Supporting Information

Cleavage of lignin β-O-4 ether bond via dehydroxylation-hydrogenation strategy over a NiMo sulfide catalyst

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1. Lignin β-O-4 model compounds synthesis

All chemicals were of analytical grade and used as purchased without further purification. The β-O-4 lignin model compounds were synthesized according to the previous procedure.
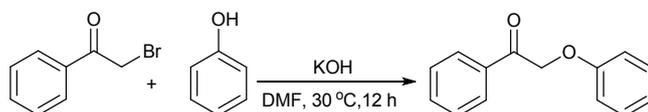
To synthesize 2-phenoxy-1-phenylethanone (β-O-4-K),[1] bromoacetophenone (9.0 g, 45 mmol) and phenol (5.0 g, 53 mmol) were dissolved in 200 mL dimethylformamide, mixed with potassium hydroxide (3.0 g, 53 mmol) and stirred 16 h at room temperature. The product was then extracted with water and ethyl ether, dried over sodium sulfate and recrystallized from ethanol.
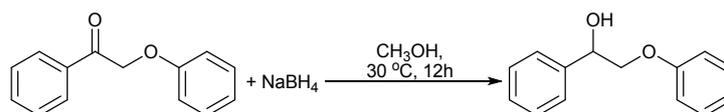
To synthesize 2-phenoxy-1-phenylethanol (β-O-4-A),[1] a solution of 2-phenoxy-1-phenylethanone (2.5 g, 11 mmol) in methanol (100 mL) was treated with sodium borohydride (11 mmol), and stirred overnight. A saturated solution of ammonium sulphate (200 mL) followed by chloroform (200 mL) was added to the reaction mixture. The organic layer was separated, washed with water (2 × 100 mL), dried and recrystallized from ethanol.
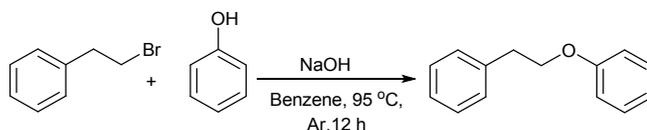
To synthesize (2-phenoxyethyl)benzene (β-O-4-H),[2] powdered caustic soda (18.0 g) was added to a solution of phenol (47.0 g) in benzene (200 g), and the resulting mixture was heated to 95 °C. 1-bromo-2-phenylethane (46.0 g) was then added, and the resulting mixture was stirred for 12 h at 95 °C. Upon completion of the reaction, the mixture was cooled, and washed and extracted with water and benzene, respectively. The solvent was then removed in vacuum

to give the crude β-O-4-H product, which was purified by silica gel column chromatography.
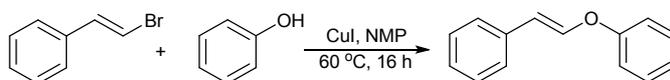
To synthesize (2-phenoxyvinyl)benzene (β-O-4-O),[3] Cs_2CO_3 (650 mg, 2.0 mmol), CuI (30 mg, 0.15 mmol, 15 mol%), ethyl 2-oxocyclohexanecarboxylate (50 mg, 0.30 mmol, 30mol%), β-bromostyrene (183.0 mg, 1 mmol), phenol (112.8 mg, 1.2 mmol), and anhydrous 1-methyl-2-pyrrolidinone (2 mL) were combined in under a stream of N_2. The reaction quickly sealed and stirred at 60 °C for 18 h. The crude reaction mixture was dissolved in H_2O and extracted with EtOAc. The combined organic layer was dried ($MgSO_4$). The product was purified by silica gel column chromatography.
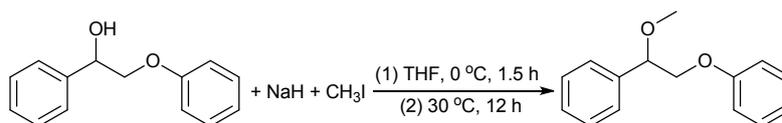
To synthesize (1-methoxy-2-phenoxyethyl)benzene (β-O-4-E),[4] A round bottom flask was charged with 2-phenoxy-1-phenylethanol (505 mg, 2.35 mmol) and tetrahydrofuran (12 mL). The resulting solution was cooled to 0 °C and sodium hydride (94 mg, 60 wt% in mineral oil, 2.35 mmol) was added in one portion. The resulting suspension was stirred at 0 °C for 1.5 h after which iodomethane (0.15 mL, 2.47 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature, stirred overnight, and the reaction was quenched with half-saturated aqueous sodium bicarbonate solution. The aqueous layer was extracted twice with ethyl acetate. The combined organic extracts were washed twice with brine, dried over $MgSO_4$, filtered, concentrated in vacuo, and purified by silica gel chromatography.

The GC-MS patterns of the β-O-4 lignin model compounds
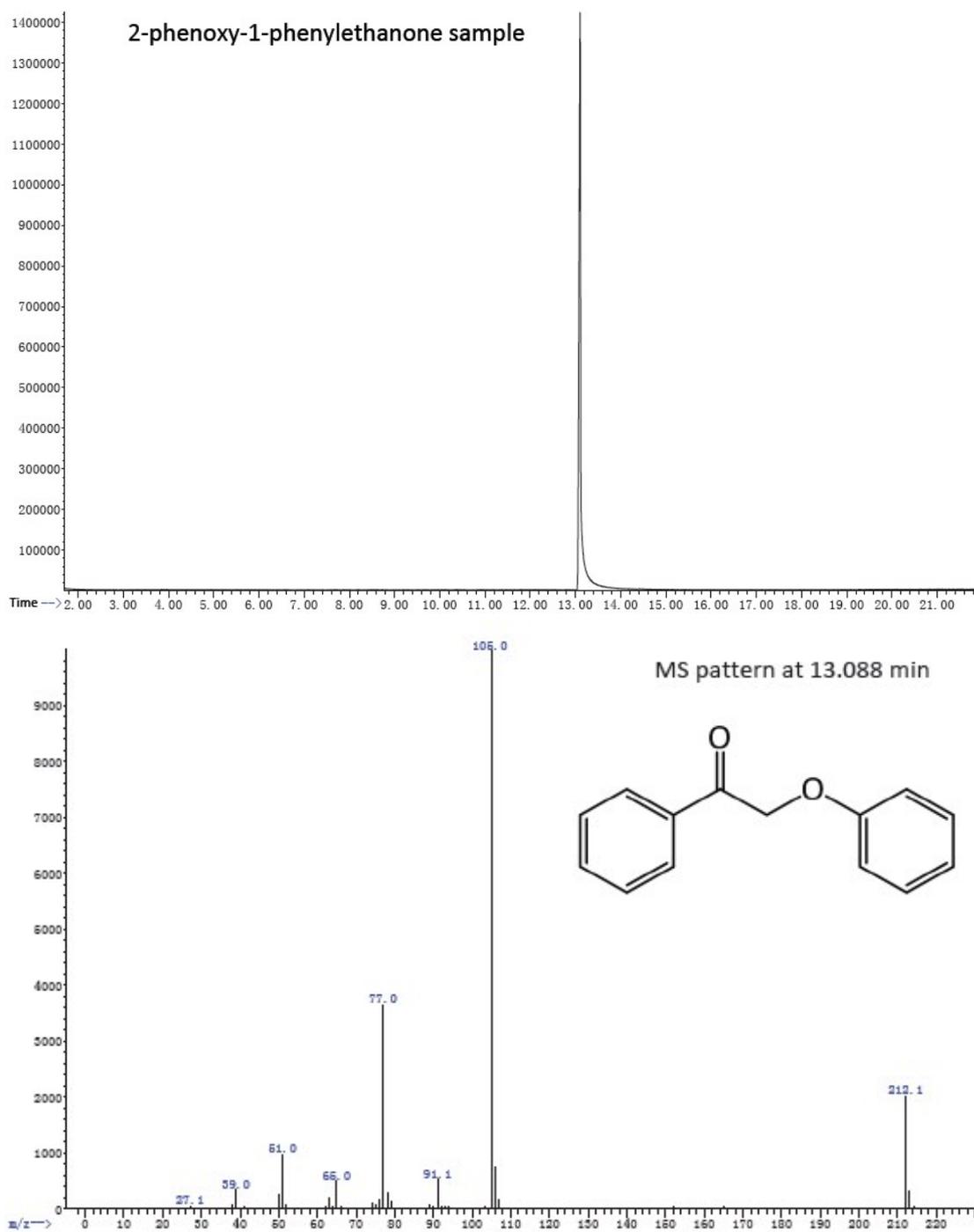
Figure S1. The GC-MS pattern of the β-O-4-K.
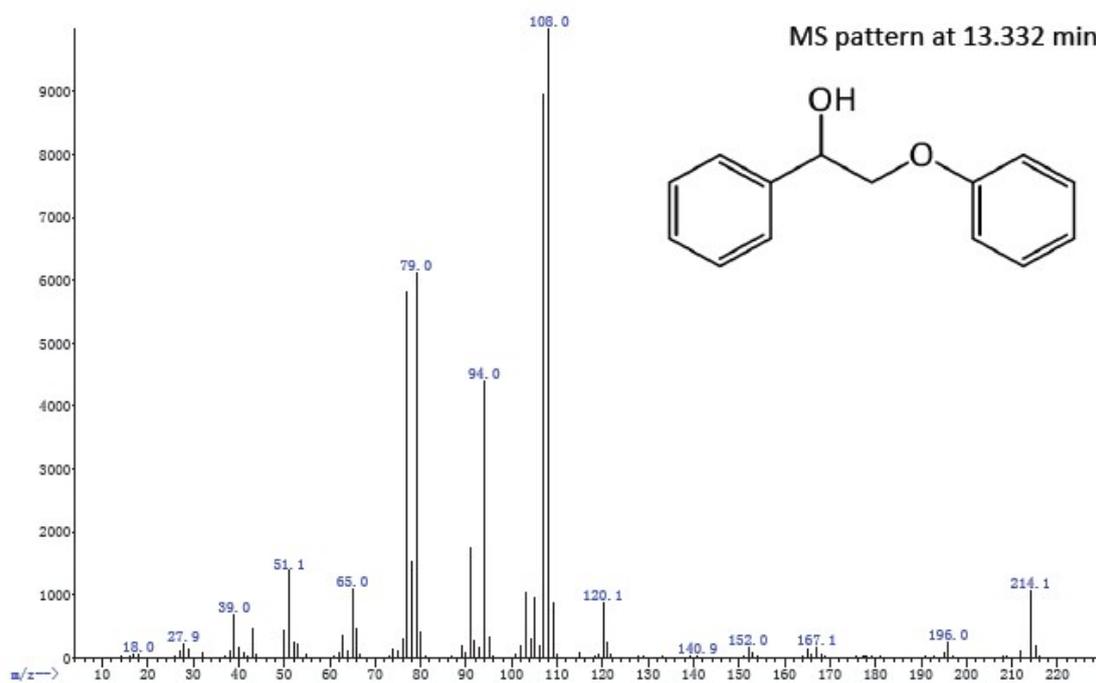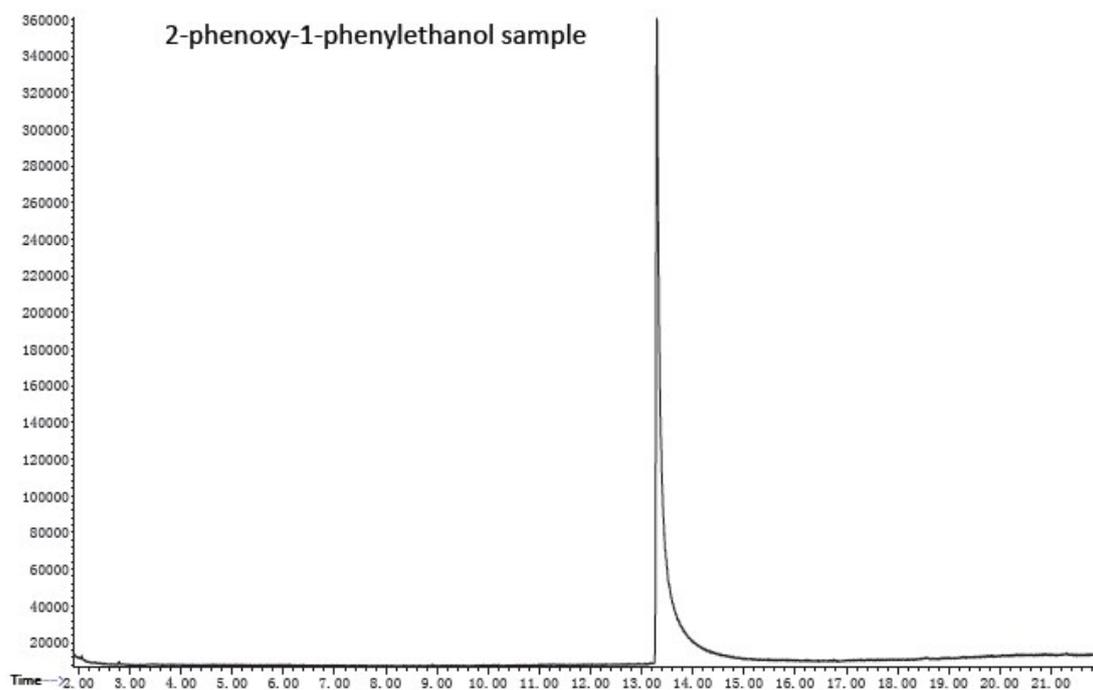
Figure S2. The GC-MS pattern of the β-O-4-A.
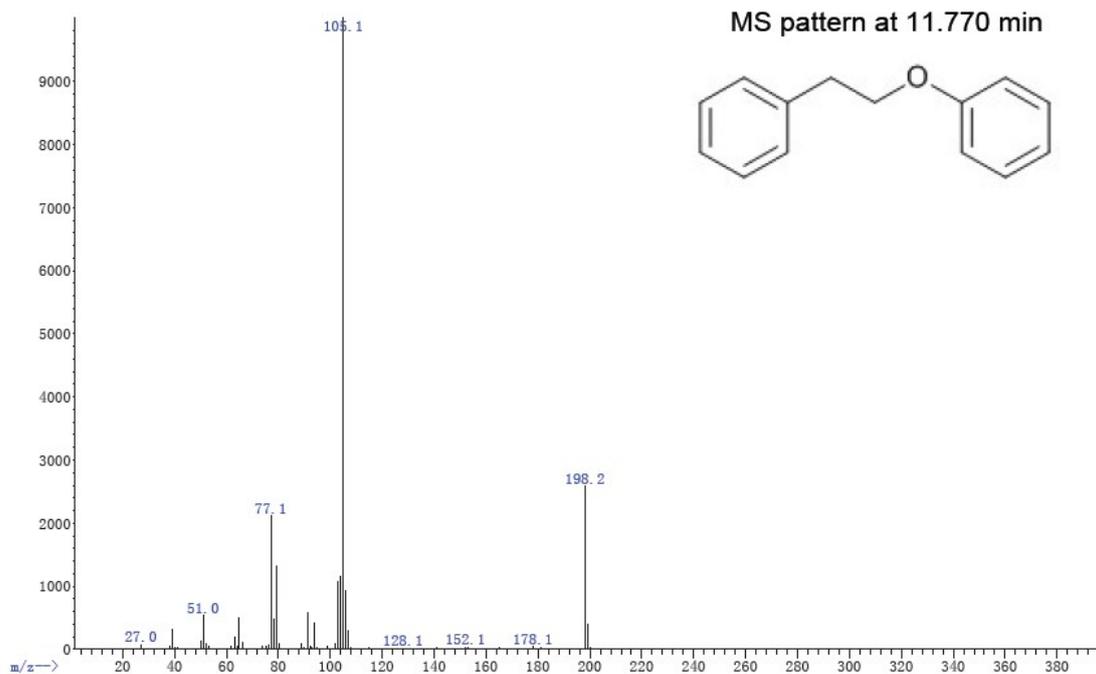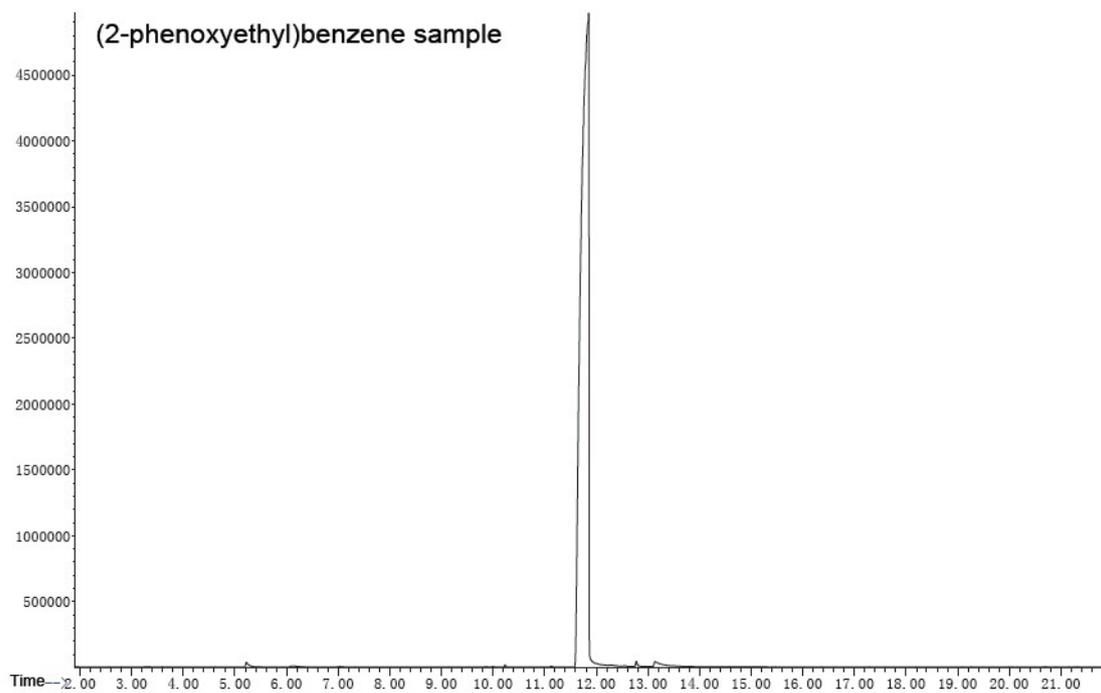
Figure S3. The GC-MS pattern of the β-O-4-H.
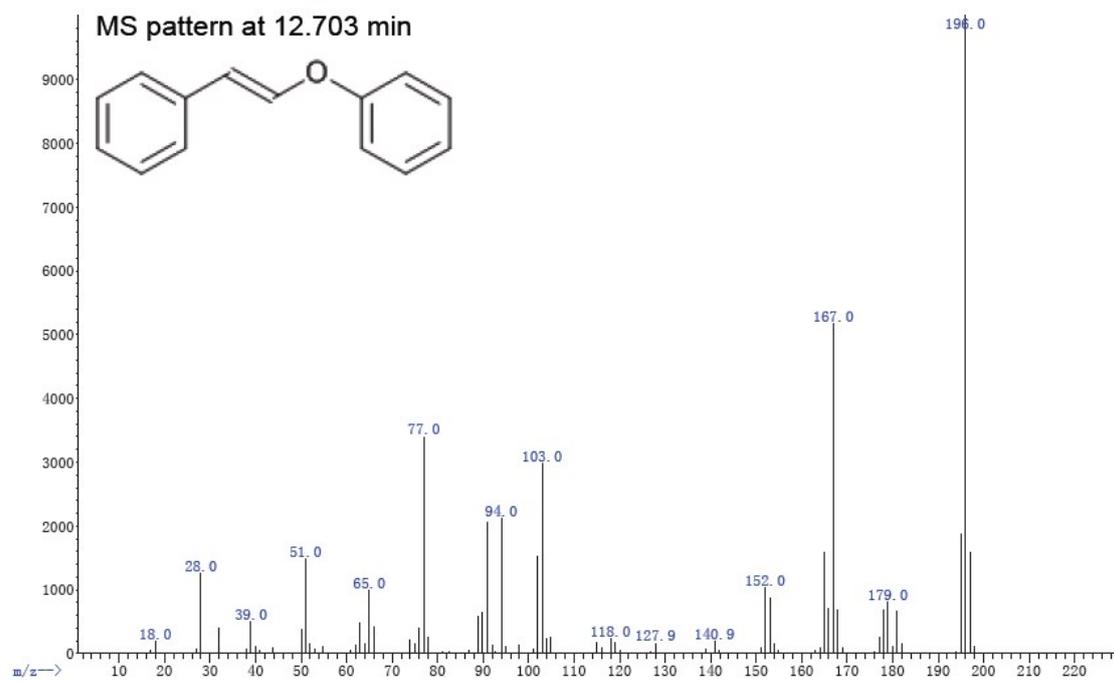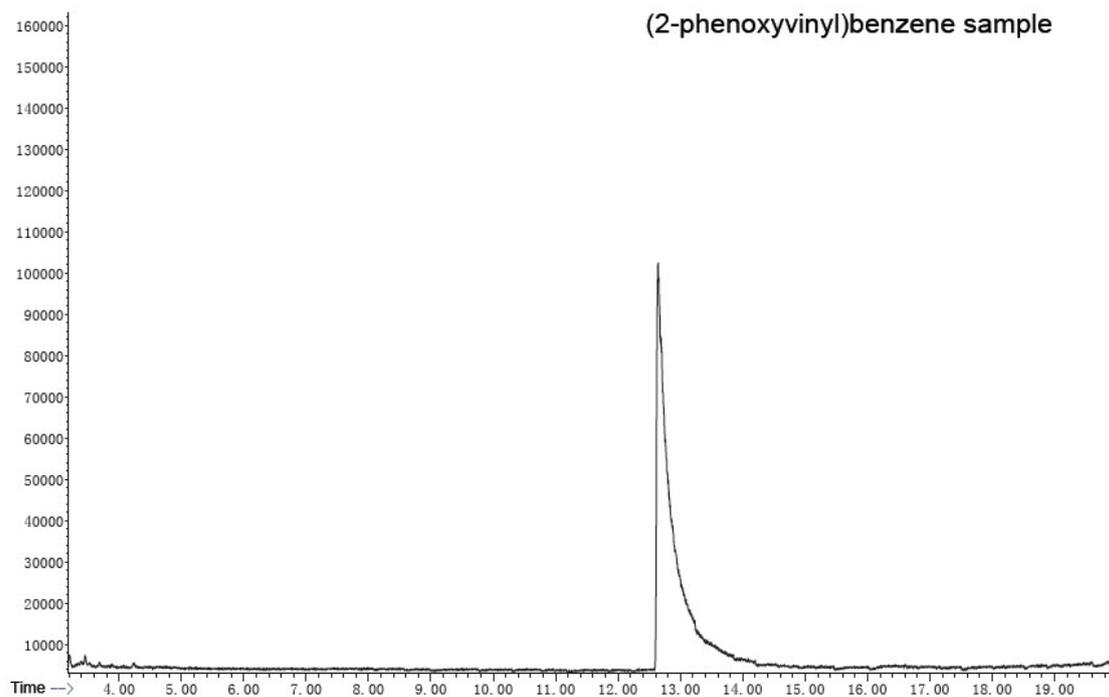
Figure S4. The GC-MS pattern of the β-O-4-O

MS pattern at 13.051 min
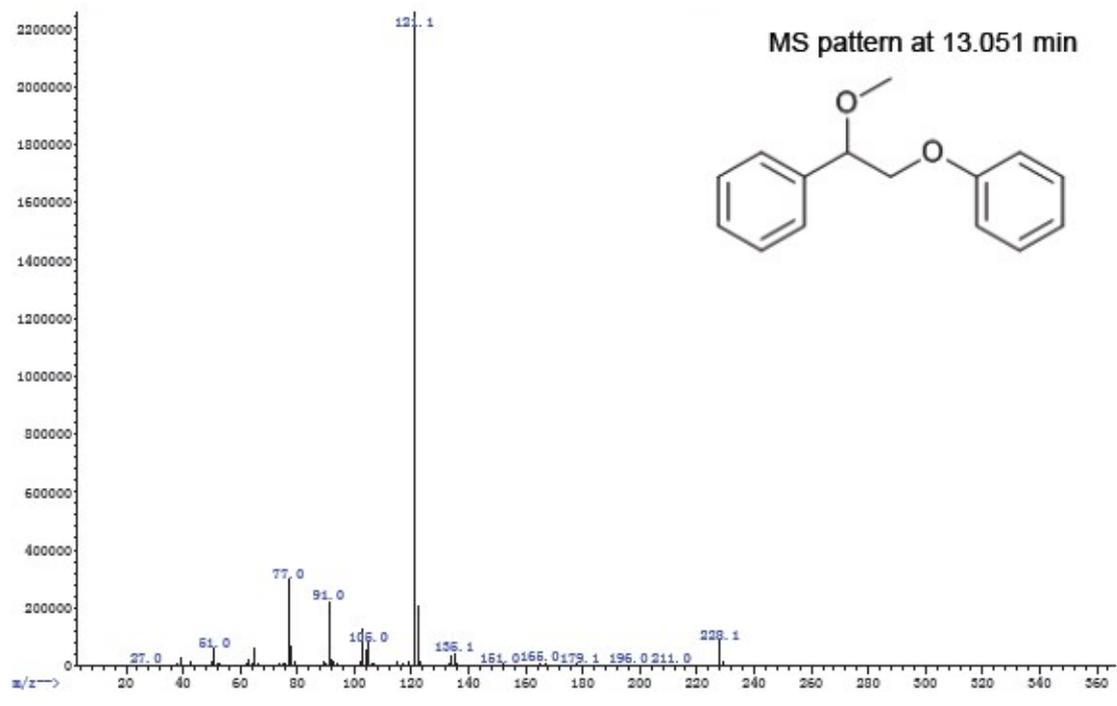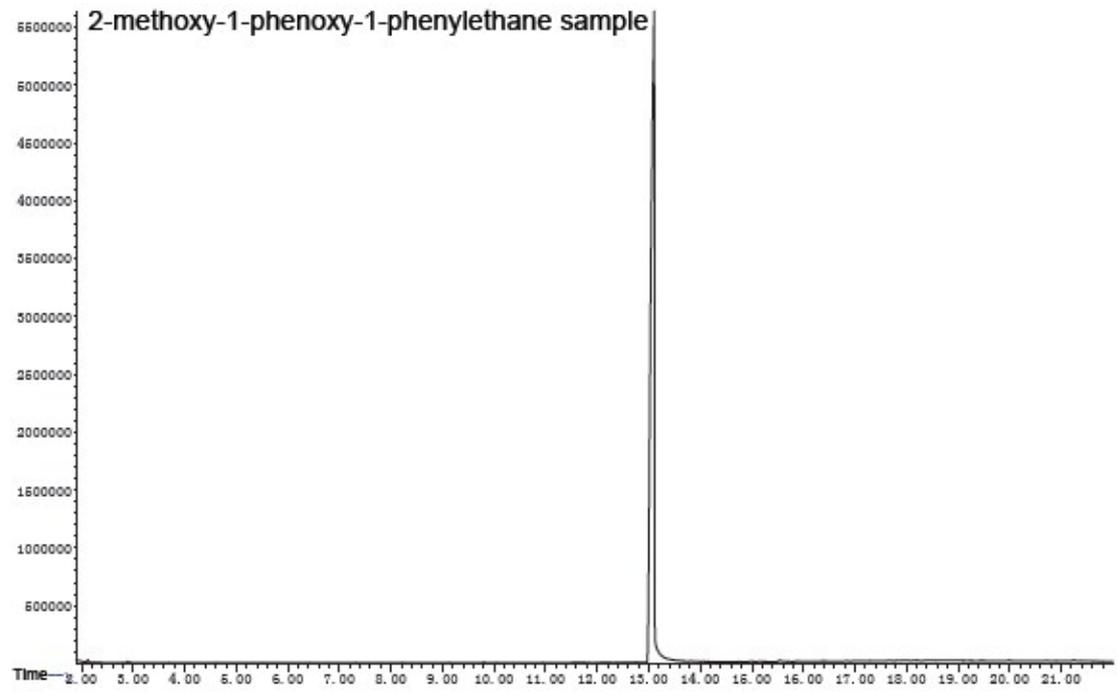
Figure S5. The GC-MS pattern of the β-O-4-E.

The synthesis of 1-(4-methoxyphenyl)-2-phenoxyethanol (β-O-4-A-OCH$_3$) referred to the produce of β-O-4-A.[1]
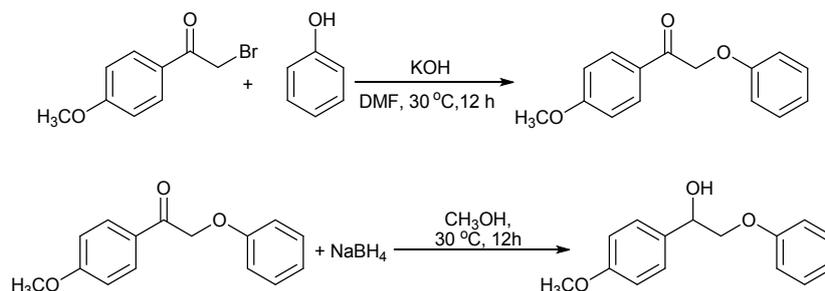
1-(4-methoxyphenyl)-2-phenoxyethanone (β-O-4-K-OCH$_3$)
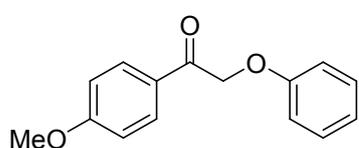
Prepared from 2-bromo-1-(4-methoxyphenyl)ethanone and phenol in 83% yield. White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.00 (d, J=8.8 Hz, 2H), 7.27 (dd, J=13.0 Hz, 4.4, 2H), 7.02 -6.90 (m, 5H), 5.20 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ = 193.13, 164.06, 158.13, 130.58, 129.56, 127.70, 121.57, 114.82, 114.02, 70.76, 55.53.

1-(4-methoxyphenyl)-2-phenoxyethanol (β-O-4-A-OCH$_3$)
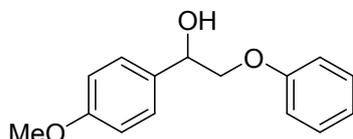
Prepared from 1-(4-methoxyphenyl)-2-phenoxyethanone and NaBH$_4$ in 90% yield. White solid. ^{1}H NMR (400 MHz, CD$_3$CN) δ = 7.44-7.31 (m, 2H), 7.31-7.23 (m, 2H), 6.98-6.88 (m, 5H), 4.94 (dt, J=7.3, 3.5 Hz, 1H), 4.02 (qd, J=9.8, 5.9 Hz, 2H), 3.77 (s, 3H), 3.59 (d, J=3.7 Hz, 1H). ^{13}C NMR (101 MHz, CD$_3$CN) δ = 159.85, 159.39, 134.10, 130.09, 128.24, 121.38, 117.88, 115.17, 114.19, 73.60, 71.95, 55.48.
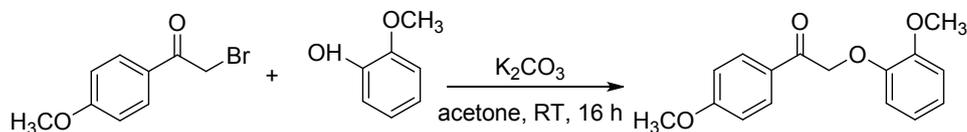
2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone
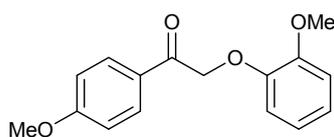
Prepared from 2-bromo-1-(4-methoxyphenyl)ethanone and guaiacol in 88% yield. White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.08 – 7.96 (m, 2H), 7.00 – 6.81 (m, 6H), 5.27 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz,

CDCl$_3$) δ = 193.15, 163.97, 149.78, 147.67, 130.52, 127.75, 122.34, 120.81, 114.79, 113.96, 112.22, 72.02, 55.93, 55.51.
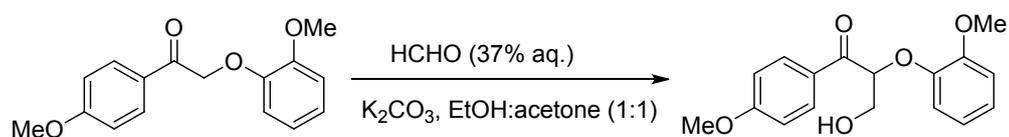
1-(4-methoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one was prepared by the literature procedures.[5] To a stirring suspension of K$_2$CO$_3$ (0.55 g, 4.0 mmol) in ethanol: acetone (v/v=1:1, 20ml) and 1-(4-methoxyphenyl)-2-(2-methoxyphenoxy)ethanone (1.13 g, 4 mmol) at 25°C, was added a water solution of formaldehyde (37%) (0.67 mL, 8.0 mmol). After 4 h the reaction mixture was filtered and was concentrated *in vacuo* to get a syrup product. The syrup was purified by column chromatography (petroleum ether/ethyl acetate, 1:1) to yielding 1-(4-methoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one as a little yellow solid.

1-(4-methoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one

^{1}H NMR (400 MHz, DMSO) δ = 8.07 (d, *J*=8.9 Hz, 2H), 7.06 (d, *J*=8.9 Hz, 2H), 6.96 (d, *J*=8.0 Hz, 1H), 6.94 – 6.87 (m, 1H), 6.79 (dt, *J*=14.4, 5.0 Hz, 2H), 5.60 (t, *J*=4.9 Hz, 1H), 5.18 (t, *J*=5.8 Hz, 1H), 3.88 (t, *J*=5.4 Hz, 3H), 3.82 (d, *J*=21.6 Hz, 2H), 3.72 (d, *J*=16.5 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 195.77, 163.92, 149.71, 147.43, 131.38, 128.56, 122.04, 121.01, 115.20, 114.46, 113.22, 81.95, 62.89, 56.06, 56.00.
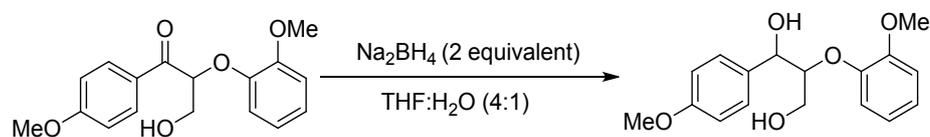
2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol

Prepared from 1-(4-methoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one and Na$_2$BH$_4$. The syrup was purified by column chromatography. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 159.52, 159.11, 151.55, 151.26, 147.65, 146.93, 132.12, 131.74, 128.35, 127.33, 124.18, 121.69, 120.95, 113.96, 112.18, 89.41, 87.20, 73.65, 72.65,

60.98, 60.69, 55.90, 55.28.

2. Catalysts preparation and characterizations

Preparation of $(NH_4)_2MoS_4$

Typically, 10 mmol ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$ and 0.5 mL NH_3 solution (28% in water) were dissolved in 100 mL ammonium sulfide solution (20% in H_2O) under vigorous stirring. Then, the solution was treated at 70 ^oC for 6 h. Then the solution was naturally cooled down to room temperature overnight. The obtained solid was collected by filtration, washed with distilled water and ethanol, and dried at 60 ^oC under vacuum.

Preparation of MoS_2 catalyst

The MoS_2 was obtained by treating the as-prepared $(NH_4)_2MoS_4$ in a horizontal furnace at 450 ^oC for 6 h in an Ar flow (50 mL·min^{-1}) with a 5 ^oC·min^{-1} heating rate from 25 ^oC.

Preparation of NiS catalyst

In a typical synthesis procedure for NiS nanobelts,[6] 2 mmol of nickel acetate tetrahydrate and 1 mmol of sodium thiosulfate were ordinally dissolved with 40 mL of distilled water in a beaker. After being stirred for 10 min, the mixture was transferred to a 50 mL Teflon-lined autoclave. Then the autoclave was sealed and heated at 200 ^oC for 12 h. After the reaction, the autoclave was allowed to cool to room temperature naturally. The obtained black products were collected by centrifugation and washed several times with distilled water and anhydrous ethanol. Finally the products were dried under vacuum at 60 ^oC.

XRD patterns of the as-synthesized materials
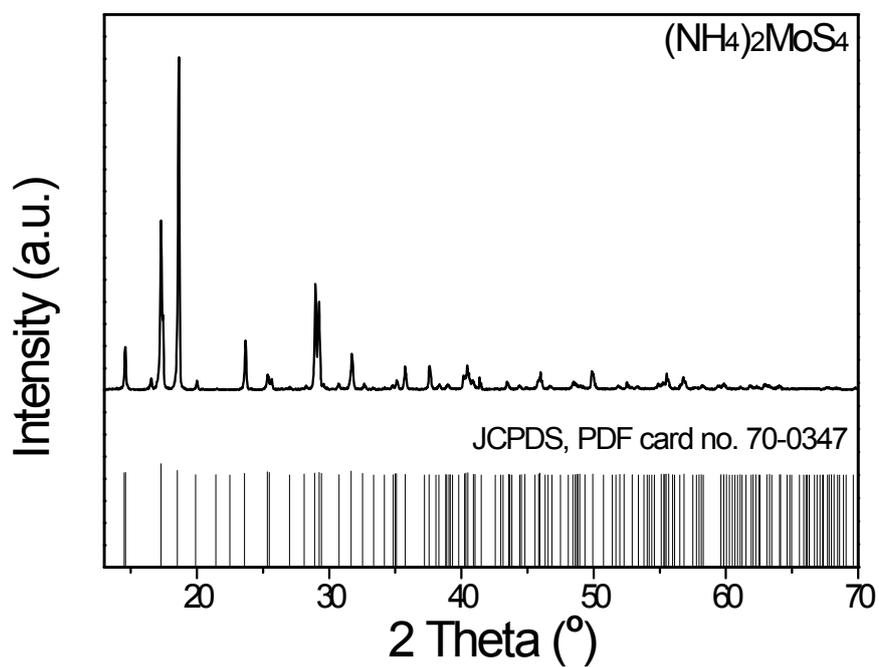
Figure S6. The XRD pattern of the as-synthesized $(NH_4)_2MoS_4$.
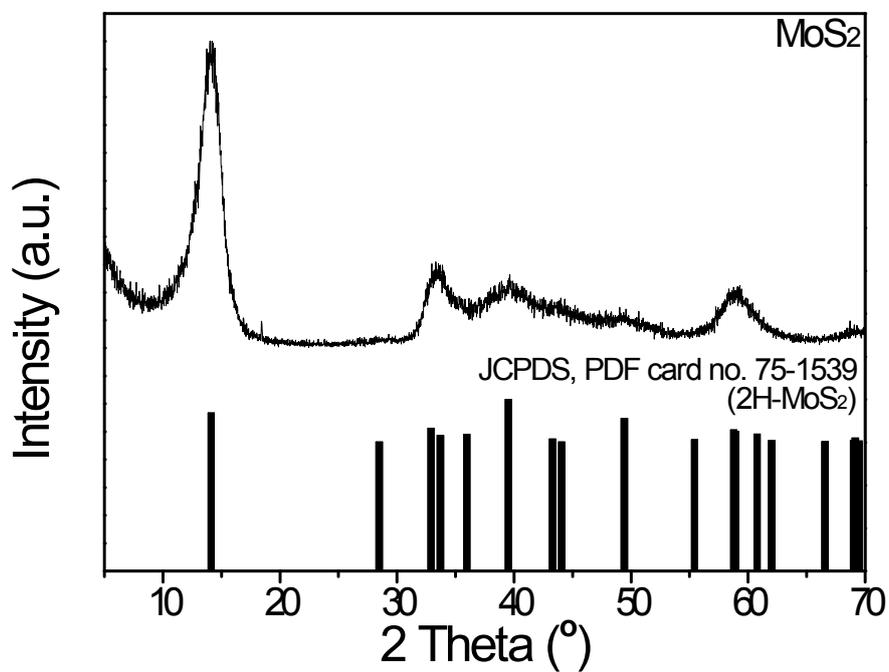
Figure S7. The XRD pattern of the as-synthesized MoS_2.
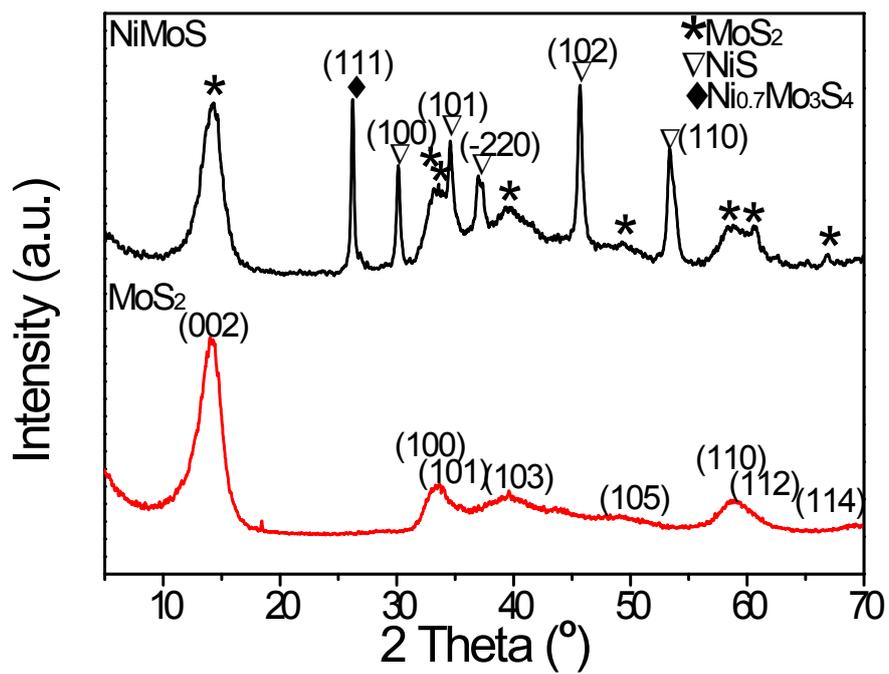
Figure S8. XRD patterns of the NiMo and MoS_2 catalysts.

The NH₃-TPD pattern of the NiMo catalyst

The desorption gas mixture was analyzed by an online mass spectrometer (THERMO$^{\text{Star}}$ gas analysis system). The sample was initially pretreated at 100 °C under an Ar gas flow (30 mL·min^{-1}) for 1 h to remove the adsorbed impurities, and then cooled down to room temperature. Then the flow gas was switched to ammonia gas (99.9%) for 30 min at room temperature, and then back to Ar gas. The reactor temperature was increased to 400 °C at a ramp rate of 10 °C·min^{-1}. The m/z 17 was recorded for NH_3 and HO* from H_2O. The pure NH_3 mass signal was the subtracted value of between m/z 17 (NH_3 and HO*) and the HO* mass signal based on the reference mass spectrum of H_2O (m/z 18) from NIST Webbook website. The quantification results were calculated by referring an ammonia standard curve.
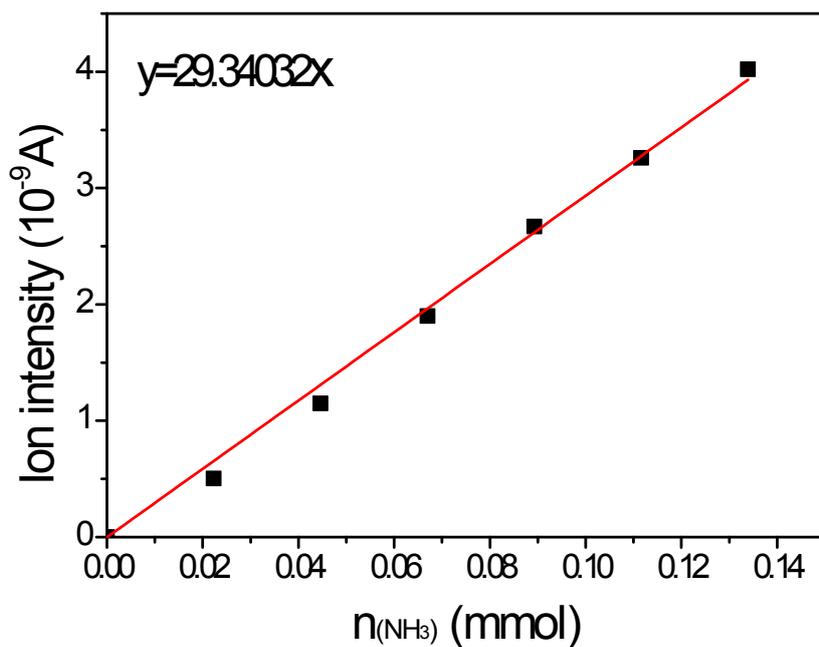
Figure S9. The standard working curve of the NH_3.
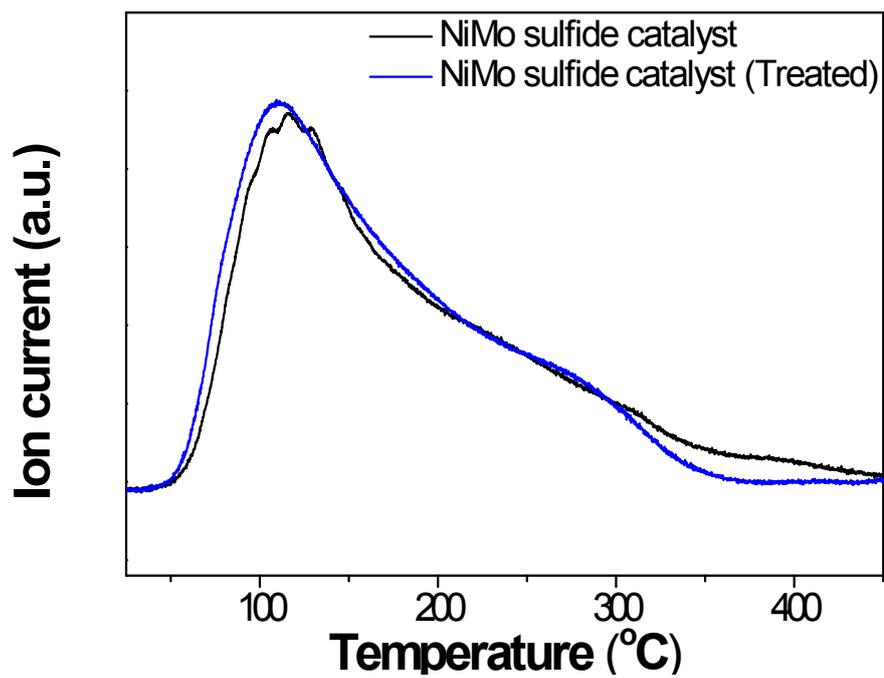
Figure S10. The NH$_3$-TPD pattern of the NiMo sulfide catalyst before (A, 90.2 μmol·g^{-1})

and after (B, 92.6 μmol·g^{-1}) treated in the CH$_3$OH at 180 °C for 1 h under 1.0 MPa H$_2$.

3. The ether bonds BDE of the lignin β-O-4 model compounds

We have calculated the bond dissociation energies by employing the Vienna Ab Initio Simulation Package (VASP),[7] a periodic plane wave based density functional theory (DFT) program. The electron-ion interactions are described by the projector-augmented wave method (PAW), which is a frozen core all-electron method using the exact shape of the valence wave functions instead of pseudo-wave functions.[8] The exchange correlation energy has been calculated within the generalized gradient approximation by the Perdew-Burke-Ernzerhof formulation (GGA-PBE).[9] The kinetic energy cutoff of plane-wave basis sets was fixed to 400 eV in all calculations. Molecules and fragments from the bond cleavage of molecules are put separately in a 20×20×20 box. Brillouin zone integration was performed using a 2×2×2 Monkhorst-Pack grid and a Gaussian smearing of 0.1 eV. Molecules and fragments from the bond cleavage of molecules were free to relax in all directions and optimized to a force less than 0.02 eV/Å on each atom. All self-consistent field (SCF) calculations were converged to $1×10^{-5}$ kJ/mol.

Table S1. The C–O bonds BDE of the β-O-4 lignin model compounds.

Ether bond	BDE (kJ·mol⁻¹)	Ether bond	BDE (kJ·mol⁻¹)
	274.0		486.9
	370.8		445.4
	227.8		401.2
	275.3		416.6
	336.3		287.0
	269.4		411.1
	294.3		125.3
	41.2		199.6
	66.9		131.7
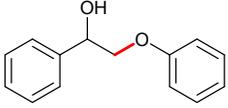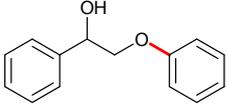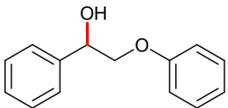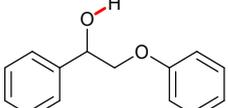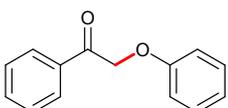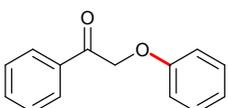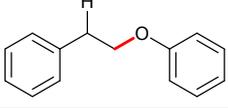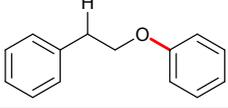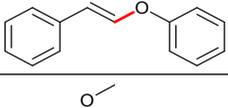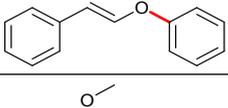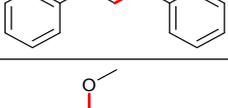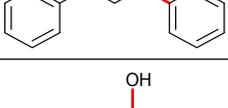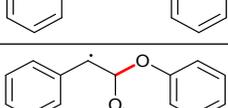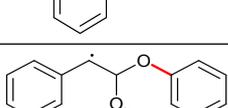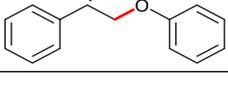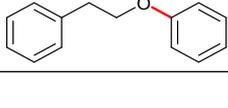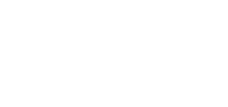
4. The possible network of stryene generation from β-O-4-A
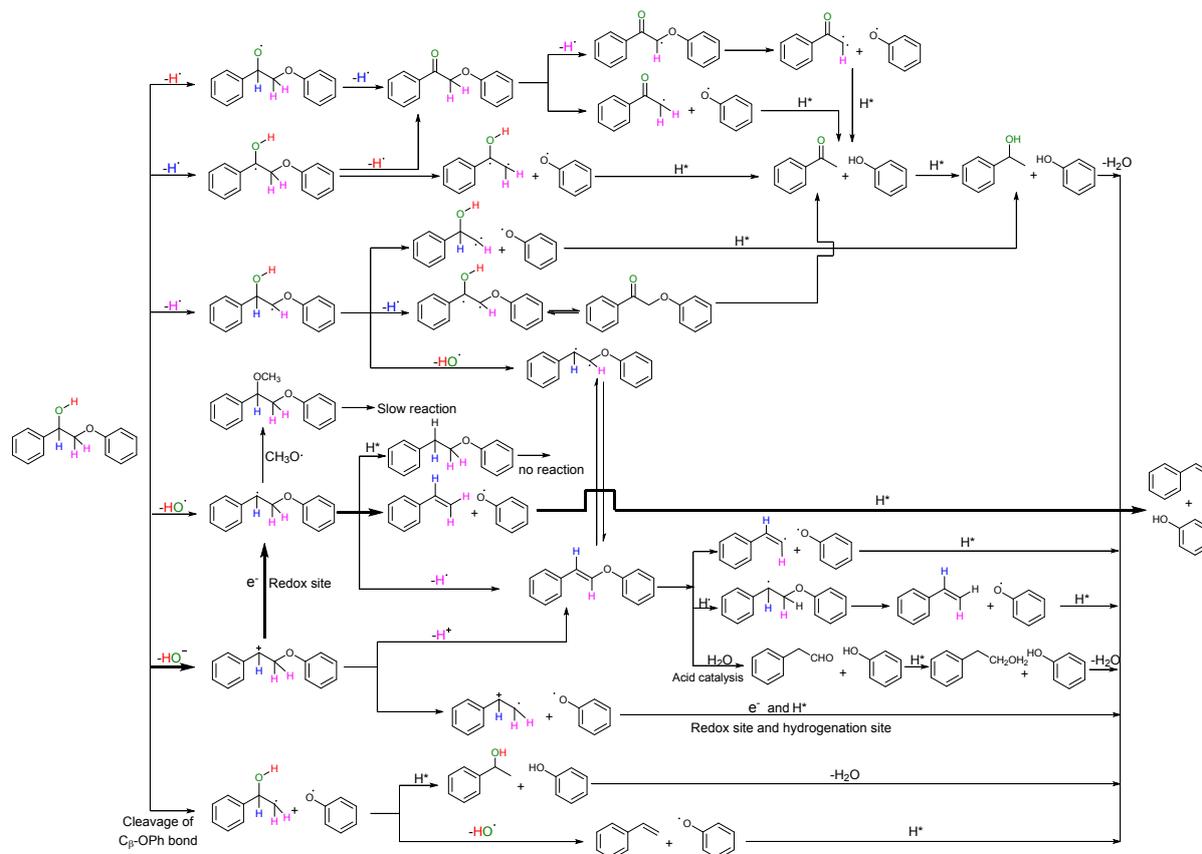
Scheme S1. The possible network of stryene generation from β-O-4-A over the NiMo sulfide.
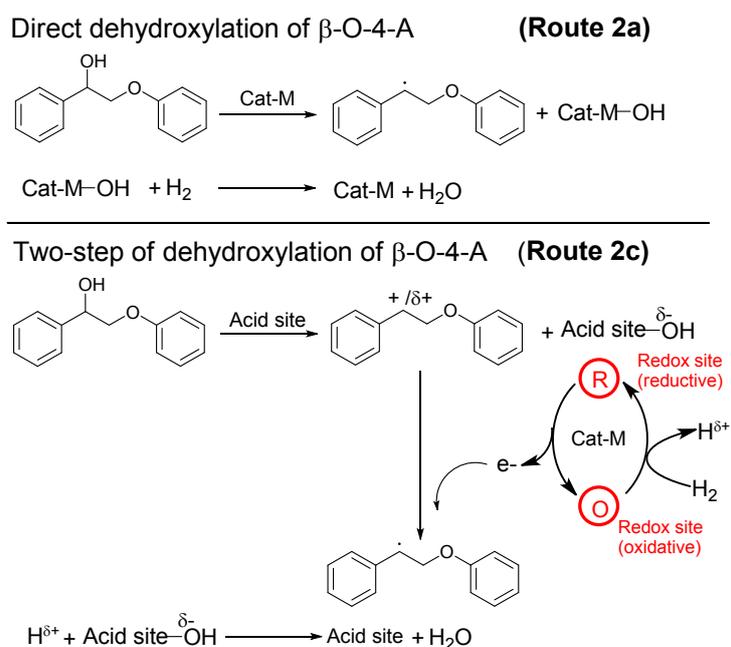
Scheme S2. Two different route of PhCH·CH₂OPh generation from β-O-4-A.

5. The control experiments
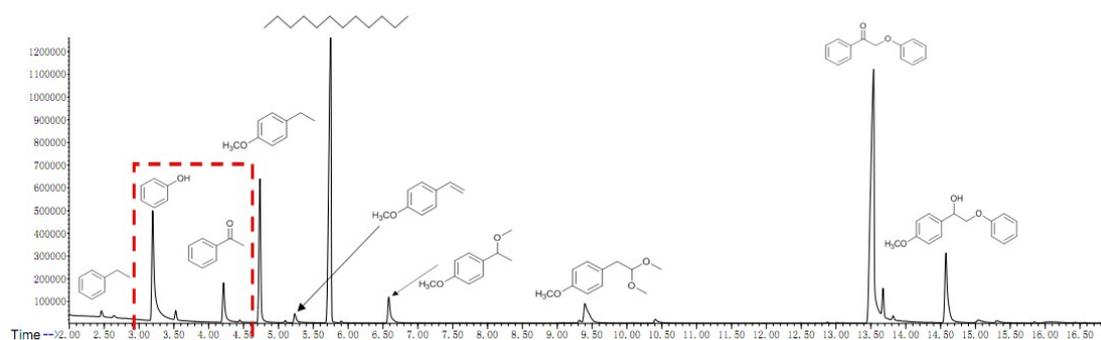
Figure S11. The conversion of β-O-4-A-(OCH$_3$) and β-O-4-K in one reactor. Reaction condition: β-O-4-A-(OCH$_3$) 0.2 mmol, β-O-4-K 0.2 mmol, NiMo sulfide 20 mg, methanol 2.0 mL, H$_2$ 1.0 MPa, 180 °C, 1 h.

Based on the peak areas of PhOH and PhCOCH$_3$ and their response factors, there were 0.15 mmol PhOH and 0.024 mmol PhCOCH$_3$ in the products.
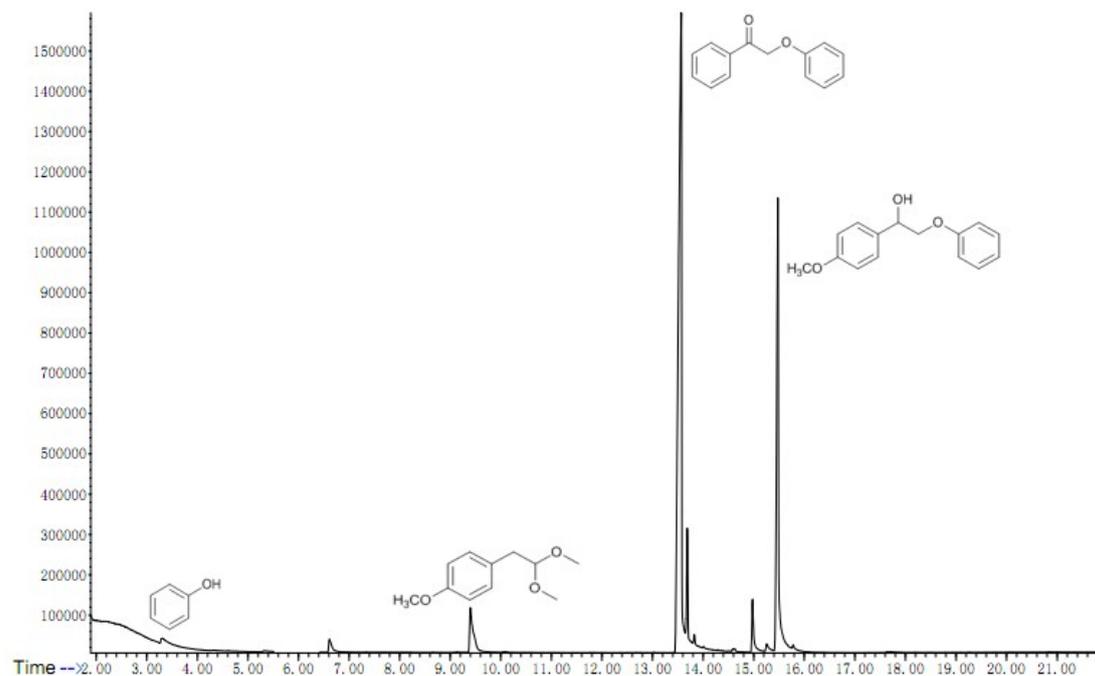
Figure S12. The conversion of β-O-4-A-(OCH$_3$) and β-O-4-K in one reactor. Reaction condition: β-O-4-A-(OCH$_3$) 0.2 mmol, β-O-4-K 0.2 mmol, NiMo sulfide 20 mg, methanol 2.0 mL, Ar 1.0 MPa, 180 °C, 1 h.

The cleavage of C$_\beta$-OPh bond in the competitive conversion of β-O-4-A-OCH$_3$ and β-O-4-K under Ar condition was < 5%.

Products distribution:

Conv. 69%

8%   10%   11%   13%

4%   1%   52 %

Conv. <1%   73%   27%
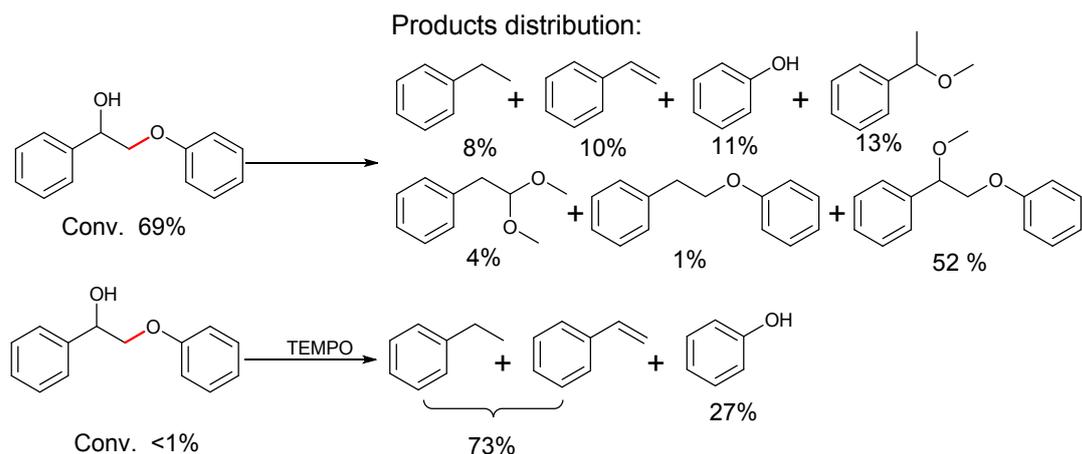
Scheme S3. The effect of the TEMPO on the β-O-4-A conversion. Reaction conditions: substrate 0.2 mmol, TEMPO 0.1 mmol, NiMo catalyst 20 mg, methanol 2.0 mL, 1.0 MPa H_2, 180 °C, 1 h.

Products distribution:

Conv. 69%

8%   10%   11%   13%

4%   1%   52 %

Conv. 1%   14%   31%   14%   19%

4%   18%

Conv. 2%   46%   54%
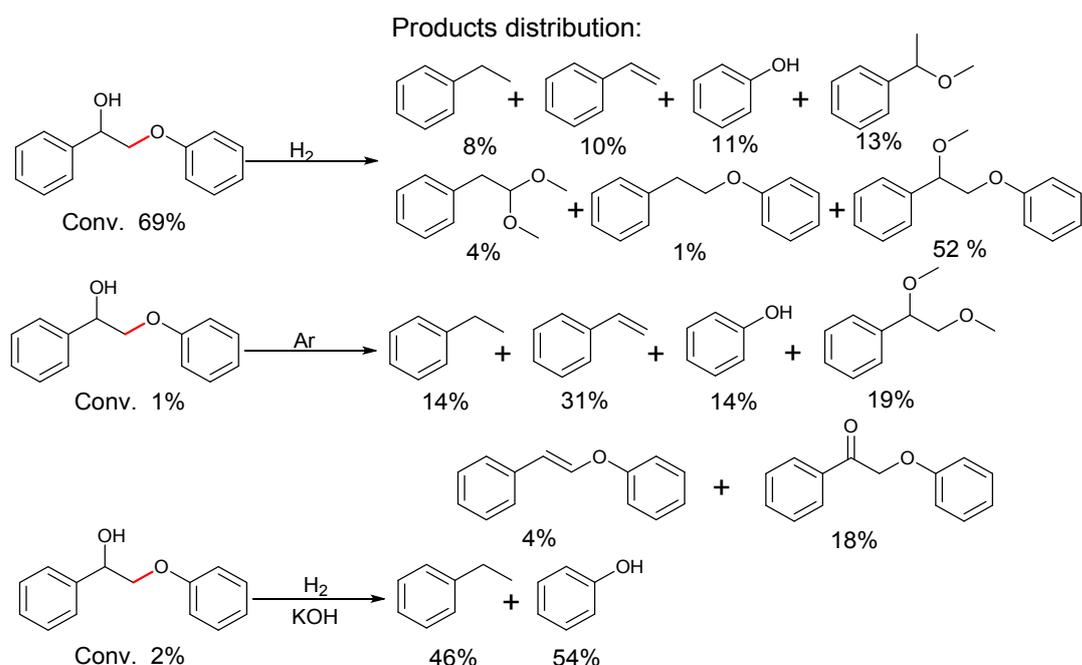
Scheme S4. The effect of the H_2 and KOH on the β-O-4-A transformation over the NiMo catalyst. Reaction conditions: substrate 0.2 mmol, NiMo catalyst 20 mg, methanol 2.0 mL, 1.0 MPa H_2 or 1.0 MPa Ar, 180 °C, 1 h. (In the reaction under Ar, the catalyst was pre-treated at 180 °C for 1 h in the methanol under 1.0 MPa H_2; In the β-O-4-A transformation with KOH, KOH 0.3 mmol.)

(A) Acid-catalyzed route
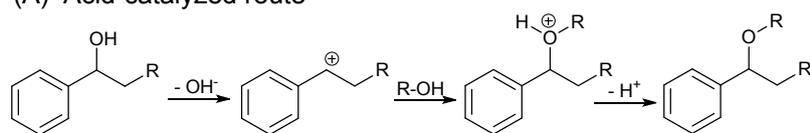
(B) Radical route
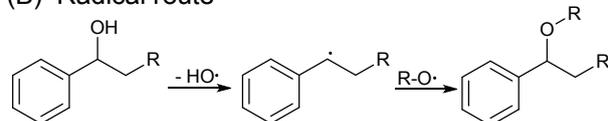
Scheme S5. The possible routes of ether compounds generation from alcohol.

Products distribution:
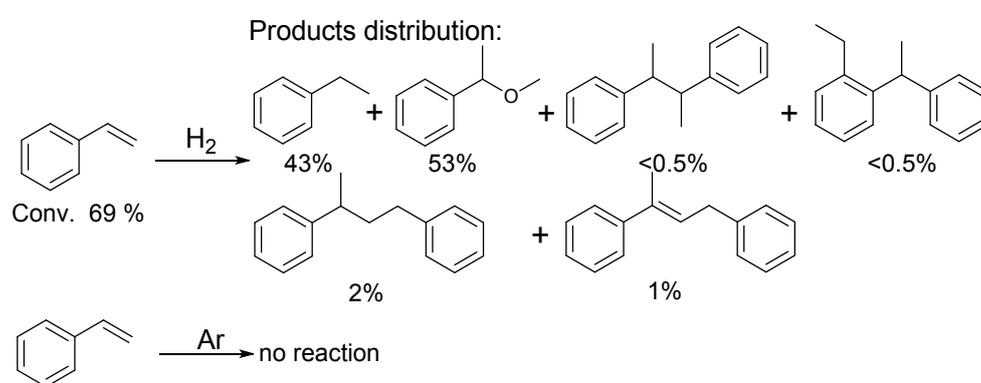
Scheme S6. The transformation of the styrene over the NiMo sulfide catalyst. Reaction conditions: substrate 0.5 mmol, NiMo sulfide catalyst 20 mg, methanol 2.0 mL, 1.0 MPa H_2(A) or 1.0 MPa Ar (B), 180 °C, 1 h.

Products distribution:
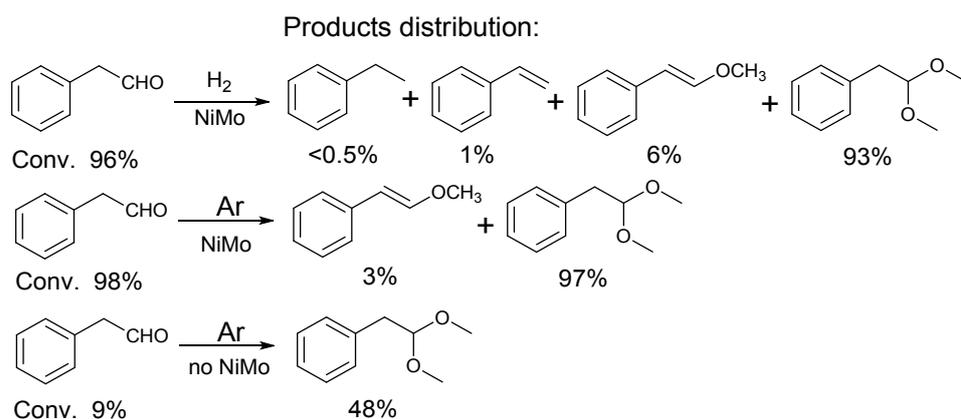
Scheme S7. The transformation of the $PhCH_2CHO$. Reaction conditions: substrate 0.5 mmol, NiMo sulfide catalyst 20 mg, methanol 2.0 mL, 1.0 MPa H_2(A) or 1.0 MPa Ar (B), 180 °C, 1 h.
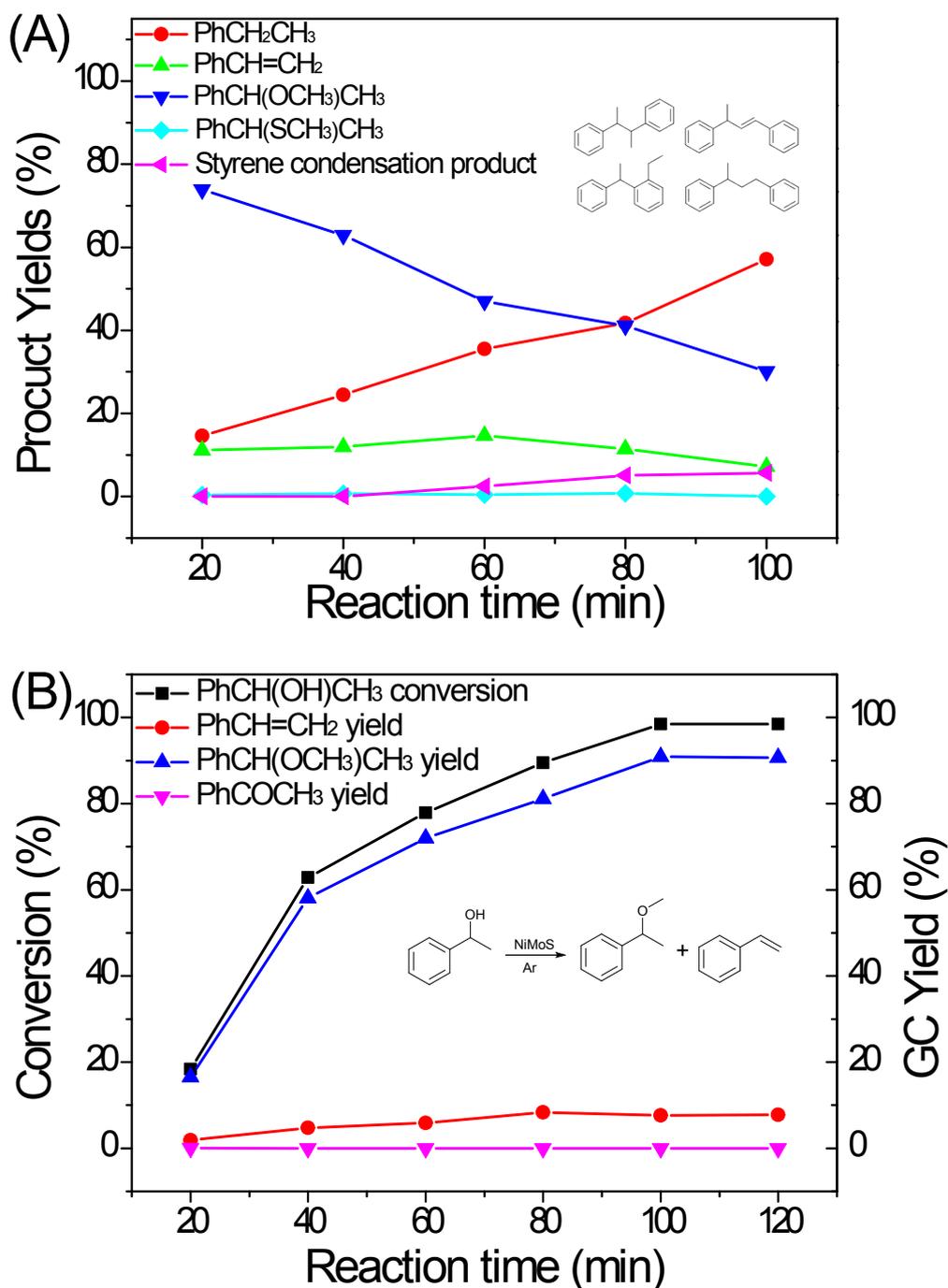
Figure S13. The transformation of 1-phenethyl alcohol over the NiMo sulfide catalyst.

Reaction conditions: substrate 0.5 mmol, catalyst 20 mg, methanol 2.0 mL, 1.0 MPa

H_2(A) or 1.0 MPa Ar (B), 180 °C. (1-phenethyl alcohol conversion was >99% at 20 min

under H_2.)
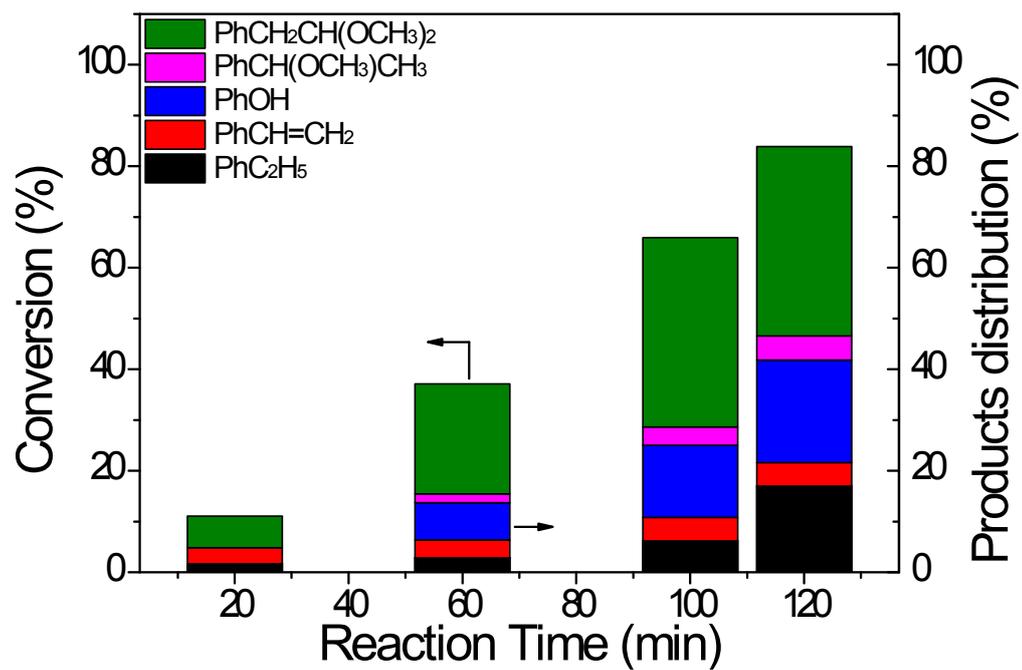
Figure S14. The transformation of β-O-4-O over the NiMo sulfide catalyst. Reaction condition: β-O-4-O 0.2 mmol, NiMo sulfide catalyst 20 mg, methanol 2.0 mL, H_2 1.0 MPa, 180 °C. The height of the histogram stands for the conversion.

6. The effect of solvents on β-O-4-A conversion

Products distribution
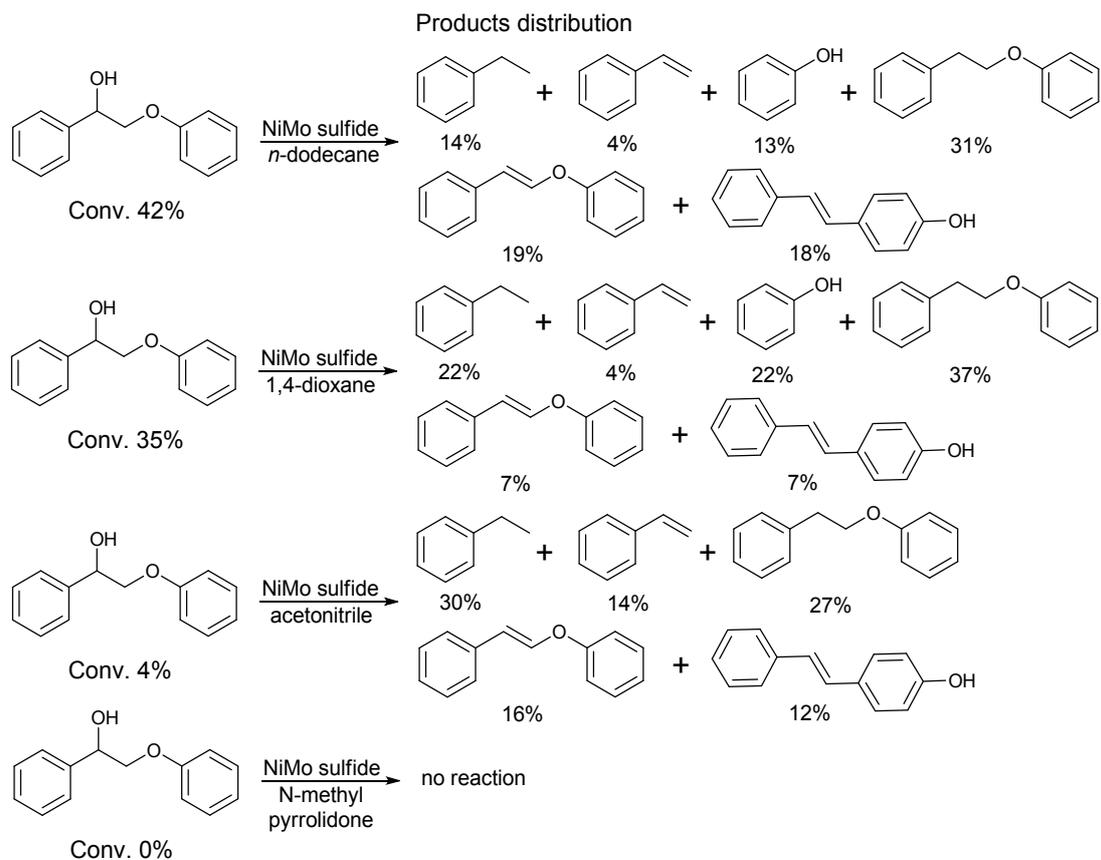
Scheme S8. The effect of non-alcohol solvents on the conversion of β-O-4-A. Reaction

condition: β-O-4-A 0.2 mmol, NiMo sulfide 20 mg, solvent 2.0 mL, H_2 1.0 MPa, 180 °C,

4 h.
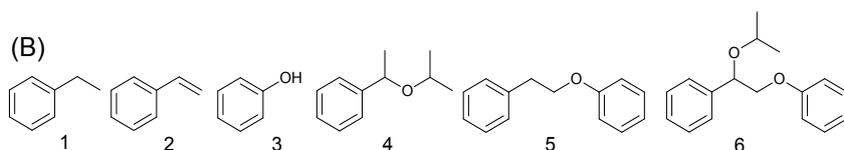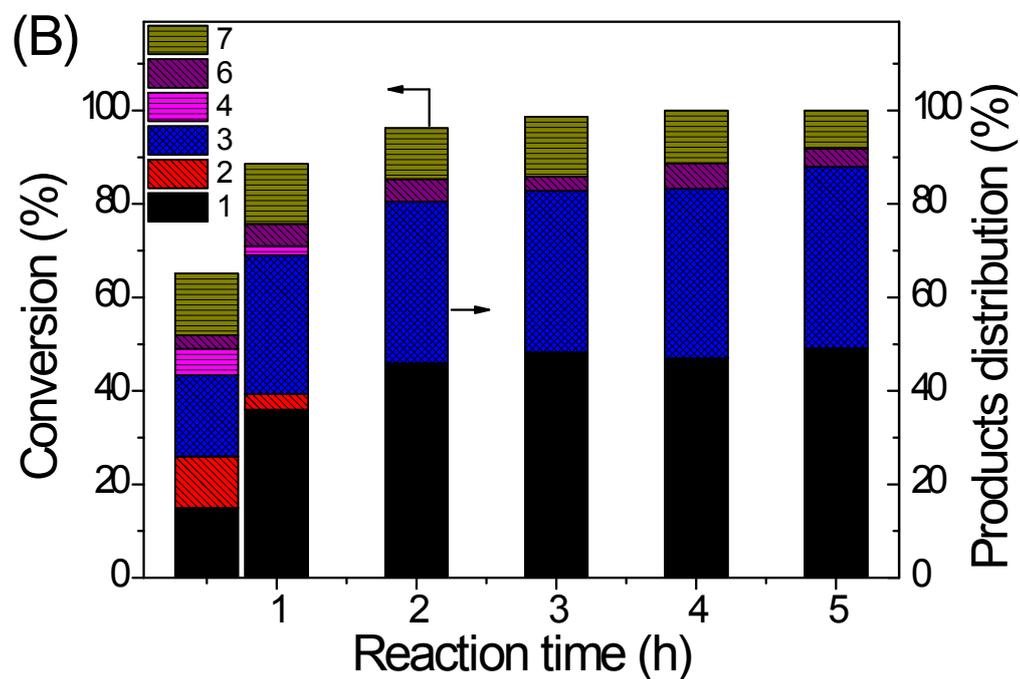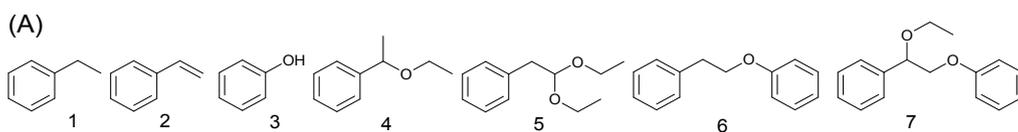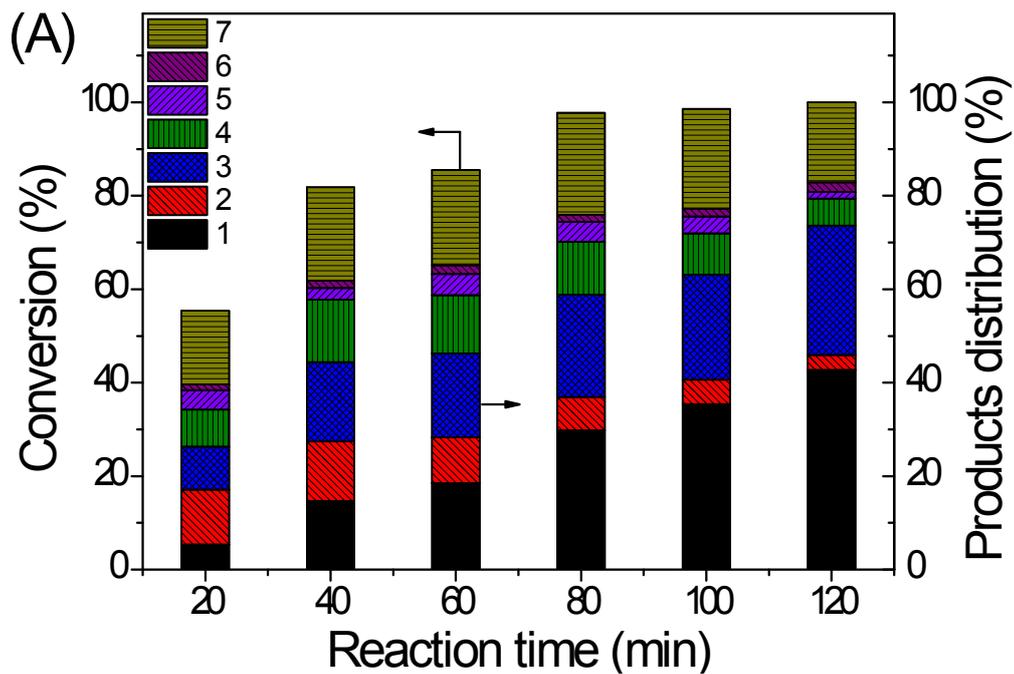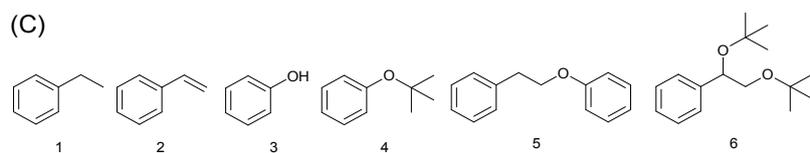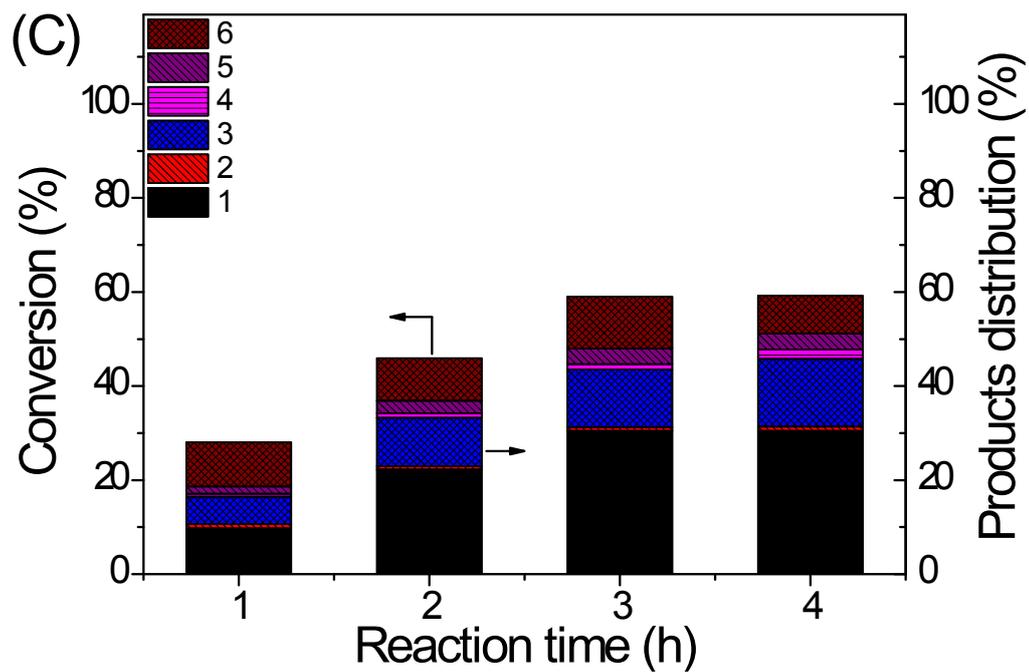
Figure S15. The effect of ethanol (A), isopropanol (B), tertiary butanol (C) as the solvent on the β-O-4-A conversion. Reaction condition: β-O-4-A 0.2 mmol, NiMo sulfide catalyst 20 mg, solvent 2.0 mL, H_2 1.0 MPa, 180 °C. The height of the histogram stands for the conversion.
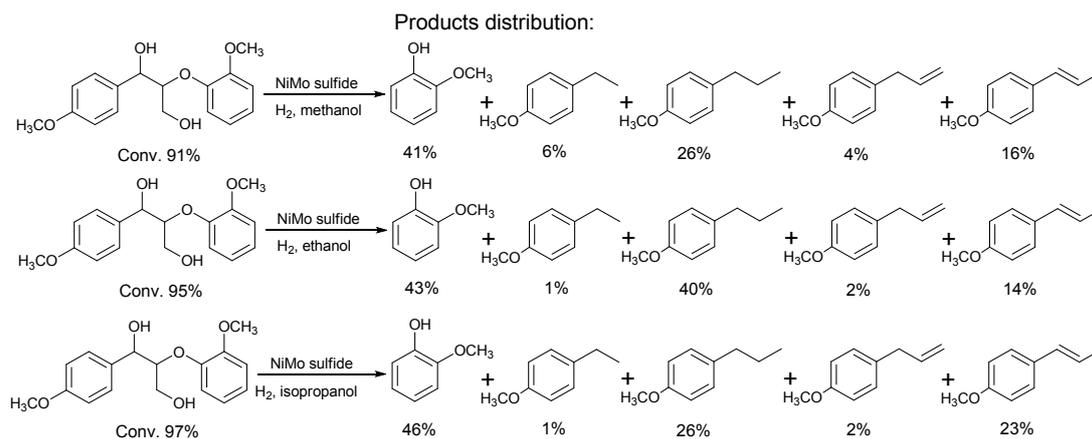
Scheme S9. The conversion of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol over the NiMo sulfide catalyst. Reaction condition: substrate 0.15 mmol, solvent 2.0 mL, NiMo sulfide catalyst 20 mg, H_2 1.0 MPa, 180 °C, 5 h.
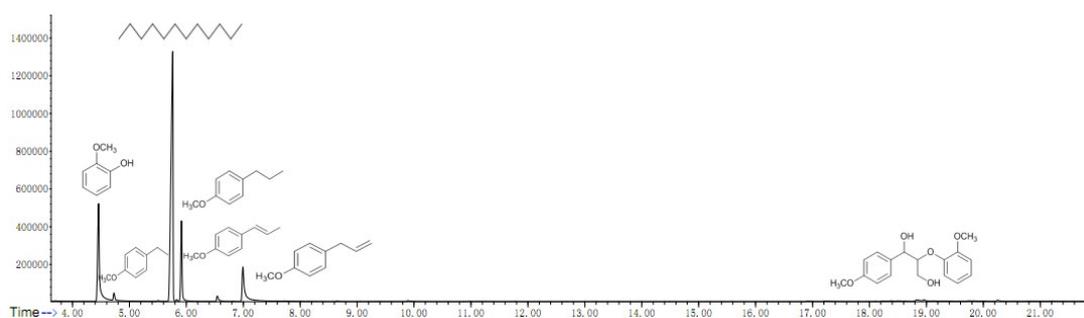
Figure S16. The conversion of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol in isopropanol.

7. The effect of introducing metal species
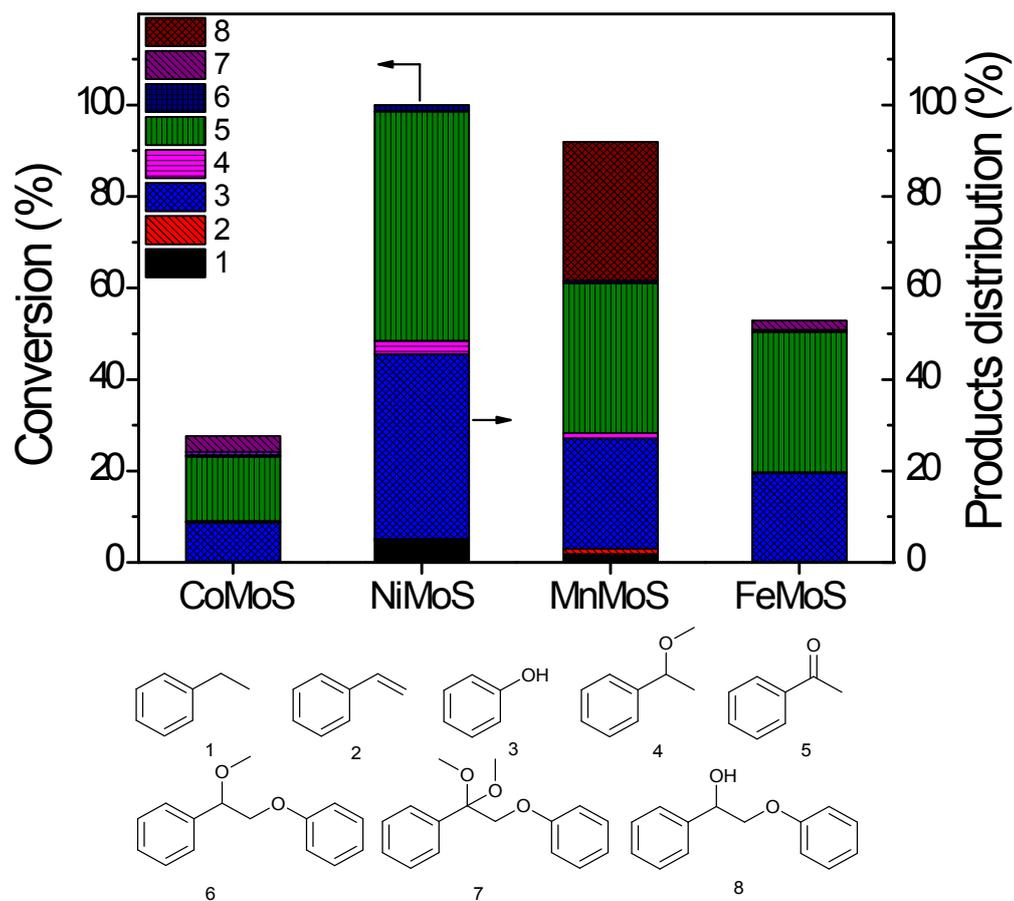
Figure S17. The conversion of β-O-4-K over the MMo sulfide catalysts. Reaction condition: β-O-4-K 0.2 mmol, catalyst 20 mg, methanol 2.0 mL, H_2 1.0 MPa, 180 °C, 6 h. The height of the histogram stands for the conversion.
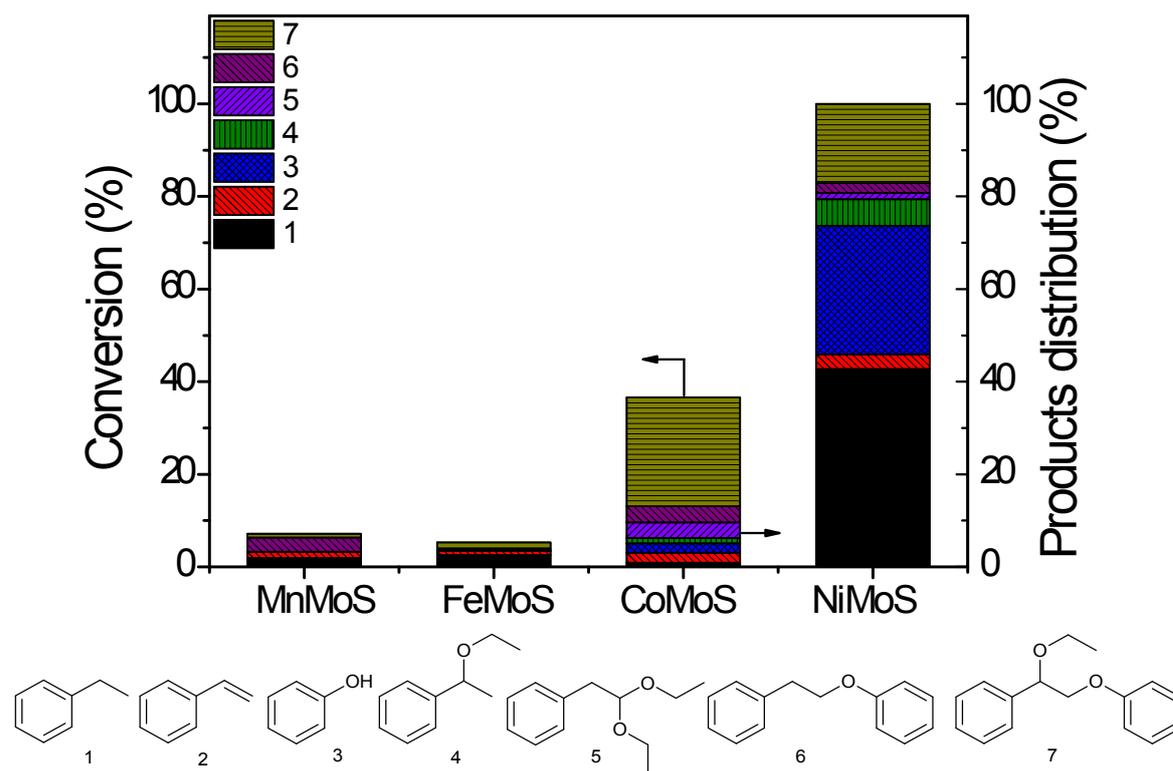
Figure S18. The conversion of β-O-4-A over the MMo sulfide catalysts. Reaction condition: β-O-4-A 0.2 mmol, catalyst 20 mg, ethanol 2.0 mL, H_2 1.0 MPa, 180 °C, 2 h. The height of the histogram stands for the conversion.

8. The effect of rotate speed on the catalytic cleavage of C_β-OPh bond
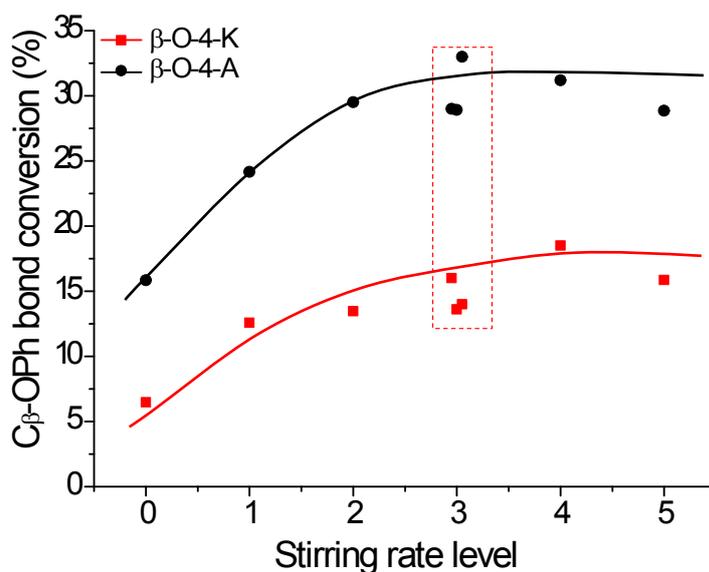
Figure S19. The effect of rotate speed on the catalytic cleavage of C_β-OPh bond of β-O-4-A and β-O-4-K. Reaction condition: substrate 0.2 mmol, methanol 2.0 mL, NiMo sulfide 20 mg, 180 °C, 1 h.

The substrate diffusion can affect reaction rate in the heterogeneous catalyzed reaction. And the sufficient stirring can promote the substrate diffusion from solution phase to the catalyst surface. We checked the effect of stirring rate on the catalytic cleavage of C_β-OPh bond. Because our magnetic stirrer can not give the real-time accurate stirring rate directly, we changed the stirring rate by controlling the rotate speed level. We carried out reactions in this work at level 3, and we repeated the β-O-4-A and β-O-4-K conversion at level 3.

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