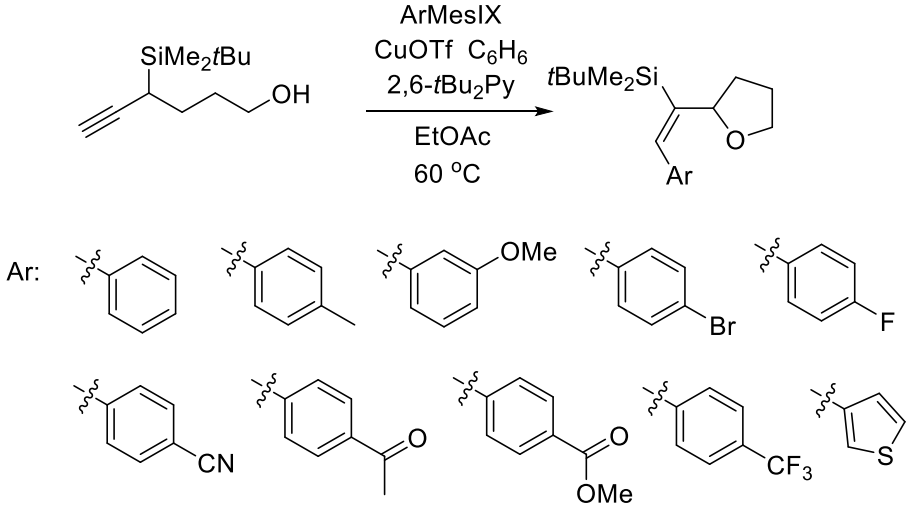
Copper-Catalyzed 1,3-Difunctionalization of Propargyl Silanes with Diaryliodanes and an Internal Nucleophile

Recently we have published preparative methods of propargyl silane 1,3-difunctionalization with concomitant silyl shift.[1] The mechanistic concept involves propargylsilane activation with an appropriate electrophile, at which point silyl group undergoes 1,2-silyl shift. This creates an electrophilic carbon center that can react with a nucleophile. Previously examined electrophiles for propargyl silane activation are proton, electrophilic halogens and selenium. Both intramolecular and intermolecular nucleophiles are viable for attacking the electrophilic carbon center.

Here we present an important extension to this methodology by the use of a formal carbon electrophile to activate the propargylsilane. In this case aryl cuprate, generated from diaryliodane, activates the propargylsilane, which undergoes a 1,2-silyl shift. This generates a carbenium ion or its equivalent, which is trapped by the intramolecular nucleophile (alcohol). Finally, arylcuprate undergoes reductive elimination, generating the target compound. Testing various diaryliodane reagents revealed that *para* and *meta* substituted aromatic groups may be introduced this way, while diaryliodanes with *ortho* substituents on both aromatic groups degrade during the reaction. Aromatic groups with electron donating and electron withdrawing substituents and some heteroaromatic groups can be used.



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References

1. a) Beļaunieks, R.; Puriņš, M.; Līpiņa, R. A.; Mishnev, A.; Turks, M. *Org. Lett.* **2023**, *25*, 4627. b) Kroņkalne, R.; Beļaunieks, R.; Ubaidullajevs, A.; Mishnev, A.; Turks, M. *J. Org. Chem.* **2023**, *88*, 13857.