Enantioselective Allyl–Allylsilane Cross-Coupling Catalyzed by Iridium

Significance: An iridium-catalyzed cross-coupling of allylic alcohols with allylsilanes is reported. A series of chiral 1,5-dienes were prepared in good yields (up to 95%) with excellent regio- (up to >25:1) and enantioselectivities (up to >99% ee).

Comment: This allyl–allylsilane cross-coupling proceeds with excellent regio- and enantioselectivity under operationally simple conditions. The utility of this reaction is demonstrated in the enantioselective synthesis of the pyrethroid insecticide protrifenbute.

Selected examples:

- 2-Naph: 79% yield >99% ee
- Ph: 87% yield >99% ee
- MeO2C: 65% yield >99% ee
- F3C: 61% yield >99% ee
- OAc: 84% yield 99% ee
- Br: 87% yield >99% ee
- MeO2C: 79% yield >99% ee
- F3C: 69% yield 99% ee
- OAc: 87% yield >99% ee
- Br: 87% yield >99% ee

Synthesis of (–)-protrifenbute:

- Cl: 75% yield regioselectivity (25:1)
- FOPh: 94% yield regioselectivity (9:1)
- OPd(dppf)Cl2: 59% yield
- AsPh3: 9-BBN regioselectivity (9:1)
- ZnEt2, CH2I2, TFA: 94% yield
- (–)-protrifenbute: >99% ee