

S1

Supplementary Material

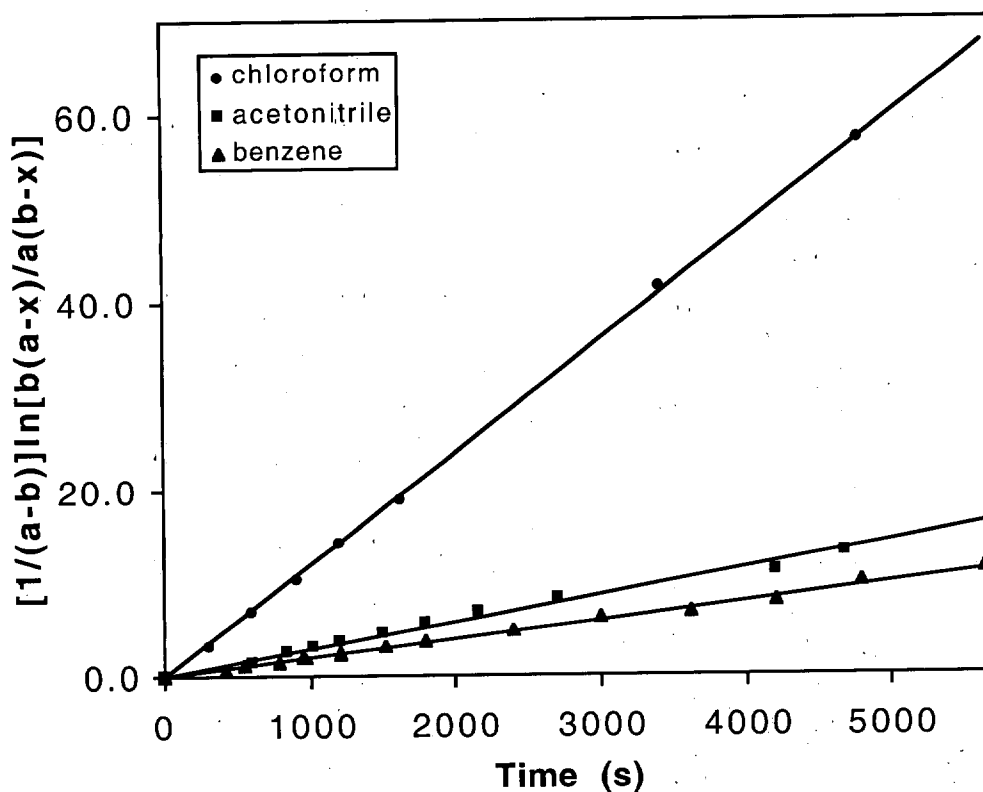


Figure 2. Kinetics of reaction of diene 1 with methacrolein at 17 °C in three Different solvents: CDCl_3 , CD_3CN , C_6D_6 .
 $[\text{diene}]_0 = 4.0\text{-}4.6 \times 10^{-2} \text{ M}$, $[\text{dienophile}]_0 = 1.1\text{-}1.4 \times 10^{-1} \text{ M}$

S2

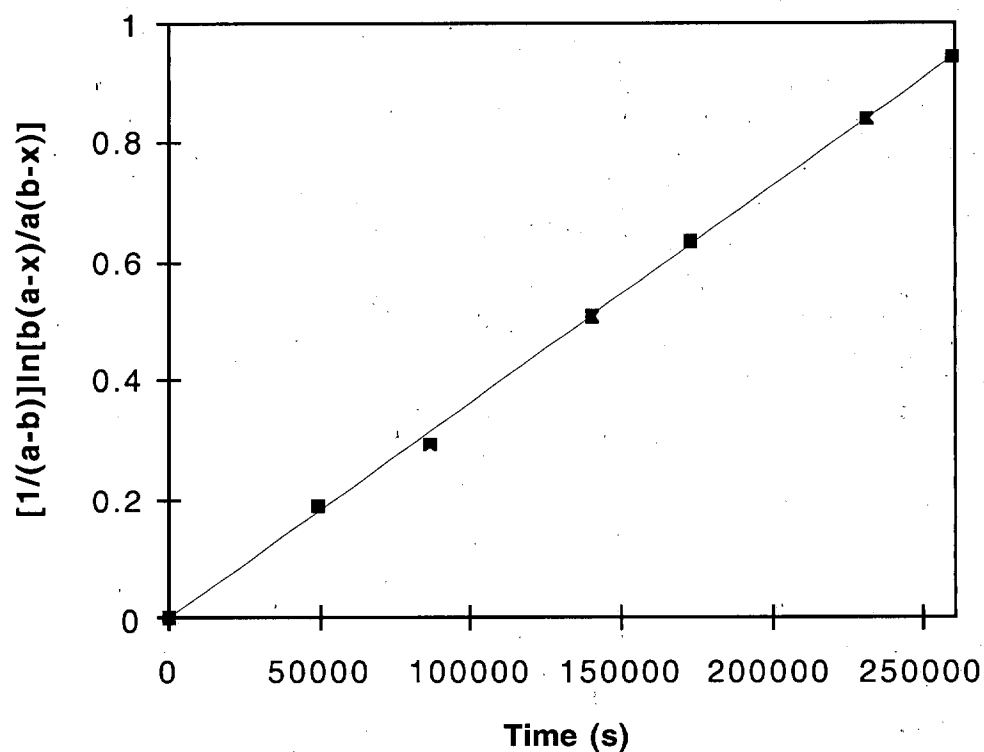


Figure 3. Kinetics of Reaction of Danishefsky's Diene (2a) with Methacrolein 20 °C in CDCl_3 . ($[\text{diene}]_0 = 4.6 \times 10^{-1} \text{ M}$, $[\text{dienophile}]_0 = 1.4 \text{ M}$).

S3

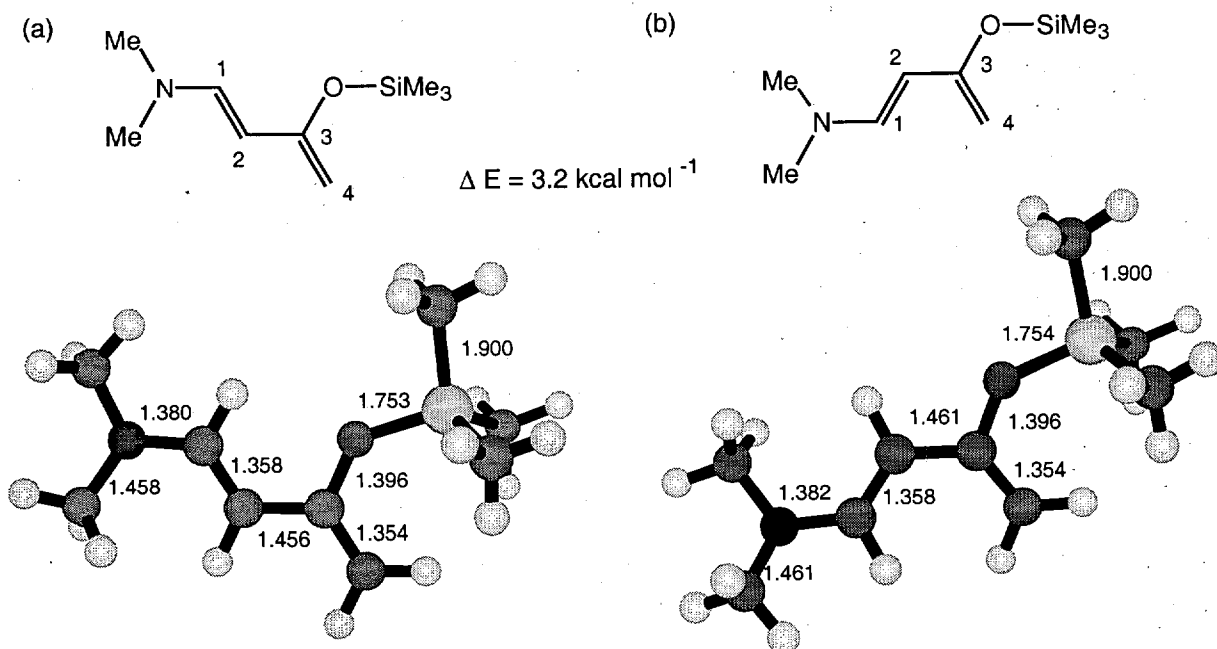


Figure 4. B3LYP/6-31G Optimized Geometry for the (a) *s-trans* and (b) *s-cis* Conformations of Diene 1a.

S4

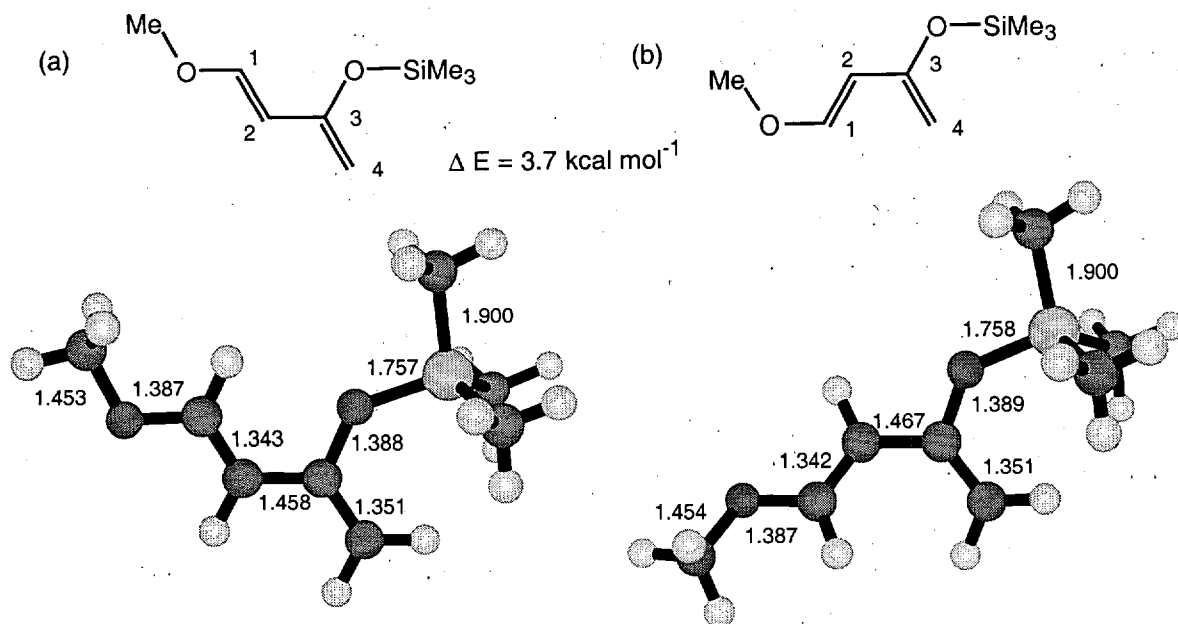


Figure 5. B3LYP/6-31G Optimized Geometry for the (a) *s-trans* and (b) *s-cis* Conformations of Danishefsky's Diene (2a).

S5

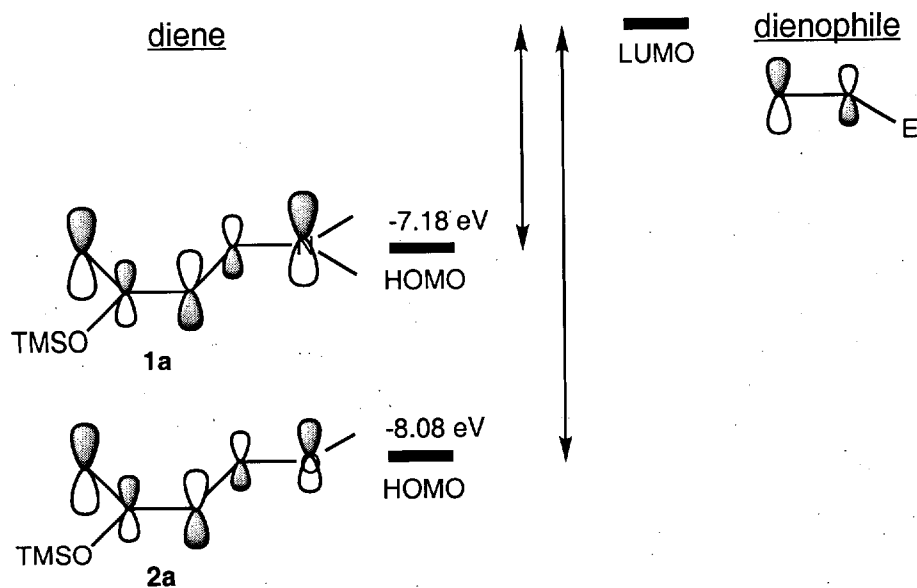


Figure 6. Frontier Molecular Orbital Representation of Dienes **1a** and **2a**.