Supporting Information

Hydrogen-Bonding-Mediated Selective Hydrogenation of Aromatic Ketones over Pd/C in Ionic Liquids at Room Temperature

Ruipeng Li[†, ‡], Yuepeng Wang[†, ‡], Yanfei Zhao[†, ‡, §, *], Fengtao Zhang[†, ‡], Wei Zeng[†, ‡], Minhao Tang[†, ‡], Junfeng Xiang[†], Xiaoyu Zhang[†], Buxing Han[†, ‡, §], and Zhimin Liu[†, ‡, §, *]

[†]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

[‡]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

[§]Physical Science Laboratory, Huairou National Comprehensive Science Center, Beijing 101400, P. R. China;

E-mails: liuzm@iccas.ac.cn； lianyi302@iccas.ac.cn.

Number of pages: 11
Number of figures: 11
Number of Table: 1

Table of Contents

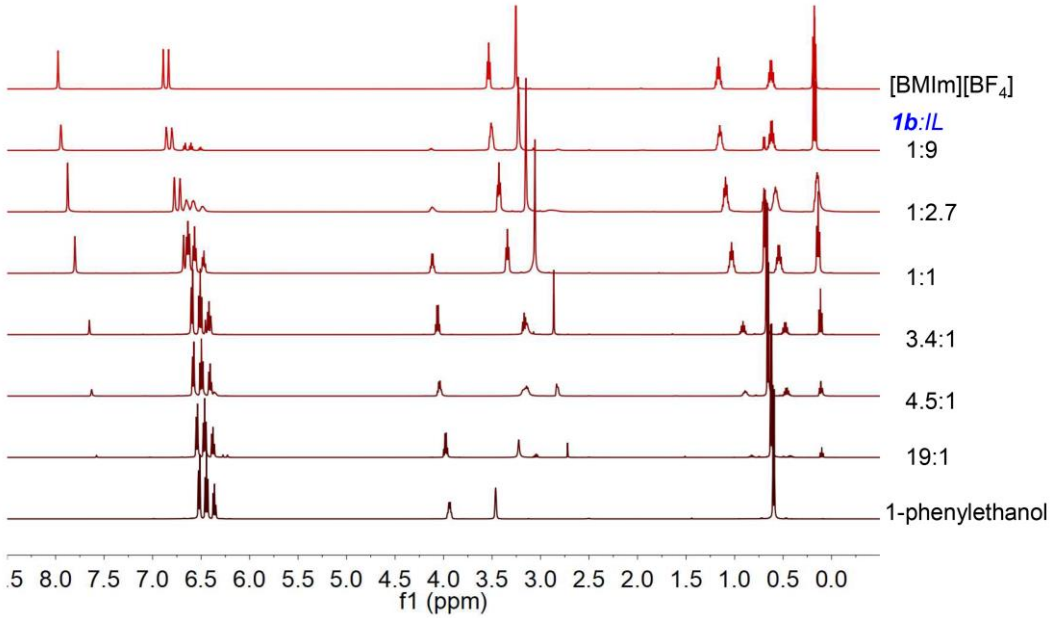

Figure S1. ^{1}H NMR (500.13 M, DMSO-d_6) spectra of 1-phenylethanol (**1b**), [BMIm][BF_4] and their mixtures with various molar ratios. (Molar ratios of **1b** to [BMIm][BF_4] were 1:9, 1:2.7, 1:1, 3.4:1, 4.5:1 and 19:1, respectively).

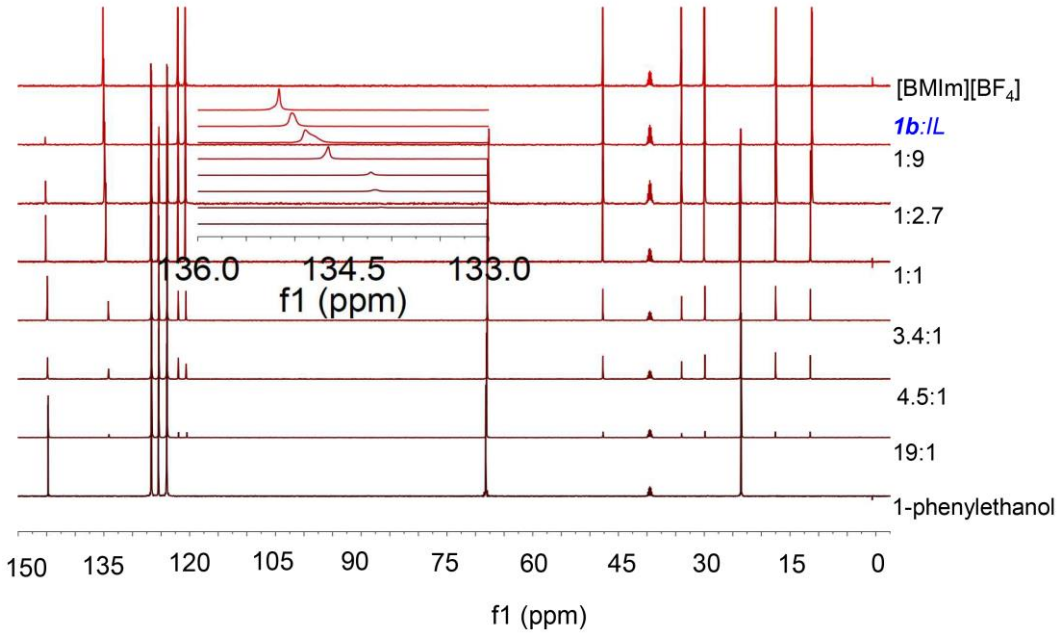

Figure S2. ^{13}C NMR (125.76 M, DMSO-d_6) spectra of **1b**, [BMIm][BF_4] and their mixtures with various molar ratios. (Molar ratios of **1b** to [BMIm][BF_4] were 1:9, 1:2.7, 1:1, 3.4:1, 4.5:1 and 19:1, respectively).

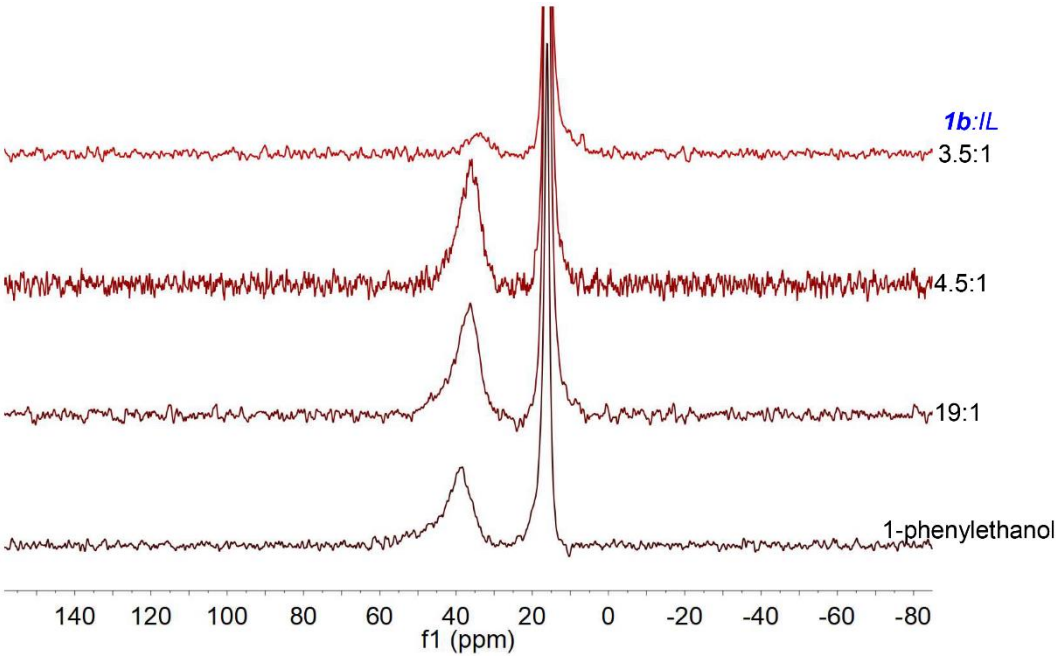

Figure S3. ^{17}O NMR (67.80 M, DMSO-d_6) spectra of **1b** and [BMIm][BF_4]-**1b** mixtures with various molar ratios. (Molar ratios of **1b** to [BMIm][BF_4] were 3.5:1, 4.5:1 and 19:1, respectively).

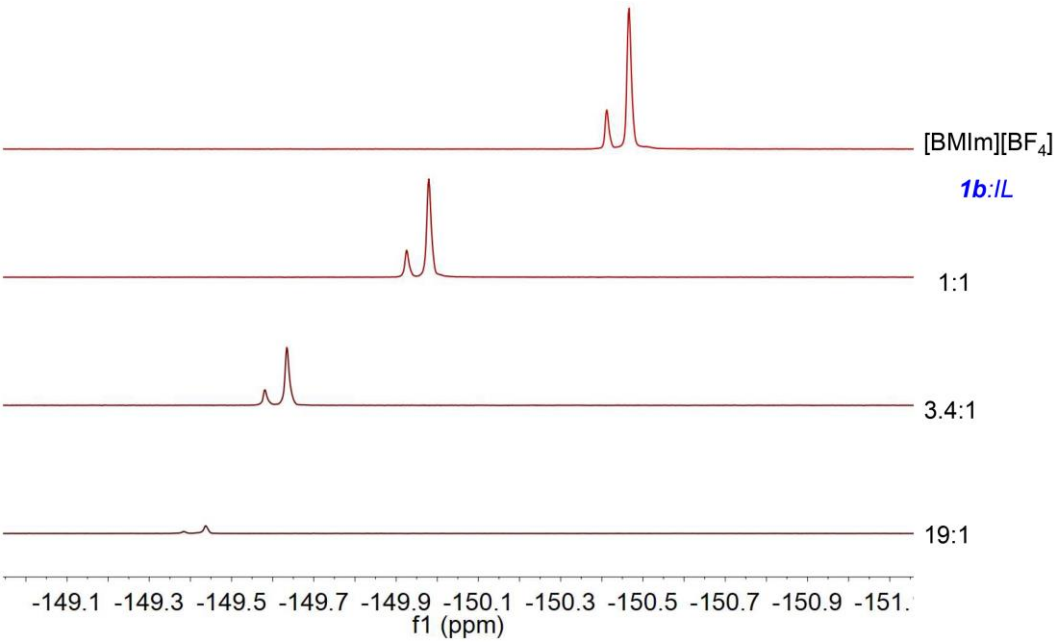

Figure S4. ^{19}F NMR (658.78 M, DMSO-d_6) spectra of [BMIm][BF_4] and [BMIm][BF4]-**1b** mixtures with various molar ratios. (Molar ratios of **1b** to [BMIm][BF_4] were 1:1, 3.4:1, and 19:1, respectively).

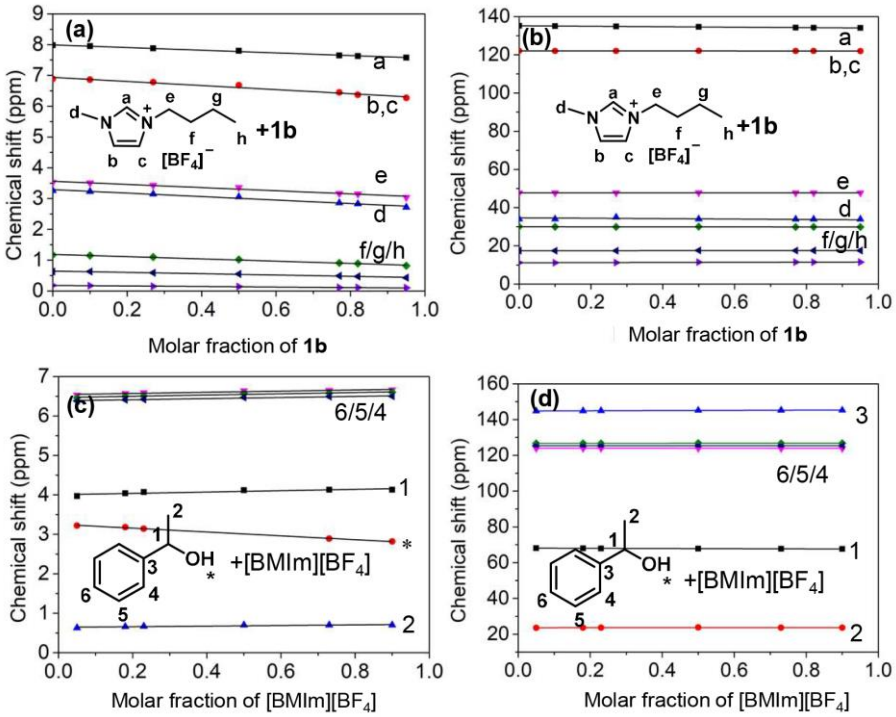

Figure S5. Correlations relationship between chemical shift for: ^{1}H (a), and ^{13}C (b) chemical shifts for [BMIm][BF_4], ^{1}H (c), and ^{13}C (d) chemical shifts for **1b**.

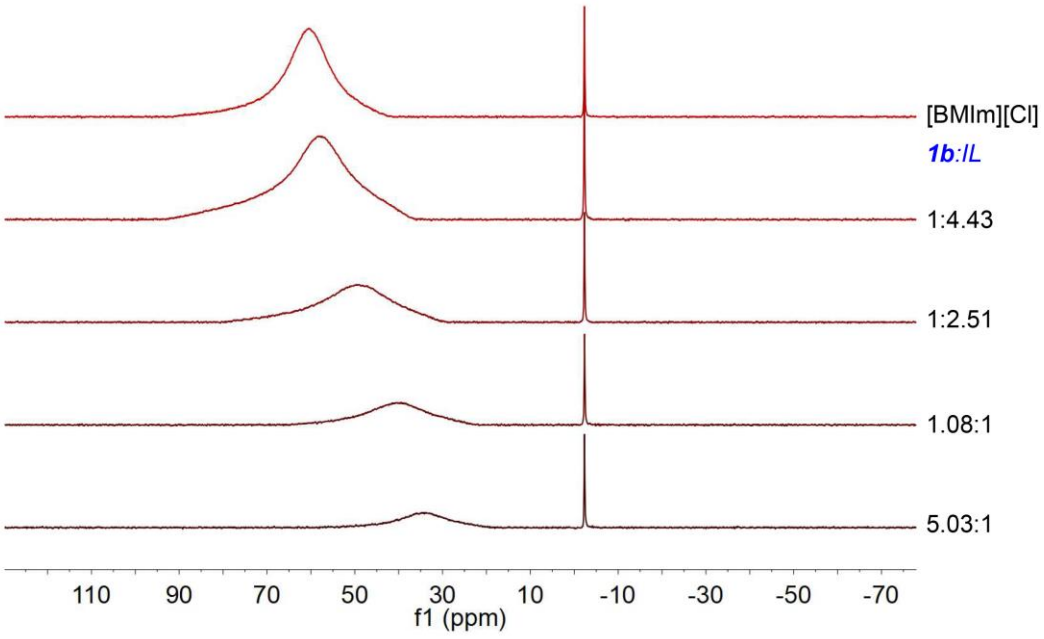

Figure S6. ^{35}Cl NMR (49.00 M, D_2O) spectra of [BMIm][Cl] and [BMIm][Cl]-**1b** mixtures with various molar ratios. (Molar ratios of **1b** to [BMIm][Cl] were 5.03:1, 1.08:1, 1:2.51, and 1:4.43, respectively).

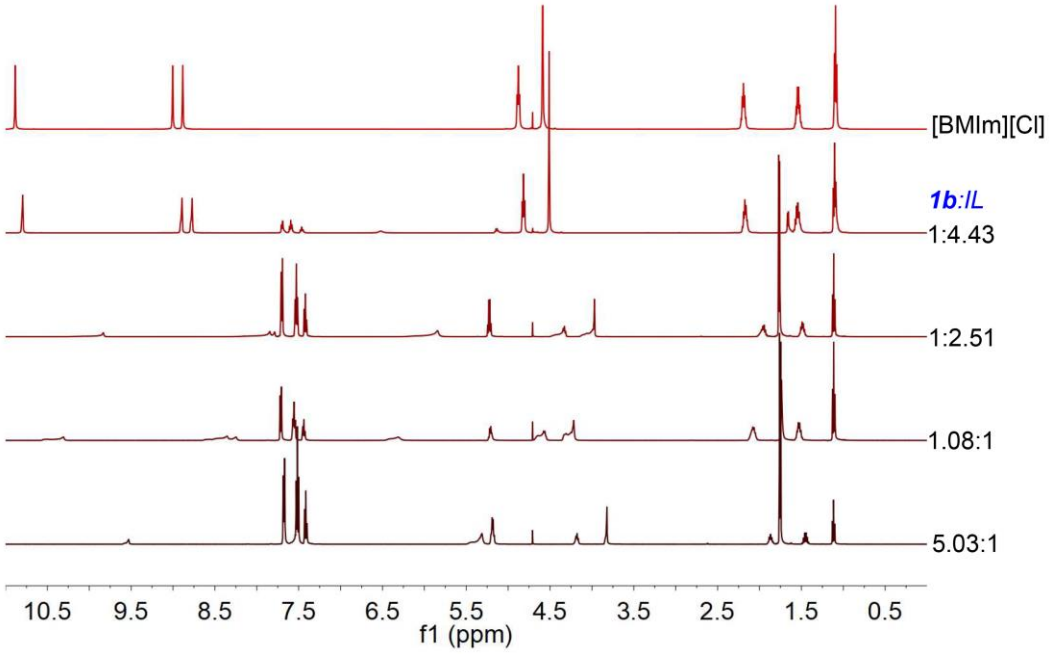

Figure S7. ^{1}H NMR (500.13 M, D_2O) spectra of [BMIm][Cl] and [BMIm][Cl]-**1b** mixtures with various molar ratios. (Molar ratios of **1b** to [BMIm][Cl] were 1:4.43, 1:2.51, 1.08:1 and 5.03:1, respectively).

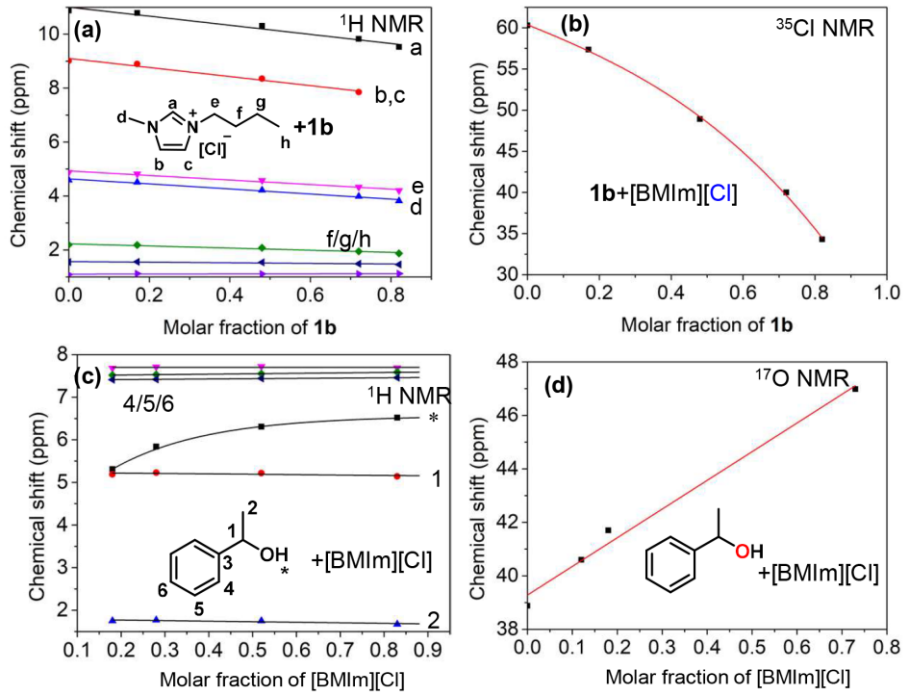

Figure S8. Correlations relationship between chemical shifts for: ^{1}H (a), and ^{35}Cl (b) chemical shifts for [BMIm][Cl], ^{1}H (c), and ^{17}O (d) chemical shifts for **1b**.

Note: The H protons of **1b** exhibit little changes except the H protons of -OH, while the H protons at the imidazolium ring have a larger change, suggesting that the hydrogen bond between -OH and IL existed. The decreased electron cloud density of H protons of -OH indicating that the O-H bond was stretched, it may be attributed to the formation of hydrogen bond between -OH and $[Cl]^-$. The electron cloud density of oxygen nuclei decreased as increasing the concentration of ILs, suggesting that hydrogen bonds between -OH and associated -OH were disrupted. The decreased electron cloud density of $[Cl]^-$ suggesting the formation hydrogen bond between **1b** and [BMIm][Cl].

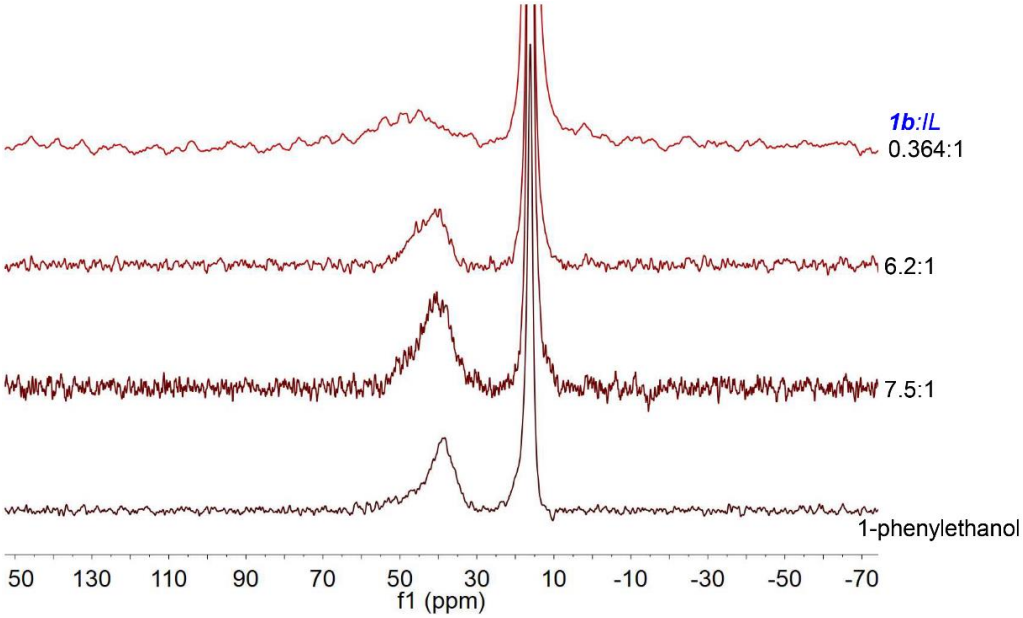

Figure S9. ^{17}O NMR (67.80 M, DMSO-d_6) spectra of **1b** and [BMIm][Cl]-**1b** mixtures with various molar ratios. (Molar ratios of **1b** to [BMIm][Cl] were 0.364:1, 6.2:1 and 7.5:1, respectively).

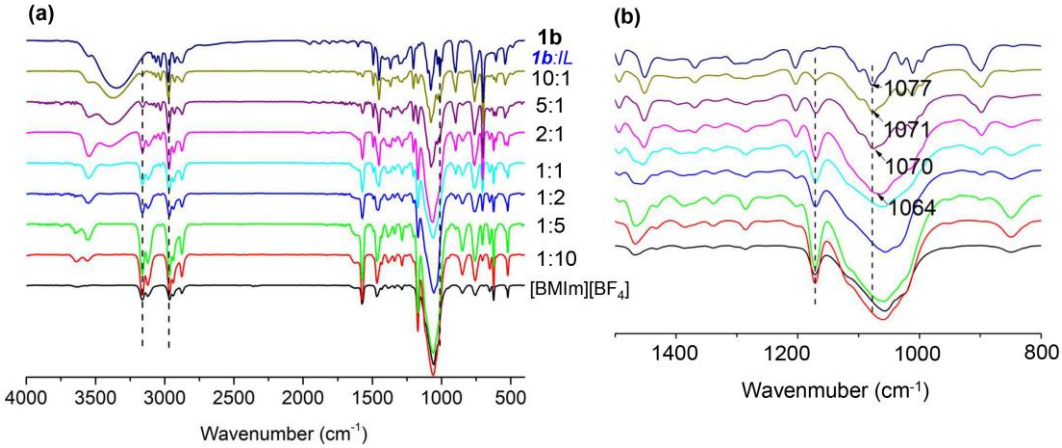

Figure S10. FT-IR spectra of **1b**, [BMIm][BF_4] and the [BMIm][BF_4]-**1b** mixtures from 4000-400 cm^{-1} (a) and 1500-800 cm^{-1} (b) at various **1b**:IL molar ratios of 10:1, 5:1, 2:1, 1:1, 1:2, 1:5, and 1:10.

Note: The [BMIm][BF_4]-**1b** mixtures with different molar ratios were prepared. After stirring completely, the sample was applied to a KBr pellet and conducted for FT-IR spectra. The peak at 3162

cm^{-1} ascribing to C-H of imidazolium ring shifts to lower wavenumbers, suggesting that C-H is activated due to the interaction with **1b**. The signals at 1077 cm^{-1} can be ascribed to the vibration of C-O bond of **1b**, which shows a more obvious red-shift for [BMIm][BF_4]-**1b**, suggesting that the C-O bond is stretched.

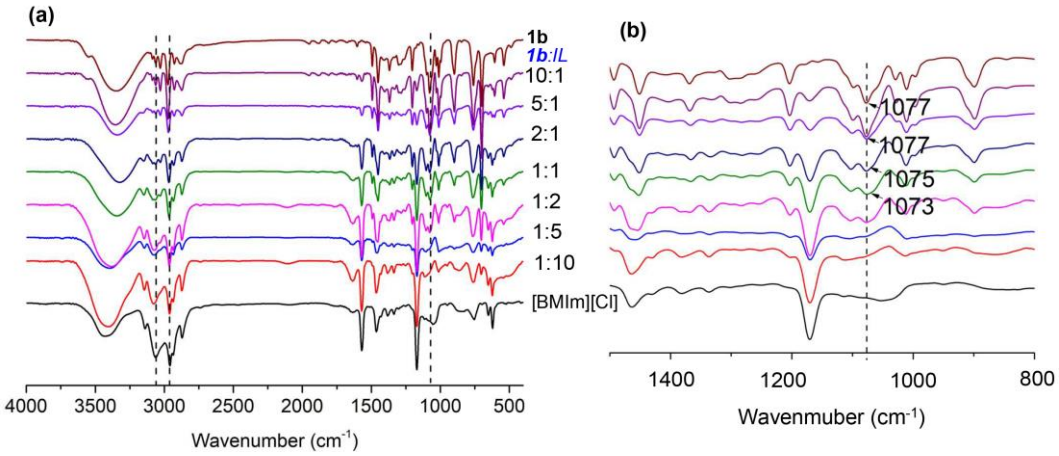

Figure S11. FT-IR spectra of **1b**, [BMIm][Cl] and the [BMIm][Cl]-**1b** mixtures at various **1b**:IL of molar ratios of 10:1, 5:1, 2:1, 1:1, 1:2, 1:5, and 1:10.

Note: The [BMIm][Cl]-**1b** mixtures with different molar ratios were prepared. After stirring completely, the sample was applied to a KBr pellet and conducted for FT-IR spectra. The signal at 1077 cm^{-1} can be ascribed to the vibration of C-O bond, and the wavenumber changes via IL concentration were not obvious compared that for [BMIm][BF_4]-**1b**, suggesting that the [BMIm][BF_4] can active C-O bond better. The signal at 3062 cm^{-1} attributed to C-H vibration have a bule-shift, suggesting that the strength of hydrogen bonds between cations and anions of the ILs may be decreased after adding **1b**.

DFT calculations:

1b

O	-2.07824500	-1.19174500	-0.55076600
C	-0.14624900	-0.03205300	0.16272800
C	0.49577700	1.19019900	-0.02926600
C	0.62780800	-1.19600600	0.21949600
C	-1.64886900	-0.15306600	0.33465400
C	1.88327700	1.24974300	-0.16254300
C	2.00933500	-1.13947700	0.08450500
C	2.64326500	0.08765500	-0.10731300
C	-2.42627700	1.12635700	0.07705700
H	-0.07777600	2.10803000	-0.07930900
H	0.13536400	-2.15122700	0.36502000
H	2.36629100	2.20874400	-0.31282700
H	2.59375900	-2.05163300	0.12942800
H	3.72114100	0.13443300	-0.21291900
H	-2.15694800	1.90470200	0.79420900
H	-3.49536300	0.92763800	0.18566800

H	-2.24232400	1.49474100	-0.93524400
H	-1.83705000	-0.47660900	1.36690800
H	-3.00953300	-1.36497200	-0.37071700

1b + [BMIm][BF_4]

O	0.85147400	1.95853800	1.36655100
C	2.31353400	1.31889100	-0.43713700
C	3.63933300	0.94643000	-0.22287200
C	1.54232300	0.57657500	-1.33706800
C	1.71244700	2.47437200	0.34414000
C	4.18990700	-0.15060700	-0.88502600
C	2.08667100	-0.51909600	-1.99884400
C	3.41296700	-0.88727300	-1.77288700
C	0.97633400	3.47400700	-0.53436900
H	4.24521700	1.51636100	0.47527800
H	0.50244500	0.84147700	-1.49992500
H	5.22283200	-0.42787800	-0.70565000
H	1.47485800	-1.09086500	-2.68904700
H	3.83584900	-1.74278200	-2.28767400
H	1.64694500	3.87510100	-1.29701100
H	0.60490600	4.30262500	0.07338000
H	0.12445600	3.00413300	-1.03372400
H	2.53253700	2.98711100	0.85647200
H	-0.05950400	2.22625600	1.18147400
C	0.46982200	-1.20781900	0.88979500
C	0.95682500	-3.20153100	0.09240700
C	1.93565800	-2.85036800	0.96732000
N	1.61061000	-1.60201100	1.44938700
H	-0.00711800	-0.25119900	1.04480000
H	0.82418800	-4.08486800	-0.50949200
H	2.82539900	-3.36724000	1.28614100
N	0.05322900	-2.16346700	0.06195000
C	2.37014500	-0.84300100	2.44167400
H	2.21816200	-1.28506900	3.42598700
H	3.42479300	-0.87644500	2.17482700
H	2.01218500	0.18485100	2.42723600
C	-1.14233000	-2.07773200	-0.78980100
H	-1.05850400	-1.16528500	-1.38192000
H	-1.10150300	-2.93645200	-1.46039700
C	-2.42361700	-2.07448200	0.03099600
H	-2.49908600	-3.01541100	0.58647100
H	-2.38153500	-1.25836100	0.75823600
C	-3.64618800	-1.88745200	-0.86266800
H	-3.66126300	-2.66920200	-1.62995400
H	-3.55919200	-0.92974000	-1.38681000
C	-4.94498000	-1.92178800	-0.06359400
H	-5.81231100	-1.77143300	-0.71028400
H	-5.06582300	-2.88321600	0.44359200
H	-4.95160700	-1.13590700	0.69589200
F	-1.85850100	2.71622300	1.03897300
F	-1.50689200	0.88093600	-0.27562900

F	-3.56032600	1.21136200	0.69720400
F	-2.86977600	2.57060500	-1.01978400
B	-2.46593100	1.84331900	0.10221000

1b +[BMIm][Cl]

O	1.08579700	1.92585100	0.88730300
C	2.79818600	0.85926500	-0.36597500
C	4.05686000	0.74567100	0.22505000
C	2.28350100	-0.23643000	-1.06393300
C	1.99956300	2.13852400	-0.18839100
C	4.79094500	-0.43446300	0.12603100
C	3.01569100	-1.41531700	-1.17129000
C	4.27123400	-1.51876500	-0.57476500
C	1.28097500	2.58789300	-1.45175700
H	4.46442900	1.59178400	0.76975200
H	1.30142500	-0.17831500	-1.52429000
H	5.76739600	-0.50467000	0.59206800
H	2.60523600	-2.25523300	-1.72110900
H	4.84094600	-2.43723600	-0.66006100
H	1.99602300	2.72258900	-2.26645900
H	0.77548800	3.54005600	-1.27364500
H	0.52798100	1.85919500	-1.76224800
H	2.70325600	2.92520300	0.10878000
H	0.22974600	2.35225800	0.69649600
C	-0.60736200	-0.63110000	0.71321200
C	-0.78690000	-2.50385700	-0.43382800
C	0.26490500	-2.63143800	0.41769800
N	0.35685600	-1.45154900	1.12040600
H	-0.78853600	0.37558500	1.06198500
H	-1.20164900	-3.18301000	-1.15999600
H	0.95778100	-3.44076400	0.57718600
N	-1.31128300	-1.24585700	-0.23546100
C	1.38813900	-1.12579400	2.10295000
H	1.20891100	-1.68996900	3.01750100
H	2.36033200	-1.38462500	1.68257200
H	1.34606200	-0.05576800	2.29321100
C	-2.48734700	-0.67628400	-0.90906500
H	-2.27574900	0.37850600	-1.09093200
H	-2.58074000	-1.19383700	-1.86440700
C	-3.74426500	-0.82861300	-0.06496000
H	-3.91746000	-1.88970400	0.14521400
H	-3.58778800	-0.32095900	0.89270300
C	-4.95555600	-0.22647800	-0.77136400
H	-5.10162400	-0.72911400	-1.73344400
H	-4.75222000	0.82672700	-0.99146900
C	-6.22181200	-0.34147200	0.07094600
H	-7.08206900	0.09151800	-0.44422200
H	-6.45199100	-1.38799000	0.28980300
H	-6.10190700	0.18225800	1.02321200
Cl	-1.96054200	2.63014800	0.59325900

Table S1. The length of C-O bond, hydrogen bond of O-H…Anion, C-H…Anion, C-H…O and charge of α-C atom of -OH, and O atom.

	Length C-O (Å)	Length O-H (Å)	Length O-H…Anion (Å)	Length C-H…Anion (Å)	Length C-H…O (Å)	Charge C	Charge O
1b	1.42805	0.96507	/	/	/	0.035	-0.518
1b-[BMIm][Cl]	1.41910	0.97859	2.16919	2.51921	2.54418	-0.029	-0.515
1b-[BMIm][BF_4]	1.42714	0.96911	1.85588	2.35923	2.27533	-0.015	-0.522