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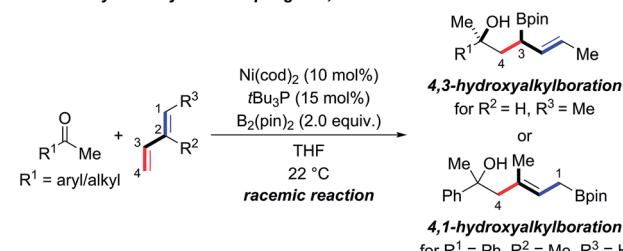
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## Introduction

The enantioselective synthesis of tertiary homoallylic alcohols<sup>1</sup> continues to attract attention as these are highly useful intermediates in complex molecule synthesis and for medicinal chemistry.<sup>2</sup> An established way to access that motif is by ketone allylation<sup>3–7</sup> where enantiofacial discrimination and low reactivity are the key challenges compared to aldehydes as electrophiles.<sup>8</sup> Many methods are based on preformed allylmetal reagents.<sup>3–6</sup> An alternative to these nucleophiles is their *in situ* formation by hydrometalation of 1,3-dienes<sup>9,10</sup> and allenes,<sup>10</sup> and examples of transition-metal-catalyzed reductive couplings with ketones were recently achieved.<sup>10–12</sup> A powerful variation of this approach is the borylation of 1,3-dienes in the presence of a carbon electrophile.<sup>13–17</sup> These and related stereoselective borylative coupling reactions of other  $\pi$ -systems form a carbon–boron and a carbon–carbon bond in a single operation.<sup>13</sup> However, reactions involving ketones as electrophiles are scarce.<sup>14,17a,d–g</sup> To the best of our knowledge, there are only three examples of the preparation of tertiary homoallylic alcohols by the borylative coupling strategy. Morken and co-workers reported a nickel-catalyzed three-component coupling of 1,3-dienes, bis(pinacolato)diboron, and ketones in racemic fashion (Scheme 1, top).<sup>14</sup> The reaction outcome was dependent on the substitution pattern of the 1,3-diene; (*E*)-penta-1,3-diene converted into 4,3-hydroxyalkylboration products while isoprene (one example) afforded the 4,1-hydroxyalkylboration product. Starting from allenes as the precursor of the allylic nucleophiles, Hoveyda and co-workers realized enantioselective borylative couplings with carbonyl

compounds with *syn* selectivity but enantiocontrol was lower for ketones than for aldehydes (Scheme 1, middle).<sup>17a</sup> Low enantioselectivity was found by Tian and Tao in an

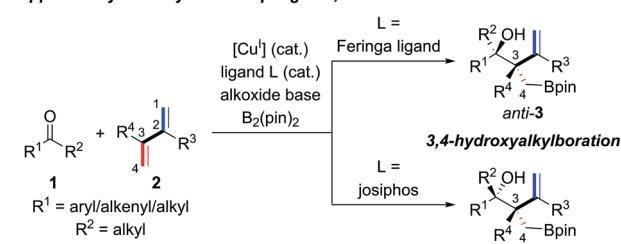
**Morken (2011):**  
*Nickel-catalyzed borylative coupling of 1,3-dienes and ketones*



**Hoveyda (2013):**  
*Enantioselective copper-catalyzed borylative coupling of allenes and ketones*



**This work:**  
*Diastereodivergent and enantioselective copper-catalyzed borylative coupling of 1,3-dienes and ketones*



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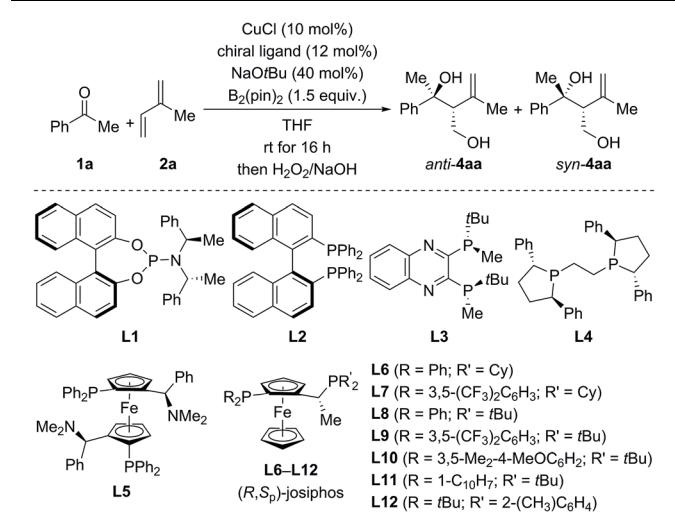
intramolecular borylative cyclization of allenes tethered to cyclohexanediolines (not shown).<sup>17f</sup> Hence, there is a demand for the development of new enantioselective borylative coupling reactions of  $\pi$ -systems and ketones to access chiral tertiary homoallylic alcohols. We disclose here such a copper-catalyzed three-component reaction with 1,3-dienes as the allylic coupling partner where the diastereoselectivity is determined by the ligand (Scheme 1, bottom).<sup>9d,e</sup>

## Results and discussion

For optimization, the three-component reaction of acetophenone (**1a**), isoprene (**2a**), and  $B_2(\text{pin})_2$  was chosen as the model reaction. The ligand effects are summarized in Table 1. In general, the reaction catalyzed by  $\text{CuCl}$  and phosphoramidite ligands afforded *anti*-**4aa** as the major diastereomer after oxidative degradation of the carbon–boron bond (see the ESI† for the complete set of data).<sup>18</sup> As an example, *anti*-**4aa** formed in decent yield and with moderate stereoselectivity at room temperature in the presence of  $\text{CuCl}/\text{L1}$  and  $\text{NaOtBu}$  (entry 1). Further optimization of the copper source, solvent, and temperature led to a system which afforded the tertiary homoallylic alcohol *anti*-**4aa** as the major diastereomer in 94% NMR yield and with 90% ee (entries 2–4). In contrast to phosphoramidite ligands, bisphosphine ligands commonly used in copper catalysis such as **L2** to **L12** furnished *syn*-**4aa** as the major diastereomer at room temperature (entries 5–17), and commercially available josiphos derivative **L9** was found to be optimal (entry 12). Lowering of reaction temperature from room temperature to  $-20\text{ }^\circ\text{C}$  increased the enantiomeric excess and diastereoselectivity significantly but was detrimental to the yield (entry 13). Finally, high yield (98% NMR yield) and stereoselectivity (93% ee and d.r. = 87 : 13 in favor of *syn*) were restored in toluene/THF 8 : 2 with 5.0 mol%  $\text{CuOAc}$  and 6.0 mol% **L9** as the catalyst–ligand combination (entry 14).

We next investigated the scope of ketones using **L1** in the *anti*-selective procedure and **L9** in the *syn*-selective setup (Conditions A and B, Scheme 2). Acetophenones with various substituents in the *para* position, including electron-donating groups (as in **1b–e**) and halogens (as in **1d–f**), exhibited high reactivity and stereoselectivity. A carboxyl group was compatible (as in **1g**), thus further emphasizing the functional-group tolerance of this reaction. **1h** and **i** with *meta*-substitution also gave satisfactory results. The reaction of *ortho*-methyl-substituted **1j** was successful under Condition B and yielded *syn*-**4ia** with 98% ee (*anti*-**4ja**: 80% ee); conversely, poor stereoselectivity was obtained under Condition A. Pyridyl-substituted **1l** reacted smoothly under Condition B and furnished *syn*-**4la** with good diastereoselectivity (d.r. = 90 : 10) and enantioselectivity (90% ee); in turn, the reaction of **1l** under Condition A produced *anti*-**4la** with a moderate ee value. Aside from aromatic methyl ketones, propiophenone (**1m**), which had not been compatible with Morken's<sup>14</sup> and Hoveyda's<sup>17a</sup> catalytic system (cf. Scheme 1), also furnished *anti*-**4ma** in excellent yield and good enantioselectivity with moderate diastereoselectivity under Condition A; B afforded the target compound in a similar

Table 1 Selected examples of the optimization of the borylative hydroxyalkylation of 1,3-dienes<sup>a</sup>



Entry	Ligand	Yield <sup>b</sup> (%)	d.r. ( <i>anti</i> : <i>syn</i> )	<i>ee</i> <sup>c</sup> (%)	
				<i>anti</i> - <b>4aa</b>	<i>syn</i> - <b>4aa</b>
1	<b>L1</b>	53	71 : 29	60	21
2 <sup>d</sup>	<b>L1</b>	88	66 : 34	64	10
3 <sup>d,e</sup>	<b>L1</b>	96	68 : 32	68	30
4 <sup>d,e,f</sup>	<b>L1</b>	94	<b>80 : 20</b>	<b>90</b>	<b>64</b>
5	<b>L2</b>	75	42 : 58	43	32 <sup>g</sup>
6	<b>L3</b>	92	35 : 65	6	35
7	<b>L4</b>	93	28 : 72	35 <sup>g</sup>	32 <sup>g</sup>
8 <sup>e</sup>	<b>L5</b>	84	44 : 56	13	22
9	<b>L6</b>	45	23 : 77	22 <sup>g</sup>	61
10	<b>L7</b>	98	23 : 77	13 <sup>g</sup>	80
11	<b>L8</b>	80	22 : 78	72 <sup>g</sup>	88
12	<b>L9</b>	98	23 : 77	74 <sup>g</sup>	88
13 <sup>h</sup>	<b>L9</b>	61	15 : 85	79 <sup>g</sup>	94
14 <sup>h,i</sup>	<b>L9</b>	98	<b>13 : 87</b>	<b>71<sup>g</sup></b>	<b>93</b>
15	<b>L10</b>	65	28 : 72	71 <sup>g</sup>	87
16	<b>L11</b>	37	47 : 53	0	37
17	<b>L12</b>	29	49 : 51	—	—

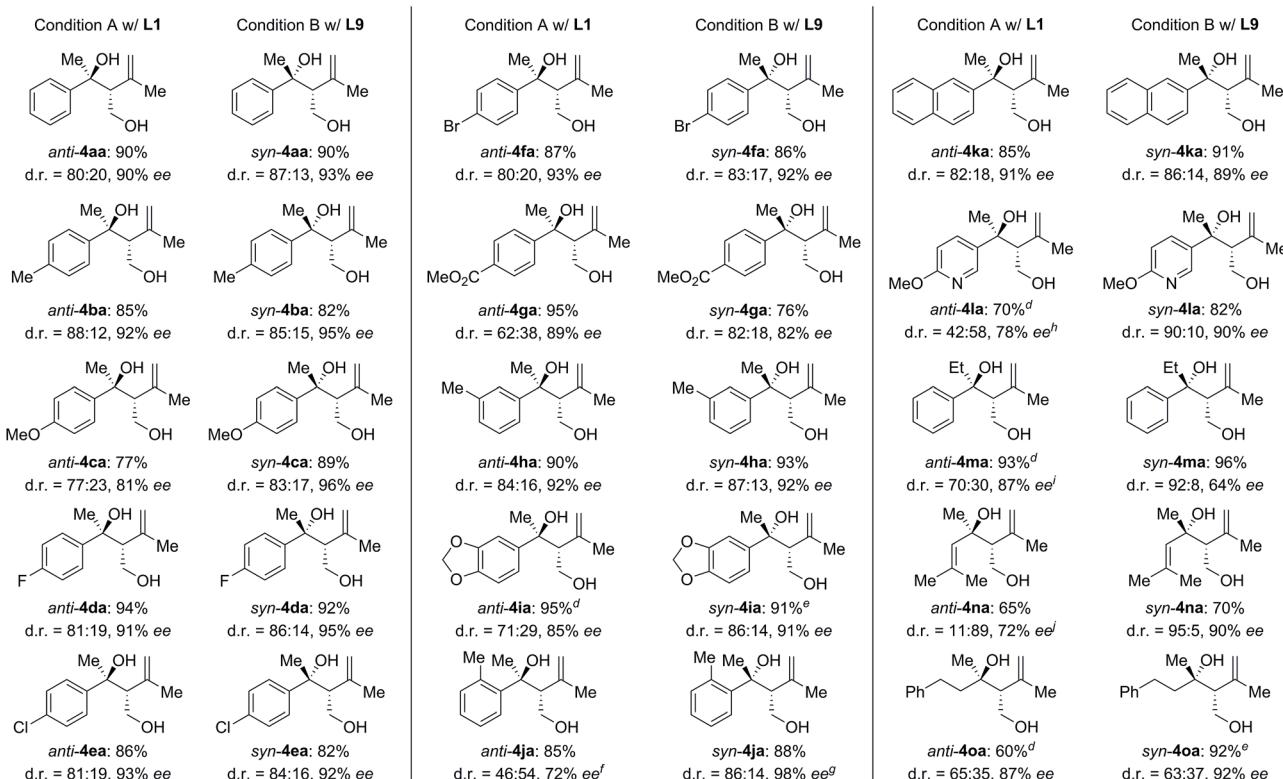
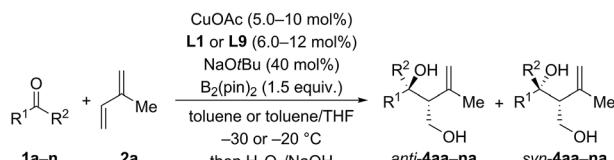
<sup>a</sup> Unless otherwise noted, the reactions were performed with **1a** (0.2 mmol), **2a** (1 mmol), and  $B_2(\text{pin})_2$  (0.3 mmol) in THF (2 mL).

<sup>b</sup> Combined NMR yield determined by  $^1\text{H}$  NMR spectroscopy with  $\text{CH}_2\text{Br}_2$  as an internal standard. <sup>c</sup> Determined by HPLC analysis on chiral stationary phases. <sup>d</sup>  $\text{CuOAc}$  instead of  $\text{CuCl}$ . <sup>e</sup> Toluene instead of THF. <sup>f</sup> Run at  $-30\text{ }^\circ\text{C}$ . <sup>g</sup> The other enantiomer was obtained. <sup>h</sup> Run at  $-20\text{ }^\circ\text{C}$ . <sup>i</sup> 0.4 mmol scale, 5.0 mol%  $\text{CuOAc}$  and 6.0 mol% **L9** were used and toluene/THF 8 : 2 instead of THF.

yield yet with a high diastereomeric ratio and a markedly diminished ee value. Interestingly,  $\alpha,\beta$ -unsaturated ketone **1n** reacted regioselectively (1,2- over 1,4-addition) with good to excellent diastereoselectivity; *syn*-**4na** was the major product under both Condition A and B. Moreover, dialkyl ketone **1o** converted into the corresponding products *anti*- and *syn*-**4oa** under A and B but with low diastereoselectivity likely due to the little steric differentiation between the methyl and methylene groups attached to the carbonyl carbon atom.

We then examined the scope of 1,3-dienes (Scheme 3). Isoprene (**2a**) could be replaced by buta-1,3-diene (**2b**),





**Scheme 2** Scope I: variation the ketone.<sup>a-c</sup> <sup>a</sup>Condition A: CuOAc (10 mol%), L1 (12 mol%), NaOtBu (40 mol%), ketone **1** (0.20 mmol), isoprene (**2a**, 1.0 mmol), and B<sub>2</sub>(pin)<sub>2</sub> (1.5 equiv.) in toluene (2 mL) at -30 °C. Condition B: CuOAc (5.0 mol%), L9 (6.0 mol%), NaOtBu (40 mol%), ketone **1** (0.40 mmol), isoprene (**2a**, 2.0 mmol), and B<sub>2</sub>(pin)<sub>2</sub> (1.5 equiv.) in toluene/THF - 8 : 2 (3.5 mL) at -20 °C. <sup>b</sup>Yields are combined isolated material; diastereomers are usually separable by flash chromatography on silica gel. <sup>c</sup>The enantiomeric excess of the major diastereomer was determined by HPLC analysis on chiral stationary phases. <sup>d</sup>CuOAc (15 mol%) and L1 (18 mol%) were used. <sup>e</sup>CuOAc (10 mol%) and L9 (12 mol%) were used. <sup>f</sup>*anti*-**4ia**: 29% ee. <sup>g</sup>*anti*-**4ia**: 80% ee. <sup>h</sup>ee value of *anti*-**4la**. <sup>i</sup>*syn*-**4ma**: 78% ee. <sup>j</sup>*syn*-**4na**: 72% ee.

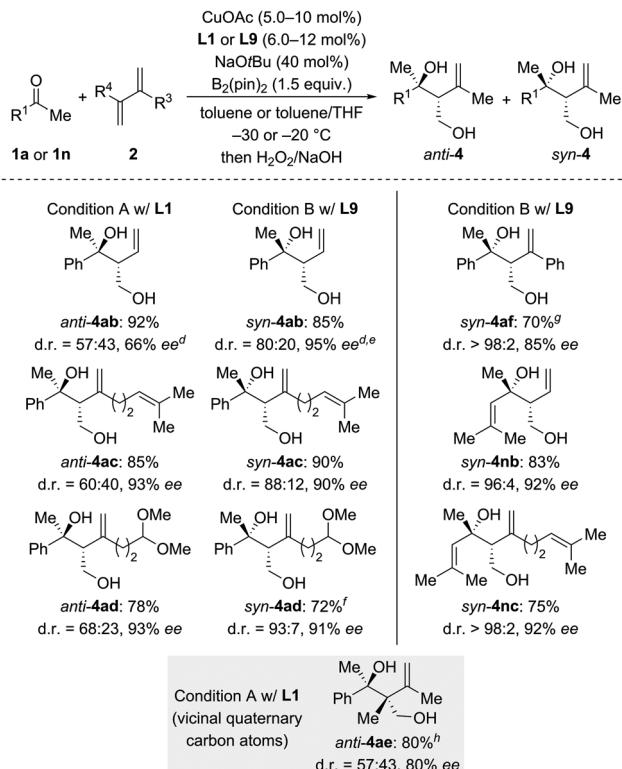
myrcene (**2c**), its functionalized derivative **2d**, and 2,3-dimethylbuta-1,3-diene (**2e**). Yields were generally good but stereoselectivities ranged from poor to good under Condition A. In contrast, good to excellent stereoselectivities were observed for these 1,3-dienes under Condition B, *e.g.*, d.r. = 96 : 4 and 92% ee for **1n**  $\rightarrow$  *syn*-**4nb** and d.r. = 93 : 7 and 91% ee for **1a**  $\rightarrow$  *syn*-**4ad**. In the case of 2-aryl-substituted 1,3-diene **1f**, diastereodivergency was not achieved. Subjecting **1f** to Condition A afforded *syn*-**4af** in low yield as a single *syn*-isomer (not shown). However, applying Condition B at  $-5\text{ }^\circ\text{C}$  significantly improved the yield and furnished the *syn*-**4af** with d.r. > 98 : 2 and 85% ee.

To explore synthetic transformations of these tertiary homoallylic alcohols (Scheme 4), a scale-up synthesis of *syn*-4aa (1.0 mmol) under Condition B was done without any loss in efficiency and selectivity (see the ESI†). The primary alkyl borane generated by the multicomponent reaction was subjected to a Suzuki–Miyaura coupling to afford *syn*-5 in 83%

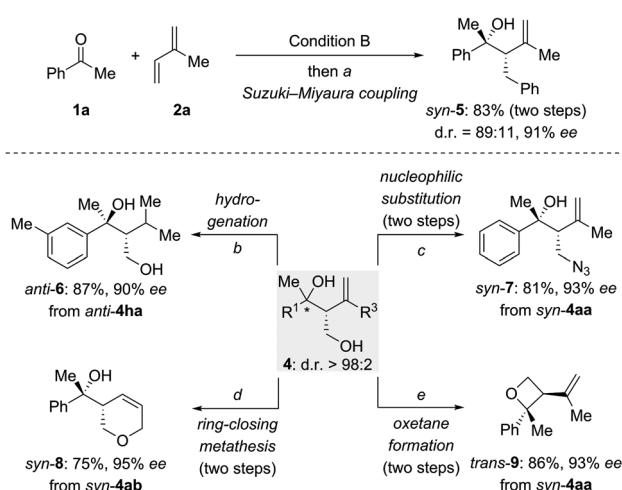
yield (Scheme 4, top). The versatility of the diol products **4** is illustrated for several transformations (Scheme 4, bottom). The 1,1-disubstituted double bond in *anti*-**4ha** was hydrogenated over Pd/C to produce *anti*-**6** in 87% yield. The hydroxy group in *syn*-**4aa** was replaced by an azide group through an  $S_N2$  reaction of an intermediate mesylate with  $NaN_3$  (*syn*-**4aa**  $\rightarrow$  *syn*-**7**). Pyran *syn*-**8** was synthesized from *syn*-**4ab** by sequential alcohol allylation and ring-closing metathesis. Of note, a chemoselective tosylation of the primary alcohol in *syn*-**4aa** followed by a 4-*exo-tet* ring closure allowed for the construction of enantioenriched, trisubstituted oxetane *trans*-**9** in 86% yield.

## Conclusion

In summary, we have developed an efficient copper-catalyzed diastereodivergent and enantioselective borylative coupling of 1,3-dienes and ketones. Using a Feringa-type ligand **L1**, the



**Scheme 3** Scope II: variation of the 1,3-diene.<sup>a–c</sup> For footnotes a–c, see Scheme 2. <sup>d</sup>The absolute configuration was assigned by chemical correlation after separation of the diastereomers by flash chromatography on silica gel (see the ESI†). <sup>e</sup>anti-4ab: 84% ee. <sup>f</sup>CuOAc (8.0 mol%) and L9 (10 mol%) were used. <sup>g</sup>Run at –5 °C with CuOAc (10 mol%), L9 (12 mol%), NaOtBu (50 mol%), and B<sub>2</sub>(pin)<sub>2</sub> (2.0 equiv.). <sup>h</sup>CuOAc (15 mol%) and L1 (18 mol%) were used.



**Scheme 4** Tertiary homoallylic alcohols as versatile building blocks. (a) PhBr (1.8 equiv.), Pd(OAc)<sub>2</sub> (5.0 mol%), RuPhos (10 mol%), KOTBu (3.0 equiv.), toluene/H<sub>2</sub>O (10/1), 80 °C, 24 h; (b) Pd/C (10%), H<sub>2</sub> (1 atm), MeOH, rt, 26 h; (c) (i) MsCl (1.5 equiv.), Et<sub>3</sub>N (1.5 equiv.), CH<sub>2</sub>Cl<sub>2</sub>, 0 °C to rt, 50 min; (ii) NaN<sub>3</sub> (2.0 equiv.), DMF/H<sub>2</sub>O (10/1), 80 °C, 12 h; (d) (i) NaH (2.0 equiv.), allyl bromide (1.1 equiv.), THF, 0 °C to rt, 14 h; (ii) Hoveyda–Grubbs II (5.0 mol%), CH<sub>2</sub>Cl<sub>2</sub>, 4, 12 h; (e) (i) TsCl (2.4 equiv.), pyridine, 0 °C to rt, 24 h; (ii) nBuLi (1.1 equiv.), –25 °C to rt, 15 h. Ms = methanesulfonyl.

reaction yielded *anti*-configured tertiary homoallylic alcohols while a switch to josiphos ligand L9 resulted in *syn* selectivity (see the ESI† for a discussion of the reaction mechanism). This three-component coupling reaction represents a useful method for the preparation of stereochemically diverse tertiary alcohols bearing versatile alkenyl and boryl motifs from feedstock 1,3-dienes, ketones, and B<sub>2</sub>(pin)<sub>2</sub>. The synthetic utility of the reaction was showcased by several transformations.

## Conflicts of interest

There are no conflicts to declare.

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