Rhodium-Catalyzed Asymmetric Dearomatization of Naphthols with Alkynes

Selected examples: (rr = alkene regioselectivity)

- 81% yield, 90% ee, rr = 17:1
- 38% yield, 78% ee, rr = 11:1
- 85% yield, 92% ee [3.2 mmol scale]
- 82% yield, 80% ee
- 72% yield, 82% ee [3.2 mmol scale]

Proposed mechanism:

Significance: Recent efforts have been extended towards the development of asymmetric C–H functionalization reactions. The authors report an asymmetric version of the previously known metal-catalyzed dearomatization of phenols.

Comment: Twenty-six dearomatized products were synthesized in moderate to high enantioselectivity by using a chiral ligand recently invented by Cramer. The use of unsymmetrical alkynes leads to regioisomeric alkene mixtures in greater than 7:1 selectivity. A primary deuterium kinetic isotope effect indicates that C–H bond cleavage is most likely the rate-determining step.