Materials and Synthesis of ILs.
Ethyl thiocyanate (EtSCN) and TMS were from TCI copr. All ILs studied in this work were prepared according to the well-established procedure, and confirmed by $^1$H NMR. They can be classified into two groups, (I) nonhydroxyl ILs, i.e., 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([BMIm][NTf$_2$]), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF$_6$]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF$_4$]), 1-butyl-3-methylimidazolium perchlorate ([BMIm][ClO$_4$]), 1-butyl-3-methylimidazolium nitrate ([BMIm][NO$_3$]), 1-butyl-3-methylimidazolium chloride ([BMIm][Cl]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF$_4$]), 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIm][BF$_4$]), 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIm][BF$_4$]), 1-decyl-3-methylimidazolium tetrafluoroborate ([DMIm][BF$_4$]), trihexyltetradecylphosphonium bis(trifluoromethanesulfonyl)amide ([P$_{666,14}$][NTf$_2$]), N-methyl-N-butyl-pyrrolidinium bis(trifluoromethanesulfonamyle)amide ([P$_{14}$][NTf$_2$]) and N-(2-methoxyethyl)-N-butyl-N,N-dimethyl-ammonium bis(trifluoromethanesulfonyl)amide [N$_{114,102}$][NTf$_2$], and (II) hydroxyl ILs, i.e., 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonamyle)amide ([HOEMIm][NTf$_2$]), 1-(2-hydroxyethyl)-3-methylimidazolium hexafluorophosphate ([HOEMIm][PF$_6$]), 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([HOEMIm][BF$_4$]), 1-(2-hydroxyethyl)-3-methylimidazolium perchlorate ([HOEMIm][ClO$_4$]), and 1-(2-hydroxyethyl)-3-methylimidazolium nitrate ([HOEMIm][NO$_3$]). All ILs were dried in vacuum at 80 °C for 10 h prior to analysis. All EtSCN-ILs solutions were made by adding 10 μL EtSCN to 1 mL ILs.

FT-IR and NMR Measurement
Infrared spectra were recorded on a Thermo-nicolet 5700 FTIR spectrometer relative to a background taken with pure ILs. The sample cell was equipped with KBr windows separated with a Teflon spacer of 160 μm. The spectra were registered 32 scanning times. All EtSCN-ILs solutions were used directly for $^{13}$C NMR spectra determination (Bruker AMX FT 400-MHz NMR spectrometer) without deuterated solvents. TMS in a capillary tube with diameter of 1.8 mm was inserted into the NMR tube.