

# Applications of Computational Chemistry to the Reactions of Lignin

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# Computational Methods

- Molecular Mechanics
- Semi-Empirical
- Ab initio
- Density Function Theory (DFT)

# Results

- Molecular geometry
- Energies of molecules and transition states
- Reactivity (electrophilicity/nucleophilicity)
- Spectra (UV, IR, NMR)

## Kinetic Analysis of the Pyrolysis of Phenethyl Phenyl Ether: Computational Prediction of $\alpha/\beta$ -Selectivities

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Computer Science and Mathematics Division, Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, Tennessee 37831-6367, and Chemical Sciences Division, Oak Ridge National Laboratory, Bethel Valley Road, Oak Ridge, Tennessee 37831-6197

## Radical Coupling Reactions in Lignin Synthesis: A Density Functional Theory Study

Amandeep K. Sangha,<sup>†</sup> Jerry M. Parks,<sup>†,§,||</sup> Robert F. Standaert,<sup>‡,||,⊥</sup> Angela Ziebell,<sup>§,#</sup> Mark Davis,<sup>§,#</sup> and Jeremy C. Smith<sup>\*,†,‡,§,||</sup>

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## Computational Study of Bond Dissociation Enthalpies for a Large Range of Native and Modified Lignins

Seonah Kim,<sup>†,‡</sup> Stephen C. Chmely,<sup>†</sup> Mark R. Nimlos,<sup>†</sup> Yannick J. Bomble,<sup>||</sup> Thomas D. Foust,<sup>†,‡</sup> Robert S. Paton,<sup>⊥</sup> and Gregg T. Beckham<sup>\*,†,‡,§</sup>

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<sup>⊥</sup>Department of Chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K.

## Theoretical Study of the Remarkably Diverse Linkages in Lignin

R. Parthasarathi,<sup>†</sup> Raymond A. Romero,<sup>†,‡</sup> Antonio Redondo,<sup>§</sup> and S. Gnanakaran<sup>\*,†</sup>

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$\pi$ -electron spin densities of lignin constituents

By OLLE MÅRTENSSON and GÖRAN KARLSSON

Reactivity and Quantum Mechanics of Lignin\*

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*Department of Wood and Polymer Chemistry University of Helsinki, Helsinki, Finland and Department of Basic Instruction in Chemistry, Medical Faculty, University of Helsinki, Helsinki, Finland.*

*Advances in Molecular Relaxation and Interaction Processes*, 14 (1979) 315-320  
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MO INVESTIGATIONS ON LIGNIN MODEL COMPOUNDS

VIII. A PCILO STUDY OF INTRAMOLECULAR HYDROGEN BOND IN GUAIACOL AND O-VANILLIN<sup>+</sup>

MILAN REMKO<sup>++</sup>

Pulp and Paper Research Institute, 890 20 Bratislava,  
Czechoslovakia

(Received 29 June 1978)

# Ongoing Projects

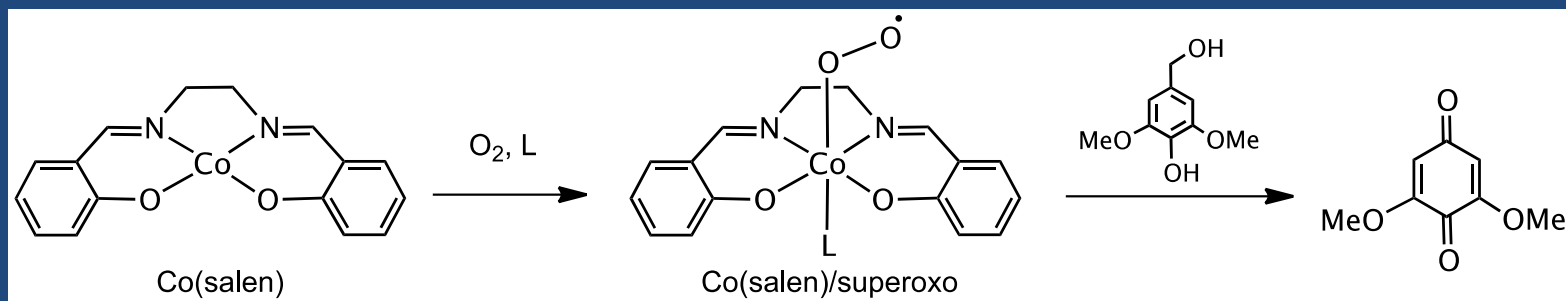
- Cobalt salen catalyzed oxidation of lignin models
- Pyrolysis reactions

# Co(salen)/O<sub>2</sub> oxidation of lignin and lignin models

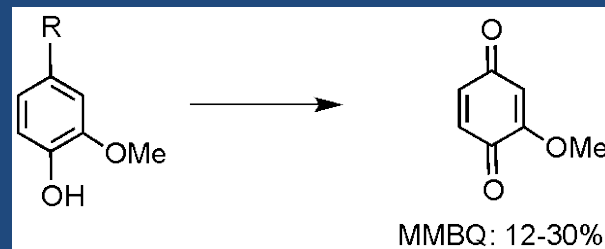
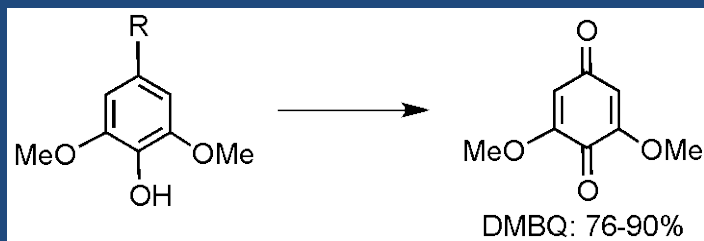
Collaboration with Joe Bozell,  
University of Tennessee

# Co(salen)/O<sub>2</sub> oxidation of lignin and lignin models

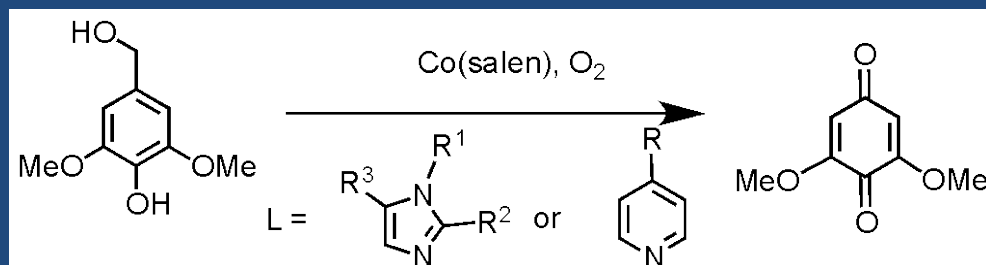
- Oxygen activation with a Co catalyst converts models to benzoquinones



- S* models work well, but *G* models oxidize in lower yield

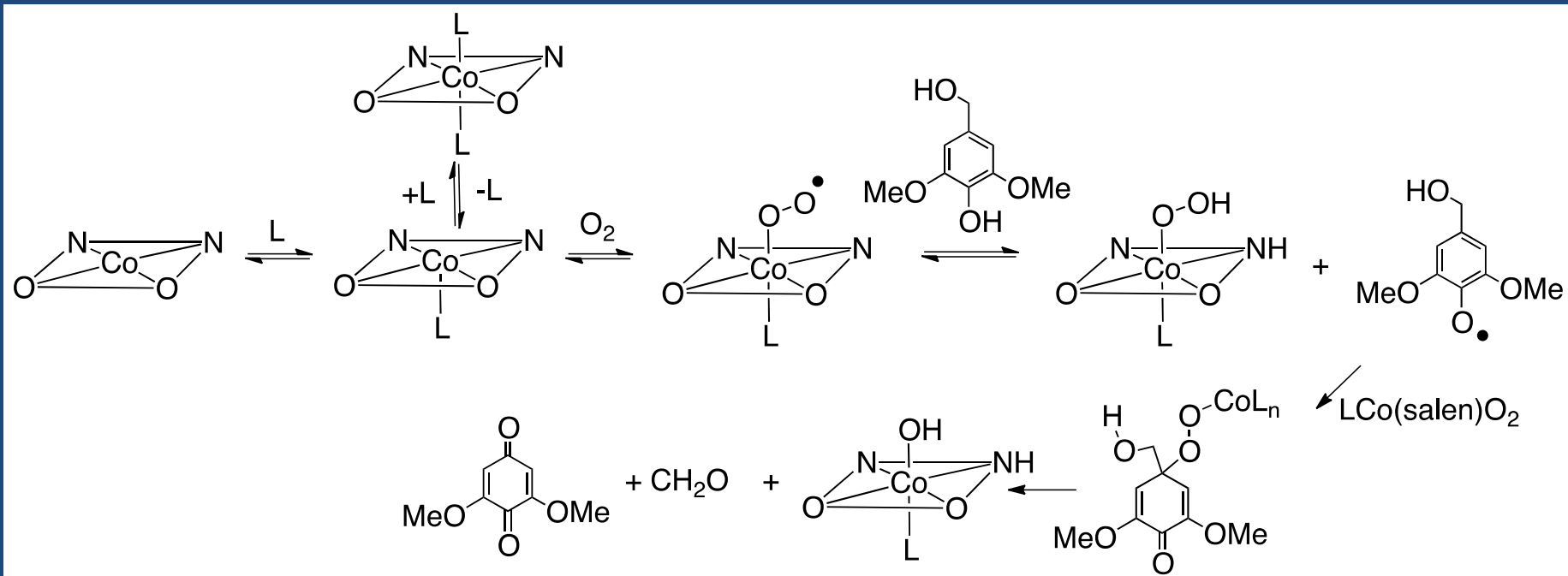


- The choice of ligand is important to the reaction





# Oxidation mechanism



# Experimental Results

Ligand	DMBQ yield	pKa
imidazole a)	5	7
1-methyl imidazole b)	29	7.33
2-methyl imidazole c)	67	7.85
1-2 dimethyl imidazole d)	72	8
2-4 dimethyl imidazole e)	71	8.38

# What goes around comes around

2398

*J. Org. Chem.* **1995**, *60*, 2398–2404

## Cobalt–Schiff Base Complex Catalyzed Oxidation of Para-Substituted Phenolics. Preparation of Benzoquinones

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Received November 4, 1994\*

Para-substituted phenolics, serving as models for lignin (a renewable source of carbon), are oxidized to the corresponding benzoquinone with oxygen in the presence of catalytic amounts of Co–Schiff base complexes. The reaction products observed depend on the structure of the catalyst. The 5-coordinate catalysts (pyridine)bis(salicylidene)ethylenediamine)cobalt [(pyr)Co(salen)] and [bis(salicylideneamino)ethyl]amine)cobalt [Co(N-Me salpr)] convert syringyl alcohol (3,5-dimethoxy-4-hydroxybenzyl alcohol) to 2,6-dimethoxybenzoquinone in high yield. In contrast, syringaldehyde (3,5-dimethoxy-4-hydroxybenzaldehyde) is unreactive toward these catalysts. However, the 4-coordinate Co(salen) converts syringaldehyde to 2,6-dimethoxybenzoquinone in 72% isolated yield. Phenols bearing a single methoxy group on the ring are unreactive toward any catalyst in MeOH. However, vanillyl alcohol (3-methoxy-4-hydroxybenzyl alcohol) is converted to 2-methoxybenzoquinone with Co(N-Me salpr) and oxygen in 43% yield in CH<sub>2</sub>Cl<sub>2</sub>, and 58% yield in CH<sub>2</sub>Cl<sub>2</sub> in the presence of 1% CuCl<sub>2</sub>. The success of the oxidations appears to be related to the ease of removal of the phenolic hydrogen by the Co/O<sub>2</sub> complex. Competitive deactivation of the catalyst occurs with substrates of lower reactivity.

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T. Elder and J.J. Bozell: MO Calculations on Phenolic Substrates

Holzforschung  
50 (1996) 24–30

## Cobalt-Schiff Base Complex Catalyzed Oxidation of *para*-Substituted Phenolics. Molecular Orbital Calculations on Phenolic Substrates

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### Keywords

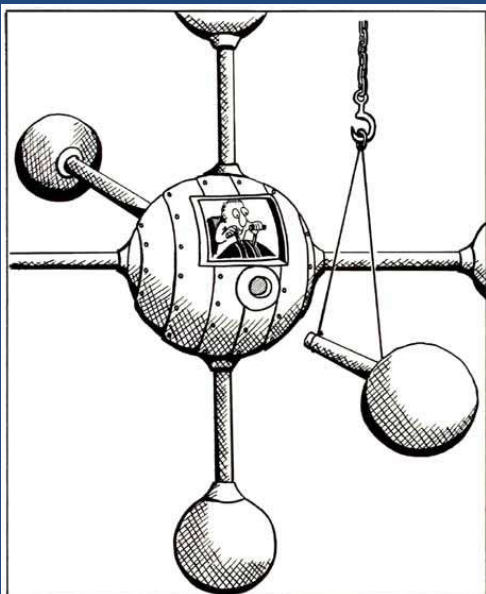
Co(salen)  
Lignin model compounds  
Oxidation  
Molecular orbital calculations

### Summary

Results from experimental oxidation reactions of lignin model compounds using Co(salen) have indicated widely differing behavior as a function of substitution. Syringyl compounds are uniformly more susceptible to oxidation than the analogous guaiacyl and *p*-hydroxyl compounds. The current work reports on the completion of molecular orbital calculations for the lignin model substrates, in an attempt to rationalize the observed differences in reactivity. The energies of the highest occupied molecular orbital (HOMO), charge on the phenolic oxygen, and frontier molecular orbital coefficients on the phenolic hydrogen are consistently greater for the syringyl compounds. In addition, syringyl compounds have lower bond dissociation energies for hydrogen abstraction.

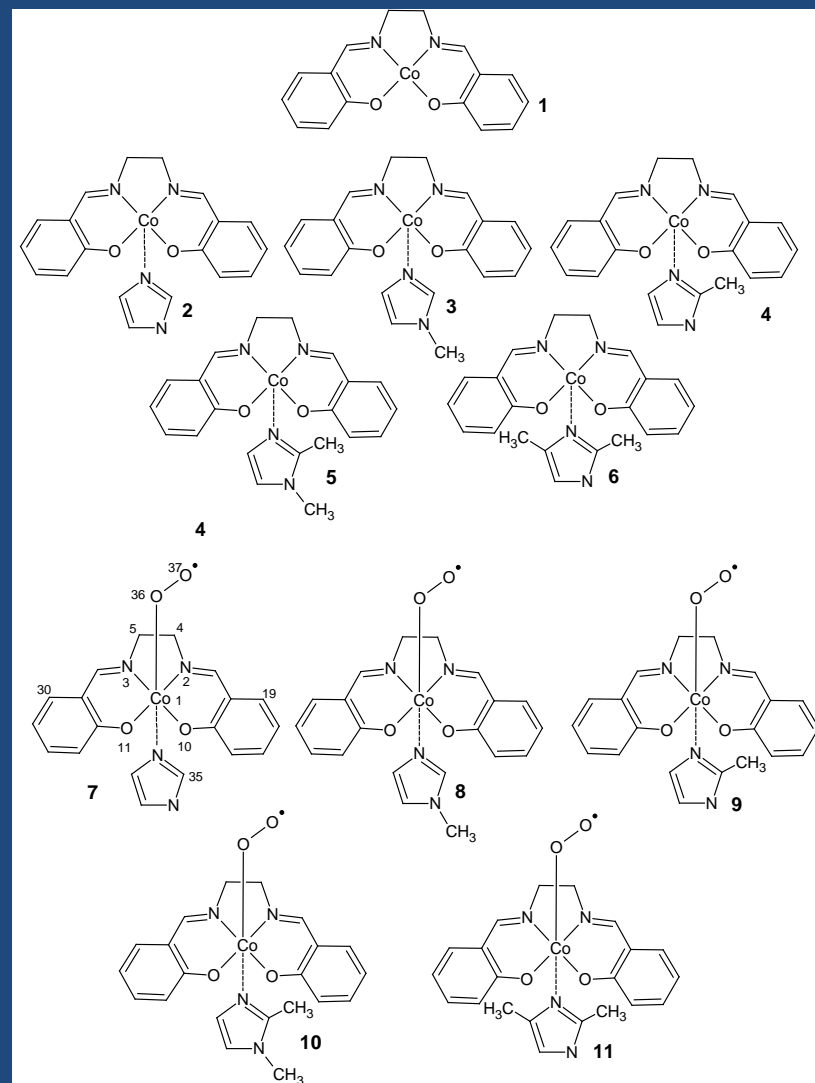


# Methods



The mysterious world of ligand substitution.

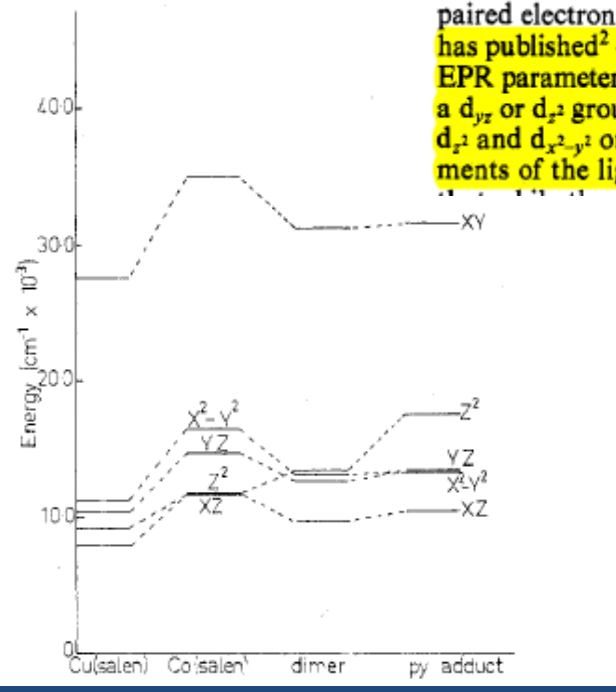
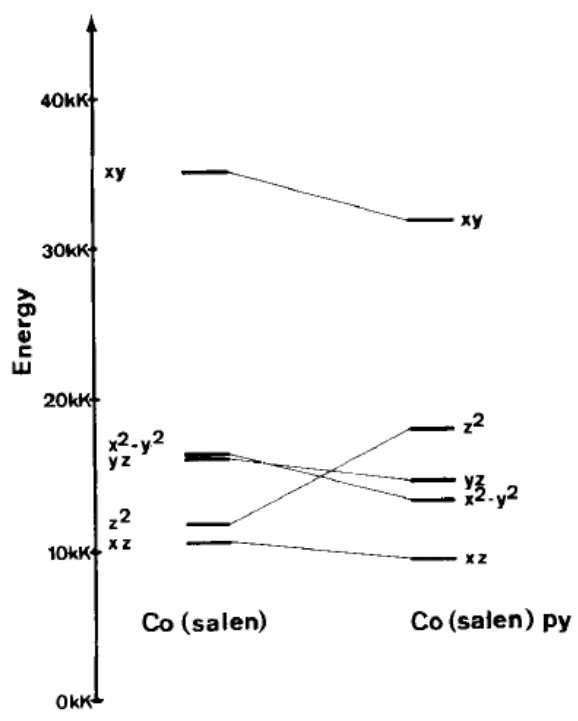
- To date, Gaussian09 has been used with UB3LYP/6-31G(d) calculations, with, NBO, full optimizations and frequency calculations
- Axial ligands that have been examined are
  - Imidazole
  - 1-methyl imidazole
  - 2-methyl imidazole
  - 1-2 dimethyl imidazole
  - 2-4 dimethyl imidazole
- All calculations were done with charge=0 and multiplicity=2 (1 unpaired electron)



# Results

- Before going too far we compared current results to the literature.





paired electron occupies the  $d_{z^2}$  orbital. Recently, McGarvey has published<sup>2</sup> detailed equations for the interpretation of the EPR parameters of a low-spin cobalt(II) complex having either a  $d_{yz}$  or  $d_{z^2}$  ground state, taking into account the fact that the  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals might be mixed by low-symmetry elements of the ligand field. Malatesta and McGarvey<sup>3</sup> found

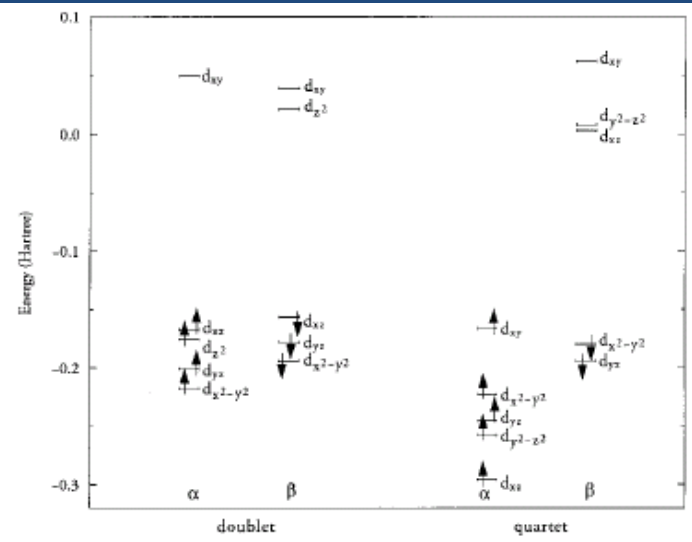


Figure 3. Quantitative molecular orbital diagram for the Co(acacen)-(pyridine) model in the doublet and quartet states.

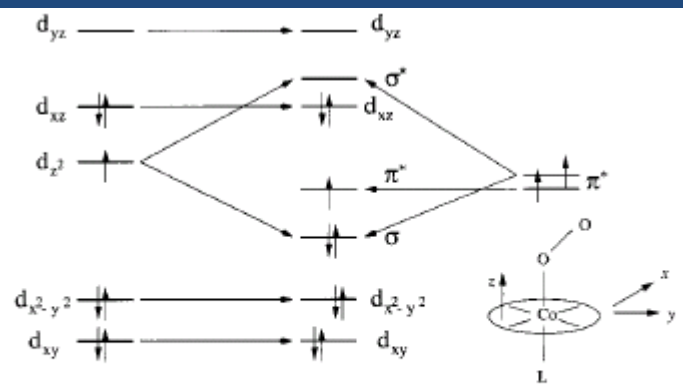


Figure 4. Schematic energy level diagram for Co(II)-dioxygen Schiff's base complexes based on an analysis of the orbital energies from density functional theory calculations.

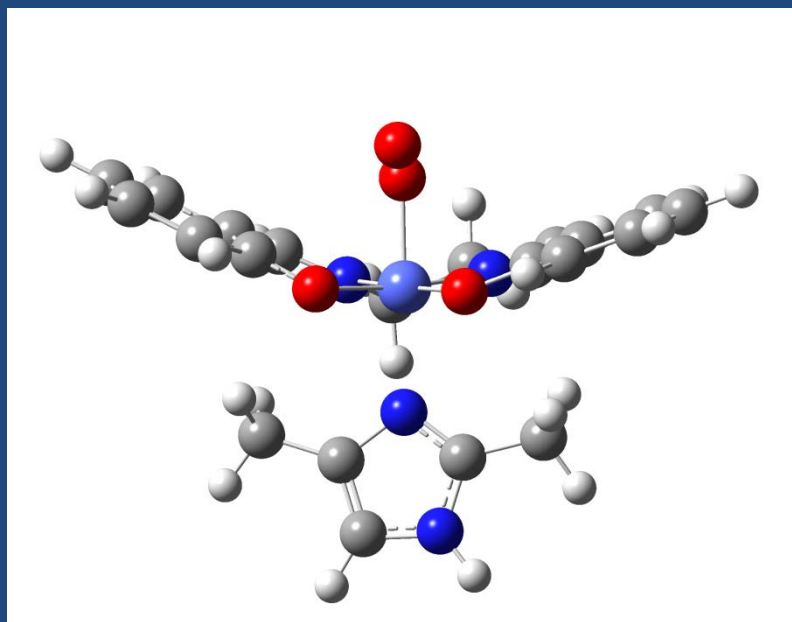
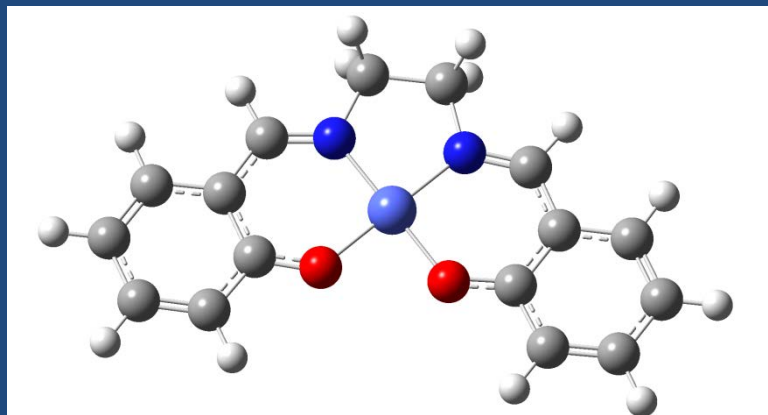


# Results

- Co(salen) the orbital population is consistent with the literature
  - The singly occupied molecular orbital is the  $d_{yz}$
  - The  $d_{xy}$  is unoccupied and the highest energy
- Co(salen)-O<sub>2</sub>-imidazole is consistent with the literature
  - The oxygen p-orbital is the singly occupied molecular orbital.
  - All axial ligands give similar results except the 2,4 dimethyl imidazole, in which there seem to be mixed orbitals
- These results are in accord with the spin density calculations

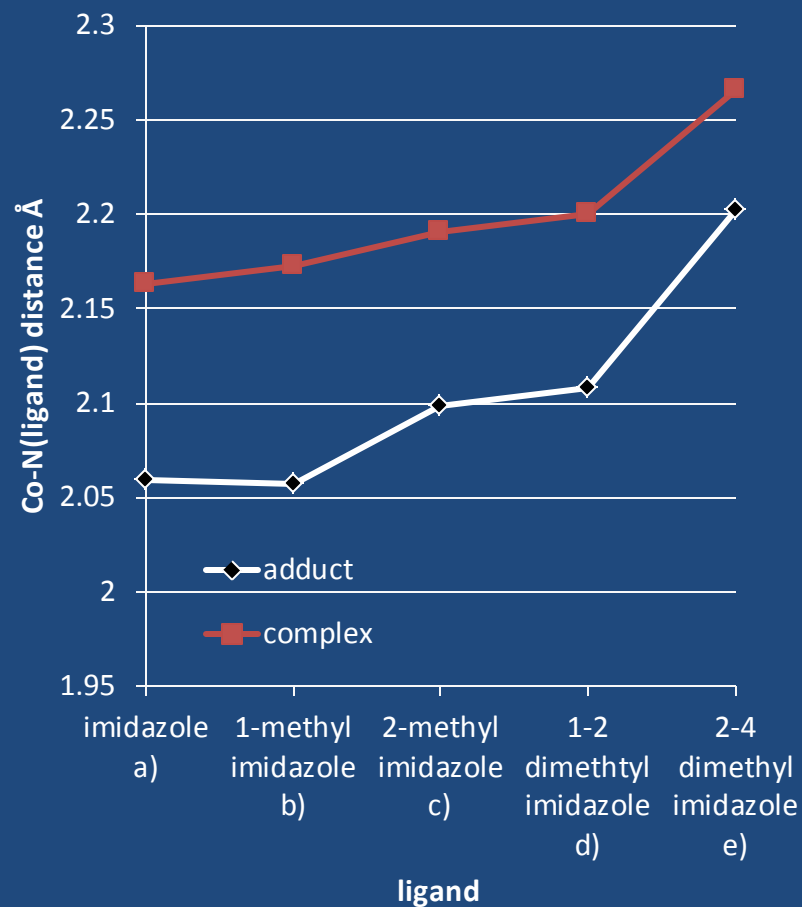
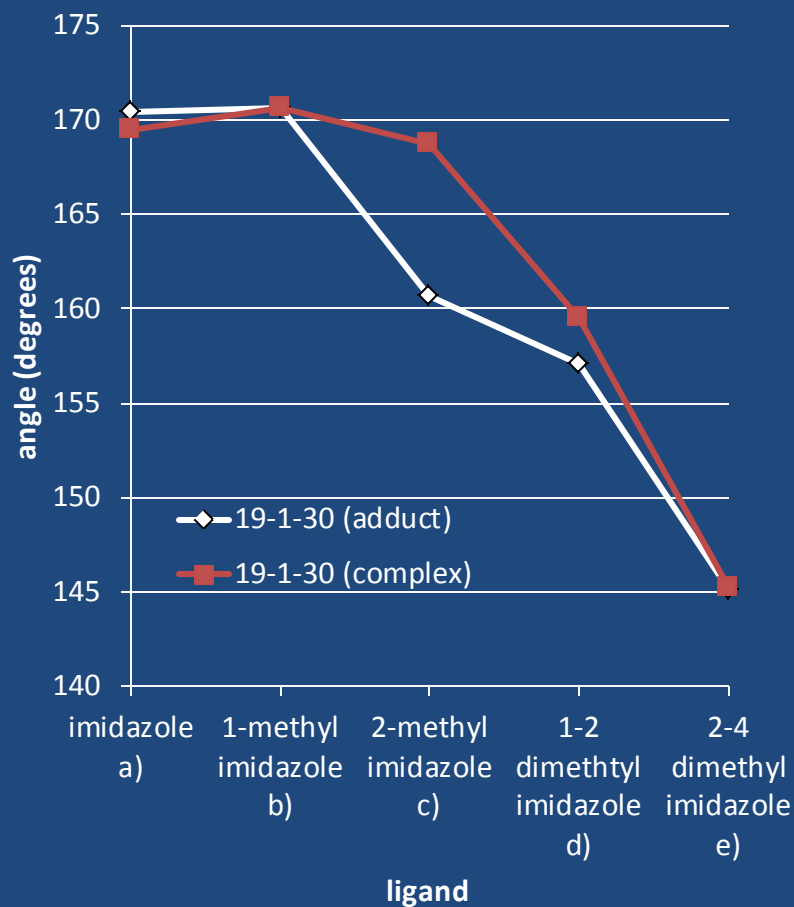
# Catalyst geometry

- The geometry of the catalyst changes with substitution
- The Co(salen) with no ligands is quite planar, while the addition of the axial ligand and oxygen distorts the structure out of planarity

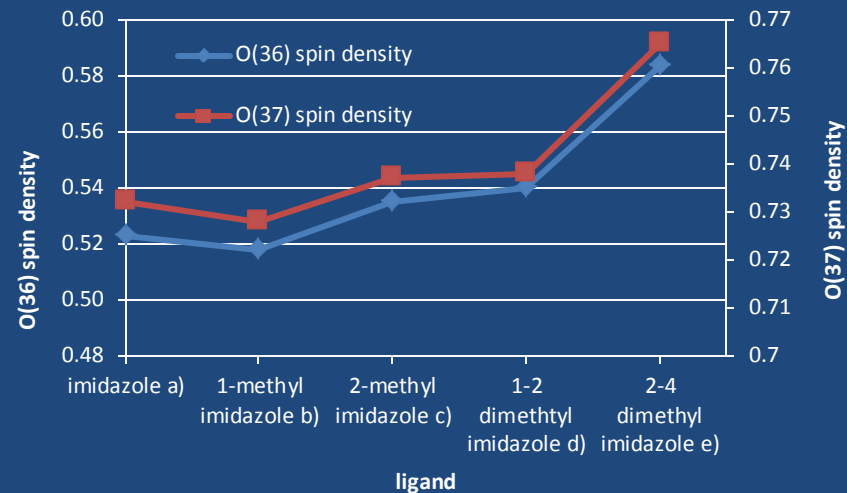
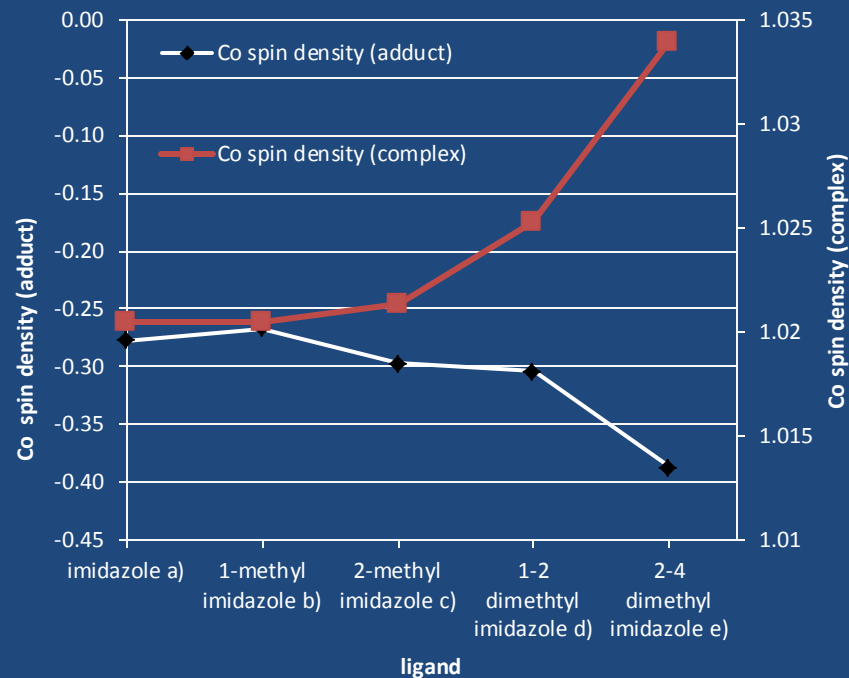
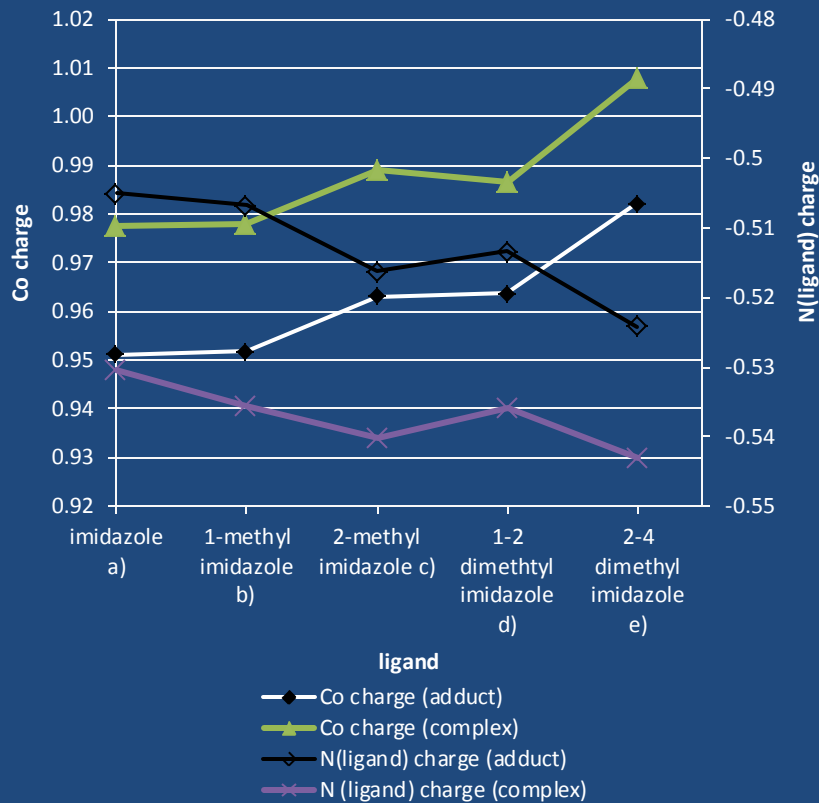




# Catalyst Geometry



# Electronic Results

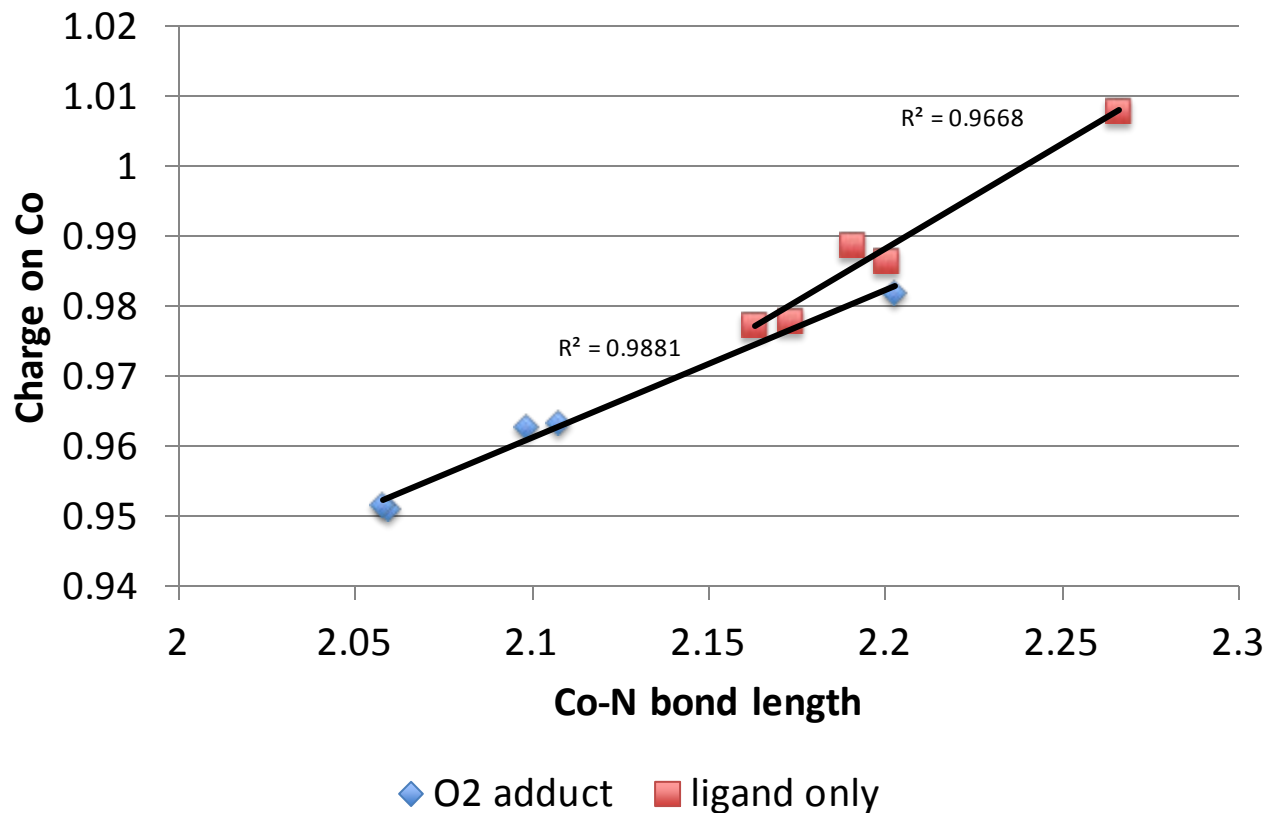


# Geometric-Electronic Relationships

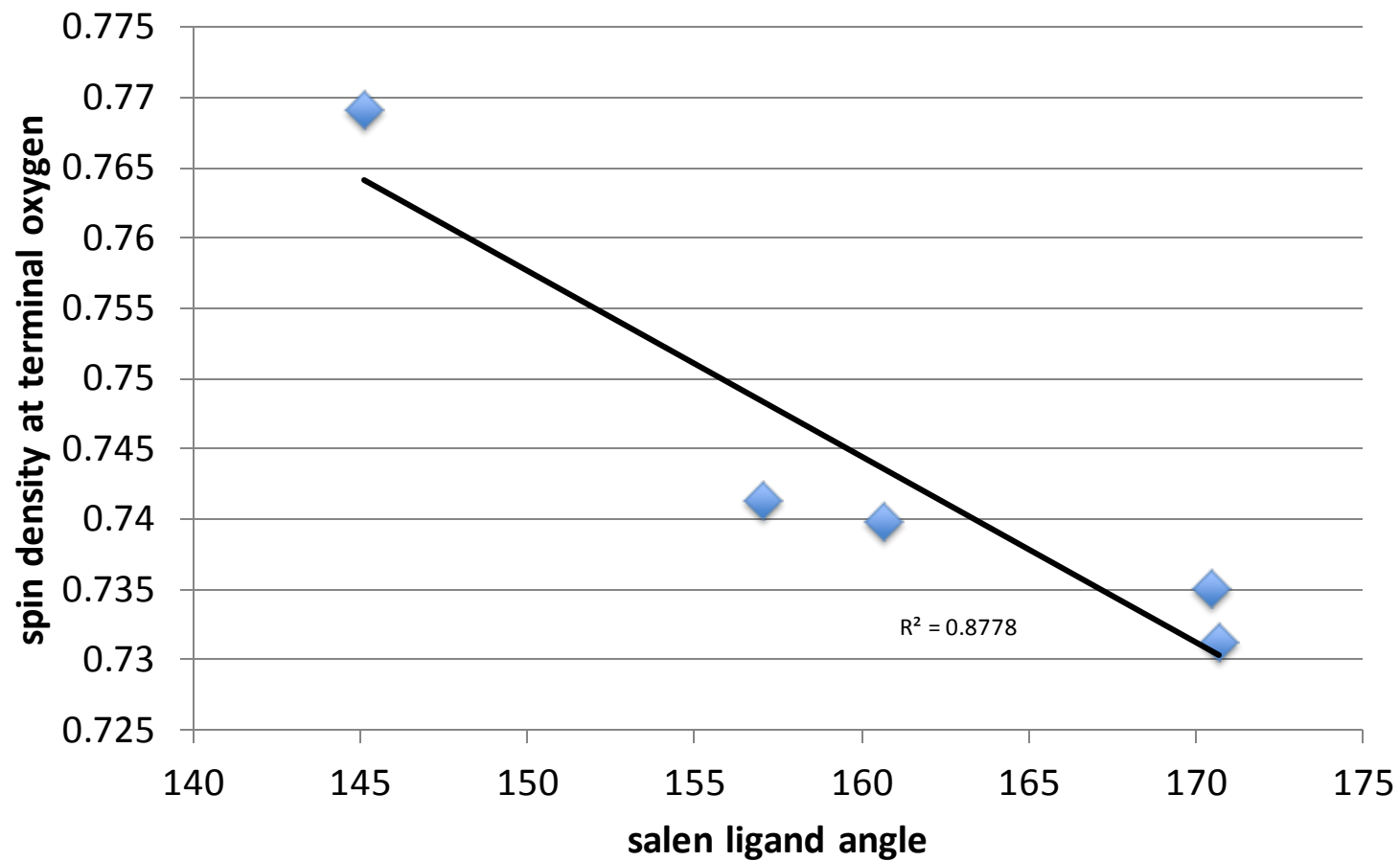
- These were done to evaluate changes in electronics as a function of geometry



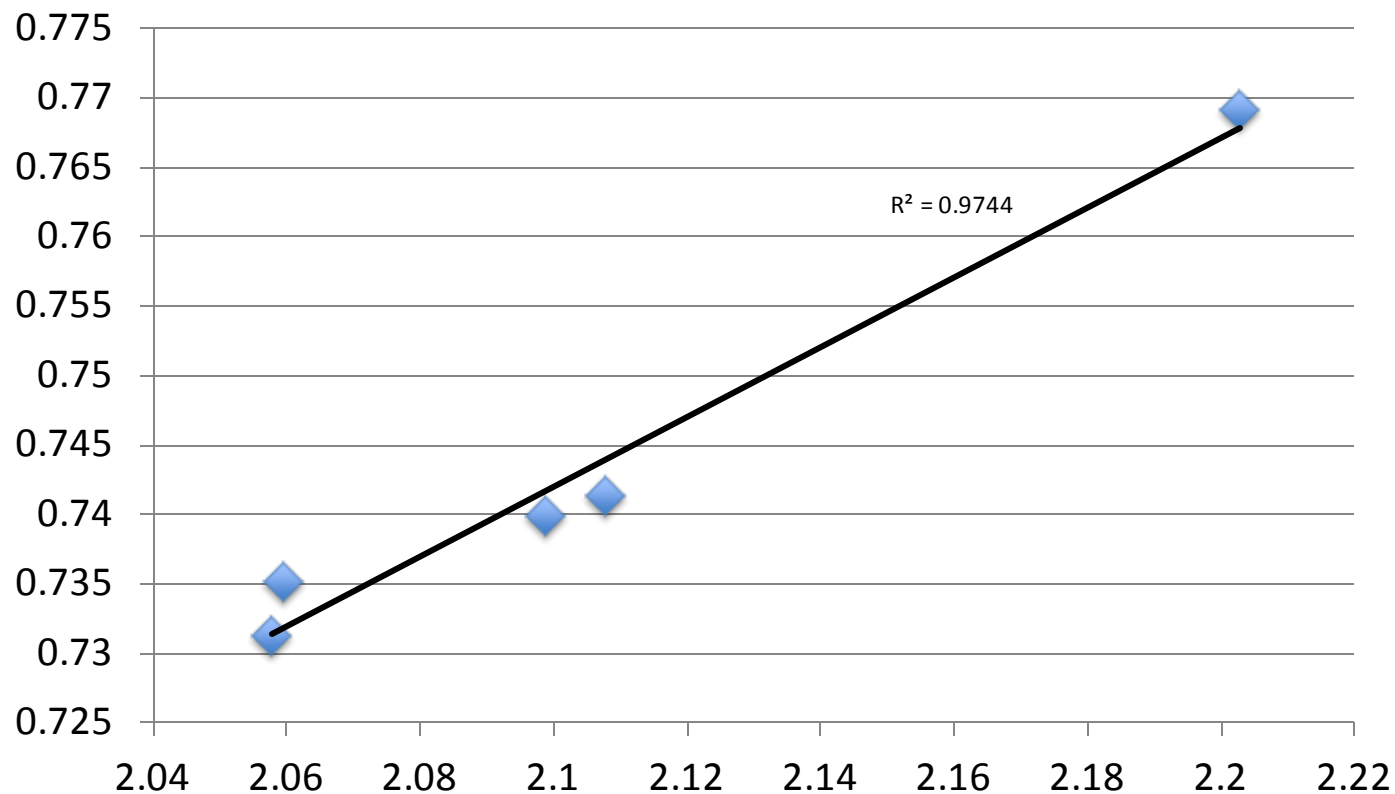
# Co charge as a function of Co-N bond length



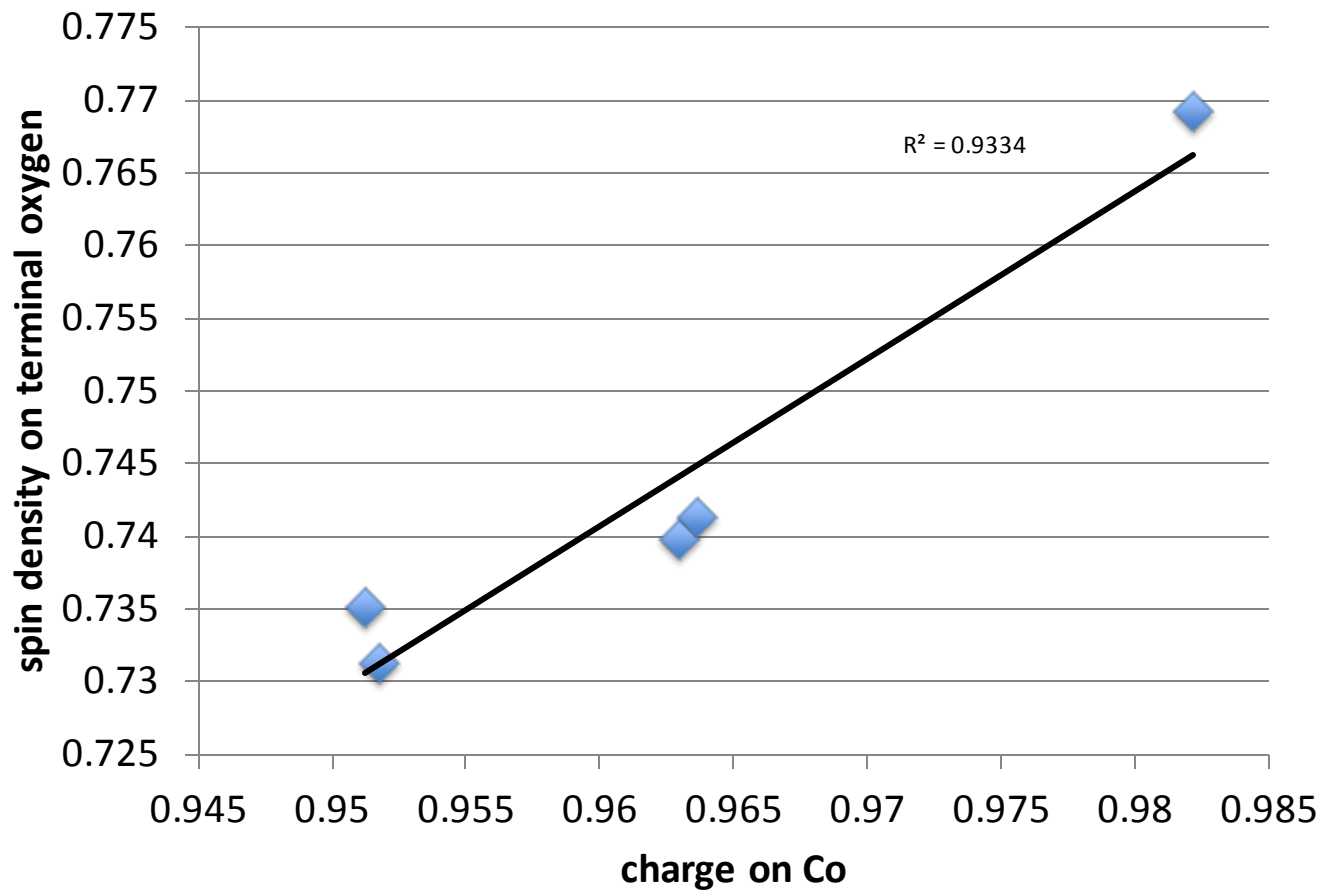
# Spin density at oxygen as a function of ligand angle



# Terminal oxygen spin density as a function of Co-axial ligand bond length

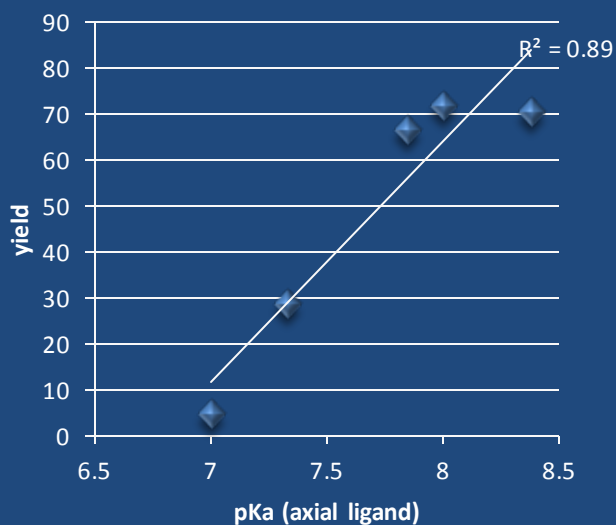


# Spin density on terminal oxygen as a function of Co charge



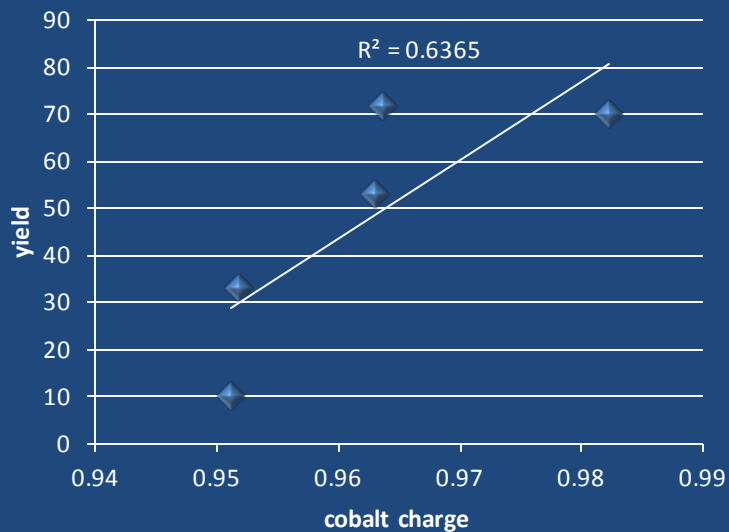
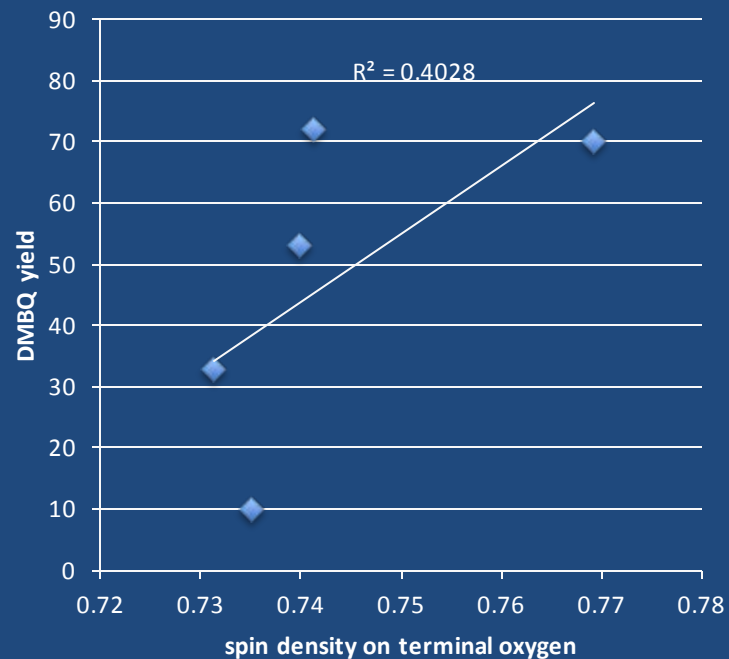
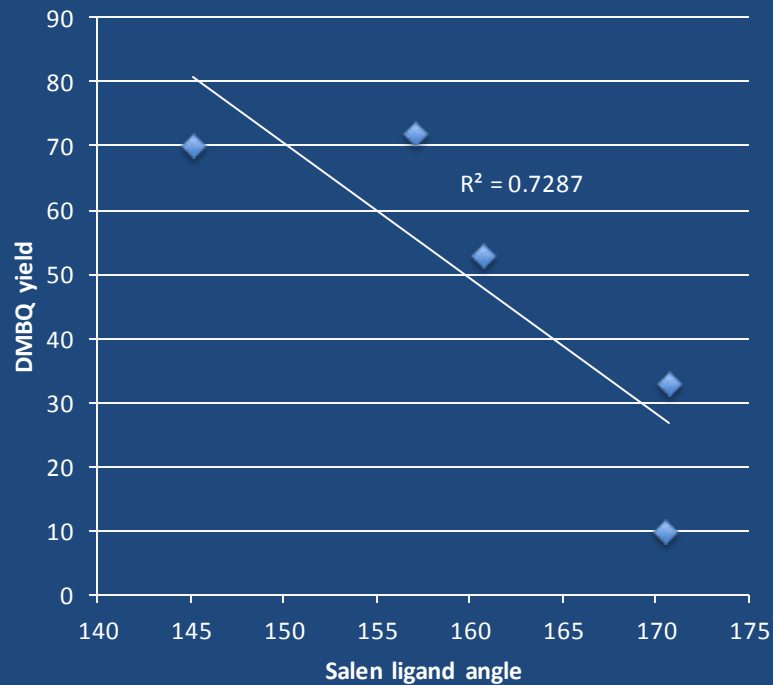
# Geometry/electronics vs Yield

Ligand	DMBQ yield	pKa
imidazole b)	5	7
1-methyl imidazole c)	29	7.33
2-methyl imidazole d)	67	7.85
1-2 dimethyl imidazole e)	72	8
2-4 dimethyl imidazole f)	71	8.38





# DMBQ yield as a function of molecular properties



# What have we learned?

- Our results are consistent with the literature in terms of orbital occupancy and ordering
- Axial substitution markedly changes the geometry of the salen ligand
  - Geometry also changes with ligand
- There are good relationships between geometry and electronics
- The relationships between geometry, electronics, energetics and yield are not as good
- This may mean that yield is controlled by more than one factor

# Pyrolysis Reactions

# Introduction

## Experimental Work on mechanisms

- Klein and Virk. 1983. Model pathways in lignin thermolysis. 1. Phenethyl phenyl ether. *Ind. Eng. Chem. Fundam.* 22:33-45
- Brežny et al. 1983, 1984. Low temperature thermolysis of lignins. I and II. *Holzforschung* 37:199-204, 38:19-24.
- Evans et al. 1986. Direct mass spectrometric studies on the pyrolysis of carbonaceous fuels. III. Primary pyrolysis of lignin. *J. Anal. Appl. Pyrolysis* 9:207-236.
- Britt and co-workers
  - 2000. Flash vacuum pyrolysis of methoxy-substituted lignin model compounds. *J. Org. Chem.* 65:1376-1389
  - 2007. Oxygen substituent effects in the pyrolysis of phenethyl phenyl ethers. *Energy and Fuels* 21:3102-3108

# Introduction

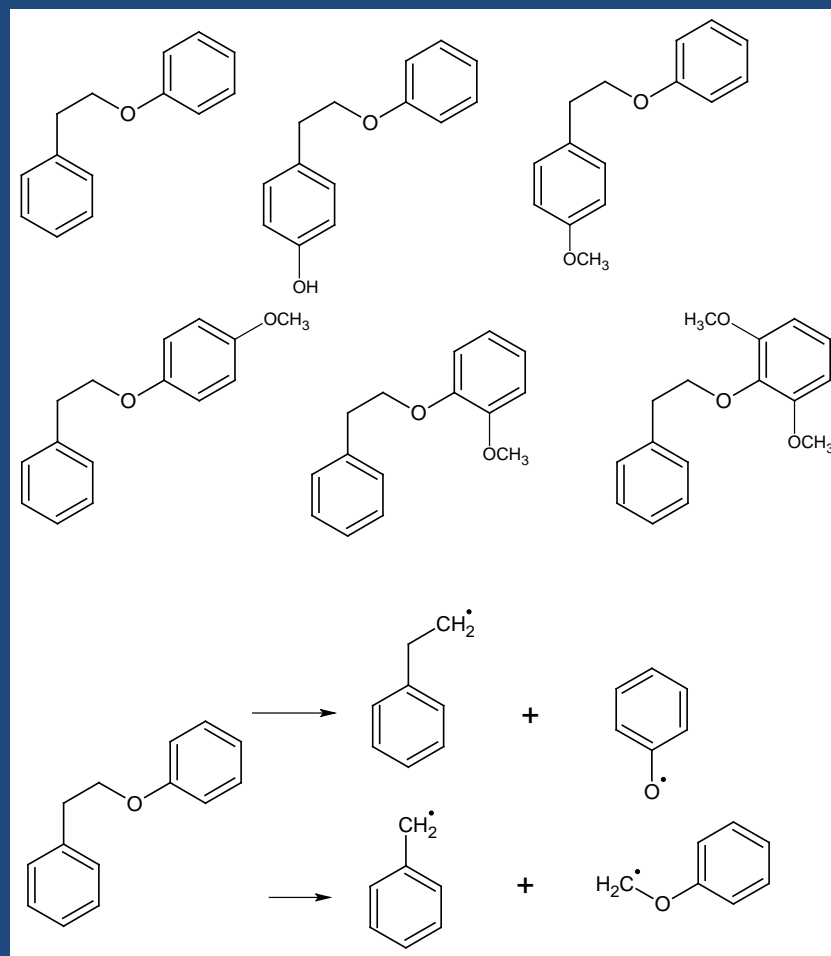
## Computational Work

- Beste, A., Buchanan, A.C. III (2009) Computational study of bond dissociation enthalpies for lignin model compounds. Substituent effect in phenylethyl phenyl ethers. *J. Org. Chem.* 74:2837–2841.
- Beste, A., Buchanan, A.C. III (2011) Computational study of bond dissociation enthalpies for substituted  $\beta$ -O-4 lignin model compounds. *ChemPhysChem* 12:3556-3565
- Younker, J.M., Beste, A., Buchanan, A.C. III. (2012) Computational study of bond dissociation enthalpies for lignin model compounds:  $\beta$ -5 arylcoumaran. *Chem. Phys. Lett.* 545:100-106
- Wang, H., Zhao, Y., Wang, C., Fu, Y., Guo, Q. (2009) Theoretical study on the pyrolysis process of lignin dimer model compounds. *Acta Chimi. Sin.* 67:893–900.

# Introduction

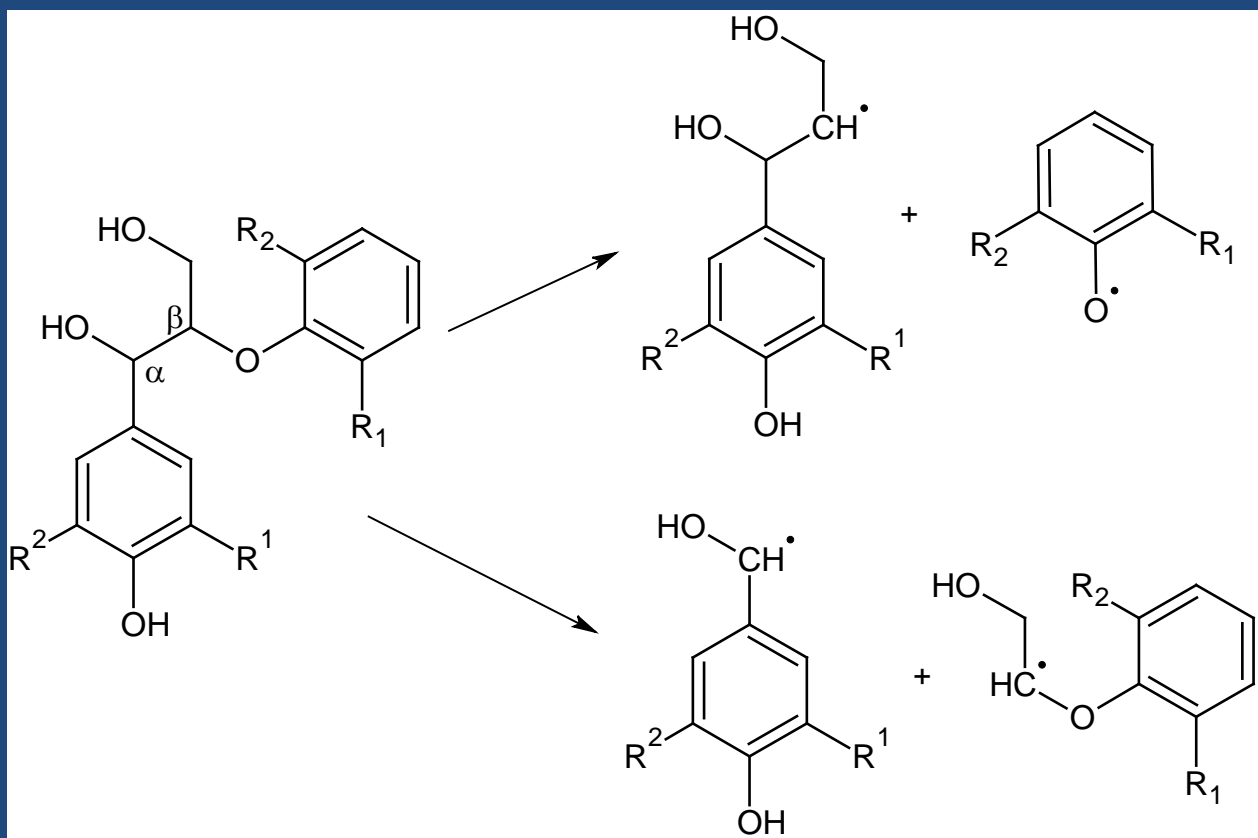
## Computational Work

- Beste, A., Buchanan, A.C. III (2009) Computational study of bond dissociation enthalpies for lignin model compounds. Substituent effect in phenylethyl phenyl ethers. *J. Org. Chem.* 74:2837–2841.
  - M06-2X/mixed basis set
    - 6-31G(d), all atoms
    - 6-311++G(d,p), atoms with unpaired electron



# Methods

- Based on the results of Beste and Buchanan (2009) on phenethyl phenyl ethers, the bond dissociation enthalpy of dilignols was evaluated



# Methods-Computational Methods

- Composite methods for accurate thermochemistry
- G3MP2
  - Curtiss et al. 1999. J. Chem. Phys. 110:4703-4709.
    - Optimizations at HF/6-31G(d) and MP2/6-31G(d)
    - Single point MP2/G3large, MP4/6-31G(d), QCISD(T)/6-31G(d)
- CBS-4m
  - Montgomery et al. 2000. J. Chem. Phys. 112:6532–6542.
    - Optimization and frequency HF/3-21G(d)
    - Single point MP4/6-31G, MP2/6-31+G(d,p), HF/CBSB1
- Gaussian09
- SGI Altix Cluster-Alabama Supercomputer Authority



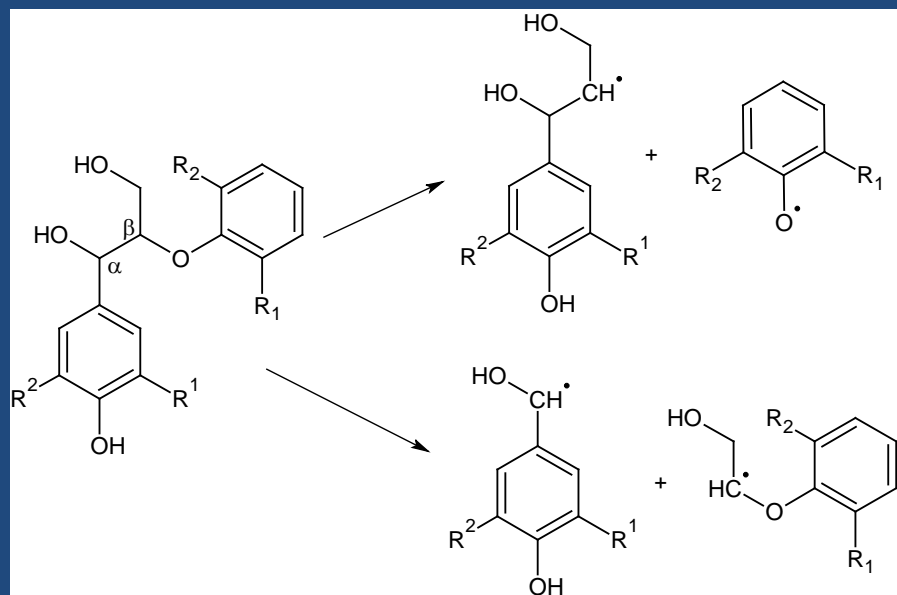
# Calibration

- Results for anisole and ppe from the literature were compared with G3MP2 and CBS-4m
  - Energetics were consistent
  - Considerable time advantage with CBS-4m

# Results

## CBS-4m

### bond dissociation enthalpy



The differences between  $\beta$ -O and  $\alpha$ - $\beta$  are smaller than for the PPEs, perhaps indicating less selectivity.

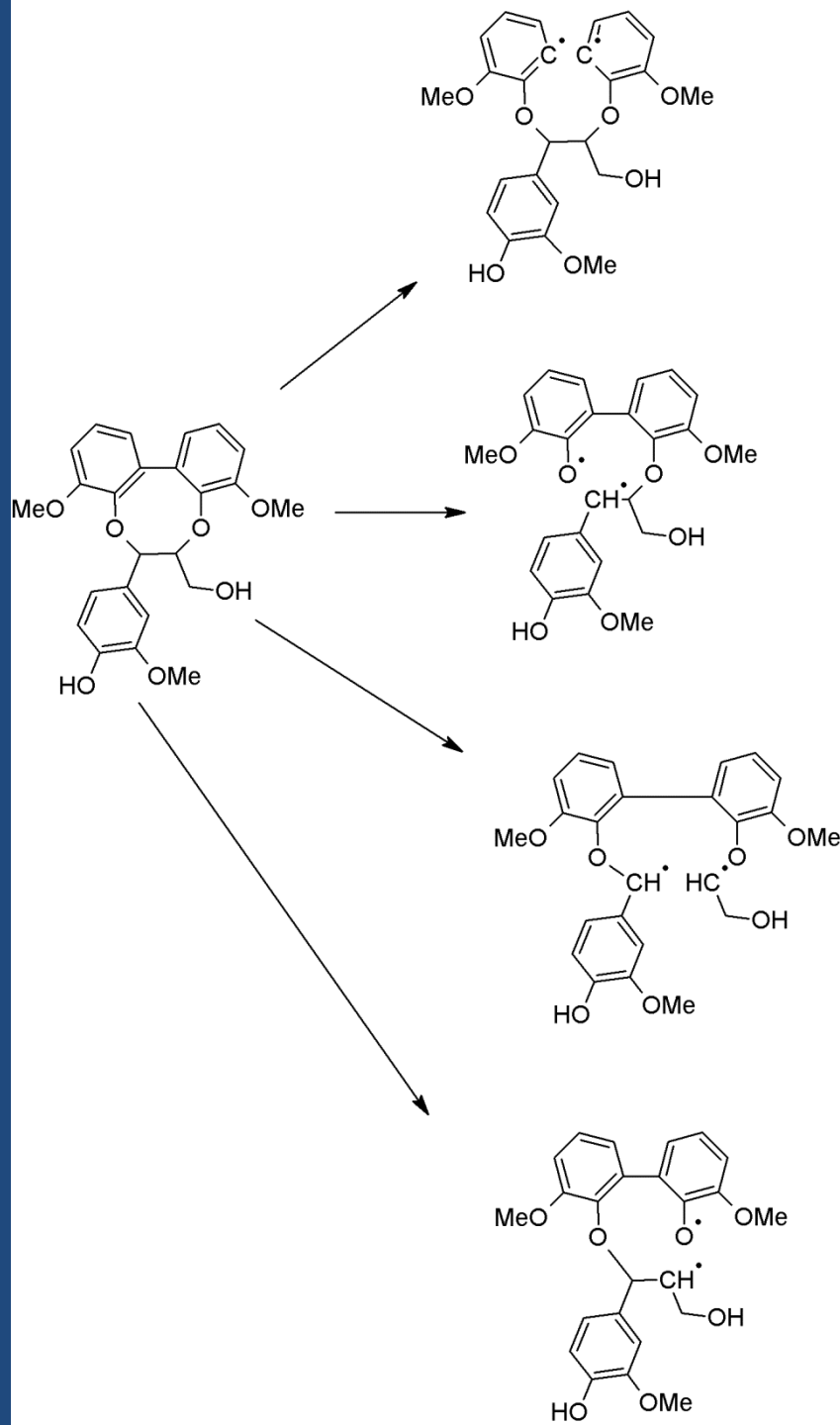
compound	temperature	$\beta$ -O	$\alpha$ - $\beta$
guaiacyl	298 K	72.3	81.1
guaiacyl M06-2x/6-311++g(d,p)	298K	70.0	81.0
syringyl	298 K	73.7	79.2
p-coumaryl	298 K	73.6	75.3
p-coumaryl	800 K	73.6	74.6
p-coumaryl (B3LYP/6-31G(d))	800 K (Wang et al. 2009)	54.5	57.6

# What Have We Learned?

- Compound methods (at least some of them) are feasible for models of reasonable size
- Compound methods are fairly consistent with respect to results
- The difference in BDE between  $\beta$ -O and  $\alpha$ - $\beta$  cleavage mechanisms is lower for dilignols than for PPE models
  - This may mean the reactions are less selective

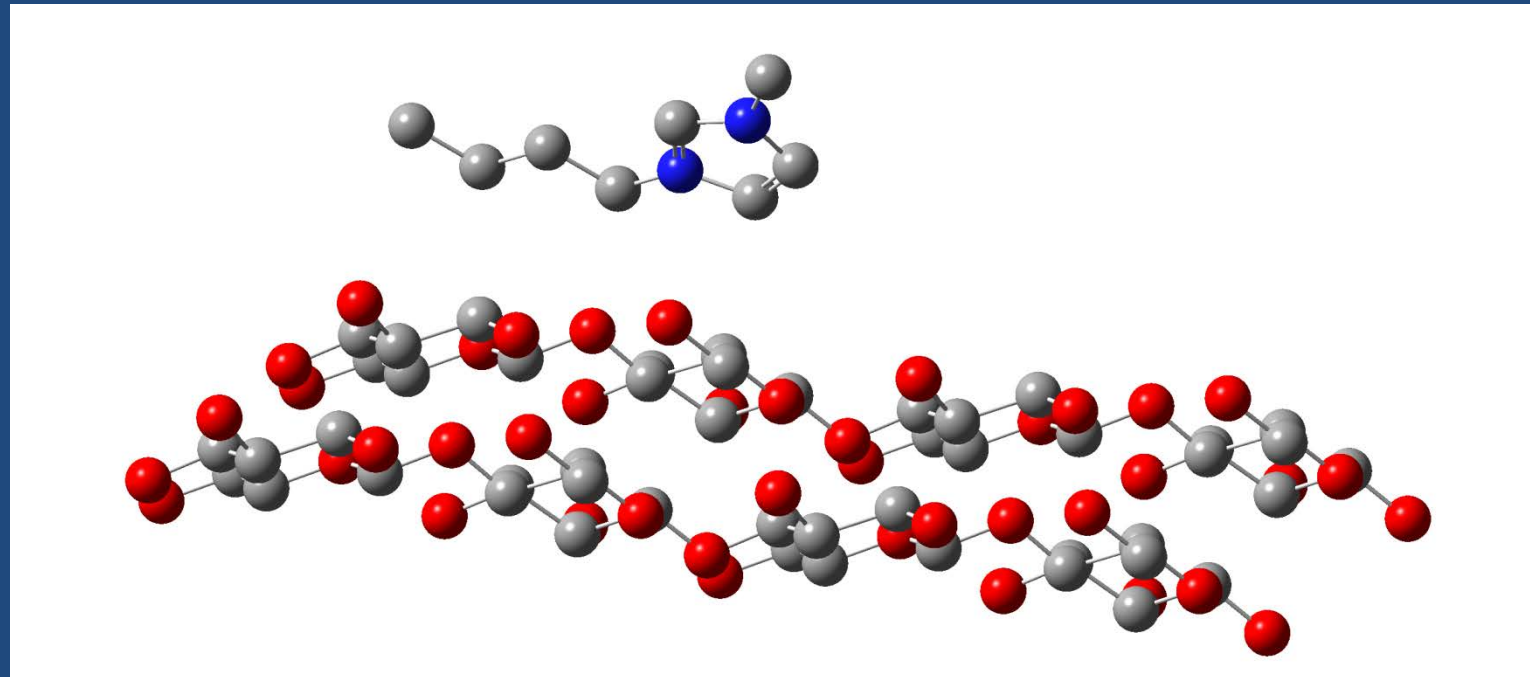
# BDEs of dibenzodioxocin

- Dibenzodioxocin structures recently discovered by Brunow and co-workers
- BDEs within the group
- Conformational analysis of open ring structures
  - 500 iteration MC search with PM3 optimization
- M06-2X/6-31+G(d), ultrafine grid, optimizations on lowest 10 conformers
- M06-2X/6-311++G(d,p) single point, frequency, ultrafine grid, on lowest energy conformer



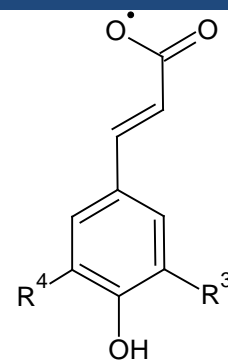
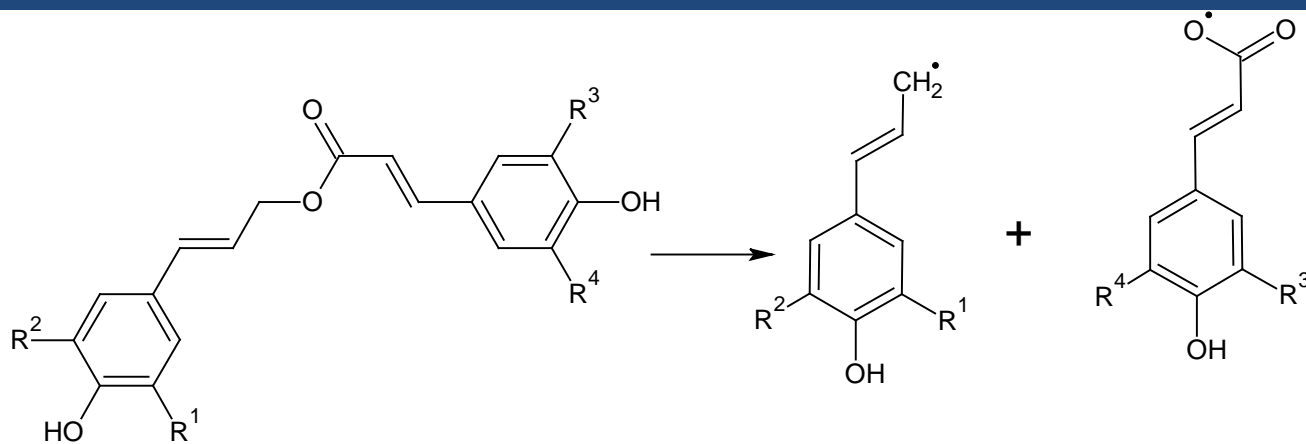
# Coming attractions (?)

- Interactions of ionic liquids with cell wall constituents

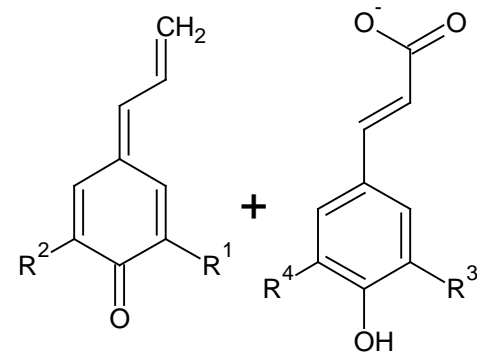
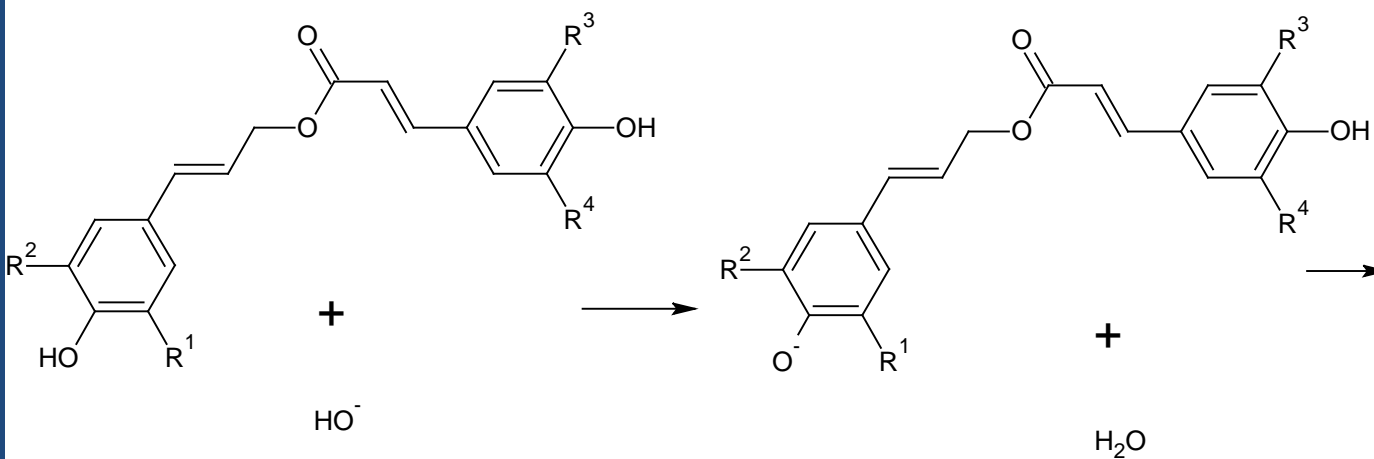


# Modified Lignins

(Grabber et al. Biomacromolecules 9:2510)



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# Questions