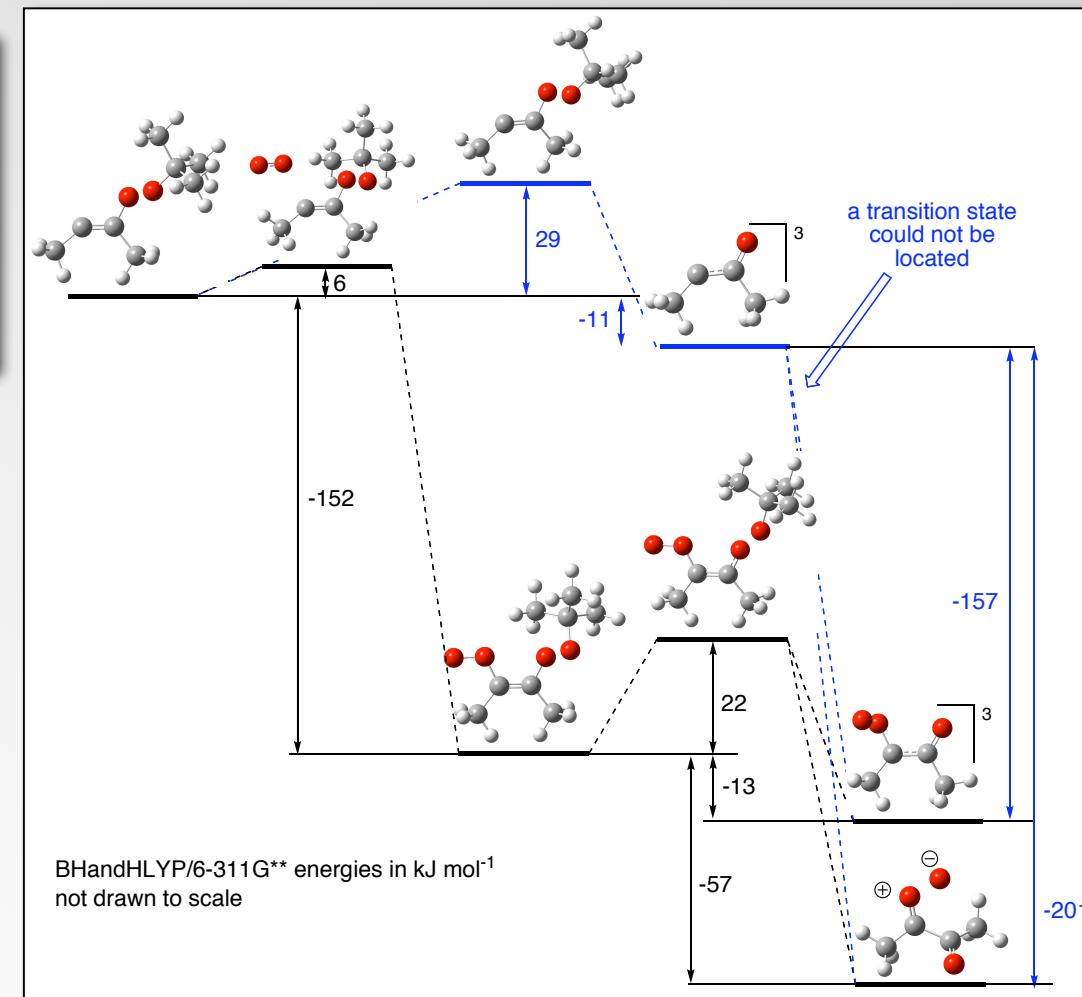
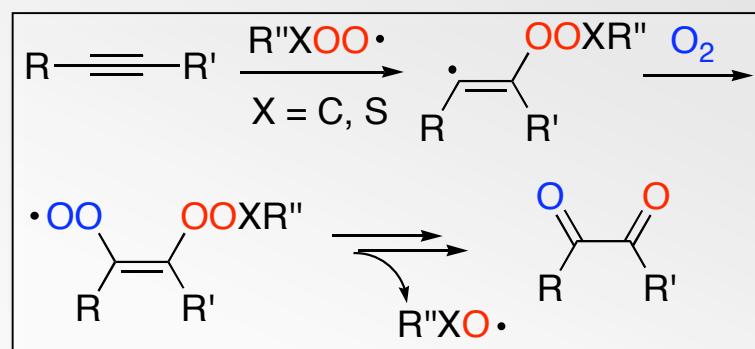


Development of new pathways for the oxidative transformation of alkynes into highly reactive carbonyl compounds.



Uta Wille, School of Chemistry, The University of Melbourne, Australia.

- ❖ A major goal in synthetic chemistry is the development of oxidation procedures that use the most abundant (and cheapest) oxidant, molecular oxygen, under non-toxic conditions.
- ❖ We have discovered a *novel mild and metal-free activation of molecular oxygen* that enables transformation of alkynes into 1,2-diketones mediated by peroxy radical intermediates.



Experimental and computational studies revealed insight into the mechanism

- ❖ addition of a peroxy radical $\text{R''XOO}\cdot$ (where $\text{X} = \text{C}$ or S) to the alkyne gives a vinyl radical, which is trapped by oxygen
- ❖ subsequent fragmentation of the peroxy O-O bond with release of an alkoyl radical $\text{R''XO}\cdot$ gives a Crigee-type intermediate, which decomposes to the 1,2-diketone
- ❖ this oxidation is the first example for the synthetic application of thiylperoxy radical $\text{R''SOO}\cdot$ reported in literature.