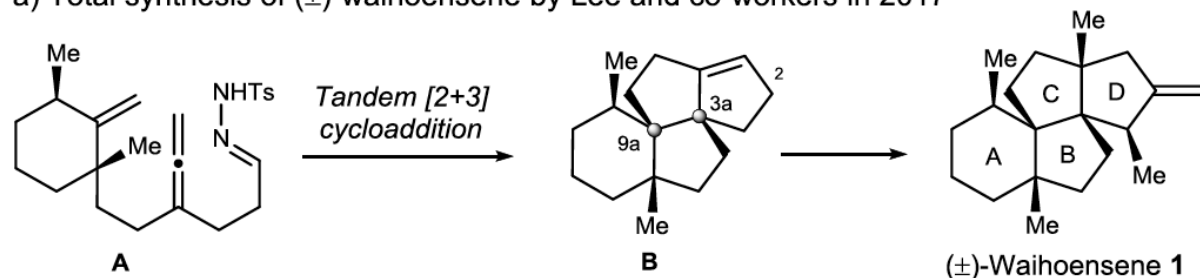


Asymmetric Total Synthesis of (+)-Waihoensene

Yongzheng Qu, Zheyuan Wang, Zhongchao Zhang, Wendou Zhang, Jun Huang,* and Zhen Yang*

a) Total synthesis of (±)-waihoensene by Lee and co-workers in 2017

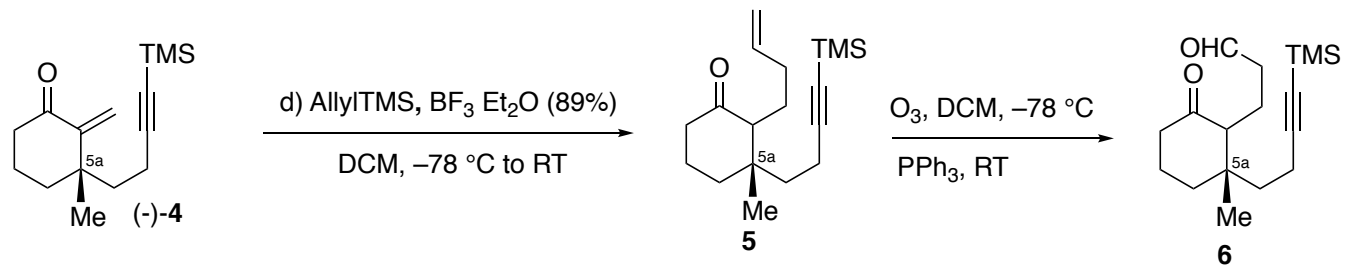


(+)-Waihoensene was isolated from the New Zealand podocarp in 1997. It is a tetracyclic diterpene containing an angular triquinane.

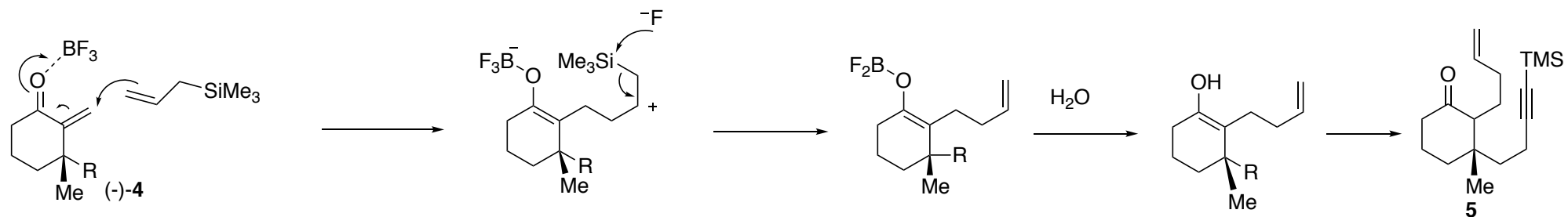
The whole structure contains a highly congested and *cis*-fused tetracyclic core decorated with 6 contiguous stereogenic centers, 4 of them are contiguous quaternary carbon.

First total synthesis of Waihoensene was achieved by Lee and co-workers in 2017 in 18 steps, featuring a tandem [2+3] cycloaddition to construct BCD ring.

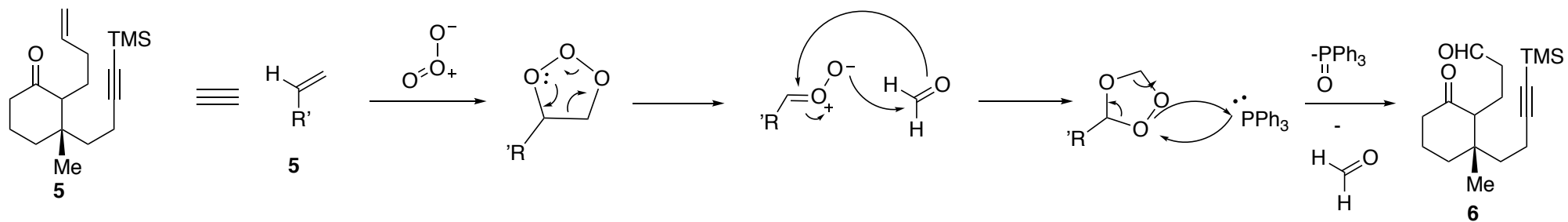
Here, they achieved the asymmetric total synthesis with 15 steps and 3.8% overall yield.

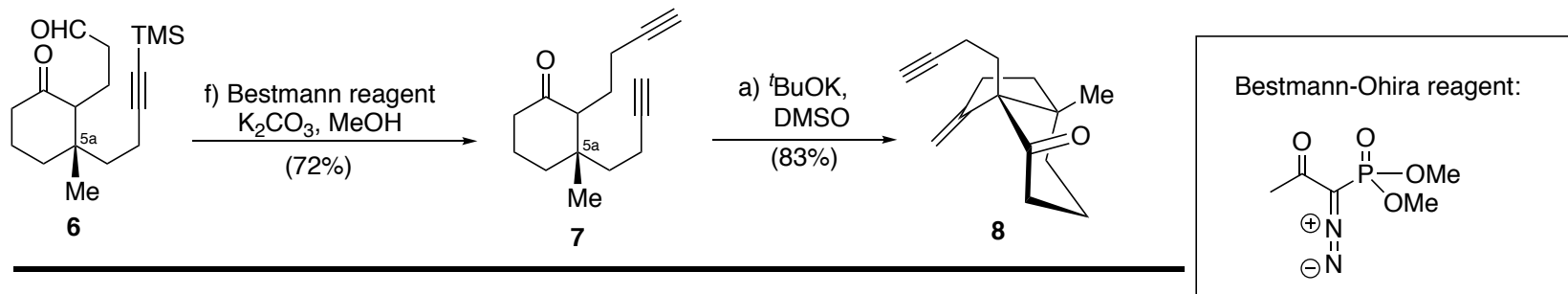


Sakurai Reaction

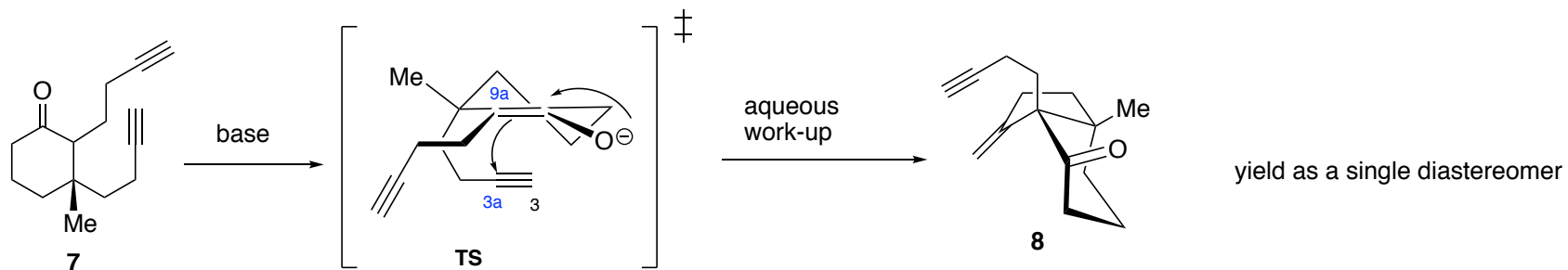
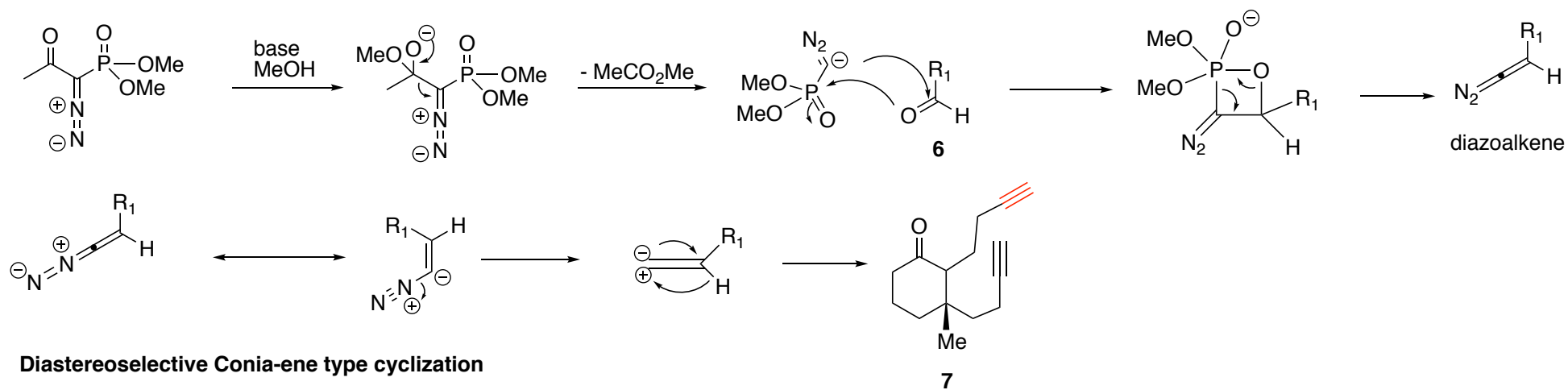


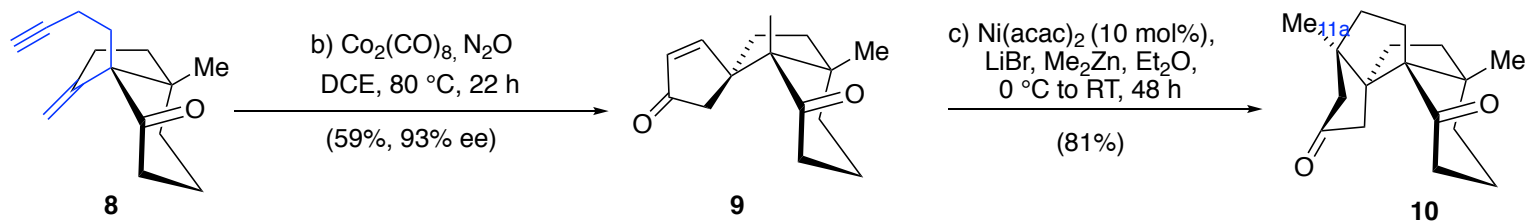
Ozonolysis



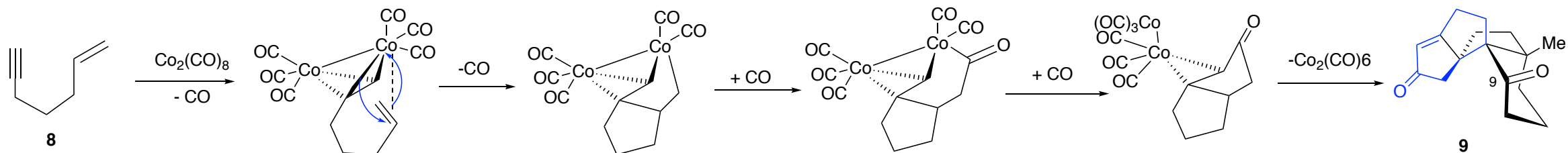


Forming diyne 7 and *in situ* desilylation

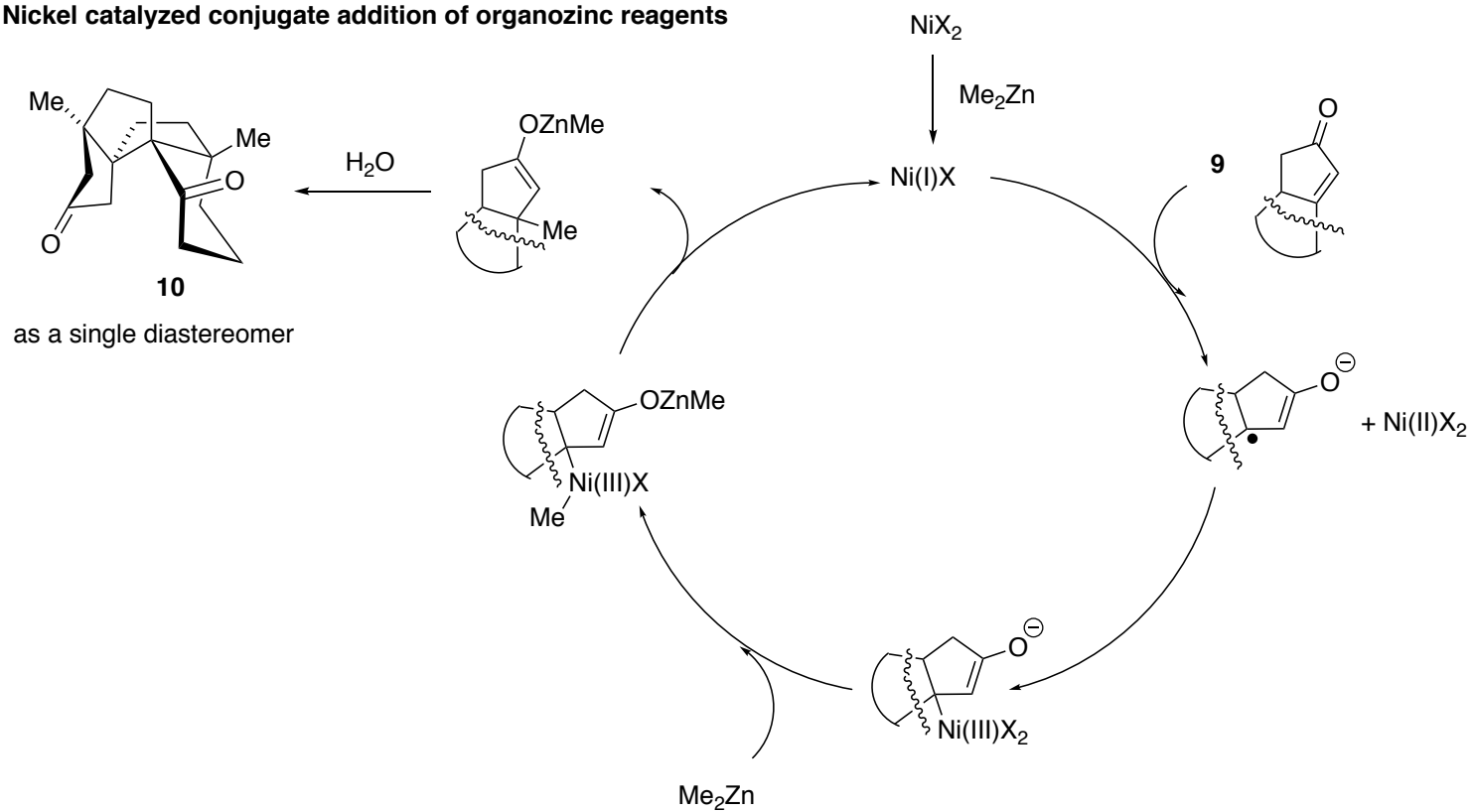


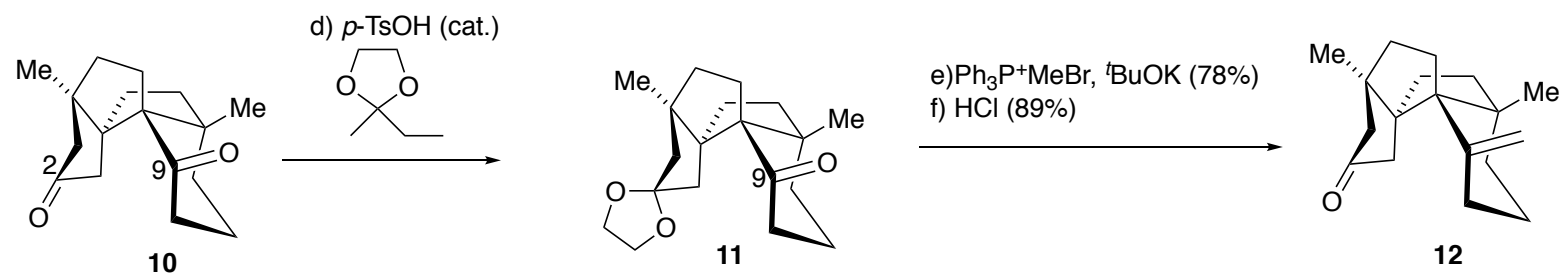


Pauson-Khand reaction

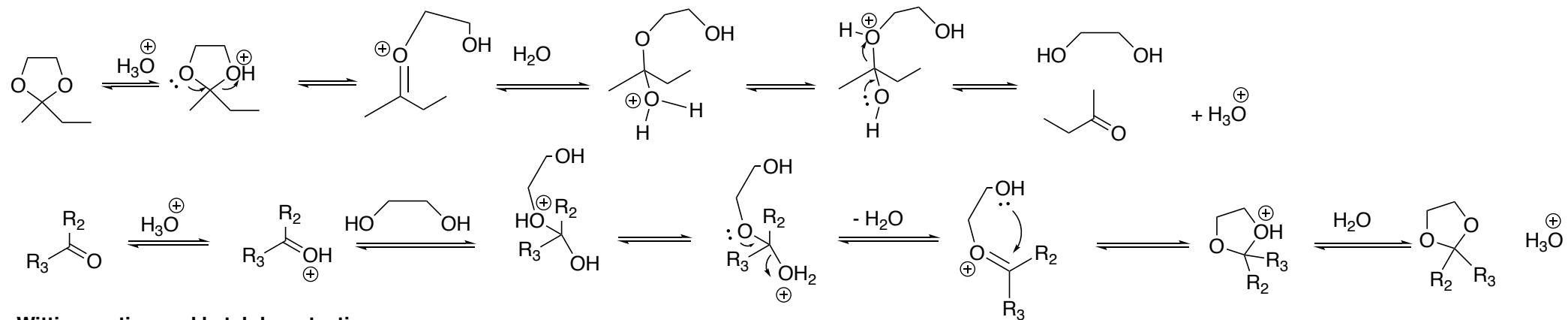


Nickel catalyzed conjugate addition of organozinc reagents

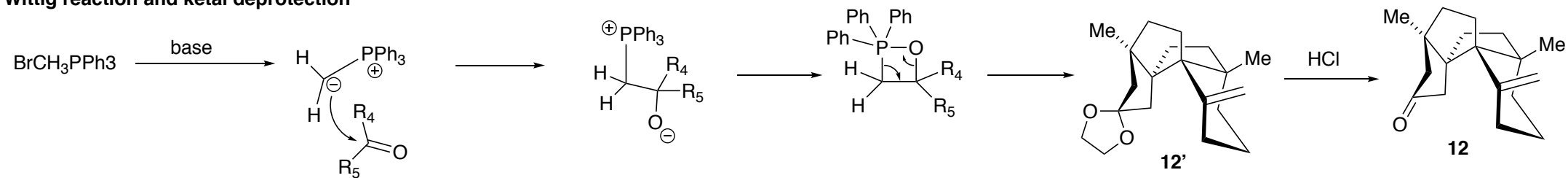


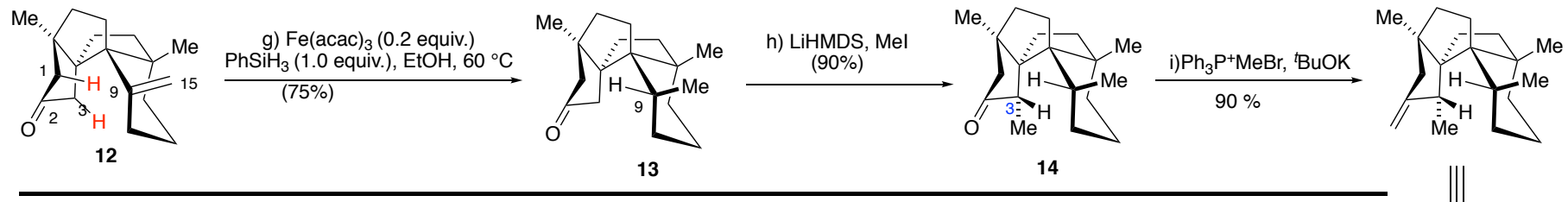


Ketal Formation

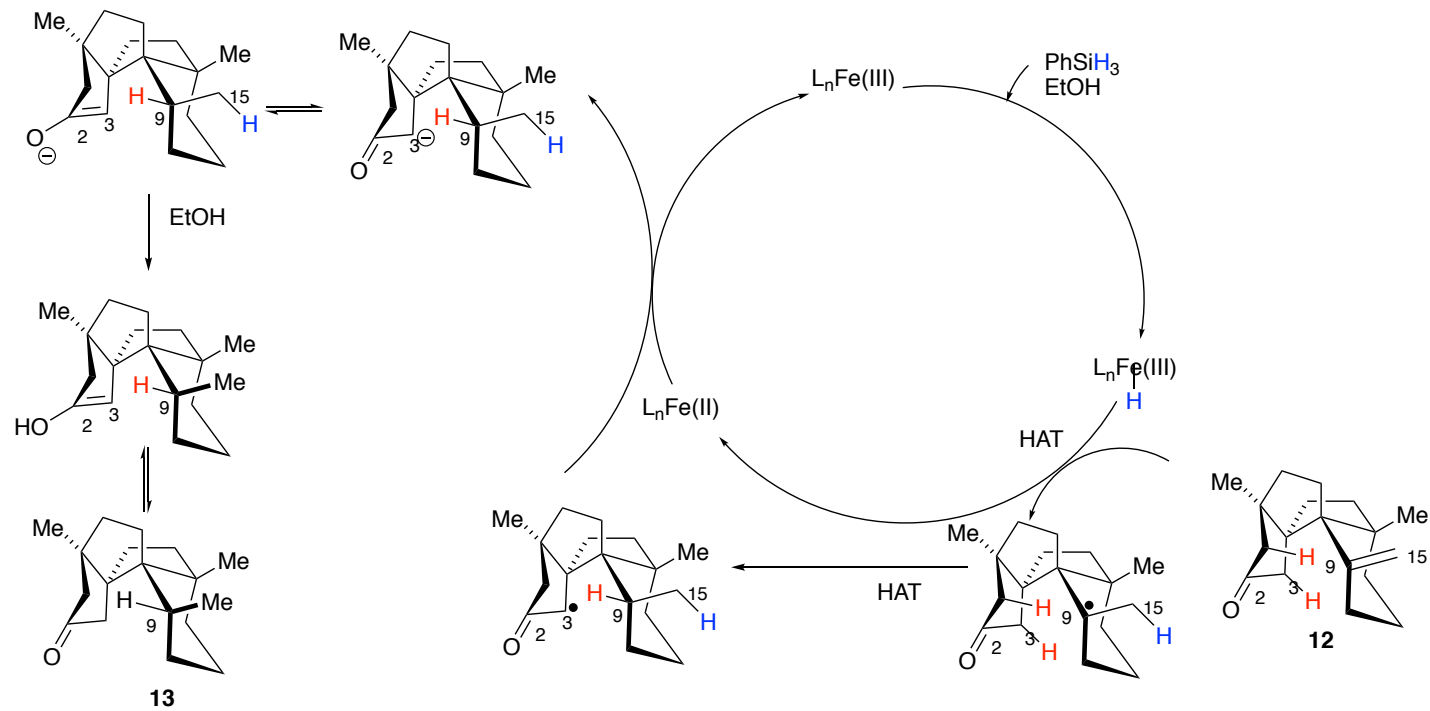


Wittig reaction and ketal deprotection





Hydrogen Atom Transfer (HAT) for olefin hydrogenation



C3 methylation and another Wittig reaction

