Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

for

Phenol-selective mass spectrometric analysis of petroleum fractions

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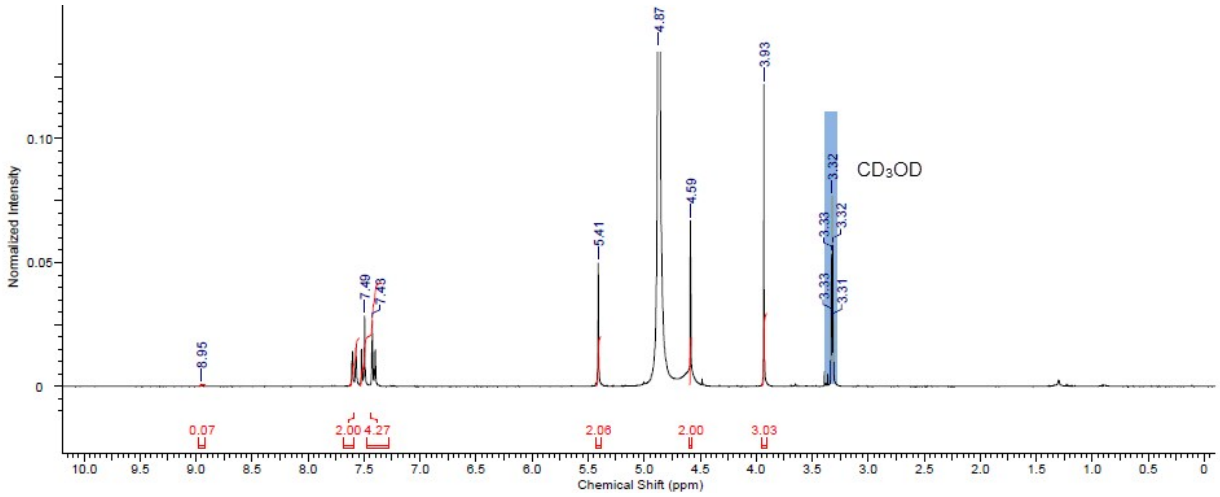


Figure S1. ^{1}H NMR (300 MHz, CD_3OD) spectra of 3-(4-(bromomethyl)benzyl)-1-methylimidazolium hexafluorophosphate, CD_3OD solvent. 298 K.

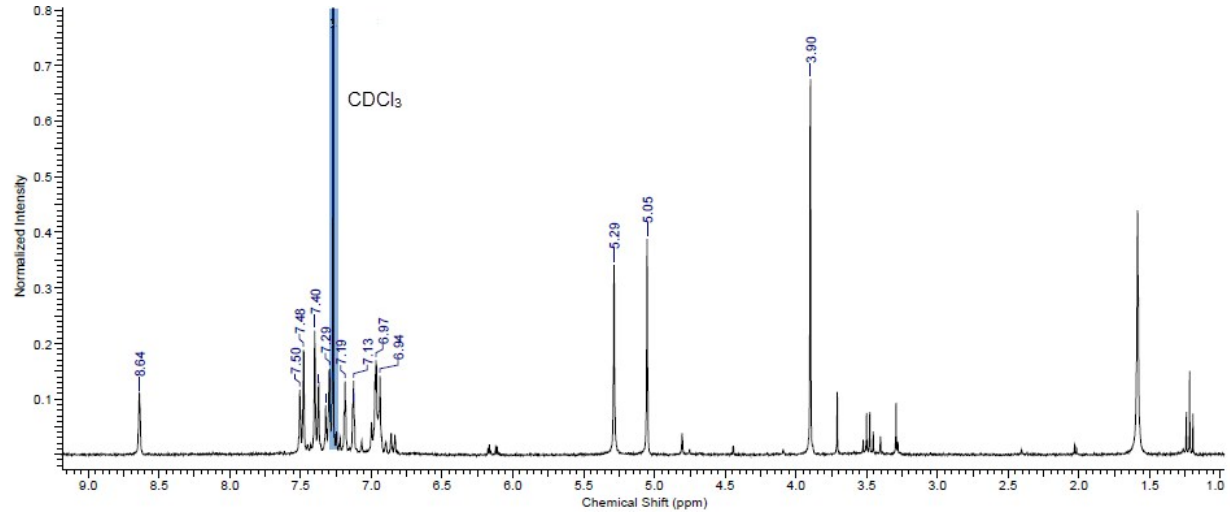


Figure S2. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of 1-methyl-3-(4-(phenoxymethyl)benzyl)-1H-imidazol -3-ium hexafluorophosphate(V), $CDCl_3$ solvent. 298 K.

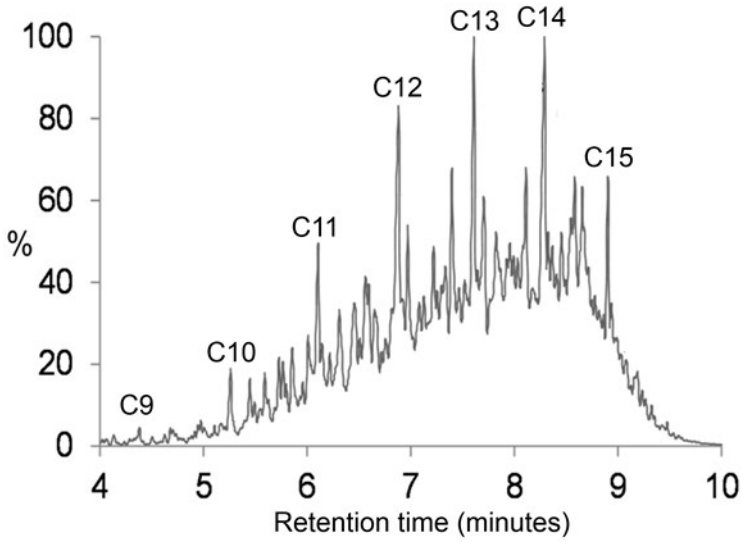


Figure S3. Cold EI GC/MS chromatogram of untreated jet fuel sample A. Major peaks are labelled with carbon number and correspond to the alkane (e.g. C13 = $C_{13}H_{28}$). Peak assignments were made using library matching. Phenols could not be identified in any of the sample studied.

GC/MS separates components of a mixture prior to analysis, and in the case of the jet fuel, the principal components are saturated hydrocarbons C_nH_{2n+2} (n = 9-16, Figure S 3). Nonane boils at 151°C and pentadecane at 271°C, so we may expect other hydrocarbons boiling in that range to also be included in the distillation fraction.[i] Predictably, the mixture contains numerous other hydrocarbon products beyond isomers of the hydrocarbons themselves - substituted benzenes and naphthalenes. For example, trimethylbenzenes have boiling points around 170°C, and naphthalene boils at 218°C. At the highest elution times, we observe alkylated naphthalenes. If we consider the phenols likely to appear in the boiling point range 150-270°C, we would expect to see phenol itself (b.p. 182°C) and variously alkylated versions, e.g. 2,5-dimethylphenol (b.p. 212°C). Naphthol sublimes at 288°C, and its alkylated derivatives have boiling points higher than this.

Table S1. The boiling points of alkylated phenols.

R group	Number of R group	Mol.Wt. of alkylated phenols	Boiling point (°C)
CH_3	0	94.1	182
CH_3	1	108.3	191~202
CH_3	2	122.2	204~218, 277
CH_3	3	136.1	213~249
CH_3	4	150.2	224~251
CH_3	5	164.2	127, 233~262
CH_3	6	178.3	138, 247~262
CH_3	7	192.3	NA

Table S2. The boiling points of thiols.

R group	Number of R group	Mol.Wt. of alkylated naphthols	Boiling point (°C)
CH_3	0	144.2	286
CH_3	1	158.1	304
CH_3	2	172.1	315
CH_3	3	186.1	335
CH_3	4	200.2	341~343
CH_3	5	214.1	357

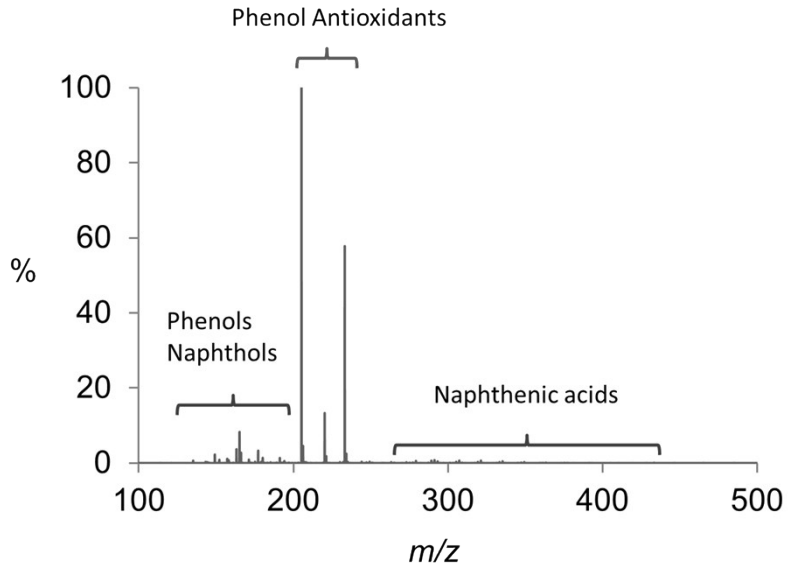


Figure S4. Negative ion mode ESI-MS of sample B after reaction with NaOH, Solvent CH_3CN/CH_2Cl_2 (v/v=1:3).

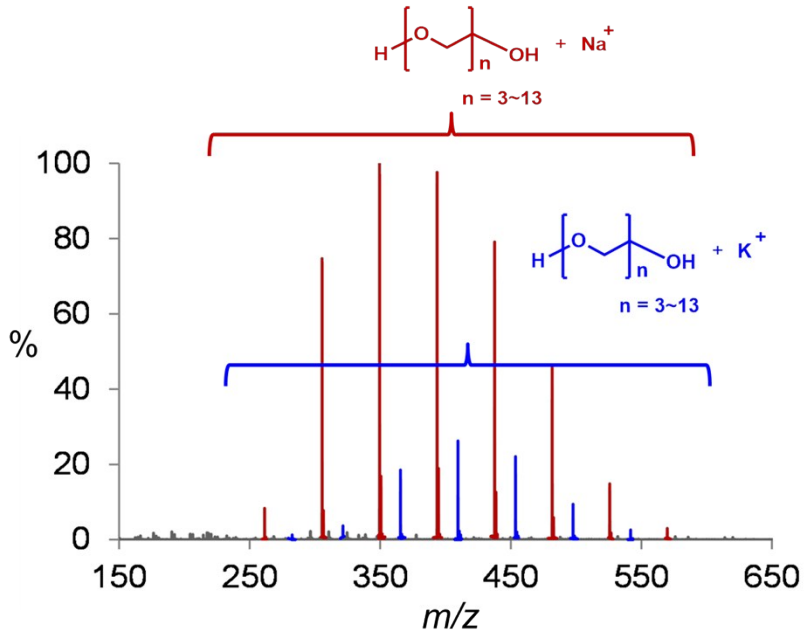


Figure S5. Positive ion mode ESI-MS of sample X2 after reaction with NaOH. Solvent CH_3CN/CH_2Cl_2 (v/v=1:3). By far the most prominent ions were based on polyethylene glycols.

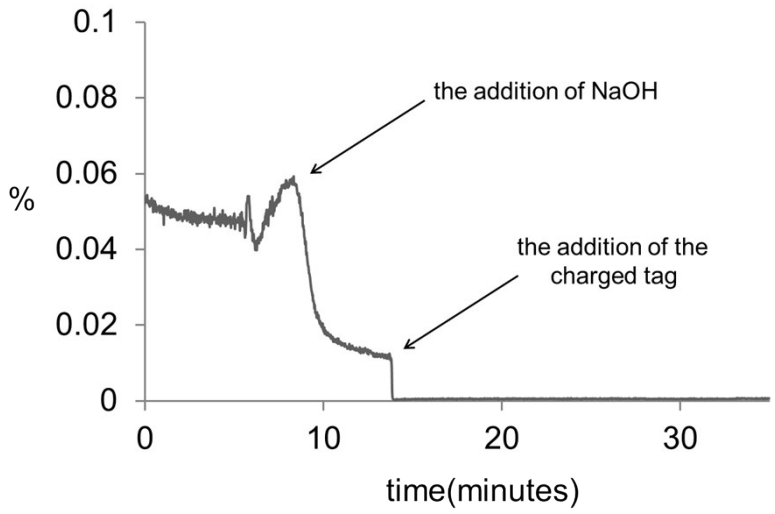
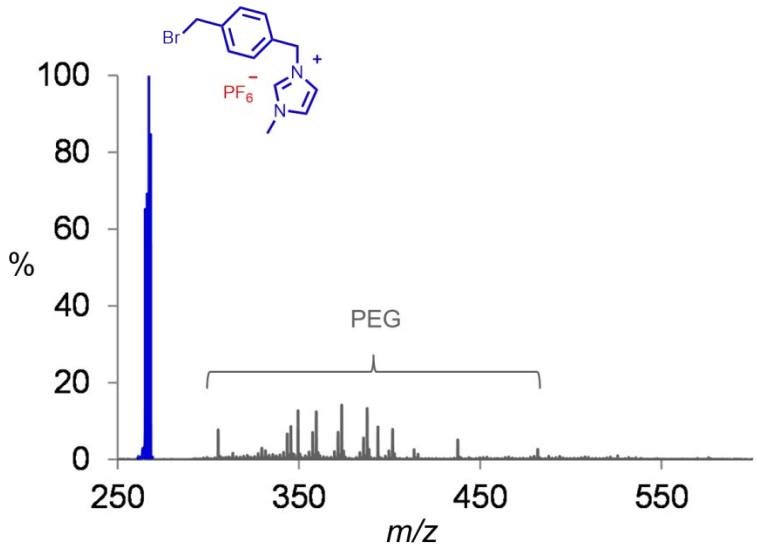


Figure S6. K^+ of the charged tag, the addition of charged tag suppresses the appearance of PEG.



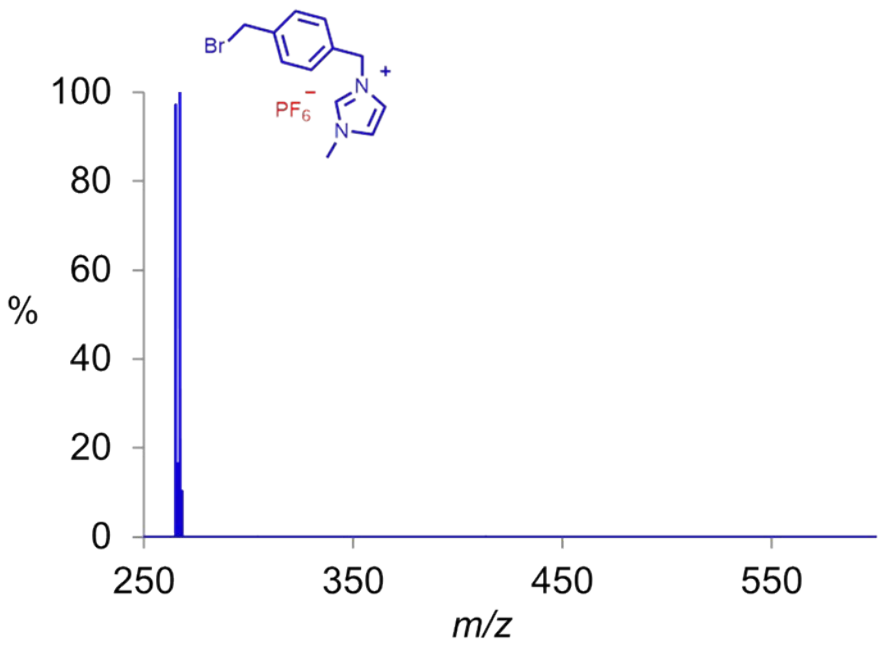


Figure S7. The spectrum of the first second of addition of charged tag further illustrates the high surface activity of the charged tag. Sample B reacted with charged tag under the base condition, solvent CH_3CN/CH_2Cl_2 (v/v=1:3).

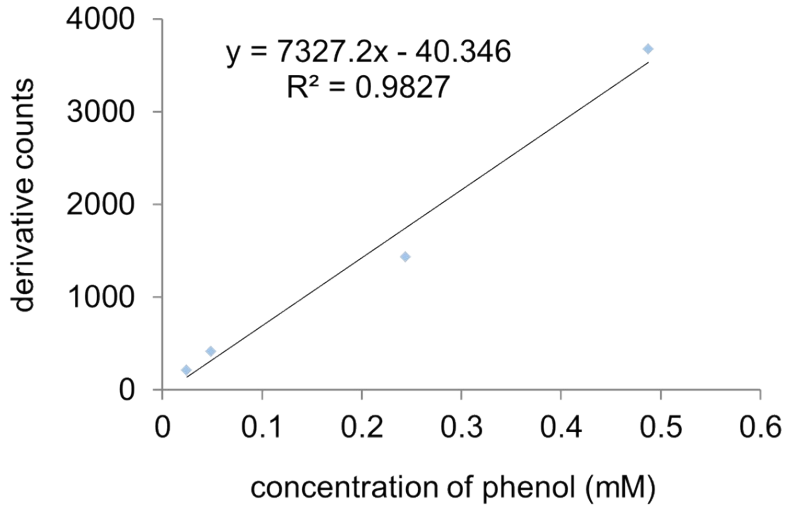


Figure S8. Response of derivative following reaction with 0.488 mM charged tag.

The average of baseline noise was determined with a method blank sample including solvent and 0.488 mM of charged tag. The eight samples analyzed in this manuscript did

not exhibit significant background noise at the region of interest (*m/z* 270 ~*m/z* 650). The response of derivative compound was found to be linear to micromolar quantities of charged tag. The derivatization process is limited by reactivity and concentration of target analytes in addition to variation in the sample matrix; therefore, the method detection limit defined here is an approximation only and will vary between samples and matrices. The general method limit was established based on a reaction with 0.488 mM of charged tag and phenol (see Equation 1). The response of the lowest identifiable derivative was then used to establish the limit detection (3 times the signal-to-noise ration) and quantitation (10 times the signal-to-noise ratio) for the jet fuel samples. The limit of detection for phenol product was examined and found to be 18 counts (8.0 μM) with a limit of quantitation of 60 counts (26.7 μM).

Table S3. The orbitrap result of series 1.

N	Experimental m/z	Calculated m/z	Composition	Accuracy (ppm)
2	307.18045	307.18104	$C_{20}H_{23}N_2O$	-1.920691459
3	321.19610	321.19669	$C_{21}H_{25}N_2O$	-1.836880698
4	335.21160	335.21234	$C_{22}H_{27}N_2O$	-2.207555963
5	349.22735	349.22799	$C_{23}H_{29}N_2O$	-1.832613703
6	363.24297	363.24364	$C_{24}H_{31}N_2O$	-1.844492033
7	377.25875	377.25929	$C_{25}H_{33}N_2O$	-1.431376282
8	391.27431	391.27494	$C_{26}H_{35}N_2O$	-1.610121006
9	405.29011	405.29059	$C_{27}H_{37}N_2O$	-1.184335417

Table S4. The orbitrap result of series 2.

N	Experimental m/z	Calculated m/z	Composition	Accuracy (ppm)
9	345.23592	345.23645	$C_{21}H_{33}N_2S$	-1.53517973
10	359.25158	359.25210	$C_{22}H_{35}N_2S$	-1.447451525
11	373.26729	373.26775	$C_{23}H_{37}N_2S$	-1.232359345
12	387.28297	387.28340	$C_{24}H_{39}N_2S$	-1.11029804
13	401.29868	401.29905	$C_{25}H_{41}N_2S$	-0.922005671
14	415.31431	415.31470	$C_{26}H_{43}N_2S$	-0.939046944

Table S5. The orbitrap result of series 3.

N	Experimental m/z	Calculated m/z	Composition	Accuracy (ppm)
6	329.20455	329.20514	$C_{20}H_{29}N_2S$	-1.79219559
7	343.22030	343.22080	$C_{21}H_{31}N_2S$	-1.456788167
8	357.23594	357.23645	$C_{22}H_{33}N_2S$	-1.427625876
9	371.25174	371.25210	$C_{23}H_{35}N_2S$	-0.969691485
10	385.26723	385.26775	$C_{24}H_{37}N_2S$	-1.349710688
11	399.28310	399.28340	$C_{25}H_{39}N_2S$	-0.751346036

Table S6. The orbitrap result of series 4.

N	Experimental m/z	Calculated m/z	Composition	Accuracy (ppm)
10	451.27955	451.27831	$C_{28}H_{39}N_2OS$	2.747750053
11	465.29411	465.29396	$C_{29}H_{41}N_2OS$	0.322376847
12	479.30943	479.30961	$C_{30}H_{43}N_2OS$	-0.375540144
13	493.32497	493.32526	$C_{31}H_{45}N_2OS$	-0.587847458
14	507.34077	507.34091	$C_{32}H_{47}N_2OS$	-0.275948573
15	521.35629	521.35656	$C_{33}H_{49}N_2OS$	-0.51787974
16	535.37194	535.37221	$C_{34}H_{51}N_2OS$	-0.50432203
17	549.38777	549.38786	$C_{35}H_{53}N_2OS$	-0.163818691

Table S7. The orbitrap result of series 5.

N	Experimental m/z	Calculated m/z	Composition	Accuracy (ppm)
9	463.27800	463.27831	$C_{29}H_{39}N_2OS$	-0.669144213
10	477.29366	477.29396	$C_{30}H_{41}N_2OS$	-0.628543466
11	491.30917	491.30961	$C_{31}H_{43}N_2OS$	-0.895565629
12	505.32479	505.32526	$C_{32}H_{45}N_2OS$	-0.930094015
13	519.34062	519.34091	$C_{33}H_{47}N_2OS$	-0.558400069
14	533.35642	533.35656	$C_{34}H_{49}N_2OS$	-0.262488569
15	547.37206	547.37221	$C_{35}H_{51}N_2OS$	-0.274036565

Table S3. Crystal data and structure refinement for $[C_{12}N_2H_{14}Br][PF_6]$.

Identification code	uvic1410
Empirical formula	$C_{12}H_{14}BrF_6N_2P$
Formula weight	411.13
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	*a* = 8.3093(6) Å α = 90°
	b = 10.6750(8) Å β = 90°
	c = 16.8309(13) Å γ = 90°
Volume	1492.93(19) $Å^3$
Z	4
Density (calculated)	1.829 $g.cm^{-3}$
Absorption coefficient (μ)	2.922 mm^{-1}
F(000)	816
Crystal color, habit	colourless, tablet
Crystal size	0.200 × 0.090 × 0.060 mm^3
θ range for data collection	2.259 to 28.493°
Index ranges	$-10 \le h \le 11$, $-14 \le k \le 14$, $-22 \le l \le 21$
Reflections collected	26499
Independent reflections	3765 [R_{int} = 0.0348]
Completeness to θ = 25.242°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.9363 and 0.7187
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3765 / 0 / 200
Goodness-of-fit on F^2	1.036
Final R indices [I>2σ(I)]	R_1 = 0.0221, wR_2 = 0.0505
R indices (all data)	R_1 = 0.0255, wR_2 = 0.0516
Absolute structure parameter	0.008(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.326 and -0.208 $e^-.Å^{-3}$

Table S5. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $[C_{12}N_2H_{14}Br][PF_6]$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br(1)	-0.18657(3)	0.60389(3)	0.43860(2)	0.026(1)
N(1)	0.5857(3)	0.2976(2)	0.57922(12)	0.017(1)
N(2)	0.6362(3)	0.2148(2)	0.69274(13)	0.020(1)
C(1)	0.5663(3)	0.1959(2)	0.62354(16)	0.019(1)
C(2)	0.6706(3)	0.3844(2)	0.62240(16)	0.024(1)
C(3)	0.7020(4)	0.3319(3)	0.69358(16)	0.026(1)
C(4)	0.5201(3)	0.3184(3)	0.49966(15)	0.020(1)
C(5)	0.3869(3)	0.4139(2)	0.49992(14)	0.015(1)
C(6)	0.3694(3)	0.4941(2)	0.43569(15)	0.017(1)
C(7)	0.2439(3)	0.5791(2)	0.43408(15)	0.018(1)
C(8)	0.1345(3)	0.5859(2)	0.49608(14)	0.015(1)
C(9)	0.1523(3)	0.5057(2)	0.56048(15)	0.019(1)
C(10)	0.2777(3)	0.4208(2)	0.56229(15)	0.018(1)
C(11)	-0.0002(3)	0.6777(3)	0.49382(16)	0.022(1)
C(12)	0.6420(4)	0.1238(3)	0.75815(18)	0.034(1)
P(1)	0.13988(8)	0.19007(6)	0.75326(4)	0.018(1)
F(1)	0.0167(2)	0.26263(17)	0.80875(10)	0.031(1)
F(2)	0.2477(2)	0.31241(15)	0.74599(10)	0.036(1)
F(3)	0.0354(2)	0.06624(16)	0.76073(11)	0.037(1)
F(4)	0.2403(2)	0.14986(15)	0.83029(10)	0.031(1)
F(5)	0.0405(2)	0.23068(18)	0.67689(9)	0.036(1)
F(6)	0.2634(2)	0.11642(19)	0.69785(11)	0.041(1)
H(1A)	0.5113	0.1219	0.6079	0.023
H(2A)	0.7014	0.4658	0.6054	0.029
H(3A)	0.7591	0.3694	0.7363	0.031
H(4A)	0.4784	0.2382	0.4785	0.024
H(4B)	0.6073	0.3473	0.4640	0.024
H(6A)	0.4436	0.4906	0.3928	0.020
H(7A)	0.2325	0.6336	0.3898	0.022
H(9A)	0.0780	0.5093	0.6034	0.022
H(10A)	0.2894	0.3666	0.6067	0.021
H(11A)	0.0348	0.7545	0.4658	0.026
H(11B)	-0.0310	0.7011	0.5487	0.026
H(12A)	0.5720	0.0526	0.7457	0.050
H(12B)	0.6052	0.1639	0.8073	0.050
H(12C)	0.7528	0.0943	0.7651	0.050

Table S6. Anisotropic displacement parameters (Å^2) for $[C_{12}N_2H_{14}Br][PF_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	0.0193(1)	0.0261(1)	0.0314(1)	-0.0063(1)	-0.0067(1)	0.0026(1)
N(1)	0.0180(11)	0.0162(10)	0.0171(11)	-0.0014(8)	-0.0031(8)	0.0019(9)
N(2)	0.0183(11)	0.0206(11)	0.0205(10)	0.0032(9)	-0.0020(9)	0.0033(9)
C(1)	0.0171(13)	0.0155(12)	0.0255(13)	-0.0028(10)	0.0001(10)	0.0033(10)
C(2)	0.0241(13)	0.0166(12)	0.0316(13)	-0.0006(10)	-0.0077(11)	-0.0044(13)
C(3)	0.0236(15)	0.0269(14)	0.0276(14)	-0.0037(11)	-0.0091(12)	-0.0013(13)
C(4)	0.0223(13)	0.0244(14)	0.0143(11)	-0.0040(11)	-0.0014(10)	0.0058(11)
C(5)	0.0156(11)	0.0160(12)	0.0136(10)	-0.0037(9)	-0.0014(9)	-0.0012(10)
C(6)	0.0162(11)	0.0227(12)	0.0119(10)	0.0000(10)	0.0038(10)	-0.0036(9)
C(7)	0.0210(12)	0.0178(12)	0.0154(11)	0.0016(10)	-0.0025(10)	-0.0037(9)
C(8)	0.0167(11)	0.0137(12)	0.0155(11)	-0.0041(9)	-0.0044(9)	0.0002(9)
C(9)	0.0181(13)	0.0254(12)	0.0120(10)	-0.0031(10)	0.0033(10)	-0.0022(10)
C(10)	0.0202(13)	0.0193(12)	0.0132(10)	0.0017(10)	0.0010(10)	-0.0007(9)
C(11)	0.0197(14)	0.0214(13)	0.0235(13)	-0.0073(11)	-0.0063(11)	0.0010(11)
C(12)	0.0303(16)	0.0385(18)	0.0317(15)	0.0183(14)	-0.0021(13)	0.0044(13)
P(1)	0.0210(3)	0.0191(3)	0.0131(3)	-0.0030(3)	0.0029(2)	-0.0017(3)
F(1)	0.0317(10)	0.0412(10)	0.0188(7)	-0.0074(7)	0.0011(7)	0.0159(8)
F(2)	0.0574(12)	0.0307(9)	0.0205(8)	-0.0014(7)	0.0013(8)	-0.0229(8)
F(3)	0.0431(11)	0.0314(10)	0.0374(10)	-0.0050(8)	0.0087(9)	-0.0192(8)
F(4)	0.0372(10)	0.0268(8)	0.0292(9)	0.0021(7)	-0.0098(7)	0.0107(8)
F(5)	0.0466(11)	0.0478(11)	0.0153(8)	-0.0018(8)	-0.0090(8)	-0.0008(10)
F(6)	0.0303(9)	0.0512(12)	0.0413(10)	-0.0250(9)	0.0140(8)	-0.0003(9)

Table S7. Bond lengths [Å] for $[C_{12}N_2H_{14}Br][PF_6]$.

atom-atom	distance	atom-atom	distance
Br(1)-C(11)	1.971(3)	N(1)-C(1)	1.327(3)
N(1)-C(2)	1.373(3)	N(1)-C(4)	1.462(3)
N(2)-C(1)	1.317(3)	N(2)-C(3)	1.364(4)
N(2)-C(12)	1.469(3)	C(2)-C(3)	1.348(4)
C(4)-C(5)	1.505(4)	C(5)-C(6)	1.387(3)
C(5)-C(10)	1.389(3)	C(6)-C(7)	1.382(4)
C(7)-C(8)	1.386(4)	C(8)-C(9)	1.389(3)
C(8)-C(11)	1.488(3)	C(9)-C(10)	1.382(3)
P(1)-F(3)	1.5863(18)	P(1)-F(1)	1.5873(17)
P(1)-F(5)	1.5882(18)	P(1)-F(2)	1.5887(17)
P(1)-F(6)	1.5940(18)	P(1)-F(4)	1.6004(18)
C(1)-H(1A)	0.9500	C(2)-H(2A)	0.9500
C(3)-H(3A)	0.9500	C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900	C(6)-H(6A)	0.9500
C(7)-H(7A)	0.9500	C(9)-H(9A)	0.9500
C(10)-H(10A)	0.9500	C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900	C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800	C(12)-H(12C)	0.9800

Symmetry transformations used to generate equivalent atoms:

Table S8. Bond angles [°] for $[C_{12}N_2H_{14}Br][PF_6]$.

atom-atom-atom	angle	atom-atom-atom	angle
C(1)-N(1)-C(2)	108.5(2)	C(1)-N(1)-C(4)	126.4(2)
C(2)-N(1)-C(4)	125.0(2)	C(1)-N(2)-C(3)	109.0(2)
C(1)-N(2)-C(12)	125.2(2)	C(3)-N(2)-C(12)	125.8(2)
N(2)-C(1)-N(1)	108.6(2)	C(3)-C(2)-N(1)	106.8(2)
C(2)-C(3)-N(2)	107.1(2)	N(1)-C(4)-C(5)	112.0(2)
C(6)-C(5)-C(10)	119.2(2)	C(6)-C(5)-C(4)	119.5(2)
C(10)-C(5)-C(4)	121.2(2)	C(7)-C(6)-C(5)	120.0(2)
C(6)-C(7)-C(8)	121.0(2)	C(7)-C(8)-C(9)	119.0(2)
C(7)-C(8)-C(11)	120.6(2)	C(9)-C(8)-C(11)	120.4(2)
C(10)-C(9)-C(8)	120.1(2)	C(9)-C(10)-C(5)	120.7(2)
C(8)-C(11)-Br(1)	109.88(17)	F(3)-P(1)-F(1)	90.42(10)
F(3)-P(1)-F(5)	90.40(11)	F(1)-P(1)-F(5)	90.45(10)
F(3)-P(1)-F(2)	178.82(11)	F(1)-P(1)-F(2)	90.45(10)
F(5)-P(1)-F(2)	90.38(10)	F(3)-P(1)-F(6)	89.28(10)
F(1)-P(1)-F(6)	179.64(12)	F(5)-P(1)-F(6)	89.76(11)
F(2)-P(1)-F(6)	89.84(10)	F(3)-P(1)-F(4)	89.87(10)
F(1)-P(1)-F(4)	89.45(9)	F(5)-P(1)-F(4)	179.71(11)
F(2)-P(1)-F(4)	89.35(10)	F(6)-P(1)-F(4)	90.35(10)
N(2)-C(1)-H(1A)	125.7	N(1)-C(1)-H(1A)	125.7
C(3)-C(2)-H(2A)	126.6	N(1)-C(2)-H(2A)	126.6
C(2)-C(3)-H(3A)	126.4	N(2)-C(3)-H(3A)	126.4
N(1)-C(4)-H(4A)	109.2	C(5)-C(4)-H(4A)	109.2
N(1)-C(4)-H(4B)	109.2	C(5)-C(4)-H(4B)	109.2
H(4A)-C(4)-H(4B)	107.9	C(7)-C(6)-H(6A)	120.0
C(5)-C(6)-H(6A)	120.0	C(6)-C(7)-H(7A)	119.5
C(8)-C(7)-H(7A)	119.5	C(10)-C(9)-H(9A)	120.0
C(8)-C(9)-H(9A)	120.0	C(9)-C(10)-H(10A)	119.6
C(5)-C(10)-H(10A)	119.6	C(8)-C(11)-H(11A)	109.7
Br(1)-C(11)-H(11A)	109.7	C(8)-C(11)-H(11B)	109.7
Br(1)-C(11)-H(11B)	109.7	H(11A)-C(11)-H(11B)	108.2
N(2)-C(12)-H(12A)	109.5	N(2)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5	N(2)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5	H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S9. Torsion angles [°] for $[C_{12}N_2H_{14}Br][PF_6]$.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(3)-N(2)-C(1)-N(1)	0.3(3)	C(12)-N(2)-C(1)-N(1)	-179.6(2)
C(2)-N(1)-C(1)-N(2)	-0.3(3)	C(4)-N(1)-C(1)-N(2)	-176.8(2)
C(1)-N(1)-C(2)-C(3)	0.2(3)	C(4)-N(1)-C(2)-C(3)	176.8(3)
N(1)-C(2)-C(3)-N(2)	0.0(3)	C(1)-N(2)-C(3)-C(2)	-0.2(3)
C(12)-N(2)-C(3)-C(2)	179.7(3)	C(1)-N(1)-C(4)-C(5)	108.9(3)
C(2)-N(1)-C(4)-C(5)	-67.1(3)	N(1)-C(4)-C(5)-C(6)	145.1(2)
N(1)-C(4)-C(5)-C(10)	-36.9(3)	C(10)-C(5)-C(6)-C(7)	-0.4(4)
C(4)-C(5)-C(6)-C(7)	177.7(2)	C(5)-C(6)-C(7)-C(8)	0.2(4)
C(6)-C(7)-C(8)-C(9)	0.0(4)	C(6)-C(7)-C(8)-C(11)	-180.0(2)
C(7)-C(8)-C(9)-C(10)	0.1(4)	C(11)-C(8)-C(9)-C(10)	-179.9(2)
C(8)-C(9)-C(10)-C(5)	-0.3(4)	C(6)-C(5)-C(10)-C(9)	0.5(4)
C(4)-C(5)-C(10)-C(9)	-177.5(2)	C(7)-C(8)-C(11)-Br(1)	87.6(3)
C(9)-C(8)-C(11)-Br(1)	-92.3(2)		

Symmetry transformations used to generate equivalent atoms:

Table S10. Crystal data and structure refinement for $[C_{18}N_2H_{18}OH][PF_6]$.

Identification code	uvic1520
Empirical formula	$C_{18}H_{19}F_6N_2OP$
Formula weight	424.32
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	*a* = 10.1719(8) Å α = 90°
	b = 17.7909(14) Å β = 110.562(3)°
	c = 11.0986(9) Å γ = 90°
Volume	1880.5(3) Å^3
Z	4
Density (calculated)	1.499 g.cm^{-3}
Absorption coefficient (μ)	0.215 mm^{-1}
F(000)	872
Crystal color, habit	colorless, tablet
Crystal size	0.271 × 0.109 × 0.050 mm^3
θ range for data collection	2.270 to 26.619°
Index ranges	-11 ≤ h ≤ 12, -22 ≤ k ≤ 22, -13 ≤ l ≤ 13
Reflections collected	26441
Independent reflections	3932 [R_{int} = 0.0563]
Completeness to θ = 25.242°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	1.0000 and 0.9382
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3932 / 0 / 254
Goodness-of-fit on F^2	1.038
Final R indices [I>2σ(I)]	R_1 = 0.0555, wR_2 = 0.1341
R indices (all data)	R_1 = 0.0882, wR_2 = 0.1521
Extinction coefficient	n/a
Largest diff. peak and hole	1.087 and -0.547 e$^-$.Å^{-3}

Table S11. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $[C_{18}N_2H_{18}OH][PF6]$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	0.0664(2)	0.35548(12)	0.03279(18)	0.026(1)
N(1)	0.6917(2)	0.56933(13)	0.5615(2)	0.023(1)
N(2)	0.6002(2)	0.57743(13)	0.3559(2)	0.023(1)
C(1)	0.7151(3)	0.55871(16)	0.4531(3)	0.023(1)
C(2)	0.5578(3)	0.59606(17)	0.5335(3)	0.028(1)
C(3)	0.5001(3)	0.60136(17)	0.4049(3)	0.027(1)
C(4)	0.7933(3)	0.55660(19)	0.6904(3)	0.032(1)
C(5)	0.5840(3)	0.57426(18)	0.2188(3)	0.029(1)
C(6)	0.4672(3)	0.52195(17)	0.1447(3)	0.024(1)
C(7)	0.3356(3)	0.55130(17)	0.0743(3)	0.026(1)
C(8)	0.2277(3)	0.50373(17)	0.0060(3)	0.025(1)
C(9)	0.2484(3)	0.42677(17)	0.0076(3)	0.023(1)
C(10)	0.3797(3)	0.39793(17)	0.0770(3)	0.025(1)
C(11)	0.4884(3)	0.44542(17)	0.1444(3)	0.025(1)
C(12)	0.1283(3)	0.37558(18)	-0.0606(3)	0.027(1)
C(13)	-0.0560(3)	0.31492(16)	-0.0090(3)	0.023(1)
C(14)	-0.1132(3)	0.29853(17)	0.0841(3)	0.026(1)
C(15)	-0.2394(3)	0.26037(17)	0.0506(3)	0.027(1)
C(16)	-0.3094(3)	0.23935(17)	-0.0764(3)	0.029(1)
C(17)	-0.2503(3)	0.25554(16)	-0.1676(3)	0.027(1)
C(18)	-0.1234(3)	0.29322(16)	-0.1358(3)	0.025(1)
P(1)	0.85285(9)	0.34884(5)	0.49272(8)	0.031(1)
F(1)	0.8499(2)	0.28843(14)	0.38719(19)	0.053(1)
F(2)	0.7555(2)	0.29755(13)	0.5425(2)	0.055(1)
F(3)	0.8574(3)	0.40953(12)	0.6010(2)	0.058(1)
F(4)	0.7219(2)	0.39176(15)	0.3977(2)	0.063(1)
F(5)	0.9858(2)	0.30982(15)	0.5921(2)	0.062(1)
F(6)	0.9532(3)	0.40038(15)	0.4461(3)	0.071(1)
H(1)	0.8000	0.5407	0.4460	0.028
H(2)	0.5142	0.6085	0.5938	0.034
H(3)	0.4080	0.6183	0.3569	0.032
H(4A)	0.8865	0.5481	0.6853	0.049
H(4B)	0.7654	0.5124	0.7283	0.049
H(4C)	0.7964	0.6007	0.7442	0.049
H(5A)	0.6731	0.5570	0.2108	0.034

H(5B)	0.5639	0.6253	0.1813	0.034
H(7)	0.3201	0.6040	0.0733	0.031
H(8)	0.1385	0.5241	-0.0427	0.030
H(10A)	0.3952	0.3452	0.0783	0.030
H(11A)	0.5784	0.4251	0.1909	0.030
H(12A)	0.0590	0.4016	-0.1347	0.032
H(12B)	0.1622	0.3302	-0.0925	0.032
H(14A)	-0.0659	0.3134	0.1708	0.031
H(15A)	-0.2783	0.2485	0.1146	0.033
H(16A)	-0.3971	0.2141	-0.1001	0.035
H(17A)	-0.2976	0.2405	-0.2542	0.032
H(18A)	-0.0835	0.3039	-0.1995	0.031

Table S12. Anisotropic displacement parameters (Å^2) for $[C_{18}N_2H_{18}OH][PF_6]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.0227(10)	0.0376(12)	0.0175(9)	-0.0010(9)	0.0070(8)	-0.0086(9)
N(1)	0.0259(13)	0.0268(13)	0.0174(11)	-0.0029(10)	0.0080(10)	-0.0039(10)
N(2)	0.0209(12)	0.0288(13)	0.0178(11)	-0.0017(10)	0.0062(10)	-0.0031(10)
C(1)	0.0241(15)	0.0243(14)	0.0222(14)	-0.0029(11)	0.0103(12)	-0.0031(12)
C(2)	0.0274(16)	0.0328(17)	0.0283(16)	-0.0066(13)	0.0149(13)	-0.0034(13)
C(3)	0.0227(15)	0.0284(16)	0.0305(16)	-0.0030(12)	0.0108(13)	-0.0010(12)
C(4)	0.0365(18)	0.0398(18)	0.0174(14)	-0.0017(13)	0.0051(13)	-0.0028(15)
C(5)	0.0280(16)	0.0381(18)	0.0186(14)	-0.0002(13)	0.0072(12)	-0.0087(13)
C(6)	0.0215(15)	0.0358(16)	0.0149(13)	-0.0008(12)	0.0062(11)	-0.0061(12)
C(7)	0.0297(16)	0.0249(15)	0.0239(14)	-0.0011(12)	0.0102(13)	-0.0015(12)
C(8)	0.0205(14)	0.0335(16)	0.0208(14)	0.0017(12)	0.0060(12)	0.0012(12)
C(9)	0.0231(15)	0.0327(16)	0.0156(13)	-0.0013(11)	0.0082(11)	-0.0046(12)
C(10)	0.0282(16)	0.0266(15)	0.0215(14)	0.0029(12)	0.0099(12)	0.0015(12)
C(11)	0.0221(15)	0.0336(16)	0.0196(14)	0.0040(12)	0.0070(12)	0.0025(12)
C(12)	0.0261(16)	0.0338(16)	0.0210(14)	-0.0012(12)	0.0083(12)	-0.0050(13)
C(13)	0.0196(14)	0.0239(14)	0.0229(14)	0.0011(11)	0.0058(11)	-0.0013(11)
C(14)	0.0247(15)	0.0298(16)	0.0214(14)	0.0005(12)	0.0059(12)	0.0006(12)
C(15)	0.0282(16)	0.0301(16)	0.0252(15)	0.0043(12)	0.0112(13)	0.0014(13)
C(16)	0.0249(16)	0.0292(16)	0.0316(16)	0.0017(13)	0.0072(13)	-0.0037(13)
C(17)	0.0272(16)	0.0254(15)	0.0237(14)	-0.0012(12)	0.0033(12)	-0.0042(12)
C(18)	0.0274(15)	0.0281(15)	0.0207(14)	0.0000(12)	0.0082(12)	-0.0020(12)
P(1)	0.0277(4)	0.0376(5)	0.0303(4)	0.0076(4)	0.0127(3)	0.0085(4)
F(1)	0.0530(13)	0.0719(15)	0.0376(11)	-0.0165(11)	0.0197(10)	-0.0041(11)
F(2)	0.0654(15)	0.0610(14)	0.0504(13)	0.0003(11)	0.0343(12)	-0.0145(12)
F(3)	0.0747(16)	0.0457(13)	0.0567(14)	-0.0073(11)	0.0263(12)	0.0129(12)
F(4)	0.0443(13)	0.0909(19)	0.0489(13)	0.0207(13)	0.0087(11)	0.0280(12)
F(5)	0.0468(13)	0.0923(19)	0.0411(12)	0.0000(12)	0.0077(10)	0.0325(12)
F(6)	0.0657(17)	0.0780(18)	0.0830(18)	0.0114(14)	0.0423(15)	-0.0186(13)

Table S13. Bond lengths [Å] for $[C_{18}N_2H_{18}OH][PF_6]$.

atom-atom	distance	atom-atom	distance
O(1)-C(13)	1.371(3)	O(1)-C(12)	1.435(3)
N(1)-C(1)	1.319(3)	N(1)-C(2)	1.372(4)
N(1)-C(4)	1.459(4)	N(2)-C(1)	1.325(4)
N(2)-C(3)	1.380(4)	N(2)-C(5)	1.472(3)
C(2)-C(3)	1.343(4)	C(5)-C(6)	1.506(4)
C(6)-C(11)	1.379(4)	C(6)-C(7)	1.392(4)
C(7)-C(8)	1.383(4)	C(8)-C(9)	1.385(4)
C(9)-C(10)	1.385(4)	C(9)-C(12)	1.498(4)
C(10)-C(11)	1.384(4)	C(13)-C(14)	1.383(4)
C(13)-C(18)	1.387(4)	C(14)-C(15)	1.383(4)
C(15)-C(16)	1.389(4)	C(16)-C(17)	1.377(4)
C(17)-C(18)	1.386(4)	P(1)-F(5)	1.575(2)
P(1)-F(4)	1.576(2)	P(1)-F(1)	1.582(2)
P(1)-F(2)	1.582(2)	P(1)-F(6)	1.588(2)
P(1)-F(3)	1.604(2)	C(1)-H(1)	0.9500
C(2)-H(2)	0.9500	C(3)-H(3)	0.9500
C(4)-H(4A)	0.9800	C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800	C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900	C(7)-H(7)	0.9500
C(8)-H(8)	0.9500	C(10)-H(10A)	0.9500
C(11)-H(11A)	0.9500	C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900	C(14)-H(14A)	0.9500
C(15)-H(15A)	0.9500	C(16)-H(16A)	0.9500
C(17)-H(17A)	0.9500	C(18)-H(18A)	0.9500

Symmetry transformations used to generate equivalent atoms:

Table S14. Bond angles [°] for $[C_{18}N_2H_{18}OH][PF_6]$.

atom-atom-atom	angle	atom-atom-atom	angle
C(13)-O(1)-C(12)	117.6(2)	C(1)-N(1)-C(2)	109.0(2)
C(1)-N(1)-C(4)	125.4(3)	C(2)-N(1)-C(4)	125.5(2)
C(1)-N(2)-C(3)	108.5(2)	C(1)-N(2)-C(5)	125.4(2)
C(3)-N(2)-C(5)	126.1(2)	N(1)-C(1)-N(2)	108.5(2)
C(3)-C(2)-N(1)	107.1(3)	C(2)-C(3)-N(2)	106.9(3)
N(2)-C(5)-C(6)	111.6(2)	C(11)-C(6)-C(7)	119.3(3)
C(11)-C(6)-C(5)	121.1(3)	C(7)-C(6)-C(5)	119.5(3)
C(8)-C(7)-C(6)	120.0(3)	C(7)-C(8)-C(9)	120.7(3)
C(8)-C(9)-C(10)	119.1(3)	C(8)-C(9)-C(12)	120.1(3)
C(10)-C(9)-C(12)	120.8(3)	C(11)-C(10)-C(9)	120.4(3)
C(6)-C(11)-C(10)	120.5(3)	O(1)-C(12)-C(9)	105.9(2)
O(1)-C(13)-C(14)	115.4(2)	O(1)-C(13)-C(18)	123.8(2)
C(14)-C(13)-C(18)	120.8(3)	C(13)-C(14)-C(15)	119.8(3)
C(14)-C(15)-C(16)	120.1(3)	C(17)-C(16)-C(15)	119.3(3)
C(16)-C(17)-C(18)	121.5(3)	C(17)-C(18)-C(13)	118.5(3)
F(5)-P(1)-F(4)	176.97(15)	F(5)-P(1)-F(1)	90.43(12)
F(4)-P(1)-F(1)	92.41(13)	F(5)-P(1)-F(2)	89.45(14)
F(4)-P(1)-F(2)	91.56(14)	F(1)-P(1)-F(2)	90.86(13)
F(5)-P(1)-F(6)	89.44(15)	F(4)-P(1)-F(6)	89.50(14)
F(1)-P(1)-F(6)	89.93(14)	F(2)-P(1)-F(6)	178.65(14)
F(5)-P(1)-F(3)	88.86(13)	F(4)-P(1)-F(3)	88.29(13)
F(1)-P(1)-F(3)	179.29(14)	F(2)-P(1)-F(3)	89.07(13)
F(6)-P(1)-F(3)	90.13(14)	N(1)-C(1)-H(1)	125.7
N(2)-C(1)-H(1)	125.7	C(3)-C(2)-H(2)	126.5
N(1)-C(2)-H(2)	126.5	C(2)-C(3)-H(3)	126.6
N(2)-C(3)-H(3)	126.6	N(1)-C(4)-H(4A)	109.5
N(1)-C(4)-H(4B)	109.5	H(4A)-C(4)-H(4B)	109.5
N(1)-C(4)-H(4C)	109.5	H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5	N(2)-C(5)-H(5A)	109.3
C(6)-C(5)-H(5A)	109.3	N(2)-C(5)-H(5B)	109.3
C(6)-C(5)-H(5B)	109.3	H(5A)-C(5)-H(5B)	108.0
C(8)-C(7)-H(7)	120.0	C(6)-C(7)-H(7)	120.0
C(7)-C(8)-H(8)	119.6	C(9)-C(8)-H(8)	119.6
C(11)-C(10)-H(10A)	119.8	C(9)-C(10)-H(10A)	119.8
C(6)-C(11)-H(11A)	119.7	C(10)-C(11)-H(11A)	119.7
O(1)-C(12)-H(12A)	110.6	C(9)-C(12)-H(12A)	110.6

O(1)-C(12)-H(12B)	110.6	C(9)-C(12)-H(12B)	110.6
H(12A)-C(12)-H(12B)	108.7	C(13)-C(14)-H(14A)	120.1
C(15)-C(14)-H(14A)	120.1	C(14)-C(15)-H(15A)	119.9
C(16)-C(15)-H(15A)	119.9	C(17)-C(16)-H(16A)	120.4
C(15)-C(16)-H(16A)	120.4	C(16)-C(17)-H(17A)	119.2
C(18)-C(17)-H(17A)	119.2	C(17)-C(18)-H(18A)	120.8
C(13)-C(18)-H(18A)	120.8		

Symmetry transformations used to generate equivalent atoms:

Table S15. Torsion angles [°] for $[C_{18}N_2H_{18}OH][PF_6]$.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(2)-N(1)-C(1)-N(2)	-0.3(3)	C(4)-N(1)-C(1)-N(2)	-178.8(3)
C(3)-N(2)-C(1)-N(1)	0.4(3)	C(5)-N(2)-C(1)-N(1)	179.4(3)
C(1)-N(2)-C(3)-C(2)	-0.3(3)	C(5)-N(2)-C(3)-C(2)	-179.4(3)
N(2)-C(3)-C(2)-N(1)	0.1(3)	C(1)-N(1)-C(2)-C(3)	0.1(3)
C(4)-N(1)-C(2)-C(3)	178.6(3)	C(1)-N(2)-C(5)-C(6)	119.9(3)
C(3)-N(2)-C(5)-C(6)	-61.3(4)	N(2)-C(5)-C(6)-C(11)	-81.9(3)
N(2)-C(5)-C(6)-C(7)	98.5(3)	C(11)-C(6)-C(7)-C(8)	0.5(4)
C(5)-C(6)-C(7)-C(8)	180.0(3)	C(6)-C(7)-C(8)-C(9)	0.7(4)
C(7)-C(8)-C(9)-C(10)	-1.1(4)	C(7)-C(8)-C(9)-C(12)	176.4(3)
C(8)-C(9)-C(10)-C(11)	0.4(4)	C(12)-C(9)-C(10)-C(11)	-177.1(3)
C(7)-C(6)-C(11)-C(10)	-1.2(4)	C(5)-C(6)-C(11)-C(10)	179.3(3)
C(9)-C(10)-C(11)-C(6)	0.7(4)	C(13)-O(1)-C(12)-C(9)	173.2(2)
C(8)-C(9)-C(12)-O(1)	-91.1(3)	C(10)-C(9)-C(12)-O(1)	86.4(3)
C(12)-O(1)-C(13)-C(14)	-178.5(3)	C(12)-O(1)-C(13)-C(18)	-0.8(4)
O(1)-C(13)-C(14)-C(15)	177.5(3)	C(18)-C(13)-C(14)-C(15)	-0.3(4)
C(13)-C(14)-C(15)-C(16)	-0.8(4)	C(14)-C(15)-C(16)-C(17)	1.4(5)
C(15)-C(16)-C(17)-C(18)	-0.9(5)	C(16)-C(17)-C(18)-C(13)	-0.2(4)
O(1)-C(13)-C(18)-C(17)	-176.8(3)	C(14)-C(13)-C(18)-C(17)	0.8(4)

Symmetry transformations used to generate equivalent atoms:

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[i] Haynes, W. M. *CRC Handbook of Chemistry and Physics, 96th ed.;* CRC Press, Taylor & Francis Group, Inc.: Abingdon, 2015.