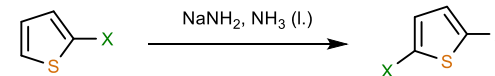
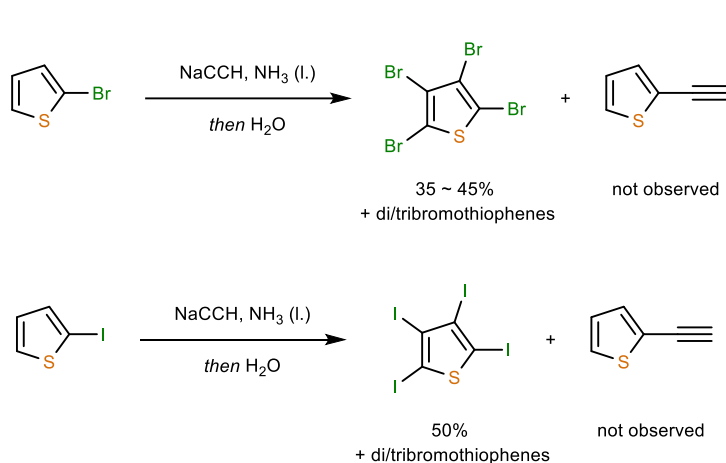


The First Halogen Dance (HD)

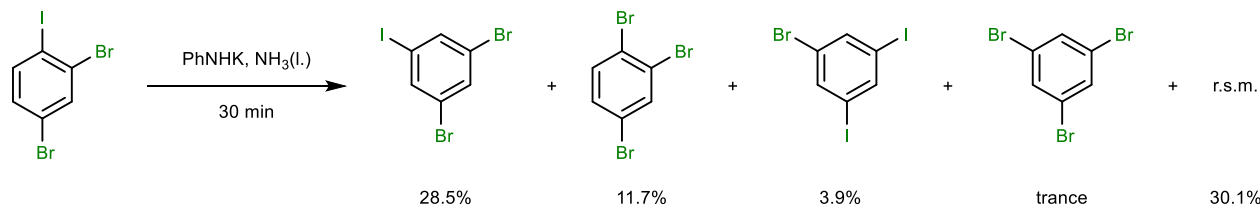


X	Eq. of NaNH ₂	Yield%	r.s.m.%
Br	2	18	10
Br	1	36	35
Br	0.2	17	70
I	2	22	12
I	1	15	45
I	0.2	15	65

Vaitiekunas, A.; Nord, F. F. *Nature* **1951**, *168*, 875. <https://doi.org/10.1038/168875a0>

Vaitiekunas, A.; Nord, F. F. *J. Am. Chem. Soc.* **1953**, *75*, 1764. <https://doi.org/10.1021/ja01103a537>

Mechanistic Studies

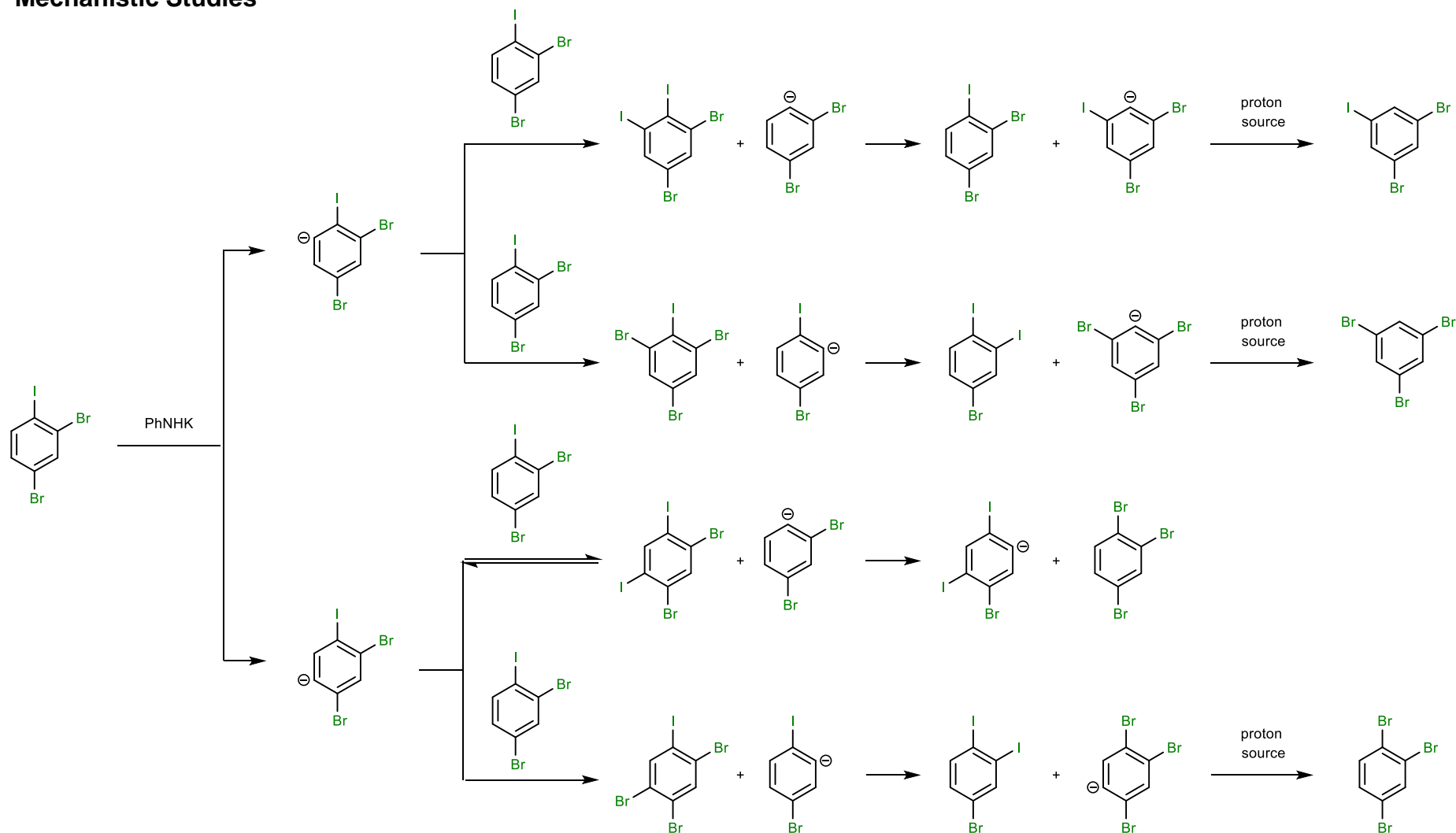


- External halogen ions did not affect the rearrangement process.
- Different patterns from addition to 3-haloarynes.
- The aryne mechanism cannot explain the formation of dihalo- and tetrahalo-products (Vaitiekunas' results).

Moyer, C. E.; Bunnett, J. F. *J. Am. Chem. Soc.* **1963**, *85*, 1891. <https://doi.org/10.1021/ja00895a058>

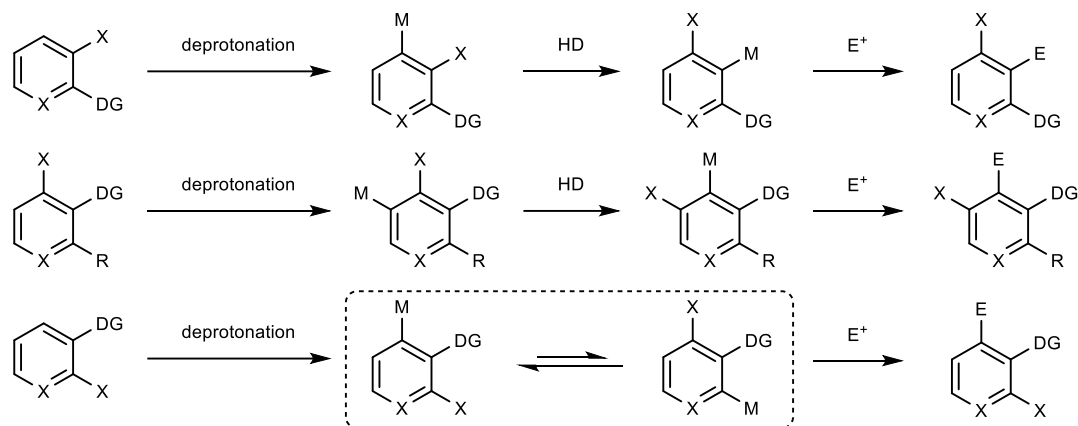
Bunnett, J. F. *Acc. Chem. Res.* **1972**, *5*, 139. <https://doi.org/10.1021/ar50052a004>

Mechanistic Studies

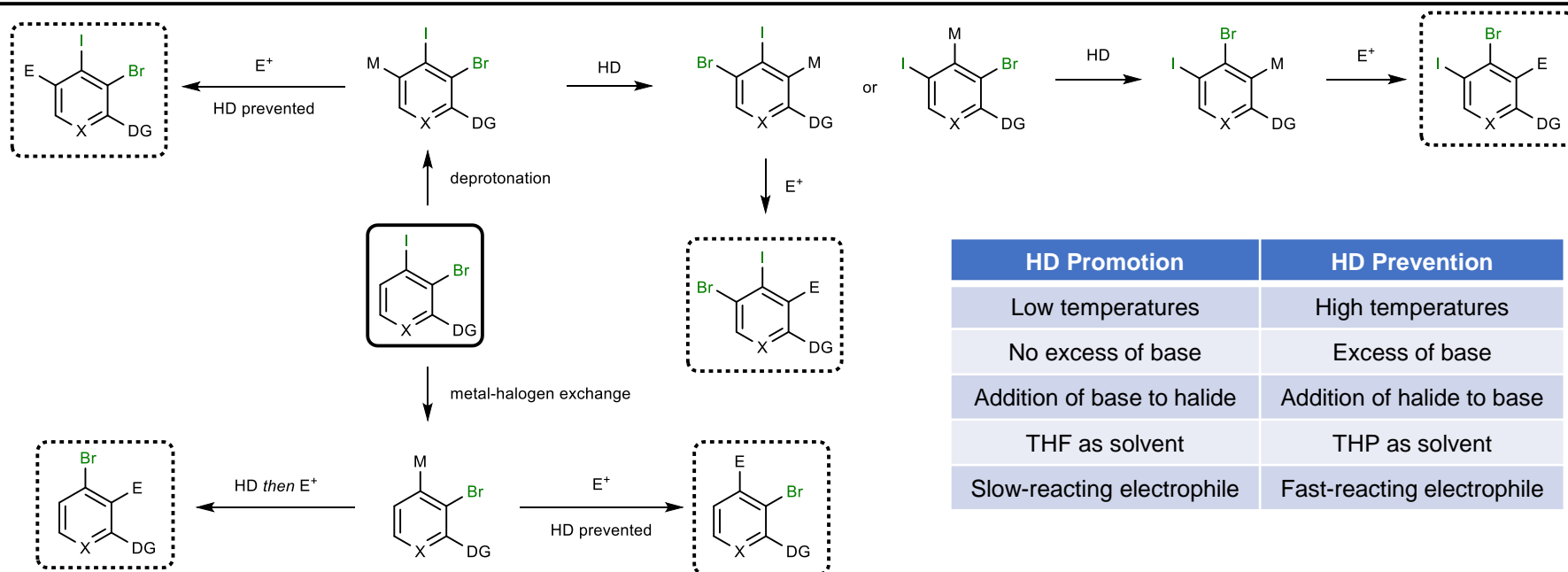


Formation of arynes not shown

General Guidelines for the Control of Halogen Dance

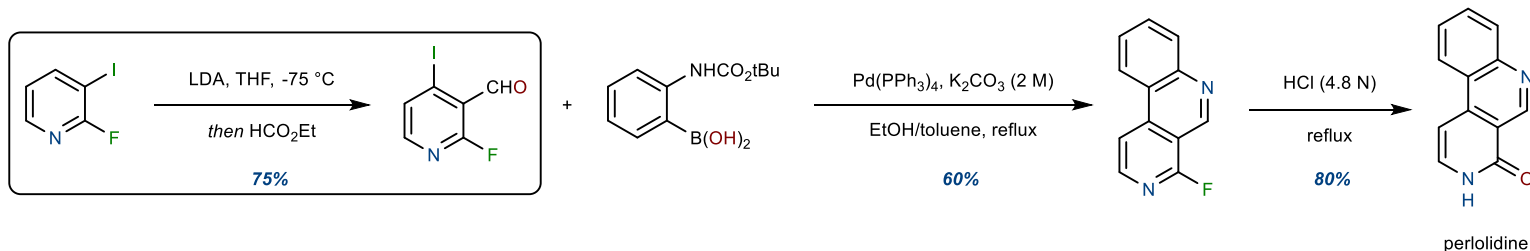


1. The thermodynamically most stable organometal species leads to the product
2. Migratory aptitude: I > Br >> Cl (F does not react)
3. HD can be minimized or completely prevented if undesired, a small amount of starting material is needed to initiate the rearrangement

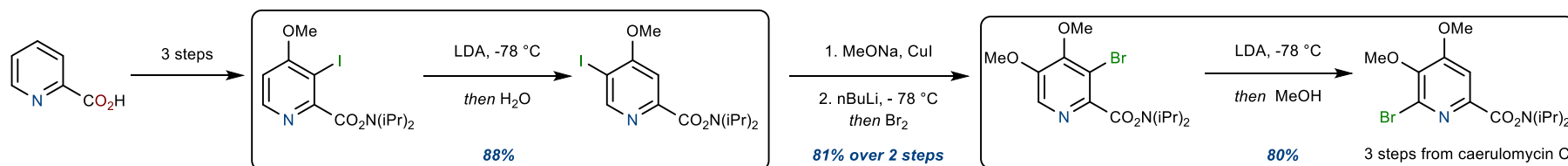


HD Promotion	HD Prevention
Low temperatures	High temperatures
No excess of base	Excess of base
Addition of base to halide	Addition of halide to base
THF as solvent	THP as solvent
Slow-reacting electrophile	Fast-reacting electrophile

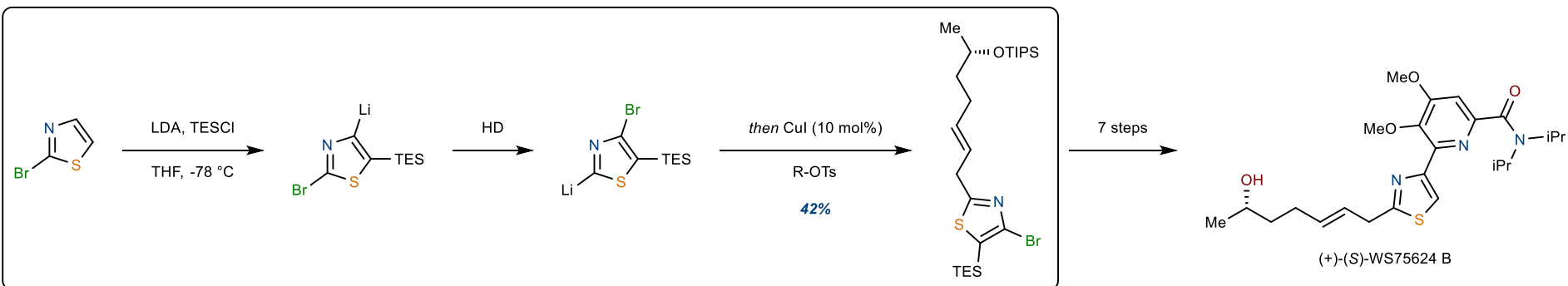
Synthetic Applications



Rocca, P.; Cochenne, C.; Marsais, F.; Thomas-dit-Dumont, L.; Mallet, M.; Godard, A.; Queguiner, G. *J. Org. Chem.* **1993**, *58*, 7832. <https://doi.org/10.1021/jo00079a031>

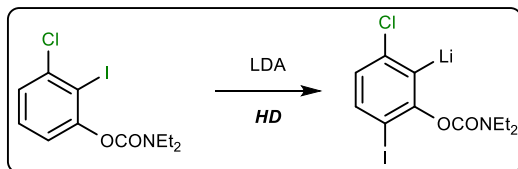


Sammakia, T.; Stangland, E. L.; Whitcomb, M. C. *Org. Lett.* **2002**, *4*, 2385. <https://doi.org/10.1021/ol026135m>



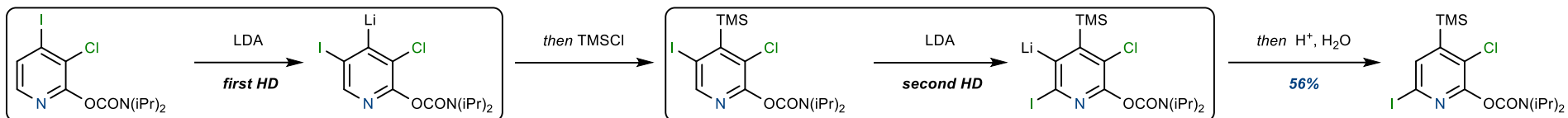
Stangland, E. L.; Sammakia, T. *J. Org. Chem.* **2004**, *69*, 2381. <https://doi.org/10.1021/jo0351217>

Synthetic Applications

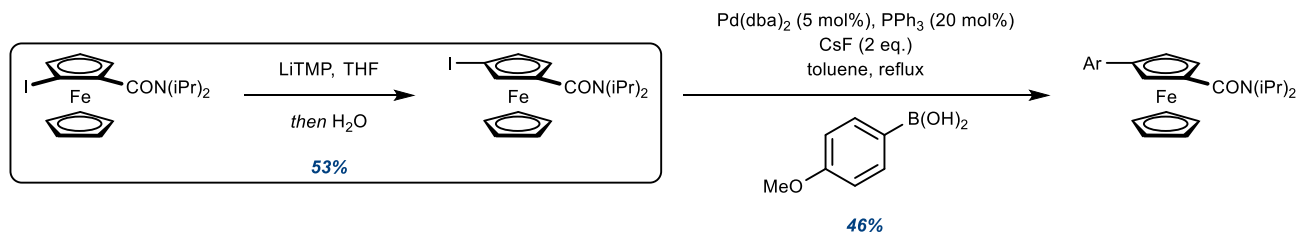


HD-Fries rearrangement cascade (left)

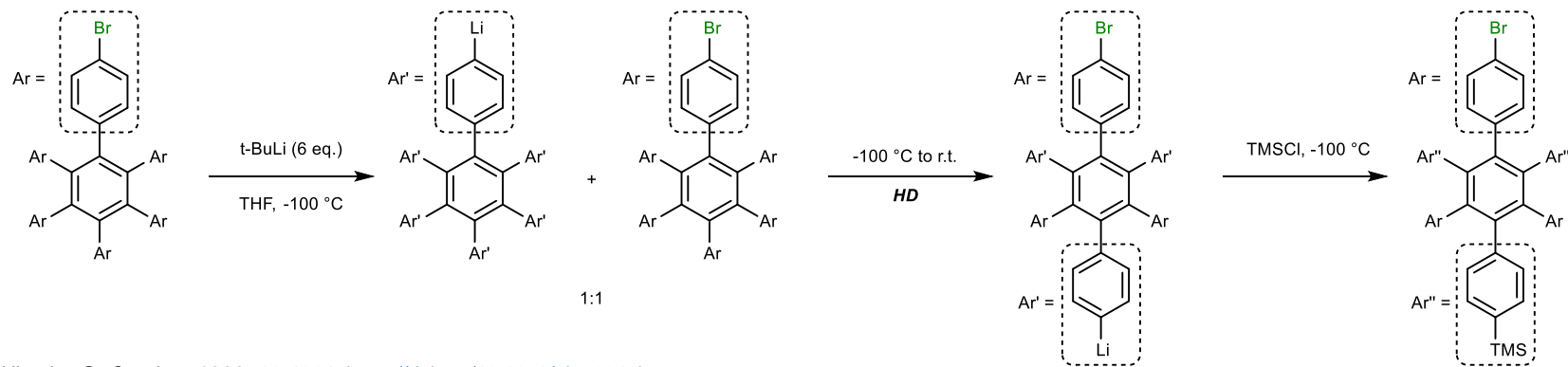
Double HD rearrangement (below)



Miller, R. E.; Rantanen, T.; Ogilvie, K. A.; Groth, U.; Snieckus, V. *Org. Lett.* **2010**, *12*, 2198. <https://doi.org/10.1021/ol100493v>



Tazi, M.; Erb, W.; Halauko, Y. S.; Ivashkevich, O. A.; Matulis, V. E.; Roisnel, T.; Dorcet, V.; Mongin, F. *Organometallics* **2017**, *36*, 4770. <https://doi.org/10.1021/acs.organomet.7b00659>



Kojima, T.; Hiraoka, S. *Org. Lett.* **2014**, *16*, 1024. <https://doi.org/10.1021/ol500041j>