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Preparation, Cation-Anion Interactions and Physicochemical Properties of Ether-Functionalized Imidazolium Ionic Liquids

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Experimental

General

All reactions were carried out under an argon atmosphere in dried glassware using standard Schlenk, syringe and septa techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova 300 MHz spectrometer in $CDCl_3$ or d6-acetone. Chemical shifts are reported relative to TMS in $CDCl_3$ (δ 0.00 for ^{1}H), residual d5-acetone (δ 2.05 for ^{1}H), $CDCl_3$ (δ 77.00 for ^{13}C), and d6-acetone (δ 30.5 for ^{13}C). Chemical shifts δ are quoted in parts per million (ppm), and coupling constants J are given in hertz (Hz). IR-spectra were recorded in a range of 4000-500 cm^{-1} using a Shimadzu FTIR-8300 Fourier Transform Infrared Spectrophotometer, and were measured as neat oil or as film (w = weak, m = medium, and s = strong). Mass spectra were recorded on a Waters Micromass Q-Tof micro quadrapole mass spectrometer in ESI-mode.

Materials

The solvents dichloromethane, acetone and diethyl ether were purchased from VETEC Química Fina LTDA and used without further purification. Triethylene glycol monomethyl ether, 2-methoxyethanol, 1-decanol, 1-butanol, methanesulfonic acid, sodium tetrafluoroborate and potassium hexafluorophosphate were used as purchased from Sigma-Aldrich. The reagents triethylamine, methanesulfonyl chloride and 1-methylimidazole were purchased from Sigma-Aldrich and distilled under argon prior to use. $CDCl_3$ and d6-acetone were purchased from Cambridge Isotope Laboratories. Activated carbon, celite, basic aluminum oxide and silica gel 60 (40-60 μm) were purchased from Merck. A procedure reported previously in the literature was used for the synthesis of **1d**,[1] **2d**[1] and **3d**,[1] and the spectral data were in accordance with the literature data.

General procedure for the synthesis of alkylating agents 1a-c

A modified literature procedure was used for the synthesis of **1a**-**c**.[1] Alcohol (1.00 equiv.), methanesulfonyl chloride (1.05 equiv.), triethylamine (1.10 equiv.) and dichloromethane. Alkylating agents **1a** and **1c** were not purified by a vacuum distillation as decomposition occurred at elevated temperatures. Instead of this, **1a** and **1c** were dissolved in dichloromethane and treated with activated carbon. Filtration over a short silica column, solvent evaporation, and vacuum drying at 70 °C for 8 hours resulted in the isolation of **1a** as a yellow liquid and **1c** as a colorless liquid. Alkylating agent **1b** was obtained as a colorless liquid after vacuum distillation. The alkylating agents **1a**-**c** were obtained in high yields (>90 %). Spectral data of **1b**[2] and **1c**[3] were in agreement with those previously reported in the literature.

General procedure for the synthesis of methanesulfonate ILs 2a-c

A modified literature procedure was used for the synthesis of **2a**-**c**.[1] The mixture of **1a**-**c** (1.000 equiv.) and 1-methylimidazole (1.001 equiv.) was heated at 60 °C for 24 hours. ILs **2a**-**b** were dissolved in dichloromethane. Methanesulfonic acid was added in order to remove excess 1-methylimidazole and the reaction mixture was stirred for 15 minutes at 25 °C. Filtration over a short basic aluminum/celite column was followed by the removal of the dichloromethane. Consecutively, **2a** and **2b** were dissolved in acetone and treated with activated carbon. Filtration over a short celite column, solvent evaporation, and vacuum dry-

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ing at 100-120 °C for 8 hours resulted in the isolation of **2a** and **2b** as yellow liquids. Room-temperature ionic salt **2c** was dissolved in hot acetone. White crystals of **2c** formed upon cooling, and diethyl ether was added to promote the crystallization. Ionic salt **2c** was vacuum dried at 30 °C for 8 hours. The very hygroscopic ILs **2a-c** were obtained in high yields (>90 %). Cyclic voltammetry experiments indicated the absence of a significant amount of water in the ILs. Spectral data of **2b**[4] were in agreement with those previously reported in the literature.

*General procedure for the synthesis of tetrafluoroborate ILs **3a-c** and hexafluorophosphate ILs **4a-b***

A modified literature procedure was used for the synthesis of **3a-c** and **4a-b**.[5] $NaBF_4$ (1.12 equiv.) or KPF_6 (1.12 equiv.) were added to a solution of IL **2a-c** (1.0 equiv.) in acetone at 25 °C. The NaO_3SCH_3 and KO_3SCH_3 salts were removed by filtration after 2 hours at 25 °C. Activated carbon was added to the acetone solution and the reaction mixture was stirred for 24 hours at 25 °C. Removal of the activated carbon by filtration was followed by the removal of the acetone. Consecutively, the ILs were dissolved in dichloromethane. Filtration over a short celite column, solvent evaporation and vacuum drying at 100-120 °C (**3a-c** and **4a**) or 75 °C (**4b**) for 8 hours resulted in the isolation of **3a-c** and **4a-b** in high yields (>90 %). The ILs **3a-b** and **4a-b** were isolated as yellow liquids and ionic liquid **3c** as a colorless liquid. Cyclic voltammetry experiments indicated the absence of a significant amount of water in the ILs. Spectral data of **3b-c**[5] and **4b**[5] were in agreement with those previously reported in the literature.

References

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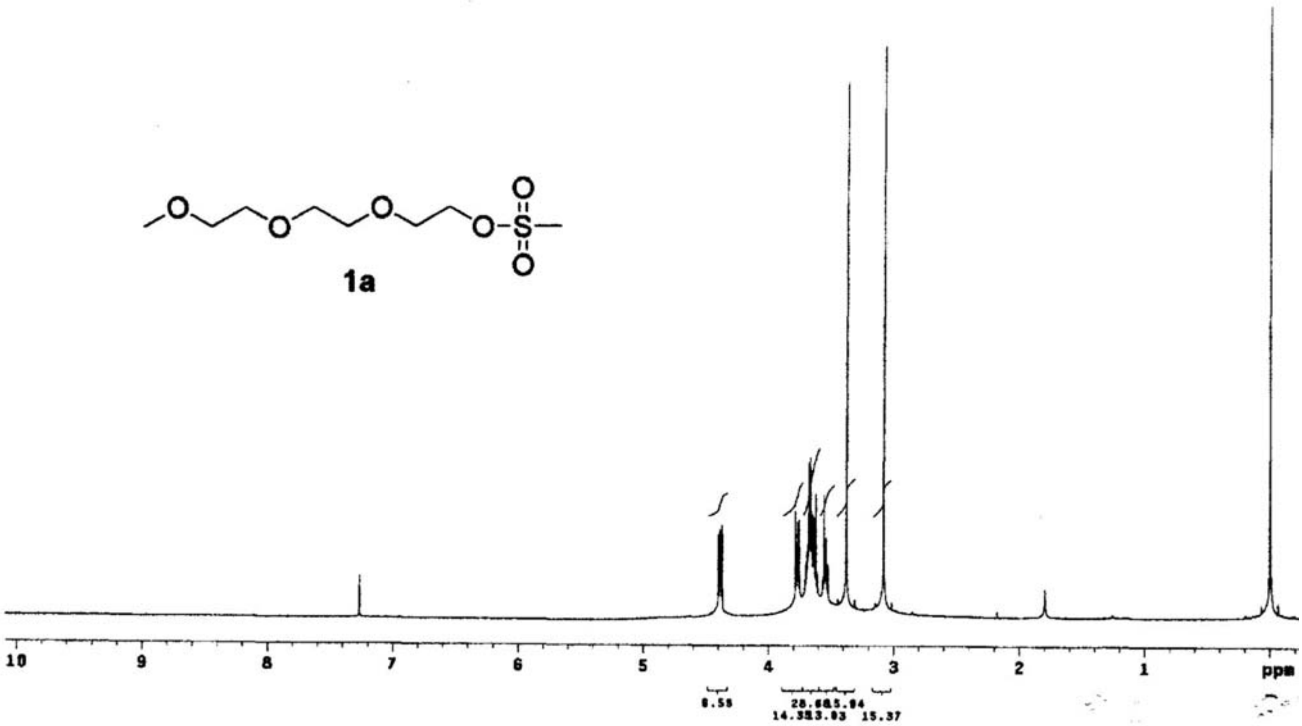

Figure S1. ^{1}H NMR spectrum of compound **1a** (300 MHz, $CDCl_3$).

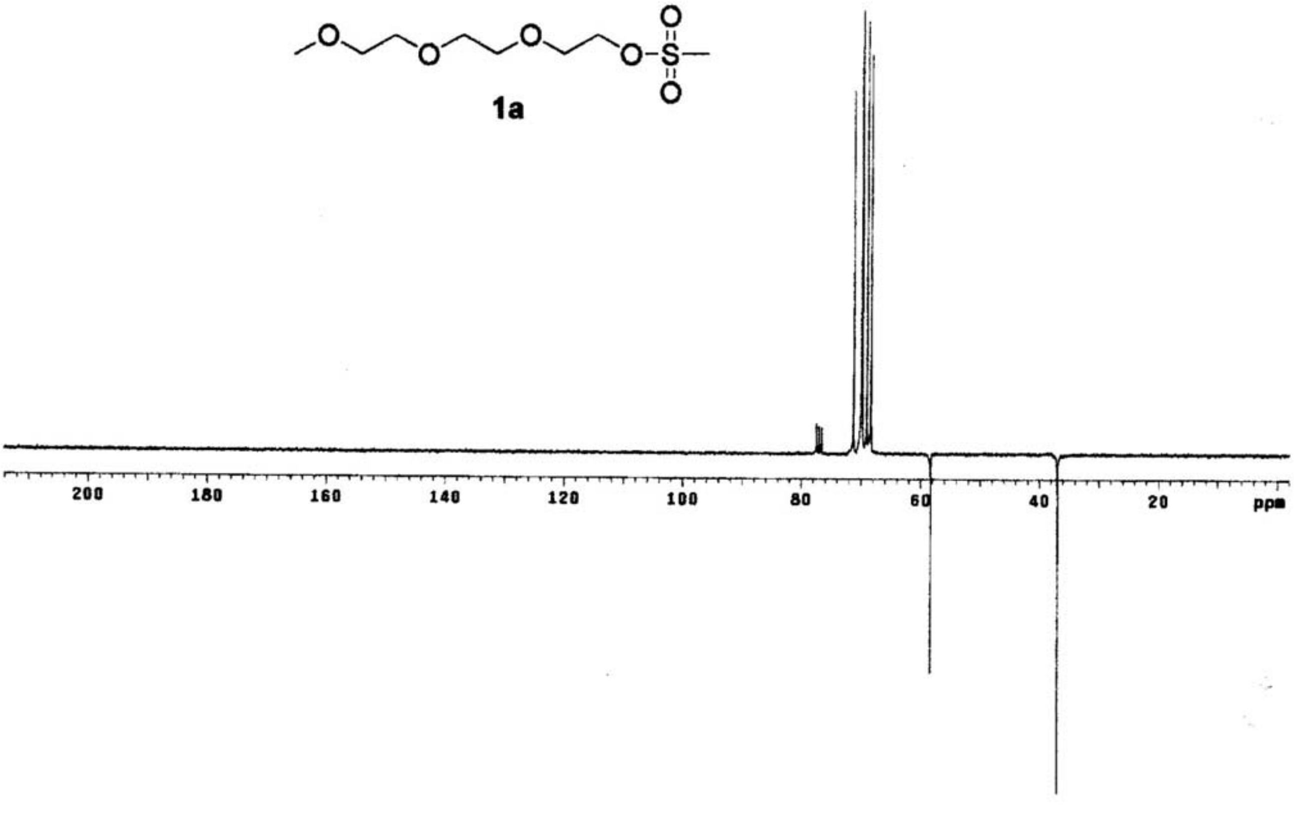

Figure S2. ^{13}C NMR spectrum of compound **1a** (75 MHz, $CDCl_3$).

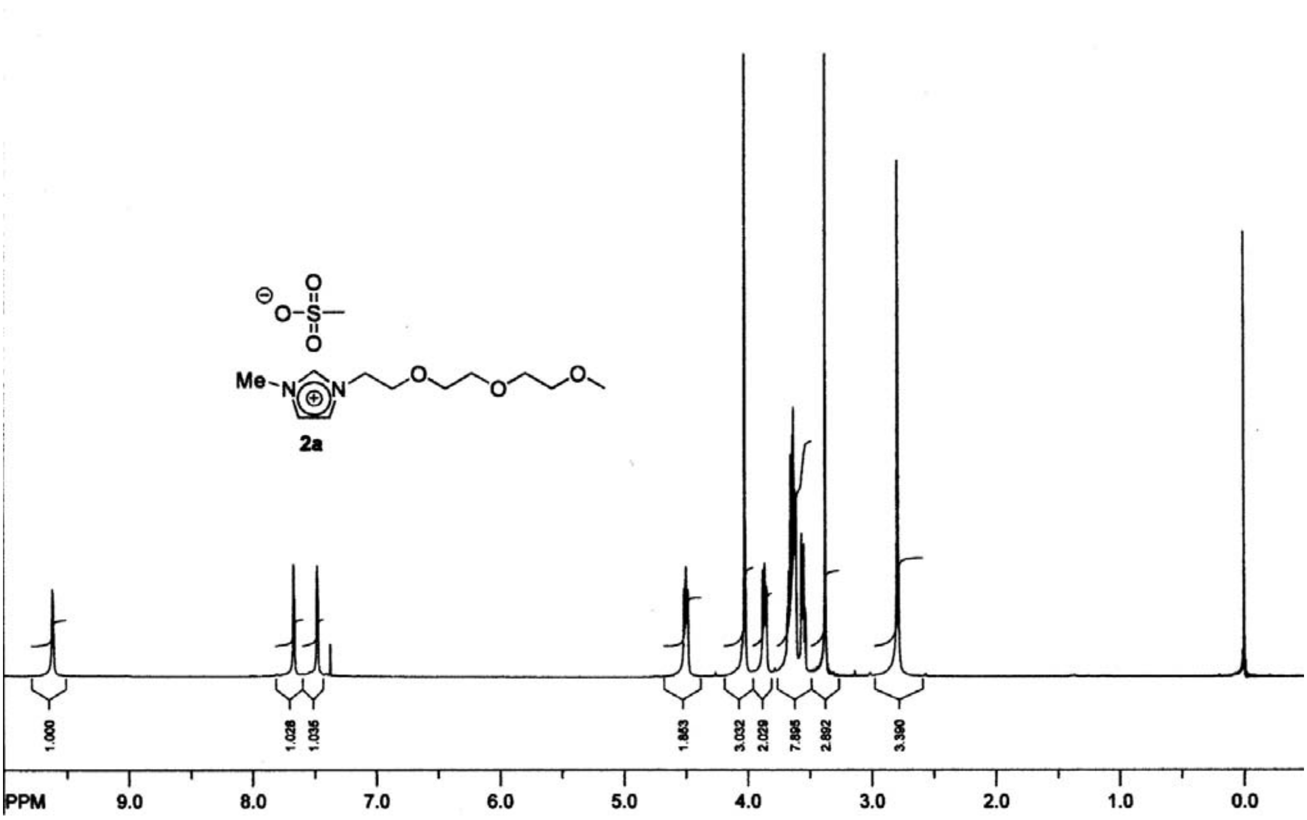

Figure S3. ^{1}H NMR spectrum of ionic liquid **2a** (300 MHz, $CDCl_3$).

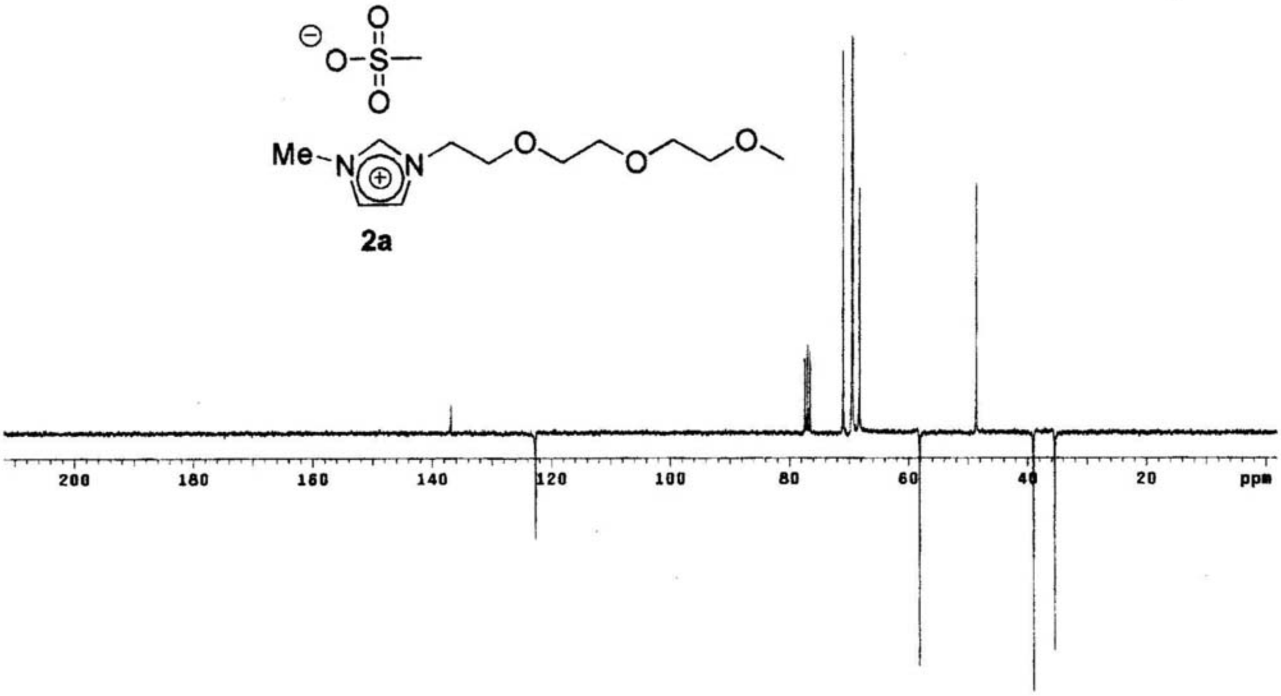

Figure S4. ^{13}C NMR spectrum of ionic liquid **2a** (75 MHz, $CDCl_3$).

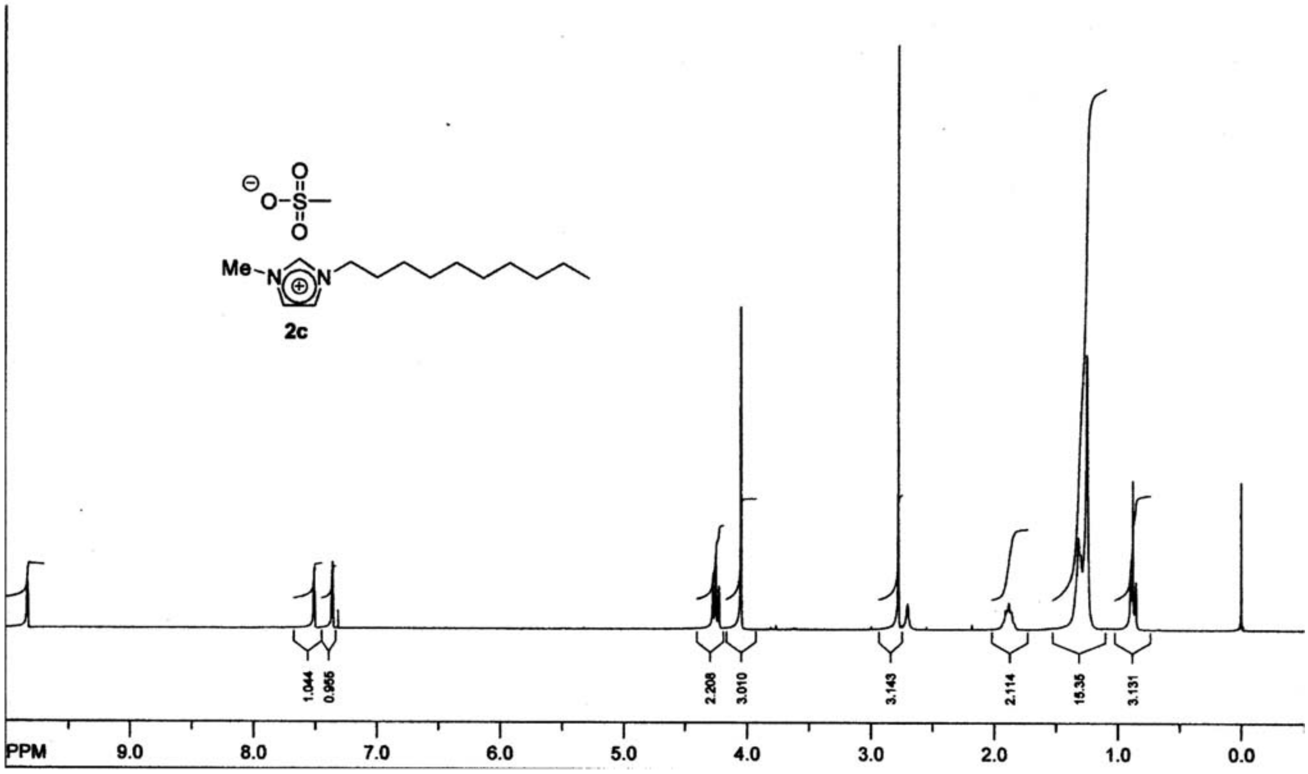

Figure S5. ^{1}H NMR spectrum of ionic liquid **2c** (300 MHz, CDCl$_3$).

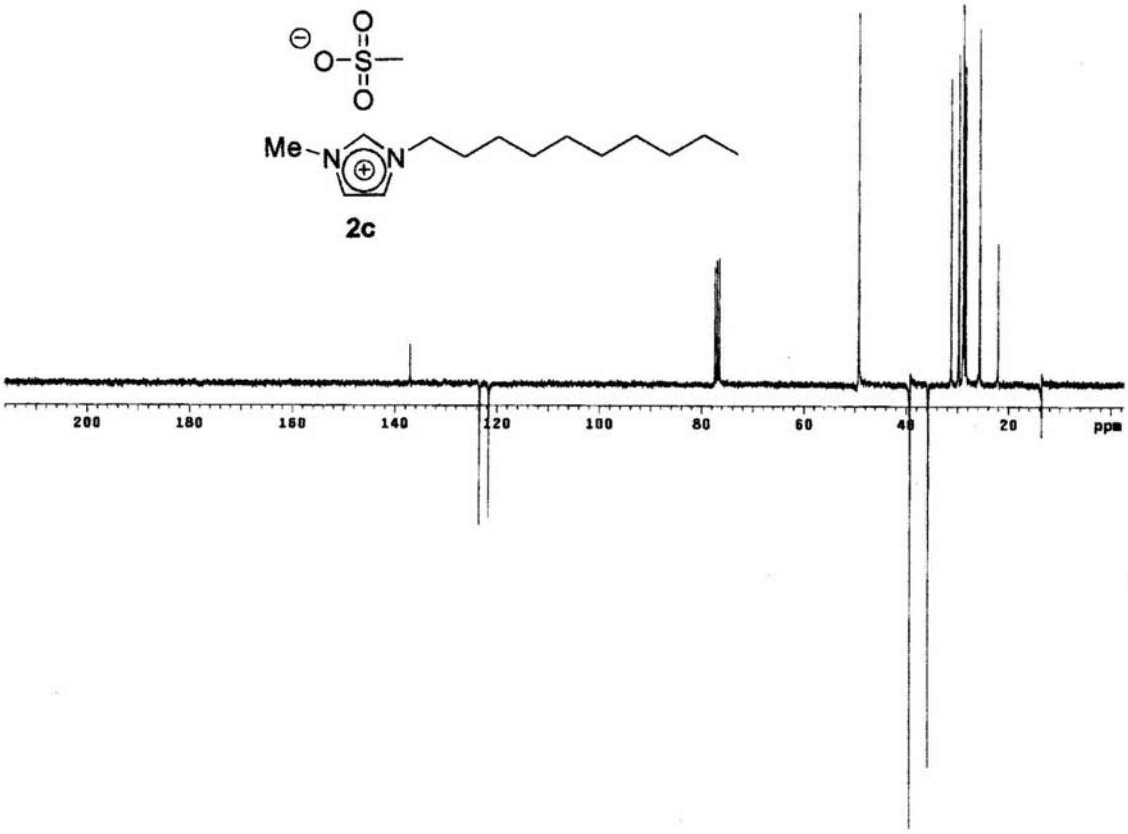

Figure S6. ^{13}C NMR spectrum of ionic liquid **2c** (75 MHz, CDCl$_3$).

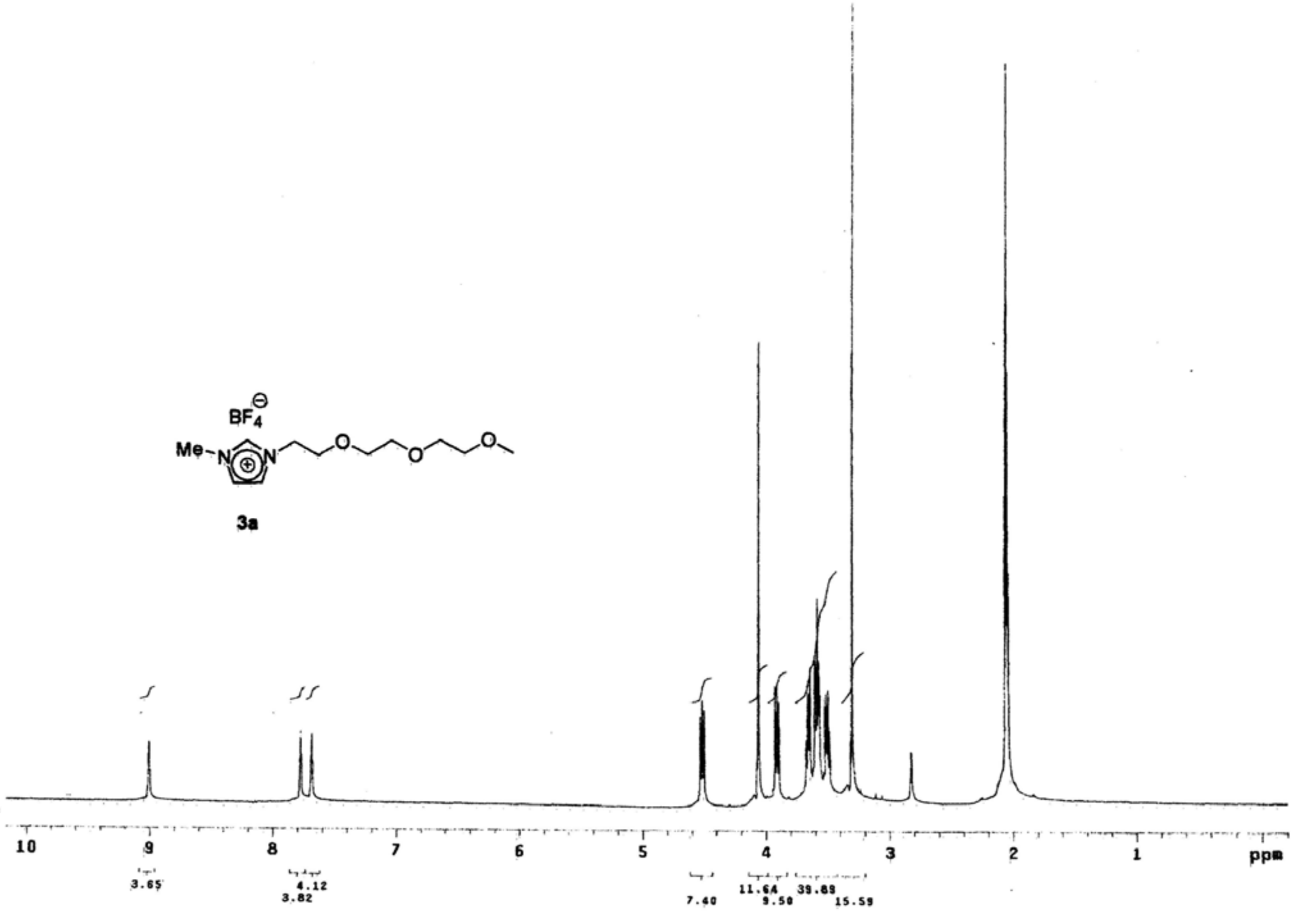

Figure S7. ^{1}H NMR spectrum of ionic liquid **3a** (300 MHz, d6-acetone).

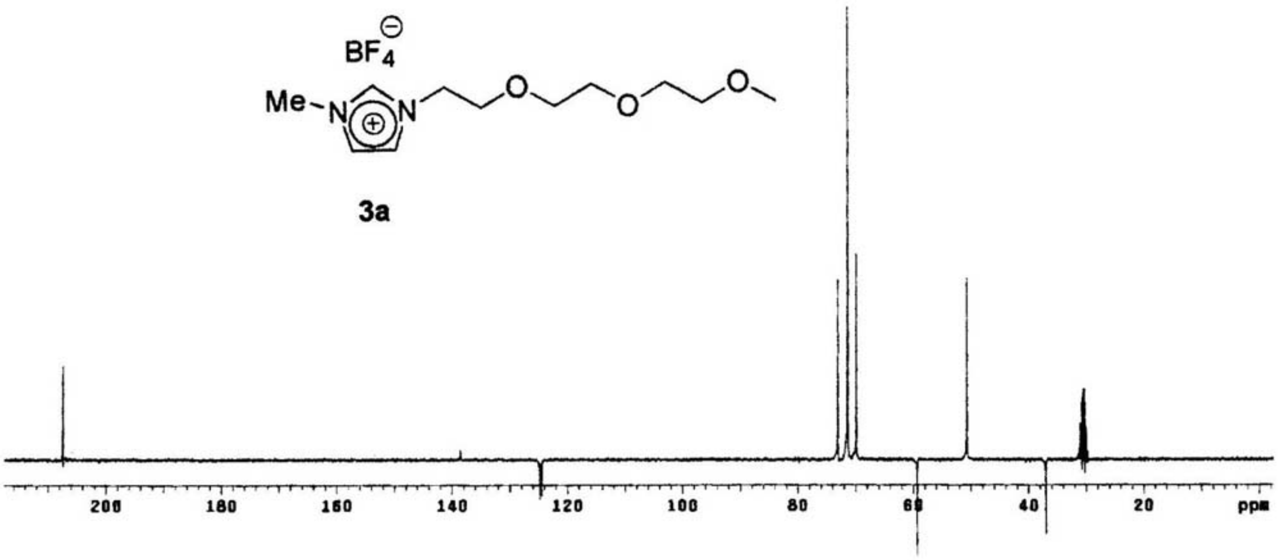

Figure S8. ^{13}C NMR spectrum of ionic liquid **3a** (75 MHz, d6-acetone).

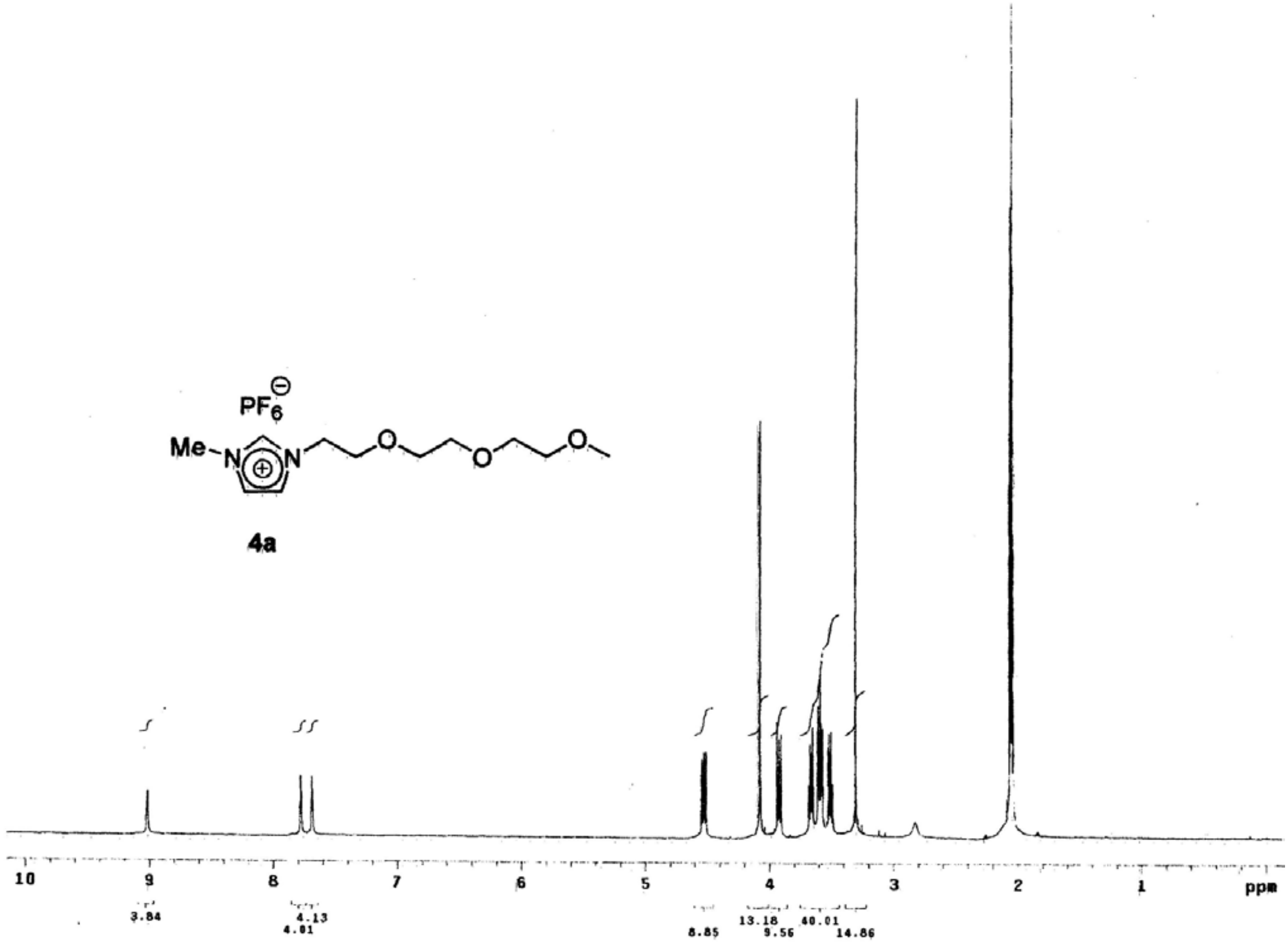

Figure S9. ^{1}H NMR spectrum of ionic liquid **4a** (300 MHz, d6-acetone).

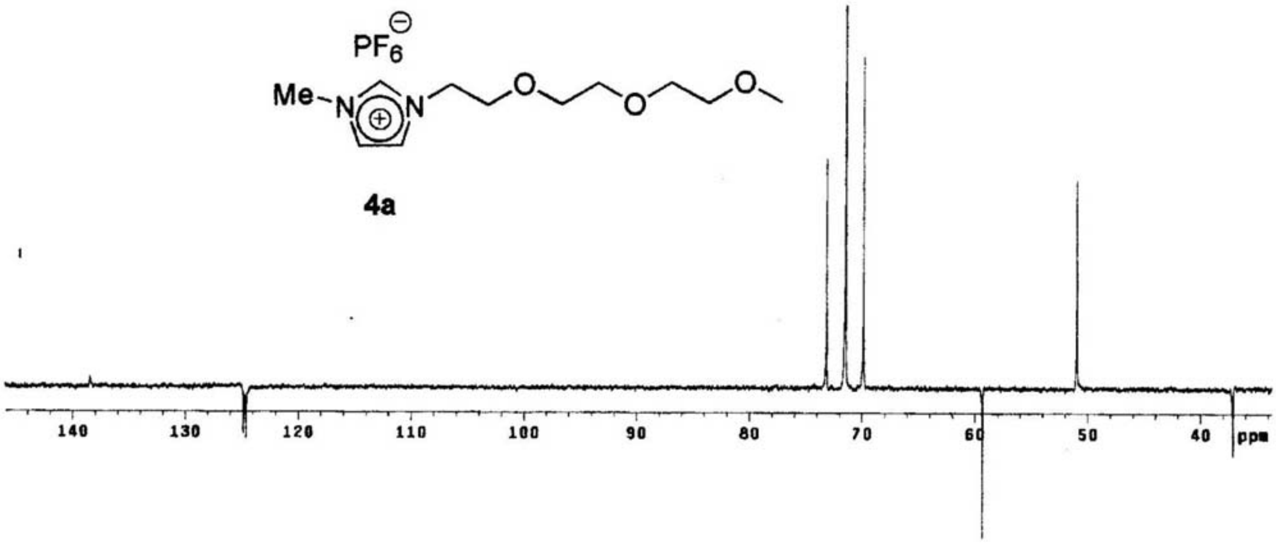

Figure S10. ^{13}C NMR spectrum of ionic liquid **4a** (75 MHz, d6-acetone).

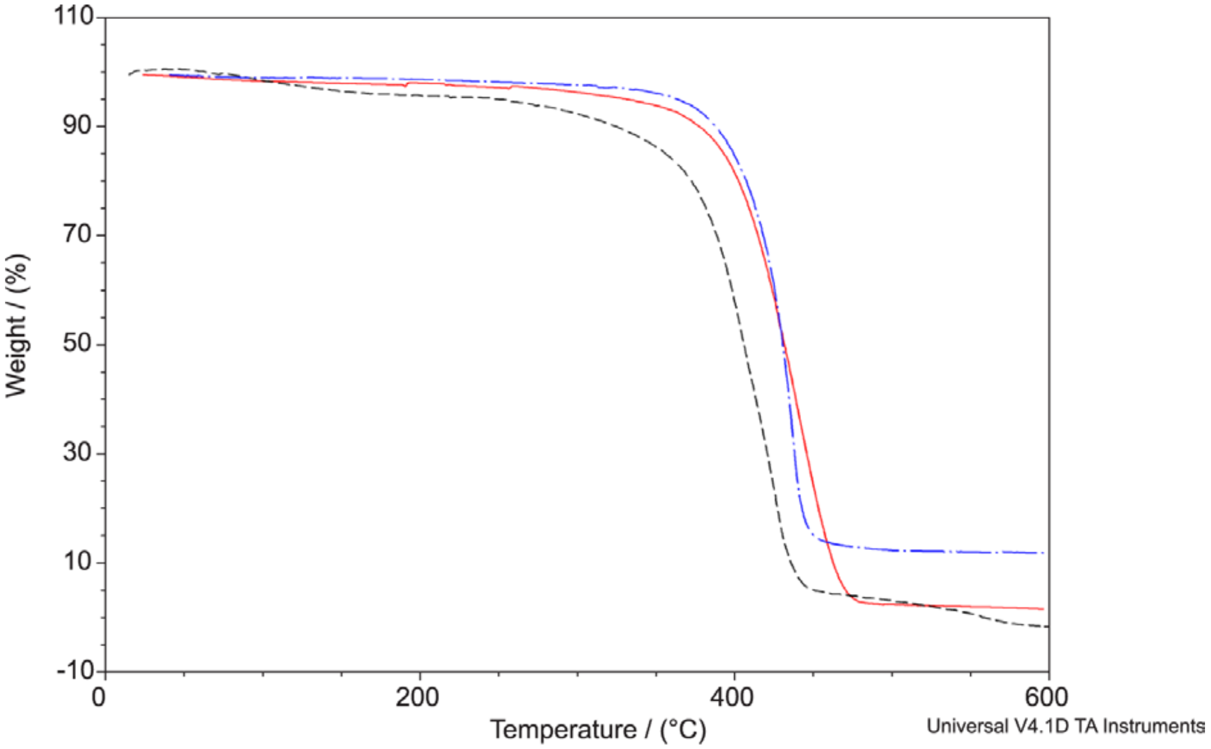

Figure S11. TGA traces of ionic liquid **2a** $[C_7O_3MIm]^+[Mes]^-$ (black line), ionic liquid **3a** $[C_7O_3MIm]^+[BF_4]^-$ (red line) and ionic liquid **4a** $[C_7O_3MIm]^+[PF_6]^-$ (blue line).

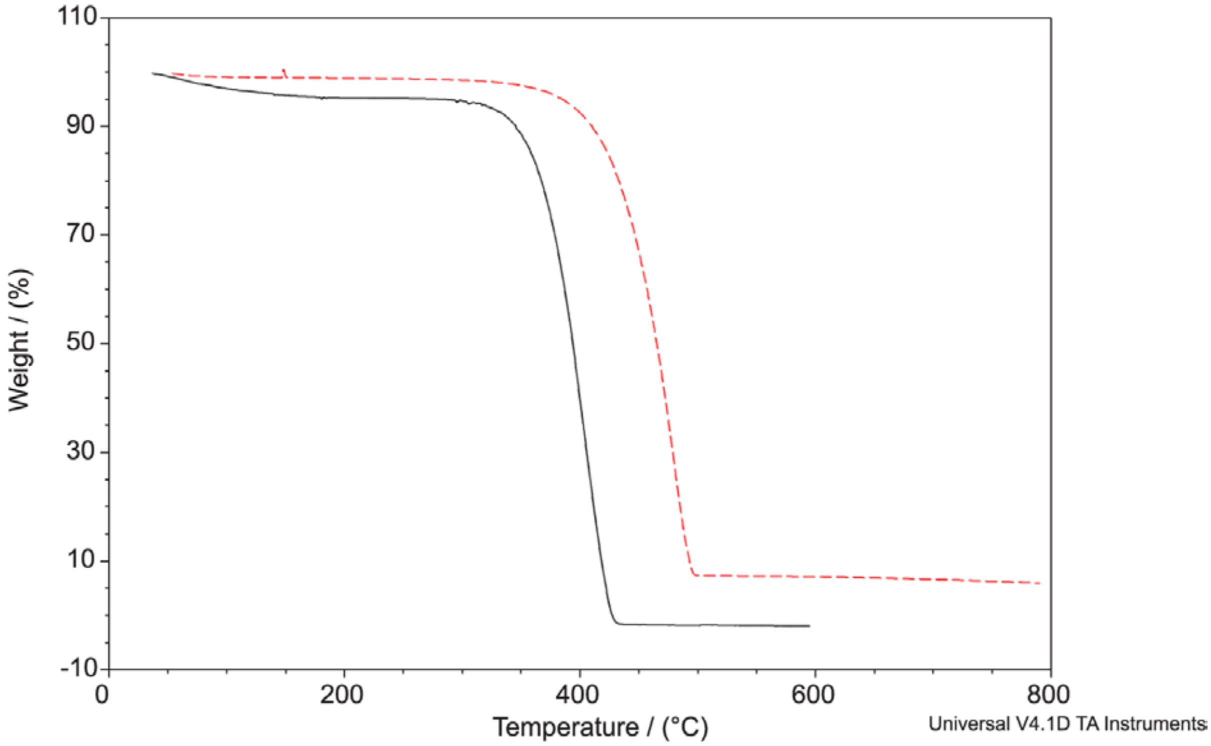

Figure S12. TGA traces of ionic liquid **2c** $[C_{10}MIm]^+[Mes]^-$ (black line) and ionic liquid **3c** $[C_{10}MIm]^+[BF_4]^-$ (red line).