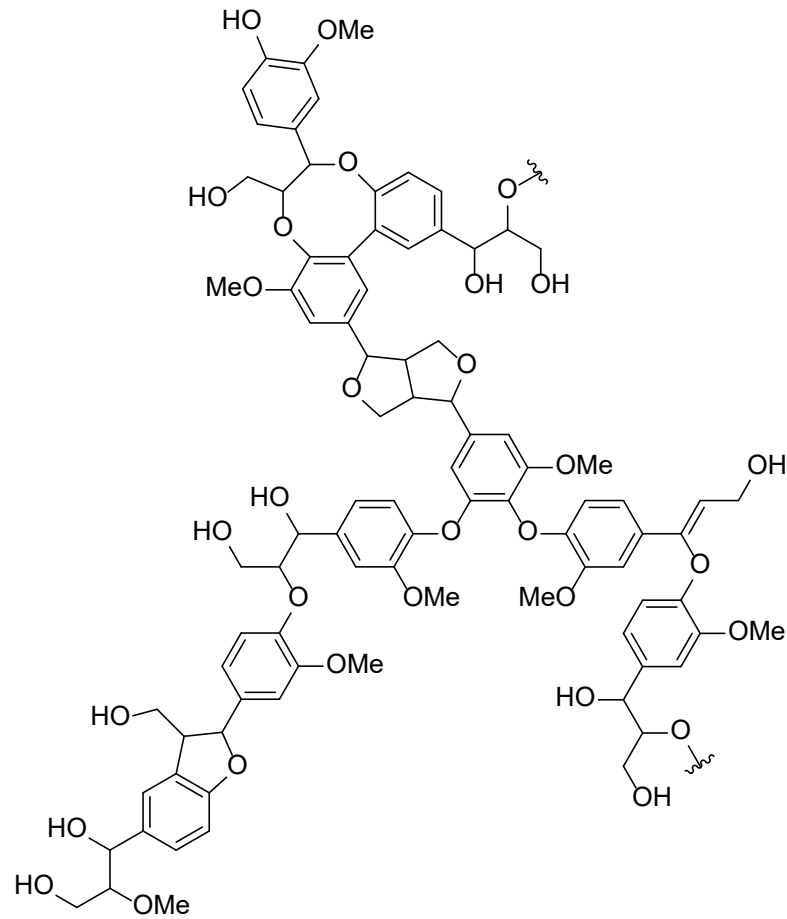


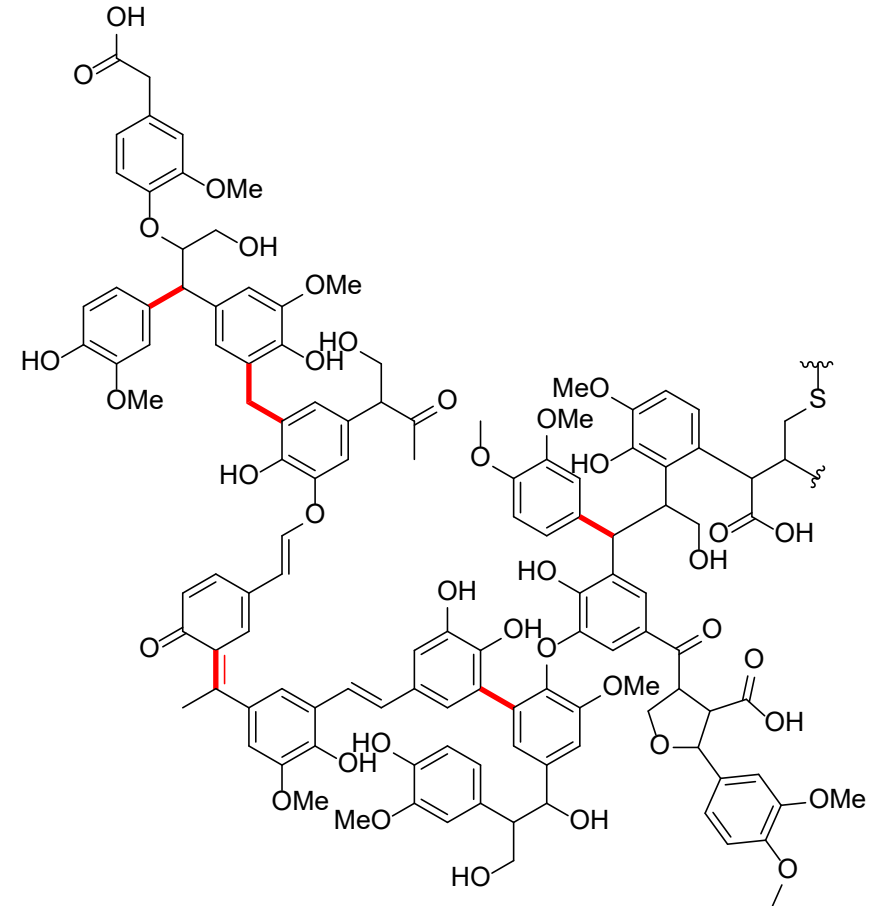
Aromatic monomer production from lignin through
catalytic carbon–carbon bond cleavage

Dr. Chad T. Palumbo
Postdoctoral Researcher

Lignin Valorization: A Case for Depolymerization



softwood native lignin



Kraft lignin

Lignin Valorization: A Case for Depolymerization

World Consumption – 1.3 million metric tons (growth 1.6% to 2024)

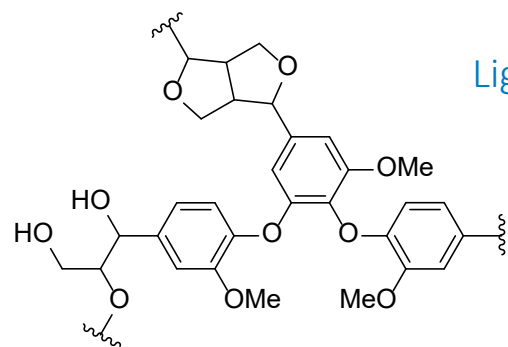
World consumption of lignosulfonates by major region and application—2019
(thousand of metric tons, 100% solids basis)

	United States	Western Europe	Mainland China	Japan	Total	Percent of total
Dispersants	111	173	103	32	418	56
Binders and adhesives	118	47	105	22	291	39
Chemicals and other	12	2	22	5	41	5
Total	241	222	229	59	751	100%

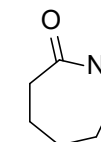
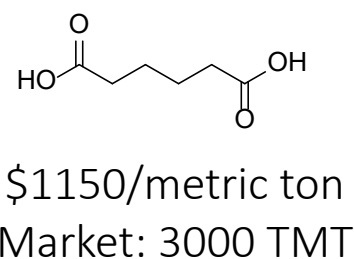
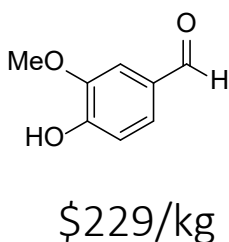
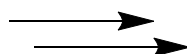
Most end uses already established

Concrete admixtures – largest sector (dispersant) – use has stagnated or even declined due to competition with polycarboxylate-based products

Value (\$/metric ton): liquid 100-300, solid 600-900



Lignin deconstruction

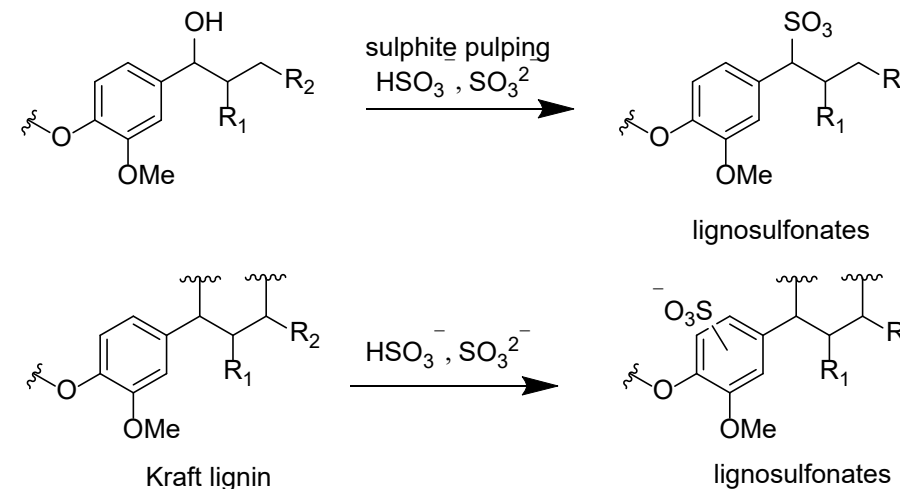


\$1400/metric ton
Market: 6000 TMT

TMT = thousand metric tons

Source: IHS Markit

Applications of Lignin – Lignosulfonates



Theoretical Yields of Monomers Through C–O Bond Cleavage Possible

Lignin First Biorefinery: active stabilization approaches that solubilize lignin from native lignocellulosic biomass while avoiding condensation reactions that lead to more recalcitrant lignin polymers

Energy Environ. Sci., 2021, 14, 262-292

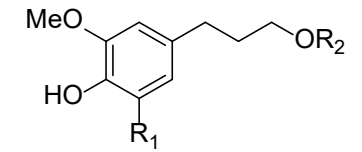
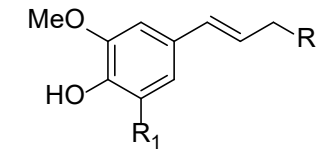
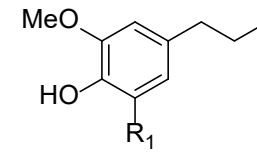


Biomass



Reductive catalytic fractionation
C–O (Aryl ether) bond cleavage

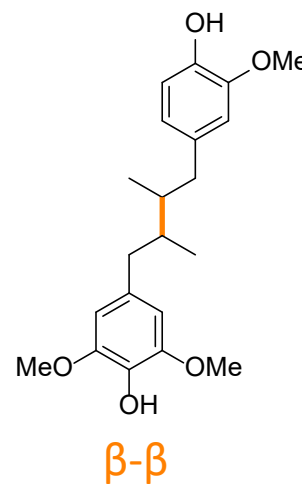
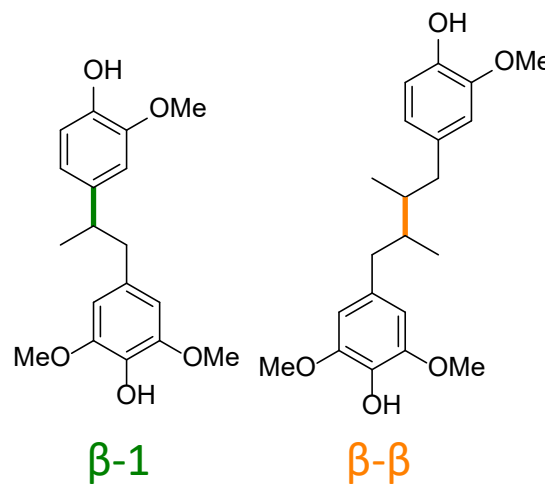
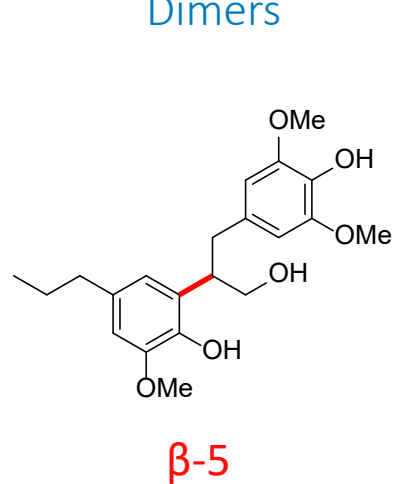
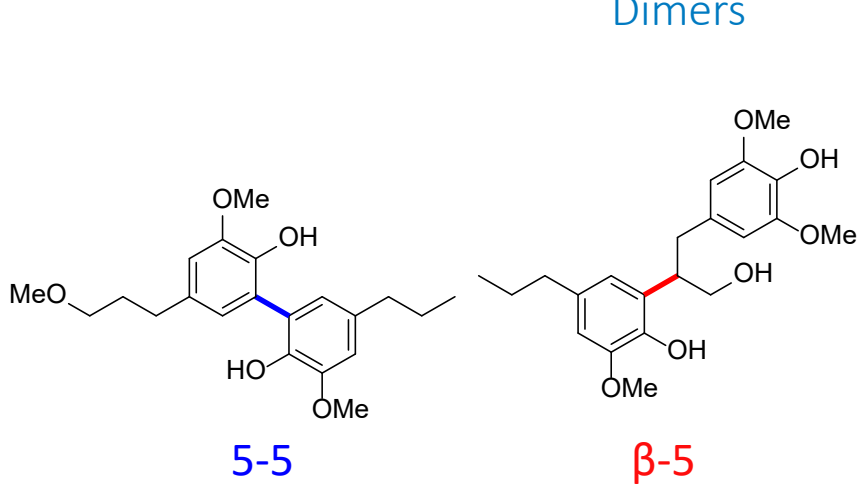
Monomers



$R_1 = \text{H, OMe}; R_2 = \text{OH, OMe}$

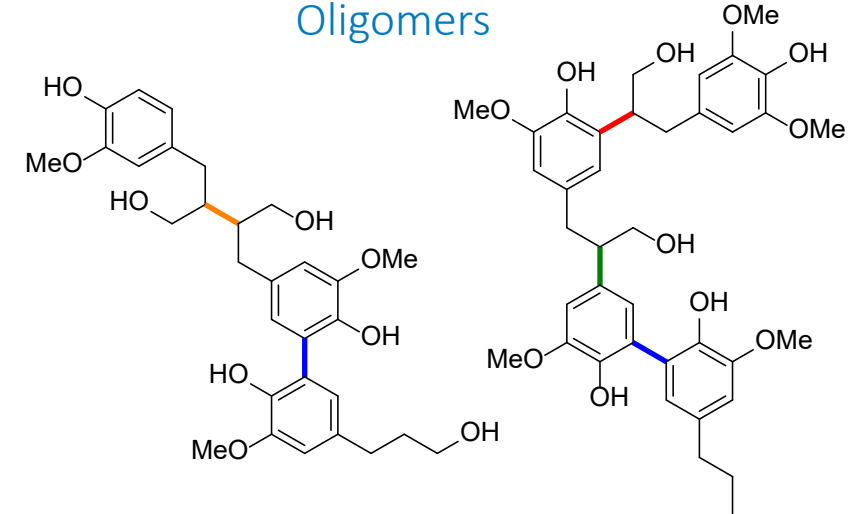
Theoretical Yields of Monomers Obtained: 20-40 wt%

Dimers

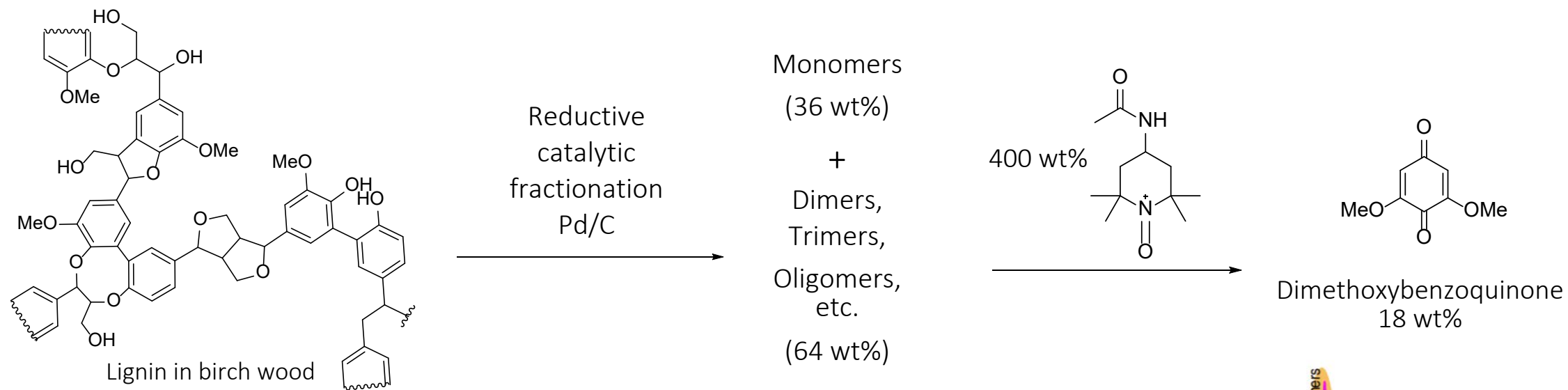


15-20 wt%

Oligomers

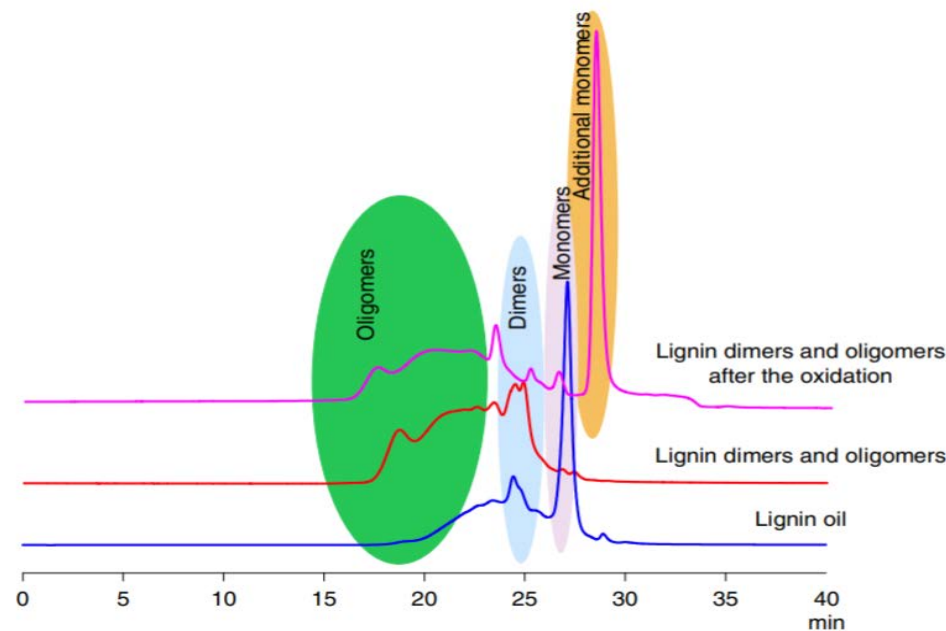


Only One Report of C–C Bond Cleavage of RCF Oligomers



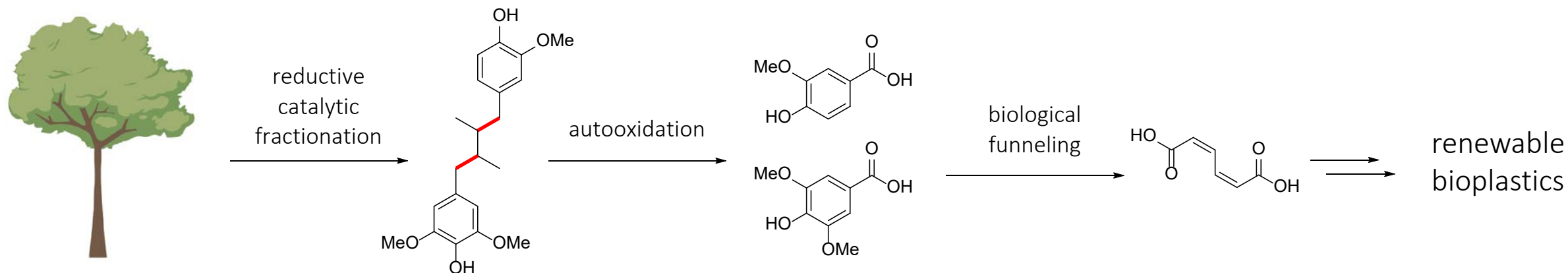
State of the Art:

- Performed with 400 wt% of oxidant
- Oxidant can be subsequently regenerated electrochemically
- Exploits the reactivity of phenols for C–C cleavage

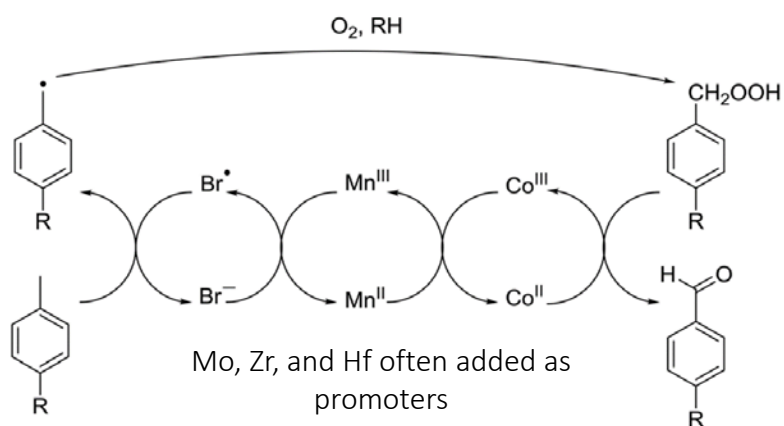


Can We Cleave C–C Bonds Catalytically into Bioavailable Products?

Our Overall Objective

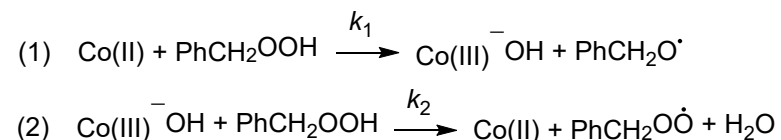


MC Process Simplified Scheme

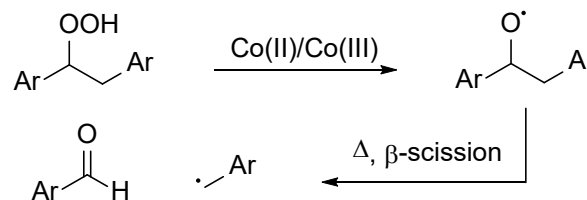


Partenheimer, W. *Catal. Today*, **1995**, *23*, 69-158

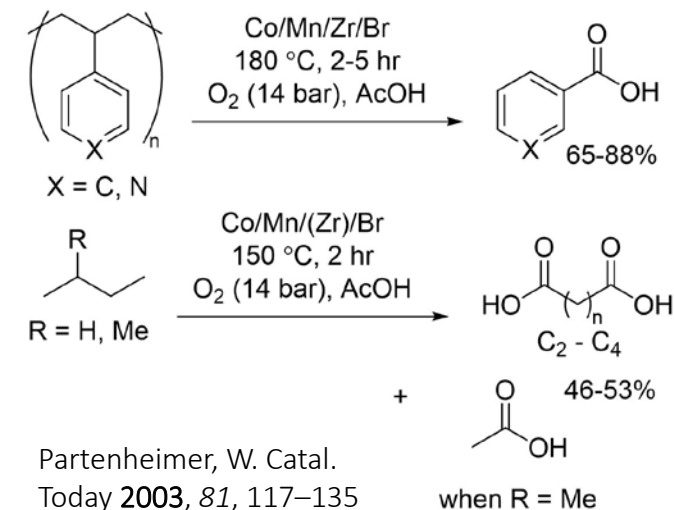
Haber-Weiss Cycle



C–C Bond Cleavage

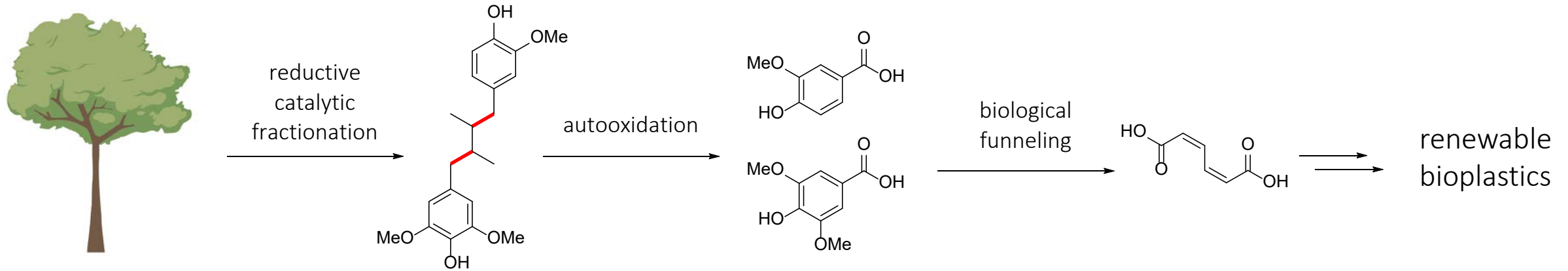


Precedent on C–C Bond Cleavage

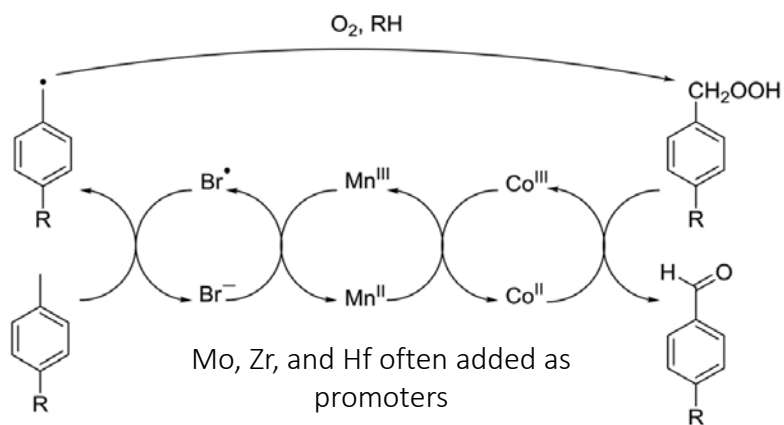


Can We Cleave C–C Bonds Catalytically into Bioavailable Products?

Our Overall Objective

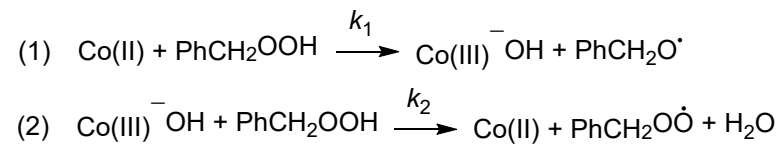


MC Process Simplified Scheme

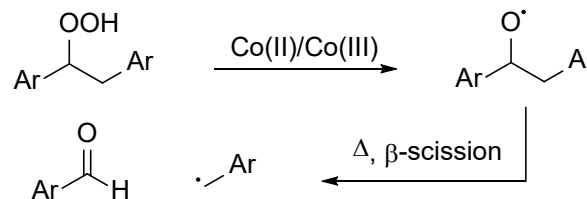


Partenheimer, W. *Catal. Today*, **1995**, *23*, 69-158

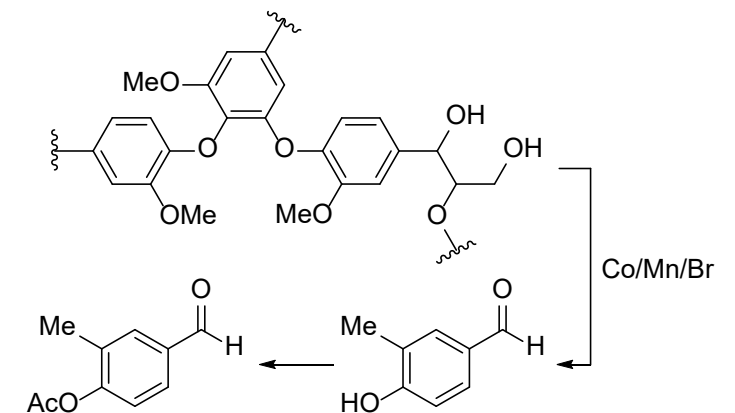
Haber-Weiss Cycle



C–C Bond Cleavage



MC Catalyst on Lignin



Partenheimer, W. *Adv. Synth. Catal.* **2009**, *351*, 456–466;
Clatworthy, E. B. *et al. Catal. Sci. Technol.* **2019**, *9*, 384–397.

Can We Cleave C–C Bonds with a Manganese Catalyst?

Ranking of Heterogeneous Catalysts Metals by Their Greenness

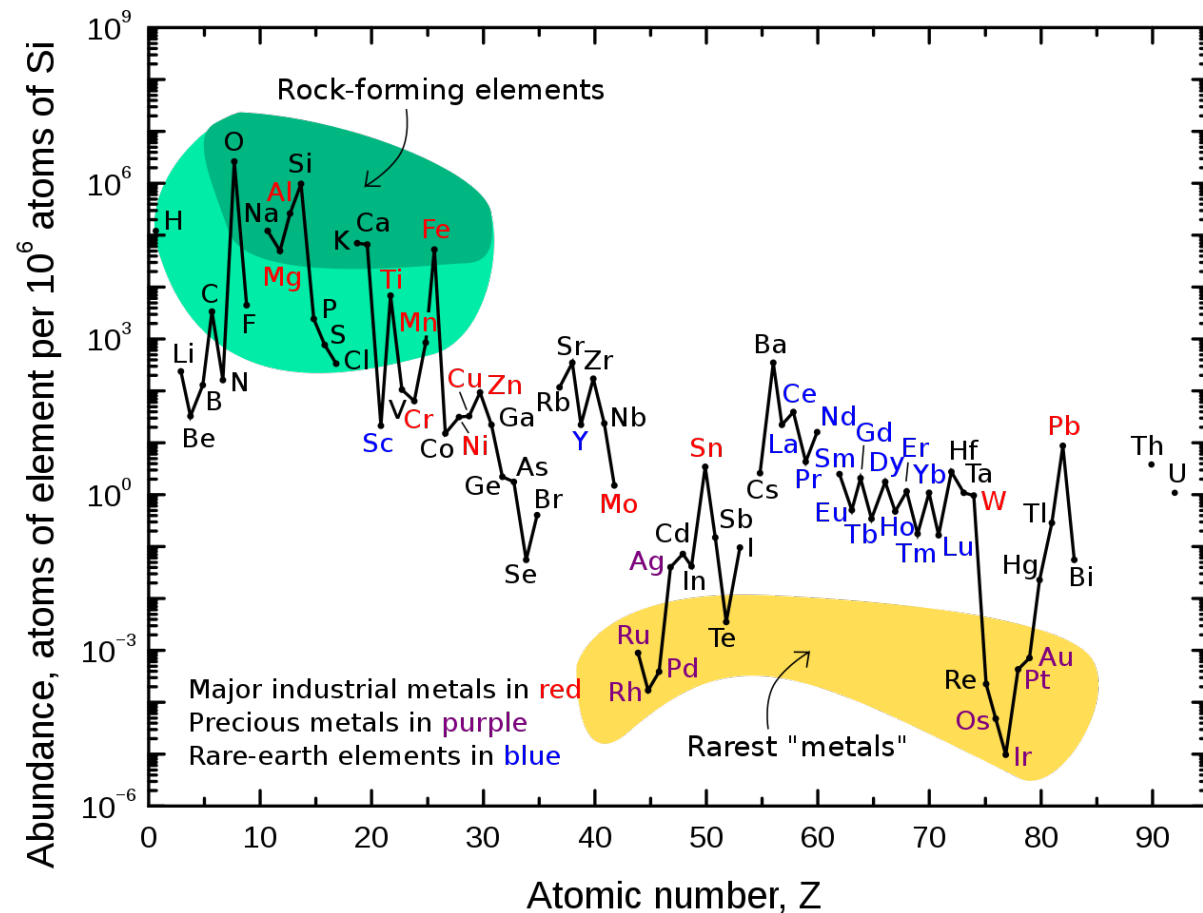
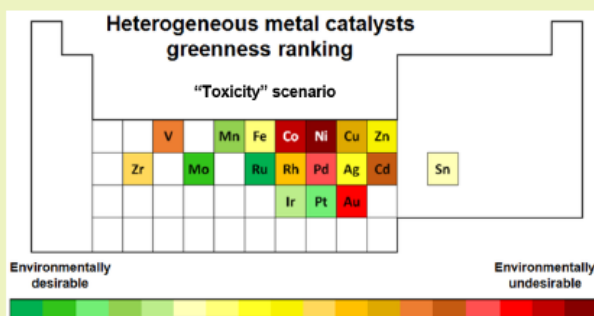
Marta Bystrzanowska,[†] Petko Petkov,[‡] and Marek Tobiszewski^{*,†}

[†]Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology (GUT), 11/12 G. Narutowicza St., 80-233 Gdańsk, Poland

[‡]Faculty of Chemistry and Pharmacy, University of Sofia, J. Bourchierblvd. 1, 1164 Sofia, Bulgaria

Supporting Information

ABSTRACT: Catalysis is a very important process in industry and laboratory practices, especially from the point of green chemistry principles. However, the eco-friendly character of heterogeneous catalysts containing transition-metal components has not yet been evaluated. Therefore, we performed a comprehensive assessment of 18 heterogeneous metal catalysts (Pd, Pt, V, Co, Ni, Mo, Ru, Mn, Au, Cu, Cd, Zr, Fe, Rh, Ir, Sn, Zn, Ag) using a multicriteria decision analysis approach. The ranking of alternatives according to relevant criteria, such as the toxicity of pure metals and metal salts toward fish, *Daphnia magna*, and algae/plants, metal toxicity toward rats via ingestion, carcinogenicity, the endangerment degree of metals, the boiling point and energy for atom detachment (estimated as metal–metal bond strength in diatomic transition-metal units), and the classification of elemental impurities according to the International Conference on Harmonization, and their degree of importance are presented. Life cycle assessment (LCA)-related parameters of metals have been also included. The assessment showed ruthenium, iron, and molybdenum as the most favorable alternatives, in contrast to nickel, cobalt, and rhodium. Results of environmental evaluation strictly depend on the chosen scenario of assessment, in terms of toxicity, endangered elements, or LCA. Sensitivity analyses toward variations in input data and applied weights prove that the results are reliable. Multicriteria decision analysis can be successfully applied in metal catalyst evaluation for particular case



Can We Cleave C–C Bonds with a Manganese Catalyst?

Ranking of Heterogeneous Catalysts Metals by Their Greenness

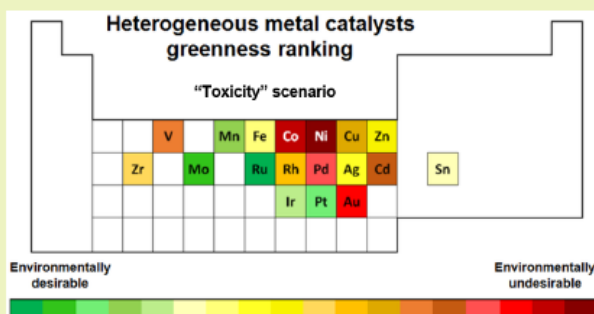
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Bystrzanowska, M. et al. *ACS Sustainable Chem. Eng.* 2019, 7, 18434–18443.

Cobalt – \$34,800 / ton
Manganese – \$1,800 / ton
Wood Mackenzie Group, Dec 2020

50 million tons of lignin produced annually in industry

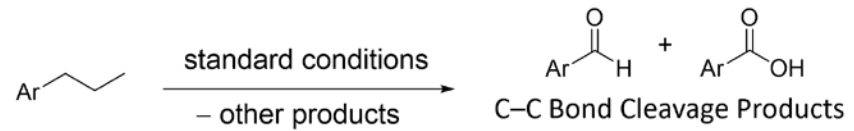
Gosselink, R.J.A. et al. *Ind. Crops Prod.* 2004, 20, 121–129.

29,400 tons Cobalt
27,400 tons Manganese

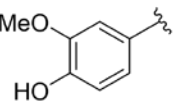
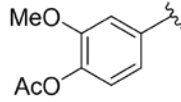
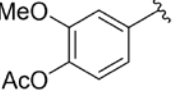
\$1.02 billion / year Cobalt
\$49.3 million / year Manganese

Our aim is to achieve lignin deconstruction to aromatic monomers using a Mn-based catalyst system

Methyl Protection and Zirconium Cocatalyst for Successful C–C Cleavage

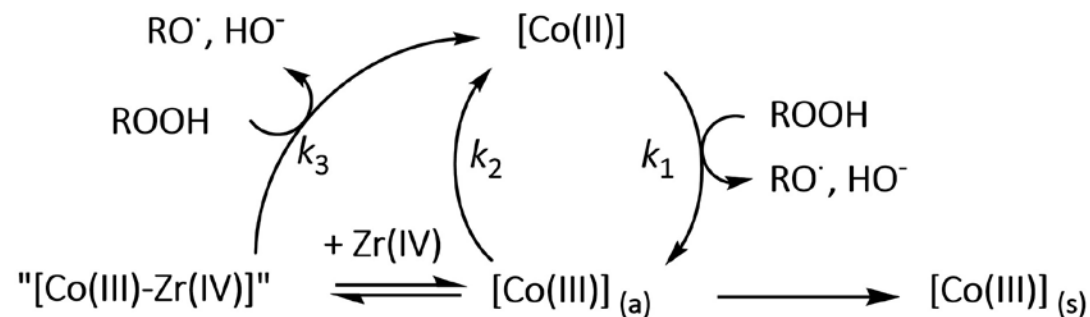


standard conditions =
8 mol% Mn(OAc)₂•4H₂O
6 mol% Zr(acac)₄
6 bar O₂, 150 °C
15 mL AcOH, 1.5 h

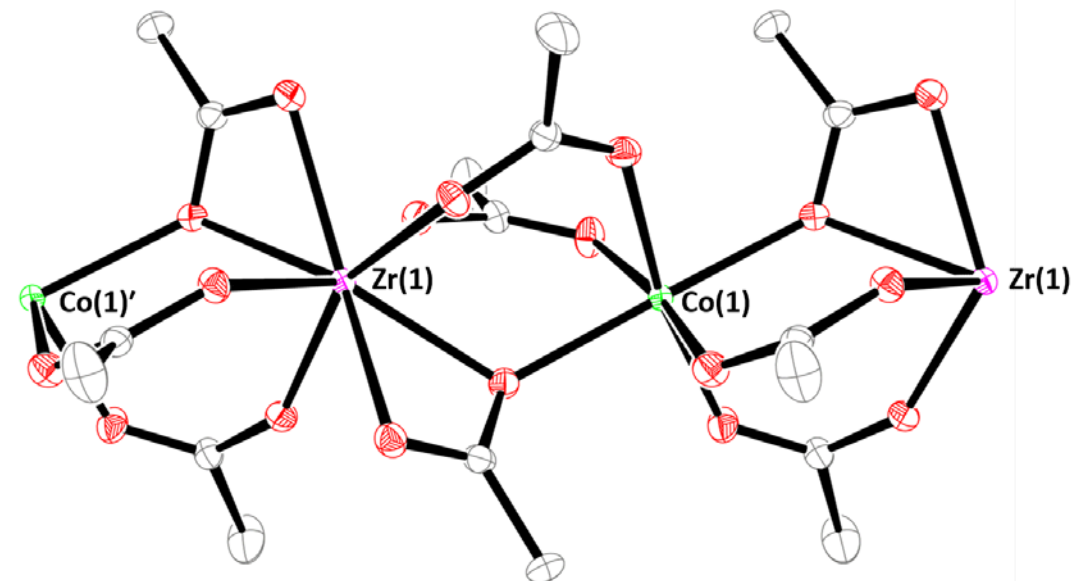
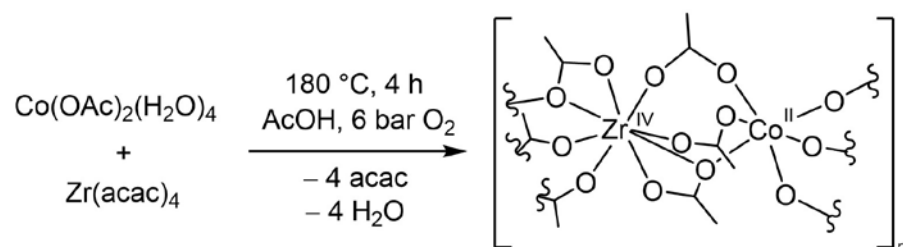
Ar =	Variation	Substrate Conversion (%)	Total C–C Cleavage Products (%)
	-	94(1)	2.1(6)
	no Zr	4.6(1)	< 1
	-	18(1)	1.9(7)

How Does Zirconium Promote Co/Mn-catalyzed Autoxidation

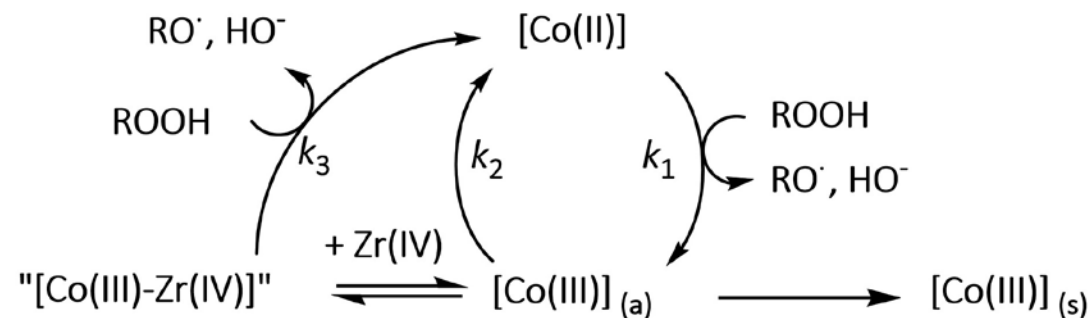
Literature on Cobalt / Zirconium Solution Kinetics



- Benson, D. et al. *Discussion Farad. Soc.* **1960**, 29, 60-72
 Steinmetz, G.R. et al. *J. Mol. Cat.* **1988**, 49, L39-L42.
 Gould, E. S. et al. *J. Am. Chem. Soc.* **1973**, 95, 5198-5204.
 Hermans, I. et al. *Chem. Eur. J.* **2010**, 16, 13226-13235.
 Jones, G. H. et al. *J. Chem. Soc., Chem Commun.* **1979**, 536-537.
 Kochi, J. K. et al. *J. Inorg. Nucl. Chem.* **1971**, 4101-4109; and refs therein.
 Chester, A. W. et al. *J. Catal.* **1977**, 46, 308-319.
 Partenheimer, W. et al. *J. Mol. Catal. Chem.* **2001**, 174, 29-33.
 Partenheimer, W. *J. Mol. Catal. Chem.* **2003**, 206, 105-119.
 Partenheimer, W. *J. Mol. Catal. Chem.* **2003**, 206, 131-144.
 Zuo, X. et al. *Ind. Eng. Chem. Res.* **2008**, 47, 546-552.
 Partenherimer, W. et al. *Adv. Synth. Catal.* **2001**, 343, 102-111.



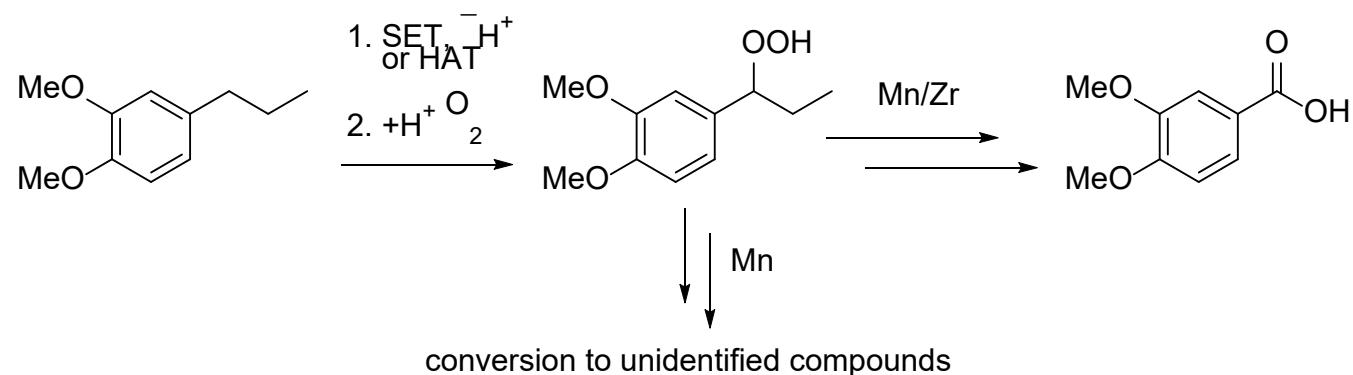
How Does Zirconium Promote Co/Mn Autoxidation



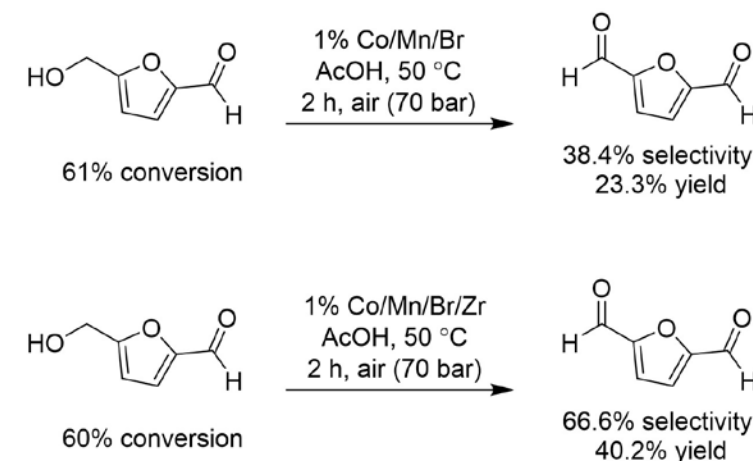
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- Partenherimer, W. et al. *Adv. Synth. Catal.* **2001**, 343, 102-111.

Zirconium allows competitive conversion to carboxylic acid products as opposed to unidentified ones



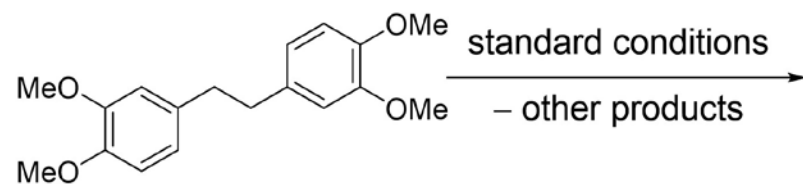
Effect of Zr on Selectivity



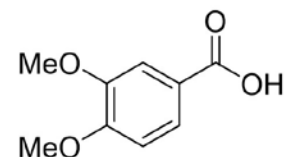
Partenherimer, W.; Grushin, V. V. *Adv. Synth. Catal.* **2001**, 343, 102-111.

Demonstration of C–C Bond Cleavage on Model Dimers

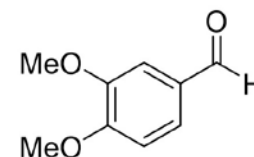
β -1



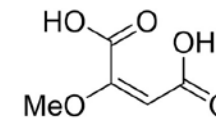
100% conversion



29(3)%



2(2)%

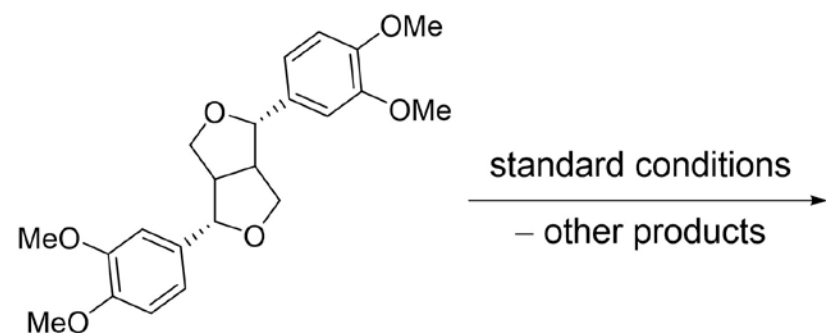


4.4(4)%

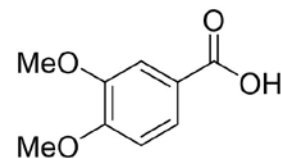
total yield = 35(4) mol%; total C–C cleavage monomers = 35(4) mol%

standard conditions =
8 mol% $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$
6 mol% $\text{Zr}(\text{acac})_4$
6 bar O_2 , 150 °C
15 mL AcOH, 1.5 h

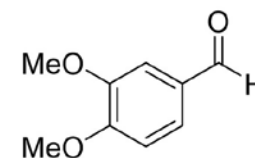
β - β



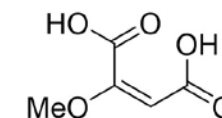
100% conversion



37(2)%



4.4(1)%

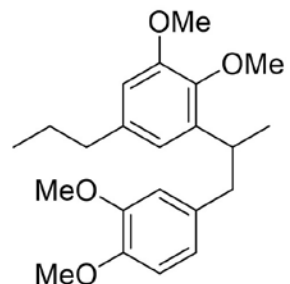


2.9(2)%

total yield = 45(2) mol%; total C–C cleavage monomers = 45(2) mol%

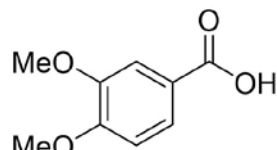
Demonstration of C–C Bond Cleavage on Model Dimers

β -5

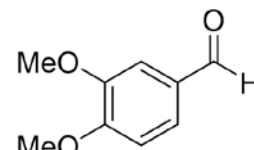


100% conversion

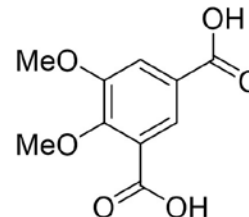
standard conditions
– other products



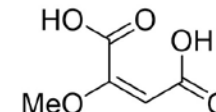
12.5(8)%



15(1)%



trace

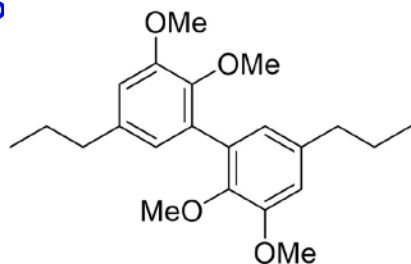


2.0(4)%

standard conditions =
8 mol% Mn(OAc)₂•4H₂O
6 mol% Zr(acac)₄
6 bar O₂, 150 °C
15 mL AcOH, 1.5 h

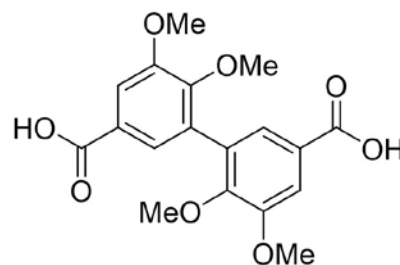
total yield = 30(1) mol%; total C–C cleavage monomers = 30(1) mol%

5-5

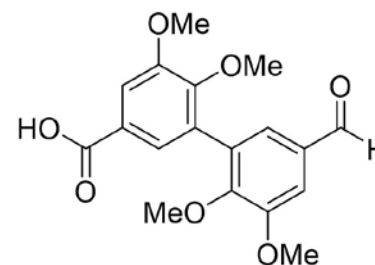


100% conversion

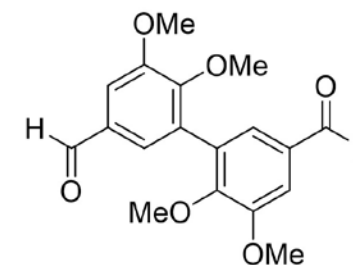
standard conditions
– other products



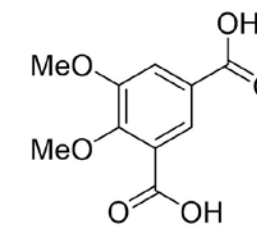
13.7(8)%



6.9(4)%



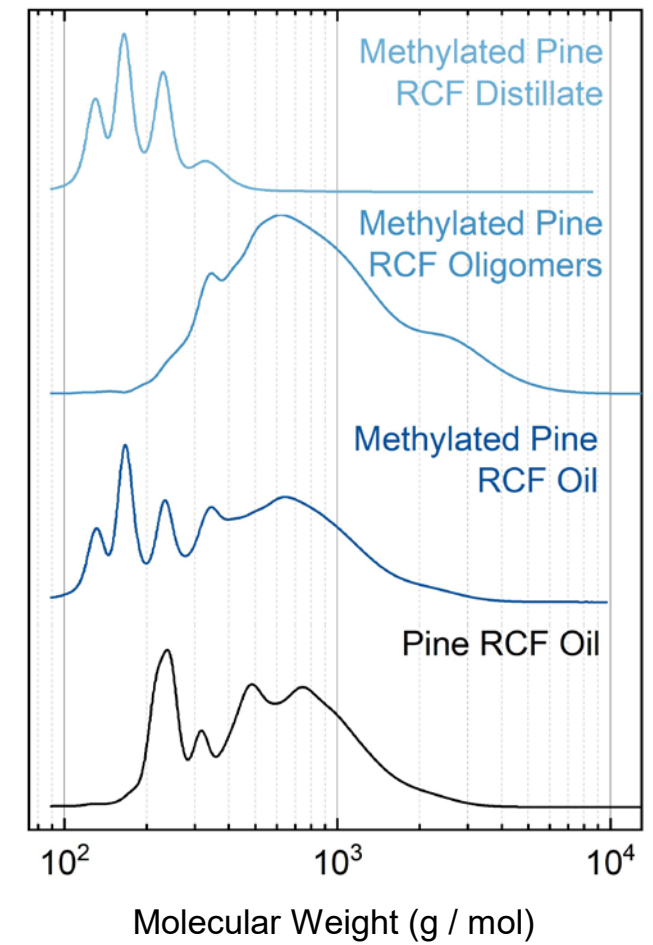
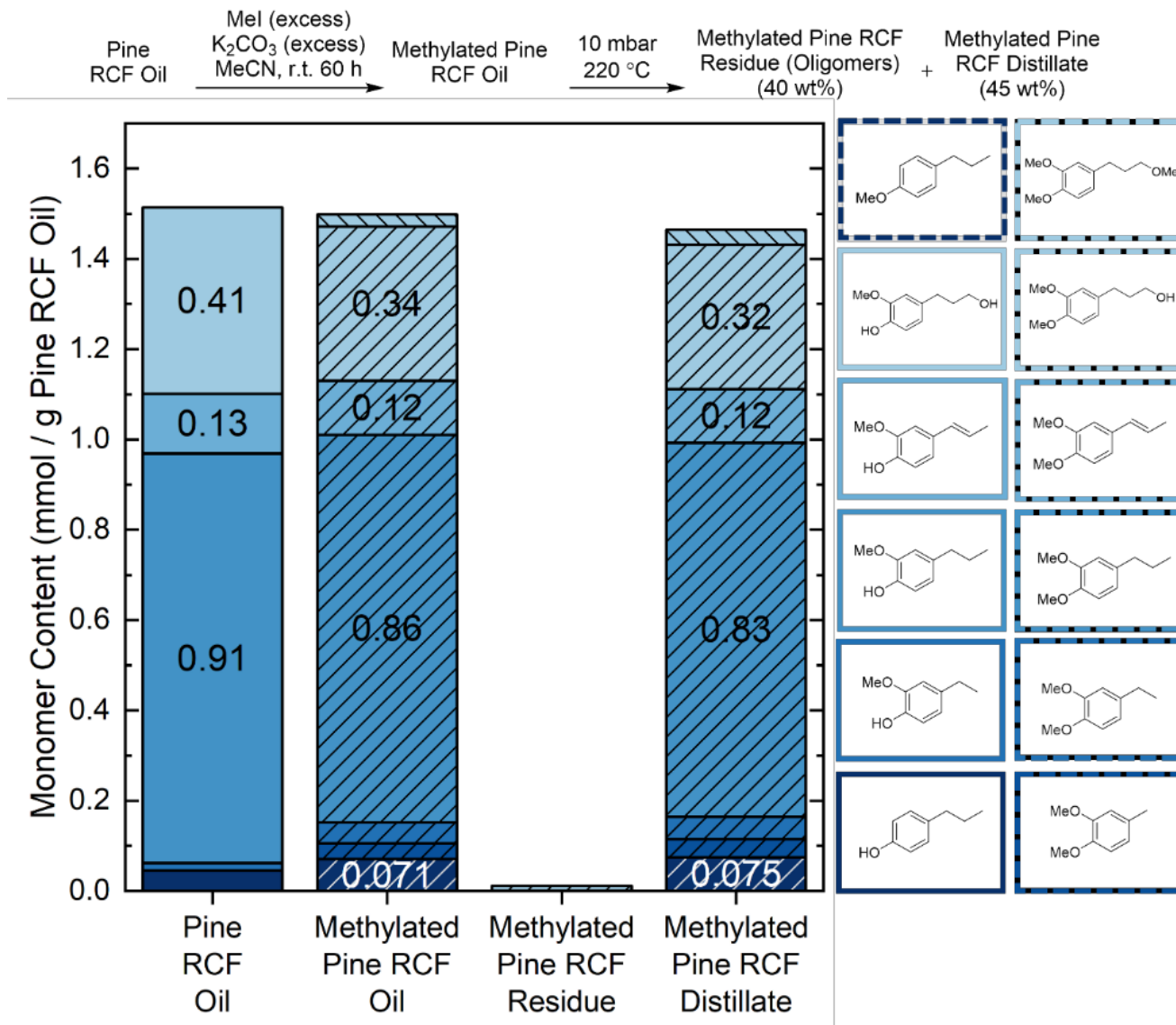
7.6(4)%



2.1(1)%

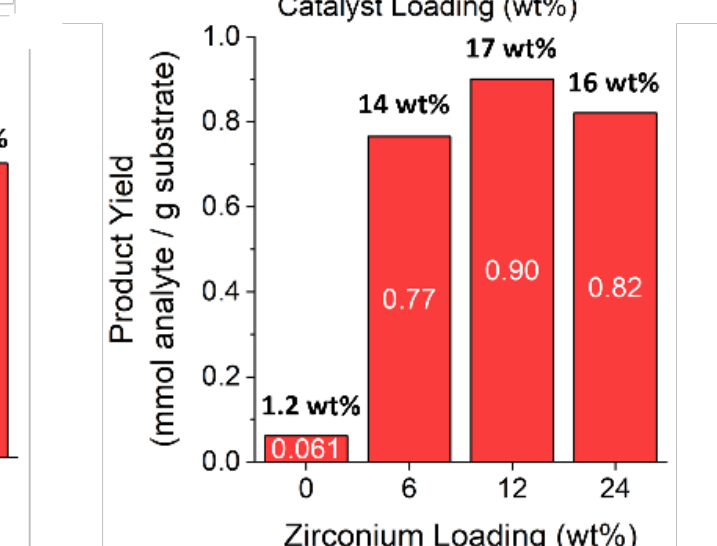
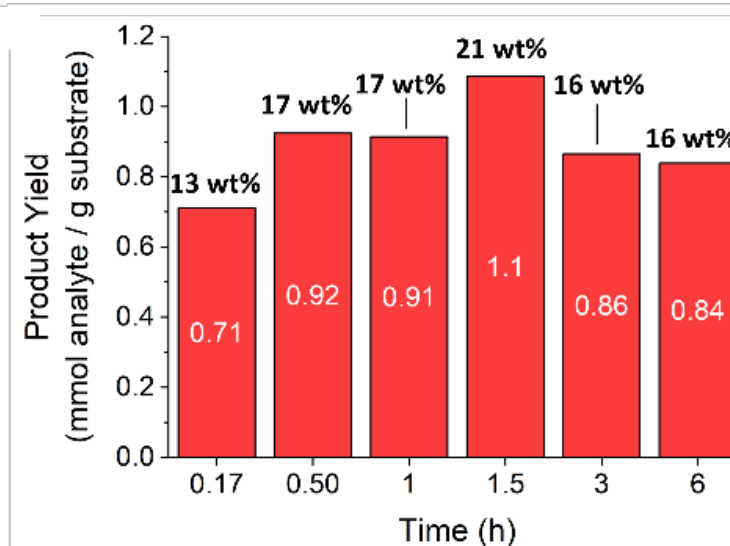
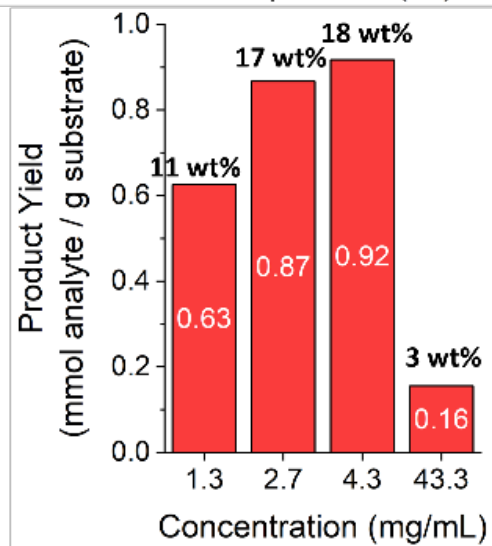
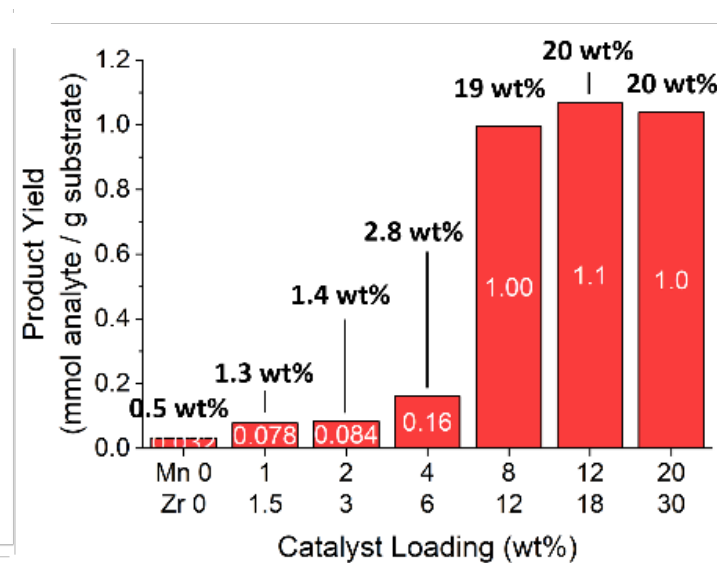
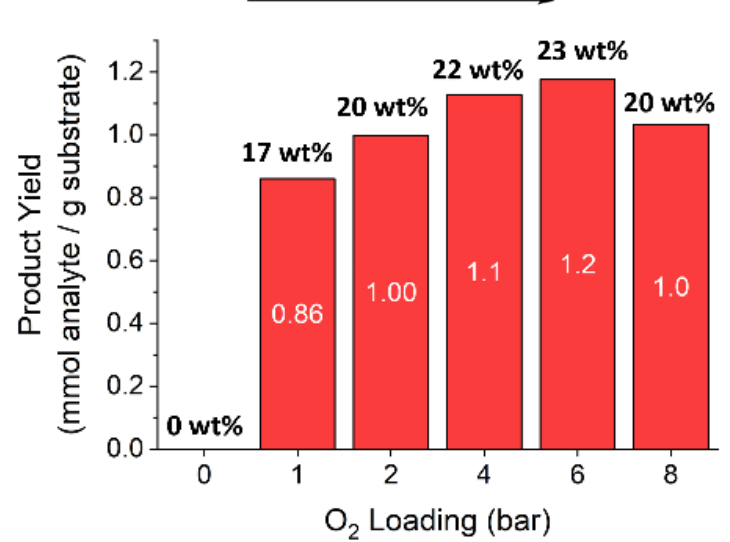
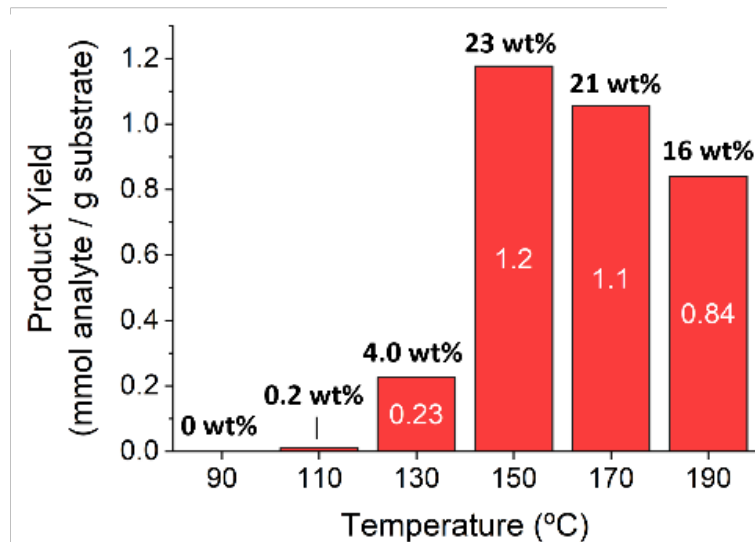
total yield = 30(1) mol%; total C–C cleavage monomers = 2.1(1) mol%

Pine Oligomer Substrate Prepared by Methylation and Distillation



Optimization of Mn-Autoxidation of Pine Oligomers in Batch

Methylated Pine Oligomers $\xrightarrow{\text{8 wt\% Mn(OAc)}_2 \cdot 4\text{H}_2\text{O}$
 $\text{12 wt\% Zr(acac)}_4$
 $\text{Acetic Acid, O}_2 \text{ (6 bar)}$
 $\text{150 }^\circ\text{C, 1.5 h}$ C-C Cleavage Product



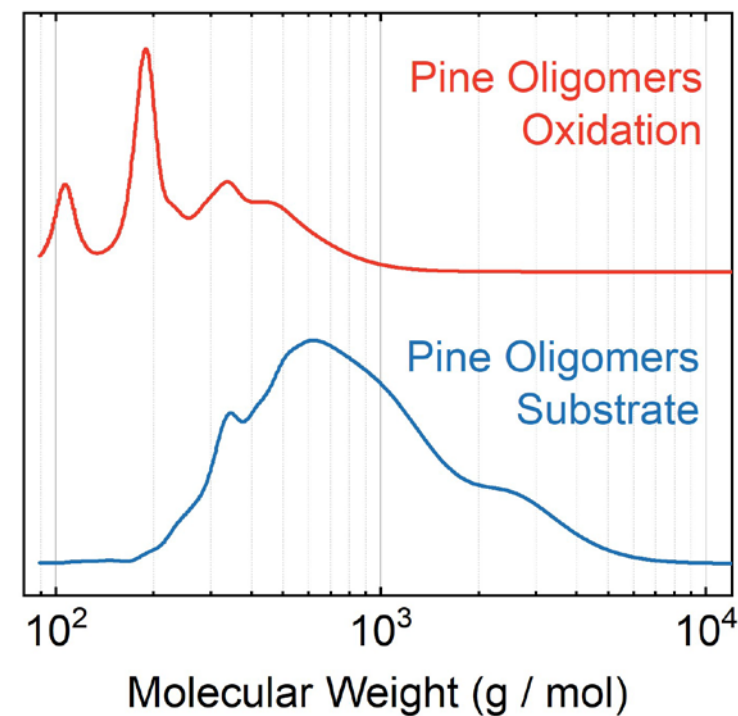
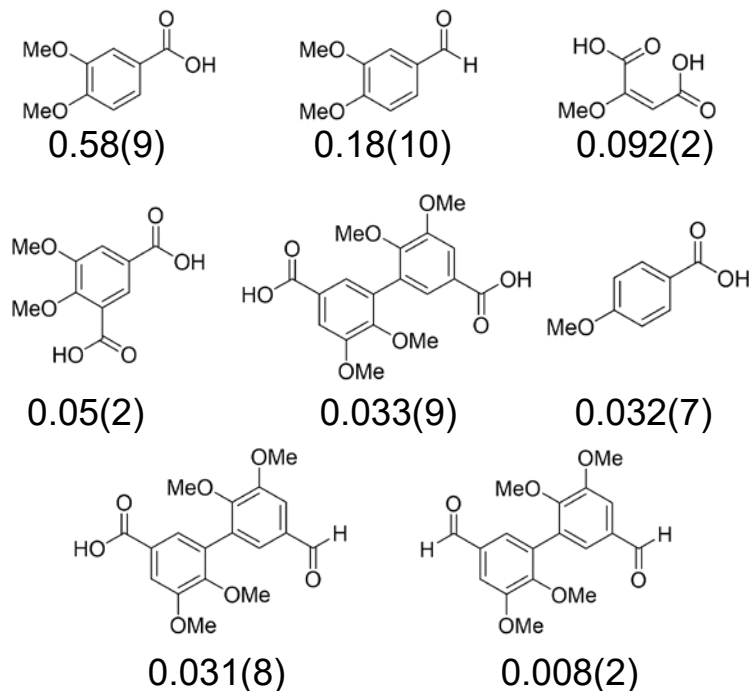
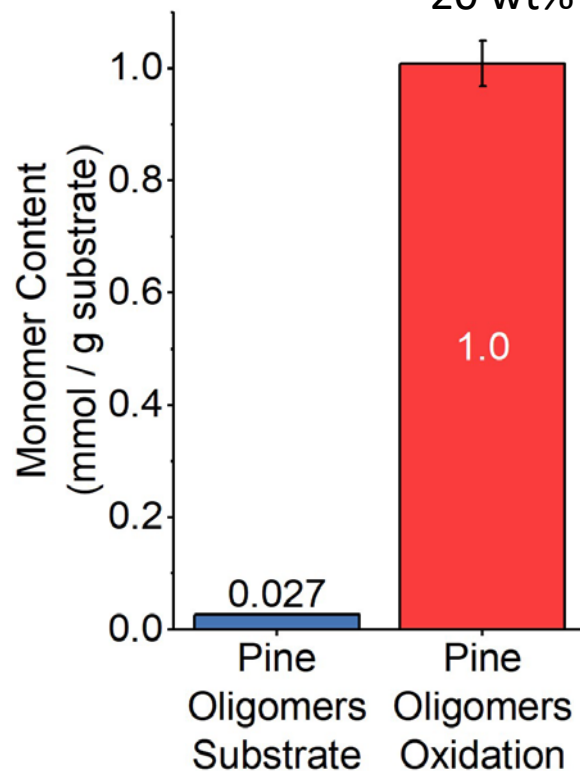
Optimized Mn-Autoxidation of Pine Oligomers in Batch

Methylated Pine Oligomers

8 wt% Mn(OAc)₂·4H₂O
 12 wt% Zr(acac)₄
 Acetic Acid, O₂ (6 bar)
 150 °C, 1.5 h

C-C Cleavage Products

~20 wt%

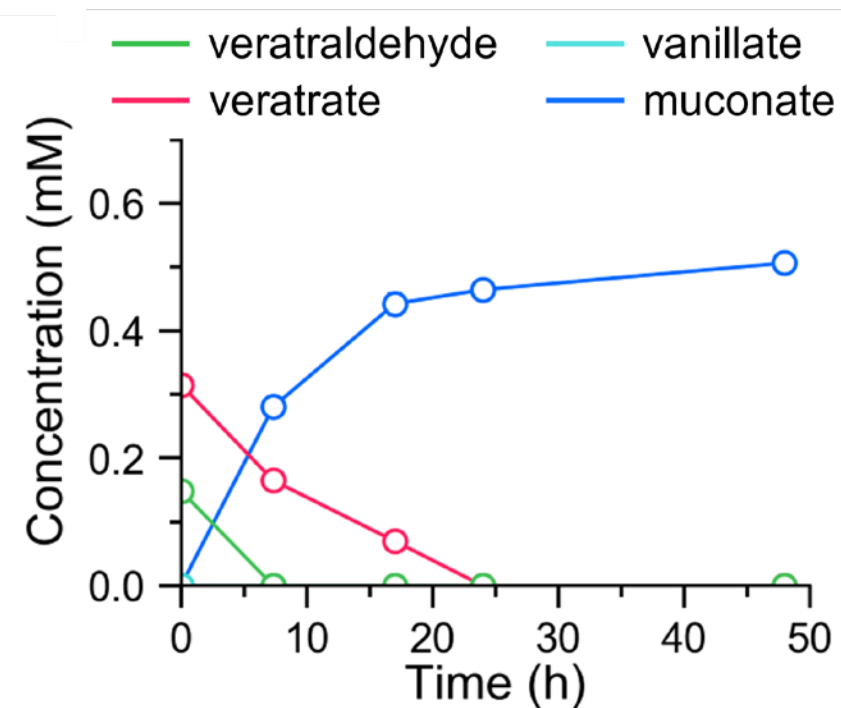
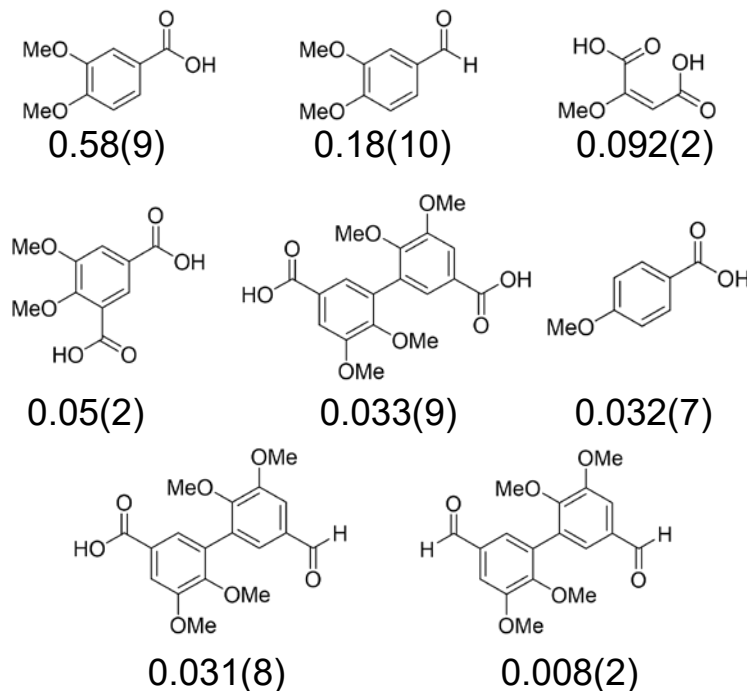
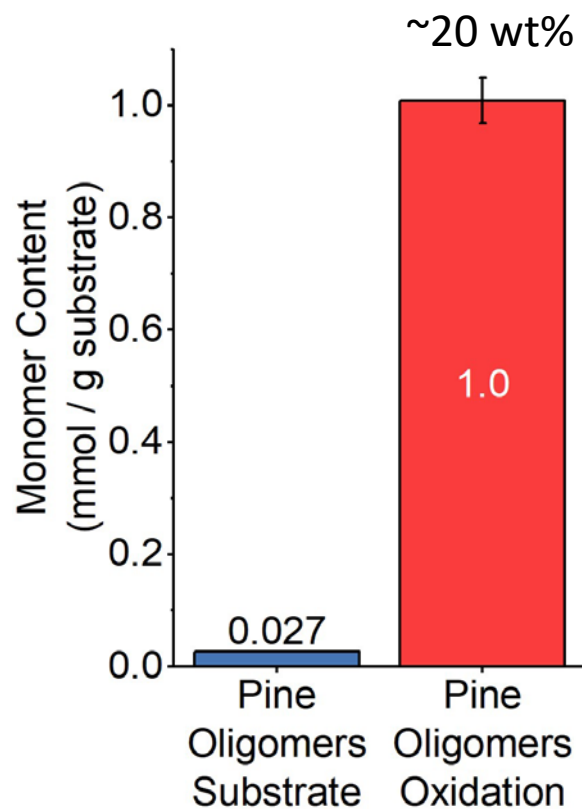
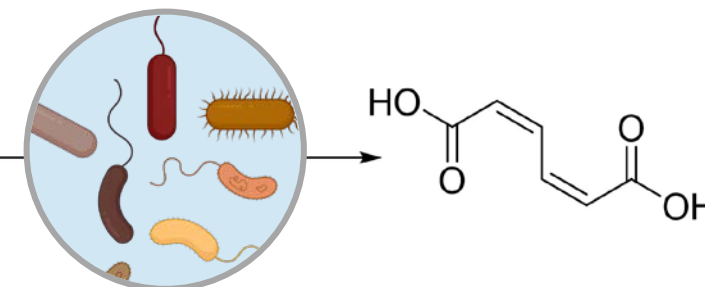


Optimized Mn-Autoxidation of Pine Oligomers in Batch

Methylated Pine Oligomers

10 wt% Mn(OAc)₂·4H₂O
 12 wt% Zr(acac)₄
 Acetic Acid, O₂ (6 bar)
 150 °C, 1.5 h

C-C Cleavage Products



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Thank You

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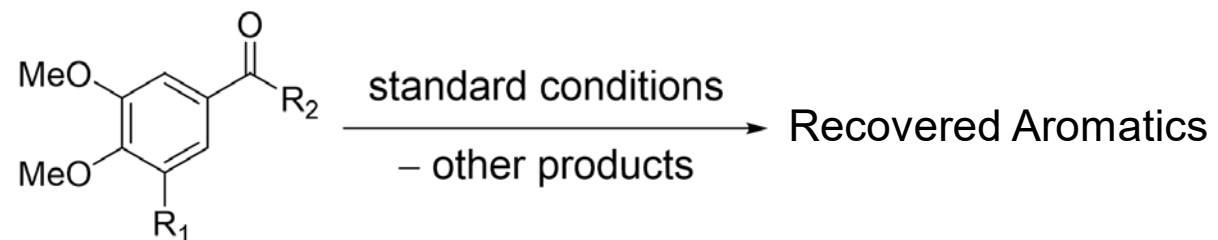


On the job market...

Chad T. Palumbo, Ph.D.
email: palumbochad@gmail.com



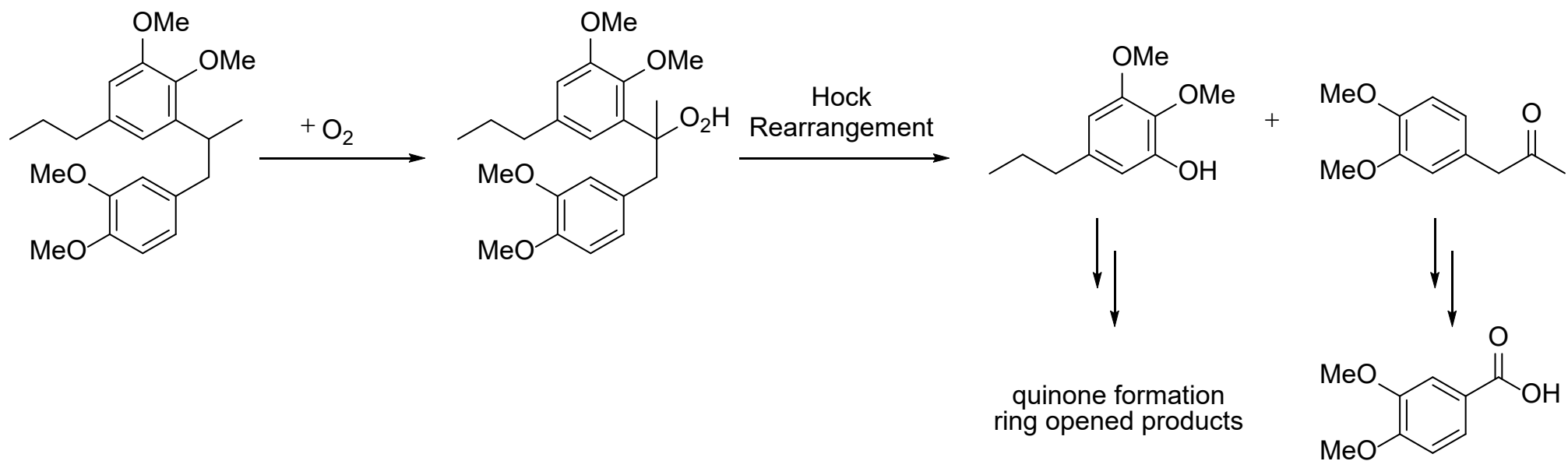
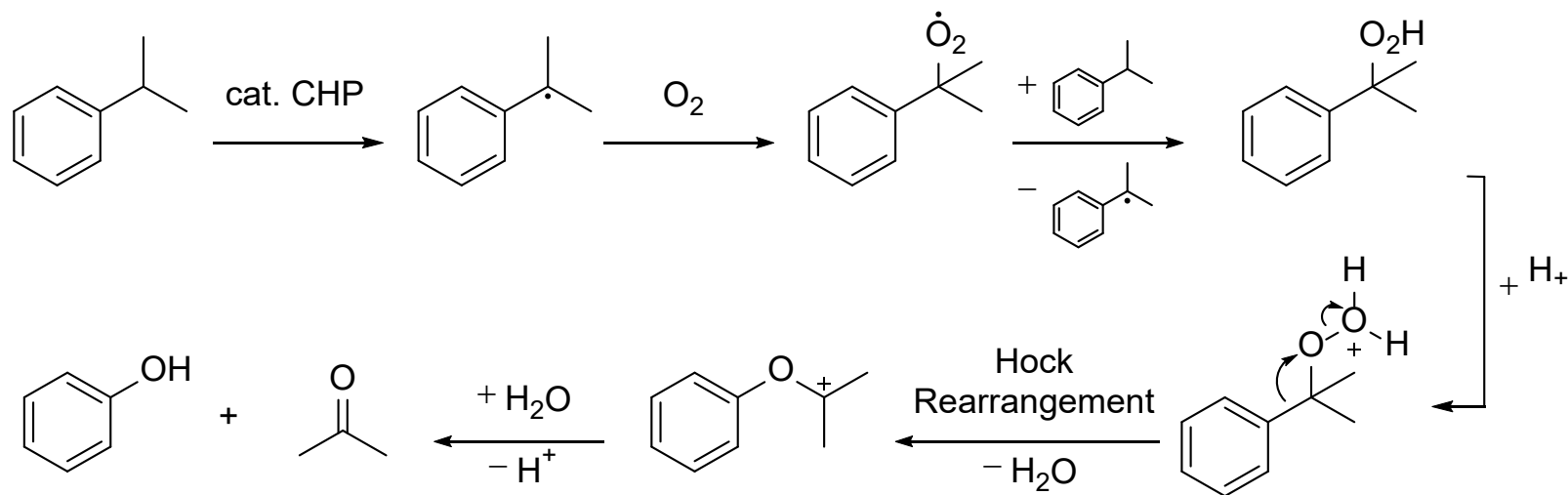
Studies of Stability of Carboxylic Acids in Autooxidation Conditions



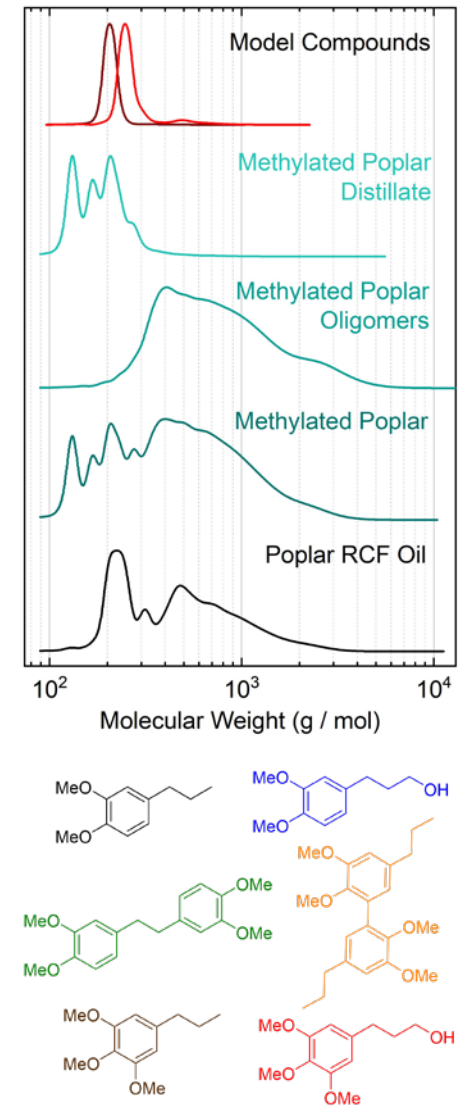
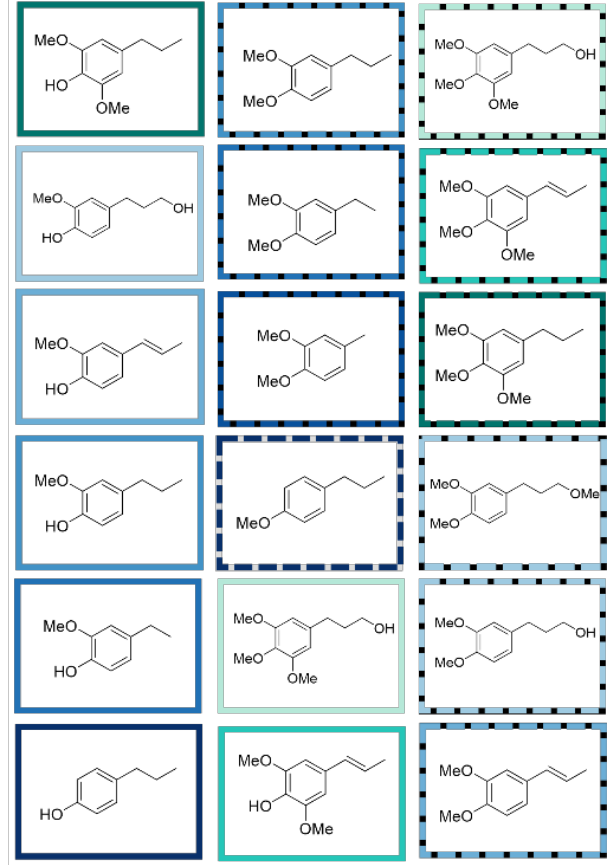
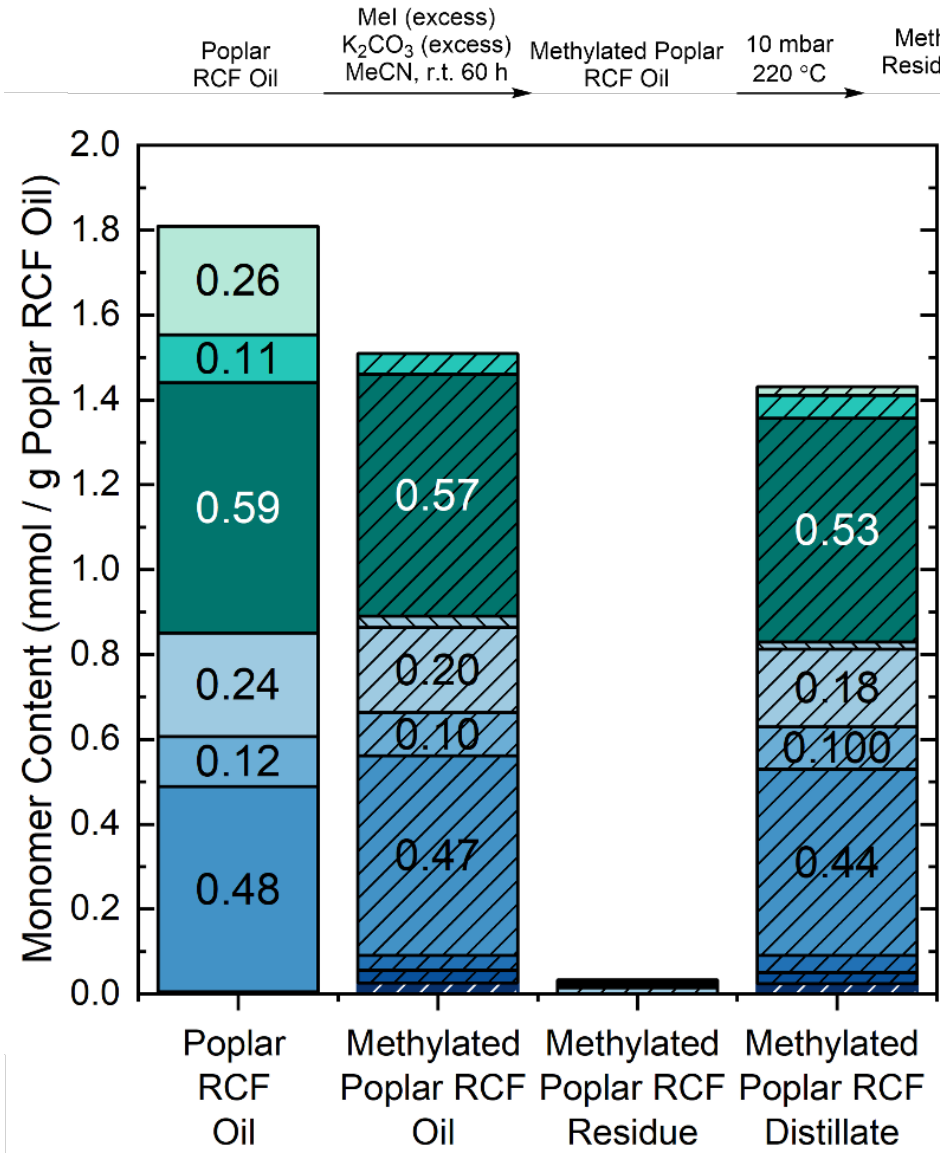
standard conditions =
8 mol% Mn(OAc)₂•4H₂O
6 mol% Zr(acac)₄
6 bar O₂, 150 °C
15 mL AcOH, 1.5 h

R ₁	R ₂	Aromatic Recovery (%)
H	H	38(4)%
H	OH	62(7)%
OMe	H	43%
OMe	OH	51(12)%

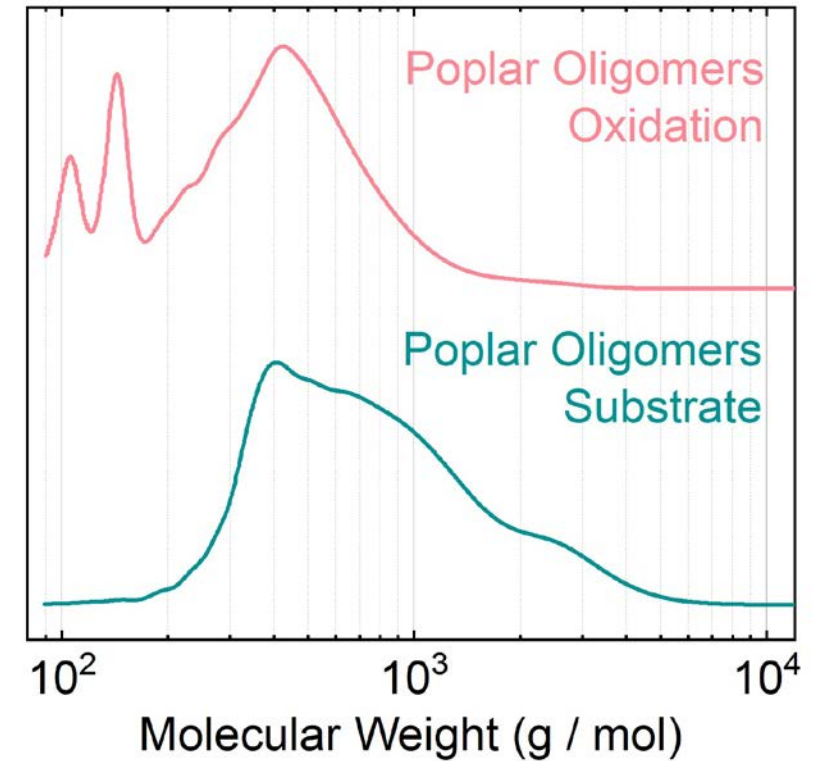
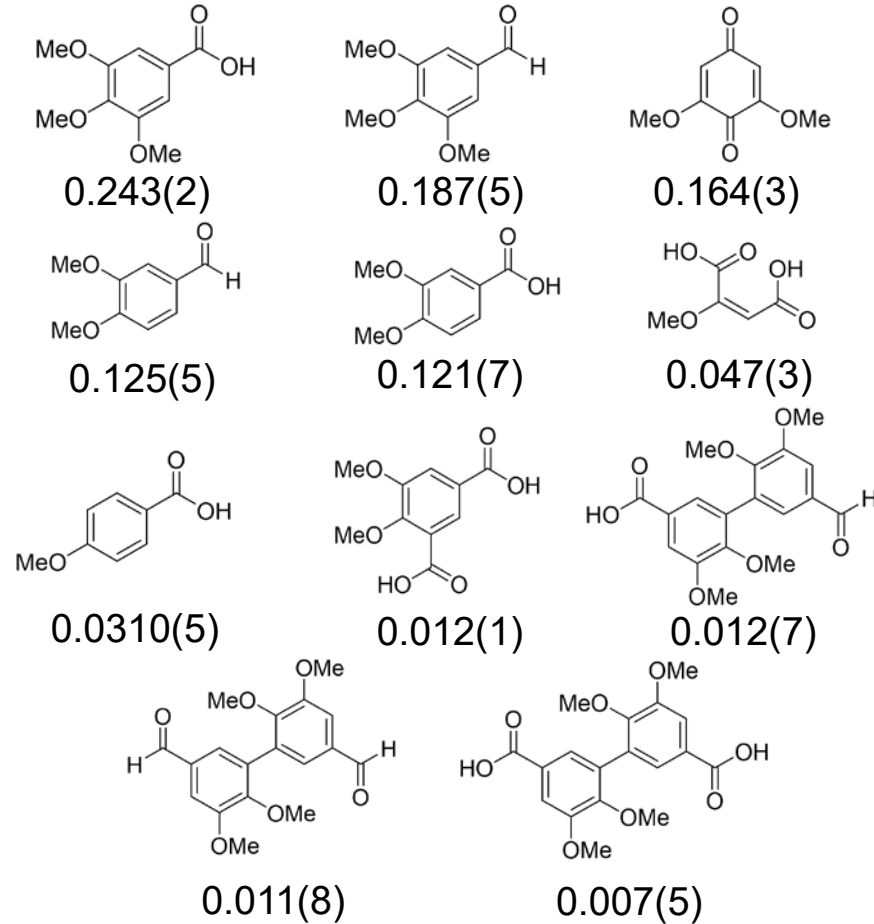
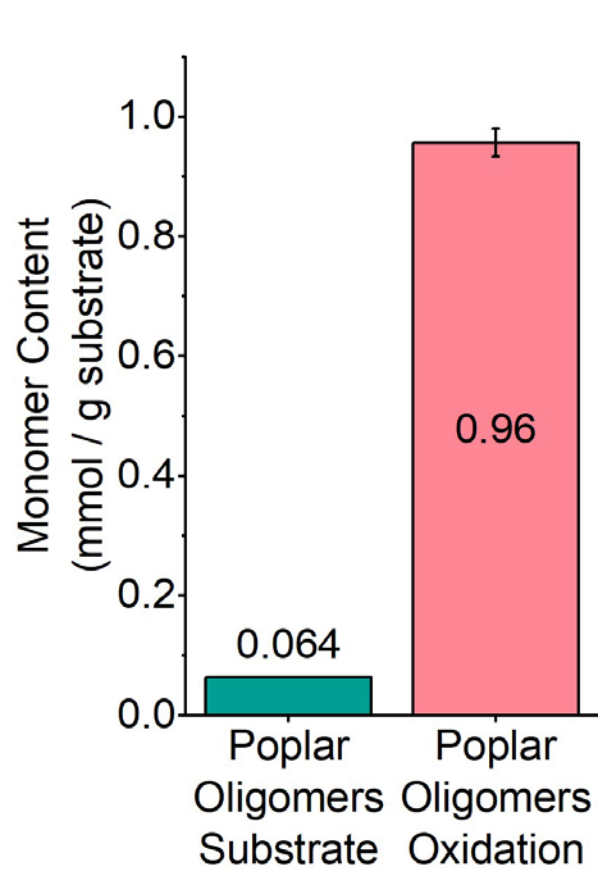
The Cumene Process and Hock Rearrangement



Preparation and Autooxidation of Methylated Poplar Oligomers



Preparation and Autooxidation of Methylated Poplar Oligomers



Bioconversion Pathway

