Supplementary Information

Synthesis of Ethanol from Aryl Methyl Ether/Lignin, CO\textsubscript{2} and H\textsubscript{2}

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Fig. S1 GC graph of the gaseous sample after the reaction of CO$_2$ and H$_2$.
Reaction condition: 20 µmol [RuCl$_2$(CO)$_3$]$_2$ (based on the metal), 20 µmol triphos, 2.2 mmol LiI, 2 mL DMI, 3 MPa CO$_2$ and 5 MPa H$_2$ (at room temperature), 190 °C, 10h.
Fig. S2 Anisole decomposition and phenol generation during the reaction. Reaction conditions: 20 μmol [RuCl\(_2\)(CO)\(_3\)]\(_2\) and 60 μmol Co\(_2\)(CO)\(_8\) (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 3 MPa CO\(_2\) and 5 MPa H\(_2\) (at room temperature), 190 °C.
Target 1

Target 2
Fig. S3 The GC-MS result of the reaction of entry 1 of Table 1. Reaction condition: 20 μmol \([\text{RuCl}_2(\text{CO})_3]_2\) and 60 μmol \(\text{CO}_2(\text{CO})_8\) (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 3 MPa CO₂ and 5 MPa H₂ (at room temperature), 190 °C, 10 h.
Target 1

Fig. S4 The GC-MS result of the reaction using 3 mmol phenol instead of 3.6 mmol anisole. Reaction condition: 20 μmol [RuCl₂(CO)₂]₂ and 60 μmol Co₂(CO)₈ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3 mmol phenol, 3 MPa CO₂ and 5 MPa H₂ (at room temperature), 190 °C, 10 h.
Fig. S5 GC graph of the liquid sample after the reaction of anisole and LiI.
Reaction condition: 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 3 MPa CO₂ and 5 MPa H₂ (at room temperature), 190 °C, 10 h.
**Fig. S6** GC graph of the liquid sample after the reaction of CH$_3$I, CO and H$_2$. Reaction condition: 20 μmol [RuCl$_2$(CO)$_3$]$_2$ and 60 μmol Co$_2$(CO)$_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 10 uL CH$_3$I, 0.8 MPa CO and 5 MPa H$_2$ (at room temperature), 190 °C, 10 h.
Fig. S7 The GC-MS result of the reaction using $^{13}\text{CO}_2$ instead of CO$_2$. Reaction condition: 20 μmol $[\text{RuCl}_2(\text{CO})_3]_2$ and 60 μmol Co$_2$(CO)$_8$ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 2 MPa $^{13}\text{CO}_2$ and 5 MPa H$_2$ (at room temperature), 190 °C, 10 h.
Fig. S8 GC graph of the gaseous sample after the reaction of CH₃I and H₂.

Reaction condition: 20 μmol [RuCl₂(CO)₃]₂ and 60 μmol Co₂(CO)₈ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 40 uL CH₃I, 5 MPa H₂ (at room temperature), 190 °C, 10 h.
**Fig. S9** GC graph of the gaseous sample after the reaction of CO and H₂.

Reaction condition: 20 μmol [RuCl₂(CO)₂]₂ and 60 μmol Co₂(CO)₈ (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 0.8 MPa CO and 5 MPa H₂ (at room temperature), 190 °C, 10 h.
(a) Total ions chromatograph

(b) deuterated ethanol

(c) standard ethanol
(d) deuterated propanol

(e) standard propanol

(f) unreacted anisole

(g) standard anisole

**Fig. S10** The GC-MS result of the reaction using D2 instead of H2: (a) total ions chromatograph, (b) deuterated ethanol and (c) standard ethanol, (d) deuterated propanol and (e) standard propanol, (f) unreacted anisole and (g) standard anisole. Reaction condition: 20 μmol [RuCl2(CO)3]2 and 60 μmol Co2(CO)8 (based on the metal), 20 μmol triphos, 2.2 mmol LiI, 2 mL DMI, 3.6 mmol anisole, 3 MPa CO2 and 5 MPa D2 (at room temperature), 190 ºC, 10 h.
Notes:

Fig. S10b: One ethanol molecule could contain at most 6 D atoms, which suggests that the H atoms on the methyl group detached from the anisole substrate could be totally substituted by the D atoms.

Fig. S10d: One propanol molecule could contain at most 8 D atoms, which suggests that the H atoms on the methyl group detached from the anisole substrate could also be totally substituted by the D atoms.

Fig. S10f: No D atom entered the anisole molecule during the reaction. This indicates that the unreacted anisole did not experience H-D exchange.
Fig. S11 The HR-ESI-MS (-) spectra of the reaction solution at condition of entry 1 of Table 1.

Notes: The HR-ESI-MS spectra revealed that the carbonyls of the Ru precursor were mainly retained in the catalyst after reaction. The Co catalyst after reaction could not be observed by HR-ESI-MS analysis, while in the literature cobalt complex with multi carbonyls were usually the active center at similar conditions¹.
Target 1

CompName: Ethanol $S$ Ethyl alcohol $S$ Alcohol $S$ Alcohol anhydrides $S$ Algin $S$ Anhydrol $S$ Denatured ethanol $S$ Ethyl hydrate

Target 2

CompName: 1-Propanol $S$ Propyl alcohol $S$ n-Propyl $-1$-ol $S$ n-Propanol $S$ n-Propyl alcohol $S$ Ethylcarbinol $S$ Optal $S$ Osmosol extra $S$ Propa
Target 3

![GC-MS spectra](image)

**Fig. S12** The GC-MS spectra of the solution after the reaction in entry 1 of Table 2.

Note: To protect the detector of the MS, the solvent DMI (retention time 8.5min-9.5min) was cut during the analysis.
Target 1

Target 2
Target 3

Fig. S13 The GC-MS spectra of the solution after the reaction in entry 2 of Table 2.
Target 3

![GC-MS spectrum of the solution after the reaction in entry 3 of Table 2.]

Target 4

![GC-MS spectrum of the solution after the reaction in entry 3 of Table 2.]

**Fig. S14** The GC-MS spectra of the solution after the reaction in entry 3 of Table 2.

**Note:** White powder was observed after the reaction because of the limited solubility of hydroquinone in DMI.
Target 1

Target 2
Target 3

Target 4

Target 5

**Fig. S15** The GC-MS spectra of the solution after the reaction in entry 4 of Table 2.

Note: White powder was observed after the reaction because of the limited solubility of hydroquinone in DMI.
Target 3

Target 4

Target 5

Fig. S16 The GC-MS spectra of the solution after the reaction in entry 5 of Table 2.
Target 1

Target 2
Target 3

Target 4

Target 5

Fig. S17 The GC-MS spectra of the solution after the reaction in entry 6 of Table 2.
Target 1

Target 2
Target 3

Fig. S18 The GC-MS spectra of the solution after the reaction in entry 7 of Table 2.
Target 1

Target 2
Target 3

Fig. S19 The GC-MS spectra of the solution after the reaction in entry 8 of Table 2.
Target 3

Target 4

Target 5

**Fig. S20** The GC-MS spectra of the solution after the reaction in entry 9 of Table 2.
Target 1

Target 2
Fig. S21 The GC-MS spectra of the solution after the reaction in entry 10 of Table 2.
Target 1

Target 2
Target 3

Target 4

Fig. S22 The GC-MS spectra of the solution after the reaction in entry 11 of Table 2.
Target 1

Target 2
Fig. S23 The GC-MS spectra of the solution after the reaction in entry 12 of Table 2.
Target 1

Target 2
Fig. S24 The GC-MS spectra of the solution after the reaction in entry 13 of Table 2.
Target 3

![GC-MS spectrum](image)

Target 4

![GC-MS spectrum](image)

**Fig. S25** The GC-MS spectra of the solution after the reaction in entry 14 of Table 2.
Table S1 Effect of reaction parameters on the reaction.$^a$

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<th>Ru (μmol)</th>
<th>Co (μmol)</th>
<th>LiI (mmol)</th>
<th>Triphos (μmol)</th>
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$^a$Reaction conditions: [RuCl₂(CO)₃]²⁺/Co₂(CO)₈ were used as the catalyst and their dosages were based on the metal, 2 mL DMI, 3.6 mmol anisole, 190 °C, 10 h. $^b$No anisole was added before the reaction. $^c$ 0.8MPa CO was used instead of 3MPa CO₂.

Note: At fixed Ru/Co ratio of 1/3, the reaction rate initially increased and then dropped with elevating catalyst dosages, and the highest TON was obtained at 20 μmol Ru and 60 μmol Co (entries 1-3). When the total Ru-Co dosage was fixed at 80 μmol, the suitable Ru/Co ratio was 1/3 (entries 2, 4-6). After testing the catalytic rate at different LiI dosages, we found that 2.2 mmol was appropriate (entries 2, 7, 8). The impact of triphos dosage was also studied and the suitable dosage was 20 μmol (entries 2, 9, 10). The anisole, CO₂ and H₂ were all essential to the reaction, because ethanol could hardly be observed without anyone of them (entries 11-13). With the rising gas pressure, the TON of ethanol increased remarkably, while the increase became minor when the pressure was high enough (entries 2, 14-17). We fixed the total pressure at 8 MPa and changed the CO₂/H₂ ratio, and found that 3 MPa CO₂ and 5 MPa H₂ were fit for the reaction (entries 2, 18-22). In short, the optimized reaction conditions were 20 μmol Ru and 60 μmol Co catalysts, 2.2 mmol LiI, 20 μmol triphos, 3 MPa CO₂ and 5 MPa H₂, 190 °C.
Table S2 Impact of the catalytic components and reactant gases on the decomposition of anisole at 190 °C.

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<th>Entry</th>
<th>Catalyst 20 μmol Ru/60 μmol Co</th>
<th>Promoter 2.2 mmol</th>
<th>Ligand 20 μmol</th>
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References