

## (4) Organic:

### 2644 - Regio- and stereoselective synthesis of vicinal (*Z*)-dihaloalkenyl silanes through *in situ* generated BrCl

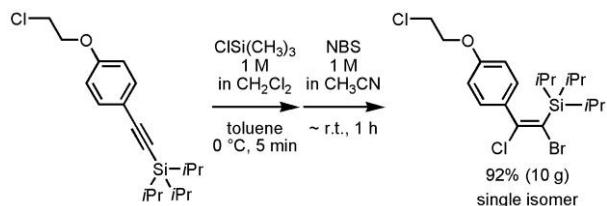
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**Abstract Body:** Vinyl substructures are one of the most fundamental moieties in organic synthesis. Dihaloalkenyl silanes are valuable building blocks in organic synthesis. The halogens and silanes can be converted into various functional groups by halogen–metal exchange and are significant for carbon–carbon bond forming reactions by way of transition-metal catalyzed reactions. Despite the utility of vicinal dihaloalkenyl silanes, their synthetic availability still remains a challenge due to the inherent difficulty in regio- and stereoselective bis-halogenation of the corresponding silyl ethynylarenes. Employment of commercially available halogens is one way, but the halogens are occasionally unpleasant to work with. Particularly, bromine monochloride (BrCl) is typically gaseous (b.p. 5 °C) and hygroscopic under an atmospheric air, which is apt to cause trouble to chemists in handling of reactions, purification, and safety.

Herein we report the simple protocol enables an efficient regio- and stereoselective bromochlorination of silyl ethynylarenes (Scheme1). The *in situ* BrCl was readily prepared by reaction of chlorotrimethylsilane with *N*-bromosuccinimide, which then perfectly added to the triple bond in a *syn*-mode. The high-yielding transformations formed each olefin as a perfectly single isomer, which occurred at 0 °C ~ room temperature in just 1 h. In addition, the reaction system has significance to generate BrCl *in situ* formally, because toxic BrCl is handling-difficult in bench experiments owing to its low boiling point of 5 °C. Thus, the methods achieved the selective bis-halogenation of silyl ethynylarenes, and provide a potentially synthetic scaffold for synthesis of differentially all-carbon tetrasubstituted olefins.



**Scheme 1.** *syn*-Selective bis-halogenation of silyl ethynylarenes.