

Electronic Supporting Information

Catalytic Hydrogenolysis of Lignin-Derived Compounds Using Sub-Nanometer Cobalt Catalysts

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1. GENERAL INFORMATION

Reagents and solvents purchased from Sigma Aldrich: Co(OAc)₂•4 H₂O 98%, MgO (≤ 50 nm), Co(PPh₃)₂Cl₂ (98%), triethylsilane (99%), formic acid (95%), triethylamine (99%), bromine, NaBH₄ 98%, methanol (99.8%), 1,4-dioxane (99.8%), isopropanol, anhydrous propylene carbonate (99.7%), CH₂Cl₂, anhydrous ethanol (99.5%), sodium sulfate (99%), magnesium sulfate (99.5%), 3,4-dimethoxyacetophenone (98%), potassium carbonate (99%), ethyl ether (99%), hexane (98.5%), isopropanol (99.5%), concentrated sulfuric acid (95-98.5%), acetone (99.5%), chloroform (99.8%), ammonium chloride (99.5%), absolute ethanol (99.5%), potassium hydroxide (85%). 5-amino-1,10-phenanthroline from TCR. **Co-2** was prepared according to previously reported methods.¹

2. CHARACTERIZATION METHODS

Diverse identification and characterization techniques were utilized for analyzing cobalt materials, alongside the organic compounds. Sample preparation adhered to detailed protocols outlined below for each set of materials.

Nuclear Magnetic Resonance (NMR) Studies

¹H, ¹³C{¹H} and HSQC NMR spectra were recorded at room temperature on a 400 or 300 MHz Bruker Avance III spectrometer in CDCl₃ or DMSO unless otherwise stated. ¹H and ¹³C{¹H} chemical shifts (δ, ppm) are reported relative to the residual proton resonance in the corresponding deuterated solvent.

Elemental Analysis

Elemental analysis of **Co-1** and **Co-2** was carried out in Thermo Scientific/Flash 2000.

3. CHARACTERIZATION OF Co-1

Table S1. Elemental composition to **Co-1**.

Source/Element	C	H	N	Co	O
EA (% mass)	60.43	3.14	12.45	-	-
EDS (at%)	91.7	-	-	0.3	8.0
XPS (at%)	82.0	-	7.9	1.3	8.9
ICP (wt%)				0.54	

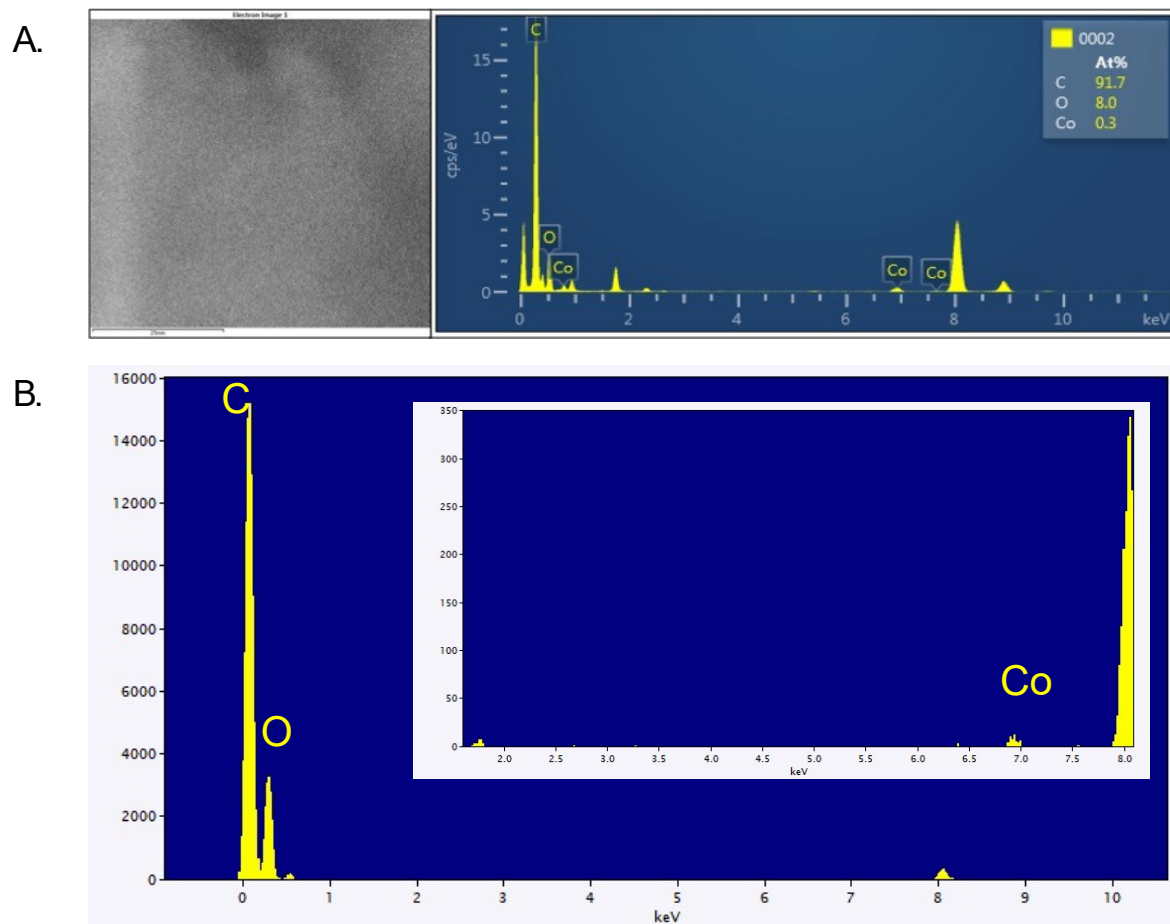


Fig. S1. A. EDS analysis of the micrographs obtained to Co-1 catalyst. B. Co-1 catalyst after 5 runs.

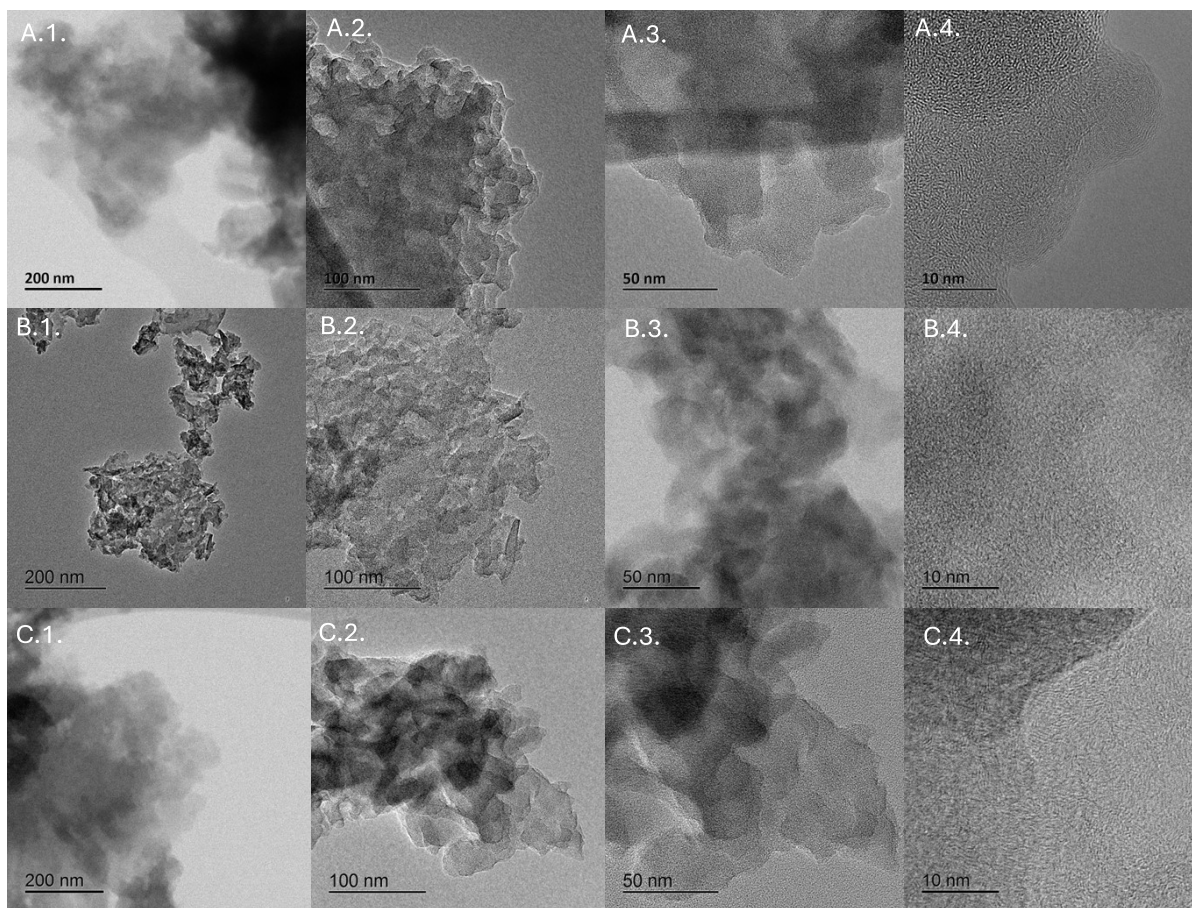


Fig. S2. TEM images from freshly Co-1, A. Batch 1, B. Batch 2 and C. Batch 3. Scale bars represent 1. 200 nm 2. 100 nm, 3. 50 nm and 4. 10 nm.

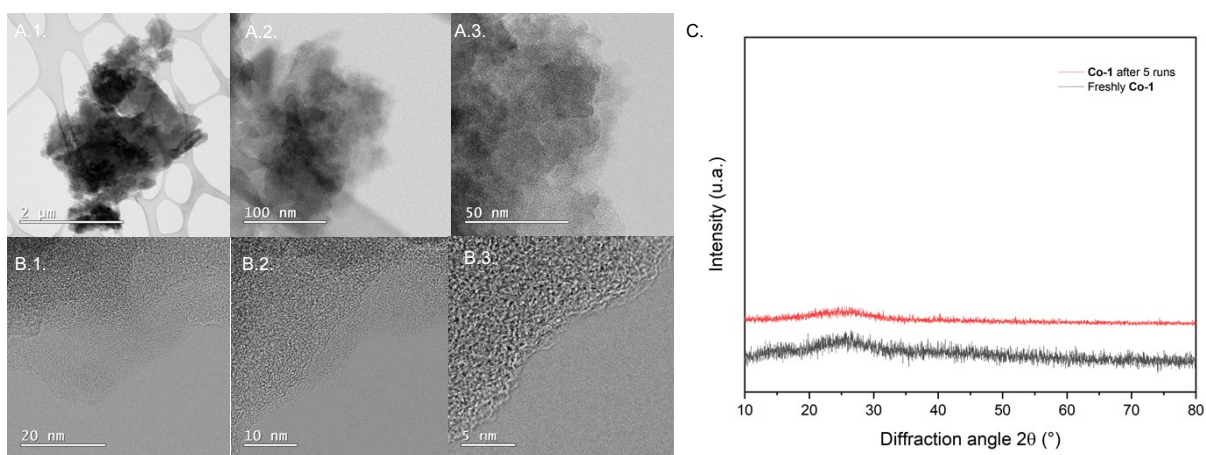
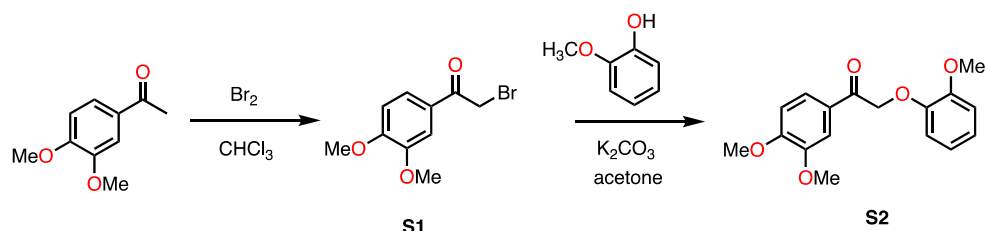


Fig. S3. A.1.-A.4. TEM images from Co-1. B.1-B.2. Co-1 after 5 runs. C. Powder X-ray diffraction (PDRX) patterns of freshly Co-1, and Co-1 after 5 runs.

4. SYNTHESIS OF SUBSTRATES

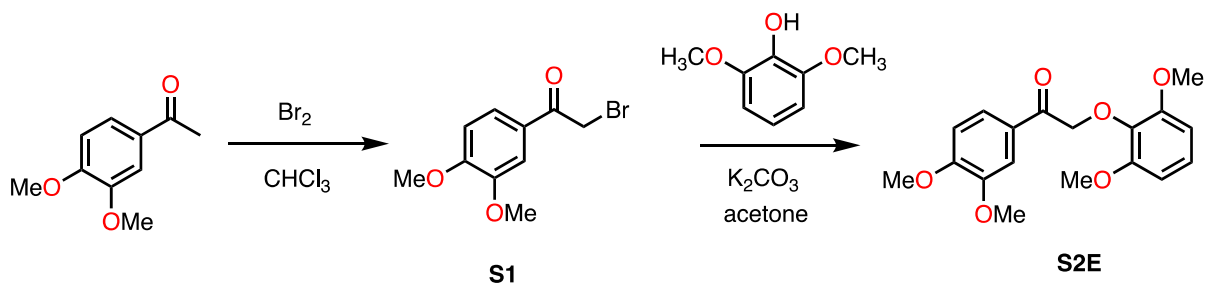
4.1. Synthesis of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (**S2**)



S2 was prepared according to a previous report with some modifications.² Briefly, the solution **S1** (11.586 g, 0.045 mol) in acetone (115 mL), prepared in a 500 mL two-neck flask, had guaiacol (5.543 g, 0.045 mol) added, followed by K_2CO_3 (12.337 g, 0.0894 mol). The system was purged with argon and refluxed at 60 °C overnight. A thin-layer chromatography was conducted for qualitative observation of the products after the reaction completion. The reaction mixture was filtered through celite. The resulting filtrate was placed in a 250 mL round-bottom flask and concentrated using a rotary evaporator at 35 °C. An orange solid was obtained, which was triturated with a spatula and suspended in cold ethanol, crystallizing a white solid. This was vacuum-filtered to obtain 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-ethanone (**S2**). 1H NMR (300 MHz, $CDCl_3$) δ : 7.67 (dd, $J = 8.4, 2.0$ Hz, 1H), 7.59 (d, $J = 2.0$ Hz, 1H), 6.99-6.80 (m, 5H), 5.28 (s, 2H), 3.93 (d, $J = 5.2$ Hz, 6H), 3.88 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ : 193.38, 153.91, 149.80, 149.30, 147.66, 127.93, 122.87, 122.44, 120.90, 114.73, 112.22, 110.51, 110.22, 72.09, 56.22, 56.11, 56.

FTIR (ATR, cm^{-1}): 3077.33, 3008.88, 2967.83, 2931.32, 2836.55, 1681.75, 1586.11, 1503.17, 1460.07, 1436.70, 1415.85, 1332.53, 1264.66, 1248.62, 1219.34, 1199.33, 1162.03, 1151.25, 1126.07, 1080.77, 1053.41, 1016.65, 919.35, 868.25, 847.86, 812.72, 797.17, 752.74, 628.52, 605.39, 578.37, 519.40, 492.75, 470.09, 413.18.

4.2 Synthesis of 2-(2,6-dimethylphenoxy)-1-(3,4-dimethoxyphenyl)ethanone (**S2E**)



S2E was prepared according to a previous report with some modifications.³ Briefly, in a round-bottom flask with a capacity of 1000 mL, a solution of **S1** (4.000 g, 0.015 mol) was prepared in 400 mL of acetone. To this solution, siringol (3.557 g, 0.023 mol) was added, and finally, K_2CO_3 (5.313 g, 0.039 mol) was added. The system was purged with argon and refluxed at 60 °C. The reaction concluded when a total consumption of the raw material was observed on the thin-layer chromatography plate. The reaction mixture was filtered over celite, and the filtrate was placed in a round-bottom flask with a capacity of 500 mL to concentrate it using a rotary evaporator at 30 °C. Once concentrated, it was suspended in cold ethanol, resulting in the formation of a white solid. This solid was left to dry under vacuum to obtain **S2E** as a white solid.

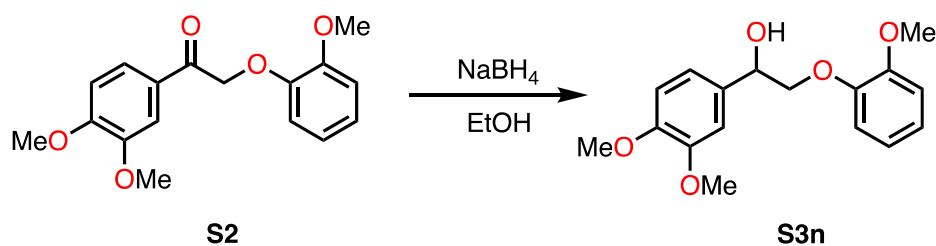
1H NMR (300 MHz, $CDCl_3$) δ : 7.71 (dd, $J = 8.4, 2$ Hz, 1H), 7.63(d, $J = 2$ Hz, 1H), 6.99 (t, $J = 8.4$ Hz, 1H), 6.88 (d, $J = 8.4$

Hz, 1H), 6.56 (d, $J = 8.4$ Hz, 2H), 5.13 (s, 2H), 3.92 (d, $J = 0.8$ Hz, 6H), 3.79 (s, 6H)

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ : 193.73, 153.41, 153.26, 149.00, 136.64, 128.39, 124.09, 123.05, 110.64, 110.05, 105.33, 75.27, 56.09, 56.05.

FTIR (ATR, cm^{-1}): 3083.93, 3002.29, 2963.76, 2938.01, 2894.21, 2837.92, 1657.58, 1584.19, 1513.01, 1492.96, 1476.12, 1459.60, 1434.47, 1422.89, 1347.18, 1305.39, 1277.58, 1254.50, 1235.35, 1204.63, 1188.60, 1174.03, 1156.54, 1107.38, 1070.87, 1022.83, 991.51, 901.02, 866.29, 833.48, 820.50, 777.89, 741.04, 715.30, 687.75, 665.90, 626.01, 612.60, 584.70, 546.75, 523.72, 460.84.

4.3. Synthesis of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-ol (**S3n**)



S3n was prepared according to a previous report with some modifications.³ In a 250 mL round-bottom flask, a solution of **S2** (3.000 g, 0.009 mol) was prepared in 50 mL of anhydrous ethanol. Slowly, NaBH₄ (0.973 g, 0.026 mol) was added to the reaction mixture, and it was stirred overnight. The reaction was monitored by thin-layer chromatography, observing the consumption of the starting material. The ethanol was then removed using a rotary evaporator to obtain a white solid. To the resulting solid, a saturated solution of NH₄Cl was added (5 °C), and the reaction mixture was diluted with 50 mL of distilled water, leading to the formation of bubbles and separation into two phases. A liquid-liquid extraction with CH₂Cl₂ was performed, and the organic phase was washed with a saturated NaCl solution. The organic phase was collected, filtered over MgSO₄, and finally concentrated with a rotary evaporator to obtain a white solid.

¹H NMR (300 MHz, CDCl₃) δ: 7.05 – 6.81 (m, 7H), 5.05 (dd, *J* = 9.3, 2.9 Hz, 1H), 4.16 (dd, *J* = 10.0, 3.0 Hz, 1H), 3.97 (dd, *J* = 10.0, 9.3 Hz, 1H), 3.91 – 3.84 (m, 9H), 3.63 – 3.56 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ: 150.17, 149.16, 148.83, 148.09, 132.29, 122.59, 121.18, 118.71, 115.98, 112.04, 111.09, 109.46, 76.38, 72.20, 56.03, 55.96, 55.92. FTIR (ATR, cm⁻¹): 3524.60, 3084.34, 3063.33, 3030.71, 3001.63, 2954.95, 2922.45, 2836.77, 1593.84, 1507.80, 1456.10, 1415.64, 1378.23, 1345.97, 1334.13, 1312.25, 1296.72, 1251.11, 1226.14, 1183.29, 1152.29, 1127.38, 1085.63, 1059.46, 1039.19, 1019.10, 914.96, 902.48, 859.66, 837.73, 803.80, 783.25, 764.76, 741.30, 646.69, 624.50, 601.49, 573.98, 526.31, 490.47, 464.32, 438.68, 413.84.

5. LIGNIN EXTRACTION

Lignin extraction was carried out according to a methodology reported previously,⁴ briefly described below. In a solution of 30 g of softwood sawdust in a 1,4-dioxane/water mixture (9:1 vol./vol.) in the presence of 0.2 M hydrochloric acid, the mixture was refluxed at 90-95 °C under inert atmosphere for 4 h. The reaction mixture was allowed to cool, then filtered, and vacuum-concentrated using a rotary evaporator. Once concentrated, the dioxane-soluble lignin was isolated by precipitation in water, purified by precipitation in diethyl ether, and vacuum-dried to obtain dioxane-soluble lignin from softwood.

6. CATALYTIC HYDROGENOLYSIS

6.1. Lignin Model Compounds Hydrogenolysis with Et₃N/HCOOH

The hydrogenolysis reactions were carried out in 10 mL borosilicate tubes equipped with a stir bar and a Teflon cap, which were loaded with **S2** (40 mg, 0.13 mmol), 2 mL of EtOH, 2 mL of deionized water, and 15 mg of cobalt catalyst, triethylamine (92 μL, 0.66 mmol), and formic acid (14.99 μL, 0.39 mmol). The flask was purged with argon. Once the tube was sealed, it was placed in the Monowave at 180 °C for 2 h. After the reaction time, a thin-layer chromatography was performed for qualitative observation of the products. Solvents were evaporated, and the sample was dissolved in CH₂Cl₂ for GC-MS. Similarly, hydrogenolysis was performed for the **S2E** and **S3n**.

6.2. Lignin Model Compounds Hydrogenolysis with hydrogen pressure

Hydrogenolysis reactions were carried out in a 22 mL stainless steel Parr® reactor equipped with a magnetic stirrer. The reactor was loaded with **S2** (80 mg, 0.26 mmol), 20 mg of cobalt catalyst, 3 mL of EtOH, and 3 mL of deionized water. The reactor was sealed using its structure for purging with argon. Once the system was purged, a pressure gauge was installed to pressurize with H₂ gas to 10 bar. The reactor was placed at 180 °C for 24 h. After the designated reaction time, the products were qualitatively observed using a thin-layer chromatography plate. The reaction mixture was filtered to separate the catalyst from the product and remove the solvents. Finally,

the dried sample was dissolved in CH_2Cl_2 for analysis by GC-MS. The same methodology was followed for the hydrogenolysis of **S2E** and **S3n**.

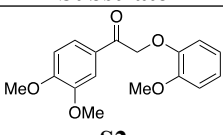
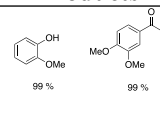
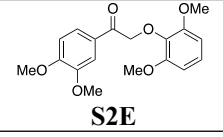
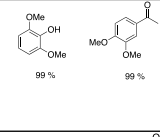
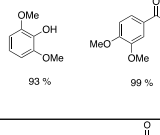
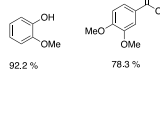
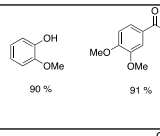
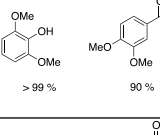
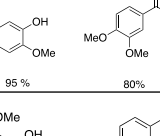
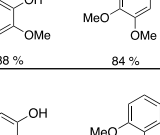
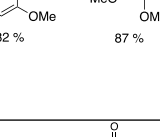
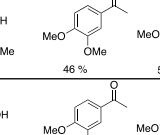
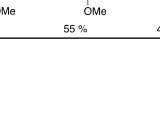
6.3. Lignin Model Compounds Hydrogenolysis with $\text{Et}_3\text{N}/\text{HCOOH}$

Lignin depolymerization/hydrogenolysis reactions were carried out using the same methodology described previously. Initially, AF/ Et_3N was used as a hydrogen source. This reaction was conducted in the Monowave, where a borosilicate tube was loaded with 50 mg of pine dioxasolv lignin or kraft lignin, 15 mg of **Co-1** catalyst, 2 mL of EtOH, 2 mL of desionized water, 14.99 μL of A.F, and 92 μL of Et_3N . The reaction mixture was placed in an argon atmosphere at 180 °C for 2 h. Once the reaction was complete, it was filtered to separate the catalyst from the reaction mixture. Solvents were evaporated, and the composition was analyzed using NMR and IR-ATR.

6.4. Lignin Model Compounds Hydrogenolysis with hydrogen pressure

A Parr® reactor equipped with a magnetic stirrer was loaded with 50 mg of pine dioxasolv lignin or kraft lignin, 15 mg of **Co-1** catalyst, 3 mL of EtOH, and 3 mL of desionized water. The reactor was purged with argon, and a pressure gauge was used to pressurize it to 10 bar with H_2 . The reaction was set at 180 °C for 24 h. After completion of the reaction, the mixture was filtered, and solvents were evaporated for subsequent composition analysis by NMR and FTIR-ATR

Table S2. Overview of catalysts for C-O lignin-derived molecules.

Catalyst	Conditions	Substrate	Products	Ref.
Co-1 15 mg	H ₂ O/EtOH, 2 h, 180 °C, Et ₃ N, HCOOH, Conv. >99%	 S2		<i>this work</i>
Co-1 20 mg	H ₂ O/EtOH, 2 h, 180 °C, Et ₃ N, HCOOH, Conv. >99%	 S2E		<i>this work</i>
Co-phen/C	H ₂ O/EtOH, 2 h, 200 °C, HCOOH (3 equiv.) Conv. >99%	S2E		5
Pd/CeO ₂ 0.02 g	H ₂ O ₂ (30 wt%, 0.5 mL), NaOH aq. (2.5 wt%, 2.5 mL), 50 °C, 3 h. Conv. 100 %	S2		6
disulfide (2,2'- dithiodiethanol) and BHT (1:1 molar ratio)	Electrolysis DMF at 5 mA 1.5 h. Conv. 97%	S2		7
disulfide (2,2'- dithiodiethanol) and BHT (1:1 molar ratio)	Electrolysis DMF at 5 mA 1.5 h. Conv. 96%	S2E		7
NaOH (5 equiv)	Ballmilling, 25 Hz, 120 min	S2		8
NaOH (5 equiv)	Ballmilling, 25 Hz, 120 min	S2E		8
CzCP33 2.0 mol%	DIPEA (5 equiv.), HCOOH (5 equiv.), MeCN, Ar, rt, 26 W CFL, 24 h. Conv. 94 %	S2		9
NiMo sulfide (20 mg)	145 psi H ₂ , MeOH, 180 °C, 6 h. Conv. >99%	S2		10
NiMo sulfide (20 mg)	145 psi H ₂ , MeOH, 180 °C, 6 h. Conv. >97%	S2E		10

7. SPECTRA AND CHROMATOGRAMS

7.1. 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (S2)

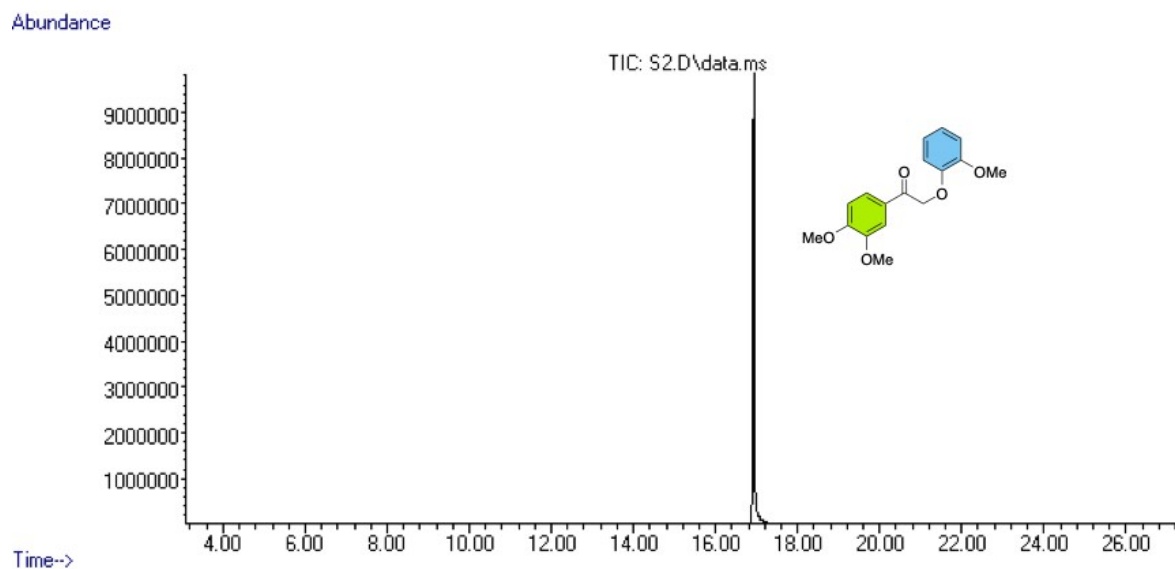


Fig. S4. Chromatogram of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethanone (S2).

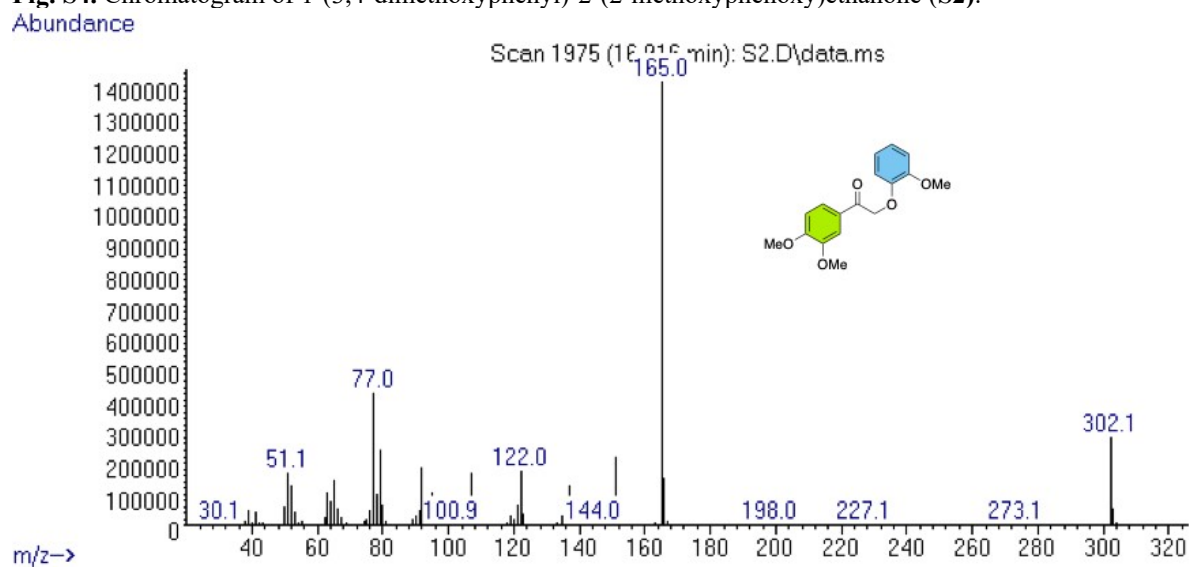


Fig. S5. Mass spectrum of compound S2.

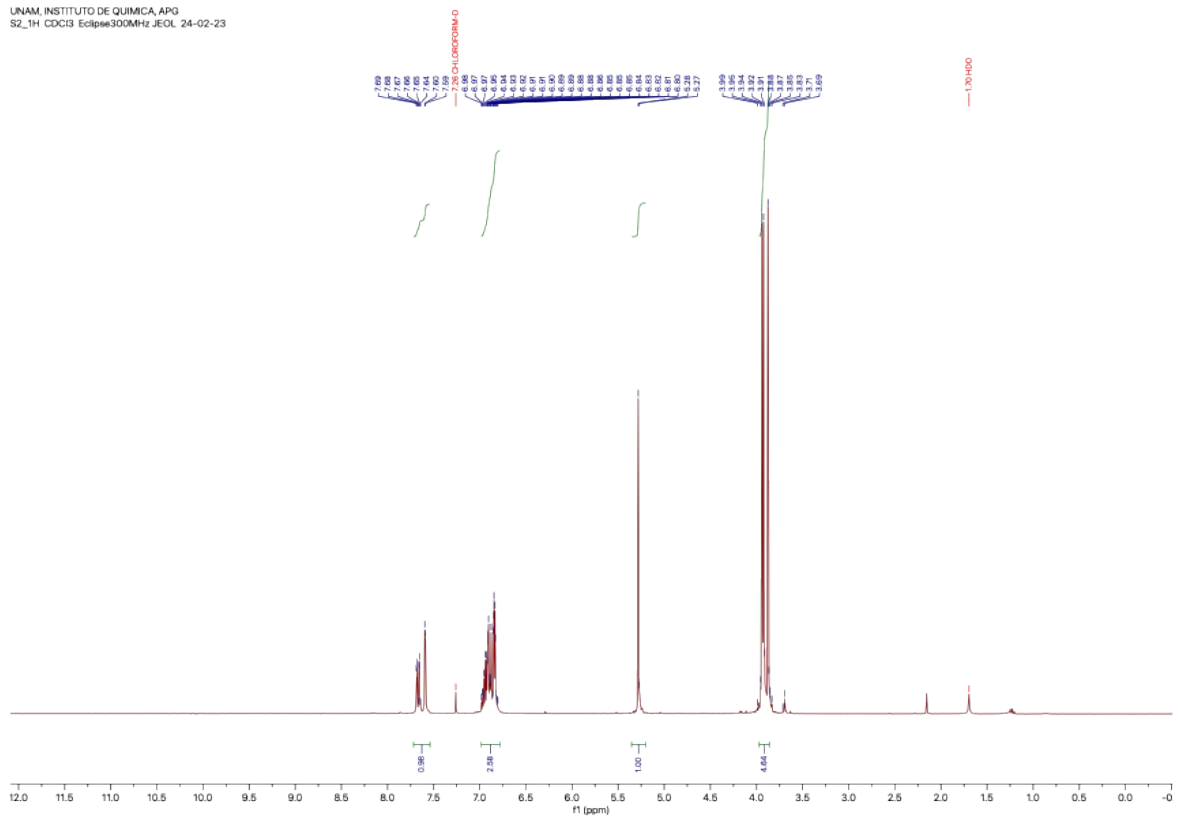


Fig. S6. ¹H NMR (300 MHz, CDCl₃) spectrum of compound S2.

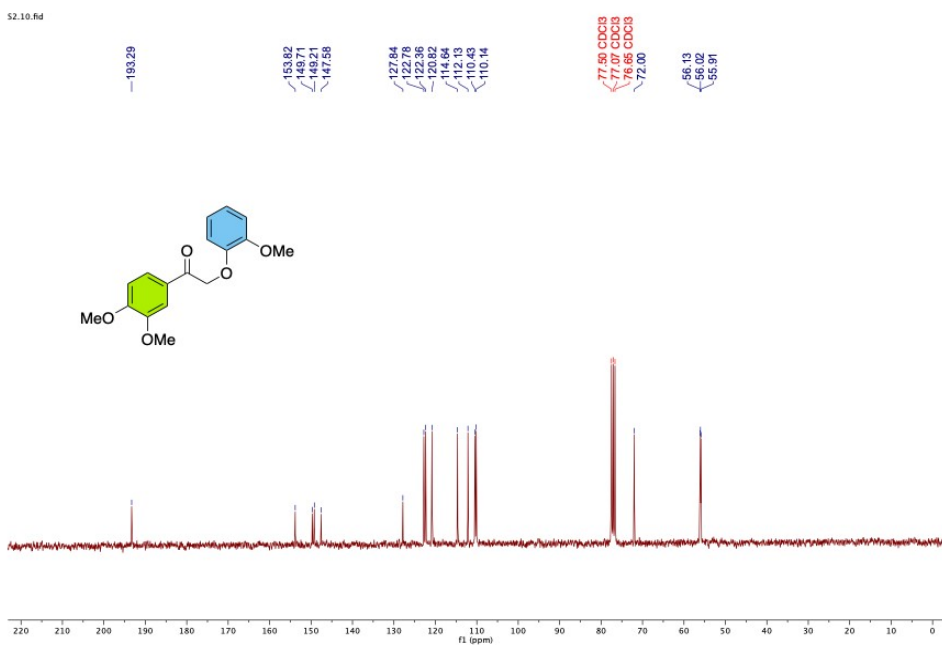


Fig. S7. ¹³C NMR (75 MHz, CDCl₃) spectrum of compound S2.

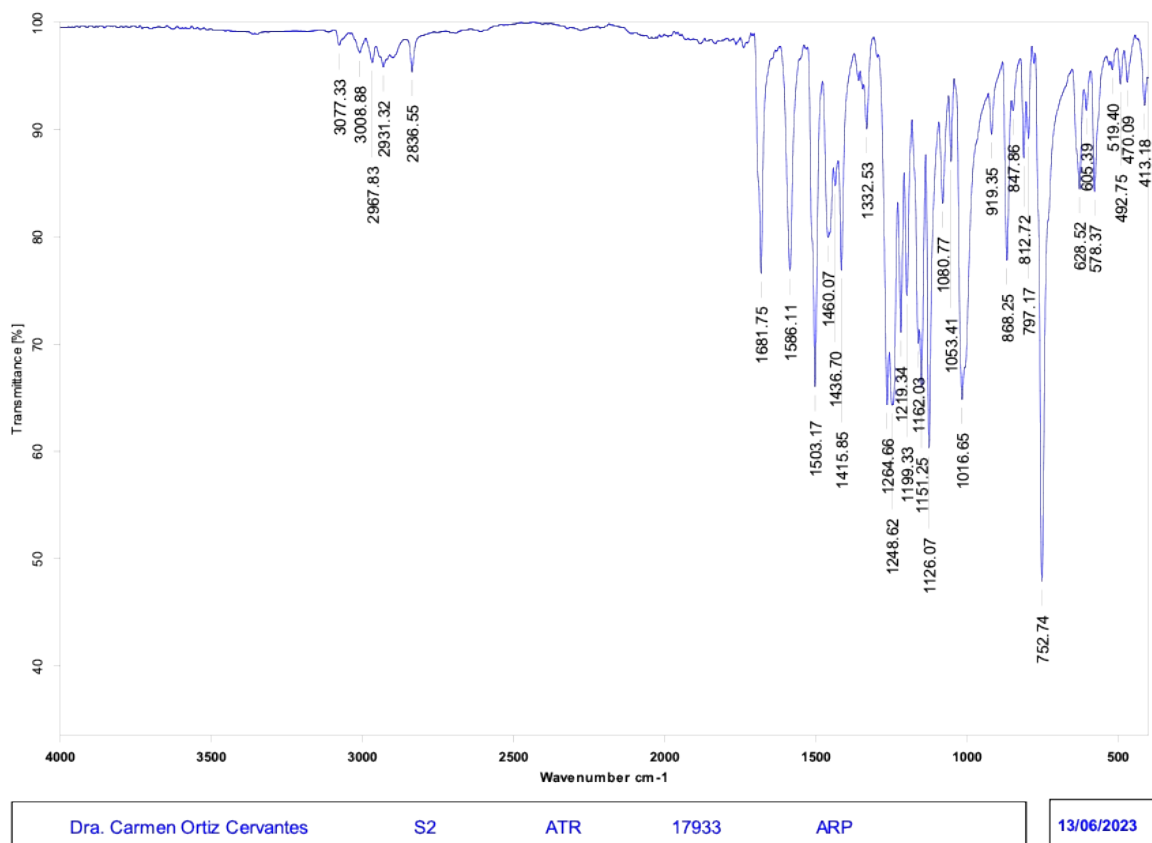


Fig. S8. ATR-FTIR spectrum of S2.

7.2. 2-(2,6-dimethylphenoxy)-1-(3,4-dimethoxyphenyl)ethanone (S2E).

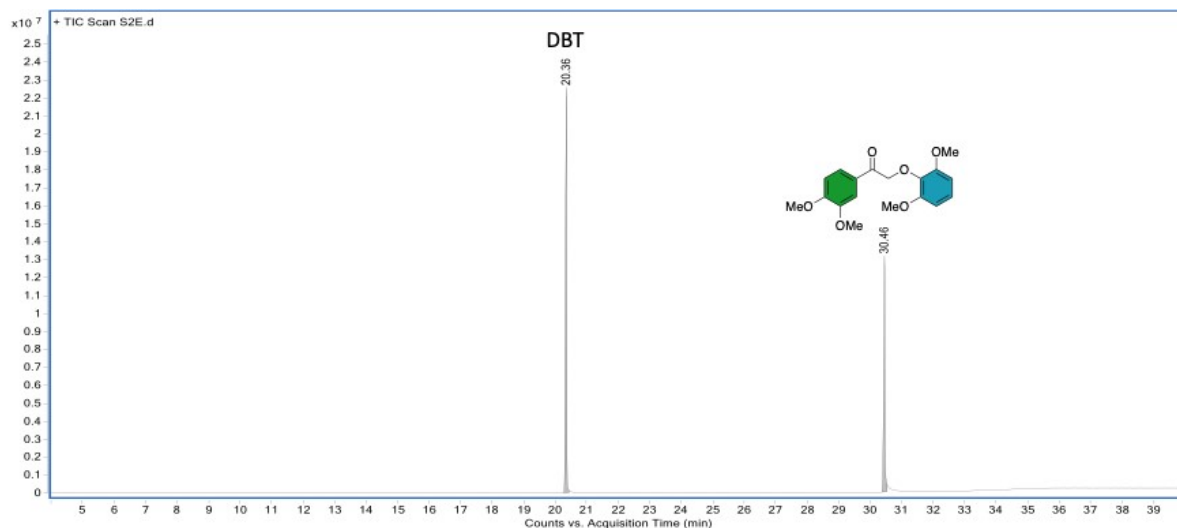


Fig. S9. Chromatogram of 2-(2,6-dimethylphenoxy)-1-(3,4-dimethoxyphenyl)ethanone (S2E).

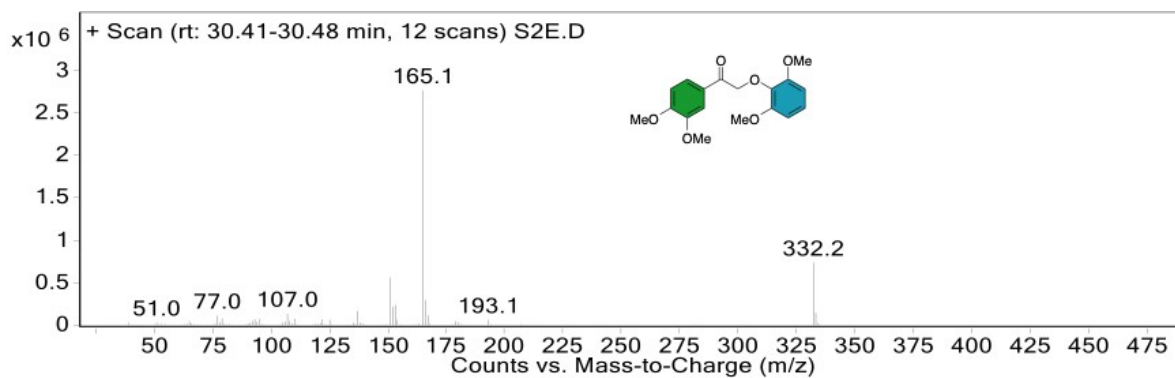


Fig. S10. Mass spectrum of compound S2E.

17930_EHuerta_23
 Instituto de Química, UNAM, E. Huerta, Dr. C. Ortiz, S2 MME, CDCI3, Jeol JNM-ECZ400S, 13-06-2023, No. reg. 17930

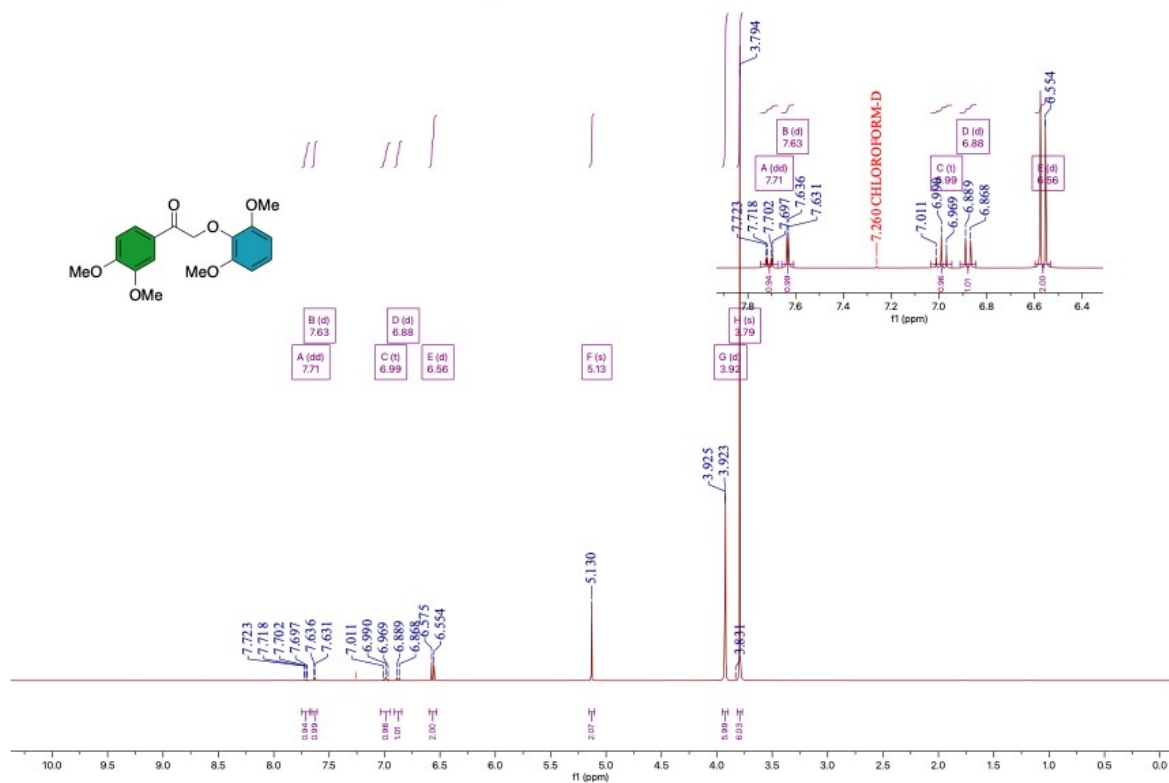


Fig. S11. ¹H NMR (400 MHz, CDCl₃) spectrum of compound S2E.

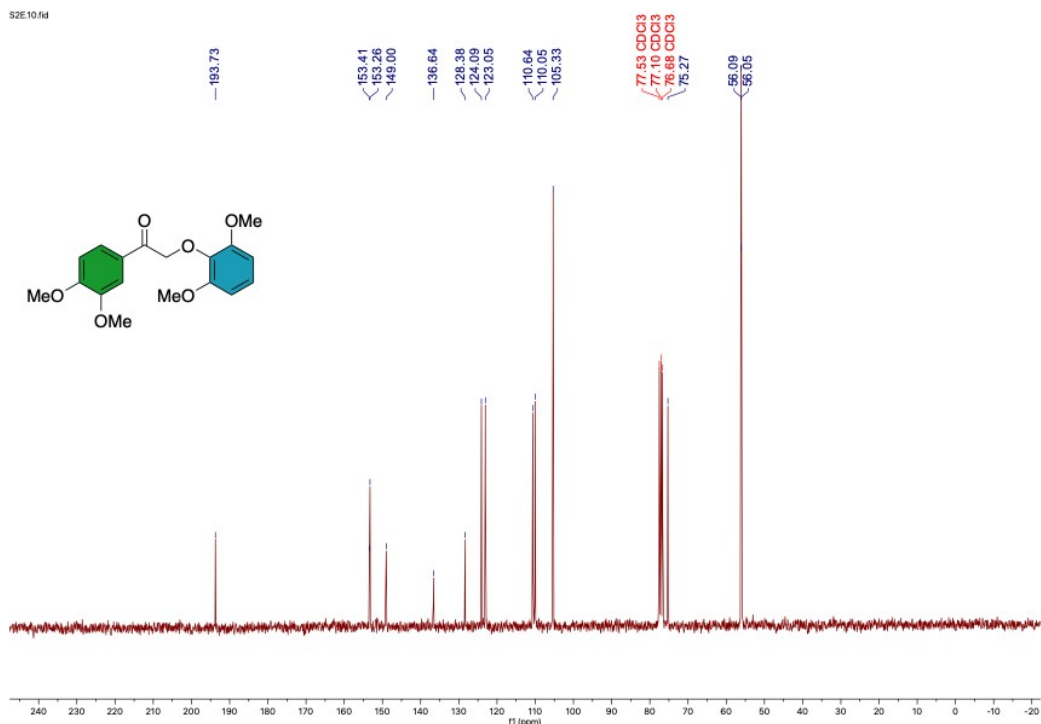


Fig. S12. ^{13}C NMR (75 MHz, CDCl_3) spectrum of compound S2E.

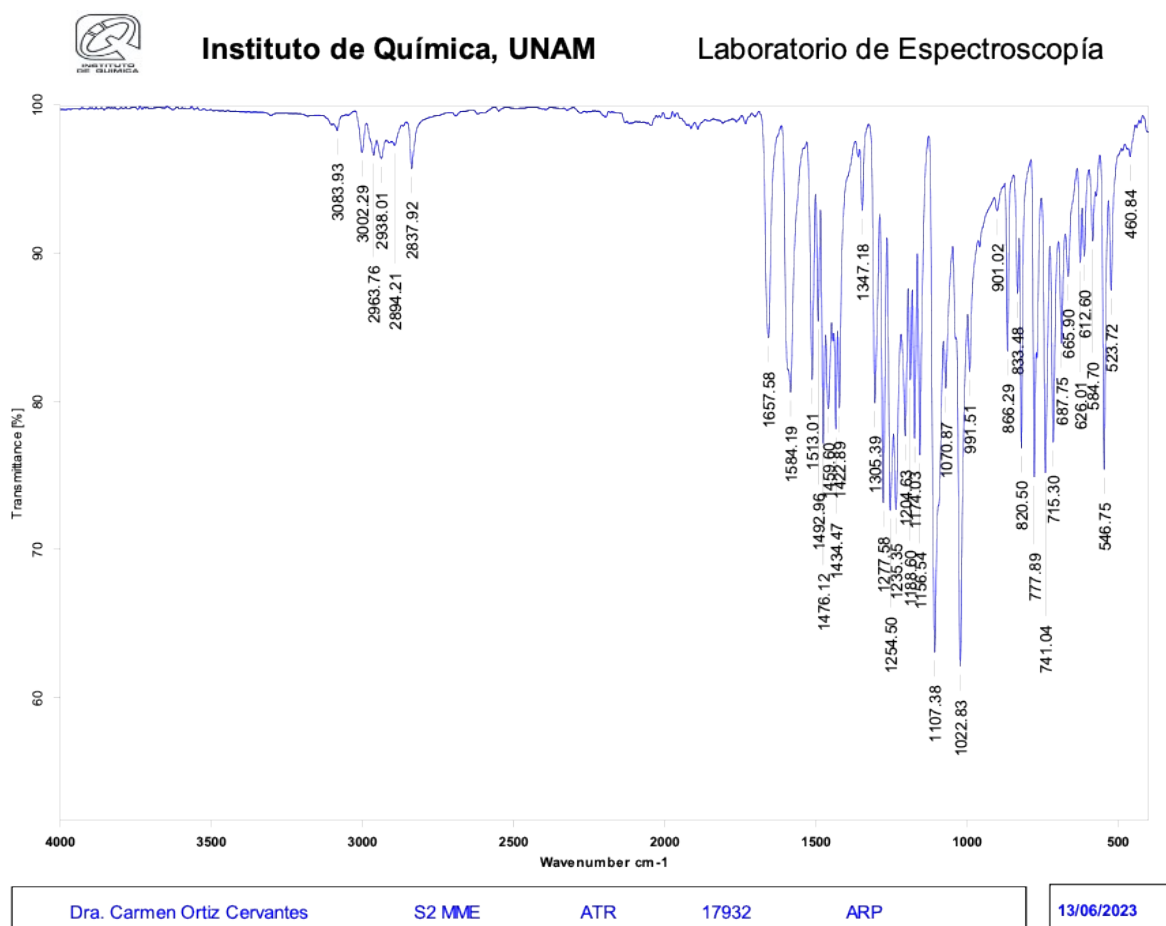


Fig. S13. ATR-FTIR spectrum of S2E.

7.3. 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-ol (**S3n**)

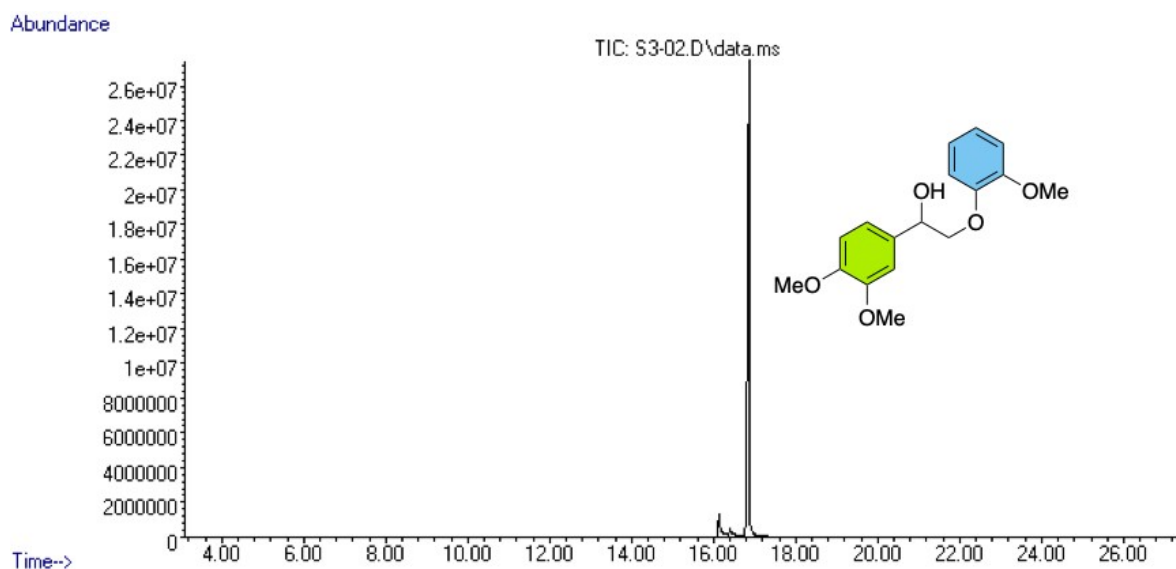


Fig. S14. Chromatogram of **S3n**.

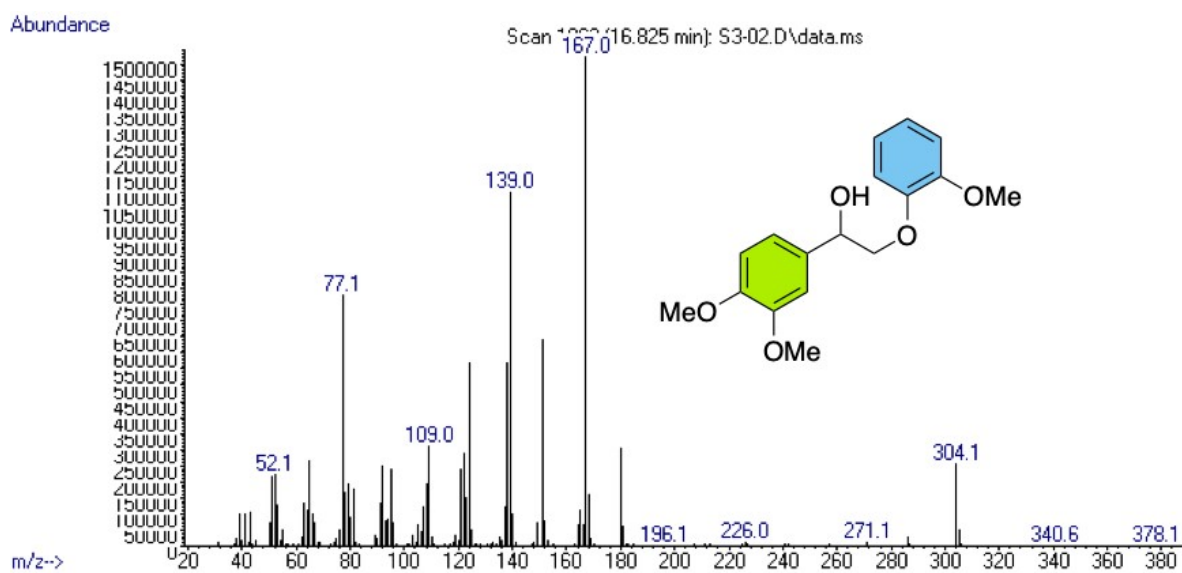


Fig. S15. Mass spectrum of compound **S3n**.

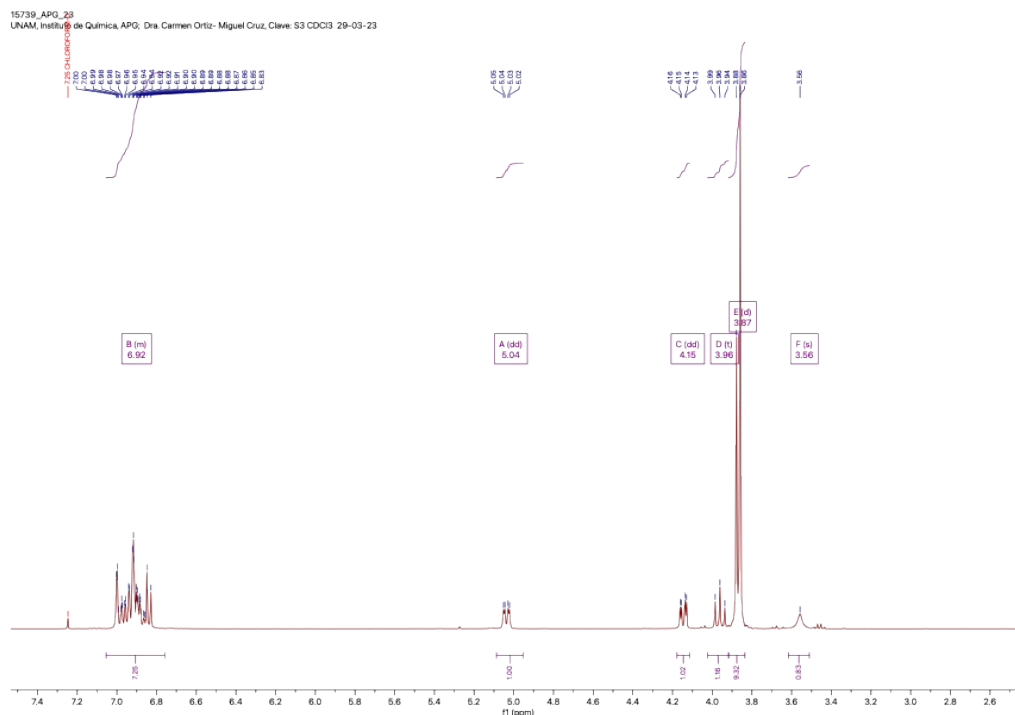


Fig. S16. ^1H NMR (400 MHz, CDCl_3) spectrum of compound S3n.

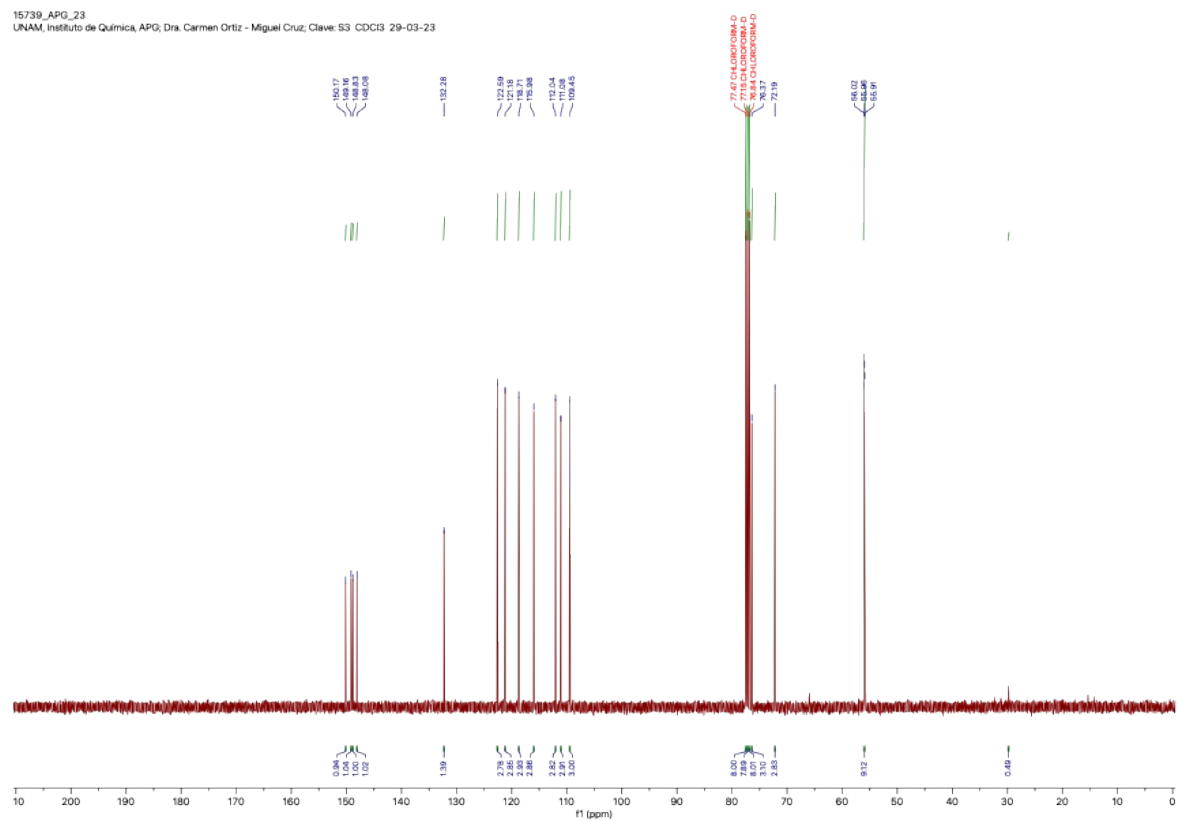


Fig. S17. ^{13}C NMR (75 MHz, CDCl_3) spectrum of compound S3n.

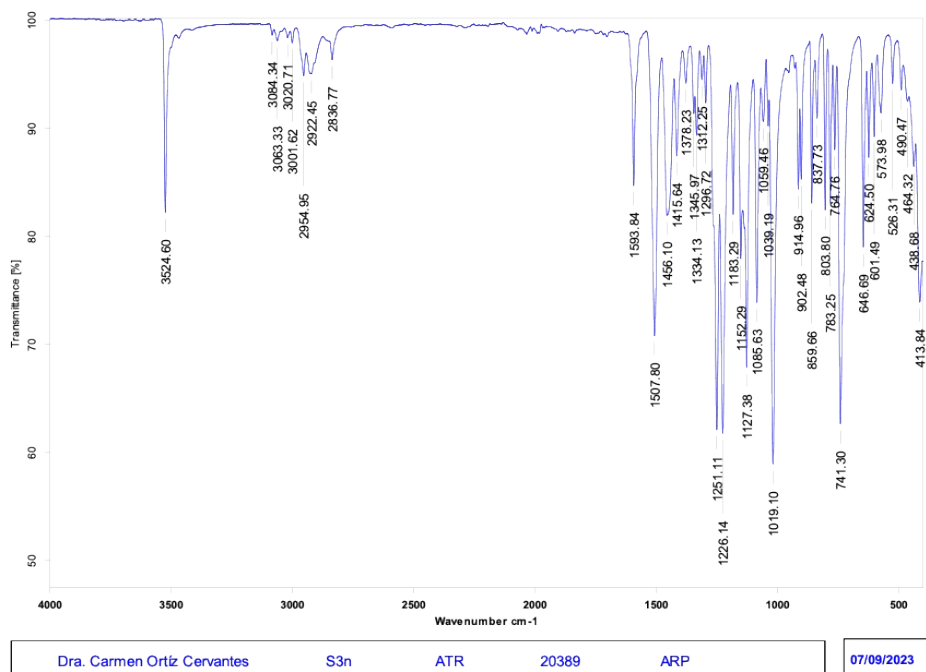


Fig. S18. ATR-FTIR spectrum of S3n.

7.4. Catalytic hydrogenolysis

Abundance

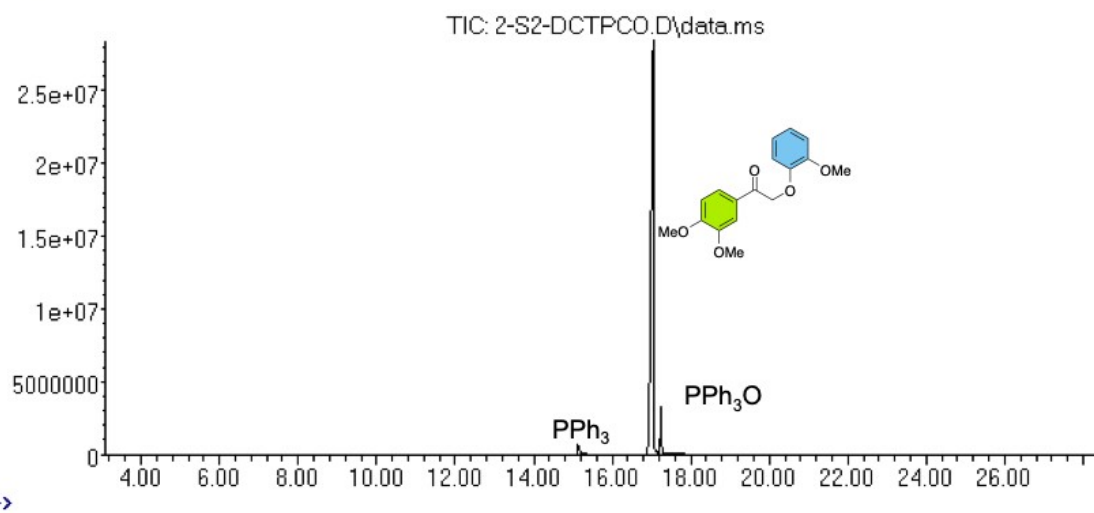


Fig. S19. Chromatogram for catalytic hydrogenolysis of S2 with $\text{Co}(\text{PPh}_3)_2\text{Cl}_2$ and $\text{HCOOH}/\text{Et}_3\text{N}$ as a hydrogen source.

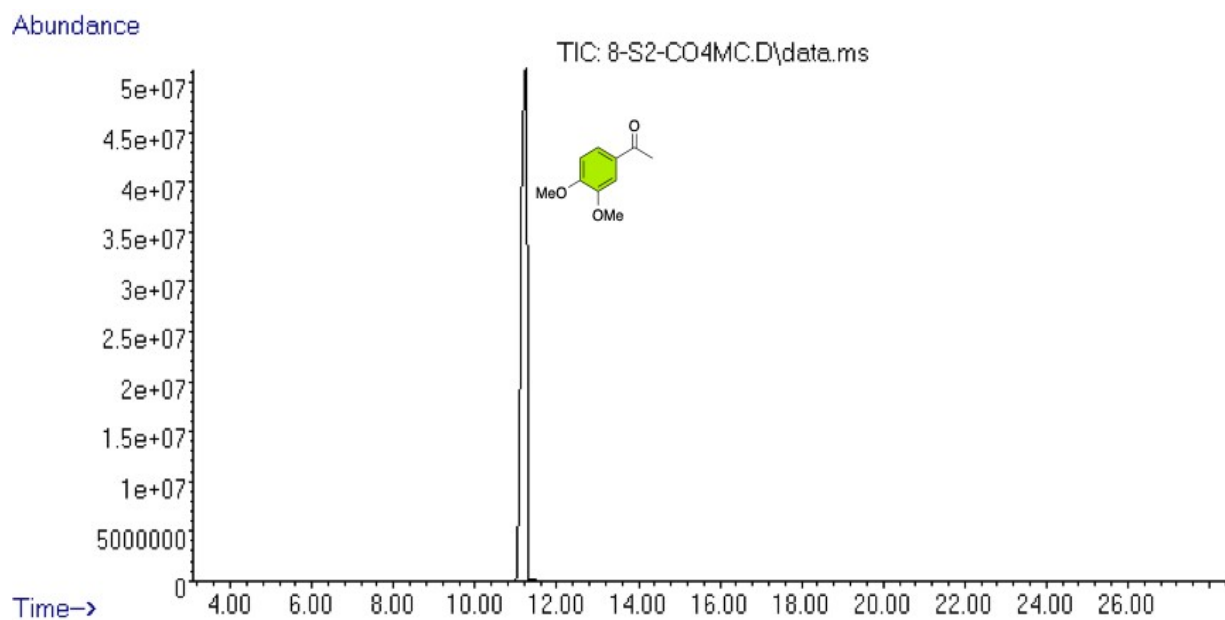


Fig. S20. Chromatogram for catalytic hydrogenolysis of **S2** with **Co-1** and HCOOH/Et₃N as a hydrogen source.

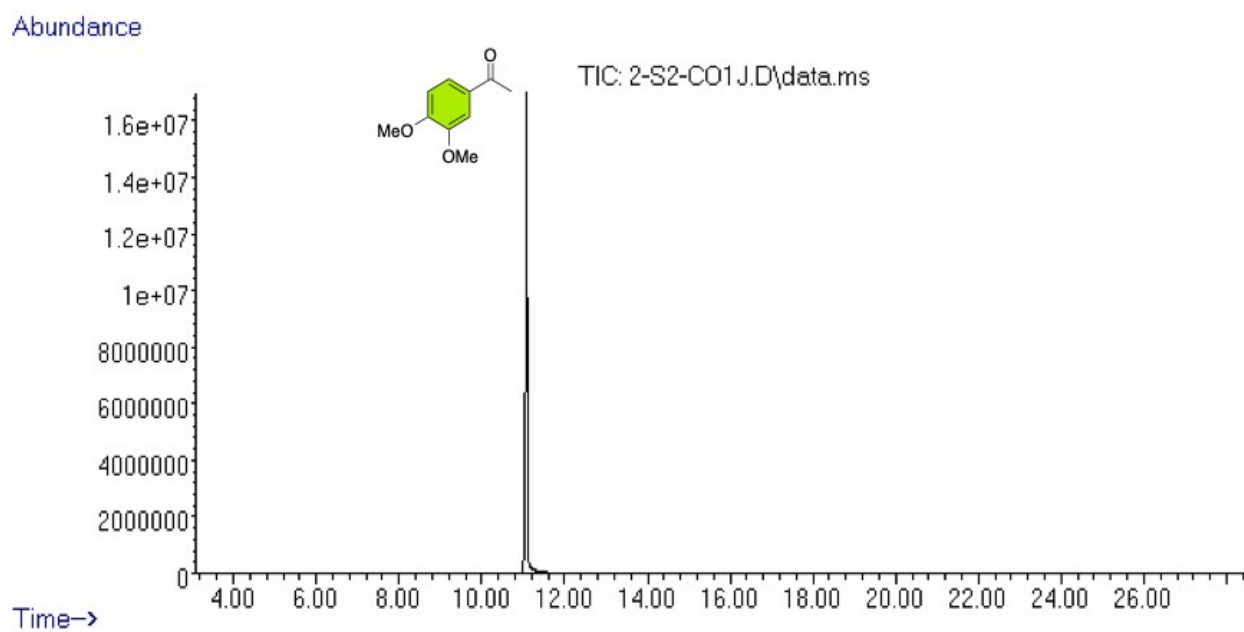


Fig. S21. Chromatogram for catalytic hydrogenolysis of **S2** with **Co-2** and HCOOH/Et₃N as a hydrogen source.

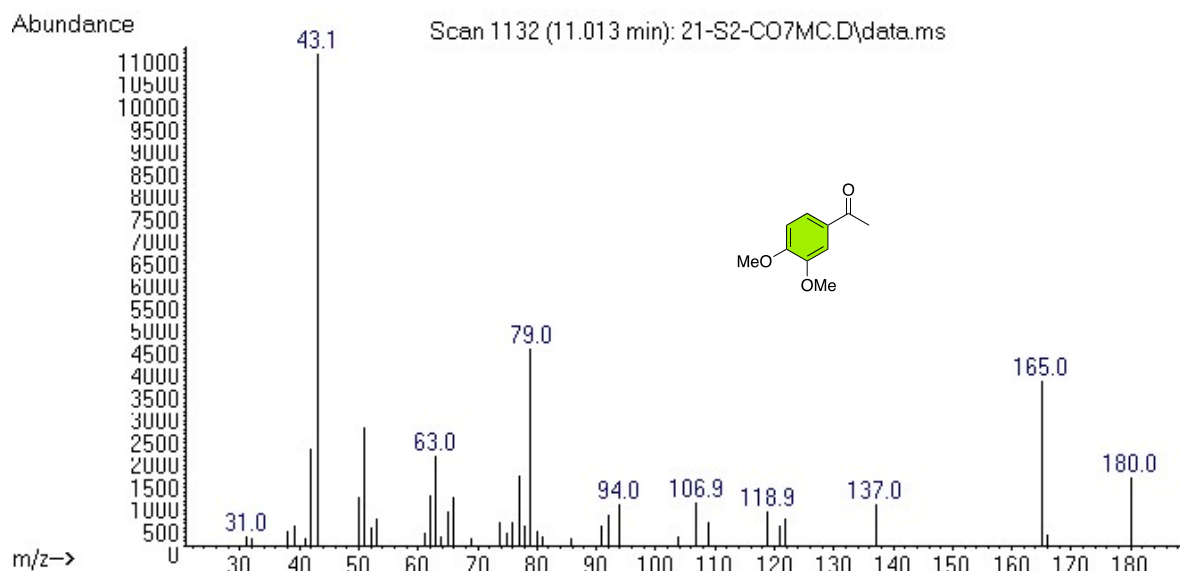


Fig. S22. Mass spectrum for ketone from the catalytic hydrogenolysis of **S2** with **Co-1** and HCOOH/ Et₃N as a hydrogen source.

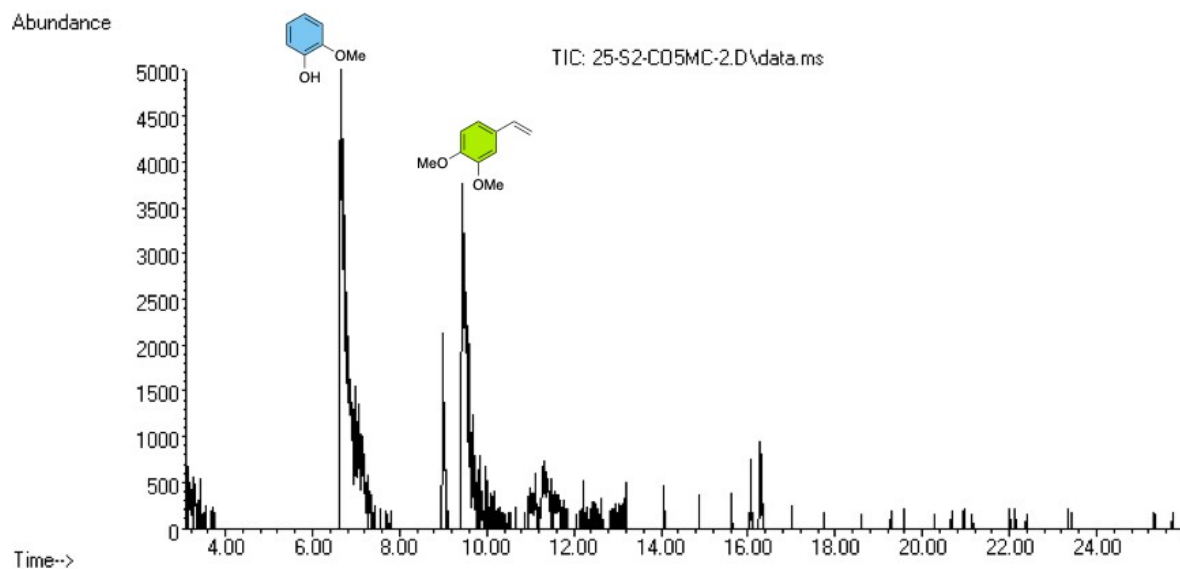


Fig. S23. Chromatogram for catalytic hydrogenolysis of **S2** with **Co-1** and IPA/KOH as a hydrogen source.

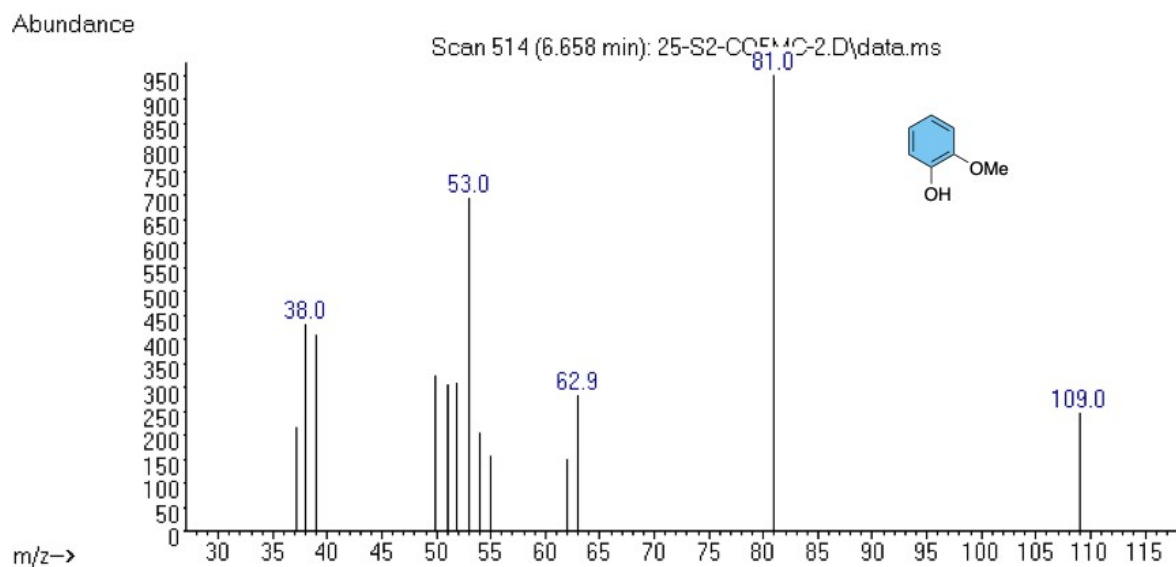


Fig. S24. Mass spectrum for 2-methoxyphenol from catalytic hydrogenolysis of **S2** with **Co-1** and IPA/KOH as a hydrogen source.

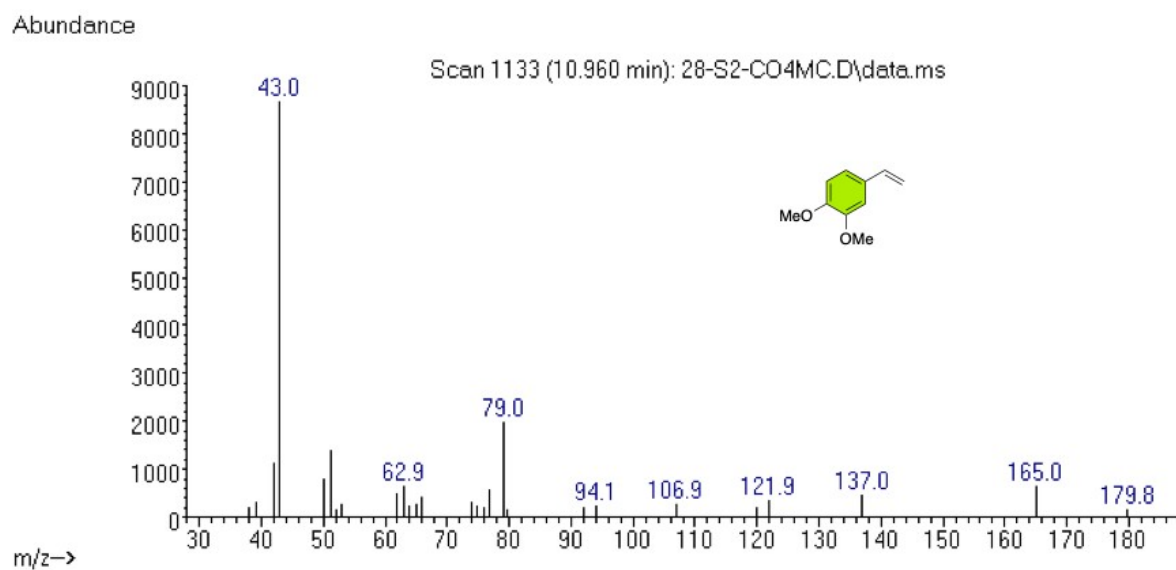


Fig. S25. Mass spectrum for alkene from catalytic hydrogenolysis of **S2** with **Co-1** and IPA/KOH as a hydrogen source.

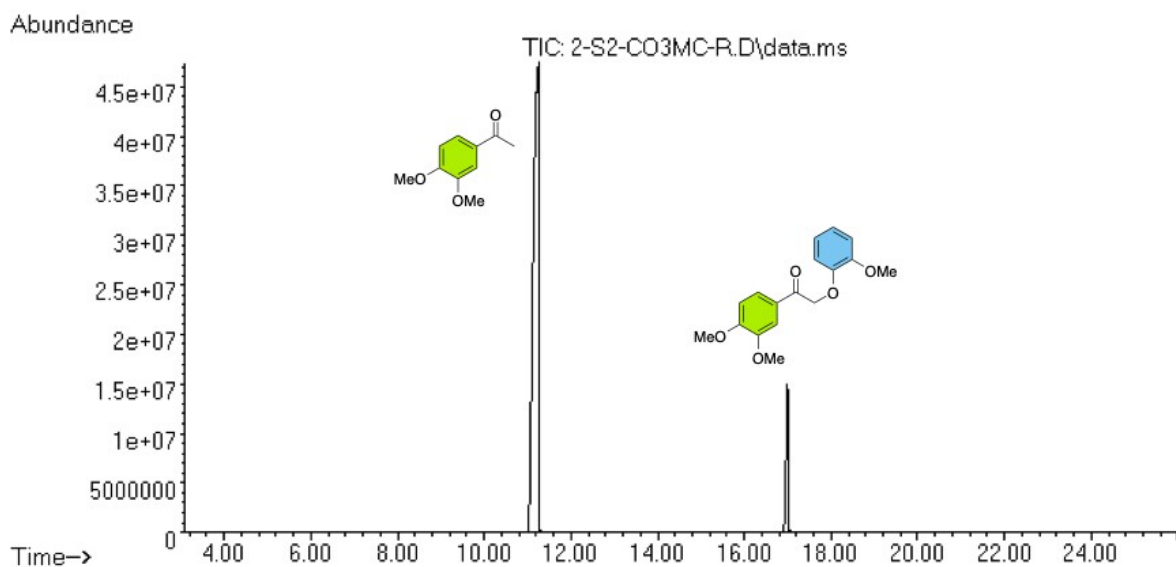


Fig. S26. Chromatogram for catalytic hydrogenolysis of S2 with Co-1 under 10 bar of hydrogen pressure

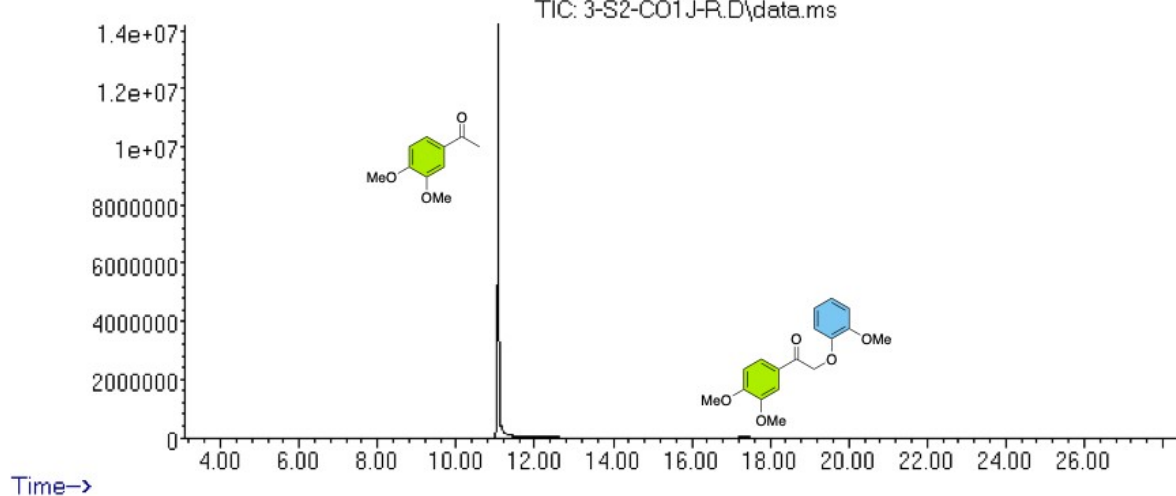


Fig. S27. Chromatogram for catalytic hydrogenolysis of S2 with Co-2 under 10 bar of hydrogen pressure.

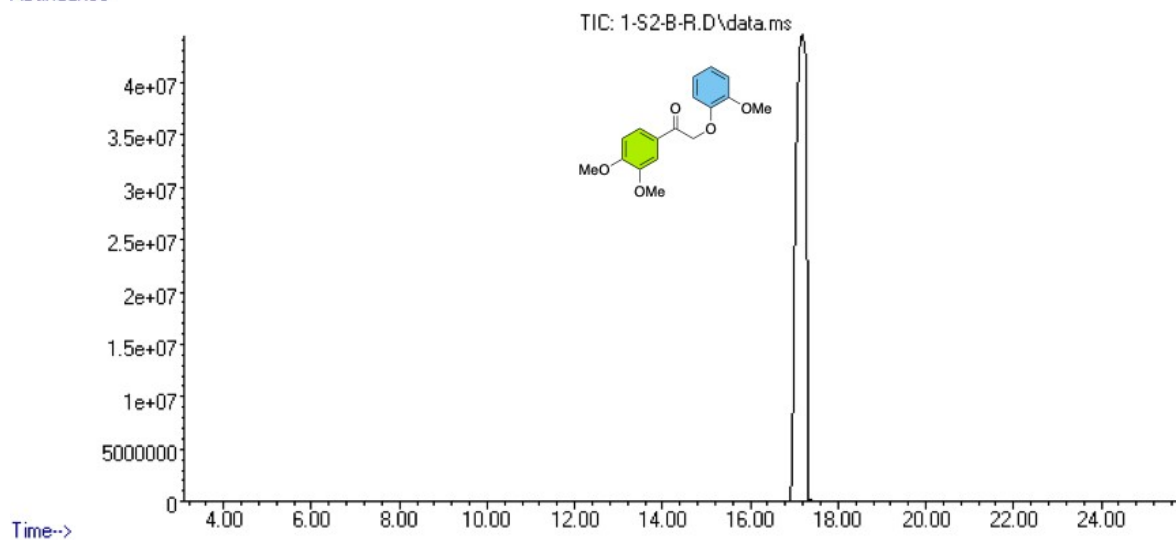


Fig. S28. Chromatogram for blank of catalytic hydrogenolysis of S2 under 10 bar of hydrogen pressure.

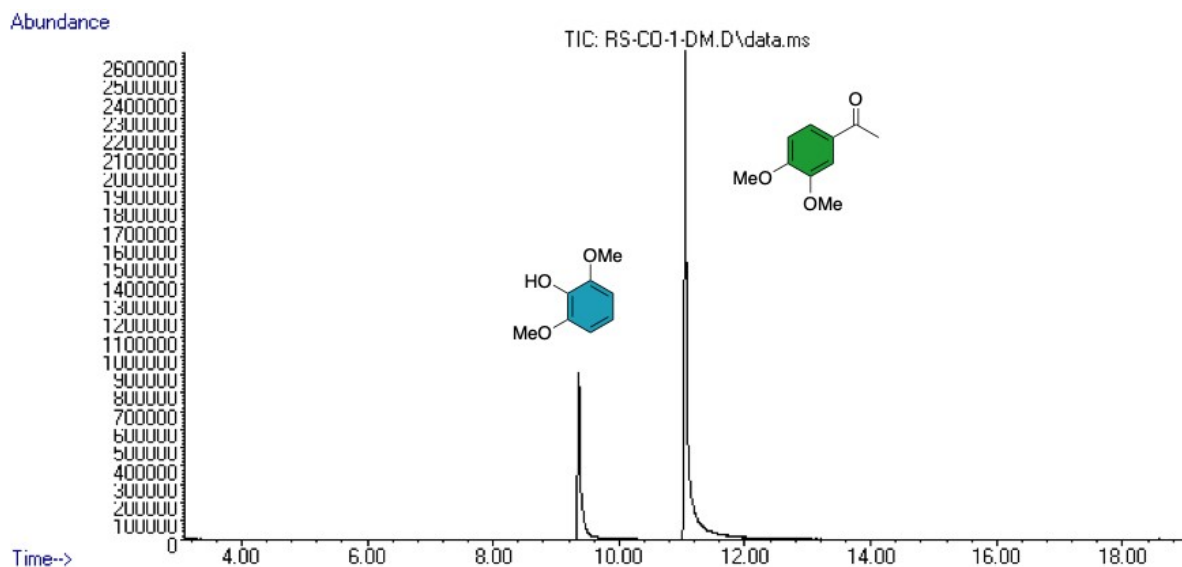


Fig. S29. Chromatogram for catalytic hydrogenolysis of **S2E** with **Co-1** and HCOOH/Et₃N as a hydrogen source.

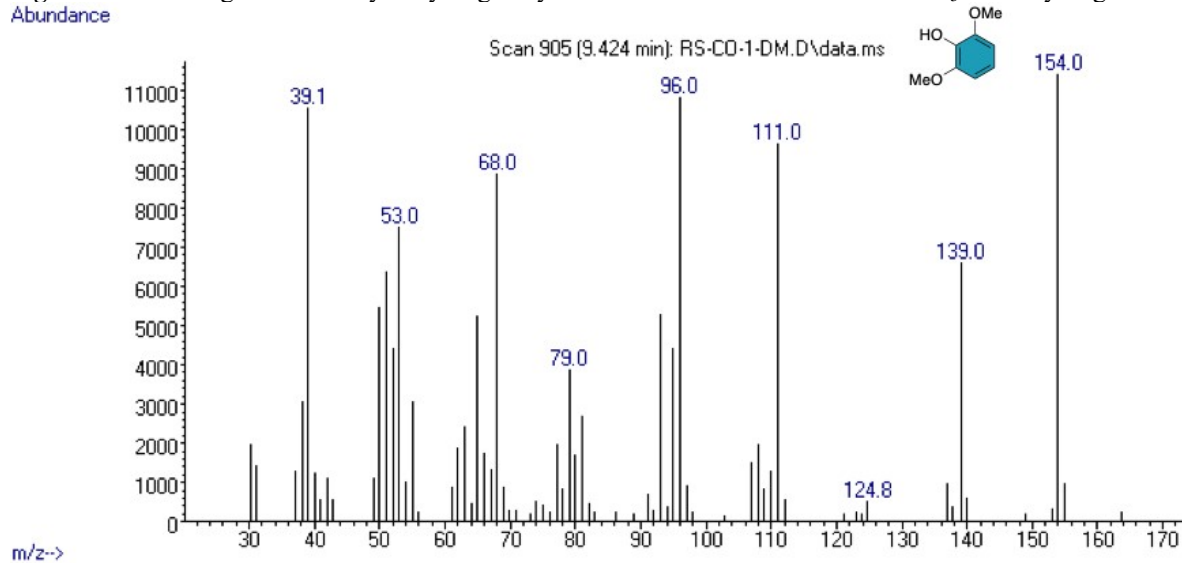


Fig. S30. Mass spectrum for 2,6-dimethoxyphenol from the catalytic hydrogenolysis of **S2E** with **Co-2** and HCOOH/ Et₃N as a hydrogen source.

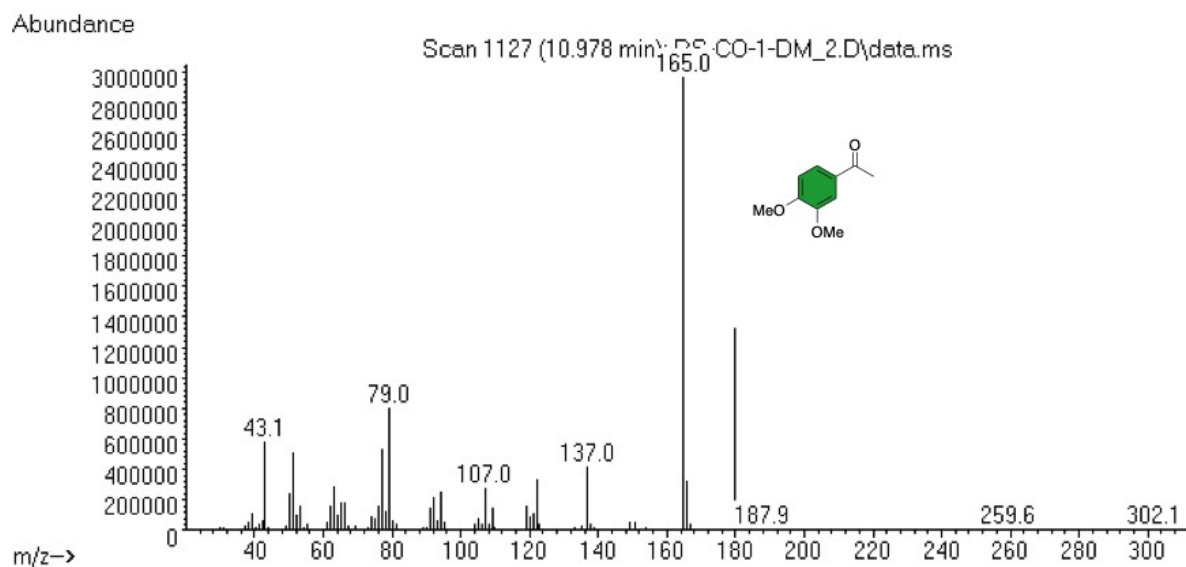


Fig. S31. Mass spectrum for ketone from the catalytic hydrogenolysis of **S2E** with **Co-2** and HCOOH/ Et₃N as a hydrogen source.

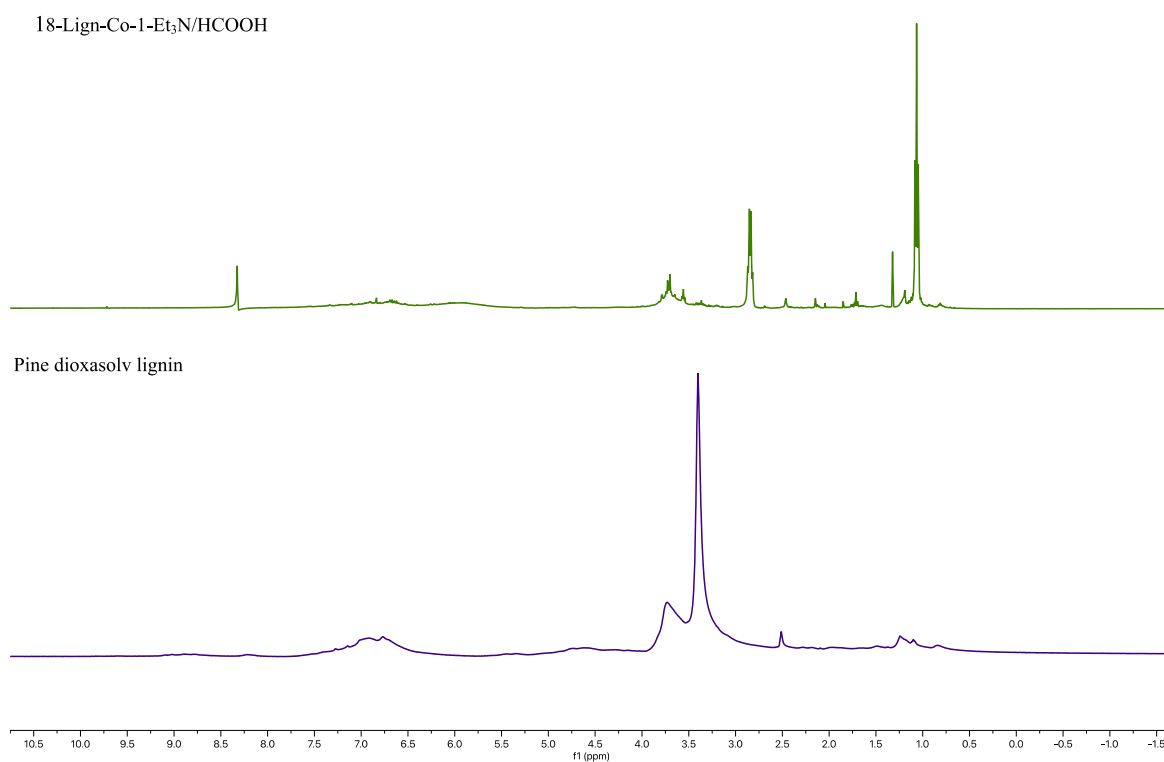


Fig. S32. ¹H NMR (300 MHz, DMSO-*d*₆) for the hydrogenolysis of pine dioxasolv lignin with **Co-1** using the AF/Et₃N as a hydrogen source.

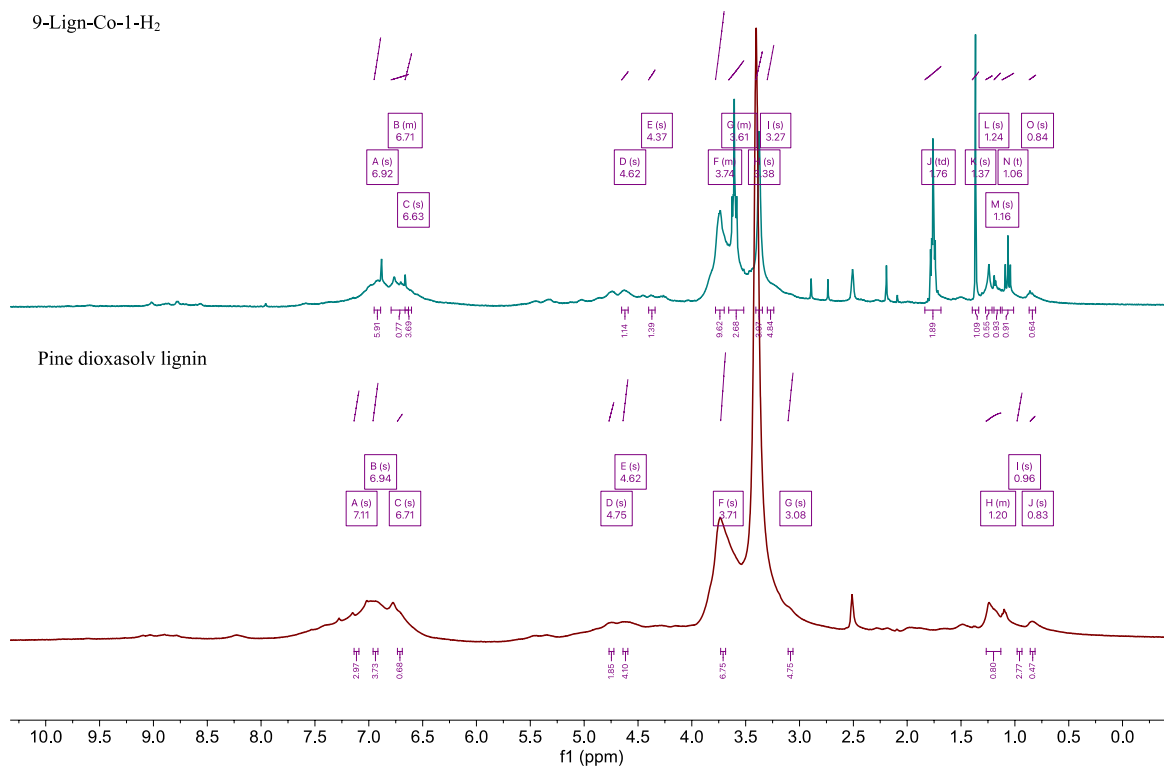


Fig. S33. ¹H NMR (400 MHz, DMSO-*d*₆) for the hydrogenolysis of pine dioxasolv lignin with Co-1 under 10 bar of hydrogen.

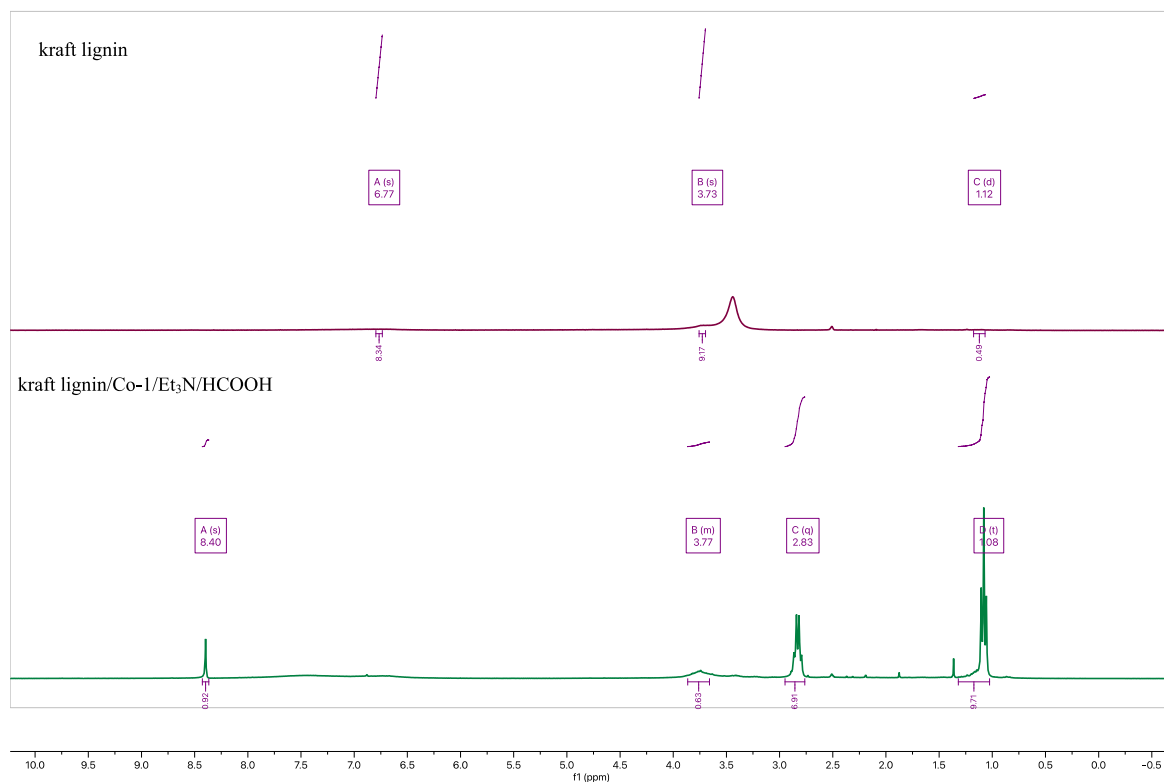


Fig. S34. ¹H NMR (300 MHz, DMSO-*d*₆) for the hydrogenolysis of kraft lignin with Co-1 using the AF/Et₃N as a hydrogen source.

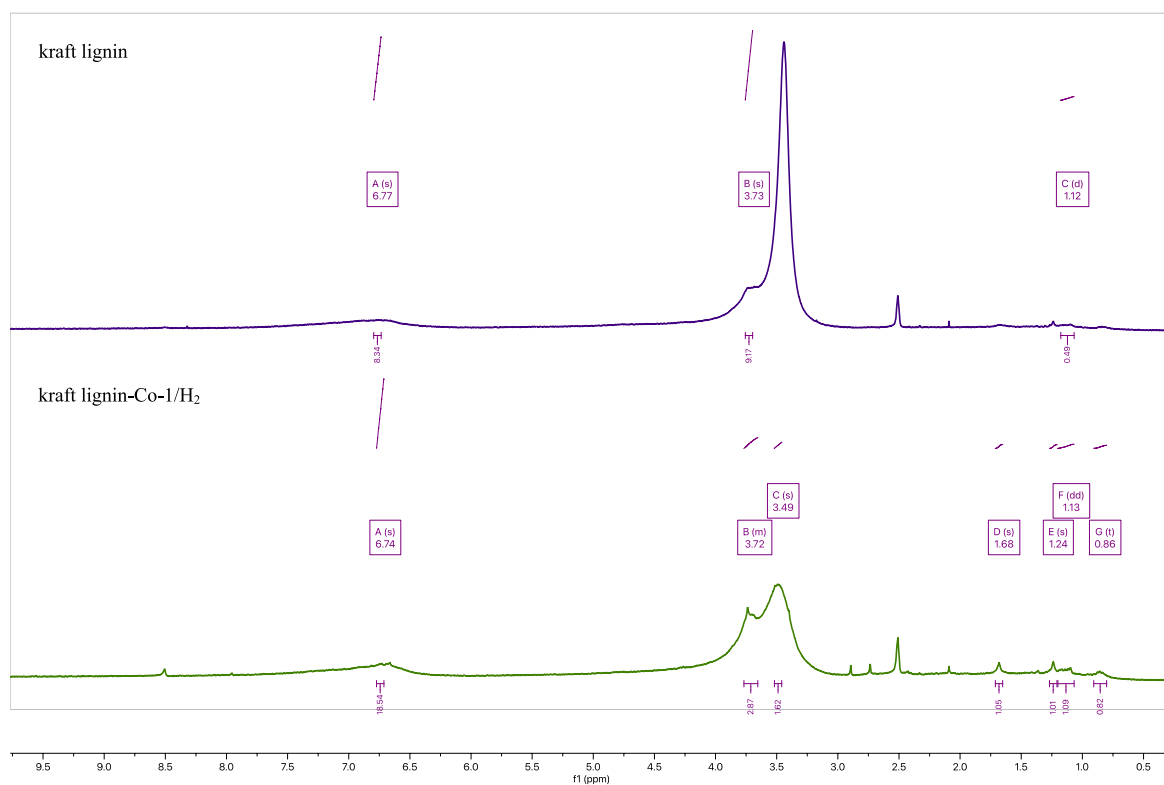


Fig. S35. ¹H NMR (300 MHz, DMSO-*d*₆) for the hydrogenolysis of kraft lignin with Co-1 under 10 bar of hydrogen.

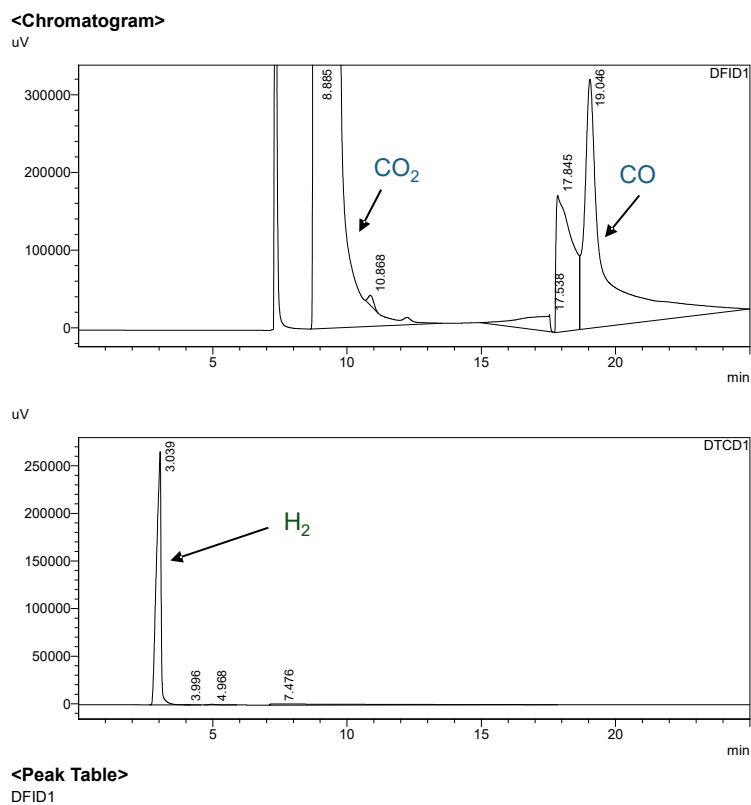


Fig. S36. GC Chromatogram from catalytic formic acid dehydrogenation by Co-1 to produce hydrogen. Co-1 (15 mg), HCOOH, 24 h at 180 °C.

Table S3. Hydrogen concentration from formic acid dehydrogenation reaction.

Entry	Conditions	Hydrogen (ppm)
1	30 min, 180 °C, Et ₃ N (5 equiv. HCOOH (3 equiv), EtOH:H ₂ O (1:1 v/v), 180 °C	1
2	30 min, EtOH:H ₂ O (1:1 v/v)	1
3	Co-1 , 180 °C, 30 min Et ₃ N (5 equiv. HCOOH (3 equiv), EtOH:H ₂ O (1:1 v/v)	135
4	Co-1 , 150 °C, 30 min Et ₃ N (5 equiv. HCOOH (3 equiv), EtOH:H ₂ O (1:1 v/v)	2

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