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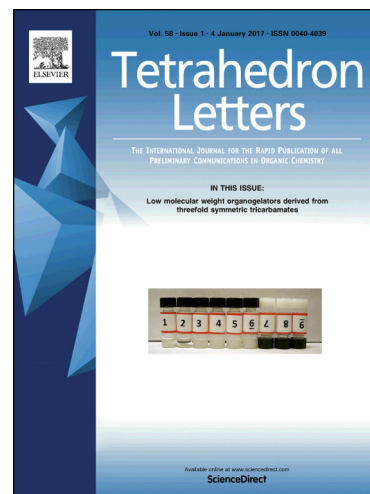
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## Enantioselective Organocatalytic Conjugate Addition of Organoboron Nucleophiles

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**Abstract**

This review covers the use of organoboron nucleophiles in enantioselective conjugate additions catalyzed by organic-based catalysts. It is divided into sections based on the type of nucleophile, with each section arranged in roughly chronological order. The categories of nucleophiles are alkynyl, alkenyl, and aryl boronates or borates. The principle modes of catalysis, iminiums formation and boron chelation, are covered.

**Keywords**

Conjugate addition, organocatalysis, organoboronates, enantioselective catalysis

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**1. Introduction**

Stabilized carbon anions have been added to electron deficient olefins for over 130 years.<sup>1</sup> Gilman's seminal report of organocuprates adding in a 1,4-addition to "benzalacetophenone" (i.e., chalcone)<sup>2</sup> established an alternative method to approach conjugate addition carbon-carbon bond formation that was later made catalytic. In the years since those discoveries, diastereoselective and enantioselective versions of those transformations have been developed. Approaches include enone activation via Lewis acids,<sup>3</sup> Brønsted acids,<sup>4</sup> or iminium<sup>5</sup> catalysis as well as catalytic control of the nucleophile, principally via asymmetric organocatalysis<sup>6</sup> or copper,<sup>7</sup> rhodium,<sup>8</sup> and palladium<sup>9</sup> complexes. Many of the latter approaches take advantage of the readily available and extraordinarily practical unsaturated organoboron nucleophiles, but their use in combination with organocatalysis has been significantly more limited. While the conjugate addition of these nucleophiles has been reviewed for organometallic catalysis, this review will address their use in organocatalytic conjugate additions. Because of the Lewis acidic nature of many of the organoboron intermediates in organocatalytic reactions, intriguing and novel reactivity is often seen along with outstanding stereocontrol.

**2. Background**

The strategy for the use of Lewis acidic nucleophiles with organocatalysis has roots in studies by H.C. Brown and Akira Suzuki conducted fifty years ago in the 1960's.<sup>10</sup> They found that alkyl boranes, readily generated via the hydroboration of alkenes, add to  $\alpha,\beta$ -unsaturated ketones and aldehydes to form  $\beta$ -alkylated products (**3**, Scheme 1). Doing so when the electrophile had prior  $\beta$ -substitution (including cyclic enones) was difficult, but finding that the mechanism of the addition was radical-based allowed them to overcome this obstacle by using catalytic oxygen, diacyl peroxide, or photoactivation.

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