Degradation Reactions of Lignin in Pyrolysis
(Computational Applications)

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Computational Literature

- Improvements in hardware and software have made high level, quantum-based calculations feasible for dilignols

- Most require supercomputer/parallel processor capabilities

- Renewed interest in bioenergy, bioproducts and the biorefinery has resulted in increased activity in this area

Kinetic Analysis of the Pyrolysis of Phenethyl Phenyl Ether: Computational Prediction of α/β-Selectivities

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

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

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Theoretical Study of the Remarkably Diverse Linkages in Lignin

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Introduction

- Biomass utilization for energy
- Biorefinery
  - Biochemical platform
  - Thermochemical platform
    - Torrefaction
    - Pyrolysis
    - Gasification
- Free radical reactions in general
  - Thermal, photochemical, mechanical, ultrasound, industrial processes

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.

Introduction
Experimental work on mechanisms

- 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
Experimental work on mechanisms

- Kawamoto and co-workers.
    - 2007. Role of side-chain hydroxyl groups in pyrolytic reactions of phenolic β-ether type of lignin dimer. J. Wood Chem. Technol. 27:113–120.
    - 2007a. Pyrolysis reactions of various lignin dimers. J. Wood Sci. 53:168–174.
    - 2007b. Effects of side-chain hydroxyl groups on pyrolytic β-ether cleavage of phenolic lignin model dimer. J. Wood Sci. 53:268–271.
    - 2008a. Different pyrolytic cleavage mechanisms of β-ether bond depending on the sidechain structure of lignin dimers. J. Anal. Appl. Pyrolysis 81:207–236.
    - 2008b Pyrolytic cleavage mechanisms of lignin-ether linkages: a study on *p-substituted* dimers and trimers. Holzforschung 62:50–56.
    - 2009 Radical chain reactions in pyrolytic cleavage of the ether linkages of lignin model dimers and a trimer. Holzforschung 63:424–430.

Introduction
Computational Work

- Beste, A., Buchanan, A.C. III (2009) Computational study of bond dissociation enthalpies for lignin model compounds. Substituent effect in phenyethyl phenyl ethers. J. Org. Chem. 74:2837–2841.

- Beste, A., Buchanan, A.C. III, Britt, P.F., Hathorn, B.C., Harrison,R.J. (2007) Kinetic analysis of the pyrolysis of phenethyl phenyl ether: computational prediction of α/β selectivities. J. Phys.Chem. A 111:12118–12126.

- Beste, A., Buchanan, A.C. III, Harrison, R.J. (2008) Computational prediction of a/b selectivities in the pyrolysis of oxygen-substituted phenethyl phenyl ethers. J. Phys. Chem. A 112:4982–498.

- 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 phenyethyl 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 upaired electron
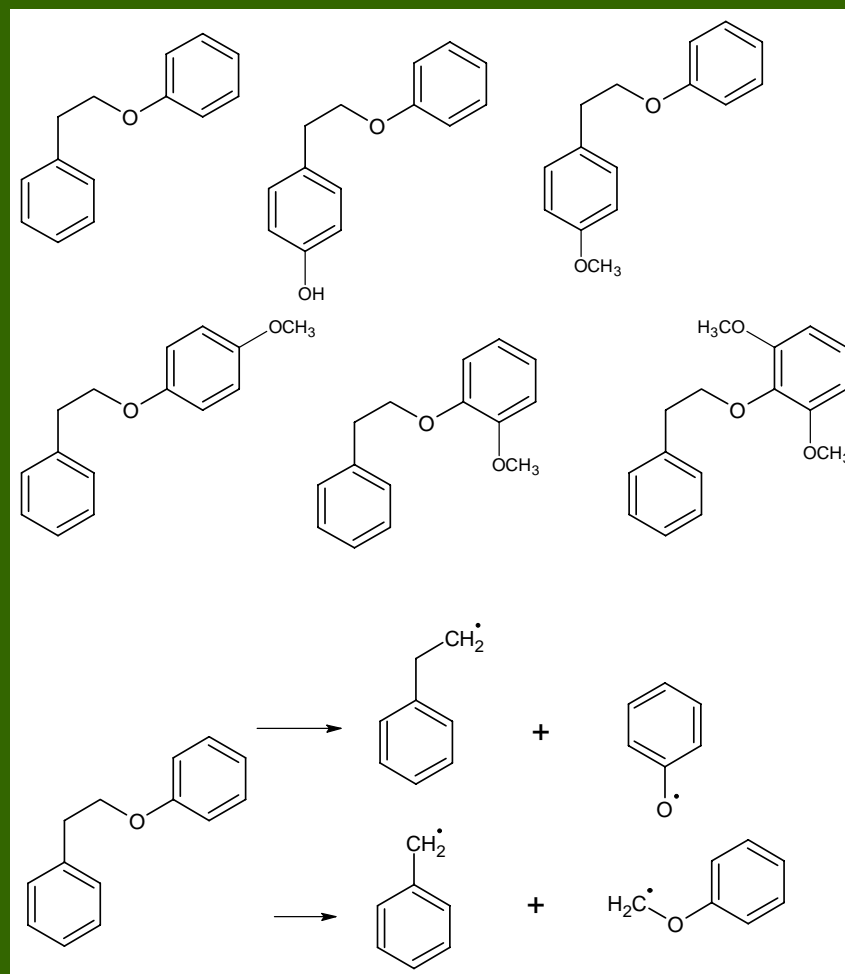
Methods

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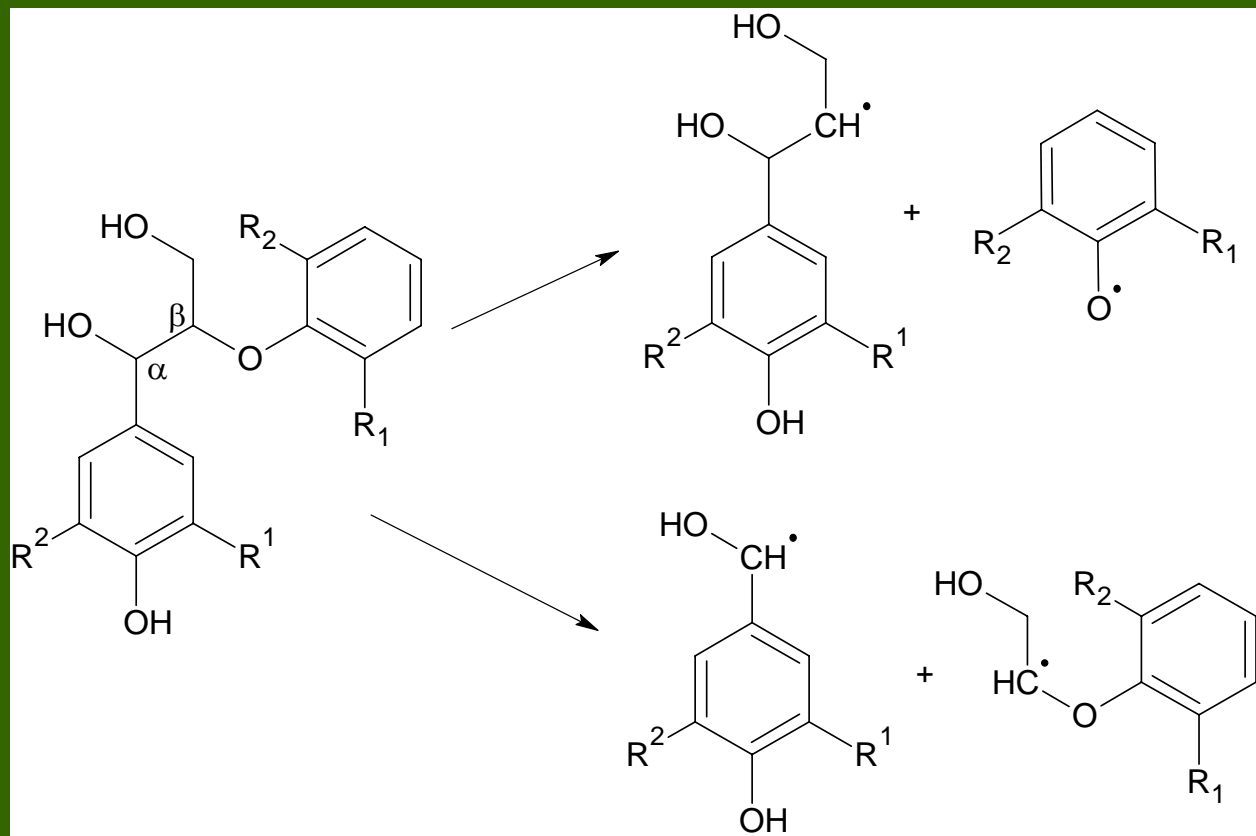
Methods

- Structures from x-ray diffraction were used as the starting geometries
  - Stomberg, R., Lundquist, K. (1994). Stereochemistry of lignin structures of the β-O-4 type. Crystal structures of model compounds. Nord. Pulp Pap. Res. J. 9:37–43.
  - Langer, V., Li, S., Lundquist, K. (2002) erythro-2-(2,6-Dimethoxyphenoxy)-1-(4-hydroxy-3,5-dimethoxyphenyl)-1,3-propanediol. Acta Cryst. E58:o42–o44.

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

Results

- **Prior to initiating work on dilignols, preliminary calculations were done on compounds from the literature**
  - Anisole experimental
    - 65.3 kcal mol^{-1}
- **CPU time**
  - PPE-oOCH3
    - G3MP2, 2300h
    - CBS-4m, 36.5h

anisole

ortho-methoxy-phenethyl phenyl ether (PPE-oOCH$_3$)
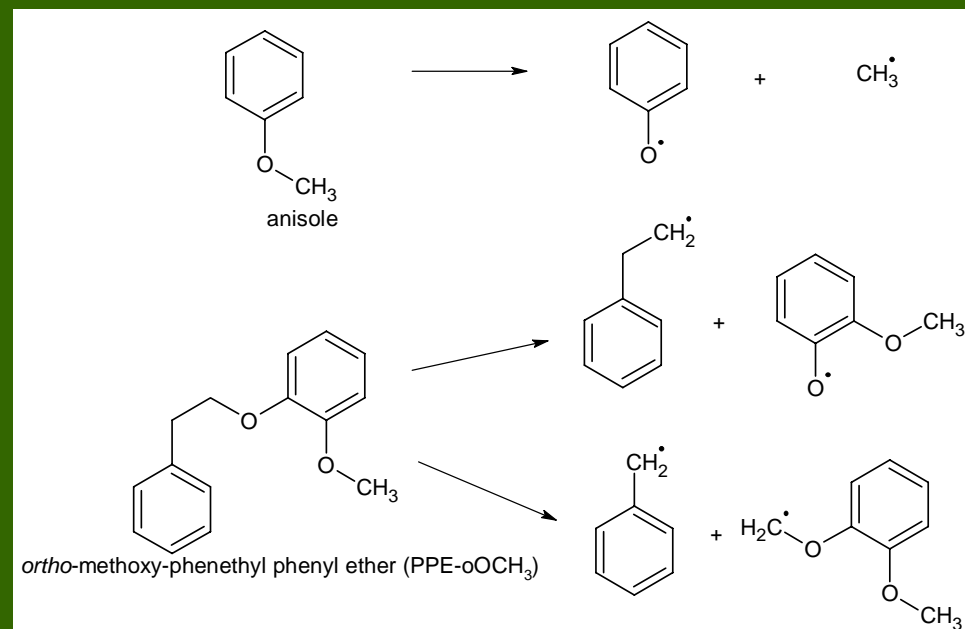
Compound/linkage	M06-2X	G3MP2	CBS-4M
Anisole	67.5	66.7	67.0
PPE-oOCH3/β-O	64.4	66.6	68.3
PPE-oOCH3/α-β	77.0	79.8	79.6

Effect of method

CBS-QB3
- B3LYP/6-311G(2d,d,p)
  - optimization
- B3LYP/CBSB7
  - frequency
- CCSD(T)/6-31+G(d')
  - Single point
- MP4SDQ/CBSB4
  - Single point
- MP2/CBSB3
  - extrapolation
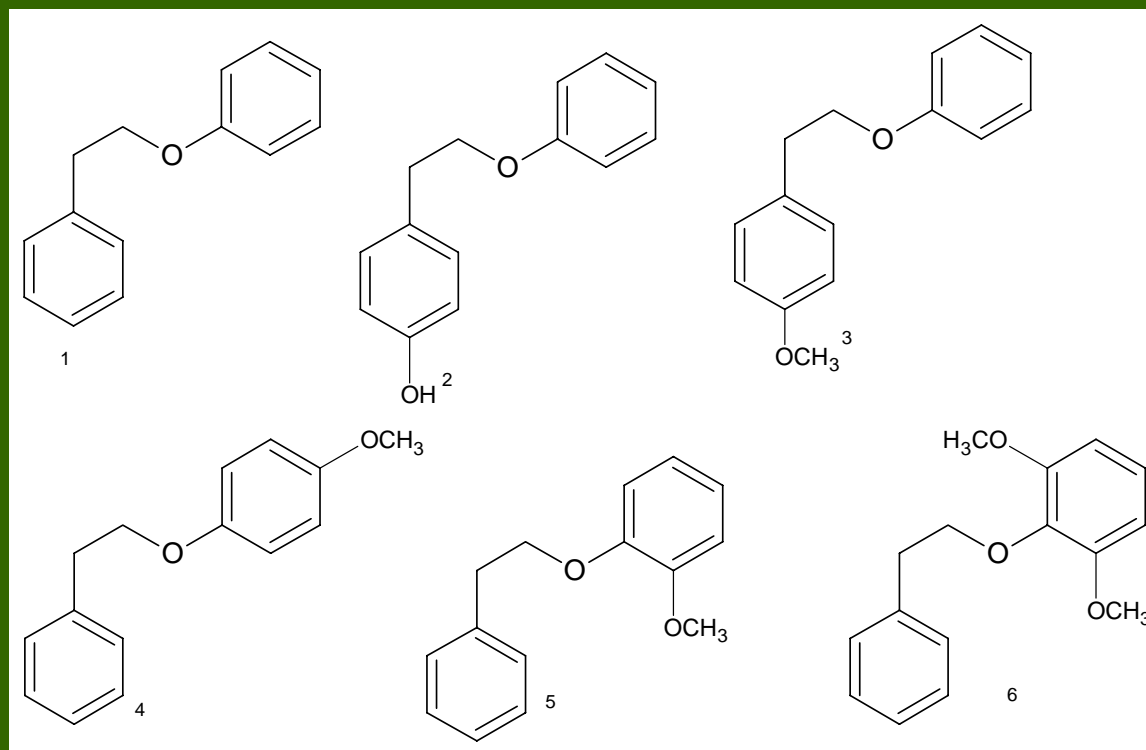
Compound	M062X (literature)	G3MP2	CBS-4m	CBS-QB3
anisole	67.5	66.7	67	65.6
1 β-O/α-β	69.5/77.1	68.8/77.1	69.8/82.8	67.8/82.8
2	69.6/76.6		69.0/82.4	
3	69.6/76.6		68.9/82.3	
4	64.1/76.7		66.4/77.1	
5	64.4/77	66.6/79.8	68.3/79.6	
6	60.9/78.0		66.7/83.1	

Results
CBS-4m
bond dissociation
enthalpy
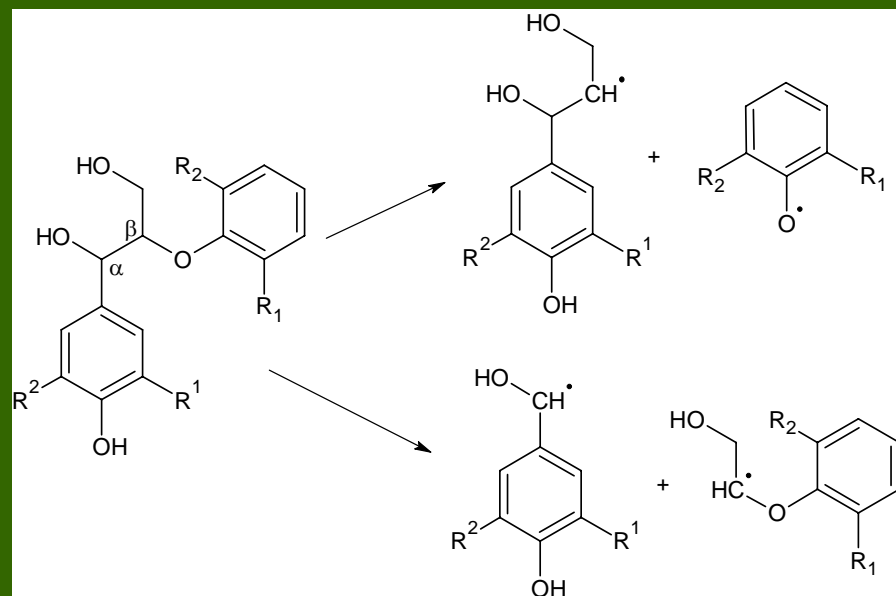
The differences between B-O and α-β are smaller than for the PPEs, perhaps indicating less selectivity.

compound	temperature	β-O	α-β
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

Effect of Substitution

Effect of Substitution

- Kawamoto et al. 2008. J. Anal. Appl. Pyrolysis 81:88
 - Proposed that γ-OH structures will form QM, while γ-deoxy will proceed via homolysis
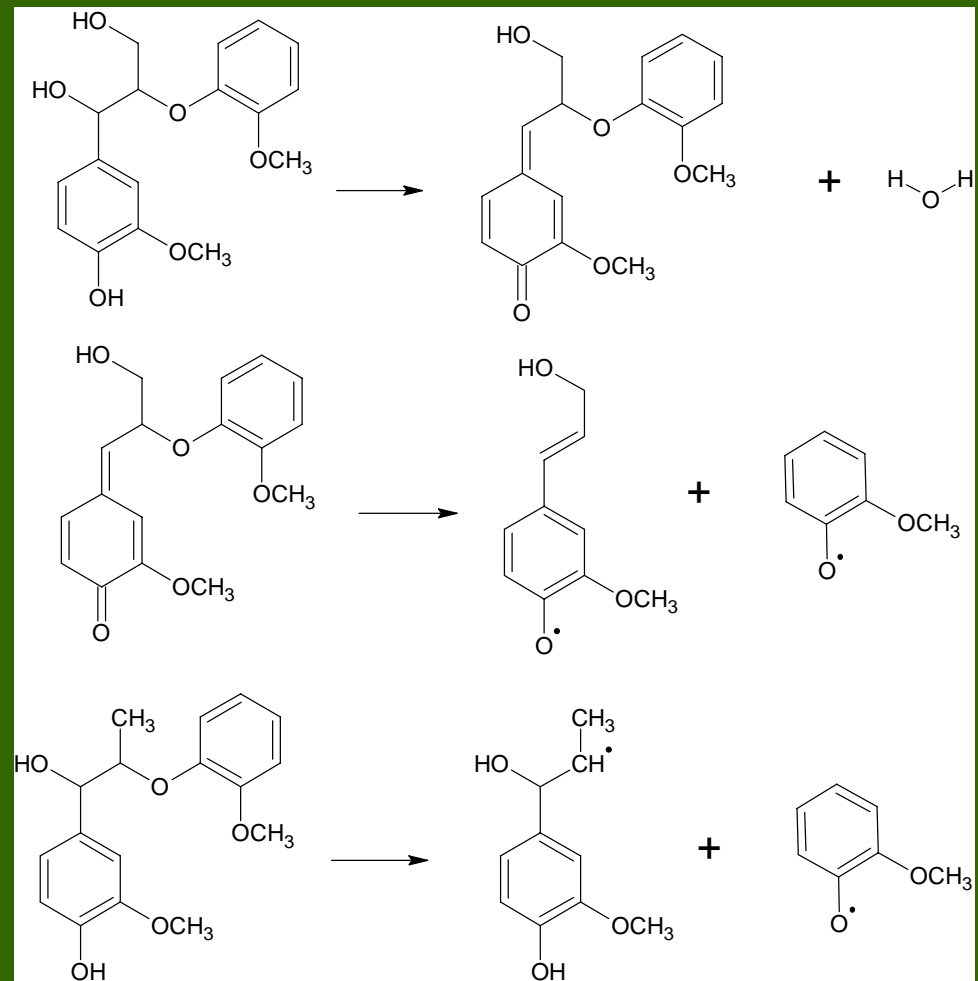
Effect of Substitution
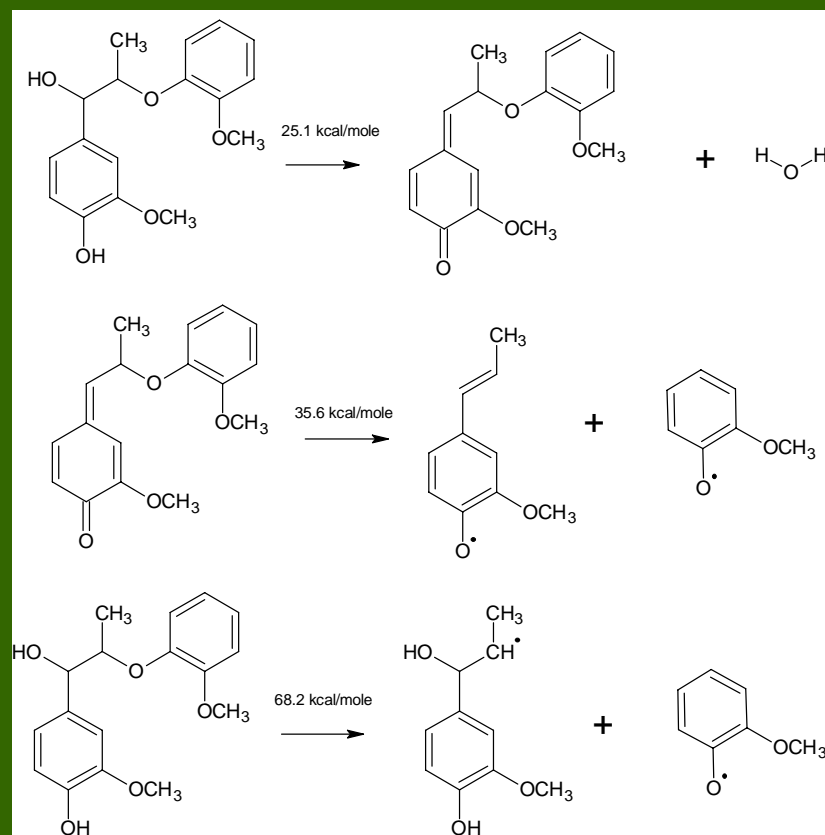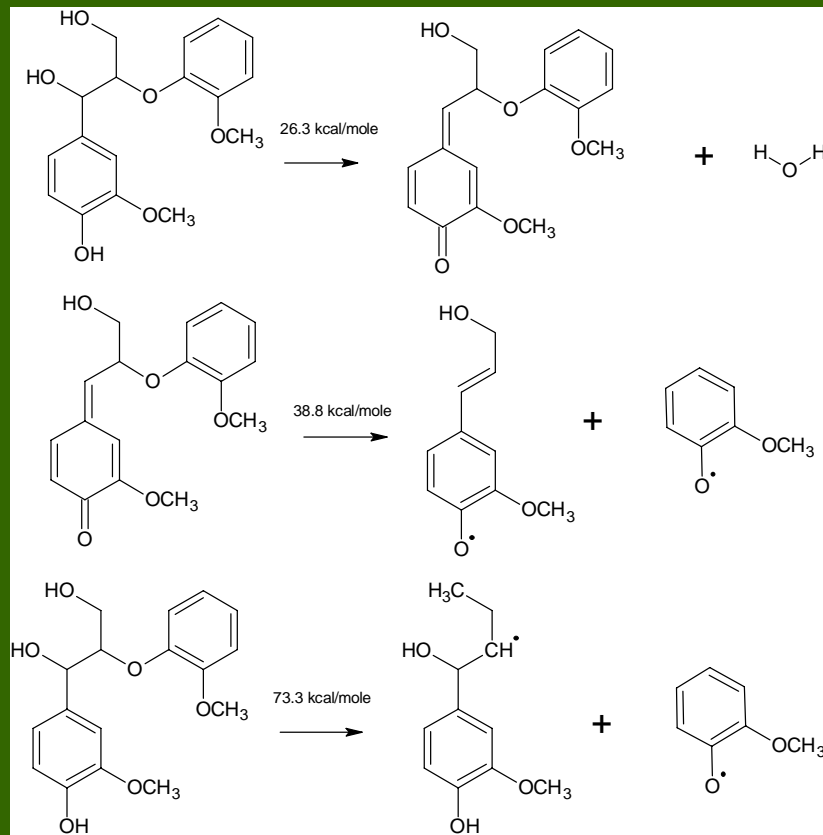
- BDE of β-O from QM is indeed lower than direct homolysis
- But when the enthalpy of reaction of QM formation is taken into account the difference is small
- Total enthalpy of reaction for the QM mechanism of the γ-deoxy is lower than direct homolysis

Effect of Substitution

- β-O = 72.3 kcal/mole

- α-β = 81.1 kcal/mole
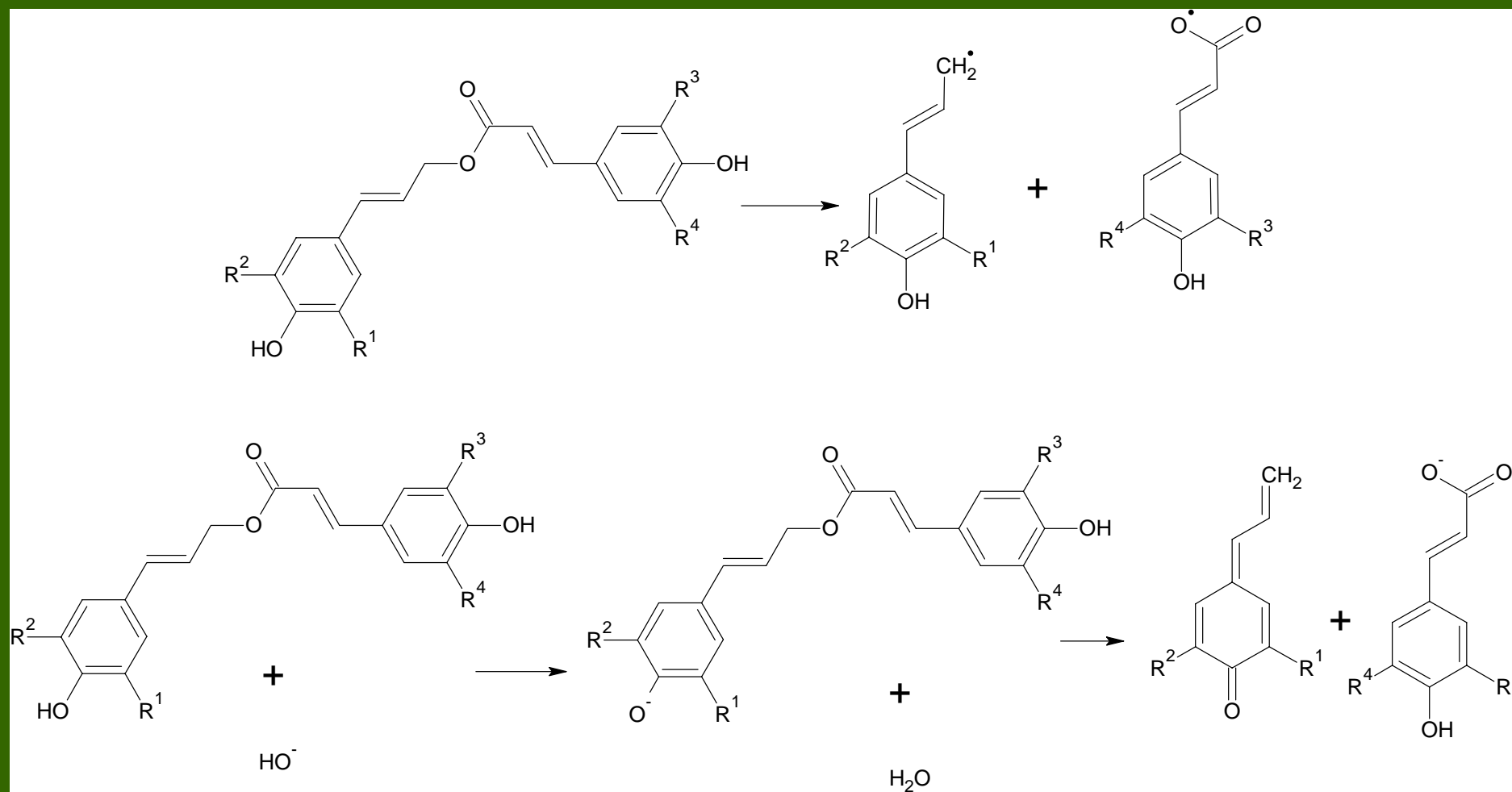

- β-O = 72.8 kcal/mole

- α-β = 82.0 kcal/mole
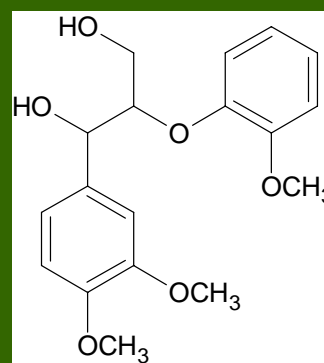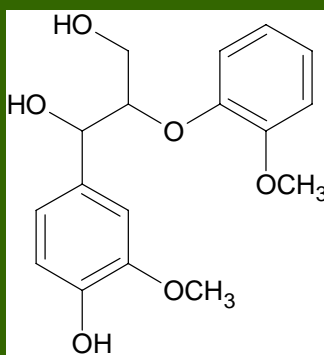
Kawamoto et al. 2008 report higher reactivity of phenolics,
Interpreted as the ability to form QM
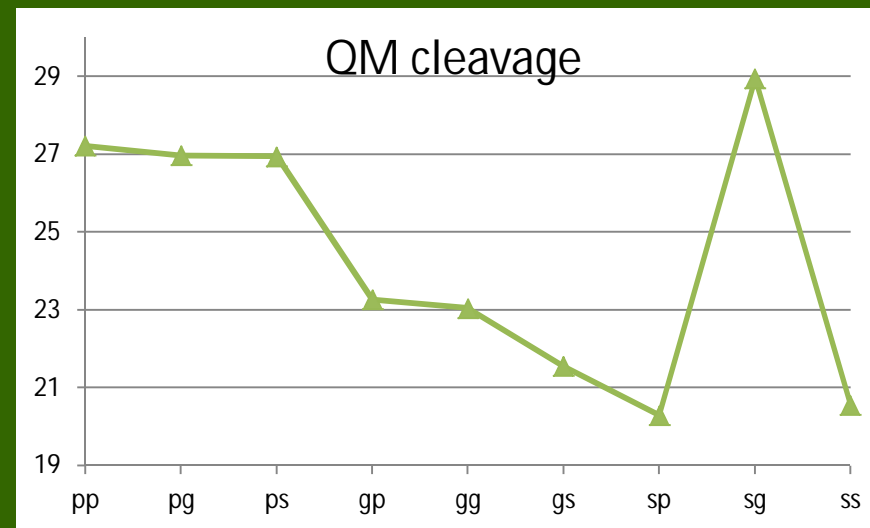
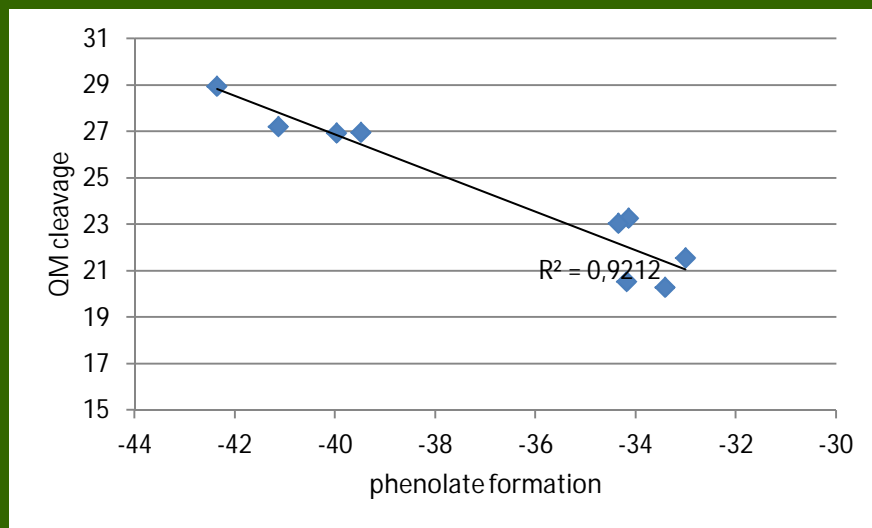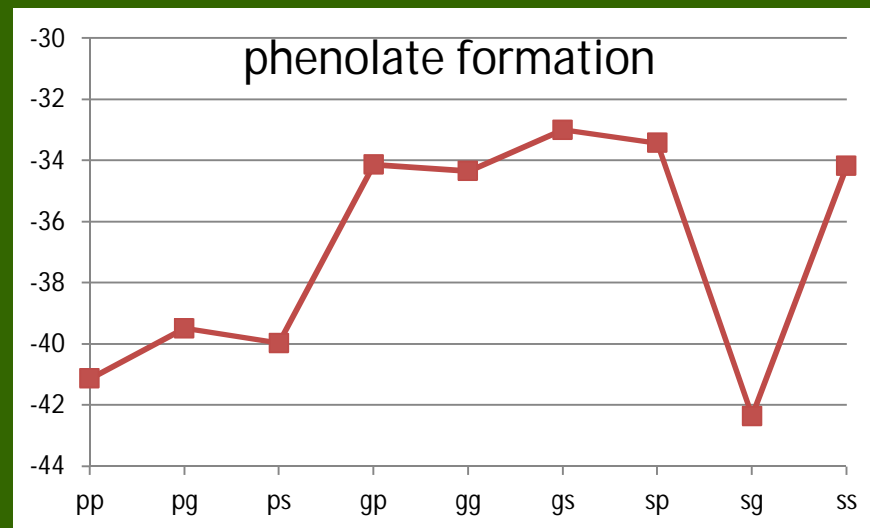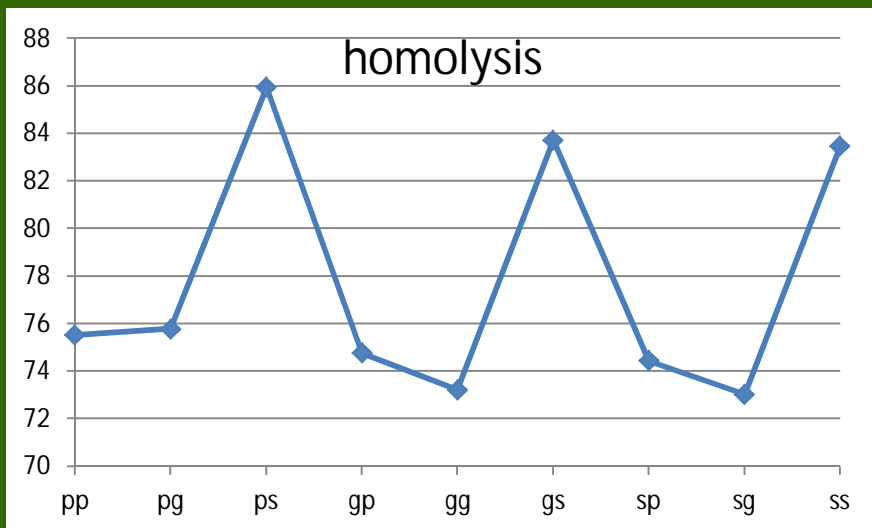# Modified Lignins

Modified Lignins
(Grabber et al. Biomacromolecules 9:2510)

Methods

- Does substitution change the energetics of the reactions?
- Can this be used to guide esterification and lignin modification to enhance removal?
- M06-2X/6-311++g(d,p) optimizations with frequency calculations
- Gaussian09

Results (kcal mol^{-1})

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 β-O and α-β cleavage mechanisms is lower for dilignols than for PPE models
  - This may mean the reactions are less selective

What Have We Learned?

- Dilignol with γ-OH can form a QM and the overall enthalpy of reaction is lower than direct homolysis

- Homolysis of dilignol with γ-deoxy group has about the same BDE as QM dilignol with γ-OH

- Etherification at phenolic position doesn't make much difference in calculated BDE

Where to next?

- Different lignin esters exhibit different energies of reaction
  - The homolytic cleavage reactions are systematic
  - Syringyl groups on the acid side are consistently higher
  - For the QM mechanism the initial dissociation reaction is exothermic, while the cleavage of the QM is endothermic (these reactions are also negatively correlated)

Questions