Category

Synthesis of Materials and Unnatural Products

Key words

hypersilyl groups cross-coupling $\sigma-\pi$ conjugation A. LESBANI, H. KONDO, J.-I. SATO, Y. YAMANOI,* H. NISHIHARA* (THE UNIVERSITY OF TOKYO, JAPAN)

Facile Synthesis of Hypersilylated Aromatic Compounds by Palladium-Mediated Arylation Reaction *Chem. Commun.* **2010**, *46*, 7784-7786.

A New Method for Hypersilyl Aromatic Compounds



Significance: Incorporation of the tris(trimethylsilyl) group, known as hypersilyl group, into π -conjugated compounds is a promising strategy for the development of unique optoelectronic materials. This super-sterically demanding functionality can not only suppress π - π stacking, which often leads to emission quenching, but also offers effective $\sigma-\pi$ conjugation with adjacent π -electron systems. Nevertheless, synthetic methods for hypersilylated compounds have been quite limited, which often accompany cleavage of weak Si–Si σ-bonds. Herein, the authors communicate the palladiumcatalyzed cross-coupling of tris(trimethyl)silane with aryl iodides to provide hypersilylated aromatic compounds, leaving the Si-Si bonds intact. Furthermore, they show that other hydrooligosilanes are applicable to this reaction.

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 Synfacts 2011, 1, 0034-0034
 Published online: 21.12.2010
 Dol: 10.1055/s-0030-1259153;
 Reg-No.: S15810SF

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Comment: It is noteworthy that 5,5'-bis(hypersilyl)bithiophene shows highly efficient solid-state blue fluorescence ($\Phi_F = 0.55$), probably due to suppression of intermolecular stacking in the solid state by bulky hypersilyl groups. A significant red shift of the UV absorption maximum of the silyl-substituted bithiophene ($\lambda_{max} = 351$ nm) compared to bithiophene ($\lambda_{max} = 304$ nm) was also observed, indicating the existence of effective σ - π conjugation.