

C-H Activation: A New Tool for the Preparation of Phenylene Scaffolding

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We have developed a new strategy for the preparation of phenylene scaffolding with potentially useful optoelectronic properties. Utilizing the iridium-catalyzed C-H activation chemistry developed by Hartwig, Miyaura and Smith, we have successfully developed a simple and rapid method for the convergent synthesis of rigid polyphenylene dendrons. We have demonstrated that an approach consisting of C-H activation/borylation followed by a Suzuki coupling with a 1,3-dihalobenzene can be iterated to build dendrons up to the third generation in good yield. This is the first example of an iterative synthetic method employing C-H activation of an arene as the main functionalization strategy.

The development of these large dendritic architectures exemplifies the limitations and possibilities of this mild and remarkably robust chemistry. The Ir-catalyzed borylation is mild and tolerant to many functional groups, proceeds in high yield, and products are typically simple to purify. Since this methodology displays selectivity that is dominated by sterics (borylation occurs at the least hindered position of the benzene ring), more highly sterically hindered moieties such as the higher-generation dendrons do not go to completion even with high initial catalyst loadings. However, we have shown that with sequential addition of catalyst, high conversions are possible using low (1-2 mol%) catalyst loadings and sequential addition. This is a surprising result that suggests alternative decomposition pathways for the Ir catalyst utilizing these substrates.

