2+2 cycloaddition of alkynyl boronates

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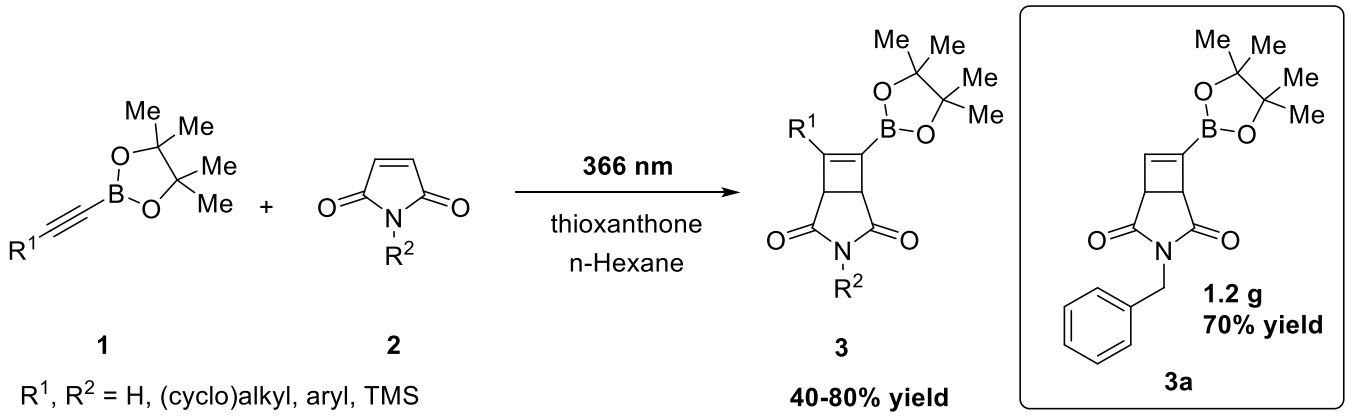
Organoboron compounds have firmly established their position as valuable synthetic intermediates in the chemists' toolbox. The scope of the known transformations is extremely wide – from Nobel prize winning Pd-catalyzed Suzuki reaction to radical photoredox couplings and nucleophilic heteroatom insertions [1].

General synthetic routes to organoboronates are also well known and include hydroboration, lithiation-borylation sequence, or the Suzuki-Miyaura reaction. However, classes of boron-containing building blocks (especially for small ring scaffolds) are still underrepresented in the literature. For exemple, cyclobutene-1-boronates have been only rarely accessed via Pd-catalyzed [2] or electrophilic borylation [3].

In this work, a number of maleimide-derived cyclobuteneboronates **3** were prepared in moderate to good yields via a light-mediated cycloaddition. The parent boronate **3a** was synthesized on a 1 g-scale and the synthetic utility of the obtained products was shown in a series of transformations, including oxidation, reduction, cycloadditions and Suzuki reactions.



1 **2** **3** **3a**

R^1, R^2 = H, (cyclo)alkyl, aryl, TMS

40-80% yield

The developed method provides an access to a variety of polyfunctionalized cyclobutene-1-boronates, that can be considered as potentially useful building blocks for medicinal chemistry.

[1] *Synthesis* **2020**, 52, 2761–2780
[2] *Bioorg. Med. Chem. Lett.* **2021**, *36*, 127823.
[3] *Angew. Chem. Int. Ed.* **2022**, *61*, e202113333.