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Chemoselective Oxidant-Free Dehydrogenation of Alcohols in Lignin Using Cp*Ir Catalysts

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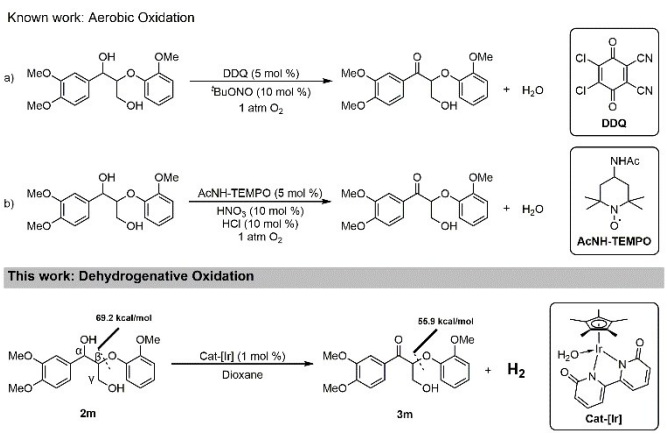
A remarkably effective method of chemoselective dehydrogenation of alcohols in lignin has been developed with iridium catalyst. And additional operation of Zn/NH_4Cl via one pot of two-step could further promote the cleavage of C-O bond in β−O−4 units in lignin. And this reaction system was also applicable to native lignin that the molecular weight of native lignin was decreased obviously detected by gel permeation chromatography (GPC). Additionally, this is the first to date to generate the by-product H_2 from native lignin and the by-product was straightforward captured by 1-decene. A probable mechanistic pathway was also proposed with the help of density functional theory (DFT) calculations.

Introduction

With the increase of the world's fossil fuel consumption rate and the decrease of fossil energy reserves, it is urgent to exploit a replacement of fossil resources for sustainable development. Lignin, as the most recalcitrant[1] part of lignocellulose biomass (cellulose, hemicellulose and lignin), is a heterogeneous aromatic biopolymer accounting for nearly 30% of non-fossil organic carbon[2] as well as the renewable sources for aromatic chemicals on the Earth.[3,4] Therefore, it is significant to make use of lignin effectively for the production of aromatic chemicals and low-molecular-mass feedstocks.[5] However, as amorphous aromatic polymer, lignin widely exists in the plants with the rigid cross-linked polymer structure.[6] Thus the physical stability and chemical inertness greatly restraint the efficient chemical conversion of lignin. Although commercial precedents have revealed that lignin sulfonate could be converted into several valuable chemicals,[7] but the yield of such progress is not gratifying, so the technological innovations are still significant to enhance the lignin's value. In this situation, that effectively degrading lignin biomass becomes popular as a novel starting for its utilization. Currently, the degradation methods of lignin mainly consists of oxidative,[8, 12] reductive[9] and redox-neutral[10] process. Although these methods have been applied into the conversion of model lignin and native lignin with good results, but pursuit of strategy with higher efficiency and atom economy is still necessary.

Previous literatures[11] revealed that C-C bond and C-O bond are the main connections in lignin. But comparing with C-O bond, cleavage of C-C bond is subjected to the radical pathways and requires a higher excitation energy due to the higher energy barrier.[12] Also, it is worth noting that within the multifaceted and heterogeneous structure, the most dominant linkage in both softwood and hardwood is the β-O-4 linkage, comprising about 50% of all linkages found in lignocelluloses.[13, 14, 15] Hence, how to more effectively make such a special connection mode (β-O-4 bond) breaking has become the key point of lignin utilization. Beckham *et al.*[16] reported that the ketone structure (such as: **Scheme 1**, substrate **3m**) could reduce the dissociation energy of C-O bond to 55.9 kcal/mol. And the experimental result[10b] indicates that, β-O-4 bond shows less tendency to cleavage as α-hydroxyl has not been oxidized. Since the oxidation of α-carbon leads to an efficient cleavage of β-O-4 bond, the selective oxidation of hydroxyl in lignin is particularly significant for the degradation of lignin.



Scheme 1 Homogeneous catalytic oxidation of lignin β-O-4 linked model compound.

Currently, various methods have been studied for the selective oxidation of lignin. Westwood *et al.*[8a] used DDQ as the oxidant to convert lignin in a good result. And Stahl et al.[8b] demonstrated a method using 4-acetamido-TEMPO to catalyze the efficient oxidation of α-hydroxyl. As α-hydroxyl has been oxidized, the formed ketone structure could bring an easier

Table 1 Optimization of reaction conditions for the dehydrogenation of lignin model compound.[a, b]

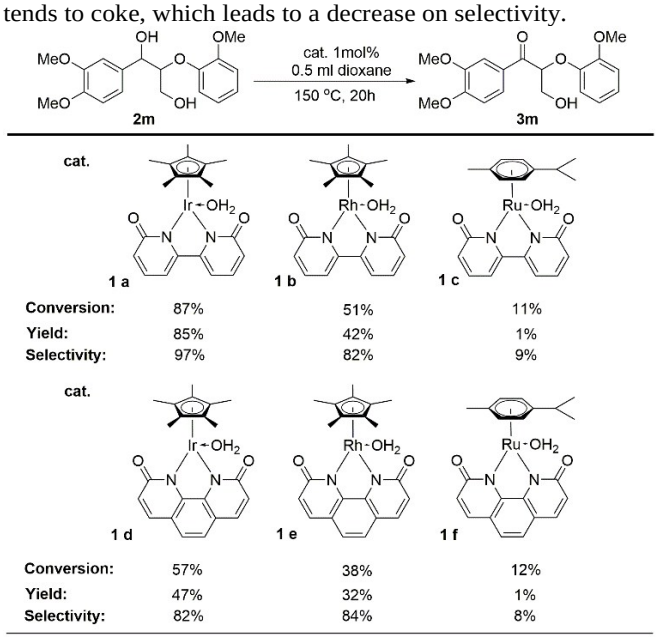
Entry	Solvent	Solvent volume [mL]	T [℃]	Addition	Conv. [%]	Yield [%]	Selectivity [%]
1	dioxane	0.5	150	none	87	85	97
2	dioxane	0.5	150	Na_2CO_3	89	27	30
3	dioxane	0.5	150	Na_2CO_3+H_2O	71	1	1
4	*tert*-butanol	0.5	150	none	73	47	64
5	*tert*-amyl alcohol	0.5	150	none	61	43	70
6	DMF	0.5	150	none	68	10	15
7	octane[c]	0.5	150	none	67	27	40
8	ethyl formate[c]	0.5	150	none	99	1	1
9	*o*-xylene	0.5	150	none	95	50	52
10	dioxane	10	150	none	13	12	91
11	dioxane	1.0	150	none	74	69	93
12	dioxane	0.5	120	none	60	58	96
13	dioxane	0.5	160	none	89	72	81
14	dioxane	0.5	180	none	95	68	71

[a] Reaction conditions: 0.5 mmol lignin model compound **2m** and 1 mol% catalyst **1a** were dissolved in the solvent. The reaction solution was stirred at certain temperature for 20h. [b] The conversion and yield of the reaction were detected by HPLC. [c] The reaction performed in the autoclave.

cleavage of β-O-4 bond via some chemical processes.[8a,10b] But considering the usage of oxidant, such catalytic system did not show any advantage on atomic economy.[17] Fujita and coworkers[18,19] have reported that iridium catalyst plays an important role in the oxidative dehydrogenation reaction of alcohols. And in recent studies we also found, Cp*Ir catalysts showed good selectivity for the dehydrogenated oxidation of α-hydroxy in lignin model compound. Herein, we successfully applied such catalysts to the dehydrogenation of lignin and the byproduct hydrogen has been trapped by 1-decene. Subsequently, we performed density functional theory (DFT) calculations to demonstrate the regioselectivity and proposed a conceivable mechanism of the dehydrogenation of alcohols in lignin. Then, successfully degradation of lignin was realized by the utilization of Zn/NH_4Cl, which was demonstrated by the gel permeation chromatography (GPC).

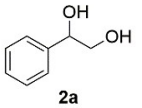
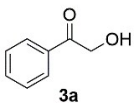
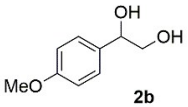
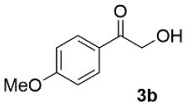
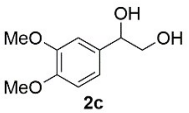
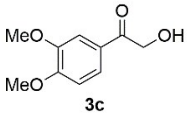
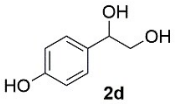
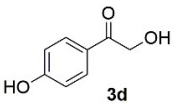
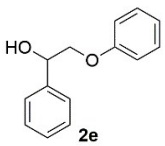
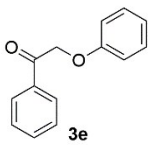
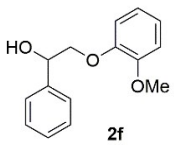
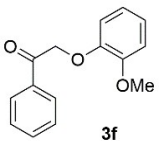
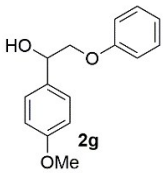
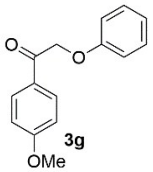
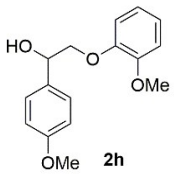
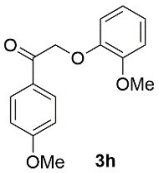
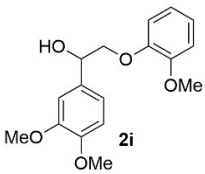
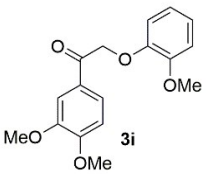
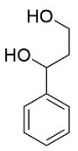
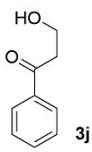
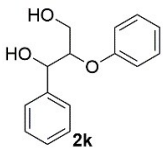
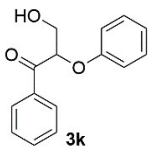
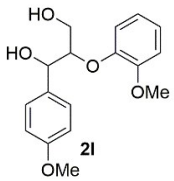
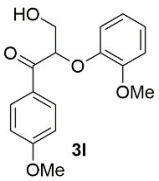
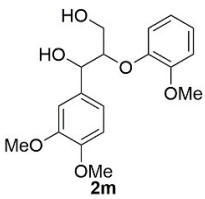
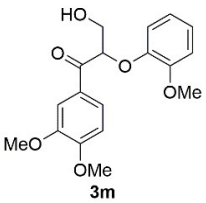
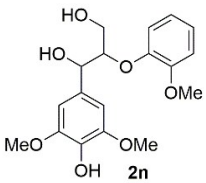
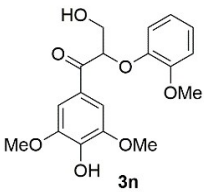
Results and Discussion

Initially, using β-O-4 linked lignin model compound **2m** as the substrate, we explored the optimal reaction conditions (**Table 1**). And we found that the addition of base or water would greatly decrease the reaction selectivity in normal conversion. Ester solvents (**Table 1**, entry 8) could improve the conversion significantly but show a bad performance in selectivity, only 1% products has been detected. Such phenomenon of high conversion with low selectivity probably caused by the transesterification between solvent and alcohols in lignin under relatively high temperature. Using tert-butyl alcohol, tert-amyl alcohol, octane and o-xylene (**Table 1**, entry 4, 5, 7, 9) as solvents respectively, the conversion could get more than 60% but also in a low selectivity. Eventually we found that under identical conditions, in 1,4-dioxane, the selectivity and yield could get nearly 97% and 85%, respectively. Also, despite the boiling point of 1,4-dioxane is 101 ℃, the conversion rate would be improved along with the increase of reaction temperature. Under low temperature, 120 ℃ (**Table 1**, entry 12), we could obtain a 60% conversion with 96% selectivity, which means the rate of dehydrogenation is unsatisfactory. And under high temperature, 160 ℃ (**Table 1**, entry 13), the coking of reaction system lead to an obvious decrease of reaction selectivity. Due to the effect of reaction temperature on selectivity, we decided to use 150 ℃ as the optimal temperature to continue our research. Later, we studied the kinetic experiments (Detailed data could be obtained from **SI**) and the effect of substrate concentration. The concentration of substrate **2m** increasing from 0.05 mol/L to 1 mol/L (**Table 1**, entry 1, 10, 11) could bring a significant enhancement on yield. Over 1 mol/L, the mass transfer deviates seriously resulting from the dense substrate, and the reaction solution tends to coke, which leads to a decrease on selectivity.



Scheme 2 Catalyst screening for selective oxidant-free dehydrogenation of substrate **2m.** The results were detected by HPLC.

Table 2 Substrate scope of lignin model compounds' conversion to ketone compunds. [a, b]

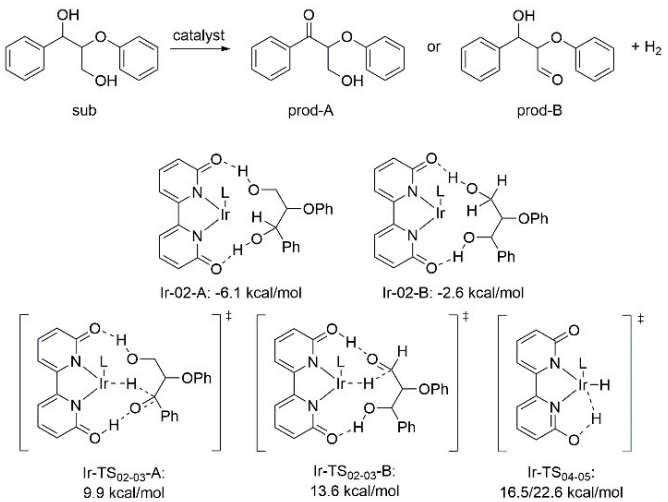
Substrate	Product	Yield	Substrate	Product	Yield
 **2a**	 **3a**	**80%**	 **2b**	 **3b**	**81%**
 **2c**	 **3c**	**85%**	 **2d**	 **3d**	**45%**
 **2e**	 **3e**	**83%**	 **2f**	 **3f**	**86%**
 **2g**	 **3g**	**84%**	 **2h**	 **3h**	**77%**
 **2i**	 **3i**	**80%**	 **2j**	 **3j**	**78%**[c]
 **2k**	 **3k**	**68%**	 **2l**	 **3l**	**73%**
 **2m**	 **3m**	**82% (85%**[d]**)**	 **2n**	 **3n**	**60%**

[a] Reaction conditions: 0.5 mmol lignin model compound **2**, 0.5mL 1, 4-dioxane, 1 mol% catalyst **1a**, 150 ºC, 20 h. [b] The results were isolated yields. [c] Reaction conditions: 0.5 mmol substrate, 0.5mL dioxane, 1 mol% catalyst 1a, 110 ºC, 20 h. [d] The yield was detected by HPLC.

Then we screened six catalysts including the central metal of iridium, rhodium and ruthenium with ligands bipyridine and 1,10-phenanthroline respectively (**Scheme 2**). For substrate **2m**, the best result was obtained over Ir catalyst with bipyridine **1a** (conversion 87%, selectivity 97%, yield 85%). Changed the central metal to Rh and Ru (catalyst **1b** and **1c**), the yield of product **3m** is 42% and 1% respectively, which indicates that the same group metal Ir and Rh perform better than Ru. This result is consistent with the report of dehydrogenation of benzyl alcohol by Fujita *et al.*[18] Changed the ligand to 1,10-phenanthroline (catalyst **1d**, **1e**, **1f**), the yield is 47%, 32% and 1%, and the selectivity is 82%, 84% and 8% respectively, which result is lower than the corresponding catalyst with bipyridine ligand. This mainly due to the structure of different ligands. Comparing with 1,10-phenanthroline, bipyridine shows more flexibility that brings about a lower steric hindrance.

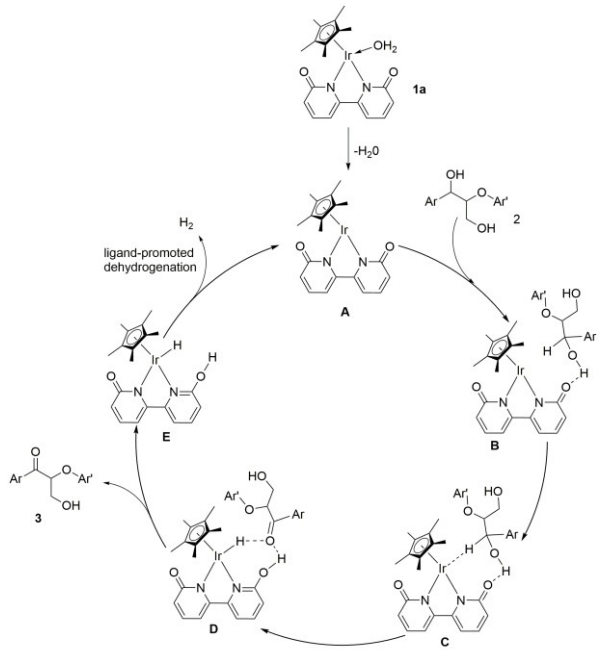
With optimal reaction conditions (as shown in **Scheme 2**) in hand, we next examined the scope of lignin model compounds with different substituents[20] in this dehydrogenation protocol (as seen in **Table 2**). First, for aryl compounds of α,β dual-hydroxyl, **2a**-**2d**, catalyst **1a** shows good chemical selectivity on the dehydrogenation of α-hydroxyl and little catalytic activity on β-hydroxyl. The reason is that once α-hydroxyl has been dehydrogenated, the formed α-carbonyl conjugated with benzene which generated a structure with better thermodynamic stability. We also found that the yield

improved along with the increase of electron donating group on benzene (**3a**-**3c**). This result is consistent with the work of Stahl.[8b] And when a phenolic hydroxyl presents on benzene (**2d**), the isolated yield of **3d** is 45%. Due to the presence of phenolic hydroxyl, side reactions generate compounds with quinone structure that severely reduces the yield of target product. Subsquently, the substrate of β-substituted compounds (**2e**-**2i**) were studied. The catalytic system also affords a satisfactory consequence and the isolated yield of the desired product is generally more than 80%. Then the catalyst of Cp*Ir **1a** was applied to the vicinal diol compounds **2j** and various β−O−4-linked diols (**2k**-**2n**). As expected, the catalyst also affords a high reactivity and selectivity for dehydrogenation of the α-hydroxyl. The above experimental studies indicated that the catalytic system could afford a high reactivity and chemoselectivity. Then to gain an insight into the mechanism of the selectivity dehydrogenation of alcohols in lignin, we have performed density functional theory (DFT) calculations on a simplified model system (as seen in **Scheme 3**). There are two different hydroxyl groups in the substrate and a selectivity between prod-A and prod-B existing. The reaction between catalyst **1a** and sub involves three elementary steps: (1) dehydrogenation of the hydroxyl group via a concerted transition state **Ir-TS$_{02\text{-}03}$-A/B** to give the product and an iridium hydride complex, (2) hydrogen transfer from the protonated bipyridine ligand to iridium via **Ir-TS$_{04\text{-}05}$**, and (3) reductive elimination and formation of H_2 via **Ir-TS$_{05\text{-}06}$**. The structure of key intermediates and transition states are presented in **Scheme 3** and the full energy profile is shown in **Figure S3** The catalyst-substrate complex **Ir-02-A** turns out to be the resting state. It is found that Step 1 controls the regioselectivity and Step 2 is a rate-determining step. For prod-A and prod-B, the energy barriers are 22.6 kcal/mol, 28.7 kcal/mol respectively. The better stability of **prod-A** results in a lower barrier. Thus, **prod-A** is the major product, which was consistent with the regioselectivity observed in experiments.



Scheme 3. The structure of key intermediates and transition states. The calculations were carried out at ωB97X-D/SDD:6-311+g(d,p)//ωB97X-D/SDD:6-31g(d,p) level and the solvent effect was considered. See **SI** for details.

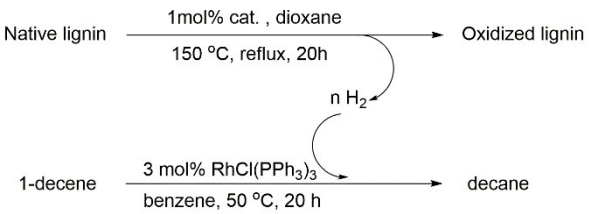
On the basis of the above results, a conceivable mechanism of the chemoselective dehydrogenation of alcohols



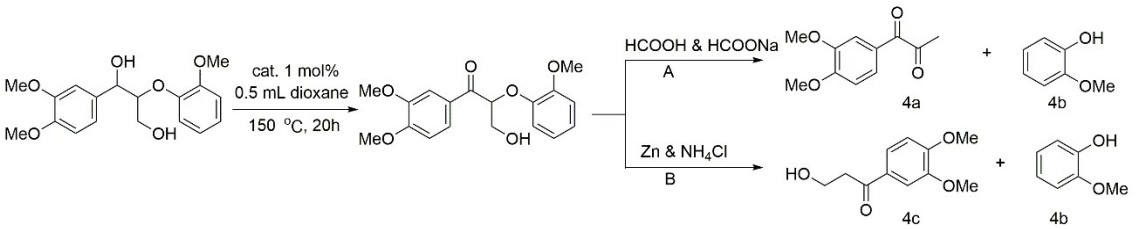
Scheme 4. A possible mechanism for the chemoselective oxidant-free dehydrogenation of alcohols in lignin**.**

in lignin can be proposed (**Scheme 4**).[18] In the initial of this reaction, the catalyst **1a** loses a molecule of water forming a vacant point on Iridium ion, affording an activated complex A. Subsequently, the hydrogen on α-carbon attacks the vacancy and hydrogen of the hydroxy couples the carbonyl on ligand, forming complex C. Then complex C transformed into the intermediate D. Later, hydrogen elimination of the substrate would occur to generate the carbonyl product **3** and the iridium species E. Finally, the reaction of the hydrogen on the iridium with the hydroxyl proton on the bipyridine ligand would occur to release one molecular hydrogen accompanied by the regeneration of A.

Based on the successful application of Cp*Ir catalyst in the dehydrogenation of β-O-4 linked lignin model compound, we attempt to conduct the dehydrogenation of native lignin. The raw lignin was extracted from birch using dioxasoly process.[8a] A mild-acid catalyzed process was employed using 0.2 N HCl in 1,4-dioxane. The lignin extracted from birch was rich of β-O-4 linkages, smaller amounts of the β–β linkage, and a very small amount of the β–5 linkage.[13] Thus the extracted lignin was used as substrate in the Cp*Ir catalytic system. To verity the generated gas is hydrogen, we designed the following dual reactions[19a] (**Scheme 5**). Linked the reaction system with a tube equipped with 1-decene and catalytic amount of $RhCl(PPh_3)_3$ to trap the hydrogen. Then we detected the existence of decane by GC which proved the good performance of Cp*Ir catalyst in the native lignin reaction.



Scheme 5. The dual reactions for capturing hydrogen gas from the dehydrogenation of native lignin by 1-decene.



Scheme 6. Degradation of lignin model compound through two-step in one pot.

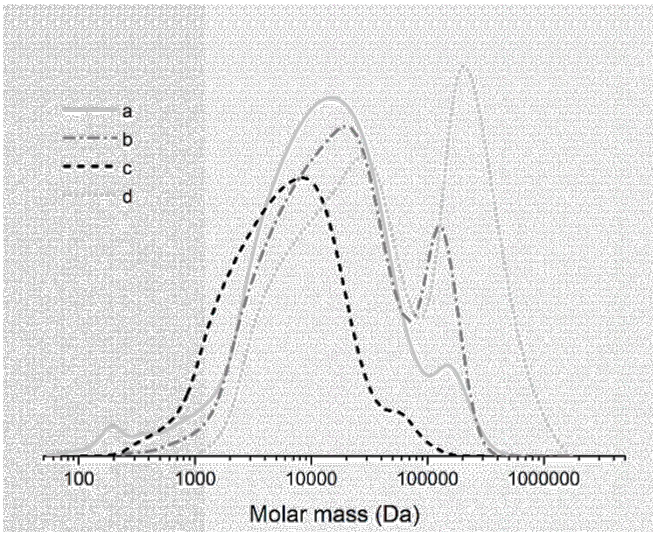


Figure 1 The GPC of the sample a, b, c & d. The sample a was the native lignin. The sample b was the dehydrogenative lignin; The sample c was processed with Zn/NH_4Cl after dehydrogenation; The sample d was the native lignin processed with Zn/NH_4Cl.

Later, to confirm that the selectively dehydrogenated lignin is more inclined to occur C-O bond cleavage, we used a two-step in one pot process to accomplish the decomposing of lignin (**Scheme 6**). According to the report of Stahl[10b], initially we utilized HCOOH/HCOONa system to directly process the dehydrogenation reaction solution. But it was found that the substrate **2m** increased significantly and only a small amount of product **4a** and **4b** were detected. A reasonable explanation is that the Cp*Ir catalyst for dehydrogenation could decompose HCOOH in good yield and generate hydrogen.[19a] Under HCOOH reducing conditions, partial **3m** could be reduced to **2m**. Therefore, the HCOOH/HCOONa system could not work efficiently in this two-step in one pot process. So then we used Zn/NH_4Cl system published by Westwood group[8a] to treat the dehydrogenation solution. Determined by HPLC, yield of **4b** and **4c** is 54% and 51% respectively without any increase of **2m**. With this good result, we applied this process into native lignin. A GPC test (**Figure 1**) was conducted to test the native lignin, dehydrogenative lignin, Zn/NH_4Cl-treated native lignin and dehydrogenative lignin. Results show that, for native lignin and dehydrogenative lignin, the molecular weight distribution is close. And that of treated dehydrogenative lignin shows an incline to low molecular weight. But the native lignin which treated by Zn/NH_4Cl directly tends to high molecular scope, which probably due to the polymerization of native lignin. Based on above data, we verified that the non-dehydrogenative lignin cannot be decomposed by Zn/NH_4Cl. Instead, the coking of lignin leads to a shift to high molecular distribution. On contrary, the dehydrogenative lignin can be decomposed by Zn/NH_4Cl in good performance, which approves the excellent dehydrogenation effect of Cp*Ir catalyst on lignin.

Conclusions

In summary, we achieved the selective dehydrogenation of β-O-4 linked lignin model compounds and native lignin over Cp*Ir catalyst. And the byproduct hydrogen has been trapped by 1-decene successfully. The dehydrogenation solution then processed by Zn/NH_4Cl confirmed that the dehydrogenated β-O-4 structure was easier to be cleavage which brings about a convenience for lignin depolymerisation detected by GPC. Moreover, by DFT calculations, we elucidated the chemoselective dehydrogenation of lignin models by Cp*Ir catalyst and demonstrated a probable reaction mechanism. Hence, we established an oxidant-free catalytic system to achieve the dehydrogenation of model lignin and native lignin.

Experimental

The reagents used in catalyst preparation and reactions were commercially available.

Catalyst preparation:

$[Cp^*Ir(H_2O)_3]SO_4$: Under argon atmosphere, the $[Cp^*IrCl_2]_2$ (480 mg, 0.60 mmol) and Ag_2SO_4 (374 mg, 1.20 mmol) were added to 4mL water. The solution was stirred at room temperature for 3 hours. Then the solution was filtered to remove the silver chloride. And the filtrate was rotary evaporated to give a pale yellow solid powder, yield: 100%.

$[Cp^*Ir(H_2O)_3(6,6'\text{-di-OH-bpy})]SO_4$: Under argon atmosphere, $[Cp^*Ir(H_2O)_3]SO_4$ (480 mg, 0.1 mmol) was dissolved in 12.5 mL water and then 0.1 mmol ligand, dipyridyl, was added. The solution was sirred at room temperature for 12 hours. Then the solution was filtered, and the filtrate was rotary evaporated to give a pale yellow solid powder, yield: 95%.

Catalyst **1a**: $[Cp^*Ir(H_2O)_3(6,6'\text{-di-OH-bpy})]SO_4$ (500 mg, 0.75mmol) was dissolved in 12 mL water and then 2 eq. potassium *tert*-butoxide was added. The solution was sirred at room temperature for 3 hours. Then the solution was filtered to get a pale dark green solid powder, catalyst **1a**, yield: 90%. (The synthesis of other catalyst, **1b**, **1c**, **1d** and **1e**, was similar with catalyst **1a**.)

General procedure for dehydrogenation of lignin model compound:
A reaction tube was linked with a reflux condenser, then substrate (0.5 mmol) and 1 mol% catalyst were added to the reaction tube dissolved in 0.5 mL 1,4-dioxane. The reaction solution was stirred at 150 °C for 20 h. After completion of the reaction, the reaction was cooled to room temperature. The reaction solution was rotary evaporated and then was separated by column chromatography. And the detailed NMR spectrum data of the products (**3a**~**3n**) could be obtained from the **SI**.

Native Lignin Extraction:
Birch sawdust was generated from kiln dried birch logs using a bandsaw and used without further processing. As reported by Sun et al.[21], the lignin content in the original birch was *ca.* 25% (w/w) and the carbohydrate analysis revealed that xylan (*ca.* 20%) and glucan (*ca.* 35%) were the dominant constituents in the original birch.

200 g of birch wood sawdust are uniformly dispersed in 1440 mL 1,4-dioxane. Then slowly added 160 mL solution of HCl (2 mol/L). Under argon atmosphere, the reaction solution was stirred for 1 h at 120 °C. Then, the reaction mixture was cooled to room temperature. The residue was filtered. And the filtrate was concentrated. The resulting concentrate was dissolved in 250 mL solvent (acetone:water=9:1). Subsequently, the solution was slowly poured into 2.5 L rapidly stirred water to get a large number of brown precipitate. The precipitate was filtered and washed. Then the precipitate was again dissolved in as little solvent (acetone: methanol = 9: 1) as possible. The solution was followed by the dropwise added rapidly stirred ether solvent, in which case a large tan solid precipitated was filtered off. And the resulting solid was vacuum dried to give 17.9 g of a tan solid powder.

Dehydrogenation reaction of native lignin:
The reaction tube **A** was linked with a reflux condenser, then 300 mg native lignin and 2.7 mg catalyst **1a** were added, dissolved in 1 mL 1,4-dioxane. 280 mg 1-decene and 3 mol% were added to the reaction tube **B**, dissolved in 3 mL benzene. The reaction tube **A** was linked with the reaction tube **B.** And the solution in reaction tube **A** was stirred at 150 °C for 20 h while the solution in tube **B** was stirred at 50 °C for 20 h. After completion of the reaction, the reaction mixture was cooled to room temperature. Then the solution in tube B was detected and decane was detected by GC analysis. Set-up diagram could be obtained from **SI**.

Degradation of the lignin model compound 2m through one pot of two-step (HCOOH/HCOONa):
After completion of the dehydrogenation reaction of lignin model compound **2m**, the reaction solution was cooled to room temperature. Then 3 eq. HCOONa and 1 mL HCOOH were directly added to the reaction tube, and the reaction solution was stirred at 110 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature for HPLC analysis.

Degradation of the lignin model compound 2m via one pot of two-step (Zn/NH_4Cl):
After completion of the dehydrogenation reaction of lignin model compound **2m**, the reaction solution was cooled to room temperature. Then the pH of the reaction system was adjusted to weak acid (5~6) with 0.5 N HCl. And 5 eq. Zn and NH_4Cl were directly added to the reaction tube, and the reaction solution was stirred at 80 °C for 1 h. After completion of the reaction, the reaction mixture was cooled to room temperature for HPLC analysis.

Degradation of native lignin via one pot of two-step (Zn/NH_4Cl):
After completion of the dehydrogenation reaction of native lignin, the reaction solution was cooled to room temperature. Then the pH of the reaction system was adjusted to weak acid (5~6) with 0.5 N HCl. And 5 eq. Zn and NH_4Cl were directly added to the reaction tube, and the reaction solution was stirred at 80 °C for 1 h. After completion of the reaction, the reaction mixture was cooled to room temperature for GPC analysis.

The computational tools for DFT calculations:
All calculations were performed using Gaussian 09[22]. Both geometry optimizations and single-point energy calculations were performed with the ωB97X-D functional[23] in 1, 4-dioxane solution using the SMD[24] solvation model. A mixed basis set of SDD[25] for transition metal (Ir) and 6-31G(d,p) for other atoms was used in geometry optimizations. Frequency calculations were carried out at the same level to confirm stationary points as minima or transition states. Single-point energy calculations were conducted using a mixed basis set of SDD for transition metal (Ir) and 6-311+G(d,p) for other atoms. All reported free energies include thermal correction to Gibbs free energy calculated at the optimized level.

The synthetic strategy of the substrate could be obtained from the **SI**.

Acknowledgements

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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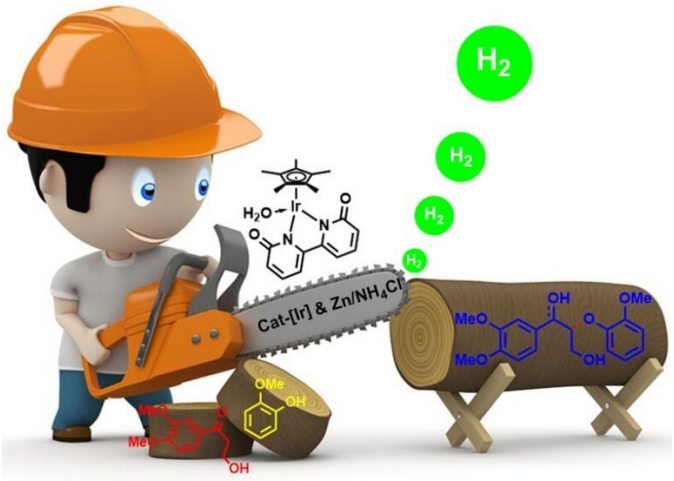
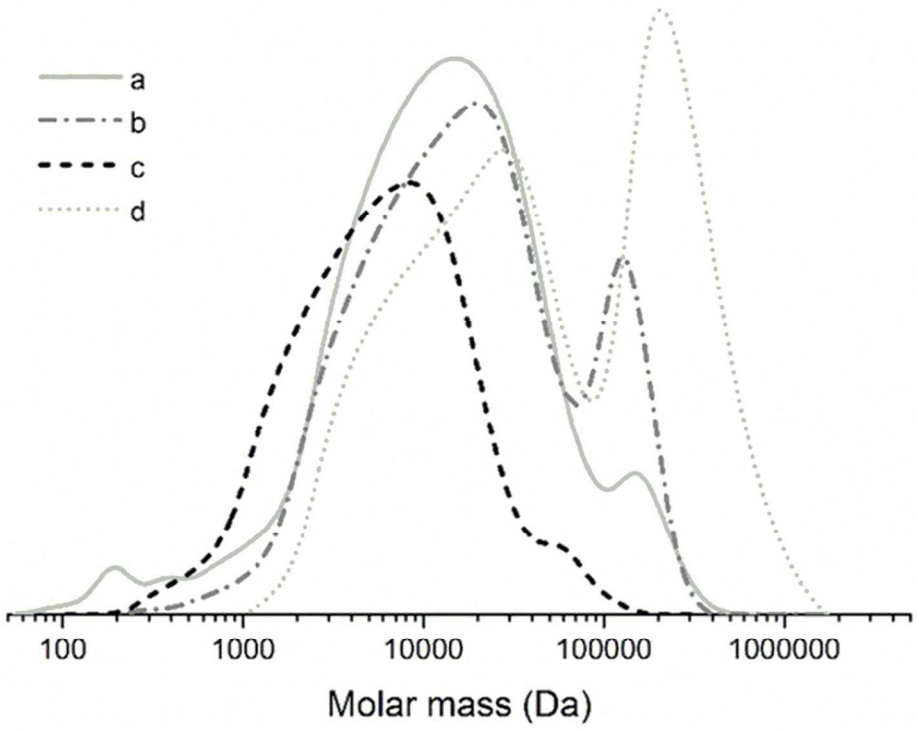
ARTICLE

Chemoselective Oxidant-Free Dehydrogenation of Alcohols in Lignin Using Cp*Ir Catalysts



Capturing hydrogen gas from the native lignin using the catalyst Cp*Ir and the dehydrogenative lignin could be further degraded with the help of Zn & NH_4Cl through one pot of two-step.



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Supplementary Information

Chemoselective Oxidant-Free Dehydrogenation of Alcohols in Lignin Using Cp*Ir Catalysts

Rui Zhu, Bing Wang, Minshu Cui, Jin Deng*, Xinglong Li, Yingbo Ma and Yao Fu*

Table of Contents

1. General Information.

All commercially available compounds and chemicals were purchased and used as received, unless otherwise noted specially. Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. High Performance Liquid Chromatography (HPLC): Hitachi L2000 HPLC; column: Alltima C18(5mm 250mm 4.6mm); mobile phase: acetonitrile : 10 mmol/L formic acid aqueous (1:1, v/v); flow rate: 1 mL/min; column temperature: 30^{o}C; detection wavelength: 280nm; ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. 2D HSQC NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer with the solvent peak used as the internal standard. Multiplicities are described using the following abbreviations: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). NMR spectra were processed using MestReNova. Column chromatography was performed using Davisil® silica (40-63 μm, 230-400 mesh). Thin layer chromatography was performed on pre-coated glass plates (Silica Gel 60A, Fluorochem) and visualised under UV light (254 nm) or by staining with $KMnO_4$.

2. Additional Screening Results.

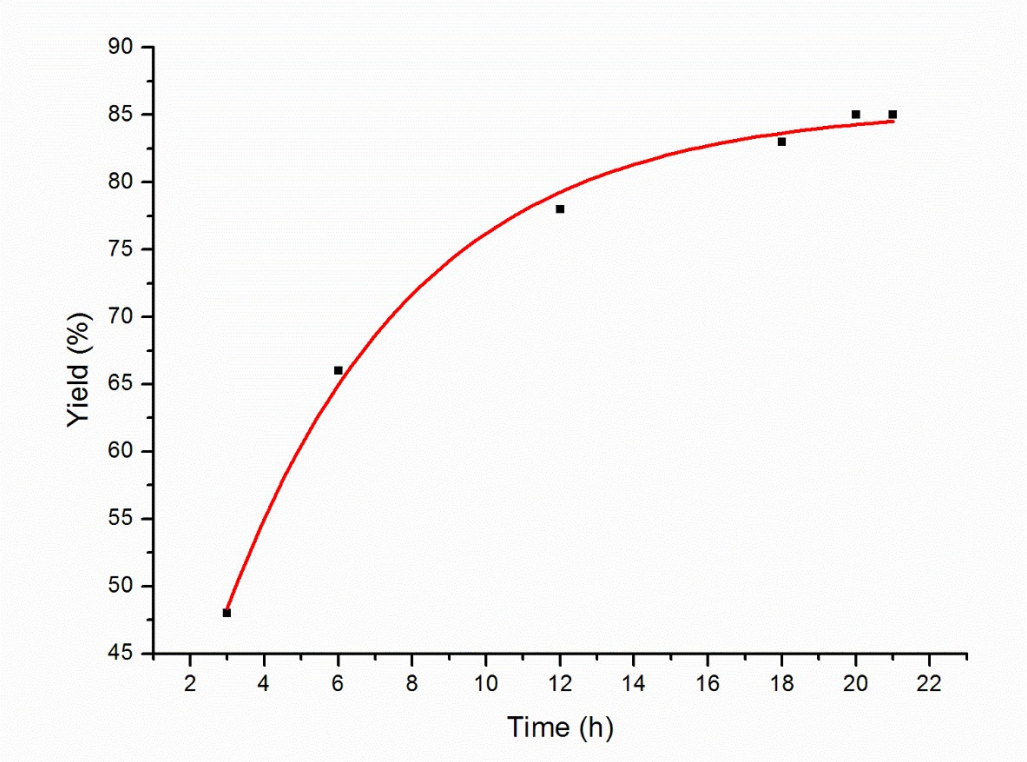


Figure S1: Screening of reaction time for dehydrogenation of alcohol in Lignin.[a,b]

[a] Reaction conditions: 0.5 mmol lignin model compound **2m**, 0.5 mL dioxane, 1 mol% catalyst **1a**, 150 °C.

[b] The yield of the reaction was detected by HPLC

3. Setup of dual reactions for dehydrogenation reactions

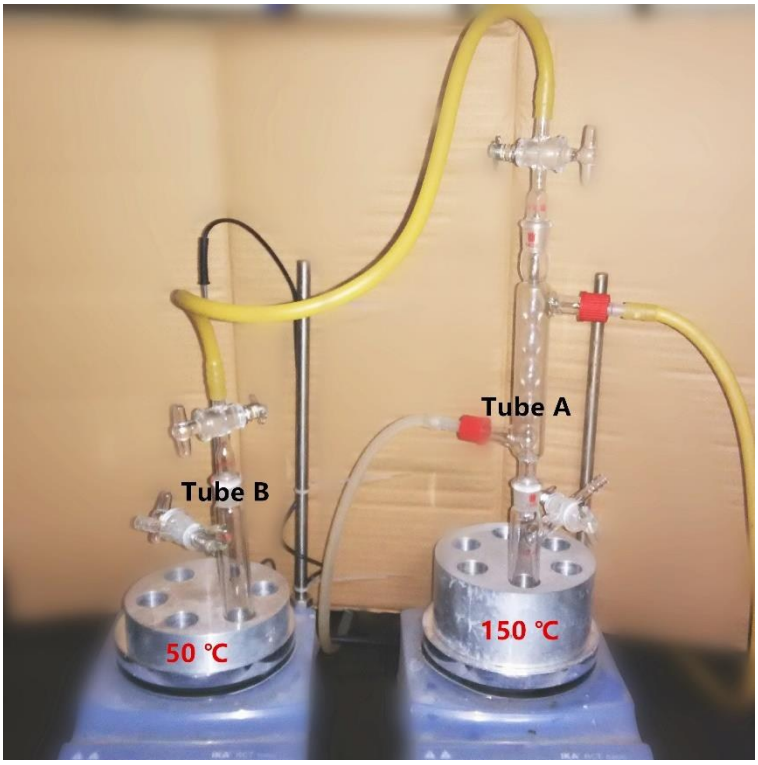


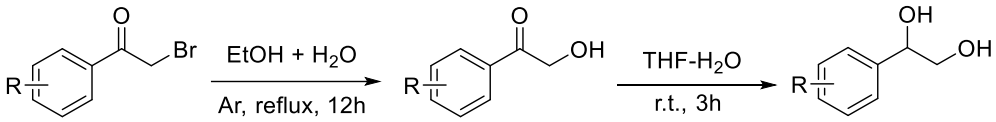
Figure S2 Setup of dual reactions for dehydrogenation reactions

4. Synthesis of Lignin Model Compounds.

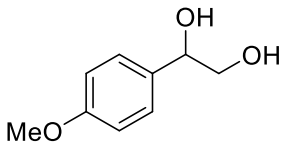
All compounds purchased commercially were not mentioned below.

General procedure for preparation of 1- arylethane-1,2-diol:

This compound was prepared according to a literature procedure.[1] Spectral data are consistent with those reported in the literature.



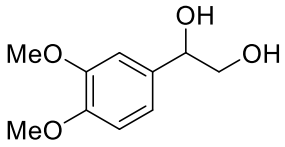
1-(4-methoxyphenyl)ethane-1,2-diol (2b):



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, *J*=8.6, 2H), 6.89 (d, *J*=8.7, 2H), 4.77 (dd, *J*=8.1, 3.7, 1H), 3.80 (s, 3H), 3.72 (dd, *J*=11.3, 3.7, 1H), 3.65 (dd, *J*=11.3, 8.2, 1H), 2.26 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.40, 132.60, 127.36, 113.95, 74.29, 68.07, 55.30.

1-(3,4-dimethoxyphenyl)ethane-1,2-diol (2c):

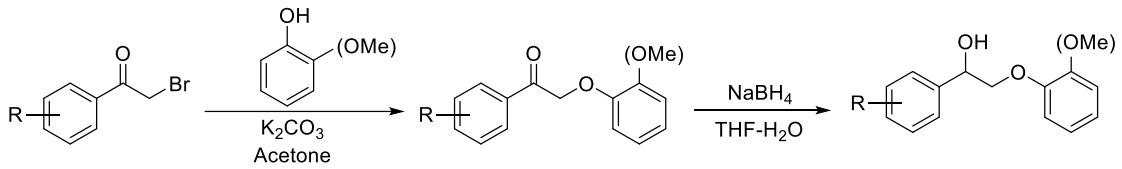


^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.82 (s, 1H), 6.76 (q, J=8.2, 2H), 4.66 (dd, J=8.1, 3.3, 1H), 3.78 (d, J=1.9, 6H), 3.65 – 3.52 (m, 2H), 2.99 (s, 2H).

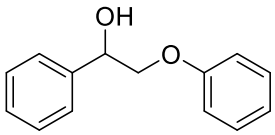
^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.0, 148.7, 133.1, 118.4, 111.1, 109.2, 74.5, 68.1, 55.9, 55.8

General procedure for preparation of 2-aryloxy-1-phenylethanols (2e-2i):

These substrates were synthesized in two-step from the corresponding phenol and 2-bromoacetophenone according to literature procedure.[2] 2-Bromoacetophenone (5 mmol, 0.990 g) was added to a stirred solution of K_2CO_3 (7.5 mmol, 1.036 g) and guaiacol (6.25 mmol, 0.776 g) in acetone (50 mL). The reaction mixture was stirred at reflux temperature for 5 h, after which it was filtered off and concentrated under vacuum. The residue was purified by column chromatography with hexane : ethyl acetate (3:1). The resulting compound (3.5 mmol, 0.847 g) was dissolved in the mixture of THF:H_2O (4:1) (25 mL), and sodium borohydride (7 mmol, 0.26 g) was added portionwise to maintain a gentle evolution of gas. Then, the mixture was stirred for 6 h at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (50 mL) and diluted with 30 mL water. The aqueous portion was extracted with ethyl acetate (3 × 30 mL). The organic parts were combined, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by column chromatography with hexane : ethyl acetate (2:1).

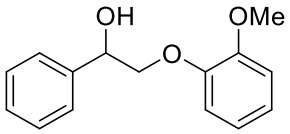


2-phenoxy-1-phenylethan-1-ol (2e):



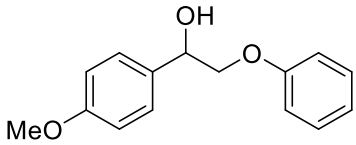
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J*=7.0, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.32 (m, 1H), 7.29 (ddd, *J*=8.5, 4.6, 1.3, 2H), 7.02 – 6.95 (m, 1H), 6.93 (dd, *J*=8.3, 2.7, 2H), 5.13 (dd, *J*=8.8, 2.9, 1H), 4.13 – 4.09 (m, 1H), 4.01 (td, *J*=9.4, 3.9, 1H), 2.78 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.39, 139.66, 129.60, 128.61, 128.23, 126.33, 121.34, 114.65, 73.30, 72.62.

2-(2-methoxyphenoxy)-1-phenylethan-1-ol (2f):



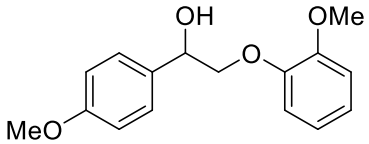
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, *J*=7.1, 2H), 7.40 – 7.24 (m, 3H), 7.01 – 6.83 (m, 4H), 5.11 (dd, *J*=9.4, 2.8, 1H), 4.16 (dd, *J*=10.0, 2.9, 1H), 3.98 (t, *J*=9.7, 1H), 3.85 (s, 3H).

1-(4-methoxyphenyl)-2-phenoxyethan-1-ol (2g):



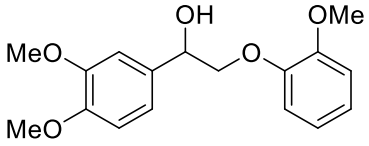
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J*=8.6, 2H), 7.27 (t, *J*=7.9, 2H), 6.99 – 6.88 (m, 5H), 5.05 (dd, *J*=8.7, 3.2, 1H), 4.05 (dd, *J*=9.6, 3.3, 1H), 3.98 (t, *J*=9.2, 1H), 3.80 (s, 3H), 2.77 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.48, 158.37, 131.78, 129.53, 127.56, 121.23, 114.60, 113.94, 73.23, 72.14, 55.29.

2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol (2h):



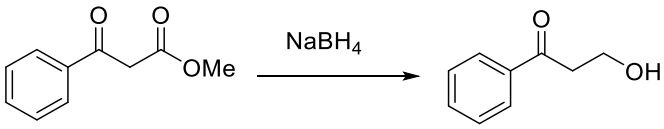
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J*=8.6, 2H), 7.04 – 6.84 (m, 6H), 5.06 (dd, *J*=9.5, 2.7, 1H), 4.14 (dd, *J*=10.0, 2.8, 1H), 3.96 (t, *J*=9.8, 1H), 3.89 (s, 3H), 3.81 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.40, 150.03, 147.95, 131.59, 128.73, 127.55, 122.45, 121.08, 115.78, 113.89, 111.93, 76.20, 71.90, 55.83, 55.30.

1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-ol (2i):

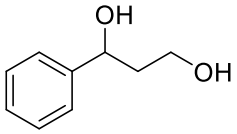


^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.94 – 6.74 (m, 7H), 4.97 (dd, *J*=9.2, 3.0, 1H), 4.06 (dd, *J*=10.0, 3.0, 1H), 3.92 – 3.87 (m, 1H), 3.83 – 3.75 (m, 9H).
13C NMR (101 MHz, CDCl3) δ = 149.91, 149.05, 148.70, 148.02, 132.41, 132.37, 122.33, 121.11, 118.62, 115.50, 115.40, 111.94, 111.01, 109.42, 76.05, 72.09, 55.93, 55.86, 55.80.

General procedure for the synthesis of 1-phenylpropane-1,3-diol (2j) from methyl 3-oxo-3-phenylpropanoate[12]:

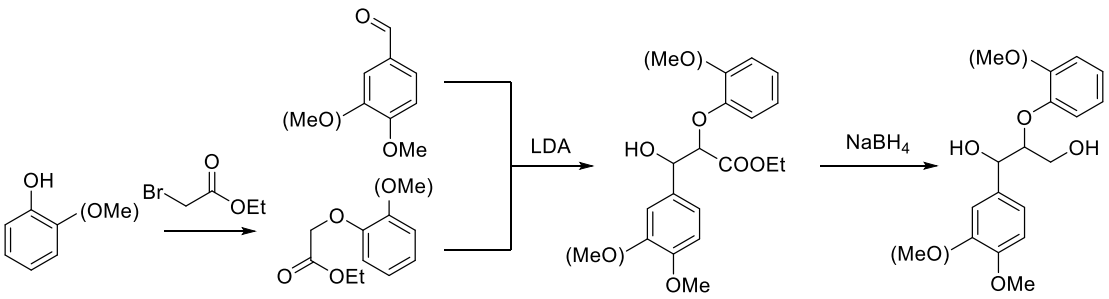


$NaBH_4$ (8 equiv) was added portion-wise to the solution of an appropriate methyl 3-oxo-3-phenylpropanoate (1.78 g) in MeOH (15 mL) at room temperature. After 20 min the heterogeneous white reaction mixture was heated to reflux until all starting material was consumed (detected by TLC). The cooled mixture was concentrated under reduced pressure and partitioned between distilled water (35 mL) and EtOAc (40 mL). The layers were separated, and the aqueous phase was back-extracted with EtOAc (3×40 mL). The combined extracts were dried (Na_2SO_4), concentrated under reduced pressure, and purified by column chromatography with hexane : ethyl acetate (3:1), yield: 80%.



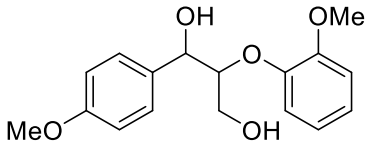
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 – 7.20 (m, 5H), 4.85 – 4.79 (m, 1H), 3.86 – 3.74 (m, 2H), 3.73 – 3.61 (m, 2H), 1.94 – 1.78 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 144.37, 128.46, 127.46, 125.73, 73.48, 60.78, 40.49.

1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (2k): This compound was prepared on the basis of a literature procedure.[5]



2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (2l): This lignin model compound was prepared on the basis of a literature procedure.[5] Substrate **2l** was prepared as a mixture of diastereomers, erythro: threo (3:2)

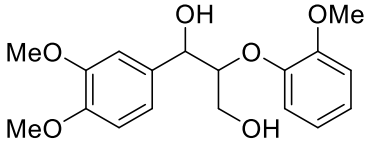
according to H-NMR. No attempt was made to separate the diastereomers. Spectral data are consistent with those reported in the literature.[3]



^{1}H NMR (400MHz, $CDCl_3$): δ 7.35 (d, J = 8.4 Hz, 2×0.6H, Ar on major diastereomer), 7.30 (d, J = 8.4 Hz, 2×0.4H, Ar on minor diastereomer), 7.12 (d, J = 1.4, 7.8 Hz, 1×0.6H, Ar on major diastereomer), 7.07-7.01 (m, 1×0.6H, Ar on major diastereomer, m, 1×0.4H, Ar on minor diastereomer, overlap), 6.95-6.85 (m, 4×0.6H, Ar on major diastereomer, m, 5×0.4H, Ar on minor diastereomer, overlap), 4.99 (m, 1×0.4H, ArC***H***OH- on minor diastereomer), 4.97 (m, 1×0.6H, ArC***H***OH- on major diastereomer), 4.16-4.12 (m, 1×0.4H, -C***H***OAr on minor diastereomer), 4.05-4.00 (td, J = 3.6, 8.0 Hz, 1×0.6H, -C***H***OAr on major diastereomer); 3.90 (dd, J = 4.0, 12.0 Hz, 1×0.4H, -C***H***$_2$OH on minor diastereomer), 3.88 (d, J = 1.2, 3×0.6H, -OMe on major diastereomer), 3.84 (d, J = 1.2, 3×0.4H, -OMe on minor diastereomer), 3.78 (s, 3×0.6H, -OMe on major diastereomer, s, 3×0.4H, -OMe on minor diastereomer, overlap), 3.65 (dd, J = 3.2, 12.0 Hz, 1×0.4H, -C***H***$_2$OH on minor diastereomer), 3.59 (dd, J = 3.2, 12.0 Hz, 1×0.6H, -C***H***$_2$OH on major diastereomer), 3.43 (dd, J = 4.0, 12.0 Hz, 1×0.6H, -C***H***$_2$OH on major diastereomer), 3.25 (brs, 2.0H, 2×-O**H**).

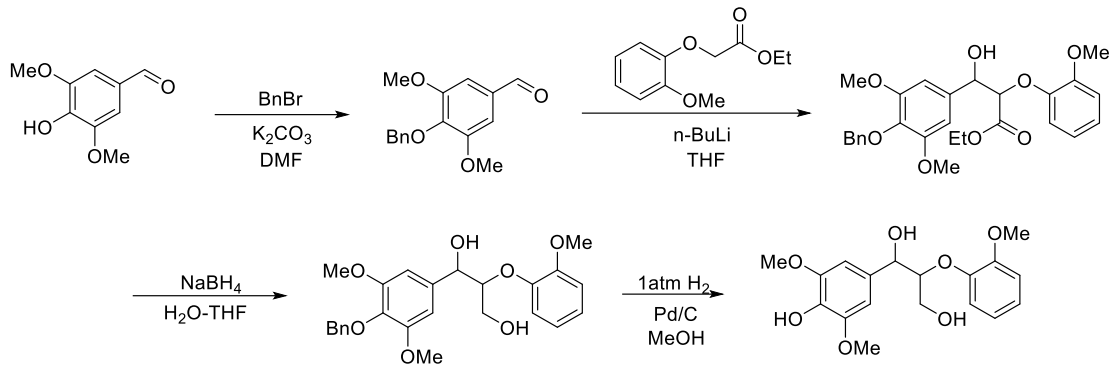
^{13}C NMR (101 MHz, $CDCl_3$) δ =159.48, 159.06, 151.52, 151.22, 147.64, 146.93, 131.74, 128.35, 127.36, 124.15, 124.08, 121.67, 121.59, 120.95, 113.93, 113.80,112.16, 112.12, 89.44, 87.23, 73.61, 72.61, 60.96, 60.70, 60.46, 55.88, 55.28

1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (2m): This lignin model compound was prepared on the basis of a literature procedure.[5] Substrate **2m** was prepared as a mixture of diastereomers, erythro: threo (3:1) according to H-NMR. No attempt was made to separate the diastereomers. Spectral data are consistent with those reported in the literature.

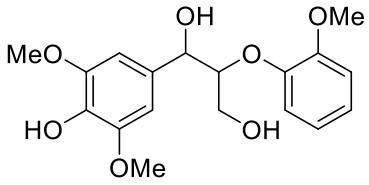


^{1}H NMR ($CDCl_3$, 400MHz): δ 7.13 (d, J = 8.0 Hz, 1×0.25H, Ar on minor diastereomer), 7.08-7.02 (m, 1×0.75H, aryl on major diastereomer, 1×0.25H, aryl on minor diastereomer, overlap); 7.01-6.89 (m, 5×0.75H, aryl on major diastereomer, 5×0.25H, aryl on minor diastereomer, overlap), 6.85-6.80 (m, 1×0.75H, aryl on major diastereomer), 4.99 (d, J = 4.8 Hz, 1×0.25H, Ar-C***H***-OH on minor diastereomer), 4.98 (t, J = 4.8 Hz, 1×0.75H, Ar-C***H***-OH on major diastereomer), 4.16 (m, 1×0.75H, C***H***OAr on major diastereomer), 4.18-4.14 (m, 1×0.25H, C***H***OAr on minor diastereomer), 3.91 (dd, J = 2.8, 12.0 Hz, 1×0.75H, -CH***H***OH on major diastereomer), 3.89 (s, 3×0.25H, -OMe on minor diastereomer), 3.86 (s, 9×0.75H, -OMe on major diastereomer, s, 6×0.25H, -OMe on minor diastereomer, overlap), 3.67 (dd, J = 3.2, 12.0 Hz, 1×0.75H, -CH***H***OH on major diastereomer), 3.63 (dd, J = 2.8, 12.0 Hz, 1×0.25H, -CH***H***OH on minor diastereomer), 3.47 (dd, J = 3.6, 12.0 Hz, 1×0.25H, -CH***H***OH on minor diastereomer).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.66, 151.34, 149.09, 149.02, 148.90, 148.45, 147.57, 146.85, 132.38, 132.04, 124.35, 124.32, 121.73, 121.67, 121.13, 119.65, 118.37, 112.15, 110.98, 109.83, 109.11, 89.62, 87.53, 73.95, 72.66, 61.04, 60.75, 55.92, 55.90.



1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol (2n): This lignin model compound was prepared on the basis of a literature procedure.[5] Substrate **2n** was prepared as a mixture of diastereomers, erythro: threo (2:1) according to H-NMR. No attempt was made to separate the diastereomers. Spectral data are consistent with those reported in the literature.



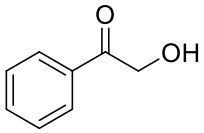
^{1}H NMR (400MHz, $CDCl_3$): δ 7.13 (dd, J = 1.6, 8.0 Hz, 1×0.6H, aryl on major diastereomer), 7.11-7.04 (m, 1×0.6H, aryl on major diastereomer, m, 1×0.4H, aryl on minor diastereomer, overlap), 6.99-6.89 (m, 2×0.6H, aryl on major diastereomer, m, 3×0.4H, aryl on minor diastereomer, overlap), 6.69 (s, 2×0.6H, aryl on major diastereomer), 6.62 (s, 2×0.4H, aryl on minor diastereomer), 5.59 (brs, 1×0.6H, Ar-O***H*** on major diastereomer), 5.57 (brs, 1×0.4H, Ar-O***H*** on minor diastereomer), 5.00-4.92 (m, 1×0.6H, ArC***H***OH- on major diastereomer, m, 1×0.4H, ArC***H***OH- on minor diastereomer, overlap), 4.17-4.14(m, 1×0.4H, -C***H***OAr on minor diastereomer), 4.03-3.98 (td, J = 4.0, 8.0 Hz, 1×0.6H, C***H***OAr on major diastereomer), 3.92 (dd, J = 4.0, 12.0 Hz, 1×0.4H, -CH***H***OH on minor diastereomer), 3.91 (s, 3×0.6H, -OMe on major diastereomer), 3.88 (s, 6×0.6H, -OMe on major diastereomer, s, 3×0.4H, -OMe on minor diastereomer, overlap), 3.87 (s, 6×0.4H, -OMe on minor diastereomer), 3.66 (dd, J = 3.2, 12.0 Hz, 1×0.4H, -CH***H***OH on minor diastereomer), 3.64 (dd, J = 3.2, 12.0 Hz, 1×0.4H, -CH***H***OH on major diastereomer), 3.49 (dd, J = 4.0, 12.0 Hz, 1×0.6H, -CH***H***OH on major diastereomer), 2.92 (brs, 2.0H, 2×-O***H***).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 151.62, 151.33, 147.51, 147.08,146.83, 134.52, 134.06, 130.95, 130.60, 124.37, 124.31, 121.74, 121.67, 121.13, 121.05, 112.15, 112.13, 103.71, 102.70, 89.58, 87.48, 74.24, 72.88, 61.00, 60.76, 56.35, 55.91, 55.89.

5. General procedure for oxidation of lignin model compounds (3a-n) and the data of NMR:

To a 10 mL reaction tube with a stir bar was added the lignin model compound (0.5 mmol) and 1 mol% of catalyst **1a** (0.005 mmol, 2.66 mg) and then 0.5 mL dioxane was added to the reaction tube. The reaction mixture was stirred for 20 h at 150 ℃. After completion of the reaction, the mixture was subjected to column chromatography to obtain the corresponding carbonyl compound.

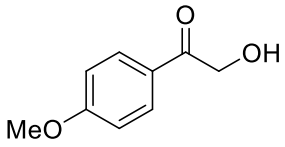
2-hydroxy-1-phenylethan-1-one (3a): Chromatography solvent: petroleum ether : ethyl acetate (2:1). Spectral data are consistent with the previous reported literature.[6]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93 (d, *J*=8.6, 2H), 7.64 (t, *J*=7.4, 1H), 7.51 (t, *J*=7.7, 2H), 4.89 (s, 2H), 3.47 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 198.41, 134.33, 133.36, 128.99, 127.71, 65.47.

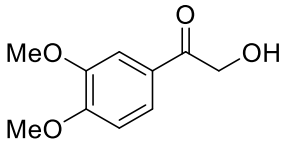
2-hydroxy-1-(4-methoxyphenyl)ethan-1-one (3b): Chromatography solvent: petroleum ether : ethyl acetate (2:1). Spectral data are consistent with the previous reported literature.[6]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J*=8.9, 2H), 6.97 (d, *J*=8.9, 2H), 4.83 (s, 2H), 3.89 (s, 3H), 3.52 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.70, 164.37, 130.02, 126.33, 114.18, 64.99, 55.58.

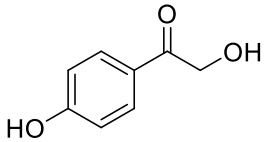
1-(3,4-dimethoxyphenyl)-2-hydroxyethan-1-one (3c): Chromatography solvent: petroleum ether : ethyl acetate (2:1). Spectral data are consistent with the previous reported literature.[6]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (d, *J*=8.2, 2H), 6.92 (d, *J*=8.0, 1H), 4.85 (s, 2H), 3.97 (s, 3H), 3.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.85, 154.22, 149.39, 126.48, 122.28, 110.30, 109.76, 64.98, 56.14.

2-hydroxy-1-(4-hydroxyphenyl)ethan-1-one (3d): Chromatography solvent: petroleum ether : ethyl acetate (4:1). Spectral data are consistent with the previous reported literature.[6]

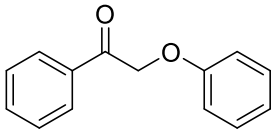


^{1}H NMR (400 MHz, d_6-Acetone) δ = 7.93 – 7.85 (m, 2H), 6.99 – 6.92 (m, 2H), 4.80 (s, 2H), 3.29 (s, 2H).

^{13}C NMR (101 MHz, d_6-Acetone) δ = 206.21, 162.73, 130.16, 125.93, 115.38, 64.64.

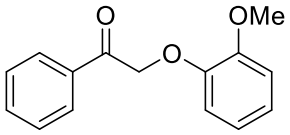
2-phenoxy-1-phenylethan-1-one (3e): Chromatography solvent: petroleum ether : ethyl acetate (7:1). Spectral data are

consistent with the previous reported literature.[6]



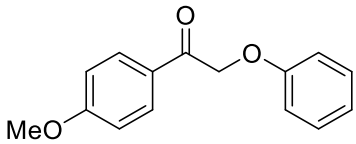
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, *J*=7.2, 2H), 7.62 (t, *J*=7.4, 1H), 7.50 (t, *J*=7.7, 2H), 7.32 – 7.26 (m, 2H), 7.02 – 6.92 (m, 3H), 5.28 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.54, 157.98, 134.56, 133.88, 129.58, 128.84, 128.14, 121.65, 114.79, 70.76.

2-(2-methoxyphenoxy)-1-phenylethan-1-one (3f): Chromatography solvent: petroleum ether : ethyl acetate (7:1). Spectral data are consistent with the previous reported literature.[6]



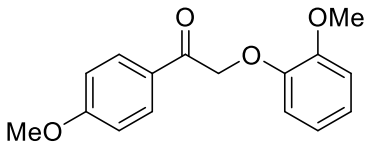
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 – 7.98 (m, 2H), 7.61 (t, *J*=7.4, 1H), 7.49 (t, *J*=7.7, 2H), 7.00 – 6.83 (m, 4H), 5.35 (s, 2H), 3.89 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.40, 150.03, 147.95, 131.59, 128.73, 127.55, 122.45, 121.08, 115.78, 113.89, 111.93, 76.20, 71.90, 55.83, 55.30.

1-(4-methoxyphenyl)-2-phenoxyethan-1-one (3g): Chromatography solvent: petroleum ether : ethyl acetate (5:1). Spectral data are consistent with the previous reported literature.[6]



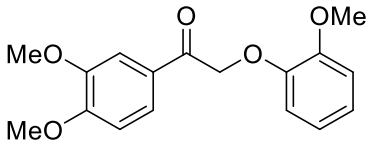
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J*=8.9, 2H), 7.31 – 7.25 (m, 2H), 7.01 – 6.92 (m, 5H), 5.21 (s, 2H), 3.88 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.13, 164.06, 158.10, 130.58, 129.58, 127.65, 121.57, 114.81, 114.02, 70.72, 55.55.

1-(4-methoxyphenyl)-2-phenoxyethan-1-one (3h): Chromatography solvent: petroleum ether : ethyl acetate (5:1). Spectral data are consistent with the previous reported literature.[6]



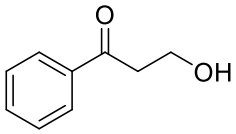
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (dd, *J*=7.0, 1.9, 2H), 6.92 (dd, *J*=16.5, 8.5, 4H), 6.84 (d, *J*=3.6, 2H), 5.28 (s, 2H), 3.88 (s, 3H), 3.86 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.14, 163.97 (s), 149.73, 147.62, 130.52, 127.70, 122.32, 120.80, 114.67, 113.97, 112.15, 71.95, 55.92, 55.53.

1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-one (3i): Chromatography solvent: petroleum ether : ethyl acetate (4:1). Spectral data are consistent with the previous reported literature.[6]



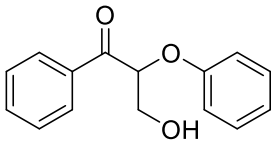
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (dt, *J*=8.4, 2.1, 1H), 7.60 (s, 1H), 6.99 – 6.94 (m, 1H), 6.94 – 6.88 (m, 2H), 6.85 (dd, *J*=3.8, 1.9, 2H), 5.30 (s, 2H), 3.96 (d, *J*=2.5, 3H), 3.94 (d, *J*=2.3, 3H), 3.89 (d, *J*=2.4, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.29, 153.81, 149.70, 149.21, 147.56, 127.83, 122.78, 122.35, 120.81, 114.61, 112.11, 110.41, 110.11, 72.00, 56.14, 56.02, 55.90.

3-hydroxy-1-phenylpropan-1-one (3j):



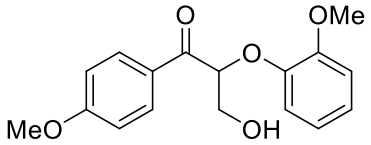
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, *J*=7.3, 2H), 7.59 (m, 1H), 7.47 (t, *J*=7.5, 2H), 4.03 (t, *J*=5.4, 2H), 3.23 (t, *J*=5.4, 2H), 2.78 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.49, 136.65, 133.53, 128.70, 128.08, 58.04, 40.44.

3-hydroxy-2-phenoxy-1-phenylpropan-1-one (3k): Chromatography solvent: petroleum ether : ethyl acetate (2:1). Spectral data are consistent with the previous reported literature.[6]



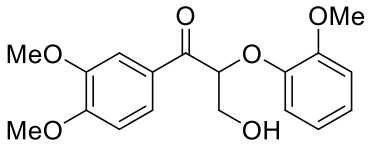
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (dd, *J*=8.3, 1.2, 2H), 7.62 (t, *J*=7.4, 1H), 7.49 (t, *J*=7.7, 2H), 7.29 – 7.23 (m, 2H), 6.98 (t, *J*=7.4, 1H), 6.90 (dd, *J*=8.7, 0.8, 2H), 5.58 (dd, *J*=6.1, 4.0, 1H), 4.15 (ddd, *J*=18.2, 12.1, 5.1, 2H), 2.00 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 196.63, 157.21, 134.68, 134.04, 129.72, 128.81, 121.99, 115.28, 81.00, 63.23.

3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one (3l): Chromatography solvent: petroleum ether : ethyl acetate (1:1). Spectral data are consistent with the previous reported literature.[5]



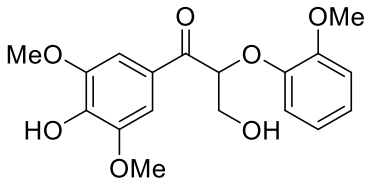
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, *J*=9.0, 2H), 7.02 – 6.98 (m, 1H), 6.94 (d, *J*=9.0, 2H), 6.93 – 6.87 (m, 2H), 6.84 – 6.79 (m, 1H), 5.39 (t, *J*=5.2, 1H), 4.06 (d, *J*=5.3, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 2.39 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 194.95, 164.05, 150.46, 146.93, 131.28, 127.88, 123.63, 121.15, 118.53, 113.97, 112.24, 84.71, 63.59, 55.80, 55.54.

1-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propan-1-one (3m): Chromatography solvent: petroleum ether : ethyl acetate (1:1). Spectral data are consistent with the previous reported literature.[1]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J*=8.6, 1H), 7.62 (s, 1H), 7.01 (t, *J*=7.6, 1H), 6.94 – 6.87 (m, 3H), 6.83 (t, *J*=7.6, 1H), 5.41 (t, *J*=5.2, 1H), 4.07 (d, *J*=5.2, 2H), 3.96 (s, 3H), 3.92 (s, 3H), 3.87 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ =194.98, 153.04, 150.33, 149.19, 146.90, 128.00, 123.63, 123.53, 121.17, 118.16, 112.24, 110.89, 110.09, 84.40, 63.74, 56.13, 55.98, 55.79.

3-hydroxy-1-(4-hydroxy-3,5-dimethoxyphenyl)-2-(2-methoxyphenoxy)propan-1-one (3n): Chromatography solvent: petroleum ether : ethyl acetate (1:1). Spectral data are consistent with the previous reported literature.[7]



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (s, 2H), 6.87 (t, *J*=7.6, 1H), 6.81 – 6.69 (m, 3H), 6.45 (s, 1H), 5.29 (t, *J*=5.1, 1H), 4.07 – 3.99 (m, 2H), 3.77 (s, 6H), 3.73 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.24, 149.95, 146.83, 146.74, 140.62, 126.19, 123.17, 121.16, 117.01, 112.18, 106.45, 84.03, 63.63, 56.35, 55.73.

6. The details for the density functional theory (DFT) calculations.

Computational Methods:

All calculations were performed using Gaussian 09[8]. Both geometry optimizations and single-point energy calculations were performed with the ωB97X-D functional[9] in 1, 4-dioxane solution using the SMD[10] solvation model. A mixed basis set of SDD[11] for transition metal (Ir) and 6-31G(d,p) for other atoms was used in geometry optimizations. Frequency calculations were carried out at the same level to confirm stationary points as minima or transition states. Single-point energy calculations were conducted using a mixed basis set of SDD for transition metal (Ir) and 6-311+G(d,p) for other atoms. All reported free energies include thermal correction to Gibbs free energy calculated at the optimized level.

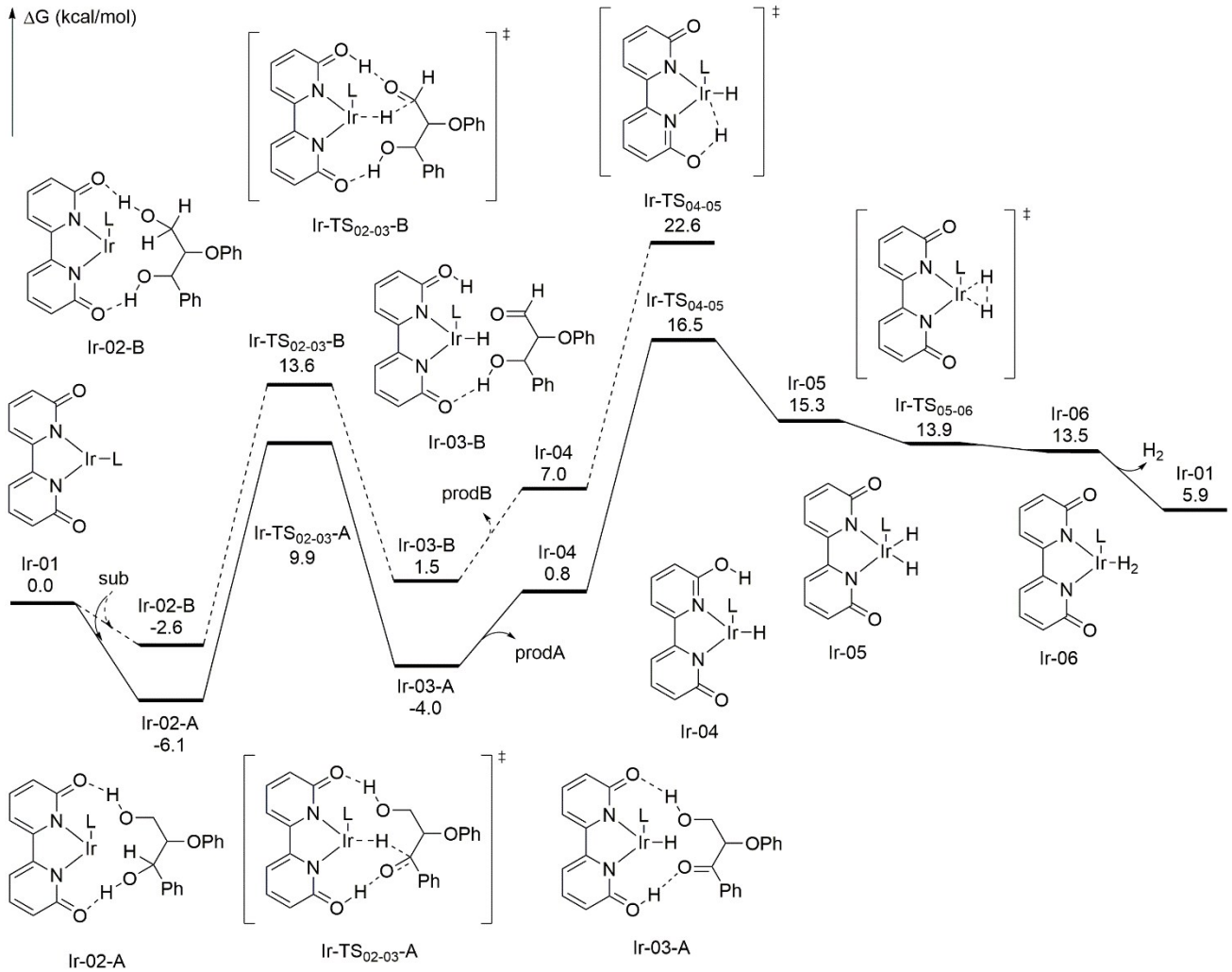


Figure S3 Full energy profile for the Ir-catalyzed dehydrogenation reaction.

The Cartesian coordinates (xyz) for all optimized structures

Ir-01

Ir	-0.36221400	-0.00282500	-0.02812300
C	1.06546200	2.67766700	-0.34691500
C	2.24388600	3.48929900	-0.11998700
C	3.44743100	2.92564300	0.16379000
C	3.57540000	1.51787300	0.24411400
C	2.45528200	0.74987100	0.07246000
C	2.46712400	-0.72730800	0.06403000
C	3.60747100	-1.47726600	0.17044100
C	3.49949300	-2.88629500	0.08490800
C	2.29229200	-3.46817000	-0.13991700
C	1.09130500	-2.67513100	-0.30505400
C	-1.99282400	0.00865900	1.36590800
C	-2.14638300	1.17417100	0.52758400
C	-2.25528500	0.71288900	-0.81289800
C	-2.24896300	-0.75514000	-0.79268200
C	-2.13863500	-1.17964000	0.55998200
C	-1.84156300	0.03011600	2.84997400
C	-2.25512900	2.57075300	1.04531100
C	-2.43276300	1.56421500	-2.02453900
C	-2.41370100	-1.64061000	-1.98141200
C	-2.24172500	-2.56279400	1.11387200
H	2.11564300	4.56119200	-0.21681000
H	4.32341700	3.55014100	0.31488000
H	4.53969700	1.06428400	0.42931100
H	4.57349300	-1.00873300	0.30079400
H	4.39300800	-3.49643200	0.18287400
H	2.17687700	-4.54134300	-0.23872700
H	-2.83123700	0.04375800	3.32072500
H	-1.29806800	0.91821300	3.17927500
H	-1.30894800	-0.85425800	3.20562900
H	-3.21337300	2.68290400	1.56617800
H	-2.19231800	3.30186300	0.24325500
H	-1.45577600	2.79589300	1.75492300
H	-3.49846800	1.75519300	-2.19392900
H	-2.03184300	1.07344300	-2.91420900
H	-1.90591800	2.50978700	-1.89362000
H	-3.47684700	-1.84431800	-2.15202000
H	-1.87958300	-2.57802900	-1.82270000
H	-2.01101300	-1.17012900	-2.88120800
H	-3.19518500	-2.66152900	1.64614100
H	-1.43541200	-2.77164800	1.82045200

H	-2.18787900	-3.31277100	0.32881200
N	1.22797200	-1.29536700	-0.10980100
N	1.21467800	1.29980200	-0.14708300
O	-0.01412300	3.16142900	-0.69928500
O	0.00445200	-3.17690900	-0.60698800

Ir-02-A

Ir	-1.85754200	-0.23141800	-0.20451800
C	-0.30326100	1.34263100	-2.29986900
C	-0.00153800	2.63169300	-2.86112600
C	-0.03006300	3.75159000	-2.08205000
C	-0.36658100	3.66817800	-0.71201100
C	-0.73978500	2.44842200	-0.21235200
C	-1.01438200	2.16607000	1.21277900
C	-0.88851600	3.08567800	2.22180800
C	-1.02847200	2.63624300	3.55252200
C	-1.24123300	1.31437400	3.82099700
C	-1.34683200	0.35168800	2.75727900
C	-3.87099000	-0.53458500	-0.76364300
C	-3.04566200	-0.97015800	-1.87745600
C	-2.21418600	-2.01761900	-1.40112100
C	-2.58105500	-2.30015100	-0.01091000
C	-3.61161100	-1.40689500	0.36991100
C	-4.91109700	0.53273000	-0.82356100
C	-3.09997500	-0.40177700	-3.25707200
C	-1.18735400	-2.78353900	-2.16391700
C	-2.04296300	-3.42947500	0.79559200
C	-4.31930000	-1.37711200	1.68460800
H	0.30609200	2.65960700	-3.89985800
H	0.24252900	4.71386000	-2.50520400
H	-0.30991800	4.54146300	-0.07599900
H	-0.65043000	4.11925100	2.00928800
H	-0.93890600	3.34897000	4.36728200
H	-1.31672000	0.93705800	4.83417000
H	-5.86850500	0.09462000	-1.12717800
H	-4.64400900	1.30414100	-1.54826300
H	-5.04681800	1.01035200	0.14913600
H	-3.91160700	-0.87744600	-3.81813700
H	-2.15672700	-0.55256300	-3.77986400
H	-3.29114700	0.67393000	-3.23064000
H	-1.56235500	-3.79221200	-2.37043700
H	-0.26061300	-2.86842700	-1.59070900
H	-0.94821400	-2.29059700	-3.10575600
H	-2.55086900	-4.35271600	0.49240700

H	-2.21662200	-3.26974300	1.85986900
H	-0.97021600	-3.55462800	0.64764300
H	-5.11087700	-2.13389000	1.69621300
H	-4.77826100	-0.40261700	1.86470700
H	-3.61887400	-1.57500000	2.49742500
N	-1.31051800	0.85213100	1.46725800
N	-0.80436200	1.33667300	-1.00934700
O	-1.45275200	-0.87813500	2.96085000
O	-0.11318100	0.26493500	-2.90359000
O	1.57876900	-1.24912700	-1.25811000
H	0.95381700	-0.73095800	-1.80585300
C	1.65751300	-0.69878400	0.03755000
H	0.64612800	-0.67699700	0.47728400
C	2.47415400	-1.67203700	0.92653800
H	2.54920000	-2.61998700	0.37898200
C	2.19867800	0.71859300	0.07674100
C	2.11370000	1.46234300	1.25678100
C	2.77782000	1.30472400	-1.04598600
C	2.60385000	2.76062500	1.31649500
H	1.64363200	1.03174400	2.13649400
C	3.25964400	2.61053100	-0.99209500
H	2.84278500	0.73449700	-1.96637100
C	3.17780400	3.34198600	0.18809800
H	2.52508000	3.32084400	2.24357100
H	3.70055700	3.05523100	-1.87921300
H	3.55818600	4.35840400	0.22950600
C	1.77926100	-1.94574000	2.26502200
H	1.68994800	-1.00900300	2.83124700
H	2.42880200	-2.60999900	2.84842600
O	0.53392500	-2.55303000	2.06148800
H	-0.18116300	-1.95200500	2.34948100
O	3.76582200	-1.20890100	1.29028900
C	4.80060700	-1.26169400	0.41200200
C	6.05645900	-0.96174600	0.95027400
C	4.68023800	-1.58183200	-0.94089500
C	7.18347100	-0.98742100	0.14172800
H	6.12480000	-0.71366100	2.00429600
C	5.82431400	-1.60487100	-1.73828400
H	3.70713700	-1.77312300	-1.37885800
C	7.07651500	-1.31289400	-1.21064500
H	8.15302100	-0.75488500	0.57247600
H	5.72172000	-1.84796700	-2.79204000
H	7.95863900	-1.33250600	-1.84280700

Ir-02-B

Ir	-2.12039900	0.08843700	-0.28034100
C	-0.79453000	2.44890000	1.15920600
C	-0.57966400	3.18649600	2.37551200
C	-0.78545700	2.60678000	3.59306700
C	-1.21052600	1.26333100	3.68356100
C	-1.45592400	0.58089300	2.51984400
C	-1.79630100	-0.85814400	2.45869100
C	-1.92746500	-1.67275500	3.55381800
C	-2.14277100	-3.05211900	3.33480000
C	-2.14244900	-3.56317700	2.06968200
C	-1.92217500	-2.71022800	0.93036800
C	-4.01949000	0.50997600	-1.10366800
C	-3.11587500	1.54910700	-1.56784700
C	-2.08578900	0.91504400	-2.30702000
C	-2.37270500	-0.52108000	-2.35975000
C	-3.58357700	-0.75982700	-1.65814100
C	-5.27143200	0.73268200	-0.32384600
C	-3.28528500	3.01173100	-1.32192800
C	-0.94639600	1.57413500	-3.00526800
C	-1.54855300	-1.51608200	-3.10377800
C	-4.31341600	-2.05547000	-1.52695900
H	-0.21508100	4.20196200	2.27460700
H	-0.59732200	3.16874500	4.50317700
H	-1.32093100	0.78278200	4.64654100
H	-1.85224200	-1.27750800	4.55819700
H	-2.27832700	-3.71216400	4.18660400
H	-2.25815000	-4.62331500	1.87711700
H	-6.09626700	0.95572000	-1.01000800
H	-5.16641400	1.57228000	0.36623100
H	-5.53917600	-0.15317600	0.25560400
H	-3.91366900	3.44542900	-2.10745900
H	-2.32077400	3.51736300	-1.30302500
H	-3.77120300	3.19403100	-0.36048000
H	-1.16842300	1.64311100	-4.07631600
H	-0.01966500	1.01259500	-2.87637500
H	-0.77937400	2.57804100	-2.61563200
H	-1.67593000	-1.35891200	-4.18071100
H	-1.84556500	-2.53497900	-2.85733200
H	-0.48678000	-1.41747800	-2.86487400
H	-5.05280700	-2.14058200	-2.33083800
H	-4.84382700	-2.11506700	-0.57360400
H	-3.62302900	-2.89655400	-1.57266600
N	-1.89271200	-1.34679300	1.18346600

N	-1.32202300	1.17411300	1.29070900
O	-1.74788700	-3.14377100	-0.22676800
O	-0.51043400	2.91013500	0.03138200
O	1.54580100	1.54904800	-1.13013500
H	0.82611300	2.08342700	-0.73685800
C	2.27562900	0.91709300	-0.10631200
H	1.72233500	0.95559000	0.84565600
C	2.36477900	-0.57572800	-0.52030900
H	2.63457900	-0.62649800	-1.58056000
C	3.62806700	1.56632300	0.11510900
C	4.35482100	1.30240900	1.27774600
C	4.18005600	2.40132900	-0.85509500
C	5.62397200	1.84219100	1.45471000
H	3.93165300	0.65258100	2.03831800
C	5.44867700	2.94666200	-0.67688000
H	3.60164900	2.61789400	-1.74701600
C	6.17690000	2.66365100	0.47521400
H	6.18260300	1.62067700	2.35927200
H	5.86860100	3.59577500	-1.44000900
H	7.16752800	3.08673000	0.61304300
C	0.99735200	-1.20180300	-0.33239600
H	0.26883900	-0.44265900	-0.66700300
H	0.84134000	-1.36106900	0.74552900
O	0.86412200	-2.38594400	-1.06572700
H	-0.02234400	-2.73730500	-0.86279100
O	3.27802900	-1.31512400	0.27498000
C	4.53079600	-1.60016100	-0.16819200
C	5.22014100	-2.56328000	0.57554500
C	5.15470100	-0.99714300	-1.26181200
C	6.51627900	-2.91781100	0.22950900
H	4.71724600	-3.02246100	1.42025800
C	6.45506100	-1.36586100	-1.59905300
H	4.65932200	-0.22145800	-1.83171400
C	7.14470900	-2.32292000	-0.86385800
H	7.03783100	-3.66809000	0.81680000
H	6.93214100	-0.88357400	-2.44721900
H	8.15939700	-2.59836800	-1.13290600

Ir-$TS_{02\text{-}03}$-A

Ir	-1.40616600	-0.46857500	-0.15775900
C	-0.41449600	1.43767200	-2.40071600
C	-0.48370000	2.66875400	-3.07729500
C	-0.88314700	3.79281500	-2.39136400
C	-1.18977900	3.70346700	-1.03237200

C	-1.15879000	2.46197700	-0.42607700
C	-1.39288500	2.24032300	1.01506900
C	-1.52263100	3.27175500	1.91669800
C	-1.65496500	2.94734600	3.27891400
C	-1.63480100	1.64046600	3.67565000
C	-1.47909300	0.57563200	2.72499300
C	-3.37380000	-0.81141800	-1.04148400
C	-2.38751200	-1.56409400	-1.80053100
C	-1.77792800	-2.50649600	-0.92546500
C	-2.36708500	-2.35727800	0.39223400
C	-3.36889200	-1.32290100	0.29592100
C	-4.28188100	0.23629000	-1.60080500
C	-2.19934700	-1.49952600	-3.28078700
C	-0.72559900	-3.48462300	-1.34309200
C	-2.19203000	-3.26348500	1.56887000
C	-4.25485000	-0.87733200	1.41301900
H	-0.16814400	2.70052100	-4.11268500
H	-0.92244600	4.75360000	-2.89418800
H	-1.45044400	4.58867500	-0.46815700
H	-1.49301800	4.30444600	1.59658200
H	-1.75885700	3.73998400	4.01418300
H	-1.71834900	1.35526600	4.71778600
H	-5.17997600	-0.22043600	-2.03147000
H	-3.78445700	0.80577900	-2.39033800
H	-4.59715200	0.94120200	-0.82810900
H	-2.95846100	-2.12981000	-3.75944600
H	-1.21500100	-1.86273400	-3.57582500
H	-2.30987900	-0.48507800	-3.66558500
H	-1.12199100	-4.16301300	-2.10580200
H	-0.38939900	-4.09338800	-0.50186900
H	0.14396000	-2.96277000	-1.75656000
H	-3.03890600	-3.95660300	1.62989300
H	-2.13452700	-2.68458800	2.49086600
H	-1.28355900	-3.86320400	1.48760100
H	-5.18311300	-1.45923200	1.40461200
H	-4.51612300	0.17901800	1.31604300
H	-3.75979500	-1.02011600	2.37432300
N	-1.39117700	0.93407000	1.39490400
N	-0.85936300	1.33717900	-1.12862400
O	-1.42759300	-0.62816400	3.07272600
O	0.08290600	0.39682400	-3.01481200
O	1.54054600	-1.01289100	-1.62939100
H	0.67931600	-0.22375600	-2.38490900
C	1.60971100	-0.67902600	-0.38609500

H	0.27632700	-0.69197300	0.12728200
C	2.25433900	-1.78044800	0.51609500
H	2.50855200	-2.58254900	-0.19017200
C	1.94577900	0.75369900	-0.03419400
C	1.81978700	1.22724800	1.27391300
C	2.36813100	1.61745400	-1.04259900
C	2.06167400	2.56551200	1.55375300
H	1.52895400	0.53544000	2.05843600
C	2.60853000	2.95938400	-0.76042300
H	2.50167300	1.23276300	-2.04805200
C	2.44332000	3.43872200	0.53533400
H	1.94307600	2.92970700	2.56968000
H	2.92603300	3.62856300	-1.55433100
H	2.62509900	4.48667300	0.75506100
C	1.38354400	-2.41083200	1.60222600
H	1.95864500	-3.25919100	1.99723300
H	0.49510000	-2.81701600	1.10976100
O	1.06215500	-1.55592400	2.65600400
H	0.11141600	-1.32022800	2.64931900
O	3.41934300	-1.31412400	1.16914800
C	4.55733200	-1.07764400	0.46341900
C	5.65139800	-0.66155400	1.22939700
C	4.69092000	-1.22911100	-0.91792500
C	6.87150300	-0.41203300	0.62003500
H	5.51780200	-0.54212000	2.29933400
C	5.92655200	-0.97507600	-1.51350500
H	3.84606500	-1.51242900	-1.53461100
C	7.02033300	-0.57097900	-0.75833500
H	7.71357900	-0.09139200	1.22642000
H	6.02377500	-1.09494000	-2.58863200
H	7.97608600	-0.37728400	-1.23448400

Ir-$TS_{02\text{-}03}$-B

Ir	1.58257600	0.00936900	-0.48529100
C	1.27139000	-2.67511600	1.00137100
C	1.69601700	-3.57581000	2.04019800
C	2.42605800	-3.13530800	3.10647500
C	2.77794100	-1.77575100	3.20729400
C	2.40529000	-0.93614600	2.18189300
C	2.64521000	0.52395700	2.21400600
C	3.40769100	1.15697600	3.17693300
C	3.49292100	2.55140200	3.15422800
C	2.77262000	3.26432700	2.22455400
C	1.99137300	2.57178000	1.27958300

C	3.37009500	0.50199000	-1.70047000
C	3.10307200	-0.88969600	-1.81217900
C	1.76881700	-1.05814400	-2.36681000
C	1.24185600	0.25745000	-2.62941400
C	2.20325500	1.22418000	-2.19903800
C	4.61276000	1.14857600	-1.17705700
C	4.00310700	-2.01941000	-1.42672600
C	1.18562600	-2.35118100	-2.83753600
C	-0.09296300	0.56162300	-3.22789100
C	2.11730900	2.69838200	-2.42977700
H	1.38800900	-4.61047800	1.94404300
H	2.72211200	-3.82756900	3.88917500
H	3.30167200	-1.40467700	4.07806300
H	3.93267700	0.58594600	3.93092700
H	4.09976000	3.07063500	3.88884900
H	2.75947200	4.34696800	2.20264100
H	5.26484000	1.45586900	-2.00211300
H	5.17732000	0.46875200	-0.53493300
H	4.37551600	2.04139900	-0.59136100
H	4.53636200	-2.39504500	-2.30667900
H	3.42721000	-2.84719300	-1.00614600
H	4.74276600	-1.71003600	-0.68517000
H	1.62852200	-2.62289000	-3.80295300
H	0.10536900	-2.26889200	-2.96713700
H	1.36641500	-3.15077500	-2.11921400
H	-0.00419300	0.67518100	-4.31390600
H	-0.49929500	1.48644400	-2.81098200
H	-0.80035400	-0.23992100	-3.00682100
H	2.49788000	2.93475400	-3.43028100
H	2.70198300	3.26016300	-1.70051300
H	1.08533900	3.04774400	-2.36651300
N	2.01450400	1.22394900	1.22879500
N	1.71871800	-1.37192700	1.09140500
O	1.26449000	3.27505000	0.44781900
O	0.54542200	-3.05360000	0.05420800
O	-1.48289600	-1.67001100	-1.01222800
H	-0.68157600	-2.14766500	-0.69583000
C	-2.16320800	-1.18906000	0.11563600
H	-1.57997700	-1.37730700	1.03040000
C	-2.31449400	0.33989300	-0.04692400
H	-2.65243500	0.55616700	-1.06516000
C	-3.52341100	-1.84921700	0.26302400
C	-4.20369800	-1.82777400	1.48157400
C	-4.13390800	-2.44130600	-0.84249400

C	-5.47986400	-2.37003400	1.58924800
H	-3.73562100	-1.37201500	2.34873200
C	-5.41173100	-2.98570100	-0.73633900
H	-3.59148000	-2.47628600	-1.78106600
C	-6.09063000	-2.94693000	0.47813200
H	-5.99867300	-2.34187800	2.54282300
H	-5.87603200	-3.44383200	-1.60493900
H	-7.08658100	-3.37154800	0.56214500
C	-1.05868000	1.16634400	0.24884500
H	-0.02809600	0.11685100	-0.14826700
H	-0.75146300	1.08539500	1.30649400
O	-0.86533500	2.24271700	-0.37610800
H	0.41867500	2.80498600	0.07518000
O	-3.21797900	0.86737600	0.92328800
C	-4.30302900	1.58632900	0.50022300
C	-4.54672600	2.79972900	1.14077800
C	-5.17835400	1.11448500	-0.47785100
C	-5.66913800	3.54603900	0.79950500
H	-3.84671800	3.14252000	1.89537500
C	-6.29274100	1.87635500	-0.81720700
H	-5.00384900	0.15242800	-0.94799500
C	-6.54437000	3.09056800	-0.18383000
H	-5.85368600	4.49258900	1.29868500
H	-6.97676600	1.50674000	-1.57524400
H	-7.41838000	3.67580400	-0.45188800

Ir-04

Ir	-0.45222700	-0.01244500	-0.35086900
C	1.04299300	2.63458800	-0.56747400
C	2.07882000	3.53141000	-0.30974500
C	3.26928400	3.02213800	0.17596400
C	3.42611800	1.64888000	0.35073700
C	2.35877700	0.81001600	0.06634500
C	2.40597700	-0.66486200	0.06425600
C	3.55768200	-1.37157200	0.32625400
C	3.51291700	-2.77303400	0.17069100
C	2.37660300	-3.37296300	-0.28482800
C	1.18969600	-2.61243500	-0.62528400
C	-1.37368100	-0.36917000	1.71285000
C	-1.70222800	0.93848200	1.27283700
C	-2.43564400	0.84913700	0.02164300
C	-2.57013400	-0.55766300	-0.29190700
C	-1.89406600	-1.29821200	0.72662800
C	-0.64998600	-0.76061400	2.96270900

C	-1.35325100	2.21374300	1.97560800
C	-3.19918200	1.96074500	-0.63622400
C	-3.37055200	-1.13798000	-1.41464000
C	-1.90528100	-2.78228900	0.89396600
H	1.92827500	4.58626100	-0.50038800
H	4.09221500	3.69329500	0.39816900
H	4.36897700	1.24135300	0.69010400
H	4.47403600	-0.87314800	0.61402000
H	4.39501000	-3.36697800	0.39406900
H	2.32130700	-4.44412500	-0.44497600
H	-1.34905500	-1.12479100	3.72446600
H	-0.10327500	0.08455200	3.38800800
H	0.07156500	-1.55806200	2.76420100
H	-2.12582500	2.46663200	2.70934800
H	-1.27225100	3.04595400	1.27308800
H	-0.40058700	2.12762000	2.50410400
H	-4.21932800	2.00603000	-0.23753300
H	-3.26983900	1.81194500	-1.71636500
H	-2.73928200	2.93633500	-0.45960700
H	-4.40061600	-1.32780100	-1.09099700
H	-2.93581400	-2.07897100	-1.75616400
H	-3.40169000	-0.45799100	-2.26859800
H	-2.76015900	-3.06051500	1.52283200
H	-0.99551900	-3.13559300	1.38241900
H	-1.97644600	-3.29353800	-0.06350400
N	1.24069300	-1.25328000	-0.31856200
N	1.16677000	1.32202000	-0.32895900
O	0.19109600	-3.12701000	-1.13998100
O	-0.11050300	3.06985600	-1.06612200
H	-0.65690400	2.26960000	-1.23046500
H	-0.30951300	-0.06380600	-1.94018900

Ir-TS_{04-05}

Ir	0.44642700	-0.12754600	-0.40174500
C	-1.26338200	-2.54120700	-0.60635100
C	-2.44549200	-3.28973500	-0.32658200
C	-3.56720100	-2.65447600	0.14540600
C	-3.58869200	-1.26183100	0.33973400
C	-2.42657000	-0.56092900	0.09882500
C	-2.28031300	0.90689400	0.08017500
C	-3.29648300	1.77462100	0.39266700
C	-3.07239200	3.15410700	0.19345000
C	-1.89129600	3.58825100	-0.32921500
C	-0.82511200	2.67199600	-0.67368300

C	1.28138100	-0.24365700	1.76938800
C	1.85153100	-1.23752300	0.89506600
C	2.58254600	-0.55482100	-0.15320800
C	2.41059700	0.85710400	0.04115900
C	1.61866500	1.03141200	1.24090800
C	0.48777900	-0.53041400	3.00414600
C	1.85489100	-2.70843900	1.16141700
C	3.46833200	-1.20446800	-1.16877700
C	3.09920400	1.94938900	-0.71241300
C	1.23805200	2.35156500	1.82520400
H	-2.43171400	-4.35390000	-0.52892500
H	-4.46720100	-3.23060800	0.33973500
H	-4.49894600	-0.75356700	0.62900700
H	-4.24800300	1.40808400	0.75539700
H	-3.85438200	3.86631800	0.44111500
H	-1.70037900	4.63844000	-0.51850500
H	1.14976900	-0.78748000	3.83844200
H	-0.19490800	-1.37010100	2.84869000
H	-0.10864200	0.33467500	3.30199400
H	2.68367100	-2.95234300	1.83554800
H	1.96468400	-3.28346700	0.24283400
H	0.92574500	-3.02563200	1.63910600
H	4.49211100	-1.26517700	-0.78374300
H	3.48474200	-0.63598500	-2.10023900
H	3.13034200	-2.21629500	-1.40052100
H	3.96686600	2.30958700	-0.14824300
H	2.40675700	2.77191600	-0.89328100
H	3.45010000	1.58977200	-1.68199800
H	1.95844800	2.62305800	2.60466700
H	0.24460700	2.32024100	2.27887300
H	1.24117600	3.12660200	1.05864800
N	-1.06355400	1.33316700	-0.37846700
N	-1.29472700	-1.20640200	-0.26858200
O	0.24512200	3.04519900	-1.17242600
O	-0.21400500	-2.99999200	-1.13125800
H	0.53394000	-1.57067300	-1.19921100
H	0.33911300	0.04152400	-1.97009300

Ir-05

Ir	-0.48033800	-0.03446100	-0.45864100
C	0.84111200	2.69659400	-0.63818700
C	1.94418400	3.57155800	-0.32481600
C	3.13009500	3.08759300	0.14557100
C	3.32038500	1.70153300	0.31672200

C	2.27308200	0.86346000	0.01718600
C	2.35547100	-0.60889000	0.04171200
C	3.49097200	-1.31750600	0.35053100
C	3.44967800	-2.72251200	0.22084600
C	2.33523900	-3.34207500	-0.26325800
C	1.16278500	-2.59253100	-0.65731700
C	-1.08561900	-0.39474700	1.72451800
C	-1.50373900	0.92434100	1.39894400
C	-2.39630000	0.84976200	0.26968200
C	-2.59359300	-0.54802000	-0.05117100
C	-1.77629100	-1.31729500	0.83495500
C	-0.15588900	-0.80155200	2.82253700
C	-1.07498600	2.19298800	2.05816000
C	-3.12990000	2.01294900	-0.31775700
C	-3.56251000	-1.09830500	-1.04909800
C	-1.79204300	-2.80242800	0.98700000
H	1.77947000	4.63086200	-0.48415300
H	3.94137100	3.77165100	0.37815400
H	4.26972400	1.30636500	0.65217700
H	4.39862300	-0.81382600	0.65527800
H	4.32620200	-3.30836900	0.48380200
H	2.29331000	-4.41515700	-0.41150400
H	-0.71987100	-1.11191400	3.70871300
H	0.50368900	0.01957600	3.11096100
H	0.47173900	-1.64120200	2.51244800
H	-1.79848300	2.46505000	2.83443400
H	-1.03004000	3.00447500	1.32983700
H	-0.09445900	2.09298500	2.52790200
H	-3.91896200	2.34011200	0.36782900
H	-3.59278200	1.74684100	-1.26975100
H	-2.43814800	2.83731100	-0.49939800
H	-4.54171400	-1.24010300	-0.57907100
H	-3.22127800	-2.06098900	-1.43368000
H	-3.68612800	-0.42248300	-1.89719400
H	-2.59891400	-3.07733900	1.67652100
H	-0.85195700	-3.17072800	1.40010200
H	-1.94470800	-3.30167600	0.03217100
N	1.20633500	-1.23015500	-0.35300400
N	1.06737700	1.34229800	-0.40453400
O	0.17866900	-3.09883000	-1.20725400
O	-0.25137900	3.10118900	-1.06661500
H	-0.78683500	0.82126900	-1.74639500
H	-0.50090500	-0.75255800	-1.86069800

Ir-TS$_{05\text{-}06}$

Ir	0.47384800	-0.06431800	-0.42768600
C	-1.24682200	-2.55646800	-0.65440300
C	-2.45491500	-3.26516300	-0.30017200
C	-3.55323300	-2.60989200	0.17664200
C	-3.54354100	-1.20747400	0.33276200
C	-2.37903500	-0.53677300	0.04563100
C	-2.24121500	0.93360400	0.03379800
C	-3.25628900	1.81384700	0.32299100
C	-3.00763000	3.19070300	0.14469200
C	-1.80615900	3.62559000	-0.33604800
C	-0.74351700	2.70366500	-0.65907900
C	1.05634400	-0.21481600	1.72421900
C	1.64624400	-1.32119700	0.99768900
C	2.53527900	-0.78279400	0.01459600
C	2.51799100	0.66215300	0.13708400
C	1.64379600	0.99516500	1.22205200
C	0.10745900	-0.33406400	2.87500600
C	1.44298200	-2.76571000	1.31716500
C	3.40725200	-1.58197500	-0.90117000
C	3.34886500	1.63775900	-0.63382400
C	1.39001700	2.36866900	1.74640200
H	-2.45342800	-4.33688400	-0.46341700
H	-4.45583500	-3.16604500	0.41464300
H	-4.43445100	-0.67519400	0.63846800
H	-4.22426700	1.45937700	0.65167000
H	-3.78998000	3.90815600	0.37599800
H	-1.60427100	4.67694200	-0.50600000
H	0.64500800	-0.56444500	3.80113800
H	-0.62269300	-1.12874300	2.70204200
H	-0.44318200	0.59640000	3.02810100
H	2.22520300	-3.09511700	2.01035200
H	1.46686500	-3.37966800	0.41801900
H	0.47609600	-2.92725600	1.79835300
H	4.37585400	-1.76764700	-0.42467200
H	3.58712000	-1.05572600	-1.84066900
H	2.94614700	-2.54272600	-1.13609900
H	4.22205500	1.94346600	-0.04734800
H	2.75488500	2.51978000	-0.88148300
H	3.70476800	1.19741000	-1.56748500
H	2.08538300	2.57063800	2.56876800
H	0.37308300	2.46784000	2.13273800
H	1.52982300	3.11742100	0.96708400
N	-1.01691400	1.36690700	-0.38090800

N	-1.25297500	-1.19614900	-0.34989700
O	0.35131900	3.04963300	-1.12842300
O	-0.26056900	-3.09201800	-1.17830100
H	0.51789300	-0.76585000	-1.86237300
H	0.61160500	0.51514400	-1.91275700

Ir-06

Ir	0.48069600	-0.01860700	-0.37368100
C	-1.08190900	-2.61418600	-0.66379800
C	-2.24360100	-3.40382500	-0.32741100
C	-3.38808400	-2.82333500	0.13982800
C	-3.47338100	-1.42394900	0.30084500
C	-2.35170700	-0.67784400	0.02591900
C	-2.30570400	0.80122200	0.02926400
C	-3.37139300	1.61652100	0.32907100
C	-3.20220100	3.00740800	0.16323000
C	-2.03349700	3.51552300	-0.32867500
C	-0.92708200	2.65589400	-0.67718100
C	1.06170200	-0.04548600	1.69260700
C	1.65835200	-1.21403400	1.06946400
C	2.52960600	-0.77005700	0.03631100
C	2.54157400	0.68990300	0.05167800
C	1.67931700	1.12394200	1.09668400
C	0.14766000	-0.05208800	2.87673800
C	1.41639300	-2.62785000	1.48142900
C	3.34850400	-1.65032200	-0.85301700
C	3.36830600	1.58438800	-0.81649600
C	1.46162100	2.53401700	1.53339000
H	-2.16809600	-4.47355000	-0.48675700
H	-4.25275400	-3.43953400	0.37129100
H	-4.39912400	-0.95247300	0.60365900
H	-4.31481600	1.20380200	0.66112800
H	-4.02084000	3.67725500	0.41203200
H	-1.89541000	4.57840800	-0.49120400
H	0.72116600	-0.09739200	3.80897500
H	-0.52492200	-0.91235300	2.85026500
H	-0.46930700	0.84882400	2.90180800
H	2.18105300	-2.92516100	2.20757400
H	1.44370800	-3.29998500	0.62446200
H	0.43912700	-2.73785600	1.95611100
H	4.32095500	-1.85492900	-0.39230000
H	3.52689600	-1.17979700	-1.82228800
H	2.83704300	-2.59781500	-1.03092500
H	4.28267300	1.88510300	-0.29386500

H	2.80369100	2.48018100	-1.08336600
H	3.65916600	1.08094000	-1.74089800
H	2.21095800	2.79276600	2.28964700
H	0.47327400	2.66248800	1.97977700
H	1.53892700	3.22300500	0.69301700
N	-1.11171300	1.31016600	-0.38280900
N	-1.18469100	-1.25958800	-0.36814800
O	0.13259300	3.05676900	-1.18552400
O	-0.04722000	-3.08056200	-1.16641400
H	0.47311300	-0.45565800	-2.06457400
H	0.50488200	0.40773600	-2.06719500

7. Degradation of the lignin model compound 2m and native lignin:

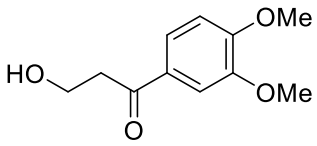
Degradation of the lignin model compound 2m through one pot of two-step (HCOOH/HCOONa):

After completion of the dehydrogenation reaction of lignin model compound **2m**, the reaction solution was cooled to room temperature. Then 3 eq. HCOONa and 1 mL HCOOH were directly added to the reaction tube, and the reaction solution was stirred at 110 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature for HPLC analysis.

Degradation of the lignin model compound 2m via one pot of two-step (Zn/NH_4Cl):

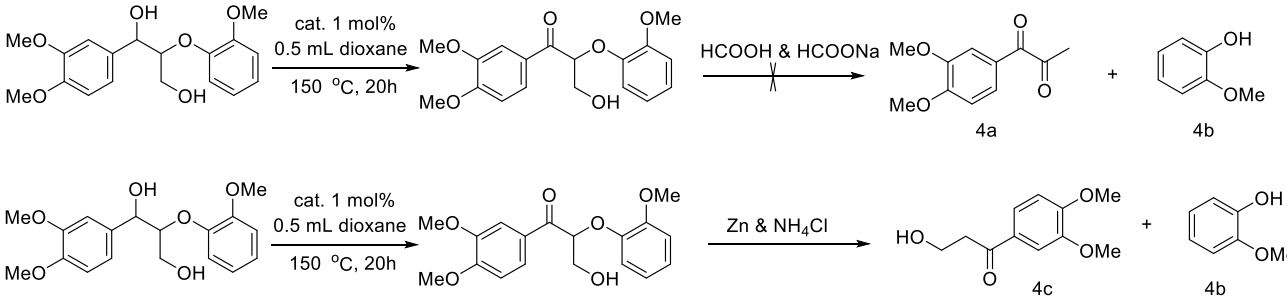
After completion of the dehydrogenation reaction of lignin model compound **2m**, the reaction solution was cooled to room temperature. Then the pH of the reaction system was adjusted to weak acid (5~6) with 0.5 N HCl. And 5 eq. Zn and NH_4Cl were directly added to the reaction tube, and the reaction solution was stirred at 80 °C for 1 h. After completion of the reaction, the reaction mixture was cooled to room temperature for HPLC analysis.

1-(3,4-dimethoxyphenyl)-3-hydroxypropan-1-one:



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (dd, *J*=8.4, 2.0, 1H), 7.53 (d, *J*=1.9, 1H), 6.91 (d, *J*=8.4, 1H), 4.03 (t, *J*=5.3, 2H), 3.96 (d, *J*=5.9, 6H), 3.21 (t, *J*=5.3, 2H), 2.35 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.17, 153.67, 149.11, 129.93, 123.01, 110.05, 109.87, 58.35, 56.13, 56.01, 39.82.



Degradation of native lignin via one pot of two-step (Zn/NH_4Cl):

After completion of the dehydrogenation reaction of native lignin, the reaction solution was cooled to room temperature. Then the pH of the reaction system was adjusted to weak acid (5~6) with 0.5 N HCl. And 5 eq. Zn and NH_4Cl were directly added to the reaction tube, and the reaction solution was stirred at 80 °C for 1 h. After completion of the reaction, the reaction mixture was cooled to room temperature for GPC analysis.

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9. NMR spectrum