Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Supplementary Information for

Polystyrene-supported imidazolium acidic ionic liquids: highly efficient catalyst for the synthesis of bisphenols

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1. Characterization

1.1 SEM analysis of polystyrene-supported acidic ionic liquids catalysts

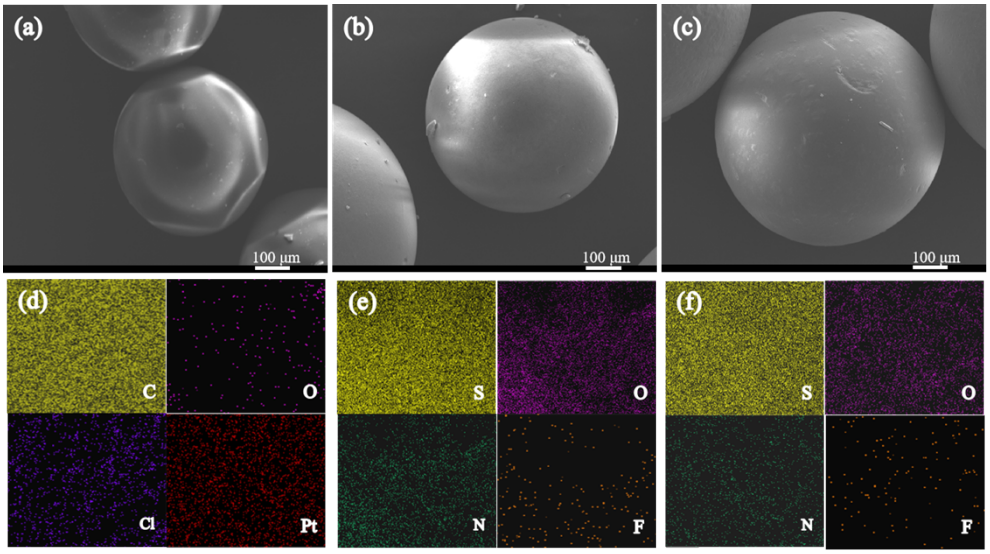

Fig. S1. SEM images of (a) CPS resin (b) [PS-PsIm][CH_3SO_3] (c) [PS-PsIm][HSO_4] and corresponding elemental mapping of (d-f).

1.2 ^{1}H NMR and ^{13}C NMR spectrum

Spectral data for 9,9-bis(4-hydroxyphenyl)fluorene (BHPF): ^{1}H NMR (600MHz, DMSO-d6, TMS) δ (ppm): 9.29 (s, 2H), 7.88-7.86 (d, 2H), 7.38-7.34 (m, 4H), 7.30-7.27 (t, 2H), 6.92-6.89 (d, 4H), 6.64-6.61 (d, 4H). ^{13}C NMR (150 MHz, DMSO-d6, TMS) δ (ppm): 156.47, 152.15, 139.80, 136.47, 129.16, 128.11, 127.74, 126.40, 120.79, 115.40, 64.09.

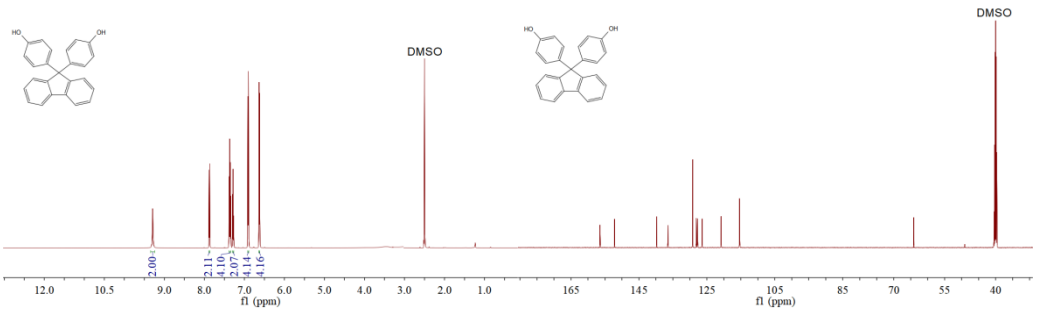

Fig. S2. ^{1}H NMR and ^{13}C NMR spectra of BHPF.

Spectral data for bis(4-hydroxyphenyl)methane (Bisphenol F): ^{1}H NMR (600MHz, DMSO-d6, TMS) δ (ppm): 9.14 (s, 2H), 7.01-6.89 (d, 4H), 6.73-6.55 (d,

4H), 3.69 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d6, TMS) δ (ppm): 155.85, 132.59, 129.89, 115.55, 40.5.

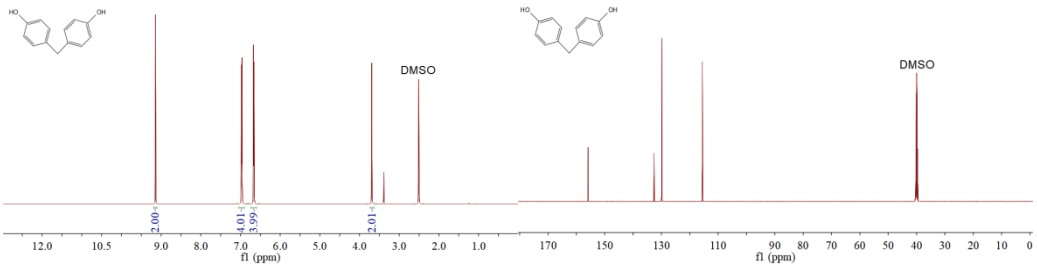

Fig. S3. ^{1}H NMR and ^{13}C NMR spectra of Bisphenol F .

Spectral data for 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A): ^{1}H NMR (600MHz, DMSO-d6, TMS) δ (ppm): 9.13 (s, 2H), 6.99-6.69 (d, 4H), 6.65-6.63 (d, 4H), 1.53 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d6, TMS) δ (ppm): 155.35, 141.53, 127.75, 115.02, 41.38, 31.35.

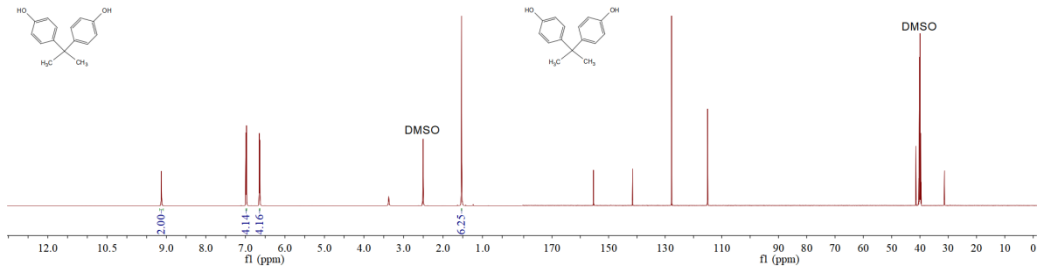

Fig. S4. ^{1}H NMR and ^{13}C NMR spectra of Bisphenol A.

Spectral data for 1,1-bis(4-hydroxyphenyl)cyclohexane (Bisphenol Z): ^{1}H NMR (600MHz, DMSO-d6, TMS) δ (ppm): δ 9.10 (s, 2H), 7.05-7.02 (d, 4H), 6.65-6.62 (d, 4H), 2.12 (s, 2H), 1.42 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d6, TMS) δ (ppm): 155.10, 139.52, 128.03, 115.28, 44.60, 37.07, 26.38, 23.03.

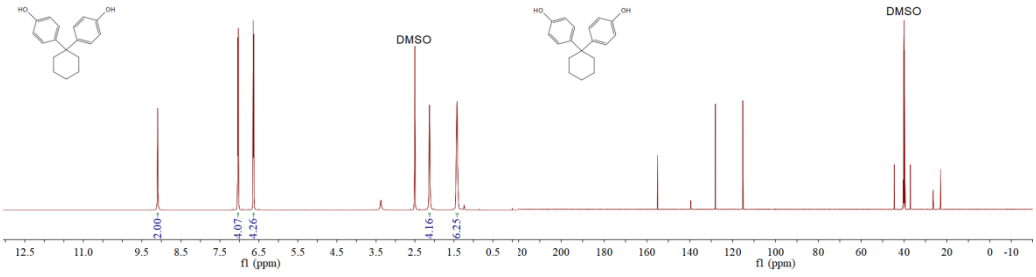

Fig. S5. ^{1}H NMR and ^{13}C NMR spectra of Bisphenol Z.

2. The quantitative analysis of the catalytic reaction

The condensation reaction was quantitative analyzed by High Performance Liquid Chromatography. The performance of the catalysts was evaluated according to the conversion of raw material and the selectivity of target product. In the established liquid chromatography, the maximum absorption wavelength of 9-fluorenone was 257 nm, while that of target product and by-product was 200 nm. Meanwhile the standardized calibration curve of raw material (9-fluorenone) in the concentration range of 0.005-0.08 mg·g^{-1} was established (Fig. S6). Therefore, based on the standard curve, the conversion was quantified using DAD detector with the absorption wavelength of 257 nm. Similarly, the selectivity was calculated by the area normalization method at the absorption wavelength of 200 nm.

Conversion of 9-fluorenone was calculated by the equation:

Conversion (%) = [m (9-fluorenone)$_I$ – m (9-fluorenone)$_T$] / m (9-fluorenone)$_I$ × 100%, which m (9-fluorenone)$_I$ and m (9-fluorenone)$_T$ were the mass of 9-fluorenone at initial and terminal reaction time.

Selectivity of target product was calculated by the equation:

Selectivity (%) = N_T / [N_T + N_B] × 100%, which N_T and N_B were the number of moles of target product and by-product.

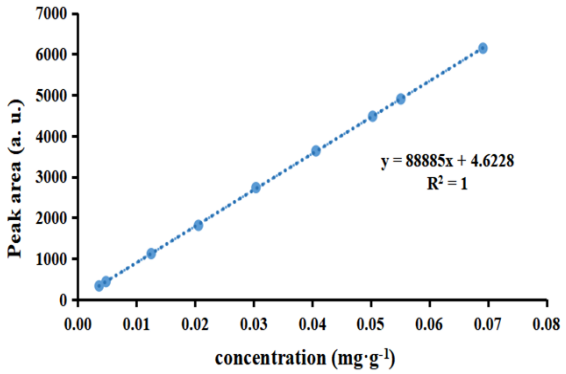

Fig. S6. The standardized calibration curve of 9-fluorenone.

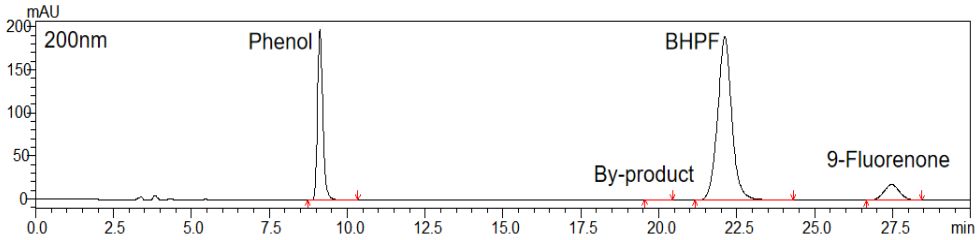

Fig. S7. The HPLC absorption peak of reaction solution.

3. Quantum chemistry theoretical calculations

Building a molecular model, by the DFT calculation of the molecular energy of the catalysts before and after deprotonation (Fig. S8), the proton donation ability of polystyrene-supported ionic liquid catalysts was compared. Based on the high-loading, [PS-PsIm][CF_3SO_3] with the minimum deprotonation energy easily provided proton to activate 9-fluorenone, which had the best catalytic effect and the highest TOF value in the condensation reaction. However, the TOF value of [PS-PsIm][HSO_4] with high proton donation ability was slightly lower than [PS-PsIm][CH_3SO_3], which might be caused by differences in the loading amount of ionic liquids.

Table S1. Proton donation ability of polystyrene-supported acidic ionic liquid catalysts.

Catalyst	Deprotonation energy (Kcal·mol^{-1})	Deprotonation energy (kJ·mol^{-1})
[PS-PsIm][CF_3SO_3]	0.49	1302.10
[PS-PsIm][CH_3SO_3]	0.51	1333.17
[PS-PsIm][HSO_4]	0.50	1318.41

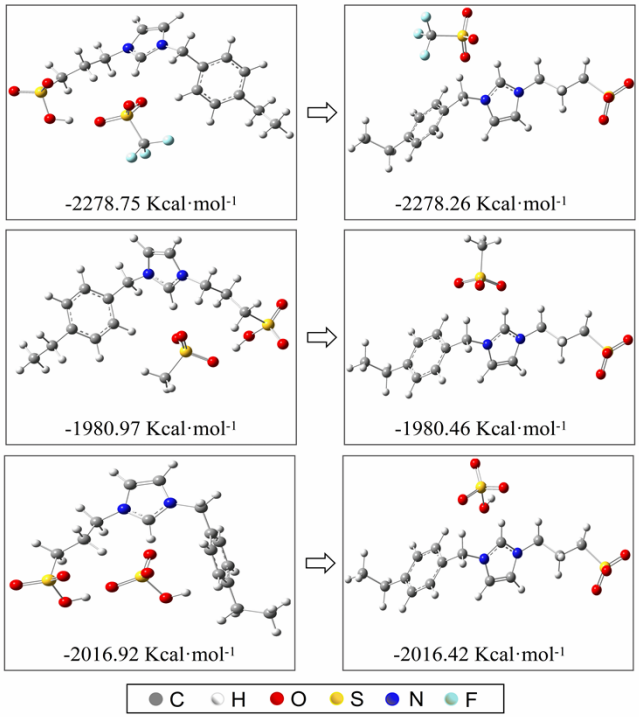

Fig. S8. Molecular energy of catalyst before and after deprotonation.