Rhodium-Catalyzed Asymmetric Vinylogous Addition to Vinylidiazooacetates

Significance: A rhodium-catalyzed asymmetric vinylogous addition of silyl enol ethers to siloxy-vinyldiazoacetates is reported. Depending on the steric of the substituents on the substrate, this method can access cyclopentenones 2 or alkynoates 3 with high yield and excellent enantioselectivity.

Comment: The use of (Z)-silyl enol ethers is critical in achieving the observed enantioselectivity. In the proposed mechanism, vinylogous adduct 5 can undergo a stereoselective 1,4-silyoxy shift to form 3. Bulkier R1 groups favor the aldol reaction to form formal [3+2] adduct 6, which in one pot, in acid, can afford 2.

Selected examples:

- 74% yield, 90% ee
- 81% yield, 95% ee
- 62% yield, 94% ee
- 29–70% yield, 90–94% ee

Proposed mechanism:

1. [RhII] → N2
2. vinylogous addition
3. aldol
4. shift
5. shift
6. shift