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Molybdenum-Catalyzed Deoxygenation Coupling of Lignin-Derived Alcohols for Functionalized Bibenzyl Chemicals

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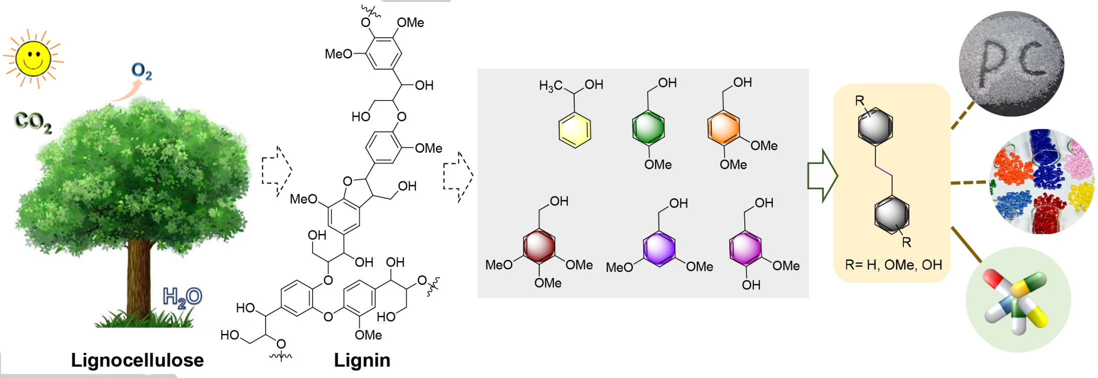
Abstract: With the growing demand for sustainability and reducing CO_2 footprint, lignocellulosic biomass has attracted much attention as a renewable, carbon-neutral and low-cost feedstock for the production of chemicals and fuels. To realize efficient utilization of biomass resource, it is essential to selectively alter the high degree of oxygen functionality of biomass-derivates. Herein, we introduced a novel procedure to transform renewable lignin-derived alcohols to various functionalized bibenzyl chemicals. This strategy relied on a concise deoxygenation coupling pathway with economical molybdenum catalyst. A well-designed H-donor experiment was performed to investigate the mechanism of this Mo-catalyzed process. It was proved that benzyl carbon-radical was the most possible intermediate to form the bibenzyl products. It was also discovered that the *para* methoxy and phenolic hydroxyl groups could stabilize the corresponding radical intermediates and then facilitate to selectively obtain bibenzyl products. Our research provides a promising application to produce functionalized aromatics from biomass-derived materials.

Biomass, especially lignocellulose, has been regarded as a promising renewable energy carrier to satisfy the continuous necessity of diversified resources for producing valuable chemicals and fuels.[1] The upgrading transformation of oxygen-rich biomass feedstocks motivates the extensive interest in developing chemical processes to re-functionalize the C-O bonds.[2] These incentives spur to explore innovative and efficient deoxygenated strategies for the selective conversion of biomass-derivates. Hydrodeoxygenation (HDO) is one such chemical procedure performed in high H_2 pressures and high temperature to remove oxygen atoms.[3] For example, in the bio-fuel refining process, HDO reaction can remove the oxygen atoms of lignin-derived bio-oils to produce hydrocarbons under noble metals and metal sulfides catalysts.[4] Deoxydehydration (DODH) reaction, as a single-step combined with dehydration and deoxygenation processes, has been used to eliminate adjacent hydroxyls in polyol and then produce olefins. This type of reaction is carried out under high-valent rhenium[5], molybdenum[6] and vanadium[7] catalysts combined with reductants, such as 1-butanol, PPh_3, H_2, metal and so on. The ability of oxo-Re, Mo and V complexes to activate C-O bonds aroused the interest of many researchers to investigate the deoxygenation of various biomass-derived alcohols.[8]

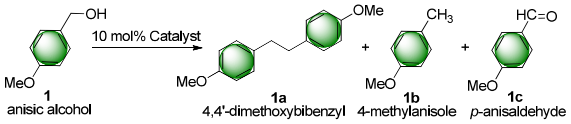
Recently, a re-functionalization of mono-alcohol has been reported via oxo-Re and V complex-catalyzed oxidation/reductive coupling reactions.[9] Compared with similar C-C bonds construction from allyl and benzyl alcohols via stoichiometric titanium-based halide[10] or La/Me_3SiCl[11] mediated pathway, this procedure discovered a new catalytic process to enhance the selectivity of C-C coupling products. Besides, different from the above-mentioned HDO and DODH methods, this deoxygenation coupling process is capable of doubling the carbon number.



Scheme 1. The conceptual outline for the production of functionalized bibenzyl chemicals from lignocellulosic feedstock.

Bibenzyls, as one type of important intermediates in chemical engineering, have been used as the aromatic monomers for the production of new type polycarbonate, thermosetting resins and thermoplastics.[12] Especially equipped with methoxy or phenolic hydroxyl groups, the functionalized bibenzyls showed a great potential as the green alternative for ubiquitous bisphenol A in similar resins.[13] Moreover, natural bibenzyls are widely known as the key motif of various important natural pharmaceuticals in bio-medical area combined with their cardioprotective, neuroprotective, anticancer and antiviral bio-activity.[14] In view of the abundant source of lignin in nature and the structural affinity between natural bibenzyls and lignin-monomer, we here described a novel procedure to produce functionalized bibenzyl chemicals from lignin-derived alcohols (Scheme 1). In this work, various molybdenum catalysts were employed in the deoxygenation coupling reactions. And a well-designed H-donor experiment was conducted to study the mechanism of molybdenum-catalyzed deoxygenation coupling reaction. The effect of different functional groups in lignin-derived substrates for the selective production of bibenzyls was also investigated.

Table 1. Comparison of different catalysts for reduced C-C coupling reaction of anisic alcohol. [a]



Entry	Catalyst	Conversion (%)	Reduced Products (**1a**, **1b**) (%)	Oxidation Products (**1c**) (%)
1	blank	-	-	-
2	MoO_3	42	22 (**7**, 15)	13
3	$(NH_4)_6Mo_7O_{24}$	67	39 (**7**, 32)	23
4	$MoO_2(acac)_2$	>99	54 (**6**, 48)	21
5	Mo-Phen	65	41 (**8**, 33)	24
6	Mo-Bipy	88	57 (**8**, 49)	25
7	Mo-Salen	>99	59 (**14**, 45)	14
8	Mo-8-HQ	>99	92 (**48**, 44)	7
9	CH_3ReO_3	>99	87 (**17**, 70)	5

[a] Reaction conditions: 1 mmol anisic alcohol, 10 mol% catalyst, 1.5 mmol triphenylphosphine and 20 mL1,4-dioxane were put into 50 mL Parr autoclave, then reacted at 220 °C for 8 h under Ar. Note: Phen: 1,10-phenanthroline, Bipy: 2,2'-bipyridine, Salen: tetradentate Schiff base, 8-HQ: 8-hydroxyquinoline.

For selectively obtaining the coupled products, we firstly investigated the viability of various Mo-based catalysts for deoxygenation coupling ability of anisic alcohol **1** (all experimental details were showed in Supporting Information). The reduced products, including the coupled product, 4,4'-dimethoxybibenzyl **1a**, deoxygenation product, 4-methylanisole **1b**, and oxidized byproduct, *para*-anisaldehyde **1c**, were detected by GC-MS as shown in Table 1. When the commercial MoO_3 and ammonium heptamolybdrate ($(NH_4)_6Mo_7O_{24}$, AHM) catalysts were used, the yields of reduced products were only 22% and 39%, respectively (Table 1, entry 2 and 3). The related coupling products formed by reductive homo-coupling of allylic alcohols and benzyl alcohol have also been observed by Fristrup and coworkers in AHM-catalyzed DODH of biomass-derived polyols.[15] Based on previous works[15-16], the weak deoxygenation ability of these Mo catalysts might be associated with the inherent multinuclear property of Mo-center.

According to our previous research, nitrogen-donor ligand was capable of enriching the electron density of Mo and improving its activity in deoxygenation reaction.[17] Therefore, several organometallic oxo-molybdenum catalysts with various nitrogen-donor ligands, including 1,10-phenanthroline (Phen), 2,2'-bipyridine (Bipy), tetradentate Schiff base (Salen) and 8-hydroxyquinoline (8-HQ), were prepared (Figure S1-3 in supporting information) and used in the deoxygenation coupling reaction. Compared with $MoO_2(acac)_2$, a slightly higher yields of reduced products were obtained with Mo-Bipy and Mo-Salen (Table 1, entry 4-7). However, it still needed to selectively enhance the yield of bibenzyl product. Mo-8-HQ, as a more stable single-site Mo-based catalyst, exhibited the excellent catalytic performance in this reaction. The total yield of reduced products was 92% with 48% yield for 4,4'-dimethoxybibenzyl **1a** and 44% yield for 4-methylanisole **1b** as shown in Table 1, entry 8 and Figure S4-10. Methyltrioxorhenium (CH_3ReO_3) has been reported to be an efficient catalyst for deoxygenation of biomass-derived alcohols.[18] In this deoxygenation coupling process, CH_3ReO_3 could give 87% yield of reduced products, but lower selectivity of bibenzyl product (Table 1, entry 9) compared with Mo-8-HQ catalyst. Therefore, Mo-8-HQ catalyst was the best candidate for the selective production of bibenzyl compounds.

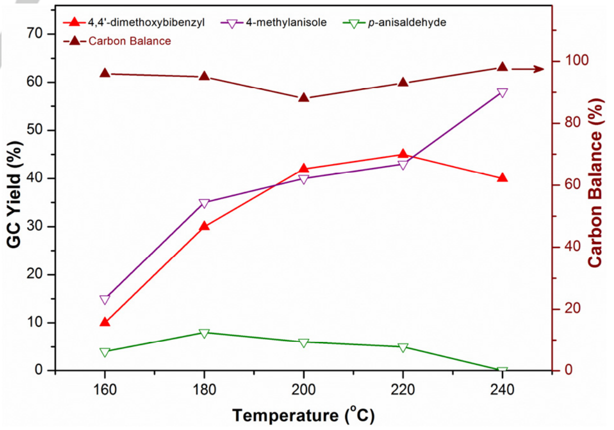


Figure 1. Reaction temperature profile of deoxygenation coupling of anisic alcohol catalyzed by Mo-8-HQ. Reaction conditions: 1 mmol anisic alcohol, 10 mol% Mo-8-HQ, 1.5 mmol PPh_3 and 20 mL1,4-dioxane were put into 50 mL Parr autoclave, then reacted at a certain temperature for 12 h under Ar.

As shown in Figure 1, a series of reaction temperatures under Mo-8-HQ catalyst were investigated. Along with the reaction temperature elevated from 180 to 240 °C, the yield of reduced products gradually increased with the decrease of the oxidized byproduct. When the reaction was run at 240 °C, the product

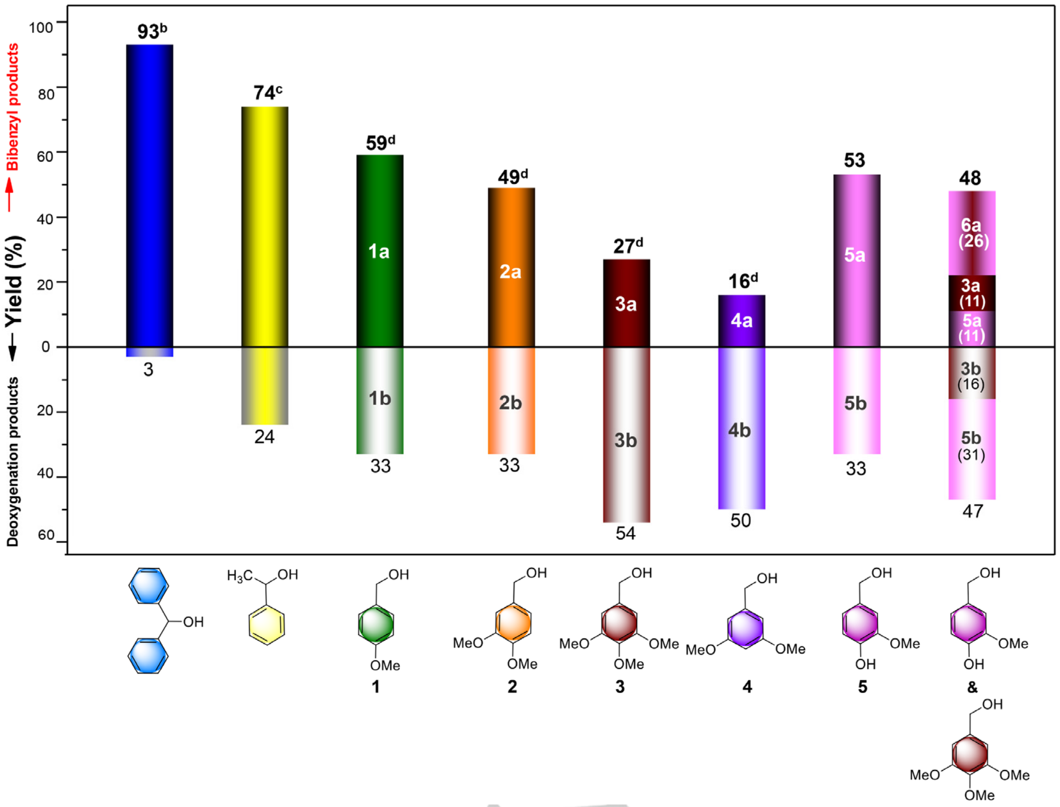


Figure 2. The distribution of reduced products from various benzylic alcohols. [a]

[a] Reaction conditions: 1 mmol alcohol substrate, 10 mol% Mo-8-HQ catalyst, 1.5 mmol triphenylphosphine and 20 mL1,4-dioxane were put into 50 mL Parr autoclave, then reacted at 220 °C for 8 h under Ar. [b] At 200 °C for 16 h. [c] At 200 °C for 14 h with adding 1 mmol 8-HQ. [d] 1 mmol 8-HQ was added under reaction condition.

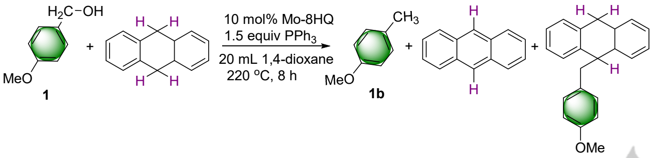
distribution was changed with the increase of 4-methylanisole **1b** and the decrease of 4,4'-dimethoxybibenzyl **1a**. It possibly resulted from the instable intermediate under high reaction temperature. It showed that suitable reaction temperature was important for the selectively formation of bibenzyl products. Depending on the further exploration, it was found that oxygen-containing reaction atmosphere could not significantly affect the product distribution (Table S1 in Supporting Information). It suggested that the Mo-based deoxygenation coupling reaction possessed strong tolerance and no need for the harsh anaerobic condition.

Based on the aforementioned condition screening results, the deoxygenation coupling procedure was also applicable to various benzyl alcohols, especially lignin-derived alcohols, with Mo-8-HQ as the catalyst. All of the results were summarized in Figure 2. The benzhydrol substrate was tested under 200 °C for 16 h. And nearly quantitatively converted into bibenzyl with four benzene rings, 1,1,2,2-tetraphenylethane (93%) (Figure 2, column 1). Interestingly, it was found that 1,1,2,2-tetraphenylethane product could be recrystallized with high purity from ice-ethanol after the solvent removed (MS and NMR analysis were shown in Figure S11-13), and the isolated yield was about 85%. α-Phenethyl alcohol was also completely converted into reduced products with a 74% selectivity of 2,3-diphenylbutane (Figure 2, column 2 and Figure S14-18) at 200 °C for 14 h. Moreover, these results were even better than the reported results with Re-based catalysts.[9a]

Because the 8-HQ ligand exhibited a special role in promoting Mo reactive activity, we tried to add 1 mmol 8-HQ into Mo-8-HQ catalyzed deoxygenation coupling reaction of anisic alcohol **1**. Interestingly, the addition of 8-HQ not only improved the yield of 4,4'-dimethoxybibenzyl **1a** (59%, in Figure 2, column 3), but also, changed the products distribution to a certain extent. Veratryl alcohol **2** with one *para*-methoxy (*p*-OMe) group and one *meta*-methoxy (*m*-OMe) group gave the corresponding reduced products in good yield (82%), in which 49% yield for 3,3',4,4'-tetramethoxybibenzyl **2a** (Figure 2, column 4, the GC and mass spectrum were shown in Figure S19-22) and 33% yield for 3,4-dimethoxytoluene **2b** were obtained. 3,4,5-Trimethoxybenzyl alcohol **3** with one *p*-OMe group and two *m*-OMe groups underwent the deoxygenation coupling reaction and afforded the natural bibenzyl product **3a** (Figure 2, column 5 and Figure S23-26), named brittonin A, in one step. 3,5-Dimethoxybenzyl alcohol **4** with two *m*-OMe groups could also produce the bibenzyl products 3,3',5,5'-tetramethoxybibenzyl **4a**, although the yield was low (Figure 2, column 6 and Figure S27-30). Obviously, these results revealed that the position of methoxy group in benzene ring affected the product distribution. It was speculated that the decreased yields of reduced products from **3** and **4** substrates were likely due to the relatively low reactivity of their corresponding reaction intermediates; this will be discussed in more details below.

In view of phenolic hydroxyl (Ar-OH) as a common functional group in lignin-derivatives, vanillyl alcohol **5** with a *p*-Ar-OH group and a *m*-OMe group was also used in the deoxygenation coupling reaction and afforded the reduced products in a good yield (86%, Figure 2, column 7 and Figure S31-34). Among these products, 53% yield was obtained for 4,4'-dihydroxy-3,3'-dimethoxybibenzyl **5a**, which, as a representative, was possibly a promising alternative for ubiquitous bisphenol A in similar resins.[13] Compared with veratryl alcohol **2**, *p*-Ar-OH in vanillyl alcohol was conductive to obtain bibenzyl products selectively.

Besides, the cross-coupling process with **3** and **5** obtained an excellent yield of reduced products and gave the mixture of homo-bibenzyls, **3a** (11%) and **5a** (11%), the hetero-bibenzyl **6a** (4-hydroxy-3,3'4'5'-tetramethoxybibenzyl, 26%, and the mass spectrum was shown in Figure S35) and deoxygenation products **3b** and **5b** (Figure 2, column 8). The hetero-bibenzyl **6a** as a type of natural bibenzyl medicine was named crepidatin. Some of our bibenzyl products, especially brittonin A and crepidatin, existed in natural *Dendrobium* plants and have been widely studied for its anticancer potential.[19] Certainly, it was considered that various functionalized bibenzyl chemicals could be synthesized through this deoxygenation coupling process with corresponding benzyl alcohols except these above-mentioned products.

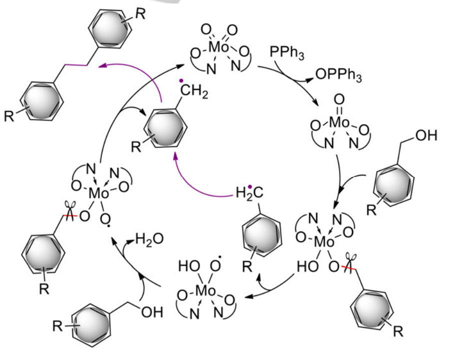


Scheme 2. Trapping Free C-radical Intermediate with 9,10-Dihydroanthracene.

The bibenzyl products were considered to be generated via homolytic decomposition of benzyl alcohol to form the free benzyl radicals process.[20] To further investigate the reaction pathway, we tried to trap the free C-radical intermediate with 9,10-dihydroanthracene (DHA), which was commonly used as H-atom donor.[21] As expected, there were no corresponding bibenzyl product, only 4-methylanisole **1b** and the DHA combined with benzyl radical product (Scheme 2, GC of the reaction mixture and mass spectrum of trapping free C-radical intermediate with DHA were shown in supporting information Figure S36 and S37). This result indicated that the benzyl radical was trapped successfully under the reaction condition and provided a mechanism evidence to understand Mo-catalyzed radical deoxygenation coupling process.

Furthermore, the results of Figure 2 illustrated that benzhydrol substrate could obtain excellent selectivity of bibenzyl product under the deoxygenation coupling reaction. The α-phenethyl alcohol substrate was also transformed into bibenzyl products with a high yield. These could be explained with the strong stability of the free benzyl 2°C-radical intermediates. Besides, *p*-Ar-OH and *p*-OMe groups in benzene ring of benzyl alcohol substrates were able to promote the yields of bibenzyl products. It might be due to the factor that these function groups could generate a stronger conjugated structure and stabilize the corresponding benzyl radicals even under 220 °C. However, the substrates with *m*-OMe group had low activity to produce bibenzyl in this process. The reason was probably that the *meta*-substituent could destabilize the intermediate benzyl radical.[22] Therefore, the stability of benzyl radical intermediate was the key point to efficient synthesis of the bibenzyl products. The type and position of the substituted groups in benzene ring significantly influenced the stability of conjugation radical intermediate. Experimental results showed that *p*-OMe and *p*-Ar-OH groups could facilitate the selectively gaining of bibenzyl products.

Based on the previous works on deoxygenation coupling reactions[9, 23], a rational catalytic cycle for the Mo-catalyzed deoxygenation coupling reaction was speculated and depicted in Scheme 3. At first, the Mo^{VI} catalyst was reduced by triphenylphosphine (PPh_3) to form Mo^{IV}. The PPh_3 reductant as an O-scavenger could avoid excessive consumption of benzyl alcohol itself as the reductant and suppress the undesired byproducts. After reaction, this reductant was converted to triphenylphosphine oxide ($OPPh_3$), which could be reduced and regenerated to PPh_3.[24] Then, Mo^{IV} and benzyl alcohol molecule were combined to form Mo-alkoxide species. Subsequently, the as-formed reduced Mo-alkoxide species were underwent in-situ C-O cleavage to benzyl radical intermediate and Mo^{VI}. Finally, two benzyl radical intermediates were coupled with each other to generate bibenzyl product. It was worthy noted that the benzyl radical intermediate with stable structure was the key factor for the selectively formation of bibenzyl products.



Scheme 3. Proposed reaction pathway of Mo-Catalyzed Deoxygenation Coupling Reaction of Benzyl Alcohol.

In summary, we took advantage of lignin-derived alcohols as the renewable resources to produce functionalized bibenzyl chemicals. It was implemented via a Mo-catalyzed deoxygenation coupling procedure. The well-designed H-donor experiment demonstrated that the benzyl carbon-radical might be the intermediate for bibenzyl products. It was also found that the methoxy and phenolic hydroxyl groups in benzene ring of lignin-derivates obviously affected the products distribution by influencing the stability of corresponding radical. This research will provide a new sustainable way to transform abundance biomass resources into value-added functionalized aromatic chemicals, especially in medicine and polymer industry.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Biomass • Lignin-derived alcohols • Molybdenum catalyst • Deoxygenation • C-C coupling

[1] a) G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* **2005**, *308*, 1446-1450; b) W. Deng, Y. Wang, S. Zhang, K. M. Gupta, M. J. Hülsey, H. Asakura, L. Liu, Y. Han, E. M. Karp, G. T. Beckham, P. J. Dyson, J. Jiang, T. Tanaka, Y. Wang, N. Yan, *Proc. Natl. Acad. Sci. USA* **2018**, *115*, 5093-5098; c) W. Luo, M. Sankar, A. M. Beale, Q. He, C. J. Kiely, P. C. A. Bruijnincx, B. M. Weckhuysen, *Nat. Commun.* **2015**, *6*, 6540; d) H. Li, S. Saravanamurugan, S. Yang, A. Riisager, *Green Chem.* **2016**, *18*, 726-734; e) L. Dong, L. Lin, X. Han, X. Si, X. Liu, Y. Guo, F. Lu, S. Rudić, S. F. Parker, S. Yang, Y. Wang, *Chem* **2019**, *5*, 1521-1536.

[2] a) A. M. Ruppert, K. Weinberg, R. Palkovits, *Angew. Chem. Int. Ed.* **2012**, *51*, 2564-2601; *Angew. Chem.* **2012**, *124*, 2614–2654; b) R. Lu, F. Lu, X. Si, H. Jiang, Q. Huang, W. Yu, X. Kong, J. Xu, *ChemSusChem* **2018**, *11*, 1621-1627; c) Y. Seo, J. M. Lowe, M. R. Gagné, *ACS Catal.* **2019**, *9*, 6648-6652.

[3] V. Zacharopoulou, E. S. Vasiliadou, A. A. Lemonidou, *ChemSusChem* **2018**, *11*, 264-275.

[4] M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B. C. Gates, M. R. Rahimpour, *Energy Environ. Sci.* **2014**, *7*, 103-129.

[5] a) R. T. Larson, A. Samant, J. Chen, W. Lee, M. A. Bohn, D. M. Ohlmann, S. J. Zuend, F. D. Toste, *J. Am. Chem. Soc.* **2017**, *139*, 14001-14004; b) M. Shiramizu, F. D. Toste, *Angew. Chem. Int. Ed.* **2012**, *51*, 8082-8086; *Angew. Chem.* **2012**, *124*, 8206–8210.

[6] J. R. Dethlefsen, D. Lupp, B. C. Oh, P. Fristrup, *ChemSusChem* **2014**, *7*, 425-428.

[7] T. V. Gopaladasu, K. M. Nicholas, *ACS Catal.* **2016**, *6*, 1901-1904.

[8] a) M. Shiramizu, F. D. Toste, *Angew. Chem. Int. Ed.* **2013**, *52*, 12905-12909; *Angew. Chem.* **2013**, *125*, 13143–13147; b) A. R. Petersen, P. Fristrup, *Chem. Eur. J.* **2017**, *23*, 10235-10243.

[9] a) G. R. Kasner, C. Boucher-Jacobs, J. Michael McClain, K. M. Nicholas, *Chem. Commun.* **2016**, *52*, 7257-7260; b) E. Steffensmeier, K. M. Nicholas, *Chem. Commun.* **2018**, *54*, 790-793.

[10] E. E. A. k. van Tamelen, B.; Sharpless, K. B. , *J. Am. Chem. Soc.* **1969**, *91*, 1552-1554.

[11] T. Nishino, Y. Nishiyama, N. Sonoda, *Tetrahedron Lett.* **2002**, *43*, 3689-3691.

[12] a) A. S. Trita, L. C. Over, J. Pollini, S. Baader, S. Riegsinger, M. A. R. Meier, L. J. Gooßen, *Green Chem.* **2017**, *19*, 3051-3060; b) I. Delidovich, P. J. C. Hausoul, L. Deng, R. Pfützenreuter, M. Rose, R. Palkovits, *Chem. Rev.* **2016**, *116*, 1540-1599.

[13] B. G. Harvey, A. J. Guenthner, H. A. Meylemans, S. R. L. Haines, K. R. Lamison, T. J. Groshens, L. R. Cambrea, M. C. Davis, W. W. Lai, *Green Chem.* **2015**, *17*, 1249-1258.

[14] a) D. C. Harrowven, S. L. Kostiuk, *Nat. Prod. Rep.* **2012**, *29*, 223-242; b) J. A. Baur, D. A. Sinclair, *Nat. Rev. Drug Discovery* **2006**, *5*, 493-506; c) Y.-S. Han, P. K. Quashie, T. Mesplède, H. Xu, Y. Quan, W. Jaeger, T. Szekeres, M. A. Wainberg, *J. Med. Virol.* **2015**, *87*, 2054-2060.

[15] J. R. Dethlefsen, D. Lupp, A. Teshome, L. B. Nielsen, P. Fristrup, *ACS Catal.* **2015**, *5*, 3638-3647.

[16] M. Stalpaert, D. De Vos, *ACS Sustainable Chem. Eng.* **2018**, *6*, 12197-12204.

[17] H. Jiang, R. Lu, X. Si, X. Luo, J. Xu, F. Lu, *ChemCatChem* **2019**, *11*, 4291-4296.

[18] X. Li, D. Wu, T. Lu, G. Yi, H. Su, Y. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4200-4204; *Angew. Chem.* **2014**, *126*, 4284–4288.

[19] a) P. L. Majumder, S. Chatterjee, *Phytochemistry* **1989**, *28*, 1986-1988; b) N. Petpiroon, N. Bhummaphan, S. Tungsukruthai, T. Pinkhien, A. Maiuthed, B. Sritularak, P. Chanvorachote, *Phytomedicine* **2019**, *58*, 152888.

[20] a) C. Boucher-Jacobs, P. Liu, K. M. Nicholas, *Organometallics* **2018**, *37*, 2468-2480; b) E. Steffensmeier, M. T. Swann, K. M. Nicholas, *Inorg. Chem.* **2019**, *58*, 844-854.

[21] Y. Lee, F. T. Sloane, G. Blondin, K. A. Abboud, R. García-Serres, L. J. Murray, *Angew. Chem. Int. Ed.* **2015**, *54*, 1499-1503; *Angew. Chem.* **2015**, *127*, 1519-1523..

[22] a) S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.* **2017**, *8*, 405-410; b) T. H. Fisher, S. M. Dershem, M. L. Prewitt, *J. Org. Chem.* **1990**, *55*, 1040-1043.

[23] D. B. Larsen, A. R. Petersen, J. R. Dethlefsen, A. Teshome, P. Fristrup, *Chem. Eur. J.* **2016**, *22*, 16621-16631.

[24] Y. Li, L.-Q. Lu, S. Das, S. Pisiewicz, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2012**, *134*, 18325-18329.

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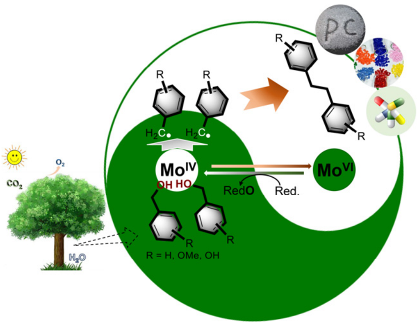

This study opens a new sight to transform abundant biomass resources into important functionalized aromatic chemicals via a concise Mo-catalyzed deoxygenation coupling procedure.