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Title: Catalytic Routes for the Conversion of Biomass Derivatives to Hydrocarbons and/or Platform Chemicals

Author(s): Silks, Louis A. III

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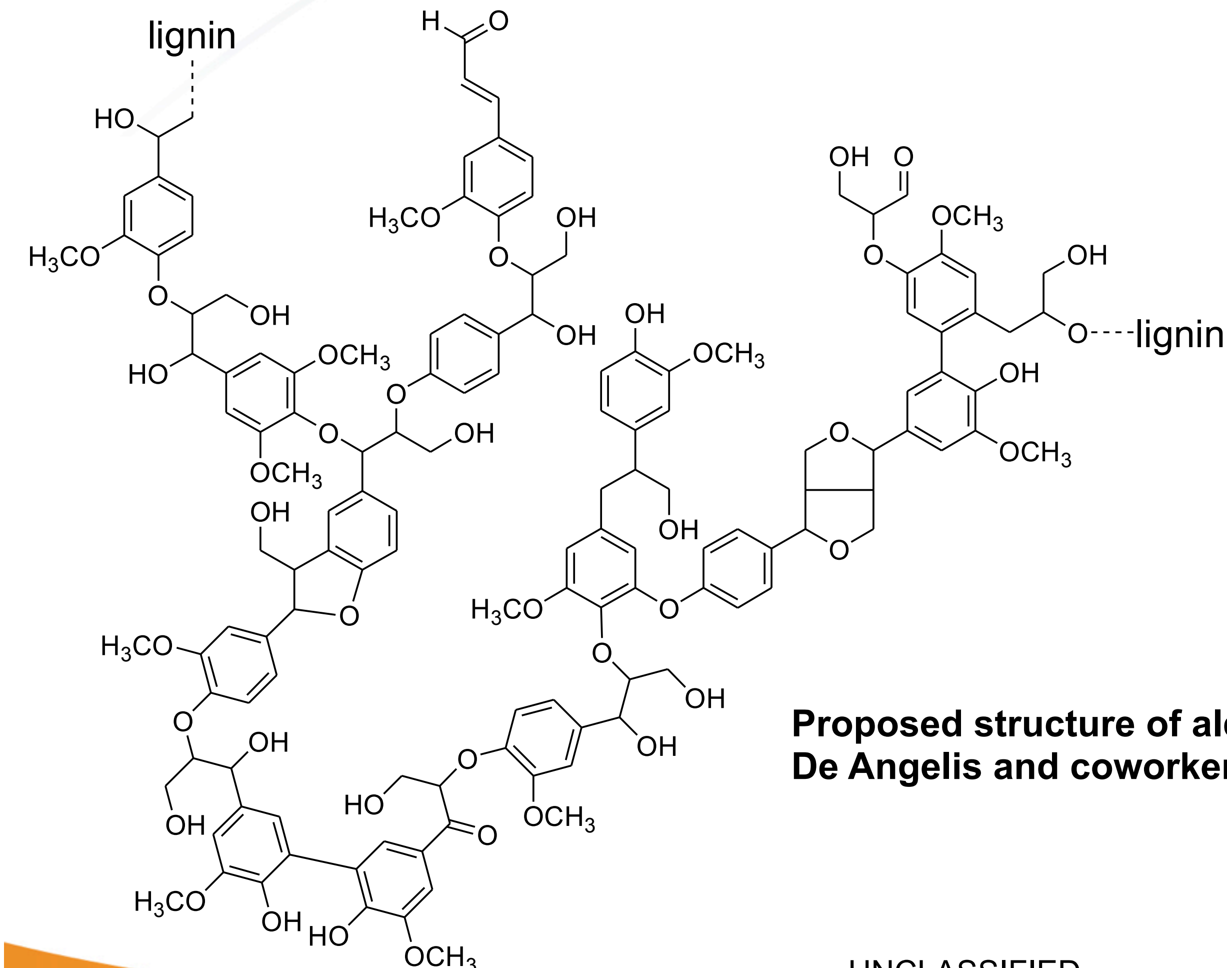
Catalytic Routes for the Conversion of Biomass Derivatives to Hydrocarbons and/or Platform Chemicals

L. A. "Pete" Silks
B11, The Biophysical and Chemistry Team
Oct 7, 2015

Hitachi Chemical Co. America Ltd. LANL Visit

Lignin Presents a Major Challenge in the Production of Biofuels from Lignocellulose. (With Susan Hanson PD to LANL Staff)



relatively little R&D

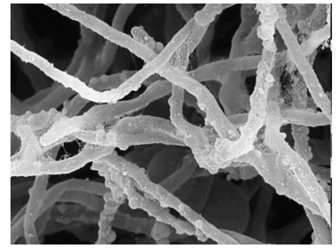
↓

need for mild, selective methods to break down lignin

Proposed structure of alder lignin:
De Angelis and coworkers: *Mass. Spec. Rev.* 2004, *23*, 87.

Biological Lignin Digestion: White Rot Fungus

Degrade lignin using enzymes lignin peroxidase and manganese-dependent peroxidase



http://genome.jgi-psf.org/whiterot1/whiterot1.home.html

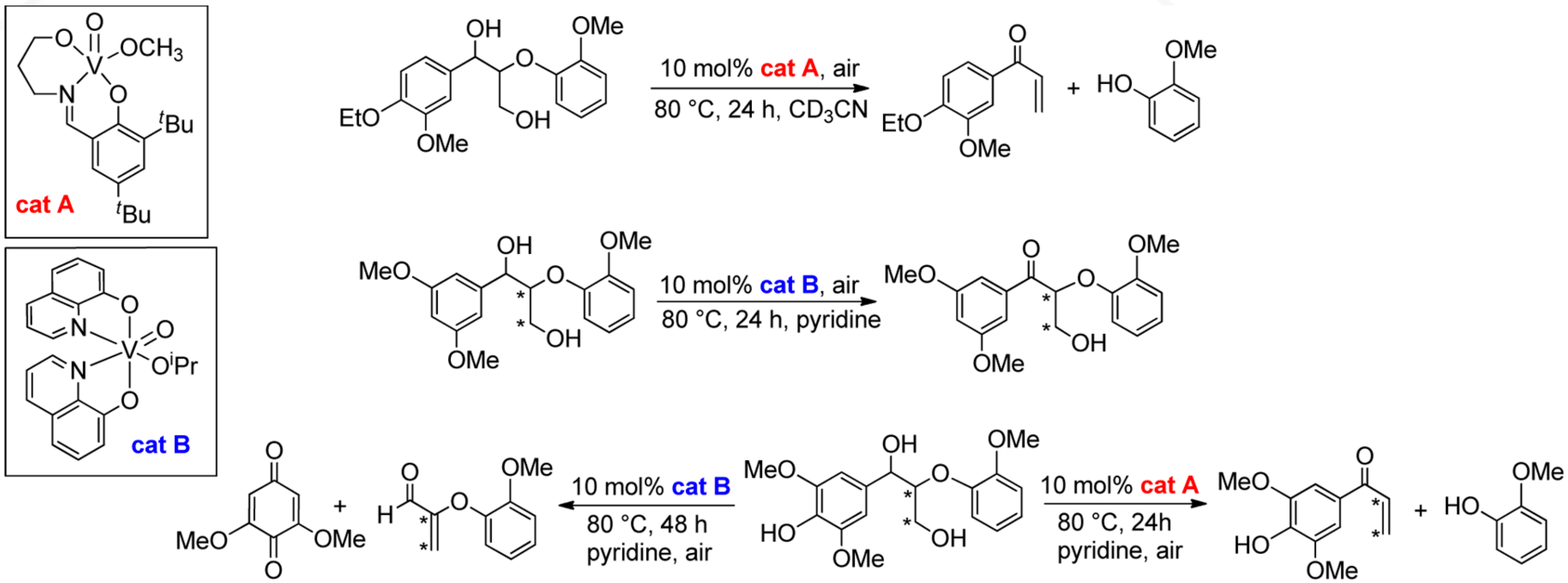
http://www.world-of-fungi.org/

Mechanism under investigation:
one-electron oxidation using radical cation mediator (veratryl alcohol)

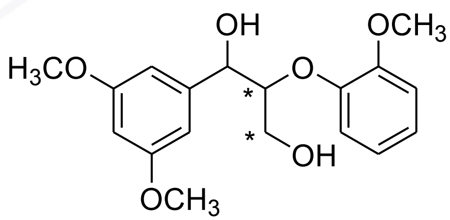
Rates are *slow*:
(pilot plant in Bangor, WA reduced levels of TNT from 1800 ppm to 1200 ppm and 1000 ppm after 30 days and 120 days, respectively)

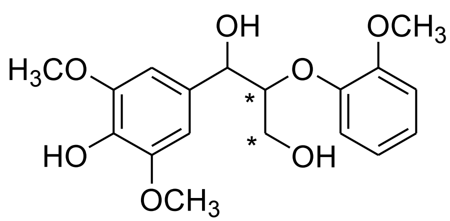
Product inhibition occurs

Issues with selectivity: can degrade many compounds, including polyaromatics


cat A
cat B
10 mol% cat A, air
80 °C, 24 h, CD3CN
10 mol% cat B, air
80 °C, 24 h, pyridine
10 mol% cat B
80 °C, 48 h
pyridine, air
10 mol% cat A
80 °C, 24h
pyridine, air

Using Model Compounds to Elucidate Catalytic Reactivity and Selectivity



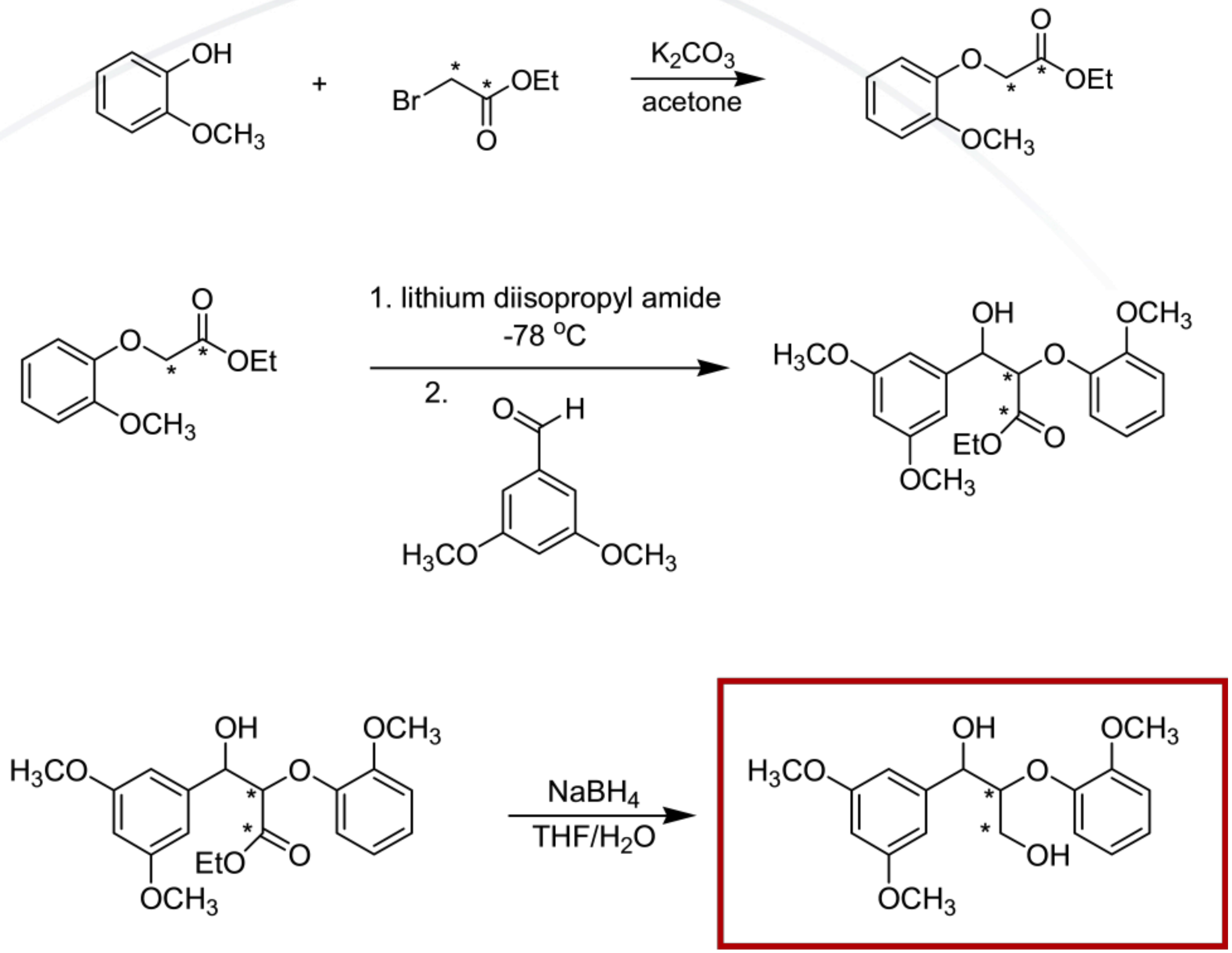


Multistep synthesis from ^{13}CO

↓

^{13}C labels allow for rapid product identification

Successful Synthesis of Labeled Compounds

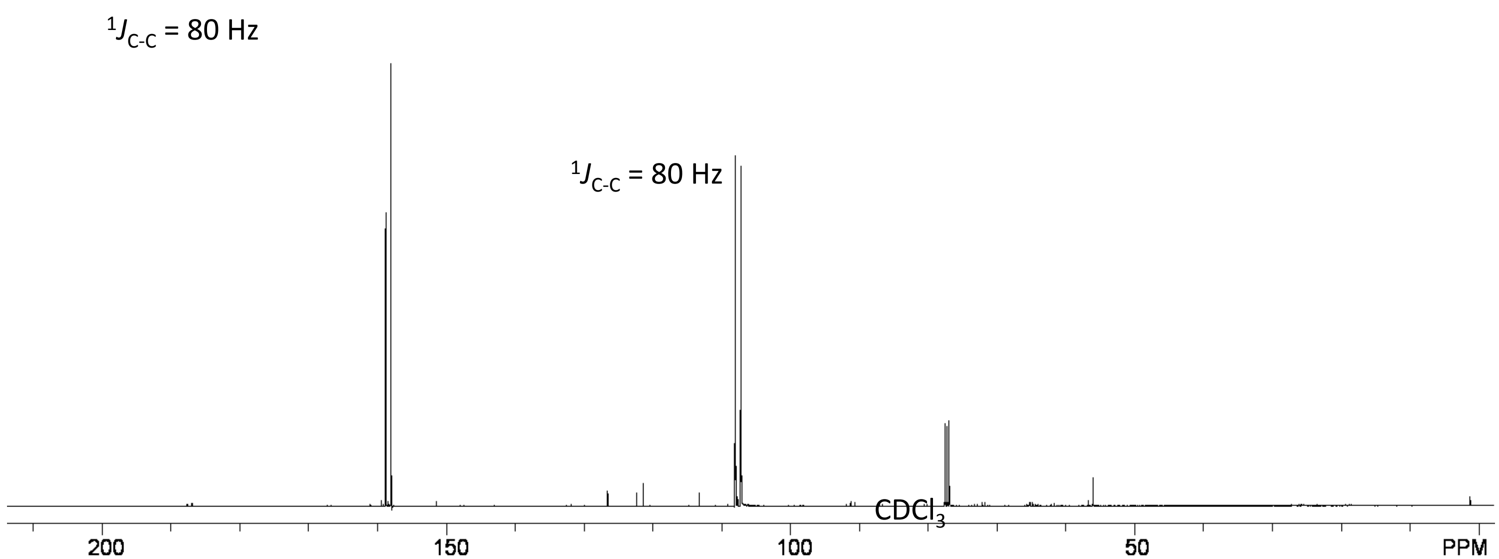


phenolic analogue also prepared

^{13}C Label Allows for Rapid Product Characterization

Isolated product from phenolic lignin model oxidation, $CDCl_3$

Reaction conditions: $(HQ)_2V(O)O^iPr$ 5 mol%, NEt_3 10 mol%, dichlorethane solvent, 80 °C, 40 h



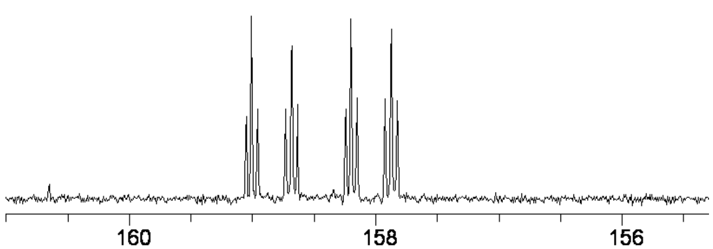
Proton-Carbon Coupling Provides Additional Insight into Molecular Structure

Proton-coupled carbon spectrum, $CDCl_3$

$^{1}J_{C\text{-}C}$ = 80 Hz

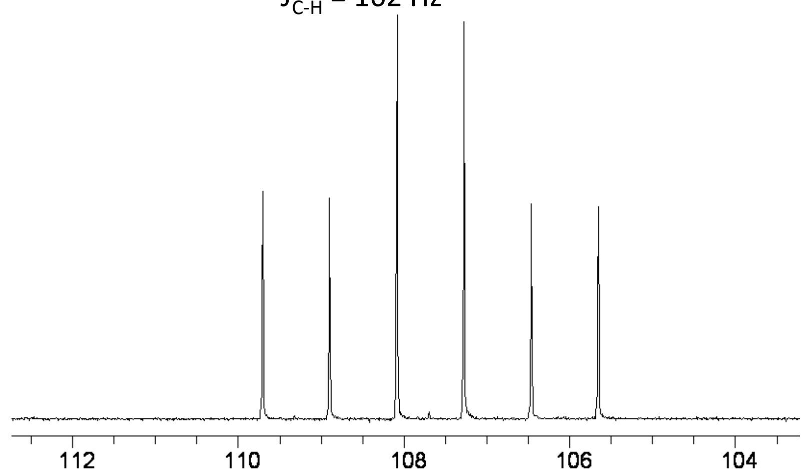
$^{2}J_{C\text{-}H}$ = 34 Hz

$J_{C\text{-}H}$ = 4 Hz

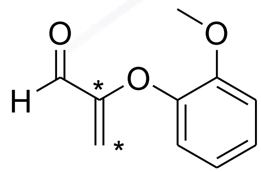


$^{1}J_{C\text{-}C}$ = 80 Hz

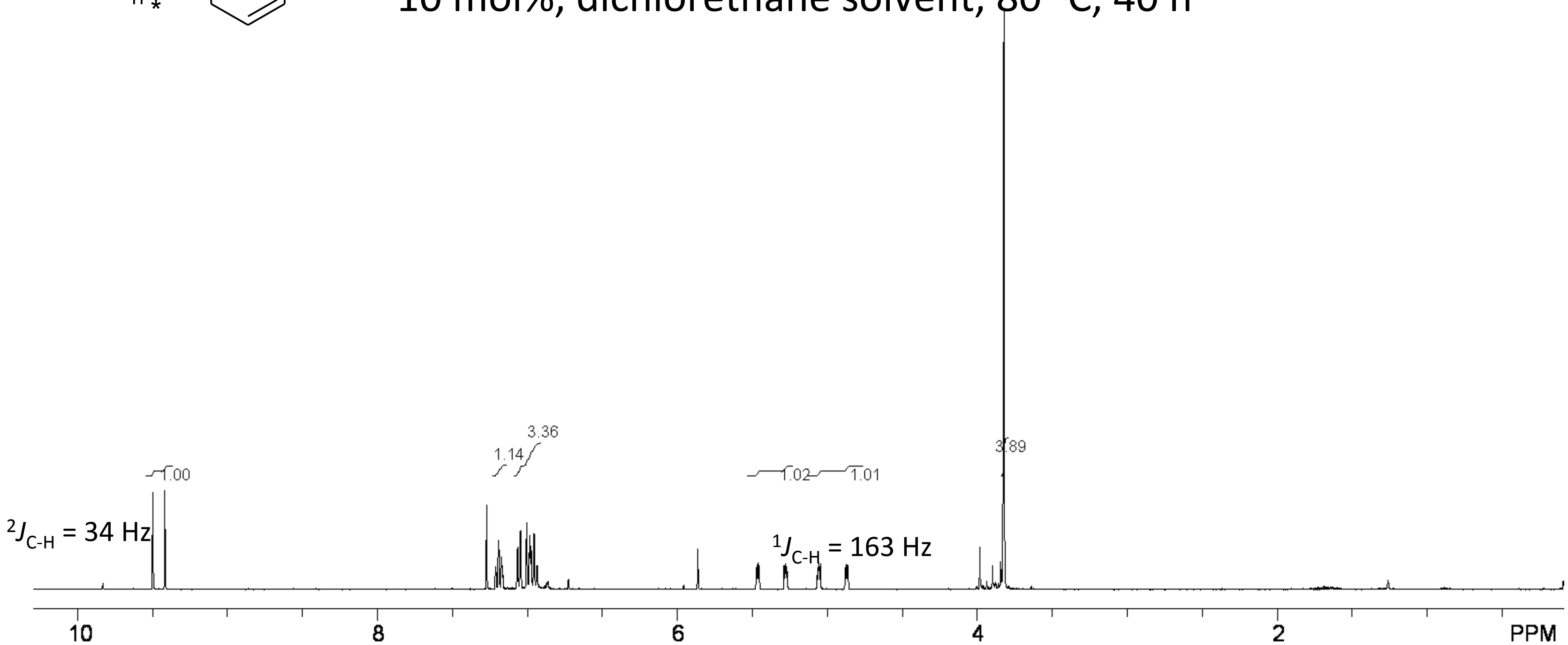
$^{1}J_{C\text{-}H}$ = 162 Hz



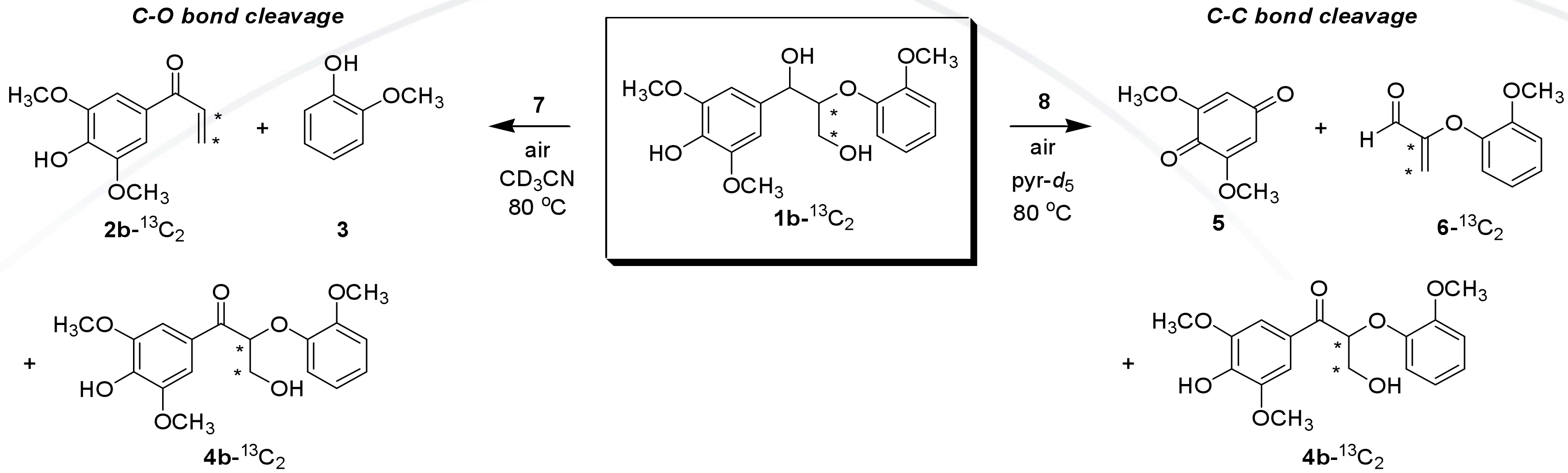
A Unique C-C Bond Fission Product



Oxidation of phenolic lignin model $(HQ)_2V(O)O^iPr$ 5 mol%, NEt_3 10 mol%, dichlorethane solvent, 80 °C, 40 h



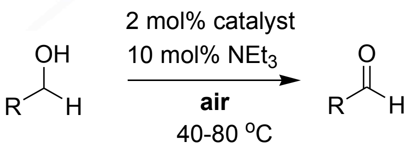
Selectivity of Lignin Model Oxidations

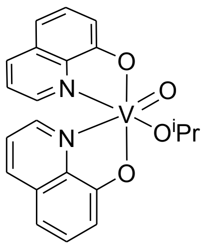


In conclusion, we have found that quinolinate complex oxidatively breaks the C_α-C_{aryl} bond in lignin model compound **1b.** This C_α-C_{aryl} bond cleavage is a new reaction mode for vanadium, and has only previously been documented for cobalt (details about mechanism?). Although a one electron pathway has also been proposed for the oxidation of a lignin model compound using Toste catalyst, the oxidation of **1b** with the Toste catalyst proceeds with a markedly different selectivity, affording C-O bond cleavage product **2b** and none of the C_α-C_{aryl} bond cleavage product.

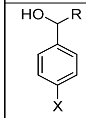
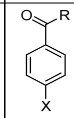
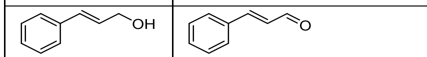
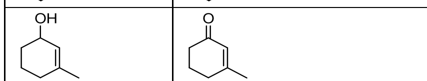
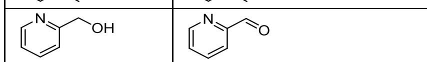
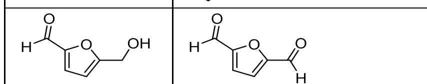
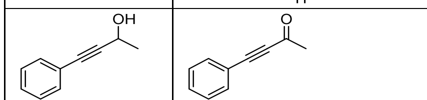
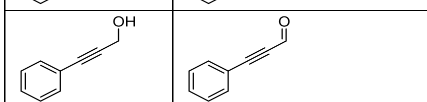
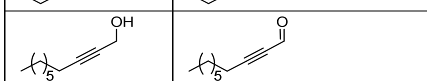
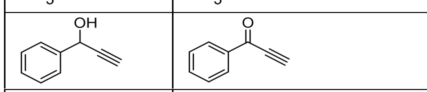
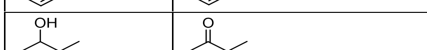
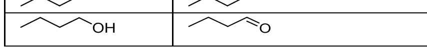
The remarkably different selectivities observed for the two vanadium catalysts reveal the complexity of vanadium mediated oxidations and supports the viability of homogeneous catalysts for controlling selectivity in the aerobic oxidation of lignin.

Expansion of the Scope of the Project



catalyst = 

-effective for benzylic, allylic, and propargylic alcohols

substrate	product	% yield
	 R = H X = H	92
	= OCH_3	96
	= NO_2	96
	X = H R = Ph	93[d]
	= CH_3	95[a,f]
	= cyclopropyl	90[a,c]
	= ^{i}Pr	(20)[a,d]
	= ^{t}Bu	0[a,d]
		98
		96[a]
		98[a]
		94
		96[a]
		(80)
		(60)
		(38)
		(5)
		(1)[b]

Substrate scope of the catalytic oxidation. Conditions: 2 mol% **8**, 10 mol% NEt_3, 1,2-dichloroethane solvent, 60 °C, 24 h. [a] = 80 °C; [b] = 100 °C, dichlorobenzene solvent; [c] = 48 h; [d] = 72 h; [f] = 1 equivalent NEt_3.

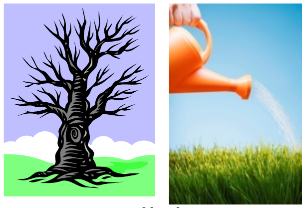
Key Application Areas	Fibers & Nonwovens	Adhesives (Hot Melt and PSA)	Films	Molded Parts	Blow Molded Bottles	Key Chemicals		
						Acrylic Acid	Surfactants	Diacids & diols
Bio-based options in Market	Natural Fibers, PLA, Cellulosics	Natural Rubber-based	TPS Blends, PLA, Cellulosics,	TPS Blends, cellulosics, Nylon 11	PLA	None	~35% of today's surfactants	1,3 PDO Sebacic Acid
Emerging materials, monomers, or other precursors	Bio-derived aliphatic polyesters, Modified or derivatized natural polymers	Bio-derived urethanes, PHA, Soy protein, Soy polyols, Sugar/acrylics, Starch derivatives.	Bio-LLDPE (via ETOH from sugar cane),	PHA, bio-derived fillers	Bio-HDPE (via ETOH from sugar cane),	Via Glycerol, Via 3-hydroxy proprionic acid (3-HPA) from sugars	Veg. Oils, Sophoro-lipids and Rhamnolipids from lipid-based substrates	**Diacids** Succinic acid, adipic acid, FDCA, Others? **Diols** Isosorbide, butanediol, Others?
Critical Needs	Cost-competitive Melt spinnable, water-resistant, bioderived fibers	Cost-competitive, bio-derived thermoplastic elastomers, tackifiers, and oil modifiers	Cost competitive bio-derived full or partial replacements for PE, PP, & PET Films.	Bio-route or non-petroleum route to propylene, or cost effective PP substitute material	Biopolymer with PE/PP-like density, barrier, heat stability, impact strength & chemical resistance	P&G's need is primarily absorbent gelling matls, but AA is also a key feedstock for plastics, paints, & coatings	Cost-competitive bio-derived fatty acids and alcohols	Cost-competitive monomers for aliphatic polyesters, polyamides, other polymers, & chemicals
What break-throughs are required to meet the need?	?	?	?	?	?	?	?	?

PLA = polylactic acid,
PSA = pressure sensitive adhesive
PHA = polyhydroxyalkanoates
PDO = propane diol

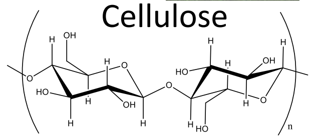
ETOH = ethanol
TPS = Thermoplastic Starch
FDCA = Furan dicarboxylic acid

Feedstocks

Wood Chips, Grasses
Stover / Husks, Sugars



Cellulose



Algal biomass: Triglycerides and Carbohydrates

Bio-Refinery

- Fermentation
- Dehydration / Acidic Treatment
- Hydrogen-based Treatments

Renewable Chemicals

Alcohols
Ethanol, Butanol
Acids/Esters
Levulinic, Acetic
Acrylic, Succinic
Ketones
Acetone,
Methyl-Vinyl
Furfurals
Hydroxy-Methyl,
Methyl,
Furfural

Direct catalytic carbon chain extension on oligosaccharides followed by HDO.

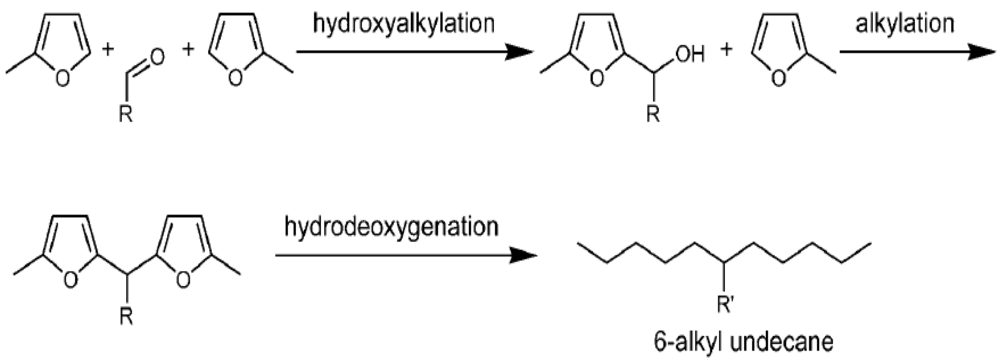
Organocatalytic chain extension, (e.g. ketone plus a furan aldehyde) then HDO to alkane.

Hydrocarbon Fuels and Advanced Chemical Feedstocks

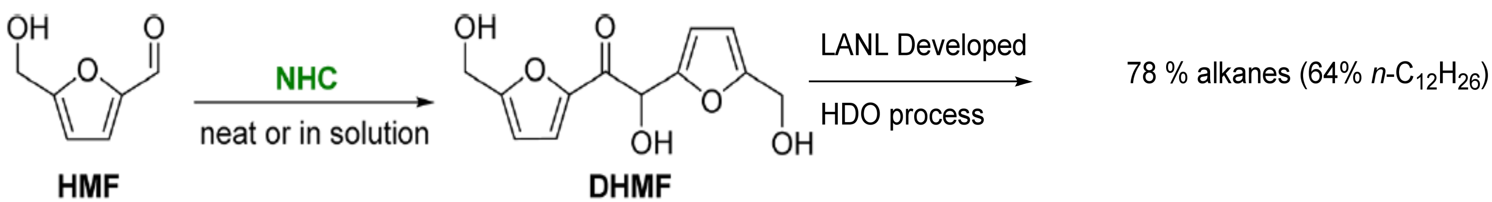
*** Companies such as xF were accessing furanics and levulinates from raw non-food based biomass with about ~10x decrease in current costs.**

*** HDO = hydrodeoxygenation (oxygen/hydrogen exchange on carbon chain).**

Current state-of-the-Art



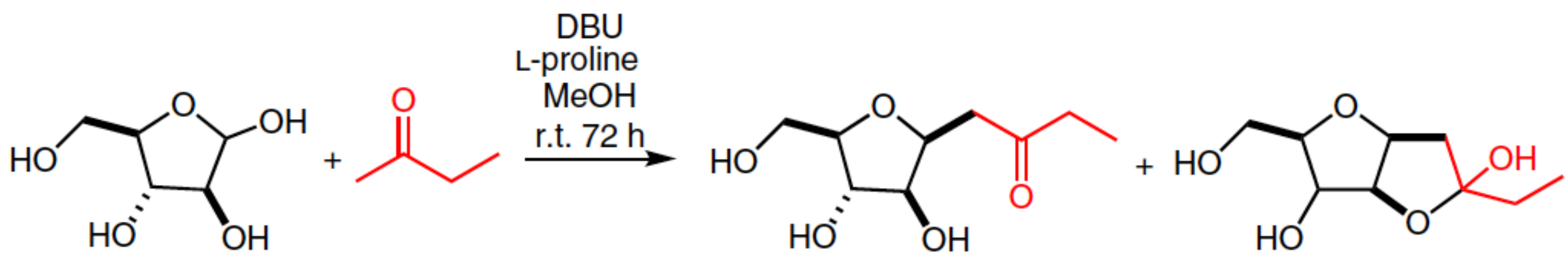
“Production of High-Quality Diesel From Biomass Waste Products,” Corma *et al.* *Angew Chem.* **2013**, *50*, 2375.



Integrated Catalytic Process for Biomass Conversion and Upgrading to C12 Furoin and Alkane Fuel,” Liu and Chen, *Catalysis*, **2014**, *4*, 1302.

UNCLASSIFIED

Current state-of-the-Art



44% overall yield, de > 98:2 (related to C-glycosylation)

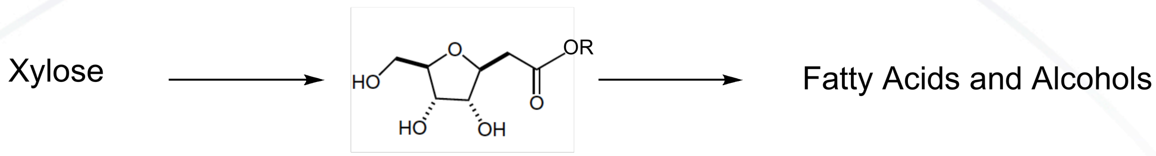
Unprotected carbohydrates were reacted in amine-catalyzed cascade reactions with various methyl ketones to give a direct access to C-glycosides by an operationally simple protocol. As the reaction mechanism,an aldol condensation followed by an intramolecular conjugate addition is assumed.

LANL Efforts:

1. Use of biomass carbonyl compounds. Levulinic acid and esters. 5+ 5,6 Carbons. Double additions of biomass carbonyl compounds will give access to higher carbon chains.

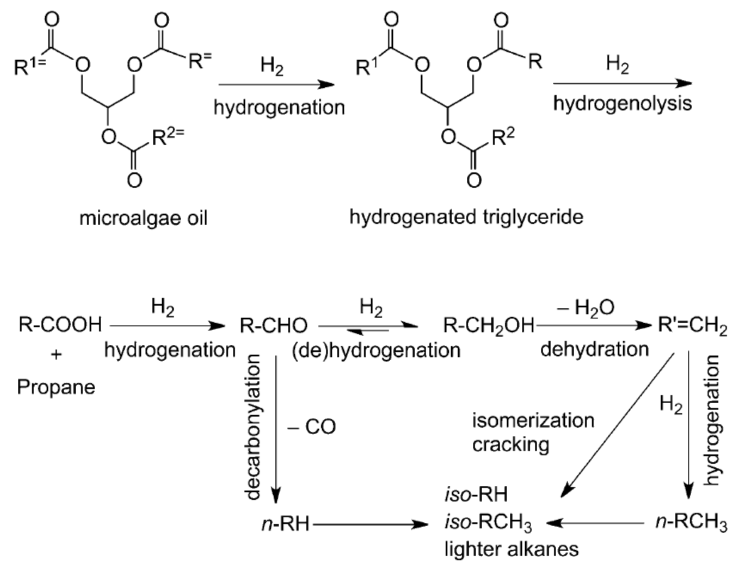
2. Other conditions which favor industrial scale up.

LANL Approach (Group B11 and C-Div)



Collaborative with J. Kiplinger (C-Div) who will be looking at actinide catalysis as model systems for potential lanthanide use.

LANL Approach (Group B11 and C-Div)



$R^{1=}$, $R^{2=}$, $R^{=}$: unsaturated alkyl chain

Methanation: $CO + H_2 = CH_4 + H_2O$

Scheme 1. Proposed reaction pathway for transformation of microalgae oil to alkanes over bifunctional Ni/HBeta catalysts.

Lercher, 2012

LANL Approach (Group B11 and C-Div)

C. Kordulis et al. / Applied Catalysis B: Environmental 181 (2016) 156–196

It seems that the use of nickel phosphide or, mainly, NiMo phosphidecatalysts with proper Ni/Mo ratio results to the impressive inhi-bition of deCO and the acceleration of HDO.

Quite promising are the studies devoted to the addition of promoters (La, Ce, P) in the traditional NiMo andNiW hydrotreatment catalysts working in their reduced form.