

Electronic Support Information

Application of Functional Metal Cationic Lewis
Acid Ionic Liquid in Alkylation of Chlorobenzene
/SOCl₂

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S1. Properties of ILs

S1.1 H₀ test method

Fully alkaline reagent: 8% (mass fraction) sulfuric acid solution ($H_0 = -0.20$). The pK_{BH^+} of H_0 and the indicator 2, 4-dinitro-6-bromoaniline given $|pK_{BH^+} - H_0| \geq 2.3$, so they can both be used as full alkaline reagents. At 25 °C, the medium was thoroughly mixed with 2, 4-dinitro-6-bromoaniline at a concentration of 8.5 mg/L, and placed away from light for 2h to reach full alkalization. Then UV was used to determine the medium.

Full protonation reagent: 97.8% sulfuric acid ($H_0 = -10.42$) with indicator 2, 4-dinitro-6-bromoaniline given $|pK_{BH^+} - H_0| \geq 2.3$, which can fully protonate the indicator. The protone-type solution was prepared by mixing 97.8% sulfuric acid with the indicator, and the concentration was 8.5 mg/L. After full mixing, the solution was placed away from light for 2h at room temperature, and then tested by UV after reaching full protonation.

Hammett acidity function value H_0 of ionic liquid can be calculated according to the following formula $H_0 = pK_a(I) + \lg([I]_s/[IH^+]_s)$, where I represents alkaline indicator, and $[IH^+]_s$ and $[I]_s$ represent indicator concentrations of protonation and unprotonation, respectively.

The tested acid was mixed with the indicator to prepare a solution with an indicator concentration of 8.5 mg/L. After the solution was fully mixed to reach equilibrium, the ultraviolet absorption spectrum of 2, 4-

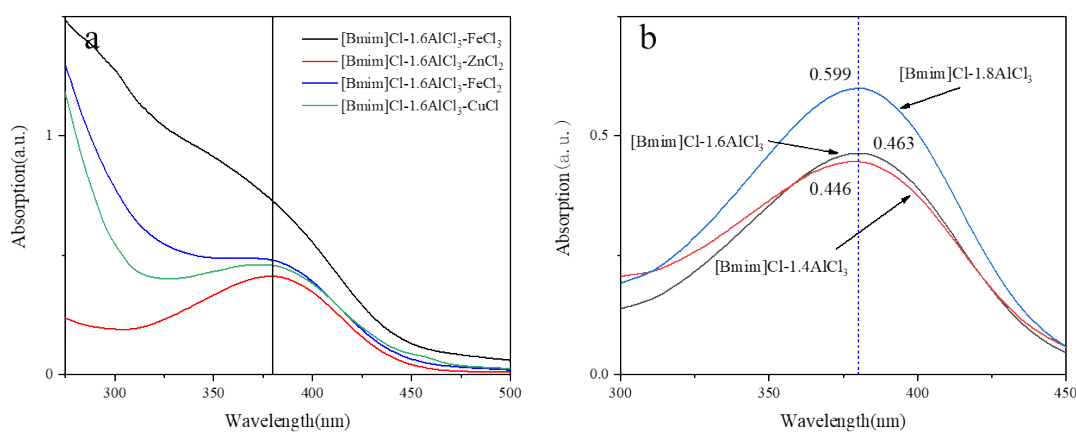


Figure S1 Uv absorption spectrum

dinitro-6-bromoaniline was scanned for determination (show as Figure. S1 and Table.S1).

Table.S1 Acid strength of metal - based ionic liquids

Catalyst	Absorption(a.u.)	H ₀
[Bmim]Cl-1.4AlCl ₃	0.446	1.08
[Bmim]Cl-1.6AlCl ₃	0.463	1.05
[Bmim]Cl-1.8AlCl ₃	0.599	0.82
[Bmim]Cl-AlCl ₃ -FeCl ₃	0.741	0.53
[Bmim]Cl-AlCl ₃ -ZnCl ₂	0.412	1.14
[Bmim]Cl-AlCl ₃ -FeCl ₂	0.482	1.02
[Bmim]Cl-AlCl ₃ -CuCl	0.459	1.06

S1.3 Acidity of IL

The acidity of ionic liquid [Bmim]Cl-1.6AlCl₃ and different complex metal-based ionic liquids was studied by Py-IR, as shown in Figure S2a. The ionic liquid [Bmim]Cl-1.6AlCl₃ has an obvious absorption band at 1540 cm⁻¹, which is attributed to the presence of Brønsted acidity. In the Py-IR spectra of [Bmim]Cl-1.6AlCl₃, bands appear near 1450 cm⁻¹, indicating the presence of Lewis acid site in the ionic liquid [Bmim]Cl-1.6AlCl₃.

The acidity of the complex ionic liquid [Bmim]Cl-1.6AlCl₃-MCl_x (molar ratio of AlCl₃: MCl_x is 12:1) was analyzed by infrared spectroscopy using pyridine as a probe (Figure S2b). The peak near 1540 cm⁻¹ in [Bmim]Cl-1.6AlCl₃ was compared with the corresponding peak in the presence of MCl_x. After the addition of IL by FeCl₃, ZnCl₂, FeCl₂ or CuCl, the wave number showed an obvious absorption peak near 1540 cm⁻¹. This indicates that IL retains the original Brønsted acidity. The acidity order of Brønsted is FeCl₃>ZnCl₂>FeCl₂>CuCl. At the same time, there was an obvious absorption peak near 1450 cm⁻¹ wave number, indicating that IL possessed Lewis acidity. Moreover, in Figure S2b, Lewis acidity improves significantly at its peak around 1450 cm⁻¹ Figure S2b with the addition of FeCl₃, ZnCl₂, FeCl₂, or CuCl.

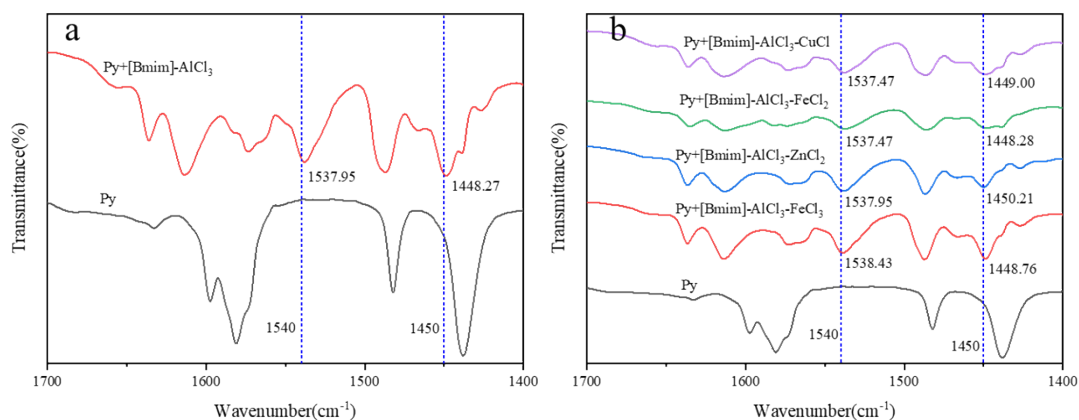


Figure S2 Py-IR spectrum

S1.4 By-product analysis

We performed LC-MS tests on the reaction system after the reaction. We analyzed the test results in conjunction with references, as shown in Figure R1. Among them are S-Aryl Arenesulfonothioate (Figure S3 a), 2,4'-dichlorodiphenyl sulfone (Figure S3 b), 2,2'-dichlorodiphenyl sulfone (Figure S3 c), and a very small amount of dimer of 4,4'-dichlorodiphenyl sulfone (Figure S3 d). The halogen atom, as a class of substituents, readily activates the benzene ring to undergo pro- and interposition substitution, resulting in the isomers with o-position substitution. At the same time, a very small fraction of 4,4'-dichlorodiphenyl sulfoxide is oxidized in an oxygen environment and polymerized in an acidic environment, resulting in the dimerization of 4,4'-dichlorodiphenyl sulfone.

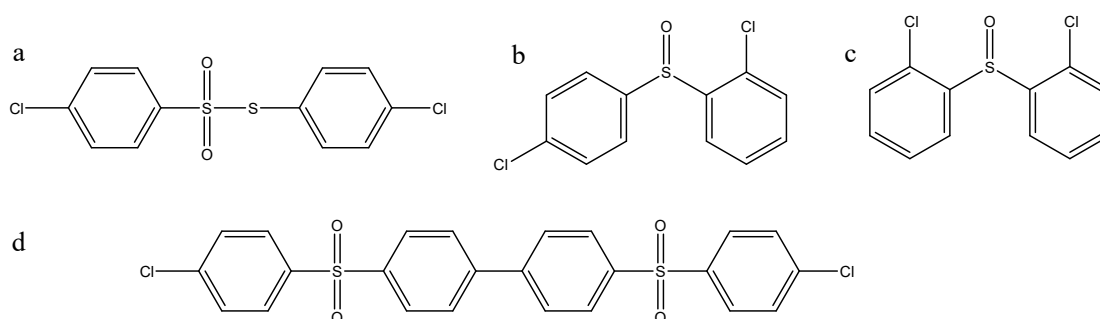


Figure S3 Structural formula of main by-products

S1.5 ICP test

The ICP test results are shown in Table S2. The tested content in the ICP test values did not differ much from the theoretical values.

Table S2 Elemental content in IL

Catalyst	Elemental content/(mg/kg)					
	Al		Fe		Zn	
	Theoretical content	Actual content	Theoretical content	Actual content	Theoretical content	Actual content
[Bmim]Cl- 1.6AlCl ₃	1.11×10^5	1.11×10^5				
[Bmim]Cl- AlCl ₃ - FeCl ₃	1.05×10^5	1.05×10^5	1.82×10^4	1.83×10^4		
[Bmim]Cl- AlCl ₃ - ZnCl ₂	1.06×10^5	1.06×10^5			2.15×10^4	2.14×10^4

S2. Blank control experiment of metal salt catalysis

Table.S3 Blank comparison of metal salt catalysis

Catalyst	Conversion/%	Selectivity/%
FeCl ₃	82.6	2.2
FeCl ₂	96.4	0.71
CuCl	100	0.21