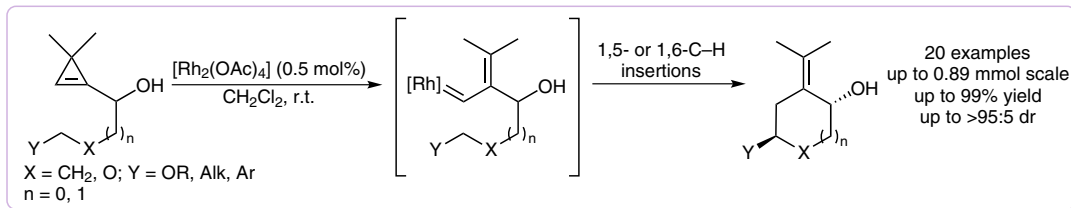


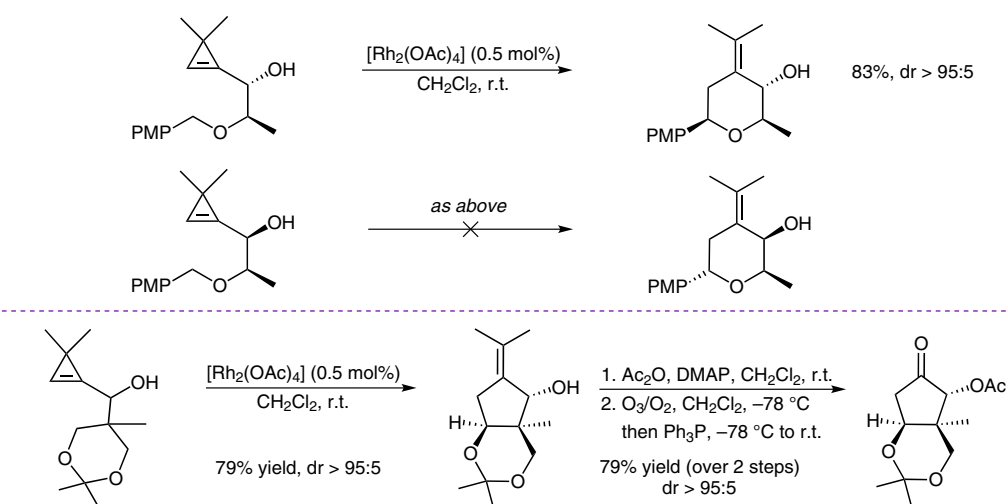
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 Highly Efficient Stereoselective Catalytic C(sp<sup>3</sup>)-H Insertions with Donor Rhodium Carbenoids Generated from Cyclopropenes  
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## C(sp<sup>3</sup>)-H Insertions with Donor Rhodium Carbenoids

### Synthesis of donor rhodium carbenoids and their use in C(sp<sup>3</sup>)-H insertions



### Differentiation of diastereotopic groups by diastereoselective 1,6-C-H insertion



**Significance:** The functionalization of unactivated C(sp<sup>3</sup>)-H bonds by insertion of transition-metal carbenoids is an attractive method of forming C-C bonds. However, while acceptor-substituted rhodium(II) carbenoids have been investigated, little is known on the reactivity of donor-substituted rhodium(II) carbenoids in C(sp<sup>3</sup>)-H insertions, due to the difficulty in handling the unstabilized diazo precursors. The authors report the facile generation of donor-substituted rhodium(II) carbenoids by ring opening of 3,3-dimethylcyclopropenylcarbinols, and their use in intramolecular C(sp<sup>3</sup>)-H insertions, which occur with high yield and diastereoselectivity.

**Comment:** Donor-substituted rhodium carbenoids were found to trigger 1,5- and 1,6-C-H insertions with high diastereoselectivity to generate a variety of functionalized carbocycles and oxygen heterocycles, which can be subsequently ozonolyzed to the corresponding ketones. Deuterium-labelling studies suggest that the reaction involves a stereospecific process at the carbenoid carbon atom, and occurs in a concerted fashion with a late transition state. Furthermore, the C-H insertion process is selective for only one of two diastereotopic methylene groups, which the authors exploited to access various bicyclic compounds.

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