Perfluorinated Ammonium and Phosphonium Ionic Liquids

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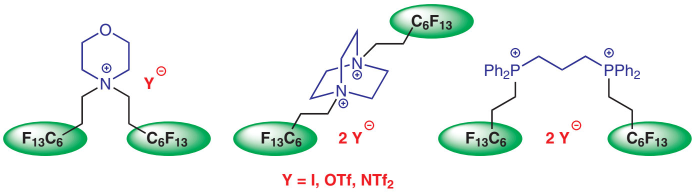

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Abstract Ammonium and phosphonium ionic liquids with perfluorinated side chains were prepared as hybrid materials for surface impregnation. Melting points of the triflimide salts range up to 95 °C. The key feature of this investigation are relatively short perfluorohexyl residues as the fluorinated part of the cations, making the target compounds beneficial alternatives to established products because of their enhanced degradability and therefore lower bioaccumulativity. In the ammonium series, pyrrolidinium, piperidinium, morpholinium triflimides as well as the dication derived from DABCO were prepared. Mono-phosphonium triflimides were obtained from triphenyl- and diphenylphosphane. Diphosphonium bistriflimides were obtained from bis(diphenylphosphano)alkanes, $Ph_2P(CH_2)_nPPh_2$ with n = 2–5. As alkylating reagents, n-$C_6F_{13}CH_2CH_2OTf$ and n-$C_6F_{13}CH_2CH_2I$ were applied.

Key words ionic liquids, fluorine compounds, phosphorus compounds, ammonium salts, phosphonium salts, triflimide

Perfluoroalkyl carboxylic and sulfonic acids with longer carbon chains ($C_nF_{2n+1}CO_2H$ and $C_nF_{2n+1}SO_3H$ with $n > 6$), so-called fluorosurfactants, represent a technologically relevant class of materials.[1] These compounds have found ubiquitous applications for surface treatment of paper, cardboard, textiles, leathers, polymeric materials, metals, etc.[2] Especially so-called fluorocarbon resins are widely used as impregnation materials for industrial as well as consumer[3] applications. The most prominent representatives for the preparation of these materials are PFOA ($C_7F_{15}CO_2H$) and PFOS ($C_8F_{17}SO_3H$).[4] Although PFOA and PFOS themselves are quite harmless since chemically inert, they are for the same reason persistent and they have become the focus of environmental concerns because they pollute the environment and are accumulated in the biosphere. Meanwhile they are detectable ubiquitously in the abiotic environment[5] as well as in animals and humans[6] and have thus attracted attention as global contaminants. These compounds were consequently listed under Annex B (restriction of production and use) of the Stockholm Convention in 2009.[7] Furthermore, the European Chemicals Agency lists PFOA on the SVHC Candidate List as a CMR substance (SVHC = substance of very high concern; CMR = carcinogenic, mutagenic, or toxic for reproduction).[8] The chemical industry began several initiatives to identify replacements for perfluoroalkyl materials with C_8F_{17} chains or higher.[9] Reasonable alternatives are shorter chain compounds with C_6F_{13} or C_4F_9 residues, which on the one hand could address the same outstanding material properties, but on the other hand do not accumulate in the environment due to their increased degradability.[10]

As a manufacturer of water repellent textile coatings, we are also aiming at identifying new compounds with shorter perfluoroalkyl side chains.[11] In particular fluorinated ionic liquids have come into focus as part of our research. Perfluorinated solvents[12] and ionic liquids[13] are so-called neoteric solvents, which are often associated with sustainable processes and green chemistry,[14] although their benefits are sometimes critically discussed.[15] The combination of both, i.e. ionic liquids with perfluorinated side chains,[16] has been realized in a few cases. Most of them utilize perfluorocarboxylic acids as anions,[17] but also perfluorinated cations have been used.[18] Among the perfluorinated cations, imidazolium,[19] triazolium,[20] and quaternary ammonium[21] species have been reported. Fluorinated quaternary phosphonium salts were reported to be super-hydrophobic materials[22] with contact angles up to 168°.[23] Herein we wish to disclose the synthesis of a small series of fluorinated ionic liquids based on cyclic ammonium, phosphonium, and diphosphonium cations. As fluorinated side chains R_F, perfluorohexyl residues were applied. In the ammonium series, pyrrolidinium **1**, piperidinium **2**, and morpholinium **3** cations, as well as the DABCO derivative **4**, were prepared (Figure 1). As phosphonium salts, the alkyltriphenyl **5** and dialkyldiphenyl congeners **6** and the diphosphonium dications **7**–**10** derived from bis(diphenylphosphano)ethane (DPPE), -propane (DPPP), -butane (DPPB), and –pentane were prepared. As anions Y, iodide or triflate (OTf) originated from the synthesis, but were both exchanged to triflimide [NTf_2, bis(trifluoromethanesulfonyl)imide anion].

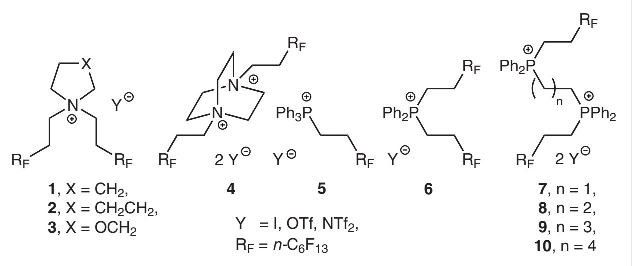
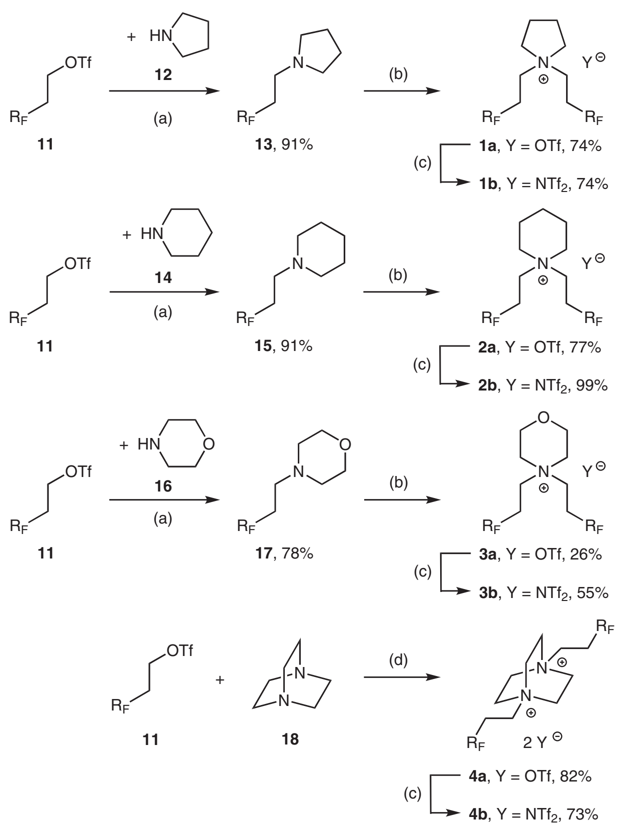


Figure 1 Target compounds of this study

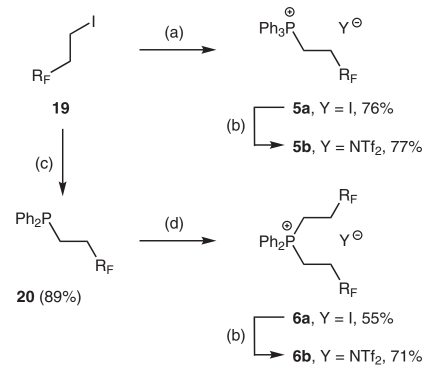
The iodide $R_FCH_2CH_2I$ **19** (see Schemes 2 and 3) and triflate $R_FCH_2CH_2OTf$ **11** (Scheme 1) were envisioned as alkylating reagents for the introduction of the 1*H*,1*H*,2*H*,2*H*-perfluorooctyl ($R_FCH_2CH_2$, $R_F = n\text{-}C_3F_{13}$) residue into amines. Whereas the iodo compound **19** was commercially available, the triflate had to be prepared from the alcohol $R_FCH_2CH_2OH$ (‘6:2 FTOH’) according to a literature procedure.[24] An initial attempt to convert $R_FCH_2CH_2I$ **19** with pyrrolidine (**12**) resulted in a complex reaction mixture. This observation is in accordance with a report by Honda and co-workers,[21a] who observed HI elimination to the respective olefin, followed by conjugated addition of the amine, followed again by HF elimination. With $R_FCH_2CH_2OTf$ **11**, however, these processes could be avoided and the envisioned alkylated amine **13** and the ammonium salt **1a** were formed (Scheme 1). After some experimentation, it was found that a stepwise approach is more practicable, since the optimal conditions for the first alkylation and the second (quaternization) were different. Thus, tertiary amines **13**,[25] **15**, and **17**[26] (78–91% yield) were obtained by conversion of the amines **12**, **14**, and **16** with K_2CO_3 as base in EtOAc at 70 °C,[27] whereas the salts **1a**, **2a**, and **3a** were obtained by heating the reaction mixtures in toluene to 130–150 °C and subsequent recrystallization from MTBE in 74% (**1a**), 77% (**2a**), and 26% (**3a**) yields, respectively. The triflate anions TfO^- were exchanged to triflimide Tf_2N^- via the hydroxide salts, prepared with the ion-exchange resin Lewatit Mono MP Plus 800. Whereas compound **2b** was directly obtained analytically pure in almost quantitative yield, compounds **1b** (74%) and **3b** (55%) required purification by recrystallization from MTBE.

For the preparation of diazonia[2.2.2]bicyclooctane derivative **4a**, DABCO (**18**) was heated with an excess of the triflate **11**; the salt **4a** was obtained in 82% yield after recrystallization from MTBE. Anion exchange was performed as above to furnish bistriflimide **4b** in 73% after recrystallization.



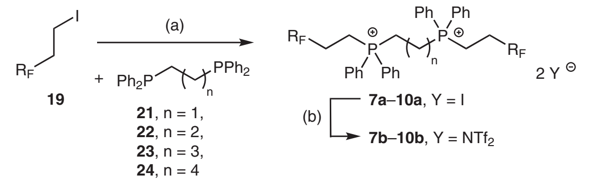
Scheme 1 Preparation of pyrrolidinium **1a**,**b**, piperidinium **2a**,**b**, morpholinium salts **3a**,**b** and DABCO derivatives **4a**,**b**. *Reagents and conditions*: (a) K_2CO_3 (2 equiv), EtOAc, 70 °C, 1 d; (b) **11** (1 equiv), toluene, 130 °C, 3 h for **1a** and **3a**; 150 °C, 3 h for **2a**; (c) 1. column of hydroxide loaded Lewatit Mono MP Plus 800, 2. $HNTf_2$ (1 equiv for **1b**, **2b**, **3b** or 2 equiv for **4b**); (d) **11** (3 equiv), toluene, 130 °C, 17 h. $R_F = n\text{-}C_6F_{13}$.

In contrast to the amines, the quaternization of phosphanes proceeded straightforwardly when using the alkyl iodide **19**. As a first example, Ph_3P was converted to furnish the salt **5a** in 76% yield after recrystallization (Scheme 2). This compound has been previously reported and used for Wittig olefinations.[28] The anion exchange, however, failed when using a hydroxy-loaded resin, presumably due to ylide formation after deprotonation. Therefore, we applied a protocol adapted from Ragogna and co-workers[23a] and stirred the iodide **5a** with $LiNTf_2$ in acetone. After equilibration, the volatiles were removed and the mixture redissolved in EtOAc. All water soluble components were extracted repeatedly with water until the aqueous extract was iodide-free (checked with $AgNO_3$). Finally, the material was recrystallized from MTBE to furnish triflimide **5b** in 77% yield. The respective dialkyldiphenyl salts **6a** (55%) and **6b** (71%) were prepared analogously from literature known phosphane **20**,[29] which we could access in 89% yield after deprotonation of Ph_2PH with *n*-BuLi and subsequent alkylation with compound **19**.



Scheme 2 Preparation of mono-phosphonium salts **5a**,**b** and **6a**,**b**. *Reagents and conditions*: (a) Ph_3P (1.1 equiv), DMF, 105 °C, 24 h; (b) 1. $LiNTf_2$ (1.5 equiv), acetone, 23 °C, 2 d; 2. EtOAc–water; (c) 1. Ph_2PH (1 equiv), *n*-BuLi (1 equiv), **19** (2.5 equiv), THF, 23 °C, 17 h; (d) **19** (1.25 equiv), DMF, 105 °C, 17 h. R_F = *n*-C_6F_{13}.

After appropriate reaction conditions had been identified for the preparation of mono-phosphonium compounds **5a** and **6a**, the commercially available diphosphanes DPPE (**21**), DPPP (**22**), DPPB (**23**) as well as the congener with pentane-1,5-diyl spacer **24** were quaternized with excess alkyl iodide **19** (Scheme 3). The salts **7a**–**10a** were obtained in 64–96% yield (Table 1) after recrystallization from MTBE. Ion exchange was accomplished with $LiNTf_2$ as established above for compounds **5b** and **6b**. Triflimide salts **7b**–**10b** were obtained in 65–88% yield (Table 1) after recrystallization.



Scheme 3 Preparation of diphosphonium salts **7a**–**10a**, **7b**–**10b**; for yields see Table 1. *Reagents and conditions*: (a) **19** (2.5 equiv), DMF, 105 °C, 24 h; (b) 1. $LiNTf_2$ (3.0 equiv), acetone, 23 °C, 2 d; 2. EtOAc–water. R_F = *n*-C_6F_{13}.

Table 1 Yields of Diphosphonium Salts after Recrystallization from MTBE

n	Y = I (yield)	Y = NTf_2 (yield)
1	**7a** (96%)	**7b** (88%)
2	**8a** (65%)	**8b** (68%)
3	**9a** (83%)	**9b** (65%)
4	**10a** (64%)	**10b** (72%)

The signals of most carbon atoms of compounds **7a**, **7b**, **8a**, and **8b** appear as higher-order multiplets in the $^{13}C\{^{1}H\}$ NMR spectra, because the respective carbon atoms define the A-part of an AXX′-system, with the two magnetically inequivalent phosphorus atoms being the X part. In these cases (n = 1, 2) the $J(^{31}P,^{31}P)$ is significantly larger than zero. For n = 3, 4 (i.e., compounds **9a**, **9b**, **10a**, and **10b**) the carbon signals are again first order (s or d), because the coupling constant $J(^{31}P,^{31}P)$ is almost zero. Anyhow, the signals of aliphatic carbon atoms are hardly detectable in the 1D spectra, but could be clearly identified by their $^{1}J(^{1}H,^{13}C)$ cross peaks in the 2D HMQC spectra (see experimental section and Supporting Information).

All ammonium and phosphonium salts **1a**,**b**–**10a**,**b** are insoluble in water and sparely soluble in MTBE, CH_2Cl_2, and $CHCl_3$ at ambient temperature. They show limited solubility in MeOH or acetone, which is however sufficient for NMR spectroscopy. Except compound **9b**, which is a wax, all compounds are solids; their melting points are listed in Table 2. However, only the triflimides **1b**–**3b** and **5b**–**10b** can be regarded as 'ionic liquids' since their melting points are below 100 °C; most of them are higher than 50 °C. The pyrrolidine derivative **1b** has the lowest melting point with 46 °C. DABCO derivatives **4a** and **4b** are high-melting materials with mp >200 °C. The triflates and iodides **1a**–**3a** and **5a**–**10a** have a melting point between 100 °C and 175 °C (mp 203 °C for compound **9a**) and are, therefore, by definition not ionic liquids. To obtain a first impression of the water repellency of the new materials, we investigated the wettability of a thin film spread on a glass surface by measuring the water contact angle.[22] The results did not fulfill our expectations at all, because all contact angles were below 110°, most of them between 50° and 100°. The highest value was obtained with pyrrolidinium triflate **1a** (104.5°), which is not an ionic liquid (mp 153 °C). The second highest value (102°) was obtained for morpholinium triflimide **3b**, which melts at 82 °C.

Table 2 Melting Points of the Ammonium and Phosphonium Salts

Cation	Anion		
	Triflate (**a**)	Iodide (**a**)	Triflimide (**b**)
1	153 °C	–	46 °C
2	139 °C	–	50 °C
3	103 °C	–	82 °C
4	>250 °C	–	206 °C
5	–	169 °C	93 °C
6	–	134 °C	95 °C
7	–	135 °C	82 °C
8	–	165 °C	54 °C
9	–	203 °C	wax
10	–	174 °C	76 °C

In the course of global efforts to replace PFOA ($C_7F_{15}CO_2H$) and PFOS ($C_8F_{17}SO_3H$) as surface active ingredients, many industrial manufacturers have begun investigations on alternative resins with shorter perfluorinated alkyl chains, hence, enhanced degradability and therefore low bioaccumulativity. Our contribution to this field is the development of novel ionic liquids with ammonium and phosphonium cations carrying perfluorinated *n*-hexyl residues ('R_F'), which were introduced by *n*-$C_6F_{13}CH_2CH_2OTf$ (**11**) and *n*-$C_6F_{13}CH_2CH_2I$ (**19**) as alkylating reagents.

In the ammonium series, pyrrolidine (**12**), piperidine (**14**), and morpholine (**16**) were first monoalkylated with triflate **11** (78–91%) and then quaternized with the same reagent furnishing the ammonium triflates **1a** (74%), **2a** (77%), and **3a** (26%), which, as they have a melting point >100 °C, are by definition not ionic liquids. However, after exchange of TfO^- by Tf_2N^- with the aid of an anion exchange resin, the triflimides **1b** (74%), **2b** (99%), and **3b** (55%) are obtained, which show melting points in the range of 46–82 °C. Furthermore, DABCO (**18**) was twice quaternized with reagent **11** furnishing the DABCOdionium bistriflate **4a** (82%) and after anion exchange the bistriflimide **4b** (73%), which are both high-melting materials (mp >200 °C).

As phosphorus-based ionic liquids, first mono-phosphonium salts **5a** (76%) and **6a** (55%) were prepared from Ph_3P or Ph_2PH and $R_FCH_2CH_2I$ **19** with one or two $R_FCH_2CH_2$ residues. Whereas the iodides **5a** and **6a** are again high-melting (mp >100 °C), ionic liquids **5b** (77%, mp 93 °C) and **6b** (71%, mp 95 °C) are obtained after ion exchange to Tf_2N^-, which now was performed with $LiNTf_2$ instead of an ion exchange resin. Furthermore, diphosphonium diiodides **7a**–**10a** (64–96%, all mp >100 °C) were prepared by twofold quaternization of diphosphanes $Ph_2P(CH_2)_nPPh_2$ (n = 2–5) with iodide **19**. Ionic liquids (mp up to 82 °C) are again obtained by anion exchange with $LiNTf_2$ yielding the bistriflimides **7b**–**10b** (65–88%).

^1H, ^{19}F, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 instrument. Multiplicities of carbon signals were determined with DEPT experiments. The ^{13}C signals of some CH_2 moieties could only be detected with 2D experiments; these are marked with 'HMQC'. ^{13}C signals of CF_2 and CF_3 moieties (including OTf) could not be individually distinguished due to extended overlapping. HRMS spectra were obtained with a Waters Q-TOF Premier (ESI, all in the +'ve mode) spectrometer. IR spectra were recorded on a Bruker Tensor 27 spectrophotometer equipped with a 'GoldenGate' 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. 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. *n*$C_6F_{13}CH_2CH_2OTf$ (**11**) was prepared according to the literature protocol.[24] All other starting materials were commercially available. In particular, *n*-$C_6F_{13}CH_2CH_2I$ (**19**) was purchased from Apollo and *n*-$C_6F_{13}CH_2CH_2OH$ from DuPont. MTBE = *t*-BuOMe.

1-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)pyrrolidine (13)

A solution of perfluorinated triflate **11** (10.0 g, 20.2 mmol, 1.0 equiv), pyrrolidine (**12**; 1.44 g, 20.2 mmol, 1.0 equiv), and K_2CO_3 (5.58 g, 40.3 mmol, 2.0 equiv) in EtOAc (15 mL) was stirred for 24 h at 70 °C. Water (20 mL) was added and the suspension was extracted with MTBE (2 × 30 mL). The combined extracts were dried ($MgSO_4$), filtered, and evaporated. Product **13** (7.63 g, 18.3 mmol, 91%) was obtained as yellow liquid.

IR (ATR): 2969 (w), 2790 (w), 1403 (w), 1358 (w), 1233 (s), 1190 (vs), 1001 (m), 732 (m), 698 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.70–1.89 (m, 4 H), 2.24–2.42 (m, 2 H), 2.50–2.61 (m, 4 H), 2.72–2.82 (m, 2 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 23.64 (s, 2 CH_2), 30.78–31.08 (m, CH_2), 47.31 (s, CH_2), 54.28 (s, 2 CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = –80.80 (tt, *J* = 2.6 Hz, *J* = 10.1 Hz), –113.58 to –114.05 (m), –121.67 to –121.97 (m), –122.67 to –122.95 (m), –123.38 to –123.67 (m), –125.97 to –126.22 (m).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{13}F_{13}N$: 418.0840; found: 418.0844.

1,1-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)pyrrolidinium Trifluoromethanesulfonate (1a)

A solution of perfluorinated triflate **11** (9.08 g, 18.3 mmol, 1.0 equiv) and amine **13** (7.63 g, 18.3 mmol, 1.0 equiv) in toluene (10 mL) was stirred in a tightly closed reaction tube for 3 h at 130 °C. After evaporation of the volatiles, the residue was recrystallized (MTBE, 20 mL) to furnish product **1a** (12.4 g, 13.6 mmol, 74%) as a colorless solid; mp 153 °C.

IR (ATR): 3056 (w), 3023 (w), 2975 (w), 1353 (w), 1318 (w), 1252 (s), 1226 (s), 1196 (s), 1142 (s), 1125 (s), 1083 (w), 1029 (m), 961 (w), 811 (w), 726 (m), 697 (m), 640 cm^{-1} (m).

^1H NMR (500 MHz, CD_3OD): δ = 2.21–2.38 (m, 4 H), 2.83–3.00 (m, 4 H), 3.66–3.77 (m, 4 H), 3.79–3.93 (m, 4 H).

$^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ = 22.94 (s, 2 CH_2), 26.32 (t, *J* = 21.9 Hz, 2 CH_2), 52.82 (s, 2 CH_2), 65.22 (s, 2 CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, CD_3OD): δ = –80.13 (s), –82.36 to –82.53 (m), –113.80 to –114.33 (m), –122.60 to –122.84 (m), –123.53 to –124.12 (m), –126.97 to –127.49 (m).

HRMS (ESI): *m*/*z* $[M - OTf^-]$ calcd for $C_{20}H_{16}F_{26}N$: 764.0868; found: 764.0871.

Exchange of Anions with $HNTf_2$; General Procedure A (GPA)

A column of ion-exchange resin Lewatit Mono MP Plus 800 (20 g, Lanxess, capacity ca. 0.95 mmol/g) was regenerated prior to each use by the following sequential washings: (1) with hydrochloric acid (10 mL, 2 mol/L) until pH 1 of the eluent, (2) with water until pH 7, (3) with aq NaOH (10 mL, 2 mol/L) until pH 13–14 and finally (4) again with water to pH 7.

A warm (ca. 65 °C) solution of the triflate salt **1a**, **2a**, **3a**, or **4a** (1.11–1.62 mmol) in MeOH (10 mL) was applied to the column and the hydroxide salt eluted with MeOH, until pH 7 of the eluent; the eluted volume was about 100 mL each time. The hydroxide salt was not isolated, but its aqueous solution was treated with $HNTf_2$ (1.0 equiv per nitrogen atom), the resulting mixture was evaporated and the residue recrystallized (MTBE) to furnish the triflimide salt **1b**, **2b**, **3b**, or **4b**.

1,1-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)pyrrolidinium Bis(trifluoromethanesulfonyl)imide (1b)

Triflate salt **1a** (1.20 g, 1.31 mmol) was converted with $HNTf_2$ (369 mg, 1.31 mmol) according to GPA to give compound **1b** (1.01 g, 0.969 mmol, 74%) after recrystallization (MTBE, 20 mL) as a colorless solid; mp 46 °C.

IR (ATR): 3153 (w), 1470 (w), 1344 (m), 1324 (m), 1185 (s), 1130 (s), 1059 (s), 698 cm^{-1} (m).

Anal. Calcd for $C_{22}H_{16}F_{32}N_2O_4S_2$: C 25.30; H, 1.54; N, 2.68; S, 6.14. Found: C, 25.41; H, 1.85; N, 2.99; S, 5.97.

1-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)piperidine (15)

A solution of perfluorinated triflate **11** (10.0 g, 20.2 mmol, 1.0 equiv), piperidine (**14**; 1.72 g, 20.2 mmol, 1.0 equiv), and K_2CO_3 (5.58 g, 40.3 mmol, 2.00 equiv) in EtOAc (15 mL) was stirred for 24 h at 70 °C. Water (20 mL) was added and the suspension was extracted with MTBE (2 × 30 mL). The combined extracts were dried ($MgSO_4$), filtered, and evaporated. Product **15** (7.88 g, 18.3 mmol, 91%) was obtained as a colorless liquid after fractionized vacuum distillation (bp 78 °C/5.2 mbar).

IR (ATR): 2939 (m), 2859 (w), 2786 (w), 1472 (w), 1446 (w), 1233 (s), 1190 (s), 1143 (s), 1079 (m), 995 (m), 810 (m), 728 (m), 708 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$): δ = 1.45 (pent, *J* = 5.9 Hz, 2 H), 1.60 (pent, *J* = 5.6 Hz, 4 H), 2.25–2.36 (m, 2 H), 2.38–2.47 (m, 4 H), 2.60–2.66 (m, 2 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 24.35 (s, CH_2), 26.13 (s, 2 CH_2), 29.13 (t, *J* = 21.5 Hz, CH_2), 50.22 (t, *J* = 3.9 Hz, CH_2), 54.62 (s, 2 CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = –80.81 (tt, *J* = 2.2 Hz, *J* = 10.0 Hz), –113.95 to –114.16 (m), –121.80 to –121.96 (m), –122.72 to –122.92 (m), –123.45 to –123.67 (m), –126.03 to –126.21 (m).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{15}F_{13}N$: 432.0991; found: 432.0983.

1,1-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)piperidinium Trifluoromethanesulfonate (2a)

A solution of perfluorinated triflate **11** (2.11 g, 4.25 mmol, 1.0 equiv) and amine **15** (1.83 g, 4.25 mmol, 1.0 equiv) in toluene (10 mL) was stirred in a tightly closed reaction tube for 3 h at 150 °C. After evaporation of the volatiles, the residue was recrystallized (MTBE, 20 mL) to furnish product **2a** (3.04 g, 3.28 mmol, 77%) as a colorless solid; mp 139 °C.

IR (ATR): 3029 (w), 2996 (w), 2970 (w), 2958 (w), 1471 (w), 1319 (w), 1227 (s), 1190 (s), 1142 (s), 1124 (s), 1084 (m), 1029 (s), 936 (m), 842 (m), 706 (m), 639 cm^{-1} (s).

^1H NMR (500 MHz, CD_3OD): δ = 1.77 (pent, *J* = 6.2 Hz, 2 H), 2.00 (pent, *J* = 6.0 Hz, 4 H), 2.83–2.96 (m, 4 H), 3.58 (t, *J* = 5.6 Hz, 4 H), 3.87–3.92 (m, 4 H).

$^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ = 20.58 (s, 2 CH_2), 21.79 (CH_2), 24.81 (t, *J* = 21.6 Hz, 2 CH_2), 49.85 (s, 2 CH_2), 61.39 (s, 2 CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, CD_3OD): δ = –80.16 (s), –82.32 to –82.51 (m), –114.25 to –114.39 (m), –122.73 to –122.98 (m), –123.73 to –123.95 (m), –127.22 to –127.40 (m).

HRMS (ESI): *m*/*z* $[M - OTf^-]$ calcd for $C_{21}H_{18}F_{26}N$: 778.1024; found: 778.1027.

1,1-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)piperidinium Bis(trifluoromethanesulfonyl)imide (2b)

Triflate salt **2a** (1.50 g, 1.62 mmol) was converted with $HNTf_2$ (455 mg, 1.62 mmol) according to GPA to furnish compound **2b** (1.69 g, 1.60 mmol, 99%) after evaporation of the solvent as a colorless solid; mp 50 °C.

IR (ATR): 3152 (w), 2969 (w), 1350 (m), 1322 (m), 1233 (m), 1181 (s), 1126 (s), 1057 (m), 731 cm^{-1} (m).

Anal. Calcd for $C_{23}H_{18}F_{32}N_2O_4S_2$: C, 26.10; H, 1.71; N, 2.65; S, 6.06. Found: C, 26.21; H, 1.83; N, 3.04; S, 6.41.

4-(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)morpholine (17)

A solution of perfluorinated triflate **11** (5.46 g, 11.0 mmol, 1.1 equiv), morpholine (**16**; 871 mg, 10.0 mmol, 1.0 equiv), and K_2CO_3 (2.76 g, 20.0 mmol, 2.00 equiv) in EtOAc (10 mL) was stirred for 24 h at 70 °C. Water (20 mL) was added and the suspension was extracted with MTBE (2 × 30 mL). The combined extracts were dried ($MgSO_4$), filtered, and evaporated. Product **17** (3.37 g, 7.78 mmol, 78%) was obtained as a yellow liquid.

IR (ATR): 2965 (w), 2914 (w), 2857 (w), 2815 (w), 1452 (w), 1410 (w), 1364 (w), 1318 (w), 1234 (s), 1188 (s), 1142 (vs), 1076 (m), 1034 (w), 1001 (m), 870 (m), 730 (m), 708 (m), 697 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$): δ = 2.25–2.36 (m, 2 H), 2.47–2.49 (m, 4 H), 2.64–2.70 (m, 2 H), 3.71–3.73 (m, 4 H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 28.86 (s, CH_2), 49.95 (s, CH_2), 53.65 (s, 2 CH_2), 67.01 (s, 2 CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$): δ = –80.76 (tt, *J* = 2.1 Hz, *J* = 10.3 Hz), –113.88 to –114.11 (m), –121.82 to –122.03 (m), –122.77 to –122.97 (m), –123.42 to –123.63 (m), –126.04 to –126.20 (m).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{13}F_{13}NO$: 434.0784; found: 434.0789.

4,4-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)morpholinium Trifluoromethanesulfonate (3a)

A solution of perfluorinated triflate **11** (4.25 g, 8.56 mmol, 1.1 equiv) and amine **17** (3.37 g, 7.78 mmol, 1.0 equiv) in toluene (5 mL) was stirred in a tightly closed reaction tube for 3 h at 130 °C. After evaporation of the volatiles, the residue was recrystallized (MTBE, 20 mL) to furnish product **3a** (1.85 g, 1.99 mmol, 26%) as a colorless solid; mp 103 °C.

IR (ATR): 3033 (w), 2779 (w), 1473 (w), 1455 (w), 1425 (w), 1367 (w), 1330 (w), 1288 (m), 1224 (s), 1201 (s), 1144 (s), 1109 (m), 1091 (m), 1024 (s), 979 (m), 708 (m), 638 cm^{-1} (s).

^1H NMR (500 MHz, CD_3OD): δ = 2.95–3.08 (m, 4 H), 3.77–3.83 (m, 4 H), 4.09–4.15 (m, 4 H), 4.15–4.21 (m, 4 H).

$^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ = 24.82 (t, *J* = 21.4 Hz, 2 CH_2), 51.77 (s, br., 2 CH_2), 60.41 (s, 2 CH_2), 61.17 (s, 2 CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, CD_3OD): δ = –80.15 (s), –82.38 (tt, *J* = 2.5 Hz, *J* = 10.2 Hz), –114.75 to –114.89 (m), –122.75 to –122.97 (m), –123.79 to –123.97 (m), –124.04 to –124.22 (m), –127.25 to –127.40 (m).

HRMS (ESI): *m*/*z* $[M - OTf^-]$ calcd for $C_{20}H_{16}F_{26}NO$: 780.0811; found: 780.0815.

4,4-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)morpholinium Bis(trifluoromethanesulfonyl)imide (3b)

Triflate salt **3a** (500 mg, 0.538 mmol) was converted with $HNTf_2$ (151 mg, 0.538 mmol) according to GPA to furnish compound **3b** (311 mg, 0.293 mmol, 55%) after evaporation of the solvent and recrystallization (MTBE, 10 mL) as a colorless solid; mp 82 °C.

IR (ATR): 1739 (w), 1463 (w), 1348 (m), 1321 (m), 1232 (m), 1181 (s), 1126 (s), 1056 (s), 905 (w), 741 (m), 618 (m), 601 cm^{-1} (m).

Anal. Calcd for $C_{22}H_{16}F_{32}N_2O_5S_2$: C, 24.92; H, 1.52; N, 2.64; S, 6.05. Found: C, 24.83; H, 1.53; N, 2.44; S, 6.04.

1,4-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,4-diazoniabicyclo[2.2.2]octane Bis(trifluoromethanesulfonate) (4a)

A solution of perfluorinated triflate **11** (6.00 g, 12.1 mmol, 3.0 equiv) and DABCO (**18**; 458 mg, 4.04 mmol, 1.0 equiv) in toluene (10 mL) was stirred in a tightly closed reaction tube for 17 h at 130 °C. After evaporation of the volatiles, the residue was recrystallized (MTBE, 20 mL) to furnish product **4a** (3.64 g, 3.30 mmol, 82%) as a colorless solid; mp >250 °C.

IR (ATR): 3033 (w), 1473 (w), 1437 (w), 1368 (w), 1323 (w), 1246 (s), 1230 (s), 1209 (s), 1189 (s), 1145 (s), 1088 (m), 1070 (w), 1027 (s), 708 (m), 630 cm^{-1} (s).

^1H NMR (500 MHz, acetone-d_6): δ = 3.18–3.33 (m, 4 H), 4.32–4.42 (m, 4 H), 4.57 (br s, 12 H).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 25.38 (t, *J* = 20.9 Hz, 2 CH_2), 52.66 (s, 6 CH_2), 57.67 (s, 2 CH_2).

$^{19}F\{^1H\}$ NMR (470 MHz, acetone-d_6): δ = –79.46 (s), –81.96 (tt, *J* = 10.3 Hz, *J* = 2.7 Hz), –113.78 to –113.99 (m), –122.61 to –122.80 (m), –123.61 to –123.96 (m), –127.00 to –1127.21 (m).

HRMS (ESI): *m*/*z* [M – 2 OTf^-] calcd for $C_{22}H_{20}F_{26}N_2$: 403.0600; found: 403.0572.

1,4-Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-1,4-diazoniabicyclo[2.2.2]octane Bis[bis(trifluoromethanesulfonyl)imide] (4b)

Triflate salt **4a** (1.23 g, 1.11 mmol) was converted with $HNTf_2$ (626 mg, 2.23 mmol) according to GPA to furnish compound **4b** (0.961 g, 0.817 mmol, 73%) after evaporation of the solvent and recrystallization (MTBE, 30 mL) as a colorless solid; mp 206 °C.

IR (ATR): 3129 (w), 3051 (w), 1474 (w), 1443 (w), 1342 (s), 1239 (m), 1187 (vs), 1119 (vs), 1055 (s), 792 (m), 742 (m), 649 (m), 571 cm^{-1} (s).

Anal. Calcd for $C_{26}H_{20}F_{38}N_4O_8S_4$: C, 22.85; H, 1.48; N, 4.10; S, 9.38. Found: C, 22.47; H, 1.84; N, 4.45; S, 9.01.

(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)triphenylphosphonium Iodide (5a)

A solution of perfluorinated iodide **19** (1.64 g, 3.46 mmol, 1.0 equiv) and Ph_3P (1.00 g, 3.81 mmol, 1.1 equiv) in DMF (2 mL) was stirred in a tightly closed reaction tube for 24 h at 105 °C. The mixture was diluted with MTBE (10 mL) and the product precipitated. It was isolated by filtration and dried under high vacuum to furnish compound **5a** (1.81 g, 2.64 mmol, 76%) as a colorless solid; mp 169 °C.

IR (ATR): 3057 (w), 2876 (w), 1741 (w), 1438 (w), 1234 (s), 1190 (s), 1115 (s), 1092 (m), 939 (m), 741 (s), 727 (s), 689 cm^{-1} (s).

^1H NMR (500 MHz, CD_3OD): δ = 2.52–2.72 (m, 2 H), 3.79–3.95 (m, 2 H), 7.74–7.99 (m, 15 H).

$^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ = 15.57 (d, *J* = 59.6 Hz, CH_2), 25.47–26.09 (m, CH_2), 118.62 (d, *J* = 88.1 Hz, 3 C), 131.79 (d, *J* = 12.2 Hz, 6 CH), 134.98 (d, *J* = 10.1 Hz, 6 CH), 136.76 (d, *J* = 3.5 Hz, 3 CH).

$^{31}P\{^1H\}$ NMR (203 MHz, CD_3OD): δ = 24.36 (s).

$^{19}F\{^1H\}$ NMR (470 MHz, CD_3OD): δ = –82.40 (tt, *J* = 9.8 Hz, *J* = 2.8 Hz), –114.77 to –114.96 (m), –122.58 to –122.92 (m), –123.61 to –123.84 (m), –127.15 to –127.36 (m).

HRMS (ESI): *m*/*z* [M – I^-] calcd for $C_{26}H_{19}F_{13}P$: 609.1017; found: 609.1015.

Exchange of Anions with $LiNTf_2$; General Procedure B (GPB)

A solution iodide salts **5a**–**10a** (0.0484–0.50 mmol) and $LiNTf_2$ (1.5 equiv per phosphorus atom) in acetone (30 mL/g) was stirred for 2 d at 23 °C. The solvent was removed in vacuo and the residue redissolved in EtOAc (100 mL/g) and filtered. The filtrate was repeatedly (ca. 3 ×) extracted with H_2O (3 × 200 mL/g) until the aqueous extract was free from iodide (monitored with a drop of aq $AgNO_3$ solution). The organic layer was dried ($MgSO_4$), filtered, and evaporated, and the crude product recrystallized (MTBE).

(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)triphenylphosphonium Bis(trifluoromethanesulfonyl)imide (5b)

Iodide salt **5a** (100 mg, 0.136 mmol, 1.0 equiv) and $LiNTf_2$ (59 mg, 0.204 mmol, 1.5 equiv) were converted according to GPB to furnish compound **5b** (93 mg, 0.105 mmol, 77%) after recrystallization (MTBE, 10 mL) as a colorless solid; mp 93 °C.

IR (ATR): 3078 (w), 2967 (w), 2936 (w), 1443 (w), 1345 (s), 1327 (m), 1237 (m), 1197 (s), 1140 (s), 1119 (s), 1052 (s), 903 (m), 740 (m), 725 (m), 614 cm^{-1} (m).

Anal. Calcd for $C_{28}H_{19}F_{19}NO_4PS_2$: C, 37.81; H, 2.15; N, 1.57; S, 7.22. Found: C, 37.59; H, 1.79; N, 1.21; S, 7.00.

(1*H*,1*H*,2*H*,2*H*-Perfluorooctyl)diphenylphosphane (20)

The entire procedure including the isolation and characterization of the product was performed under an inert atmosphere (N_2). *n*-BuLi (0.94 mL, 2.4 mmol, 1.0 equiv, 2.5 mol/L solution in hexane) was added at r.t. to a solution of Ph_2PH (438 mg, 2.40 mmol, 1.0 equiv) in abs THF (2 mL). After stirring the mixture for 5 min at 23 °C, perfluorinated iodide **19** (1.12 g, 2.40 mmol, 1.0 equiv) was added and the mixture was further stirred for 17 h at 23 °C. The mixture was then filtered using a reversible frit and the resulting solution was evaporated to furnish the product **20** (1.11 g, 2.09 mmol, 89%) as an off-white solid; mp 40 °C.

IR (ATR): 3072 (w), 1482 (w), 1439 (w), 1364 (w), 1235 (m), 1182 (s), 1139 (s), 1121 (m), 1070 (m), 1028 (w), 925 (w), 847 (w), 746 (m), 735 (m), 723 (m), 693 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.05–2.23 (m, 2 H), 2.24–2.37 (m, 2 H), 7.33–7.41 (m, 6 H), 7.42–7.51 (m, 4 H).

$^{31}P\{^1H\}$ NMR (203 MHz, $CDCl_3$): δ = –16.05 (s).

The ^{13}C NMR spectrum was in accordance with literature data.[29]

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{14}F_{13}NaP$: 555.0523; found: 555.0529.

Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonium Iodide (6a)

A solution of perfluorinated iodide **19** (557 mg, 1.17 mmol, 1.25 equiv) and phosphane **20** (500 mg, 0.94 mmol, 1.0 equiv) in DMF (2 mL) was stirred in a tightly closed reaction tube for 17 h at 105 °C. The mixture was diluted with MTBE (10 mL); the crude material precipitated and was collected by filtration. The residue was recrystallized (MTBE, 10 mL) to furnish product **6a** (521 mg, 0.517 mmol, 55%) as a colorless solid; mp 134 °C.

IR (ATR): 2890 (w), 2875 (w), 1140 (w), 1405 (w), 1231 (s), 1187 (s), 1120 (s), 1071 (m), 808 (m), 737 (m), 688 cm^{-1} (m).

^1H NMR (500 MHz, CD_3OD): δ = 2.37–2.62 (m, 4 H), 3.51–3.69 (m, 4 H), 7.74–7.89 (m, 4 H), 7.89–8.12 (m, 6 H).

$^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ = 12.25–15.26 (m, 2 CH_2; HMQC), 22.77–27.04 (m, 2 CH_2; HMQC), 116.81 (d, *J* = 85.3 Hz, 2 C), 131.86 (d, *J* = 14.5 Hz, 4 CH), 134.47 (d, *J* = 11.8 Hz, 4 CH), 137.10 (d, *J* = 3.3 Hz, 2 CH).

$^{31}P\{^1H\}$ NMR (203 MHz, CD_3OD): δ = 29.20 (s).

$^{19}F\{^1H\}$ NMR (470 MHz, CD_3OD): δ = –82.35 to –82.47 (m), –114.77 to –115.08 (m), –122.65 to –122.92 (m), –123.65 to –123.97 (m), –127.15 to –127.39 (m).

HRMS (ESI): *m*/*z* [M – I^-] calcd for $C_{28}H_{18}F_{26}P$: 879.0731; found: 879.0718.

Bis(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonium Bis(trifluoromethanesulfonyl)amide (6b)

Iodide salt **6a** (500 mg, 0.50 mmol, 1.0 equiv) and $LiNTf_2$ (72 mg, 0.75 mmol, 1.5 equiv) were converted according to GPB to furnish compound **6b** (410 mg, 0.354 mmol, 71%) after recrystallization (MTBE, 20 mL) as a colorless solid; mp 95 °C.

IR (ATR): 2962 (w), 2931 (w), 1440 (w), 1345 (m), 1329 (m), 1179 (s), 1129 (s), 1062 (m), 950 (m), 922 (m), 692 (m), 609 cm^{-1} (m).

Anal. Calcd for $C_{30}H_{18}F_{32}NO_4PS_2$: C, 31.08; H, 1.56; N, 1.21; S, 5.53. Found: C, 31.18; H, 1.64; N, 0.84; S, 5.17.

1,2-Bis[(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonio]ethane Diiodide (7a)

A solution of perfluorinated iodide **19** (11.9 g, 25.0 mmol, 2.6 equiv) and DPPE (**21**; 3.88 g, 9.70 mmol, 1.00 equiv) in DMF (10 mL) was stirred in a tightly closed reaction tube for 24 h at 105 °C. The mixture was diluted with MTBE (50 mL); the crude product precipitated and was collected by filtration. The residue was recrystallized (MTBE, 100 mL) to furnish product **7a** (12.5 g, 9.29 mmol, 96%) as a colorless solid; mp 135 °C.

IR (ATR): 2867 (w), 1437 (w), 1339 (w), 1198 (s), 1142 (s), 1122 (m), 736 (m), 685 cm^{-1} (m).

^1H NMR (500 MHz, CD_3OD): δ = 2.36–2.50 (m, 4 H), 3.54–3.62 (m, 4 H), 3.64–3.72 (m, 4 H), 7.74–7.83 (m, 8 H), 7.89–7.99 (m, 12 H).

$^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ = 14.82–15.40 (m, 2 CH_2), 16.89 (t, *J* = 25.1 Hz, 2 CH_2), 25.28 (t, *J* = 22.8 Hz, 2 CH_2), 115.26–116.35 (m, 4 C), 131.83–132.14 (m, 8 CH), 134.99–135.32 (m, 8 CH), 137.23 (s, 4 CH).

$^{31}P\{^1H\}$ NMR (203 MHz, CD_3OD): δ = 31.25 (s).

$^{19}F\{^1H\}$ NMR (470 MHz, CD_3OD): δ = –82.40 (tt, *J* = 9.9 Hz, *J* = 2.6 Hz), –114.40 to –114.67 (m), –122.69 to –122.87 (m), –123.49 to –123.69 (m), –123.69 to –123.91 (m), –127.19 to –127.35 (m).

HRMS (ESI): *m*/*z* [M – 2 I^-] calcd for $C_{42}H_{32}F_{26}P_2$: 546.0782; found: 546.0763.

1,2-Bis[(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonio]ethane Bis[bis(trifluoromethanesulfonyl)imide] (7b)

Iodide salt **7a** (100 mg, 74.3 μmol, 1.0 equiv) and $LiNTf_2$ (64 mg, 0.223 mmol, 3.0 equiv) were converted according to GPB to furnish compound **7b** (108 mg, 65.3 μmol, 88%) after recrystallization (MTBE, 10 mL) as a colorless solid; mp 82 °C.

IR (ATR): 3071 (w), 2964 (w), 2928 (w), 1440 (w), 1350 (m), 1333 (m), 1231 (m), 1182 (s), 1142 (s), 1127 (s), 1092 (m), 1051 (m), 738 (m), 649 (m), 610 cm^{-1} (m).

Anal. Calcd for $C_{46}H_{32}F_{38}N_2O_8P_2S_4$: calcd.: C, 33.43; H, 1.95; N, 1.69; S, 7.76. Found: C, 33.10; H, 1.83; N, 1.51; S, 7.57.

1,3-Bis[(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonio]propane Diiodide (8a)

A solution of perfluorinated iodide **19** (1.44 g, 3.03 mmol, 2.5 equiv) and DPPP (**22**; 500 mg, 1.21 mmol, 1.0 equiv) in DMF (5 mL) was stirred in a tightly closed reaction tube for 24 h at 105 °C. The mixture was diluted with MTBE (20 mL); the crude product precipitated and was collected by filtration. The residue was recrystallized (MTBE, 50 mL) to furnish product **8a** (1.07 g, 0.786 mmol, 65%) as a colorless solid; mp 165 °C.

IR (ATR): 2911 (w), 2875 (w), 1739 (w), 1438 (w), 1228 (s), 1189 (s), 1143 (s), 1116 (s), 737 (m), 689 cm^{-1} (m).

^1H NMR (500 MHz, CD_3OD): δ = 1.65–1.82 (m, 2 H), 2.34–2.60 (m, 4 H), 3.42–3.57 (m, 4 H), 3.58–3.73 (m, 4 H), 7.65–7.83 (m, 8 H), 7.83–7.98 (m, 12 H).

$^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD): δ = 12.61–15.32 (m, 2 CH_2; HMQC), 14.14–18.85 (m, CH_2; HMQC), 19.56–24.98 (m, 2 CH_2; HMQC), 25.10 (t, *J* = 22.3 Hz, 2 CH_2), 116.87–117.56 (m, 4 C), 131.67–131.77 (m, 8 CH), 134.42–134.49 (m, 8 CH), 136.73–136.84 (m, 4 CH).

$^{31}P\{^1H\}$ NMR (203 MHz, CD_3OD): δ = 27.69 (s).

$^{19}F\{^1H\}$ NMR (470 MHz, CD_3OD): δ = –82.42 (tt, *J* = 10.4 Hz, *J* = 2.6 Hz), –114.79 to –115.17 (m), –122.66 to –123.04 (m), –123.49 to –123.76 (m), –123.76 to –124.08 (m), –127.18 to –127.42 (m).

HRMS (ESI): *m*/*z* [M – 2 I^-] calcd for $C_{43}H_{34}F_{26}P_2$: 553.0855; found: 553.0842.

1,3-Bis[(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonio]propane Bis[bis(trifluoromethanesulfonyl)imide] (8b)

Iodide salt **8a** (100 mg, 73.5 μmol, 1.0 equiv) and $LiNTf_2$ (63 mg, 0.22 mmol, 3.0 equiv) were converted according to GPB to furnish compound **8b** (83 mg, 50 μmol, 68%) after recrystallization (MTBE, 5 mL) as a colorless solid; mp 54 °C.

IR (ATR): 3071 (w), 2998 (w), 2959 (w), 2928 (w), 1441 (w), 1347 (m), 1328 (m), 1228 (m), 1181 (s), 1133 (s), 1054 (s), 1054 (s), 738 (m), 614 (m), 601 cm^{-1} (m).

Anal. Calcd for $C_{47}H_{34}F_{38}N_2O_8P_2S_4$: C, 33.87; H, 2.06; N, 1.68; S, 7.68. Found: C, 33.58; H, 2.42; N, 1.57; S, 7.42.

1,4-Bis[(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonio]butane Diiodide (9a)

A solution of perfluorinated iodide **19** (1.39 g, 2.93 mmol, 2.5 equiv) and DPPB (**23**; 500 mg, 1.17 mmol, 1.0 equiv) in DMF (5 mL) was stirred in a tightly closed reaction tube for 24 h at 105 °C. The mixture was diluted with MTBE (20 mL); the crude material precipitated and was collected by filtration. The residue was recrystallized (MTBE, 50 mL) to furnish product **9a** (1.33 g, 0.968 mmol, 83%) as a colorless solid; mp 203 °C.

IR (ATR): 2876 (w), 1438 (m), 1230 (s), 1189 (s), 1142 (s), 1116 (s), 1087 (m), 736 (s), 687 cm^{-1} (s).

^{1}H NMR (500 MHz, CD_3OD): δ = 1.84–1.97 (m, 4 H), 2.49–2.64 (m, 4 H), 3.43–3.48 (m, 4 H), 3.50–3.60 (m, 4 H), 7.82–7.91 (m, 8 H), 7.96–8.11 (m, 12 H).

^{13}C{^{1}H} NMR (125 MHz, CD_3OD): δ = 14.45 (d, *J* = 55.0 Hz, 2 CH_2), 21.18 (d, *J* = 50.2 Hz, 2 CH_2), 23.61 (d, *J* = 18.9 Hz, 2 CH_2), 25.31 (t, *J* = 23.0 Hz, 2 CH_2), 117.85 (d, *J* = 84.9 Hz, 4 C), 131.66 (d, *J* = 12.7 Hz, 8 CH), 134.55 (d, *J* = 9.8 Hz, 8 CH), 136.59 (d, *J* = 2.2 Hz, 4 CH).

^{31}P{^{1}H} NMR (203 MHz, CD_3OD): δ = 28.43 (s).

^{19}F{^{1}H} NMR (470 MHz, CD_3OD): δ = –82.41 (tt, *J* = 10.9 Hz, *J* = 3.3 Hz), –114.72 to –115.09 (m), –122.53 to –122.91 (m), –123.49 to –123.71 (m), –123.71 to –124.09 (m), –126.99 to –127.42 (m).

HRMS (ESI): *m*/*z* [M – 2 I^-] calcd for $C_{44}H_{36}F_{26}P_2$: 560.0939; found: 560.0923.

1,4-Bis[(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonio]butane Bis[bis(trifluoromethanesulfonyl)imide] (9b)

Iodide salt **9a** (100 mg, 72.8 μmol, 1.0 equiv) and $LiNTf_2$ (63 mg, 0.22 mmol, 3.0 equiv) were converted according to GPB to furnish compound **9b** (79 mg, 47 μmol, 65%) after recrystallization (MTBE, 5 mL) as a colorless wax.

IR (ATR): 3070 (w), 2933 (w), 1441 (w), 1347 (m), 1327 (m), 1226 (m), 1182 (s), 1133 (s), 1055 (s), 738 (m), 614 (m), 600 cm^{-1} (m).

Anal. Calcd for $C_{48}H_{36}F_{38}N_2O_8P_2S_4$: C, 34.30; H, 2.16; N, 1.67; S, 7.62. Found: C, 34.29; H, 2.00; N, 1.52; S, 7.97.

1,5-Bis[(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonio]pentane Diiodide (10a)

A solution of perfluorinated iodide **19** (1.35 g, 2.84 mmol, 2.5 equiv) and 1,5-bis(diphenylphosphano)pentane (**24**; 500 mg, 1.14 mmol, 1.0 equiv) in DMF (5 mL) was stirred in a tightly closed reaction tube for 24 h at 105 °C. The mixture was diluted with MTBE (20 mL); the crude product precipitated and was collected by filtration. The residue was recrystallized (MTBE, 50 mL) to furnish product **10a** (1.00 g, 0.722 mmol, 64%) as a colorless solid; mp 174 °C.

IR (ATR): 2891 (w), 2869 (w), 1437 (m), 1232 (s), 1188 (s), 1120 (s), 1072 (m), 737 (s), 688 (s), 648 cm^{-1} (m).

^{1}H NMR (500 MHz, CD_3OD): δ = 1.54–1.65 (m, 4 H), 1.73–1.81 (m, 2 H), 2.37–2.54 (m, 4 H), 3.16–3.26 (m, 4 H), 3.40–3.50 (m, 4 H), 7.72–7.80 (m, 8 H), 7.86–7.98 (m, 12 H).

^{13}C{^{1}H} NMR (125 MHz, CD_3OD): δ = 14.35 (d, *J* = 54.4 Hz, 2 CH_2), 21.30 (d, *J* = 49.7 Hz, 2 CH_2), 22.36–22.43 (m, 2 CH_2), 25.25 (t, *J* = 22.9 Hz, 2 CH_2), 31.97–32.25 (m, CH_2), 118.11 (d, *J* = 84.7 Hz, 4 C), 131.61 (d, *J* = 12.6 Hz, 8 CH), 134.47 (d, *J* = 9.9 Hz, 8 CH), 136.51 (d, *J* = 3.0 Hz, 4 CH).

^{31}P{^{1}H} NMR (203 MHz, CD_3OD): δ = 28.34 (s).

^{19}F{^{1}H} NMR (470 MHz, CD_3OD): δ = –82.40 (tt, *J* = 10.3 Hz, *J* = 3.1 Hz), –114.59 to –115.25 (m), –122.53 to –123.02 (m), –123.36 to –124.30 (m), –126.88 to –127.69 (m).

HRMS (ESI): *m*/*z* [M – 2 I^-] calcd for $C_{45}H_{38}F_{26}P_2$: 567.1011; found: 567.0996.

1,5-Bis[(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)diphenylphosphonio]pentane Bis[bis(trifluoromethanesulfonyl)imide] (10b)

Iodide salt **10a** (93 mg, 67 μmol, 1.0 equiv) and $LiNTf_2$ (58 mg, 0.20 mmol, 3.0 equiv) were converted according to GPB to furnish compound **10b** (82 mg, 48 μmol, 72%) after recrystallization (MTBE, 5 mL) as a colorless solid; mp 76 °C.

IR (ATR): 3071 (w), 2950 (w), 2931 (w), 1441 (w), 1343 (m), 1328 (m), 1230 (m), 1184 (s), 1138 (s), 1057 (s), 739 (m), 611 cm^{-1} (m).

Anal. Calcd for $C_{49}H_{38}F_{38}N_2O_8P_2S_4$: C, 34.72; H, 2.26; N, 1.65; S, 7.58. Found: C, 34.33; H, 2.66; N, 1.42; S, 7.88.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610072.

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