**Supporting Information – jo-2019-02493g**

**Characterizing Cation Chemistry for Anion Exchange Membranes -- A Product Study of Benzylimidazolium Salt Decompositions in Base**
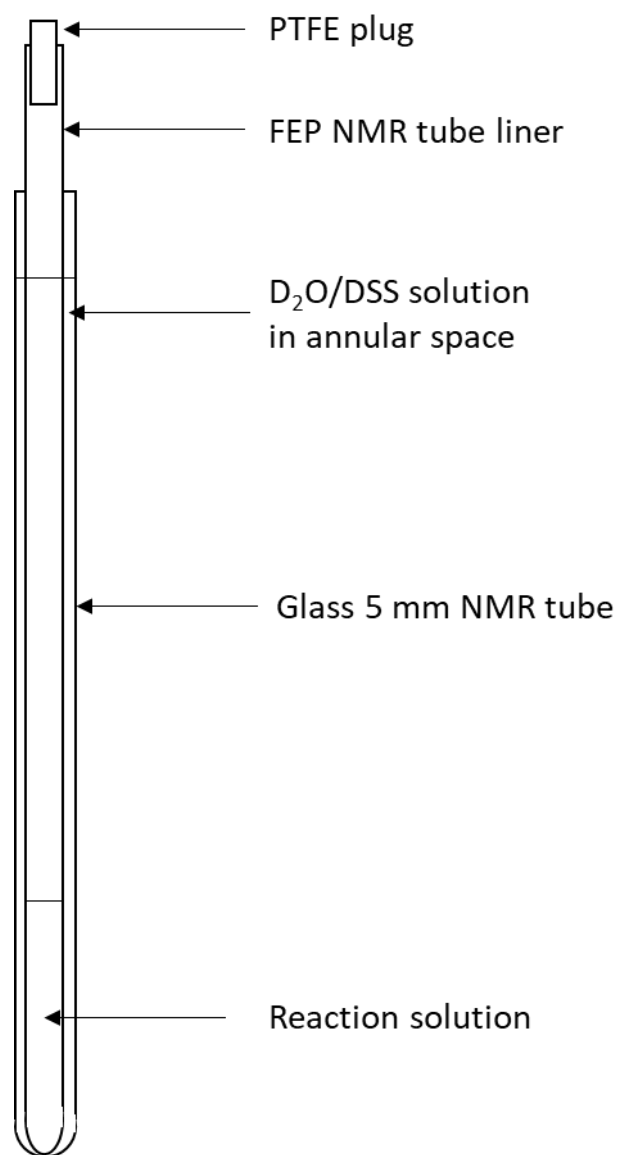
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**Figure S1 –** Schematic of nested NMR tube setup.

PTFE plug

FEP NMR tube liner

$D_2O$/DSS solution
in annular space

Glass 5 mm NMR tube

Reaction solution

**Table S1** – Table of chemical shift data in 1 M and 4.25 M KOH for starting salts and products. $^{1}$H shifts vs DSS external reference, $^{13}$C vs TMS internal instrument reference.   NM = not measured.  Assignments were confirmed using 2-D HMQC and HMBC $^{1}$H-$^{13}$C correlations.

| Species | 1 M KOH | | 4.25 M KOH | |
|---|---|---|---|---|
| | $^{1}$H (ppm) | $^{13}$C (ppm) | $^{1}$H (ppm) | $^{13}$C (ppm) |
| **2** | 3.78, 5.29, 7.38, 8.66 (br) | 52.8 ($CH_2$) | NM | NM |
| **3** | 2.47, 3.69, 5.26 | NM | 2.27, 3.50, 5.12 | 50.9 ($CH_2$) |
| **4** | NM | NM | 1.83, 1.95, 2.25, 3.37, 6.82, 7.14 | 7.7, 7.7, 9.4, 31.4 ($CH_3$); 47.5 ($CH_2$)[#] |
| $CH_3CO_2^-$ | 1.83 | NM | 1.65 | 23.6, 181.1 |
| $HCO_2^-$ (*) | 8.36 | 170.9 | 8.19 | 170.8 |
| $HOCH_2CO_2^-$ | 3.85 | 61.3, 180.2 | 3.67 | 61.5, 181.3 |
| $(CH_3)_2C(OH)CO_2^-$ | NM | NM | 1.08 | 26.5, 73.6, 183.8 |
| $PhCH_2NH_2$ | 3.70 ($CH_2$) | 44.8 ($CH_2$) | 3.50 ($CH_2$) | 44.7 ($CH_2$) |
| $PhCH_2OH$ | --- | --- | 4.31 ($CH_2$) | NM |
| $CH_3NH_2$ (*) | 2.19 | 26.8 | 2.01 | 26.9 |
| $PhCO_2^-$ | 7.77, 7.47, 7.39 | NM | 7.54, 7.24, 7.17 | 174.9 (C=O) |
| $(CH_3)_3CO_2^-$ | 1.00 | 27.4, 39.7, 188.8 | 0.83 | 27.4, 39.5, 188.4 |
| $CO_3^=$ | -- | 168.1 | -- | 168.1 |
| $CH_3CH(OH)CO_2^-$ | 1.23 (d), 4.03 (q) | NM | -- | -- |

**\***Assignments also further confirmed by measurement of $^{1}$H-$^{13}$C coupling constants: 195 Hz for formate (agreed with identical measurement on authentic sample), 135 Hz for methylamine (literature value 133 Hz (S. Watanabe, I. Ando, Y. Sakamoto, J. Mol. Struc. **82** (1982), 237-243)).

[#]Only imidazolium methyl and benzylic methylene chemical shifts listed.
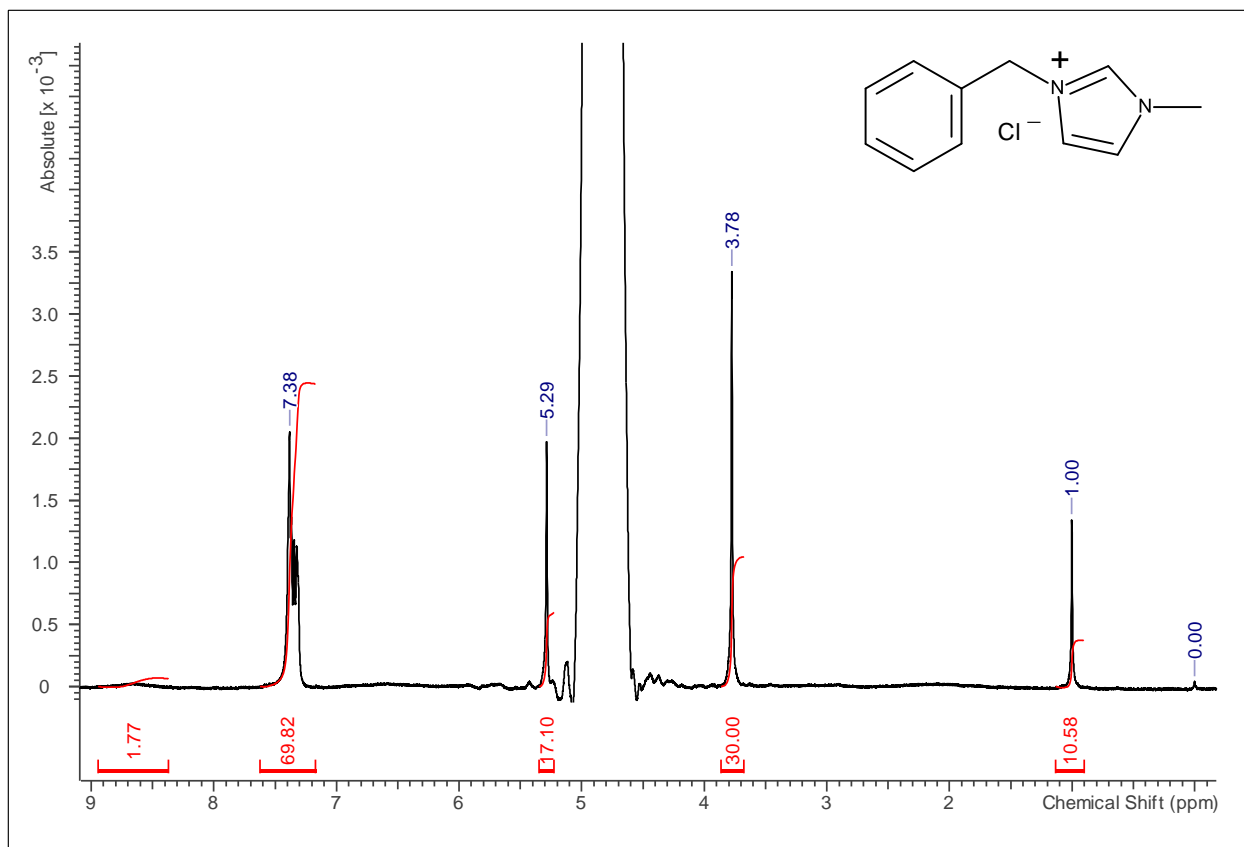
**Figure S2 –** Proton NMR spectrum of 0.83 wt % benzylmethylimidazolium chloride **2** in 1 M KOH containing 0.05 wt % pivalic acid, before start of decomposition reaction.  Peak at 1.00 ppm is pivalate internal standard; C2 proton signal at 8.6 ppm is broadened and attenuated by rapid exchange into water signal; and, while it was easily visible, obtaining accurate integrals on the benzylic methylene signal at 5.29 ppm even after baseline correction was difficult due to extensive overlap with water signal.  Thus, integrals of the N-methyl and aromatic region signals were used in the kinetic analysis.
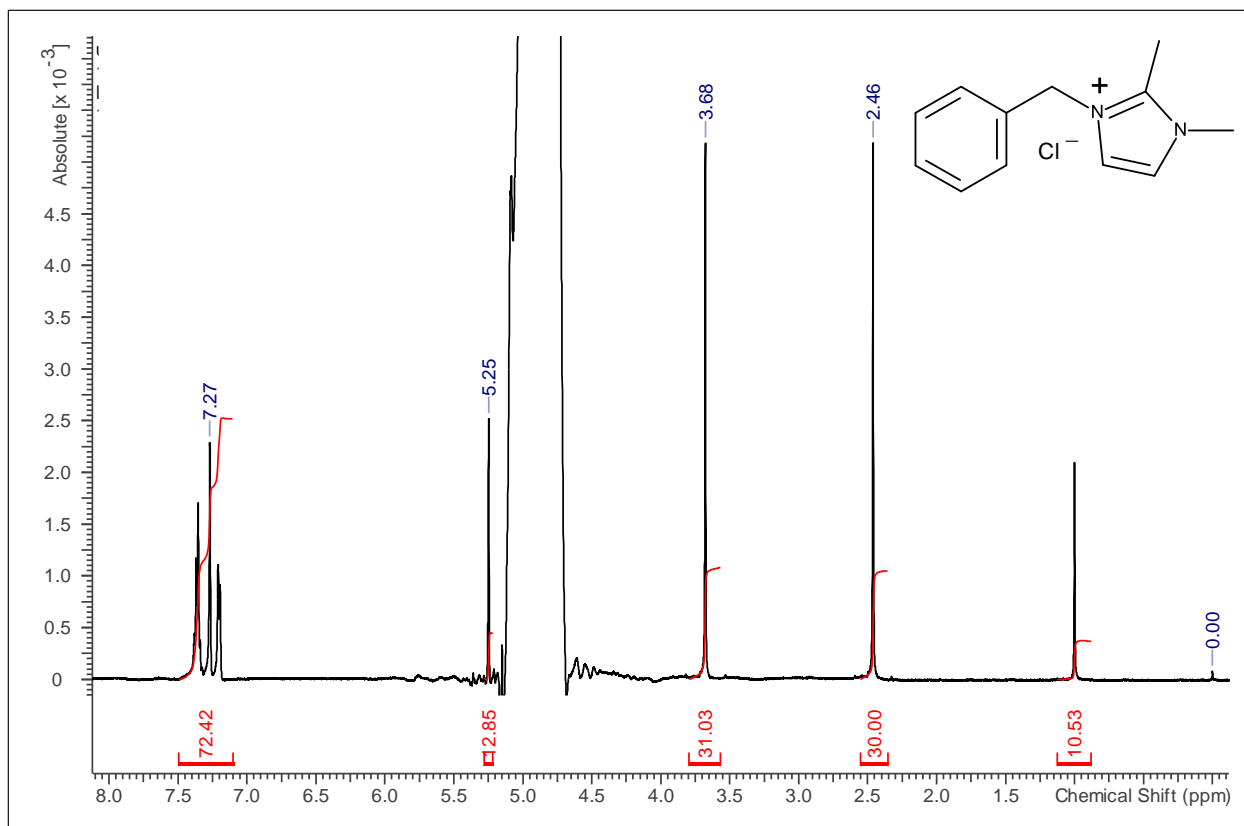
**Figure S3 –** Proton NMR spectrum of 0.89 wt % benzyldimethylimidazolium chloride **3** in 1 M KOH containing 0.05 wt % pivalic acid, before start of decomposition reaction.  Peak at 1.00 ppm is pivalate internal standard; and, while it was easily visible, obtaining accurate integrals on the benzylic methylene signal at 5.25 ppm even after baseline correction was difficult due to extensive overlap with water signal.  Thus, integrals of the N-methyl and aromatic region signals were used in the kinetic analysis.
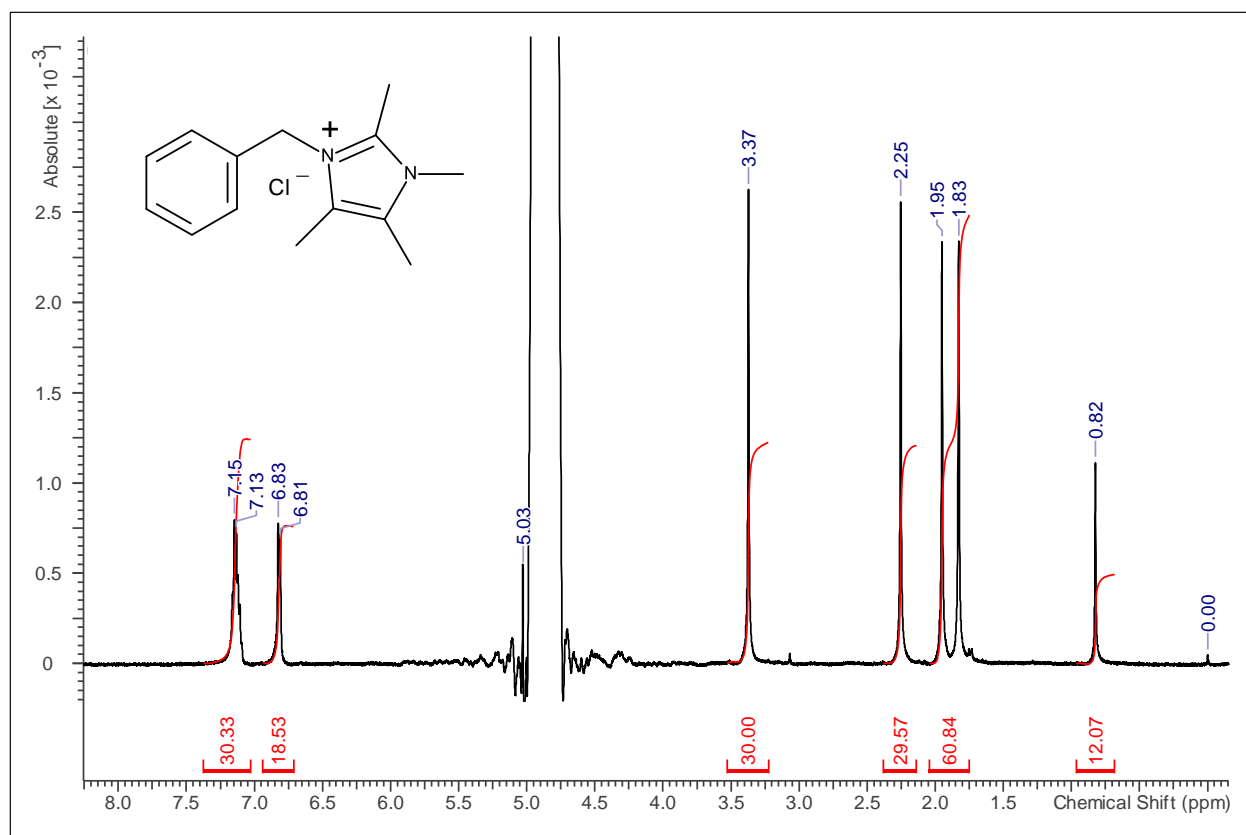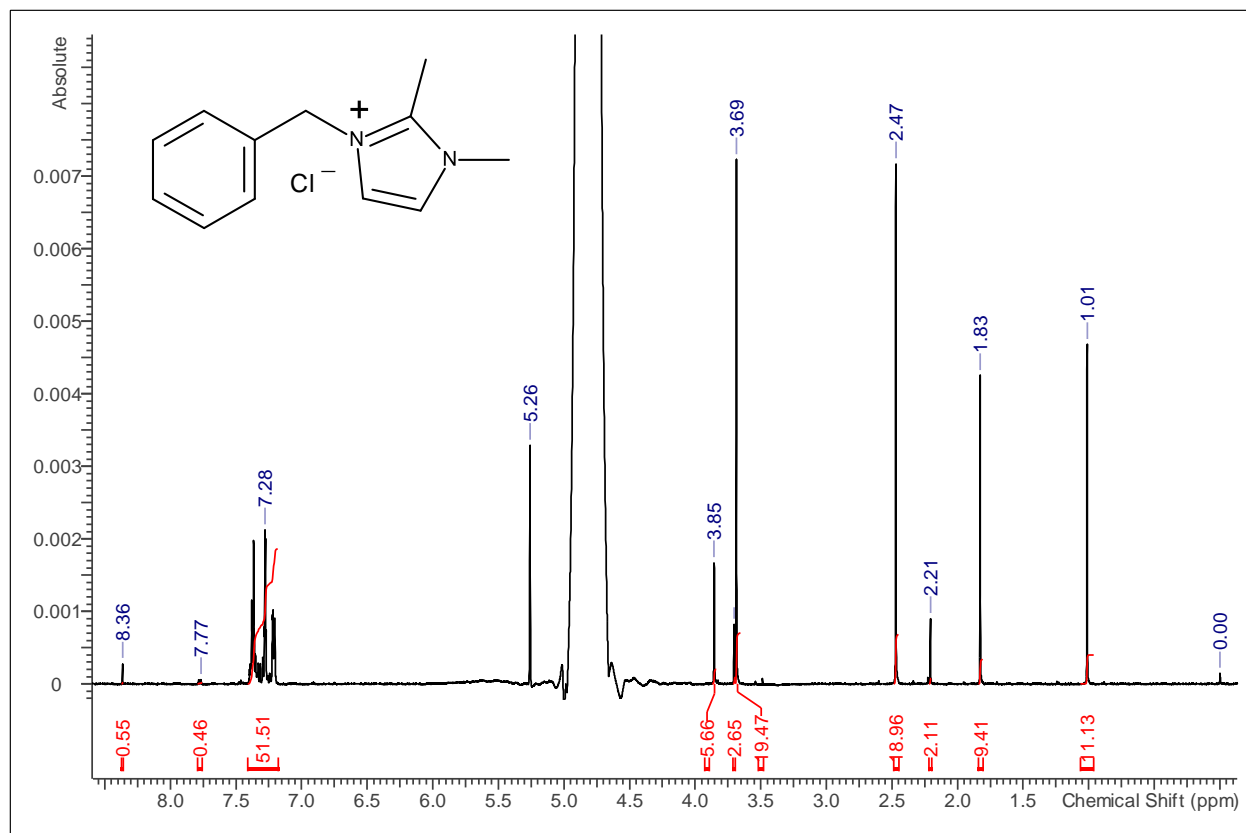
**Figure S4 –** Proton NMR spectrum of 1.00 wt % benzyltetramethylimidazolium chloride **4** in 4.25 M KOH containing 0.05 wt % pivalic acid, before start of decomposition reaction. Peak at 0.82 ppm is pivalate internal standard; and, although it was observable, the benzylic methylene signal at 5.03 ppm was severely overlapped with the water signal, could not be integrated reliably even after baseline correction, and was not used in the kinetic analysis.
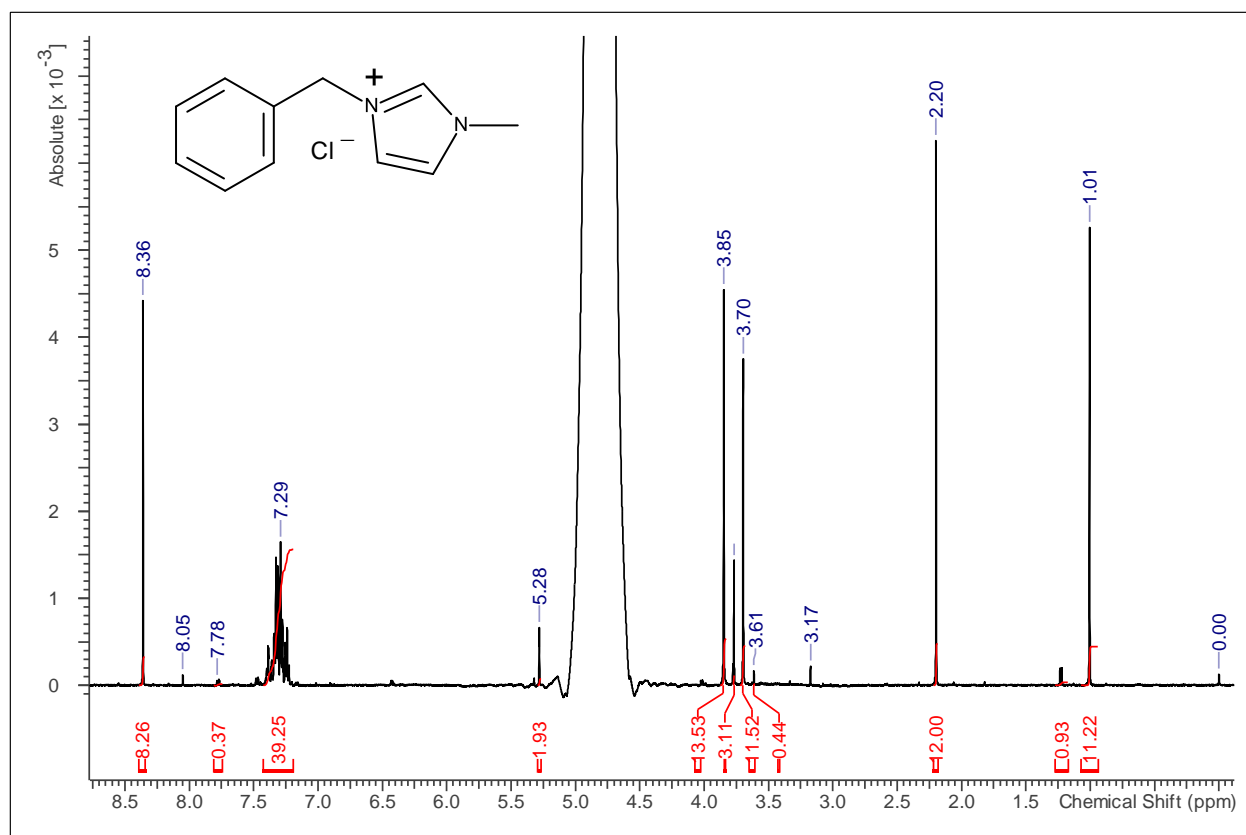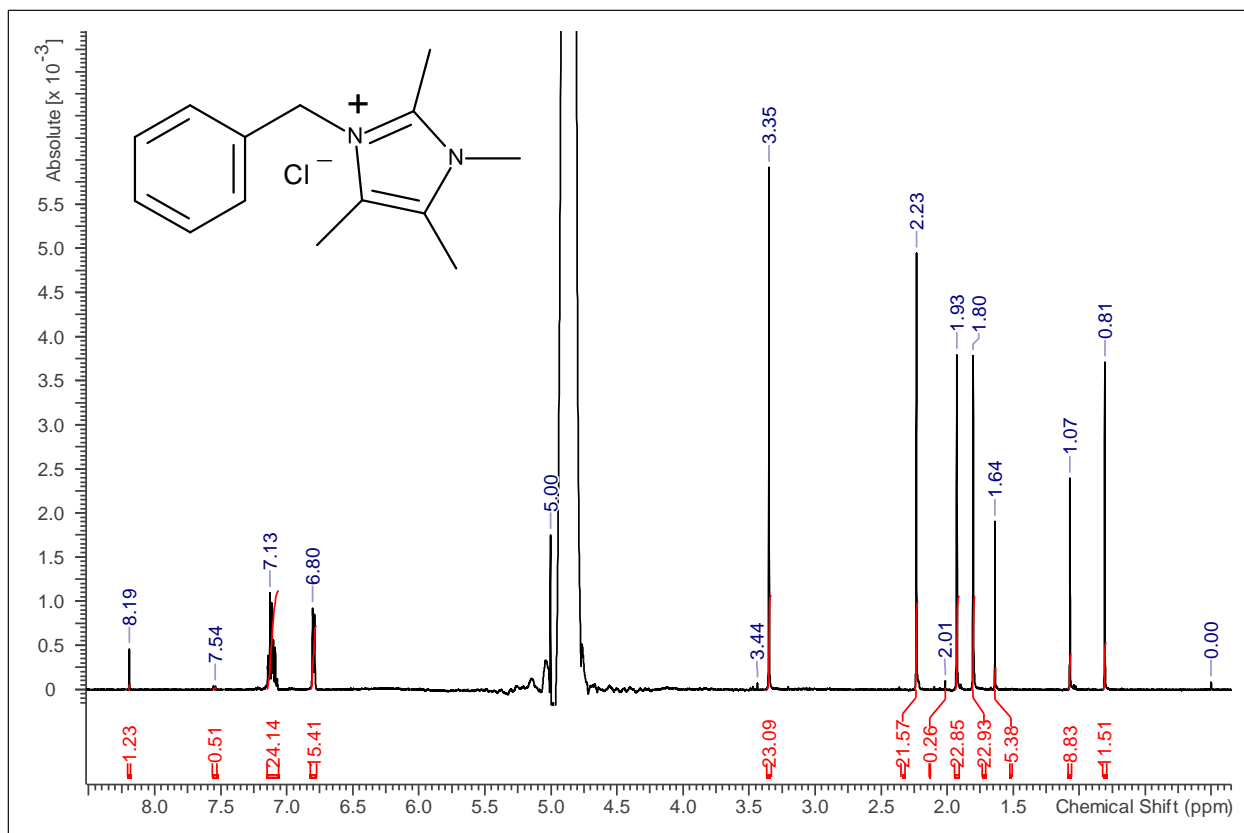
**Figure S5** – Sample proton NMR spectrum of reaction mixture from benzylmethylimidazolium chloride **2** decomposition in 1 M KOH solution in FEP – 2 days/80 °C, 90 mole % consumption of **2**. Assignments: starting material , 3.77, 5.28 ppm; pivalate internal standard, 1.01 ppm; methylamine, 2.2 ppm; benzylamine, 3.70, 7.25-7.3 ppm; glycolate, 3.85 ppm; benzoate, 7.78 ppm; formate, 8.36 ppm; lactate, 1.22 ppm; unassigned, 3.17, 3.61, 8.05 ppm (see text for discussion of latter peak).

**Figure S6** – Sample proton NMR spectrum of reaction mixture from benzyldimethylimidazolium chloride **3** decomposition in 1M KOH solution in FEP – 20 days/80 °C, 38 mole % consumption of **3**. Assignments: starting material , 2.47, 3.69, 5.26, 7.2-7.4 ppm; pivalate internal standard, 1.01 ppm; acetate, 1.83 ppm; methylamine, 2.21 ppm; benzylamine, 3.69, 7.25-7.3 ppm; glycolate, 3.85 ppm; benzoate, 7.77 ppm; formate, 8.36 ppm.

**Figure S7** – Proton NMR spectrum of reaction mixture from benzyltetramethylimidazolium chloride **4** decomposition in 4.25 M KOH solution in FEP – 44 days/80 °C, 23 mole % consumption of **4.** Assignments:  starting material , 1.80, 1.93, 2.23, 3.35, 6.80, 7.13 ppm; pivalate internal standard, 0.81 ppm; 2-hydroxyisobutyrate, 1.07 ppm; acetate, 1.64 ppm; methylamine, 2.01 ppm; benzoate, 7.54 ppm; formate, 8.19 ppm; unassigned, 3.44 ppm.

**Table S2** – Degradation of BTMImCl (**4**) in 4.25 M KOH solution, comparison of runs in PTFE and FEP (data for latter from Table 3).

| Reactor | Mole Frac 4 Reacted | Product Analysis | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Mole Products per Mole 4 Reacted | | | | | | |
| | | Acetate | 2-HIB | Methylamine | Formate | Benzoate | Benzylamine | Benzyl Alcohol |
| PTFE | 0.13 | 0.73 | 0.50 | 0.30 | 0.21 | 0.10 | 0.31 | 0.11 |
| FEP | 0.15 | 0.81 | 0.68 | 0.05 | 0.44 | 0.04 | -- | -- |
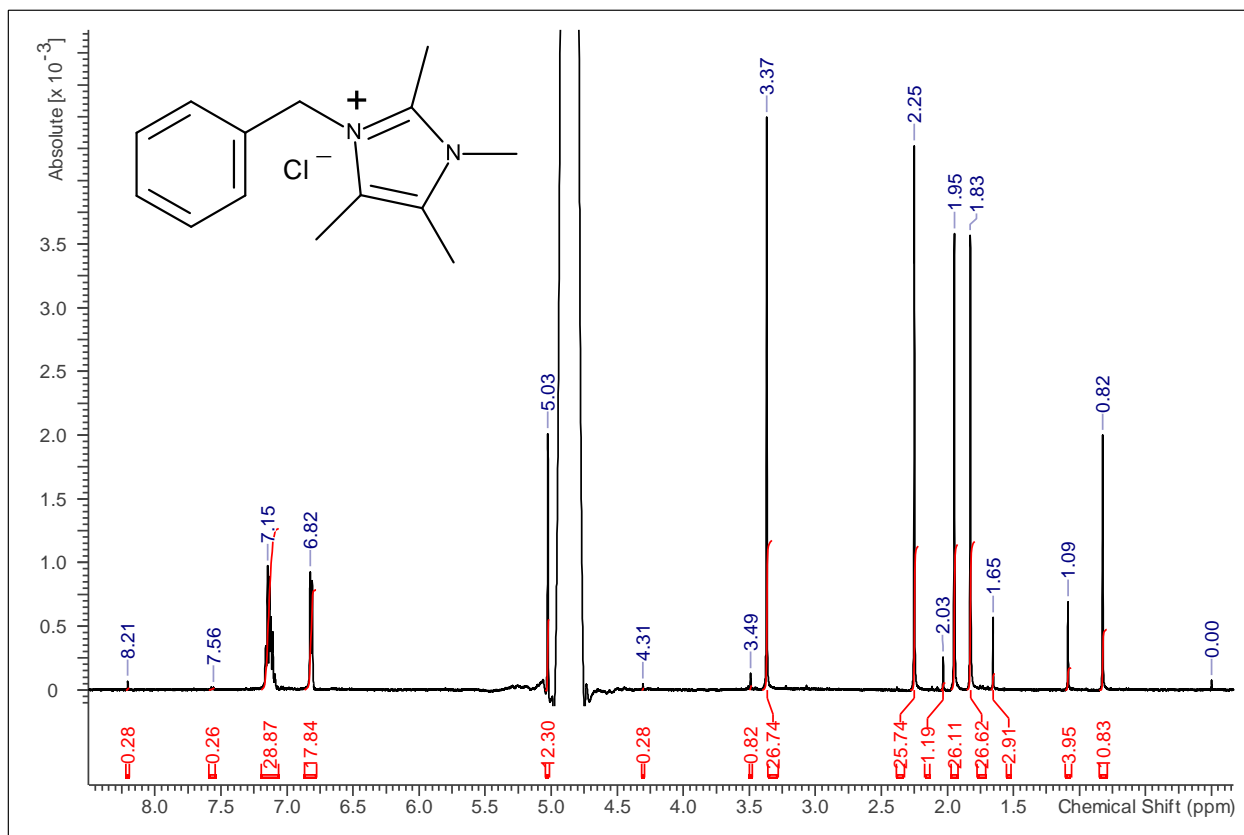


**Figure S8** – Reaction solution from decomposition of **4**/KOH solution in PTFE sealed reactor – 27 days/80 °C, 13 mole % consumption of **4**. Assignments: 1.83, 1.95, 2.25, 3.37, 5.03, 6.82, 7.15 ppm – starting material **4**; 0.82 ppm, pivalate internal integration standard; 1.09 ppm, 2-hydroxyisobutyrate; 1.65 ppm, acetate; 2.03 ppm, methylamine; 3.49 ppm, benzylamine; 4.31 ppm, benzyl alcohol; 7.56 ppm, benzoate; 8.21 ppm, formate. Assignments for benzyl alcohol and benzylamine were confirmed by spiking with authentic samples.