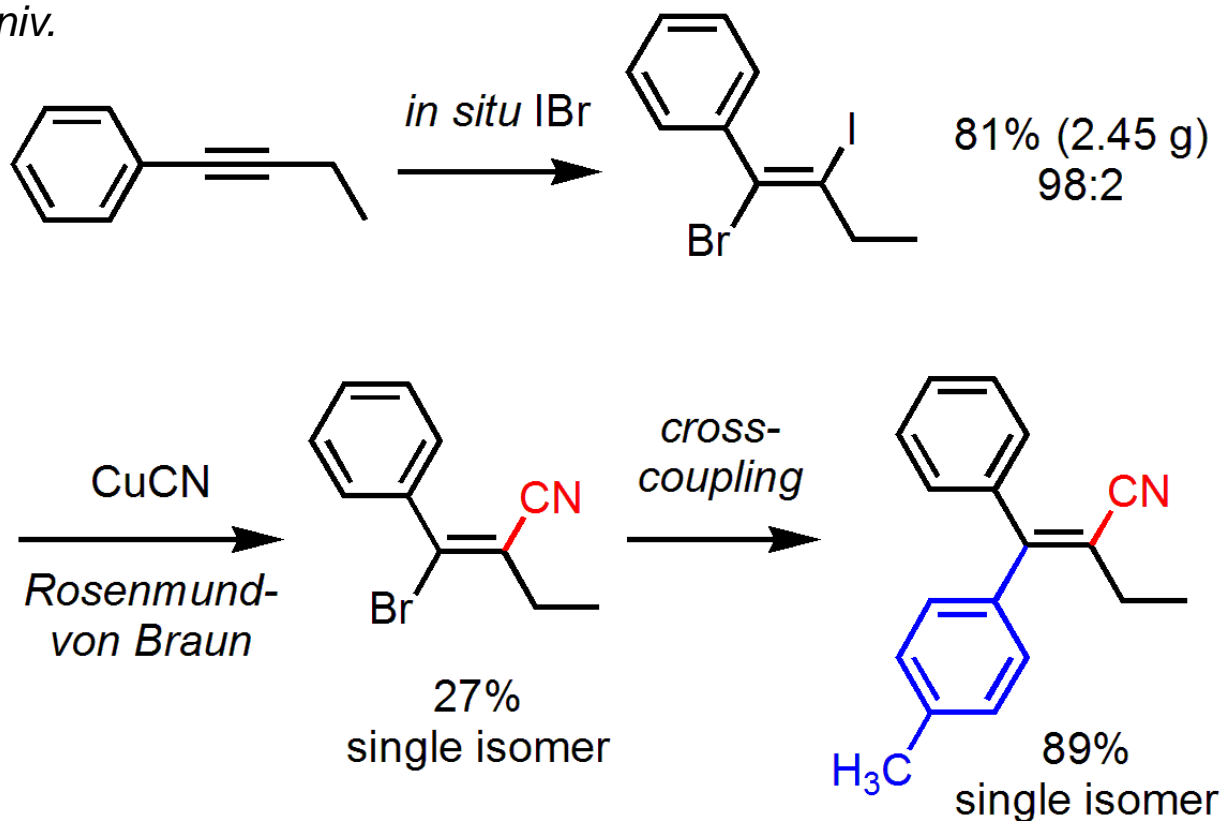


Elucidation of Reaction Process through β -Halogen Elimination in Vinylic Rosenmund–von Braun Reaction of (*E*)-(1-bromo-2-iodo-but-1-en-1-yl)benzene



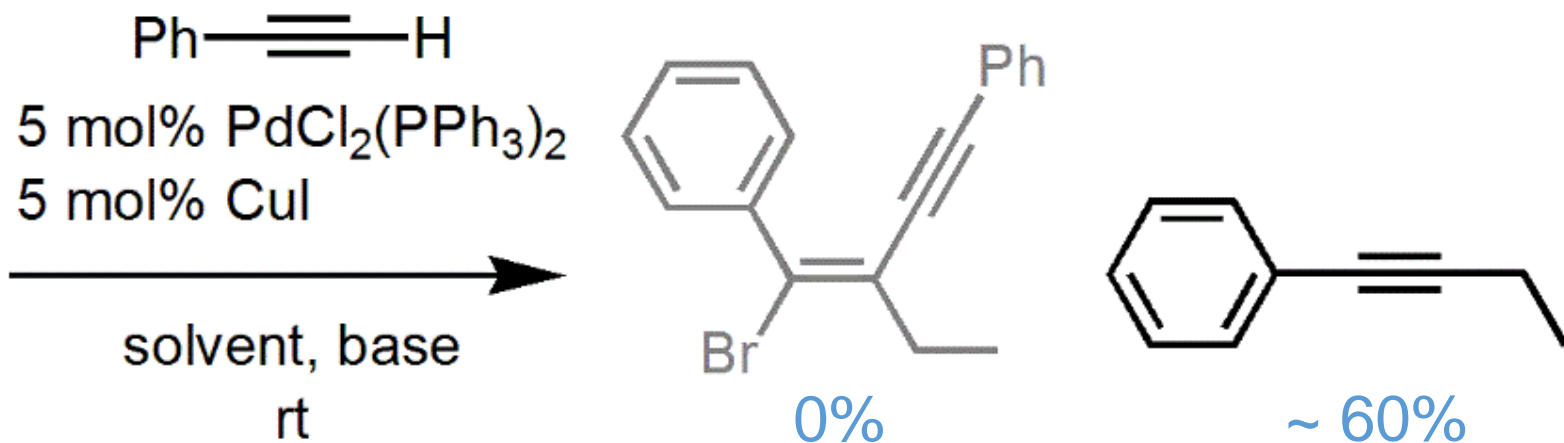
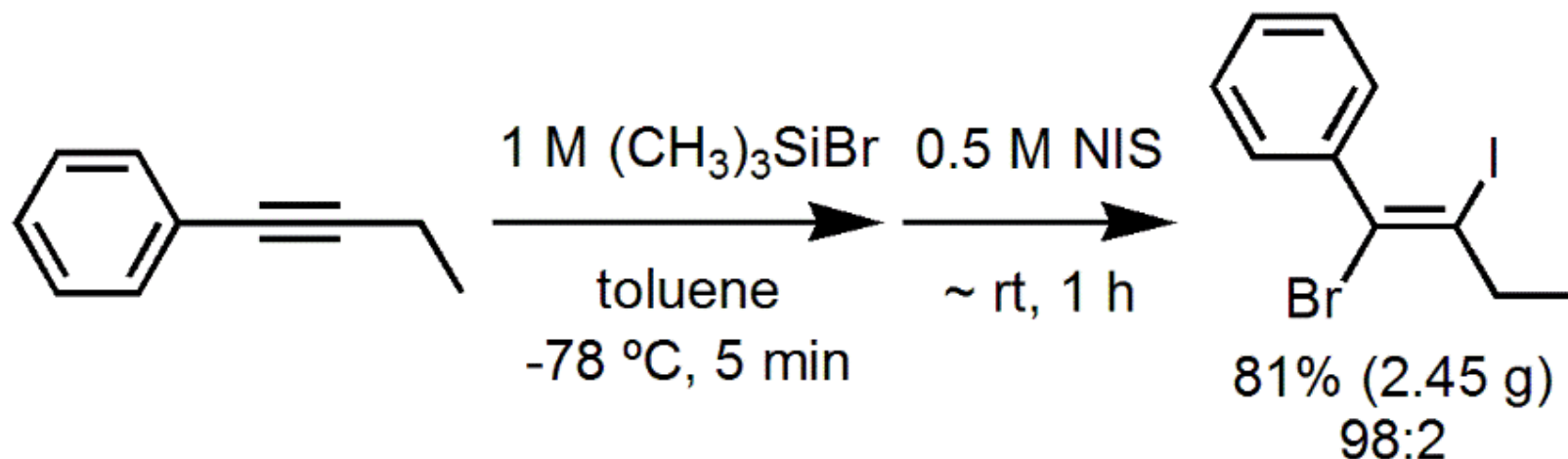
Ryukoku Univ.

Naoki Endo, Mao Kanaura, & Tetsuo Iwasawa*



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

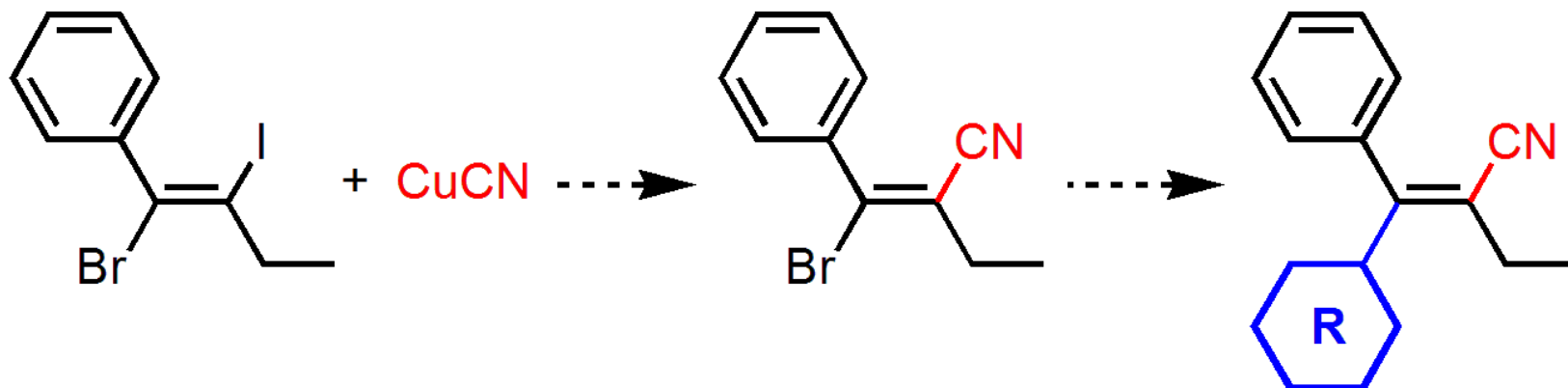
Background



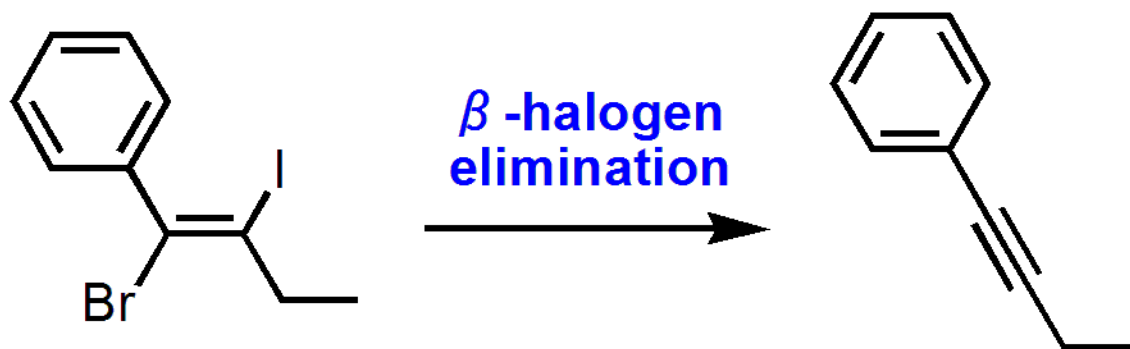
- Ide, M.; Yauchi, Y.; Iwasawa, T. *Eur. J. Org. Chem.* **2014**, 3262-3267.
- Ide, M.; Yauchi, Y.; Shiogai, R.; Iwasawa, T. *Tetrahedron* **2014**, 70, 8532-8538.
- 特願 2014-014060, 特願 2014-153644

Approach

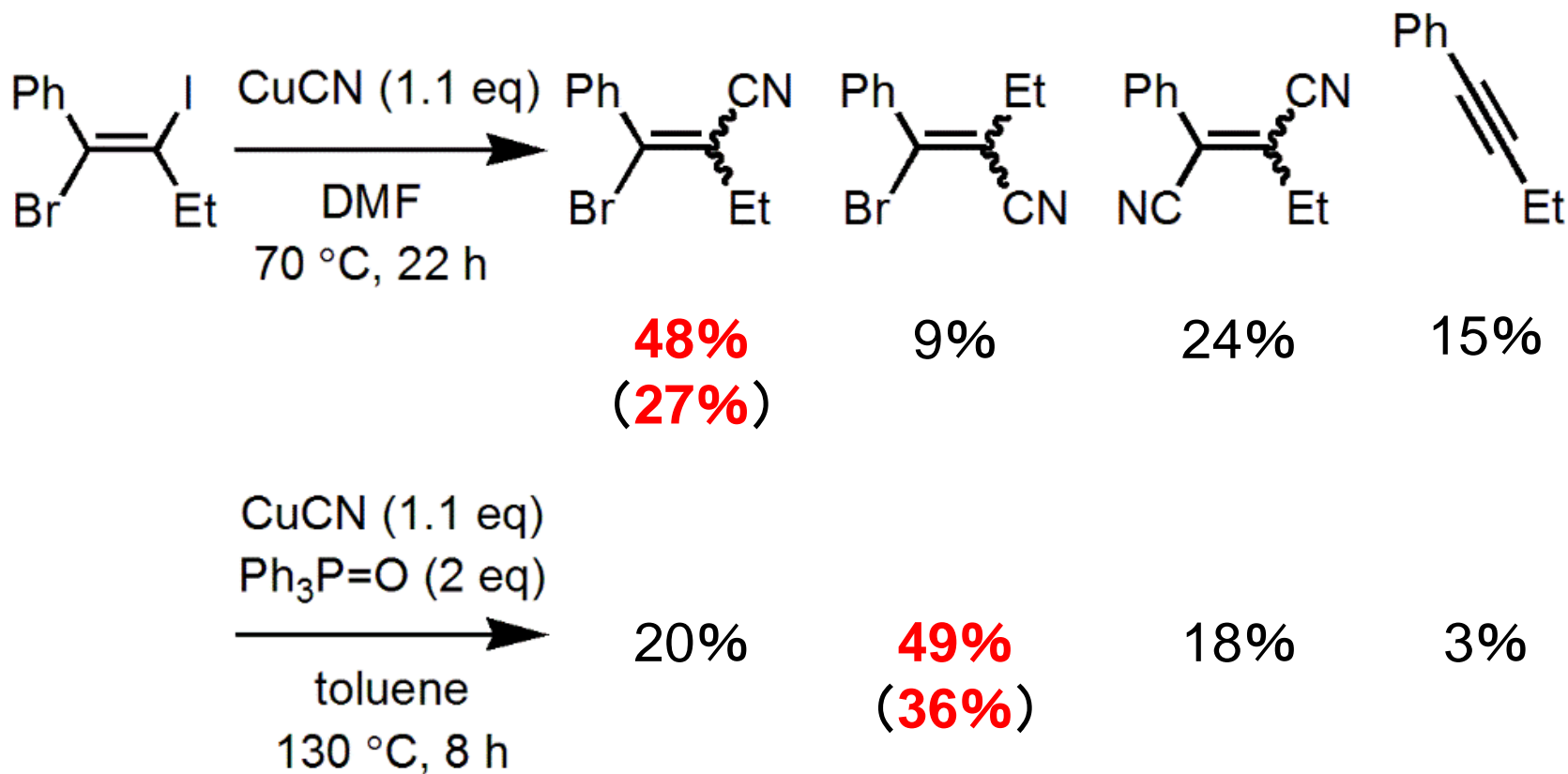
Vinylic Rosenmund–von Braun reaction



Differentially Substituted Olefin Template Strategy

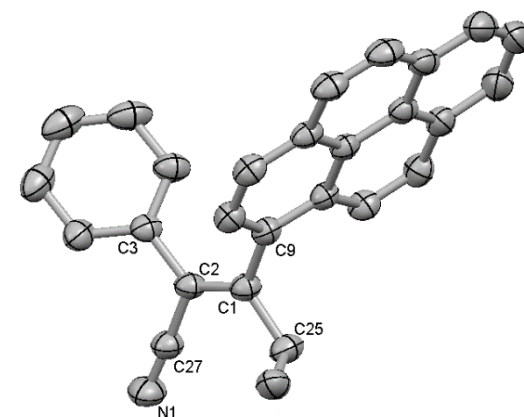
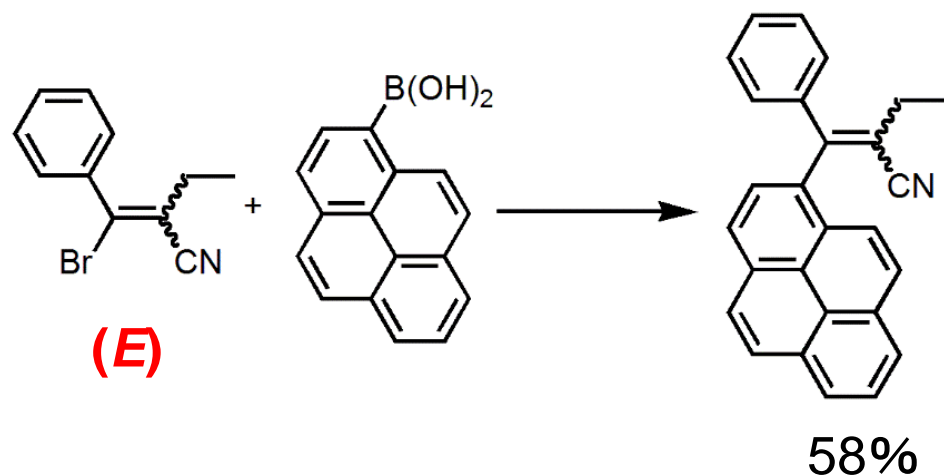
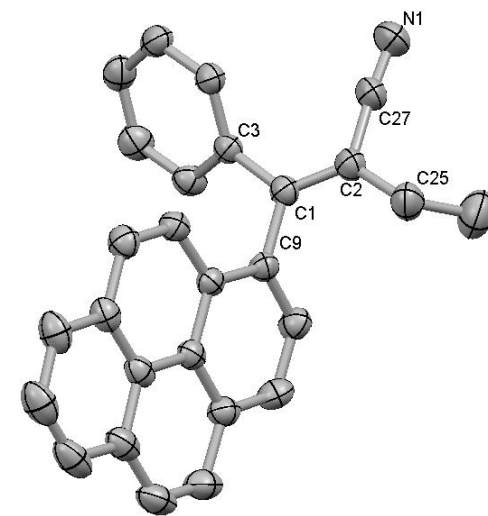
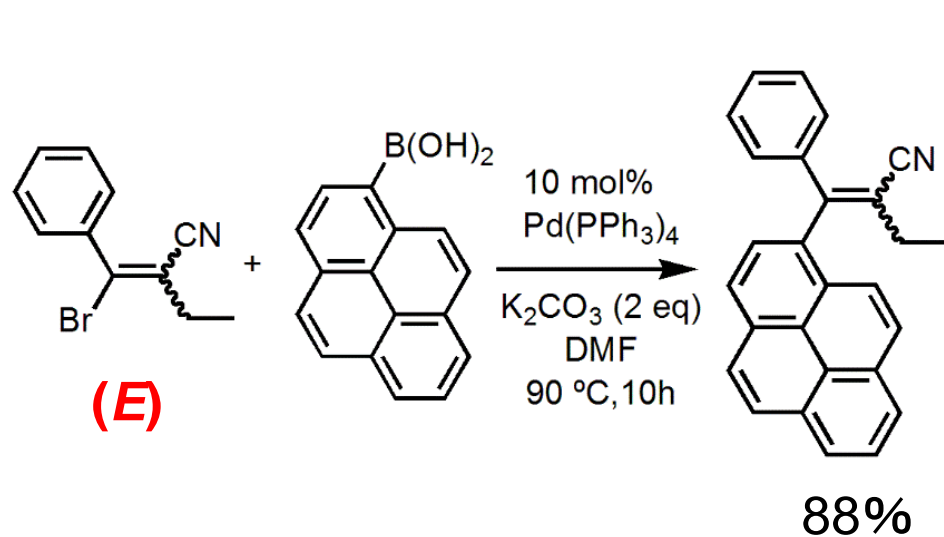


In real

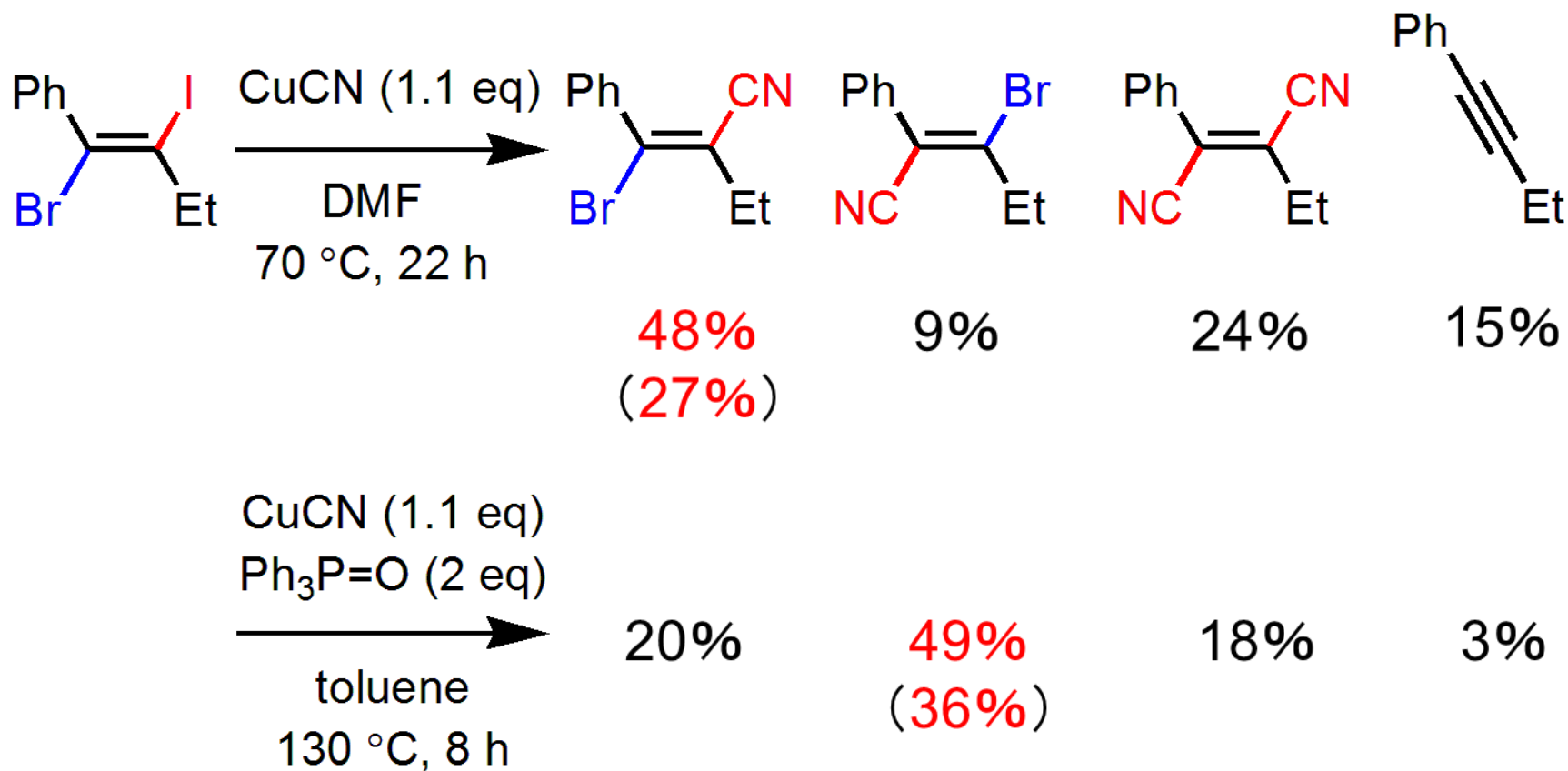


Ligand-controllable System

Palladium-catalyzed synthesis of pyrene derivatives

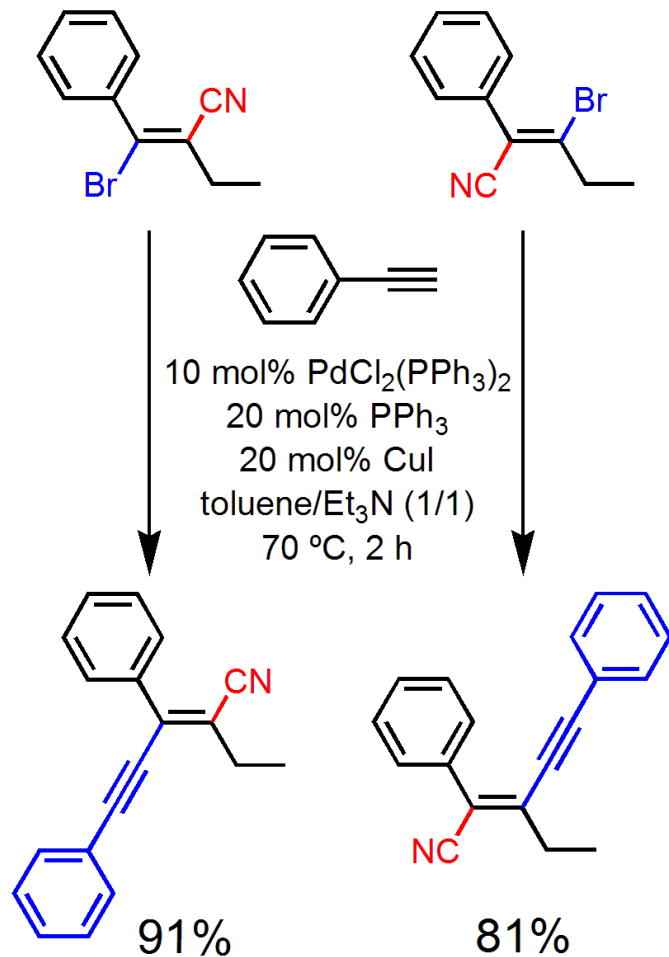


X-ray structure; result of both (*E*)-forms !

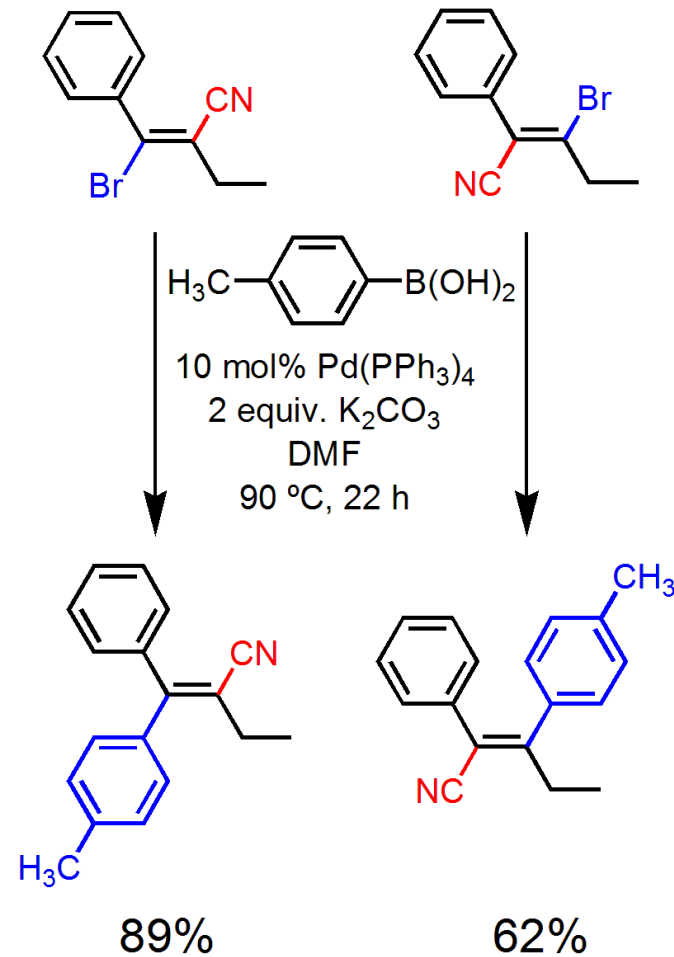


Stereo-defined synthesis of differentially tetrasubstituted acrylonitriles

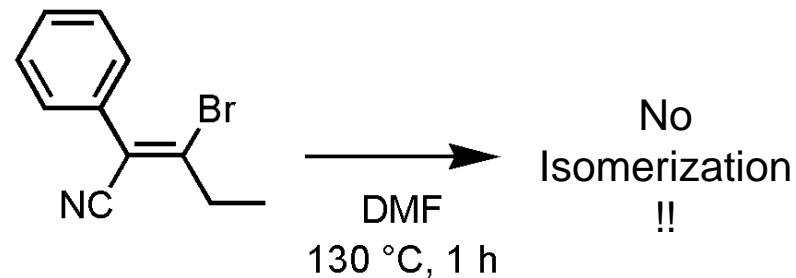
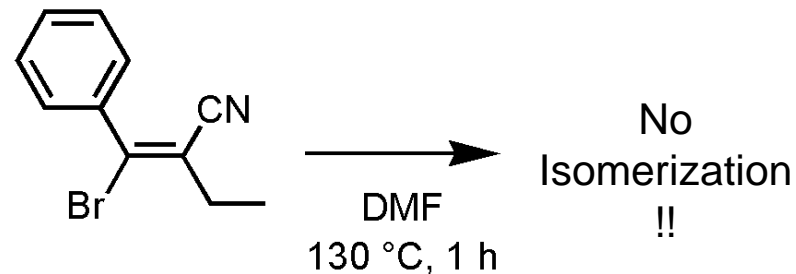
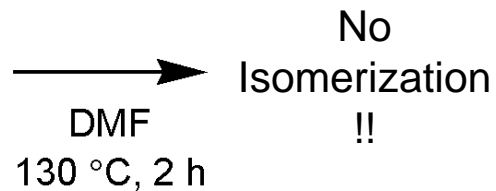
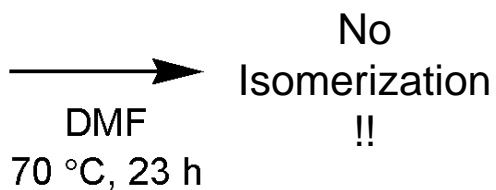
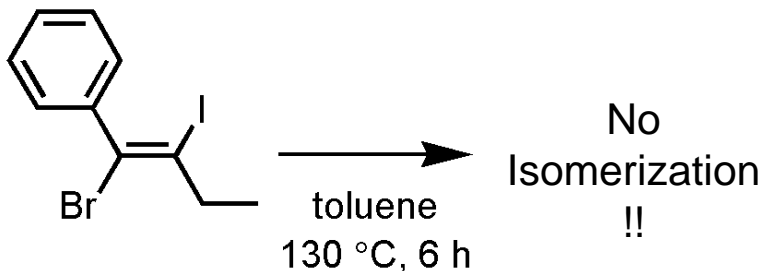
Sonogashira



Suzuki-Miyaura

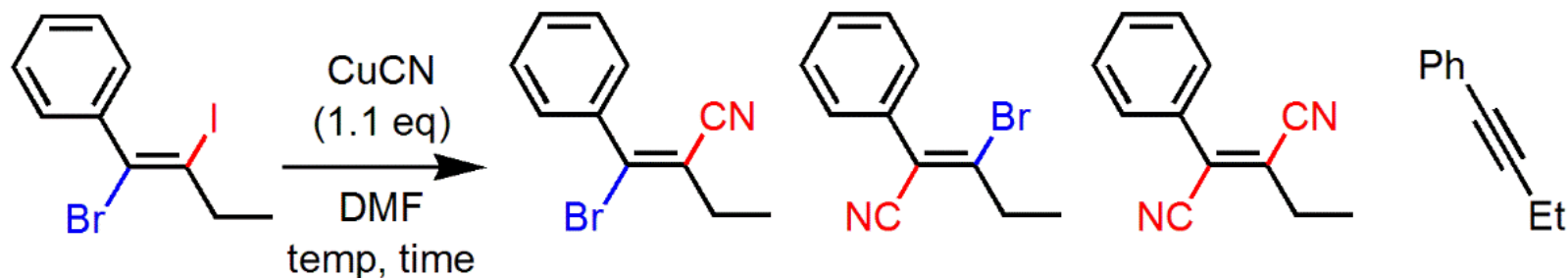


No tautomerization



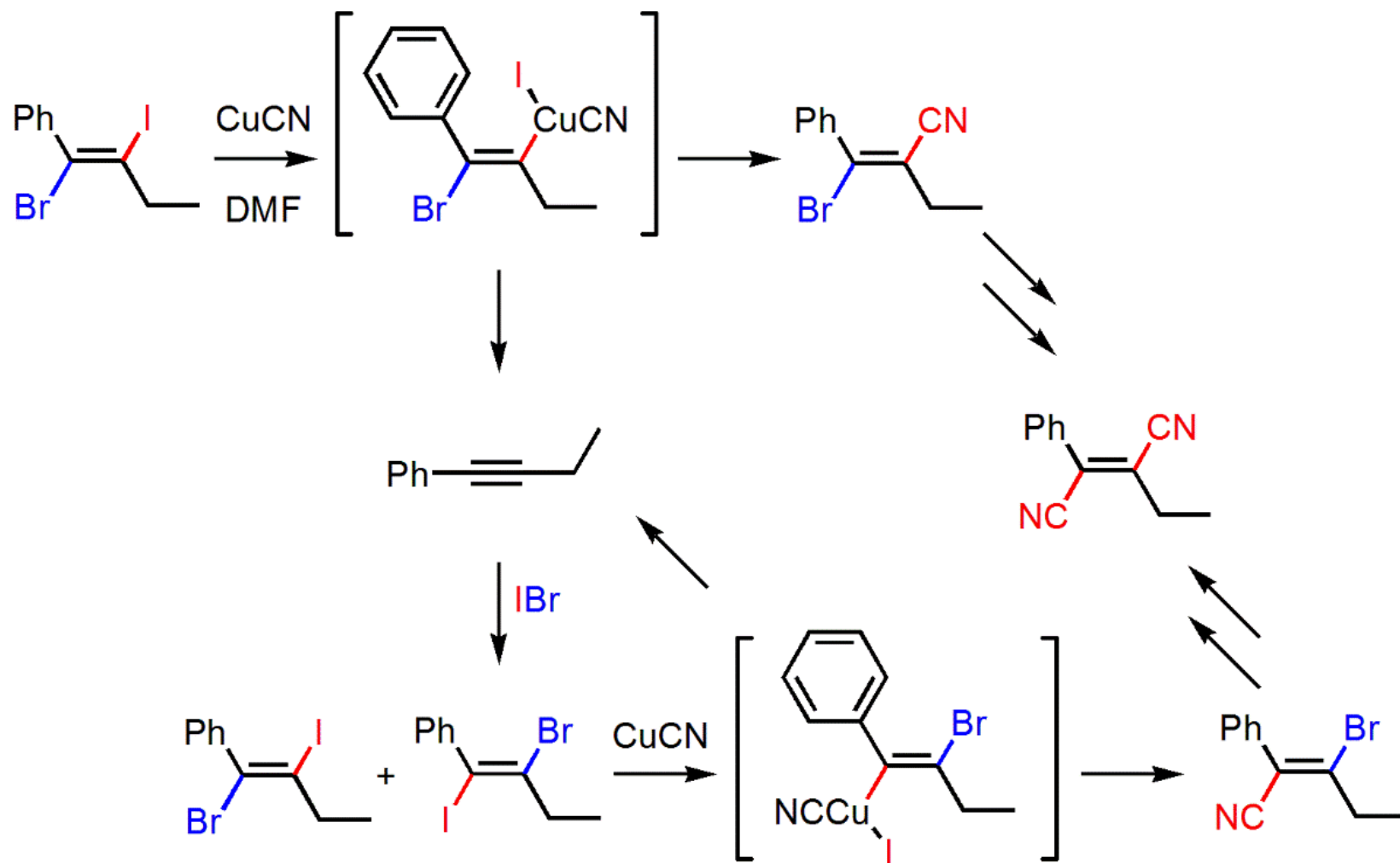
Heating doesn't cause tautomerization.

Temperature-dependent reactivity

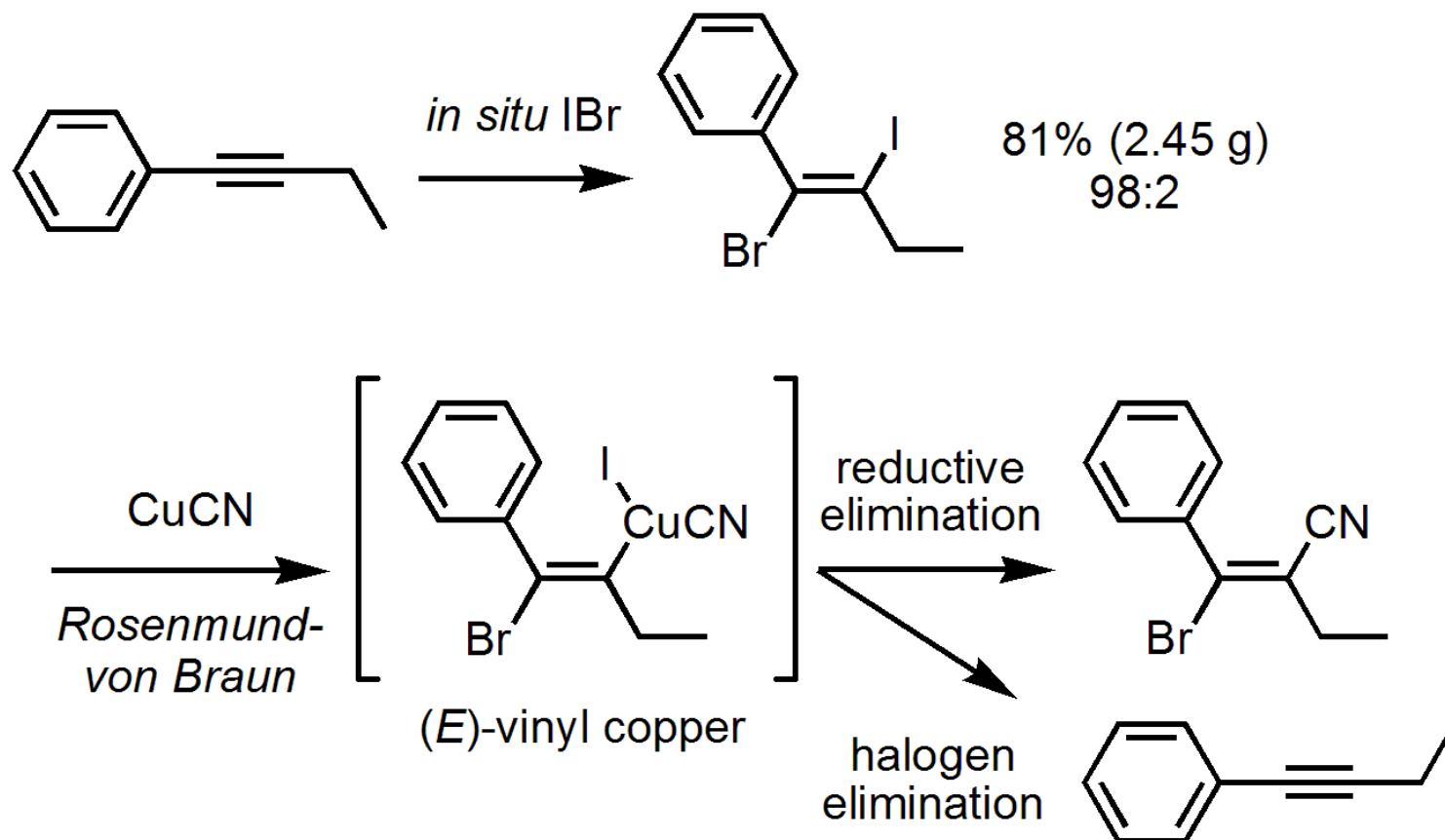


82%	→ r.t., 74 h	2%	0%	0%	2%
74%	→ 50°C, 22 h	9%	0%	0%	7%
0%	→ 70°C, 22 h	48%	9%	24%	15%
0%	→ 90°C, 5 h	40% ↓	18% ↑	26%	16%
0%	→ 130°C, 1 h	32% ↓	26% ↑	24%	5%

Plausible reaction paths



Summary



- Endo, N.; Kanaura, M.; Iwasawa, T. *Tetrahedron Letters* **2016**, 57, 483-486.
- Iwasawa, T. *J. Synth. Org. Chem.* **2015**, 73, 1212-1225.