Accepted Article

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Selective Oxidation of Lignin Model Compounds

Ruili Gao,*,[a],[b] Yanding Li,[b],[c] Hoon Kim,[a],[b] Justin K. Mobley,†,[b] and John Ralph*,[a],[b]

Abstract: Lignin, the planet's most abundant renewable source of aromatic compounds, is difficult to degrade efficiently to well-defined aromatics. We developed a microwave-assisted catalytic Swern oxidation system using an easily prepared catalyst, $MoO_2Cl_2(DMSO)_2$, and DMSO as the solvent and oxidant. It demonstrated high efficiency in transforming lignin model compounds containing the units and functional groups found in native lignins. The aromatic ring substituents strongly influenced the selectivity of β-ether phenolic dimer cleavage to generate sinapaldehyde and coniferaldehyde, monomers not usually produced by oxidative methods. Time-course studies on two key intermediates provided insight into the reaction pathway. Due to the broad scope of this oxidation system and the insight gleaned with regard to its mechanism, this strategy could be adapted and applied in a general sense to the production of useful aromatic chemicals from phenolics and lignin.

In recent years, lignin, the largest source of renewable aromatic compounds on the planet, has received increased attention in academia and industry for its potential to be converted into commodity chemicals. Whereas lignin has historically been burned to provide energy, new efforts have focused on utilizing and manipulating its inherent structure and functionality.[1-6] For example, various strategies have shown promise in deriving valuable chemicals from the lignin portion of biomass feedstocks, including lignin catalytic cracking, hydrolysis, reduction/ hydrogenolysis, and oxidation.[2,7-10] Of these methods, oxidative treatments present several advantages and have the potential to yield more highly functionalized monomers or oligomers that could be useful within the chemical industry.[11-14] As this subfield of lignin valorization continues to mature, some promising homogeneous catalytic oxidation methods have emerged. Hanson *et al.* developed a series of oxovanadium catalysts featuring various ligands and successfully applied them to the oxidative cleavage of lignin.[15-18] Depending on which catalyst they employed, the researchers were able to selectively cleave C–C or C–O bonds in phenolic lignin model compounds. Mottweiler successfully used vanadium acetylacetonate and copper (II) nitrate as catalysts to cleave lignin model compounds and generate carboxylic acids in modest yields.[19] Bozell and coworkers improved the performance of cobalt-Schiff base complexes in the oxidation of lignin model compounds.[20] They demonstrated that Co(salen) complexes can selectively convert phenolic lignin models into benzoquinones in good yields. Due to

the low abundance of free phenolic moieties in lignin, however, this method generates these benzoquinones from isolated lignins in relatively low yields.

Although each of these catalytic oxidation methods, in which O_2 was used as the ultimate oxidant, offers unique opportunities for selective chemical synthesis depending on the transition metal and ligand scaffold, they are all limited by the long reaction times required for even the simplest of lignin model compounds. Efficient catalytic conversion of both lignin model compounds and lignin to well-defined aromatics represents a key challenge that has considerably limited the valorization of lignin. We therefore sought to tackle this primary issue by developing a rapid oxidative method that could efficiently degrade lignin model compounds with functional groups found in native and processed lignins, and eventually natural lignin itself. The justification for the use of model compounds is that, although the corollary is not valid, any scheme that fails to produce decent yields on a representative model compound will have little-to-no chance of working on actual lignin.

Dioxomolybdenum compounds have been reported as efficient catalysts for the oxidation of alcohols,[21-26] but they have not been widely used on lignin or even simple lignin model compounds. Recently, Sanz and coworkers reported on the oxidative cleavage of glycols catalyzed by a common and easily prepared dioxomolybdenum (VI) complex in dimethyl sulfoxide (DMSO) using microwave irradiation.[27] As an efficient and direct manner of heating the reaction mixture rapidly, microwave irradiation has already been successfully explored in organic synthesis and lignin pretreatments. To that end, several studies have suggested that oxidation kinetics can be considerably enhanced by microwave assistance that, in some cases, even increases the conversion or selectivity over that of conventional catalytic oxidation methods.[28-30] Inspired by these breakthroughs, we have applied microwave irradiation to the oxidation of lignin model compounds, with interesting outcomes. Herein we report a selective and efficient catalytic approach to the oxidation of lignin model compounds using microwave irradiation technology.

We initially performed reactivity studies on an all-syringyl (S–S) β–O–4-linked phenolic dimer **6**SS (Table 1) with the easily prepared dioxomolybdenum (VI) complex, $MoO_2Cl_2(DMSO)_2$ in DMSO as solvent and oxidant. We found that the oxidation of these dimers, which model major structures in lignin, in DMSO at 160 °C for 4 h [catalyzed by the addition of 5 mol% $MoO_2Cl_2(DMSO)_2$] could generate sinapaldehyde **12**S (3,5-dimethoxy-4-hydroxycinnamaldehyde) in an isolated yield of 85%. When we replaced traditional heating with microwave irradiation in this catalytic system, we obtained similar results after only 10 minutes at the same temperature (with a ramp-up time of 1 min). These findings are all the more remarkable in light of the fact that no other reported method can oxidize β–O–4 phenolic dimers in such an efficient and selective manner. Moreover, this method is the first to generate sinapaldehyde **12**S directly from the oxidation of these model dimers, suggesting that it may have synthetic and commercial value.

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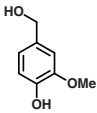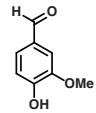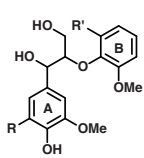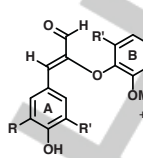   E-mail: rgao@wisc.edu, jralph@wisc.edu
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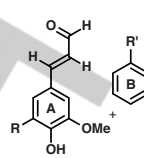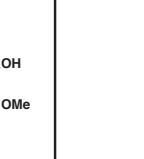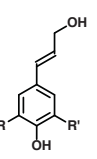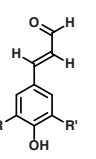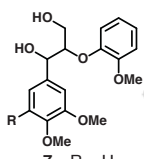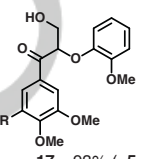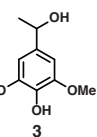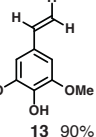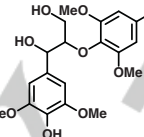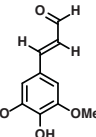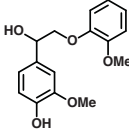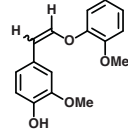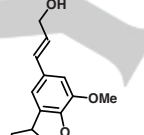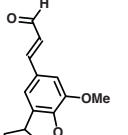
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Table 1. Oxidation of lignin model compounds in DMSO catalyzed by MoO₂Cl₂(DMSO)₂.

substrate	t (min)	products[a]	substrate	t (min)	products[a]
1	10	**11** 92%	**6**$_{GG}$ R = R' = H **6**$_{GS}$ R = H, R' = OMe **6**$_{SG}$ R = OMe, R' = H **6**$_{SS}$ R = R' = OMe	10	**16**$_{GG}$ 81% **12**$_{G}$ 0 **18**$_{G}$ 0 **16**$_{GS}$ 0 **12**$_{G}$ 83% **18**$_{S}$ 76% **16**$_{SG}$ 32% **12**$_{S}$ 53% **18**$_{G}$ 49% **16**$_{SS}$ 0 **12**$_{S}$ 87% **18**$_{S}$ 81%
2$_{H}$ R = R' = H **2**$_{G}$ R = H, R' = OMe **2**$_{S}$ R = R' = OMe	10	**12**$_{H}$ 97% **12**$_{G}$ 91% **12**$_{S}$ 87%	**7**$_{G'}$ R = H **7**$_{S'}$ R = OMe	10	**17**$_{G'}$ 93% (=**5**$_{G'}$) **17**$_{S'}$ 93%
3	10	**13** 90%	**8**	10	**12**$_{S}$ 91%[b]
4	10	**14** 65% (*cis:trans* = 97:3)	**9**	15	**19** 87%
5$_{G}$ R = H **5**$_{G'}$ R = Me	20	**15**$_{G}$ 86% **15**$_{G'}$ 85%	**10**	15	**NR**

Note that substrates are numbered **1**-**10** and their corresponding products from **11**-**19**. [a]Reactions were conducted with 0.5 mmol model compounds, 5 mol% MoO₂Cl₂(DMSO)₂ in 5 mL DMSO under microwave irradiation (400 W), isolated yields given. [b]Two equivalents of sinapaldehyde **12**$_{S}$ were formed.

Encouraged by these initial results, we worked to optimize the microwave reaction conditions using this same phenolic S–S-β-ether dimer **6**$_{SS}$ [details on the catalyst, solvent, oxidants, and temperature screening data, and full reaction conditions, are included in the Supporting Information (Table S1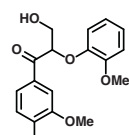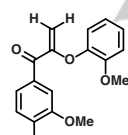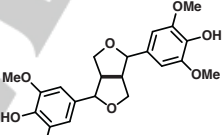)]. After screening at various microwave temperatures, we found that the reaction generated sinapaldehyde **12**$_{S}$ most efficiently between 130 °C and 160 °C; we observed no reaction at temperatures below 120 °C. Even so, although yields of sinapaldehyde were acceptable in that range, we observed the α-ketone (not shown, but the S–S analog of **5** or **17**, Table 1) as a byproduct at temperatures below 160 °C. Due to the high temperatures required for this reaction, we quickly identified DMSO as the most suitable solvent. γ-Valerolactone (GVL), dimethylformamide

(DMF), and cyclohexanone (each containing 3.0 equivalents of DMSO as oxidant) did not perform as well, with cyclohexanone being the worst (approximately 30% conversion) presumably due to its ready ability to coordinate to the molybdenum center, thus blocking the catalytic site. Other oxidants, such as O₂, hydrogen peroxide, benzoyl peroxide, and ammonium persulfate, failed to afford sinapaldehyde **12**$_{S}$ in significant yields, nor did additives improve the formation of the desired product. In fact, NMR spectral analysis revealed that the addition of a Brønsted acid or base (Table S1, entries 12 and 13) fully suppressed the oxidation. Under the optimized reaction conditions (Table S1, entry 5), other commercially available molybdenum complexes (such as MoO₃, Na₂MoO₄·2H₂O, and MoO₂Cl₂) showed high oxidative reactivity but lower selectively, affording sinapaldehyde **12**$_{S}$ in yields of 50-

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75%, with the corresponding α-ketone (not shown, but the S–S analog of **5** or **17**, Table 1) and unknown polymeric byproducts comprising the remainder.

With these optimized conditions in hand, we evaluated the reaction scope by using a range of lignin model compounds containing the key units and functional groups commonly found in native and processed lignins (Table 1). We first evaluated a series of simple model compounds, on which our catalytic system performed very well: oxidation of the primary benzylic alcohol **1** (entry 1) and the three "traditional" lignin monomers (*p*-coumaryl alcohol **2**$_H$, coniferyl alcohol **2**$_G$, and sinapyl alcohol **2**$_S$) afforded the corresponding aldehydes, *p*-coumaraldehyde **12**$_H$ (4-hydroxycinnamaldehyde), coniferaldehyde **12**$_G$ (4-hydroxy-3-methoxycinnamaldehyde) and sinapaldehyde **12**$_S$ (3,5-dimeth-oxy-4-hydroxycinnamaldehyde), in isolated yields of 87-97%; no acids, resulting from over-oxidation, were detected. This oxidation, with its high yields of hydroxycinnamaldehydes **12** from the hydroxycinnamyl alcohols (monolignols, **2**), is considered to be synthetically useful, competing with the likes of DDQ oxidation to elicit such oxidations.[31] In contrast to our observance of the α-ketone **17** in product mixtures from the oxidation of non-phenolic dimers **7**, we saw evidence of dehydration of the benzylic alcohols **3** or **4** to form styrene **13** or styryl ether **14** products in good yields.

More significantly, these oxidation conditions proved to be highly effective on β-ether dimers containing diols, i.e., with the full 3-carbon sidechain that is the common chemical motif in lignin. Both the syringyl- and guaiacyl-type phenolic dimers **6** demonstrated good reactivity but with strikingly different product profiles. Oxidation of phenolic G–G–β-ether dimer **6**$_{GG}$ afforded the cinnamaldehyde-β-aryl ether **16**$_{GG}$ in a yield of 81% without any cleavage products being detectable by NMR. Conversely, the oxidation of phenolic G–S- and S–S–β–O–4 dimers **6**$_{GS}$ and **6**$_{SS}$ yielded solely the cinnamaldehydes **12**$_G$ and **12**$_S$, corresponding to C$_β$–O bond cleavage, and syringol **18**$_S$ (2,6-dimethoxyphenol) in high yields, whereas oxidation of the S–G-model **6**$_{SG}$ afforded both the cinnamaldehyde-β-aryl ether **16**$_{SG}$ (32%) and partial C$_β$–O bond cleavage to produce sinapaldehyde **12**$_S$ and guaiacol **18**$_G$. These results provided important insight into the dependence of the product distribution on either the electron density in the various moieties of the reactant or perhaps just the sterics in-volved in aiding the cleavage; substrates with more electron-rich B-rings produced a less-stable cinnamaldehyde-β-aryl ether, which cleaved to form the respective cinnamaldehyde and phenol. As evidence of this dependence, two equivalents of sinap-aldehyde **12**$_S$ were obtained in an isolated yield of 91% following the oxidation of the authentic sinapyl alcohol β–O–4 dimer **8** under the optimized conditions; the analogous guaiacyl dimer (not shown) again did not fully cleave, producing **16**$_{GG}$ in addition to **12**$_G$. In the case of both G-type and S-type non-phenolic β-ether dimers **7**$_{G'}$ and **7**$_{S'}$, the α-ketone was detected in high yield (93%) after 10 min, although dehydration of the γ-alcohol began to occur after a reaction time of 25 min. As expected based on these results, oxidation of α-keto-γ-hydroxy model compounds **5**$_G$ and **5**$_{G'}$ offered further proof that benzylic oxidation takes place first, followed by dehydration to afford the alkene. The oxidation of another important lignin model **9** featuring the β–5-linkage showed highly selective oxidation of the cinnamyl alcohol side-chain moiety to yield the corresponding cinnamaldehyde; as usual for these oxidations, the primary alcohol (that is neither benzylic nor allylic) was not oxidized. This reaction system did not cleave

a sinapyl alcohol β–β-coupled dimer **10** (syringaresinol), regard-less of reaction time; in this case, only the starting material was detected.
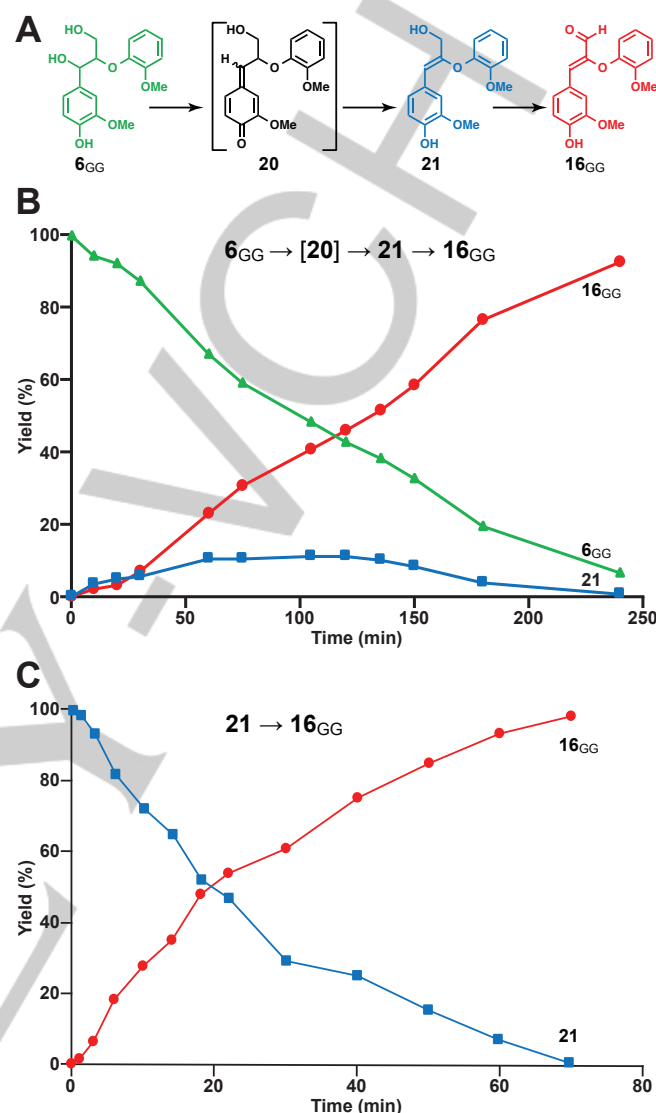
Figure 1. Mechanistic study of oxidation of G–G–β–O–4 phenolic dimers. (**A**) Overall reaction pathway. (**B**) Overall time-course plot of the reaction **6**$_{GG}$→[**20**]→**21**→**16**$_{GG}$. (**C**) Time-course plot of the reaction **21**→**16**$_{GG}$.

We next probed the mechanistic details of the catalytic cycle using the phenolic G–G–β-ether dimer model compound **6**$_{GG}$ (Fig. 1). Quinone methide **20**[32-34] and cinnamyl alcohol-β-aryl ether **21** were synthesized and fully characterized as important inter-mediates, and we used ^{1}H NMR spectroscopy to obtain reaction time-course data (Supporting Information). Direct investigation of the oxidation of β-ether dimer **6**$_{GG}$ revealed a low steady-state concentration of the cinnamyl alcohol-β-ether **21** throughout the formation of the cinnamaldehyde-β-aryl ether **16**$_{GG}$ (Fig. 1b). The data also indicated that the oxidation process begins with the conversion of the starting dimer **6**$_{GG}$ to its quinone methide **20**, which quickly undergoes conversion to cinnamyl alcohol-β-aryl ether **21**, followed by oxidation to afford the final product **16**$_{GG}$ (Fig. 1a). Independent studies following the oxidation of both authentic synthesized quinone methide **20** to final product **16**$_{GG}$, and the

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cinnamyl alcohol-β-aryl ether **21** to final product **16**$_{GG}$, also confirmed these findings. Our kinetic studies, which provide evidence of the rapid conversion of **20** to **21**, and which demonstrate that intermediate **21** is consumed more rapidly than the overall conversion of the starting dimer into the product, suggest that the formation of quinone methide **20** is the rate-limiting step in this reaction.
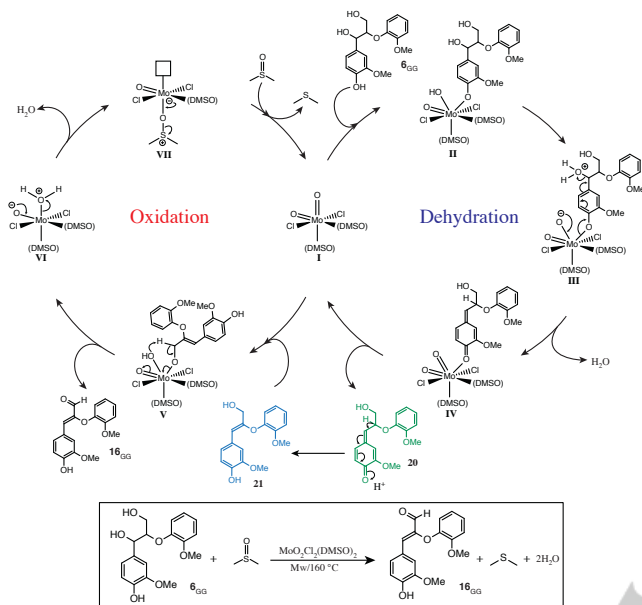
Scheme 1. Proposed mechanism for oxidation of G-G-β–O–4 phenolic dimer **6**$_{GG}$ by MoO$_2$Cl$_2$(DMSO)$_2$ in DMSO.

Any proposed mechanism has to be consistent with the above observations. A plausible mechanism for the formation of cinnam-aldehyde-β-aryl ether **16**$_{GG}$ from β-ether dimer **6**$_{GG}$ is given in Scheme 1. In the catalytic cycle, the first step is a dehydration, which begins with the coordination of the phenol to the molybdenum center to form **II**, and is then followed by proton transfer to generate intermediate **III**. Next, a quinone methide-catalyst complex **IV** forms by water elimination involving the cleavage of the C–O. The intermediate quinone methide **20** rapidly undergoes H$_β$ elimination to form intermediate **21**,[35] which will coordinate to the Mo center and undergo the oxidation process to produce the product **16**$_{GG}$ and metal complex **VI**. It is not clear whether the quinone methide **20** is in any way coordinated with the Mo, but we confirm that **20** does produce **21** (at least partially), rather than undergo formaldehyde elimination in a retro-aldol reaction, under these conditions but without the added Mo catalyst. The intermediate **VI** eliminates one molecule of water to generate complex **VII**. DMSO then occupies the empty site to regenerate the catalyst **I**, with the release of dimethyl sulfide as a byproduct (which is evidenced by its smell and its ^{1}H NMR peak at 2.08 ppm). In summary, the overall process of the oxidation of a phenolic β-ether dimer involves dehydration and the oxidation of an alcohol by DMSO, generating two molecules of water and one molecule of dimethyl sulfide as the only byproducts. Oxidation of non-phenolic β-ether dimers **7** cannot follow this mechanism; the reaction stops after benzylic oxidation to produce the α-ketone (e.g., compounds **7** to **17**). Similar results were seen in a previous

study on the stoichiometric Swern oxidation of lignin model compounds.[35] Although the cleavage of β-ether model compounds to form cinnamaldehyde derivatives was not elucidated in that paper, it has been noted that benzyl-oxidized lignin model compounds are thermodynamically less stable than their alcohol analogues (~87 KJ mol^{-1}).[14,36–41] Highly conjugated and electron-rich substrates such as **16**$_{SS}$, **16**$_{SG}$, and **16**$_{GS}$ would therefore logically undergo thermolytic cleavage of the C$_β$–O bond at temperatures between 120 °C and 160 °C.

Although not the aim of the present work, these model studies provided the basis for the testing the reactivity of actual lignin; β-ether units are the most prevalent in lignin. Preliminary studies on Aspen lignin showed that more than 25 wt% of the original lignin was oxidatively converted to well-defined monomers, with sinapaldehyde and coniferaldehyde being the two major products (totaling 15% yield) with the ratio of 70:30. Moreover, the oxidation of a high-syringyl lignin from F5H-upregulated transgenic poplar[42,43] produced 31 wt% monomers, with sinapaldehyde as the major product in 22% yield; other monomers included syringaldehyde and syringic acid, along with the *p*-hydroxybenzoic acid that acylates poplar lignins. These yields are too high to have resulted solely from cleaving phenolic end-groups, so it is clear that processive depolymerization is occurring. However, the yields are lower than would be expected from cleaving all β-ethers,[8] so it is also clear that benzylic oxidation is occurring and preventing full depolymerization. We are now attempting to laboriously delineate conditions that allows peeling from the phenolic end to occur in preference to benzylic oxidation of etherified units to enhance the yields of monomers to really practically compelling levels.

In conclusion, we have capitalized on the pioneering work of other researchers to develop an effective and efficient method for the oxidation of lignin model compounds to novel products using easily prepared and environmentally friendly MoO$_2$Cl$_2$(DMSO)$_2$ as a catalyst and DMSO as the solvent and oxidant. We demonstrated that this strategy can oxidize a broad range of lignin model compounds, and its ability to cleave the C–O bond in phenolic β-ether dimers to form sinapaldehyde or coniferaldehyde has potential for industrial applications; the acid derivatives, *p*-coumaric and ferulic acid, are already mildly valuable commodity chemicals.[10] Reaction time-course studies of two key synthetic intermediates provided important insights into the mechanism. Extrapolating from its broad reaction scope and the mechanistic details, we contend that this new catalytic system could facilitate depolymerization of lignin into commodity chemicals, as already preliminarily demonstrated here. Studies on dealing with the attributes of this reaction to deliver efficient lignin depolymerization are currently ongoing and proving promising but are meeting with the often-encountered obstacles; successful high-yielding depolymerization will hopefully be reported in due course. Moreover, we envision that this method could be used in place of the laborious conventional Swern oxidation as a facile and selective oxidation system for the conversion of alcohols to carbonyl compounds, and recommend its use for producing hydroxycinnamaldehydes from hydroxycinnamyl alcohols.

Supporting Information

Full catalyst screening data, experimental procedures, time-course studies of the reactions, and characterization data for all

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products is provided in pdf format. This material is available free of charge via the Internet at http://onlinelibrary.wiley.com

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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COMMUNICATION

Entry for the Table of Contents

COMMUNICATION

6$_{GG}$ R = R' = H
6$_{GS}$ R = H, R' = OMe
6$_{SG}$ R = OMe, R' = H
6$_{SS}$ R = R' = OMe

16$_{GG}$ 81%
16$_{GS}$ 0
16$_{SG}$ 32%
16$_{SS}$ 0

12$_G$ 0
12$_G$ 83%
12$_S$ 53%
12$_S$ 87%

18$_G$ 0
18$_S$ 76%
18$_G$ 49%
18$_S$ 81%
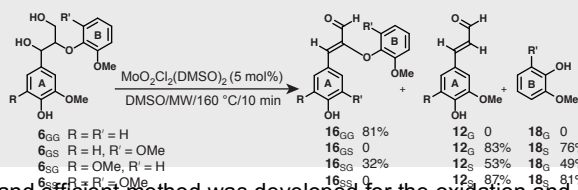
Ruili Gao,* Yanding Li, Hoon Kim, Justin K. Mobley, and John Ralph*

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Selective Oxidation of Lignin Model Compounds

An effective and efficient method was developed for the oxidation and cleavage of lignin model compounds using easily prepared and environmentally friendly MoO$_2$Cl$_2$(DMSO)$_2$ as catalyst under microwave irradiation.

I'm sorry! I have been engaged in desktop publishing since its inception, but I have NEVER understood graphics in MS Word and I can not for the life of me size this graphic and place it properly into the above space!!

6$_{GG}$ R = R' = H
6$_{GS}$ R = H, R' = OMe
6$_{SG}$ R = OMe, R' = H
6$_{SS}$ R = R' = OMe

16$_{GG}$ 81%
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