



Progress Towards the Design and Synthesis of Vinyl-Sulfone Functionalized Polymers

Sophie Wazlowski and Brian Northrop

Department of Chemistry, Wesleyan University, Middletown, CT 06459



Introduction

The Diels-Alder reaction forms covalent bonds through a thermodynamically favorable and sometimes reversible mechanism. Stephen Frayne, PhD, previously investigated the possibility of using this reaction to add and remove protecting groups during dendrimer synthesis (highly branched molecules with extensive biological applications).¹

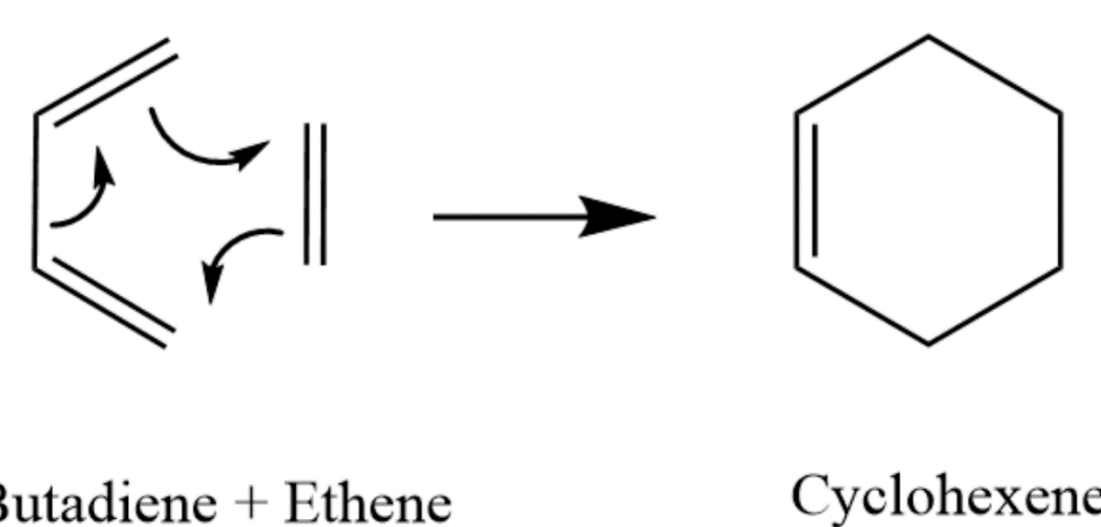


Figure 1: General Diels-Alder reaction between butadiene and ethene

The dendrimers (synthesized with furan-maleimide derivatives) were mostly insoluble, greatly limiting the number of possible applications. Consequently, the prospect of synthesizing dendrimers using vinyl sulfone derivatives was investigated.

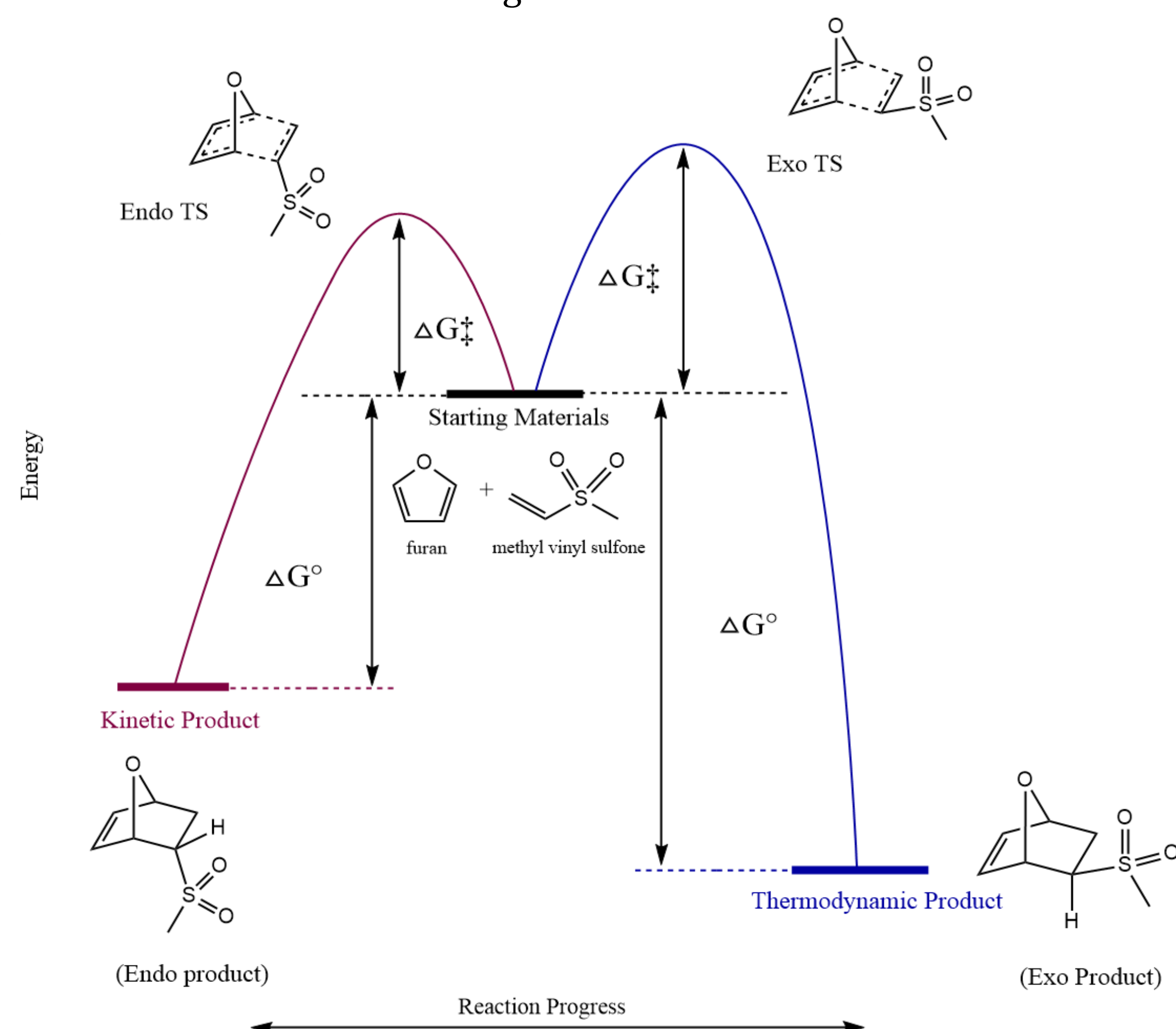


Figure 2: Reaction scheme for Diels-Alder reaction between furan (diene) and methyl vinyl sulfone (dienophile)

The relative Gibbs free energy values for different dienes were calculated as shown in Figure 3 below. Based on the results, the dienes furan and dimethyl fulvene were selected for synthetic study. The reaction between ethyl vinyl sulfone and furan was found to not be reversible, and thus could not be used to add and remove protecting groups in dendrimer synthesis. Consequently, the direction of the project was shifted towards norbornene monomer synthesis with the end goal of designing and creating different polymers through ROMP.

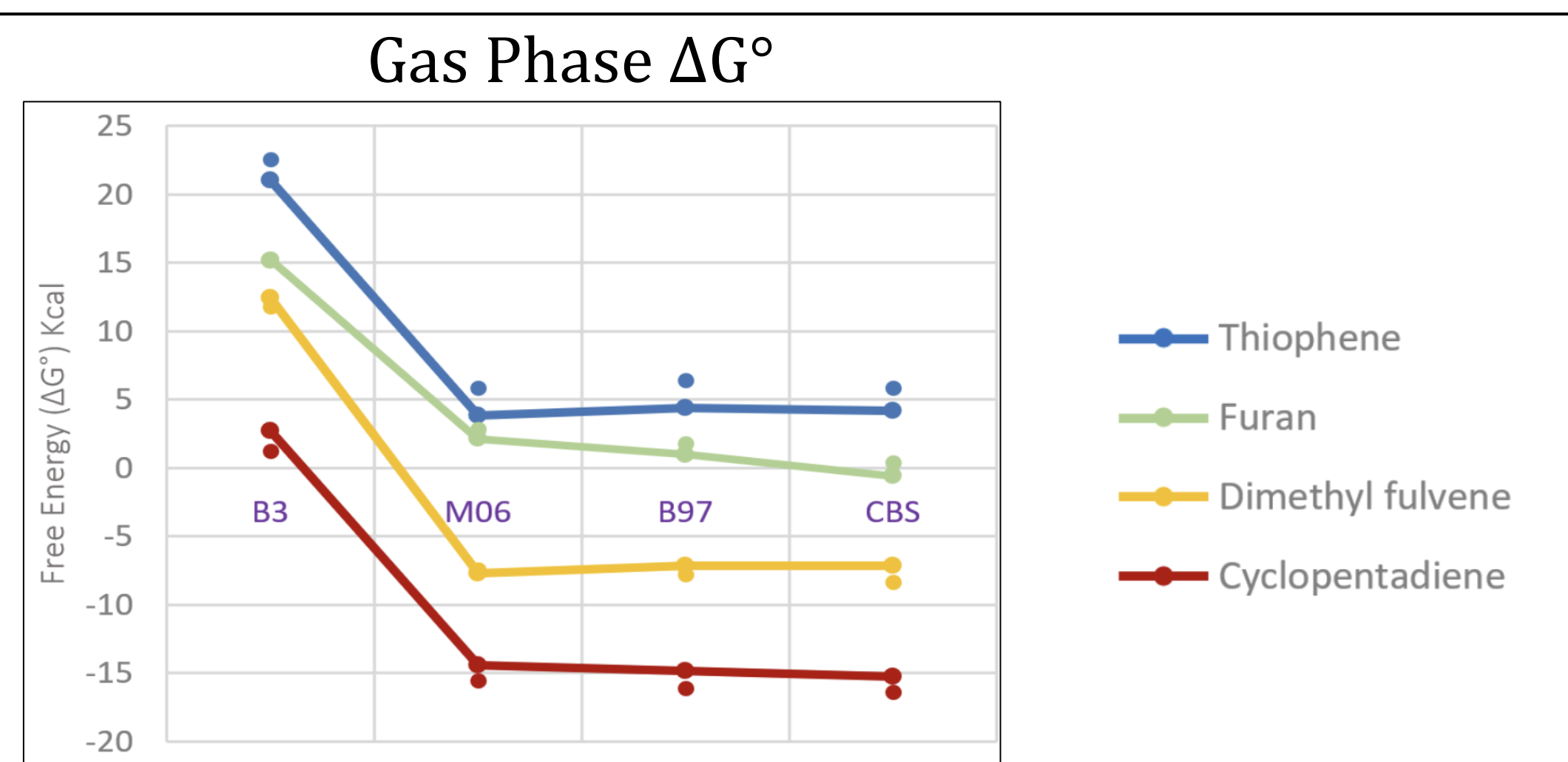
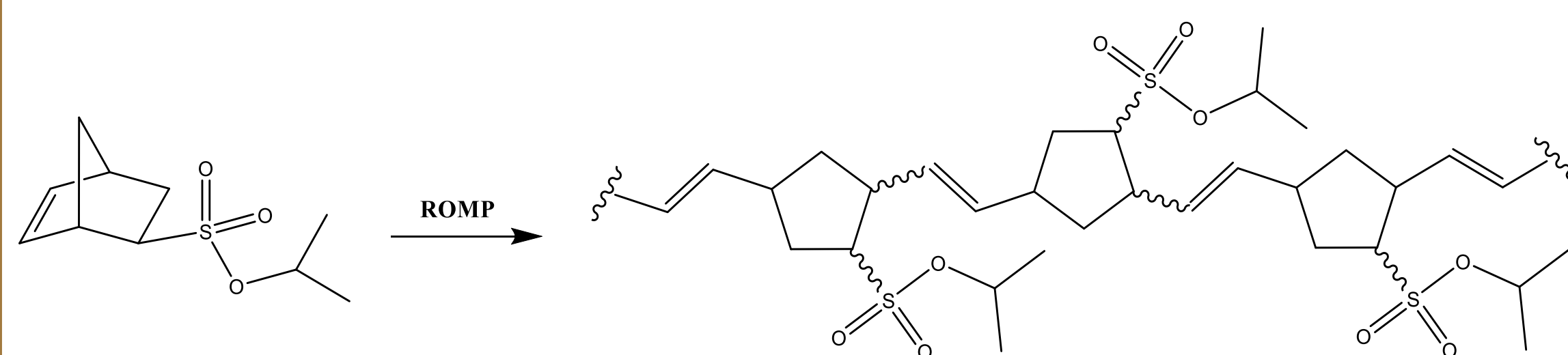


Figure 3: Graphs of both endo and exo product free energies at the B3LYP/6-31G(d), M062x/6-311G(2d,p), wB97xd/6-311G(2d,p) and CBS-QB3 levels of theory

Vinyl-Sulfone Monomer Synthesis

1. ROMP and Norbornene Monomer Synthesis



❖ **Living polymerization:** Energetic cost of connecting monomers and forming polymers outweighed by the gains of both relieving ring strain through ring opening + converting double to single bonds²

❖ **ROMP:** Metathesis reaction commonly used for the design in synthesis of polymers, including materials used to make baseball bats, bathroom fixtures and ballistic panels, among others³

- ❖ **Vinyl-sulfone functionalized monomers:** there has been little exploration of ROMP with cyclic alkenes containing vinyl sulfone derivatives. Butoxy-, isopropoxy-, and hexyloxy- vinyl sulfone were synthesized and reacted with cyclopentadiene and furan. A total of 9 vinyl-sulfone monomers were made.
- ❖ Reaction between ethyl vinyl sulfone and furan still did not progress; furan is aromatic while cyclopentadiene is not, making it less reactive

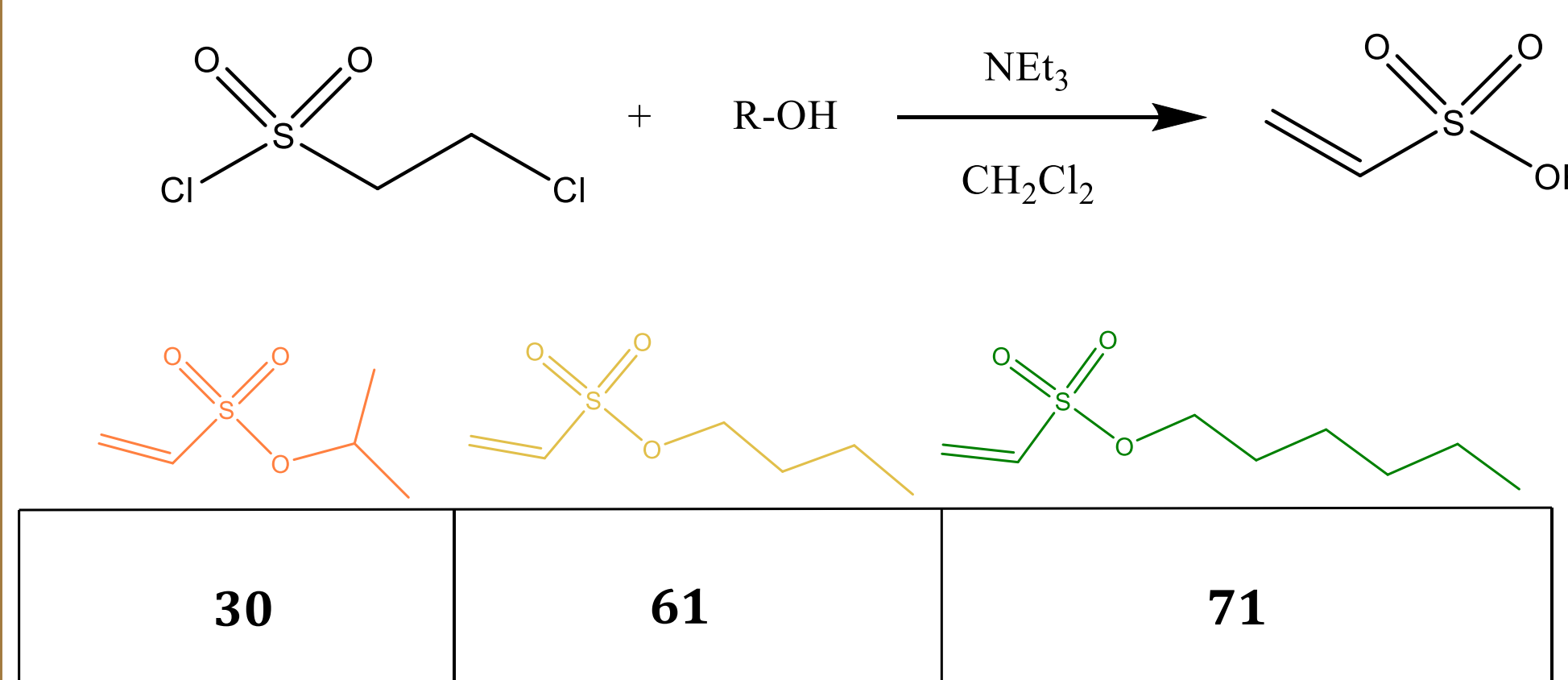


Figure 4: Percent yield synthesis of butoxy-, hexyloxy- and isopropoxy- vinyl sulfone derivatives

X = -O-, -CH₂-R

30	61	71	89	8.9	8.9	103	80
			N/A	21	33	31	43

Figure 5: Percent yield for reactions between furan, cyclopentadiene and the corresponding dienophile

2. COSY Analysis of Furan and Isopropoxy Vinyl Sulfone Diels-Alder Adduct

- ❖ **2D NMR COSY** spectra of isopropoxy vinyl sulfone + furan showing through-bond proton-proton coupling used to identify ¹H NMR peaks
- ❖ When H_d proton is in exo position (i.e. the endo product), it has a higher ppm based off of NMR of crystal structures analyzed in previous literature⁴
- ❖ Exo product favored for furan-reacted products; endo favored for cyclopentadiene

- ❖ H_c, H_e coupling observed for endo product
- ❖ H_c must be coupled to H_a

Absences in observed coupling:

- ❖ Protons with dihedral angles close to 90° typically do not exhibit coupling

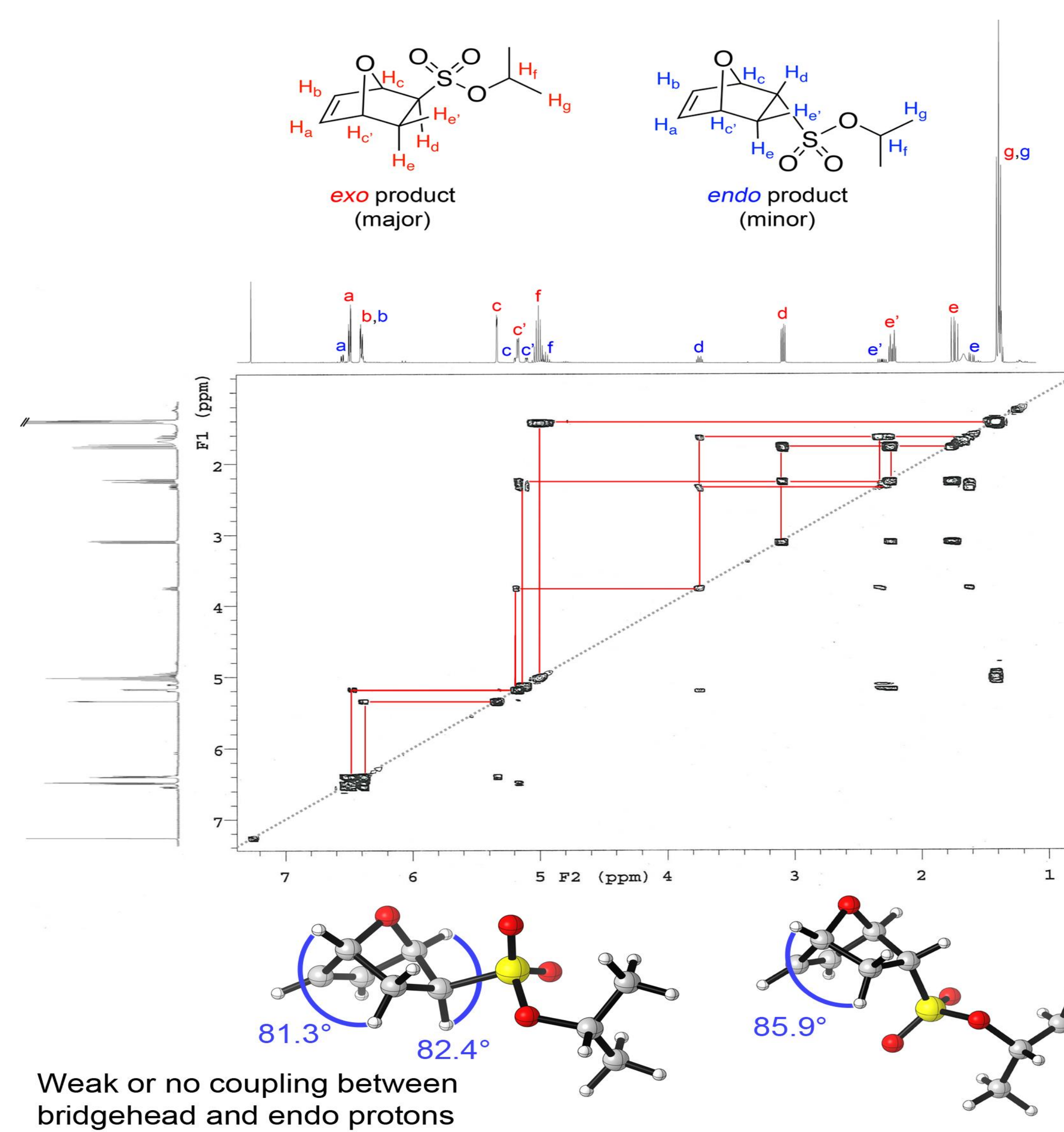
Exo product:

- ❖ No H_c, H_d coupling observed

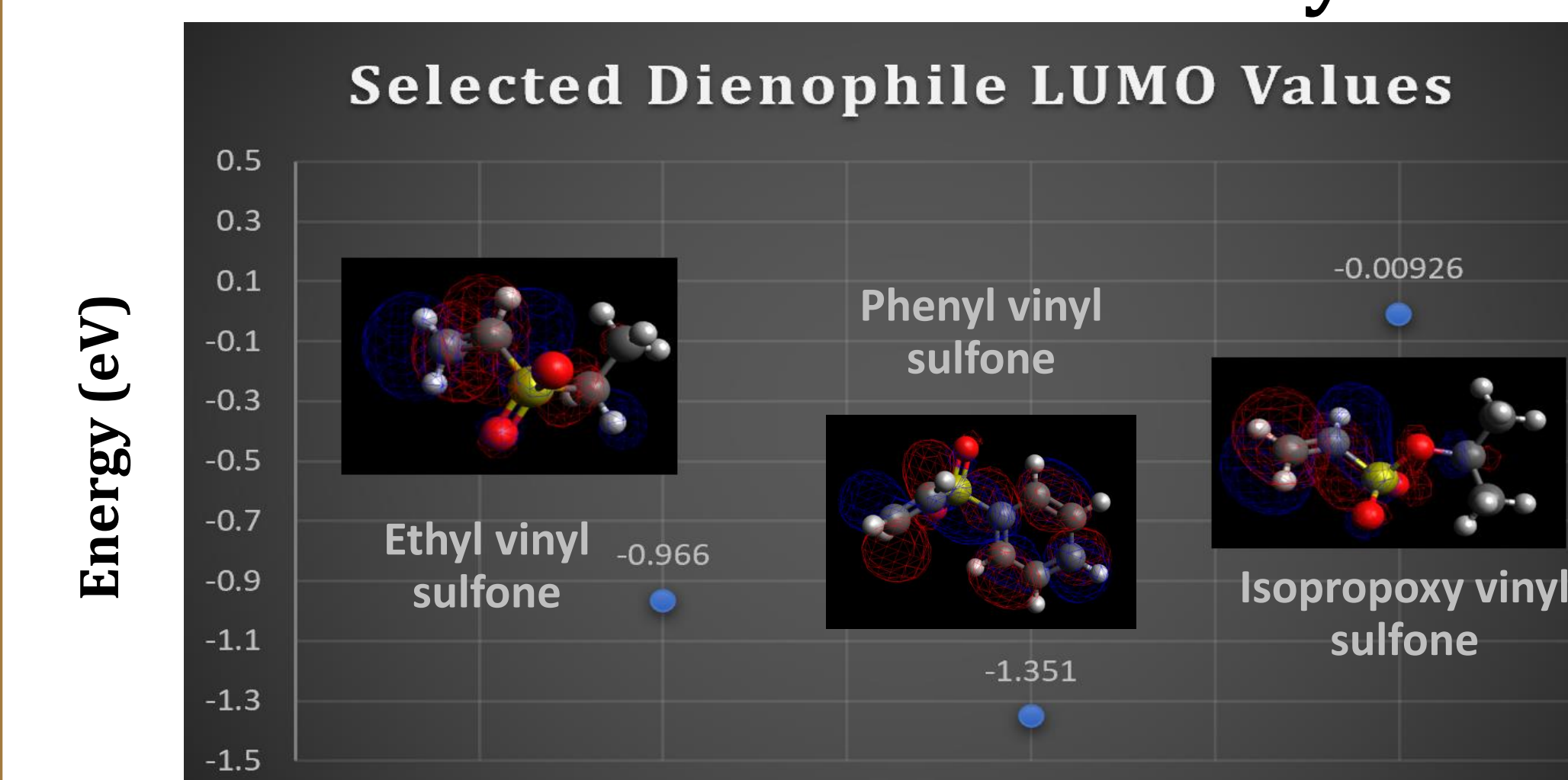
- ❖ No H_c, H_d coupling

Endo product:

- ❖ No H_c, H_e coupling

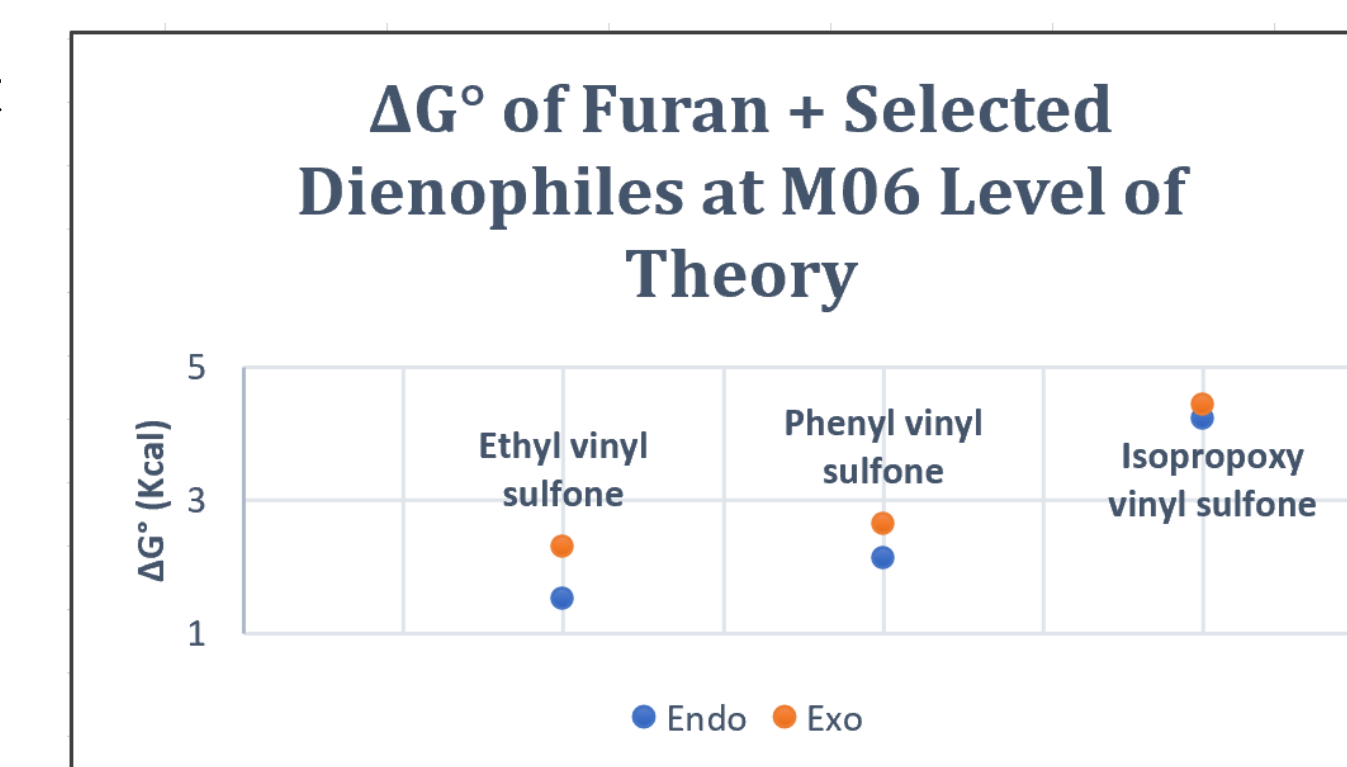


3. Molecular Orbital Analysis



- ❖ LUMO \rightarrow measure of how electron-withdrawing a dienophile is
- ❖ Lower LUMO = less electron density in dienophile, so reaction is expected to be more favorable
- ❖ Ethyl and phenyl vinyl sulfone have lower LUMOs, a trend reflected in the reaction ΔG° values

- ❖ Phenyl vinyl sulfone has a lower LUMO, but higher ΔG° value
- ❖ The ΔG° values are within 1 kcal of error, accounting for this discrepancy
- ❖ Regardless, the more electron-rich isopropoxy vinyl sulfone has a higher LUMO and ΔG° value



Future Directions

- ❖ Reducing each norbornene monomer to thioethers and sulfoxides to explore affects of oxidations states on polymer properties (thioethers, sulfoxides are electron rich and would not react through Diels-Alder)
- ❖ Synthesizing polymers with each monomer derivative using ROMP -Trans isomers favored because ROMP is thermodynamically driven
- ❖ Testing the physical properties of the polymers:
 - **Glass transition:** measure of which temperatures cause a material to transition from its brittle, "glassy" state to a viscous or rubbery state. Used to determine a temperature range at which the material can be used.
 - **Rheology:** Studying how polymers react to applied forces

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