

Supporting Information

Metal Triflates for the Production of Aromatics from Lignin

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1. General

1.1 Materials

Chemicals were obtained from Acros, Aldrich or Strem at the highest available purity, unless stated otherwise. The synthesis of **1**^{[1][2][3]}, **1b**^{[1][2]}, **1c**^{[1][2]}, **6**^{[2][4][5]}, **7**^{[5][6]}, **8**^[5], **9**^[5] and **10**^[5] were described elsewhere as well as the procedures for the isolation of products **5**, **5c**, **11**, **12**, **13** and **14**.^[5] The isolation and fractionation of methanosolv walnut lignin was done according to a published procedure.^[5] Iron(III) triflate, used in all experiments in this work, was obtained from Aldrich (90%). We did test other sources of iron(III) triflate (with remarkably different appearance, Figure S1) and found some variations in activity for the cleavage of **1** in the presence of ethylene glycol depending on iron(III) triflate source used (Table S1).



A = Aldrich 90%
B = Alfa 90%
C = Santa Cruz 95%

Figure S1. Difference in appearance of Fe(OTf)₃ from different suppliers.

Table S1. Cleavage of β -O-4 model compound **1** using different batches of Fe(OTf)₃ in the presence of ethylene glycol.

Entry ^[a]	Fe(OTf) ₃ batch	Conversion 1 (%) ^[b]		Yield 4 (%) ^[b]		Yield 3 (%) ^[b]	
		1 h	2 h	1 h	2 h	1 h	2 h
1	Aldrich (90%) old ^[c]	89	100	85	93	75	92
2	Aldrich (90%) fresh	95	100	94	91	89	99
3	Santa Cruz (95%)	57	92	51	85	46	84
4	Alfa Aesar (90%)	71	99	63	92	58	89

[a] Conditions: 0.1 mmol substrate, 10 mol% catalysts, 1,4-dioxane, 140°C, 1.5 eq. ethylene glycol (see SI section 3.1 for procedure) [b] determined by GC-FID using n-octadecane as internal standard [c] after 6 month use (stored in glovebox but handled under air).

1.2 Methods

Gas chromatography with a flame ionisation detector (GC/FID) was performed using an Agilent 6890 series equipped with a 6890N FID, a HP5 column (30m x 0.25mm) with 0.25 µm film and using nitrogen as carrier gas. The standard method for analysis and quantification for which retention times are provided in the text below is a 1 µL injection, a split ratio of 50 : 1, a nitrogen flow of 1 mL/s with a temperature profile starting with 60 °C 5 min isotherm followed by a 10 °C/min ramp for 20 minutes, finishing the ramp at 260 °C, a temperature that was held for 5 minutes.

Gas chromatography-mass spectrometry (GC/MS) was performed using either an Agilent 6890 series GC system equipped with a HP973 mass detector and a HP1-column (25 m x 0.25 mm x 0.25 µm) or a Shimadzu GC-2010 plus system equipped with a GCMS QP2010 GC SE detector and a HP5 column (30 m x 0.25 mm x 0.25 µm). Both GC/MS systems use helium as the carrier gas. High performance liquid chromatography (HPLC) was performed using a Shimadzu prominence system equipped with a photodiode detector (Shimadzu SPD-M10A) and a fraction collector (Shimadzu FRC-10A).

High performance liquid chromatography (HPLC) was performed using a Shimadzu UFLC system equipped with a photodiode detector (Shimadzu SPD-M20A Prominence) and an Agilent Eclipse XDB-C18 5 Column (5 µm 4.6 x 150 mm). Analysis was performed using Shimadzu Lab solutions Version 5.51 software. All samples were analysed using (A) MeCN (0.1% v/v formic acid) and (B) H₂O (0.1% v/v formic acid) as mobile phase at a flowrate of 1.0 mL/min. HPLC gradient: 5% A/95% B for 10 minutes followed by gradient to 95% A/5% B over 30 minutes followed by 10 minutes at 95% A/5% B followed by a gradient to 5% A/95% B over 5 minutes followed by 5 minutes at 5% A/95% B.

2. Metal triflate catalyzed cleavage of lignin β -O-4 model compounds

2.1 Procedure

Substrate (e.g. **1**, 48.9 mg, 0.2 mmol) was weighed out in a 20 mL microwave vial, equipped with a magnetic stirring bar. Solvent (e.g. 1,4-dioxane, 2 mL) and n-octadecane (25 μ mol from a 0.25 M stock solution in the appropriate solvent) were added and the vial was sealed. The solution was stirred and heated to the appropriate temperature and catalyst (e.g. triflic acid, 10 mol%, 1 μ L, 0.02 mmol or 200 μ L of a freshly prepared 5 mg/mL Fe(OTf)₃ stock in 1,4-dioxane, 10 mol%, 0.02 mmol) was added by syringe with a thin needle through the septum of the microwave vial. If samples were taken, this was done by syringe equipped with a long thin needle. The samples (100-150 μ L) were filtered, diluted in DCM and analyzed by GCFID and GCMS (Figure 2). Otherwise the reaction was stopped by cooling on ice. The crude reaction mixture was filtered through celite and an aliquot was taken for GCFID and GCMS analysis (Results in Table S2).

GCFID retention times: n-octadecane (IS) 19.9 min, **1**: 22.4 min, **2**: 9.8 min, **3**: 10.6 min.

Quantification was performed using GCFID peak areas and calibration curves with authentic samples containing known amounts of internal standard (n-octadecane). From these calibration curves relative response factors to the internal standard (n-octadecane) were calculated and used to determine unknown quantities in samples obtained from the cleavage reactions.

2.2 Results

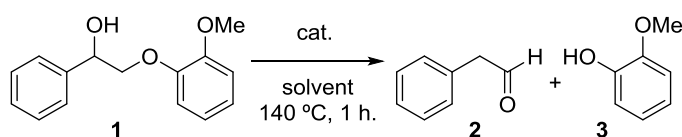


Table S2. Cleavage of β -O-4 model compound **1** using Brønsted or Lewis acid catalysts (Scheme S1).^[a]

Entry	Catalyst	Solvent	Additive	Conversion 1 (%) ^[b]	Yield 2 (%) ^[b]	Yield 3 (%) ^[b]
1	HOTf	Toluene	-	100	trace	54
2	HOTf	1,4-dioxane	-	100	11	96
3	H ₂ SO ₄	Toluene	-	100	<2	59
4	MeSO ₃ H	Toluene	-	100	5	77
5	NaOTf	Toluene	-	<5	-	-
6	NaOTf ^[c]	1,4-dioxane	-	<5	-	-
7	AgOTf	Toluene	-	<5	<2	<2
8	AgOTf ^[c]	1,4-dioxane	-	<5	-	-

9	Al(OTf) ₃	Toluene	-	100	<2	57
10	Al(OTf) ₃	1,4-dioxane	-	89	32	73
11	Al(OTf) ₃	Toluene	50 mol% DTBMP ^[d]	<5	-	-
12 ^[e]	AlCl ₃	Toluene	-	15	-	-
13	Cu(OTf) ₂	Toluene	-	100	<2	78
14	Cu(OTf) ₂	1,4-dioxane	-	41	7	7
15	Cu(OTf) ₂	Toluene	50 mol% DTBMP ^[d]	<5	-	-
16	Sc(OTf) ₃	Toluene	-	100	<5	67
17	Sc(OTf) ₃	1,4-dioxane	-	98	<2	84
18	Sc(OTf) ₃	Toluene	50 mol% DTBMP ^[d]	<5	-	-
19	Fe(OTf) ₃	Toluene	-	100	<2	57
20	Fe(OTf) ₃	1,4-dioxane	-	100	14	92
21	Fe(OTf) ₃	Toluene	50 mol% DTBMP ^[d]	<5	-	-
22	Fe(OTf) ₃	1,4-dioxane	50 mol% DTBMP ^[d]	<5	-	-
23	Fe(OTf) ₃	Toluene	1 eq. NaHCO ₃	<5	-	-
24	Fe(OTf) ₃	1,4-dioxane	1 eq. NaHCO ₃	<5	-	-
25 ^[e]	Fe(OTf) ₂	Toluene	-	11	-	-
26	FeCl ₃	Toluene	-	<5	<2	<2
27 ^[e]	FeCl ₃	Toluene	-	100	16	40
28 ^[e]	FeCl ₃	1,4-dioxane	-	37	-	8
29	Eu(OTf) ₃	Toluene	-	>99	25	61
30	Eu(OTf) ₃	1,4-dioxane	-	26	7	12
31	Eu(OTf) ₃	Toluene	50 mol% DTBMP ^[d]	<5	-	-
32	La(OTf) ₃	Toluene	-	<5	-	-
33	La(OTf) ₃	1,4-dioxane	-	7	-	-
34	Yb(OTf) ₃	Toluene	-	98	7	46
34	Yb(OTf) ₃	1,4-dioxane	-	12	-	-
35	Yb(OTf) ₃	Toluene	50 mol% DTBMP ^[d]	<5	-	-
36	Hf(OTf) ₄	Toluene	-	96	-	46
37	Hf(OTf) ₄	1,4-dioxane	-	95	-	68
38	Hf(OTf) ₄	Toluene	50 mol% DTBMP ^[d]	<5	-	-
39	Ni(OTf) ₂	Toluene	-	<5	-	-
40	Ni(OTf) ₂	1,4-dioxane	-	<5	-	-
41	Bi(OTf) ₃	Toluene	-	>99	-	72
42	Bi(OTf) ₃	1,4-dioxane	-	>99	<2	96
43	Bi(OTf) ₃	Toluene	50 mol% DTBMP ^[d]	<5	-	-
45	Zn(OTf) ₂	Toluene	-	<5	-	-
46	Zn(OTf) ₂	1,4-dioxane	-	<5	-	-

[a] Conditions: 0.1 mmol substrate, 10 mol% catalysts, toluene, 1 h, 140°C [b] determined by GC/FID using n-octadecane as internal standard [c] 20 mol% [d] DTBMP = 2,6-ditertbutyl-4-methylpyridine [e] 16 hours.

3. Metal triflate catalyzed cleavage of lignin β -O-4 model compounds with in situ decarbonylation

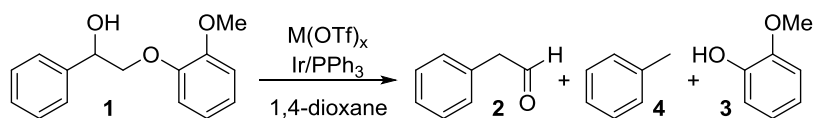
3.1 Procedure

Inside a glovebox a 20 mL microwave vial was charged with substrate (e.g. **1**, 12.2 mg, 0.05 mmol) and n-octadecane (6,25 μ mol) from a stock solution in 1,4-dioxane. A premixed solution of PPh₃ and [IrCl(cod)]₂ in 1,4-dioxane (mixed for 15 minutes prior to addition) was added to this mixture and the vial was sealed. The vial was stirred and heated to the appropriate temperature and catalyst from a stock solution in 1,4-dioxane was added by syringe with a thin needle through the septum of the microwave vial. Upon completion the reaction mixtures were cooled on ice and filtered through celite. Aliquots of the reaction mixtures were diluted in DCM and analyzed by GCFID and GCMS (Results in Table S3-5). Comment: The use of a glovebox is not necessary. The use of semi-inert techniques with degassed solvents and in sealed microwave vials is sufficient.

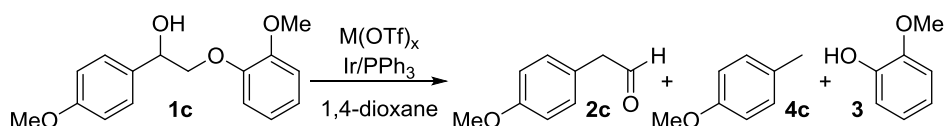
GCFID retention times: n-octadecane (internal standard) 19.9 min, **1**: 22.4 min, **1c**: 24.8 min, **2**: 9.8 min, **3**: 10.6 min, **4**: 4.0 min, **4c**: 9.7 min.

Quantification was performed using GCFID peak areas and calibration curves with authentic samples containing known amounts of internal standard (n-octadecane). From these calibration curves relative response factors to the internal standard (n-octadecane) were calculated and used to determine unknown quantities in samples obtained from the cleavage reactions

3.2 Results



Scheme S2. Metal triflate catalyzed cleavage of lignin β -O-4 model compound **1** with in situ decarbonylation.



Scheme S3. Metal triflate catalyzed cleavage of lignin β -O-4 model compound **1c** with in situ decarbonylation.

Table S3. Iron(III)triflate catalyzed cleavage of lignin β -O-4 model compound **1** and in situ decarbonylation with Ir/PPh₃ (Scheme S2).^[a]

Entry	Fe(OTf) ₃	[IrCl(cod)] ₂	PPh ₃	T	Time	Conversion ^[b]	2 ^[b]	4 ^[b]	3 ^[b]
1	10 mol%	2.5 mol%	5 mol%	120°C	16 hours	100%	2%	23%	89%
2	10 mol%	5 mol%	10 mol%	120°C	16 hours	100%	1%	43%	88%
3	5 mol%	5 mol%	10 mol%	120°C	16 hours	62%	4%	29%	50%
4	2 mol%	5 mol%	10 mol%	120°C	16 hours	20%	-	11%	13%
5 ^[c]	5 mol%	5 mol%	10 mol%	120°C	40 hours	79%	5%	60%	73%
6	2 mol%	5 mol%	10 mol%	120°C	40 hours	16%	3%	6%	10%

[a] 0.05 mmol substrate in 1 mL 1,4-dioxane (50 mM), iridium and triphenyl phosphane were incubated for 15 minutes in 1,4-dioxane at room temperature prior to the reaction [b] quantified by GCFID with n-octadecane as internal standard and calibration curves based on authentic standards [c] 0.05 mmol substrate in 2 mL 1,4-dioxane (25 mM).

Table S4. Aluminium(III) triflate catalyzed cleavage of lignin β -O-4 model compound **1** and in situ decarbonylation with Ir/PPh₃ (Scheme S2).^[a]

Entry	Al(OTf) ₃	[IrCl(cod)] ₂	PPh ₃	T	Time	Conversion ^[b]	2 ^[b]	4 ^[b]	3 ^[b]
1	10 mol%	2.5 mol%	5 mol%	120°C	16 hours	86%	8%	34%	72%
2	10 mol%	5 mol%	10 mol%	120°C	16 hours	80%	4%	38%	58%
3	5 mol%	5 mol%	10 mol%	120°C	16 hours	52%	6%	27%	44%
4	2 mol%	5 mol%	10 mol%	120°C	16 hours	20%	1%	10%	15%
5 ^[c]	5 mol%	5 mol%	10 mol%	120°C	40 hours	68%	7%	36%	57%
6	2 mol%	5 mol%	10 mol%	120°C	40 hours	51%	2%	32%	41%

[a] 0.05 mmol substrate in 1 mL 1,4-dioxane (50 mM), iridium and triphenyl phosphane were incubated for 15 minutes in 1,4-dioxane at room temperature prior to the reaction [b] quantified by GCFID with n-octadecane as internal standard and calibration curves based on authentic standards [c] 0.05 mmol substrate in 2 mL 1,4-dioxane (25 mM).

Table S5. Iron(III) triflate catalyzed cleavage of lignin β -O-4 model compound **1c** and in situ decarbonylation with Ir/PPh₃ (Scheme S3).^[a]

Entry	FeOTf ₃	[IrCl(cod)] ₂	PPh ₃	T	Time	Conversion ^[b]	2c ^[b]	4c ^[b]	3 ^[b]
1	5 mol%	5 mol%	10 mol%	120°C	16 hours	100%	-	44%	97%
2	2 mol%	5 mol%	10 mol%	120°C	16 hours	100%	-	68%	99%
3	1 mol%	5 mol%	10 mol%	120°C	16 hours	100%	-	73%	>99%
4	1 mol%	5 mol%	10 mol%	140°C	16 hours	100%	-	82%	>99%

[a] 0.05 mmol substrate in 1 mL 1,4-dioxane (50 mM), iridium and triphenyl phosphane were incubated for 15 minutes in 1,4-dioxane at room temperature prior to the reaction [b] quantified by GCFID with n-octadecane as internal standard and calibration curves based on authentic standards.

4. Metal triflate catalyzed cleavage of lignin β -O-4 model compounds with in situ acetal formation

4.1 Procedure

Substrate (e.g. **1**, 48.9 mg, 0.2 mmol) was weighed out in a 20 mL microwave vial, equipped with a stirring bar. Solvent (e.g. 1,4- dioxane, 2 mL) and n-octadecane (25 μ mol from a 0.25 M stock solution in the appropriate solvent), diol (e.g. ethylene glycol 16 μ L 0.3 mmol) were added and the vial was sealed. The solution was stirred and heated to the appropriate temperature and catalyst (e.g. triflic acid, 10 mol%, 1 μ L, 0.02 mmol or 200 μ L of a freshly prepared 5 mg/mL Fe(OTf)₃ stock in 1,4-dioxane, 10 mol%, 0.02 mmol) was added by syringe with a thin needle through the septum of the microwave vial. If samples were taken, this was done by syringe equipped with a long thin needle. The samples (100-150 μ L) were filtered, diluted in DCM and analyzed by GCFID and GCMS (See Figures 3 & S2-4). Otherwise the reaction was stopped by cooling on ice. The crude reaction mixture was filtered through celite and an aliquot was taken for GCFID and GCMS analysis (Results in Table S6).

GCFID retention times: n-octadecane (internal standard) 19.9 min, **1**: 22.4 min, **1b**: 20.6 min, **1c**: 24.8 min, **3**: 10.6 min, **3b**: 8.5 min, **5**: 14.2 min, **5c**: 17.5 min.

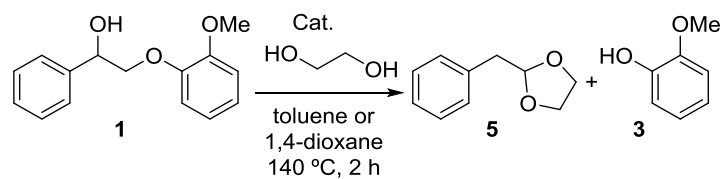
Quantification was performed using GCFID peak areas and calibration curves with authentic samples containing known amounts of internal standard (n-octadecane). From these calibration curves relative response factors to the internal standard (n-octadecane) were calculated and used to determine unknown quantities in samples obtained from the reactions.

Reactions with model compounds **6**, **7**, **8** and **9** were analyzed using HPLC. The reaction mixtures were quenched by addition of a drop of Et₃N and 1 mL of a 0.01 M 4-ethoxyphenol (internal standard) stock in MeCN was added. An aliquot of the reaction mixture was then diluted in MeCN/H₂O and analyzed by HPLC.

HPLC retention times: 4-ethoxyphenol 17.1 min, **3**: 15.8 min, **6**: 18.6, **7**: 19.3, **8**: 20.2/20.3 min, **9**: 18.7/18.9 min, **11**: 19.0 min, **12**: 22.5 min, **13**: 24.6 min, **14**: 22.7 min..

Quantification was performed by integration of the peak areas at 270 nm using calibration curves of authentic samples containing known amounts of internal standard (4-ethoxyphenol). From these calibration curves relative response factors to the internal standard (n-octadecane) were calculated and used to determine unknown quantities in samples obtained from the reactions.

4.2 Results



Scheme S4. Acid/metal triflate catalyzed cleavage of lignin β -O-4 model compound **1** in the presence of ethylene glycol.

Table S6. Cleavage of β -O-4 model compound **1** using Brønsted or Lewis acid catalysts in the presence of ethylene glycol (Scheme S4).^[a]

Entry	Catalyst	Solvent	Conversion 1 (%) ^[b]	Yield 5 (%) ^{[b][c]}	Yield 3 (%) ^[b]
1	HOTf	Toluene	100	17	46
2	HOTf	1,4-dioxane	100	99	94
3	H ₂ SO ₄	Toluene	100	71	66
4	Fe(OTf) ₃	Toluene	100	43	57
5	Fe(OTf) ₃	1,4-dioxane	100	93	92
6	Al(OTf) ₃	Toluene	5	5	5
7	Al(OTf) ₃	1,4-dioxane	82	52 (3)	57
8	Cu(OTf) ₂	Toluene	<5	-	-
9	Cu(OTf) ₂	1,4-dioxane	9	-	-
10	Sc(OTf) ₃	Toluene	30	18	17
11	Sc(OTf) ₃	1,4-dioxane	48	3 (9)	25
12	Eu(OTf) ₃	Toluene	<5	<2	<2
13	Eu(OTf) ₃	1,4-dioxane	14	4 (<2)	7
14	Hf(OTf) ₄	Toluene	96	9	47
15	Hf(OTf) ₄	1,4-dioxane	99	71 (<2)	83
16	Bi(OTf) ₃	Toluene	100	71	88
17	Bi(OTf) ₃	1,4-dioxane	100	83 (2)	95
18	Yb(OTf) ₃	Toluene	<5	<2	<2
18	Yb(OTf) ₃	1,4-dioxane	15	3	5

[a] Conditions 0.1 mmol substrate 10 mol% catalysts, toluene, 2 h, 140°C, 1.5 eq. ethylene glycol [b] determined by GC/FID using n-octadecane as internal standard [c] yield 2-phenylacetaldehyde **2** (%) between brackets

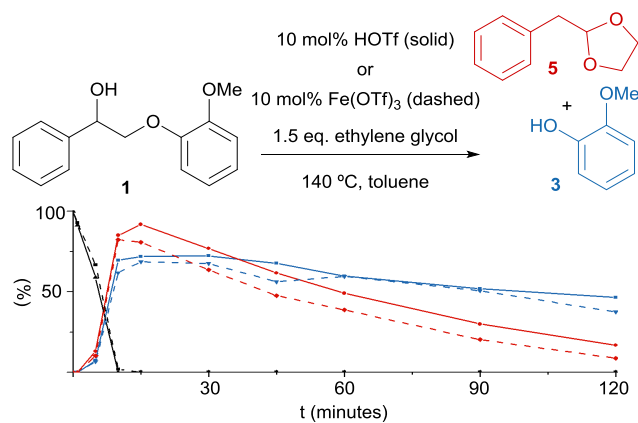


Figure S2. Comparison between activity of HOTf and Fe(OTf) in the cleavage of β -O-4 model compound **1** in toluene.

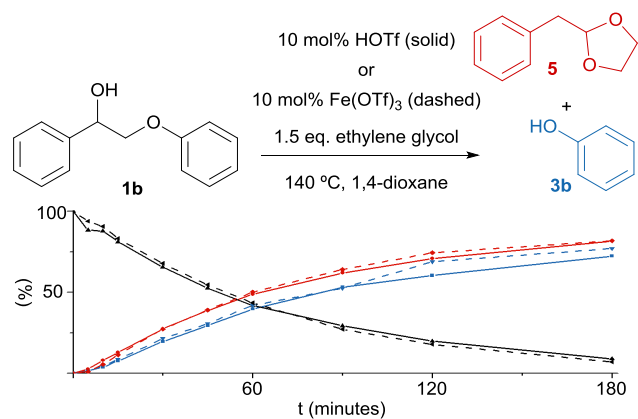


Figure S3. Comparison between activity of HOTf and Fe(OTf) in the cleavage of β -O-4 model compound **1b**.

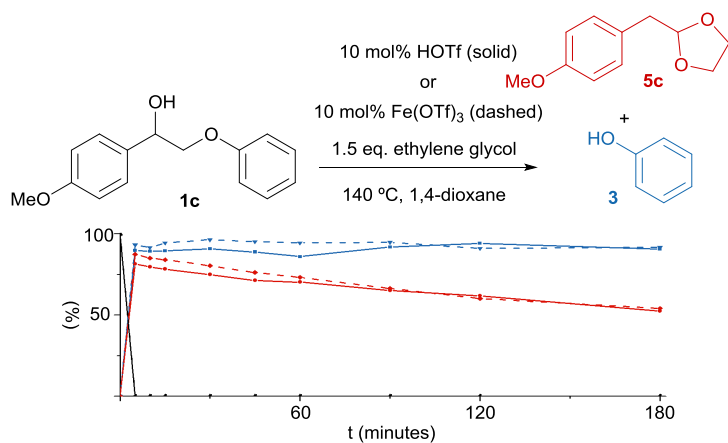


Figure S4. Comparison between activity of HOTf and Fe(OTf) in the cleavage of β -O-4 model compound **1c**.

5. Metal triflate catalyzed cleavage acetal formation and acetal stability

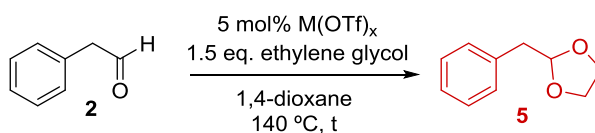
5.1 Procedure

Substrate (**2**, 24 mg, 0.2 mmol), n-octadecane (25 μmol) and ethylene glycol (1.5 eq. 0.3 mmol) were added from a stock solution in 1,4-dioxane to a 20 mL microwave vial, equipped with a stirring bar. Solvent (e.g. 1,4-dioxane) was added to give a total volume of 3.9 mL and the vial was sealed. The solution was stirred and heated to the appropriate temperature and catalyst (e.g. 100 μL of a freshly prepared 50 mg/mL $\text{Fe}(\text{OTf})_3$ stock in 1,4-dioxane, 5 mol%, 0.01 mmol) was added by syringe with a thin needle through the septum of the microwave vial. Samples were taken by syringe equipped with a long thin needle. The samples (100-150 μL) were filtered, diluted in DCM and analyzed by GCFID and GCMS (See Figures S5).

GCFID retention times: n-octadecane (internal standard 19.9 min, **2**: 9.8 min, **3**: 10.6 min).

Quantification was performed using GCFID peak areas and calibration curves with authentic samples containing known amounts of internal standard (n-octadecane). From these calibration curves relative response factors to the internal standard (n-octadecane) were calculated and used to determine unknown quantities in samples obtained from the reactions.

5.2 Results



Scheme S5. Acid catalyzed acetal formation of **5** from **2b** and ethylene glycol.

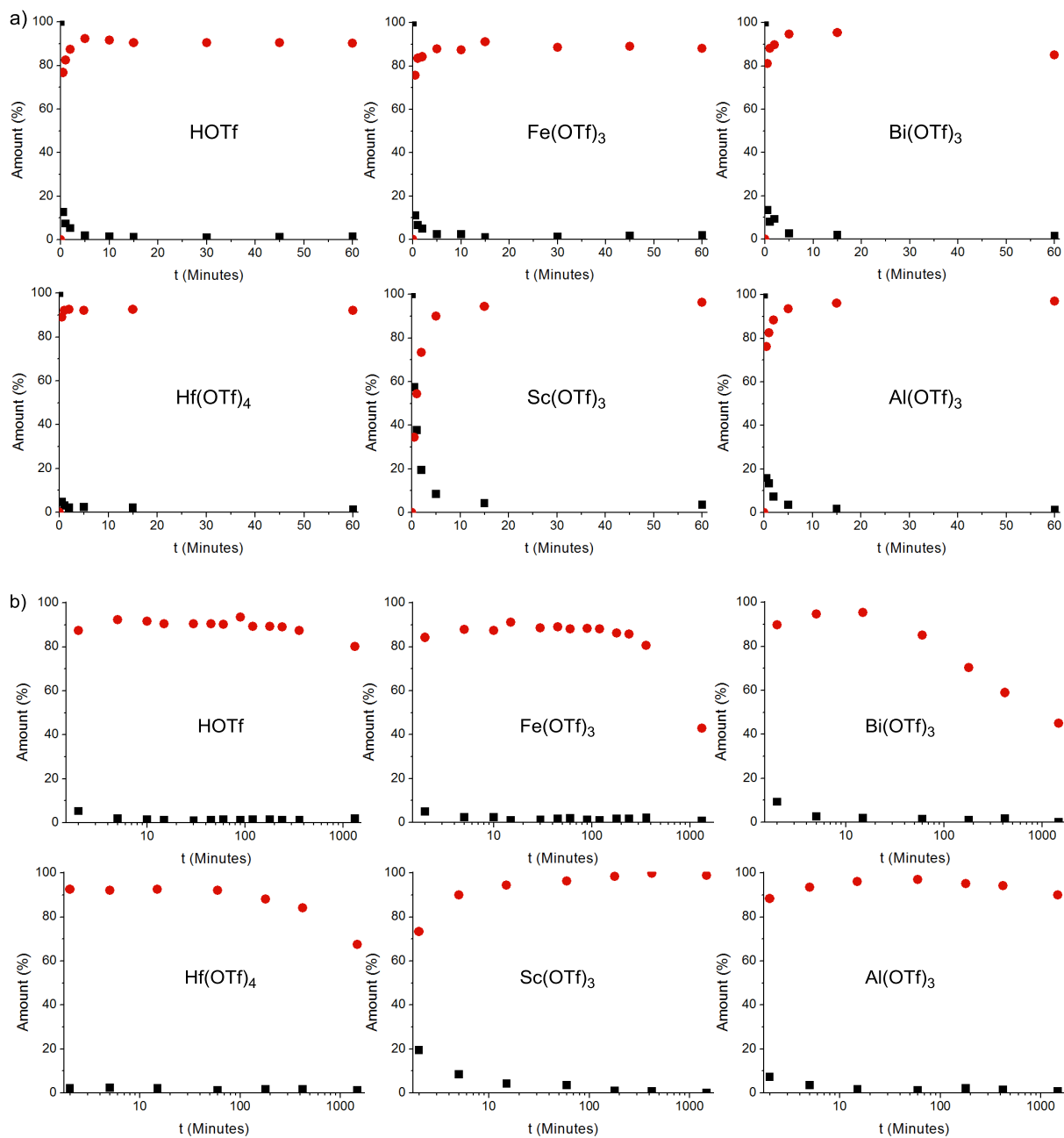


Figure S5. a) Comparison of the formation of **5** from **2** and ethylene glycol and b) the stability of **5** over time in these reaction mixtures (Log₁₀ scale).

5.3 Metal triflates

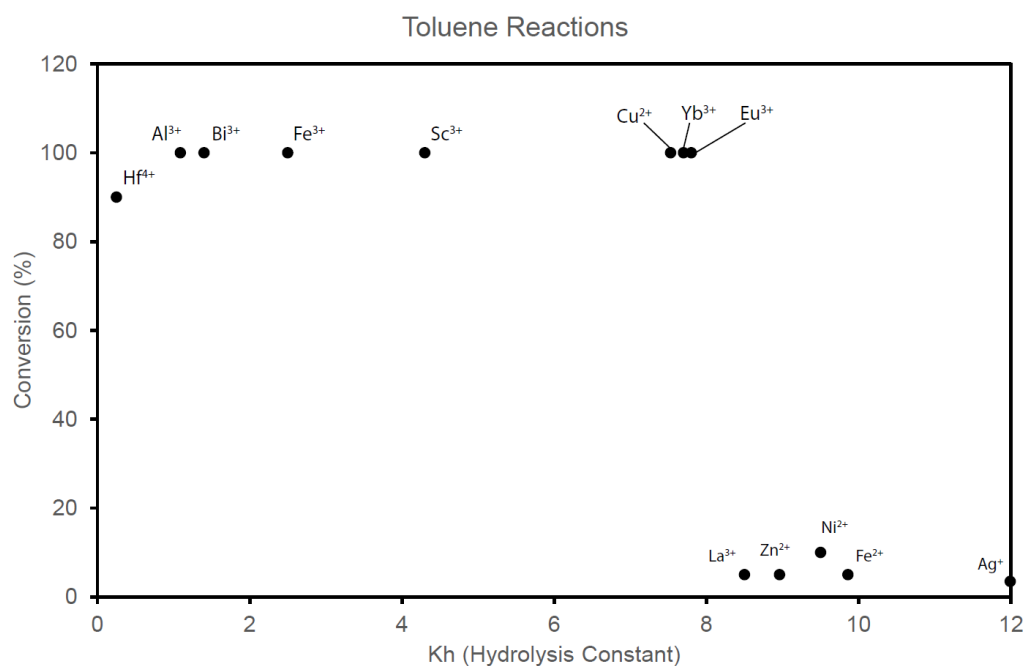


Figure S6. Correlation between the conversion of model compound **1** and the Kh (Hydrolysis Constant) of the metal triflates used for reactions in toluene. Kh values for triflates see also ref [7].

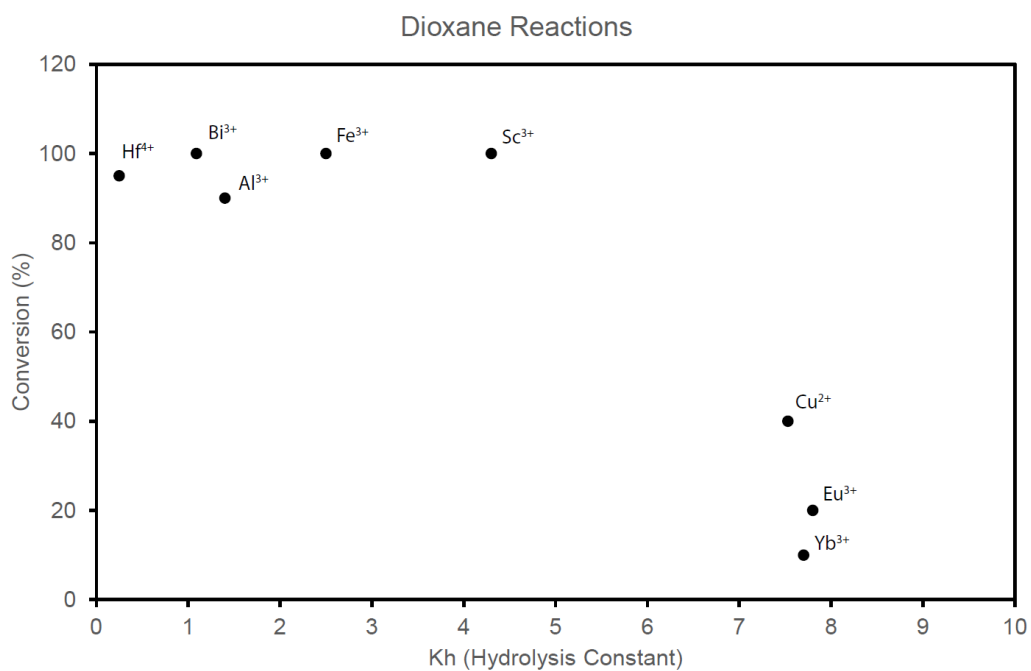


Figure S7. Correlation between the conversion of model compound **1** and the Kh (Hydrolysis Constant) of the metal triflates used for reactions in dioxane. Kh values for triflates see also ref [7].

6. Metal triflate catalyzed depolymerization of walnut methanosolv lignin with in situ acetal formation

6.1 Procedure

Walnut methanosolv lignin (50 mg) isolated by a reported procedure^[5] was placed in a 20 mL microwave vial equipped with a magnetic stirring bar. Solvent (1,4-dioxane, 1 mL), internal standard (n-octadecane, 10 μ L from a 0.25 M stock in 1,4-dioxane, 2.5 μ mol) and ethylene glycol (145 μ L from a 7.1 M stock in 1,4-dioxane) were added. The catalyst $M(\text{OTf})_x$ (23 μ mol) was added as a solid (HOTf was added from a 0.23 M stock solution in 1,4-dioxane) and the vial was sealed. The reaction was stirred at 140 $^{\circ}\text{C}$ for 15 minutes before being cooled rapidly in an ice bath. The mixture was filtered through a plug of celite and the flask and filter washed with about 0.5 mL 1,4-dioxane in 3 portions. The combined filtrate was evaporated to dryness over 16 hours at 40 $^{\circ}\text{C}$ in a Univapo 150 ECH rotational vacuum concentrator. The residue was suspended in 150 μ L dichloromethane by extensive mixing (by vortex) after which 1.35 mL toluene was added. The samples were vortexed and subsequently centrifuged for 10 minutes at 13400 rpm using an Eppendorf minispin tabletop centrifuge. The light organic liquid and solid or thick oily residue were separated. This procedure for suspension/washing with 10% DCM and 90% toluene was repeated three times after which both the combined extracted fractions and the residue were dried for 24 hours at 40 $^{\circ}\text{C}$ in an Univapo 150 ECH rotational vacuum concentrator (dried weights see Table S7). The oil containing the low molecular weight components was dissolved in DCM and analyzed by GCFID for quantification of **P1-3** (Figure 7 and Table S8).

6.2 Results

Table S7. Weight analysis of lignin fractions.

Entry	Catalyst	Weight extracted residue (mg) ^[a]	Weight solid (oily) residue (mg) ^[b]
1	HOTf	10.5	45.0
2	HOTf	12.7	47.0
3	HOTf	13.0	55.0
4	$\text{Bi}(\text{OTf})_3$	17.5	87.6
5	$\text{Bi}(\text{OTf})_3$	17.2	85.6
6	$\text{Fe}(\text{OTf})_3$	13.3	82.2
7	$\text{Fe}(\text{OTf})_3$	16.9	89.5
8	$\text{Hf}(\text{OTf})_4$	11.2	90.6
9	$\text{Hf}(\text{OTf})_4$	14.9	96.3

[a] Weight of the oil obtained from extraction with toluene/DCM after drying in vacuo [b] Weight of the residue after extraction with toluene/DCM after drying in vacuo.

Table S8. Quantities of **P1-3** obtained from the metal triflate catalyzed depolymerization of walnut methanosolv.^[a]

Entry	Catalyst	P1	P2	P3	Total P1-3
1	HOTf	0.5 Wt%	5.0 Wt%	9.6 Wt%	15.1 Wt%
2	HOTf	0.6 Wt%	4.9 Wt%	9.2 Wt%	14.7 Wt%
3	HOTf	0.4 Wt%	3.9 Wt%	7.0 Wt%	11.3 Wt%
4	Bi(OTf) ₃	0.6 Wt%	5.7 Wt%	10.2 Wt%	16.4 Wt%
5	Bi(OTf) ₃	0.6 Wt%	4.9 Wt%	9.0 Wt%	14.4 Wt%
6	Fe(OTf) ₃	0.7 Wt%	5.7 Wt%	10.6 Wt%	17.0 Wt%
7	Fe(OTf) ₃	0.6 Wt%	7.2 Wt%	13.8 Wt%	21.6 Wt%
8	Hf(OTf) ₄	0.4 Wt%	3.4 Wt%	6.2 Wt%	10.0 Wt%
9	Hf(OTf) ₄	0.5 Wt%	4.9 Wt%	9.2 Wt%	14.6 Wt%

[a] From reactions with 50 mg of lignin, quantities of **P1-3** determined by GCFID using n-octadecane as internal standard.

7. References

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