

# ALTERNATING RADICAL STABILITIES. A CONVERGENT ROUTE TO TERMINAL AND INTERNAL BORONATES

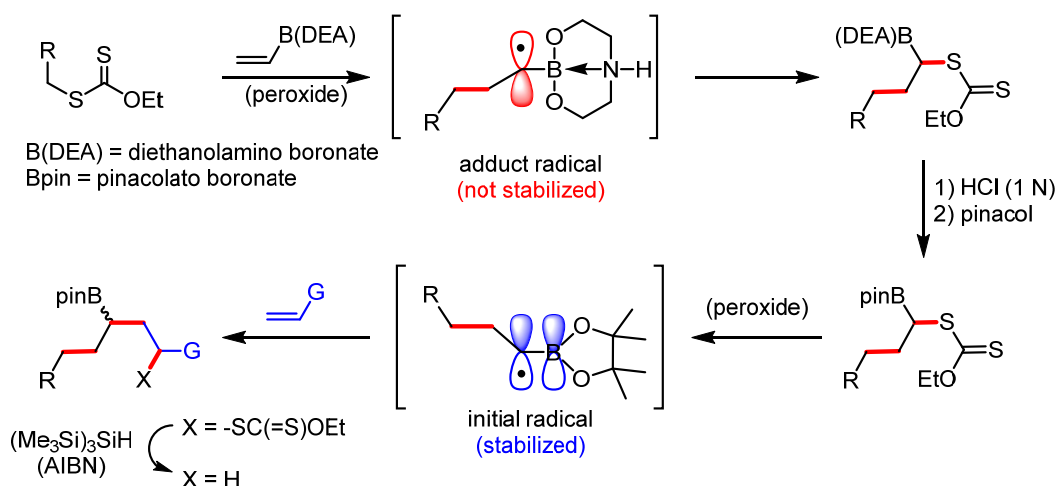
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Boronic acids and esters have long proven their importance; in the field of catalysis, as bioactive substances or as synthetic intermediates, all thanks to the reactivity of the boron center.<sup>1</sup> So far, accessing such compounds has mostly relied on traditional ionic and organometallic reactions, however, radical processes have recently found interest to tackle this synthetic challenge.<sup>2</sup>

The xanthate addition-transfer process has already shown great efficiency in the construction of highly functionalized boronates.<sup>3</sup> Its broad tolerance for polar group makes it a powerful method for the construction of previously hardly accessible organoboron compounds. However, the lack of an efficient method to obtain diverse  $\alpha$ -boronyl xanthates has limited the study of such promising substrates.

We developed a method to tune the stability of the carbon radical adjacent to the boron to perform two successive xanthate addition-transfer reaction and obtain highly decorated boronates.<sup>3</sup> The diethanolamino boronate, being  $sp^3$  hybridized, does not stabilize the radical, however the pinacolato boronate stabilize the radical in alpha position thanks to its empty p-orbital. By alternating the substituent on the boron, it is possible to control the behavior of the  $\alpha$ -boronyl xanthates and obtain a large variety of internal and terminal boronates.



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