# Electronic Supporting Information

## Unraveling the Cation and Anion Effects and Kinetics for Ionic Liquid Catalyzed Direct Synthesis of Methyl Acrylate at Mild Condition

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## I. Purity of [Cation]F-type ionic liquid

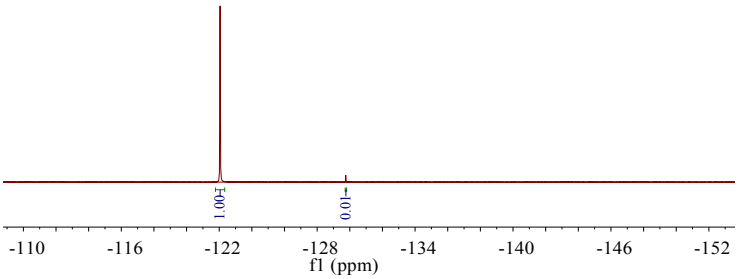
**Table S1** Purity of [Cation]F-type ionic liquids

| [Cation]F | Purity /% [a] | [Cation]F | Purity /% [a] |
|---|---|---|---|
| [EMIM]F | 99 | [Hpy]F | 99 |
| [PMIM]F | 99 | [Opy]F | 98 |
| [BMIM]F | 99 | [N2,2,2,2]F | 99 |
| [HMIM]F | 99 | [N3,3,3,3]F | 99 |
| [Epy]F | 98 | [N4,4,4,4]F | 98 |
| [Bpy]F | 98 | [N8,8,8,8]F | 99 |

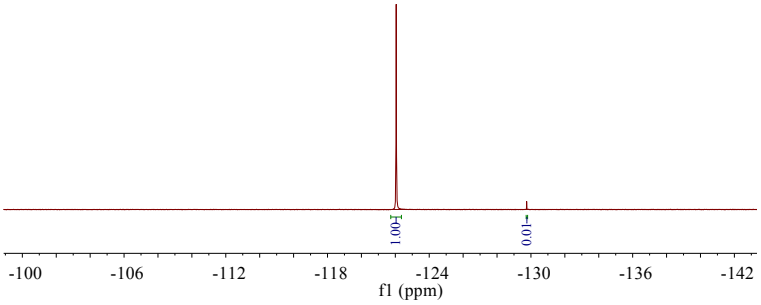
[a] The purity of ILs-F were determined with $^{19}$F-NMR.

## II. $^{19}$F-NMR spectra for purity determination of [Cation]F-type ionic liquid

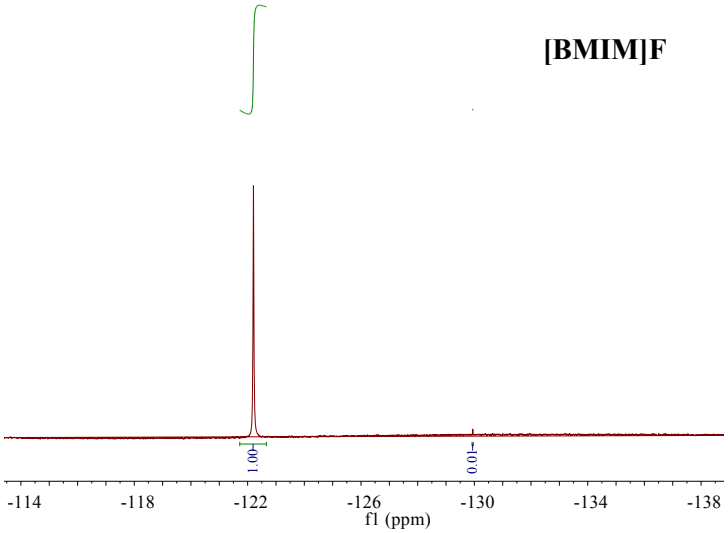
**[EMIM]F**



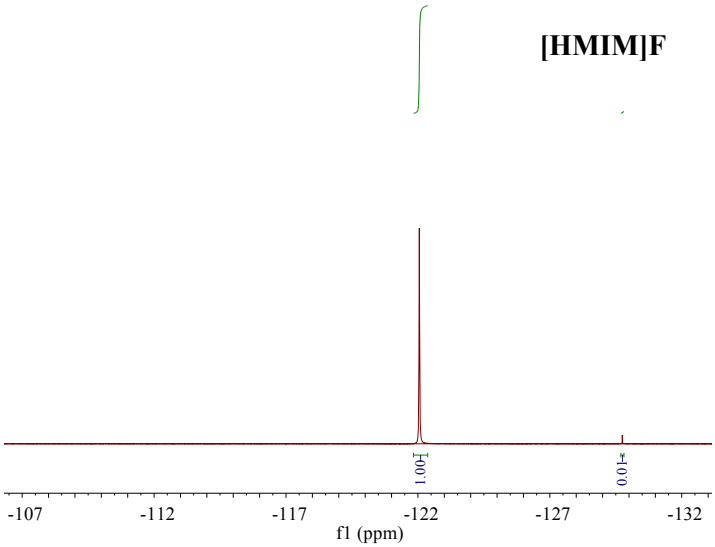

**[PMIM]F**



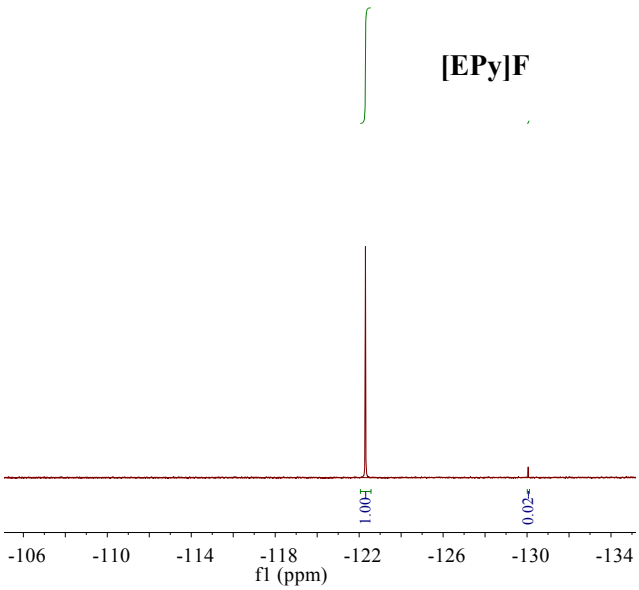
**[BMIM]F**



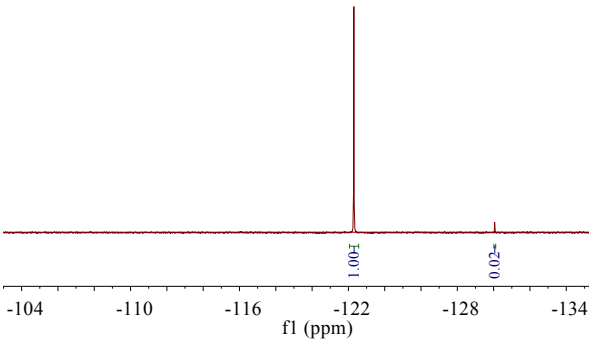

**[HMIM]F**



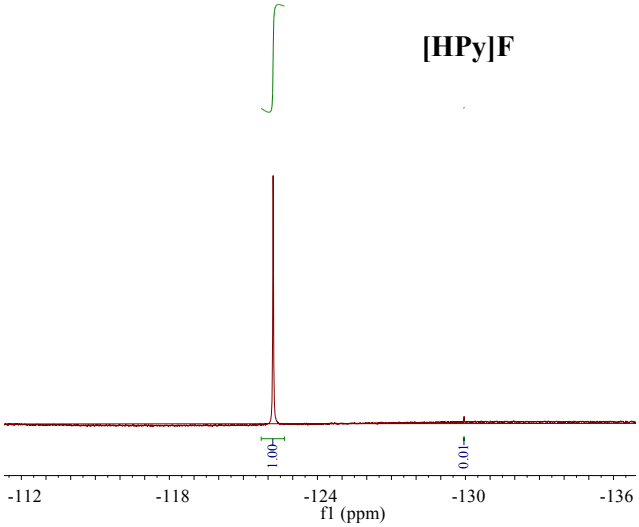

**[EPy]F**



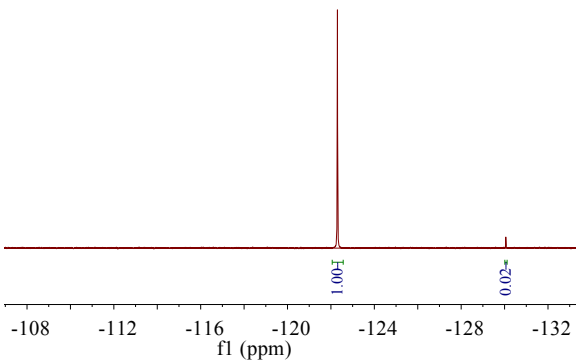
**[BPy]F**



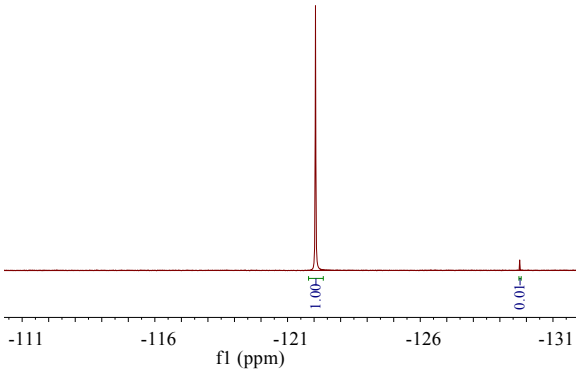

**[HPy]F**



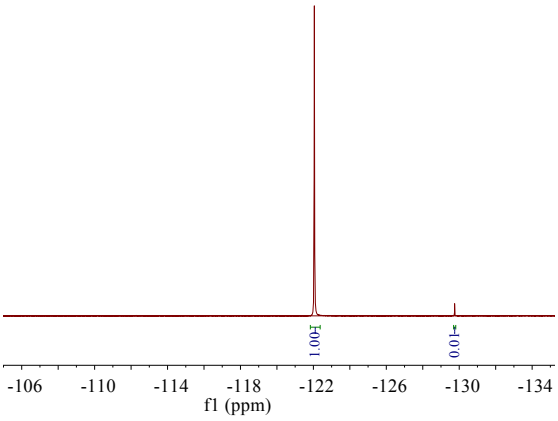

**[OPy]F**



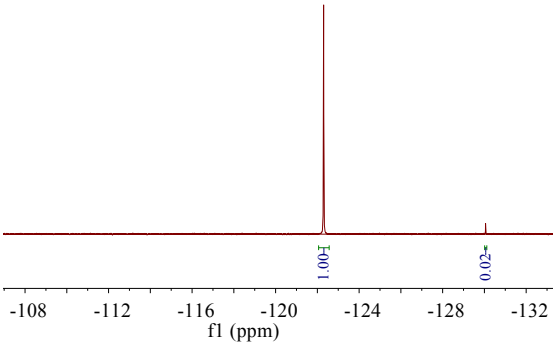
**[N2,2,2,2]F**

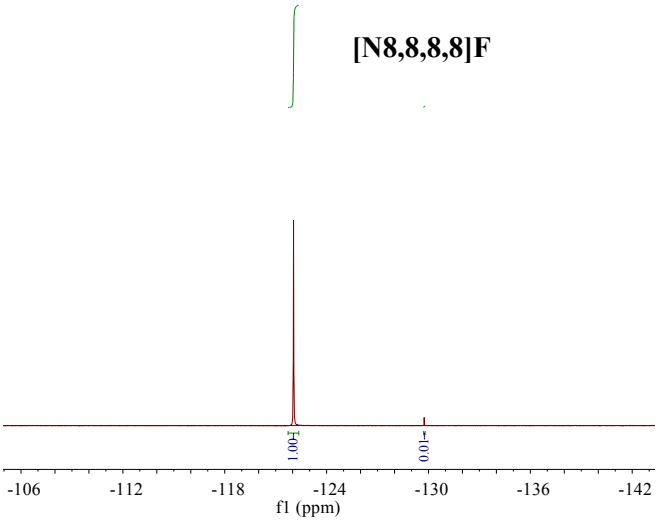



**[N3,3,3,3]F**




**[N4,4,4,4]F**






## III. Supplementary experiments for catalytic system evaluation

**Table S2** Yield of 1-methoxy-1-trimethylsilyloxyethene and MA during synthesis reaction with catalysis of [Cation]F [a]

| Ionic liquid | Yield of 1-methoxy-1-trimethylsilyloxyethene /% [b] | Yield of MA /% |
|---|---|---|
| [EMIM]F | 51.1 | 0 |
| [PMIM]F | 53.9 | 0 |
| [BMIM]F | 56.8 | 0 |
| [HMIM]F | 51.7 | 0 |
| [EPy]F | 44.1 | 0 |
| [BPy]F | 46.9 | 0 |
| [HPy]F | 50.7 | 0 |
| [OPy]F | 48.1 | 0 |
| [N2,2,2,2]F | 57.3 | 0 |
| [N3,3,3,3]F | 60.9 | 0 |
| [N4,4,4,4]F | 56.7 | 0 |
| [N8,8,8,8]F | 53.8 | 0 |

[a] Reaction condition: 0.1 mol/L methyl acetate, trioxane and BSA in the solvent of $CH_2Cl_2$, 5 wt.% [Cation]F ionic liquid catalyst, 25°C, 3 h.

[b] The yield was calculated based on methyl acetate.

**Table S3** Conversion of trioxane during the decomposition reaction without methyl acetate [a]

| Ionic liquid | Conversion of trioxane /% | Selectivity of formaldehyde /% |
|---|---|---|

| | | |
|---|---|---|
| [N3,3,3,3]Cl/CuCl | 77.4 | 100 |
| [N3,3,3,3]Cl/$FeCl_3$ | 84.5 | 100 |
| [N3,3,3,3]Cl/$ZnCl_2$ | 88.3 | 100 |
| [N3,3,3,3]Cl/$AlCl_3$ | 93.6 | 100 |

[a] Reaction condition: 0.1 mol/L trioxane in $CH_2Cl_2$, 5 wt.% [N3,3,3,3]Cl/$MCl_x$ ionic liquid catalyst, 25°C, 3 h.

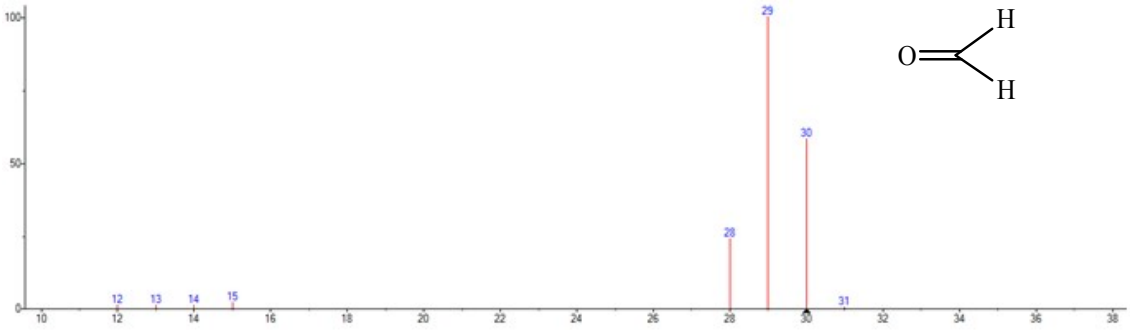
**Table S4** Yield and selectivity of MA during the aldol reaction between 1-methoxy-1-trimethylsilyloxyethene and trioxane [a]

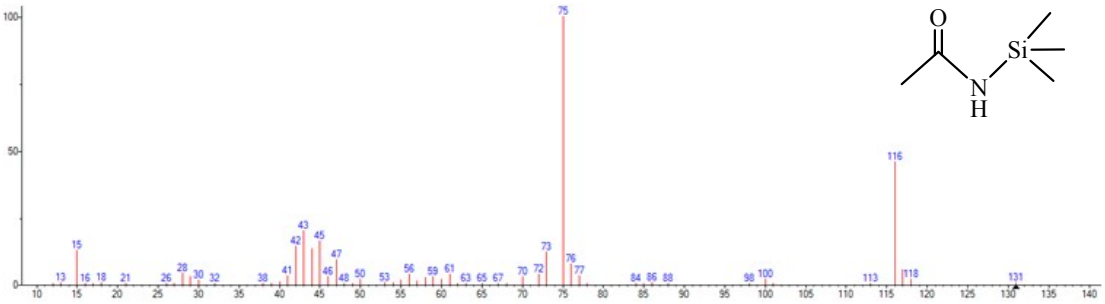
| Ionic liquid | Yield of MA /% [b] | Selectivity of MA /% [b] |
|---|---|---|
| [N3,3,3,3]Cl/CuCl | 48.8 | 99.7 |
| [N3,3,3,3]Cl/$FeCl_3$ | 60.3 | 99.8 |
| [N3,3,3,3]Cl/$ZnCl_2$ | 72.5 | 100 |
| [N3,3,3,3]Cl/$AlCl_3$ | 83.2 | 100 |

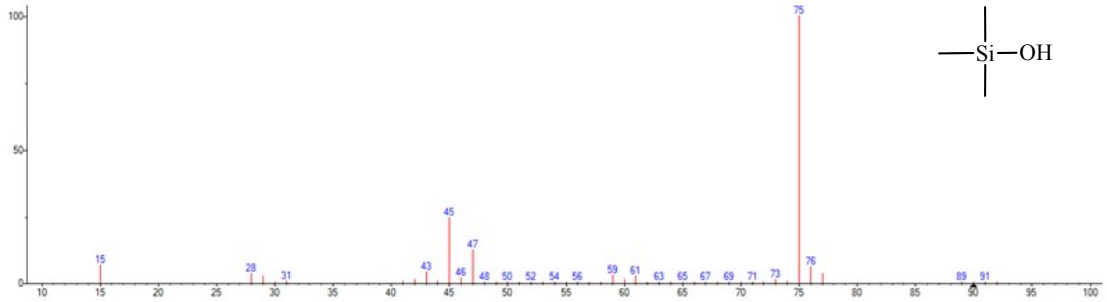
[a] Reaction condition: 0.1 mol/L 1-methoxy-1-trimethylsilyloxyethene and trioxane in $CH_2Cl_2$, 5 wt.% [N3,3,3,3]Cl/$MCl_x$ ionic liquid catalyst, 25°C, 2.5 h.

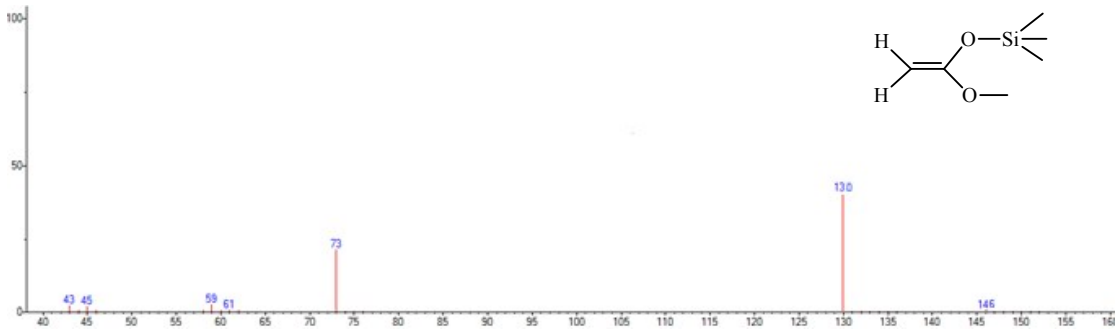
[b] The yield and selectivity were calculated based on 1-methoxy-1-trimethylsilyloxyethene

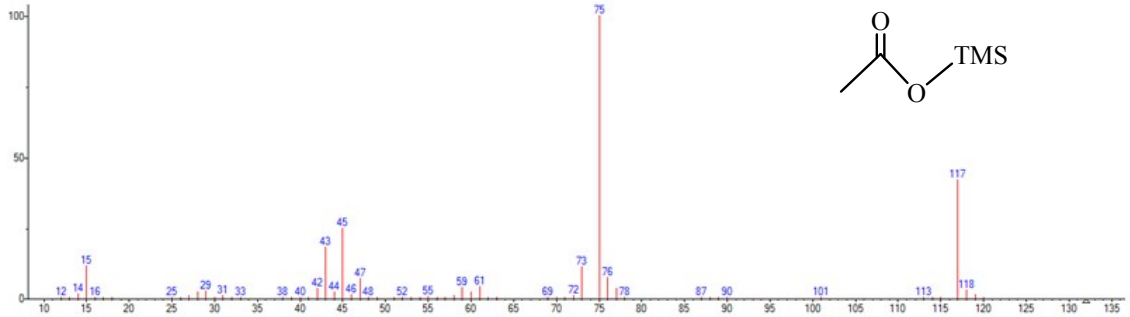
## IV. MS information of intermediates

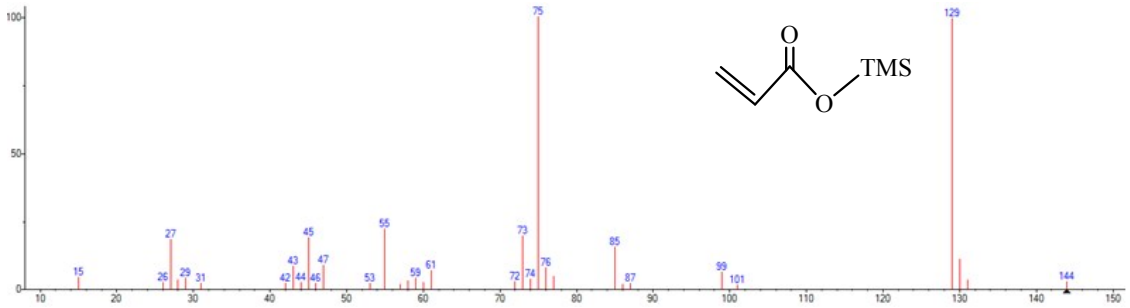



Si—OH


H
O—Si
H
O—


O
TMS
O


O
TMS
O