Enantioselective synthesis of optically active homoallylamines by nucleophilic addition of chirally modified allylboranes to *N*-silylimines

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Enantioselectivity in the allylboration of *N*-silylimines with a variety of chirally modified allylboron reagents has been examined. Optically active *N*-sulfonylamino alcohols (**16**, **17** and **19**) derived from D-camphor and norephedrine were found to be efficient chiral ligands for the allylboration reagent. These reagents smoothly reacted with *N*-silylimines to give the corresponding homoallylic amines in a high level of enantioselectivity up to 96% ee.

Introduction

In recent years, considerable progress has been made in the asymmetric addition of carbon nucleophiles to prochiral carbonyl compounds. Especially, enantioselective allylation of aldehydes has been extensively studied and various efficient chiral allylating agents have been developed.[1] Chirally modified allylboron reagents have been particularly important for allylations.[2] By comparison, the asymmetric addition of carbon nucleophiles to prochiral imines leading to optically active amines is a field which is still in its infancy. Optically active amines are important compounds utilized extensively in organic synthesis as starting materials in the preparation of biologically active substances, resolving agents, and chiral auxiliaries for asymmetric synthesis.[3] Although the enantioselective synthesis of optically active amines by nucleophilic addition of organometallic reagents toward imines is a topic of current interest,[4] the enantioselective addition of allylmetallic reagents to the C=N double bond is quite underdeveloped.[5] There are only a few reports on the asymmetric allylation of aldimines.[6–8] We have recently found that some chirally modified allylboron reagents could asymmetrically add to *N*-metalloimines such as *N*-silylimines[9] and *N*-aluminioimines[10] to afford the corresponding enantioenriched homoallylamines. Since this methodology appeared to be potentially useful for preparing certain enantioenriched homoallylamines, we have examined the scope and limitation of this procedure. We report herein the details of our efforts to find suitable conditions for preparing highly enantioenriched homoallylamines by nucleophilic addition of chirally modified allylboron reagents to *N*-silylimines.

Results and discussion

Before our study of asymmetric allylboration of imines, we surveyed the reactivity of various imines toward triallylboranes (Scheme 1, Table 1). Allylboration of *N*-arylimine **1** gave the secondary homoallylic amine in moderate yield after 16 h at room temperature. Bulky N-substituents such as a trityl group completely prevented the allylboration reaction even after 24 h at room temperature (entry 2). Oxime ether **3** reacted with triallylborane slowly to give the corresponding methoxyamine in low yield. Sulfenimine **5** was converted to the sulfenamide that

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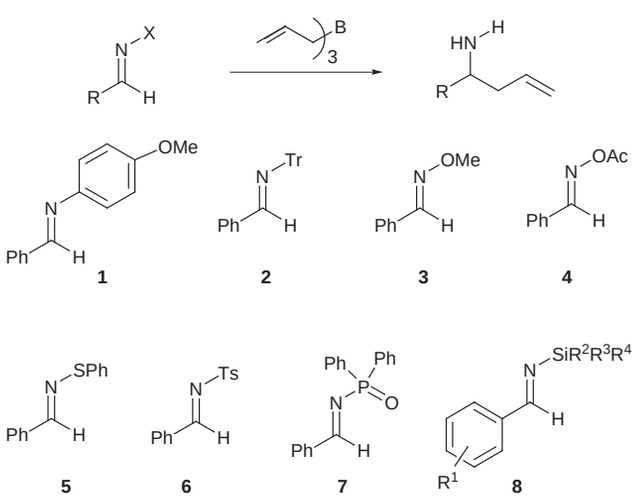
Table 1 Allylboration of various *N*-substituted imines with triallylborane in THF at room temperature

Entry	Imine	*N*-Substituent	Reaction time (*t*/h)	Yield of homoallylamine (%)[a]
1	**1**	4-$MeOC_6H_4$	16	55[b]
2	**2**	Tr	24	NR[c]
3	**3**	MeO	24	36[d]
4	**4**	Ac	24	NR[c]
5	**5**	PhS	30	55
6	**6**	Ts	20	Complex mixture
7	**7**	$Ph_2P(O)$	20	NR[c]
8[e]	**8a**	Me_3Si	3	90

[a] Isolated yields. [b] The corresponding 4-methoxyphenylamine was obtained. [c] No reaction. [d] The corresponding methoxyamine was obtained. [e] At 0 °C.



8a: R^1 = H, R^2 = R^3 = R^4 = Me
8b: R^1 = *o*-Cl, R^2 = R^3 = R^4 = Me
8c: R^1 = *p*-Cl, R^2 = R^3 = R^4 = Me
8d: R^1 = *o*-OMe, R^2 = R^3 = R^4 = Me
8e: R^1 = *p*-OMe, R^2 = R^3 = R^4 = Me
8f: R^1 = H, R^2 = R^3 = Me, R^4 = ^{t}Bu
8g: R^1 = H, R^2 = R^3 = R^4 = ^{i}Pr

Scheme 1

Table 2 Enantioselective allylboration of *N*-(trimethylsilyl)imines with chirally modified allylborane **10**

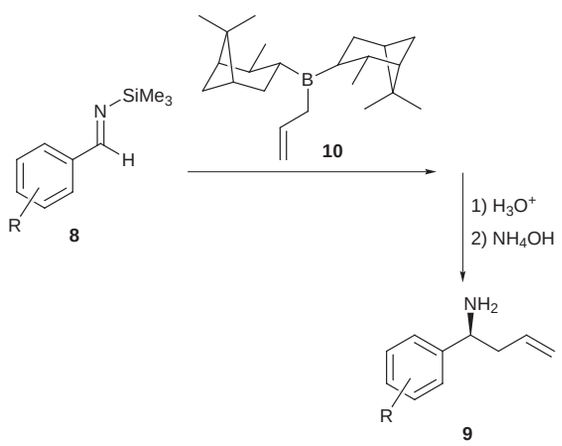
				Homoallylamine **9**		
Entry	Silylimine	Solvent	*T*/°C	Yield (%)[a]	ee (%)[b]	Config.[c]
1	**8a**	THF	−78	65	64	*S*
2	**8a**	Ether	−78	70	73	*S*
3	**8a**	Ether	−30	76	43	*S*
4	**8a**	Ether	0	84	29	*S*
5	**8b**	THF	−78	62	46	*S*
6	**8c**	THF	−78	72	8	*S*
7	**8d**	THF	−78	65	52	*S*
8	**8e**	THF	−78	70	14	*S*

[a] Isolated yields. [b] Determined by HPLC analysis with a chiral stationary-phase column. See Experimental section. [c] The absolute configuration of the product was determined by comparison of the specific rotation with the reported value (ref. 19).

Table 3 Enantioselective allylboration of *N*-(trimethylsilyl)benzaldimine **8a** with chirally modified allylboron reagents for 3 h at −78 °C

			1-Phenylbut-3-enamine **9a**		
Entry	Chiral ligand	Solvent	Yield (%)[a]	ee (%)[b]	Config.[c]
1	**11a**	THF	89	39	*R*
2	**11b**	THF	70	25	*R*
3	**11c**	THF	83	32	*R*
4	**12**	THF	92	32	*R*
5	**13**	THF	26	28	*R*
6	**14**	THF	14	14	*S*
7	**15**	THF	90	40	*R*
8	**16a**	Ether	65	65	*S*
9	**17**	Ether	93	72	*R*
10	**18**	THF	81	53	*S*
11	**19a**	Ether	88	78	*S*
12	**21**	Ether	12	10	*R*
13	**22**	THF	72	27	*R*

[a] Isolated yields. [b] Determined by HPLC analysis with a chiral stationary-phase column. See Experimental section. [c] The absolute configuration of the product was determined by comparison of the specific rotation with the reported value (ref. 19).



Scheme 2

could be elaborated to the primary homoallylamine by acid treatment. Although *N*-*p*-tolylsulfonyl-[11,12] and *N*-diphenylphosphinoylimines[13] are known to react with some organometallic reagents to give the corresponding amines, the reaction of *N*-tosylimine **6** with triallylborane yielded only a complex mixture. *N*-Diphenylphosphinoylimine **7** showed no reaction with triallylborane at room temperature. Finally we found that *N*-trimethylsilylimine **8a** was relatively highly reactive toward triallylborane, and gave the homoallylamine in high yield as shown in Table 1 (entry 8). The trimethylsilyl group was easily removed during the usual aqueous work-up procedure to give the primary amine. The high reactivity of the *N*-trimethylsilylimine toward triallylborane prompted us to apply this reaction to its asymmetric version. Since various excellent chiral allylboron reagents have been developed for the enantioselective allylboration of aldehydes to prepare homoallylic alcohols,[1] we first chose one of these chiral reagents for the enantioselective allylboration of *N*-silylimines.

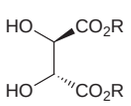
In the first place, enantiopure allyldiisopinocampheylborane[14] **10** developed by Brown was employed as enantioselective allylboration agent for **8a** (Scheme 2). This reagent is known as one of the most effective allylborating agents for aldehydes. Another advantage of this reagent is its easy accessibility from commercially available (−)-chlorodiisopinocampheylborane [(−)-DIP-Chloride™]. Table 2 showed that enantioselective allylboration of several *N*-(trimethylsilyl)-imines with **10**. Allylboration of **8a** with **10** in THF at −78 °C afforded the enantioenriched homoallylamine **9a** in satisfactory yield with 64% ee (entry 1). The use of diethyl ether (hereinafter abbreviated simply as ether) as solvent gave somewhat higher enantioselectivity. The enantioselectivity decreased with increasing temperature as expected (Table 2, entries 2–4). In all cases the *si*-face of the imine was attacked by **10** to yield the *S*-homoallylamine. However, the enantioselectivities were very much affected by the substituents on the aromatic ring of the imine. Very recently, Brown and co-workers reported a modified method for the asymmetric allylboration of *N*-silylimines, which showed higher enantioselectivities.[15] They claimed that *N*-trimethylsilylimines were not reactive toward **10**, and suggested that aldimines generated *in situ* from *N*-trimethylsilylimines by addition of 1 mol equiv. of water could react with **10**. From these observations, the reaction in our case might occur during aqueous work-up.

To examine the enantioselectivity in allylboration of *N*-silylimines, we have prepared various kinds of chirally modified allylboron reagents other than **10**. These reagents were readily prepared from the reaction of triallylborane with chiral bidentate ligands such as chiral diols **11** and **12**, hydroxy acid **13**, *N*-sulfonylamino acid **14**, and *N*-sulfonylamino alcohols **15**–**22**. As shown in Table 3, asymmetric allylboration of **8a** took place smoothly with these chirally modified allylboron reagents at −78 °C to give the corresponding primary homoallylamine **9a**. Although tartrate ligands **11** developed by Roush showed high efficiency in the allylboration of aldehydes,[1g,16] not very good selectivity was obtained in the allylboration of the imine (entries 1–3). Enantiopure *N*-sulfonylamino alcohols derived from D-camphor and norephedrine showed relatively higher enantioselectivity in the allylboration (entries 8–11). However, contrary to the reaction with **10**, addition of water severely prevented the allylboration with these reagents giving benzaldehyde instead. *N*-Trimethylsilylimine is reactive enough toward these reagents. GC analysis of the reaction mixture showed that the *N*-trimethylsilylimine was consumed before aqueous work-up, which also supported the above mentioned reactivity of the reagents.

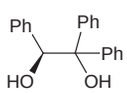
Table 4 Enantioselective allylboration of *N*-(trialkylsilyl)benzaldimines **8** with chirally modified allylboron reagents derived from **16** and **17** at −78 °C for 3 h

Entry	Trialkylsilyl group (imine)	Chiral ligand	Solvent	1-Phenylbut-3-enamine		
				Yield (%)[a]	ee (%)[b]	Config.[c]
1	TMS (**8a**)	**16a**	Ether	65	65	*S*
2	TMS (**8a**)	**16b**	Ether	90	89	*S*
3	TBDMS (**8f**)	**16b**	Ether	83	67	*S*
4	TIPS (**8g**)	**16b**	Ether	54	55	*S*
5	TMS (**8a**)	**16c**	Ether	37	86	*S*
6	TBDMS (**8f**)	**16c**	Ether	73	83	*S*
7	TIPS (**8g**)	**16c**	Ether	20	58	*S*
8	TMS (**8a**)	**17**	Ether	93	72	*R*
9[d]	TMS (**8a**)	**17**	Ether	92	76	*R*
10	TMS (**8a**)	**17**	THF	92	64	*R*
11	TMS (**8a**)	**17**	Toluene	73	53	*R*
12	TMS (**8a**)	**17**	Hexane	67	35	*R*

[a] Isolated yields. [b] Determined by HPLC analysis with a chiral stationary-phase column. See Experimental section. [c] The absolute configuration of the product was determined by comparison of the specific rotation with the reported value (ref. 19). [d] At −100 °C.



11a R = Me
11b R = Et
11c R = ^{i}Pr



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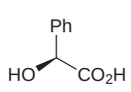

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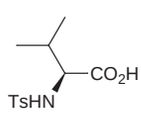

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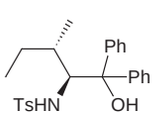

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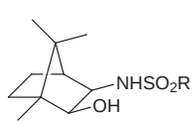
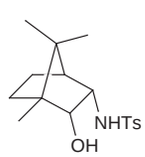


16a R = Me
16b R = Tol
16c R = 2-Naph



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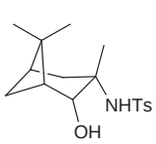

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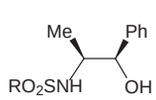
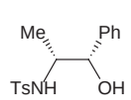


19a R = Me
19b R = Tol
19c R = *o*-NO_2Ph
19d R = 1-Naph
19e R = 2-Naph



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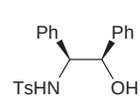

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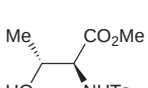

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The effect of the silyl substituent of *N*-silylimines **8** was then investigated by using camphor-derived chiral allylboron reagents (Table 4). The synthesis of *N*-(trialkylsilyl)imines possessing bulky silyl groups such as *tert*-butyldimethylsilyl (TBDMS) and triisopropylsilyl (TIPS) has recently been reported by Cainelli *et al.*[17] Enantioselective allylboration of these *N*-silylimines with the reagents derived from sulfonamides **16** was tested. In spite of a bulky substituent on the imine nitrogen, the reaction occurred at −78 °C. In the case of the TIPS imine, both the yield and ee decreased. By using these bulky trialkylsilyl groups, aromatic as well as aliphatic enolizable imines could be prepared.[17] Although we have prepared such aliphatic *N*-(*tert*-butyldimethylsilyl)imines, unfortunately, no reaction occurred when they were treated with **16a**. The solvent effect was examined by using chiral ligand **17** as shown in Table 4 (entries 8–12). From these results ether is the choice of solvent. A similar tendency was observed when the chiral ligand **19b** was employed (Table 5). In the case of camphor-based enantiopure *N*-sulfonylamino alcohols, *exo*-derivatives **16** preferred *si*-face attack to give *S*-homoallylamine, while *endo*-derivative **17** preferred *re*-face attack to give *R*-homoallylamine in all solvents tested.

Table 5 Effect of N-substituent in the chiral ligand **19** on the allylboration of **8a**

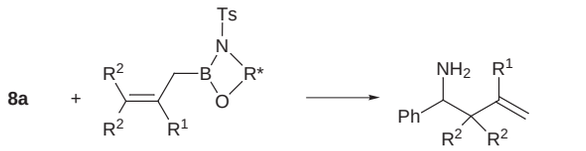
Entry	Chiral ligand	Solvent	1-Phenylbut-3-enamine		
			Yield (%)[a]	ee (%)[b]	Config.[c]
1	**19a**	Ether	88	78	*S*
2	**19b**	Ether	89	92	*S*
3[d]	**19b**	Ether	80	96	*S*
4	**19b**	THF	91	87	*S*
5	**19b**	Toluene	76	77	*S*
6	**19b**	Hexane	64	68	*S*
7	**19c**	Ether	91	87	*S*
8	**19d**	Ether	92	88	*S*
9	**19e**	Ether	93	91	*S*
10	**20**	Ether	90	92	*R*

[a] Isolated yields. [b] Determined by HPLC analysis with a chiral stationary-phase column. See Experimental section. [c] The absolute configuration of the product was determined by comparison of the specific rotation with the reported value (ref. 19). [d] At −100 °C.

Among the various chiral ligands used in this study, those represented by structure **19** derived from norephedrine appeared to be the most suitable for the allylboration of the imine (Table 3). The effect of the substituent of the enantiopure *N*-sulfonylamino alcohols **19** on the reactivity and selectivity has then been investigated. The results are shown in Table 5. Of various substituents investigated tolylsulfonyl **19b** gave the best result. It is noteworthy that this reaction occurred even at −100 °C in high yield (entry 3). Enantioselectivity obtained at this temperature was always somewhat higher than that obtained at −78 °C (Table 4 entry 9, Table 5 entry 3, Table 6 entry 5). Thus, the highest ee (96% ee) for the allylboration of **8a** was attained by using **19b** in ether at −100 °C (Table 5, entry 3). Both enantiomers of norephedrine are commercially available. From (1*R*,2*S*)-norephedrine, *S*-homoallylamine was obtained, while *R*-homoallylamine with the same ee was obtained from (1*S*,2*R*)-norephedrine (entries 2, 10).

Not only allylboration, but also methallyl- and prenylboration were possible in this system. Instead of an allylboron reagent, methallyl- or prenylboron reagents were prepared using **17** and **19b** as chiral ligands. They also reacted smoothly with imine **8a** to give the corresponding homoallylamines with high ee as shown in Table 6. In the case of methallylboration of **8a** with the chiral reagent prepared from **19b** the homoallylamine was obtained in 94% yield with 96% ee at −100 °C (entry 5).

Table 6 Enantioselective allylboration of *N*-(trimethylsilyl)benzaldimine **8a** with chirally modified allylboron reagents in ether at −78 °C



Entry	Chiral ligand	R¹	R²	Homoallylamine Yield (%)[a]	ee (%)[b]	Config.[c]
1[d]	**17**	Me	H	89	72	*R*
2	**17**	Me	H	89	80	*R*
3	**17**	H	Me	91	68	*R*
4	**19b**	Me	H	92	94	*S*
5[e]	**19b**	Me	H	94	96	*S*
6	**19b**	H	Me	89	87	*S*

[a] Isolated yields. [b] Determined by HPLC analysis with a chiral stationary-phase column. See Experimental section. [c] The absolute configuration of the product was determined by comparison of the specific rotation with the reported value (ref. 19). [d] THF was used as solvent. [e] At −100 °C.

In conclusion, we have investigated the enantioselectivity in the reaction of chirally modified allylboron reagents with *N*-silylimines. Of various chiral ligands developed in this study, *N*-sulfonylamino alcohols such as **16**, **17** and **19** showed high levels of enantioselectivity with good yields of the primary homoallylic amines. These chiral ligands were readily prepared and recovered in high yield after the reaction. The foregoing results clearly demonstrate that our methodology provides a practical way of obtaining optically active primary homoallylic amines with high ee. Related reactions by using the polymer-supported *N*-sulfonylamino alcohols as solid phase chiral ligands are in progress.

Experimental

General

All reactions were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) and ether were freshly distilled from sodium benzophenone ketyl under nitrogen immediately before use. (−)-Chlorodiisopinocampheylborane [(−)-DIP-Chloride™] was purchased from Aldrich, Inc. Reactions were monitored by TLC using Merck precoated silica gel plates (Merck 5554, $60F_{254}$). Flash column chromatography was performed over Wako silica gel (Wakogel C-200, 100–200 mesh). Mps were measured on a Yanaco micro melting point apparatus and are uncorrected. Microanalyses were obtained using YANACO MT-3 CHN CORDER. ^{1}H NMR spectra were measured on a JEOL JNM-GX270 spectrometer using Me_4Si as an internal standard, and *J* values are reported in Hz. IR spectra were recorded with a JEOL JI*R*-7000 FT-IR spectrometer and are reported in reciprocal centimeters (cm^{-1}). Optical purity was determined by HPLC analysis with a TOSOH HLC-8020 or JASCO HPLC system composed of 3-Line Degasser DG-980-50, HPLC Pump PV-980, and Column oven CO-965, equipped with a chiral column (Chiralcel OD-H, Daicel) using hexane–propan-2-ol–diethylamine (90 : 10 : 0.1). A UV detector (TOSOH UV-8011 for TOSOH HPLC system, JASCO UV-975 for JASCO HPLC system) was used for chromatographic peak detection. Optical rotations were taken on a JASCO DIP-140 digital polarimeter using a 10 cm thermostatted microcell. $[\alpha]_D$-Values are given in units of 10^{-1} deg cm^2 g^{-1}.

All *N*-trimethylsilylimines **8a–8e** were obtained by reaction of the corresponding aldehydes with lithium hexamethyldisilazide according to the literature procedure.[18] *N*-Trialkylsilylimines **8f** and **8g** were prepared according to Cainelli's procedure.[17]

General procedure for the preparation of the *N*-sulfonylamino alcohols 15–22

The preparation of **19b** is typical. To a solution of (1*R*,2*S*)-norephedrine (1.51 g, 10 mmol) in THF (50 cm^3) were added triethylamine (1.4 cm^3, 10 mmol) and toluene-*p*-sulfonyl chloride (1.9 g, 10 mmol) at 0 °C. After being stirred for 3 h at room temperature, the reaction mixture was poured into 1 M aq. HCl (50 cm^3), and the THF was evaporated under vacuum. The resulting aqueous solution was extracted with ether (3 × 25 cm^3). The combined extracts were dried over $MgSO_4$ and evaporated at reduced pressure to give the crude product. Recrystallization from ethanol–water gave **19b** in 96% yield; $[\alpha]_D^{25}$ −15.93 (*c* 2.48 in $CHCl_3$); mp 82 °C; ν_{max}(KBr) 3500, 3255, 1591, 1456, 1324, 1160; δ_H($CDCl_3$; 270 MHz) 0.82 (3H, d, *J* 6.8), 2.41 (3H, s), 2.86 (1H, br), 3.52–3.58 (1H, m), 4.79 (1H, d, *J* 3.4), 5.16 (1H, d, *J* 8.8), 7.21–7.33 (7H, m), 7.77 (2H, d, *J* 8.3) (Found: C, 62.82; H, 6.28; N, 4.25. $C_{16}H_{19}NO_3S$ requires C, 62.92, H, 6.28; N, 4.59%).

14. Yield 83%; $[\alpha]_D^{25}$ +17.1 (*c* 2.23 in $CHCl_3$); mp 150–153 °C; ν_{max}(KBr) 3332, 3178, 2962, 1727, 1691, 1468, 1346, 1141, 1089; δ_H($CDCl_3$; 270 MHz) 0.85 (3H, d, *J* 6.8), 0.94 (3H, d, *J* 6.8), 2.09 (1H, br), 2.40 (3H, s), 3.77 (1H, dd, *J* 9.8 and 4.4), 5.43 (1H, d, *J* 9.8), 7.26 (2H, d, *J* 7.8), 7.71 (2H, d, *J* 8.3) (Found: C, 53.29; H, 6.28; N, 4.86. $C_{12}H_{17}NO_4S$ requires C, 53.14; H, 6.27; N, 5.17%).

15; Yield 84%; $[\alpha]_D^{25}$ +20.06 (*c* 2.81 in THF); mp 195–198 °C; ν_{max}(KBr) 3530, 3300, 2960, 1455, 1325, 1158, 1098; δ_H($CDCl_3$; 270 MHz) 0.67 (3H, t, *J* 7.3), 0.84–0.95 (1H, m), 0.98 (3H, d, *J* 6.8), 1.16–1.22 (1H, m), 1.58–1.64 (1H, m), 2.37 (3H, s), 2.66 (1H, s), 4.37 (1H, d, *J* 9.8), 4.66 (1H, d, *J* 9.3), 7.10–7.43 (14H, m) (Found: C, 70.89; H, 6.94; N, 3.31. $C_{25}H_{29}NO_3S$ requires C, 70.92; H, 6.98; N, 3.31%).

16a. Yield 83%; $[\alpha]_D^{25}$ +31.46 (*c* 2.30 in $CHCl_3$); mp 128–130 °C; ν_{max}(KBr) 3498, 3239, 2959, 1481, 1306, 1151; δ_H($CDCl_3$; 270 MHz) 0.82 (3H, s), 0.95 (3H, s), 1.08 (3H, s), 1.50–1.84 (5H, m), 2.40 (1H, br s), 2.98 (3H, s), 3.48 (1H, t, *J* 7.3), 3.70–3.80 (1H, m), 5.08 (1H, br s) (Found: C, 53.44; H, 8.50; N, 5.67. $C_{11}H_{21}NO_3S$ requires C, 53.41; H, 8.56; N, 5.66%).

16b. Yield 90%; $[\alpha]_D^{25}$ −25.03 (*c* 1.73 in EtOH); mp 144–147 °C; ν_{max}(KBr) 3516, 3330, 2960, 1597, 1483, 1340, 1095; δ_H($CDCl_3$; 270 MHz) 0.76 (3H, s), 0.89 (3H, s), 1.05 (3H, s), 1.39–1.68 (5H, m), 2.03 (1H, d, *J* 4.4), 2.44 (3H, s), 3.24 (1H, t, *J* 7.3), 3.56 (1H, dd, *J* 7.3 and 3.9), 5.24 (1H, d, *J* 6.3), 7.31 (2H, d, *J* 8.3), 7.76 (2H, d, *J* 8.3) (Found: C, 63.15; H, 7.78; N, 4.33. $C_{17}H_{25}NO_3S$ requires C, 63.16; H, 7.74; N, 4.33%).

16c. Yield 75%; $[\alpha]_D^{25}$ +16.1 (*c* 1.59 in $CHCl_3$); mp 165 °C; ν_{max}(KBr) 3529, 3336, 2956, 1589, 1482, 1344, 1093; δ_H($CDCl_3$; 270 MHz) 0.72 (3H, s), 0.86 (3H, s), 1.05 (3H, s), 1.23–1.70 (5H, m), 2.14 (1H, d, *J* 4.4), 3.26–3.33 (1H, m), 3.53–3.58 (1H, m), 5.42 (1H, d, *J* 6.3), 7.57–7.97 (7H, m) (Found: C, 66.90; H, 7.00; N, 3.90. $C_{20}H_{25}NO_3S$ requires C, 66.85; H, 6.96; N, 3.90%).

17. Yield 79%; $[\alpha]_D^{25}$ +34.4 (*c* 2.77 in CH_2Cl_2); mp 134–136 °C; ν_{max}(KBr) 3527, 3342, 2929, 1599, 1495, 1321, 1094; δ_H($CDCl_3$; 270 MHz) 0.80 (3H, s), 0.83 (3H, s), 0.85 (3H, s), 1.06–1.74 (5H, m), 2.03 (1H, d, *J* 3.9), 2.43 (3H, s), 3.67–3.78 (2H, m), 5.24 (1H, d, *J* 6.4), 7.30 (2H, d, *J* 8.3), 7.77 (2H, d, *J* 8.3) (Found: C, 63.05; H, 7.72; N, 4.17. $C_{17}H_{25}NO_3S$ requires C, 63.16; H, 7.74; N, 4.33%).

19a. Yield 97%; $[\alpha]_D^{25}$ −27.12 (*c* 2.81 in $CHCl_3$); mp 98–100 °C; ν_{max}(KBr) 3505, 3280, 1593, 1160; δ_H($CDCl_3$; 270 MHz) 1.07 (3H, d, *J* 6.8), 2.89 (3H, s), 3.18 (1H, d, *J* 3.9), 3.68–3.80 (1H, m), 4.82–4.88 (1H, m), 4.97 (1H, d, *J* 8.8), 7.25–7.34 (5H, m)

(Found: C, 52.39; H, 6.58; N, 6.11. $C_{10}H_{15}NO_3S$ requires C, 52.38; H, 6.61; N, 6.11%).

19c. Yield 96%; $[\alpha]_D^{25}$ +41.97 (*c* 2.33 in $CHCl_3$); mp 111–113 °C; ν_{max}(KBr) 3527, 3342, 1535, 1417, 1356, 1317; δ_H($CDCl_3$; 270 MHz) 0.97 (3H, d, *J* 6.8), 2.51 (1H, d, *J* 4.4), 3.70–3.90 (1H, m), 4.75–4.82 (1H, m), 5.62 (1H, d, *J* 8.3), 7.21–7.33 (5H, m), 7.69–7.88 (3H, m) (Found: C, 53.54; H, 3.93; N, 8.38. $C_{15}H_{16}N_2O_5S$ requires C, 53.56; H, 3.90; N, 8.32%).

19d. Yield 94%; $[\alpha]_D^{25}$ −28.64 (*c* 2.56 in $CHCl_3$); mp 92 °C; ν_{max}(KBr) 3532, 3317, 1432, 1155, 1093; δ_H($CDCl_3$; 270 MHz) 0.74 (3H, d, *J* 6.8), 2.60 (1H, d, *J* 3.9), 3.47–3.59 (1H, m), 4.62–4.68 (1H, m), 5.2 (1H, d, *J* 8.8), 7.12–7.27 (5H, m), 7.52–7.69 (3H, m), 7.93 (1H, d, *J* 8.3), 8.07 (1H, d, *J* 8.3), 8.32 (1H, d, *J* 7.3), 8.62 (1H, d, *J* 8.8) (Found: C, 66.91; H, 5.58; N, 4.13. $C_{19}H_{19}NO_3S$ requires C, 66.84; H, 5.62; N, 4.10%).

19e. Yield 97%; $[\alpha]_D^{25}$ +14.95 (*c* 2.48 in CH_2Cl_2); mp 82 °C; ν_{max}(KBr) 3523, 3315, 1433, 1155, 1092; δ_H($CDCl_3$; 270 MHz) 0.85 (3H, d, *J* 6.8), 2.71 (1H, br s), 3.61–3.72 (1H, m), 4.76–4.84 (1H, m), 5.11 (1H, d, *J* 8.8), 7.18–7.30 (5H, m), 7.57–7.67 (2H, m), 7.82–7.96 (4H, m), 8.47 (1H, s) (Found: C, 66.80; H, 5.71; N, 4.11. $C_{19}H_{19}NO_3S$: C, 66.84; H, 5.62; N, 4.10%).

20. Yield 96%; $[\alpha]_D^{25}$ +15.93 (*c* 2.48 in $CHCl_3$); mp 93–95 °C; ν_{max}(KBr) 3504, 3257, 1591, 1457, 1324, 1160; δ_H($CDCl_3$; 270 MHz) 0.82 (3H, d, *J* 6.8), 2.41 (3H, s), 2.86 (1H, br s), 3.52–3.58 (1H, m), 4.79 (1H, d, *J* 3.4), 5.16 (1H, d, *J* 8.8), 7.21–7.33 (7H, m), 7.77 (2H, d, *J* 8.3) (Found: C, 62.88; H, 6.21; N, 4.58. $C_{16}H_{19}NO_3S$ requires C, 62.92; H, 6.28; N, 4.59%).

21. Yield 87%; $[\alpha]_D^{25}$ +75.3 (*c* 2.03 in THF); mp 224–228 °C; ν_{max}(KBr) 3470, 3320, 1310, 1150; δ_H($CDCl_3$; 270 MHz) 2.29 (1H, d, *J* 4.9), 2.34 (3H, s), 4.55 (1H, dd, *J* 7.8 and 4.9), 4.99 (1H, t, *J* 4.6), 5.20 (1H, d, *J* 7.8), 6.80–7.22 (12H, m), 7.48 (2H, d, *J* 8.3) (Found: C, 68.70; H, 5.75; N, 3.80. $C_{21}H_{21}NO_3S$ requires C, 68.66; H, 5.72; N, 3.81%).

22. Yield 79%; $[\alpha]_D^{25}$ −4.66 (*c* 2.13 in $CHCl_3$); mp 102 °C; ν_{max}(KBr) 3400, 3240, 1710, 1370, 1170; δ_H($CDCl_3$; 270 MHz) 1.26 (3H, d, *J* 6.4), 2.17 (1H, br s), 2.42 (3H, s), 3.52 (3H, s), 3.82 (1H, dd, *J* 9.8 and 2.9), 4.13 (1H, br s), 5.48 (1H, d, *J* 9.3), 7.29 (2H, d, *J* 8.8), 7.73 (2H, d, *J* 8.3) (Found: C, 50.15; H, 5.95; N, 4.85. $C_{12}H_{17}NO_5S$: C, 50.17; H, 5.92; N, 4.88%).

General procedure for enantioselective allylboration of 10 to *N*-silylimines

The transformation of **8a** to **9a** is typical. To a solution of **10** (12 mmol), prepared from (−)-DIP-Chloride™ (3.8 g, 12 mmol) and allylmagnesium chloride (12 mmol), was added dropwise a THF (5 cm^3) solution of **8a** (1.42 g, 8 mmol) at −78 °C. The reaction mixture was then stirred for 3 h at −78 °C and quenched with 1 M HCl. The aqueous phase was separated, and washed with ether. The aqueous phase was then neutralized with NH_4OH and extracted with ether. The combined ether layer was dried over $MgSO_4$ and evaporated under reduced pressure. The residual product was purified by flash chromatography (Et_2O–hexane, 4:1) to yield **9a** as a colorless liquid (0.76 g, 65%), δ_H($CDCl_3$; 270 MHz) 7.34–7.22 (5H, m), 5.82–5.68 (1H, m), 5.15–5.06 (2H, m), 3.98 (1H, dd, *J* 7.8 and 5.4), 2.46–2.32 (2H, m), 1.53 (2H, br s). The enantioselectivity of 64% ee was determined by HPLC analysis using a chiral stationary-phase column (Daicel, Chiralcel OD-H; hexane–propan-2-ol–diethylamine 90:10:0.1, flow rate 0.5 cm^3 min^{-1}); t_R = 16.3 min (*R*), t_R = 20.7 min (*S*). The absolute configuration of the product was correlated to that described in the literature.[19]

General procedure for enantioselective allylboration of *N*-silylimines with chirally modified allylboron reagents

The transformation of **8a** to **9a** is typical. To a THF (5 cm^3) solution of (1*R*,2*S*)-*N*-(*p*-tolylsulfonyl)norephedrine **19b** (1.22 g, 4 mmol) and triethylamine (0.05 cm^3) was added a THF solution (15 cm^3) of triallylborane (5 mmol) prepared from BF_3·OEt_2 (0.61 cm^3, 5 mmol) and allylmagnesium chloride (15 mmol, 1.2 M) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and then heated under reflux for 1 h to complete the formation of the oxazaborolidine ring. After cooling to room temperature, the solvent was removed *in vacuo* and dry ether (20 cm^3) was introduced. At −78 °C an ethereal (2 cm^3) solution of *N*-silylimine **8a** (0.53 g, 3 mmol) was added dropwise and the mixture was stirred for 3 h. The reaction was quenched with 1 M HCl and the organic phase was separated, from which chiral ligand **19b** was recovered (93%). The aqueous phase was then neutralized with NH_4OH and extracted with ether. The combined ether layer was dried ($MgSO_4$) and evaporated. Chromatography (Et_2O–hexane, 4:1) gave 1-phenylbut-3-enamine as a colorless oil. (89%). The enantioselectivity (92% ee) was determined by HPLC analysis using a chiral stationary-phase column as shown before.

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