

## 論文内容の要旨

論文題目      Synthesis, Properties and Applications of Functionalized Benzo[*b*]siloles

[ベンゾ[*b*]シロール誘導体の合成, 物性および応用]

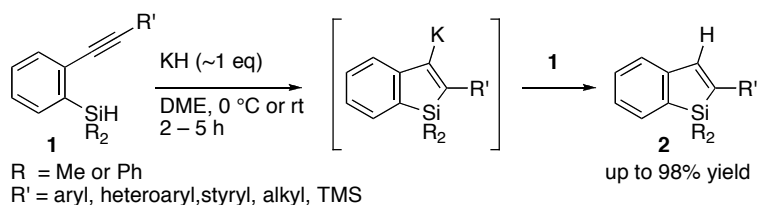
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The present thesis describes the development of two novel synthetic methods for benzo[*b*]silole (hereinafter benzosilole) derivatives, together with the investigation of their properties and applications as organic semiconductors.

Chapter 1 describes the potential of benzosiloles for materials science, based on their low LUMO level. In order to investigate their potential, efficient preparation methods for benzosilole-based materials are necessary, and therefore development of synthetic methodologies for benzosilole is the primary motivation of the author.

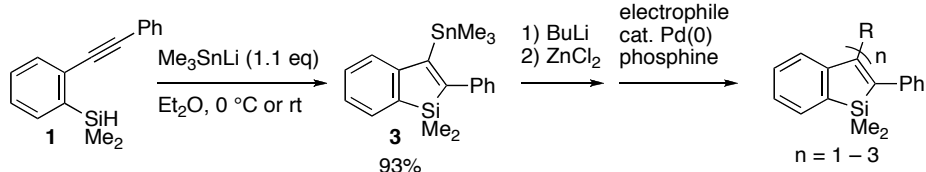
In Chapter 2, base-promoted cyclization of (2-alkynylphenyl)silane **1** into benzosilole was investigated. The author has found that potassium hydride in 1,2-dimethoxyethane promotes the cyclization reaction in good yield. The reaction showed broad scope and afforded a variety of 2-substituted benzosiloles **2** in good yield. It is assumed that the silane moiety was deprotonated first, and then the resulting silyl anion added across the triple bond in intramolecular fashion to generate a 3-potassiobenzosilole. Subsequent protonation of this intermediate by unreacted **1** yielded the product.

**Scheme 1.**



Based on the concept of modular synthesis, in Chapter 3 the generation of a stable 3-metallobenzosilole was investigated, in order to obtain various 2,3-substituted benzosiloles. Trimethylstannyl lithium in diethyl ether promoted the cyclization of **1** into a stable 3-stannylbenzosilole **3** in excellent yield. The reaction is assumed to be initiated by the stannyl lithium addition across the triple bond, and then the generated vinyl lithium attacked the silicon atom, promoting cyclization together with elimination of hydride. The obtained 3-stannylbenzosilole **3** was transmetalated into the corresponding zinc intermediate, which was cross-coupled with electrophiles in the presence of Pd(0) to obtain a variety of 2,3-disubstituted benzosiloles as well as molecules containing multiple benzosilole units.

**Scheme 2.**



In Chapter 4, properties of benzosiloles and their applications are described. These compounds were found to show high electron affinity and form stable amorphous films showing high electron-drift mobility. Based on these properties, selected benzosiloles were used as *n*-type organic semiconductors for organic light-emitting diodes.

