Titanium-Catalyzed Stereoselective Formal [3+2] Cycloaddition

Selected examples:

- 98% yield, dr > 19:1, 97% ee
- 75% yield, dr = 12:1, 96% ee
- 91% yield, dr > 19:1, 97% ee
- 96% yield, dr > 19:1, 96% ee
- 92% yield, dr > 19:1, 96% ee
- 87% yield, dr > 19:1, 79% ee
- 92% yield, dr = 6:1, 88% ee
- 96% yield, dr > 19:1, 96% ee
- 89% yield, dr > 19:1, 96% ee
- 81% yield, dr > 19:1, 90% ee
- 87% yield, dr = 9:1, 80% ee
- 90% yield, dr = 4:1, 96% ee
- 91% yield, dr = 11:1, 96% ee
- 95% yield, dr > 19:1, 65% ee
- 81% yield, dr > 19:1, 51% ee
- 79% yield, dr > 19:1, 46% ee
- 90% yield, dr = 45% ee
- 82% yield, dr = 5:1, 13% ee

* with 5 mol% of catalyst

**at -25 °C for 48 h

**a with 5 mol% of catalyst

**b at –25 °C for 48 h

Significance: The discovery of new reactions mediated by organic radical intermediates continues to provide solutions to challenging synthetic problems in conventional two-electron chemistry. The authors have developed a Ti-catalyzed stereoselective formal [3+2] cycloaddition of cyclopropyl ketones and alkenes.

Comment: This catalytic cycloaddition through a radical-redox-relay mechanism provides chiral polysubstituted cyclopentane derivatives containing two contiguous stereogenic centers in high yields and with high diastereo- and enantioselectivities.

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titanium catalysis
cycloaddition
cyclopropyl ketones
alkenes