## **Supporting Information**



S-Figure 1. <sup>1</sup>H NMR of IL [mmim][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 2. <sup>1</sup>H NMR of the six recyle IL [mmim][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 3. <sup>13</sup>C NMR of IL [mmim][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 4.  $^{13}\!C$  NMR of the six recyle IL [mmim][Me\_2PO\_4]



S-Figure 5. FT-IR spectra of IL [mmim][Me<sub>2</sub>PO<sub>4</sub>] (a: New IL, b: Reused IL for six times)



S-Figure 6. <sup>1</sup>H NMR of IL [mPy][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 7. <sup>13</sup>C NMR of IL [mPy][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 8. <sup>1</sup>H NMR of IL [mtetn][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 9. <sup>13</sup>C NMR of IL [mtetn][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 10. <sup>1</sup>H NMR of IL [mmo][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 11. <sup>13</sup>C NMR of IL [mmo][Me<sub>2</sub>PO<sub>4</sub>]



S-Figure 12. LC spectra of the products in NaOH aqueous solution

1: Methanol; 2: Unkown I (EIC = 257); 3: Unkown II (EIC = 301); 4: Syringe aldehyde (EIC = 181); 5: Unkown III (EIC = 271); 6: *p*-Hydroxybenzaldehyde (EIC = 121); 7: Vanillin (EIC = 151); 8: Unkown III (EIC = 165); 9: 3,5-Dimethoxybenzoic acid (EIC = 181); 10: Syringate (EIC = 197); 11: Unkown IV (EIC = 287); 12: *p*-Hydroxybenzoate (EIC = 137).



S-Figure 13. LC spectra of the products in the coupled process of reaction-separation