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Chemicals from lignin by diol-stabilized acidolysis: reaction pathways and kinetics

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Contents

S 1.0 Analytical procedures

Ultra-high performance liquid chromatography-mass spectrometry (UPLCMS) was performed using a Waters Acquity Ultra Performance LC system equipped with a TQ detector and an Acquity UPLC HSS T3 Column (1.8 µm 2.1 × 150 mm). Analysis was performed using MassLynx V4.1 software.

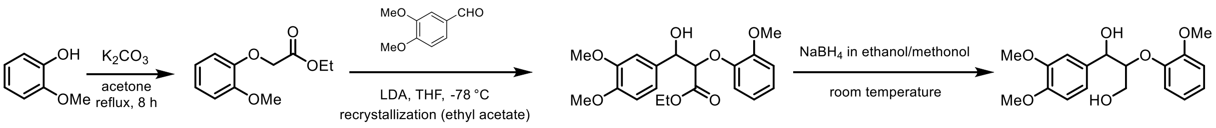
Gas chromatography-mass spectrometry (GC-MS) was performed using an Agilent 6890 series GC system equipped with a HP973 mass detector with helium as carrier gas.

NMR: NMR spectra were recorded on a Varian Oxford Mercury AS 400, an Agilent Technologies 400/54 Premium shielded spectrometer or a Bruker Ascend 600 using CDCl$_3$ or DMSO-d_6 as solvent at room temperature. Chemical shift values are reported in part per million (ppm) with the solvent resonance as the internal standard. Data report followed the bellowing pattern: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br. = broad, m = multiplet), coupling constants (Hz), and integration.

Thin layer chromatography was performed on pre-coated aluminum plates (60/kieselguhr F$_{254}$ Merk) and visualized under UV light (254 nm) or by staining with KMnO$_4$.

S 2.0 Synthesis of standard compounds

Compound **A**: Ethyl 3-(3,4-dimethoxyphenyl)-3-hydroxy-2-(2-methoxyphenoxy)propanoate

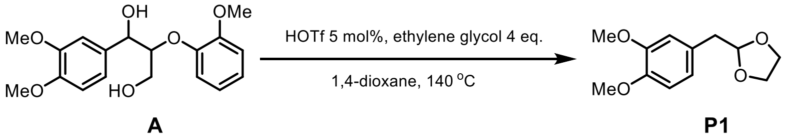


Compound **A** was synthesized following a literature procedure.[1]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10–7.03 (m, 1H), 7.01–6.87 (m, 5H), 6.84 (d, *J* = 8.2 Hz, 1H), 4.98 (d, *J* = 4.6 Hz, 1H), 4.22–4.12 (m, 1H), 3.98–3.83 (m, 10H), 3.66 (dd, *J* = 12.2, 3.4 Hz, 1H).

Spectral data were consistent with the values reported in literature.[1]

Compound **P1**: 2-(3,4-dimethoxybenzyl)-1,3-dioxolane

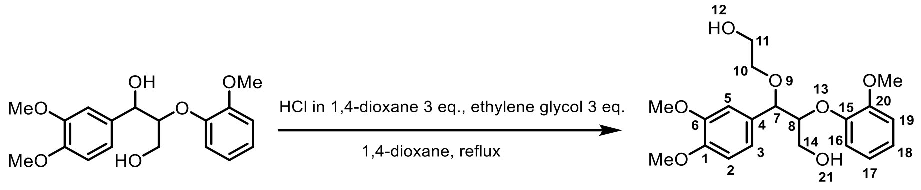


Substrate (e.g., compound **A**, 50 mg, 0.15 mmol) was placed in a 20 mL microwave vial, equipped with a magnetic stirring bar. Solvent (1,4-dioxane, 10 mL) and ethylene glycol (37 mg, 0.6 mmol, 4 eq.) were added and the vial was sealed. The solution was stirred and heated to 140 °C. HOTf (5 mol%, 50 µL, from a 0.15 mmol/mL stock solution in 1,4-dioxane) was added by syringe with a thin needle through the septum of the microwave vial. The reaction was stirred at 140 °C for 15 min before being cooled rapidly in an ice bath and quenched with a drop of trimethylamine, transferred to a round bottomed flask and concentrated in *vacuo*. Purification was carried out via column chromatography (20–50% EtOAc/heptane) yielding the product as an off-white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 (s, 3H, Ar-$\underline{H}$), 5.04 (t, *J* = 4.8 Hz, 1H), 3.98–3.93 (m, 2H), 3.88 (s, 3H), 3.87–3.82 (m, 5H), 2.91 (d, *J* = 4.8 Hz, 2H).

Spectral data were consistent with the values reported in literature.[2]

Compound **B**: 3-(3,4-dimethoxyphenyl)-3-(2-hydroxyethoxy)-2-(2-methoxyphenoxy)propan-1-ol



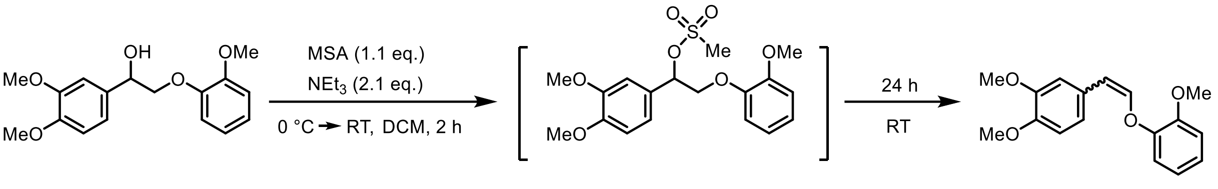
A **B**

Substrate **A** (100 g, 0.2991 mmol) was dissolved in 1,4-dioxane (5 mL) and EG (5 mL). 3 eq. of HCl (from a 4 N HCl in 1,4-dioxane solution) was added to the mixture and the reaction refluxed for 2 h, after which no more starting material was visible by TLC. The reaction was quenched by addition of 10 mL sat. aqueous $NaHCO_3$ and extracted into EtOAc. The organic layers were combined and washed with brine and dried over $MgSO_4$ prior to being filtered and concentrated in *vacuo*. The crude product was purified via column chromatography (30–60% Acetone/PET Ether) to obtain the product as a clear semi-solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.14 (m, 0.25H, Ar-$\underline{H}$), 7.05–6.83 (m, 5H, Ar-$\underline{H}$), 6.78 (m, 1H, Ar-$\underline{H}$), 6.57 (d, 0.75H, Ar-$\underline{H}$), 4.70 (d, *J* = 7.2 Hz, 0.75H, H7), 4.64 (d, *J* = 7.8 Hz, 0.25H, H7), 4.25 (dt, 0.25H, H8), 4.10 (dt, 0.25H, H8), 3.98 (dd, 1H, H14), 3.91–3.82 (m, 9H, 3 × -OCH_3), 3.81–3.39 (m, 5H, H10, H11 and H14).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 149.5, 149.2, 148.9, 147.3, 131.9, 123.8, 123.5, 121.6, 121.5, 120.2, 120.2, 120.1, 119.8, 112.3, 112.2, 111.2, 111.1, 110.3, 87.2 (C8, minor), 86.6 (C8, major), 82.9 (C7, minor), 80.6 (C7, major), 77.5, 70.6, 70.6, 61.9 (C11), 61.9, 61.1, 56.1 (-O$\underline{C}H_3$), 56.1(-O$\underline{C}H_3$), 55.9 (-O$\underline{C}H_3$).

Compound **I1**: 1,2-dimethoxy-4-(2-(2-methoxyphenoxy)vinyl)benzene



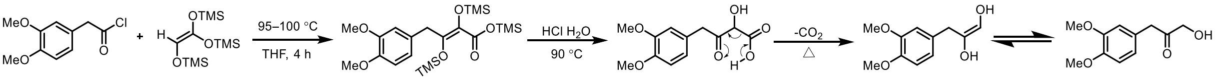
B-OH **I1**

1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-ol (**B-OH**) was synthesized following the literature procedure.[3] To a DCM (5 mL) solution of **B-OH** (100 mg, 0.329 mmol), cooled to 0 °C, was added methanesulfonic anhydride (MSA = 63 mg, 0.361 mmol, 1.1 eq.) and triethylamine (0.1 mL, 2.1 eq.). The resulted mixture was stirred at 0 °C for 30 min and then allowed to warm up to room temperature. After stirring overnight, the reaction mixture was diluted with water (5 mL) and extracted with DCM. The organic phase was successively washed with 10 mL of a 1M HCl solution, brine (15 mL) and water and dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by column chromatography (pentane/acetone = 97/3) to obtain a cis/trans isomer mixture (*cis*/*trans* = 7.7/1). Quantitative proton NMR result of the mixture was used for HPLC calibration.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.0 Hz, 1H), 7.16–7.04 (m, 3H), 7.02 (d, *J* = 12.5 Hz, 0.115H, *trans*), 7.00–6.91 (m, 2H), 6.87–6.80 (m, 1H), 6.55 (d, *J* = 6.8 Hz, 0.885H, *cis*), 6.29 (d, *J* = 12.5 Hz, 0.115H, *trans*), 5.56 (d, *J* = 6.8 Hz, 0.885H, *cis*), 3.91 (s, 3H), 3.89 (s, 6H).

Spectral data were consistent with the values reported in the literature.[3]

Compound **R**: 1-(3,4-dimethoxyphenyl)-3-hydroxypropan-2-one



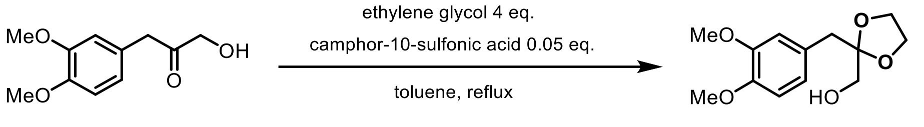
DBC **R**

R was synthesized following a literature procedure.[4] To THF in a sealed round bottom flask, were successively added 3,4-dimethoxybenzeneacetyl chloride (**DBC**, 1.0 g, 4.66 mmol) and tris(trimethyl-siloxy)ethylene (3.0 g, 10.25 mmol, 2.2 eq.) via syringe. The mixture was then heated to 110 °C refluxing for 4 h under a N_2 atmosphere. After cooling, THF and 2M HCl were successively added into the solution, which was then heated at 85 °C for 30 min. After cooling to the room temperature, the water phase was saturated by NaCl and washed 3 times with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated in *vacuo*. The product was purified by column chromatography.

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.80 (d, 1H, Ar-H), 6.74–6.68 (m, 2H, Ar-H), 4.25 (s, 2H), 3.84–3.82 (m, 6H, -OCH$_3$), 3.62 (s, 2H).

Spectral data were consistent with the values reported in literature.[5]

Compound **R1**: 2-[(3,4-Dimethoxyphenyl)methyl]-1,3-dioxolane-2-methanol



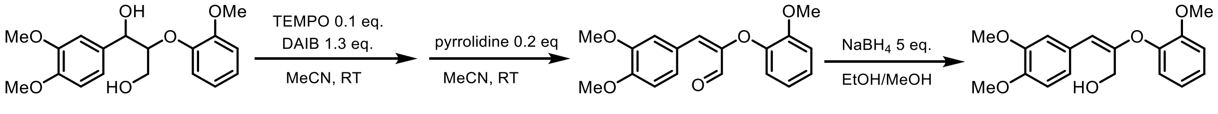
R **R1**

R1 was synthesized following a literature procedure.[6] To a stirred solution of Hibbert ketone (**R**, 150.0 mg, 0.714 mmol, 1 eq.) and ethylene glycol (177.2 mg, 2.854 mmol, 4 eq.) in toluene (5 mL), was added camphor-10-sulfonic acid (8.3 mg, 0.036 mmol, 0.05 eq.). The resulted mixture was heated and refluxing for 3 h, after which cooled to room temperature and concentrated *in vacuo*. The crude mixture was dissolved in DCM (20 mL) and washed with water (2 × 10 mL) and brine (2 × 10 mL). The combined organic phase was dried over MgSO$_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (15–40% Acetone/PET Ether) to afford the product as an orange oil.

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.87–6.75 (m, 3H), 3.95–3.89 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.74–3.67 (m, 2H), 3.51 (s, 2H), 2.91 (s, 2H).

Spectral data were consistent with the values reported in the literature.[6]

Compound **I2**: 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-1-propene-3-ol



A **BI** **I2**

To a 20 mL microwave vial with 15 mL ACN, were added substrate **A** (500.0 mg, 1.5 mmol, 1 eq.), 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 23.4 mg, 0.15 mmol, 0.1 eq.) and (Diacetoxyiodo)benzene (DAIB, 626.2 mg, 1.94 mmol, 1.3 eq.). The resulting solution was stirred at room temperature for 7 h, after which pyrrolidine (25.5 μL, 0.3 mmol, 0.2 eq.) was added, and the solution was stirred for another 5 h at room temperature. The resulted mixture was diluted with 15 mL water and washed with EtOAc (3 × 15 mL). The combined organic phase was dried over MgSO$_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (30–60% EtOAc/Heptane) to afford **BI**. To a round-bottom flask, was added 5 mL ethanol and **BI** (100 mg, 0.32 mmol, 1 eq.). NaBH$_4$ (143.6 mg, 1.59 mmol, 5 eq.) was then added in 5 min. MeOH (193 μL, 4.77 mmol, 15 eq.) was added slowly under N$_2$. The reaction was stirred for 24 h after which no starting material (**BI**) was visible by TLC. The reaction was quenched with an aqueous solution of sat. NH_4Cl (5 mL). An additional 5 mL H_2O was added to solubilize the precipitated salts. The quenched reaction was then extracted with EtOAc (3 × 5 mL). The organic layers were combined, washed with H_2O and brine prior to being dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification was carried out by column chromatography (1–3% MeOH/DCM) to afford the product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (sf, 1H, Ar-H), 7.11–6.95 (m, 4H, Ar-H), 6.87–6.76 (m, 2H, Ar-H), 6.10 (s, 1H, Cα-H), 4.17 (s, 2H, Cγ-H), 3.92 (s, 3H, -OCH_3), 3.85 (s, 3H, -OCH_3), 3.75 (s, 3H, -OCH_3).

Spectral data were consistent with the values reported in the literature, and the spectra implies that the compound is in Z-isomer form.[7]

S 3.0 Time course reactions

S 3.1 Carbon balance calculation

$$\text{C balance} = \frac{\text{C amount in identified products+C amount in remaining starting substrate}}{\text{C amount in the starting substrate}}$$ in detail:

$$\text{C balance} = \frac{(\text{Yield}_{\beta-O-4} \times 17) + (\text{Yield}_{\text{EG adduct}} \times 17) + (\text{Yield}_{\text{C2-vinyl ethers}} \times 17) + (\text{Yield}_{\text{Guaiacol}} \times 7) + (\text{Yield}_{\text{C2-acetal}} \times 10)}{17}$$

S 3.2 C3 β-O-4 model acidolysis with different metal triflates

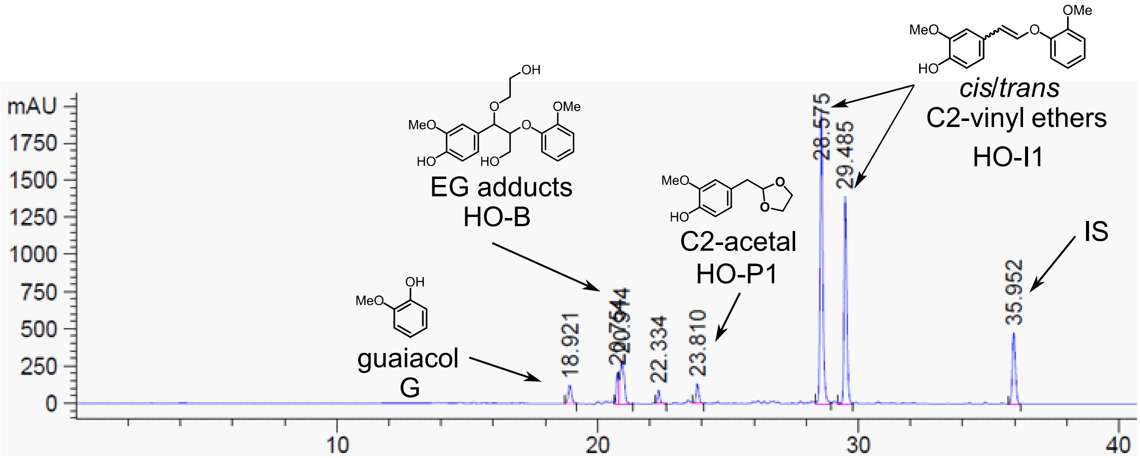


Fig. S1. HPLC Chromatograph resulting from the treatment of compound **HO-A** with 10 mol% $Yb(OTf)_3$ for 60 min (Table S1, Entry 13).

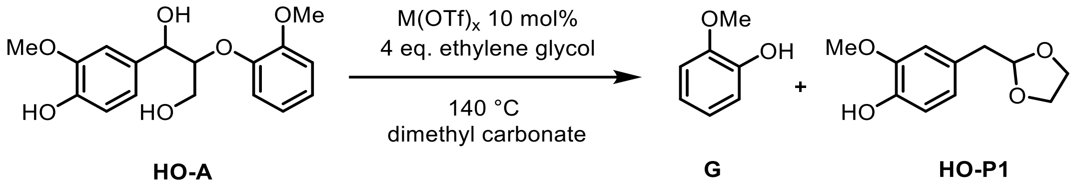


Table S1. Screening of the cleavage of phenolic C3 β-O-4 model compound **HO-A** with metal triflate salts in DMC to phenolic products **G** and **HO-P1**.

Entry	Catalyst	mol %	Time	% Conversion	% Yield (**G**)	% Yield (**HO-P1**)
1	$Fe(OTf)_3$	10	15 mins	100	77	55
2	$Fe(OTf)_3$	10	20 mins	100	80	56
3	$Fe(OTf)_3$	10	30 mins	100	81	53
4	$Fe(OTf)_3$	10	1 hour	100	81	43
5	$Fe(OTf)_3$	10	2 hour	100	77	32
6	$Sc(OTf)_3$	5	15 mins	100	25	0
7	$Sc(OTf)_3$	10	15 mins	100	60	49
8	$Sc(OTf)_3$	10	30 mins	100	69	61
9	$Sc(OTf)_3$	10	60 mins	100	74	65
10	$Yb(OTf)_3$	5	15 mins	96	9	0
11	$Yb(OTf)_3$	10	15 mins	97	10	0
12	$Yb(OTf)_3$	10	30 mins	100	14	0
13	$Yb(OTf)_3$	10	60 mins	100	18	3
14	$Ag(OTf)_3$	5	15 mins	100	84	38
15	$Ag(OTf)_3$	10	15 mins	100	86	74
16	$Ag(OTf)_3$	10	30 mins	100	92	75
17	$Sn(OTf)_3$	5	15 mins	98	77	68
18	$Sn(OTf)_3$	10	15 mins	100	82	71
19	$Sn(OTf)_3$	10	30 mins	100	86	72
20	$Bi(OTf)_3$	5	15 mins	100	84	73
21	$Bi(OTf)_3$	10	15 mins	100	85	69
22	$Bi(OTf)_3$	10	30 mins	100	83	66
23	$Sm(OTf)_3$	5	15 mins	36	2	0
24	$Sm(OTf)_3$	10	15 mins	53	3	0
25	$Sm(OTf)_3$	10	30 mins	83	5	0
26	$Zn(OTf)_2$	5	15 mins	11	0	0
27	$Zn(OTf)_2$	10	15 mins	54	3	0
28	$Zn(OTf)_2$	10	30 mins	71	4	0
29	$Cu(OTf)_2$	5	15 mins	100	45	17
30	$Cu(OTf)_2$	10	15 mins	100	78	54
31	$Cu(OTf)_2$	10	30 mins	100	92	40
32	$Al(OTf)_3$	5	15 mins	100	69	48
33	$Al(OTf)_3$	10	15 mins	100	81	67
34	$Al(OTf)_3$	10	30 mins	100	85	71
35	$In(OTf)_3$	5	15 mins	100	74	67
36	$In(OTf)_3$	10	15 mins	100	78	70
37	$In(OTf)_3$	10	30 mins	100	81	71

The conversion and yield were obtained via HPLC analysis.

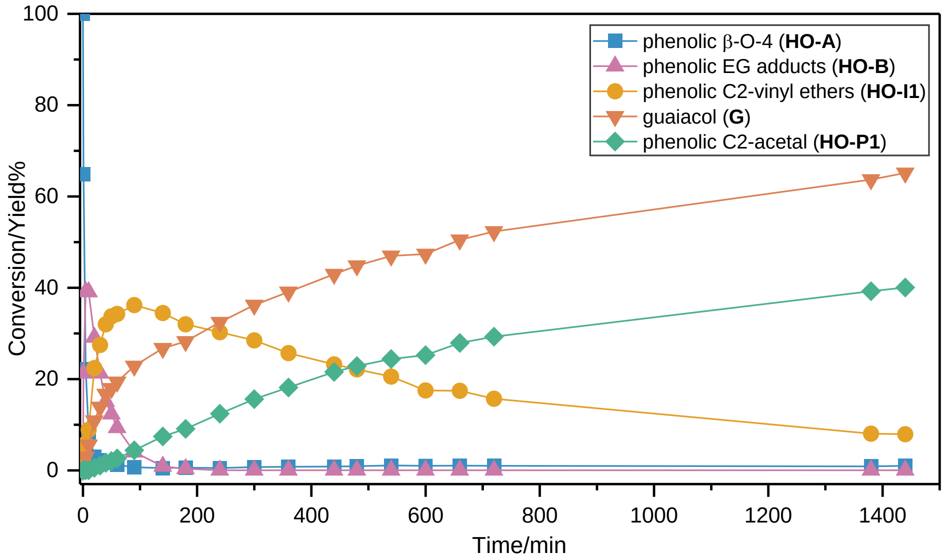


Fig. S2. Graph of time course of the reaction of phenolic β-O-4 model compound **HO-A** with 10 mol% Yb(OTf)$_3$, 4 eq. ethylene glycol, in 1,4-dioxane, at 140 °C.

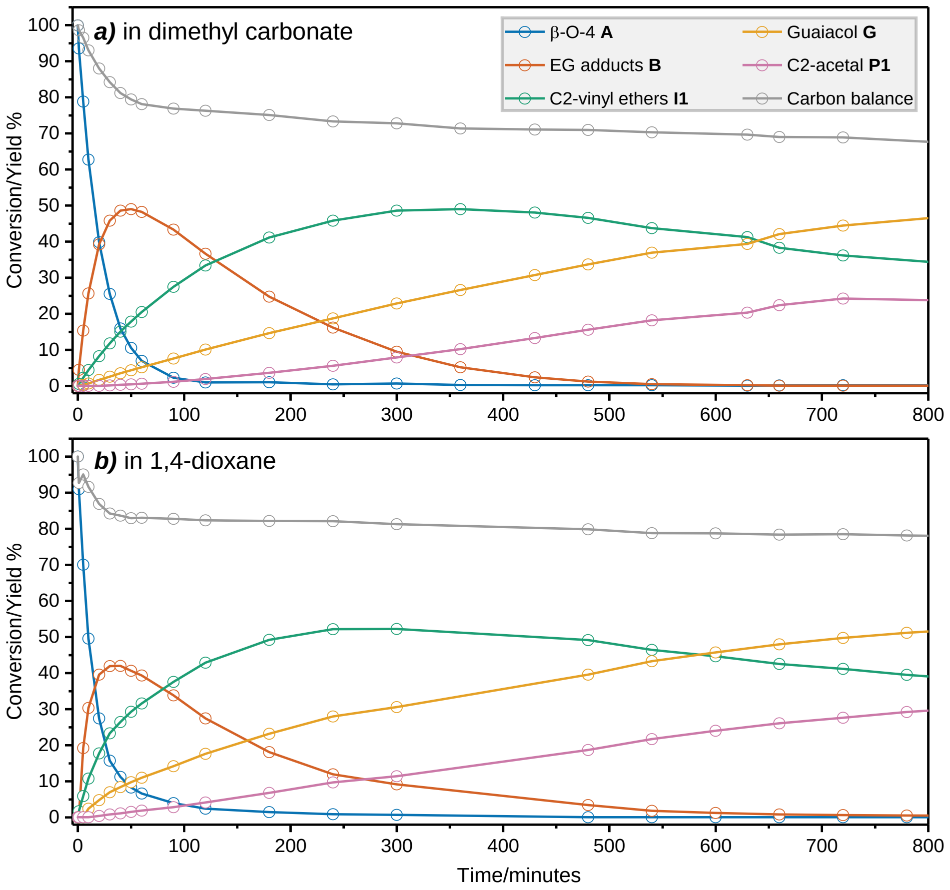


Fig. S3. Graphs of time course of the reaction of non-phenolic model compound **A** with 10 mol% Yb(OTf)$_3$, 4 eq. ethylene glycol, a) in dimethyl carbonate b) in 1,4-dioxane at 140 °C (heating block). Conversion and yields were obtained via HPLC analysis using 1,2,4,5-tetramethylbenzene as internal standard. Symbols: measured; lines: for illustrative purposes only.

S 3.3 Time course reaction profiles at different temperatures

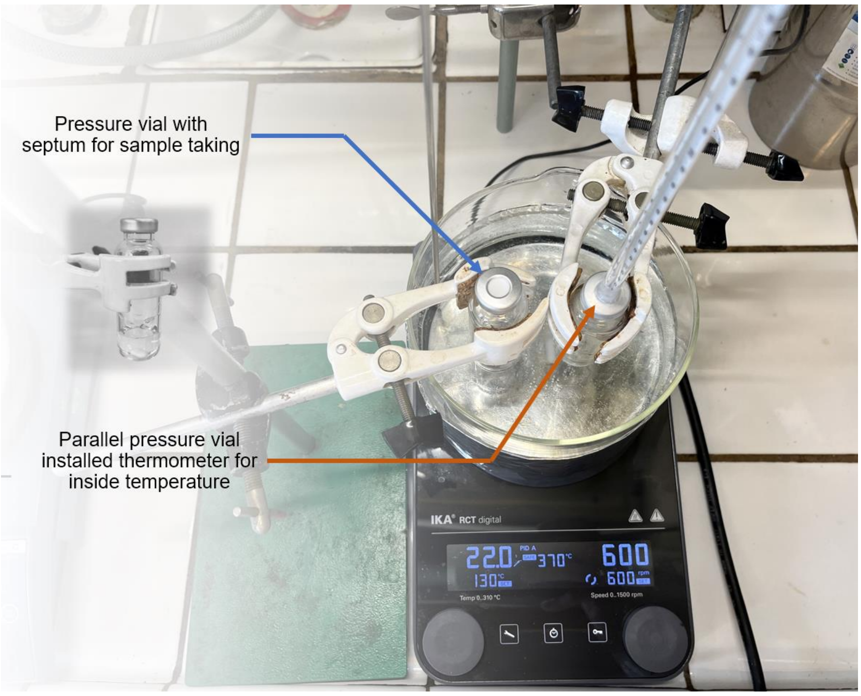


Fig. S4. Reactor vessel and reaction set up for the time course reaction with the precise monitoring of the internal reaction temperature in the reaction vessels.

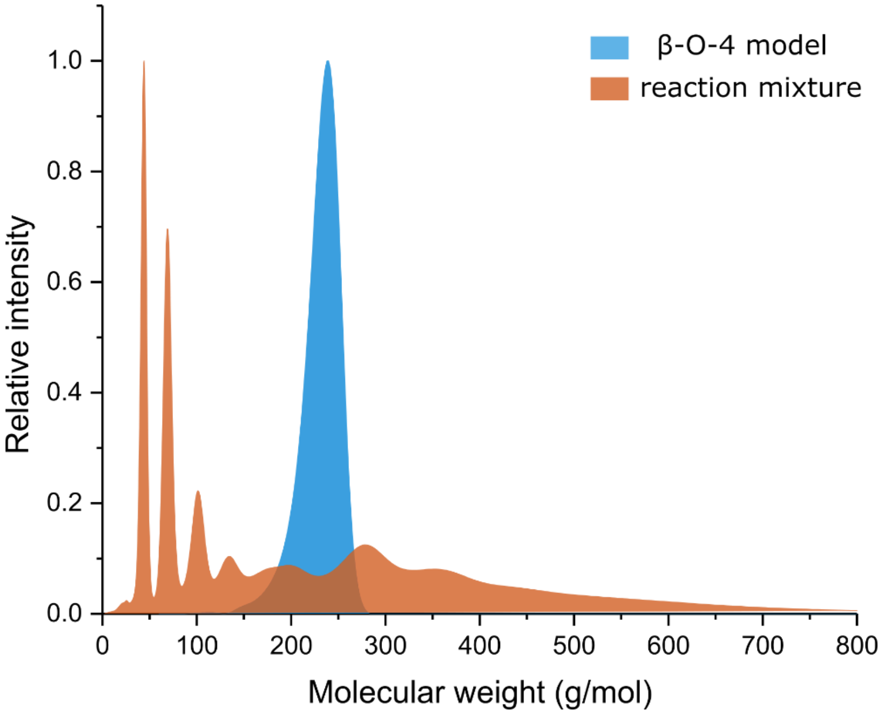


Fig. S5. GPC traces of lignin β-O-4 model **A** and product mixtures obtained after catalytic treatment of **A**. Reaction condition: 10 mol% $Yb(OTf)_3$, 4 eq. ethylene glycol at 140 °C in 1,4-dioxane.

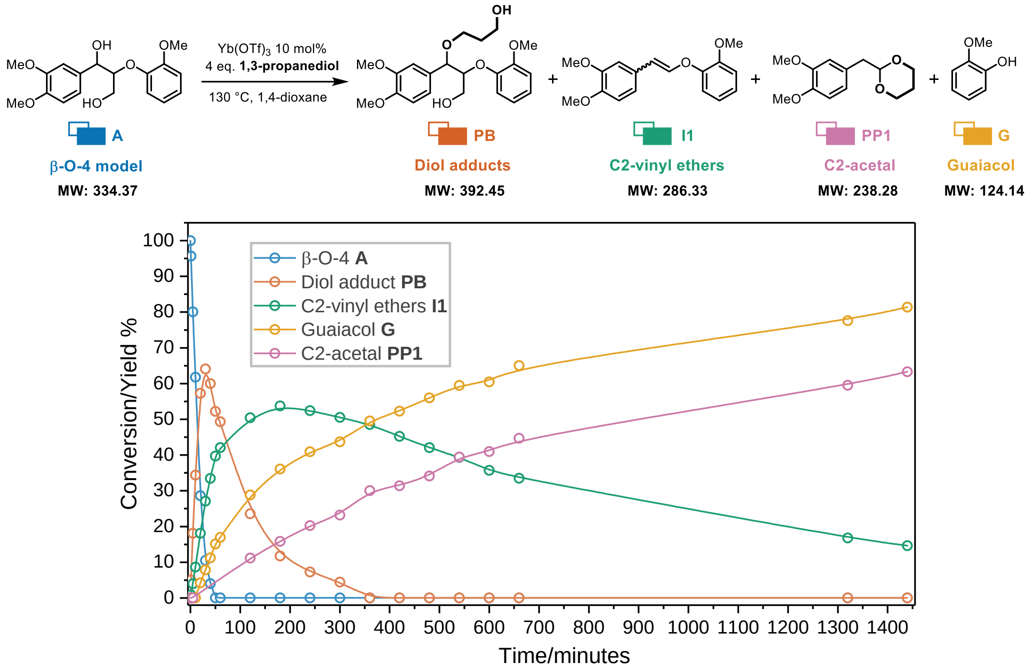


Fig. S6. Graph of time course of the reaction of non-phenolic model compound **A** with 10 mol% Yb(OTf)$_3$, 4 eq. 1,3-propanediol in 1,4-dioxane at 130 °C. Quantifications of **PB** and **PP1** are estimated by using response factors of **B** and **P1**.

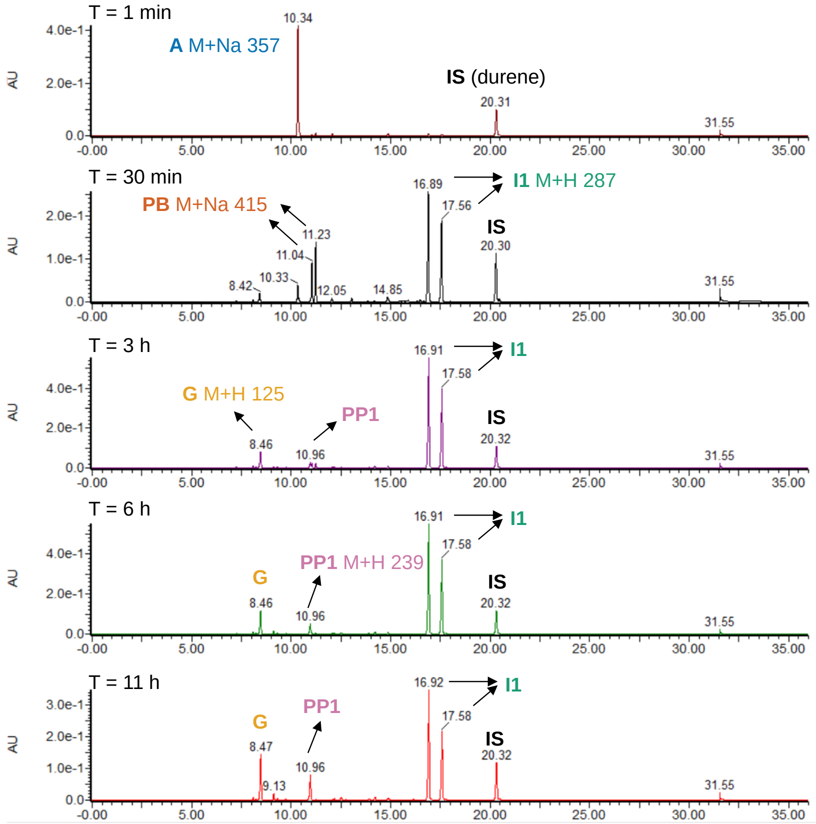


Figure S7: Selected UPLC-MS chromatographs recorded at 270 nm taken during the reaction monitoring experiment.

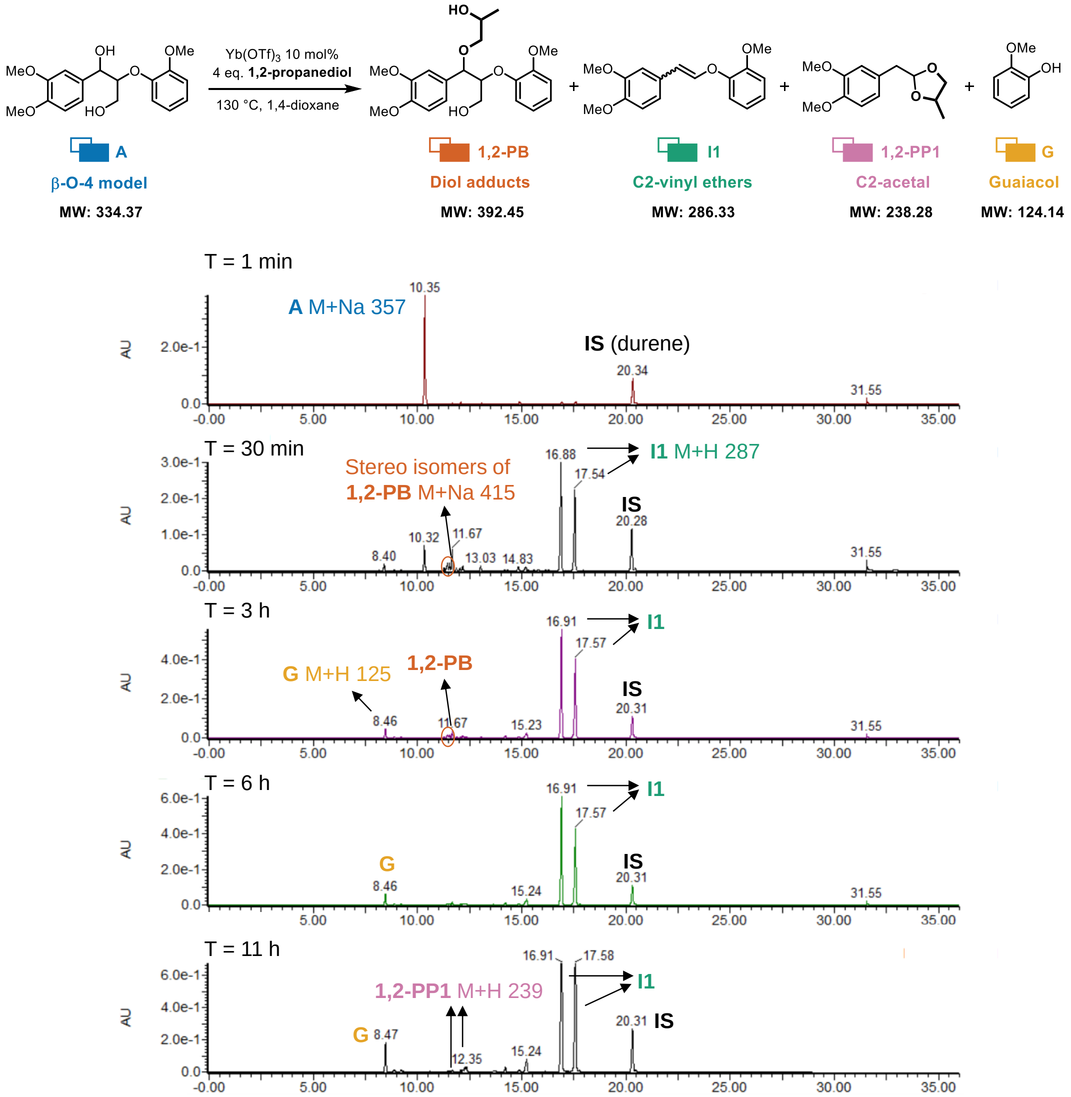


Figure S8: Selected UPLC-MS chromatographs recorded at 270 nm taken during the reaction monitoring experiment. Reaction conditions are indicated in the reaction scheme.

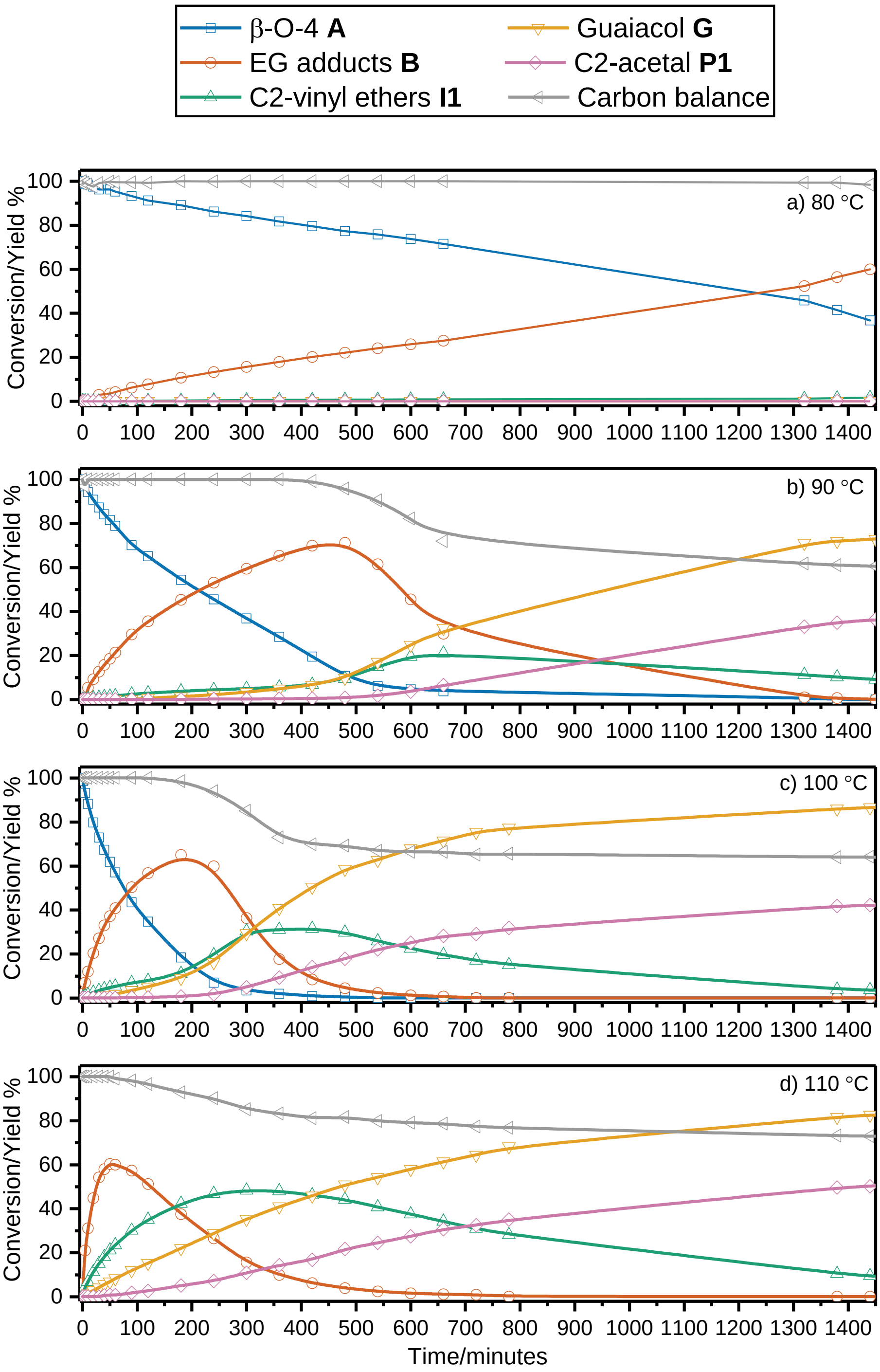


Fig. S9. Graphs of time course of the reaction of β-O-4 model compound with 10 mol% Yb(OTf)$_3$, 4 eq. ethylene glycol, in 1,4-dioxane at a) 80 °C, b) 90 °C, c) 100 °C, d) 110 °C. Conversion and yield obtained via HPLC analysis using 1,2,4,5 tetramethylbenzene as internal standard. Symbols: measured; lines: for illustrative purposes only. Accurate temperature control was found to be extremely important to get trustworthy reaction profiles for kinetic modeling. The reaction profile is sensitive to temperature fluctuations. For example, temperature fluctuation was observed for the reaction after 200 min at 100 °C, therefore only reaction profile between 0 to 200 min was used for kinetic modeling at 100 °C.

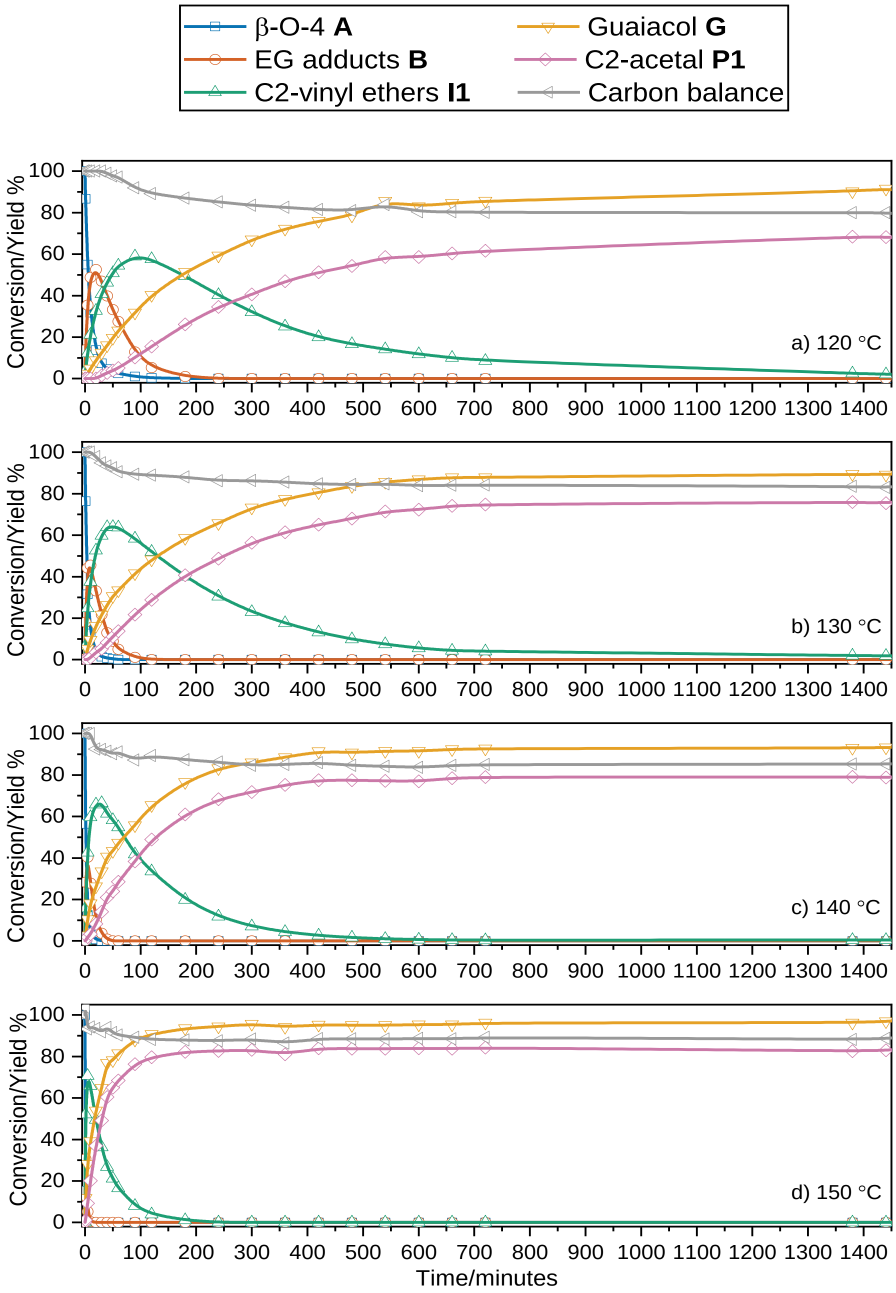


Fig. S10. Graphs of time course of the reaction of β-O-4 model compound **A** with 10 mol% Yb(OTf)$_3$, 4 eq. ethylene glycol, in 1,4-dioxane at a) 120 °C, b) 130 °C, c) 140 °C, d) 150 °C. Conversion and yield obtained via HPLC analysis using 1,2,4,5 tetramethylbenzene as internal standard. Symbols: measured; lines: for illustrative purposes only.

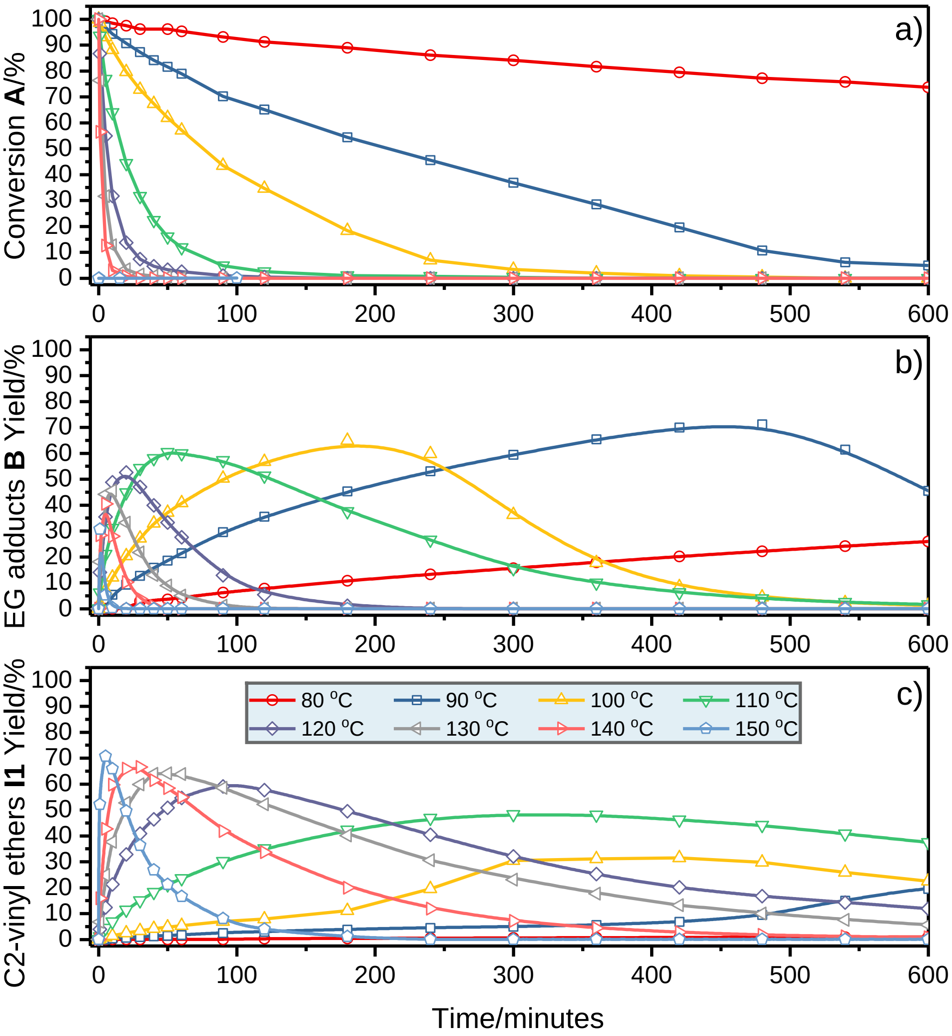
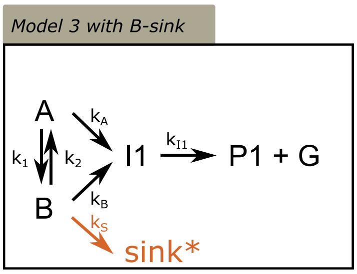
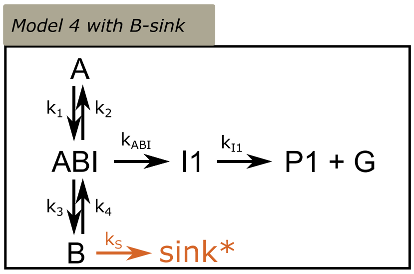


Fig. S11. Time course profiles of a) the conversion of non-phenolic model compound **A**, b) the yield of ethylene glycol **B**, c) the yield of C2-vinyl ethers **I1** over time at different temperatures. Conversion and yields obtained via HPLC analysis using 1,2,4,5 tetramethylbenzene as internal standard. Reaction condition: 10 mol% Yb(OTf)$_3$, 4 eq. ethylene glycol, in 1,4-dioxane. Symbols: measured; lines: for illustrative purposes only.

S 4.0 Kinetic modeling details



Model 3 with B-sink



Model 4 with B-sink

*sink denotes reaction pathways that lead to unidentified side cleavage or condensation products. From the kinetic schemes of Fig. 5 it appears that Model 4 has one more parameter than Model 3: The model equations for Model 3 are given in the main text as Eqs (3)–(6). In the case of Model 4, the number of parameters is reduced by applying the steady-state hypothesis to the intermediate species **ABI**. Since species **ABI** could not be detected, its concentration profile is unknown and inclusion of its concentration in the model would result in an undetermined situation; the optimum value of the objective function can be achieved with (infinitely) many parameter combinations. Elimination of the **ABI** concentration resolves the situation, resulting in the following set of equations for Model 4:

$$\frac{dC_A}{dt} = (\kappa_2 - 1)k_1 C_A + \kappa_2 k_4 C_B \qquad (C_A)_{t=0} = C_{A,0} \qquad \text{(S1)}$$

$$\frac{dC_B}{dt} = \kappa_3 k_1 C_A + (k_4(\kappa_3 - 1) - k_s)C_B \qquad (C_B)_{t=0} = 0 \qquad \text{(S2)}$$

$$\frac{dC_{I_1}}{dt} = (1 - \kappa_2 - \kappa_3)(k_1 C_A + k_4 C_B) - k_{I_1} C_{I_1} \qquad (C_{I_1})_{t=0} = 0 \qquad \text{(S3)}$$

$$\frac{dC_{P_1}}{dt} = k_{I_1} C_{I_1} \qquad (C_{P_1})_{t=0} = 0 \qquad \text{(S4)}$$

$$\kappa_i = \frac{k_i}{k_2 + k_3 + k_{\text{ABI}}} \quad (i = 2,3) \qquad \text{(S5)}$$

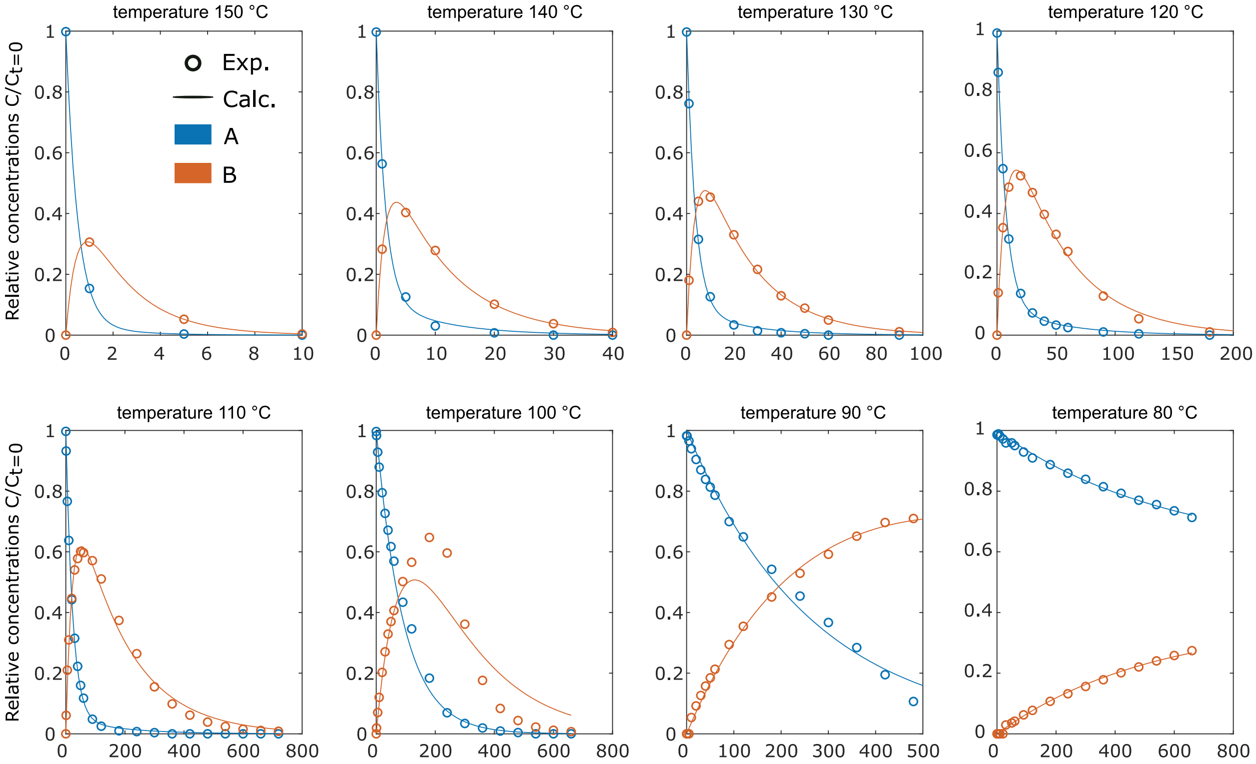


Fig. S12. Initial kinetic model fitting of C_A and C_B with Model 3 at different temperatures. Symbols: measured data; lines: calculated according to the model.

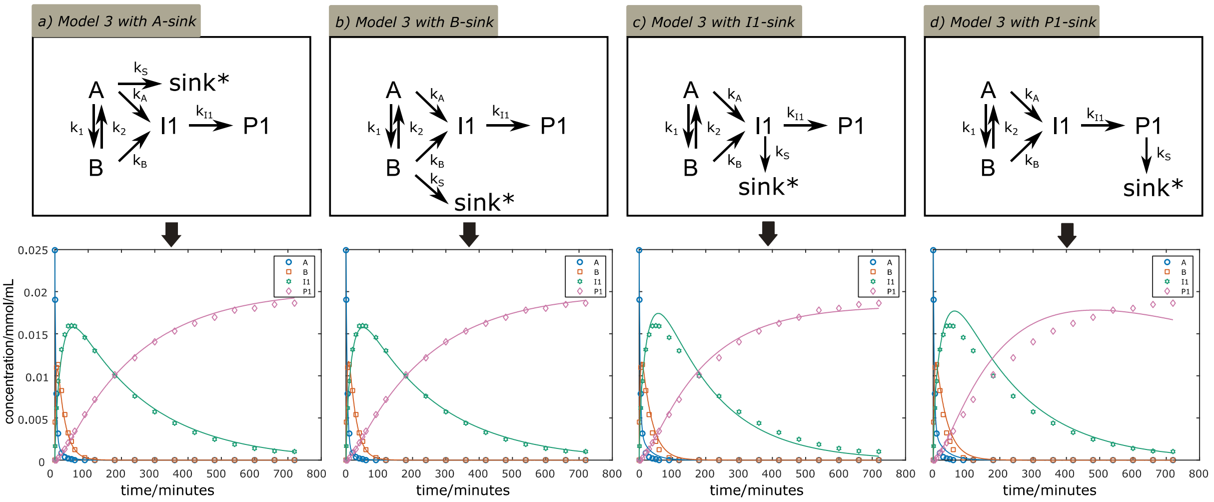


Fig. S13. Kinetic fitting results of the time course profile at 130 °C using Model 3 with a sink route a) from **A**, b) from **B**, c) from **I1**, d) from **P1**. Symbols: measured data; lines: calculated according to the model. *sink denotes reaction pathways that lead to unidentified side cleavage or condensation products.

Table S2. Rate constants (130 °C) calculated under different sink route for Model 3.

Sink route	**k_1**	**k_2**	**k_A**	**k_B**	**k_{I1}**	**k_S**	**ssr 10^5**
A-sink	186	31	61	37	4.3	38	1.155
B-sink	181	16	69	32	4.3	14	0.266
I1-sink	190	48	83	24	4.2	1.5	2.349
P1-sink	190	55	89	18	4.9	0.7	6.941

Units of k_1, k_2, k_A, k_B, k_{I1}, and k_S: 10^3 min^{-1}

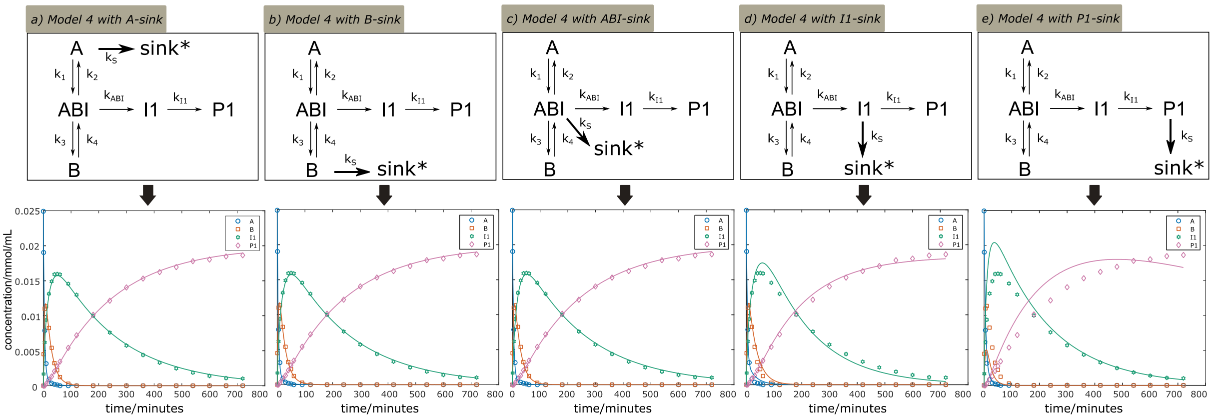


Fig. S14. Kinetic fitting results of time course profile at 130 °C using Model 4 with a sink route a) from **A**, b) from **B**, c) from **ABI**, d) from **I1**, e) from **P1**. Symbols: measured data; lines: calculated according to the model. *sink denotes reaction pathways that lead to unidentified side cleavage or condensation products.

Table S3. Rate constants (130 °C) calculated under different sink route for Model 4.

Sink route	k_1 (10^3 min^{-1})	K_2	K_3	k_4 (10^3 min^{-1})	k_{I1} (10^3 min^{-1})	k_S (10^3 min^{-1})	ssr 10^5
A-sink	304	0.185	0.614	182	4.3	37	1.153
B-sink	284	0.121	0.636	130	4.3	14	0.266
ABI-sink	277	0.078	0.642	162	4.3	0.225 (*)	0.489
I1-sink	444	0.385	0.428	126	4.2	1.5	2.349
P1-sink	548	0.499	0.34	109	4.9	0.73	6.945

(*) K_{ABI}

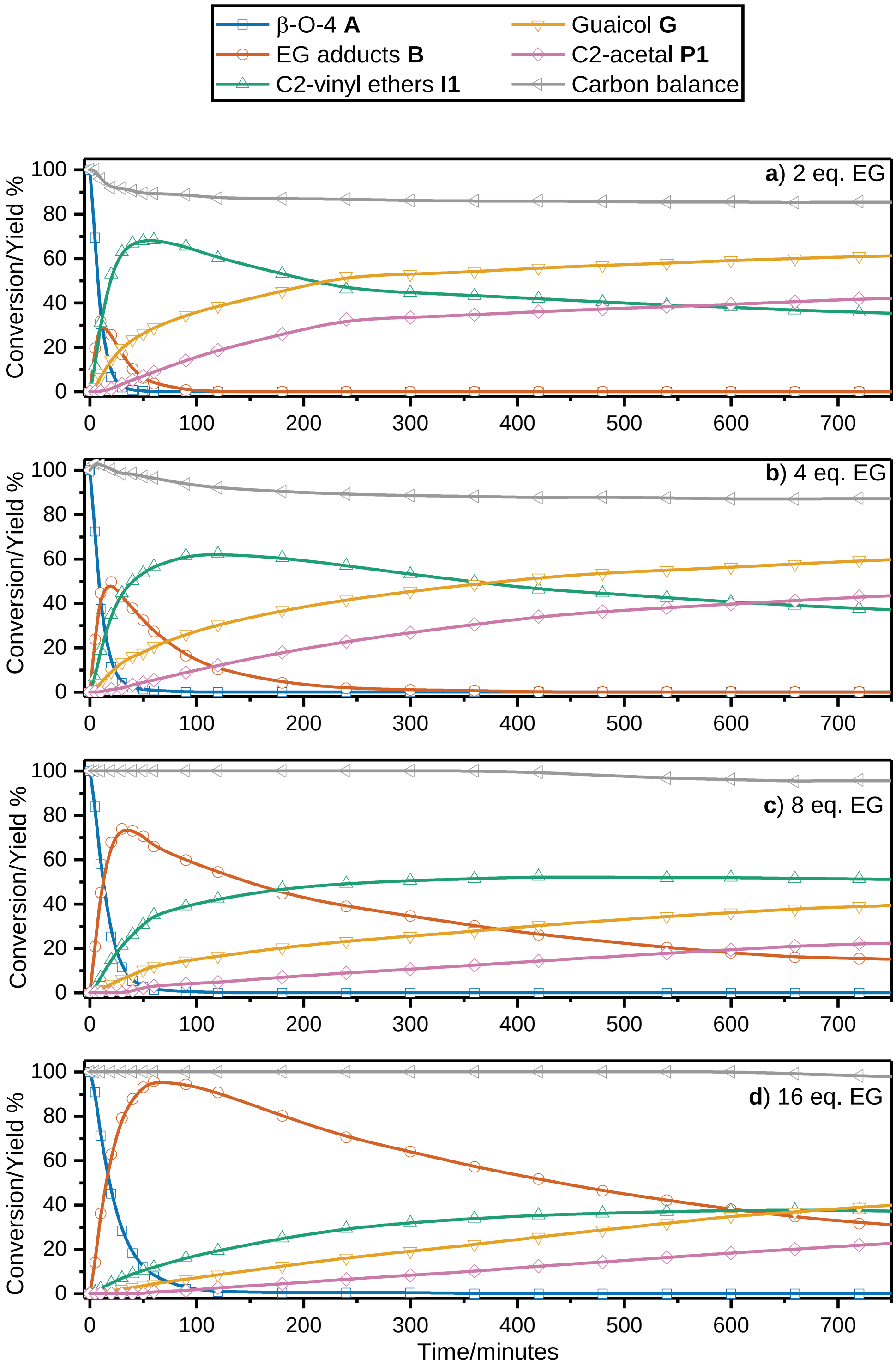


Fig. S15. Graphs of time course of the reaction of β-O-4 model compound **A** with 10 mol% Yb(OTf)$_3$ in 1,4-dioxane at 130 °C under a) 2 eq. ethylene glycol, b) 4 eq. ethylene glycol, c) 8 eq. ethylene glycol, d) 16 eq. ethylene glycol. Symbols: measured; lines: for illustrative purposes only.

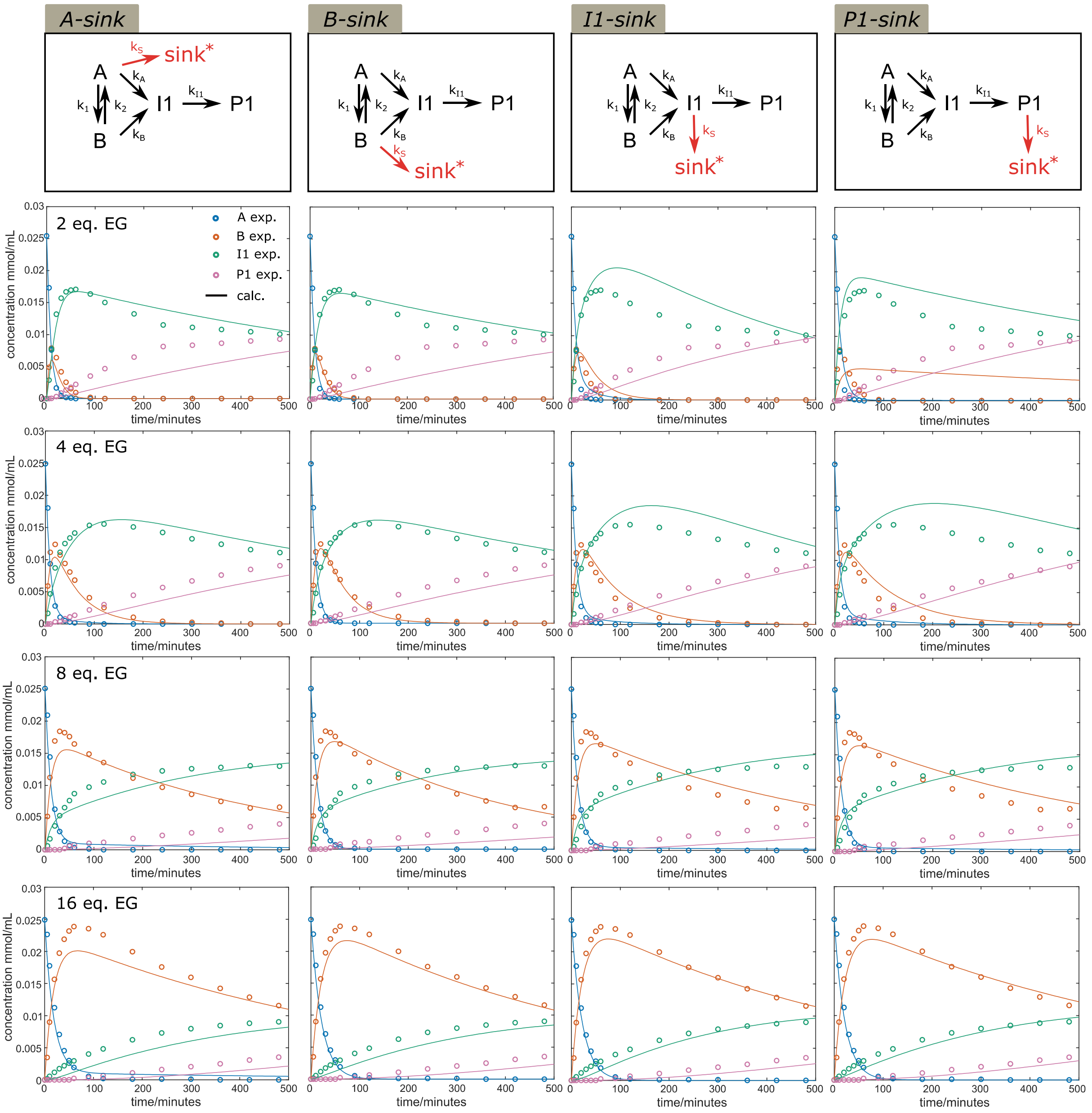


Fig. S16. Kinetic fitting results of time course profiles under different ethylene glycol amounts at 130 °C under Model 3 with a sink route from **A**, **B**, **I1** and **P1**, respectively. Symbols: measured data; lines: calculated according to the model. *sink denotes reaction pathways that lead to unidentified side cleavage or condensation products.

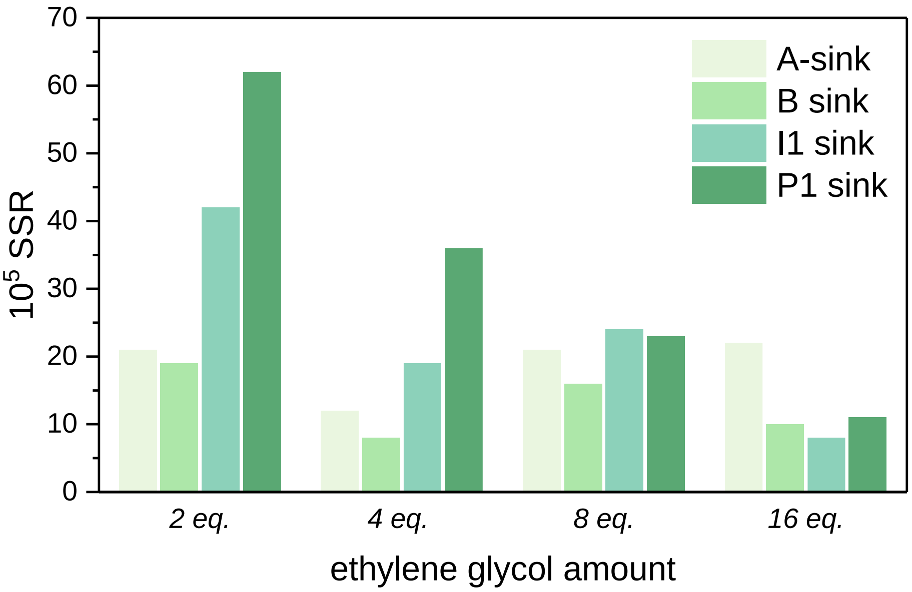
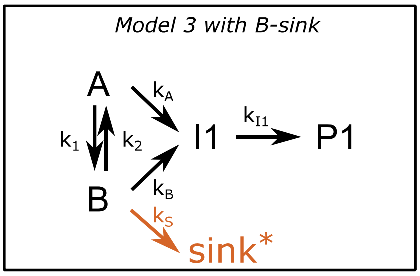
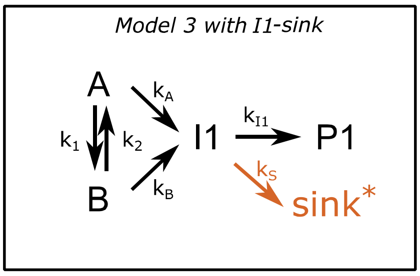


Fig. S17. Comparison of residual sum of squares under different ethylene glycol amounts and sink routes.



related to Table S4



related to Table S5

Table S4. Rate constants calculated under sink route from **B** in the simplified Model 3. *sink denotes reaction pathways that lead to unidentified side cleavage or condensation products.

Ethylene glycol content	k_1	k_2	k_A	k_B	k_{I1}	k_S
EG 2 eq.	70	small	39	38	1.11	34
EG 4 eq.	69	small	27	14	1.11	6.9
EG 8 eq.	54	small	17	1.82	0.35	0.78
EG 16 eq.	46	small	0.67	1.3	0.9	0.42

Rate constant unit: (10^3 min^{-1})

Table S5. Rate constants calculated under sink route from **I1** in the simplified Model 3. *sink denotes reaction pathways that lead to unidentified side cleavage or condensation products.

Water content	k_1	k_2	k_A	k_B	k_{I1}	k_S
392 ppm	194	40	75	48	5.22	1.77
6209 ppm	44	small	small	42	2.98	9.23
11209 ppm	15	small	small	22	1.48	6.65

Rate constant unit: (10^3 min^{-1})

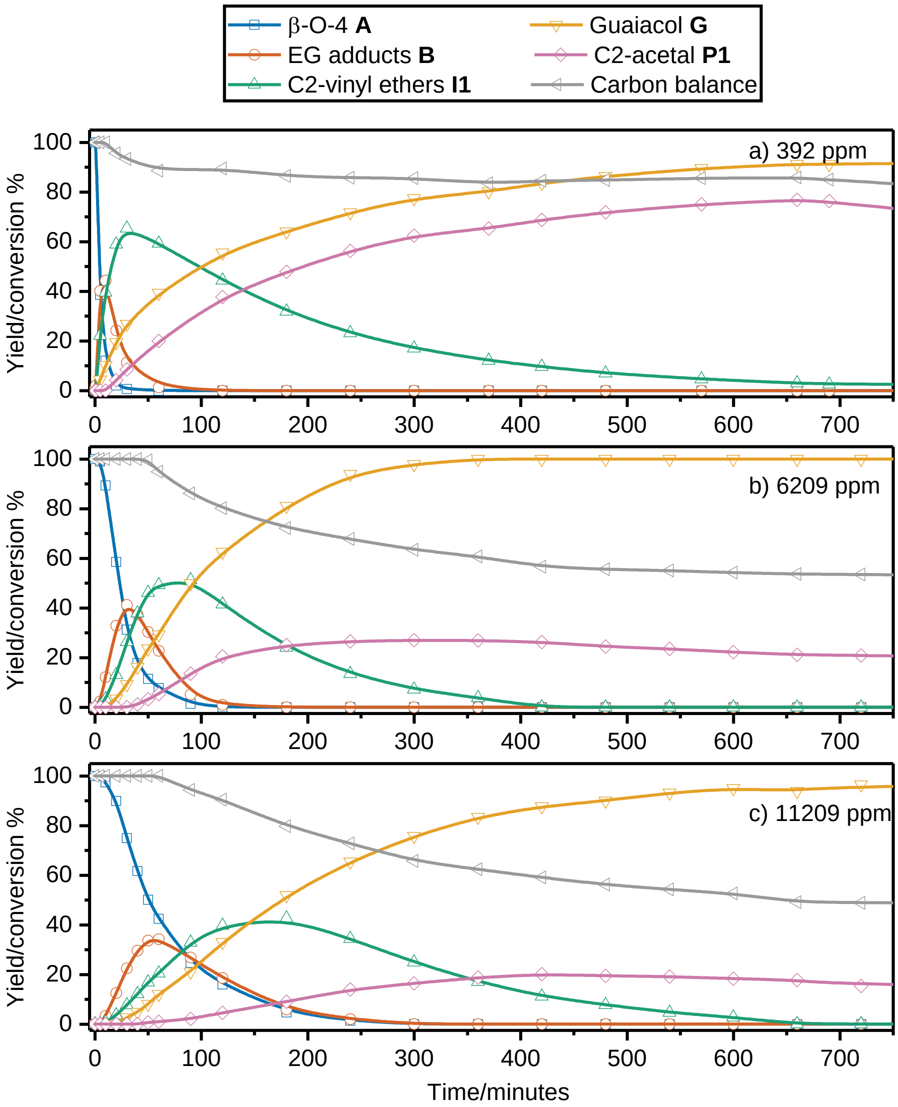
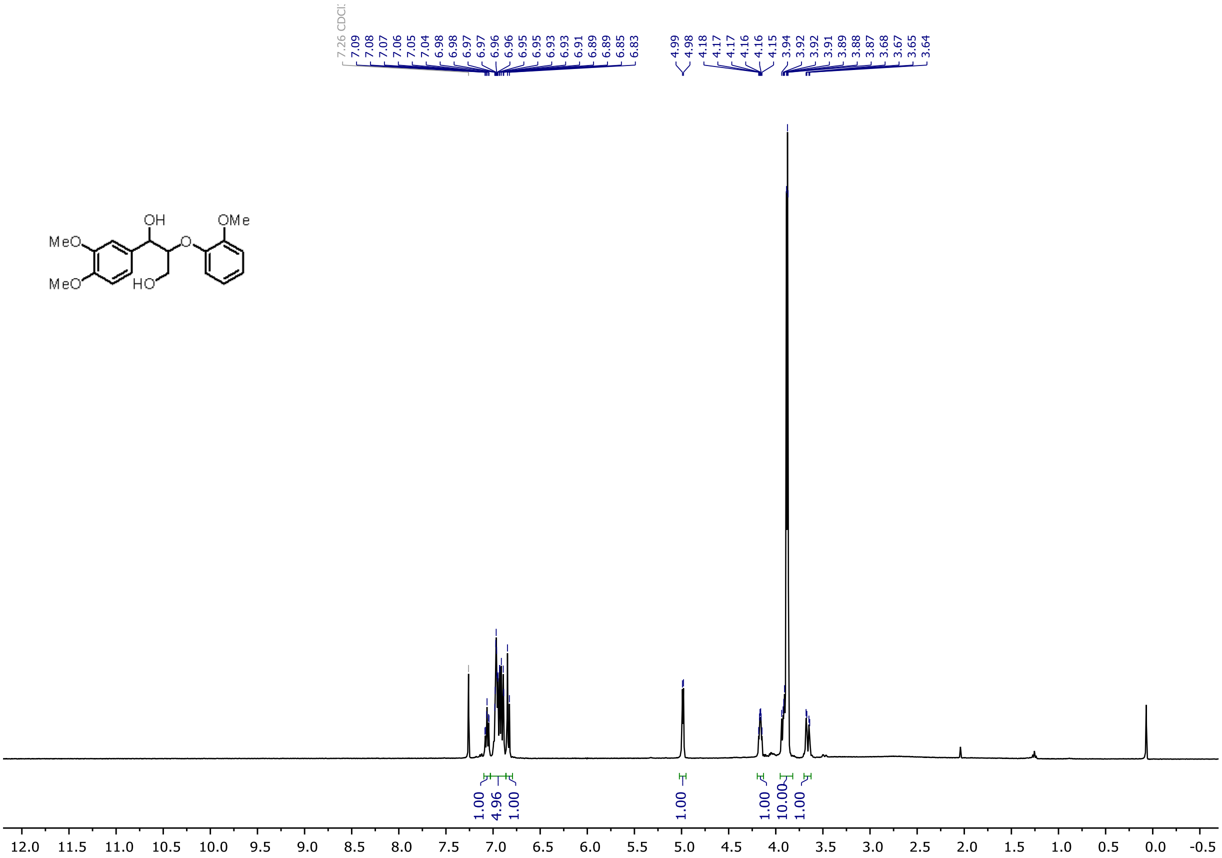


Fig. S18. Graphs of time course of the reaction of β-O-4 model compound with 10 mol% Yb(OTf)$_3$, 4 eq. ethylene glycol, in 1,4-dioxane at 130 °C under a) 392 ppm, b) 6209 ppm, c) 11209 ppm water. Symbols: measured; lines: for illustrative purposes only.

S 5.0 NMRs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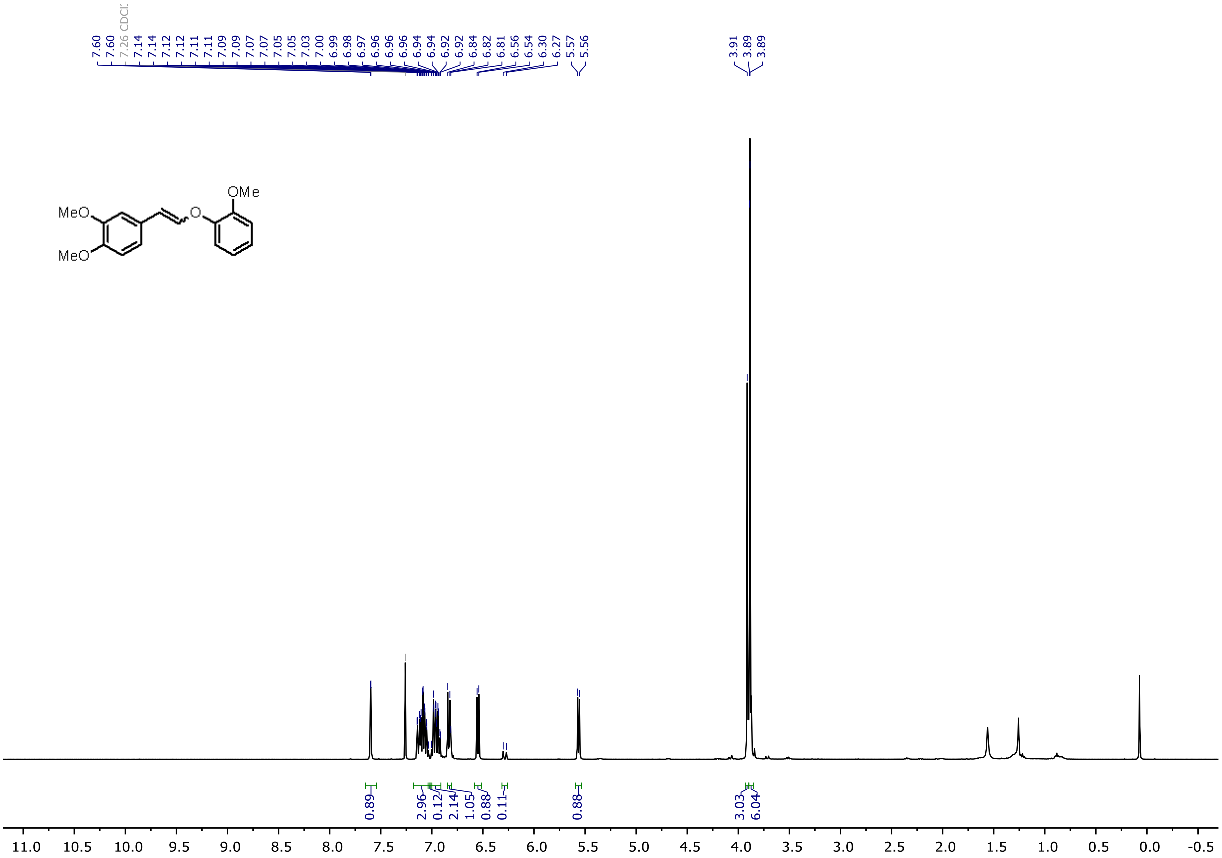
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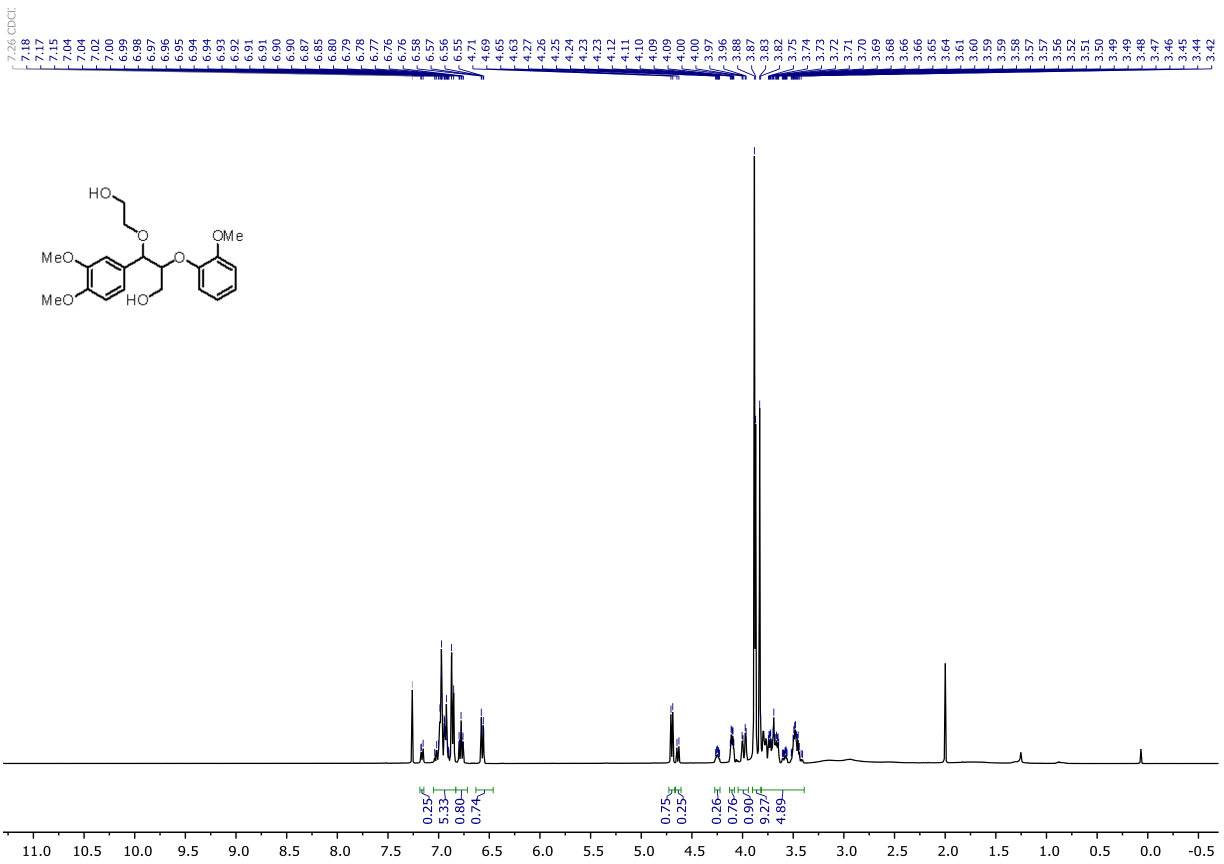
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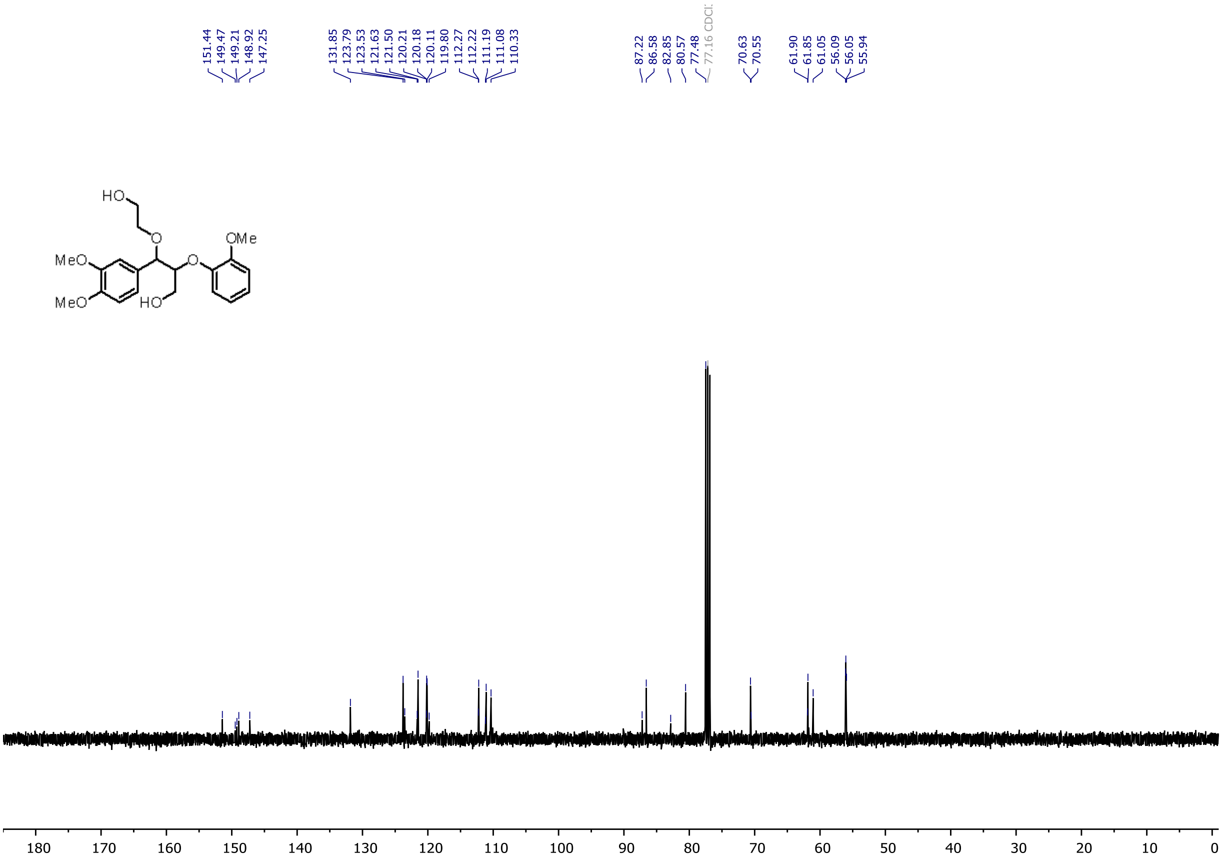
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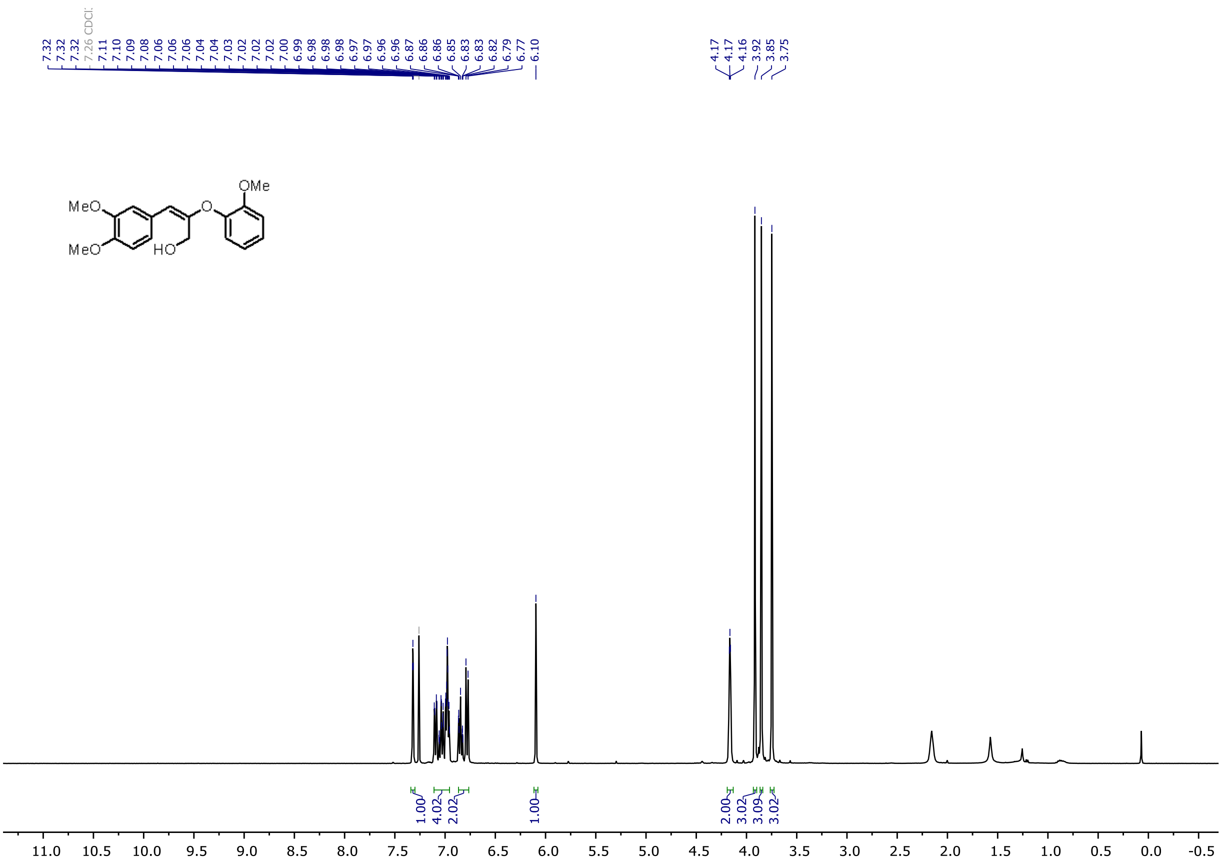
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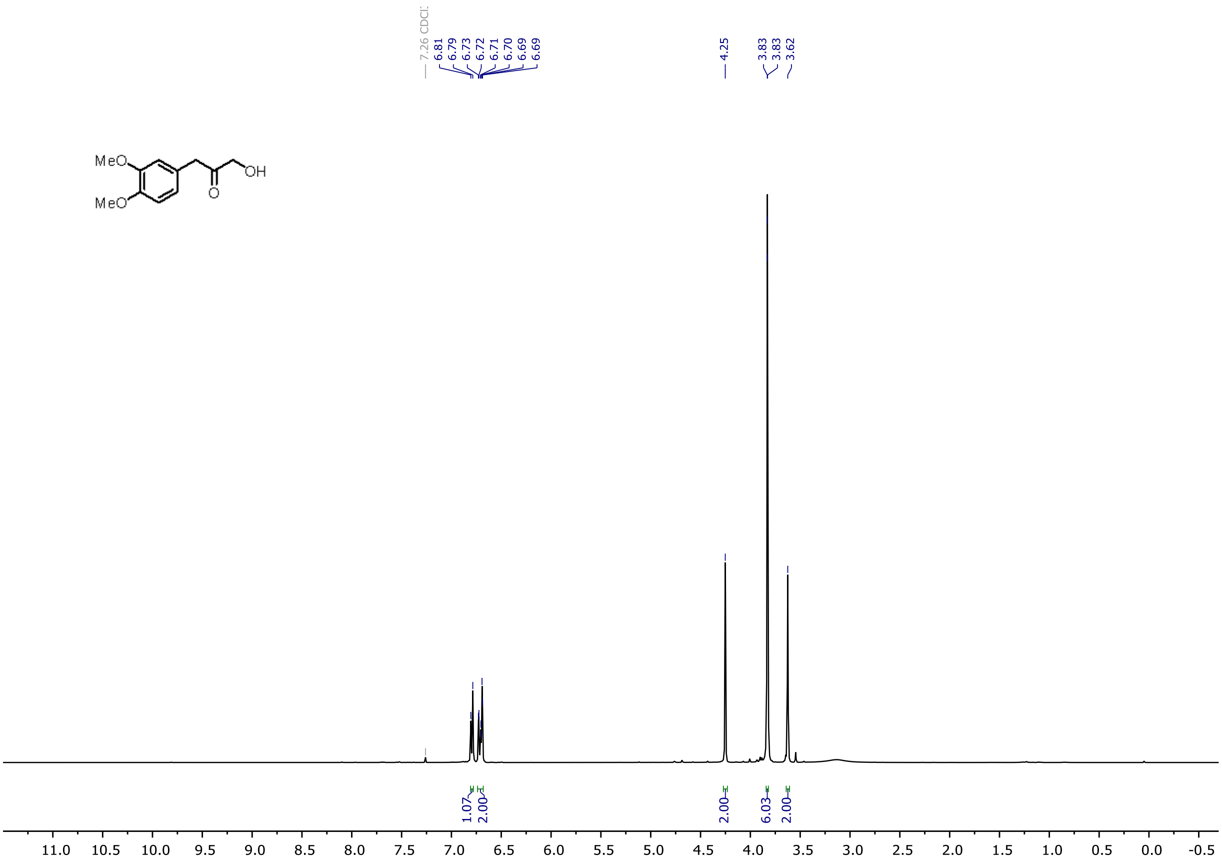
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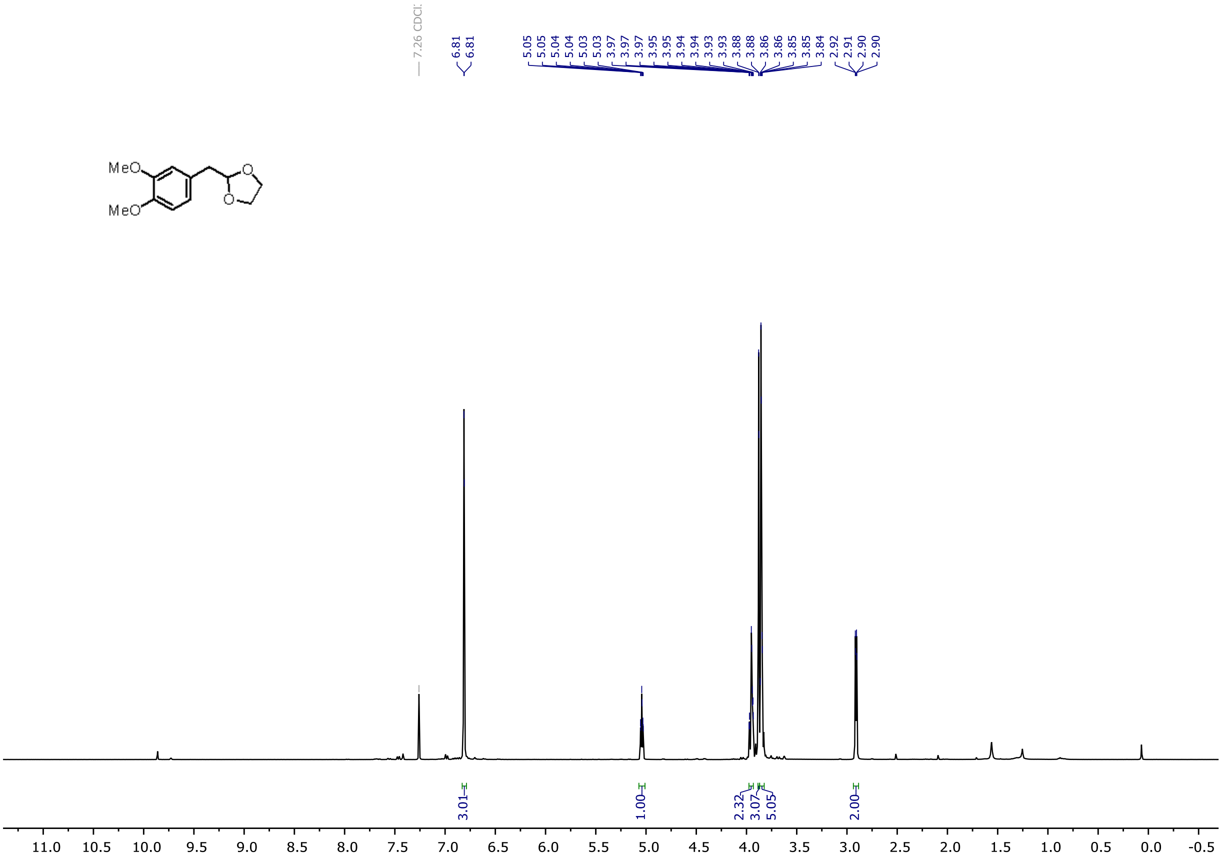
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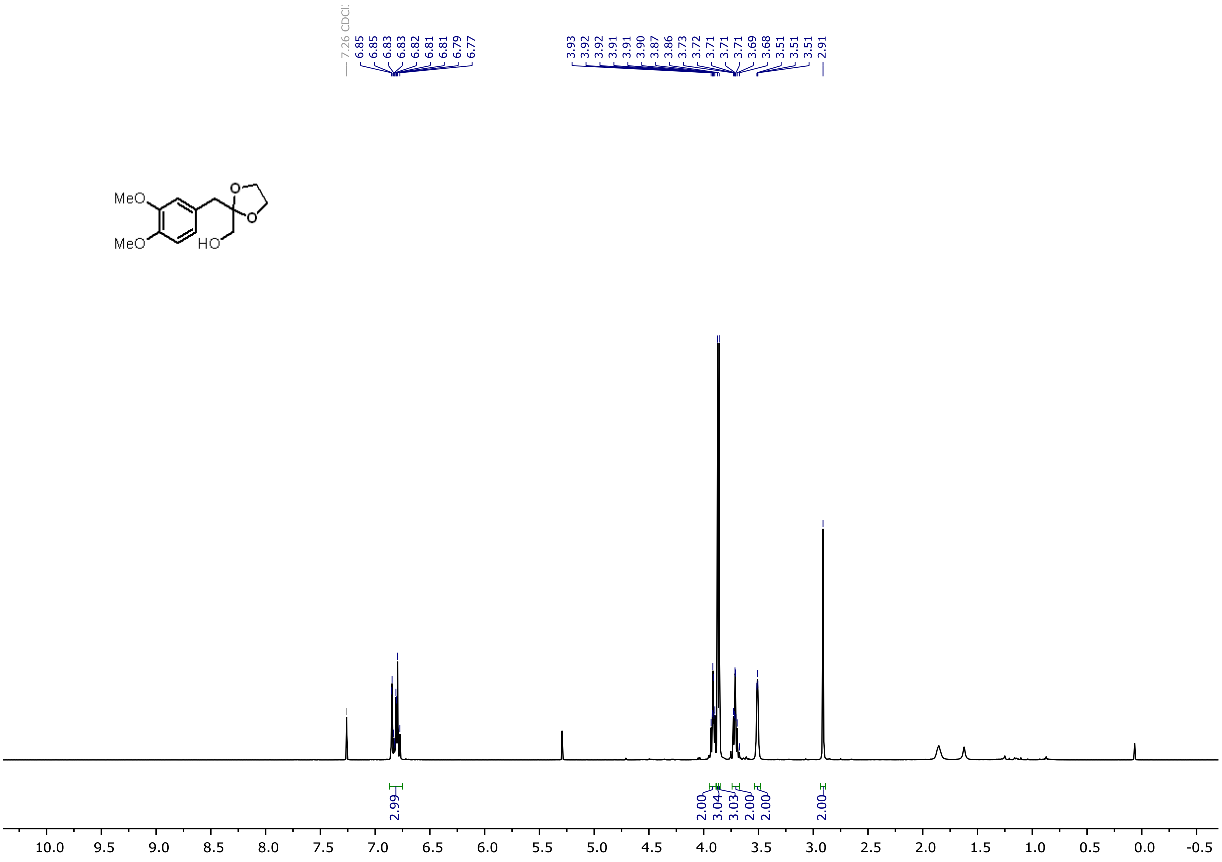
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S 6.0 References

1. J. Buendia, J. Mottweiler and C. Bolm, *Chemistry*, 2011, **17**, 13877-13882.
2. C. W. Lahive, P. J. Deuss, C. S. Lancefield, Z. Sun, D. B. Cordes, C. M. Young, F. Tran, A. M. Slawin, J. G. de Vries, P. C. Kamer, N. J. Westwood and K. Barta, *J Am Chem Soc*, 2016, **138**, 8900-8911.
3. S. Dabral, J. Mottweiler, T. Rinesch and C. Bolm, *Green Chemistry*, 2015, **17**, 4908-4912.
4. M. J. P. Vaismaa, M. V. Leskinen and M. K. Lajunen, *Synthetic Communications*, 2009, **39**, 2042-2052.
5. F. Hayat, L. Kang, C.-Y. Lee and D. Shin, *Tetrahedron*, 2015, **71**, 2945-2950.
6. D. M. Miles-Barrett, A. R. Neal, C. Hand, J. R. Montgomery, I. Panovic, O. S. Ojo, C. S. Lancefield, D. B. Cordes, A. M. Slawin, T. Lebl and N. J. Westwood, *Org Biomol Chem*, 2016, **14**, 10023-10030.
7. H. Ito, T. Imai, K. Lundquist, T. Yokoyama and Y. Matsumoto, *Journal of Wood Chemistry and Technology*, 2011, **31**, 172-182.