

## Supplementary Information

### **A remarkable anion effect on palladium nanoparticle formation and stabilization in hydroxyl-functionalized ionic liquids**

Xiao Yuan,<sup>a,b</sup> Ning Yan,<sup>a</sup> Sergey A. Katsyuba,<sup>c</sup> Elena E. Zvereva,<sup>c</sup> Yuan Kou,<sup>b,\*</sup> and Paul J. Dyson<sup>a,\*</sup>

<sup>a</sup> *Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. Email: paul.dyson@epfl.ch.*

<sup>b</sup> *PKU Green Chemistry Centre, Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China. Email: yuankou@pku.edu.cn*

<sup>c</sup> *A.E.Arbusov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, Arbuzov str. 8, 420088 Kazan, Russia.*

#### **FT-IR analysis**

##### **Samples**

- 1) [C<sub>2</sub>OHmim][Tf<sub>2</sub>N].
- 2) Pd(OAc)<sub>2</sub> (0.1 mM) dissolved in [C<sub>2</sub>OHmim][Tf<sub>2</sub>N].
- 3) Pd NPs (0.1 mM) dispersed in [C<sub>2</sub>OHmim][Tf<sub>2</sub>N], prepared by thermal decomposition of Pd(OAc)<sub>2</sub> at 393 K for 30 min with rapid stirring.

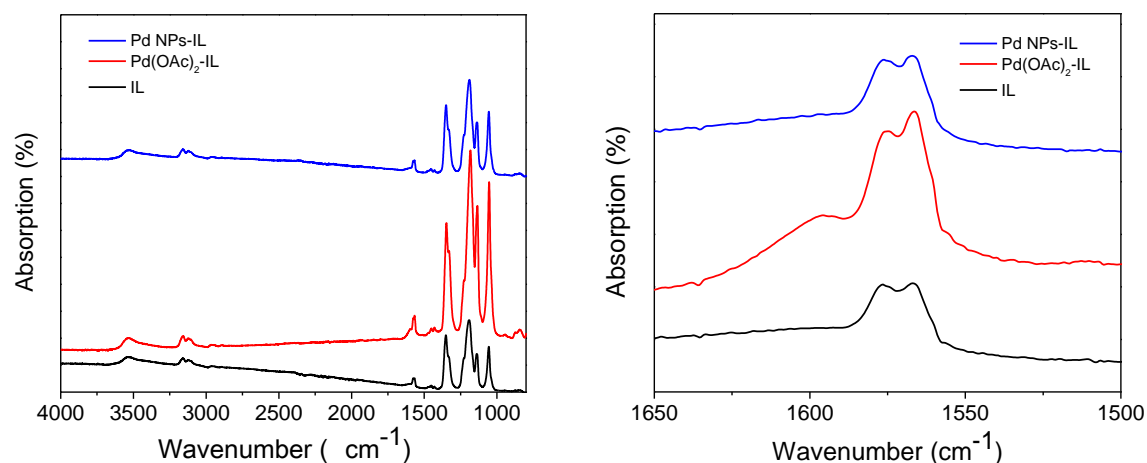


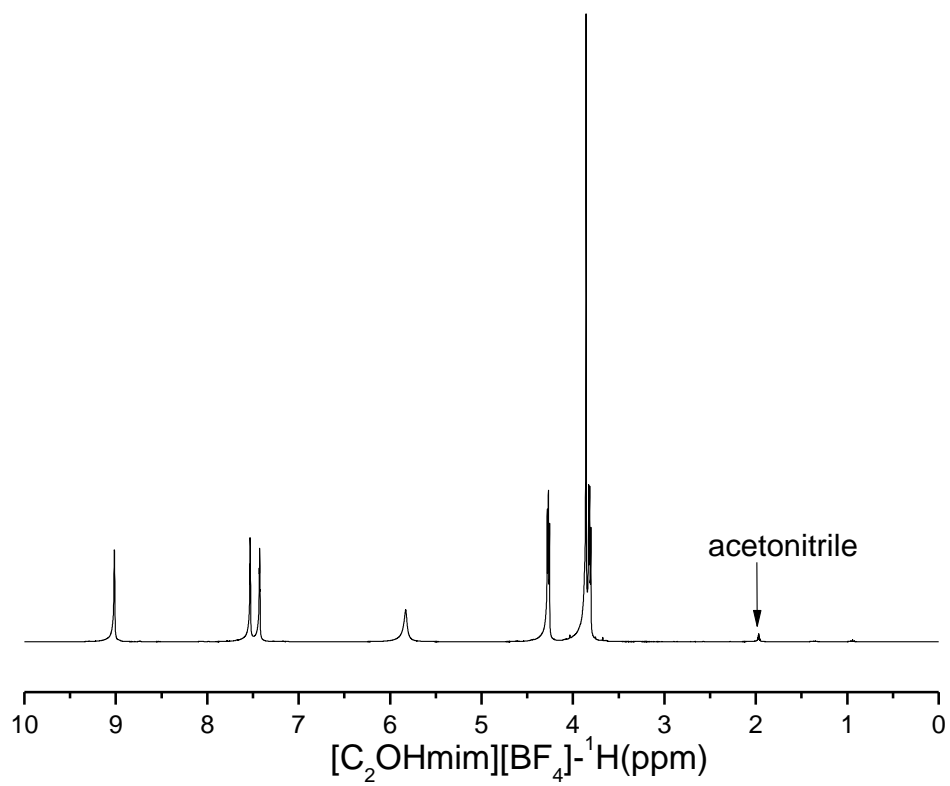
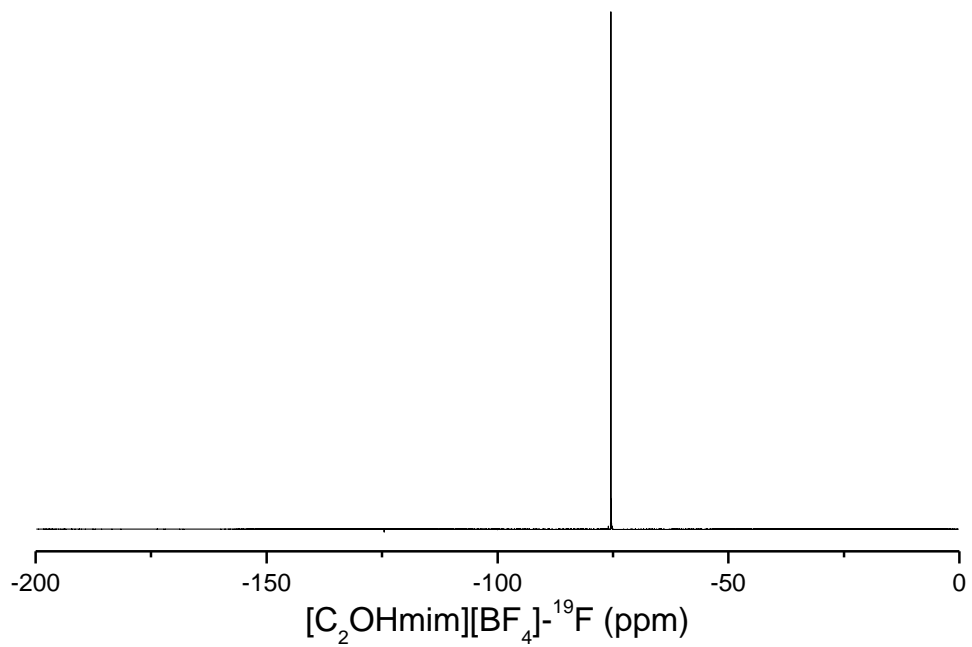
Fig S1 FT-IR spectroscopy of [C<sub>2</sub>OHmim][Tf<sub>2</sub>N], Pd(OAc)<sub>2</sub>-[C<sub>2</sub>OHmim][Tf<sub>2</sub>N] and Pd NPs-[C<sub>2</sub>OHmim][Tf<sub>2</sub>N] left) full spectra; and right) the C=O band region. Spectra were recorded on a Perkin Elmer Spectrum (600-4000 cm<sup>-1</sup>) installed with the ATR accessory (IR-ATR).

The IR spectra reveal: 1) the decomposition of Pd(OAc)<sub>2</sub> was complete, as the characteristic absorption band at ca. 1600 cm<sup>-1</sup> disappears after thermal decomposition; and 2) [C<sub>2</sub>OHmim] does not act as the reductant as no new absorption band for a C=O functionality was observed after the formation of Pd NPs.

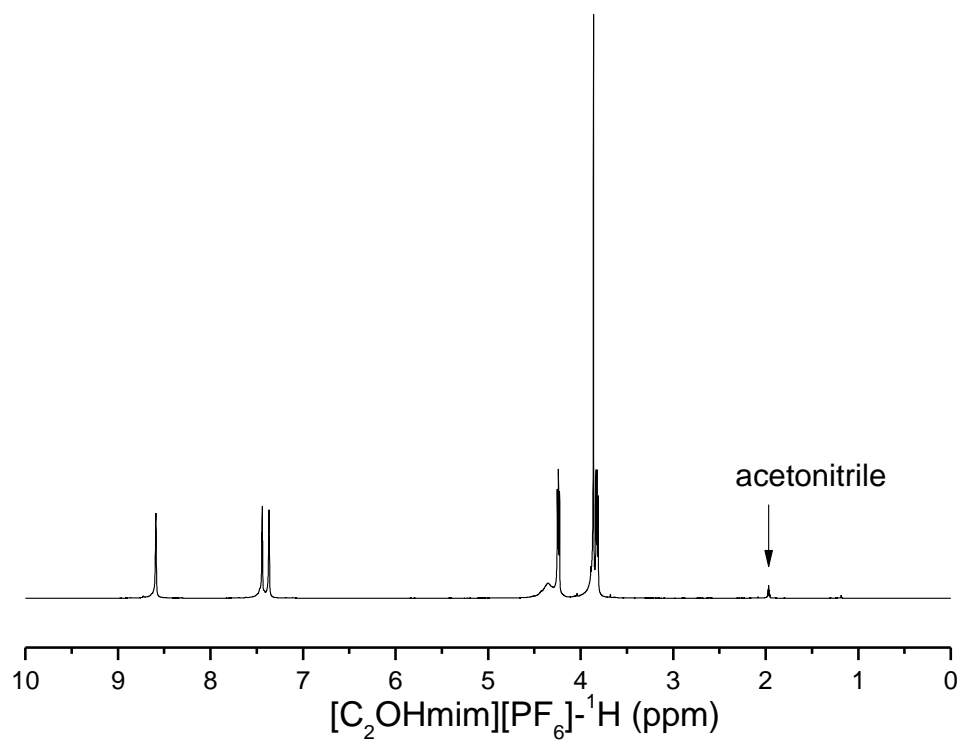
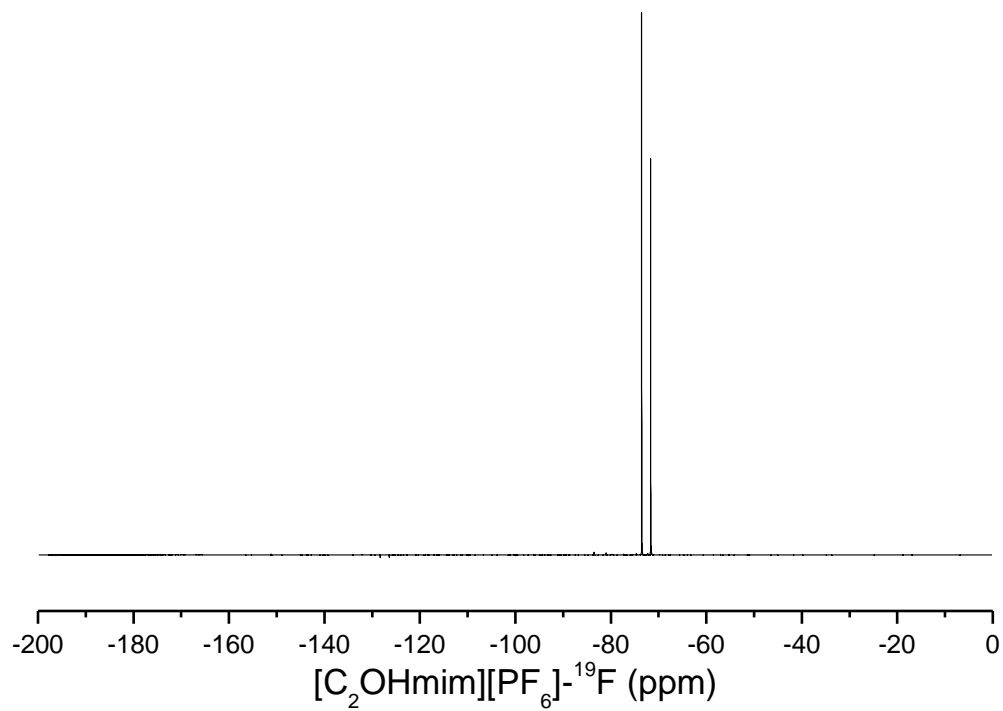
### NMR analysis of the ionic liquids

NMR spectra of the ionic liquid dissolved in CD<sub>3</sub>CN were obtained at 20°C with a Bruker AVANCE-400 instrument.

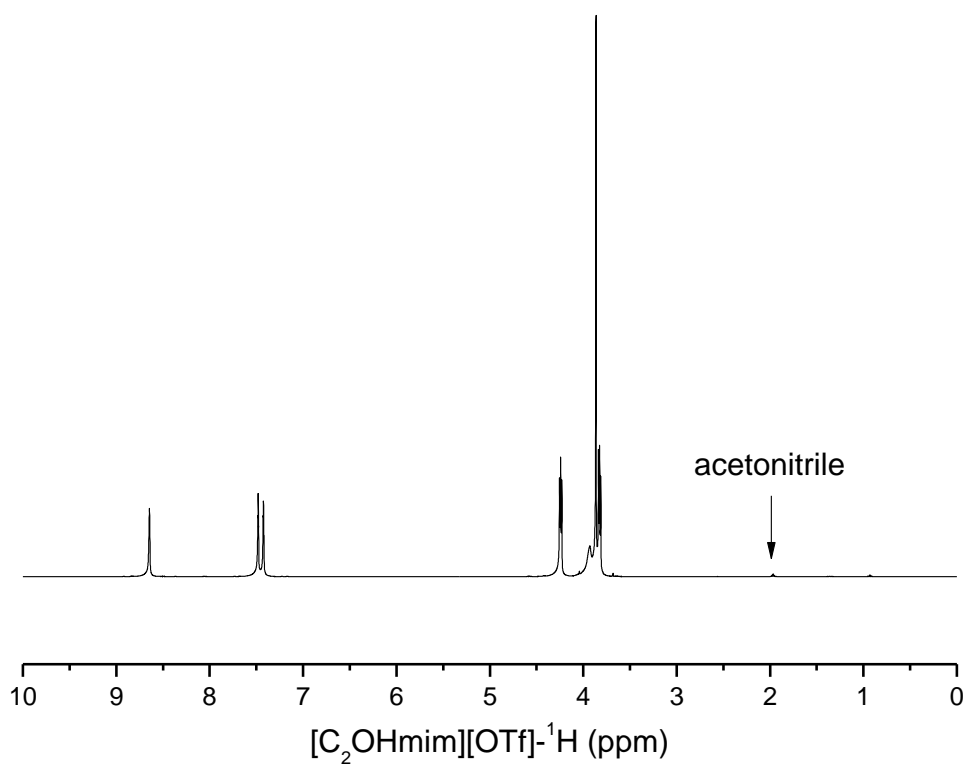
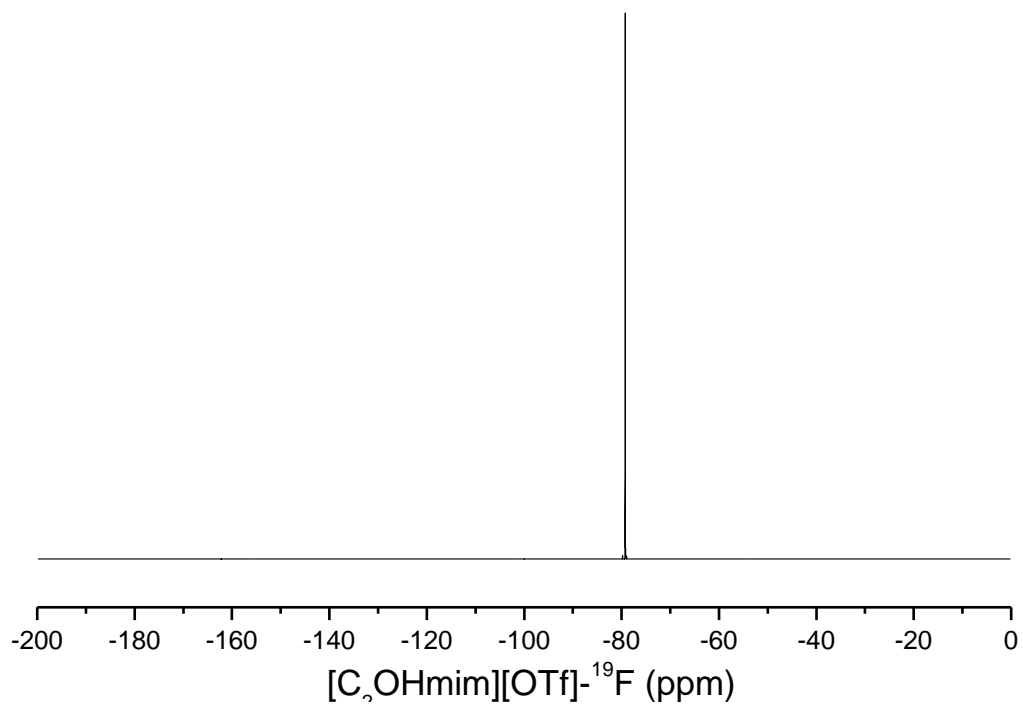
**[C<sub>2</sub>OHmim][BF<sub>4</sub>]**



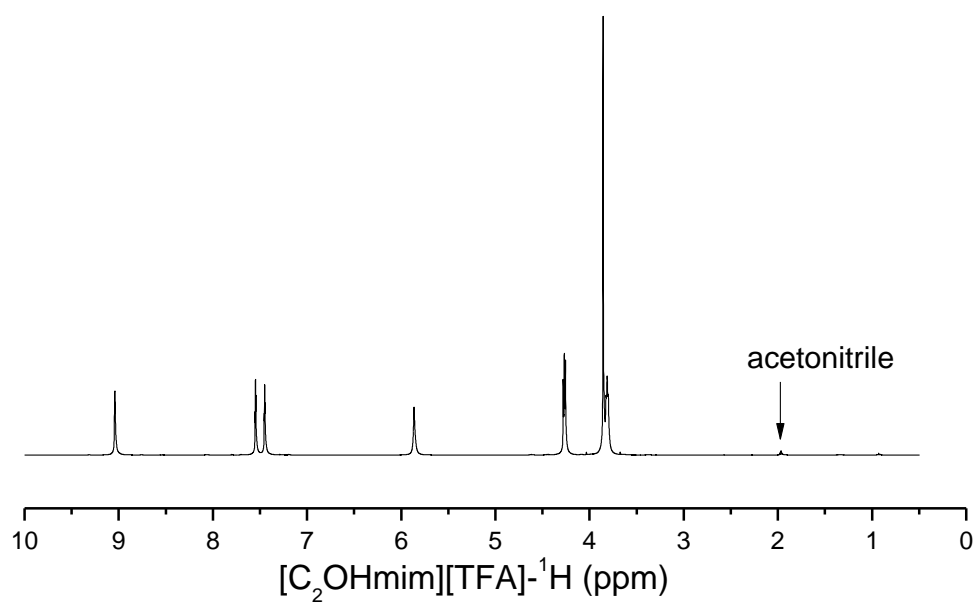
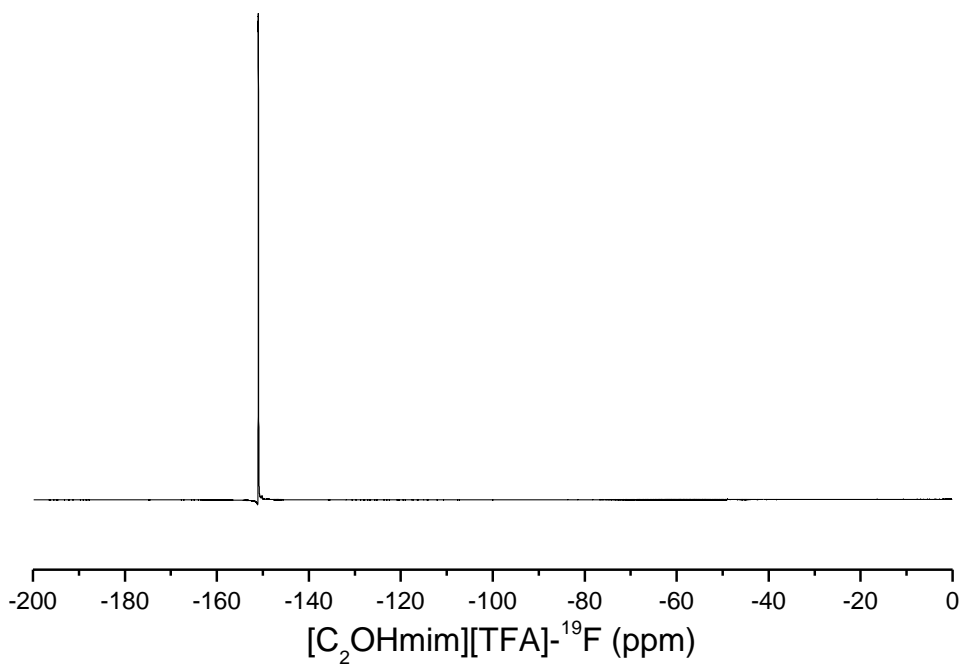
**[C<sub>2</sub>OHmim][PF<sub>6</sub>]**



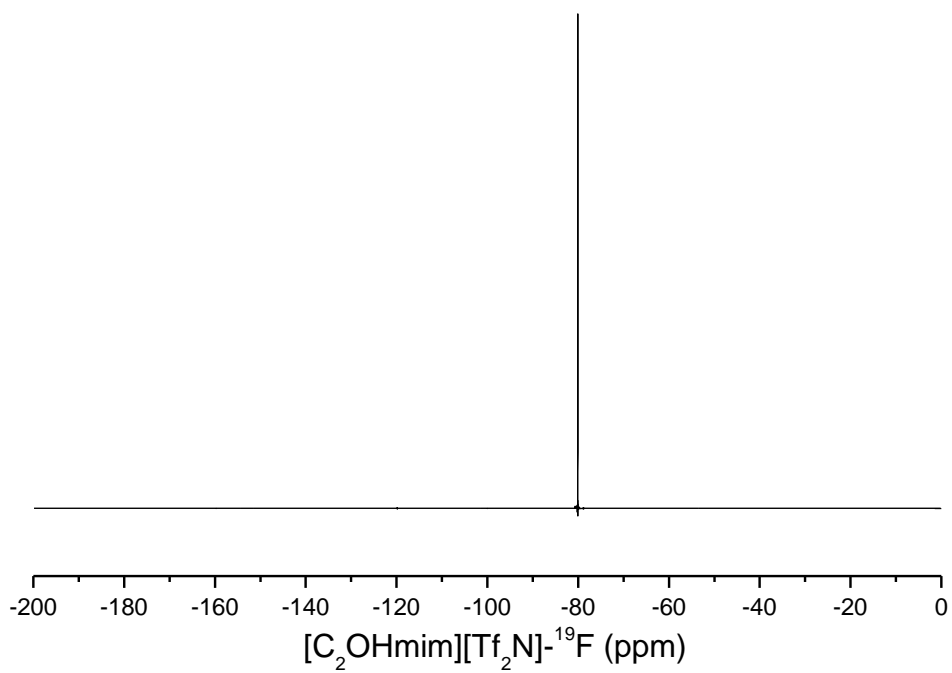
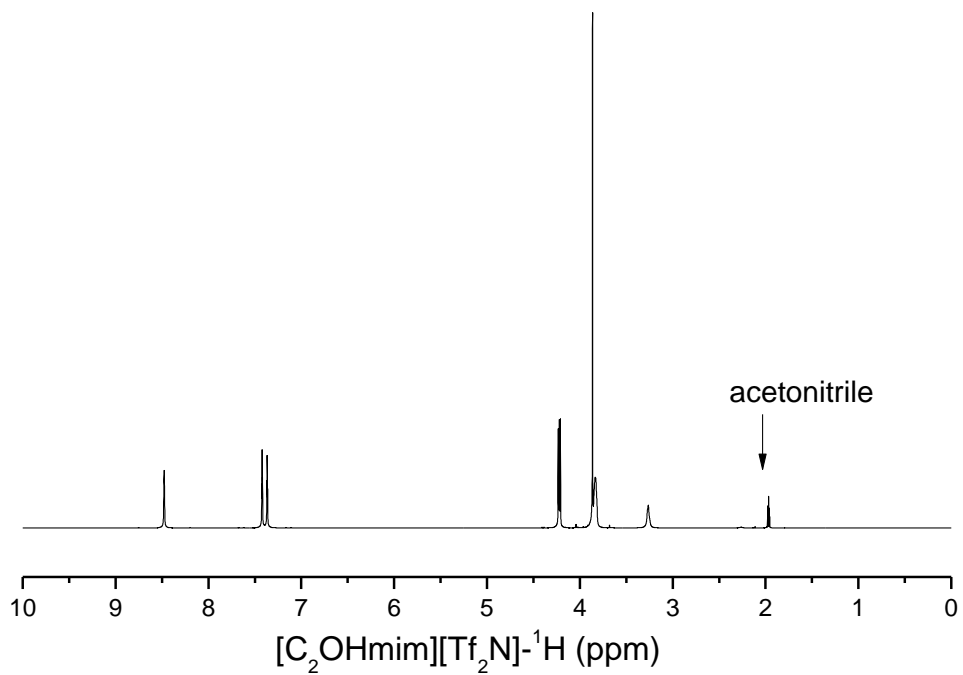
**[C<sub>2</sub>OHmim][OTf]**



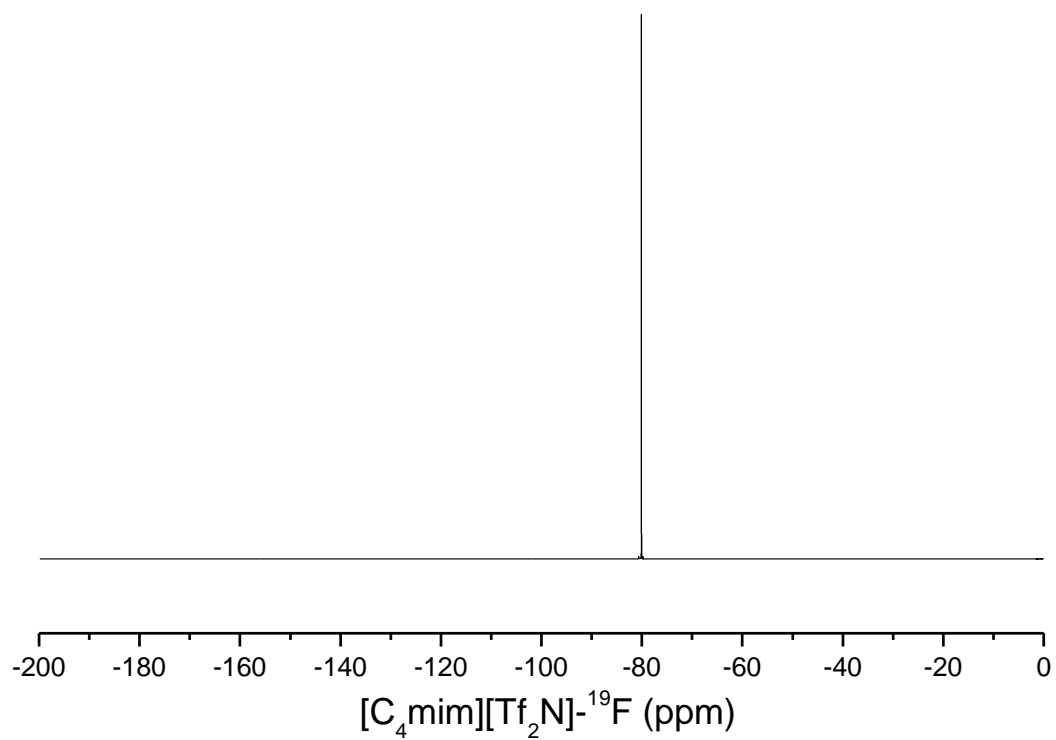
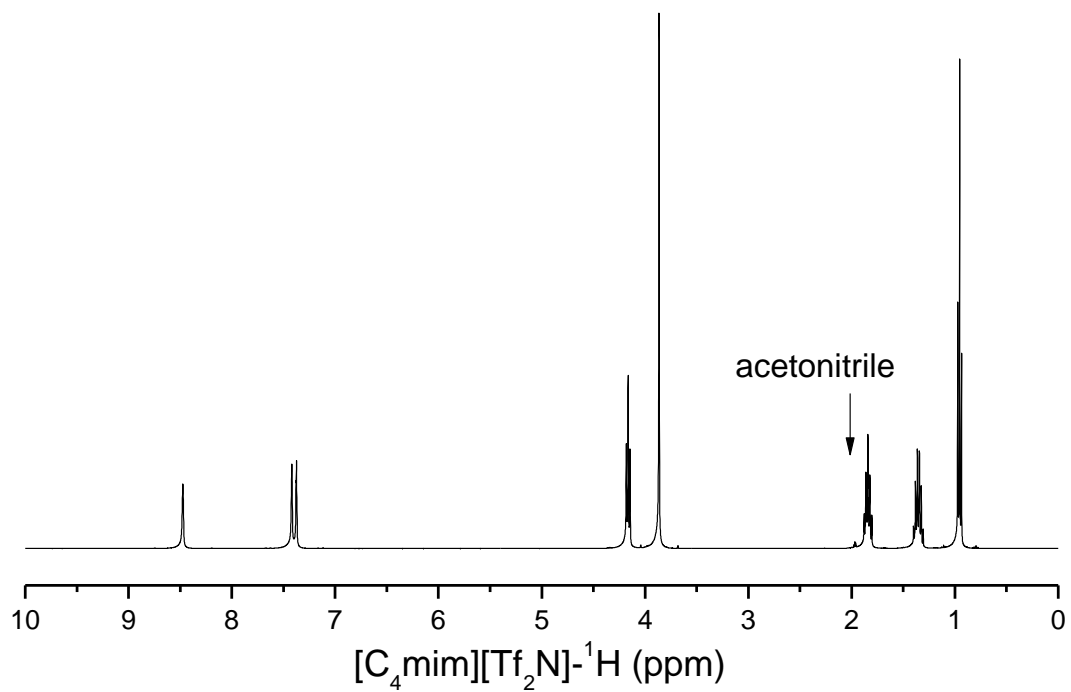
**[C<sub>2</sub>OHmim][TFA]**



**[C<sub>2</sub>OHmim][Tf<sub>2</sub>N]**



**[C<sub>4</sub>mim][Tf<sub>2</sub>N]**





## References

- 1 X. Yang, N. Yan, Z. F. Fei, R. M. Crespo-Quesada, G. Laurenczy, L. Kiwi-Minsker, Y. Kou, Y. D. Li and P. J. Dyson, *Inorg. Chem.*, 2008, **47**, 7444-7446.
- 2 A. H. Jalili, A. Mehdizadeh, M. Shokouhi, H. Sakhaeinia and V. Taghikhani, *J. Chem. Thermodyn.*, 2010, **42**, 787-791.
- 3 L. C. Branco, J. N. Rosa, J. J. M. Ramos and C. A. M. Afonso, *Chem. Eur. J.*, 2002, **8**, 3671-3677.