Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information to:

Tuning transport properties of phosphonium ionic liquids

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Content

1. Experimental parameters for PFGSTE-measurements

1.1 General remarks an additional experimental details

The gradient unit for the PFGSTE-measurements was calibrated prior to the measurements by determining the self-diffusion coefficients of water and bis(2-ethylhexyl) phthalate (DEHP) und comparing them to the reported literature values. Calibration with water was performed since its self-diffusion coefficient is well known from various experimental techniques,[1–3] while DEHP requires long gradient pulses due to its viscosity which is comparable to that of ionic liquids and was suggested in literature.[4] As check for spectrometer and operator performance as well as reliability of the measurements the ^{1}H and ^{19}F self-diffusion coefficients of hexyltrifluoroacetate were measured since this compound contains both active NMR nuclei of interest. The obtained self-diffusion coefficients for hexyltrifluoroacetate were found to be $D(^{1}H) = 1.82 \times 10^{-5}$ cm^{2} s^{-1} and $D(^{19}F) = 1.80 \times 10^{-5}$ cm^{2} s^{-1} which are identical within experimental error.

As different parameter sets for the diffusion time Δ and the overall gradient duration δ should yield the same values for the obtained self-diffusion coefficients this procedure can be used as a test for the applicability of the Stejskal-Tanner equation. Figure S1 shows the obtained signal decrease with increasing gradient strength for $[P_{4442}][NTf_2]$ at 25°C choosing a different parameter set for Δ and δ obtaining virtually the same values.

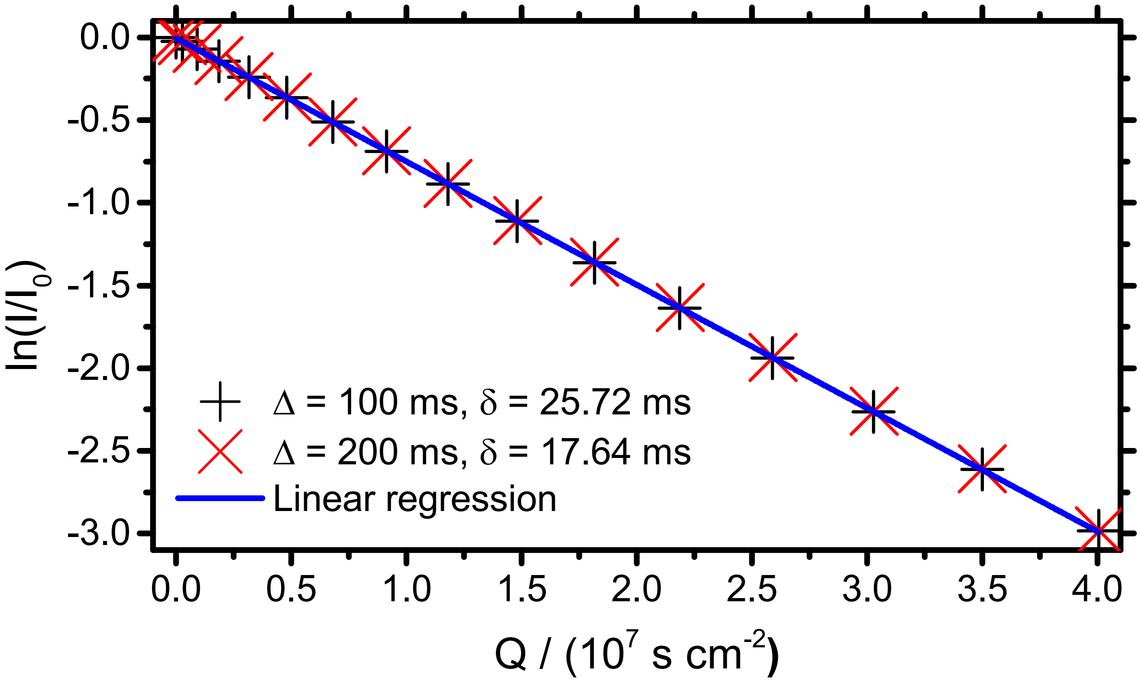

Figure S1: Linear regression of logarithmic intensity decreasing in with increasing gradient for $[P_{4442}][NTf_2]$ in the ^{19}F PFGSTE experiment at 25°C using two different parameter sets of diffusion time Δ and overall gradient duration δ to show the validity of the Stejskal-Tanner equation.

The pulse program used for the PFGSTE measurements including the notation given in the Bruker library is shown in Figure S2.

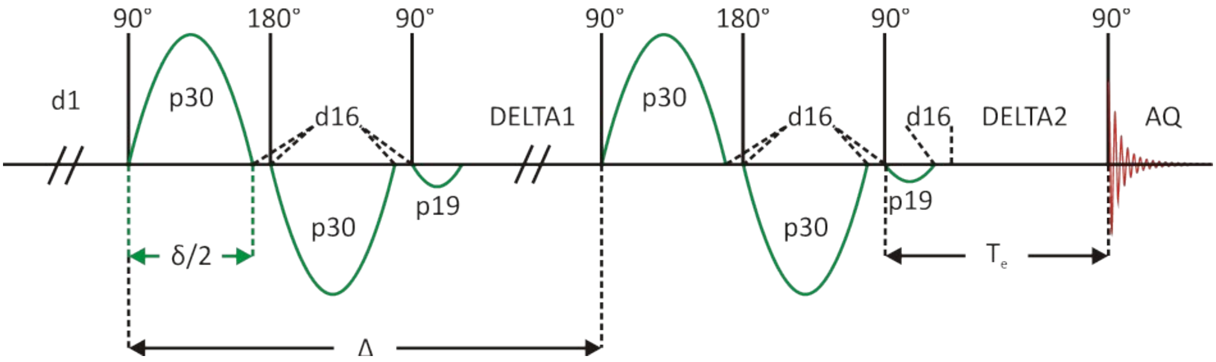

Figure S2: Pulse program for the PFGSTE measurements in the notation from the Bruker library.

The total relaxation delay consisting of relaxation delay d1 and acquisition time AQ should be long enough to restore equilibrium conditions prior to the first pulse and was for this purpose chosen to be five to seven times the spin lattice relaxation T1. The value for the T1 was roughly obtained from the zero crossing in an inversion recovery experiment. Pulse durations were determined using the automatic pulsecal routine for ^{1}H and manually by quartering the pulse duration required for a 360° pulse for ^{19}F. Relaxation effects don't have to be taken into account when the total experiment time is held fixed, which is hence desirable. This can be easily be achieved by changing the gradient strength while keeping the diffusion time Δ and the gradient duration time δ fixed. During the experiments, the gradient strength was increased from 2% to 95% in equidistant steps. Each experiment consisted of 16 transients and 4 additional dummy scans. One should also make sure to use integer multiples of 16 as number of scans to ensure a complete phase cycle.[5] The spoiler gradient duration p19 is commonly set to twice the gradient duration p30. For the rather viscous ionic liquids, this would lead to unacceptably high values for p19 and therefore also for the longitudinal eddy current delay T_e, especially with the rather large spoiler gradients of 9.1 G cm^{-1} and 7.0 G cm^{-1}. To avoid artefacts and excessive attenuation of wanted signals, p19 was set fixed to 2 ms and T_e to 5 ms.[6] The parameters are summarised in Table S1. From the set of spectra thus obtained within one experiment, the one with the smallest gradient strength was phase corrected manually and the same phase correction applied to the other spectra at higher gradients. Line broadening with the apparent line width was also applied, as well as a baseline correction.

Table S1: Parameters and values for the PFGSTE measurements and abbreviation in the Bruker library.

Parameter	Abbreviation in Bruker library	Value
Number of scans	ns	16
Number of dummy scans	ds	4
Relaxation delay	d1	varied
Pulse duration of the 90° pulse	p1	varied
Pulse duration of the 180° pulse	p2	varied
Gradient pulse duration	p30	varied
Diffusion time	d20	varied
Gradient recovery delay	d16	200 µs
Spoiler gradient duration	p19	2 ms
LED delay T_e	d21	5 ms
Strength of first spoiler gradient	GPZ7	-17.13%
Strength of second spoiler gradient	GPZ8	-13.17%
Strength of diffusion gradient	GPZ6	varied from 2 to 95%

The values for Δ and δ should be chosen so that the desired signal for the largest gradient strength has about 5% of the intensity of the same signal with the lowest gradient. This was achieved in our case by first guessing both parameters reasonably, recording the spectra at 2% and 95% gradient strength, calculating the corresponding self-diffusion coefficient with the Stejskal-Tanner equation and subsequently altering Δ and δ so that the attenuation is adequate. By this procedure, the experimental parameters can be set up in the minimum amount of time, and a smooth Gaussian decay as shown in Figure S3 is obtained.

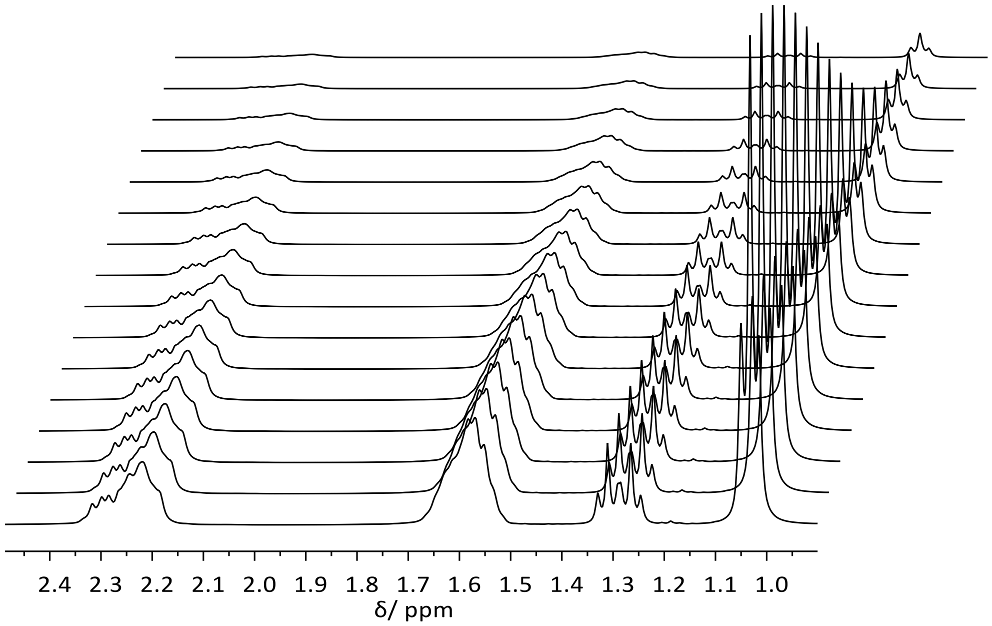

Figure S3: Obtained Gaussian decay of the signal intensity for ^{1}H NMR measurements of the ionic liquid [P_{4442}][NTf_2] with increasing diffusion gradient strength as stacked plot.

1.2 NMR diffusometry on the investigated phosphonium ionic liquids using the PFGSTE pulse sequence

As mentioned in the previous section the gradient pulse duration p30, the diffusion time d20 along with the pulse duration of the 90° pulse p1 and the relaxation delay d1 were individually varied for each experiment in order to obtain a parameter set for the appropriate signal attenuation with varying diffusion gradient strength. The values used for the PFGSTE measurements at 25°C are listed in Table S2. Varied parameters for the temperature dependent measurements can be found in Table S3. Results of the obtained self-diffusion coefficients for the gradient calibration with water and DEHP at 25°C are listed in Table S4 while values for the temperature-dependent measurements are given in Table S5. Derived quantities in the main manuscript refer to the calibration with water. The highest derivation from the linear fit of the logarithmic intensity decrease with increasing gradient was found to be 0.6 % but in most cases in the range of 0.01 - 0.1 %.

Table S2 : Parameters used for the PFGSTE-measurements on the ionic liquids at 25°C.

Ionic liquid	^{1}H				^{19}F			
	p30 / ms	d20 / ms	p1 / µs	d1 / s	p30 / ms	d20 / ms	p1 / µs	d1 / s
[P_{222202}][NTf_2]	7.30	80	11.64	5	8.31	70	18.47	2
[P_{2225}][NTf_2]	9.40	100	11.53	4	9.70	100	18.36	3
[P_{2228}][NTf_2]	9.30	150	11.40	4	11.34	100	18.00	2
[P_{444202}][TFA]	9.37	250	10.80	5	13.26	120	17.03	2
[P_{444202}][OMs]	17.19	300	11.41	4	-	-	-	-
[P_{444202}][NTf_2]	8.13	250	10.82	5	7.32	250	18.04	3
[P_{444202}][OTf]	13.01	250	10.71	5	12.55	250	16.29	3
[P_{4442}][NTf_2]	8.36	250	10.85	4	8.82	200	17.90	3
[P_{4446}][NTf_2]	10.81	250	10.74	4	10.84	200	17.08	3
[P_{4448}][NTf_2]	11.40	250	10.65	4	10.30	250	16.80	3
[P_{44410}][NTf_2]	12.46	250	10.70	4	12.58	200	16.43	3

Table S3: Parameters used for the PFGSTE-measurements on the ionic liquids at variable temperatures.

Ionic liquid	Temp. / °C	^{1}H				^{19}F			
		p30 / ms	d20 / ms	p1 / µs	d1 / s	p30 / ms	d20 / ms	p1 / µs	d1 / s
$[P_{4442O2}][NTf_2]$	25	8.13	250	10.82	5	7.32	250	18.04	3
	35	6.57	200	11.02	5	7.02	150	19.08	3
	45	5.80	150	11.11	5	6.70	100	19.44	3
	55	4.36	150	11.20	5	5.23	100	19.38	3
	65	3.78	100	11.40	5	3.63	100	19.18	3
	75	3.55	80	11.53	5	3.59	80	18.76	3
$[P_{4442}][NTf_2]$	25	8.36	250	10.85	4	8.82	200	17.90	3
	35	6.90	200	10.95	5	9.47	100	18.53	2
	45	6.26	150	11.07	5	7.41	100	19.09	2
	55	5.10	100	11.29	4	5.45	100	19.49	2
	65	4.77	80	11.44	5	4.11	100	18.81	3
	75	3.71	80	11.51	4	3.26	100	18.57	3
$[P_{4448}][NTf_2]$	25	11.40	250	10.65	4	10.30	250	16.80	3
	35	8.36	250	10.86	5	8.46	200	17.63	3
	45	7.10	200	10.98	6	6.33	200	18.55	3
	55	5.74	200	11.47	6	5.63	150	19.42	2
	65	5.35	150	11.53	7	5.23	100	19.81	2
	75	4.26	150	11.69	8	4.06	100	20.25	2

Table S4: Self-diffusion coefficients D of the ionic liquids obtained via PFGSTE measurements for different calibration substances at 25°C from ^{1}H and ^{19}F NMR.

Ionic liquid	$D(^1H)$ / 10^{-8} cm^2 s^{-1}			$D(^{19}F)$ / 10^{-8} cm^2 s^{-1}		
	Non calibrated	H_2O	DEHP	Non calibrated	H_2O	DEHP
[P_{2222O2}][NTf_2]	25.1	23.3	22.3	25.3	23.5	22.5
[P_{2225}][NTf_2]	12.0	11.2	10.7	13.0	12.1	11.6
[P_{2228}][NTf_2]	8.11	7.54	7.21	9.47	8.80	8.45
[P_{4442O2}][TFA]	4.65	4.32	4.14	5.73	5.32	5.09
[P_{4442O2}][OMs]	1.02$^{1)}$	0.948$^{1)}$	0.908$^{1)}$	-	-	-
	1.17$^{2)}$	1.09$^{2)}$	1.04$^{2)}$			
[P_{4442O2}][NTf_2]	6.30	5.86	5.61	8.70	8.07	7.72
[P_{4442O2}][OTf]	2.45	2.27	2.18	2.96	2.75	2.63
[P_{4442}][NTf_2]	5.90	5.48	5.25	7.46	6.93	6.64
[P_{4446}][NTf_2]	3.55	3.30	3.16	4.99	4.64	4.44
[P_{4448}][NTf_2]	3.11	2.89	2.77	4.36	4.06	3.88
[P_{44410}][NTf_2]	2.67	2.48	2.37	3.73	3.47	3.32

$^{1)}$ Cation self-diffusion coefficient. $^{2)}$ Anion self-diffusion coefficient.

Table S5: Self-diffusion coefficients D of the ionic liquids obtained via PFGSTE measurements for different calibration substances at different temperatures from ^{1}H and ^{19}F NMR.

Ionic liquid	Temp. / °C	**D(^{1}H) / 10^{-8} cm^2 s^{-1}**			**D(^{19}F) / 10^{-8} cm^2 s^{-1}**		
		Non calibrated	H_2O	DEHP	Non calibrated	H_2O	DEHP
$[P_{4442O2}][NTf_2]$	25	6.30	5.86	5.61	8.70	8.07	7.72
	35	9.75	9.06	8.67	15.8	14.6	14.0
	45	19.8	18.4	17.5	26.2	24.4	23.3
	55	35.0	32.5	31.1	42.6	39.6	37.9
	65	61.5	57.2	54.8	77.2	71.8	68.7
	75	105	97.9	93.7	126	117	112
$[P_{4442}][NTf_2]$	25	5.90	5.48	5.25	7.46	6.93	6.64
	35	10.9	10.1	9.70	13.4	12.5	12.0
	45	17.4	16.1	15.4	21.7	20.2	19.3
	55	33.7	31.3	30.0	38.6	35.9	34.4
	65	60.3	56.1	53.7	77.0	71.5	68.5
	75	95.2	88.5	84.7	120	111	107
$[P_{4448}][NTf_2]$	25	3.11	2.89	2.77	4.36	4.06	3.88
	35	5.93	5.51	5.27	8.14	7.56	7.24
	45	10.2	9.46	9.06	14.4	13.4	12.8
	55	15.5	14.4	13.8	24.3	22.6	21.6
	65	23.9	22.2	21.3	42.1	39.1	37.5
	75	37.5	34.9	33.4	71.8	66.8	63.9

Plot of the temperature dependent self-diffusion coefficients of anion and cation for $[P_{4442O2}][NTf_2]$, $[P_{4442}][NTf_2]$ and $[P_{4442O2}][NTf_2]$ are shown in Figure S4 to Figure S6. The measured temperature-dependent self-diffusion coefficients were fitted with the Arrhenius equation S1 and the obtained fitting parameters are listed in Table S6.

$$D = A\exp\left(\frac{-E_a}{RT}\right) \tag{S1}$$

A number of different approaches for the fitting of temperature dependent self-diffusion data can be found in the literature, first and foremost the VFT equation. However only marginal deviations from the linear behaviour in the Arrhenius plot were found for the temperature dependent self-diffusion measurements. Therefore fitting using Arrhenius equation was preferred. The only parameters required are the pre-exponential factor A and E_a, which is frequently interpreted as activation energy for the position exchange of two molecules.

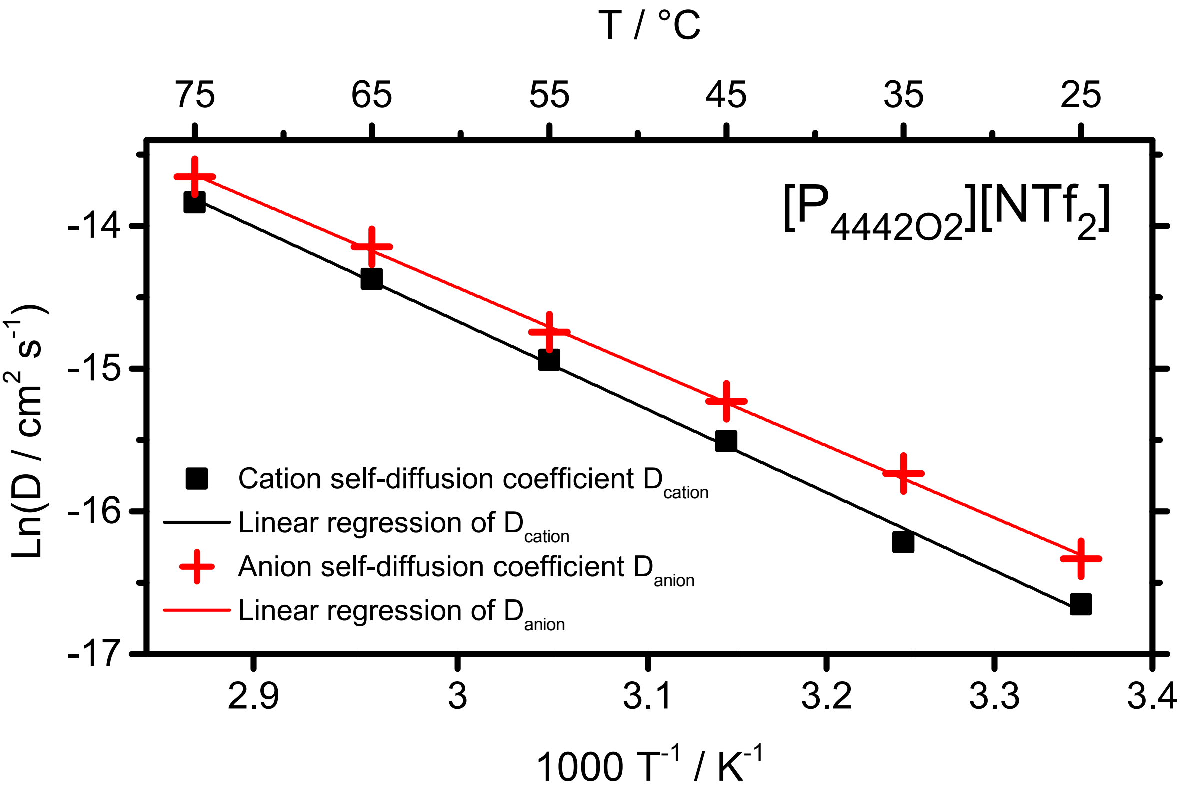

Figure S4: Linear regression of cation and anion self-diffusion coefficients of the ionic liquid $[P_{444202}][NTf_2]$ with temperature.

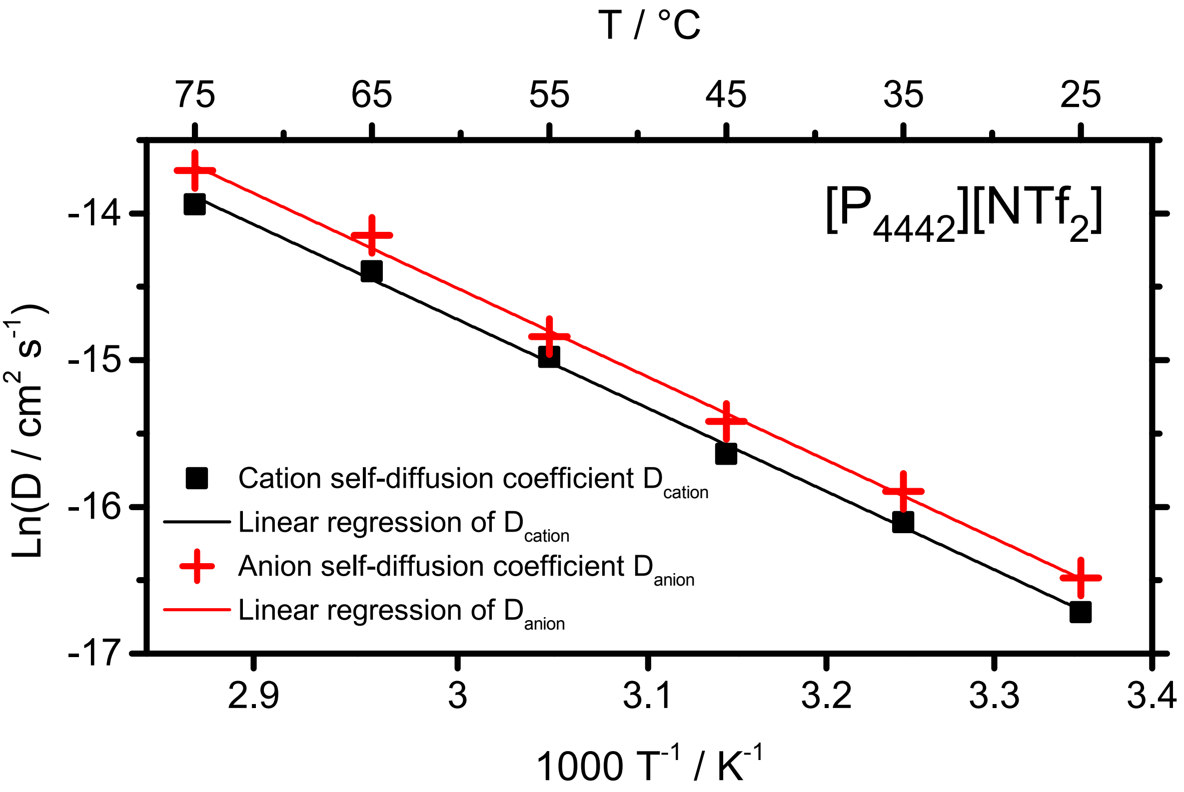

Figure S5: Linear regression of cation and anion self-diffusion coefficients of the ionic liquid $[P_{4442}][NTf_2]$ with temperature.

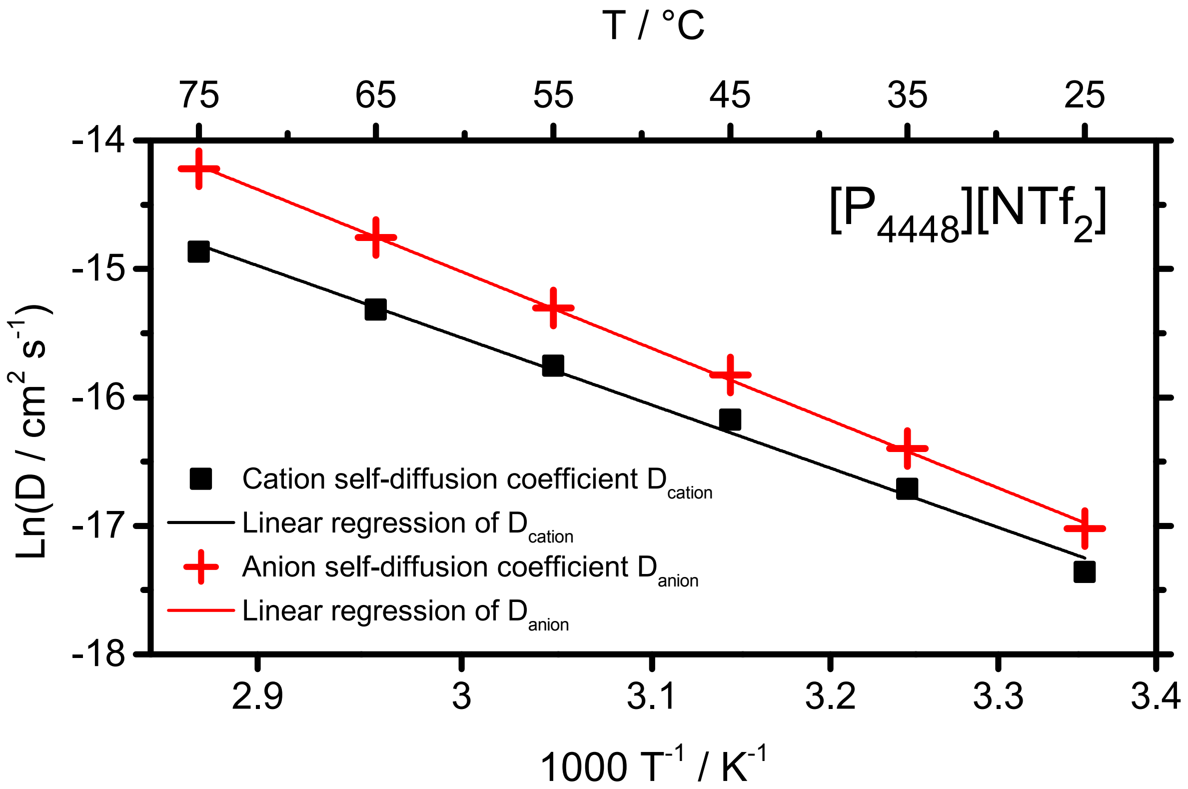

Figure S6: Linear regression of cation and anion self-diffusion coefficients of the ionic liquid $[P_{4448}][NTf_2]$ with temperature.

Table S6: Arrhenius fitting parameters of the temperature dependent self-diffusion coefficients.

Ionic Liquid	Nucleus	A / $cm^2 s^{-1}$	ΔA / %	E_a /kJ mol^{-1}	$ΔE_a$ / %
$[P_{4442O2}][NTf_2]$	^1H (D_{cation})	61.4	22	52.0	1
	^{19}F (D_{anion})	24.4	40	48.8	2
$[P_{4442}][NTf_2]$	^1H (D_{cation})	21.6	46	49.2	3
	^{19}F (D_{anion})	41.9	80	50.5	5
$[P_{4448}][NTf_2]$	^1H (D_{cation})	0.596	29	41.6	2
	^{19}F (D_{anion})	23.4	30	50.3	2

2. Density

Experimental values for the temperature-dependent densities ρ exhibited highly linear behaviour. Experimental values are presented in Table S7 and are plotted in Figure S7. Linear fits of the ionic liquid densities using equation S2 are given in Table S8.

$$\rho = (a + b * T) \qquad \text{(S2)}$$

The largest deviation of the fit from the experimental value was as low as 0.06 %. Besides the linear fit, models based on exponential or quadratic equations were used in the literature.[7–11] The quadratic corrections were found to be negligible in our case, and we therefore preferred the linear equation because the fit can be performed analytically.

Table S7: Densities ρ in g mL^{-1} of the investigated ILs at different temperatures.

Ionic Liquid	Temperature / °C					
	25	35	45	55	65	75
$[P_{2222O2}][NTf_2]$	1.340	1.331	1.321	1.312	1.303	1.293
$[P_{2225}][NTf_2]$	1.301	1.293	1.284	1.275	1.265	1.257
$[P_{2228}][NTf_2]$	1.244	1.235	1.225	1.218	1.209	1.201
$[P_{4442O2}][TFA]$	1.056	1.049	1.042	1.035	1.027	1.020
$[P_{4442O2}][OMs]$	1.027	1.021	1.014	1.007	1.001	0.994
$[P_{4442O2}][NTf_2]$	1.224	1.215	1.206	1.198	1.189	1.180
$[P_{4442O2}][OTf]$	1.111	1.103	1.096	1.088	1.081	1.074
$[P_{4442}][NTf_2]$	1.244	1.235	1.227	1.218	1.209	1.199
$[P_{4446}][NTf_2]$	1.182	1.174	1.166	1.157	1.148	1.140
$[P_{4448}][NTf_2]$	1.162	1.154	1.145	1.138	1.129	1.120
$[P_{44410}][NTf_2]$	1.142	1.132	1.124	1.117	1.109	1.099

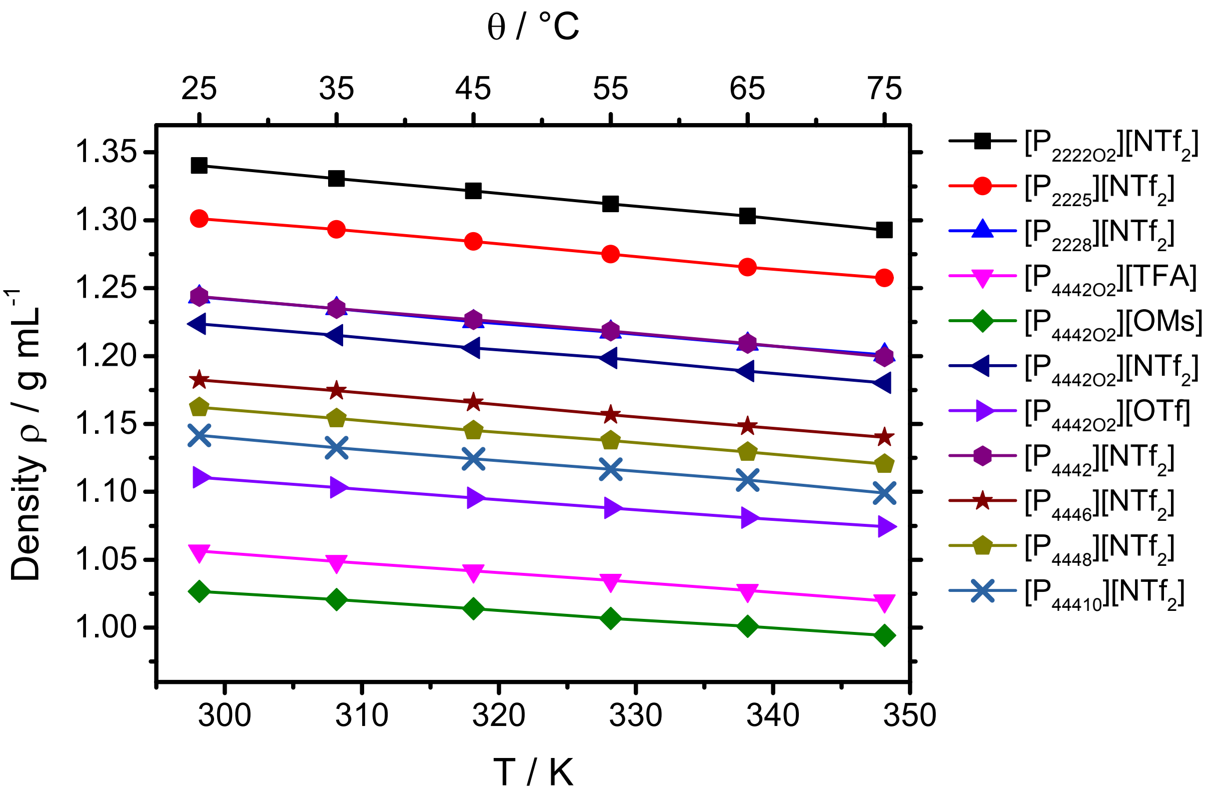

Figure S7: Density progression of the investigated ILs with temperature.

Table S8: Fitting parameters a and b for the linear regression of ionic liquids densities.

Ionic Liquid	a / g mL^{-1}	Δa / %	b / 10^{-4} K^{-1}	Δb / %	R^2
$[P_{2222O2}][NTf_2]$	1.622	0.18	-9.43	1.0	0.99963
$[P_{2225}][NTf_2]$	1.568	0.26	-8.92	1.5	0.99909
$[P_{2228}][NTf_2]$	1.498	0.27	-8.56	1.6	0.99897
$[P_{4442O2}][TFA]$	1.273	0.16	-7.26	0.8	0.99974
$[P_{4442O2}][OMs]$	1.221	0.25	-6.51	1.2	0.99943
$[P_{4442O2}][NTf_2]$	1.483	0.20	-8.69	1.2	0.99944
$[P_{4442O2}][OTf]$	1.328	0.23	-7.30	1.2	0.99937
$[P_{4442}][NTf_2]$	1.506	0.33	-8.79	1.1	0.99886
$[P_{4446}][NTf_2]$	1.437	0.07	-8.52	0.5	0.99972
$[P_{4448}][NTf_2]$	1.409	0.21	-8.29	1.1	0.99956
$[P_{44410}][NTf_2]$	1.390	0.29	-8.34	1.2	0.99882

3. Specific conductivity

The conductivity cell with the sample was placed in the tempered vessel shown schematically in Figure S8 to ensure temperature stability and exclusion of oxygen and moisture. Experimental specific conductivity κ values are summarized in Table S9 and plots are displayed in Figure S9.

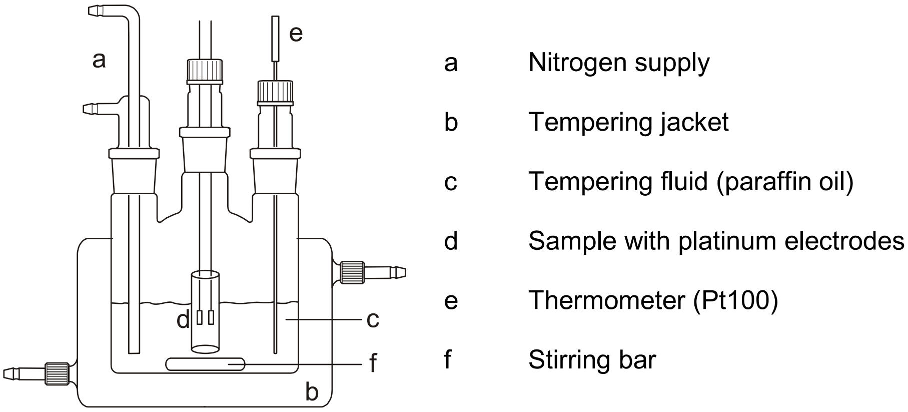

Figure S8: Sketch of the conductivity cell used for the determination of specific conductivity.

Table S9: Specific conductivity κ in µS cm^{-1} of the investigated ILs at different temperatures.

Ionic Liquid	Temperature / °C					
	25	35	45	55	65	75
$[P_{2222O2}][NTf_2]$	3351	4716	6486	8548	10843	13446
$[P_{2225}][NTf_2]$	1642	2508	3582	4934	6615	8544
$[P_{2228}][NTf_2]$	891	1407	2110	2968	4037	5332
$[P_{4442O2}][TFA]$	463	765	1210	1808	2612	3591
$[P_{4442O2}][OMs]$	106	210	383	641	1005	1530
$[P_{4442O2}][NTf_2]$	763	1209	1775	2639	3624	4797
$[P_{4442O2}][OTf]$	275	487	808	1240	1829	2582
$[P_{4442}][NTf_2]$	792	1301	1948	2769	3805	5098
$[P_{4446}][NTf_2]$	391	629	985	1442	2044	2821
$[P_{4448}][NTf_2]$	307	480	742	1094	1554	2165
$[P_{44410}][NTf_2]$	226	380	598	903	1309	1828

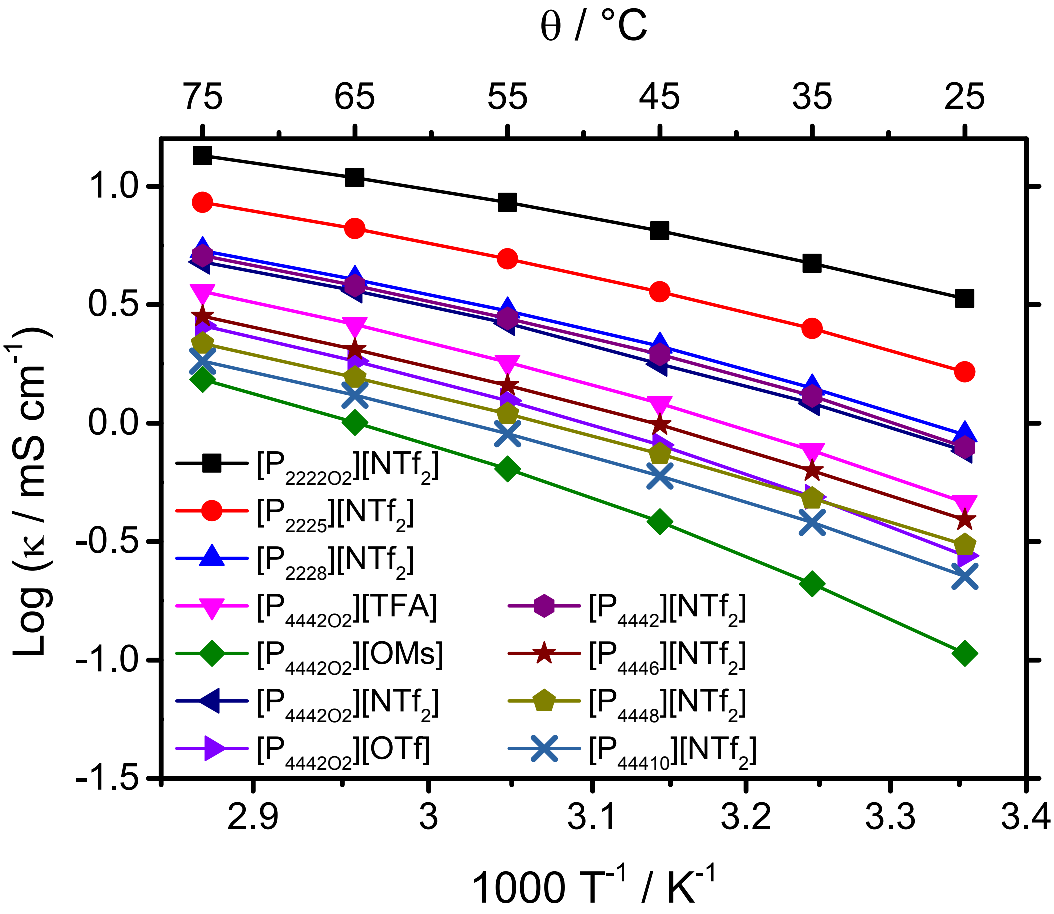

Figure S9: Progression of specific conductivity κ of the investigated ILs with temperature.

Vogel-Fulcher-Tammann (VFT) equation fit parameters of the specific conductivity following equation S3 with κ_0, B and T_0 being fit parameters are given in Table S10.

$$\kappa = \kappa_0 \exp (B / T\text{-}T_0) \qquad \text{(S3)}$$

The largest deviation of the fit from the experimental data was 2.5%, in most cased this deviation was below 1%.

Table S10: VFT fitting parameters of the investigated ILs specific conductivity κ.

Ionic liquid	κ_0 / S cm^{-1}	$\Delta\kappa_0$ / %	B / K	ΔB / %	T_0 / K	ΔT_0 / %	R^2
$[P_{222201}][NTf_2]$	0.55	16	-681	8	165.0	4	0.99983
$[P_{2225}][NTf_2]$	1.07	31	-952	11	151.2	7	0.99973
$[P_{2228}][NTf_2]$	0.67	40	-896	15	162.7	8	0.99948
$[P_{4442O2}][TFA]$	1.45	43	-1172	13	152.7	7	0.99970
$[P_{4442O2}][OMs]$	3.05	49	-1472	12	154.4	7	0.99979
$[P_{4442O2}][NTf_2]$	0.70	39	-915	14	164.4	7	0.99955
$[P_{4442O2}][OTf]$	1.04	50	-1105	15	164.0	7	0.99957
$[P_{4442}][NTf_2]$	0.97	35	-1014	12	155.2	6	0.99968
$[P_{4446}][NTf_2]$	2.24	45	-1462	15	129.1	12	0.99966
$[P_{4448}][NTf_2]$	7.64	65	-2111	14	89.8	19	0.99981
$[P_{44410}][NTf_2]$	1.52	34	-1417	9	137.4	7	0.99988

4. Molar conductivity

Calculated molar conductivities Λ_M of the investigated ionic liquids at different temperatures are given in Table S11. VFT fitting parameters $\Lambda_{M,0}$, B and T_0 following equation S4 are given in Table S12.

$$\Lambda_M = \Lambda_{M,0} \exp (B / T-T_0) \qquad (S4)$$

Table S11: Molar conductivity Λ_M in S cm^2 mol^{-1} of the investigated ILs at different temperatures.

Ionic Liquid	Temperature / °C					
	25	35	45	55	65	75
$[P_{2222O2}][NTf_2]$	1.179	1.671	2.314	3.072	3.922	4.903
$[P_{2225}][NTf_2]$	0.630	0.969	1.393	1.933	2.611	3.394
$[P_{2228}][NTf_2]$	0.367	0.583	0.881	1.247	1.708	2.271
$[P_{4442O2}][TFA]$	0.170	0.283	0.451	0.679	0.987	1.368
$[P_{4442O2}][OMs]$	0.038	0.076	0.140	0.236	0.372	0.570
$[P_{4442O2}][NTf_2]$	0.347	0.553	0.818	1.223	1.694	2.258
$[P_{4442O2}][OTf]$	0.105	0.187	0.313	0.484	0.718	1.020
$[P_{4442}][NTf_2]$	0.326	0.539	0.812	1.163	1.609	2.174
$[P_{4446}][NTf_2]$	0.188	0.304	0.480	0.707	1.010	1.404
$[P_{4448}][NTf_2]$	0.157	0.248	0.386	0.573	0.820	1.151
$[P_{44410}][NTf_2]$	0.123	0.209	0.332	0.504	0.737	1.038

Table S12: VFT fitting parameters for the molar conductivity Λ_M of the investigated ILs.

Ionic liquid	$\Lambda_{M,0}$ / S cm^2 mol^{-1}	$\Delta\Lambda_{M,0}$ / %	B / K	ΔB / %	T_0 / K	ΔT_0 / %	R^2
$[P_{2222O2}][NTf_2]$	256.1	19	743.8	9	160.1	4	0.99996
$[P_{2225}][NTf_2]$	531.2	22	1012.2	8	147.8	5	0.99998
$[P_{2228}][NTf_2]$	347.8	21	947.9	7	159.8	4	0.99998
$[P_{4442O2}][TFA]$	712.8	30	1245.7	9	149.0	5	0.99997
$[P_{4442O2}][OMs]$	1413	56	1533.1	13	152.0	8	0.99995
$[P_{4442O2}][NTf_2]$	411.0	68	973.6	23	161.0	12	0.99976
$[P_{4442O2}][OTf]$	488.0	16	1147.4	5	162.2	2	0.99999
$[P_{4442}][NTf_2]$	568.3	44	1105.9	14	149.5	9	0.99992
$[P_{4446}][NTf_2]$	1458	37	1546.3	10	125.5	8	0.99997
$[P_{4448}][NTf_2]$	6187	51	2278.2	11	82.9	16	0.99998
$[P_{44410}][NTf_2]$	1236	10	1533.9	3	131.6	2	1

5. Viscosity

Experimental values for the viscosity of the ionic liquids at different temperatures are displayed in Table S13. The data were fitted following equation S5 yielding the VFT fitting parameters $\eta_{0,}$ B and T_0 that are summarized in Table S14.

$$\eta = \eta_0 \exp (B / T - T_0) \tag{S5}$$

Table S13: Viscosity η in mPa s of the investigated ILs at different temperatures.

Ionic Liquid	Temperature / °C							
	25	35	45	55	65	75	85	95
$[P_{2222O2}][NTf_2]$	49.56	33.95	24.47	18.35	14.26	11.42	9.42	7.96
$[P_{2225}][NTf_2]$	97.95	60.38	40.65	28.57	20.94	15.85	12.49	10.13
$[P_{2228}][NTf_2]$	119.42	72.00	47.38	32.80	23.63	17.71	13.68	10.93
$[P_{4442O2}][TFA]$	207.23	126.03	78.28	54.91	38.97	28.60	21.89	17.45
$[P_{4442O2}][OMs]$	766.52	393.81	227.67	140.37	92.04	62.26	43.81	31.74
$[P_{4442O2}][NTf_2]$	155.02	92.69	60.68	4.15	29.96	22.61	17.91	14.74
$[P_{4442O2}][OTf]$	405.35	227.35	134.55	89.62	60.20	41.99	30.66	23.34
$[P_{4442}][NTf_2]$	163.68	100.77	65.58	44.35	31.19	22.70	17.14	13.37
$[P_{4446}][NTf_2]$	257.33	146.74	91.31	59.90	41.08	29.33	21.79	16.63
$[P_{4448}][NTf_2]$	266.46	153.89	97.35	64.08	44.07	31.45	23.26	17.77
$[P_{44410}][NTf_2]$	301.06	174.98	107.98	70.00	47.68	33.79	24.81	18.86

Table S14: VFT fitting parameters for the viscosity η of the investigated ILs..

Ionic liquid	η_0/ mPa s	$\Delta\eta_0$/ %	B / K	ΔB / %	T_0 / K	ΔT_0 / %	R^2
$[P_{2222O2}][NTf_2]$	0,2995	6	636,1	3	173,6	1	0,99999
$[P_{2225}][NTf_2]$	0,2367	14	699,7	5	182,0	2	0,99995
$[P_{2228}][NTf_2]$	0,2021	13	749,6	5	180,7	2	0,99997
$[P_{4442O2}][TFA]$	0,1727	46	915,5	15	169,0	6	0,99973
$[P_{4442O2}][OMs]$	0,1855	28	968,4	8	181,8	3	0,99994
$[P_{4442O2}][NTf_2]$	0,3685	13	651,6	5	190,3	2	1
$[P_{4442O2}][OTf]$	0,1226	36	1046,7	10	169,0	4	0,99990
$[P_{4442}][NTf_2]$	0,0371	12	1368,2	3	135,1	2	0,99999
$[P_{4446}][NTf_2]$	0,1083	15	1006,1	4	168,7	2	1
$[P_{4448}][NTf_2]$	0,0929	26	1089,9	7	161,2	3	1
$[P_{44410}][NTf_2]$	0,0411	11	1366,3	3	144,6	2	0,99999

6. Materials and synthesis of the investigated ionic liquids

6.1 Materials

The phosphines triethylphosphine (99%) and tri-n-butylphosphine (99%) were obtained from Strem Chemicals (Kehl, Germany) and used as received. Alkylation reagents 2-chloroethyl ethyl ether (99%) and 2-bromoethyl ethyl ether (95%) from Sigma Aldrich (St. Louis, USA), bromoethane (98%) from Acros Organics (Geel, Belgium) and 1-bromopentane (99%), 1-bromohexane (99%), 1-bromooctane (98%+), 1-bromodecane (98%) delivered from Alfa Aesar (Karlsruhe, Germany) were used as received. Acetonitrile (>99.9%, Chromasolv HPLC grade) and acetone (99.9% p.a.) from Fisher Scientific (Schwerte, Germany) were dried and stored over molecular sieves (MeCN: 4Å; acetone: 3Å). Alkali metal salts for the anion metathesis, lithium bis(trifluoromethylsulfonyl)imide $LiNTf_2$ (99%) from IoLiTec (Heilbronn, Germany) and sodium trifluoromethanesulfonate NaOTf (98%) were used a received. Dichloromethane (>99% puriss. p.a.) delivered from Fisher Scientific was used without further purification. Synthesis of the 2-ethoxy ethyl methanesulfonate[12,13] and silver trifluoroacetate[14] were carried out according to literature preparations. $CDCl_3$ (99.8% D) from Sigma Aldrich was stored over 4 Å molecular sieves and silver foil.

6.2 Synthesis of the ionic liquids

6.2.1 Synthesis of (2-ethoxyethyl)triethylphosphonium chloride $[P_{2222O2}][Cl]$

In a dried Schlenk flask were added 6.00 mL of triethylphosphine (40.7 mmol / 1.0 eq / 4.81 g), 6.12 mL of 2-chloroethyl ethyl ether (57.0 mmol / 1.4 eq / 6.19 g) and 20 mL acetonitrile under an inert atmosphere of argon. The reaction mixture was heated to 50°C for two weeks. The organic solvent and excess of reagents were removed by rotary evaporation and the residue dried in oil pump-vacuum (5 x 10^{-3} mbar) at 50°C for two days to give 8.06 g of an colourless solid (57.0 mmol / 87% yield).

^{1}H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.83 (dt, $^3J_{H/P}$ = 19.9 Hz, $^3J_{H/H}$ = 5.9 Hz, 2H, P-(CH$_2$)$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 3.49 (q, $^3J_{H/H}$ = 7.0 Hz, 2H, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 2.96 (dt, $^2J_{H/P}$ = 12.3 Hz, $^3J_{H/H}$ = 5.9 Hz, 2H, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 2.51 (dq, $^2J_{H/P}$ = 13.7 Hz, $^3J_{H/H}$ = 7.7 Hz, 6H, P-***CH$_2$***-CH$_3$), 1.29 (dt, $^3J_{H/P}$ = 18.2 Hz, $^3J_{H/H}$ = 7.7 Hz, 9H, P-CH$_2$-***CH$_3$***), 1.15 (t, $^3J_{H/H}$ = 7.0 Hz, 3H, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 67.0 (s, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 63.7 (d, $^2J_{C/P}$ = 7.8 Hz, P-(CH$_2$)$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 20.4 (d, $^1J_{C/P}$ = 49.7 Hz, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 15.1 (s, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***), 13.2 (d, $^1J_{C/P}$ = 48.8 Hz, P-***CH$_2$***-CH$_3$), 6.2 (d, $^2J_{C/P}$ = 5.5 Hz, P-CH$_2$-***CH$_3$***).

^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 38.7 (s).

6.2.2 Synthesis of (2-ethoxyethyl)triethylphosphonium bis(trifluoromethanesulfonyl)imide [P$_{2222O2}$][NTf2]

4.99 g (22.0 mmol / 1.0 eq) of [P$_{2222O2}$][Cl] and 8.21 g (28.6 mmol / 1.3 eq) LiNTf$_2$ were stirred overnight together with 30 mL of H$_2$O and 250 mL of dichloromethane. The organic phase was separated, washed with another 30 mL of H$_2$O and dried over a small amount of 4 Å molecular sieves overnight. The organic solvent was removed by means of rotary evaporation and the remainder dried in oil pump vacuum to yield 10.2 g of colourless, supercooled liquid (21.6 mmol / 98% yield).

^{1}H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.73 (dt, $^3J_{H/P}$ = 19.6 Hz, $^3J_{H/H}$ = 5.9 Hz, 2H, P-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 3.48 (q, $^3J_{H/H}$ = 7.0 Hz, 2H, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 2.43 (dt, $^2J_{H/P}$ = 12.0 Hz, $^3J_{H/H}$ = 5.9 Hz, 2H, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 2.18 (dq, $^2J_{H/P}$ = 13.0 Hz, $^3J_{H/H}$ = 7.7 Hz, 6H, P-***CH$_2$***-CH$_3$), 1.23 (dt, $^3J_{H/P}$ = 18.4 Hz, $^3J_{H/H}$ = 7.7 Hz, 9H, P-CH$_2$-***CH$_3$***), 1.15 (t, $^3J_{H/H}$ = 7.0 Hz, 3H, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 119.9 (q, $^1J_{C/F}$ = 321.3 Hz, ***CF$_3$***), 67.0 (s, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 62.9 (d, $^2J_{C/P}$ = 7.7 Hz, P-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 19.2 (d, $^1J_{C/P}$ = 49.9 Hz, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 14.9 (s, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***), 12.6 (d, $^1J_{C/P}$ = 49.2 Hz, P-***CH$_2$***-CH$_3$), 5.5 (d, $^2J_{C/P}$ = 5.5 Hz, P-CH$_2$-***CH$_3$***).

^{19}F{^{1}H} NMR (CDCl$_3$, 376 MHz, δ in ppm): -79.9 (s, ***CF$_3$***).

^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 38.9 (s).

6.2.3 Synthesis of triethylpentylphosphonium bromide [P_{2225}][Br]

6.00 mL of triethylphosphine (40.7 mmol / 1.0 eq / 4.81 g), 7.50 mL of 1-bromopentane (60.5 mmol / 1.5 eq / 9.14 g) and 80 mL acetonitrile were placed in a dry Schlenk flask under argon and stirred at 50°C for three days. The solvent was removed on a rotary evaporator, the excess reagents removed in vacuum and the residue dried on a vacuum line (5×10^{-3} mbar) to yield 10.4 g colourless solid (38.7 mmol / 95% yield)

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.54 (dq, $^2J_{H/P}$ = 13.2 Hz, $^3J_{H/H}$ = 7.7 Hz, 6H, P-$\boldsymbol{CH_2}$-CH_3), 2.40 (dt, $^2J_{H/P}$ = 13.0 Hz, $^3J_{H/H}$ = 8.4 Hz, 2H, P-$\boldsymbol{CH_2}$-$(CH_2)_4$-H), 1.64 – 1.51 (m, 2H, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 1.51 – 1.41 (m, 2H, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 1.39 – 1.21 (m, 11H, P-$(CH_2)_3$-$\boldsymbol{CH_2}$-CH_3 and P-$(CH_2)_4$-$\boldsymbol{CH_3}$), 0.89 (t, $^3J_{H/H}$ = 7.2 Hz, 3H, P-$(CH_2)_4$-$\boldsymbol{CH_3}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 33.0 (d, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-$(CH_2)_2$-H, $^3J_{C/P}$ = 14.5 Hz), 22.2 (s, P-$(CH_2)_3$-$\boldsymbol{CH_2}$-CH_3), 21.5 (d, $^2J_{C/P}$ = 4.8 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 18.3 (d, $^1J_{C/P}$ = 47.1 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_4$-H), 13.9 (s, P-$(CH_2)_4$-$\boldsymbol{CH_3}$), 12.6 (d, $^1J_{C/P}$ = 48.8 Hz, P-$\boldsymbol{CH_2}$-CH_3), 6.2 (d, $^2J_{C/P}$ = 5.5 Hz, P-CH_2-$\boldsymbol{CH_3}$).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, δ in ppm): 38.1 (s).

6.2.4 Synthesis of triethylpentylphosphonium bis(trifluoromethanesulfonyl)imide [P_{2225}][NTf_2]

10.4 g of triethylpentylphosphonium bromide [P_{2225}][Br] (38.6 mmol / 1.0 eq) and 14.4 g $LiNT_2$ (50.2 mmol / 1.3 eq) were stirred in a two phase system of 50 mL water and 250 mL dichloromethane overnight. The organic phase was separated and washed four times with 50 mL of water. Absence of bromide anions in the aqueous phase was confirmed by testing with 0.1 mol $AgNO_3$-solution. After drying over 4 Å molecular sieves overnight the solvent was removed by rotary evaporation and the residue dried in oil-pump vacuum at 60°C for two days yielding 18.0 g of a colourless liquid (38.2 mmol / 99%).

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.15 (dq, $^2J_{H/P}$ = 12.9 Hz, $^3J_{H/H}$ = 7.7 Hz, 6H, P-$\boldsymbol{CH_2}$-CH_3), 2.06 (dt, $^2J_{H/P}$ = 12.8 Hz, $^3J_{H/H}$ = 8.4 Hz, 2H, P-$\boldsymbol{CH_2}$-$(CH_2)_4$-H), 1.57 – 1.28 (m, 6H, P-CH_2-$\boldsymbol{(CH_2)_3}$-CH_3), 1.22 (dt, $^3J_{H/P}$ = 18.1 Hz, $^3J_{H/H}$ = 7.7 Hz, 9H, P-CH_2-$\boldsymbol{CH_3}$), 0.88 (t, $^3J_{H/H}$ = 7.2 Hz, 3H, P-$(CH_2)_4$-$\boldsymbol{CH_3}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 119.9 (q, $^1J_{C/F}$ = 321.4 Hz, $\boldsymbol{CF_3}$), 32.7 (d, $^3J_{C/P}$ = 14.5 Hz, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 21.8 (s, P-$(CH_2)_3$-$\boldsymbol{CH_2}$-CH_3), 21.0 (d, $^2J_{C/P}$ = 4.7 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 17.5 (d, $^1J_{C/P}$ = 47.6 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_4$-H), 13.6 (s, P-$(CH_2)_4$-$\boldsymbol{CH_3}$), 11.6 (d, $^1J_{C/P}$ = 49.3 Hz, P-$\boldsymbol{CH_2}$-CH_3), 5.4 (d, $^2J_{C/P}$ = 5.5 Hz, P-CH_2-$\boldsymbol{CH_3}$).

^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz, δ in ppm): -79.0 (s, $\boldsymbol{CF_3}$).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, δ in ppm): 38.3 (s).

6.2.5 Synthesis of triethyloctylphosphonium bromide [P_{2228}][Br]

To 80 mL acetonitrile in a dried Schlenk flask were added 6.00 mL of triethylphosphine (40.7 mmol / 1.0 eq / 4.81 g) and 9.00 ml 1-bromooctane (52.1 mmol / 1.3 eq / 10.1 g) under argon. The reaction mixture was heated to 50°C for three days and the solvent removed on a rotary evaporator. The excess of reagents were removed in oil pump vacuum and the product dried at 50°C at 3 x 10^{-3} mbar for two days to yield 12.3 g of product (39.5 mmol / 97% yield) obtained as colourless solid.

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.54 (dq, $^2J_{H/P}$ = 13.1 Hz, $^3J_{H/H}$ = 7.7 Hz, 6H, P-***CH₂***-CH₃), 2.39 (dt, $^2J_{H/P}$ = 13.0 Hz, $^3J_{H/H}$ = 8.3 Hz, 2H, P-$\boldsymbol{CH_2}$-$(CH_2)_7$-H), 1.57 (dt, $^3J_{H/P}$ = 16.0 Hz, $^3J_{H/H}$ = 7.4 Hz, 2H, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_6$-H), 1.47 (dt, $^4J_{H/P}$ = 14.9 Hz, $^3J_{H/H}$ = 6.8 Hz, 2H, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-$(CH_2)_5$-H), 1.35 – 1.17 (m, 17H, P-$(CH_2)_3$-$\boldsymbol{(CH_2)_4}$-CH_3 and P-CH_2-$\boldsymbol{CH_3}$), 0.85 (t, $^3J_{H/H}$ = 6.8 Hz, 3H, P-$(CH_2)_7$-$\boldsymbol{CH_3}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 31.8 (s, P-$(CH_2)_5$-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 31.0 (d, $^3J_{C/P}$ = 14.5 Hz, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-$(CH_2)_5$-H), 29.1 (s, P-$(CH_2)_3$-$\boldsymbol{CH_2}$-$(CH_2)_4$-H and P-$(CH_2)_4$-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 22.7 (s, P-$(CH_2)_6$-$\boldsymbol{CH_2}$-CH_3), 21.9 (d, $^2J_{C/P}$ = 4.7 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_6$-H), 18.4 (d, $^1J_{C/P}$ = 47.0 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_7$-H), 14.2 (s, P-$(CH_2)_7$-$\boldsymbol{CH_3}$), 12.6 (d, $^1J_{C/P}$ = 48.8 Hz, P-$\boldsymbol{CH_2}$-CH_3), 6.3 (d, $^2J_{C/P}$ = 5.5 Hz, P-CH_2-$\boldsymbol{CH_3}$).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, δ in ppm): 38.0 (s).

6.2.6 Synthesis of triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide [P_{2228}][NTf_2]

To a flask containing 50 mL water and 250 mL dichlormethane were added 12.1 g of triethyloctylphosphonium bromide [P_{2228}][Br] (38.9 mmol / 1.0 eq) and 14.5 g of $LiNTf_2$ (50,4 mmol / 1.3 eq). The mixture was vigorrously stirred overnight, the organic phase separated, washed three times with 50 mL of water until no halides could be detected in the aqueous phase by testing with 0.1 mol $AgNO_3$ solution and dried over 4 Å molecular sieves overnight. The organic solvent was removed under reduced pressure and the product dried at 60°C for 48 hours in oil-pump vacuum to obtain 19.9 g of the product as colourless liquid (38.9 mmol / 100 % yield).

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.16 (dq, $^2J_{H/P}$ = 12.8 Hz, $^3J_{H/H}$ = 7.7 Hz, 6H, P-$\boldsymbol{CH_2}$-CH_3), 2.06 (dt, $^2J_{H/P}$ = 12.7 Hz, $^3J_{H/H}$ = 8.1 Hz, 2H, P-$\boldsymbol{CH_2}$-$(CH_2)_7$-H), 1.58 – 1.37 (m, 4H, P-CH_2-$\boldsymbol{(CH_2)_2}$-$(CH_2)_5$-H), 1.36 – 1.08 (m, 17H, P-$(CH_2)_3$-$\boldsymbol{(CH_2)_4}$-CH_3 and P-CH_2-$\boldsymbol{CH_3}$), 0.85 (t, $^3J_{H/H}$ = 6.8 Hz, 3H, P-$(CH_2)_7$-$\boldsymbol{CH_3}$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, δ in ppm): 119.9 (q, $^1J_{C/F}$ = 321.4 Hz, ***CF_3***), 31.7 (s, P-$(CH_2)_5$-***CH_2***-$(CH_2)_2$-H) 30.7 (d, P-$(CH_2)_2$-***CH_2,*** $^3J_{C/P}$ = 14.6 Hz), 28.9 (s, P-$(CH_2)_3$-***CH_2***-$(CH_2)_4$-H) 28.8 (s, P-$(CH_2)_4$-***CH_2***-$(CH_2)_3$-H), 22.6 (s, P-$(CH_2)_6$-***CH_2***-CH_3), 21.3 (d, $^2J_{C/P}$ = 4.7 Hz, P-CH_2-***CH_2***-$(CH_2)_6$-H), 17.6 (d, $^1J_{C/P}$ = 47.5 Hz, P-***CH_2***-$(CH_2)_7$-H), 14.1 (s, P-$(CH_2)_7$-***CH_3***), 11.6 (d, $^1J_{C/P}$ = 49.2 Hz, P-***CH_2***-CH_3), 5.4 (d, $^2J_{C/P}$ = 5.5 Hz, P-CH_2-***CH_3***).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz, δ in ppm): -79.0 (s, ***CF_3***).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, δ in ppm): 38.3 (s).

6.2.7 Synthesis of (2-ethoxyethyl)tributylphosphonium bromide [P_{4442O2}][Br]

160 mL acetonitrile, 40 mL tributylphosphine (158 mmol / 1.0 eq / 32.0 g) and 24 mL 2-bromoethyl ethyl ether (214 mmol / 1.4 eq / 32.8 g) were placed in a dried Schlenk flask under argon. The mixture was heated to 55°C for four days and the solvent removed under reduced pressure. The residue was dissolved in 200 mL water and neutralized with saturated sodium bicarbonate solution. The aqueous solution was washed two times with 50 mL of hexane and extracted two times with 150 mL of dichloromethane. The combined dichloromethane phases were dried with $MgSO_4$, filtered and the solvent removed by rotary evaporation. After drying at 60°C for one day 53.6 g of the product (151 mmol / 96% yield) were obtained as slightly yellowish solid.

^1H NMR ($CDCl_3$, 400 MHz, δ in ppm): 3.79 (dt, $^3J_{H/P}$ = 20.0 Hz, $^3J_{H/H}$ = 5.9 Hz, 2H, P-CH_2-***CH_2***-O-$(CH_2)_2$-H), 3.46 (q, $^3J_{H/H}$ = 7.0 Hz, 2H, P-$(CH_2)_2$-O-***CH_2***-CH_3), 2.92 (dt, $^2J_{H/P}$ = 12.1 Hz, $^3J_{H/H}$ = 5.9 Hz, 2H, P-***CH_2***-CH_2-O-$(CH_2)_2$-H), 2.49 – 2.28 (m, 6H, P-***CH_2***-$(CH_2)_3$-H), 1.61 – 1.35 (m, 12H, P-CH_2-***$(CH_2)_2$***-CH_3), 1.13 (t, $^3J_{H/H}$ = 7.0 Hz, 3H, P-$(CH_2)_2$-O-CH_2-***CH_3***), 0.92 (t, $^3J_{H/H}$ = 7.1 Hz, 9H, P-$(CH_2)_3$-***CH_3***).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, δ in ppm): 66.9 (s, P-$(CH_2)_2$-O-***CH_2***-CH_3), 63.7 (d, $^2J_{C/P}$ = 7.8 Hz, P-CH_2-***CH_2***-O-$(CH_2)_2$-H), 24.0 (d, $^3J_{C/P}$ = 15.5 Hz, P-(CH_2)-***CH_2***-CH_3), 23.8 (d, $^2J_{C/P}$ = 4.8 Hz, P-CH_2-***CH_2***-$(CH_2)_2$-H), 21.2 (d, $^1J_{C/P}$ = 49.5 Hz, P-***CH_2***-CH_2-O-$(CH_2)_2$-H), 20.0 (d, $^1J_{C/P}$ = 47.3 Hz, P-***CH_2***-$(CH_2)_3$-H), 15.1 (s, P-$(CH_2)_2$-O-CH_2-***CH_3***), 13.5 (s, P-$(CH_2)_3$-***CH_3***).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, δ in ppm): 33.3 (s).

6.2.8 Synthesis of (2-ethoxyethyl)tributylphosphonium trifluoroacetate [P_{4442O2}][TFA]

5.08 g (2-ethoxyethyl)tributylphosphonium bromide [P_{4442O2}][Br] (14.3 mmol / 1.0 eq) were dissolved in 25 mL ethanol and a solution of 3.80 g silver trifluoroacetate (17.2 mmol/ 1.2 eq) in 25 mL ethanol was added and stirred for 20 h under exclusion of light. After filtration the solvent was removed under reduced pressure and the residue dissolved in 20 mL water. The aqueous solution was extracted two times with 100 mL dichloromethane. The organic phase was washed two times with 20 mL water whereby the absence of halide and silver was confirmed by testing with 0.1 mol $AgNO_3$ and 0.1 mol NaCl solution separately. The organic solvent was removed by rotary evaporation and the residue dried in oil-pump vacuum for two days yielding 5.14 g of the product (13.2 mmol / 93% yield) as slightly brown liquid.

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 3.62 (dt, $^{3}J_{H/P}$ = 19.9 Hz, $^{3}J_{H/H}$ = 5.9 Hz, 2H, P-CH_2-***CH_2***-O-$(CH_2)_2$-H), 3.33 (q, $^{3}J_{H/H}$ = 7.0 Hz, 2H, P-$(CH_2)_2$-O-***CH_2***-CH_3), 2.55 (dt, $^{2}J_{H/P}$ = 12.0 Hz, $^{3}J_{H/H}$ = 5.9 Hz, 2H, P-***CH_2***-CH_2-O-$(CH_2)_2$-H), 2.19 – 2.02 (m, 6H, P-***CH_2***-$(CH_2)_3$-H), 1.49 – 1.23 (m, 12H, P-CH_2-***$(CH_2)_2$***-CH_3), 1.01 (t, $^{3}J_{H/H}$ = 7.0 Hz, 3H, P-$(CH_2)_2$-O-CH_2-***CH_3***), 0.79 (t, $^{3}J_{H/H}$ = 7.1 Hz, 9H, P-$(CH_2)_3$-***CH_3***).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 160.2 (q, $^{2}J_{C/F}$ = 32.3 Hz), 117.2 (q, $^{1}J_{C/F}$ = 297.7 Hz, ***CF_3***), 66.6 (s, P-$(CH_2)_2$-O-***CH_2***-CH_3), 63.2 (d, $^{2}J_{C/P}$ = 7.7 Hz, P-CH_2-***CH_2***-O-$(CH_2)_2$-H), 23.7 (d, $^{3}J_{C/P}$ = 15.7 Hz, P-$(CH_2)_2$-***CH_2***-CH_3), 23.3 (d, $^{2}J_{C/P}$ = 4.8 Hz, P-CH_2-***CH_2***-$(CH_2)_2$-H), 20.3 (d, $^{1}J_{C/P}$ = 49.6 Hz, P-***CH_2***-CH_2-O-$(CH_2)_2$-H), 19.2 (d, $^{1}J_{C/P}$ = 47.5 Hz, P-***CH_2***-$(CH_2)_3$-H), 14.7 (s, P-$(CH_2)_2$-O-CH_2-***CH_3***), 13.0 (s, P-$(CH_2)_3$-***CH_3***).

^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz, δ in ppm): -74.8 (s, ***CF_3***).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, δ in ppm): 33.5 (s).

6.2.9 Synthesis of (2-ethoxyethyl)tributylphosphonium trifluoromethanesulfonate [P_{4442O2}][OTf]

To a solution of of 8.94 g (2-ethoxyethyl)tributylphosphonium bromide [P_{4442O2}][Br] (25.2 mmol / 1.0 eq) dissolved in 10 mL dry acetone was added a solution of 5.20 g sodium triflate (30.2 mmol / 1.2 eq) in 30 mL dry acetone. The obtained suspension was stirred for 24 hours, filtered and the solvent removed under reduced pressure. The residue was dissolved in 200 mL dichloromethane, 0.5 g Celite® added and the solution stored in a refrigerator for three hours while shaking from time to time. After filtration the organic phase was washed with 50 mL water and the absence of bromide was confirmed by testing with 0.1 mol $AgNO_3$ solution. The organic phase was dried over 4 Å molecular sieves for 24 hours, filtered and the solvent removed by means of rotary evaporation. After drying for 24 hours on a Schlenk line 9.32 g of the product (22.0 mmol / 87% yield) were obtained as slightly yellow liquid.

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 3.71 (dt, $^{3}J_{H/P}$ = 19.9 Hz, $^{3}J_{H/H}$ = 5.9 Hz, 2H, P-CH_2-***CH_2***-O-$(CH_2)_2$-H), 3.44 (q, $^{3}J_{H/H}$ = 7.0 Hz, 2H, P-$(CH_2)_2$-O-***CH_2***-CH_3), 2.50 (dt, $^{2}J_{H/P}$ = 12.0 Hz, $^{3}J_{H/H}$ = 5.9 Hz, 2H, P-***CH_2***-CH_2-O-$(CH_2)_2$-H), 2.21 – 2.04 (m, 6H, P-***CH_2***-$(CH_2)_3$-H), 1.59 – 1.37 (m, 12H, P-CH_2-***$(CH_2)_2$***-CH_3), 1.12 (t, $^{3}J_{H/H}$ = 7.0 Hz, 3H, P-$(CH_2)_2$-O-CH_2-***CH_3***), 0.90 (t, $^{3}J_{H/H}$ = 7.1 Hz, 9H, P-$(CH_2)_3$-***CH_3***).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 120.8 (q, $^{1}J_{C/F}$ = 320.7 Hz, ***CF$_3$***), 66.8 (s, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 63.3 (d, $^{2}J_{C/P}$ = 7.6 Hz, P-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 23.8 (d, $^{3}J_{C/P}$ = 15.7 Hz, P-CH$_2$-CH$_2$-***CH$_2$***), 23.5 (d, $^{2}J_{C/P}$ = 4.8 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_2$-H), 20.2 (d, $^{1}J_{C/P}$ = 49.8 Hz, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 19.4 (d, $^{1}J_{C/P}$ = 47.5 Hz, P-***CH$_2$***-(CH$_2$)$_3$-H), 15.0 (s, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***), 13.3 (s, P-(CH$_2$)$_3$-***CH$_3$***).

^{19}F{^{1}H} NMR (CDCl$_3$, 376 MHz, δ in ppm): -78.4 (s, ***CF$_3$***).

^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 33.5 (s).

6.2.10 Synthesis of (2-ethoxyethyl)tributylphosphonium bis(trifluoromethanesulfonyl)-imide [P$_{4442O2}$][NTf$_2$]

5.11 g of (2-ethoxyethyl)tributylphosphonium bromide [P$_{4442O2}$][Br] (14.4 mmol/ 1.0 eq) and 4.95 g of LiNTf$_2$ (17.3 mmol/ 1.2 eq) were dissolved in 50 mL dry acetone and stirred for one hour. The solvent was removed by rotary evaporation and the residue dissolved in 100 mL dichlormethane. The precipitate was filtered off and the organic phase washed two times with about 50 mL of water. The solvent was removed under reduced pressure and the product dried in oil-pump-vacuum for 2 days to obtain 7.81 g of the product (14.1 mmol / 98% yield) as a slightly yellowish liquid.

^{1}H NMR (DMSO-d$_6$, 400 MHz, δ in ppm): 3.69 (dt, $^{3}J_{H/P}$ = 19.0 Hz, $^{3}J_{H/H}$ = 6.1 Hz, 2H, P-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 3.47 (q, $^{3}J_{H/H}$ = 7.0 Hz, 2H, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 2.54 (dt, $^{2}J_{H/P}$ = 12.5 Hz, $^{3}J_{H/H}$ = 6.1 Hz, 2H, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 2.25 – 2.08 (m, 6H, P-***CH$_2$***-(CH$_2$)$_3$-H), 1.57 – 1.31 (m, 12H, P-CH$_2$-***(CH$_2$)$_2$***-CH$_3$), 1.13 (t, $^{3}J_{H/H}$ = 7.0 Hz, 3H, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***), 0.92 (t, $^{3}J_{H/H}$ = 7.2 Hz, 9H, P-(CH$_2$)$_3$-***CH$_3$***).

^{13}C{^{1}H} NMR (DMSO-d$_6$, 101 MHz, δ in ppm): 119.5 (q, $^{1}J_{C/F}$ = 321.9 Hz, ***CF$_3$***), 65.7 (s, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 62.6 (d, $^{2}J_{C/P}$ = 6.2 Hz, P-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 23.3 (d, $^{3}J_{C/P}$ = 16.0 Hz, P-(CH$_2$)$_2$-***CH$_2$***-CH$_3$), 22.6 (d, $^{2}J_{C/P}$ = 4.5 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_2$-H), 19.2 (d, $^{1}J_{C/P}$ = 48.8 Hz, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 18.2 (d, $^{1}J_{C/P}$ = 47.6 Hz, P-***CH$_2$***-(CH$_2$)$_3$-H), 14.7 (s, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***), 13.1 (s, P-(CH$_2$)$_3$-***CH$_3$***).

^{19}F{^{1}H} NMR (DMSO-d$_6$, 376 MHz, δ in ppm): -78.8 (s, ***CF$_3$***).

^{31}P{^{1}H} NMR (DMSO-d$_6$, 162 MHz, δ in ppm): 33.7 (s).

6.2.11 Synthesis of (2-ethoxyethyl)tributylphosphonium methanesulfonate [P$_{4442O2}$][OMs]

To a dried Schlenk flask were added under argon 15.9 g 2-ethoxy ethyl methanesulfonate (94.5 mmol / 1.0 eq), 28.3 mL tributylphosphine (113 mmol / 1.2 eq / 28.4 g) and 100 mL acetonitrile. The mixture was heated at 50°C for 14 days and the solvent removed by means of rotary evaporation. The residue was then dissolved in 100 mL water and the aqueous phase washed three times with 100 mL diethyl ether. The water was rotated off and the product dried at 80°C for 24 hours in oil pump vacuum to yield 27.9 g of the product (75.3 mmol / 80% yield) as colourless liquid.

^{1}H NMR (CDCl$_3$, 400 MHz, δ in ppm): 3.67 (dt, $^3J_{H/P}$ = 20.1 Hz, $^3J_{H/H}$ = 5.9 Hz, 2H, P-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 3.34 (q, $^3J_{H/H}$ = 7.0 Hz, 2H, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 2.61 (dt, $^2J_{H/P}$ = 12.1 Hz, $^3J_{H/H}$ = 5.9 Hz, 2H, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 2.54 (s, 3H, SO$_3$-***CH$_3$***), 2.24 – 2.07 (m, 6H, P-***CH$_2$***-(CH$_2$)$_3$-H), 1.47 – 1.28 (m, 12H, P-CH$_2$-***(CH$_2$)$_2$***-CH$_3$), 1.02 (t, $^3J_{H/H}$ = 7.0 Hz, 3H, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***), 0.81 (t, $^3J_{H/H}$ = 7.1 Hz, 9H, P-(CH$_2$)$_3$-***CH$_3$***).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 66.1 (s, P-(CH$_2$)$_2$-O-***CH$_2$***-CH$_3$), 63.0 (d, $^2J_{C/P}$ = 7.7 Hz, P-CH$_2$-***CH$_2$***-O-(CH$_2$)$_2$-H), 39.0 (s, SO$_3$-CH$_3$), 23.3 (d, $^3J_{C/P}$ = 15.7 Hz, P-CH$_2$-CH$_2$-***CH$_2$***), 23.0 (d, $^2J_{C/P}$ = 4.8 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_2$-H), 19.8 (d, $^1J_{C/P}$ = 49.5 Hz, P-***CH$_2$***-CH$_2$-O-(CH$_2$)$_2$-H), 18.8 (d, $^1J_{C/P}$ = 47.4 Hz, P-***CH$_2$***-(CH$_2$)$_3$-H), 14.4 (s, P-(CH$_2$)$_2$-O-CH$_2$-***CH$_3$***), 12.8 (s, P-(CH$_2$)$_3$-***CH$_3$***).

^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 33.2 (s).

6.2.12 Synthesis of ethyltributylphosphonium bromide [P$_{4442}$][Br]

To a dried Schlenk flask were added 35.0 mL tributylphosphine (140 mmol/ 1.0 eq / 28.0 g), 12.5 mL 1-bromoethane (0.168 mmol/ 1.2 eq / 18.3 g) and 150 mL acetonitrile. The reaction was stirred at 25°C for two days, the solvent and excess of reagents were removed under reduced pressure and the residue was dried in oil-pump vacuum at 50°C for two days. 42.3 g of the product (136 mmol / 97% yield) were obtained as a colourless solid.

^{1}H NMR (CDCl$_3$, 400 MHz, δ in ppm): 2.52 (dq, $^2J_{H/P}$ = 15.4 Hz, $^3J_{H/H}$ = 7.7 Hz, 2H, P-***CH$_2$***-CH$_3$), 2.47 – 2.33 (m, 6H, P-***CH$_2$***-(CH$_2$)$_3$-H), 1.59 – 1.42 (m, 12H, P-CH$_2$-***(CH$_2$)$_2$***-CH$_3$), 1.25 (dt, $^3J_{H/P}$ = 18.1 Hz, $^3J_{H/H}$ = 7.7 Hz, 3H, P-CH$_2$-***CH$_3$***), 0.93 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, P-(CH$_2$)$_3$-***CH$_3$***).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 24.0 (d, $^3J_{C/P}$ = 15.2 Hz, P-(CH$_2$)$_2$-***CH$_2$***-CH$_3$), 23.8 (d, $^2J_{C/P}$ = 4.8 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_2$-H), 18.8 (d, $^1J_{C/P}$ = 47.3 Hz, P-***CH$_2$***-(CH$_2$)$_3$-H), 13.5 (s, P-(CH$_2$)$_3$-***CH$_3$***), 13.3 (d, $^1J_{C/P}$ = 48.9 Hz, P-***CH$_2$***-CH$_3$), 6.3 (d, $^2J_{C/P}$ = 5.5 Hz, P-CH$_2$-***CH$_3$***).

^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 34.6 (s).

6.2.13 Synthesis of ethyltributylphosphonium bis(trifluoromethanesulfonyl)imide $[P_{4442}][NTf_2]$

8.5 g ethyltributylphosphonium bromide $[P_{4442}][Br]$ (27.3 mmol / 1.0 eq) and 8.62 g $LiNTf_2$ (30.0 mmol / 1.1 eq) were dissolved in 150 mL dry acetone and stirred for 24 hours. The solvent was removed by rotary evaporation, the residue dissolved in 200 mL dichloromethane, filtered and washed four times with 150 mL deionised water. Afterwards the organic solvent was removed under reduced pressure and the residue dried on a Schlenk line at 50°C for two days yielding 13.7 g of product (26.8 mmol / 98% yield) obtained as colourless, supercooled liquid.

^1H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.16 (dq, $^2J_{H/P}$ = 12.9 Hz, $^3J_{H/H}$ = 7.8 Hz, 2H, P-***CH_2***-CH_3), 2.12 – 2.02 (m, 6H, P-***CH_2***-$(CH_2)_3$-H), 1.57 – 1.43 (m, 12H, P-CH_2-***$(CH_2)_2$***-CH_3), 1.23 (dt, $^3J_{H/P}$ = 18.2 Hz, $^3J_{H/H}$ = 7.7 Hz, 3H, P-CH_2-***CH_3***), 0.95 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, P-$(CH_2)_3$-***CH_3***).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, δ in ppm): 120.0 (q, $^1J_{C/F}$ = 323.9 Hz, ***CF_3***), 23.8 (d, $^3J_{C/P}$ = 15.2 Hz, P-$(CH_2)_2$-***CH_2***-CH_3), 23.4 (d, $^2J_{C/P}$ = 4.7 Hz, P-CH_2-***CH_2***-$(CH_2)_2$-H), 18.1 (d, $^1J_{C/P}$ = 47.8 Hz, P-***CH_2***-$(CH_2)_3$-H), 13.3 (s, P-$(CH_2)_3$-***CH_3***), 12.4 (d, $^1J_{C/P}$ = 49.1 Hz, P-***CH_2***-CH_3), 5.6 (d, $^3J_{C/P}$ = 5.5 Hz, P-CH_2-***CH_3***).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz, δ in ppm): -78.9 (s, ***CF_3***).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, δ in ppm): 34.9 (s).

6.2.14 Synthesis of tributylhexylphosphonium bromide $[P_{4446}][Br]$

20.0 mL tributylphosphine (80.1 mmol / 1.0 eq / 16.2 g) and 13.5 mL 1-bromohexane (96.1 mmol / 1.2 eq / 15.9 g) were added to 100 mL acetonitrile in a dried Schlenk flask under argon atmosphere. The reaction mixture was stirred for two days at 50°C and the solvent removed on a rotary evaporator. The excess of reagents was removed in vacuum and the residue dried at 50°C for two day to obtain the 29.1 g of the product (79.3 mmol / 99% yield) as a colourless solid.

^1H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.25 – 2.02 (m, 8H, P-***CH_2***-$(CH_2)_3$-H and P-***CH_2***-$(CH_2)_5$-H), 1.35 – 1.13 (m, 16H, P-CH_2-***$(CH_2)_2$***-CH_3 and P-CH_2-***$(CH_2)_2$***-$(CH_2)_3$-H), 1.05 – 0.94 (m, 4H, P-$(CH_2)_3$-***$(CH_2)_2$***-CH_3), 0.66 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, P-$(CH_2)_3$-***CH_3***), 0.57 (t, $^3J_{H/H}$ = 6.9 Hz, 3H, P-$(CH_2)_5$-***CH_3***).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, δ in ppm): 30.4 (s, P-$(CH_2)_3$-***CH_2***-$(CH_2)_2$-H), 29.8 (d, $^3J_{C/P}$ = 14.7 Hz P-$(CH_2)_2$-***CH_2***-$(CH_2)_3$-H), 23.3 ($^3J_{C/P}$ = 15.3 Hz, P-$(CH_2)_2$-***CH_2***-CH_3), 23.2 (d, $^2J_{C/P}$ = 4.8 Hz, P-CH_2-***CH_2***-$(CH_2)_2$-H), 21.7 (s, P-$(CH_2)_4$-***CH_2***-CH_3), 21.2 (d, $^2J_{C/P}$ = 4.7 Hz, P-CH_2-***CH_2***-$(CH_2)_4$-H), 18.7 (d, $^1J_{C/P}$ = 47.1 Hz, P-***CH_2***-$(CH_2)_5$-H), 18.5 (d, $^1J_{C/P}$ = 47.3 Hz, P-***CH_2***-$(CH_2)_3$-H), 13.3 (s, P-$(CH_2)_5$-***CH_3***), 12.9 (s, P-$(CH_2)_3$-***CH_3***).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, δ in ppm): 32.5 (s).

6.2.15 Synthesis of tributylhexylphosphonium bis(trifluoromethanesulfonyl)imide [P_{4446}][NTf_2]

9.0 g of tributylhexylphosphonium bromide [P_{4446}][Br] (24.5 mmol / 1.0 eq) and 8.5 g lithium bis(trifluoromethanesulfonyl)imide (29.4 mmol / 1.2 eq) were dissolved in 100 mL dry acetone and stirred at 25°C for one day. The solvent was removed under reduced pressure. The residue was dissolved in 250 mL dichloromethane, filtered and washed three times with about 150 mL of deionised water. The organic phase was separated, the solvent removed on a rotary evaporator and the residue dried in oil-pump vacuum (3×10^{-3} mbar) to yield 13.6 g of the ionic liquid (24.0 mmol / 98% yield) as colourless liquid.

^1H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.16 – 2.01 (m, 8H, P-$\boldsymbol{CH_2}$-$(CH_2)_3$-H and P-$\boldsymbol{CH_2}$-$(CH_2)_5$-H), 1.54 – 1.36 (m, 16H, P-CH_2-$\boldsymbol{(CH_2)_2}$-CH_3 and P-CH_2-$\boldsymbol{(CH_2)_2}$-$(CH_2)_3$-H), 1.34 – 1.20 (m, 4H, P-$(CH_2)_3$-$\boldsymbol{(CH_2)_2}$-CH_3), 0.92 (t, $^3J_{H/H}$ = 6.9 Hz, 9H, P-$(CH_2)_3$-$\boldsymbol{CH_3}$), 0.85 (t, $^3J_{H/H}$ = 7.0 Hz, 3H, P-$(CH_2)_5$-$\boldsymbol{CH_3}$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz, δ in ppm): 119.9 (q, $^1J_{C/F}$ = 321.5 Hz, $\boldsymbol{CF_3}$), 30.9 (s, P-$(CH_2)_3$-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 30.2 (d, $^3J_{C/P}$ = 14.8 Hz P-$(CH_2)_2$-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 23.7 ($^3J_{C/P}$ = 15.3 Hz, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-CH_3), 23.4 (d, $^2J_{C/P}$ = 4.7 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 22.3 (s, P-$(CH_2)_4$-$\boldsymbol{CH_2}$-CH_3), 21.4 (d, $^2J_{C/P}$ = 4.7 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_4$-H), 18.6 (d, $^1J_{C/P}$ = 47.4 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_5$-H), 18.4 (d, $^1J_{C/P}$ = 47.7 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 13.8 (s, P-$(CH_2)_5$-$\boldsymbol{CH_3}$), 13.2 (s, P-$(CH_2)_3$-$\boldsymbol{CH_3}$).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz, δ in ppm): -78.9 (s, $\boldsymbol{CF_3}$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, δ in ppm): 33.1 (s).

6.2.16 Synthesis of tributyloctylphosphonium bromide [P_{4448}][Br]

To 150 mL acetonitrile in a dried Schlenk flask were added 20.0 mL tributylphoshpine (80.1 mmol / 1.0 eq / 16.2 g) and 16.6 mL 1-bromooctane (96.1 mmol / 1.2 eq / 18.6 g) under an atmosphere of argon. The mixture was heated at 55°C for two days and the solvent removed by rotary evaporation. The excess of reagents was removed in vacuum and the residue dried on a Schlenk line at 55°C for three days to obtain 30.4 g product (76.8 mmol / 96%) as a colourless solid.

^1H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.53 – 2.29 (m, 8H, P-$\boldsymbol{CH_2}$-$(CH_2)_3$-H and P-$\boldsymbol{CH_2}$-$(CH_2)_7$-H), 1.59 – 1.41 (m, 16H, P-CH_2-$\boldsymbol{(CH_2)_2}$-CH_3 and P-CH_2-$\boldsymbol{(CH_2)_2}$-$(CH_2)_5$-H), 1.35 – 1.17 (m, 8H, P-$(CH_2)_3$-$\boldsymbol{(CH_2)_4}$-CH_3), 0.95 (t, $^3J_{H/H}$ = 6.6 Hz, 9H, P-$(CH_2)_3$-$\boldsymbol{CH_3}$), 0.85 (t, $^3J_{H/H}$ = 6.6 Hz, 3H, P-$(CH_2)_7$-$\boldsymbol{CH_3}$).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 31.8 (s, P-(CH$_2$)$_5$-***CH$_2$***-(CH$_2$)$_2$-H), 30.9 (d, ^{3}J$_{C/P}$ = 14.6 Hz, P-(CH$_2$)$_2$-***CH$_2$***-(CH$_2$)$_5$-H), 29.1 (s, P-(CH$_2$)$_4$-***CH$_2$***-(CH$_2$)$_3$-H), 29.0 (d, ^{4}J$_{C/P}$ = 1.0 Hz, P-(CH$_2$)$_3$-***CH$_2$***-(CH$_2$)$_4$-H), 24.1 (^{3}J$_{C/P}$ = 15.3 Hz, P-(CH$_2$)$_2$-***CH$_2$***-CH$_3$), 24.0 (d, ^{2}J$_{C/P}$ = 4.8 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_2$-H), 22.7 (s, P-(CH$_2$)$_6$-***CH$_2$***-CH$_3$), 22.0 (d, ^{2}J$_{C/P}$ = 4.8 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_4$-H), 19.5 (d, ^{1}J$_{C/P}$ = 47.2 Hz, P-***CH$_2$***-(CH$_2$)$_7$-H), 19.3 (d, ^{1}J$_{C/P}$ = 47.3 Hz, P-***CH$_2$***-(CH$_2$)$_3$-H), 14.2 (s, P-(CH$_2$)$_7$-***CH$_3$***), 13.6 (s, P-(CH$_2$)$_3$-***CH$_3$***).

^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 32.7 (s).

6.2.17 Synthesis of tributyloctylphosphonium bis(trifluoromethanesulfonyl)imide [P$_{4448}$][NTf$_2$]

In 200 mL dry acetone were dissolved 8.5 g of tributyloctylphosphonium bromide [P$_{4448}$][Br] (21.5 mmol / 1.0 eq) and 6.8 g LiNTf$_2$ (23.6 mmol / 1.1 eq). The solution was stirred for 12 hours, the solvent removed by rotary evaporation, the residue dissolved in 200 mL dichloromethane, filtered and washed three times with 100 mL deionised water. The organic phase was separated, the solvent removed on a rotary evaporator and the obtained ionic liquid dried at 50°C for two days yielding 12.7 g of the product (21.3 mmol / 99% yield) obtained as colourless liquid.

^{1}H NMR (CDCl$_3$, 400 MHz, δ in ppm): 2.18 – 2.00 (m, 8H, P-***CH$_2$***-(CH$_2$)$_3$-H and P-***CH$_2$***-(CH$_2$)$_7$-H), 1.57 – 1.39 (m, 16H, P-CH$_2$-**(*CH$_2$*)$_2$**-CH$_3$ and P-CH$_2$-**(*CH$_2$*)$_2$**-(CH$_2$)$_5$-H), 1.36 – 1.21 (m, 8H, P-(CH$_2$)$_3$-**(*CH$_2$*)$_4$**-CH$_3$), 0.96 (t, ^{3}J$_{H/H}$ = 7.1 Hz, 9H, P-(CH$_2$)$_3$-***CH$_3$***), 0.87 (t, ^{3}J$_{H/H}$ = 6.6 Hz, 3H, P-(CH$_2$)$_7$-***CH$_3$***).

^{13}C{^{1}H} NMR (CDCl$_3$, 101 MHz, δ in ppm): 121.6 (q, ^{1}J$_{C/F}$ = 322.9 Hz, ***CF$_3$***), 31.7 (s, P-(CH$_2$)$_5$-***CH$_2$***-(CH$_2$)$_2$-H), 30.7 (d, ^{3}J$_{C/P}$ = 14.7 Hz P-(CH$_2$)$_2$-***CH$_2$***-(CH$_2$)$_5$-H), 29.0 (s, P-(CH$_2$)$_4$-***CH$_2$***-(CH$_2$)$_3$-H), 28.8 (d, ^{4}J$_{C/P}$ = 1.0 Hz, P-(CH$_2$)$_3$-***CH$_2$***-(CH$_2$)$_4$-H), 23.9 (^{3}J$_{C/P}$ = 15.3 Hz, P-(CH$_2$)$_2$-***CH$_2$***-CH$_3$), 23.5 (d, ^{2}J$_{C/P}$ = 4.7 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_2$-H), 22.7 (s, P-(CH$_2$)$_6$-***CH$_2$***-CH$_3$), 21.6 (d, ^{2}J$_{C/P}$ = 4.7 Hz, P-CH$_2$-***CH$_2$***-(CH$_2$)$_6$-H), 18.8 (d, ^{1}J$_{C/P}$ = 47.3 Hz, P-***CH$_2$***-(CH$_2$)$_7$-H), 18.5 (d, ^{1}J$_{C/P}$ = 47.6 Hz, P-***CH$_2$***-(CH$_2$)$_3$-H), 14.1 (s, P-(CH$_2$)$_7$-***CH$_3$***), 13.3 (s, P-(CH$_2$)$_3$-***CH$_3$***).

^{19}F{^{1}H} NMR (CDCl$_3$, 376 MHz, δ in ppm): -78.9 (s, ***CF$_3$***).

^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz, δ in ppm): 33.1 (s).

6.2.18 Synthesis of tributyldecylphosphonium bromide [P$_{44410}$][Br]

Under argon atmosphere, 15.0 mL tributylphoshpine (60.0 mmol / 1.0 eq / 12.2 g), 16.2 mL 1-bromooctane (78.0 mmol / 1.3 eq / 17.3 g) along with 80 mL acetonitrile were placed in a dried Schlenk flask. After heating the reaction mixture at 50°C for three days the solvent was removed under reduced pressure and the excess of reagents distilled off in vacuum. The residue was dried in oil-pump vacuum (5 x 10^{-3} bar) at 50°C for two days yielding 24.2 g of the product (57.1 mmol / 95% yield) as colourless solid.

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.53 – 2.31 (m, 8H, P-$\boldsymbol{CH_2}$-$(CH_2)_3$-H and P-$\boldsymbol{CH_2}$-$(CH_2)_9$-H), 1.59 – 1.39 (m, 16H, P-CH_2-$\boldsymbol{(CH_2)_2}$-CH_3 and P-CH_2-$\boldsymbol{(CH_2)_2}$-$(CH_2)_7$-H), 1.36 – 1.14 (m, 12H, P-$(CH_2)_3$-$\boldsymbol{(CH_2)_6}$-CH_3), 0.95 (t, $^3J_{H/H}$ = 7.0 Hz, 9H, P-$(CH_2)_3$-$\boldsymbol{CH_3}$), 0.85 (t, $^3J_{H/H}$ = 6.9 Hz, 3H, P-$(CH_2)_7$-$\boldsymbol{CH_3}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 31.9 (s, P-$(CH_2)_7$-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 30.9 (d, $^3J_{C/P}$ = 14.6 Hz, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-$(CH_2)_{7z}$-H), 29.5 (s, P-$(CH_2)_5$-$\boldsymbol{CH_2}$-$(CH_2)_4$-H), 29.4 (s, P-$(CH_2)_4$-$\boldsymbol{CH_2}$-$(CH_2)_5$-H), 29.3 (s, P-$(CH_2)_6$-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 29.1 (d, $^4J_{C/P}$ = 0.8 Hz, P-$(CH_2)_3$-$\boldsymbol{CH_2}$-$(CH_2)_6$-H), 24.1 (d, $^3J_{C/P}$ = 14.7 Hz, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-CH_3), 24.0 (d, $^2J_{C/P}$ = 4.5 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 22.7 (s, P-$(CH_2)_8$-$\boldsymbol{CH_2}$-CH_3), 22.0 (d, $^2J_{C/P}$ = 4.8 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_8$-H), 19.5 (d, $^1J_{C/P}$ = 47.0 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_9$-H), 19.3 (d, $^1J_{C/P}$ = 47.3 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 14.2 (s, P-$(CH_2)_9$-$\boldsymbol{CH_3}$), 13.6 (s, P-$(CH_2)_3$-$\boldsymbol{CH_3}$).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, δ in ppm): 32.8 (s).

6.2.19 Synthesis of tributyldecylphosphonium bis(trifluoromethanesulfonyl)imide [P_{44410}][NTf_2]

For the anion metathesis reaction 8.0 g tributyldecylphosphonium bromide [P_{44410}][Br] (18.9 mmol / 1.0 eq) and 6.0 g of $LiNTf_2$ (20.8 mmol / 1.1 eq) were dissolved in 120 mL of dry acetone and stirred at 25°C for 24 hours. The solvent was removed on a rotary evaporator, the residue dissolved in 150 mL dichloromethane, filtered and washed three times with about 75 mL of deionised water. The organic phase was separated, the solvent removed under reduced pressure and finally dried on a Schlenk line at 50°C for 2 days to obtain 11.7 g of the colourless ionic liquid (18.8 mmol / 99% yield).

^{1}H NMR ($CDCl_3$, 400 MHz, δ in ppm): 2.18 – 1.97 (m, 8H, P-$\boldsymbol{CH_2}$-$(CH_2)_3$-H and P-$\boldsymbol{CH_2}$-$(CH_2)_9$-H), 1.58 – 1.37 (m, 16H, P-CH_2-$\boldsymbol{(CH_2)_2}$-CH_3 and P-CH_2-$\boldsymbol{(CH_2)_2}$-$(CH_2)_7$-H), 1.36 – 1.15 (m, 12H, P-$(CH_2)_3$-$\boldsymbol{(CH_2)_6}$-CH_3), 0.97 (t, $^3J_{H/H}$ = 6.9 Hz, 9H, P-$(CH_2)_3$-$\boldsymbol{CH_3}$), 0.87 (t, $^3J_{H/H}$ = 7.0 Hz, 3H, P-$(CH_2)_7$-$\boldsymbol{CH_3}$).

^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz, δ in ppm): 120.0 (q, $^1J_{C/F}$ = 321.4 Hz, $\boldsymbol{CF_3}$), 32.0 (s, P-$(CH_2)_7$-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 30.7 (d, $^3J_{C/P}$ = 14.6 Hz P-$(CH_2)_2$-$\boldsymbol{CH_2}$-$(CH_2)_7$-H), 29.5 (s, P-$(CH_2)_5$-$\boldsymbol{CH_2}$-$(CH_2)_4$-H), 29.4 (s, P-$(CH_2)_4$-$\boldsymbol{CH_2}$-$(CH_2)_5$-H), 29.3 (s, P-$(CH_2)_6$-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 28.9 (d, $^4J_{C/P}$ = 0.9 Hz, P-$(CH_2)_3$-$\boldsymbol{CH_2}$-$(CH_2)_6$-H), 23.9 (d, $^3J_{C/P}$ = 15.2 Hz, P-$(CH_2)_2$-$\boldsymbol{CH_2}$-CH_3), 23.6 (d, $^2J_{C/P}$ = 4.8 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_2$-H), 22.8 (s, P-$(CH_2)_8$-$\boldsymbol{CH_2}$-CH_3), 21.6 (d, $^2J_{C/P}$ = 4.7 Hz, P-CH_2-$\boldsymbol{CH_2}$-$(CH_2)_8$-H), 18.8 (d, $^1J_{C/P}$ = 47.4 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_9$-H), 18.6 (d, $^1J_{C/P}$ = 47.6 Hz, P-$\boldsymbol{CH_2}$-$(CH_2)_3$-H), 14.2 (s, P-$(CH_2)_9$-$\boldsymbol{CH_3}$), 13.4 (s, P-$(CH_2)_3$-$\boldsymbol{CH_3}$).

$^{19}F\{^1H\}$ NMR ($CDCl_3$, 376 MHz, δ in ppm): -78.8 (s, ***CF_3***).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz, δ in ppm): 33.1 (s).

7. NMR Spectra

7. 1 NMR spectra of [P_{222202}][Cl]

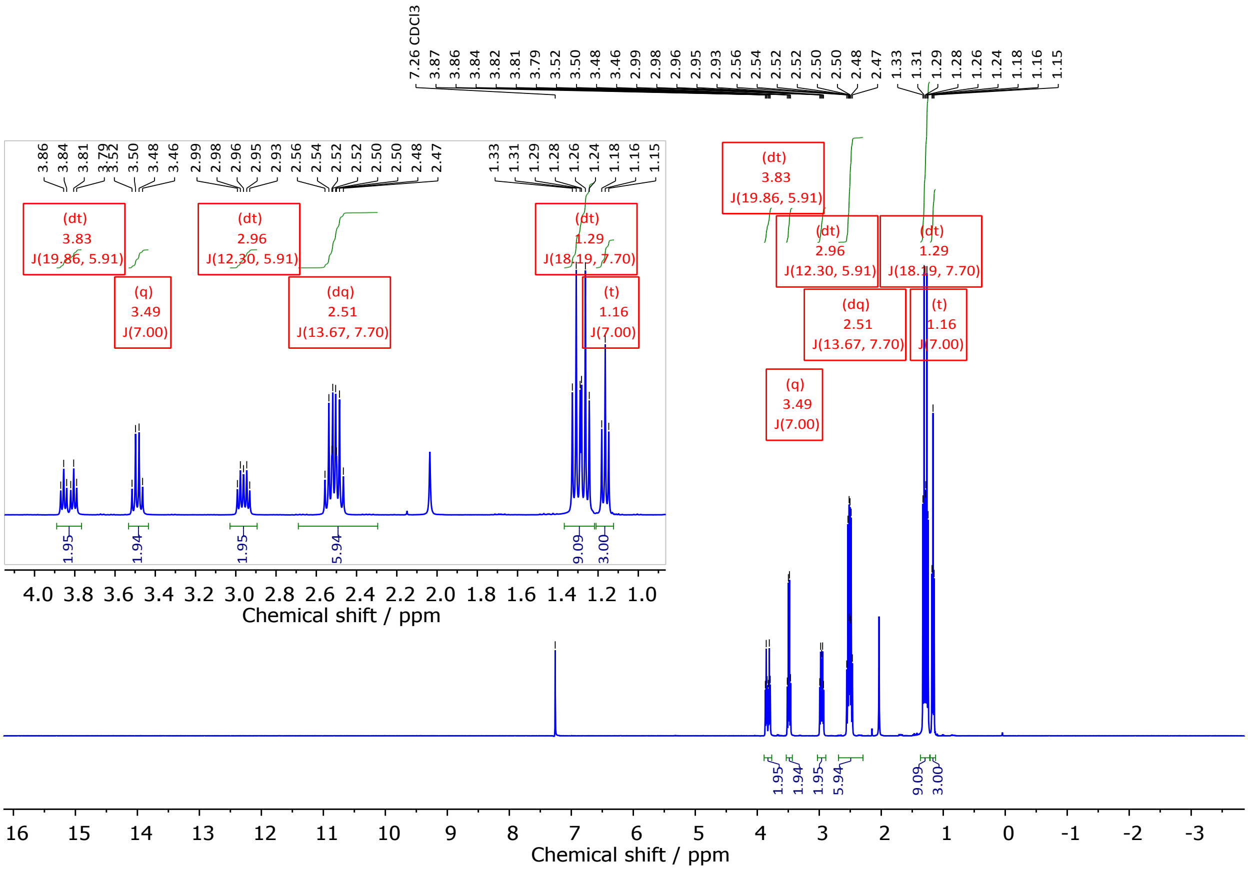

Figure S10: ^{1}H NMR spectrum of [P_{222202}][Cl].

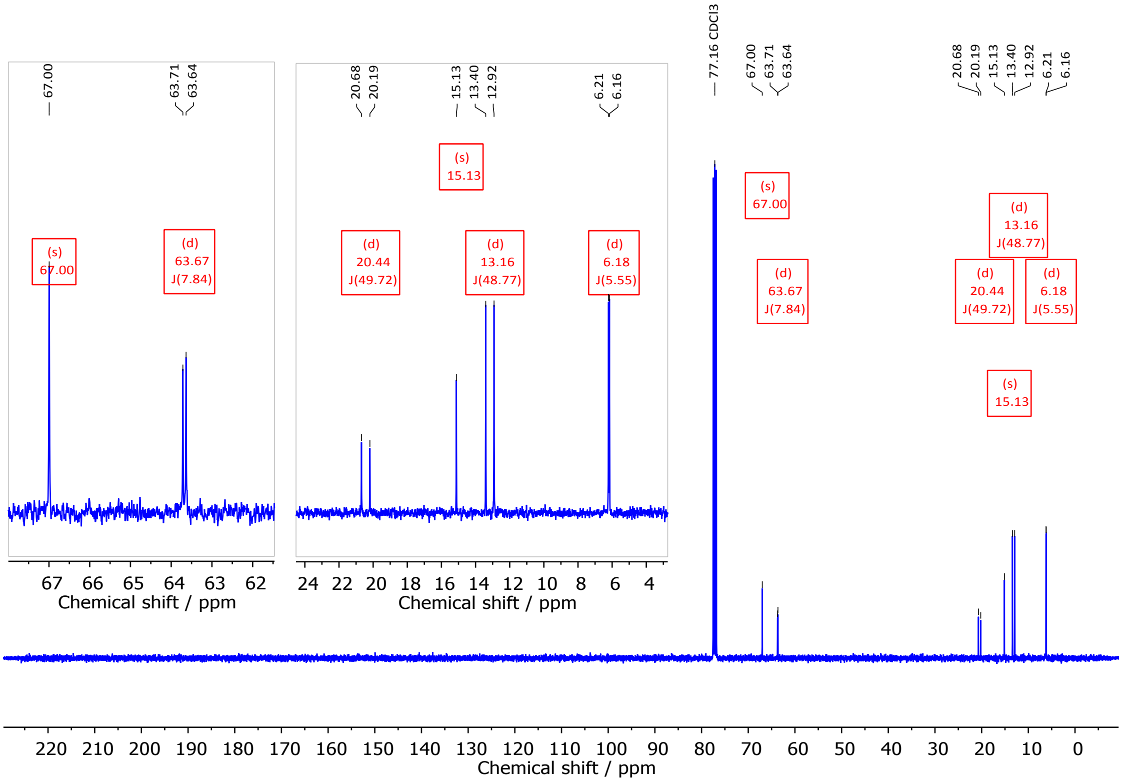

Figure S11: ^{13}C{^{1}H} NMR spectrum of [P$_{2222O2}$][Cl].

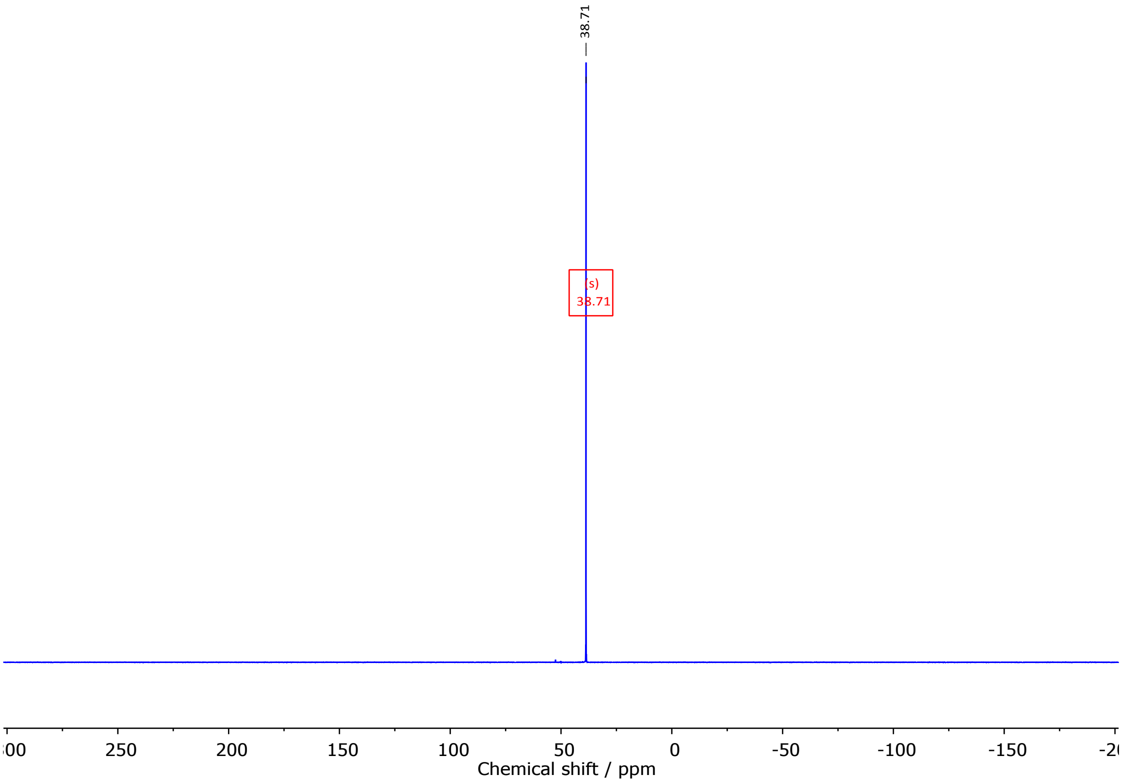

Figure S12: ^{31}P{^{1}H} NMR spectrum of [P$_{2222O2}$][Cl].

7.2 NMR spectra of [P_{222202}][NTf_2]

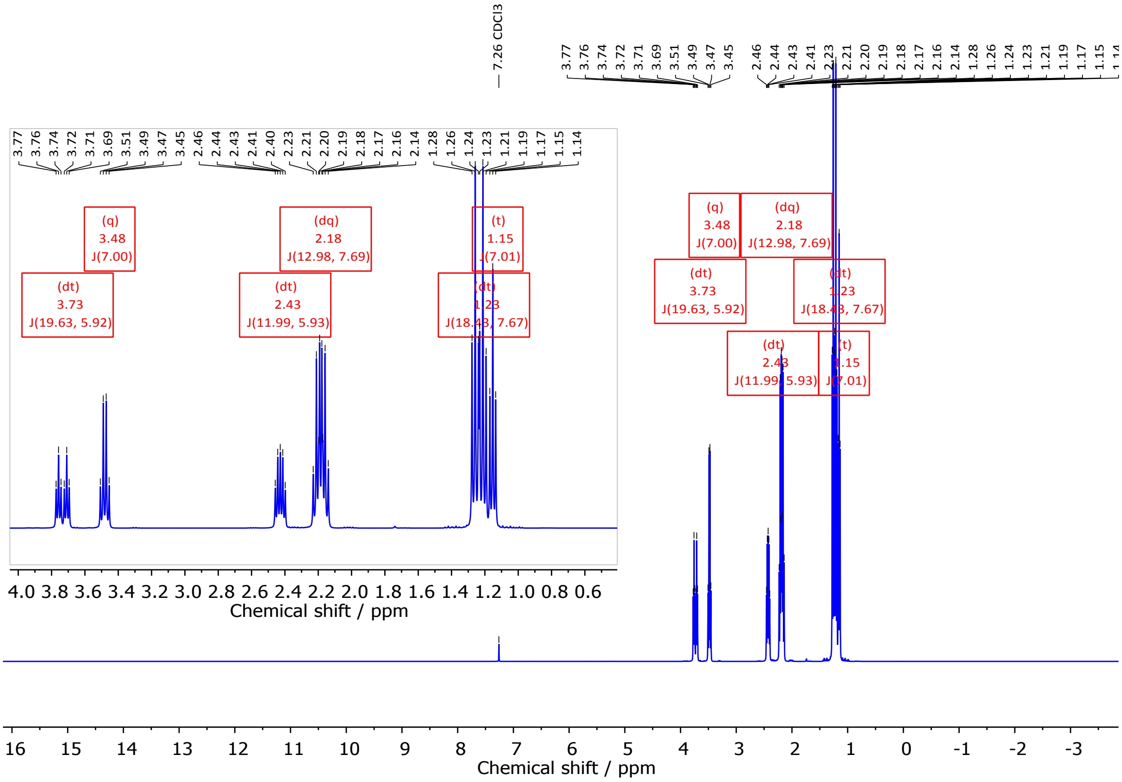

Figure S13: ^{1}H NMR spectra of [P_{222202}][NTf_2].

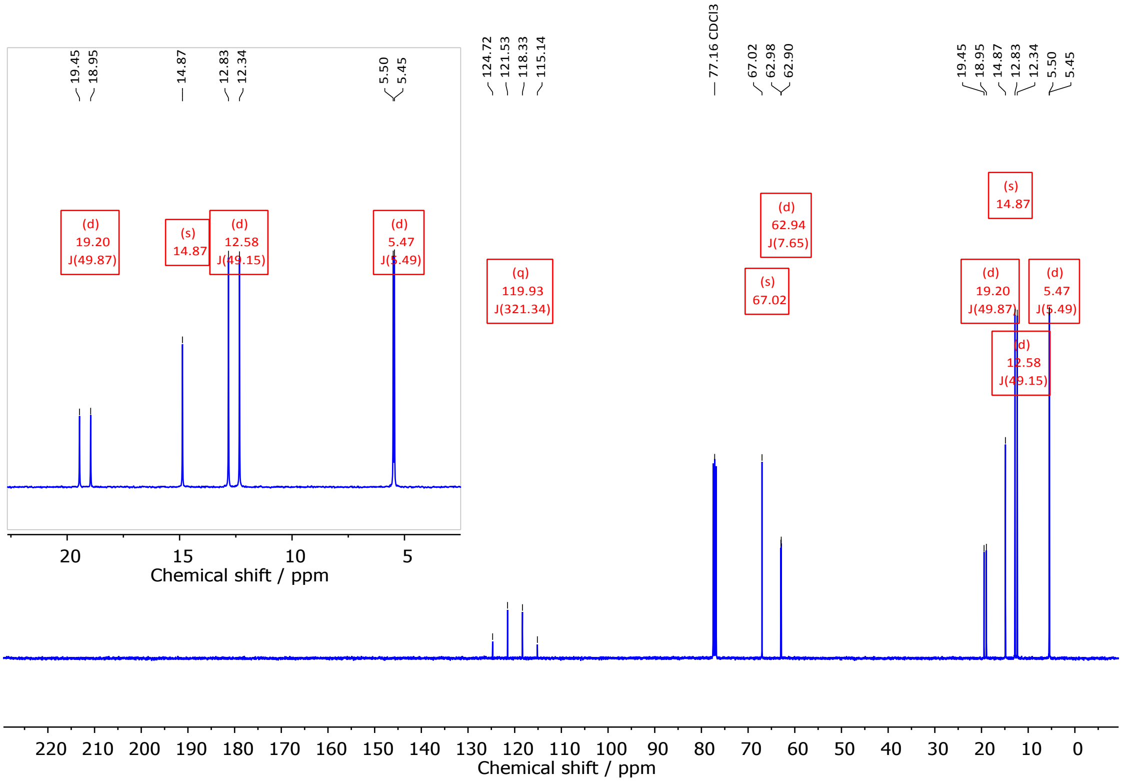

Figure S14: ^{13}C{^{1}H} NMR spectrum of [P_{222202}][NTf_2].

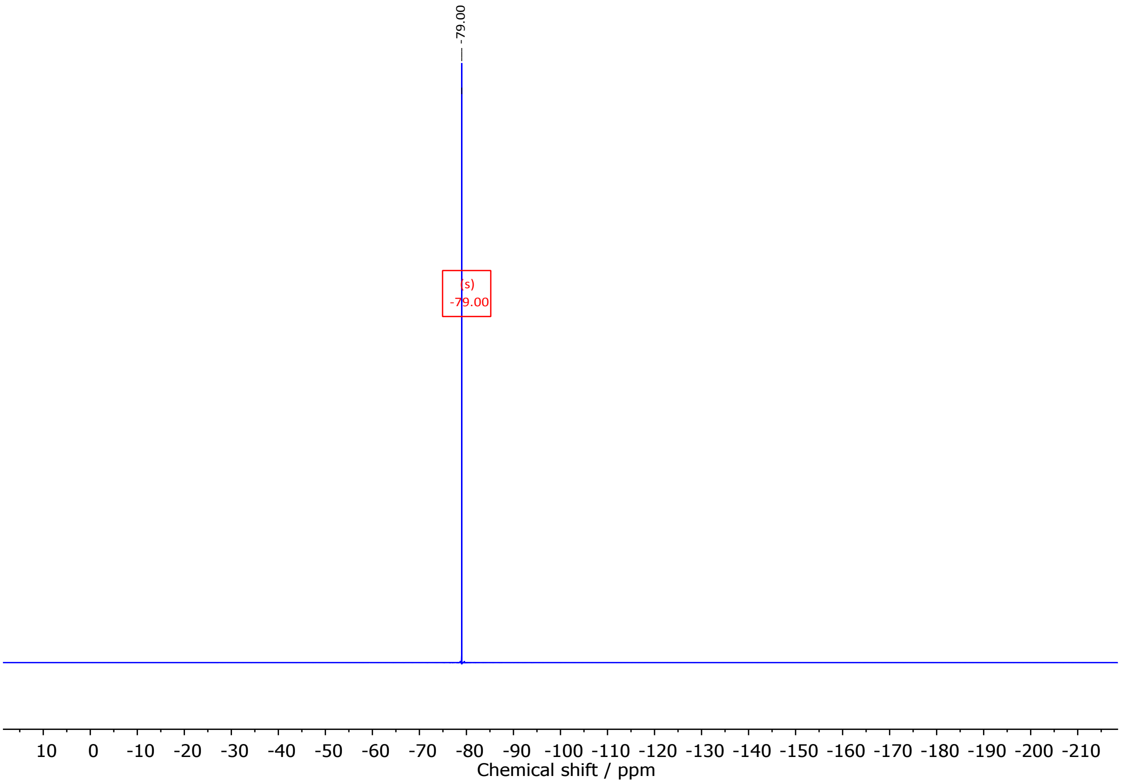

Figure S15: $^{19}F\{^1H\}$ NMR spectrum of $[P_{222202}][NTf_2]$.

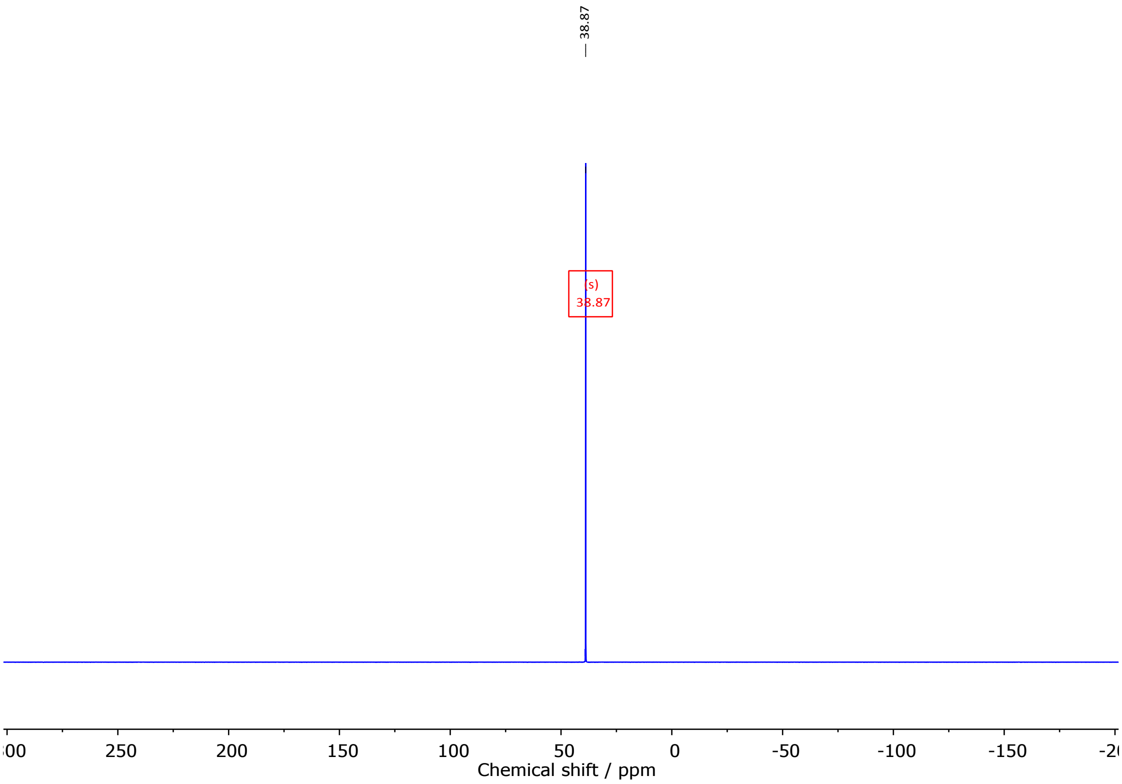

Figure S16: $^{31}P\{^1H\}$ NMR spectrum of $[P_{222202}][NTf_2]$.

7.3 NMR spectra of $[P_{2225}][Br]$

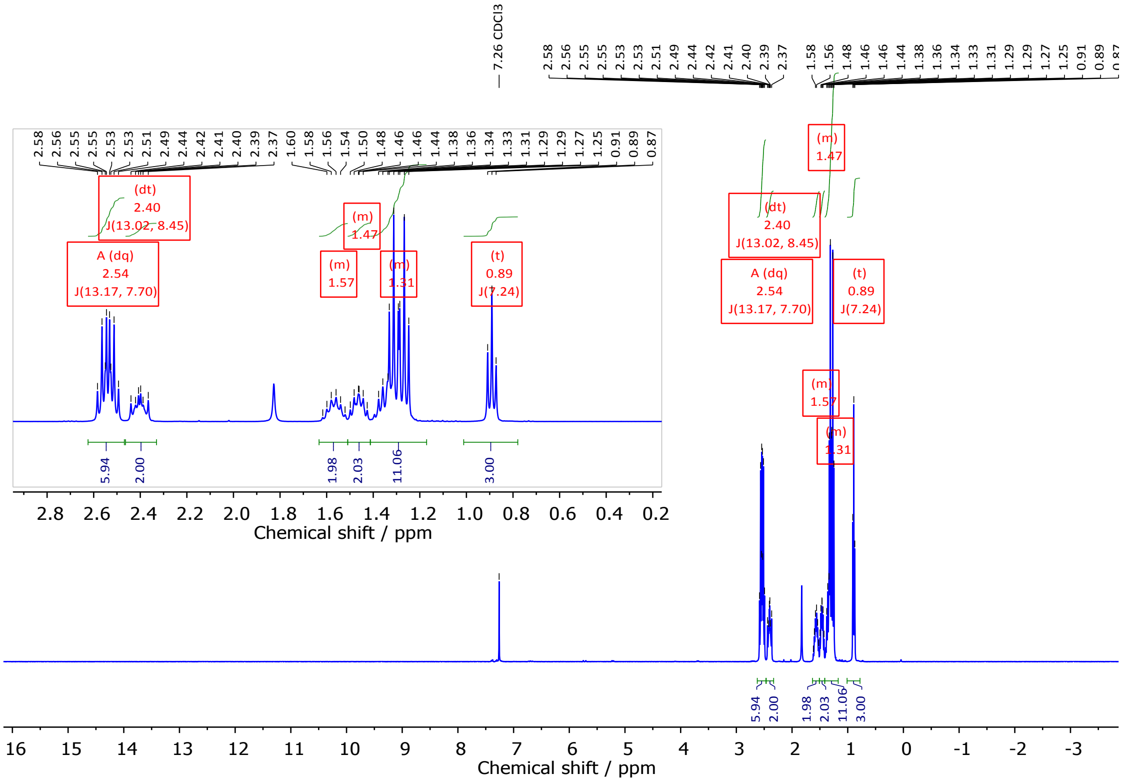

Figure S17: ^{1}H NMR spectrum of $[P_{2225}][Br]$.

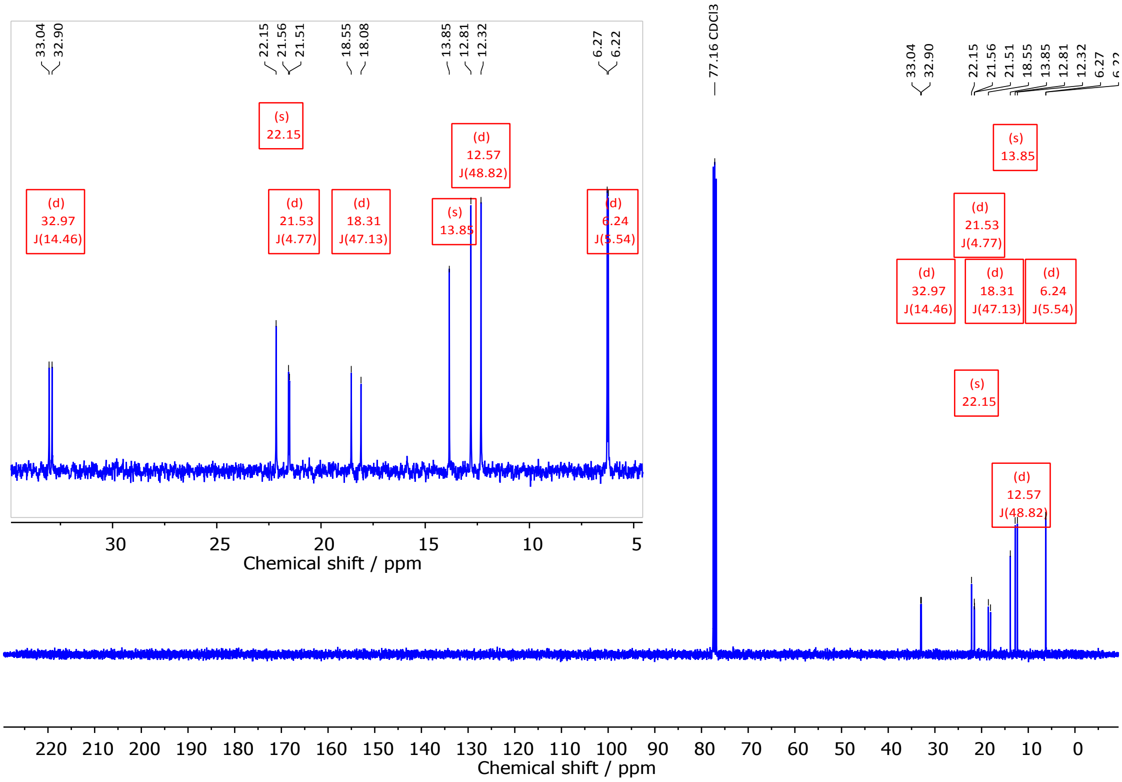

Figure S18: ^{13}C{^{1}H} NMR spectrum of $[P_{2225}][Br]$.

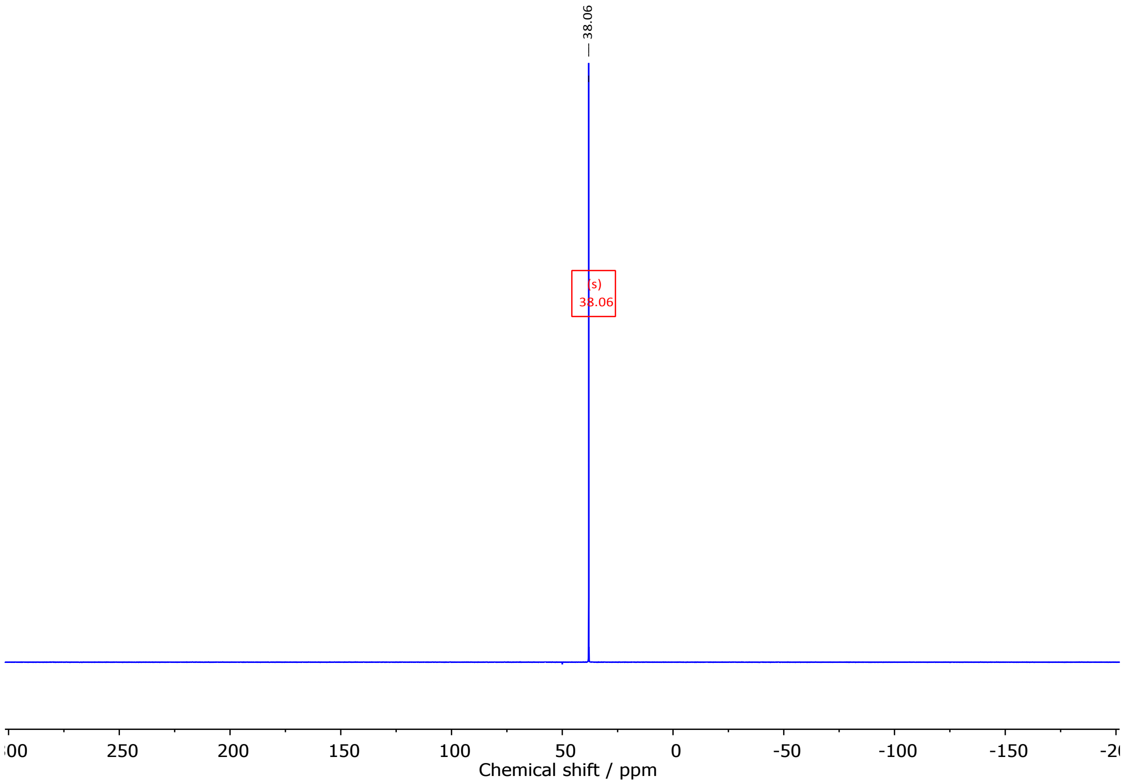

Figure S19: $^{31}P\{^1H\}$ NMR spectrum of $[P_{2225}][Br]$.

7.4 NMR spectra of $[P_{2225}][NTf_2]$

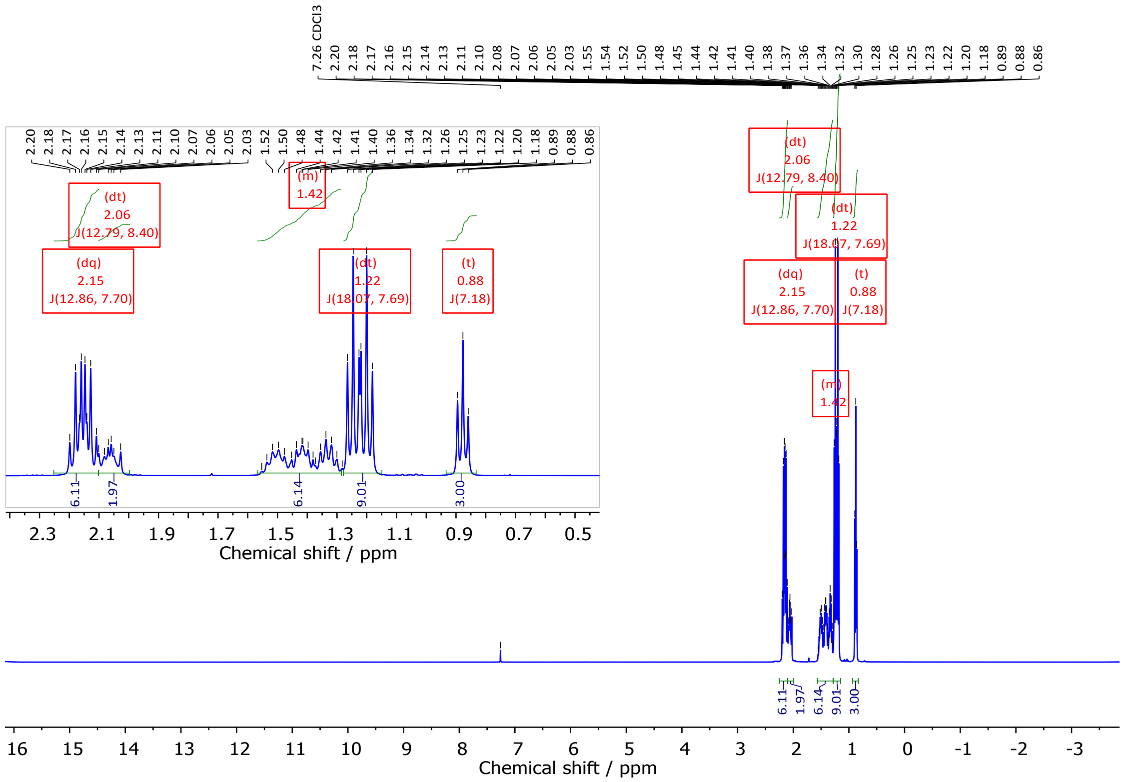

Figure S20: ^1H NMR spectrum of $[P_{2225}][NTf_2]$

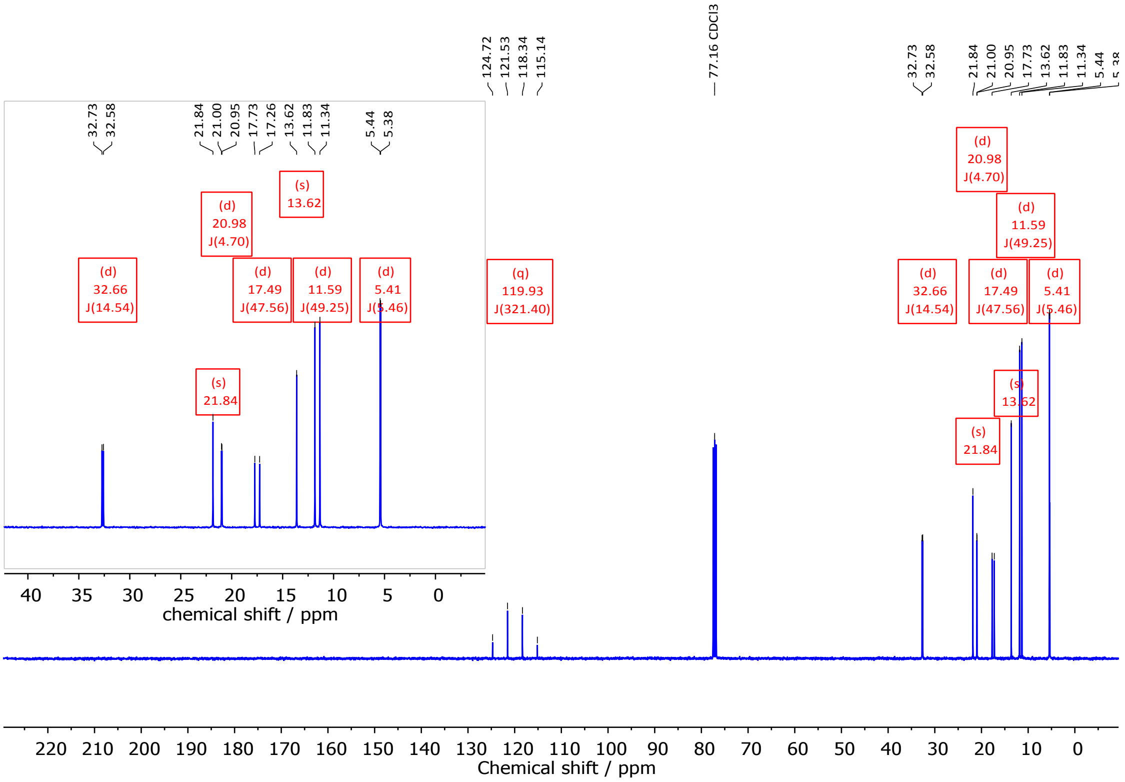

Figure S21: $^{13}C\{^1H\}$ NMR spectrum of $[P_{2225}][NTf_2]$.

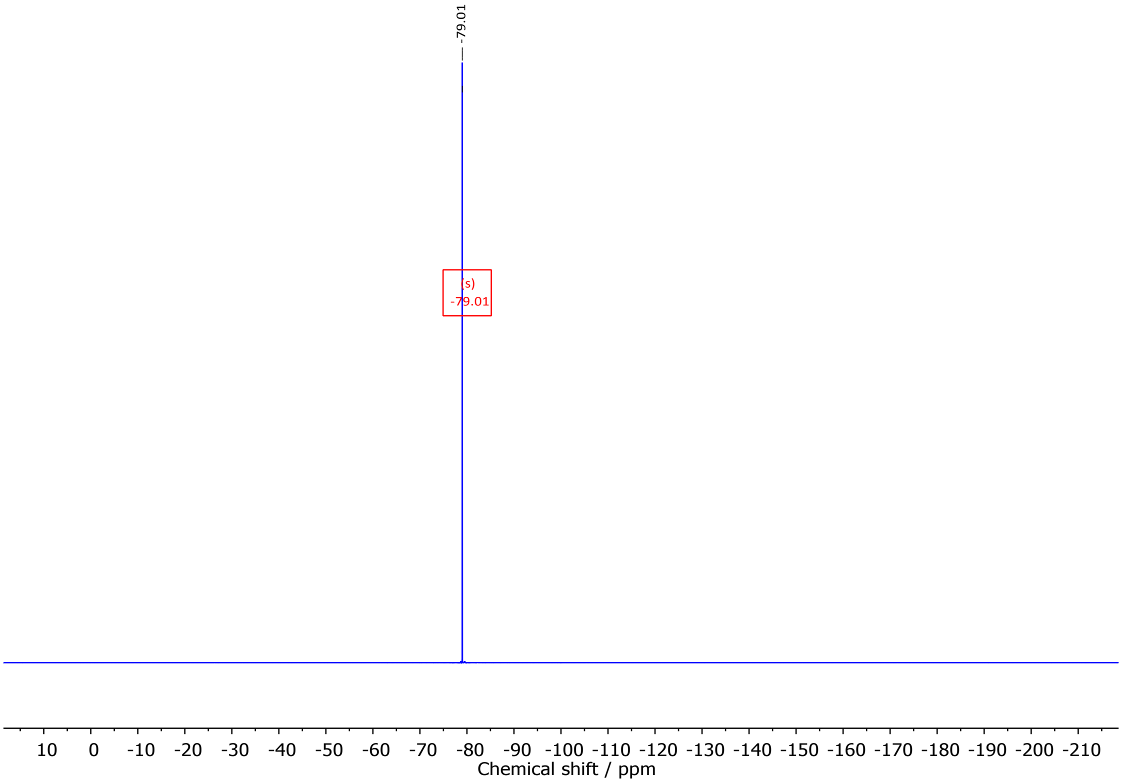

Figure S22: $^{19}F\{^1H\}$ NMR spectrum of $[P_{2225}][NTf_2]$.

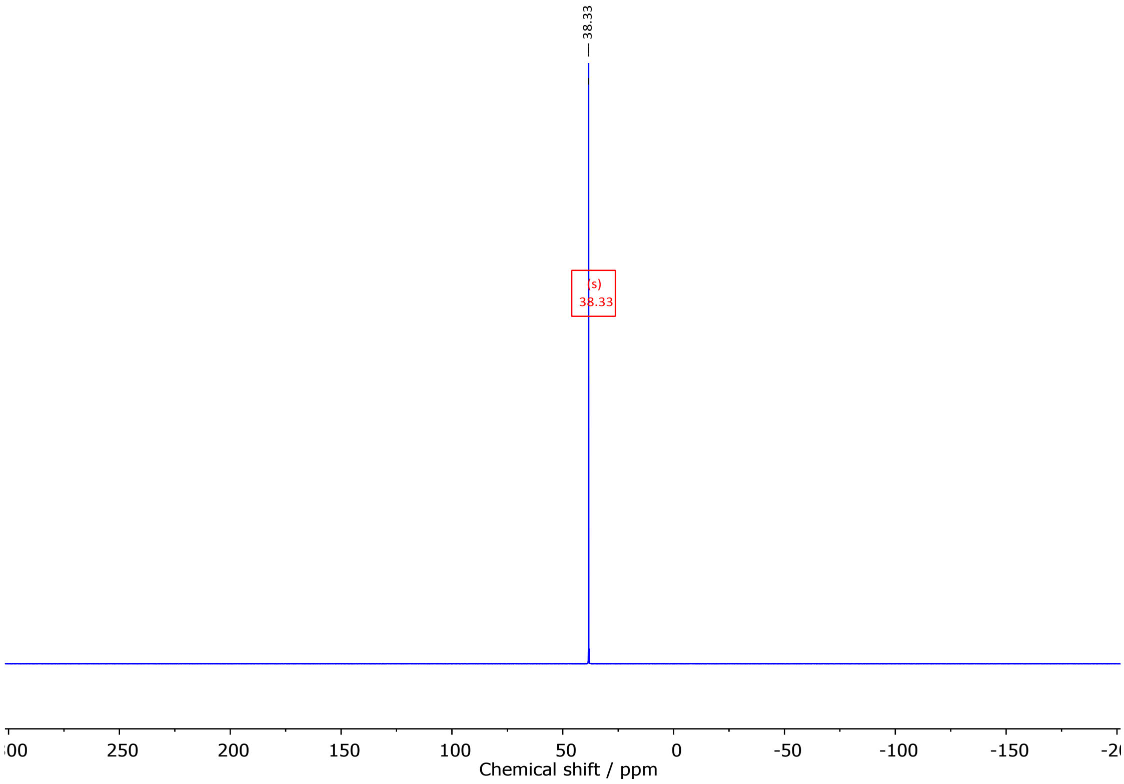

Figure S23: $^{31}P\{^1H\}$ NMR spectrum of $[P_{2225}][NTf_2]$.

7.5 NMR spectra of $[P_{2228}][Br]$

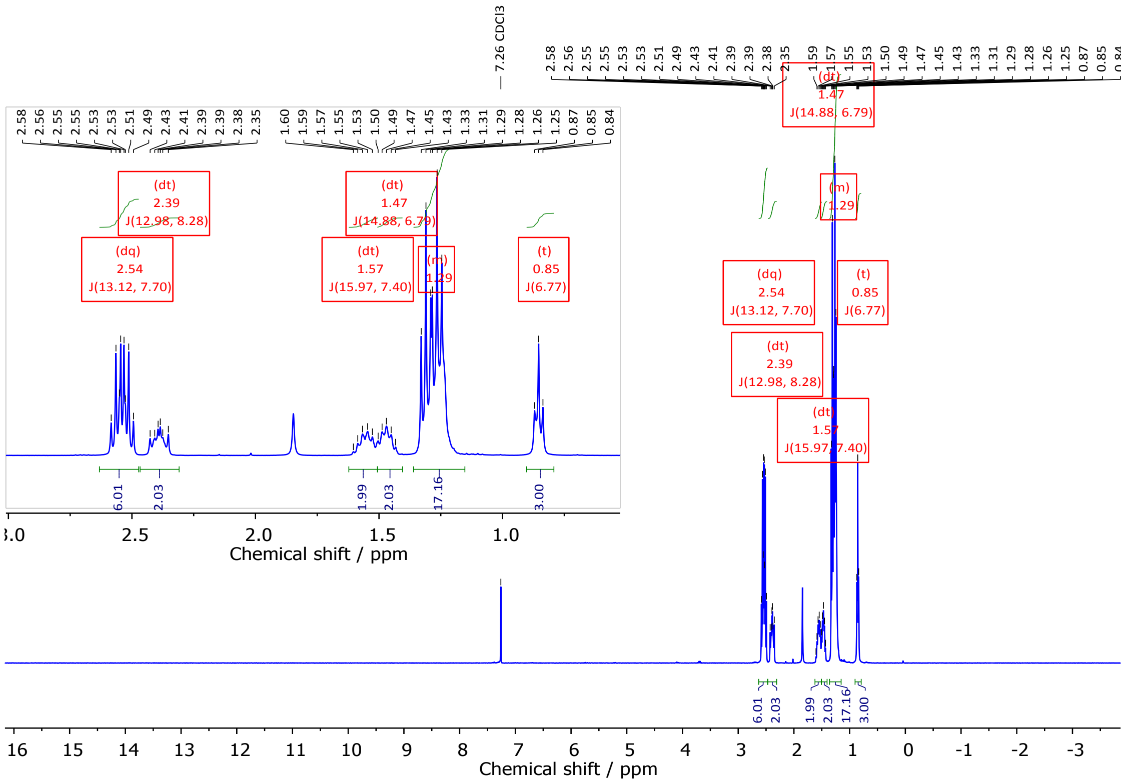

Figure S24: ^1H NMR spectrum of $[P_{2228}][Br]$.

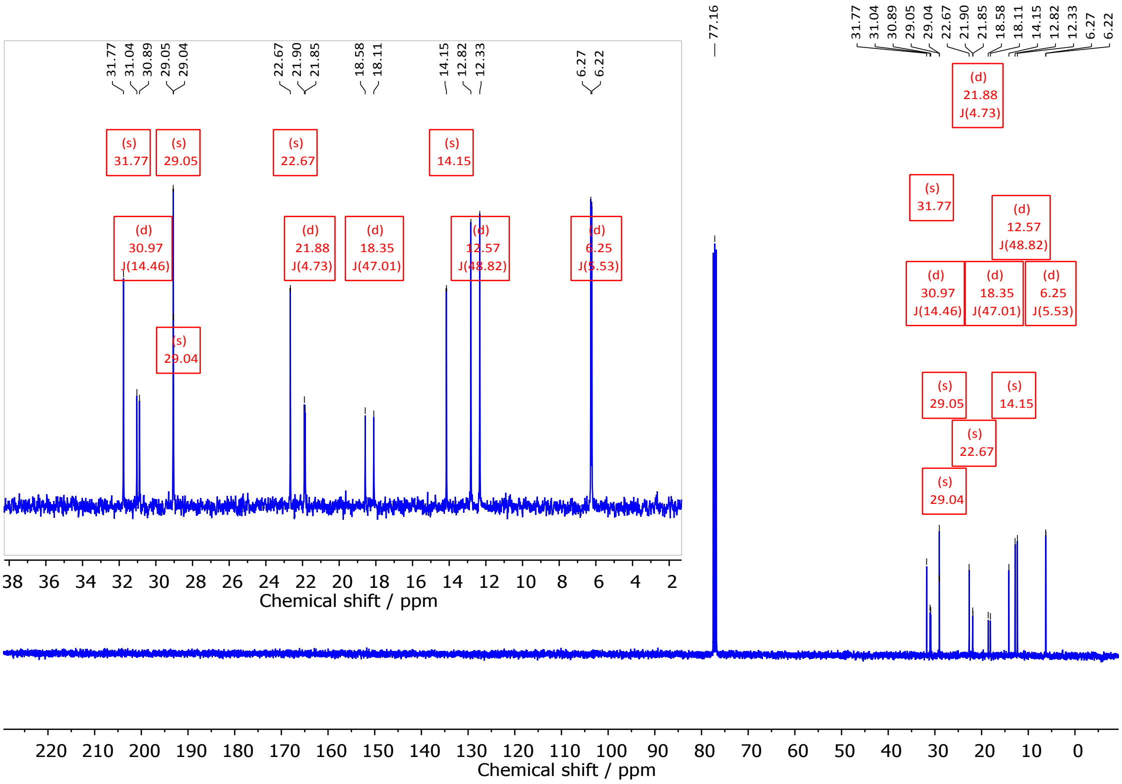

Figure S25: $^{13}C\{^1H\}$ NMR spectrum of $[P_{2228}][Br]$.

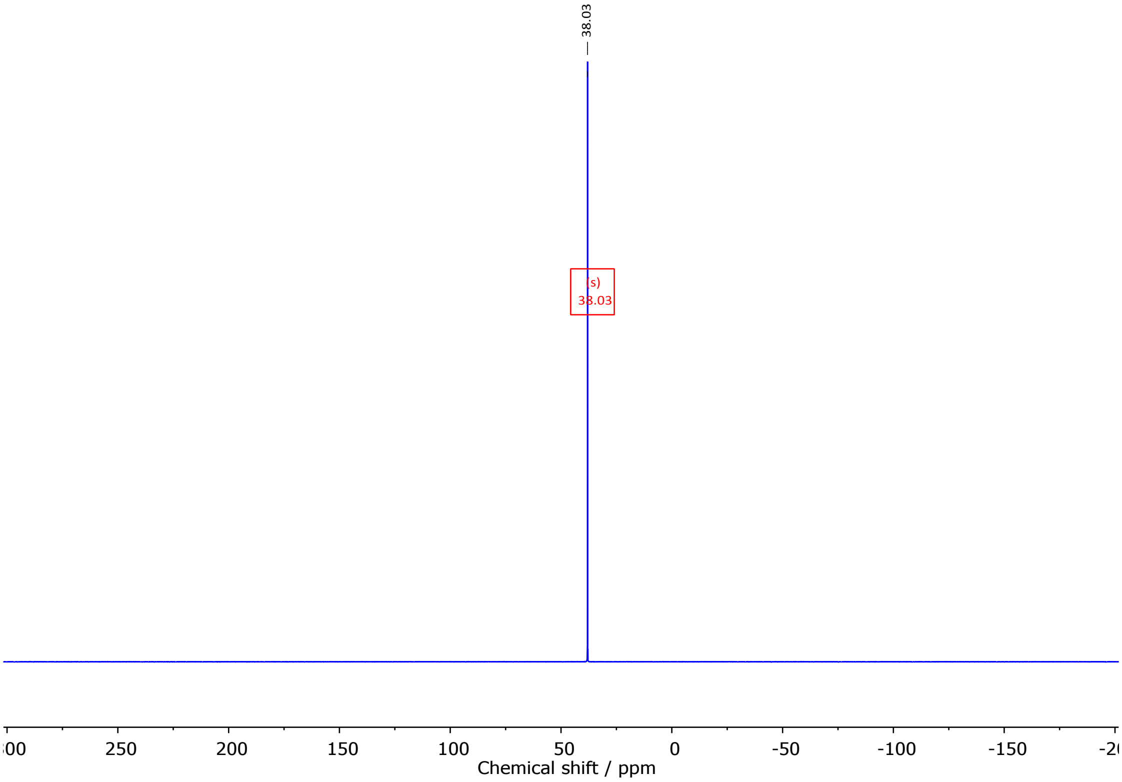

Figure S26: $^{31}P\{^1H\}$ NMR spectrum of $[P_{2228}][Br]$.

7.6 NMR spectra of $[P_{2228}][NTf_2]$

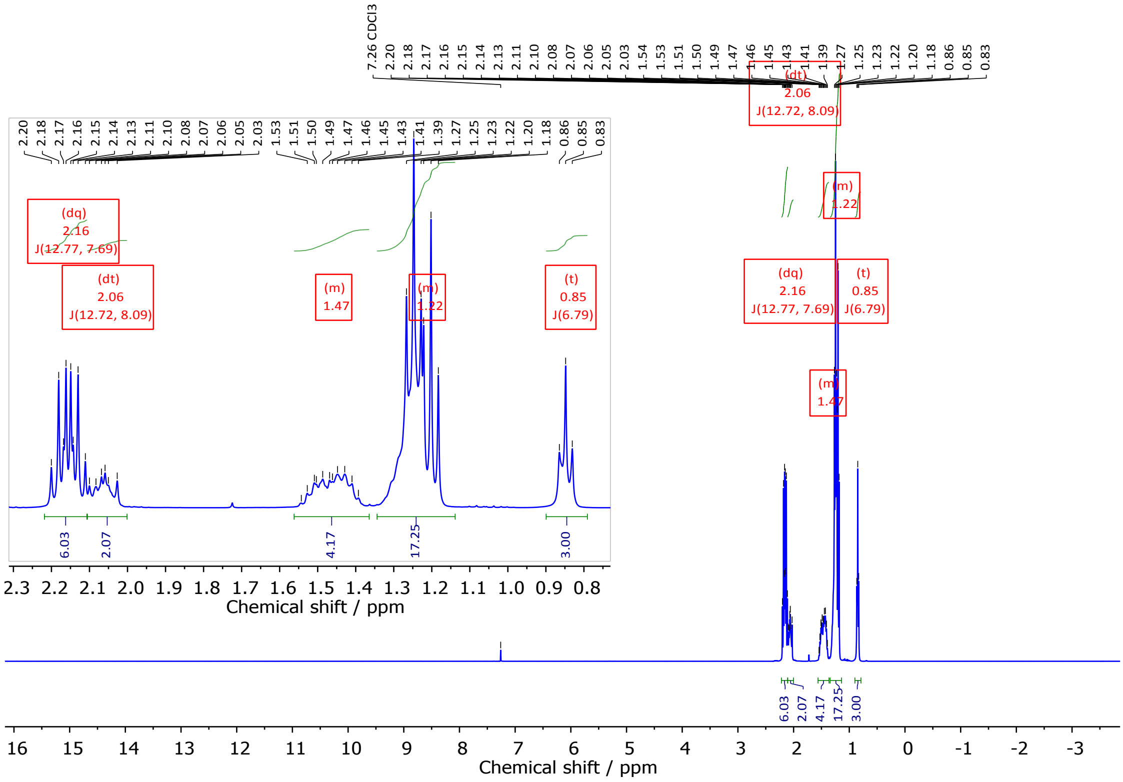

Figure S27: ^{1}H NMR spectrum of $[P_{2228}][NTf_2]$

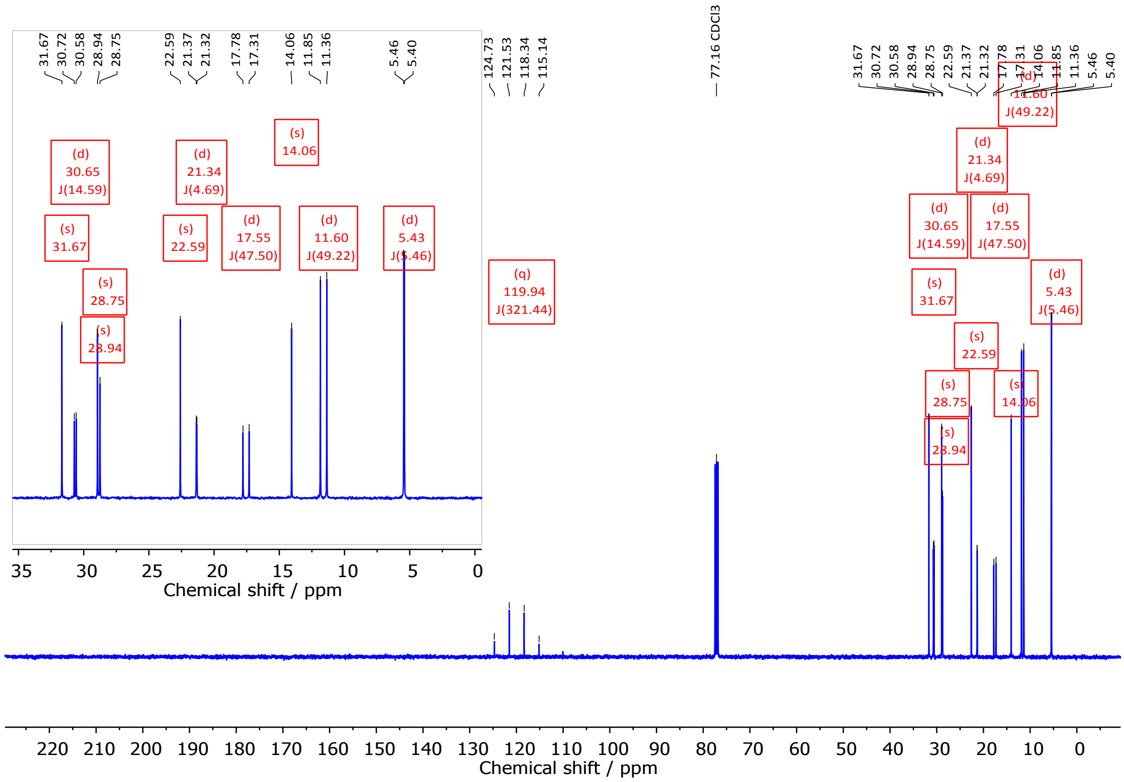

Figure S28: $^{13}C\{^{1}H\}$ NMR spectrum of $[P_{2228}][NTf_2]$.

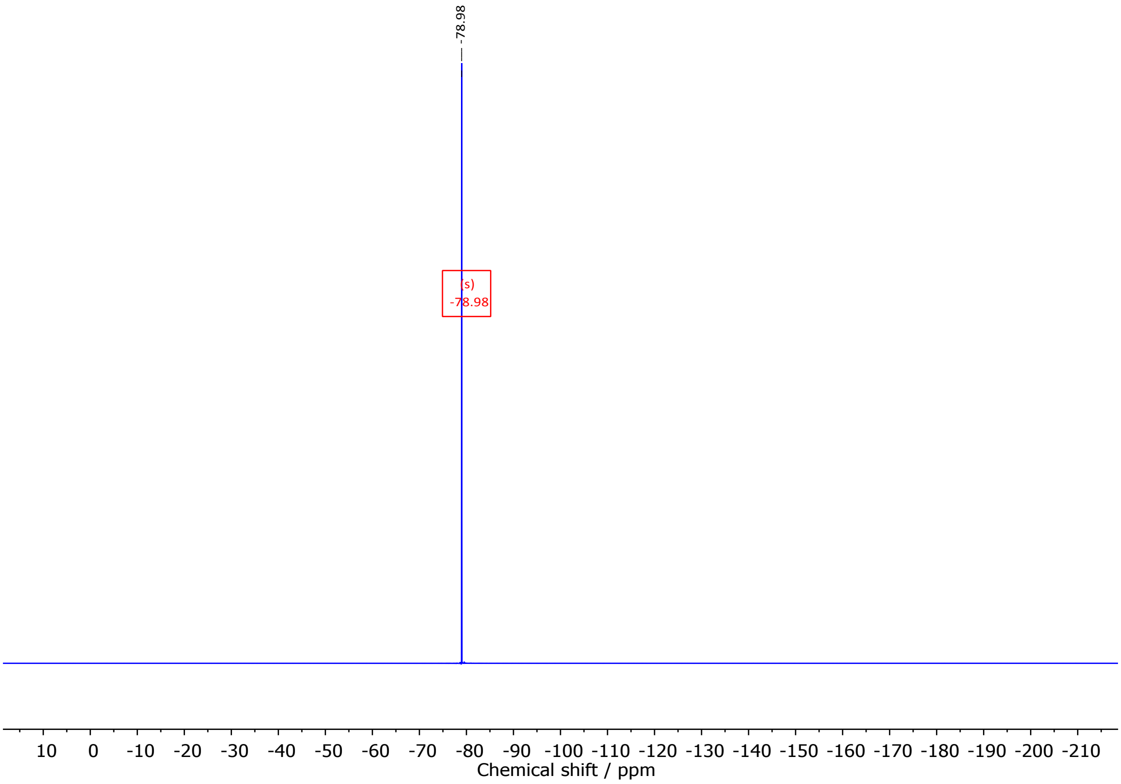

Figure S29: $^{19}F\{^1H\}$ NMR spectrum of $[P_{2228}][NTf_2]$.

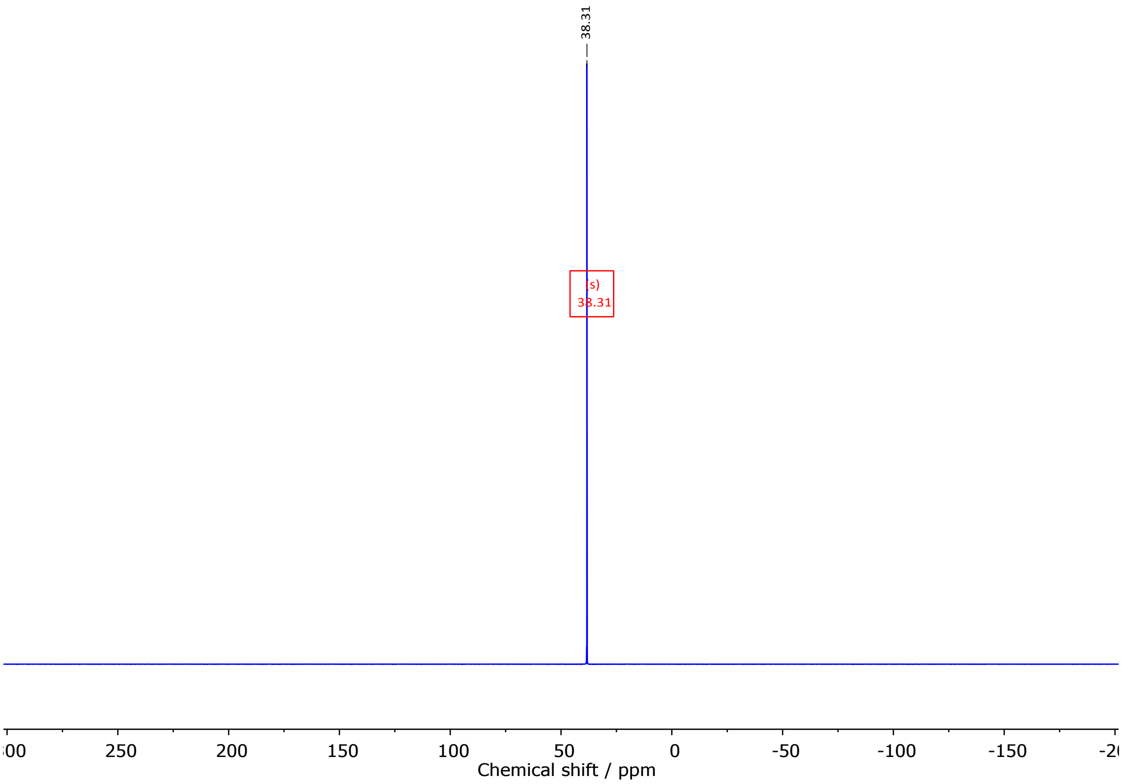

Figure S30: $^{31}P\{^1H\}$ NMR spectrum of $[P_{2228}][NTf_2]$.

7.7 NMR spectra of [P_{4442O2}][Br]

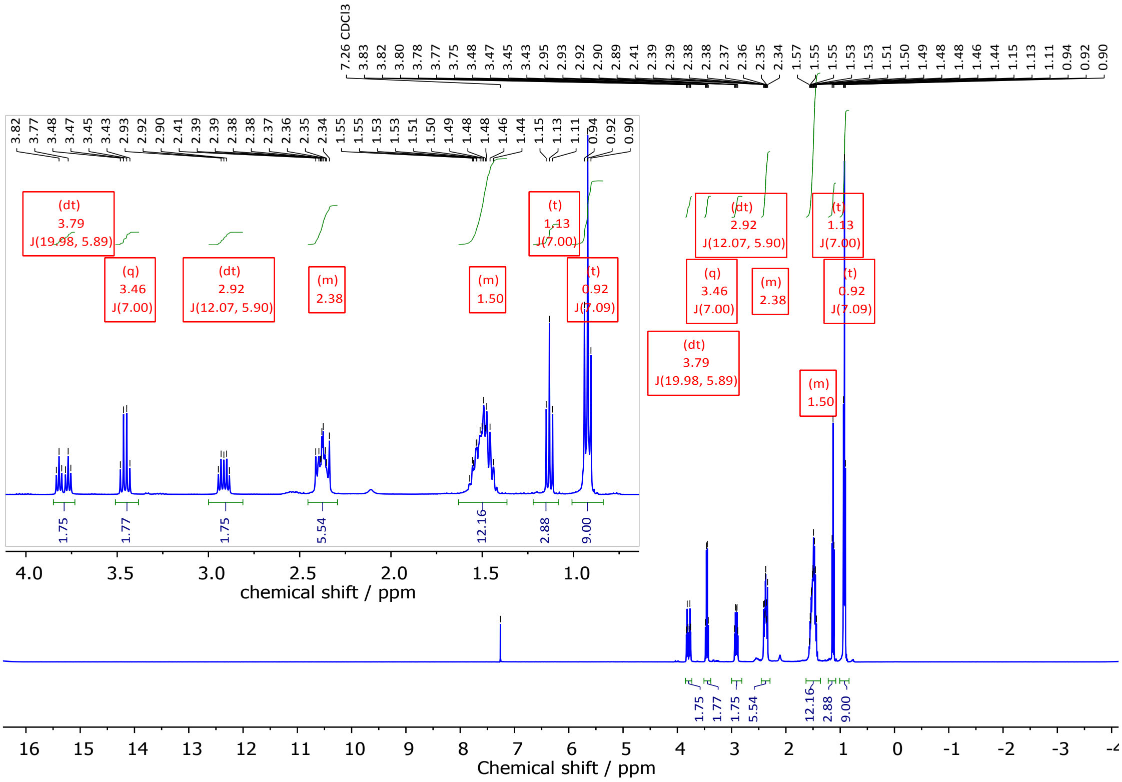

Figure S31: ^{1}H NMR spectrum of [P_{4442O2}][Br].

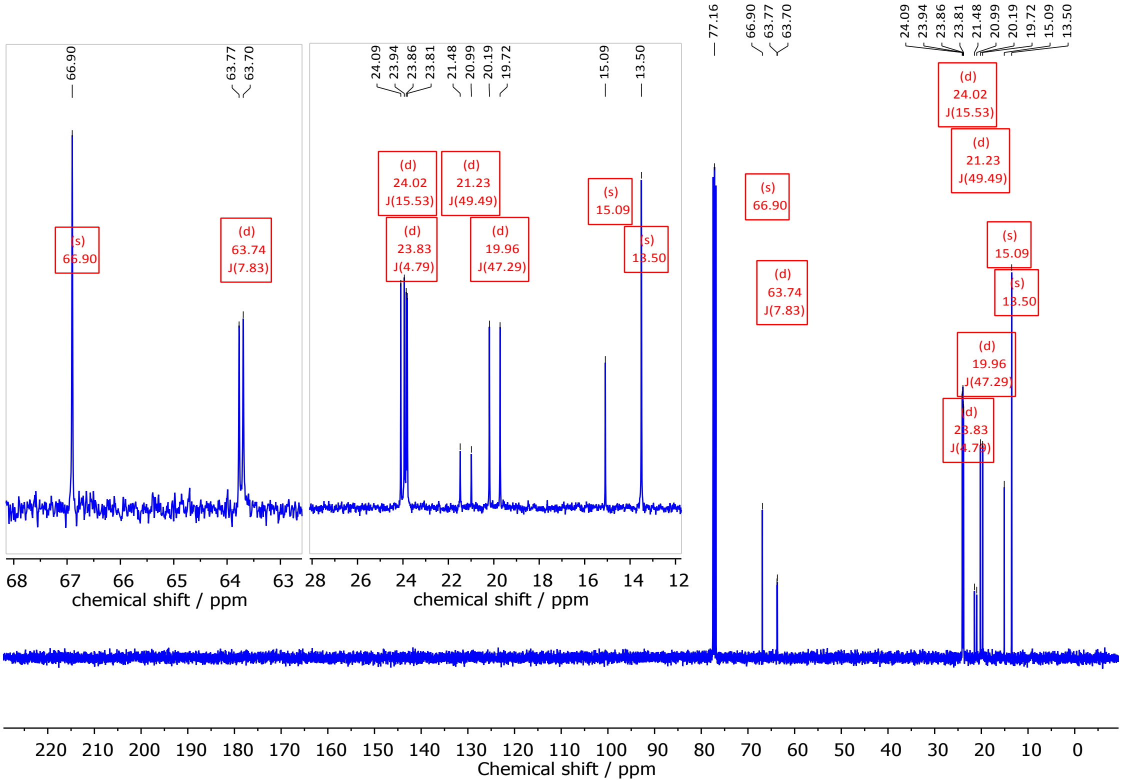

Figure S32: $^{13}C\{^{1}H\}$ NMR spectrum of [P_{4442O2}][Br].

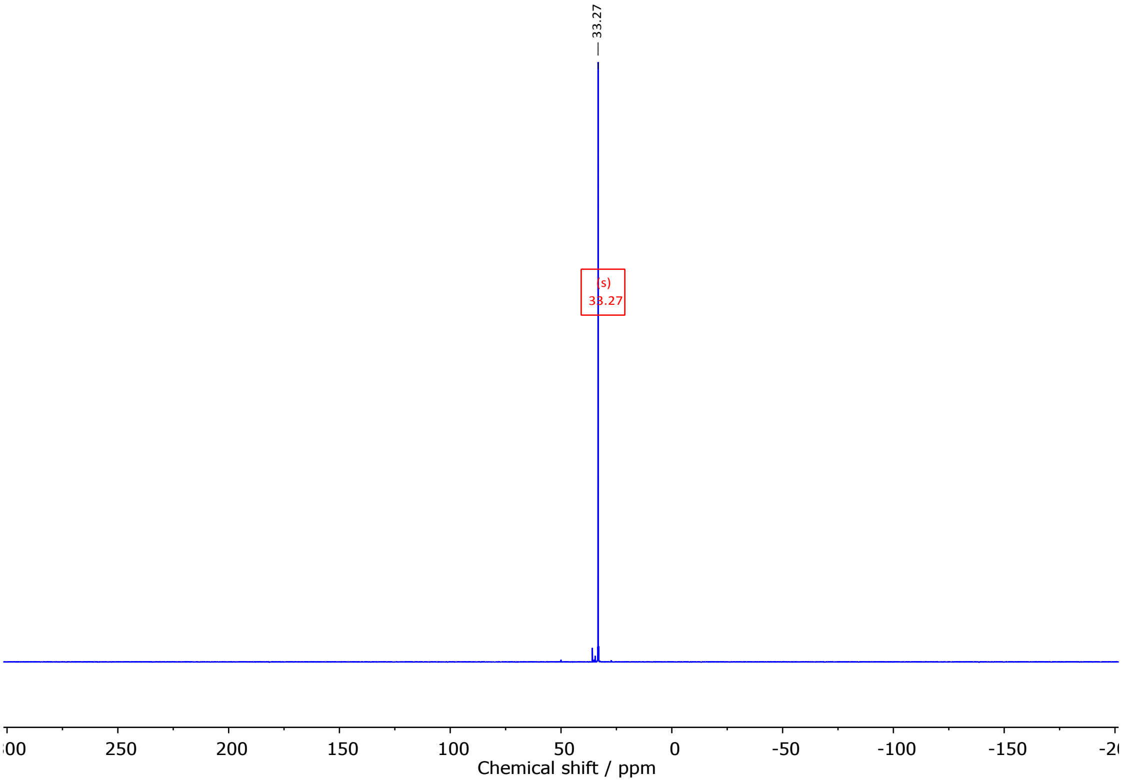

Figure S33: $^{31}P\{^1H\}$ NMR spectrum of $[P_{444202}][Br]$.

7.8 NMR spectra of $[P_{444202}][TFA]$

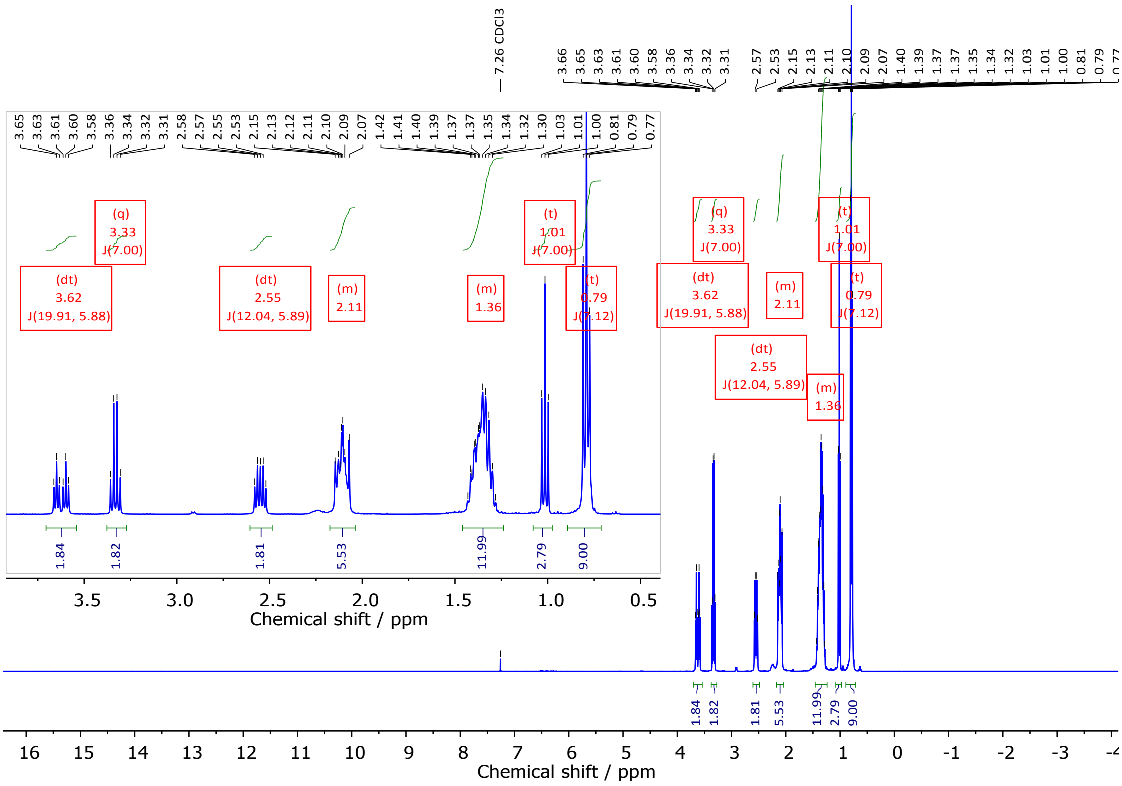

Figure S34: ^1H NMR spectrum of $[P_{444202}][TFA]$.

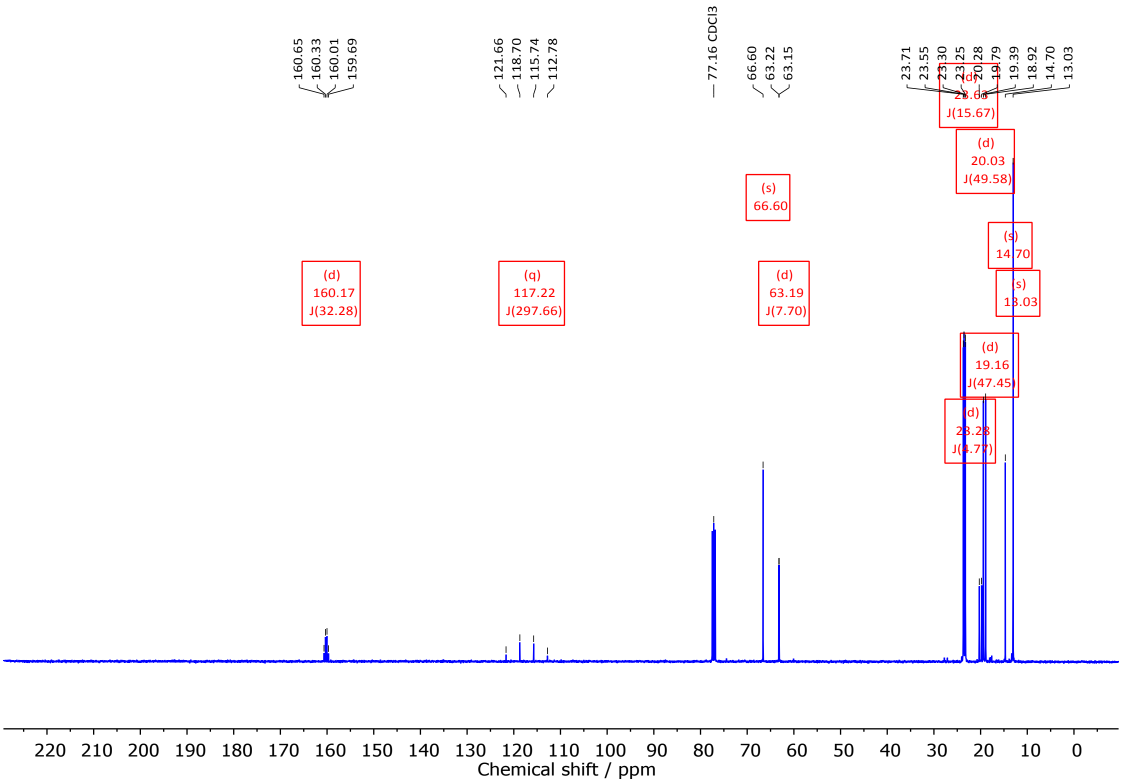

Figure S35: $^{13}C\{^1H\}$ NMR spectrum of $[P_{444202}][TFA]$.

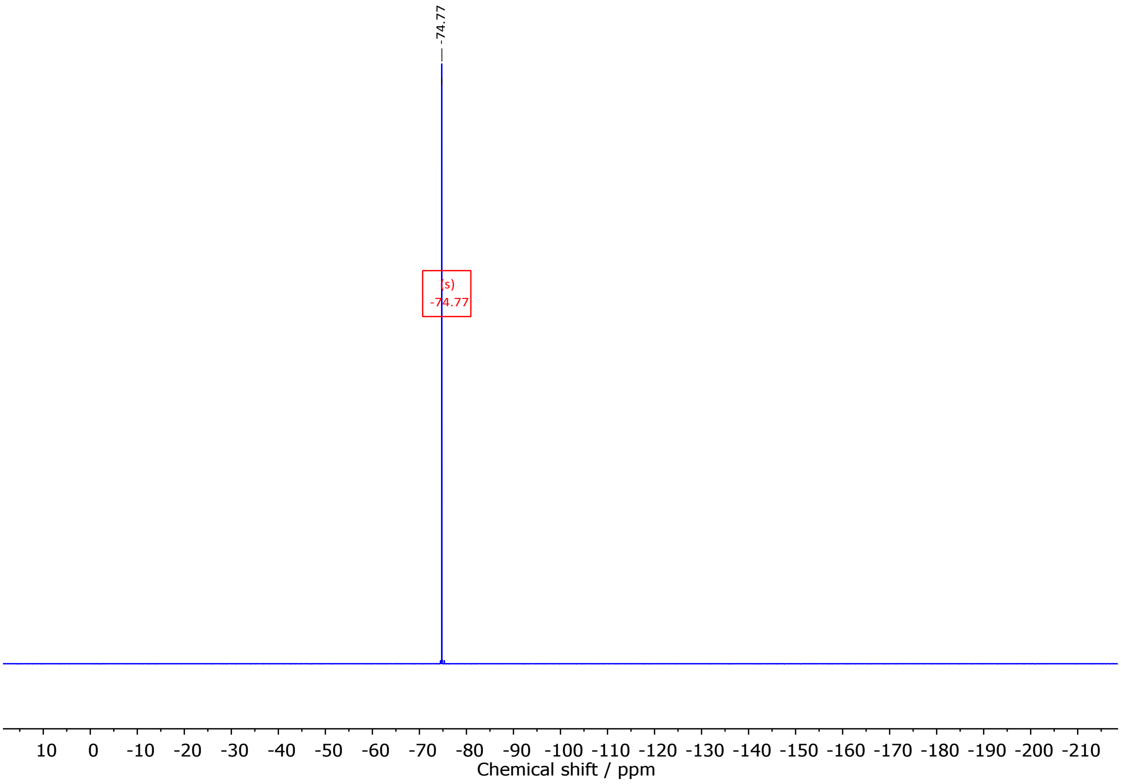

Figure S36: $^{19}F\{^1H\}$ NMR spectrum of $[P_{444202}][TFA]$.

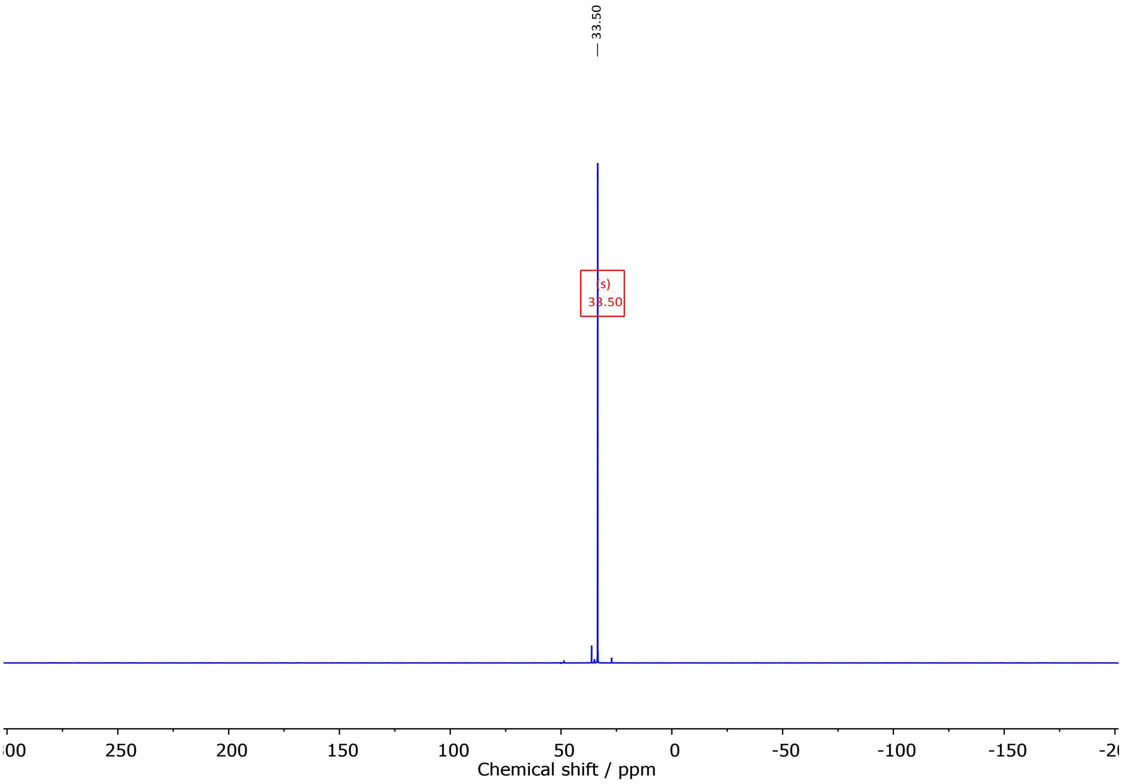

Figure S37: $^{31}P\{^1H\}$ NMR spectrum of $[P_{444 2O2}][TFA]$.

7.9 NMR spectra of $[P_{444 2O2}][OTf]$

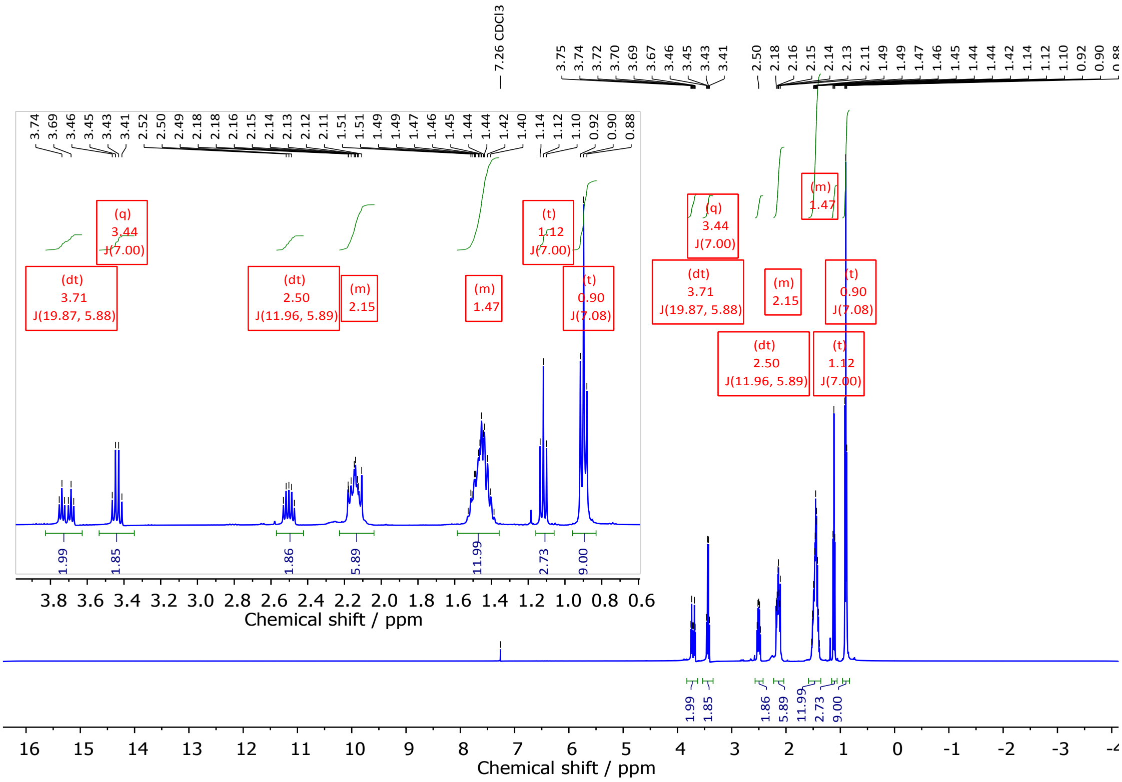

Figure S38: ^1H NMR spectrum of $[P_{444 2O2}][OTf]$.

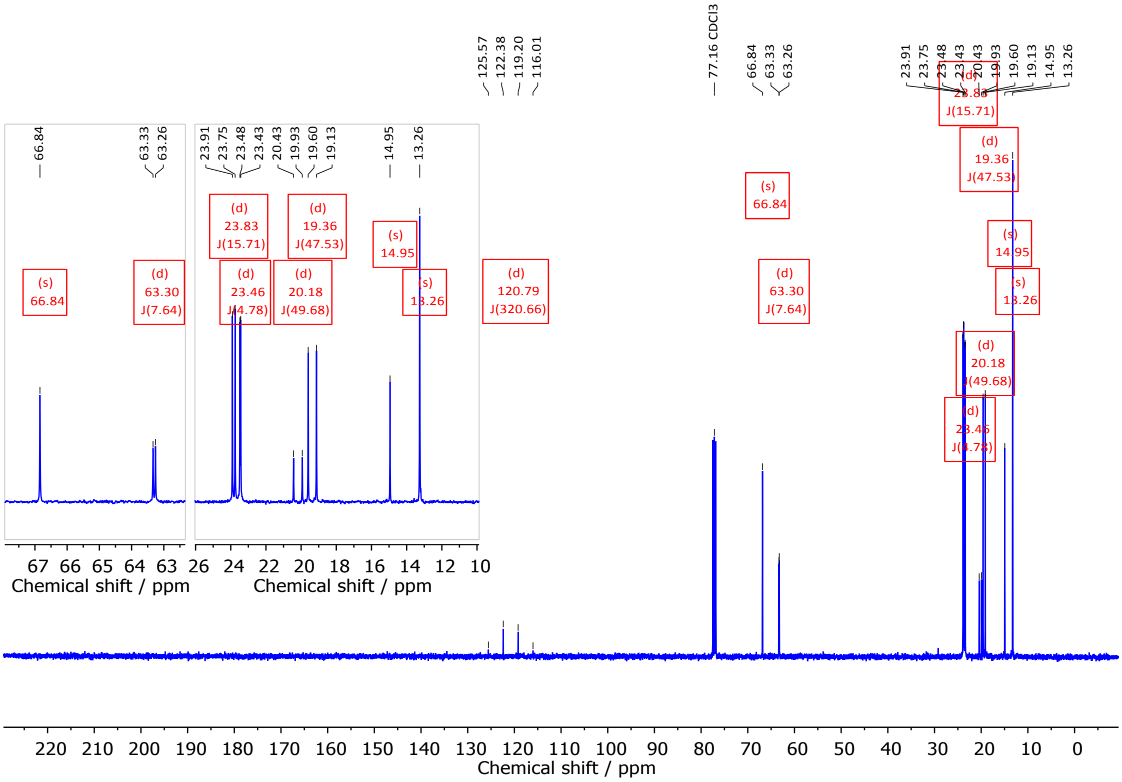

Figure S39: $^{13}C\{^{1}H\}$ NMR spectrum of $[P_{4442O2}][OTf]$.

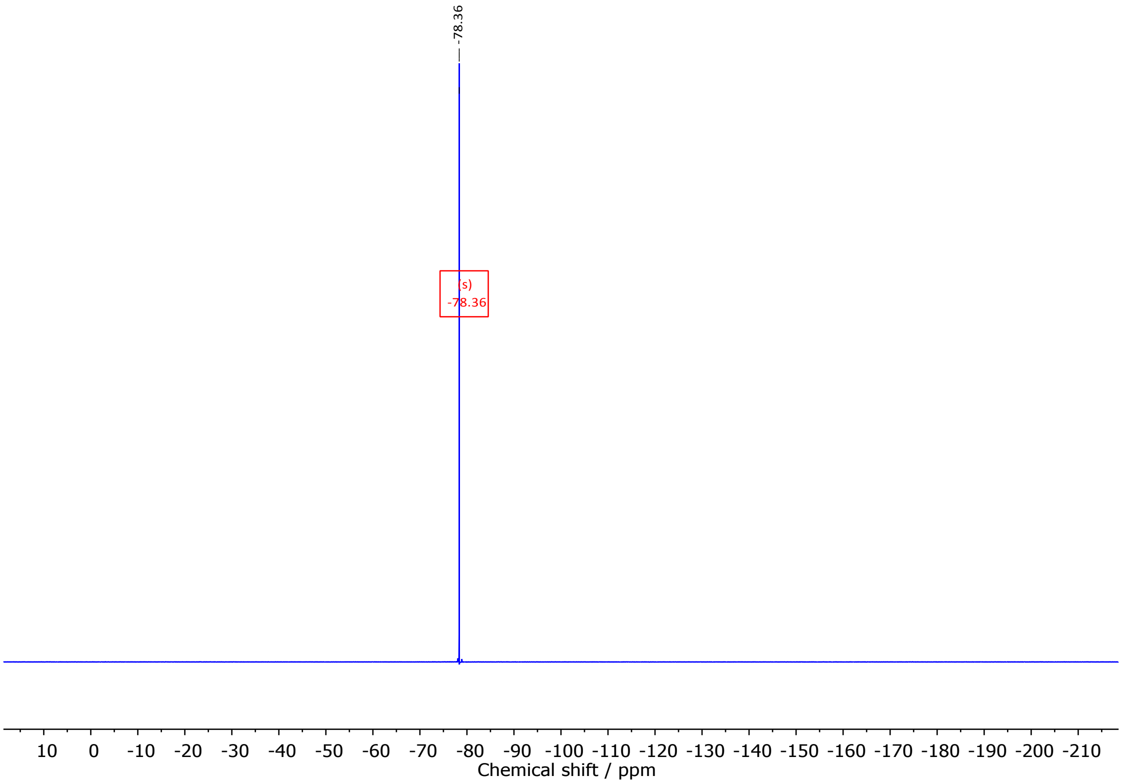

Figure S40: $^{19}F\{^{1}H\}$ NMR spectrum of $[P_{4442O2}][OTf]$.

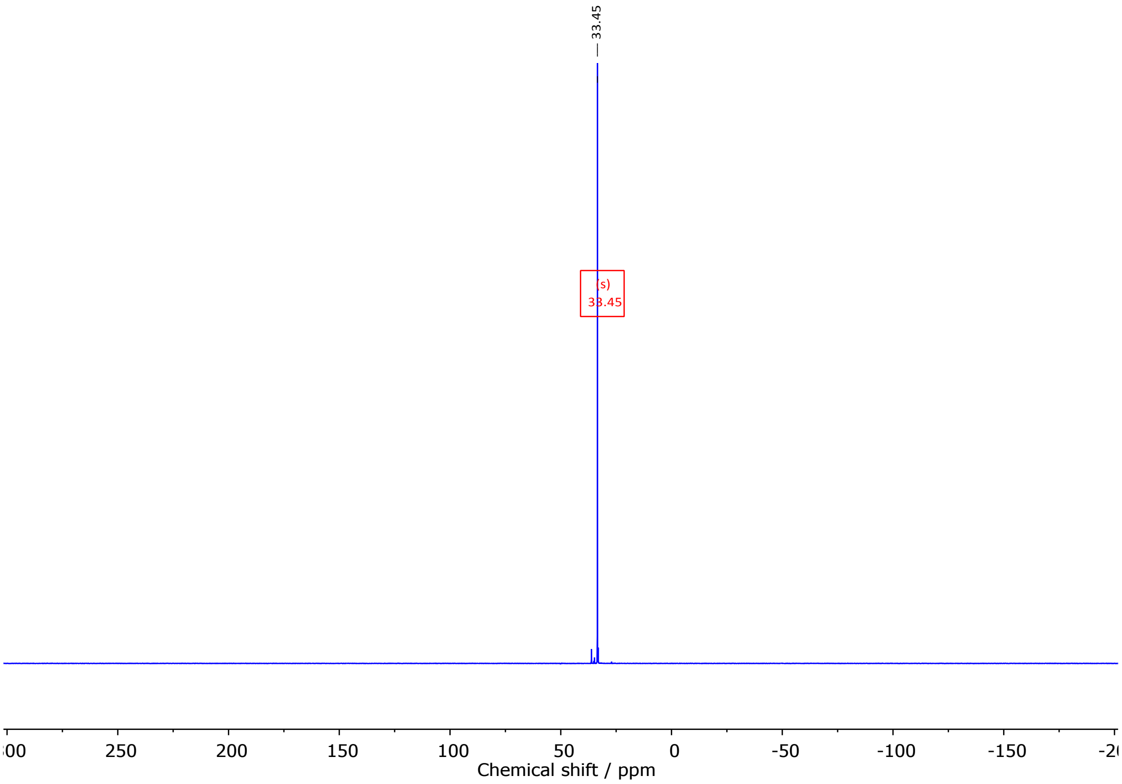

Figure S41: $^{31}P\{^{1}H\}$ NMR spectrum of $[P_{444202}][OTf]$.

7.10 NMR spectra of $[P_{444202}][NTf_2]$

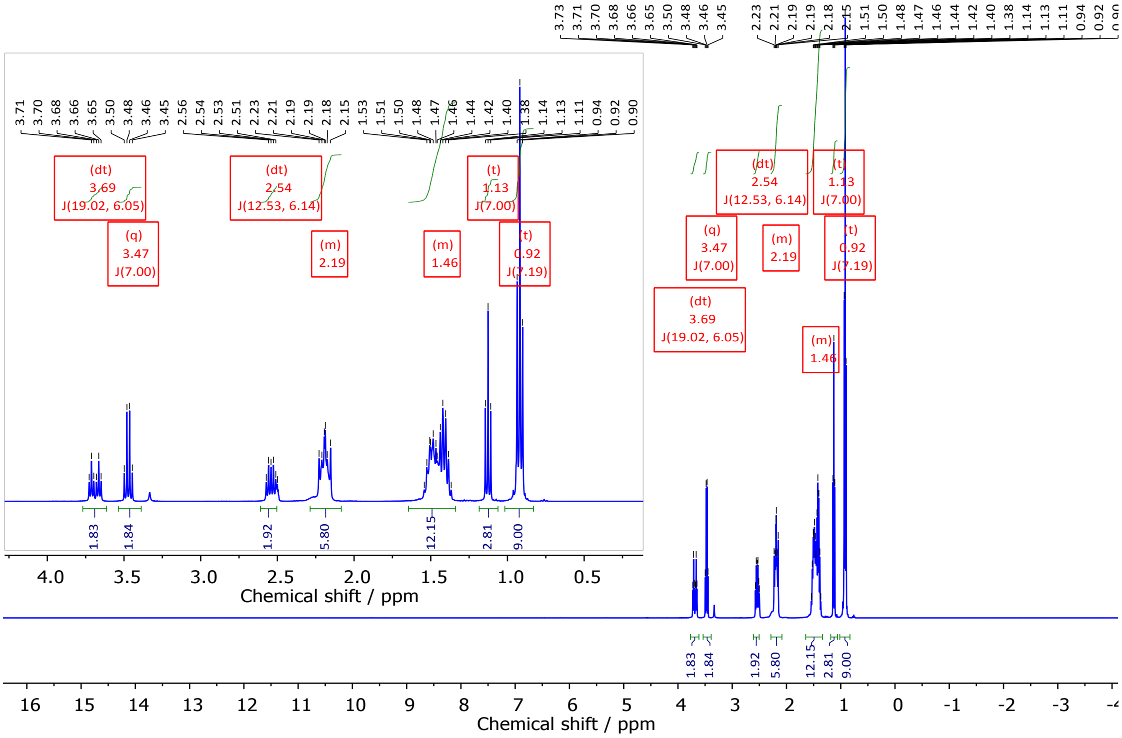

Figure S42: ^{1}H NMR spectrum of $[P_{444202}][NTf_2]$.

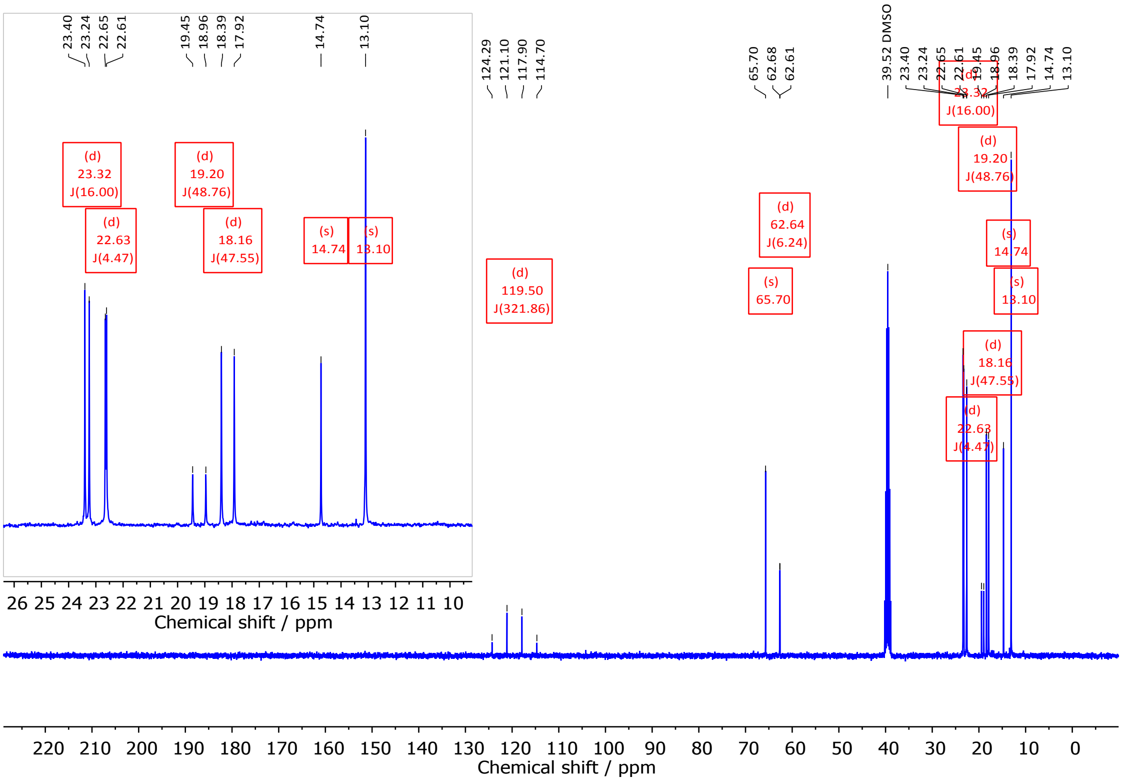

Figure S43: $^{13}C\{^1H\}$ NMR spectrum of $[P_{4442O2}][NTf_2]$.

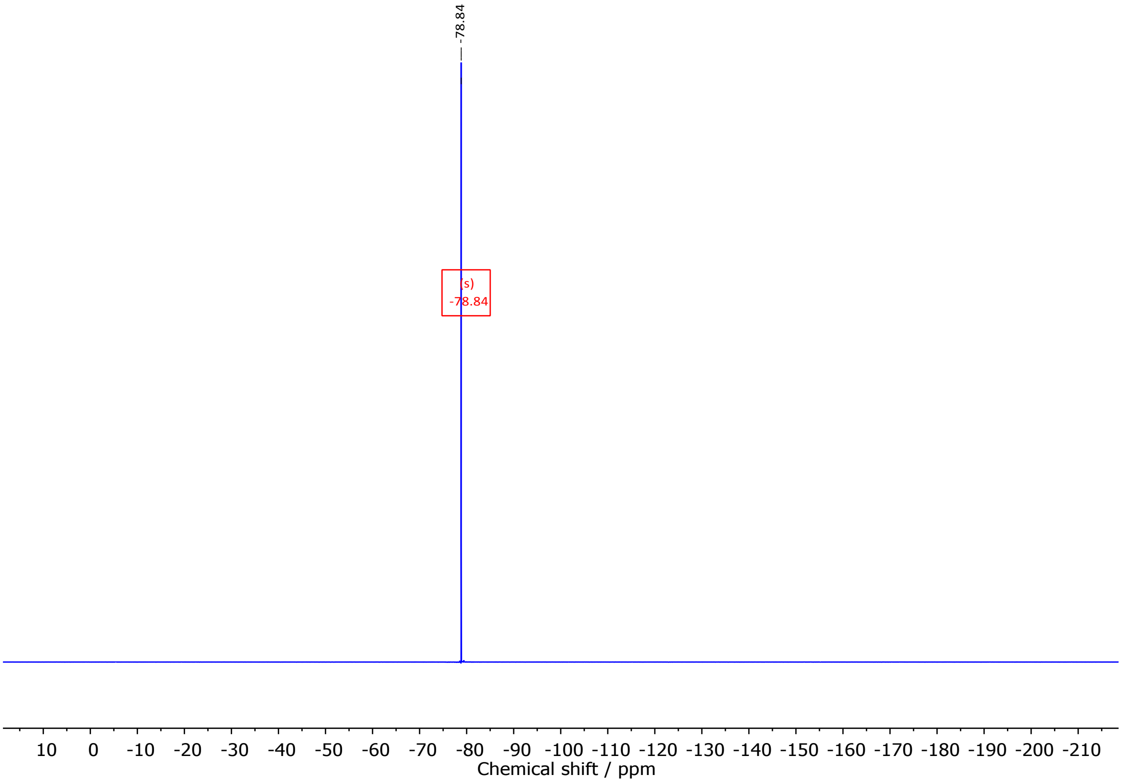

Figure S44: $^{19}F\{^1H\}$ NMR spectrum of $[P_{4442O2}][NTf_2]$.

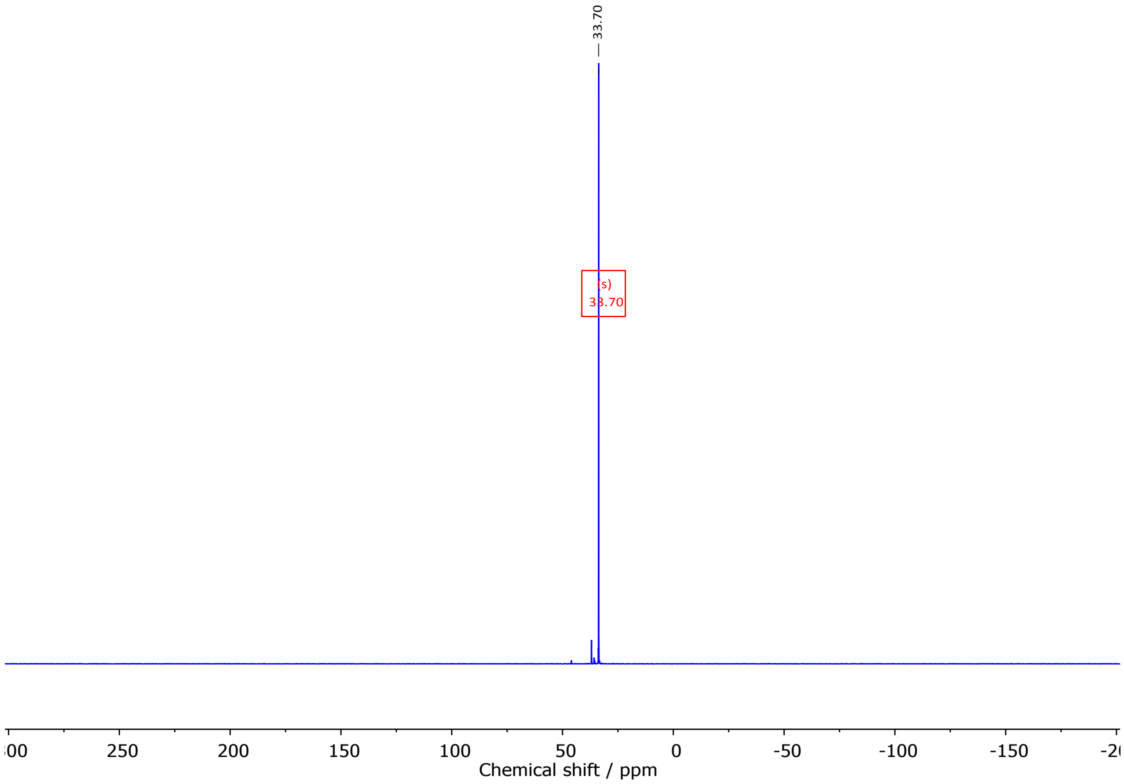

Figure S45: $^{31}P\{^{1}H\}$ NMR spectrum of $[P_{4442O2}][NTf_2]$.

7.11 NMR spectra of $[P_{444202}][OMs]$

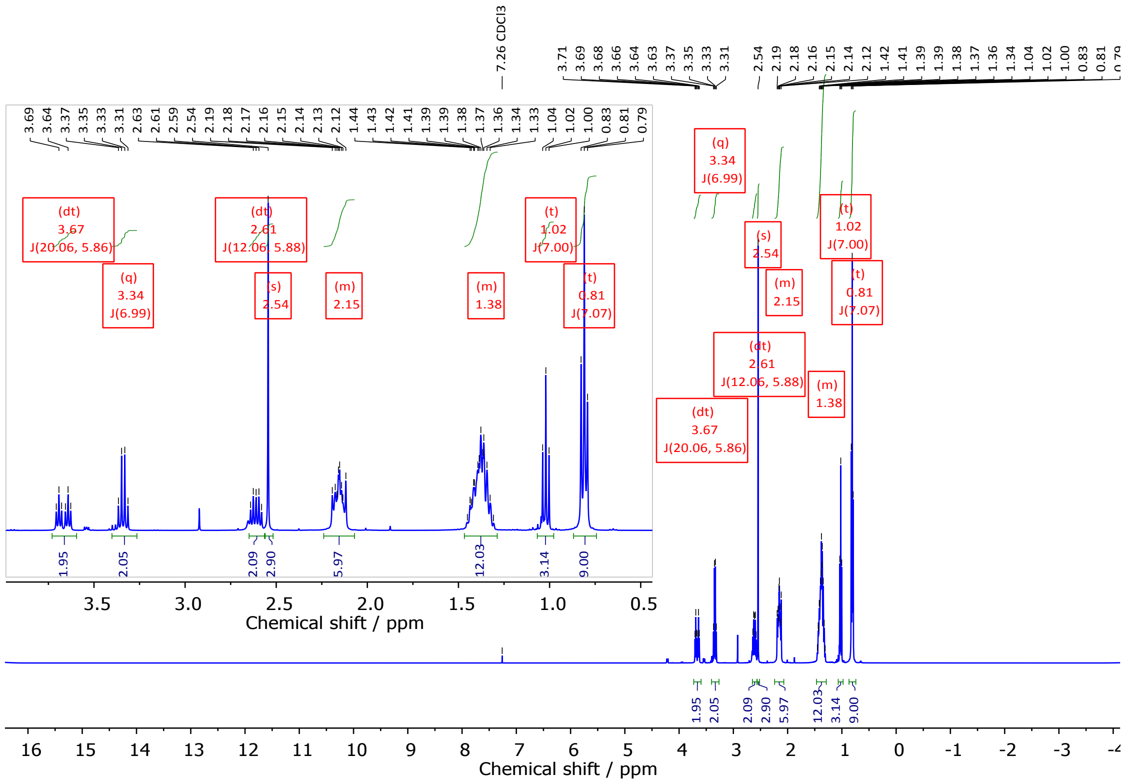

Figure S46: ^{1}H NMR spectrum of $[P_{444202}][OMs]$.

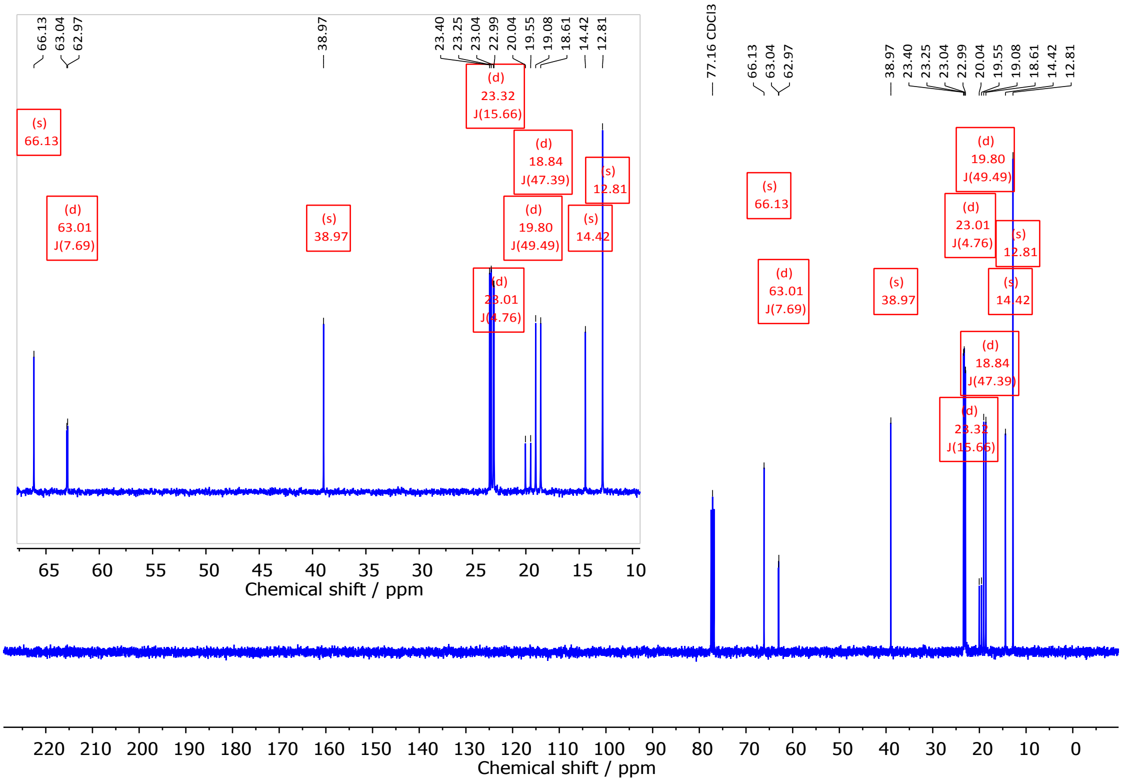

Figure S47: $^{13}C\{^{1}H\}$ NMR spectrum of [P_{4442O2}][OMs].

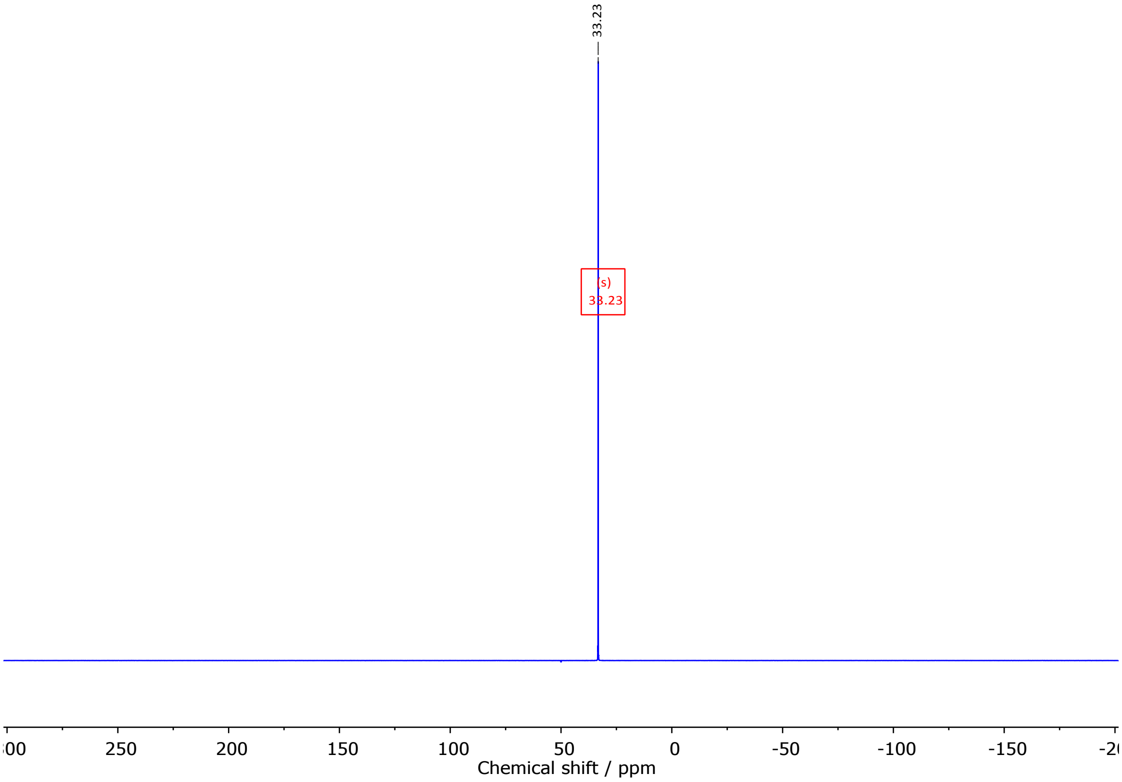

Figure S48: $^{31}P\{^{1}H\}$ NMR spectrum of [P_{4442O2}][OMs].

7.12 NMR spectra of [P_{4442}][Br]

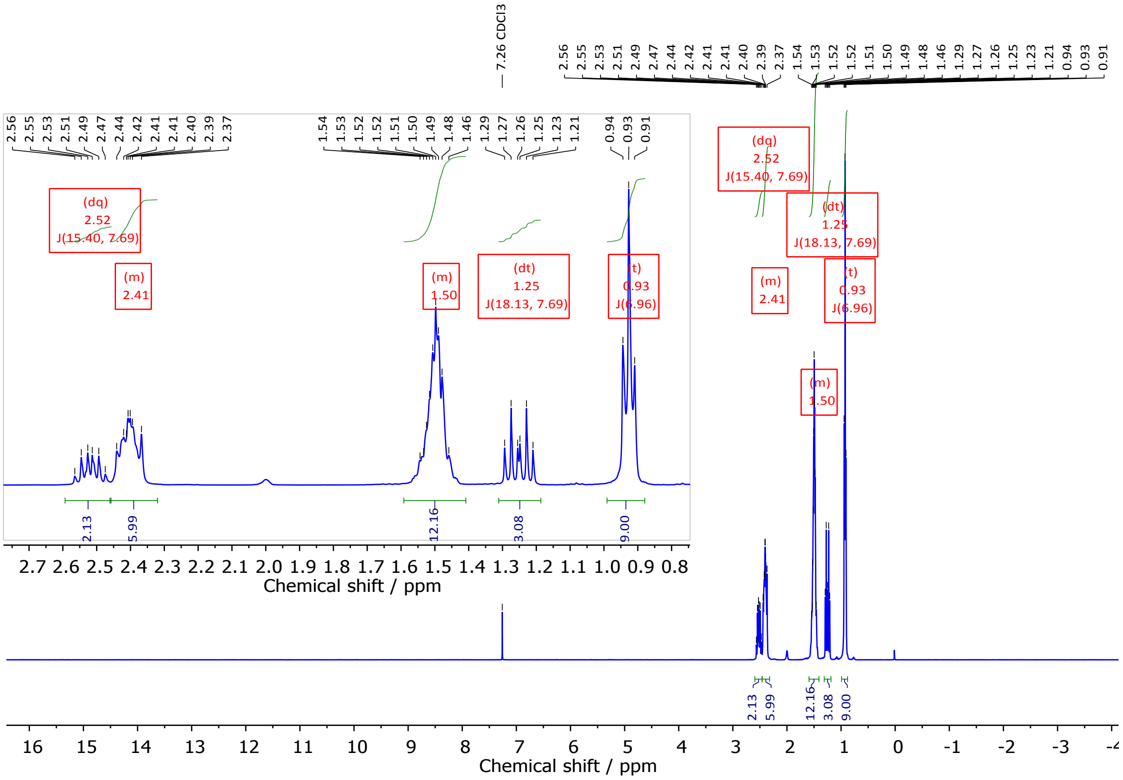

Figure S49: ^{1}H NMR spectrum of [P_{4442}][Br].

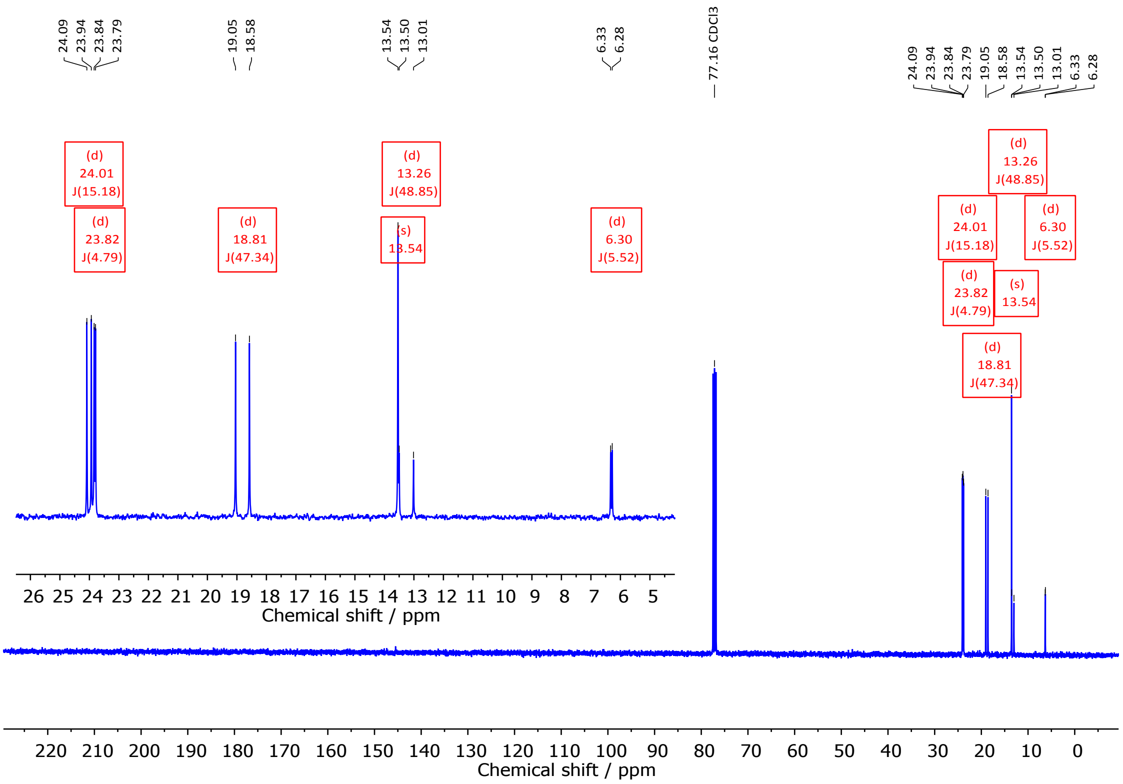

Figure S50: ^{13}C{^{1}H} NMR spectrum of [P_{4442}][Br].

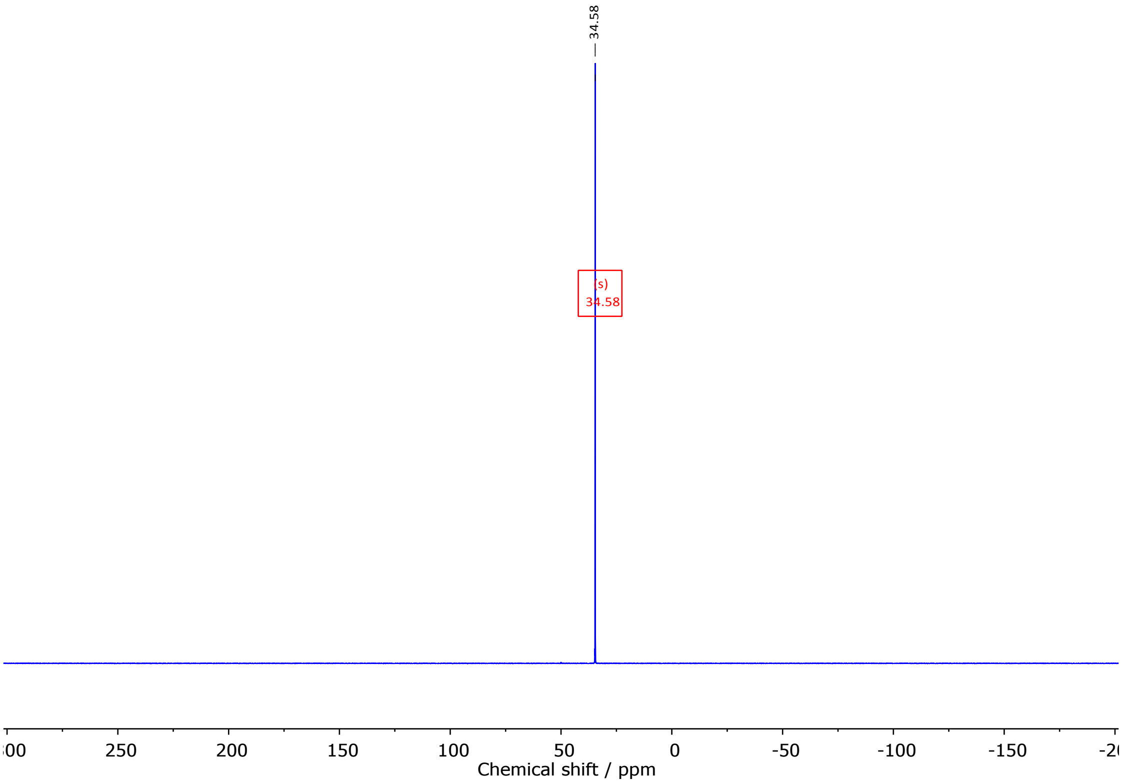

Figure S51: $^{31}P\{^{1}H\}$ NMR spectrum of $[P_{4442}][Br]$.

7.13 NMR spectra of $[P_{4442}][NTf_2]$

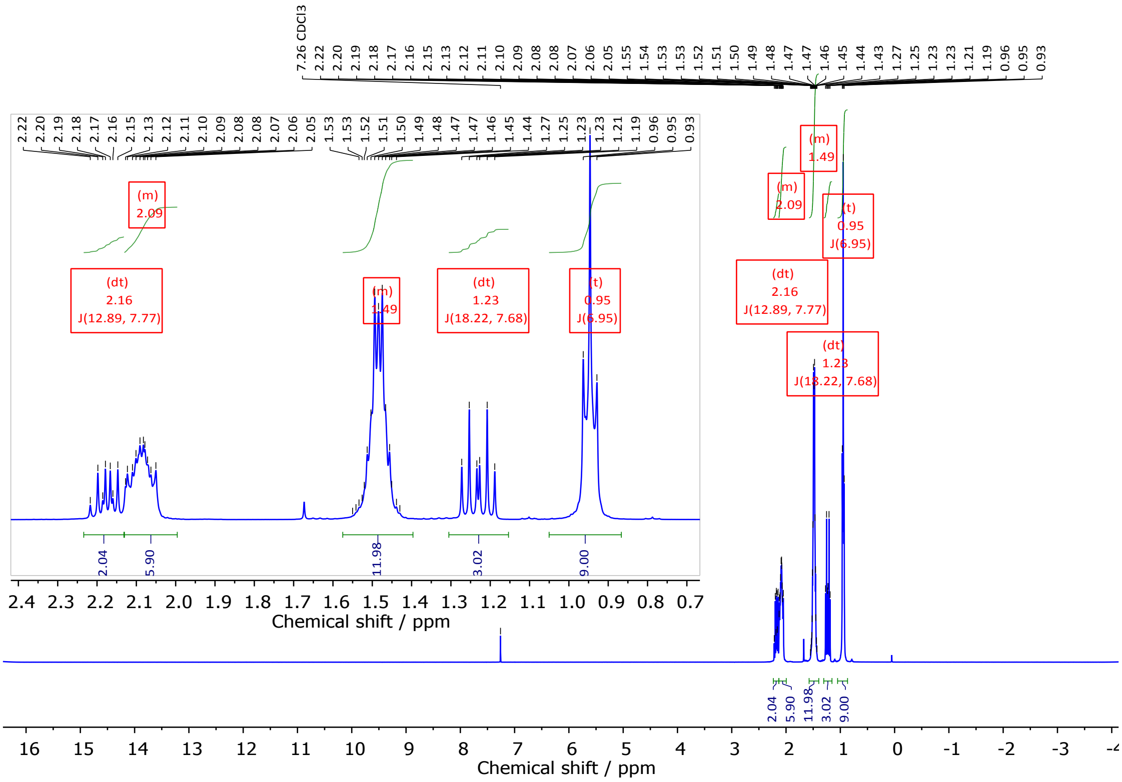

Figure S52: ^{1}H NMR spectrum of $[P_{4442}][NTf_2]$.

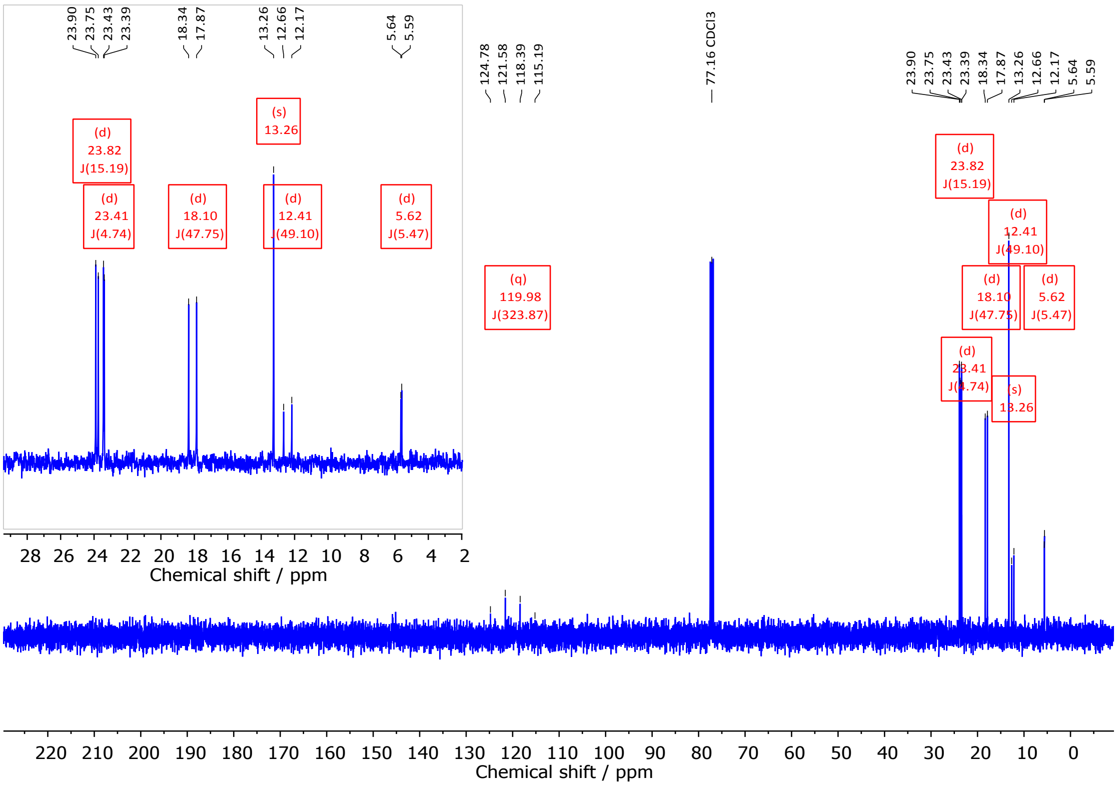

Figure S53: $^{13}C\{^1H\}$ NMR spectrum of $[P_{4442}][NTf_2]$.

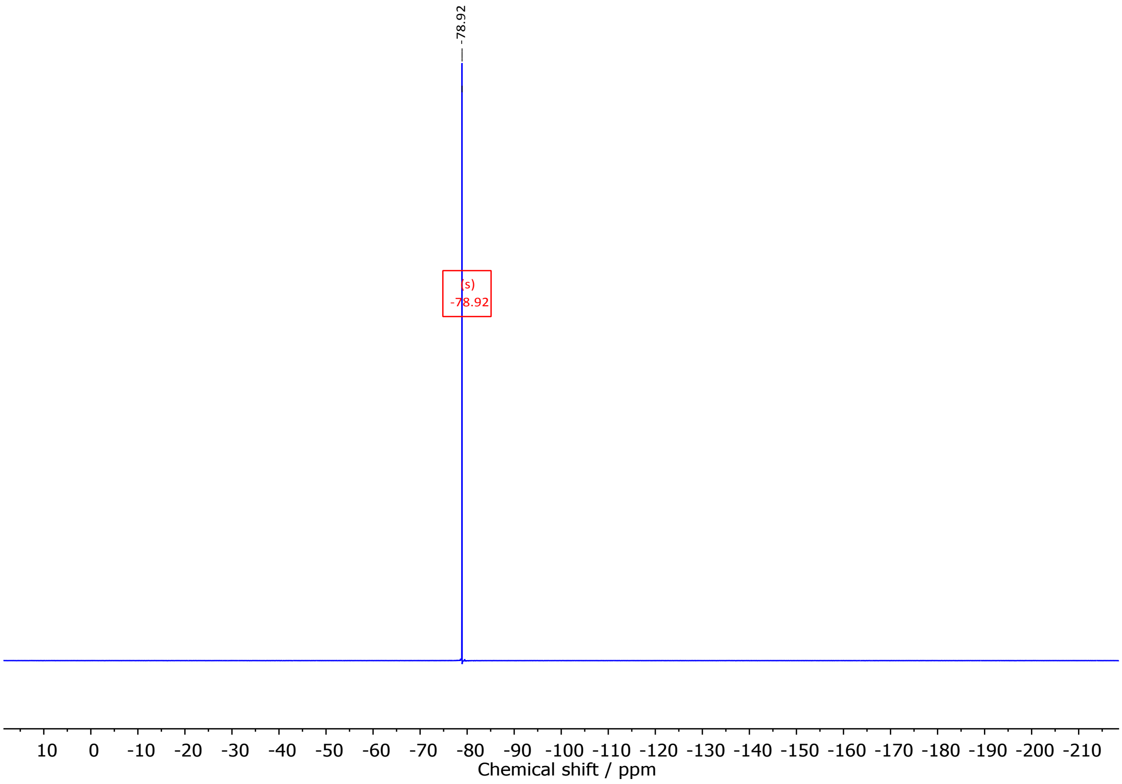

Figure S54: $^{19}F\{^1H\}$ NMR spectrum of $[P_{4442}][NTf_2]$.

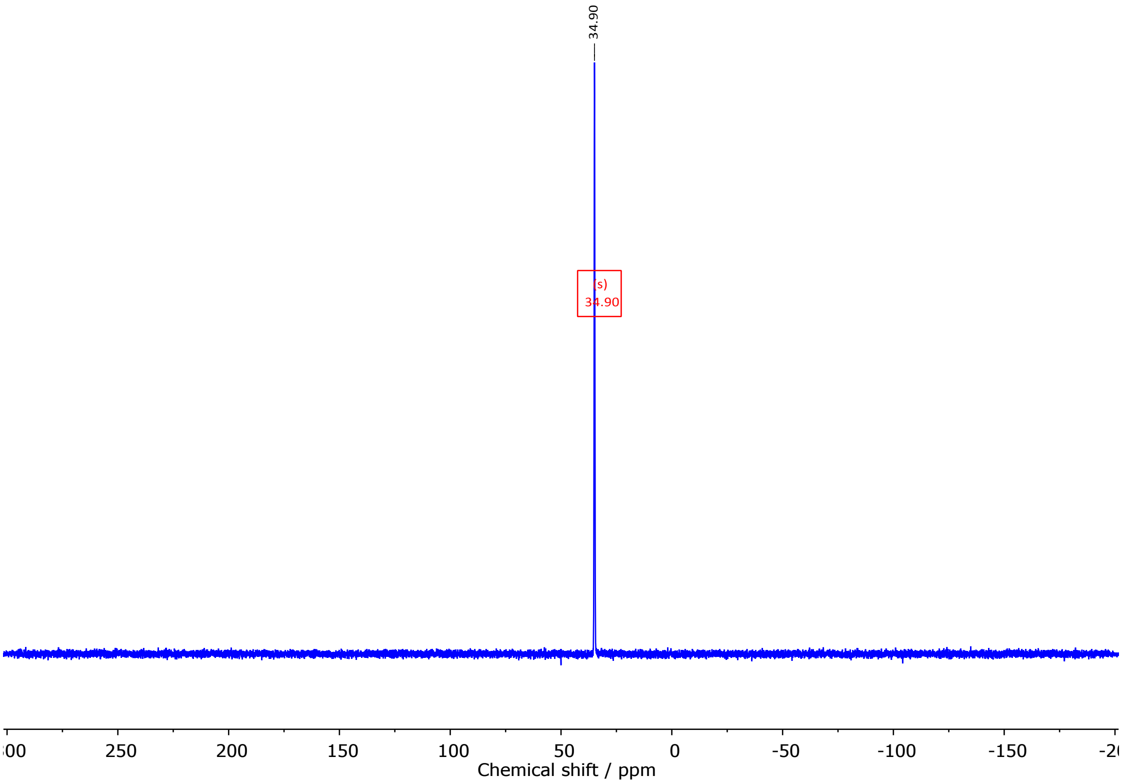

Figure S55: $^{31}P\{^1H\}$ NMR spectrum of $[P_{4442}][NTf_2]$.

7.14 NMR spectra of $[P_{4446}][Br]$

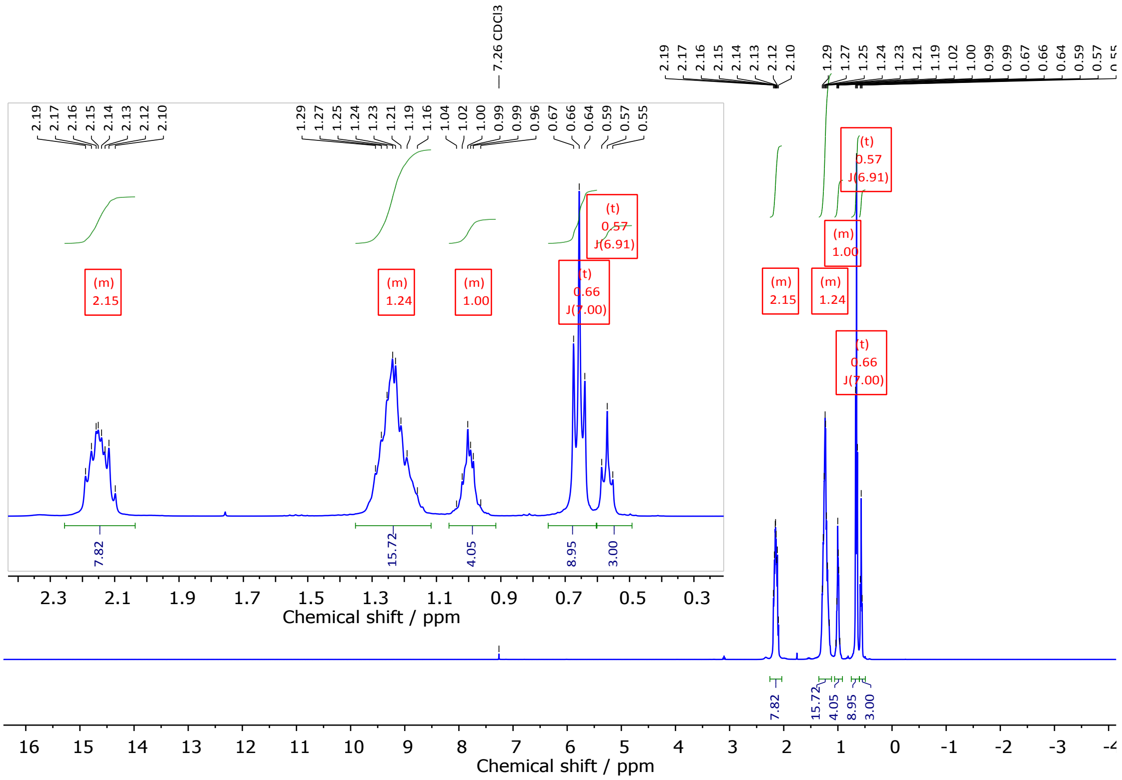

Figure S56: ^1H NMR spectrum of $[P_{4446}][Br]$.

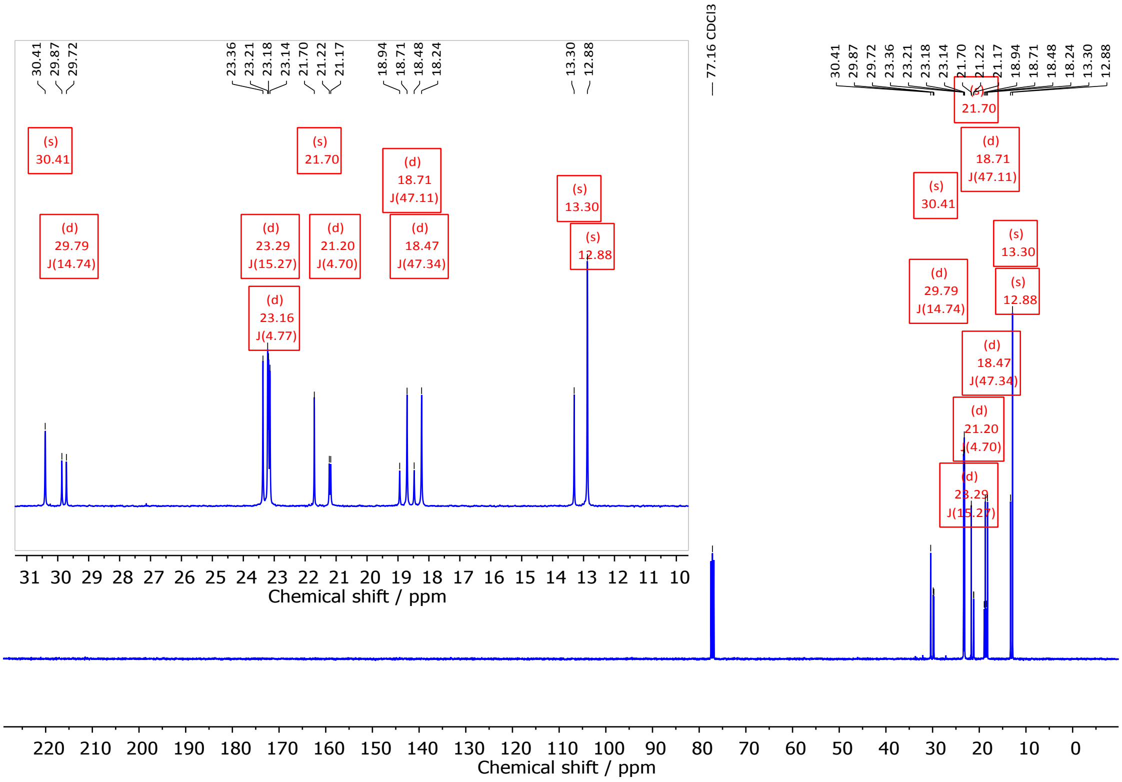

Figure S57: $^{13}C\{^{1}H\}$ NMR spectrum of $[P_{4446}][Br]$.

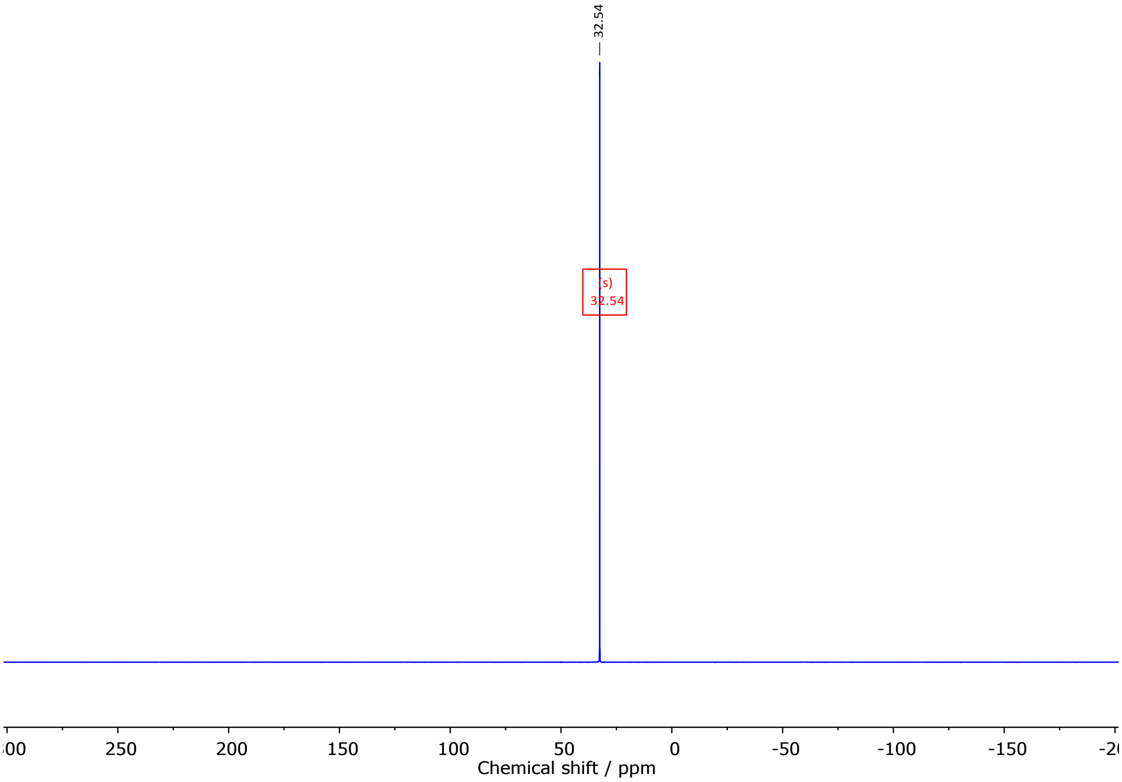

Figure S58: $^{31}P\{^{1}H\}$ NMR spectrum of $[P_{4446}][Br]$.

7.15 NMR spectra of [P_{4446}][NTf_2]

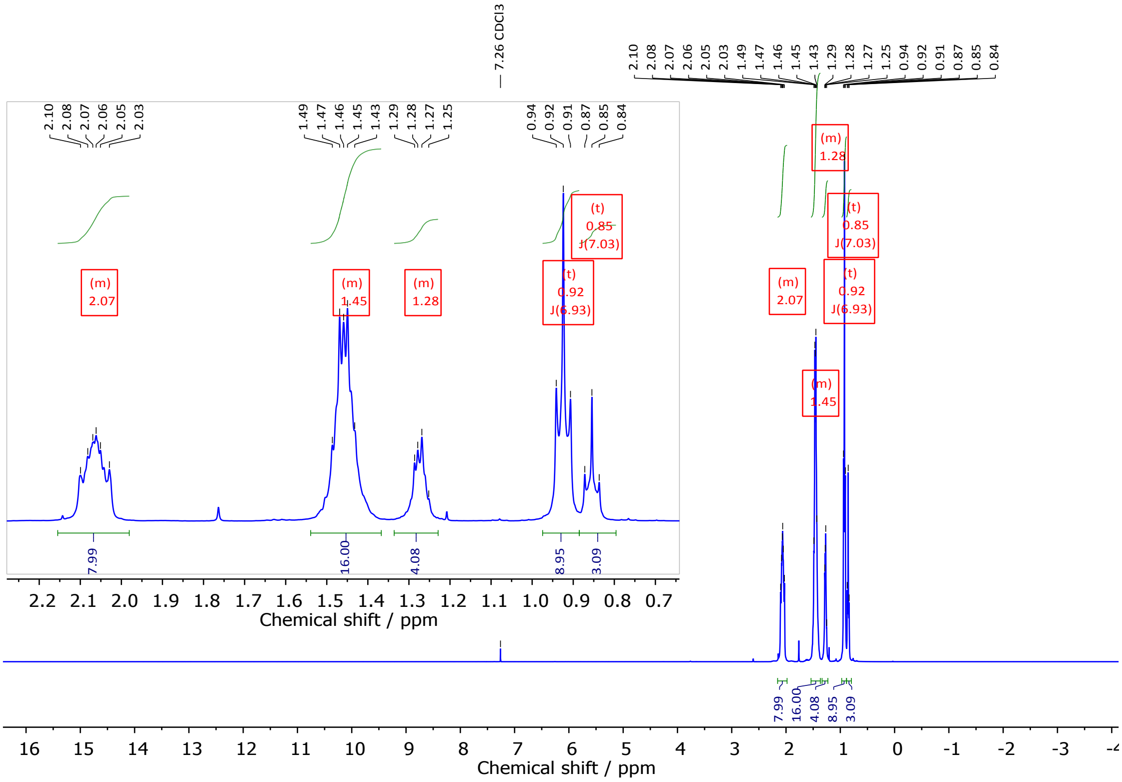

Figure S59: ^{1}H NMR spectrum of [P_{4446}][NTf_2].

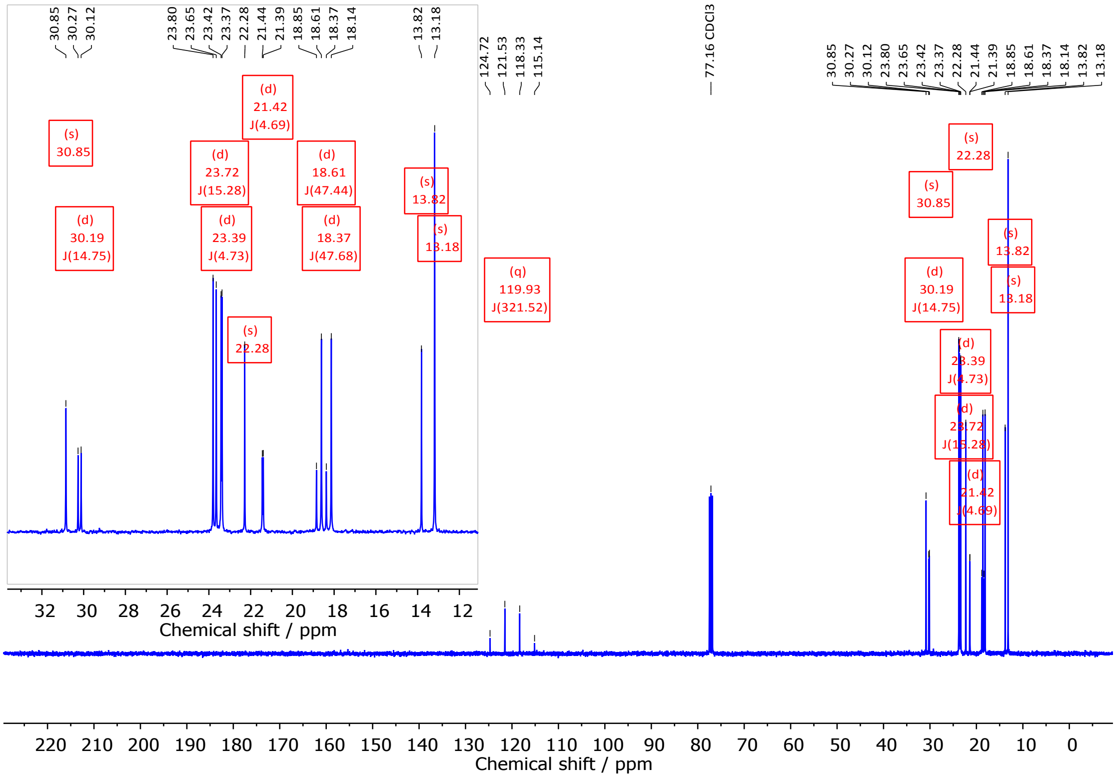

Figure S60: ^{13}C{^{1}H} NMR spectrum of [P_{4446}][NTf_2].

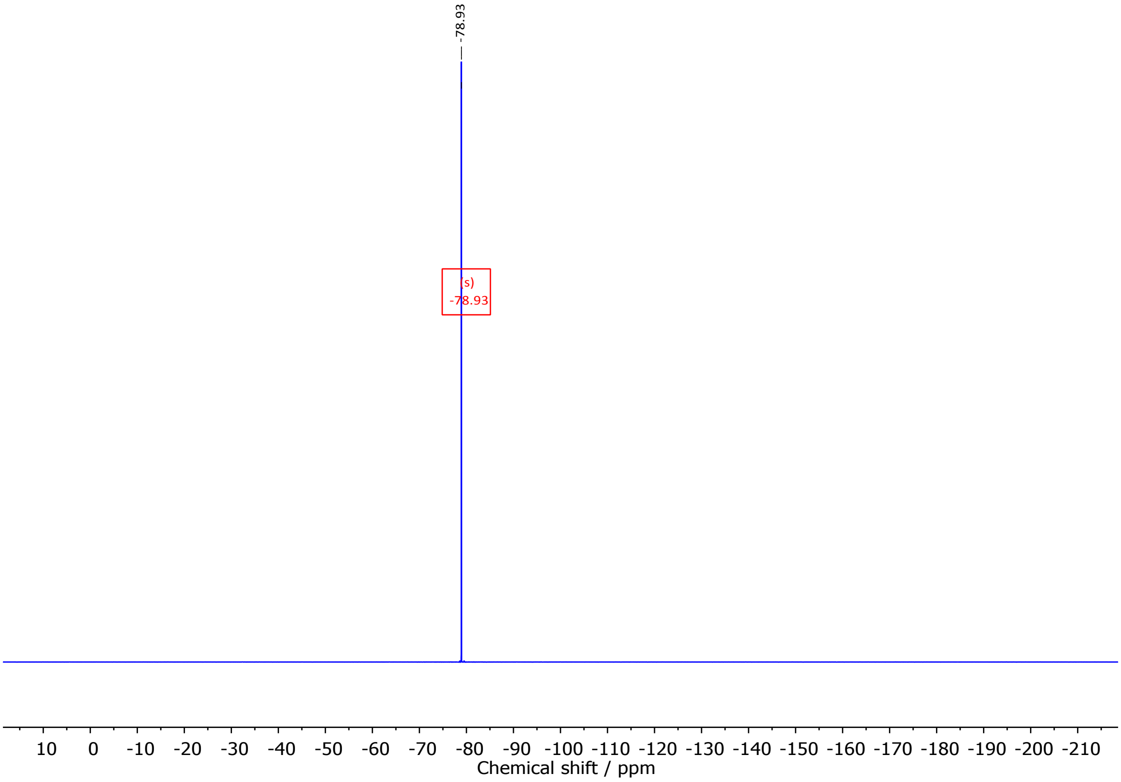

Figure S61: $^{19}F\{^1H\}$ NMR spectrum of $[P_{4446}][NTf_2]$.

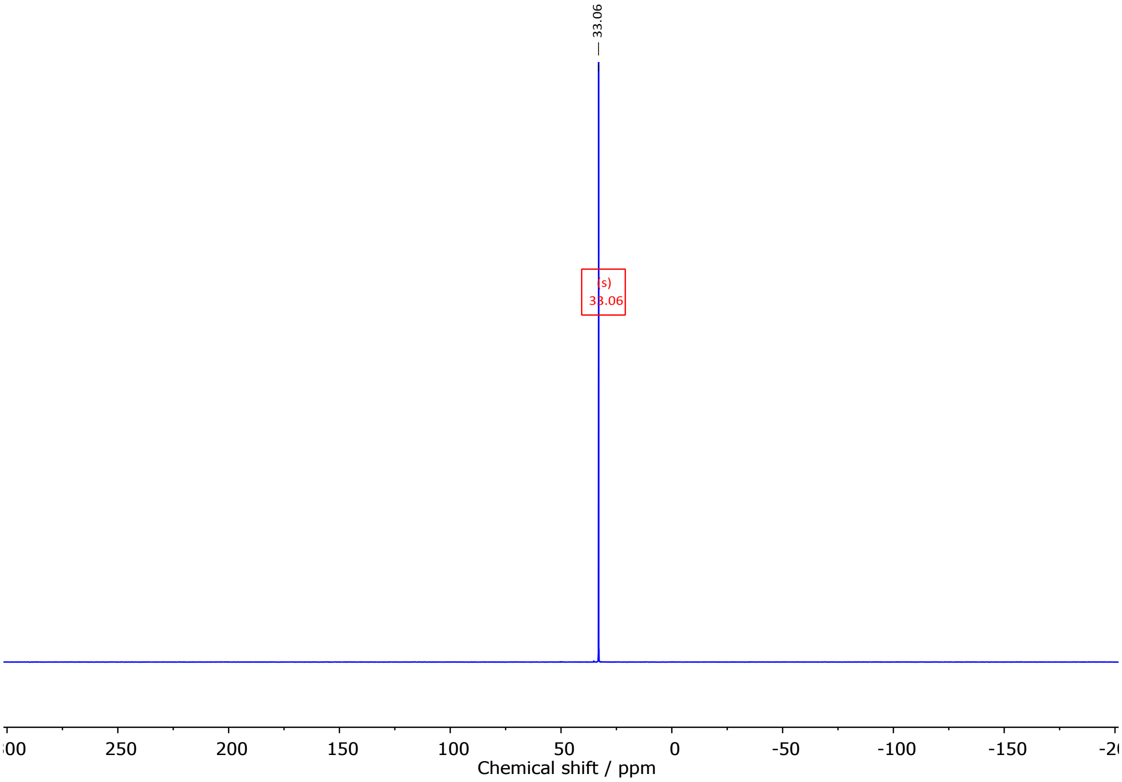

Figure S62: $^{31}P\{^1H\}$ NMR spectrum of $[P_{4446}][NTf_2]$.

7.16 NMR spectra of [P_{4448}][Br]

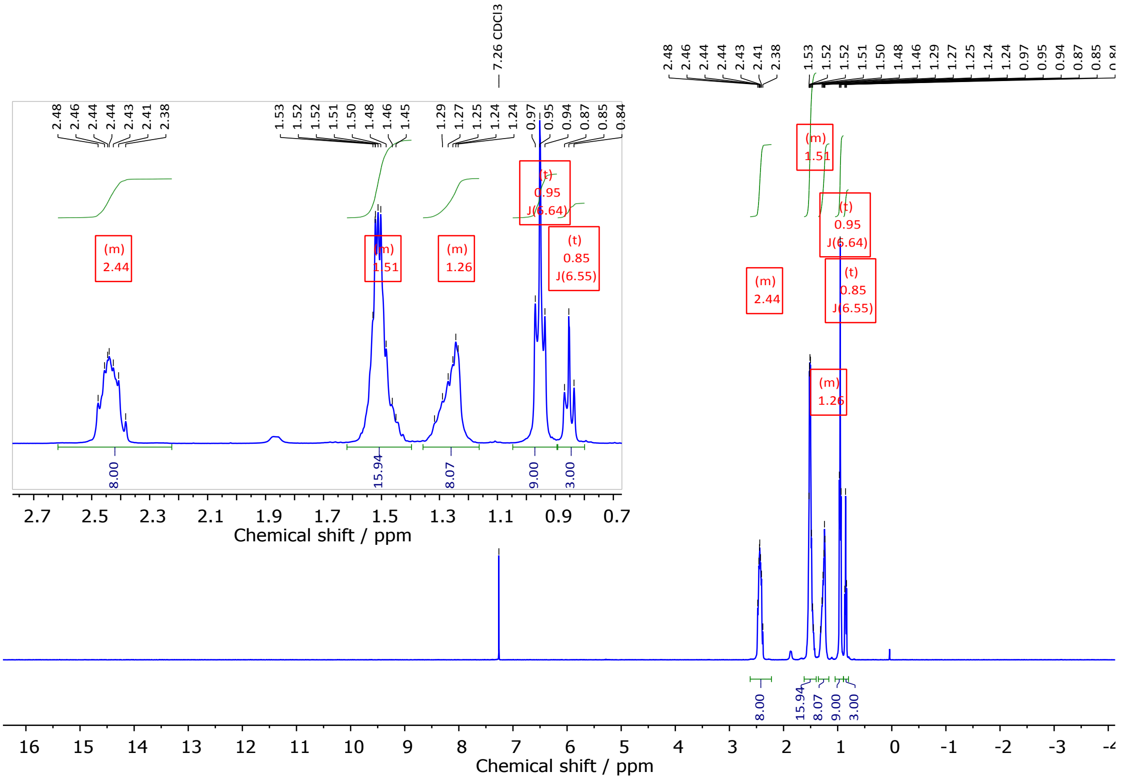

Figure S63: ^{1}H NMR spectrum of [P_{4448}][Br].

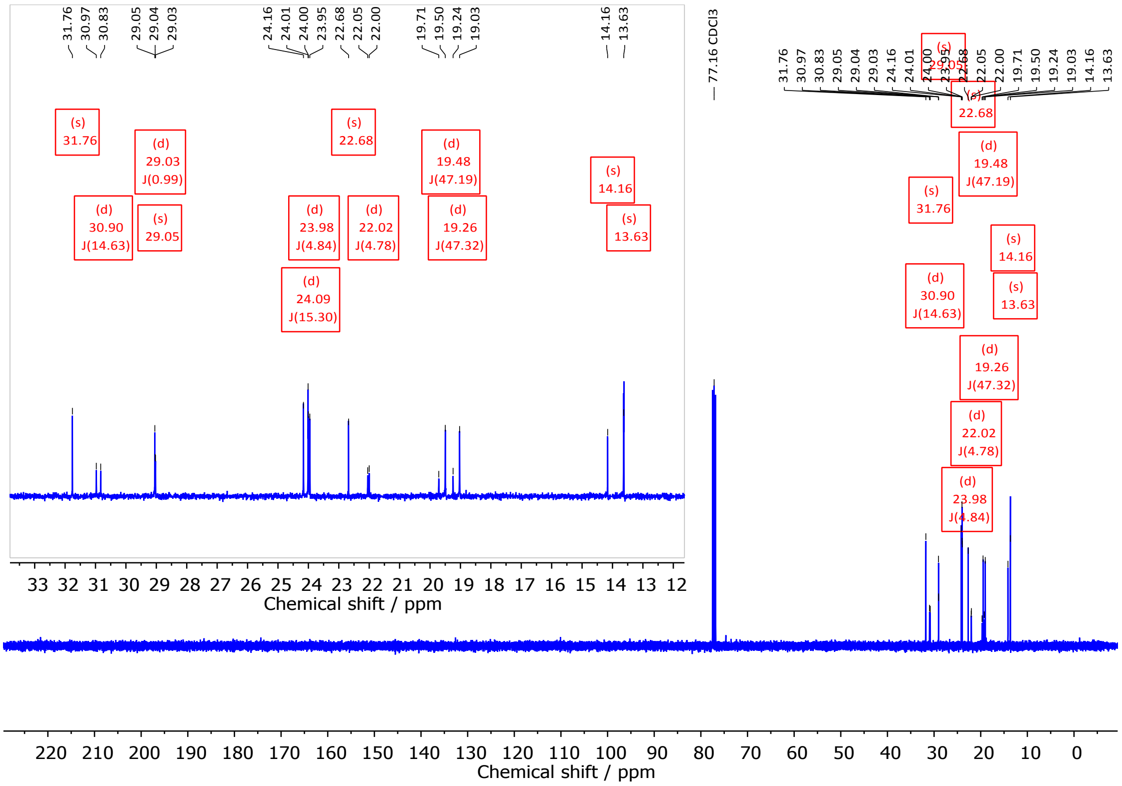

Figure S64: ^{13}C{^{1}H} NMR spectrum of [P_{4448}][Br].

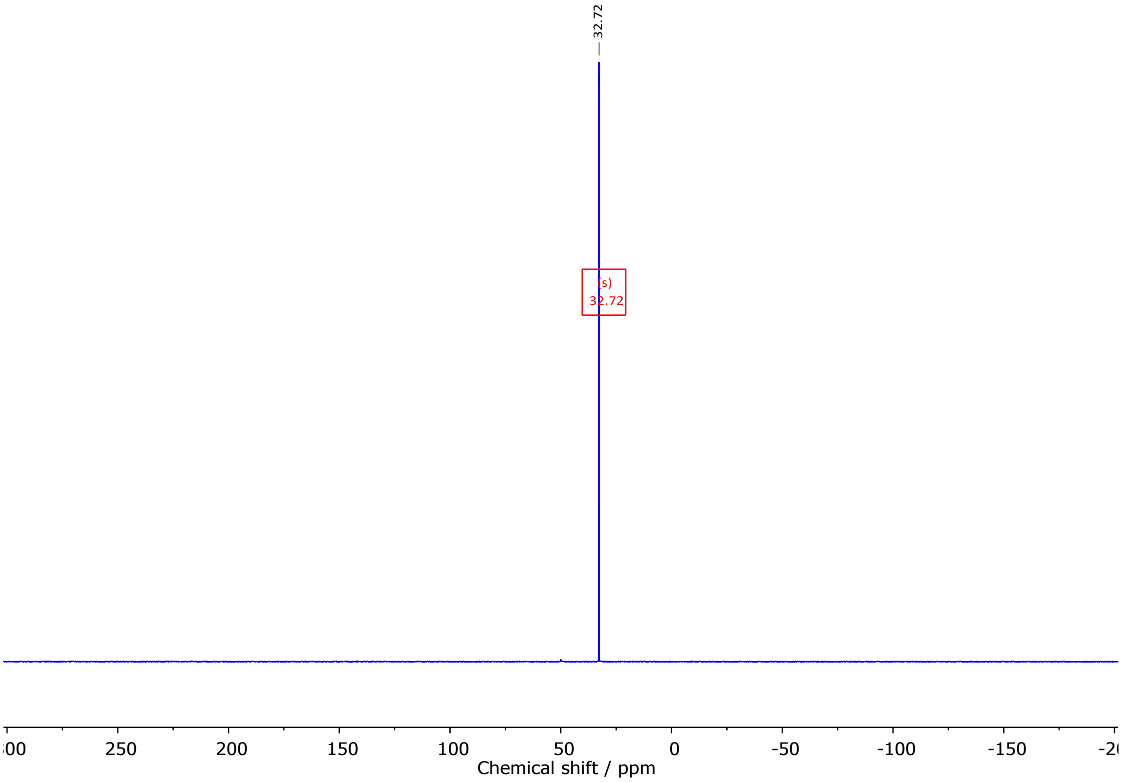

Figure S65: $^{31}P\{^{1}H\}$ NMR spectrum of $[P_{4448}][Br]$.

7.17 NMR spectra of $[P_{4448}][NTf_2]$

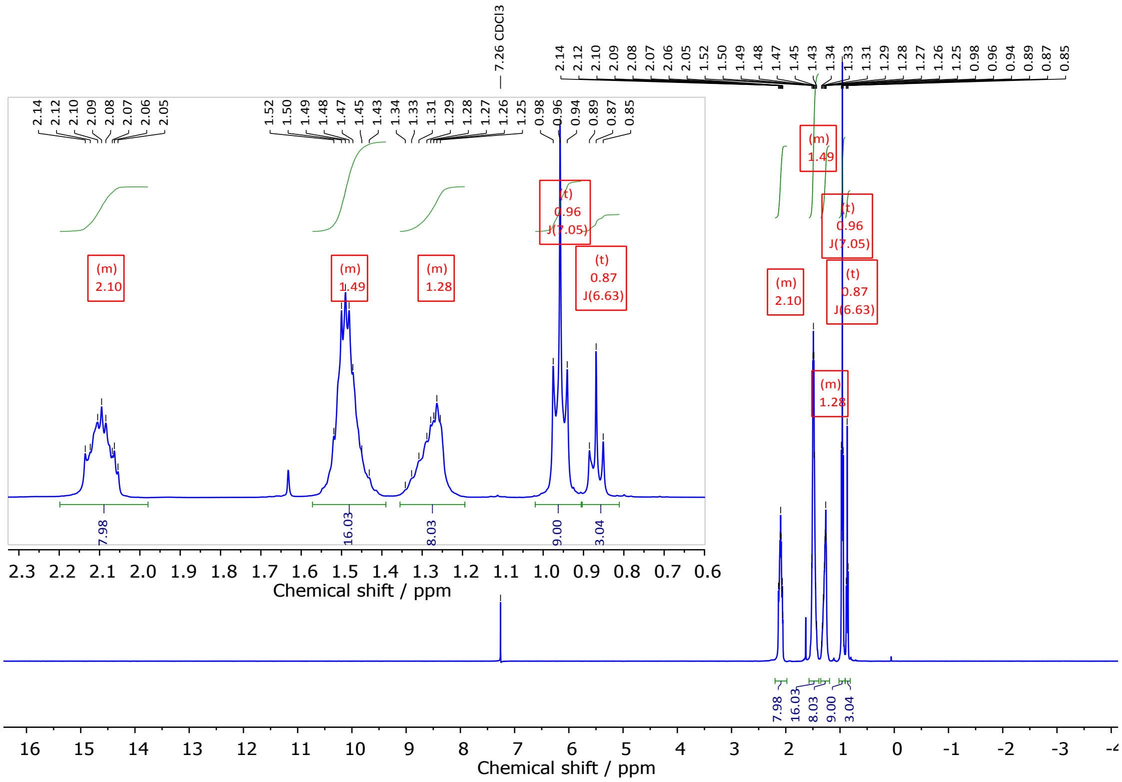

Figure S66: ^{1}H NMR spectrum of $[P_{4448}][NTf_2]$.

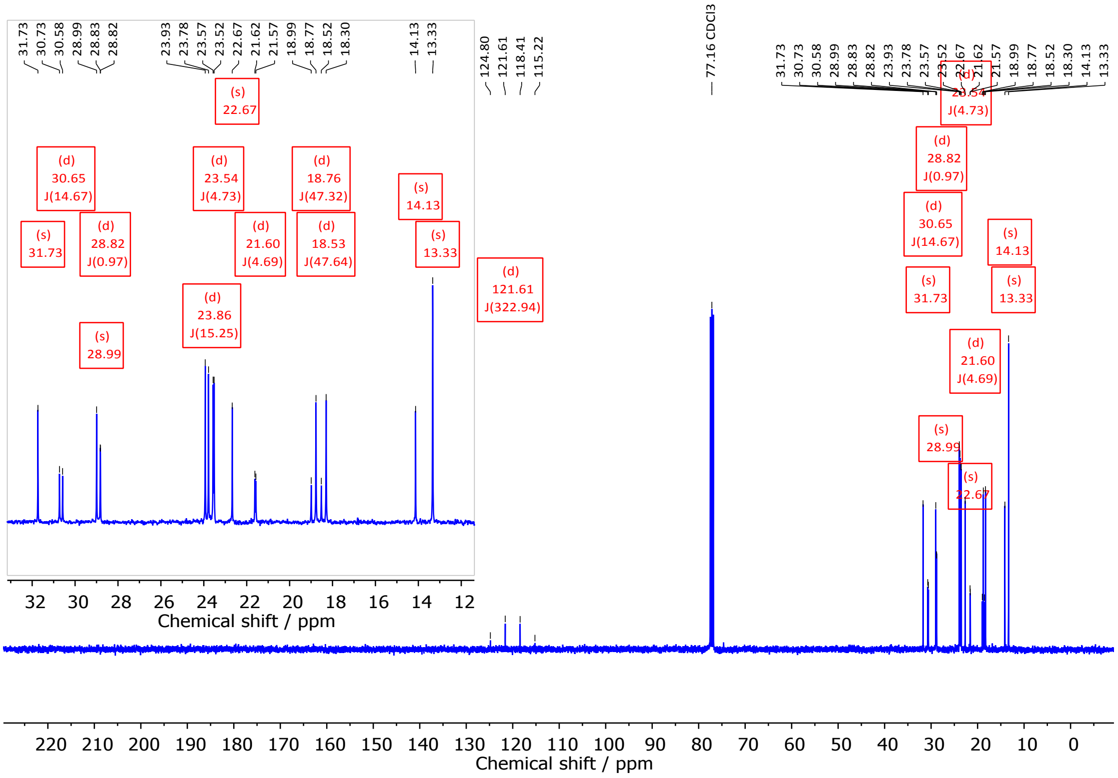

Figure S67: $^{13}C\{^1H\}$ NMR spectrum of [P_{4448}][NTf_2].

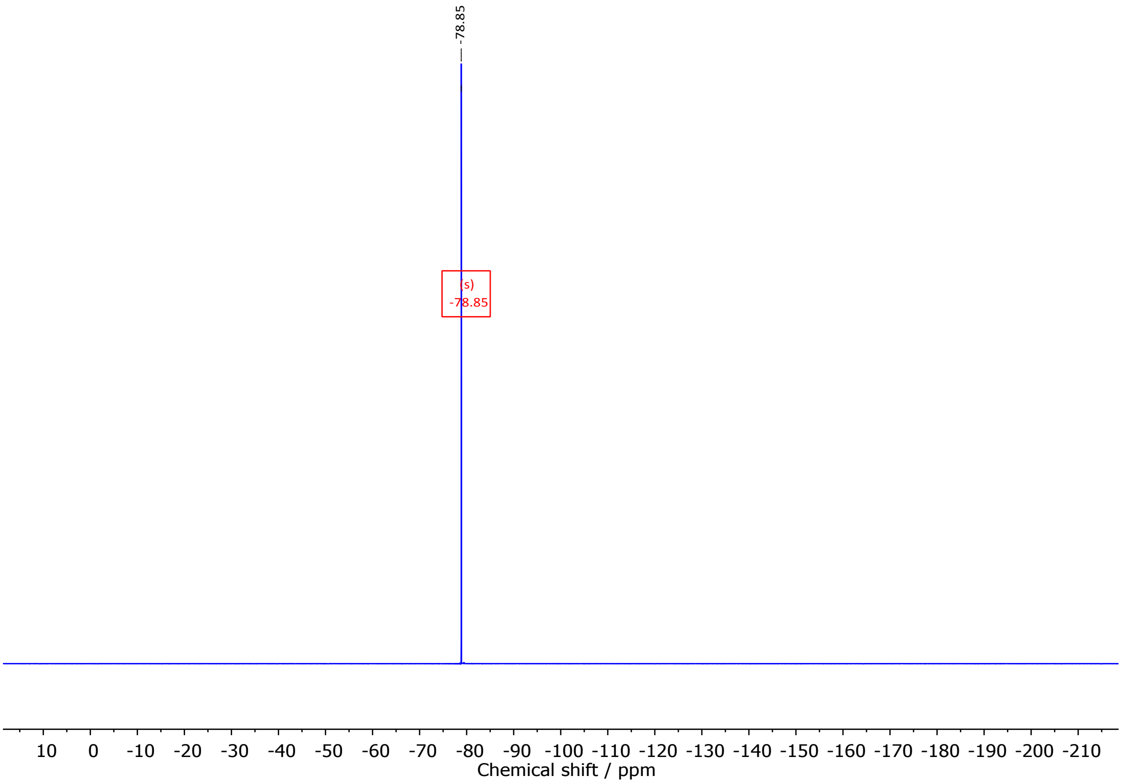

Figure S68: $^{19}F\{^1H\}$ NMR spectrum of [P_{4448}][NTf_2].

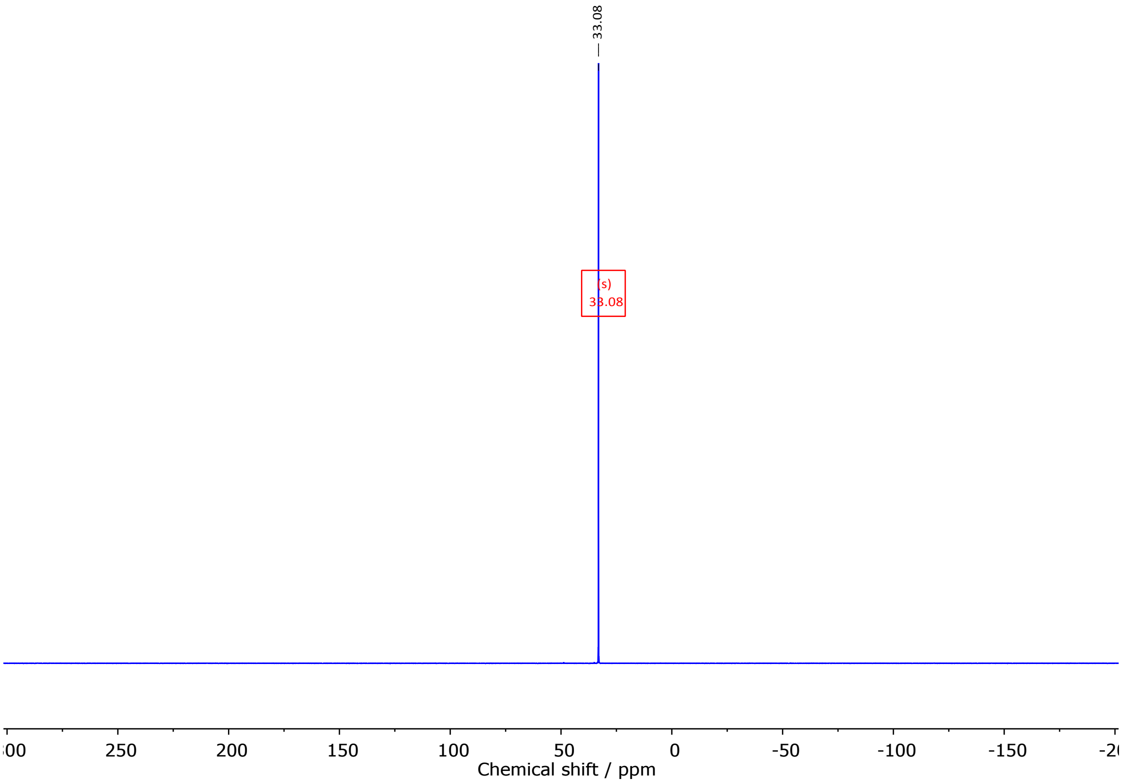

Figure S69: $^{31}P\{^{1}H\}$ NMR spectrum of $[P_{4448}][NTf_2]$.

7.18 NMR spectra of $[P_{44410}][Br]$

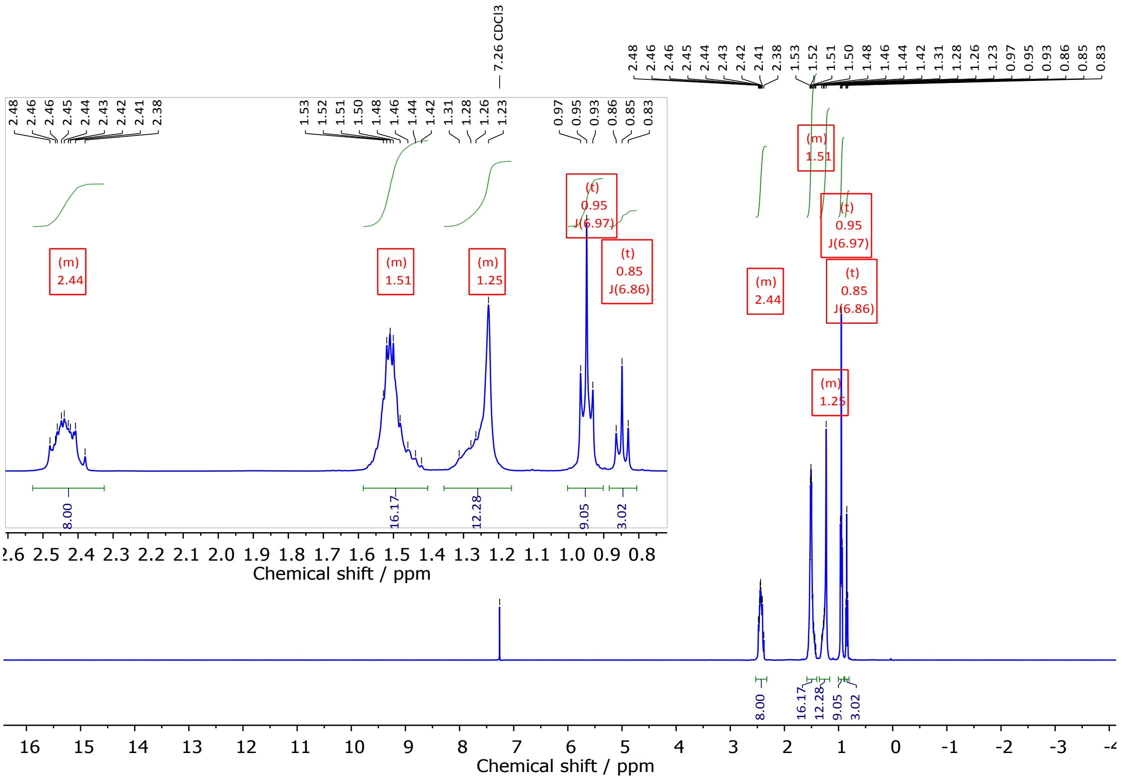

Figure S70: ^{1}H NMR spectrum of $[P_{44410}][Br]$.

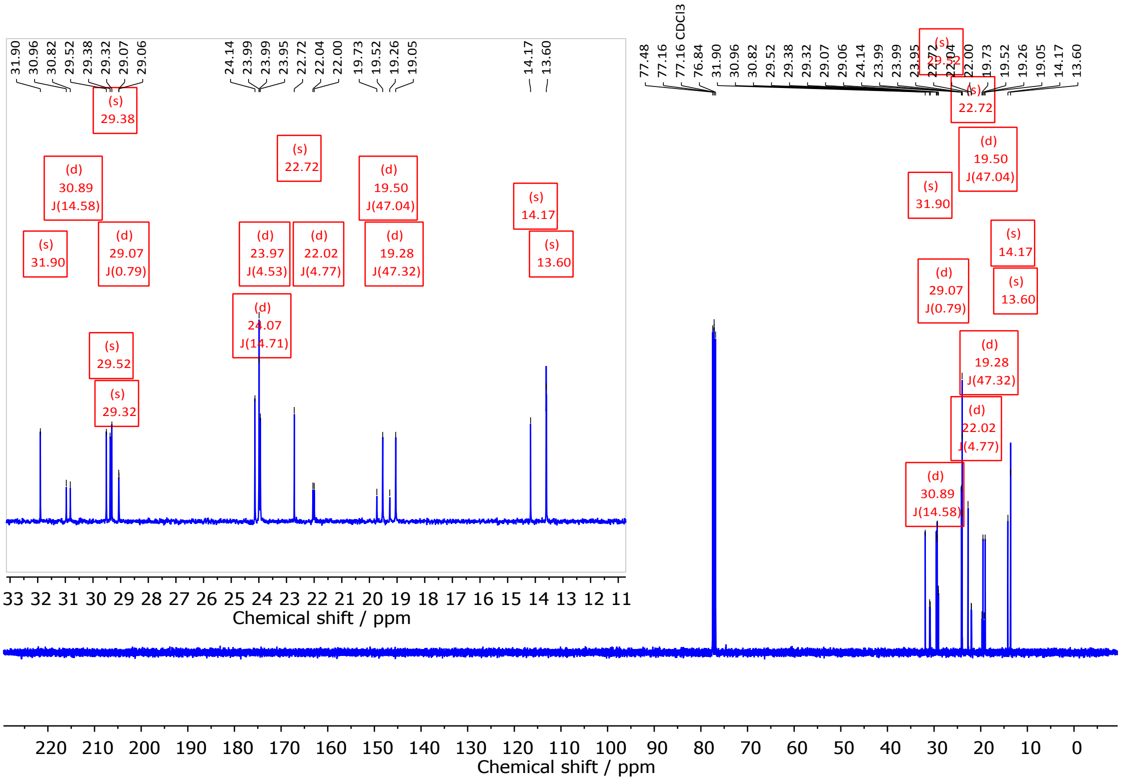

Figure S71: $^{13}C\{^1H\}$ NMR spectrum of $[P_{44410}][Br]$.

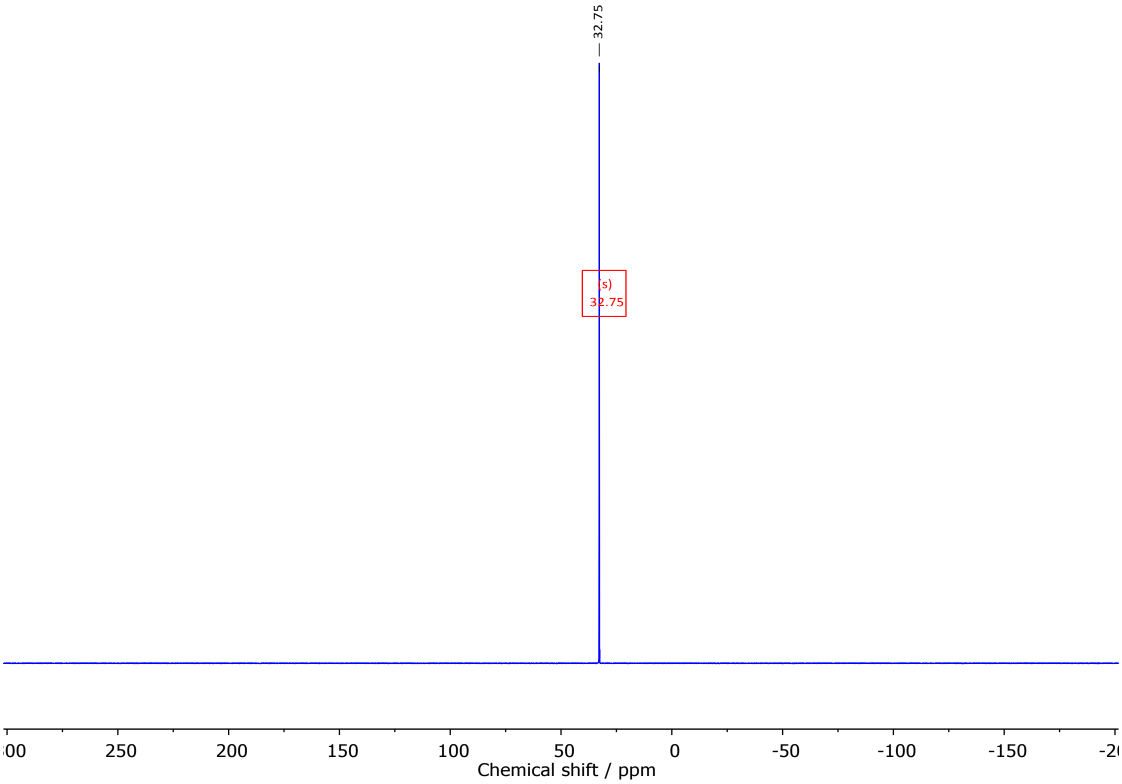

Figure S72: $^{31}P\{^1H\}$ NMR spectrum of $[P_{44410}][Br]$.

7.19 NMR spectra of [P_{44410}][NTf_2]

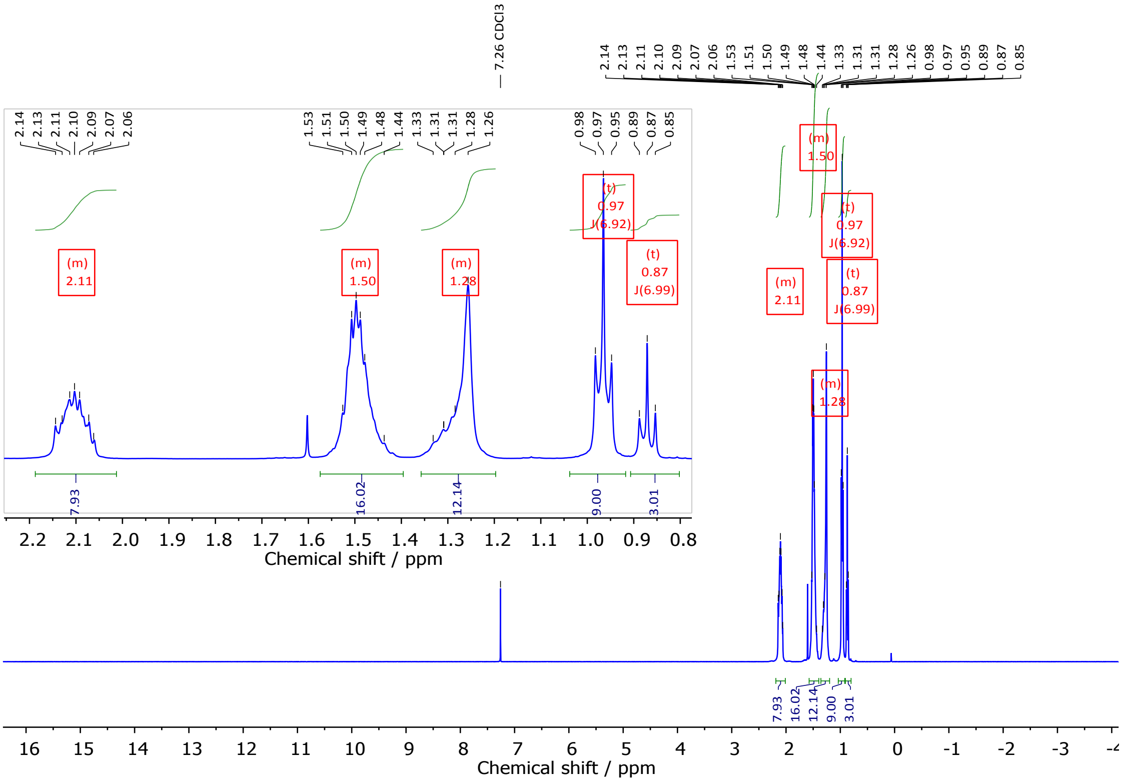

Figure S73: ^{1}H NMR spectrum of [P_{44410}][NTf_2].

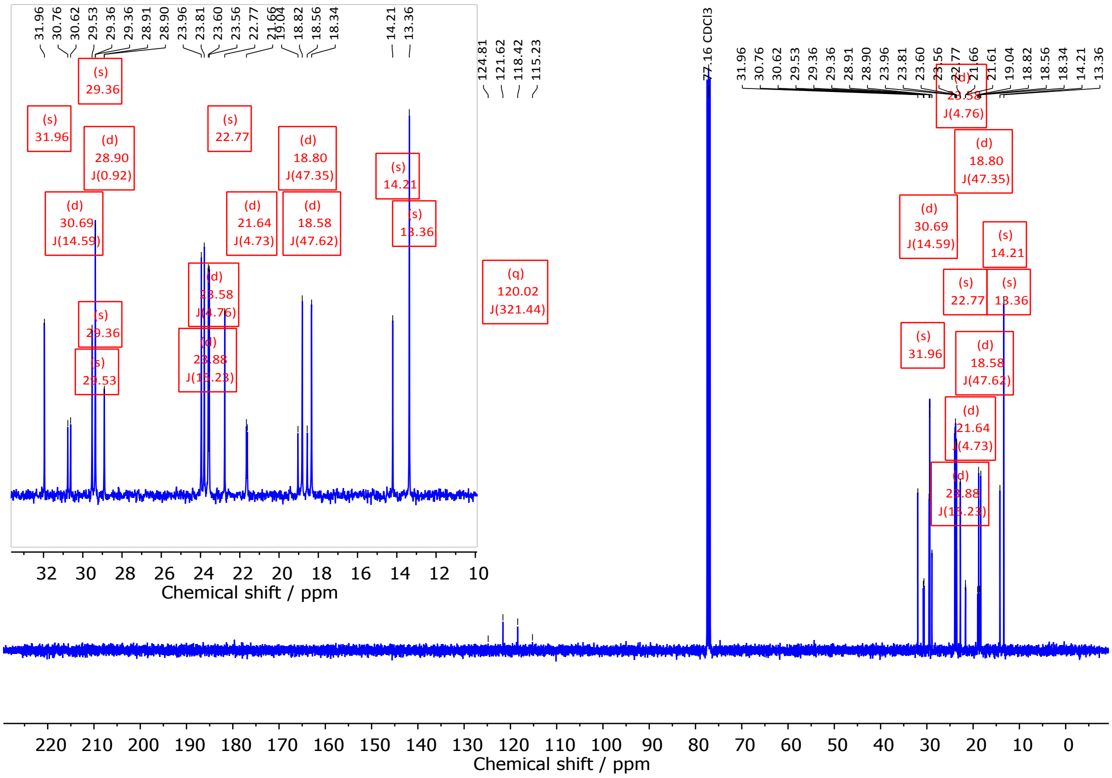

Figure S74: ^{13}C{^{1}H} NMR spectrum of [P_{44410}][NTf_2].

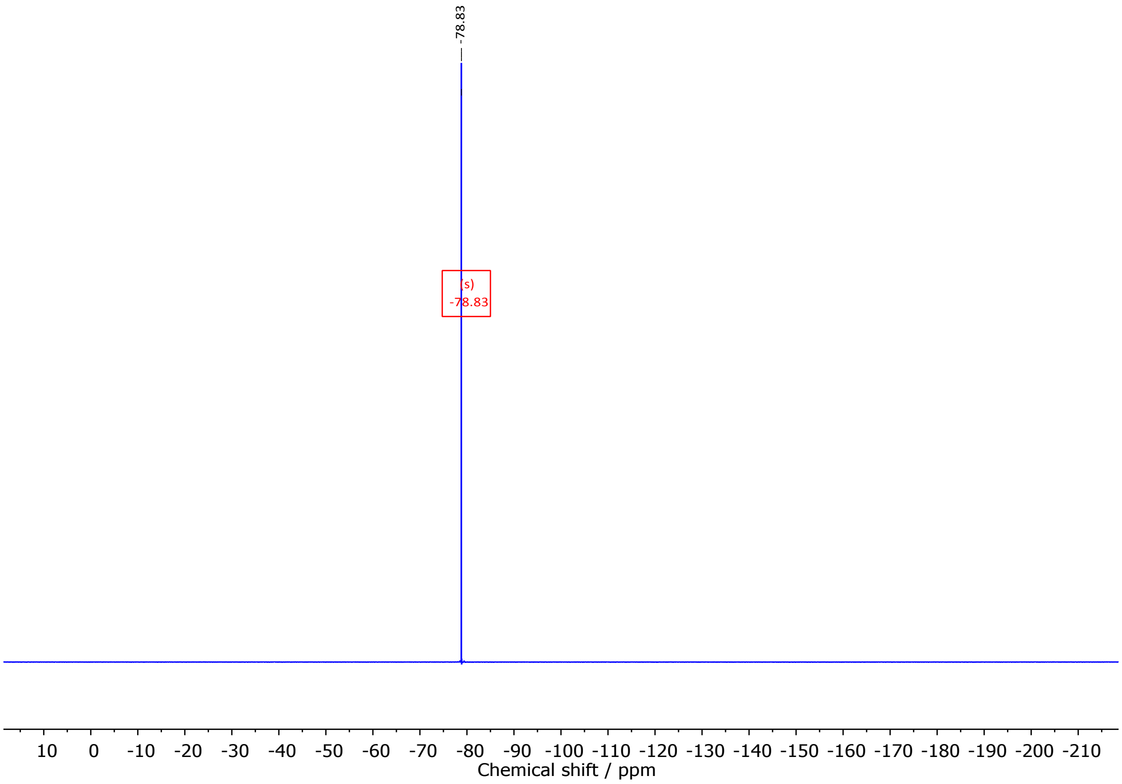

Figure S75: $^{19}F\{^1H\}$ NMR spectrum of $[P_{44410}][NTf_2]$.

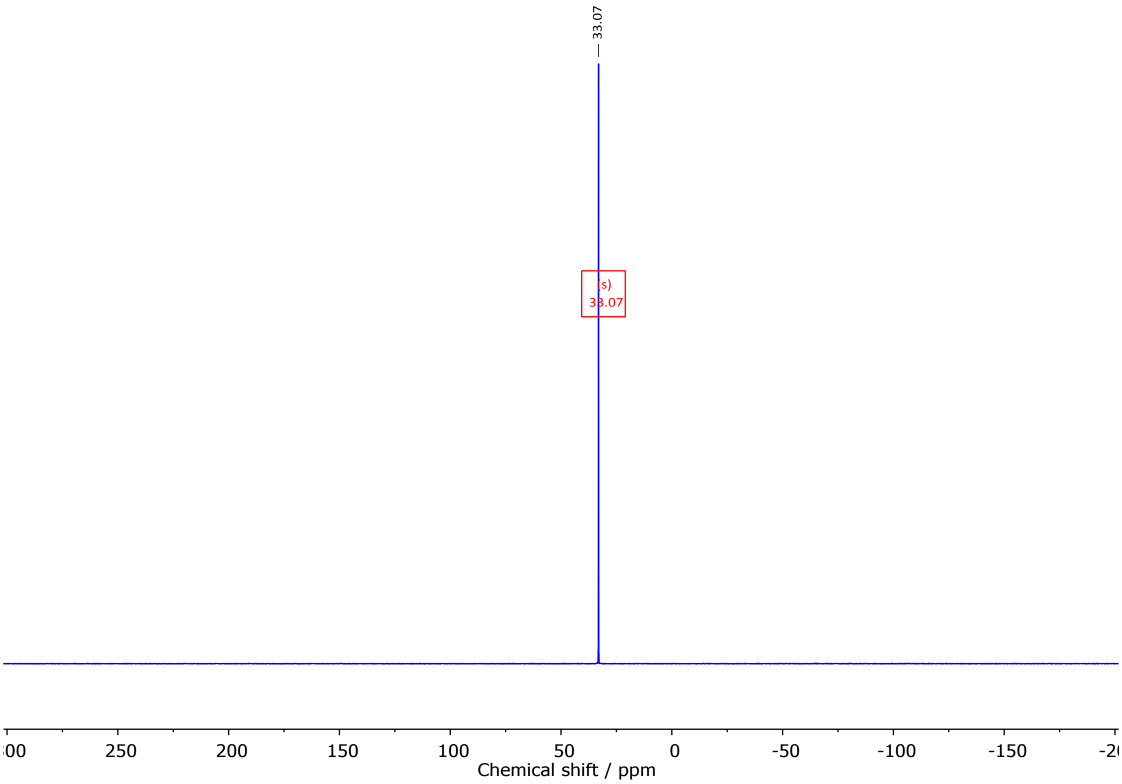

Figure S76: $^{31}P\{^1H\}$ NMR spectrum of $[P_{44410}][NTf_2]$.

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