Electronic Supplementary Information (ESI)

Ionic-Liquid Buffers: A Kind of NewChemicals Potential for Controlling pH in Non-Aqueous Media

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I. General

Cyclohexene (99%, Alfa Aesar) and 1-hexene (98%, Fluka) were used as received without further purification. Styrene was passed through a neutral alumina column before use. DMF was purified by drying overnight over KOH pellets and then distilled under reduced pressure. The ^1H NMR spectra were obtained on a Brüker AM-500 Fourier transform NMR spectrometer at 500 MHz. ^1H NMR spectra were referenced to tetramethylsilane in deuterated DMSO. Mass spectra were acquired using a Bruker ESQUIRE-3000 *plus* ion trap spectrometer equipped with a gas nebulizer probe, capable of analyzing ions up to m/z 6000.

II. NMR measurements of active catalytic species

24.0 mg of $[RuCl_2(PPh_3)_3]$, 25 mg of ionic-liquid buffer ([BMIM][HP] with Log_{10} ([Base]/[Acid]) of 0.000, 0.315) and 0.50 mL of solvent were introduced into a stainless steel autoclave. The autoclave was flushed with high purity hydrogen consecutively for three times. The autoclave was then filled with hydrogen to 2.5 MPa. The mixture was stirred at 800 rpm at 50 ℃ for 2.5 h. NMR measurements were carried out using microprobe NMR tubes with coaxial insert stems that D_2O was filled up in the lower 4 cm of the capillary for external locking. ^1H NMR spectra were recorded on a Bruker AV 400 instrument. ^1H NMR spectra were referenced to tetramethylsilane.

Ⅲ. Phase transition analysis

The calorimetric measurements were performed with a differential scanning calorimeter (NETZSCH DSC 204 equipped with a liquid nitrogen cryostatic cooling) in the temperature range -150 °C to a predetermined temperature. An average sample weight of 5–10 mg was sealed in an aluminum pan, and then heated and cooled at a rate of 10 °C min^{-1} under a flow of helium. The glass transition temperature (T_g, onset of the heat capacity change), crystallization temperature (Tc, onset of the exothermic peak), solid–solid transition temperature (T_s, onset of the endothermic peak), and melting point (T_m, onset of the endothermic peak) were taken during heating in the second heating–cooling cycle.

IV. Thermal gravimetric analysis (TGA)

TGA was performed with Simultaneous Thermal Analysis-STA 409EP. An average sample weight of 5 mg was placed in a platinum pan and heated at 10 °C min^{-1} from 40 °C to 600 °C under a flow of nitrogen. The onset of decomposition was defined as the decomposition temperature (T_d).

V. Specific conductivity

The ionic conductivity (k) of the neat ionic liquid buffers was measured by a conductivity meter (Shanghai Precision & Scientific Instrument Co., Ltd. REX Instrument Factory, model DDB-303A) at 25 °C.

VI. pH titration procedure

Titrations were carried out using a custom-built autotitrator. Place a clean and dry magnetic stirring bar in the beaker and set the beaker over a magnetic stirring motor. An appropriate amount of acid (~1 mM) was dissolved in 20 mL of the solvent. Immerse the electrodes connected to the in the solution and start the stirring. A peristaltic pump (Shanghai Hu Xi analysis instrument factory Co., Ltd., model HL-2) (running at 1 mL min^{-1}) titrated the solution with 0.1 M [RMIM][OH] solution over a period of approximately 20 min. The pH was recorded with a pH meter (ORION, model 828) interfaced to a computer. A combination pH electrode (ORION, CHN060, a glass electrode and a reference electrode) was used. Glass electrodes cells are calibrated by two-point calibration using two standard buffer solutions (potassium hydrogen phthalate and mixed phosphate). The accuracy of pH measurements was ±0.01 pH unit.

VII. Solubility determination

All solubility determinations are carried out at the laboratory temperature in small test tubes (*e.g.* 100×12 mm) but of sufficient size to permit vigorous shaking of the solvent and the solute. Treat 0.10 g portion of the solid with successive l.00 mL portions of the solvent, shaking vigorously after each addition, until 3.00 mL have been added. If the compound does not dissolve completely in 3.00 mL of the solvent, it may be regarded as insoluble in the solvent. When dealing with a liquid, add 0.20 mL of the compound to 3.00 mL of the solvent and shake.

VIII. Density determination

The densities of the ionic liquids were determined at 25 °C by placing 1.00 mL of the ionic liquid in a 1.00 mL volumetric tube and weighing the difference.

IX. Water content

The water content in the ILs was detected by Karl-Fischer titration (Metrohm ltd., model 787 KF Titrino).

X. Spectral data

1-butyl-3-methylimidazolium hydrogen phthalate ([BMIM][HP]). From 0.9 g (5.4 mmol) of [BMIM]Cl and 0.83 g (5.0 mmol) of phthalic acid, 1.49 g of [BMIM][HP] was obtained (Yield : 91.1%). ^{1}H-NMR (DMSO, δ/ppm relative to TMS) : 0.80 (t, 3H, J = 7.2 Hz), 1.18 (d, 2H, J = 7.4 Hz), 1.71 (d, 2H, J = 7.3 Hz), 3.89 (s, 3H), 4.13 (t, 2H, J = 7.3 Hz), 7.51 (t, 2H, J = 5.6 Hz), 7.69 (s, 1H), 7.75 (s, 1H), 8.17 (t, 2H, J = 5.6 Hz), 9.16 (s, 1H); ESI-MS (m/z) calcd for [BMIM] 139.2 obsd 139.1; cald for [HP] 165.1 obsd 164.8.

1-butyl-3-methylimidazolium hydrogen tartrate ([BMIM][HT]). From 0.9 g (5.4 mmol) of [BMIM]Cl and 0.75 g (5.0 mmol) of tartaric acid, 1.44 g of [BMIM][HT] was obtained (Yield : 92.5%). ^{1}H-NMR (DMSO, δ/ppm relative to TMS) : 0.86 (t, 3H, J = 7.4 Hz), 1.22 (t, 2H, J = 7.3 Hz), 1.74 (t, 2H, J = 7.4 Hz), 3.84 (s, 3H), 4.03 (s, 2H), 4.15 (t, 2H, J = 7.1 Hz), 4.64 (s, 2H), 7.66 (s, 1H), 7.73 (s, 1H), 9.19 (s, 1H); ESI-MS (m/z) calcd for [BMIM] 139.2 obsd 139.1; cald for [HT] 149.1 obsd 148.8.

1-methyl-3-octylimidazolium hydrogen phthalate ([OMIM][HP]). From 1.94 g (5.4 mmol) of [OMIM][Br] and 0.83 g (5.0 mmol) of hydrogen phthalate, 1.80 g of [OMIM][HP] was obtained (Yield : 92.7%). ^{1}H-NMR (DMSO, δ/ppm relative to TMS) : 0.80 (t, 3H, J = 6.7 Hz), 1.18 (t, 10H, J= 5.1 Hz), 1.73 (t, 2H, J = 6.0 Hz), 3.84 (s, 3H), 4.12 (t, 2H, J = 7.1 Hz), 7.51 (t, 2H, J = 3.1 Hz), 7.66 (S, 1H), 7.73 (s, 1H), 8.09 (t, 2H, J = 3.0 Hz), 9.10 (s, 1H); ESI-MS (m/z) calcd for [OMIM] 195.3 obsd 195.1; cald for [HP] 165.1 obsd 164.8.

XI. Spectra

[BMIM][HP]

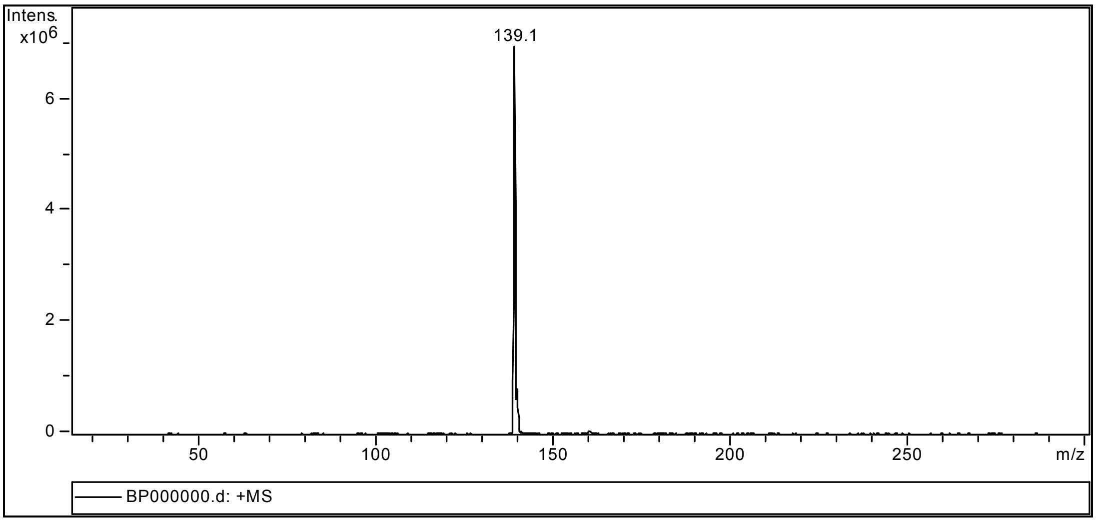

Fig. 1S Positive ion ESI spectrum of [BMIM][HP].

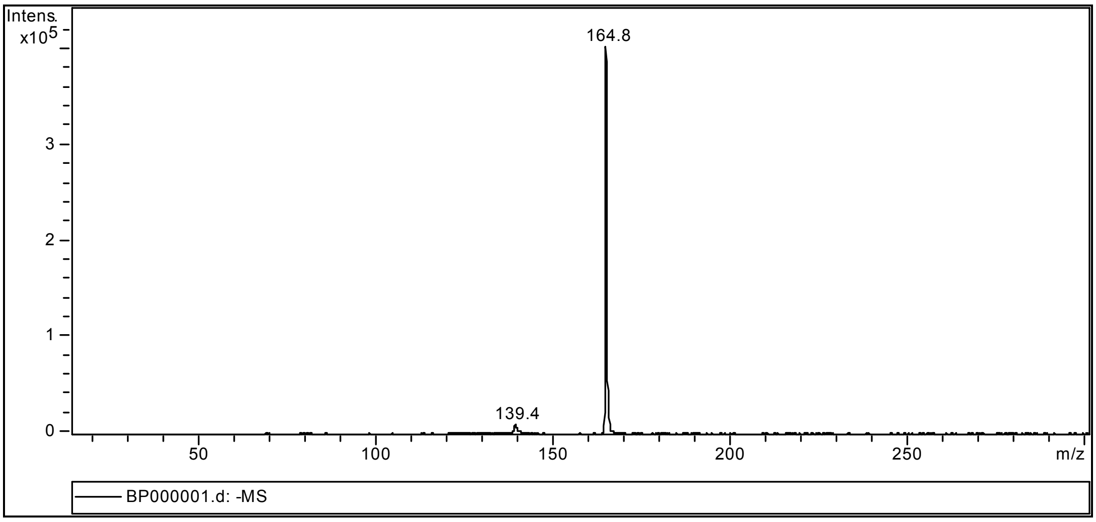

Fig. 2S Negative ion ESI spectrum of [BMIM][HP].

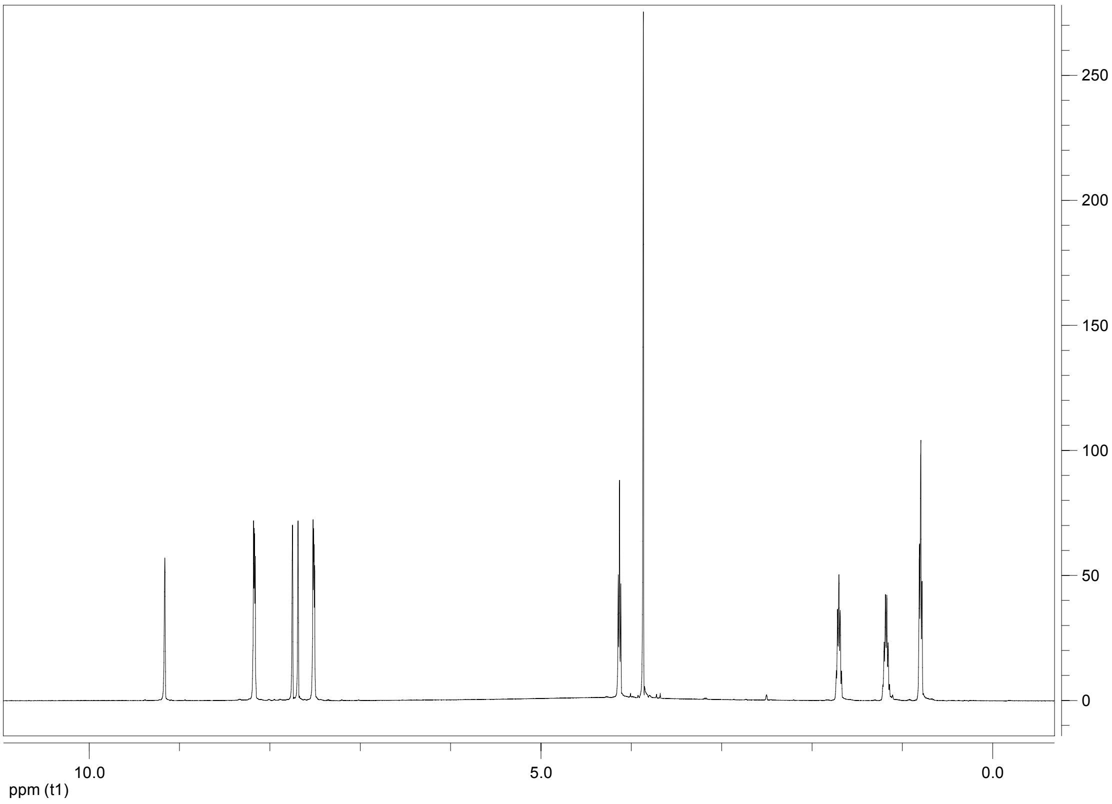

Fig. 3S ^{1}H NMR spectrum of [BMIM][HP].

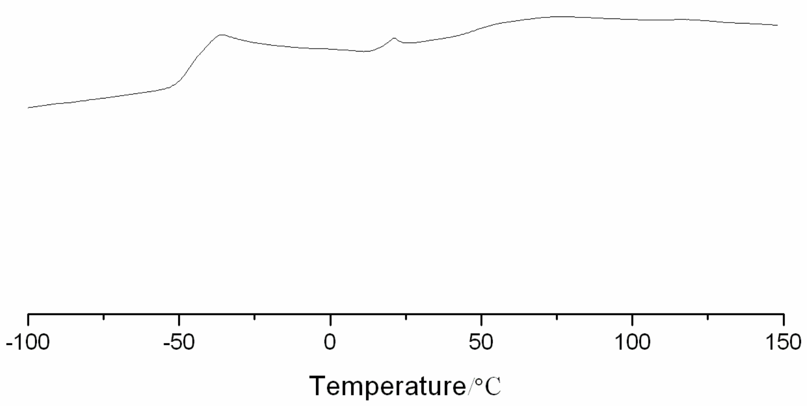

Fig. 4S DSC traces on heating for ionic-liquid buffer [BMIM][HP].

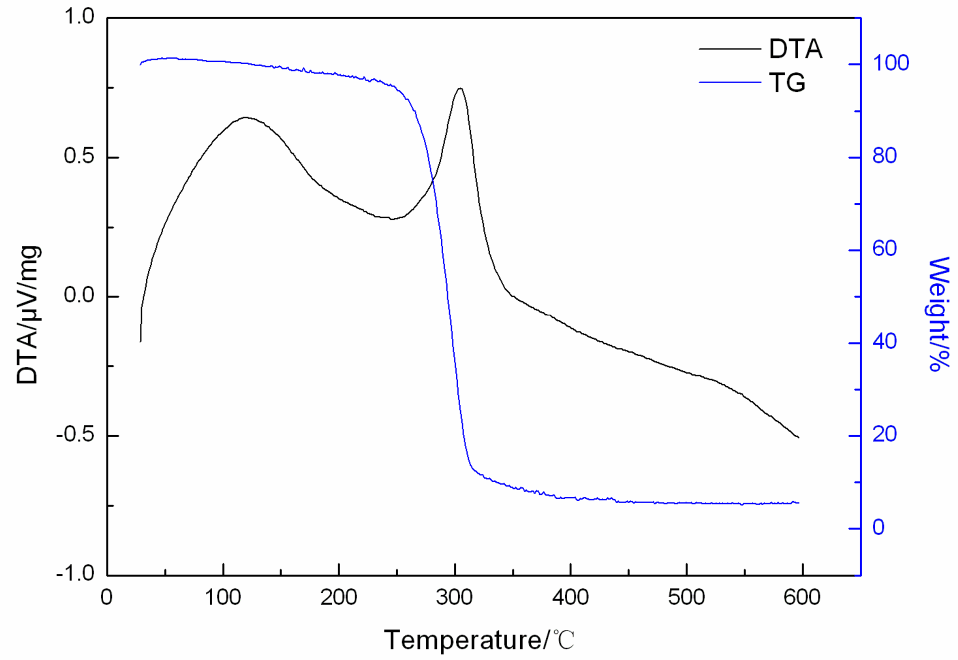

Fig. 5S DTA and TG traces of [BMIM][HP].

[BMIM][HT]

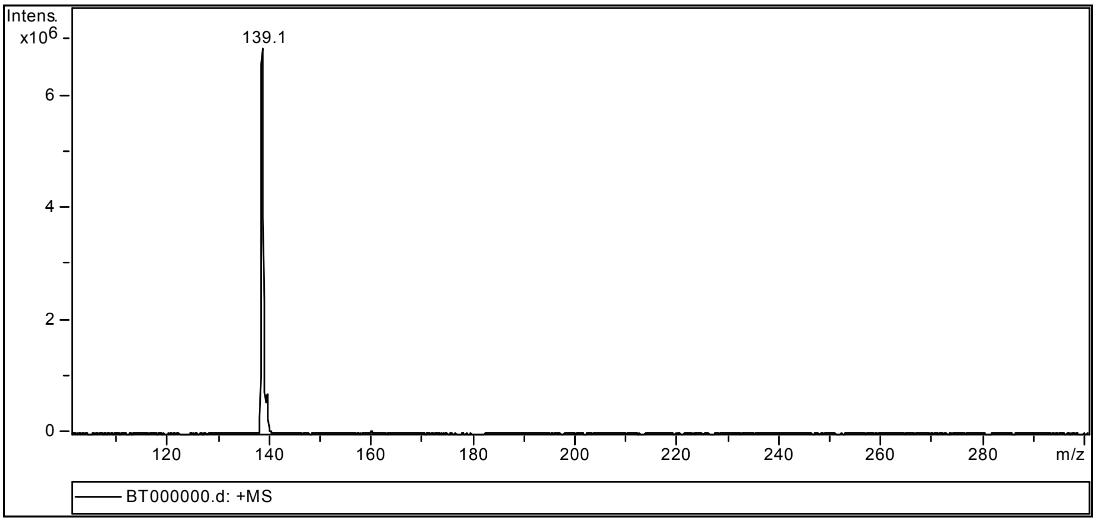

Fig. 6S Positive ion ESI spectrum of [BMIM][HT].

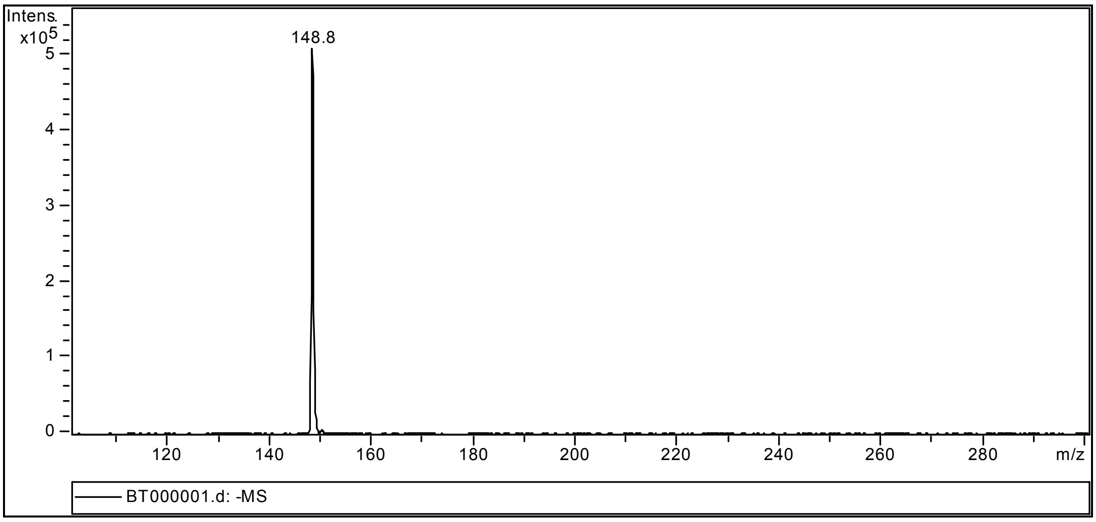

Fig. 7S Negative ion ESI spectrum of [BMIM][HT].

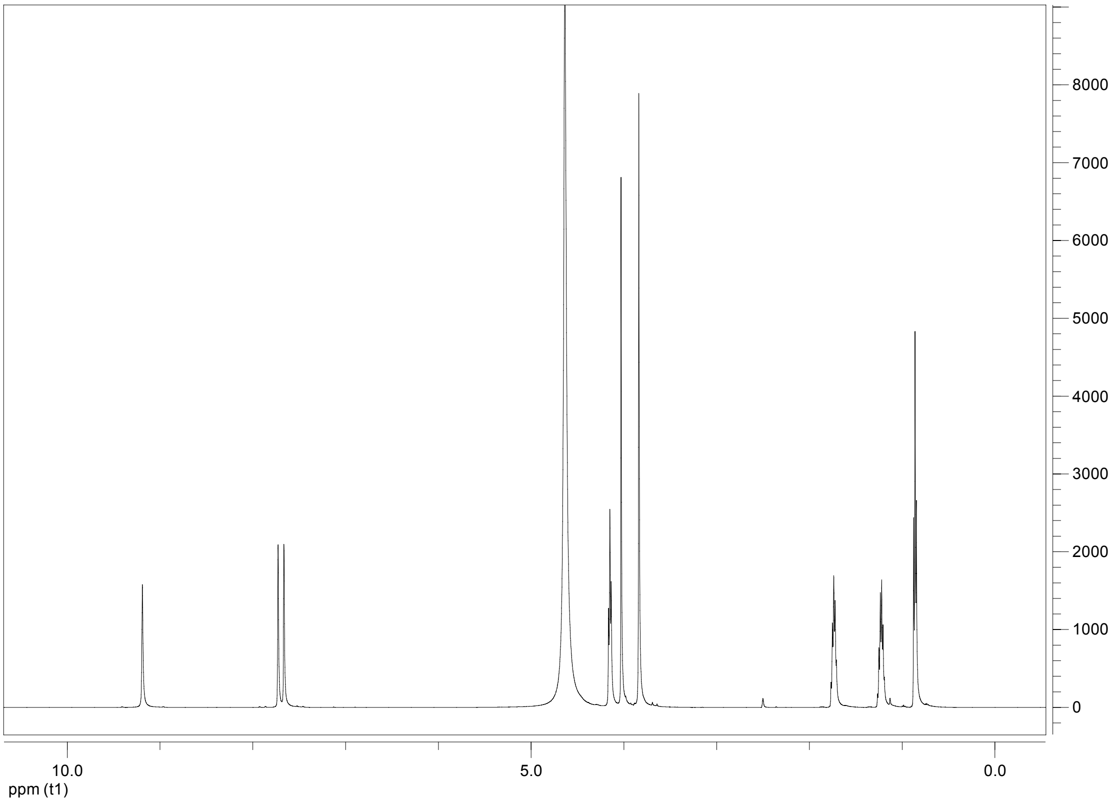

Fig. 8S ^{1}H NMR spectrum of [BMIM][HT].

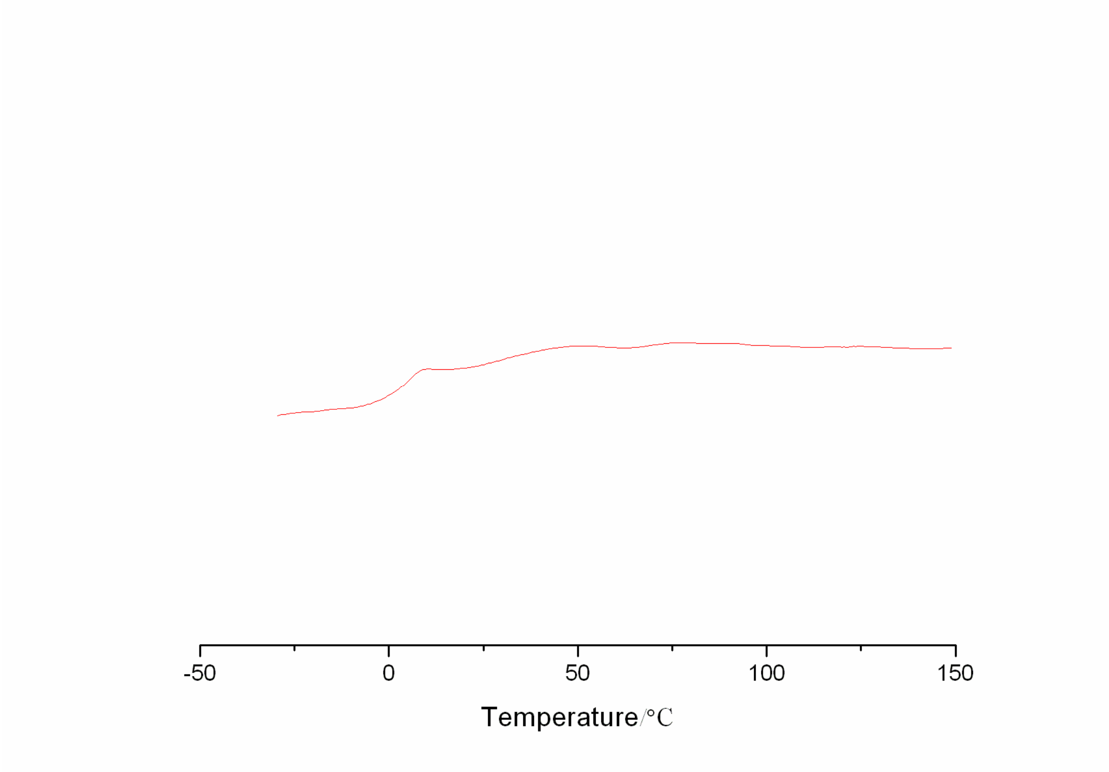

Fig. 9S DSC traces on heating for ionic-liquid buffer [BMIM][HT].

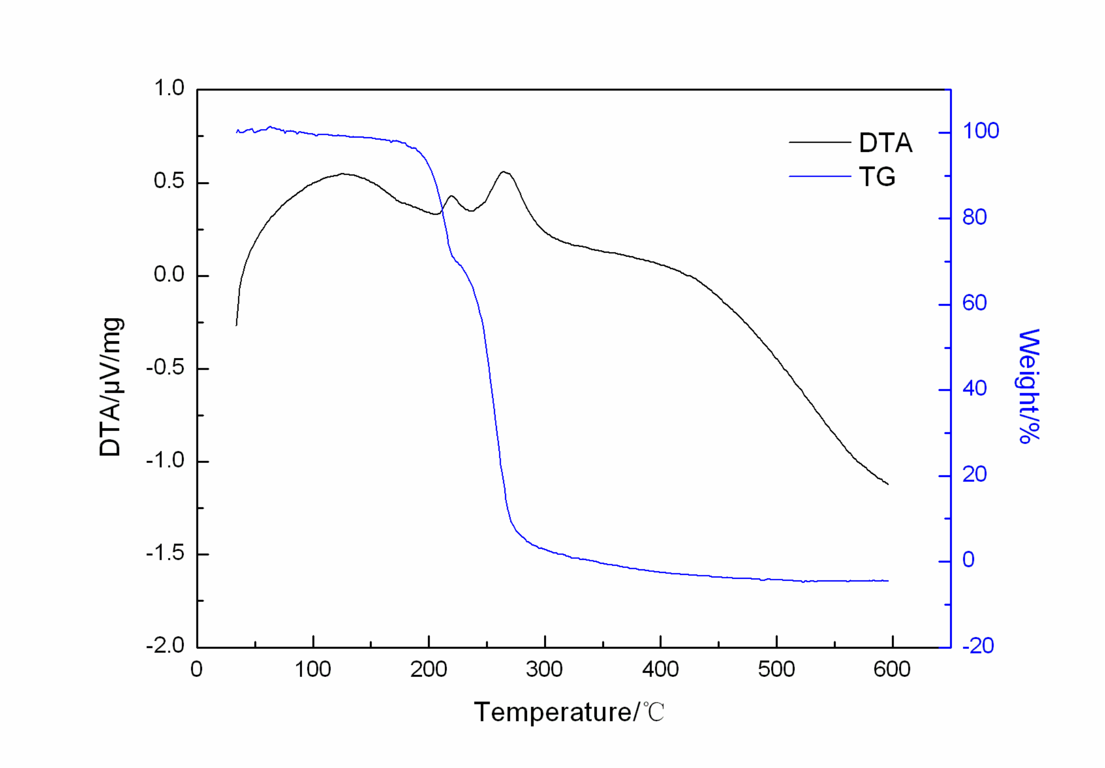

Fig. 10S DTA and TG traces of [BMIM]HT.

[OMIM][HP]

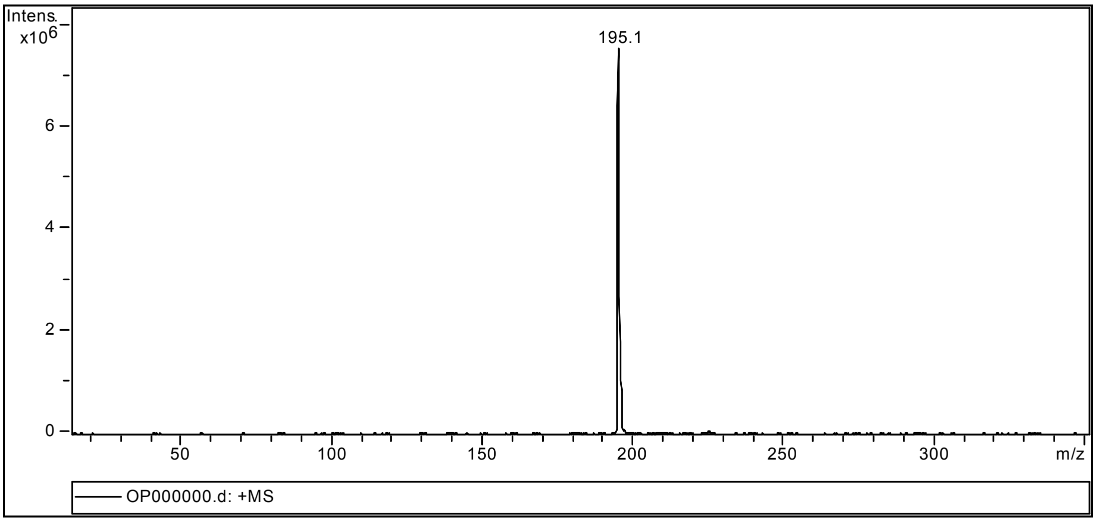

Fig. 11S Positive ion ESI spectrum of [OMIM][HP].

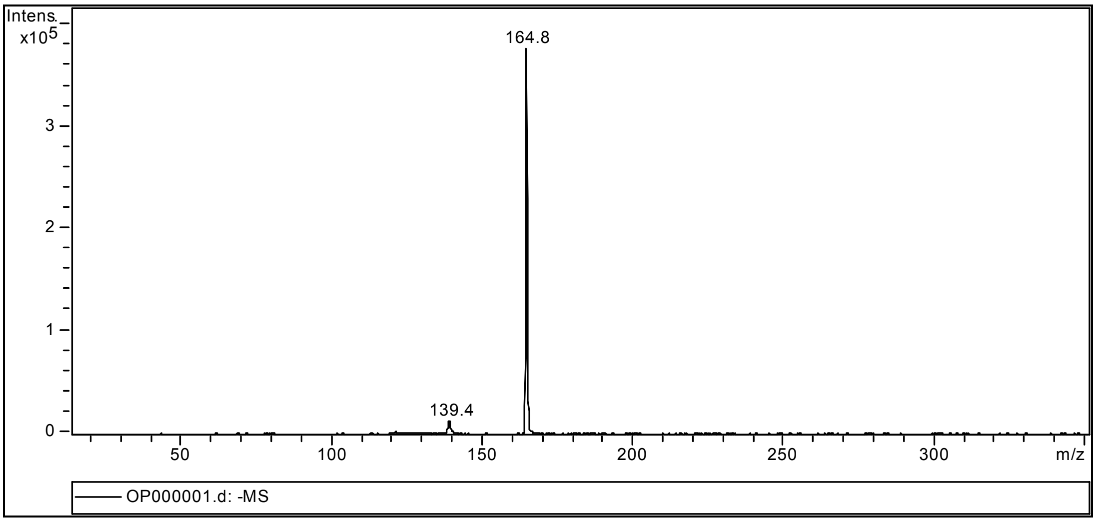

Fig. 12S Negative ion ESI spectrum of [OMIM][HP].

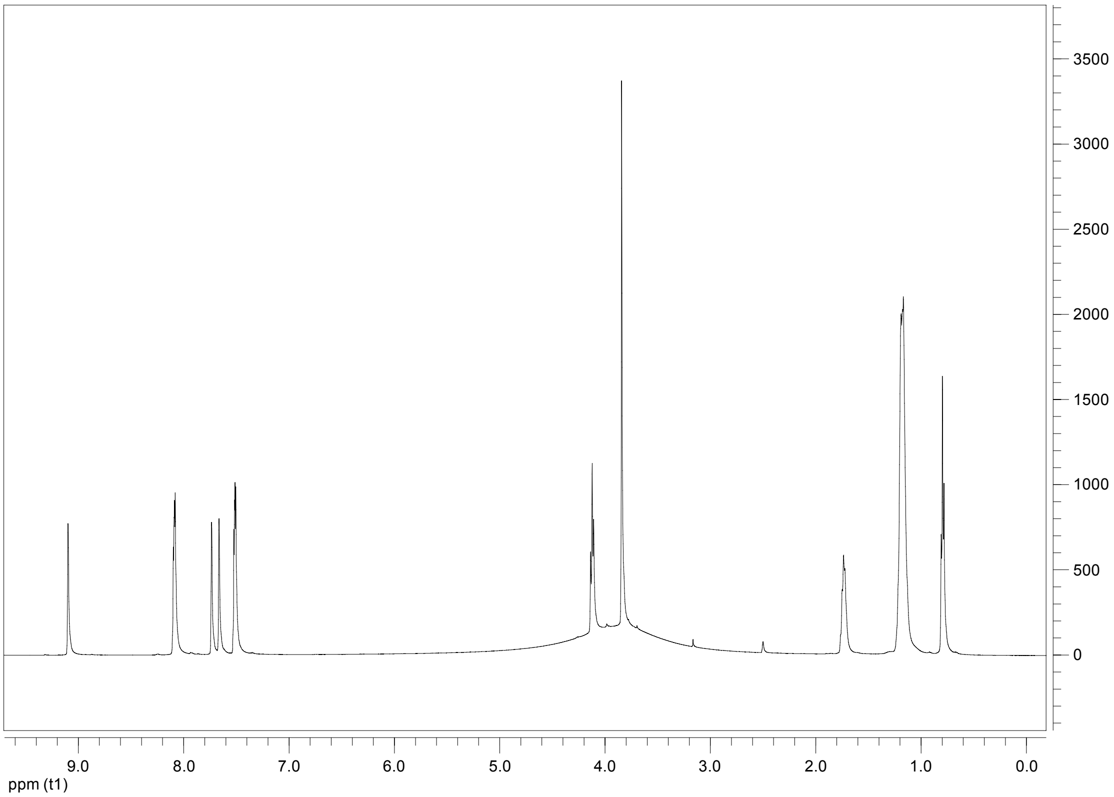

Fig. 13S ^{1}H NMR spectrum of [OMIM][HP].

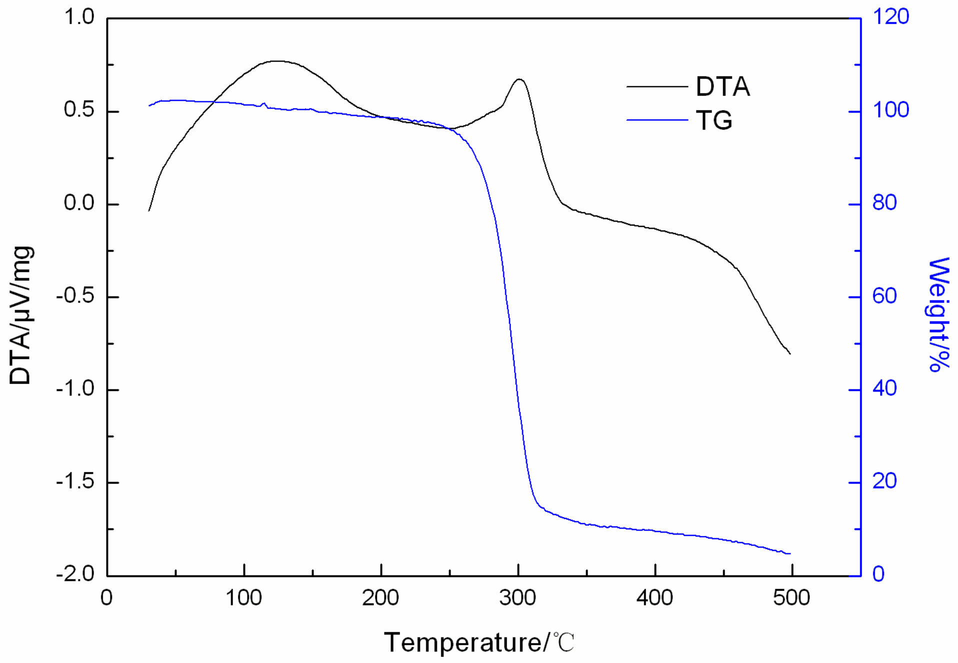

Fig. 14S DTA and TG traces of [OMIM][HP].

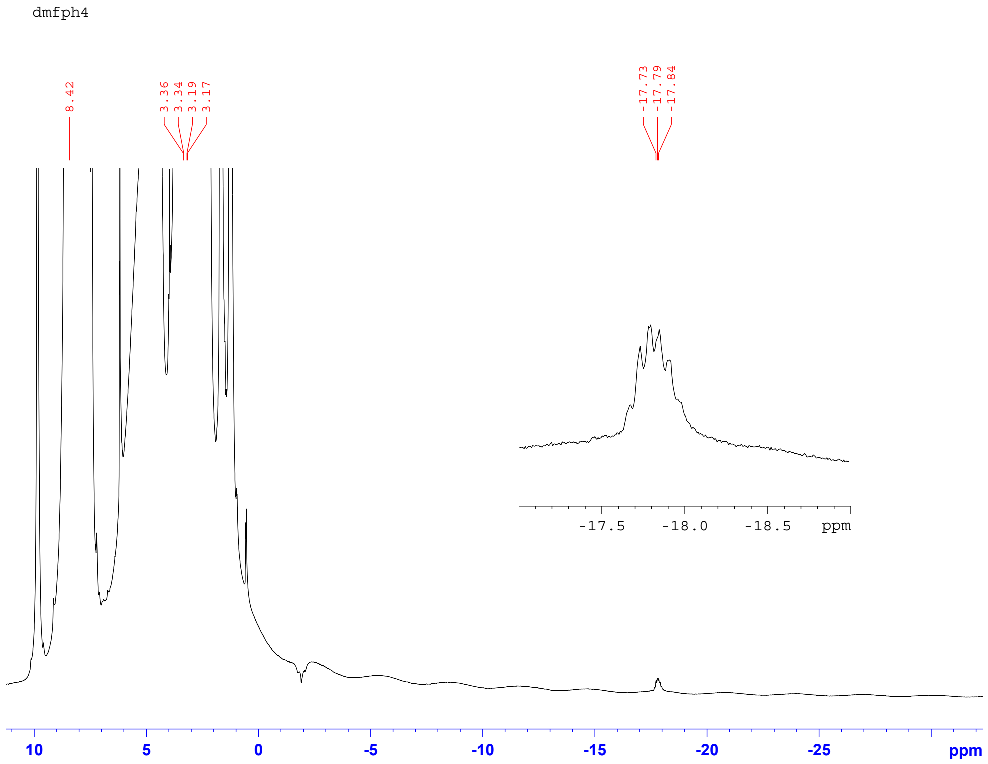

Fig. 15S ^{1}H NMR spectrum of Ru complex in DMF buffered by [BMIM][HP] with Log$_{10}$ ([Base]/[Acid]) of 0.0.

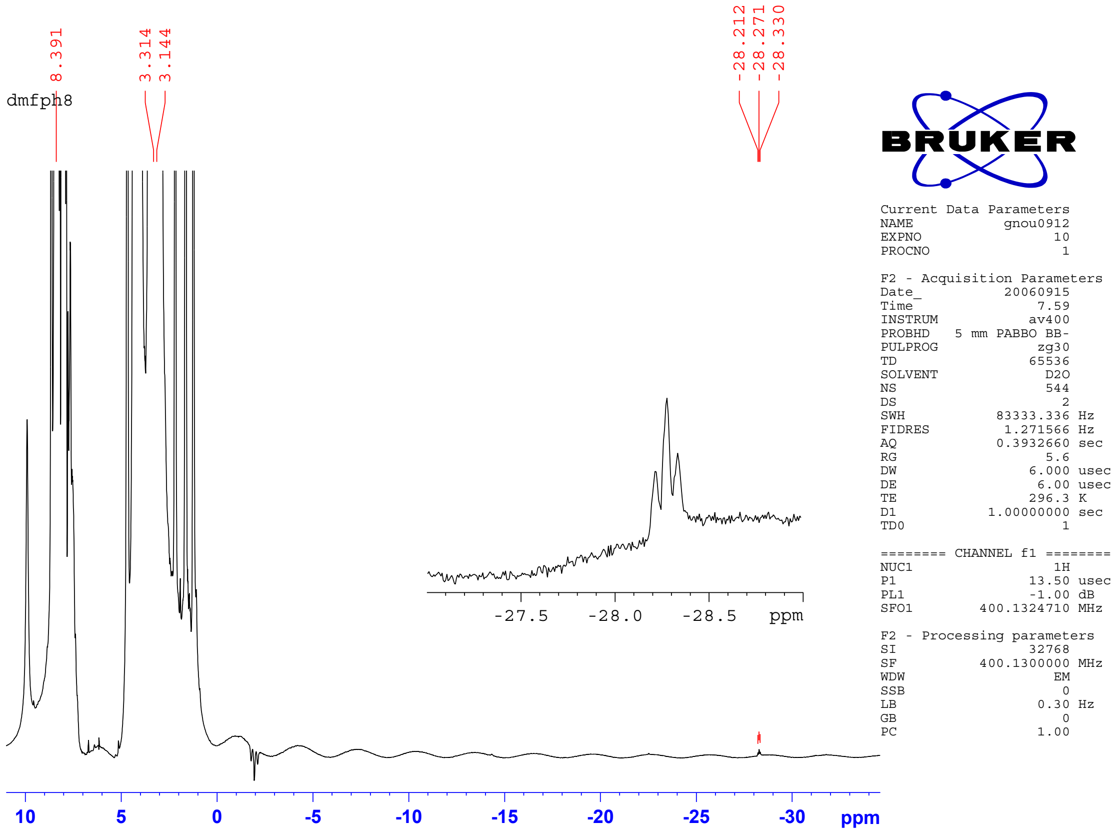

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Fig. 16S ^{1}H NMR spectrum of Ru complex in DMF buffered by[BMIM][HP] with Log$_{10}$ ([Base]/[Acid]) at 0.315.

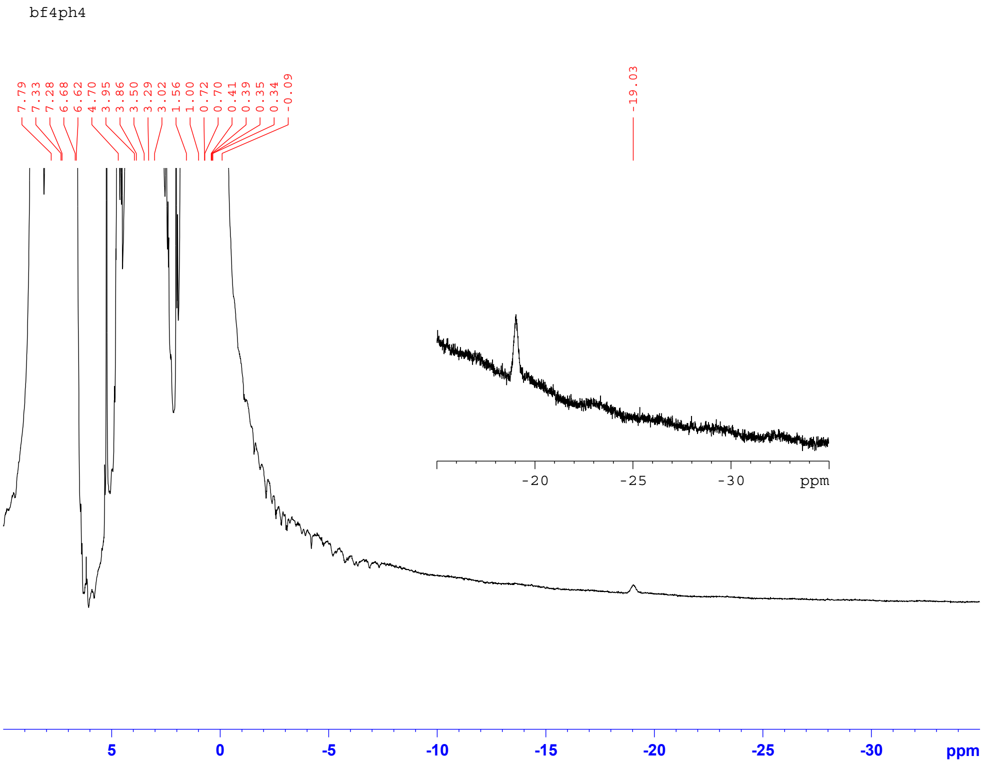

Fig. 17S ^{1}H NMR spectrum of Ru complex in [BMIM][BF_4] buffered by[BMIM][HP] with Log_{10} ([Base]/[Acid]) of 0.0.

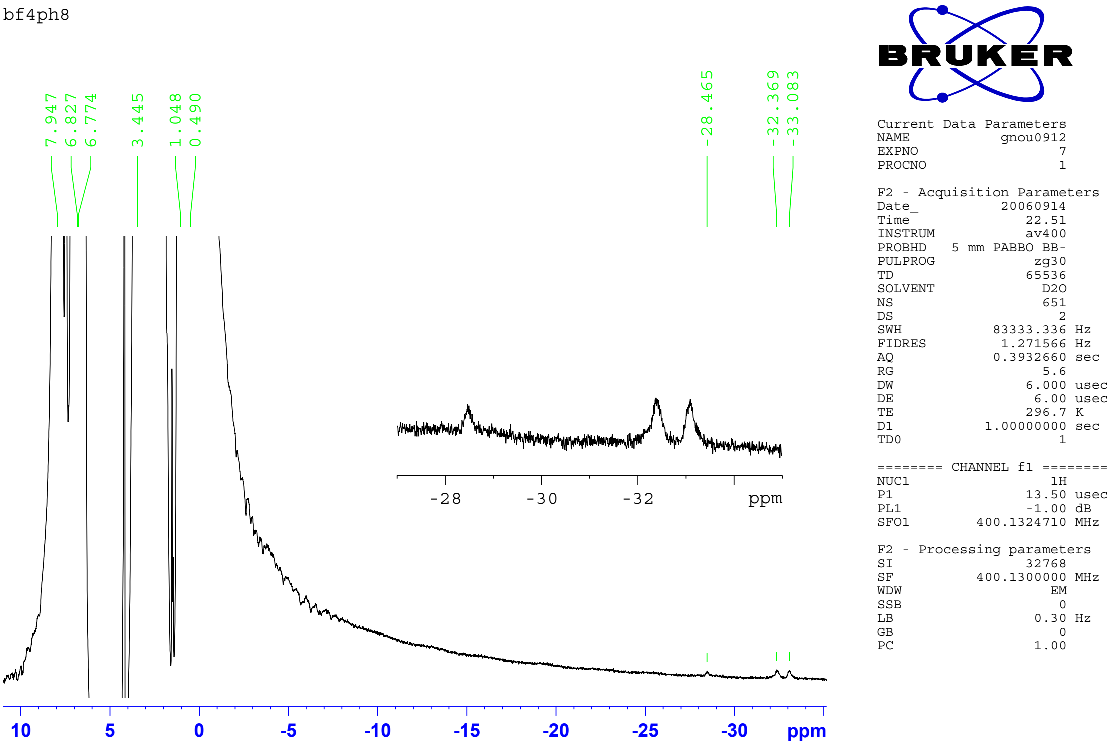

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Fig. 18S ^{1}H NMR spectrum of Ru complex in [BMIM][BF_4] buffered by[BMIM][HP] with Log_{10} ([Base]/[Acid]) of 0.315.

XII. Table 1S.

Table 1S Thermal properties, density, ionic conductivity, and solubility data of IL buffers [a)]

IL buffer	T_g / °C [b)]	T_d / °C [c)]	T_m / °C [d)]	K / mS cm^{-1} [e)]	Solubility in solvent		
					MeOH	DMF	CH_2Cl_2
[BMIM][HP] [f)]	-37	305		0.477	Miscible	Miscible	Miscible
[OMIM][HP]		305	42.0–44.4		Miscible	Miscible	Miscible
[BMIM][HT][g)]	8	220			Miscible	Miscible	Miscible

[a] Abbreviations: BMIM = 1-butyl-3-methylimidazole, OMIM = 1-octyl-3-methylimidazole, HP = hydrogen phthalate, HT = hydrogen tartrate. [b] glass transition temperature by DSC on heating. [c] Decomposition temperature by TGA. [d] Melting point by digital melting-point apparatus. [e] Specific conductivity at 25 °C. [f] Density of [BMIM][HP] at 25 °C is 1.25 g mL^{-1}. [g] Sticky liquid at room temperature.

XIII. Table 2S.

Table 2S Water content of ionic-liquid buffers and solvents

Sunstance	Water content / %
DMF	0.28
[BMIM][HP]	0.49
[OMIM][HP]	0.24
[BMIM][HT]	0.95
[BMIM][BF_4]	0.49