ELECTRONIC SUPPLEMENTARY INFORMATION

Transition Metal- and Photoredox-catalyzed Valorization of Lignin Subunits

Amrita Das and Burkhard König

Address: Department of Chemistry and Pharmacy, Institute of Organic Chemistry, University of Regensburg,
Universitätsstraße 31, 93053 Regensburg, Germany

Email: Burkhard König* - Burkhard.Koenig@chemie.uni-regensburg.de

* Corresponding author

Table of contents

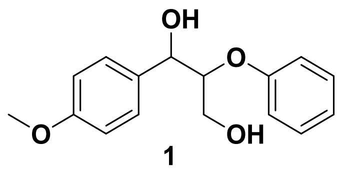
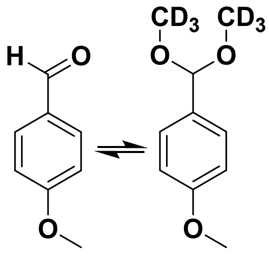
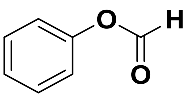
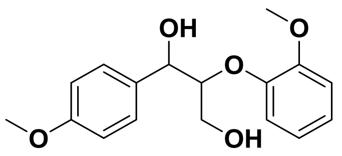
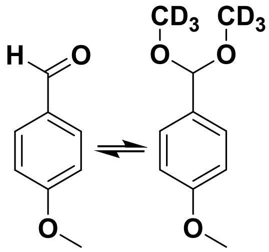
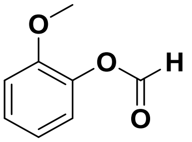
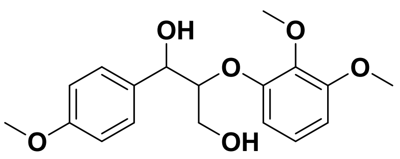
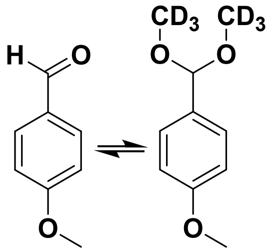
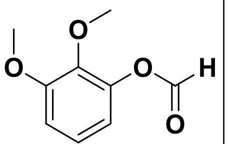
General Information

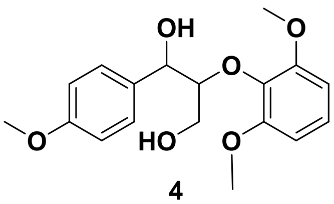
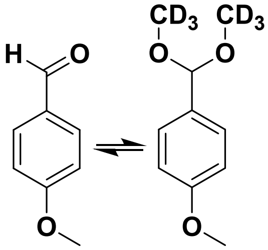
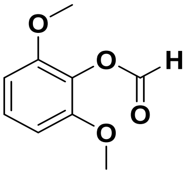
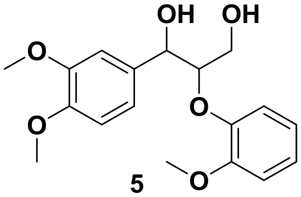
The lignin model substrates were synthesized according to the literature procedures.[1-3] The photocatalyst riboflavin tetraacetate (RFTA) was synthesized according to the literature procedure.[4] Thin-layer chromatography was performed using silica gel plates 60 F254: Visualization was accomplished with short wavelength UV light (254 nm). Standard flash chromatography was performed on an Isolera™ Spektra Systems automated with high performance flash purification system using silica gel of particle size 40−63 µm or a reverse column (specification: Biotage SNAP KP-C18-HS-12g). Preparative high-pressure liquid chromatography (HPLC) was performed using a C18 reverse column and water/acetonitrile mixtures with a UV detector. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance spectrometers (300 MHz and 75 MHz or 400 MHz and 101 MHz) in $CDCl_3$ and MeOH-d_4 solution with internal solvent signal as reference (7.26 and 77.26, 3.31, 4.78 and 49.15 respectively). Proton NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, hept = heptet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, qd = quartet of doublets, m = multiplet, br. s. = broad singlet), coupling constants (Hz) and numbers of protons. Data for ^{13}C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. High resolution mass spectra (HRMS) were obtained from the central analytic mass spectrometry facilities of the Faculty of Chemistry and Pharmacy, Regensburg University and are reported according to the IUPAC recommendations 2013. Quantification of oxidation products was performed by ^{1}H and ^{13}C NMR analysis using internal standards. Electrochemical studies were carried out under argon atmosphere. The measurements were performed in acetonitrile (MeCN) containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate using ferrocene/ferrocenium (Fc/Fc^+) as an internal reference. A glassy carbon electrode (working electrode), platinum wire (counter electrode), and silver wire (quasi-reference electrode) were employed. Spectroelectrochemical studies were carried out in an optically transparent thin layer electrochemical cell (OTTLE). Photooxidation reactions were performed with 455 nm LEDs (OSRAM Oslon SSL 80 royal-blue LEDs (λ = 455 nm (± 15 nm), 3.5 V, 700 mA.

Photocatalytic oxidation of the lignin model compounds

Table 1:

Benzylic oxidation and C_α-C_β bond cleavage of model compounds (reaction in CD_3OD):

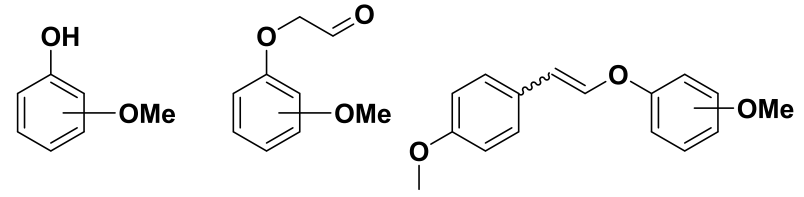
Substrate	Products[a]		Recovered starting material
 **1**	 **1a, 65%**	 **1b, 15%**	**54%**
 **2**	 **2a, 29%**	 **2b, 4%**	**35%**
 **3**	 **3a, 13%**	 **3b, 1%**	**51%**

 **4**	 **4a, 26%**	 **4b, 6%**	**26%**
 **5**	Very difficult to predict the NMR. Degradation of the starting material is observed.		

The reactions were performed with 0.1 mmol of substrate, CD_3OD (1 mL), 10 mol% RFTA under blue light irradiation (455 nm) in air for 8 hours.

[a]the yields were calculated by **^{1}H NMR** (300 MHz) using 1,3,5-trimethoxybenzene as an internal standard.

The other fragments obtained from the oxidation of compounds **1-4** were confirmed by GC-MS analysis. However, we were not able to quantify these fragments (**Figure 1**).

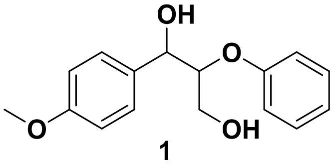
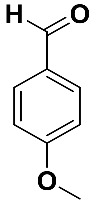
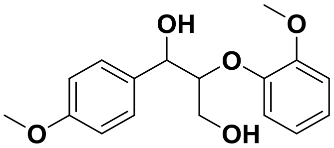
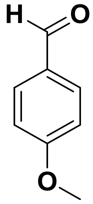
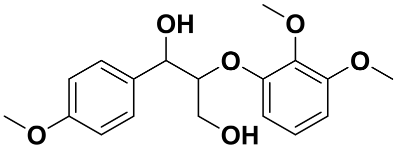
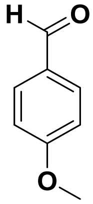
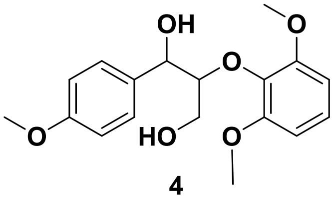
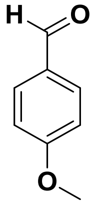


1c, 2c, 3c, 4c **1d, 2d, 3d, 4d** **1e, 2e, 3e, 4e**

Figure 1: Fragments obtained from oxidation of compounds **1-4**.

Table 2:

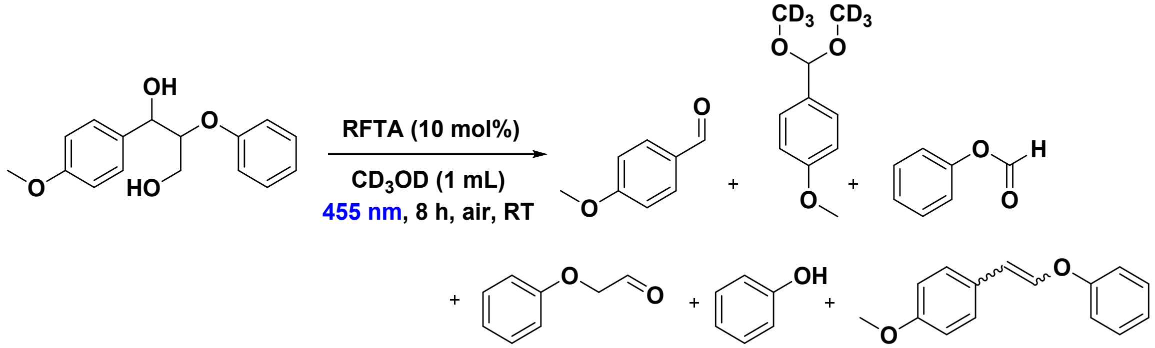
Benzylic oxidation of model substrates in CH_3CN: H_2O (1:1):

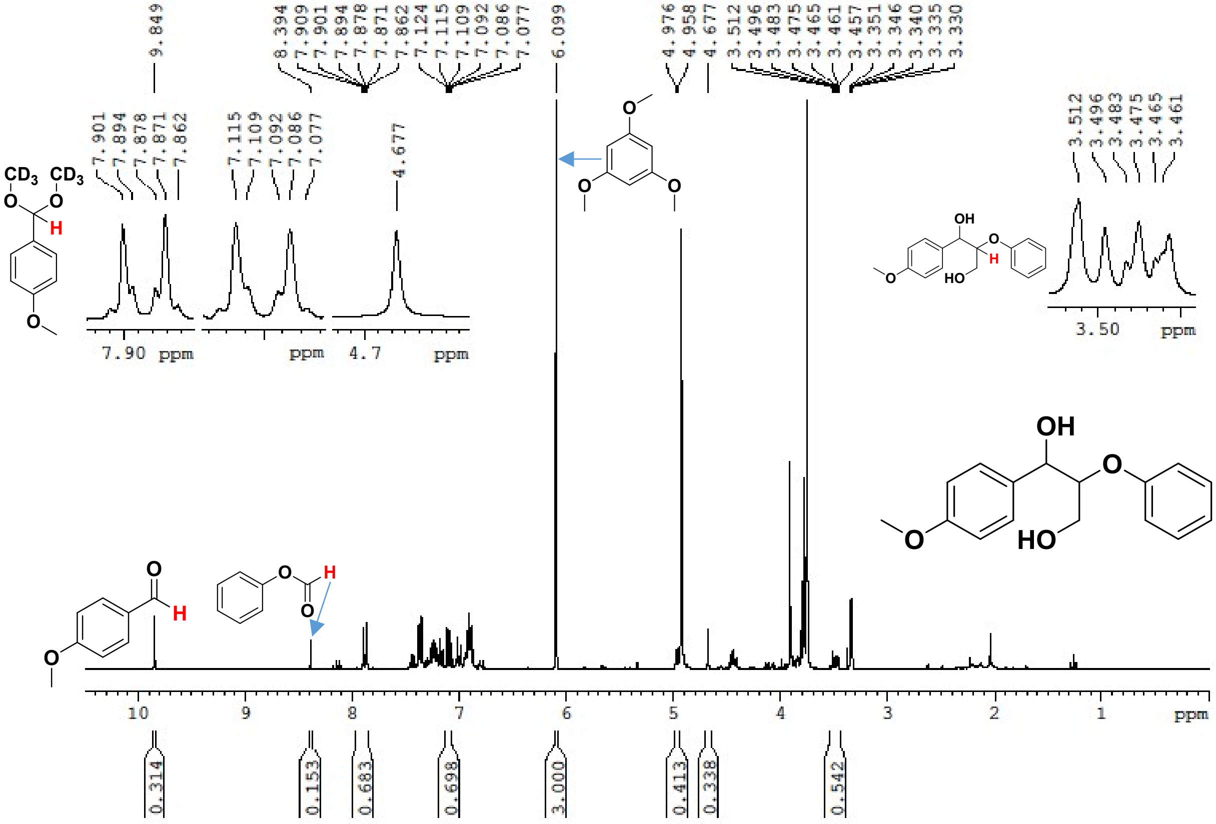
Substrate	Product	Yield[b] (%)	Recovered starting material (%)
 **1**		**55**	**29**
 **2**		**40**	**30**
 **3**		**30**	**57**
 **4**		**15**	**31**

The reactions were performed with 0.1 mmol of substrate, CH_3CN: H_2O (1:1) (1 mL), 10 mol% RFTA under blue light irradiation (455 nm) in air for 18 hours.

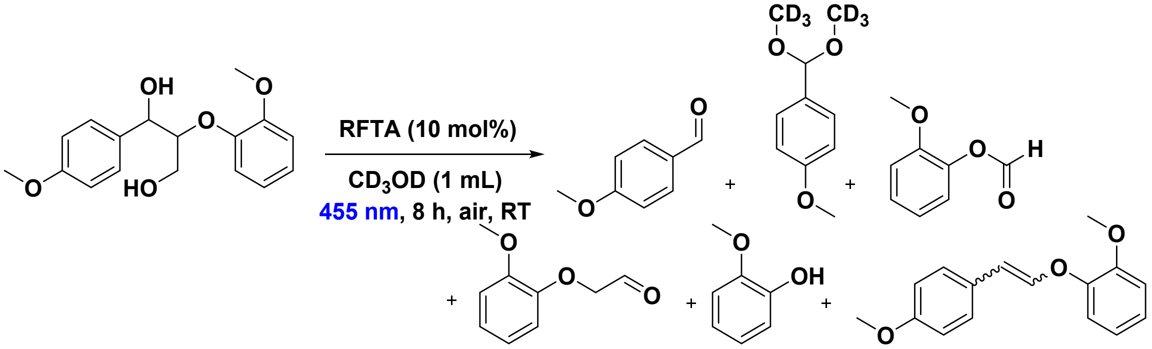
[b] yields were determined by column chromatography over silica gel.

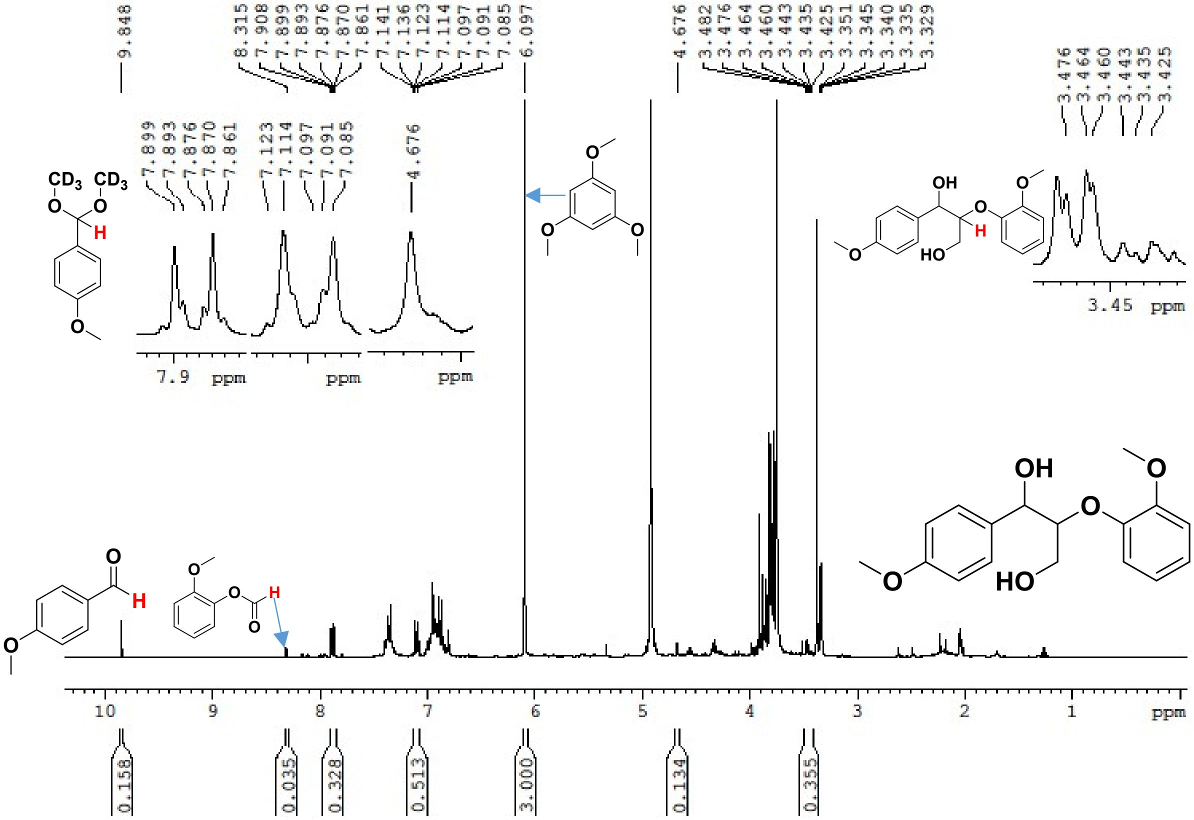
Photocatalytic conversion of 1-(4-methoxyphenyl)-2-phenoxypropane-1,3-diol (1) to different fragments



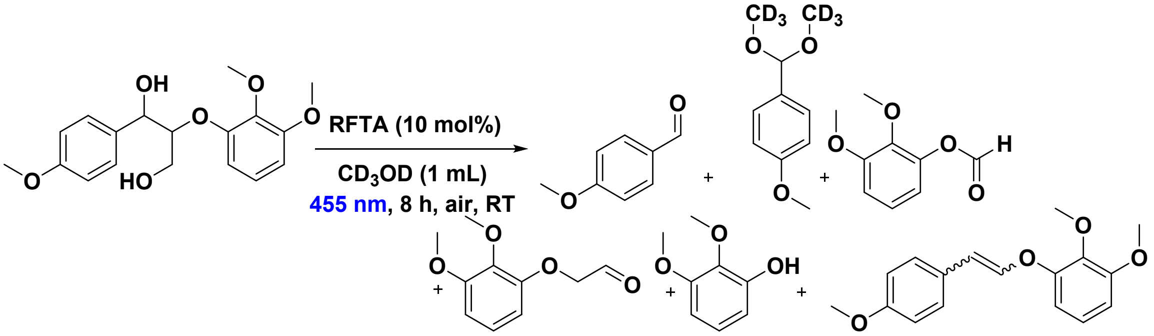


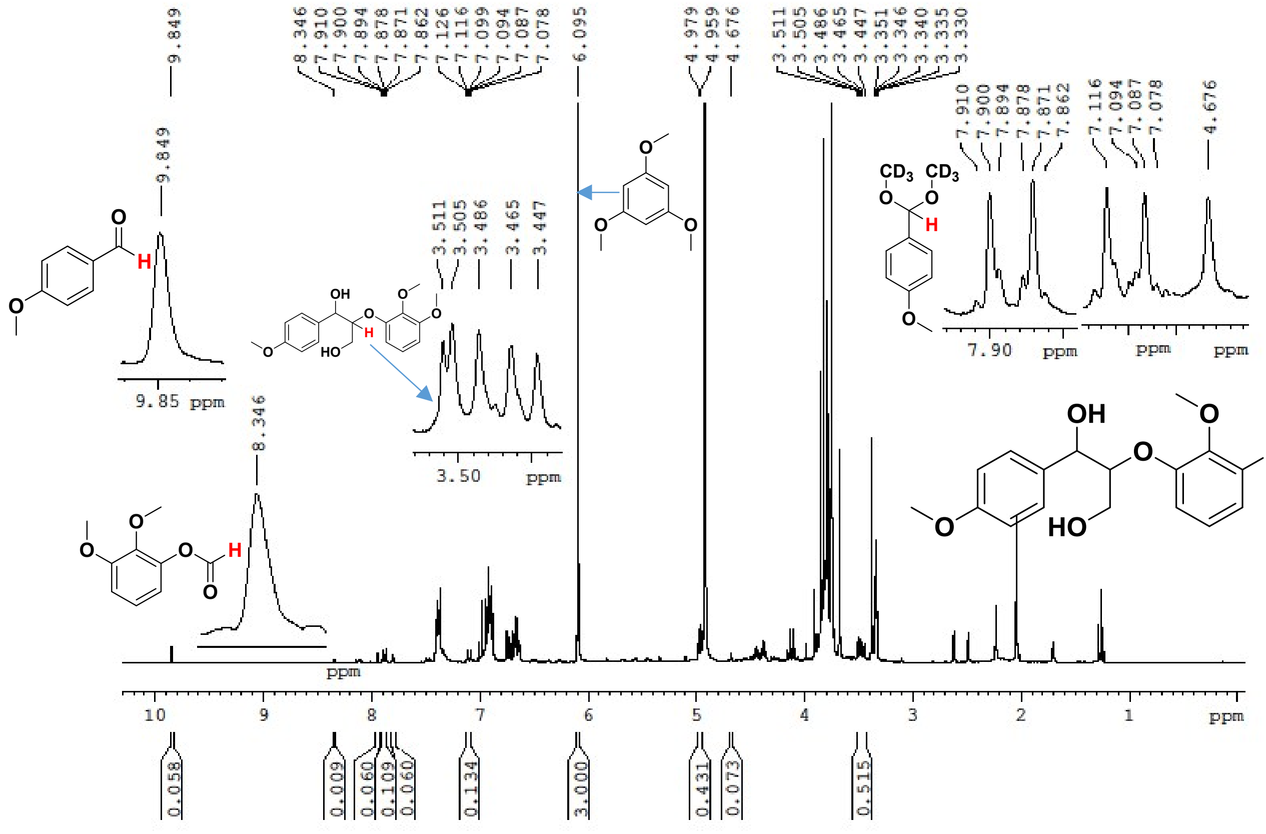
Photocatalytic conversion of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (2) to different fragments



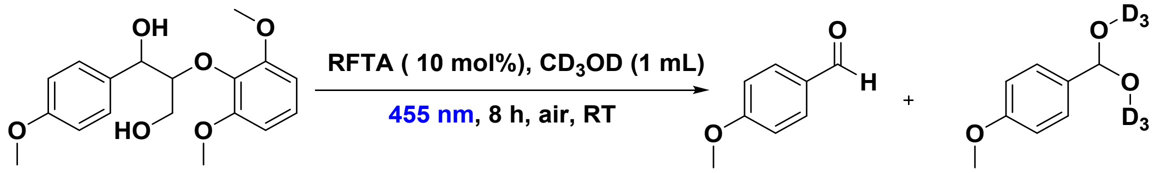


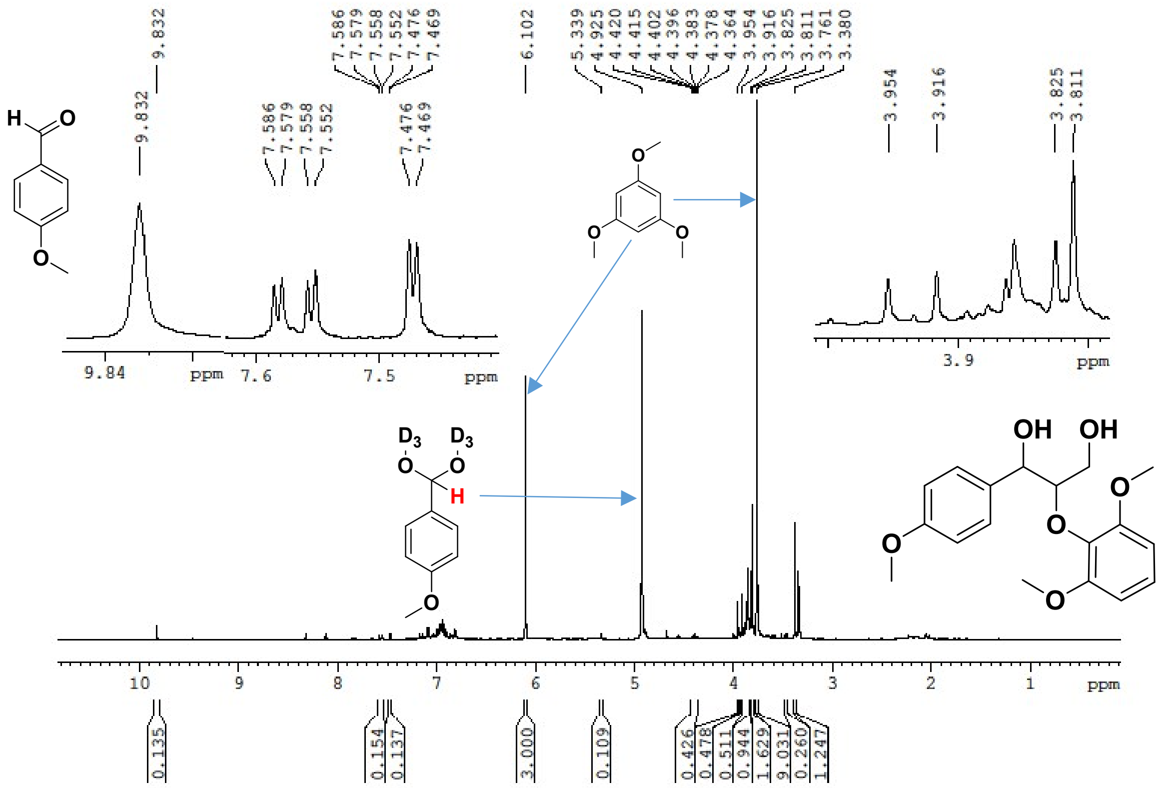
Photocatalytic conversion of 2-(2,3-dimethoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (3) to different fragments





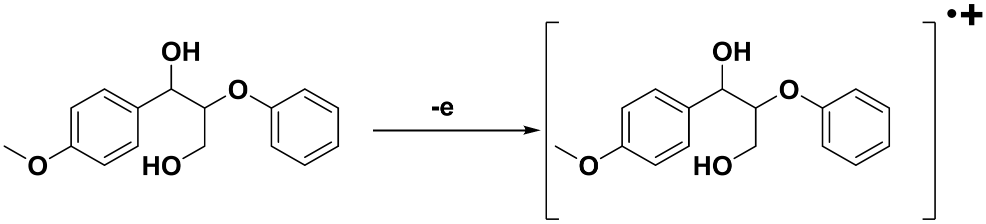
Photocatalytic conversion of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (4) to 4-methoxybenzaldehyde



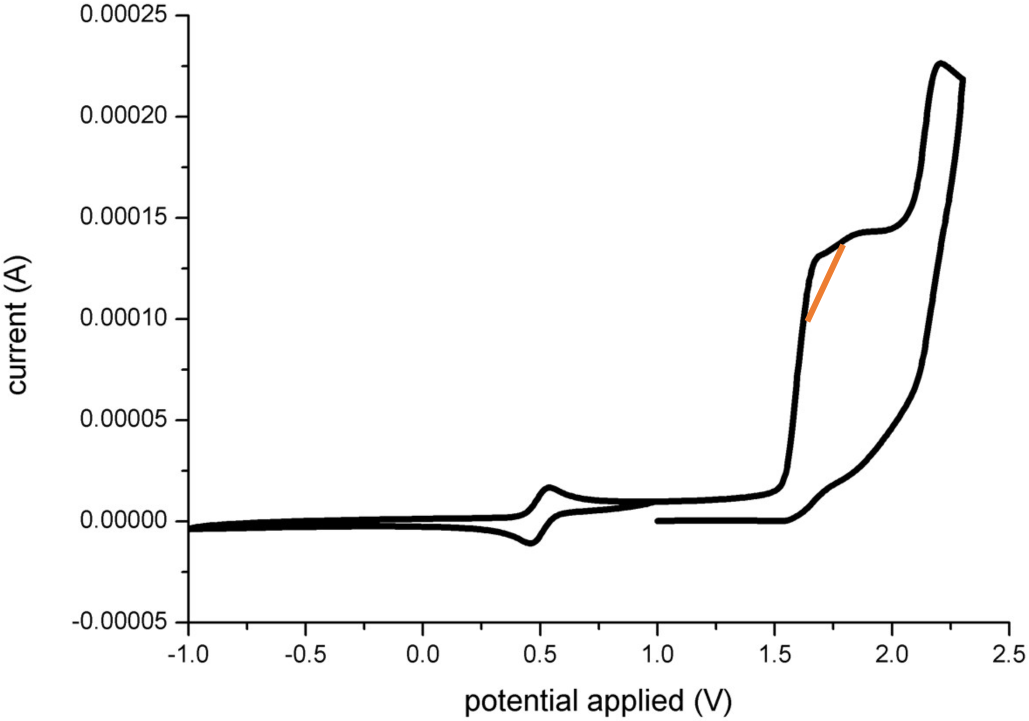


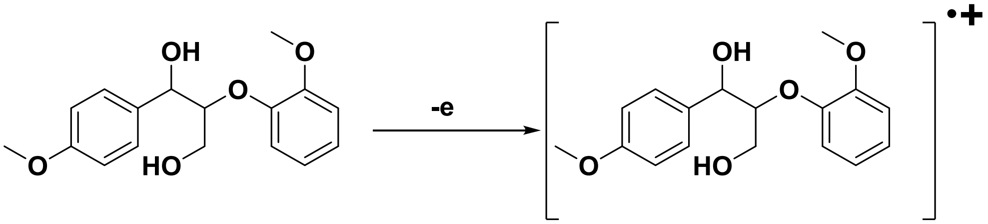
26% of the aldehyde and the corresponding acetal in total are in equilibrium with each other. Rest is the starting material.

Cyclic voltammetry measurements of compounds 1-5

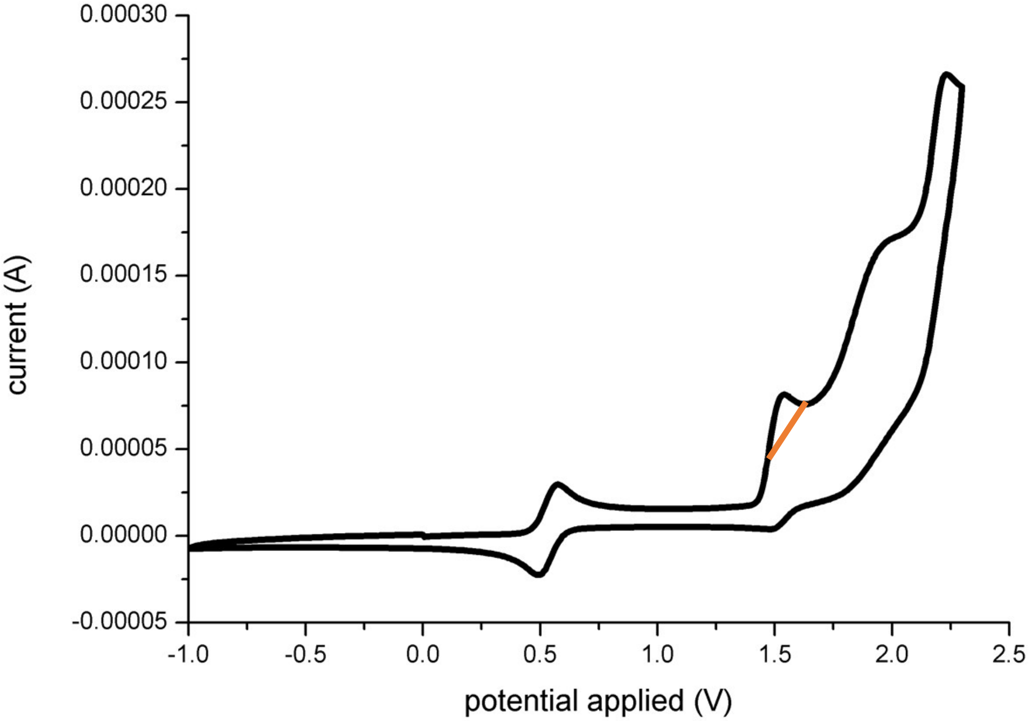


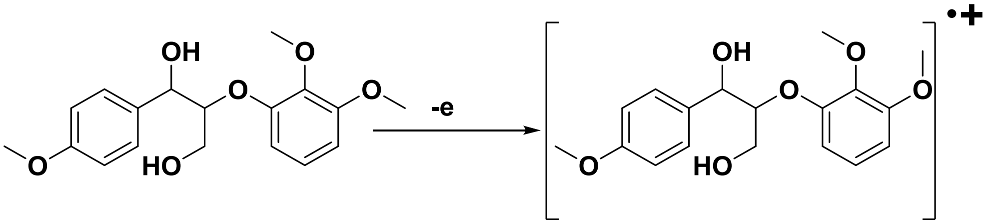
E^0 = 1.56 V *vs* SCE



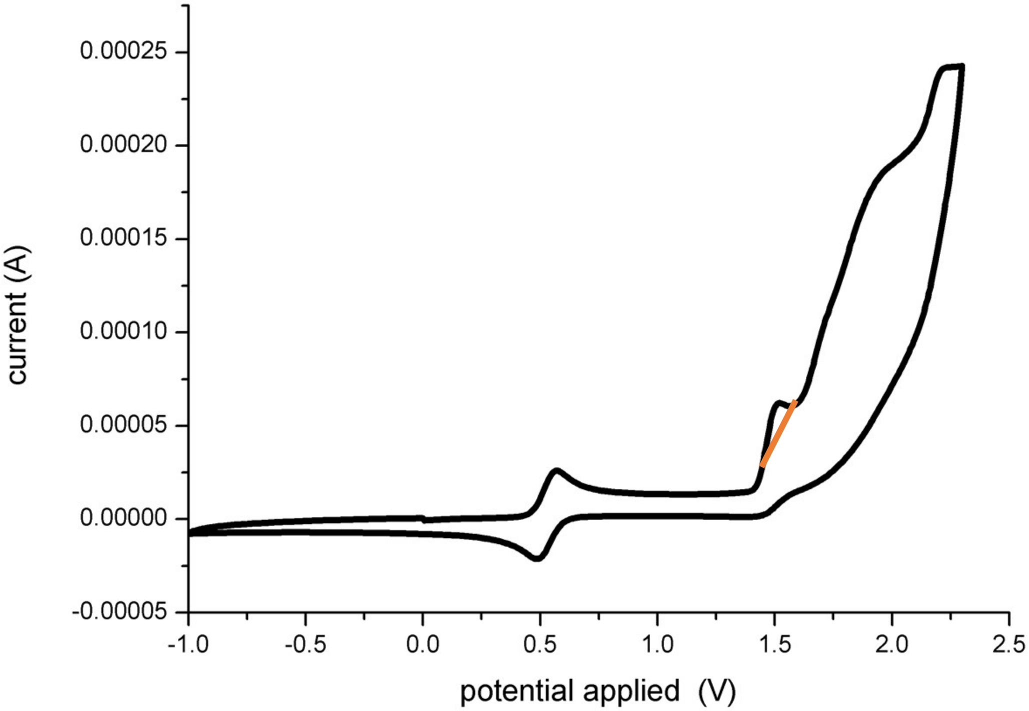


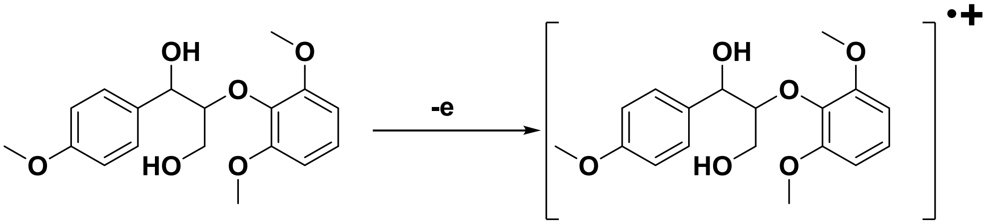
E^0 = 1.37 V *vs* SCE



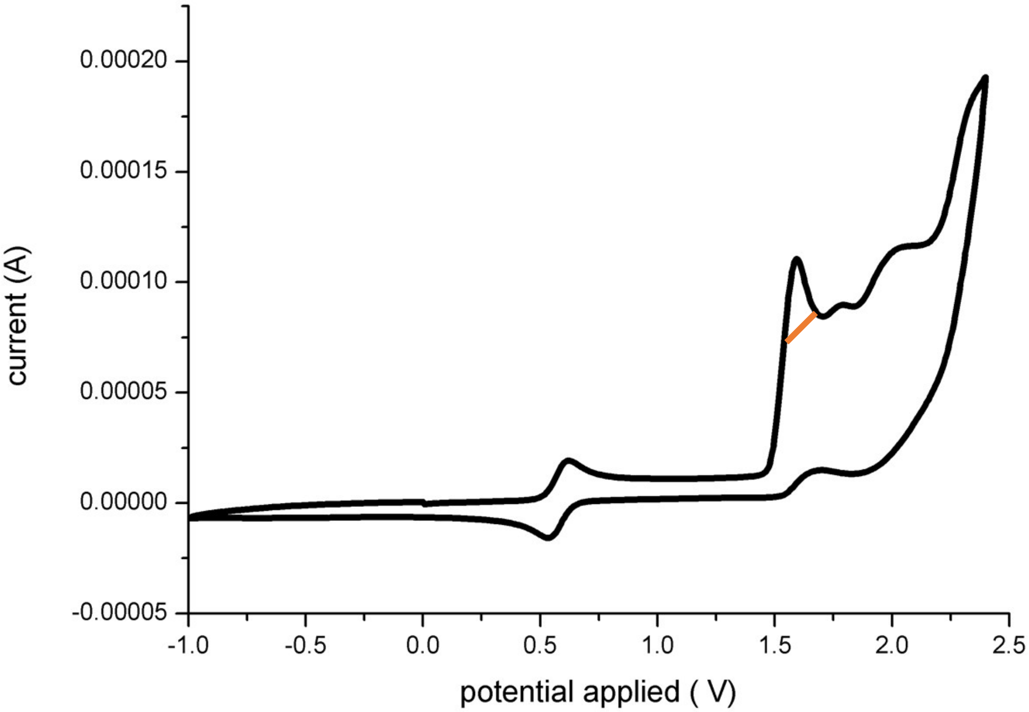


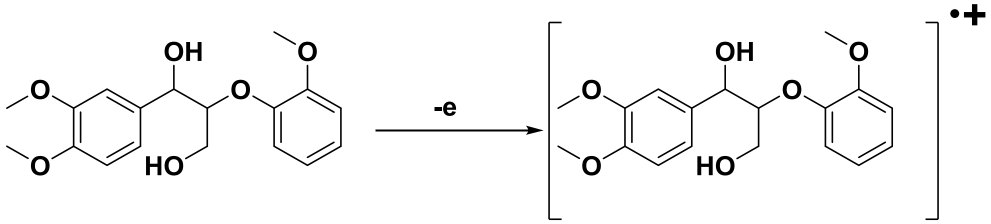
E^0 = 1.39 V *vs* SCE




OH
O
HO
-e
•+

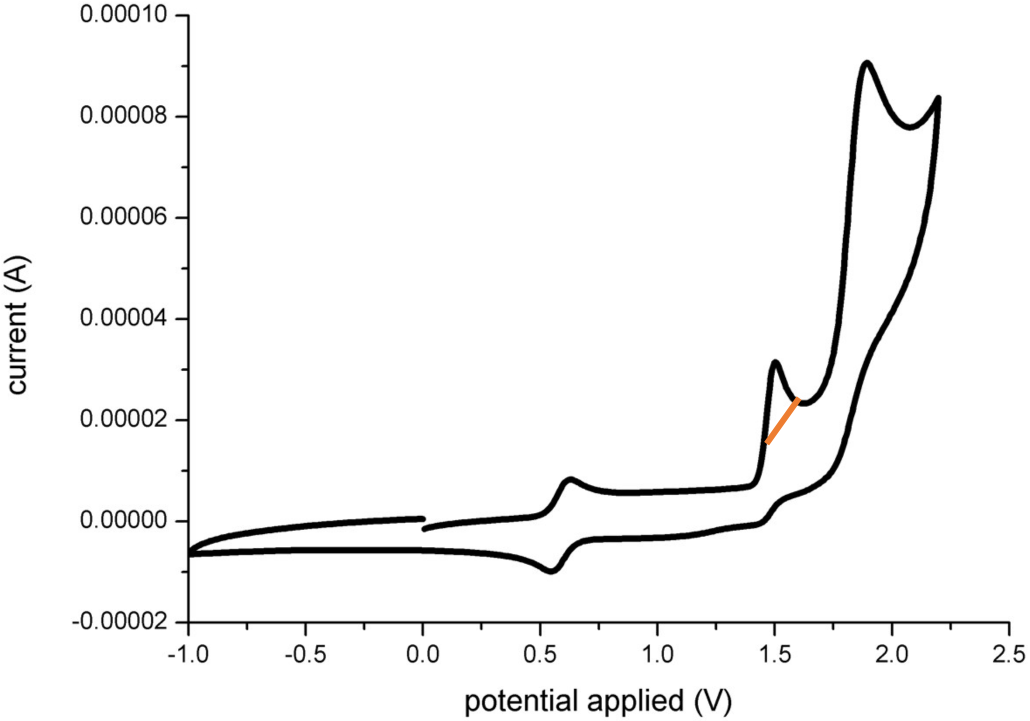
E^0 = 1.4 V *vs* SCE


current (A)
0.00020
0.00015
0.00010
0.00005
0.00000
-0.00005
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
potential applied (V)



-e

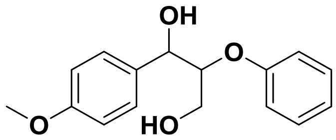
E^0 = 1.3 V *vs* SCE



current (A)
0.00010
0.00008
0.00006
0.00004
0.00002
0.00000
-0.00002
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
potential applied (V)

Synthesis of the lignin model compounds

Synthesis of 1-(4-methoxyphenyl)-2-phenoxypropane-1,3-diol (1)[1]

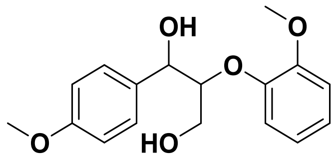


The compound synthesized according to the literature procedure. The compound was obtained as a 3:1 mixture of diasteromers as a white sticky solid.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28-7.13 (m, 5.6H), 6.91-6.76 (m, 6.6H), 4.93 (d, *J* = 4 Hz, 0.3H), 4.89 (d, *J* = 5.2 Hz, 1H), 4.31-4.27 (m, 1.3 H), 3.83 (dd, *J* = 12 Hz, 4.4 Hz, 0.3H), 3.75 (dd, *J* = 12 Hz, 4 Hz, 0.3H), 3.85 (s, 3.3H), 3.84 (s, 1H), 3.44 (dd, *J* = 12.4Hz, 4 Hz, 1.6 Hz).

^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 159.7, 159.5, 158.2, 157.8, 132.6, 131.8, 129.9, 129.8, 128.3, 127.6, 122.2, 122.0, 116.8, 116.7, 114.2, 114.1, 83.3, 82.0, 74.0, 73.8, 61.5, 61.2, 55.5.

Synthesis of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (2)[2]

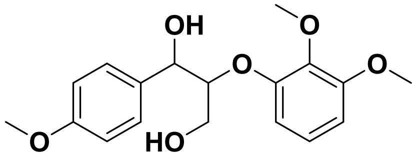


The compound is synthesized according to the literature procedure. The compound was obtained as a 1.68:1 mixture of diasteromers as a sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37-7.33 (m, 1H), 7.32-7.28 (m, 2H), 7.13-7.10 (m, 0.5H), 7.07-7.01 (m, 1.5H), 6.94-6.85 (m, 7.2H), 4.99-4.97 (m, 1.5H), 4.16-4.12 (m, 1H), 4.03 (q, *J* = 3.6 Hz, 0.6H), 3.91 (d, *J* = 5.8 Hz, 0.5H), 3.88 (s, 1.8H), 3.87 (s, 0.3H), 3.85 (s, 3H), 3.79-3.78 (m, 4.5H), 3.65 (dd, *J* = 12.1 Hz, 3.3 Hz, 1H), 3.60 (dd, *J* = 12.4 Hz, 3.3 Hz, 0.6H), 3.44 (dd, *J* = 12.5 Hz, 4 Hz, 0.6H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 159.6, 159.2, 151.7, 151.4, 147.8, 147.1, 132.3, 131.9, 128.5, 127.5, 124.3, 124.2, 121.8, 121.7, 121.1, 121.0, 114.1, 114.0, 112.3, 112.3, 89.6, 87.4, 73.8, 72.8, 61.1, 60.0, 56.0, 55.4.

Synthesis of 2-(2,3-dimethoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (3)[3]



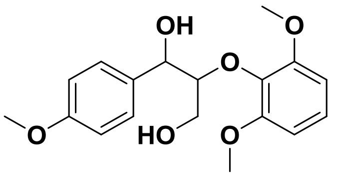
The compound is synthesized according to the literature procedure. The compound was obtained as a 1.58:1 mixture of diasteromers as a sticky oil.

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.25-7.15 (m, 3.5H), 6.90-6.47 (m, 8.3H), 5.18 (bs, 0.6H), 4.89-4.87 (m, 1.5H), 4.09 (q, *J* = 4.8 Hz, 0.6H), 4.03-3.99 (m, 0.4H), 3.95 (q, *J* = 3.8 Hz, 1H), 3.82-3.67 (m, 15.3H), 3.57 (dd, *J* = 12.2 Hz, 3.4 Hz, 0.7H), 3.46 (dd, *J* = 12.5 Hz, 3.2 Hz, 1H), 3.32 (dd, *J* = 12.5 Hz, 4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 159.6, 159.2, 153.8, 153.8, 152.3, 151.6, 141.0, 132.6, 132.0, 128.7, 128.4, 127.5, 124.6, 124.4, 114.1, 113.9, 113.2, 112.6, 107.6, 107.3, 88.9, 86.0, 73.9, 73.2, 61.7, 61.6, 61.1, 61.0, 56.1, 55.4.

HRMS [M+NH$_4$]+ $C_{18}H_{22}O_6$ calculated 352.1755 found 352.1761.

Synthesis of 2-(2,6-dimethoxyphenoxy)-1-(4-methoxyphenyl)propane-1,3-diol (4).[3]



The compound is synthesized according to the literature procedure. The compound was obtained as a 1:0.5 mixture of diasteromers as a sticky oil.

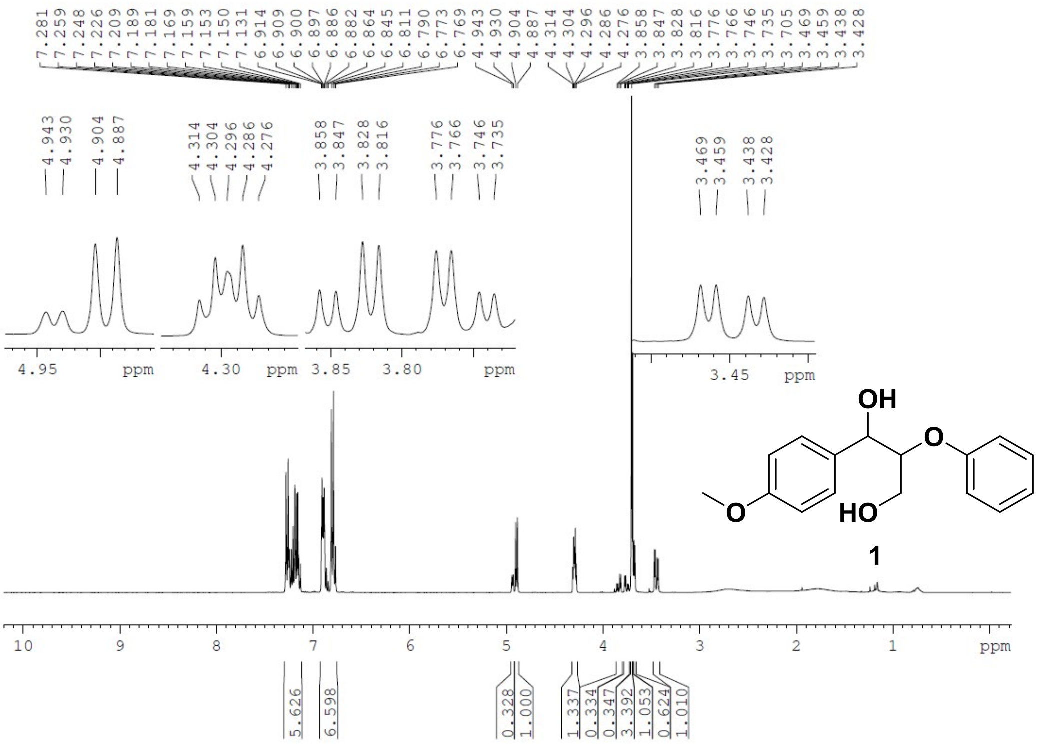
^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.40-7.36 (m, 2H), 7.28-7.25 (m, 0.4H), 7.08-7.03 (m, 1.4H), 6.89-6.85 (m, 3H), 6.64-6.62 (m, 3H), 5.07 (d, *J* = 8.8 Hz, 1H), 5.02 (d, *J* = 3.6 Hz, 0.5H), 4.15 (q, *J* = 3 Hz, 0.5H), 4.12-4.08 (m, 0.3H), 3.92-3.89 (m, 10H), 3.87 (s, 3H), 3.79 (s, 2.7H), 3.78 (s, 1.7H), 3.55 (dd, *J* = 12.2 Hz, 2.7 Hz, 1H), 3.49 (dd, *J* = 12 Hz, 2.7 Hz, 0.6H), 3.29-3.26 (m, 1.2H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 159.5, 159.0, 153.7, 153.4, 135.5, 135.1, 132.4, 131.7, 128.7, 127.2, 124.6, 124.6, 114.0, 113.9, 105.5, 89.2, 87.1, 73.9, 72.6, 60.7, 60.6, 56.3, 55.4.

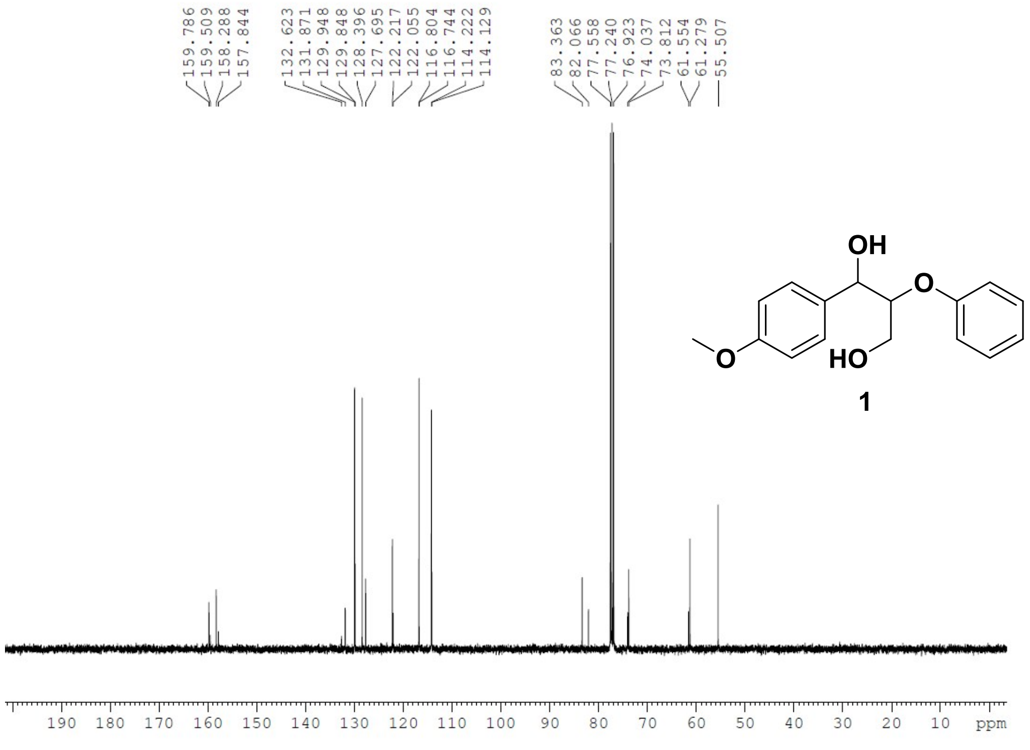
HRMS [M+Na]+ $C_{18}H_{22}O_6$ calculated 357.1309 found 357.1311.

^{1}H and ^{13}C spectra of synthesized compounds

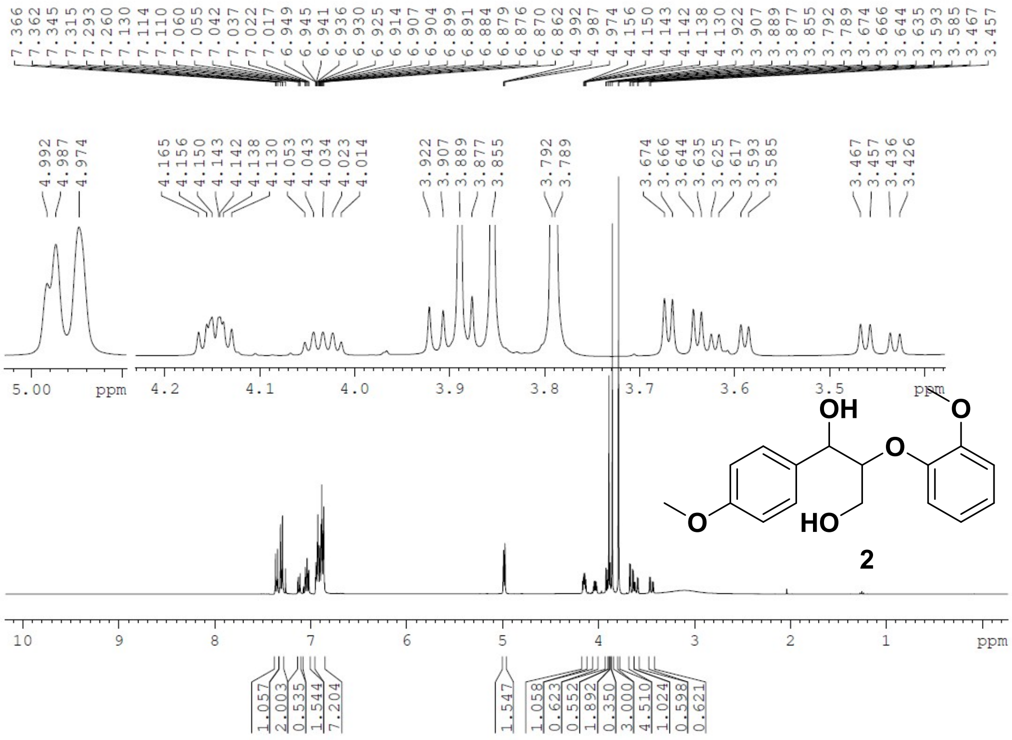
^{1}H spectra of compound 1 ($CDCl_3$, 400 MHz)



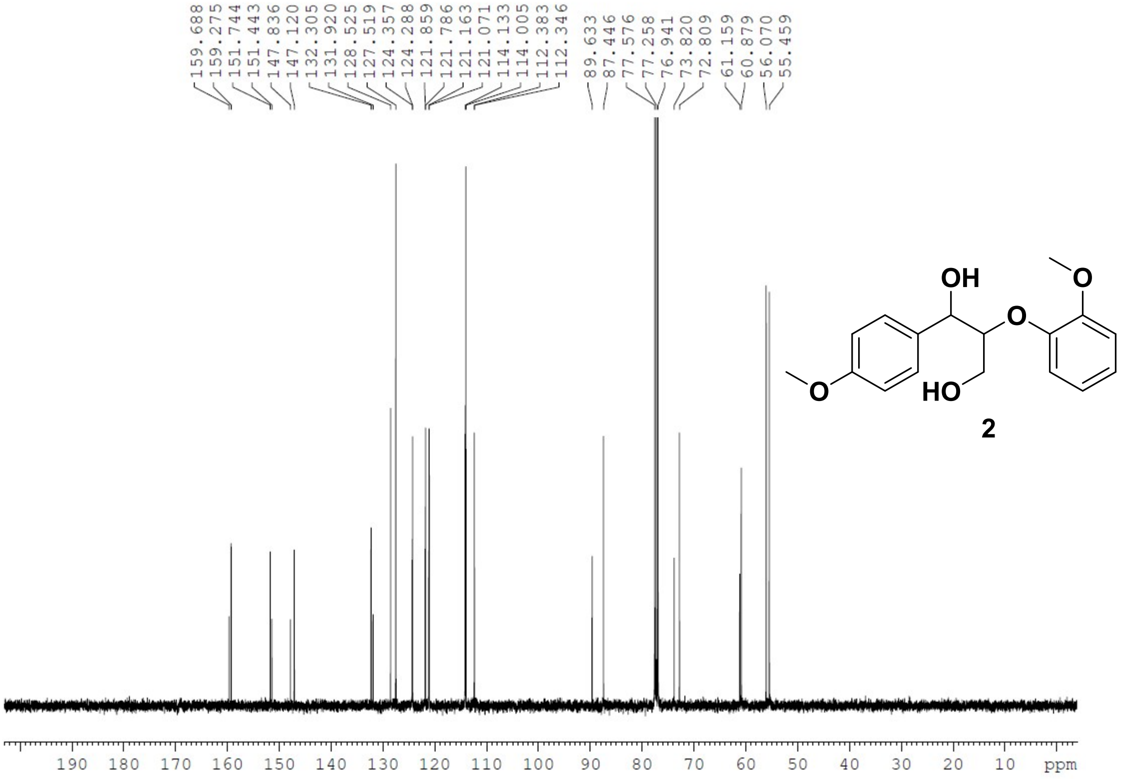
^{13}C spectra of compound 1 ($CDCl_3$, 101 MHz)



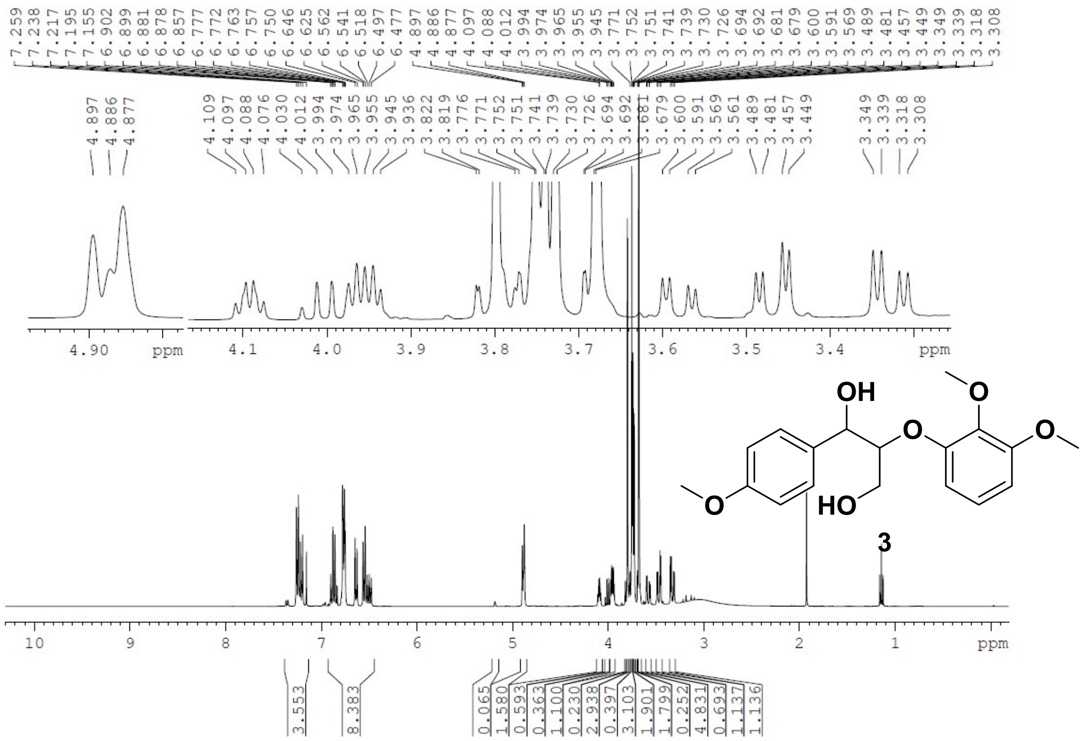
^{1}H spectra of compound 2 (CDCl$_3$, 400 MHz)



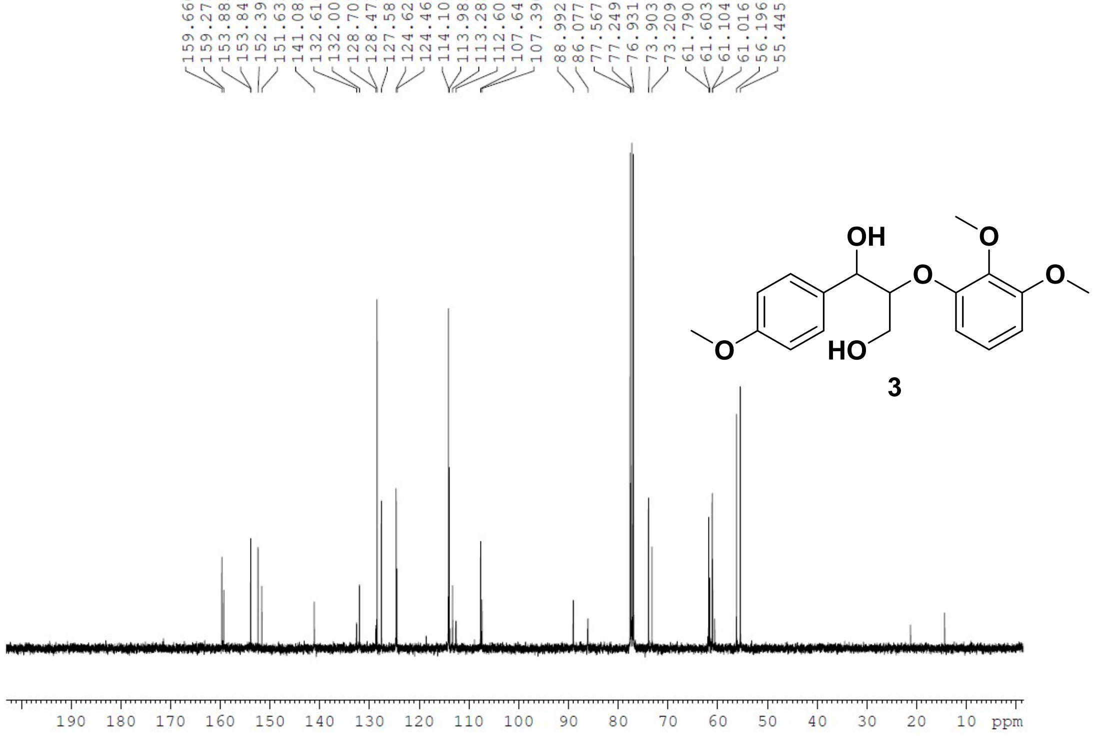
^{13}C spectra of compound 2 (CDCl$_3$, 101 MHz)



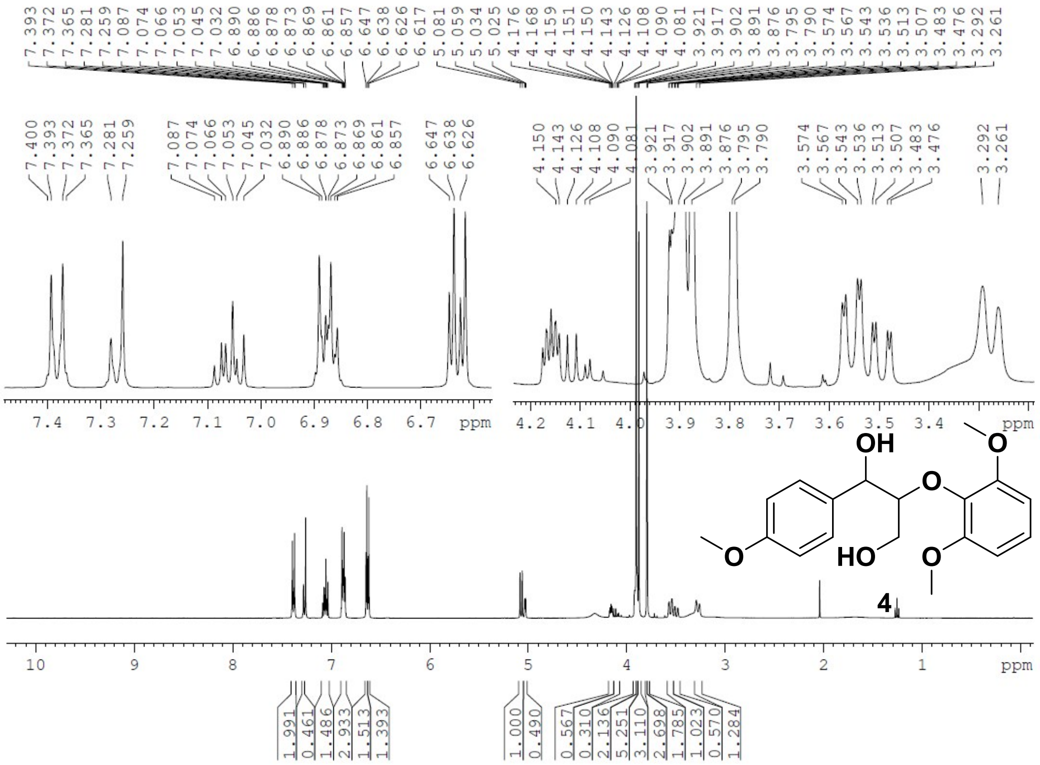
^{1}H spectra of compound 3 ($CDCl_3$, 400 MHz)



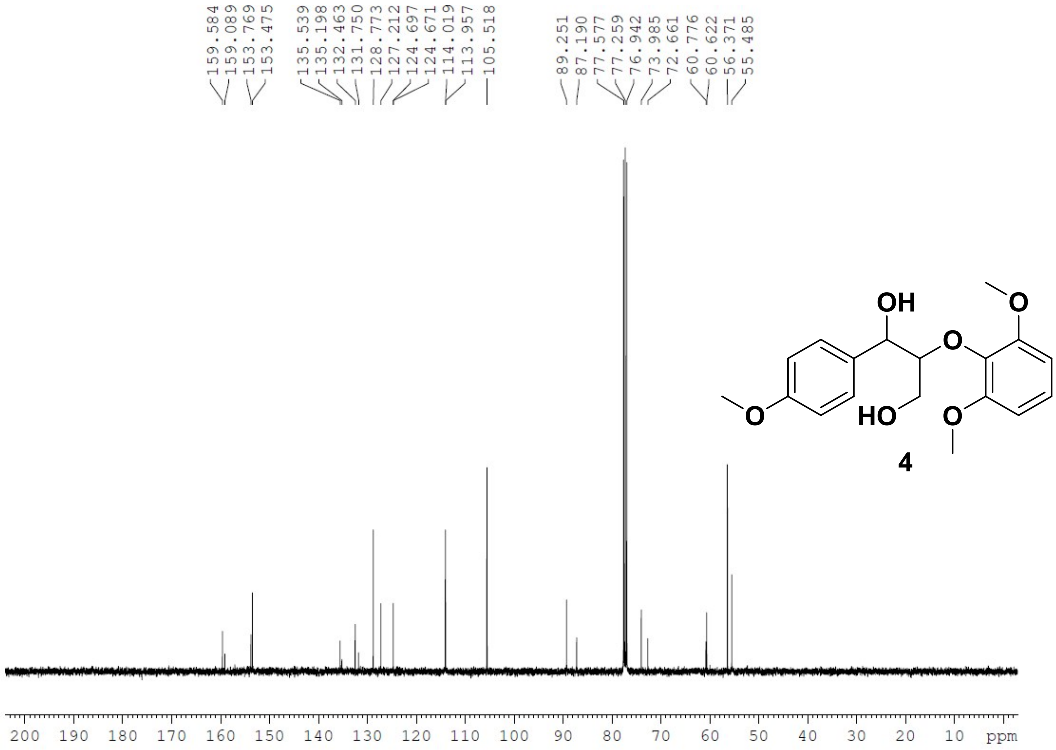
^{13}C spectra of compound 3 ($CDCl_3$, 101 MHz)



^{1}H spectra of compound 4 ($CDCl_3$, 400 MHz)



^{13}C spectra of compound 4 ($CDCl_3$, 101 MHz)



References

1. N. D. Patil and N. Yan, *Tetrahedron Lett.*, 2016, **57**, 3024-3028.

2. J. Luo, X. Zhang, J. Lu and J. Zhang, *ACS Catal.*, 2017, **7**, 5062-5070.

3. M. J. Kurth, L. A. A. Randall, C. Chen, C. Melander, R. B. Miller, K. McAlister, G. Reitz, R. Kang, T. Nakatsu and C. Green, *J. Org. Chem.*, 1994, **59**, 5862-5864.

4. A. Barthel, L. Trieschmann, D. Ströhl, R. Kluge, G. Böhm and R. Csuk, *Arch. Pharm.*, 2009, **342**, 445-452.