

Ion pairing in 1-butyl-3-methylpyridinium halides ionic liquids studied by NMR and DFT calculations

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Electronic Supporting Information

Additional NMR spectra	p. 2
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xyz coordinates of optimized structures	p. 21

NMR of the pure samples

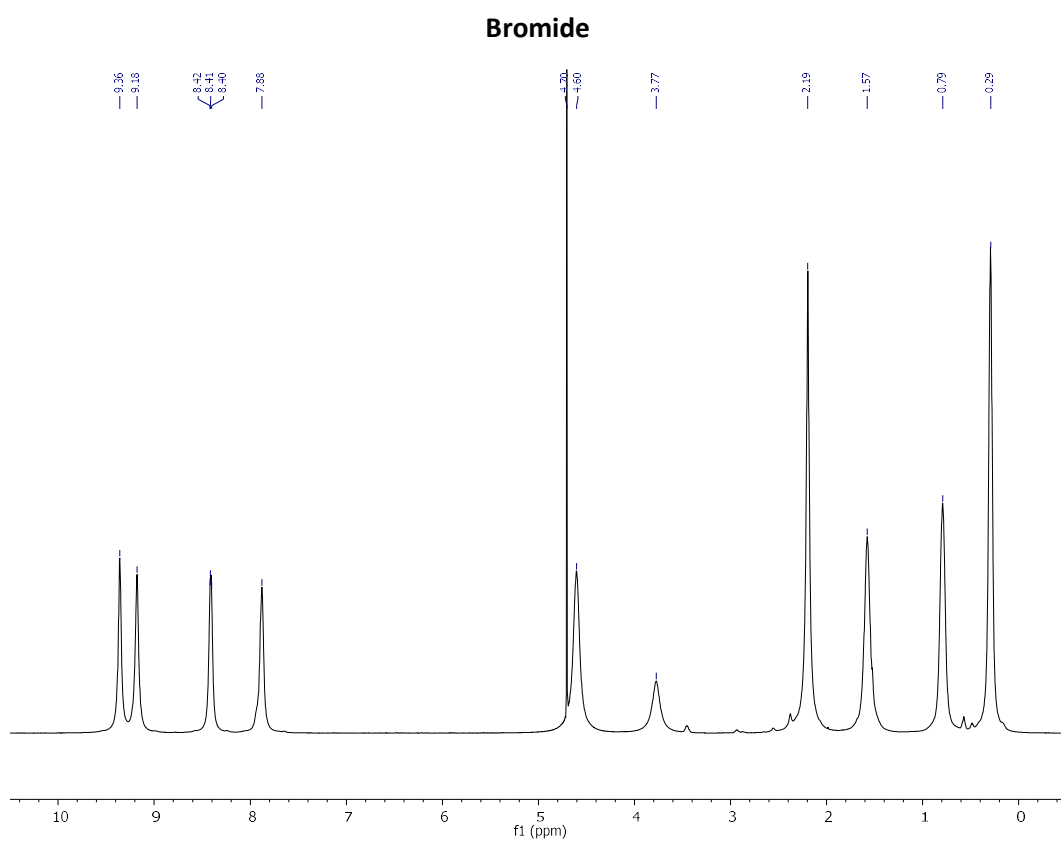


Fig. S1. ^1H NMR spectrum of neat [BMP][Br]. T = 313.1K

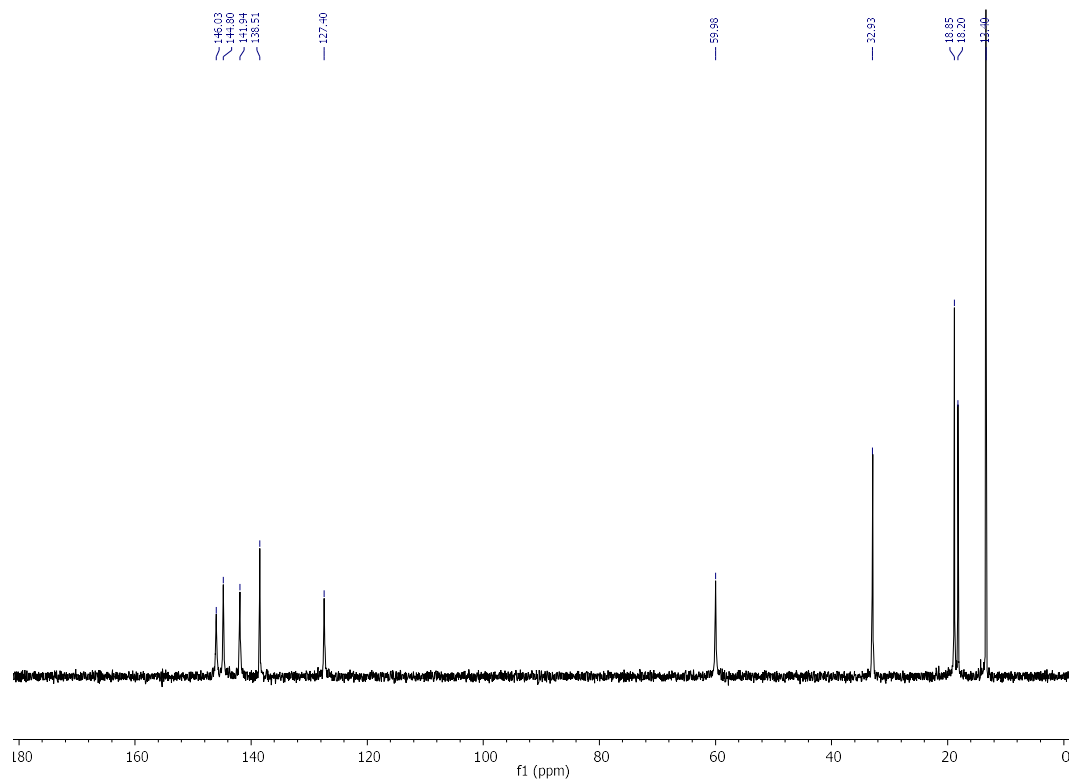


Fig. S2. ^{13}C NMR spectrum of neat [BMP][Br]. T = 313.1K

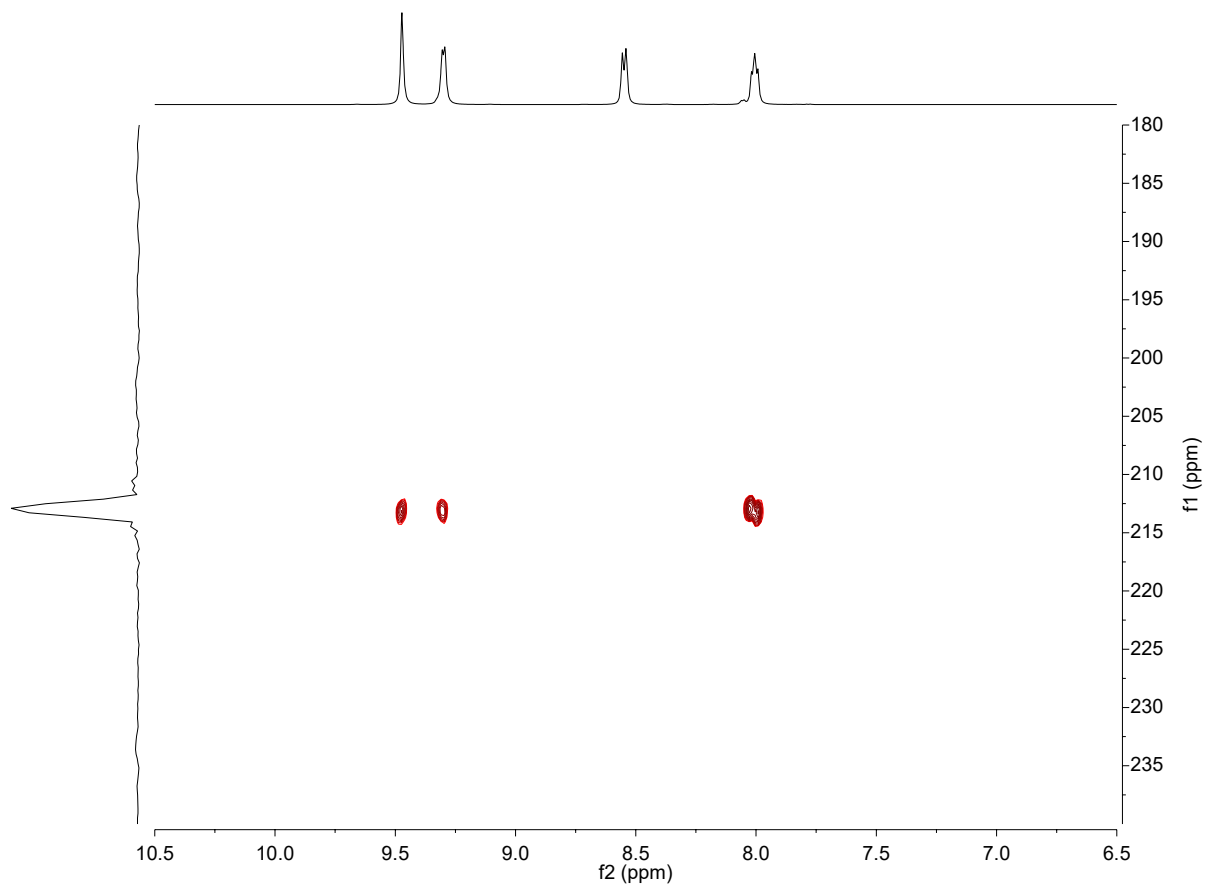


Fig. S3. ^1H - ^{15}N HMBC sub-spectrum of neat[BMP][Br].T = 313.1K

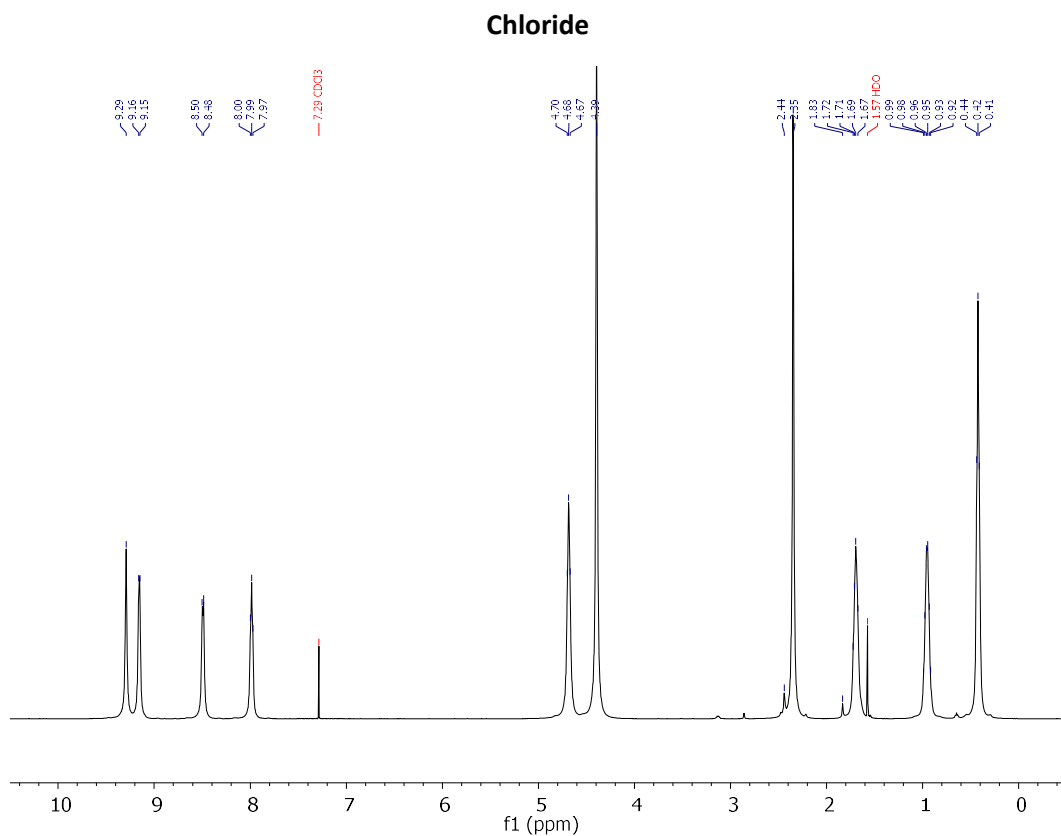


Fig. S4. ^1H NMR spectrum of neat [BMP][Cl]. T = 298.1K

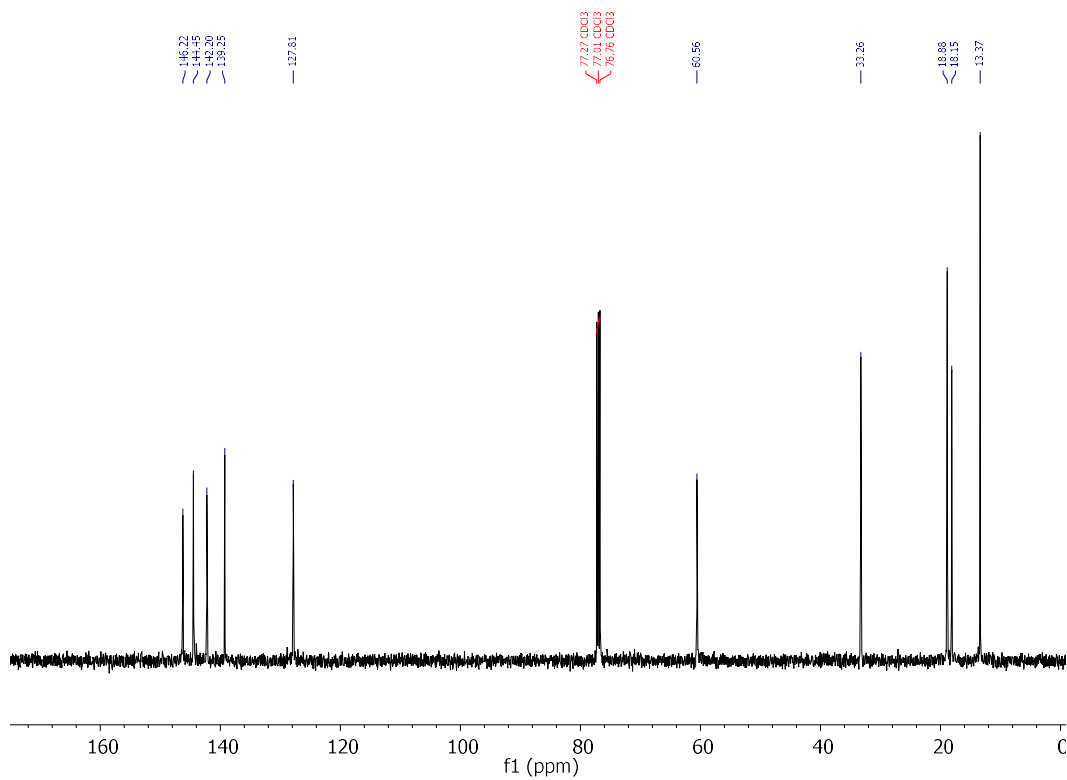


Fig. S5. ^{13}C NMR spectrum of neat [BMP][Cl]. T = 298.1K

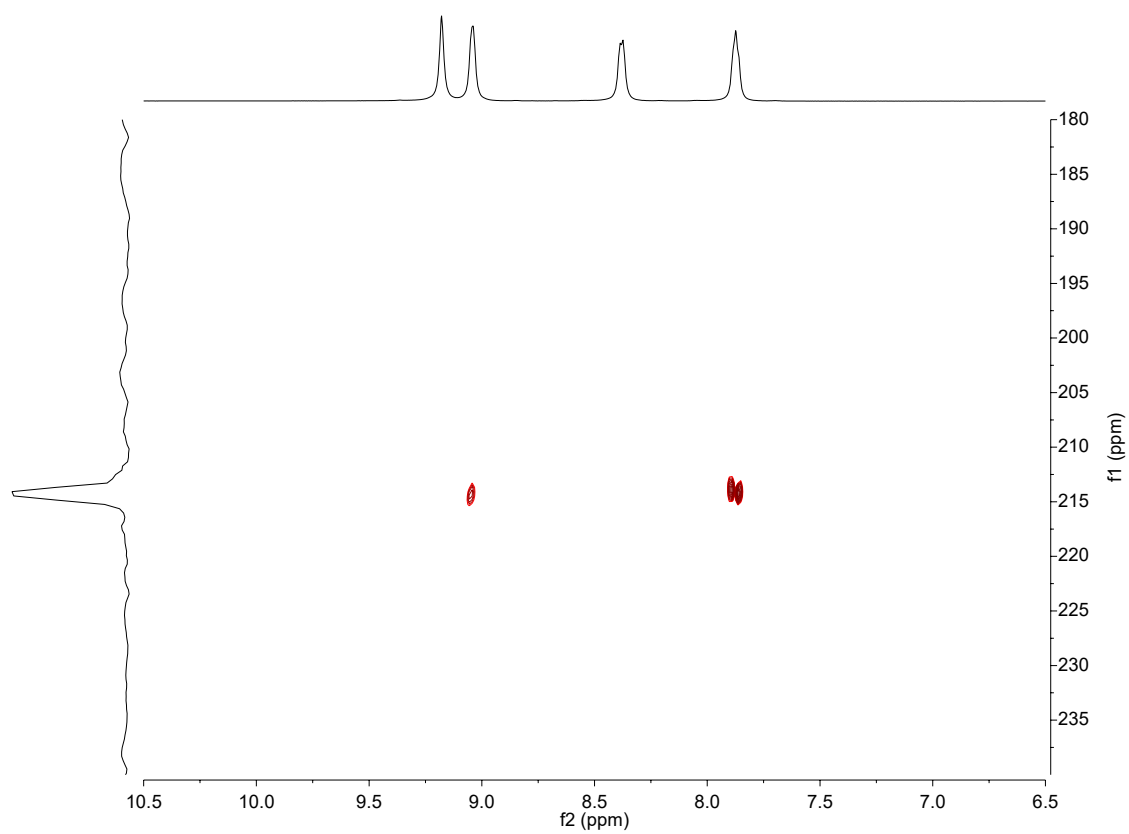


Fig. S6. ^1H - ^{15}N HMBC sub-spectrum of neat[BMP][Cl].T = 298.1K

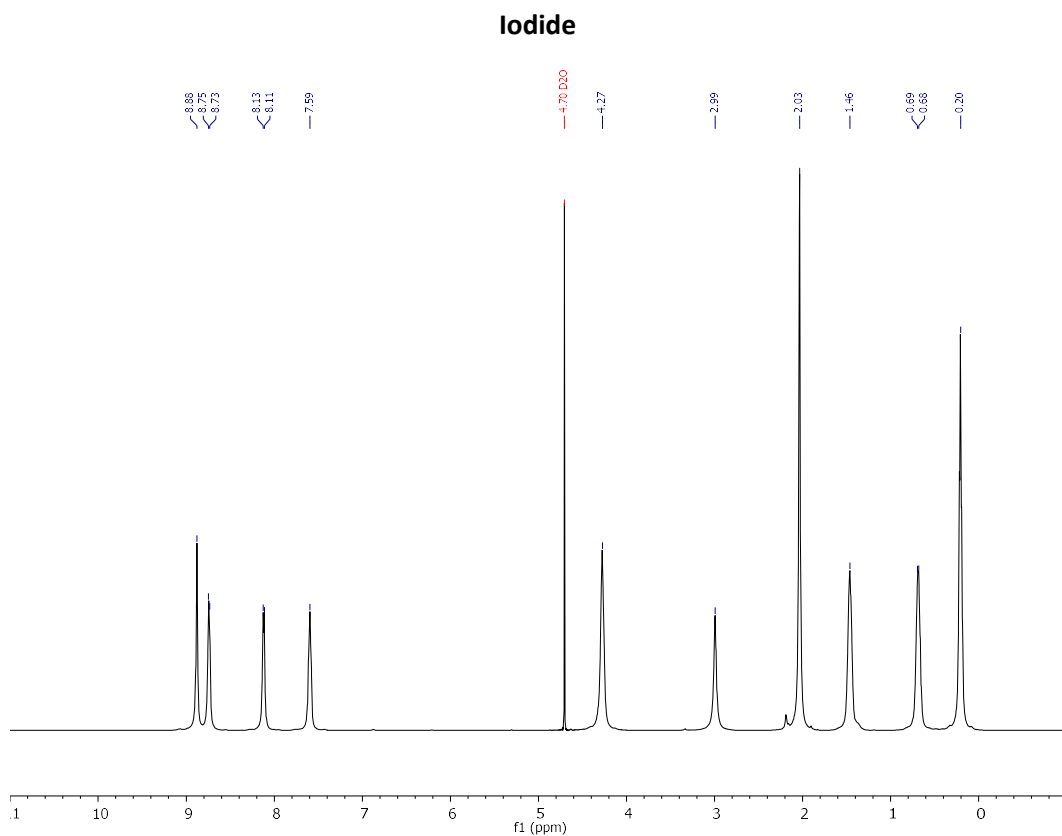


Fig. S7. ^1H NMR spectrum of neat [BMP][I]. T = 298.1K

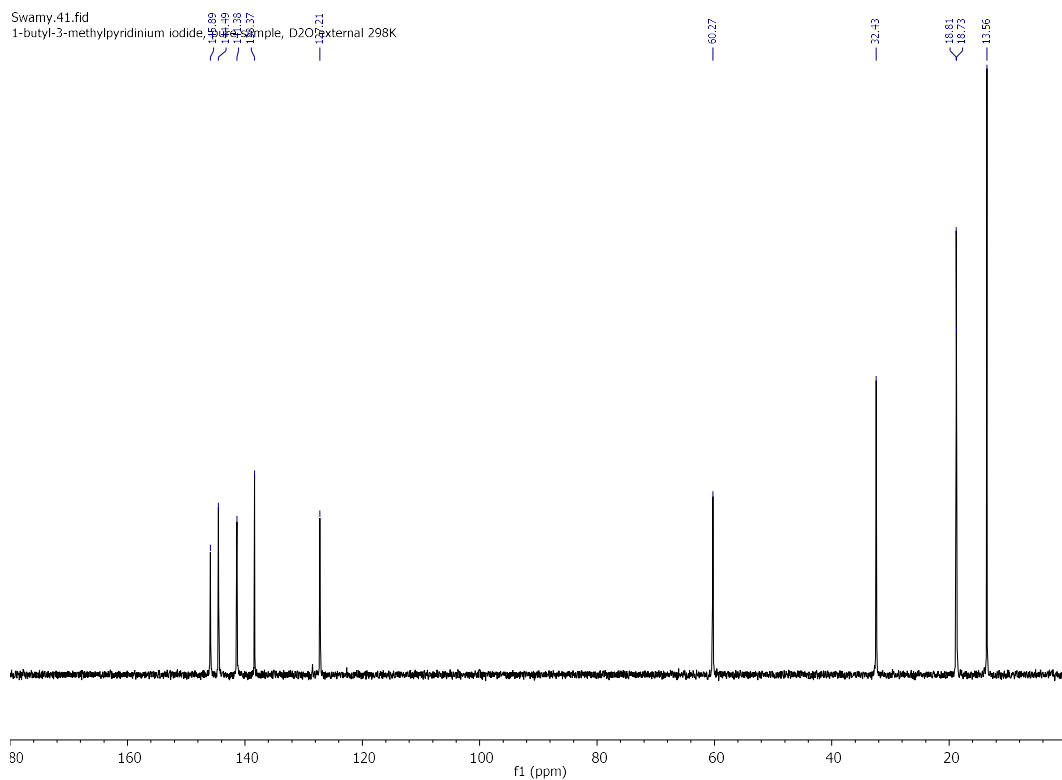


Fig. S8. ^{13}C NMR spectrum of neat [BMP][I]. T = 298.1K

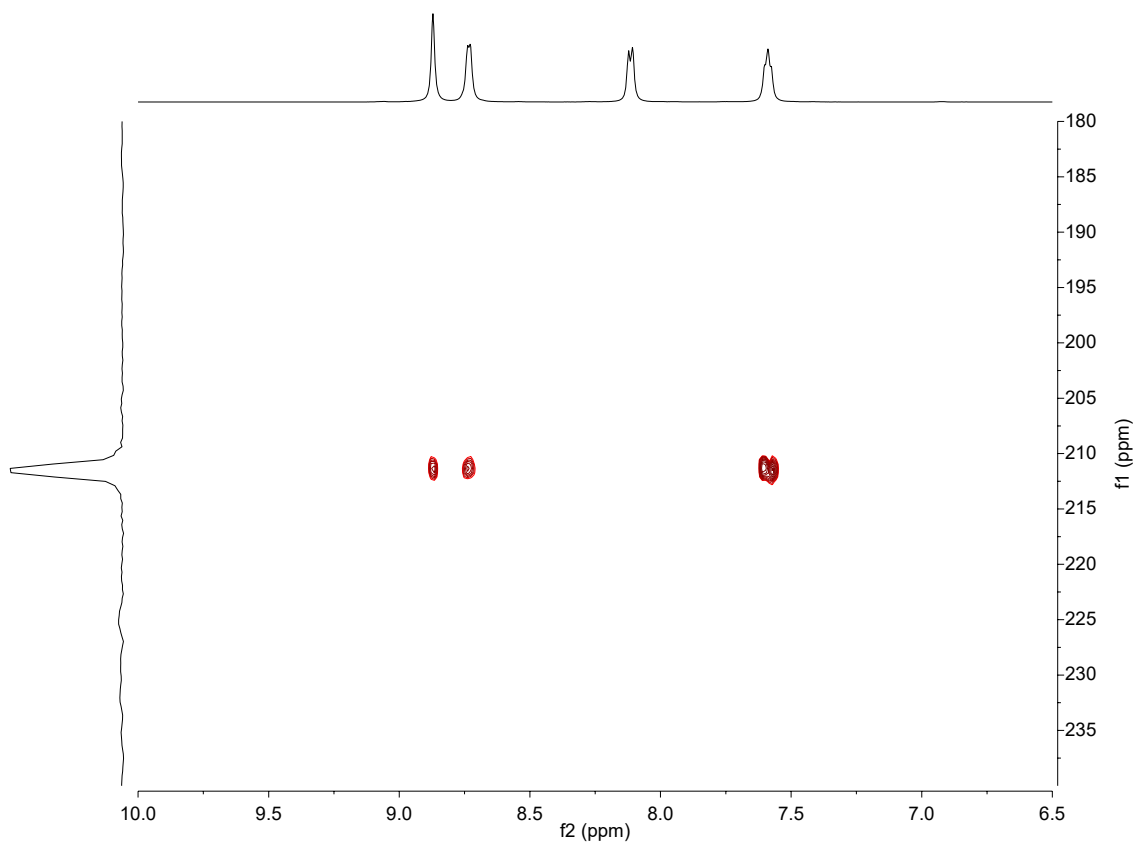


Fig. S9. ^1H - ^{15}N HMBC sub-spectrum of neat[BMP][I]. T = 298.1 K

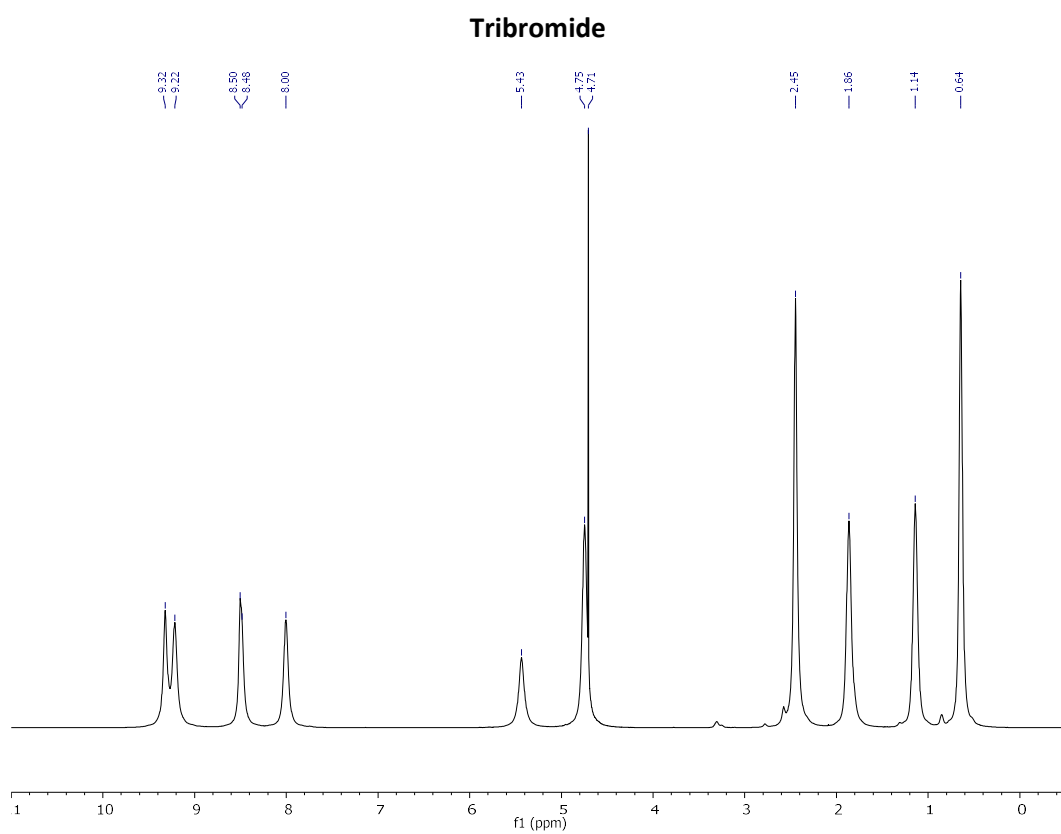


Fig. S10. ^1H NMR spectrum of neat [BMP][Br₃⁻]. T = 308.1K

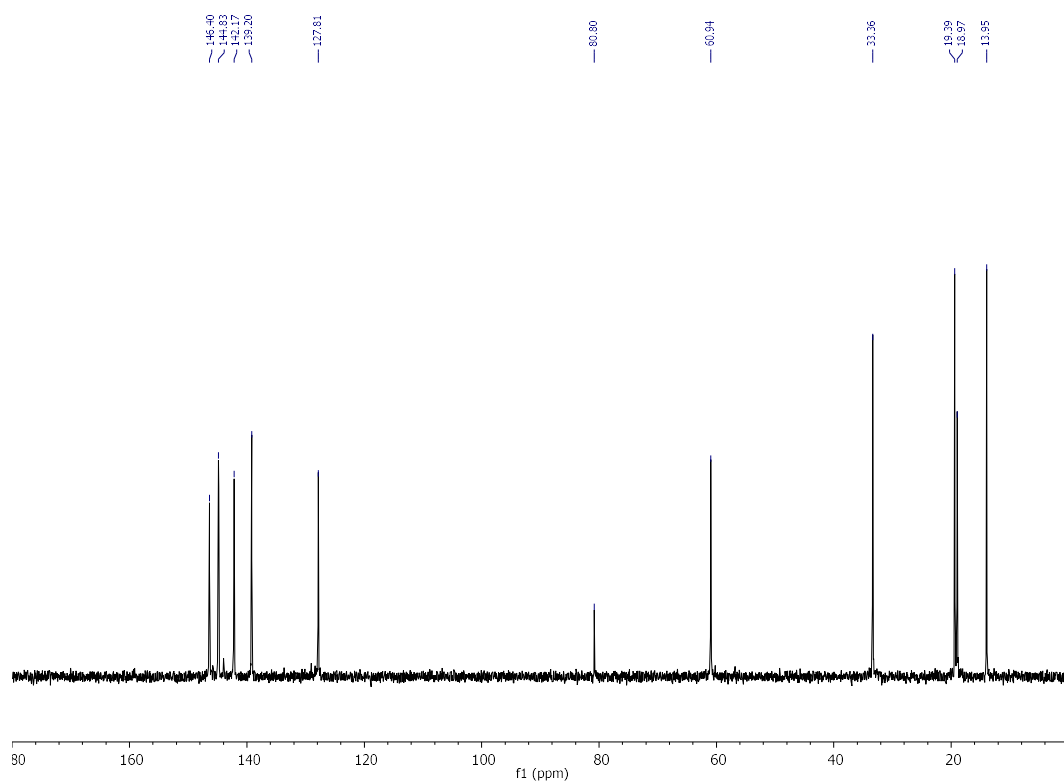


Fig. S11. ^{13}C NMR spectrum of neat $[\text{BMP}][\text{Br}_3^-]$. $T = 308.1\text{K}$

Chloride in CD₃OD

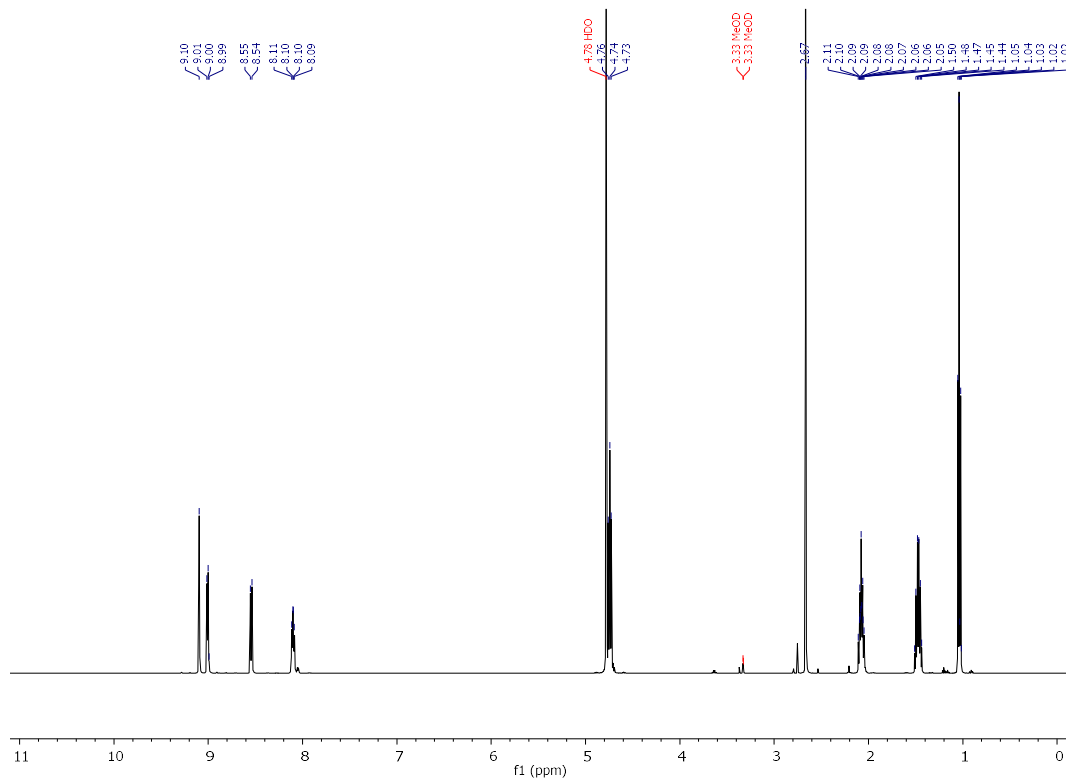


Fig. S12. ¹H NMR spectrum of [BMP][Cl] in CD₃OD. T = 298.1K

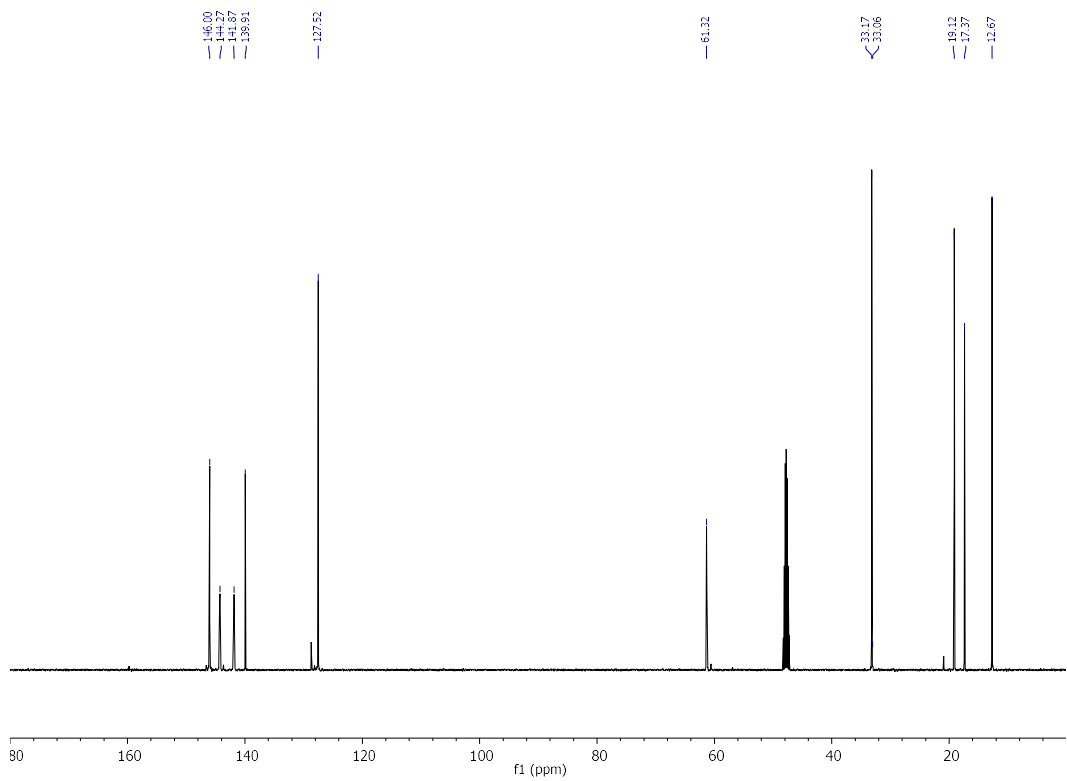


Fig. S13. ¹³C NMR spectrum of [BMP][Cl] in CD₃OD. T = 298.1K

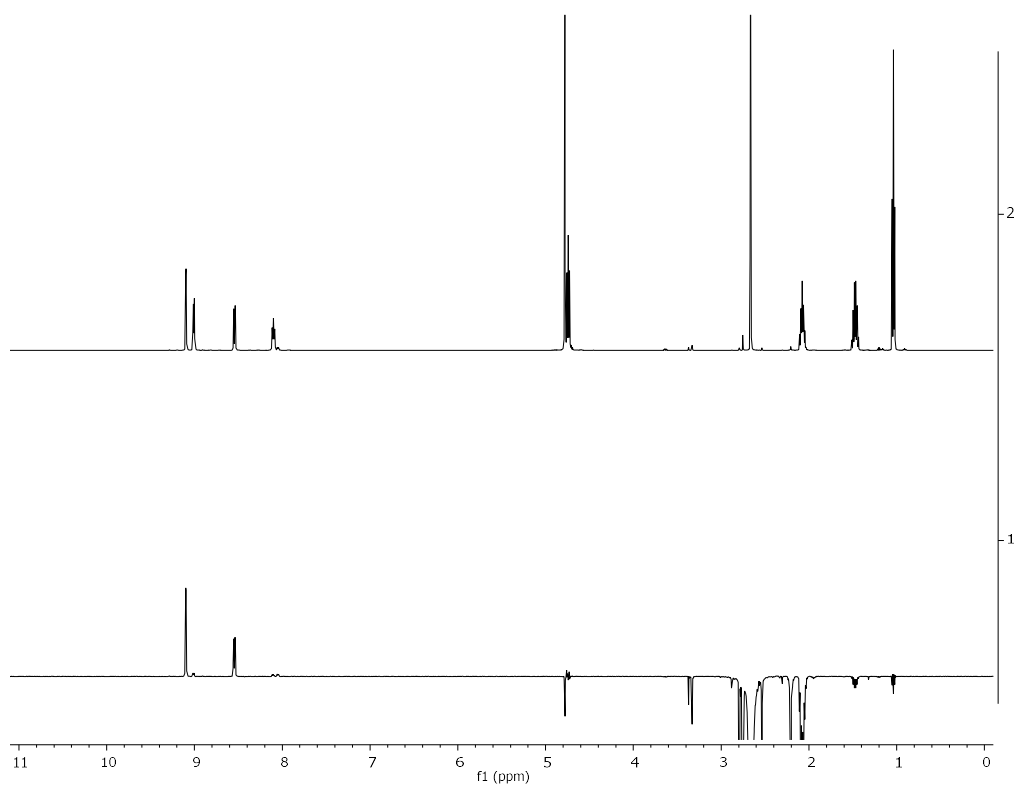


Fig. S14. Top: ^1H NMR spectrum of [BMP][Cl] in CD_3OD . Bottom: ^1H NOESY spectrum of the same sample, with selective inversion of the pyridinium CH_3 resonance (see text). $T = 298.1\text{K}$

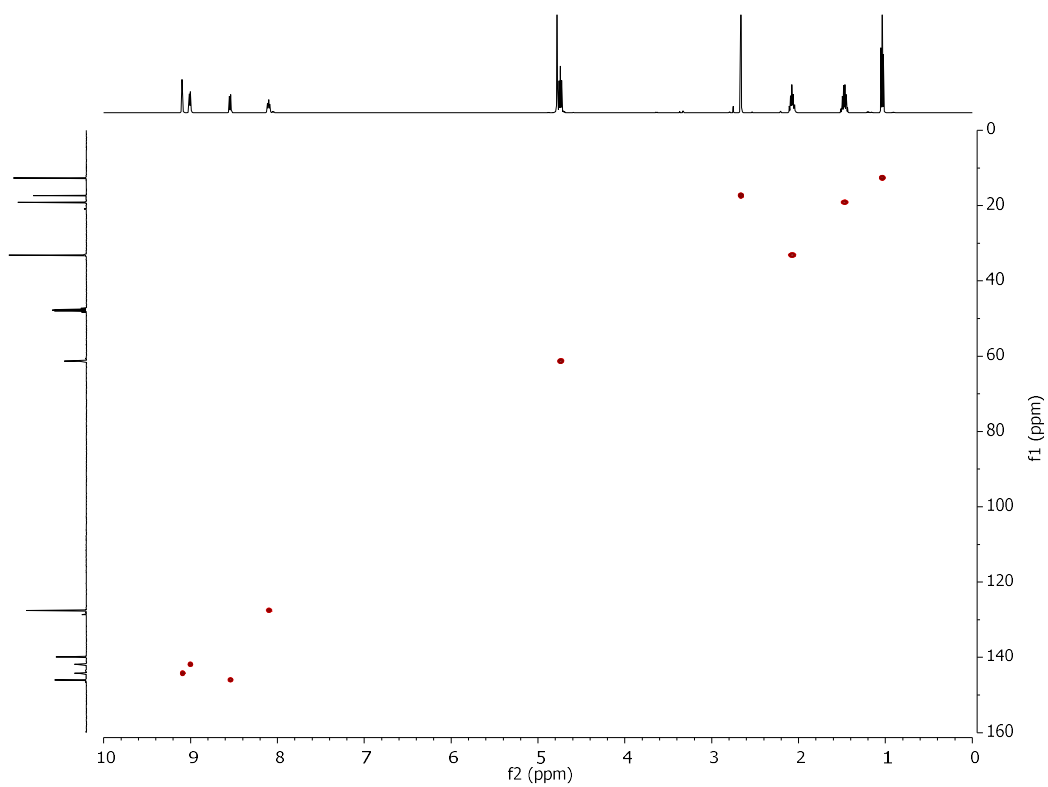
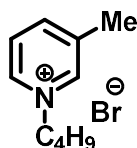


Fig. S15. ^1H - ^{13}C HSQC spectrum of [BMP][Cl] in CD_3OD . $T = 298.1\text{K}$

Synthesis and characterization

1. 1-Butyl-3-methylpyridinium bromide [BMPy]Br:



To a stirred solution of 3-picoline (10.0 g, 0.1 mol) and *n*-butylbromide (17.65g, 0.128 mol) was heated and refluxed at 90 °C for 4 h. After completion of the reaction (monitored by TLC), excess *n*-butylbromide was distilled off at 80 °C under reduced pressure (10 mm Hg) over 4 h leaving behind the product [BMPy]Br as a brownish viscous liquid (24.06 g; 97 %).

Molecular formula : C₁₀H₁₆BrN

Nature : Brownish viscous liquid

¹H NMR (CDCl₃, 200 MHz) : d 0.94 (t, *J* = 7.20 Hz, 3H), 1.34-1.45 (m, 2H), 1.96-2.04 (m, 2H), 2.63 (s, 3H), 4.94 (t, *J* = 7.45 Hz, 2H), 8.00 (t, *J* = 6.57 Hz, 1H), 8.20 (d, *J* = 8.09 Hz, 1H), 9.31 (d, *J* = 5.81 Hz, 1H), 9.38 (s, 1H) ppm.

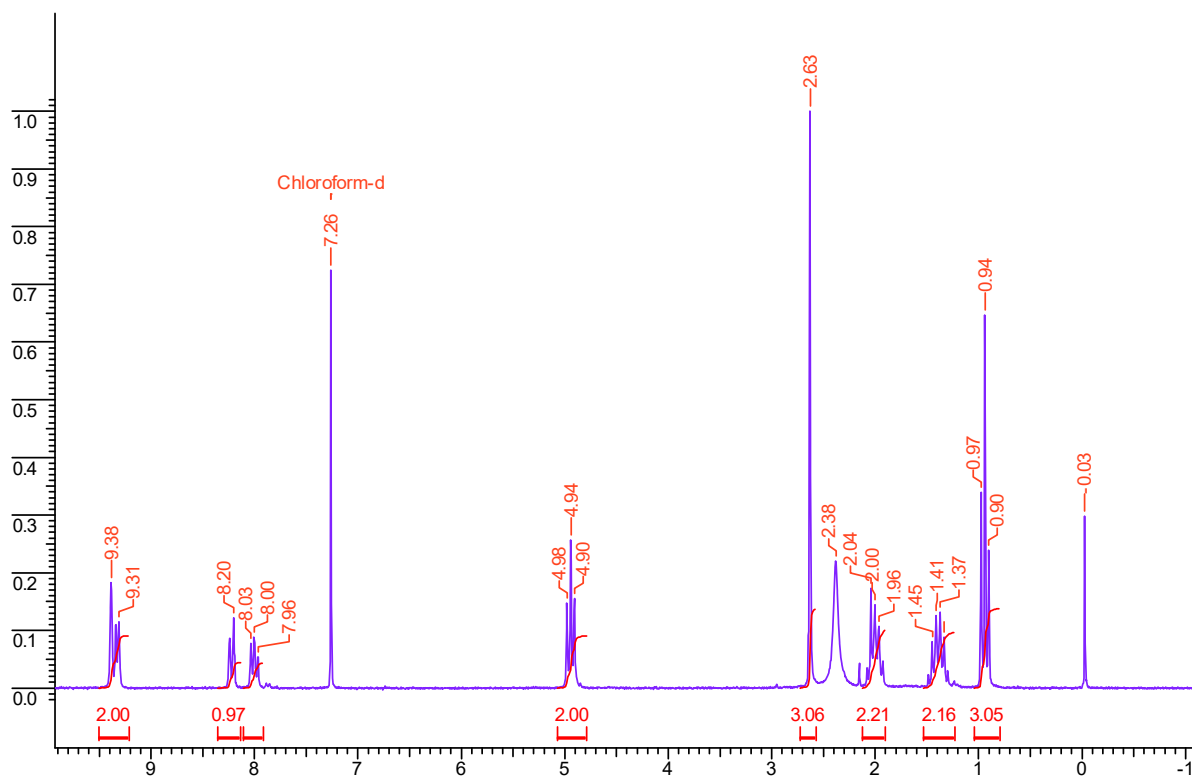
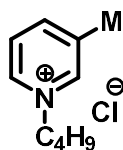


Fig. S16. ¹H-NMR of 1-Butyl-3-methylpyridinium bromide

2 1-Butyl-3-methylpyridinium chloride [BMPy]Cl:



To a stirred solution of 3-picoline (10.0 g, 0.1 mol) and *n*-butylchloride(11.85 g, 0.128 mol) was heated and refluxed at 90 °C for 24 h. After completion of the reaction (monitored by TLC), excess *n*-butylchloride was distilled off at 80 °C under reduced pressure (10 mm Hg) over 4 h leaving behind the product [BMPy]Cl as a brownish viscous liquid (18.94 g; 93 %).

Molecular formula : C₁₀H₁₆ClN

Nature : Brownish viscous liquid

¹H NMR (CDCl₃, 200 MHz) : d 0.94 (t, *J* = 7.20 Hz, 3H), 1.34-1.45 (m, 2H), 1.96-2.04 (m, 2H), 2.63 (s, 3H), 4.94 (t, *J* = 7.45 Hz, 2H), 8.00 (t, *J* = 6.57 Hz, 1H), 8.20 (d, *J* = 8.09 Hz, 1H), 9.31 (d, *J* = 5.81 Hz, 1H), 9.38 (s, 1H) ppm.

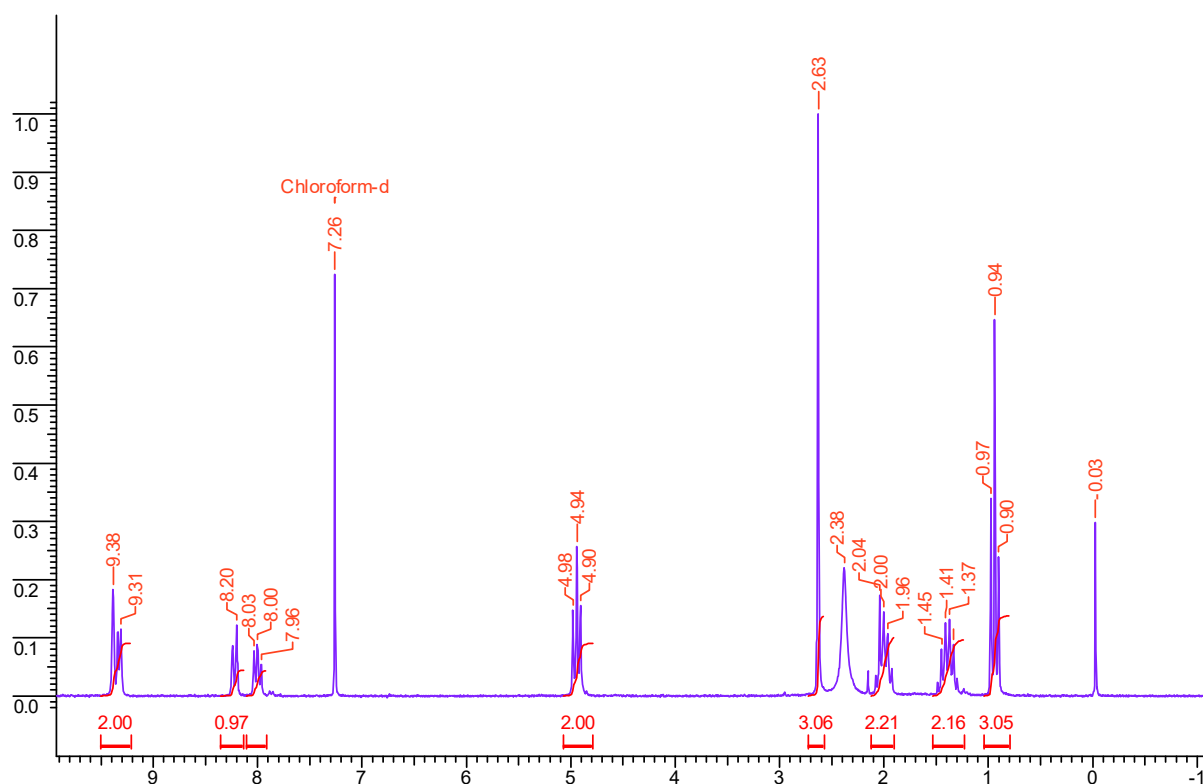
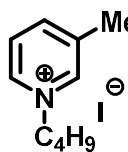


Fig. S17. ¹H NMR of 1-Butyl-3-methylpyridinium chloride

(3) 1-Butyl-3-methylpyridinium iodide [BMPy]I:



To a stirred solution of 3-picoline (10.0 g, 0.1 mol) and *n*-butyliodide (23.7 g, 0.107 mol) was heated at 90 °C for 24 h. After completion of the reaction (monitored by TLC), excess *n*-butyliodide was distilled off at 80 °C under reduced pressure (10 mm Hg) over 4 h leaving behind the product [BMPy]Cl as a dark reddish viscous liquid (27 g; 93 %).

Molecular formula : C₁₀H₁₆IN

Nature : Dark Reddish viscous liquid

¹H NMR (CDCl₃, 200 MHz) : d 0.94 (t, *J* = 7.20 Hz, 3H), 1.34-1.42 (m, 2H), 1.96-2.04 (m, 2H), 2.63 (s, 3H), 4.96 (t, *J* = 7.45 Hz, 2H), 8.00 (t, *J* = 6.57 Hz, 1H), 8.26 (d, *J* = 8.09 Hz, 1H), 9.12 (d, *J* = 5.81 Hz, 1H), 9.32 (s, 1H) ppm.

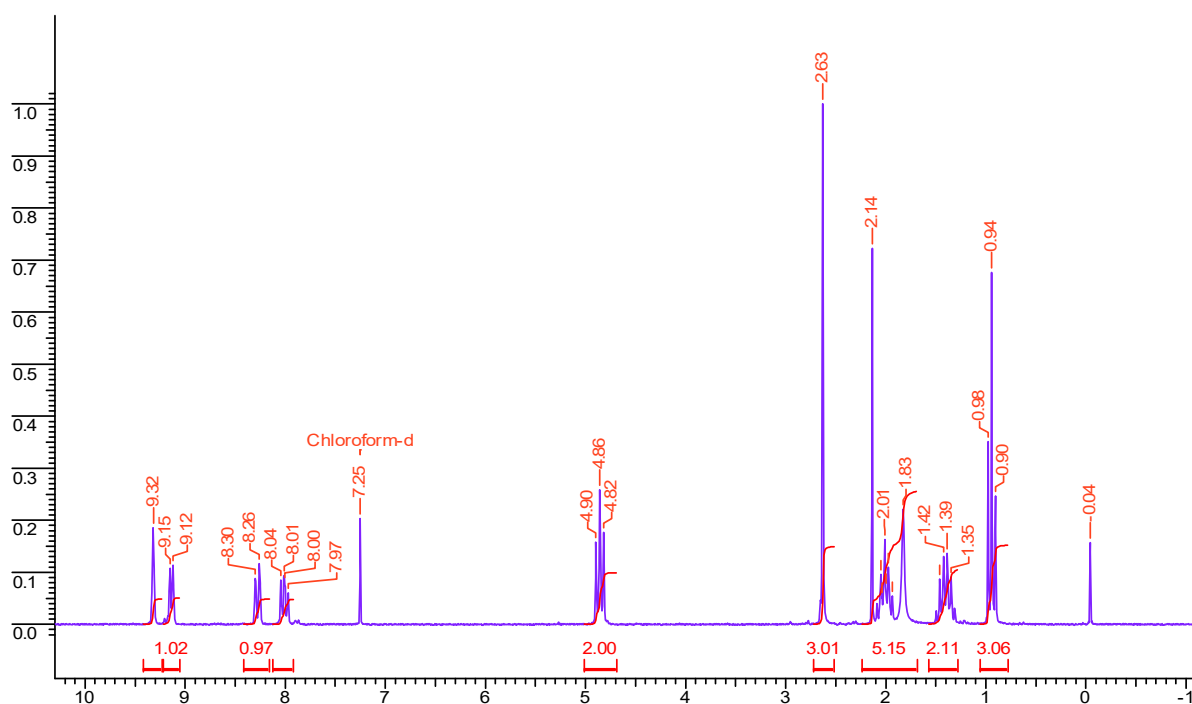
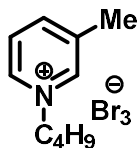


Fig. S18. ¹H NMR of 1-Butyl-3-methylpyridinium iodide

4. 1-Butyl-3-methylpyridinium tribromide



Molecular bromine (1.043 g, 0.652 mmol) was added slowly to 1-butyl-3-methylpyridinium bromide [BMPy]Br (1.0 g, 0.434 mmol) at ice-cooled temperature under stirring to give a deep red liquid. The stirring was continued for another 2 h.

The excess bromine was removed under reduced pressure over 5 h at 60 °C gave pure [BMPy]Br₃ as a red oil (1.62 g; 95%).

Molecular formula : C₁₀H₁₆Br₃N

Nature: Red oil

¹H NMR (CDCl₃, 200 MHz) : δ 0.96 (t, *J* = 7.20 Hz, 3H), 1.37-1.45 (m, 2H), 1.8-2.05 (m, 2H), 2.65 (s, 3H), 4.88 (t, *J* = 7.58 Hz, 2H), 8.01 (t, *J* = 7.83 Hz, 1H), 8.26 (d, *J* = 8.09 Hz, 1H), 9.14 (d, *J* = 6.07 Hz, 1H), 9.25 (s, 1H) ppm.

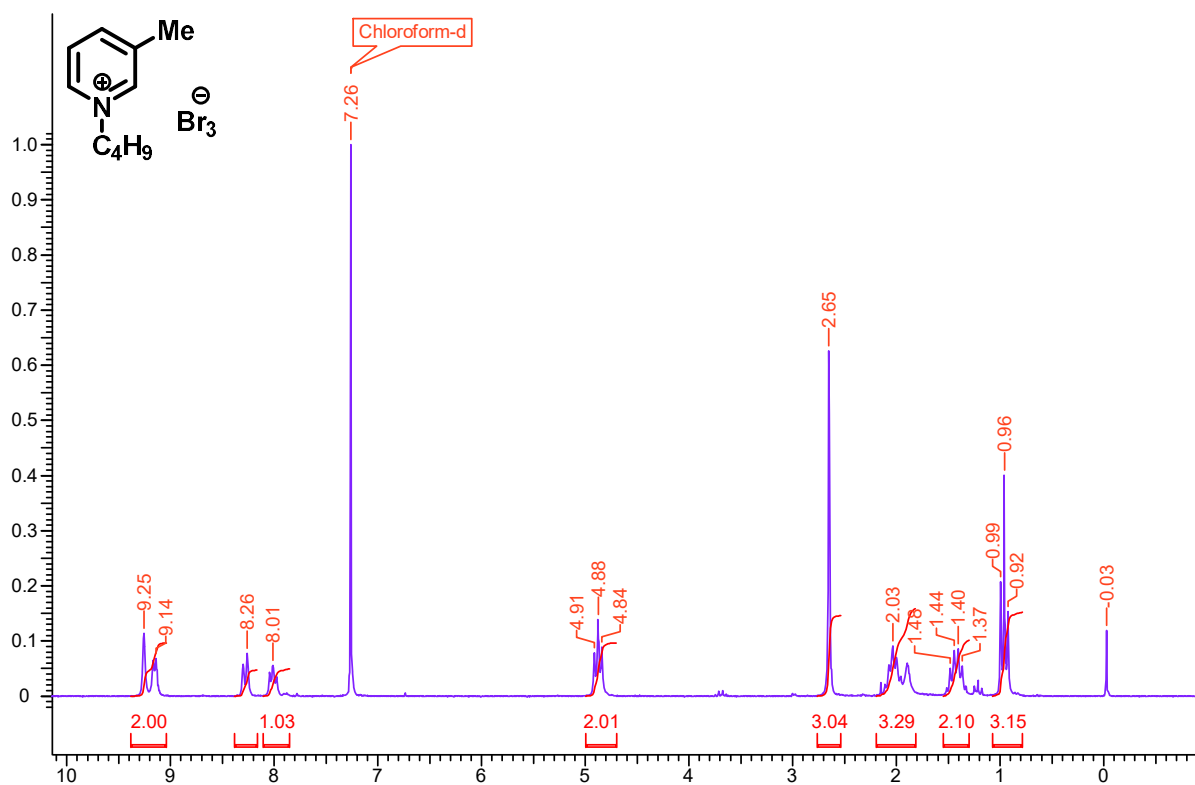
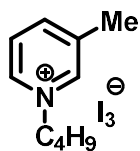


Fig. S19. ¹H NMR of 1-Butyl-3-methylpyridinium tribromide

5. 1-Butyl-3-methylpyridinium triiodidide



Molecular iodine (13.75 g, 0.108 mol) was added slowly to 1-butyl-3-methylpyridinium iodide [BMPy]I (10 g, 0.0361 mol) in 50ml chloroform, at ice-cooled temperature under stirring for 5 h. It was then left to attain room temperature

and left overnight at room temperature. The excess iodine was removed under reduced pressure over 5 h at 60 °C to afford crude product. This was pet ether (5 x 25 nl) to afford pure [BMPy]I₃ as a dark red oil (18 g; 94%).

Molecular formula : C₁₀H₁₆I₃N

Nature: Dark red oil

¹H NMR (CDCl₃, 200 MHz) : δ 1.06 (t, *J* = 7.20 Hz, 3H), 1.42-1.61 (m, 2H), 2.04-2.2 (m, 2H), 2.74 (s, 3H), 4.71 (t, *J* = 7.58 Hz, 2H), 8.0 (t, *J* = 7.83 Hz, 1H), 8.36 (d, *J* = 8.09 Hz, 1H), 8.61 (d, 2H) ppm.

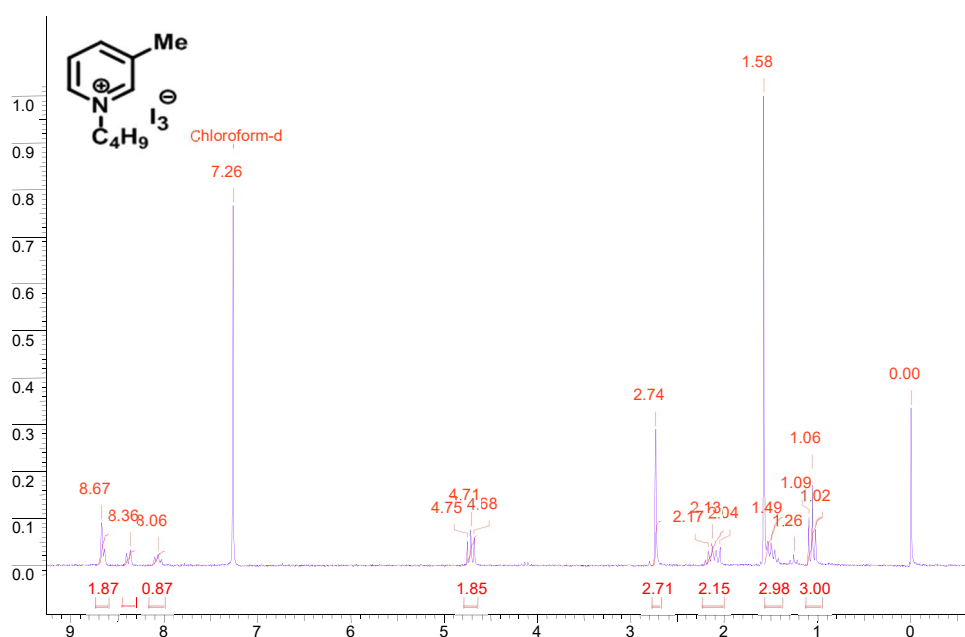
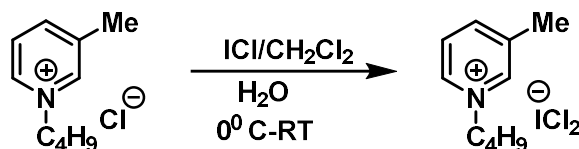


Fig. S20. ¹H NMR of 1-Butyl-3-methylpyridinium triiodide

6. 1-butyl-3-methylpyridinium dichloroiodate



A black solution of ICl (3.14 g, 19.39 mmol) in dichloromethane (35 ml), was added drop wise to an ice cold solution of 1-butyl-3-methylpyridinium chloride¹ (3.0 g, 16.16 mmol) in water (16 ml) under stirring and then left to attain room temperature. After the reaction mixture was stirred for 1 hour at room temperature, the dichloromethane layer was separated and dried with sodium sulphate and then evaporated under vacuum to afford water soluble dark reddish brown ionic liquid 1-butyl-3-methylpyridinium dichloroiodate (BMPDCI) in quantitative yields (5.5 g, 98%). This ionic liquid was stable and stored in dark at 10 °C (in refrigerator) for several months without any change in colour, loss of reactivity and degradation (checked by ¹H NMR).

¹H NMR (200 MHz, DMSO-*d*₆ δ/ppm): 8.87 (s, 1H, Ar-H), 8.80 (d, 1H, *J* = 5.94 Hz, Ar-H), 8.35 (d, 1H, *J* = 7.96 Hz, Ar-H), 7.97 (dd, 1H, *J* = 8.42, 1.37 Hz, Ar-H), 4.43 (t, 2H, CH₂), 2.40 (s, 3H, Ar-CH₃), 1.87 – 1.72 (m, 2H, -CH₂-CH₂), 1.28 - 1.09 (m, 2H, CH₂-CH₃), 0.81 (t, 3H, CH₃); **¹³C NMR** (50 MHz, CDCl₃+DMSO-*d*₆): 12.51, 17.77, 18.41, 32.44, 60.83, 126.96, 138.99, 140.84, 143.18, 145.15; **IR** (thin film, cm⁻¹): 3058, 2962, 2933, 2873, 1633, 1504, 1465, 1382, 1325, 1251, 1201, 1157, 804, 752, 684; **Viscosity** 43.6 cP at 25 °C. (Revolutions per minute (RPM): 550, Full Scale Range (FSR): 12.8%, Shear rate: 3197); **HRMS-ESI** Positive mode: [M⁺-ICl₂]⁺ calcd for C₁₀H₁₆N [M-ICl₂]⁺ 150.1282, found 150.1276.

AD-21#561 RT: 2.50 AV:1 NL: 4.52E9
T: FTMS + p ESI Full ms [60.00-900.00]

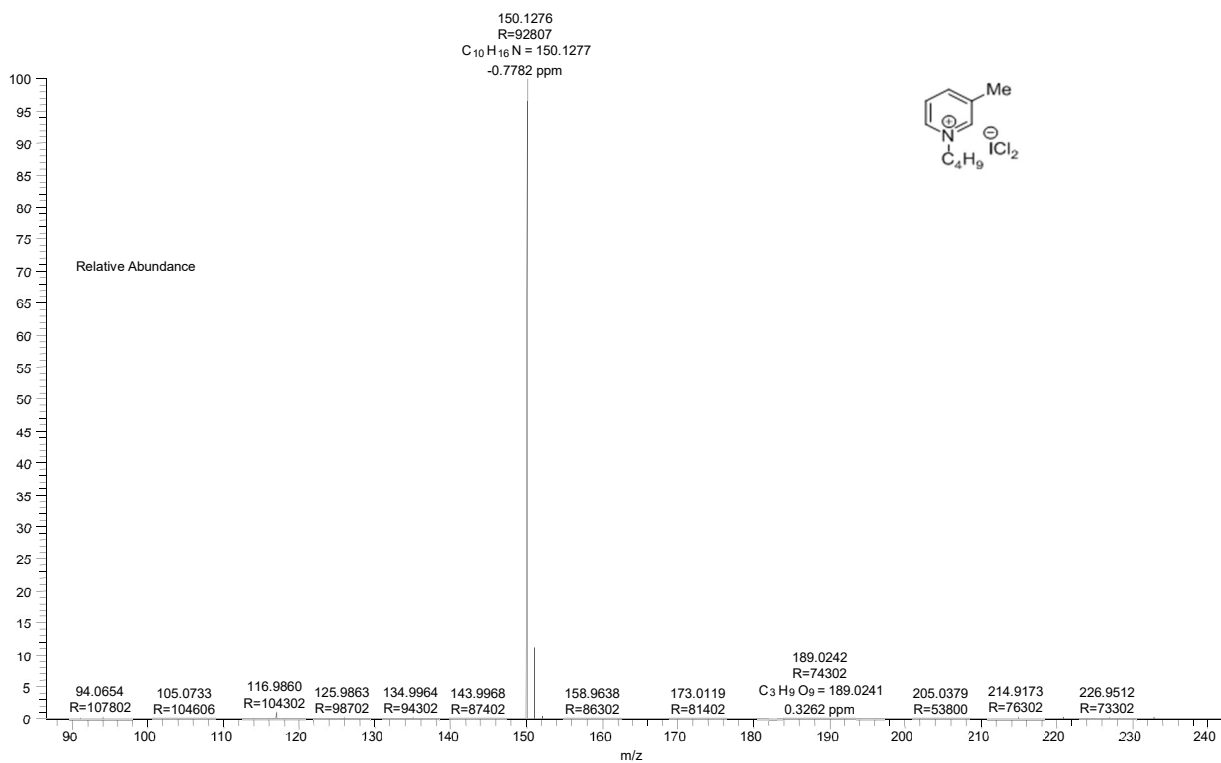


Fig. S21. HRMS of 1-butyl-3-methylpyridinium dichloroiodate

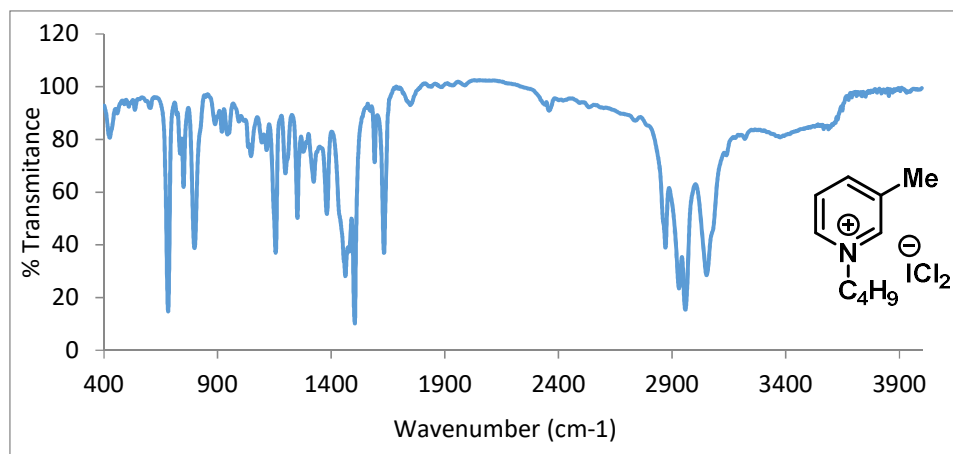
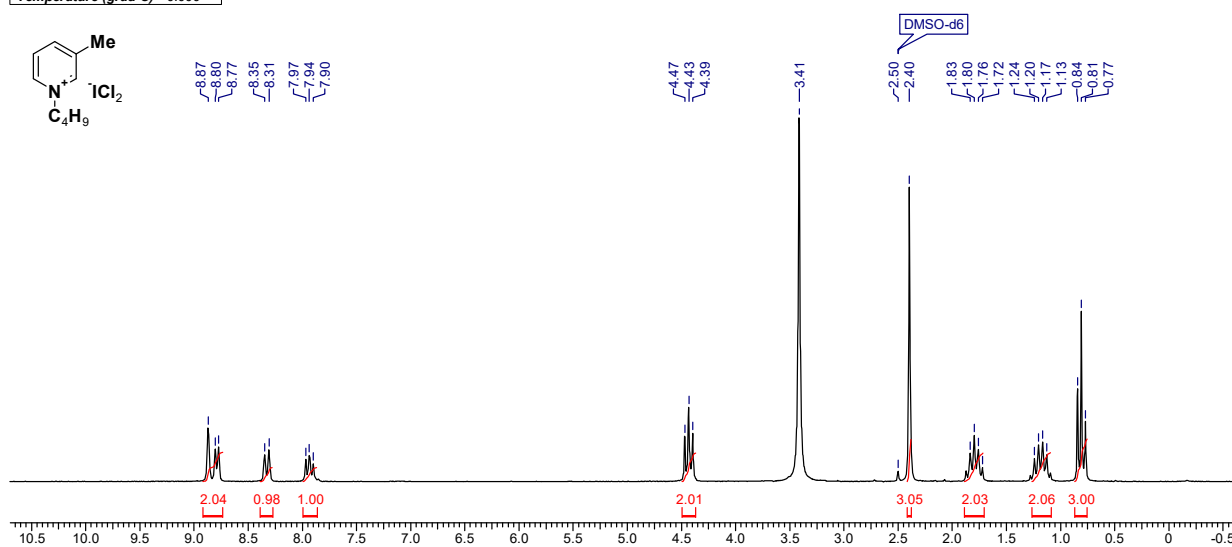
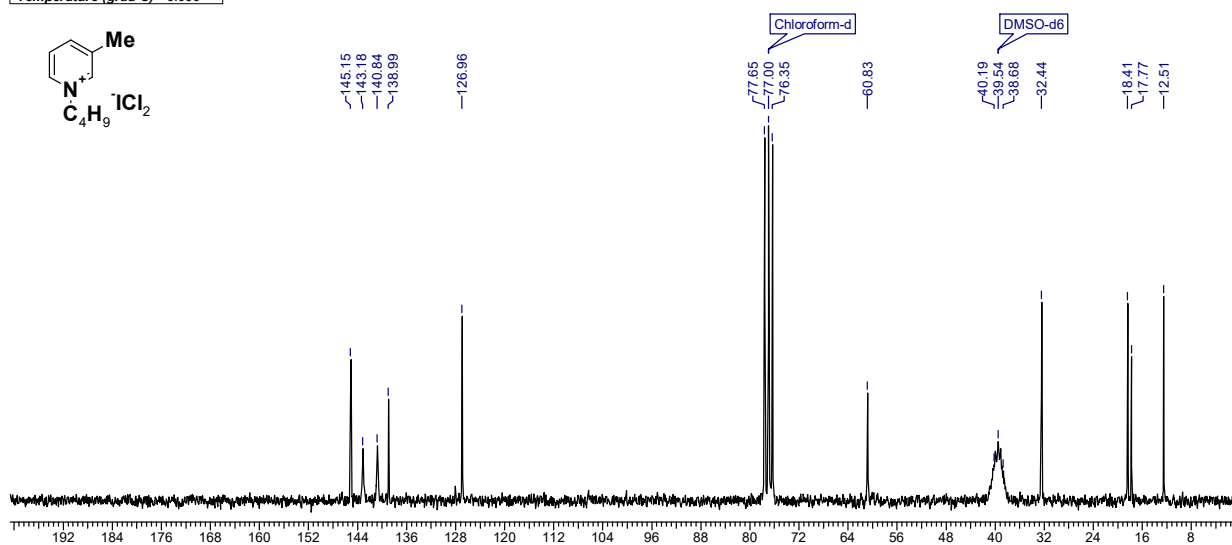


Fig. S22. IR of 1-butyl-3-methylpyridinium dichloroiodate

Acquisition Time (sec)	Comment	Date	Frequency (MHz)
7.9167	amar	27/05/2014 03:55:36	200.13
Nucleus	1H	Original Points Count	Points Count
		32768	32768
Temperature (grad C)	0.000	Sweep Width (Hz)	4139.07

Fig. S23. ^1H NMR of 1-butyl-3-methylpyridinium dichloroiodate

Acquisition Time (sec)	Comment	Date	Frequency (MHz)
2.7329	amar	27/05/2014 06:17:24	50.32
Nucleus	^{13}C	Original Points Count	Points Count
		32768	32768
Temperature (grad C)	0.000	Sweep Width (Hz)	11990.41

Fig. S24. ^{13}C NMR of 1-butyl-3-methylpyridinium dichloroiodate

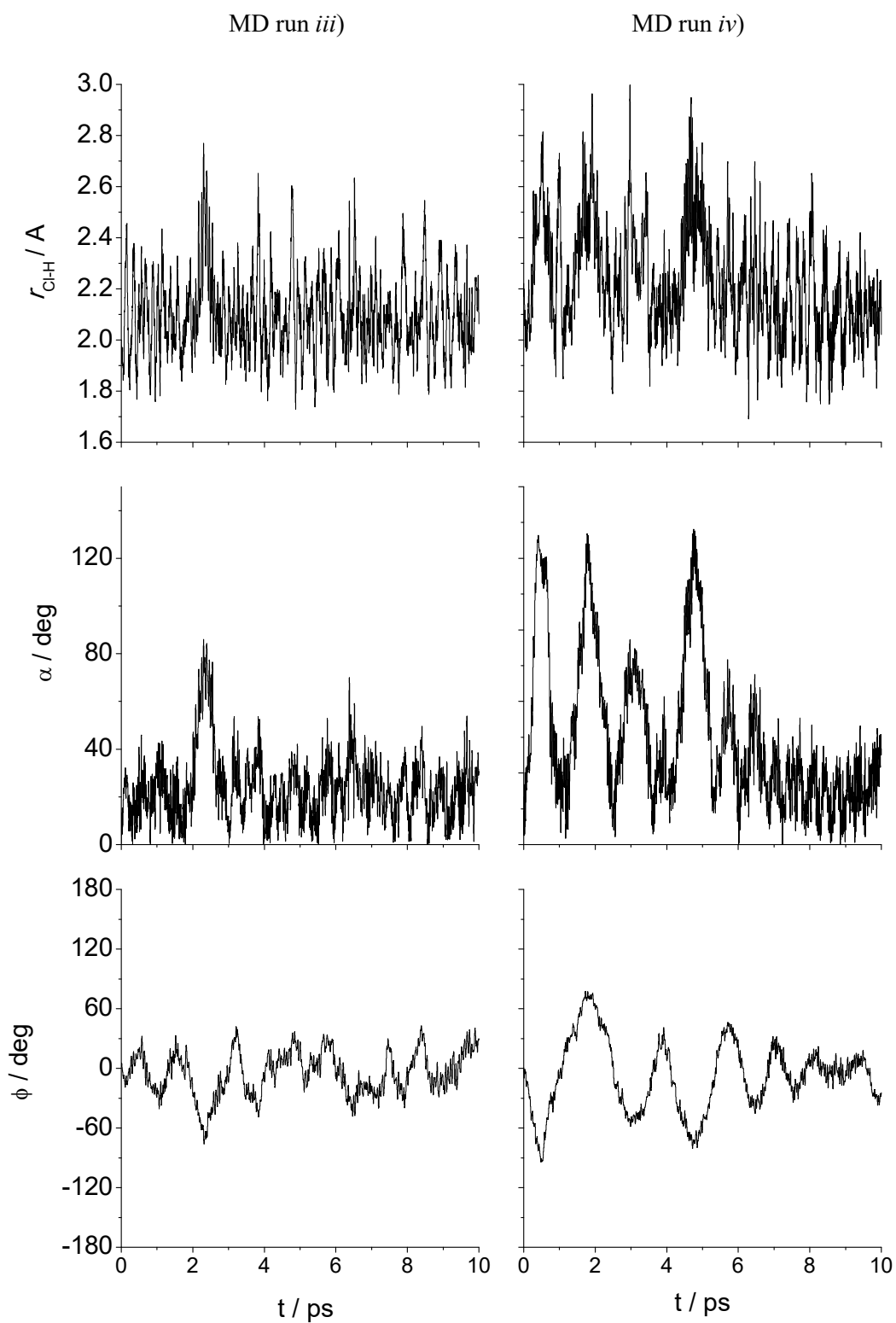


Fig. S25. Time evolution of (top): H-bond distance, $r(\text{Cl-H})$ between Chloride and the H2, in MD run *iii*), or H6, in MD run *iv*) hydrogen; (middle) angle α between the Cl-H2/6-C2/6 atoms; (bottom): out-of-plane bending angle ϕ of the chloride anion with respect to the aromatic ring (dihedral angle Cl-H2/6-C2/6-C8)

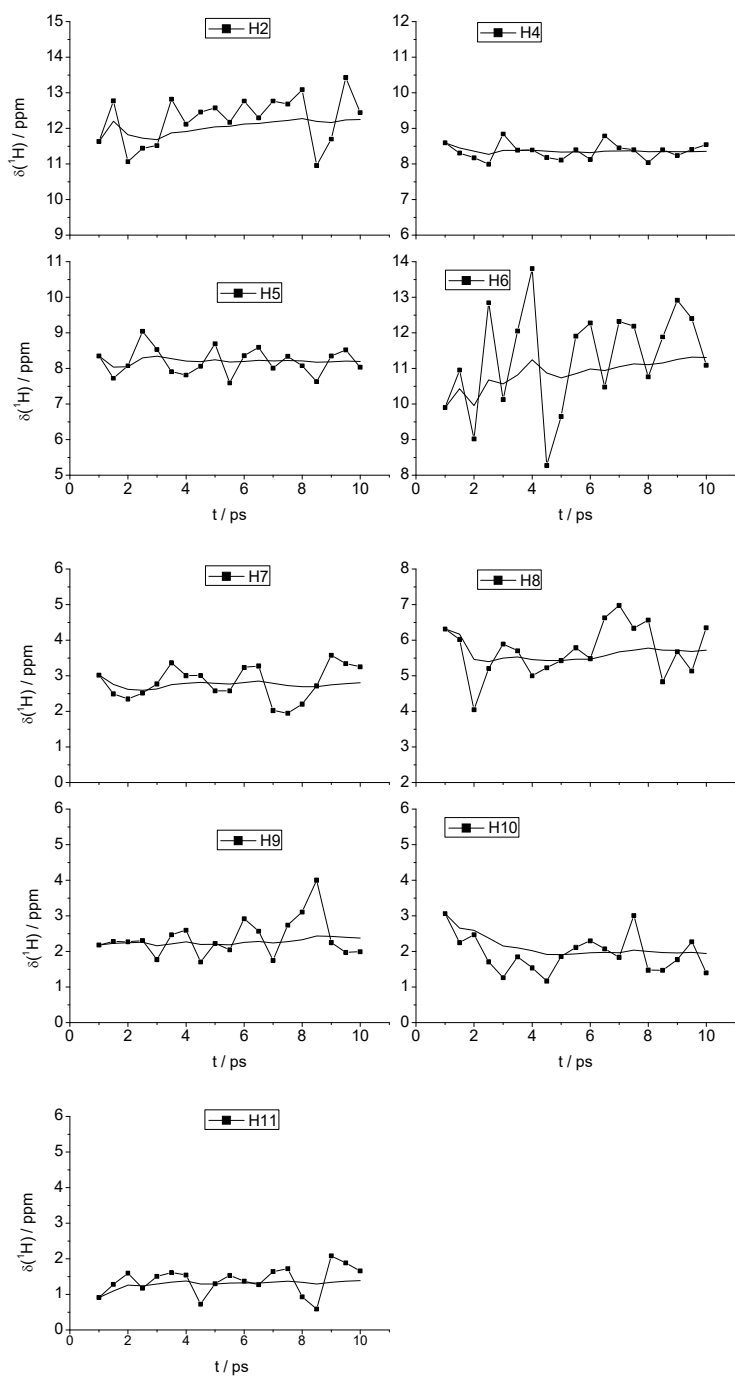


Fig. S26. Time evolution of the BMP protons during the 10 ps ADMP dynamics. Values are averaged of the MD run *iii*) and MD run *iv*). Symbols: instantaneous values; line: running average.

With reference to Figure 5 of the manuscript.

BMP, *o*)

27

C	-0.088896	0.069042	0.104997
C	-0.162918	-0.128677	1.474422
C	1.001572	-0.219039	2.205090
N	2.191576	-0.117197	1.592462
C	2.277806	0.077080	0.262987
C	1.150431	0.175884	-0.529130
H	-1.113396	-0.216844	1.981246
H	1.019044	-0.373007	3.274826
C	3.431965	-0.153564	2.402598
H	3.278566	0.146977	-0.141539
C	1.263843	0.391937	-2.009123
H	-0.998247	0.140253	-0.480273
H	4.211098	-0.596033	1.782309
C	3.822261	1.239368	2.879057
H	3.247773	-0.824909	3.241007
C	5.088908	1.197377	3.731593
H	3.978373	1.888386	2.010904
H	2.998209	1.668447	3.458888
C	5.498653	2.582147	4.223483
H	4.924751	0.535724	4.588932
H	5.903538	0.756377	3.147300
H	6.405532	2.529295	4.830011
H	5.695056	3.254344	3.383256
H	4.709820	3.030080	4.834453
H	0.711339	-0.379807	-2.548304
H	0.835682	1.359700	-2.279767
H	2.302192	0.370129	-2.338968

BMP Cl, *i*)

28

C	-0.241796	-0.344581	0.415827
C	-0.126594	-0.788831	1.723142
C	1.094938	-0.713004	2.354414
N	2.161631	-0.224931	1.702026
C	2.058442	0.224644	0.438837
C	0.862633	0.185579	-0.249944
H	-0.973907	-1.193842	2.257811
H	1.257025	-1.040251	3.371347
C	3.468377	-0.130465	2.393704
H	2.966879	0.613318	-0.001534
C	0.762084	0.727902	-1.643946
H	-1.197115	-0.402274	-0.092434
H	4.235887	-0.410285	1.671181
C	3.711266	1.265165	2.951132

H	3.466327	-0.878749	3.185879
C	5.051561	1.345368	3.678901
H	3.687453	1.993171	2.134002
H	2.896697	1.529075	3.633270
C	5.321250	2.742857	4.228612
H	5.064173	0.617338	4.497395
H	5.855488	1.057674	2.992288
H	6.281063	2.783749	4.748468
H	5.342051	3.481961	3.422801
H	4.541474	3.041280	4.935142
H	0.193656	0.049719	-2.282347
H	0.242125	1.689087	-1.624843
H	1.746423	0.881690	-2.086129
Cl	0.425917	3.310808	1.654491

BMP Cl, *ii*)

28

C	2.205605	0.169287	0.061256
C	1.117573	0.312555	-0.778622
C	-0.148525	0.157562	-0.215714
C	-0.286918	-0.128711	1.133572
C	0.841456	-0.258849	1.911678
N	2.057215	-0.106085	1.366997
C	1.309677	0.581497	-2.242051
C	3.257382	-0.242257	2.219850
C	3.637419	1.083786	2.864619
C	4.879101	0.936615	3.741734
C	5.269471	2.248828	4.414804
Cl	2.465356	-3.321972	0.413373
H	-1.259497	-0.257395	1.586923
H	0.809721	-0.487451	2.967395
H	3.223575	0.263984	-0.291176
H	-1.028596	0.256363	-0.840354
H	4.054917	-0.629665	1.587005
H	3.033208	-1.002746	2.967470
H	3.820337	1.829360	2.083308
H	2.798196	1.447044	3.467639
H	4.693801	0.171876	4.503836
H	5.711379	0.572883	3.129606
H	6.159911	2.123259	5.034832
H	5.483760	3.022021	3.671186
H	4.462418	2.614759	5.056194
H	0.581378	1.310932	-2.599302
H	2.311603	0.956689	-2.451178
H	1.167314	-0.341804	-2.809376

BMP Cl, iii)
28

C	0.586466	0.374121	-0.214664
C	-0.284980	-0.538471	0.379454
C	0.114217	-1.271460	1.487249
C	1.381232	-1.086921	1.994506
N	2.215925	-0.207758	1.417304
C	1.843693	0.515031	0.344676
C	3.557320	0.028692	2.000650
C	3.524840	1.170602	3.006832
C	4.912673	1.434293	3.586263
C	4.912720	2.591590	4.580136
C	0.198453	1.174703	-1.423363
Cl	4.563713	2.560729	-0.547128
H	-0.545795	-1.984355	1.960934
H	1.758739	-1.623314	2.853690
H	2.593149	1.204479	-0.042137
H	-1.280098	-0.674903	-0.027973
H	4.226939	0.266476	1.173873
H	3.879959	-0.905690	2.460155
H	3.159048	2.072632	2.504969
H	2.820643	0.932626	3.811758
H	5.281358	0.526142	4.075992
H	5.604304	1.652676	2.765625
H	5.914941	2.769505	4.976653
H	4.571488	3.515123	4.103448
H	4.248400	2.384561	5.424433
H	-0.762734	1.666747	-1.263967
H	0.947000	1.933956	-1.650006
H	0.099115	0.519736	-2.292252

BMP Cl, iv)
28

C	0.645579	0.377212	-0.255787
C	-0.253477	-0.473784	0.391635
C	0.121713	-1.146429	1.542386
C	1.392564	-0.968305	2.048966
N	2.251866	-0.150618	1.420091
C	1.901620	0.512068	0.301154
C	3.590467	0.075504	2.014517
C	3.547415	1.195017	3.045926
C	4.927311	1.439839	3.652274
C	4.901769	2.525810	4.723565
C	0.270226	1.116096	-1.506915
H	-0.561049	-1.809089	2.055322
H	1.765737	-1.458060	2.946398
H	2.661462	1.150157	-0.130203
H	-1.250437	-0.606885	-0.012456

H	4.273375	0.307003	1.197161
H	3.896722	-0.861997	2.479393
H	3.174969	2.112942	2.577928
H	2.841563	0.917301	3.835994
H	5.299369	0.504910	4.084674
H	5.627921	1.720249	2.858000
H	5.898904	2.691537	5.137891
H	4.546504	3.475577	4.312877
H	4.237637	2.245476	5.546134
H	-0.612823	1.733988	-1.331845
H	1.080399	1.759052	-1.850350
H	0.029163	0.409715	-2.304404
Cl	3.125296	-2.364234	4.778777

BMP Cl, v)
29

C	0.593985	0.375186	-0.217621
C	-0.280885	-0.527123	0.389629
C	0.116161	-1.245392	1.506608
C	1.385292	-1.062151	2.014216
N	2.220301	-0.194789	1.419612
C	1.851753	0.516339	0.337223
C	3.560333	0.040398	2.006078
C	3.523405	1.205284	2.984806
C	4.897436	1.452365	3.601260
C	4.892086	2.630124	4.570978
C	0.200990	1.169587	-1.429377
Cl	4.545705	2.590133	-0.622020
H	-0.547987	-1.948932	1.988915
H	1.775188	-1.583189	2.885692
H	2.603651	1.197396	-0.058562
H	-1.276494	-0.665551	-0.016358
H	4.241653	0.247798	1.180481
H	3.857241	-0.880399	2.508944
H	3.186400	2.104457	2.457260
H	2.793809	0.989411	3.773607
H	5.226508	0.546122	4.121747
H	5.622505	1.637564	2.800821
H	5.883232	2.789948	5.001724
H	4.593207	3.551888	4.062999
H	4.191092	2.457169	5.392927
H	-0.672013	1.788734	-1.211379
H	1.012388	1.819712	-1.757182
H	-0.062137	0.501310	-2.252256
Cl	3.169373	-2.486054	4.741637

BMP Br, *i*)
28

C	-0.252483	-0.351694	0.477870
C	-0.089396	-0.753968	1.796008
C	1.157348	-0.680548	2.372429
N	2.204057	-0.229591	1.659732
C	2.054819	0.181140	0.390217
C	0.829697	0.135791	-0.249830
H	-0.919787	-1.126245	2.379231
H	1.358569	-0.980410	3.390973
C	3.529641	-0.115326	2.310376
H	2.947622	0.547387	-0.097881
C	0.684561	0.646024	-1.651257
H	-1.229619	-0.407809	0.012752
H	4.282269	-0.238147	1.531463
C	3.681859	1.221879	3.021960
H	3.623608	-0.952524	3.002493
C	5.064942	1.364429	3.652100
H	3.501543	2.030703	2.307156
H	2.908714	1.309675	3.793040
C	5.235322	2.704898	4.361152
H	5.228992	0.546898	4.362984
H	5.830180	1.260326	2.874875
H	6.229490	2.791116	4.805595
H	5.103606	3.535402	3.661784
H	4.497534	2.821209	5.160268
H	-0.063077	0.070782	-2.198401
H	0.360644	1.690045	-1.618189
H	1.629864	0.601179	-2.192732
Br	0.988191	3.573193	1.196070

BMP Br, *ii*)
Not a minimum

BMP Br, *iii*)
28

C	0.595476	0.362050	-0.216342
C	-0.266259	-0.574529	0.354760
C	0.138695	-1.325279	1.448305
C	1.401646	-1.136027	1.964740
N	2.226925	-0.234359	1.409734
C	1.848237	0.505539	0.351086
C	3.562021	0.013369	2.003272
C	3.509296	1.152701	3.011499
C	4.894989	1.454973	3.576181
C	4.871021	2.618747	4.562287
C	0.201726	1.187403	-1.406307

Br	4.582542	2.832515	-0.436958
H	-0.514333	-2.055544	1.904921
H	1.782618	-1.685987	2.813596
H	2.587107	1.216310	-0.015680
H	-1.258188	-0.714766	-0.059207
H	4.234333	0.263355	1.181897
H	3.893415	-0.919117	2.460064
H	3.118684	2.045046	2.511475
H	2.817888	0.896673	3.822036
H	5.293858	0.560253	4.066888
H	5.569556	1.689504	2.745932
H	5.870936	2.828393	4.949098
H	4.499630	3.528147	4.081059
H	4.219563	2.399331	5.413482
H	-0.750031	1.690278	-1.224689
H	0.957065	1.940736	-1.630359
H	0.079800	0.549663	-2.284995

BMP Br, *iv*)
28

C	0.631906	0.362146	-0.259935
C	-0.249944	-0.531805	0.352491
C	0.135585	-1.235922	1.480674
C	1.400542	-1.047803	1.998526
N	2.244302	-0.190994	1.402240
C	1.882942	0.503442	0.306286
C	3.578708	0.041694	2.003388
C	3.536885	1.189155	3.003146
C	4.905090	1.412583	3.642722
C	4.887344	2.547014	4.662575
C	0.246355	1.136888	-1.485844
H	-0.534135	-1.931326	1.966722
H	1.777958	-1.557640	2.881964
H	2.631499	1.170318	-0.100794
H	-1.241419	-0.673551	-0.061820
H	4.271891	0.242621	1.186296
H	3.871560	-0.884429	2.498953
H	3.202167	2.104393	2.502383
H	2.802471	0.951825	3.780313
H	5.225142	0.484359	4.127609
H	5.640708	1.630756	2.860418
H	5.874116	2.689002	5.109128
H	4.590244	3.490808	4.195746
H	4.180726	2.334558	5.470107
H	-0.643439	1.738668	-1.289563
H	1.048662	1.800642	-1.807517
H	0.013231	0.454816	-2.306387
Br	3.241638	-2.425534	4.905300

BMP Br, v)
29

C	0.593956	0.365857	-0.221698
C	-0.260842	-0.577206	0.351480
C	0.148222	-1.317634	1.449270
C	1.409195	-1.117392	1.970651
N	2.227244	-0.214987	1.405984
C	1.845378	0.518797	0.343606
C	3.563086	0.030595	1.998824
C	3.518393	1.196101	2.976308
C	4.888904	1.446920	3.600195
C	4.865777	2.611098	4.586009
C	0.189274	1.188651	-1.410280
Br	4.511251	2.869419	-0.620860
H	-0.500329	-2.050689	1.908258
H	1.800810	-1.649770	2.834046
H	2.580371	1.230155	-0.029096
H	-1.249770	-0.729023	-0.065940
H	4.247108	0.239352	1.175511
H	3.864520	-0.887991	2.503233
H	3.184339	2.094683	2.446316
H	2.786425	0.978259	3.761788
H	5.225692	0.537178	4.109433
H	5.613634	1.651806	2.804468
H	5.851898	2.776452	5.026249
H	4.559671	3.536042	4.088485
H	4.161541	2.419006	5.400973
H	-0.745523	1.715788	-1.208502
H	0.954961	1.923202	-1.661114
H	0.029164	0.546881	-2.279714
Br	3.139824	-2.514206	4.938526

BMP I, i)
28

C	-0.239697	-0.363932	0.482515
C	-0.070054	-0.744686	1.805958
C	1.179558	-0.662812	2.375178
N	2.223044	-0.225020	1.649731
C	2.067847	0.164781	0.374319
C	0.839221	0.110201	-0.258936
H	-0.897424	-1.106354	2.399858
H	1.384658	-0.946604	3.397759
C	3.553695	-0.109821	2.290259
H	2.959977	0.518276	-0.125040
C	0.692972	0.597724	-1.668780
H	-1.218886	-0.428720	0.023060
H	4.300262	-0.234717	1.506082
C	3.714794	1.226186	3.002229

H	3.651292	-0.946187	2.982788
C	5.092507	1.348494	3.648703
H	3.557621	2.038764	2.285953
H	2.934854	1.325430	3.764697
C	5.268422	2.681434	4.370206
H	5.238126	0.524397	4.355924
H	5.864864	1.241230	2.879185
H	6.256883	2.754359	4.829367
H	5.155103	3.518432	3.675415
H	4.520445	2.798828	5.159617
H	-0.153591	0.119418	-2.161429
H	0.518849	1.677583	-1.658241
H	1.594491	0.405803	-2.251956
I	0.647126	3.668560	1.403825

BMP I, ii)
28

C	2.162030	0.215995	0.122905
C	1.103162	0.429580	-0.739082
C	-0.182396	0.305609	-0.214079
C	-0.367735	-0.020428	1.120709
C	0.733049	-0.215487	1.924769
N	1.968623	-0.091187	1.416538
C	1.345347	0.740470	-2.186144
C	3.146960	-0.283719	2.290017
C	3.643230	1.040698	2.854414
C	4.853967	0.836889	3.763136
C	5.369091	2.151492	4.341051
I	2.732745	-3.491523	-0.125280
H	-1.356652	-0.127224	1.543222
H	0.662972	-0.470823	2.972440
H	3.191899	0.280082	-0.200889
H	-1.041739	0.461250	-0.855764
H	3.906866	-0.784045	1.689110
H	2.849647	-0.969630	3.082994
H	3.907730	1.711529	2.029928
H	2.833385	1.520957	3.414043
H	4.583144	0.156450	4.577553
H	5.652037	0.344810	3.196856
H	6.236263	1.983392	4.983576
H	5.669190	2.838567	3.544519
H	4.597783	2.646435	4.938211
H	0.685081	1.540667	-2.524250
H	2.377836	1.042481	-2.361430
H	1.140777	-0.144358	-2.794264

BMP I, *iii*)
28

C	0.562261	0.352739	-0.196945
C	-0.255265	-0.637027	0.350404
C	0.190827	-1.406992	1.413482
C	1.451148	-1.184941	1.923994
N	2.234388	-0.233512	1.392329
C	1.813678	0.525677	0.363578
C	3.567400	0.041766	1.978004
C	3.500676	1.175288	2.991615
C	4.883023	1.480873	3.563186
C	4.850131	2.630774	4.564802
C	0.123096	1.198140	-1.356246
I	4.706892	3.154519	-0.454927
H	-0.426636	-2.178949	1.850403
H	1.862749	-1.748115	2.749590
H	2.517397	1.274798	0.011200
H	-1.244637	-0.803814	-0.059627
H	4.232548	0.302050	1.154017
H	3.920143	-0.884454	2.431030
H	3.106110	2.069313	2.497184
H	2.807611	0.907703	3.796677
H	5.286643	0.582144	4.042388
H	5.557017	1.732366	2.737274
H	5.847375	2.835553	4.960975
H	4.481416	3.546136	4.092868
H	4.193170	2.399492	5.408567
H	-0.855907	1.638189	-1.158120
H	0.833377	2.001629	-1.551511
H	0.039318	0.586338	-2.257586

BMP I, *iv*)
28

C	0.593530	0.331948	-0.292384
C	-0.257137	-0.561834	0.361867
C	0.164765	-1.225704	1.502110
C	1.435438	-0.997760	1.985975
N	2.251139	-0.142542	1.349414
C	1.853492	0.513745	0.243288
C	3.593855	0.122898	1.917425
C	3.528597	1.171598	3.019074
C	4.913944	1.442831	3.600156
C	4.866274	2.437208	4.756018
C	0.166958	1.068840	-1.527951
H	-0.479242	-1.920871	2.022025
H	1.837985	-1.476925	2.873227
H	2.579820	1.183534	-0.197370
H	-1.252782	-0.736445	-0.029291

H	4.235544	0.440755	1.095908
H	3.970471	-0.822897	2.308774
H	3.096427	2.096325	2.621063
H	2.865341	0.809493	3.811912
H	5.343889	0.497225	3.947999
H	5.573152	1.820639	2.810902
H	5.865704	2.626895	5.154122
H	4.444418	3.394255	4.434748
H	4.246727	2.053564	5.571901
H	-0.693478	1.705423	-1.310697
H	0.969485	1.696052	-1.915703
H	-0.128506	0.362975	-2.306893
I	3.457253	-2.404262	5.141674

BMP I, *v*)
29

C	0.557116	0.357472	-0.220604
C	-0.255450	-0.634357	0.331750
C	0.192525	-1.392662	1.401609
C	1.451744	-1.162392	1.913789
N	2.231494	-0.214972	1.369987
C	1.808379	0.536657	0.336484
C	3.566829	0.057715	1.951694
C	3.499058	1.179791	2.976744
C	4.872698	1.447577	3.585130
C	4.838037	2.581015	4.605332
C	0.107118	1.200851	-1.377540
I	4.638892	3.198048	-0.596821
H	-0.423122	-2.162583	1.844990
H	1.867825	-1.706391	2.754798
H	2.510642	1.284256	-0.021340
H	-1.242637	-0.809418	-0.080428
H	4.230360	0.320828	1.127011
H	3.913366	-0.867945	2.411681
H	3.124708	2.088219	2.491856
H	2.791234	0.902060	3.765706
H	5.235514	0.530750	4.062164
H	5.578484	1.692751	2.783827
H	5.825721	2.751478	5.040032
H	4.509171	3.514619	4.139364
H	4.146926	2.350508	5.421725
H	-0.828910	1.708932	-1.136427
H	0.853534	1.953169	-1.633077
H	-0.068685	0.576324	-2.256270
I	3.471600	-2.464955	5.189242