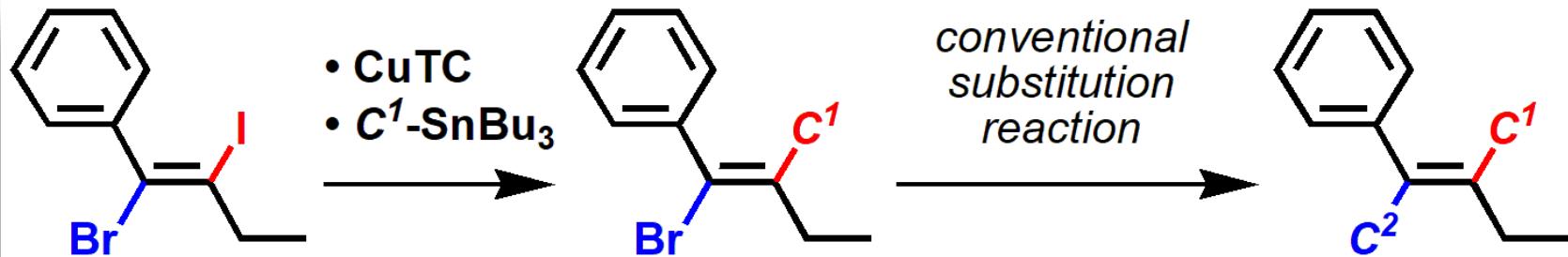


Stereo-defined Synthesis of Tetrasubstituted Olefins via Vicinal Dihaloalkenyl Scaffolds



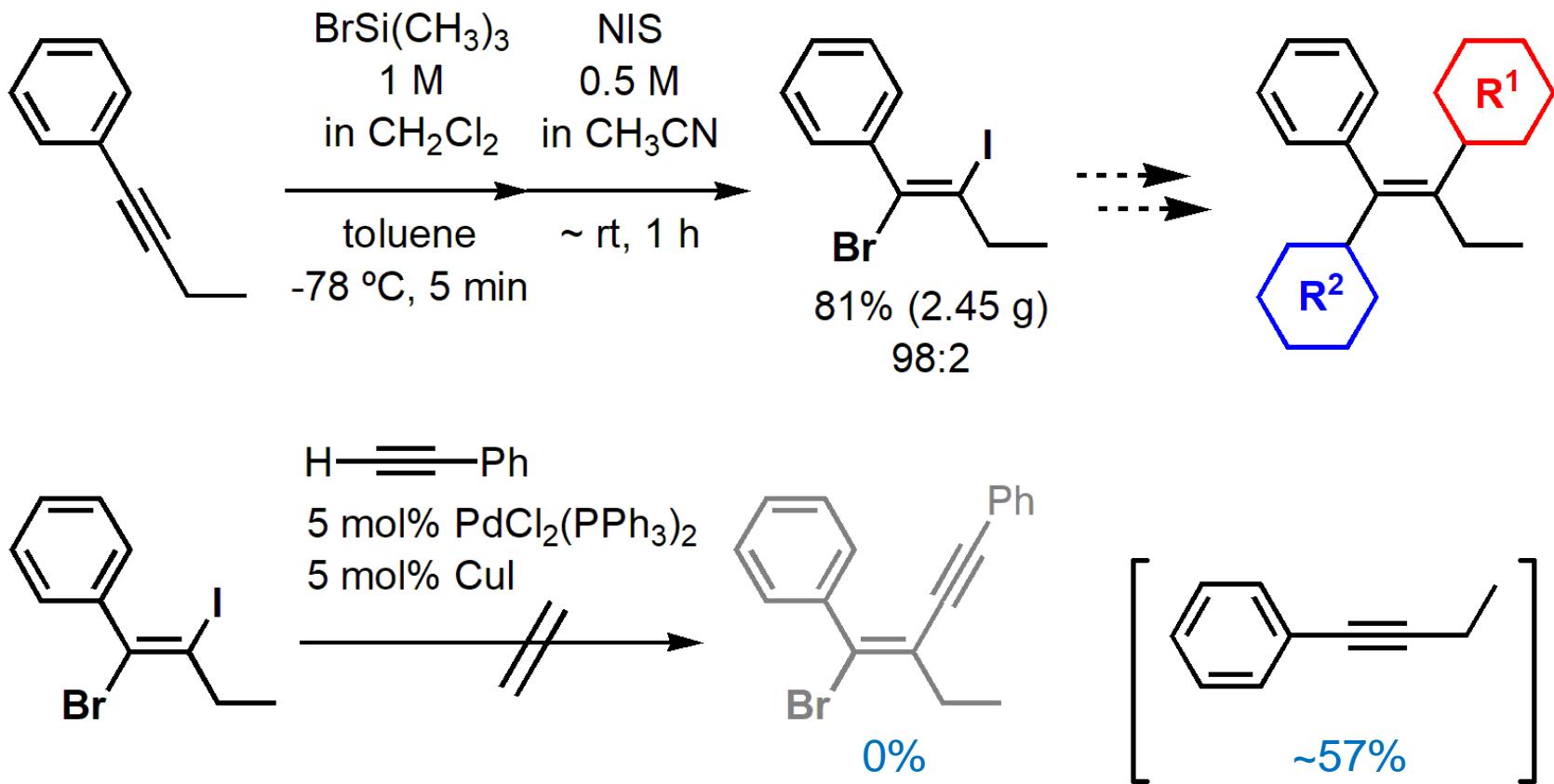
Ryukoku Univ., Naoki Endo and Tetsuo Iwasawa*



Differentially Substituted Olefin Template Strategy

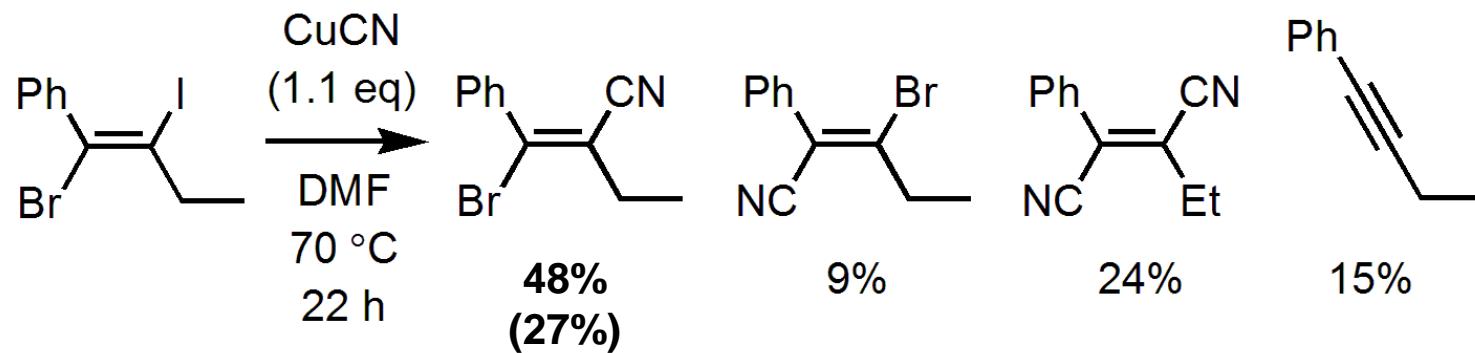
Endo, N.; Iwasawa, T. *Tetrahedron* 2017, 73, 5833-5840.

Background

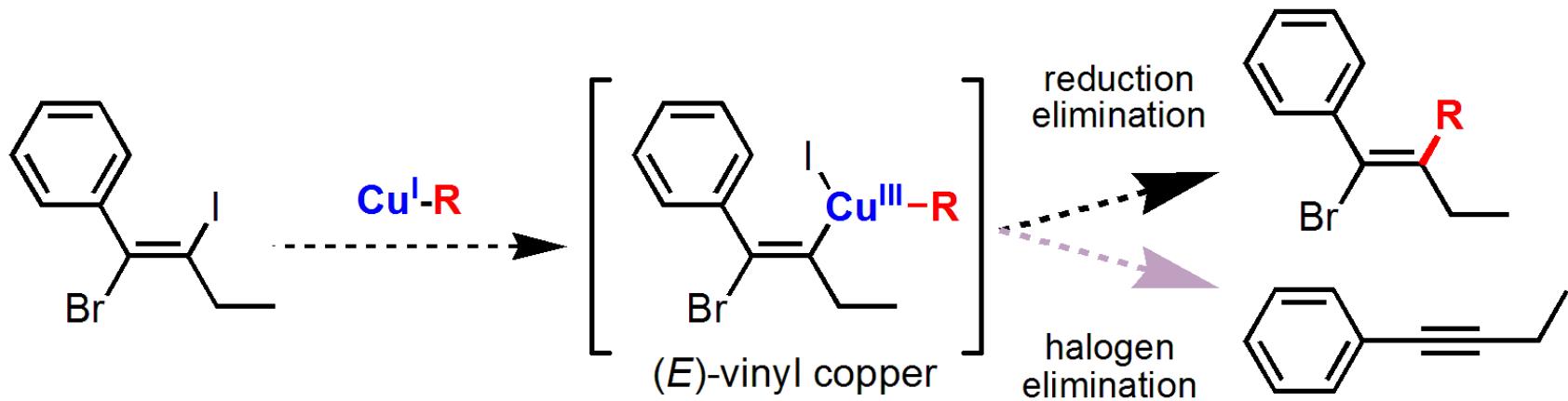


Ide, M.; Yauchi, Y.; Shiogai, R.; Iwasawa, T. *Tetrahedron* **2014**, *70*, 8532-8538.

Approach

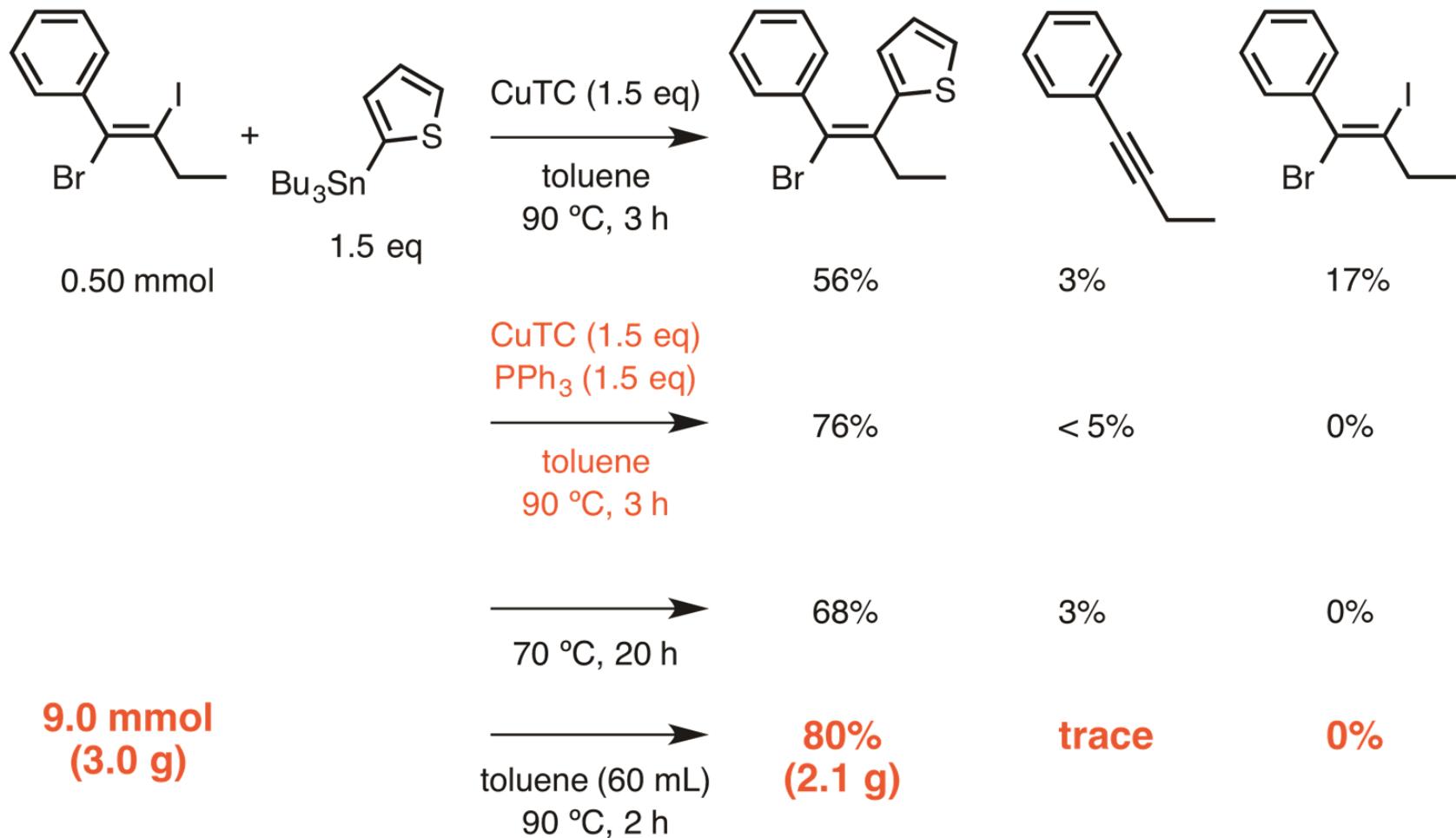


Endo, N.; Kanaura, M.; Iwasawa, T. *Tetrahedron Lett.* 2016, 57, 483-486.

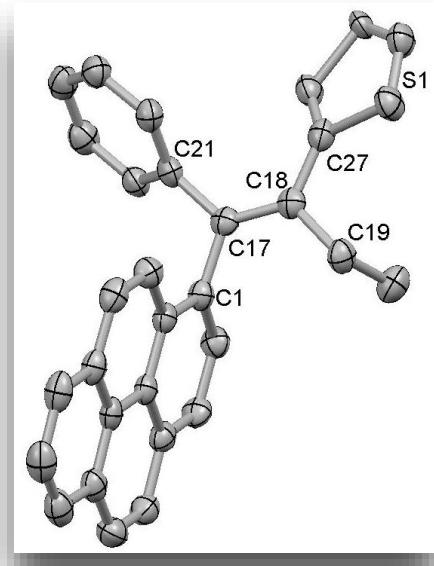
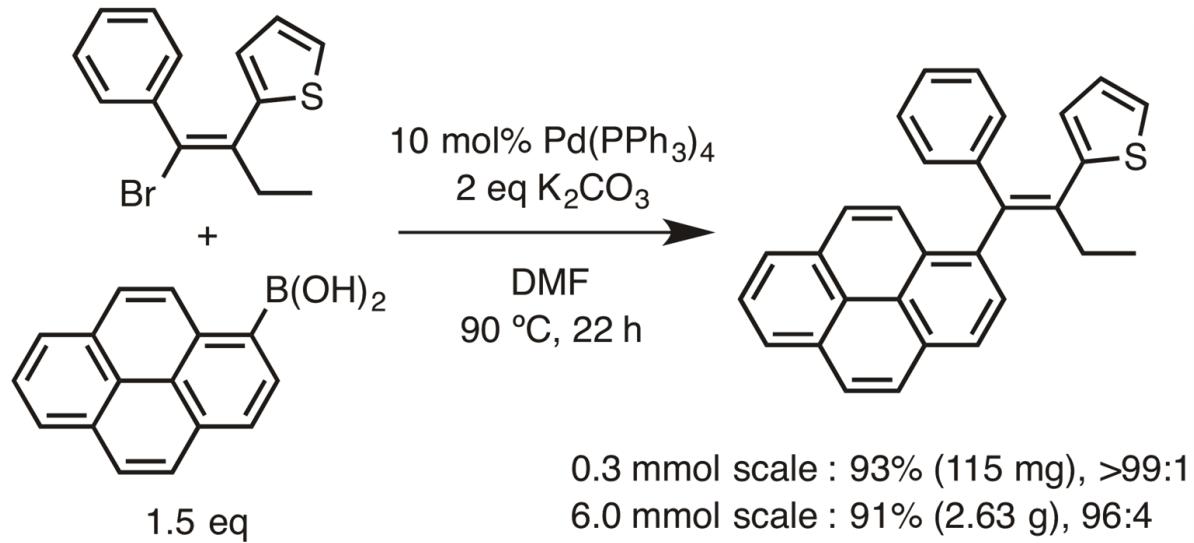


G. D. Allred, L. S. Liebeskind, *J. Am. Chem. Soc.* 1996, 118, 2748-2749.

In real

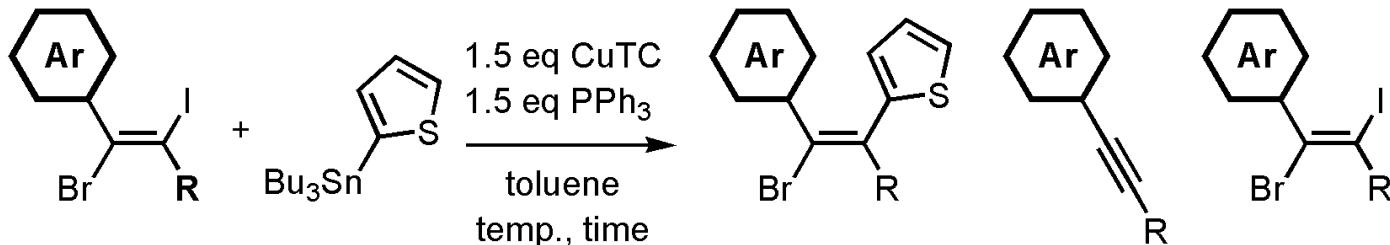


Single formation of the olefin was demonstrated with nearly full retention of stereochemistry.



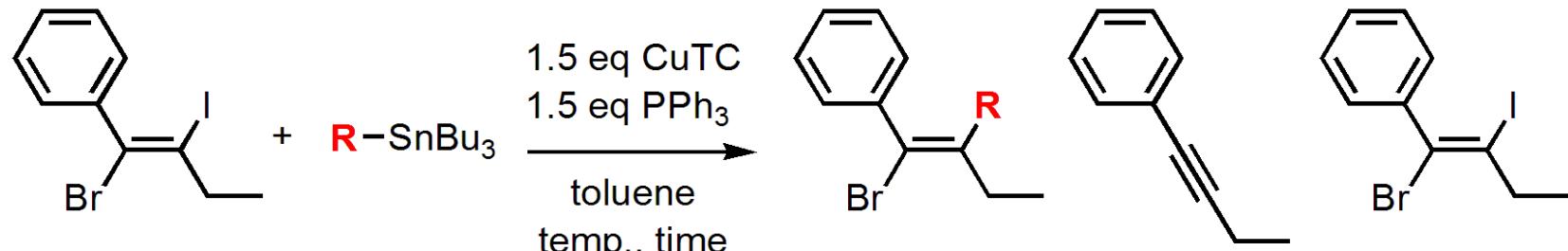
CCDC-1546653 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Monoclinic, space group $P\bar{1}/n$, colorless, $a = 14.3026(7)$ Å, $b = 11.8400(5)$ Å, $c = 25.2918(12)$ Å, $\alpha = 90^\circ$, $\beta = 96.499(7)^\circ$, $\gamma = 90^\circ$, $V = 4255.5(3)$ Å 3 , $Z = 8$, $T = 123$ K, $d_{\text{calcd.}} = 1.294$ g cm $^{-3}$, $\mu(\text{Mo-}\text{K}\alpha) = 0.167$ mm $^{-1}$, $R_1 = 0.0746$, $wR_2 = 0.1770$, GOF = 1.027.

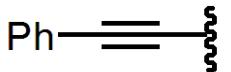
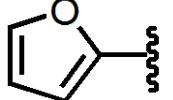
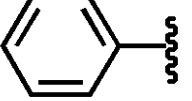
Substrate Scope



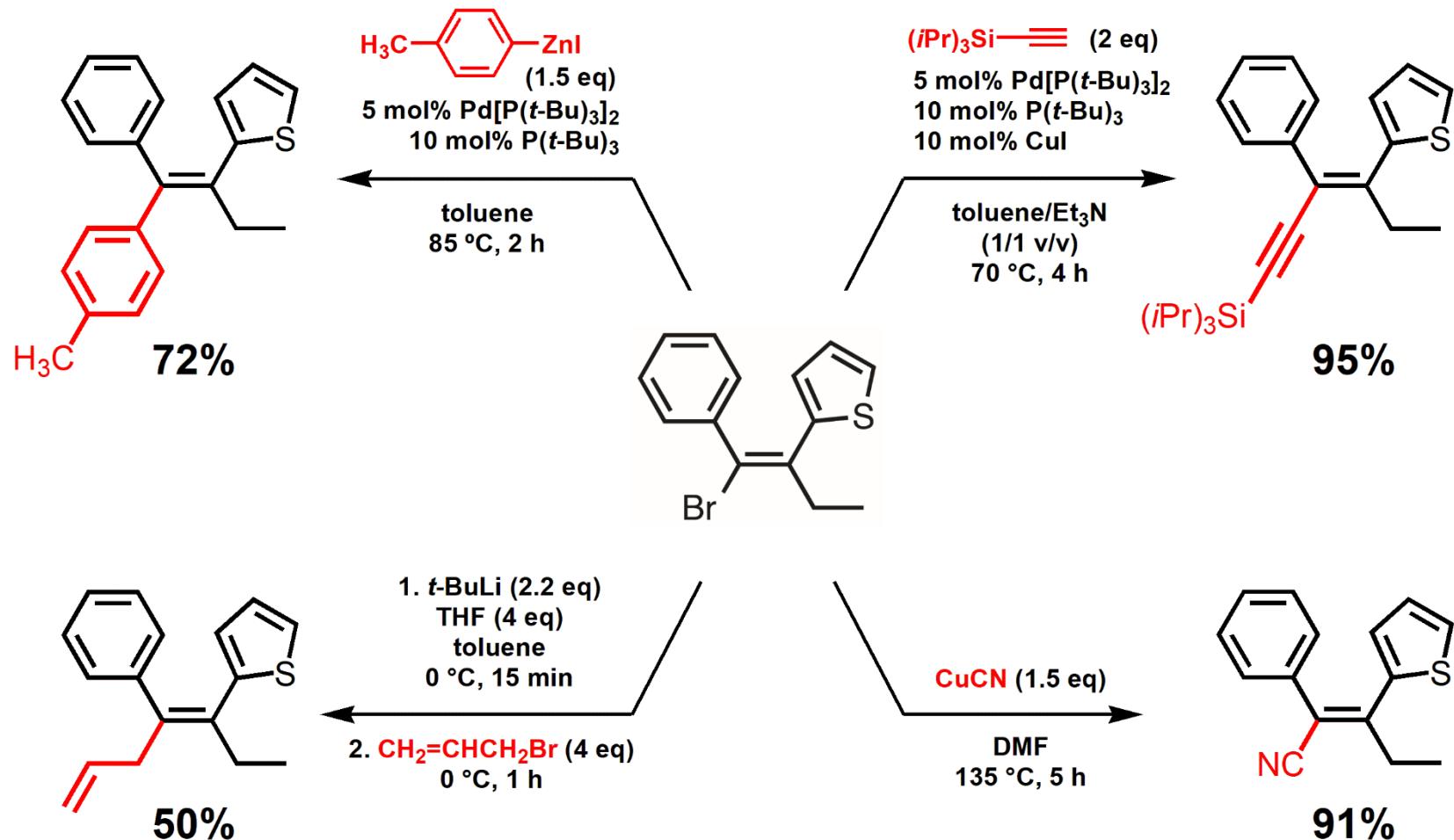
Ar	R	temp./°C	time/h	Yield (%)	Yield (%)	Yield (%)
		85	23	65%	11%	trace
		70	19	61%	11%	0%
		90	11	60%	17%	0%
		90	23	<25%	21%	14%

Substrate Scope

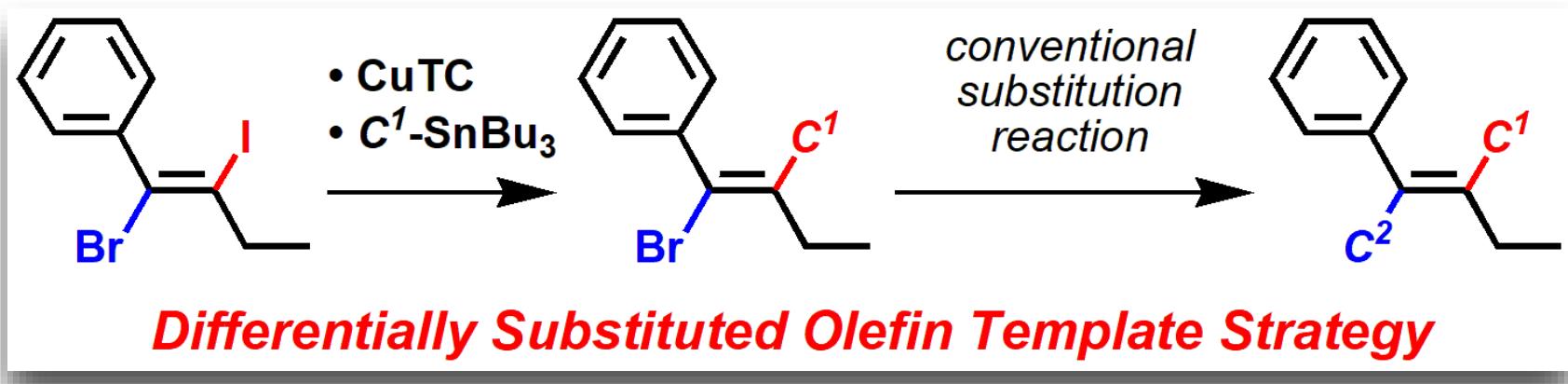
Reaction scheme:  A substituted alkene (with a phenyl ring, a bromine atom, and an iodine atom) reacts with R-SnBu₃ under the following conditions: 1.5 eq CuTC, 1.5 eq PPh₃, toluene, at a certain temperature for a certain time. The products are three isomers: one where the R-group is attached to the carbon bearing the iodine (R-alkene), one where the R-group is attached to the terminal carbon (alkyne), and one where the R-group is attached to the carbon bearing the bromine (I-alkene).

R	temp./°C	time/h	Yield (%)	Yield (%)	Yield (%)
	110	20	51%	10%	4%
	90	2	75%	3%	6%
	90	11	<10%	-	-
	110	17	0%	-	-

Synthesis of the differentially all-carbon tetrasubstituted olefins



Summary



Endo, N.; Iwasawa, T. *Tetrahedron* 2017, 73, 5833-5840.