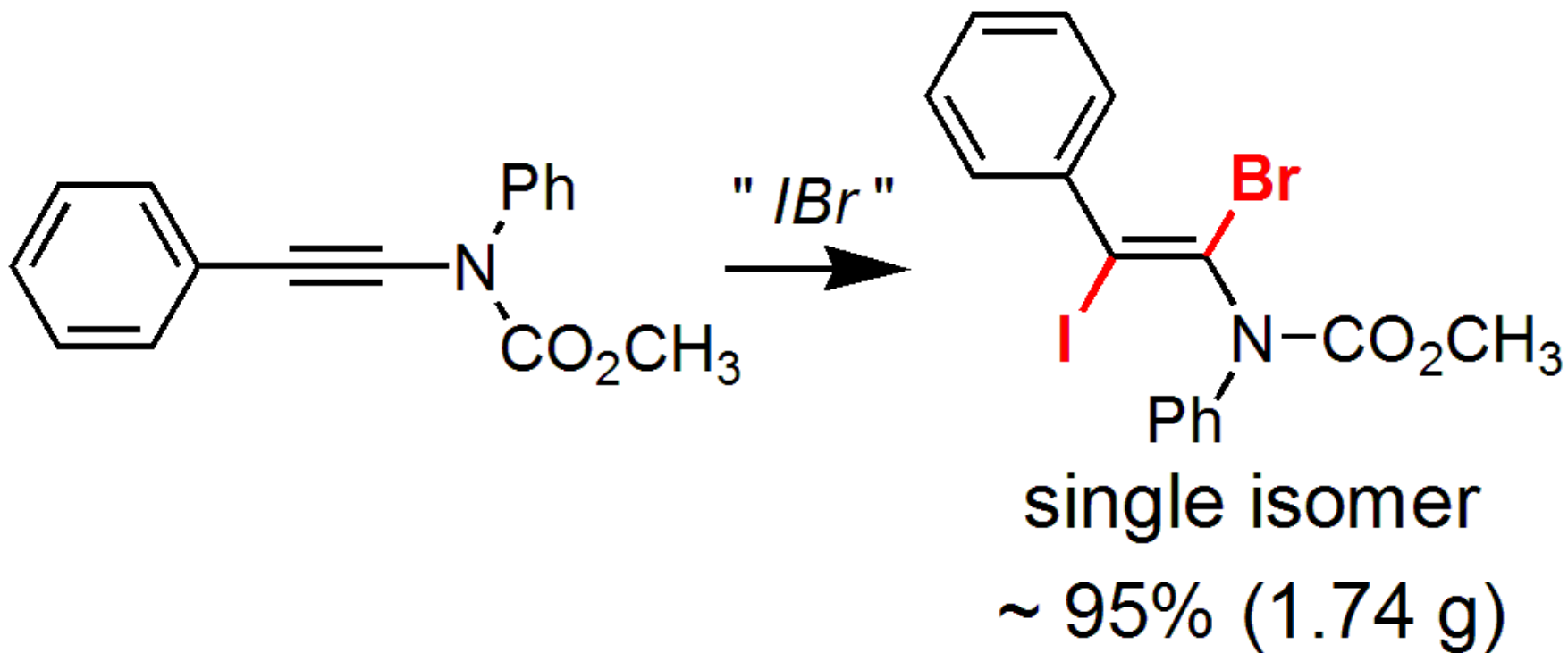
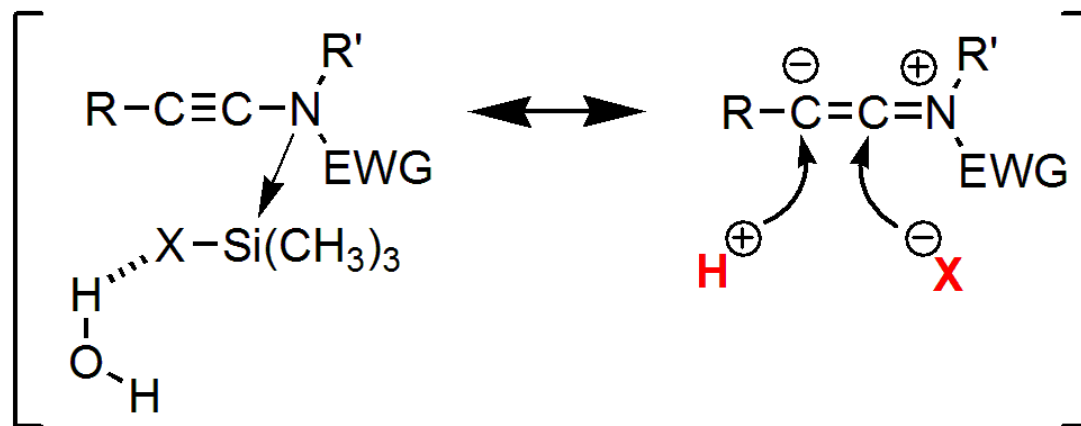
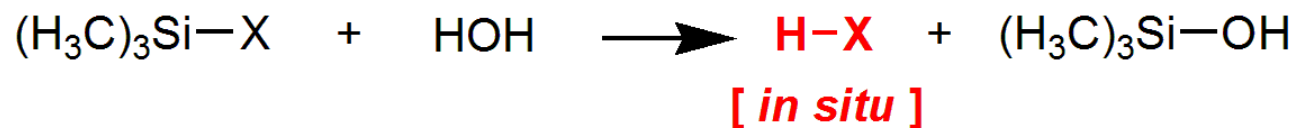
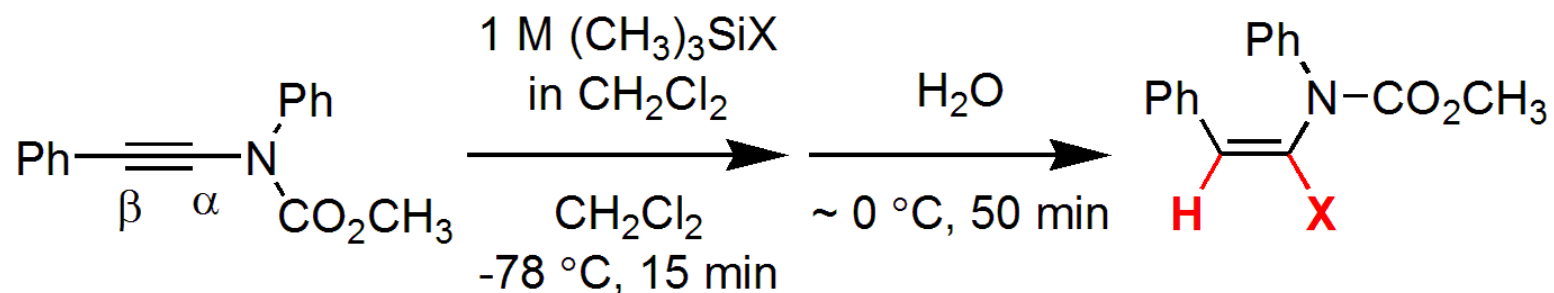


Regio-, and Stereoselective Iodobromination of Ynamides for Synthesis of (*E*)-1-Bromo-2-Iodoenamides



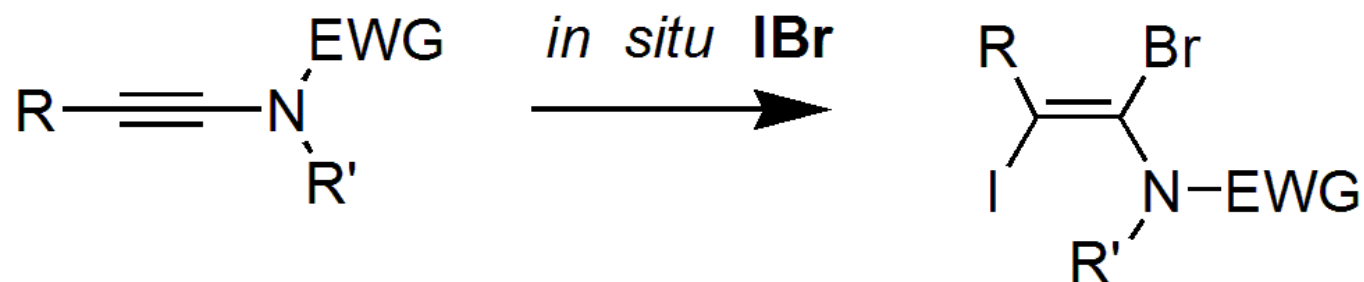
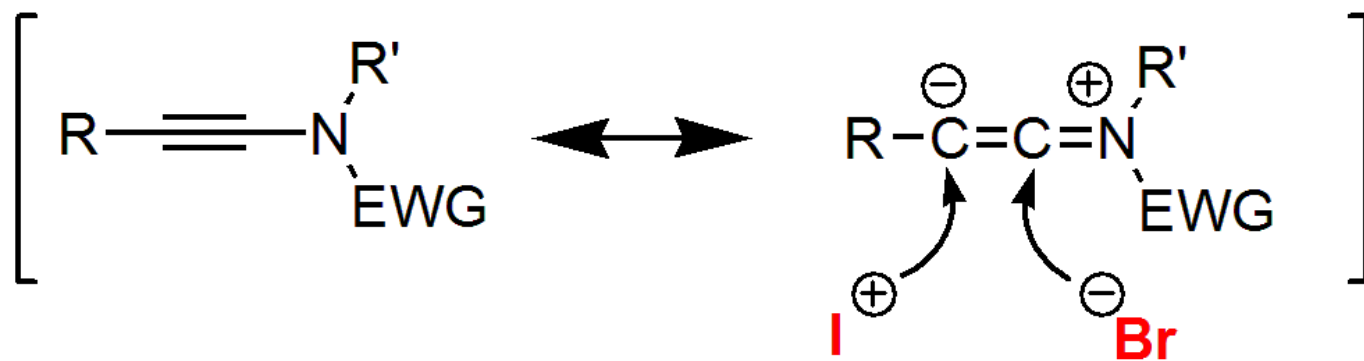
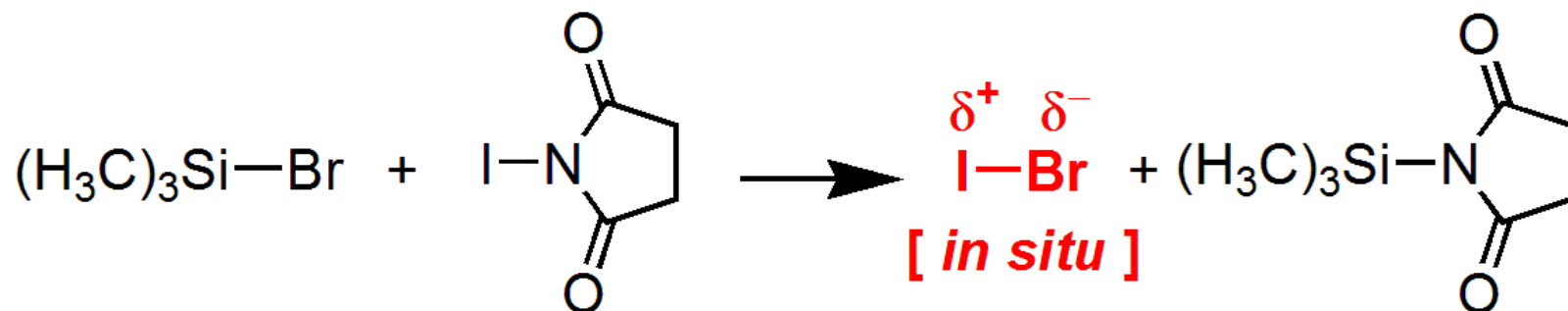
- Ide, M.; Yauchi, Y.; Iwasawa, T. *Eur. J. Org. Chem.* **2014**, 3262-3267.
- 特願 2014-014060, (2014年1月 出願)

Background

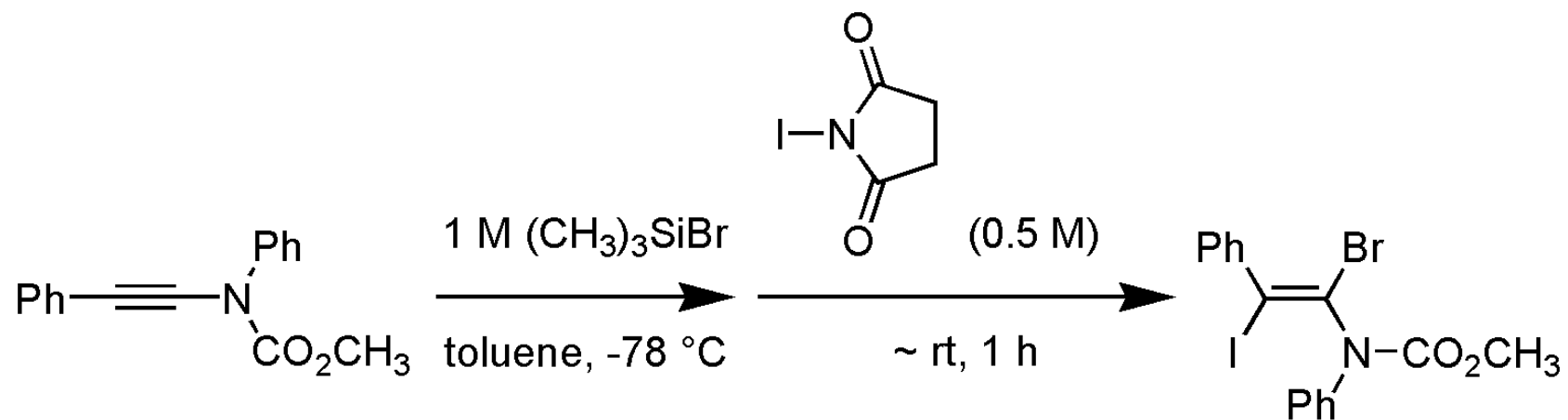


1. Sato, A. H.; Ohashi, K.; Iwasawa, T. *Tetrahedron Lett.* **2013**, *54*, 1309-1311.
2. Sato, A. H.; Ohashi, K.; Ito, K.; Iwasawa, T. *Tetrahedron Lett.* **2013**, *54*, 2878-2881.
3. Ohashi, K.; Mihara, S.; Sato, A. H.; Ide, M.; Iwasawa, T. *Tetrahedron Lett.* **2014**, *55*, 632-635.

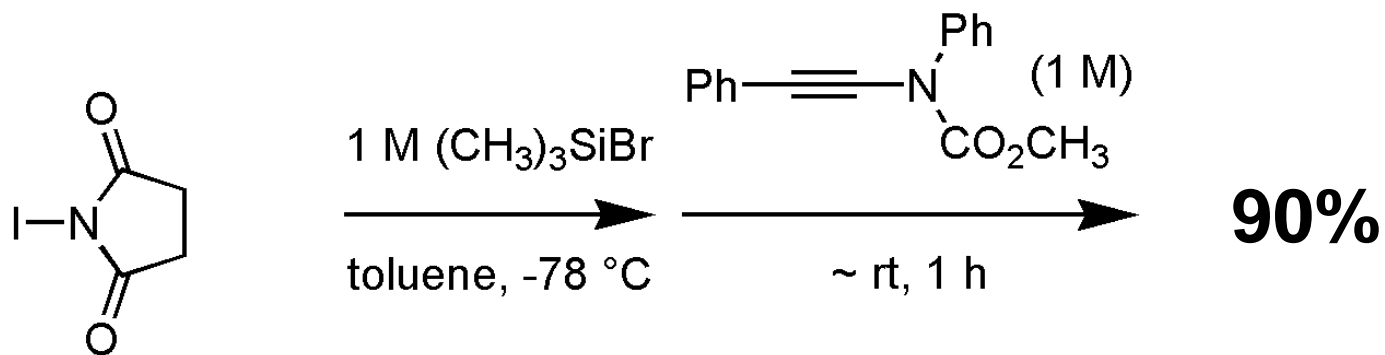
Approach



Real, *in situ* IBr

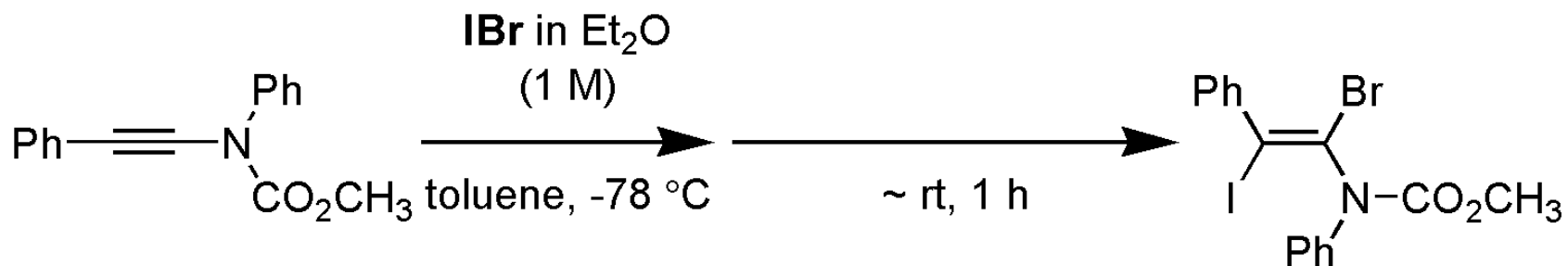


83%

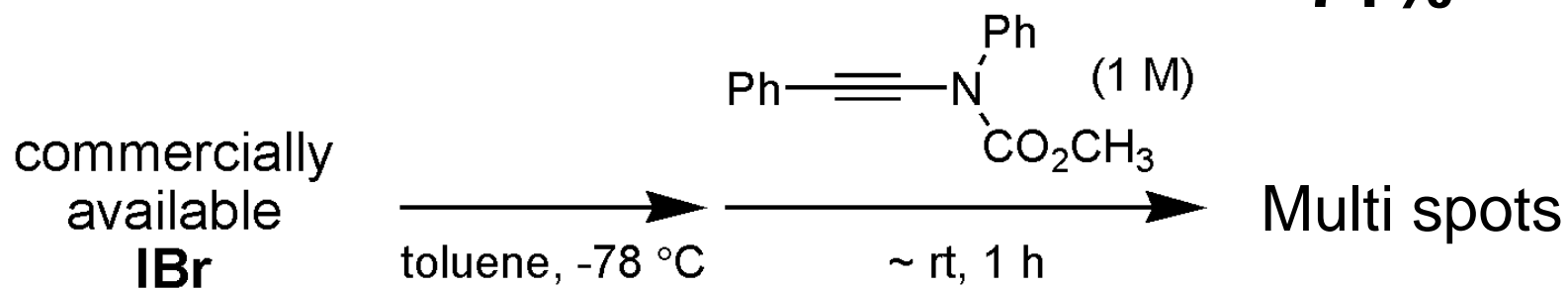


90%

Commercially available IBr (neat)



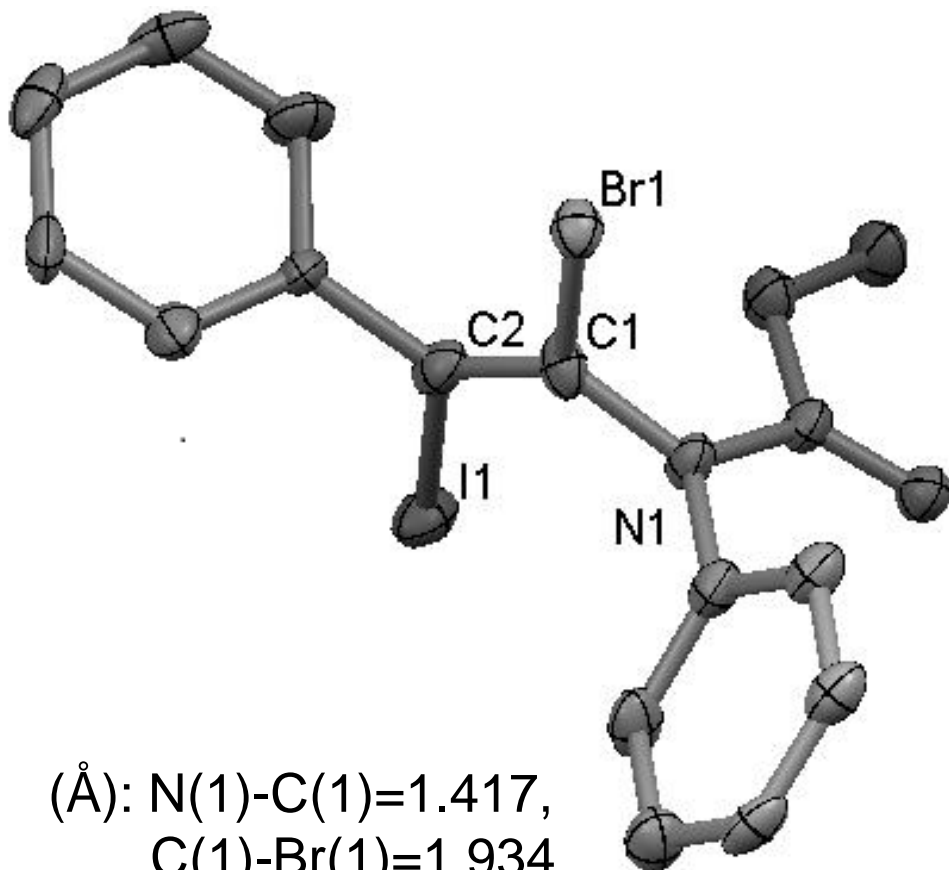
71%



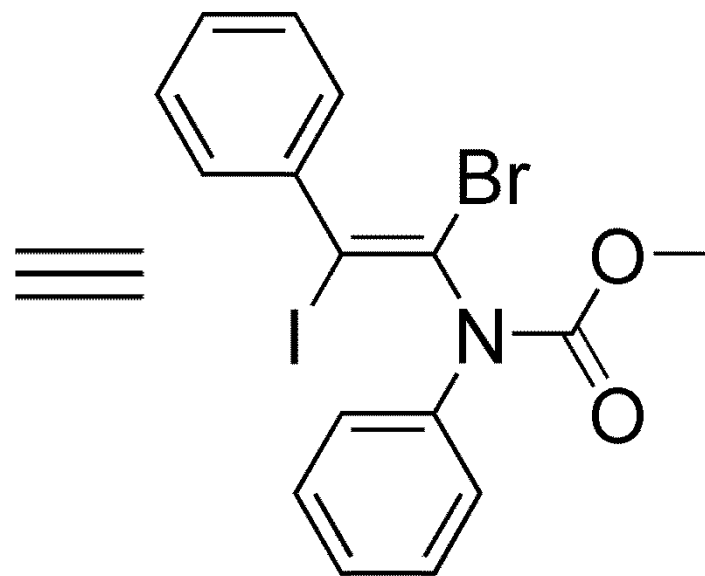
neat IBr; nasty to operate.



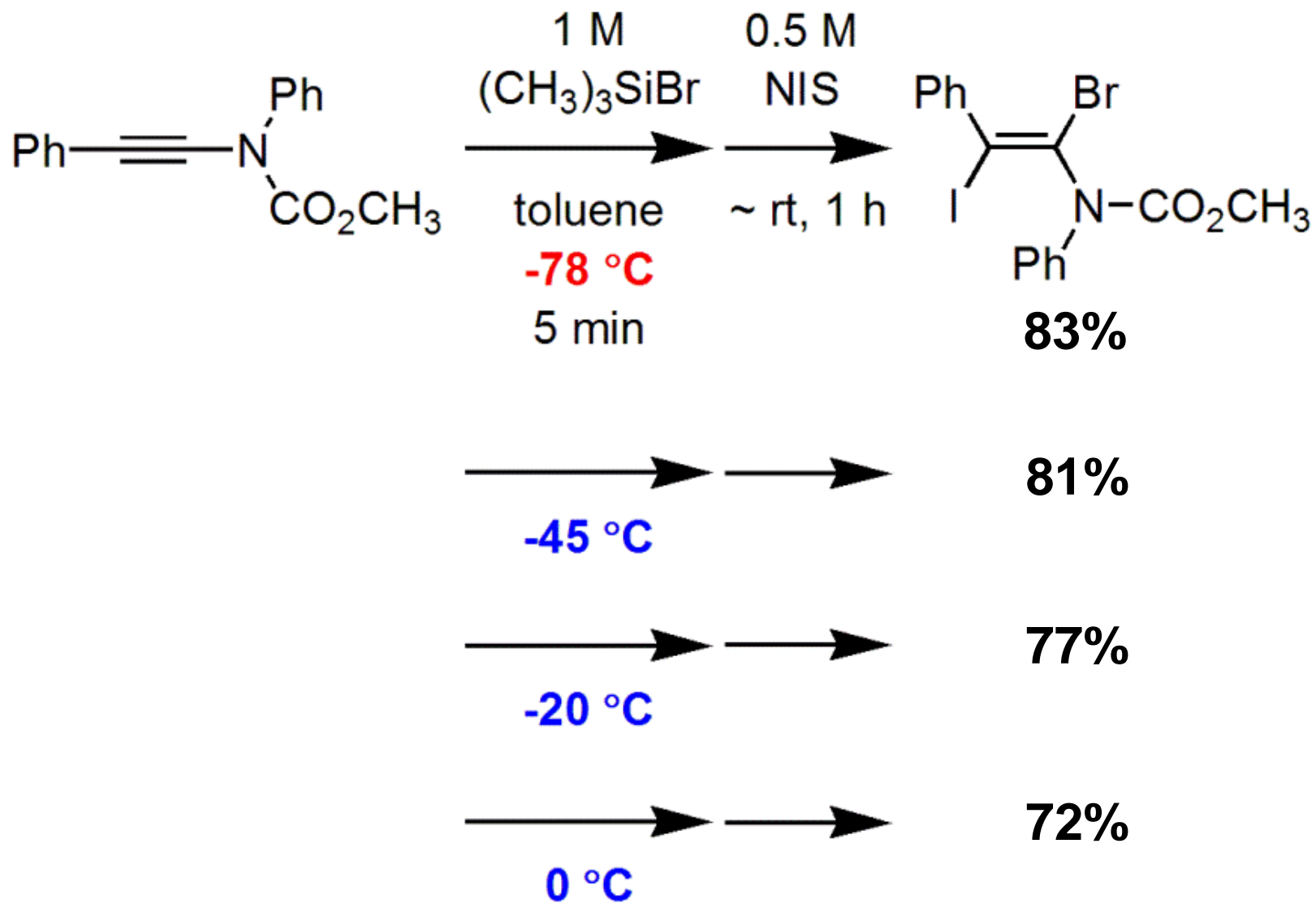
ORTEP drawing



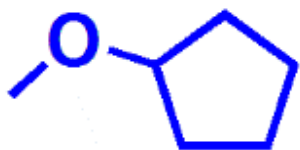
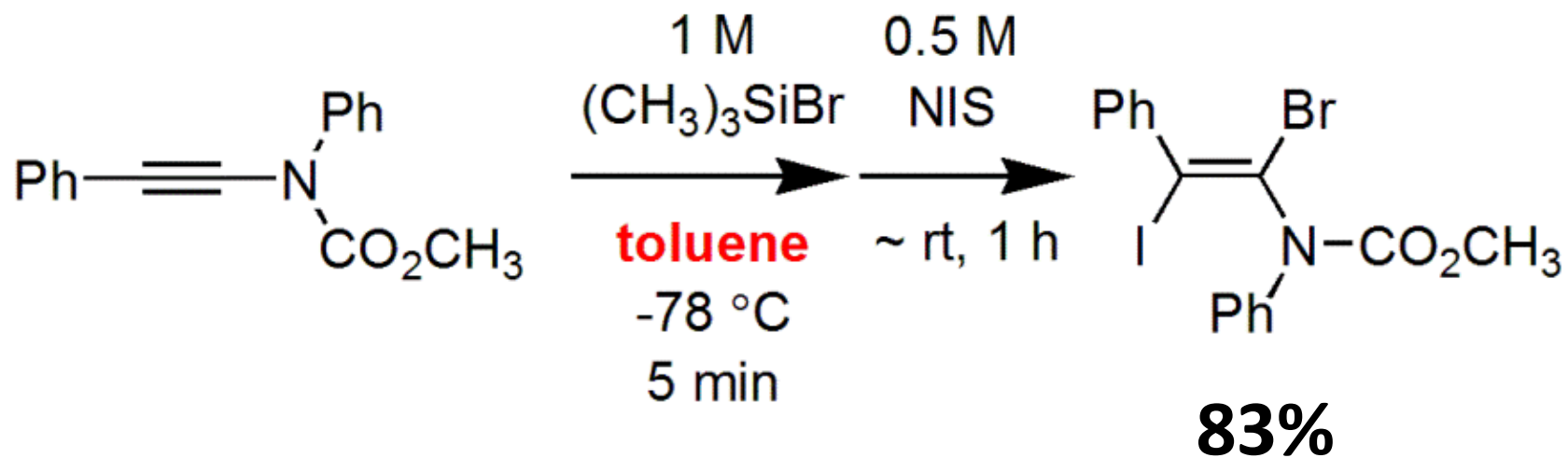
(Å): N(1)-C(1)=1.417,
C(1)-Br(1)=1.934,
C(2)-I(1)=2.114,
C(1)-C(2)=1.304.



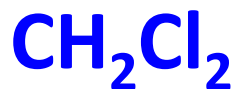
Temperature



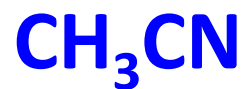
Solvent



72%



70%

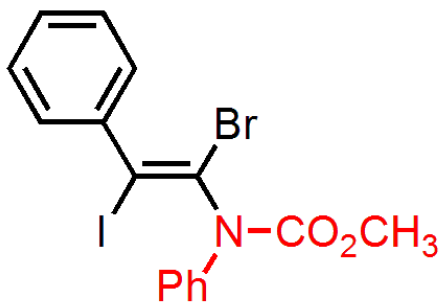


65%

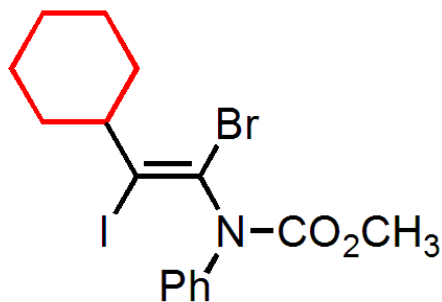


36%

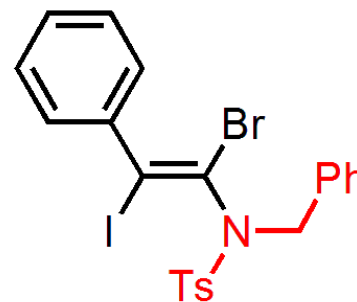
Substrate scope



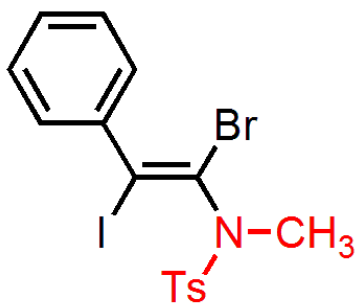
95% (1.74 g)



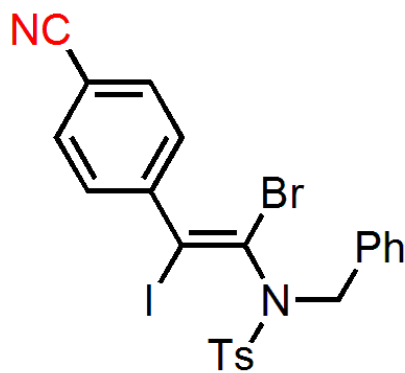
92% (1.66 g)



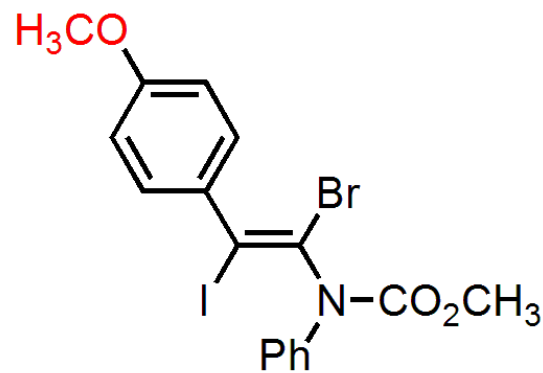
62%



57%

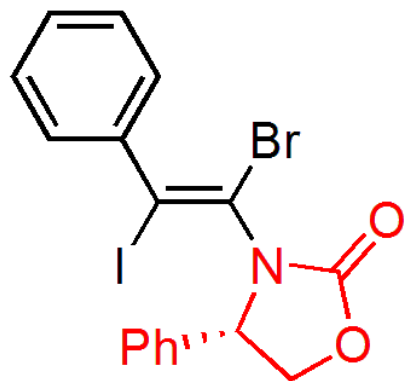


78%

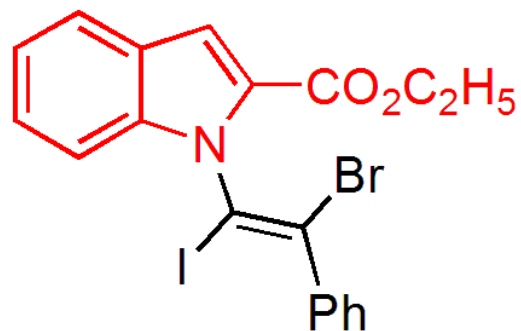


62%

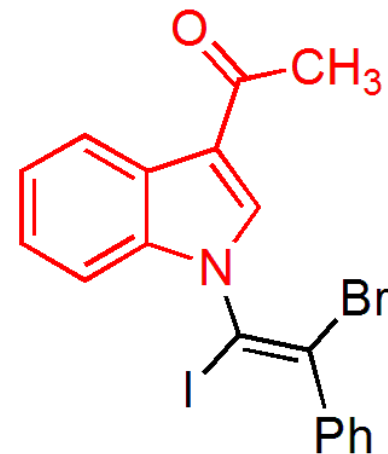
Substrate scope



75%



60%

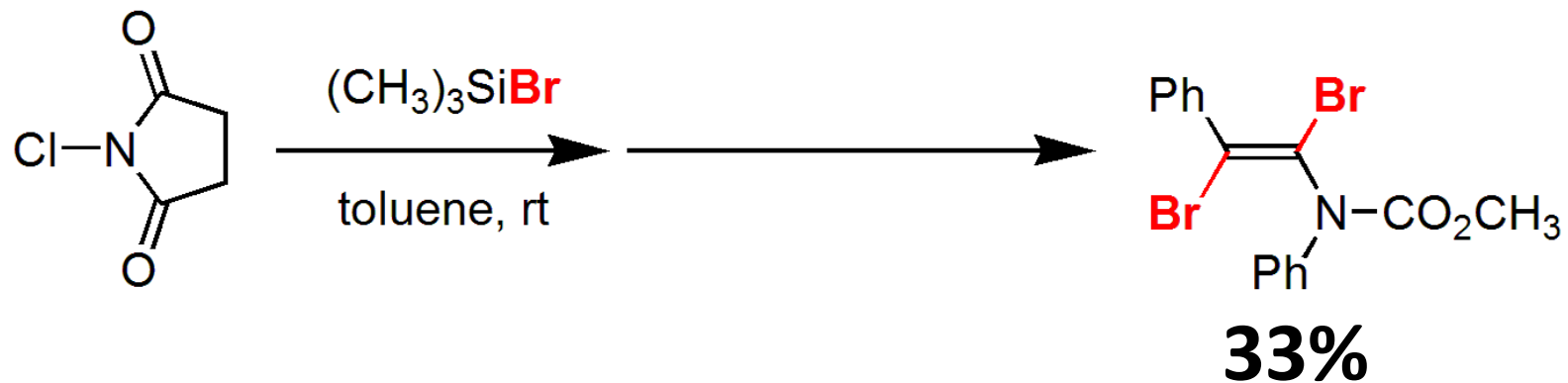
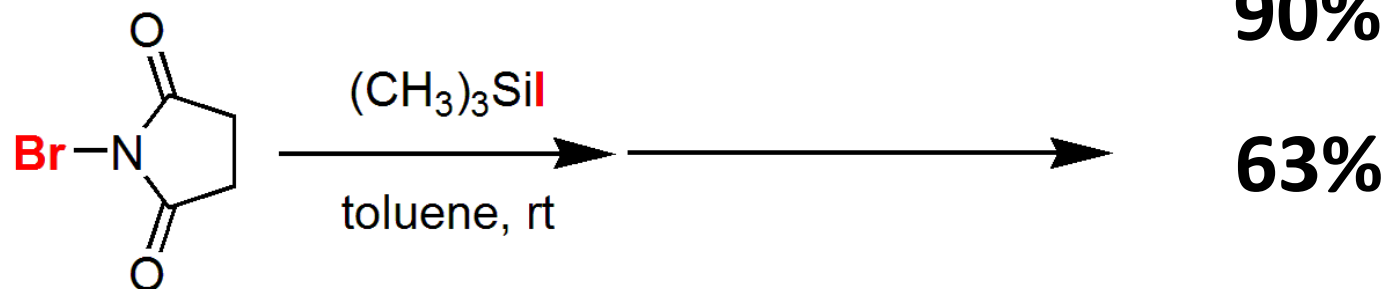
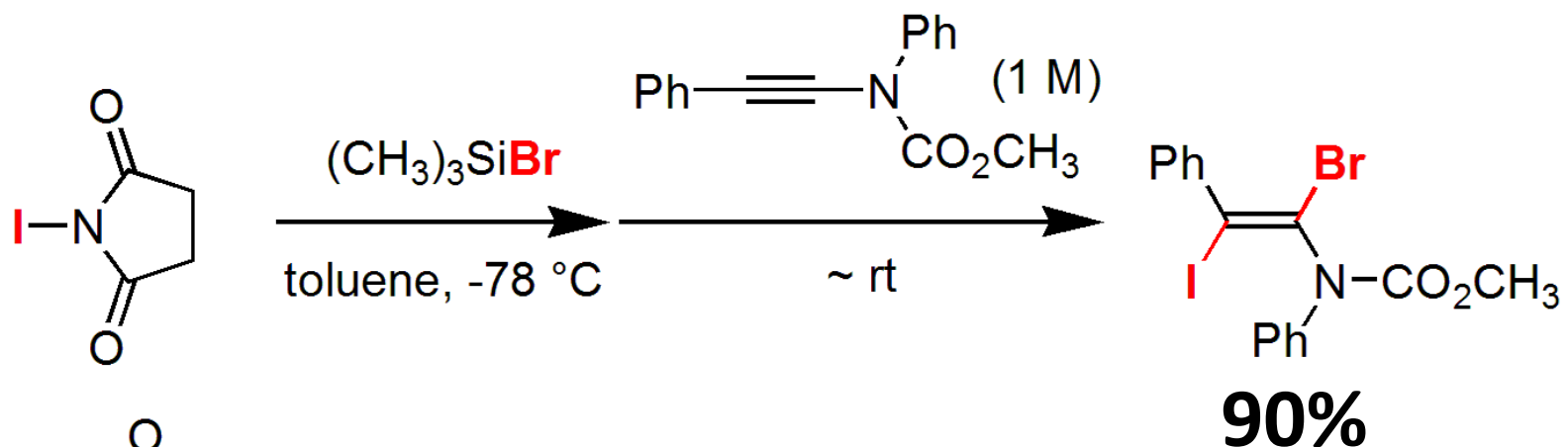


75%

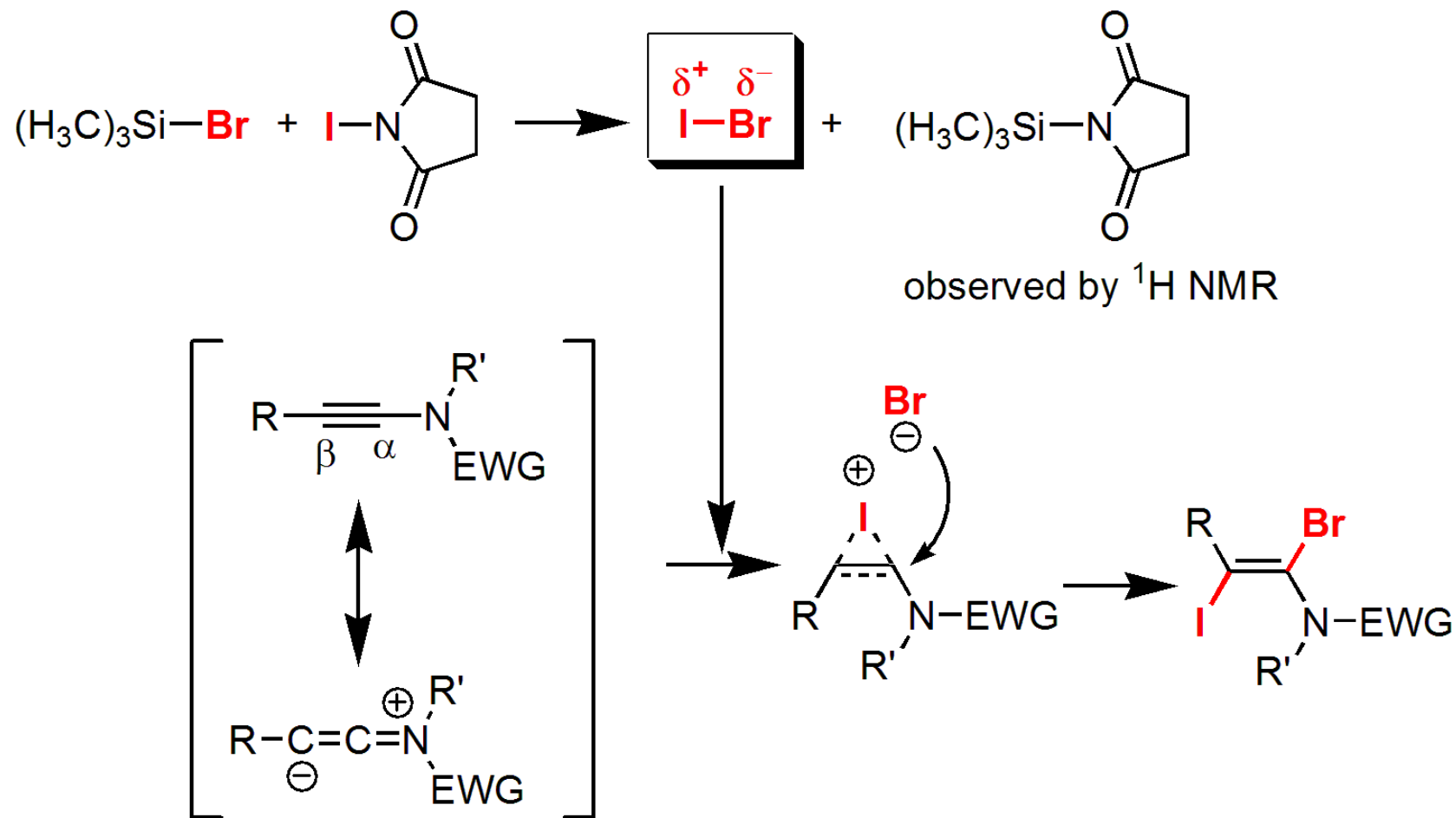
56% (83:17)

neat

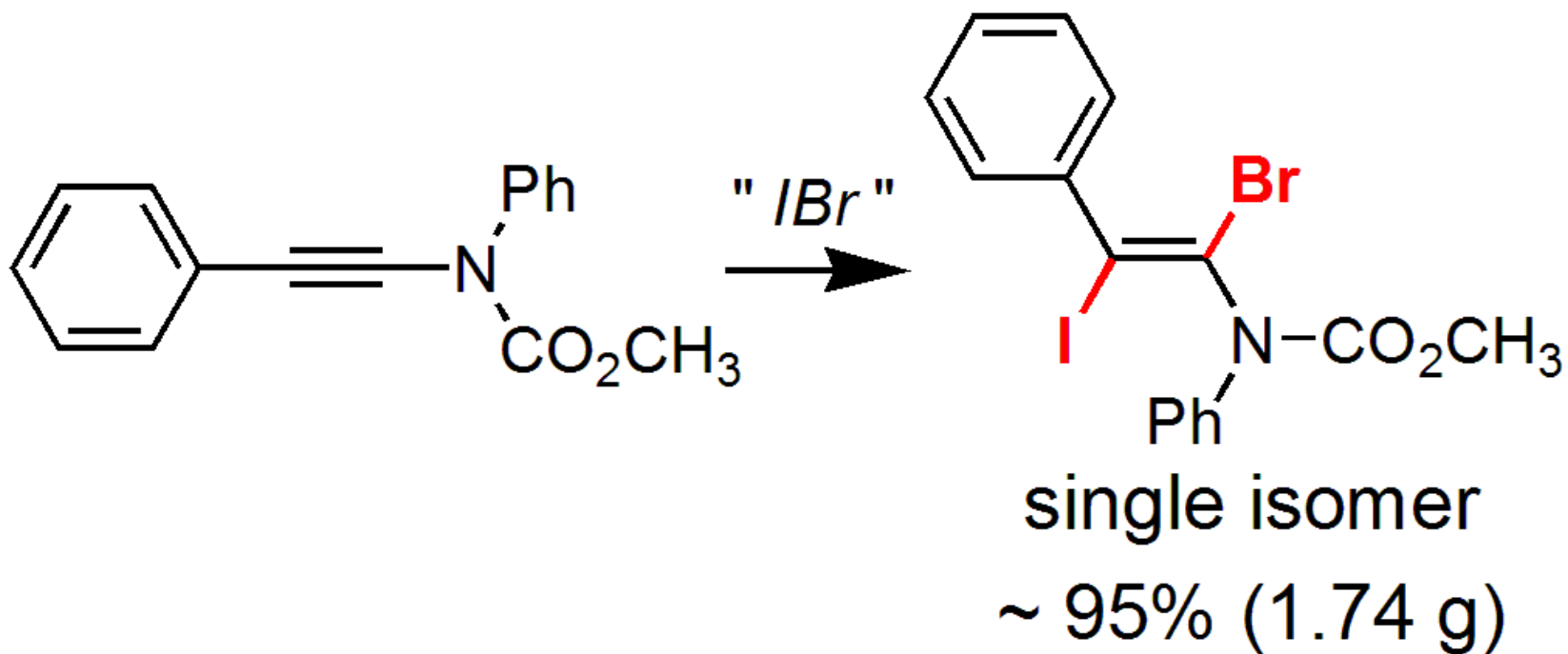
Other halogen sources



Plausible mechanism



Summary



- Ide, M.; Yauchi, Y.; Iwasawa, T. *Eur. J. Org. Chem.* **2014**, 3262-3267.
- Chikugo, T.; Yauchi, Y.; Ide, M.; Iwasawa, T. *Tetrahedron* **2014**, 70 (26), 3988-3993.
- Shiogai, R.; Yauchi, Y.; Ide, M.; Iwasawa, T. *Tetrahedron* **2014**, 70 (45), 8532-8538.
- Yauchi, Y.; Ide, M.; Iwasawa, T. *Eur. J. Org. Chem.* **2015**, 938-943.