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14. ABSTRACT Recently, a new class of high-energy-containing materials, <i>gem</i> -bis(difluoramino)-substituted heterocyclic nitramines, has gained attention as high-energy oxidizers: HNF ^X ^[1,2] and TNFX ^[3] have been successfully synthesized under strongly acidic conditions from their corresponding ketone derivatives using an excess of difluoramine. ^[4] HNF ₂ is an unpredictably shock-sensitive and thermally unstable, gaseous compound ^[5,6] which can be generated from different precursors, e.g., tetrafluorohydrazine, ^[7] <i>N,N</i> -difluorourea, ^[8] <i>N,N</i> -difluorocarbamates, ^[9] or trityldifluoramine. ^[10] Out of these precursors, only trityldifluoramine is a stable storable solid. However, it is not useful as a general reagent for the preparation of larger quantities of <i>gem</i> -bis(difluoramines) because its synthesis requires the use of expensive N ₂ F ₄ which is commercially unavailable and must be prepared from difluoramine, and of equivalent amounts of mercury in an organic solvent. The use of mercury presents environmental problems, and working with N ₂ F ₄ in an organic solvent can be hazardous. Therefore, it is highly desirable to develop a stable, solid, readily accessible difluoramine source. Obvious candidates for HNF ₂ sources were difluorosulfamate salts. Although the parent free acid, HOSO ₂ NF ₂ , had been known since 1961 and has been widely used as a difluoroaminating reagent, ^[11,12] no reports could be found on the existence of its salts. In this paper, we report the results from two independent studies.					
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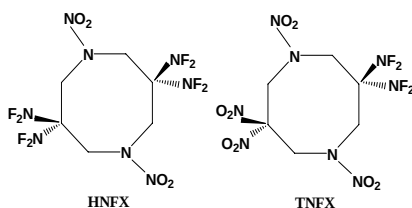
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Preparation, Characterization, and Crystal Structures of the SO_3NHF^- and SO_3NF_2^- Anions**

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Dedicated to Dr. Carl Schack on the occasion of his 70th birthday

Recently, a new class of high-energy-containing materials, *gem*-bis(difluoramino)-substituted heterocyclic nitramines, has gained attention as high-energy oxidizers: $\text{HNFX}^{[1,2]}$ and $\text{TNFX}^{[3]}$ have been successfully synthesized under strongly acidic conditions from their corresponding ketone derivatives using an excess of difluoramine.^[4]



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HNF_2 is an unpredictably shock-sensitive and thermally unstable, gaseous compound^[5,6] which can be generated from different precursors, e.g., tetrafluorohydrazine,^[7] *N,N*-difluorourea,^[8] *N,N*-difluorocarbamates,^[9] or trityldifluoramine.^[10] Out of these precursors, only trityldifluoramine is a stable storable solid. However, it is not useful as a general reagent for the preparation of larger quantities of *gem*-bis(difluoramines) because its synthesis requires the use of expensive N_2F_4 which is commercially unavailable and must be prepared from difluoramine, and of equivalent amounts of mercury in an organic solvent. The use of mercury presents environmental problems, and working with N_2F_4 in an organic solvent can be hazardous. Therefore, it is highly desirable to develop a stable, solid, readily accessible difluoramine source. Obvious candidates for HNF_2 sources were difluorosulfamate salts. Although the parent free acid, HOSO_2NF_2 , had been known since 1961 and has been widely used as a difluoroaminating reagent,^[11,12] no reports could be found on the existence of its salts. In this paper, we report the results from two independent studies.

At TPL, Inc., $\text{Na}^+\text{SO}_3\text{NF}_2^-$ was first isolated by fluorinating aqueous sulfamic acid at 0 °C, neutralizing the product with concentrated aqueous sodium hydroxide, filtering off the less-soluble sodium fluoride by-product, and drying the neutral solution under vacuum. This process was improved by utilizing aqueous sodium sulfamate as a reactant, which is even more soluble than sulfamic acid. This modification required removal of less water for isolation. Maintaining neutral or slightly basic conditions with added sodium hydroxide or sodium carbonate during the aqueous fluorination proved beneficial, as the stability of acidic difluorosulfamic acid is poorer than that of neutral salt solutions. Sodium difluorosulfamate of ~96% purity could be prepared in this manner.

After storage in a refrigerator at ~0 °C for one month, solid sodium difluorosulfamate that was prepared in this way showed signs of degradation, as evidenced by its ¹⁹F NMR spectrum in D_2O . However, dilute aqueous solutions maintained at pH 7–8 (with dilute aqueous NaHCO_3) appeared to be stable for several weeks at room temperature, according to ¹⁹F NMR, and, after 64 days at room temperature, only slight changes were apparent. After nine years, one such sample showed no residual difluorosulfamate content.

At USC, the synthesis of the SO_3NF_2^- and SO_3NHF^- anions was achieved by direct fluorination of SO_3NH_2^- salts with diluted elemental fluorine in unbuffered aqueous solutions at 0 °C [Eq. (1)].



The reaction conditions were similar to those previously used successfully for the fluorination of urea,^[8a] carbamates^[9a] and sulfamide.^[13] The acidic reaction mixture was not stable above ~5 °C, and fast hydrolysis of the difluorosulfamate [Eq. 2] occurred upon warming to ambient temperature.



The ease of this acid-catalyzed hydrolysis can account for the lack of previous reports to isolate salts of the difluorosulfamate anion. The successful isolation of difluorosulfamate salts required careful control of the reaction conditions and rapid removal of the water and HF by-product at 0 °C in a vacuum. This method resulted in the isolation of pure, colorless NaSO_3NF_2 in 94% yield. The dry sodium salt is stable at room temperature but decomposes when exposed to atmospheric moisture. It was stored in the dry argon atmosphere of a glove box for a period of 4 months without showing any sign of decomposition. The identity of the compound was established by the observed material balance, vibrational and

multinuclear NMR spectroscopy, electronic structure calculations, and by converting it into [PNP][SO₃NF₂] $\cdot$ CH₂Cl₂ (PNP = bis-(triphenylphosphoranylidene)ammonium) and determining its crystal structure.

The observed Raman and IR spectra of solid NaSO₃NF₂ are shown in Figure 1, and the observed frequencies and intensities are listed in Table 1. They were assigned by comparison with those calculated at the MP2^[14] level of theory using the 6-311+G(d) basis set.

Table 1. Comparison of observed and unscaled calculated MP2/6-311+G(d) vibrational frequencies (cm⁻¹) and intensities for SO₃NF₂⁻ in point group C_s.

mode		approx. mode description in point group C _s	observed ^{[a],[e]}		calculated ^[b]
			IR	Raman	calcd (IR) [Raman]
a'	v ₁	v _{as} SO ₃	1309	1304	1286 (364)
			vs	[0.8]	[7.2 dp]
	v ₂	v _s SO ₃	1080 s	1089	1051 (59)
				[10.0]	[38 p]
	v ₃	v _s NF ₂	968 w	997	979 (72)
				[4.0]	[4.4 p]
				971	
				[0.9]	
v ₄		v SN	715 m	722	671 (64)
				[5.5]	[17 p]
	v ₅	δ _{sciss} SO ₂	627 s	630	601 (140)
			617 s	[1.1]	[0.6 dp]
	v ₆	δ _{umbrella} SO ₂		526	521 (1.6)
				[2.6]	[7.3 p]
	v ₇	δ _{sciss} NF ₂	525 vw		501 (25)
					[4.6 p]
v ₈		δ _{rock} SO ₂	[c]	337	298 (1.6)
				[4.3]	[8.6 p]
	v ₉	δ _{rock} NF ₂	[c]	264	224 (0.5)
				[1.3]	[2.4 p]
	v ₁₀	v _{as} SO ₃	1284	1267	1282 (362)
			vs	[0.7]	[7.7 dp]
	v ₁₁	v _{as} NF ₂	869 m	868	829 (75)
				[1.6]	[2.1 dp]
v ₁₂		δ _{sciss} SO ₂	532 w	537	532 (35)
				[2.0]	[3.5 dp]
	v ₁₃	δ _{rock} SO ₂	[c]	390	325 (0.8)
				[2.6]	[0.8 dp]
	v ₁₄	δ _{wag} NF ₂	[c]	186	154 (0.02)
				[1.3]	[6.1 dp]
	v ₁₅	τ SN	[c]	37	37 (0.00)
				[d]	[2.0 dp]

[a] As Na⁺ salt. Relative IR and Raman intensities given in parentheses and brackets, respectively. [b] IR intensities given in km mol⁻¹ and Raman intensities given in Å⁴ amu⁻¹. [c] Not observed, IR spectrum recorded only between 4000 and 400 cm⁻¹. [d] Not observed, Raman spectrum recorded only between 3600 and 80 cm⁻¹. [e] In addition to the listed bands, IR bands at 1627 m, 1209 w, 1184 m, 565 w, and Raman bands at 1618 [0.5], 1321 [0.7], 572 [1.2] cm⁻¹ were observed which were not assigned.

While the ¹⁹F NMR spectrum of naturally abundant [¹⁴N]NaSO₃NF₂ in CD₃CN gives only a broad resonance at δ = 34 ppm, the spectrum of an ¹⁵N-labeled sample in the same solvent shows a sharp doublet at δ = 33.8 ppm with ¹J(¹⁹F–¹⁵N) = 138 Hz. In the ¹⁵N NMR spectrum of the sample, a sharp triplet at δ = –20.4 ppm with the same ¹J(¹⁵N–¹⁹F) coupling constant was observed.

Colorless and air stable [PNP][SO₃NF₂] was obtained by neutralizing the fluorination reaction mixture, adding PNP⁺Cl⁻ and extracting with methylene chloride [Eq (3)]. Single crystals of [PNP][SO₃NF₂] $\cdot$ CH₂Cl₂ suitable for X-ray crystal structure determination were obtained by recrystallization from CH₂Cl₂.

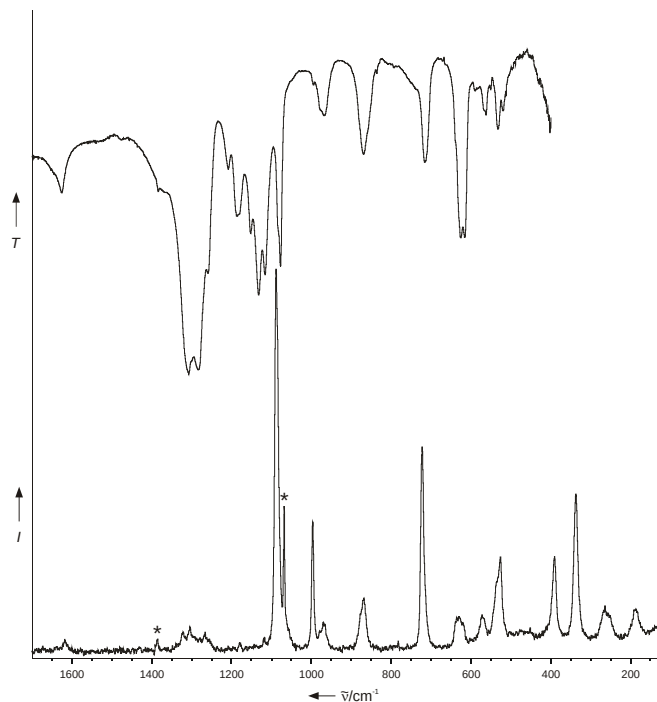


Figure 1. IR and Raman spectra of solid NaSO₃NF₂. Bands marked with asterisks (*) are due to an impurity of NO₃⁻.



[PNP][SO₃NF₂] $\cdot$ CH₂Cl₂, containing one molecule of methylene chloride, crystallizes in the triclinic space group *P*1̄. The X-ray structure analysis^[15] reveals the presence of two isolated [PNP]⁺ and [SO₃NF₂]⁻ units together with two disordered CH₂Cl₂ molecules in the unit cell (packing diagrams are given in the Supplementary Figures S1 and S2). The closest F $\cdots$ H and O $\cdots$ H contacts between neighboring cations and anions are 2.682 Å and 2.349 Å, respectively. The SO₃NF₂⁻ anion is depicted in Figure 2. The dimen-

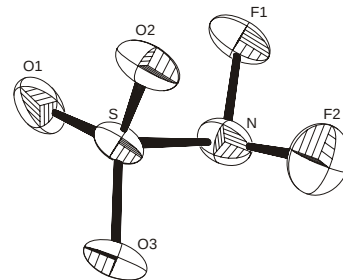


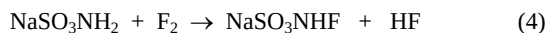
Figure 2. ORTEP drawing of the anion part of [PNP][SO₃NF₂] $\cdot$ CH₂Cl₂. Thermal ellipsoids are shown at the 50% probability level. Bond lengths [Å] and angles [°]: S–O(1) 1.428(4), S–O(2) 1.424(3), S–O(3) 1.424(3), S–N 1.772(4), F(1)–N 1.412(5), F(2)–N 1.463(6), O(1)–S–O(2) 114.7(2), O(1)–S–O(3) 116.1(2), O(2)–S–O(3) 116.8(2), O(1)–S–N 100.1(2), O(2)–S–N 106.1(2), O(3)–S–N 99.3(2), F(1)–N–F(2) 99.0(3), F(1)–N–S 104.5(3), F(2)–N–S 99.6(3).

sions of the SO₃N skeleton are more similar to those of sulfamic acid^[16] than to the ones reported for salts with the SO₃NH₂⁻ anion.^[17] Estimations of the double-bond character of the S–N bond are frequently made by comparison of the observed lengths with that predicted from Pauling's covalent radii, 1.74 Å,^[18] or with the bond length in sulfamic acid, 1.772(1) Å.^[16b] In the solid state, the latter has the zwitterionic structure ⁺NH₃–SO₃⁻ which possesses a formal

S–N single bond. The observed S–N bond length of 1.772(4) Å in SO_3NF_2^- is similar to the one in sulfamic acid and larger than the typical values found in the SO_3NH_2^- anion (1.64 Å). The S–O bond lengths of 1.428(8) Å and 1.424(3) Å are shorter than the values reported for sulfamates (1.44–1.45 Å)^[17] and sulfamic acid (1.438(1) Å, 1.436(1) Å, and 1.435(1) Å).^[16b] The average O–S–O and O–S–N angles of 115.9° and 101.8°, respectively, are in good agreement with the ones reported for sulfamic acid.

The marked differences in the S–N and S–O bond lengths between SO_3NF_2^- and SO_3NH_2^- can be readily reconciled by the large difference between the electronegativities of hydrogen and fluorine. The strongly electron withdrawing fluorine atoms pull some of the negative charges away from the oxygen atoms, thereby increasing the S=O double bond character and shortening the S–O bonds. By contrast, the electron-donating hydrogen atoms increase the electron density on the nitrogen atom, which passes it on to the S=O bonds. This results in partial N=S double bond character and increased negative charges on the oxygen atoms with concomitant lengthening of the S–O bonds.

When only one equivalent of fluorine was used in the fluorination reaction of SO_3NH_2^- , the SO_3NHF^- anion was formed [Eq. (4)].



Colorless and somewhat moisture sensitive NaSO_3NHF was obtained when the acidic reaction mixture was evaporated in a vacuum at 0 °C. The compound was identified and characterized by its vibrational spectra and, as $[\text{PPh}_4][\text{SO}_3\text{NHF}]$, by its crystal structure. The observed Raman and IR spectra of NaSO_3NHF are shown in Figure 3. The observed frequencies and intensities are listed in Table 2 and were assigned by comparison with those calculated at the MP2^[11] level of theory using the 6-311+G(d) basis set.

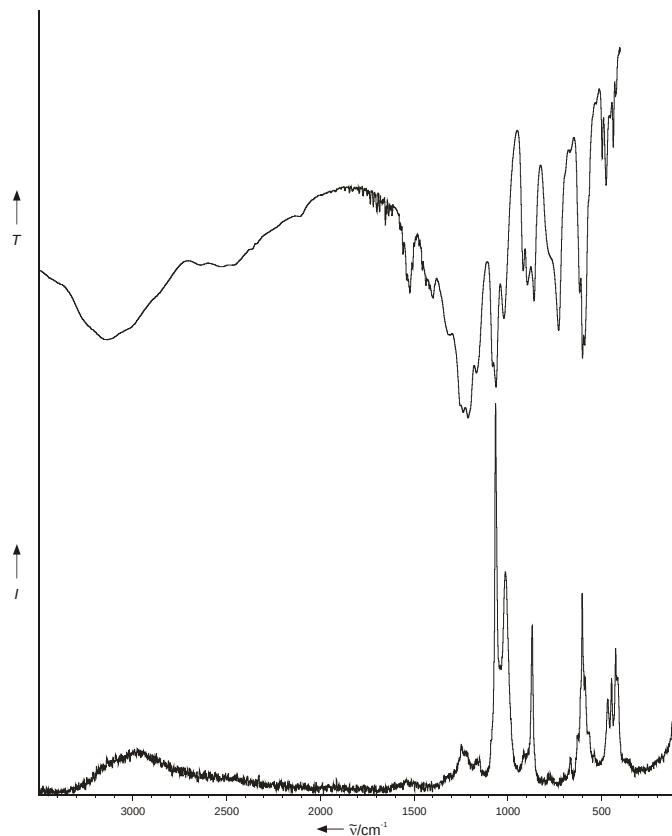


Figure 3. IR and Raman spectra of solid NaSO_3NHF .

Table 2. Comparison of observed and unscaled calculated MP2/6-311+G(d) vibrational frequencies (cm^{-1}) and intensities for SO_3NHF^- in point group C_1 .

mode	approx. mode description in point group C_1	observed ^{[a],[d]}		calculated ^[b]
		IR	Raman	calcd (IR) [Raman]
ν_1	ν_s NHF	3100 s, br	3000 [1.3]	3481 (2.4) [69]
ν_2	ν_{as} NHF	1522 w		1410 (30) [2.8]
ν_3	ν_{as} SO_3	1242 vs	1246 [1.3]	1270 (368) [7.3]
ν_4	ν_{as} SO_3	1213 vs	1225 [1.2]	1240 (401) [7.1]
ν_5	ν_s SO_3	1064 s	1065 [10.0]	1041 (82) [27]
ν_6	δ NHF	1021 m	1014 [5.9]	1033 (45) [18]
ν_7	δ NHF	863 m	869 [4.3]	923 (38) [14]
ν_8	ν SN	602 s	602 [5.0]	699 (161) [16]
ν_9	δ_{sciss} SO_2	590 s		584 (66) [4.5]
ν_{10}	δ_{sciss} SO_2	497 w	466 [2.6]	520 (26) [3.4]
ν_{11}	$\delta_{umbrella}$ SO_2	477 w	445 [3.0]	509 (26) [5.9]
ν_{12}	δ_{rock} SO_2	438 w	424 [3.7]	371 (0.1) [4.7]
ν_{13}	δ_{rock} SO_2	[c]	411 [3.0]	343 (8.1) [2.6]
ν_{14}	δ NHF	[c]		215 (1.2) [1.1]
ν_{15}	τ SN	[c]	122 [2.0]	118 (1.9) [0.4]

[a] As Na^+ salt. Relative IR and Raman intensities given in parentheses and brackets, respectively. [b] IR intensities given in km mol^{-1} and Raman intensities given in $\text{\AA}^4 \text{amu}^{-1}$. [c] Not observed, IR spectrum recorded only between 4000 and 400 cm^{-1} . [d] In addition to the listed bands, IR bands at 1313 m, 1168 s, 1082 s, 918 m, 897 m, 773 m, 731 s, 617 m and Raman bands at 1168 [1.0], 1153 [1.0], 913 [1.2], 666 [1.0] cm^{-1} were observed which were not assigned.

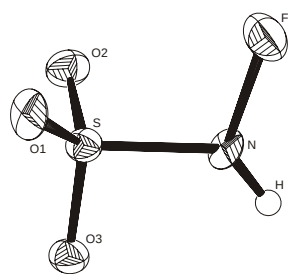


Figure 4. ORTEP drawing of the anion part of $[\text{PPh}_4][\text{SO}_3\text{NHF}]$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [°]: S–O(1) 1.433(4), S–O(2) 1.457(4), S–O(3) 1.447(3), S–N 1.694(5), F(1)–N 1.474(5), O(1)–S–O(2) 114.4(2), O(1)–S–O(3) 115.3(2), O(2)–S–O(3) 114.1(2), O(1)–S–N 108.5(2), O(2)–S–N 104.3(2), O(3)–S–N 98.0(2), F–N–S 106.4(3).

The $[\text{PPh}_4][\text{SO}_3\text{NHF}]$ salt was obtained by metathesis in the same manner as shown in Eq. 3. It crystallizes disordered in the triclinic space group $P\bar{1}$. The X-ray structure analysis^[19] reveals the presence of two non-equivalent $[\text{PPh}_4]^+$ and $[\text{SO}_3\text{NHF}]^-$ units (packing diagrams are given in the Supplementary Figures S3 and S4). While one SO_3NHF^- anion could be refined well, the second one suffers from a disorder in the SO_3 -group. This results in a relatively high R factor of 8.16% for the refined structure. The closest $\text{F}\cdots\text{H}$ and $\text{O}\cdots\text{H}$ contacts between neighboring cations and anions are 2.566 Å and 2.373 Å, respectively. The ordered SO_3NHF^- anion is depicted in Figure 4. The observed S–N bond

length of 1.694(5) Å in SO_3NHF^- lies between those observed for SO_3NF_2^- (1.772(4) Å) and SO_3NH_2^- (1.64 Å). This is in accord with the expectation that the electronic effect of an $-\text{NHF}$ group is intermediate between those of an $-\text{NF}_2$ and an $-\text{NH}_2$ group.

The presence of one hydrogen atom and one fluorine atom attached to the same nitrogen atom was further established by proton and fluorine NMR spectroscopy. The proton and fluorine spectra showed doublets at $\delta = 8.69$ and -103.0 ppm, respectively, with the same $^2J(^1\text{H}-^{19}\text{F})$ coupling constant of 49 Hz.

The utility of NaSO_3NF_2 as an alternative source of difluoramine in organic difluoramination reactions was demonstrated by both research groups. At TPL, qualitative reactions of cyclohexanone and of 3-pentanone with the reagent in $\sim 100\%$ H_2SO_4 showed in both cases formation of the expected *gem*-bis(difluoramino)alkane by ^{19}F NMR spectroscopy. A quantitative comparison was conducted using 1,3-dibromoacetone as a model ketone. Using NaSO_3NF_2 in anhydrous H_2SO_4 containing $\sim 1\%$ SO_3 , 1,3-dibromo-2,2-bis(difluoramino)propane was formed in 38% nonoptimized yield. This compares with a yield of 37% for conventional difluoramination (HNF_2 in oleum) of 1,3-dibromoacetone.

At USC, the potential of NaSO_3NF_2 for the transformation of carbonyl into *gem*-bis(difluoramino) groups was demonstrated for acetone and 1-acetylpiperidin-4-one using 2.5 equivalents of the reagent in CDCl_3 containing 30% oleum. The formation of the desired *gem*-bis(difluoramino) compounds was established by ^{19}F , ^1H , and ^{13}C NMR spectroscopy. In the case of 1-acetylpiperidin-4-one, only the oxygen of the ring-carbonyl group was replaced, while the carbonyl oxygen of the acetyl group did not react.

In summary, the elusive difluorosulfamate and monofluorosulfamate anions have been isolated and characterized for the first time. They can be prepared in high yield by direct fluorination of sulfamates in aqueous solution. The absence of prior reports of isolation of these salts may be attributed to rapid acid-catalyzed hydrolysis of these solutions above 0 °C. The NaSO_3NF_2 salt is a stable, storable reagent for the *in-situ* generation of HNF_2 and preparation of *gem*-bis(difluoramino) compounds, eliminating the hazards involved in the isolation and handling of treacherous difluoramine.

Experimental Section

Sodium difluorosulfamate (TPL): Sulfamic acid (16.42 g, 0.169 mol) was dissolved in 30 mL H_2O , and NaOH (8.1 g, 0.20 mol), was added. Fluorine (10% in nitrogen) was bubbled through the solution at 0 °C. The progress of the fluorination of sulfamate was monitored by ^{19}F NMR analysis of reaction aliquots, observing the conversion of monofluorosulfamate ($\delta = -102.1$ ppm vs. external CFCl_3 in $[\text{D}_6]\text{acetone}$) to difluorosulfamate ($\delta = 36.6$ ppm). After 1.5 h, the fluorination was complete, and the cloudy mixture was neutralized with concentrated aqueous NaOH . The NaF precipitate was removed by filtration. Based on its ^{19}F NMR spectrum, the filtrate appeared to be a 96 : 4 mixture of NaSO_3NF_2 and NaF . The viscous filtrate was quickly dried at room temperature in a vacuum desiccator over excess P_2O_5 . After 24 h, ^{19}F NMR analysis of the dried solid showed the same $\text{SO}_3\text{NF}_2^-/\text{F}^-$ ratio as the initial filtrate.

1,3-Dibromo-2,2-bis(difluoramino)propane (TPL): 1,3-Dibromoacetone (24.72 g, 0.114 mol) was added to a mixture of sodium difluorosulfamate (61 g, ≤ 0.39 mol) in 310 mL of sulfuric acid containing $\sim 1\%$ SO_3 (made from 30% oleum plus conc. H_2SO_4) plus 100 mL dichloromethane. After stirring for 4 days at 0 °C, the reaction was quenched in water, neutralized, and extracted with dichloromethane. Removal of the solvent produced 13.2 g of solute, the major constituent of which was 1,3-dibromo-2,2-bis(difluoramino)propane (38% crude yield). Three short-path distillations (room temperature at 1–3 torr) produced material that was $>95\%$ pure (elemental analysis

and ^1H NMR) with residual 1,3-dibromoacetone as the main impurity. ^1H NMR (200 MHz, CDCl_3 , TMS): δ 3.98 (quintet, 1.25 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 23.75 (quintet, 5.5 Hz), 99 (m). ^{19}F NMR (CDCl_3): δ 29.9 (s). ^1H NMR (C_6D_6): δ 3.24 (quintet, 1.27 Hz). ^{13}C NMR (C_6D_6): δ 23.69 (quintet, 5.7 Hz), 95.37 (quintet, 6.4 Hz). ^{19}F NMR (C_6D_6): δ 30.26 (s). Anal. Calcd. for $(0.953)\text{C}_3\text{H}_4\text{F}_4\text{N}_2\text{Br}_2 + (0.047)\text{C}_3\text{H}_4\text{Br}_2\text{O}$: C, 12.08; H, 1.35; N, 8.78; F, 23.83. Found: C, 12.12; H, 1.30; N, 8.93; F, 23.53.

Materials and Apparatus (USC): All reactions were carried out in Teflon-FEP ampules closed by stainless steel valves or Pyrex glass vessels closed by grease-free Kontes glass-Teflon valves. Volatile materials were handled in stainless steel/Teflon-FEP^[20] or Pyrex glass vacuum lines. Nonvolatile solids were handled in the dry argon atmosphere of a glove box. Infrared spectra were recorded in the range 4000–400 cm^{-1} on a Midac, M Series, FT-IR spectrometer using KBr pellets. The pellets were prepared inside the glove box using an Econo mini-press (Barnes Engineering Co.) and transferred in a closed container to the spectrometer before placing them quickly into the sample compartment which was purged with dry nitrogen to minimize exposure to atmospheric moisture and potential hydrolysis of the sample. Raman spectra were recorded on a Bruker Equinox 55 FT-RA spectrometer using a Nd-YAG laser at 1064 nm with power levels of 100–200 mW and Pyrex melting point capillaries as sample containers.

Nuclear magnetic resonance spectra were recorded unlocked on Bruker AMX 500 and Varian Mercury/VX 400 NMR spectrometers at room temperature. The ^{19}F and ^{15}N NMR spectra were referenced to external samples of neat CFCl_3 and neat nitromethane, respectively.

The starting materials $\text{H}_2\text{NSO}_3\text{H}$, H_2SO_4 , $[\text{P}(\text{C}_6\text{H}_5)_4]\text{Cl}$, $[\text{PNP}]\text{Cl}$, NaOH (all Aldrich), $^{15}\text{N}_2$ urea (MSD Isotopes), and fluorine (Air Products and Chemicals Inc.) were used without further purification. Solvents were dried by standard methods and freshly distilled prior to use. NaSO_3NH_2 was obtained by neutralization of HSO_3NH_2 with NaOH . $^{15}\text{N}[\text{HSO}_3\text{NH}_2]$ was prepared from $^{15}\text{N}_2$ urea and H_2SO_4 according to a modified literature method.^[21]

Preparation of NaSO_3NHF (USC): A solution of NaSO_3NH_2 (0.380 g, 3.19 mmol) in 4 mL water was placed into a Teflon-FEP ampule equipped with a Teflon-coated magnetic stirring bar and a Teflon gas inlet tube. After cooling to 0 °C, fluorine (3.19 mmol), diluted by 90 vol.% nitrogen, was introduced at a rate of 110 mL/min. The reaction mixture was pumped to dryness at 0 °C, leaving behind a colorless solid (0.391 g, weight calculated for 3.19 mmol $\text{NaSO}_3\text{NHF} = 0.437$ g).

Preparation of $[\text{PPh}_4][\text{SO}_3\text{NHF}]$ (USC): A solution of NaSO_3NH_2 (0.695 g, 5.00 mmol) in 10 mL water was placed into a Teflon-FEP ampule equipped with a magnetic stirring bar and a Teflon gas inlet tube. After cooling to 0 °C, fluorine (5.00 mmol), diluted by 90 vol.% nitrogen, was introduced at a rate of 110 mL/min. The reaction mixture was neutralized by adding cold solid NaHCO_3 and filtered through a cold porcelain frit. A cold solution of 5.00 mmol PPh_4Cl in 50 mL water was added to the clear filtrate. The resulting milky solution was extracted three times with 50 mL of cold CH_2Cl_2 . The combined organic phases were dried over MgSO_4 and pumped to dryness at ambient temperature, leaving behind a colorless solid (2.039 g, weight calculated for 5.00 mmol $\text{PPh}_4\text{SO}_3\text{NHF} = 2.267$ g). Crystals were grown from CH_2Cl_2 solution by slow evaporation of the solvent using a stream of dry nitrogen.

Preparation of NaSO_3NF_2 (USC): A solution of NaSO_3NH_2 (0.236 g, 1.98 mmol) in 7 mL water was placed into a Teflon-FEP ampule equipped with a magnetic stirrer and a Teflon gas inlet tube. After cooling to 0 °C, fluorine, diluted by 90 vol.% nitrogen, was introduced at a rate of 110 mL/min. After 45 min, the fluorination was discontinued, and the reaction mixture pumped to dryness at 0 °C, leaving behind a colorless solid (0.288 g, weight calculated for 1.98 mmol $\text{NaSO}_3\text{NF}_2 = 0.307$ g).

Preparation of $[\text{A}][\text{SO}_3\text{NF}_2]$ ($\text{A} = \text{PNP}$, PPh_4 , AsPh_4) (USC): A solution of NaSO_3NH_2 (0.357 g, 3.00 mmol) in 10 mL water was placed into a Teflon-FEP ampule equipped with a magnetic stirring bar and a Teflon gas inlet tube. After cooling to 0 °C, fluorine, diluted by 90 vol.% nitrogen, was introduced at a rate of 110 mL/min. After 60 min, the fluorination was discontinued, and the reaction mixture was

neutralized by adding cold solid NaHCO_3 . The reaction mixture was filtered through a cold porcelain frit, and a cold aqueous solution of 3.00 mmol A^+Cl^- was added to the clear filtrate. The resulting milky solution was extracted three times with 10 mL of cold CH_2Cl_2 . The combined organic phases were dried over MgSO_4 and pumped to dryness at ambient temperature, leaving behind colorless solids ($[\text{PPh}_4][\text{SO}_3\text{NF}_2]$: 1.283 g, calculated weight for 3.00 mmol = 1.414 g; $[\text{AsPh}_4][\text{SO}_3\text{NF}_2]$: 1.466 g, calculated weight for 3.00 mmol = 1.543 g; $[\text{PNP}][\text{SO}_3\text{NF}_2]$: 2.071 g, calculated weight for 3.00 mmol = 2.011 g). Crystals were grown from CH_2Cl_2 solution by slow evaporation of the solvent using a stream of dry nitrogen.

2,2-Bis(difluoramino)propane and 1-acetyl-4,4-bis(difluoramino)piperidine (USC): To a vigorously stirred mixture of CDCl_3 (1.5 mL), 30% oleum (1.5 mL), and the ketone starting material (1.0 mmol), 2.5 equivalents of NaSO_3NF_2 were added in increments at 4 °C. Immediate gas evolution was observed. After 15 min, the upper organic phase was analyzed by ^{19}F , ^1H , and ^{13}C NMR spectroscopy, showing the formation of the desired *gem*-bis(difluoramines).

Theoretical Methods: The molecular structures and harmonic vibrational frequencies were calculated using second-order many-body perturbation theory^[14] (denoted as MP2, but also known as MBPT(2)) and a 6-311+G(d) basis set. Hessians (energy second derivatives) were calculated for the final equilibrium structures to determine if they are minima (positive definite hessian) or *n*th-order transition states ("*n*" negative eigenvalues). All calculations were performed using the electronic structure code GAMESS.^[22]

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- [15] Crystal data for $\text{C}_{37}\text{H}_{32}\text{Cl}_2\text{F}_2\text{N}_2\text{O}_3\text{P}_2\text{S}$: $M_r = 755.55$, triclinic, space group $P\bar{1}$, $a = 11.8650(12)$, $b = 11.9167(12)$, $c = 14.5180(15)$ Å, $\alpha = 66.755(2)$, $\beta = 68.964(2)$, $\gamma = 71.034(2)^\circ$, $V = 1719.7(3)$ Å³, $F(000) = 780$, $\rho_{\text{calcd.}} (Z = 2) = 1.459$ g·cm⁻³, $\mu = 0.395$ mm⁻¹, approximate crystal dimensions $0.29 \times 0.21 \times 0.05$ mm³, θ range = 1.58 to 27.49° , index ranges $-15 \leq h \leq 12$, $-15 \leq k \leq 12$, $-18 \leq l \leq 18$, $\text{Mo}_{\text{K}\alpha}$ ($\lambda = 0.71073$ Å), $T = 133(2)$ K, 10657 measured reflections (Bruker 3-circle, SMART APEX CCD with χ -axis fixed at 54.74° , using the SMART V 5.625 program, Bruker AXS: Madison, WI, 2001), of which 7433 ($R_{\text{int}} = 0.0487$) were unique. Lorentz and polarization correction (SAINT V 6.22 program, Bruker AXS: Madison, WI, 2001), structure solution by direct methods (SHELXTL 5.10, Bruker AXS: Madison, WI, 2000), full-matrix least-squares refinement on F^2 , data to parameters ratio = 16.9 : 1, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0731$, $wR2 = 0.1949$, R indices (all data): $R1 = 0.1087$, $wR2 = 0.2102$, GOF on $F^2 = 1.012$. Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 274108.
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1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 274109.

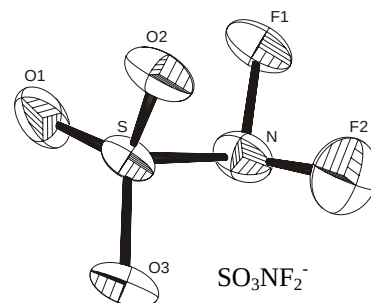
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Synopsis

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Preparation, Characterization, and
Crystal Structures of the SO_3NHF^-
and SO_3NF_2^- Anions

Safe difluoroaminating reagents: Salts of the elusive SO_3NF_2^- anion were prepared by aqueous fluorination of SO_3NH_2^- with F_2 , characterized, and shown to be excellent reagents for the preparation of *gem*-bis(difluoramines). Salts of the intermediate SO_3NHF^- anion were also isolated and characterized.



Supplementary Material

Preparation, Characterization, and Crystal Structures of the SO_3NHF^- and SO_3NF_2^- Anions

Ralf Haiges, Ross Wagner, Jerry A. Boatz, Muhammed Yousufuddin, Markus Etzkorn, G. K. Surya Prakash, Karl O. Christe,* Robert D. Chapman,* Mark F. Welker, Charles B. Kreutzberger*

Figure S1. Crystal packing of $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ along the a-axis.

Figure S2. Crystal packing of $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$ along the b*-axis.

Table S1. Crystal data and structure refinement for $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$.

Table S3. Bond lengths and angles for $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$.

Table S4. Anisotropic displacement parameters for $[\text{PNP}][\text{SO}_3\text{NF}_2]\cdot\text{CH}_2\text{Cl}_2$.

Figure S3. Crystal packing of $[\text{PPh}_4][\text{SO}_3\text{NFH}]$ along the a-axis.

Figure S4. Crystal packing of $[\text{PPh}_4][\text{SO}_3\text{NFH}]$ along the b*-axis.

Table S5. Crystal data and structure refinement for $[\text{PPh}_4][\text{SO}_3\text{NFH}]$.

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Table S6. Atomic coordinates and equivalent isotropic displacement parameters for $[\text{PPh}_4][\text{SO}_3\text{NFH}]$.

Table S7. Bond lengths and angles for $[\text{PPh}_4][\text{SO}_3\text{NFH}]$.

Table S8. Anisotropic displacement parameters for $[\text{PPh}_4][\text{SO}_3\text{NFH}]$

Figure S1. Crystal packing of [PNP][SO₃NF₂] $\cdot$ CH₂Cl₂ along the a-axis.

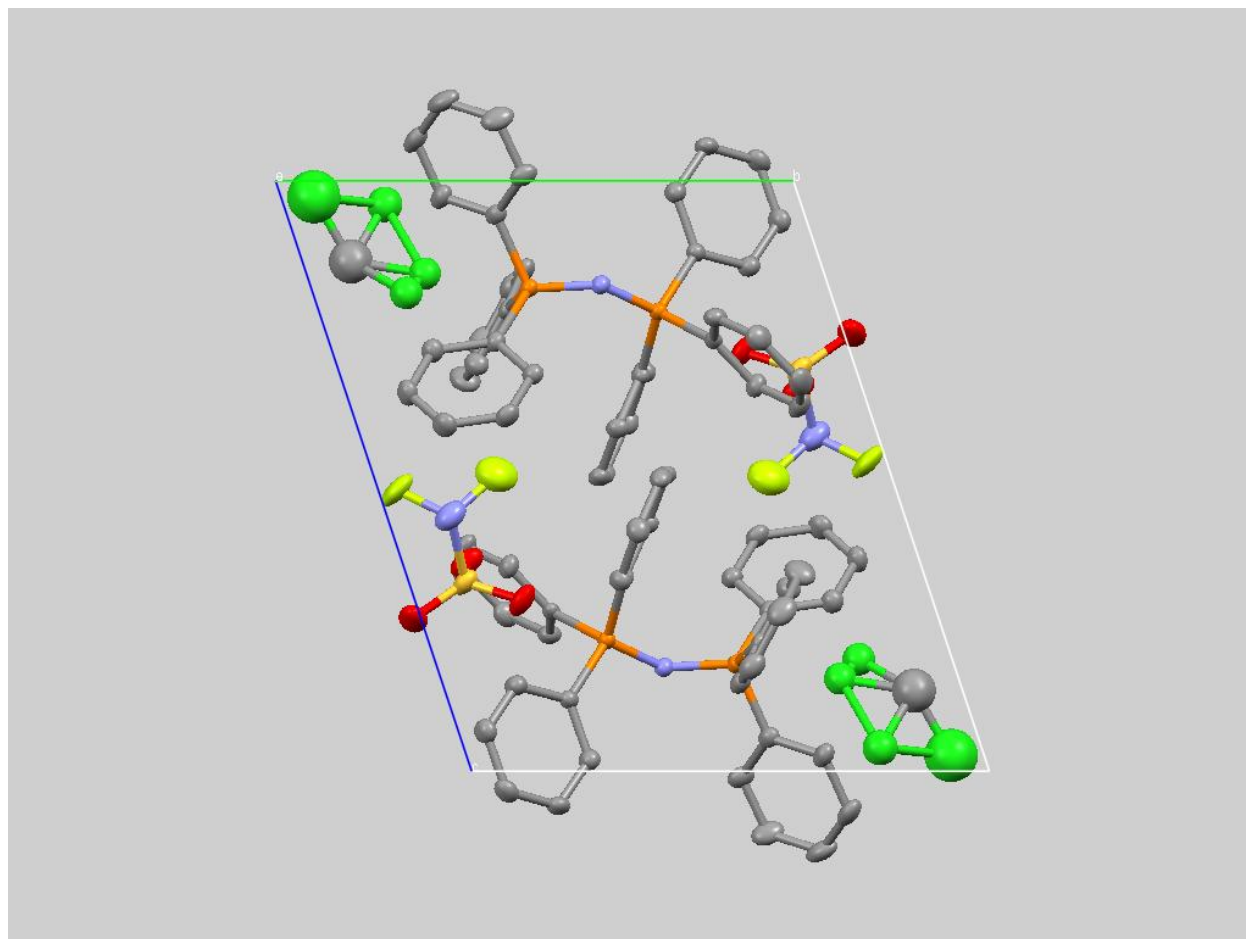


Figure S2. Crystal packing of [PNP][SO₃NF₂] $\cdot$ CH₂Cl₂ along the b*-axis.

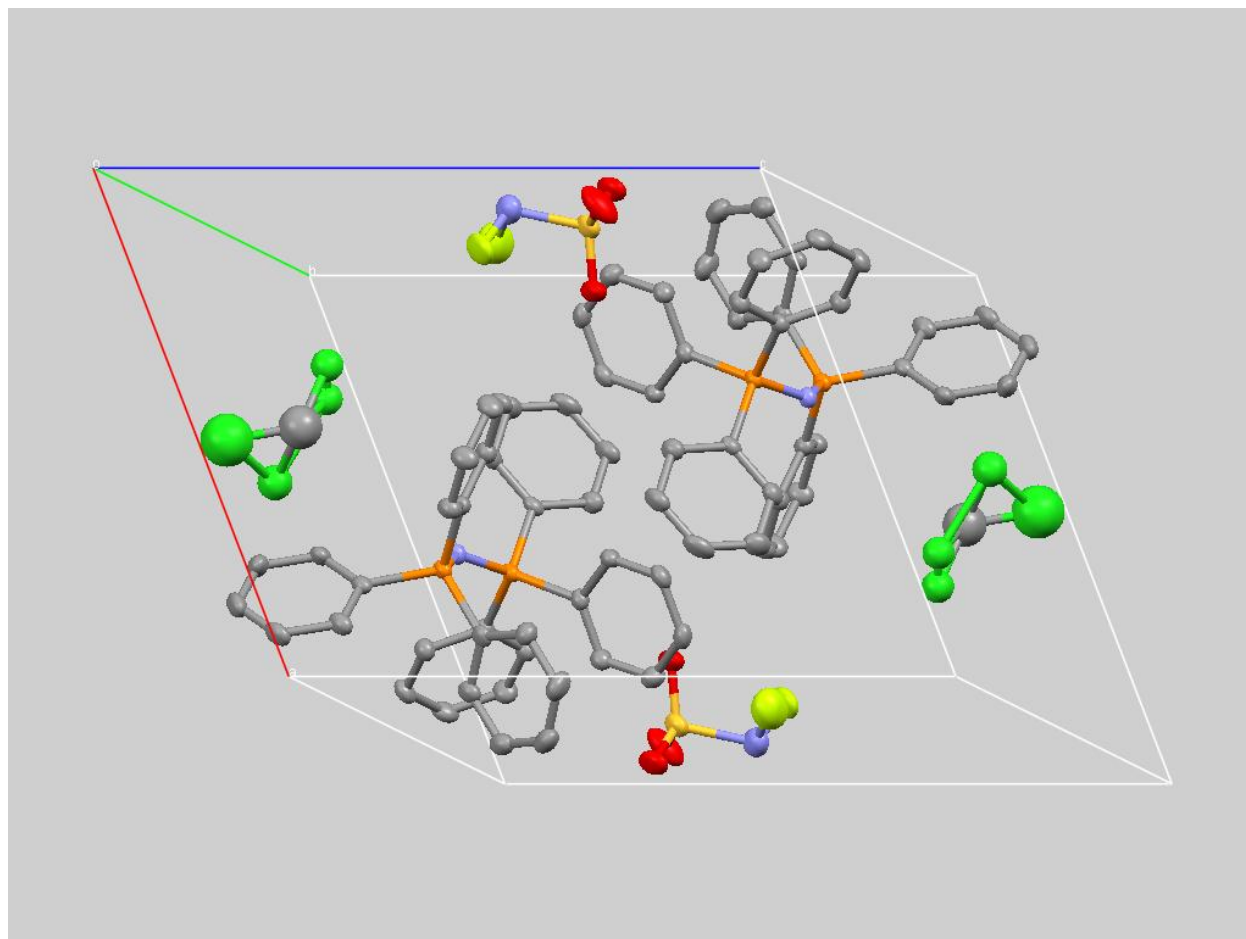


Table S1. Crystal data and structure refinement for [PNP][SO₃NF₂] $\cdot$ CH₂Cl₂.

Identification code	pnpnf2m	
Empirical formula	C ₃₇ H ₃₂ Cl ₂ F ₂ N ₂ O ₃ P ₂ S	
Formula weight	755.55	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.8650(12) Å	$\alpha = 66.755(2)^\circ$
	b = 11.9167(12) Å	$\beta = 68.964(2)^\circ$
	c = 14.5180(15) Å	$\gamma = 71.034(2)^\circ$
Volume	1719.7(3) Å ³	
Z	2	
Density (calculated)	1.459 Mg/m ³	
Absorption coefficient	0.395 mm ⁻¹	
F(000)	780	
Crystal size	0.29 x 0.21 x 0.05 mm ³	
Theta range for data collection	1.58 to 27.49°	
Index ranges	-15 ≤ h ≤ 12, -15 ≤ k ≤ 12,	
	-18 ≤ l ≤ 18	
Reflections collected	10657	
Independent reflections	7433 [R(int) = 0.0487]	
Completeness to theta = 27.49°	94.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7433 / 0 / 439	
Goodness-of-fit on F ²	1.012	
Final R indices [I > 2σ(I)]	R1 = 0.0731, wR2 = 0.1949	
R indices (all data)	R1 = 0.1087, wR2 = 0.2102	
Largest diff. peak and hole	2.141 and -0.956 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [PNP][SO₃NF₂] $\cdot$ CH₂Cl₂. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	9080(1)	8911(1)	3198(1)	33(1)
P(1)	6575(1)	6553(1)	2214(1)	18(1)
P(2)	7010(1)	4204(1)	1823(1)	19(1)
F(1)	8484(3)	9637(3)	4760(2)	54(1)
F(2)	9027(3)	7620(4)	5028(3)	82(1)
O(1)	9241(4)	10151(3)	2582(3)	61(1)
O(2)	7839(3)	8757(3)	3531(3)	42(1)
O(3)	10023(3)	7924(3)	2894(3)	41(1)
N(1)	6408(3)	5618(3)	1759(2)	20(1)
N(2)	9444(4)	8771(4)	4326(3)	47(1)
Cl(1)	5775(2)	1958(3)	400(2)	63(1)
Cl(2)	3499(3)	1805(3)	1898(2)	54(1)
Cl(3)	5216(5)	638(5)	269(5)	144(3)
Cl(4)	4060(5)	2288(5)	1569(4)	53(2)
C(1)	7440(3)	7663(4)	1214(3)	19(1)
C(2)	7860(4)	7649(4)	191(3)	25(1)
C(3)	8489(4)	8545(4)	-583(3)	28(1)
C(4)	8704(4)	9453(4)	-336(3)	30(1)
C(5)	8293(4)	9474(4)	677(3)	30(1)
C(6)	7658(4)	8594(4)	1450(3)	26(1)
C(7)	5076(3)	7436(3)	2706(3)	19(1)
C(8)	4889(4)	7971(4)	3466(3)	26(1)
C(9)	3748(4)	8680(4)	3804(4)	32(1)
C(10)	2791(4)	8856(4)	3404(4)	37(1)
C(11)	2955(4)	8324(4)	2660(4)	33(1)
C(12)	4093(4)	7619(4)	2315(3)	26(1)
C(13)	7258(4)	5804(4)	3290(3)	20(1)
C(14)	6615(4)	5020(4)	4190(3)	23(1)
C(15)	7116(4)	4356(4)	5015(3)	27(1)
C(16)	8267(4)	4462(4)	4968(3)	27(1)
C(17)	8906(4)	5239(4)	4085(3)	29(1)

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C(18)	8419(4)	5903(4)	3237(3)	25(1)
C(19)	5957(3)	3219(4)	2723(3)	20(1)
C(20)	6282(4)	1943(4)	2877(3)	27(1)
C(21)	5452(4)	1195(4)	3588(4)	31(1)
C(22)	4326(4)	1700(4)	4135(4)	32(1)
C(23)	3999(4)	2970(4)	3979(3)	29(1)
C(24)	4806(4)	3728(4)	3278(3)	24(1)
C(25)	7338(4)	4042(4)	568(3)	22(1)
C(26)	6609(4)	4827(4)	-94(3)	29(1)
C(27)	6838(4)	4679(5)	-1051(4)	37(1)
C(28)	7804(4)	3750(5)	-1349(4)	38(1)
C(29)	8536(4)	2972(4)	-700(4)	35(1)
C(30)	8311(4)	3098(4)	269(3)	28(1)
C(31)	8442(4)	3632(4)	2177(3)	21(1)
C(32)	8589(4)	2708(4)	3100(3)	29(1)
C(33)	9685(5)	2384(5)	3362(4)	40(1)
C(34)	10632(4)	2982(5)	2710(4)	40(1)
C(35)	10507(4)	3908(4)	1780(4)	34(1)
C(36)	9415(4)	4230(4)	1512(3)	27(1)
C(37)	4897(7)	940(8)	1366(7)	98(3)

Table S3. Bond lengths [Å] and angles [°] for [PNP][SO₃NF₂] $\cdot$ CH₂Cl₂.

Cl(1)-C(37)	1.718(9)	C(15)-C(16)	1.387(6)
Cl(2)-C(37)	1.735(9)	C(16)-C(17)	1.377(6)
Cl(3)-C(37)	1.656(10)	C(17)-C(18)	1.386(6)
Cl(3)-Cl(3)#1	2.216(11)	C(19)-C(20)	1.387(5)
Cl(4)-C(37)	1.667(9)	C(19)-C(24)	1.393(5)
S(1)-O(2)	1.424(3)	C(20)-C(21)	1.394(6)
S(1)-O(3)	1.424(3)	C(21)-C(22)	1.368(6)
S(1)-O(1)	1.428(4)	C(22)-C(23)	1.379(6)
S(1)-N(2)	1.772(4)	C(23)-C(24)	1.381(6)
P(1)-N(1)	1.593(3)	C(25)-C(26)	1.382(6)
P(1)-C(1)	1.791(4)	C(25)-C(30)	1.403(5)
P(1)-C(13)	1.798(4)	C(26)-C(27)	1.388(6)
P(1)-C(7)	1.801(4)	C(27)-C(28)	1.387(6)
P(2)-N(1)	1.581(3)	C(28)-C(29)	1.370(7)
P(2)-C(31)	1.792(4)	C(29)-C(30)	1.393(6)
P(2)-C(19)	1.793(4)	C(31)-C(32)	1.384(6)
P(2)-C(25)	1.796(4)	C(31)-C(36)	1.403(6)
F(1)-N(2)	1.412(5)	C(32)-C(33)	1.378(6)
F(2)-N(2)	1.463(6)	C(33)-C(34)	1.375(7)
C(1)-C(2)	1.392(5)	C(34)-C(35)	1.387(7)
C(1)-C(6)	1.403(5)	C(35)-C(36)	1.378(6)
C(2)-C(3)	1.389(6)		
C(3)-C(4)	1.384(6)	C(37)-Cl(3)-Cl(3)#1	137.9(6)
C(4)-C(5)	1.382(6)	O(2)-S(1)-O(3)	116.78(19)
C(5)-C(6)	1.380(6)	O(2)-S(1)-O(1)	114.7(2)
C(7)-C(12)	1.394(5)	O(3)-S(1)-O(1)	116.1(2)
C(7)-C(8)	1.400(5)	O(2)-S(1)-N(2)	106.1(2)
C(8)-C(9)	1.377(6)	O(3)-S(1)-N(2)	99.3(2)
C(9)-C(10)	1.376(6)	O(1)-S(1)-N(2)	100.1(2)
C(10)-C(11)	1.383(6)	N(1)-P(1)-C(1)	111.00(18)
C(11)-C(12)	1.374(6)	N(1)-P(1)-C(13)	114.57(17)
C(13)-C(18)	1.393(5)	C(1)-P(1)-C(13)	109.73(18)
C(13)-C(14)	1.395(5)	N(1)-P(1)-C(7)	109.01(18)
C(14)-C(15)	1.367(6)	C(1)-P(1)-C(7)	106.65(18)

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C(13)-P(1)-C(7)	105.44(18)	C(16)-C(17)-C(18)	120.7(4)
N(1)-P(2)-C(31)	113.78(17)	C(17)-C(18)-C(13)	119.4(4)
N(1)-P(2)-C(19)	110.66(18)	C(20)-C(19)-C(24)	119.3(4)
C(31)-P(2)-C(19)	109.00(19)	C(20)-C(19)-P(2)	120.4(3)
N(1)-P(2)-C(25)	109.02(18)	C(24)-C(19)-P(2)	120.3(3)
C(31)-P(2)-C(25)	106.69(18)	C(19)-C(20)-C(21)	119.4(4)
C(19)-P(2)-C(25)	107.44(18)	C(22)-C(21)-C(20)	121.0(4)
P(2)-N(1)-P(1)	134.0(2)	C(21)-C(22)-C(23)	119.7(4)
F(1)-N(2)-F(2)	99.0(3)	C(22)-C(23)-C(24)	120.2(4)
F(1)-N(2)-S(1)	104.5(3)	C(23)-C(24)-C(19)	120.4(4)
F(2)-N(2)-S(1)	99.6(3)	C(26)-C(25)-C(30)	119.7(4)
C(2)-C(1)-C(6)	119.1(4)	C(26)-C(25)-P(2)	119.9(3)
C(2)-C(1)-P(1)	120.9(3)	C(30)-C(25)-P(2)	120.3(3)
C(6)-C(1)-P(1)	119.9(3)	C(25)-C(26)-C(27)	120.0(4)
C(3)-C(2)-C(1)	120.3(4)	C(26)-C(27)-C(28)	120.2(4)
C(4)-C(3)-C(2)	119.9(4)	C(29)-C(28)-C(27)	120.2(4)
C(5)-C(4)-C(3)	120.3(4)	C(28)-C(29)-C(30)	120.4(4)
C(6)-C(5)-C(4)	120.2(4)	C(29)-C(30)-C(25)	119.4(4)
C(5)-C(6)-C(1)	120.2(4)	C(32)-C(31)-C(36)	119.6(4)
C(12)-C(7)-C(8)	119.1(4)	C(32)-C(31)-P(2)	123.1(3)
C(12)-C(7)-P(1)	120.2(3)	C(36)-C(31)-P(2)	117.1(3)
C(8)-C(7)-P(1)	120.7(3)	C(33)-C(32)-C(31)	120.0(4)
C(9)-C(8)-C(7)	119.7(4)	C(32)-C(33)-C(34)	120.1(5)
C(10)-C(9)-C(8)	120.2(4)	C(33)-C(34)-C(35)	120.9(4)
C(9)-C(10)-C(11)	120.9(4)	C(36)-C(35)-C(34)	119.2(4)
C(12)-C(11)-C(10)	119.3(4)	C(35)-C(36)-C(31)	120.2(4)
C(11)-C(12)-C(7)	120.7(4)	Cl(3)-C(37)-Cl(4)	124.3(6)
C(18)-C(13)-C(14)	119.4(4)	Cl(3)-C(37)-Cl(1)	72.3(4)
C(18)-C(13)-P(1)	123.2(3)	Cl(4)-C(37)-Cl(1)	79.6(4)
C(14)-C(13)-P(1)	117.3(3)	Cl(3)-C(37)-Cl(2)	124.2(5)
C(15)-C(14)-C(13)	120.5(4)	Cl(4)-C(37)-Cl(2)	30.5(2)
C(14)-C(15)-C(16)	120.3(4)	Cl(1)-C(37)-Cl(2)	108.4(5)
C(17)-C(16)-C(15)	119.6(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{PNP}][\text{SO}_3\text{NF}_2] \cdot \text{CH}_2\text{Cl}_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	29(1)	40(1)	32(1)	-22(1)	1(1)	-8(1)
P(1)	19(1)	18(1)	16(1)	-6(1)	-1(1)	-5(1)
P(2)	20(1)	20(1)	18(1)	-9(1)	-1(1)	-6(1)
F(1)	51(2)	70(2)	52(2)	-48(2)	4(2)	-12(2)
F(2)	86(3)	84(3)	64(3)	-11(2)	-29(2)	-9(2)
O(1)	77(3)	39(2)	39(2)	-8(2)	16(2)	-17(2)
O(2)	25(2)	66(2)	44(2)	-34(2)	1(2)	-12(2)
O(3)	30(2)	48(2)	51(2)	-36(2)	3(2)	-6(2)
N(1)	22(2)	20(2)	19(2)	-8(2)	-5(1)	-4(1)
N(2)	42(3)	60(3)	46(3)	-31(3)	-10(2)	-6(2)
C(1)	19(2)	19(2)	17(2)	-5(2)	-2(2)	-4(2)
C(2)	28(2)	25(2)	23(2)	-9(2)	-5(2)	-7(2)
C(3)	32(2)	29(2)	17(2)	-6(2)	1(2)	-8(2)
C(4)	25(2)	27(2)	27(3)	-2(2)	0(2)	-10(2)
C(5)	33(2)	26(2)	31(3)	-8(2)	-5(2)	-13(2)
C(6)	30(2)	27(2)	22(2)	-9(2)	-3(2)	-9(2)
C(7)	20(2)	16(2)	16(2)	-4(2)	2(2)	-4(2)
C(8)	25(2)	25(2)	30(3)	-14(2)	-4(2)	-5(2)
C(9)	30(2)	33(3)	32(3)	-20(2)	5(2)	-9(2)
C(10)	26(2)	30(3)	39(3)	-13(2)	6(2)	0(2)
C(11)	25(2)	32(3)	35(3)	-7(2)	-8(2)	0(2)
C(12)	27(2)	28(2)	18(2)	-6(2)	-4(2)	-5(2)
C(13)	25(2)	19(2)	18(2)	-6(2)	-5(2)	-6(2)
C(14)	20(2)	27(2)	20(2)	-7(2)	-2(2)	-8(2)
C(15)	31(2)	26(2)	18(2)	-7(2)	0(2)	-8(2)
C(16)	33(2)	27(2)	22(2)	-9(2)	-12(2)	-1(2)
C(17)	26(2)	30(2)	33(3)	-10(2)	-10(2)	-6(2)
C(18)	26(2)	25(2)	23(2)	-6(2)	-4(2)	-9(2)
C(19)	19(2)	21(2)	22(2)	-9(2)	-4(2)	-5(2)
C(20)	25(2)	27(2)	29(2)	-10(2)	-3(2)	-8(2)
C(21)	31(2)	22(2)	36(3)	-9(2)	-3(2)	-9(2)

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C(22)	34(3)	30(3)	30(3)	-7(2)	0(2)	-17(2)
C(23)	23(2)	34(3)	27(2)	-16(2)	2(2)	-6(2)
C(24)	25(2)	25(2)	23(2)	-9(2)	-4(2)	-7(2)
C(25)	20(2)	25(2)	22(2)	-10(2)	0(2)	-10(2)
C(26)	19(2)	42(3)	25(2)	-16(2)	0(2)	-6(2)
C(27)	27(2)	60(3)	31(3)	-20(3)	-10(2)	-9(2)
C(28)	38(3)	60(3)	27(3)	-25(3)	2(2)	-22(3)
C(29)	31(3)	39(3)	35(3)	-25(2)	6(2)	-10(2)
C(30)	28(2)	28(2)	30(3)	-16(2)	1(2)	-9(2)
C(31)	23(2)	18(2)	22(2)	-12(2)	-3(2)	-1(2)
C(32)	30(2)	31(3)	28(2)	-8(2)	-10(2)	-9(2)
C(33)	47(3)	44(3)	35(3)	-3(2)	-24(2)	-13(2)
C(34)	31(3)	54(3)	46(3)	-26(3)	-16(2)	-4(2)
C(35)	26(2)	44(3)	38(3)	-23(2)	-3(2)	-9(2)
C(36)	25(2)	29(2)	28(2)	-16(2)	1(2)	-6(2)

Figure S3. Crystal packing of $[\text{PPh}_4][\text{SO}_3\text{NFH}]$ along the a-axis.

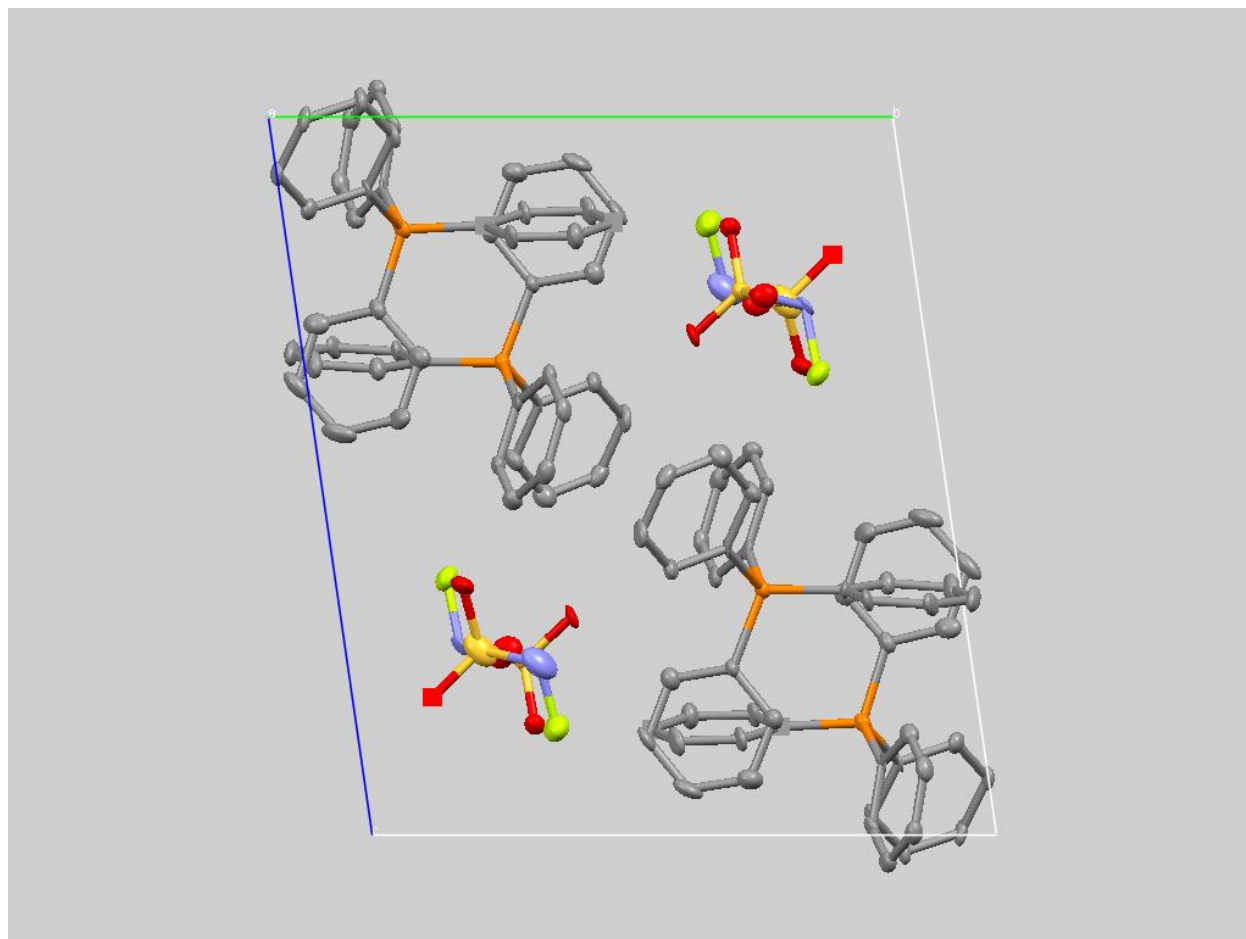


Figure S4. Crystal packing of [PPh₄][SO₃NFH] along the b*-axis.

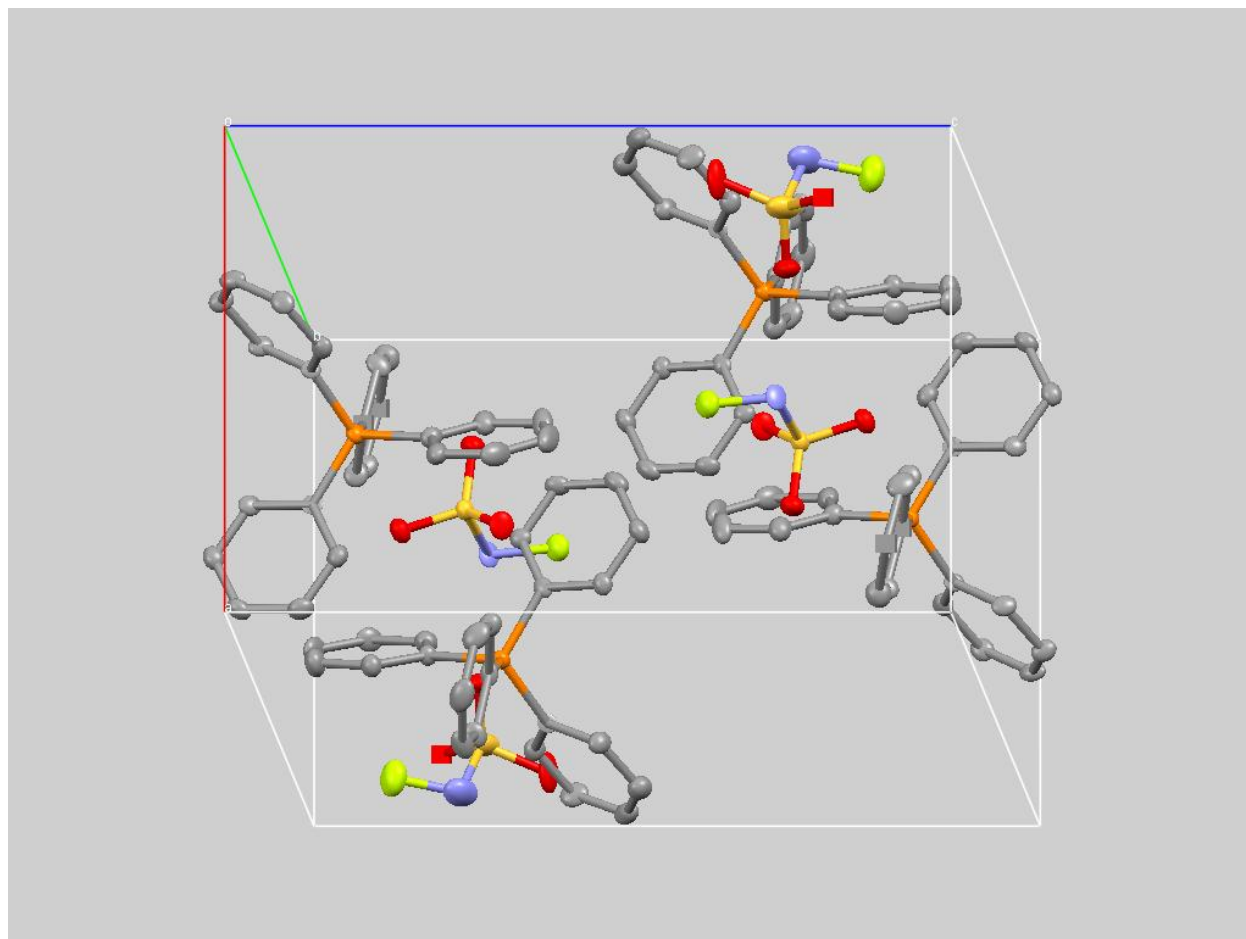


Table S5. Crystal data and structure refinement for [PPh₄][SO₃NFH].

Identification code	nf23m	
Empirical formula	C ₂₄ H ₂₁ FNO ₃ PS	
Formula weight	453.45	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3914(18) Å	$\alpha = 82.221(3)^\circ$
	b = 14.094(2) Å	$\beta = 89.994(3)^\circ$
	c = 15.505(3) Å	$\gamma = 71.066(3)^\circ$
Volume	2125.8(6) Å ³	
Z	4	
Density (calculated)	1.417 Mg/m ³	
Absorption coefficient	0.263 mm ⁻¹	
F(000)	944	
Crystal size	0.33 x 0.18 x 0.11 mm ³	
Theta range for data collection	1.33 to 27.52°	
Index ranges	-13 ≤ h ≤ 5, -13 ≤ k ≤ 10,	
	-19 ≤ l ≤ 19	
Reflections collected	6552	
Independent reflections	6136 [R(int) = 0.0364]	
Completeness to theta = 27.48°	62.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6136 / 0 / 559	
Goodness-of-fit on F ²	1.019	
Final R indices [I > 2σ(I)]	R1 = 0.0816, wR2 = 0.2126	
R indices (all data)	R1 = 0.1134, wR2 = 0.2307	
Largest diff. peak and hole	2.993 and -1.094 e.Å ⁻³	

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [PPh₄][SO₃NFH]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	5508(1)	1891(1)	1566(1)	18(1)
P(2)	9581(1)	3176(1)	3418(1)	16(1)
S(1)	4745(1)	7171(1)	2424(1)	19(1)
S(2)	9273(2)	7842(2)	2576(1)	46(1)
F(1)	5062(3)	8211(3)	3572(2)	32(1)
F(2)	10421(4)	6800(3)	1487(2)	46(1)
O(1)	5447(4)	6299(3)	3038(2)	26(1)
O(2)	3271(3)	7529(3)	2489(2)	29(1)
O(3)	5186(4)	7139(3)	1540(2)	24(1)
O(4)	9791(5)	7976(4)	3475(2)	43(1)
O(5)	8204(4)	7407(3)	2581(2)	34(1)
O(6)	9085(4)	8715(3)	1918(2)	37(1)
N(1)	5234(4)	8155(4)	2635(3)	22(1)
N(2)	10657(5)	6925(5)	2393(3)	52(2)
C(1)	4716(5)	3216(5)	1512(3)	17(2)
C(2)	5464(6)	3877(6)	1334(3)	23(2)
C(3)	4848(6)	4911(7)	1306(4)	30(2)
C(4)	3485(6)	5288(6)	1471(4)	30(2)
C(5)	2731(6)	4636(6)	1659(4)	28(2)
C(6)	3332(6)	3613(6)	1673(3)	23(2)
C(7)	7060(5)	1663(5)	1001(3)	15(1)
C(8)	8342(5)	1163(5)	1409(3)	23(2)
C(9)	9491(5)	1000(5)	923(3)	25(2)
C(10)	9361(5)	1316(5)	33(3)	23(2)
C(11)	8091(5)	1805(5)	-376(3)	22(2)
C(12)	6937(5)	1982(5)	100(3)	20(2)
C(13)	5830(5)	1309(5)	2682(3)	21(2)
C(14)	6611(6)	295(6)	2885(3)	28(2)
C(15)	6824(6)	-164(6)	3746(4)	35(2)
C(16)	6256(7)	403(7)	4402(4)	41(2)
C(17)	5500(7)	1401(6)	4204(3)	32(2)

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C(18)	5289(6)	1862(5)	3352(3)	28(2)
C(19)	4397(5)	1402(5)	1016(3)	14(2)
C(20)	3671(5)	1955(5)	256(3)	21(2)
C(21)	2937(5)	1522(6)	-235(3)	22(2)
C(22)	2920(5)	567(6)	37(3)	21(2)
C(23)	3629(5)	8(5)	796(3)	22(2)
C(24)	4364(5)	437(6)	1284(3)	21(2)
C(25)	10664(5)	3675(5)	3989(3)	14(2)
C(26)	11308(5)	3136(5)	4776(3)	23(2)
C(27)	12049(5)	3550(6)	5279(4)	28(2)
C(28)	12175(5)	4464(6)	4984(3)	26(2)
C(29)	11551(5)	5005(5)	4198(4)	27(2)
C(30)	10799(5)	4600(5)	3700(3)	20(2)
C(31)	9204(5)	3841(5)	2320(3)	16(2)
C(32)	9647(5)	3301(5)	1614(3)	22(2)
C(33)	9359(6)	3819(6)	776(3)	32(2)
C(34)	8650(6)	4835(6)	637(3)	33(2)
C(35)	8203(5)	5370(5)	1330(3)	26(2)
C(36)	8474(5)	4858(5)	2175(3)	23(2)
C(37)	8028(5)	3328(5)	3975(3)	16(2)
C(38)	6765(5)	3903(5)	3596(3)	19(2)
C(39)	5618(5)	4047(5)	4084(3)	22(2)
C(40)	5739(5)	3621(5)	4947(3)	24(2)
C(41)	7000(5)	3026(5)	5332(3)	24(2)
C(42)	8158(5)	2873(5)	4850(3)	18(2)
C(43)	10452(5)	1859(5)	3413(3)	17(2)
C(44)	9750(6)	1165(6)	3509(3)	24(2)
C(45)	10425(6)	153(6)	3446(4)	32(2)
C(46)	11790(6)	-171(6)	3287(4)	33(2)
C(47)	12495(6)	516(6)	3210(3)	27(2)
C(48)	11844(5)	1526(6)	3267(3)	22(2)

Table S7. Bond lengths [Å] and angles [°] for [PPh₄][SO₃NFH].

P(1)-C(1)	1.770(7)	C(16)-C(17)	1.362(9)
P(1)-C(7)	1.791(5)	C(17)-C(18)	1.375(8)
P(1)-C(19)	1.792(5)	C(19)-C(24)	1.378(8)
P(1)-C(13)	1.794(5)	C(19)-C(20)	1.391(7)
P(2)-C(43)	1.783(7)	C(20)-C(21)	1.402(8)
P(2)-C(37)	1.795(5)	C(21)-C(22)	1.360(8)
P(2)-C(25)	1.797(5)	C(22)-C(23)	1.387(8)
P(2)-C(31)	1.804(5)	C(23)-C(24)	1.395(8)
S(1)-O(1)	1.433(4)	C(25)-C(30)	1.372(8)
S(1)-O(3)	1.447(3)	C(25)-C(26)	1.390(7)
S(1)-O(2)	1.457(4)	C(26)-C(27)	1.400(8)
S(1)-N(1)	1.694(5)	C(27)-C(28)	1.354(8)
S(2)-O(5)	1.432(4)	C(28)-C(29)	1.384(8)
S(2)-O(6)	1.448(4)	C(29)-C(30)	1.393(7)
S(2)-O(4)	1.551(4)	C(31)-C(36)	1.374(8)
S(2)-N(2)	1.648(6)	C(31)-C(32)	1.410(7)
F(1)-N(1)	1.473(5)	C(32)-C(33)	1.382(7)
F(2)-N(2)	1.470(6)	C(33)-C(34)	1.368(9)
C(1)-C(2)	1.396(8)	C(34)-C(35)	1.389(9)
C(1)-C(6)	1.399(8)	C(35)-C(36)	1.390(7)
C(2)-C(3)	1.383(9)	C(37)-C(38)	1.381(7)
C(3)-C(4)	1.379(9)	C(37)-C(42)	1.407(7)
C(4)-C(5)	1.392(9)	C(38)-C(39)	1.385(7)
C(5)-C(6)	1.370(9)	C(39)-C(40)	1.379(7)
C(7)-C(8)	1.394(7)	C(40)-C(41)	1.389(8)
C(7)-C(12)	1.401(6)	C(41)-C(42)	1.388(7)
C(8)-C(9)	1.384(7)	C(43)-C(44)	1.390(8)
C(9)-C(10)	1.384(7)	C(43)-C(48)	1.397(7)
C(10)-C(11)	1.382(7)	C(44)-C(45)	1.387(9)
C(11)-C(12)	1.379(7)	C(45)-C(46)	1.376(8)
C(13)-C(14)	1.388(8)	C(46)-C(47)	1.384(9)
C(13)-C(18)	1.393(8)	C(47)-C(48)	1.379(8)
C(14)-C(15)	1.386(7)		
C(15)-C(16)	1.392(9)		

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C(1)-P(1)-C(7)	108.5(3)	C(12)-C(7)-P(1)	116.7(4)
C(1)-P(1)-C(19)	108.2(3)	C(9)-C(8)-C(7)	119.7(5)
C(7)-P(1)-C(19)	108.5(2)	C(8)-C(9)-C(10)	120.0(5)
C(1)-P(1)-C(13)	109.9(3)	C(11)-C(10)-C(9)	120.5(5)
C(7)-P(1)-C(13)	111.1(2)	C(12)-C(11)-C(10)	120.2(5)
C(19)-P(1)-C(13)	110.6(3)	C(11)-C(12)-C(7)	119.6(5)
C(43)-P(2)-C(37)	109.1(3)	C(14)-C(13)-C(18)	119.3(5)
C(43)-P(2)-C(25)	108.0(3)	C(14)-C(13)-P(1)	120.1(4)
C(37)-P(2)-C(25)	109.6(2)	C(18)-C(13)-P(1)	120.6(5)
C(43)-P(2)-C(31)	110.8(3)	C(15)-C(14)-C(13)	120.1(6)
C(37)-P(2)-C(31)	109.8(2)	C(14)-C(15)-C(16)	119.4(7)
C(25)-P(2)-C(31)	109.6(3)	C(17)-C(16)-C(15)	120.5(6)
O(1)-S(1)-O(3)	115.3(2)	C(16)-C(17)-C(18)	120.4(6)
O(1)-S(1)-O(2)	114.4(2)	C(17)-C(18)-C(13)	120.3(7)
O(3)-S(1)-O(2)	114.1(2)	C(24)-C(19)-C(20)	119.3(5)
O(1)-S(1)-N(1)	108.5(2)	C(24)-C(19)-P(1)	120.6(4)
O(3)-S(1)-N(1)	98.0(2)	C(20)-C(19)-P(1)	119.7(5)
O(2)-S(1)-N(1)	104.3(2)	C(19)-C(20)-C(21)	119.8(6)
O(5)-S(2)-O(6)	114.6(3)	C(22)-C(21)-C(20)	120.1(5)
O(5)-S(2)-O(4)	116.6(2)	C(21)-C(22)-C(23)	120.9(5)
O(6)-S(2)-O(4)	113.3(3)	C(22)-C(23)-C(24)	119.1(6)
O(5)-S(2)-N(2)	104.8(3)	C(19)-C(24)-C(23)	120.8(5)
O(6)-S(2)-N(2)	109.4(3)	C(30)-C(25)-C(26)	119.3(5)
O(4)-S(2)-N(2)	95.7(3)	C(30)-C(25)-P(2)	121.9(4)
F(1)-N(1)-S(1)	106.4(3)	C(26)-C(25)-P(2)	118.7(5)
F(2)-N(2)-S(2)	103.1(3)	C(25)-C(26)-C(27)	120.2(6)
C(2)-C(1)-C(6)	119.0(7)	C(28)-C(27)-C(26)	119.8(5)
C(2)-C(1)-P(1)	120.8(5)	C(27)-C(28)-C(29)	120.7(5)
C(6)-C(1)-P(1)	120.2(5)	C(28)-C(29)-C(30)	119.7(6)
C(3)-C(2)-C(1)	120.7(6)	C(25)-C(30)-C(29)	120.4(5)
C(4)-C(3)-C(2)	119.5(6)	C(36)-C(31)-C(32)	120.4(5)
C(3)-C(4)-C(5)	120.4(7)	C(36)-C(31)-P(2)	120.3(4)
C(6)-C(5)-C(4)	120.3(6)	C(32)-C(31)-P(2)	119.2(5)
C(5)-C(6)-C(1)	120.1(6)	C(33)-C(32)-C(31)	118.8(6)
C(8)-C(7)-C(12)	120.0(4)	C(34)-C(33)-C(32)	120.5(6)
C(8)-C(7)-P(1)	123.3(4)	C(33)-C(34)-C(35)	121.0(5)

C(34)-C(35)-C(36)	119.2(6)
C(31)-C(36)-C(35)	120.1(5)
C(38)-C(37)-C(42)	120.5(4)
C(38)-C(37)-P(2)	122.9(4)
C(42)-C(37)-P(2)	116.5(4)
C(37)-C(38)-C(39)	119.8(5)
C(40)-C(39)-C(38)	120.1(5)
C(39)-C(40)-C(41)	120.7(5)
C(42)-C(41)-C(40)	119.8(5)
C(41)-C(42)-C(37)	119.0(5)
C(44)-C(43)-C(48)	119.5(6)
C(44)-C(43)-P(2)	120.8(5)
C(48)-C(43)-P(2)	119.6(5)
C(45)-C(44)-C(43)	120.1(6)
C(46)-C(45)-C(44)	120.4(7)
C(45)-C(46)-C(47)	119.5(7)
C(48)-C(47)-C(46)	121.1(6)
C(47)-C(48)-C(43)	119.4(6)

Table S8. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{PPh}_4][\text{SO}_3\text{NFH}]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	21(1)	15(2)	18(1)	0(1)	1(1)	-8(1)
P(2)	17(1)	13(2)	16(1)	-1(1)	1(1)	-4(1)
S(1)	21(1)	19(2)	17(1)	-1(1)	1(1)	-6(1)
S(2)	25(1)	49(2)	56(1)	13(1)	-4(1)	-9(1)
F(1)	37(2)	28(3)	32(2)	-13(2)	4(1)	-10(2)
F(2)	67(3)	35(4)	36(2)	-11(2)	-3(2)	-14(2)
O(1)	37(2)	7(4)	27(2)	6(2)	-1(2)	-2(2)
O(2)	23(2)	36(4)	29(2)	-5(2)	4(2)	-11(2)
O(3)	29(2)	21(4)	21(2)	-2(2)	6(2)	-6(2)
O(4)	78(3)	27(4)	17(2)	4(2)	2(2)	-9(3)
O(5)	21(2)	45(4)	37(2)	-8(2)	1(2)	-14(2)
O(6)	44(2)	14(4)	35(2)	21(2)	-1(2)	3(2)
N(1)	36(3)	13(5)	18(2)	7(2)	2(2)	-13(3)
N(2)	33(3)	57(6)	52(3)	17(3)	-5(2)	-4(3)
C(1)	30(3)	0(6)	20(2)	0(2)	0(2)	-4(3)
C(2)	32(3)	8(7)	29(3)	1(3)	-2(2)	-7(4)
C(3)	37(3)	14(8)	41(3)	4(3)	-5(3)	-14(4)
C(4)	44(4)	0(6)	42(3)	-3(3)	-3(3)	0(3)
C(5)	34(3)	15(7)	34(3)	-3(3)	4(2)	-5(4)
C(6)	30(3)	9(7)	30(3)	0(3)	8(2)	-9(3)
C(7)	21(2)	3(5)	23(2)	-2(2)	1(2)	-7(3)
C(8)	28(3)	19(5)	22(3)	-2(3)	-3(2)	-10(3)
C(9)	21(3)	16(6)	34(3)	-1(3)	-3(2)	-2(3)
C(10)	22(3)	17(5)	29(3)	-5(3)	8(2)	-5(3)
C(11)	30(3)	15(5)	22(3)	-2(3)	4(2)	-10(3)
C(12)	23(3)	11(5)	24(3)	5(3)	0(2)	-8(3)
C(13)	23(3)	14(6)	23(3)	2(3)	-2(2)	-7(3)
C(14)	30(3)	35(7)	23(3)	-4(3)	0(2)	-18(4)
C(15)	32(3)	29(6)	39(3)	18(3)	-8(3)	-13(3)
C(16)	54(4)	58(8)	20(3)	10(4)	-4(3)	-36(5)
C(17)	56(4)	26(7)	23(3)	-7(3)	5(3)	-25(4)
C(18)	35(3)	25(6)	26(3)	-1(3)	1(2)	-16(3)

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C(19)	18(3)	4(6)	19(2)	3(3)	1(2)	-5(3)
C(20)	23(3)	9(5)	31(3)	3(3)	-2(2)	-8(3)
C(21)	24(3)	10(7)	31(3)	-1(3)	-4(2)	-4(3)
C(22)	18(3)	11(6)	36(3)	-10(3)	0(2)	-6(3)
C(23)	29(3)	10(5)	29(3)	-4(3)	5(2)	-8(3)
C(24)	22(3)	16(7)	23(3)	-6(3)	3(2)	-2(3)
C(25)	18(2)	1(6)	19(2)	3(2)	2(2)	-2(3)
C(26)	27(3)	18(5)	24(3)	5(3)	-2(2)	-9(3)
C(27)	26(3)	27(7)	29(3)	0(3)	-2(2)	-8(3)
C(28)	20(3)	25(7)	32(3)	-15(3)	0(2)	-4(3)
C(29)	32(3)	11(6)	41(3)	-5(3)	-2(2)	-10(3)
C(30)	24(3)	11(6)	23(3)	-1(3)	-1(2)	-2(3)
C(31)	19(3)	10(6)	17(2)	1(2)	-1(2)	-2(3)
C(32)	26(3)	17(5)	21(3)	-2(3)	2(2)	-6(3)
C(33)	39(3)	34(7)	21(3)	0(3)	3(2)	-9(4)
C(34)	35(3)	41(7)	19(3)	13(3)	-6(2)	-13(4)
C(35)	26(3)	14(6)	31(3)	12(3)	-3(2)	-2(3)
C(36)	23(3)	21(7)	26(3)	-1(3)	2(2)	-6(3)
C(37)	23(3)	8(5)	20(2)	-6(2)	5(2)	-7(3)
C(38)	21(3)	11(5)	24(3)	-3(3)	0(2)	-5(3)
C(39)	18(3)	13(5)	33(3)	-3(3)	1(2)	-2(3)
C(40)	25(3)	19(6)	32(3)	-8(3)	11(2)	-10(3)
C(41)	30(3)	22(6)	21(2)	-2(3)	7(2)	-9(3)
C(42)	25(3)	10(5)	20(2)	-2(2)	2(2)	-5(3)
C(43)	27(3)	5(5)	16(2)	-3(2)	2(2)	0(3)
C(44)	28(3)	14(7)	27(3)	-2(3)	-3(2)	-5(4)
C(45)	41(4)	15(7)	39(3)	-4(3)	-8(3)	-10(4)
C(46)	44(4)	12(6)	34(3)	-7(3)	-7(3)	5(4)
C(47)	30(3)	13(7)	26(3)	0(3)	6(2)	7(4)
C(48)	28(3)	7(6)	25(3)	1(3)	5(2)	0(3)
