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Enantioselective Catalysis of Ketoester-ene Reaction of Silyl Enol Ether to Construct Quaternary Carbons by Chiral Dicationic Palladium(II) Complexes
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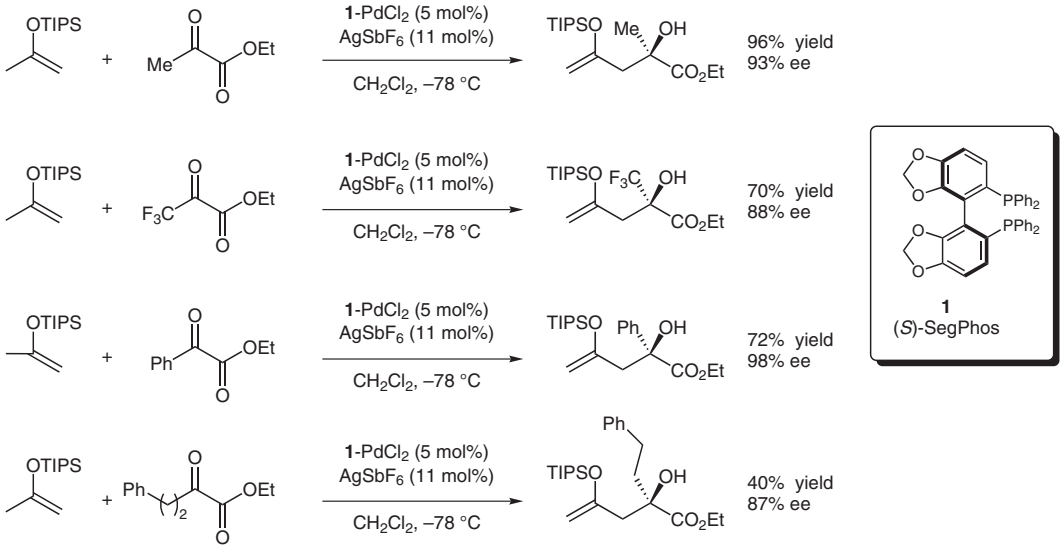
Ketoester-Ene Reaction of Silyl Enol Ether to Construct Quaternary Carbons



Significance: The authors describe a highly enantioselective ketoester-ene reaction that generates optically active β-hydroxy silyl enol ethers containing tertiary alcohols. This is a very nice reaction because the product not only contains a chiral quaternary carbon, but also a useful silyl enol ether. A reasonable amount of α-ketoester substrates works well with this reaction. A SegPhos-Pd-Ag catalyst system is used with the silver's likely role to generate the cationic palladium species.

Comment: This is a fantastic report for the construction of a very useful compound. The study of silyl enol ether starting materials revealed that the TMS enol ether gave only Mukaiyama-aldol-type products. Using TBS resulted in good yield and moderate enantiomeric excess (85%). TIPS and TBDPS gave high ee values (93% and 96%, respectively), but with TIPS much higher yields were achieved (96% vs 68%). The authors showed an example of lowering the catalyst loading to 0.01 mol% without serious decrease in ee or yield.

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