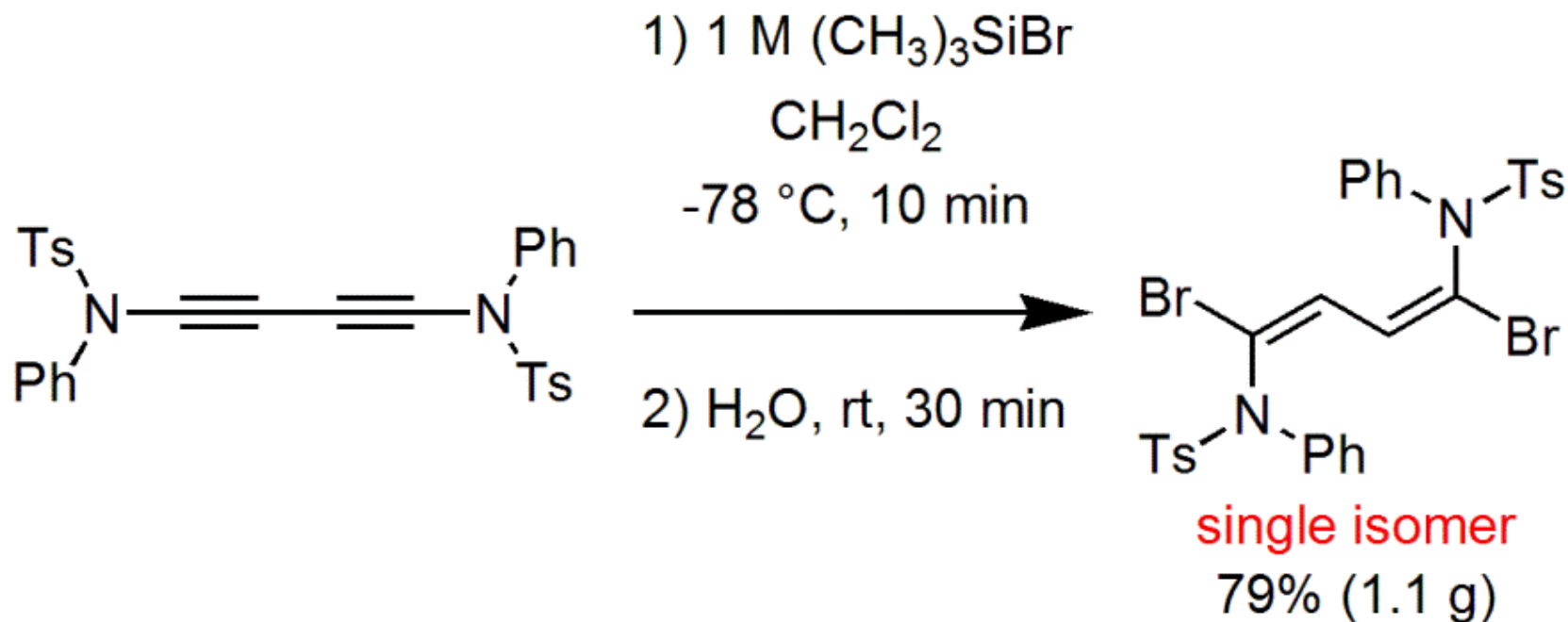
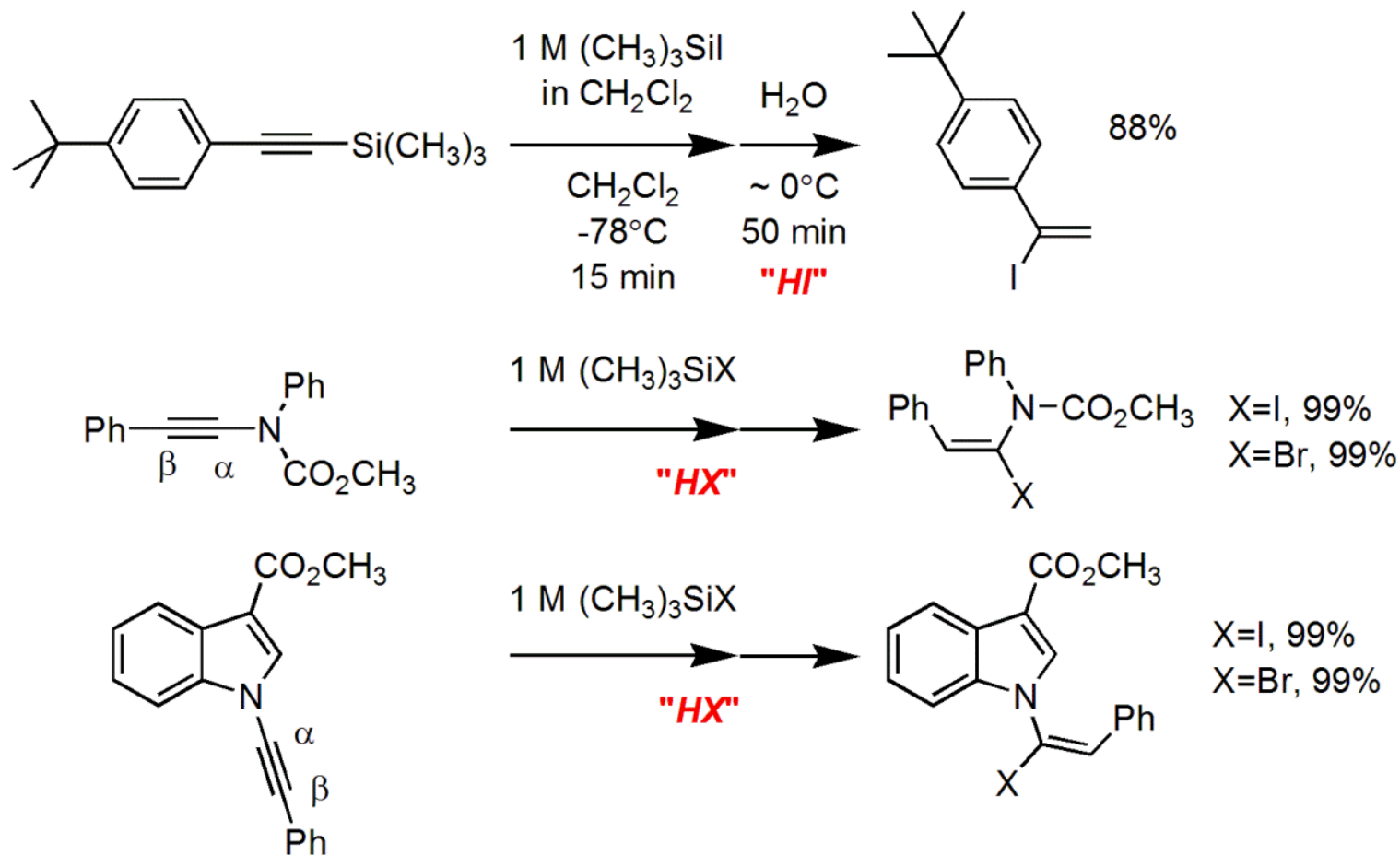


Regio- and Stereoselective Hydrohalogenation of Ynamide Components in 1,3-Butadiynes with *in situ* Generated HX



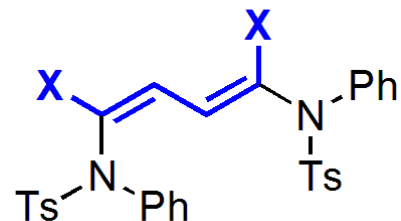
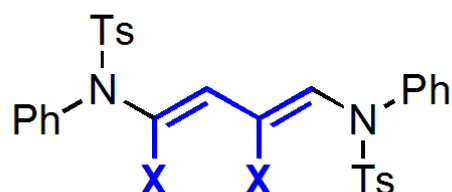
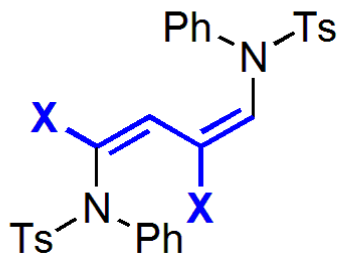
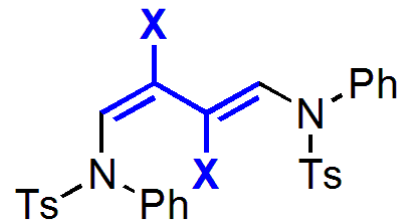
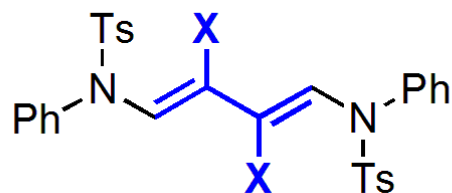
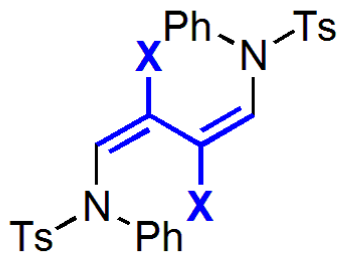
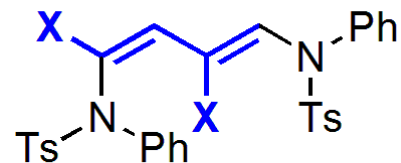
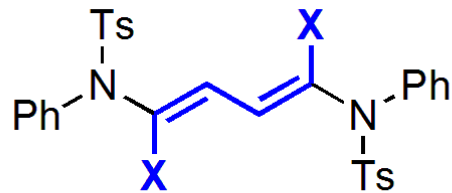
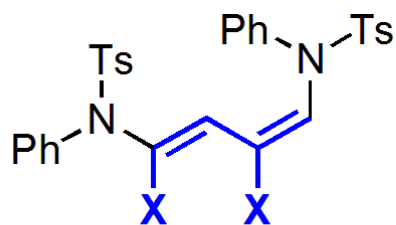
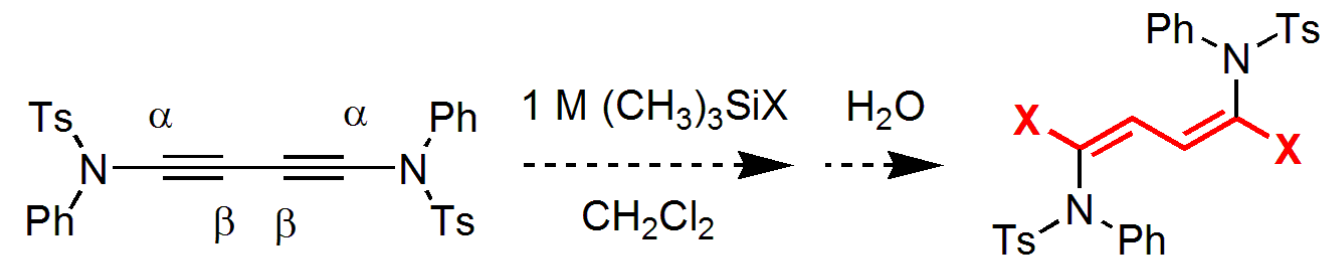
- Ohashi, K.; Ide, M.; Mihara, S.; Iwasawa, T. *Tetrahedron Lett.* **2014**, 55, 2130-2133.
- 特願 2012-278613

Background

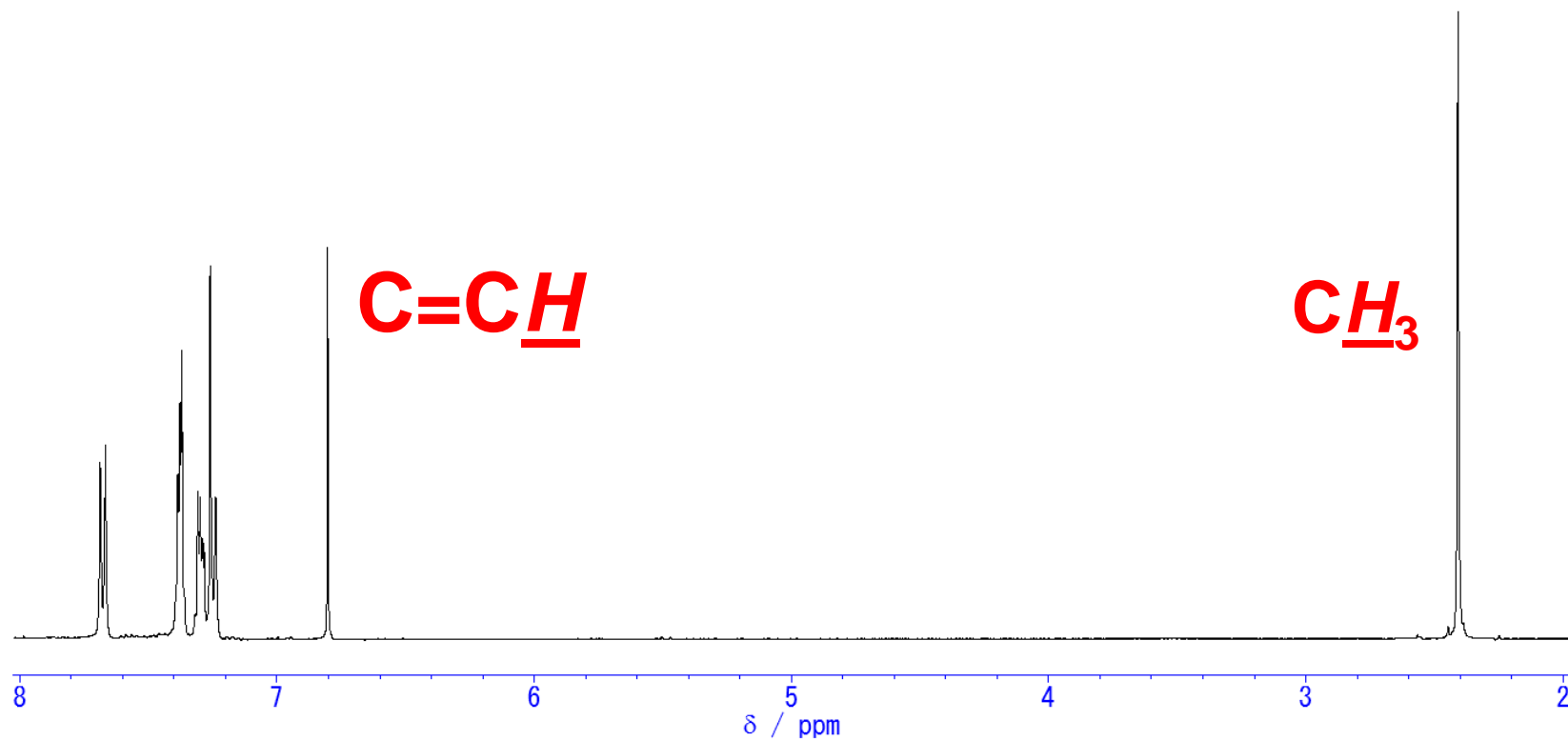
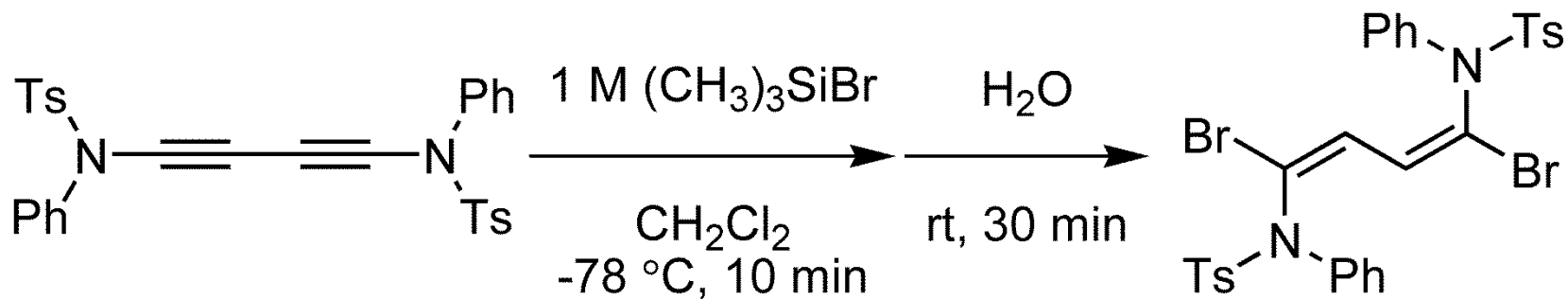


1. Sato, A. H.; Mihara, S.; Iwasawa, T. *Tetrahedron Lett.* **2012** 53, 3585-3589.
2. Sato, A. H.; Ohashi, K.; Iwasawa, T. *Tetrahedron Lett.* **2013** 54, 1309-1311.
3. Sato, A. H.; Ohashi, K.; Iwasawa, T. *Tetrahedron Lett.* **2013** 54, 2878-2881.

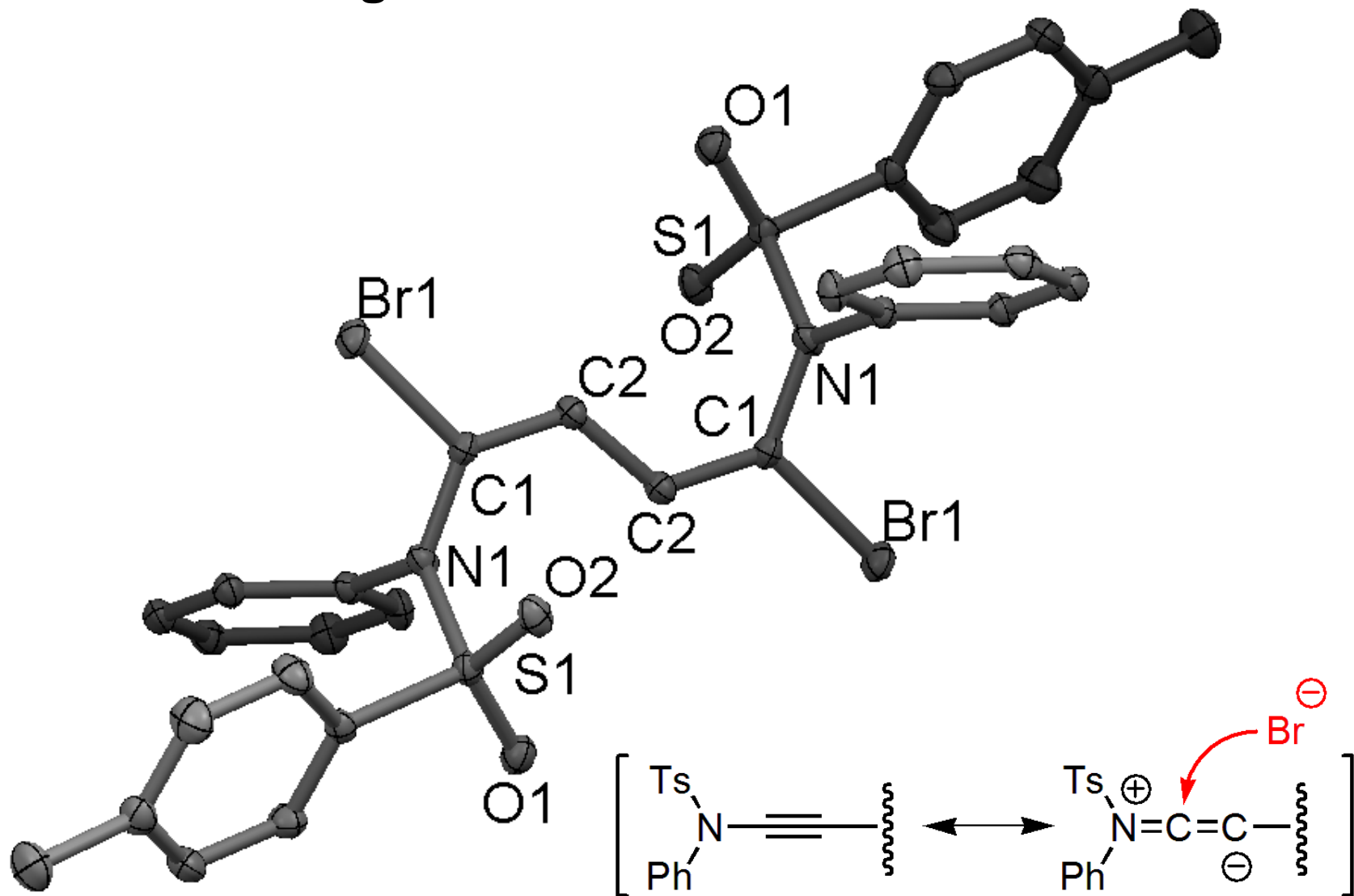
Approach



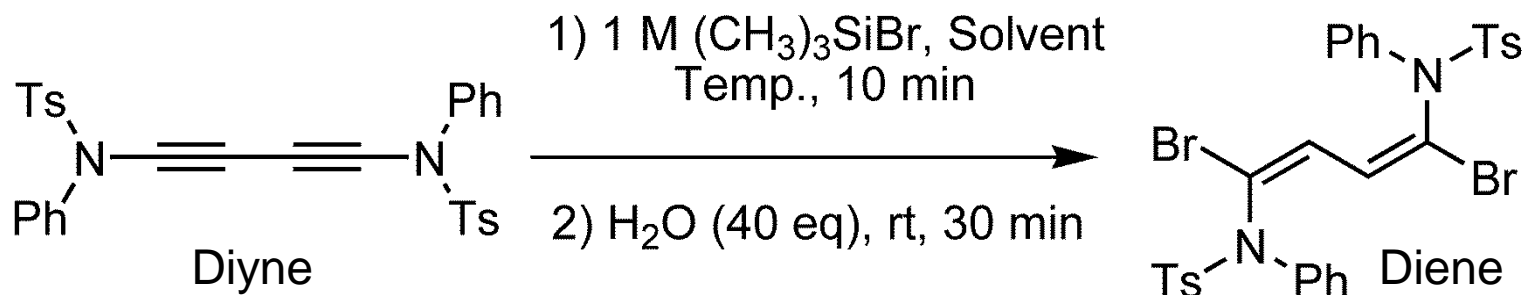
Single product



ORTEP drawing

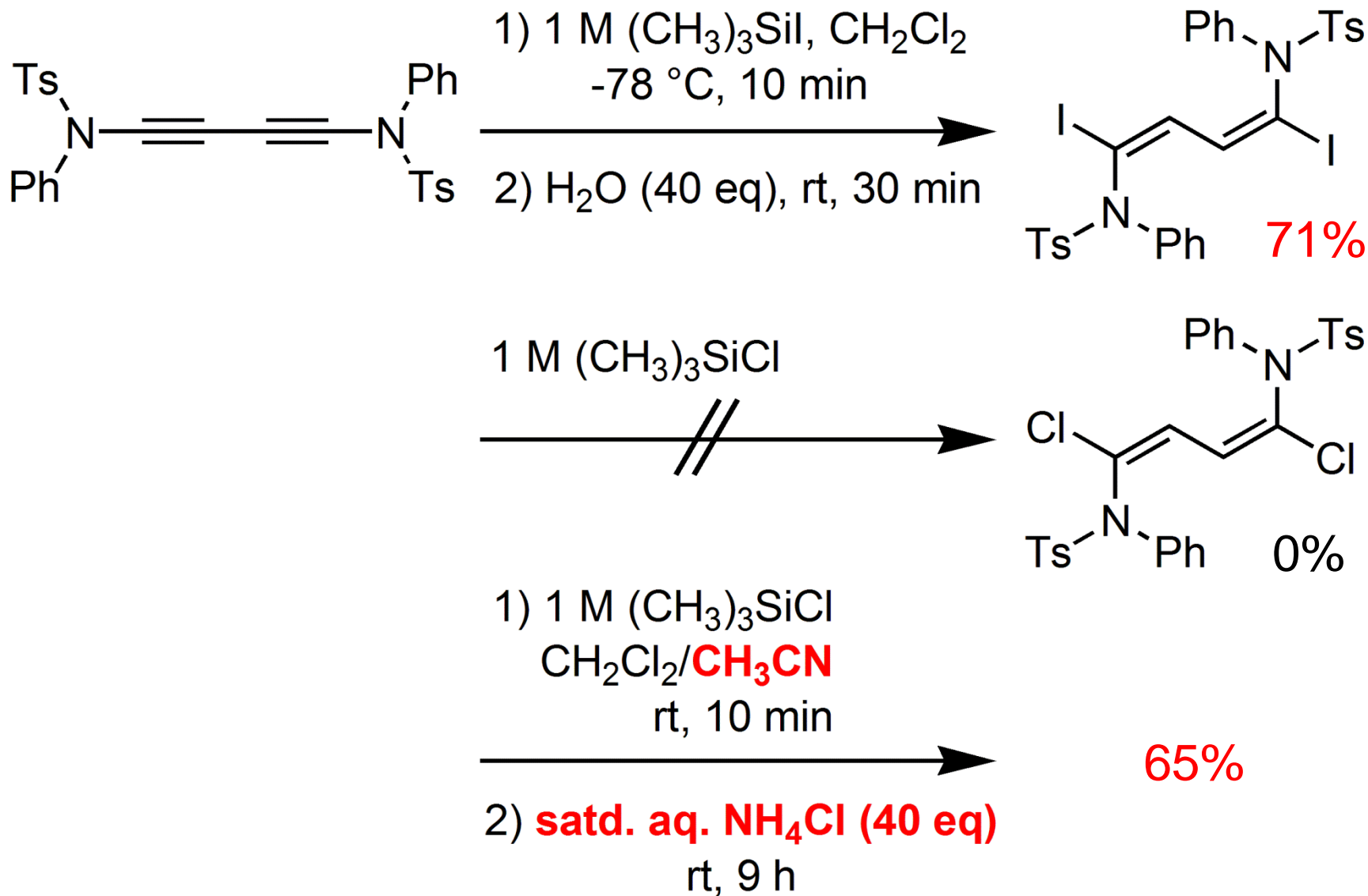


Screening of conditions

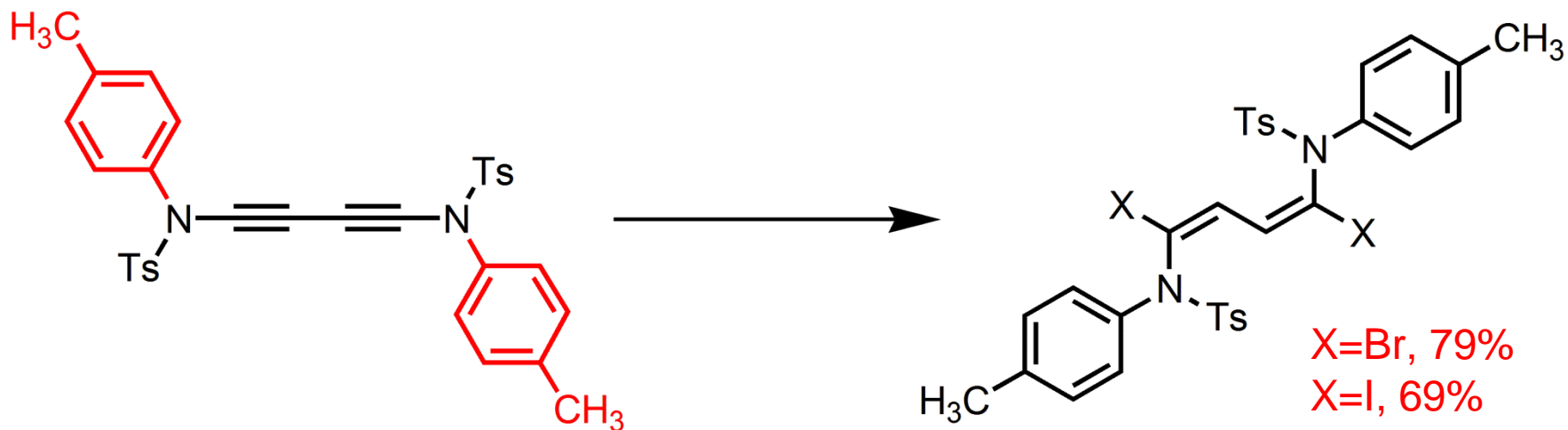
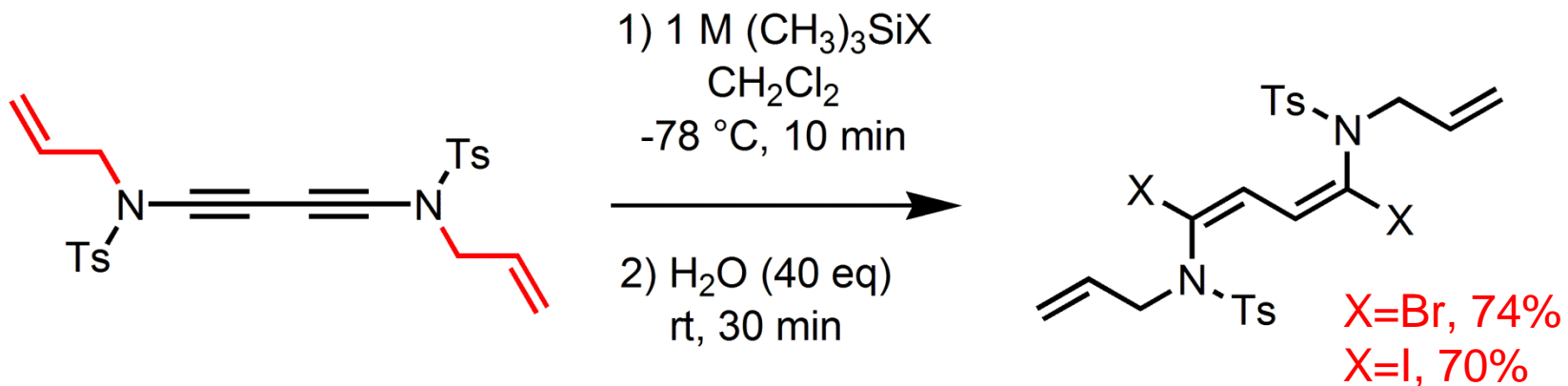


TMSBr (eq)	Solvent	Temp/ $^{\circ}\text{C}$	Yield/%	
			Diene	Diene
3.2	CH_2Cl_2	-78	0	79
3.2	CH_2Cl_2	0	2	68
1.2	CH_2Cl_2	0	28	44
2.4	CH_2Cl_2	0	12	60
4.0	CH_2Cl_2	0	2	64
3.2	Acetone	rt	4	60
3.2	Toluene	rt	28	52
3.2	THF	rt	72	24

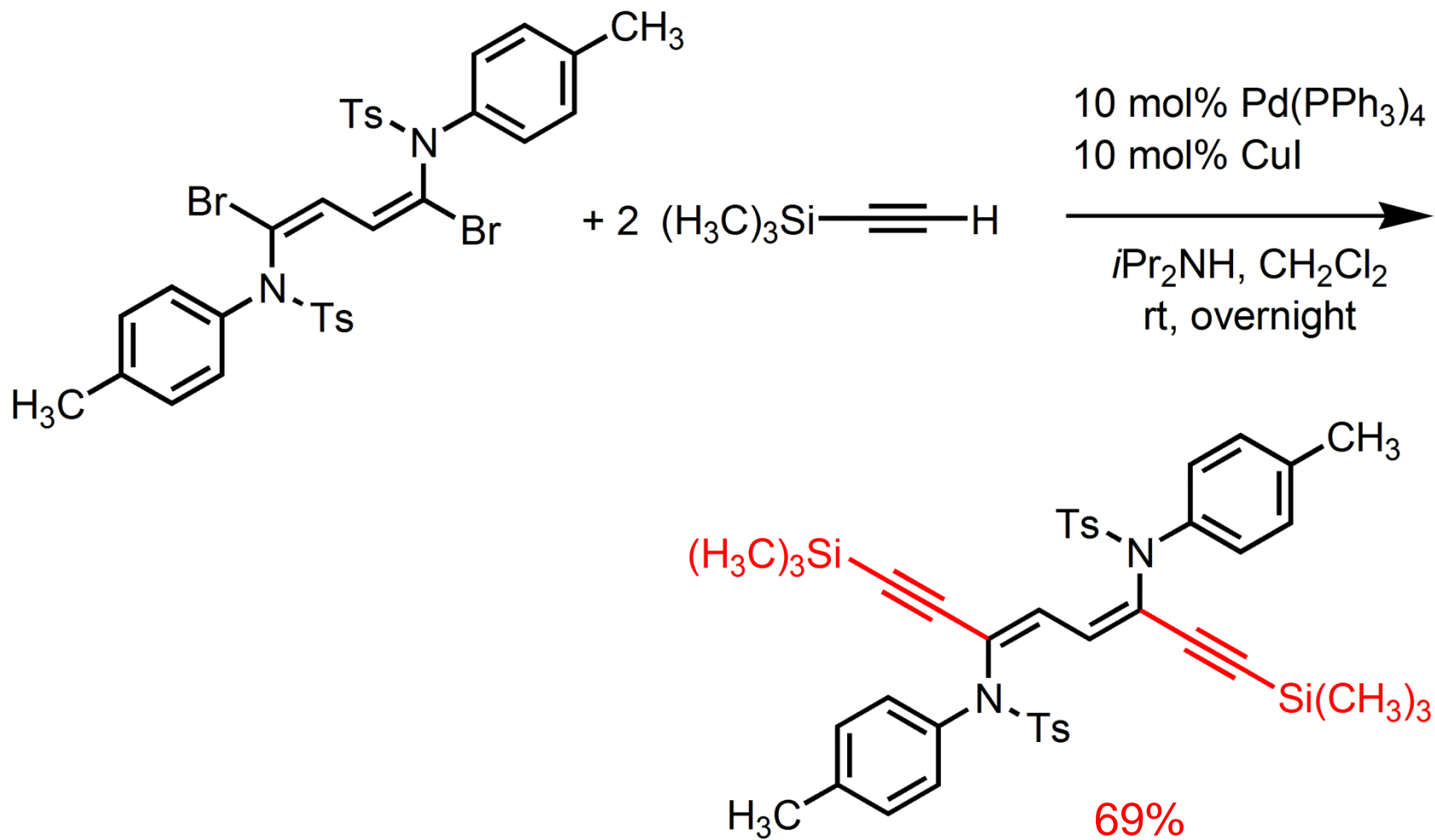
In situ HI & HCl



N-allyl and *N*-tolyl

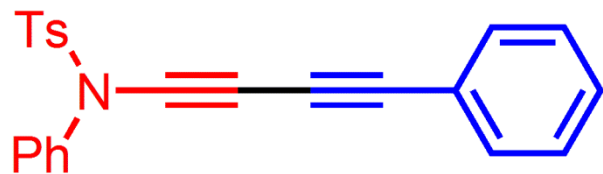


Synthetic application

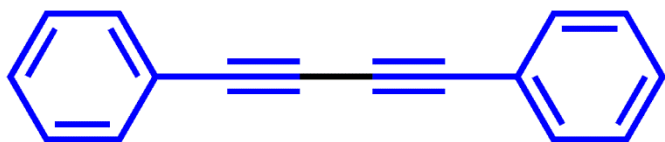
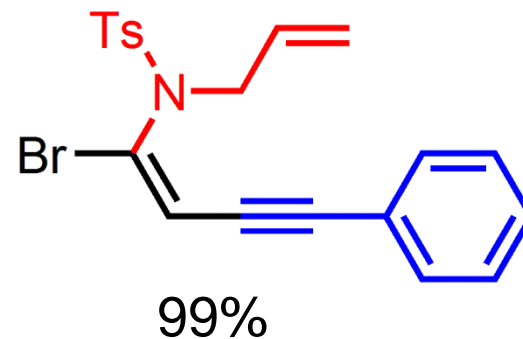
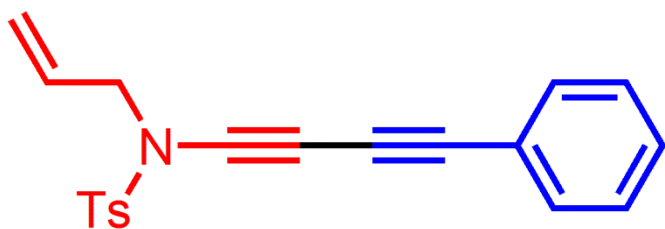
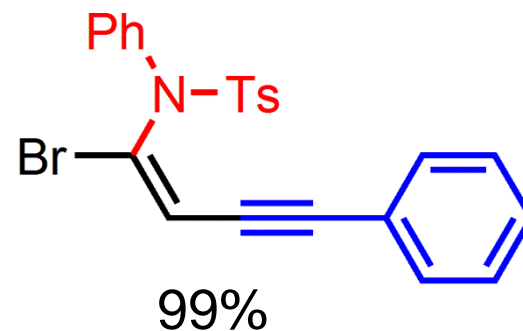


Unsymmetrical diyne

1) 1 M $(\text{CH}_3)_3\text{SiBr}$
 CH_2Cl_2 ,
 -78°C , 10 min

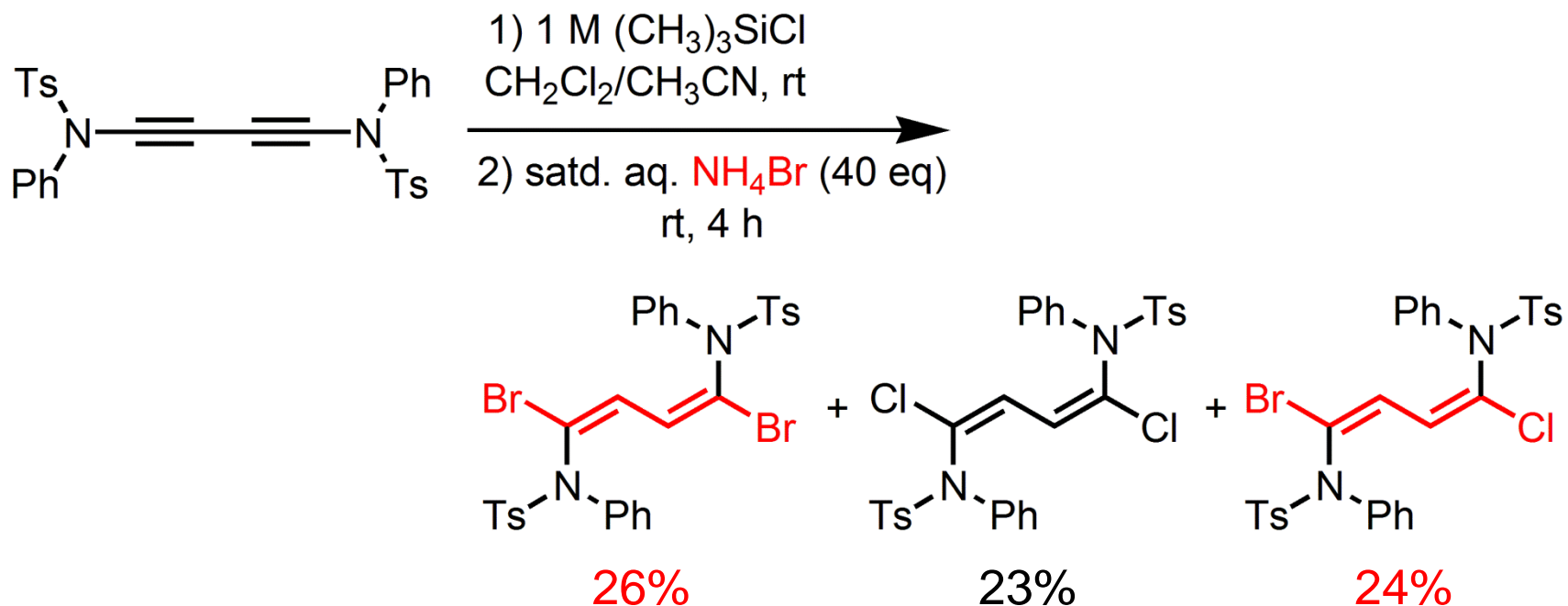
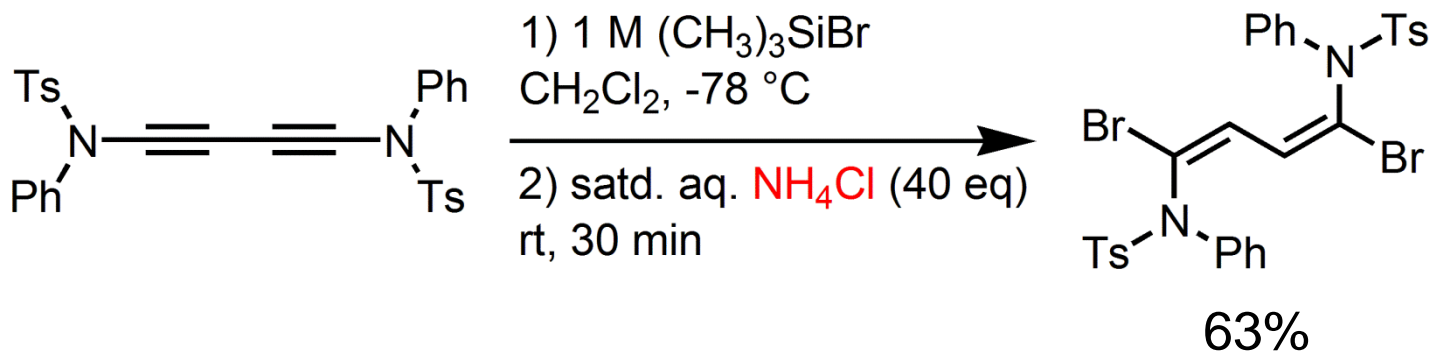


2) H_2O
rt, 30 min

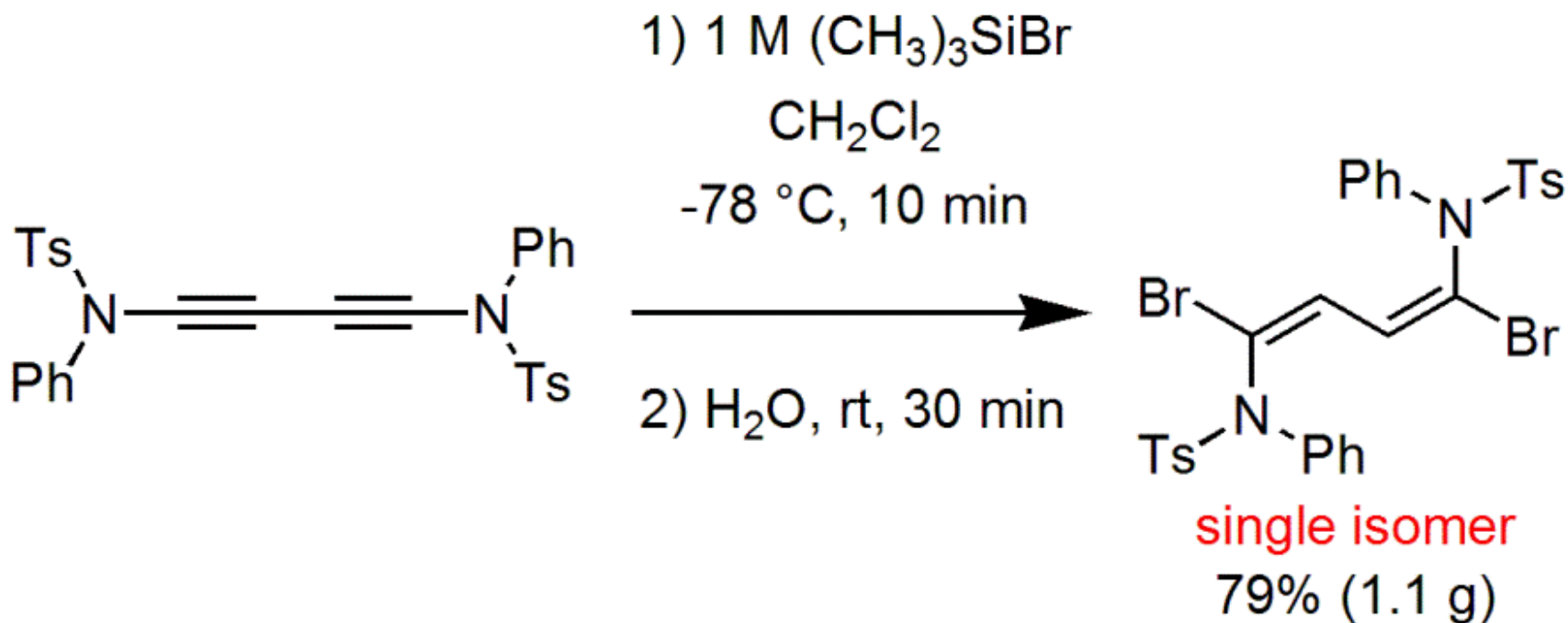


No Reaction

Ionic mechanism?



Summary



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