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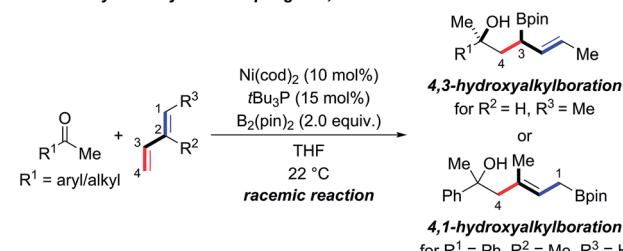
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Introduction

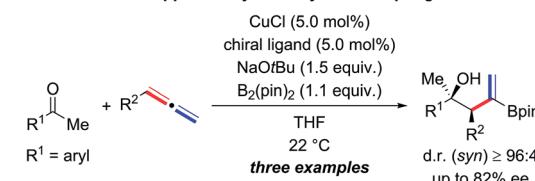
The enantioselective synthesis of tertiary homoallylic alcohols¹ continues to attract attention as these are highly useful intermediates in complex molecule synthesis and for medicinal chemistry.² An established way to access that motif is by ketone allylation^{3–7} where enantiofacial discrimination and low reactivity are the key challenges compared to aldehydes as electrophiles.⁸ Many methods are based on preformed allylmetal reagents.^{3–6} An alternative to these nucleophiles is their *in situ* formation by hydrometalation of 1,3-dienes^{9,10} and allenes,¹⁰ and examples of transition-metal-catalyzed reductive couplings with ketones were recently achieved.^{10–12} A powerful variation of this approach is the borylation of 1,3-dienes in the presence of a carbon electrophile.^{13–17} These and related stereoselective borylative coupling reactions of other π -systems form a carbon–boron and a carbon–carbon bond in a single operation.¹³ However, reactions involving ketones as electrophiles are scarce.^{14,17a,d–g} 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).¹⁴ 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).^{17a} Low enantioselectivity was found by Tian and Tao in an

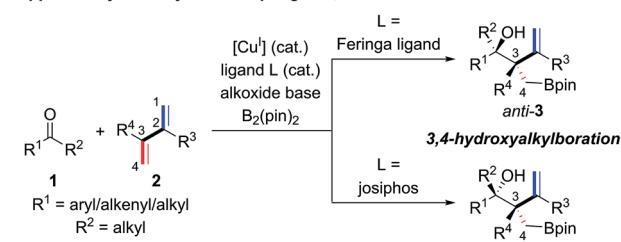
Morken (2011):
Nickel-catalyzed borylative coupling of 1,3-dienes and ketones



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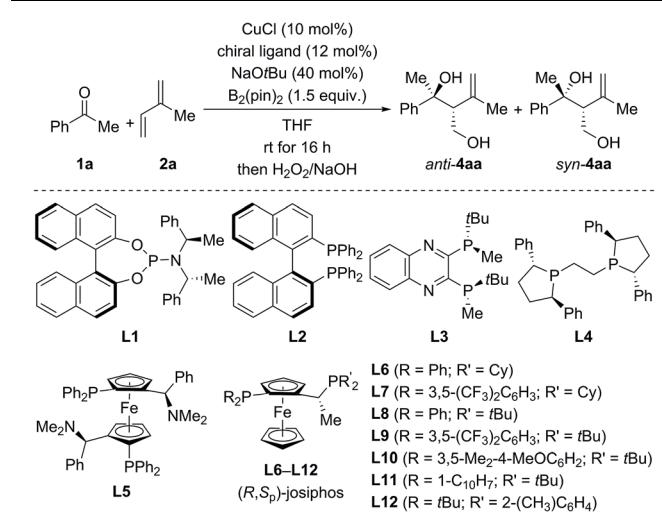
intramolecular borylative cyclization of allenes tethered to cyclohexanediolines (not shown).^{17f} Hence, there is a demand for the development of new enantioselective borylative coupling reactions of π -systems and ketones to access chiral tertiary homoallylic alcohols. We disclose here such a copper-catalyzed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

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 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).¹⁸ 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 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% 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's¹⁴ and Hoveyda's^{17a} 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^a



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

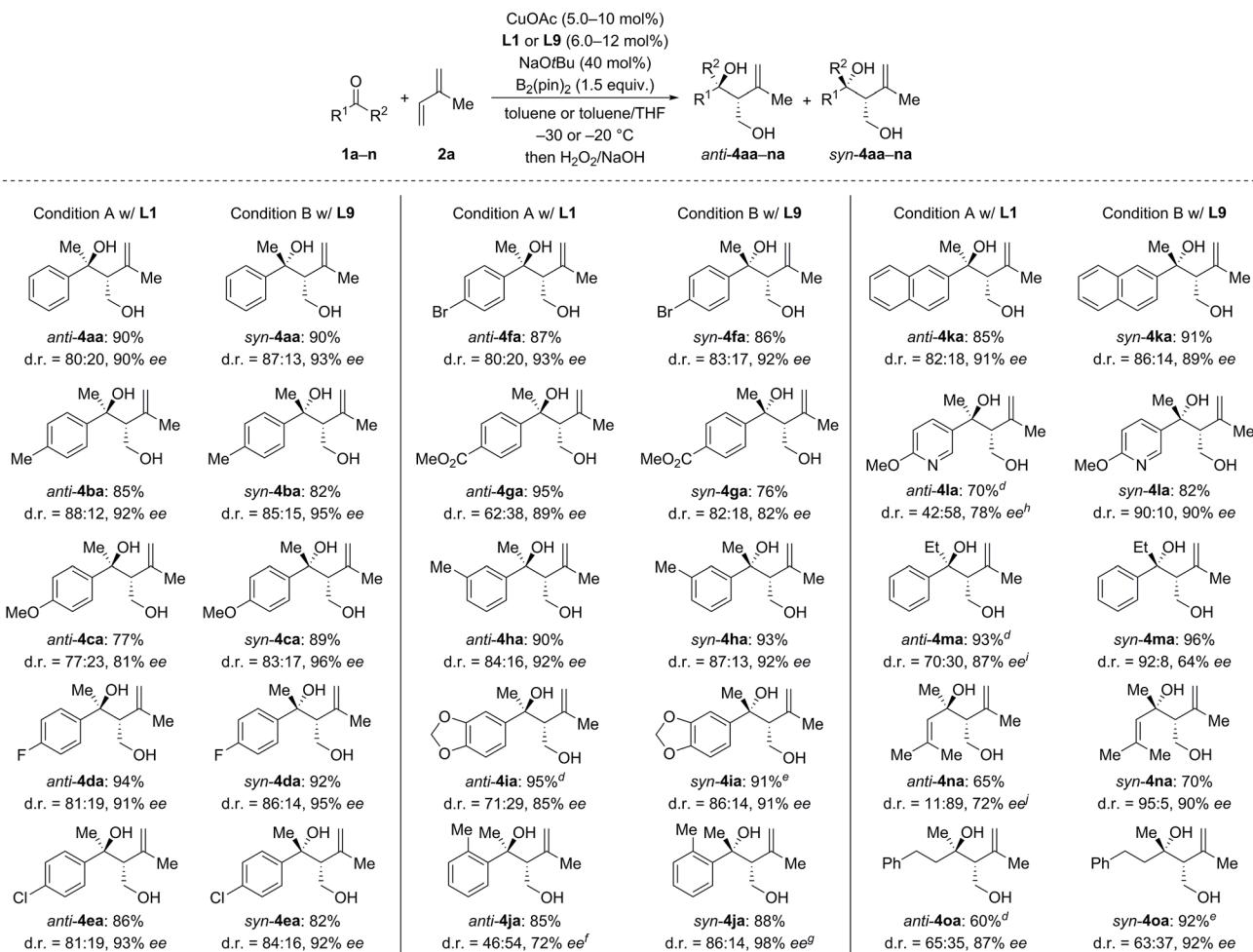
^a Unless otherwise noted, the reactions were performed with **1a** (0.2 mmol), **2a** (1 mmol), and $B_2(\text{pin})_2$ (0.3 mmol) in THF (2 mL).

^b Combined NMR yield determined by ^1H NMR spectroscopy with CH_2Br_2 as an internal standard. ^c Determined by HPLC analysis on chiral stationary phases. ^d CuOAc instead of CuCl . ^e Toluene instead of THF. ^f Run at $-30\text{ }^\circ\text{C}$. ^g The other enantiomer was obtained. ^h Run at $-20\text{ }^\circ\text{C}$. ⁱ 0.4 mmol scale, 5.0 mol% 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, α,β -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 of the ketone.^{a–c} ^aCondition A: CuOAc (10 mol%), L1 (12 mol%), NaOtBu (40 mol%), ketone 1 (0.20 mmol), isoprene (2a, 1.0 mmol), and B2(pin)2 (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 B2(pin)2 (1.5 equiv.) in toluene/THF – 8 : 2 (3.5 mL) at -20 °C. ^bYields are combined isolated material; diastereomers are usually separable by flash chromatography on silica gel. ^cThe enantiomeric excess of the major diastereomer was determined by HPLC analysis on chiral stationary phases. ^dCuOAc (15 mol%) and L1 (18 mol%) were used. ^eCuOAc (10 mol%) and L9 (12 mol%) were used. ^fanti-4ja: 29% ee. ^ganti-4ja: 80% ee. ^hee value of anti-4la. ⁱsyn-4ma: 78% ee. ^jsyn-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 → syn-4nb and d.r. = 93 : 7 and 91% ee for 1a → 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 °C significantly improved the yield and furnished the syn-4af with d.r. > 98 : 2 and 85% ee.

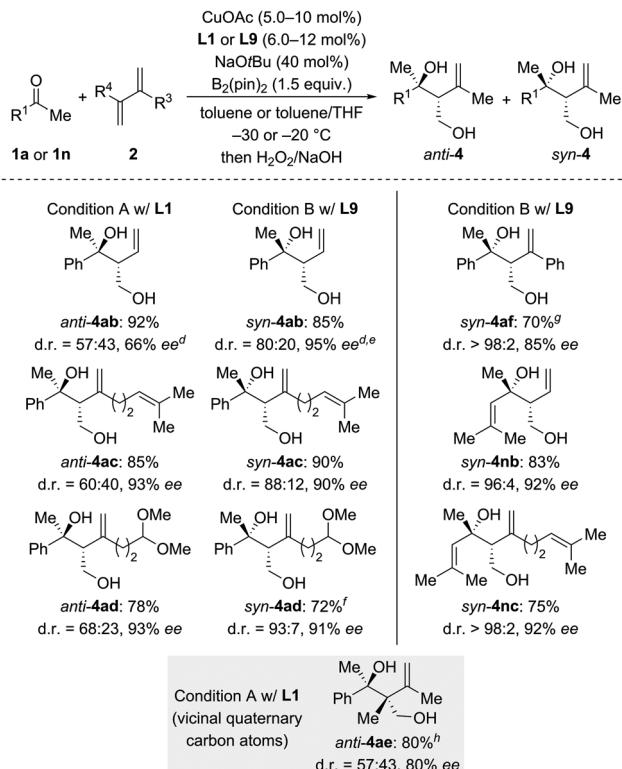
To explore synthetic transformations of these tertiary homoallylic alcohols (Scheme 4), a scale-up synthesis of syn-4aa (1.0 mmol) under Condition B was done without any loss in efficiency and selectivity (see the ESI†). The primary alkyl borane generated by the multicomponent reaction was subjected 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 hydroxyl group in syn-4aa was replaced by an azide group through an S_N2 reaction of an intermediate mesylate with NaN₃ (syn-4aa → 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.

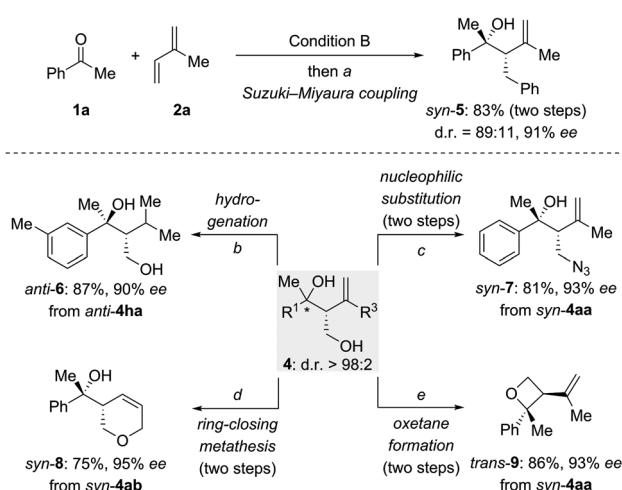
Conclusion

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.^{a–c} For footnotes a–c, see Scheme 2. ^dThe absolute configuration was assigned by chemical correlation after separation of the diastereomers by flash chromatography on silica gel (see the ESI†). ^eanti-4ab: 84% ee. ^fCuOAc (8.0 mol%) and L9 (10 mol%) were used. ^gRun at –5 °C with CuOAc (10 mol%), L9 (12 mol%), NaOtBu (50 mol%), and B₂(pin)₂ (2.0 equiv.). ^hCuOAc (15 mol%) and L1 (18 mol%) were used.



Scheme 4 Tertiary homoallylic alcohols as versatile building blocks. (a) PhBr (1.8 equiv.), Pd(OAc)₂ (5.0 mol%), RuPhos (10 mol%), KOTBu (3.0 equiv.), toluene/H₂O (10/1), 80 °C, 24 h; (b) Pd/C (10%), H₂ (1 atm), MeOH, rt, 26 h; (c) (i) MsCl (1.5 equiv.), Et₃N (1.5 equiv.), CH₂Cl₂, 0 °C to rt, 50 min; (ii) NaN₃ (2.0 equiv.), DMF/H₂O (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%), CH₂Cl₂, 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 B₂(pin)₂. The synthetic utility of the reaction was showcased by several transformations.

Conflicts of interest

There are no conflicts to declare.

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