Electronic Supplementary Material (ESI) for Green Chemistry

Supplementary Information for:

Ruthenium nanoparticle catalysts stabilized in phosphonium and imidazolium ionic liquids: Dependence of catalyst stability and activity on the ionicity of the ionic liquid

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Transmission Electron Microscopic Data

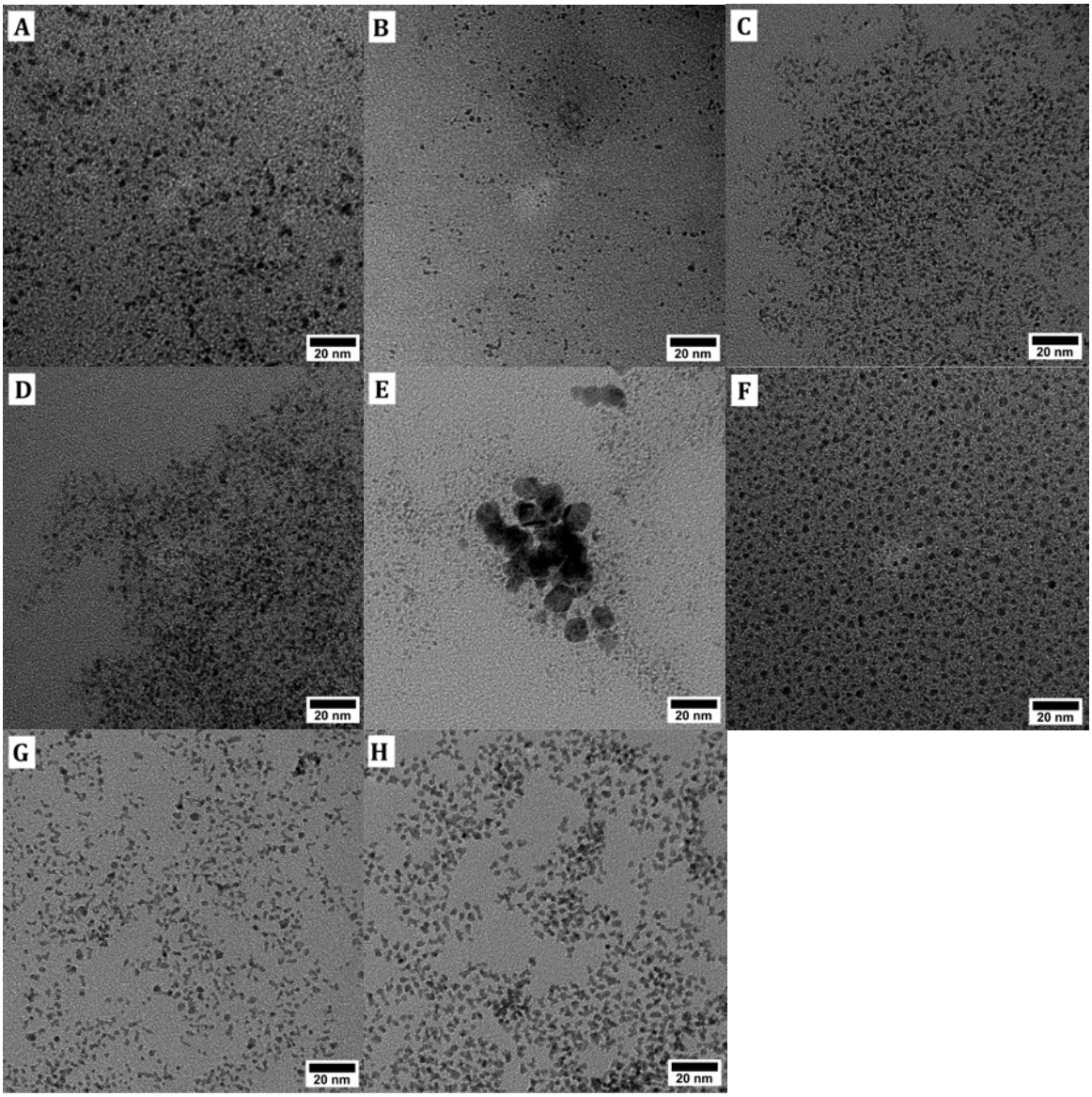

Fig. S1 TEM images for Ru NPs before catalysis prepared in (A) $[P_{4,4,4,1}]NTf_2$, (B) $[P_{4,4,4,8}]NTf_2$, (C) $[P_{4,4,4,14}]NTf_2$, (D) $[P_{4,4,4,1}]OTf$, (E) $[P_{4,4,4,1}]PF_6$, (F) $[P_{4,4,4,1}]Cl$, (G) $[BMI]NTf_2$ and (H) $[BDMI]NTf_2$.

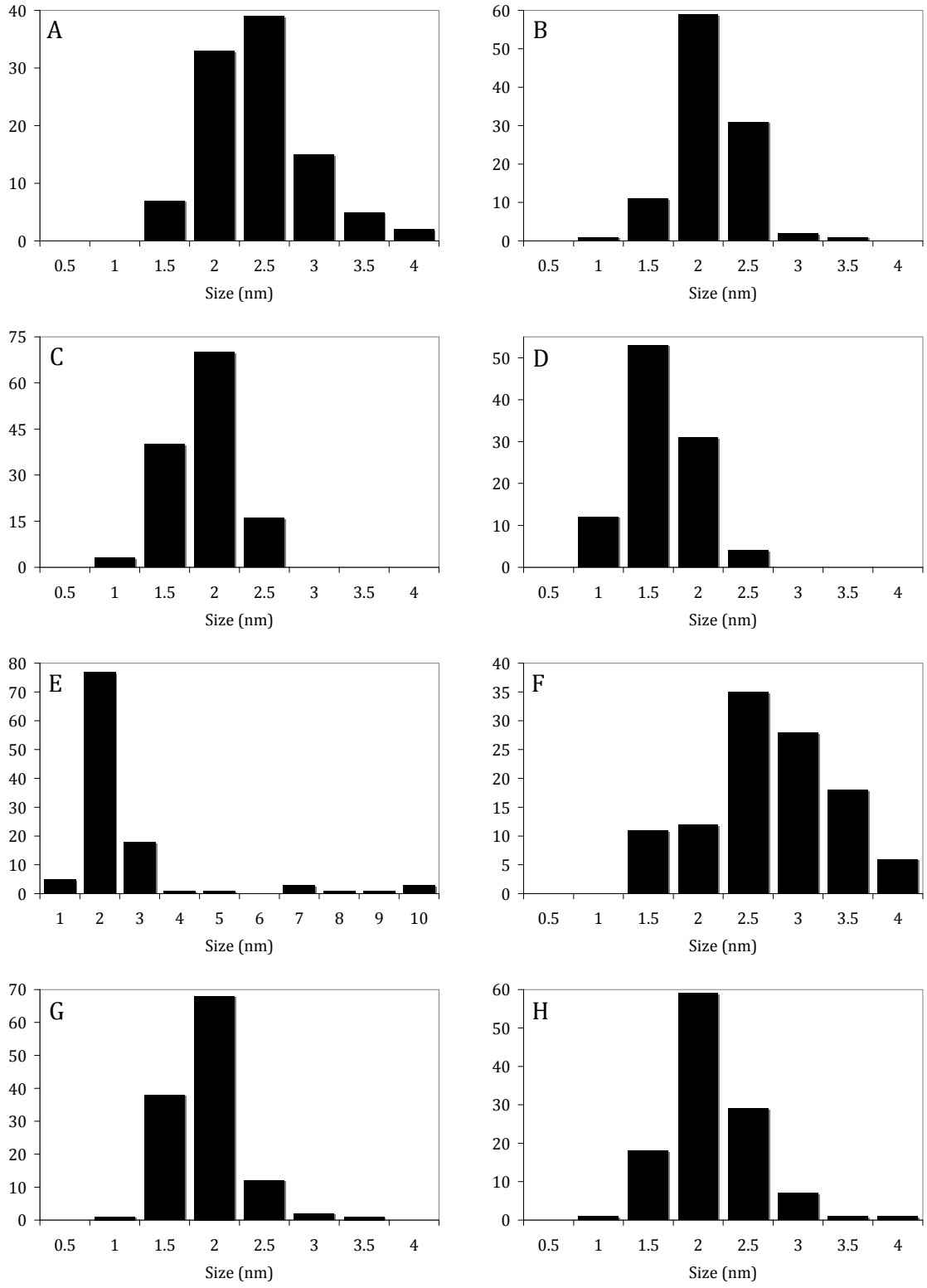

Fig. S2 TEM histograms for Ru NPs before catalysis prepared in (A) $[P_{4,4,4,1}]NTf_2$, (B) $[P_{4,4,4,8}]NTf_2$, (C) $[P_{4,4,4,14}]NTf_2$, (D) $[P_{4,4,4,1}]OTf$, (E) $[P_{4,4,4,1}]PF_6$, (F) $[P_{4,4,4,1}]Cl$, (G) $[BMI]NTf_2$ and (H) $[BDMI]NTf_2$.

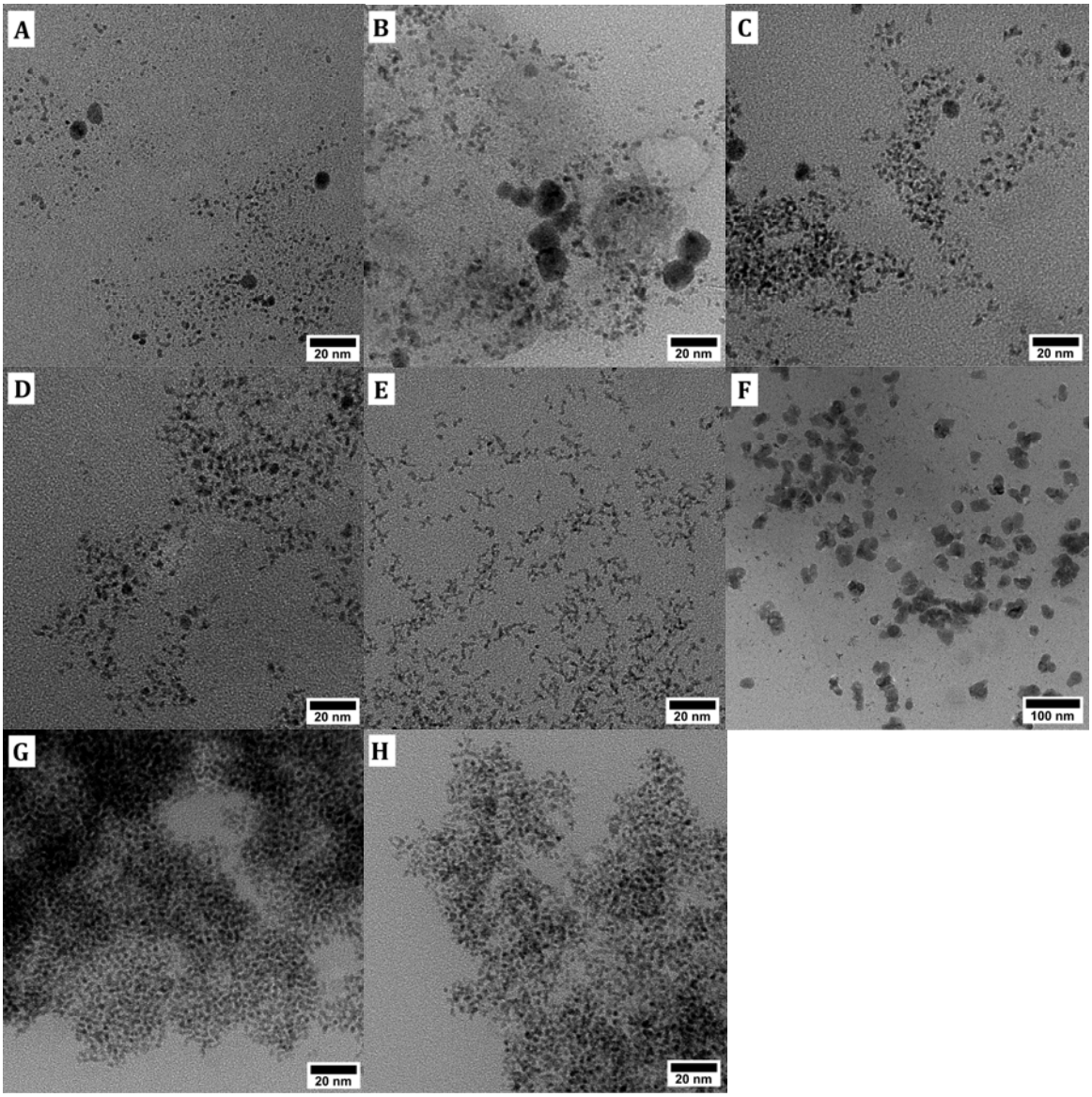

Fig. S3 TEM images for Ru NPs after catalysis prepared in (A) $[P_{4,4,4,1}]NTf_2$, (B) $[P_{4,4,4,8}]NTf_2$, (C) $[P_{4,4,4,14}]NTf_2$, (D) $[P_{4,4,4,1}]OTf$, (E) $[P_{4,4,4,1}]PF_6$, (F) $[P_{4,4,4,1}]Cl$, (G) $[BMI]NTf_2$ and (H) $[BDMI]NTf_2$.

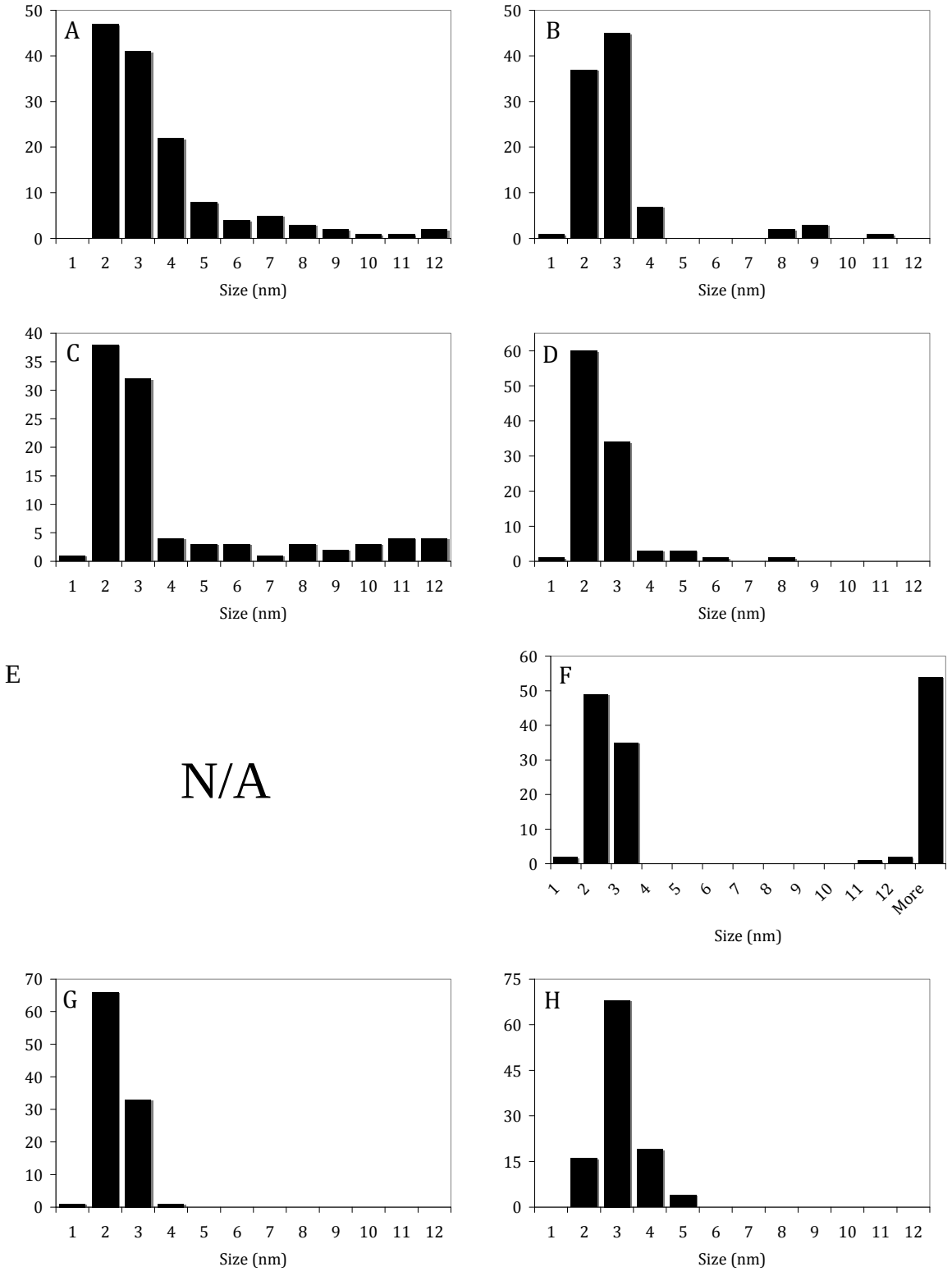

Fig. S4 TEM histograms for Ru NPs after catalysis prepared in (A) $[P_{4,4,4,1}]NTf_2$, (B) $[P_{4,4,4,8}]NTf_2$, (C) $[P_{4,4,4,14}]NTf_2$, (D) $[P_{4,4,4,1}]OTf$, (E) $[P_{4,4,4,1}]PF_6$, (F) $[P_{4,4,4,1}]Cl$, (G) $[BMI]NTf_2$ and (H) $[BDMI]NTf_2$.

Walden Plot Data

Table S1. Experimental Density (ρ_{exp}) for Phosphonium and Imidazolium Ionic Liquids as a Function of Temperature (T)

Ionic Liquid	ρ_{exp} (g·cm^{-3}) at T (K)				
	293.15	298.15	303.15	308.15	313.15
$[P_{4,4,4,1}]NTf_2$	1.254	1.250	1.245	1.241	1.237
$[P_{4,4,4,8}]NTf_2$	1.159	1.156	1.151	1.147	1.143
$[P_{4,4,4,14}]NTf_2$	1.107	1.104	1.100	1.096	1.092
$[BMI]NTf_2$	1.433	1.428	1.423	1.418	1.413
$[BDMI]NTf_2$	1.416	1.412	1.407	1.402	1.397

Table S2. Calculated Density (ρ_{calc}) for Phosphonium and Imidazolium Ionic Liquids as a Function of Temperature (T) Employing the Parameters of the Linear Fit ($\rho_{exp} = aT - b$)

Ionic Liquid	Parameters		ρ_{calc} (g·cm^{-3}) at T (K)		
	a	b	333.15	343.15	353.15
$[P_{4,4,4,1}]NTf_2$	-0.0009	1.5061	1.206	1.197	1.188
$[P_{4,4,4,8}]NTf_2$	-0.001	1.7261	1.133	1.125	1.117
$[P_{4,4,4,14}]NTf_2$	-0.001	1.6978	1.064	1.056	1.048
$[BMI]NTf_2$	-0.0008	1.3302	1.393	1.383	1.373
$[BDMI]NTf_2$	-0.0008	1.3998	1.365	1.355	1.345

Table S3. Experimental Viscosity (η) for Phosphonium and Imidazolium Ionic Liquids as a Function of Temperature (T)

Ionic Liquid	η (mPa·s) at T (K)		
	333.15	343.15	353.15
$[P_{4,4,4,1}]NTf_2$	38.7492	27.0152	19.7248
$[P_{4,4,4,8}]NTf_2$	47.9135	33.4342	24.1951
$[P_{4,4,4,14}]NTf_2$	62.1429	43.1084	30.7070
$[BMI]NTf_2$	15.0970	11.7808	9.5035
$[BDMI]NTf_2$	24.4223	18.1637	13.9608

Table S4. Specific Conductivity (κ) for Phosphonium and Imidazolium Ionic Liquids as a Function of Temperature (T)

Ionic Liquid	κ(mS·cm^{-1}) at T (K)		
	333.15	343.15	353.15
$[P_{4,4,4,1}]NTf_2$	2.4975	3.1745	3.8825
$[P_{4,4,4,8}]NTf_2$	1.2405	1.5796	1.9524
$[P_{4,4,4,14}]NTf_2$	0.6754	0.8858	1.1178
$[BMI]NTf_2$	10.5484	11.8184	13.2366
$[BDMI]NTf_2$	7.1790	8.4258	9.5600

Table S5. Calculated Molar Conductivity (Λ_m) for Phosphonium and Imidazolium Ionic Liquids as a Function of Temperature (T)

Ionic Liquid	Λ_m (S·cm^2·mol^{-1}) at T (K)		
	333.15	343.15	353.15
$[P_{4,4,4,1}]NTf_2$	38.7492	27.0152	19.7248
$[P_{4,4,4,8}]NTf_2$	47.9135	33.4342	24.1951
$[P_{4,4,4,14}]NTf_2$	62.1429	43.1084	30.7070
$[BMI]NTf_2$	15.0970	11.7808	9.5035
$[BDMI]NTf_2$	24.4223	18.1637	13.9608

The molar conductivity was calculated according to: $\Lambda_m = \kappa \frac{M}{\rho}$

where κ is the specific conductivity, M is the molar mass and ρ is the density.

Table S6. Deviation from the Ideal Line (ΔW) as a Function of Temperature (T) and the Fitting Parameters for the Fractional Walden Plot ($\log \Lambda_m = \log C' + \alpha \log \eta^{-1}$) for Phosphonium and Imidazolium Ionic Liquids

Ionic Liquid	Parameters		ΔW at T (K)		
	α	log C'	333.15	343.15	353.15
$[P_{4,4,4,1}]NTf_2$	0.6759	0.2649	0.40	0.45	0.49
$[P_{4,4,4,8}]NTf_2$	0.6847	0.4042	0.51	0.55	0.60
$[P_{4,4,4,14}]NTf_2$	0.7365	0.5157	0.57	0.61	0.65
$[BMI]NTf_2$	0.5208	0.0730	0.32	0.37	0.42
$[BDMI]NTf_2$	0.5391	0.0290	0.25	0.31	0.37

Nuclear Magnetic Resonance Data

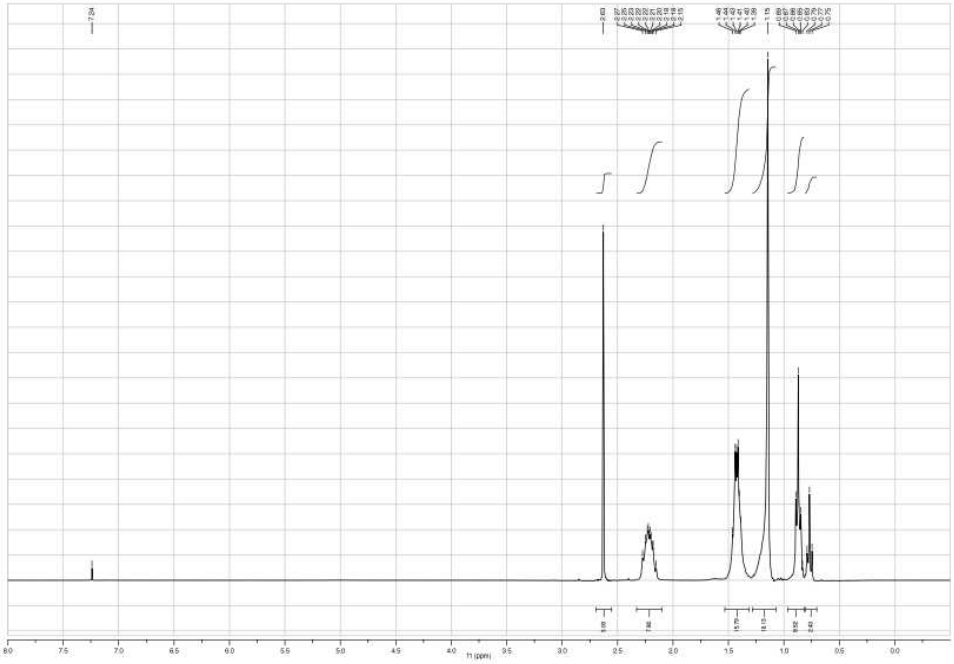

Fig. S5 ^{1}H NMR spectrum of tetradecyl(tributyl)phosphonium methanesulfonate, $[P_{4,4,4,14}]O_3SMe$, in $CDCl_3$ obtained using a 300 MHz spectrometer.

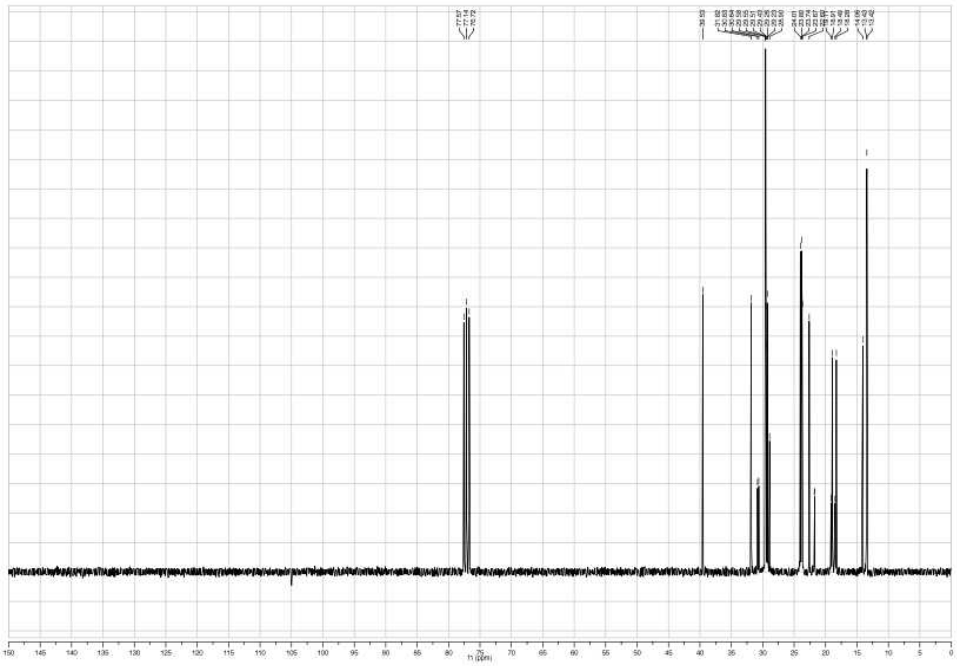

Fig. S6 ^{13}C NMR spectrum of tetradecyl(tributyl)phosphonium methanesulfonate, $[P_{4,4,4,14}]O_3SMe$, in $CDCl_3$ obtained using a 75.5 MHz spectrometer.

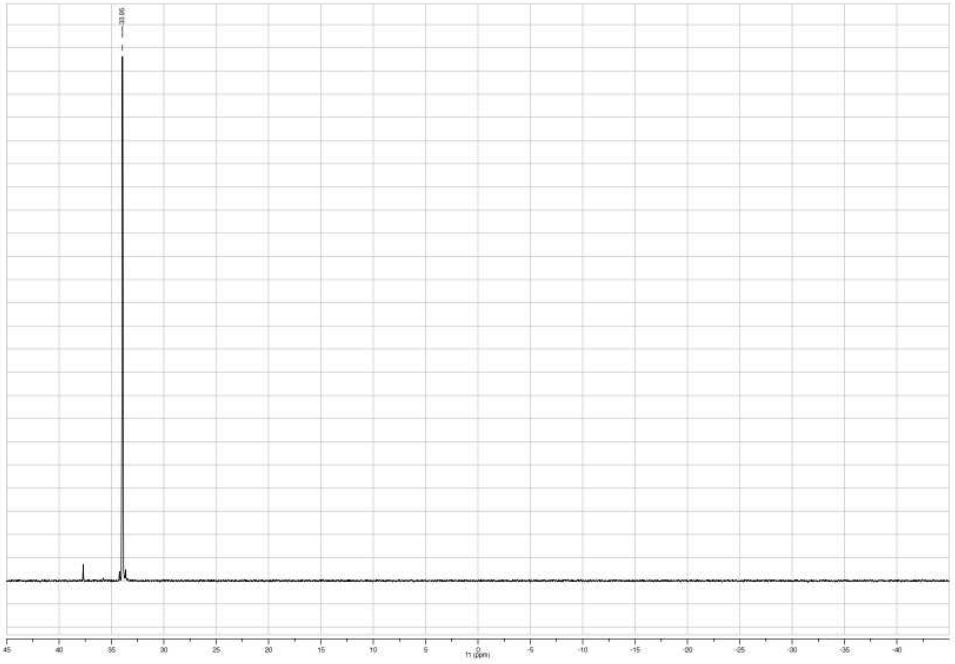

Fig. S7 ^{31}P NMR spectrum of tetradecyl(tributyl)phosphonium methanesulfonate, $[P_{4,4,4,14}]O_3SMe$, in $CDCl_3$ obtained using a 81.0 MHz spectrometer.

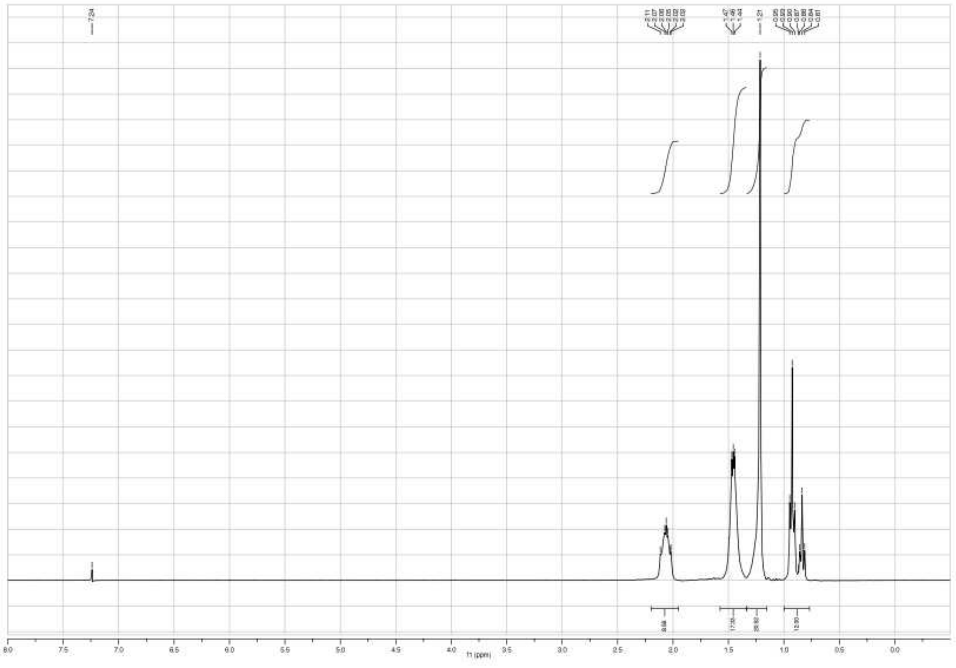

Fig. S8 ^{1}H NMR spectrum of tetradecyl(tributyl)phosphonium bis(trifluoromethyl-sulfonyl)amide, $[P_{4,4,4,14}]NTf_2$, in $CDCl_3$ obtained using a 300 MHz spectrometer.

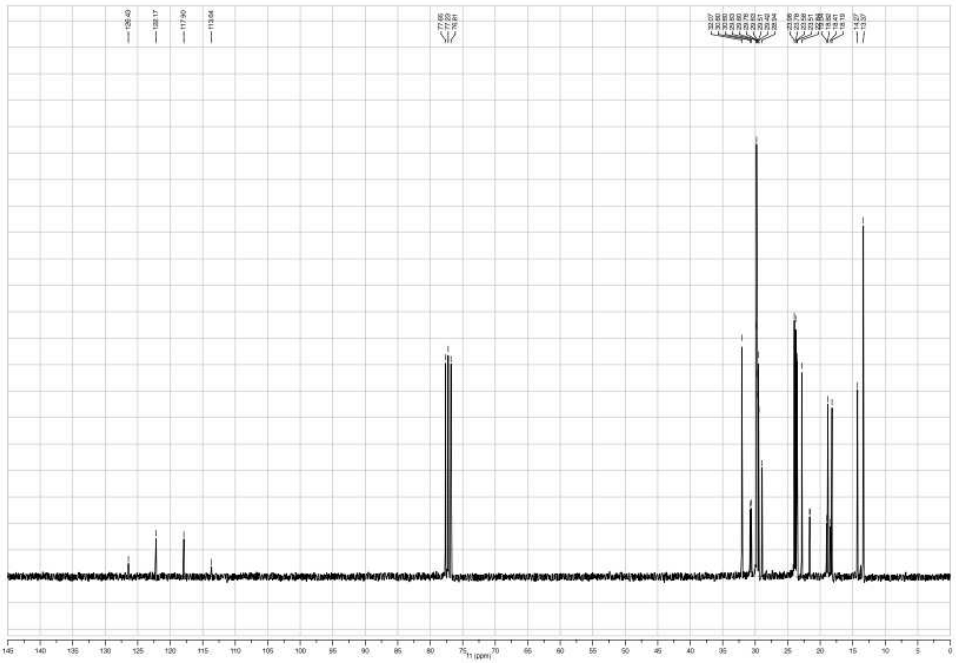

Fig. S9 ^{13}C NMR spectrum of tetradecyl(tributyl)phosphonium bis(trifluoromethylsulfonyl)amide, $[P_{4,4,4,14}]NTf_2$, in $CDCl_3$ obtained using a 75.5 MHz spectrometer.

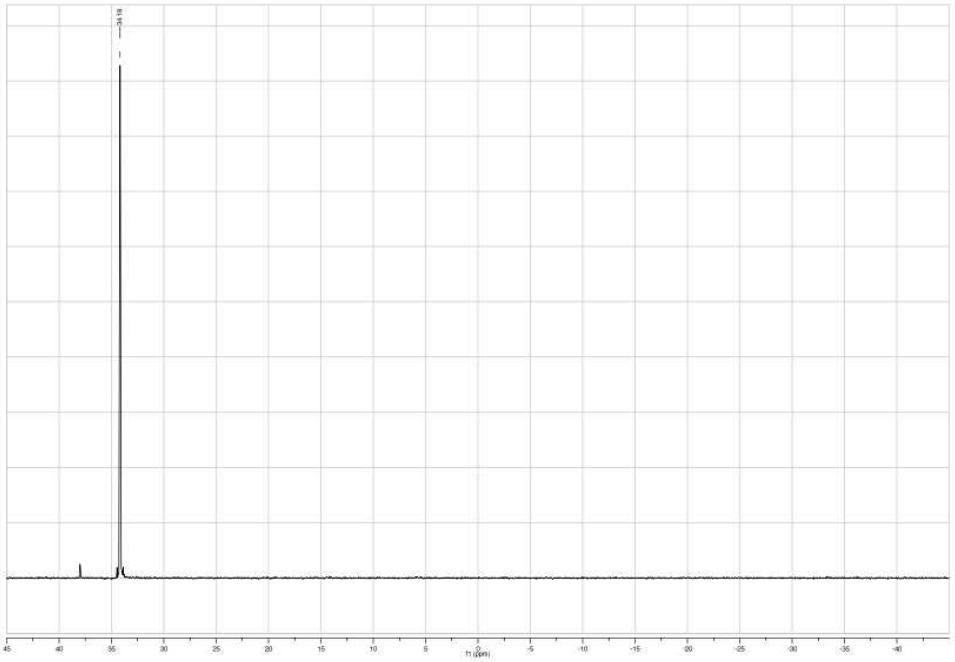

Fig. S10 ^{31}P NMR spectrum of tetradecyl(tributyl)phosphonium bis(trifluoromethylsulfonyl)amide, $[P_{4,4,4,14}]NTf_2$, in $CDCl_3$ obtained using a 81.0 MHz spectrometer.