 (tt, 1H, J=6.1 and 5.3 Hz); 5.93 (tt, 1H, J_{HF}=53.2 and 5.0 Hz) ppm. ^{13}C NMRe δ: 25.8; 27.2; 66.8; 69.8 (t, J=28.2 Hz); 73.8; 75.1; 109.8 (tt, J=249.2 and 34.3 Hz); 110.3 (tt, J=249.6 and 26.5 Hz) ppm. ^{19}F NMRb δ: −140.3 (dtt, 2F, J=4.8 Hz, J_{FH}=53.0 and 1.6 Hz, dec. t, J=3.6 Hz); −125.75 to −125.8 (m, 2F, dec. t, J=3.6 Hz).

*4.2.2.3. 2,2-Dimethyl-4-[(2,2,2-trifluoroethoxy)methyl]-1,3-dioxolane (**13**)*

^{1}H NMRd δ: 1.36 (s, 3H); 1.43 (s, 3H); 3.67 (d, 2H, J=5.3 Hz); 3,77 (dd, 1H, J=8.4 and 6.2 Hz); 3.92 (q, 2H, J_{HF}=8.6 Hz); 4.06 (dd, 1H, J=8.4 and 6.5 Hz); 4.28 (tt, 1H, J=5.3 and 6.4 Hz) ppm. ^{13}C NMRe δ: 26.0; 27.3; 66.9; 69.5 (q, J=25.5 Hz); 73.8; 75.2; 110.2; 124.4 (q, J=279.4 Hz) ppm. ^{19}F NMRg δ: −74.8 (t, J_{FH}=8.6 Hz, dec. s) ppm.

*4.2.2.4. 2,2-Dimethyl-4-[(3,3,4,4,5,5,6,6-octafluoro-pentoxy)methyl]-1,3-dioxolane (**14**)*

^{1}H NMRd δ: 1.36 (s, 3H); 1.42 (s, 3H); 3.67 (d, 2H, J=5.2 Hz); 3.77 (dd, 1H, J=8.4 and 6.2 Hz); 4.03 (tt, 2H, J_{HF}=14.0 and 1.8 Hz); 4.06 (dd, 1H, J=8.4 and 6.5 Hz); 4.28 (tt, 1H, J=5.3 and 6.3 Hz); 6.07 (tt, 1H, J_{HF}=52.0 and 5.5 Hz) ppm. ^{13}C NMRc δ: 25.3; 26.65; 66.3; 68.3 (t, J=25.5 Hz); 73.5; 74.6; 107.8 (tt, J=254.2 and 30.5 Hz); 109.8; 110.2 (ttt, J=263.8 and 26.5 and 30.8 Hz); 111.0 (ttt, J=264.6 and 36.3 and 30.6 Hz); 115.5 (tt, J=256.7 and 30.6 Hz) ppm. ^{19}F NMRg δ: −137.9 (dm, 2F, J_{FH} ~ 52 Hz, dec. m); −130.85 to −131.0 (m, 2F); −126.3 (t, 2F, J=7.9 Hz); −120.5 (q, 2F, J=11.6 Hz, dec. t, J=11.6 Hz) ppm.

*4.3. General procedure for the preparation of diols **15–17***

Into a round-bottom flask (250 ml) equipped with a distillation splitter-head and magnetic spinbar containing a solution of ether **12–14** (Table 4) in methanol, concentrated hydrochloric acid was added dropwise and the mixture was refluxed for 4 h. Then, volatile components were distilled off by fraction distillation and the residue was distilled in vacuo to afford the diol (**15–17**). Diols **16** and **17** were subsequently purified as in the procedure of Section 4.2.1. For amounts of reactants, yields, boiling points and elemental analyses of products see Table 4.

*4.3.1.1. 3-(2,2,3,3-Tetrafluoropropoxy)propane-1,2-diol (**15**)*

^{1}H NMRa δ: 3.55–3.69 (m, 4H); 3.84–3.90 (m, 1H); 3.88 (tt, 2H, J_{HF}=12.9 and 1.6 Hz); 4.14 (bs, 2H, D_2O); 5.96 (tt, 1H, J_{HF}=53.1 and 4.8 Hz) ppm. ^{13}C NMRc δ: 63.55;

Table 4
Preparation of fluorodiols **15–17**

Starting compounds				Fluorodiols							
Ethers		MeOH g	HCl ml	Yield		B.p. °C	Purity dist [a]	Elemental analyses			
No.	g mmol	mmol		No.	g %	kPa (Torr)	chrom [b]	Formula M.w.	Calculated/Found		
									%C	%H	%F
12	7.66	4.00	0.5	**15**	5.78	105–107	99.5%	$C_6H_{10}F_4O_3$	34.96	4.89	36.87
	31.1	124.8			90.1	33.3 (0.3)	99.8%	206.14	35.34	4.92	36.52
13	4.77	3.57	0.3	**16**	3.23	75–76	98.5%	$C_5H_6F_3O_3$	34.49	5.21	32.74
	22.3	111.4			83.2	26.7 (0.2)	99.3%	174.12	35.17	5.21	34.79
14	0.30	0.12	0.1	**17**	0.17	> 120 [c]	98.6%	$C_8H_{10}F_8O_3$	31.39	3.29	49.64
	0.87	3.75			61.8	13.3 (0.1)	98.9%	306.15	31.43	3.32	49.66

[a] Purity (GCb) achieved by distillation.
[b] Purity (GCb) achieved by the subsequent short-column chromatography.
[c] Approximate value.

68.3 (t, J=27.8 Hz); 71.0; 73.8; 109.5 (tt, J=249.1 and 35.0 Hz); 115.2 (tt, J=249.7 and 27.0 Hz) ppm. ^{19}F NMRb δ: −139.9 (d, 2F, J_{FH}=53.1 Hz, dec. bs); −125.5 (m, 2F, dec. bs) ppm.

4.3.1.2. 3-(2,2,2-Trifluoroethoxy)propane-1,2-diol (16)

^{1}H NMRa δ: 2.95 (bs, 2H, D_2O); 3.59–3.72 (m, 4H); 3.88 (q, 2H); 3.85–3.92 (m, 1H) ppm. ^{13}C NMRc δ: 63.51; 68.9 (q, J=34.2 Hz); 70.9; 73.9; 124.0 (q, J=279.5 Hz) ppm. ^{19}F NMRb δ: −74.8 (t, J=8.6 Hz, dec. s) ppm.

4.3.1.3. 3-(2,2,3,3,4,4,5,5-Octafluoropentoxy)-propane-1,2-diol (17)

^{1}H NMRa δ: 2.85 (bs, 1H, D_2O); 3.24 (bs, 1H, D_2O); 3.60–3.73 (m, 4H); 3.84–3.92 (m, 1H); 4.00 (tt, 2H, J_{HF}=13.9 and 1.4 Hz); 6.06 (tt, 1H, J_{HF}=52.0 and 5.5 Hz) ppm. ^{13}C NMRc δ: 63.5; 68.3 (t, J=25.5 Hz); 70.7; 74.3; 107.7 (tt, J=254.4 and 30.7 Hz); 110.2 (ttt, J=263.8 and 30.9 and 26.8 Hz); 111. (ttt, J=264.5 and 31.0 and 33.5 Hz); 115.5 (tt, J=256.8 and 30.7 Hz) ppm. ^{19}F NMRb δ: −137.8 (d, 2F, J_{FH}=51.6 Hz, dec. bs); −130.8 (m, 2F, dec. bs); −126.1 (kv, 2F, J=7.0 Hz); −120.4 (kv, 2F, J=12.1 Hz) ppm.

*4.4. General procedure for the preparations of monomethacrylates **18, 19, 23** and bis-methacrylates **20, 21, 24***

The reactions were carried out under a nitrogen atmosphere in a two-necked round-bottom flask equipped with a Claisen adapter (with septum on one neck), to which was attached a Dimroth reflux condenser with a drying tube (calcium chloride) and magnetic spinbar.

4.4.1. Procedure A [55]

Into the mixture of pyridine (0.384 g, 4.85 mmol), diol **15** (0.5 g, 2.43 mmol), diethyl ether (5 ml) and diphenyl picryl hydrazyl (DPPH, 6 mg), a solution of methacryloyl chloride (0.507 g, 4.85 mmol) and DPPH (ca. 5 mg) in diethyl ether (3 ml) was added dropwise into the flask cooled to 0 °C (ice water) over 0.5 h while stirring and the mixture was stirred for 2 h under cooling. The mixture was then heated to r.t. and reacted under reflux for 28 h and the mixture composition was checked by GC, which showed the content of monomethacrylate **18** and bis-methacrylate **20** in an approximate ratio 2:1. After cooling to r.t., diethyl ether (10 ml) was added to the mixture which was treated with dilute hydrochloric acid (1 M, 10 ml), then with water (10 ml) and with sodium hydrogen carbonate (5% solution, 10 ml) and with water (10 ml). The ether layer was dried with magnesium sulfate and the ether removed in vacuo at 40 °C (r.e.). The residue of 282 mg was separated by column chromatography (40 g of silicagel L 40/100, column diameter 20 mm, chloroform) to obtain 78 mg (11.7% yield) of monoester **18** and 42 mg (yield 5.04%) of diester **20**.

4.4.2. Procedure B

Into the mixture of pyridine (3.36 g, 29.1 mmol), diol **22** (6 g, 28.3 mmol), diethyl ether (60 ml) and diphenyl picryl hydrazyl (DPPH, 40 mg), a solution of methacryloyl chloride (2.96 g, 28.3 mmol) and DPPH (ca. 10 mg) in diethyl ether (10 ml) was added dropwise into the flask cooled to 0 °C (ice water) over 10 min while stirring. After 15 min, the mixture composition was checked by GC; ether was then removed (rotary evaporator), dichloromethane (30 ml) was added to the residue and also evaporated together with a part of unreacted pyridine (the operation was repeated three times). The residue was diluted with dichloromethane (25 ml), washed with water and the oily layer was separated, dried with magnesium sulfate and the solvent was then removed (rotary evap.). The residue obtained (7.78 g), which consisted of (GCc) pyridine (33%), starting diol **22** (17%), monoester **23** (46%), diester **24** (4%), was (after adding DPPH, 20 mg, and tert.octylpyrocatechol, 25 mg)

distilled in vacuo to obtain three fractions with a different composition of the compounds **22–24** (GCc): fr.1, 66–67 °C, 1.36 g; fr.2, 77–85 °C, 1.58 g; fr.3, 85 °C, 0.68 g; all at 0.4 mmHg (53.3 Pa). The calculated yields were 33% for monoester **23** and 3% for diester **24**. Crystalline fractions 2 and 3 were combined together and crystallised three times from 1,1,2-trichlorotrifluoroethane to give monoester **23** in a yield of 0.453 g, m.p. 55–60 °C. Pure products **23** and **24** for analyses were isolated by column chromatography (silica, chloroform), purity ca. 98% (GCc).

Products **18**, **20** (GCc) were prepared analogously and were reacted with diol **15** (4 g, 19.4 mmol), pyridine (2.3 g, 29.1 mmol) and methacryloyl chloride (2.03 g, 19.4 mmol). The calculated yields were 54% for monoester **18** and 11% for diester **20**. Pure products for analyses were obtained as above, purity 97% and 98% (GCc).

Products **19**, **21** (GCc) were prepared analogously and were reacted with diol **16** (6.56 g, 37.7 mmol), pyridine (4.47 g, 56.5 mmol) and methacryloyl chloride (3.94 g, 37.7 mmol). The calculated yields were 43% for monoester **19** and 3% for diester **21**. Pure products for analyses were obtained as above, purity 98% and 97% (GCc).

*4.4.2.1. 3-(2,2,3,3-Tetrafluoropropoxy)-2-hydroxypropyl methacrylate (**18**)*

^{1}H NMRa δ: 1.68 (dd, 3H, J = 1.5 and 1.0 Hz); 2.40 (bs, 1H, temp.); 3.66 (dd, 1H, J = 9.9 and 5.8 Hz); 3.70 (dd, 1H, J = 9.9 and 4.4 Hz); 3.91 (tt, 2H, J_{HF} = 12.6 and 1.7 Hz); 4.08 (tt, 1H, J = 5.6 and 4.7 Hz); 4.23 (dd,1H, J = 11.6 and 5.7 Hz); 4.27 (dd, 1H, J = 11.6 and 4.7 Hz); 5.62 (qi, 1H, J = 1.6 Hz); 5.91 (tt, 1H, J_{HF} = 53.2 and 4.7 Hz); 6.14 (dq, 1H, J = 1.5 and 1.0 Hz) ppm. ^{13}C NMRc δ: 18.3; 65.4; 68.5 (t, J = 28.1 Hz); 69.0; 73.5; 109.3 (tt, J = 249.8 and 34.9 Hz); 115.0 (tt, J = 250.0 and 27.1 Hz); 126.3; 135.9; 167.5 ppm. ^{19}F NMRg δ: −139.51 (dtt, 2F, J_{FH} = 53.8 and 1.6 Hz, dec. t, J = 3.7 Hz); −125.1 (dtt, 2F, J_{FH} = 12.7 and 4.3 Hz, dec. t, J = 3.7 Hz) ppm.

MS (M_r = 274), m/z/% rel. int.: EI: 275/5, 257/40, 171/7, 145/16, 143/13, 129/27, 100/8, 99/11, 69/100, 51/20, 43/20, 41/83, 40/8; CI (CH_4): 275/8, 258/49, 257/100, 143/34, 69/44; CI(CH_3CN): 275/8, 258/10, 257/100, 143/16.

*4.4.2.2. 2-Hydroxy-3-(2,2,2-trifluoroethoxy)propyl methacrylate (**19**)*

^{1}H NMRa δ: 1.96 (s, 3H); 2.40 (bs, 1H, temp.); 3.69 (dd, 1H, J = 9.8 and 5.9 Hz); 3.75 (dd, 1H, J = 9.8 and 4.3 Hz); 3.91 (q, 2H, J_{HF} = 8.6 Hz); 4.10 (tt, 1H, J = 4.8 and 5.5 Hz); 4.24 (dd, 1H, J = 11.6 and 5.5 Hz); 4.28 (dd, 1H, J = 11.6 and 4.9 Hz); 5.62 (s, 1H); 6.14 (s, 1H) ppm. ^{13}C NMRc δ: 18.9; 66.2; 69.7 (q, J = 34.3 Hz); 69.8; 74.25; 124.6 (q, J = 273.7 Hz); 126.7; 136.7; 168.15 ppm. ^{19}F NMRg δ: −74.8 (t, J = 8.4 Hz, dec. s) ppm.

MS (M_r = 342), m/z/% rel. int.: EI: 243/8, 225/30, 143/5, 129/26, 113/17, 100/9, 99/10, 85/5, 83/8, 69/100, 58/5, 43/19, 41/83; CI(CH_4): 243/12, 226/58, 225/100, 143/12, 87/5, 69/53; CI(CH_3CN): 243/18, 226/10, 225/100, 143/12.

*4.4.2.3. 3-(2,2,3,3-Tetrafluoropropoxy)propane-1,2-diyl bis-methacrylate (**20**)*

^{1}H NMRd δ: 1.94 (bs, 6H); 3.80 (d, 2H, J = 5.0 Hz); 3.88 (tt, 2H, J_{HF} = 12.5 and 4.5 Hz); 4.31 (dd, 1H, J = 12.2 and 6.0 Hz); 4.41 (dd, 1H, J = 12.2 and 4.6 Hz); 5.31 (qi, 1H, J = 5.0 Hz); 5.60 (bs, 1H); 5.62 (bs, 1H); 5.89 (tt, 1H, J_{HF} = 52.4 and 4.9 Hz); 6.10 (bs, 1H); 6.13 (bs, 1H) ppm. ^{13}C NMRe δ: 18.2; 62.4; 68.5 (t, J = 28.6); 70.1; 70.8; 109.0 (tt, J = 249.5 and 34.6 Hz); 114.8 (tt, J = 249.9 and 27.1 Hz); 126.1; 126.3; 135.7; 135.9; 166.3; 166.7 ppm. ^{19}F NMRg δ: −139.5 (dtt, 2F, J_{FH} = 51.8 and 1.6 Hz, dec. t, J = 4.2 Hz); −125.7 (dtt, 2F, J_{FH} = 12.4 and 4.5 Hz, dec. t, J = 4.2 Hz) ppm.

MS (M_r = 342), m/z/% rel. int.: EI: 257/10, 211/8, 171/12, 69/100, 51/8, 41/71, 40/7; CI(CH_4): 258/100, 257/52, 211/9, 271/18, 69/38; CI(CH_3CN): 258/6, 257/100.

*4.4.2.4. 3-(2,2,2-Trifluoroethoxy)propane-1,2-diyl bis-methacrylate (**21**)*

^{1}H NMRa δ: 1.93 (dd, 3H, J = 1.5 and 1.0 Hz); 1.95 (dd, 3H, J = 1.5 and 1.0 Hz); 3.81–3.95 (m, 4H); 4.33 (dd, 1H, J = 11.9 and 6.0 Hz); 4.44 (dd, 1H, J = 11.9 and 4.2 Hz); 5.31 (qi, 1H, J = 5.1 Hz); 5.59 (qi, 1H, J = 1.5 Hz); 5.62 (qi, 1H, J = 1.5 Hz); 6.10 (bs, 1H), 6.13 (bs, 1H) ppm. ^{13}C NMRc δ: 18.2; 62.5; 68.9 (q, J = 34.3 Hz); 70.2; 70.8; 123.8 (q, J = 279.9 Hz); 126.1; 126.4; 135.8; 135.9; 166.5; 166.8 ppm. ^{19}F NMRg δ: −74.8 (t, J_{FH} = 8.4 Hz, dec. s).

MS (M_r = 310), m/z/% rel. int.: EI: 225/15, 224/5, 179/7, 139/13, 69/100, 41/73; CI(CH_4): 226/100, 225/50, 139/19, 69/45; CI(CH_3CN): 225/100.

*4.4.2.5. 3,3,4,5,5,5-Hexafluoro-2-hydroxypent-1-yl methacrylate (**23**)*

^{1}H NMRa δ: 1.97 (s, 3H); 3.49 (bs, 1H, temp.); 4.24–4.56 (m, 3H); 5.20 (ddq, 1H, J_{HF} = 42.7 and 20.5 and 6.0 Hz); 5.68 (s, 1H); 6.20 (s, 1H) ppm. ^{13}C NMRc δ: 18.2; 63.2; 68.65 (dd, J = 22.0 and 31.1 Hz); 82.9 (dddq, J = 193.4 and 37.7 and 34.7 and 23.8 Hz); 117.6 (ddd, J = 253.8 and 282.9 and 25.8 Hz); 120.8 (dq, J = 282.6 and 25.6 Hz); 127.1; 135.45; 168.46 ppm. ^{19}F NMRb δ: diester. A: −213.3 (dqi, 1F, J_{FH} = 41.7 Hz, dec. qi, J = 10.8 Hz); −128.8 to −129.65 (dm, 1F, J ~ 272 Hz, dec. dd, J = 11.0 Hz); −125.4 to −126.3 (dm, 1F, J ~ 273 Hz, dec. dqi, J = 10.6 Hz); −74.2 (m, 3F, dec. q, J = 10.8 Hz); diester. B: −217.3 (dqi, 1F, J_{FH} = 43.3 Hz, dec. qi, J = 10.7 Hz); −124.1 to −124.9 (dm, 1F, J ~ 275 Hz, dec. dqi, J = 10.1 Hz); −119.4 to −120.2 (dm, 1F, J ~ 275 Hz, dec. dqi, J = 11.0 Hz); −74.8 (m, 3F, dec. q, J = 10.7 Hz) ppm.

MS (M_r = 280), m/z/% rel. int.: EI: 129/5, 113/5, 87/20, 69/100, 51/5, 43/10, 41/66; CI(CH_4): 281/7, 263/30, 69/100; CI(CH_3CN): 282/6, 281/100, 263/50.

*4.4.2.6. 3,3,4,5,5,5-Hexafluoropentane-1,2-diyl bis-methacrylate (**24**)*

^{1}H NMRa δ: 1.92 (dd, 3H, J=2.5 and 1.1 ppm); 1.98 (bs, 3H); 4.40–4.70 (m, 3H); 4.80–5.10 (m, 1H); 5.60–5.62 (m, 1H); 5.70–5.74 (m, 1H); 6.10 (bs, 1H); 6.19–6.21 (m, 1H) ppm. ^{13}C NMRc δ: 18.2; 68.0 (dd, J=25.6 and 30.2 Hz); 82.1–86.0 (m); 115.5–122.0 (m); 126.7; 126.8; 134.7; 134.8; 166.47; 166.54 ppm. ^{19}F NMRg δ: −209 to −216 (m, 1F); 137–109 (m, 2F); −70 to −76 (m, 3F) ppm.

MS (M_r=348), m/z/% rel. int.: EI: 320/6, 263/32, 69/100, 41/58, 40/10; CI(CH_4): 264/42, 263/65, 70/29, 69/100; CI(CH_3CN): 263/100, 264/10.

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