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Radical addition reactions of fluorinated species. Part 7. Highly selective two-step synthesis of 1-(polyfluoroalkyl)ethane-1,2-diols; regioselectivity of the additions of methylated 1,3-dioxolanes to perfluoroolefins

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Abstract

The two-step synthesis of the diols is based on the radical addition of 2,2-dimethyl-1,3-dioxolane (**1**), a protected ethane-1,2-diol, to perfluoroalk-1-enes R_F–CF=CF_2 (R_F=CF_3, C_9F_{19}; **2**, **3**) and perfluoro[trifluorovinyl (poly)ethers] R_FO–CF=CF_2 (R_F=C_3F_7, $C_3F_7O[CF(CF_3)CF_2]$, $CF_3(OCF_2CF_2)_4$; **4**–**6**) with preparative yields above 90% in each step. The additions were initiated photochemically or by dibenzoyl peroxide and were completely chemoselective and almost completely regioselective. 4-Fluoroalkylated dioxolanes obtained (**7**–**11**) were deprotected by acid methanolysis to afford 1-polyfluoroalkylethane-1,2-diols (**12**–**16**). 1,3-Dioxolane (**27**) or 2,2,4-trimethyl-1,3-dioxolane (**30**) reacted at two centers to yield regioisomeric mixtures of fluoroalkylated dioxolanes. The factors influencing fluoroolefin and dioxolane regioselectivity are discussed.

Keywords: Fluoroolefins; Regioselective radical addition; Photo-addition; Hydrolysis of fluoroalkylated 1,3-dioxolanes; 1-(Polyfluoroalkyl)ethane-1,2-diols; 1-(Poly-fluoroalkyl)ethane-1,2-diyl bis-methacrylates; Radical stability; Steric effects

1. Introduction

Fluoroalkyl diols are versatile intermediate compounds in preparations of a variety of special monomers [2]. Typical examples of their applications are polyesters [3–5] polyurethanes [6–9], polyethers [10], and polymethacrylates [2] in various technical fields including optical fiber coatings. Monoesters of fluoroalkylated glycols in a polymeric form are also claimed for medicinal applications, e.g. as materials for contact lenses [11–15].

Several methods are described in the literature for syntheses and preparations of fluorine-containing 1,2-diols bearing three or four-carbon initial non-fluorinated groups in the chain (e.g. R_F–$(CH_2)n$–CHOH–CH_2OH, n=1,2). The diols were obtained by acid hydrolysis of the corresponding 1,2-epoxides [16–20], by transformation of the epoxides to acetates and then by subsequent base hydrolysis [21,22] and also by the catalytic oxidation of fluorinated terminal olefins [23,24]. 1-(Fluoroalkyl)ethane-1,2-diols were also obtained from the corresponding 1,2-epoxides by their hydrolysis [25–28]. Another method used was *cis*-hydroxylation of 1-perfluoroalkylethenes [24,29] by potassium permanganate. In the patent literature, there is also mentioned a synthesis of the fluoroalkylated 1,2-diol by the reaction of ethane-1,2-diol with hexafluoropropene [30,31].

The synthesis of 1-fluoroalkylethane-1,2-diols can also be performed in two steps (Scheme 1). The first step is a radical addition of 2,2-dimethyl-1,3-dioxolane to fluorine-containing 1-alkenes, the second step is hydrolysis of the addition products. Some radical additions of 2,2-dimethyl-1,3-dioxolane [32–34] to several types of olefins have been reported, but the results were not satisfactory from the preparative point of view: additions to non-fluorinated 1-olefins afforded mixtures of regioisomers in yields below 25% [32,33]; in the case of chlorotrifluoroethene [34], only a 31% yield of the 1:1 addition product was obtained owing to telomerization and side reactions.

2. Results

We now report [35] a convenient synthesis of 1-(polyfluoroalkyl)ethane-1,2-diols (Scheme 1) via 4-fluoroalkyl-2,2-dimethyl-1,3-dioxolane intermediates (**7**–**11**), which is highly regio- and chemoselective and can be accomplished with preparative yields above 90% in each of the two steps.

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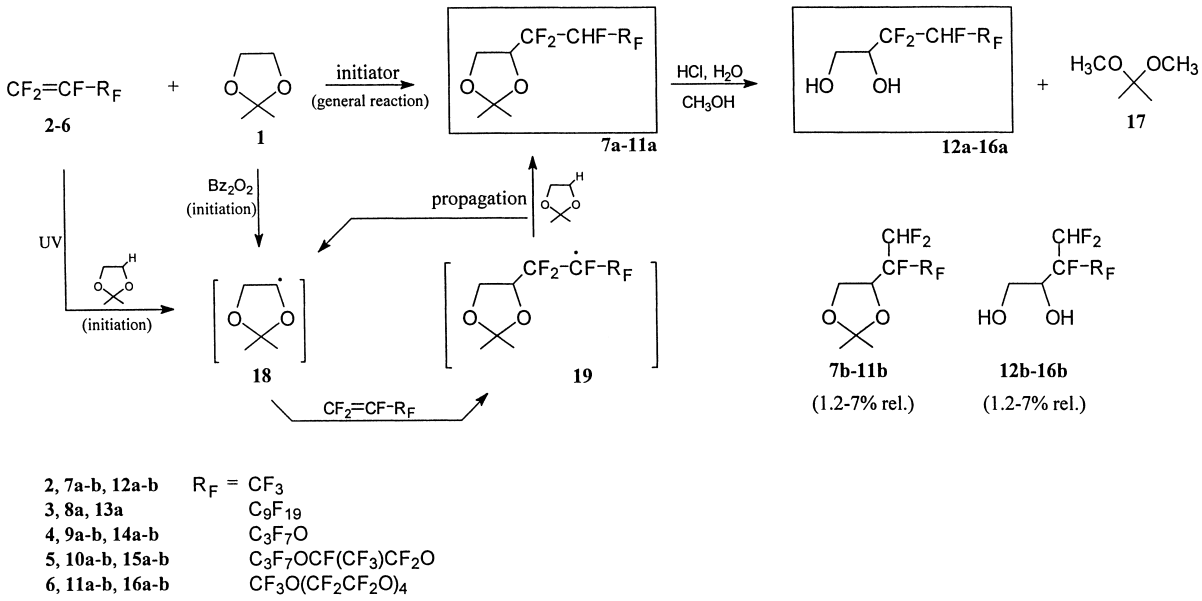


2, 7a-b, 12a-b	R_F = CF_3
3, 8a, 13a	C_9F_{19}
4, 9a-b, 14a-b	C_3F_7O
5, 10a-b, 15a-b	$C_3F_7OCF(CF_3)CF_2O$
6, 11a-b, 16a-b	$CF_3O(CF_2CF_2O)_4$

Scheme 1. Synthesis of 1-(polyfluoroalkyl)ethane-1,2-diols.

The addition reaction was performed with hexafluoropropene (**2**) or perfluoroundec-1-ene (**3**) as examples of perfluoroalk-1-enes, and with perfluoro vinyl ether **4** or perfluoro vinyl polyethers (**5,6**) (Scheme 1). The radical additions were initiated with UV light or dibenzoyl peroxide. In the photochemical reactions, fluoroolefins are excited [36,37] to a diradical-like triplet state that can abstract hydrogen from dioxolane **1** to generate an intermediate radical (**18**, Scheme 1), which starts a chain reaction. Perfluoroolefins **2–6** reacted easily by direct UV irradiation with almost complete conversion of the olefins. A great advantage of this procedure has been the possibility of carrying out the reactions under atmospheric pressure with gaseous olefins. Reactions of fluoroolefins **2–6** with the peroxide initiator also proceeded with complete conversions of the olefins and gave high preparative yields (Table 1). The only preparative disadvantage was the formation of a small amount of decomposition products (mainly benzoic acid) from the initiator.

Methanolysis of fluoroalkyl dioxolanes (**7–11**) was accomplished with a mixture of hydrochloric acid and methanol. Acetone dimethyl acetal (**17**) was formed as a volatile compound in this re-acetalization reaction. In contrast to the previous report on a similar reaction [34], we used a much higher relative amount of methanol. All the fluoroalkylated dioxolanes (**7–11**) were easily hydrolyzed to the corresponding fluoroalkyldiols **12–16** with preparative yields above 90% (Table 2). No fluorinated by-products were detected in the reaction mixture. The transformations of the diols **12–16** to the corresponding methacrylates **20–24** were performed by their reaction with methacryloyl chloride as reported previously [38,39] (Scheme 2).

Table 1
Radical addition reactions of 2,2-dimethyl-1,3-dioxolane (**1**) with perfluoroolefins **2–6** (Scheme 1)

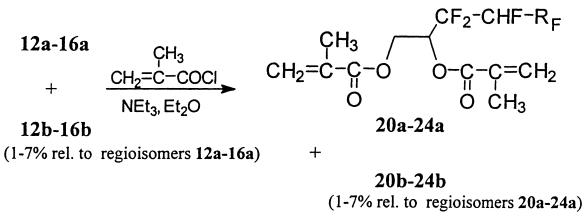
Olefin	Initiation	Time (h)	Conversion of olefin (%)	fluoroalkylated dioxolanes **7–11**				
				No.	**b** (% rel. to **a**)	Yield (%)	Purity[a] (%)	B.p. (M.p.) (°C/mmHg)
2[b]	UV	2	99	**7a–b**	1	95	99	(86–88)/200
3[c]	UV	2	98	**8a**	0	92	98	(83–85)/7 (22)
4[c]	UV	2	98	**9a–b**	6	94	99	(92–93)/200
4[c]	Bz_2O_2	4	96	**9a–b**	6	92	98	(77–79)/100
5[c]	UV	2	98	**10a–b**	6	93	99	(94–96)/20
5[c]	Bz_2O_2	4	96	**10a–b**	6	91	98	(90–92)/15
6[c]	UV	2	98	**11a–b**	7	93	99	(95–97)/2
6[c]	Bz_2O_2	4	97	**11a–b**	7	92	98	(84–86)/1

[a] Including regioisomer.
[b] Olefin 0.10 mol, dioxolane **1** 0.50 mol.
[c] Olefin 0.02 mol, dioxolane **1** 0.10 mol.

Table 2
Preparation of 1-fluoroalkyl-1,2-ethanediols **12–16** (Scheme 1) and the corresponding bis-methacrylates **20–24** (Scheme 2)

	Fluoroalkylated diols **12–16** and bis-methacrylates **20–24**			
	b[a] (% rel.)	Yield (%)	Purity[b] (%)	B.p., (M.p.) (°C/mmHg), (°C)
12a–b	1	93	99	(88–89)/20
13a	0	92	98	(111–113)
14a–b	6	92	99	(97–99)/7
15a–b	6	90	99	(95–96)/2
16a–b	7	91	99	(96–98)/0.1
20a–b	1	88	98	(97–99)/1
21a	0	85	98	(98–99)/0.008
22a–b	6	86	98	(94–96)/0.6
23a–b	6	85	98	(82–83)/0.012
24a–b	7	84	98	(95–97)/0.005

[a] Regioisomer content.
[b] Including regioisomer.



12a-b, 20a-b $R_F = CF_3$
13a, 21a C_9F_{19}
14a-b, 22a-b C_3F_7O
15a-b, 23a-b $C_3F_7OCF(CF_3)CF_2O$
16a-b, 24a-b $CF_3O(CF_2CF_2O)_4$

Scheme 2. The conversion of diols to bis-methacrylates.

In the literature, there is described [40,41] selective monoacylation of polyfluoroalkylated 1,2-diols with methacryloyl chloride. In contrast to the previous report [40], in which only mono-methacrylates of perfluoroalkylated 1,2-diols were obtained in refluxing diethyl ether, we obtained only bis-methacrylates by the acylation of diols **12–16** at room temperature (Table 3). Similarly, bis-methacrylates were formed almost exclusively by the acylation of similar (polyfluoroalkyl)ethane-1,2-diols [38]. The difference between previous [40,41] and present results could be caused by a slightly different structure of the acylated diols (Table 3) or by fast isomerization of monoesters during the reaction or workup [42–45], or rapid acylation of the monomethacrylates to bis-methacrylates.

3. Discussion

3.1. Polar effects in radical additions

It is known [46–54] that radical additions are highly favored if reaction partners are of opposite Lewis acid–base character. In our reactions (Scheme 1), the intermediate radical **18** formed from dioxolane **1** (Scheme 1) is nucleophilic while the double bond in perfluoroolefins **2–6** is relatively electrophilic. Similar reaction partners, i.e. nucleophilic radical and electrophilic double bond, reacted in Schemes 4 and 5. Very probably, this is the main reason that the additions proceeded easily, rapidly and were completed with almost total conversion of fluoroolefins. Additions of similar nucleophilic radicals generated from alicyclic ethers (oxolane [1,55–60], 1,3-dioxolane [55,59,60], 1,4-dioxane [57,59,60]) also proceeded easily with perfluoroolefins [55–58] or methyl trifluoroacrylate [59,60]. In contrast, the previously reported radical additions of dioxolane **1** to non-fluorinated olefins [32,33] proceeded with low yields and partial regioselectivity. This observation can be explained by unfavorable interactions between nucleophilic radicals and electron rich double bonds.

3.2. Regioselectivity of additions to perfluoroolefins **2–6**, **25** and **33**

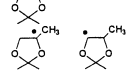
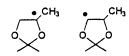
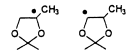
It is known [1,44,46,55,62,63] that the regioselectivity of radical additions to fluorinated propenes and higher per-

Table 3
Selectivity of the monoacylation of diols R_F–$(CH_2)_n$–CH(OH)–CH_2OH with methacryloyl chloride

R_F	*n*	Conditions	Monoester/diester	Yield (%)	Reference
C_4F_9, C_6F_{13}, C_8F_{17}	0	Pyridine, Et_2O, reflux, 72 h	100/0	68–71/0	[40]
CF_3CHFCF_2	0	Pyridine, Et_2O, 0°C, 0.5 h	100/10	46/4	[38]
CF_3CH_2O	1	Pyridine, Et_2O, reflux, 28 h	20/10	12/5	[38]
As in Scheme 1	0	NEt_3, Et_2O, r.t., 2 h	0/100	0/84–88	[a]

[a] This paper (see Table 2).

Table 4
Regioselectivity of additions of some radicals to fluoroolefins

Entry		Olefin	Radical R$^{\bullet}$	Initiation	Regioisomeric adduct-radicals (% rel.)		References
					R_F-$\dot{C}$F-CF_2 R	R_F-CF-$\dot{C}F_2$ R	
1		CF_3–CH=CH_2	$CH_3^{\bullet}$		77	33	[49,50]
2		CF_3–CH=CH_2	$CF_3^{\bullet}$		98	2	[46,49,50,61]
3	**2**	CF_3–CF=CF_2	$CF_3^{\bullet}$		79	21	[46,49,50,61]
4	**2**	CF_3–CF=CF_2	$(OH)H_2C^{\bullet}$	UV, peroxide	95.5–98	2–4.5	[64–66]
5	**2**	CF_3–CF=CF_2	$(CH_3)_2(OH)C^{\bullet}$	UV, peroxide	100	0	[64–66]
6	**2**	CF_3–CF=CF_2		UV	98	2	[63]
7	**2**	CF_3–CF=CF_2		UV	99	1	[a]
8	**2**	CF_3–CF=CF_2		UV	99	1	[a]
9	**2**	CF_3–CF=CF_2		UV	100	0	[a]
10	**33**	C_5F_{11}–CF=CF_2		UV, peroxide	100	0	[a] [67]
11	**25**	C_7F_{15}–CF=CF_2	$(OH)H_2C^{\bullet}$	UV, peroxide	100	0	[a] [67]
12	**3**	C_9F_{19}–CF=CF_2		UV	100	0	[a]
13	**4**	C_3F_7–O–CF=CF_2	$(OH)H_2C^{\bullet}$	UV	93	7	[62]
14	**4**	C_3F_7–O–CF=CF_2	$(CH_3)_2(OH)C^{\bullet}$	UV	99	1	[62]
15	**4**	C_3F_7–O–CF=CF_2		UV, peroxide	93	7	[62,63]
16	**4**	C_3F_7–O–CF=CF_2		UV, peroxide	94	6	[a]
17	**4**	C_3F_7–O–CF=CF_2		UV	96.5	3.5	[a]
18	**5**	$C_3F_7OCF(CF_3)CF_2O$–CF=CF_2	$(OH)H_2C^{\bullet}$	UV	95	5	[63]
19	**5**	$C_3F_7OCF(CF_3)CF_2O$–CF=CF_2	$(CH_3)_2(OH)C^{\bullet}$	UV	100	0	[63]
20	**5**	$C_3F_7OCF(CF_3)CF_2O$–CF=CF_2		UV	94	6	[64,65]
21	**5**	$C_3F_7OCF(CF_3)CF_2O$–CF=CF_2		UV, peroxide	94	6	[a]
22	**6**	$C_3F_7OCF(CF_3)CF_2O$–CF=CF_2		UV, peroxide	93	7	[a]

[a] This paper.

fluoroolefins is influenced by steric and polar effects of substituents attached to the double bond as well as by the character of radicals added (e.g. Table 4, entries 1–3).

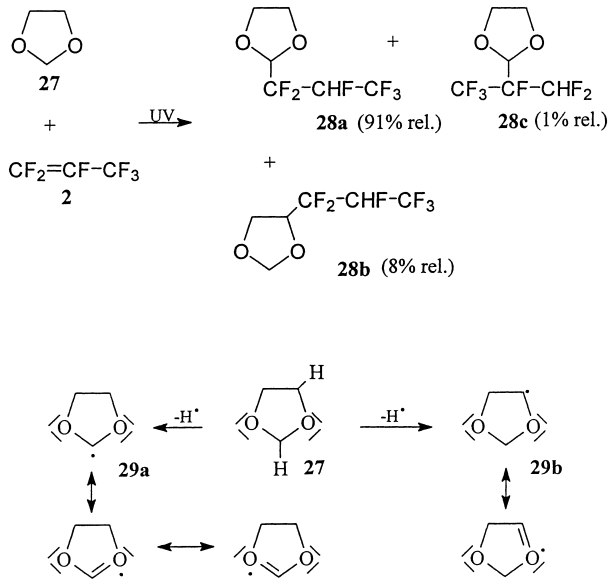
Nucleophilic radicals tend to add to the terminal position of perfluoroalk-1-enes. This regioselectivity is probably the result of a steric effect together with favorable interactions of frontier orbitals of the reacting species [1]. In this report, the additions to all perfluoroolefins **2**–**6**, **25** and **33** were highly or completely regioselective (93–100% rel., Table 4, entries 4–22). From the point of view of olefins, better regioselectivity was evidently achieved in reactions of perfluoroalk-1-enes by comparison with perfluoro vinyl ethers **4**–**6** (Table 4, comparable entries: 6–8 with 15,16; 10 and 12 with 21–22). The data in Table 4 also show an increasing regioselectivity effect of a longer perfluorinated chain in perfluoroalk-1-enes **3**, **25** and **33** reacting with the complete regioselectivity (entries 4 and 11, 8 and 12). Such effect is almost unobserved in the series of perfluoro vinyl ethers **4**–**6** (Table 4, comparable entries 15 and 18, 16 and 19 or 20). Both observations have been reported and discussed for similar additions in our preceding paper [62] as a steric (or stereoelectronic) ''tail effect'' of a perfluorinated chain. To verify this tail effect we carried out the addition of methanol to perfluorononon-1-ene (Table 4, entry 11) that proceeded with 100% regioselectivity (Scheme 3).

$$\underset{\mathbf{25}}{C_7F_{15}\text{-}CF{=}CF_2} + CH_3OH \xrightarrow{UV} \underset{\mathbf{26}}{C_7F_{15}\text{-}CHF\text{-}CF_2\text{-}CH_2OH}$$

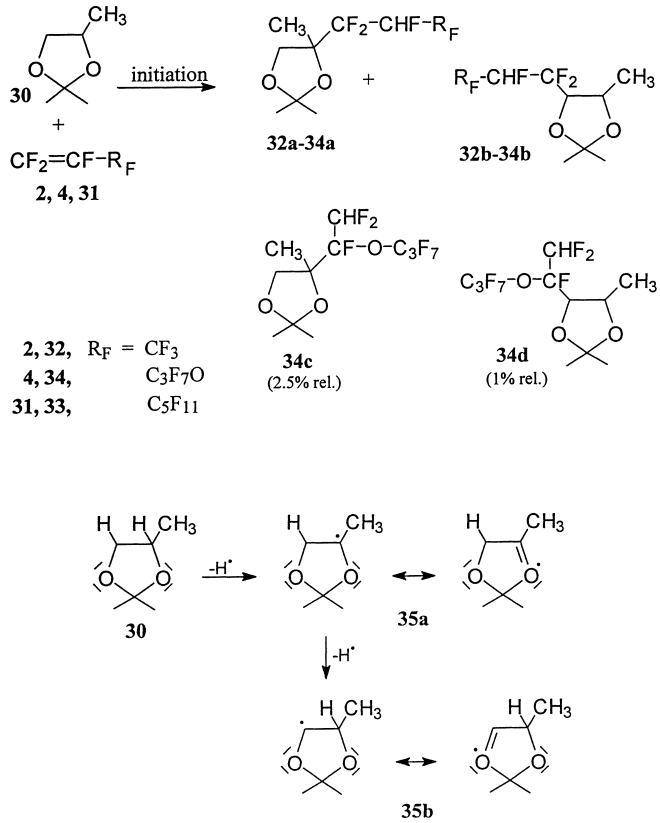
Scheme 3. Complete regioselective addition to perfluorononon-1-ene.

3.3. Regioselectivity on the 1,3-dioxolane ring

All the additions of 2,2-dimethyl-1,3-dioxolane (**1**) to fluoroolefins **2**–**6** were completely regioselective from the point of view of dioxolane **1** which reacted exclusively at C_4 (Table 4, Scheme 1) and no reaction took place on the methyl groups. This observation is in agreement with the general stabilising effect of alkoxy groups on carbon-centered radicals [54,68]. In the addition of 1,3-dioxolane (**27**), it could be supposed that the stabilising effect of the two oxygen atoms in intermediate radical **29a** (Scheme 4) would be much higher than in intermediate **27b** and would favor the exclusive formation of radical **27a** (Scheme 4). How-



Scheme 4. Regioselectivity of the addition of 1,3-dioxolane to hexafluoropropene.



Scheme 5. Regioselectivity of the additions of 2,2,4-trimethyldioxolane.

ever, radical additions of dioxolane **27** to various fluoroolefins showed also that the C_4–H bond in 1,3-dioxolane is cleaved leading to the minor addition products (hexafluoropropene, 92:8 (Scheme 4); perfluoroallyl chloride, 92:8 [1]; perfluorocyclohexene, 90:10 [56,58]; methyl trifluoroacrylate 91:9 [59]).

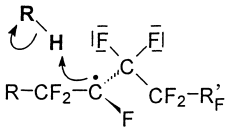
When 2,2,4-trimethyl-1,3-dioxolane (**30**) was used as an additive, the additions were completely regioselective on perfluoroolefins (Table 4, entries 9 and 10), but both C–H bonds at C_4 and C_5 in the dioxolane **30** were cleaved (intermediate radicals **35a** and **35b**, Scheme 5). Ratios of the regioisomeric adducts **32a–34a** and **32b–34b** (Table 5) revealed that the tertiary C–H bond at C_4 is much more reactive in all the additions than the secondary C–H bond at C_5. A similar observation has been reported previously [58] for the radical addition of 2-methyloxolane to hexafluoropropene (product ratio 2:1, γ-ray initiation).

In the additions of dioxolane **30**, regioisomers formed by the addition of tertiary radical **35a** to fluoroolefins were formed (Table 5, products **32–34**). Such a result can be the consequence of an easier hydrogen abstraction from the tertiary C–H bond in **30** supported by a better stabilization of the radical **35a** by the adjacent 4-methyl group [47,48,51,52,54,68].

Table 5
Products and regioselectivity of radical addition reactions of 1,3-dioxolanes **27** and **30** with fluoroolefins (Schemes 4 and 5)

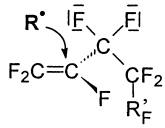
Olefin[a]		Initiation	Time (h)	Conversion (%)	Addition products							
R_F					Regioisomers (% rel.)					Yield (%)	Purity (%)	B.p. (°C/mmHg)
						a	**b**	**c**	**d**			
2[a]	CF_3	*hν*	2	99	**28**[c]	91	8	1		92	99	(75–77)/200
2[a]	CF_3	*hν*	2	99	**32**[d]	87	13			95	99	(77–79)/100
31[b]	$CF_3(CF_2)_4$	*hν*	2	98	**33**[d]	87	13			92	98	(84–86)/15
31[b]	$CF_3(CF_2)_4$	Bz_2O_2	4	97	**33**[d]	80	20			90	98	(80–82)/10
4[b]	C_3F_7O	*hν*	2	98	**34**[d]	84.5	12	2.5	1	94	99	(95–99)/150

[a] Olefin, 0.10 mol; 1,3-dioxolane, 0.50 mol.
[b] Olefin, 0.02 mol; 2,2,3-trimethyl-1,3-dioxolane, 0.10 mol.
[c] Reaction of 1,3-dioxolane (**27**) (Scheme 4).
[d] Reaction of 2,2,4-trimethyl-1,3-dioxolane (Scheme 5).



A

Outer access of trivalent carbon radical to least bulky and monovalent hydrogen atom, low steric shielding of the reactivity site.



B

C-C Bond formation between trivalent carbon radical and inner C atom of the double bond, high steric shielding of the reactivity site.

Scheme 6. (A) Outer access of trivalent carbon radical to least bulky and monovalent hydrogen atom, low steric shielding of the reactivity site. (B) C–C Bond formation between trivalent carbon radical and inner C atom of the double bond, high steric shielding of the reactivity site.

It is interesting that the ratio of regioisomeric products formed by the addition of radicals **35a** and **35b** was not dependent, within experimental error, on the olefin character and the chain length of fluoroolefins (Table 5, UV initiation: ratios of **32a**:**32b**, **33a**:**33b**, (**34a**+**34c**):(**34b**+**34d**) are all 87:13; increased content of the minor regioisomer **33b** (20%) in the peroxide-induced reaction of olefin **3** could be caused by higher reaction temperature). This observation is in sharp contrast with the chain-length effect (the ''tail effect'', [1,62], Section 3.2) in perfluoroolefins on the regioselectivity of additions (Table 5). As mentioned above, a constant ratio of regioisomeric adducts has also been obtained in the additions of 1,3-dioxolane (**27**) to very different perfluoroolefins (see Section 3.2, [1,56,59,60]). Both these observations can be explained by structures in Scheme 6: the formation of dioxolane radicals, e.g. **29a** and **29b** (Scheme 4) or **35a** and **35b** (Scheme 5), by hydrogen abstraction in the propagation step (**A**, Scheme 6) proceeds more easily and rapidly than the formation of the adduct-radical (**B**, Scheme 6). The ratio of the dioxolane radicals formed is thus given by the relative reactivity of the C–H bonds in the hydrogen-abstraction step.

4. Structure elucidation of new compounds

4-Fluoroalkyldioxolanes **7–11** and fluoroalkyl diols **12–16** and their bis-methacrylates **20–24** are new compounds. The structures of all compounds were elucidated on the basis of their ^{1}H and ^{19}F NMR spectra and elemental microanalyses. The compounds **7–11**, **12–16** and **20–24** contain two newly formed asymmetric carbon atoms. The pairs of diastereoisomers can be detected by GC and by their ^{1}H and ^{19}F NMR signals, but the stereoisomers were not separated and the relative configurations have not been assigned to the individual diastereoisomers. Asymmetric centers in the starting 4-fluoroalkyl-2,2-dimethyl-1,3-dioxolanes **7–11** were transformed into the corresponding 1-fluoro-alkylethane-1,2-diols **12–16** and subsequently into the bis-methacrylates **20–24** without any change (see Section 5).

5. Experimental

5.1. General comments

The temperature data were not corrected. Distillations of high boiling compounds were carried out using a Vacuubrand RC5 high vacuum oil pump. GC analyses were performed on a Chrom 5 instrument (Laboratorní přístroje, Prague; FID, 380×0.3 cm packed column, silicone elastomer E-301 on Chromaton N-AW-DMCS (Lachema, Brno), nitrogen) and on Delsi apparatus (model 330, equipped with SE30 column, 100 cm×1/8 in. (i.d.); nitrogen, temperature programme in the range 50–250°C) with a Hewlett-Packard integrator (model 33990). NMR spectra were recorded on Bruker 400 AM (FT, ^{19}F at 376.5 MHz) and Bruker WP 80 SY (FT, ^{19}F at 75 MHz) instruments: TMS and $CFCl_3$ as the internal standards, chemical shifts in ppm (s singlet, bs broad singlet, d doublet, t triplet, q quadruplet, qi quintuplet, sex sextuplet, sep septuplet, m multiplet), coupling constants J in Hz, solvents $CDCl_3$, acetone-d_6 and DMSO-d_6. Mass spectra were scanned on a GC-Mass Spectrometer tandem JEOL D X-303 (JMA 5000, single focus, 70 eV, helium), GC inlet via a 1 m capillary column coated with silicone elastomer.

The chemicals used were as follows: 1,3-dioxolane (Fluka), 2,2-dimethyl-1,3-dioxolane [67] and 2,2,4-trimethyl-1,3-dioxolane [69] (yield 83–85%; 1,1,2-trichlorotrifluoroethane (CFC-113) was used as azeotropic solvent) were prepared according to the literature. Silicagel L40/100 (Merck), 2,2-diphenyl-1-picrylhydrazyl (Aldrich); methacryloyl chloride (Fluka) was distilled before use. Oxolane (Fluka) and acetone were dried and purified according to the standard procedures [70]. Dibenzoyl peroxide (Merck) was precipitated from its chloroform solution by methanol and dried in vacuo. Hexafluoropropene (Fluorochem); perfluorovinyl ethers **4** and **5** were prepared from hexafluoropropene-1,2-oxide according to the literature [62,71], perfluoroether **6** was a gift of the Institute of Organoelement Compounds, Moscow.

5.1.1. NMR and MS spectra of perfluoro-3,6,9,12,15-pentaoxahexadec-1-ene (**6**)

^{19}F NMR ($CDCl_3$+Et_2O, 10:1) δ: −55.95 (t, 3F, CF_3O, $^{4}J_{FF} = 9$); −88.67 (t, 1F(a), CF_2OCF, $^{3}J_{FF} = 7$); −88.71 (s, 1F(b), CF_2OCF); −89.26 (t, 1F(a), CF_2CF_2OCF, $^{3}J_{FF} = 7$); −89.29 (s, 1F(b), CF_2CF_2OCF); −89.37 (s, 8F, $4CF_2O$); −91.08 (s, 2F, $CF_2CF_2OCF_3$); −91.36 (q, 2F, CF_2OCF_3, $^{4}J_{FF} = 9$); −113.90 (dd, 1F(*cis*), CF_2=, $^{2}J_{FF} = 84$, $^{3}J_{FF} = 66$); −122.21 (dd, 1F(*trans*), CF_2=, $^{2}J_{FF} = 84$, $^{3}J_{FF} = 113$); −135.71 (dd, 1F, CF=, $^{3}J_{FF} = 113$ and 66) ppm.

MS *m/z* (% rel. int.): 630(9, M^+); 313(3, $C_6F_{11}O_2^+$); 251(3, $C_4F_9O_2^+$); 213(19, $C_4F_7O_2^+$); 197(10, $C_4F_7O^+$); 185(46, $C_3F_7O^+$); 170(5); 169(100, $C_3F_7^+$); 163(11); 147(36, $C_3F_5O^+$); 135(77, $C_2F_5O^+$); 131(7, $C_3F_5^+$); 120(27); 119(99, $C_2F_5^+$); 101(6); 100(99, $C_2F_4^+$); 98(5);

97(99, $C_2F_3O^+$); 81(23, $C_2F_3^+$); 78(34, $C_2F_2O^+$); 75(19); 70(8); 69(99, CF_3^+); 48(24).

5.2. Radical additions to perfluoroolefins (products **7–11**, **26**, **28** and **32–34**)

5.2.1. General procedure for photo-induced additions of dioxolanes to hexafluoropropene (**2**) in an immersion-well photoreactor (products **7**,**28**,**32**)

Apparatus: An immersion-well photoreactor (75 ml) cooled externally from −15°C to −5°C, a medium-pressure UV lamp (Tesla, RVK 125) in a water-cooled double jacket (quartz and Simax® glass, sintered-glass inlet at the bottom of the reactor); a dry-ice cooled spiral cooler was connected to a dry-ice cooled trap (through a hydraulic seal with silicon oil) that was connected to the atmosphere through a hydraulic seal with sulfuric acid.

Reaction: Prior to the reaction, the whole apparatus, filled with dioxolane (**1**, **27**, **30**; 0.5 mol), was carefully flushed with argon. Hexafluoropropene (15.0 g, 0.1 mol) was introduced into the dioxolane (0.5 mol) in the photoreactor over 2 h at such a flow-rate that it was totally consumed. Dioxolane was then distilled off on a packed column (15 cm, Berle saddles) and the crude product was distilled under reduced pressure to give pure product.

5.2.2. Photoreaction of 2,2-dimethyl-1,3-dioxolane (**1**) with hexafluoropropene (**2**) (products **7a** and **7b**)

For apparatus and procedure see Section 5.2.1 (for yields and b.p., see Table 1). Analysis (**7a**+**7b**): Found: C, 38.48; H, 4.33; F, 45.49%. $C_8H_{10}F_6O_2$ requires: C, 38.11; H, 4.00; F, 45.21%. M, 252.16.

*4-(1,1,2,3,3,3-Hexafluoropropan-1-yl)-2,2-dimethyl-1,3-dioxolane (***7a**, 98.8% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers A(55% rel.), B(45% rel.): 1.37, 1.38, 1.46, 1.48 (4×s, 6H, $2CH_3$); 4.16 and 4.18, 4.27 and 4.29 (4×t, 2H(B,A), CH_2O, $^2J_{HH} = ^3J_{HH} = 6$); 4.35 (dddd, 1H (B), CHO, $^3J_{HF} = 15$ and 6, $^3J_{HH} = 4$ and 2); 4.43 (dddt, 1H(A), CHO, $^3J_{HF} = 23$ and 2, $^3J_{HH} = 4$ and 2, $^4J_{HH} = 3.5$); 5.05 (dddq, 1H(A), CHF, $^2J_{HF} = 43$,$^3J_{HF} = 20$, 6(func q) and 1.5); 5.06 (dddq, 1H(B), CHF, $^2J_{HF} = 43$,$^3J_{HF} = 12$, 8 and 6(func q)) ppm. ^{19}F NMR ($CDCl_3$) δ: −74.41 (dq, 3F(A), CF_3, $^3J_{FF} = ^4J_{FF} = 11$,$^3J_{HF} = 6$); −74.82 (ddt, 3F(B), CF_3, $^3J_{FF} = 11$,$^4J_{FF} = 11$ and 8, $^3J_{HF} = 6$); −120.01 (dddqi, 1F(F(a), B), CF_2, $^2J_{FF} = 273$,$^3J_{HF} = 12$, 6, $^3J_{FF} = ^4J_{FF} = 11$ (qi)); −125.11 (dddqi, 1F(F(b), B), CF_2, $^2J_{FF} = 273$,$^3J_{HF} = 20$ and 8, $^3J_{FF} = 11$,$^4J_{FF} = 8$); −126.72 (dddqi, 1F(F(a), A), CF_2, $^2J_{FF} = 270$,$^3J_{HF} = 20$ and 2, $^3J_{FF} = ^4J_{FF} = 12$ (qi)); −130.93 (ddddq, 1F(F(b), A), CF_2, $^2J_{FF} = 270$,$^3J_{HF} = 23$ and 1.5, $^4J_{FF} = 11$ (q), $^3J_{FF} = 4$); −213.42 (ddddq, 1F(A), CHF, $^2J_{HF} = 43$,$^3J_{FF} = 12$, 11(q) and 4, $^4J_{HF} = 3$); −218.43 (dsext,1F(B), CHF, $^2J_{HF} = 43$,$^3J_{FF} = 11$ (sext)) ppm. MS *m/z* (% rel. int.): 253 (30, $(M+1)^+$); 238 (51, $(M–CH_2)^+$); 237 (62,$(M–CH_3)^+$); 233 (5,$(M–F)^+$); 222 (40,$(M–2CH_3)^+$); 203 (30); 175(26); 155 (25); 151 (3, $C_3HF_6^+$); 121 (33); 101 (53, $C_5H_9O_2^+$); 77 (41, $C_3H_3F_2^+$); 72 (63, $C_4H_5F^+$); 69 (100, CF_3^+); 59 (72, $C_2H_3O_2^+$); 56 (98).

*4-(1,1,2,3,3,3-Hexafluoropropan-2-yl)-2,2-dimethyl-1,3-dioxolane (***7b**, 1,2% rel.to **7a**). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A(56% rel.), B(44% rel.): 1.35–1.50 (m, 6H, $2CH_3$); 4.15–4.30 (m, 2H, CH_2O); 4.45–4.60 (m, 1H, CHO); 6.20, 6.23 (2×t, 1H(A,B), CHF_2, $^2J_{HF} = 52$ and 54) ppm. ^{19}F NMR ($CDCl_3$) δ: −74.14, −74.58 (2×dt, 3F(A,B), CF_3, $^4J_{FF} = 10$,$^3J_{FF} = 7$ and 3); −133.96 (dtq, 2F(A), CHF_2, $^2J_{HF} = 52$,$^4J_{FF} = 10$(q),$^3J_{FF} = ^4J_{HF} = 2.2$(t)); −136.35 (dqi, 2F(B), CHF_2, $^2J_{HF} = 54$, $^3J_{FF} = ^4J_{FF} = 11$); −193.20 and −197.51 (2×dm, 1F(B,A), CF, $^3J_{HF} = 19$) ppm.

5.2.3. General procedure for photo-induced additions of dioxolanes to perfluorolefins in quartz cell (products **8–11**, **26**, **33–34**)

Apparatus: the reactions were carried out in a round-shaped two-necked (with septa) quartz cell of volume ca. 20 ml (diameter 5 cm, thickness 1 cm, plane-parallel sites) irradiated externally by a medium pressure UV lamp (Tesla, RVK 400 W), placed in a reflecting-metal cylindrical housing, with a round window (diameter 5 cm) made of a quartz lens.

Reaction: the reaction mixture consisted of dioxolane (**1**, **27**, **30**; 0.1 mol) and the perfluoroolefin (**4–6**, **31**; 0.02 mol) was deaerated for 1 h at ca. −10°C with a stream of argon (inlet–outlet by needles through septa). The mixture was then irradiated at r.t. for 2 h (ca. 98% conversion of the olefin, monitoring by GC) while stirring (magnetic spinbar). Dioxolane was then distilled off (5 cm column packed with Berle saddles) and the crude product was distilled to afford pure product (for reaction amounts, conversion, yields, product purity and b.p., see Table 1 or Table 5.

5.2.4. Photo-induced reaction of 2,2-dimethyl-1,3-dioxolane (**1**) with perfluoroundec-1-ene (**3**) (product **8a**)

For apparatus and procedure see Section 5.2.3 (for yield and boiling point, see Table 1).

*4-(1,1,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Docosafluoroundecan-1-yl)-2,2-dimethyl-1,3-dioxolane (***8a**). Analysis (**11**): Found: C, 29.84; H, 1.63; F, 63.44%. $C_{16}H_{10}F_{22}O_2$ requires: C, 29.46; H, 1.55; F, 64.08%. M, 652.22. ^{1}H NMR (acetone -d_6) δ, 2 diastereoisomers, A (60% rel.), B (40% rel.): 1.38, 1.40, 1.46, 1.48 (4×s, 6H, $2CH_3$); 4.31, 4.33 (2×dm, 2H, CH_2O, $^2J_{HH} = 6$); 4.64, 4.70 (2×m, 1H, CHO); 5.72, 5.79 (2×dm, 1H, CHF, $^2J_{HF} = 46$) ppm. ^{19}F NMR (acetone -d_6) δ: −81.37 (t, 3F, CF_3, $^3J_{FF} = 10$); −122.13 (m, 10F, $5CF_2$); −117.59 and −122.32 (2×dm, 1F(a), CF_2CH, $^2J_{FF} = 273$); −123.01 and −129.83 (2×dm, 1F(b), CF_2CH, $^2J_{FF} = 273$); −123.10, −126.52 (2×m, 6F, $3CF_2$); −212.51 and −217.53 (2×dm, 1F(A,B), CHF, $^2J_{HF} = 46$) ppm.

5.2.5. General procedure for peroxide-induced additions of dioxolanes to perfluorolefins (products **9–11** *and* **33***)*

A homogenous mixture of perfluoroolefin (**4–6**, **31**; 0.02 mol), dioxolane (**1**, **30**; 0.1 mol) and dibenzoyl peroxide (0.48 g; 2 mmol) was deaerated for 0.5 h at ca. −20°C with a stream of argon (inlet–outlet by two needles through the septa) in a flask (25 ml) equipped with a dry-ice cooled spiral reflux condenser with a hydraulic seal (sulfuric acid). The reaction mixture was refluxed for 4 h while stirring intensively (96–97% conversion of olefins, monitoring by GC). Excess of dioxolane was distilled off (column 5 cm packed with Berle saddles) and the crude product was distilled in vacuo to afford pure product (for reaction amounts, conversion, yields, product purity and b.p., see Table 1 or Table 5).

*5.2.6. Photo- and peroxide-induced reaction of 2,2-dimethyl-1,3-dioxolane (***1***) with perfluoro-3-oxahex-1-ene (***4***) (products* **9a** *and* **9b***)*

For apparatus and procedure see Sections 5.2.3 and 5.2.5 (for yield and b.p., see Table 1). Analysis (**9a**+**9b**). Found: C, 32.94; H, 2.86; F, 52.10%. $C_{10}H_{10}F_{10}O_3$ requires: C, 32.62; H, 2.74; F, 51.60%. M, 368.17.

*4-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahexan-1-yl)-2,2-dimethyl-1,3-dioxolane (***9a**, 93% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers A (56% rel.), B (44% rel.): 1.36, 1.38, 1.46, 1.47 (4×s, 6H, $2CH_3$); 4.16 and 4.18 (2×t, 2H(B), CH_2O, $^2J_{HH} = ^3J_{HH} = 7$); 4.25 and 4.27 (2×t, 2H(A), CH_2O, $^2J_{HH} = ^3J_{HH} = 4.5$); 4.34 (ddt, 1H(A), CHO, $^3J_{HF} = 19$ and 4, $^3J_{HH} = 4.5$); 4.42 (ddt, 1H(B), CHO, $^3J_{HF} = 17$ and 8, $^3J_{HH} = 7$); 6.10 (ddd, 1H(A), CHF, $^2J_{HF} = 55$,$^3J_{HF} = 9$ and 1.5); 6.12 (ddd, 1H(B), CHF, $^2J_{HF} = 53$,$^3J_{HF} = 8$ and 3.5) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.81, −81.87 (2×t, 3F, CF_3, $^3J_{FF} = 7$); −85.15, −85.52, −87.31 and −88.17 (4×dm, 2F(a,b), CF_2O, $^2J_{FF} = 146$); −129.00 (ddt, 1F(F(a), A), CF_2CH, $^2J_{FF} = 268$,$^3J_{HF} = 9$ and 4, $^3J_{FF} = 9$); −131.13 (dddd, 1F(F(b), A), CF_2CH, $^2J_{FF} = 268$,$^3J_{HF} = 19$ and 1.5, $^3J_{FF} = 11$); −131.59 (dq, 1F(F(a), B), CF_2CH, $^2J_{FF} = 269$,$^3J_{HF} = ^3J_{FF} = 8$); −131.94 (ddd, 1F(F(b), B), CF_2CH, $^2J_{FF} = 269$,$^3J_{HF} = 17$ and 3.5); −130.24, −130.30 (2×m, 2F, CF_2CF_3); −144.33 (dd, 1F(B), CHF, $^2J_{HF} = 53$,$^3J_{FF} = 8$); −151.34 (dddd, 1F(A), CHF, $^2J_{HF} = 55$,$^4J_{HF} = 15$,$^3J_{FF} = 11$ and 9) ppm.

MS *m/z* (% rel. int.): 369(1.5, $(M+1)^+$); 368(1, M^+); 354(26, $(M–CH_2)^+$); 353(100, $(M–CH_3)^+$); 338(6, $(M–2CH_3)^+$); 319(3, $C_8H_4F_9O_3^+$); 183(19, $(M–C_3F_7O)^+$); 169(21, $C_3F_7^+$); 101(43, $C_5H_9O_2^+$); 77(16, $C_3H_3F_2^+$); 69(34, CF_3^+); 61(22, $C_2H_5O_2^+$); 59(67, $C_2H_3O_2^+$).

*4-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahexan-2-yl)-2,2-dimethyl-1,3-dioxolane (***9b**, 7% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (50% rel.), B (50% rel.): 1.36−1.47 (m, 6H, $2CH_3$); 4.16–4.27 (m, 2H, CH_2O); 4.45–4.55 (m, 1H, CHO); 6.05 (ddt, 1H(B), CHF_2, $^2J_{HF} = 53$,$^3J_{HF} = 5.6$,$^4J_{HH} = 1$); 6.07 (dt, 1H(A), CHF_2, $^2J_{HF} = 54$,$^4J_{HH} = 1$) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.65, −81.74 (2×t, 3F(A,B), CF_3, $^3J_{FF} = 7$); −85.15, −88.17 (2×m, 2F(A,B), CF_2O); −129.95 and −130.12 (2×m, 2F(A,B), CF_2–CF_3); −134.48 (ddd, 1F(F(a), A), CHF_2, $^2J_{FF} = 301$,$^2J_{HF} = 54$,$^3J_{FF} = 4$); −135.32 (ddd, 1F(F(a), B), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 53$,$^3J_{FF} = 4$); −136.24 (ddd, 1F(F(b), B), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 53$,$^3J_{FF} = 9$); −137.33 (m, 1F(B), CF); −139.37 (dddt, 1F(F(b), A), $^2J_{FF} = 301$,$^2J_{HF} = 54$,$^3J_{HF} = 23$,$^5J_{FF} = 8$); −145.12 (m, 1F(A), CF) ppm.

*5.2.7. Photo- and peroxide-induced reaction of 2,2-dimethyl-1,3-dioxolane (***1***) with perfluoro(5-trifluoromethyl-3,6-dioxanon-1-ene (***5***) (products* **10a** *and* **10b***)*

For apparatus and procedure see Sections 5.2.3 and 5.3.5 (for yield and b.p., see Table 1).

Analysis (**10a**+**10b**): Found: C, 29.45; H, 1.98; F, 57.76%. $C_{13}H_{10}F_{16}O_4$ requires: C, 29.23; H, 1.89; F, 56.90%. M, 534.19.

*4-(1,1,2,4,4,5,7,7,8,8,9,9,9-Tridecafluoro-5-trifluoromethyl-3,6-dioxanonan-1-yl)-2,2-dimethyl-1,3-dioxolane (***10a**, 94% rel.). ^{1}H NMR ($CDCl_3$) δ, 4 diastereoisomers, A,B (56% rel.), C,D (44% rel.): 1.38, 1.39, 1.45, 1.46 (4×s, 6H, $2CH_3$); 4.17, 4.19, 4.25, 4.27 (4×d, 2H, CH_2O, $^2J_{HH} = 9$); 4.29, 4.41 (2×m, 1H, CHO); 6.11 (ddd, 1H(A,B), CHF, $^2J_{HF} = 55$,$^3J_{HF} = 12$ and 2); 6.09 and 6.26 (2×ddd, 1H(C,D), CHF, $^2J_{HF} = 53$,$^3J_{HF} = 12$ and 1) ppm. ^{19}F NMR ($CDCl_3$) δ: −80.51, −80.53, −80.61, −80.64 (4×d, 3F, CF_3CF, $^3J_{FF} = 8$); −81.82, −81.84, −81.85, −81.87 (4×t, 3F, CF_3, $^3J_{FF} = 7$); −81.92, −82.44 (2×dm, 2F, CF_2CF_2O, $^2J_{FF} = 139$); −83.78, −83.85, −84.46, −86.02 (4×dm, 1F(a), $CFCF_2O$, $^2J_{FF} = 143$); −84.39, −86.26, −86.55, −87.22 (4×dm, 1F(b), $CFCF_2O$, $^2J_{FF} = 143$); −128.96 and −129.22 (2×ddt, 1F(F(a), A,B), CF_2CH, $^2J_{FF} = 268$, $^3J_{HF} = 12$ and 9, $^3J_{FF} = 9$); −130.15, −130.20 (2×m, 2F, CF_2CF_3); −131.19 and −131.47 (2×dddd, 1F(F(b), A,B), CF_2CH, $^2J_{FF} = 268$,$^3J_{HF} = 11$ and 2, $^3J_{FF} = 19$); −132.22 (dt, 2F(C,D), CF_2CH, $^3J_{FF} = 12$(t) and 1); −144.45 and −144.54 (2×dt, 1F(C,D), CHF, $^2J_{HF} = 53$,$^3J_{FF} = 12$); −145.69 (t, 1F, CF, $^3J_{FF} = 22$); −151.45 and −151.67 (2×ddd, 1F(A,B), CHF, $^2J_{HF} = 55$,$^3J_{FF} = 19$ and 9) ppm.

*4-[1,1,2,4,4,5,7,7,8,8,9,9,9-Tridecafluoro-3,6-dioxa-5-(trifluoromethyl)nonan-2-yl]-2,2-dimethyl-1,3-dioxolane (***10b**, 6% rel.). ^{1}H NMR ($CDCl_3$) δ, 4 diastereoisomers, A,B (65% rel.), C,D (35% rel.): 1.35–1.50 (m, 6H, $2CH_3$); 4.15–4.30 (m, 2H, CH_2O); 4.40–4.55 (m, 1H, CHO); 6.05, 6.07 (2×dt, 1H(A,B), CHF_2, $^2J_{HF}$=53, $^3J_{HF} = 13$); 6.20, 6.22 (2×dt, 1H(C,D), CHF_2, $^2J_{HF} = 53$,$^3J_{HF} = 10$) ppm. ^{19}F NMR ($CDCl_3$) δ: −80.10, −80.30 (2×m, 3F, CF_3CF); −81.80, −81.90 (2×m, 3F, CF_3CF_2); −82.00, −82.50 (2×m, 2F, CF_2CF_2O); −83.5, −87.30 (2×m, 2F, $CFCF_2O$); −130.11 (m, 2F, CF_2CF_3); −134.75 (ddd, 1F(F(a), A,B), CHF_2, $^2J_{FF} = 301$,$^2J_{HF} = 53$,$^3J_{FF} = 12$); −135.92 (dm, 2F(C,D), CHF_2, $^2J_{HF} = 53$); −136.50 (m, 1F(A,B), CF); −139.91 (ddm, 1F(F(b), A,B), CHF_2,

$^2J_{FF} = 301$,$^2J_{HF} = 53$); −140.89 (m, 1F(C,D), CF); −145.50 (m, 1F, CF_3–CF) ppm.

*5.2.8. Photo- and peroxide-induced reaction of 2,2-dimethyl-1,3-dioxolane (**1**) with perfluoro-3,6,9,12,15-pentaoxahexadec-1-ene (**6**) (products **11a** and **11b**)*

For apparatus and procedure see Sections 5.2.3 and 5.3.5 (for yield and b.p., see Table 1).

Analysis (**11a**+**11b**): Found: C, 26.32; H, 1.45; F, 57.22%. $C_{16}H_{10}F_{22}O_7$ requires: C, 26.25; H, 1.38; F, 57.08%. M, 732.22.

*4-(1,1,2,4,4,5,5,7,7,8,8,10,10,11,11,13,13,14,14,16,16,1-6-Docosafluoro-3,6,9,12,15-pen-taoxahexadecan-1-yl)-2,-2-dimethyl-1,3-dioxolane (***11a**, 93% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (54% rel.), B (46% rel.): 1.34, 1.38, 1.45, 1.46 (4×s, 6H, $2CH_3$); 4.13, 4.24 (2×dd, 2H(B), CH_2O, $^2J_{HH} = 9$,$^3J_{HH} = 2$ or 1); 4.17, 4.26 (2×dd, 2H(A), CH_2O, $^2J_{HH} = 9$,$^3J_{HH} = 7$ or 2); 4.32 (dt, 1H(A), CHO, $^3J_{HF} = 6$,$^3J_{HH} = 7$ and 2); 4.40 (dd, 1H(B), CHO, $^3J_{HH} = 2$ and 1); 6.04 (ddd, 1H(A), CHF, $^2J_{HF} = 54$,$^3J_{HF} = 11$ and 1.6); 6.06 (dt, 1H(B), CHF, $^2J_{HF} = 53$,$^3J_{HF} = 6$) ppm. ^{19}F NMR ($CDCl_3$) δ: −56.08 (t, 3F, CF_3, $^4J_{FF} = 9$); −88.93, −89.03 (2×m, 2F, CF_2O); −89.90, −90.07 (2×dd, 1F(a), CF_2O, $^2J_{FF} = 143$,$^3J_{FF} = 10$); −91.41 (q, 2F, CF_2OCF_3, $^4J_{FF} = 9$); −92.00, −92.60 (2×dd, 1F(b), CF_2O, $^2J_{FF} = 143$,$^3J_{FF} = 5$); −89.42 (m, 10F, $5CF_2O$); −129.51 (ddd, 1F(F(a), A), CF_2CH, $^2J_{FF} = 267$,$^3J_{FF} = 15$,$^3J_{HF} = 1.6$); −131.48 (dddd, 1F(F(b), A), CF_2CH, $^2J_{FF} = 267$,$^3J_{FF} = 15$,$^3J_{HF} = 11$ and 6); −132.03 (dd, 2F(B), CF_2CH, $^3J_{HF} = 6$,$^3J_{FF} = 5$); −144.41 and −151.63 (2×dt, 1F(B,A), CHF, $^2J_{HF} = 53$ or 54, $^3J_{FF} = 5$ or 15) ppm. MS *m/z* (% rel. int.): 732(0.5, M^+); 731(1, $(M–H)^+$); 718(17, $(M–CH_2)^+$); 717(98, $(M–CH_3)^+$); 702(4, $(M–2CH_3)^+$); 531(3, $(M–C_3F_7O_2)^+$); 365(3, $(M–C_6F_{13}O_3)^+$); 299(5, $(M–C_7F_{15}O_4)^+$); 269(4, $C_5F_{11}^+$); 183(12, $C_4H_2F_7^+$); 169(6, $C_3F_7^+$); 135(8, $C_2F_5O^+$); 119(100, $C_2F_5^+$); 101(38, $C_5H_9O_2^+$); 100(11, $C_2F_4^+$); 97(6, $C_2F_3O^+$); 77(15, $C_3H_3F_2^+$); 69(57, CF_3^+); 61(52, $C_2H_5O_2^+$); 59(94, $C_2H_3O_2^+$).

*4-(1,1,2,4,4,5,5,7,7,8,8,10,10,11,11,13,13,14,14,16,16,1-6-Docosafluoro-3,6,9,12,15-pen-taoxahexadec-2-yl)-2,2-dimethyl-1,3-dioxolane (***11a**, 93% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (75% rel.), B (25% rel.): 1.36–1.47 (m, 6H, $2CH_3$); 4.16–4.27 (m, 2H, CH_2O); 4.45–4.55 (m, 1H, CHO); 6.08 and 6.10 (2×dt, 1H(B,A), CHF_2, $^2J_{HF} = 54$ or 53, $^3J_{HF} = 6$) ppm. ^{19}F NMR ($CDCl_3$) δ: −56.08 (t, 3F, CF_3O, $^4J_{FF} = 9$); −88.90, −89.05 (2×m, 2F, CF_2O); −89.90, −90.10 (2×dm, 1F(a), CF_2O, $^2J_{FF} = 143$); −91.41 (q, 2F, CF_2OCF_3, $^4J_{FF} = 9$); −92.00, −92.60 (2×dm, 1F(b), CF_2O, $^2J_{FF} = 143$); −89.42 (m, 10F, $5CF_2O$); −134.51, −136.05 (2×ddm, 2F(A), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 53$); −137.83 (ddtt, 1F(A), CFCH, $^3J_{FF} = 19$,$^3J_{HF} = 16$ and 6, $^4J_{FF} = 4$); −138.12 (m, 1F(B), CFCH); −139.62 (2×ddm, 2F(B), CHF_2, $^2J_{FF} = 301$,$^2J_{HF} = 54$) ppm.

*5.2.9. Photo-induced reaction of 1,3-dioxolane (**27**) with hexafluoropropene (**2**) (products **28a**–**28c**)*

For apparatus and procedure see Section 5.2.1 (for yield and b.p., see Table 5).

Analysis (**28a**+**28b**+**28c**): Found: C, 32.29; H, 2.79; F, 51.11%. $C_6H_6F_6O_2$ requires: C, 32.16; H, 2.70; F, 50.87%. M, 224.10.

*2-(1,1,2,3,3,3-Hexafluoropropan-1-yl)-1,3-dioxolane (***28a**, 91% rel.). ^{1}H NMR ($CDCl_3$) δ: 4.00–4.15 (m, 4H, $2CH_2O$); 5.03 (dddq, 1H, CHF, $^2J_{HF} = 43$,$^3J_{HF} = 16$, 6(q) and 5); 5.29 (ddd, 1H, CHO, $^3J_{HF} = 12$ and 4, $^4J_{HF} = 2$) ppm. ^{19}F NMR ($CDCl_3$) δ: −74.71 (ddt, 3F, CF_3, $^3J_{FF} = 11$,$^4J_{FF} = 10$(t),$^3J_{HF} = 6$); −129.24 (ddddq, 1F(a), CF_2, $^2J_{FF} = 272$,$^3J_{FF} = 11$,$^4J_{FF} = 10$(q), $^3J_{HF} = 12$ and 5); −130.63 (ddddq, 1F(b), CF_2, $^2J_{FF} = 272$,$^3J_{HF} = 16$ and 4, $^4J_{FF} = 10$(q),$^3J_{FF} = 8.5$); −216.44 (dddqi, 1F, CHF, $^2J_{HF} = 43$,$^3J_{FF} = 11$(qi) and 8.5, $^4J_{HF} = 2$) ppm.

*2-(1,1,2,3,3,3-Hexafluoropropan-2-yl)-1,3-dioxolane (***28b**, 8% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (54% rel.), B (46% rel.): 4.18–4.35 (m, 2H, CH_2O); 4.38–4.50 (m, 1H, CHO); 4.90–5.00 (m, 2H, CH_2O_2); 5.05 and 5.06 (2×dm, 1H(A,B), CHF, $^2J_{HF} = 43$) ppm. ^{19}F NMR ($CDCl_3$) δ: −74.48, −74.86 (2×ddt, 3F(A,B), CF_3, $^4J_{FF(a)} = 12$ or 8, $^4J_{FF(b)} =^3 J_{FF} = 11$(t),$^3J_{HF} = 6$); −118.58 (ddqi, 1F(F(a), A), CF_2, $^2J_{FF} = 277$, $^3J_{FF} =^4 J_{FF} = 12$(qi),$^3J_{HF} = 6$); −121.48 (dddq, 1F(F(a), B), CF_2, $^2J_{FF} = 275$,$^3J_{FF} = 11$,$^4J_{FF} = 8$(q),$^3J_{HF} = 6$); −127.76, −129.84 (2×dddq, 2F(F(b), B,A), CF_2, $^2J_{FF} = 275$ or 277, $^4J_{FF} = 11$(q),$^3J_{FF} = 10$ or 5.8, $^3J_{HF} = 12$); −213.33 (ddddq, 1F(A), CHF, $^2J_{HF} = 43$,$^3J_{FF(a)} = 12$,$^3J_{FF} = 11$(q),$^3J_{FF(b)} = 5.8$,$^4J_{HF} = 2.5$); −217.32 (dddqi, 1F(B), CHF, $^2J_{HF} = 43$,$^3J_{FF} = 11$(qi), $^3J_{FF(b)} = 10$,$^4J_{HF} = 2.5$) ppm.

*4-(1,1,2,3,3,3-Hexafluoropropan-1-yl)-1,3-dioxolane (***28c**, 1% rel.). ^{1}H NMR ($CDCl_3$) δ: 4.00–4.15 (m, 4H, $2CH_2O$); 5.38 (d, 1H, CHO, $^3J_{HF} = 14$); 6.08 (dt, 1H, CHF_2, $^2J_{HF} = 53$,$^3J_{HF} = 6$) ppm. ^{19}F NMR ($CDCl_3$) δ: −73.65 (ddt, 3F, CF_3, $^4J_{FF} = 9$(t),$^3J_{FF} = 6.6$,$^4J_{HF} = 1$); −134.35 (ddq, 1F(a), CHF_2, $^2J_{HF} = 53$,$^4J_{FF} = 9$(q),^3J FF = 6.6); −134.84 (dqi, 1F(b), CHF_2, $^2J_{HF} = 53$, $^4J_{FF} =^3 J_{FF} = 9$); −198.27 (dddqi, 1F, CF, $^3J_{FF} = 9$ and 6.6(qi), $^3J_{HF} = 14$ and 6) ppm.

*5.2.10. Photo-induced reaction of 2,2,4-trimethyl-1,3-dioxolane (**30**) with hexafluoropropene (**2**) (products **32a** and **32b**)*

For apparatus and procedure see Section 5.2.1 (for yield and b.p., see Table 5).

Analysis (**32a**+**32b**): Found: C, 40.43; H, 4.66; F, 43.72%. $C_9H_{12}F_6O_2$ requires: C, 40.61; H, 4.54; F, 42.82%. M, 266.18.

*4-(1,1,2,3,3,3-Hexafluoropropan-1-yl)-2,2,4-trimethyl-1-,3-dioxolane (***32a**, 87% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (74% rel.), B (26% rel.): 1.43, 1.45, 1.46, 1.47 (4×s, 6H, $2CH_3$); 1.49 (s, 3H, CH_3); 3.80, 3.83, 4.39, 4.42

(4×d, 2H, CH_2O, $^2J_{HH} = 9$); 5.12 and 5.15 (2×dddq, 1H(A,B), CHF, $^2J_{HF} = 43$,$^3J_{HF} = 18$, 6(q) and 1.5) ppm. ^{19}F NMR ($CDCl_3$) δ: −74.26, −74.54 (2×ddt, 3F, CF_3, $^4J_{FF} = 14$ and 10, $^3J_{FF} = 10$,$^3J_{HF} = 6$); −119.20 and −124.03 (2×dddq, 1F(F(a), A,B), CF_2, $^2J_{FF} = 284$ or 273, $^4J_{FF} = 10$,$^3J_{FF} = 8$,$^3J_{HF} = 1.5$); −124.90 and −126.33 (2×dddq, 1F(F(b), A,B), CF_2, $^2J_{FF} = 284$ or 273, $^4J_{FF} = 14$,$^3J_{FF} = 10$,$^3J_{HF} = 17.6$); −208.92 and −209.87 (2×ddqi, 1F(A,B), CHF, $^2J_{HF} = 43$,$^3J_{FF} =$ 10(qi) and 8) ppm. MS *m/z* (% rel. int.): 267(1, $(M+1)^+$); 252(31, $(M–CH_2)^+$); 251(100, $(M–CH_3)^+$); 191(24, $C_6H_5F_6^+$); 151(9, $C_3HF_6^+$); 141(5, $C_5H_5F_4^+$); 121(6, $C_5H_4F_3^+$); 115(45, $(M–C_3HF_6)^+$); 109(55, $C_4H_4F_3^+$); 101(6, $C_5H_9O_2^+$); 91(11, $C_4H_5F_2^+$); 77(17, $C_3H_3F_2^+$); 72(83, $C_4H_5F^+$); 69(43, CF_3^+); 64(10, $C_2H_2F_2^+$); 59(21, $C_2H_3O_2^+$); 56(99, $C_2O_2^+$); 55(73); 54(99); 52(11, $CH_2F_2^+$).

*4-(1,1,2,3,3,3-Hexafluoropropan-1-yl)-2,2,5-trimethyl-1-,3-dioxolane (***32b**, 13% rel.). ^{1}H NMR ($CDCl_3$) δ, 4 diastereoisomers, A (6% rel.), B (46% rel.), C (44% rel.), D (4% rel.): 1.42–1.48 (m, 9H, $3CH_3$); 3.92 (m, 1H, C*H*CH_3); 4.48 (dt, 1H, C*H*CF_2, $^3J_{HF} = 6$,$^3J_{HH} = 1.7$); 5.00, 5.05, 5.22, 5.27 (4×dddq, 1H, CHF, $^2J_{HF} = 43$,$^3J_{HF} = 18$, 6(q) and 1.5) ppm.

^{19}F NMR ($CDCl_3$) δ: −74.70, −74.75 (2×ddt, 3F, CF_3, $^4J_{FF} = 11$ and 7, $^3J_{FF} = 11$,$^3J_{HF} = 5$); −119.92, −124.33, −125.40, −126.22 (4×ddq, 1F(a), CF_2, $^2J_{FF} =$ 270,$^4J_{FF} = 11$,$^3J_{FF} = 2$); −123.08, −127.40, −127.57, −128.37 (4×dqi, 1F(b), CF_2, $^2J_{FF} = 270$,$^4J_{FF} =$ $^3J_{FF} = 7$); −212.63 and −213.39 (2×dddq, 1F(A,B), CHF, $^2J_{HF} = 43$,$^3J_{FF} = 12$(q), 7 and 2); −217.56 and −221.29 (2×dsex, 1F(C,D), CHF, $^2J_{HF} = 44$,$^3J_{FF} = 11$) ppm.

MS *m/z* (% rel. int.): 267(1, $(M+1)^+$); 252(31, $(M–CH_2)^+$); 251(100, $(M–CH_3)^+$); 223(5, $(M\text{-}C_3H_7^+$); 222(91, $(M–C_3H_8)^+$); 191(28, $C_6H_5F_6^+$); 171(25, $C_6H_4F_5^+$); 151(12, $C_3HF_6^+$); 145(26, $C_4H_5F_4O^+$); 127(50, $C_4H_3F_4^+$); 121(30, $C_5H_4F_3^+$); 115(23, $(M–C_3HF_6)^+$); 109(15, $C_4H_4F_3^+$); 101(3, $C_5H_9O_2^+$); 91(10, $C_4H_5F_2^+$); 77(22, $C_3H_3F_2^+$); 71(23, $C_4H_4F^+$); 69(32, CF_3^+); 56(99, $C_2O_2^+$); 55(51); 54(32); 52(10, $CH_2F_2^+$).

5.2.11. Photo- and peroxide-induced reaction of 2,2,4-trimethyl-1,3-dioxolane (30) with perfluorohept-1-ene (31) (products 33a and 33b)

For apparatus and procedure see Sections 5.2.3 and 5.2.5 (for yields and b.p., see Table 5).

Analysis (**33a**+**33b**): Found: C, 33.38; H, 2.76; F, 57.55%. $C_{13}H_{12}F_{14}O_2$ requires: C, 33.49; H, 2.59; F, 57.05%. M, 466.21.

*2,2,4-Trimethyl-4-(1,1,2,3,3,4,4,5,5,6,6,7,7,7-tetradeca-fluoroheptan-1-yl)- 1,3-dioxolane (***33a**, 87% or 80% rel.).

^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (52% rel.), B (48% rel.): 1.42, 1.43, 1.44, 1.46 (4×s, 6H, $2CH_3$); 1.49 (s, 3H, CH_3); 3.80, 4.42 (2×d, 2H(B), CH_2O, $^2J_{HH} = 9$); 3.83 (dt, 1H(H(a), A), CH_2O, $^2J_{HH} = 9$,$^4J_{HF} = 2.4$); 4.39 (d, 1H(H(b), A), CH_2O, $^2J_{HH} = 9$); 5.35 and 5.37 (2×dtt, 1H, CHF, $^2J_{HF} = 43$,$^3J_{HF} = 18$ and 3) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.44 (t, 3F, CF_3, $^3J_{FF} = 10$); −117.63 and −119.39 (2×dm, 1F(a), CF_2C, $^2J_{FF} = 273$); −123.12 (m, 6F, $3CF_2$); −123.51 and −125.67 (2×dm, 1F(b), CF_2C, $^2J_{FF} = 273$); −126.60 (m, 2F, CF_2CF_3); −209.11 and −210.06 (2×dm, 1F, CHF, $^2J_{HF} = 43$) ppm.

*2,2,5-Trimethyl-4-(1,1,2,3,3,4,4,5,5,6,6,7,7,7-tetradeca-fluoroheptan-1-yl)- 1,3-dioxolane (***33b**, 13 or 20% rel.).

^{1}H NMR ($CDCl_3$) δ, 4 diastereoisomers, A (44% rel.), B (3% rel.), C (50% rel.), D (3% rel.): 1.42–1.48 (m, 9H, $3CH_3$); 3.93 (m, 1H, C*H*CH_3); 4.48 (t, 1H, C*H*CF_2, $^3J_{HF} = 6$); 5.20–52 (4×m, 1H, CHF) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.44 (t, 3F, CF_3, $^3J_{FF} = 10$); −117.63 and −119.39 (2×dm, 1F(a), CF_2C, $^2J_{FF} = 273$); −123.12 (m, 6F, $3CF_2$); −123.51 and −125.67 (2×dm, 1F(b), CF_2C, $^2J_{FF} = 273$); −126.60 (m, 2F, CF_2CF_3); −212.49, −213.57, −217.09, −220.22 (4×dm, 1F, CHF, $^2J_{HF} = 43$) ppm.

5.2.12. Photo-induced reaction of 2,2,4-trimethyl-1,3-dioxolane (30) with perfluoro-3-oxahext-1-ene (4) (products 34a–34d)

For apparatus and procedure see Sections 5.2.3 and 5.2.5 (for yields and boiling points, see Table 5).

Analysis (**34a**+**34b**+**34c**+**34d**): Found: C, 34.49; H, 3.22; F, 49.95%. $C_{11}H_{12}F_{10}O_3$ requires: C, 34.57; H, 3.16; F, 49.71%. M, 382.20.

*4-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahexan-1-yl)-2,2,-4-trimethyl-1,3-dioxolane (***34a**, 84.5% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A(56% rel.), B(44% rel.): 1.38, 1.41, 1.42, 1.45 (4×s, 6H, $2CH_3$); 1.49 (s, 3H, CH_3); 3.78, 3.80, 4.37, 4.39 (4×d, 2H, CH_2O, $^2J_{HH} = 9$); 6.14 (ddd, 1H(B), CHF, $^2J_{HF} = 53$,$^3J_{HF} = 8$ and 3.5); 6.16 (ddd,1H(A), CHF, $^2J_{HF} = 54$,$^3J_{HF} = 14$ and 5) ppm. ^{19}F NMR ($CDCl_3$) δ: −81.83, −81.92 (2×t, 3F, CF_3, $^3J_{FF} = 7$); −85.11, −85.42, −87.42, −88.19 (4×dm, 2F(a,b), CF_2O, $^2J_{FF} = 146$); −129.11 (ddd,1F(F(a),A), CF_2C, $^2J_{FF} = 268$,$^3J_{HF} = 5$,$^3J_{FF} = 9$); −130.15 (ddd,1F(F(b),A), CF_2C, $^2J_{FF} = 268$,$^3J_{HF} = 14$,$^3J_{FF}$ $= 11$); −130.57 (dt,1F(F(a),B), CF_2C, $^2J_{FF} = 269$,$^3J_{HF}$ $=^3J_{FF} = 8$); −130.92 (dd,1F(F(b),B), CF_2C, $^2J_{FF} = 269$, $^3J_{HF} = 3.5$); −130.2, −130.3 (2×m,2F,CF_2CF_3); −140.65(dd,1F(B), CHF, $^2J_{HF} = 53$,$^3J_{FF} = 8$); −144.45(d,1F(A), CHF, $^2J_{HF} = 54$) ppm.

*4-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahexan-1-yl)-2,2,-5-trimethyl-1,3-dioxolane (***34b**, 12% rel.). ^{1}H NMR ($CDCl_3$) δ, 4 diastereoisomers, A(45% rel.), B(13% rel.), C(25% rel.), D(17% rel.): 1.4–1.5 (m, 9H, $3CH_3$); 3.89 (m, 1H, C*H*CH_3); 4.45 (dd, 1H, C*H*CF_2, $^3J_{HF} = 6$ and 3); 6.10–6.15 (dm,1H, CHF, $^2J_{HF} = 55$) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.8 (t, 3F, CF_3, $^3J_{FF} = 7$); −85.15 to −88.17 (4×dm, 2F(a,b), CF_2O, $^2J_{FF} = 146$); −129.11 (ddt, 1F (a), CF_2CH, $^2J_{FF} = 268$,$^3J_{HF} = 6$ and 4, $^3J_{FF} = 6$); −131.15 (dddd, 1F(b), CF_2CH,

$^2J_{FF} = 268$,$^3J_{HF} = 19$ and 3, $^3J_{FF} = 11$); −130.30 (m, 2F, CF_2CF_3); −150.64 (ddd, 1F(A), CHF, $^2J_{HF} = 55$,$^3J_{FF} = 11$ and 6); −150.98, −151.13, −154.27 (3×dm, 1F(B,C,D), CHF, $^2J_{HF} = 55$) ppm.

*4-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahexan-2-yl)-2,2,-4-trimethyl-1,3-dioxolane (***34c**, 2.5% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A(50% rel.), B(50% rel.): 1.4–1.5 (m, 9H, $3CH_3$); 3.8–4.4 (m, 2H, CH_2O); 6.05, 6.07 (2×t, 1H(B,A), CHF, $^2J_{HF} = 53$) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.62, −81.68 (2×t, 3F (A,B), CF_3, $^3J_{FF} = 7$); −85.2 to −88.2 (2×m, 2F(A,B), CF_2O); −130.0, −130.1 (2×m, 2F(A,B), CF_2–CF_3); −133.28 (dd, 1F(F(a), A), CHF_2, $^2J_{FF} = 301$,$^2J_{HF} = 54$); −135.22 (dd,1F(F(a), B), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 53$); −136.3 (dd, 1F(F(b), B), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 53$); −138.3 (m, 1F(B), CF); −139.21 (dd, 1F(F(b), A), $^2J_{FF} = 301$,$^2J_{HF} = 54$); −145.12 (m, 1F (A), CF) ppm.

*4-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahexan-2-yl)-2,2,-5-trimethyl-1,3-dioxolane (***34d**, 1% rel.). ^{1}H NMR ($CDCl_3$) δ, 4 diastereoisomers, A(50% rel.), B(35% rel.), C(10% rel.), D(5% rel.): 1.4–1.5 (m, 9H, 3 CH_3); 3.9 (m, 1H, C*H*CH_3); 4.5 (m, 1H, C*H*CF); 6.1–6.2 (dm, 1H, CHF, $^2J_{HF} = 55$) ppm. ^{19}F NMR ($CDCl_3$) δ: −81.6 (t, 3F, CF_3, $^3J_{FF} = 7$); −85.2 to −88.2 (2×m,2F(A,B),CF_2O); −130.0, −130.1 (2×m,2F(A,B), *CF_2*–CF_3); −133.5 (dd,1F(F(a),A), CHF_2, $^2J_{FF} = 303$,$^2J_{HF} = 55$); −135.7 (dd, 1F(F(a), B), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 55$); −136.3 (dd, 1F(F(b), B), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 55$); −138.3 (m,1F (B), CF); −139.2 (dd, 1F(F(b), A), $^2J_{FF} = 303$,$^2J_{HF} = 55$); −145.2 (m, 1F (A), CF) ppm.

5.2.13. Photo-induced reaction of methanol with perfluorononon-1-ene (25) (product 26)

For apparatus and procedure see Section 5.2.3 A mixture of methanol (6.4 g; 0.2 mol) and (**3**) (0.9 g; 2 mmol) was irradiated at r.t. for 3 h (conversion of **3**, 99%). After evaporation of methanol, crude product **26** was twice recrystallized from hexane to give pure **26** in a 90% yield (0.87 g), m.p. 80–81°C (lit. value [67], m.p. 80–81°C), purity ca. 99%.

1H,1H,3H-Perfluorodecan-1-ol (**26**). ^{19}F NMR ($CDCl_3$) δ: −81.3 (t, 3F, CF_3, $^3J_{FF} = 7$); −119.0 to −130.0 (7×m, 14F, 7 CF_2); −214.5 (dm, 1H, CHF, $^2J_{HF} = 55$) ppm.

5.3. General procedure for hydrolysis of fluoroalkylated dioxolanes 7–11 to the corresponding diols 12–16

Apparatus: The reactions were carried out in a round-bottomed flask (25 ml) equipped with a Dimroth reflux condenser, a drying tube (potassium hydroxide) and with a magnetic spinbar.

Reaction: A mixture of fluoroalkylated dioxolane (**7–11**, as a mixture of regioisomers if any; 0.02 mol), methanol (12.8 g, 0.40 mol) and conc. hydrochloric acid (0.5 g) was refluxed for 3 h while stirring (the complete conversion of the dioxolane was checked by ^{19}F NMR). Methanol was removed on a rotary evaporator and toluene (ca. 50 ml) was then added to the residue and the mixture was fractionated on a packed column (15 cm, Berle saddles, heated jacket). After distilling off toluene under atmospheric pressure, the residue was then distilled in vacuo and the product (**12–16**, as a mixture of regioisomers if any) was taken as the last fraction (for yields, purity, b.p. and m.p., see Table 2).

5.3.1. Hydrolysis of dioxolane 7 (isomeric products 12a–b)

For apparatus and procedure see Section 5.3 (for yields, purity and b.p., see Table).

Analysis (**12a**+**12b**): Found: C, 28.26; H, 3.04; F, 53.75%. $C_5H_6F_6O_2$ requires: C, 28.32; H, 2.85; F, 53.75%. M, 212.09.

*3,3,4,5,5,5-Hexafluoropentane-1,2-diol (***12a**), 98.8% rel.). ^{1}H NMR (DMSO-d_6) δ, 2 diastereoisomers, A (56% rel.), B (44% rel.): 3.52–3.71 (m, 2H, CH_2O); 3.90 (m, 1H, CHO); 5.00, 5.10 (2×t, 1H, CH_2O*H*, $^3J_{HH} = 6$); 5.81, 5.84 (2×dddq, 1H, CHF, $^2J_{HF} = 42$,$^3J_{HF} = 10$, 4 and 3); 6.20, 6.23 (2×d, 1H, CHO*H*, $^3J_{HH} = 6$) ppm.

^{19}F NMR (DMSO -d_6) δ: −72.70 (dq, 3F(A), CF_3, $^3J_{FF} = ^4J_{FF} = 11$,$^3J_{HF} = 8$); −73.00 (qi, 3F(B), CF_3, $^3J_{FF} = ^4J_{FF} = ^3J_{HF} = 11$); −121.02 (dddq, 1F(F(a), B), CF_2, $^2J_{FF} = 268$,$^4J_{FF} = 11$,$^3J_{FF} = 9$,$^3J_{HF} = 3$); −122.05 (dddq, 1F(F(b), B), CF_2, $^2J_{FF} = 268$,$^4J_{FF} = 11$,$^3J_{FF} = 5$,$^3J_{HF} = 4$); −123.41 (ddqi, 1F(F(a), A), CF_2, $^2J_{FF} = 268$,$^4J_{FF} = ^3J_{FF} = 11$,$^3J_{HF} = 3$); −126.20 (ddq, 1F(F(b), A), CF_2, $^2J_{FF} = 268$,$^4J_{FF} = 11$,$^3J_{HF} = 4$); −213.32 (dqi, 1F(A), CHF, $^2J_{HF} = 42$,$^3J_{FF} = 11$); −214.56 (dddq, 1F(B), CHF, $^2J_{HF} = 42$,$^3J_{FF} = 11$(q), 9 and 5) ppm.

*3-(Difluoromethyl)-3,4,4,4-tetrafluorobutane-1,2-diol (***12b**,1.2% rel.). ^{1}H NMR (DMSO-d_6) δ, 2 diastereoisomers, A (62% rel.), B (38% rel.): 3.50–3.70 (m, 2H, CH_2O); 4.11 (m, 1H, CHO); 5.00–5.10 (2×m, 1H, CH_2O*H*); 6.20, 6.21 (2×dt, 1H(A,B), CHF_2, $^2J_{HF} = 53$,$^3J_{HF} = 6$); 6.27, 6.31 (2×d, 1H, CHO*H*, $^3J_{HH} = 6$) ppm.

^{19}F NMR (DMSO -d_6) δ: −72.38, −72.67 (2×m, 3F, CF_3); −133.79 (dqi, 2F(A), CHF_2, $^2J_{HF} = 51$,$^3J_{FF} = ^4J_{FF} = 9$); −134.94 (dq, 2F(B), CHF_2, $^2J_{HF} = 52$,$^4J_{FF} = 9$); −191.54, −192.87 (2×m, 1F(B,A), CF) ppm.

5.3.2. Hydrolysis of dioxolane 8 (product 13a)

For apparatus and procedure see Section 5.3 (for yield, purity and m.p., see Table 2).

*3,3,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Docosafluorotridecane-1,2-diol (***13a**). Analysis: Found: C, 25.49; H, 1.05; F, 67.87%. $C_{13}H_6F_{22}O_2$ requires: C, 25.51; H, 0.99; F, 68.28%. M, 612.15.

^{1}H NMR (DMSO -d_6) δ, 2 diastereoisomers, A (53% rel.), B (47% rel.): 3.50–3.70 (m, 2H, CH_2O); 3.90 (m, 1H, CHO); 4.91, 5.02 (2×t, 1H, CH_2O*H*, $^3J_{HH} = 5$); 5.65 and 5.73 (2×dm, 1H(A,B), CHF, $^2J_{HF} = 42$); 6.10, 6.17 (2×d, 1H, CHO*H*, $^3J_{HH} = 6$) ppm.

^{19}F NMR (DMSO -d$_6$) δ: −81.10 (t, 3F, CF_3, $^3J_{FF} = 10$); −119.48 and −120.31 (2×dm, 1F(a), CF_2CH, $^2J_{FF} = 273$); −121.97 (m, 10F, $5CF_2$); −122.76, −126.36 (2×m, 6F, $3CF_2$); −124.95 and −125.87 (2×dm, 1F(b), CF_2CH, $^2J_{FF} = 273$); −212.88 and −214.23 (2×dm, 1F(A,B), CHF, $^2J_{HF} = 42$) ppm.

5.3.3. Hydrolysis of dioxolane **9** *(products* **14a–b***)*

For apparatus and procedure see Section 5.3 (for yield, purity and b.p., see Table 2).

Analysis (**14a**+**14b**): Found: C, 25.54; H, 1.94; F, 57.18%. $C_7H_6F_{10}O_3$ requires: C, 25.62; H, 1.84; F, 57.90%. M, 328.11.

*3,3,4,6,6,7,7,8,8,8-Decafluoro-5-oxaoctane-1,2-diol (***14a**, 93% rel.). ^{1}H NMR (DMSO-d$_6$) δ, 2 diastereoisomers, A (58% rel.), B (42% rel.): 3.52, 3.64 (2×m, 2H, CH_2O); 3.85 (m, 1H, CHO); 5.08 (bs, 1H, CH_2OH); 6.13, 6.19 (2×d, 1H, CHO*H*, $^3J_{HH} = 6.5$); 6.75 and 6.79 (2×dt, 1H(A,B), CHF, $^2J_{HF} = 53$,$^3J_{HF} = 6$) ppm.

^{19}F NMR (DMSO -d$_6$) δ: −80.50, −80.53 (2×t, 3F, CF_3, $^3J_{FF} = 7$); −83.91, −84.02 (2×dm, 1F(a), CF_2O, $^2J_{FF} = 147$); −85.04 (dm, 1F(b), CF_2O, $^2J_{FF} = 147$); −127.32 (dt, 1F(F(a), A), CF_2CH, 2JFF=265, 3JHF=6); −128.23 (dt, 2F(B), CF_2CH, $^3J_{FF} = 8$,$^3J_{HF} = 6$(t)); −128.87 (ddt, 1F(F(b), A), CF_2CH, $^2J_{FF} = 265$,$^3J_{HF} = 9$ and 6, $^3J_{FF} = 9$); −129.14 (m, 2F, CF_2CF_3); −145.40 and −148.30 (2× dqi, 1F(B,A), CHF, $^2J_{HF} = 53$,$^3J_{FF} = {}^4J_{FF} = 8$ or 9) ppm.

MS *m/z* (% rel. int.): 329(1.5, $(M+1)^+$); 311(1, $(M–OH)^+$); 288(2, $(M–2HF)^+$); 278(66, $(M–CF_2)^+$); 259(10, $(M–CF_3)^+$); 258(94, $(M–CHF_3)^+$); 248(10, $C_5HF_9O^+$); 229(5, $C_5H_4F_7O_2^+$); 169(45, $C_3F_7^+$); 119(12, $C_2F_5^+$); 100(11, $C_2F_4^+$); 93(26, $C_3F_3^+$); 92(70, $C_3H_5FO_2^+$); 91(18); 77(23, $C_3H_3F_2^+$); 75(20); 69(71, CF_3^+); 64(11, $C_2H_2F_2^+$); 61(100, $C_2H_5O_2^+$); 51(13, CHF_2^+).

*3-(Difluoromethyl)-3,5,5,6,6,7,7,7-octafluoro-4-oxaheptane-1,2-diol (***14b**, 7% rel. to **14a**). ^{1}H NMR (DMSO-d$_6$) δ, 2 diastereoisomers, A (50% rel.), B (50% rel.): 3.50–3.70 (m, 2H, CH_2O); 4.18 (m, 1H, CHO); 4.48 (bs, 1H, CH_2OH); 6.27, 6.36 (2×d, 1H, CHOH, $^3J_{HH} = 6.2$); 6.55 and 6.57 (2×dt, 1H(B,A), CHF_2, $^2J_{HF} = 52.5$,$^3J_{HF} = 3$) ppm.

^{19}F NMR (DMSO -d$_6$) δ: −80.37, −80.48 (2×t, 3F, CF_3, $^3J_{FF} = 7$); −83.90, −85.00 (2×m, 2F, CF_2O); −129.22 (m, 2F, CF_2CF_3); −136.05 (ddd, 1F(F(a), A), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 52.5$,$^3J_{FF} = 7$); −136.66 (dt, 2F(B), CHF_2, $^2J_{HF} = 52.5$,$^3J_{FF} = {}^4J_{HF} = 12$); −137.11 (ddt, 1F(F(b), A), CHF_2, $^2J_{FF} = 300$,$^2J_{HF} = 52.5$,$^3J_{FF} = {}^4J_{HF} = 7$); −138.62 and −142.29 (2×ddtt, 1F(B,A), CF, $^4J_{FF} = 19$,$^3J_{FF} = 7$,$^3J_{HF} = 6$ and 3) ppm.

5.3.4. Hydrolysis of dioxolane **10** *(products* **15a–b***)*

For apparatus and procedure see Section 5.3 (for yield, purity and b.p., see Table 2).

Analysis (**15a**+**15b**): Found: C, 24.51; H, 1.33; F, 61.06%. $C_{10}H_6F_{16}O_4$ requires: C, 24.31; H, 1.22; F, 61.52%. M, 494.13.

*3,3,4,6,6,7,9,9,10,10,11,11,11-Tridecafluoro-7-(trifluoromethyl)-5,8-dioxaundecane-1,2-diol (***15a**, 94% rel.). ^{1}H NMR (DMSO -d$_6$) δ, 4 diastereoisomers A,B (60% rel.), C,D (40% rel.): 3.51, 3.54, 3.61, 3.65 (4×q, 2H, CH_2O, $^2J_{HH} = {}^3J_{HH} = 5.6$); 3.82, 3.88 (2×m, 1H, CHO); 5.02, 5.03, 5.10, 5.11 (4×t, 1H, CH_2OH, $^3J_{HH} = 5.6$); 6.09, 6.11, 6.18, 6.19 (4×d, 1H, CHO*H*, $^3J_{HH} = 6.2$); 6.70 (ddd, 1H(C,D), CHF, $^2J_{HF} = 52$,$^3J_{HF} = 8.5$ and 4); 6.75 (dt, 1H(A,B), CHF, $^2J_{HF} = 52$,$^3J_{HF} = 6.5$) ppm.

^{19}F NMR (DMSO -d$_6$) δ: −79.80, −79.86, −79.87, −79.89 (4×d, 3F, CF_3CF, $^3J_{FF} = 8$); −81.02, −81.04, −81.05, −81.07 (4×t, 3F, CF_3CF_2, $^3J_{FF} = 7$); −81.07, −81.65 (2×dm, 2F, CF_2CF_2O, $^2J_{FF} = 140$); −83.37, −83.67 (2×dm, 2F, $CFCF_2O$, $^2J_{FF} = 142$); −127.51 (ddt, 1F(F(a), A,B), CF_2CH, $^2J_{FF} = 265$,$^3J_{HF} = 12$ and 6.5, $^3J_{FF} = 6.5$); −128.84 (dddd, 1F(F(a), C,D), CF_2CH, $^2J_{FF} = 266$,$^3J_{HF} = 17$ and 8.5, $^3J_{FF} = 6$); −129.42 (ddd, 1F(F(b), A,B), CF_2CH, $^2J_{FF} = 265$,$^3J_{HF} = 8$ and 6.5); −129.44, −129.46, −129.48, −129.49 (4×m, 2F, CF_2CF_3); −129.52 (ddd, 1F(F(b), C,D), CF_2CH, $^2J_{FF} = 266$,$^3J_{HF} = 6$ and 4); −144.96 (q, 1F, CF, $^3J_{FF} = 22$); −145.37 and −145.51 (2×dd, 1F(C,D), CHF, $^2J_{HF} = 52$,$^3J_{FF} = 6$); −147.88 and −148.21 (2×dd, 1F(A,B), CHF, $^2J_{HF} = 52$,$^3J_{FF} = 6.5$) ppm.

*3-(Difluoromethyl)-3,5,5,6,8,8,9,9,10,10,10-undecafluoro-6-(trifluoromethyl)-4,7-dioxa decane-1,2-diol (***15b**, 6% rel.). ^{1}H NMR (DMSO -d$_6$) δ, 4 diastereoisomers, A,B (50% rel.), C,D (50% rel.): 3.50–3.70 (m, 2H, CH_2O); 4.04, 4.22 (2×m, 1H, CHO); 4.84, 4.87 (2×t, 1H, CH_2OH, $^3J_{HH} = 4$); 6.25, 6.27, 6.35, 6.37 (4×d, 1H, CHO*H*, $^3J_{HH} = 5$); 6.48, 6.50, 6.51, 6.53 (4×dt, 1H, CHF_2, $^2J_{HF} = 51$,$^3J_{HF} = 2$) ppm.

^{19}F NMR (DMSO −d$_6$) δ: −79.80 (m, 3F, CF_3CF); −81.05 (m, 3F, CF_3CF_2); −81.00, −81.65 (2×m, 2F, CF_2CF_2O); −83.40, −83.70 (2×m, 2F, $CFCF_2O$); −129.45 (m, 2F, CF_2CF_3); −136.08 (dd, 1F(F(a), A,B), CHF_2, $^2J_{FF} = 302$,$^2J_{HF} = 51$); −136.75 and −137.51 (2×ddd, 2F(C,D), CHF_2, $^2J_{FF} = 301$,$^2J_{HF} = 52$,$^3J_{FF} = 11$); −137.87 (dm, 1F(F(b), A,B), CHF_2, $^2J_{FF} = 302$); −138.20, −142.74 (2×m, 1F, CFCH); −144.96 (m, 1F, CF) ppm.

5.3.5. Hydrolysis of fluoroalkyldixolane **11** *(products* **16a–b***)*

For apparatus and procedure see Section 5.3 (for yields, purity and b.p., see Table 2).

Analysis (**16a**+**16b**): Found: C, 22.42; H, 0.93; F, 60.03%. $C_{13}H_6F_{22}O_7$ requires: C, 22.56; H, 0.87; F, 60.39%. M, 692.15.

*3,3,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15,16,16,18,18,1-8-Docosafluoro-5,8,11,14,17-pen-taoxaoctadecane-1,2-diol (***16a**, 93% rel.). ^{1}H NMR (DMSO -d$_6$) δ, 2 diastereoisomers, A (56% rel.), B (44% rel.): 3.54, 3.57 (2×q, 1H(a), CH_2O, $^2J_{HH} = {}^3J_{HH} = 5.7$); 3.64, 3.67 (2×dt, 1H(b), CH_2O, $^2J_{HH} = 5.7$,$^3J_{HH} = 11$); 3.86, 3.90 (2×dq, 1H, CHO, $^3J_{HH} = 11$ and 6.4, $^3J_{HF} = 6.4$); 4.99, 5.07 (2×t, 1H, CH_2OH, $^3J_{HH} = 5.7$); 6.06, 6.16 (2×d, 1H, CHO*H*,

$^3J_{HH} = 6.4$); 6.48 (ddd, 1H(B), CHF, $^2J_{HF} = 52$,$^3J_{HF} = 9$ and 4); 6.55 (dt, 1H(A), CHF, $^2J_{HF} = 53$,$^3J_{HF} = 6.5$) ppm.

^{19}F NMR (DMSO -d_6) δ: −56.70, −56.73 (2×t, 3F, CF_3O, $^4J_{FF} = 9$); −88.78 (m, 2F, CF_2O); −89.44, −89.62, −89.65 (3×m, 10F, $5CF_2O$); −89.81, −90.28 (2×m, 2F, CF_2O); −91.68, −91.71 (2×q, 2F, CF_2O, $^4J_{FF} = 9$); −127.64 (ddd, 1F(F(a), A), CF_2CH, $^2J_{FF} = 266$,$^3J_{HF} = 6.4$,$^3J_{FF} = 5$); −129.71 (ddd, 1F(F(a), B), CF_2CH, $^2J_{FF} = 268$,$^3J_{HF} = 6.4$,$^3J_{FF} = 17$); −130.08 (ddt, 1F(F(b), A), CF_2CH, $^2J_{FF} = 266$,$^3J_{HF} = 6.4$(t), $^3J_{FF} = 5$); −130.24 (ddt, 1F(F(b), B), CF_2CH, $^2J_{FF} = 268$,$^3J_{HF} = 6.4$(t),$^3J_{FF} = 13$); −145.78 (ddd, 1F(B), CHF, $^2J_{HF} = 51$,$^3J_{FF} = 17$ and 13); −148.38 (dt, 1F(A), CHF, $^2J_{HF} = 51$,$^3J_{FF} = 5$(t)) ppm.

MS *m/z* (% rel. int.): 652(1, $(M–2HF)^+$); 642(16, $(M–CF_2)^+$); 622(29, $(M–CHF_3)^+$); 185(6, $C_3F_7O^+$); 135(11, $C_2F_5O^+$); 123(26, $C_4H_5F_2O_2^+$); 119(100, $C_2F_5^+$); 100(33, $C_2F_4^+$); 97(16, $C_2F_3O^+$); 93(23, $C_3F_3^+$); 92(45, $C_3H_5FO_2^+$); 77(33, $C_3H_3F_2^+$); 69(83, CF_3^+); 61(92, $C_2H_5O_2^+$); 59(6, $C_2H_3O_2^+$); 51(7, CHF_2^+).

*3-(Difluoromethyl)-3,5,5,6,6,8,8,9,9,11,11,12,12,14,14,-15,15,17,17,17-eicosafluoro-4,7,10, 13,16-pentaoxaheptadecane-1,2-diol (***16b**, 7% rel.). ^{1}H NMR (DMSO -d_6) δ, 2 diastereoisomers, A (50% rel.), B (50% rel.): 3.50–3.70 (m, 2H, CH_2O); 4.20, 4.25 (2×m, 1H, CHO); 5.02, 5.05 (2×t, 1H, CH_2OH, $^3J_{HH} = 4$); 6.20, 6.32 (2×d, 1H, $CHOH$, $^3J_{HH} = 6.3$); 6.41 (dt, 1H, CHF_2, $^2J_{HF} = 52$,$^3J_{HF} = 4$) ppm.

^{19}F NMR (DMSO -d_6) δ: −56.75 (m, 3F, CF_3O); −88.80 (m, 2F, CF_2O); −89.55 (m, 10F, $5CF_2O$); −89.80, −90.30 (2×m, 2F, CF_2O); −91.73 (m, 2F, CF_2O); −136.75 and −137.08 (2×ddd, 1F(a), CHF_2, $^2J_{FF} = 301$, $^2J_{HF} = 52$, $^3J_{FF} = 10$); −138.11 and −138.42 (2×dd, 1F(b), CHF_2, $^2J_{FF} = 301$,$^2J_{HF} = 52$); −138.27, −143.81 (2×m, 1F, CF) ppm.

5.4. Bis-methacrylates of fluoroalkylated diols **12–16** (products **20–24**)

5.4.1. General procedure for the preparation of bis-methacrylates **20–24**

The reaction was carried out in a round-bottomed flask (25 ml) equipped with a Dimroth reflux condenser connected to the atmosphere through a drying tube (potassium hydroxide) and with a magnetic spinbar, (for apparatus see Section 5.3, flask 100 ml).

Reaction: a mixture of methacryloyl chloride (6.28 g, 60 mmol), fluoroalkylated diol (**12–16**, as a mixture of regioisomers if any; 10 mmol), triethylamine (7.1 g, 70 mmol), diethyl ether (60 ml) and a stabilizer (di-tert.octylpyrocatechol, 33.5 mg, 0.1 mmol) was stirred at r.t. for 2 h (the complete conversion of a diol was checked by ^{19}F NMR). Methanol (1.3 g, 40 mmol) was then added and the mixture was stirred for an additional hour. Water (2×100 ml) was then added slowly to the mixture, the ethereal layer was separated, the water layer was extracted with ether (40 ml), ethereal solutions were combined and dried with magnesium sulfate. After evaporation of diethyl ether (rotary evaporator), triethylamine and methyl methacrylate were removed in vacuo (water pump) and the residue was distilled under high vacuum pump to give pure product (for yields, purity of products **20–24**, b.p. and m.p., see Table 2).

5.4.2. Reaction of fluoroalkyldiol **12** (products **20a–b**)

For apparatus and procedure see Section 5.4.1 (for yields, purity and b.p., see Table 2).

Analysis (**20a**+**20b**): Found: C, 45.32; H, 4.29; F, 33.31%. $C_{13}H_{14}F_6O_4$ requires: C, 44.84; H, 4.05; F, 32.73%. M, 348.24.

3,3,4,5,5,5-Hexafluoropentane-1,2-diyl bis-methacrylate (**20a**, 98.8% rel.).

^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (56% rel.), B (44% rel.): 1.91, 1.93 (2×s, 6H, 2 CH_3); 4.43 (t, 1H(H(a), A), CH_2O, $^2J_{HH} = ^3J_{HH} = 12.2$); 4.44 (d, 1H(H(a), B), CH_2O, $^2J_{HH} = 12.2$); 4.59, 4.68 (2×dd, 1H(H(b), B, A), CH_2O, $^2J_{HH} = 12.2$,$^3J_{HH} = 3.8$); 4.89, 5.03 (2×dddq, 1H(A, B), CHF, $^2J_{HF} = 43.5$,$^3J_{HF} = 20$, 6(q) and 1.5 or 15(B)); 5.61, 5.73 (2×m, 2H(E), 2 CH_2=); 5.70 (m, 1H, CH); 6.10, 6.21 (2×m, 2H(Z), 2 CH_2=) ppm.

^{19}F NMR ($CDCl_3$) δ: −74.24 (dq, 3F(A), CF_3, $^3J_{FF} = ^4J_{FF} = 11$,$^3J_{HF} = 6$); −74.50 (ddt, 3F(B), CF_3, $^3J_{FF} = ^4J_{FF} = 11$,$^4J_{FF} = 10$,$^3J_{HF} = 6$); −116.56 (dddqi, 1F(F(a), B), CF_2, $^2J_{FF} = 272$,$^3J_{HF} = 15$ and 6,$^3J_{FF} = ^4J_{FF} = 11$(qi)); −121.48 (dddqi, 1F(F(a), A), CF_2, $^2J_{FF} = 269$,$^3J_{HF} = 20$ and 2, $^3J_{FF} = ^4J_{FF} = 11$(qi)); −121.65 (dddqi, 1F(F(b), B), CF_2, $^2J_{FF} = 272$,$^3J_{HF} = 20$ and 8, $^3J_{FF} = ^4J_{FF} = 10$(qi)); −122.00 (dddqi, 1F(F(b), A), CF_2, $^2J_{FF} = 269$,$^3J_{HF} = 23$ and 1.5, $^3J_{FF} = ^4J_{FF} = 11$(qi)); −212.19 (dsex, 1F(A), CHF, $^2J_{HF} = 43.5$,$^3J_{FF} = 11$ (sex)); −212.90 (ddqi, 1F(B), CHF, $^2J_{HF} = 43.5$,$^3J_{FF} = 11$ (qi) and 10) ppm.

*3-(Difluoromethyl)-3,4,4,4-tetrafluorobutane-1,2-diyl bis-methacrylate (***20b**, 1.2% rel. to **20a**). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (62% rel.), B (38% rel.): 1.95 (m, 6H, 2 CH_3); 4.40–4.70 (m, 2H, CH_2O); 5.61, 5.73 (2×m, 2H(E), 2 CH_2=); 5.70 (m, 1H, CH); 6.10, 6.20 (2×m, 2H(Z), CH_2=); 6.21, 6.25 (2×t, 1H(A, B), CHF_2, $^2J_{HF} = 52$ and 53) ppm.

^{19}F NMR ($CDCl_3$) δ: −74.01 (dq, 3F(A), CF_3, $^3J_{FF} = ^4J_{FF} = 8$,$^4J_{HF} = 5$); −74.19 (d, 3F(B), CF_3, $^4J_{HF} = 3$); −132.03, −133.42 (2×ddqi, 2F(A), CHF_2, $^2J_{FF} = 305$, $^2J_{HF} = 52$,$^3J_{FF} = ^4J_{FF} = 8$(qi)); −132.08, −133.83 (2×ddm, 2F(B), CHF_2, $^2J_{FF} = 304$,$^2J_{HF} = 53$); −188.73 (m, 1F(B), CF); −189.70 (sex, 1F(A), CF, $^3J_{FF} = 8$) ppm.

5.4.3. Reaction of fluoroalkyldiol **13a**

For apparatus and procedure see Section 5.4.1 (for yield, purity and m.p., see Table 2).

*3,3,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-Docosafluorotridecane-1,2-diyl bis-methacrylate (***21a**). Ana-

lysis: Found: C, 33.86; H, 1.95; F, 56.12%. $C_{21}H_{14}F_{22}O_4$ requires: C, 33.71; H, 1.89; F, 55.85%. M, 748.30.

^{1}H NMR (acetone $-d_6$) δ, 2 diastereoisomers, A (53% rel.), B (47% rel.): 1.91, 1.92 (2×s, 6H, 2 CH_3); 4.31, 4.33 (2×dm, 2H, CH_2O, $^2J_{HH} = 6$); 5.70, 5.75 (2×dm, 1H, CHF, $^2J_{HF} = 46$); 5.60, 5.72 (2×m, 2H(E), 2 CH_2=); 5.82 (m, 1H, CH); 6.10, 6.22 (2×m, 2H(Z), 2 CH_2=) ppm.

^{19}F NMR (acetone $-d_6$) δ: −81.36 (t, 3F, CF_3, $^3J_{FF} = 10$); −122.10 (m, 10F, $5CF_2$); −117.57 and −122.30 (2×dm, 1F(a), CF_2CH, $^2J_{FF} = 273$); −123.00 and −129.81 (2×dm, 1F(b), CF_2CH, $^2J_{FF} = 273$); −123.08, −126.49 (2×m, 6F, $3CF_2$); −212.44 and −217.47 (2×dm, 1F(A,B), CHF, $^2J_{HF} = 46$) ppm.

5.4.4. Reaction of fluoroalkyldiol **14** *(products* **22a**–**b***)*

For apparatus and procedure see Section 5.4.1 (for yield, purity and b.p., see Table 2).

Analysis (**22a**+**22b**): Found: C, 39.10; H, 3.14; F, 41.22%. $C_{15}H_{14}F_{10}O_5$ requires: C, 38.81; H, 3.04; F, 40.92%. M, 464.26.

*3,3,4,6,6,7,7,8,8,8-Decafluoro-5-oxaoctane-1,2-diyl bis-methacrylate (***22a**,93% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (58% rel.), B (42% rel.): 1.92, 1.96, 1.97 (3×m, 6H, 2 CH_3); 4.41 (dd, 1H(H(a), A), CH_2O, $^2J_{HH} = 12.8$, $^3J_{HH} = 15$); 4.42 (d, 1H(H(a), B), CH_2O, $^2J_{HH} = 12.8$); 4.62, 4.65 (2×dd, 1H(H(b), B, A), CH_2O, $^2J_{HH} = 12.8$,$^3J_{HH} = 3.6$); 5.61, 5.71 (2×m, 2H(E), 2 CH_2=); 5.68 (m, 1H, CH); 6.03 (dd, 1H(B), CHF, $^2J_{HF} = 54$, $^3J_{HF} = 6.3$); 6.07 (ddd, 1H(A), CHF, $^2J_{HF} = 54$, $^3J_{HF} = 5.9$ and 4.6); 6.10, 6.18, 6.20 (3×m, 2H(Z), 2 CH_2=) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.76 (t, 3F, CF_3, $^3J_{FF} = 7$); −85.43, −87.78 (2×ddm, 2F(A), CF_2O, $^2J_{FF} = 146$, $^4J_{FF} = 8$); −85.45, −87.48 (2×ddm, 2F(B), CF_2O, $^2J_{FF} = 146$, $^4J_{FF} = 4$); −122.28 (ddd, 10F(F(a), A), CF_2CH, $^2J_{FF} = 278$, $^3J_{HF} = 13$ and 6); −123.41 (ddd, 1F(F(a), B), CF_2CH, $^2J_{FF} = 279$, $^3J_{HF} = 15$ and 6); −123.83 (dd, 1F(F(b), B), CF_2CH, $^2J_{FF} = 279$, $^3J_{HF} = 15$); −125.15 (dddd, 1F(F(b), A), CF_2CH, $^2J_{FF} = 278$, $^3J_{HF} = 13$ and 4.6, $^3J_{FF} = 8$); −130.12 (m, 2F, CF_2CF_3); −143.40 (dd, 1F(B), CHF, $^2J_{HF} = 54$, $^4J_{FF(b)} = 4$); −146.84 (dq, 1F(A), CHF, $^2J_{HF} = 54$, $^3J_{FF(b)} = {}^4J_{FF} = 8$(q)) ppm.

*3-(Difluoromethyl)-3,5,5,6,6,7,7,7-octafluoro-4-oxaheptane-1,2-diyl bis-methacrylate (***22b**, 7% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (50% rel.), B (50% rel.): 1.96 (m, 6H, 2 CH_3); 4.40–4.70 (m, 2H, CH_2O); 5.61, 5.71 (2×m, 2H(E), 2 CH_2=); 5.68 (m, 1H, CH); 6.03, 6.07 (2×dt, 1H, CHF_2, $^2J_{HF} = 53$(t), $^3J_{HF} = 9$); 6.10, 6.20 (2×m, 2H(Z), CH_2=) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.64 (t, 3F, CF_3, $^3J_{FF} = 7$); −85.40 to −87.80 (4×dm, 2F, CF_2O, $^2J_{FF} = 146$); −130.57 (m, 2F, CF_2); −133.22, −133.60 (2×ddd, 2F(A), CHF_2, $^2J_{FF} = 306$, $^2J_{HF} = 53$, $^3J_{FF} = 9$); −133.61 (dd, 2F(B), CHF_2, $^2J_{HF} = 53$, $^3J_{FF} = 9$); −135.29, −136.63 (2×sep, 1F, CF, $^3J_{FF} = {}^3J_{HF} = {}^4J_{FF} = 9$) ppm.

5.4.5. Reaction of fluoroalkyldiol **15** *(products* **23a**–**b***)*

For apparatus and procedure see Section 5.4.1 (for yields, purity and b.p., see Table 2).

Analysis (**23a**+**23b**): Found: C, 34.87; H, 2.41; F, 47.98%. $C_{18}H_{14}F_{16}O_6$ requires: C, 34.30; H, 2.24; F, 48.23%. M, 630.28.

*3,3,4,6,6,7,9,9,10,10,11,11,11-Tridecafluoro-7-(trifluoromethyl)-5,8-dioxaundecane-1,2-diyl bis-methacrylate (***23a**, 94% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (28% rel.), B (31% rel.), C (20% rel.), D (21% rel.): 1.92, 1.96, 1.97 (3×s, 6H, 2 CH_3); 4.38, 4.43 (2×dd, 1H(H(a), C,D and A,B), CH_2O, $^2J_{HH} = 12.3$, $^3J_{HH} = 7$(A,B) and 2(C,D)); 4.61, 4.66 (2×dd, 1H(H(b), A,B and C,D), CH_2O, $^2J_{HH} = 12.3$, $^3J_{HH} = 3.7$); 5.61, 5.70 (2×m, 2H(E), 2 CH_2=); 5.68 (m, 1H, CH); 6.01 (ddd, 1H(C,D), CHF, $^2J_{HF} = 53$, $^3J_{HF} = 7$ and 3.2); 6.07 (dt, 1H(A,B), CHF, $^2J_{HF} = 54$, $^3J_{HF} = 5.4$(t)); 6.10, 6.18, 6.19 (3×m, 2H(Z), 2 CH_2=) ppm.

^{19}F NMR ($CDCl_3$) δ: −80.46, −80.48 (2×m, 3F, CF_3CF); −81.33, −81.84 (2×t, 3F, CF_3, $^3J_{FF} = 7$); −81.93, −82.33 (2×dm, 2F, CF_2O, $^2J_{FF} = 143$); −84.09, −84.38, −84.47 and −85.95, −86.16, −86.33 (6×dm, 2F(A, C,D, B), CFCF_2O, $^2J_{FF} = 143$); −122.38, −122.65 (2×ddt, 1F(F(a), B, A), CF_2CH, $^2J_{FF} = 278$, $^3J_{FF} = 5$, $^3J_{HF} = 7$ and 5); −124.11, −124.15 (2×ddd, 1F(F(a), C, D), CF_2CH, $^2J_{FF} = 280$, $^3J_{HF} = 16$ and 3.2); −124.60, −124.64 (2×ddt, 1F(F(b), C, D), CF_2CH, $^2J_{FF} = 280$, $^3J_{FF} = 7$, $^3J_{HF} = 13$ and 7); −125.72, −125.85 (2×dddd, 1F(F(b), A, B), CF_2CH, $^2J_{FF} = 278$, $^3J_{FF} = 9$, $^3J_{HF} = 13$ and 5); −130.10, −130.14 (2×m, 2F, CF_2); −143.63 (ddt, 1F(C, D), CHF, $^2J_{HF} = 53$, $^3J_{FF(b)} = 7$, $^4J_{FF} = 5$(t)); −145.37, −145.43, −145.53 (3×t, 1F(B, C,D, A), CF, $^3J_{FF} = 21$); −146.38, −146.83 (2×ddq, 1F(B, A), CHF, $^2J_{HF} = 54$, $^3J_{FF} = 9$ and 5, $^4J_{FF} = 5$) ppm.

*3-(Difluoromethyl)-3,5,5,6,8,8,9,9,10,10,10-undecafluoro-6-(trifluoromethyl)-4,7-dioxa decane-1,2-diyl bis-methacrylate (***23b**, 6% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (25% rel.), B (25% rel.), C, D (50% rel.): 1.96 (m, 6H, 2 CH_3); 4.35–4.70 (m, 2H, CH_2O); 5.61, 5.70 (2×m, 2H(E), 2 CH_2=); 5.68 (m, 1H, CH); 6.10, 6.20 (2×m, 2H(Z), CH_2=); 6.17, 6.22 (2×dt, 1H(A,B and C,D), CHF_2, $^2J_{HF} = 53$(t), $^3J_{HF} = 13$ and 10) ppm.

$_{19}$F NMR ($CDCl_3$) δ: −80.32, −80.34 (2×m, 3F, CF_3CF); −81.81 (m, 3F, CF_3); −81.90, −82.30 (2×dm, 2F, CF_2O, $^2J_{FF} = 143$); −84.00 to −86.50 (3×dm, 2F, CFCF_2O, $^2J_{FF} = 143$); −130.08 (m, 2F, CF_2); −133.28, −133.35 and −133.71, −133.78 (4×ddd, 2F(A, B), CHF_2, $^2J_{FF} = 305$, $^2J_{HF} = 53$, $^3J_{FF} = 22$ and 15); −133.53 (dd, 2F(C, D), CHF_2, $^2J_{HF} = 53$, $^3J_{FF} = 19$); −135.14, −135.33 (2×m, 1F(A, B), CFCH, ^{3}JFF = 22(d) and 15(d)); −136.47 (m, 1F(C,D), CFCH, $^3J_{FF} = 19$(t), $^4J_{FF} = 7$(t)); −145.20 (m, 1F, CF) ppm.

5.4.6. Reaction of fluoroalkyldiol **16** *(products* **24a**–**b***)*

For apparatus and procedure see Section 5.4.1 (for yields, purity and b.p., see Table 2).

*3,3,4,6,6,7,7,9,9,10,10,12,12,13,13,15,15,16,16,18,18,1-8-Docosafluoro-5,8,11,14,17-pentaoxaoctadecane-1,2-diyl bis-methacrylate (***24a**, 93% rel.). Analysis (**24a**+**24b**): Found: C, 31.18; H, 1.91; F, 49.70%. $C_{21}H_{14}F_{22}O_9$ requires: C, 30.45; H, 1.70; F, 50.46%. M, 828.30.

^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (56% rel.), B (44% rel.): 1.92, 1.95, 1.96 (3×m, 6H, 2 CH_3); 4.40, 4.42 and 4.60, 4.65 (4×dd, 1H(B, A), CH_2O, $^2J_{HH} = 12.2$, $^3J_{HH} = 9.4$ and 3.6); 5.60, 5.69, 5.70 (3×m, 2H(E), 2 CH_2=); 5.68 (m, 1H, CHO); 5.96, 6.00 (2×dt, 1H(A, B), CHF, $^2J_{HF} = 53.5$, $^3J_{HF} = 5$(t)); 6.10, 6.17, 6.19 (3×m, 2H(Z), 2 CH_2=) ppm.

^{19}F NMR ($CDCl_3$) δ: −55.97 (t, 3F, CF_3O, $^4J_{FF} = 9$); −88.62, −88.72 (2×m, 2F, CF_2O); −89.28 (m, 10F, 5 CF_2O); −90.08, −90.17 and −91.94, −92.11 (4×dd, 2F, CF_2O, $^2J_{FF} = 143$, $^3J_{FF} = 10$ and 5); −91.30 (q, 2F, CF_2OCF_3, $^4J_{FF} = 9$); −122.12 (dq, 1F(F(a), A), CF_2CH, $^2J_{FF} = 278$, $^3J_{FF}$=$^3J_{HF} = 5$); −124.07 (dt, 2F(B), CF_2CH, $^3J_{FF} = 6$, $^3J_{HF} = 12$ and 6); −125.68 (ddm, 1F(F(b), A), CF_2CH, $^2J_{FF} = 278$, $^3J_{FF} = 8$); −143.47, −146.78 (2×ddq, 1F(B, A), CHF, $^2J_{HF} = 53.5$, $^3J_{FF}$=$^4J_{FF} = 7$(q), $^3J_{FF} = 5$) ppm.

*3-(Difluoromethyl)-3,5,5,6,6,8,8,9,9,11,11,12,12,14,14,-15,15,17,17,17-eicosafluoro-4,7,10, 13,16-pentaoxaheptadecane-1,2-diyl bis-methacrylate (***24b**, 7% rel.). ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (50% rel.), B (50% rel.): 1.94 (m, 6H, 2 CH_3); 4.40–4.70 (m, 2H, CH_2O); 5.60, 5.70 (2×m, 2H(E), 2 CH_2=); 5.68 (m, 1H, CH); 6.09, 6.12 (2×dt, 1H, CHF_2, $^2J_{HF} = 53$(t), $^3J_{HF} = 10$); 6.10, 6.20 (2×m, 2H(Z), CH_2=) ppm.

^{19}F NMR ($CDCl_3$) δ: −56.00 (t, 3F, CF_3O, $^4J_{FF} = 9$); −88.60 to −92.20 (m, 16F, 8 CF_2O); −133.33, −133.49 (2×ddd, 1F(a), CHF_2, $^2J_{FF} = 300$, $^2J_{HF} = 53$, $^3J_{FF} = 9$); −134.05 (dd, 1F(b), CHF_2, $^2J_{FF} = 300$, $^2J_{HF} = 53$); −135.32, −137.13 (2×m, 1F, CF, $^3J_{FF} = 19$(t), $^4J_{FF} = 4$(t)) ppm.

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References

[1] O. Paleta, V. Církva, Z. Budková, S. Böhm, J. Fluorine Chem. 86 (1997) 155.
[2] B. Boutevin, J.J. Robin, Adv. Polym. Sci. 102 (1992) 105.
[3] F.D. Trischler, J. Hollander Jr., , J. Polym. Sci., Part A-1, Polym. Chem. 7 (1969) 971.
[4] P. Johncock, S.P. Barnett, P.A. Rickard, J. Polym. Sci., Part A-1, Polym. Chem. 24 (1969) 971.
[5] A.E. Mera, J.R. Griffith, J. Fluorine Chem. 69 (1994) 151.
[6] R.A. Mitsch, J.L. Zollinger, US Patent 3 972 856 (1976).
[7] R.A. Mitsch, J.L. Zollinger, Ger. Offen. 2 011 774 (1970).
[8] R.A. Mitsch, J.L. Zollinger, Chem. Abs. 74 (1971) 13999.
[9] J.G. Orear, J.R. Griffith, S.A. Reines, J. Paint. Technol. 552 (1971) 873.
[10] J. Hollander Jr., F.D. Trischler, J. Am. Chem. Soc., Div. Polym. Chem. 8 (1967) 491.
[11] M.F. Refojo, in: M. Ruben, M. Guillon (Eds.), Contact Lens Practise, Chapter 2, Chapman and Hall, London, 1994.
[12] F. Yamamoto, T. Suzuki, M. Ikari, S. Saito, A. Ohmori, T. Yasuhara, Eur. Patent Appl. EP 213 412 (1987).
[13] F. Yamamoto, T. Suzuki, M. Ikari, S. Saito, A. Ohmori, T. Yasuhara, Chem. Abs. 108 (1988) 26994.
[14] T. Hogi, N. Osawa, Jpn. Kokai Tokkyo Koho JP 0 497 117 (1992).
[15] T. Hogi, N. Osawa, Chem. Abs. 117 (1992) 118550.
[16] J.D. Park, F.E. Rogers, J.R. Lacher, J. Org. Chem. 26 (1961) 2089.
[17] K. von Werner, Ger. Offen. DE 3 525 494 (1987).
[18] K. von Werner, Chem. Abs. 106 (1987) 155891.
[19] M. Yoshizumi, A. Nakamura, Y. Yamashita, K. Kaneko, Jpn. Kokai Tokkyo Koho JP 1 305 045 (1989).
[20] M. Yoshizumi, A. Nakamura, Y. Yamashita, K. Kaneko, Chem. Abs. 112 (1990) 197619.
[21] Y. Animoto, S. Daimon, M. Okamoto, Jpn. Patent 7 884 909 (1978).
[22] Y. Animoto, S. Daimon, M. Okamoto, Chem. Abs. 89 (1978) 214891.
[23] W.A. Herrmann, S.J. Eder, W. Scherer, Angew. Chem. 104 (1992) 1371.
[24] W.A. Herrmann, S.J. Eder, Chem. Ber. 126 (1993) 31.
[25] E.T. McBee, T.M. Burton, J. Am. Chem. Soc. 74 (1952) 3022.
[26] D.A. Rausch, A.M. Lovelace, L.E. Coleman, J. Org. Chem. 21 (1956) 1328.
[27] P.V. Ramachandran, B. Gong, H.C. Brown, J. Org. Chem. 60 (1995) 41.
[28] T. Kubota, H. Shirakura, T. Tanaka, J. Fluorine Chem. 54 (1991) 286.
[29] A. Ayari, S. Szönyi, E. Rouvier, A. Cambon, J. Fluorine Chem. 50 (1990) 67.
[30] M. Tanaka, J. Agou, M. Kuwahara, J. Sakashita, T. Shimoda, M. Sudou, Eur. Patent Appl. EP297 822 (1989).
[31] M. Tanaka, J. Agou, M. Kuwahara, J. Sakashita, T. Shimoda, M. Sudou, Chem. Abs. 111 (1989) 135008.
[32] B. Maillard, M. Cazaux, R. Lalande, Bull. Soc. Chim. Fr. (1971) 467.
[33] B. Maillard, M. Cazaux, R. Lalande, Bull. Soc. Chim. Fr. (1973) 1368.
[34] V. Dědek, I. Hemer, Collect. Czech. Chem. Commun. 50 (1985) 2743.
[35] O. Paleta, V. Církva, J. Kvíčala, Czech. Patent 282 756 (1997).
[36] O. Paleta, Z. Budková, J. Kvíčala, H.J. Timpe, Collect. Czech. Chem. Commun. 60 (1995) 636.
[37] A. Gilbert, J. Baggot, Essentials of Molecular Photochemistry, Blackwell, London, 1991, p. 168 and 229.
[38] J. Kvíčala, B. Dolenský, O. Paleta, J. Fluorine Chem. 85 (1997) 117.
[39] O. Paleta, L. Štěpán, A. Danda, J. Kvíčala, V. Dědek, J. Fluorine Chem. 45 (1989) 331.
[40] A. Ayari, S. Szönyi, E. Rouvier, A. Cambon, Bull. Soc. Chim. Fr. 129 (1992) 315.
[41] K. Ishihara, H. Kurihara, H. Yamamoto, J. Org. Chem. 58 (1993) 3791.
[42] T. Cohen, M. Dughi, V.A. Notaro, G. Pinkus, J. Org. Chem. 27 (1962) 814.
[43] M. Hirano, T. Morimoto, J. Chem. Soc., Perkin Trans. 2 (1984) 1033.
[44] L.J. Sauty, S. Azer, R.A. McClelland, J. Am. Chem. Soc. 110 (1988) 2909.
[45] R.A. McClelland, N.E. Seaman, D. Cramm, J. Am. Chem. Soc. 106 (1984) 4511.
[46] J.M. Tedder, J.C. Walton, Acc. Chem. Res. 9 (1976) 183.
[47] B. Giese, Angew. Chem., Int. Ed. Engl. 16 (1977) 125.
[48] B. Giese, Angew. Chem., Int. Ed. Engl. 22 (1983) 753.

[49] J.M. Tedder, J.C. Walton, Tetrahedron 36 (1980) 701.
[50] J.M. Tedder, J.C. Walton, Tetrahedron 38 (1982) 313.
[51] J.M. Tedder, Angew. Chem. 94 (1982) 433.
[52] J.M. Tedder, Angew. Chem., Int. Ed. Engl. 22 (1982) 401.
[53] C. Walling, Tetrahedron 41 (1985) 3887.
[54] B. Giese, in: M. Regitz, B. Giese (Eds.), Methoden der Organischen Chemie (Houben-Weyl), vol. E19a, Part 1, Thieme, Stuttgart, 1989, p. 1.
[55] T.N. Abroskina, A.D. Sorokin, R.V. Kudryavcev, I.A. Cheburkov, Izv. Akad. Nauk. USSR, Ser. Khim. 23 (1974) 1823.
[56] J. Courtieu, J. Jullien, N.T. Lai, P. Gonord, S.K. Kan, Tetrahedron 32 (1976) 669.
[57] W. Dmowski, H. Voelbnagel-Neugebauer, J. Fluorine Chem. 81 (1981) 223.
[58] R.D. Chambers, B. Grievson, J. Chem. Soc., Perkin Trans. 1 (1985) 2215.
[59] V.P. Šendrik, O. Paleta, V. Dědek, Collect. Czech. Chem. Commun. 39 (1974) 1061.
[60] V.P. Šendrik, O. Paleta, V. Dědek, Collect. Czech. Chem. Commun. 42 (1977) 2530.
[61] D.C. Nonhebel, J.C. Walton, Free-Radical Chemistry, Chapter 8, Cambridge University Press, Cambridge, 1974.
[62] O. Paleta, V. Církva, J. Kvíčala, J. Fluorine Chem. 80 (1996) 125.
[63] V. Církva, R. Polák, O. Paleta, J. Fluorine Chem. 80 (1996) 135.
[64] O. Paleta, V. Dědek, S. Neuenfeld, H.-J. Timpe, Czech. Patent 268 247 (1989).
[65] O. Paleta, V. Dědek, S. Neuenfeld, H.-J. Timpe, Chem. Abs. 114 (1991) 206556.
[66] R.N. Haszeldine, R. Rowland, R.P. Sheppard, A.E. Tipping, J. Fluorine Chem. 28 (1985) 291.
[67] J.D. LaZerte, R.J. Koshar, J. Am. Chem. Soc. 77 (1955) 910.
[68] F.G. Bordwell, X.-M. Zhang, M.S. Alnajjar, J. Am. Chem. Soc. 114 (1992) 7623.
[69] J. Dauben, B. Löken, J. Am. Chem. Soc. 76 (1954) 1362.
[70] B.S. Furniss, A.J. Hammford, P.W.G. Smith, A.R. Tatchell, Vogel's Textbook of Practical Organic Chemistry, 5th ed., Chapter 6, Wiley, New York, 1991.
[71] J. Kvíčala, O. Paleta, V. Dědek, J. Fluorine Chem. 47 (1990) 441.