

Electronic Supplementary Information (ESI)

**Enthalpic Interactions in Aqueous Strong Electrolytes upon Addition of Ionic
Liquids**

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Table S1. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for aqueous solution of NaCl.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.100	-80.04	-80.29
2.185	-38.19	-150.9
3.254	-23.60	-215.0
4.309	-16.65	-273.9
5.350	-12.99	-328.4
6.376	-10.41	-379.0
7.388	-8.292	-426.1
8.387	-6.973	-470.0
9.372	-6.074	-511.0
10.34	-5.215	-549.4
11.30	-4.736	-585.2
12.25	-4.268	-618.7
13.19	-4.033	-650.1
14.11	-3.739	-679.4

Table S2. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for aqueous solution of [MIM]Cl.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.156	-24.09	-3.247
2.295	-18.31	-6.449
3.419	-14.26	-9.606
4.527	-10.85	-12.72
5.620	-8.649	-15.79
6.698	-7.335	-18.82
7.761	-5.916	-21.81
8.810	-5.140	-24.76
9.845	-4.636	-27.67
10.87	-4.092	-30.54
11.87	-3.604	-33.37
12.87	-3.337	-36.16
13.85	-3.068	-38.92
14.82	-2.869	-41.65

Table S3. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for mixing of aqueous solution of [MIM]Cl-NaCl.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.118	71.79	91.31
2.220	26.40	171.3
3.306	15.37	243.7
4.377	10.18	310.0
5.434	6.828	371.2
6.475	5.097	427.9
7.503	4.175	480.5
8.517	3.340	529.4
9.517	2.698	574.9
10.50	2.320	617.3
11.48	1.940	656.8
12.44	1.715	693.6
13.39	1.454	727.9
14.32	1.210	759.9

Table S4. The Experimental H_{IL}^{E} values and the calculated relative apparent molar enthalpy, ϕ_{L} values for aqueous solution of [Py]Cl.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{\text{IL}}^{\text{E}} / \text{kJ mol}^{-1}$	$\phi_{\text{L}} / \text{kJ mol}^{-1}$
0	-	-
2.136	60.24	207.0
3.182	29.98	295.6
4.214	18.05	377.3
5.231	12.00	453.2
6.234	8.743	523.9
7.224	6.265	590.0
8.201	4.837	651.9
9.164	3.600	709.9
10.12	2.867	764.3
11.05	2.288	815.4
11.98	1.732	863.5
12.89	1.547	908.6
13.80	1.085	951.1

Table S5. The Experimental H_{IL}^{E} values and the calculated relative apparent molar enthalpy, ϕ_{L} values for mixing of aqueous solution of [Py]Cl-NaCl.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{\text{IL}}^{\text{E}} / \text{kJ mol}^{-1}$	$\phi_{\text{L}} / \text{kJ mol}^{-1}$
0	-	-
1.118	256.3	335.2
2.219	93.45	628.5
3.305	49.87	894.0
4.376	31.21	1137
5.433	21.46	1361
6.474	15.48	1569
7.502	11.87	1761
8.515	9.288	1940
9.515	7.501	2106
10.50	6.139	2261
11.47	5.203	2405
12.43	4.276	2539
13.38	3.707	2664
14.32	3.025	2780

Table S6. The Experimental H_{IL}^{E} values and the calculated relative apparent molar enthalpy, ϕ_{L} values for aqueous solution of [MPyrr]Cl.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{\text{IL}}^{\text{E}} / \text{kJ mol}^{-1}$	$\phi_{\text{L}} / \text{kJ mol}^{-1}$
0	-	-
1.071	-74.53	-89.33
2.127	-30.49	-167.6
3.168	-17.27	-238.5
4.195	-11.36	-303.6
5.207	-8.477	-363.6
6.206	-6.624	-419.2
7.192	-5.321	-470.8
8.164	-4.233	-518.9
9.123	-3.529	-563.6
10.07	-2.888	-605.3
11.00	-2.555	-644.2
11.93	-2.308	-680.5
12.84	-1.919	-714.3
13.73	-1.833	-745.8

Table S7. The Experimental H_{IL}^{E} values and the calculated relative apparent molar enthalpy, ϕ_{L} values for mixing of aqueous solution of [MPyrr]Cl-NaCl.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{\text{IL}}^{\text{E}} / \text{kJ mol}^{-1}$	$\phi_{\text{L}} / \text{kJ mol}^{-1}$
0	-	-
1.104	-36.73	-54.80
2.192	-11.06	-102.7
3.266	-4.802	-146.0
4.324	-2.495	-185.6
5.367	-1.531	-222.0
6.396	-1.026	-255.8
7.411	-0.5277	-287.0
8.413	-0.3183	-316.0
9.400	-0.3840	-343.0
10.37	-0.3971	-368.0
11.33634	-0.0474	-391.3
12.29	-0.1354	-412.9
13.22	-0.0586	-433.1
14.15	-0.3409	-451.8

Table S8. The Experimental H_{IL}^{E} values and the calculated relative apparent molar enthalpy, ϕ_{L} values for aqueous solution of NaBF_4 .

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{\text{IL}}^{\text{E}} / \text{kJ mol}^{-1}$	$\phi_{\text{L}} / \text{kJ mol}^{-1}$
0	-	-
1.075	463.4	291.3
2.149	280.7	552.5
3.224	211.0	794.0
4.298	172.3	1020
5.373	147.7	1231
6.448	128.5	1431
7.522	115.0	1620
8.600	105.0	1798
9.671	95.47	1966
10.75	87.82	2126
10.96	81.45	2276
11.88	75.61	2419
12.79	70.38	2553
13.68	65.89	2680

Table S9. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for aqueous solution of [MIM][BF₄].

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.071	-130.2	-156.5
2.127	-51.86	-293.6
3.169	-27.25	-417.7
4.196	-16.83	-531.5
5.209	-11.2110	-636.5
6.209	-7.033	-733.6
7.195	-4.508	-823.8
8.167	-1.985	-907.6
9.127	-0.7171	-985.7
10.07	0.7761	-1058
11.01	2.262	-1126
11.93	3.694	-1189
12.84	3.984	-1248
13.74	3.968	-1303

Table S10. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for mixing of aqueous solution of [MIM][BF₄]-NaBF₄.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.160	31.82	29.44
2.303	15.98	55.33
3.430	10.34	78.88
4.541	7.450	100.5
5.637	5.270	120.6
6.717	4.375	139.2
7.783	3.656	156.5
8.834	2.787	172.7
9.870	2.554	187.8
10.89	2.085	201.9
11.90	1.955	215.1
12.90	1.394	227.5
13.88	1.375	239.1
14.85	1.145	249.9

Table S11. The Experimental H_{IL}^{E} values and the calculated relative apparent molar enthalpy, ϕ_{L} values for aqueous solution of [EMIM][BF₄].

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{\text{IL}}^{\text{E}} / \text{kJ mol}^{-1}$	$\phi_{\text{L}} / \text{kJ mol}^{-1}$
0	-	-
1.074	11.60	5.816
2.133	7.159	10.97
3.177	6.110	15.68
4.207	5.093	20.04
5.223	3.933	24.09
6.225	3.475	27.88
7.214	3.183	31.42
8.189	2.672	34.74
9.151	2.381	37.87
10.10	2.289	40.80
11.04	2.141	43.57
11.96	1.858	46.17
12.87	1.798	48.62
13.78	1.537	50.93

Table S12. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for mixing of aqueous solution of [EMIM][BF₄]-NaBF₄.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.120	341.1	323.4
2.224	170.6	607.4
3.312	113.2	865.4
4.385	83.67	1102
5.442	67.18	1321
6.485	55.22	1525
7.514	47.10	1714
8.529	40.65	1890
9.530	36.01	2054
10.52	32.34	2208
11.49	28.97	2351
12.45	26.36	2486
13.40	24.00	2611
14.34	22.15	2728

Table S13. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for aqueous solution of [BMIM][BF₄].

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.056	-42.99	-46.69
2.098	-19.30	-87.66
3.125	-12.17	-124.9
4.138	-8.290	-159.0
5.137	-6.012	-190.5
6.122	-5.119	-219.8
7.095	-4.254	-247.0
8.054	-3.712	-272.3
9.000	-3.173	-295.9
9.934	-2.823	-318.0
10.86	-2.526	-338.6
11.76	-2.456	-357.8
12.66	-2.110	-375.8
13.55	-1.919	-392.5

Table S14. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for mixing of aqueous solution of [BMIM][BF₄]-NaBF₄.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.083	309.8	296.5
2.151	152.9	556.9
3.203	102.1	793.4
4.241	75.14	1011
5.264	60.32	1211
6.272	49.59	1398
7.267	41.92	1571
8.249	36.24	1733
9.217	32.09	1883
10.17	28.60	2024
11.11	25.72	2156
12.04	23.28	2279
12.96	21.36	2394
13.87	19.56	2502

Table S15. The Experimental H_{IL}^{E} values and the calculated relative apparent molar enthalpy, ϕ_{L} values for aqueous solution of [HMIM][BF₄].

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{\text{IL}}^{\text{E}} / \text{kJ mol}^{-1}$	$\phi_{\text{L}} / \text{kJ mol}^{-1}$
0	-	-
1.069	-90.70	-93.70
2.124	-42.72	-175.9
3.164	-26.46	-250.6
4.189	-20.06	-319.1
5.201	-15.92	-382.4
6.198	-12.87	-441.1
7.182	-10.72	-495.7
8.153	-9.217	-546.6
9.111	-8.069	-594.0
10.06	-7.286	-638.2
10.99	-6.574	-679.6
11.91	-5.855	-718.2
12.82	-5.383	-754.3
13.72	-5.081	-788.0

Table S16. The Experimental H_{IL}^E values and the calculated relative apparent molar enthalpy, ϕ_L values for mixing of aqueous solution of [HMIM][BF₄]-NaBF₄.

$m \times 10^6 / \text{mol kg}^{-1}$	$H_{IL}^E / \text{kJ mol}^{-1}$	$\phi_L / \text{kJ mol}^{-1}$
0	-	-
1.078	293.8	280.9
2.141	146.4	527.5
3.188	96.30	751.6
4.221	71.95	957.3
5.240	57.46	1148
6.244	47.54	1324
7.235	40.16	1488
8.212	34.83	1641
9.175	30.80	1784
10.13	27.52	1917
11.06	24.81	2042
12.00	22.31	2159
12.90	20.63	2268
13.80	18.84	2369

Table S17. The Adjustable parameters for fitting excess partial molar enthalpy data ($H^E_{II}/\text{kJ mol}^{-1}$) of different aqueous solution of ionic liquid-salt systems using equation 2.

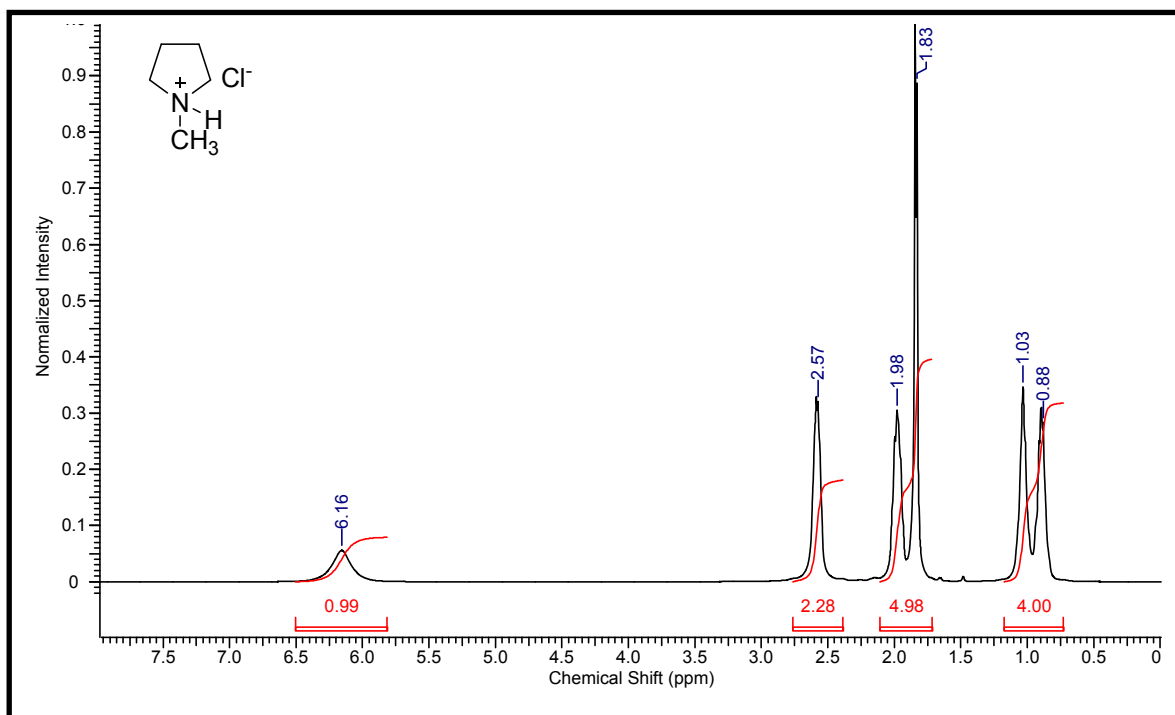
system	$10^{-4}a_0$ (kJ mol ^{-1.5} kg ^{0.5})	$10^{-7}a_1$ (kJ mol ⁻² kg)	$10^{-9}a_2$ (kJ mol ^{-2.5} kg ^{1.5})
NaCl	24.9±1.81	-8.3±0.79	9.2±1.1
[MIM]Cl	2.1±0.05	-0.28±0.01	-
[MIM]Cl- NaCl	-27.0±2.6	9.3±1.1	-10.5±1.5
[Py]Cl	-35.4±3.0	11.5±1.2	-12.4±1.5
[Py]Cl- NaCl	-99±8.8	34.1±3.8	-38.8±5.2
[MPyrr]Cl	27.3±2.3	-9.5±1.0	10.9±1.4
[MPyrr]Cl- NaCl	16.0±1.6	-5.7±0.67	6.5±0.90
NaBF ₄	-98±6.7	30.5±2.9	32.7±3.8
[MIM][BF ₄]	48.2±4.0	-16.6±1.8	19.2±2.5
[MIM][BF ₄]- NaBF ₄	-9.1±0.58	2.9±0.25	-3.1±0.33
[EMIM][BF ₄]	-2.1±0.27	0.61±0.12	-0.64±0.16
[EMIM][BF ₄]- NaBF ₄	-100±7.2	32.7±3.1	-36.1±4.2
[BMIM][BF ₄]	14.6±1.1	-5.0±0.48	5.7±0.67
[BMIM][BF ₄]- NaBF ₄	-93±7.0	31.0±3.1	-34.9±4.3
[HMIM][BF ₄]	29.2±2.3	-9.9±1.0	11.3±1.4
[HMIM][BF ₄]- NaBF ₄	-88.1±6.5	29.5±2.9	-33.2±3.9

Table S18. The adjustable parameters for fitting relative apparent molar enthalpy data ($\phi_L/\text{kJ mol}^{-1}$) of different aqueous solution of ionic liquid-salt systems using equation 6 with correlation coefficient $r^2 > 0.99$.

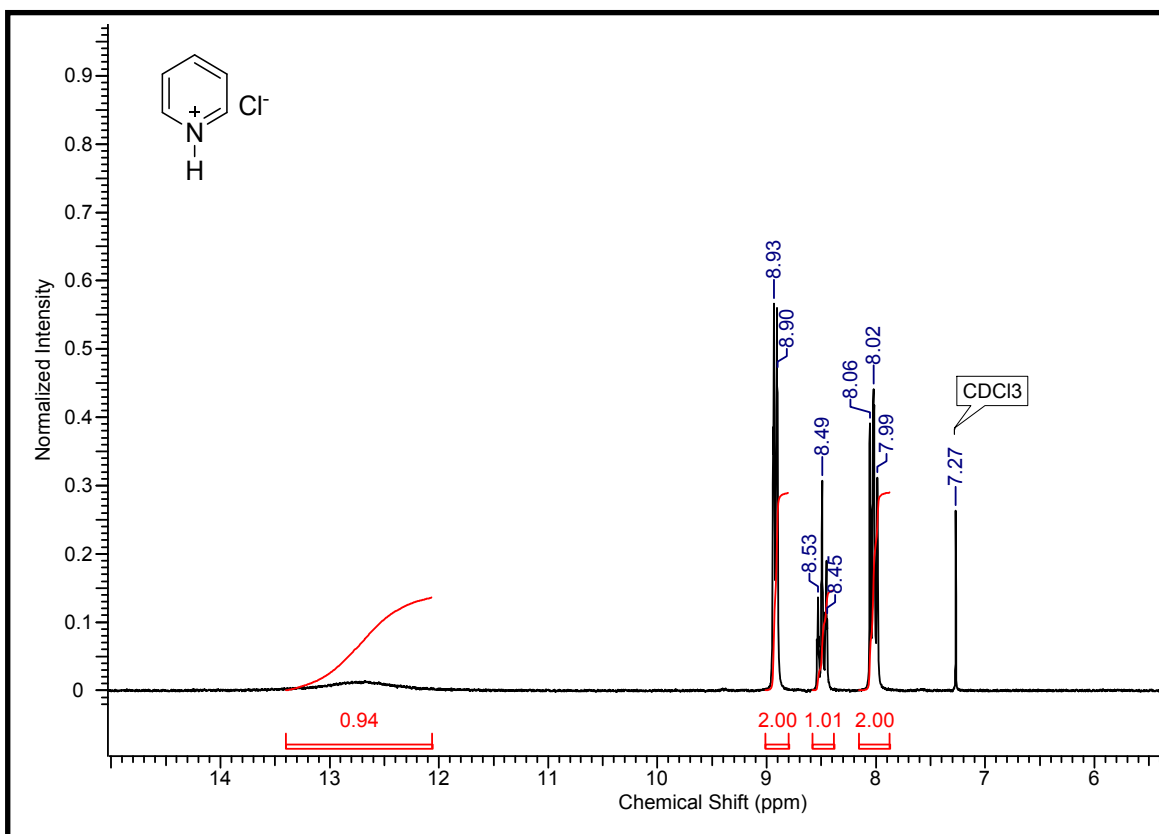
system	$10^{-7}q$	system	$10^{-7}q$
NaCl	-5.421 ± 0.121	[MIM][BF ₄]	-10.55 ± 0.242
[MIM]Cl	-0.452 ± 0.009	[MIM][BF ₄]- NaBF ₄	1.659 ± 0.030
[MIM]Cl- NaCl	5.627 ± 0.126	[EMIM][BF ₄]	22.11 ± 0.003
[Py]Cl	7.288 ± 0.151	[EMIM][BF ₄]- NaBF ₄	20.56 ± 0.439
[Py]Cl- NaCl	21.07 ± 0.490	[BMIM][BF ₄]	-3.340 ± 0.783
[MPyrr]Cl	-6.113 ± 0.141	[BMIM][BF ₄]- NaBF ₄	19.48 ± 0.415
[MPyrr]Cl- NaCl	-3.676 ± 0.089	[HMIM][BF ₄]	-6.446 ± 0.146
NaBF ₄	19.27 ± 0.416	[HMIM][BF ₄]- NaBF ₄	18.53 ± 0.395

¹H NMR of Ionic Liquids

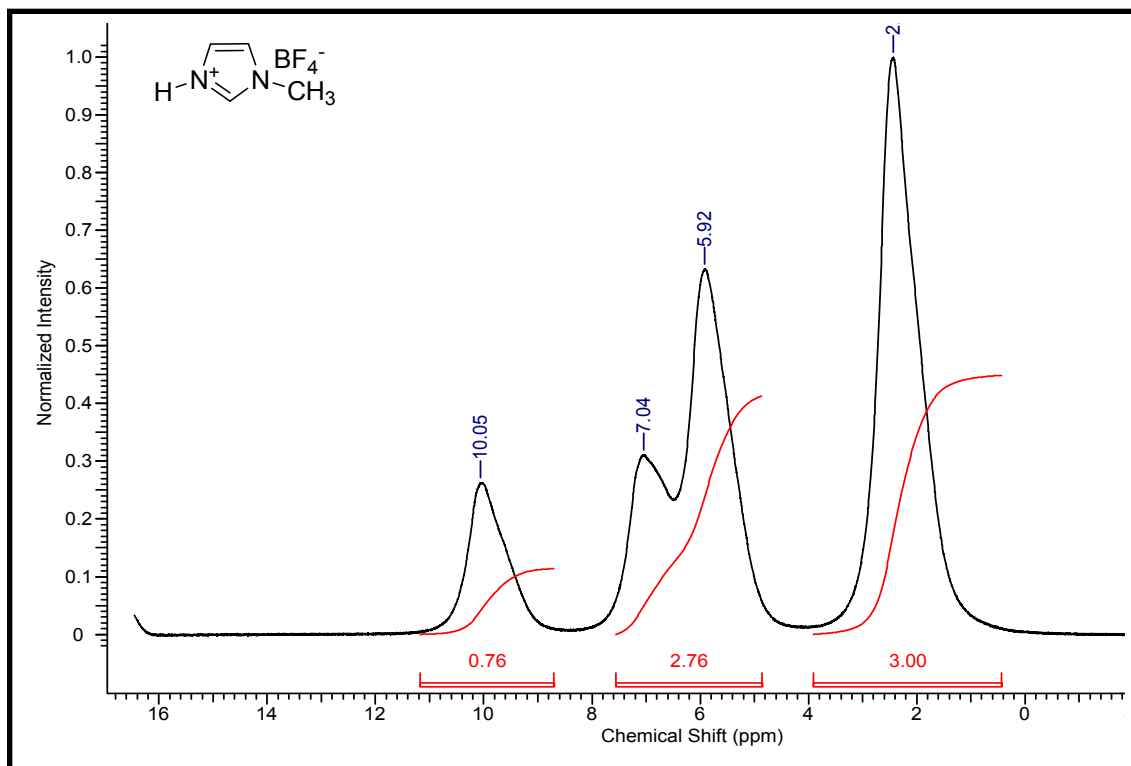
1. [MPyrr]Cl - ¹H NMR, 200 MHz



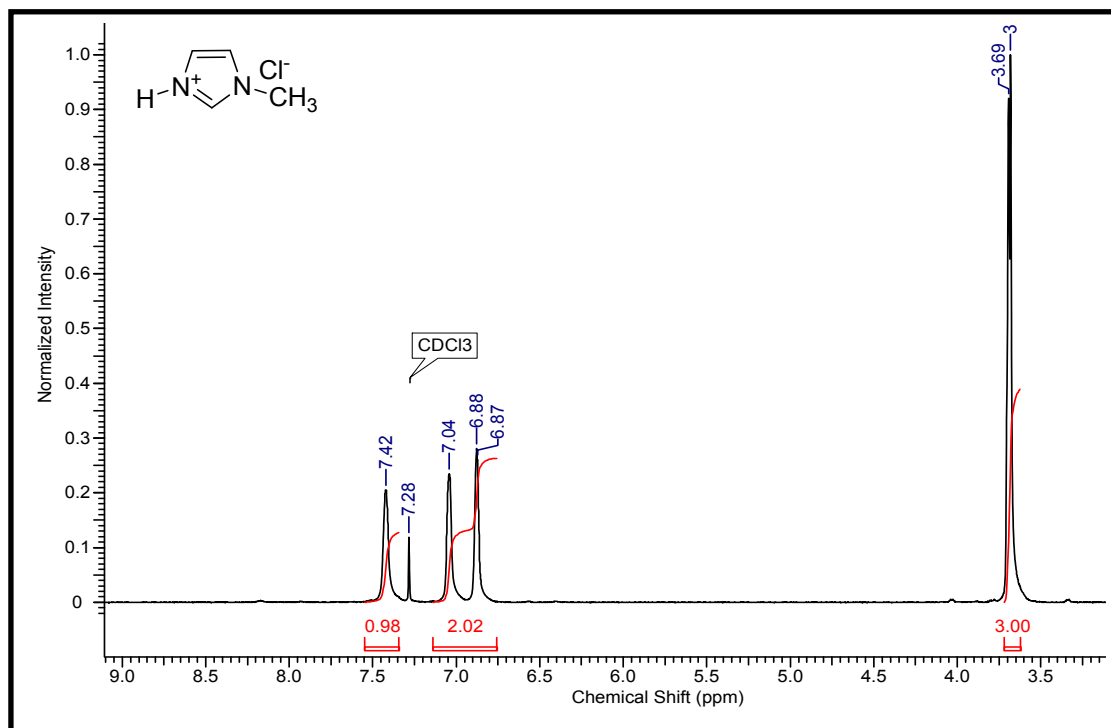
2. [Py]Cl - ^1H NMR, 200 MHz, CDCl_3



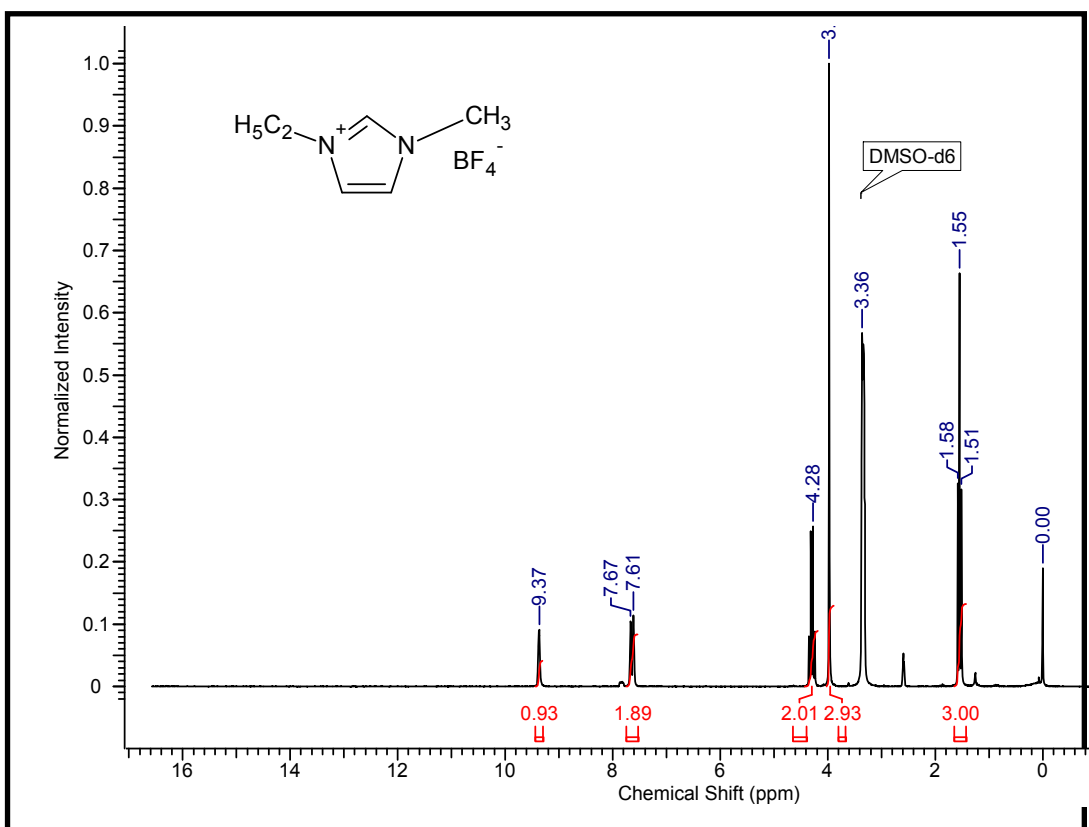
3. [MIM][BF₄] - ¹H NMR, 400 MHz



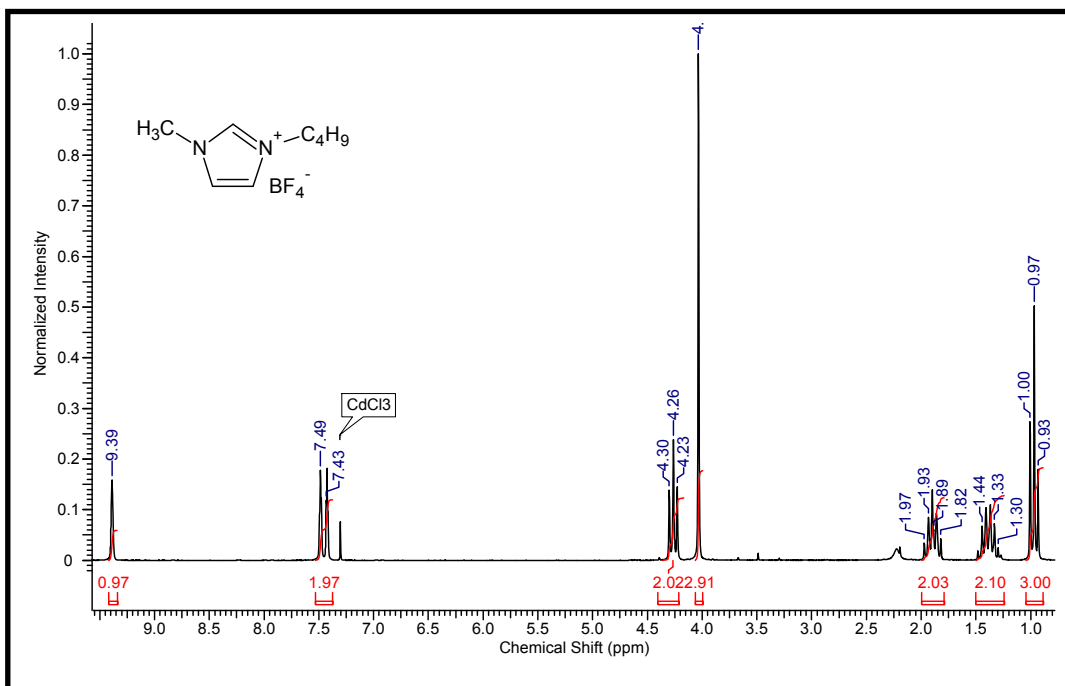
4. [MIM]Cl - ^1H NMR, 200 MHz, CDCl_3



5. [EMIM][BF₄] - ¹H NMR, 200 MHz, DMSO-d₆



6. [BMIM][BF₄] - ¹H NMR, 200 MHz, CDCl₃



7. [HMIM][BF₄] - ¹H NMR, 200 MHz, CDCl₃

