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Metal Triflates for the Production of Aromatics from Lignin

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The depolymerization of lignin into valuable aromatic chemicals is one of the key goals towards establishing economically viable biorefineries. In this contribution we present a simple approach for converting lignin to aromatic monomers in high yields under mild reaction conditions. The methodology relies on the use of catalytic amounts of easy-to-handle metal triflates (M(OTf)$_x$). Initially, we evaluated the reactivity of a broad range of metal triflates using simple lignin model compounds. More advanced lignin model compounds were also used to study the reactivity of different lignin linkages. The product aromatic monomers were either phenolic C2-acetals obtained by stabilization of the aldehyde cleavage products by reaction with ethylene glycol or methyl aromatics obtained by catalytic decarbonylation. Notably, when the method was ultimately tested on lignin, especially Fe(OTf)$_3$ proved very effective and the phenolic C2-acetal products were obtained in an excellent, 19.3 ± 3.2 wt % yield.

Introduction

The development of fundamentally new catalytic methods is of central importance for the production of bulk and fine chemicals from renewable lignocellulose feedstocks.[1,2] In this context, it is very important to valorize all main constituents of lignocellulose, including lignin.[3] However, despite recent efforts, the catalytic conversion of lignin has proven very challenging.[4] Acidolysis is an efficient method for the cleavage of the most abundant β-O-4 linkage in lignin (Scheme 1).[5] In addition, acid-catalyzed depolymerization is a highly relevant method especially in relation to the future biorefinery concept as the most common organosolv lignin extraction methodologies also use acidic media.[6] One of the main challenges with acid-mediated degradation of lignin is the reconstitution of reactive fragments leading to more robust oligomeric structures often referred to as biochar. In essence, acidolysis leads to phenolic C2-acetaldehydes that are notoriously unstable under acidic conditions. This is the major reason why this acidolysis pathway has largely escaped attention for the production of aromatic monomers from lignin until recently. In new studies by our group and others, it was shown that by capturing these reactive intermediates formed upon acidolysis, lignin can be effectively depolymerized with suppression of recondensation pathways leading to improved monomer yields (Scheme 1 b).[7]

Of the different in situ stabilization methodologies applied, in particular acetal formation with ethylene glycol led to a defined set of major products in good yields from models and lignin. The cleavage of the β-O-4 linkage was most efficiently promoted by strong acids with non-coordinating anions such as triflic acid (HOTf).[7a,d] However, HOTf is corrosive and inconvenient to handle, which may lead to inconsistent results. On the other hand, metal triflates (M(OTf)$_x$) are weighable solids that are less corrosive than HOTf and therefore much less hazardous in handling.[8]

Additionally, in the case of other homogeneous catalysts used, for example, in the iridium-catalyzed decarbonylation to yield *p*-cresol and mono- and di-methoxylated cresols, the strongly acidic conditions may affect the stability of the iridium catalyst.[7a] For this reason, we were interested to assess the usefulness of Lewis acids such as metal triflates and their compatibility with the homogeneous metal catalysts used.

In this contribution, we evaluate the reactivity of different metal triflate salts for the cleavage of β-O-4, β-5, and β-β lignin model compounds. We determine the quantities of ethylene glycol acetals or methyl aromatics obtained after stabilization of reactive intermediates by acetal formation or decarbonylation upon bond cleavage. Ultimately, the depolymerization of walnut methanosolv lignin was successfully carried out and the use of Fe(OTf)$_3$ led to results surpassing those obtained with HOTf.

Results and Discussion

Metal triflate-catalyzed cleavage of β-O-4 model compound 1

Acid-catalyzed cleavage of the β-O-4 model compound **1** results in the formation of 2-phenyl acetaldehyde (**2**) and guaia-

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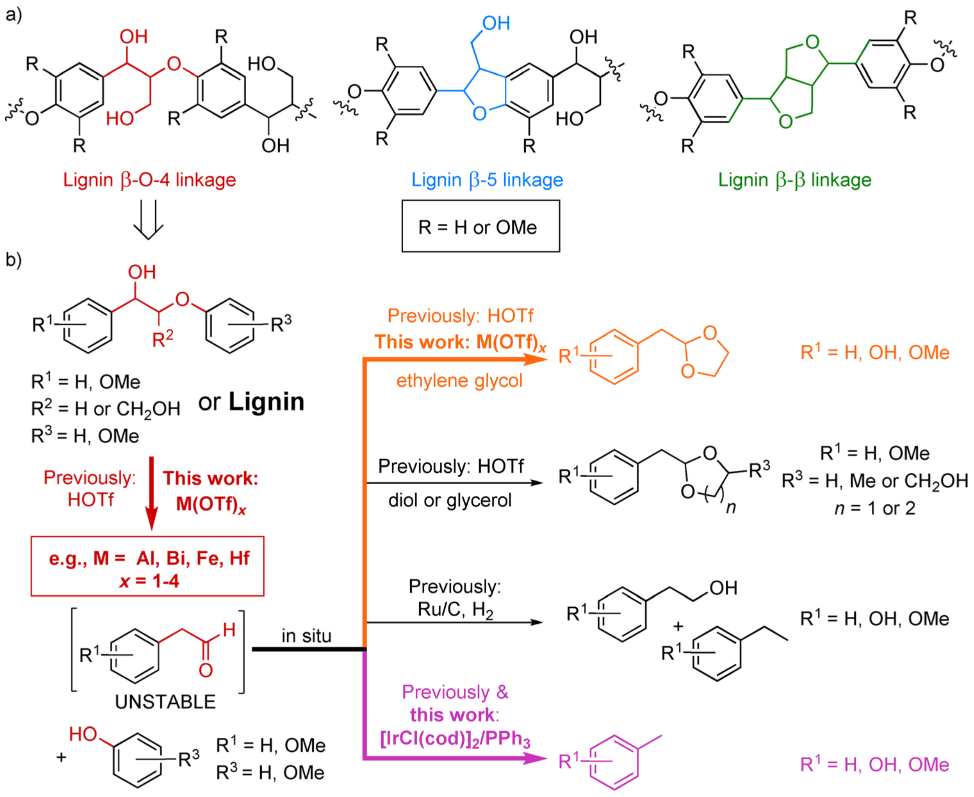
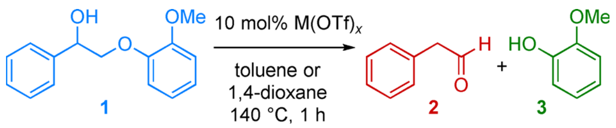


Scheme 1. a) Major linkage motifs in lignin. b) Acid-catalyzed cleavage of β-O-4 motif in model compounds and lignin with in situ conversion of reactive aldehyde intermediates. cod = 1,5-cyclooctadiene



Scheme 2. Metal triflate-catalyzed cleavage of lignin β-O-4 model compound **1**.

col (**3**) (Scheme 2),[5b,7a–b,9] and **2** is rapidly converted into its aldol condensation products under these reaction conditions.[7a,b] After evaluating a range of metal triflates, we found that several metal triflates successfully catalyzed the cleavage of **1** (Table S2 in the Supporting Information). In toluene (Figure 1 a), yields of **3** were similar or slightly higher for $Al(OTf)_3$,

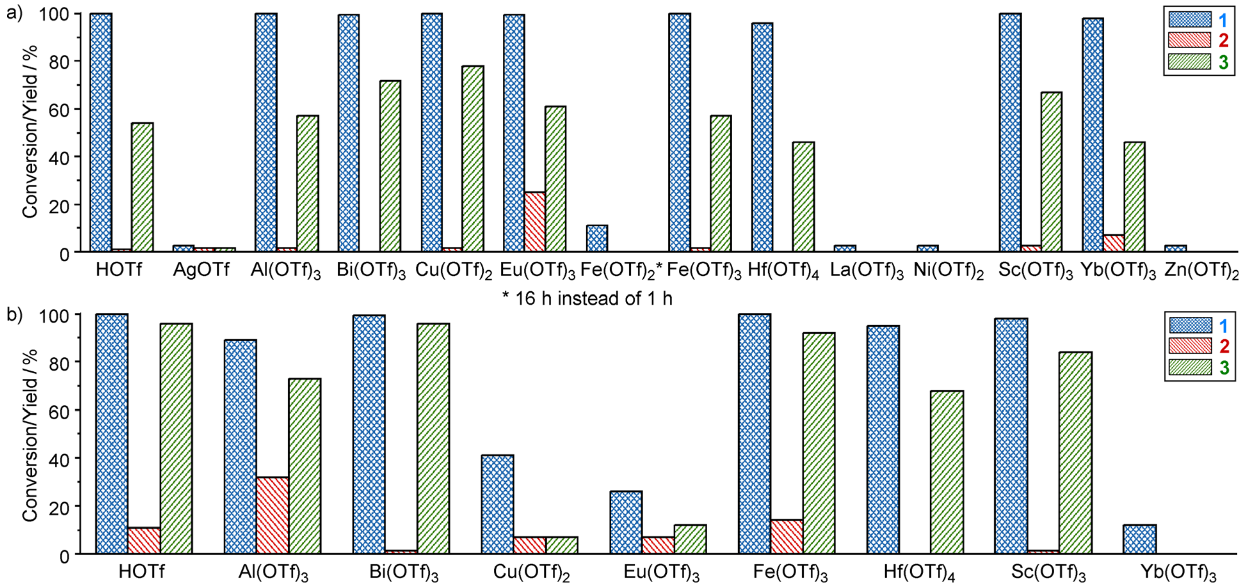


Figure 1. Cleavage of β-O-4 model compound **1** using metal triflates as catalysts in a) toluene and b) 1,4-dioxane (Reaction conditions shown in Scheme 2).

$Bi(OTf)_3$, $Cu(OTf)_2$, $Eu(OTf)_3$, $Fe(OTf)_3$, $Hf(OTf)_4$, $Sc(OTf)_3$, and $Yb(OTf)_3$ when compared to HOTf. No significant reactivity was detected for other metal triflate salts such as AgOTf, $Fe(OTf)_2$, $Zn(OTf)_2$, and $Ni(OTf)_2$. As expected, typically, only small amounts of **2** were detected in these reactions in toluene.

Several metal triflates that showed significant cleavage activity in toluene were subsequently tested in 1,4-dioxane, which is a suitable solvent for solubilizing lignin (Figure 1 b). Here, only $Al(OTf)_3$, $Bi(OTf)_3$, $Fe(OTf)_3$, $Hf(OTf)_4$, and $Sc(OTf)_3$ showed good reactivity compared to HOTf. Other metal triflates such as $Cu(OTf)_3$, $Eu(OTf)_3$, and $Yb(OTf)_3$ led to significantly lower conversion of **1**. Overall, higher yields of **2** and **3** were obtained using 1,4-dioxane as solvent. Indeed, it is well-known that 1,4-dioxane is a Lewis base and can form stable complexes with Lewis acids;[10] therefore, it is expected that its use further reduces the acidity of the reaction medium, allowing the formation of substantial quantities of **2**. To evaluate the higher stability of **2** more quantitatively in 1,4-dioxane, we monitored the reactions over time using $Fe(OTf)_3$ and HOTf (Figure 2).[7a] The reaction rates and product formation profiles for these reactions showed a remarkably similar pattern, with only slightly higher overall yields of **2**. Additionally, the practical advantage of using the triflate salt compared to HOTf was apparent during this experiment. The metal triflate catalyst could easily be weighed and added using a stock solution in 1,4-dioxane or as a solid to the reaction. Because of this more accurate data is provided compared to experiments that required the addition of microliter quantities of smoking HOTf using a microsyringe either directly to the reaction mixture or through a stock solution in the appropriate solvent.

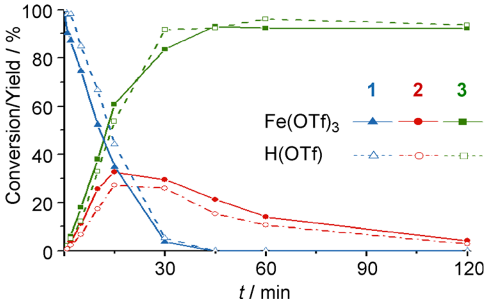
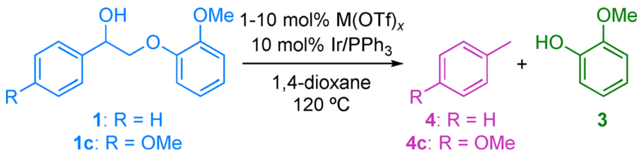


Figure 2. Reaction profiles for the cleavage of **1**, using 10 mol% $Fe(OTf)_3$ (solid lines) and 10 mol% HOTf (dotted lines) in 1,4-dioxane at 140 °C.

All metal triflates that catalyzed the cleavage of **1** are known to be strong Lewis acids and have already found many applications in organic synthesis.[11] Therefore, the question is whether the cleavage of **1** is catalyzed by the metal triflates as Lewis acids or alternatively by in situ formation of HOTf from the triflate salts.[12] Other strong Lewis acids such as $AlCl_3$ and $FeCl_3$ did not show any significant activity in the cleavage of **1** in 1,4-dioxane or toluene (Table S2). The addition of non-nucleophilic bases such as 2,6-di-*tert*-butyl-4-methylpyridine[13] or $NaHCO_3$ completely quenched all reactivity for metal triflates that were previously successful in the cleavage of **1** (Table S2). These results, combined with the similar reaction progress, led us to conclude that the triflate salts ($Al(OTf)_3$, $Bi(OTf)_3$, $Cu(OTf)_2$, $Sc(OTf)_3$, $Fe(OTf)_3$, $Eu(OTf)_3$, $Yb(OTf)_3$, and $Hf(OTf)_4$) likely form triflic acid in situ and are therefore capable of catalyzing the acidolysis of **1**. Nevertheless, the presence of the metal seems to modulate the acidity somewhat, depending on the stability of the triflate salt applied. Remarkably, a good correlation between the conversion of **1** and the hydrolysis constant of several metal triflates were found in both toluene as well as dioxane (displayed in the Supporting Information, Figures S6 and S7).

Metal triflate-catalyzed cleavage of β-O-4 model compounds combined with decarbonylation

After establishing that metal triflates are attractive alternatives to HOTf, we focused on the in situ catalytic decarbonylation of aldehyde **2** towards highly desirable methyl aromatics (Scheme 3).[7a,14] Thus, $Fe(OTf)_3$ and $Al(OTf)_3$ were tested under decarbonylation conditions using $[IrCl(cod)]_2$ and PPh_3 in 1,4-dioxane (Figure 3, Tables S3 and S4).[7a,15] In these reactions,



Scheme 3. Metal triflate-catalyzed cleavage of lignin β-O-4 model compound **1** combined with in situ decarbonylation.

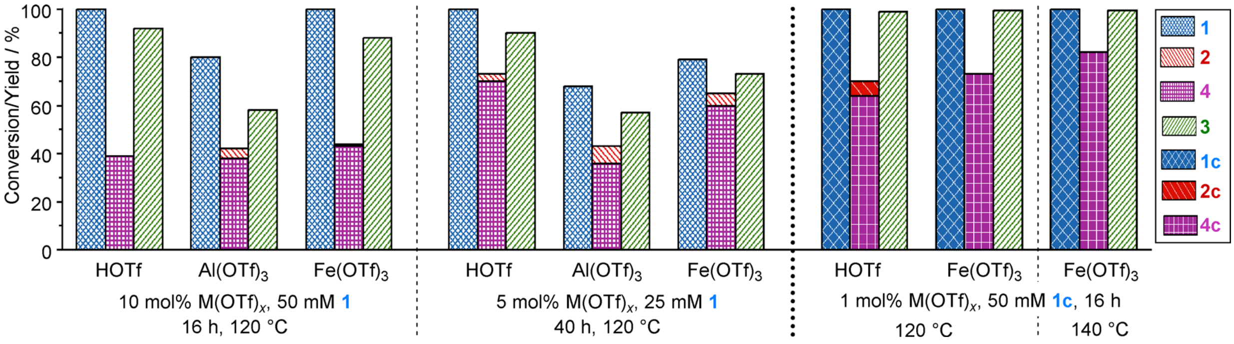
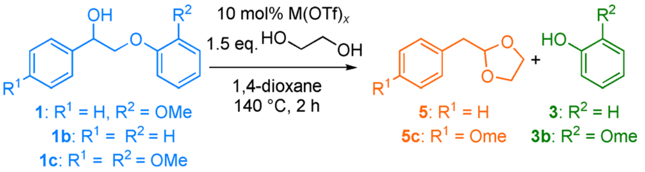


Figure 3. Cleavage of β-O-4 model compounds **1** and **1 c** catalyzed by metal triflates and in situ decarbonylation of **2** and **2 c** using 5 mol% $[IrCl(cod)]_2$ and 10 mol% PPh_3.

a lower metal triflate loading and milder temperature were used to prevent the build-up of aldehyde **2**, which was necessary as the decarbonylation of **2** forming toluene **4** catalyzed by Ir/PPh_3 was found to be relatively slow. The results for $Fe(OTf)_3$ and HOTf at 50 mM substrate concentration and 10 mol% catalyst loading were similar. Higher yields of **3** could be achieved with 25 mM substrate concentration and 5 mol% catalyst loading but with prolonged reaction time. At this substrate concentration, $Fe(OTf)_3$ resulted in slightly better selectivity towards **4** (76% vs. 70%). Using $Al(OTf)_3$, the conversion of **1** and selectivities towards **3** and **4** were significantly lower. The same trends were observed for a similar β-O-4 model compound **1c**, yielding up to 83% **4c** and showing a small increase in decarbonylation efficiency in the presence of $Fe(OTf)_3$ over HOTf (Figure 3, Table S5). The results demonstrate that the balance between the rate of aldehyde formation and the rate of decarbonylation is crucial to achieve high product yields.

Metal triflate-catalyzed cleavage of β-O-4 model compounds combined with ethylene glycol acetal formation

Next, we turned our attention to the cleavage of **1** with in situ conversion of the formed aldehyde **2** to its more stable 1,3-dioxolane acetal **5** (Scheme 4) using ethylene glycol. Several triflates such as $Bi(OTf)_3$, $Fe(OTf)_3$, and $Hf(OTf)_4$ showed excellent yields of 1,3-dioxolane acetal product **5** and guaiacol **3** (Figure 4 and Table S6). Other triflate salts tested showed significantly lower activity in the presence of ethylene glycol compared to the previous runs in 1,4-dioxane alone (compare Figure 4 and Figure 1b). In particular, $Sc(OTf)_3$ showed much lower conversion of **1** and only traces of **5** with some build-up of **2** under these reaction conditions. In a separate set of experiments, we showed that in particular $Sc(OTf)_3$ is relatively inefficient in catalyzing the formation of acetal **5** from **2** and ethylene glycol (Figure S5a).



Scheme 4. Cleavage of lignin β-O-4 model compounds **1**, **1b**, and **1c** in the presence of ethylene glycol to form **5** and **5c** catalyzed by $M(OTf)_x$.

Next, the reaction profiles for the cleavage of **1** and acetal formation with $Fe(OTf)_3$, $Hf(OTf)_3$ and $Bi(OTf)_3$ were compared to HOTf (Figure 5). HOTf and $Fe(OTf)_3$ again showed very similar conversion of **1** and yields of **3** and **5** (compare Figure 5a and b). This similarity between HOTf and $Fe(OTf)_3$ was also observed for reactions in toluene as well as other β-O-4 model compounds (**1b** and **1c**, Figures S2–S4). With 10 mol% $Hf(OTf)_4$, full substrate conversion was seen, but in this case within 1 h and a slight buildup of **2** was observed in the first

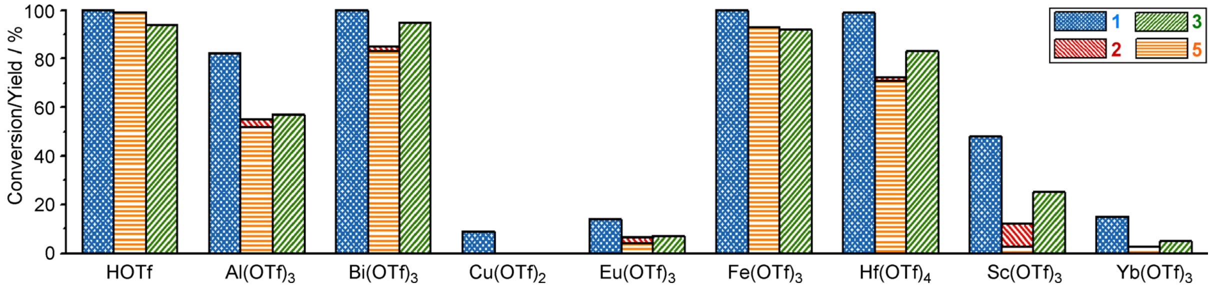


Figure 4. Cleavage of β-O-4 model compound **1** using metal triflate catalysts. Reaction conditions shown in Scheme 4. (Slightly different results were obtained with $Fe(OTf)_3$ from different commercial sources, see Table S1).

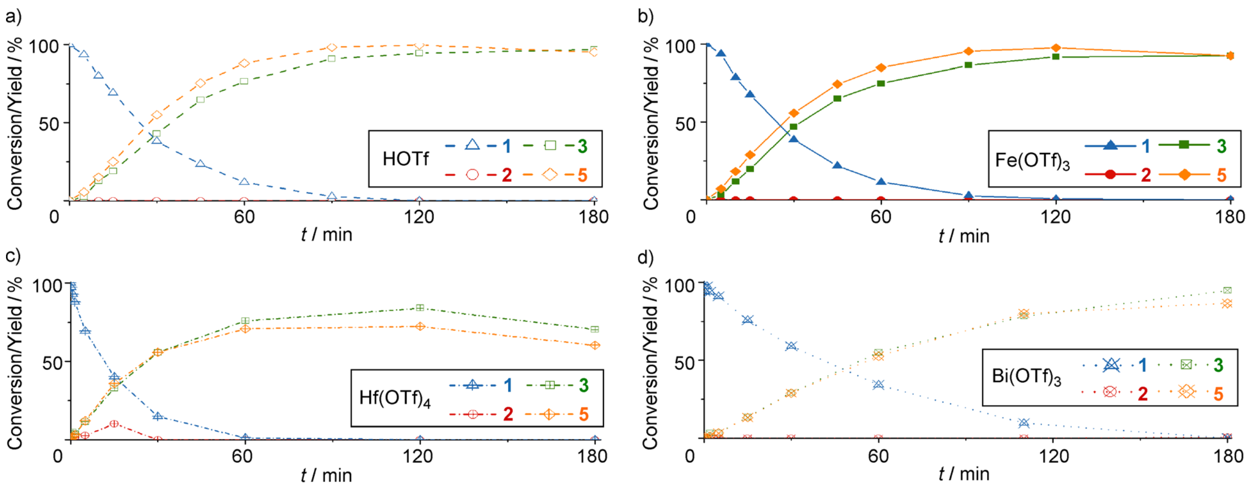


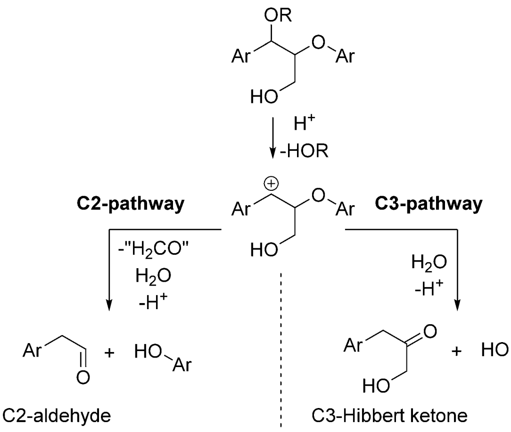
Figure 5. Reaction progress of the cleavage of **1** and in situ acetal formation with ethylene glycol catalyzed by a) 10 mol% HOTf, b) 10 mol% $Fe(OTf)_3$, c) 10 mol% $Hf(OTf)_4$, and d) 10 mol% $Bi(OTf)_3$.

15 min (Figure 5 c). As aldehyde **2** was already shown to be unstable in the experiments above, this explains the overall lower selectivity of **5** with $Hf(OTf)_4$ as catalyst. The use of $Bi(OTf)_3$ resulted in slower reactions but similar product yields upon 180 min reaction time (Figure 5 d). Overall, these reactions showed a clear trend in the rate of cleavage of **1**: $Hf(OTf)_4 > HOTf = Fe(OTf)_3 > Bi(OTf)_3$.

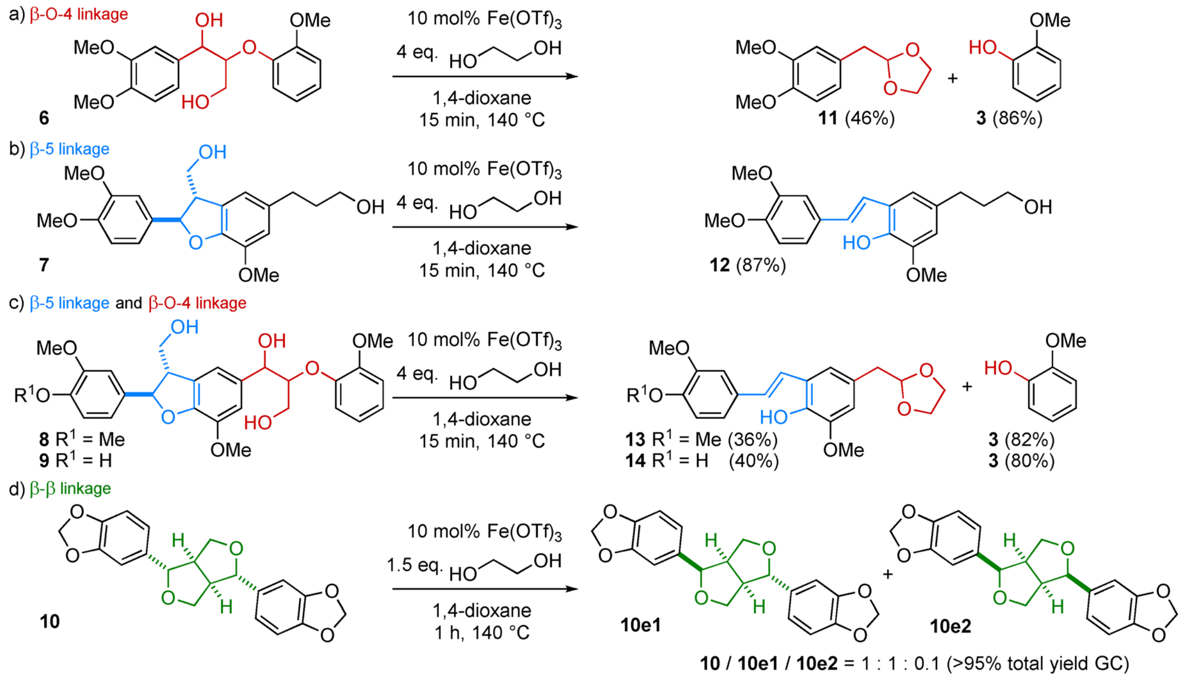
Reactivity of advanced lignin β-O-4, β-5, and β-β model compounds

Next, we turned our attention to the reactivity of a more complex β-O-4 motif containing all functionalities (carbinol-group and additional electron-donating aromatic-ring substituents) as well as other types of lignin linkages (β-5 and β-β) in the presence of metal triflates. For this purpose, we used a set of advanced lignin model compounds previously developed and employed by our groups for mechanistic investigations.[7d] These compounds contain β-O-4 (**6**, **8** and **9**), β-5 (**7**) and β-β (**10**) linkages comprising relevant functional groups that reflect the structure of these linkages in lignin (Scheme 5). Model compounds of this level of complexity are rarely used due to limited accessibility and analytical challenges associated with product analysis. Herein, we have a unique opportunity to gain more detailed insight into the effectiveness of the methodology employed prior to testing lignin.[7d]

Model compounds **6**–**10** were exposed to the cleavage and in situ acetal formation conditions in the presence of $Fe(OTf)_3$ (Scheme 5). The β-O-4 linkages in compounds **6**, **8**, and **9** were fully cleaved within 15 min and provided the corresponding phenolic product **3** in high yields as determined by HPLC (Scheme 5 a and c). The ethylene glycol acetals **11**, **13**, and **14** of the corresponding C2-aldehydes were detected as major cleavage products, albeit at lower yields. This is due to a competing cleavage pathway that leads to C3 aromatic products that relate to the so-called Hibbert ketones detected in traditional acidolysis reaction mixtures (Scheme 6).[5c,16] It was also shown that the β-5 linkage in **7**–**9** undergoes ring opening to ultimately form the corresponding *trans*-stilbenes **12**–**14** as major product (Scheme 5b and c). The product yields indicate a preference for the cleavage of the β-O-4 moiety via a pathway that releases the carbinol group as formaldehyde. The β-5 linkage is almost exclusively modified via a similar mechanism.[17] This also implies that the formaldehyde released during these reactions is probably trapped in the form of its



Scheme 6. Competing "C2" and "C3" β-O-4 cleavage pathways after formation of the benzylic carbocation.



Scheme 5. Reaction of a) Complex β-O-4 model compound **6**, b) β-5 model compound **7**, c) Advanced β-O-4-β-5 model compounds **8** and **9**, d) β-β model compound **10.** Reaction conditions: 10 mol% $Fe(OTf)_3$, ethylene glycol, in 1,4-dioxane.

ethylene-glycol acetal 1,3-dioxolane as also confirmed in our earlier studies.[7d]

The β-β model compound **10** underwent epimerization upon reaction with $Fe(OTf)_3$ in the presence of ethylene glycol forming a mixture of epimers **10**/**10 e1**/**10 e2** at a ratio of 1:1:0.1 as determined by gas chromatography–flame ionization detector (GC–FID; Scheme 5 d). We have previously obtained the same results using 10 mol% HOTf as catalyst in the same solvent.[7d] Overall, it can be concluded that a very similar reactivity was observed for the advanced model compounds **6**–**10** both in the presence of $Fe(OTf)_3$ and HOTf. Regarding the different types of linkages, the β-O-4 linkage model compounds were efficiently cleaved to two aromatic monomers (acetal and phenol product); however, the β-5 and β-β linkage models resulted in the formation of modified aromatic dimers. This means that when applying these methods using lignin as substrate, only the scission of the β-O-4 moiety will allow depolymerization. This highlights the importance of having a high β-O-4 content in the lignin used to achieve high aromatic monomer yields using the presented methodology.

Metal triflate-catalyzed depolymerization of walnut methanosolv lignin

Finally, after studying the reactivity of all main types of linkages, the metal triflates $Bi(OTf)_3$, $Fe(OTf)_3$, and $Hf(OTf)_4$ that showed the most promising results in the model compound studies were tested in lignin depolymerization in the presence of ethylene glycol. The results were compared to those obtained with HOTf (Scheme 7). For these reactions, methanosolv walnut lignin was isolated from walnut shells. This lignin has a higher β-O-4 content (26 β-O-4 linkage per 100 aromatic units) compared to other organosolv lignins tested previously by our group.[7a,d] The very simple catalytic methodology consisted of runs using 50 mg lignin, 60 wt% ethylene glycol, and catalytic amounts of $M(OTf)_x$ at 140 °C for 15 min in 1,4-dioxane. The depolymerization mixtures were subjected to a fractionation procedure in which the low-molecular weight material was extracted using toluene (Table S7).

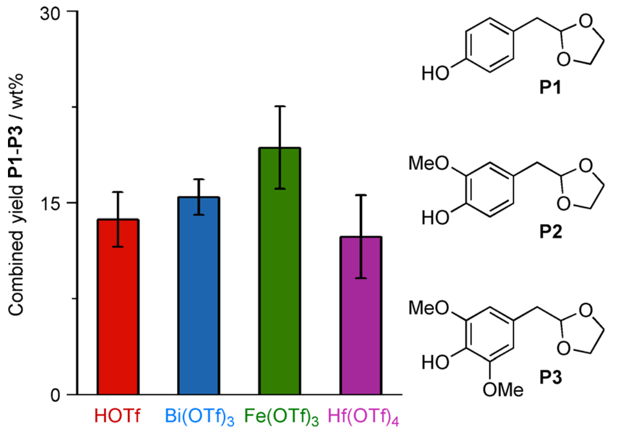
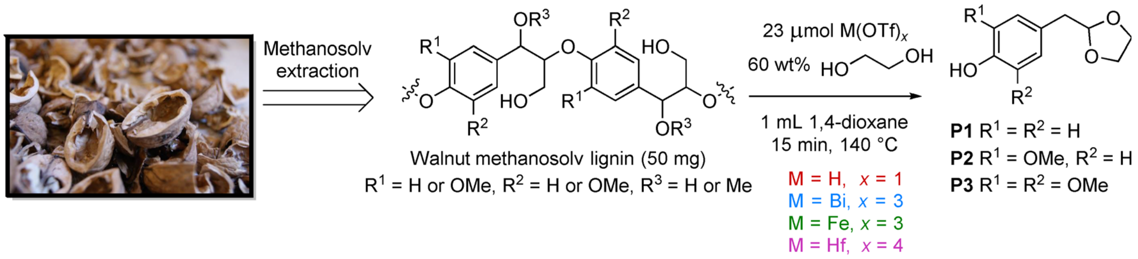


Figure 6. Yields of **P1**-**3** after depolymerization of 50 mg walnut methanosolv lignin with 23 μmol $M(OTf)_x$ in 1 mL 1,4-dioxane with 60 wt% ethylene glycol for 15 min at 140 °C (Shown data are averages of 2–3 identical experiments).

To evaluate the effectiveness of the metal triflate catalysts, we focused on the major monomeric products **P1**–**P3**, which were quantified by GC–FID using an internal standard (Figure 6, Table S8). The ratio of **P1**/**P2**/**P3** was found to be 4:33:63 for all experiments, in almost perfect agreement with the H/G/S ratio of 6:29:65 determined by 2D-HSQC NMR analysis of the starting lignin.[7d] Overall, excellent yields of **P1**–**P3** were obtained, reaching over 10 wt% for all metal triflate-catalyzed reactions. Interestingly, $Fe(OTf)_3$ performed better than the other triflates and HOTf, reaching an excellent yield of **P1**-**P3** of 19.3 ± 3.2 wt%. Thus far, only a few reports exist with such high yields of aromatic monomers, especially of product mixtures with limited complexity;[3a–d,18] thus, this method further contributes to achieving the highly efficient valorization of renewable resources and the production of distinct valuable monomers in high yields.[19]

Conclusions

Overall, this study shows that several metal triflates ($M(OTf)_x$) can be excellent substitutes for HOTf in the depolymerization of lignin. The general reactivities of lignin model compounds compared well to those observed with triflic acid, and preliminary studies suggest that triflic acid formed in situ is responsible for the reactivity of these metal triflates. While model compounds mirroring all three major lignin linkages (β-O-4, β-β, β-5) showed similar behavior in the presence of triflates and triflic acid, there were variations in substrate conversion and product yields depending on the type of metal triflate used. For example, $Hf(OTf)_4$ showed higher activity for the cleavage of β-O-4 model compounds but lower product selectivity, whereas other triflate salts such as $Bi(OTf)_3$ showed lower activity but



Scheme 7. Metal triflate-catalyzed depolymerization of walnut methanosolv lignin (representive structure shown) in the presence of ethylene glycol to yield acetal phenols **P1**–**P3**.

similar selectivities. In the depolymerization of organosolv lignin, Bi(OTf)$_3$, Fe(OTf)$_3$ and Hf(OTf)$_4$ all showed promising results and three main aromatic products were clearly identified as major products. Interestingly, the best aromatic monomer yields 19.3 ± 3.2 wt% were obtained with Fe(OTf)$_3$, reflecting differences in reactivity in this case in favor of the metal triflate compared to triflic acid. More specific reasons for this behavior are currently investigated in our laboratories. Future studies should also address the possibility of catalyst recycling[20a] either by immobilization of the triflate salts[20b] or HOTf[20c].

Experimental Section

Metal triflate-catalyzed cleavage of β-O-4 model compounds: Substrate (e.g., **1**, 48.9 mg, 0.2 mmol) was weighed in a 20 mL microwave vial equipped with a magnetic stirring bar. Solvent (e.g., 1,4-dioxane, 2 mL) and *n*-octadecane (25 μmol 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 the catalyst (e.g., triflic acid, 10 mol%, 1 μL, 0.02 mmol or 200 μL of a freshly prepared 5 mg mL^{-1} Fe(OTf)$_3$ stock in 1,4-dioxane, 10 mol%, 0.02 mmol) was added by a syringe with a thin needle through the septum of the microwave vial. If samples were taken, this was done by using a syringe equipped with a long thin needle. The samples (100–150 μL) were filtered, diluted in dichloromethane (DCM) and analyzed by GC–FID and GC–MS (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 GC–FID and GC–MS analysis (Table S2).

Metal triflate-catalyzed cleavage of β-O-4 model compounds in combination with in situ decarbonylation: 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 μmol) from a stock solution in 1,4-dioxane. A premixed solution of PPh$_3$ and [IrCl(cod)]$_2$ in 1,4-dioxane (mixed for 15 min 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 a 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 GC–FID and GC–MS (Results in Tables S3–S5).

Metal triflate catalyzed cleavage of β-O-4 model compounds in combination with in situ acetal formation: Substrate (e.g., **1**, 48.9 mg, 0.2 mmol) was weighed in a 20 mL microwave vial equipped with a stirring bar. Solvent (e.g., 1,4-dioxane, 2 mL) and *n*-octadecane (25 μmol from a 0.25 M stock solution in the appropriate solvent), diol (e.g., ethylene glycol 16 μL 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 μL, 0.02 mmol or 200 μL of a freshly prepared 5 mg mL^{-1} Fe(OTf)$_3$ stock in 1,4-dioxane, 10 mol%, 0.02 mmol) was added by a syringe with a thin needle through the septum of the microwave vial. If samples were taken, this was done by using syringe equipped with a long thin needle. The samples (100–150 μL) were filtered, diluted in DCM, and analyzed by GC–FID and GC–MS (see Figures 3 and S2–S4). Otherwise the reaction was stopped by cooling on ice. The crude reaction mixture was filtered over Celite and an aliquot was taken for GC–FID and GC–MS analysis (Results in Table S6).

Metal triflate-catalyzed depolymerization of walnut methanosolv lignin in combination with in situ acetal formation: Walnut methanosolv lignin (50 mg) isolated by a reported procedure[7c] 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 μL from a 0.25 M stock in 1,4-dioxane, 2.5 μmol) and ethylene glycol (145 μL from a 7.1 M stock in 1,4-dioxane) were added. The catalyst M(OTf)$_x$ (23 μmol) 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 °C for 15 min before being cooled rapidly in an ice bath. The mixture was filtered over a plug of Celite and the flask and filter washed with about 0.5 mL 1,4-dioxane in three portions. The combined filtrate was evaporated to dryness over 16 h at 40 °C in a Univapo 150 ECH rotational vacuum concentrator. The residue was suspended in 150 μL DCM by extensive mixing (by vortex) after which 1.35 mL toluene was added. The samples were vortexed and subsequently centrifuged for 10 min at 13 400 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 h at 40 °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 GC–FID for quantification of **P1**–**P3** (Table S8).

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Keywords: acidolysis · aromatics · depolymerization · lignin · metal triflates

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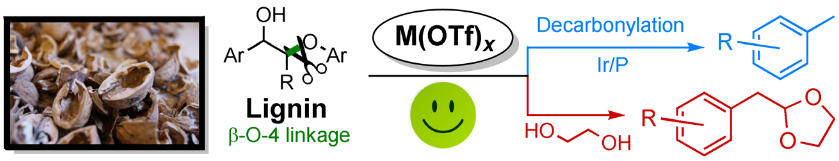

Nutty triflates: Metal triflates are introduced as an easy-to-handle alternative to triflic acid for the cleavage of lignin β-O-4 linkages in conjunction with stabilization of reactive intermediates. The reactivity of several model compounds and lignin is studied. In particular, iron(III) triflate proved effective, providing as much as 19.3 ± 3.2 wt% yield of a set of three aromatic C2-acetals from lignin.

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Metal Triflates for the Production of Aromatics from Lignin