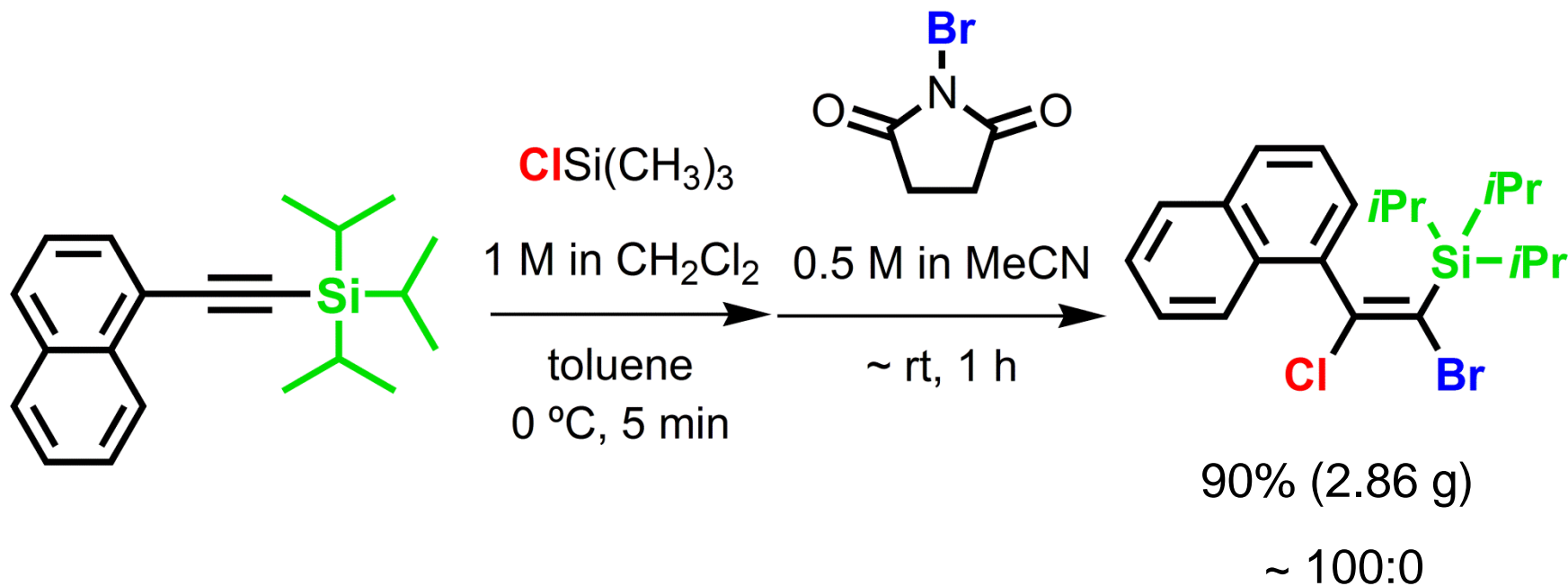


# Regio- and Stereoselective Synthesis of Vicinal (Z)-Dihaloalkenyl Silanes from Silyl Ethynylarenes

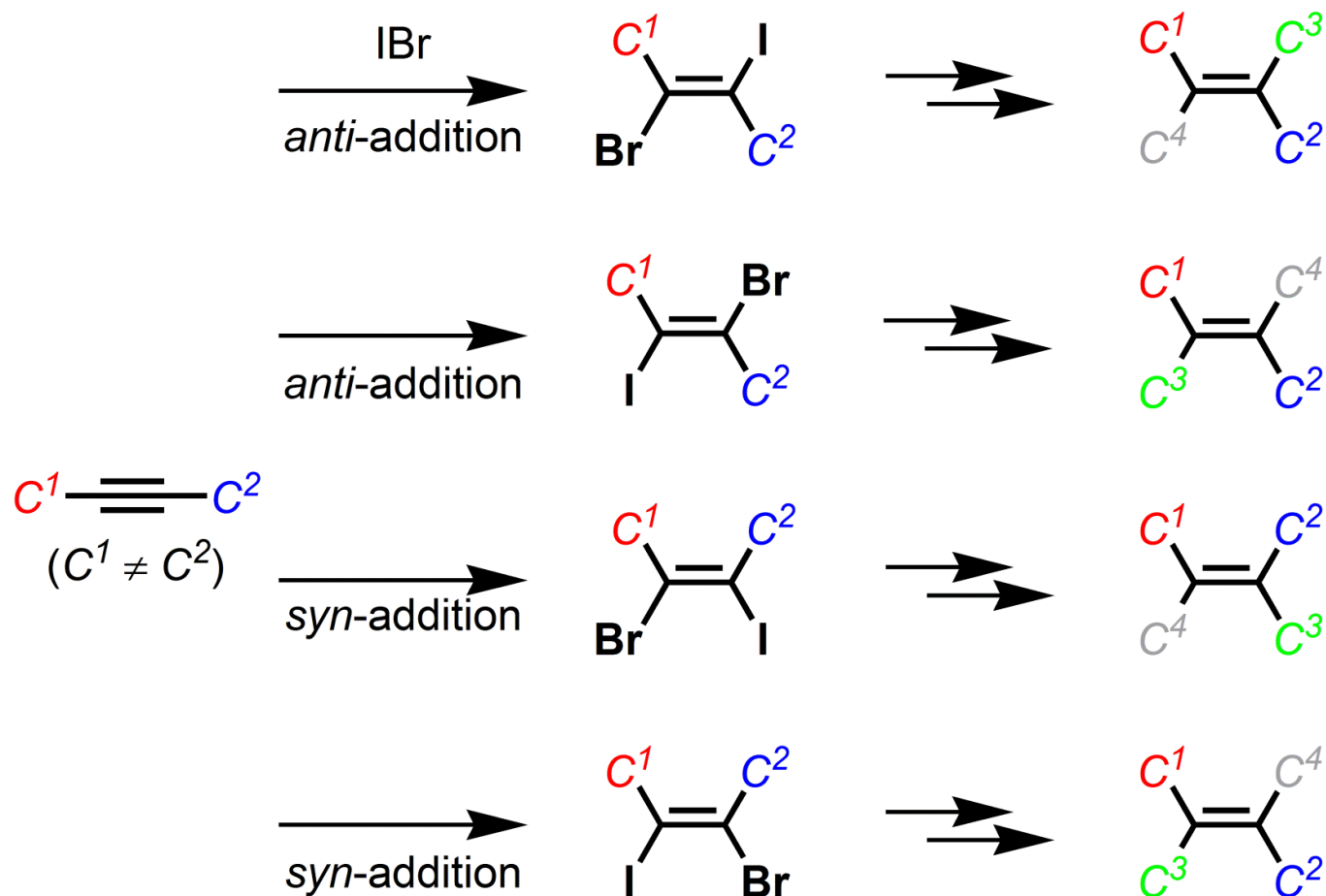
Masataka Ide, Tetsuo Iwasawa\*



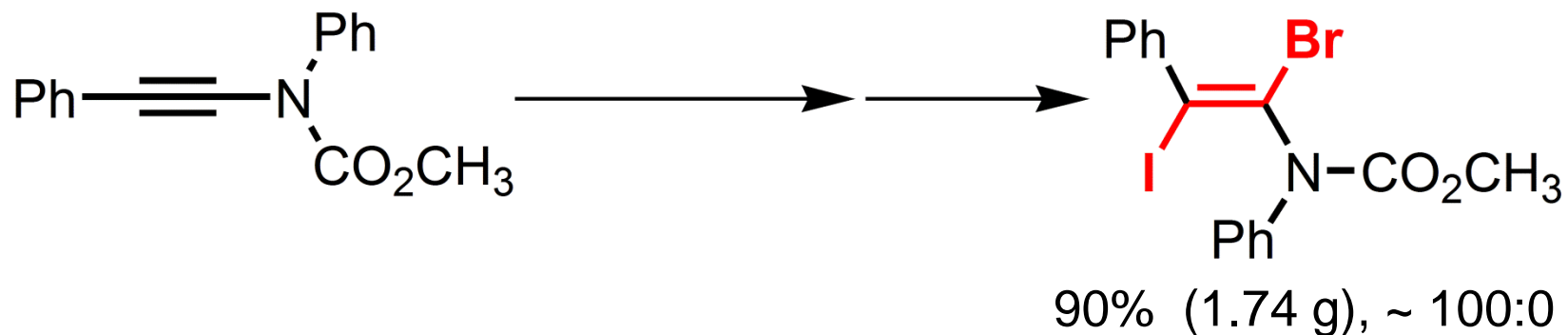
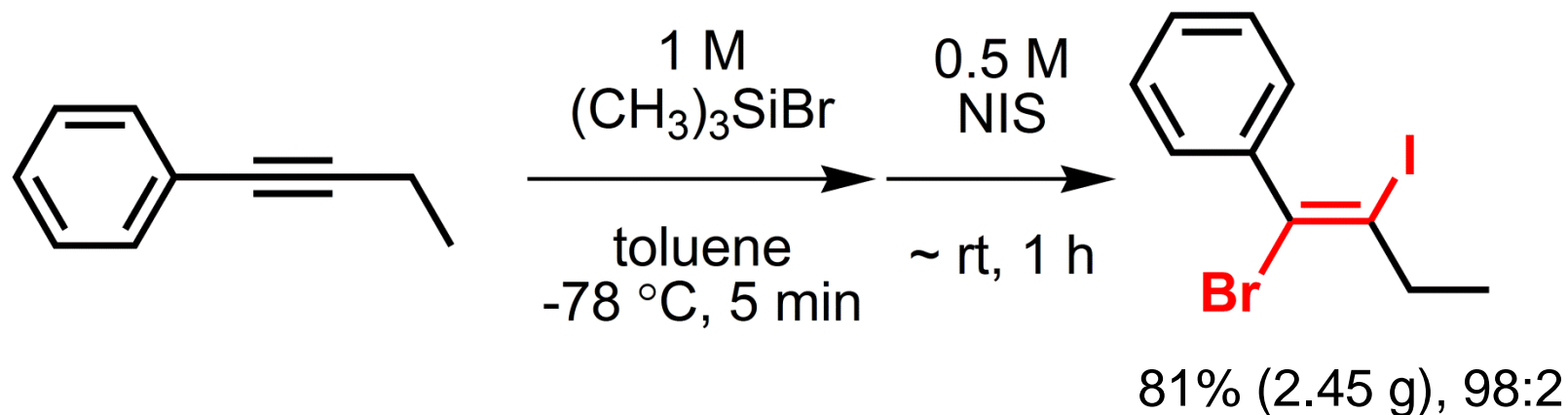
- Yauchi, Y.; Ide, M.; Shiogai, R.; Chikugo, T.; Iwasawa, T. *Eur. J. Org. Chem.* **2015**, 938-943.
- 特願 2015-247030(2015年12月5日 出願)

# Background

- Ogilvie, *et al.*, *Chem. Rev.* **2007**, *107*, 4698-4745.
- Differentially Substituted Olefin Template

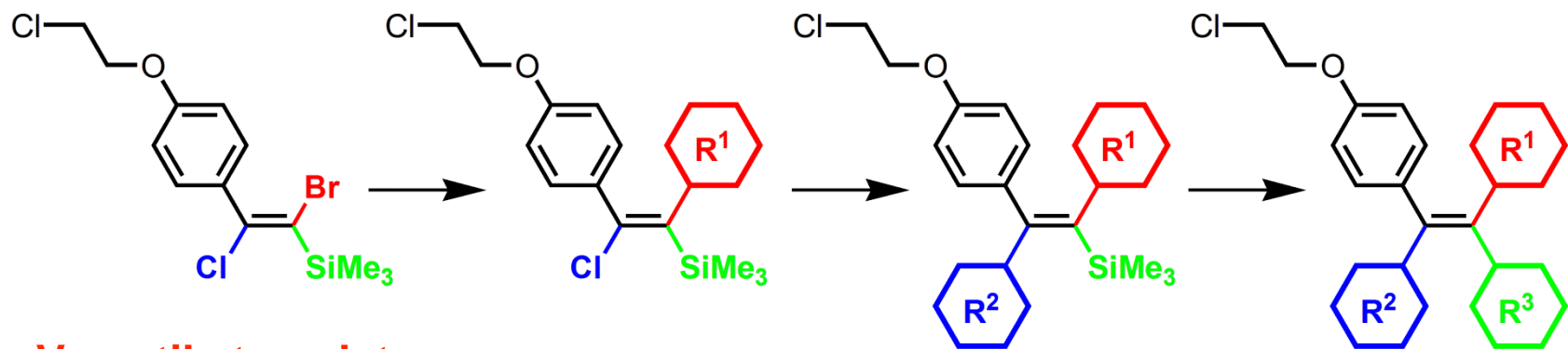


# Background

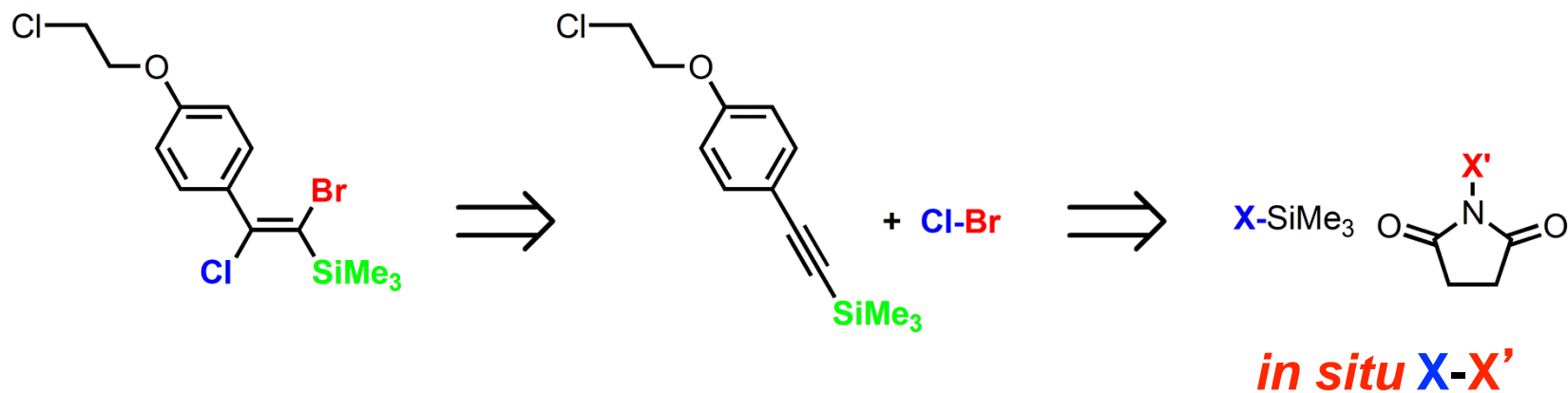


1. Ide, M.; Yauchi, Y.; Iwasawa, T. *Eur. J. Org. Chem.* **2014**, 3262-3267.
2. Ide, M.; Yauchi, Y.; Shiogai, R.; Iwasawa, T. *Tetrahedron* **2014**, 70, 8532-8538.
3. 特願 2014-014060, 特願 2014-153644

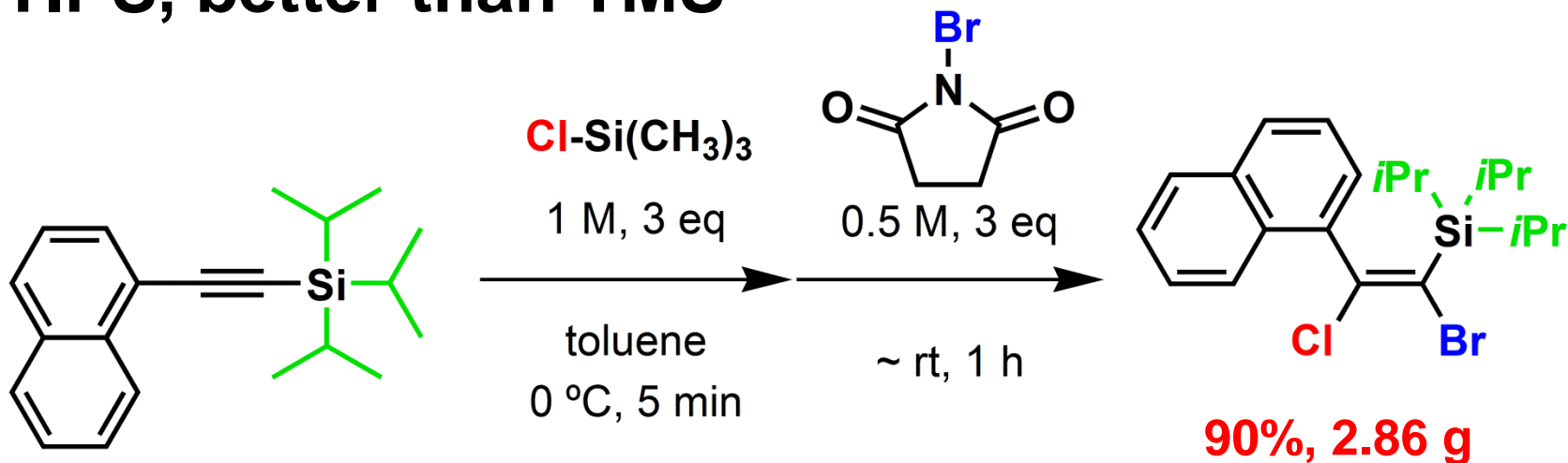
# New approach



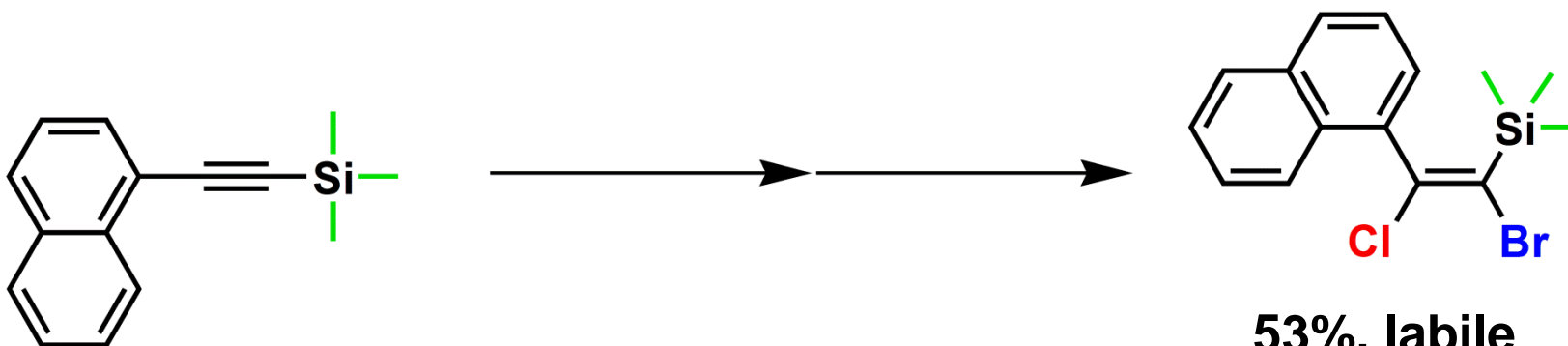
**Versatile template**



# TIPS, better than TMS

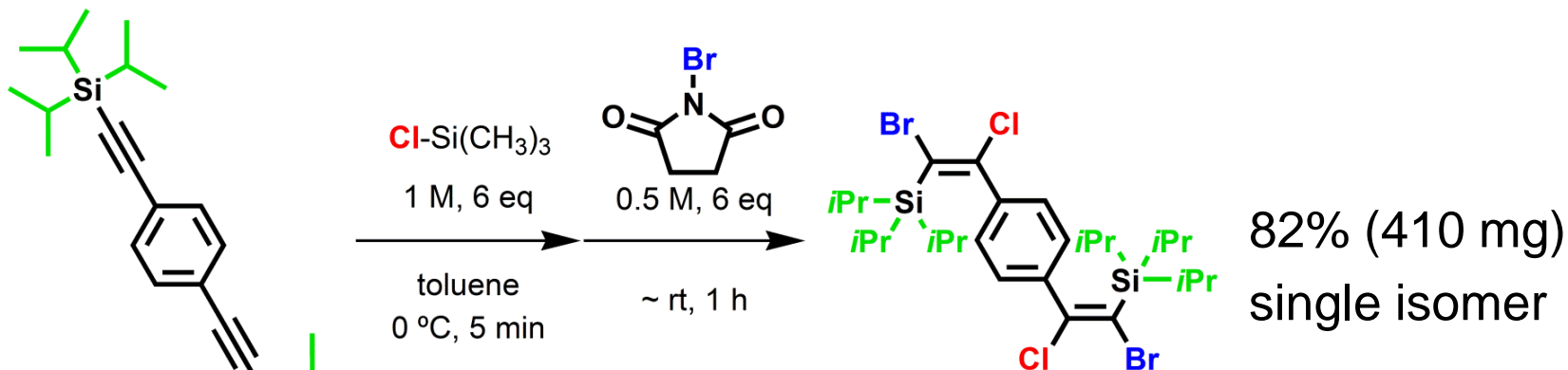


**90%, 2.86 g  
single isomer**

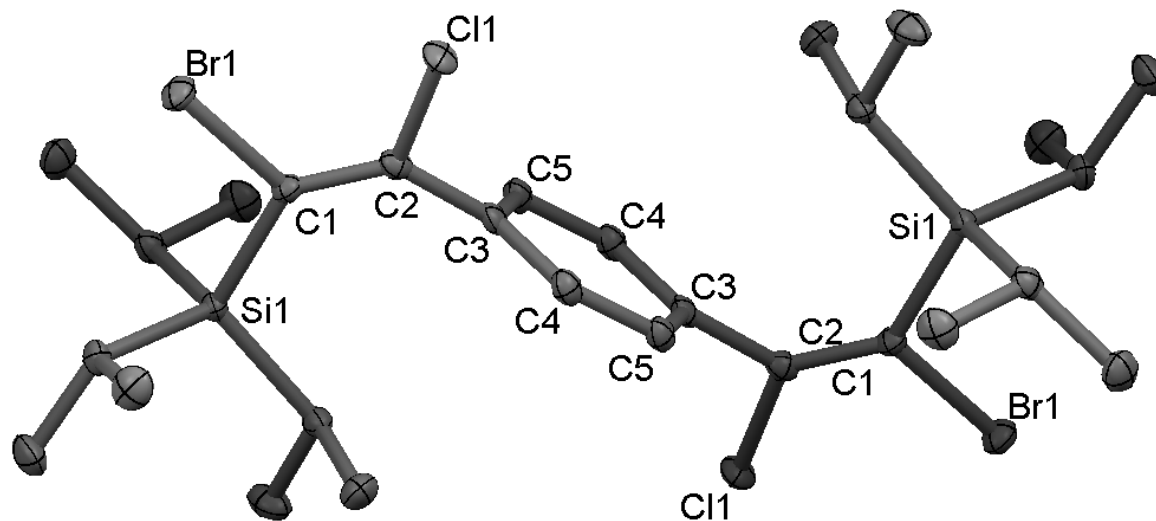


**53%, labile  
alkyne ~ 0%**

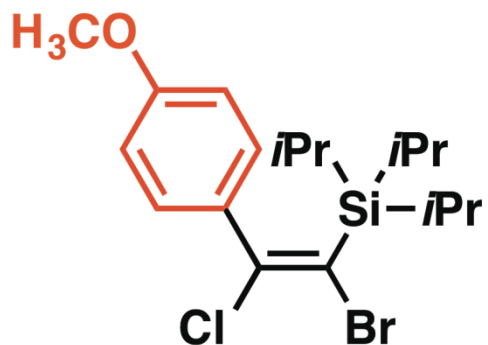
# X-ray structure; result of *syn*-addition



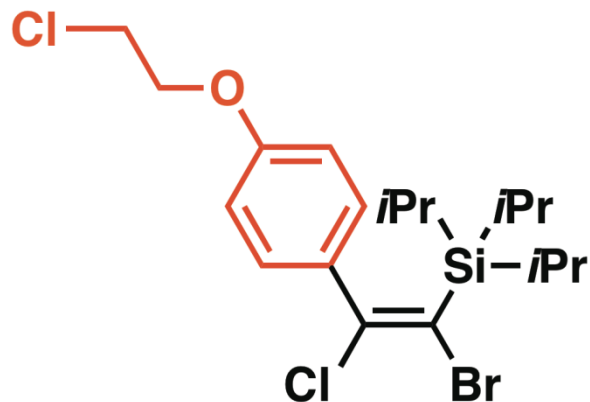
**(Z)-fashion**



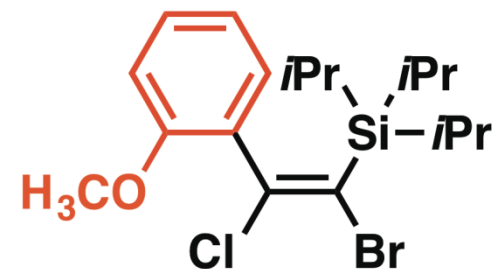
# Product scope



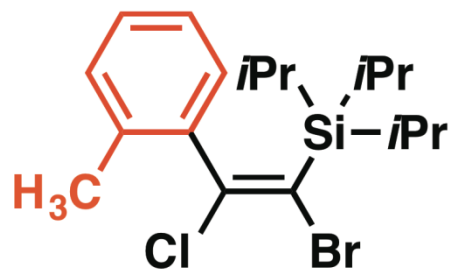
98%, 397 mg



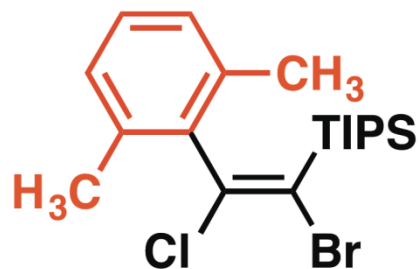
92%, 10.0 g



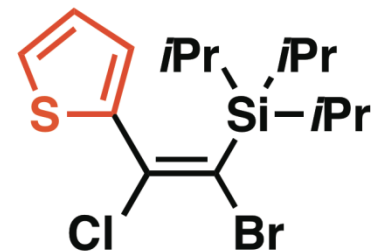
88%, 356 mg



95%, 369 mg

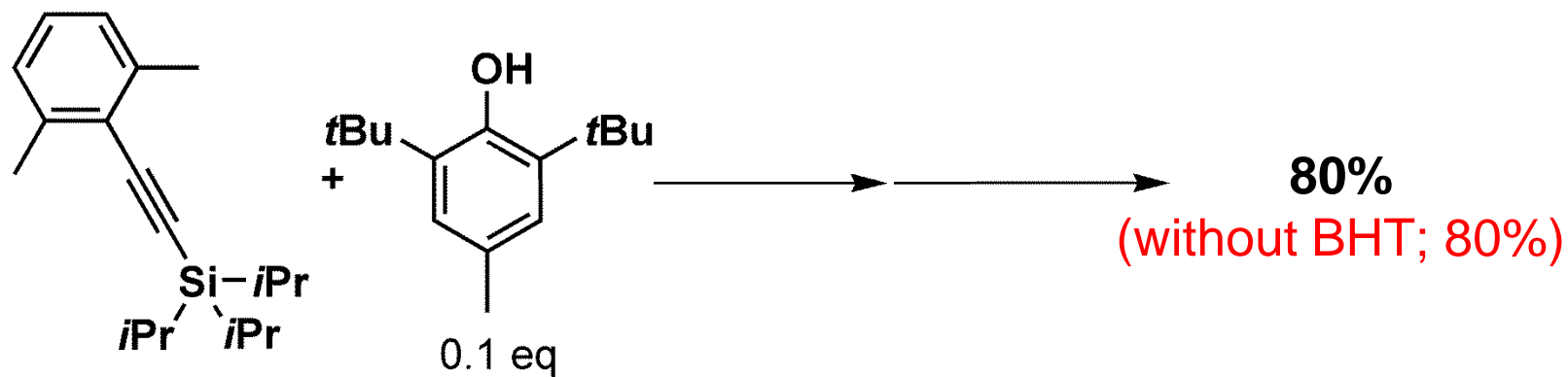
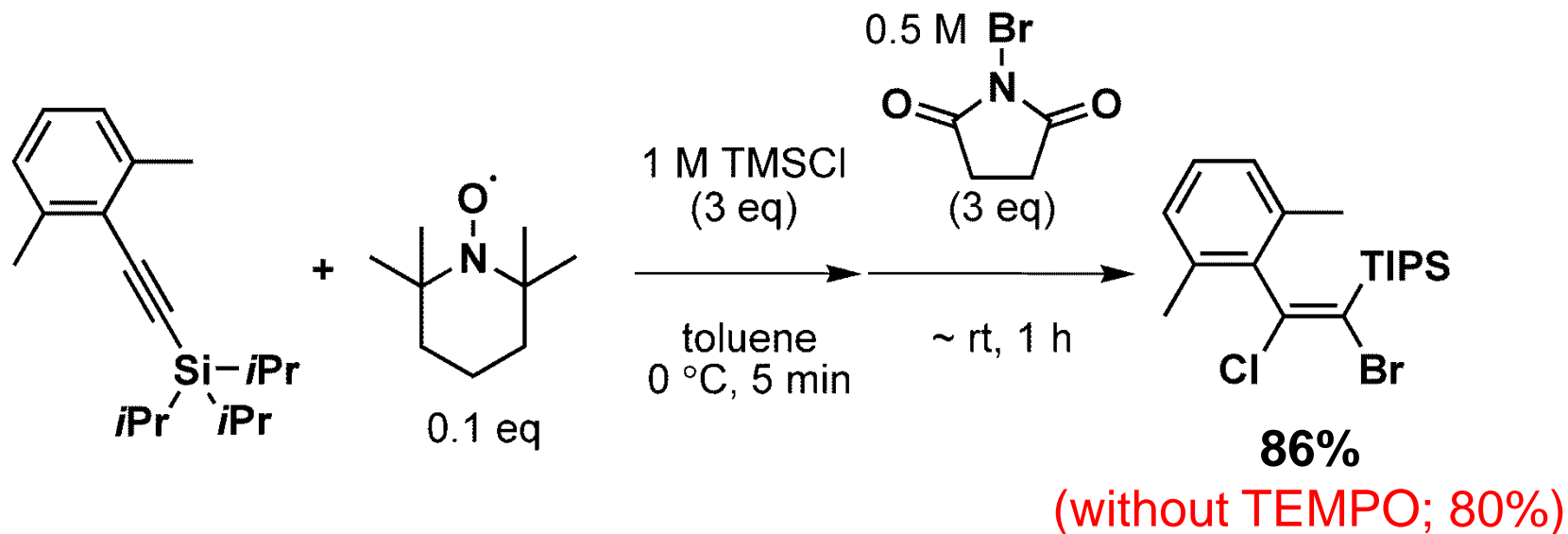


80%, 161 mg



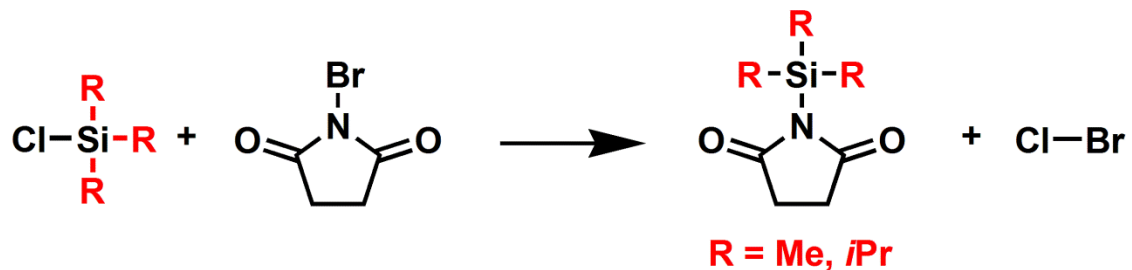
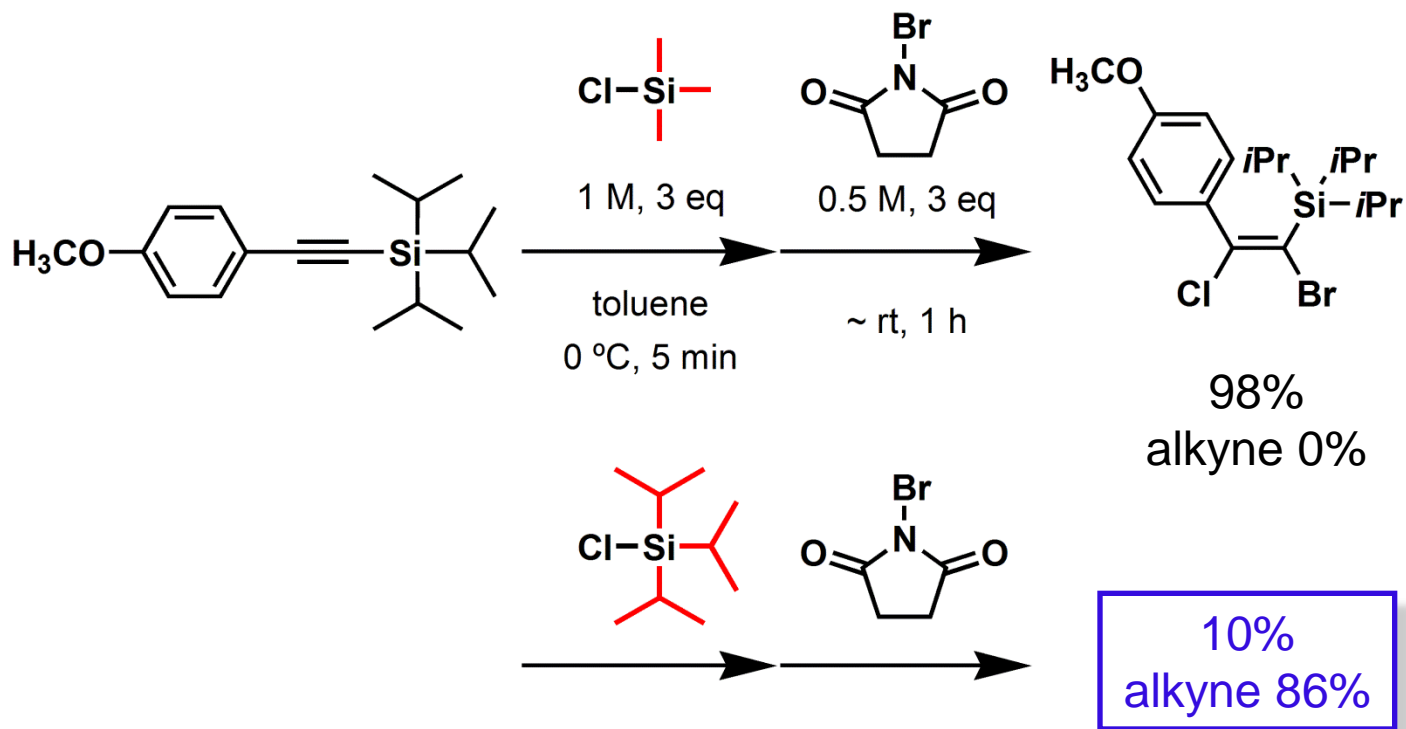
38%, 143 mg

# Radical process ? No...

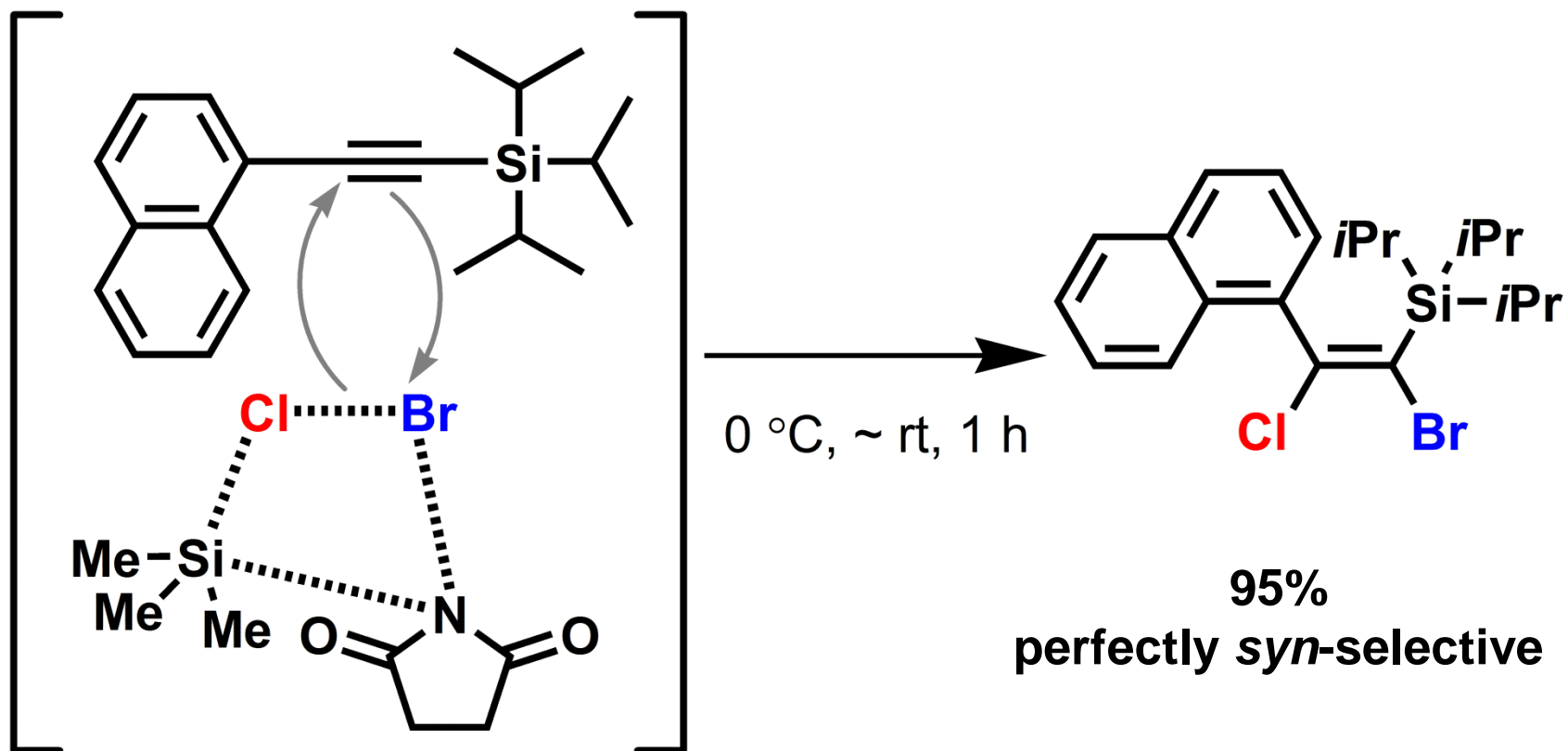




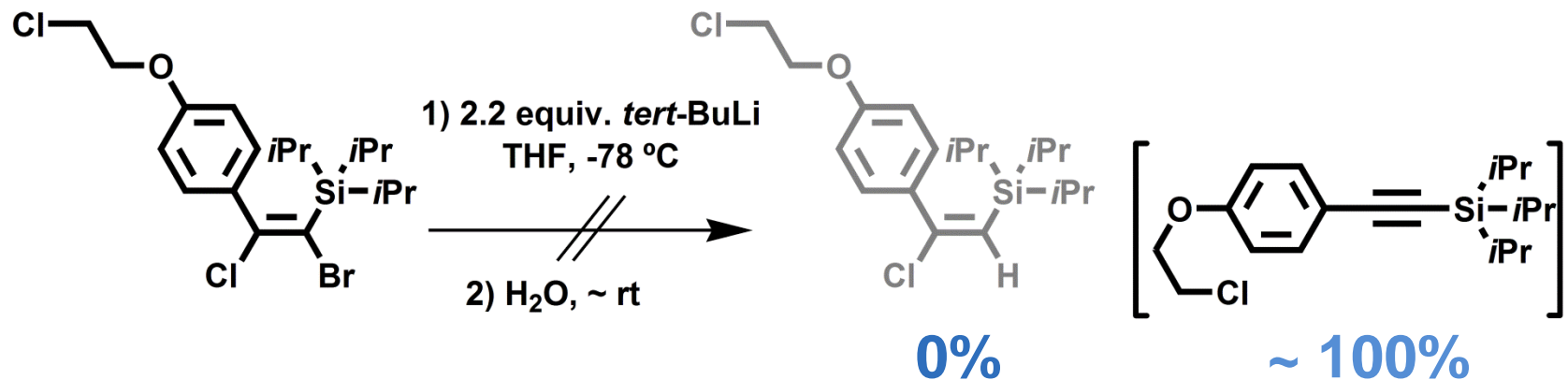
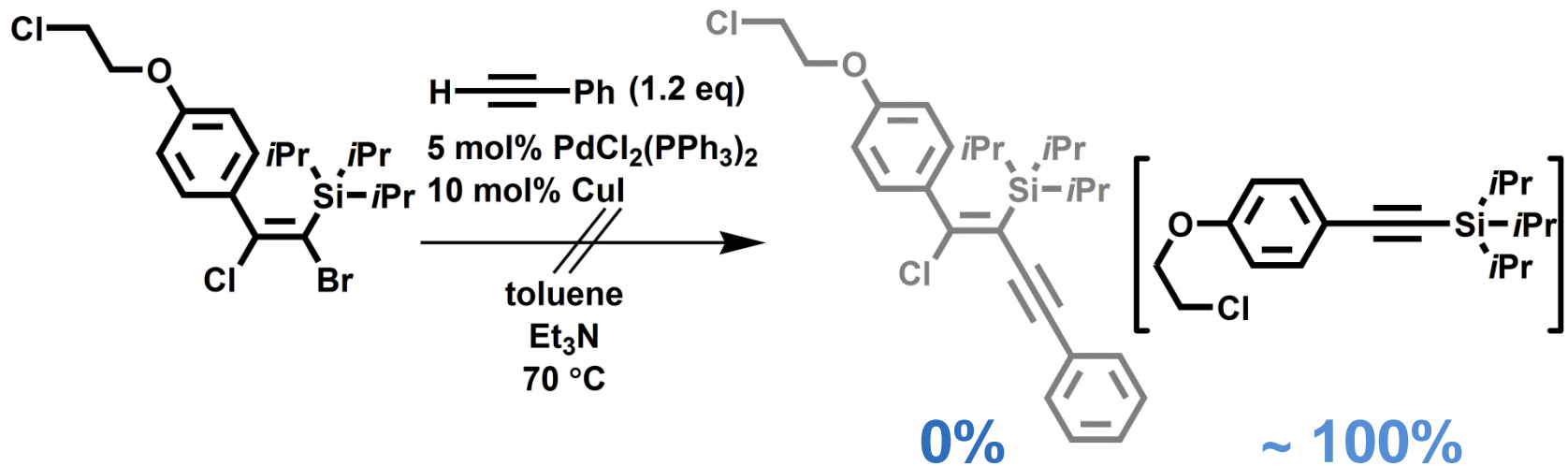
# TMS-Cl vs. TIPS-Cl



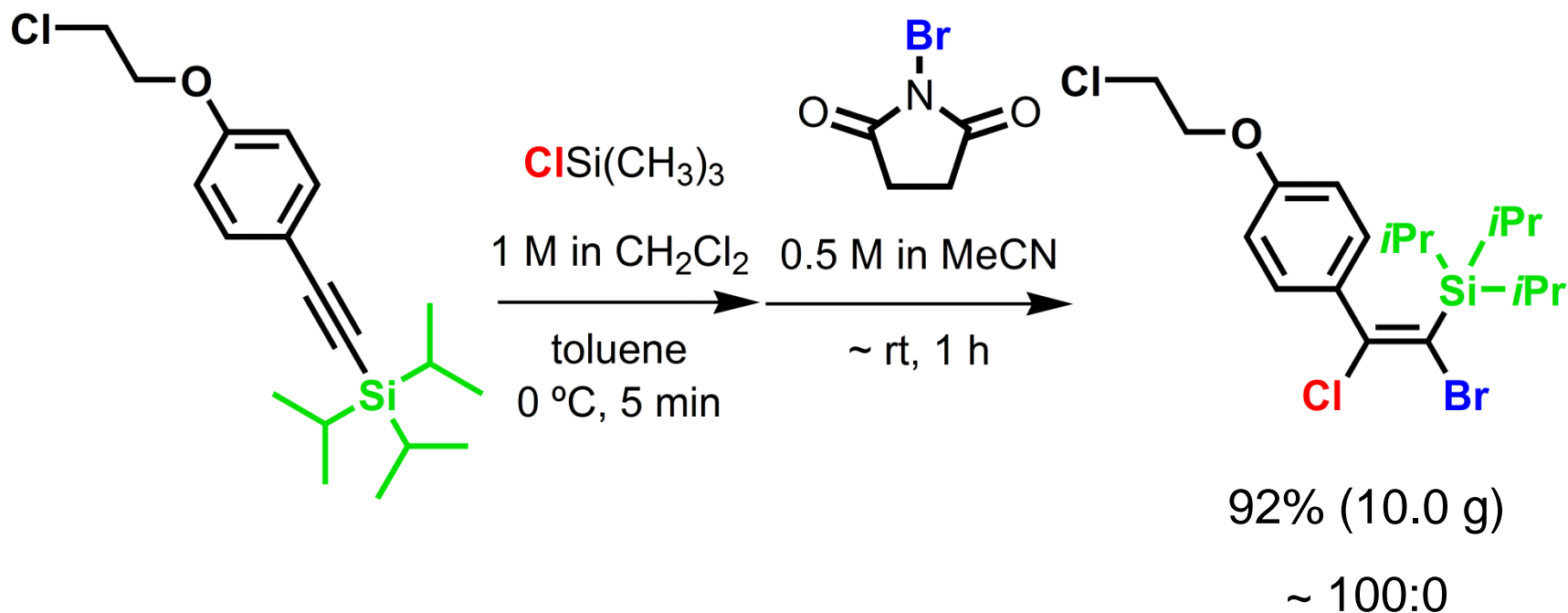
# Plausible mechanism



# Cross-coupling remains our major challenge.



# Summary



- Yauchi, Y.; Ide, M.; Shiogai, R.; Chikugo, T.; Iwasawa, T. *Eur. J. Org. Chem.* **2015**, 938-943.
- 特願 2015-247030 (2015年12月5日 出願)