EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

Title: Fluorinated Alkyl Aryl Esters, Carbinols and Derivatives Thereof as Alternatives to Perfluoroalkyl Carboxylic and Sulfonic Acids

Authors: Jens Christoffers; Torben Alpers; Thomas W. T. Muesmann; Oliver Temme

To be cited as: Eur. J. Org. Chem. 10.1002/ejoc.201601298

Link to VoR: https://doi.org/10.1002/ejoc.201601298

Supported by
ACES Asian Chemical Editorial Society

WILEY-VCH

Fluorinated Alkyl Aryl Esters, Carbinols and Derivatives Thereof as Alternatives to Perfluoroalkyl Carboxylic and Sulfonic Acids

Torben Alpers,[a,b] Thomas W. T. Muesmann,[b] Oliver Temme,[b] Jens Christoffers*[a]

[a] MSc. T. Alpers, Prof. Dr. J. Christoffers, Institut for Chemie, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany. Fax: +49(0)441 798 3873. Email: jens.christoffers@uni-oldenburg.de. Homepage: www.christoffers.chemie.uni-oldenburg.de

[b] MSc. T. Alpers, Dr. T. Muesmann, Dr. O. Temme, Ferdinand Eimermacher GmbH & Co. KG, Westring 24, 48356 Nordwalde, Germany.

Graphical Abstract

Key topic: Fluorinated Compounds

Short, but still repellent. Aromatic esters and carbinols with perfluorohexyl residues and some derivatives thereof were prepared as novel, biodegradable materials for textile impregnation.

Abstract: Perfluorohexyl carbinols were prepared from the respective Grignard reagent and benz-, terephthal-, isophthal- and trimesalydehyde (four products). The corresponding secondary alcohols were further transformed by ether (methyl, ethyl,

propyl and *n*-hexyl) and ester formation (with acetyl chloride and 2-ethylhexanoyl chloride) yielding 14 derivatives. Furthermore, perfluoroalkyl esters were prepared from aromatic, heteroaromatic and aliphatic mono-, di-, tri- and tetracarboxylic acids and tridecafluorooctanol. The wettability of all 29 materials was investigated by water contact angle measurements of a thin film on a glass surface. In up to six cases, contact angles >130° were observed indicating, that the products might be suitable candidates for the impregnation of surfaces. With their relatively short perfluoroalkyl side chains and therefore low bioaccumulativity, the target compounds might be beneficial alternatives to established products.

Keywords: Fluorine compounds, wettability, esters, alkohols, ethers, Grignard reagent.

Introduction

Perfluoroalkyl carboxylic and sulfonic acids with longer carbon chains ($C_nF_{2n+1}CO_2H$ and $C_nF_{2n+1}SO_3H$ with n > 6) and derivatives thereof have found ubiquitous applications for surface treatment of textiles, leathers, cardboard, paper, polymeric materials, metals etc.[1] Especially so called fluorocarbon resins are widely in use as impregnation materials for industrial as well as consumer[2] applications. The manufacturing of impregnation materials, especially for the car industry is still based on PFOA ($C_7F_{15}CO_2H$) and PFOS ($C_8F_{17}SO_3H$). While the final impregnation products are quite harmless, their purification in the industrial scale is not thorough enough to eliminate all of the very persistent PFOA and PFOS residues. During their use the impregnation products pollute the environment with these residues of PFOA and PFOS. Due to their persistency and bioaccumulativity, they are detectable

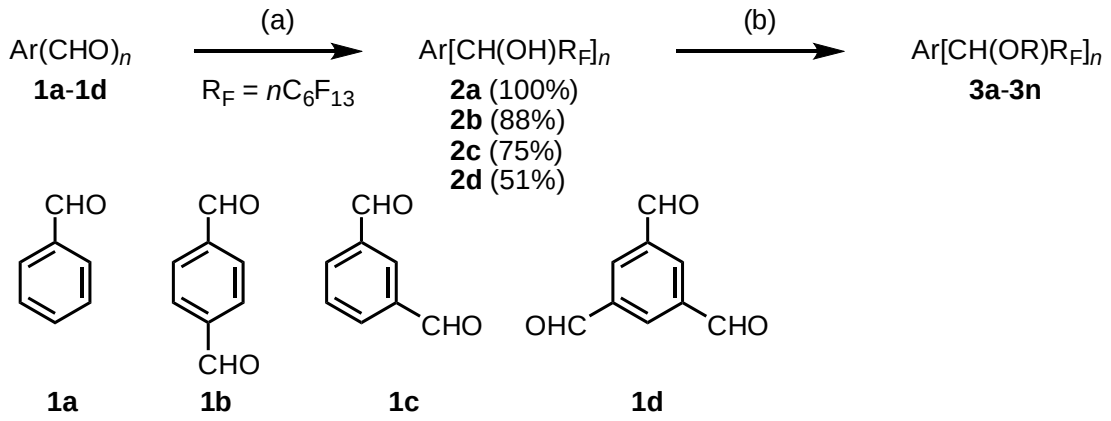
ubiquitously in the abiotic environment[3] as well as in animals and humans[4] and have thus attracted attention as global contaminants. As a result, these compounds were listed under Annex B (restriction of production and use) of the Stockholm Convention in 2009.[5] PFOA is furthermore listed on the SVHC-candidates list of the European Chemicals Agency as CMR-substance.[6] Shorter chain compounds with C_6F_{13} and C_4F_9 residues are also quite persistent, although their dwell time in organisms is much shorter. Actually, a recent study on the cytotoxicity and bioaccumulation of C_6 to C_{10} perfluoroalkanoic acids showed, that compounds with C_6 to C_8 are not cytotoxic in concentrations up to 200 mg/L, whereas C_9 and C_{10} compounds are already harmful at 25 mg/L. Furthermore, the C_6 compound could not – in contrast to the longer chain compounds – be detected by mass spectrometry inside the cells.[7] It was furthermore proposed in the literature, that compounds with C_6F_{13} and C_4F_9 residues possess improved biodegradability.[8] Therefore, several industrial initiatives started off identifying replacements for perfluoroalkyl materials, being e.g. shorter chain homologues or other types of fluorinated and non-fluorinated chemicals.[9] Having the great advantages of perfluorinated compounds with their outstanding material properties in view, we would like to contribute to this field with new environmentally optimized compounds being readily accessible.

As a manufacturer of water repellent textile coatings, we are also aiming at identifying new compounds with attributes fitting into on the one hand our property characteristics and being on the other hand degradable after exposure into the environment. We propose that both features will be addressed by compounds with a secondary alcohol function possessing an aromatic scaffold and a perfluorohexyl chain (n-C_6F_{13}) as well as ethers and esters thereof. Furthermore, we prepared perfluorinated alkyl esters of aromatic oligocarboxylic acids. Herein we wish to disclose the synthesis of two small libraries of such compounds and their basic

physical properties.

Results and Discussion

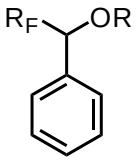
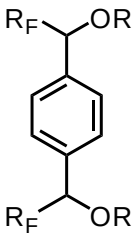
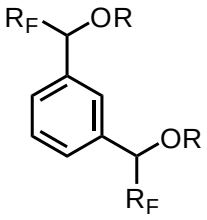
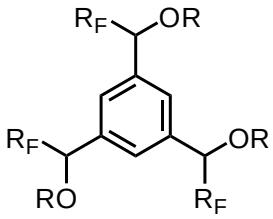
Perfluorohexylcarbinols and derivatives thereof. Our first synthetic approach to access a small library of compounds of potential interest started from perfluorohexyl iodide and is given in Scheme 1. Aromatic aldehydes **1a**–**1d** were converted with perfluorohexyl Grignard reagent ($n$$C_6F_{13}MgX$) to furnish the secondary alcohols **2a**–**2d**. After some experimentation with activated elemental Mg, it turned out that the Grignard reagent was conveniently prepared by magnesium-iodine exchange at low temperature from MeMgBr-solution and $n$$C_6F_{13}I$, as recommended in the literature.[10] Although compounds **2b** and **2c** possess two, and compound **2d** even three stereocenters no duplication of signal sets in the NMR spectra was observed, presumably due to line broadening by strong association in the NMR solvent.



Scheme 1. Synthesis of products **2a**–**2d** and **3a**–**3n** from aldehydes **1a**–**1d**. Reagents and conditions: (a) m equiv. MeMgBr, m equiv. $n$$C_6H_{13}I$, Et_2O, –78°C, 8 h; m = 1.5 for **1a**, m = 4 for **1b** and **1c**, m = 8 for **1d**; (b) For conditions, constitution of products and yields see Table 1. Ethx = 2-ethylhexanoyl, R_F = $n$$C_6F_{13}$.

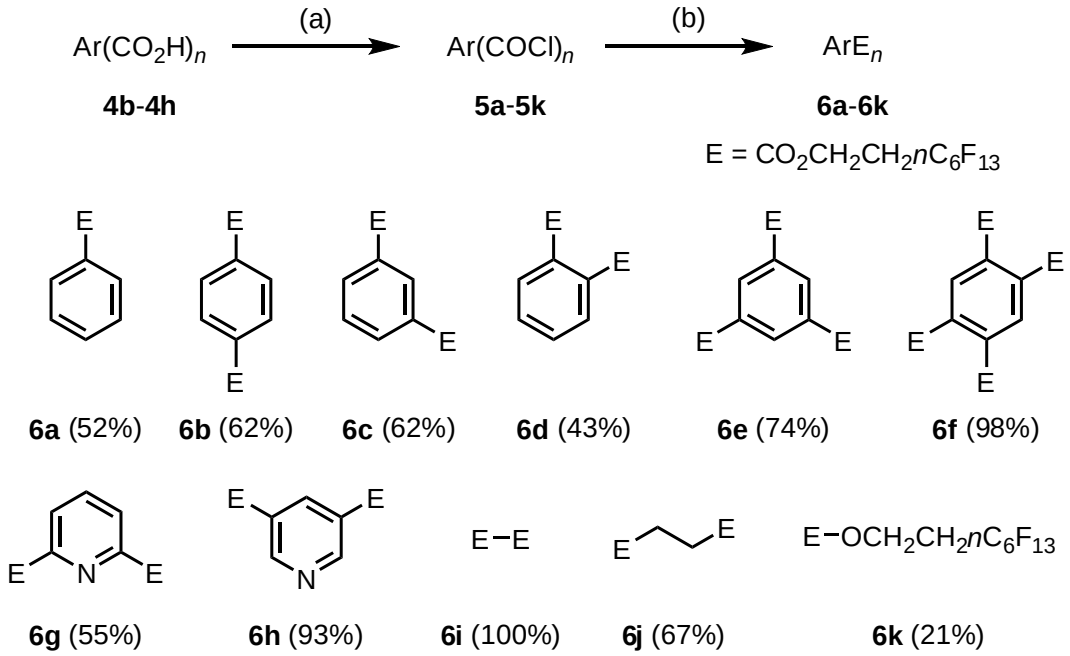
Since alcohols **2** are relatively polar compounds and moreover could associate with water by hydrogen bonding, we explored further transformations by either alkylation or acylation. Suitable conditions were first elaborated for the simplest scaffold represented by compound **2a** (for constitutions of products, yields and conditions see Table 1). After deprotonation with a small excess of NaH, alkylation was achieved with a large excess of MeI, EtI, *n*PrBr or *n*HexBr in THF at 50°C. The highest yield was achieved for product **3a** (entry 1), which is not surprising since MeI is the sterically least hindered electrophile. Surprisingly, the yields for the ethyl, propyl and hexyl ethers do neither correlate with the leaving group (iodide vs. bromide) nor with the lengths of the alkyl chains (range 8–42%, entires 3–5). Best results for acylations were achieved when treating the alcohol **2a** with an excess of the respective acid chloride (AcCl or 2-ethylhexanoylchloride = EthxCl) in pyridine. Yields were satisfying in both cases (52% and 62%, resp., entries 5 and 6). Compound **3f** has two stereocenters, thus, a doubled signal set (ratio 1 : 1) is observed in the NMR spectra. Alkylation of the disubstituted scaffolds **2b** and **2c** were performed with 5 equiv. of NaH and 5 equiv of MeI or EtI. For the *para*-isomer **2b** the methylation proceeded straightforwardly and product **3g** was obtained in 85% yield (entry 7). In analogy to the ethylation of compound **3b**, the yield of the ethyl ether **3h** was low (9%, entry 8). The ethylation was therefore not performed for the *meta*-isomer **2c**. In this case, only the methyl ether **3k** was prepared (66%, entry 11). Acylation of the *para*- and *meta*-dialcohols **2b** and **2c** were performed with 6 equiv. of acid chlorides yielding the esters **3i**, **3j**, **3l**, **3m** in 29-41% yield (entries 9, 10, 12, 13). The NMR spectra of products in entries 7–13 showed at least doubled (for Ethx-esters multiple) signal sets due to diastereoisomers (see experimental section for details). The triple functionalization of compound **2d** turned out to be rather difficult. The triacetyl-compound **3n** (64%, entry 14) was the only derivative which could be obtained.

Table 1. Etherification and esterification of alcohols **2a**–**2d**; R_F = nC_6F_{13}.

Scaffold	Entry	Product	R	Yield	Conditions
	1	**3a**	Me	75%	1.5 equiv. NaH, 6.0 equiv. MeI, EtI, *n*PrBr, or *n*HexBr, THF, 0°C→50°C, 17 h
	2	**3b**	Et	21%	
	3	**3c**	*n*Pr	8%	
	4	**3d**	*n*Hex	42%	
	5	**3e**	Ac	52%	1.5 equiv. AcCl, pyridine, 0°C→23°C, 24 h
	6	**3f**	Ethx	62%	2.0 equiv. EthxCl, pyridine, 0°C→23°C, 24 h
	7	**3g**	Me	85%	5.0 equiv. NaH, 5.0 equiv. MeI or EtI, THF, 0°C→50°C, 17 h
	8	**3h**	Et	9%	
	9	**3i**	Ac	45%	6.0 equiv. RCl, pyridine, 0°C→23°C, 24 h
	10	**3j**	Ethx	33%	
	11	**3k**	Me	66%	5.0 equiv. NaH, 5.0 equiv. MeI, THF, 0°C→50°C, 17 h
	12	**3l**	Ac	41%	6.0 equiv. RCl, pyridine, 0°C→23°C, 24 h
	13	**3m**	Ethx	29%	
	14	**3n**	Ac	64%	6.0 equiv. AcCl, pyridine, 0°C→23°C, 24 h

It has to be pointed out, that we were not able to obtain mass spectrometric data of most of compounds **3**, neither by using EI, CI or ESI techniques. In these cases, matching elemental analyses were obtained from respective products in order to have proof for the elemental compositions.

Esters of oligocarboxylic acids. As a second building block we utilized 2-(perfluorohexyl)ethanol for the preparation of esters from several oligocarboxylic acids. The acid chlorides were either prepared by treating the carboxylic acids with an excess of $SOCl_2$,[11] if they were not commercially available like PhCOCl (**5a**), $(COCl)_2$ (**5i**) or the solution of phosgene (**5k**) in toluene. The acid chlorides were then reacted with the alcohol $nC_6F_{13}CH_2CH_2OH$ in pyridine solution to yield the corresponding esters **6a**–**6k** after acidic workup, extraction and crystallization from CH_2Cl_2.



Scheme 2. Synthesis of esters and from carboxylic acids **4b**–**4h** *via* the acid chlorides **5a**–**5k**; for products **6a**, **6i** and **6k** acid chlorides were used directly (yield given over one step); compound **5j** was prepared from succinic anhydride and $SOCl_2$; in case of compound **6k** a solution of phosgene (**5k**) in toluene was used. For products **6b**–**6h** and **6i** the given yield is over two steps. Reagents and conditions: (a) xs. $SOCl_2$, 4 h, 80°C; (b) 1.5 equiv. (per COCl group) $nC_6F_{13}CH_2CH_2OH$, pyridine, 3 h, 90°C. E = $CO_2CH_2CH_2nC_6F_{13}$.

Physical Properties. In order to obtain a first impression of water repellency of the new products we have investigated the wettability of a thin film spread on a glass surface by measuring the water contact angle. Figure 1 shows a representative photograph of the droplet on the impregnated surface. Table 2 lists the average of left and right angle together with the melting point and the fluorine content. Obviously, no correlation can be derived from the angles and the two other pieces of data. A great influence, however, seems to have the constitution of the compound: As an example, the angle for the constitutional *ortho*, *meta* and *para* isomers (compounds **6b**, **6c**, **6d**) jumps from ca. 120° *via* 135° to 75°. These results make clear, that predictions cannot be made, and all compounds must instead be investigated individually, which will be our main task within the near future. Anyhow, although we have prepared no compound with a contact angle >150°, which is normally regarded as "super-hydrophobic",[12] with six out of 29 compounds with a contact angle >130° we seem to be on the right way in order to obtain hydrophobic compounds suitable for textile impregnation, which are expected to be – as a benefit of shorter perfluoroalkyl chains – bio-degradable.

Table 2. Selected properties of fluorinated compounds: Melting points, fluorine content (% w/w) and water contact angles (the average value between left and right angle together with its span width is given).

Compound	contact angle	Fluorine content / % w/w	mp.
2a	111.4±0.3°	58	53°C
2b	126.9±0.2°	64	133°C
2c	136.5±0.1°	64	86°C
2d	103.8±0.5°	66	131°C

3a	27.5±1.0°	56	–[a]
3b	64.6±0.8°	54	–[a]
3c	30.9±1.0°	53	–[a]
3d	33.3±1.4°	48	–[a]
3e	140.3±0.0°	53	43°C
3f	118.3±0.4°	45	41°C
3g	123.2±0.6°	62	70°C
3h	42.1±0.2°	59	–[a]
3i	116.0±0.1°	58	109°C
3j	130.9±0.2°	48	99°C
3k	126.1±0.2°	62	45°C
3l	133.0±0.7°	58	66°C
3m	82.8±0.6°	48	–[a]
3n	119.1±0.1°	59	–[a]
6a	47.2±1.1°	58	–[a]
6b	121.1±0.2°	58	161°C
6c	133.9±0.1°	58	47°C
6d	74.3±0.2°	58	36°C
6e	112.8±0.2°	58	73°C
6f	117.8±0.1°	60	114°C
6g	118.6±0.9°	57	127°C
6h	117.2±1.0°	57	132°C
6i	136.0±0.0°	63	43°C
6j	85.3±2.0°	61	–[a]
6k	43.8±0.2°	65	–[a]

[a] not a solid at ambient temperature.

Figure 1. Shape of a water droplet on a glass surface coated with compound **2c**; contact angles are 136.4° and 136.5°, resp.

Summary. We have prepared 29 new compounds with up to four perfluoro-*n*-hexyl moieties, which shall serve as materials for textile coatings. As a first survey of their property profile, we have investigated their wettability by water contact angle measurements of a thin film on a glass surface. In up to six cases, contact angles >130° were observed indicating, that the products might be suitable candidates for the impregnation of surfaces. Further studies are in progress in our laboratories, in particular, studies on the biodegradability of the new compounds. The latter shall actually be the key property of the new materials. With their relatively short perfluoroalkyl side chains and therefore low bioaccumulativity, the target compounds might be beneficial alternatives to established products, like PFOA ($C_7F_{15}CO_2H$) and PFOS ($C_8F_{17}SO_3H$).

The compounds prepared in this study divide into two classes: Perfluorohexyl carbinols were prepared from the respective Grignard reagent and benz-, terephthal-,

isophthal- and trimesalydehyde (four products). The corresponding secondary alcohols were further transformed by ether (methyl, ethyl, propyl and *n*-hexyl) and ester formation (with acetyl chloride and 2-ethylhexanoyl chloride) yielding 14 derivatives. As a second set of 15 compounds, we have prepared perfluoroalkyl esters from aromatic, heteroaromatic and aliphatic mono-, di-, tri- and tetracarboxylic acids and tridecafluorooctanol.

Experimental Section

General: Preparative column chromatography was carried out using Merck SiO_2 (35–70 µm, type 60 A) with hexanes, *tert*-butyl methyl ether (MTBE), and ethyl acetate (EtOAc) as eluents. TLC was performed on Merck aluminium plates coated with SiO_2 F_{254}. ^{1}H-, ^{19}F- and ^{13}C-NMR spectra were recorded on a Bruker Avance DRX 500 instrument. Multiplicities of carbon signals were determined with DEPT experiments. MS and HRMS spectra of products were obtained with a Waters Q-TOF Premier (ESI) spectrometer. IR spectra were recorded on a Bruker Tensor 27 spectrometer equipped with a "GoldenGate" diamond ATR unit. Elemental analyses were determined with a Euro EA-CHNS instrument from HEKAtech. Contact angle measurements were performed with a Contact Angle System OCA, model 15plus from dataphysics and a Teli ccd camera, model CS8620C1. The droplet volume was 9 µL and photograph was taken after 2 s. All starting materials were commercially available. In particular, *n*$C_6F_{13}I$ was purchased from Apollo, *n*$C_6F_{13}CH_2CH_2OH$ from DuPond, and MeMgBr solution from Sigma-Aldrich.

2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-phenyl-1-heptanol (2a).[13] Under an inert atmosphere (N_2) and exclusion of moisture, MeMgBr (15.0 mL, 44.7 mmol, 3 mol L^{-1} solution in Et_2O, 1.5 equiv.) was added at –78°C (dry ice-acetone bath) to a solution of $nC_6F_{13}I$ (19.9 g, 44.7 mmol, 1.5 equiv.) in Et_2O (60 mL) and the resulting mixture was stirred for 2 h at the same temperature. Subsequently, freshly distilled PhCHO (**1a**) (3.16 g, 29.8 mmol, 1.00 equiv.) was added at –78°C and the solution was stirred for further 8 h at the same temperature. Saturated, aqueous NH_4Cl solution (25 mL) was added to the mixture. After warming to ambient temperature, the layers were separated and the aqueous layer extracted with MTBE (3 x 30 mL). The combined organic layers were washed with water (2 x 30 mL) and brine (2 x 30 mL), dried ($MgSO_4$) and evaporated after filtration. The residue was purified by chromatography (SiO_2, hexanes/MTBE 5 : 1, R_f = 0.45) to furnish the product **2a** (12.7 g, 29.8 mmol, 100%) as a colorless solid, mp. 53°C (lit. 47°C[13a]). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.43 (d, *J* = 5.1 Hz, 1H), 5.21 (dt, *J* = 17.8 Hz, *J* = 5.7 Hz, 1H), 7.39–7.51 (m, 5H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 72.37–72.78 (m, CH), 128.17 (2 CH), 128.81 (2 CH), 129.89 (CH), 134.13 (C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.80 (tt, *J* = 9.6 Hz, *J* = 2.6 Hz), (–117.55)–(–126.84) (m) ppm. IR (ATR): nu(tilde) = 3438 (m), 1497 (w), 1458 (s), 1365 (m), 1316 (w), 1227 (s), 1201 (s), 1141 (s), 1058 (m), 1047 (s), 1028 (m), 1004 (w), 827 (w), 776 (m), 734 (m), 717 (s), 698 (s), 662 (m), 626 (m) cm^{-1}. MS (ESI, neg. mode): m/z (%) = 851 (25) [2 M – H^+], 471 (100), 319 (20). All spectroscopic data are in accordance with the literature.[13] $C_{13}H_7F_{13}O$ (426.18): calcd. C 36.64%, H 1.66%; found C 36.32%, H 1.51%.

1,4-Bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-hydroxyheptyl)benzene (2b). Following the procedure given above for compound **2a**, *n*$C_6F_{13}I$ (26.8 g, 60.0 mmol, 4.0 equiv.), MeMgBr (20.0 mL, 60.0 mmol, 3 mol L^{-1} solution in Et_2O, 4.0 equiv.) and terephthalaldehyde (**1b**) (2.10 g, 15.0 mmol, 1.0 equiv.) were converted to give the title compound **2b** (10.3 g, 13.3 mmol, 88%) as a colorless solid (mp. 133°C) after chromatography (SiO_2, hexanes/MTBE 1 : 1, R_f = 0.61). ^{1}H-NMR (500 MHz, acetone-d_6): δ = 5.46 (dd, *J* = 20.4 Hz, *J* = 5.2 Hz, 2H), 7.64 (s, 4H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, acetone-d_6): δ = 71.75–72.20 (m, 2 CH), 129.13 (4 CH), 137.36 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, acetone-d_6): δ = 49.86–61.06 (m), 95.72 (tt, *J* = 10.3 Hz, *J* = 2.7 Hz) ppm. IR (ATR): nu(tilde) = 3404 (m), 2925 (m), 1426 (w), 1365 (m), 1318 (m), 1230 (s), 1187 (s), 1142 (s), 1118 (s), 1066 (s), 1051 (m), 1019 (w), 942 (w), 914 (w), 863 (w), 846 (w), 813 (m), 785 (m), 764 (m), 738 (m), 717 (s), 709 (s), 691 (s), 654 (s) cm^{-1}. HR-MS (ESI, neg. mode): calcd. 773.0031 (for $C_{20}H_7F_{26}O_2$), found 773.0042 [M – H^+]. $C_{20}H_8F_{26}O_2$ (774.24).

1,3-Bis(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-hydroxyheptyl)benzene (2c). Following the procedure given above for compound **2a**, *n*$C_6F_{13}I$ (26.8 g, 60.0 mmol, 4.0 equiv.), MeMgBr (20.0 mL, 60.0 mmol, 3 mol L^{-1} solution in Et_2O, 4.0 equiv.) and isophthalaldehyde (**1c**) (2.10 g, 15.0 mmol, 1.0 equiv.) were converted to give the title compound **2c** (8.67 g, 11.2 mmol, 75%) as a colorless solid (mp. 86°C) after chromatography (SiO_2, hexanes/MTBE 1 : 1, R_f = 0.61). Due to two diastereoisomers (ratio ca. 1 : 1), the ^{13}C-NMR spectrum shows a partly doubled signal set. ^{1}H-NMR (500 MHz, acetone-d_6): δ = 5.48 (dd, *J* = 19.8 Hz, *J* = 5.7 Hz, 2H), 7.50 (t, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.78 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, acetone-d_6): δ = 71.85–72.26 (m, 2 CH), 128.99 (CH), 129.27 (½ CH), 129.31 (½ CH), 129.95 (2 CH), 136.52 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, acetone-d_6): δ = 49.77–60.73 (m),

95.66 (t, *J* = 10.1 Hz) ppm. IR (ATR): nu(tilde) = 3576 (w), 1366 (w), 1317 (w), 1231 (s), 1194 (s), 1138 (s), 1120 (s), 1067 (s), 907 (w), 781 (w), 756 (m), 733 (w), 719 (m), 706 (s), 662 (m), 633 (m) cm^{-1}. HR-MS (ESI, neg. mode): calcd. 773.0031 (for $C_{20}H_7F_{26}O_2$), found 773.0031 [M – H^+]. $C_{20}H_8F_{26}O_2$ (774.24).

1,3,5-Tris(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-hydroxyheptyl)benzene (2d). Following the procedure given above for compound **2a**, *n*$C_6F_{13}I$ (22.0 g, 49.3 mmol, 8.00 equiv.), MeMgBr (16.6 mL, 49.3 mmol, 3 mol L^{-1} in Et_2O, 8.00 equiv.) and trialdehyde **1d** (1.00 g, 6.17 mmol, 1.00 equiv.) were converted to give the title compound **2d** (3.51 g, 3.12 mmol, 51%) as a colorless solid (mp. 131°C) after recrystallization from CH_2Cl_2 (50 mL). ^{1}H-NMR (500 MHz, acetone-d_6): δ = 5.55 (dt, *J* = 18.9 Hz, *J* = 6.1 Hz, 3H), 6.03 (d, *J* = 6.0 Hz, 3H), 7.82 (s, 3H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, acetone-d_6): δ = 71.84–72.30 (m, 3 CH), 129.88 (3 CH), 136.63 (3 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, acetone-d_6): δ = 50.07–60.57 (m), 95.73 (t, *J* = 10.4 Hz) ppm. IR (ATR): nu(tilde) = 3368 (w), 1367 (w), 1319 (w), 1231 (s), 1192 (s), 1174 (s), 1121 (s), 1057 (m), 903 (w), 698 (s) cm^{-1}. $C_{27}H_9F_{39}O_3$ (1122.30): calcd. C 28.90%, H 0.81%; found C 29.01%, H 0.52%.

(2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-methoxyheptyl)benzene (3a). NaH (14 mg, 60% *w/w* dispersion in mineral oil, 0.35 mmol, 1.5 equiv.) was washed with hexanes (2 x 5 mL), dried in vacuum and then added to a solution of alcohol **2a** (100 mg, 0.235 mmol, 1.0 equiv.) in THF (2 mL). The resulting mixture was stirred at 50°C for 3 h and then cooled to 0°C. MeI (200 mg, 1.40 mmol, 6.0 equiv.) was added and the mixture warmed to ambient temperature and stirred for 17 h. Subsequently, the mixture was diluted with MTBE (10 mL) and washed with water (2 x 10 mL) and brine (2 x 10 mL). The organic layer was dried ($MgSO_4$) and evaporated after filtration to yield the title compound **3a** (78.0 mg, 0.177 mmol, 75%) as a colorless oil. ^{1}H-NMR

(500 MHz, $CDCl_3$): δ = 3.35 (s, 3H), 4.66 (dd, *J* = 19.7 Hz, *J* = 4.3 Hz, 1H), 7.42–7.45 (m, 5H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 57.76 (CH_3), 80.56–81.12 (CH), 128.69 (2 CH), 129.05 (2 CH), 129.83 (CH), 131.72 (C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.78 (tt, *J* = 9.9 Hz, *J* = 2.7 Hz), (–115.51)–(–126.96) (m) ppm. IR (ATR): nu(tilde) = 2924 (m), 2855 (m), 1716 (w), 1458 (m), 1365 (m), 1352 (m), 1237 (s), 1145 (s), 1121 (s), 1068 (m), 1030 (w), 988 (w), 860 (w), 789 (w), 776 (w), 731 (m), 716 (m), 699 (m), 664 (w), 620 (w) cm^{-1}. $C_{14}H_9F_{13}O$ (440.20): calcd. C 38.20%, H 2.06%; found C 38.58%, H 2.22%.

(1-Ethoxy-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)benzene (3b). Following the procedure given above for product **3a**, alcohol **2a** (200 mg, 0.470 mmol, 1.0 equiv.) was deprotonated with NaH (28 mg, 60% *w/w* dispersion in mineral oil, 0.71 mmol, 1.5 eq) and alkylated with ethyl iodide (440 mg, 2.82 mmol, 6.0 equiv.) to furnish the title compound **3b** (44 mg, 0.097 mmol, 21%) as a colorless oil after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.45). ^1H-NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.0 Hz, 3H), 3.45 (dq, *J* = 9.2 Hz, *J* = 7.2 Hz, 1H), 3.53 (dq, *J* = 9.2 Hz, *J* = 7.0 Hz, 1H), 4.77 (dd, *J* = 19.9 Hz, *J* = 4.6 Hz, 1H), 7.40–7.45 (m, 5H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 14.98 (CH_3), 65.91 (CH_2), 78.86–79.26 (CH), 128.60 (2 CH), 128.98 (2 CH), 129.66 (CH), 132.49 (C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.84 (tt, *J* = 10.3 Hz, *J* = 3.1 Hz), (–115.26)–(–127.12) (m) ppm. IR (ATR): nu(tilde) = 2985 (w), 2888 (w), 2361 (w), 2338 (w), 1644 (w), 1497 (w), 1458 (w), 1408 (w), 1351 (w), 1315 (w), 1234 (s), 1195 (s), 1144 (s), 1106 (s), 1075 (m), 1068 (m), 1034 (m), 968 (w), 944 (w), 898 (w), 856 (w), 817 (w), 787 (w), 776 (w), 729 (m), 714 (m), 698 (s), 663 (m) cm^{-1}. $C_{15}H_{11}F_{13}O$ (454.23): calcd. C 39.66%, H 2.44%; found C 39.26%, H 2.33%.

[2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-(propyloxy)heptyl]benzene (3c). Following the procedure given above for product **3a**, alcohol **2a** (200 mg, 0.470 mmol, 1.0 equiv.) was deprotonated with NaH (28 mg, 60% *w/w* dispersion in mineral oil, 0.71 mmol, 1.5 eq) and alkylated with 1-bromopropane (347 mg, 2.82 mmol, 6.0 equiv.) to furnish the title compound **3c** (18 mg, 0.038 mmol, 8%) as a colorless oil after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.43). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.4 Hz, 3H), 1.57–1.65 (m, 2H), 3.33 (dt, *J* = 8.9 Hz, *J* = 6.5 Hz, 1H), 3.42 (dt, *J* = 8.9 Hz, *J* = 6.4 Hz, 1H), 4.75 (dd, *J* = 20.1 Hz, *J* = 4.6 Hz, 1H), 7.40–7.44 (m, 5H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 10.56 (CH_3), 22.88 (CH_2), 72.08 (CH_2), 79.14–79.54 (CH), 128.59 (2 CH), 129.02 (2 CH), 129.64 (CH), 132,46 (C) ppm. ^{19}F{^{1}H}-NMR (470 MHz, $CDCl_3$): δ = –80.81 (tt, *J* = 10.1 Hz, *J* = 2.9 Hz), (–115.33)–(–127.03) (m) ppm. IR (ATR): nu(tilde) = 3077 (w), 2971 (w), 2885 (w), 2364 (w), 2345 (w), 1640 (m), 1459 (m), 1354 (m), 1236 (s), 1198 (s), 1146 (s), 1123 (s), 1078 (m), 1033 (m), 1003 (w), 968 (m), 913 (w), 858 (m), 818 (m), 789 (m), 778 (m), 730 (m), 700 (s), 666 (m) cm^{-1}. $C_{16}H_{16}F_{13}O$ (468.26): calcd. C 41.04%, H 2.80%; found C 40.70%, H 2.90%.

[2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoro-1-(hexyloxy)heptyl]benzene (3d). Following the procedure given above for product **3a**, alcohol **2a** (200 mg, 0.470 mmol, 1.0 equiv.) was deprotonated with NaH (28 mg, 60% *w/w* dispersion in mineral oil, 0.71 mmol, 1.5 eq) and alkylated with 1-bromohexane (465 mg, 2.82 mmol, 6.0 equiv.) to furnish the title compound **3d** (100 mg, 0.196 mmol, 42%) as a colorless oil after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.43). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3H), 1.21–1.37 (m, 6H), 1.55–1.61 (m, 2H), 3.36 (dt, *J* = 8.9 Hz, *J* = 6.5 Hz, 1H), 3.44 (dt, *J* = 9.0 Hz, *J* = 6.5 Hz, 1H), 4.74 (dd, *J* = 19.8 Hz, *J* = 4.6 Hz, 1H), 7.40–7.44 (m, 5H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 14.08

(CH_3), 22.67 (CH_2), 25.63 (CH_2), 29.54 (CH_2), 31.59 (CH_2), 70.48 (CH_2), 79.15–79.56 (CH), 128.58 (2 CH), 129.02 (2 CH), 129.64 (CH), 132.47 (C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.81 (tt, *J* = 10.5 Hz, *J* = 2.1 Hz), (–115.31)–(–126.99) (m) ppm. IR (ATR): nu(tilde) = 2938 (w), 2866 (w), 1459 (w), 1353 (w), 1236 (s), 1199 (s), 1146 (s), 1122 (s), 1069 (m), 700 (s) cm^{-1}. $C_{19}H_{19}F_{13}O$ (510.34): calcd. C 44.72%, H 3.75%; found C 44.37%, H 3.49%.

(1-Acetoxy-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-phenyl)heptan (3e). AcCl (553 mg, 7.04 mmol, 1.5 equiv.) was added to ice-cooled pyridine (4 mL) and the resulting mixture stirred for 10 min at 0°C. Subsequently, alcohol **2a** (2.00 g, 4.69 mmol, 1.0 equiv.) was added and the mixture stirred for 1 d at ambient temperature. Finally, water (20 mL) was added and the mixture acidified to pH 3 with conc. hydrochloric acid (10 mL). After extraction with MTBE (2 x 20 mL) the combined organic layers were dried ($MgSO_4$) and the solvent evaporated after filtration. Chromatographic purification of the residue (SiO_2, hexanes/MTBE 50 : 1, R_f = 0.39) gave the title compound **3e** (1.14 g, 2.43 mmol, 52%) as a colorless solid, mp. 43°C. ^1H-NMR (500 MHz, $CDCl_3$): δ = 2.17 (s, 3H), 6.30 (dd, *J* = 17.7 Hz, *J* = 6.6 Hz, 1H), 7.39–7.48 (m, 5H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 20.63 (CH_3), 71.08–71.49 (CH), 128.78 (2 CH), 128.77 (2 CH), 130.11 (CH), 131.07 (C), 168.45 (C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.84 (tt, *J* = 9.6 Hz, *J* = 2.6 Hz), (–115.99)–(–126.82) (m) ppm. IR (ATR): nu(tilde) = 3047 (w), 2971 (w), 1762 (m), 1375 (m), 1357 (m), 1216 (s), 1205 (s), 1145 (s), 1122 (m), 1091 (m), 1065 (m), 738 (m), 728 (m), 716 (m), 699 (s), 660 (m) 609 (m) cm^{-1}. $C_{15}H_9F_{13}O_2$ (468.21): calcd. C 38.48%, H 1.94%; found C 38.42%, H 1.76%.

2-Ethylhexanoic acid [(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-phenyl)heptyl]-ester (3f). According to the procedure reported above for the preparation of compound **3e**, the alcohol **2a** (2.00 g, 4.69 mmol, 1.0 equiv.), 2-ethylhexanoyl chloride (1.53 g, 9.38 mmol, 2.0 equiv.) and pyridine (5 mL) were converted to yield the title compound **3f** (1.95 g, 3.53 mmol, 62%) as a colorless solid, mp. 41°C, after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.52). The products is obtained as a mixture of two diastereoisomers; two signal sets (ratio 1 : 1) were observed in the NMR spectra. ^{1}H-NMR (500 MHz, acetone-d_6): δ = 0.79–0.97 (m, 6H), 1.10–1.38 (m, 4H), 1.38–1.50 (m, 4H), 2.39–2.50 (m, 1H), 6.45 (dd, *J* = 19.6 Hz, *J* = 5.9 Hz, 1H), 7.48–7.49 (m, 3H), 7.57–7.61 (m, 2H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, acetone-d_6); isomer A: δ = 11.83 (CH_3), 14.05 (CH_3), 23.18 (CH_2), 25.56 (CH_2), 29.97 (CH_2), 31.84 (CH_2), 47.91 (CH), 71.63–72.05 (CH), 129.51 (2 CH), 129.65 (2 CH), 130.93 (CH), 132.13 (C), 172.39 (C) ppm; isomer B: δ = 11.84 (CH_3), 14.06 (CH_3), 23.21 (CH_2), 25.85 (CH_2), 30.05 (CH_2), 32.24 (CH_2), 47.96 (CH), 71.63–72.05 (CH), 129.51 (2 CH), 129.66 (2 CH), 130.93 (CH), 132.13 (C), 173.90 (C) ppm. ^{19}F{^{1}H}-NMR (470 MHz, acetone-d_6): δ = 49.93–61.52 (m), 95.77 (tt, *J* = 10.1 Hz, *J* = 2.8 Hz) ppm. IR (ATR): nu(tilde) = 2965 (w), 2944 (w), 2874 (w), 1743 (s), 1458 (w), 1229 (s), 1190 (s), 1148 (s), 1122 (s), 1070 (s), 699 (s) cm^{-1}. $C_{21}H_{21}F_{13}O_2$ (552.38): calcd. C 45.66%, H 3.83%; found C 45.32%, H 4.06%.

1,4-Bis[(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-methoxy)heptyl]benzene (3g). Following the procedure given above for product **3a**, alcohol **2b** (100 mg, 0.129 mmol, 1.00 equiv.) was deprotonated with NaH (26 mg, 60% *w/w* dispersion in mineral oil, 0.65 mmol, 5.0 eq) and alkylated with methyl iodide (92 mg, 0.65 mmol, 5.0 equiv.) to furnish the title compound **3g** (85 mg, 0.11 mmol, 85%) as a colorless solid, mp. 70°C, after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.29). ^{1}H-

NMR (500 MHz, $CDCl_3$): δ = 3.37 (s, 6H), 4.66 (dd, *J* = 19.6 Hz, *J* = 4.3 Hz, 2H), 7.50 (s, 4H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 58.02 (2 CH_3), 80.28–80.72 (2 CH), 129.18 (4 CH), 133.38 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.86 (tt, *J* = 10.6 Hz, *J* = 2.2 Hz), (–115.45)–(–127.10) (m) ppm. IR (ATR): nu(tilde) = 2949 (w), 1451 (w), 1424 (w), 1369 (w), 1354 (w), 1318 (w), 1234 (s), 1194 (s), 1143 (s), 1097 (s), 1069 (s), 1051 (m), 1023 (w), 988 (m), 944 (w), 916 (w), 882 (w), 846 (w), 818 (w), 801 (w), 770 (w), 739 (w), 719 (m), 691 (m), 657 (s), 607 (m) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 803.0500 (for $C_{22}H_{13}F_{26}O_2$), found 803.0500 [M + H^+]. $C_{22}H_{12}F_{26}O_2$ (802.29).

1,4-Bis[(1-ethoxy-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro)heptyl]benzene (3h). Following the procedure given above for product **3a**, alcohol **2b** (200 mg, 0.258 mmol, 1.00 equiv.) was deprotonated with NaH (52 mg, 60% *w/w* dispersion in mineral oil, 1.3 mmol, 5.0 eq) and alkylated with ethyl iodide (403 mg, 2.58 mmol, 10 equiv.) to furnish the title compound **3h** (19 mg, 0.023 mmol, 9%) as a colorless oil after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.41). ^1H-NMR (500 MHz, acetone-d_6): δ = 1.21 (t, *J* = 7.0 Hz, 6H), 3.56 (q, *J* = 7.0 Hz, 4H), 5.22 (dd, *J* = 20.6 Hz, *J* = 4.3 Hz, 2H), 7.65 (s, 4H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, acetone-d_6): δ = 15.19 (2 CH_3), 66.48 (2 CH_2), 78.75–78.98 (2 CH), 129.94 (4 CH), 134.89 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, acetone-d_6): δ = 49.81–64.82 (m), 95.79 (tt, *J* = 10.3 Hz, *J* = 2.3 Hz) ppm. IR (ATR): nu(tilde) = 2957 (m), 2925 (m), 2855 (m), 1715 (w), 1459 (w), 1365 (m), 1313 (w), 1231 (s), 1190 (s), 1143 (s), 1109 (s), 1081 (m), 1068 (m), 1037 (m), 1022 (m), 970 (w), 874 (w), 859 (w), 811 (w), 792 (w), 744 (m), 735 (m), 718 (m), 709 (m), 689 (m) cm^{-1}. $C_{24}H_{16}F_{26}O_2$ (830.35): calcd. C 34.72%, H 1.94%; found C 34.85%, H 2.12%.

1,4-Bis(1-acetoxy-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)benzene (3i). According to the procedure reported above for the preparation of compound **3e**, the alcohol **2b** (2.00 g, 2.58 mmol, 1.0 equiv.), acetyl chloride (1.22 g, 15.5 mmol, 6.0 equiv.) and pyridine (10 mL) were converted to yield the title compound **3i** (1.00 g, 1.17 mmol, 45%) as a colorless solid, mp. 109°C, after chromatography (SiO_2, hexanes/MTBE 25 : 1, R_f = 0.52). Due to two diastereoisomers (ratio ca. 1 : 1), the ^{13}C-NMR spectrum shows a partly doubled signal set. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.18 (s, 6H), 6.32 (dd, *J* = 18.3 Hz, *J* = 5.3 Hz, 2H), 7.51 (s, 4H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 20.60 (2 CH_3), 70.56–70.97 (2 CH), 129.05 (½ x 4 CH), 129.11 (½ x 4 CH), 132.91 (C), 132.94 (C), 168.32 (2 C) ppm. ^{19}F{^{1}H}-NMR (470 MHz, $CDCl_3$): δ = –80.79 (tt, *J* = 10.4 Hz, *J* = 2.7 Hz), (–115.78)–(–127.16) (m) ppm. IR (ATR): nu(tilde) = 2975 (w), 1762 (s), 1377 (m), 1202 (s), 1184 (s), 1122 (s), 1062 (s), 1023 (m), 920 (m), 689 (s) cm^{-1}. $C_{24}H_{12}F_{26}O_4$ (858.31): calcd. C 33.58%, H 1.41%; found C 33.84%, H 1.13%.

1,4-Bis[1-(2-ethylhexanoyloxy)(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)]benzene (3j). According to the procedure reported above for the preparation of compound **3e**, the alcohol **2b** (2.00 g, 2.58 mmol, 1.0 equiv.), 2-ethylhexanoyl chloride (2.52 g, 15.5 mmol, 6.0 equiv.) and pyridine (5 mL) were converted to yield the title compound **3j** (867 mg, 0.845 mmol, 33%) as a colorless solid, mp. 99°C, after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.17). The product is obtained as a mixture of several diastereoisomers; two signal sets (ratio 1.2 : 1) were observed in the NMR spectra. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.75–0.85 (m, 12H), 1.07–1.34 (m, 8H), 1.45–1.70 (m, 8H), 2.39 (tt, *J* = 5.4 Hz, *J* = 8.8 Hz, 2H), 6.32 (dd, *J* = 5.6 Hz, *J* = 17.4 Hz, 2H), 7.50 (s, 4H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$); isomer A: δ = 11.58 (2 CH_3), 13.78 (2 CH_3), 22.58 (2 CH_2), 25.27 (2 CH_2), 29.44 (2

CH_2), 31.54 (2 CH_2), 47.28 (2 CH), 70.05–71.14 (2 CH), 129.04 (4 CH), 133.13 (2 C), 173.77 (2 C) ppm; isomer B: δ = 11.62 (2 CH_3), 13.80 (2 CH_3), 22.63 (2 CH_2), 25.48 (2 CH_2), 29.44 (2 CH_2), 31.73 (2 CH_2), 47.28 (2 CH), 70.05–71.14 (2 CH), 129.04 (4 CH), 133.13 (2 C), 173.78 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.83 (tt, *J* = 9.7 Hz, *J* = 2.8 Hz), (–115.87)–(–127.17) (m) ppm. IR (ATR): nu(tilde) = 2968 (w), 2943 (w), 2869 (w), 1746 (s), 1461 (w), 1384 (w), 1366 (w), 1317 (w), 1281 (w), 1230 (s), 1188 (vs), 1173 (s), 1150 (vs), 1132 (s), 1086 (m), 1070 (s), 1020 (w), 954 (w), 690 (s), 646 (s) cm^{-1}. $C_{36}H_{36}F_{26}O_4$ (1026.64): calcd. C 42.12%, H 3.53%; found C 42.41%, H 3.60%.

1,3-Bis[(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-1-methoxy)heptyl]benzene (3k). Following the procedure given above for product **3a**, alcohol **2c** (2.00 g, 2.58 mmol, 1.0 equiv.) was deprotonated with NaH (516 mg, 60% w/w dispersion in mineral oil, 12.9 mmol, 5.0 equiv.) and alkylated with methyl iodide (1.83 g, 12.9 mmol, 5.00 equiv.) to furnish the title compound **3k** (1.36 mg, 1.69 mmol, 66%) as a brownish solid after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.55), mp. 45°C. Due to two diastereoisomers (ratio ca. 1 : 1), the ^1H-and ^{13}C-NMR spectra show partly doubled signal sets. ^1H-NMR (500 MHz, $CDCl_3$): δ = 3.36 (s, ½ x 6H), 3.37 (s, ½ x 6H), 4.71 (dd, *J* = 19.1 Hz, *J* = 4.9 Hz, 2H), 7.49–7.53 (m, 4H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 57.89 (2 CH_3), 80.41–80.84 (2 CH), 128.95 (½ CH), 129.01 129.31 129.47 (½ CH), 130.27 (½ x 2 CH), 130.34 (½ x 2 CH), 132.32 (½ x 2 C), 132.36 (½ x 2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.88 (tt, *J* = 9.8 Hz, *J* = 2.5 Hz), (–115.77)–(–126.97) (m) ppm. IR (ATR): nu(tilde) = 2256 (w), 1243 (m), 1209 (m), 1150 (w), 905 (s), 726 (s), 652 (m), 586 (w) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 825.0320 (for $C_{22}H_{12}F_{26}NaO_2$), found 825.0320 [M + Na^+]. $C_{22}H_{12}F_{26}O_2$ (830.35).

1,3-Bis(1-acetoxy-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)benzene (3l). According to the procedure reported above for the preparation of compound **3e**, the alcohol **2c** (2.00 g, 2.58 mmol, 1.00 equiv.), acetyl chloride (1.22 g, 15.5 mmol, 6.00 equiv.) and pyridine (10 mL) were converted to yield the title compound **3l** (910 mg, 1.06 mmol, 41%) as a colorless solid, mp. 66°C, after chromatography (SiO_2, hexanes/MTBE 50 : 1, R_f = 0.43). Due to two diastereoisomers (ratio ca. 1 : 1), the ^{1}H-NMR spectrum shows a partly doubled signal set. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.17 (s, ½ x 6H), 2.18 (s, ½ x 6H), 6.34 (dt, *J* = 5.8 Hz, *J* = 17.1 Hz, 2H), 7.45–7.49 (m, 1H), 7.52–7.56 (m, 3H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 20.54 (CH_3), 20.60 (CH_3), 70.61–71.04 (2 CH), 128.84 (CH), 129.14 (CH), 130.47 (2 CH), 131.78 (2 C), 168.27 (C), 168.39 (C) ppm. ^{19}F{^{1}H}-NMR (470 MHz, $CDCl_3$): δ = –80.85 (tt, *J* = 9.7 Hz, *J* = 2.1 Hz), (–116.65)–(–126.99) (m) ppm. IR (ATR): nu(tilde) = 3020 (w), 2980 (w), 2974 (w), 1770 (s), 1761 (s), 1434 (w), 1371 (m), 1314 (w), 1231 (s), 1190 (vs), 1140 (vs), 1122 (s), 1066 (s), 1039 (m), 919 (m), 707 (s) cm^{-1}. $C_{24}H_{12}F_{26}O_4$ (858.31): calcd. C 33.58%, H 1.41%; found C 33.61%, H 1.29%.

1,3-Bis[1-(2-ethylhexanoyloxy)(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)]benzene (3m). According to the procedure reported above for the preparation of compound **3e**, the alcohol **2c** (2.00 g, 2.58 mmol, 1.00 equiv.), 2-ethylhexanoyl chloride (2.52 g, 15.5 mmol, 6.00 equiv.) and pyridine (5 mL) were converted to yield the title compound **3m** (772 mg, 0.752 mmol, 29%) as a colorless oil after chromatography (SiO_2, hexanes/MTBE 100 : 1, R_f = 0.17). Three signal sets (ratio 5 : 4 : 1) were observed in the NMR spectra due to the six possible diastereoisomers of this compound. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.68–0.91 (m, 12H), 1.02–1.28 (m, 8H), 1.37–1.67 (m, 8H), 2.26–2.37(m, 2H), 6.23–6.30 (m, 2H), 7.34–7.47 (m, 3H),

7.53 (s, 1H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$); signal set A: δ = 11.58 (2 CH_3), 13.74 (2 CH_3), 22.55 (CH_2), 22.58 (CH_2), 25.00 (2 CH_2), 29.41 (2 CH_2), 31.21 (2 CH_2), 47.18 (2 CH), 70.36–71.08 (2 CH), 128.54 (CH), 128.89 (CH), 130.70 (2 CH), 131.85 (2 C), 173.70 (2 C) ppm; signal set B: δ = 11.63 (2 CH_3), 13.84 (2 CH_3), 22.60 (CH_2), 22.62 (CH_2), 25.23 (2 CH_2), 29.44 (2 CH_2), 31.48 (2 CH_2), 47.40 (2 CH), 70.36–71.08 (2 CH), 128.54 (CH), 130.16 (CH), 130.70 (2 CH), 131.85 (2 C), 173.78 (2 C) ppm; signal set C: δ = 11.77 (2 CH_3), 14.01 (2 CH_3), 22.76 (CH_2), 22.77 (CH_2), 25.45 (2 CH_2), 29.51 (2 CH_2), 31.62 (2 CH_2), 48.38 (2 CH), 70.36–71.08 (2 CH), 128.54 (CH), 129.05 (CH), 130.70 (2 CH) 131.85 (2 C), 173.85 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.88 (tt, *J* = 10.0 Hz, *J* = 2.6 Hz), (–116.39)–(–126.73) (m) ppm. IR (ATR): nu(tilde) = 2964 (m), 2937 (m), 2866 (w), 1812 (w), 1756 (m), 1463 (m), 1235 (s), 1195 (s), 1156 (s), 1069 (m), 1040 (m), 1026 (m), 703 (m) cm^{-1}. $C_{36}H_{36}F_{26}O_4$ (1026.64): calcd. C 42.12%, H 3.53%; found C 41.88%, H 1.57%.

1,3,5-Tris(1-acetoxy-2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)benzene (3n). According to the procedure reported above for the preparation of compound **3e**, the alcohol **2d** (1.00 g, 0.891 mmol, 1.00 equiv.), acetyl chloride (0.57 mL, 8.0 mmol, 9.0 equiv.) and pyridine (3 mL) were converted to yield the title compound **3n** (711 mg, 0.570 mmol, 64%) as a colorless oil after chromatography (SiO_2, hexanes/MTBE 20 : 1, R_f = 0.34). Three signal sets (ratio 2 : 3 : 4) were observed in the NMR spectra due to the two possible diastereoisomers of this compound; the major diastereoisomer possesses furthermore two diastereotopic side chains in the ratio 1 : 2. ^1H-NMR (500 MHz, $CDCl_3$): δ = 2.18–2.21 (m, 9H), 6.37 (dd, *J* = 8.3 Hz, *J* = 15.6 Hz, 3H), 7.61–7.63 (m, 3H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$); signal set A: δ = 20.46 (CH_3), 69.82–70.45 (m, 3 CH), 130.42 (3 CH), 132.46 (3 C), 168.11 (C) ppm; signal set B: δ = 20.52 (CH_3), 69.82–70.45 (m, 3 CH), 130.49 (3 CH), 132.50 (3 C), 168.21 (C) ppm;

signal set C: δ = 20.58 (CH_3), 69.82–70.45 (m, 3 CH), 130.53 (3 CH), 132.55 (3 C), 168.35 (C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = (–80.86)–(–80.94) (m), (–117.17)–(–127.16) (m) ppm. IR (ATR): nu(tilde) = 2976 (w), 1768 (s), 1374 (m), 1192 (vs), 1144 (vs), 1122 (s), 1066 (s), 896 (m), 735 (m), 708 (m) cm^{-1}. $C_{33}H_{15}F_{39}O_6$ (1248.41): calcd. C 31.75%, H 1.21%; found C 31.64%, H 1.33%.

(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoroctyl) benzoate (6a). The alcohol $nC_6F_{13}CH_2CH_2OH$ (1.16 mL, 5.34 mmol, 1.50 eq.) was added to an ice-cooled solution of PhCOCl (**5a**) (500 mg, 3.56 mmol, 1.00 eq.) in pyridine (5 mL) and the mixture was subsequently stirred for 96 h at ambient temperature. It was then diluted with water (30 mL) and acidified with conc. hydrochloric acid (7 mL) until pH 3. The mixture was extracted with MTBE (2 x 30 mL) and the combined organic extracts dried ($MgSO_4$) and evaporated after filtration. The oily residue was treated with CH_2Cl_2 (5 mL) in order to extract impurities. The oily layer was separated and dried to furnish the title compound **6a** (879 mg, 1.88 mmol, 52%) as a colorless oil. ^1H-NMR (500 MHz, $CDCl_3$): δ = 2.62 (tt, *J* = 18.1 Hz, *J* = 6.3 Hz, 2H), 4.64 (t, *J* = 6.4 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 8.04 (d, *J* = 6.9 Hz, 2H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 30.09 (CH_2), 56.97 (CH_2),128.63 (2 CH), 129.70 (C), 129.84 (2 CH), 133.48 (CH), 166.29 (C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.79 (tt, *J* = 2.7 Hz, *J* = 10.1 Hz), (–113.37)–(–113.46) (m), (–121.75)–(–121.92) (m), (–122.72)–(–122.93) (m), (–123.39)–(–123.59) (m), (–125.98)–(–126.20) (m) ppm. IR (ATR): nu(tilde) = 3066 (w), 2978 (w), 1726 (s), 1274 (s), 1233 (vs), 1190 (vs), 1117 (s), 708 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 491.0293 (for $C_{15}H_9F_{13}NaO_2$), found 491.0284 [M + Na^+]. $C_{15}H_9F_{13}O_2$ (468.21).

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)terephthalate (6b). A mixture of terephthalic acid (**4b**) (5.00 g, 30.1 mmol, 1.00 eq.) and $SOCl_2$ (10.7 g, 90.2 mmol, 3.00 eq.) was stirred for 4 h at 80°C. Excess of $SOCl_2$ was then removed by distillation and the residue dried in high vacuum to yield the acid chloride **5b** (5.55 g, 27.4 mmol, 91%) as colorless solid. A portion of compound **5b** (2.00 g, 9.85 mmol, 1.00 eq.) was dissolved in pyridine (5 mL) and $nC_6F_{13}CH_2CH_2OH$ (7.89 g, 21.7 mmol, 2.2 eq.) was added to this mixture while cooling with an ice-water bath. After stirring the mixture for 3 h at 90°C, it was diluted with water (50 mL) and acidified with conc. hydrochloric acid (14 mL) until pH 3. The mixture was extracted with MTBE (2 x 50 mL) and the combined organic extracts dried ($MgSO_4$) and evaporated after filtration. Product **6b** (5.71 g, 6.66 mmol, 68%) was obtained as a colorless solid, mp. 161°C, after recrystallization from CH_2Cl_2 (50 mL). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.63 (tt, *J* = 18.1 Hz, *J* = 6.4 Hz, 4H), 4.67 (t, *J* = 6.4 Hz, 4H), 8.11 (s, 4H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 30.83 (2 CH_2), 57.41 (2 CH_2), 129.91 (4 CH), 133.78 (2 C), 165.37 (2 C) ppm. ^{19}F{^{1}H}-NMR (470 MHz, $CDCl_3$): δ = –80.77 (tt, *J* = 10.2 Hz, *J* = 2.3 Hz), (–113.32)–(–113.48) (m), (–121.63)–(–121.92) (m), (–122.66)–(–122.87) (m), (–123.42)–(–123.58) (m), (–126.00)–(–126.19) (m) ppm. IR (ATR): nu(tilde) = 2975 (w), 2842 (w), 1718 (s), 1686 (m), 1280 (s), 1233 (s), 1182 (s), 1139 (vs), 1120 (vs), 1078 (s), 728 (s), 695 (s), 649 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 881.0218 (for $C_{24}H_{12}F_{26}NaO_4$), found 881.0228 [M + Na^+]. $C_{24}H_{12}F_{26}O_4$ (858.31).

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) isophthalate (6c). Following the procedure given above for compound **6b**, isophthalic acid (**4c**) (5.00 g, 30.1 mmol, 1.00 eq.) and $SOCl_2$ (6.6 mL, 90 mmol, 3.0 eq.) were converted to give compound **5c** (6.11 g, 30.1 mmol, 100%). A portion of the acid chloride **5c** (500 mg, 2.46 mmol,

1.00 eq.) and *n*$C_6F_{13}CH_2CH_2OH$ (1.60 mL, 7.39 mmol, 3.00 eq.) were converted to give the title compound **6c** (1.30 g, 1.52 mmol, 62%) as a colorless solid, mp. 47°C, after recrystallization from CH_2Cl_2 (20 mL). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.63 (tt, *J* = 18.2 Hz, *J* = 6.4 Hz, 4H), 4.67 (t, *J* = 6.4 Hz, 4H), 7.57 (t, *J* = 7.8 Hz, 1H), 8.25 (dd, *J* = 7.8 Hz, *J* = 1.7 Hz, 2H), 8.67 (t, *J* = 1.7 Hz, 1H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 30.82 (2 CH_2), 57.37 (2 CH_2), 129.06 (CH), 130.29 (2 C), 131.01 (CH), 134.41 (2 CH), 165.30 (2 C) ppm. ^{19}F{^{1}H}-NMR (470 MHz, $CDCl_3$): δ = –80.87 (tt, *J* = 2.4 Hz, *J* = 9.5 Hz), (–113.40)–(–113.59) (m), (–121.75)–(–121.99) (m), (–122.76)–(–122.95) (m), (–123.48)–(–123.63) (m), (–126.07)–(–126.23) (m) ppm. IR (ATR): nu(tilde) = 2975 (w), 2836 (w), 1717 (s), 1679 (m), 1283 (m), 1232 (s), 1184 (s), 1139 (vs), 1077 (s), 727 (s), 696 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 859.0399 (for $C_{24}H_{13}F_{26}O_4$), found 859.0356 [M + H^+]. $C_{24}H_{12}F_{26}O_4$ (858.31).

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) phthalate (6d). Following the procedure given above for compound **6b**, phthalic anhydride **4d** (5.00 g, 33.8 mmol, 1.00 eq.) and $SOCl_2$ (7.4 mL, 100 mmol, 3.0 eq.) were converted to give compound **5d** (4.03 g, 21.2 mmol, 63%). A portion of the acid chloride **5d** (500 mg, 2.46 mmol, 1.00 eq.) and *n*$C_6F_{13}CH_2CH_2OH$ (1.17 mL, 5.41 mmol, 2.20 eq.) were converted to give the title compound **6d** (1.46 g, 1.70 mmol, 69%) as a colorless solid, mp. 36°C, after recrystallization from CH_2Cl_2 (20 mL). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.63 (tt, *J* = 18.1 Hz, *J* = 6.3 Hz, 4H), 4.65 (t, *J* = 6.5 Hz, 4H), 7.55–7.61 (m, *2*H), 7.68–7.76 (m, 2H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 30.57 (2 CH_2), 57.54 (2 CH_2), 129.17 (2 CH), 131.66 (2 C), 131.67 (2 CH), 167.00 (2 C) ppm. ^{19}F{^{1}H}-NMR (470 MHz, $CDCl_3$): δ = –80.87 (tt, *J* = 2.4 Hz, *J* = 10.4 Hz), (–113.54)–(–113.73) (m), (–121.79)–(–121.97) (m), (–122.73)–(–123.06) (m), (–123.49)–(–123.73) (m), (–125.97)–(–126.44) (m) ppm. IR (ATR): nu(tilde) = 2978 (w), 1732 (m), 1232 (s), 1189 (vs), 1141

(vs), 1079 (s), 842 (m), 809 (m), 733 (m), 697 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 881.0218 (for $C_{24}H_{12}F_{26}NaO_4$), found 881.0205 [M + Na^+]. $C_{24}H_{12}F_{26}O_4$ (858.31).

Tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)trimesate (6e). Following the procedure given above for compound **6b**, trimesic acid **4e** (3.00 g, 14.3 mmol, 1.00 eq.) and $SOCl_2$ (4.7 mL, 64 mmol, 4.5 eq.) were converted to give compound **5e** (3.78 g, 14.3 mmol, 100%). A portion of the acid chloride **5e** (500 mg, 1.88 mmol, 1.00 eq.) and $nC_6F_{13}CH_2CH_2OH$ (1.35 mL, 6.20 mmol, 3.30 eq.) were converted to give the title compound **6e** (1.73 g, 1.39 mmol, 74%) as a colorless solid, mp. 73°C, after recrystallization from CH_2Cl_2 (20 mL). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.65 (tt, *J* = 18.2 Hz, *J* = 6.4 Hz, 6H), 4.70 (t, *J* = 6.3 Hz, 6H), 8.87 (s, 3H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 30.76 (3 CH_2), 57.76 (3 CH_2), 131.07 (3 CH), 135.15 (3 C), 164.36 (3 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.87 (tt, *J* = 2.6 Hz, *J* = 9.8 Hz), (–113.45)–(–113.55) (m), (–121.76)–(–121.94) (m), (–122.74)–(–122.97) (m), (–123.47)–(–123.67) (m), (–126.09)–(–126.23) (m) ppm. IR (ATR): nu(tilde) = 3069 (w), 2969 (w), 1748 (m), 1729 (s), 1320 (m), 1229 (s), 1193 (vs), 1139 (vs), 1122 (s), 1079 (s), 1006 (m), 708 (s), 696 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 1271.0144 (for $C_{24}H_{12}F_{26}NaO_4$), found 1271.0126 [M + Na^+]. $C_{33}H_{15}F_{39}O_6$ (1248.41).

Pyromellitic acid tetrakis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl) ester (6f). A solution of pyromellitic acid (**4f**) (1.00 g, 3.93 mmol, 1.00 eq.) in $SOCl_2$ (20 mL, 280 mmol) and catalytic amounts of DMF (38 mg) was stirred under exclusion of moisture (N_2 atmosphere) for 16 h at 90°C. Subsequently, all volatiles were removed by distillation and the alcohol $nC_6F_{13}CH_2CH_2OH$ (8.59 g, 23.6 mmol, 6.00 eq.) was added to the residue. The mixture was stirred for further 96 h at 90°C and

subsequently diluted with water (100 mL), at which most of the crude product precipitated. The suspension was extracted with MTBE (2 x 100 mL) and the solid material separated by filtration and washed with H_2O (30 mL) and MTBE (30 mL). The combined organic layers were dried ($MgSO_4$) and evaporated after filtration. The combined solid products were recrystallized from CH_2Cl_2 (60 mL) to furnish product **6f** (6.31 g, 3.85 mmol, 98%) as a colorless solid, mp. 114°C. Due to poor solubility in acetone or $CDCl_3$, no well resolved 1D-^{13}C-NMR spectrum was obtained. The ^{13}C-signals were therefore assigned by $^1J(^1H,^{13}C)$ and $^3J(^1H,^{13}C)$ correlations out of the HMQC and HMBC spectra. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.60 (tt, *J* = 18.2 Hz, *J* = 6.5 Hz, 8H), 4.66 (t, *J* = 6.4 Hz, 8H), 8.06 (s, 2H), ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 29.55 (4 CH_2), 57.60 (4 CH_2), 128.96 (2 CH), 134.01 (4 C), 165.10 (4 C) ppm; the ^{13}C resonances were indentified by ^1J, ^2J and $^3J(^1H,^{13}C)$ correlations out of the HMQC and HMBC spectra (see supporting information). $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.88 (tt, *J* = 2.5 Hz, *J* = 10.7 Hz), –113.65 (tq, *J* = 13.9 Hz, *J* = 5.4 Hz), (–121.80)–(–122.00) (m), (–122.81)–(–122.96), (–123.52)–(–123.64) (m), (–126.12)–(–126.25) (m) ppm. IR (ATR): nu(tilde) = 3082 (w), 2982 (w), 1744 (m), 1723 (s), 1291 (m), 1234 (s), 1183 (s), 1139 (vs), 1108 (s), 1073 (m), 1006 (m), 697 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 1661.0069 (for $C_{42}H_{18}F_{52}NaO_8$), found 1661.0063 [M + Na^+]. $C_{42}H_{18}F_{52}O_8$ (1638.52).

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) pyridine-2,6-dicarboxylate (6g). Following the procedure given above for compound **6f**, 2,6-pyridinedicarboxylic acid **4g** (500 mg, 2.99 mmol, 1.00 eq.), $SOCl_2$ (2.2 mL, 29.9 mmol, 10.0 eq.), DMF (16 mg) and *n*$C_6F_{13}CH_2CH_2OH$ (1.43 mL, 6.58 mmol, 2.2 eq.) were converted to give the title compound **6g** (1.41 g, 1.64 mmol, 55%) as a colorless solid, mp. 127°C, after recrystallization from CH_2Cl_2 (20 mL). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.70 (tt, *J* =

18.2 Hz, *J* = 6.8 Hz, 4H), 4.73 (t, *J* = 6.7 Hz, 4H), 8.04 (t, *J* = 7.8 Hz, 1H), 8.30 (d, *J* = 7.8 Hz, 2H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 30.70 (2 CH_2), 58.13 (2 CH_2), 128.42 (2 CH), 138.62 (CH), 148.08 (2 C), 164.17 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.82 (tt, *J* = 2.5 Hz, *J* = 10.1 Hz), (–112.40)–(–114.40) (m), (–121.35)–(–124.08) (m), (–125.85)–(–126.54) (m) ppm. IR (ATR): nu(tilde) = 3064 (w), 1741 (s), 1235 (s), 1200 (s), 1178 (s), 1079 (s), 1079 (s), 999 (m), 867 (m), 768 (m), 693 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 860.0351 (for $C_{23}H_{12}F_{26}NO_4$), found 860.0328 [M + H^+]. $C_{23}H_{11}F_{26}NO_4$ (859.30).

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) pyridine-3,5-dicarboxylate (6h). Following the procedure given above for compound **6f**, 3,5-pyridine dicarboxylic acid **4h** (4.00 g, 23.9 mmol, 1.00 eq.), $SOCl_2$ (17.6 mL, 240 mmol, 10.0 eq.), DMF (ca. 38 mg) and *n*$C_6F_{13}CH_2CH_2OH$ (11.4 mL, 52.8 mmol, 2.2 eq.) were converted to give the title compound **6h** (19.09 g, 22.2 mmol, 93%) as a colorless solid, mp. 132°C, after recrystallization from CH_2Cl_2 (50 mL). ^1H-NMR (500 MHz, $CDCl_3$): δ = 2.66 (tt, *J* = 18.2 Hz, *J* = 6.4 Hz, 4H), 4.73 (t, *J* = 6.3 Hz, 4H), 8.93 (t, *J* = 1.9 Hz, 1H), 9.41 (d, *J* = 2.0 Hz, 2H) ppm. $^{13}C\{^1H\}$-NMR (135 MHz, $CDCl_3$): δ = 30.71 (2 CH_2), 58.10 (2 CH_2), 126.46 (2 CH), 139.57 (CH), 153.13 (2 C), 163.36 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.80 (tt, *J* = 2.6 Hz, *J* = 10.2 Hz), –113.42 (ddt, *J* = 4.9 Hz, *J* = 15.0 Hz, *J* = 19.9 Hz), (–121.33)–(–122.07) (m), (–122.37)–(–123.04) (m), (–123.28)–(–123.84) (m), (–125.73)–(–126.55) (m) ppm. IR (ATR): nu(tilde) = 3057 (w), 3008 (w), 2937 (w), 2860 (w), 1738 (s), 1343 (m), 1307 (m), 1284 (m), 1232 (s), 1194 (s), 1140 (s), 1122 (s), 1090 (s), 999 (m), 651 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 860.0351 (for $C_{23}H_{12}F_{26}NO_4$), found 860.0331 [M + H^+]. $C_{23}H_{11}F_{26}NO_4$ (859.30).

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) oxalate (6i). Following the procedure given above for compound **6a**, *n*$C_6F_{13}CH_2CH_2OH$ (1.88 mL, 8.67 mmol, 2.20 eq.) pyridine (3 mL), and $(COCl)_2$ (**5i**) (500 mg, 3.94 mmol, 1.00 eq.) were converted to give the title compound **6i** (3.08 mg, 3.94 mmol, 100%) as a colorless solid, mp. 43°C, after recrystallization from CH_2Cl_2 (10 mL). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.59 (tt, *J* = 17.6 Hz, *J* = 6.4 Hz, 4H), 4.60 (t, *J* = 6.5 Hz, 4H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 30.50 (2 CH_2), 58.98 (2 CH_2), 156.73 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.82 (tt, *J* = 2.5 Hz, *J* = 10.4 Hz), (–113.47)–(–113.67) (m), (–121.78)–(–122.01) (m), (–122.76)–(–123.02) (m), (–123.43)–(–123.69) (m), (–126.06)–(–126.26) (m) ppm. IR (ATR): nu(tilde) = 1764 (s), 1317 (w), 1184 (s), 1139 (s), 1121 (s), 1005 (m), 804 (m), 697 (s), 652 (s) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 804.9905 (for $C_{18}H_8F_{26}NaO_4$), found 804.9880 [M + Na^+]. $C_{18}H_8F_{26}O_4$ (782.22).

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) succinate (6j). Following the procedure given above for compound **6b**, succinic anhydride (10.0 g, 100 mmol, 1.00 eq.) and $SOCl_2$ (16.7 g, 140 mmol, 1.40 eq.) were converted to give compound **5j** (14.3 g, 92.5 mmol, 93%). A portion of the acid chloride **5j** (300 mg, 1.94 mmol, 1.00 eq.) and *n*$C_6F_{13}CH_2CH_2OH$ (1.76 g, 4.84 mmol, 2.50 eq.) were converted to give the title compound **6j** (1.13 g, 1.39 mmol, 72%) as a brownish oil after washing with CH_2Cl_2 (20 mL). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.47 (tt, *J* = 18.4 Hz, *J* = 6.6 Hz, 4H), 2.66 (s, 4H), 4.40 (t, *J* = 6.5 Hz, 4H) ppm. $^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$): δ = 28.98 (2 CH_2), 30.67 (t, *J* = 21.9 Hz, 2 CH_2), 56.79 (2 CH_2), 171.79 (2 C) ppm. $^{19}F\{^1H\}$-NMR (470 MHz, $CDCl_3$): δ = –80.89 (tt, *J* = 10.2 Hz, *J* = 2.3 Hz), (–113.60)–(–126.21) (m) ppm. IR (ATR): nu(tilde) = 2927 (w), 2857 (w), 1743 (m), 1420 (w), 1363 (w), 1319 (w), 1232 (s), 1189 (s), 1164 (s), 1123 (s), 1082 (m), 1011 (w), 961

(w), 913 (w), 842 (w), 809 (w), 781 (w), 746 (w), 733 (m), 708 (m), 698 (m) cm^{-1}. $C_{20}H_{12}F_{26}O_4$ (810.27): calcd. C 29.03%, H 1.33%; found. C 29.19%, H 1.23%.

Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoroctyl)carbonate (6k). The alcohol $n$$C_6F_{13}CH_2CH_2OH$ (4.60 g, 12.6 mmol, 2.50 eq.) and pyridine (7 mL) was added to a solution of $COCl_2$ in toluene **5k** (20% w/w, 1.4 mL, 2.5 mmol, 1.0 eq) and the mixture was stirred for 1 d at ambient temperature. It was then diluted with water H_2O (30 mL), acidified with conc. hydrochloric acid (6 mL) until pH 3 and then extracted with MTBE (2 x 30 mL). The combined extracts were dried ($MgSO_4$) and evaporated after filtration. The residue was extracted with CH_2Cl_2 (20 mL). After separation of the CH_2Cl_2 layer the product layer was dried in high vacuum to furnish compound **6k** (153 mg, 0.203 mmol, 21%) as a colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 2.39 (tt, *J* = 19.0 Hz, *J* = 6.4 Hz, 4H), 3.99 (t, *J* = 6.4 Hz, 4H) ppm. ^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$): δ = 34.14 (2 CH_2), 55.43 (2 CH_2), 154.44 (1 C) ppm. ^{19}F{^{1}H}-NMR (470 MHz, $CDCl_3$): δ = –80.97 (tt, *J* = 2.5 Hz, *J* = 9.4 Hz), (–113.40)–(–113.68) (m), (–121.84)–(–122.21) (m), (–122.84)–(–123.02) (m), (–123.60)–(–123.88) (m), (–126.14)–(–126.31) (m) ppm. IR (ATR): nu(tilde) = 1768 (w), 1232 (s), 1188 (vs), 1142 (vs), 1121 (s), 1079 (m), 1049 (m), 732 (m), 696 (m) cm^{-1}. HR-MS (ESI, pos. mode): calcd. 776.9956 (for $C_{17}H_8F_{26}NaO_3$), found 776.9974 [M + Na^+]. $C_{17}H_8F_{26}O_3$ (754.21).

Acknowledgement

We are grateful to Malena Hillje for experimental support and to Dr. Izabella Brand for helping us with contact angle measurements. MTBE was obtained as a generous gift from Evonik Industries, Marl, Germany.

References

[1] a) F. M. Hekster, R. W. P. M. Laane, P. de Voogt, *Rev. Environ. Contam. Toxicol.* **2003**, *179*, 99–121; b) C. A. Huset, M. A. Barlaz, D. F. Barofsky, J. A. Field, *Chemosphere* **2011**, *82*, 1380–1386; c) E. Goosey, S. Harrad, *Environ. Int.* **2011**, *37*, 86–92.

[2] a) S. T. Washburn, T. S. Bingman, S. K. Braithwaite, R. C. Buck, L. W. Buxton, H. J. Clewell, L. A. Haroun, J. E. Kester, R. W. Rickard, A. M. Shipp, *Environ. Sci. Technol.* **2005**, *39*, 3904–3910; b) S. Fiedler, G. Pfister, K.-W. Schramm, *Toxicol. Environ. Chem.* **2010**, *92*, 1801–1811.

[3] C. A. Moody, G. N. Hebert, S. H. Strauss, J. A. Field, *J. Environ. Monit.* **2003**, *5*, 341–345.

[4] a) C. Kubwabo, N. Vais, F. M. Benoit, *J. Environ. Monit.* **2004**, *6*, 540–545; b) K. Kannan, J. C. Franson, W. W. Bowerman, K. J. Hansen, P. D. Jones, J. P. Giesy, *Environ. Sci. Technol.* **2001**, *35*, 3065–3070.

[5] a) L. Vierke, C. Schulte, *Nachr. Chem.* **2016**, *64*, 969–971; b) J. W. Martin, B. J. Asher, S. Beesoon, J. P. Benskin, M. S. Ross, *J. Environ. Monit.* **2010**, *12*, 1979–2004.

[6] L. Vierke, C. Staude, A. Biegel-Engler, W. Drost, C. Schulte, *Environm. Sci. Europe* **2012**, *24*, 16.

[7] M. C. Kasuya, K. Hatanaka, *J. Fluorine Chem.* **2016**, *188*, 1–4.

[8] a) V. Ochoa-Herrera, J. A. Field, A. Luna-Velasco, R. Sierra-Alvarez, *Environ. Sci.: Processes Impacts* **2016**, *18*, 1236–1246; b) W. Sun, V. M. Gamez, L. Otero-Gonzalez, Y. Cho, C. K. Ober, R. Sierra-Alvarez, *Arch. Environ. Contam. Toxicol.* **2013**, *64*, 187–197.

[9] a) S. C. Gordon, *Regulatory Toxicol. Pharmacol.* **2011**, *59*, 64–80; b) Z. Wang, I. T. Cousins, M. Scheringer, K. Hungerbühler, *Environ. Int.* **2013**, *60*, 242–248.

[10] M. Yang, J. Hao, H. Li, *J. Fluorine Chem.* **2014**, *165*, 81–90.

[11] a) K. Griesar, E. A. Soto-Bustamante, W. Haase, *Z. Naturforsch. B* **2000**, *55b*, 567–575; b) M. Gomes, A. Gandini, A. J. D. Silvestre, B. Reis, *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 3759–3768; c) M. C. Davis, *Synth. Commun.* **2007**, *37*, 1457–1462.

[12] Review: N. Cohen, A. Dotan, H. Dodiuk, S. Kenig, *Mater. Manufac. Proc.* **2016**, *31*, 1143–1155.

[13] a) M. Tordeux, C. Francese, C. Wakselman, *J. Chem. Soc., Perkin Trans. 1* **1990**, 1951–1957; b) M. Fujiu, K. Negishi, J. Guang, P. G. Williard, S. Kuroki, K. Mikami, *Dalton Trans.* **2015**, *44*, 19464–19468; c) K. Mikami, T. Murase, Y. Itoh, *J. Am. Chem. Soc.* **2007**, *129*, 11686–11687.