EurJOC
European Journal of Organic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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Authors: Christoph Kahrs, Mathias Wickleder, and Jens Christoffers

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201800882

Link to VoR: http://dx.doi.org/10.1002/ejoc.201800882

Supported by ACES Asian Chemical Editorial Society

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10.1002/ejoc.201800882

Biphenyl Sulfonic and Disulfonic Acids with Perfluorinated Alkyl Residues

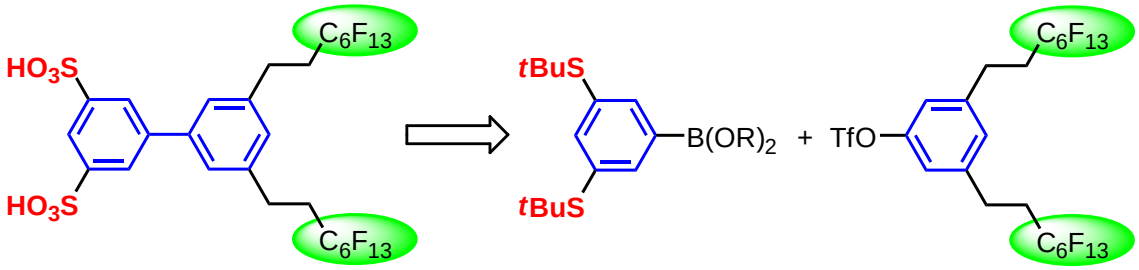
Christoph Kahrs,[a] Mathias S. Wickleder,[b] Jens Christoffers*[a]

[a] M.Sc. C. Kahrs, Prof. Dr. J. Christoffers, Institut für Chemie, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany. Fax: +49(0)441 798 3873. Email: jens.christoffers@uol.de. Homepage: www.christoffers.chemie.uni-oldenburg.de

[b] Prof. Dr. M. S. Wickleder, Universität zu Köln, 50939 Köln, Germany

Graphical Abstract

Key topic: Fluorinated Biphenyl Sulfonic Acids



Hybrid materials consisting of polar sulfonic acids, crystalline biphenyl scaffolds and amorphous fluorinated side chains are prepared by Suzuki cross coupling.

Abstract: Sulfonic acids serve as interesting, yet not intensively studied alternatives to carboxylic acids as linker units in coordination polymers. In this study, we present the synthesis of hybrid sulfonic acids with polar, rigid biphenyl moieties and disordered highly fluorinated alkyl chains. Consequently, eight biphenyl sulfonic and disulfonic acids with one or two perfluoroalkyl chains were prepared. The key steps within the synthesis include two palladium catalyzed C–C bond formations: The perfluoroalkyl residue is installed by Heck reaction (up to 91%) using 1*H*,1*H*,2*H*-perfluorinated alkenes (C_6 and C_8) and the biphenyl unit is established by a Suzuki coupling (up to 88%) of boronic acids bearing one or two protected thiol groups. Finally, these thiol groups are converted into the sulfonic acids by *N*-chlorosuccinimid mediated oxidation followed by hydrolysis of the respective sulfonyl chloride.

Keywords: Sulfonic acids, Fluorine compounds, Biaryl compounds, Suzuki coupling, Heck reaction, Boron compounds, Palladium catalysis, Cross coupling

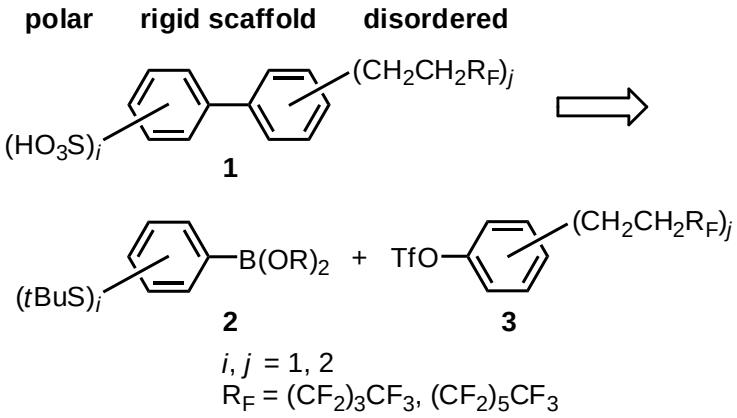
Introduction

Aromatic oligocarboxylic acids are the leading structural motif for linker molecules in metal organic frameworks and coordination polymers.[1] The key advantage of this compound class is the flexible accessibility of various structural subtypes with different symmetries, which is based on a rich and well developed synthetic organic chemistry targeting benzene carboxylic acids. In contrast, the synthesis of aromatic sulfonic acids is much less developed, which is mainly due to the electronically deactivating character of a sulfo group making a second sulfonation (electrophilic aromatic substitution) very difficult. However, advantageous features of sulfonic acids compared to carboxylic acids are their higher acidity and pronounced thermal stability of their salts, making them attractive target structures for the preparation of new materials. For this reason, we have initiated a research program for the development of aromatic sulfonic acids as linker compounds in coordination polymers.[2]

Two types of sulfonic acids have found wide spread industrial as well as consumer applications: First, alkane and alkylbenzene sulfonates are the most common anion tensides.[3] Secondly, perfluoroalkane sulfonic acids, so-called fluorosurfactants like perfluorooctane sulfonic acid (PFOS),[4] represent a technologically relevant class of materials. These compounds have found ubiquitous applications for surface treatment and impregnation.[5]

Benzoic acid derivatives with perfluoroalkyl residues have been reported to exhibit extraordinary interesting properties as crystalline as well as liquid crystalline materials.[6] In extension of our efforts towards sulfonic acids as linker molecules for coordination polymers, we report herein on the development of new hybrid materials **1** consisting of three entities (Scheme 1): (1) polar, hydrophilic aromatic sulfonic acids, which might define proton conducting materials[7] in the solid state or could form crystalline salts with various metal cations; (2) a rigid biphenyl scaffold being the structural element for inducing crystallinity of the material; and (3) hydrophobic perfluorinated residues creating domains without well-defined crystalline order.[8] The retrosynthetic approach to target compounds **1** is based on a Suzuki coupling for the biaryl unit starting from boronic acid derivatives **2** with one or two sulfur moieties protected as *tert*-butyl thioethers and phenyl triflates **3**[9] carrying one or two perfluorinated alkyl chains. An established strategy for introduction of such perfluoroalkyl

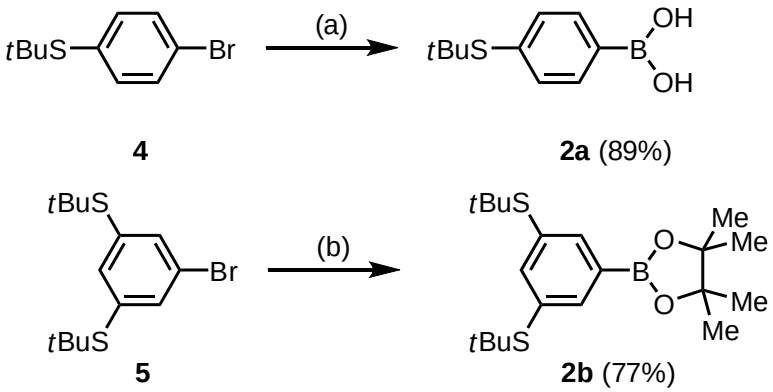
chains is the Heck reaction of an aryl halide with 1*H*,1*H*,2*H*-perfluoro α-olefins followed by catalytic hydrogenation.[10]



Scheme 1. Target compounds of this study are biphenyl mono- and disulfonic acids **1** with one or two perfluoroalkyl residues R_F. Their preparation is based on Suzuki coupling reactions of building blocks **2** and **3.**

Results and Discussion

Boronic acids 2. *para*-(*tert*-Butylthio)benzene boronic acid (**2a**) was literature known[11] and prepared accordingly from the respective *para*-bromo thioether **4**[12] by lithium-halogen exchange, reaction with $B(OMe_3)$ and subsequent hydrolysis. Respective bis(*tert*-butyl)benzene derivative **2b** was not literature known. Therefore, we prepared it by palladium-catalyzed borylation of bromobenzene bisthioether **5**[13] with bispinacol-diborane (B_2pin_2) following a literature procedure (Scheme 2).[14] Pinacol boronate **2b** was obtained with 77%.



Scheme 2. Preparation of boronic acid **2a** and pinacol boronate **2b**; reagents and conditions: (a) 1. 1.1 equiv. *n*BuLi, THF, –78°C, 0.5 h; 2. 2.0 equiv. $B(OMe)_3$, –78°C→23°C, 2 h; 3. HCl–H_2O, 23°C, 5 min; (b) 1.2 equiv. B_2pin_2, 2.0 equiv. KOAc, 5 mol% $Pd(OAc)_2$, 10 mol% DPPF, DMSO, 80°C, 16 h.

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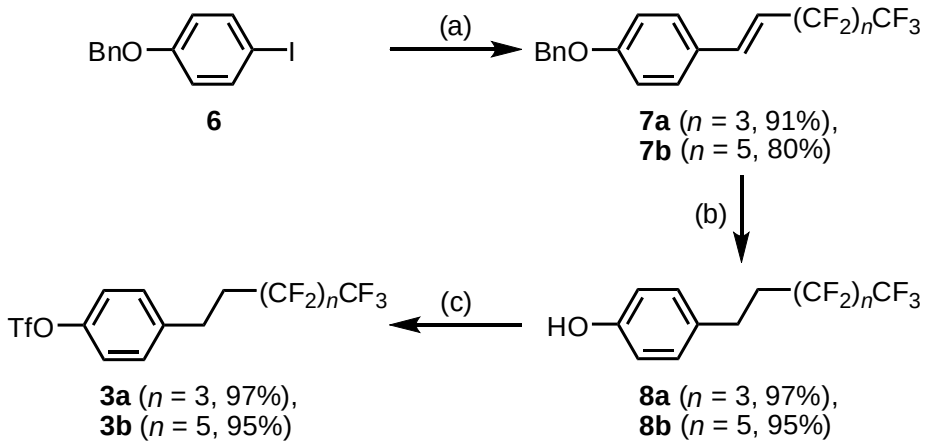
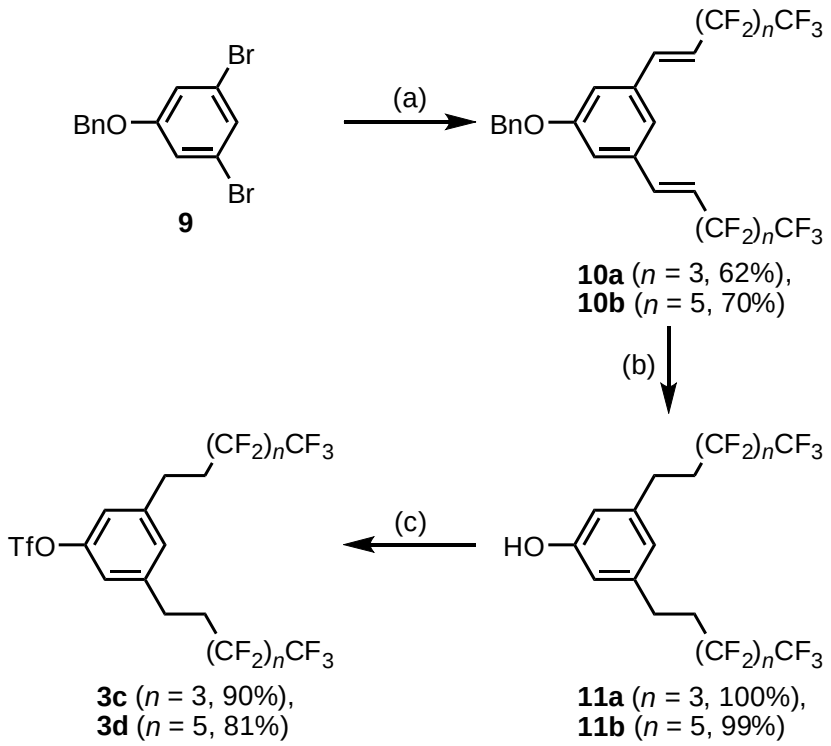
Fluorinated building blocks 3. For the preparation of compounds **3a** and **3b** with one perfluoroalkyl residue a Heck reaction of a respective aromatic compound with 1*H*,1*H*,2*H*-perfluoro α-olefins was envisioned. In order to circumvent regioselectivity problems with consecutive Heck and Suzuki reactions, we planned to install the triflate leaving group after the Heck reaction by esterification of the respective phenol. In a first exploration of this route it turned out, that a free phenol unit leads to unsatisfactory results in the Heck reaction. Therefore, we decided to protect the hydroxyl function as benzyl ether. Consequently, we started from *para*-iodo benzyl ether **6**, which was accessed according to a literature protocol,[15] and converted it with the respective polyfluorinated 1-hexene and 1-octene. We started with recently published reaction conditions [$Pd(OAc)_2$, PPh_3, NEt_3, DMA, 100°C],[16] which had to be optimized for product **7a** (ligands, solvents, temperature) and finally identified optimal conditions [$Pd(OAc)_2$, P(*o*tol)$_3$, K_2CO_3, DMF, 140°C; Scheme 3].[17] Compounds **7a** and **7b** were isolated with 91% and 80% yields, resp., after column chromatography exclusively as (*E*)-isomers. Catalytic hydrogenation of the olefins also cleaved the benzyl protective groups and gave saturated compounds **8a** and **8b** both in almost quantitative yields. Introduction of the triflate leaving group (Tf_2O, pyridine) proceeded smoothly and also in almost quantitative yields (97% for **3a**, 95% for **3b**).



Scheme 3. Synthesis of the triflates **3a**, **3b**. Reagents and conditions: (a) 10 equiv. $CH_2{=}CH(CF_2)_nCF_3$, 10 mol% $Pd(OAc)_2$, 20 mol% P(*o*tol)$_3$, 5 equiv. K_2CO_3, DMF, 140°C, 18 h; (b) 10 mol% Pd–C, 4 bar H_2, EtOAc, 70°C, 18 h; (c) 1.2 equiv. Tf_2O, 2.0 equiv. pyridine, CH_2Cl_2, 23°C, 1.5 h.

The synthesis of congeners **3c** and **3d** with two fluorinated side chains started from (dibromophenyl) ether **9**, which was accessed from the respective dibromophenol as

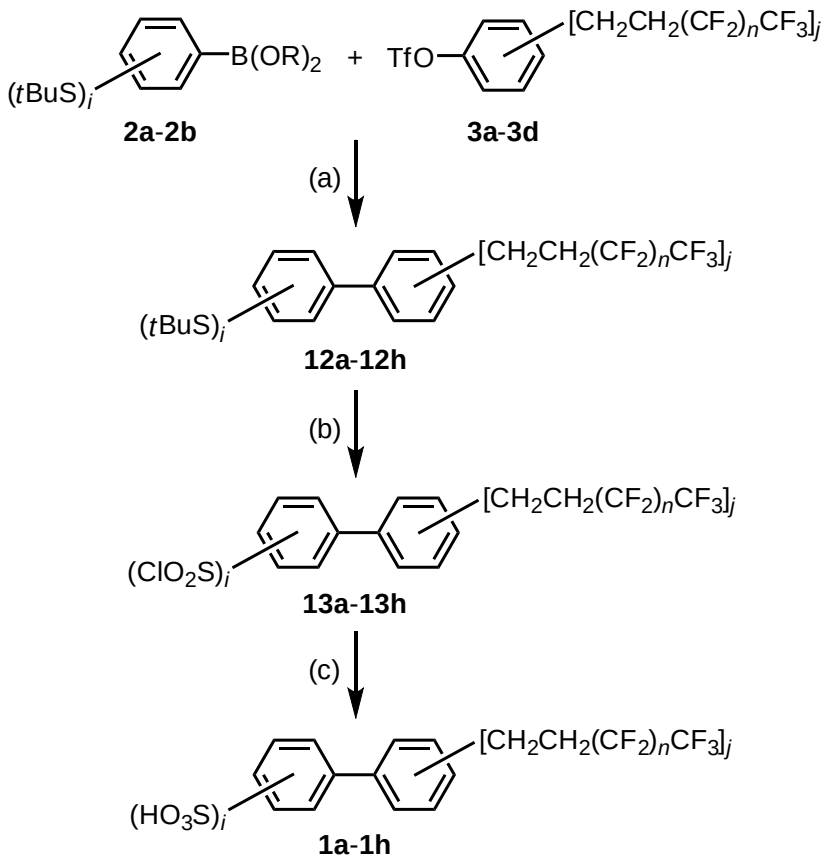
reported in the literature (Scheme 4).[18] The same reaction conditions as for compounds in Scheme 3 were chosen for all three steps, but yields are naturally a little bit lower since all transformations had to occur twice within this scaffold. Practically, the Heck reaction proceeded in 62% (product **10a**) and 70% (product **10b**). Catalytic hydrogenations inclusive debenzylations were again quantitative (100% for **11a** and 99% for **11b**). The introduction of the triflate group proceeded with good yields (90% for **3c** and 81% for **3d**).



Scheme 4. Synthesis of the triflates **3c**, **3d**. Reagents and conditions: (a) 10 equiv. $CH_2=CH(CF_2)_nCF_3$, 10 mol% $Pd(OAc)_2$, 20 mol% P(*o*tol)$_3$, 5.0 equiv. K_2CO_3, DMF, 140°C, 18 h; (b) 10 mol% Pd–C, 4 bar H_2, EtOAc, 70°C, 18 h; (c) 1.2 equiv. Tf_2O, 2.0 equiv. pyridine, CH_2Cl_2, 23°C, 1.5 h.

Suzuki coupling and elaboration of the sulfur functions. We applied previously published conditions for a Suzuki coupling reaction {[$Pd(PPh_3)_4$] as precatalyst and Na_2CO_3 as base in EtOH–toluene–water at 100°C}[19] to start off optimizations for the conversion of boronic acid **2a** with triflate **3a**, which gave however only low yield of product **12a**. After variation of catalyst, base, solvent and temperature we found [Pd_2dba_3] as precatalyst, SPhos [2-(dicyclohexylphosphano)-2',6'-dimethoxybiphenyl] as ligand[20] and K_2CO_3 as base in toluene–water at 140°C as suitable conditions to furnish product **12a** in 76% yield (Scheme 5, Table 1). When adopting these conditions to the conversions of boronic acid derivatives **2a** and **2b** with all four triflates

3a–**3d**, biphenyl products **12a**–**12f** were obtained in the range of 82–59% yield. Products **12g** and **12h** were isolated with significantly lower yields (43% and 36%, resp.). The *tert*-butyl protective group was then oxidatively cleaved from the sulfur moiety with a method generating chlorine *in situ* from NCS and HCl.[21] Sulfonyl chlorides **13a**–**13h** were obtained with good to excellents yields (77–100%) after purification by column chromatography. Upon heating in water, the sulfonyl chlorides **13a**–**13h** were hydrolyzed to sulfonic acids **1a**–**1h**, which were obtained after evaporation to dryness as microcrystalline materials (90–100% yields) being hardly soluble in water and organic solvents. As expected, the mono and disulfonic acids **1a**–**1h** crystallize as the mono or dihydrate, respectively.



Scheme 5. Suzuki coupling of boronic acid derivatives **2a** (*i* = 1) and **2b** (*i* = 2) with triflates **3a**, **3b** (*j* = 1) and **3c**, **3d** (*j* = 2) and further transformation of the thioethers to sulfonic acids. For constitution of products **1a**–**1h** and all yields see Table 1. Reagents and conditions: (a) 5 mol% [Pd_2dba_3], 20 mol% SPhos, 2.0 equiv. K_2CO_3, toluene/H_2O 1:1, 140°C, 18 h; (b) 4 x *i* equiv. NCS, 1.1 x *i* equiv. HCl, MeCN, 0°C, 1 h, 23°C, 1 h; (c) H_2O, 100°C, 18 h.

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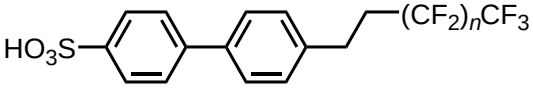
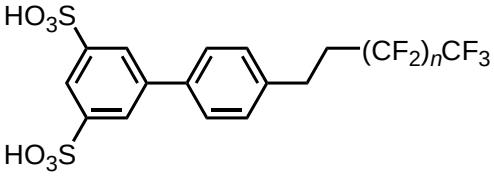
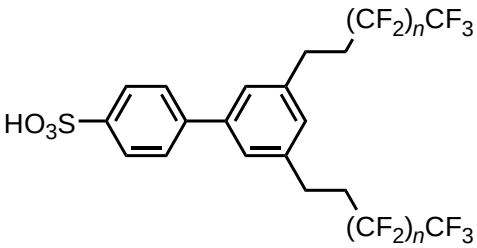
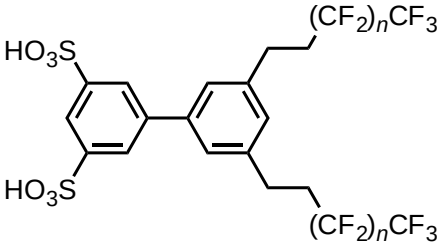
Table 1. Constitutions and yields of products **1a**–**1h**, yields for intermediate products **12a**–**12h** and **13a**–**13h**.

Product **1**	Yield of **1**	Yield of **12**	Yield of **13**
	**1a** (*n* = 3, 100%), **1b** (*n* = 5, 98%),	**12a** (76%), **12b** (88%),	**13a** (77%), **13b** (80%),
	**1c** (*n* = 3, 97%), **1d** (*n* = 5, 91%),	**12c** (81%), **12d** (76%),	**13c** (85%), **13d** (78%),
	**1e** (*n* = 3, 90%), **1f** (*n* = 5, 91%),	**12e** (79%), **12f** (82%),	**13e** (78%), **13f** (77%),
	**1g** (*n* = 3, 90%), **1h** (*n* = 5, 90%)	**12g** (43%), **12h** (36%)	**13g** (100%), **13h** (85%)

Conclusion

A series of eight biphenyl sulfonic and disulfonic acids **1a**–**1h** with either one of two perfluoroalkyl residues was prepared. Within the framework of our research program on sulfonic acids as linker units in metal organic frameworks, these materials shall serve as linker molecules for preparing coordination polymers with polar, crystalline and disordered fluorinated domains in the solid state. Two palladium catalyzed transformations were the key transformations for the formation of C–C bonds: First, the fluorinated side chains were introduced by Heck reaction (yields 62–91%) of 1*H*,1*H*,2*H*-perfluoro α-olefins to the aromatic ring (followed by catalytic hydrogenation to the saturated side chains). Secondly, the biphenyl scaffold was established by Suzuki coupling (yields 36–88%) of boronic acid derivatives **2a**–**2b** holding either one or two *tert*-butylthio groups with phenyl triflates carrying the perfluoro alkyl chains. In

two subsequent functional group interconversions, the *tert*-butylthio functions were oxidatively transformed to the sulfonyl chlorides, which were finally hydrolyzed to the final sulfonic acids. As a further element of diversity the lengths of the side chains was either C_6 or C_8.

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 CH_2Cl_2 as eluents. TLC was performed on aluminum plates coated with SiO_2 F_{254}. ^1H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 300 and 500 instruments. Multiplicities of carbon signals were determined with DEPT experiments. Due to the high multiplicity of the carbon signals of the perfluorinated chains, we were not able to identify these carbon atoms in the ^{13}C NMR spectra. MS and HRMS spectra were obtained with Thermo Scientific DFS (EI) and Waters Q-TOF Premier (ESI and APCI) spectrometers. IR spectra were recorded on a Bruker Tensor 27 spectrometer equipped with a diamond ATR unit. Elemental analyses were determined with a Euro EA-CHNS instrument from HEKAtech. Melting points were obtained with a Gallenkamp device; values are uncorrected. Compounds **4**,[12] **5**,[13] **6**[15] and **9**[18] were prepared according to literature protocols. All other starting materials were commercially available. In particular, $n$$C_4F_9CH=CH_2$ and $n$$C_6F_{13}CH=CH_2$ were purchased from Apollo.

4-(*tert*-Butylthio)benzeneboronic acid (2a). With exclusion of moisture and air (nitrogen atmosphere), *n*-BuLi (2 mol/L in *n*-hexane, 0.90 mL, 2.24 mmol, 1.1 equiv.) was added to a solution of thioether **4** (500 mg, 2.04 mmol, 1.0 equiv.) in THF (5 mL) at –78°C. After stirring the mixture for 30 min at –78°C, $B(OMe)_3$ (0.46 mL, 0.43 g, 4.1 mmol, 2.0 equiv.) was added. The solution was stirred for 15 min at –78°C and for further 1.5 h at ambient temperature. Hydrochloric acid (1 mol/L, 10 mL) was added and the suspension was stirred for 5 min at ambient temperature. The layers were separated and the aqueous layer was extracted with MTBE (3 x 20 mL). The combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed *in vacuo* to furnish the title compound **2a** (381 mg, 1.81 mmol, 89%) as a colorless solid, which did not require further purification. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 9 H), 7.66–7.69 (m, 2 H), 8.17–8.20 (m, 2 H) ppm. The protons of the boronic acid

were not observed. The data were in accordance with literature values.[11] $C_{10}H_{15}BO_2S$ (210.10).

2-[3,5-Bis(*tert*-butylthio)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b). With exclusion of moisture and air (nitrogen atmosphere), bisthioether **5** (100 mg, 0.30 mmol, 1.0 equiv.) was added to a mixture of B_2pin_2 (91 mg, 0.36 mmol, 1.2 equiv.), $Pd(OAc)_2$ (3 mg, 15 µmol, 5 mol%), DPPF (17 mg, 30 µmol, 10 mol%) and KOAc (59 mg, 0.60 mmol, 2.0 equiv.) in DMSO (3 mL). The resulting mixture was stirred at 80°C for 16 h. MTBE (25 mL) was then added and the solution was washed with brine (3 x 15 mL). The organic layer was dried ($MgSO_4$) and filtered. The solvent was removed *in vacuo* and the crude product purified by column chromatography (SiO_2, CH_2Cl_2, R_f = 0.92) to yield the title compound **2b** (88 mg, 0.23 mmol, 77%) as a colorless solid (mp 111°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 18 H), 1.34 (s, 12 H), 7.82–7.83 (m, 1 H), 7.94–7.94 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 25.02 (4 CH_3), 31.19 (6 CH_3), 46.21 (2 C), 84.17 (2 C), 132.63 (2 C), 143.92 (2 CH), 148.88 (CH) ppm. Due to the quadrupole moment of the boron atom, we were not able to identify the *ipso*-carbon atom. IR (ATR): nu(tilde) = 2972 (m), 2924 (w), 2862 (w), 1361 (s), 1337 (vs), 1312 (s), 1160 (s), 1141 (vs), 1124 (s), 712 (s) cm^{-1}. HRMS (ESI, pos. mode): calcd. 381.2088 (for $C_{20}H_{34}BO_2S_2^+$); found 381.2087 [M + H^+]. $C_{20}H_{33}BO_2S_2$ (380.41).

General procedure A (GPA). With exclusion of moisture and air (nitrogen atmosphere), the alkene (10 equiv.) was added to a suspension of the bromo- (**6**) or iodobenzene (**9**) derivative (1.0 equiv.), $Pd(OAc)_2$ (10 mol%), P(*o*tol)$_3$ (20 mol%) and K_2CO_3 (5.0 equiv.) in anhydrous DMF (3 L/mol). The resulting mixture was heated to 140°C for 18 h. Brine (15 L/mol) was added and the mixture was extracted with MTBE (3 x 15 L/mol). The organic layer was dried ($MgSO_4$) and filtered. The solvent was removed *in vacuo* and the crude product was purified by column chromatography to give the alkenes **7** or **10**.

(*E*)-1-(Benzyloxy)-4-(1*H*,2*H*-perfluoro-1-hexenyl)benzene (7a). According to the GPA, 1*H*,1*H*,2*H*-perfluoro-1-hexene (0.54 mL, 0.79 g, 3.2 mmol), 1-(benzyloxy)-4-iodobenzene (**6**) (100 mg, 0.32 mmol), $Pd(OAc)_2$ (7 mg, 32 µmol), P(*o*tol)$_3$ (19 mg, 64 µmol) and K_2CO_3 (221 mg, 1.60 mmol) were converted to furnish compound **7a** (125

mg, 0.29 mmol, 91%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.38) as a colorless solid (mp 52°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.11 (s, 2 H), 6.05 (dt, *J* = 16.1 Hz, *J* = 12.3 Hz, 1 H), 6.98–7.01 (m, 2 H), 7.11 (dt, *J* = 16.1 Hz, *J* = 1.8 Hz, 1 H), 7.32–7.44 (m, 7 H) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 70.24 (CH_2), 111.89 (t, *J* = 22.8 Hz, CH), 115.39 (2 CH), 126.62 (C), 127.59 (2 CH), 128.32 (CH), 128.82 (2 CH), 129.35 (2 CH), 136.57 (C), 139.28 (t, *J* = 9.9 Hz, CH), 160.48 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–125.76)–(–125.68) (m, CF_2), (–124.12)–(–124.06) (m, CF_2), (–110.84)–(–110.79) (m, CF_2), (–81.10)–(–81.06) (m, CF_3) ppm. IR (ATR): nu(tilde) = 2888 (w), 2857 (w), 1656 (w), 1609 (m), 1223 (vs), 1203 (vs), 1130 (vs) cm^{-1}. HRMS (EI, 70 eV): calcd. 428.0817 (for $C_{19}H_{13}F_9O^+$); found 428.0815 [M^+]. $C_{19}H_{13}F_9O$ (428.30).

(*E*)-1-(Benzyloxy)-4-(1*H*,2*H*-perfluoro-1-octenyl)benzene (7b). According to the GPA, 1*H*,1*H*,2*H*-perfluoro-1-octene (7.3 mL, 11.1 g, 32.2 mmol), 1-(benzyloxy)-4-iodobenzene (**6**) (1.00 g, 3.22 mmol), $Pd(OAc)_2$ (72 mg, 0.32 mmol), P(*o*tol)$_3$ (196 mg, 644 µmol) and K_2CO_3 (2.23 g, 16.1 mmol) were converted to furnish compound **7b** (1.37 g, 2.59 mmol, 80%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.35) as a colorless solid (mp 60°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.11 (s, 2 H), 6.08 (dt, *J* = 16.1 Hz, *J* = 12.4 Hz, 1 H), 7.00–7.02 (m, 2 H), 7.11 (dt, *J* = 16.1 Hz, *J* = 1.9 Hz, 1 H), 7.35–7.46 (m, 7 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 70.26 (CH_2), 112.07 (t, *J* = 23.1 Hz, CH), 115.43 (2 CH), 126.70 (C), 127.60 (2 CH), 128.32 (CH), 128.83 (2 CH), 129.37 (2 CH), 136.66 (C), 139.27 (t, *J* = 9.5 Hz, CH), 160.55 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–126.23)–(–126.15) (m, CF_2), (–123.25)–(–123.20) (m, CF_2), (–122.94)–(–122.83) (m, CF_2), (–121.67)–(–121.54) (m, CF_2), (–110.64)–(–110.56) (m, CF_2), (–80.94)–(–80.90) (m, CF_2) ppm. IR (ATR): nu(tilde) = 3041 (w), 2860 (w), 1235 (s), 1191 (vs), 1141 (s), 738 (s), 714 (s), 706 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 528.0753 (for $C_{21}H_{13}F_{13}O^+$); found 528.0767 [M^+]. $C_{21}H_{13}F_{13}O$ (528.31).

(*E*)-1-(Benzyloxy)-3,5-bis(1*H*,2*H*-perfluoro-1-hexenyl)benzene (10a). According to the GPA, 1*H*,1*H*,2*H*-perfluoro-1-hexene (2.5 mL, 3.6 g, 15 mmol), 1-(benzyloxy)-3,5-dibromobenzene (**9**) (500 mg, 1.46 mmol), $Pd(OAc)_2$ (33 mg, 0.15 mmol), P(*o*tol)$_3$ (89 mg, 0.29 mmol) and K_2CO_3 (1.01 g, 7.30 mmol) were converted to furnish compound **10a** (608 mg, 0.90 mmol, 62%) after column chromatography (SiO_2, hexanes/CH_2Cl_2

10:1, R_f = 0.35) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.14 (s, 2 H), 6.22 (dt, *J* = 16.0 Hz, *J* = 12.0 Hz, 2 H), 7.11–7.17 (m, 5 H), 7.35–7.38 (m, 1 H), 7.41–7.46 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 70.65 (CH_2), 115.53 (2 CH), 116.04 (t, *J* = 23.0 Hz, 2 CH), 120.15 (CH), 127.66 (2 CH), 128.52 (CH), 128.92 (2 CH), 135.81 (2 C), 136.29 (C), 139.06 (t, *J* = 9.2 Hz, 2 CH), 159.80 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–125.70)–(–125.61) (m, CF_2), (–124.06)–(–124.00) (m, CF_2), (–111.52)–(–111.47) (m, CF_2), (–81.09)–(–81.04) (m, CF_3) ppm. IR (ATR): nu(tilde) = 3069 (w), 3039 (w), 1221 (vs), 1170 (s), 1130 (vs), 885 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 672.0752 (for $C_{25}H_{14}F_{18}O^+$); found 672.0744 [M^+]. $C_{25}H_{14}F_{18}O$ (672.36).

(*E*)-1-(Benzyloxy)-3,5-bis(1*H*,2*H*-perfluoro-1-octenyl)benzene (10b). According to the GPA, 1*H*,1*H*,2*H*-perfluoro-1-octene (3.4 mL, 5.1 g, 15 mmol), 1-(benzyloxy)-3,5-dibromobenzene (**9**) (500 g, 16.4 mmol), $Pd(OAc)_2$ (33 mg, 0.15 mmol), P(*o*tol)$_3$ (89 mg, 0.29 mmol) and K_2CO_3 (1.01 g, 7.30 mmol) were converted to furnish compound **10b** (889 mg, 1.02 mmol, 70%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.39) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.13 (s, 2 H), 6.22 (dt, *J* = 16.1 Hz, *J* = 12.0 Hz, 2 H), 7.11–7.17 (m, 5 H), 7.35–7.37 (m, 1 H), 7.40–7.45 (m, 4 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 70.66 (CH_2), 115.53 (2 CH), 116.13 (t, *J* = 23.1 Hz, 2 CH), 120.16 (CH), 127.66 (2 CH), 128.52 (CH), 128.92 (2 CH), 135.81 (2 C), 136.28 (C), 139.03 (t, *J* = 9.6 Hz, 2 CH), 159.79 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–126.12)–(–126.04) (m, 2 CF_2), (–123.14)–(–123.08) (m, 2 CF_2), (–122.83)–(–122.74) (m, 2 CF_2), (–121.58)–(–121.46) (m, 2 CF_2), (–111.26)–(–111.21) (m, 2 CF_2), (–80.82)–(–80.78) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 3072 (w), 3039 (w), 1231 (s), 1192 (vs), 1169 (s), 1142 (vs), 1119 (s), 699 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 872.0624 (for $C_{29}H_{14}F_{26}O^+$); found 872.0622 [M^+]. $C_{29}H_{14}F_{26}O$ (872.39).

General procedure B (GPB). Pd–C (10 w/w%, 10 mol%) was added to a solution of the alkene **7** or **10** (1.0 equiv.) in EtOAc (5 L/mol). The resulting suspension was stirred at 70°C under a H_2 atmosphere (3 bar excess) for 18 h. The suspension was filtered using SiO_2 (MTBE). The solvent was removed *in vacuo* to give the phenols **8** and **11**.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)phenol (8a). According to the GPB, Pd–C (10 w/w%, 132 mg, 124 µmol) and alkene **7a** (531 mg, 1.24 mmol) were converted to furnish compound **8a** (419 mg, 1.23 mmol, 99%) after filtration (SiO_2, MTBE, R_f = 0.92) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24–2.42 (m, 2 H), 2.82–2.88 (m, 2 H), 5.10 (br s, 1 H), 6.78–6.81 (m, 2 H), 7.07–7.10 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 25.69 (t, J = 4.3 Hz, CH_2), 33.25 (t, J = 22.2 Hz, CH_2), 115.78 (2 CH), 129.64 (2 CH), 131.61 (C), 154.30 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.08)–(–126.03) (m, CF_2), (–124.52)–(–124.46) (m, CF_2), (–114.95)–(–114.89) (m, CF_2), (–81.08)–(–81.04) (m, CF_3) ppm. IR (ATR): nu(tilde) = 3283 (w), 2970 (w), 2956 (w), 2868 (w), 1216 (vs), 1169 (s), 1131 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 340.0504 (for $C_{12}H_9F_9O^+$); found 340.0502 [M^+]. $C_{12}H_9F_9O$ (340.19).

4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)phenol (8b). According to the GPB, Pd–C (10 w/w%, 239 mg, 225 µmol) and alkene **7b** (1.19 g, 2.25 mmol) were converted to furnish compound **8b** (963 mg, 2.19 mmol, 97%) after filtration (SiO_2, MTBE, R_f = 0.94) as a colorless solid (mp 43°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28–2.39 (m, 2 H), 2.84–2.87 (m, 2 H), 5.12 (br s, 1 H), 6.79–6.81 (m, 2 H), 7.07–7.09 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 25.76 (t, J = 4.0 Hz, CH_2), 33.41 (t, J = 22.1 Hz, CH_2), 115.79 (2 CH), 129.61 (2 CH), 131.55 (C), 154.46 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.25)–(–126.17) (m, CF_2), (–123.63)–(–123.56) (m, CF_2), (–123.00)–(–122.83) (m, CF_2), (–122.04)–(–121.86) (m, CF_2), (–114.76)–(–114.61) (m, CF_2), (–80.95)–(–80.89) (m, CF_2) ppm. IR (ATR): nu(tilde) = 3402 (w), 3029 (w), 2943 (w), 2876 (w), 1228 (s), 1204 (s), 1187 (vs), 1139 (vs), 1073 (s), 693 (s), 637 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 440.0440 (for $C_{14}H_9F_{13}O^+$); found 440.0457 [M^+]. $C_{14}H_9F_{13}O$ (440.20).

3,5-Bis(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phenol (11a). According to the GPB, Pd–C (10 w/w%, 15 mg, 14 µmol) and alkene **10a** (96 mg, 0.14 mmol) were converted to furnish compound compound **11a** (83 mg, 0.14 mmol, 100%) after filtration (SiO_2, MTBE, R_f = 0.94) as a colorless solid (mp 52°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.31–2.41 (m, 2 H), 2.84–2.87 (m, 2 H), 4.87 (br s, 1 H), 6.58 (s, 2 H), 6.65 (s, 1 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.44 (t, J = 3.9 Hz, 2 CH_2), 32.88 (t, J = 22.1 Hz, 2 CH_2), 113.84 (2 CH), 121.00 (CH), 141.74 (2 C), 156.32 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.07)–(–126.01) (m, 2 CF_2), (–124.48)–(–124.42)

(m, 2 CF_2), (–114.87)–(–114.81) (m, 2 CF_2), (–81.18)–(–81.13) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 3396 (w), 2963 (w), 2893 (w), 2851 (w), 1209 (s), 1127 (s), 1097 (s), 1063 (s), 1051 (vs), 1035 (s), 1000 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 586.0595 (for $C_{18}H_{12}F_{18}O^+$); found 586.0583 [M^+]. $C_{18}H_{12}F_{18}O$ (586.26).

3,5-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phenol (11b). According to the GPB, Pd–C (10 w/w%, 109 mg, 102 µmol) and alkene **10b** (889 g, 1.02 mmol) were converted to furnish compound **11b** (798, 1.01 mmol, 99%) after filtration (SiO_2, MTBE, R_f = 0.94) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.31–2.41 (m, 2 H), 2.84–2.87 (m, 2 H), 4.75 (br s, 1 H), 6.58 (s, 2 H), 6.64 (s, 1 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.46 (t, *J* = 4.7 Hz, 2 CH_2), 32.97 (t, *J* = 21.7 Hz, 2 CH_2), 113.82 (2 CH), 120.97 (CH), 141.70 (2 C), 156.33 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.12)–(–126.05) (m, 2 CF_2), (–123.49)–(–123.43) (m, 2 CF_2), (–122.88)–(–122.76) (m, 2 CF_2), (–121.89)–(–121.77) (m, 2 CF_2), (–114.56)–(–114.49) (m, 2 CF_2), (–80.83)–(–80.79) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 3344 (w), 2948 (w), 1231 (s), 1187 (vs), 1142 (vs), 1120 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 786.0467 (for $C_{22}H_{12}F_{26}O^+$); found 786.0457 [M^+]. $C_{22}H_{12}F_{26}O$ (786.30).

General procedure C (GPC). At 0°C, Tf_2O (1.2 equiv.) was added to a solution of pyridine (2.0 equiv.) and phenol **8** or **11** (1.0 equiv.) in anhydrous CH_2Cl_2 (5 L/mol). A colorless solid precipitated immediately. The resulting suspension was stirred at ambient temperature for 1.5 h. MTBE (25 L/mol) and hydrochloric acid (1 mol/L, 15 L/mol) were added and the layers were separated. The organic layer was washed with saturated aqueous $NaHCO_3$ (15 L/mol) and brine (15 L/mol). The organic layer was dried ($MgSO_4$) and filtered. The solvent was removed *in vacuo* to give the triflates **3**.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)phenyl trifluoromethanesulfonate (3a). According to the GPC, Tf_2O (124 mg, 0.44 mmol), pyridine (59 mg, 0.74 mmol) and phenol **8a** (126 mg, 0.37 mmol) were converted to furnish compound **3a** (171 mg, 0.36 mmol, 97%) as a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.33–2.43 (m, 2 H), 2.94–2.98 (m, 2 H), 7.23–7.25 (m, 2 H), 7.30–7.31 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ = 26.05 (t, *J* = 4.5 Hz, CH_2), 32.73 (t, *J* = 22.1 Hz, CH_2), 118.92 (q, *J* = 320.7 Hz, C), 121.04 (2 CH), 130.28 (2 CH), 139.82 (C), 148.52 (C) ppm. $^{19}F\{^1H\}$

NMR (470 MHz, $CDCl_3$): δ = (–126.07)–(–126.02) (m, CF_2), (–124.47)–(–124.41) (m, CF_2), (–114.88)–(–114.82) (m, CF_2), (–81.08)–(–81.04) (m, CF_3), (–72.88) (s, CF_3) ppm. IR (ATR): nu(tilde) = 2957 (w), 2922 (w), 2858 (w), 1208 (vs), 1131 (vs), 881 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 471.9997 (for $C_{13}H_8F_{12}O_3S^+$); found 471.9998 [M^+]. $C_{13}H_8F_{12}O_3S$ (472.24).

4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)phenyl trifluoromethanesulfonate (3b). According to the GPC, Tf_2O (0.41 mL, 0.68 g, 2.42 mmol), pyridine (0.33 mL, 0.32 g, 4.04 mmol) and phenol **8b** (888 mg, 2.02 mmol) were converted to furnish compound **3b** (1.10 g, 1.92 mmol, 95%) as a yellow liquid. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.33–2.44 (m, 2 H), 2.94–2.98 (m, 2 H), 7.23–7.25 (m, 2 H), 7.30–7.31 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.09 (t, *J* = 4.3 Hz, CH_2), 32.84 (t, *J* = 22.2 Hz, CH_2), 118.91 (q, *J* = 320.7 Hz, C), 121.87 (2 CH), 130.27 (2 CH), 139.81 (C), 148.51 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.18)–(–126.10) (m, CF_2), (–123.53)–(–123.42) (m, CF_2), (–122.90)–(–122.80) (m, CF_2), (–121.95)–(–121.82) (m, CF_2), (–114.63)–(–114.48) (m, CF_2), (–80.84)–(–80.79) (m, CF_2), (–72.89) (CF_3) ppm. IR (ATR): nu(tilde) = 2953 (w), 1203 (s), 1137 (vs), 886 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 571.9933 (for $C_{15}H_8F_{16}O_3S^+$); found 571.9937 [M^+]. $C_{15}H_8F_{16}O_3S$ (572.26).

3,5-Bis(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)phenyl trifluoromethanesulfonate (3c). According to the GPC, Tf_2O (305 mg, 1.08 mmol), pyridine (142 mg, 1.80 mmol) and phenol **11a** (530 mg, 0.90 mmol) were converted to furnish compound **3c** (583 mg, 0.81 mmol, 90%) as a yellow oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.34–2.44 (m, 4 H), 2.95–2.98 (m, 4 H), 7.03 (s, 2 H), 7.11 (s, 1 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.46 (t, *J* = 4.5 Hz, 2 CH_2), 32.56 (t, *J* = 22.3 Hz, 2 CH_2), 118.90 (q, *J* = 320.5 Hz, C), 119.81 (2 CH), 128.59 (CH), 142.64 (2 C), 150.06 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.00)–(–125.94) (m, 2 CF_2), (–124.35)–(–124.29) (m, 2 CF_2), (–114.62)–(–114.56) (m, 2 CF_2), (–81.08)–(–81.03) (m, 2 CF_3), (–72.92) (s, CF_3) ppm. IR (ATR): nu(tilde) = 2960 (w), 1211 (vs), 1132 (vs), 987 (s), 884 (s), 728 (s), 611 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 718.0088 (for $C_{19}H_{11}F_{21}O_3S^+$); found 718.0079 [M^+]. $C_{19}H_{11}F_{21}O_3S$ (718.32).

3,5-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)phenyl trifluoromethanesulfonate (3d). According to the GPC, Tf_2O (341 mg, 1.21 mmol), pyridine (160 mg, 2.02 mmol) and

phenol **11b** (798 mg, 1.01 mmol) were converted to furnish compound **3d** (751 mg, 0.82 mmol, 81%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.34–2.45 (m, 4 H), 2.95–2.98 (m, 4 H), 7.03 (s, 2 H), 7.12 (s, 1 H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.45 (t, *J* = 4.5 Hz, 2 CH_2), 32.61 (t, *J* = 22.7 Hz, 2 CH_2), 118.87 (q, *J* = 321.9 Hz, C), 119.81 (2 CH), 128.62 (CH), 142.62 (2 C), 150.03 (C) ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.13)–(–126.05) (m, 2 CF_2), (–123.40)–(–123.34) (m, 2 CF_2), (–122.87)–(–122.77) (m, 2 CF_2), (–121.89)–(–121.76) (m, 2 CF_2), (–114.37)–(–114.30) (m, 2 CF_2), (–80.84)–(–80.79) (m, 2 CF_3), (–72.91) (s, CF_3) ppm. IR (ATR): nu(tilde) = 2952 (w), 1235 (s), 1212 (s), 1186 (vs), 1158 (s), 1139 (vs), 1117 (s), 985 (s), 700 (s), 613 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 917.9960 (for $C_{23}H_{11}F_{29}O_3S^+$); found 917.9956 [M^+]. $C_{23}H_{11}F_{29}O_3S$ (918.35).

General procedure D (GPD). With exclusion of moisture and air (nitrogen atmosphere), triflate **3** (1.0 equiv) was added to a suspension of boronic acid derivative **2** (1.1 equiv.), Pd_2dba_3 (5 mol%), SPhos (20 mol%) and K_2CO_3 (2.0 equiv.) in degassed toluene (20 L/mol). Degassed water (20 L/mol) was added and the vial was tightly closed. The resulting mixture was stirred at 140°C for 18 h. The layers were separated and the aqueous layer was extracted with MTBE (2 x 40 L/mol). The combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed *in vacuo* and the crude product was purified by column chromatography to give the biphenyl derivatives **12**.

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)-4-(*tert*-butylthio)biphenyl (12a). According to the GPD, triflate **3a** (100 mg, 0.21 mmol), boronic acid **2a** (48 mg, 0.23 mmol), Pd_2dba_3 (10 mg, 11 µmol), SPhos (17 mg, 42 µmol) and K_2CO_3 (58 mg, 0.42 mmol) were converted to furnish compound **12a** (78 mg, 0.16 mmol, 76%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.24) as a colorless solid (mp 87°C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 9 H), 2.37–2.47 (m, 2 H), 2.95–2.99 (m, 2 H), 7.30–7.31 (m, 2 H), 7.53–7.55 (m, 2 H), 7.56–7.58 (m, 2 H), 7.59–7.61 (m, 2 H) ppm. $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.23 (t, *J* = 4.1 Hz, CH_2), 31.14 (3 CH_3), 32.96 (t, *J* = 22.0 Hz, CH_2), 46.24 (C), 127.11 (2 CH), 127.60 (2 CH), 128.95 (2 CH), 131.90 (C), 137.99 (2 CH), 138.68 (C), 139.03 (C), 141.11 (C) ppm. $^{19}F\{^{1}H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.02)–(–125.96) (m, CF_2), (–124.44)–(–124.37) (m, CF_2), (–114.86)–(–114.80) (m, CF_2), (–81.01)–(–80.97) (m, CF_3) ppm. IR (ATR): nu(tilde) =

2971 (w), 1232 (s), 1210 (s), 1189 (s), 1167 (s), 1131 (vs), 814 (s), 712 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 488.1215 (for $C_{22}H_{21}F_9S^+$); found 488.1223 [M^+]. $C_{22}H_{21}F_9S$ (488.46).

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-4-(*tert*-butylthio)biphenyl (12b). According to the GPD, triflate **3b** (100 mg, 0.17 mmol), boronic acid **2a** (40 mg, 0.19 mmol), Pd_2dba_3 (8 mg, 9 µmol), SPhos (14 mg, 34 µmol) and K_2CO_3 (47 mg, 0.34 mmol) were converted to furnish compound **12b** (90 mg, 0.15 mmol, 88%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.30) as a colorless solid (mp 83°C). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 9 H), 2.37–2.48 (m, 2 H), 2.96–2.99 (m, 2 H), 7.30–7.31 (m, 2 H), 7.54–7.55 (m, 2 H), 7.56–7.58 (m, 2 H), 7.60–7.61 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.27 (t, J = 4.1 Hz, CH_2), 31.14 (3 CH_3), 33.08 (t, J = 22.0 Hz, CH_2), 46.22 (C), 127.12 (2 CH), 127.60 (2 CH), 128.95 (2 CH), 131.96 (C), 137.99 (2 CH), 138.71 (C), 139.05 (C), 141.13 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.17)–(–126.10) (m, CF_2), (–123.52)–(–123.44) (m, CF_2), (–122.92)–(–122.81) (m, CF_2), (–121.93)–(–121.82) (m, CF_2), (–114.64)–(–114.50) (m, CF_2), (–80.84)–(–80.80) (m, CF_2) ppm. IR (ATR): nu(tilde) = 2964 (w), 2925 (w), 2865 (w), 1230 (s), 1184 (s), 1141 (vs), 698 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 588.1151 (for $C_{24}H_{21}F_{13}S^+$); found 588.1155 [M^+]. $C_{24}H_{21}F_{13}S$ (588.47).

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)-3,5-bis(*tert*-butylthio)biphenyl (12c). According to the GPD, triflate **3a** (100 mg, 0.21 mmol), boronic acid **2b** (87 mg, 0.23 mmol), Pd_2dba_3 (10 mg, 11 µmol), SPhos (17 mg, 42 µmol) and K_2CO_3 (58 mg, 0.42 mmol) were converted to furnish compound **12c** (96 mg, 0.17 mmol, 76%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.19) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 18 H), 2.36–2.48 (m, 2 H), 2.94–3.01 (m, 2 H), 7.31–7.34 (m, 2 H), 7.56–7.58 (m, 2 H), 7.74–7.75 (m, 1 H), 7.77–7.78 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.25 (t, J = 4.0 Hz, CH_2), 31.19 (6 CH_3), 32.97 (t, J = 22.1 Hz, CH_2), 46.46 (C), 127.68 (2 CH), 129.04 (2 CH), 133.61 (CH), 136.33 (2 CH), 138.44 (C), 138.95 (C), 141.28 (C), 144.71 (2 C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.02)–(–125.97) (m, CF_2), (–124.46)–(–124.37) (m, CF_2), (–114.84)–(–114.71) (m, CF_2), (–81.06)–(–81.02) (m, CF_3) ppm. IR (ATR): nu(tilde) = 2964 (w), 2924 (w), 2900 (w), 2861 (w), 1220 (s), 731 (vs) cm^{-1}. HRMS (APCI): calcd. 577.1640 (for $C_{26}H_{30}F_9S_2^+$); found 577.1621 [M + H^+]. $C_{26}H_{29}F_9S_2$ (576.92).

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)-3,5-bis(*tert*-butylthio)biphenyl (12d). According to the GPD, triflate **3b** (100 mg, 0.21 mmol), boronic acid **2b** (72 mg, 0.19 mmol), Pd_2dba_3 (8 mg, 9 µmol), SPhos (14 mg, 34 µmol) and K_2CO_3 (47 mg, 0.34 mmol) were converted to furnish compound **12d** (89 mg, 0.13 mmol, 76%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.29) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 18 H), 2.36–2.46 (m, 2 H), 2.96–2.99 (m, 2 H), 7.31–7.32 (m, 2 H), 7.55–7.56 (m, 2 H), 7.72–7.73 (m, 1 H), 7.75–7.76 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 26.28 (t, J = 3.9 Hz, CH_2), 31.20 (6 CH_3), 33.08 (t, J = 22.1 Hz, CH_2), 46.47 (C), 127.69 (2 CH), 129.05 (2 CH), 133.60 (CH), 136.35 (2 CH), 138.44 (C), 138.97 (C), 141.29 (C), 144.72 (2 C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–126.14)–(–126.08) (m, CF_2), (–123.53)–(–123.42) (m, CF_2), (–122.89)–(–122.80) (m, CF_2), (–121.92)–(–121.79) (m, CF_2), (–114.61)–(–114.48) (m, CF_2), (–80.82)–(–80.78) (m, CF_2) ppm. IR (ATR): nu(tilde) = 2962 (w), 2942 (w), 2924 (w), 2864 (w), 1237 (vs), 1165 (s), 1144 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 676.1498 (for $C_{28}H_{29}F_{13}S_2^+$); found 676.1491 [M^+]. $C_{28}H_{29}F_{13}S_2$ (676.64).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-4-(*tert*-butylthio)biphenyl (12e). According to the GPD, triflate **3c** (100 mg, 0.14 mmol), boronic acid **2a** (32 mg, 0.15 mmol), Pd_2dba_3 (6 mg, 7 µmol), SPhos (11 mg, 28 µmol) and K_2CO_3 (39 mg, 0.28 mmol) were converted fo furnish compound **12e** (78 mg, 0.11 mmol, 79%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.29) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (s, 9 H), 2.38–2.49 (m, 4 H), 2.97–3.00 (m, 4 H), 7.08 (s, 1 H), 7.33 (s, 2 H), 7.53–7.55 (m, 2 H), 7.61–7.63 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 26.67 (t, J = 3.9 Hz, 2 CH_2), 31.17 (3 CH_3), 33.12 (t, J = 22.3 Hz, 2 CH_2), 46.29 (C), 125.80 (2 CH), 127.31 (2 CH), 127.69 (CH), 132.53 (C), 138.00 (2 CH), 140.56 (2 C), 141.04 (C), 141.92 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–126.00)–(–125.95) (m, 2 CF_2), (–124.38)–(–124.32) (m, 2 CF_2), (–114.75)–(–114.70) (m, 2 CF_2), (–81.10)–(–81.05) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 2965 (w), 2900 (w), 1217 (vs), 1167 (s), 1131 (vs), 1109 (s), 880 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 734.1306 (for $C_{28}H_{24}F_{18}S^+$); found 734.1301 [M^+]. $C_{28}H_{24}F_{18}S$ (734.53).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-4-(*tert*-butylthio)biphenyl (12f). According to the GPD, triflate **3d** (100 mg, 0.11 mmol), boronic acid **2a** (25 mg, 0.12 mmol),

Pd_2dba_3 (5 mg, 6 µmol), SPhos (9 mg, 22 µmol) and K_2CO_3 (30 mg, 0.22 mmol) were converted to furnish compound **12f** (80 mg, 90 µmol, 82%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.41) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (s, 9 H), 2.37–2.48 (m, 4 H), 2.96–3.00 (m, 4 H), 7.08 (s, 1 H), 7.33 (s, 2 H), 7.53–7.54 (m, 2 H), 7.60–7.62 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.65 (t, J = 3.2 Hz, 2 CH_2), 31.13 (3 CH_3), 33.16 (t, J = 22.5 Hz, 2 CH_2), 46.30 (C), 125.79 (2 CH), 127.31 (2 CH), 127.71 (CH), 132.39 (C), 138.02 (2 CH), 140.52 (2 C), 141.01 (C), 141.85 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.12)–(–126.05) (m, 2 CF_2), (–123.45)–(–123.36) (m, 2 CF_2), (–122.85)–(–122.75) (m, 2 CF_2), (–121.87)–(–121.75) (m, 2 CF_2), (–114.50)–(–114.44) (m, 2 CF_2), (–80.84)–(–80.80) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 2963 (w), 2924 (w), 1233 (s), 1189 (vs), 1142 (vs), 1120 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 934.1178 (for $C_{32}H_{24}F_{26}S^+$); found 934.1181 [M^+]. $C_{32}H_{24}F_{26}S$ (934.56).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)-3,5-bis(*tert*-butylthio)biphenyl (12g). According to the GPD, triflate **3c** (100 mg, 0.14 mmol), boronic acid **2b** (57 mg, 0.15 mmol), Pd_2dba_3 (6 mg, 7 µmol), SPhos (11 mg, 28 µmol) and K_2CO_3 (39 mg, 0.28 mmol) were converted to furnish compound **12g** (50 mg, 60 µmol, 43%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.21) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.35 (s, 18 H), 2.38–2.49 (m, 4 H), 2.97–3.00 (m, 4 H), 7.09 (s, 1 H), 7.30 (s, 2 H), 7.73–7.76 (m, 3 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.65 (t, J = 3.7 Hz, 2 CH_2), 31.23 (6 CH_3), 33.07 (t, J = 22.4 Hz, 2 CH_2), 46.57 (2 C), 125.88 (2 CH), 127.87 (CH), 133.82 (2 C), 136.44 (2 CH), 140.69 (2 C), 141.25 (2 C), 144.97 (CH) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–125.97)–(–125.92) (m, 2 CF_2), (–124.34)–(–124.28) (m, 2 CF_2), (–114.71)–(–114.66) (m, 2 CF_2), (–81.09)–(–81.02) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 2964 (w), 2925 (w), 2900 (w), 1217 (vs), 1166 (s), 1131 (vs), 879 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 822.1653 (for $C_{32}H_{32}F_{18}S_2^+$); found 822.1645 [M^+]. $C_{32}H_{32}F_{18}S_2$ (822.70).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-3,5-bis(*tert*-butylthio)biphenyl (12h). According to the GPD, triflate **3d** (100 mg, 0.11 mmol), boronic acid **2b** (46 mg, 0.12 mmol), Pd_2dba_3 (5 mg, 6 µmol), SPhos (9 mg, 22 µmol) and K_2CO_3 (30 mg, 0.22 mmol) were converted to furnish compound **12h** (46 mg, 40 µmol, 36%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.24) as a colorless oil. ^{1}H NMR

(500 MHz, $CDCl_3$): δ = 1.34 (s, 18 H), 2.38–2.49 (m, 4 H), 2.97–3.00 (m, 4 H), 7.09 (s, 1 H), 7.29 (s, 2 H), 7.73–7.75 (m, 3 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.67 (t, *J* = 3.9 Hz, 2 CH_2), 31.23 (6 CH_3), 33.16 (t, *J* = 22.5 Hz, 2 CH_2), 46.57 (2 C), 125.87 (2 CH), 127.88 (CH), 133.81 (2 C), 136.44 (2 CH), 140.69 (2 C), 141.23 (C), 141.25 (C), 144.96 (CH) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.11)–(–126.04) (m, 2 CF_2), (–123.40)–(–123.35) (m, 2 CF_2), (–122.84)–(–122.74) (m, 2 CF_2), (–121.85)–(–121.74) (m, 2 CF_2), (–114.47)–(–114.40) (m, 2 CF_2), (–80.83)–(–80.78) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 2960 (w), 2923 (w), 2864 (w), 1231 (s), 1189 (s), 1141 (vs), 1073 (s), 723 (s), 708 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 1022.1525 (for $C_{36}H_{32}F_{26}S_2^+$); found 1022.1525 [M^+]. $C_{36}H_{32}F_{26}S_2$ (1022.73).

General procedure E (GPE). NCS (4.0 equiv. per thioether unit) and hydrochloric acid (1 mol/L, 1.1 equiv. per thioether unit) were added in portions at 0°C to a solution of thioether **12** (1.0 equiv.) in CH_3CN (30 L/mol). The resulting solution was stirred at 0°C for 1 h and at ambient temperature for 1 h. Water (30 L/mol) was added and the mixture was extracted with CH_2Cl_2 (3 x 30 L/mol). The combined organic layers were dried ($MgSO_4$) and filtered. The solvent was removed *in vacuo* and the crude product was purified by column chromatography to give the sulfonyl chlorides **13**.

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)biphenyl-4-sulfonyl chloride (13a). According to the GPE, NCS (69 mg, 0.52 mmol), hydrochloric acid (1 mol/L, 0.15 mL, 0.15 mmol) and thioether **12a** (64 mg, 0.13 mmol) were converted to furnish compound **13a** (52 mg, 0.10 mmol, 77%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.11) as a colorless solid (mp 75°C). ^1H NMR (500 MHz, $CDCl_3$): δ = 2.38–2.49 (m, 2 H), 2.99–3.02 (m, 2 H), 7.36–7.38 (m, 2 H), 7.59–7.61 (m, 2 H), 7.79–7.81 (m, 2 H), 8.09–8.11 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.36 (t, *J* = 3.8 Hz, CH_2), 32.84 (t, *J* = 22.2 Hz, CH_2), 127.78 (2 CH), 128.02 (2 CH), 128.17 (2 CH), 129.37 (2 CH), 137.22 (C), 140.56 (C), 143.09 (C), 147.95 (2 C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–125.98)–(–125.90) (m, CF_2), (–124.37)–(–124.30) (m, CF_2), (–114.68)–(–114.61) (m, CF_2), (–81.05)–(–80.99) (m, CF_2) ppm. IR (ATR): nu(tilde) = 2956 (w), 2928 (w), 2854 (w), 1233 (s), 1209 (vs), 1190 (s), 1165 (vs), 1127 (vs), 1085 (s), 715 (s), 581 (vs), 561 (vs) cm^{-1}. HRMS (EI, 70 eV): calcd. 498.0097 (for $C_{18}H_{12}ClF_9O_2S^+$); found 498.0083 [M^+]. $C_{18}H_{12}ClF_9O_2S$ (498.79).

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)biphenyl-4-sulfonyl chloride (13b). According to the GPE, NCS (80 mg, 0.60 mmol), hydrochloric acid (1 mol/L, 0.2 mL, 0.2 mmol) and thioether **12b** (90 mg, 0.15 mmol) were converted to furnish compound **13b** (72 mg, 0.12 mmol, 80%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.14) as a colorless solid (mp 90°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34–2.52 (m, 2 H), 2.98–3.03 (m, 2 H), 7.36–7.38 (m, 2 H), 7.58–7.61 (m, 2 H), 7.78–7.81 (m, 2 H), 8.09–8.12 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 26.38 (t, *J* = 3.9 Hz, CH_2), 32.94 (t, *J* = 22.2 Hz, CH_2), 127.78 (2 CH), 128.02 (2 CH), 128.17 (2 CH), 129.38 (2 CH), 137.22 (C), 140.58 (C), 143.09 (C), 147.96 (2 C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–126.12)–(–126.04) (m, CF_2), (–123.45)–(–123.39) (m, CF_2), (–122.85)–(–122.75) (m, CF_2), (–121.87)–(–121.76) (m, CF_2), (–114.46)–(–114.39) (m, CF_2), (–80.84)–(–80.80) (m, CF_2) ppm. IR (ATR): nu(tilde) = 2920 (w), 2850 (w), 1235 (s), 1178 (vs), 1139 (vs), 1108 (s), 696 (s), 568 (s), 556 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 598.0033 (for $C_{20}H_{12}ClF_{13}O_2S^+$); found 598.0018 [$M^+$]. $C_{20}H_{12}ClF_{13}O_2S$ (598.80).

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)biphenyl-3,5-disulfonyl dichloride (13c). According to the GPE, NCS (139 mg, 1.04 mmol), hydrochloric acid (1 mol/L, 0.3 mL, 0.3 mmol) and thioether **12c** (76 mg, 0.13 mmol) were converted to furnish compound **13c** (66 mg, 0.11 mmol, 85%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.03) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.39–2.50 (m, 2 H), 3.02–3.05 (m, 2 H), 7.43–7.45 (m, 2 H), 7.64–7.66 (m, 2 H), 8.52–8.53 (m, 2 H), 8.60–8.61 (m, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 26.42 (t, *J* = 4.0 Hz, CH_2), 32.71 (t, *J* = 22.5 Hz, CH_2), 123.55 (CH), 127.95 (2 CH), 129.90 (2 CH), 130.83 (2 CH), 134.67 (C), 141.86 (C), 145.56 (C), 146.42 (2 C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–125.96)–(–125.88) (m, CF_2), (–124.34)–(–124.27) (m, CF_2), (–114.58)–(–114.51) (m, CF_2), (–81.03)–(–80.97) (m, CF_2) ppm. IR (ATR): nu(tilde) = 3079 (w), 1211 (s), 1169 (vs), 1129 (s), 611 (vs) cm^{-1}. HRMS (EI, 70 eV): calcd. 595.9327 (for $C_{18}H_{11}Cl_2F_9O_4S_2^+$); found 595.9345 [$M^+$]. $C_{18}H_{11}Cl_2F_9O_4S_2$ (597.29).

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)biphenyl-3,5-disulfonyl dichloride (13d). According to the GPE, NCS (96 mg, 0.72 mmol), hydrochloric acid (1 mol/L, 92 mg, 90 µmol) and thioether **12d** (64 mg, 90 µmol) were converted to furnish compound **13d**

(50 mg, 70 µmol, 78%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.05) as a colorless solid (dec. 112°C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35–2.53 (m, 2 H), 3.01–3.06 (m, 2 H), 7.42–7.45 (m, 2 H), 7.64–7.66 (m, 2 H), 8.52–8.53 (m, 2 H), 8.60–8.61 (m, 1 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 26.44 (t, *J* = 4.2 Hz, CH_2), 32.80 (t, *J* = 22.4 Hz, CH_2), 123.55 (CH), 127.95 (2 CH), 129.90 (2 CH), 130.83 (2 CH), 134.67 (C), 141.87 (C), 145.56 (C), 146.42 (2 C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–126.10)–(–126.02) (m, CF_2), (–123.42)–(–123.32) (m, CF_2), (–122.85)–(–122.73) (m, CF_2), (–121.87)–(–121.74) (m, CF_2), (–114.35)–(–114.29) (m, CF_2), (–80.80)–(–80.76) (m, CF_2) ppm. IR (ATR): nu(tilde) = 3079 (w), 2921 (w), 2851 (w), 1245 (s), 1215 (s), 1173 (vs), 1136 (vs), 1118 (s), 603 (vs), 563 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 695.9263 (for $C_{20}H_{11}Cl_2F_{13}O_4S_2^+$); found 695.9263 [$M^+$]. $C_{20}H_{11}Cl_2F_{13}O_4S_2$ (697.30).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)biphenyl-4-sulfonyl chloride (13e). According to the GPE, NCS (48 mg, 0.36 mmol), hydrochloric acid (1 mol/L, 0.10 mL, 0.10 mmol) and thioether **12e** (63 mg, 90 µmol) were converted to furnish compound **13e** (51 mg, 70 µmol, 78%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.13) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34–2.52 (m, 4 H), 2.98–3.04 (m, 4 H), 7.18 (s, 1 H), 7.35 (s, 2 H), 7.78–7.81 (m, 2 H), 8.10–8.13 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 26.65 (t, *J* = 4.2 Hz, 2 CH_2), 32.99 (t, *J* = 22.2 Hz, 2 CH_2), 126.18 (2 CH), 127.78 (2 CH), 128.47 (2 CH), 129.23 (CH), 140.08 (C), 141.11 (2 C), 143.45 (C), 147.84 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$): δ = (–125.97)–(–124.91) (m, 2 CF_2), (–124.34)–(–124.28) (m, 2 CF_2), (–114.66)–(–114.61) (m, 2 CF_2), (–81.06)–(–81.01) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 2957 (w), 2926 (w), 2852 (w), 1216 (vs), 1192 (s), 1170 (s), 1126 (vs), 569 (vs) cm^{-1}. HRMS (EI, 70 eV): calcd. 744.0188 (for $C_{24}H_{15}ClF_{18}O_2S^+$); found 744.0183 [$M^+$]. $C_{24}H_{15}ClF_{18}O_2S$ (744.86).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)biphenyl-4-sulfonyl chloride (13f). According to the GPE, NCS (17 mg, 0.13 mmol), hydrochloric acid (1 mol/L, 41 mg, 40 µmol) and thioether **12f** (31 mg, 33 µmol) were converted to furnish compound **13f** (24 mg, 25 µmol, 76%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.22) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.39–2.49 (m, 4 H), 3.00–3.03 (m, 4 H), 7.18 (s, 1 H), 7.34 (s, 2 H), 7.78–7.80 (m, 2 H), 8.11–8.13 (m, 2 H)

ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.66 (t, *J* = 3.0 Hz, 2 CH_2), 33.00 (t, *J* = 22.4 Hz, 2 CH_2), 126.19 (2 CH), 127.79 (2 CH), 128.48 (2 CH), 129.24 (CH), 140.09 (C), 141.12 (2 C), 143.46 (C), 147.85 (C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–126.10)–(–126.03) (m, 2 CF_2), (–123.39)–(–123.33) (m, 2 CF_2), (–122.84)–(–122.72) (m, 2 CF_2), (–121.83)–(–121.72) (m, 2 CF_2), (–114.41)–(–114.34) (m, 2 CF_2), (–80.81)–(–80.76) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 2962 (w), 2928 (w), 1233 (s), 1191 (vs), 1178 (vs), 1142 (vs), 1122 (s), 707 (s), 568 (vs), 560 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 944.0061 (for $C_{28}H_{15}ClF_{26}O_2S^+$); found 944.0062 [$M^+$]. $C_{28}H_{15}ClF_{26}O_2S$ (944.89).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)biphenyl-3,5-disulfonyl dichloride (13g). According to the GPE, NCS (43 mg, 320 µmol) hydrochloric acid (1 mol/L, 92 mg, 90 µmol) and thioether **12g** (37 mg, 40 µmol, 1.0 equiv.) were converted to furnish compound **13g** (37 mg, 40 µmol, 100%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.07) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.36–2.55 (m, 4 H), 3.02–3.08 (m, 4 H), 7.27 (s, 1 H), 7.38 (s, 2 H), 8.51–8.51 (m, 2 H), 8.63–8.65 (m, 1 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.67 (t, *J* = 3.7 Hz, 2 CH_2), 32.94 (t, *J* = 22.3 Hz, 2 CH_2), 123.95 (CH), 126.16 (2 CH), 130.31 (CH), 131.09 (2 CH), 137.49 (C), 141.87 (2 C), 145.47 (C), 146.47 (2 C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = (–125.96)–(–125.90) (m, 2 CF_2), (–124.32)–(–124.22) (m, 2 CF_2), (–114.78)–(–114.53) (m, 2 CF_2), (–81.08)–(–81.00) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 2950 (w), 2922 (w), 2854 (w), 1218 (vs), 1178 (s), 1132 (vs) cm^{-1}. HRMS (EI, 70 eV): calcd. 841.9418 (for $C_{24}H_{14}Cl_2F_{18}O_4S_2^+$); found 841.9416 [$M^+$]. $C_{24}H_{14}Cl_2F_{18}O_4S_2$ (843.36).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)biphenyl-3,5-disulfonyl dichloride (13h). According to the GPE, NCS (29 mg, 0.22 mmol), hydrochloric acid (1 mol/L, 61 mg, 60 µmol) and thioether **12h** (29 mg, 28 µmol) were converted to furnish compound **13h** (23 mg, 22 µmol, 79%) after column chromatography (SiO_2, hexanes/CH_2Cl_2 10:1, R_f = 0.05) as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.41–2.51 (m, 4 H), 3.04–3.07 (m, 4 H), 7.27 (s, 1 H), 7.38 (s, 2 H), 8.51–8.51 (m, 2 H), 8.64–8.64 (m, 1 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 26.67 (t, *J* = 3.7 Hz, 2 CH_2), 32.94 (t, *J* = 22.3 Hz, 2 CH_2), 123.95 (CH), 126.16 (2 CH), 130.31 (CH), 131.09 (2 CH), 137.49 (C), 141.87 (2 C), 145.47 (C), 146.47 (2 C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz,

$CDCl_3$): δ = (–126.09)–(–126.02) (m, 2 CF_2), (–123.33)–(–123.27) (m, 2 CF_2), (–122.85)–(–122.72) (m, 2 CF_2), (–121.82)–(–121.72) (m, 2 CF_2), (–114.32)–(–114.26) (m, 2 CF_2), (–80.80)–(–80.76) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 2961 (w), 2923 (w), 2854 (w), 1235 (s), 1184 (vs), 1143 (s) cm^{-1}. HRMS (EI, 70 eV): calcd. 1041.9290 (for $C_{28}H_{14}Cl_2F_{26}O_4S_2^+$); found 1041.9292 [$M^+$]. $C_{28}H_{14}Cl_2F_{26}O_4S_2$ (1043.39).

General procedure F (GPF). A suspension of sulfonyl chloride **13** (1.0 equiv.) in water (20 L/mol) was heated to reflux for 18 h. The solvent was removed *in vacuo* to furnish the sulfonic acids **1**.

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)biphenyl-4-sulfonic acid monohydrate (1a). According to the the GPF, sulfonyl chloride **13a** (39 mg, 78 µmol) was converted to furnish compound **1a** (39 mg, 78 µmol, 100%) as a colorless solid (dec. 165°C). ^{1}H NMR (500 MHz, acetone-d_6): δ = 2.55–2.66 (m, 2 H), 3.01–3.05 (m, 2 H), 7.47–7.49 (m, 2 H), 7.68–7.70 (m, 2 H), 7.81–7.82 (m, 2 H), 7.93–7.95 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ = 26.54 (t, *J* = 3.9 Hz, CH_2), 32.84 (t, *J* = 21.8 Hz, CH_2), 127.88 (2 CH), 127.92 (2 CH), 128.27 (2 CH), 130.06 (2 CH), 138.64 (C), 140.49 (C), 141.45 (C), 144.91 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, acetone-d_6): δ = (–126.64)–(–126.58) (m, CF_2), (–124.88)–(–124.82) (m, CF_2), (–114.98)–(–114.92) (m, CF_2), (–81.95)–(–81.90) (m, CF_2) ppm. IR (ATR): nu(tilde) = 2954 (w), 2922 (w), 2853 (w), 1210 (vs), 1194 (s), 1130 (vs), 805 (s), 710 (s) cm^{-1}. HRMS (ESI, pos. mode): calcd. 481.0514 (for $C_{18}H_{14}F_9O_3S^+$); found 481.0527 [M – OH]$^+$. $C_{18}H_{13}F_9O_3S \cdot H_2O$ (498.36).

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)biphenyl-4-sulfonic acid monohydrate (1b). According to the GPF, sulfonyl chloride **13b** (49 mg, 82 µmol) was converted to furnish compound **1b** (48 mg, 80 µmol, 98%) as a colorless solid (dec. 91°C). ^{1}H NMR (500 MHz, acetone-d_6): δ = 2.56–2.67 (m, 2 H), 3.02–3.05 (m, 2 H), 7.48–7.49 (m, 2 H), 7.69–7.70 (m, 2 H), 7.82–7.84 (m, 2 H), 7.94–7.96 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ = 26.64 (t, *J* = 3.9 Hz, CH_2), 33.02 (t, *J* = 21.7 Hz, CH_2), 127.98 (2 CH), 128.04 (2 CH), 128.32 (2 CH), 130.09 (2 CH), 138.62 (C), 140.62 (C), 141.00 (C), 145.25 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, acetone-d_6): δ = (–126.74)–(–126.66) (m, CF_2), (–123.92)–(–123.87) (m, CF_2), (–123.41)–(–123.29) (m, CF_2), (–122.42)–(–

122.31) (m, CF_2), (–114.74)–(–114.67) (m, CF_2), (–81.71)–(–81.66) (m, CF_2) ppm. IR (ATR): nu(tilde) = 3032 (w), 2950 (w), 1229 (s), 1181 (s), 1140 (vs), 1124 (vs), 1073 (s), 1036 (s), 594 (s), 562 (s) cm^{-1}. HRMS (ESI, neg. mode): calcd. 579.0305 (for $C_{20}H_{12}F_{13}O_3S^-$); found 579.0280 [M – H_3O^+]. $C_{20}H_{13}F_{13}O_3S \cdot H_2O$ (598.38): calcd. C 40.15, H 2.53, S 5.36; found C 40.31, H. 2.60, S 5.10.

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorohexyl)biphenyl-3,5-disulfonic acid dihydrate (1c). According to the GPF, sulfonyl chloride **13c** (15 mg, 22 µmol) was converted to furnish compound **1c** (20 mg, 34 µmol, 97%) as a yellow solid (dec. 138°C). ^{1}H NMR (500 MHz, acetone-d_6): δ = 2.59–2.70 (m, 2 H), 3.08–3.11 (m, 2 H), 7.61–7.63 (m, 2 H), 7.97–7.98 (m, 2 H), 8.64–8.65 (m, 1 H), 8.81–8.82 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 26.62 (t, *J* = 4.3 Hz, CH_2), 32.65 (t, *J* = 21.1 Hz, CH_2), 124.12 (CH), 128.90 (2 CH), 130.56 (2 CH), 132.05 (2 CH), 135.28 (C), 142.56 (C), 146.48 (C), 146.65 (2 C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, acetone-d_6): δ = (–126.63)–(–126.57) (m, CF_2), (–124.87)–(–124.81) (m, CF_2), (–114.91)–(–114.85) (m, CF_2), (–81.94)–(–81.89) (m, CF_2) ppm. IR (ATR): nu(tilde) = 3404 (w), 2927 (w), 1714 (m), 1217 (s), 1130 (vs), 1030 (s) cm^{-1}. HRMS (ESI, neg. mode): calcd. 558.9937 (for $C_{18}H_{12}F_9O_6S_2^-$); found 558.9938 [M – 2 H_2O – H^+]. $C_{18}H_{13}F_9O_6S_2 \cdot 2\ H_2O$ (596.43).

4'-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)biphenyl-3,5-disulfonic acid dihydrate (1d). According to the GPF, sulfonyl chloride **13d** (15 mg, 22 µmol) was converted to furnish compound **1d** (14 mg, 20 µmol, 91%) as a colorless solid (dec. 125°C). ^{1}H NMR (500 MHz, acetone-d_6): δ = 2.61–2.71 (m, 2 H), 3.08–3.12 (m, 2 H), 7.61–7.62 (m, 2 H), 7.96–7.97 (m, 2 H), 8.64–8.65 (m, 1 H), 8.81–8.81 (m, 2 H) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 26.72 (t, *J* = 4.4 Hz, CH_2), 32.84 (t, *J* = 21.5 Hz, CH_2), 124.15 (CH), 128.94 (2 x CH), 130.60 (2 CH), 132.07 (2 CH), 134.35 (C), 142.63 (C), 146.57 (C), 146.76 (2 C) ppm. $^{19}F\{^1H\}$ NMR (470 MHz, acetone-d_6): δ = (–126.73)–(–126.65) (m, CF_2), (–123.92)–(–123.87) (m, CF_2), (–123.42)–(–123.31) (m, CF_2), (–122.39)–(–122.31) (m, CF_2), (–114.74)–(–114.61) (m, CF_2), (–81.70)–(–81.65) (m, CF_2) ppm. IR (ATR): nu(tilde) = 3343 (w), 3079 (w), 2945 (w), 1215 (s), 1172 (vs), 1135 (vs), 1118 (s), 610 (vs), 602 (vs) cm^{-1}. HRMS (ESI, neg. mode): calcd. 328.9900 (for $C_{20}H_{11}F_{13}O_6S_2^{2-}$); found 328.9881 [M – 2 H_3O^+]. $C_{20}H_{13}F_{13}O_6S_2 \cdot 2\ H_2O$ (696.45): calcd. C 34.49, H 2.46, S 9.21; found C 34.84, H 2.30, S 9.35.

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)biphenyl-4-sulfonic acid monohydrate (1e). According to the GPF, sulfonyl chloride **13e** (22 mg, 30 µmol) was converted to furnish compound **1e** (20 mg, 27 µmol, 90%) as a colorless solid (dec. 101°C). ^{1}H NMR (500 MHz, acetone-d_6): δ = 2.61–2.72 (m, 4 H), 3.07–3.10 (m, 4 H), 7.52 (s, 1 H), 7.73 (s, 2 H), 8.11–8.13 (m, 2 H), 8.19–8.20 (m, 2 H) ppm. ^{13}C{^{1}H} NMR (125 MHz, acetone-d_6): δ = 26.94 (t, *J* = 3.7 Hz, 2 CH_2), 32.99 (t, *J* = 21.9 Hz, 2 CH_2), 127.04 (2 CH), 128.48 (2 CH), 129.51 (2 CH), 130.59 (CH), 139.96 (C), 141.85 (2 C), 143.71 (C), 149.04 (C) ppm. ^{19}F{^{1}H} NMR (470 MHz, acetone-d_6): δ = (–126.66)–(–126.59) (m, 2 CF_2), (–124.86)–(–124.79) (m, 2 CF_2), (–115.00)–(–114.95) (m, 2 CF_2), (–81.97)–(–81.93) (m, 2 CF_3) ppm. IR (ATR): nu(tilde) = 3426 (w), 2957 (w), 2932 (w), 1216 (vs), 1192 (s), 1176 (s), 1126 (vs), 568 (vs) cm^{-1}. HRMS (ESI, neg. mode): calcd. 726.0460 (for $C_{24}H_{15}F_{18}O_3S^-$); found 726.0453 [M – H_3O^+]. $C_{24}H_{16}F_{18}O_3S \cdot H_2O$ (744.44): calcd. C 38.72, H 2.44, S 4.31; found C 39.11, H 2.44, S 4.50.

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)biphenyl-4-sulfonic acid monohydrate (1f). According to the GPF, sulfonyl chloride **13f** (10 mg, 11 µmol) was converted to furnish compound **1f** (9 mg, 10 µmol, 91%) as a colorless solid (dec. 91°C). Due to no solubility in any solvent, we were not able to obtain NMR spectra. IR (ATR): nu(tilde) = 3417 (w), 2954 (w), 1186 (vs), 1142 (s), 1122 (s), 630 (s) cm^{-1}. HRMS (ESI, neg. mode): calcd. 925.0332 (for $C_{28}H_{15}F_{26}O_3S^-$); found 925.0317 [M – H_3O^+]. $C_{28}H_{16}F_{26}O_3S \cdot H_2O$ (944.47).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorohexyl)biphenyl-3,5-disulfonic acid dihydrate (1g). According to the GPF, sulfonyl chloride **13g** (22 mg, 30 µmol) was converted to furnish compound **1g** (23 mg, 27 µmol, 90%) as a colorless solid (dec. 107°C). Due to no solubility in any solvent, we were not able to obtain NMR spectra. IR (ATR): nu(tilde) = 2936 (w), 1625 (s), 1396 (s), 1372 (s), 1006 (s), 979 (s), 831 (vs), 703 (vs) cm^{-1}. HRMS (ESI, neg. mode): calcd. 401.9978 (for $C_{24}H_{14}F_{18}O_6S_2^{2-}$); found 401.9966 [M – 2 H_3O^+]. $C_{24}H_{16}F_{18}O_6S_2 \cdot 2\ H_2O$ (842.51).

3',5'-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)biphenyl-3,5-disulfonic acid dihydrate (1h). According to the GPF, sulfonyl chloride **13h** (10 mg, 10 µmol) was converted to furnish compound **1h** (9 mg, 9 µmol, 90%) as a colorless solid (dec. 93°C). Due to no solubility in any solvent, we were not able to obtain NMR spectra. IR (ATR): nu(tilde)

= 3458 (w), 2924 (w), 1233 (s), 1189 (vs), 1143 (s) cm^{-1}. HRMS (ESI, neg. mode): calcd. 501.9914 (for $C_{28}H_{14}F_{26}O_6S_2^{2-}$); found 501.9893 [M – 2 H_3O^+]. $C_{28}H_{16}F_{26}O_6S_2 \cdot 2\ H_2O$ (1042.54).

Acknowledgement

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. MTBE was obtained as a generous gift from Evonik Industries, Marl, Germany.

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