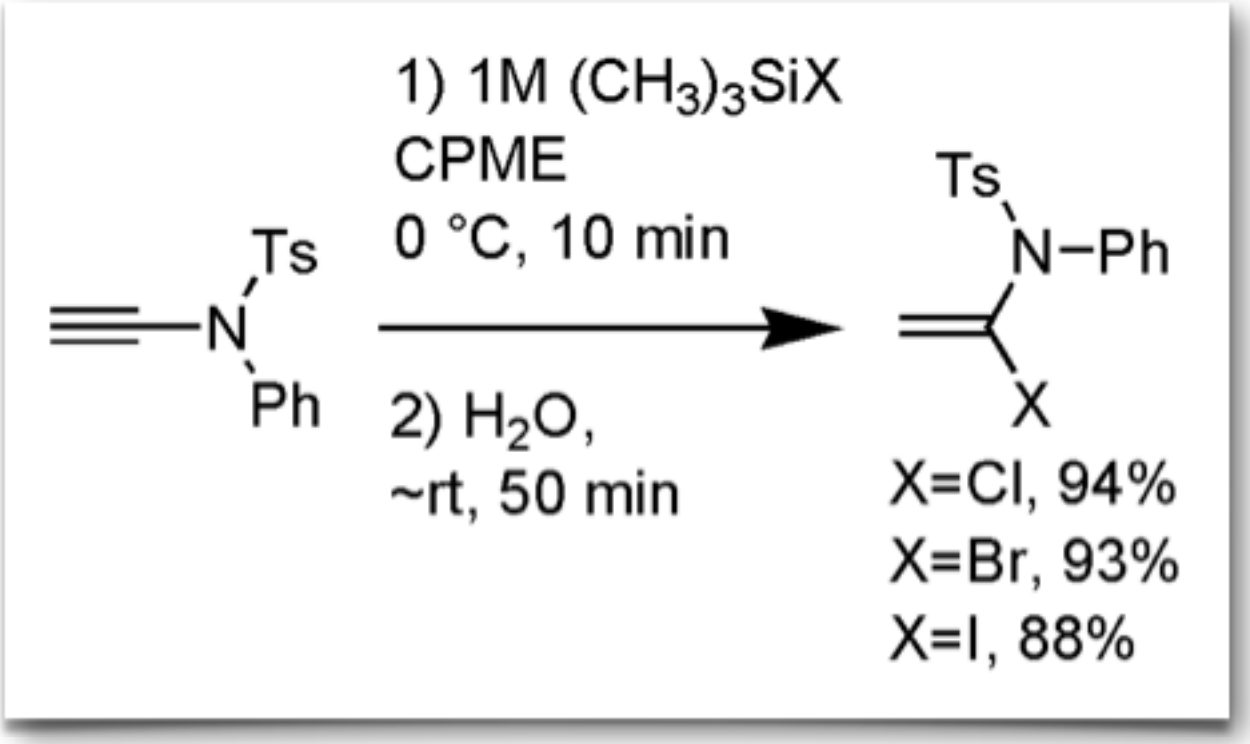
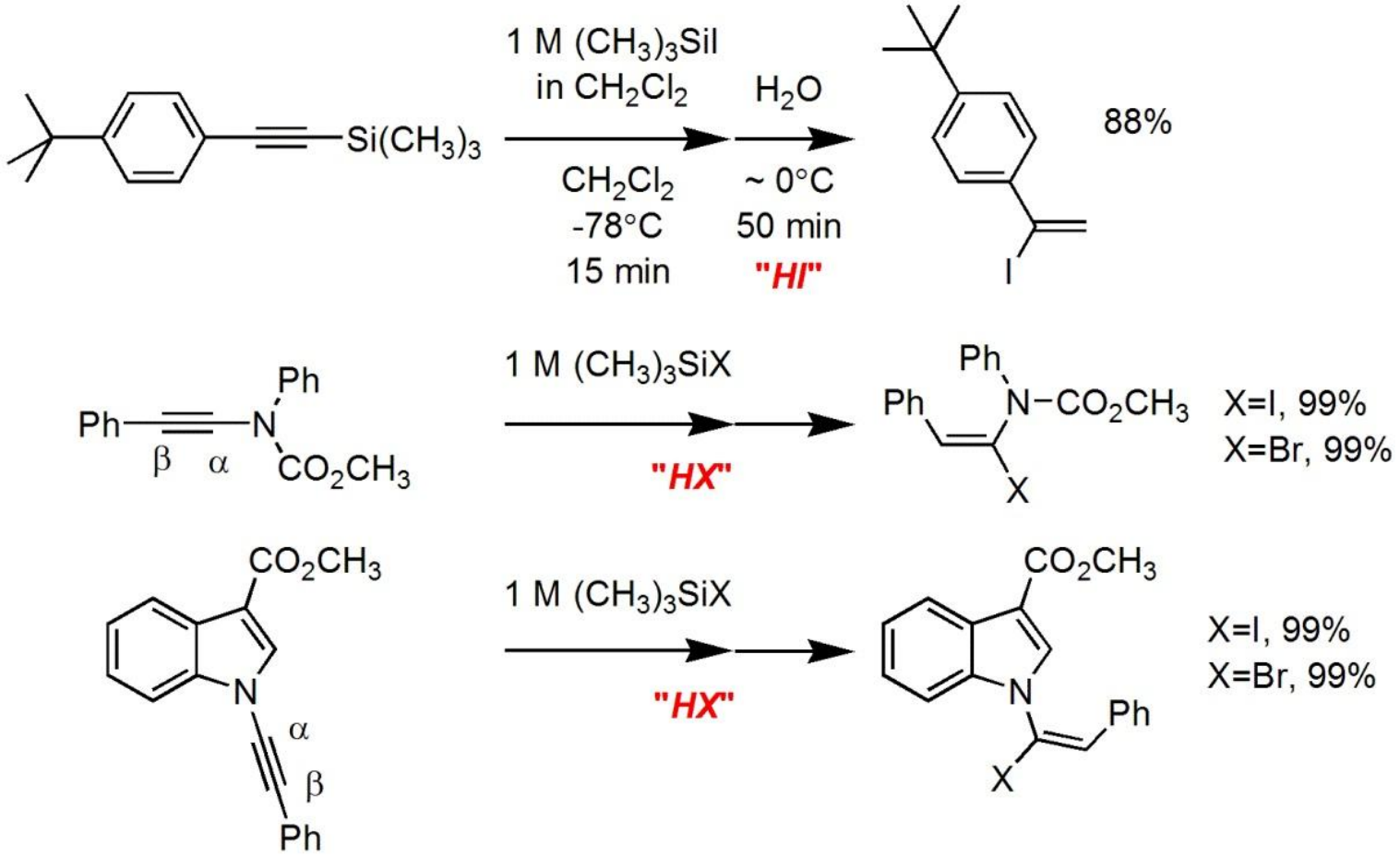
Synthesis of 1-Haloethenamides from Ynamides through TMSX-mediated Hydrohalogenation



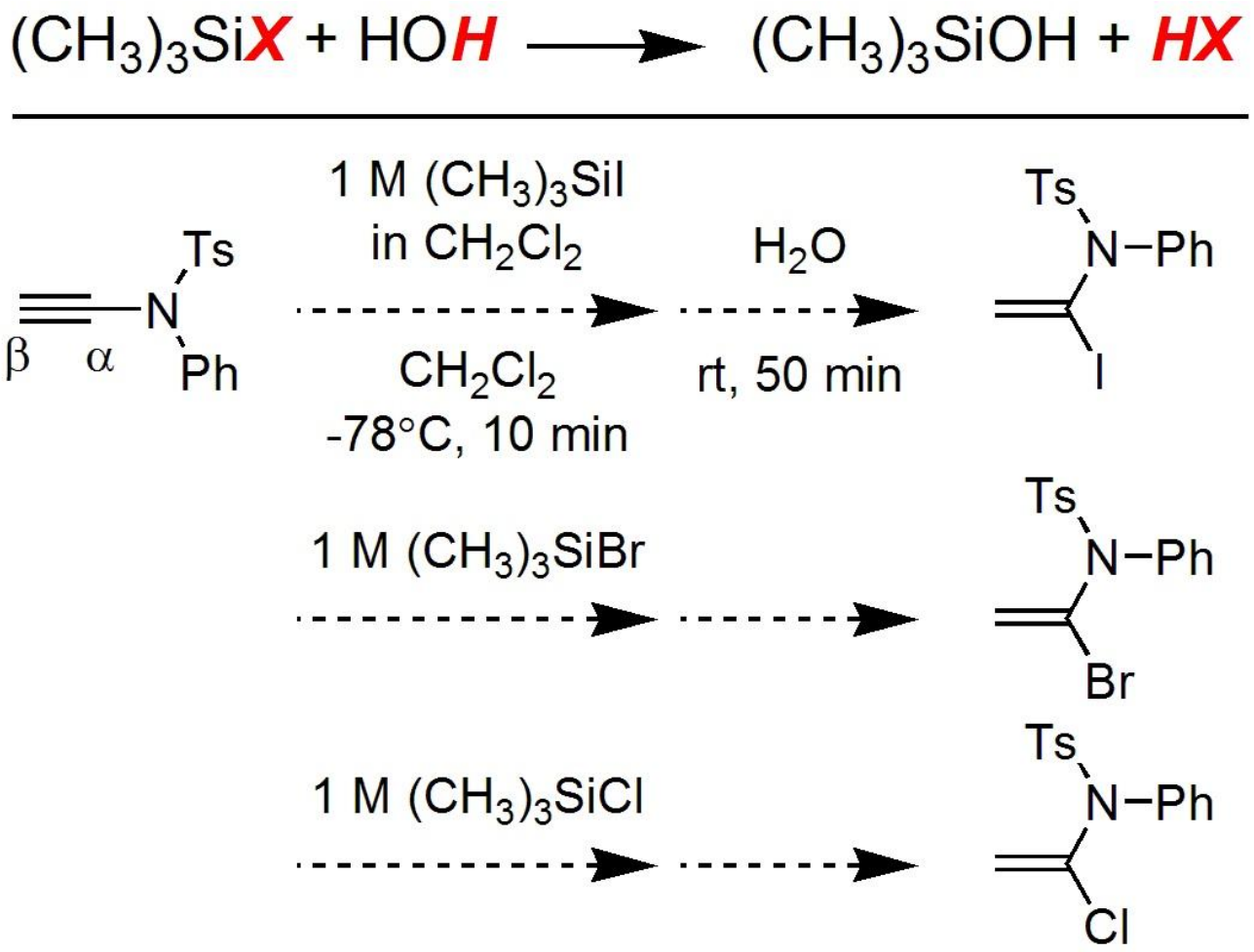
Ohashi, K.; Mihara, S.; Sato, A. H.; Ide, M.; Iwasawa, T. *Tetrahedron Lett.* **2014,** *55,* 632-635**.**

Background



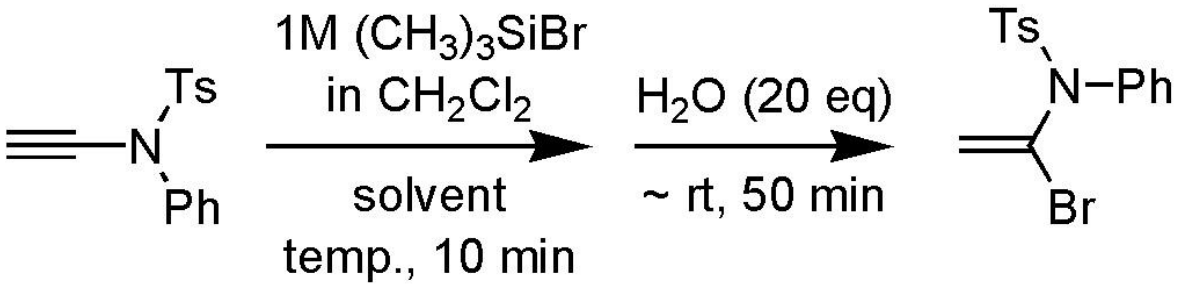
1. Sato, A.H.; Mihara, S.; Iwasawa, T. *Tetrahedron Lett.* **2012**, *53*, 3585-3589.
2. Sato, A.H.; Ohashi, K.; Iwasawa, T. *Tetrahedron Lett.* **2013**, *54*, 1309-1311.
3. Sato, A.H.; Ohashi, K.; Ito, K.; Iwasawa, T. *Tetrahedron Lett.* **2013**, *54*, 2878-2881.

Approach



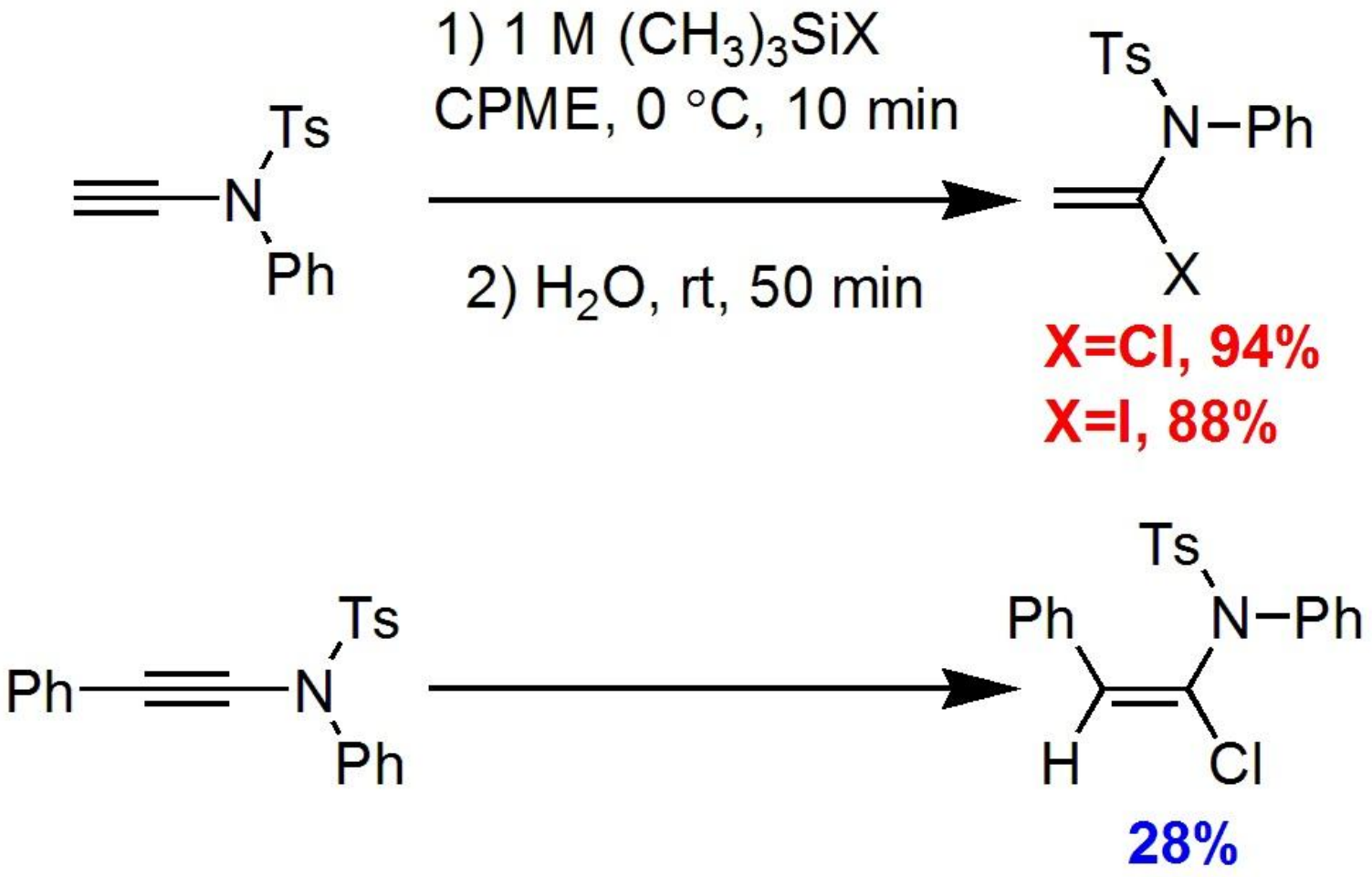
1-Haloethenamide

Hydrobromination

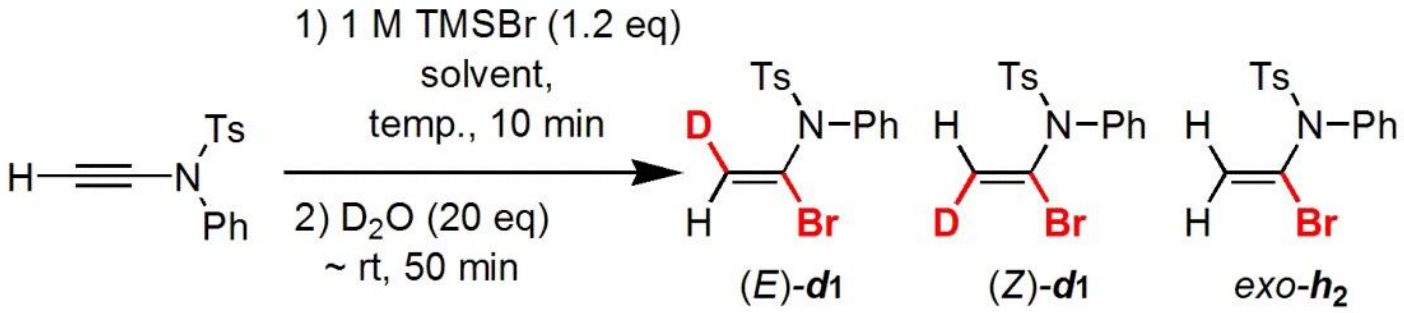


TMSBr (eq)	Solvent	Temp/ ^{o}C	Yield/%
2.0	**CH_2Cl_2**	**-78**	**56**
1.2	CH_2Cl_2	-78	89
1.2	THF	-78	91
1.2	diethyl ether	-78	94
1.2	CPME	-78	95
1.2	**CPME**	**0**	**93**

In situ HI and HCl

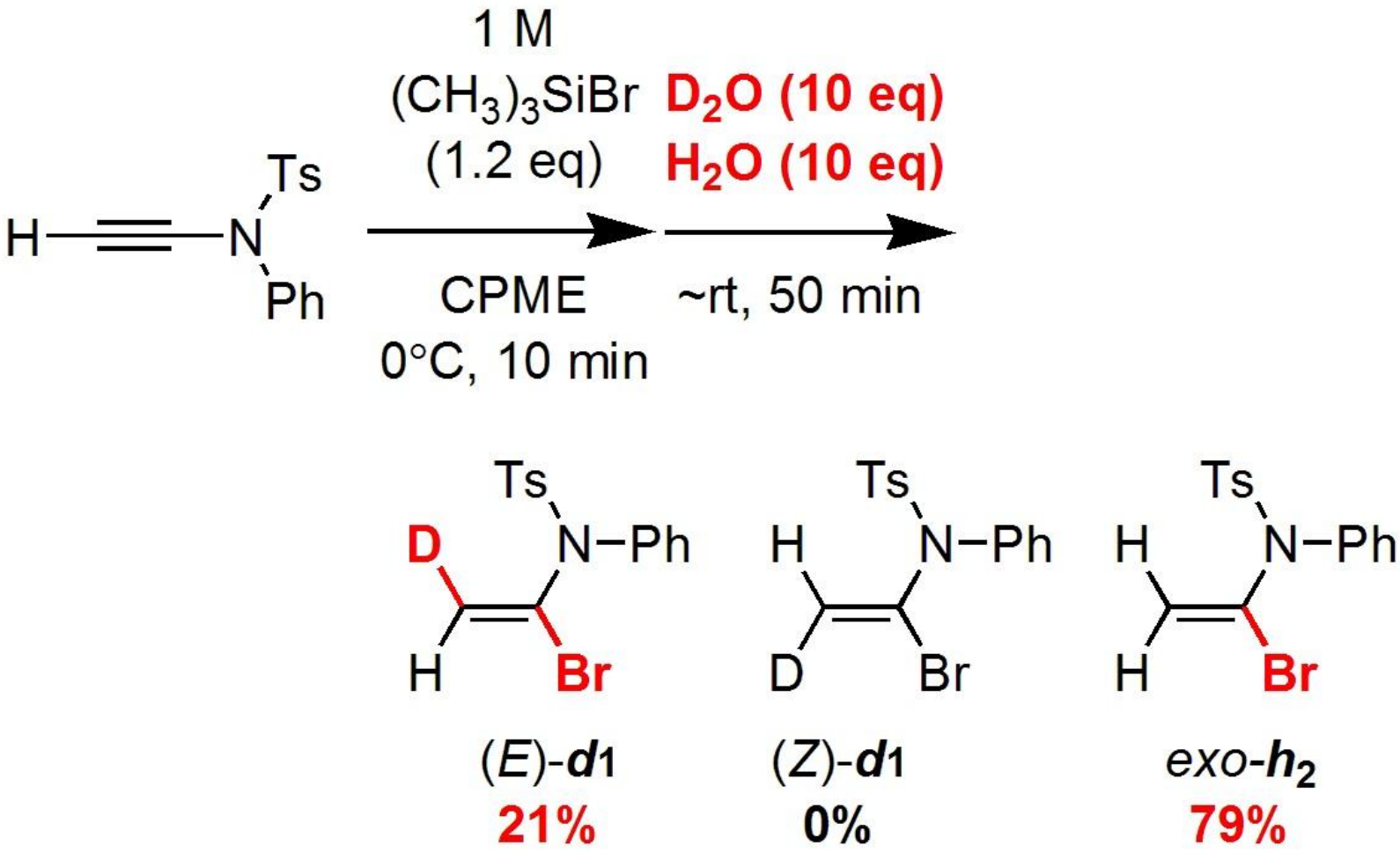


Deuteriobromination

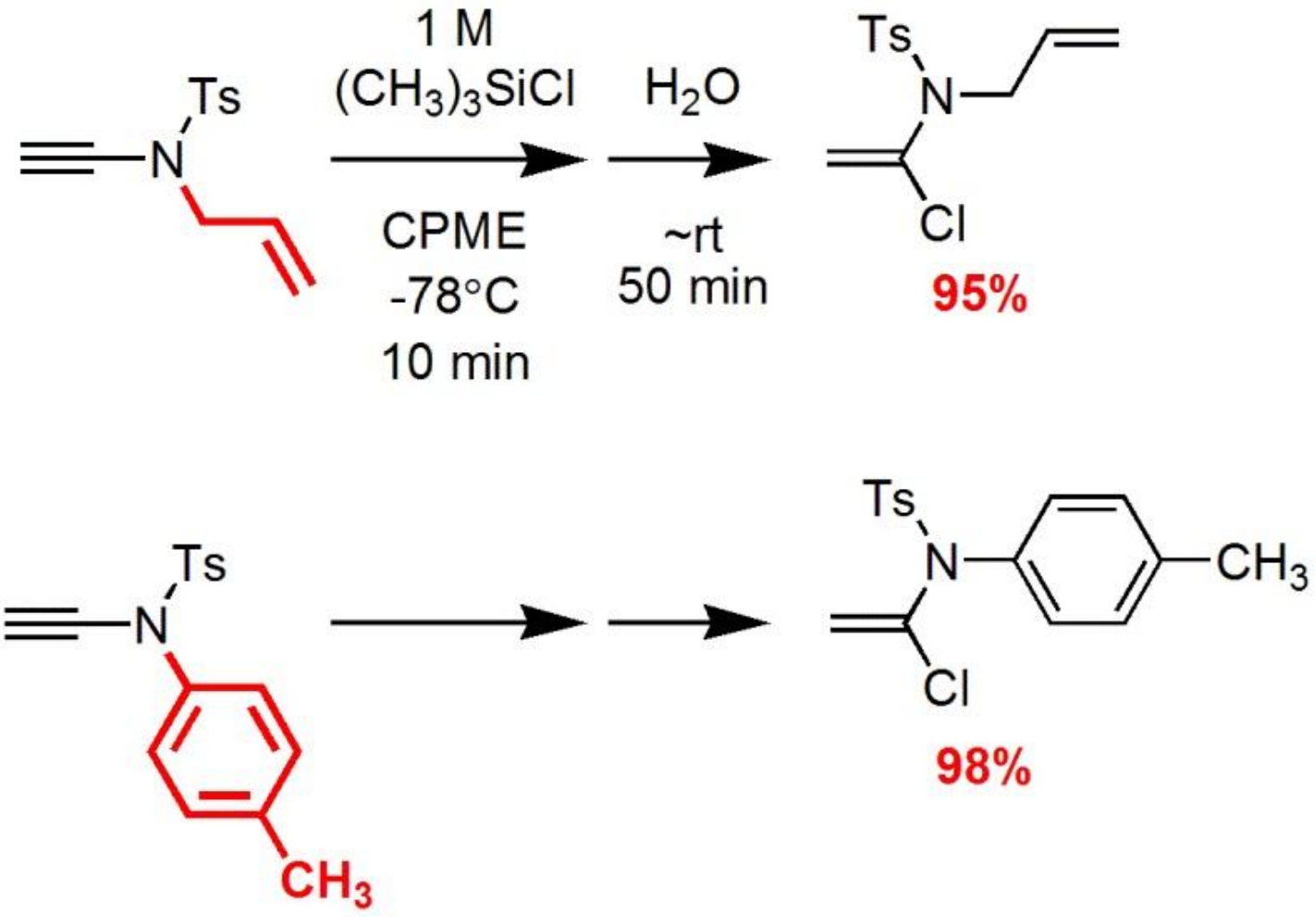


Solvent	Yield/%		
	(*E*)-$\boldsymbol{d}_1$	(*Z*)-$\boldsymbol{d}_1$	*exo*-$\boldsymbol{h}_2$
CPME	**85**	**0**	**9**
Diethyl ether	72	18	14
Acetone	65	14	8
CH_2Cl_2	26	24	14
CH_3CN	64	14	16

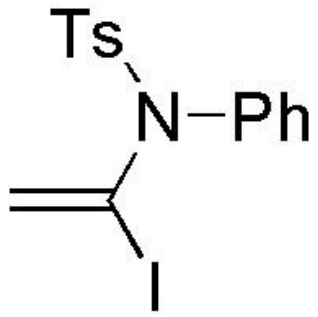
Rate-determining step



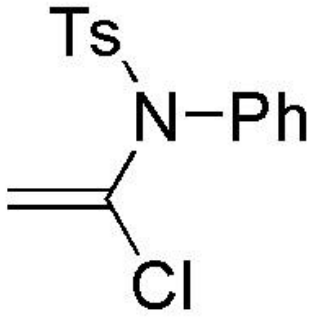
N-allyl and *N*-tolyl



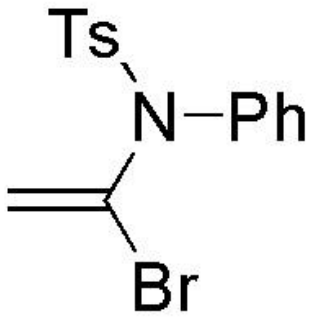
They are quite labile…



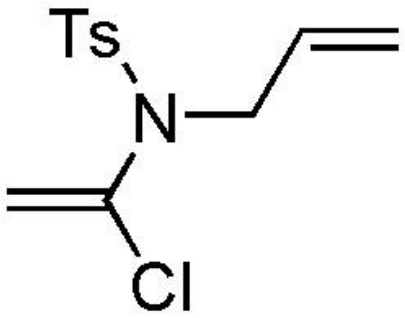
Decomposed in 2 d



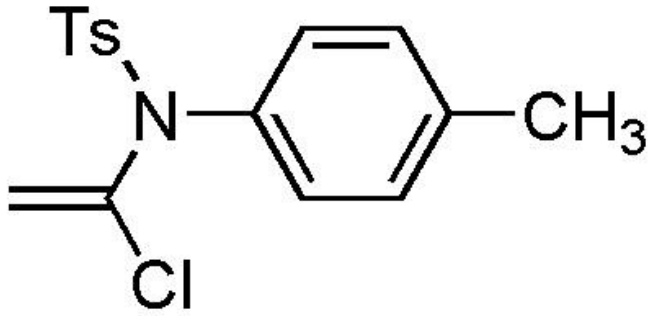
70% Remained in 1 week



Decomposed in 10 d

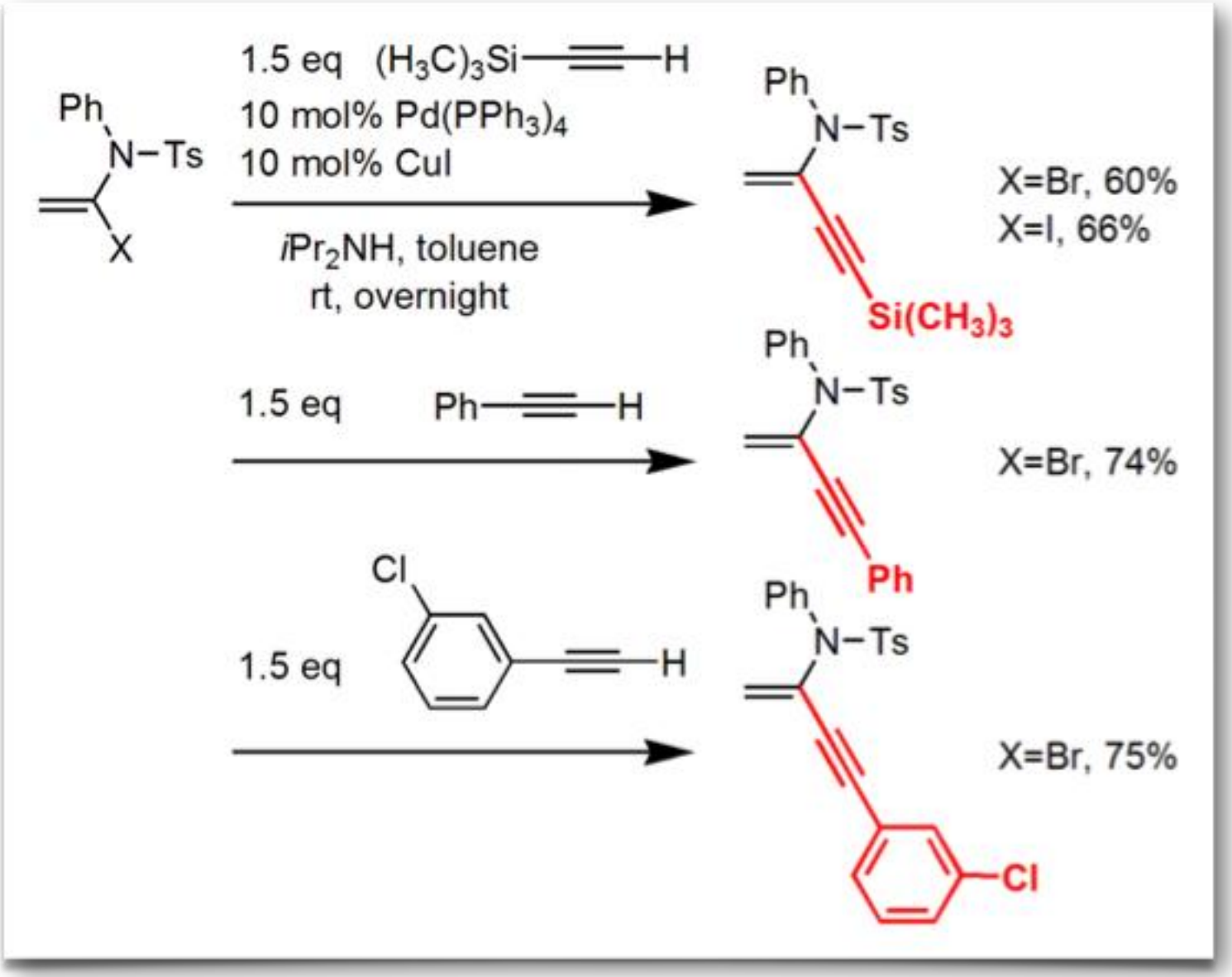


No appreciable decomposition in 1 week

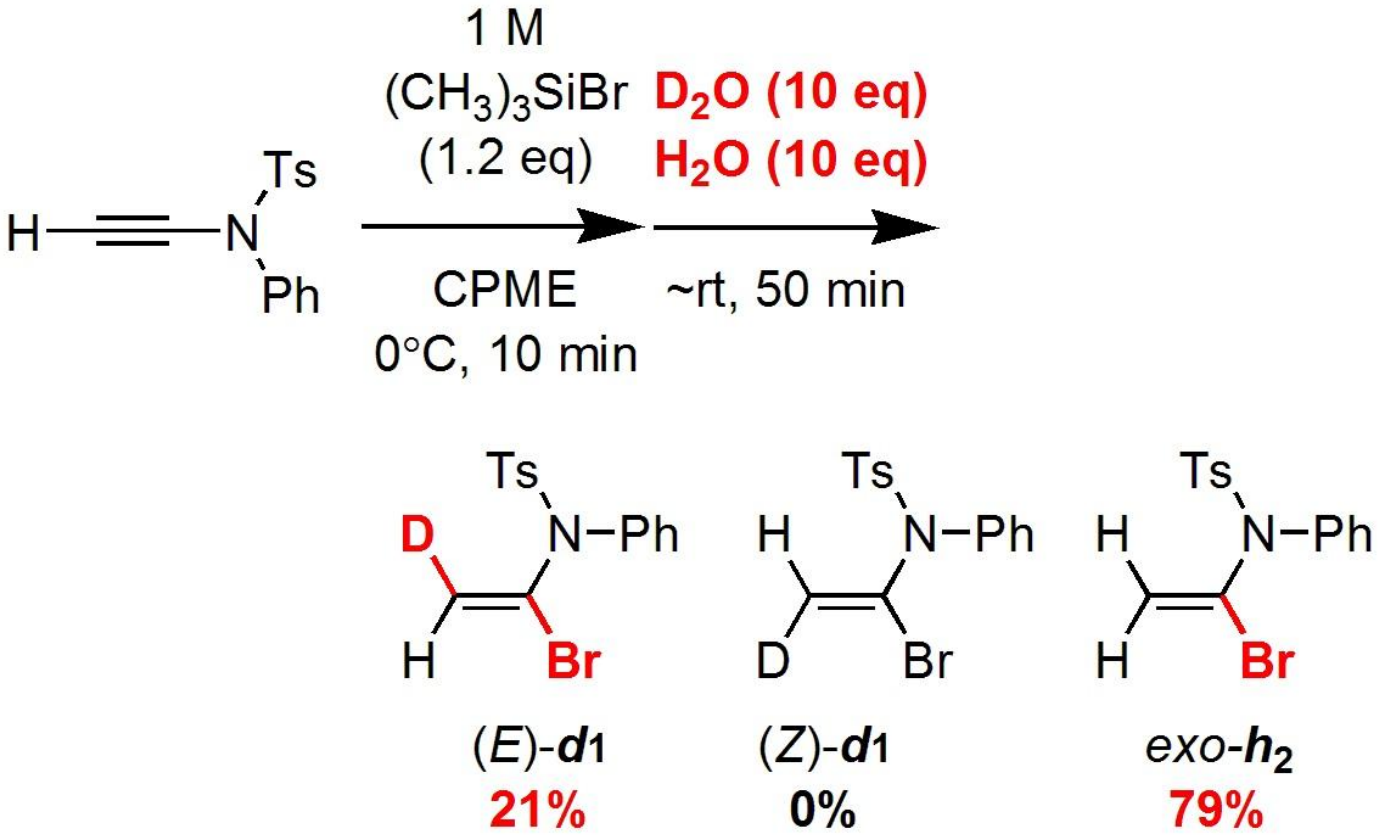


Decomposed in 4 h

Synthetic application



Summary



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