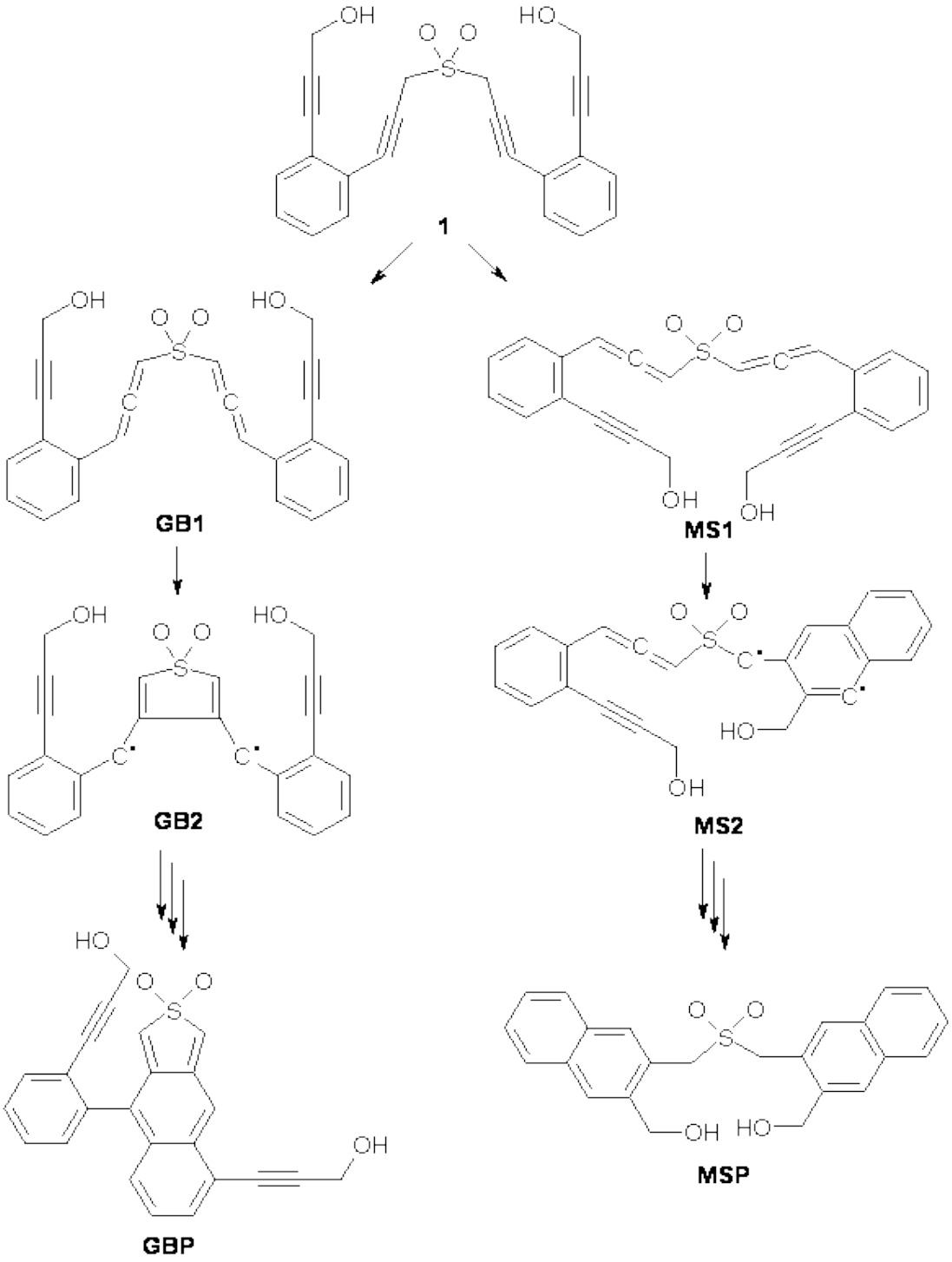
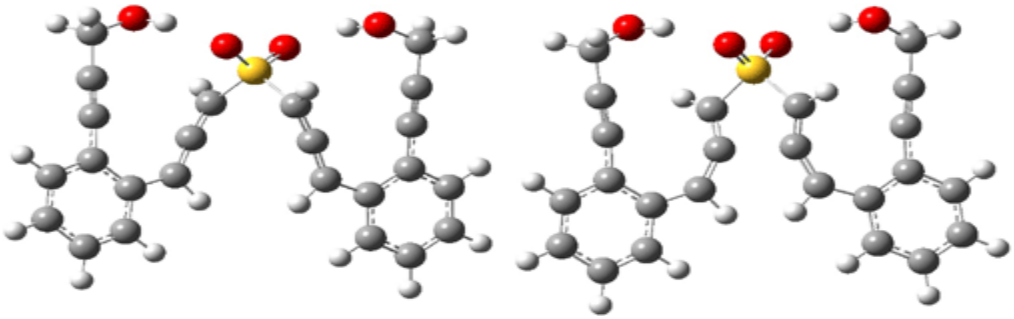
GARRAT-BRAVERMAN VS MYERS-SAITO CYCLIZATION

The competition between Bergman cyclization and Myers-Saito cyclization of ene-ynes and related species is discussed in Chapter 3.3 of my book and also in these posts. Yet another variation, the Garratt-Braverman cyclization[1-3] has now been examined in terms of competition with the Myers-Saito cyclization for **1** using both experiments and computations.[4] Subjecting **1** to base should cause the rearrangement to either **GB1** or **MS2**. These can undergo either the Garratt-Braverman cyclization to give **GB2** or the Myers-Saito cyclization to **MS2**.

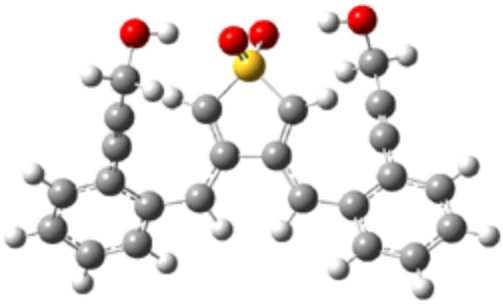


B3LYP/6-31G(d) predicts that **GB1** is only slightly higher in energy than **MS1** (by 0.7 kcal mol^{-1}).

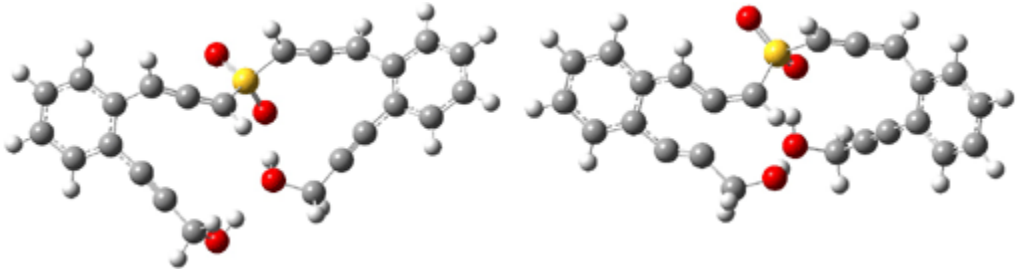
The transition states (**GB1toGB2** or **MS1toMS2** – see Figure 1) each lie 24.4 kcal mol^{-1} above their respective reactants. However, the diradical **GB2** is 7.2 kcal mol^{-1} below **GB1** but **MS2** is only 0.3 kcal mol^{-1} below **MS1**. So while the two reactions are of similar kinetic probability, having identical activation barriers, the GB route leads to the more thermodynamically stable intermediate. Furthermore, the GB route ultimately results in **GBP**, via an intramolecular cyclization of the diradical, while the MS route, which ends with **MSP**, requires intermolecular abstraction of 4 hydrogens. Thus, the unimolecularity of the GB path further favors the GB route over the MS pathway. In fact, experimental studies of **1** and related compounds all give rise to the GB product only.



GB1 **GB1toGB2**

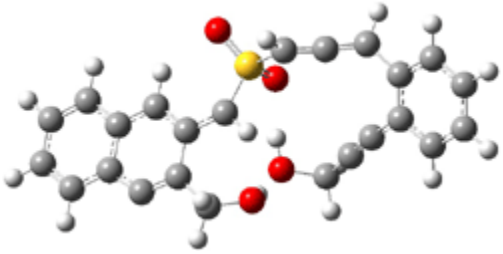


GB2



MS1

MS1toMS2



MS2

Figure 1. B3LYP/6-31G(d) optimized structures.[4]

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