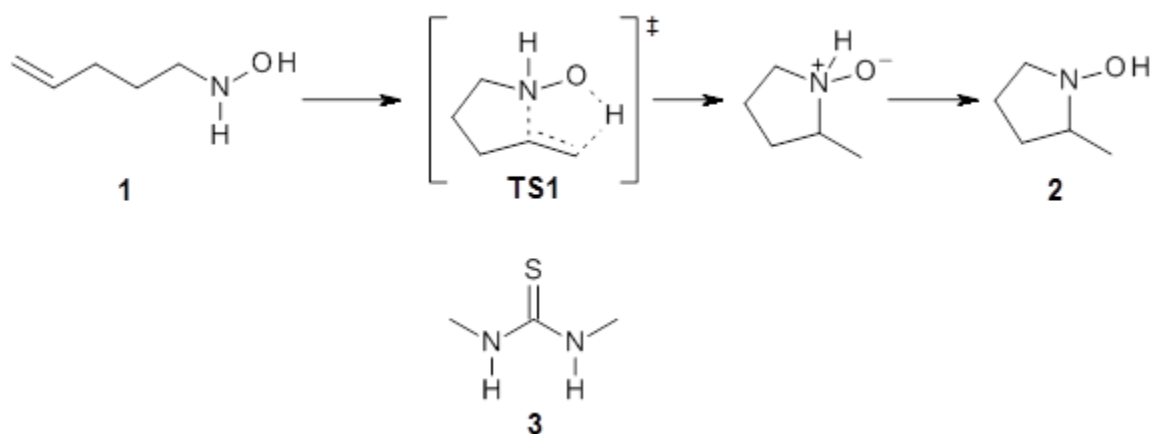


THIOUREA-CATALYZED HYDROAMINATION

Jacobsen reports on another application of thiourea-based organocatalysts, this time for the catalysis of hydroamination.¹ To support the synthetic effort, he examined the uncatalyzed intramolecular hydroamination that takes **1**, through **TS1** into product **2**. The geometry of **TS1** optimized at B3LYP/6-31+G(d,p) is shown in Figure 1. The computed barrier for this reaction is 22.2 kcal mol⁻¹. Using a model thiourea as the catalyst (MeHN)₂C=S, **3**, Jacobsen locates a catalyzed transition state **TS2** shown in Figure 1. The activation barrier for this catalyzed reaction is 19.1 kcal mol⁻¹, suggesting that a thiourea can afford a real catalytic effect.



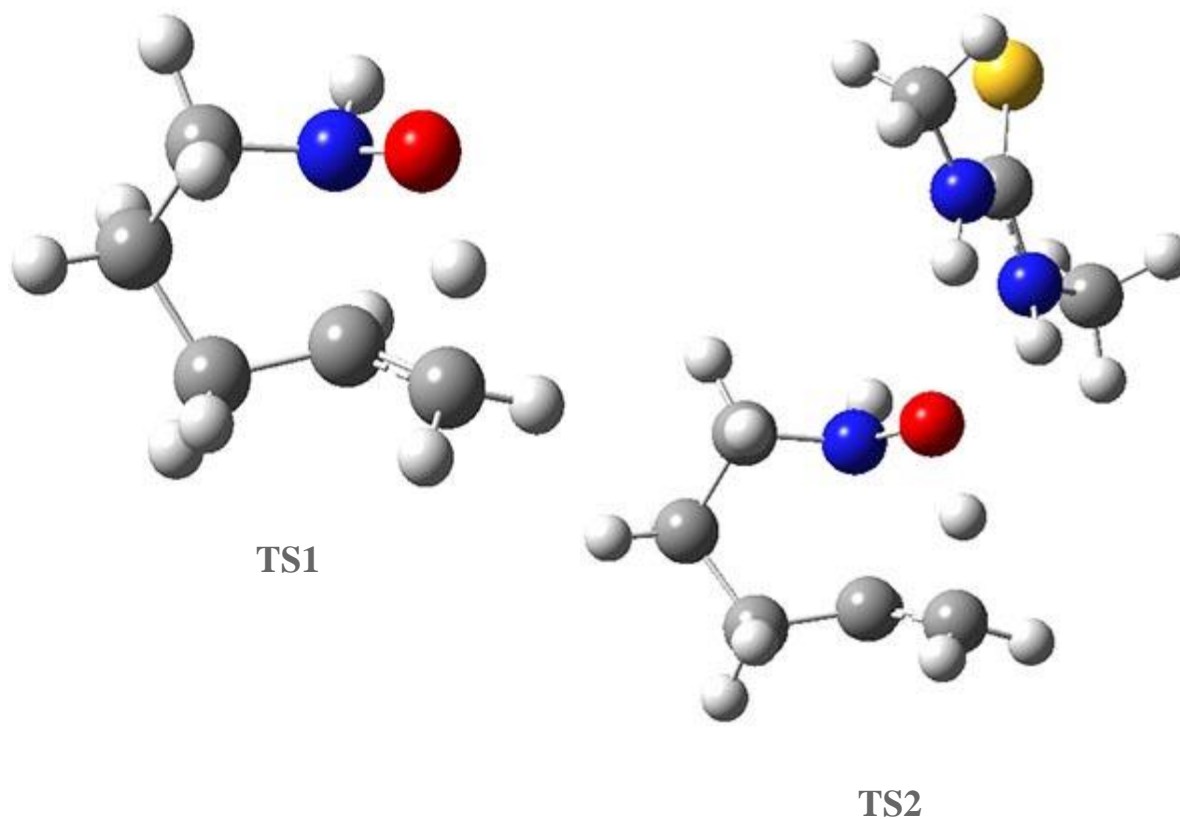
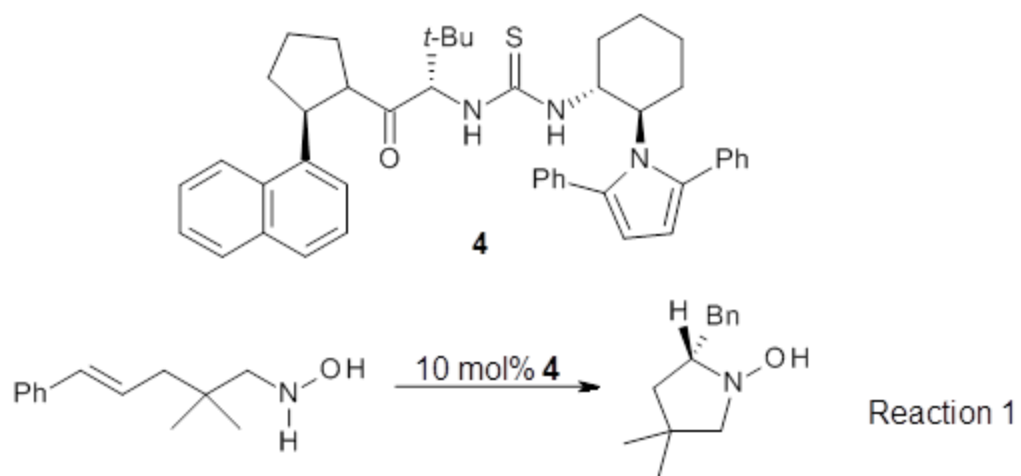


Figure 1. B3LYP/6-31+G(d,p) optimized geometries of TS1 and TS2(the catalyzed transition state).

Jacobsen then goes on to show that **4** can act as both an excellent catalyst for the hydroamination reaction along with inducing significant enantioselectivity. An example is Reaction 1, where 10 mol% of catalyst **3** gives an overall yield of 83% and an ee of 91%, while in the absence of catalyst the yield is only 8%.



Source: <http://comporgchem.com/blog/?p=2708>