Electronic Supplementary Information for

Selective Hydrogenation of Phenol and Derivatives over an Ionic Liquid-like Copolymer Stabilized Palladium catalyst in Aqueous Media

Aibing Chen,[a] Guoying Zhao,[b,a] Jinzhu Chen,*[b] Limin Chen,[c] and Yifeng Yu[a]

[a]College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology. Shijiazhuang 050018, P. R. China

[b]Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences. Guangzhou 510640, P. R. China. Tel./Fax: +86-20-3722-3380; E-mail: chenjz@ms.giec.ac.cn.

[c]College of Environmental Science and Engineering, South China University of Technology. Guangzhou 510006, P. R. China

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1. Experimental Details

1.1. Chemicals

Unless otherwise stated, all chemicals in this work were commercial available and used without further purification. Phenol, cyclohexanone, cyclohexanol, ethyl acetate, phosphotungstic acid ($H_3PW_{12}O_{40}\cdot xH_2O$), silicotungstic acid ($H_4SiW_{12}O_{40}\cdot xH_2O$) and phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot xH_2O$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P. R. China). *n*-Octane (internal standard, ≥99.5%), 1-vinylimidazole, 1,3-propanesulfonate, *n*-butylchloride, 1-vinyl-2-pyrrolidone, sodium styrene sulfonate, 2,2'-azobis(2-methylpropionitrile) (AIBN), *o*-cresol, *m*-cresol, *p*-cresol, 4-*tert*-butylphenol, 4-methoxyphenol, 4-cholrophenol, salicylic acid, catechol, resorcinol and hydroquinone were purchased from Aladdin Industrial Inc. (Shanghai, P. R. China). Potassium tetrachloropalladate(II) (K_2PdCl_4), potassium tetrachloroplatinate(II) (K_2PtCl_4), ruthenium(III) chloride hydrate ($RuCl_3\cdot xH_2O$), rhodium(III) chloride hydrate ($RhCl_3\cdot xH_2O$) were provided by Kunming Boren Precious Metals Co. Ltd (Kunming, P. R. China). Hydrogen gas (>99.999%) was obtained from Huate Co. Ltd (foshan, P. R. China). De-ionized pure water from Millipore-Milli Q Plus System was used as solvent.

1.2. Instruments

1H NMR spectra were recorded on a Bruker AVANCE Digital 400 MHz spectrometer at 25°C with D_2O and $CDCl_3$ as solvent. Gas chromatography (GC) was performed on an Agilent 6890 or Shimadzu 2010 gas chromatograph equipped with a 30 m (0.32-mm-i.d) KB-5 column with a flame ionization detector (FID). GC-mass spectroscopy (GC-MS) analysis was performed on a FINNIGAN TRACE GC-MS 2000 GC-mass spectroscopy, equipped with a 30 m (0.53-mm-i.d) DB-5 column. High-resolution transmission electron microscopy (HRTEM) was recorded on a JEM-2010HR at 20 keV. IR spectra were measured on a Bruker Tensor 27 FT-IR spectrometer as KBr pellets.

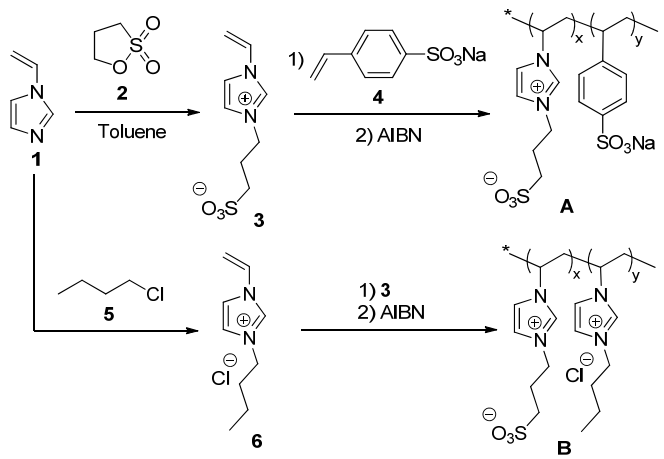

Figure S1-1. Synthetic route to **A** and **B**.

1.3. Synthetic procedure

Unless otherwise stated, all of the synthetic operations were performed under the protection of nitrogen with standard Schlenk techniques.

1.3.1. Synthesis of 3-(1-vinyl-imidazoliumyl)propanesulfonate 3

In a 250 mL round-bottomed flask equipped with stirring bar and magnetic stirrer, 1,3-propanesulfonate **2** (6.47 g, 53 mmol) was added to 60 mL toluene and stirred vigorously to be dissolved completely. The solution was cooled to 0c in ice-water bath and 1-vinyl-imidazole **1** (5.00 g, 53 mmol) was added dropwise under vigorous stirring, the mixture was then stirred for 10 minutes in ice-water and 12 hours at the room temperature. The white precipitate formed was isolated by filtration, and washed three times with 60 mL toluene and ether. The solid was then dried at 60°C under vacuum for 2 hours to give a white product 9.17 g (Yield 80%). ^{1}H NMR (400 MHz, D_2O): δ = 9.04 (s, 1H), 7.74 (s, 1H), 7.58 (s, 1H), 7.11 (m, 1H), 5.76 (dd, 1H, *J* = 15.6 Hz, 2.8 Hz), 5.38 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz), 4.36 (t, 2H, *J* = 7.2 Hz), 2.90 (t, 2H, *J* = 7.6 Hz), 2.30 (m, 2H). IR (KBr, cm^{-1}): ν = 3445 (O−H, H_2O, vs); 3109 (C−H, w); 1655 (w), 1574 (vs), 1406 (m) (C=N and C=C); 1184 (SO_3^-, vs); 1043 (SO_3^-, vs); 592 (C−H, w).

1.3.2. Synthesis of 1-vinyl-3-butyl-1*H*-imidazolium chloride ([VBIM]Cl) 6

In a 25 mL round-bottomed Schlenk flask equipped with condenser and magnetic stirrer, butylchloride **5** (18.50 g, 200 mmol) was added to 1-vinyl-imidazole **1** (5.00 g, 53 mmol), the mixture was then refiluxed for 24 hours in an oil bath at 70°C under vigorous stirring. After cooling down to room temperature, the upper phase was poured out and the solid residue was washed three times with 30 mL ethyl acetate. Then the solid was dried at 60°C under a vacuum for 2 hours to give a pale yellow product 7.74 g (Yield 75%, calculated on 1-vinyl-1*H*-imidazole). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 11.35 (s, 1H), 7.88 (s, 1H), 7.54 (dd, *J* = 14.7 Hz, 8.8 Hz, 2H), 6.02 (dd, *J* = 14.7 Hz, 2.7 Hz, 1H), 5.39 (dd, *J* = 8.6 Hz, 3.0 Hz, 1H), 4.40 (t, 2H), 1.95 (m, 2H), 1.41 (m, 2H), 0.98 (t, 3H).

1.3.3. Synthesis of poly[(3-(1-vinyl-imidazoliumyl)propanesulfonate)-*co*-(sodium 4-styrene sulfonate)] A

A mixture of zwitterions **3** (0.97 g, 4.5 mmol), sodium styrene sulfonate **4** (0.93 g, 4.5 mmol) and 2,2′-azobis(isobutyronitrile) (AIBN, 15 mg), methanol (5 mL) and distilled water (5 mL) was poured in a 50 mL Schlenk flask equipped with condenser. The whole reaction system was degassed by three freeze/thaw cycles, and then the mixture was stirred at 600 rpm in a preheated oil bath at 60°C for 24 h. The whole mixture was collected and residue monomers were removed from the mixture by dialysis for three days in 1000 mL × 6 water. After dialysis, the water solvent was removed by a rotavapor under vacuum, and the final product was dried in vacuum at room temperature. A total of 1.22 g of colorless solid **A** was obtained (yield: 64%). The purity and the copolymer compositions were checked by ^{1}H NMR spectroscopy (Figure 2). IR (KBr, cm^{-1}): ν = 3439 (O−H, H_2O, vs); 3140 (C−H, m); 2928 (C−H, w); 1641 (m), 1560 (w), 1421 (w) (C=N and C=C); 1180 (SO_3^-, s); 1042 (SO_3^-, s); 586

(C−H, m).

1.3.4 Synthesis of poly-[(3-(1-vinyl-imidazoliumyl)propanesulfonate)-*co*-(1-vinyl-3-butyl-1*H*-imidazolium chloride))] B

zwitterions **3** (0.97 g, 4.5 mmol), 1-vinyl-3-butylimidazolium **6** (0.84 g, 4.5 mmol), and 2,2′-azobis(isobutyronitrile) (AIBN) (25 mg, 0.15 mmol) were mixed in methanol (10 mL) and degassed by three freeze/thaw cycles. The mixture was then stirred at 600 rpm in a preheated oil bath at 60°C for 24 h. The resulting solution diluted with 10 mL water and filtrated with filter paper, then removed three-quarters of solvent under vacuum. The residual monomers were removed by dialysis in distilled water for three days in 1000 mL × 6 water, and the solvent was removed under reduced pressure. Finally, the final product was dried under vacuum at room temperature. A total of 1.00 g of colorless solid **B** was obtained (yield: 40%). The purity and copolymer compositions were checked by ^{1}H NMR spectroscopy.

1.4. Selective hydrogenation of phenol

1.4.1. Preparation of Pd nanoparticles

IL-like copolymer **A** (15 mg, 7.00×10^{-2} mmol), K_2PdCl_4 (6 mg, 1.75×10^{-2} mmol) and water (3 mL) were placed in a Schlenk flask (25 mL). The flask was purged with H_2 to remove the air for three times, the reaction was then stirred at 600 rpm at 80°C for 2 hours under a hydrogen balloon at atmospheric pressure to give a dark brown solution.

1.4.2. Pd catalyzed phenol hydrogenation

The reaction was conducted in a Schlenk flask (25 mL) with a magnetic stir bar. A typical procedure was as follows: phenol (33 mg, 0.35 mmol), K_2PdCl_4 (6 mg, 1.75×10^{-2} mmol, 5 mol% relative to phenol), copolymer **A** (15 mg, 7.00×10^{-2} mmol, 20 mol% relative to phenol), phosphotungstic acid ($H_3PW_{12}O_{40}\cdot xH_2O$, 101 mg, 10 mol% relative to phenol), and water (3 mL) were placed in a flask. The flask was purged with H_2 to remove the air for three times, the reaction was then stirred at 600 rpm under a hydrogen balloon under atmospheric pressure. For the reaction conducted in compressed hydrogen pressure, the hydrogenation was carried out in a Teflon-lined stainless steel batch reactor (50 mL total volume) with a magnetic stirrer. In a typical experiment, phenol, catalyst, and solvents were loaded into the reactor. The reactor was sealed and purged with H_2 to remove the air for three times, and then hydrogen was introduced into the reactor at the desired pressure. The reactor was placed in the oil bath that had been heated to the desired temperature. After reaction the reactor was placed in ice water to quench the reaction, and then a known amount of internal standard *n*-octane was added to the reactor if used. The products were extracted with ethyl acetate and the organic phase was analyzed using a GC (Agilent 6890) or GC (Shimadzu 2010) equipped with a flame ionization detector (FID) and a KB-5 capillary column (0.32 mm in diameter, 30 m in length) using nitrogen as the carry gas. Identification of the products and reactant was performed a GC-MS (Trace GC-MS 2000) as well as by comparing the retention times to respective standards in

GC traces. The GC and GC-MS conditions for the product analysis were: Injector Port Temperature: 250°C; Column Temperature: Initial temperature: 45°C (4 min); Gradient Rate: 25°C /min (7 min); Final Temperature: 220°C (3 min); Flow Rate: 75 ml/min.

1.4.3. Pt catalyzed phenol hydrogenation

Pt catalyzed phenol hydrogenation was conducted by the same procedure of Pd with K_2PtCl_4 as Pt precursor instead of K_2PdCl_4.

1.4.4. Rh and Ru catalyzed phenol hydrogenation

Hydrogenation gas under atmospheric pressure is not efficient to reduce Rh^{3+} and Ru^{3+} ions to its elemental state at 80°C. Therefore, Rh/**A** and Ru/**A** catalysts were prepared by hydrogenation reduction of $RhCl_3$ and $RuCl_3$, respectively, in the presence of IL-like copolymer **A** in aqueous media under 1 MPa hydrogen at 100°C for 2 hours. The as-prepared Rh/**A** and Ru/**A** catalysts was used for the subsequent phenol hydrogenation.

1.4.5. Calculation of the conversion and selectivity

The composition of the reaction mixture was determined by equation E1.

$$X_i = \frac{A_i f_i}{\sum_i A_i f_i} \times 100\% \qquad \text{(E1)}$$

Where *Xi* is the mole fraction of component *i*, *fi* is the response factor of component *i*, and *Ai* is the peak area of component *i*. The conversion of phenol is defined as the ratio of number of moles of phenol consumed in the reaction to the total moles of phenol initially added (Eq. E2). The selectivity to cyclohexanone is defined as the ratio of number of moles of cyclohexanone produced to the total number of moles of all products (Eq. E3).

$$\text{Conversion of phenol} = \frac{\text{Moles of phenol consumed}}{\text{Moles of phenol initially added}} \qquad \text{(E2)}$$

$$\text{Selectivity to cyclohexanone} = \frac{\text{Moles of cyclohexanone}}{\text{Moles of all products}} \qquad \text{(E3)}$$

Unless otherwise noticed, cyclohexanone and the cyclohexanol were the only reaction products observed. Selectivities and conversions were determined according to the literature methods (Lit. Liu, H. Z.; Jiang, T.; Han, B. X.; Liang, S. G.; Zhou, Y. X. *Science*, **2009**, *326*, 1250–1252.).

1.4.6. Temperature-conversion and time-conversion profiles

The effect of the reaction temperature on cyclohexanone selectivity was further investigated as described in Figure S2-1. The conversion of phenol increased with the temperature investigated. The cyclohexanone selectivity increased as the temperature increased with a maximum of >99% at 80°C. A further increased temperature, however, led to reduced cyclohexanone selectivity, owing to the over-reduction of cyclohexanone to cyclohexanol. The time-conversion profile reveals that the yield of cyclohexanone has a maximum (selectivity >99%) with a complete phenol conversion after 7 hours at 80°C

(Figure S2-2). After this time the second hydrogenation of the cyclohexanone to cyclohexanol is initiated also, while the selectivity of cyclohexanone declines with the concomitant production of cyclohexanol.

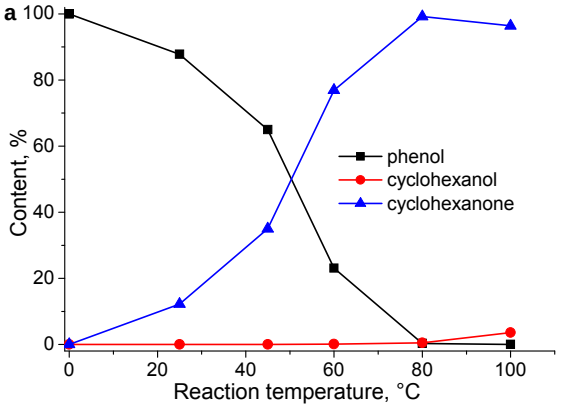

Figure S2-1 temperature-conversion profile. Reactions conditions: phenol (33 mg, 0.35 mmol), K_2PdCl_4 (5 mol% relative to phenol), **A** (20 mol% relative to phenol), HPA (10 mol% relative to phenol), H_2 (0.1 MPa), water (3 mL), reaction time, (7 h).

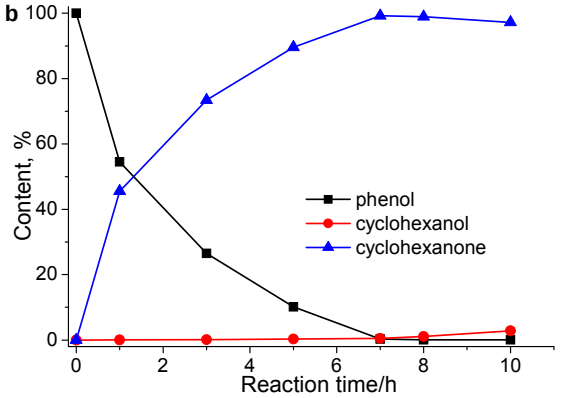

Figure S2-2 time-conversion profile. Reactions conditions: phenol (33 mg, 0.35 mmol), K_2PdCl_4 (5 mol% relative to phenol), **A** (20 mol% relative to phenol), HPA (10 mol% relative to phenol), H_2 (0.1 MPa), water (3 mL), reaction temperature, (80°C).

1.5. Mercury poisoning experiments

Mercury poisoning experiments were performed in order to determine that the catalyst is heterogeneous or homogeneous (Lit. Widegren, J. A.; Bennett, M. A.; Finke, R. G. *J. Am. Chem. Soc.*, **2003**, *125*, 10301–10310).

Step 1: Preparation of Pd nanoparticles

IL-like copolymer **A** (15 mg, 7.00×10^{-2} mmol), K_2PdCl_4 (6 mg, 1.75×10^{-2} mmol) and water (3 mL) were placed in a Schlenk flask (25 mL). The flask was purged with H_2 to remove the air for three times, the reaction was then stirred at 600 rpm at 80°C for 2 hours under a hydrogen balloon at atmospheric pressure. After the reaction was halted, the reactor was cooled to room temperature.

Step 2: Mercury poisoning experiments

Mercury (3.51 g, 17.5 mmol, 1000 equiv to Pd), phenol (33 mg, 0.35 mmol), phosphotungstic acid ($H_3PW_{12}O_{40}\cdot xH_2O$, 101 mg, 10 mol% relative to phenol) were added to the Schlenk flask. After purging the reactor several times with hydrogen, the reactor was connected again to a hydrogen balloon at atmospheric pressure, and the reaction mixture was stirred at a speed of about 600 rpm at 80°C for 7 hours.

1.6. Recycling experiments

The reusability of catalyst system was tested for phenol hydrogenation in water. Phenol (33 mg, 0.35 mmol), K_2PdCl_4 (6 mg, 1.75×10^{-2} mmol, 5 mol% relative to phenol), copolymer **A** (15 mg, 7.00×10^{-2} mmol, 20 mol% relative to phenol), phosphotungstic acid ($H_3PW_{12}O_{40}\cdot xH_2O$, 101 mg, 10 mol% relative to phenol), and water (3 mL) were placed in a flask. The flask was purged with H_2 to remove the air for three times, the reaction was then stirred at 600 rpm under a hydrogen balloon under atmospheric pressure for 7 hours. After the reaction, the aqueous phase was extracted several times by cyclohexane until no products was analyzed on GC from the organic phase. Then the residual cyclohexane was removed under reduced pressure from the aqueous phase at room temperature. The catalyst system was then reused under the same conditions with the freshly added phenol (33 mg, 0.35 mmol). It was found that the conversion of phenol slightly decreased from >99 to 97% after three time recycling, but the selectivity to cyclohexanone was the same as the fresh catalyst.

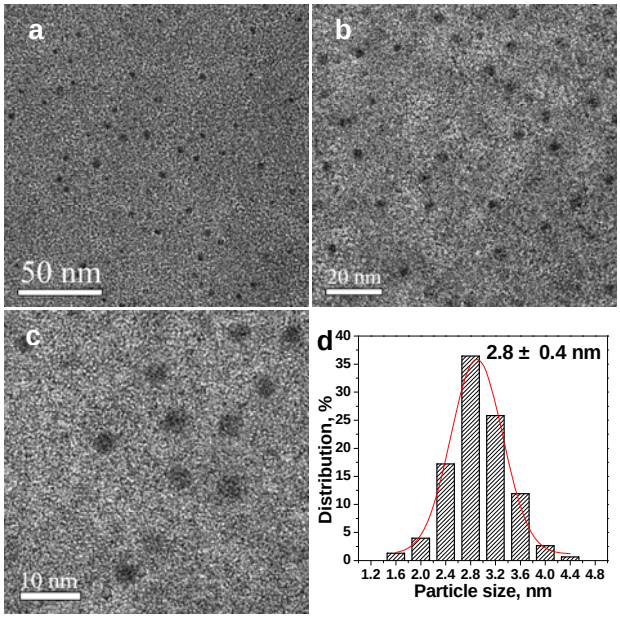

Figure S3-1. TEM micrographs (a-c) and size distributions (d) of fresh Pd

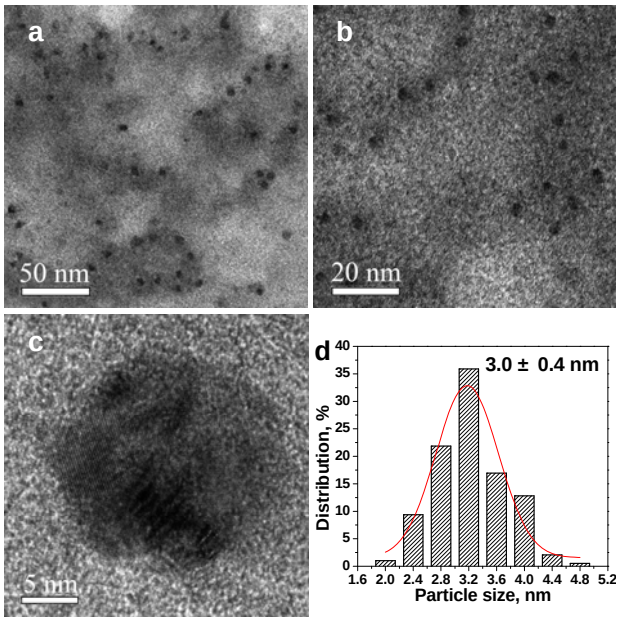

Figure S3-2. TEM micrographs (a-c) and size distributions (d) of recovered Pd after three times recycling.

1.7. High-resolution transmission electron microscopy (HRTEM)

The freshly prepared and recycled Pd catalysts were analyzed by HRTEM. After the phenol hydrogenation reaction was quenched, 0.2 mL of Pd nanoparticle-containing aqueous solution was diluted with 5 mL methanol and ultrasonicated for 1 h, and then one drop of the solution was placed on a copper grid coated by a carbon film and analyzed by TEM. More than 200 particles were counted to determine the size distribution.

Figure S4. GC analysis of the data listed in Table 1

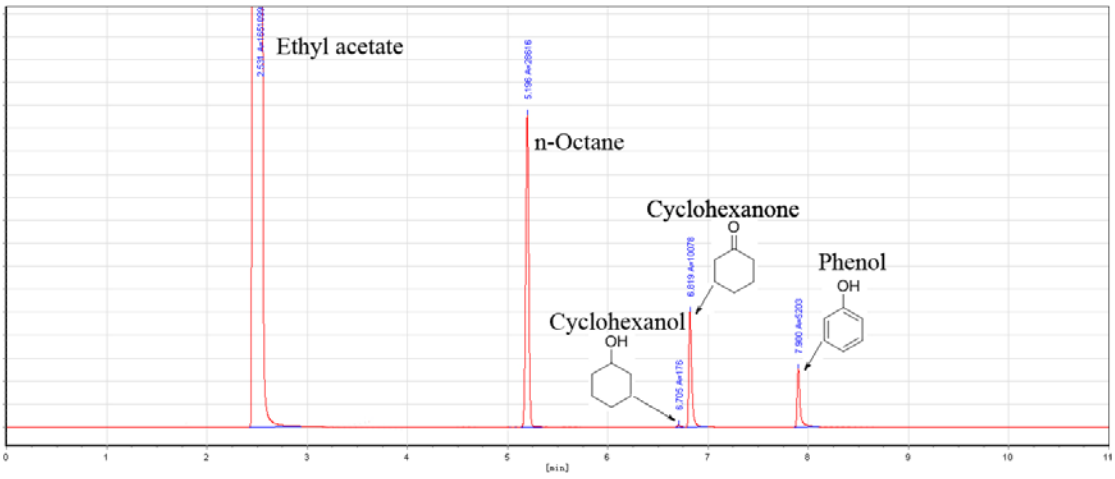

Figure S4-1. GC of phenol hydrogenation (Table 1, run 1)

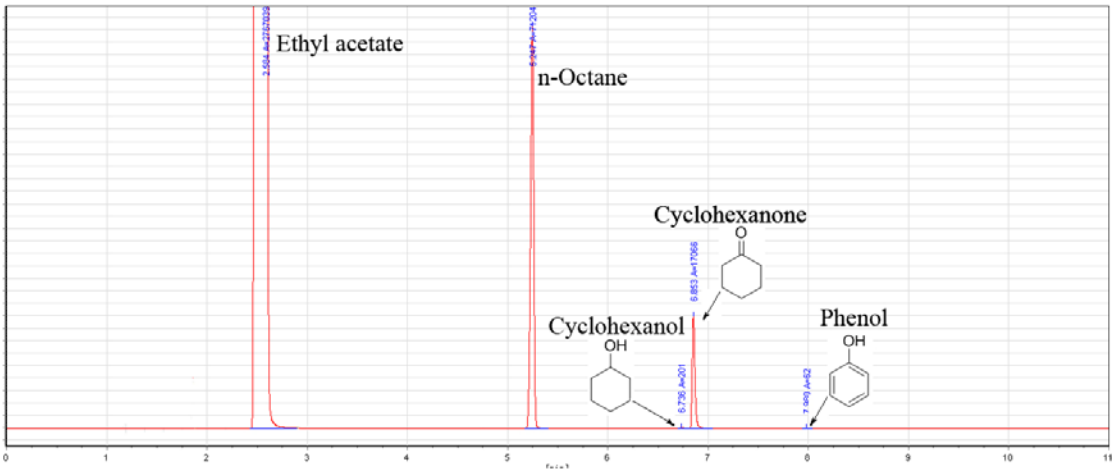

Figure S4-2. GC of phenol hydrogenation (Table 1, run 2)

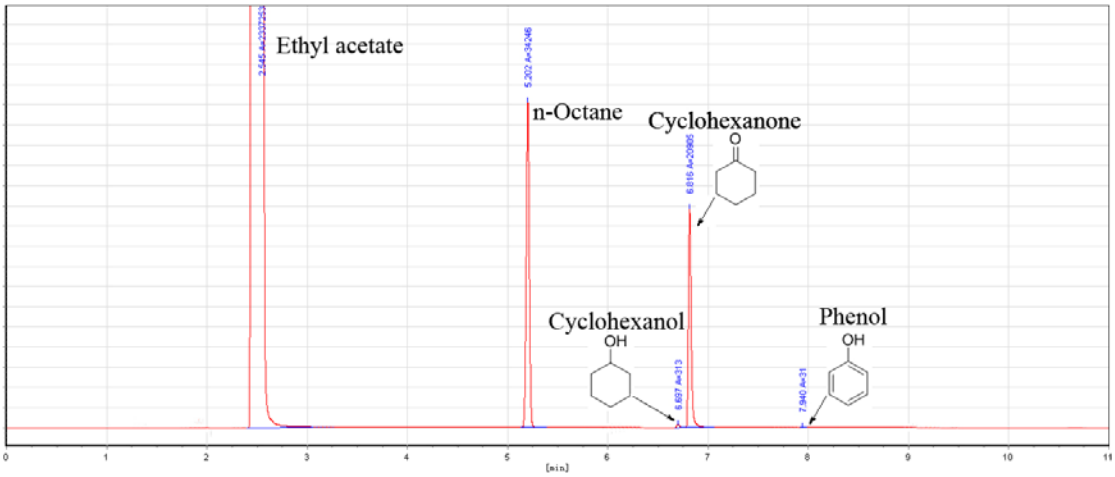

Figure S4-3. GC of phenol hydrogenation (Table 1, run 3)

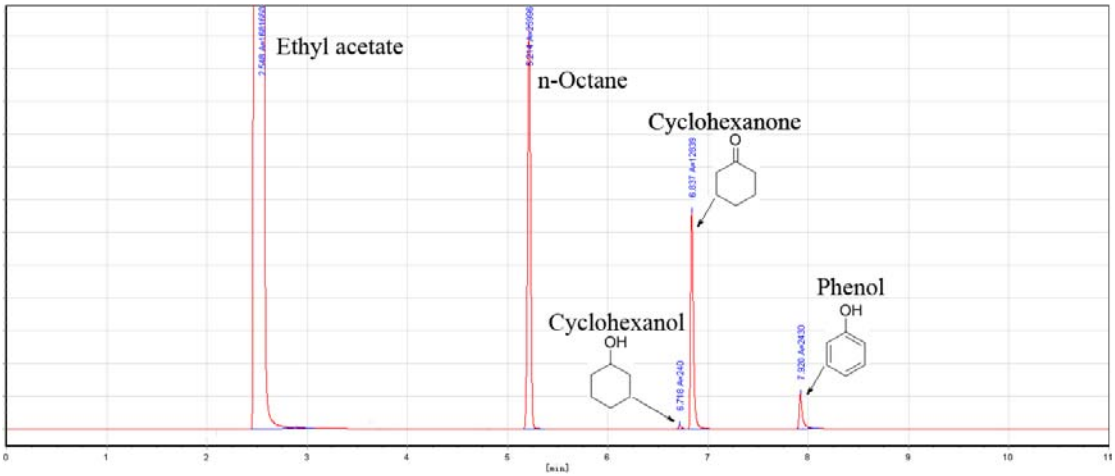

Figure S4-4. GC of phenol hydrogenation (Table 1, run 4)

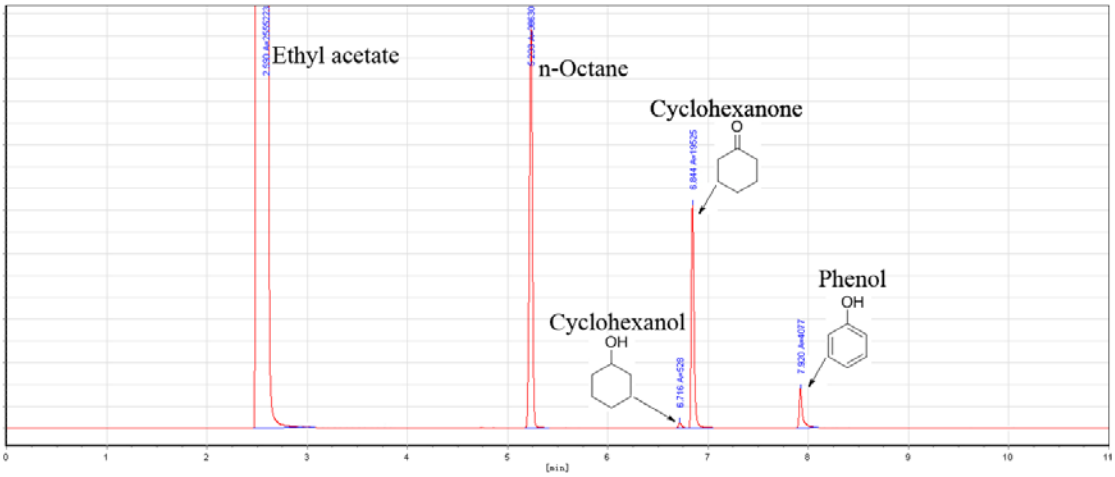

Figure S4-5. GC of phenol hydrogenation (Table 1, run 5)

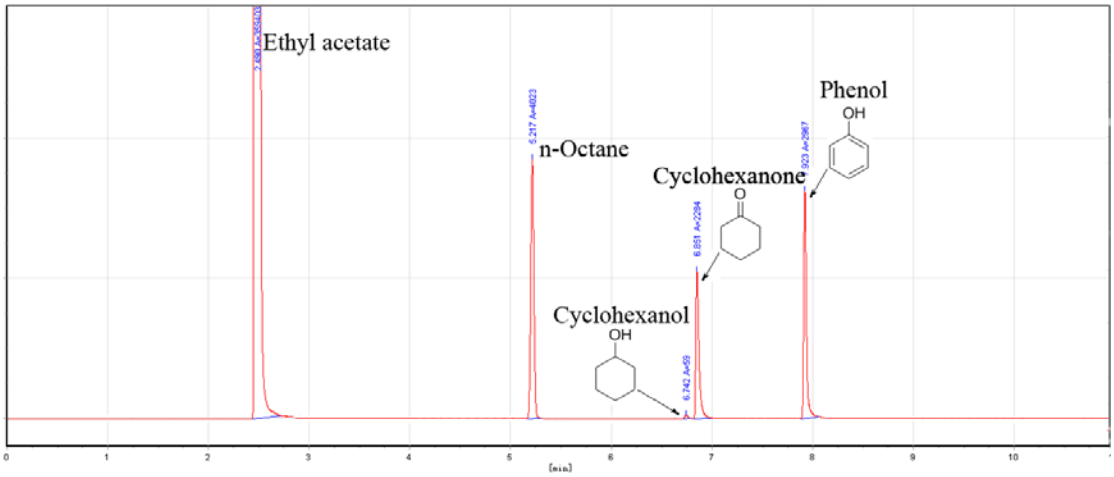

Figure S4-6. GC of phenol hydrogenation (Table 1, run 6)

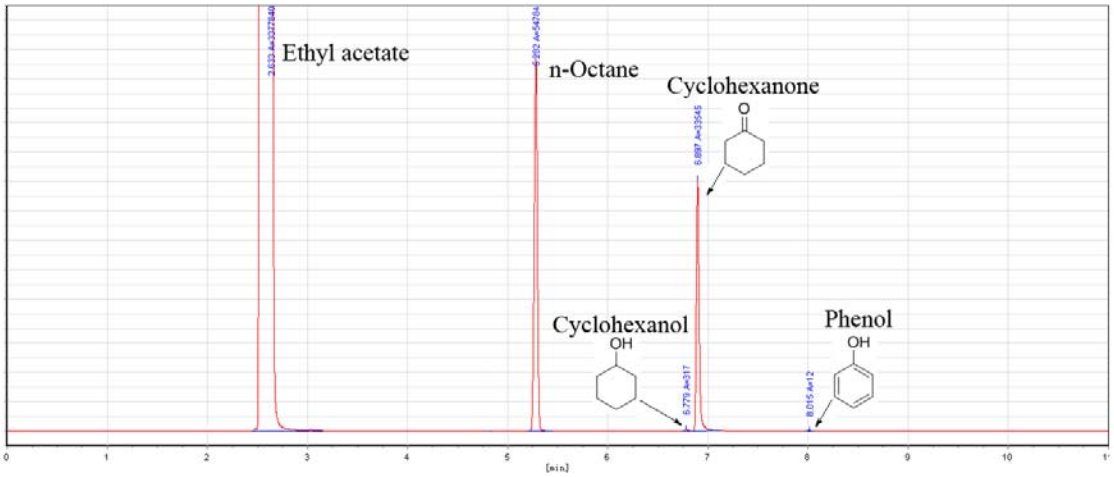

Figure S4-7. GC of phenol hydrogenation (Table 1, run 7)

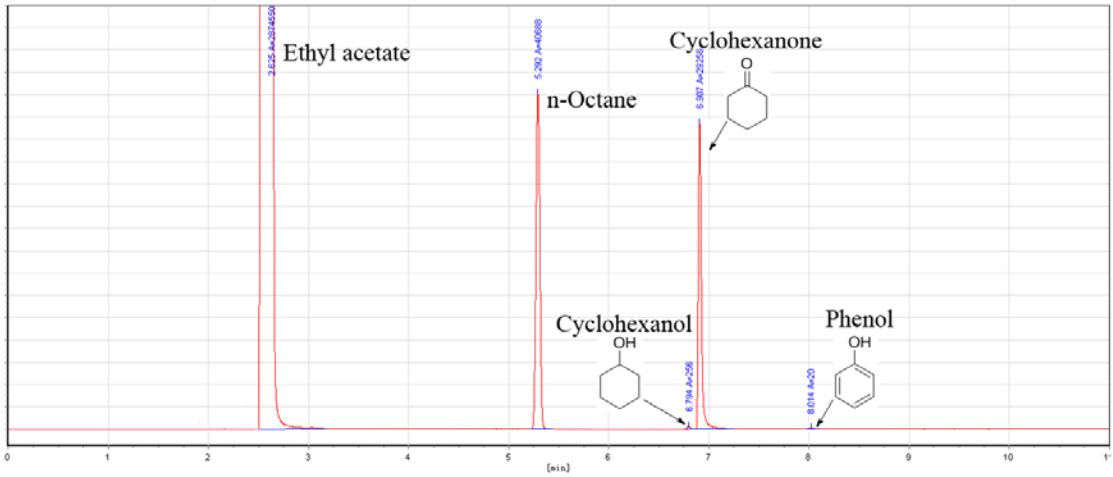

Figure S4-8. GC of phenol hydrogenation (Table 1, run 8)

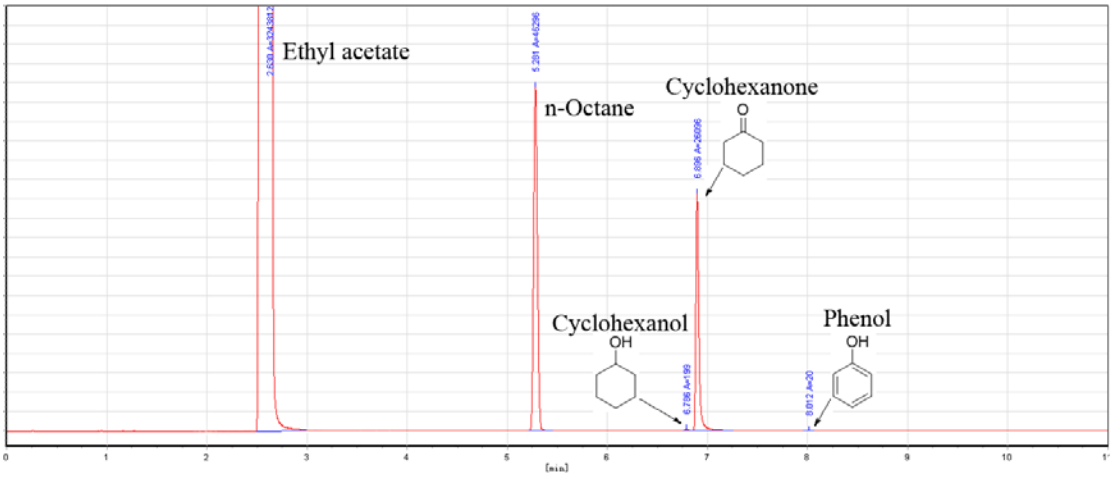

Figure S4-9. GC of phenol hydrogenation (Table 1, run 9)

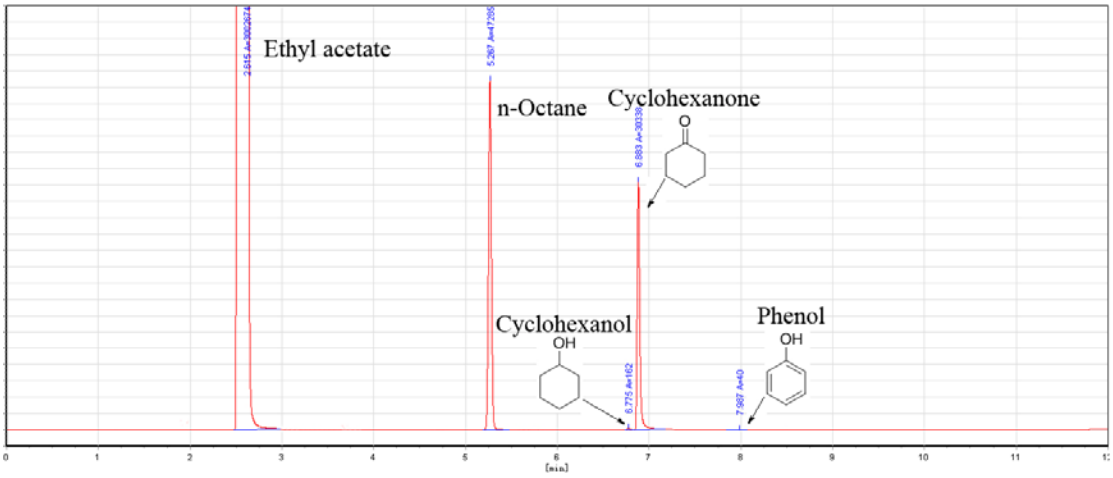

Figure S4-10. GC of phenol hydrogenation (Table 1, run 10)

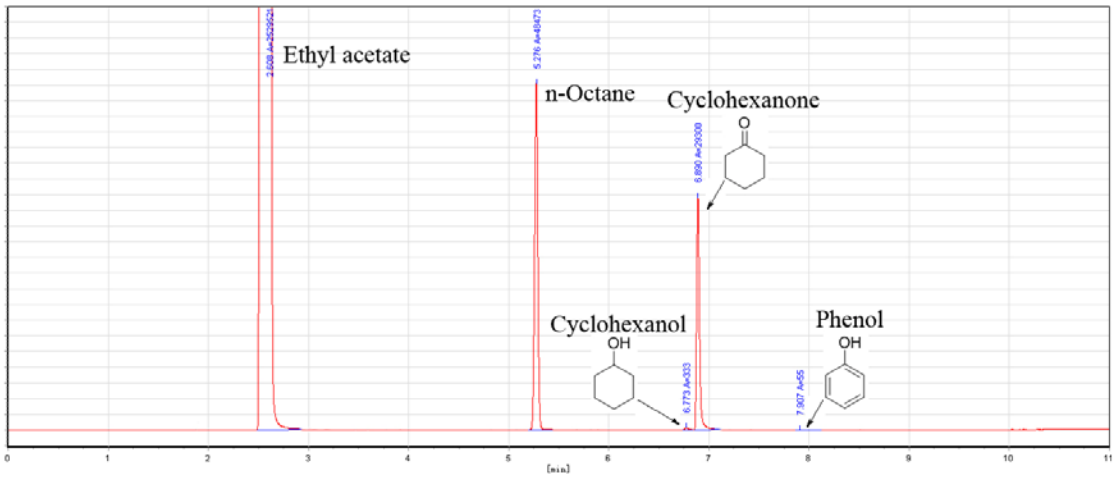

Figure S4-11. GC of phenol hydrogenation (Table 1, run 11)

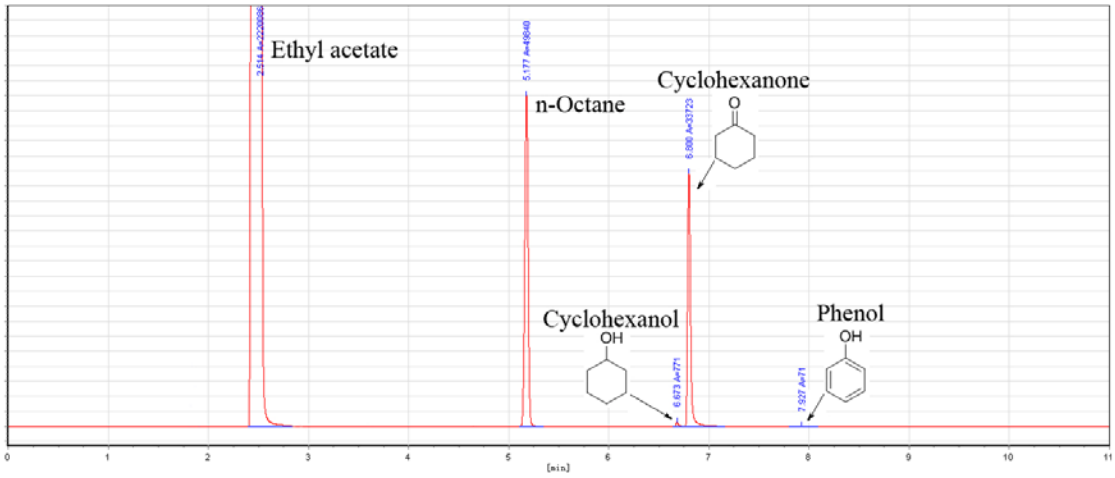

Figure S4-12. GC of phenol hydrogenation (Table 1, run 12)

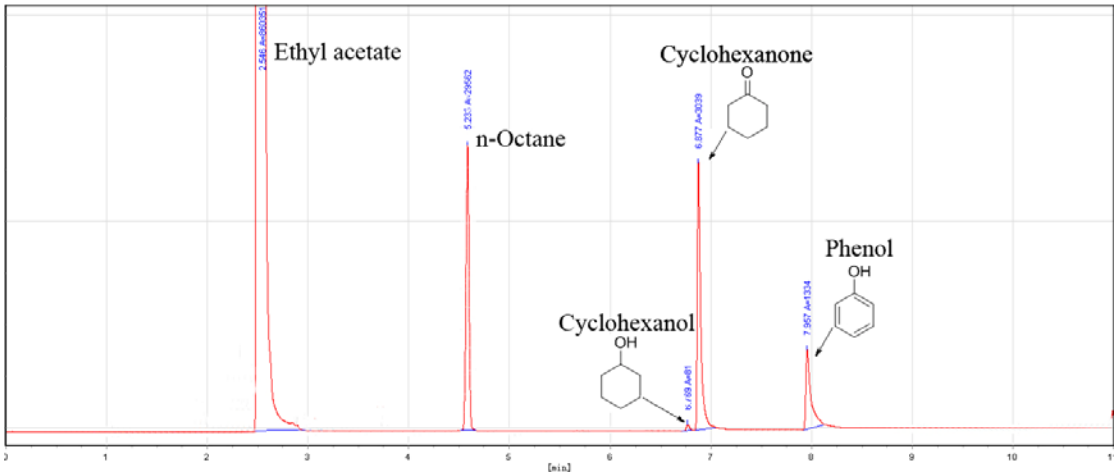

Figure S4-13. GC of phenol hydrogenation (Table 1, run 13)

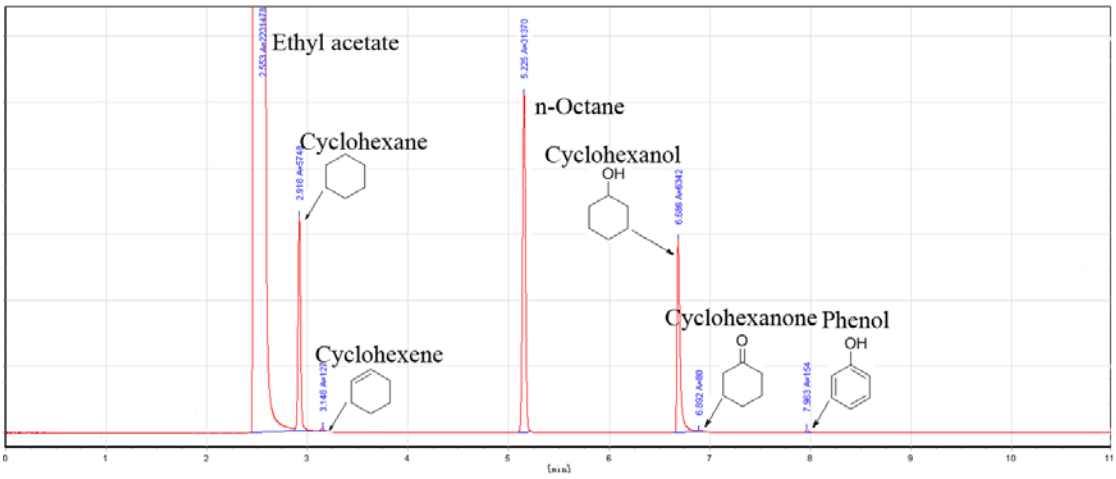

Figure S4-14. GC of phenol hydrogenation (Table 1, run 14)

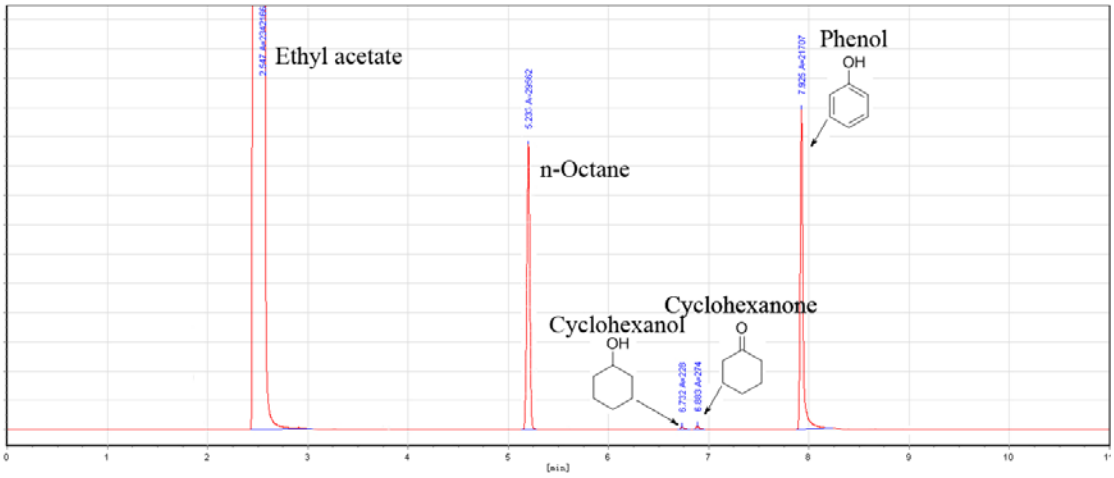

Figure S4-15. GC of phenol hydrogenation (Table 1, run 15)

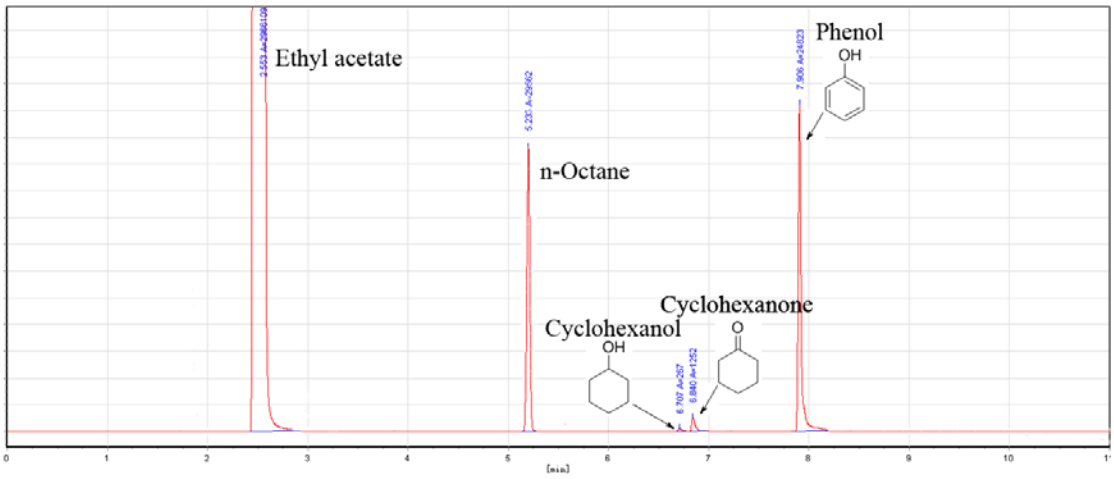

Figure S4-16. GC of phenol hydrogenation (Table 1, run 16)

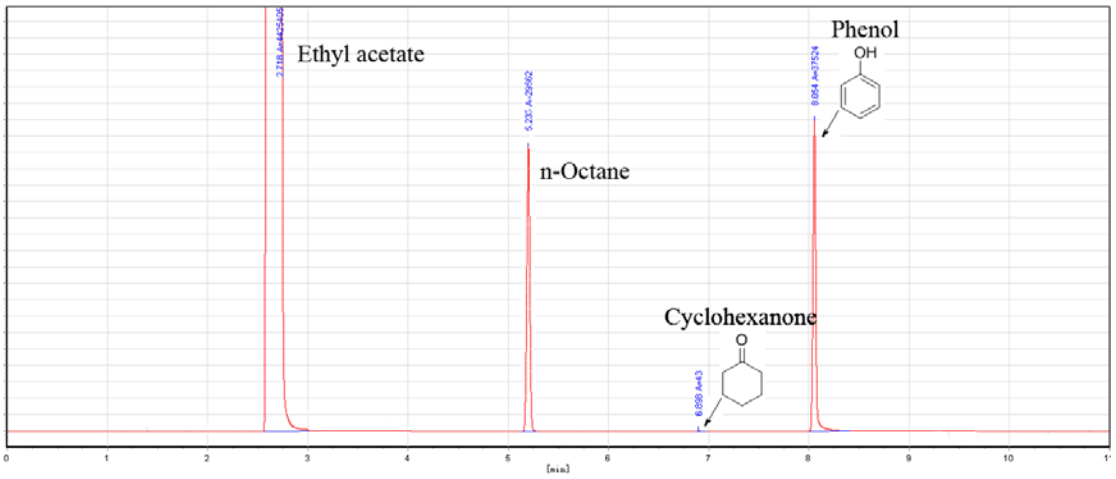

Figure S4-17. GC of phenol hydrogenation (Table 1, run 17)

Figure S5. GC analysis of the data listed in Table 2

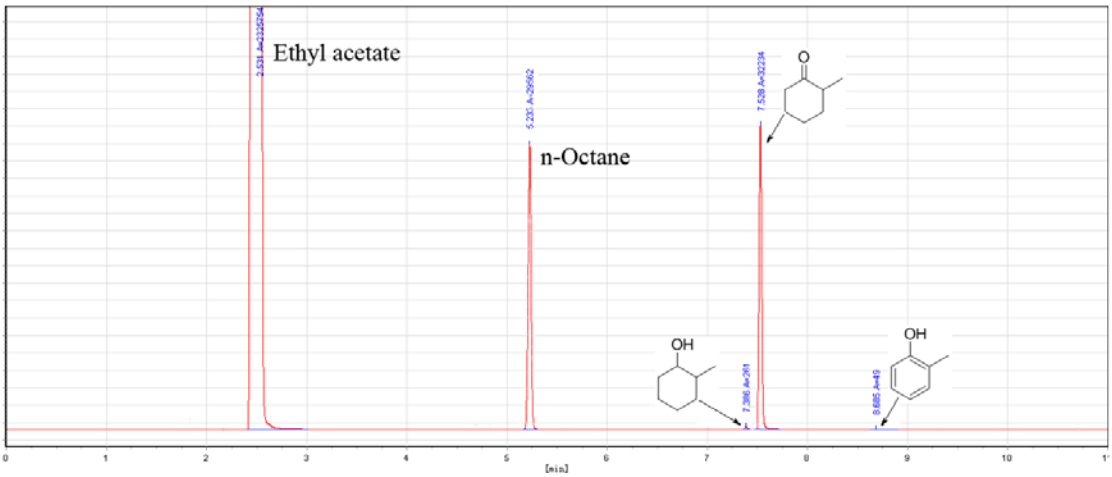

Figure S5-1. GC of 2-methylphenol hydrogenation (Table 2, run 1)

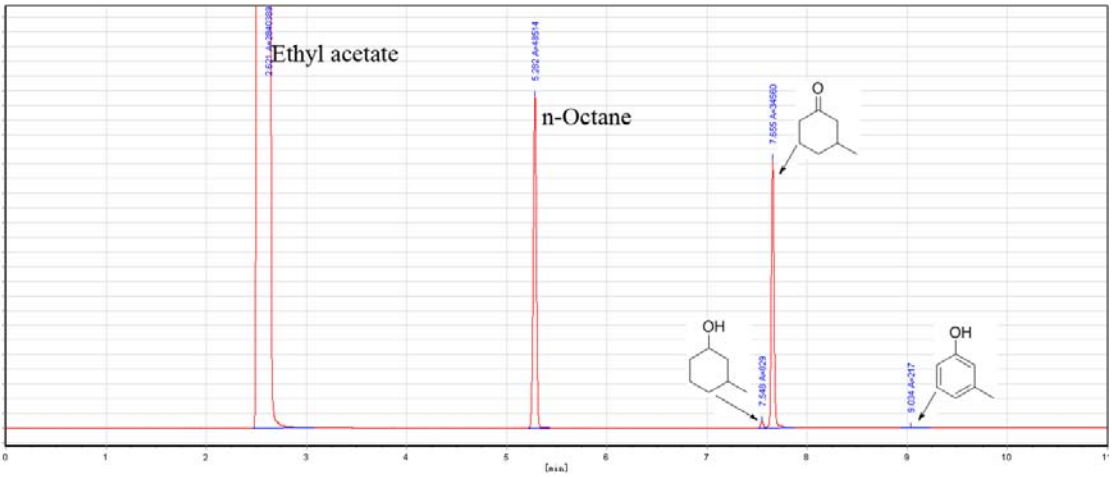

Figure S5-2. GC of 3-methylphenol hydrogenation (Table 2, run 2)

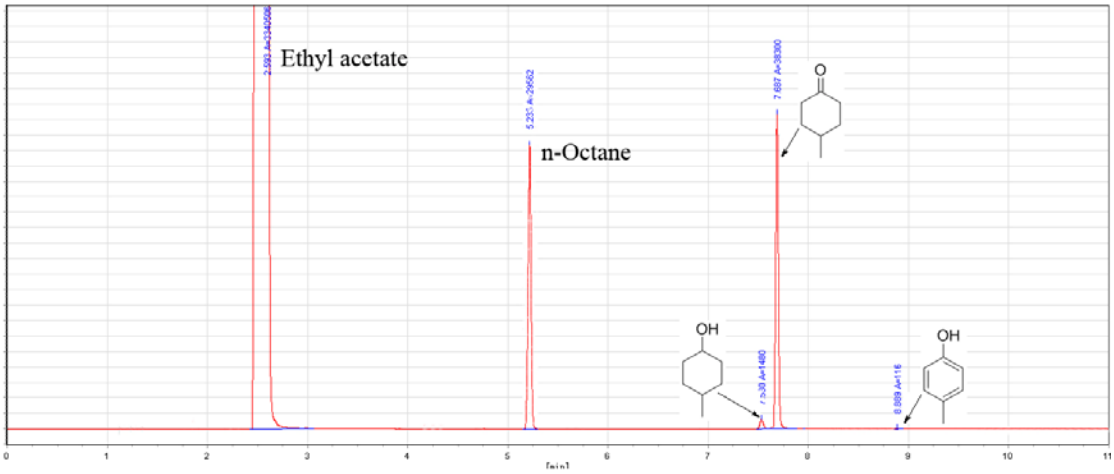

Figure S5-3. GC of 4-methylphenol hydrogenation (Table 2, run 3)

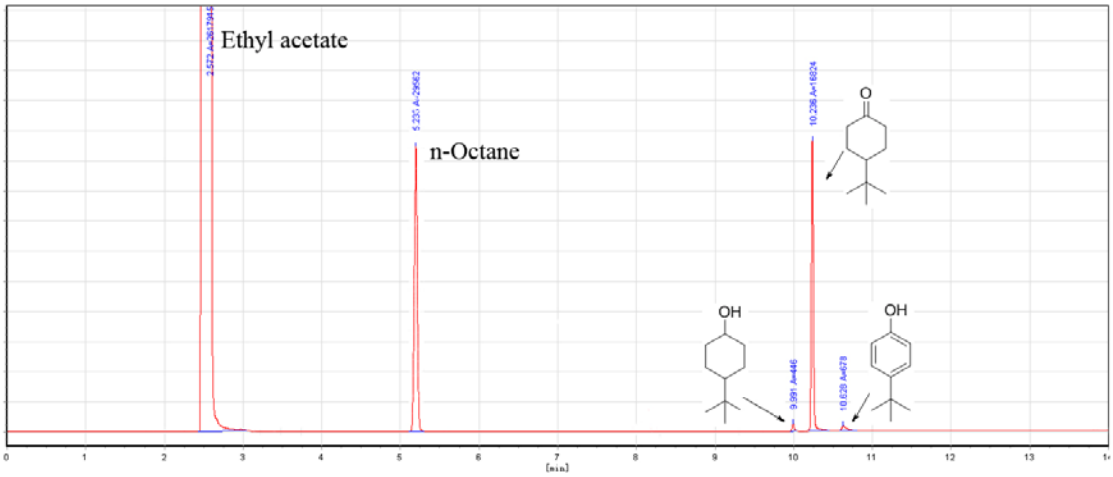

Figure S5-4. GC of 4-tert-butylphenol hydrogenation (Table 2, run 4)

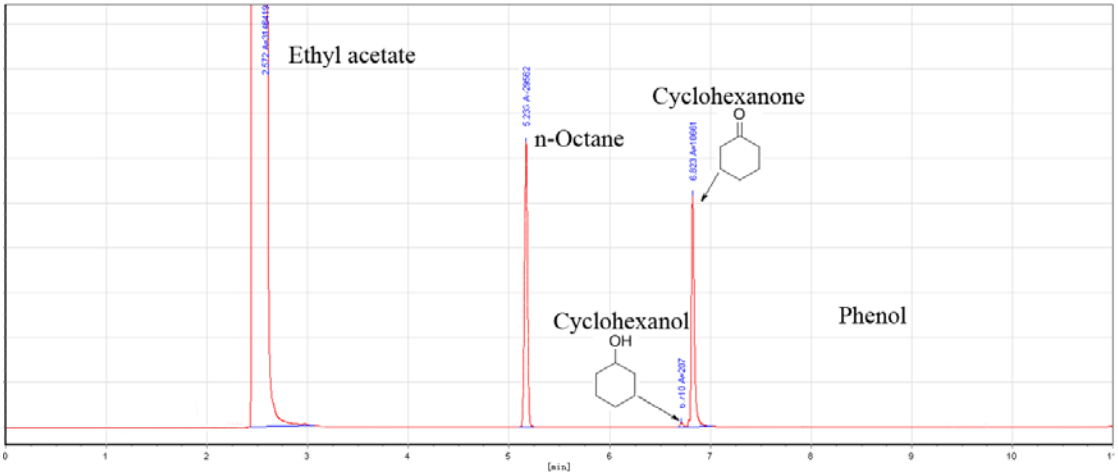

Figure S5-5. GC of hydroquinone hydrogenation (Table 2, run 5)

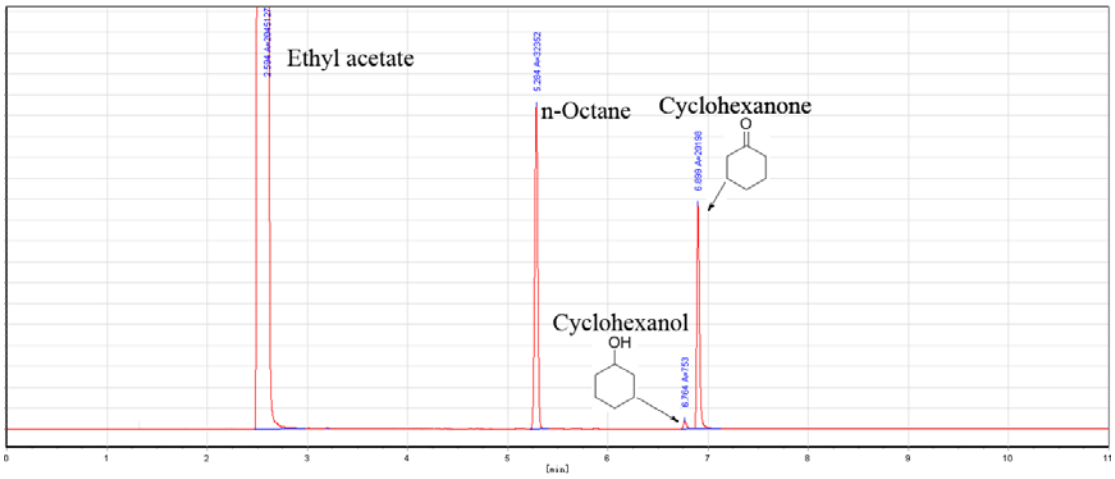

Figure S5-6. GC of resorcinol hydrogenation (Table 2, run 6)

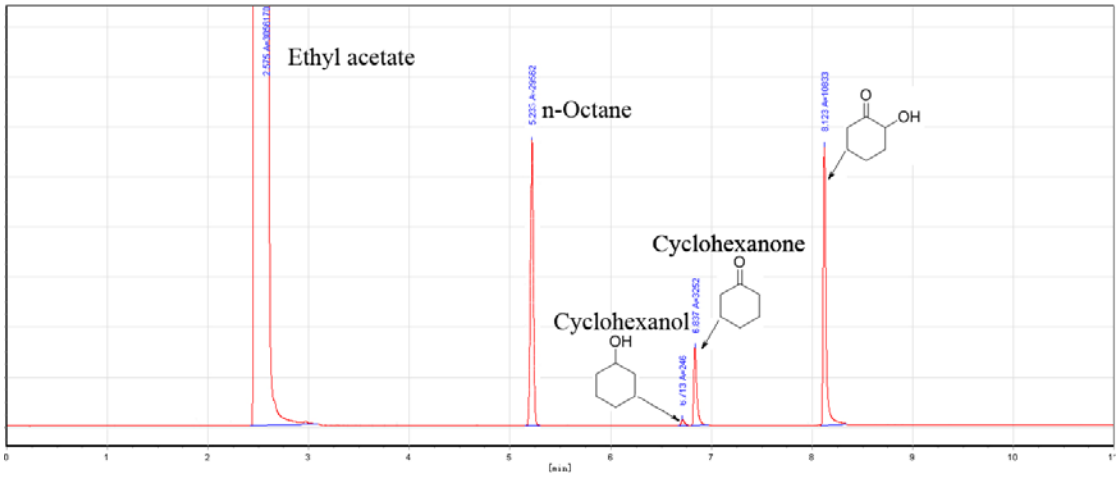

Figure S5-7. GC of pyrocatechol hydrogenation (Table 2, run 7)

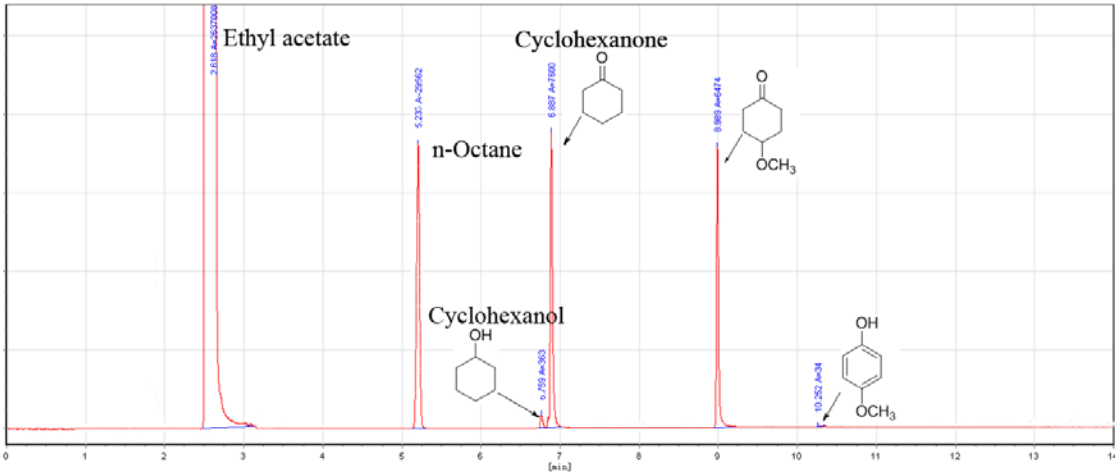

Figure S5-8. GC of 4-methoxyphenol hydrogenation (Table 2, run 8)

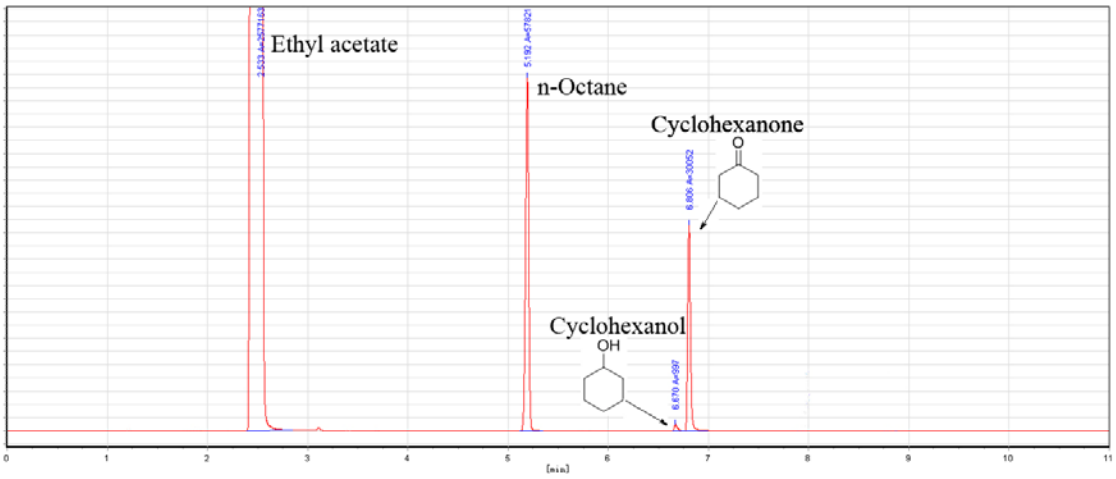

Figure S5-9. GC of 4-chlorophenol hydrogenation (Table 2, run 9)

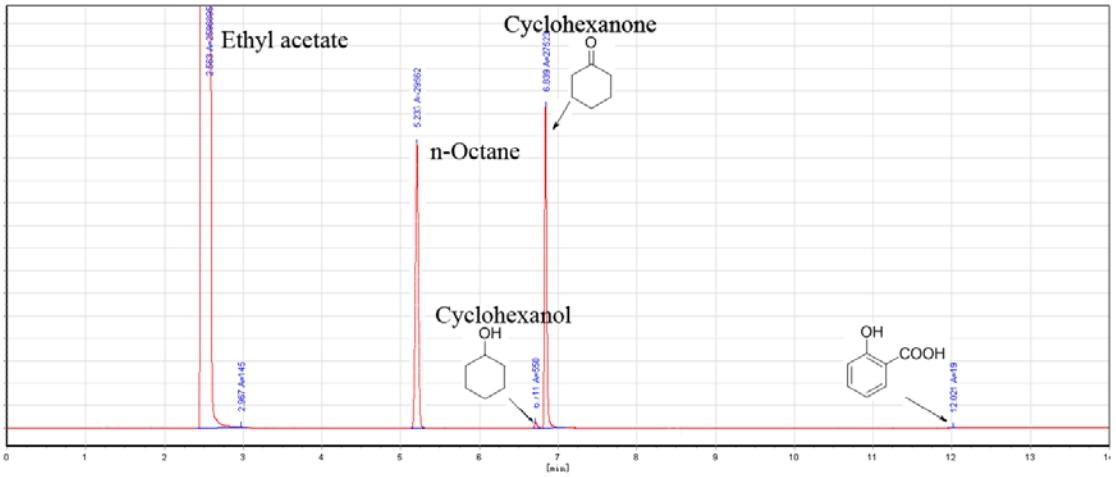

Figure S5-10. GC of salicylic acid hydrogenation (Table 2, run 10)

Figure S6. GC-MS analysis of the data listed in Tables 1 and 2

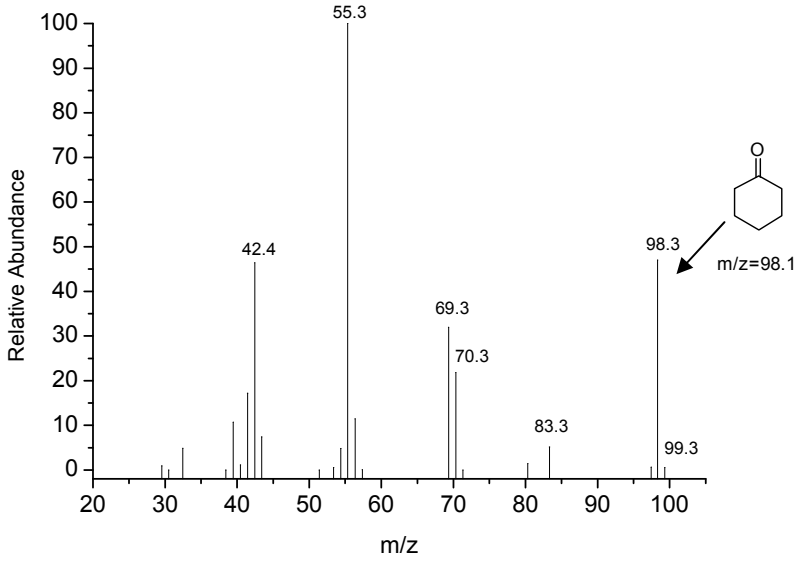

Figure S6-1. GC-MS of cyclohexanone (Table 1; Table 2, runs 5-10)

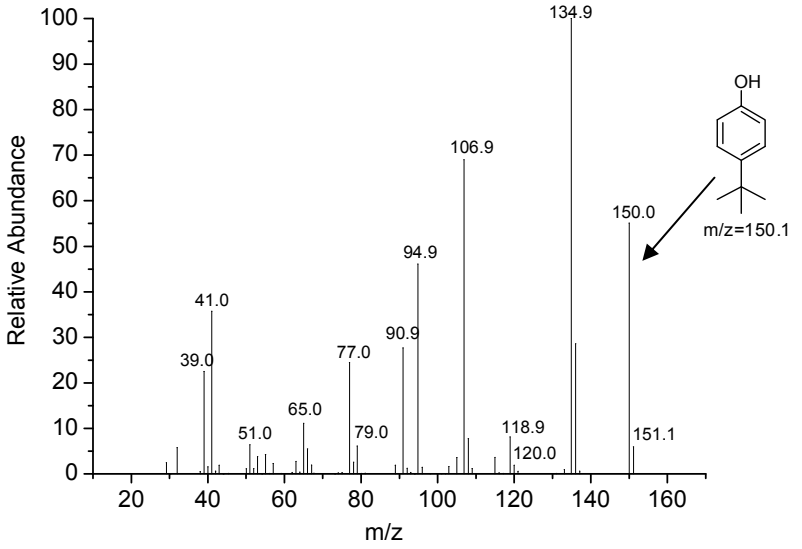

Figure S6-2. GC-MS of 4-tert-butylphenol (Table 2, run 4)

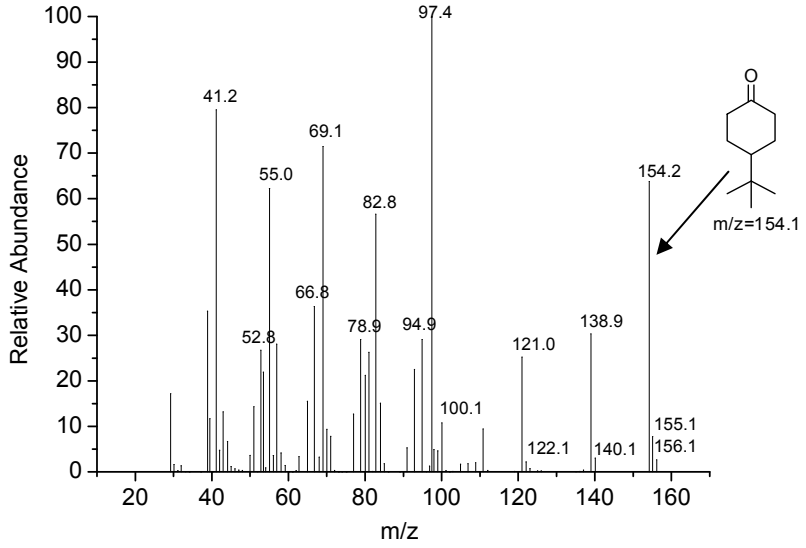

Figure S6-3. GC-MS of 4-tert-butylcyclohexanone (Table 2, run 4)

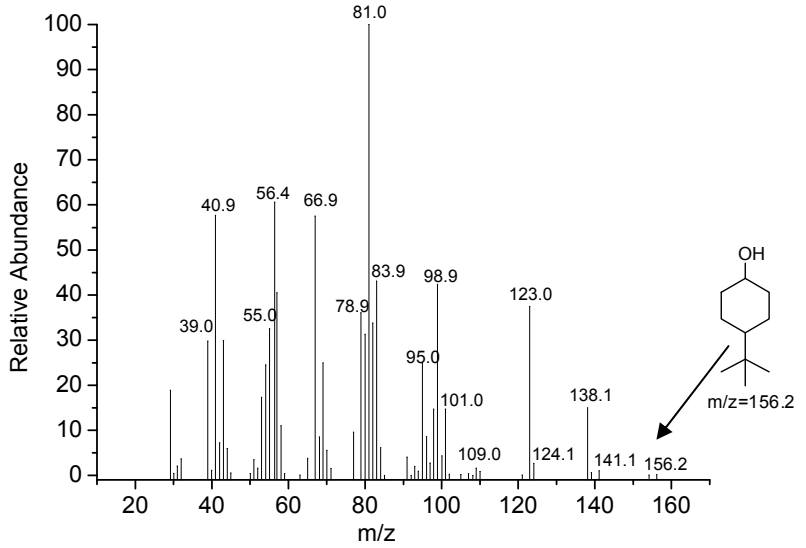

Figure S6-4. GC-MS of 4-tert-butylcyclohexanol (Table 2, run 4)

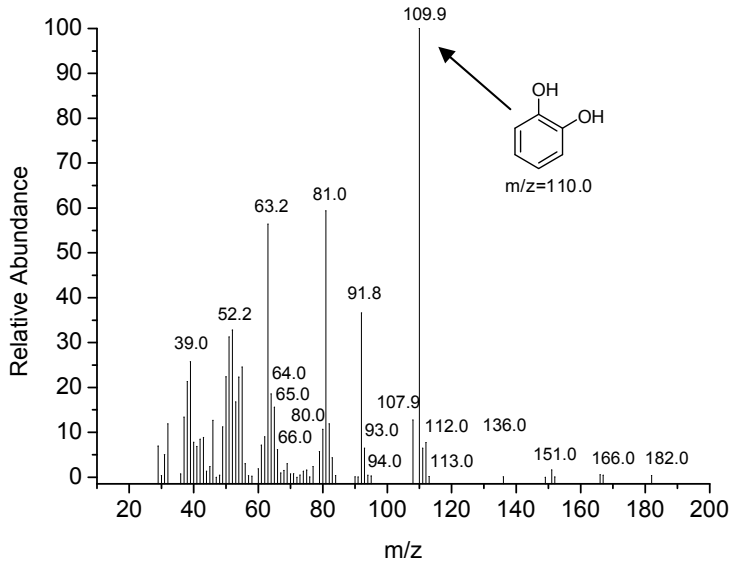

Figure S6-5. GC-MS of pyrocatechol (Table 2, run 7)

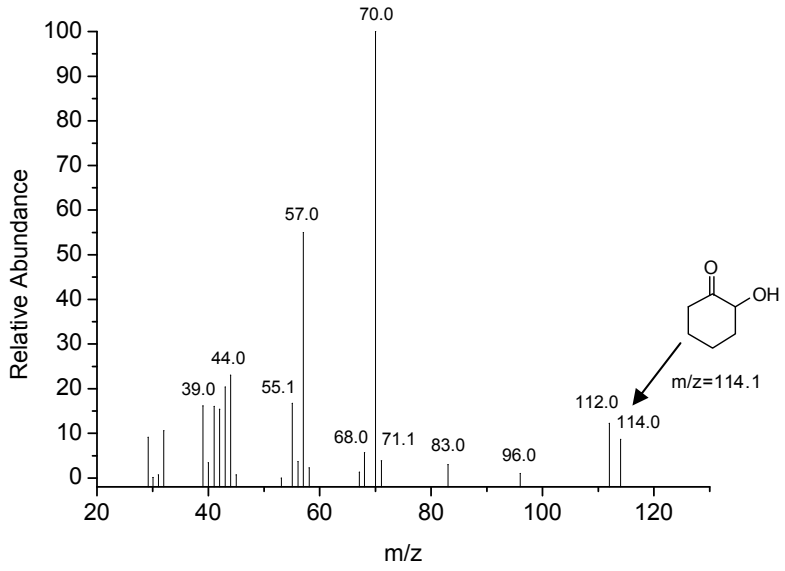

Figure S6-6. GC-MS of 2-hydroxycyclohexanone (Table 2, run 7)

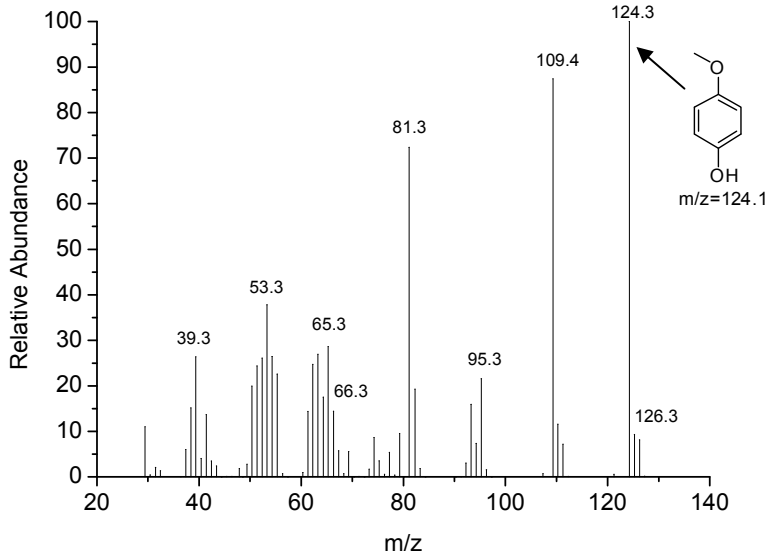

Figure S6-7. GC-MS of 4-methoxyphenol (Table 2, run 8)

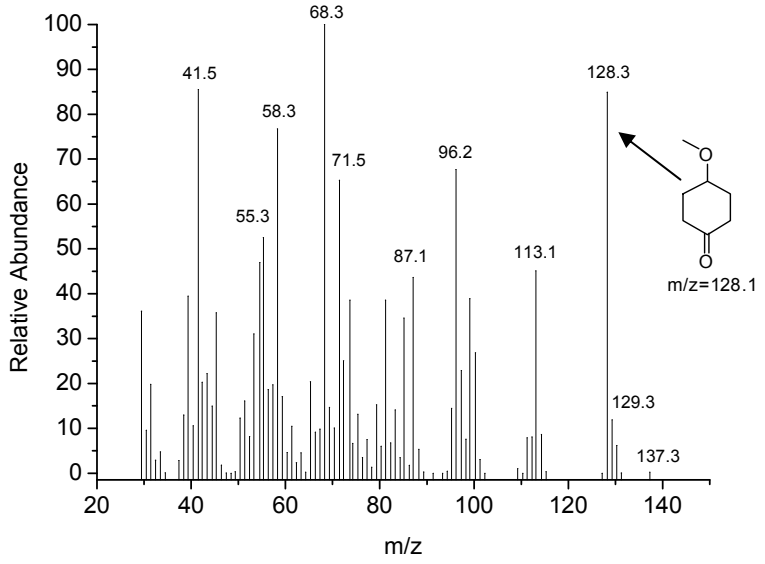

Figure S6-8. GC-MS of 4-methoxycyclohexanone (Table 2, run 8)

Figure S7. NMR and IR analysis of A and B

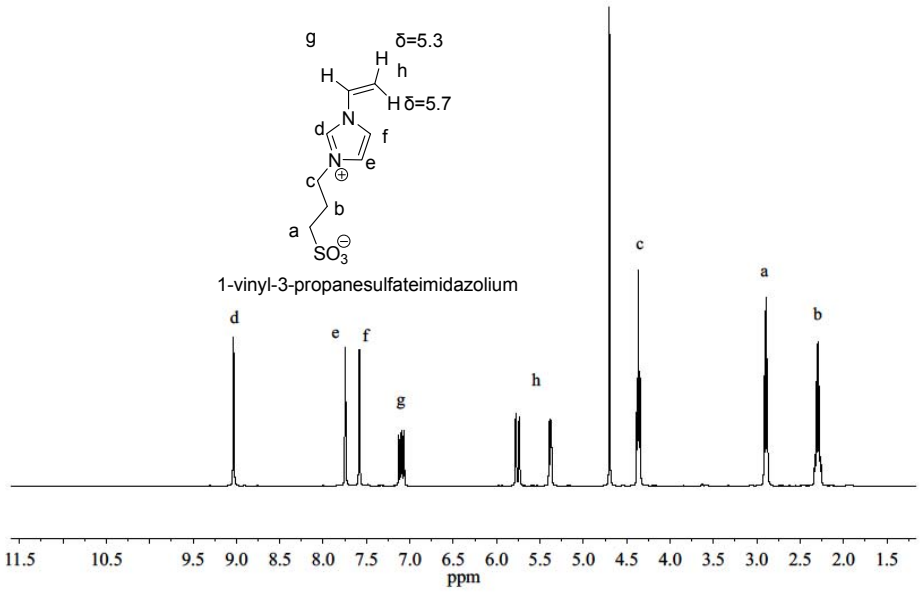

Figure S7-1. ^{1}H NMR of 3-(1-vinyl-1*H*-imidazoliumyl)propanesulfonate **3** in D_2O. ^{1}H NMR (400 MHz, D_2O): δ = 9.04 (s, 1H), 7.74 (s, 1H), 7.58 (s, 1H), 7.11 (m, 1H), 5.76 (dd, 1H, *J* = 15.6 Hz, 2.8 Hz), 5.38 (dd, 1H, *J* = 8.8 Hz, 2.4 Hz), 4.36 (t, 2H, *J* = 7.2 Hz), 2.90 (t, 2H, *J* = 7.6 Hz), 2.30 (m, 2H).

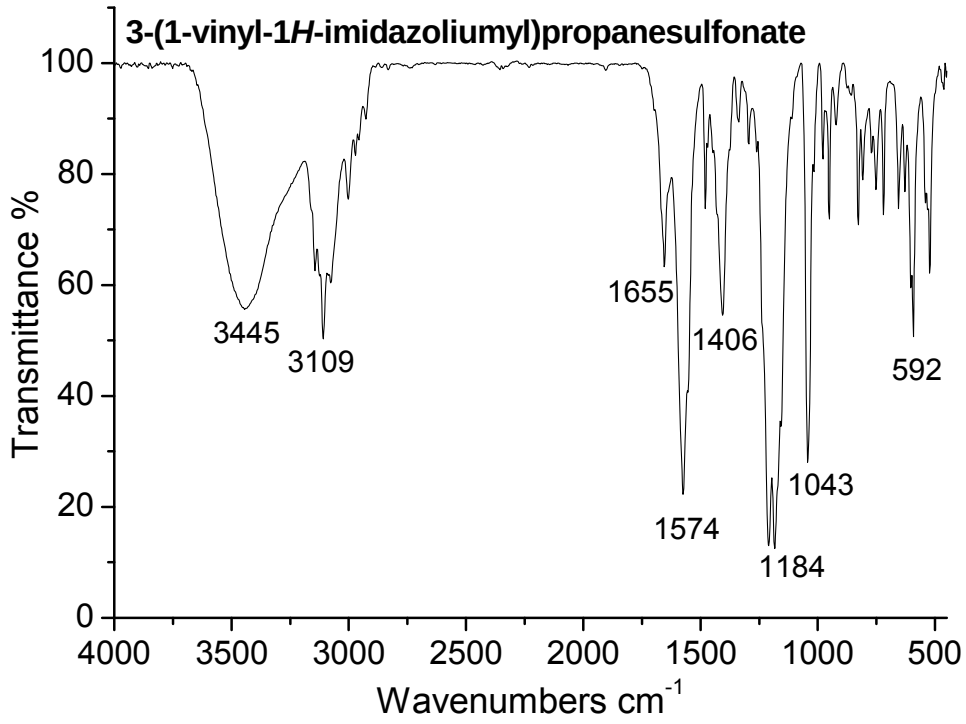

Figure S7-2. IR of 3-(1-vinyl-1*H*-imidazoliumyl)propanesulfonate **3** on KBr Pellet. IR (KBr, cm^{-1}): ν = 3445 (O−H, vs); 3109 (C−H, w); 1655 (w), 1574 (vs), 1406 (m), (C=N and C=C); 1184 (SO_3^-, vs); 1043 (SO_3^-, vs); 592 (C−H, w).

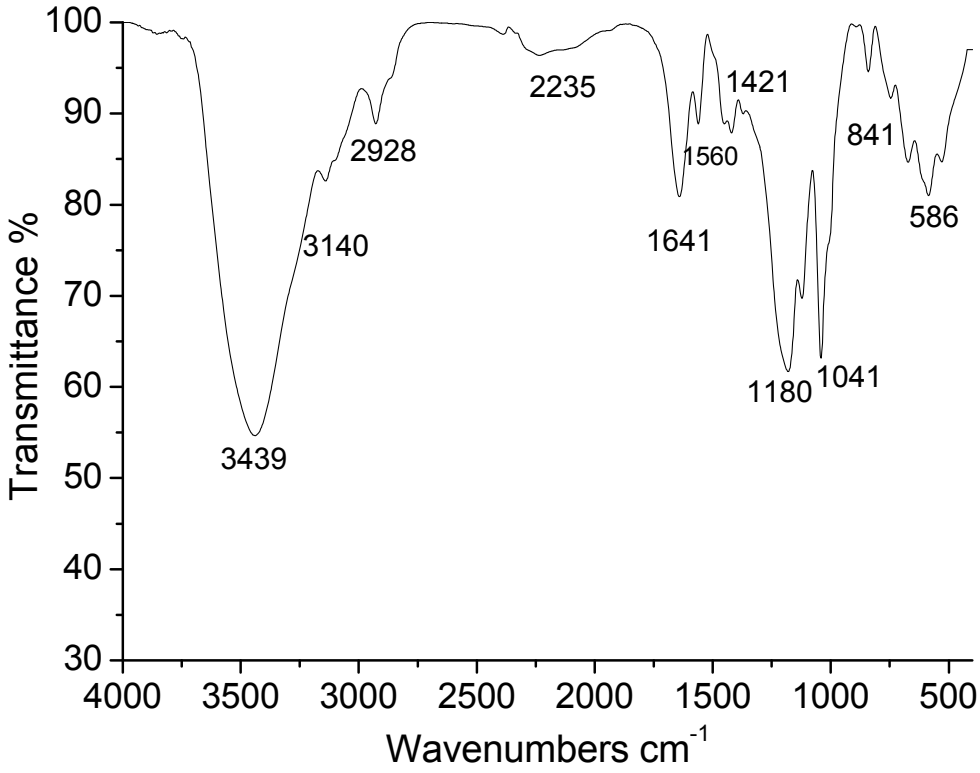

Figure S7-3. IR of poly[(3-(1-vinylimidazoliumyl)propanesulfonate)-*co*-(sodium 4-styrene sulfonate)] **A** on KBr Pellets. IR (KBr, cm^{-1}): ν = 3439 (O−H, H_2O, vs); 3140 (C−H, m); 2928 (C−H, w); 1641 (m), 1560 (w), 1421 (w), (C=N and C=C); 1180 (SO_3^-, s); 1042 (SO_3^-, s); 586 (C−H, m).

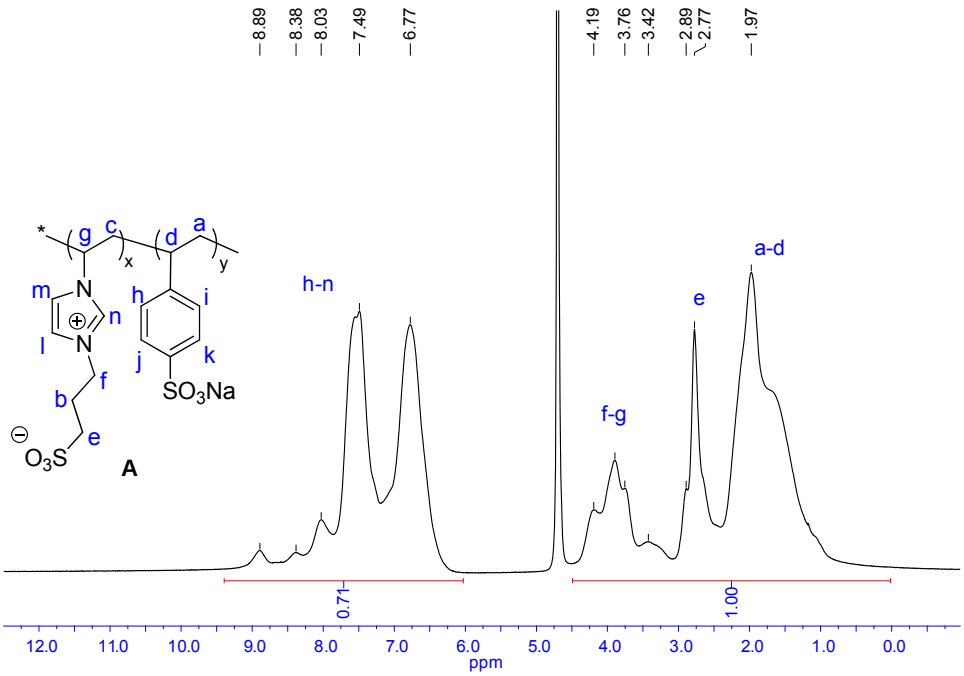

Figure S7-4. ^1H NMR (400 MHz, D_2O) of poly[(3-(1-vinylimidazoliumyl) propanesulfonate)-*co*-(sodium 4-styrene sulfonate)] **A**,

Based on the integration in ^{1}H NMR of copolymer A, the molar ratio of "x : y" is "1 : 1.8".
Asserts that the molar of monomer 3-(1-vinylimidazoliumyl) propanesulfonate is "x", while the molar of monomer sodium styrene sulfonate is "y":
three aromatic protons (l, m, n) from monomer 3-(1-vinylimidazoliumyl) propanesulfonate and four aromatic protons (h, I, j, K) from monomer sodium styrene sulfonate are observed with an integration area of 0.71 and chemical shift from 6.0 to 9.5 ppm. Thus, the equation "3 x + 4 y = 0.71" is obtained.
nine aliphatic (sp^3) protons (2c, 1g, 2f, 2b, 2e) from monomer 3-(1-vinylimidazoliumyl) propanesulfonate and three aliphatic (sp^3) protons (2a, 1d) from monomer sodium styrene sulfonate are observed with an integration area of 1 and chemical shift from 0 to 4.5 ppm. Thus, the equation "9 x + 3 y = 1" is obtained.

solving the equations
3 x + 4 y = 0.71
9 x + 3 y = 1

x = 0.069
y = 0.126

thus, x : y = 1 : 1.8

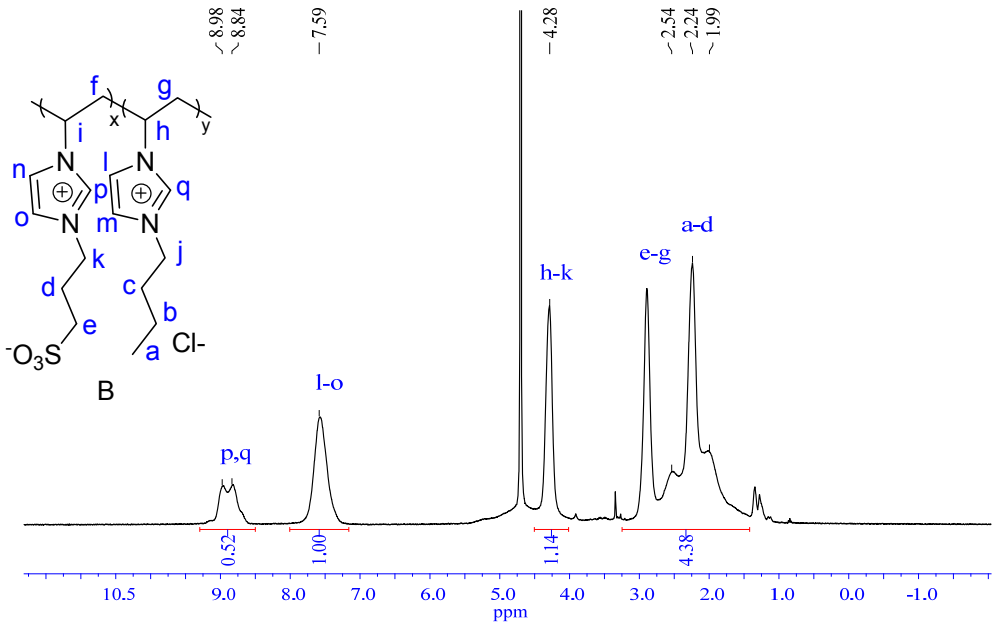

Figure S7-5. ^{1}H NMR of **B** in D_2O. Based on the integration in ^{1}H NMR of copolymer **B**, the molar ratio of "x : y" is "1 : 1.7".