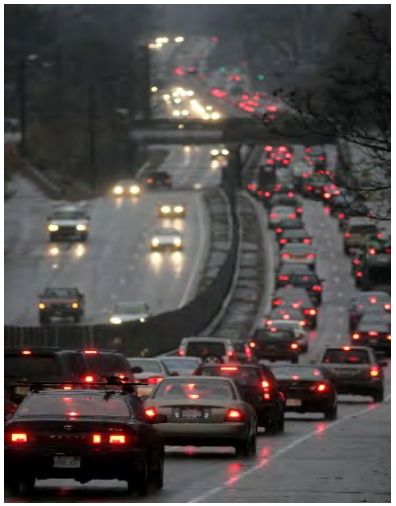
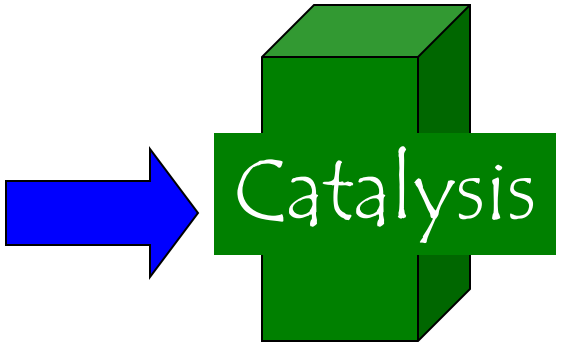
The Petrochemical Industry: A 20th Century Success Story

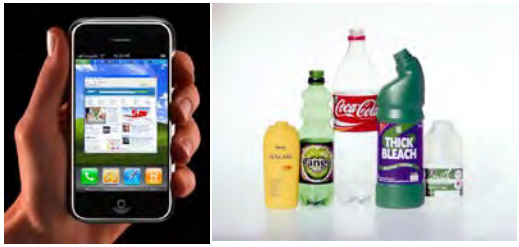
fuel



Interesting Materials

Catalysis Enabling 21st Century E²





Energy

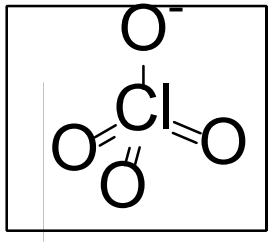
Environment

- Reactions of chlorine oxyanions
- Biomass conversion
- Kinetics of olefin polymerization

Perchlorate: Rocket Science

Rocket fuel, missiles, and fireworks.

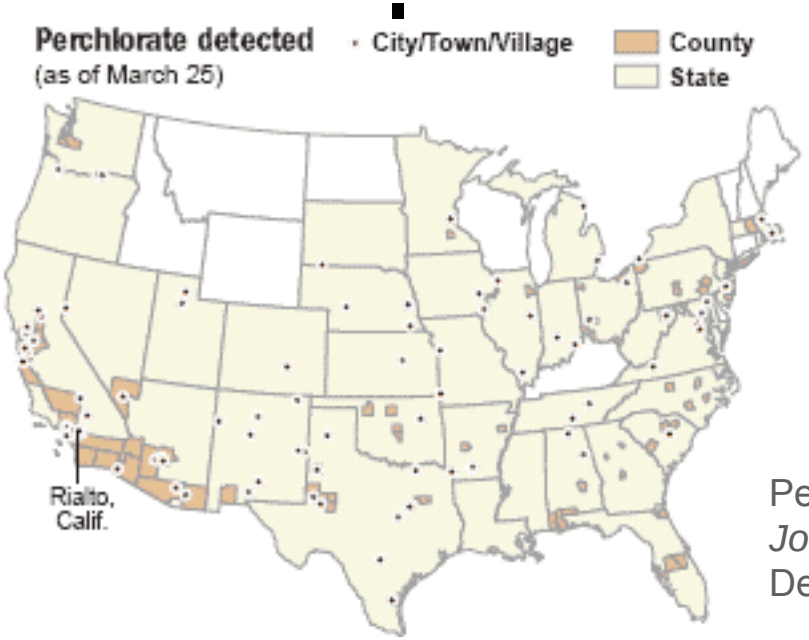
Uses



Water Contaminant

Toxicity

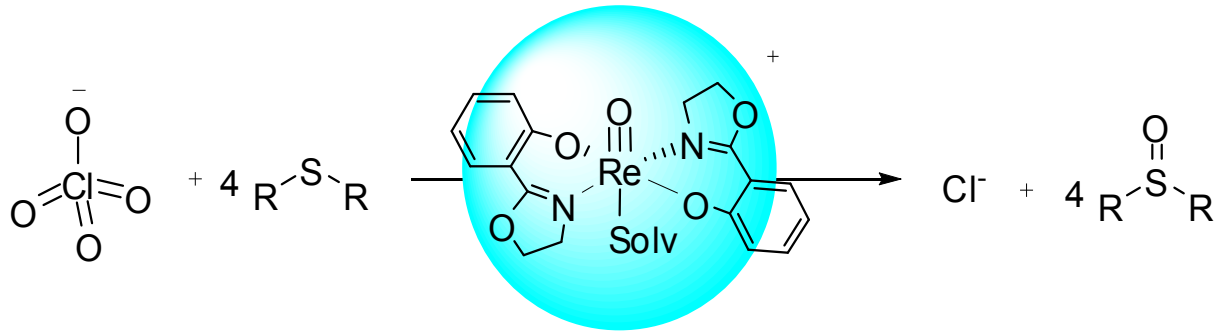
Interferes with the functioning of the thyroid.

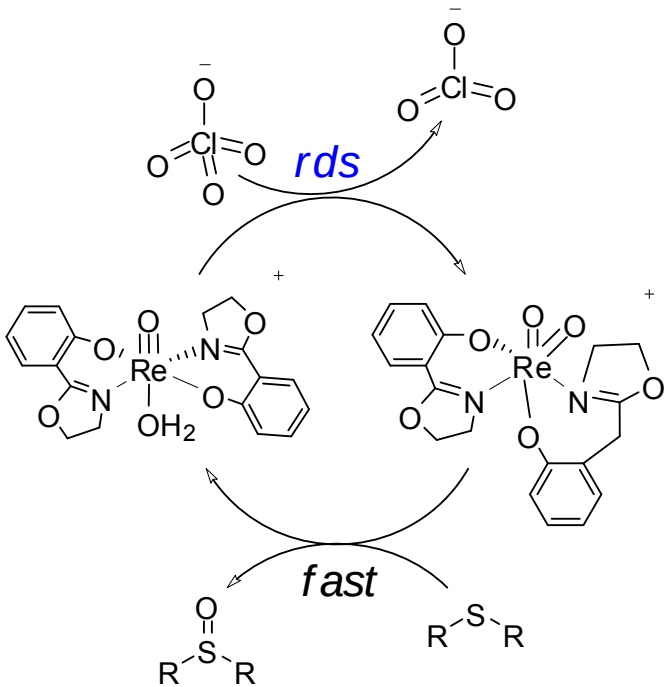


Peter Waldman, *The Wall Street Journal- Online* (WSJ.com), December 16, 2002.

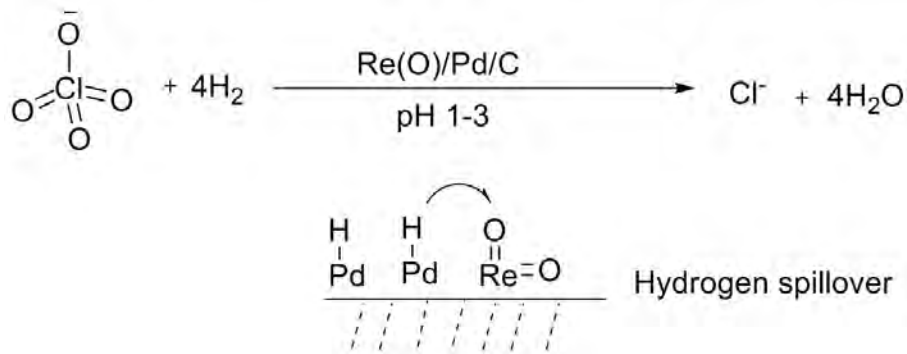
Reduction Via Oxygen Atom Transfer (OAT)

Mechanism





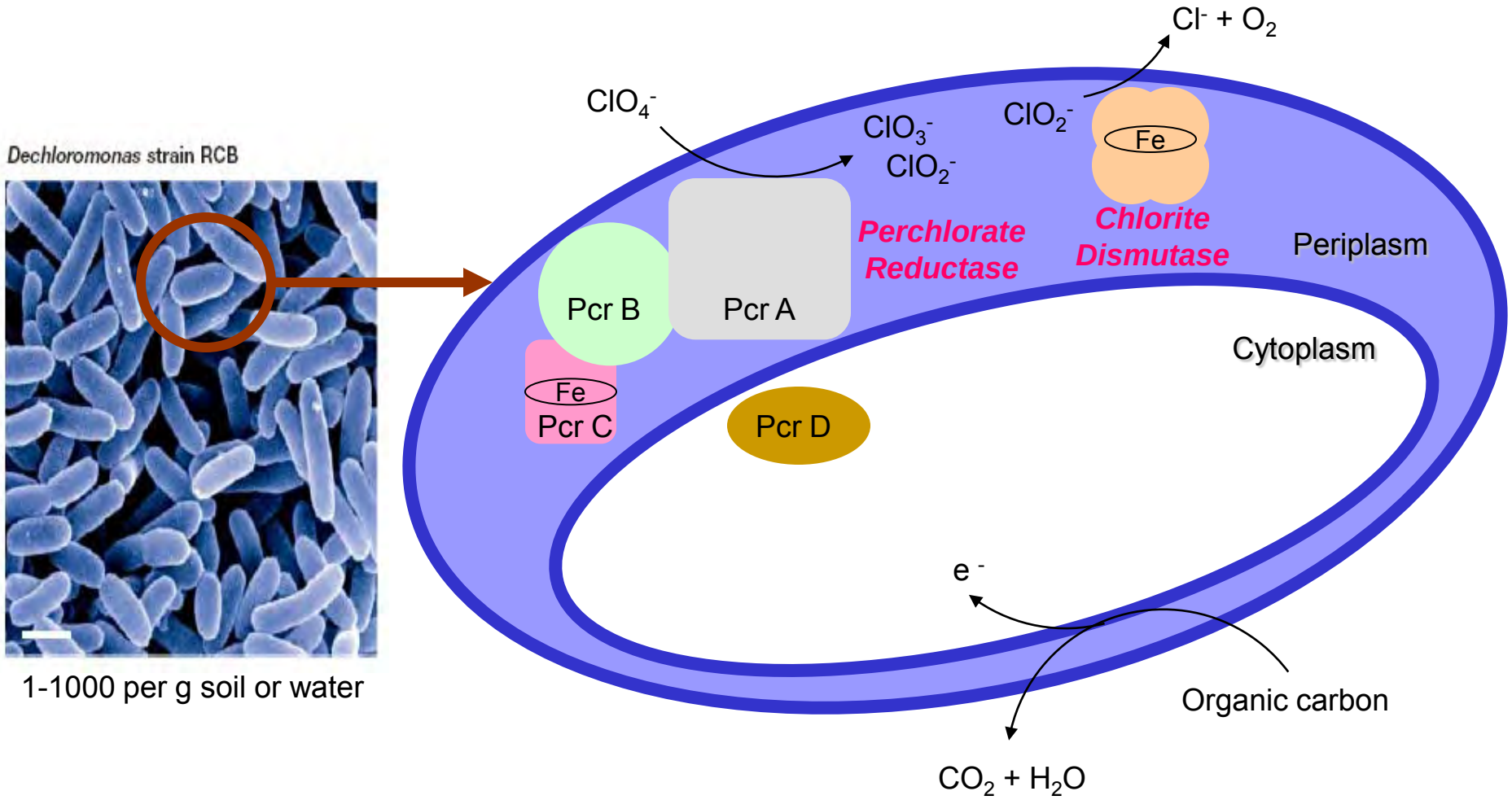
John Shapley (UICU)



Environ. Sci. Tech. **2007**, *41*, 2044.

Abu-Omar, *Chem. Comm.* **2003**, 2102.
Abu-Omar *et al Inorg. Chem.* **2004**, *43*, 4036.

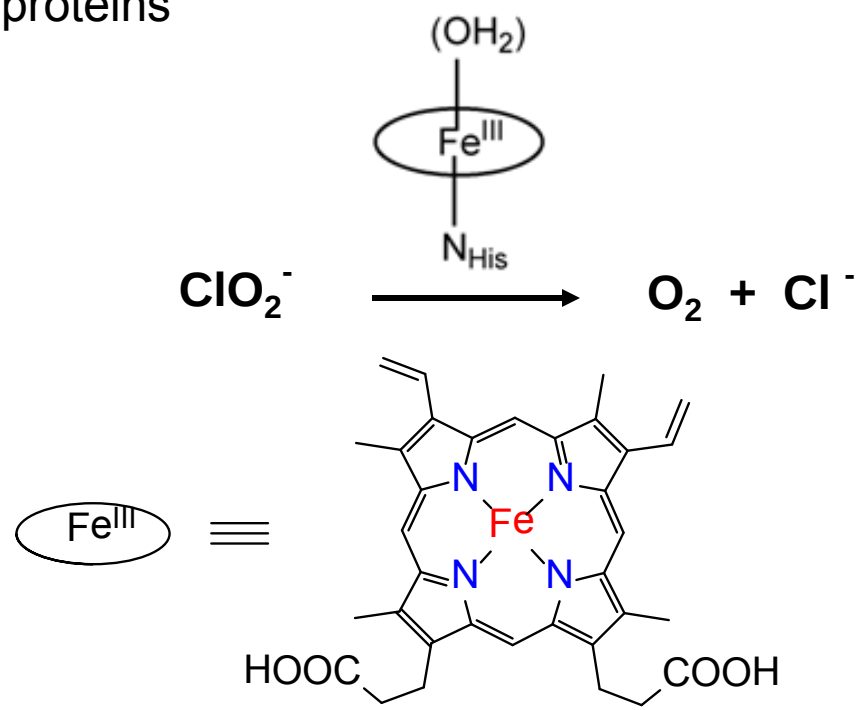
Perchlorate-Reducing Bacteria (PRB)



Coates et al, *Nature Reviews Microbiology* **2005**, *2*, 596.

Chlorite Dismutase

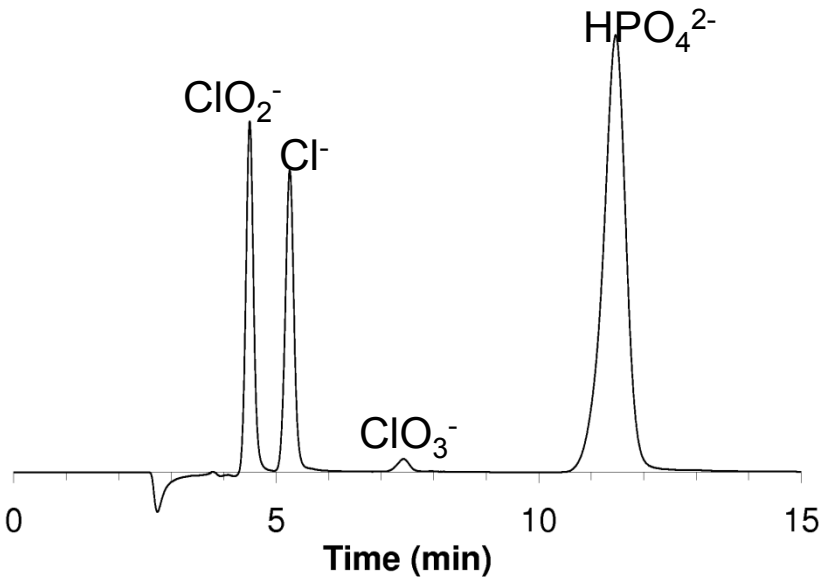
- Homotetramer, 100 -120 kDa
- 1 heme *b* per monomer
- Histidine ligated heme
- No sequence homology with other proteins
- K_m ~ 215 μM
- k_{cat} ~ 7500 s^{-1}
- k_{cat}/K_m = 3.5 x 10^7 $M^{-1}s^{-1}$



$$ClO_2^- \xrightarrow[\text{0.050 M}]{\text{85 nM cld}} O_2 + Cl^-$$

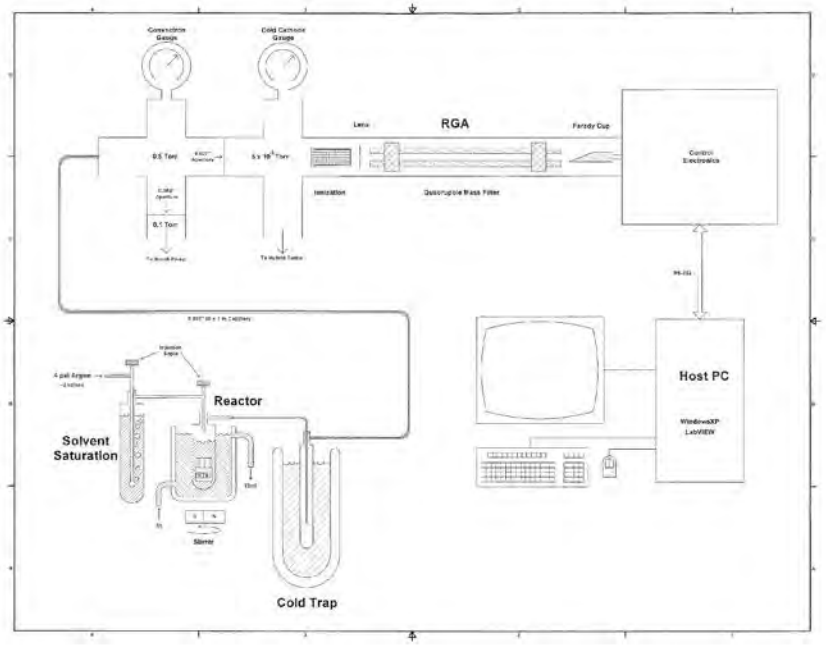
Amanda

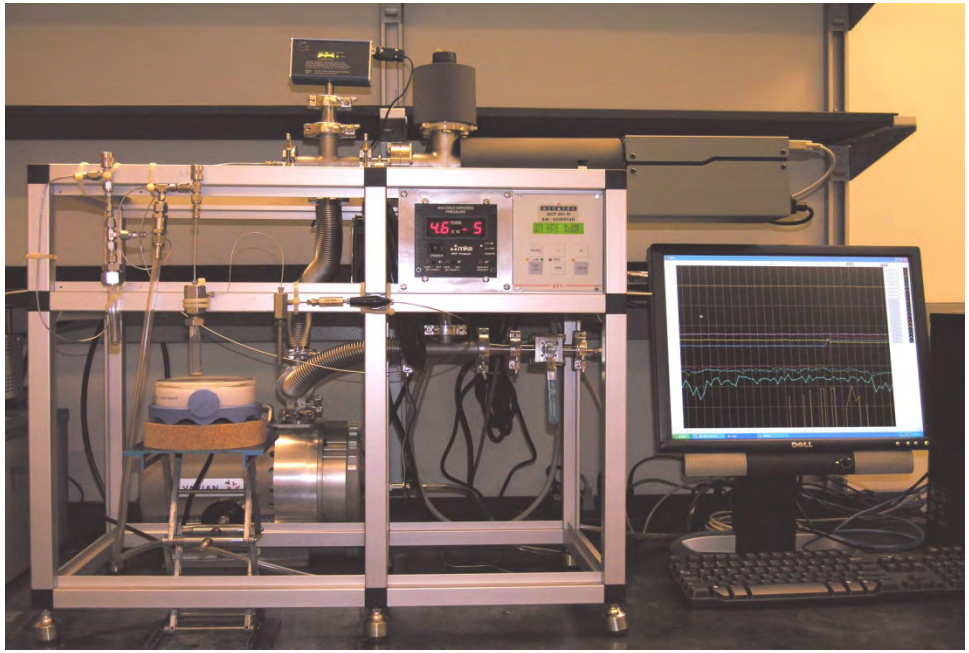
Mike



Compound	C_i mM	C_∞	Recovery	% Yield
O_2	0	4.6 mL	4.6 mL	41
Cl^-	2.8	25.7 mM	22.9 mM	49
ClO_3^-	1.6	1.4 mM	0	0
ClO_2^-	46.7	26.4 mM	26.4 mM	51

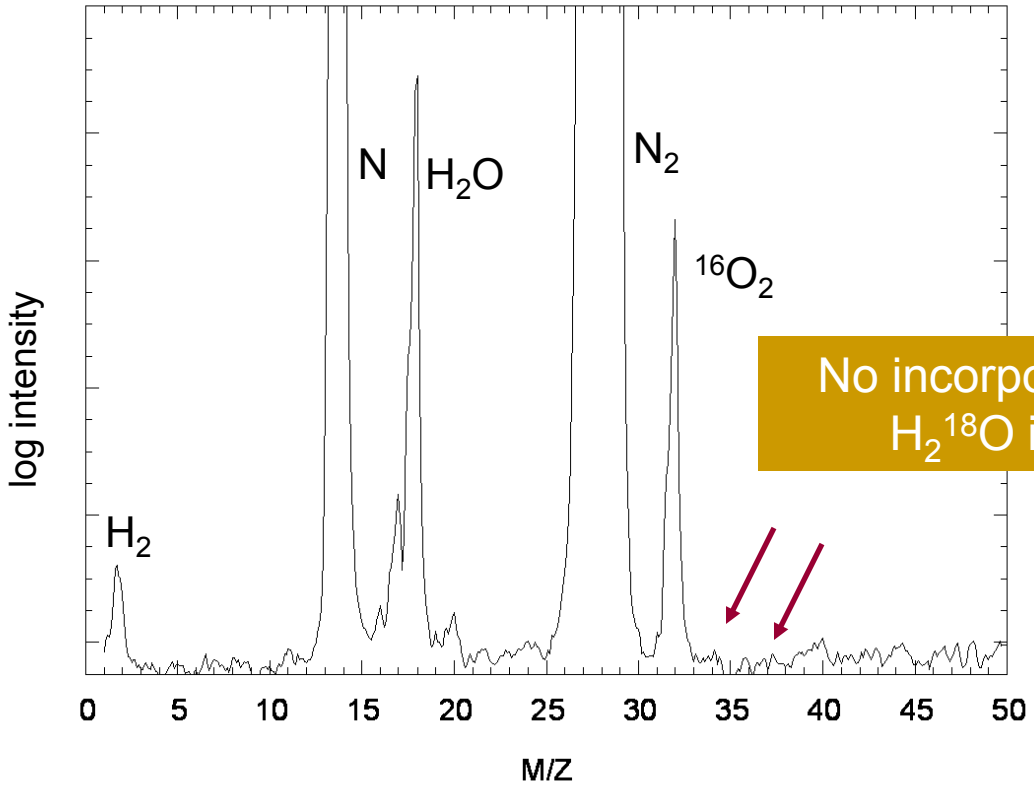
19th Century mass spectrometry





Isotope Labeling

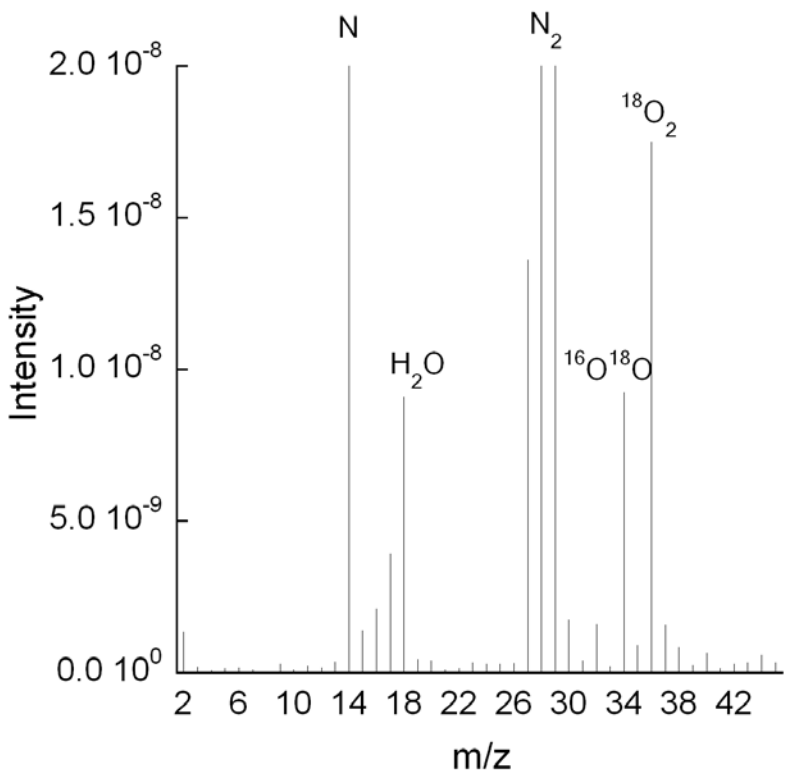
$$ClO_2^- \xrightarrow[H_2{}^{18}O]{Cld} O_2 + Cl^-$$



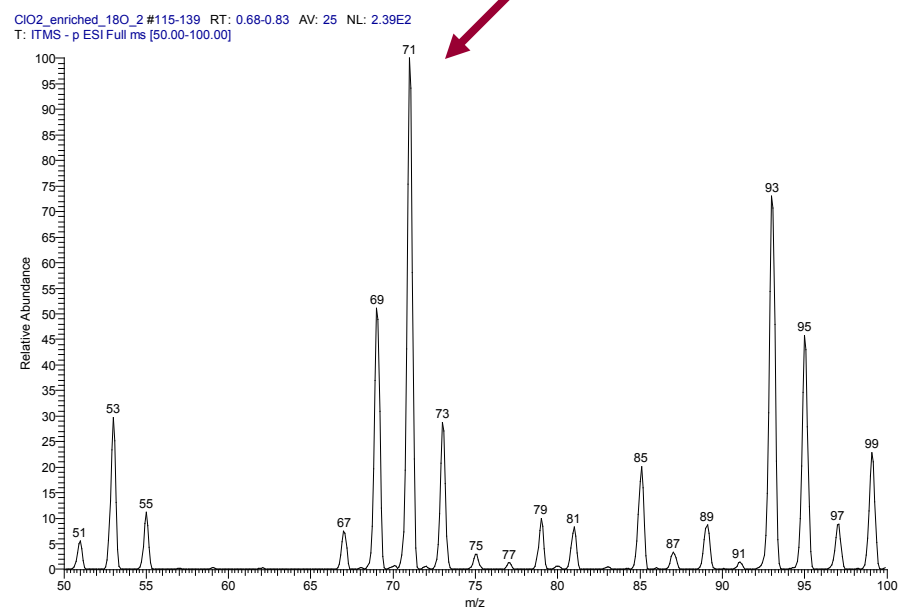
No incorporation of ^{18}O from $H_2{}^{18}O$ into O_2 product

$$Cl^{18}O_2^- \xrightarrow[H_2O]{Cld} O_2 + Cl^-$$

77%

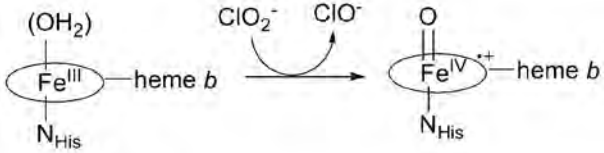


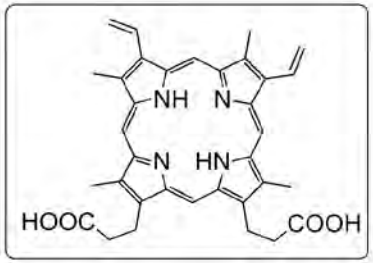
$Cl^{18}O_2^-$

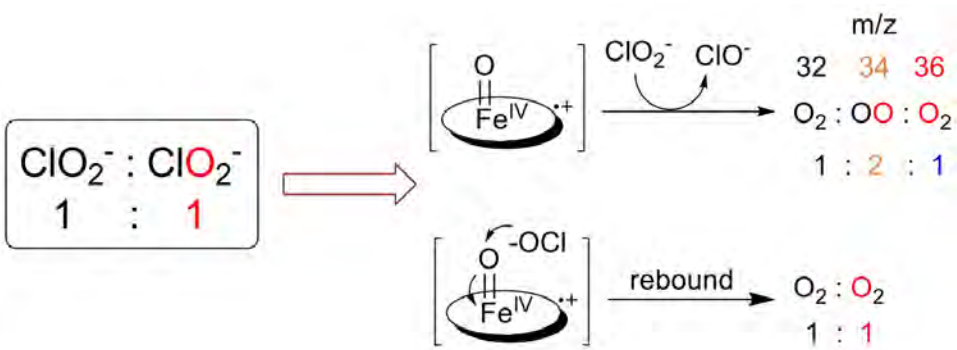


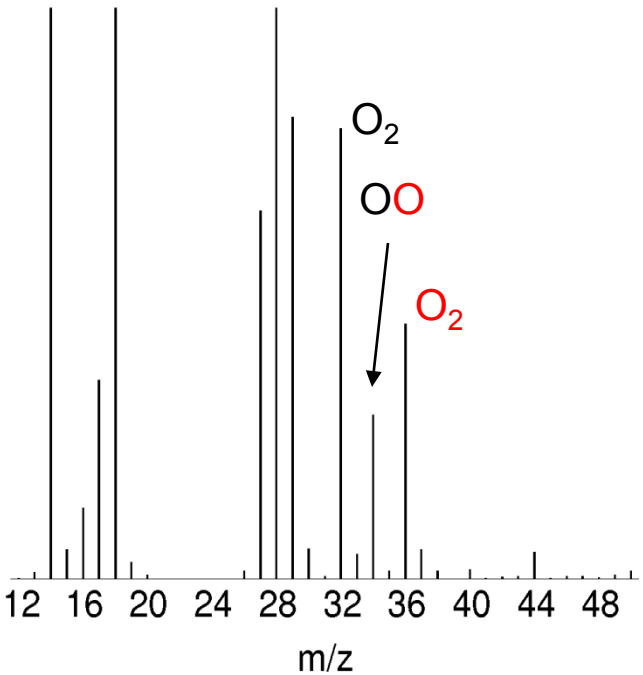
Both O atoms in the evolved O_2 derive from chlorite

Cross Over Experiment

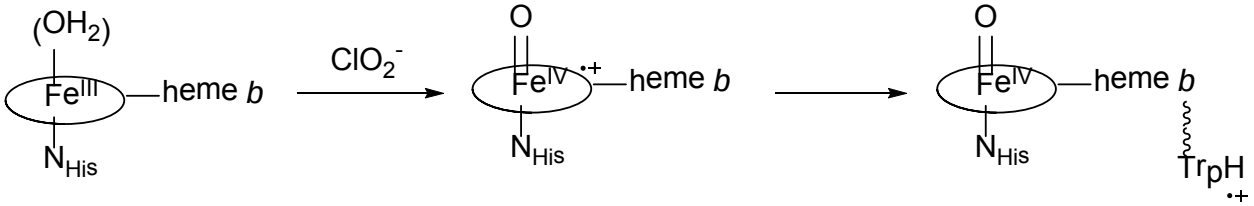


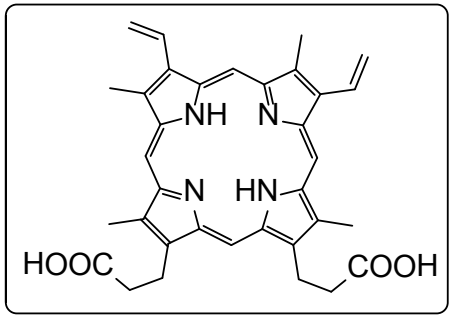


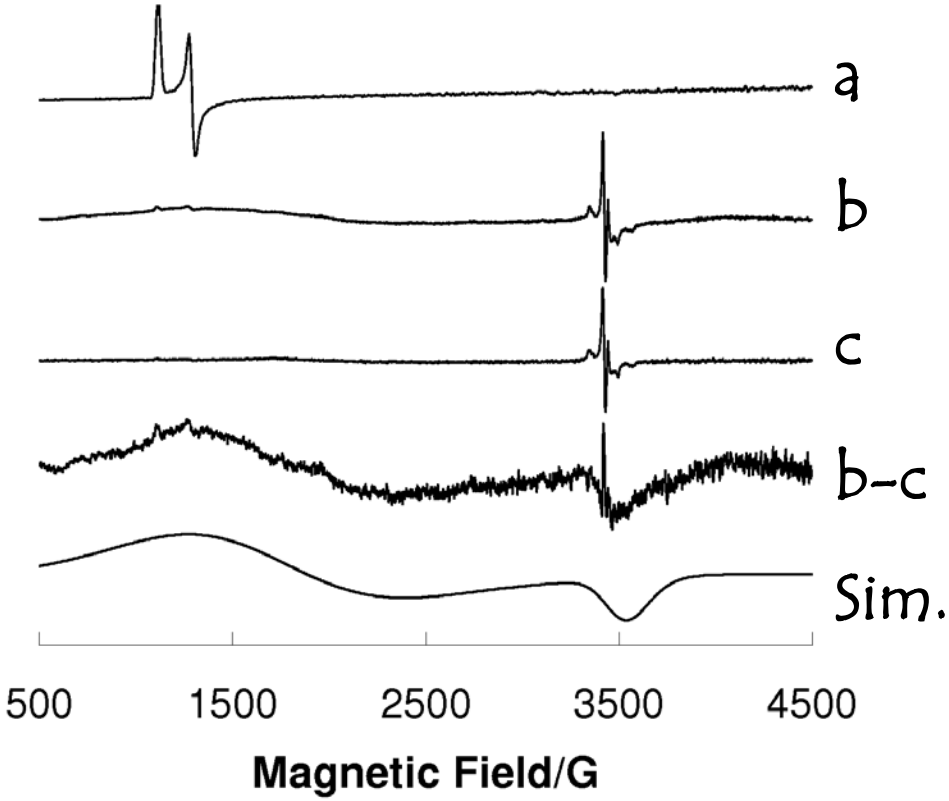




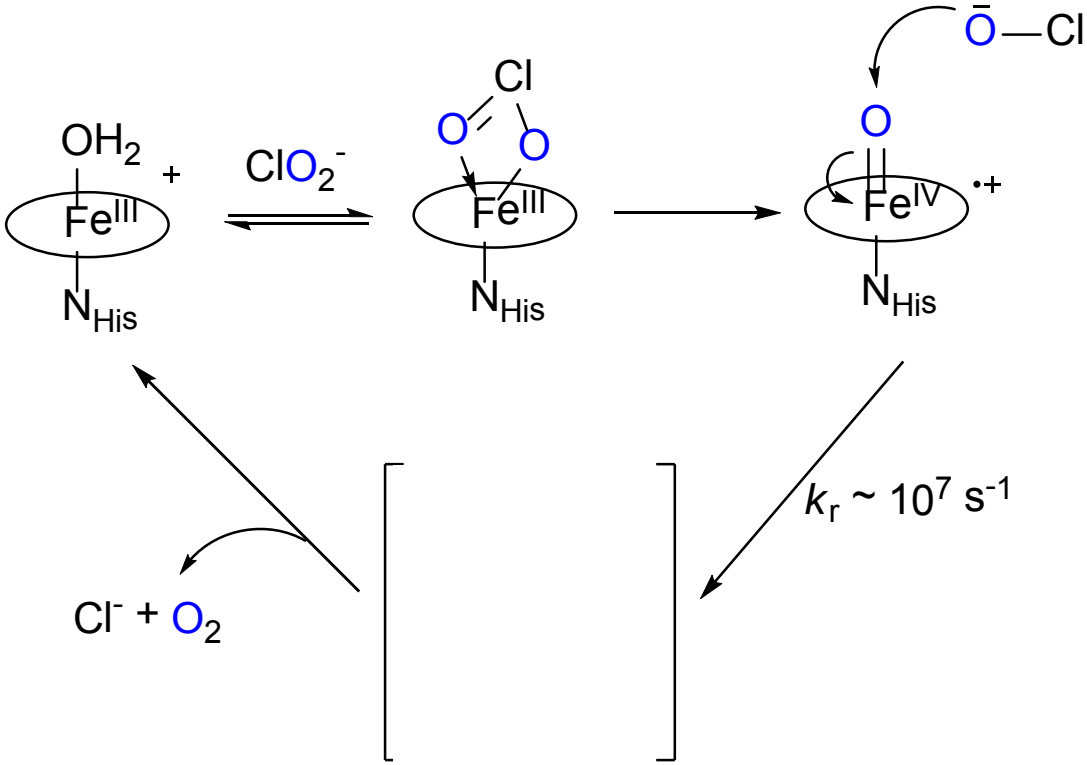
Freeze-Quench EPR





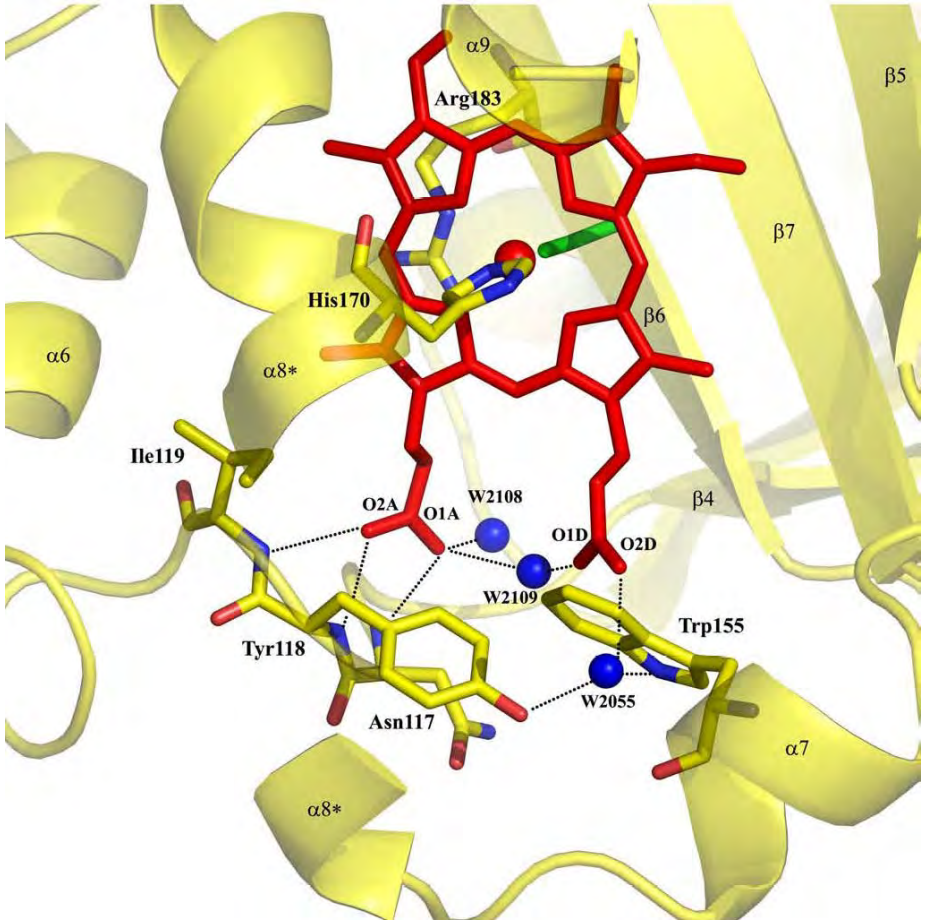


Mechanistic Insight



Proc. Natl. Acad. Sci. USA **2008**, *105*, 15654–15659.

Structural Confirmation

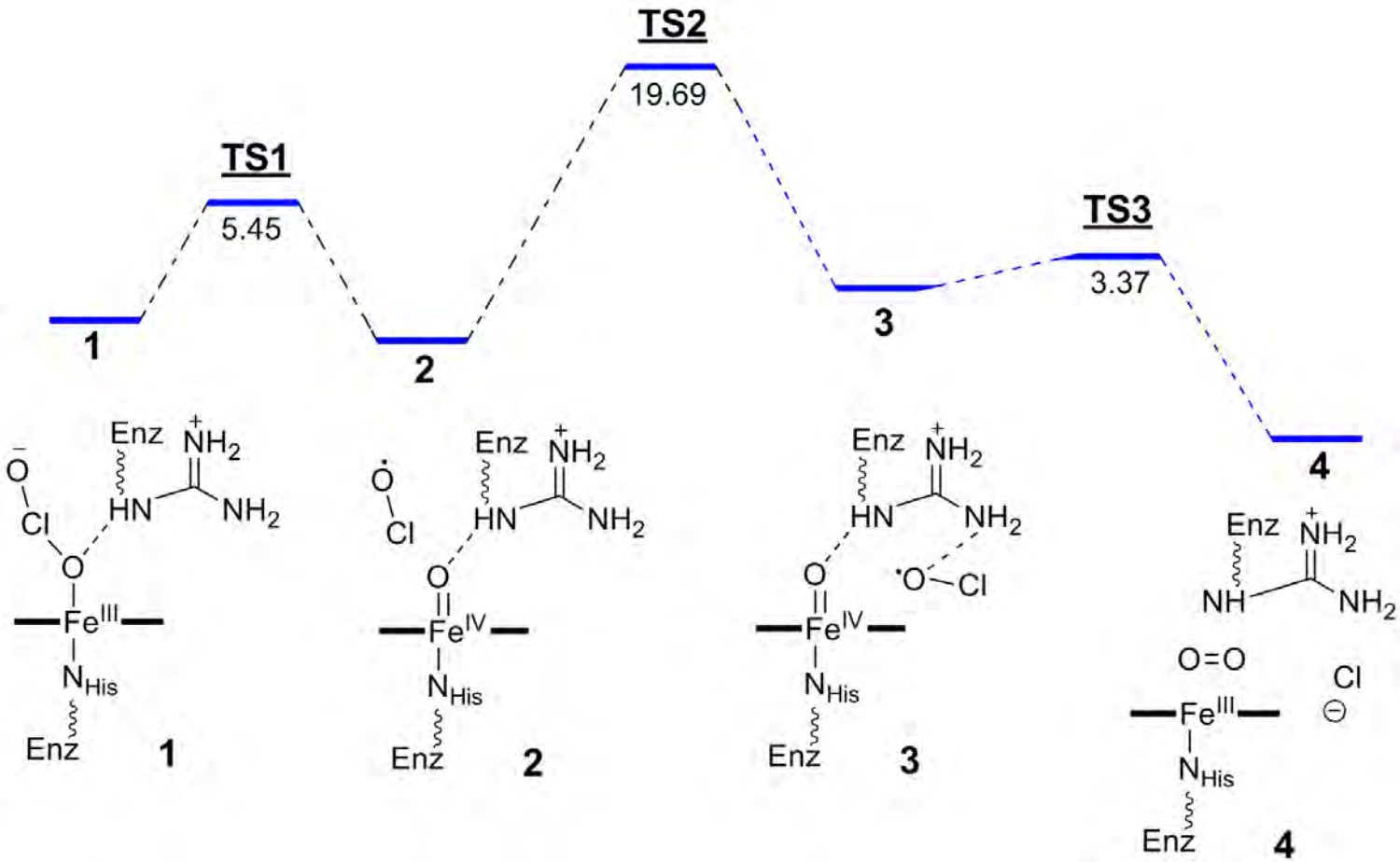


- *Azospira oryzae* Cld

- "The heme active-site pocket is solvent accessible both from the inside and the outside of the ring. Moreover, a second anion binding site that could accommodate the assumed reaction intermediate ClO^- for further transformation has been identified near the active site. The current crystal structure confirms and complements a recently proposed catalytic mechanism that proceeds via a ferryl species and a ClO^- anion."

Daniël C. de Geus *et al J. Mol. Biol.* **2009**, *387*, 192-206.

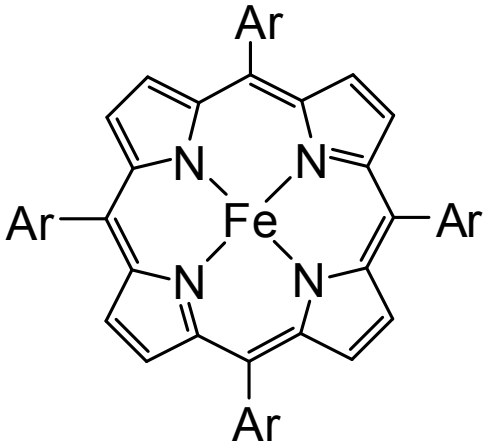
Density Functional Theory



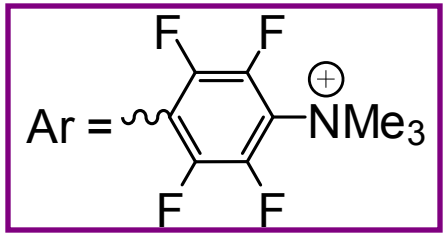
QM/MM
B3LYP

With Derat, Submitted for publication.

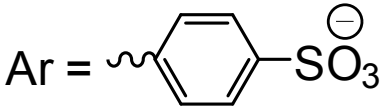
First Generation Cld Model Complexes



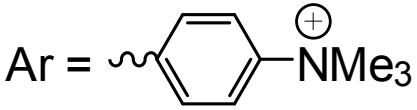
$[Fe(TF4TMAP)]^{5+}[OTf^{-}]_5$

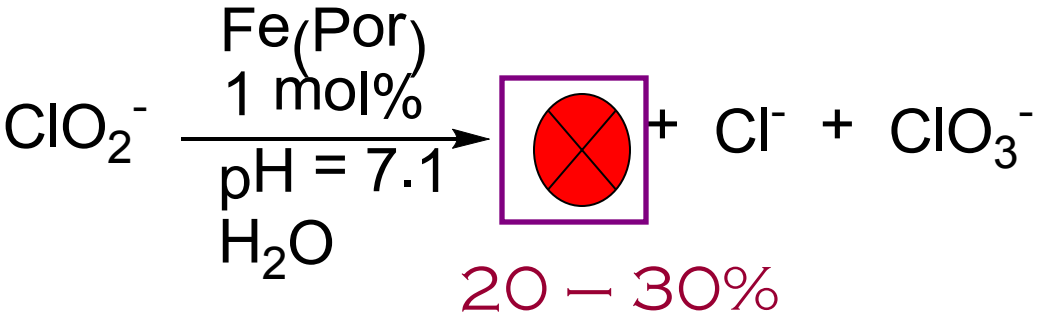


$[Na^{+}]_3[Fe(TPPS)]^{3-}$

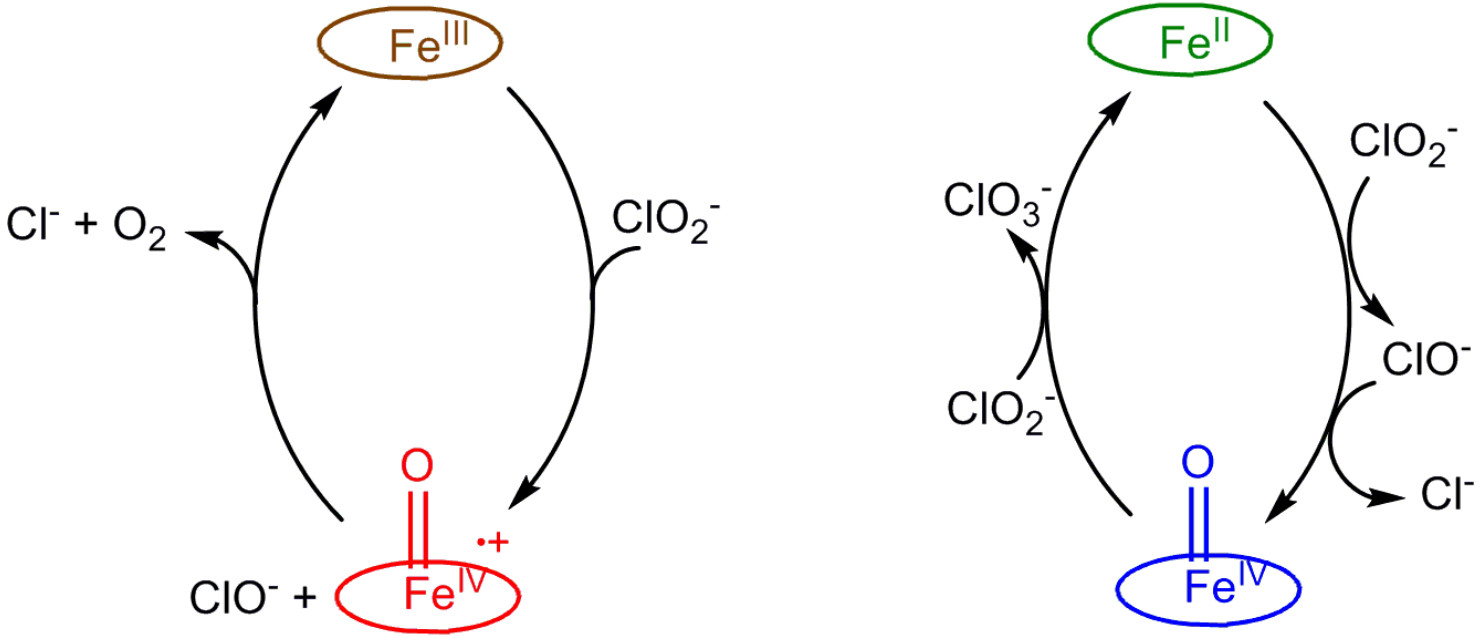


$[Fe(TMAP)]^{5+}[Cl^{-}]_5$



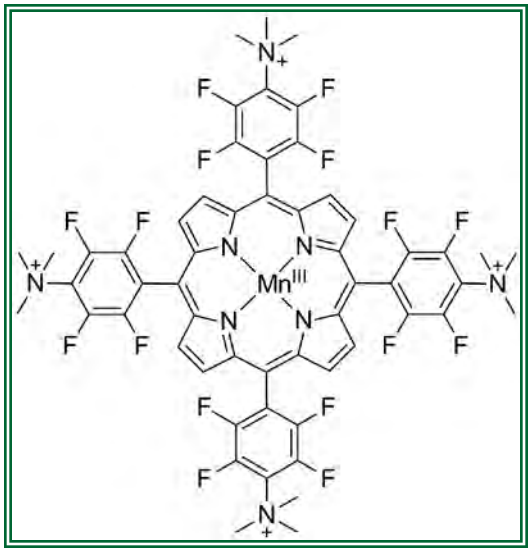


Catalysis via Two Pathways



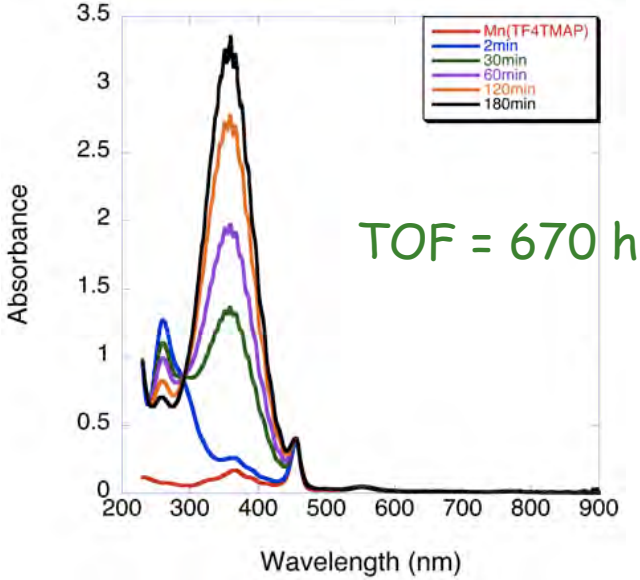
Angew. Chem. Int. Ed. **2008**, *47*, 7697-7700.
Inorg. Chem. **2009**, *48*, 2260-68.

Mn versus Fe

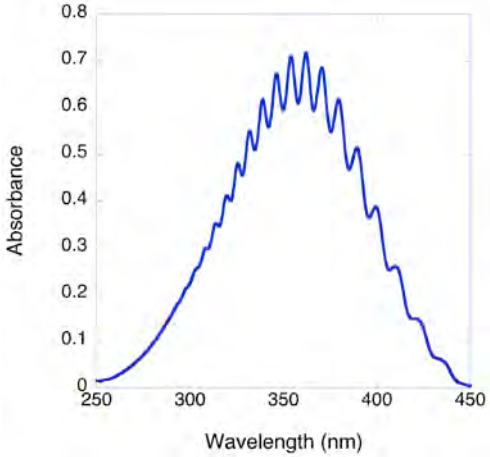


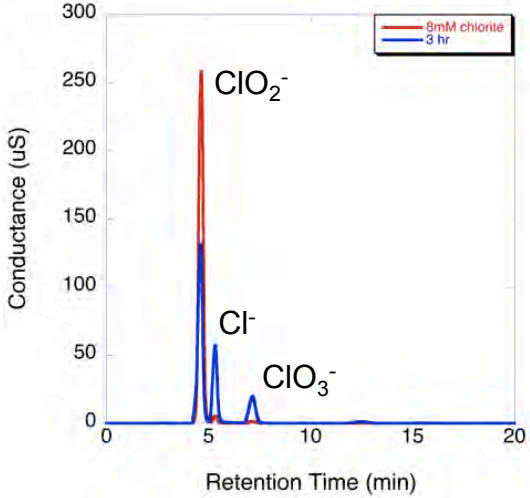
Scott

pH = 5.0

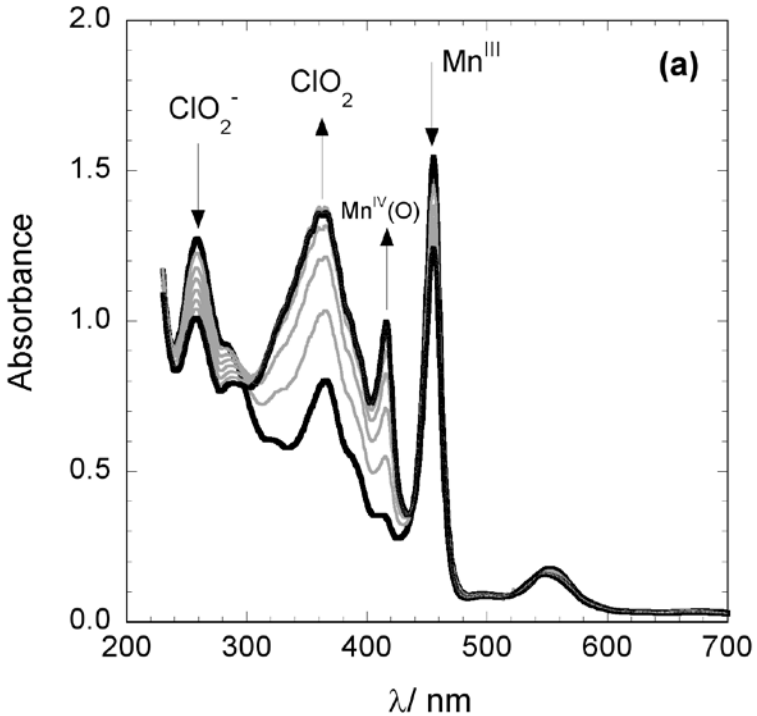


TOF = 670 h^{-1}

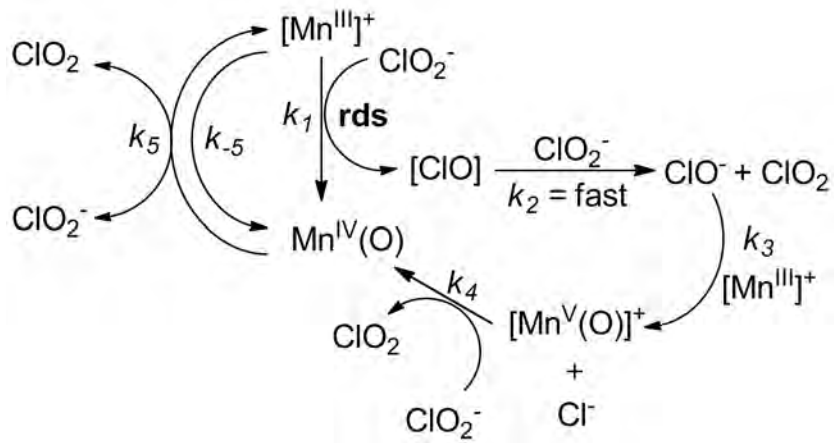




ClO_2 gas even at pH 7



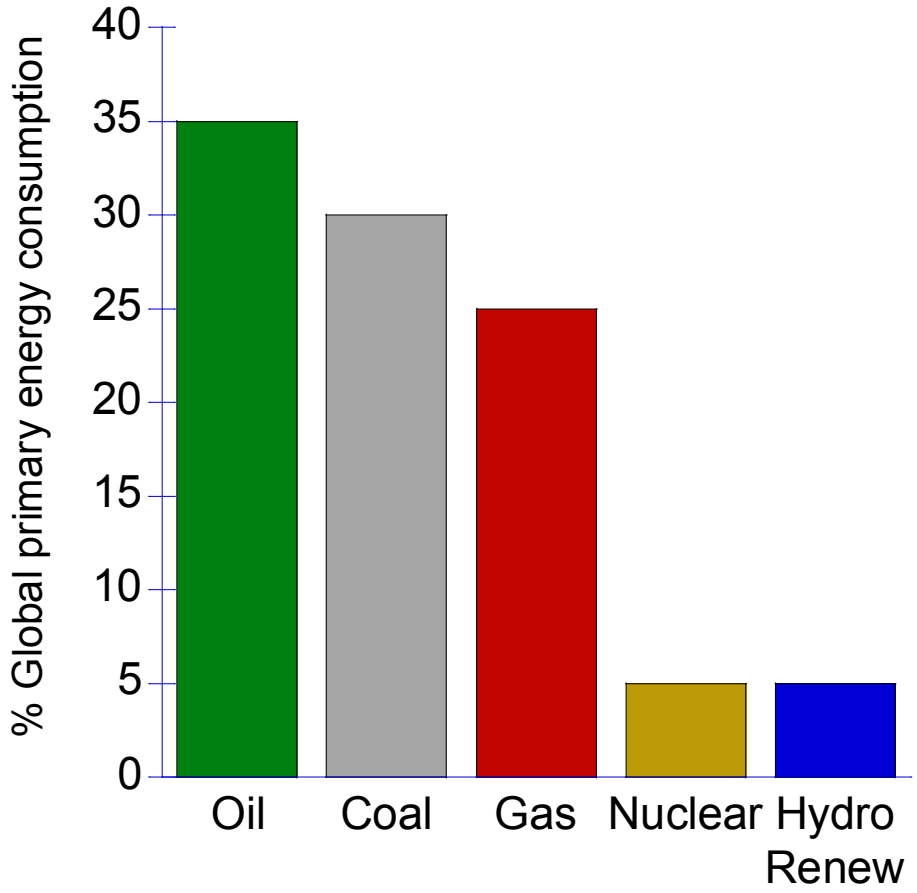
Mechanism



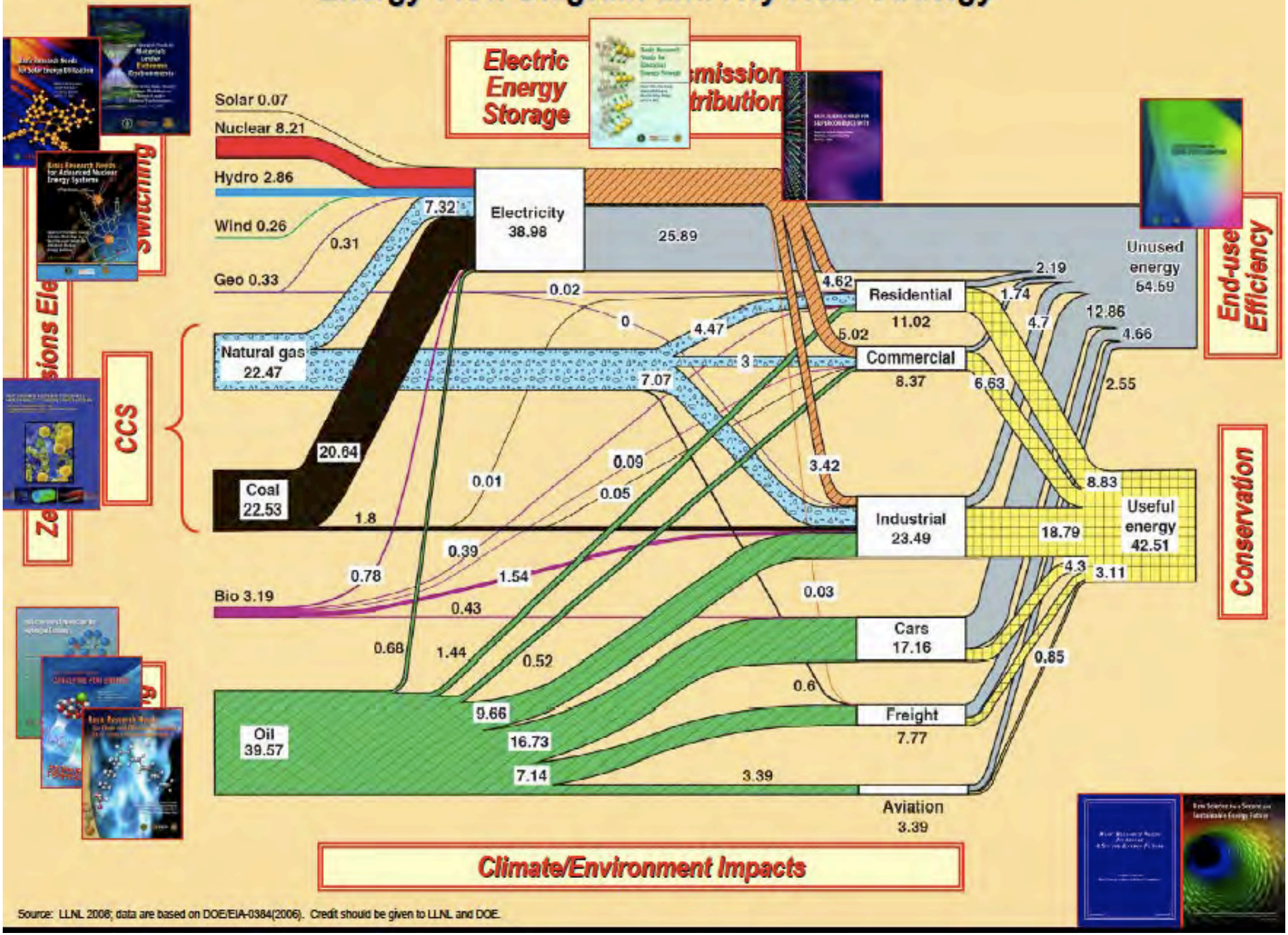
Angew. Chem. Int. Ed. **2011**, *50*, 699.

Groves *Angew. Chem. Int. Ed.* **2011**, *50*, 695.

Global Energy Consumption



Energy Flow Diagram and Key R&D Strategy



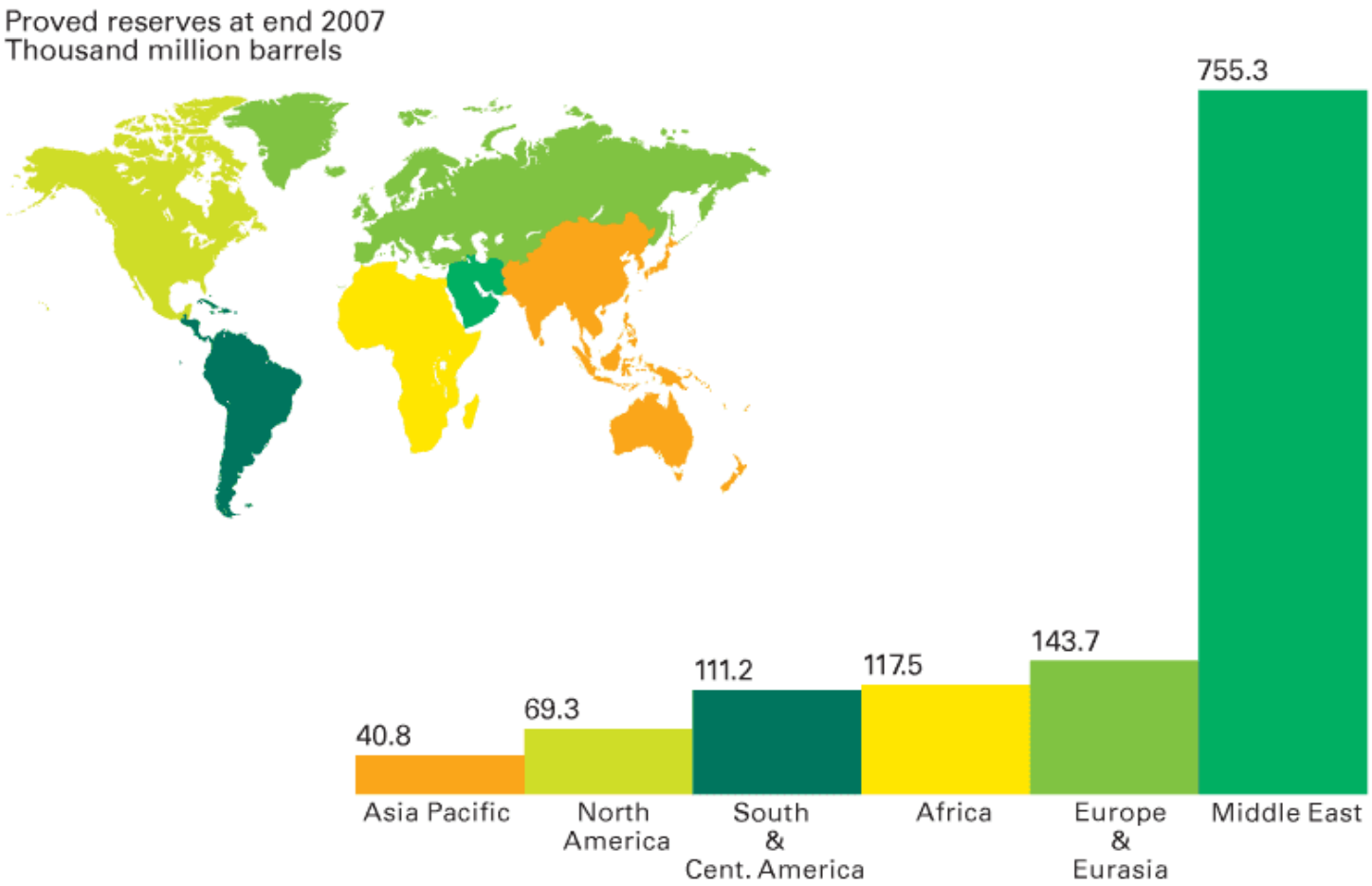
Source: LLNL 2006; data are based on DOE/EIA-0384(2006). Credit should be given to LLNL and DOE.

Planes, Trains, & Automobiles

US Oil Imports in 2009

Country/Region	Million tons	Percent (%)
South America	119	19
Middle East	120	19
Canada	122	20
Mexico	65	11
Norway	43	7
Africa	124	20
Old Russia	24	4
Total	617	100

But Where is the Proven Oil Reserves



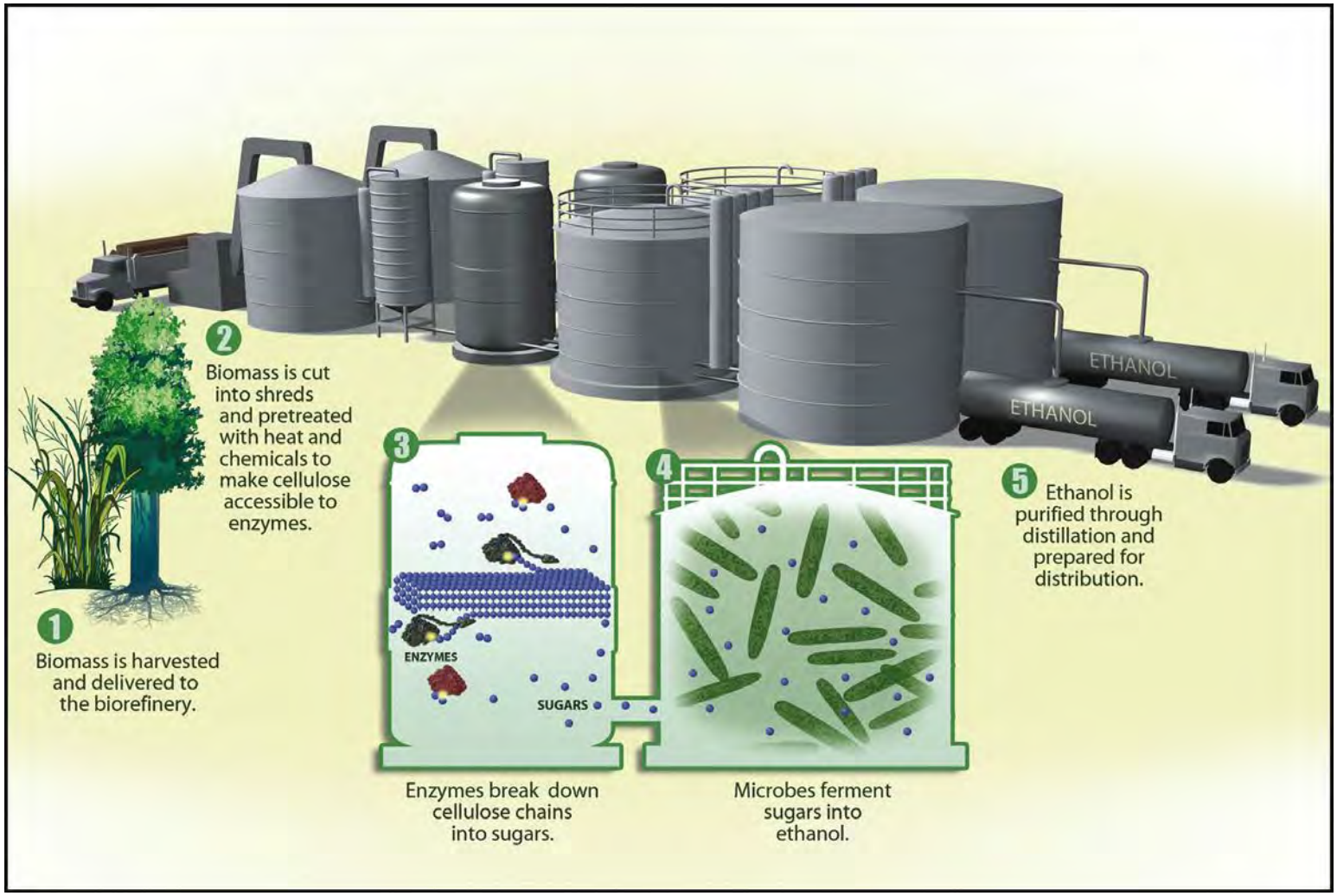
Proven Oil Reserves

Country	Reserves (10^9 bbl)
Saudi Arabia	260
Canada	179
Iraq	115
Iran	105
Kuwait	99
UAE	97
Venezuela	80
Russia	60
Libya	42
Nigeria	36
U.S.	21

- 5 out of the top 6 countries are in the Middle East.

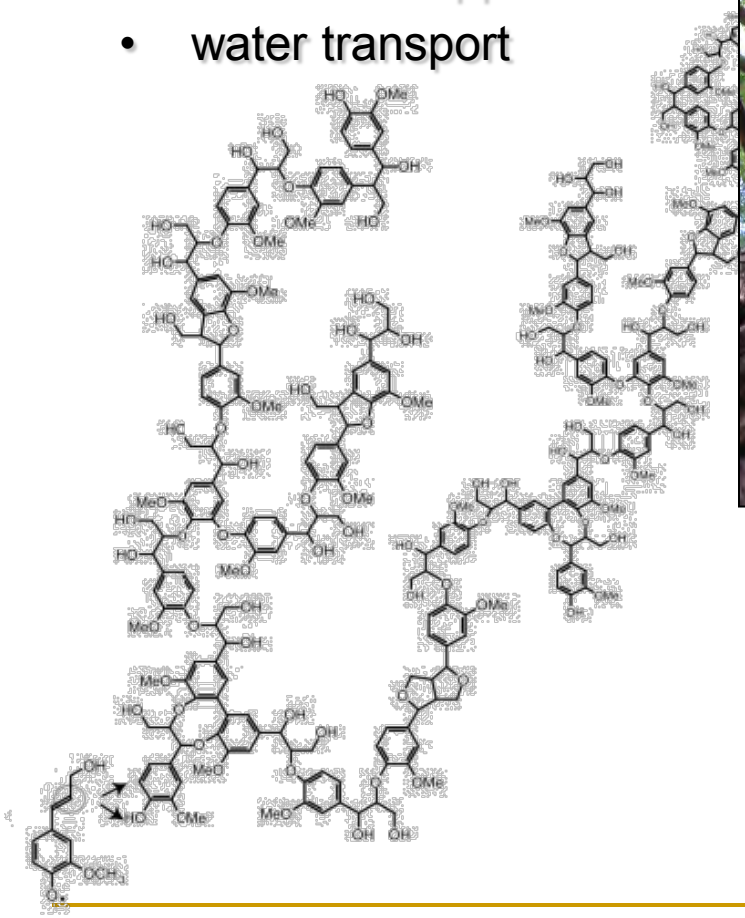
The agronomic footprint of biofuel feedstock to displace 30% gasoline by 2030 with ethanol

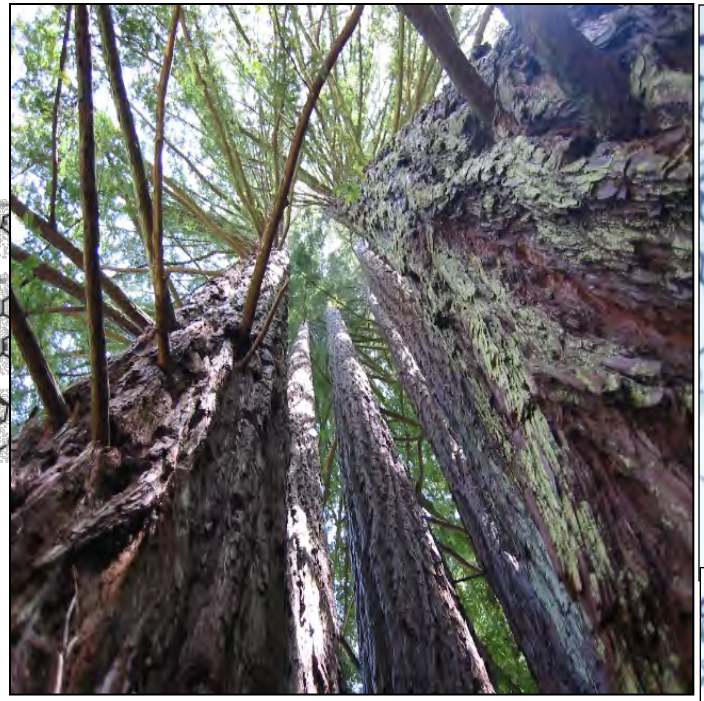
Biological conversion of biomass to biofuel



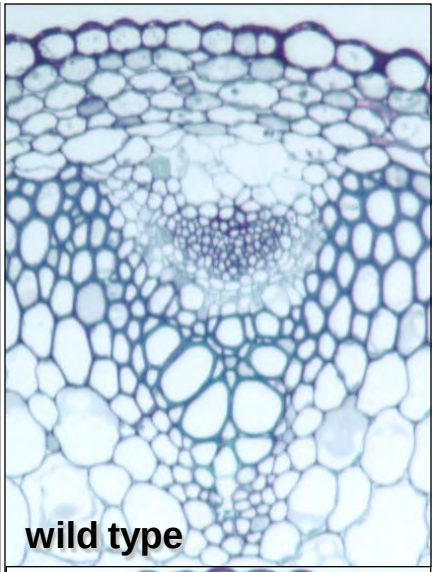
Phenylpropanoid metabolism is critical for plant survival

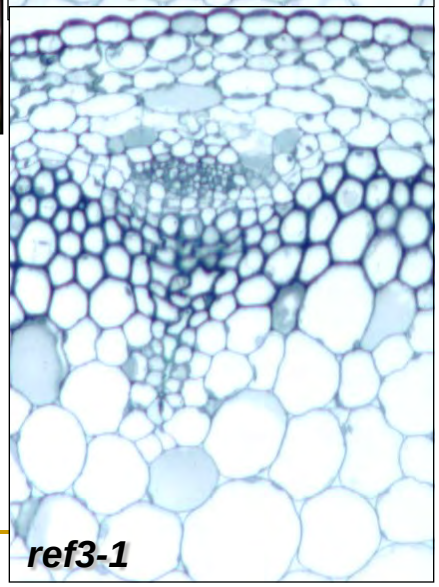
- UV resistance
- structural support
- water transport





http://givingspace.org/benlomond/up%20redwoods.jpg

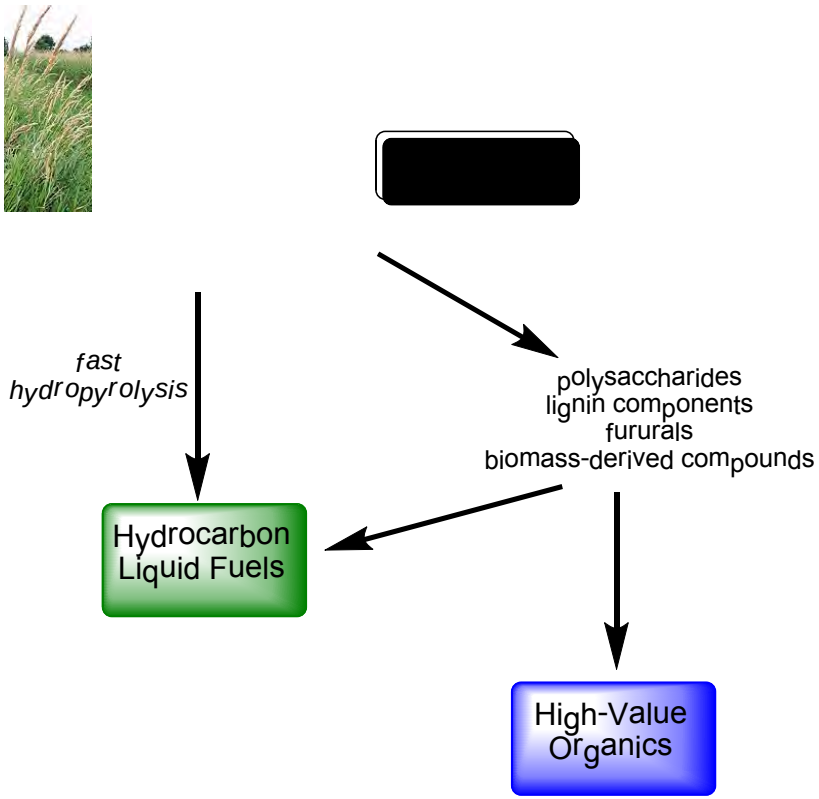




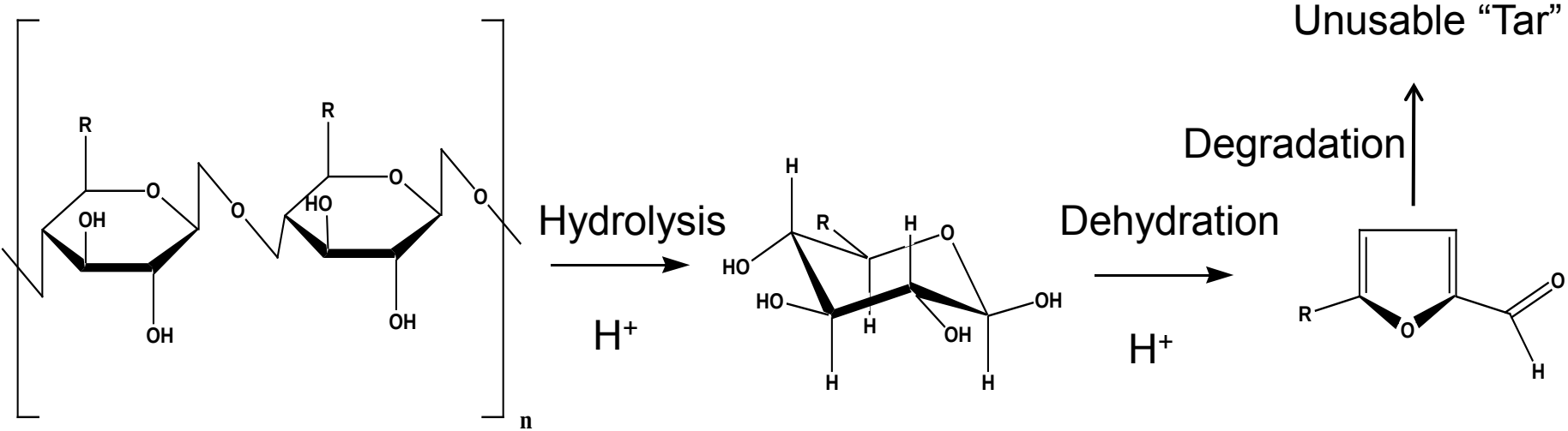
Hatfield and Vermerris *Plant Physiol.* **2001**, *126*, 1351-1357.

Catalytic Conversion Processes

- Apply and optimize catalytic transformations to a range of biomass components and genetic variants.



The Acid Route Dilemma



R: - CH_2OH	Cellulose
R: - OH	Hemicellulose

Cellulosic Biomass

R: - CH_2OH	Glucose
R: - OH	Xylose

Simple Sugars

R: - CH_2OH	HMF
R: - H	Furfural

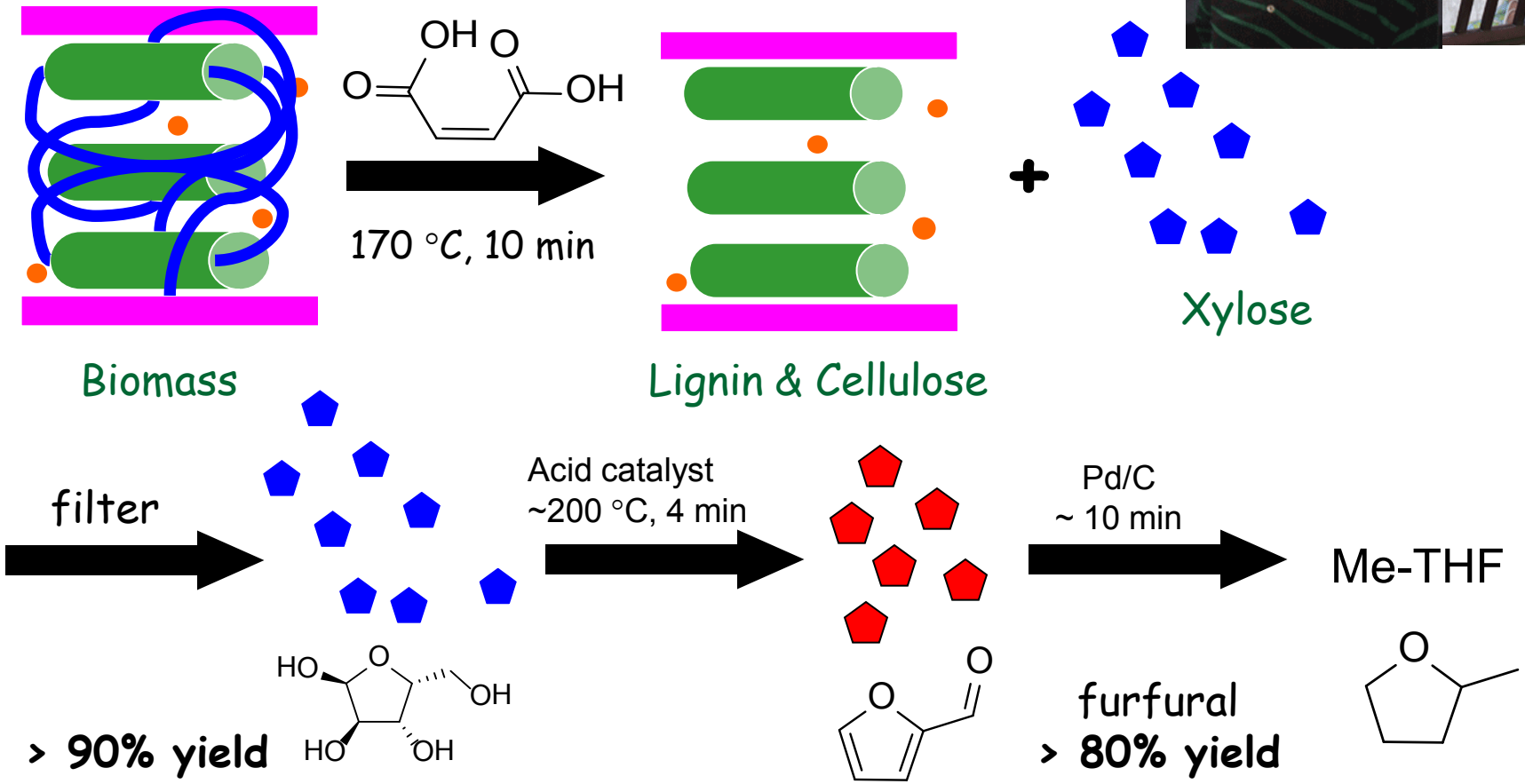
Aldehydes

Controlling reaction selectivity towards hydrolysis and dehydration vs degradation critical to biofuel production

Leaving lignin unmodified

Selective Hydrolysis and Conversion

Eurick & Shuo



With Prof. Nate Mosier

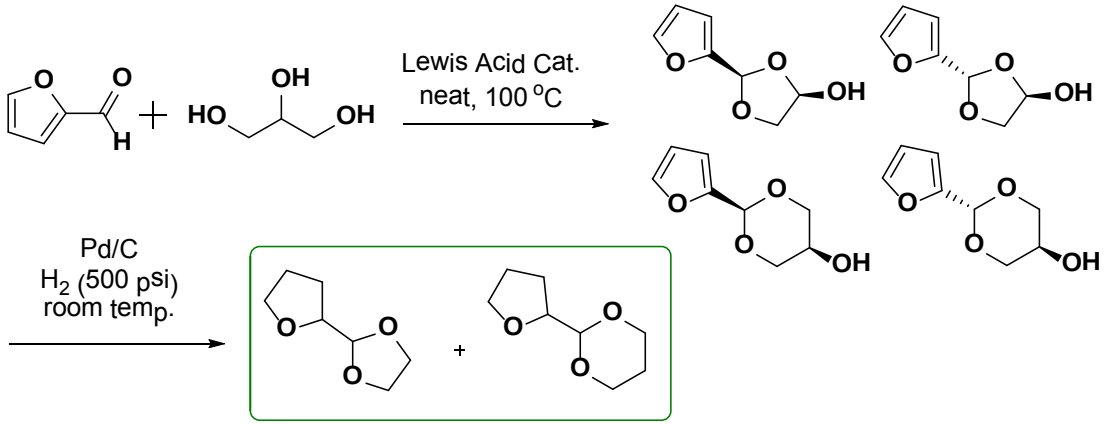
Biomass variants

Biomass	Glucan (Cellulose)	Xylan (Hemi-cellulose)	Other Structural Carbo-hydrates	Lignin	Extractives	Other (Ash, protein, etc.)
Switchgrass	35%	21%	3%	20%	10%	11%
Lodgepole Pine	25%	18%	2%	28%	12%	15%
Hybrid Poplar	45%	18%	4%	21%	8%	4%

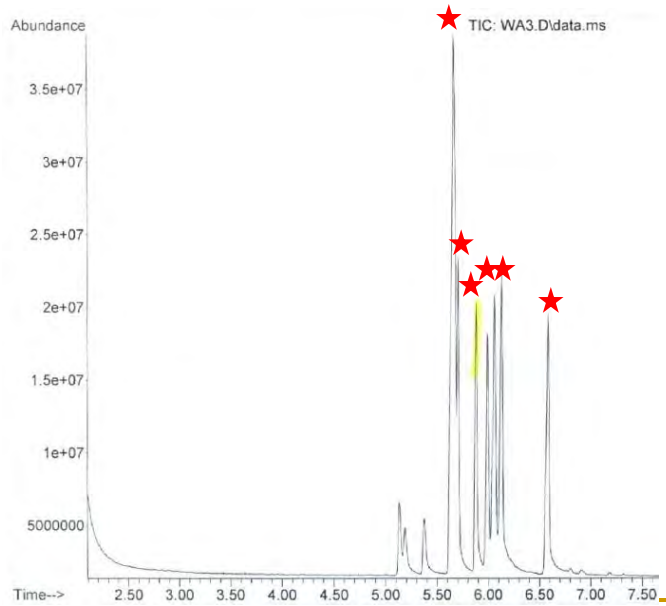
One-pot furfural from biomass

Sample	Reagent/ Catalyst	T (@ 200 °C)/ min	Xylose % conversion	% Yield furfural
Pure xylose (10 g/L)	$ZnCl_2$	10	100	50
	Maleic acid	10	100	90
	Maleic acid + $ZnCl_2$	10	100	90
	H_2SO_4	5	100	65
Switchgrass	Maleic acid	10	100	85
	Maleic acid + $ZnCl_2$	10	100	80
	H_2SO_4	5	100	55
Poplar	Maleic acid	10	55	93
	Maleic acid + $ZnCl_2$	10	100	85
	H_2SO_4	5	100	57
Pine	Maleic acid + $ZnCl_2$	10	100	53
	H_2SO_4	5	97	34

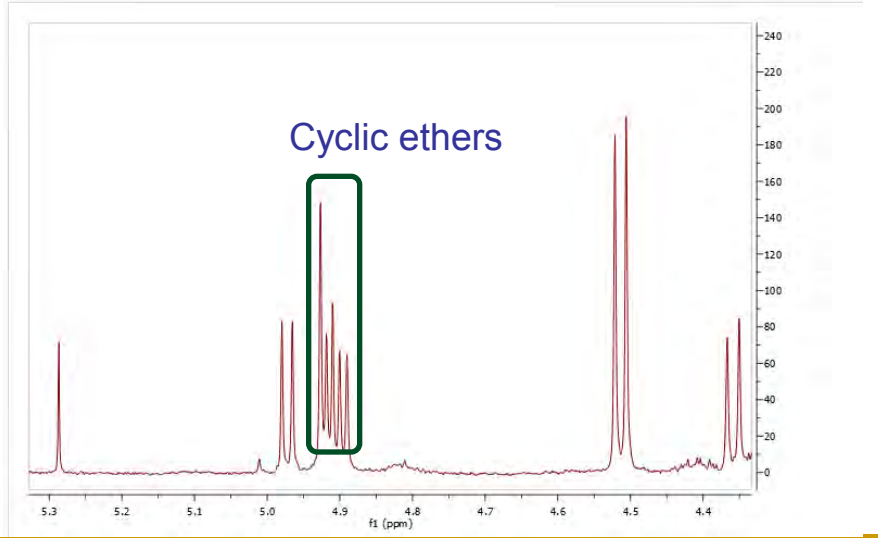
Tandem hydrogenation of acetal products from Ff



GC

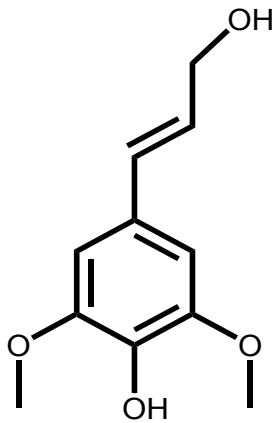


^{1}H NMR

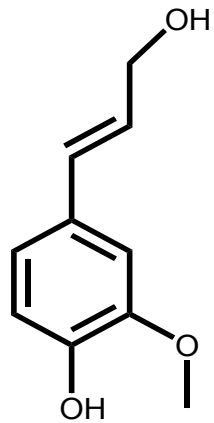


★ Ether hydrocarbon products including isomers

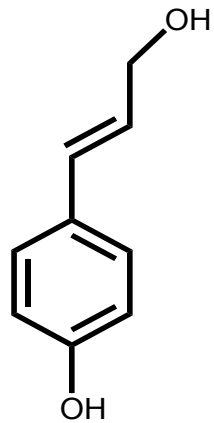
Lignin Structure



Sinapyl alcohol

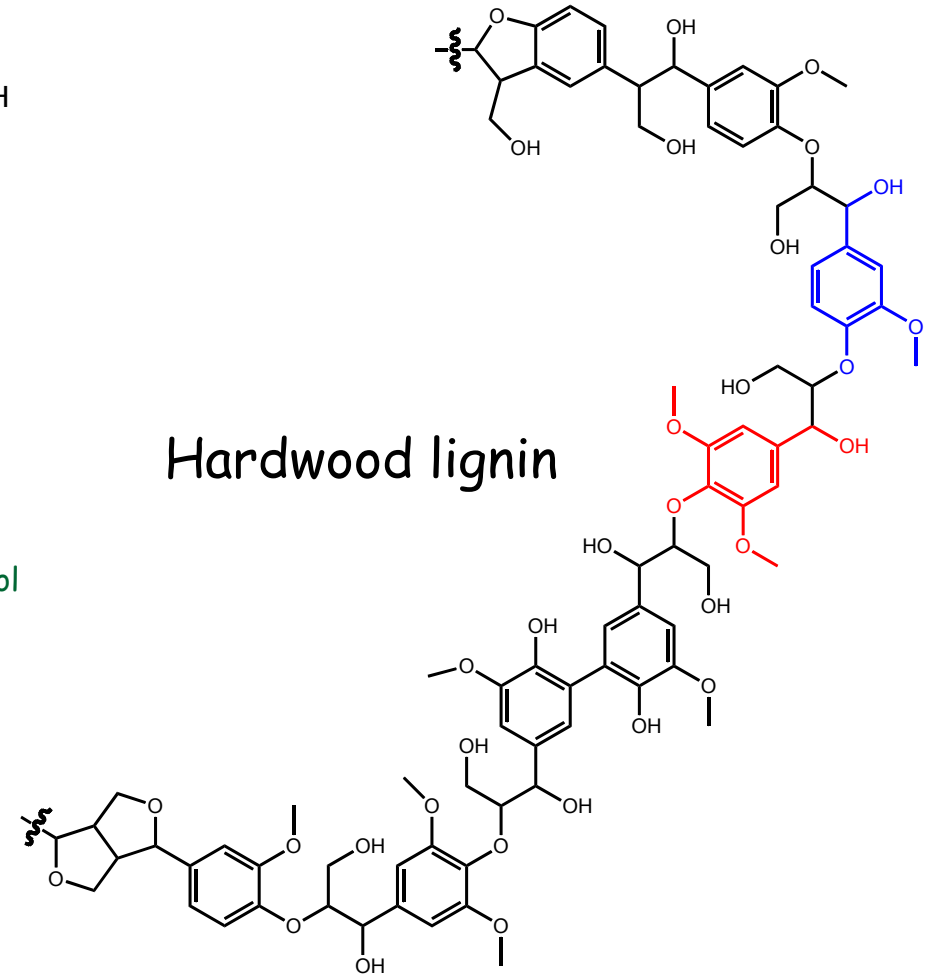


conifryl alcohol



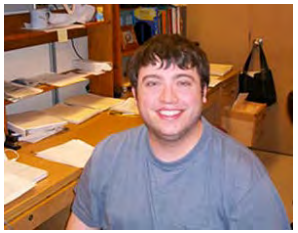
p-coumaryl alcohol

Hardwood lignin

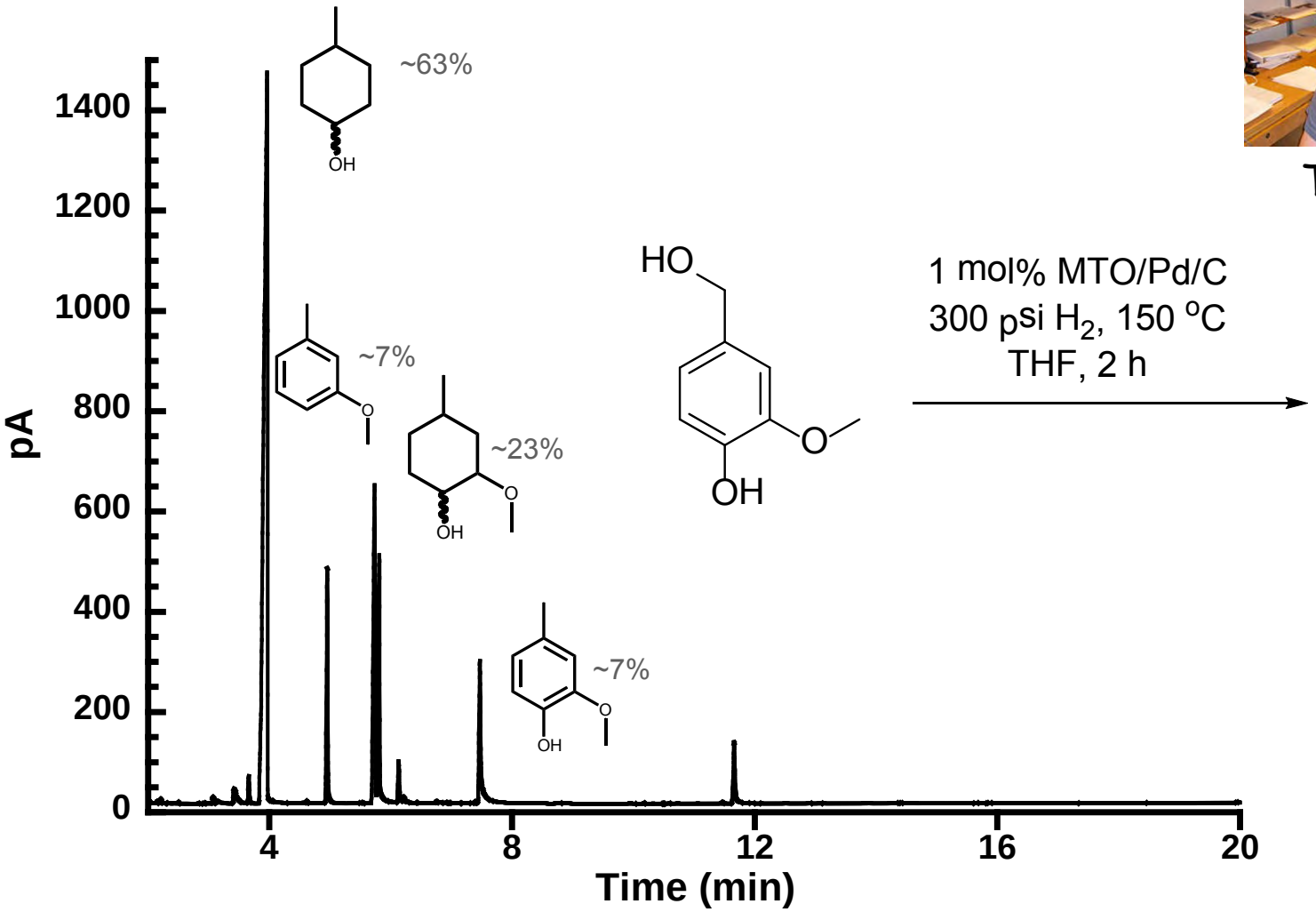


- UV resistance
- structural support
- water transport

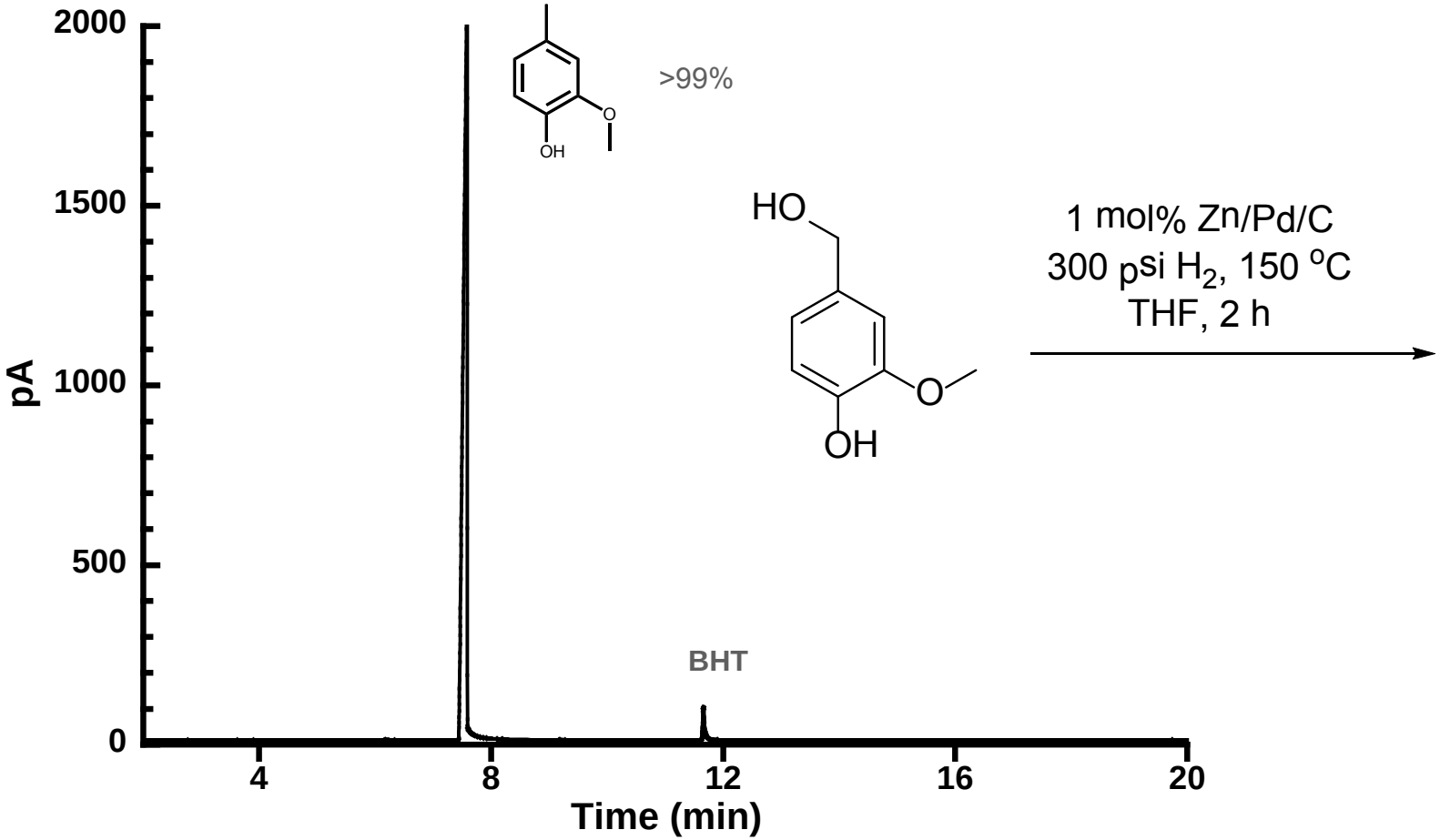
Vanillyl Alcohol (a lignin monomer model)



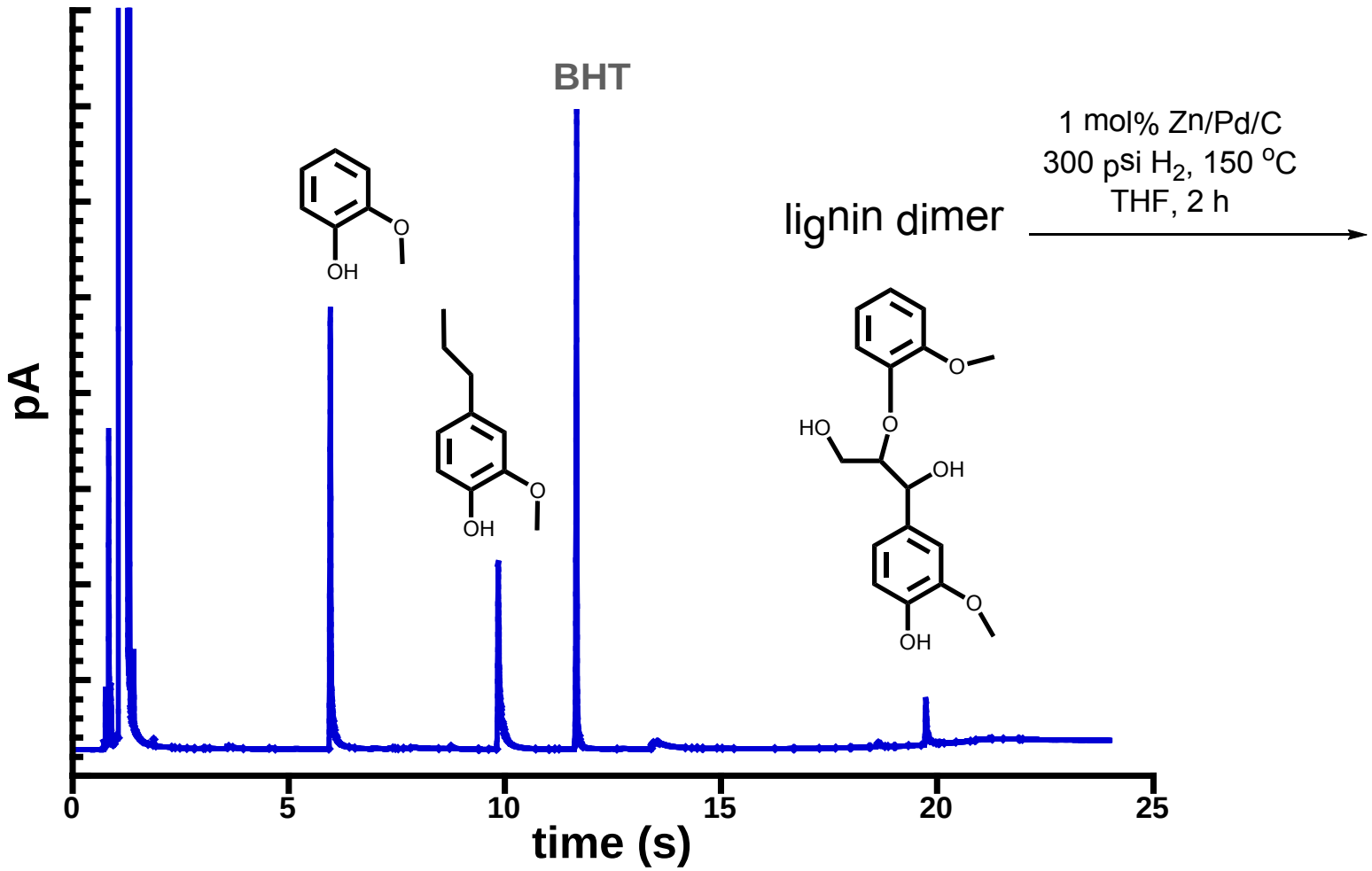
Trenton



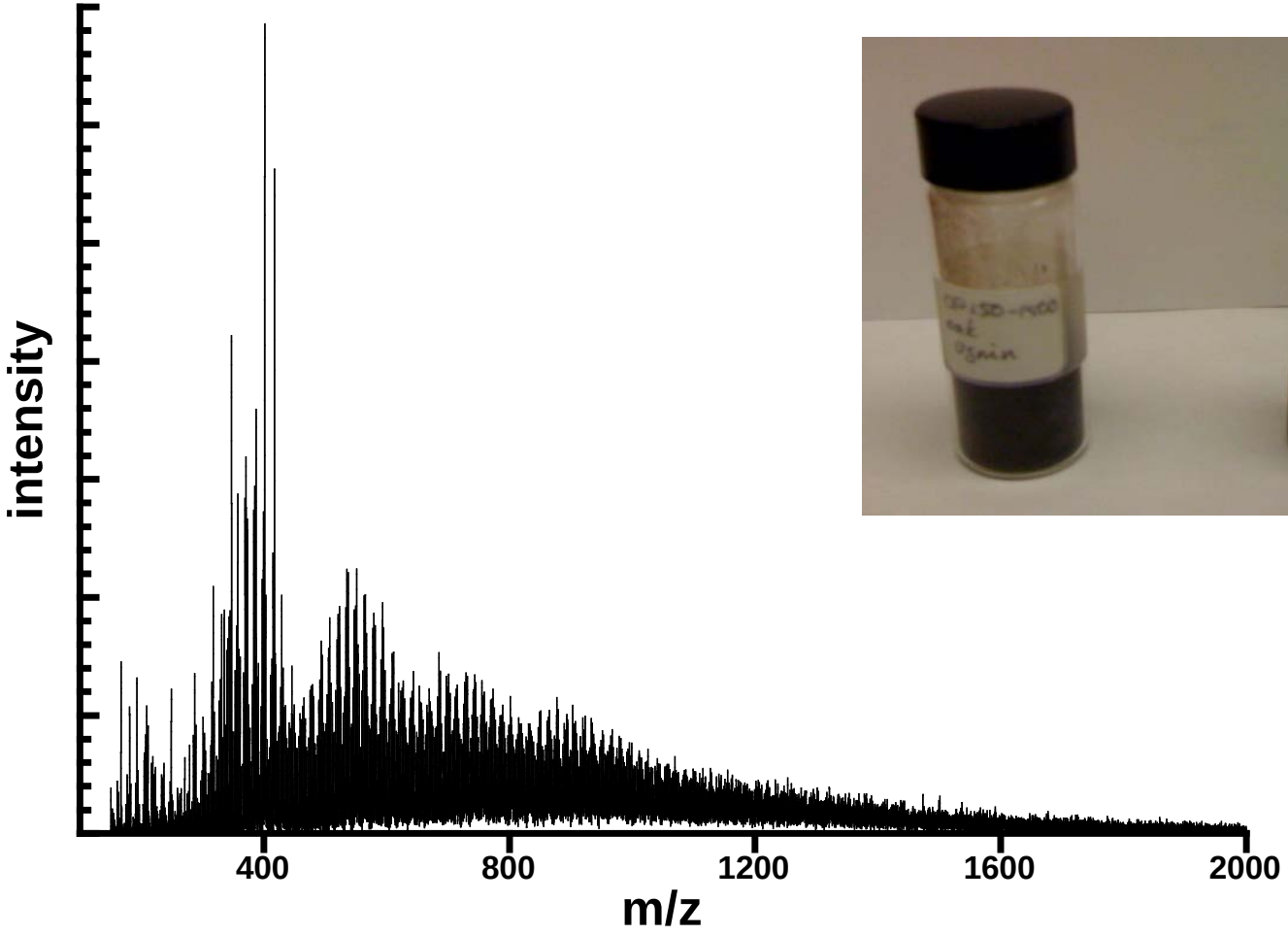
Preserving the aromatic group!

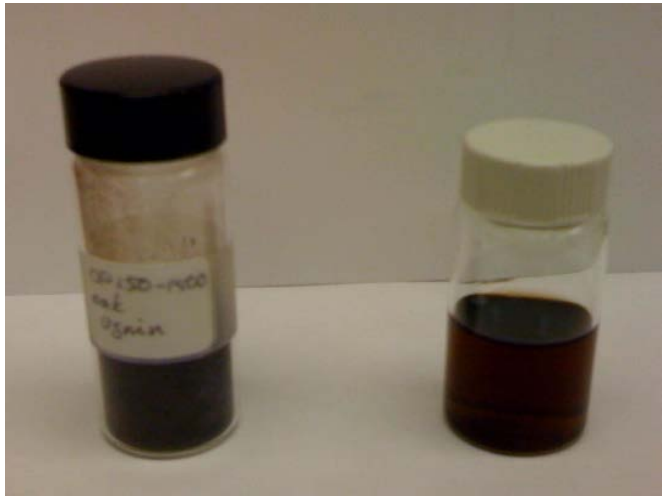


Lignin dimer



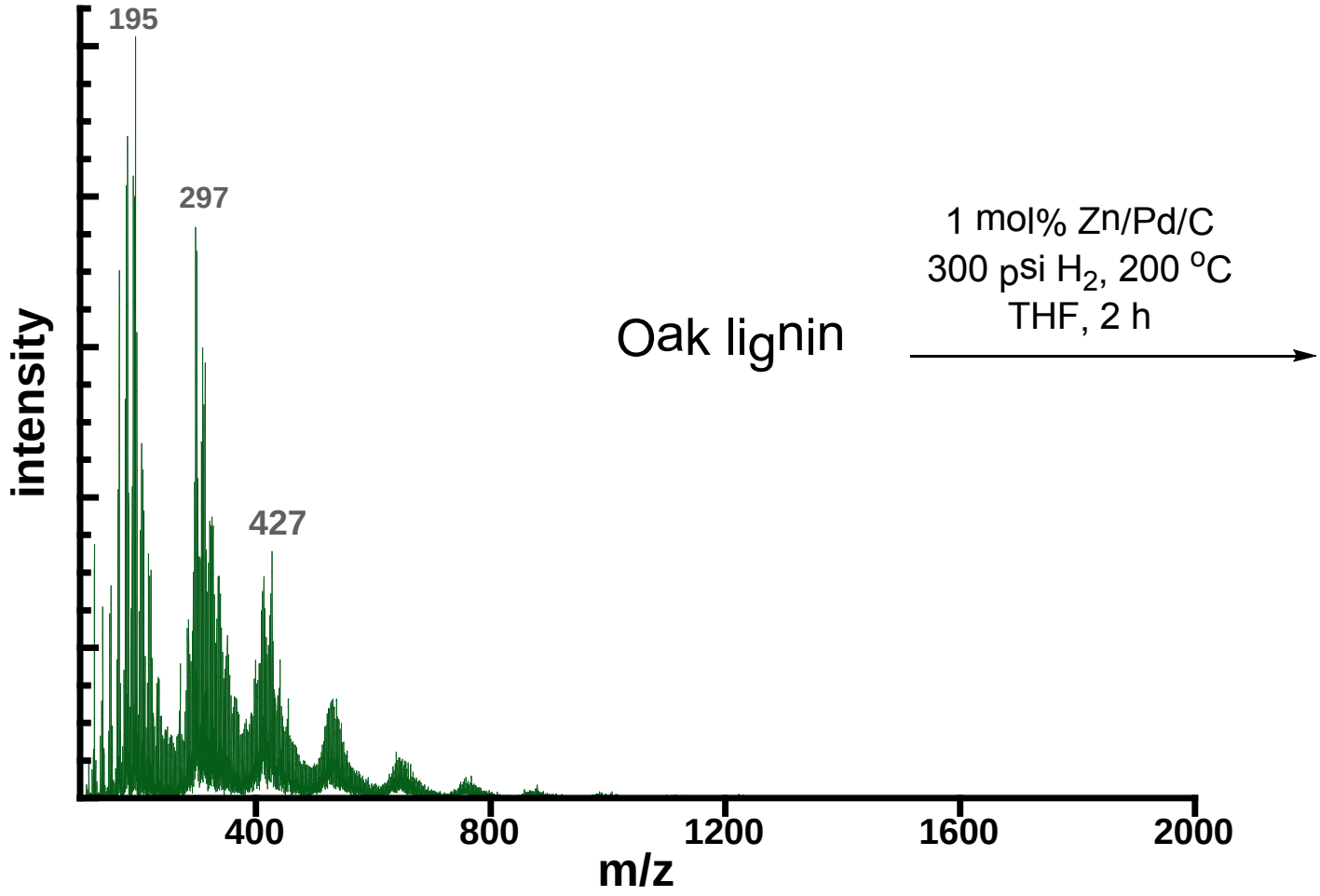
MS of oak lignin



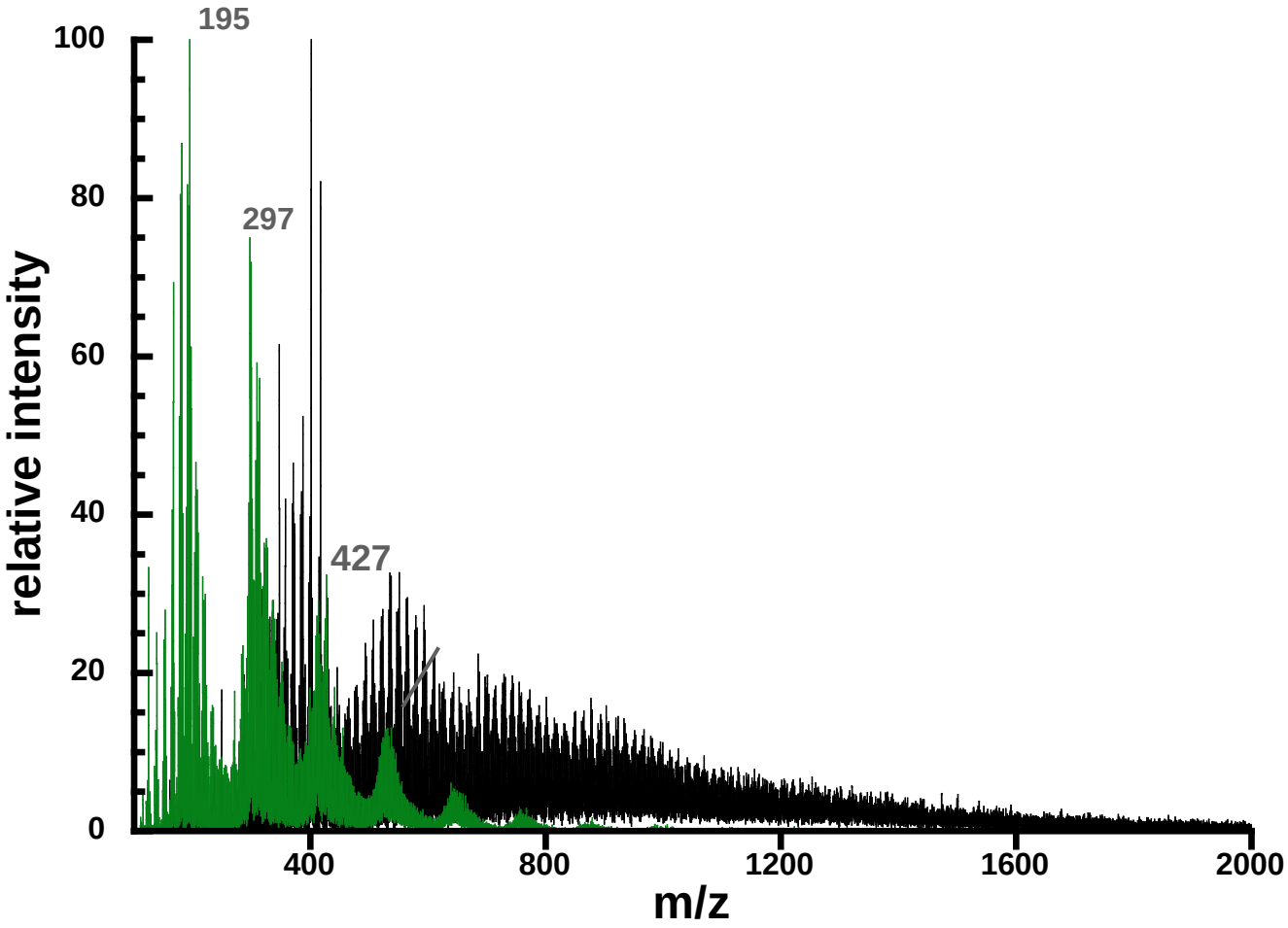


With Profs. Joe Bozell and Hilkka Kenttämaa

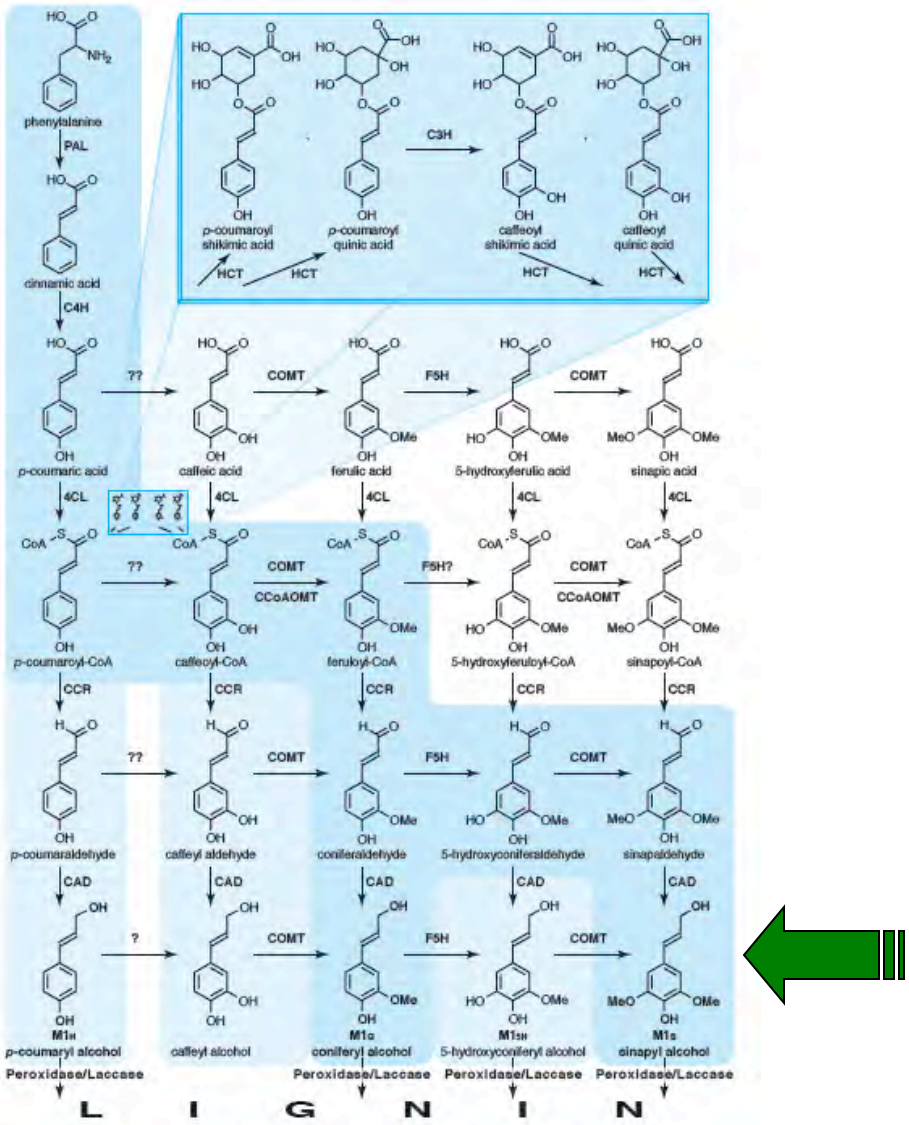
Degradation of oak lignin



Degradation of oak lignin



Tailored biomass



With Clint Chapple

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