Electronic Supplementary Material (ESI) for RSC Advances.

Prediction of ^{1}H NMR Chemical Shifts for Ionic Liquids: Strategy and Application of Relative Reference Standard

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SUPPLEMENTARY INFORMATION

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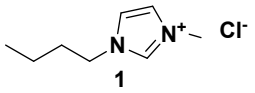
--Test set of ionic liquids



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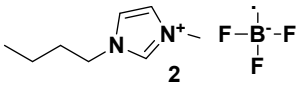
1-butyl-3-methylimidazolium chloride
[C_4mim]Cl



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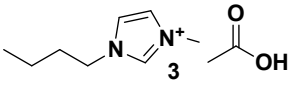
1-butyl-3-methyl imidazolium tetrafluoroborate
[C_4mim][BF_4]



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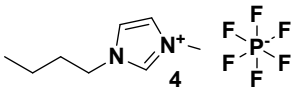
1-butyl-3-methylimidazolium acetate
[C_4mim][OAc]



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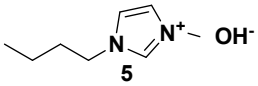
1-butyl-3-methylimidazolium
hexafluorophosphate
[C_4mim][PF_6]



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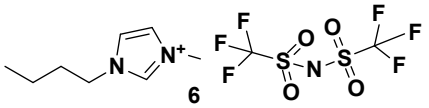
Hydroxide 1-butyl-3-methyl imidazolium
[C_4mim]OH



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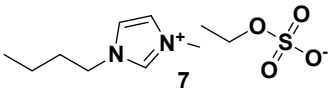
1-butyl-3-methylimidazolium
bis(trifluoromethylsulfonyl)imide
[C_4mim][Tf_2N]



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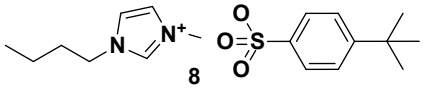
1-butyl-3-methylimidazolium ethylsulphate
[C_4mim][$MeSO_4$]



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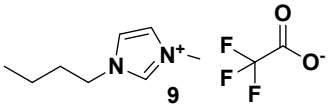
1-butyl-3-methyl imidazolium toslayte
[C_4mim][OTs]



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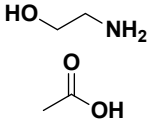
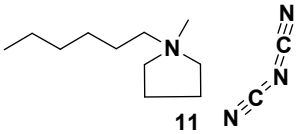
1-butyl-3-methyl imidazolium trifluoroacetate
[C_4mim][TFA]



ethanolamine acetate



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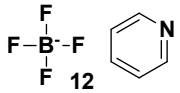
N-butyl-N-methylpyrrolidinium dicyanamide
[P16][DCA]



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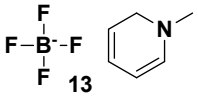
pyridine Tetrafluoroborate
[py][BF_4]



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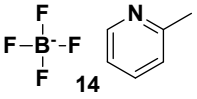
1-methyl pyridine tetrafluoroborate
[1-Me-py][BF_4]



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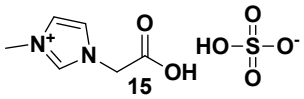
2-methyl pyridine tetrafluoroborate
[2-Me-py][BF_4]



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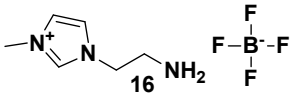
1-Carboxymethyl-3-methylimidazol-3-ium Hydrogen Sulfate
[CMI][HSO_4]



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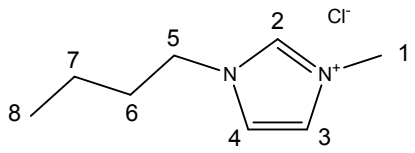
Amine 1-ethyl-3-methylimidazolium tetrafluoroborate
[NH_2-Emim][BF4]

Figure S1. A test set of ionic liquids

--Example of the RRS approach for the calculation of [C_4mim]Cl.



1-butyl-3-methylimidazolium chloride

Scheme S1. Structure of 1-Butyl-3-methylimidazolium Chloride and 1-Methylimidazole with Hydrogen Atoms Numbered.

(1) The organic molecule similar to the cation of the studied IL was used as the reference compound. In this case, 1-methlyimidozle was employed as a corresponding reference compound.

(2) The ^{1}H absolute magnetic shielding values of H2', H3', and H4' protons in 1-methylimidazole ring were calculated at the certain level of theory.

(3) The shielding constants of [C_4mim]Cl with a single ion pair were calculated at the same level as the 1-methylimidazole calculations.

(4) Once the shielding constants were computed, the ^{1}H NMR chemical shifts can be calculated in accordance with the following equation:

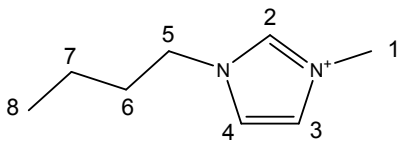
$$\delta_{calc}^{x} = \sigma_{ref,x} - \sigma_x + \delta_{ref,x}$$

(5) Where $\sigma_{ref,x}$ and σ_x are the NMR isotropic magnetic shielding values. Generally, the x hydrogen atoms for the given molecule and for the reference compound have similar structure. And $\delta_{ref,x}$ is the certain proton chemical shift of the reference compound in deuterated chloroform, which was taken from the Spectral Data Base for Organic Compounds (SDBS). For instance, the δ_{calc}^{H2} of [C_4mim]Cl would include the calculated values of $\sigma_{1\text{-methylimidazole,H2'}}$ and $\sigma_{[C_4mim]Cl,H2}$, and the experimental data of $\delta_{1\text{-methylimidazole,H2'}}$

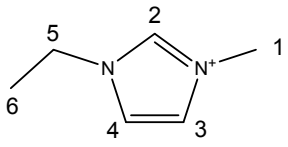
(6) H3 and H4 calculations of [C_4mim]Cl have the similar procedure of H2, but x in the equation should be replaced by H3 and H4, respectively. The $-CH_2-$ or $-CH_3$ hydrogens (H5−H8) in the $[C_4mim]^+$ cation were calculated by using TMS (δ=0.00 ppm) as the reference compound.

--Example of the RRS approach for the calculation of [C_4mim][BF_4].

Another example of the RRS approach exhibits as follows.



1-butyl-3-methylimidazolium



1-ethyl-3-methylimidazolium

Scheme S2. **Structure of [C_4mim][BF_4] and [C_2mim][BF_4] with Hydrogen Atoms Numbered.**

$\delta_{calc}^{x} = \sigma_{ref,x} - \sigma_x + \delta_{ref,x}$

	$\sigma_{calc,x}$	$\sigma_{ref,x}$	$\delta_{ref,x}$	$\delta_{calc,x}$ (RRS)	$\delta_{calc,x}$ (TMS)	$\delta_{exp,x}$	RRS	TMS
H2	22.525	22.864	8.55	8.89	9.03	8.77	0.118	0.259
H3	23.791	23.862	7.35	7.42	7.76	7.63	0.208	0.133
H4	23.665	23.937	7.41	7.68	7.89	7.69	0.008	0.199
H1	27.715	27.520	4.14	3.95	3.84	4.04	0.094	0.200
H5	27.351	27.574	3.84	4.06	3.98	4.32	0.257	0.339
H6	29.773	27.574	3.84	1.64	1.78	1.93	0.288	0.148
H7	30.0194	27.574	3.84	1.39	1.53	1.38	0.014	0.154
H8	30.4186	29.869	1.41	0.86	1.14	0.94	0.079	0.195
						RMS	0.167	0.214
						MAE	0.134	0.204

Herein, the reference compound is [C_2mim][BF_4]. $\sigma_{ref,x}$ and $\sigma_{calc,x}$ are the calculated magnetic shielding tensors of the reference compound and the studied IL, respectively. $\delta_{calc,x}$ and $\delta_{ref,x}$ are the calculated chemical shifts of the studied IL [C_4mim][BF_4] and the experimental chemical shifts of [C_2mim][BF_4], respectively.

According to the structure similarity, H1-H5 of [C_4mim][BF_4] can be calculated through $\delta_{calc}^{x} = \sigma_{ref,x} - \sigma_x + \delta_{ref,x}$ directly. H6 and H7 of [C_4mim][BF_4] cannot be directly calculated by the above equation due to the absence of H6 and H7 in [C_2mim][BF_4]. But they can be obtained by using the values of H5 in [C_2mim][BF_4] because of their similar structures (−CH_2−). Meanwhile, H8 of [C_4mim][BF_4] can be calculated through H6 of [C_2mim][BF_4] for their similar structures.

--Boltzmann averaging

The Boltzmann distribution is generally defined as below.

$$P_i = \frac{n_i}{\sum n_j} = \frac{e^{-G_i/RT}}{\sum e^{-G_j/RT}} = \frac{Q_i}{Q_j}$$

Eq. 1

Furthermore, the equation 1 is mathematically equivalent to the equation 3 for calculating the Boltzmann distribution (probability) of the *i*-th configuration of the IL.

$$e^{-G_i/RT} = e^{-(\Delta G_i + G_{Referece})/RT} = Ce^{-\Delta G_i/RT}$$

Eq. 2

$$P_i = \frac{n_i}{\sum n_j} = \frac{e^{-\Delta G_i/RT}}{\sum e^{-\Delta G_j/RT}} = \frac{Q_{i(Relative)}}{Q_{(Relative)}}$$

Eq. 3

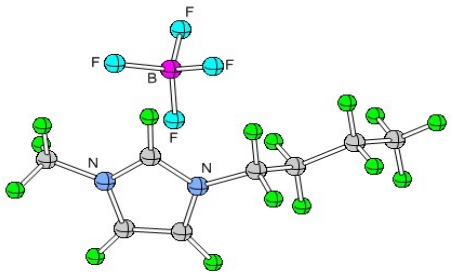
In addition, Boltzmann averaging is defined as:

$$\delta_{obs} = \sum_i P_i \delta_i$$

Eq. 4

Where ΔG_i is the free energy difference between the *i*-th configuration and the configuration with the minimal energy.

Boltzmann averaging for [C_4mim][BF_4] configurations



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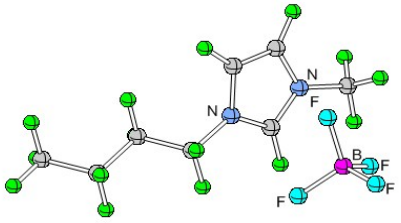

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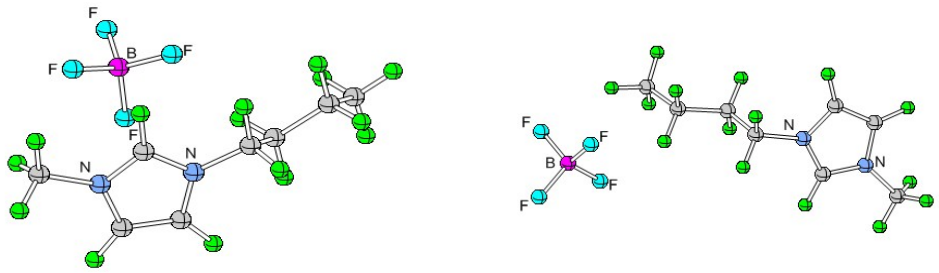


3 4

Figure S2. Four energetically preferred configurations of $[C_4mim][BF_4]$

Table S1. Boltzmann Distribution of Configurations for the IL $[C_4mim][BF_4]$ at 298 K

Temperature (K)	298.15	$Q_{(Relative)}$	1.452892
Configuration index	ΔE	$Q_{i(Relative)}$	Percent
3	0	1	68.83%
2	0.469	0.453	31.17%
1	10.238	0.000000	0.00%
4	21.027	0.000000	0.00%

Table S2. **Calculated Proton Chemical Shifts for Different Configurations of $[C_4mim][BF_4]$**[a]

Configuration	$\sigma_{calc,x}$	$\delta_{calc,x}$ (TMS)	$\delta_{exp,x}$	absolute errors
Configuration 3				
H2	22.823	8.731	8.77	0.039
H3	23.885	7.669	7.63	0.039
H4	23.731	7.823	7.69	0.133
H1	27.521	4.034	4.04	0.006
H5	27.548	4.006	4.32	0.314
H6	29.782	1.772	1.93	0.158
H7	30.179	1.376	1.38	0.004
H8	30.394	1.161	0.94	0.221
			RMS	0.155
			MAE	0.114
Configuration 2				
H2	23.060	8.494	8.77	0.276
H3	23.842	7.713	7.63	0.083
H4	23.744	7.811	7.69	0.121
H1	27.505	4.050	4.04	0.010

H5	27.612	3.942	4.32	0.378
H6	29.891	1.664	1.93	0.266
H7	30.236	1.319	1.38	0.061
H8	30.208	1.346	0.94	0.406
			RMS	0.245
			MAE	0.200
Boltzmann averaging				
H2	22.897	8.657	8.77	0.113
H3	23.871	7.683	7.63	0.053
H4	23.735	7.820	7.69	0.130
H1	27.516	4.039	4.04	0.001
H5	27.568	3.986	4.32	0.334
H6	29.816	1.738	1.93	0.192
H7	30.196	1.358	1.38	0.022
H8	30.336	1.219	0.94	0.279
			RMS	0.179
			MAE	0.140

[a] **m06-2x/aug-cc-pvdz** functional basis was used for geometry optimization and ^{1}H NMR calculations; reference compound was TMS.

Boltzmann averaging for [C_4mim][NTF_2] configurations

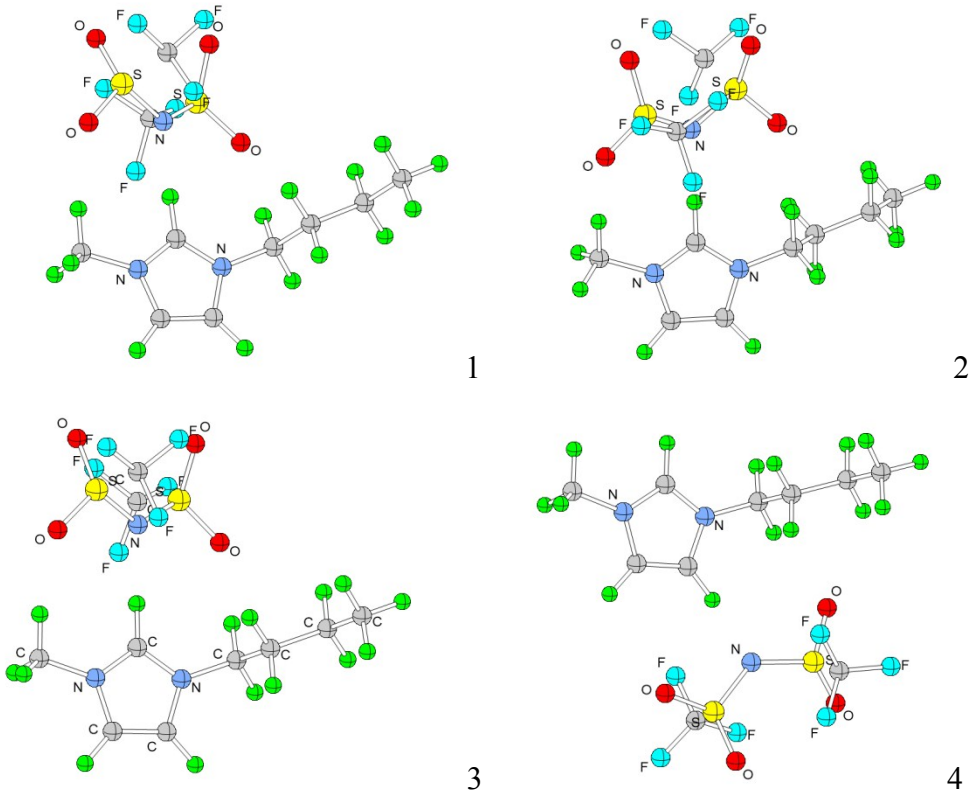


Figure S3. Four energetically preferred configurations of [C_4mim][NTf_2]

Table S3. Boltzmann Distribution of Configurations for $[C_4mim][NTf_2]$ at 298 K

Temperature (K)	298.15	$Q_{(Relative)}$	2.307
Configuration index	ΔE	$Q_{i(Relative)}$	Percent
3	0	1	43.33%
1	0.035	0.943	40.88%
2	0.598	0.364	15.78%
4	7.062	6.608E-06	0.0003%

Table S4. Calculated Proton Chemical Shifts for Different Configurations of $[C_4mim][NTf_2]$[a]

Configuration	$\sigma_{calc,x}$	$\delta_{calc,x}$ (TMS)	$\delta_{exp,x}$	absolute errors
Configuration 3				
H2	19.834	11.720	8.63	3.090
H3	23.562	7.992	7.54	0.452
H4	23.784	7.770	7.46	0.310
H1	27.356	4.198	4.24	0.042
H5	27.080	4.475	3.96	0.515
H6	29.962	1.593	1.92	0.327
H7	30.216	1.338	1.40	0.062
H8	30.330	1.224	0.97	0.254
			RMS	1.134
			MAE	0.632
Configuration 1				
H2	19.834	11.721	8.63	3.091
H3	23.558	7.996	7.54	0.456
H4	23.785	7.769	7.46	0.309
H1	27.365	4.189	4.24	0.051
H5	27.082	4.472	3.96	0.512
H6	29.960	1.595	1.92	0.325
H7	30.217	1.337	1.40	0.063
H8	30.330	1.224	0.97	0.254
			RMS	1.134
			MAE	0.633
Configuration 2				
H2	19.841	11.714	8.63	3.084
H3	23.691	7.863	7.54	0.323
H4	23.546	8.008	7.46	0.548
H1	27.248	4.306	4.24	0.066
H5	27.062	4.493	3.96	0.533
H6	29.890	1.664	1.92	0.256

H7	30.249	1.306	1.40	0.095
H8	30.294	1.261	0.97	0.291
			RMS	1.138
			MAE	0.649
Boltzmann averaging				
H2	19.833	11.722	8.63	3.092
H3	23.579	7.976	7.54	0.436
H4	23.745	7.810	7.46	0.350
H1	27.340	4.214	4.24	0.026
H5	27.075	4.479	3.96	0.519
H6	29.947	1.608	1.92	0.312
H7	30.219	1.336	1.40	0.065
H8	30.321	1.233	0.97	0.263
			RMS	1.135
			MAE	0.633

[a] **m06-2x/aug-cc-pvdz** functional basis was used for geometry optimization and ^{1}H NMR calculations; reference compound was TMS.

--Calculation data of Table 1

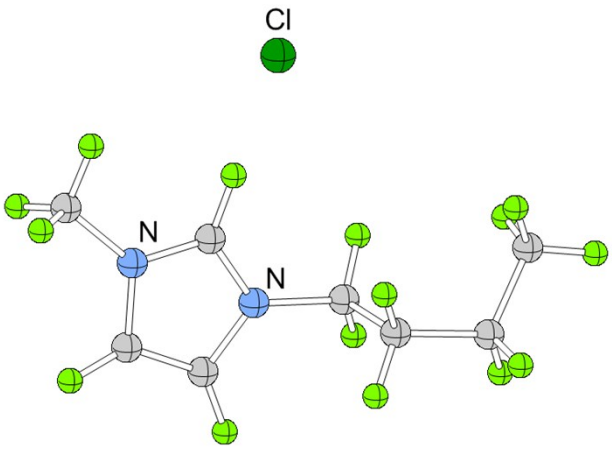


Figure S4. Structure of [C_4mim]Cl

Table S5. Calculated ^{1}H NMR Chemical Shifts of [C_4mim]Cl

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	19.162	23.567	7.385	11.790	12.530	8.630	3.160	3.900
H3	24.077	24.053	7.011	7.035	7.616	7.540	0.505	0.076
H4	23.975	24.000	6.863	6.888	7.718	7.460	0.572	0.258
H1	27.779	27.919	3.641	3.782	3.914	4.240	0.459	0.326
H5	27.144				4.549	3.960		0.589
H6	30.037				1.656	1.920		0.264
H7	30.345				1.347	1.400		0.053
H8	32.154				0.462	0.970		0.508
reference compound: 1-methylimidazole					RMS, ppm		1.197	1.417
level of theory: **mp2/aug-cc-pvdz**					MAE, ppm		0.764	0.747

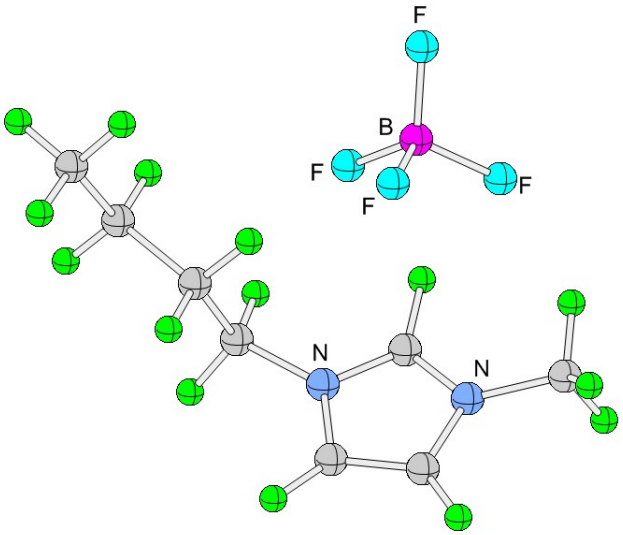


Figure S5. Structure of [C_4mim][BF_4]

Table S6. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][BF_4]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	21.892	23.567	7.385	9.060	9.801	8.630	0.430	1.171
H3	24.357	24.053	7.011	7.315	7.336	7.540	0.225	0.204
H4	24.323	24.000	6.863	7.187	7.370	7.460	0.273	0.090
H1	27.810	27.919	3.641	3.750	3.882	4.240	0.490	0.358
H5	28.532				3.161	3.960		0.799
H6	30.158				1.535	1.920		0.385
H7	30.661				1.032	1.400		0.368
H8	30.878				0.814	0.970		0.156
reference compound: 1-methylimidazole					RMS, ppm		0.371	0.558
level of theory: **mp2/aug-cc-pvdz**					MAE, ppm		0.354	0.441

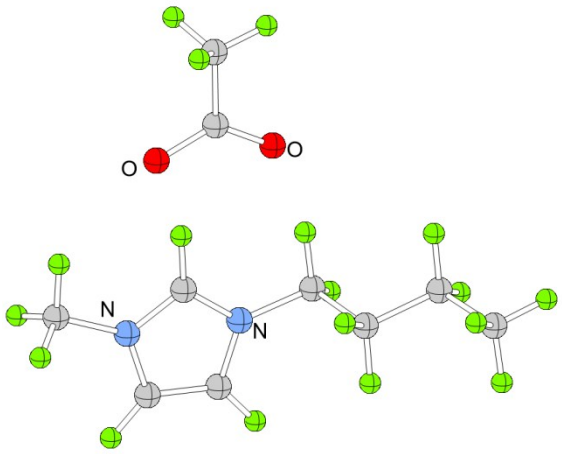


Figure S6. Structure of [C_4mim][OAc]

Table S7. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][OAc]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	17.735	23.661	7.385	13.311	13.819	10.18	3.131	3.639
H3	23.816	23.832	7.011	7.027	7.738	7.880	0.853	0.142
H4	23.709	23.758	6.863	6.912	7.845	7.960	1.048	0.115
H1	27.298	27.653	3.641	3.996	4.256	4.200	0.204	0.056
H5	26.954	27.653	3.641	4.341	4.601	3.890	0.451	0.711
H6	29.882	27.653	3.641	1.412	1.672	1.600	0.188	0.072
H7	30.178	27.653	3.641	1.116	1.376	1.210	0.094	0.166
H8	30.422	27.653	3.641	0.872	1.132	0.840	0.032	0.292
reference compound: 1-methylimidazole					RMS, ppm		1.221	1.318
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.750	0.649

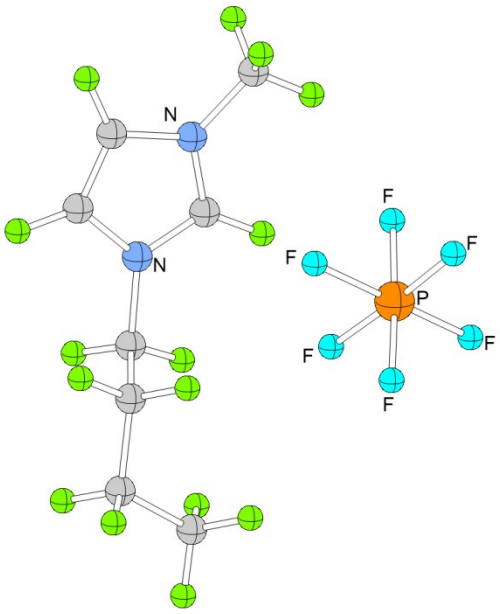


Figure S7. Structure of [C_4mim][PF_6]

Table S8. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][PF_6]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	22.952	23.661	7.385	8.094	8.603	8.520	0.426	0.083
H3	23.677	23.832	7.011	7.166	7.878	7.490	0.324	0.388
H4	23.737	23.758	6.863	6.884	7.817	7.520	0.636	0.297
H1	27.432	27.653	3.641	3.862	4.123	4.250	0.388	0.127
H5	27.193	27.653	3.641	4.101	4.362	3.970	0.131	0.392
H6	29.604	27.653	3.641	1.690	1.950	1.930	0.240	0.020
H7	30.634	27.653	3.641	0.660	0.920	1.380	0.720	0.460
H8	30.463	27.653	3.641	0.831	1.091	0.940	0.109	0.151
reference compound: 1-methylimidazole					RMS, ppm		0.425	0.285
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.372	0.240

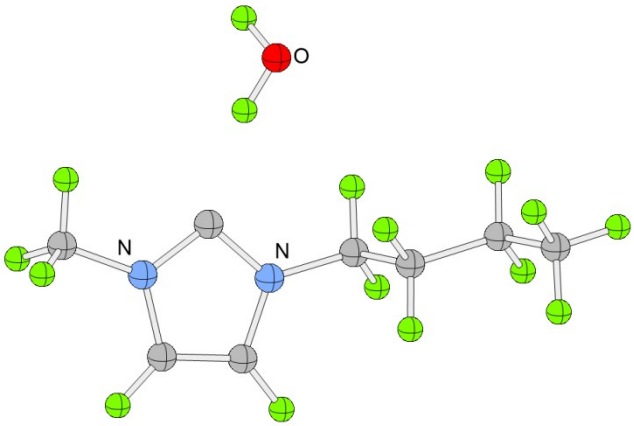


Figure S8. Structure of $[C_4mim]OH$

Table S9. Calculated ^1H NMR Chemical Shifts of $[C_4mim]OH$

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	23.661	24.614	7.385	8.338	7.893	9.270	0.932	1.377
H3	23.779	23.832	7.011	7.064	7.775	7.820	0.756	0.045
H4	23.742	23.758	6.863	6.879	7.812	7.750	0.871	0.062
H1	27.325	27.653	3.641	3.969	4.229	4.200	0.231	0.029
H5	27.564	27.653	3.641	3.730	3.990	3.860	0.130	0.130
H6	30.093	27.653	3.641	1.201	1.461	1.780	0.579	0.319
H7	30.189	27.653	3.641	1.105	1.365	1.250	0.145	0.115
H8	30.419	27.653	3.641	0.875	1.136	0.900	0.025	0.236
reference compound: 1-methylimidazole					RMS, ppm		0.573	0.511
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.459	0.289

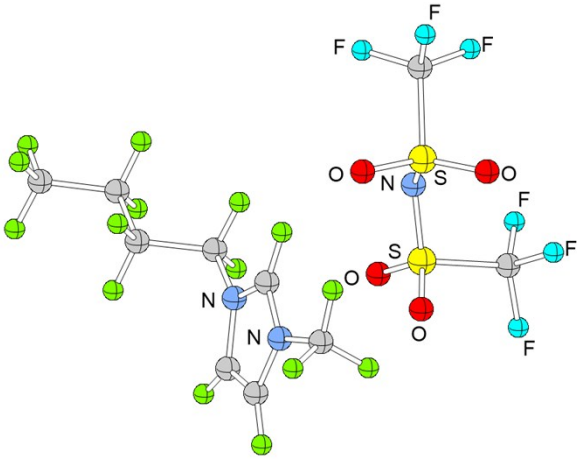


Figure S9. Structure of $[C_4mim][Tf_2N]$

Table S10. Calculated ^1H NMR Chemical Shifts of $[C_4mim][Tf_2N]$

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	19.834	23.661	7.385	11.212	11.720	8.630	2.582	3.090
H3	23.562	23.832	7.011	7.281	7.992	7.540	0.259	0.452
H4	23.784	23.758	6.863	6.837	7.770	7.460	0.623	0.310
H1	27.356	27.678	3.641	3.963	4.198	4.240	0.277	0.042
H5	27.080			4.475	4.475	3.960	0.515	0.515
H6	29.962			1.593	1.593	1.920	0.327	0.327
H7	30.216			1.338	1.338	1.400	0.062	0.062
H8	30.330			1.224	1.224	0.970	0.254	0.254
reference compound: 1-methylimidazole					RMS, ppm		0.977	1.134
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.612	0.632

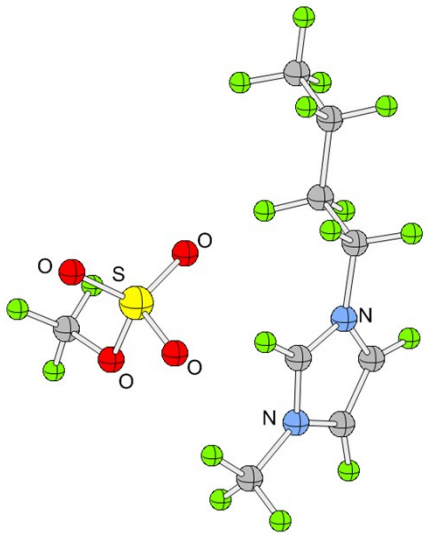


Figure S10. Structure of [C_4mim][$MeSO_4$]

Table S11. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][$MeSO_4$]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	20.987	23.661	7.385	10.059	10.567	9.418	0.641	1.149
H3	23.831	23.832	7.011	7.012	7.723	7.630	0.618	0.093
H4	23.681	23.758	6.863	6.940	7.874	7.580	0.640	0.294
H1	27.482	27.653	3.641	3.812	4.072	4.260	0.448	0.188
H5	27.232	27.653	3.641	4.062	4.323	3.370	0.692	0.953
H6	29.986	27.653	3.641	1.308	1.568	1.881	0.573	0.313
H7	30.113	27.653	3.641	1.181	1.441	1.352	0.171	0.089
H8	30.410	27.653	3.641	0.884	1.144	0.935	0.051	0.209
reference compound: 1-methylimidazole					RMS, ppm		0.530	0.560
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.479	0.411

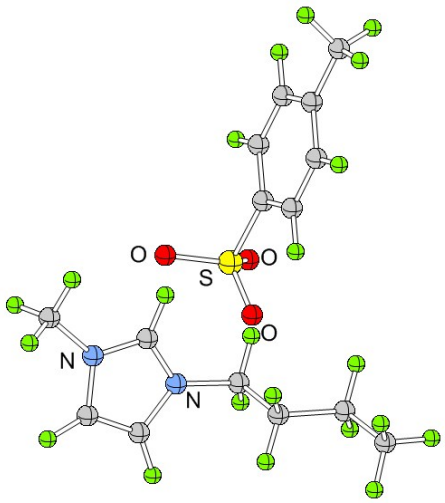


Figure S11. Structure of [C_4mim][OTS]

Table S12. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][OTS]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	23.735	23.661	7.385	7.311	7.887	8.530	1.219	0.643
H3	24.339	23.832	7.011	6.504	7.284	7.660	1.156	0.376
H4	24.088	23.758	6.863	6.533	7.534	7.290	0.757	0.244
H1	28.291	27.653	3.641	3.003	3.331	4.020	1.017	0.689
H5	27.714	27.653	3.641	3.580	3.909	3.780	0.200	0.128
H6	29.546	27.653	3.641	1.748	2.076	1.710	0.038	0.366
H7	30.058	27.653	3.641	1.236	1.564	1.220	0.016	0.344
H8	30.463	27.653	3.641	0.831	1.159	0.870	0.039	0.289
reference compound: 1-methylimidazole					RMS, ppm		0.748	0.424
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.555	0.385

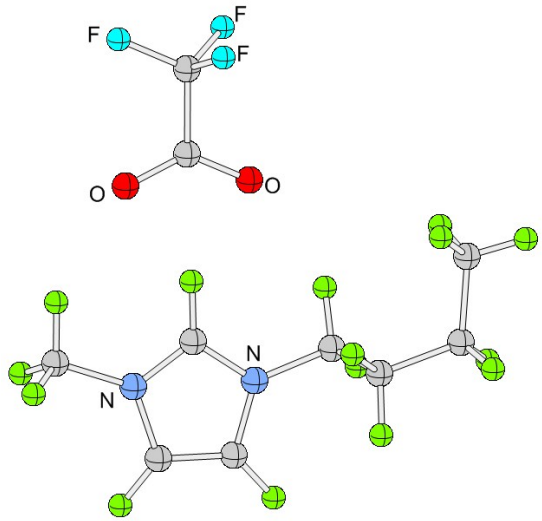


Figure S12. Structure of [C_4mim][TFA]

Table S13. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][TFA]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	19.041	23.661	7.385	12.005	12.513	8.670	3.335	3.843
H3	24.257	23.832	7.011	6.586	7.297	7.430	0.844	0.133
H4	24.154	23.758	6.863	6.467	7.401	7.390	0.923	0.011
H1	27.841	27.653	3.641	3.453	3.713	4.140	0.687	0.427
H5	27.554	27.653	3.641	3.740	4.000	3.850	0.110	0.150
H6	29.850	27.653	3.641	1.444	1.704	1.790	0.346	0.086
H7	30.164	27.653	3.641	1.130	1.390	1.260	0.130	0.130
H8	30.596	27.653	3.641	0.698	0.959	0.860	0.162	0.099
reference compound: 1-methylimidazole					RMS, ppm		1.291	1.370
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.817	0.610

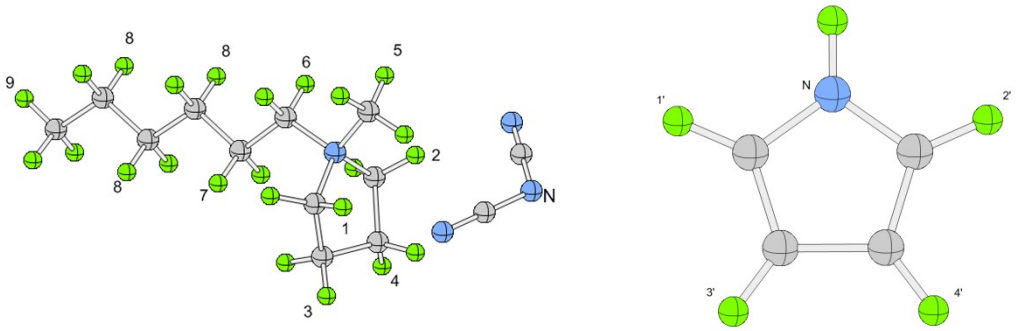


Figure S13. Structure of *N*-hexyl-*N*-methylpyrrolidinium dicyanamide ([P16][DCA], left) and pyrrole (right)

Table S14. Calculated ^{1}H NMR Chemical Shifts of *N*-hexyl-*N*-methylpyrrolidinium Dicyanamide ([P16][DCA])

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	27.649	23.891	6.737	2.979	3.889	3.450	0.471	0.439
H2	27.629	23.891	6.737	3.000	3.910	3.450	0.450	0.460
H3	29.180	24.442	6.235	1.497	2.358	2.080	0.583	0.278
H4	29.007	24.442	6.235	1.670	2.532	2.080	0.410	0.452
H5	28.238			3.317	3.301	2.980	0.337	0.321
H6	28.547			3.007	2.991	3.290	0.283	0.299
H7	30.007			1.547	1.532	1.680	0.133	0.148
H8	30.383			1.171	1.155	1.310	0.139	0.155
H9	30.241			1.314	1.298	0.880	0.434	0.418
reference compound: pyrrole					RMS, ppm		0.387	0.350
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.360	0.330

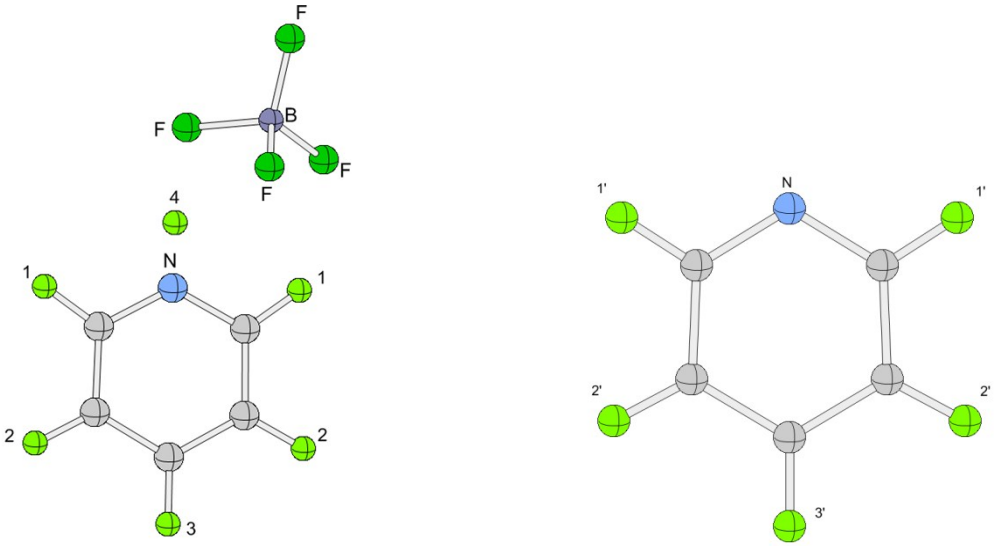


Figure S14. Structure of pyridinium tetrafluoroborate ([Py][BF_4], left) and pyridine (right)

Table S15. Calculated ^{1}H NMR Chemical Shifts of [Py][BF_4]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	22.886	23.369	8.59	9.075	9.771	8.71	0.365	1.061
H2	24.424	24.864	7.23	7.672	8.233	8.06	0.389	0.173
H3	23.185	24.055	7.62	8.487	9.472	8.62	0.133	0.852
H4	17.037			15.620	15.620	13.09	2.530	2.530
reference compound: pyridine					RMS, ppm		1.295	1.439
level of theory: **HF/631G(d)**					MAE, ppm		0.854	1.154

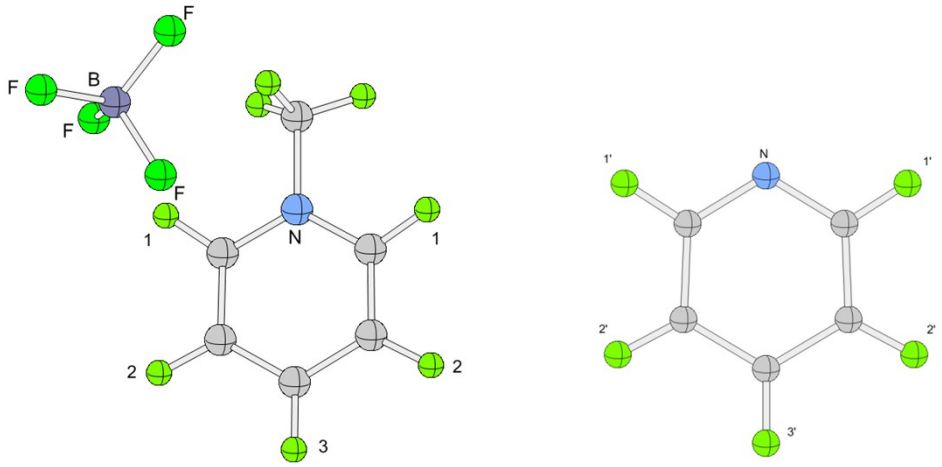
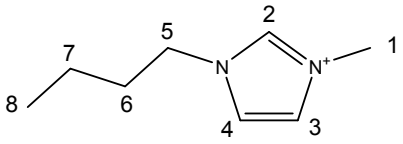


Figure S15. Structure of 1-methyl-pyridinium tetrafluoroborate ([1-me-Py][BF_4], left) and pyridine (right)

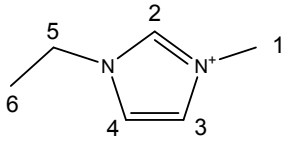
Table S16. Calculated ^{1}H NMR Chemical Shifts of [1-me-Py][BF_4]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	23.192	22.713	8.710	8.231	8.430	8.640	0.409	0.210
H2	23.520	23.832	8.060	8.372	8.103	8.010	0.362	0.093
H3	23.079	23.428	8.620	8.969	8.543	8.490	0.479	0.053
H4	27.249			4.373	4.373	4.310	0.063	0.063
reference compound: pyridine					RMS, ppm		0.365	0.122
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.328	0.105

--Calculation data of Tables 2&3



1-butyl-3-methylimidazolium



1-ethyl-3-methylimidazolium

Table S17. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) for the $[C_4mim]^+$-based IL Chemical Shifts Using the Modification of RRS Approach.

$[C_4mim][PF_6]$								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	24.192	24.209	8.820	8.837	8.390	8.520	0.317	0.130
H3	25.620	25.647	7.240	7.267	6.963	7.520	0.253	0.557
H4	25.633	25.654	7.290	7.311	6.949	7.490	0.179	0.541
H1	28.659	28.678	4.260	4.279	3.924	3.970	0.309	0.046
H5	28.591	28.578	3.970	3.983	3.991	4.250	0.267	0.259
H6	30.892	30.984	1.590	1.683	1.691	1.930	0.247	0.239
H7	31.701				0.882	1.380		0.498
H8	31.780				0.802	0.940		0.138
Reference Compound: $[C_2mim][PF_6]$					RMS, ppm		0.266	0.356
level of theory: **wp04/6-31+g(d)**					MAE, ppm		0.262	0.301
$[C_4mim][PF_6]$								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	22.569	22.848	8.820	9.099	9.054	8.520	0.579	0.534
H3	24.103	24.179	7.290	7.366	7.519	7.490	0.124	0.029
H4	24.094	24.078	7.240	7.224	7.529	7.520	0.296	0.009
H1	27.606	27.650	4.260	4.304	4.017	4.250	0.054	0.233
H5	27.427	27.459	3.970	4.003	4.196	3.970	0.032	0.226
H6	29.865	30.104	1.590	1.829	1.757	1.930	0.101	0.173
H7	30.489	30.104	1.590	1.205	1.134	1.380	0.175	0.246
H8	30.597	30.104	1.590	1.096	1.025	0.940	0.156	0.085
Reference Compound: $[C_2mim][PF_6]$					RMS, ppm		0.252	0.247
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.190	0.192
$[C_4mim][PF_6]$								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	22.952	22.010	8.820	7.879	8.603	8.520	0.641	0.083
H3	23.677	23.860	7.290	7.474	7.878	7.490	0.016	0.388
H4	23.737	23.655	7.240	7.158	7.817	7.520	0.362	0.297
H1	27.432	27.665	4.260	4.494	4.123	4.250	0.244	0.127
H5	27.193	27.378	3.970	4.156	4.362	3.970	0.186	0.392
H6	29.604	29.844	1.590	1.830	1.950	1.930	0.100	0.020
H7	30.634	29.844	1.590	0.800	0.920	1.380	0.580	0.460
H8	30.463	29.844	1.590	0.971	1.091	0.940	0.031	0.151

Reference Compound: $[C_2mim][PF_6]$					RMS, ppm		0.351	0.285
level of theory: **m062x/aug-cc-pvdz**					MAE, ppm		0.270	0.240
$[C_4mim][MeSO_4]$								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	23.086	23.079	9.440	9.432	9.496	9.310	0.122	0.186
H3	25.649	25.630	7.620	7.640	6.933	8.000	0.360	1.067
H4	25.672	25.636	7.620	7.656	6.910	7.920	0.264	1.010
H1	28.552	28.533	4.330	4.350	4.030	4.140	0.210	0.110
H5	28.430	28.275	4.030	4.185	4.152	4.420	0.235	0.268
H6	31.145	30.335	1.280	2.089	1.437	1.950	0.139	0.513
H7	31.397				1.185	1.370		0.185
H8	31.699				0.883	0.930		0.047
Reference Compound: $[C_2mim][EtSO_4]$					RMS, ppm		0.236	0.567
level of theory: **wp04/6-31+g(d)**					MAE, ppm		0.222	0.423
$[C_4mim][MeSO_4]$								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	21.587	21.298	9.440	9.151	10.036	9.418	0.267	0.618
H3	24.225	24.195	7.620	7.590	7.397	7.630	0.040	0.233
H4	24.126	24.079	7.620	7.573	7.497	7.580	0.007	0.084
H1	27.753	27.670	4.330	4.247	3.869	4.260	0.013	0.391
H5	26.601	26.168	4.030	3.597	5.455	3.370	0.227	2.085
H6	29.860	30.183	1.280	1.603	1.762	1.881	0.278	0.119
H7	30.094	30.183	1.280	1.370	1.529	1.352	0.018	0.177
H8	30.623	30.183	1.280	0.841	1.000	0.935	0.094	0.065
Reference Compound: $[C_2mim][EtSO_4]$					RMS, ppm		0.162	0.790
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.118	0.471
$[C_4mim][MeSO_4]$								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	20.987	20.697	9.440	9.149	10.512	9.418	0.269	1.094
H3	23.831	23.740	7.620	7.528	7.668	7.630	0.102	0.038
H4	23.681	23.599	7.620	7.538	7.818	7.580	0.042	0.238
H1	27.482	27.506	4.330	4.354	4.016	4.260	0.094	0.244
H5	27.232	26.823	4.030	3.621	4.267	3.370	0.251	0.897
H6	29.986	29.998	1.280	1.291	1.512	1.881	0.590	0.369
H7	30.113	29.998	1.280	1.164	1.386	1.352	0.188	0.034
H8	30.410	29.998	1.280	0.868	1.089	0.935	0.067	0.154
Reference Compound: $[C_2mim][EtSO_4]$					RMS, ppm		0.261	0.534
level of theory: **m062x/aug-cc-pvdz**					MAE, ppm		0.200	0.383
$[C_4mim][BF_4]$								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	24.144	24.102	8.550	8.508	8.438	8.770	0.262	0.332
H3	26.699	25.689	7.350	8.359	5.884	7.690	0.669	1.806
H4	25.697	25.681	7.410	7.426	6.885	7.630	0.204	0.745

H1	28.402	28.680	4.140	4.418	4.180	4.040	0.378	0.140
H5	28.424	28.564	3.830	3.970	4.158	4.320	0.350	0.162
H6	30.617	30.972	1.410	1.765	1.965	1.930	0.165	0.035
H7	31.123				1.459	1.380		0.079
H8	31.377				1.205	0.940		0.265
Reference Compound: [C_2mim][BF_4]					RMS, ppm		0.377	0.712
level of theory:**wp04/6-31+G(d)**					MAE, ppm		0.338	0.446

[C_4mim][BF_4]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	22.058	22.050	8.550	8.542	9.565	8.770	0.228	0.795
H3	24.183	24.210	7.350	7.377	7.440	7.630	0.253	0.190
H4	24.109	24.132	7.410	7.434	7.514	7.690	0.256	0.176
H1	27.728	27.727	4.140	4.139	3.894	4.040	0.099	0.146
H5	26.565	26.761	3.840	4.037	5.058	4.320	0.284	0.738
H6	29.780	30.177	1.410	1.806	1.842	1.930	0.124	0.088
H7	30.123	30.177	1.410	1.464	1.500	1.380	0.084	0.119
H8	30.616	30.177	1.410	0.970	1.006	0.940	0.030	0.066
Reference Compound: [C_2mim][BF_4]					RMS, ppm		0.192	0.402
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.170	0.290

[C_4mim][BF_4]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	22.525	22.864	8.550	8.889	9.030	8.770	0.119	0.260
H3	23.791	23.862	7.350	7.421	7.764	7.630	0.209	0.134
H4	23.665	23.937	7.410	7.682	7.890	7.690	0.008	0.200
H1	27.715	27.520	4.140	3.945	3.839	4.040	0.095	0.201
H5	27.351	27.574	3.840	4.063	3.981	4.320	0.257	0.339
H6	29.773	27.574	3.840	1.641	1.782	1.930	0.289	0.148
H7	30.019	27.574	3.840	1.394	1.535	1.380	0.014	0.155
H8	30.419	29.869	1.410	0.860	1.136	0.940	0.080	0.196
Reference Compound: [C_2mim][BF_4]					RMS, ppm		0.167	0.214
level of theory: **m062x/aug-cc-pvdz**					MAE, ppm		0.134	0.204

[C_4mim][OTs]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	23.735	23.662	8.590	8.517	7.887	8.530	0.013	0.643
H3	24.339	24.380	7.700	7.742	7.284	7.660	0.082	0.376
H4	24.088	24.093	7.370	7.375	7.534	7.290	0.085	0.244
H1	28.291	28.358	4.160	4.227	3.331	4.020	0.207	0.689
H5	27.714	27.537	3.830	3.653	3.909	3.780	0.127	0.128
H6	29.546	29.961	1.470	1.885	2.076	1.710	0.175	0.366
H7	30.058	29.961	1.470	1.373	1.564	1.220	0.153	0.344
H8	30.463	29.961	1.470	0.968	1.159	0.870	0.098	0.289
Reference Compound: [C_2mim][OTs]					RMS, ppm		0.131	0.424
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.117	0.385

[C_4mim][OAC]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	17.459	17.470	9.890	9.901	14.164	10.18	0.279	3.984
H3	24.265	24.297	7.880	7.912	7.358	7.880	0.032	0.522
H4	24.195	24.268	7.780	7.852	7.427	7.960	0.108	0.533
H1	27.745	27.751	4.210	4.216	3.878	4.200	0.016	0.323
H5	24.876	24.843	3.860	3.827	6.747	3.890	0.063	2.857
H6	29.882	30.256	1.390	1.765	1.741	1.600	0.165	0.141
H7	30.178	30.256	1.390	1.468	1.444	1.210	0.258	0.234
H8	30.594	30.256	1.390	1.052	1.028	0.840	0.212	0.188
Reference Compound: [C_2mim][OAC]					RMS, ppm		0.171	1.761
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.142	1.098
[C_4mim][OAC]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	17.735	17.798	9.890	9.953	13.819	10.180	0.227	3.639
H3	23.816	23.786	7.880	7.850	7.738	7.880	0.030	0.142
H4	23.709	23.746	7.780	7.817	7.845	7.960	0.144	0.115
H1	27.298	27.306	4.210	4.218	4.256	4.200	0.018	0.056
H5	26.954	26.918	3.860	3.824	4.601	3.890	0.066	0.711
H6	29.882	29.995	1.390	1.503	1.672	1.600	0.097	0.072
H7	30.178	29.995	1.390	1.207	1.376	1.210	0.003	0.166
H8	30.422	29.995	1.390	0.962	1.132	0.840	0.122	0.292
Reference Compound: [C_2mim][OAC]					RMS, ppm		0.113	1.318
level of theory: **m062x/aug-cc-pvdz**					MAE, ppm		0.088	0.649
[C_4mim][TFA]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	19.041	19.101	8.810	8.870	12.513	8.670	0.200	3.843
H3	24.257	24.238	7.580	7.561	7.297	7.430	0.131	0.133
H4	24.154	24.133	7.510	7.490	7.401	7.390	0.100	0.011
H1	27.841	27.699	4.310	4.168	3.713	4.140	0.028	0.427
H5	27.554	27.303	3.980	3.729	4.000	3.850	0.121	0.150
H6	29.850	30.175	1.280	1.604	1.704	1.790	0.186	0.086
H7	30.164	30.175	1.280	1.291	1.390	1.260	0.031	0.130
H8	30.596	30.202	1.280	0.886	0.959	0.860	0.026	0.099
Reference Compound: [C_2mim][TFA]					RMS, ppm		0.122	1.370
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.103	0.610

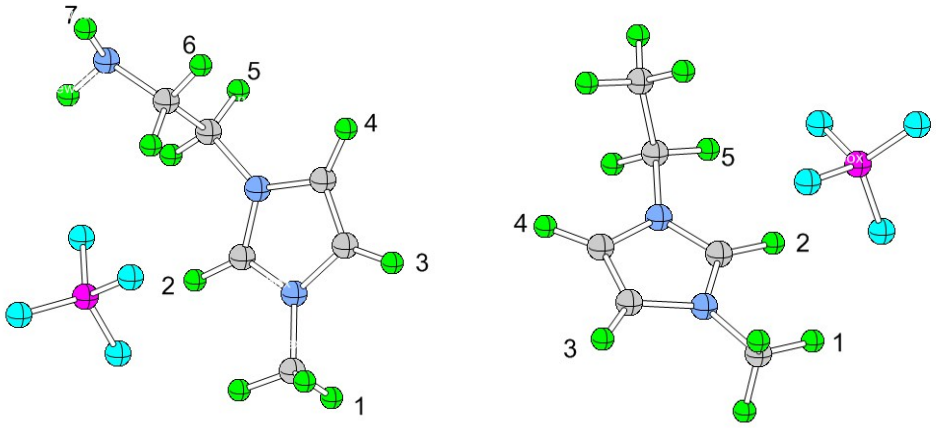


Figure S16. Structure of Amine 1-ethyl-3-methylimidazolium tetrafluoroborate ([NH_2-emim][BF_4], left) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([C_2mim][BF4], right)

Table S18. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the [NH_2-emim][BF_4] Chemical Shifts Using the Modification of RRS Approach.

[NH_2-emim][BF_4]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	22.864	23.204	8.550	8.890	8.759	9.120	0.230	0.361
H3	23.858	23.937	7.350	7.429	7.765	7.450	0.021	0.315
H4	23.844	23.862	7.410	7.428	7.778	7.200	0.228	0.578
H1	27.520	27.434	4.140	4.054	4.102	3.720	0.334	0.382
H5	27.389	29.869	1.410	3.890	4.233	3.410	0.480	0.823
H6	28.570	29.869	1.410	2.710	3.053	2.770	0.060	0.283
H7	30.849	29.869	1.410	0.430	0.773	2.070		
Reference Compound: [C_2mim][BF_4]					RMS, ppm		0.274	0.495
level of theory: **m062x/aug-cc-pvdz**					MAE, ppm		0.225	0.457

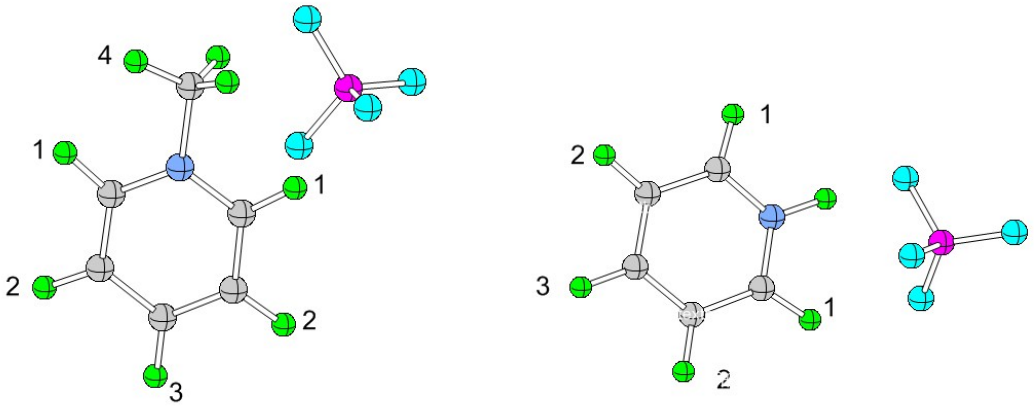


Figure S17. Structure of 1-methyl-pyridinium tetrafluoroborate ([1-me-Py][BF_4], left) and pyridinium tetrafluoroborate ([Py][BF_4],right)

Table S19. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the [1-me-Py][BF_4] Chemical Shifts Using the Modification of RRS Approach.

[1-me-Py][BF_4]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	23.341	23.486	8.710	8.570	8.871	8.640	0.0743	0.231
H2	24.517	24.371	8.060	8.210	7.695	8.010	0.196	0.315
H3	23.986	23.779	8.620	8.410	8.227	8.490	0.0766	0.263
H4	27.796			4.420	4.416	4.310	0.106	0.106
Reference Compound: [Py][BF_4]					RMS, ppm		0.124	0.241
level of theory: **wp04/6-31+G(d)**					MAE, ppm		0.113	0.229
[1-me-Py][BF_4]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	23.192	22.747	8.710	8.265	8.430	8.640	0.375	0.210
H2	23.520	23.287	8.060	7.828	8.103	8.010	0.183	0.093
H3	23.079	22.667	8.620	8.208	8.543	8.490	0.282	0.053
H4	27.249			4.373	4.373	4.310	0.063	0.063
Reference Compound: [Py][BF_4]					RMS, ppm		0.254	0.122
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.226	0.105

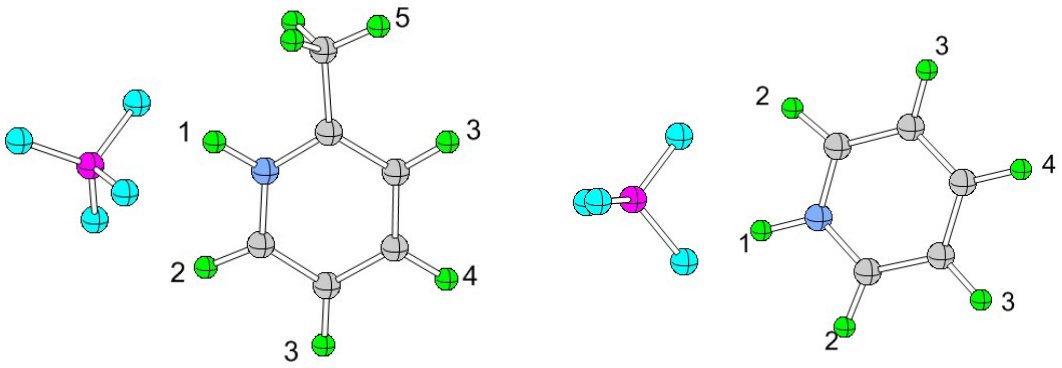


Figure S18. Structure of 2-methyl-pyridinium tetrafluoroborate ([2-me-Py][BF_4], left) and pyridinium tetrafluoroborate ([Py][BF_4],right)

Table S20. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the [2-me-Py][BF4] Chemical Shifts Using the Modification of RRS Approach.

[2-me-Py][BF_4]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	18.209	17.755	13.09	12.64	14.003	12.42	0.2156	1.583
H2	23.332	23.486	8.710	8.560	8.881	8.540	0.016	0.341
H3	24.588	24.371	8.060	7.840	7.625	7.850	0.0066	0.225
H4	23.997	23.779	8.620	8.400	8.216	8.450	0.048	0.234
H5	29.541			2.670	2.671	2.750	0.0788	0.0788
Reference Compound: [Py][BF_4]					RMS, ppm		0.105	0.740
level of theory: **wp04/6-31+G(d)**					MAE, ppm		0.0729	0.493
[2-me-Py][BF_4]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	22.621	22.747	8.710	8.584	9.001	8.540	0.044	0.461
H2	23.633	23.287	8.060	7.715	7.990	7.850	0.135	0.140
H3	23.067	22.667	8.620	8.220	8.555	8.450	0.230	0.105
H4	18.110	17.495	13.090	12.48	13.513	12.42	0.056	1.093
H5	28.821			2.801	2.801	2.750	0.051	0.051
Reference Compound: [Py][BF_4]					RMS, ppm		0.126	0.537
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.103	0.370

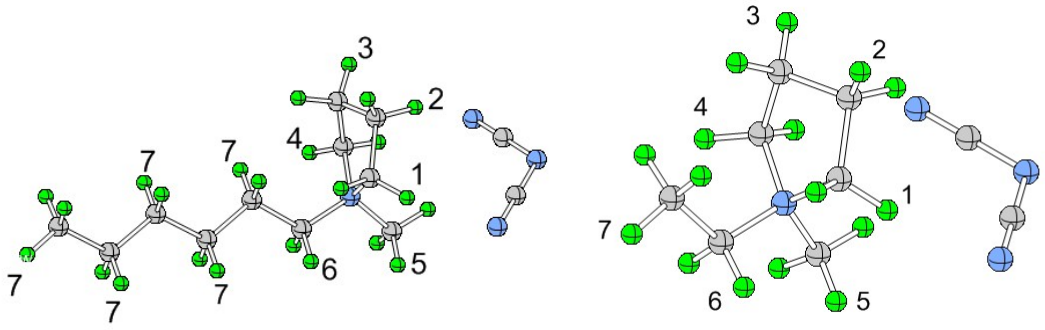


Figure S19. Structure of N-butyl-N-methylpyrrolidinium dicyanamide (P16-DCA, left) and N-Ethyl-N-methylpyrrolidinium dicyanamide (P12-DCA, right)

Table S21. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the P16-DCA Chemical Shifts Using the Modification of RRS Approach.

P16-DCA								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	27.949	27.897	3.420	3.368	3.605	3.450	0.082	0.155
H2	27.746	28.039	3.420	3.714	3.809	3.450	0.264	0.359
H3	29.585	29.579	2.070	2.065	1.970	2.080	0.016	0.111
H4	29.278	29.240	2.070	2.032	2.276	2.080	0.048	0.196
H5	28.541	28.463	2.950	2.873	3.014	2.980	0.107	0.034
H6	28.609	28.482	3.360	3.234	2.946	3.290	0.056	0.344
H7	29.910	30.284	1.270	1.644	1.644	1.680	0.036	0.036
Reference Compound: P12-DCA					RMS, ppm		0.107	0.192
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.081	0.151

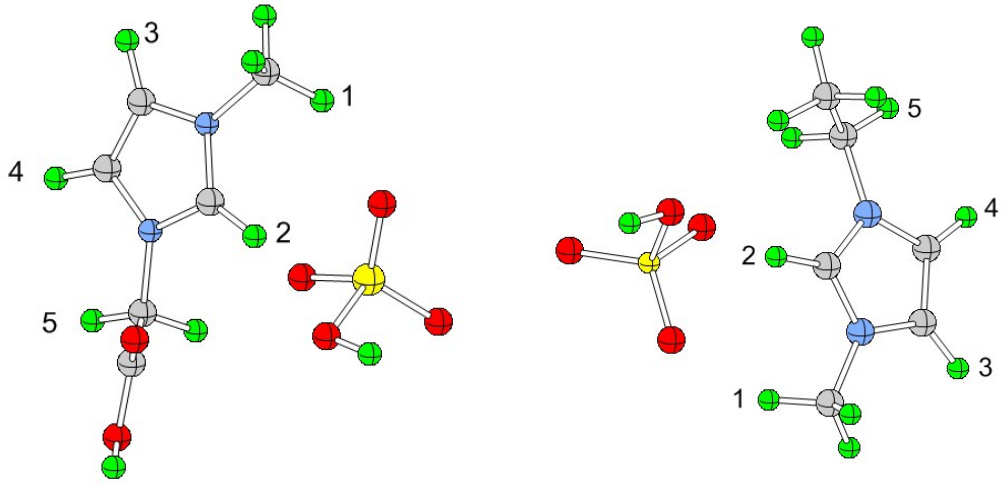


Figure S20. Structure of 1-Carboxymethyl-3-methylimidazol-3-ium Hydrogen Sulfate ([CMI][HSO_4], left) and 1-Ethyl-3-methylimidazolium Hydrogen Sulfate ([EMIM][HSO_4],right)

Table S22. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the [CMI][HSO_4] Chemical Shifts Using the Modification of RRS Approach.

[CMI][HSO_4]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	23.3413	23.4856	8.71	8.57	8.8711	8.64	0.0743	0.2311
H2	24.5172	24.3711	8.06	8.21	7.6952	8.01	0.1962	0.3148
H3	23.9858	23.7792	8.62	8.41	8.2266	8.49	0.0766	0.2634
H4	27.7964			4.42	4.4160	4.31	0.1060	0.1060
Reference Compound:[EMIM][HSO_4]					RMS, ppm		0.1236	0.2414
level of theory:B3LYP/6-31+G(d)					MAE, ppm		0.1133	0.2288
[CMI][HSO_4]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	22.285	23.327	8.310	9.352	9.253	8.680	0.672	0.573
H2	23.605	24.049	7.110	7.554	7.933	7.390	0.164	0.543
H3	23.497	23.971	7.050	7.524	8.041	7.370	0.154	0.671
H4	27.533	27.732	3.860	4.060	4.005	3.820	0.240	0.185
H5	26.170	27.396	3.520	4.746	5.368	4.990	0.244	0.378
Reference Compound:[EMIM][HSO_4]					RMS, ppm		0.352	0.500
level of theory: **b3lyp/6-31++g(d,p)-d3**					MAE, ppm		0.295	0.470
[CMI][HSO_4]								
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	22.032	22.864	8.310	9.141	9.506	8.680	0.461	0.826
H2	23.483	23.611	7.110	7.238	8.055	7.390	0.152	0.665
H3	23.554	23.592	7.050	7.088	7.984	7.370	0.282	0.614
H4	27.442	27.494	3.860	3.912	4.096	3.820	0.092	0.276

H5	26.233	27.364	3.520	4.651	5.305	4.990	0.339	0.315
Reference Compound:[EMIM][HSO_4]						RMS, ppm	0.296	0.579
level of theory: **m062x/aug-cc-pvdz**						MAE, ppm	0.265	0.539

Table S23. Calculated ^{1}H NMR Chemical Shifts of the [C_4mim]$^+$-Based ILs

entry	Studied IL	Refence IL	Level of theory		MAE	RMS
1	[C_4mim][BF_4]	[C_2mim][BF_4]	b3lyp/6-31gd+	RRS, ppm	0.2480	0.2198
				TMS, ppm	0.3492	0.2864
2	[C_4mim][BF_4]	[C_2mim][BF_4]	b3lyp/6-311gdp++	RRS, ppm	0.2084	0.1864
				TMS, ppm	0.3763	0.2483
3	[C_4mim][BF_4]	[C_2mim][BF_4]	b3lyp/aug-cc-pvdz	RRS, ppm	0.2108	0.1909
				TMS, ppm	0.4091	0.2625
4	[C_4mim][BF_4]	[C_2mim][BF_4]	m062x/6-31gd+	RRS, ppm	0.2726	0.2147
				TMS, ppm	0.2497	0.1668
5	[C_4mim][BF_4]	[C_2mim][BF_4]	mpw1pw91/6-31gd+	RRS, ppm	0.2480	0.2198
				TMS, ppm	0.3492	0.2864
6	[C_4mim][PF_6]	[C_2mim][PF_6]	b3lyp/6-31gd+	RRS, ppm	0.2471	0.2288
				TMS, ppm	0.2825	0.1869
7	[C_4mim][PF_6]	[C_2mim][PF_6]	b3lyp/6-311gdp++	RRS, ppm	0.2216	0.1963
				TMS, ppm	0.3548	0.2018
8	[C_4mim][PF_6]	[C_2mim][PF_6]	b3lyp/aug-cc-pvdz	RRS, ppm	0.2358	0.2151
				TMS, ppm	0.4496	0.2377
9	[C_4mim][PF_6]	[C_2mim][PF_6]	m062x/6-31gd+	RRS, ppm	0.2001	0.1765
				TMS, ppm	0.3486	0.2238
10	[C_4mim][PF_6]	[C_2mim][PF_6]	mpw1pw91/6-31gd+	RRS, ppm	0.2481	0.2299
				TMS, ppm	0.2710	0.1872
11	[C_4mim][$MeSO_4$]	[C_2mim][$MeSO_4$]	b3lyp/6-31gd+	RRS, ppm	0.2678	0.2563
				TMS, ppm	0.6671	0.5336
12	[C_4mim][$MeSO_4$]	[C_2mim][$MeSO_4$]	b3lyp/6-311gdp++	RRS, ppm	0.2423	0.2164
				TMS, ppm	0.7216	0.4756
13	[C_4mim][$MeSO_4$]	[C_2mim][$MeSO_4$]	b3lyp/aug-cc-pvdz	RRS, ppm	0.2671	0.2457
				TMS, ppm	0.8714	0.4978
14	[C_4mim][$MeSO_4$]	[C_2mim][$MeSO_4$]	m062x/6-31gd+	RRS, ppm	0.2319	0.2226
				TMS, ppm	0.5818	0.3659
15	[C_4mim][$MeSO_4$]	[C_2mim][$MeSO_4$]	mpw1pw91/6-31gd+	RRS, ppm	0.2406	0.2316
				TMS, ppm	0.5868	0.4421
16	[C_4mim][Tf_2N]	[C_2mim][Tf_2N]	b3lyp/6-31gd+	RRS, ppm	0.3196	0.3013
				TMS, ppm	0.6867	0.4402
17	[C_4mim][Tf_2N]	[C_2mim][Tf_2N]	b3lyp/6-311gdp++	RRS, ppm	0.3200	0.3092
				TMS, ppm	1.0197	0.5166
18	[C_4mim][Tf_2N]	[C_2mim][Tf_2N]	b3lyp/aug-cc-pvdz	RRS, ppm	0.3300	0.3212
				TMS, ppm	0.9956	0.5051
19	[C_4mim][Tf_2N]	[C_2mim][Tf_2N]	m062x/6-31gd+	RRS, ppm	0.3645	0.3432

				TMS, ppm	0.7989	0.3733
20	$[C_4mim][Tf_2N]$	$[C_2mim][Tf_2N]$	mpw1pw91/6-31gd+	RRS, ppm	0.3230	0.3049
				TMS, ppm	0.6865	0.4172
21	$[C_4mim][OTs]$	$[C_2mim][OTs]$	b3lyp/6-31gd+	RRS, ppm	0.2335	0.2128
				TMS, ppm	0.8559	0.5345
22	$[C_4mim][OTs]$	$[C_2mim][OTs]$	b3lyp/6-311gdp++	RRS, ppm	0.2328	0.2161
				TMS, ppm	1.1166	0.6415
23	$[C_4mim][OTs]$	$[C_2mim][OTs]$	b3lyp/aug-cc-pvdz	RRS, ppm	0.2617	0.2211
				TMS, ppm	1.2185	0.6725
24	$[C_4mim][OTs]$	$[C_2mim][OTs]$	m062x/6-31gd+	RRS, ppm	0.2290	0.2103
				TMS, ppm	1.0051	0.5948
25	$[C_4mim][OTs]$	$[C_2mim][OTs]$	mpw1pw91/6-31gd+	RRS, ppm	0.2260	0.2062
				TMS, ppm	0.8633	0.5267
26	$[C_4mim][TFA]$	$[C_2mim][TFA]$	b3lyp/6-31gd+	RRS, ppm	0.3871	0.3565
				TMS, ppm	1.4080	0.6910
27	$[C_4mim][TFA]$	$[C_2mim][TFA]$	b3lyp/6-311gdp++	RRS, ppm	0.3563	0.3246
				TMS, ppm	1.8407	0.8342
28	$[C_4mim][TFA]$	$[C_2mim][TFA]$	b3lyp/aug-cc-pvdz	RRS, ppm	0.3953	0.3101
				TMS, ppm	1.9288	0.8555
29	$[C_4mim][TFA]$	$[C_2mim][TFA]$	m062x/6-31gd+	RRS, ppm	0.3940	0.3321
				TMS, ppm	1.6299	0.8290
30	$[C_4mim][TFA]$	$[C_2mim][TFA]$	mpw1pw91/6-31gd+	RRS, ppm	0.3772	0.3467
				TMS, ppm	1.4139	0.6546
31	$[C_4mim][OAC]$	$[C_2mim][OAC]$	b3lyp/6-31gd+	RRS, ppm	0.4017	0.3243
				TMS, ppm	1.5720	0.9384
32	$[C_4mim][OAC]$	$[C_2mim][OAC]$	b3lyp/6-311gdp++	RRS, ppm	0.4834	0.3431
				TMS, ppm	2.0822	1.0864
33	$[C_4mim][OAC]$	$[C_2mim][OAC]$	b3lyp/aug-cc-pvdz	RRS, ppm	0.4619	0.3149
				TMS, ppm	2.1653	1.1157
34	$[C_4mim][OAC]$	$[C_2mim][OAC]$	m062x/6-31gd+	RRS, ppm	0.4412	0.3697
				TMS, ppm	1.7177	0.9193
35	$[C_4mim][OAC]$	$[C_2mim][OAC]$	mpw1pw91/6-31gd+	RRS, ppm	0.4206	0.3353
				TMS, ppm	1.5497	0.8931

--Calculation of IL clusters

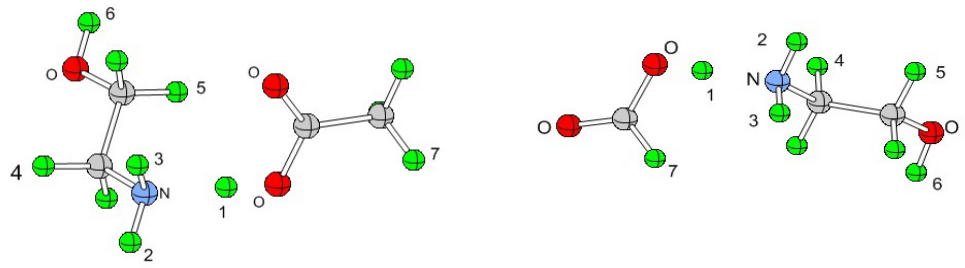


Figure S21. Structure of Ethanolamine Acetate (left) and Ethanolamine Formate (right)

Table S24. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the Ethanolamine Acetate Chemical Shifts Using the Modification of RRS Approach.

ethanolamine acetate

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	13.357	14.593	5.600	6.836	18.197	6.720	0.116	11.477
H2	29.573	29.804	6.150	6.381	1.982	6.550	0.169	4.568
H3	29.714	30.143	5.950	6.379	1.840	6.550	0.171	4.710
H4	28.927	28.642	3.160	2.874	2.627	2.800	0.074	0.173
H5	27.791	27.893	3.430	3.532	3.763	3.560	0.028	0.203
H6	30.820	30.983	7.600	7.763	0.734	7.800	0.037	7.066
H7	29.521	22.692	8.400	1.572	2.033	1.750	0.179	0.283
Reference Compound: ethanolamine formate					RMS, ppm		0.126	5.668
level of theory: **m062x/aug-cc-pvdz**					MAE, ppm		0.111	4.069

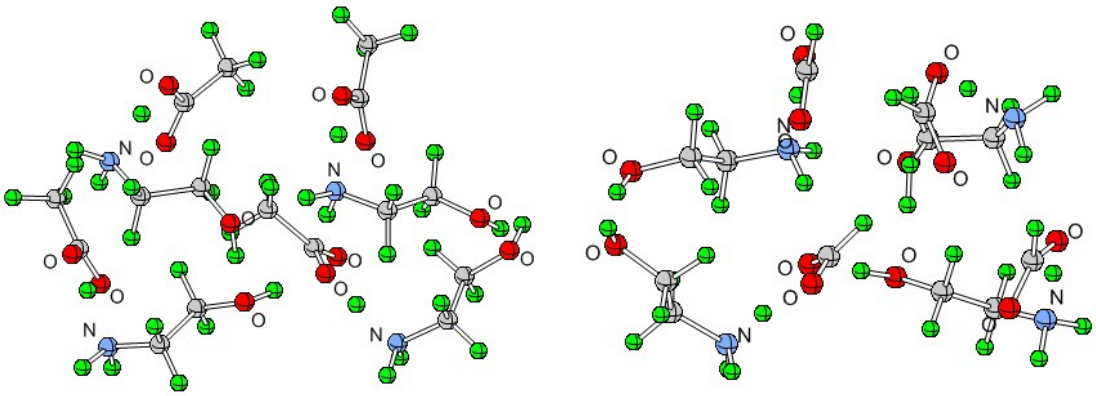


Figure S22. Structure of 4 IP Ethanolamine Acetate (left) and 4 IP Ethanolamine Formate (right)

Table S25. Mean Value of the 4 IP Ethanolamine Acetate Chemical Shifts

4IP ethanolamine acetate

H1	AVERAGE	H2	AVERAGE	H3	AVERAGE
14.1689	13.0831	28.9835	28.8571	28.5098	29.3141
13.8030		29.0025		29.9486	
13.3752		28.1450		29.2008	
10.9854		29.2974		29.5970	

level of theory: **m062x/aug-cc-pvdz**

Table S26. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the 4 IP Ethanolamine Acetate Chemical Shifts Using the Modification of RRS Approach.

4IP ethanolamine acetate

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	13.083	13.125	5.600	5.642	18.581	6.720	1.078	11.861
H2	28.857	28.426	6.150	5.719	2.807	6.550	0.831	3.743
H3	29.314	28.385	5.950	4.939	2.269	6.550	1.611	4.281
H4	28.732	28.498	3.160	2.926	2.932	2.800	0.126	0.132
H5	28.127	27.195	3.430	2.498	3.537	3.560	1.062	0.023
H6	27.716	27.097	7.600	6.981	3.948	7.800	0.819	3.852
H7	29.605	22.865	8.400	1.660	2.059	1.750	0.090	0.309
Reference Compound: 4 IP ethanolamine formate					RMS, ppm		0.947	5.182
level of theory: **m062x/aug-cc-pvdz**					MAE, ppm		0.921	3.457

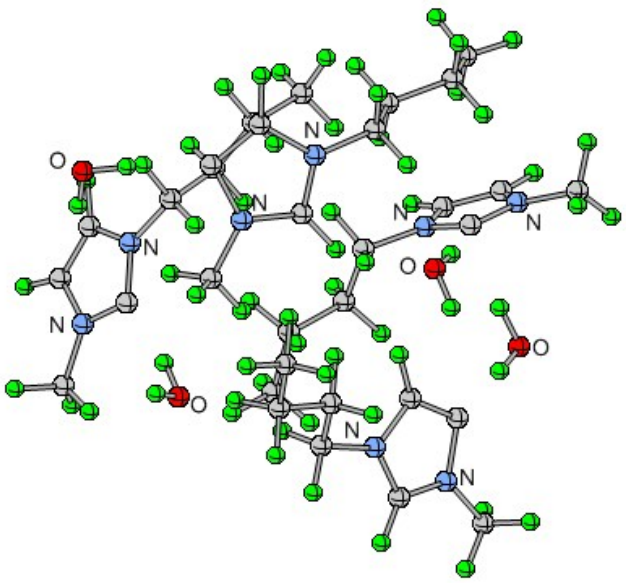


Figure S23. Structure of 4 IP [C_4mim][OH]

Table S27. Mean Value of the 4 IP [C_4mim][OH] Chemical Shifts

4 IP [C_4mim][OH]					
H2	AVERAGE	H3	AVERAGE	H4	AVERAGE
21.0759	23.8225	22.2115	23.4900	24.1447	23.8264
24.0320		24.0328		23.5173	
23.1604		23.9306		23.7704	
23.0218		23.7851		23.8730	
level of theory: **m062x/aug-cc-pvdz**					

Table S28. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the 4 IP [C_4mim][OH] Chemical Shifts Using the Modification of TMS Approach.

4 IP [C_4mim][OH]							
Atom	σ calc.x	Atom	σ ref.x	δ ref.x	δ calc.x (TMS)	δ exp.x	TMS
H2	23.825	H2'	24.701	9.23	8.676	9.27	0.593
H3	23.490	H3'	23.814	7.79	8.008	7.82	0.188
H4	23.826	H4'	23.707	7.75	7.672	7.75	0.077
H1	27.686	H1'	27.645	4.24	3.812	4.20	0.387
H5	27.276	H5'	27.489	3.72	4.222	3.86	0.362
H6	29.961	H6'	30.223	1.25	1.537	1.78	0.242
H7	30.388				1.111	1.25	0.139
H8	31.051				0.447	0.90	0.452
Reference Compound: TMS					RMS, ppm		0.609
level of theory: **m062x/aug-cc-pvdz**					MAE, ppm		0.410

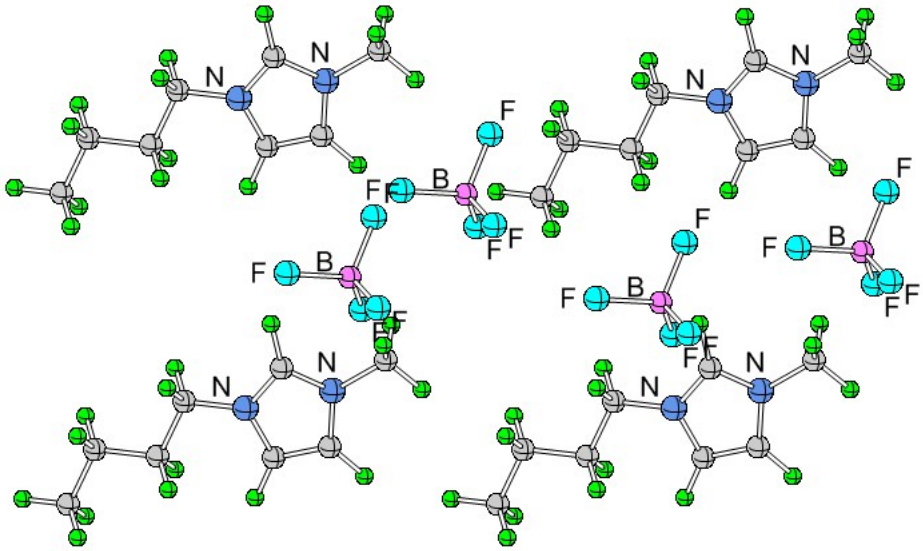


Figure S24. Structure of 4 IP [C_4mim][BF_4]

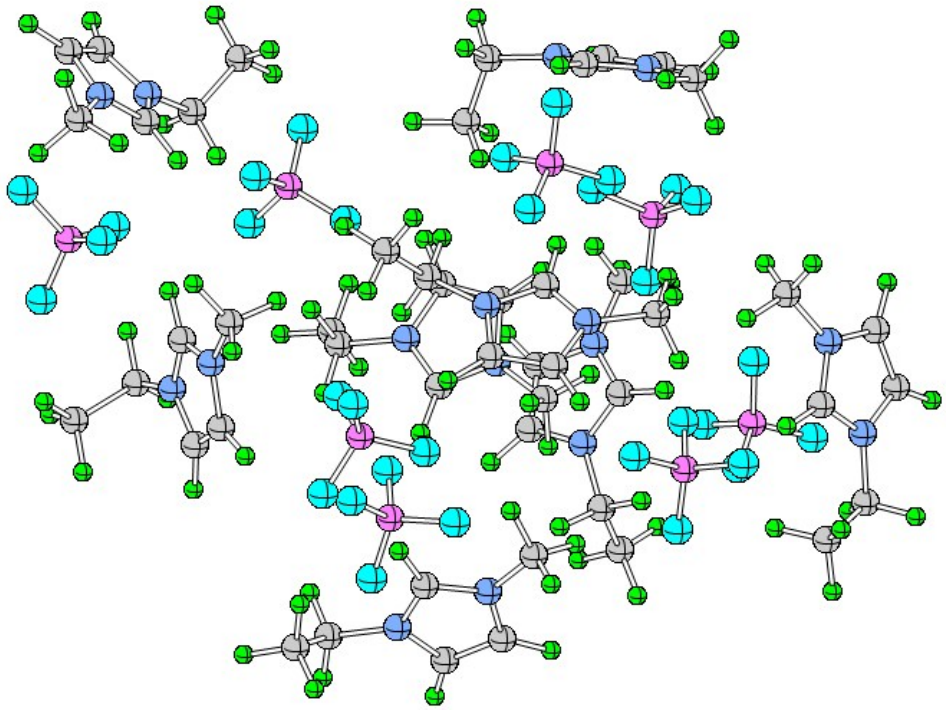


Figure S25. Structure of 8 IP [C_2mim][BF_4]

Table S29. Mean Value of the 4 IP [C_4mim][BF_4] Chemical Shifts

4 IP [C_4mim][BF_4]					
H2	AVERAGE	H3	AVERAGE	H4	AVERAGE
22.9579	22.9998	25.1438	25.0761	24.2722	24.8225
22.7141		25.2079		25.1010	
23.2889		24.5681		24.6092	
23.0382		25.3844		25.3075	

level of theory: **mp2/aug-cc-pvdz**

Table S30. Mean Absolute Errors (MAE) and Root Mean Square Deviations (RMS) of the 4IP [C_4mim][BF_4] Acetate Chemical Shifts Using the Modification of RRS Approach.

4 IP [C_4mim][BF_4]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H1	23.000	23.028	8.550	8.713	9.157	8.770	0.057	0.387
H2	25.077	25.541	7.350	7.814	6.944	7.690	0.123	0.746
H3	24.823	24.916	7.410	7.452	7.148	7.630	0.178	0.482
H4	28.383	28.264	4.140	4.259	3.638	4.040	0.219	0.402
H5	28.039	27.950	3.830	3.920	3.982	4.320	0.400	0.338
H6	30.123	30.509	1.410	1.796	1.898	1.930	0.134	0.032
H7	30.628				1.393	1.380		0.013
H8	31.150				0.872	0.940		0.068
Reference Compound: 8 IP [C_2mim][BF_4]					RMS, ppm		0.214	0.390
level of theory: **mp2/aug-cc-pvdz**					MAE, ppm		0.185	0.308

--Cartesian coordinates of optimized ILs

Table S31. Cartesian coordinates

1-methylimidazole	m062x/aug-cc-pvdz	*x*	*y*	*z*
	C	0.1905	-1.0845	0.0002
	N	1.4713	-0.7677	-0.0001
	C	1.5021	0.6064	-0.0001
	C	0.2223	1.1084	-0.0001
	N	-0.6040	0.0138	-0.0001
	C	-2.0563	0.0345	0.0001
	H	-0.2226	-2.0877	0.0003
	H	2.4359	1.1583	-0.0002
	H	-0.1677	2.1197	-0.0002
	H	-2.4245	0.5451	0.8965
	H	-2.4245	0.5504	-0.8933
	H	-2.4193	-0.9969	-0.0030
TMS	m062x/aug-cc-pvdz			
	Si	0.0000	0.0000	0.0000
	C	1.0890	1.0890	1.0890
	C	-1.0890	-1.0890	1.0890
	C	-1.0890	1.0890	-1.0890
	C	1.0890	-1.0890	-1.0890
	H	1.7356	1.7356	0.4793
	H	0.4793	1.7356	1.7356
	H	1.7356	0.4793	1.7356
	H	-1.7356	-0.4793	1.7356
	H	-1.7356	-1.7356	0.4793
	H	-0.4793	-1.7356	1.7356
	H	-1.7356	0.4793	-1.7356
	H	-1.7356	1.7356	-0.4793
	H	-0.4793	1.7356	-1.7356
	H	1.7356	-1.7356	-0.4793
	H	1.7356	-0.4793	-1.7356
	H	0.4793	-1.7356	-1.7356
$[C_2mim][BF_4]$	m062x/aug-cc-pvdz			
	C	-1.7276	-2.1042	-0.9164
	N	-2.1749	-1.2338	0.0512
	C	-1.1475	-0.8900	0.8230

N	-0.0580	-1.5189	0.3930
C	-0.3937	-2.2837	-0.7016
C	-3.5179	-0.6682	0.1364
C	1.2964	-1.3129	0.9195
C	2.2127	-0.7160	-0.1405
F	-0.5566	1.0290	-1.1699
B	-0.6565	1.9357	-0.0901
F	0.2976	1.5792	0.8983
F	-1.9510	1.8263	0.4789
F	-0.4286	3.2436	-0.5277
H	-1.1811	-0.1722	1.6313
H	0.3326	-2.8875	-1.2281
H	-2.3902	-2.5175	-1.6648
H	-4.2474	-1.4720	0.0132
H	-3.6335	-0.1986	1.1144
H	-3.6347	0.0889	-0.6431
H	1.6704	-2.2772	1.2820
H	1.1953	-0.6267	1.7654
H	2.3595	-1.4414	-0.9535
H	1.7179	0.1672	-0.5611
H	3.1602	-0.4488	0.2788

$[C_2mim][EtSO_4]$	m062x/aug-cc-pvdz			
	C	1.5170	-0.4083	0.0472
	N	2.6860	-1.0212	-0.1375
	C	3.7041	-0.1143	0.0512
	C	3.1161	1.0779	0.3551
	N	1.7562	0.8672	0.3507
	C	2.8499	-2.4343	-0.4667
	C	0.7264	1.8913	0.5812
	C	0.4910	2.7250	-0.6668
	H	0.5383	-0.8789	-0.0470
	H	4.7459	-0.3946	-0.0389
	H	3.5456	2.0468	0.5776
	H	3.4162	-2.5204	-1.3983
	H	3.3810	-2.9349	0.3477
	H	1.8580	-2.8744	-0.5908
	H	1.0775	2.5054	1.4161
	H	-0.1748	1.3536	0.8904
	H	0.1211	2.0954	-1.4845

H	1.4126	3.2264	-0.9869
S	-2.1043	-0.8255	0.1557
O	-1.2390	-1.8058	-0.5552
O	-1.5374	-0.3690	1.4583
O	-1.9654	0.4934	-0.8500
O	-3.5457	-1.1593	0.2003
C	-2.7377	1.6211	-0.4356
H	-2.5883	2.3908	-1.1991
H	-3.8018	1.3609	-0.3837
H	-2.3991	1.9904	0.5421
H	-0.2591	3.4939	-0.4483

[C_2mim][OAC] m062x/aug-cc-pvdz

C	-0.6121	0.3551	-0.0816
N	-1.1420	1.5713	0.0418
C	-2.5085	1.4858	-0.1075
C	-2.7997	0.1708	-0.3246
N	-1.6019	-0.5084	-0.3073
C	-0.3687	2.7860	0.2905
C	-1.4110	-1.9570	-0.4575
C	-1.8549	-2.7051	0.7882
H	0.4498	0.0940	-0.0174
H	-3.1478	2.3579	-0.0546
H	-3.7445	-0.3293	-0.4959
H	-0.6892	3.2256	1.2397
H	0.6860	2.4982	0.3361
H	-0.5391	3.4925	-0.5272
H	-0.3427	-2.1001	-0.6474
H	-1.9793	-2.2684	-1.3397
H	-2.9179	-2.5342	0.9976
H	-1.2636	-2.3885	1.6555
C	2.7857	-0.1731	0.0045
C	4.2800	-0.4522	-0.1332
O	2.4203	1.0099	0.2410
O	2.0050	-1.1555	-0.1471
H	4.8772	0.4110	0.1764
H	4.5519	-1.3334	0.4604
H	4.4991	-0.6830	-1.1847
H	-1.7001	-3.7792	0.6354

[C_2mim][OTs] b3lyp/6-31++g(d,p)-d3

C	1.0137	-0.7682	1.2570
N	1.9170	0.1766	1.5428
C	3.0971	-0.1194	0.8832
C	2.8907	-1.2822	0.2001
N	1.5870	-1.6746	0.4551
C	1.6907	1.3423	2.3976
C	0.9024	-2.8693	-0.0803
C	1.2318	-3.1199	-1.5438
H	-0.0093	-0.7963	1.6050
H	3.9650	0.5156	0.9602
H	3.5508	-1.8512	-0.4332
H	1.9790	2.2431	1.8564
H	0.6332	1.3871	2.6514
H	2.2886	1.2465	3.3058
H	-0.1654	-2.6950	0.0591
H	1.1934	-3.7245	0.5354
H	2.2865	-3.3716	-1.6838
H	0.9907	-2.2515	-2.1617
O	-3.8191	0.8283	0.5938
S	-2.7960	-0.1960	0.2052
O	-2.2697	-0.9523	1.3950
O	-3.2652	-1.1116	-0.8843
C	-1.3890	0.7040	-0.4508
C	-1.0442	1.9408	0.0985
C	0.1269	2.5708	-0.3200
C	0.9725	1.9765	-1.2687
C	2.2804	2.6198	-1.6438
C	0.5926	0.7447	-1.8209
C	-0.5807	0.1071	-1.4197
H	-1.6755	2.4039	0.8487
H	0.3985	3.5302	0.1105
H	2.2327	3.7080	-1.5458
H	3.0797	2.2627	-0.9818
H	2.5690	2.3704	-2.6690
H	1.2301	0.2704	-2.5613
H	-0.8534	-0.8531	-1.8413
C	0.3922	-4.3152	-2.0316

[C_2mim][PF_6] b3lyp/6-31++g(d,p)-d3

C	1.6587	-0.4133	-0.6940
N	1.9387	-1.5801	-0.1036
C	3.0830	-1.4297	0.6598
C	3.4891	-0.1350	0.5177
N	2.5871	0.4799	-0.3333
C	1.1476	-2.8073	-0.2215
C	2.5865	1.9085	-0.6989
C	2.0970	2.7798	0.4517
H	0.8024	-0.2157	-1.3176
H	3.4992	-2.2474	1.2265
H	4.3275	0.3951	0.9402
H	0.8482	-3.1338	0.7754
H	0.2589	-2.5934	-0.8117
H	1.7473	-3.5798	-0.7068
H	1.9426	2.0094	-1.5741
H	3.6072	2.1636	-0.9936
H	2.1025	3.8274	0.1353
H	2.7466	2.6835	1.3270
H	1.0769	2.5090	0.7363
P	-2.0240	0.0961	0.0517
F	-2.5779	1.0381	1.2725
F	-1.4444	-0.8476	-1.1801
F	-0.8429	-0.4961	1.0388
F	-3.1839	0.6819	-0.9474
F	-1.0036	1.3039	-0.4242
F	-3.0196	-1.1220	0.5133

$[C_2mim][Tf_2N]$	b3lyp/6-31++g(d,p)-d3			
	C	1.5783	-1.8093	2.2754
	C	2.1568	-2.3267	0.9636
	C	3.7347	1.5948	-1.6099
	N	3.0641	-1.3418	0.3408
	C	4.4354	-1.2720	0.5062
	C	4.8659	-0.1789	-0.1899
	N	3.7461	0.4001	-0.7612
	C	2.6686	-0.3203	-0.4284
	H	0.9330	-2.5787	2.7102
	H	2.3693	-1.5739	2.9946
	H	0.9744	-0.9137	2.1073
	H	1.3664	-2.5343	0.2413

H	2.7427	-3.2356	1.1116
H	4.2639	2.4002	-1.0982
H	4.2232	1.3715	-2.5605
H	2.6993	1.8888	-1.7796
H	4.9753	-1.9986	1.0924
H	5.8534	0.2307	-0.3312
H	1.6402	-0.1087	-0.6939
N	-0.4502	0.0905	-0.5153
S	-1.3314	-1.1062	-1.1449
S	-0.8168	1.6675	-0.6022
O	-2.1459	2.0162	-1.1120
O	-2.1044	-0.7690	-2.3433
O	-0.4743	-2.3005	-1.1491
C	-2.6205	-1.5052	0.1685
C	-0.8674	2.0811	1.2329
F	-3.4836	-0.4931	0.3174
F	-3.3001	-2.6037	-0.1952
F	-2.0239	-1.7431	1.3487
F	-1.8151	1.3703	1.8580
F	-1.1375	3.3864	1.3816
F	0.3164	1.8213	1.8134
O	0.3613	2.4041	-1.0852

[C_2mim][TFA] b3lyp/6-31++g(d,p)-d3

C	1.6598	-0.4393	-0.0602
N	2.4826	-1.4928	0.0463
C	3.7908	-1.0608	-0.0972
C	3.7390	0.2887	-0.2929
N	2.4028	0.6546	-0.2680
C	2.0195	-2.8665	0.2705
C	1.8506	2.0208	-0.4247
C	2.1436	2.8982	0.7905
H	0.5570	-0.5152	0.0046
H	4.6299	-1.7383	-0.0533
H	4.5283	1.0075	-0.4509
H	2.4266	-3.2437	1.2122
H	0.9290	-2.8512	0.3186
H	2.3437	-3.5034	-0.5565
H	0.7723	1.8922	-0.5660
H	2.2871	2.4386	-1.3377

H	1.7104	3.8901	0.6236
H	3.2187	3.0226	0.9671
H	1.6842	2.4789	1.6915
C	-1.7098	0.0151	-0.1002
C	-3.2705	-0.0509	-0.0057
O	-1.2098	1.1262	-0.3699
O	-1.1314	-1.0792	0.1368
F	-3.8839	1.0451	-0.5014
F	-3.7743	-1.1204	-0.6718
F	-3.6633	-0.1712	1.2936

Conf1.[C_4mim][BF_4] m062x/aug-cc-pvdz Energy= -847.6574

C	-1.7455	-2.0583	-0.9057
N	-2.2000	-1.1750	0.0477
C	-1.1804	-0.8412	0.8352
N	-0.0941	-1.4955	0.4350
C	-0.4231	-2.2604	-0.6620
C	-3.5183	-0.5450	0.0647
C	1.2638	-1.2759	0.9563
C	2.1830	-0.7272	-0.1305
C	3.5268	-0.2912	0.4508
C	4.4918	0.1623	-0.6426
F	-0.4673	0.9447	-1.1355
B	-0.6069	1.8968	-0.0944
F	0.2655	1.5022	0.9609
F	-1.9344	1.8010	0.3998
F	-0.3153	3.1651	-0.5286
H	-1.2109	-0.0968	1.6167
H	0.3050	-2.8709	-1.1720
H	-2.3962	-2.4538	-1.6698
H	-4.2701	-1.3033	-0.1581
H	-3.6923	-0.1219	1.0526
H	-3.5305	0.2634	-0.6670
H	1.6291	-2.2253	1.3616
H	1.1665	-0.5510	1.7662
H	2.3466	-1.4952	-0.8994
H	1.6808	0.1210	-0.6063
H	3.3546	0.5292	1.1579
H	3.9750	-1.1172	1.0211
H	5.4468	0.4893	-0.2210

H	4.6954	-0.6526	-1.3463
H	4.0687	0.9977	-1.2097

Conf2.[C_4mim][BF_4] m062x/aug-cc-pvdz		Energy=	-847.6582
C	0.6475	2.9312	0.4830
N	1.3237	2.0275	-0.3210
C	0.5957	0.9110	-0.4112
N	-0.5210	1.0656	0.3025
C	-0.5089	2.3263	0.8746
C	2.6603	2.1798	-0.9062
C	-1.4946	-0.0199	0.5361
C	-2.8256	0.2207	-0.1785
C	-3.8187	-0.9204	0.0810
C	-5.1602	-0.7105	-0.6281
F	1.3938	-1.1557	1.2687
B	1.8951	-1.7919	0.1136
F	2.4329	-3.0215	0.3825
F	2.8451	-0.9252	-0.5001
F	0.7928	-1.8995	-0.8086
H	0.8660	0.0039	-0.9363
H	-1.3042	2.6726	1.5153
H	1.0501	3.9054	0.7112
H	3.2663	2.7927	-0.2365
H	3.0951	1.1818	-0.9852
H	2.5944	2.6597	-1.8865
H	-1.6288	-0.0979	1.6195
H	-1.0032	-0.9345	0.1980
H	-3.2634	1.1737	0.1515
H	-2.6422	0.3153	-1.2571
H	-3.3714	-1.8678	-0.2468
H	-3.9860	-1.0181	1.1627
H	-5.8465	-1.5395	-0.4250
H	-5.6465	0.2147	-0.2952
H	-5.0286	-0.6455	-1.7147

Conf3.[C_4mim][BF_4] m062x/aug-cc-pvdz		Energy=	-847.6530
C	-2.2181	-2.2367	-0.5901
N	-2.3977	-0.9552	-0.0965
C	-0.9728	-2.6378	-0.2075
C	-1.2967	-0.6082	0.5600

N	-0.4168	-1.5993	0.5202
C	-3.5399	-0.0615	-0.3173
H	-3.8819	-0.1762	-1.3452
H	-4.3522	-0.3061	0.3713
H	-3.1866	0.9658	-0.1578
C	0.9833	-1.4746	0.9781
C	1.9292	-1.1584	-0.1851
C	3.3133	-0.7387	0.3252
C	4.3010	-0.4755	-0.8147
H	5.2736	-0.1558	-0.4280
H	4.4619	-1.3754	-1.4194
H	3.9302	0.3120	-1.4787
H	3.1904	0.1719	0.9237
H	3.7203	-1.5095	0.9951
H	2.0135	-2.0325	-0.8454
H	1.4874	-0.3394	-0.7604
H	0.9937	-0.6466	1.6903
H	1.2481	-2.4016	1.4958
H	-1.1010	0.5082	1.0923
H	-2.9734	-2.7388	-1.1603
H	-0.4430	-3.5539	-0.3905
B	-0.1174	2.1746	-0.0219
F	0.3940	3.4135	-0.2947
F	0.5763	1.5481	1.0620
F	-0.0421	1.3021	-1.1325
F	-1.4935	2.2512	0.3729

Conf4.[C_4mim][BF_4] m062x/aug-cc-pvdz		Energy =	-847.6300
C	-1.74549	-2.05826	-0.90571
N	-2.19996	-1.17497	0.04773
C	-1.18038	-0.84117	0.83523
N	-0.09412	-1.49553	0.43499
C	-0.42307	-2.26037	-0.66197
C	-3.51832	-0.54502	0.06465
C	1.26375	-1.27587	0.95633
C	2.18296	-0.72719	-0.13053
C	3.52676	-0.29121	0.45081
C	4.49177	0.16226	-0.64257
F	7.68053	0.60883	-1.13552
B	8.01211	1.5121	-0.0944

	F	8.59052	0.7491	0.9609
	F	6.79978	2.06142	0.3998
	F	8.87354	2.48764	-0.52861
	H	-1.21086	-0.09679	1.61674
	H	0.30498	-2.87089	-1.17198
	H	-2.39618	-2.45383	-1.66976
	H	-4.27012	-1.30327	-0.15814
	H	-3.69233	-0.12191	1.05264
	H	-3.53052	0.26336	-0.66703
	H	1.62908	-2.22529	1.36157
	H	1.16654	-0.55098	1.76619
	H	2.34659	-1.49517	-0.89944
	H	1.68076	0.121	-0.60633
	H	3.35459	0.52918	1.15794
	H	3.97498	-1.11721	1.02112
	H	5.44678	0.48927	-0.22103
	H	4.69541	-0.65259	-1.34627
	H	4.06865	0.99773	-1.20972
[C_4mim][$MeSO_4$]	m062x/aug-cc-pvdz			
	C	-1.8307	-0.1561	-0.4319
	N	-2.9388	-0.4819	0.2306
	C	-3.5883	0.6706	0.6107
	C	-2.8321	1.7143	0.1632
	N	-1.7466	1.1719	-0.4867
	C	-3.3687	-1.8506	0.5048
	C	-0.5962	1.9095	-1.0251
	C	0.3947	2.2561	0.0780
	C	1.6556	2.8964	-0.4947
	C	2.5968	3.3879	0.6002
	H	-1.1021	-0.8544	-0.8284
	H	-4.5194	0.6493	1.1623
	H	-2.9744	2.7842	0.2488
	H	-3.5974	-1.9399	1.5702
	H	-4.2535	-2.0848	-0.0943
	H	-2.5430	-2.5183	0.2456
	H	-0.9878	2.8078	-1.5143
	H	-0.1270	1.2610	-1.7697
	H	0.6563	1.3321	0.6124
	H	-0.0815	2.9378	0.7980

H	1.3770	3.7395	-1.1439
H	2.1669	2.1598	-1.1306
H	3.5178	3.8046	0.1745
H	2.8760	2.5672	1.2739
H	2.1170	4.1702	1.2035
S	1.2649	-1.8714	-0.3090
O	-0.0005	-2.6252	-0.0960
O	1.1174	-0.7374	-1.2720
O	1.4633	-1.1465	1.1704
O	2.4759	-2.6957	-0.5249
C	2.6780	-0.4015	1.2828
H	2.6041	0.1572	2.2214
H	3.5405	-1.0775	1.3206
H	2.7872	0.2939	0.4395

[C_4mim][OAc] m062x/aug-cc-pvdz

C	0.8052	0.9868	-0.1688
N	1.4346	2.1004	0.2034
C	0.5625	3.1628	0.1191
C	-0.6281	2.6587	-0.3169
N	-0.4475	1.3045	-0.4920
C	2.8318	2.1444	0.6262
C	-1.4660	0.3285	-0.8993
C	-2.4657	0.0687	0.2190
C	-3.4956	-0.9776	-0.1966
C	-4.5134	-1.2515	0.9052
H	1.2486	-0.0135	-0.1957
H	0.8591	4.1734	0.3694
H	-1.5733	3.1458	-0.5204
H	2.8873	2.5352	1.6464
H	3.2169	1.1210	0.5911
H	3.3963	2.7873	-0.0554
H	-0.9210	-0.5870	-1.1527
H	-1.9608	0.7239	-1.7934
H	-2.9729	1.0065	0.4901
H	-1.9178	-0.2796	1.1061
H	-2.9715	-1.9075	-0.4583
H	-4.0141	-0.6365	-1.1046
H	-5.2408	-2.0104	0.5914
H	-5.0667	-0.3386	1.1646

H	-4.0144	-1.6155	1.8134
C	1.9618	-2.2414	-0.1102
C	2.4221	-3.6739	0.1454
O	2.7625	-1.3087	0.1801
O	0.7973	-2.0781	-0.5670
H	3.5144	-3.7470	0.1195
H	2.0806	-3.9705	1.1474
H	1.9742	-4.3605	-0.5813

[C_4mim][OTs] b3lyp/6-31++g(d,p)-d3

C	2.4587	-1.3122	-0.5456
N	2.9229	-2.3537	0.1554
C	4.1854	-2.0403	0.6288
C	4.4695	-0.7749	0.2035
N	3.3784	-0.3402	-0.5288
C	2.1568	-3.5806	0.4125
C	3.1572	1.0165	-1.0756
C	2.8938	2.0440	0.0302
H	1.4710	-1.2081	-0.9976
H	4.7605	-2.7323	1.2244
H	5.3375	-0.1546	0.3643
H	2.4699	-3.9873	1.3758
H	1.0992	-3.3051	0.4563
H	2.3450	-4.3125	-0.3780
H	2.2884	0.9403	-1.7339
H	4.0362	1.2746	-1.6767
H	3.7577	2.0872	0.7100
H	2.0231	1.7132	0.6097
O	-0.1623	0.7448	1.0609
S	-0.6564	-0.3307	0.1580
O	-0.1513	-0.1923	-1.2568
O	-0.4082	-1.7172	0.6742
C	-2.4479	-0.1354	0.0613
C	-3.1057	0.7281	0.9344
C	-4.4977	0.8513	0.8645
C	-5.2457	0.1214	-0.0673
C	-6.7489	0.2627	-0.1507
C	-4.5594	-0.7441	-0.9366
C	-3.1737	-0.8764	-0.8768
H	-2.5275	1.2986	1.6542

H	-5.0069	1.5287	1.5474
H	-7.1348	0.9031	0.6497
H	-7.0556	0.7052	-1.1078
H	-7.2480	-0.7113	-0.0712
H	-5.1197	-1.3207	-1.6708
H	-2.6531	-1.5431	-1.5578
C	2.6258	3.4384	-0.5534
H	1.7547	3.3835	-1.2199
H	3.4781	3.7570	-1.1730
C	2.3649	4.4837	0.5375
H	3.2294	4.5852	1.2064
H	2.1638	5.4686	0.1001
H	1.4988	4.2020	1.1476

$[C_4mim][PF_6]$ b3lyp/6-31++g(d,p)-d3

C	1.0405	1.3134	0.5525
N	1.2308	2.3613	-0.2562
C	2.5591	2.3801	-0.6460
C	3.1660	1.3131	-0.0515
N	2.1980	0.6584	0.6925
C	0.1757	3.2827	-0.6996
C	2.3727	-0.5899	1.4694
C	2.8266	-1.7720	0.6050
H	0.0956	1.0205	0.9860
H	2.9503	3.1385	-1.3066
H	4.1870	0.9681	-0.0972
H	0.1498	3.2931	-1.7914
H	-0.7796	2.9153	-0.3243
H	0.3805	4.2857	-0.3165
H	1.4028	-0.7983	1.9265
H	3.0967	-0.3802	2.2640
H	2.9907	-2.6095	1.2973
H	3.8094	-1.5532	0.1612
P	-2.2033	-0.2853	0.0317
F	-2.3033	-1.7941	-0.5604
F	-2.0064	1.2629	0.6490
F	-0.9803	0.0611	-1.0468
F	-3.3487	-0.5826	1.1400
F	-1.0268	-0.7873	1.1154
F	-3.2989	0.2732	-1.0281

C	1.8292	-2.1888	-0.4851
H	1.6638	-1.3564	-1.1813
H	0.8529	-2.3906	-0.0292
C	2.3054	-3.4184	-1.2667
H	1.5764	-3.6933	-2.0364
H	3.2659	-3.2327	-1.7658
H	2.4346	-4.2857	-0.6066

[C4mim][Tf2N] b3lyp/6-31++g(d,p)-d3

C	-3.4892	0.6380	-1.2736
C	-3.0577	1.1553	0.1026
C	-1.1732	-2.4615	2.9321
N	-2.9608	0.0712	1.1064
C	-4.0063	-0.4601	1.8396
C	-3.4908	-1.4663	2.6033
N	-2.1386	-1.5378	2.3184
C	-1.8398	-0.5977	1.4100
H	-2.7615	-0.1096	-1.6158
H	-4.4612	0.1293	-1.1958
H	-3.7722	1.8846	0.4976
H	-2.0743	1.6288	0.0484
H	-0.9917	-2.1634	3.9682
H	-1.5848	-3.4728	2.9023
H	-0.2442	-2.4301	2.3593
H	-5.0128	-0.0794	1.7579
H	-3.9601	-2.1260	3.3169
H	-0.8502	-0.4068	0.9833
N	0.9024	-0.0556	0.1309
S	1.2844	1.4730	-0.2822
S	1.8475	-1.3663	-0.0657
O	3.2906	-1.1452	-0.0953
O	2.2688	1.6406	-1.3479
O	0.0047	2.2021	-0.3373
C	2.1012	2.1571	1.2787
C	1.3912	-1.9822	-1.7936
F	3.2403	1.5150	1.5506
F	2.3630	3.4603	1.1074
F	1.2721	2.0247	2.3344
F	2.0223	-3.1395	-2.0352
F	1.7320	-1.0944	-2.7314

F	0.0614	-2.1988	-1.8739
O	1.2749	-2.4009	0.8154
C	-3.5758	1.7792	-2.2978
H	-4.2955	2.5325	-1.9456
H	-2.6016	2.2816	-2.3564
C	-3.9882	1.2896	-3.6907
H	-4.0361	2.1232	-4.4003
H	-3.2686	0.5605	-4.0826
H	-4.9754	0.8101	-3.6712

[C4mim][TFA] b3lyp/6-31++g(d,p)-d3

C	-1.0148	-1.3133	0.2174
N	-1.0911	-2.5863	-0.1911
C	-2.4139	-2.9929	-0.1601
C	-3.1464	-1.9285	0.2781
N	-2.2544	-0.8959	0.5107
C	0.0518	-3.4129	-0.5922
C	-2.6071	0.4679	0.9387
C	-3.1015	1.3235	-0.2272
H	-0.1049	-0.7109	0.3041
H	-2.7092	-3.9910	-0.4427
H	-4.2056	-1.8172	0.4479
H	-0.0999	-3.7595	-1.6164
H	0.9551	-2.8021	-0.5326
H	0.1302	-4.2687	0.0816
H	-1.7135	0.9012	1.3920
H	-3.3717	0.3734	1.7143
H	-3.9707	0.8395	-0.6909
H	-2.3142	1.3741	-0.9892
C	2.4071	-0.0846	0.0620
C	3.6690	0.8429	0.0152
O	1.3815	0.4926	0.4989
O	2.5654	-1.2503	-0.3505
F	3.5202	1.8169	-0.9289
F	3.8808	1.4795	1.1986
F	4.8176	0.1910	-0.2818
C	-3.4754	2.7375	0.2280
H	-4.2535	2.6770	1.0009
H	-2.6023	3.2070	0.6995
C	-3.9664	3.6125	-0.9273

H	-4.8550	3.1793	-1.4024
H	-4.2299	4.6169	-0.5785
H	-3.1937	3.7183	-1.6978

[2-me-Py][BF_4] b3lyp/6-31++g(d,p)-d3

C	-1.8337	0.9418	0.0375
C	-3.0986	0.3851	-0.1476
C	-3.2535	-1.0027	-0.1523
C	-2.1438	-1.8329	0.0261
C	-0.9002	-1.2467	0.2071
N	-0.7924	0.0963	0.2124
H	-3.9503	1.0416	-0.2900
H	-4.2397	-1.4346	-0.2984
H	-2.2339	-2.9132	0.0212
H	0.0344	-1.7812	0.3464
B	2.4194	-0.0823	-0.0675
F	1.6354	1.0424	0.4886
F	2.0818	-1.2058	0.7267
F	1.9326	-0.2804	-1.3692
F	3.7542	0.2228	-0.0178
H	0.1729	0.5041	0.3377
C	-1.5383	2.4123	0.0491
H	-1.0810	2.7101	0.9996
H	-0.8256	2.6677	-0.7436
H	-2.4532	2.9905	-0.0978

[1-me-Py][BF_4] b3lyp/6-31++g(d,p)-d3

C	-2.1618	0.8865	-0.7671
C	-2.9205	-0.2344	-1.0385
C	-2.8219	-1.3353	-0.1975
C	-1.9721	-1.2817	0.9086
C	-1.2361	-0.1384	1.1447
N	-1.3257	0.9144	0.3014
C	-0.4413	2.0911	0.4865
H	-2.1897	1.7854	-1.3708
H	-3.5649	-0.2367	-1.9096
H	-3.4176	-2.2208	-0.3873
H	-1.8595	-2.1290	1.5743
H	-0.4975	-0.0555	1.9292
H	-1.0363	3.0111	0.4140

H	0.3346	2.0634	-0.2794
H	0.0374	2.0124	1.4581
B	2.2159	-0.2562	-0.1655
F	2.7249	1.0326	-0.3780
F	1.8217	-0.3805	1.1915
F	1.0970	-0.4665	-1.0086
F	3.2137	-1.2164	-0.4639

Pyridine hf-6-31g(d)

C	1.1441	-0.7232	0
C	1.2000	0.6737	0.0000
C	-0.0000	1.3869	0.0000
C	-1.2001	0.6736	0.0000
C	-1.1441	-0.7232	-0.0000
N	0.0000	-1.4206	0.0000
H	2.0603	-1.3112	-0.0003
H	2.1595	1.1834	0.0001
H	-0.0000	2.4740	-0.0007
H	-2.1596	1.1832	0.0001
H	-2.0602	-1.3113	-0.0003

[Py][BF_4] b3lyp/6-31++g(d,p)-d3

C	1.4645	-0.9982	-0.0309
C	2.8058	-1.3417	0.0037
C	3.7654	-0.3261	0.0294
C	3.3655	1.0131	0.0194
C	2.0128	1.3085	-0.0162
N	1.1155	0.3032	-0.0400
H	0.6525	-1.7133	-0.0510
H	3.0882	-2.3874	0.0114
H	4.8206	-0.5769	0.0573
H	4.0877	1.8202	0.0386
H	1.6112	2.3137	-0.0269
H	0.1155	0.5461	-0.0675
B	-2.5195	-0.0119	0.0084
F	-1.5926	1.0745	-0.1132
F	-3.2083	0.1103	1.2267
F	-3.4195	0.0330	-1.0689
F	-1.7875	-1.2177	-0.0176
C	1.4645	-0.9982	-0.0309

C	2.8058	-1.3417	0.0037
C	3.7654	-0.3261	0.0294

Pyrrole b3lyp/6-31++g(d,p)-d3

N	-1.1128	0.0000	0.0000
C	-0.3260	-1.1127	0.0000
C	0.9717	-0.7133	0.0000
C	0.9718	0.7132	0.0000
C	-0.3259	1.1127	0.0000
H	-2.1053	0.0001	0.0001
H	-0.7553	-2.0929	-0.0001
H	1.8281	-1.3567	0.0000
H	1.8282	1.3566	0.0000
H	-0.7552	2.0929	0.0000

[P16][DCA] b3lyp/6-31++g(d,p)-d3

N	0.5274	-0.2652	-0.4861
C	0.6979	1.2435	-0.6163
C	0.7614	1.7653	0.8101
C	1.5238	0.6475	1.5250
C	0.9004	-0.6165	0.9513
C	1.4609	-0.9468	-1.4270
C	-0.8746	-0.7096	-0.8138
C	-1.9845	0.0158	-0.0697
H	-0.1122	1.6352	-1.2353
H	1.6560	1.4110	-1.1157
H	1.2851	2.7252	0.8451
H	-0.2410	1.8887	1.2371
H	1.4214	0.6761	2.6135
H	2.5898	0.6978	1.2753
H	1.5717	-1.4782	0.9315
H	-0.0196	-0.8785	1.4771
H	1.3106	-2.0270	-1.3523
H	2.4835	-0.6869	-1.1451
H	1.2522	-0.5932	-2.4405
H	-0.9029	-1.7843	-0.5986
H	-0.9908	-0.5670	-1.8945
H	-1.9557	1.0906	-0.2880
H	-1.8744	-0.1017	1.0157
N	5.2205	-0.0787	0.2091

C	4.5389	-1.1457	0.5560
N	3.9808	-2.1190	0.8946
C	4.5930	0.8696	-0.4448
N	4.0811	1.7516	-1.0229
C	-3.3444	-0.5395	-0.4945
C	-4.4996	0.1444	0.2308
H	-3.3771	-1.6211	-0.2962
H	-3.4677	-0.4102	-1.5801
H	-4.3846	-0.0024	1.3159
H	-4.4482	1.2296	0.0524
C	-5.8667	-0.3734	-0.2067
C	-7.0144	0.3101	0.5298
H	-5.9122	-1.4590	-0.0362
H	-5.9791	-0.2191	-1.2899
H	-7.9873	-0.0691	0.1930
H	-6.9413	0.1391	1.6126
H	-6.9971	1.3951	0.3582

P12-DCA b3lyp/6-31++g(d,p)-d3

N	-1.1730	-0.3689	-0.3976
C	-1.2522	1.1163	-0.7198
C	-1.3040	1.8276	0.6242
C	-0.3833	0.9689	1.4921
C	-0.6591	-0.4656	1.0420
C	-0.2111	-1.0289	-1.3365
C	-2.4946	-1.0675	-0.5587
C	-3.6781	-0.4769	0.1954
H	-2.0962	1.2875	-1.3716
H	-0.3393	1.3790	-1.2304
H	-0.9452	2.8433	0.5245
H	-2.3106	1.8617	1.0248
H	-0.5714	1.0825	2.5522
H	0.6467	1.2298	1.2986
H	0.2156	-1.0960	1.0549
H	-1.4341	-0.9313	1.6295
H	-0.1208	-2.0721	-1.0772
H	0.7454	-0.5480	-1.2510
H	-0.5870	-0.9180	-2.3435
H	-2.3276	-2.0911	-0.2518
H	-2.7077	-1.0711	-1.6189

H	-4.5339	-1.1150	0.0059
H	-3.9321	0.5174	-0.1472
H	-3.5267	-0.4466	1.2664
N	3.6133	0.0372	0.0180
C	2.9955	-1.0443	0.4340
N	2.4487	-1.9887	0.7983
C	2.8102	0.9190	-0.5199
N	2.0945	1.6913	-0.9877

[CMI][HSO_4] b3lyp/6-31++g(d,p)-d3

C	-0.5983	0.9519	0.3828
N	-0.5996	2.2850	0.3318
C	-1.5192	2.6921	-0.6212
C	-2.0734	1.5650	-1.1469
N	-1.4880	0.4901	-0.5020
C	0.3210	3.1346	1.0965
C	-1.6204	-0.9233	-0.8394
H	0.0336	0.3362	1.0063
H	-1.6885	3.7336	-0.8425
H	-2.8125	1.4341	-1.9211
H	1.2755	2.6061	1.1576
H	-0.0874	3.3347	2.0906
H	0.4508	4.0737	0.5567
H	-2.3286	-1.0247	-1.6644
H	-0.6321	-1.2734	-1.1703
S	2.2299	-0.5021	-0.2332
O	3.4563	-1.2886	-0.3839
O	1.3134	-0.4352	-1.3966
O	1.2533	-1.4225	0.8407
O	2.3804	0.7924	0.4815
H	1.8591	-1.7558	1.5259
C	-2.0873	-1.7367	0.3570
O	-2.2277	-1.3197	1.4817
O	-2.3146	-3.0080	-0.0202
H	-2.5568	-3.5039	0.7847

[EMIM][HSO_4] b3lyp/6-31++g(d,p)-d3

C	1.1571	0.5098	-0.7801
N	1.0751	1.7189	-0.2139
C	1.6381	1.6572	1.0492

C	2.0855	0.3806	1.2243
N	1.7776	-0.3167	0.0686
C	0.3918	2.8802	-0.7850
C	2.0953	-1.7304	-0.1955
C	3.5881	-1.9437	-0.4060
H	0.7954	0.2485	-1.7615
H	1.6657	2.5166	1.7000
H	2.5842	-0.0896	2.0565
H	0.1746	2.6768	-1.8324
H	1.0438	3.7507	-0.7051
H	-0.5364	3.0603	-0.2407
H	1.7276	-2.3059	0.6566
H	1.5229	-2.0195	-1.0775
H	3.7744	-3.0060	-0.5894
H	3.9457	-1.3736	-1.2688
H	4.1578	-1.6421	0.4780
S	-2.2311	-0.3397	0.1025
O	-3.6132	-0.7805	0.4344
O	-1.4483	0.1496	1.2609
O	-1.4009	-1.7232	-0.2979
O	-2.1651	0.5331	-1.1004
H	-1.8419	-2.1524	-1.0542

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ethanolamine formate m062x/aug-cc-pvdz

N	0.3439	1.1173	0.2358
H	-1.1439	0.8179	-0.2512
C	2.6561	0.1774	0.2230
C	1.1987	-0.0044	-0.1787
O	3.4684	-0.8946	-0.2279
H	0.6762	1.9828	-0.1885
H	3.0600	1.0849	-0.2451
H	2.7306	0.2971	1.3166
H	0.7992	-0.9237	0.2718
H	1.1268	-0.1097	-1.2680
H	3.1984	-1.6992	0.2325
C	-2.6229	-0.3076	0.2550
O	-3.7192	-0.7987	0.1024
O	-2.0818	0.5474	-0.5862
H	-1.9925	-0.5509	1.1342
H	0.4078	1.2541	1.2441

ethanolamine acetate	m062x/aug-cc-pvdz		
N	-0.9229	-1.6381	0.2205
C	-1.7577	0.6546	0.1701
C	-2.0284	-0.7818	-0.2330
O	-2.8612	1.4331	-0.2810
H	-1.1025	-2.6030	-0.0502
H	-0.8794	-1.6326	1.2391
H	-1.6561	0.7209	1.2649
H	-0.8195	1.0068	-0.2851
H	-2.0895	-0.8479	-1.3263
H	-2.9952	-1.0969	0.1852
H	-2.7036	2.3506	-0.0304
C	1.9325	0.0828	0.1196
C	3.1726	0.7308	-0.4310
O	1.5089	0.2814	1.2473
O	1.3410	-0.7264	-0.7444
H	3.6421	1.3551	0.3328
H	3.8711	-0.0433	-0.7713
H	2.9031	1.3414	-1.3019
H	0.4657	-1.1068	-0.3300

4ip ethanolamine formate	m062x/aug-cc-pvdz		
N	-4.0004	1.3444	1.5533
C	-1.7194	0.6776	2.2356
C	-3.2165	0.4676	2.4430
O	-0.9678	-0.2202	3.0385
H	-4.8686	1.6201	2.0064
H	-4.2665	0.8184	0.7194
H	-1.4633	0.5573	1.1702
H	-1.4437	1.6968	2.5283
H	-3.4611	0.6959	3.4841
H	-3.4615	-0.5888	2.2673
H	-0.8505	-1.0397	2.5183
C	-2.1213	2.8085	-0.6450
O	-2.5821	1.8185	-1.1971
O	-2.5325	3.2342	0.5356
H	-3.1820	2.5239	0.9575
N	-4.0301	-3.3118	0.5079
C	-1.7921	-2.3508	0.4029

C	-2.7292	-3.2494	1.1892
O	-0.5961	-2.1977	1.1596
H	-4.6988	-3.8268	1.0774
H	-3.9387	-3.8263	-0.3683
H	-1.5710	-2.7969	-0.5760
H	-2.2721	-1.3751	0.2318
H	-2.8838	-2.8237	2.1861
H	-2.2741	-4.2393	1.3111
H	0.1242	-1.9185	0.5613
C	-4.7686	-0.8724	-1.5719
O	-4.2207	-1.7277	-2.2498
O	-4.9297	-0.9877	-0.2594
H	-4.5674	-1.9191	0.0674
N	1.6940	0.5705	1.7720
C	4.0955	0.4716	1.3614
C	2.9758	0.0914	2.3154
O	5.3128	-0.1054	1.8052
H	0.9395	0.4127	2.4423
H	1.4718	0.0153	0.9425
H	3.8340	0.1220	0.3544
H	4.1852	1.5664	1.3074
H	3.1385	0.5542	3.2937
H	2.9777	-0.9986	2.4520
H	5.8047	-0.3654	1.0098
C	2.2489	2.9095	-0.4406
O	2.4417	1.8560	-1.0329
O	1.8389	2.9748	0.8123
H	1.7597	2.0010	1.2221
N	3.2184	-3.2384	-0.8700
C	4.9135	-1.5621	-1.3909
C	4.4936	-2.6527	-0.4230
O	6.0490	-0.9119	-0.8194
H	2.9842	-4.0443	-0.2913
H	3.3004	-3.5841	-1.8267
H	5.1740	-2.0008	-2.3627
H	4.0922	-0.8496	-1.5452
H	4.3354	-2.2205	0.5711
H	5.2839	-3.4071	-0.3470
H	6.3731	-0.2441	-1.4390
C	1.1251	-0.8404	-1.7367

O	1.7020	-1.0745	-2.7847
O	1.4214	-1.4793	-0.6051
H	2.1955	-2.2565	-0.7688
H	-1.3553	3.4220	-1.0714
H	-5.1806	0.0325	-1.9672
H	0.3112	-0.1521	-1.6423
H	2.4284	3.8652	-0.8870

4IP ethanolamine acetate	m062x/aug-cc-pvdz		
N	4.0838	1.5346	-1.7584
C	1.6800	1.0196	-2.0614
C	3.0827	0.8924	-2.6638
O	0.7708	0.1356	-2.7511
H	4.8589	1.9241	-2.2705
H	4.4324	0.8668	-1.0792
H	1.7186	0.7886	-1.0083
H	1.3221	2.0313	-2.1754
H	3.1089	1.3762	-3.6297
H	3.3107	-0.1566	-2.8089
H	0.7437	-0.7160	-2.2623
C	2.4488	2.8024	0.8898
C	1.8285	3.8387	1.7860
O	2.4532	1.6005	1.1317
O	2.9797	3.3266	-0.1955
H	1.4469	3.3759	2.6816
H	2.5698	4.5882	2.0314
H	1.0289	4.3345	1.2490
H	3.4255	2.6521	-0.8445
N	4.2076	-3.1339	-0.9679
C	2.0378	-2.1396	-0.3444
C	2.7760	-3.0205	-1.3514
O	0.7571	-1.8425	-0.9403
H	4.7485	-3.6546	-1.6383
H	4.3414	-3.5091	-0.0398
H	1.9145	-2.6637	0.5961
H	2.5961	-1.2358	-0.1628
H	2.7230	-2.5434	-2.3188
H	2.2799	-3.9817	-1.4211
H	0.0872	-1.5859	-0.2727
C	5.1568	-1.0141	1.2639

C	5.3869	0.2472	2.0348
O	5.0317	-2.1249	1.7315
O	5.0532	-0.7887	-0.0642
H	5.5943	0.0140	3.0668
H	6.2065	0.8010	1.5962
H	4.4873	0.8456	1.9574
H	4.8160	-1.6421	-0.5649
N	-1.9266	0.5368	-1.7439
C	-4.3679	0.1409	-1.8264
C	-3.0032	-0.2629	-2.3996
O	-5.2712	-0.9805	-1.9327
H	-1.0603	0.5235	-2.2737
H	-1.7438	0.1646	-0.8205
H	-4.2393	0.4198	-0.7938
H	-4.7576	0.9991	-2.3599
H	-2.9629	-0.0883	-3.4649
H	-2.8672	-1.3224	-2.2252
H	-5.7874	-1.0332	-1.1104
C	-3.1300	2.7999	0.2755
C	-3.5241	4.1474	0.8233
O	-3.2057	1.7613	0.9261
O	-2.7078	2.8593	-0.9647
H	-3.8647	4.0494	1.8415
H	-2.6735	4.8156	0.7714
H	-4.3046	4.5679	0.2014
H	-2.3755	1.9357	-1.3732
N	-2.9214	-3.2437	0.8897
C	-4.5563	-1.4442	1.3118
C	-4.2937	-2.7543	0.5721
O	-5.8300	-0.9701	0.7897
H	-2.6842	-4.0677	0.3608
H	-2.7958	-3.4145	1.8773
H	-4.6185	-1.6072	2.3799
H	-3.7825	-0.7236	1.1097
H	-4.3600	-2.5571	-0.4847
H	-5.0563	-3.4751	0.8418
H	-6.0665	-0.1229	1.1897
C	-1.1349	-0.9184	2.1899
C	-0.4930	0.4139	2.3994
O	-1.6266	-1.6196	3.0442

	O	-1.1920	-1.2902	0.8778
	H	-0.3650	0.5810	3.4576
	H	0.4564	0.5034	1.8901
	H	-1.1768	1.1518	1.9946
	H	-1.8449	-2.0912	0.7564

4IP [C_4mim]OH	m062x/aug-cc-pvdz			
	C	-0.6543	1.7000	2.2680
	N	-1.9646	1.4274	2.2980
	C	-2.7548	2.5890	2.2957
	C	-1.7928	3.5795	2.2405
	N	-0.5196	3.0251	2.2245
	C	-2.5007	0.0758	2.3844
	C	0.7531	3.7333	2.0693
	C	1.0601	4.0017	0.6004
	C	2.4693	4.5402	0.3850
	C	2.7584	4.7654	-1.0963
	H	0.1737	0.9979	2.2753
	H	-4.5569	2.1555	1.9451
	H	-1.8961	4.6559	2.2094
	H	-3.2848	-0.0496	1.6373
	H	-1.7030	-0.6488	2.2102
	H	-2.9244	-0.0890	3.3795
	H	1.5300	3.1030	2.5116
	H	0.6802	4.6628	2.6401
	H	0.3172	4.6968	0.1859
	H	0.9398	3.0595	0.0471
	H	3.1888	3.8186	0.7943
	H	2.6024	5.4747	0.9451
	H	3.7988	5.0621	-1.2664
	H	2.1125	5.5496	-1.5073
	H	2.5737	3.8461	-1.6660
	O	-5.4452	1.7754	1.6780
	H	-5.9968	1.8252	2.4677
	C	-4.1315	-1.3907	-1.1152
	N	-5.0642	-1.9955	-1.8958
	C	-5.6215	-1.1304	-2.8179
	C	-5.0213	0.0713	-2.6189
	N	-4.1141	-0.1156	-1.5900
	C	-5.4214	-3.4022	-1.7963

C	-3.2801	0.9458	-1.0255
C	-2.5632	1.7778	-2.0806
C	-1.6715	2.8348	-1.4273
C	-0.7695	3.5330	-2.4406
H	-3.0787	-2.3581	0.1752
H	-6.3805	-1.4404	-3.5213
H	-5.1663	1.0207	-3.1119
H	-6.4871	-3.5051	-1.5789
H	-5.1917	-3.9154	-2.7333
H	-4.8405	-3.8460	-0.9874
H	-2.5430	0.4507	-0.3852
H	-3.9046	1.5817	-0.3876
H	-3.2879	2.2720	-2.7381
H	-1.9544	1.1141	-2.7106
H	-1.0625	2.3502	-0.6495
H	-2.2989	3.5754	-0.9160
H	-0.1856	4.3317	-1.9733
H	-1.3642	3.9763	-3.2470
H	-0.0667	2.8248	-2.8970
O	-2.5735	-2.9073	0.8370
H	-3.1801	-3.0080	1.5813
C	2.5751	-4.3980	0.6213
N	3.6776	-3.9885	-0.0154
C	3.8225	-2.5933	0.0173
C	2.7020	-2.2119	0.7304
N	1.9506	-3.3214	1.0885
C	4.6177	-4.9032	-0.6536
C	0.6837	-3.3226	1.8285
C	0.7226	-2.3563	3.0065
C	-0.4961	-2.5294	3.9093
C	-0.5644	-1.4517	4.9860
H	2.2391	-5.4179	0.7426
H	4.9403	-1.7113	-1.2087
H	2.3607	-1.2226	1.0012
H	5.3680	-4.2999	-1.1631
H	5.1035	-5.5342	0.0940
H	4.0994	-5.5312	-1.3811
H	0.5134	-4.3481	2.1700
H	-0.1314	-3.0572	1.1468
H	0.7569	-1.3232	2.6322

H	1.6432	-2.5186	3.5825
H	-0.4637	-3.5230	4.3742
H	-1.4013	-2.5016	3.2908
H	-1.4470	-1.5730	5.6220
H	-0.6098	-0.4530	4.5345
H	0.3225	-1.4836	5.6290
O	5.4676	-1.2569	-1.9319
H	4.8612	-0.5922	-2.2843
C	2.9909	1.0920	-0.5109
N	4.0707	1.6155	-1.1463
C	3.9269	1.6100	-2.5216
C	2.7084	1.0615	-2.7720
N	2.1641	0.7543	-1.5387
C	5.2659	2.0910	-0.4686
C	0.8417	0.1627	-1.3569
C	0.6853	-1.2086	-2.0021
C	-0.7164	-1.7510	-1.7324
C	-0.9162	-3.1741	-2.2392
H	2.6281	0.9925	1.3156
H	4.6864	1.9943	-3.1871
H	2.1904	0.8751	-3.7015
H	5.5070	3.1027	-0.8042
H	5.0722	2.0983	0.6042
H	6.1062	1.4248	-0.6819
H	0.0966	0.8480	-1.7756
H	0.6760	0.1010	-0.2754
H	1.4429	-1.8924	-1.6016
H	0.8513	-1.1310	-3.0844
H	-1.4545	-1.0864	-2.2007
H	-0.9198	-1.7182	-0.6522
H	-1.9416	-3.5144	-2.0620
H	-0.2404	-3.8706	-1.7289
H	-0.7151	-3.2392	-3.3147
O	2.3760	0.9302	2.2872
H	3.0460	0.3732	2.7021

4IP $[C_4mim][BF_4]$ mp2/aug-cc-pvdz

C	-5.5231	-1.8890	1.2827
N	-4.9621	-1.2354	2.3041
C	-4.9609	0.1183	2.0134

C	-5.5446	0.2649	0.7938
N	-5.8898	-1.0008	0.3552
C	-4.3318	-1.8914	3.4505
C	-6.3866	-1.3478	-0.9887
C	-5.3212	-1.1341	-2.0683
C	-5.8655	-1.4761	-3.4611
C	-4.8147	-1.2827	-4.5591
H	-5.6090	-2.9623	1.2148
H	-4.4867	0.8486	2.6478
H	-5.6364	1.1358	0.1651
H	-3.2907	-1.5684	3.5111
H	-4.8630	-1.6302	4.3697
H	-4.3538	-2.9668	3.2766
H	-7.2795	-0.7414	-1.1760
H	-6.6841	-2.3981	-0.9481
H	-4.4680	-1.7760	-1.8277
H	-4.9672	-0.0978	-2.0402
H	-6.7434	-0.8507	-3.6812
H	-6.2166	-2.5175	-3.4716
H	-5.2211	-1.5329	-5.5456
H	-3.9420	-1.9220	-4.3830
H	-4.4646	-0.2442	-4.5917
B	-3.6113	-4.2847	0.6269
F	-4.4977	-4.6092	1.6884
F	-2.7911	-5.3609	0.3126
F	-4.3767	-3.8846	-0.4852
F	-2.8200	-3.1796	1.0578
C	-0.4863	3.9035	0.9711
N	0.0584	3.9684	2.1893
C	-0.2560	5.1929	2.7515
C	-1.0151	5.8650	1.8434
N	-1.1463	5.0422	0.7376
C	0.9190	2.9437	2.7848
C	-1.9559	5.3187	-0.4651
C	-3.4543	5.3653	-0.1492
C	-4.2950	5.4493	-1.4294
C	-5.7980	5.4447	-1.1376
H	-0.4006	3.0750	0.2841
H	0.0904	5.4743	3.7333
H	-1.4683	6.8424	1.8850

H	0.5640	2.7223	3.7941
H	0.8769	2.0552	2.1583
H	1.9492	3.3009	2.7988
H	-1.7457	4.5086	-1.1636
H	-1.5980	6.2606	-0.8946
H	-3.6755	6.2218	0.5043
H	-3.7102	4.4528	0.3975
H	-4.0532	4.5857	-2.0585
H	-4.0270	6.3532	-1.9957
H	-6.3802	5.5269	-2.0622
H	-6.0875	6.2782	-0.4851
H	-6.0848	4.5097	-0.6436
B	-2.9410	1.7614	-0.4672
F	-1.8154	2.2754	-1.1682
F	-2.8937	0.3671	-0.4720
F	-2.9105	2.2504	0.8605
F	-4.1237	2.2112	-1.0955
C	1.2401	-2.2924	-1.6006
N	0.9935	-1.0187	-1.9269
C	-0.2271	-0.6469	-1.3907
C	-0.7244	-1.7342	-0.7364
N	0.2088	-2.7509	-0.8807
C	1.8662	-0.1613	-2.7314
C	0.1228	-4.1007	-0.2953
C	0.3550	-4.0983	1.2182
C	0.2669	-5.5181	1.7944
C	0.4853	-5.5514	3.3101
H	2.1399	-2.8427	-1.8486
H	-0.6262	0.3488	-1.5008
H	-1.6418	-1.8806	-0.1878
H	2.0311	0.7744	-2.1990
H	2.8213	-0.6623	-2.8836
H	1.3857	0.0346	-3.6947
H	0.8744	-4.7096	-0.8065
H	-0.8664	-4.5056	-0.5172
H	-0.4147	-3.4728	1.6838
H	1.3344	-3.6519	1.4382
H	1.0127	-6.1610	1.3046
H	-0.7191	-5.9292	1.5501
H	0.4156	-6.5738	3.6985

H	-0.2683	-4.9467	3.8293
H	1.4733	-5.1576	3.5807
B	2.6153	2.5368	-0.0436
F	2.3796	3.8691	0.2994
F	3.2442	2.4511	-1.3065
F	3.4508	1.9286	0.9201
F	1.3854	1.8364	-0.0937
C	5.7620	0.6902	-0.7326
N	6.3962	0.9902	-1.8694
C	7.6401	0.3867	-1.8562
C	7.7458	-0.2747	-0.6721
N	6.5691	-0.0658	0.0177
C	5.7746	1.6442	-3.0212
C	6.1775	-0.6946	1.2926
C	6.0084	0.3246	2.4217
C	5.6247	-0.3578	3.7415
C	5.4258	0.6424	4.8847
H	4.7659	1.0075	-0.4641
H	8.3202	0.4641	-2.6891
H	8.5348	-0.8914	-0.2738
H	6.5005	2.3111	-3.4916
H	5.4544	0.8668	-3.7184
H	4.9128	2.2107	-2.6707
H	6.9570	-1.4252	1.5239
H	5.2556	-1.2421	1.0884
H	5.2313	1.0443	2.1404
H	6.9436	0.8873	2.5516
H	6.4001	-1.0852	4.0212
H	4.7017	-0.9345	3.5940
H	5.1467	0.1332	5.8140
H	4.6338	1.3614	4.6439
H	6.3429	1.2121	5.0785
B	4.7543	-2.2896	-1.7018
F	4.9766	-1.4086	-2.7900
F	3.9866	-1.5845	-0.7296
F	4.0100	-3.3984	-2.1394
F	5.9644	-2.6824	-1.1343

8IP $[C_2mim][BF_4]$	mp2/aug-cc-pvdz			
	N	0.7977	-0.5024	-0.0619

C	-0.2289	-1.3338	-0.2268
N	-1.1649	-0.7178	-0.9434
C	-0.7271	0.5533	-1.2460
C	0.5123	0.6903	-0.6937
C	-2.4763	-1.2868	-1.2655
C	-2.6981	-1.3801	-2.7649
C	1.9802	-0.8002	0.7410
H	-0.3117	-2.3274	0.1989
H	-1.3544	1.2621	-1.7734
H	1.2027	1.5276	-0.6723
H	1.7238	-0.7603	1.8046
H	2.3212	-1.8133	0.5000
H	2.7645	-0.0762	0.4984
H	-3.2210	-0.6315	-0.7970
H	-2.4953	-2.2777	-0.7939
H	-3.7111	-1.7672	-2.9499
H	-2.6320	-0.3915	-3.2438
H	-1.9712	-2.0678	-3.2169
B	-0.4393	-4.5007	-0.9490
F	-0.4886	-5.8783	-1.1536
F	-1.3316	-4.1352	0.0997
F	-0.7811	-3.7844	-2.1083
F	0.8740	-4.1149	-0.5518
N	1.9469	-4.8008	2.0795
C	0.6393	-5.0142	2.2135
N	0.3314	-6.1638	1.6111
C	1.4707	-6.6835	1.0449
C	2.4899	-5.8293	1.3440
C	-1.0166	-6.7503	1.5603
C	-1.6168	-6.8773	2.9507
C	2.6841	-3.6659	2.6349
H	-0.0683	-4.3492	2.7031
H	1.4502	-7.5916	0.4549
H	3.5443	-5.8525	1.0923
H	3.4465	-3.3399	1.9195
H	1.9732	-2.8576	2.8311
H	3.1794	-3.9693	3.5663
H	-0.8999	-7.7250	1.0711
H	-1.6215	-6.1107	0.9102
H	-2.6001	-7.3615	2.8741

H	-0.9804	-7.4871	3.6078
H	-1.7657	-5.8864	3.4020
B	-1.5133	-2.2043	2.7954
F	-1.8213	-1.3834	3.8808
F	-2.1609	-1.7383	1.6330
F	-1.9163	-3.5390	3.0496
F	-0.1092	-2.1906	2.5597
N	2.6393	-0.1660	-2.9468
C	3.4536	-0.8233	-2.1256
N	2.9899	-2.0617	-1.9698
C	1.8321	-2.2056	-2.7069
C	1.6139	-1.0096	-3.3230
C	3.7188	-3.1237	-1.2646
C	4.3288	-4.0940	-2.2638
C	2.8437	1.2053	-3.3874
H	4.3525	-0.4266	-1.6609
H	1.2457	-3.1187	-2.6987
H	0.8163	-0.6845	-3.9808
H	3.8449	1.5153	-3.0757
H	2.7702	1.2355	-4.4811
H	2.0960	1.8647	-2.9298
H	2.9974	-3.6225	-0.6034
H	4.4922	-2.6210	-0.6731
H	4.9628	-4.8154	-1.7290
H	3.5471	-4.6500	-2.8021
H	4.9467	-3.5378	-2.9806
B	6.2726	-0.9033	-3.2300
F	7.5537	-0.9709	-3.7850
F	6.2465	-1.6588	-2.0168
F	5.2997	-1.4107	-4.0957
F	5.9543	0.4463	-2.8960
N	7.3512	1.7043	-0.8621
C	7.5616	0.4524	-0.4657
N	8.5591	-0.0601	-1.1827
C	8.9854	0.8879	-2.0850
C	8.2272	1.9991	-1.8812
C	9.0251	-1.4531	-1.1243
C	8.4478	-2.1902	0.0681
C	6.2459	2.5354	-0.3997
H	7.0045	-0.0505	0.3189

H	9.7522	0.6715	-2.8185
H	8.2079	2.9524	-2.3952
H	5.6550	2.8565	-1.2654
H	5.6054	1.9210	0.2411
H	6.6250	3.4060	0.1487
H	10.1230	1 -1.4157	6 -1.08435
H	8.7077	-1.9138	-2.0684
H	8.8617	-3.2069	0.0851
H	8.7007	-1.6980	1.0182
H	7.3556	-2.2663	-0.0107
B	5.2059	-1.2172	1.6853
F	4.1188	-1.0710	2.5712
F	5.3962	-2.5806	1.3898
F	6.3695	-0.6529	2.2238
F	4.9138	-0.5258	0.4708
N	-8.6937	2.6639	-0.1506
C	-7.6010	2.2682	-0.7977
N	-7.7352	2.5683	-2.0847
C	-8.9629	3.1637	-2.2752
C	-9.5697	3.2167	-1.0570
C	-6.7438	2.2446	-3.1157
C	-6.1003	3.4990	-3.6805
C	-8.9734	2.3508	1.2450
H	-6.7678	1.7368	-0.3509
H	-9.3011	3.4872	-3.2526
H	-10.5456	6 3.5824	4 -0.7615
H	-9.5755	1.4355	1.2785
H	-8.0178	2.1811	1.7518
H	-9.4982	3.1980	1.7013
H	-7.2658	1.6536	-3.8802
H	-6.0065	1.5982	-2.6261
H	-5.3750	3.2154	-4.4556
H	-6.8438	4.1681	-4.1387
H	-5.5658	4.0301	-2.8828
B	-4.3690	1.8818	-0.2064
F	-3.0342	1.5753	0.1030
F	-4.9516	0.7500	-0.8656
F	-4.4410	2.9749	-1.0870
F	-5.1078	2.1372	0.9589
N	-4.9349	-1.9817	0.8272

C	-5.6534	-1.9238	-0.2915
N	-5.5846	-3.1023	-0.9077
C	-4.7866	-3.9448	-0.1576
C	-4.3734	-3.2370	0.9321
C	-6.3357	-3.4319	-2.1238
C	-7.3705	-4.5133	-1.8595
C	-4.7732	-0.8448	1.7362
H	-6.1794	-1.0496	-0.6595
H	-4.5598	-4.9578	-0.4689
H	-3.6966	-3.5008	1.7389
H	-3.9399	-0.2183	1.3986
H	-5.7065	-0.2731	1.7222
H	-4.5528	-1.2302	2.7370
H	-5.6100	-3.7384	-2.8911
H	-6.8227	-2.4978	-2.4345
H	-7.9141	-4.7290	-2.7893
H	-6.8996	-5.4454	-1.5147
H	-8.0876	-4.1568	-1.1100
B	-8.5119	-0.5977	-0.7504
F	-9.6970	0.1228	-0.8741
F	-7.6485	-0.3030	-1.8560
F	-8.7072	-1.9784	-0.7082
F	-7.8385	-0.1777	0.4393
N	2.1834	6.5287	0.4101
C	0.8915	6.3065	0.6330
N	0.2959	6.0419	-0.5284
C	1.2444	6.0813	-1.5269
C	2.4326	6.3844	-0.9358
C	-1.0944	5.5894	-0.6612
C	-1.1727	4.0902	-0.8957
C	3.1657	6.7918	1.4570
H	0.4133	6.3375	1.6094
H	1.0090	5.8439	-2.5575
H	3.4315	6.4579	-1.3479
H	2.6334	6.8144	2.4137
H	3.8765	5.9595	1.4642
H	3.6623	7.7487	1.2543
H	-1.5517	6.1646	-1.4784
H	-1.5973	5.8583	0.2759
H	-2.2242	3.7785	-0.9662

	H	-0.6428	3.8119	-1.8198
	H	-0.6956	3.5773	-0.0515
	B	3.1225	3.3402	-0.6451
	F	3.3598	1.9491	-0.4857
	F	1.7497	3.5602	-0.3660
	F	3.4255	3.7334	-1.9536
	F	3.9206	4.0667	0.2604
	N	2.4246	1.5098	3.0055
	C	1.3663	1.8522	2.2739
	N	0.3007	1.1970	2.7306
	C	0.6822	0.4201	3.8019
	C	2.0222	0.6143	3.9694
	C	-1.0612	1.3317	2.1921
	C	-2.0332	1.8324	3.2442
	C	3.7682	2.0488	2.8394
	H	1.3693	2.5889	1.4726
	H	-0.0291	-0.2220	4.3108
	H	2.7295	0.1760	4.6629
	H	3.7771	2.6732	1.9408
	H	4.0052	2.6736	3.7090
	H	4.4724	1.2131	2.7482
	H	-1.3648	0.3533	1.7926
	H	-0.9910	2.0412	1.3627
	H	-2.9999	2.0184	2.7545
	H	-2.1775	1.0789	4.0306
	H	-1.6553	2.7667	3.6795
	B	0.7779	4.5925	3.2089
	F	0.5855	5.9518	3.5440
	F	-0.1779	4.2459	2.2006
	F	0.6364	3.7521	4.3000
	F	2.0730	4.4659	2.6397
$[NH_2\text{-Emim}][BF_4]$	m062x/aug-cc-pvdz			
	C	-0.3232	-1.2378	0.8721
	N	0.7456	-1.7149	0.2415
	C	0.4317	-1.9024	-1.0838
	C	-0.8707	-1.5316	-1.2390
	N	-1.3220	-1.1297	-0.0027
	C	2.0373	-2.0069	0.8566
	C	-2.6432	-0.5667	0.2792

C	-2.7016	0.9188	-0.0591
N	-4.0575	1.3920	0.2137
H	-0.3675	-0.9673	1.9191
H	1.1573	-2.2749	-1.7950
H	-1.5083	-1.5165	-2.1135
H	2.8056	-1.4182	0.3509
H	1.9903	-1.7208	1.9089
H	2.2394	-3.0782	0.7643
H	-2.8501	-0.7327	1.3423
H	-3.3755	-1.1244	-0.3125
H	-2.4910	1.0510	-1.1271
H	-1.9157	1.4473	0.4994
H	-4.1970	1.4874	1.2177
B	1.6982	1.3398	-0.0854
F	2.5566	0.5214	-0.8545
F	2.1240	2.6762	-0.1551
F	0.3819	1.2273	-0.5835
F	1.7216	0.9032	1.2624
H	-4.1794	2.3230	-0.1756

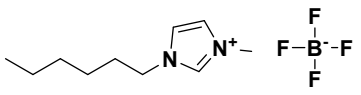
$[NH_2\text{-Emim}][BF_4]\text{-}SO_2$	m062x/aug-cc-pvdz		
C	-2.7383	-0.8225	-0.7413
N	-3.6835	-0.9922	0.1786
C	-3.2075	-1.8405	1.1514
C	-1.9399	-2.1872	0.7893
N	-1.6724	-1.5402	-0.3961
C	-4.9660	-0.2976	0.2119
C	-0.3917	-1.5408	-1.1070
C	0.7353	-1.0678	-0.1942
N	1.9226	-0.8623	-1.0202
H	-2.8052	-0.1716	-1.6025
H	-3.8041	-2.1173	2.0111
H	-1.2162	-2.8334	1.2689
H	-4.9314	0.4768	0.9837
H	-5.1382	0.1620	-0.7631
H	-5.7545	-1.0231	0.4288
H	-0.5027	-0.8529	-1.9506
H	-0.1963	-2.5498	-1.4851
H	0.9583	-1.8447	0.5475
H	0.3974	-0.1680	0.3380

H	1.8121	-0.0020	-1.5544
B	-1.7611	1.9717	0.0509
F	-3.0877	2.0435	-0.4369
F	-1.3200	3.2460	0.4343
F	-1.7230	1.0933	1.1565
F	-0.9271	1.4629	-0.9764
S	5.8694	0.2617	-0.0542
O	7.1746	0.2317	0.6093
O	4.8182	-0.5701	0.5434
H	2.7359	-0.7256	-0.4263

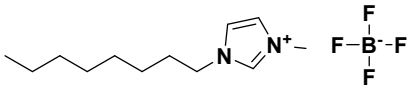
--Effects of long alkyl chains on the prediction

Holbrey and Seddon (*J. Chem. Soc., Dalton Trans.* 1999, 2133−2140) studied a series of 1-alkyl-3-methylimdazolium ([C$_n$mim][BF$_4$] with n =0−18) in deuterated propanone and found that the NMR peaks of protons changed only slightly, indicating that the proton chemical shifts were relatively insensitive to increasing alkyl chain length.

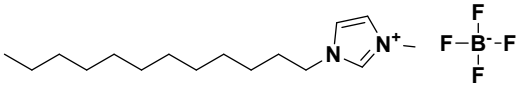
However, the effects of long alkyl chain on the prediction of the calculated proton chemical shifts is still ambiguous. Therefore, we set out to calculate ^{1}H NMR chemical shifts of a series of 1-alkyl-3-methylimdazolium ([C$_n$mim][BF$_4$] with n = 6, 8, 12) ILs by means of RRS method. In the study, [C$_4$mim][BF$_4$], the ionic liquids with relatively short alkyl chain, was used as the relative reference standard due to its structural similarity. It is found that the length of alkyl chains in the imidazolium ring has little effect on the accuracy of calculated chemical shifts. The RMS of [C$_{12}$mim][BF$_4$] ionic liquid is less than 0.25 ppm.



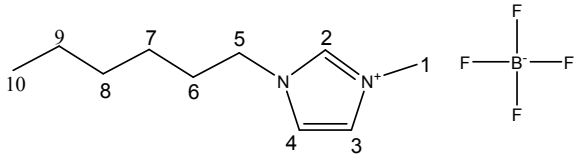
1-hexyl-3-methylimidazolium Tetrafluoroborate
[C$_6$mim][BF$_4$]



1-octyl-3-methylimidazolium Tetrafluoroborate
[C$_8$mim][BF$_4$]



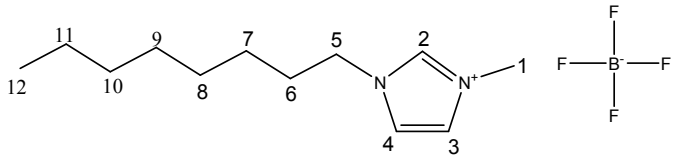
1-Dodecyl-3-methylimidazolium Tetrafluoroborate
[C$_{12}$mim][BF$_4$]



Scheme S3. Structure of [C_6mim][BF_4] and Hydrogen Atoms Numbered.

Table S32. Calculated ^{1}H NMR Chemical Shifts of [C_6mim][BF_4]

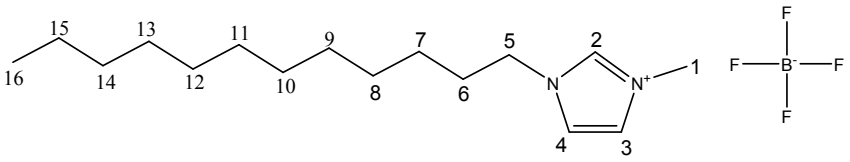
H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	23.618	23.611	8.550	8.543	9.632	8.670	0.127	0.962
H3	26.186	26.134	7.350	7.298	7.064	7.420	0.122	0.356
H4	26.173	26.146	7.410	7.383	7.077	7.470	0.087	0.393
H1	29.318	29.297	4.140	4.119	3.932	4.040	0.079	0.108
H5	29.188	29.007	3.840	3.660	4.062	4.180	0.520	0.118
H6	31.877	31.979	1.410	1.512	1.373	1.840	0.328	0.467
H7	32.200	31.979	1.410	1.189	1.050	1.840	0.651	0.790
H8	32.290	31.979	1.410	1.098	0.959	1.840	0.742	0.881
H9	32.202	31.979	1.410	1.187	1.048	1.840	0.653	0.792
H10	32.462	31.979	1.410	0.927	0.788	0.850	0.077	0.062
reference compound: [C_4mim][BF_4]					RMS, ppm		0.428	0.590
level of theory: **HF/6-311++g(d,p)**					MAE, ppm		0.339	0.493



Scheme S4. Structure of [C_8mim][BF_4] and Hydrogen Atoms Numbered.

Table S33. Calculated ^{1}H NMR Chemical Shifts of [C_8mim][BF_4]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	23.621	23.611	8.770	8.760	9.629	8.430	0.330	1.199
H3	26.191	26.173	7.630	7.612	7.059	7.280	0.332	0.221
H4	26.183	26.161	7.690	7.668	7.067	7.280	0.388	0.213
H1	29.320	29.315	4.040	4.035	3.930	3.880	0.155	0.050
H5	29.193	29.180	4.320	4.307	4.057	4.090	0.217	0.033
H6	31.887	31.880	1.930	1.924	1.363	1.850	0.074	0.487
H7	32.207	32.112	1.380	1.285	1.043	1.280	0.005	0.237
H8	32.294	32.112	1.380	1.198	0.956	1.280	0.082	0.324
H9	32.278	32.112	1.380	1.214	0.971	1.280	0.066	0.309
H10	32.346	32.112	1.380	1.146	0.903	1.280	0.134	0.377
H11	32.268	32.112	1.380	1.224	0.982	1.280	0.056	0.298
H12	32.502	32.381	0.940	0.820	0.748	0.840	0.020	0.092
reference compound: [C_4mim][BF_4]					RMS, ppm		0.200	0.435
level of theory: **HF/6-311++g(d,p)**					MAE, ppm		0.155	0.320



Scheme S5. Structure of $[C_{12}mim][BF_4]$ and Hydrogen Atoms Numbered.

Table S34. Calculated ^1H NMR Chemical Shifts of $[C_{12}mim][BF_4]$

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	23.628	23.611	8.770	8.753	9.622	9.090	0.337	0.532
H3	26.196	26.173	7.630	7.607	7.054	7.680	0.073	0.626
H4	26.190	26.161	7.690	7.662	7.060	7.750	0.088	0.690
H1	29.323	29.315	4.040	4.032	3.927	3.840	0.192	0.087
H5	29.199	29.180	4.320	4.301	4.051	4.150	0.150	0.099
H6	31.894	31.880	1.930	1.917	1.356	1.850	0.067	0.494
H7	32.226	32.112	1.380	1.266	1.024	1.310	0.044	0.286
H8	32.315	32.112	1.380	1.177	0.935	1.310	0.133	0.375
H9	32.289	32.112	1.380	1.203	0.961	1.310	0.107	0.349
H10	32.368	32.112	1.380	1.124	0.882	1.250	0.126	0.368
H11	32.352	32.112	1.380	1.140	0.898	1.250	0.110	0.352
H12	32.387	32.112	1.380	1.105	0.863	1.250	0.145	0.387
H13	32.384	32.112	1.380	1.108	0.866	1.250	0.142	0.384
H14	32.384	32.112	1.380	1.109	0.866	1.250	0.141	0.384
H15	32.313	32.112	1.380	1.179	0.937	1.250	0.071	0.313
H16	32.532	32.381	0.940	0.790	0.718	0.840	0.050	0.122
reference compound: $[C_4mim][BF_4]$					RMS, ppm		0.141	0.401
level of theory: **HF/6-311++g(d,p)**					MAE, ppm		0.124	0.365

--Details of generalizing reference standard

A generalised standard might be proposed when the ILs have the weakly coordinating anions. if the IL [C_2mim][BF_4] were used as a reference standard, the proton NMR chemical shifts of ILs with weakly interacting anions could be well predicted. For example, the RMSs of [C_4mim][PF_6] and [C_2mim][PF_6] are 0.242 and 0.284, respectively.

Moreover, an order that representing the intensity of anion interactions might also be obtained by means of RMS analysis. That is, larger RMS usually indicates stronger interaction between the cation and the anion. According to the RMS results, the intensity order of the anion interaction is: [C_4mim][PF_6] (RMS is 0.242) ≈ [C_2mim][PF_6] (0.284) < [C_4mim][NTf_2] (0.374)< [C_4mim][Ots] (0.477) ≈ [C_4mim][$MeSO_4$] (0.495) < [C_4mim][TFA] (1.064) < [C_4mim][OAc] (1.272).

Table S35. Calculated ^{1}H NMR Chemical Shifts of [C_2mim][PF_6]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	22.010	22.864	8.550	9.403	9.544	8.820	0.583	0.724
H3	23.860	23.862	7.350	7.351	7.694	7.290	0.061	0.404
H4	23.655	23.937	7.410	7.691	7.899	7.240	0.451	0.659
H1	27.665	27.520	4.140	3.995	3.889	4.260	0.265	0.371
H5	27.378	27.574	3.840	4.036	4.176	3.970	0.066	0.206
H6	29.844	27.574	3.840	1.569	1.710	1.590	0.021	0.120
H7	29.844	27.574	3.840	1.569	1.710	1.590	0.021	0.120
H8	29.844	29.869	1.410	1.435	1.710	1.590	0.155	0.120
reference compound: [C_2mim][BF_4]					RMS, ppm		0.284	0.410
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.203	0.340

Table S36. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][PF_6]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	22.952	22.864	8.550	8.462	8.603	8.520	0.058	0.083
H3	23.677	23.862	7.350	7.535	7.878	7.490	0.045	0.388
H4	23.737	23.937	7.410	7.610	7.817	7.520	0.090	0.297
H1	27.432	27.520	4.140	4.229	4.123	4.250	0.021	0.127
H5	27.193	27.574	3.840	4.221	4.362	3.970	0.251	0.392
H6	29.604	27.574	3.840	1.810	1.950	1.930	0.120	0.020
H7	30.634	27.574	3.840	0.779	0.920	1.380	0.601	0.460
H8	30.463	29.869	1.410	0.816	1.091	0.940	0.124	0.151
reference compound: [C_2mim][BF_4]					RMS, ppm		0.242	0.285
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.164	0.240

Table S37. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][OTS]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	23.735	22.864	8.550	7.679	7.887	8.530	0.851	0.643
H3	24.339	23.862	7.350	6.873	7.284	7.660	0.787	0.376
H4	24.088	23.937	7.410	7.258	7.534	7.290	0.032	0.244
H1	28.291	27.520	4.140	3.369	3.331	4.020	0.651	0.689
H5	27.714	27.574	3.840	3.700	3.909	3.780	0.080	0.128
H6	29.546	27.574	3.840	1.867	2.076	1.710	0.157	0.366
H7	30.058	27.574	3.840	1.356	1.564	1.220	0.136	0.344
H8	30.463	29.869	1.410	0.816	1.159	0.870	0.054	0.289
reference compound: [C_2mim][BF_4]					RMS, ppm		0.477	0.424
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.343	0.385

Table S38. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][Tf_2N]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	21.832	22.864	8.550	9.581	9.790	8.630	0.951	1.160
H3	23.815	23.862	7.350	7.396	7.807	7.540	0.144	0.267
H4	23.675	23.937	7.410	7.672	7.947	7.460	0.212	0.487
H1	27.452	27.520	4.140	4.208	4.170	4.240	0.032	0.070
H5	27.533	27.574	3.840	3.880	4.089	3.960	0.080	0.129
H6	29.711	27.574	3.840	1.702	1.911	1.920	0.218	0.009
H7	30.306	27.574	3.840	1.108	1.317	1.400	0.292	0.084
H8	30.220	29.869	1.410	1.059	1.402	0.970	0.089	0.432
reference compound: [C_2mim][BF_4]					RMS, ppm		0.374	0.483
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.252	0.330

Table S39. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][OAC]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	17.735	22.864	8.550	13.679	13.819	10.18	3.499	3.639
H3	23.816	23.862	7.350	7.396	7.738	7.880	0.484	0.142
H4	23.709	23.937	7.410	7.638	7.845	7.960	0.322	0.115
H1	27.298	27.520	4.140	4.362	4.256	4.200	0.162	0.056
H5	26.954	27.574	3.840	4.460	4.601	3.890	0.570	0.711
H6	29.882	27.574	3.840	1.532	1.672	1.600	0.068	0.072
H7	30.178	27.574	3.840	1.236	1.376	1.210	0.026	0.166
H8	30.422	29.869	1.410	0.857	1.132	0.840	0.017	0.292
reference compound: [C_2mim][BF_4]					RMS, ppm		1.272	1.318
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.644	0.649

Table S40. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][TFA]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	19.041	22.050	8.550	11.558	12.513	8.670	2.888	3.843
H3	24.257	24.210	7.350	7.303	7.297	7.430	0.128	0.133
H4	24.154	24.132	7.410	7.389	7.401	7.390	0.001	0.011
H1	27.841	27.727	4.140	4.026	3.713	4.140	0.114	0.427
H5	27.554	26.761	3.840	3.047	4.000	3.850	0.803	0.150
H6	29.850	30.177	1.410	1.736	1.704	1.790	0.054	0.086
H7	30.164	30.177	1.410	1.423	1.390	1.260	0.163	0.130
H8	30.596	30.177	1.410	0.991	0.959	0.860	0.131	0.099
reference compound: [C_2mim][BF_4]					RMS, ppm		1.064	1.370
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.535	0.610

Table S41. Calculated ^{1}H NMR Chemical Shifts of [C_4mim][$MeSO_4$]

H	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
H2	20.987	22.864	8.550	10.426	10.512	9.418	1.008	1.094
H3	23.831	23.862	7.350	7.381	7.668	7.630	0.250	0.038
H4	23.681	23.937	7.410	7.666	7.818	7.580	0.086	0.238
H1	27.482	27.520	4.140	4.178	4.016	4.260	0.082	0.244
H5	27.232	27.574	3.840	4.182	4.267	3.370	0.812	0.897
H6	29.986	27.574	3.840	1.427	1.512	1.881	0.454	0.369
H7	30.113	27.574	3.840	1.301	1.386	1.352	0.052	0.034
H8	30.410	29.869	1.410	0.869	1.089	0.935	0.066	0.154
reference compound: [C_2mim][BF_4]					RMS, ppm		0.4956	0.5337
level of theory: **m06-2x/aug-cc-pvdz**					MAE, ppm		0.3511	0.3833

--Details on Case Study

In the first stage of this case study, the structure of $[NH_2\text{-Emim}][BF_4]\text{-}SO_2$ and $[NH_2\text{-Emim}][BF_4]$ were optimized at the level of theory m062x/aug-cc-pvdz. Vibrational analysis (frequency calculation) was followed after geometry optimization. The absence of negative or imaginary frequencies indicated that the structures were at a global minimum. In order to investigate the reaction between SO_2 and $[NH_2\text{-Emim}][BF_4]$, SO_2 molecule was used to attack the different position of $[NH_2\text{-Emim}][BF_4]$ and thus optimized the possible geometric configurations (Figure S26-S27).

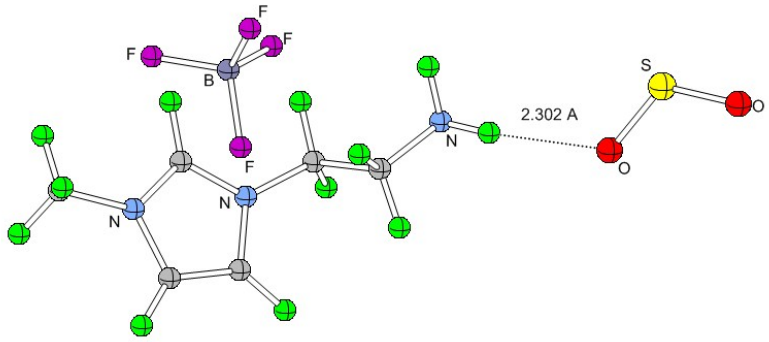


Figure S26. SO_2 molecule absorb the H of $–NH_2–$ in $[NH_2\text{-Emim}][BF_4]$ (configuration 1)

First, the oxygen atom on SO_2 molecule was supposed to absorb the H of $–NH_2–$ in $[NH_2\text{-Emim}][BF_4]$, as shown in Figure S26. Meanwhile, the ^1H NMR chemical shifts was calculated according to this optimized structure (Table S42).

Table S42. Calculated ^1H NMR Chemical Shifts of $[NH_2\text{-Emim}][BF_4]–SO_2$ (Configuration 1)

H position	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
N─CH─N	22.749	23.204	9.12	9.57	8.87	9.19	0.385	0.317
H in ring	23.765	23.844	7.45	7.53	7.86	7.45	0.079	0.407
H in ring	23.050	23.858	7.200	8.01	8.57	8.100	0.093	0.472
ring-CH_3	27.206	27.434	3.72	3.95	4.42	3.72	0.228	0.696
ring-CH_2─	27.500	27.389	3.41	3.30	4.12	3.41	0.110	0.713
─CH_2─	28.473	28.570	2.77	2.87	3.15	2.35	0.517	0.800
─NH_2	29.264	30.849	2.07	3.65	2.36	3.35	0.305	0.992
─NH_2	30.780	30.160	2.07	1.45	0.84	1.45	0.000	0.608
Reference Compound: $[NH_2\text{-Emim}][BF_4]$						RMS	0.271	0.563
level of theory: **m062x-aug-cc- pvdz**						MAE	0.215	0.527

Second, SO_2 molecule was supposed to absorb the H of $–CH_3$ in [NH_2-Emim][BF_4]. The optimized configuration of this proposed reaction was illustrated in Figure S27, and the data of proton chemical shifts was collected in Table S43.

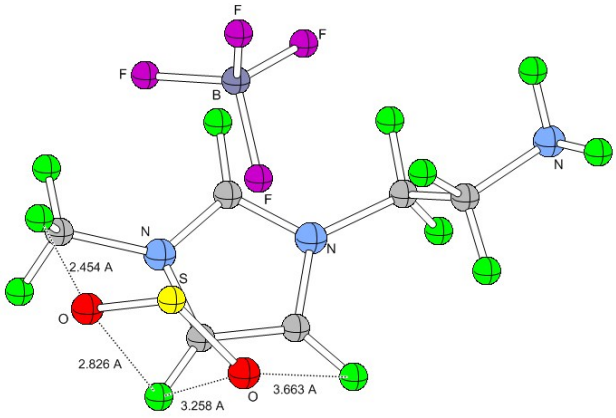


Figure S27. Configuration 2 of [NH_2-Emim][BF_4]

Table S43. Calculated ^{1}H NMR Chemical Shifts of [NH_2-Emim][BF_4]–SO_2 (Configuration 2)

H position	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
N–CH–N	23.034	23.204	9.12	9.29	8.59	9.19	0.099	0.602
H in ring	23.535	23.844	7.45	7.76	8.09	7.45	0.309	0.637
H in ring	23.981	23.858	7.20	7.08	7.64	8.10	1.024	0.459
ring-CH_3	27.619	27.434	3.72	3.53	4.00	3.72	0.185	0.283
ring-CH_2–	27.478	27.389	3.41	3.32	4.14	3.41	0.089	0.735
–CH_2–	28.428	28.570	2.77	2.91	3.19	2.35	0.562	0.845
–NH_2	30.371	30.849	2.07	2.55	3.19	3.35	0.802	0.155
–NH_2	30.761	30.160	2.07	1.47	0.86	1.45	0.019	0.589
Reference Compound: [NH_2-Emim][BF_4]						RMS	0.519	0.579
level of theory: **m062x-aug-cc-pvdz**						MAE	0.386	0.538

Another configuration was also proposed, in which the sulfur atom of SO_2 molecule was attracted by the nitrogen atom of NH_2–. The data and the configuration were listed in Table S44 and Figure S28, respectively.

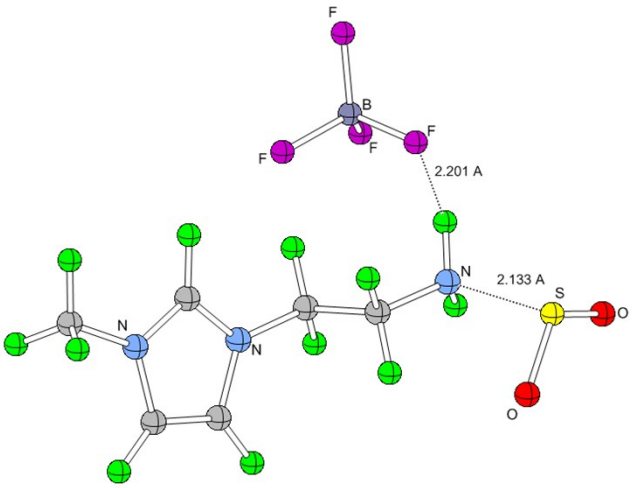


Figure S28. Configuration 3 of $[NH_2\text{-Emim}][BF_4]$

Table S44. Calculated ^{1}H NMR Chemical Shifts of $[NH_2\text{-Emim}][BF_4]$–SO_2 (Configuration 3)

H position	σ_{cal}	σ_{ref}	δ_{ref}	δ_{cal} (RRS)	δ_{cal} (TMS)	δ_{exp}	AE (RRS)	AE (TMS)
N–CH–N	22.361	23.204	9.12	9.96	9.26	9.19	0.773	0.072
H in ring	23.665	23.844	7.45	7.63	7.96	7.45	0.179	0.508
H in ring	23.650	23.858	7.20	7.41	7.97	8.10	0.693	0.128
ring-CH_3	27.257	27.434	3.72	3.90	4.37	3.72	0.177	0.645
ring-CH_2–	27.025	27.389	3.41	3.77	4.60	3.41	0.364	1.187
–CH_2–	28.582	28.570	2.77	2.76	3.04	2.35	0.408	0.690
–NH_2	25.654	30.849	2.07	7.26	3.04	3.35	3.915	0.310
–NH_2	30.010	30.160	2.07	2.22	1.61	1.45	0.771	0.163
Reference Compound: $[NH_2\text{-Emim}][BF_4]$						RMS	1.473	0.581
level of theory: **m062x-aug-cc-pvdz**						MAE	0.910	0.463

However, only the first configuration of $[NH_2\text{-Emim}][BF_4]$–SO_2 and its ^{1}H NMR chemical shifts are most consistent with the experimental values. The predicted spectral data reveal that the proton chemical shifts of –NH_2 group were significantly changed after the SO_2 absorption: from 2.07 to 1.45 and to 3.35 ppm, respectively. Meanwhile, the chemical shift of H (unsaturated C–H in the imidazole ring, with N–CH_2–CH_2–NH_2 connected to the right) moved downfield from 7.20 to 8.10 ppm due to the impact of $[BF_4]^-$ anion. Particularly, the study shows that the $[BF_4]^-$ anion of $[NH_2\text{-Emim}][BF_4]$-SO_2 was not combined with the H of NH_2, which only moved to the center of imidazolium ring and over the imidazolium plane, as Figure S26 shown.