Clean Beckmann Rearrangement of Cyclohexanone Oxime in caprolactam Based Brønsted Acidic Ionic Liquids

Shu Guo, Zhengyin Du, Shiguo Zhang, Dongmei Li, Zuopeng Li, Youquan Deng*

Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China

Fax: (+86)-931-4968116, e-mail: ydeng@lzb.ac.cn

Supporting information

Differential scanning calorimetry (DSC) measurements were performed using a DSC-Q100 differential scanning calorimeter (TA Instruments Inc.). The samples were sealed in aluminum pans and scanned between 173K and 393K with a scanning rate of 10°C/min. The glass transition temperature (T_g) determined from the midpoint of the heat capacity change is at -74.0 °C.

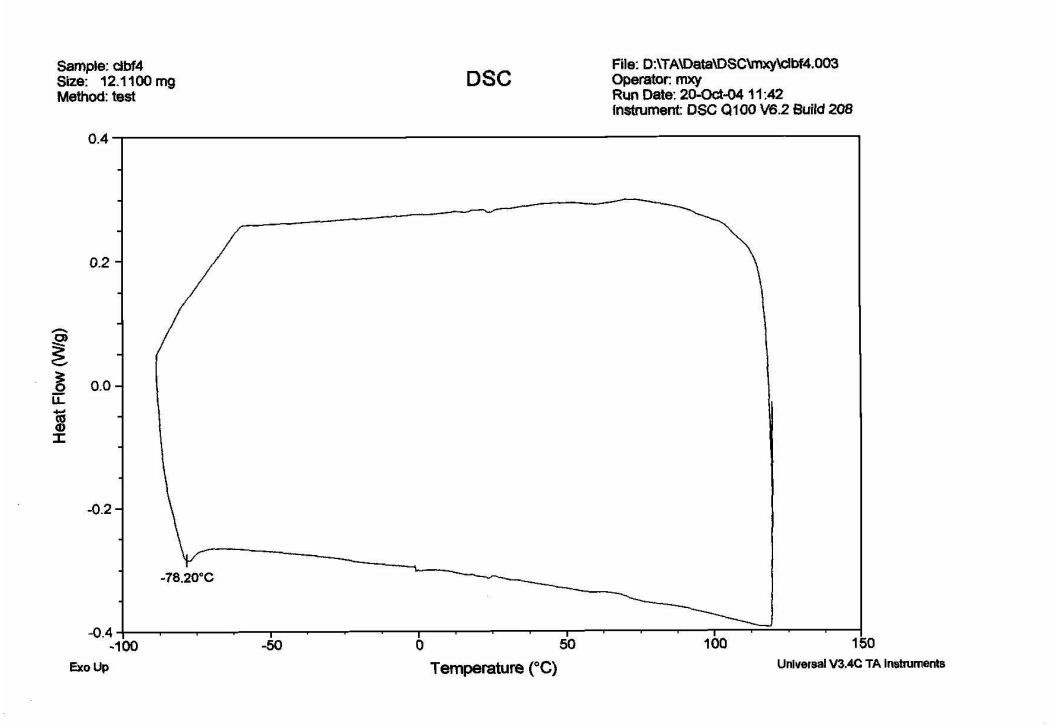

Figure S1. Differential scanning calorimetry (DSC) curves for the [NHC][BF_4]

The thermal stability was measured dynamically under N_2 with rate of 20 ^oC /min, using Perkin Elmer co. Pyrid Dimond TG. The thermo gravimetric (TG) curves of $[NHC]BF_4$ showed weight loss processes with 10% weight loss at 239^oC. It indicated that the IL has stability enough under reaction conditions.

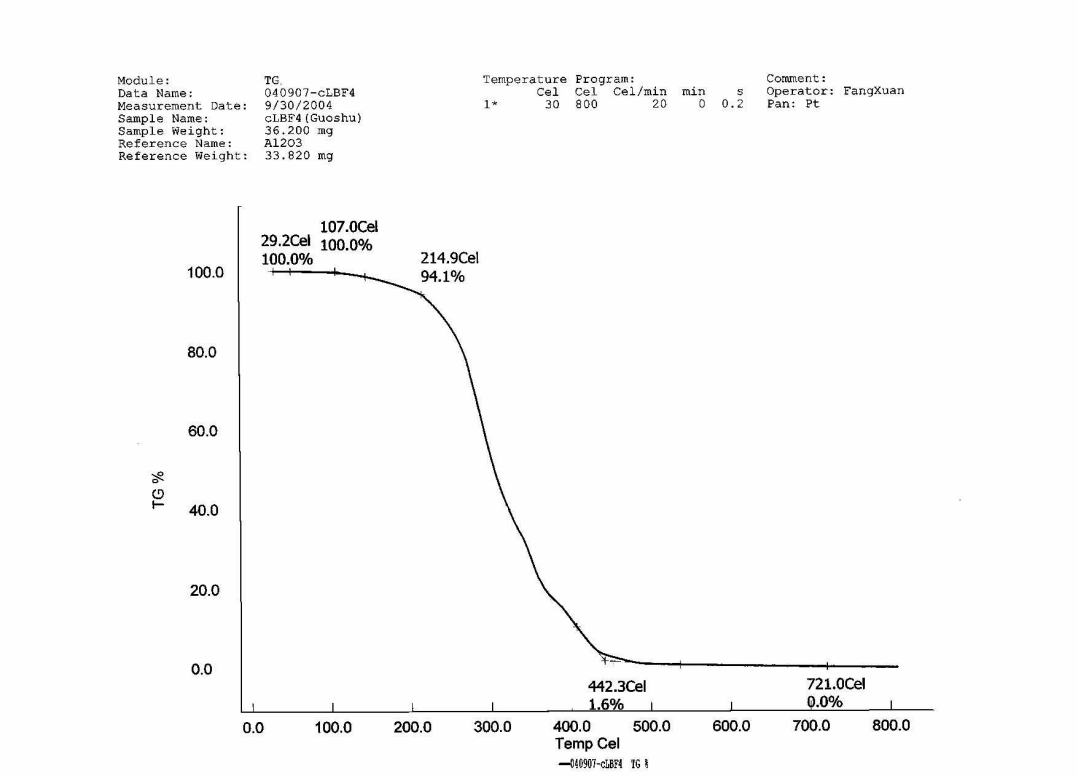

Figure S2. TG trace of the $[NHC][BF_4]$

Electrochemical stability was analyzed using a cyclic voltammetry (CHI660A Instruments Electrochemical Work Station) at room temperature. A glassy carbon working electrode of 3 mm diameter was used with a platinum wire as the counter electrode and a Ag/AgCl as the reference electrode. The electrochemical stability behavior of $[NHC][BF_4]$ was stable to potentials from -0.5V to +1.5v versus Ag/Ag^+. The reduction current observed in the vicinity of -0.3v is resulted from the reduction of active H in $[NHC][BF_4]$.

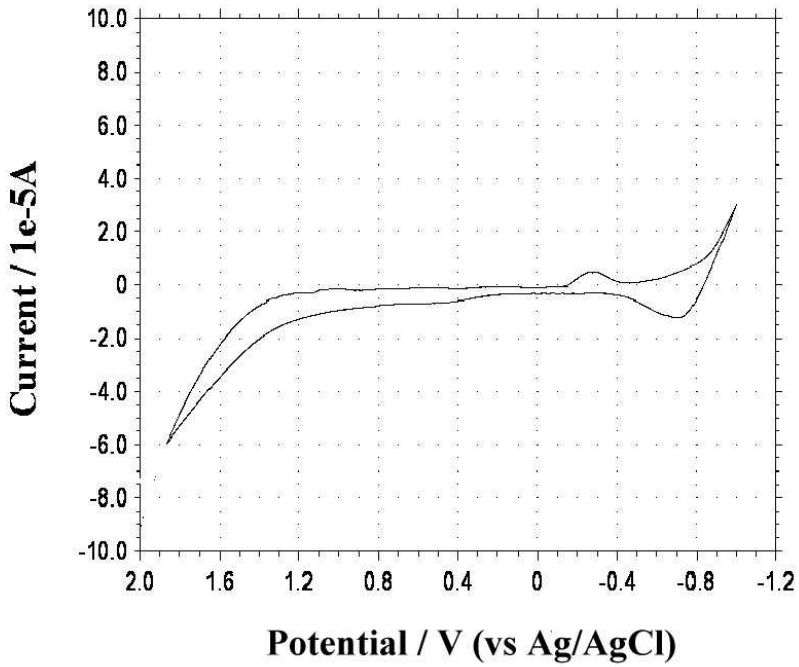

Figure S3. Cyclic voltammograms of [NHC][BF_4] at 20 ^oC

In ^{1}H-NMR of [NHC][BF_4] (**Figure S6**), there are two active H (A, δ=8.26ppm and 12.0ppm) which shift to low field in comparison with corresponding H (B, δ=6.9ppm) in caprolactam, indicating that such acidic H do not bond covalently to N but dissociate around caprolactam and BF_4^-. When exchanged by D_2O, two active H disappeared and DHO signals appeared (C, δ=5.94ppm).

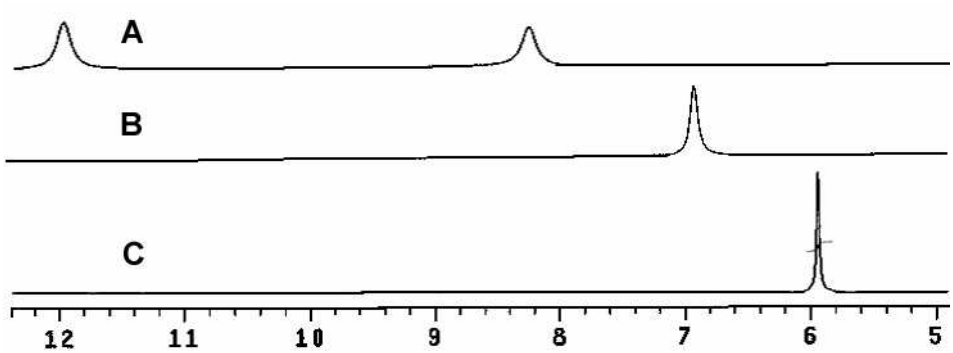

Figure S4. ^{1}H-NMR (400MHz, d_6-DMSO) spectra of active H in (A) [NHC][BF_4], (B) ε-caprolactam, and (C) (A) was added D_2O for exchanging active H

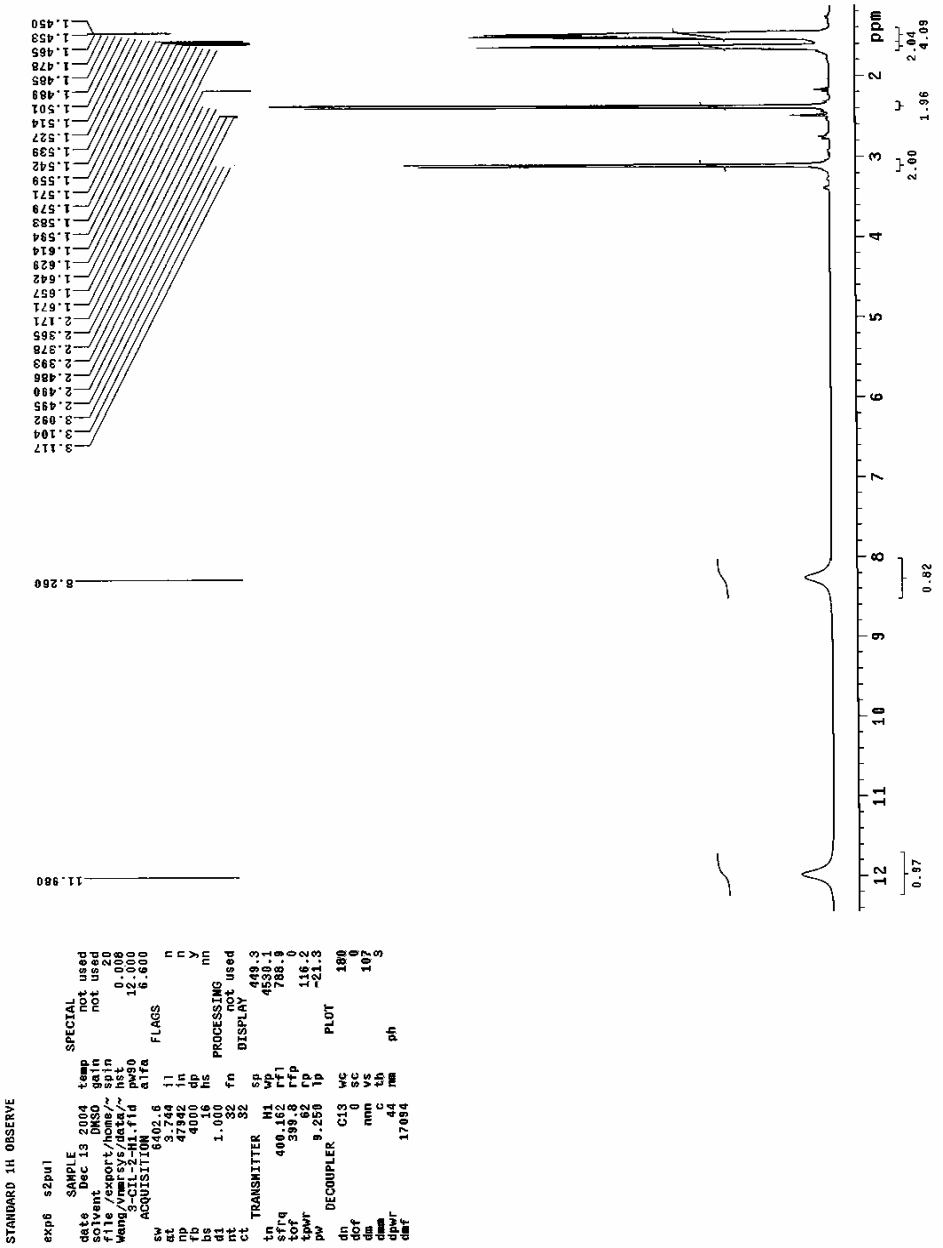

Figure S5. [1]HNMR spectra of [NHC][BF_4], Spectral data: ^{1}H NMR (400 MHz, d_6-DMSO) δ 1.453 (2H, -CH_2-), 1.485 (2H, -CH_2-), 1.657 (2H, -CH_2-), 2.378 (2H, NCH_2-), 3.104 (2H, -$COCH_2$-), 8.260 and 11.980 (2H, -NH- and HBF_4).

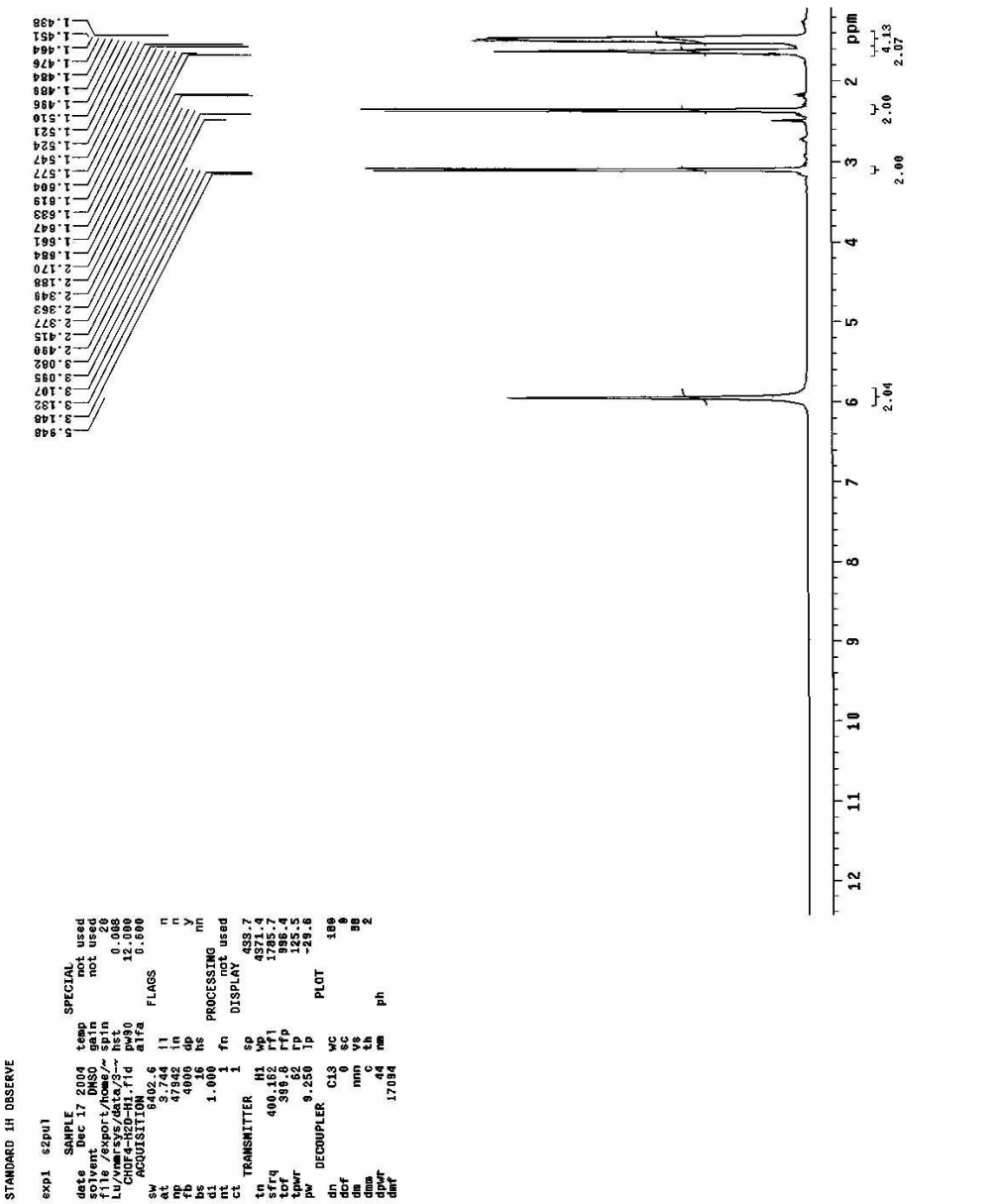

Figure S6. ^{1}HNMR spectra of [NHC][BF_4], a few drops of D_2O were added for exchanging active H. Spectral data: ^{1}H NMR (400 MHz, d_6-DMSO): δ 1.453 (2H, -CH_2-), 1.485 (2H, -CH_2-), 1.657 (2H, -CH_2-), 2.378 (2H, NCH_2-), 3.104 (2H, -COCH_2-), 5.944 (2H, DHO).

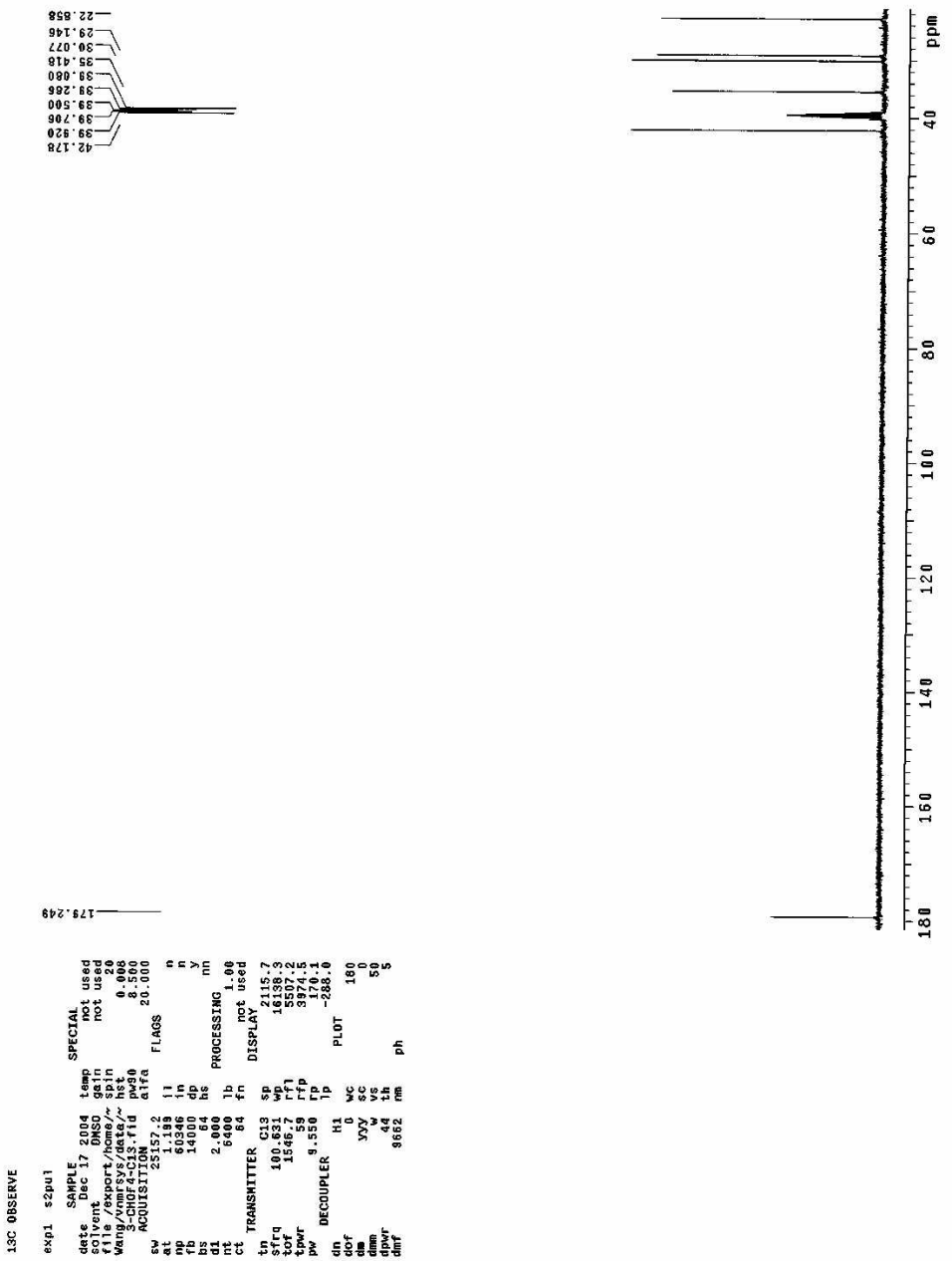

Figure S7. ^{13}CNMR spectra of [NHC][BF_4], Spectral data: ^{13}C NMR (100MHz, d_6-DMSO): δ 22.858, 29.146, 30.077, 35.418, 42.178, 179.249.

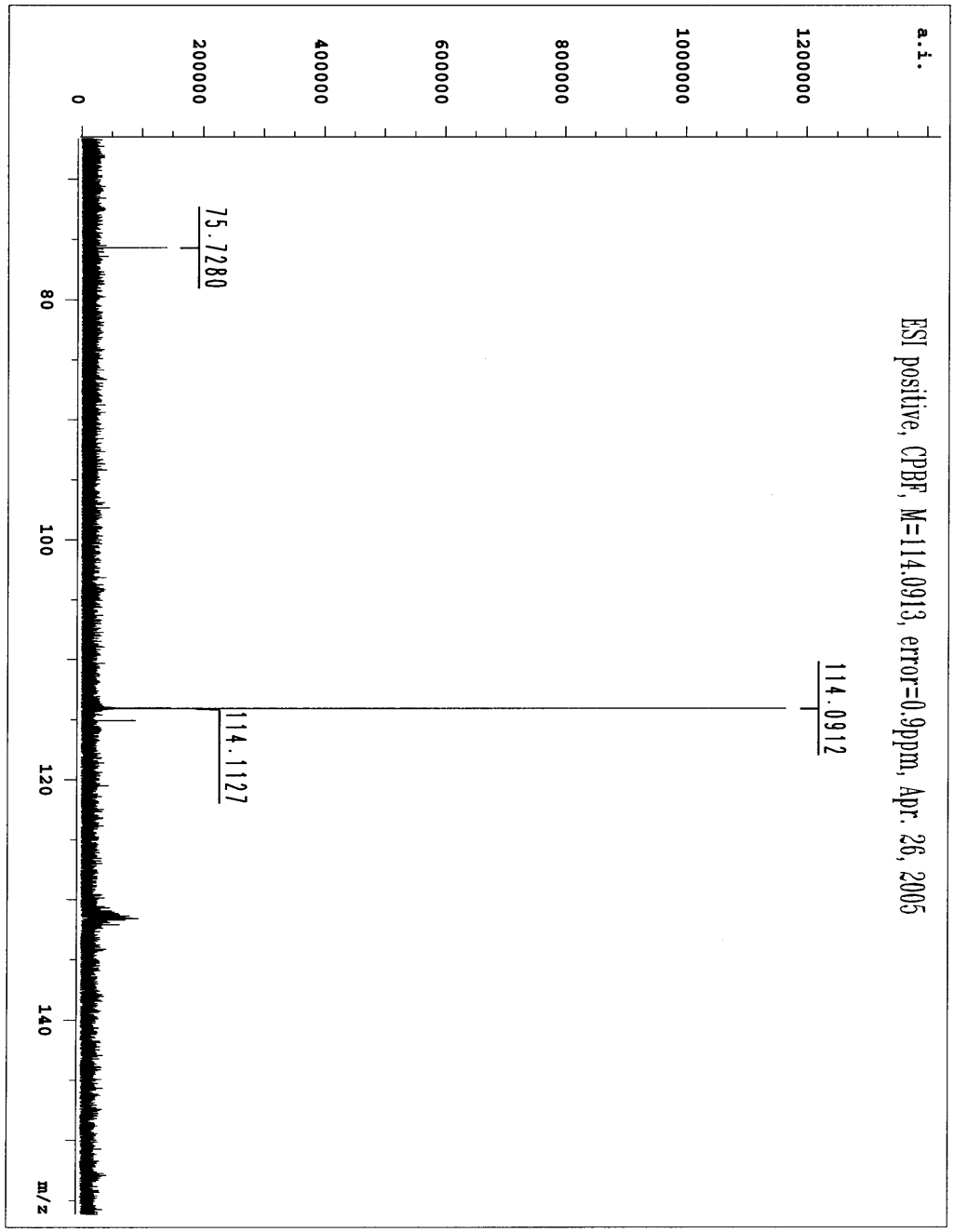

Figure S8. Electrospray ionization mass spectrum (ESI-MS) of [NHC][BF_4]