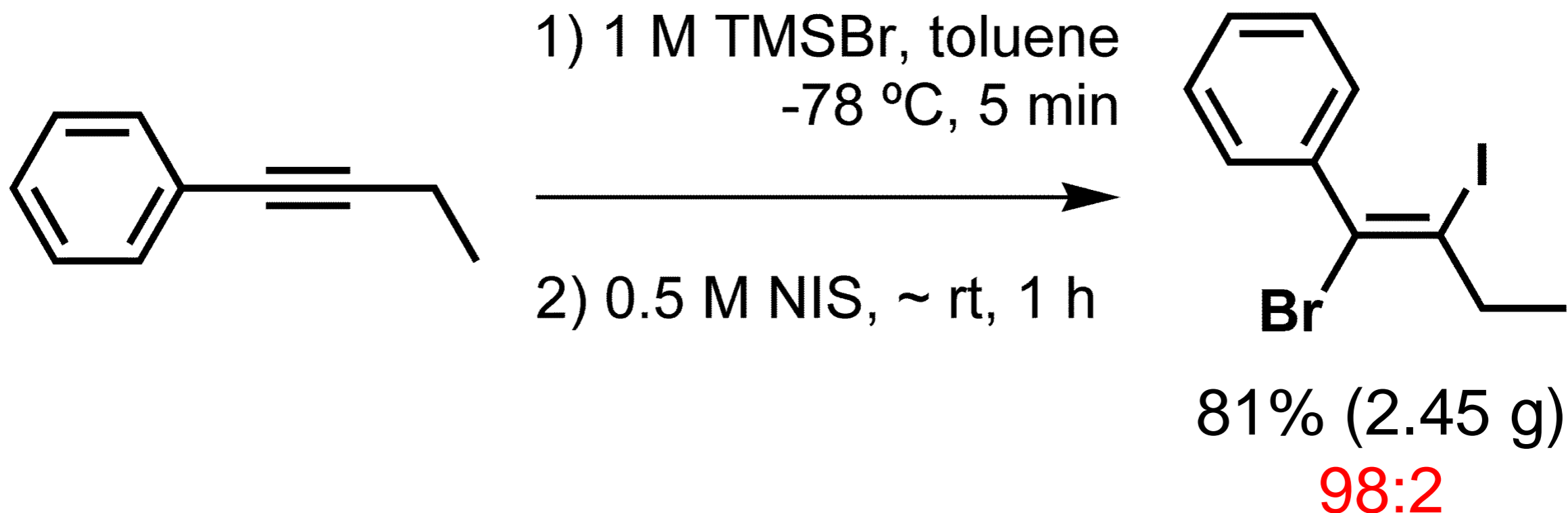


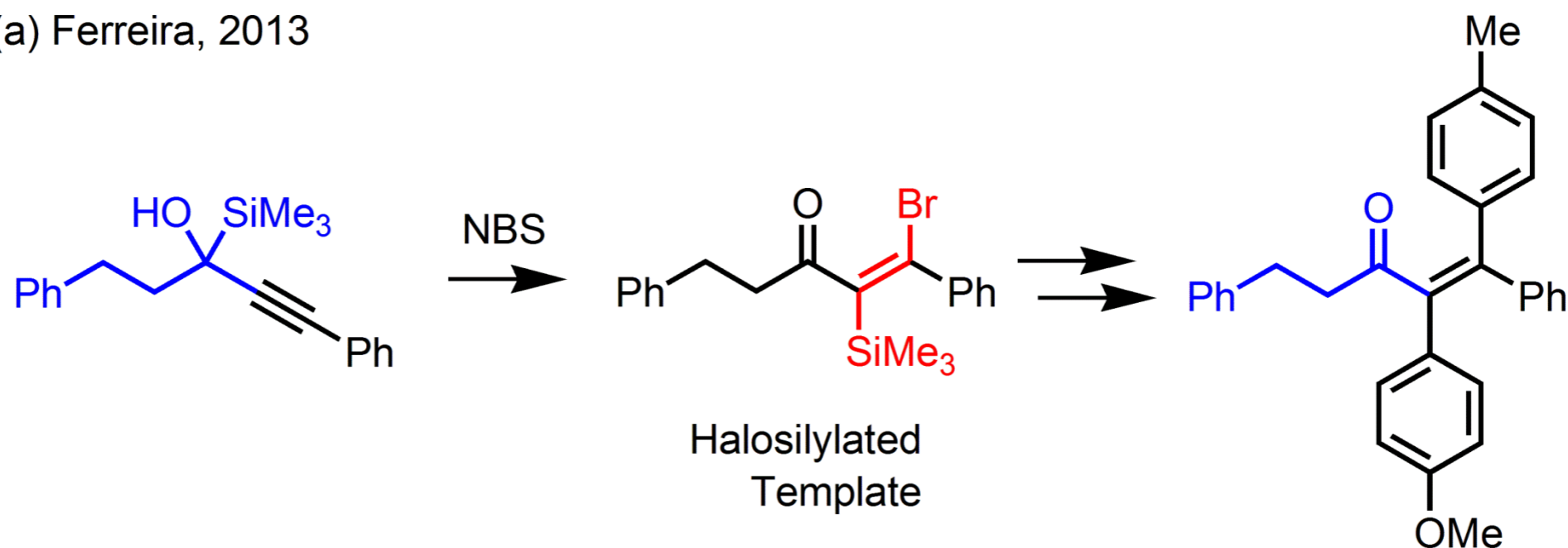
# Regio- and Stereoselective Iodobromination of Internal Alkynes for Tetrasubstituted Olefins



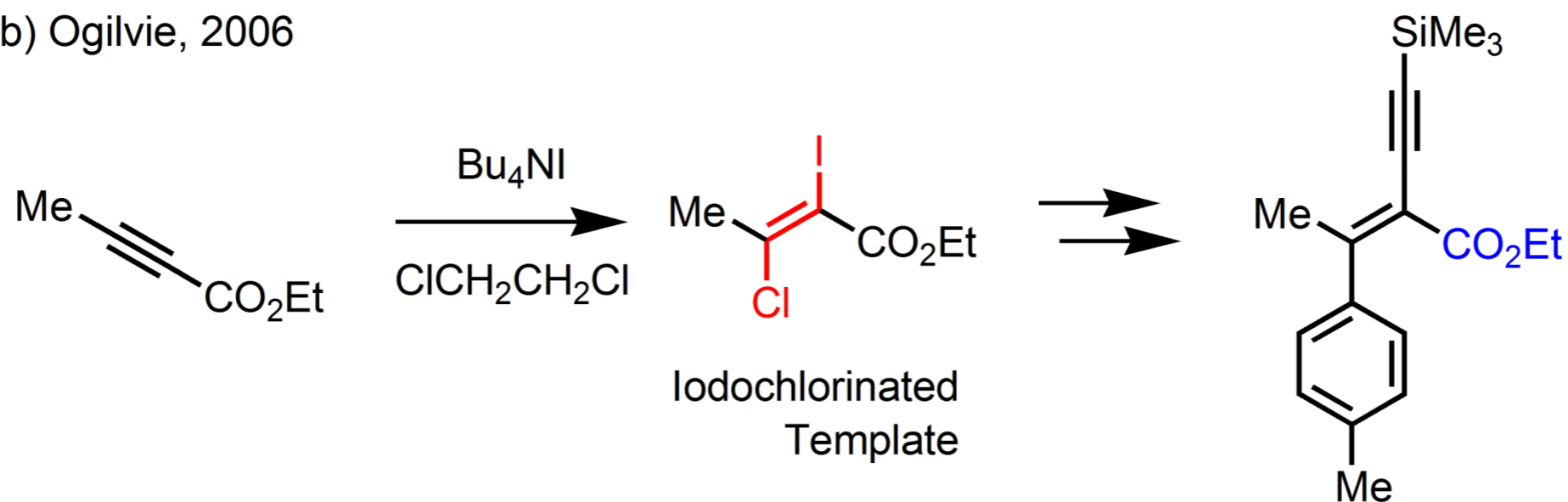
- Ide, M.; Yauchi, Y.; Shiogai, R.; Iwasawa, T. *Tetrahedron* **2014**, *70*, 8532-8538.
- 特願 2014-153644

# Background

(a) Ferreira, 2013



(b) Ogilvie, 2006

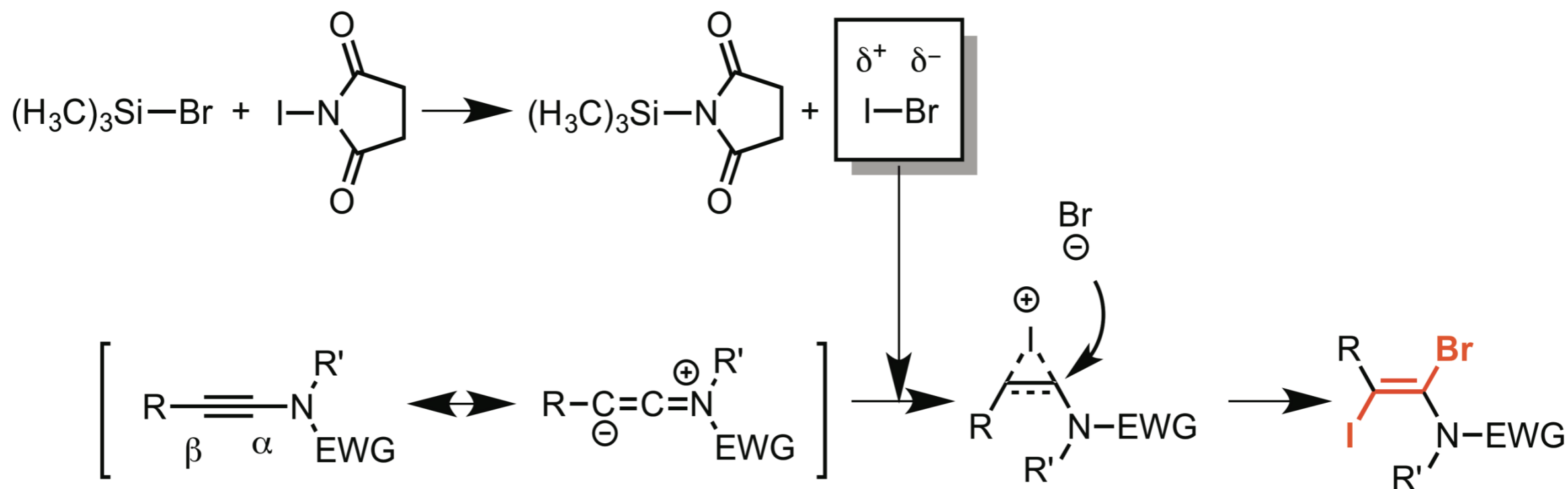
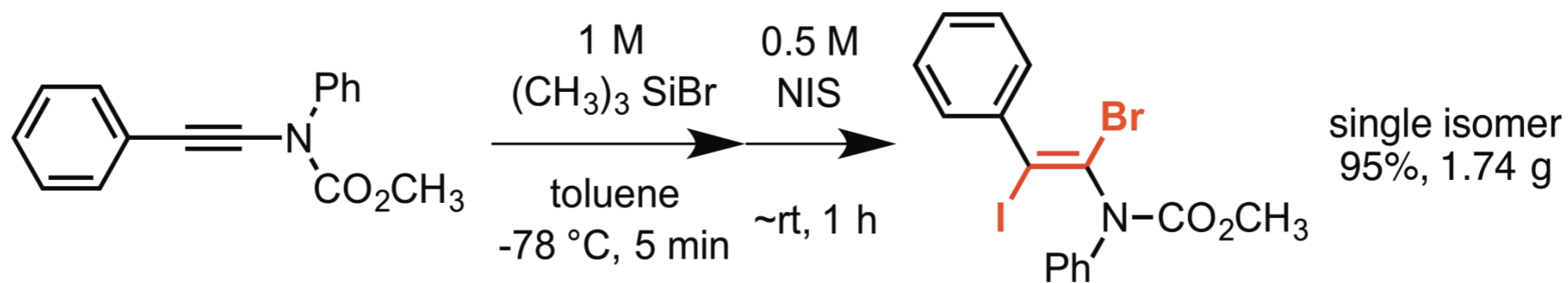


A. N. T. Barczak, D. A. Rooke, Z. A. Menard, E. M. Ferreira, *Angew. Chem., Int. Ed.* **2013**, *52*, 7579-7582.

B. a) A. B. Lemay, K. S. Vulic, W. W. Ogilvie, *J. Org. Chem.* **2006**, *71*, 3615;

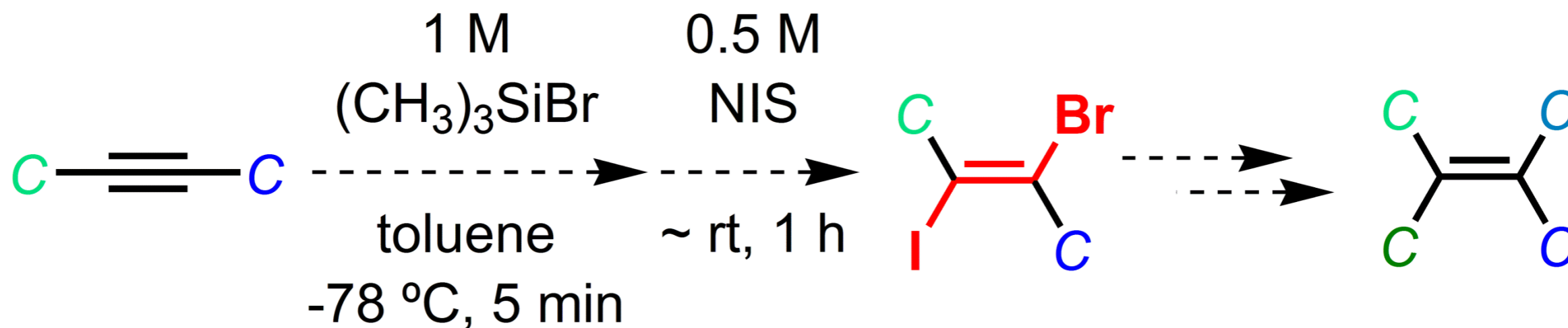
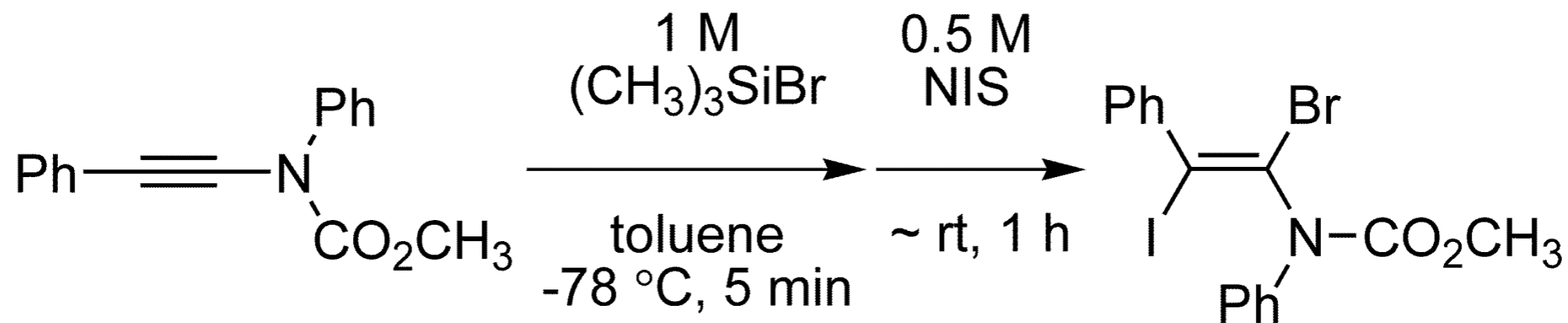
b) M. N. Ho, A. B. Lemay, W. W. Ogilvie, *J. Org. Chem.* **2007**, *72*, 977.

# Background



- Ide, M.; Yauchi, Y.; Iwasawa, T. *Eur. J. Org. Chem.* **2014**, 3262-3267.
- 特願 2014-014060 (2014年1月29日 出願)

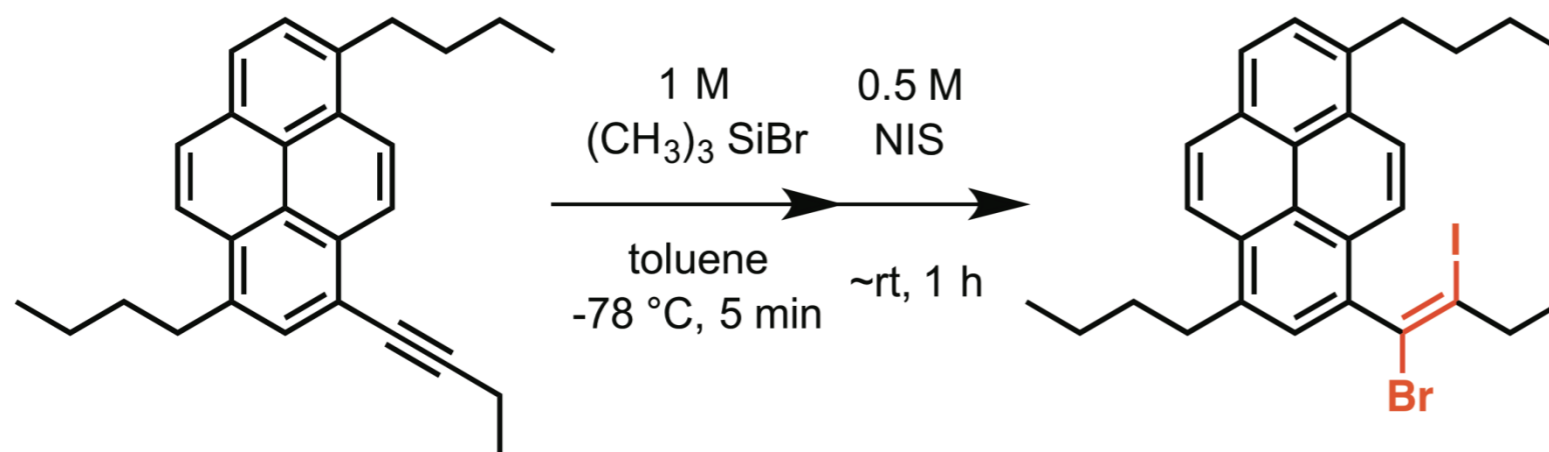
# Approach



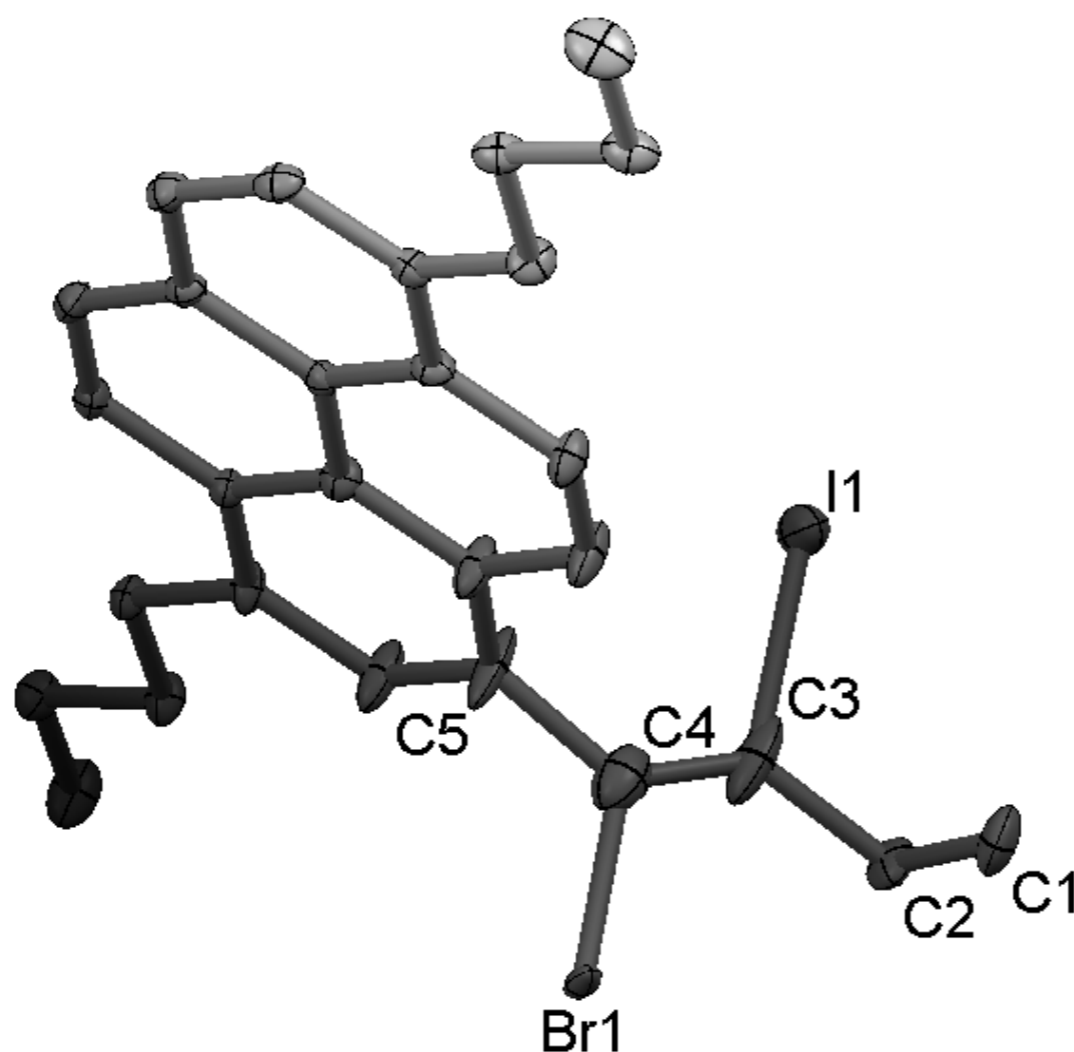
Ref) Flynn, A. B.; Ogilvie, W. W. *Chem. Rev.* **2007**, *107*, 4698-4745.

“Stereocontrolled Synthesis of Tetrasubstituted Olefins”

# (*E*)-1-bromo-2-iodo olefin

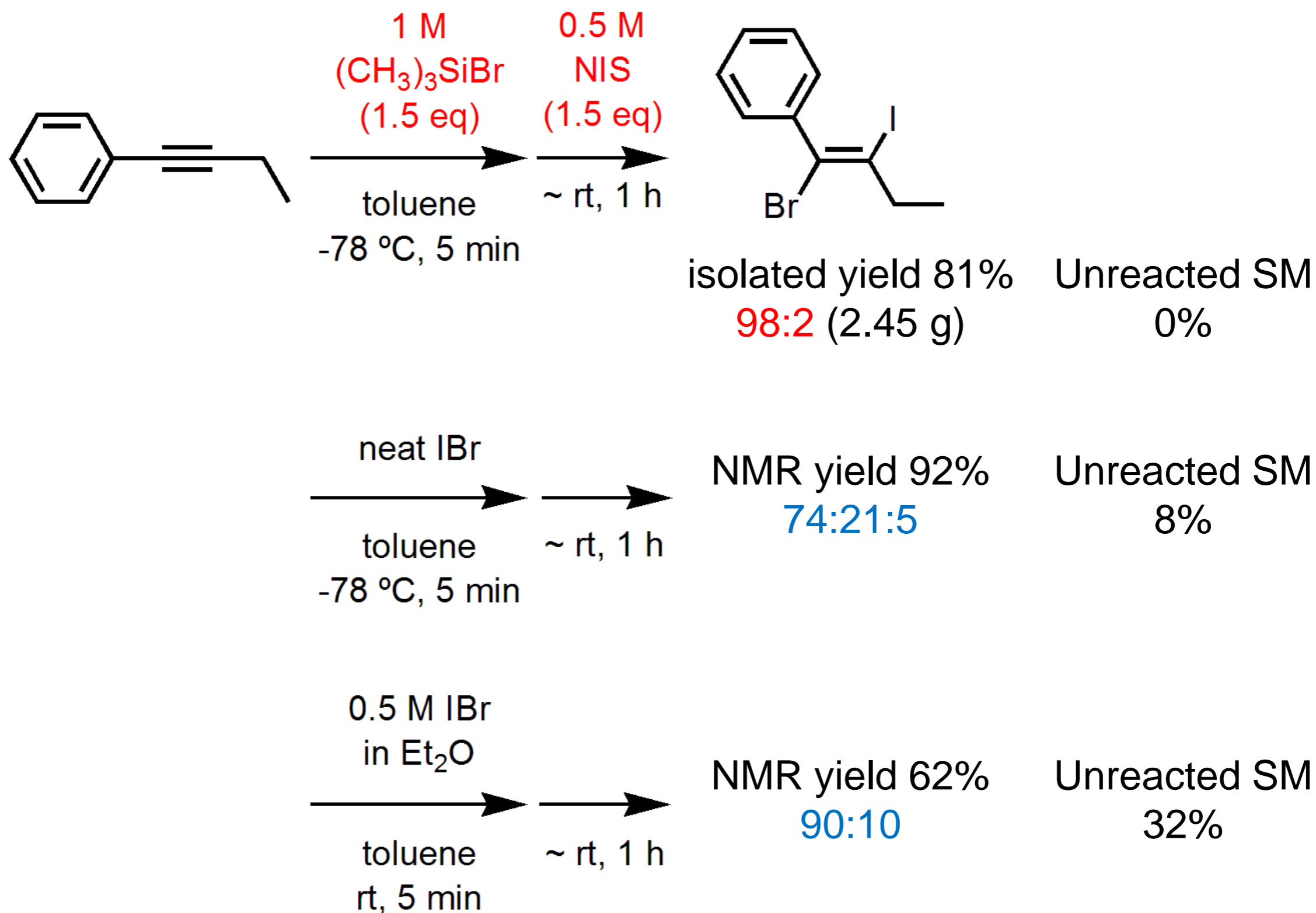


77% (443 mg)  
94:6  
(*E*)-, 1-bromo-2-iodo

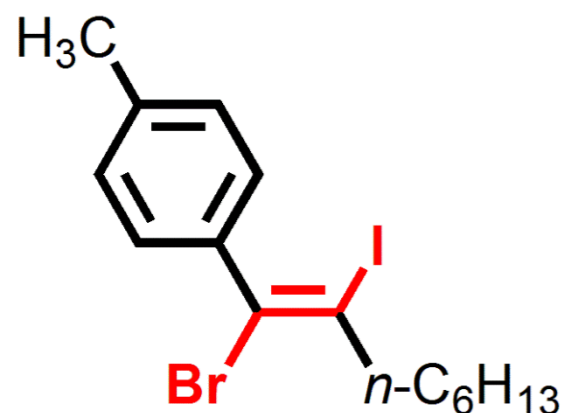


(Å): C(2)-C(3) = 1.507  
C(3)-I(1) = 2.168  
C(3)-C(4) = 1.267  
C(4)-Br(1) = 1.905  
C(4)-C(5) = 1.501

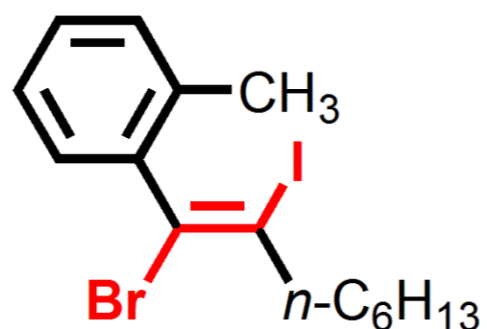
# I<sub>2</sub>, *in situ* or not



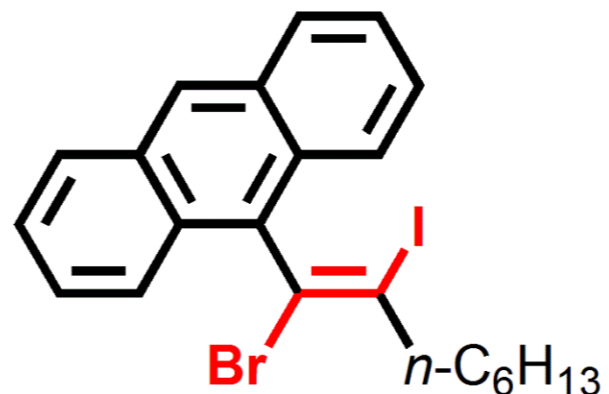
# Scope



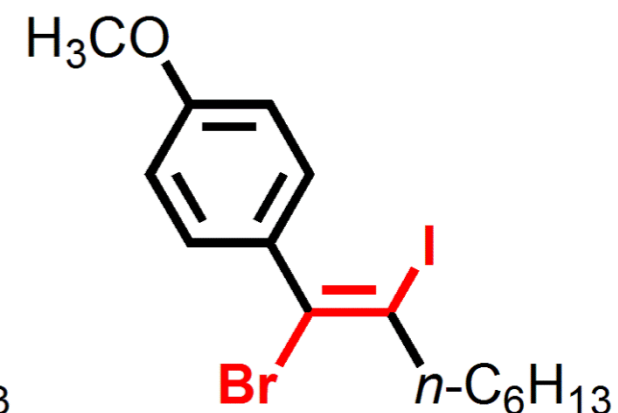
81%, 98:2



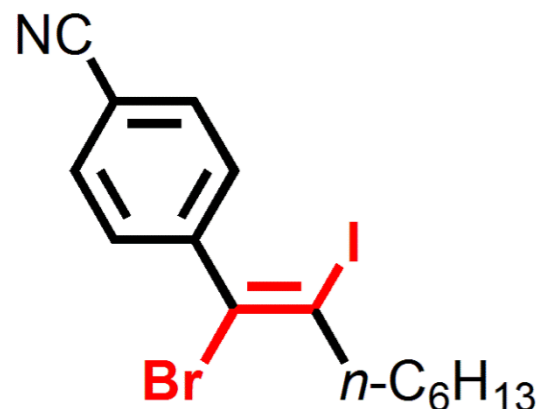
97%, 97:3



70%, ~100:0

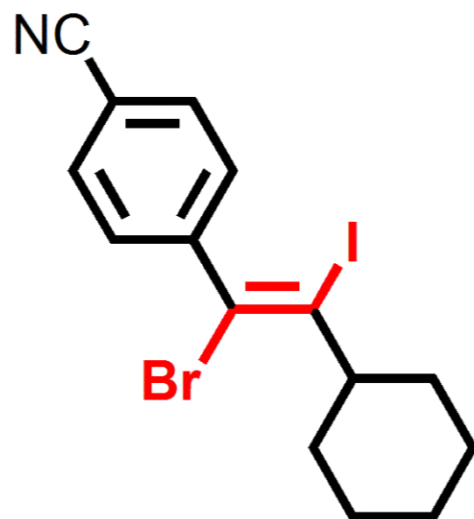


99%, > 99:1



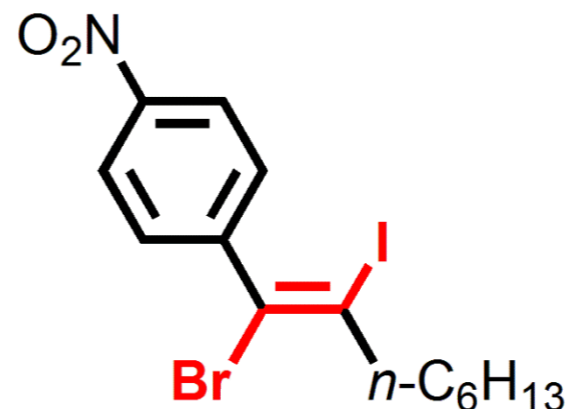
52%, 87:13

Recovered alkyne  
48%



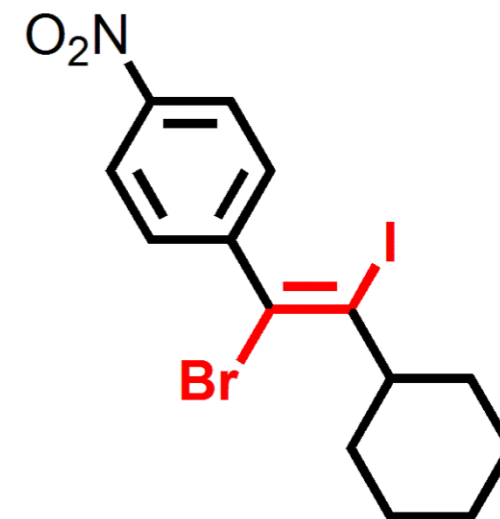
59%, 97:3

Recovered alkyne  
32%



55%, 76:24

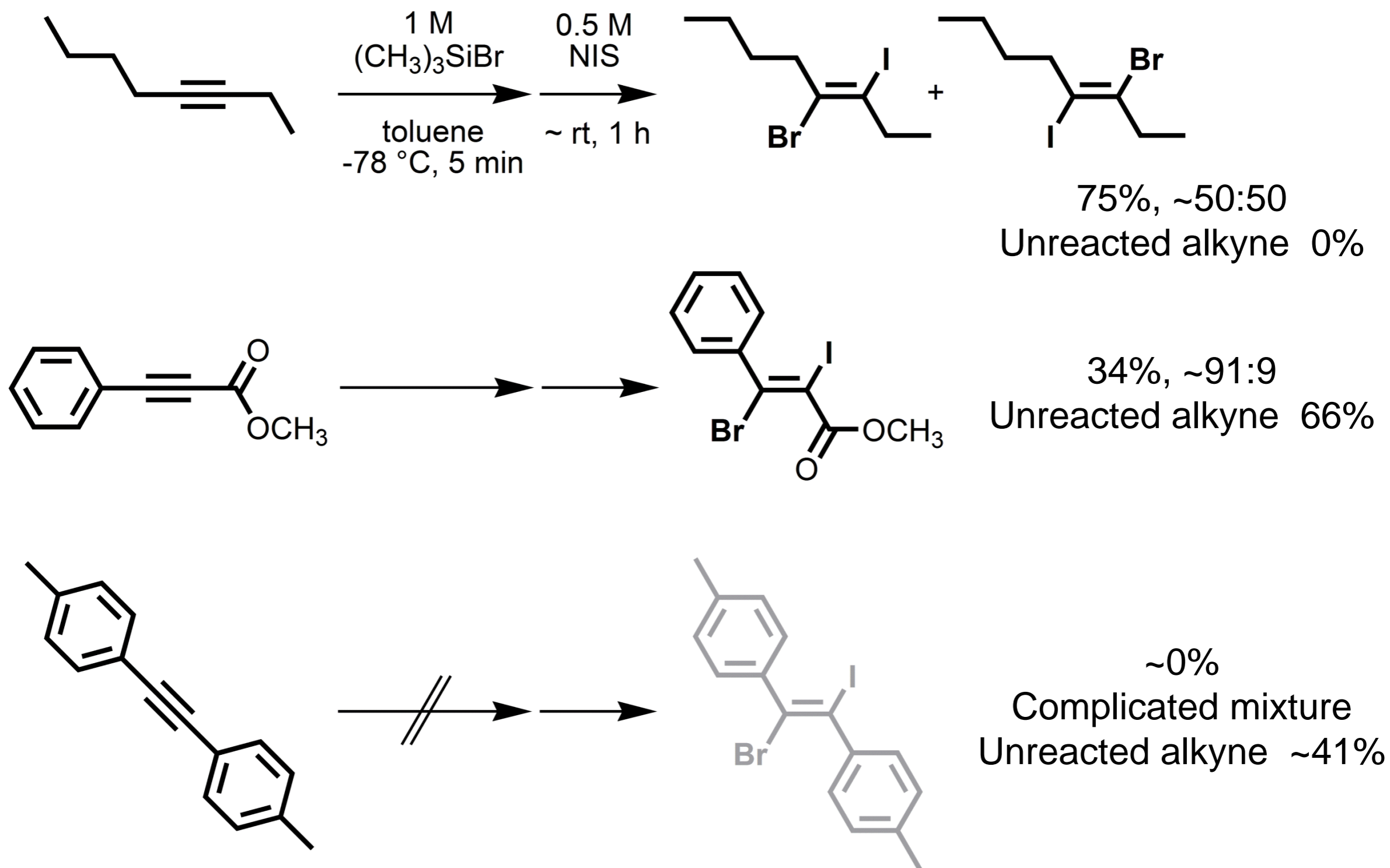
Recovered alkyne  
22%



37%, 95:5

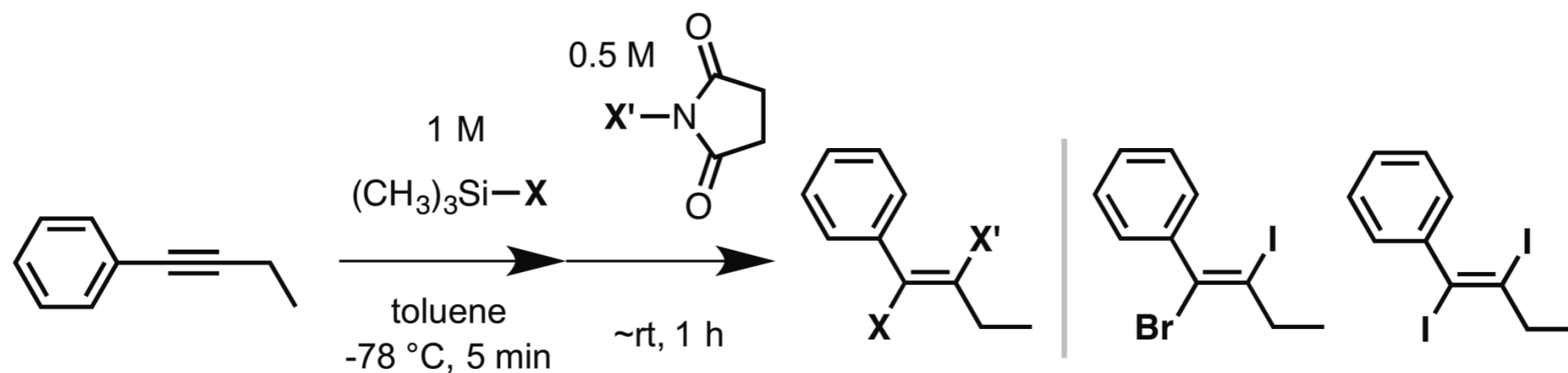
Recovered alkyne  
47%

# Limitation



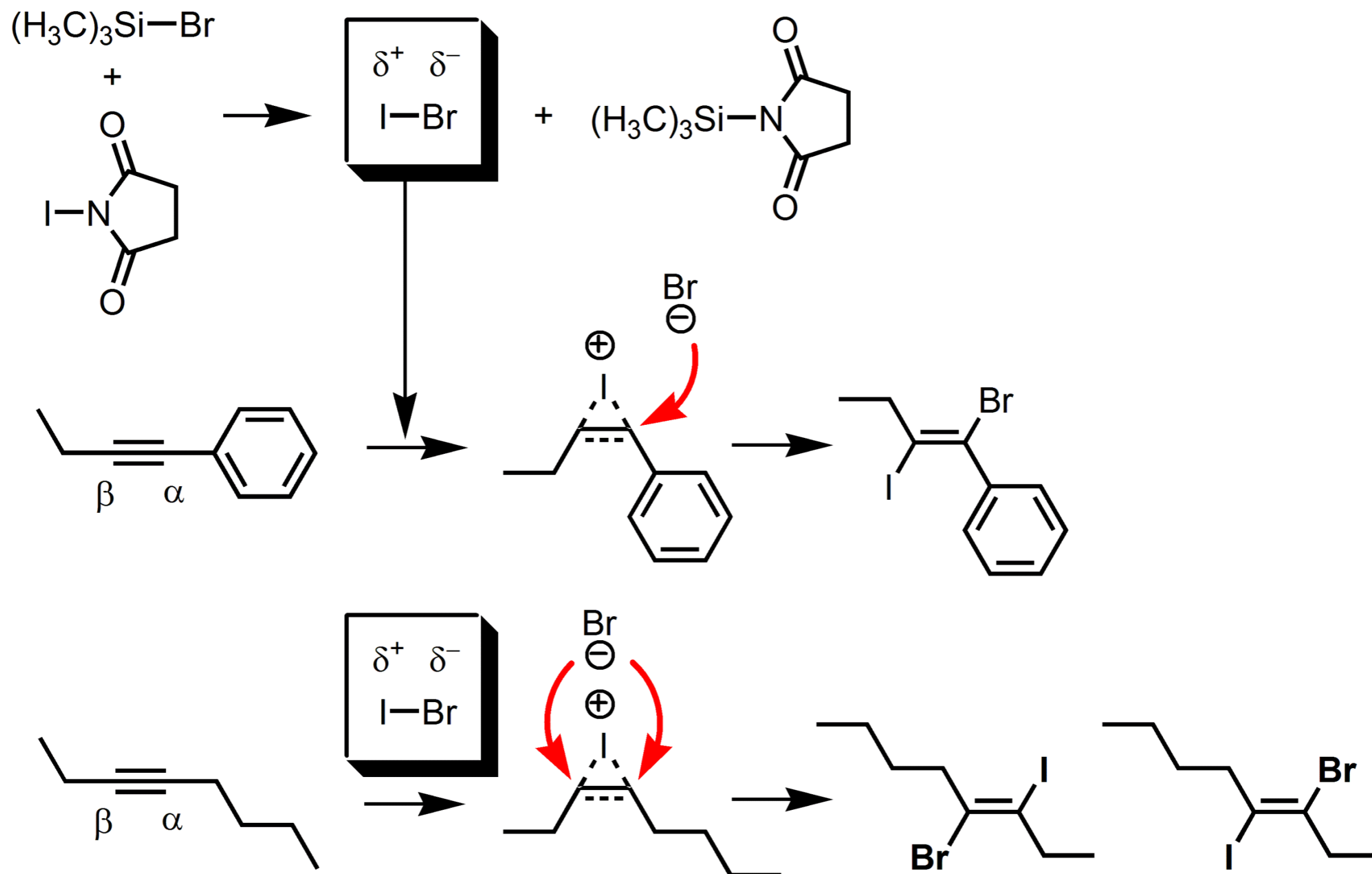


# Halogen sources (TMSX/NX'S)

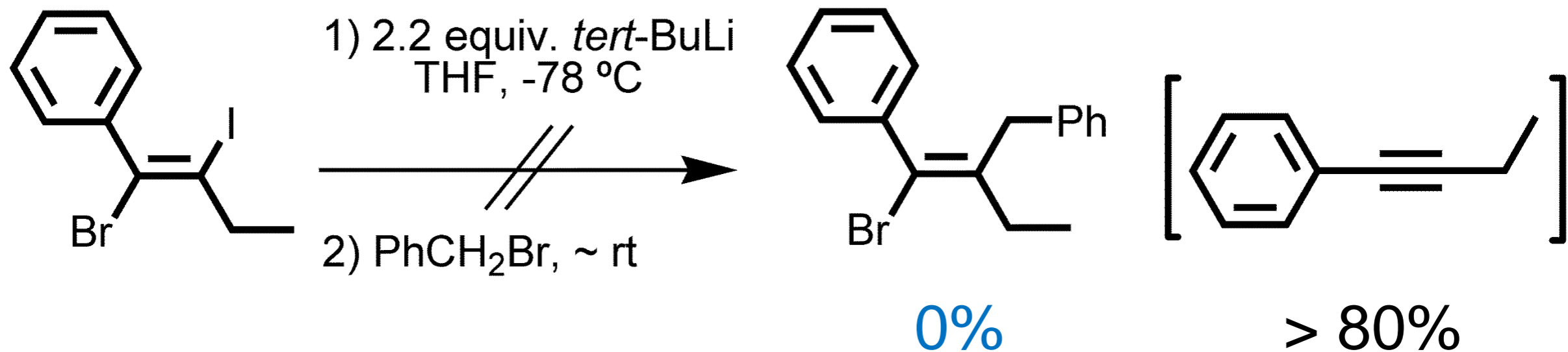
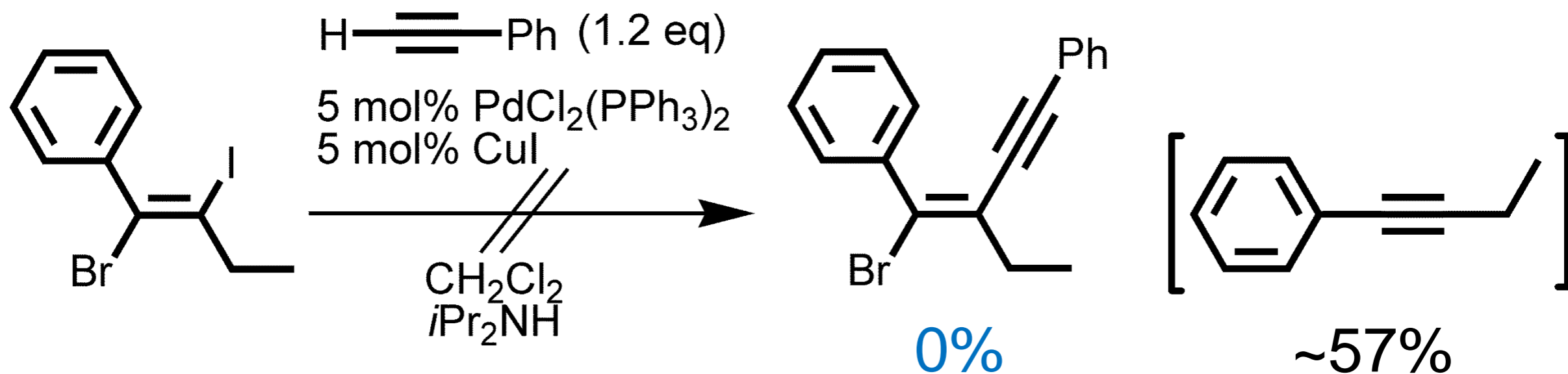


X	X'	Product	%Yield	Ratio	Recovered Alkyne (%)
I	I	I, I	26	$\sim 100:0$	60
I	Br	Br, I	76	87:13	19
I	Cl	I, I	24	$\sim 100:0$	32
Br	I	Br, I	81	98:2	0
Br	Br	-	-	-	0
Br	Cl	-	-	-	0
Cl	I	I, I	30	$\sim 100:0$	11
Cl	Br	-	-	-	0
Cl	Cl	-	-	-	0

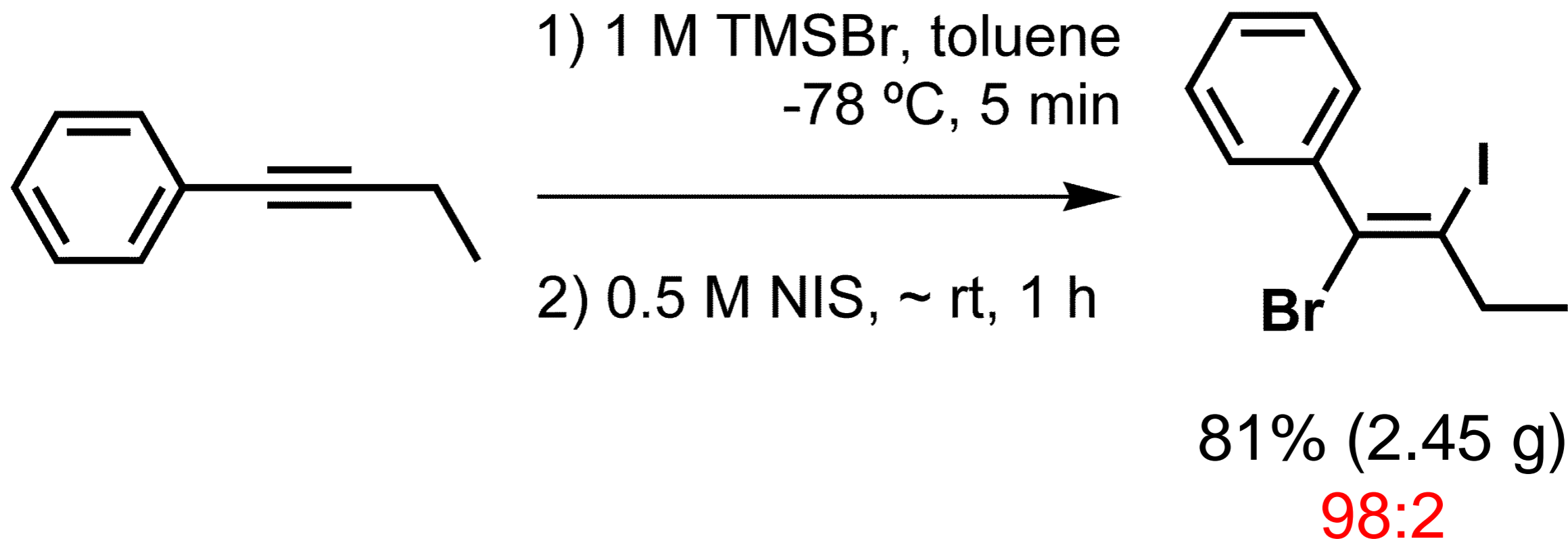
# Plausible mechanism



# Unworkable on conventional protocols



# Summary



- Ide, M.; Yauchi, Y.; Shiogai, R.; Iwasawa, T. *Tetrahedron* **2014**, *70*, 8532-8538.
- 特願 2014-153644