Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Stepwise Degradation of Hydroxyl Compounds to Aldehydes via Successive C–C Bond Cleavage

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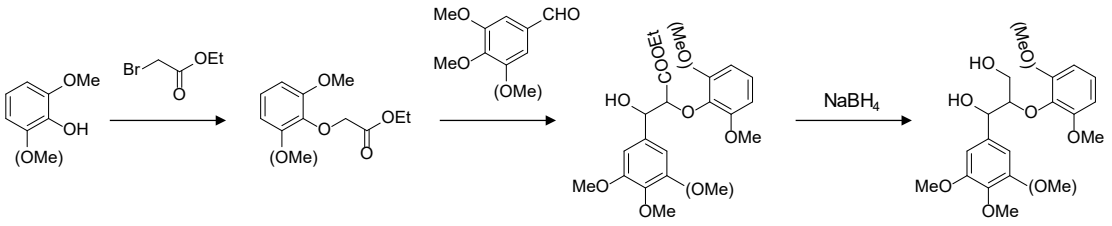
Experimental Procedures

Chemicals: Commercially available compounds (purity: >99.5%) were purchased from Sigma-Aldrich, Acros, J&K, or Alfa Aesar and used as received, unless stated otherwise. Specifically, extra dry (AcroSeal) methyl sulfoxide (DMSO), tetrahydrofuran (THF), diisopropylamine were purchased from Acros. *n*-Butyllithium solution (2.0 M in cyclohexane) was purchased from Sigma-Aldrich. 1-phenylethanol (**1a**), 1-(4-methylphenyl)ethanol (**1d**), 1-[4-(trifluoromethyl)phenyl]ethanol (**1f**), 1-(4-biphenylyl)ethanol (**1g**), 1-(4-methoxyphenyl)ethanol (**1i**), 1-(3-methoxyphenyl)ethanol (**1j**), 1-(2-methoxyphenyl)ethanol (**1k**), 1-(4-chlorophenyl)Ethanol (**1l**), 1-(3-chlorophenyl)ethanol (**1m**), 1-(2-chlorophenyl)ethanol (**1n**), 1-(2,4-diethoxyphenyl)ethanol (**1r**), 2-chloro-1-phenylethanol (**1s**), 1,2-ethanediol (**1t**), 2-phenoxy-1-phenylethanol (**1u**), 1-phenyl-1-propanol (**1v**), 1-phenyl-1-hexanol (**1w**), 1-phenyl-2-propanol (**1y**), 4-phenyl-2-butanol (**1z**), 2-phenylethyl alcohol (**1aa**), 4-phenylbutan-1-ol (**1bb**), 6-phenyl-1-hexanol (**1cc**), 8-phenyl-1-octanol (**1dd**), phenetole (**1ee**), 2-phenoxyethanol (**1ff**), 4-phenoxybutanol (**1gg**) were obtained from Sigma-Aldrich or Acros. Other alcohol substrates were synthesized according to the following procedure.

Synthesis of alcohol substrates: The alcohols were synthesized by reduction of corresponding aldehydes or ketones with sodium borohydride. Typically, aldehydes or ketones (15 mmol) was dissolved in 100 mL THF. $NaBH_4$ solution (30 mol $NaBH_4$ in 20 mL water) was added into the THF solution dropwise. Then the cloudy mixture was stirred at room temperature until the substrate was fully consumed. Subsequently, 100 mL saturated aqueous NH_4Cl was added to quench the reaction. The aqueous phase was extracted with ethyl acetate for three times (3×100 mL). The organic phase was washed three times with brine, dried with anhydrous Na_2SO_4, concentrated *in vacuo* to yield the corresponding alcohols. Further purification was conducted using gel column chromatography if necessary.

Synthesis of β-O-4 type lignin oligomers: As shown in the following equation, β-O-4 type lignin oligomer model compounds were synthesized via three steps according to previous work.[1] For example, 2-(2,6-dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)propane-1,3-diol (**3c**) was synthesized according to the following procedure, others were synthesized in the same way unless using different starting materials.



A **B** **C** **D**

Preparation of **B**: 2,6-dimethoxyphenol (4.63 g, 30 mmol), ethyl bromoacetate (5.02 g, 30 mmol) and K_2CO_3 (9.30 g, 60 mmol) were added into 50 mL acetone. The mixture was refluxed at 60 °C for 14 h. After cooled to room temperature, the mixture was filtered and concentrated *in vacuo* to yield the solid product **B** (Ethyl 2-(2,6-dimethoxyphenoxy)acetate).

Preparation of **C**: veratraldehyde (1.66 g, 10 mmol) and **B** (2.64 g, 11 mmol) were dissolved in 30 mL toluene and dried by azeotropic distillation thrice. Then the solid mixture was dissolved in dry THF (12 mL) and cooled to -78 °C. Freshly prepared lithium diisopropylamide (LDA) solution was added dropwise into the mixture at -78 °C, and the reaction mixture was kept stirring at -78 °C for 2 h. After warmed to 0 °C, the reaction was quenched by 100 mL saturated aqueous NH_4Cl. The aqueous phase was extracted with ethyl acetate (3×100 mL). The organic phase was washed thrice with brine, dried with anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified using silica gel column chromatography, generating colorless oil **C**. LDA solution was prepared using the following procedure: a solution of diisopropylamine (1.11 g, 11 mmol) in THF (18 mL) was cooled to -78 °C, *n*-butyllithium solution (2.0 M in cyclohexane, 5.5 mL) was added at -78 °C. The LDA solution was obtained after warmed to 0 °C,

Preparation of **D**. the product **D** was generated by the reduction of **C** with sodium borohydride, following the same procedure for the synthesis of alcohol substrates as described above.

General procedure for Oxidative degradation reaction. In a typical experiment, desired amounts of alcohol substrate, $PdCl_2$, CuCl, internal standard and DMSO was mixed under O_2 atmosphere (oxygen balloon was used). Different *n*-alkanes were used as internal standard, according to the boiling point of reactants and products. Then the mixture was heated in an oil bath to targeted temperature, and kept stirring for a desired time. After reaction, the reactor was quenched in ice-water bath, followed by addition of ethyl acetate and saturated brine. Subsequently, the organic matter was extracted using ethyl acetate twice, and combined for qualitative and quantitative analysis. For HPLC analysis, the ethyl acetate solution was concentrated *in vacuo* and re-dissolved in DMSO.

Characterization methods: The qualitative analysis of products was conducted using GC-MS (Agilent 5975C-7890A, equipped with a mass detector) and by comparing with authentic samples. The conversion and yields of corresponding aldehyde products were quantitatively analyzed using GC (Agilent 7820, equipped with a hydrogen flame-ionization detector, full electric pneumatic control, 280 °C) based on internal standard curves and areas of integrated peak area. The qualitative analysis of gas products was conducted using GC (Agilent 7820 equipped with a thermal conductivity detector). The acid products were quantitatively analyzed by high

performance liquid chromatography (HPLC). HPLC traces were recorded by the Agilent 1260 Infinity II LC system equipped with a refractive index detector. NMR spectra were recorded on a Bruker Avance 400 or Bruker Avance 600 spectrometer equipped with 5 mm pulsed-field-gradient (PFG) probes. The resonance band of TMS or solvents was used as the internal standard. The spectra were recorded at 303 K. NMR spectra were analyzed and presented using MestReNova software.

Results and Discussion

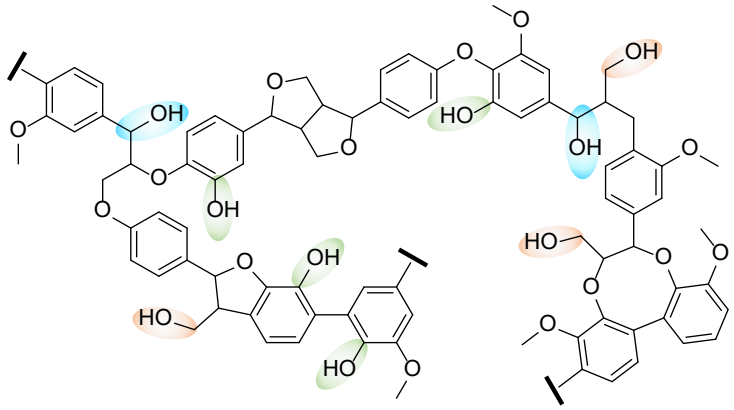


Figure S1. Representative structure of native lignin.[2] Three types of hydroxyl groups are highlighted by different colors.

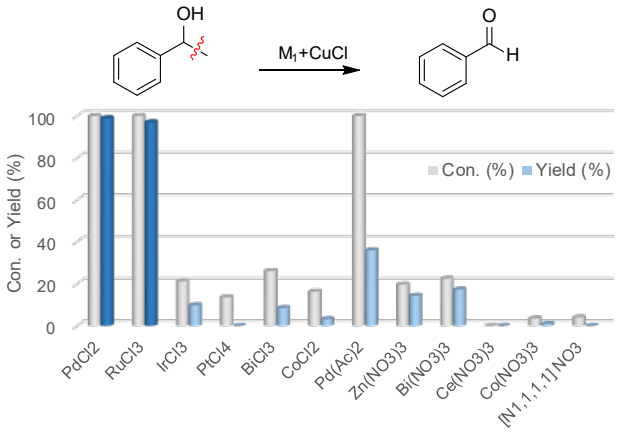


Figure S2. Catalyst screening for the oxidative conversion of 1-phenylehtanol to benzaldehyde. Tested anhydrous inorganic salts include $PdCl_2$, $RuCl_3$, $IrCl_3$, $PtCl_4$, $BiCl_3$, $CoCl_2$, $Pd(OAc)_2$, $Zn(NO_3)_2$, $Bi(NO_3)_3$, $Ce(NO_3)_3$, $Co(NO_3)_3$ and tetramethylammonium nitrate ($[N_{1,1,1,1}]$ NO_3). Reaction conditions: 0.5 mmol 1-phenylethanol, 20 mol% metal salt 1, 30 mol% metal salt 2, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C, 10 h. Yield and conversion were determined by gas chromatography (GC).

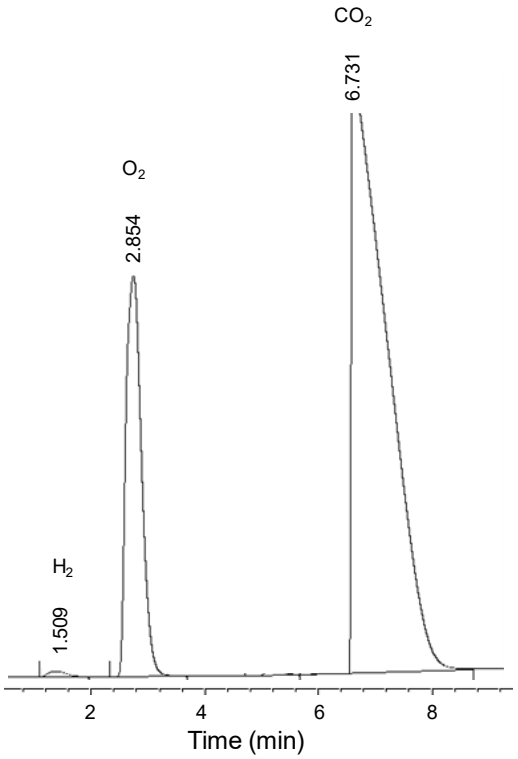


Figure S3. Qualitative GC analysis of the gaseous product released during the conversion of 1-phenylethanol to benzaldehyde (the reaction in Table 1, entry 1). It was found that H_2 and CO_2 were released during the reaction, which is similar to previous work in that H_2 and CO_2 were produced during the degradation of secondary alcohols.[3] Reaction conditions: 0.5 mmol 1-phenylethanol, 20 mol% $PdCl_2$, 30 mol% CuCl, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C, 10 h.

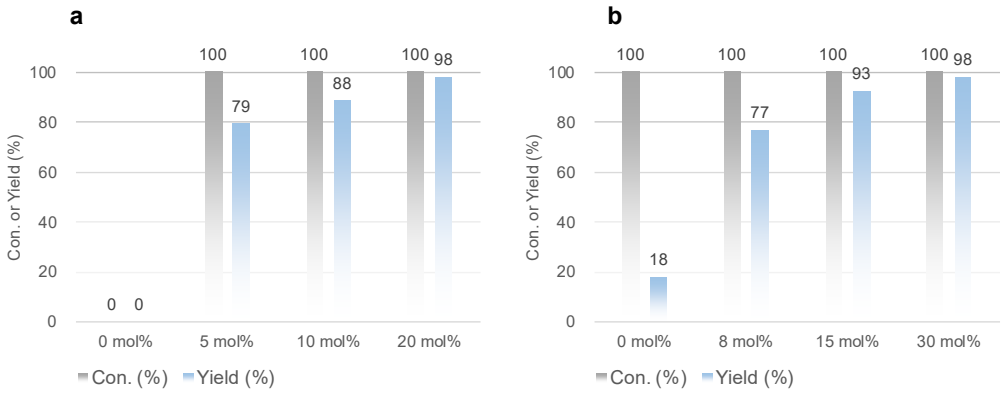
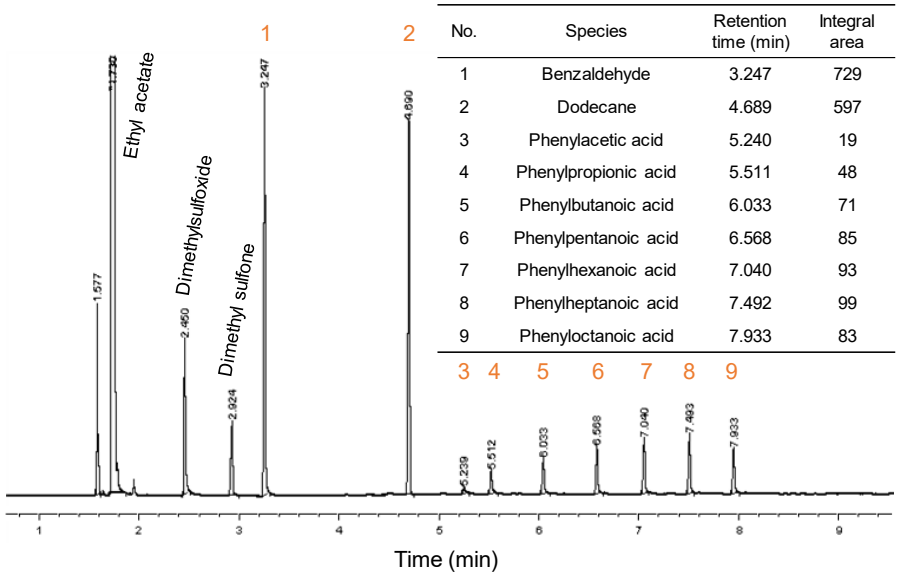


Figure S4. Optimization of the relative amounts of $PdCl_2$ and CuCl in the catalytic system for the conversion of 1-phenylethanol to benzaldehyde. (**a**) Effect of $PdCl_2$ amount (from 0 mol% to 20 mol%) on the reaction. The amount of CuCl is 30 mol%. (**b**) Effect of CuCl amount (from 0 mol% to 30 mol%) on the reaction. The amount of $PdCl_2$ is 20 mol%. The optimized catalyst contains 20 mol% $PdCl_2$ and 30 mol% CuCl. Reaction conditions: 0.5 mmol 1-phenylethanol, 0-20 mol% $PdCl_2$, 0-30 mol% CuCl, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C, 10 h.

Moreover, we studied the effects of amounts and relative ratios of the two metal salts ($PdCl_2$ and CuCl) on the reaction (Fig. S4). In the absence of $PdCl_2$, CuCl did not show any catalytic activity for the reaction (Fig. S4a). In the absence of CuCl, **1a** could also be fully converted whereas the yield of benzaldehyde is only 18%, under identical reaction conditions (Fig. S4b). By varying the relative amounts of $PdCl_2$ and CuCl, the catalyst combination was optimized (20 mol% $PdCl_2$ and 30 mol% CuCl).



No.	Species	Retention time (min)	Integral area
1	Benzaldehyde	3.247	729
2	Dodecane	4.689	597
3	Phenylacetic acid	5.240	19
4	Phenylpropionic acid	5.511	48
5	Phenylbutanoic acid	6.033	71
6	Phenylpentanoic acid	6.568	85
7	Phenylhexanoic acid	7.040	93
8	Phenylheptanoic acid	7.492	99
9	Phenyloctanoic acid	7.933	83

Figure S5. GC trace of the products obtained from oxidative degradation of 8-phenyl-1-octanol (Table 2, **1dd**). The main product benzaldehyde and carboxylic acids with various carbon chain lengths were detected and summarized in the insert table.

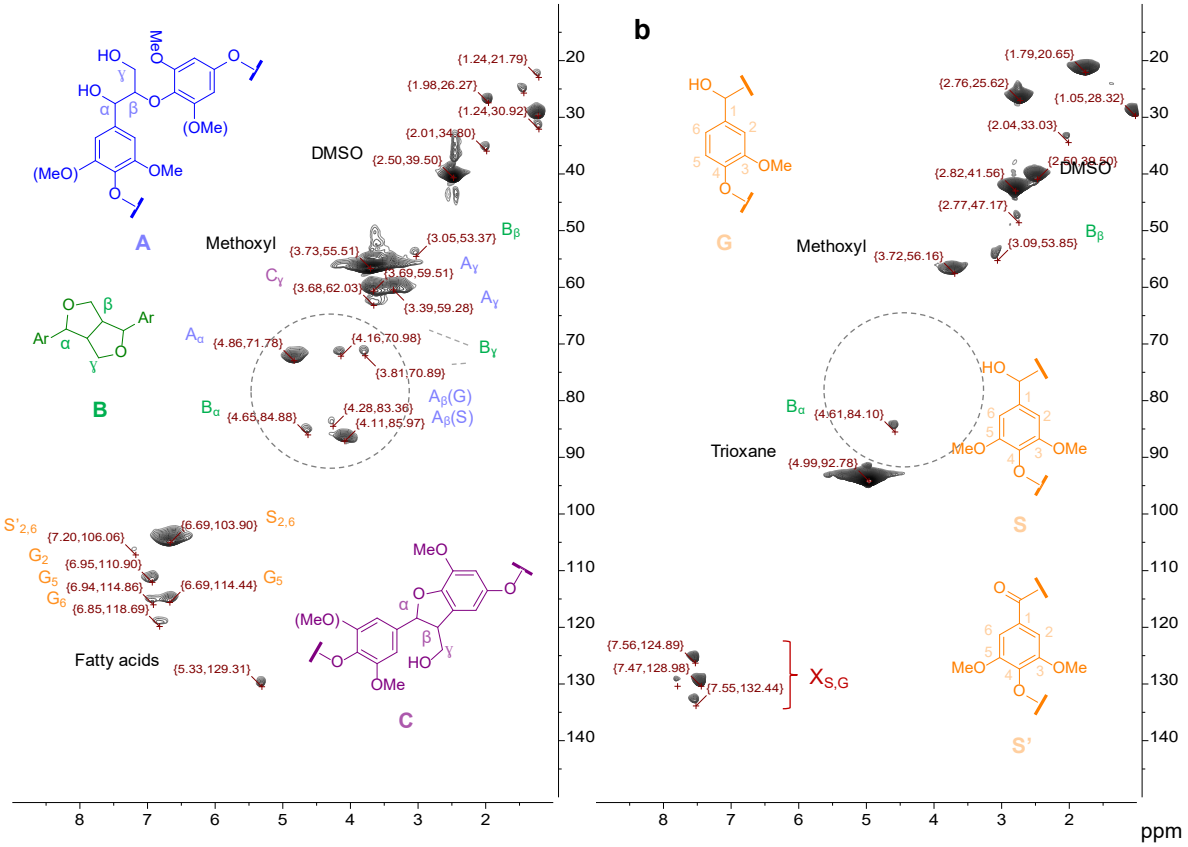


Figure S6. Full 2D HSQC NMR spectra of the cellulolytic enzyme birch lignin before (**a**) and after degradation (**b**). The Contours are labeled according to the presented linkage structures. DMSO (**a**, δ_H/δ_C, 2.50/39.50 ppm) or trioxane (**b**, δ_H/δ_C, 5.00/92.78 ppm) was used as internal standard. Signals of $X_{S,G}$ are assigned to S and G unit of the probable carboxyl and aldehyde group rich products. Reaction conditions: 100 mg Poplar lignin powder, 20 mol% $PdCl_2$, 30 mol% CuCl, 2 mL DMSO-d_6, 1 atm O_2, 120 °C, 12 h.

Table S1. Assignments of the resonance signals shown in 2D HSQC NMR spectra.

No.	Label	δ_H/δ_C (ppm)	Assignments
1	A_α	4.86/71.75	C_α-H_α in β-O-4 substructures linked to a S unit (A)
2	A_β(G)	4.28/83.36	C_β-H_β in β-O-4 substructures linked to a G unit (A)
3	A_β(S)	4.11/85.85	C_β-H_β in β-O-4 substructures linked to a S unit (A)
4	A_γ	3.70/59.51, 3.39/59.29	C_γ-H_γ in β-O-4 substructures (A)
5	B_α	4.65/84.85	C_α-H_α in β-β (resinol) substructures (B)
6	B_β	3.05/53.37	C_β-H_β in β-β (resinol) substructures (B)
7	B_γ	4.16/70.98, 3.81/70.89	C_γ-H_γ in β-β (resinol) substructures (B)
8	C_γ	3.68/62.03	C_γ-H_γ in phenylcoumaran substructures (C)
9	G_2	6.95/110.90	C_2-H_2 in guaiacyl units (G)
10	G_5	6.94/114.86, 6.69/114.44	C_5-H_5 in guaiacyl units (G)
11	G_6	6.85/118.69	C_6-H_6 in guaiacyl units (G)
12	$S_{2,6}$	6.69/103.90	$C_{2,6}$-$H_{2,6}$ in syringyl units (S)
13	$S'_{2,6}$	7.20/106.06	$C_{2,6}$-$H_{2,6}$ in oxidized syringyl units (S')
14	Methoxyl	3.70/55.57	C-H in methoxyls
15	DMSO	2.50/39.50	C-H in methyl of DMSO
16	Trioxane	5.00/92.78	C-H of -CH_2- units

Mechanism study

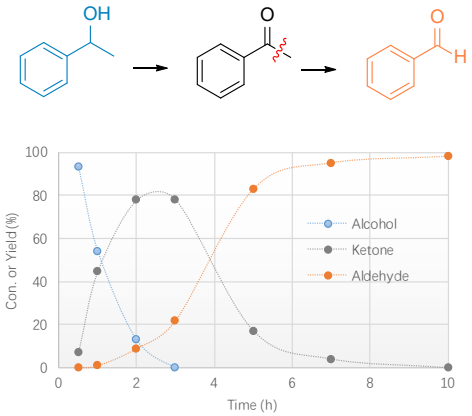


Figure S7. Time-course product distributions for the oxidative degradation of 1-phenylethanol. Reaction conditions: 0.5 mmol 1-phenylethanol, 20 mol% metal salt 1, 30 mol% metal salt 2, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C, 10 h. Yield and conversion were determined by GC.

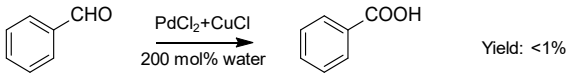


Figure S8. Stability of benzaldehyde in the reported catalytic system. Reaction condition was the same to that shown in Table 1, expect additional water was added. Trace amount of benzoic acid (yield: <1%) was generated. Reaction conditions: 0.5 mmol substrate, 20 mol% $PdCl_2$, 30 mol% CuCl, 200 mol% H_2O, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C, 24 h. Yield was determined by GC.

It has been reported that benzaldehyde could stay stable in Cu[4] or Pd[5] catalyzed oxidative systems, under similar reaction conditions. Nucleophilic attack of carbonyl group by external hydroxyl group and following β-hydride elimination is essential for oxidizing aldehyde substrates to acids.[6] Additional alkaline or other additives are generally necessay for this transformation. For instance, selective aerobic oxidation of alcohols to aldehydes or acids could be mediated by the addition of KOH in Ag-NHC Complex catalyzed reactions.[7] The addition of KOH is crucial for generating acids. While in our neutral Pd/Cu catalyzed system without any additives, benzaldehyde is stable under given reaction conditions (Fig. S8).

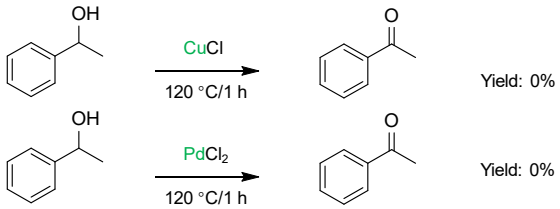


Figure S9. The catalytic activity of individual CuCl or $PdCl_2$ for the oxidative conversion of 1-phenylethanol to acetophenone was investigated. None of them could catalyze the reaction under given reaction conditions. Reaction conditions: 0.5 mmol substrate, 20 mol% $PdCl_2$ or 30 mol% CuCl, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C, 1 h. Yield was determined by GC

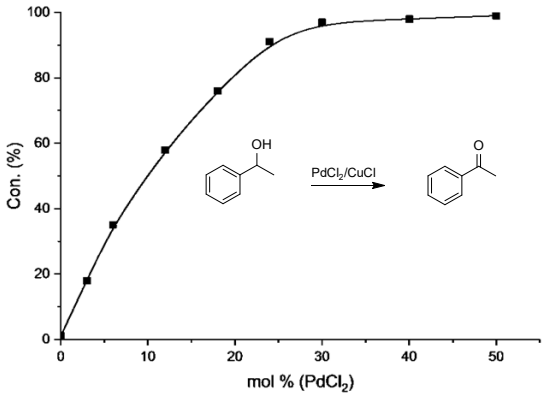


Figure S10. Effect of $PdCl_2$ concentration on the conversion of the oxidation of 1-phenylethanol to acetophenone. Reaction conditions: 0.5 mmol substrate, 0-50 mol% $PdCl_2$, 30 mol% CuCl, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C, 1 h. Yield was determined by GC.

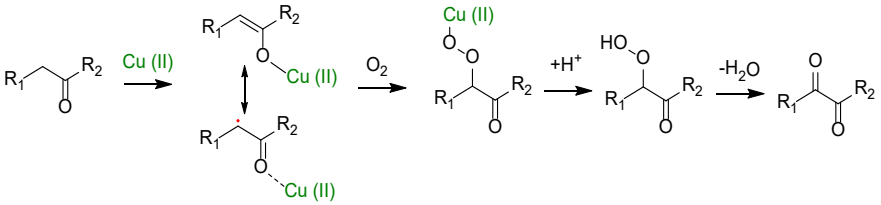


Figure S11. Cu catayzed transformation of carbonyl componds to dicarbonyl componds.[8]

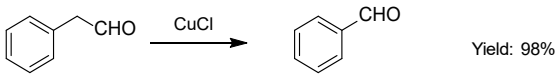


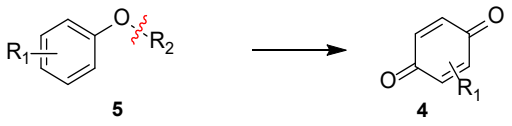
Figure S12. Transformation of phenylacetaldehyde to benzaldehyde. Reaction conditions: 0.5 mmol substrate, 30 mol% CuCl, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C, 10 h. Yield was determined by GC.

Herein, we also investigated the reactivities of phenoxy group containing phenolic esters (**5a-f**) and aliphatic alcohols (**5g-i**) in the catalytic system (Table S2). In the presence of carbonyl and hydroxyl functional group, the C−C bonds in the substrates could also be cleaved. The substrate was oxidatively degraded via C−C cleavage, finally affording benzoquinone in relatively high yields ranging from 55% to 97%. On contrast, in the absence of hydroxyl group on the carbon chain, the C−C bond of phenetole (**5g**) cannot be cleaved in the applied catalytic system.

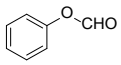
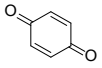
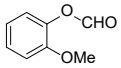
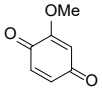
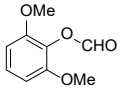
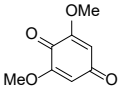
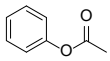
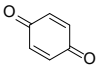
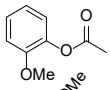
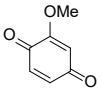
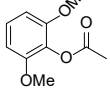
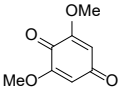
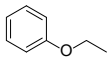
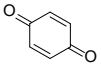
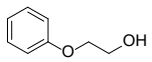
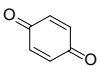
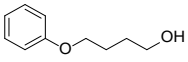
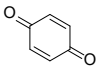
For the phenoxy substituted aliphatic alcohols (**5g-i**), the substrates were transformed to phenolic esters followed by decomposition to phenols (Fig. S13, Table S2). Then phenols were quickly converted to benzoquinones catalyzed by CuCl.[9] For verification, we conducted the oxidative reaction of phenol in the catalytic system, and it was quickly converted to benzoquinone in 1 h at 100 °C in the catalytic system (yield: 95%, Fig. S14). In addition to benzoquinone, phenoxy group containing aliphatic acids were generated under given conditions (Figure S15). Since benzoquinone tends to form oligomers and/or polymers in the presence of O_2 and Cu-containing species, the overall yields of benzoquinone is not very high in these cases (Table S2).[9]

As a kind of polyhydroxy compound, β−O−4 linkages of lignin model oligomers were first degraded into phenolic ester and aldehyde parts by the cleavage of C_α−C_β bonds. During the reaction, phenolic esters were further converted to phenols and benzoquinones finally by cleavage of C−O bonds (Table 3, Fig. S16).

Table S2. The oxidative degradation of phenolic esters to benzoquinones.



5 **4**

	Substrate	Reaction time		Product	Yield
5a:		2 h	**4a:**		95%
5b:		2 h	**4b:**		97%
5c:		2 h	**4c:**		94%
5d:		24 h	**4a:**		67%
5e:		24 h	**4b:**		69%
5f:		24 h	**4c:**		64%
5g:		24 h	4a:		n.p.
5h:		6 h	4a:		74%
5i:		6 h	4a:		55%

Reaction conditions: 0.5 mmol substrate, 30 mol% CuCl, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 120 °C. Yield was determined by GC.

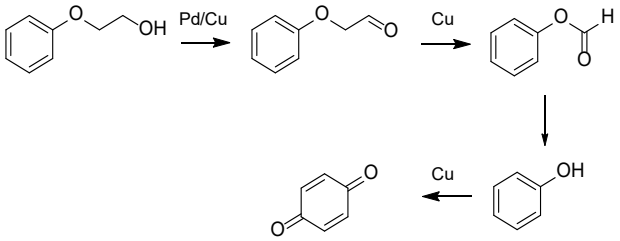


Figure S13. Possible transformation pathway from 2-phenoxyethanol (**5h**) to benzoquinone (**3a**).[9]

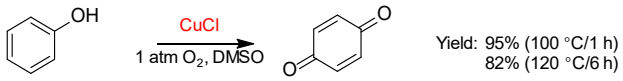
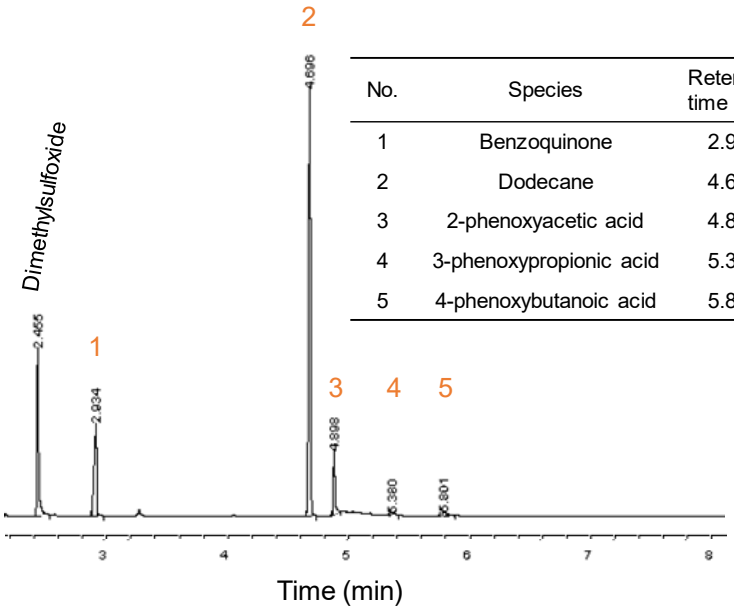


Figure S14. Oxidation conversion of phenol to benzoquinone. The yield of benzoquinone decreased with the increasing of reaction temperature, owning to the generation of oligomers and/or polymers. Reaction conditions: 0.5 mmol phenol, 30 mol% CuCl, 2 mL DMSO, 0.5 mmol internal standard, 1 atm O_2, 100-120 °C. Yields were determined by GC.



No.	Species	Retention time (min)	Integral area
1	Benzoquinone	2.934	251
2	Dodecane	4.696	699
3	2-phenoxyacetic acid	4.898	103
4	3-phenoxypropionic acid	5.380	9
5	4-phenoxybutanoic acid	5.801	20

Figure S15. GC trace of the products obtained from oxidative degradation of 1-phenoxy-4-butanol (**5i**). The products including acids with various carbon chain lengths were detected and summarized in the insert table.

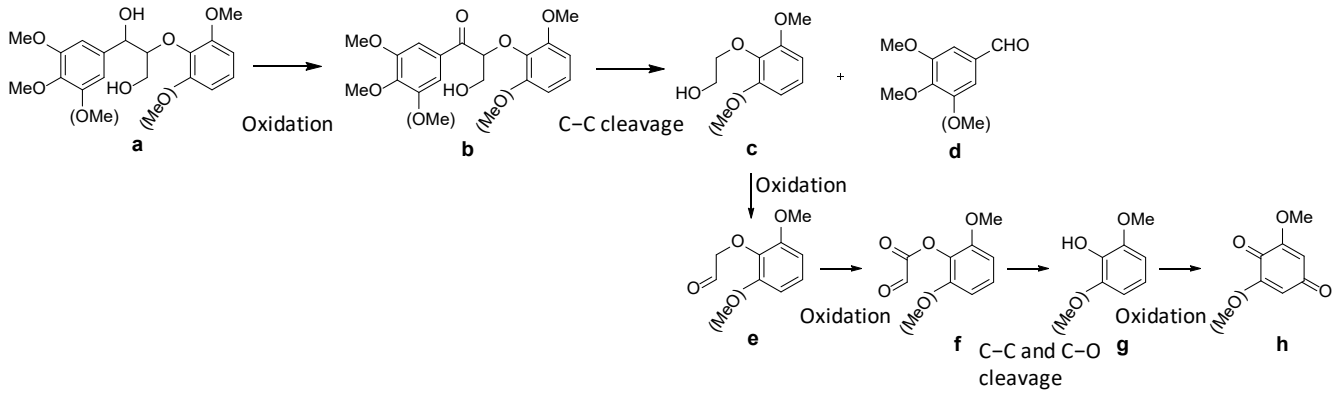


Figure S16. Possible transformation pathway for cleavage of β-O-4 linkages in lignin oligomers.

For the oxidative transformation of β-O-4 type lignin model compoundss (**a**), the benzyl hydroxyl was first oxidized to carbonyl group catalyzed by Pd/Cu catalyst. 1,2-hydride shift of carbonyl compond (**b**) initiated the first C−C bonds cleavage, followed by the generation of benzyl aldehyde (**d**) and phenoxyl substituted alcohols (**c**). As primary alcohols, **c** was oxidized to **f**. Further C-C and C-O bond cleavage affords phenols (**g**), which was further transformed to benzoquinones (**h**) in the applied catalytic system.

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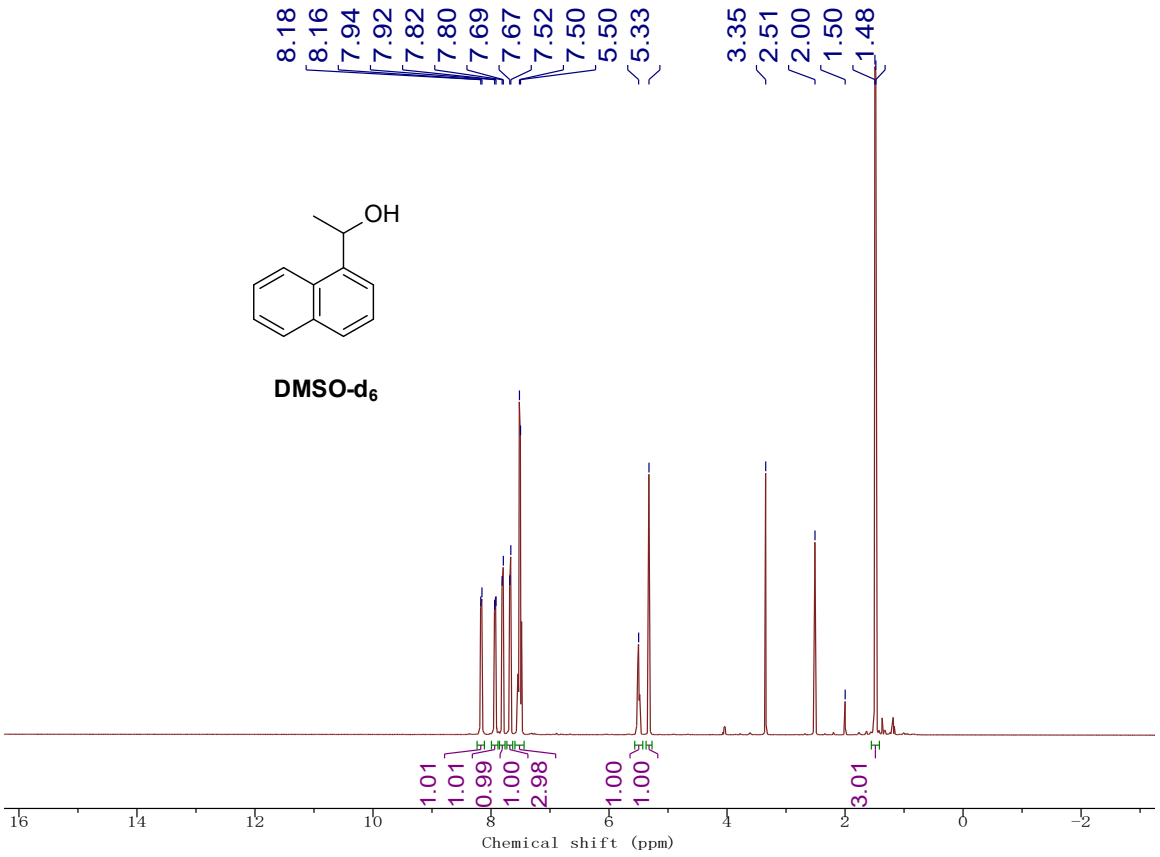
NMR Spectra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2.51
2.00
1.50
1.48
OH
DMSO-d6
1.01
1.01
0.99
1.00
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4
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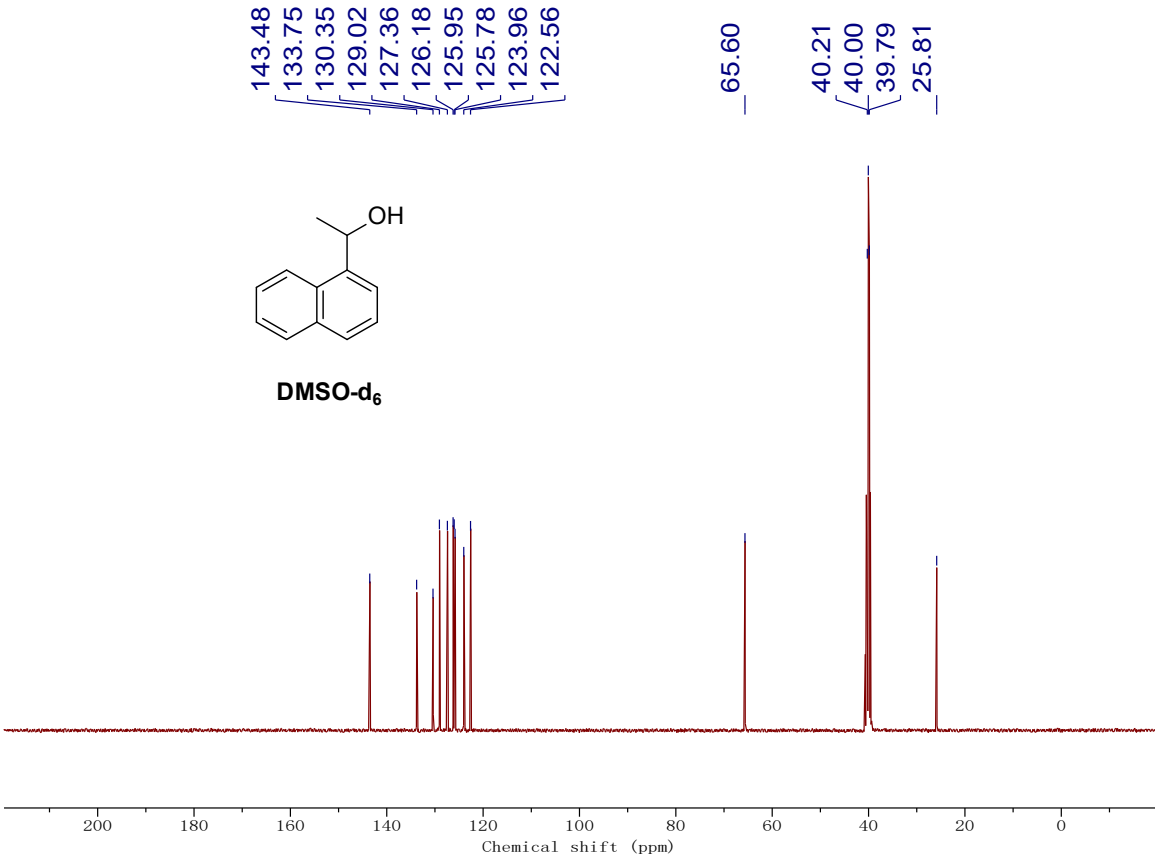
Chemical shift (ppm)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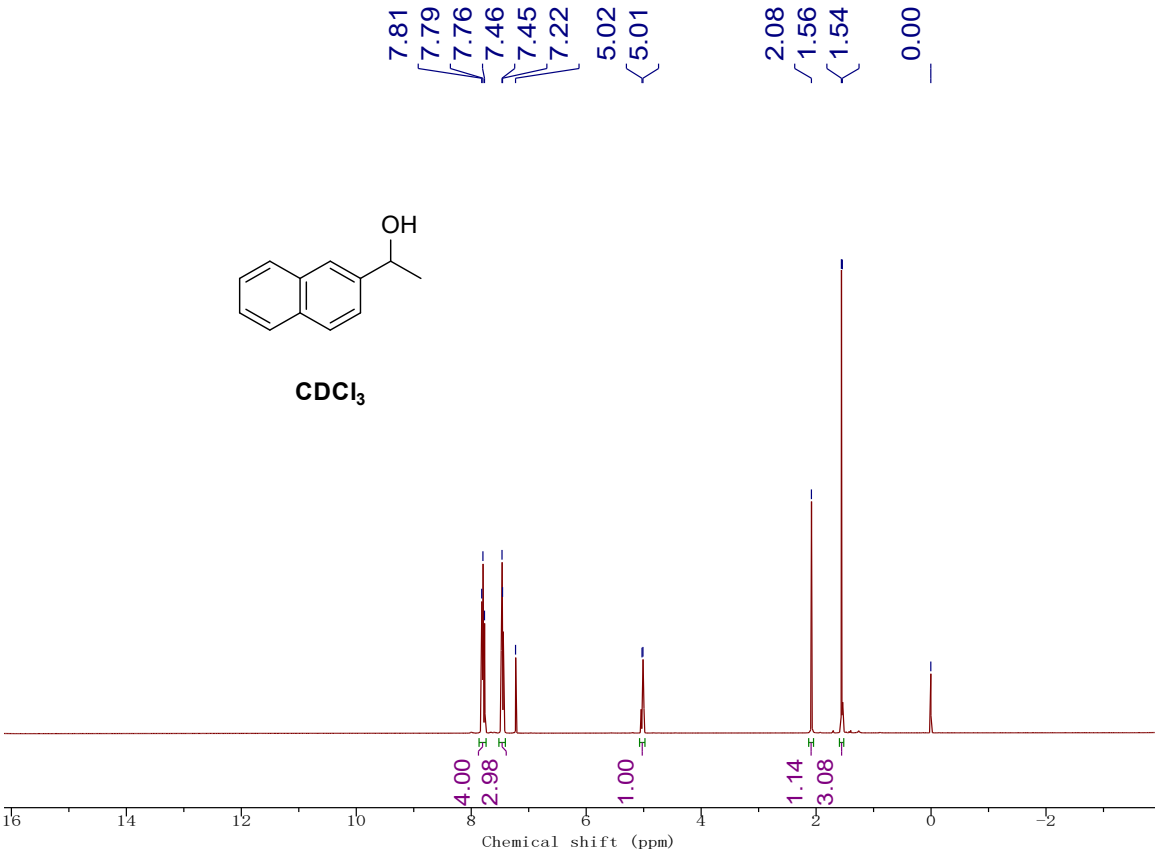
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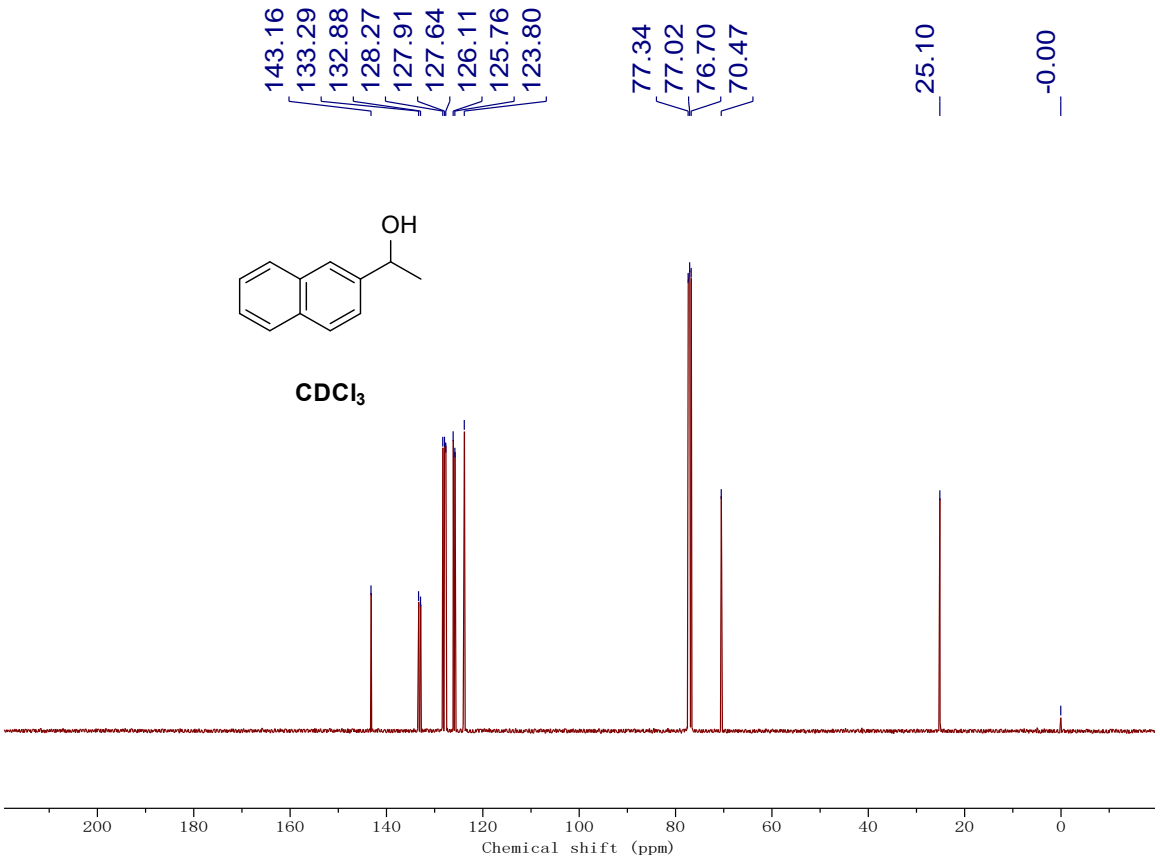
Chemical shift (ppm)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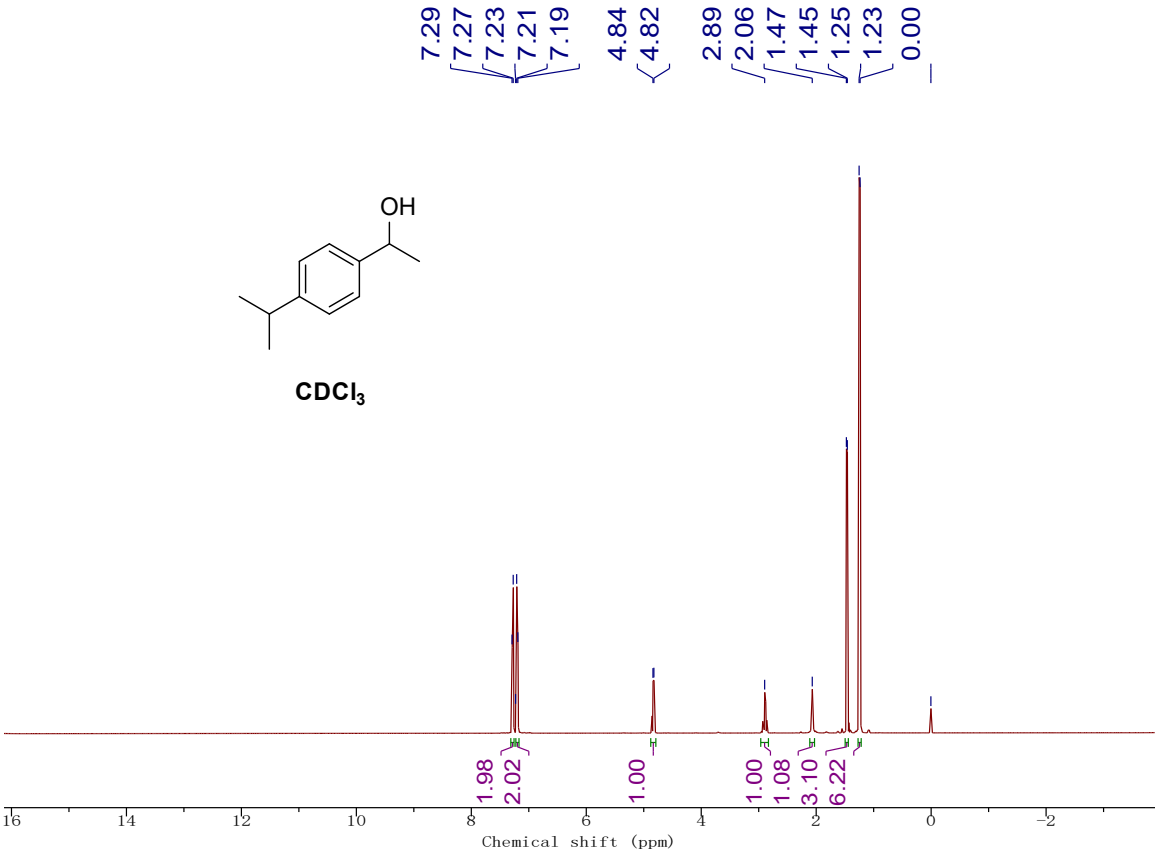
Chemical shift (ppm)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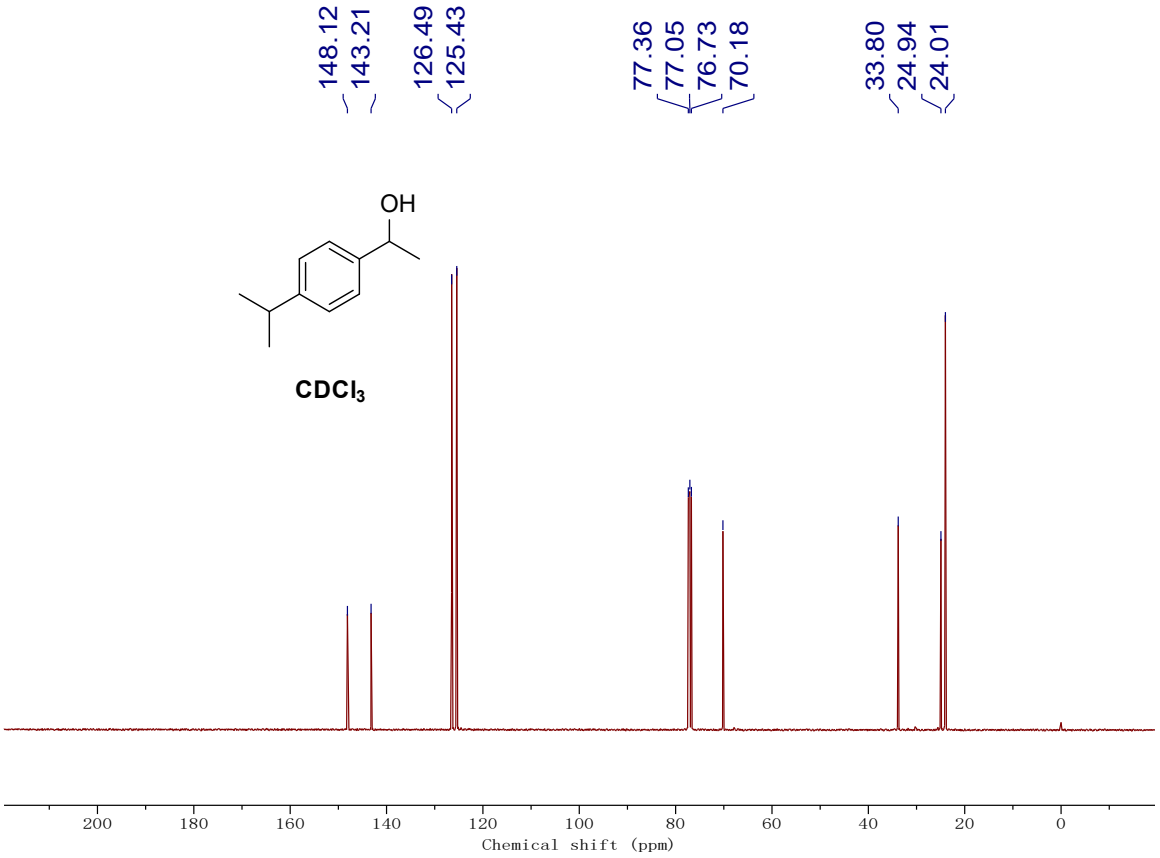
Chemical shift (ppm)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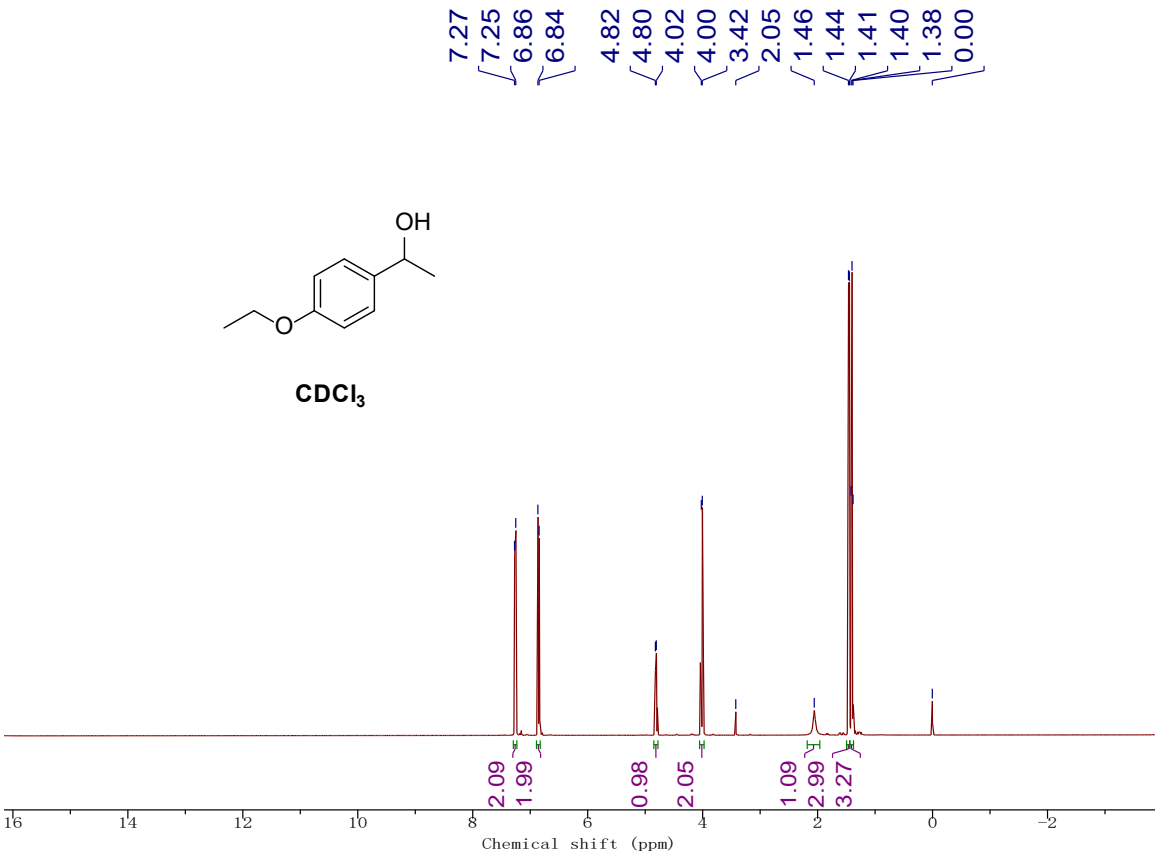
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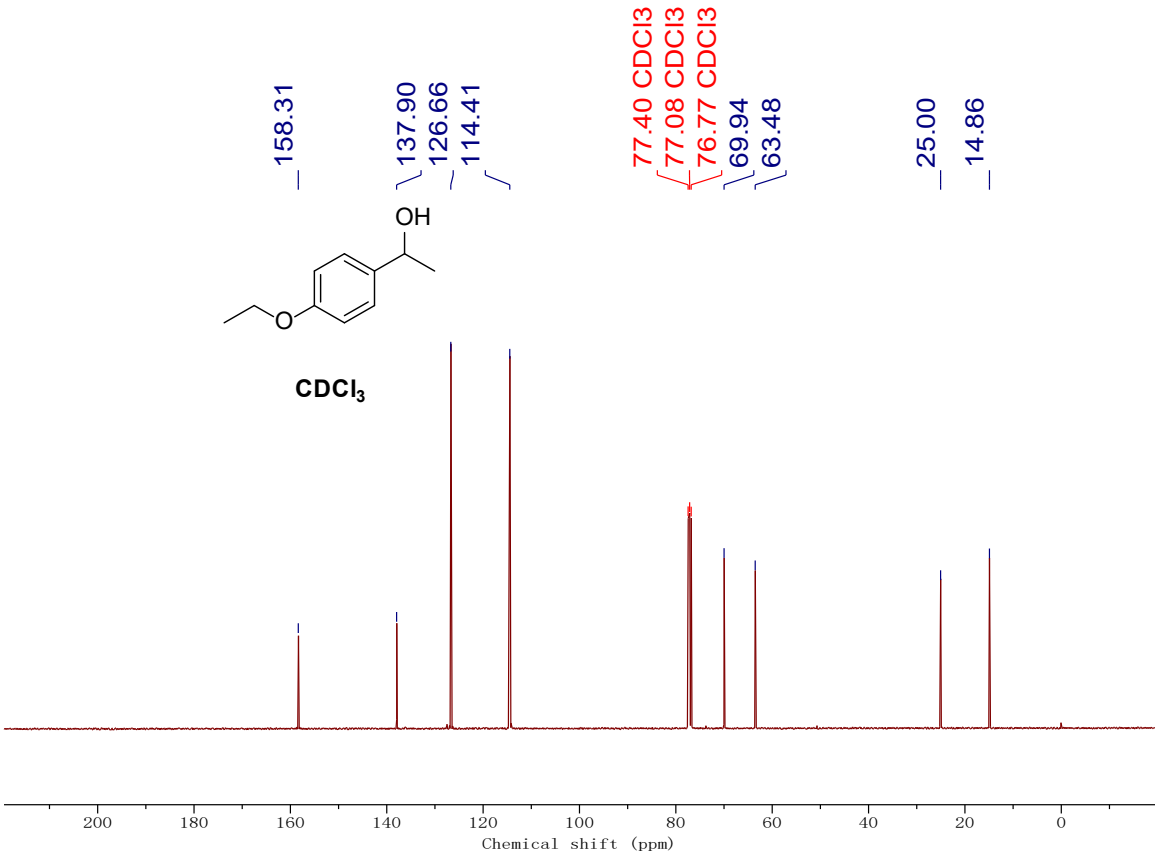
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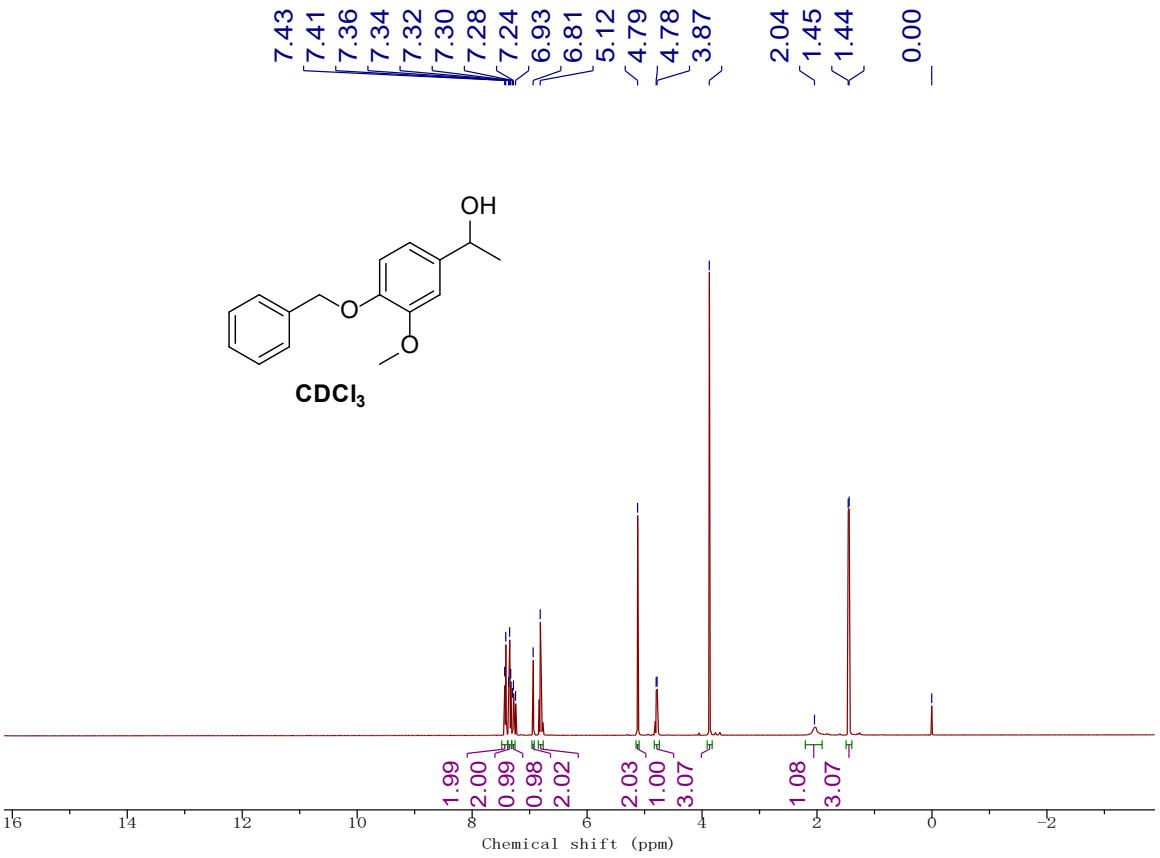
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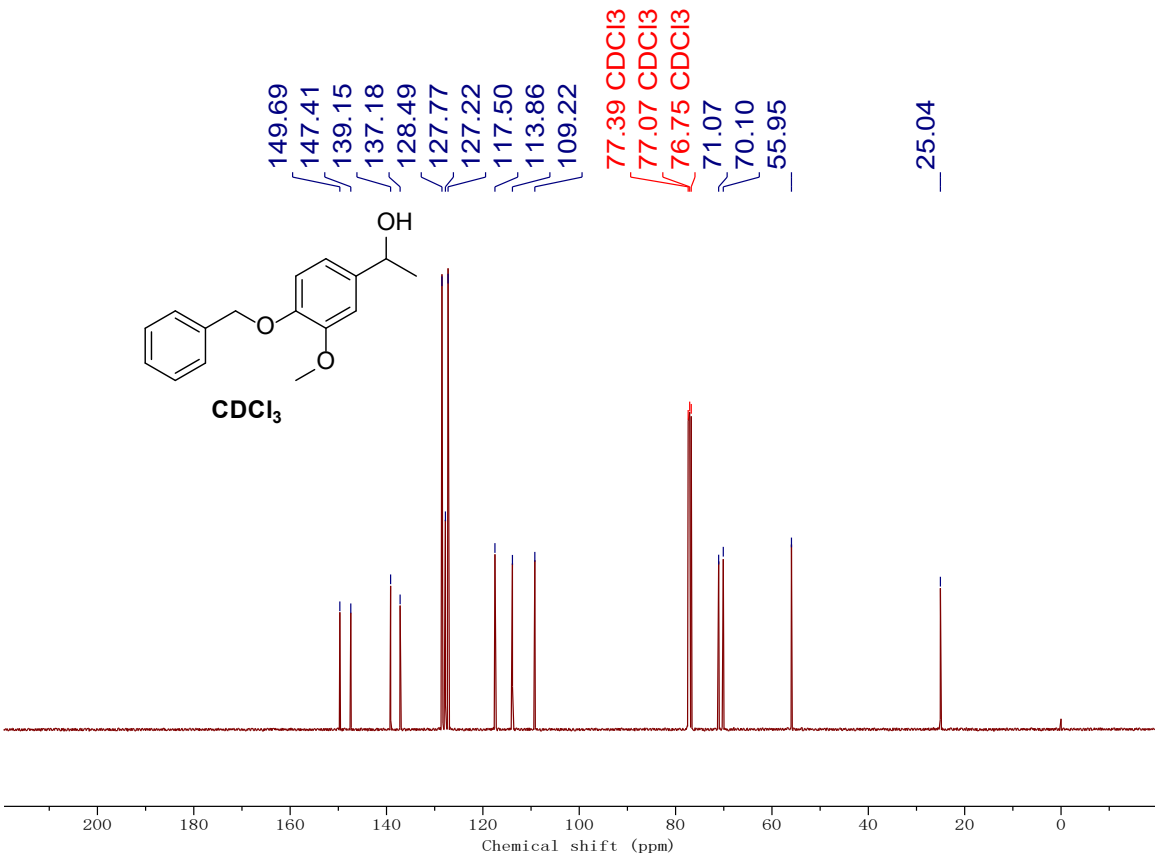
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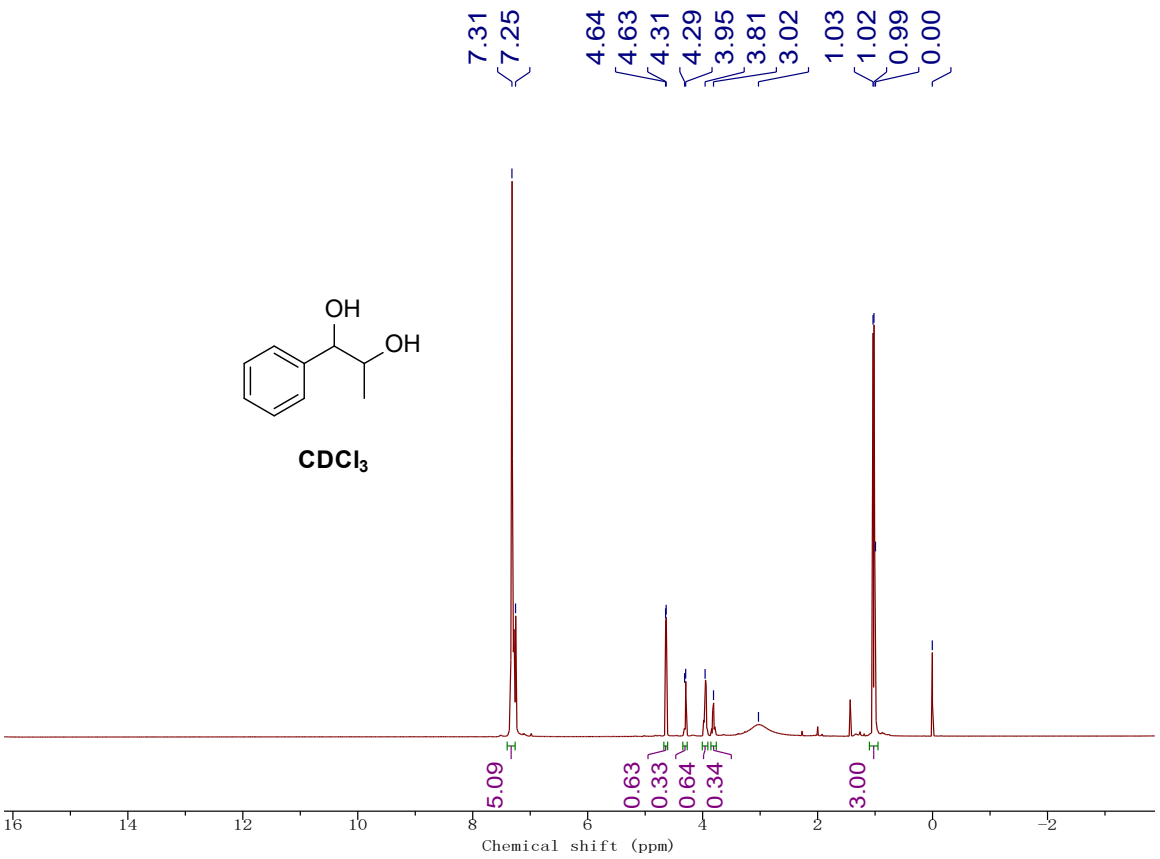
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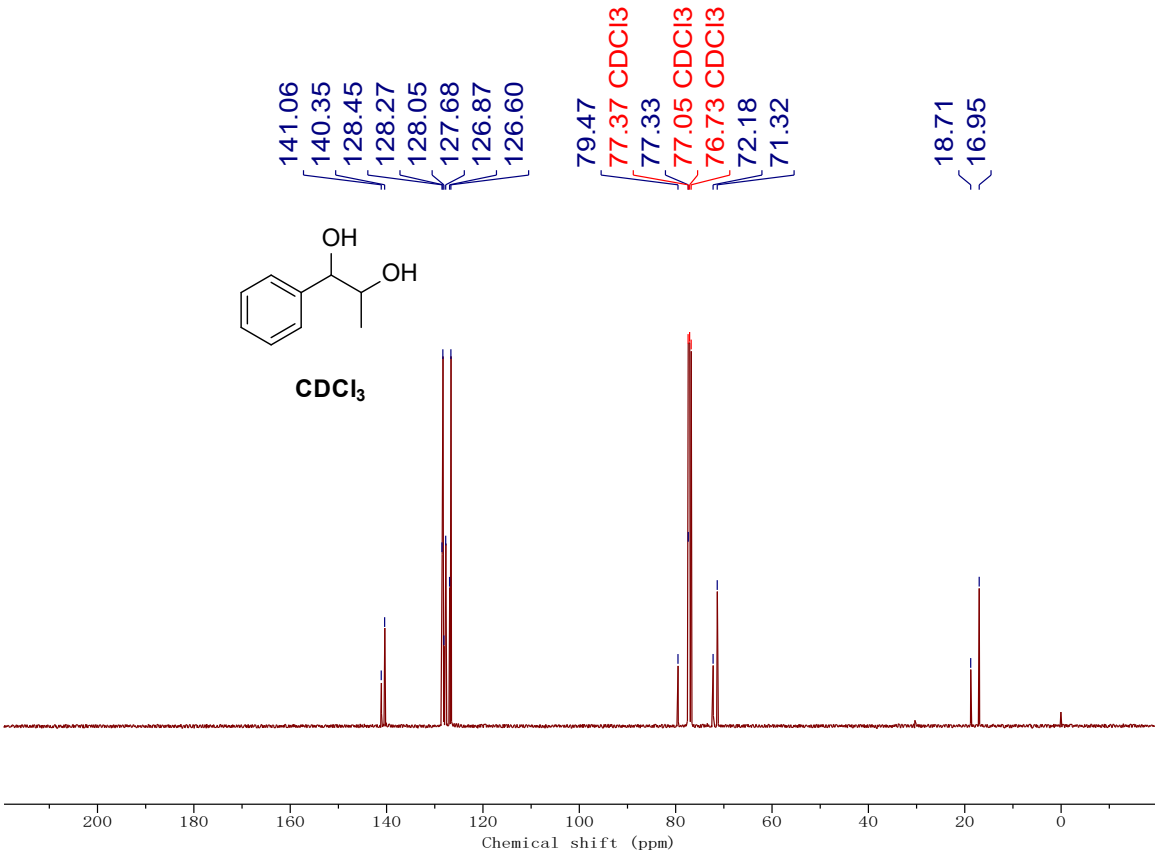
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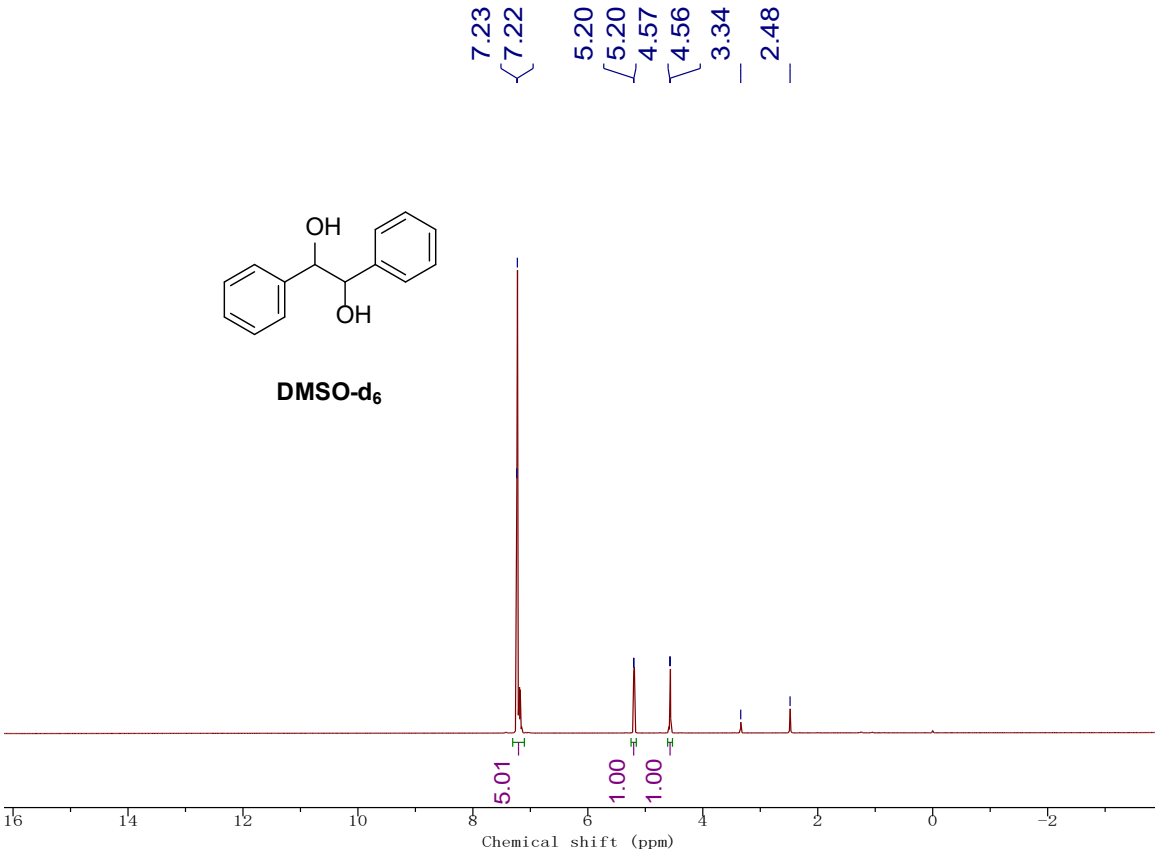
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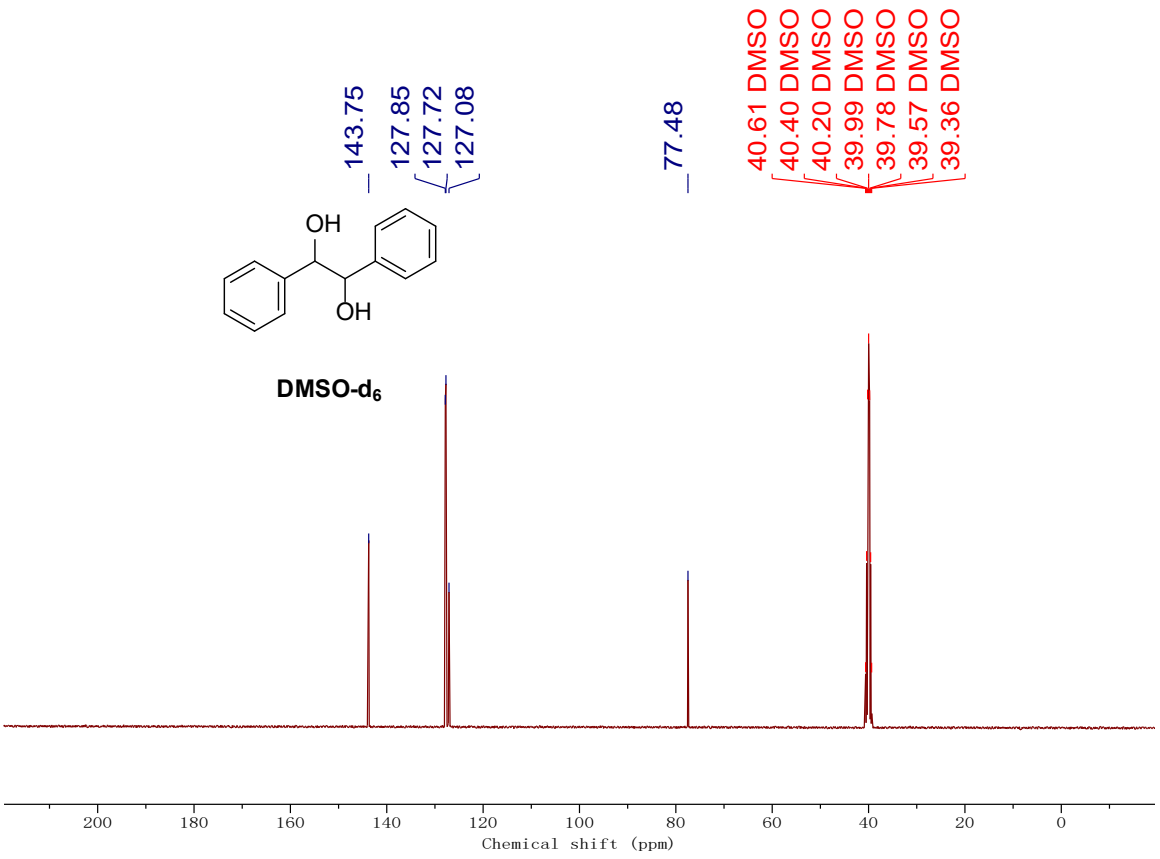
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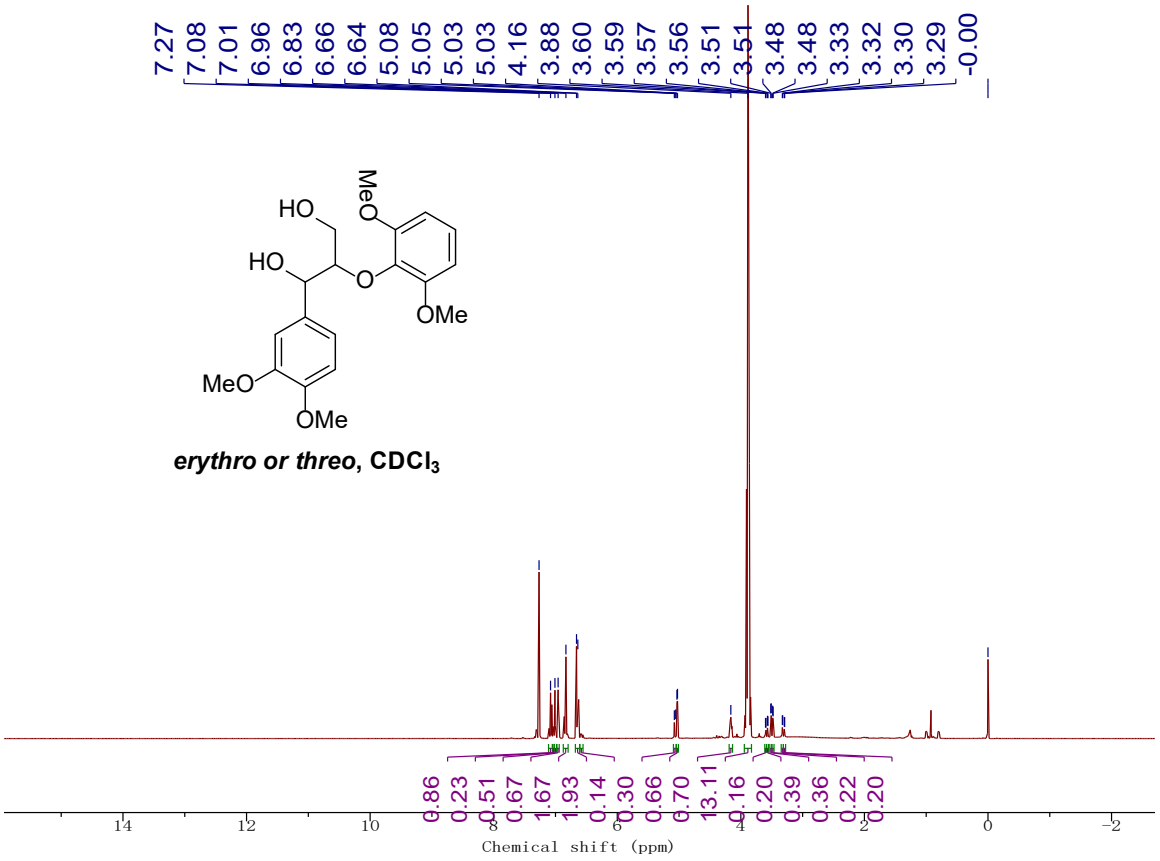

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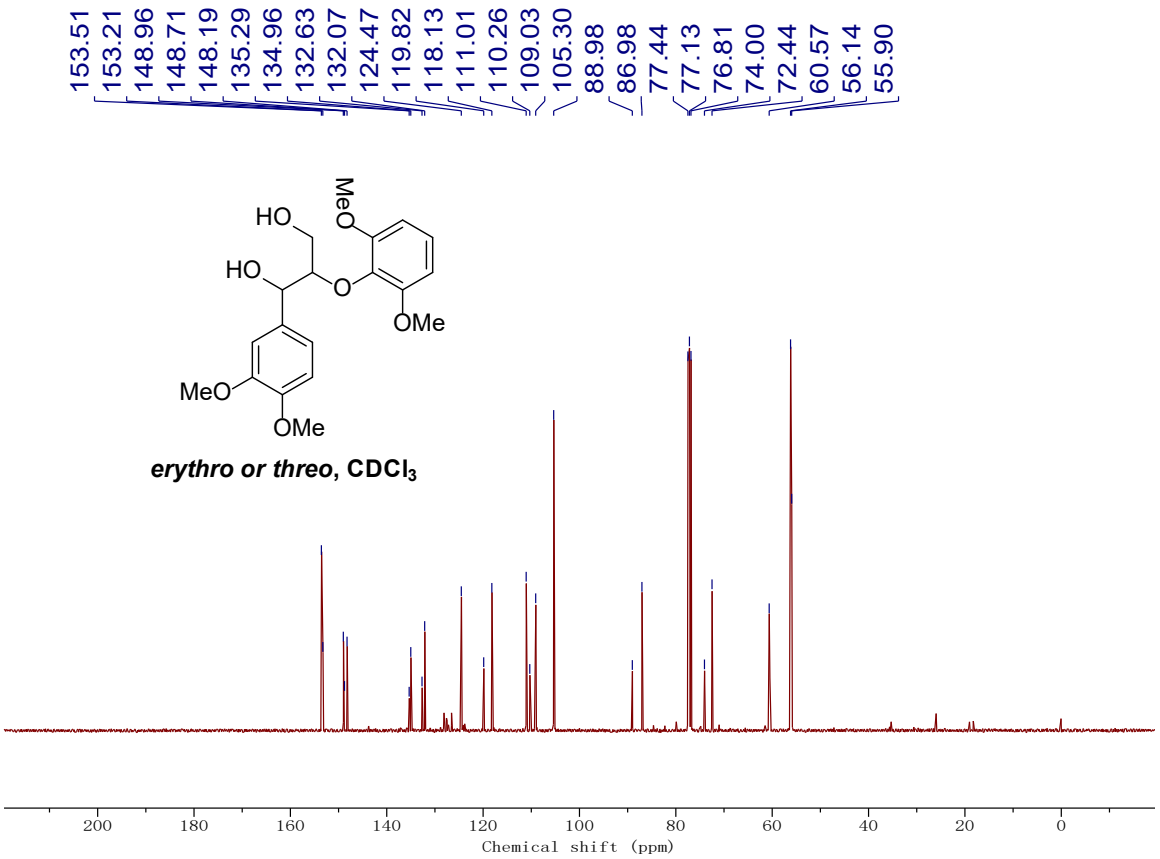

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