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Hosomi–Sakurai Reaction

A Catalytic Asymmetric Borono Variant of Hosomi–Sakurai Reactions with N,O-Aminals**

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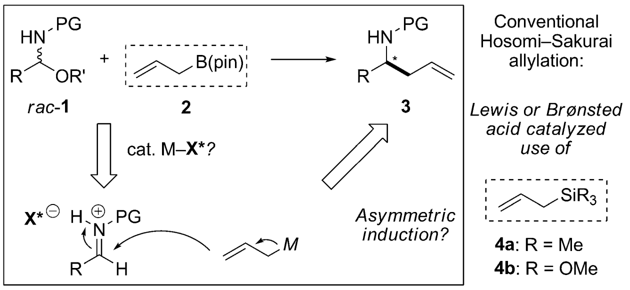
Catalytic intermolecular cross-couplings between C_{sp^3} centers, such as O,O-acetals and N,O-aminals, and allyl species are challenging, but provide convenient access to various important substance classes such as homoallyl ethers and amines.[1] For these transformations, Hosomi–Sakurai reactions using allyl silicon-based reagents are generally employed.[2,3] These carbon–carbon bond formations proceed through either Lewis acid or Brønsted acid activation of the electrophile to generate a stabilized carbenium ion intermediate that can react with a silicon-based nucleophile. However, catalytic asymmetric Hosomi–Sakurai allylations of C_{sp^3} centers have proved to be challenging.[2f,j,4]

Allyl boronates are typically employed for additions to C_{sp^2} centers,[5] although a few C_{sp^3}–C_{sp^3} cross-couplings have been reported.[6,7] These nontoxic reagents are intrinsically less nucleophilic than silicon-based compounds and have been neglected in the context of allylation of C_{sp^3} centers. However, allyl boronates may offer significant advantages such as superior stability and unique reactivity and selectivity. During a project initially aimed at the catalytic activation of allyl boronates for selective C–C coupling with more complex electrophiles, we observed a peculiar reactivity with C_{sp^3} intermediates such as N,O-aminals. These electrophiles are abundant in natural products[8a] and play an important role in organic synthesis.[2f,8b–e] Thus, the development of catalytic asymmetric carbon–carbon bond formations with N,O-aminals is worthwhile.[1] Intrigued by the unexpected reactivity, we started more detailed investigations with a view towards asymmetric catalysis. We report herein an approach to address the challenge of catalytic asymmetric Hosomi–Sakurai reactions involving C_{sp^3} centers by employing boronates instead of silicon-based reagents.



Scheme 1. Asymmetric borono variant of Hosomi–Sakurai reactions? B(pin) = pinacolatoboron, PG = protecting group.

In an initial screen of various Lewis and Brønsted acids for the reaction of N,O-aminal *rac*-**1a** with allyl boronate **2** indium(I) triflate[6a] was identified as the best catalyst for the formation of homoallyl amide *rac*-**3a** (Scheme 1; R = phenyl, PG = benzoyl, R′ = methyl).[9] In contrast, the corresponding Hosomi–Sakurai allylations with silicon-based reagents **4a** and **4b** barely proceeded,[9] which stands in sharp contrast to our earlier study.[6a] The substantially higher reactivity of **2** over **4** under mildly Lewis acidic conditions constitutes a prerequisite for asymmetric catalysis. We postulated a dual catalytic activation[6a] of *rac*-**1a** and **2** to generate iminium ion and allyl indium(I) intermediates (Scheme 1), thus we screened potential indium(I) catalysts bearing chiral counteranions[9] rather than chiral ligands.[10] In these experiments the combination of indium(I) chloride and chiral silver binol phosphate (*R*)-**5a**-Ag[11] was found to be the most promising chiral catalyst system for the formation of product (*R*)-**3a** (e.r. = 88:12).[9] Also, allyl silane **4a** proved to be substantially less effective than allyl boronate **2** in terms of both reactivity and selectivity.[9] Thus, these results demonstrate the viability of our originally envisaged asymmetric concept, in which we proposed the use of boronates instead of silanes. At this stage, we explain the success of **2** based on its higher propensity to undergo transmetalation, thereby forming a more reactive allyl indium species.

Next, we further optimized the reaction conditions (Table 1). A screen of silver binol phosphates identified (*R*)-**5b**-Ag as the best chiral source (Table 1, entries 1–5). The use of an apolar cosolvent (cyclopentylmethyl ether) and a slight excess of the chiral silver salt further improved the asymmetric induction even at a lower catalyst loading (Table 1, entries 6–8). We then conducted several control experiments. In the absence of indium(I) chloride, (*R*)-**5b**-Ag displayed low reactivity and low asymmetric induction (Table 1, entry 10). The use of chiral Brønsted acid (*R*)-**5b**-H, which may be generated in situ under the present catalysis conditions, did not lead to any reaction (Table 1, entry 11).[4g,8c] The combination of indium(I) chloride and (*R*)-**5b**-H provided low asymmetric induction (Table 1, entry 12), thereby demonstrating that an achiral metal salt and a chiral Brønsted

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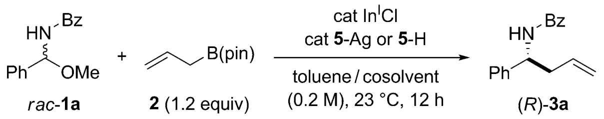
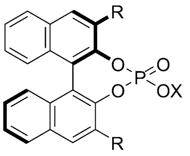
Table 1: Optimization study and control experiments .



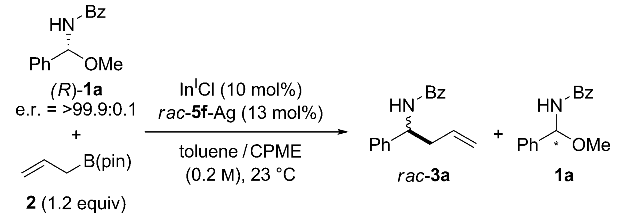
Entry	In^{I}Cl [mol %]	**5** [mol %]	Cosolvent	Yield[a] [%]	e.r.[b]
1[c]	10	(*R*)-**5a**-Ag (10)	–	81	88:12
2[c]	10	(*R*)-**5b**-Ag (10)	–	96	94.5:5.5
3[c]	10	(*R*)-**5c**-Ag (10)	–	90	44.5:55.5
4[c]	10	(*R*)-**5d**-Ag (10)	–	91	49.5:50.5
5[c]	10	(*R*)-**5e**-Ag (10)	–	94	49.5:50.5
6[c]	10	(*R*)-**5b**-Ag (10)	CPME	96	95.5:4.5
7[c]	10	(*R*)-**5b**-Ag (13)	CPME	98	98.5:1.5
8[c,d]	5	(*R*)-**5b**-Ag (6.5)	CPME	96	97.5:2.5
9[d]	5	–	CPME	1	–
10[d]	–	(*R*)-**5b**-Ag (6.5)	CPME	5	57:43
11[d]	–	(*R*)-**5b**-H (6.5)	CPME	NR[e]	–
12[c,d]	5	(*R*)-**5b**-H (6.5)	CPME	88	62.5:37.5

[a] Yields of isolated (*R*)-**3a** after purification by preparative TLC on silica gel. [b] Enantiomeric ratios were determined by HPLC on a chiral staionary phase. [c] The chiral catalyst was preformed in toluene at RT. [d] Reaction time: 18 h. [e] NR = no reaction (detected by ^{1}H NMR spectroscopy). CPME = Cyclopentyl methyl ether.



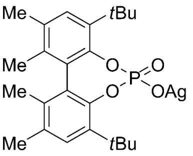
(*R*)-**5a**-Ag: R = 3,5-(tBu)$_2$C$_6$H$_3$, X = Ag
(*R*)-**5b**-Ag: R = 3,5-(tBu)$_2$-4-MeOC$_6$H$_2$, X = Ag
(*R*)-**5b**-H: R = 3,5-(tBu)$_2$-4-MeOC$_6$H$_2$, X = H
(*R*)-**5c**-Ag: R = 3,5-(Me)$_2$C$_6$H$_3$, X = Ag
(*R*)-**5d**-Ag: R = 2,4,6-(iPr)$_3$C$_6$H$_2$, X = Ag
(*R*)-**5e**-Ag: R = SiPh$_3$, X = Ag

Table 2: Mechanistic control experiment.



t [min]	**3a**		**1a**	
	Yield [%][a]	e.r.[b]	Yield [%][a]	e.r.[b]
15	1	50:50	95	97.5:2.5
60	15	50:50	82	91:9
120	28	50:50	67	80:20
180	39	50:50	57	68:32
300	52	50:50	43	56.5:43.5
480	80	50:50	16	50:50
640	93	50:50	5	50:50

[a] Yields of isolated *rac*-**3a** and **1a** after purification by preparative TLC on silica gel. [b] Enantiomeric ratios were determined by HPLC on a chiral stationary phase. Bz = benzoyl.



rac-**5f**-Ag

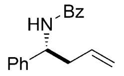
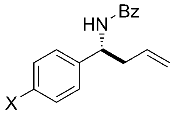
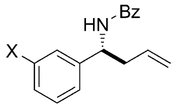
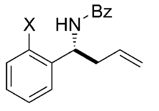
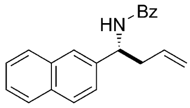
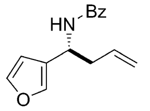
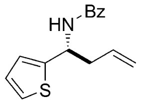
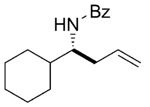
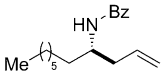
acid are ineffective.[12,13] Importantly, we confirmed that redox disproportionation of indium(I), which would generate indium(0) and indium(III) in situ,[14] did not occur in the present catalysis.[15] Thus, the combination of indium(I) chloride and (*R*)-**5b**-Ag was shown to be crucial for the highly enantioselective formation of homoallyl amide (*R*)-**3a** under mild reaction conditions. The results of our control experiments (Table 1, entries 9–12)[13,15] suggest the in situ generation of a chiral low-oxidation-state indium species as the active catalyst.

Next, we carried out a control experiment to investigate the reaction mechanism (Table 2). We employed the optically enriched aminal (*R*)-**1a** (e.r. = > 99.9:0.1) and allyl boronate **2** under standard reaction conditions using indium(I) chloride (10 mol %) combined with racemic silver phosphate *rac*-**5f**-Ag (13 mol %) as the catalyst system. This experiment was carefully analyzed over time by determining yields and enantiomeric ratios for both the generated product **3a** and the recovered substrate **1a** (15–640 min). Although the starting aminal (*R*)-**1a** was optically pure, the product **3a** proved to be racemic at all stages of the reaction. At the same time, the racemization of (*R*)-**1a** proceeded relatively slowly under mildly Lewis acidic conditions. For example, we isolated product **3a** in 15 % yield as a racemate (e.r. = 50:50) after a reaction time of 60 min, while substrate (*R*)-**1a** was recovered in 82 % yield with high optical purity (e.r. = 91:9). These results strongly indicate an iminium ion intermediate for this reaction (S_N1 pathway). In turn, these data provide proof that the catalytic asymmetric C–C bond formation (see, Table 1) proceeds by the postulated S_N1 mechanism with an iminium ion species as a key intermediate, thus confirming the critical role of the chiral counteranion (see, Scheme 1).[10,16,17] Overall, the present C–C bond-forming method relies on the generation of a chirally modified electrophile (acyclic transition state), and represents therefore an orthogonal approach compared with our related earlier study, in which we proposed a chirally modified nucleophile as a key intermediate (cyclic transition state).[10]

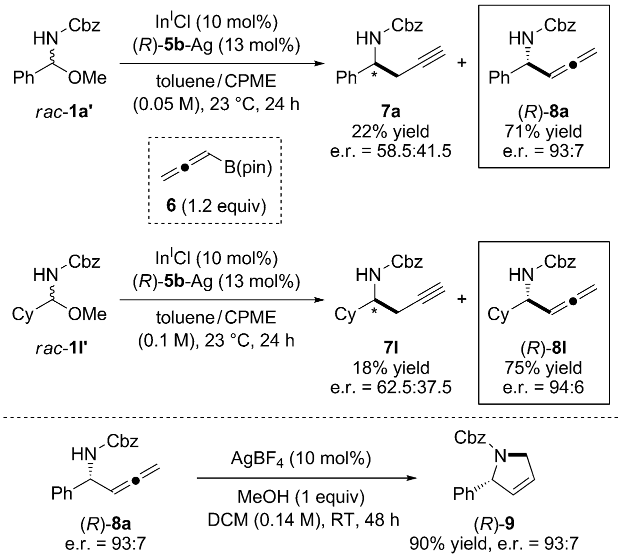
We then examined the scope of this catalytic asymmetric transformation (Table 3). Under the optimized reaction conditions the reactions between substituted aromatic or heteroaromatic aminals *rac*-**1a**–**k** and allyl boronate **2** proceeded smoothly to provide the desired products (*R*)-**3a**–**k** with high asymmetric induction (Table 3, entries 1–12). In addition, even the challenging aliphatic aminals *rac*-**1l** and *rac*-**1m** proved to be good substrates for this new catalytic asymmetric method. Product (*R*)-**3l** was formed with excellent asymmetric induction (Table 3, entry 13), which demonstrates a dramatic improvement compared with our earlier related study.[10] Product (*S*)-**3m** was obtained in high yield albeit with lower asymmetric induction (Table 3, entry 14). Overall, we consider these results remarkable as the levels of asymmetric induction exceed[4c,e,g] or equal[18b,c] even those of the corresponding catalytic asymmetric allylations of unactivated aldimines (C_{sp^2} centers) with boronate **4** or silicon-based reagents **2**.[18]

In addition, we were pleased to find that the novel chiral catalyst system was applicable to asymmetric allenylation

Table 3: Scope for the catalytic asymmetric N,O-aminal allylation.

Entry[a]	Product (*R*)-**3**		Yield [%][b]	e.r.[c]
1		(*R*)-**3a**	96	97.5:2.5
2			96[d]	98.5:1.5[d]
3		(*R*)-**3b**: X = OMe	98	97.5:2.5
4		(*R*)-**3c**: X = Me	98	98:2
5		(*R*)-**3d**: X = F	96	97:3
6		(*R*)-**3e**: X = Me	99	98:2
7		(*R*)-**3f**: X = CF$_3$	94	97:3
8		(*R*)-**3g**: X = Me	96	96.5:3.5
9		(*R*)-**3h**: X = F	98	95:5
10		(*R*)-**3i**	99	97.5:2.5
11		(*R*)-**3j**	98	95:5
12		(*R*)-**3k**	99	97.5:2.5
13		(*R*)-**3l**	96	98:2
14		(*S*)-**3m**	88	86:14

[a] Reaction conditions: *rac*-**1a–m** (1 equiv), In^{I}Cl (5 mol%), (*R*)-**5b**-Ag (6.5 mol%), **2** (1.2 equiv), toluene/CPME (0.2 M), 23 °C, 18 h. [b] Yields of isolated (*R*)-**3a–l** and (*S*)-**3m** after purification by preparative TLC on silica gel. [c] Enantiomeric ratios were determined by HPLC on a chiral stationary phase. [d] Modified reaction conditions: In^{I}Cl (10 mol%), (*R*)-**5b**-Ag (13 mol%), 12 h.



Scheme 2. Catalytic asymmetric allenylation and subsequent cyclization. Cbz = benzyloxycarbonyl, Cy = Cyclohexyl.

(Scheme 2). The reactions of aromatic and aliphatic aminals *rac*-**1a′** and *rac*-**1l′** with allenyl boronate **6** afforded the homoallenyl carbamates (*R*)-**8a** and (*R*)-**8l** in 71% and 75% yields, respectively, with high asymmetric induction (e.r. = 93:7 and 94:6, respectively). The homopropargyl carbamates **7a** and **7l** were obtained as the minor regioisomers, which were separated from (*R*)-**8a** and (*R*)-**8l** by chromatography. The observed regioselectivity is unprecedented for the use of allenyl boronate **6** in asymmetric catalysis. Thus, our work is clearly distinct from related studies.[6a,19] The utility of highly functionalized compounds of type **8** was demonstrated by a catalytic intramolecular hydroamination with (*R*)-**8a**[20] to generate azaheterocycle (*R*)-**9**[21] (Scheme 2). This 5-*endo-trig* cyclization occurred smoothly without loss of optical purity (e.r. = 93:7), and constitutes a straightforward method to access optically enriched 2-substituted 2,5-dihydropyrroles.

This report features several notable characteristics: 1) Under mildly Lewis acidic conditions, boronates proved to be dramatically more reactive and selective than classic silicon-based reagents. 2) The described transformations represent the first highly enantioselective Hosomi–Sakurai reactions with C$_{sp^3}$ centers.[2f,j] 3) This study also constitutes the first main-group-metal-catalyzed activation of allyl boronates for asymmetric C–C bond formation with C$_{sp^3}$ centers.[6] 4) Chiral Brønsted acid catalysis either with[12] or without[4g,8c] achiral metal salts proved to be inefficient. 5) In the context of asymmetric intermolecular C–C bond formation, the chemistry presented herein is a rare example not only of chiral-counteranion-directed metal catalysis,[10,12] but also of dynamic kinetic resolution.[22] Current investigations include elucidation of the catalyst structure and application to other reactions.

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Keywords: asymmetric catalysis · boron · chiral counteranion · Hosomi–Sakurai reaction · indium

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