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Copper-Catalyzed Diastereoselective Addition of Diborylmethane to *N-tert*-Butanesulfinyl Aldimines: Synthesis of β-Aminoboronates

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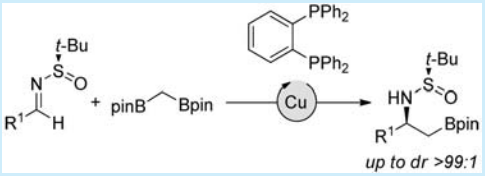
Supporting Information

ABSTRACT: We have developed a highly chemo- and diastereoselective alkylation of *N-tert*-butanesulfinyl aldimines with diborylmethane. Whereas the addition of diborylmethane under metal-free conditions shows poor diastereoselectivity, the use of a copper catalyst and a bidentate phosphine ligand significantly enhances the diastereoselectivity, providing chiral β-aminoboronates in good yields. On the basis of the stereochemical outcome, we propose that the reaction likely proceeds via a boron-chelating six-membered chairlike transition state.



The nucleophilic addition of organometallic reagents to imines bearing a chiral auxiliary is a powerful synthetic strategy that provides access to chiral α-branched amines, which are prevalent in natural products, pharmaceuticals, and asymmetric catalysts.[1] The diastereoselective addition of organometallics to *N-tert*-butanesulfinyl imines is one of the more reliable and efficient methods in this context.[2,3] However, these reagents typically suffer from drawbacks such as limited functional group tolerance and air and moisture sensitivity.

Recent progress of metal-catalyzed 1,2-addition of boronic acids or potassium organotrifluoroborates to *N-tert*-butanesulfinyl imines has significantly expanded the scope of this transformation. In particular, Ellman[4] and others[5] established a highly efficient transition-metal-catalyzed diastereoselective 1,2-addition reaction using aryl,[4a−e,5a−c] alkenyl,[4f] propargyl,[5f] and allyl[1b,5d,e] boron reagents (Scheme 1A). Despite these significant advances, the diastereoselective 1,2-addition using alkylboron reagents remains largely undeveloped.[6,7]

1,1-Diboron compounds, which contain two boryl groups at the same sp^3 carbon center, have been successfully employed in the synthesis of alkylboron compounds.[8,9] Because of their great synthetic potential, the enantio- and diastereoselective transformations of 1,1-diboron reagents are particularly appealing.[10] Hall[11a,b] and Yun[11c] independently reported the stereospecific cross-coupling of optically pure 1,1-diboron compounds. Morken and co-workers described the Pd-catalyzed enantioselective Suzuki−Miyaura coupling of 1,1-diborylalkanes with aryl[10a] and vinyl halides.[10b] The same group also reported the stereoselective deborylative alkylation of 1,1,2-tris(boronates) with alkyl halides to afford enantiomerically enriched internal 1,2-diboryl compounds through the intermediacy of an α-borylcarbanion.[10c] More recently, Meek reported the enantio- and diastereoselective addition of 1,1-diborylalkanes to aldehydes to afford 1,2-hydroxyboronates in the presence of a copper−chiral monodentate phosphoramidite complex.[10d,e] These examples illustrate interesting features of the chemo-, enantio-, and stereoselective coupling of 1,1-diboron compounds; yet, the discovery of new reactivity would be of utmost synthetic importance.

Herein, we describe the first chemo- and diastereoselective alkylation of *N-tert*-butanesulfinyl aldimines with diborylmethane catalyzed by a copper salt and an achiral bidentate phosphine ligand (Scheme 1B), likely via an uncommon six-membered transition state in metal-catalyzed 1,2-addition of organoboron reagents to *N-tert*-butanesulfinyl aldimines. The reaction provides β-aminoboronates, which can be further functionalized to generate synthetically valuable intermediates.

Inspired by developments utilizing 1,1-diborylalkanes in stereoselective transformations, we initially reasoned that the α-borylcarbanion generated from 1,1-diborylalkanes could react with *N*-sulfinyl aldimines to provide β-aminoboronates.[8e,12] To probe the viability of this envisioned strategy, at first we investigated the reaction of (*R*)-*N*-(benzylidene)-2-methylpropane-2-sulfinamide (**1a**) with diborylmethane (**2a**) under metal-free conditions. When **1a** was treated with **2a** in toluene

Scheme 1. Addition of Organometallics to *N-tert*-Butanesulfinylimine

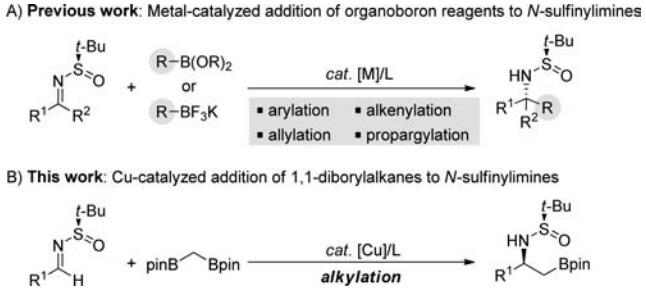


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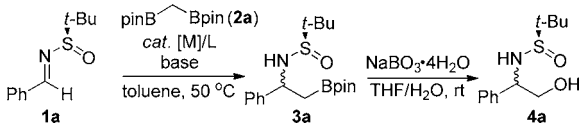
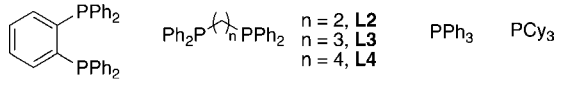
Table 1. Optimization Study[a]



entry	base	[M]	L	conv (%)	yield (%)[b]	dr[c]
1	LiO*t*Bu	–	–	<1	<1	n.d.
2	NaO*t*Bu	–	–	100	96	77:23
3	KO*t*Bu	–	–	100	86	54:46
4	LiO*t*Bu	$[Rh(COD)Cl]_2$	**L1**	39	15	83:17
5	LiO*t*Bu	$Cu(OTf)_2$	**L1**	78	66	97:3
6	LiO*t*Bu	$Cu(OTf)_2$	**L2**	46	20	95:5
7	LiO*t*Bu	$Cu(OTf)_2$	**L3**	51	32	94:6
8	LiO*t*Bu	$Cu(OTf)_2$	**L4**	56	54	95:5
9	LiO*t*Bu	$Cu(OTf)_2$	**L5**	33	15	96:4
10	LiO*t*Bu	$Cu(OTf)_2$	**L6**	62	50	95:5
11	LiO*t*Bu	CuCl	**L1**	90	61	98:2
12	LiO*t*Bu	CuBr	**L1**	100	91	99:1
13[d]	LiO*t*Bu	CuBr	–	50	24	n.d.
14[e]	–	CuBr	**L1**	<1	<1	n.d.
15[f]	LiO*t*Bu	CuBr	**L1**	100	45	85:15
16[g]	LiO*t*Bu	CuBr	**L1**	84	40	95:5

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (1.5 equiv), catalyst (10 mol %) and ligand (10 mol %) in toluene (1.0 mL) at 50 °C for 12 h, then $NaBO{\cdot}4H_2O$, THF/H_2O, rt for 2 h. [b]Determined by ^1H NMR analysis using dibromomethane as an internal standard. [c]Diastereomeric ratio was determined by HPLC (see the Supporting Information). [d]Without ligand. [e]Without LiO*t*Bu. [f]THF was used instead of toluene as a solvent. [g]5 mol % of CuBr and **L1** was used. n.d. = not detected.



at 50 °C in the presence of a stoichiometric amount of LiO*t*Bu as a base, no desired product was formed (Table 1, entry 1). In contrast, when NaO*t*Bu (entry 2) or KO*t*Bu (entry 3) were employed, the corresponding *β*-amino alcohol **4a** was obtained after oxidation of **3a** in high yields albeit with poor diastereoselectivity. On the basis of these observations, we envisioned that generation of the metal *α*-boryl species and suppression of the formation of *α*-borylcarbanion would promote the diastereoselective 1,2-addition to *N*-sulfinyl aldimines.[10d]

Thus, we set out to investigate the effect of various metal complexes on the diastereoselective 1,2-addition of **2a** to **1a** in the presence of LiO*t*Bu as a base. The reaction using $[Rh(COD)Cl]_2$ and 1,2-bis(diphenylphosphino)benzene (**L1**) ligand forms the corresponding *β*-amino alcohol (**4a**) in low yield with moderate diastereoselectivity (entry 4).[4] Switching the metal precursor from rhodium to copper yielded **4a** in 66% yield with excellent diastereoselectivity (97:3 dr, entry 5). Further screening of phosphine ligands showed lower conversion (entries 6–10) with a diastereoselectivity comparable to that obtained with **L1**. The yield of the desired product was significantly improved by changing from Cu(II) to Cu(I) salts (entries 11 and 12). In particular, copper bromide (entry 12) provided excellent yield with excellent diastereomeric ratio (99:1 dr). Reactions with CuBr in the absence of a phosphine ligand and LiO*t*Bu base resulted in very low conversion of **1a** (entries 13 and 14).[13] Moreover, poor results were obtained when the solvent was switched from toluene to THF (entry 15).[14] The catalyst loading of the reaction could be reduced, albeit in lower yield (entry 16).

The relative stereochemistry of the major isomer was assigned as (Rs, R), as determined by single-crystal X-ray analysis of **4f** (Figure 1). On the basis of the observed

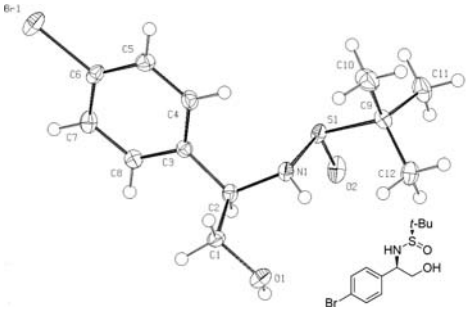
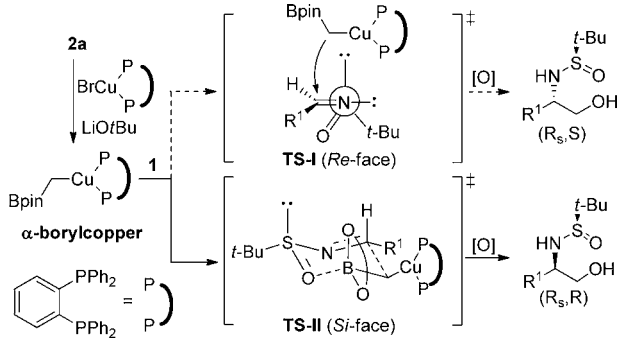


Figure 1. X-ray structure of product **4f**.

diastereoselectivity, we assumed that the reaction proceeds via a chairlike six-membered cyclic transition state, in which the boron species was coordinated to the oxygen atom of the sulfinyl moiety (Scheme 2).[15,16] This is particularly noteworthy considering that previously developed diastereoselective 1,2-addition reactions of organoboron reagents to *N-tert*-butanesulfinyl imines completely favored an open transition state (**TS-I**), because of the steric congestion caused by the ligand bound to the metal species.[4,5] A similar boron-chelated transition state was reported in the diastereoselective reduction of *N-tert*-butanesulfinyl imines employing 9-BBN as a reducing reagent.[17]

Scheme 2. Rationale for the Diastereoselectivity: Open Transition State (TS-I) and Chairlike Transition State (TS-II)



With the optimal conditions in hand, we then examined the scope of *N-tert*-butanesulfinyl aldimines **1** with diborylmethane **2a** (Table 2).[18] In all cases, the crude mixtures were directly oxidized to the corresponding *β*-amino alcohols to facilitate chromatographic separation and HPLC determination of the diastereomeric ratio. The 1,2-addition to the substrate bearing a methyl group in the para position of the aromatic ring proceeded in good yield and moderate diastereoselectivity. However, the reaction of substrate **1b** at room temperature afforded **4b** with almost complete diastereoselectivity (99:1 dr), albeit with slightly lower efficiency after a prolonged reaction time (24 h). In addition, the electron-poor substrate bearing a

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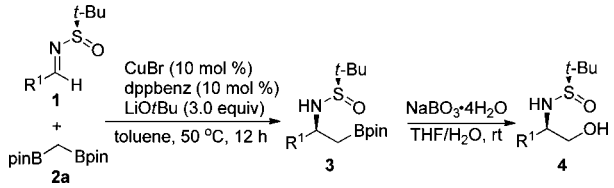
Table 2. Substrate Scope[a,b,c]



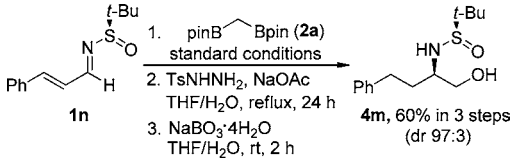
entry	R^1	product	yield (%)[b]	dr[c]
1	C_6H_5	**4a**	85	99:1
2	(4-Me)C_6H_4	**4b**	76	90:10
3[d]	(4-Me)C_6H_4	**4b**	57	99:1
4	(4-CF_3)C_6H_4	**4c**	87	97:3
5	(4-F)C_6H_4	**4d**	75	98:2
6	(4-Cl)C_6H_4	**4e**	82	97:3
7	(4-Br)C_6H_4	**4f**	70	98:2
8	(3-Me)C_6H_4	**4g**	61	97:3
9	(3-Cl)C_6H_4	**4h**	69	97:3
10	(3-Br)C_6H_4	**4i**	73	96:4
11	(2-Me)C_6H_4	**4j**	53	96:4
12	2-furyl	**4k**	67	98:2
13	2-thienyl	**4l**	96	94:6
14	$PhCH_2CH_2$	**4m**	<1	–

[a]Reaction conditions: **1** (0.2 mmol), **2a** (1.5 equiv), CuBr (10 mol %), **L1** (10 mol %) and LiO*t*Bu in toluene (1.0 mL) at 50 °C for 12 h, then $NaBO_3·4H_2O$, THF/H_2O, rt for 2 h. [b]Isolated yields of the corresponding 1,2-amino alcohol. [c]Diastereoselectivity was determined by HPLC (see the Supporting Information). [d]Runs at room temperature for 24 h.

trifluoromethyl group in the para position gave product **4c** in 87% yield with excellent diastereoselectivity (97:3 dr). The reactions of *N*-*tert*-butanesulfinyl aldimines with halides in the para position provided the corresponding *β*-amino alcohols with satisfactory yield and diastereoselectivity (70−82%, 97:3−98:2 dr). *N*-*tert*-Butanesulfinyl aldimines with substituents at the meta or ortho position of the aromatic ring also reacted smoothly to produce **4g**−**4j** with good diastereomeric ratios (96:4−97:3 dr). The reactions of heteroaryl-substituted *N*-sulfinyl aldimines were also examined. The substrate containing a furyl group reacted with **2a** to deliver **4k** in acceptable yield (67%) and excellent diastereoselectivity (98:2 dr). The *N*-sulfinyl aldimine containing a thienyl group also resulted in the formation of desired product **4l** in high yield (96%) with moderate diastereoselectivity (94:6 dr). Unfortunately, an aliphatic *N*-*tert*-butanesulfinyl aldimine failed to provide the corresponding product under the standard conditions.

It should be noted that the developed chemo- and diastereoselective alkylation reaction could be applied also to *α*,*β*-unsaturated *N*-*tert*-butanesulfinyl aldimines (Scheme 3). When **1n** was treated with **2a** under the standard conditions, the corresponding *α*,*β*-unsaturated *β*-aminoboronate product was formed, which was directly subjected to hydrogenation and

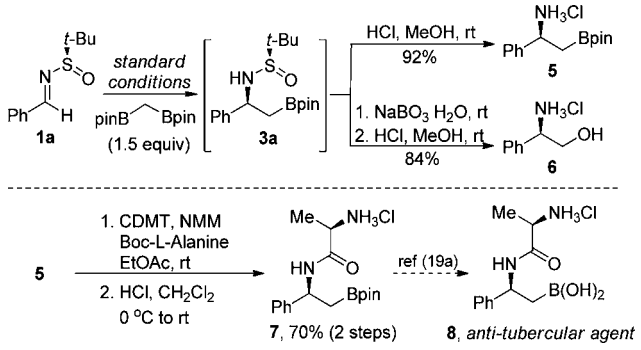
Scheme 3. Copper-Catalyzed Diastereoselective Addition of 2b to *α*,*β*-Unsaturated *N*-*tert*-Butanesulfinylimine



oxidation to give aliphatic *β*-amino alcohol **4m** in 60% yield (over 3 steps) with good diastereoselectivity (97:3 dr). Thus, in view of the poor conversion of aliphatic *N*-sulfinyl aldimine **1m** under our reaction conditions, this strategy provides a useful alternative for the preparation of aliphatic *β*-amino alcohol.

Because our method provides *N*-protected *β*-aminoboronates, a tandem diastereoselective alkylation/deprotection sequence was examined. As depicted in Scheme 4, this strategy

Scheme 4. Deprotection of *N*-Sufinyl Group and Synthesis of Antitubercular Agent



provided the corresponding *β*-aminoboronate hydrochloride **5** in 92% yield over two steps. Notably, in the event, the Bpin unit remained intact. In addition, the Cu-catalyzed diastereoselective alkylation of **1a** with diborylmethane followed by the sequential oxidation of Bpin and deprotection of the sulfinyl group afforded the corresponding *β*-amino alcohol hydrochloride **6** in 84% overall yield.

The *β*-aminoboronate motif is commonly found in pharmacologically active agents; thus, the synthetic utility of product **5** can be highlighted by its application to the synthesis of *β*-substituted *β*-aminoboron compound **8**, a highly potent antitubercular agent.[19] The reaction of *β*-aminoboronate hydrochloride **5** with Boc-L-alanine in the presence of 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) and *N*-methylmorpholine (NMM)[20] followed by deprotection of the Boc group under acidic conditions gave **7** in 70% yield, without epimerization of the stereocenter. The obtained product **7** could be converted into the corresponding antitubercular agent **8** following literature procedures.[19a]

In summary, we have developed the first example of a copper-catalyzed chemo- and diastereoselective addition of 1,1-diborylalkanes to *N*-*tert*-butanesulfinyl aldimines. Whereas the reaction proceeds with low diastereoselectivity under metal-free conditions, when a copper catalyst and a bidentate phosphine ligand are employed, the corresponding *β*-aminoboronates are obtained in good yields and high diastereoselectivity. On the basis of the observed diastereoselectivity, we propose that the reaction likely proceeds through a boron-chelating chairlike transition state.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00376.

Experimental details, spectral data for all compounds, and crystallographic data for **4f** (PDF)

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Notes

The authors declare no competing financial interest.

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(14) A significant amount of *trans*-2-phenylvinylboronate (53%) was detected as a side product in THF.

(15) We assumed that copper species are not involved in a chairlike transition state because of the steric hindrance between the ligand bound to copper and the substrate. For related works, see refs 4 and 5.

(16) In contrast to copper-catalyzed conditions, the in situ generated α-borylcarbanion can presumably access both the less-hindered *Re*-face through the noncoordinate **TS-I** and the *Si*-face of the *N*-sulfinyl imine through the six-membered **TS-II** to form the corresponding diastereomeric mixtures under metal-free conditions.

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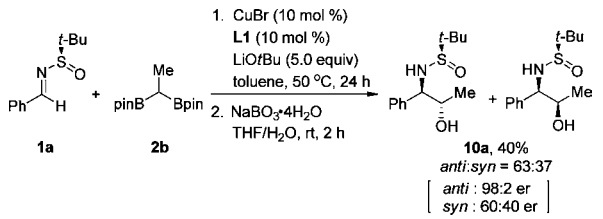

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