



Cycloisomerization of Dienynes by a Planar-chiral Gold(I) Complex

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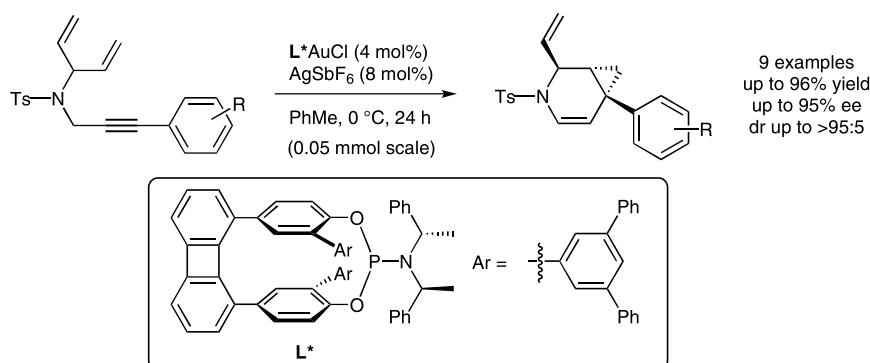
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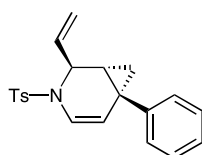
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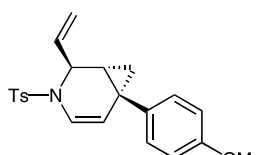
Cycloisomerization of Dienynes by a Planar-chiral Gold(I) Complex



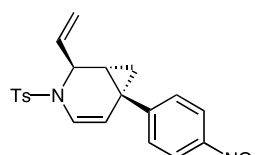
Selected examples:



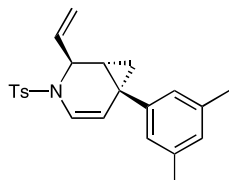
92% yield, 90% ee, dr = 95:5



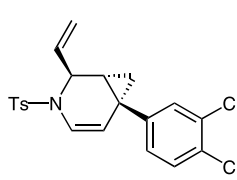
93% yield, 83% ee, dr = 95:5



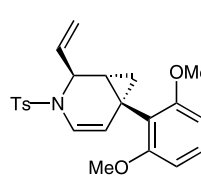
33% yield, 67% ee, dr = 95:5



95% yield, 88% ee, dr > 95:5



71% yield, 84% ee, dr = 95:5



94% yield, 95% ee, dr > 95:5

Significance: The gold(I) catalyst shows a strong affinity for unsaturated (triple) bonds, and subsequent cycloisomerization reactions with various nucleophiles (carbon, heteroatom) are a powerful tool for the construction of cyclic molecules. However, asymmetric variants of these reactions are challenging because of the nature of a linear coordination of the gold complex. The authors describe new chiral phosphoramidite ligands based on a planar-chiral paracyclophane scaffold. The cycloisomerization reaction of diene-yne substrates afforded the bicyclic products in high yield with good to excellent diastereo- and enantioselectivity.

Comment: By using the reported phosphoramidite ligand, dienynes having enantiotopic vinyl groups were successfully transformed into the products bearing three contiguous stereocenters (platinum-catalyzed reaction of this type of substrates gave moderate yield, see: *Adv. Synth. Catal.* **2011**, 353, 1109). The unactivated substrates bearing an electron-deficient aryl group were also tolerated and gave the desired product in moderate yield with excellent diastereoselectivity and good enantioselectivity.