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. 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.

The xanthate addition-transfer process has already shown great efficiency in the construction of highly functionalized boronates. 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 α-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. The diethanolamino boronate, being sp³ 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 α-boronyl xanthates and obtain a large variety of internal and terminal boronates.

\[ \text{B(DEXA) = diethanolamino boronate} \]
\[ \text{Bpin = pinacolato boronate} \]

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[4] Huang, Q.; Michalland, J.; Zard, S. Z. manuscript submitted for publication