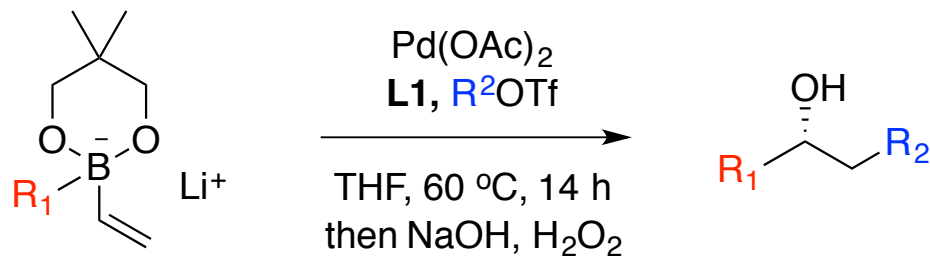
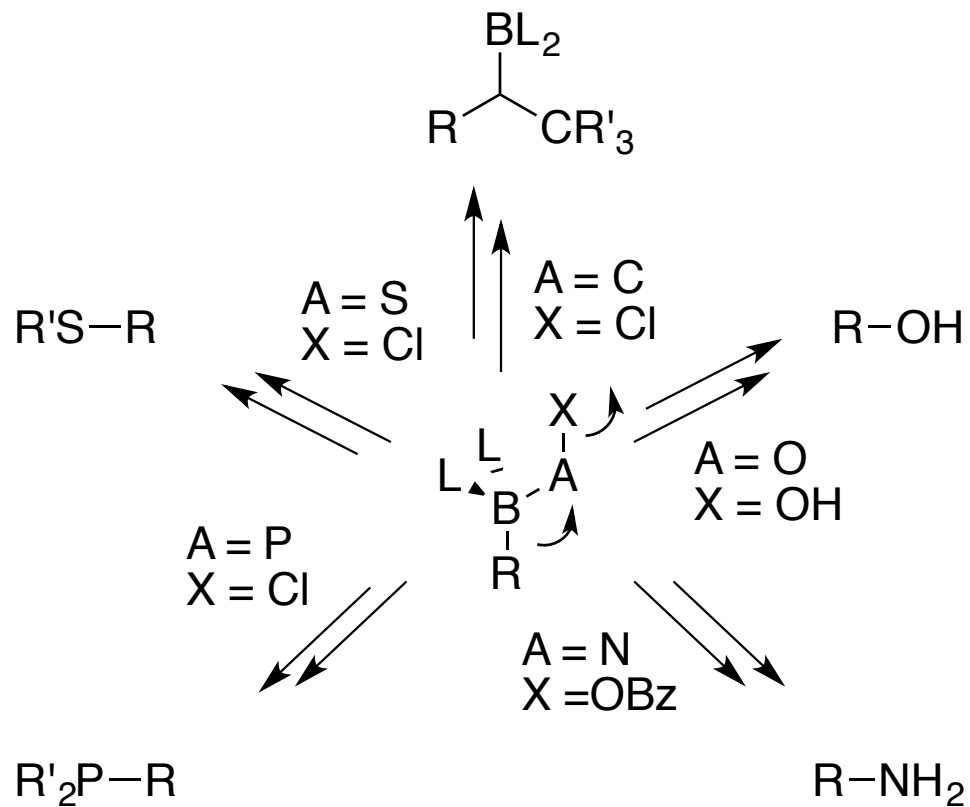


Catalytic Conjunctive Cross-Coupling enabled by Metal-Induced Metallate Rearrangement

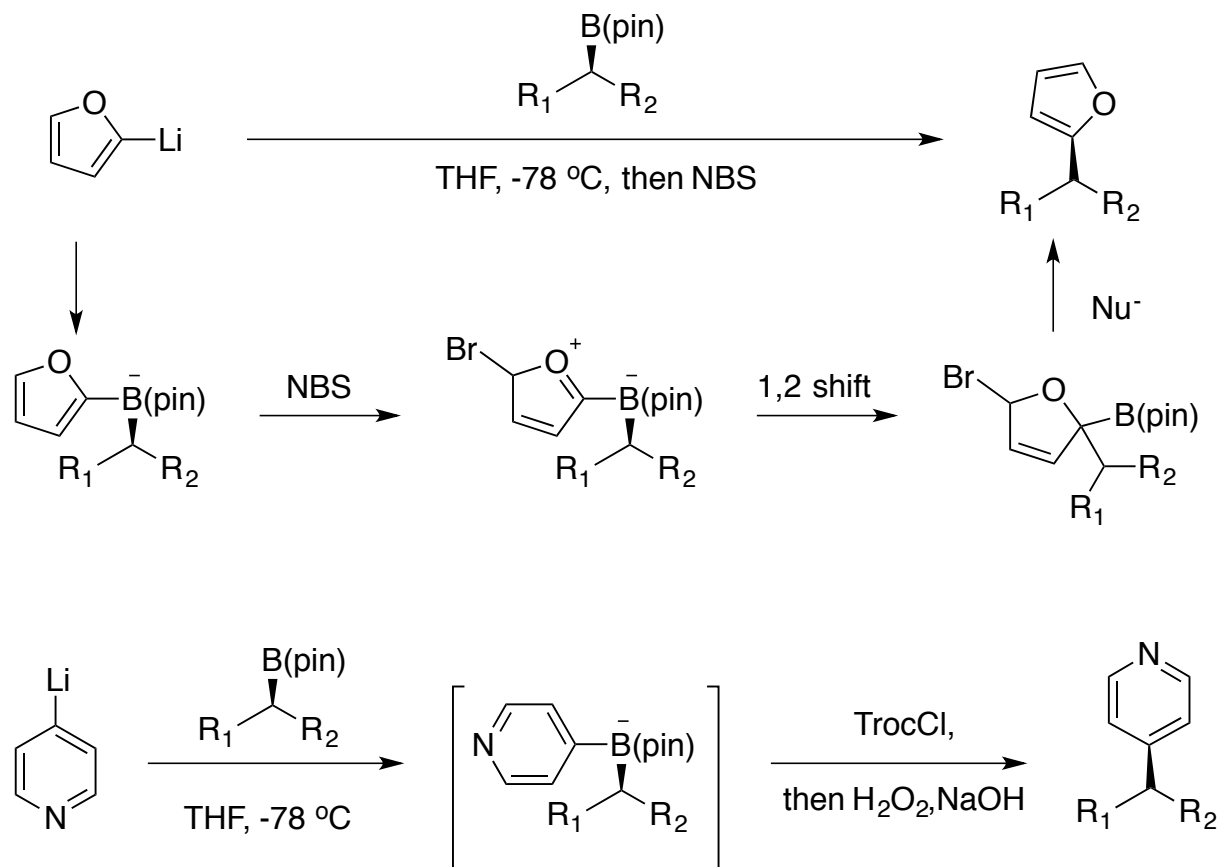
L. Zhang, G. J. Lovinger, E. K. Edelstein, A. A. Szymaniak, M. P. Chierchia, J. P. Morken
Science **2016**, *351*, 70-74.



1,2-Metallate Shifts with Boron

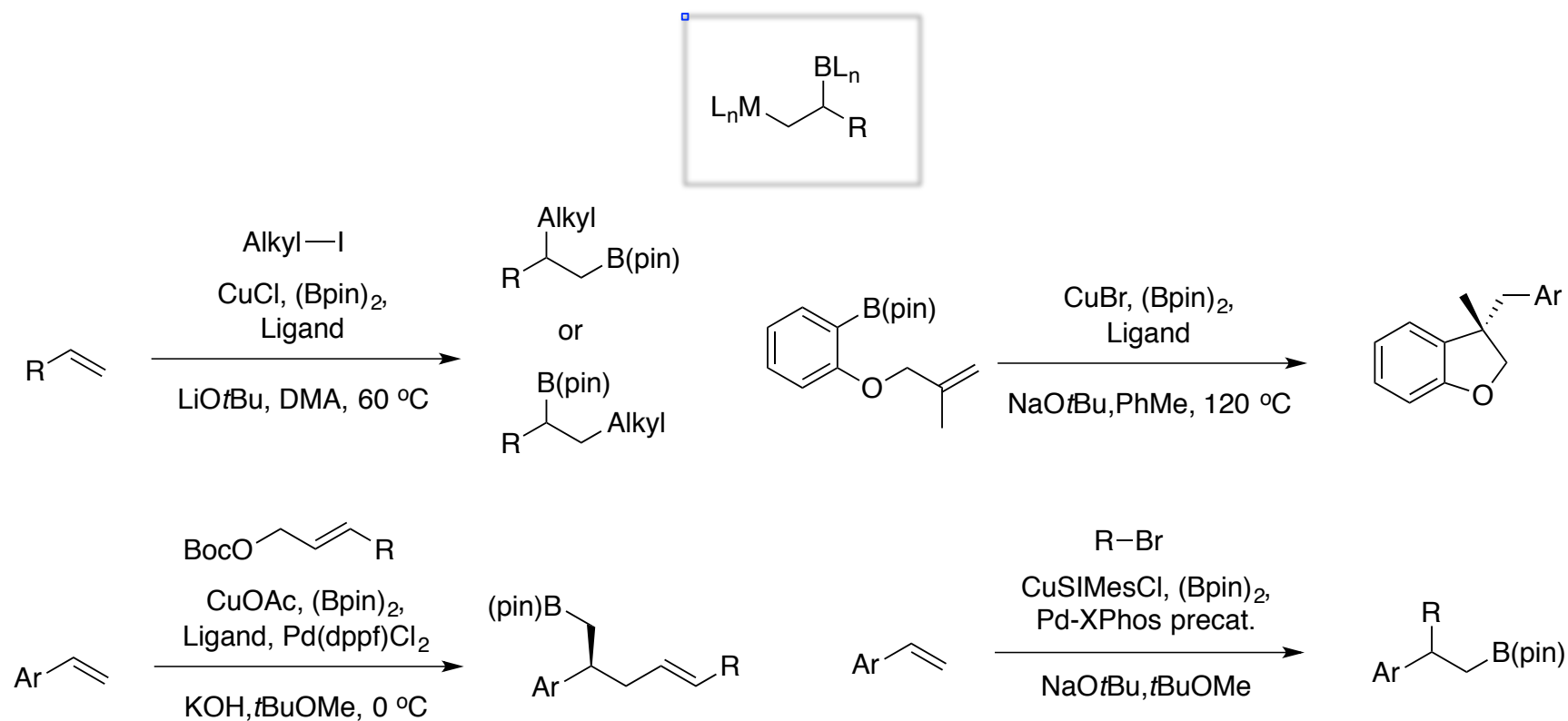


Recent 1,2-Metallate Shifts from Boron to Carbon



Nature Chem. **2014**, *6*, 584-589.
J. Am. Chem. Soc. **2015**, *137*, 10958-10961.

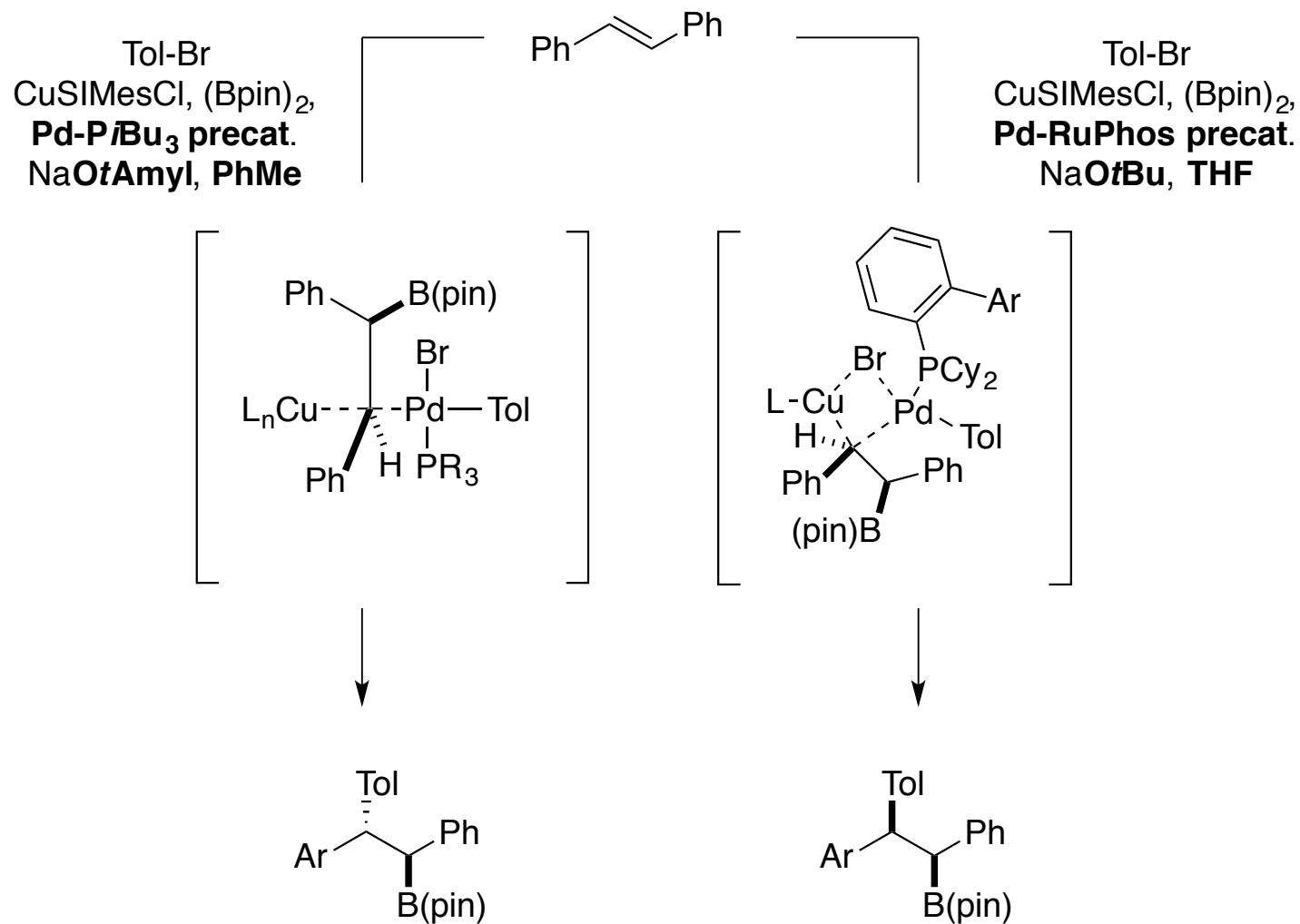
Alkyl-Metal Regents Generated from Alkenes



Angew. Chem. Int. Ed. **2015**, *54*, 12957-12961.
J. Am. Chem. Soc. **2015**, *137*, 13760-13764.

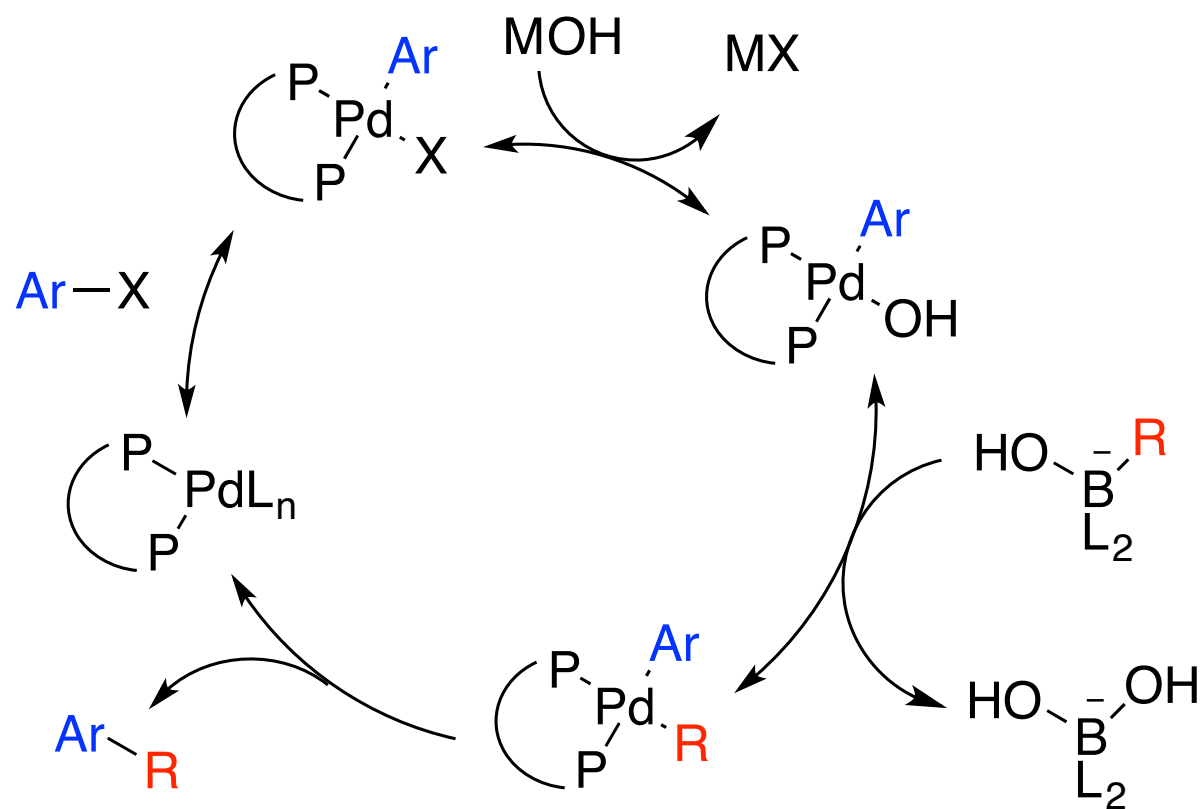
J. Am. Chem. Soc. **2015**, *137*, 14578-14581.
Chem. Eur. J. **2014**, *20*, 12032-12036.

Stereoinvertive vs. Stereoretentive Transmetalation

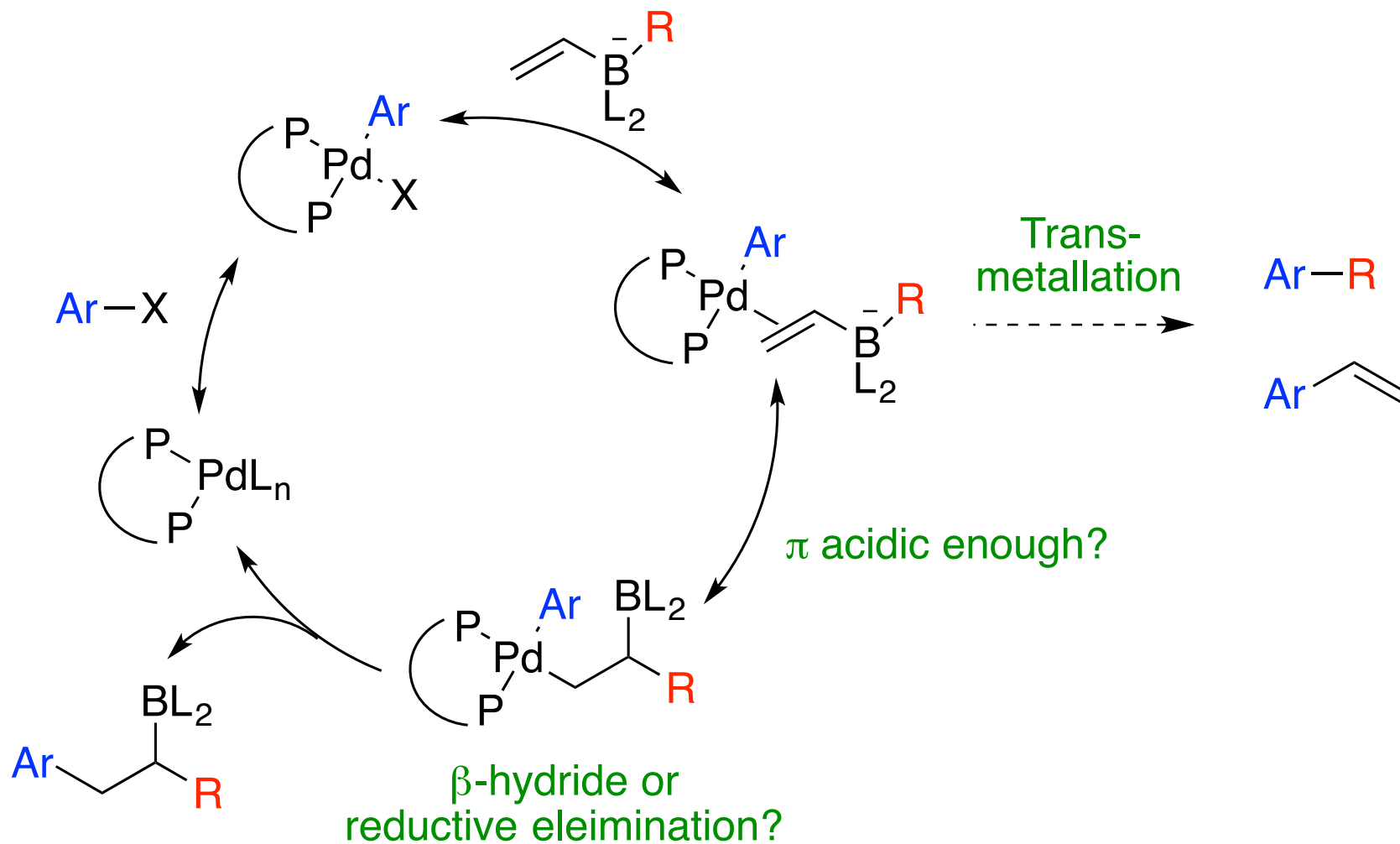


Angew. Chem. Int. Ed. **2015**, *54*, 5228-5231.

Suzuki Catalytic Cycle

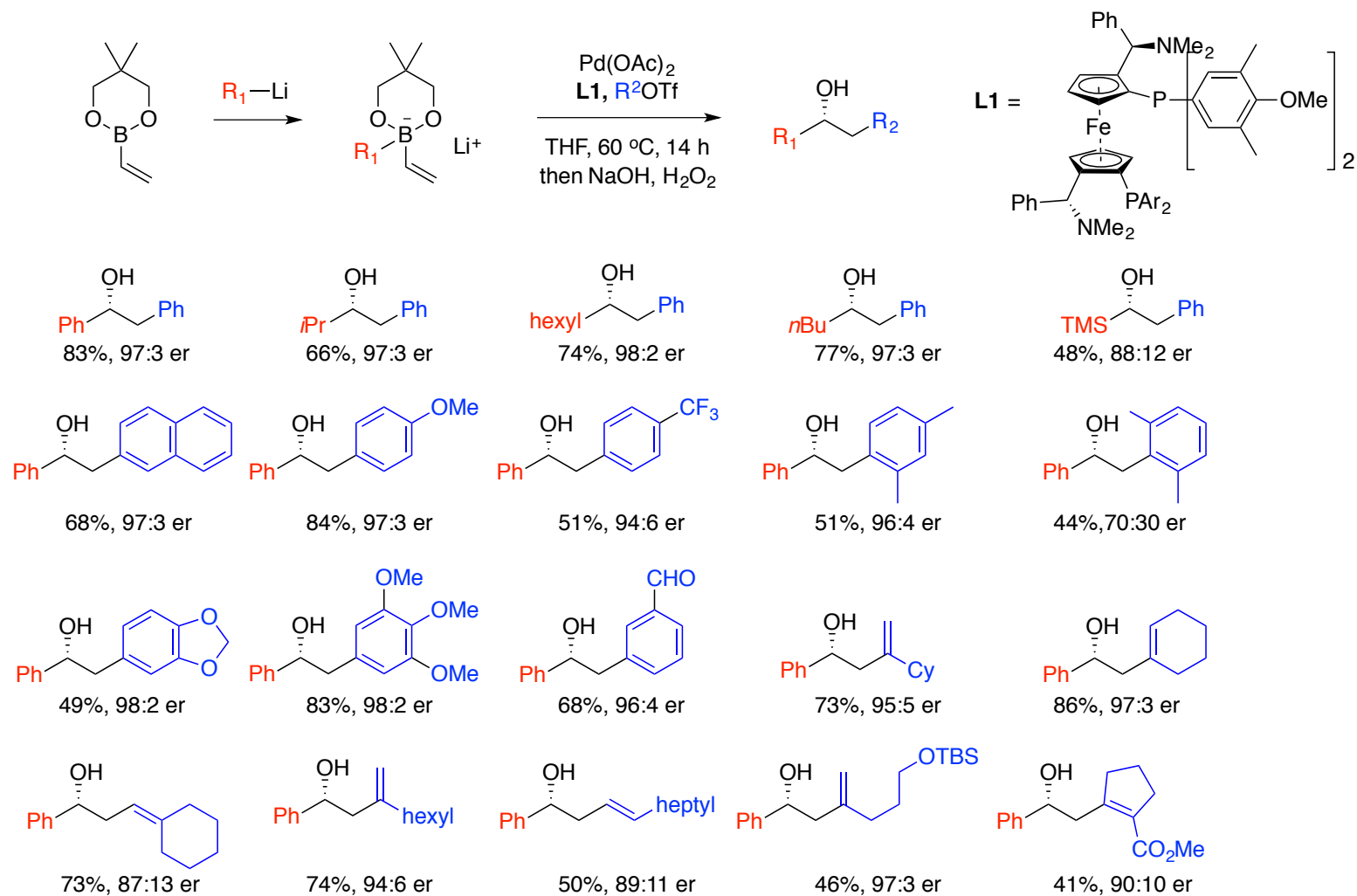


Proposed Catalytic Cycle



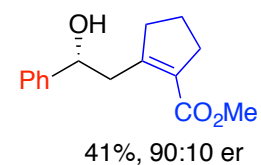
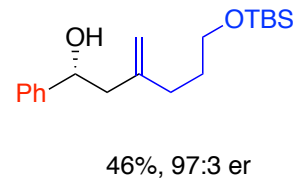
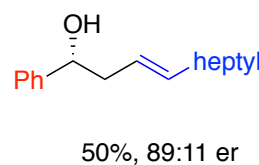
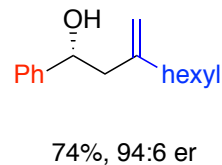
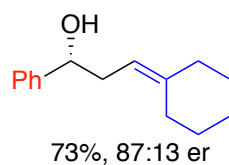
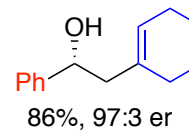
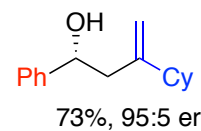
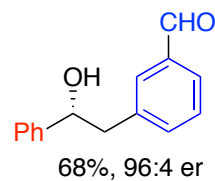
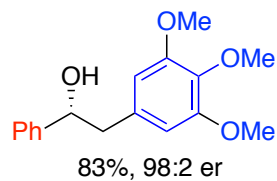
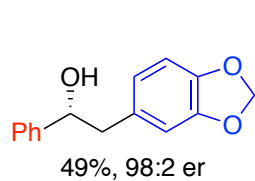
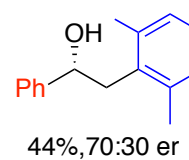
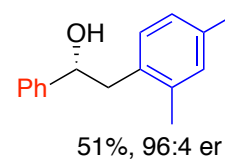
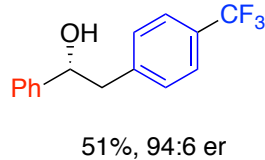
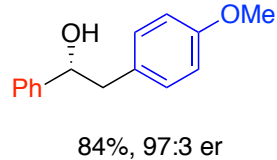
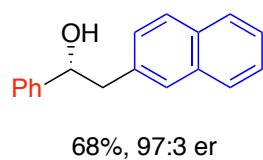
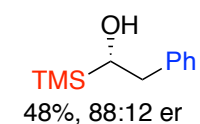
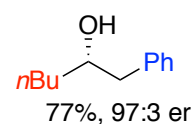
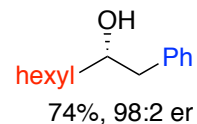
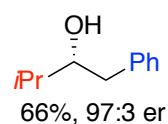
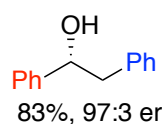
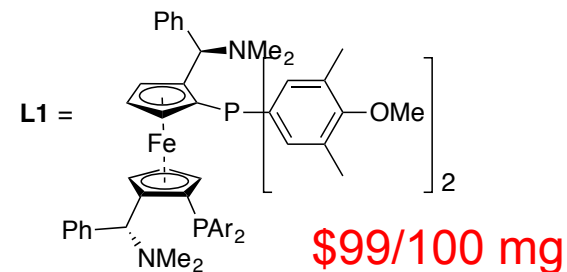
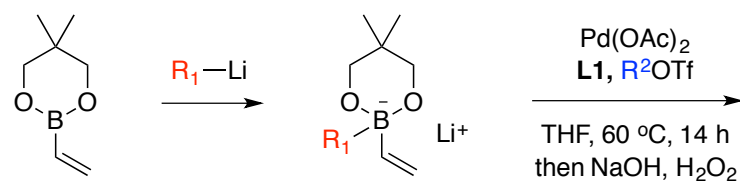
Science. 2016, 351, 70-74.

R-Li Method: Reaction Scope



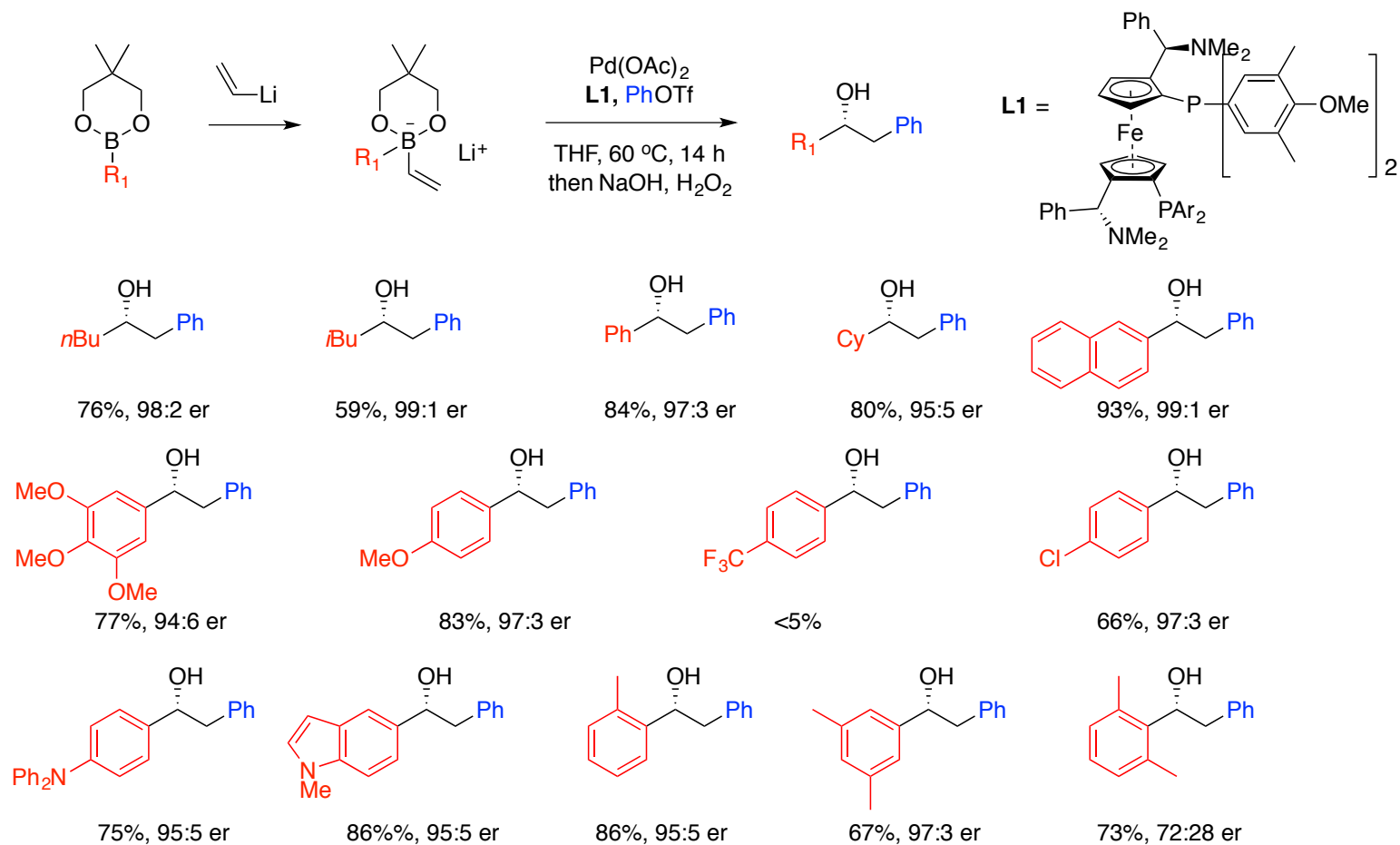
Science. 2016, 351, 70-74.

R-Li Method: Reaction Scope



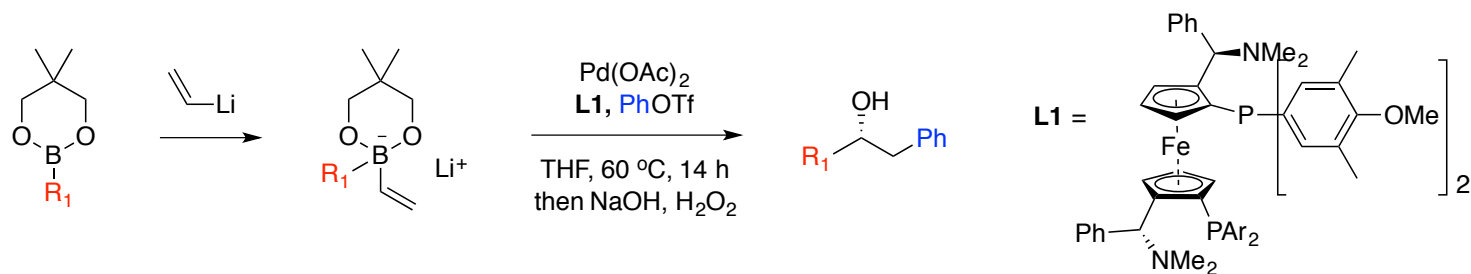
Science. 2016, 351, 70-74.

Vinyl-Li Method: Reaction Scope



Science. 2016, 351, 70-74.

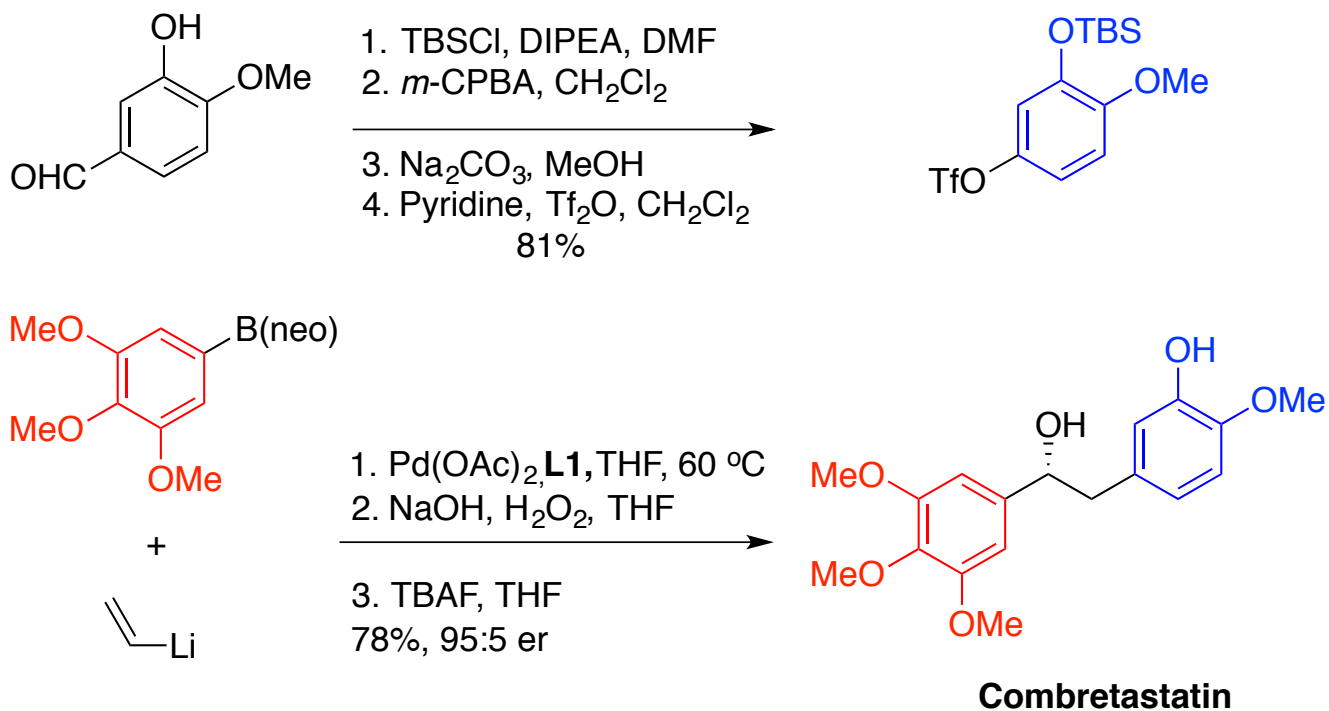
Vinyl-Li Method: Interesting Notes



- 1-2 mol% halide ion detrimental
 - Solution: "...lithium-halogen exchange with *n*-BuLi followed by low temperature crystallization of vinyl lithium."
- Alternatives
 - Increase catalyst loading by 2.5x
 - Li-Sn exchange

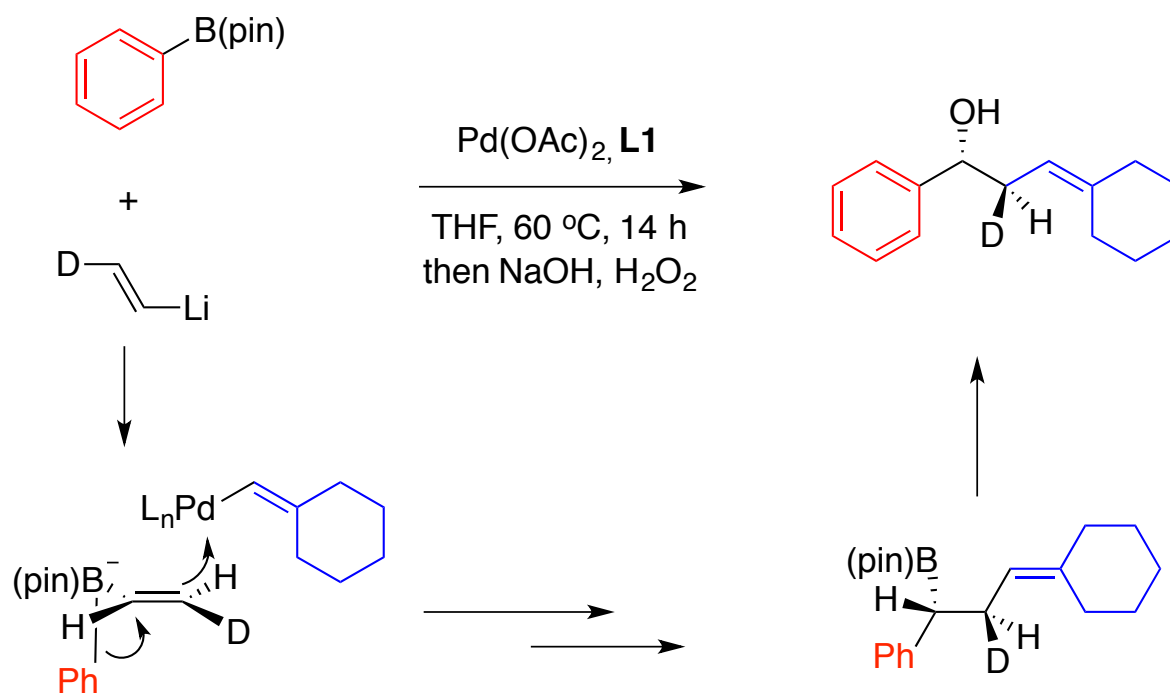
Science. 2016, 351, 70-74.

Preparation of Combretastatin



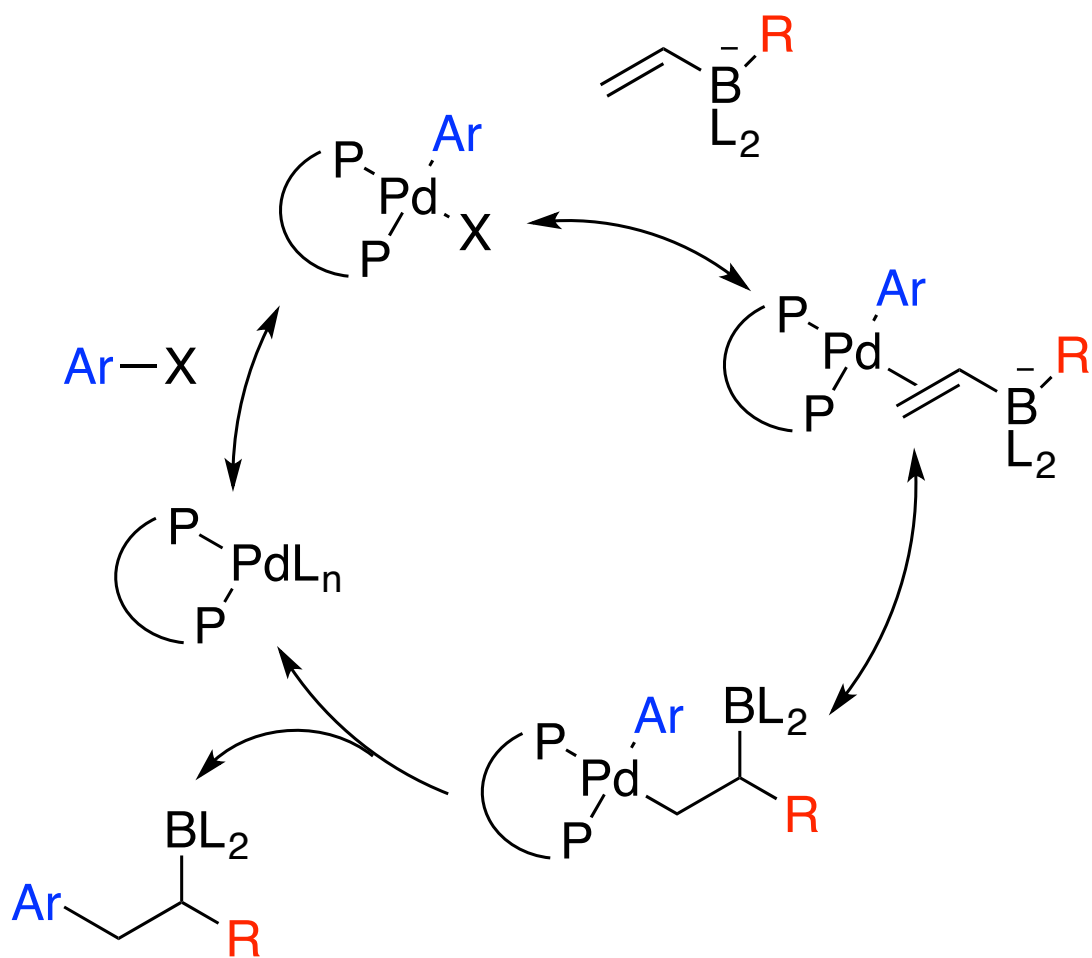
Science. 2016, 351, 70-74.

D-Labeling Experiment

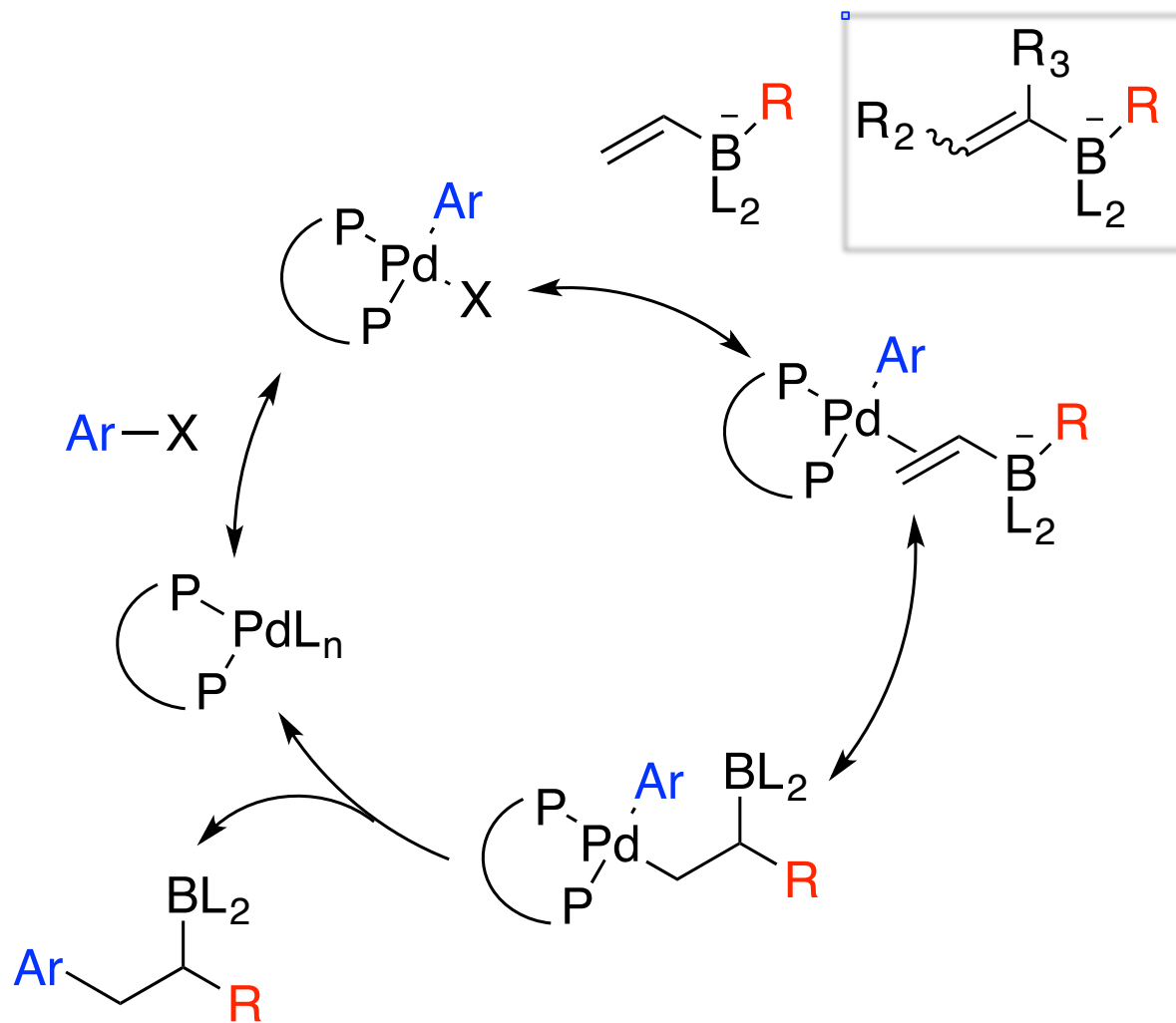


Science. 2016, 351, 70-74.

Interesting Future Directions



Interesting Future Direction



Current Drawbacks

- Sensitivity to counterions
- Laborious reaction setup
- 1,2-shift of electron deficient aromatics