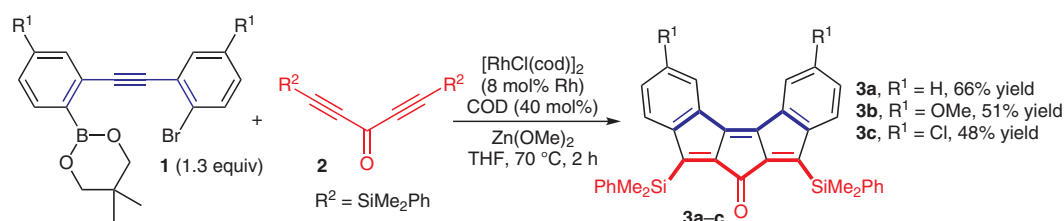


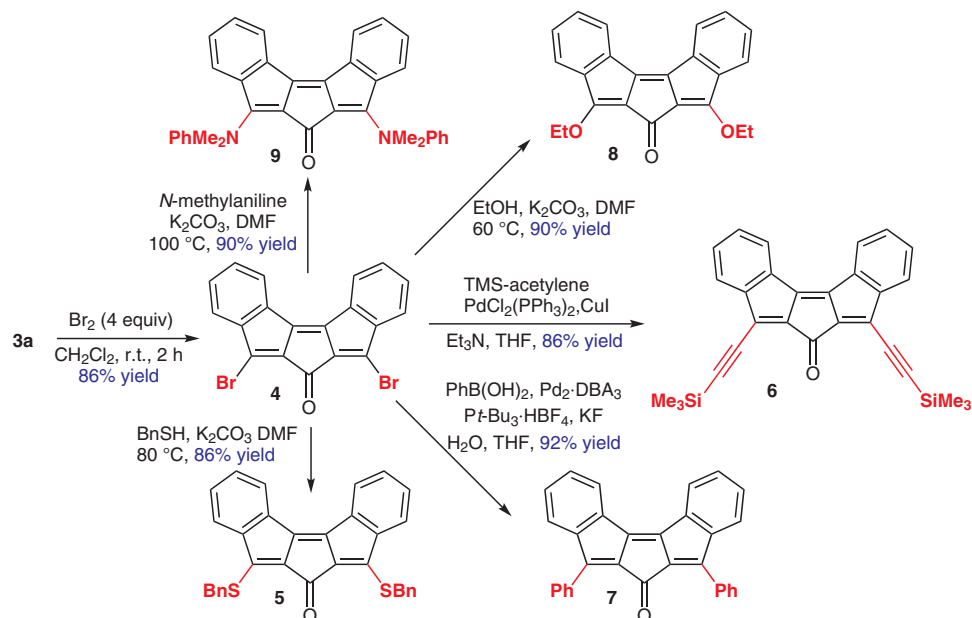
R. SHINTANI*, S. KISHIKAWA, K. NAKAMURA, T. TSUDA, K. NOZAKI* (OSAKA UNIVERSITY, TOYONAKA AND THE UNIVERSITY OF TOKYO, JAPAN)

Synthesis of Carbonyl-Bridged Dibenzofulvalenes and Related Compounds by Rhodium-Catalyzed Stitching Reaction
Chem. Commun. **2019**, 55, 1072–1075.

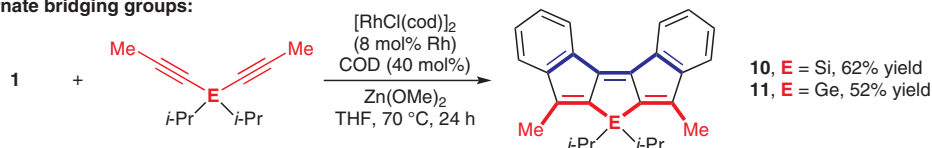
Rhodium Cross-Stitching Sews Up Dibenzofulvalenes



Selected examples of product diversification:



Alternate bridging groups:



Significance: Extended conjugated aromatic molecules possess unique optoelectronic properties that have proven critical for the development of functional materials. Conventional methods for the construction of such polycyclic structures are often linear, iterative processes that hinder scale-up and further development. This method provides hitherto unreported carbonyl-bridged dibenzofulvalenes in a single step by an alkyne insertion cascade.

Comment: Zinc methoxide uniquely enables boronic ester **1** and ketone **2** to undergo coupling and cyclization via rhodium(I) catalysis, affording a modest variety of products. Compound **3a** can be efficiently transformed into dibromide **4**, and the latter compound is easily diversified into a variety of substituted compounds possessing a range of optical and electronic properties. Finally, this method proved able to furnish C-, Si-, Ge-, S-, and P-bridged structures.

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Synfacts 2019, 15(03), 0241 Published online: 15.02.2019
DOI: 10.1055/s-0037-1612220; Reg-No.: S00319SF

Category

Synthesis of
Materials and
Unnatural Products

Key words

polycyclic aromatic
hydrocarbons

alkynylbenzenes

rhodium catalysis

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