

ABSTRACT

Novel approaches to utilizing alkynes in transition metal-catalyzed [2+2+2] cycloadditions and photochemical [2+2] cycloadditions were investigated with respect to the potential applications of these transformations.

First, a chemo- and regioselective fully intermolecular cocyclootrimerization of internal alkynes with a commercially available ethynyl boronate was developed using Ru-catalysis and its mechanism was examined using DFT calculations. The established method allows for a straightforward preparation of various 1,4-diborylated benzenes, which can serve as multifunctional building blocks in organic synthesis. In particular, the products can be used in cross-coupling, carbonylation and oxidation reactions to access a broad variety of contiguously substituted arenes, such as natural products mirandamycin and violaceoid C.

Second, a comparative study of catalytic and uncatalyzed photocycloadditions between alkynes and quinones was undertaken. Contrary to the recent reports, irradiation with visible light alone is sufficient to obtain not only the [2+2] cycloaddition products, but also several products of cascade transformations. Thus, depending on the structure of the quinone used, either carbo- or heterocycloaddition pathway is mainly realized, giving rise either to annulated cyclobutenes or reactive *para*-quinone methides, respectively. The investigation of the chemo- and regioselectivity of these reactions allowed to correct three previously reported product structures and establish a connection between the non-catalytic and catalytic protocols. Chiefly, the photochemically generated *para*-quinone methides were found to react smoothly with carbon and heteroatom nucleophiles even in the absence of additional reagents, hence creating opportunities for the development of new cascade transformations involving alkynes and quinones.

Overall, the present work illustrates how new synthetically useful intermediates can be assembled from alkynes and other readily available starting materials by the means of catalytic and photochemical cycloaddition reactions.