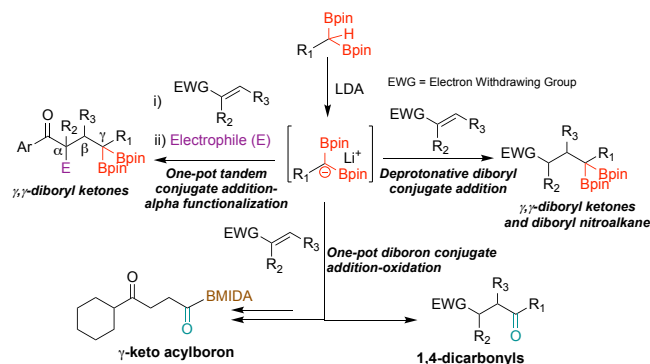


# Boron-promoted Deprotonative Conjugate Addition: Development of Geminal diborons as Versatile Soft Pronucleophiles and Acyl Anion Equivalents

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**ABSTRACT:** Conjugate addition of  $\alpha$ -boron stabilized carbanions is an underexplored reaction modality. Existing methods require deborylation of geminal di/triboryl alkanes and/or the presence of additional activating groups. We report the 1,4-addition of  $\alpha,\alpha$ -diboryl carbanions generated via deprotonation of corresponding geminal diborons. The methodology provided a general route to highly substituted and synthetically useful  $\gamma,\gamma$ -diboryl ketones. The development of geminal diborons as soft pronucleophiles also enabled their use as acyl anion equivalents via one-pot tandem conjugate addition-oxidation sequence.

Geminal diborons have emerged as versatile building blocks for preparation of a variety of structurally complex organic compounds.<sup>1</sup> In comparison to other 1,1-organodimetallic reagents, the geminal organodiborons possess several advantages such as enhanced stability, ease of handling and easy accessibility from abundantly available substrates. Various creative methods have been reported for synthesis and synthetic applications of these reagents.<sup>1-3</sup> These organoborons can be activated via two complimentary strategies. Treatment of a geminal diboryl alkane with an alkoxide or hydroxide base provides boron stabilized carbanion via monodeborylation.<sup>4-6</sup> On the other hand, the use of a hindered base leads to  $\alpha,\alpha$ -diboryl carbanion via deprotonation.<sup>1</sup> Matteson and others have shown that the  $\alpha$ -boryl and  $\alpha,\alpha$ -diboryl carbanions can be used as hard nucleophiles in C-C bond formation with electrophiles via metal catalyzed cross-coupling, nucleophilic substitution or 1,2-addition pathway (Boron-Wittig reaction).<sup>1,2,7,8</sup>

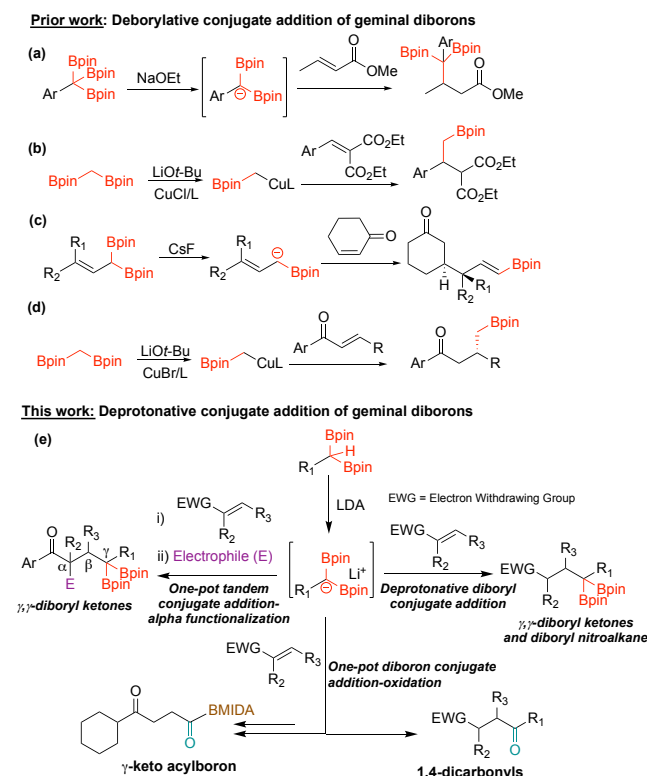
In contrast to the above mentioned well-established reactivity of  $\alpha$ -boryl carbanions, the feasibility of 1,4-addition of these nucleophiles is beginning to emerge only recently. Two pioneering reports<sup>9,10</sup> demonstrated the deborylative conjugate addition of geminal diboryl/triboryl alkanes (Figure 1, a-b). Thereafter, an elegant application of this concept was reported via the 1,4-addition of  $C(sp^3)$ -carbanions stabilized by boron and allyl groups (Figure 1c).<sup>11</sup> In a

related study, the Rh catalyzed conjugate addition of  $\alpha$ -boryl  $C(sp^2)$  nucleophiles and its application for synthesis of 1,4-dicarbonyls was disclosed.<sup>12</sup> Recently, the scope of deborylative conjugate addition was extended to enones<sup>13a</sup> (Figure 1d) and vinyl epoxides.<sup>13b</sup>

Despite the above advances, the full synthetic potential of  $\alpha$ -boryl carbanion-based conjugate additions remain untapped. For instance, majority of the currently available methods for 1,4-addition of  $\alpha$ -boryl carbanions involve deborylation of geminal triboryl<sup>9</sup> and diboryl<sup>13</sup> alkanes besides requiring activation by neighboring benzylic,<sup>9</sup> allylic<sup>11</sup> or  $Cu^{10,13}$  groups (Figure 1a-d). In contrast, general strategies for conjugate addition of  $\alpha,\alpha$ -diboryl stabilized carbanions produced by deprotonation of geminal diborons lacking any other electron-withdrawing groups remain scarce. In view of the tremendous synthetic utility of 1,4-addition reactions,<sup>14</sup> the development of a diboron-retentive conjugate addition would provide a valuable tool to the emerging chemistry of geminal diboryl alkanes.

In the course of our ongoing work on new synthetic applications of geminal diborons,<sup>15-17</sup> we became interested to develop a tandem deprotonation-conjugate addition of readily available geminal diboryl alkanes. This approach would preserve the synthetically useful diboron motif in the product while avoiding the installation/removal<sup>9</sup> of an

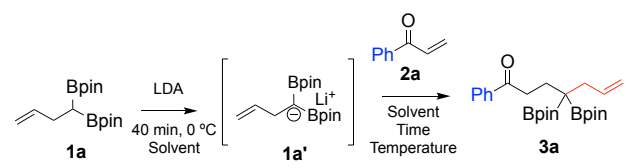
**Figure 1.** Previous approaches for conjugate addition of geminal di/triborons via deborylation (a-d); New deprotonative diboryl conjugate addition and its synthetic applications (e).



additional boronate group for activating the geminal diboron as soft pronucleophile. Furthermore, the deprotonative 1,4- addition is expected to open-up a general route to synthetically useful and highly functionalized  $\gamma,\gamma$ -diboryl ketones that would be difficult to prepare using conventional methods. Existing methods<sup>18</sup> to access these diboryl ketones involve mainly unsubstituted geminal diborons, require expensive catalyst or limit the installation of functional group diversity at the  $\alpha$ - and  $\beta$ - positions. Herein, we describe a rapid and convenient diboron-retentive conjugate addition reaction of  $\alpha,\alpha$ -diboryl pronucleophiles and its application to access a wide variety of  $\gamma,\gamma$ -diboryl ketones (Figure 1e). This strategy also led to the development of geminal diborons as masked acylanion equivalents via one-pot conjugate addition-oxidation to provide the valuable 1,4-dicarbonyl frameworks.

We began our studies on the feasibility of deprotonative conjugate addition of diborylalkanes by treating **1a** with LDA in THF at 0 °C followed by the addition of enone **2a** to the same pot. We were pleased to isolate the desired conjugate addition product **3a** in 55% yield (entry 1, Table 1). TLC monitoring of the reaction showed that the enone was consumed within 3-5 min. A screen of the reaction conditions revealed that maintaining a low temperature (0 °C) during the reaction of enone with deprotonated **1a'** and quenching the reaction mixture after 5 min improved the yield (entry 2). A further lowering of the reaction temperature to -20 °C or increasing the amount of LDA (entries 3-4) diminished the reaction efficiency. Replacing THF with

**Table 1. Optimization of 1,4-conjugation addition conditions.**



Entry	Time Temperature	Base (equiv) Solvent	Isolated yield <b>3a</b> (%) <sup>a</sup>
1	25 min 23 °C	LDA (1.1) THF	55
2	5 min 0 °C	LDA (1.1) THF	59
3	5 min -20 °C	LDA (1.1) THF	46
4	5 min 0 °C	LDA (1.5) THF	39
5	5 min 0 °C	LDA (1.1) Toluene	NR <sup>b</sup>
6	5 min 0 °C	LDA (1.1) 1,4-dioxane	NR <sup>b</sup>
7	5 min 0 °C	LDA (1.1) 1,2-dimethoxyethane	45
8	5 min 0 °C	LDA (1.1) THF/HMPA (2:1 v/v)	53
9	5 min 0 °C	LDA (1.1) THF	70 <sup>c</sup>

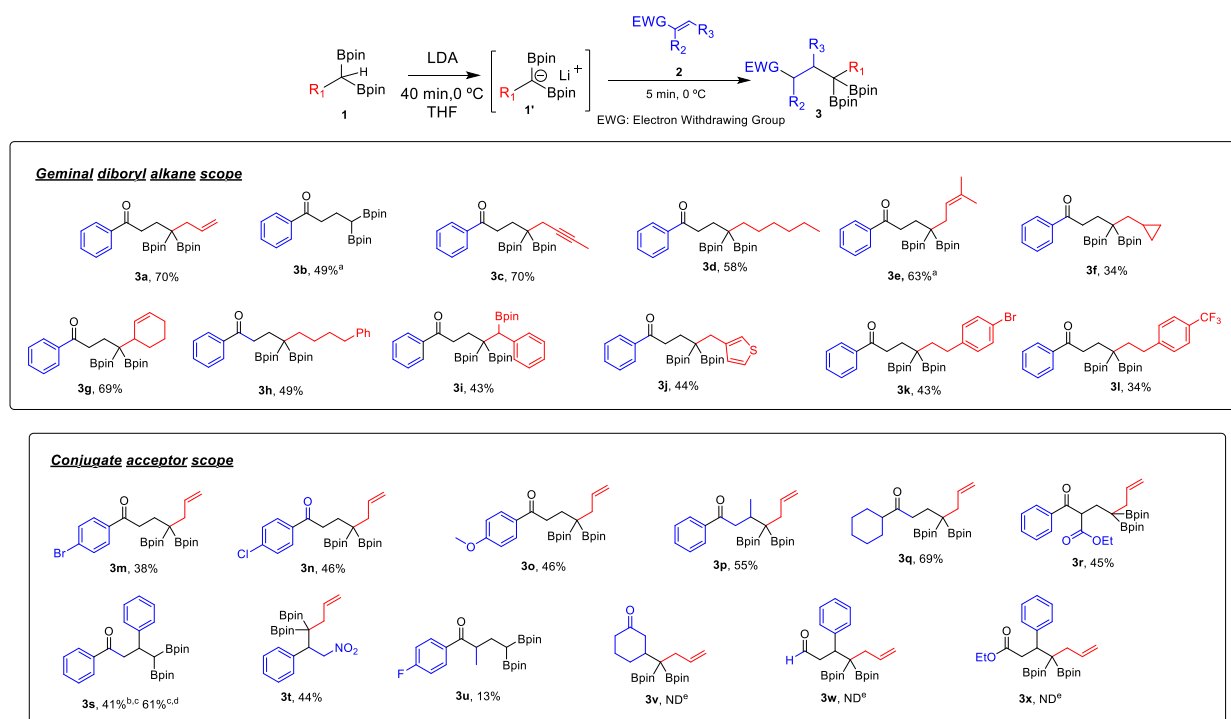
<sup>a</sup>Isolated yield after aqueous work-up and silica gel column chromatography. <sup>b</sup>No reaction observed based on TLC analysis.

<sup>c</sup>Isolated yield after quenching with methanol followed by silica gel column chromatography.

other solvents or using HMPA as additive was not beneficial (entries 5-8). The yield of **3a** was improved to 70% by quenching the reaction with methanol and avoiding aqueous workup (entry 9).

The above optimized conditions were used to investigate the scope of the reaction. Geminal diborons having alkene (Scheme 1, **3a** and **3e**), alkyl (**3d**), alkyne (**3c**), aromatic (**3h**, **3k**, **3l**) and heteroaromatic groups (**3j**) were amenable to the developed protocol. Significantly, the reaction was not limited to geminal diborons as the unsubstituted bis[(pinacolato)boryl]methane also underwent conjugate addition to enone after deprotonation with LDA (**3b**). To evaluate the feasibility of chemoselective generation and reaction of  $\alpha$ -boryl stabilized soft nucleophiles from multiboryl alkanes, we prepared the 1,1,2-triboryl alkane (**1i**) that can undergo LDA-mediated deprotonation at the geminal diboron and/or the  $\alpha$ -boryl benzylic carbon. Reaction of **1i** with the enone **2a** exclusively provided the  $\gamma,\gamma,\delta$ -triboryl ketone **3i** indicating the preferential deprotonation and 1,4-addition of geminal diboryl anion. The above result and the recently

## Scheme 1. Scope of conjugate addition reaction.



Reaction conditions: **1** (1 equiv.), **2** (1 equiv.), LDA (1.1 equiv.), THF. All reactions were conducted at 0.6 mmol scale unless otherwise specified. <sup>a</sup>Average yield of three independent experiments. <sup>b</sup>Isolated yield at 0.6 mmol scale. <sup>c</sup>The conjugate addition step was conducted at -30 °C. <sup>d</sup>Average yield of two independent experiments at 1.9 mmol scale. <sup>e</sup>1,4-conjugate addition product was not detected; the 1,2-addition products (via Boron-Wittig reaction) were observed instead

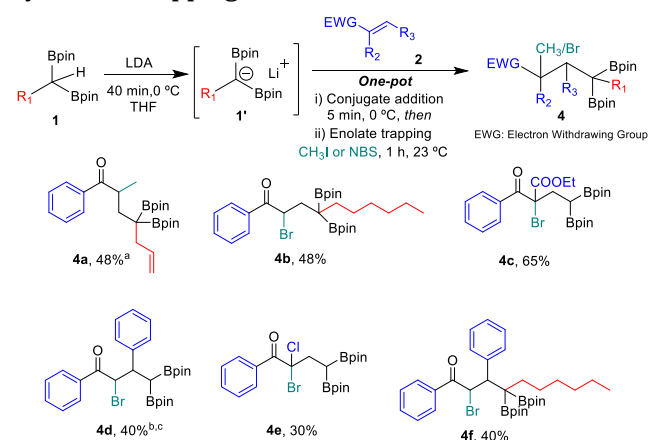
reported deborylative conjugate addition of benzylic triborons<sup>9</sup> collectively suggest that in comparison to the benzylic group the presence of an additional boryl group provides greater soft nucleophilic character to the  $\alpha$ -boryl stabilized anion. Multiborylated alkanes such as 1,1,2-tris-borons<sup>19</sup> have been previously shown to be valuable building blocks for site-selective installation of molecular diversity via sequential transformations of boryl groups. The successful conjugate addition of **3i** allows access to multifunctional tris-borons having ketones as additional synthetic handles.

Next, we evaluated the ability of other conjugate acceptors to participate in deprotonative 1,4-addition. A variety of  $\alpha,\beta$ -unsaturated ketones bearing aromatic and aliphatic substituents were found to be compatible with the deprotonative conjugate addition of diboryl alkanes. Cyclohexyl enone provided the desired product **3q** in 69% yield (Scheme 1) while aromatic enones having electron-donating or withdrawing groups were also competent reaction partners (**3m-3o**). Notably, substituents at the  $\alpha$ - or  $\beta$ -position of enones were tolerated (**3p, 3r, 3s, 3u**). The reaction was successfully scaled up to 1.9 mmol and an increase in yield was observed at this larger scale (**3s**). The developed protocol was also compatible with nitroalkenes as conjugate acceptors (**3t**). This reaction provided rare  $\gamma,\gamma$ -diboryl nitroalkanes which can be elaborated into other useful scaffolds.<sup>20</sup> Cyclic enones,  $\alpha,\beta$ -unsaturated aldehydes and esters were not compatible substrates as they provided the 1,2-addition product (Boron-Wittig reaction, **3v-3x**).<sup>7</sup> The above results highlight the complimentary nature of deprotonative conjugate addition (Scheme 1) to the

deborylative<sup>9,13</sup> 1,4-addition of geminal diboron pronucleophiles which was reported to be applicable to mainly enoates<sup>6</sup> or  $\beta$ -substituted enones and unsubstituted<sup>10</sup> geminal diborons (Figure 1a-d).

The developed approach also allowed late-stage installation of additional structural diversity (Scheme 2). For instance, the enolates resulting from the deprotonative

## Scheme 2. Scope of tandem conjugate addition followed by enolate trapping.

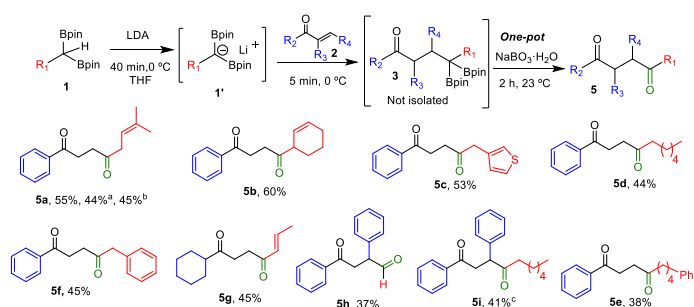


Reaction conditions: **1** (1 equiv.), **2** (1 equiv.), LDA (1.1 equiv.), THF; then electrophile (MeI 3 equiv. or NBS 1.1 equiv.) was added and stirred for 1 h at 23 °C. <sup>a</sup>Upon conjugate addition completion, HMPA (2 mL) was added. <sup>b</sup>Combined yield of two diastereomers. <sup>c</sup>The conjugate addition reaction was conducted at -30 °C.

addition of geminal diborons were successfully quenched with electrophiles in the same pot. This strategy allowed access to highly functionalized  $\gamma,\gamma$ -diboryl ketones (**4a-f**) including scaffolds having geminal halo-ester **4c**, vicinal halo-aryl (**4d**) or geminal dihalo groups (**4e**) which would be difficult to install using the existing methods.<sup>18</sup> Interestingly, the tandem conjugate addition and  $\alpha$ -functionalization of  $\beta$ -substituted enone using unsubstituted geminal diboron and NBS provided a mixture of two diastereomeric products (**4d**) while the use of substituted geminal diboryl alkane as Michael donor afforded only one diastereomer (**4f**).

To further expand the synthetic utility of geminal diboryl stabilized carbanions, we envisioned their use as acyl anion equivalents. There has been considerable interest in development of new types of umpolung reagents due to their utility in accessing carbonyl compounds having 1,4 functional group relationships.<sup>21, 22</sup> Given the facile reactivity of **1** as soft nucleophiles (Scheme 1-2) and the mild conditions required for oxidation of boronate group,<sup>12, 15</sup> we hypothesized that a one-pot conjugate addition-diboron oxidation sequence could be feasible. The resulting 1,4-dicarbonyl products are privileged intermediates for synthesis of bioactive compounds.<sup>23</sup> To this end, the deprotonated diboron **1'** was treated with enone **2** followed by the addition of  $\text{NaBO}_3$  to the same pot (Scheme 3). The above tandem reaction successfully provided the desired 1,4-diketone **5**. The protocol was compatible with geminal diboryl alkanes having saturated (**5d**, **5i**, **5e**), unsaturated (**5a**, **5b**) and heteroaromatic groups (**5c**).

#### Scheme 3. Scope of one-pot diboron conjugate addition-oxidation.



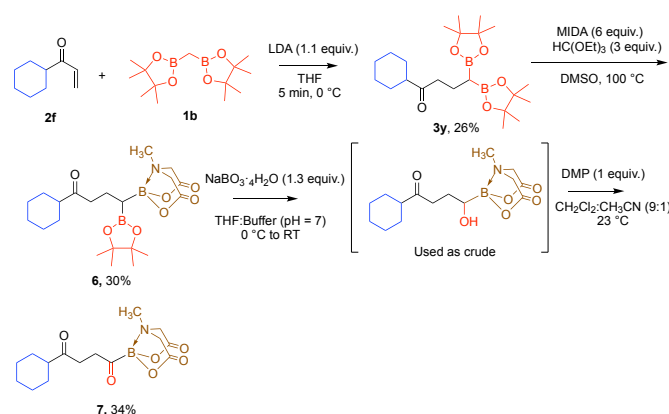
Reaction conditions: **1** (1 equiv.), **2** (1 equiv.), LDA (1.1 equiv.), THF; then  $\text{NaBO}_3 \cdot \text{H}_2\text{O}$  (1.3 equiv.),  $\text{H}_2\text{O}$ , 2 h, 23 °C. All reactions were performed at 0.6 mmol scale unless otherwise specified. <sup>a</sup>Isolated yield after 2-pot protocol. <sup>b</sup>Isolated yield after 2.6 mmol scale reaction. <sup>c</sup> $\text{H}_2\text{O}_2$  (2 mL, 30% solution in  $\text{H}_2\text{O}$ ) and NaOH (2 mL, 2M solution in  $\text{H}_2\text{O}$ ) were used instead of  $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ .

The geminal diboron framework of 1,1,2-trisboryl alkane **1i** also participated in the desired one-pot reaction while its benzylic boronate component underwent protodeborylation under the oxidation conditions (**5f**). Interestingly, the tandem conjugate addition-diboron oxidation of **1a** and **2f** afforded the conjugated 1,4-diketone via isomerization of terminal olefin (**5g**). Furthermore, unsubstituted diboron could be used thereby providing  $\alpha$ -substituted 1,4-ketoaldehydes (**5h**) which represents one of the more challenging<sup>24</sup> 1,4-dicarbonyls. The benefit of the one-pot conjugate addition-oxidation was evaluated by conducting the corresponding two-pot reaction sequence involving isolation of  $\gamma,\gamma$ -diboryl ketone (**3e**) followed by its oxidation.

This two-pot approach provided lower yield (44%) of the 1,4-diketone (**5a**, Scheme 3) in comparison to the one-pot protocol (55%). Finally, the one-pot reaction was successfully scaled up to 2.6 mmol without a significant decrease in reaction yield (**5a**, 45%, Scheme 3).

To investigate the utility of the diboryl conjugate addition-oxidation approach in enabling access to rare 1,4-dicarbonyls, we became interested in developing a synthetic route to  $\gamma$ -keto acylborons (Scheme 4). The unique chemical reactivity and applications of acylborons in organic synthesis and bioconjugation have inspired several creative synthetic methods.<sup>25, 26</sup> While the  $\alpha$ -keto<sup>27</sup> and  $\beta$ -keto acylborons<sup>28</sup> can be prepared using several approaches, methods to access  $\gamma$ -keto acylborons are scarce.<sup>29</sup> Inspired by our recently developed route to MIDA acylborons,<sup>15, 16</sup> the geminal diboron motif in the conjugate addition product **3y** (Scheme 4) was successfully transformed into the unsymmetrical diboron **6**. Chemoselective oxidation<sup>15</sup> of **6** provided the desired  $\gamma$ -keto MIDA acylboron **7** in 34% yield. In view of the ready availability of  $\alpha$ - and  $\beta$ -substituted  $\gamma,\gamma$ -diboryl ketones (Scheme 1-2), the above chemoselective oxidation approach is expected to enable a general route to  $\gamma$ -keto acylborons.

#### Scheme 4. Synthesis of $\gamma$ -keto acylboron via conjugate addition-oxidation sequence.



In conclusion, the diboron-retentive conjugate addition of geminal diboryl alkanes with enones and nitroolefin has been developed for the first time. The methodology is applicable on both terminal and internal enones as conjugate acceptors while  $\alpha$ -substituents on these substrates are also tolerated. A variety of substituted as well as unsubstituted geminal diborons were compatible reaction partners and installation of additional functional group diversity was feasible by trapping the enolate with electrophiles. This reaction afforded a general route to highly substituted and synthetically useful  $\gamma,\gamma$ -diboryl ketones. Furthermore, geminal diborons were shown to be effective acyl anion equivalents via a one-pot conjugate addition-oxidation sequence. Collectively, these studies provide geminal diboryl alkanes as versatile soft pronucleophiles for rapid C-C bond formation with enones and nitroolefins and eliminate the requirement of installing/removing an additional geminal boronate group for activating the pronucleophile towards 1,4-addition.



## ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, characterization data, NMR spectra (PDF).

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### Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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