Journal of Fluorine Chemistry 132 (2011) 760–766

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis of bi- and tetracatenar highly fluorinated compounds for grafting on silicone materials

Stéphane Malfait [a], Stéphane Gérard [a], Richard Plantier-Royon [a], Gérard Mignani [b,1], Charles Portella [a,*]

[a] Institut de Chimie Moléculaire de Reims, Université de Reims-Champagne-Ardenne – CNRS (UMR 6229), UFR Sciences, BP 1039, 51687 Reims Cedex 2, France
[b] Rhodia Usines silicones, 55 rue des frères Perret, BP 22-69191, Saint-Fons Cedex, France[2]

ARTICLE INFO

Article history:
Received 23 March 2011
Received in revised form 13 May 2011
Accepted 17 May 2011
Available online 25 May 2011

Dedicated to Alain Tressaud, in honor of his ACS award, and for his great contribution to the development and promotion of fluorine chemistry.

Keywords:
Epichlorhydrin
Fluorine
Highly fluorinated compounds
Poly(perfluoroalkylated) diethers
Poly(perfluoroalkylated) diesters
Hydrosilylation
Functionalized silicones

ABSTRACT

A series of highly fluorinated compounds bearing two or four perfluoroalkyl (R_F) chains, with a flexible or rigid core have been synthesized. Radical additions, nucleophilic addition or condensation reactions were implemented for these synthesis, using perfluoroalkylated iodides and alcohols and various type of substrates: bis(allylic) derivatives, epichlorhydrin, diacid derivatives. All compounds contain an unsaturated moiety (vinyl, allyl or internal double bond) to be grafted on silicone materials by a catalyzed hydrosilylation reaction.

1. Introduction

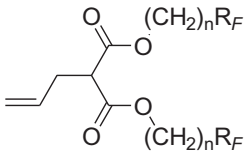
Due to the strong electronegativity, the small size and low polarisability of fluorine atom, perfluoroalkyl (R_F) moieties exhibit properties of great interest (chemical and thermal stability, low surface energy, self organization ability) for a wide variety of applications [1]. A property of particular interest is the possibility to induce both water- and oil-repellency to materials treated with compounds bearing such substituents.

Fluorinated polysiloxanes based on linear polysiloxane backbone with grafted aliphatic fluorocarbon groups have attracted increasing attention in recent years due to their heat and solvent resistance. Another interesting property is their low surface tension. Many fluorinated polysiloxanes, containing perfluoroalkyl, perfluoroalkyl ether and perfluoroalkyl ester moieties, have been studied in detail. Some of these fluorinated silicone polymers exhibit mesomorphic surface textures. These structures are attributed to the organization of the fluorocarbon–hydrocarbon grafts along the silicone backbone forming well-defined supramolecular architectures on the surface. The organization of these perfluorinated chains is crucial to obtain very low surface energy [2].

In the framework of a research programme dedicated to new silicone materials for textile treatment, we have investigated a series of innovative structures bearing at least two perfluoroalkyl moieties and an unsaturation for the subsequent grafting by an hydrosilylation reaction. The background of this programme has both practical and computational bases. Rhodia-Silicones company had previously developed effective hydrophobic and oleophobic silicone oils for coating, by hydrosilylation of bis(R_F) compounds (among others) with silicones containing Si–H moieties [3]. Good properties were obtained in particular with the allylmalonic ester **1**. On the other hand, an exploratory computational study indicated the interest of accumulating R_F chains, preferably with a symmetrical and/or rigid core, to favour the self-organization of fluorinated chains and to enhance the repellency character and decrease the ratio of introduced fluorine [4].

* Corresponding author. Tel.: +33 326 913234; fax: +33 326 913166.
E-mail address: charles.portella@univ-reims.fr (C. Portella).
[1] Current address: Rhoda, Centre de Recherches et de Technologies de Lyon, 85 rue des frères Perret, 69192, Saint-Fons Cedex, France.
[2] Now: Bluestar Silicones, 55 rue des frères Perret, BP 62, 69192 Saint-Fons, France.

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.05.020



1

We report herein the preparation of a variety of unsaturated compounds bearing two or four perfluorooctyl chains. For any possible practical applications, an easy and cheap access to starting materials was required. Epichlorhydrin and common diacids (tartaric, malic, fumaric and maleic acids) were considered as good candidates. The reported compounds as well as the saturated precursors could also be of interest for different purposes, i.e. including fluorous technologies, justifying also to disclose these results.

2. Results and discussion

2.1. Synthesis of bicatenar derivatives

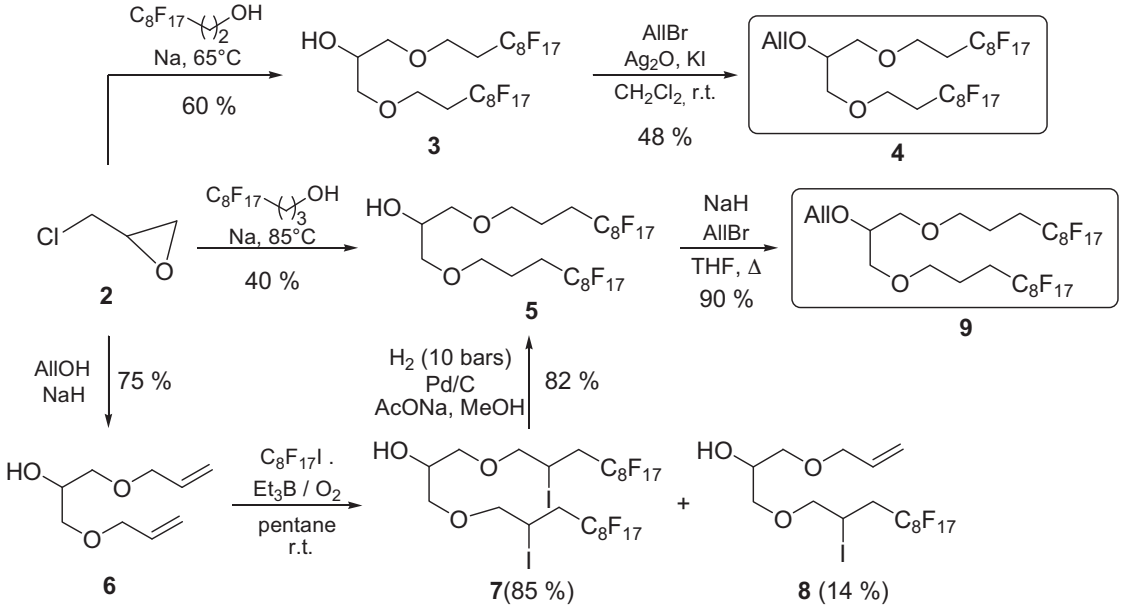
2.1.1. Glycerol type triethers prepared from epichlorhydrin

Epichlorhydrin **2** is a starting material of choice for derivatization towards glycerol-type derivatives, including fluorinated ones [5]. However, *O*-allyl-bis(*O*-$R_F$alkyl)ethers with the structures proposed here (Scheme 1) were not yet reported. As classical procedures such as deprotonation with sodium hydride led to degradation of the starting alcohol, the intermediate alcohol **3** was prepared in a solvent-free procedure by direct reaction of **2** with an excess of melt 2-(perfluorooctyl)ethanol and sodium metal [6]. The reaction should be performed with caution (see Section 4) and even if some degradation was observed, the hydroxy diether **3** was obtained in a reasonable yield of 60%. The allylation step proved also to be problematic using classical Williamson conditions (NaH, THF). The desired triether **4** was finally obtained with a yield of 48% (conversion: 52%) using freshly prepared silver oxide [7] as activating agent.

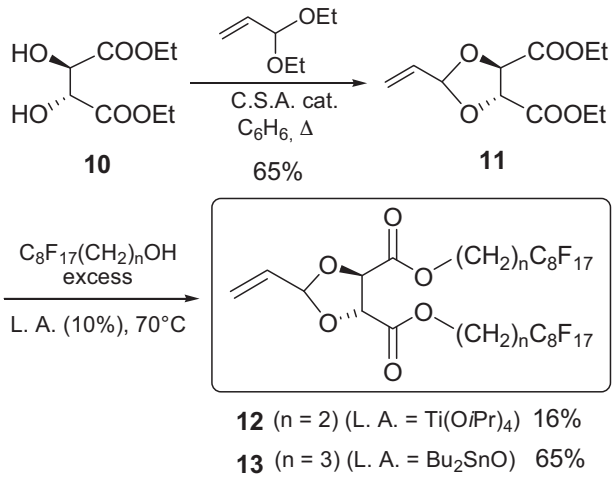
Two approaches were considered to synthesize the homologous alcohol **5** with a three carbons spacer (Scheme 1). The similar direct procedure was applied to (perfluorooctyl)propanol with the same shortcomings and, moreover, the need of a higher excess of alcohol for only a 40% yield, mainly due to the difficulties in the separation of the desired compound **5** and the excess of 3-perfluorooctyl propanol. In spite of the three steps from **2**, the second approach proved to be more convenient. Epichlorhydrin was first converted into the bis(1,3-*O*-allyl) ether **6**. Radical addition of perfluorooctyliodide was effectively performed using triethylborane as initiator [8]. The bis(adduct) **7** was isolated in 85% yield from a mixture containing a minor amount of the mono-adduct **8**. Hydrogenolysis of C–I bonds was conveniently performed under Pd/C catalysis, which was preferred to reduction with tributyltin hydride. Finally, the hydroxydiether **5** with three-carbon spacers was easily and effectively converted into the desired triether **9** under classical Williamson reaction conditions.

2.1.2. Tartaric and malic acid derived compounds

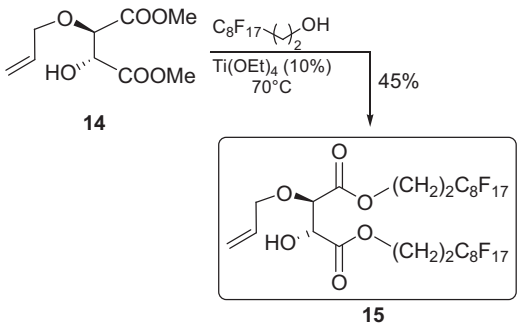
It was interesting to include in this panel of building-blocks a compound having both a C_2-symmetry axis and a rigid core. L-tartaric acid was the ideal starting material for such a purpose. The goal was to make a rigid structure by means of an unsaturated acetal like the one from acroleine. We initially attempted the sequence to prepare this acetal from the diester of L-tartaric acid with (perfluorooctyl)ethanol which was easily prepared [9]. The trans acetalization with acroleine diethylacetal failed, whatever the acid catalyst attempted (pyridinium *p*-toluenesulfonate (PPTS), camphorsulfonic acid, $Yb(OTf)_3$). Thus, the sequence was reversed: the acetal was prepared prior to esterification by the fluorinated alcohol (Scheme 2). Transacetalization between diethyl or dimethyl tartrate **10** [10] and acroleine diethylacetal catalyzed by camphorsulfonic acid afforded the acetal **11**, which was reacted with an excess of the fluorinated alcohol or perfluorooctyl propanol under Lewis acid catalysis. The reaction with perfluorooctyl ethanol yielded an intractable mixture of the desired ester **12** and the reactants. At the best, **12** was isolated in only 16% yield after crystallization in an ether/pentane mixture [11]. On the other hand, the synthesis of the analogue compound **13** derived from (perfluorooctyl)propanol was achieved in satisfactory yield using dibutyltin oxide as catalyst and the following procedure: the



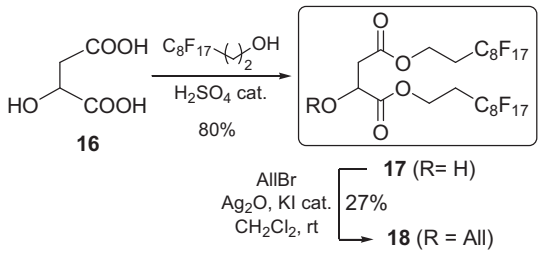
Scheme 1. Synthesis of 2-*O*-allyl-1,3-bis[*O*-(perfluorooctyl)alkyl]propanetriol.



Scheme 2. Synthesis of di-*O*-[(perfluorooctyl)alkyl 2,3-*O*-prop-2-enylidene tartrates.



Scheme 3. Synthesis of di((perfluorooctyl)ethyl) 2-*O*-allyl tartrate.



Scheme 4. Synthesis of di[(perfluorooctyl)ethyl] *O*-allyl malate.

reaction led first the desired diester **13** easily separated from the mixture of remaining reactants (52% conversion) which was reacted again after introduction of an additional amount of dibutyltin oxide, to eventually afford **13** with an overall yield of 65%.

To possibly assess the influence of the rigidity of the structure, the allyl tartaric and allyl malic derivatives **15** and **18** were synthesized (Schemes 3 and 4). The best way to **14** was the sequence allylation–transesterification whereas the reversed sequence esterification–allylation proved better for the malic acid derivative. The *O*-allyl dimethyl tartrate **14** was quantitatively prepared [12] and submitted to transesterification conditions ($Ti(OEt)_4$ cat.) to afford **15** in 45% isolated yield (Scheme 3). Synthesis of compound **17** was achieved by the prior direct esterification of DL-malic acid **16** with (perfluorooctyl)ethanol. A solvent free procedure under sulfuric acid catalysis gave much better results than a reported procedure with APTS in toluene [13]. The resulting diester **17** was converted to the corresponding *O*-allyl ether **18** with a low isolated yield (Scheme 4).

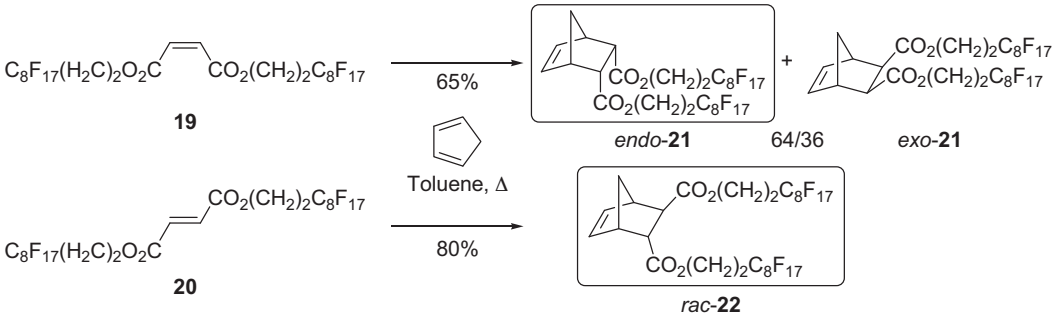
2.1.3. Bicyclo[2.2.1]heptene dicarboxylic derivatives

Norbornene bicyclic system also constitutes an interesting rigid core for our purpose; moreover it includes the double bond for further hydrosilylation. Dicarboxylic esters may be prepared easily by Diels–Alder cycloadditions. Fluorine containing compounds of this type were already used in ROMP for block copolymers synthesis [14]. We propose here a shorter strategy for their synthesis (Scheme 5). Maleic- and fumaric acid-derived fluorinated esters **19** and **20** were obtained in good yields and purity by reacting the corresponding acid in neat (perfluorooctyl)ethanol under sulfuric acid catalysis and removal of the excess of alcohol by vacuum sublimation. Diels–Alder reaction of **19** with cyclopentadiene led to a 64/36 mixture of the bicylic cycloadducts *endo*-**21**/*exo*-**21** in 65% yield for 70% conversion yield. The major *endo* isomer was determined by comparison with a pure sample obtained by esterification of the commercially available pure *cis*-5-norbornene-*endo*-2,3-dicarboxylic acid. Cycloaddition performed from the fumaric diester **20** led to the cycloadduct (*rac*)-**22** in 80% yield (85% conv.)

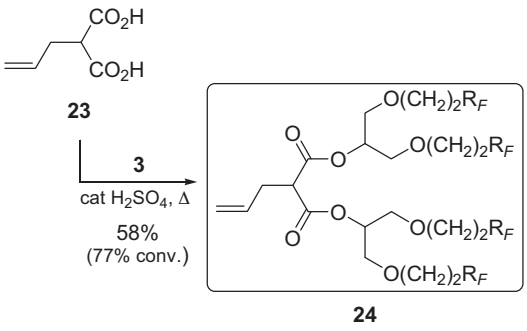
2.2. Synthesis of tetracatenar derivatives

As mentioned in the introduction, allylmalonic acid moiety is an interesting source of bicatenar perfluorinated compounds [3]. Having in hand the bicatenar alcohol **3**, we were keen to use it to prepare a tetracatenar malonic ester. Iminoacetic acid is another building block of interest to prepare diesters and then to have access to tetracatenar malonamide derivatives.

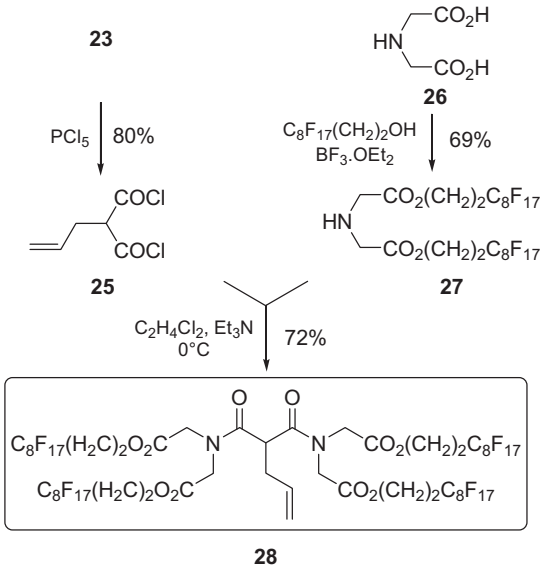
Thus allylmalonic acid **23** was treated at 75 °C by neat alcohol **3** (excess) under sulfuric acid catalysis to afford the tetracatenar allylmalonic ester **24** in 58% yield for a 77% conversion yield. The reaction needed a long time favouring some decarboxylation, giving the corresponding pentenoic ester as a by-product (10%) (Scheme 6).



Scheme 5. Synthesis of di[(perfluorooctyl)ethyl] esters of norbornene dicarboxylic acids.



Scheme 6. Synthesis of tetracatenar allylmalonic diester **24**.

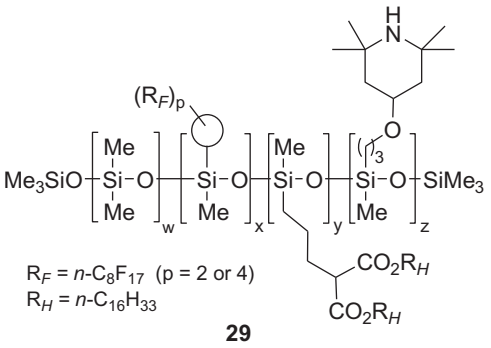


Scheme 7. Synthesis of tetracatenar allylmalonamide **28**.

Acid **23** was activated as its dichloride **25** prior to its conversion to the malonamide **28** [15] (Scheme 7). In parallel, iminodiacetic acid **26** was converted into the fluorinated iminodiacetate **27** (Scheme 7). Usual acid catalysts (H_2SO_4, *p*-toluenesulfonic acid, PPTS) proved to be unsuccessful for this esterification. Satisfactory yield was achieved using $BF_3{\cdot}Et_2O$, previously reported to give good results for similar reactions [16]. Then **25** and **27** were reacted in dichloroethane in the presence of triethylamine to afford the expected tetracatenar malonamide **28** in 72% yield (Scheme 7).

2.3. Grafting on silicone bearing SiH moieties

Grafting of the prepared unsaturated di- and tetracatenar R_F derivatives along with non-fluorinated grafts bearing either two long alkyl chains (R_H) or an amine function was attempted by catalytic hydrosilylation reaction from SiH containing polysiloxanes. The additional grafts contribute to increase hydrophobic properties and affinity for textiles, respectively. Karstedt catalyst was effective for hydrosilylation of allylic and vinylic compounds, with conversion yields ranging from 80 to 100%. Norbornenyl derivatives with *vic*-disubstituted double bond were less reactive, and needed chloroplatinic acid as catalyst to achieve high conversion yields (>94%). The result was a polydimethylsiloxane with the general formula of the type **29**, with a statistical distribution of the substituents [17].



For a large number of industrial textile applications the following properties were required: (i) strong oleophobic and hydrophobic character; (ii) good durability/permanence of their properties after washing machine; (iii) good chemical stability in the washing medium; (iv) good softness and non-yellowing properties; (v) applicability in the form of a stable emulsion or microemulsion; (vi) safe and reproductible processing; (vii) good patent position; and (viii) attractive price. These parameters are fully satisfied using **29** type oligomer structures.

3. Conclusion

A panel of bicatenar and tetracatenar highly fluorinated compounds with a wide structural diversity have been synthesized. They are characterized by an ether or ester linkage between the perfluoroalkyl(alkyl) chain and the core, and the presence of an unsaturation which allows their hydrosilylation by an Si–H containing polysiloxane. The syntheses generally gave satisfactory yields, notably because of the easy recovery, in most cases, of the excess and/or unreacted fluorinated starting material. These compounds along with aliphatic ones were effectively grafted on silicone oligomers to bring to them both hydrophobic and oleophobic character. Beyond the aim of this work, all compounds presented here are of potential interest for any surface modification purpose, for materials elaboration and for fluorous chemistry.

4. Experimental

4.1. General remarks

All starting materials were obtained from commercial suppliers. All solvents were dried using literature procedures. Analytical TLC was performed on Merck silica gel F254 (0.2 mm), detection being carried out by spraying with an alcoholic solution of phosphomolybdic acid or an aqueous solution of $KMnO_4$ (2%)/Na_2CO_3 (4%), followed by heating. Flash column chromatography was performed over silica gel Merck 9385 (40–63 μm) Kieselgel 60. NMR spectra were recorded on a Bruker AC 250 spectrometer (250 MHz for ^1H, 62.5 MHz for ^{13}C and 235 MHz for ^{19}F) in the deuterated solvent stated. Chemical shifts are expressed in parts per million using TMS and $CFCl_3$ as internal standards. Coupling constants are in Hz and splitting pattern abbreviations are: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; quint, quintuplet; m, multiplet. In the ^{13}C NMR spectra, the carbon signals of the *F*-octyl chain are not mentioned owing to their too low intensity (splitting due to fluorine coupling). FTIR spectra were recorded with an IR^{TM} plus MIDAC spectrophotometer and are expressed in cm^{-1}. Optical rotations were determined at 20 °C with a Perkin-Elmer Model 241 polarimeter in the specified solvents. Mass spectra were performed on Q-TOF Micro micromass positive ESI

(CV = 30 V). Elementary analyses were taken on a Perkin-Elmer CHN 2400 elementary analysis instrument. Melting points were determined with a Büchi apparatus in open capillary tubes and are uncorrected.

4.2. 1,3-Bis[2-(perfluorooctyl)ethyloxy]propan-2-ol (3)

Caution: this reaction must be carried out carefully, with control of the temperature in the heart of the reaction mixture. To 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecan-1-ol (40 g, 86.2 mmol) heated to 65 °C was carefully added sodium (810 mg, 35 mmol) and freshly distilled epichlorhydrin (1.25 mL, 11.5 mmol) over 3 hours. After 18 h of stirring, the solution was cooled to r.t. and was quenched carefully with isopropanol (5 mL), methanol (5 mL) and water (30 mL). The solution was then extracted with ether and the organic layer was dried over anhydrous Na_2SO_4. Evaporation and elimination of the residual alcohol by sublimation (1 mm Hg, 100 °C), afforded crude mixture which was purified by flash chromatography (petroleum ether/EtOAc, 80/20) to yield **3** (10.1 g, 60%) as pale yellow solid; mp 48–50 °C; IR (KBr) ν 1655, 1147, 1116, 704, 656 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 2.32–2.58 (4H, tt, $^3J_{H,F}$ = 18.7 Hz, J = 6.5 Hz, CH_2R_f), 3.55 (4H, m, CH_2CH_2O), 3.72 (4H, t, J = 6.5 Hz, OCH_2), 4.05 (1H, m, CHOH); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 32.0 (CH_2), 63.5 (CH_2), 70.9 (CH_2), 72.5 (CHOH); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.5 (3F, CF_3), −114.0 (2F, CF_2), −122.3 (6F, CF_2), −123.5 (2F, CF_2), −124.9 (2F, CF_2), −126.5 (2F, CF_2). MS (EI) *m/z*: 966 [M^+−18], 551, 507 (100), 477, 427; Anal. calcd for $C_{23}H_{14}F_{34}O$: C, 28.04; H, 1.40; found: C, 27.98; H, 1.18.

4.3. 2-Allyloxy-1,3-bis[2-(perfluorooctyl)ethyloxy]propane (4)

In a round-bottomed flask under argon, silver oxide (16 g) and potassium iodide (1.6 g) were successively added to a solution of **3** (11.86 g, 12 mmol) in dry dichloromethane (120 mL). Allyl bromide (4.6 mL, 53.15 mmol) was added dropwise to the solution and the mixture was stirred three days in the dark and then filtered through a pad of celite. Concentration of the filtrate under vacuum and purification by flash chromatography (petroleum ether/EtOAc, 80/20) afforded **4** as pale yellow oil (5.9 g, 48%); ^1H NMR (250 MHz, $CDCl_3$): δ 2.30–2.65 (4H, m, CH_2R_f), 3.52–3.75 (4H, m), 3.85 (4H, t, J = 6.5 Hz, OCH_2), 4.20 (1H, m, CHOH), 5.22–5.47 (2H, m, CH_{2all}), 6.03 (1H, m, CH_{all}); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 32.0 (CH_2), 63.5 (CH_2), 71.2 (CHOH), 72.5 (OCH_2), 117.3 (CH_{2all}), 135.0 (CH_{all}); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.4 (3F, CF_3), −114.5 (2F, CF_2), −122.5 (6F, CF_2), −123.5 (2F, CF_2), −124.0 (2F, CF_2), −126.5 (2F, CF_2); MS (EI) *m/z*: 1024 [M^+], 591, 547, 504, 477 (100), 427. Anal. calcd for $C_{28}H_{18}F_{34}O_3$: C, 30.46; H, 1.75; found: C, 30.01; H, 1.82.

4.4. 1,3-Bis[3-(perfluorooctyl)propyloxy]propan-2-ol (5)

Sodium acetate (132 mg, 1.6 mmol, 6.4 equiv.) and Pd/C (50 mg/mmol) were successively added to a solution of bis(iodoperfluoroalkylated) compound **7** (316 mg, 0.25 mmol) in solution in methanol (30 mL) in a reactor. The mixture was stirred under hydrogen (10 bars) at room temperature and the reaction was monitored by TLC. After completion, the mixture was filtered and concentred *in vacuo*. The crude mixture was diluted in ether and washed with an aqueous solution of sodium thiosulfate. The aqueous layer was extracted with ether (3 × 50 mL). The solution was dried over anhydrous Na_2SO_4 and the solvent was removed. Purification by flash chromatography (petroleum ether/EtOAc, 90/10) afforded **5** as white solid (206 mg, 82%); mp 41–43 °C; IR (KBr) ν 3485, 1147, 1116, 721, 657 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 1.82–1.98 (4H, m, $CH_2CH_2R_f$), 2.14–2.19 (4H, m, CH_2R_f), 2.36 (1H, s, OH), 3.47–3.52 (8H, m, CH_2O), 3.95 (1H, quint., J = 4.8 Hz, CHOH); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 20.7 (CH_2), 27.9 (t, $^2J_{C,F}$ = 23.6 Hz, CH_2R_f), 69.4 (CHOH), 69.8 (CH_2), 75.9 (CH_2); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.1 (3F, CF_3), −114.5 (2F, CF_2), −122.1 (6F, CF_2), −122.9 (2F, CF_2), −123.7 (2F, CF_2), −126.3 (2F, CF_2); Anal. calcd for $C_{25}H_{18}F_{34}O_3$: C, 29.65; H, 1.78; found: C, 30.00; H, 1.60.

4.5. 1,3-Bis[2-iodo-3-(perfluorooctyl)propyloxy]propan-2-ol (7) and 1-allyloxy-3-O-[2-iodo-3-(perfluorooctyl)propyloxy]propan-2-ol (8)

A round-bottomed flask in the dark was charged with the starting 1,3-diallylpropan-2-ol (0.34 g, 2 mmol) in solution in pentane and perfluorooctyl iodide (3.28 g, 6 mmol, 3 equiv.). Successive amounts of Et_3B 1 M in hexane (0.06 mL, 0.4 mmol, 0.2 equiv. up to 0.8 equiv.) were added. The reaction was monitored by TLC. After completion of the reaction (20 h), the solution was poured into brine and extracted with ether (3 × 50 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed and the crude product was purified by flash chromatography (petroleum ether/EtOAc, 85/15) to yield bis(perfluoroalkylated) product **7** (2.12 g, 85%) as white solid and minor product **8** (14%); Compound **7**: mp 61–63 °C; IR (KBr) ν 3420, 1147, 707, 659, 559 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 2.43 (1H, d, J = 4.5 Hz, OH), 2.61–3.13 (4H, m, CH_2R_f), 3.61–3.82 (8H, m, CH_2O), 4.02 (1H, quint., J = 4.5 Hz, CHOH), 4.41 (2H, quint., J = 5.7 Hz, CHI); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.6 (CHI), 37.8 (t, $^2J_{C,F}$ = 21.7 Hz, CH_2R_f), 69.4 (CHOH), 71.8 (CH_2), 75.9 (CH_2); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.3 (3F, CF_3), −113.8 (2F, CF_2), −121.3 (4F, CF_2), −122.1 (2F, CF_2), −122.4 (2F, CF_2), −123.3 (2F, CF_2), −124.0 (2F, CF_2). MS (EI) *m/z*: 1264 [M^+], 1136, 677, 587, 551 (100); Anal. calcd for $C_{25}H_{16}F_{34}I_2O_3$: C, 23.74; H, 1.27; found: C, 23.90; H, 1.04. Compound **8**: ^1H NMR (250 MHz, $CDCl_3$): δ 2.41–2.45 (1H, m, OH), 2.58–3.18 (2H, m, CH_2R_f), 3.45–3.78 (6H, m), 3.94–4.01 (1H, m, CHOH), 4.04 (4H, dt, J = 1.5 Hz, J = 5.7 Hz, CH_2O), 4.38 (1H, quint., J = 5.7 Hz, CHI), 5.21 (1H, dq, J = 1.5 Hz, J = 10.3 Hz, CH_2=), 5.28 (1H, dq, J = 1.5 Hz, J = 17.2 Hz, CH_2=), 5.91 (1H, ddt, J = 5.7 Hz, J = 10.3 Hz, J = 17.2 Hz, CH=); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.6 (CHI), 37.7 (t, $^2J_{C,F}$ = 21.2 Hz, CH_2R_f), 69.4 (CHOH), 71.0 (CH_2), 72.1 (CH_2), 72.4 (CH_2), 76.0 (CH_2), 117.3 (CH_2=), 134.3 (CH=); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.3 (3F, CF_3), −113.9 (2F, CF_2), −122.0 (2F, CF_2), −122.3 (4F, CF_2), −123.2 (2F, CF_2), −124.0 (2F, CF_2), −126.6 (2F, CF_2); MS (EI) *m/z*: 718 [M^+] (15), 587 (100), 459, 389.

4.6. 2-Allyloxy-1,3-bis[3-(perfluorooctyl)propyloxy]propane (9)

To a suspension of sodium hydride (0.14 g, 5.94 mmol, 1.2 equiv.) in dry THF (30 mL) was added a solution of **5** (5 g, 4.95 mmol) in dry THF (10 mL). The mixture was stirred for 1 h at room temperature and allyl bromide (0.51 mL, 5.94 mmol, 1.2 equiv.) was added dropwise. The solution was then stirred and heated overnight at reflux. The mixture was diluted in ether and washed with brine. The aqueous layer was extracted with ether (3 × 50 mL). After drying over sodium sulfate and concentration, flash chromatography (petroleum ether/EtOAc, 90/10) gave **9** as a colourless oil (4.73 g, 90%); IR (neat) ν 1655, 1147, 1116, 704, 656 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ 1.83–1.94 (4H, m, $CH_2CH_2R_f$), 2.09–2.33 (4H, m, CH_2R_f), 3.48–3.56 (8H, m, CH_2O), 3.64 (1H, quint., J = 4.4 Hz, CHOH), 4.13 (4H, dt, ^4J = 1.5 Hz, ^3J = 5.7 Hz, $CHCH_2O$), 5.17 (1H, dq, ^4J = J = 1.5 Hz, J = 10.7 Hz, CH_{2all}), 5.28 (1H, dq, ^4J = J = 1.5 Hz, J = 17.2 Hz, CH_{2all}), 5.91 (1H, ddt, J = 5.7 Hz, J = 10.7 Hz, J = 17.2 Hz, CH_{all}); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 20.7 (CH_2), 27.8 (t, $^2J_{C,F}$ = 22.7 Hz, CH_2R_f), 69.8 (CH_2), 70.7 (CH_2), 71.4 (CH_2), 76.9 (CHOH), 116.8 (CH_{2all}), 135.0 (CH_{all}); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.1 (3F, CF_3), −114.5 (2F, CF_2), −122.1 (6F, CF_2), −122.9 (2F, CF_2), −123.7 (2F, CF_2), −126.3 (2F, CF_2); Anal. calcd for $C_{28}H_{22}F_{34}O_3$: C, 32.00; H, 2.09; found: C, 32.39; H, 2.03.

4.7. Di[3-(perfluoocty)lpropyl] (2R, 3R)-2,3-O-allylidenetartrate (13)

To 3-(perfluorooctyl)propanol (40 g, 86.2 mmol) heated to 80 °C under argon was added compound **11** (9.4 g, 38.5 mmol) and Bu_2SnO (0.9 g, 3.6 mmol). The mixture was stirred at 80 °C for 16 h. After separation by flash chromatography over silica gel (petroleum ether/EtOAc, 80/20), fluorinated diester **13** (8.4 g, 42%; 52% conversion) was isolated. The recovered mixture of acetal **11** and fluorinated alcohol was reacted similarly after addition of Bu_2SnO (0.3 g, 1.2 mmol). The overall procedure yielded **13** as a white solid (13.0 g, 65%); mp 73–74 °C; $[\alpha]_D^{20} = -10$ (*c* 1.08, $CHCl_3$); IR (neat) ν 1763, 1215, 1034, 1011, 960, 704, 653 cm^{-1}; ^1H NMR (250 MHz, CD_3COCD_3): δ 1.96–2.12 (4H, m), 2.30–2.52 (4H, m), 4.32–4.50 (4H, m), 4.87 (1H, d, *J* = 3.4 Hz), 4.98 (1H, d, *J* = 3.4 Hz), 5.41 (1H, dd, *J* = 1.5 Hz, *J* = 10.3 Hz), 5.57 (1H, dd, *J* = 1.5 Hz, *J* = 17.0 Hz, CH_{2all}), 5.59 (1H, d, *J* = 6.5 Hz), 5.92 (1H, ddd, *J* = 6.5 Hz, *J* = 10.3 Hz, *J* = 17.0 Hz, CH_{all}); ^{13}C NMR (62.5 MHz, CD_3COCD_3): δ 20.7, 28.3 (t, $^2J_{C,F}$ = 21.7 Hz, CH_2R_f), 64.9, 77.8, 78.2, 107.7, 121.8 (CH_{2all}), 135.1 (CH_{all}), 169.8, 170.1; ^{19}F NMR (235 MHz, CD_3COCD_3): δ −80.7 (3F, CF_3), −113.8 (2F, CF_2), −121.4 (6F, CF_2), −122.2 (2F, CF_2), −122.8 (2F, CF_2), −125.7 (2F, CF_2); MS (EI) *m/z*: 1108 [M^+] (55), 1081, 603 (100), 547, 441; Anal. calcd for $C_{29}H_{18}F_{34}O_6$: C, 31.41; H, 1.62; found: C, 31.16; H, 1.34.

4.8. Di[(perfluorooctyl)ethyl] (2R,3R)-2-O-allyltartrate (15)

2-(Perfluorooctyl)ethanol (25 g, 75 mmol) and dimethyl allyloxytartrate **14** (6.54 g, 30 mmol) were melt in a round-bottomed flask under argon. Then, titanium (IV) tetraethoxide (1.5 mL) of were added and the solution was heated at 130 °C under reduce pressure (80 mm Hg). The reaction was monitored by TLC. After 21 h, the residual perfluoroalkylated alcohol was recovered by sublimation and crystallization of the crude mixture (petroleum ether) gave a white solid (15.0 g, 80%); mp 56 °C; $[\alpha]_D^{20} = +10.6$ (*c* 0.119; $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 2.54 (4H, tt, *J* = 5.4 Hz, $^3J_{H,F}$ = 17.9 Hz, CH_2R_f), 3.90 (1H, dd, *J* = 6.5 Hz, *J* = 12.5 Hz, CH_2CHCH_2), 4.30 (1H, dd, *J* = 5.4 Hz, *J* = 12.5 Hz, CH_2CHCH_2), 4.34 (1H, d, *J* = 2.2 Hz, CHOH), 4.45–4.55 (4H, m, CH_2), 4.63–4.70 (1H, m, CHOH), 5.15–5.30 (2H, m, CH_{2all}), 5.75–5.90 (1H, m, CH_{all}); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 30.5 (CH_2), 57.3, 58.5, 68.0, 72.0, 118.3, 133.5, 168.2, 170.5; ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.5 (3F, CF_3), −114.0 (2F, CF_2), −122.5 (6F, CF_2), −123.4 (2F, CF_2), −124.0 (2F, CF_2), −126.6 (2F, CF_2); Anal. calcd for $C_{27}H_{16}F_{34}O_6$: C, 29.94; H, 1.48; found: C, 30.08; H, 1.27.

4.9. Di[(perfluorooctyl)ethyl] malate (17)

2-(perfluorooctyl)ethanol (80 g, 168 mmol) and DL-malic acid (7.78 g, 56 mmol) were melt in a reactor equipped with a refrigerant. Catalytic amount of sulfuric acid was added and the mixture was stirred and heated to 110 °C for 20 h. Residual alcohol was then eliminated by sublimation (110 °C, 0.5 mm Hg). After recrystallization from toluene, compound **17** was isolated as a white solid (46 g, 80%); mp 68–70 °C; ^1H NMR (250 MHz, $CDCl_3$): δ 2.44–2.65 (4H, m, CH_2R_f), 2.80–2.95 (2H, m, CH_2), 3.10 (1H, bs, OH), 4.42–4.52 (4H, m, CH_2CH_2O), 4.54–4.65 (1H, m, CHOH); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.3 (3F, CF_3), −114.1 (2F, CF_2), −122.3 (6F, CF_2), −123.2 (2F, CF_2), −124.0 (2F, CF_2), −126.6 (2F, CF_2); MS (EI) *m/z*: 1026 [M^+] (10), 989, 535 (100), 493, 427, 169, 131; Anal. calcd for $C_{24}H_{12}F_{34}O_5$: C, 28.07; H, 1.17; found: C, 28.17; H, 1.23.

4.10. Di[(perfluorooctyl)ethyl] O-allylmalate (18)

In a round-bottomed flask under argon, silver oxide (9 g, 39 mmol) and potassium iodide (0.86 g, 5.2 mmol) were successively added to a solution of **17** (26.7 g, 26 mmol) in dry dichloromethane (70 mL). Allyl bromide (2.5 mL, 28.9 mmol) was added dropwise to the solution and the mixture was stirred three days at room temperature and then filtered through a pad of celite. After concentration the crude mixture was purified flash chromatography (petroleum ether/EtOAc, 80/20) to afford **18** as a white solid (7.4 g, 27%); mp 73 °C; ^1H NMR (250 MHz, $CDCl_3$): δ 2.38–2.65 (4H, m, CH_2R_f), 2.82 (2H, d, *J* = 6.5 Hz, CH_2), 4.00–4.10 (1H, m), 4.28–4.50 (5H, m), 4.65–4.75 (1H, m, $CHOCH_2$), 5.18–5.41 (2H, m, CH_{2all}), 5.85–6.02 (1H, m, CH_{all}); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 30.0 (CH_2), 37.5 (CH_2), 72.5, 73.2, 118.1 (CH_{2all}), 133.0 (CH_{all}), 170.2; ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.0 (3F, CF_3), −114.2 (2F, CF_2), −122.0 (6F, CF_2), −123.8 (2F, CF_2), −124.5 (2F, CF_2), −126.7 (2F, CF_2); MS (EI) *m/z*: 1066 [M^+] (15), 1010, 989, 966, 939 (100), 909; Anal. calcd for $C_{27}H_{16}F_{34}O_5$: C, 30.39; H, 1.50; found: C, 30.58; H, 1.27.

4.11. General procedure for the synthesis of fluorinated maleic acid and fumaric esters

2-(Perfluorooctyl)ethanol (21 g, 45.2 mmol) and maleic or fumaric acid (2.3 g, 20 mmol) were melt in a reactor equipped with a refrigerant. A catalytic amount of sulfuric acid was added and the mixture was stirred and heated to 110 °C for 20 h. Residual alcohol was then eliminated by sublimation (110 °C, 0.5 mm Hg). Compounds were purified by recrystallization from toluene.

4.12. Di[(perfluorooctyl)ethyl] maleate (19)

(21.6 g, 92%); mp 62–63 °C; ^1H NMR (250 MHz, $CDCl_3$): δ 2.41–2.62 (4H, m, CH_2R_f), 4.52 (4H, t, *J* = 6.8 Hz, CH_2), 6.33 (2H, s, CH); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 30.2 (CH_2), 57.1 (CH_2), 129.8, 164.5; ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.4 (3F, CF_3), −114.3 (2F, CF_2), −122.4 (6F, CF_2), −123.3 (2F, CF_2), −124.1 (2F, CF_2), −126.7 (2F, CF_2).

4.12.1. Di[(perfluorooctyl)ethyl] fumarate (20)

(17.9 g, 88%); mp 81–83 °C; ^1H NMR (250 MHz, CD_3COCD_3): δ 2.66 (4H, dt, *J* = 6.1 Hz, *J* = 12.2 Hz, *J* = 19.1 Hz, CH_2R_f), 4.47 (4H, t, *J* = 6.1 Hz, CH_2), 6.71 (2H, s, CH); ^{19}F NMR (235 MHz, CD_3COCD_3): δ −80.6 (3F, CF_3), −112.9 (2F, CF_2), −121.4 (6F, CF_2), −122.2 (2F, CF_2), −123.1 (2F, CF_2), −125.7 (2F, CF_2); MS (EI) *m/z*: 1008 [M^+] (8), 989, 639, 545 (100), 427, 131.

4.13. General procedure for the Diels–Alder reactions

A toluene (150 mL) solution of esters **19** or **20** (15 g, 14.9 mmol) and freshly distilled cyclopentadiene (1.33 g, 20 mmol) was refluxed for 2 h. After filtration through a pad of silice and removal of the solvent *in vacuo*, the crude product was recrystallized (petroleum ether/EtOAc, 90/10).

4.13.1. Di[(perfluorooctyl)ethyl] (cis,endo)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (endo-21) and di[(perfluorooctyl)ethyl] (cis,exo)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (exo-21)

(10.4 g, 65% from **19**), (*ratio* endo/exo 64/36); mp 56–58 °C; major isomer **endo-21** was purified by flash chromatography over silica gel; Compound **endo-21**: mp 68–70 °C; ^1H NMR (250 MHz, $CDCl_3$): δ 1.32 (1H, d, *J* = 8.8 Hz, CH_2), 1.52 (1H, d, *J* = 8.8 Hz, CH_2), 2.44 (4H, tt, *J* = 6.5 Hz, *J* = 12.5 Hz, *J* = 18.4 Hz, CH_2R_f), 3.21 (2H, s, CH), 3.30 (2H, s, CH), 4.30–4.45 (4H, m, CH_2), 6.30 (2H, m, CHCH); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 25.2, 46.5, 47.3, 48.9, 56.2, 135.2, 172.0; ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.3 (3F, CF_3), −114.1 (2F, CF_2), −122.5 (6F, CF_2), −123.5 (2F, CF_2), −124.1 (2F, CF_2), −126.0 (2F, CF_2); MS (EI) *m/z*: 1074 [M^+] (4), 1055, 1009, 939, 611, 545 (100), 505, 169; Anal. calcd for $C_{29}H_{16}F_{34}O_4$: C, 32.46; H, 1.49; found: C, 32.04; H, 1.21; Compound **exo-21**: ^1H NMR (250 MHz, $CDCl_3$): δ 1.50 (1H, d, *J* = 9.1 Hz, CH), 2.05 (1H, d, *J* = 9.1 Hz, CH),

2.20–2.53 (4H, m, CH_2R_f), 2.65 (2H, d, J = 1.9 Hz, CH), 3.11 (2H, t, J = 1.9 Hz, CH), 4.32–4.40 (4H, m, CH_2), 6.22 (2H, t, J = 1.9 Hz, CHCH); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.4 (3F, CF_3), −114.0 (2F, CF_2), −122.6 (6F, CF_2), −123.5 (2F, CF_2), −124.0 (2F, CF_2), −126.0 (2F, CF_2).

4.13.2. (±)-Di[(perfluorooctyl)ethyl] (exo,endo)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (rac-22)

(13.0 g, 80% from **20**); mp 82–83 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.50 (1H, dd, J = 1.9 Hz, J = 8.8 Hz, CH_2), 1.60 (1H, d, J = 8.8 Hz, CH_2), 2.48–2.55 (4H, m, CH_2R_f), 2.72 (1H, dd, J = 1.5 Hz, J = 4.6 Hz), 3.12 (1H, m, CH), 3.33 (1H, ma, CH), 3.35 (1H, t, J = 4.6 Hz), 4.35 (2H, t, J = 6.1 Hz, CH_2), 4.43 (2H, dt, J = 1.9 Hz, J = 5.5 Hz, CH_2), 6.08 (1H, dd, J = 2.7 Hz, J = 5.7 Hz, CHCH), 6.29 (1H, dd, J = 3.0 Hz, J = 5.7 Hz, CHCH); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 30.5 (CH_2), 31.3, 45.0, 47.2, 48.5, 56.3, 57.5, 135.2, 138.3, 174.0; ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.0 (3F, CF_3), −114.2 (2F, CF_2), −122.6 (6F, CF_2), −123.8 (2F, CF_2), −124.4 (2F, CF_2), −126.6 (2F, CF_2); Anal. calcd for $C_{29}H_{16}F_{34}O_4$: C, 32.46; H, 1.49; found: C, 31.97; H, 1.38.

4.14. Di-[1,3-bis((perfluorooctyl)ethyloxy)propan-2-yl] 2-allylmalonate (24)

A mixture of alcohol **3** (27 g, 28.3 mmol), allylmalonic acid (1.63 g, 11.34 mmol) and a catalytic amount of concentrated sulfuric acid was stirred for 18 h at 75 °C. The crude product, after cooling, was directly purified by flash chromatography (petroleum ether/EtOAc, 80/20) to afford **24** as a colorless oil (13.7 g, 58%); IR (neat) ν 2878, 1736, 1323, 1234, 1145 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.20–2.51 (8H, tt, $^3J_{H,F}$ = 18.3 Hz, J = 6.3 Hz, CH_2R_f), 2.65 (2H, t, J = 6.9 Hz, CH_2CHCH_2), 3.54 (1H, t, J = 7.3 Hz, $CH(COO)_2$), 3.66 (8H, d, J = 7.3 Hz, CH_2), 3.78–3.82 (8H, m, CH_2), 5.03–5.21 (4H, t, J = 21 Hz, CH_{2all}), 5.65–5.85 (1H, m, CH_{all}); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 31.3, 32.6, 51.4, 63.2, 68.7, 68.8, 71.9, 117.5, 133.6, 168.1 (CO); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.5 (3F, CF_3), −114.1 (2F, CF_2), −122.6 (6F, CF_2), −123.4 (2F, CF_2), −124.3 (2F, CF_2), −126.8 (2F, CF_2); Anal. calcd for $C_{52}H_{34}F_{68}O_4$: C, 30.05; H, 1.64; found: C, 29.84; H, 1.37.

4.15. Di[2-(perfluorooctyl)ethyl] iminodiacetate (27)

2-(Perfluorooctyl)ethanol (65 g, 140 mmol) was melt with iminodiacetic acid **26** (3.72 g, 28 mmol) in a round-bottomed flask under argon. $BF_3{\cdot}Et_2O$ (10.6 mL) was slowly added and the mixture was stirred for 96 h. After addition of ethyl acetate, the solution was washed with an aqueous solution of ammonium chloride. Residual alcohol was eliminated by sublimation (110 °C, 0.5 mm Hg) and the crude mixture was purified by flash chromatography over silica gel to furnish **27** as a white solid (19.8 g, 69%); mp 68–69 °C; IR (KBr) ν 1743, 1203, 1140, 663 cm^{-1}; ^{1}H NMR (250 MHz, CD_3COCD_3): δ 2.51–2.85 (4H, m, CH_2R_f), 3.58 (4H, s, NCH_2), 4.13 (4H, t, J = 5.1 Hz, CH_2); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.3 (3F, CF_3), −114.2 (2F, CF_2), −122.7 (6F, CF_2), −123.1 (2F, CF_2), −124.8 (2F, CF_2), −126.3 (2F, CF_2); Anal. calcd for $C_{24}H_{13}F_{34}NO_4$: C, 28.09; H, 1.26; found: C, 28.08; H, 1.24.

4.16. 2-Allyl-N^1,N^1,N^3,N^3-tetra[2(-perfluorooctyl)ethyl]malonamide (28)

To a cold mixture (0 °C) of ester **27** (22 g, 21.5 mmol) and triethylamine (2.8 mL) in 1,1,2,2-tetrachloroethane (150 mL) was added acylchloride **25** [18] (1.93 g, 10.7 mmol) dropwise. The mixture was stirred and heated 41 h and then poured into ice-cold water and extracted with ethyl acetate. The pale yellow precipitate was filtered and rinsed twice with acetone. After recrystallization from acetone, compound **28** was isolated as a white solid (16.6 g, 72%); mp 90–91 °C; IR (KBr) ν 3123, 1755, 1666, 1404, 1203 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.40–2.75 (8H, m, CH_2R_f), 2.85 (2H, t, J = 10.0 Hz, CH_2CHCH_2), 3.90 (1H, t, J = 10.0 Hz, $CHCH_2$), 4.05–4.30 (8H, m, CH_2), 4.41–4.50 (8H, m, NCH_2COO), 5.05–5.23 (2H, m, CH_{2all}), 5.85 (1H, m, CH_{all}); ^{19}F NMR (235 MHz, $CDCl_3$): δ −81.3 (3F, CF_3), −114.1 (2F, CF_2), −122.3 (6F, CF_2), −123.2 (2F, CF_2), −124.0 (2F, CF_2), −126.6 (2F, CF_2); Anal. calcd for $C_{54}H_{30}F_{68}N_2O_{10}$: C, 30.02; H, 1.39; found: C, 29.93; H, 1.12.

Acknowledgments

The authors acknowledge the contribution of Dr. Paul Branlard, Dr. Caroll Vergelati, Dr. Alfred Greiner and Dr. Philippe Olier to fruitful discussions during the development of this project. We are grateful to Rhodia Silicones (now Bluestar Silicones) for financial support of this work.

References

[1] Recent reviews on various aspects of fluorous chemistry:
(a) K.L. O'Neal, H. Zhang, Y. Yang, L. Hong, D. Lu, S.G. Weber, J. Chromatogr. A 1217 (2010) 2287–2295;
(b) W. Zhang, Chem. Rev. 109 (2009) 749–795;
(c) W. Zhang, Green Chem. 11 (2009) 911–920;
See also:, J.A. Gladysz, D.P. Curran, I.T. Hiraki (Eds.), Handbook of Fluorous Chemistry, Wiley-VCH, Weinheim, 2004.
[2] S. Breuning, J. Chardon, N. Ghennouni, G. Mignani, P. Olier, A. van der Spuy, C. Vergelati, in: N. Auner, J. Weis (Eds.), Organosilicon Chemistry, from Molecules to Materials, IV, Wiley-VCH, 2000, pp. 645–658.
[3] G. Guichard, G. Mignani, P. Olier, PCT Int. Appl. WO 2000005315 A1 20000203 CAN 132:124038 (2000).
[4] C. Vergelati, C.G. Mignani, unpublished results
[5] (a) W. Huang, C. Jin, D.K. Derzon, T.A. Huber, J.A. Last, P.P. Provencio, A.S. Gopalan, M. Dugger, D.Y. Sasaki, J. Colloid Interf. Sci. 272 (2004) 457–464;
(b) H. Tamiaki, T. Nishiyama, R. Shibata, Bioorg. Med. Chem. Lett. 17 (2007) 1920–1923.
[6] The preparation of compounds similar to **3** was reported from epichlorhydrine via a stepwise procedure and the intermediate glycidyl ether. See Ref. [5a].
[7] M. Tanabe, R.H. Peters, Org. Synth. Coll. 7 (1990) 386.
[8] E. Rogalska, R. Bilewicz, T. Brigaud, C. El Moujahid, G. Foulard, C. Portella, M.-J. Stébé, Chem. Phys. Lipids 105 (2000) 71–91.
[9] Z. Szlávik, G. Tárkányi, G. Tarczay, A. Gömöry, R.J. Rábai, J. Fluorine Chem. 98 (1999) 83–87.
[10] Y. Tsuzuki, M. Koyama, K. Tanabe, Bull. Chem. Soc. Jpn. 41 (1968) 1008–1013.
[11] Compound **12** is a white solid; mp 73–75 °C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.57–2.86 (4H, m, CH_2R_f), 4.52–4.63 (4H, m, CH_2O), 4.85 (1H, d, J = 3.4 Hz), 4.97 (1H, d, J = 3.4 Hz), 5.42 (1H, d, J = 10.3 Hz), 5.56 (1H, d, J = 17.2 Hz, CH_{2all}), 5.59 (1H, d, J = 6.5 Hz), 5.93 (1H, ddd, J = 6.5 Hz, J = 10.3 Hz, J = 17.2 Hz, CH_{all}); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 30.9 (t, $^2J_{C,F}$ = 21.7 Hz, CH_2R_f), 58.3, 77.5, 78.0, 107.0, 122.0, 135.0, 169.5, 169.7; ^{19}F NMR (235 MHz, $CDCl_3$): δ −80.6 (3F, CF_3), −112.9 (2F, CF_2), −121.2 (6F, CF_2), −122.2 (2F, CF_2), −123.1 (2F, CF_2), −125.7 (2F, CF_2).
[12] N. Magashima, M. Ohno, Chem. Lett. (1987) 141–144.
[13] T. Nishimura, Y. Maeda, N. Kakiuchi, S. Uemura, J. Chem. Soc., Perkin Trans. 1 (2000) 4301–4305.
[14] K. Wewerka, A. Wewerka, F. Stelzer, B. Gallot, L. Andruzzi, G. Galli, Macromol. Rapid Commun. 24 (2003) 906–910.
[15] Direct condensation of iminodiacetate **27** with commercially available dimethyl allylmalonate using various Lewis acids or bases as catalyst failed.
[16] G.C.R. Ellis-Davies, J.H. Kaplan, J. Org. Chem. 53 (1988) 1966–1969.
[17] This paper being devoted to the synthesis of unsaturated fluorinated grafts, hydrosilylation procedures and analytical methods are nor further detailed. These procedures and methods are similar to the ones exemplified in the patent given in Ref. [3].
[18] F. Sorm, J. Beranek, J. Smrt, J. Sicher, Coll. Czech. Chem. Commun. 20 (1955) 593–596.