Supporting information

Efficient Hydrodeoxygenation of Lignin-Derived Phenols and Dimeric Ethers with Synergistic [Bmim]PF_6-Ru/SBA-15 Catalysis Under Acid Free Conditions

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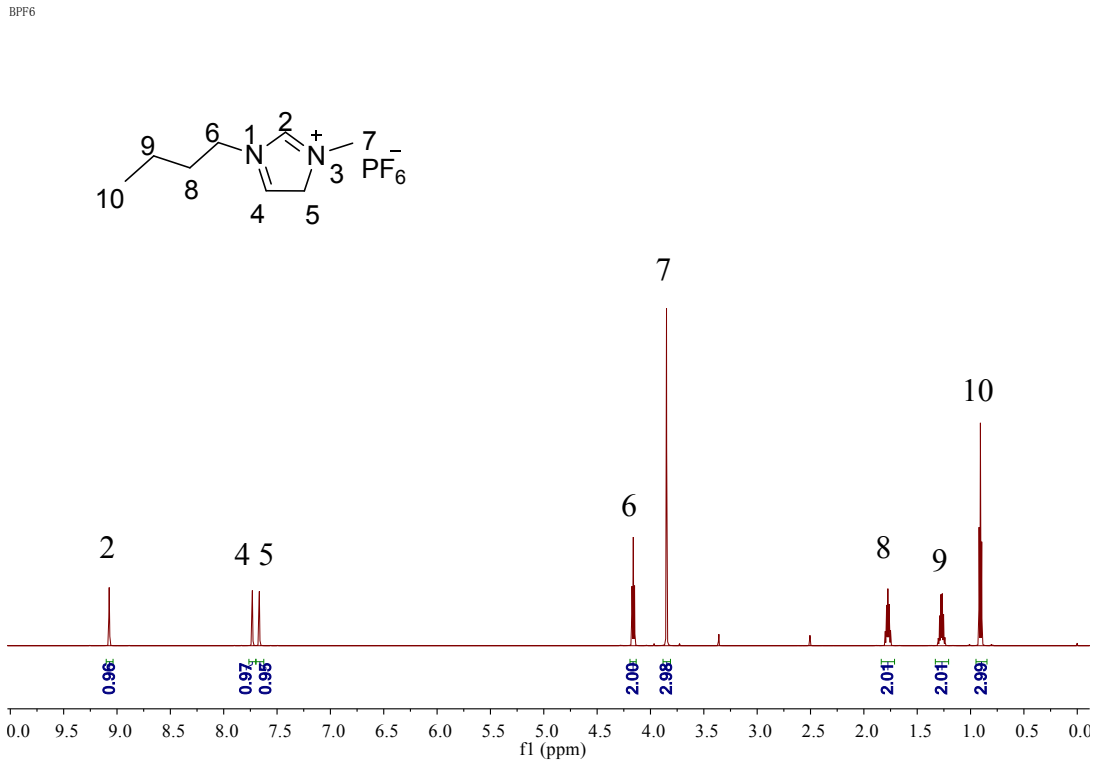
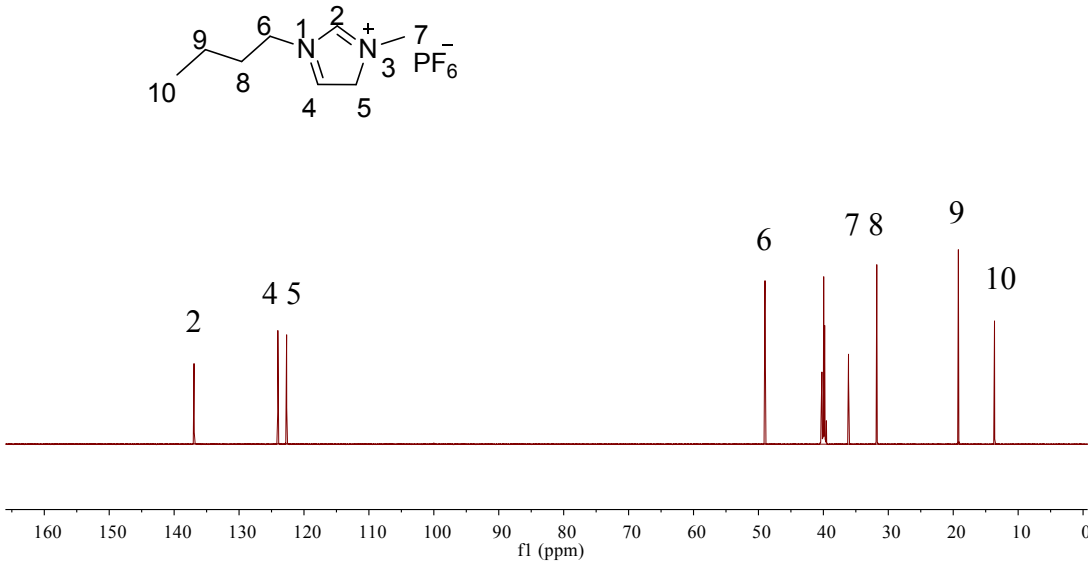
1. $^{1}H/^{13}C$ NMR spectrum of the ILs

1.1. $[Bmim]PF_6$

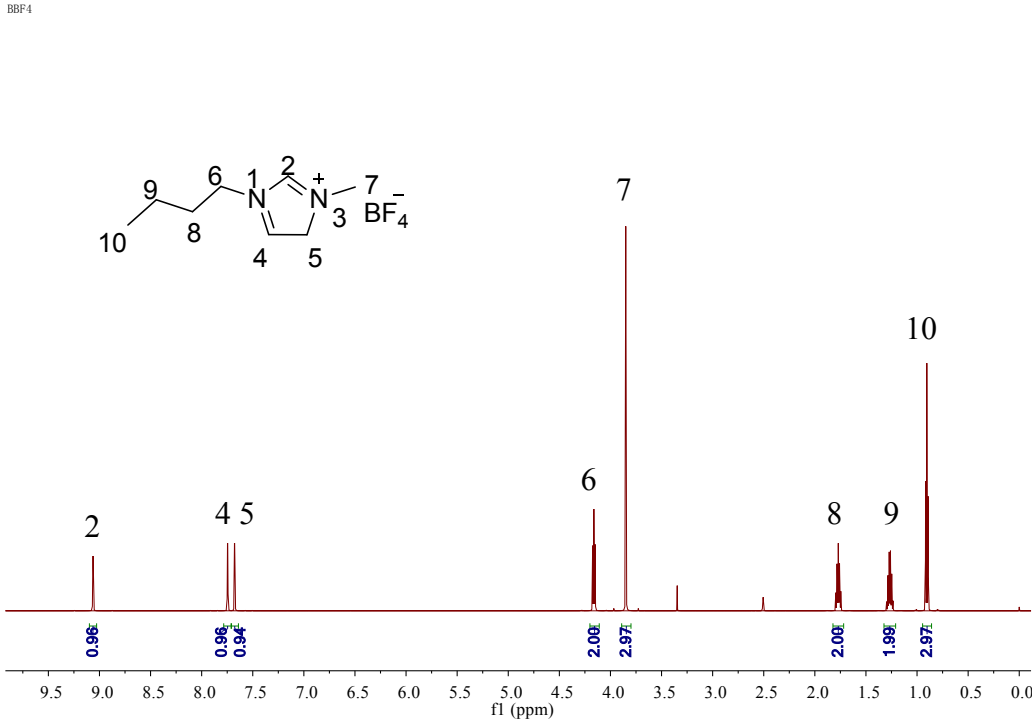


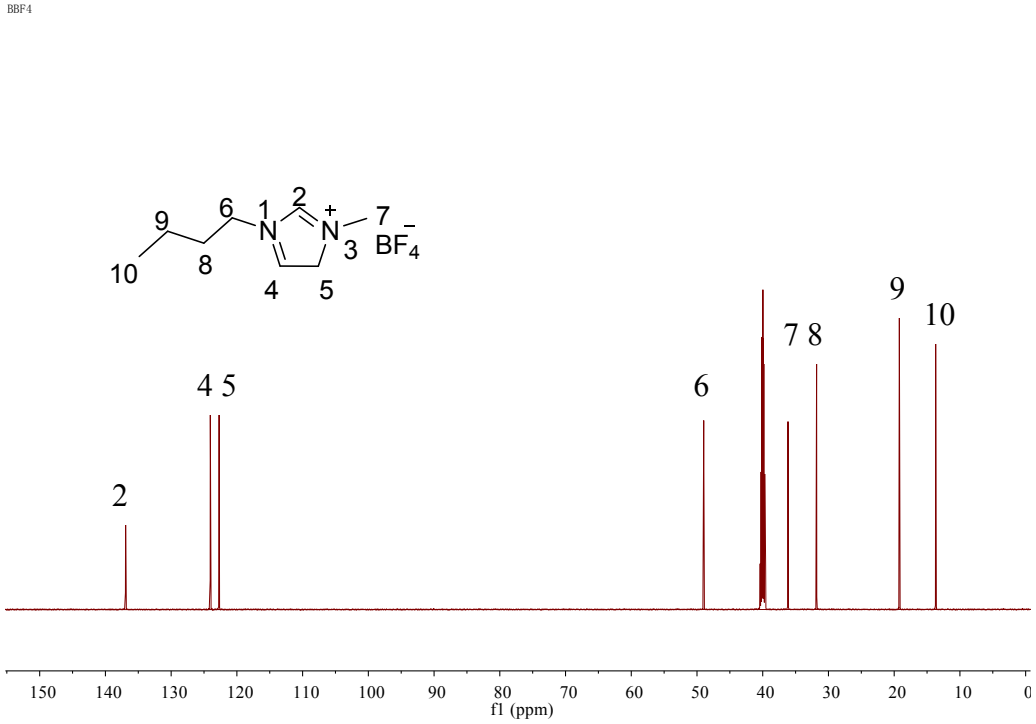


1-Butyl-3-methylimidazolium hexafluorophosphate ($[Bmim]PF_6$): Colorless liquid, ^{1}H-NMR (DMSO, 600MHz): δ (ppm) = 9.07 (s, 1H), 7.73 (d, *J* = 1.1Hz 1H), 7.67 (d,

J = 1.0Hz, 1H), 4.16 (t, J = 7.2Hz, 2H), 3.85 (s, 3H), 1.84-1.71 (m, 2H), 1.33-1.21 (m, 2H), 0.91 (t, J = 7.4Hz, 3H); ^{13}C NMR (D_2O, 600MHz) δ (ppm) = 136.93, 124.03, 122.67, 48.99, 36.13, 31.78, 19.21, 13.64. HRMS (m/z, micrOTOF-Q II): calculated for [Bmim]$^+$ 139.1230, found 139.1259, calculated for PF_6^- 144.9647, found 144.9618.

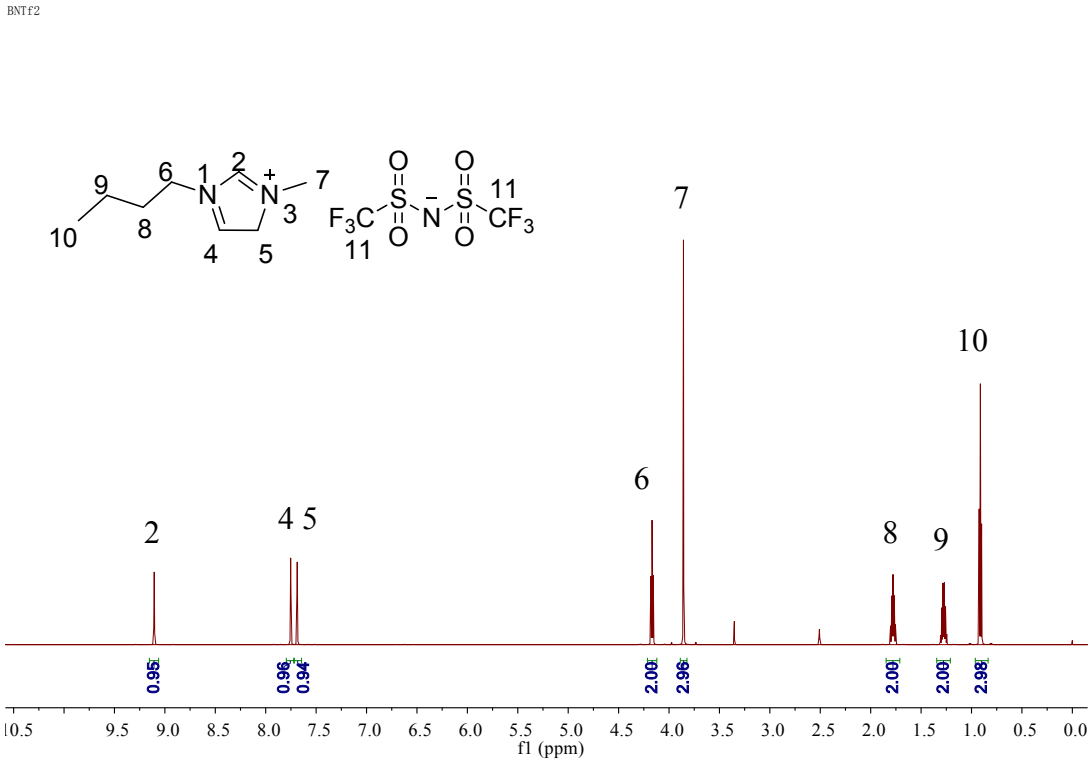
1.2. [Bmim]BF_4



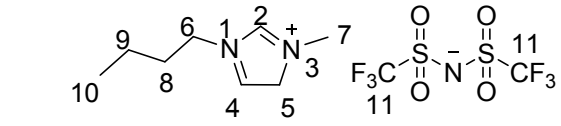


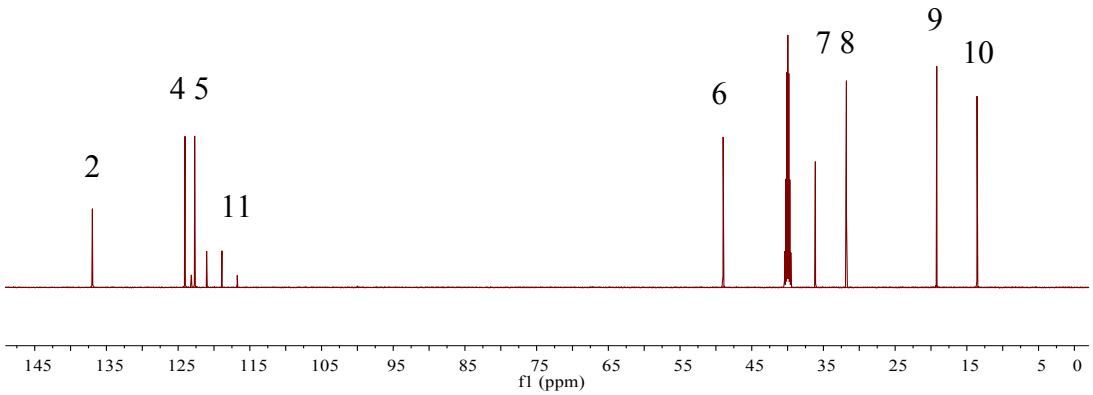
1-n-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4): Colorless liquid, ^{1}H-NMR (DMSO, 600MHz): δ (ppm) = 9.06 (s, 1H), 7.75 (t, *J* = 1.7Hz, 1H), 7.68 (t, *J* = 1.7Hz, 1H), 4.16 (t, *J* = 7.2Hz, 2H), 3.85 (s, 3H), 1.82-1.72 (m, 2H), 1.32-1.21 (m, 2H), 0.90 (t, *J* = 7.4Hz, 3H); ^{13}C NMR (D_2O, 600MHz) δ (ppm) = 136.93, 124.05, 122.70, 48.97, 36.15, 31.80, 19.22, 13.68. HRMS (m/z, micrOTOF-Q II): calculated for $[Bmim]^+$ 139.1230, found 139.1254, calculated for BF_4^- 87.0035, found 86.9970.

1.3. $[Bmim]NTf_2$



BNTf2

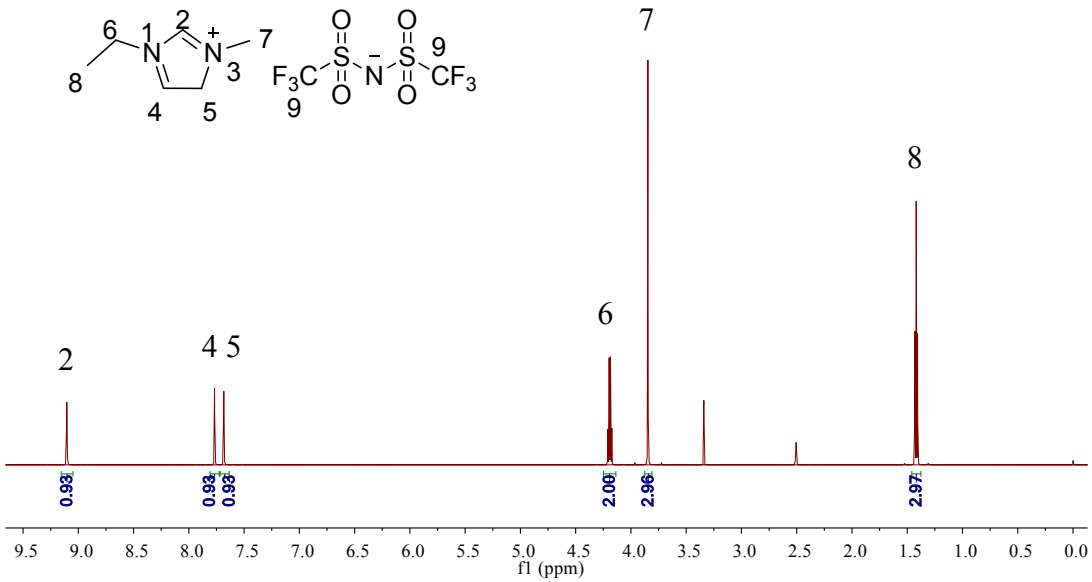




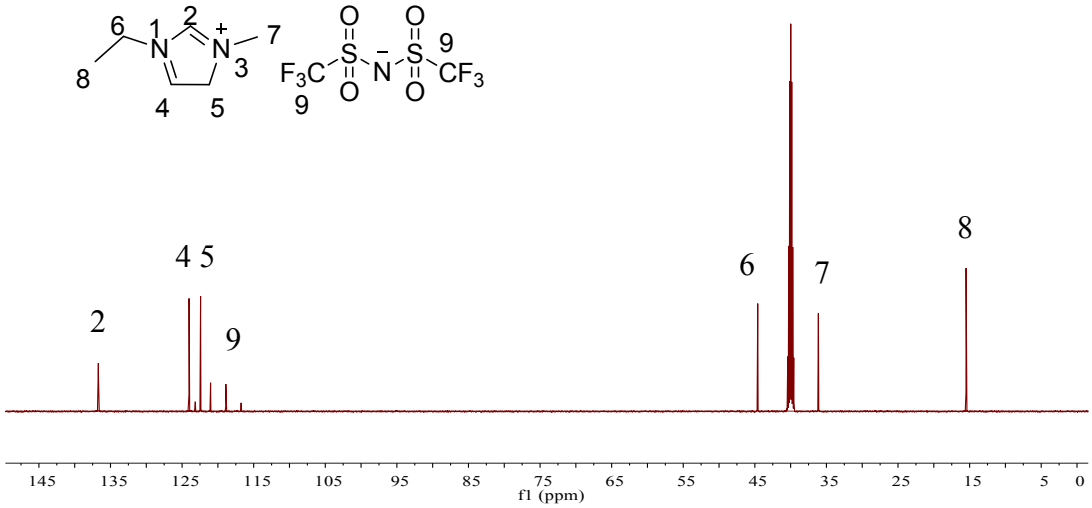
1-n-butyl-3-methylimidazolium N-bis-(trifluoromethanesulfonyl) imidate ([Bmim]NTf$_2$): Colorless liquid, ^{1}H-NMR (DMSO, 600MHz): δ (ppm) = 9.11 (s, 1H), 7.75 (t, J = 1.7Hz, 1H), 7.69 (t, J = 1.7Hz, 1H), 4.17 (t, J = 7.2Hz, 2H), 3.86 (s, 3H), 1.85-1.71 (m, 2H), 1.34-1.21 (m, 2H), 0.91 (t, J = 7.4Hz, 3H); ^{13}C NMR (D_2O, 600MHz) δ (ppm) = 136.96, 124.04, 122.69, 123.16-116.76 (m), 48.99, 36.13, 31.80, 19.20, 13.58. HRMS (m/z, micrOTOF-Q II): calculated for [Bmim]$^+$ 139.1230, found 139.1259, calculated for $^{NTf_2^-}$ 279.9178, found 279.9099.

1.4. [Emim]NTf$_2$

ENTf2



ENTf2



1-ethyl-3-methylimidazolium N-bis-(trifluoromethanesulfonyl) imidate ([Bmim]NTf$_2$): Colorless liquid, ^{1}H-NMR (DMSO, 600MHz): δ (ppm) = 9.10 (s, 1H), 7.77 (t, *J* = 1.7Hz, 1H), 7.68 (t, *J* = 1.7Hz, 1H), 4.19 (q, *J* = 7.3Hz, 2H), 3.85 (s, 3H), 1.42 (t, *J* = 7.3Hz, 3H); ^{13}C NMR (D$_2$O, 600MHz) δ (ppm) = 136.69, 124.03, 122.42, 123.15-116.75 (m), 44.60, 36.13, 15.49. HRMS (m/z, micrOTOF-Q II): calculated for [Emim]$^+$ 111.0917, found 111.0927, calculated for NTf_2^- 279.9178, found 279.9038.

2. Characterization of the catalysts

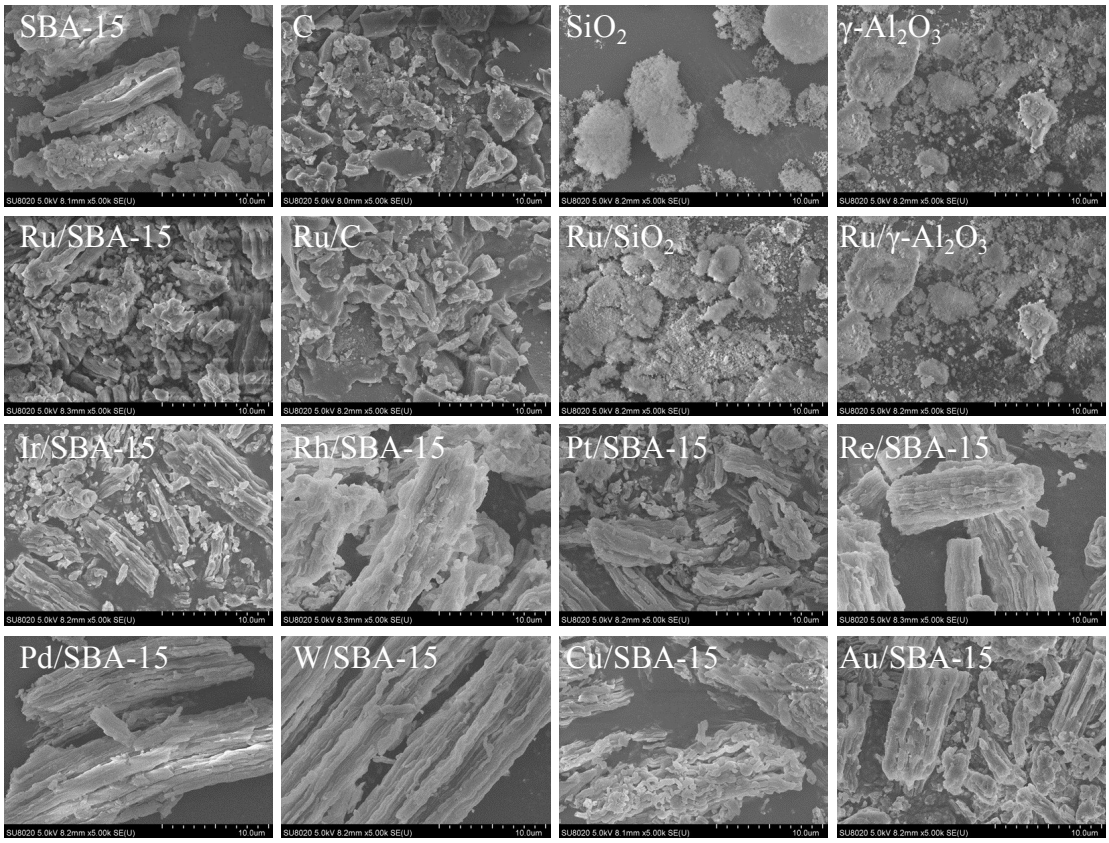


Figure S1. SEM graphics of catalysts.

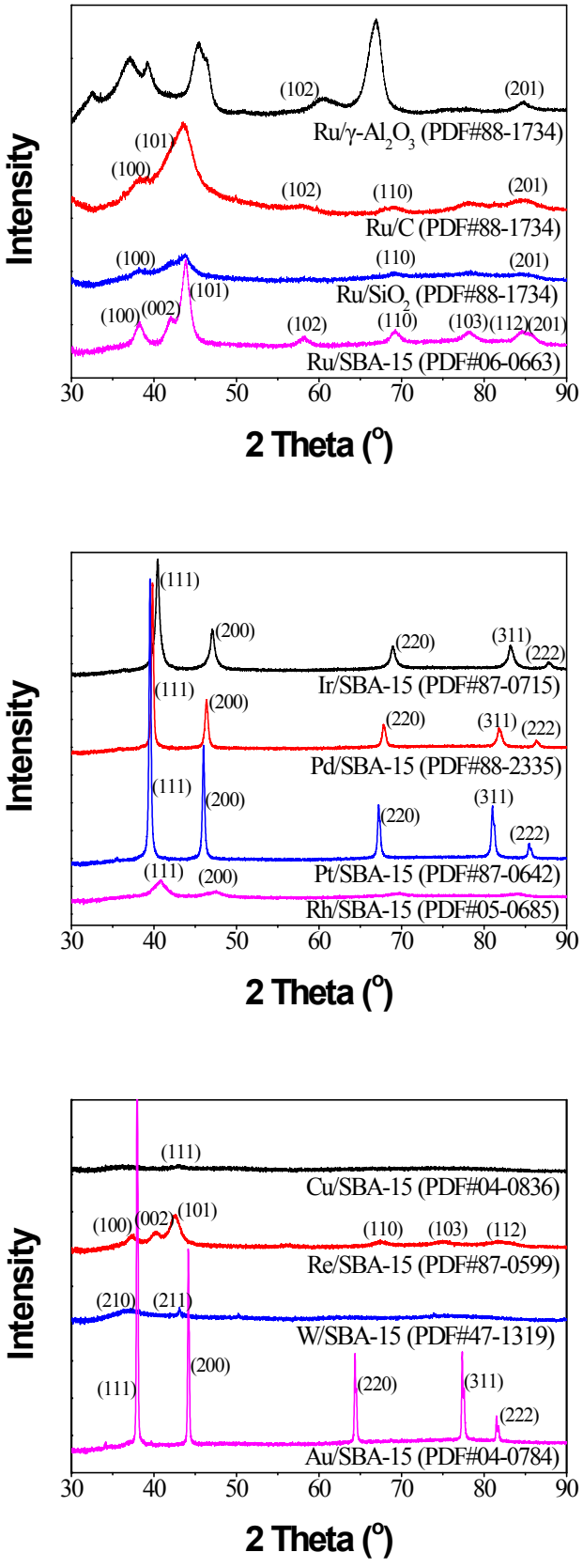


Figure S2. XRD patterns of the catalysts.

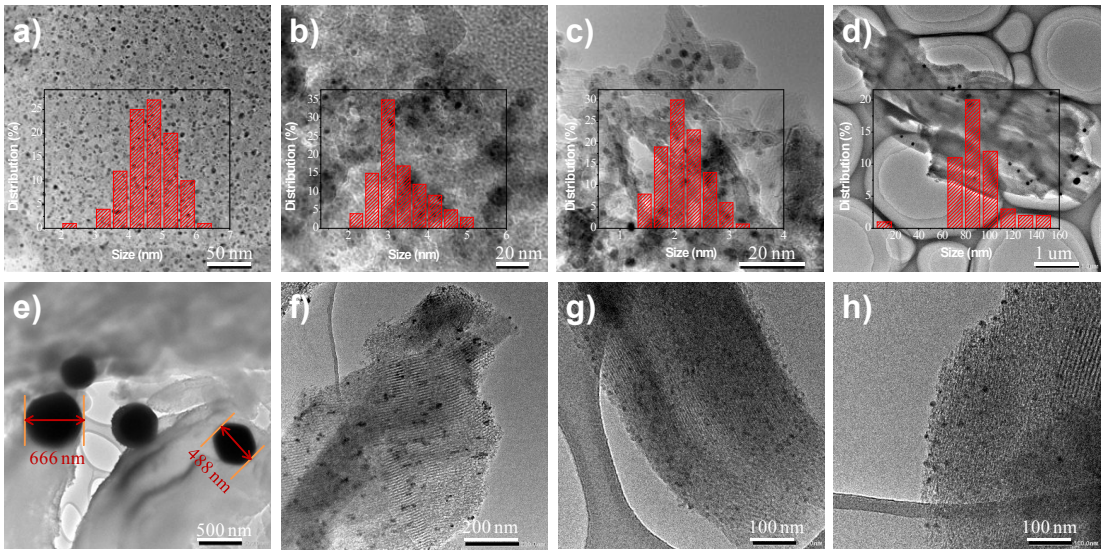


Figure S3. TEM images of (a) Ru/C, (b) Ru/SiO_2, (c) Ru/γ-Al_2O_3, (d) Pd/SBA-15, (e) Au/SBA-15, (f) Re/SBA-15, (g) W/SBA-15, (h) Cu/SBA-15.

3. Experimental section

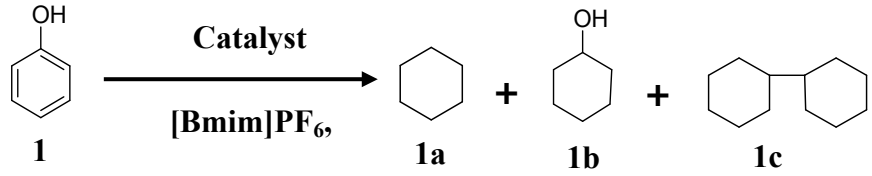
The conversions of substrates and yields of corresponding aliphatic alkanes were calculated based on the following formulas:

$$Conversion = \frac{Moles\ of\ phenols\ \ used - \ Moles\ of\ phenols\ remimed}{Moles\ of\ phenols\ used} \times 100\%$$

$$Conversion = \frac{Moles\ of\ dimeric\ ethers\ \ used - \ Moles\ of\ dimeric\ ethers\ remimed}{Moles\ of\ dimeric\ ethers\ used} \times 100\%$$

$$Yield\ of\ alkanes = \frac{Moles\ of\ alkanes\ generated}{Moles\ of\ phenols\ (dimeric\ ethers\ \times 2)\ used} \times 100\%$$

Table S1. Catalytic activity of different catalysts for the HDO of phenol.[a]

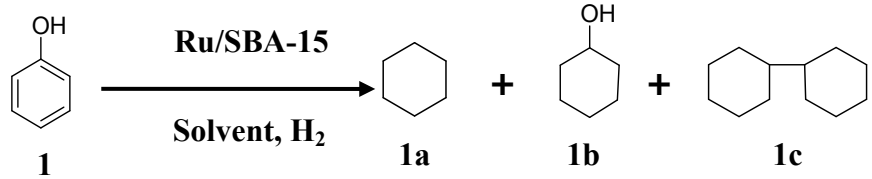


1 **1a** **1b** **1c**

Entry	Catalyst	Conversion (%)[b]	Yield (%)[b]		
			1a	1b	1c
1	None	0	0	0	0
2	SBA-15	0	0	0	0
3	Re/SBA-15	34.7	15.9	0	0
4	Pd/SBA-15	28.2	7.1	0	0
5	W/SBA-15	3.2	1.2	0	0
6	Cu/SBA-15	5.7	1.0	0	0
7	Au/SBA-15	1.0	0.7	0	0

[a] Reaction conditions: Phenol, 1 mmol; catalyst 0.1 g; [Bmim]PF_6, 2.0 g; reaction temperature, 130 °C; reaction time, 6 h; pressure of H_2, 2 MPa. [b] The conversion and yields were determined by GC with n-dodecane as a internal standard.

Table S2. The effect of different solvents for the HDO of phenol.[a]



1 **1a** **1b** **1c**

Entry	Solvent	Conversion (%)[b]	Yield (%)[b]		
			1a	1b	1c
1	[BHEM]mesy[c]	100	7.0	59.8	0
2	Methanol[d]	31.2	2.2	28.1	0
3	Ethanol[d]	6.3	4.6	0	0
4	n-Propanol[d]	100	1.6	67.8	0
5	n-Hexane[d]	100	3.4	76.5	0

[a] Reaction conditions: Phenol, 1 mmol; Ru/SBA-15, 0.1 g; [c] IL, 2.0 g, [d] solvent, 4.0 g; reaction temperature, 130 °C; reaction time, 6 h; pressure of H_2, 2 MPa. [c] Refer to *Cellulose* **2018**, *25*, 3241-3254.

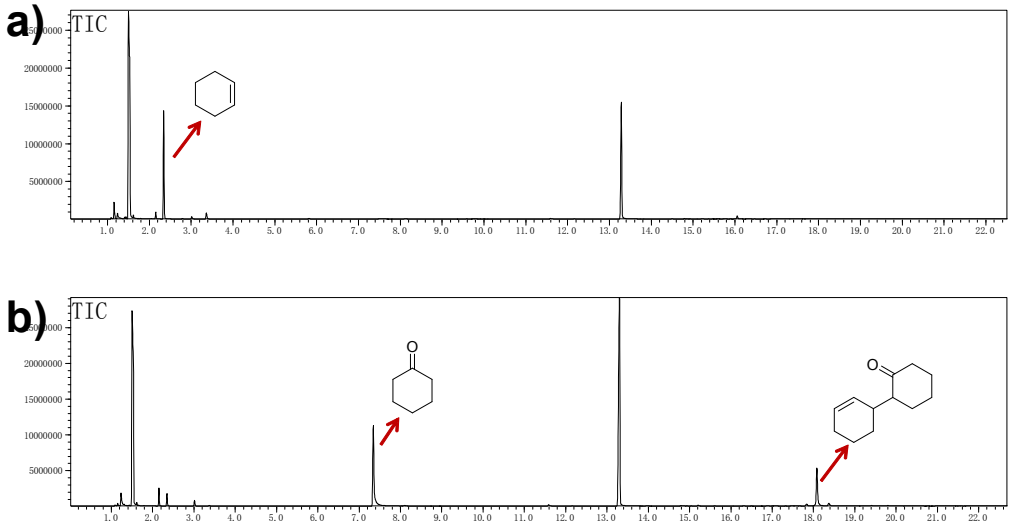


Figure S4. a) GC-MS of cyclohexanol HDO result, b) GC-MS of cyclohexanone HDO result. Reaction conditions: substrate, 1 mmol; [Bmim]PF_6, 2.0 g, reaction temperature, 130 ^oC; reaction time, 6 h; pressure of H_2, 2 MPa. N-dodecane was used as an internal standard.

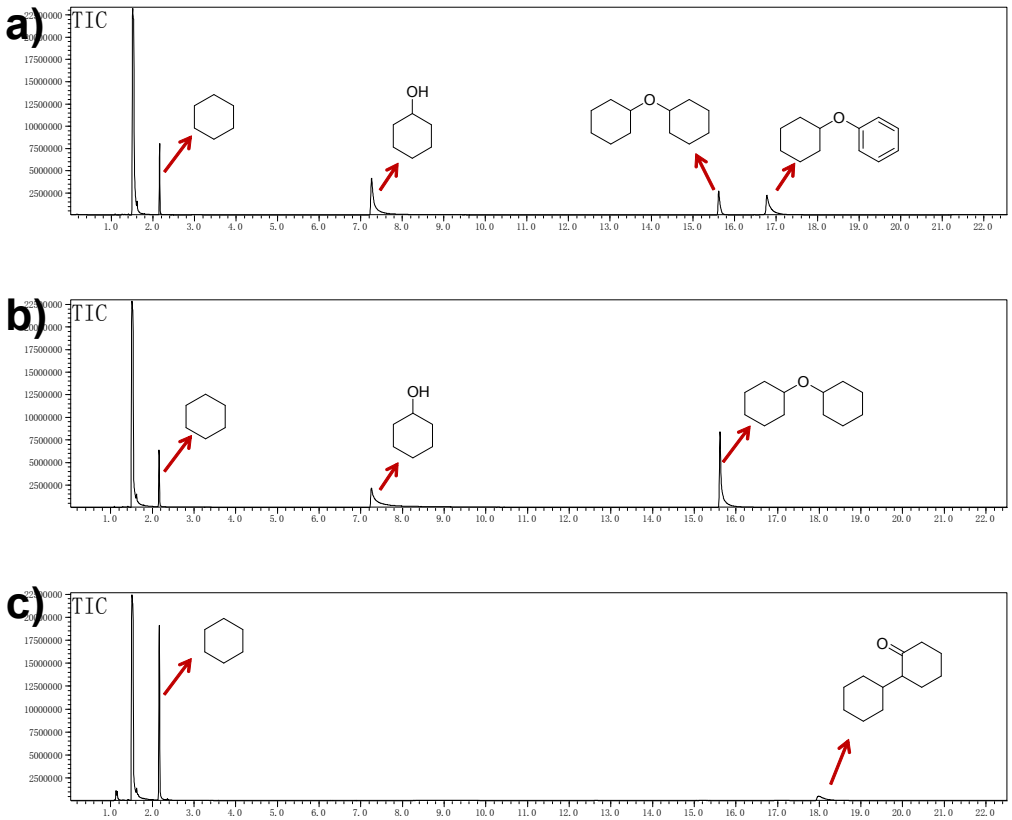


Figure S5. GC-MS of diphenyl ether HDO result. Reaction conditions: diphenyl ether, 1 mmol; [Bmim]PF_6, 2.0 g, reaction temperature, 130 ^oC; reaction time, a) 0.2 h, b) 1

h, c) 4 h; pressure of H_2, 2 MPa. N-dodecane was used as an internal standard.

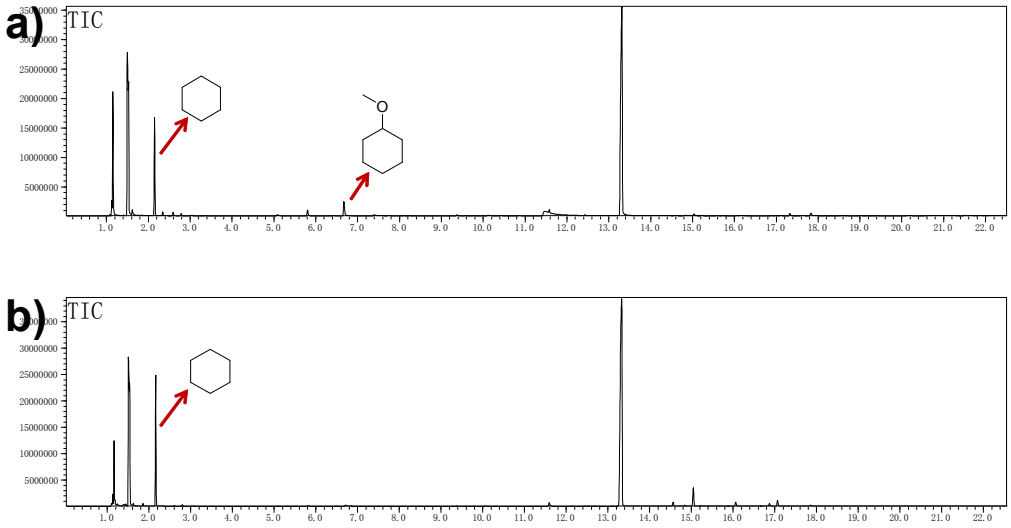


Figure S6. HDO of guaiacol at a) 130 ºC for 6 hours, b) 150 ºC for 6 hours. Reaction conditions: guaiacol, 1 mmol; [Bmim]PF_6, 2.0 g, Ru/SBA-15, 0.1 g; pressure of H_2, 2 MPa. N-dodecane was used as an internal standard.

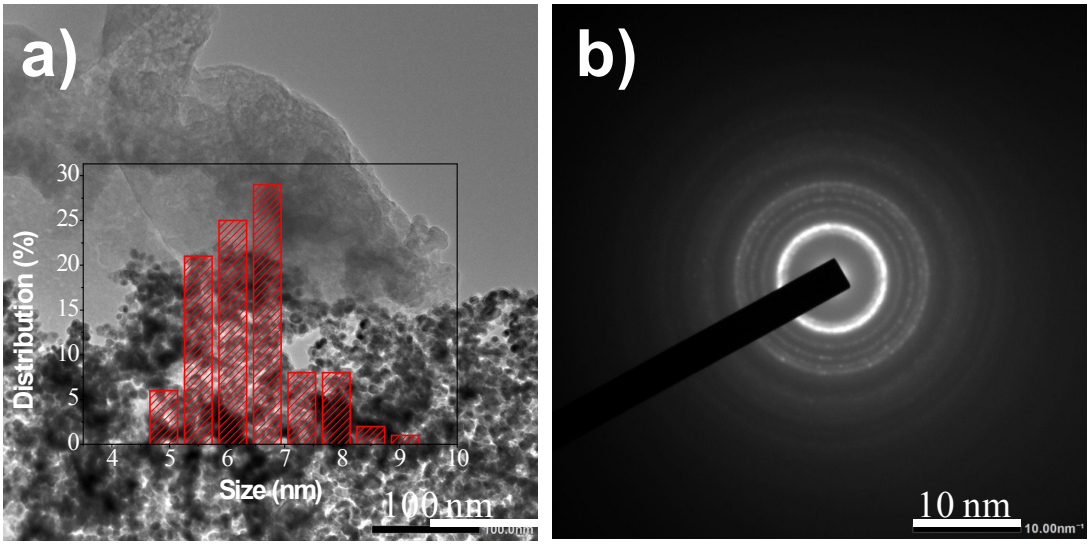


Figure S7. a) TEM images of recycle Ru/SBA-15, B) Electron diffraction rings for Ru NPs falling off from SBA-15.

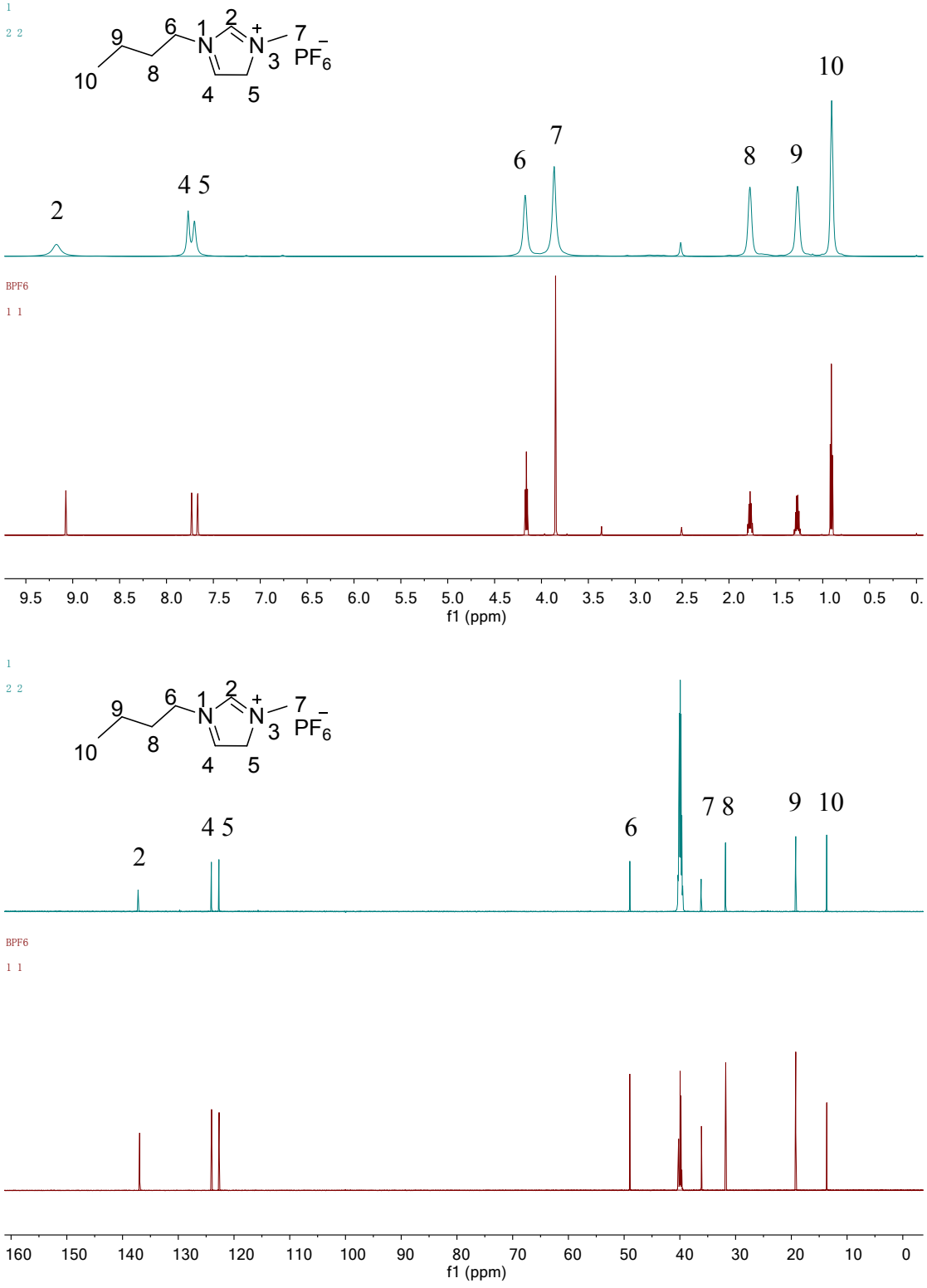


Figure S8. The $^{1}H/^{13}C$ NMR spectroscopy of neat and recycled [Bmim]PF_6.