Enantioselective Rhodium-Catalyzed Allylation of Cyclic Imines with Potassium Allyltrifluoroborates

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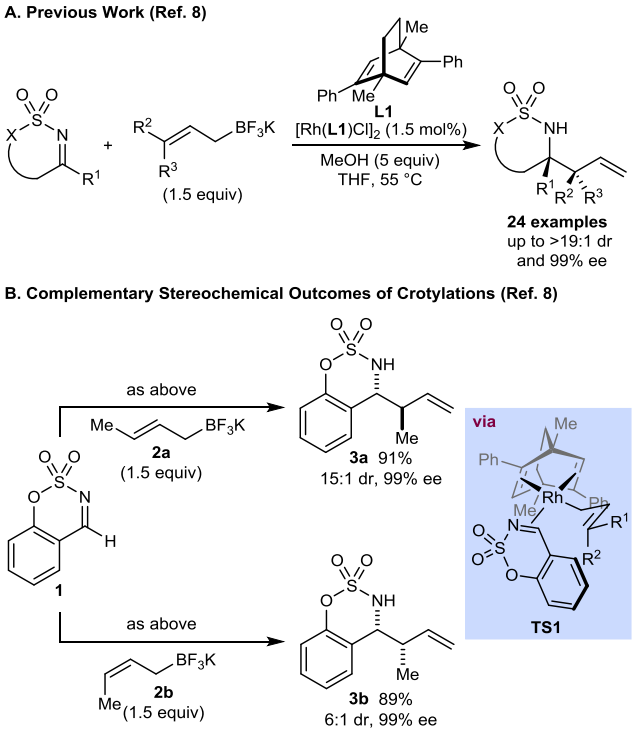
Abstract: This Article presents further examples of the enantioselective rhodium-catalyzed addition of potassium allyltrifluoroborates to cyclic imines. A wide range of substituted allyltrifluoroborates are compatible with this process, and provide protected homoallylic amines with high levels of diastereo- and enantioselection. The reactions display a strong preference for carbon–carbon bond formation at the more substituted terminus of the allyl fragment of the allyltrifluoroborate, regardless of the position of the boron atom. Representative examples of manipulation of the products are also described.

Key words: allyltrifluoroborates, asymmetric catalysis, enantioselectivity, imines, rhodium

Introduction

The enantioselective rhodium(I)-catalyzed addition of organoboron reagents to π-electrophiles is now a well-established method for the synthesis of enantioenriched chiral compounds.[1] The stability, functional group tolerance, and usually low toxicity of organoboron compounds, coupled with the ability of a broad range of chiral ligands to impart high levels of enantioselection across several classes of reactions, has resulted in this method being widely applied in synthesis. Thus far, efforts have focused mainly upon nucleophilic arylations[1] and alkenylations[2] using the corresponding organoboron reagents, though one example of the use of alkynylboron reagents[3] has also been described.[4,5] Although catalytic enantioselective nucleophilic allylations occupy a prominent position in organic synthesis,[6,7] it was not until our recent investigation[8] that an enantioselective rhodium-catalyzed allylboration[9,10] was achieved. Prompted by the general utility of chiral homoallylic amines in synthesis,[6b,11,12] along with the increasing body of work describing the catalytic enantioselective allylborations of imines,[11] we developed[8] the enantioselective addition of potassium allyltrifluoroborates to cyclic imines,[13] catalyzed by a rhodium complex based upon the chiral diene **L1**[14,15] (Scheme 1A). In this study, the reactions using substituted allyltrifluoroborates displayed two notable features. First, clean allylic transposition was observed,



Scheme 1 Previously reported rhodium(I) catalyzed allylation of cyclic imines.

resulting in C–C bond formation at the γ-carbon of the allyltrifluoroborate. Second, high levels of stereochemical transfer were observed. For example, the reactions of aldimine **1** with (*E*)- and (*Z*)-crotyltrifluoroborates **2a** and **2b** proceeded with different stereochemical outcomes to provide diastereomeric products **3a** and **3b**, respectively, with high diastereo- and enantioselectivities (Scheme 1B).[8] A cyclic chairlike transition state **TS1** was invoked to rationalize the stereochemical outcomes.

This Article presents further examples of this process, using classes of imines and substituted allyltrifluoroborates additional to those described in our original study.[8] As well as providing a more thorough understanding of the substrate scope, some of the results using allyltrifluoroborates reveal cases of α-selectivity in the reactions, which we have not observed previously. Finally, representative examples of manipulations of the allylation products are presented.

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Further Evaluation of Substrate Scope

In our original investigation, four distinct classes of cyclic imines were shown to undergo enantioselective allylation. These were benzoxathiazine-2,2-dioxides, 1,2,6-thiadiazine-1,1-dioxides, 1,2,5-thiadiazolidine-1,1-dioxides, and cyclic sulfamidates.[8] We have since found that other cyclic *N*-sulfonyl ketimines **4a**–**4c** are also effective substrates (Scheme 2). For example, using the rhodium complex derived from *ent*-**L1**[14] (the enantiomer of the chiral diene employed in our original study[8]), methyl- and *n*-butyl-substituted ketimines underwent allylation with potassium allyltrifluoroborate (**2c**) under our established conditions[8] to give benzosultams **5a** and **5b**, respectively, in moderate yields but with high enantioselectivities. It appears that the allylations of imines containing electron-withdrawing substituents proceed with lower enantioselectivities. For example, a substrate **4c** containing an ethyl ester underwent allylation in only 21% ee (product **5c**). In addition, ketimine **6** containing a trifluoromethyl group underwent allylation in 85% yield but the product **7** was racemic (Scheme 3). In our previous study, benzoxathiazine-2,2-dioxides containing electron-withdrawing substituents on the benzene ring were also allylated in lower enantioselectivities under our standard conditions using MeOH (5 equiv) in THF/dioxane, but fortunately the use of *i*-PrOH (13 equiv) in toluene/dioxane gave better

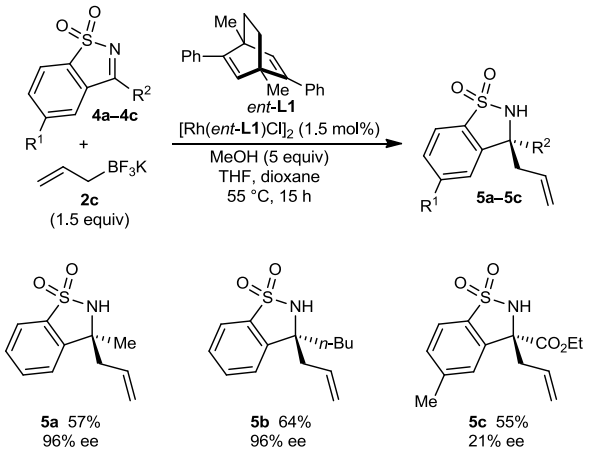
Biographical Sketches

Hamish B. Hepburn was born in 1988 in Dundee, Scotland. He completed a master's degree in chemistry at the University of Edinburgh in 2011, which included a one year placement at AstraZeneca. He is currently conducting Ph.D. studies in the group of Dr. Hon Wai Lam at the University of Edinburgh, investigating rhodium-catalyzed enantioselective transformations.

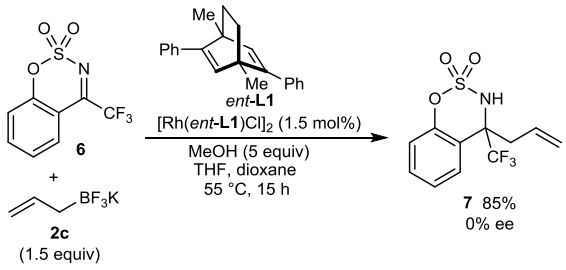
Nawasit Chotsaeng was born in 1982 in Roi Et, Thailand. After attaining a bachelor's degree at King Mongkut's Institute of Technology Ladkrabang in 2005, he completed a master's degree at the same institution in 2009. He is currently conducting Ph.D. research on new transition-metal-catalyzed reactions in the group of Dr. Hon Wai Lam at the University of Edinburgh, funded by a Royal Thai Government Scholarship.

Yunfei Luo was born in 1975 in Yunnan Province, China. He received a bachelor's degree in chemistry from Fudan University in 1998 and a master's degree from the same institution in 2001. He was a research associate at the Shanghai Institute of Organic Chemistry between 2001 and 2004, and worked in industry between 2004 and 2006. He obtained a Ph.D. degree in 2010 under the supervision of Dr. Andrew Carnell at the University of Liverpool, and is currently undertaking postdoctoral research in the group of Dr. Hon Wai Lam at the University of Edinburgh, focusing on asymmetric catalysis.

Hon Wai Lam was born in 1976 in Harrow, England. He received an M.Chem. degree in chemistry from the University of Oxford in 1998. He then moved to the University of Nottingham to carry out his Ph.D. under the direction of Gerald Pattenden. In January 2002, he moved to Harvard University as a GSK Postdoctoral Fellow to work with David A. Evans. In October 2003, he joined the School of Chemistry at the University of Edinburgh where he is now a Reader in Organic Chemistry. In October 2013, Hon will take up a new appointment at the University of Nottingham as the GSK Chair of Sustainable Chemistry. His group's research interests are based around the development of new synthetic methodology, including enantioselective catalysis and C–H functionalization chemistry.



Scheme 2 Enantioselective allylation of imines **4a**–**4c**.



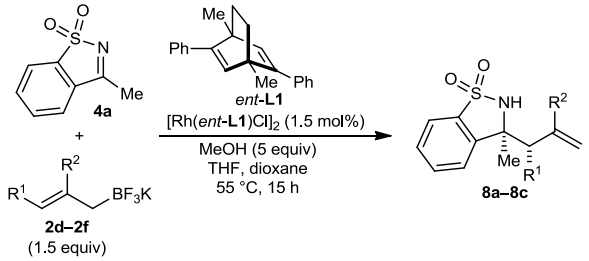
Scheme 3 Allylation of imine **6**.

results.[8] However, application of these modified conditions to the synthesis of products **5c** and **7** did not offer any improvement in enantioselection.

Table 1 presents the reactions of cyclic ketimine **4a** with a range of substituted potassium allyltrifluoroborates.[16] Consistent with our previous report,[8] the β-*n*-propyl-substituted allyltrifluoroborate **2d** was an effective allylating agent, and reacted with **4a** to provide **8a** in high diastereo- and enantioselectivity, though in a modest yield (entry 1). Allyltrifluoroborates not reported in our original investigation were also effective. For example, the γ-phenyl-substituted allyltrifluoroborate **2e** gave **8b** in 86% yield as one observable diastereomer in 91% ee (entry 2), while β-methylallyltrifluoroborate **2f** provided **8c** in 56% yield and 98% ee (entry 3).

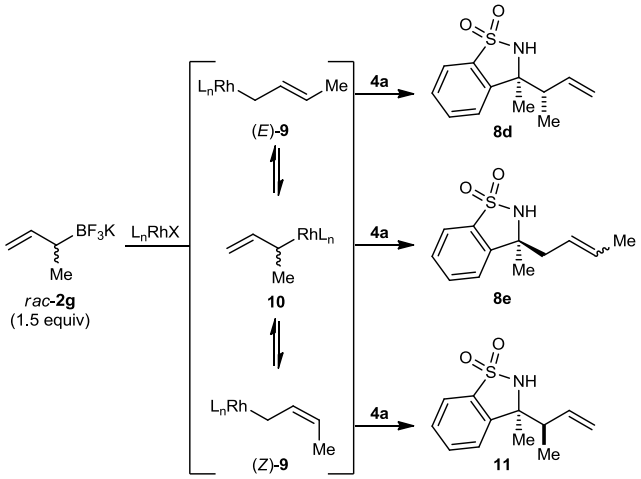
Up until this point, all of the reactions that we have studied that involve substituted allyltrifluoroborates have employed reagents in which boron is bonded to a primary carbon atom. In these cases, C–C bond formation occurred exclusively at the γ-carbon of the allyltrifluoroborate. It was therefore of interest to examine the reactions using racemic α-methyl-substituted allyltrifluoroborate **2g**, where boron is bonded to a secondary carbon atom. On the basis of an experiment using a deuterated potassium allyltrifluoroborate, we speculate that these allylations proceed *via* the intermediacy of allylrhodium species.[8] According to this hypothesis, transmetallation of *rac*-**2g** with the chiral rhodium complex could therefore, in principle, lead to several interconverting isomeric

Table 1 Enantioselective Allylation of Imine **4a** with Substituted Potassium Allyltrifluoroborates.[a]



Entry	Allyltrifluoroborate	Product	Yield (%)[b]	dr[c]	ee (%)[d]
1	**2d**	**8a**	48	>19:1	98
2	**2e**	**8b**	86	>19:1	91
3	**2f**	**8c**	56	–	98

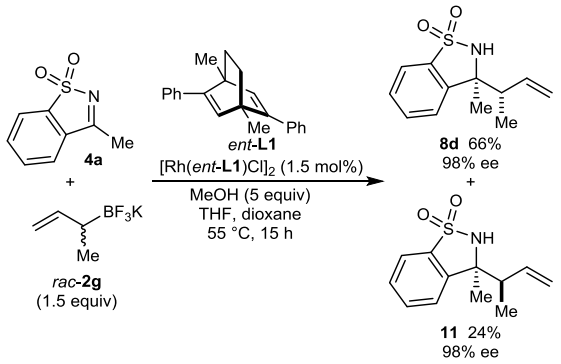
[a] Reactions were conducted using 0.30 mmol of **4a**. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis of the unpurified reaction mixtures. [d] Determined by chiral HPLC analysis.



Scheme 4 Possible outcomes of reactions using α-methyl-substituted allyltrifluoroborate **2g**.

allylrhodium species, each of which would provide different products upon reaction with imine **4a** (Scheme 4). As such, it was not clear whether the γ-selectivity observed previously[8] would be maintained using *rac*-**2g**.

In the event, allylation of **4a** with *rac*-**2g** provided a mixture of diastereomeric products **8d** and **11** with high enantioselectivities, where C–C bond formation occurred at the α-carbon of *rac*-**2g** (Scheme 5).[16] Other isomeric products such as **8e** were not observed. In addition to

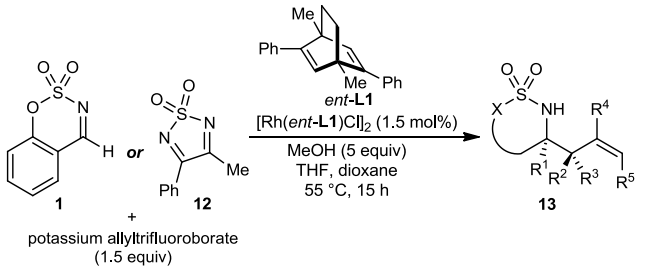


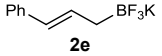
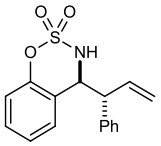
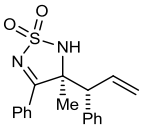
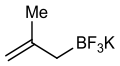
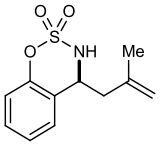
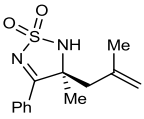
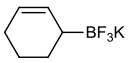
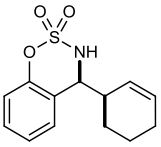
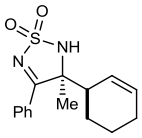
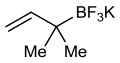
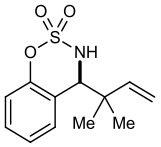
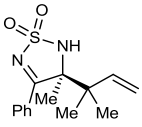
Scheme 5 Reaction of imine **4a** with the α-methyl-substituted allyltrifluoroborate **2g**.

providing further evidence that these allylations proceed *via* allylrhodium intermediates, this result indicates that the contributions to the observed products are greatest for crotylrhodium species (*E*)-**9**, followed by (*Z*)-**9**, while the contribution of **10** is negligible. If the interconversion between the different allylrhodium species is rapid compared with the rates of imine allylation, the product ratio will depend only upon the relative rates of allylation from (*E*)-**9**, **10**, and (*Z*)-**9**, and not upon their equilibrium distribution (Curtin–Hammett-type kinetics[17]). However, the high degrees of stereochemical transfer observed in the allylations of imine **1** using (*E*)- and (*Z*)-crotyltrifluoroborates **2a** and **2b** (see Scheme 1B) suggests that isomerization between (*E*)-**9** and (*Z*)-**9** is slow compared with the rate of allylation. Therefore, if a similar scenario is operative in the allylation of imine **4a** with *rac*-**2g**, it is likely that the ratio of **8d** and **11** obtained depends significantly on the ratio of (*E*)-**9** and (*Z*)-**9** formed in the initial transmetallation.

Next, the allylations of aldimine **1** and ketimine **12** with a range of substituted allyltrifluoroborates not reported in our original study[8] were conducted, and these reactions generally proceeded with high diastereo- and enantioselectivities (Table 2).[16] In certain cases, the use of *i*-PrOH (5 equiv) in toluene/dioxane provided higher enantioselectivities compared with our standard conditions of MeOH (5 equiv) in THF/dioxane (products **13a**, **13b**, and **13d**). Consistent with the result shown in Table 1, entry 2, **2e** was a highly effective allylating agent, and reacted with imines **1** and **12** to give **13a** and **13e**, respectively, in good yields and high stereoselectivities. Although β-methyl substituted allyltrifluoroborate **2f** reacted with ketimine **12** to give **13f** in good yield and high enantioselectivity, the ee was lower in the reaction with aldimine **1** (**13b** obtained in 79% ee). As an example of an allyltrifluoroborate containing substitution at both the α- and γ-carbons, cyclohexenyltrifluoroborate **2h** was evaluated. This reagent was only moderately effective, as the reaction with aldimine **1** provided **13c** in only 36% yield, though with good diastereo- and enantioselectivity.[16] The reaction of **2h** with ketimine **12** was completely

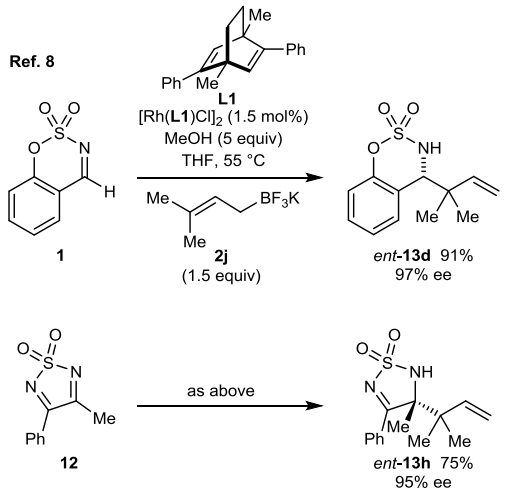
Table 2 Reaction of Imines **1** and **12** with Substituted Allyltrifluoroborates.[a]



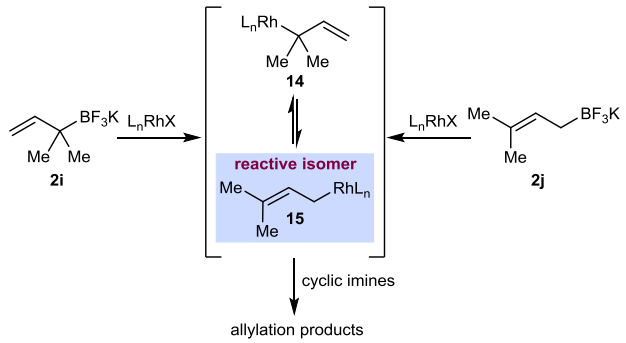
Allyltrifluoroborate	Product using **1**	Product using **12**
 **2e**	 **13a** 90%[b] 19:1 dr, 95% ee	 **13e** 86% 19:1 dr, 95% ee
 **2f**	 **13b** 65%[b] 79% ee	 **13f** 90% 97% ee
 **2h**	 **13c** 36% 10:1 dr, 93% ee	 **13g** <5%
 **2i**	 **13d** 71%[b] 90% ee	 **13h** 87% 91% ee

[a] Reactions were conducted using 0.30 mmol of **1** or **12**. Cited yields are of isolated products. Diastereomeric ratios were determined by ^{1}H NMR analysis of the unpurified reaction mixtures. Enantiomeric excesses were determined by chiral HPLC analysis. [b] Reaction conducted using *i*-PrOH (5 equiv) in toluene/dioxane instead of MeOH in THF/dioxane.

unsuccessful, and provided a complex mixture of unidentified products. The α,α-dimethyl- substituted allyltrifluoroborate **2i** resulted in C–C bond formation at the α-carbon exclusively, and provided reverse prenylation products **13d** and **13h** with good yields and high enantiomeric excesses. Interestingly, our previous study demonstrated that prenyltrifluoroborate **2j**, the isomer of **2i**, resulted in the formation of the enantiomers of **13d** and **13h** when **L1** was used (Scheme 6).[8] The formation of the reverse prenylation products **13d** and **13h** from both allyltrifluoroborates **2i** (α-selectivity) and **2j** (γ-selectivity) suggests that allylation proceeds *via* allylrhodium species **15** rather than the isomeric species **14** (Scheme 7).

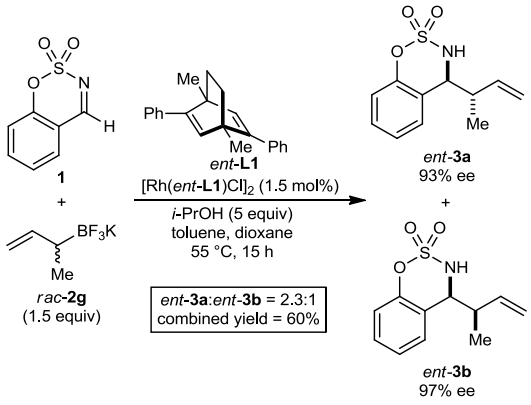


Scheme 6 Allylation of imines **1** and **12** with prenyltrifluoroborate **2j**.

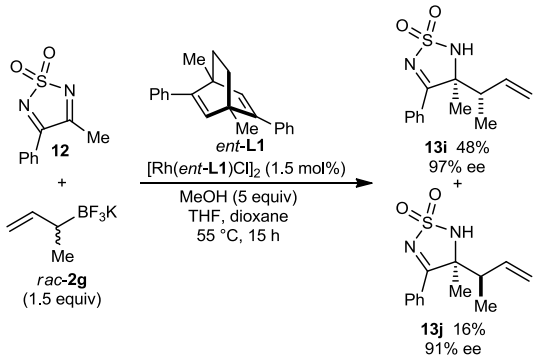


Scheme 7 Allylrhodium species from allyltrifluoroborates **2i** and **2j**.

The reactions of imines **1** and **12** with α-methyl-substituted allyltrifluoroborate **2g** proceeded with similar outcomes to the corresponding reaction with imine **4a** (Schemes 8 and 9, compare with Scheme 5). In the case of imine **1**, two products *ent*-**3a** and *ent*-**3b** were produced as an inseparable 2.3:1 mixture in 60% combined yield, and with enantiomeric excesses of 93% ee and 97% ee, respectively (Scheme 8). With imine **12**, the two products **13i** and **13j** were separable, and were isolated in 48% and 16% yields, respectively, and in high enantioselectivities (Scheme 9).



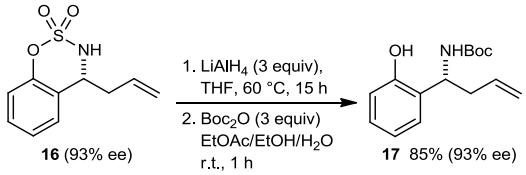
Scheme 8 Reaction of imine **1** with the α-methyl-substituted allyltrifluoroborate **2g**.



Scheme 9 Reaction of imine **12** with the α-methyl-substituted allyltrifluoroborate **2g**.

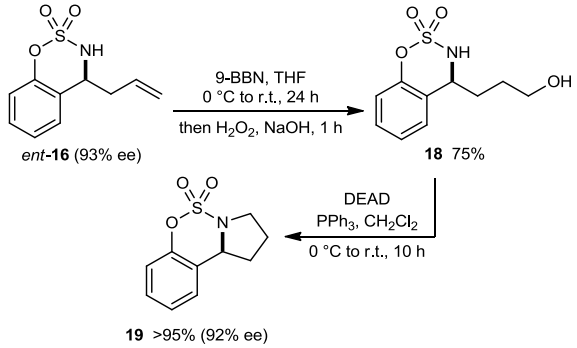
Functionalizations of the Allylation Products

To demonstrate the utility of the allylation products, representative transformations were conducted. For example, removal of the sulfonyl group of **16** (obtained in our original investigation using ligand **L1**[8]) was readily accomplished by treatment with $LiAlH_4$; *in situ* reaction of the resulting amine with Boc_2O then provided carbamate **17** in 85% overall yield (Scheme 10).



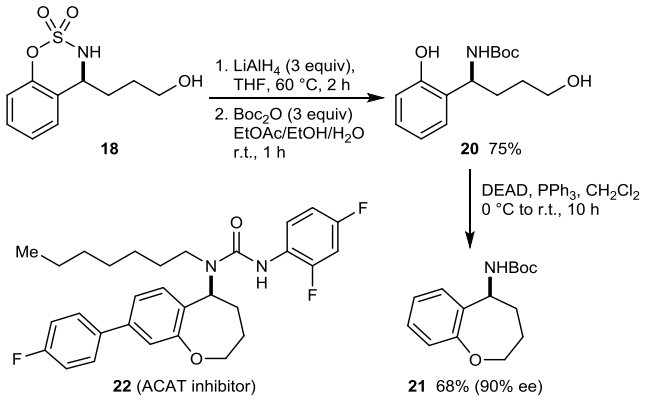
Scheme 10 Removal of the sulfonyl group of **16**.

A hydroboration/oxidation sequence of the alkene of *ent*-**16** (prepared as described previously[8] by the reaction of imine **1** with potassium allyltrifluoroborate, but using chiral diene *ent*-**L1**) provided primary alcohol **18**, which was transformed into the tricyclic sulfamate **19** by a Mitsunobu cyclization (Scheme 11).



Scheme 11 Conversion of *ent*-**16** into tricyclic sulfamate **19**.

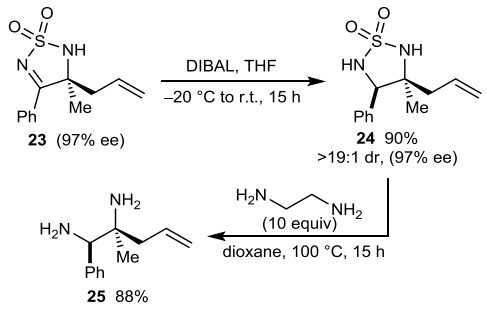
Alternatively, treatment of **18** with $LiAlH_4$ followed by Boc_2O provided carbamate **20**, which was converted into the tetrahydrobenzoxepine **21** by a Mitsunobu cyclization. Amino-substituted tetrahydrobenzoxepines have been shown to exhibit interesting biological



Scheme 12 Conversion of **18** into amino-substituted tetrahydrobenzoxepine **22**.

activities; compound **22**, for example, is a strong ACAT (acyl coenzyme A, cholesterol *O*-acyltransferase) inhibitor.[18]

Finally, the imine of the allylation product **23** (prepared as described previously[8] by the reaction of imine **12** with potassium allyltrifluoroborate, but using chiral diene *ent*-**L1**) underwent a highly diastereoselective reduction upon treatment with DIBAL at –20 °C to give **24** in 90% yield as a single observable diastereomer (Scheme 13).[19] Heating **24** in dioxane in the presence of ethylene diamine (10 equiv) removed the sulfonyl group to provide 1,2-diamine **25** in 88% yield.



Scheme 13 Conversion of **23** into 1,2-diamine **25**

Conclusion

In summary, the reactions described herein, using imines and potassium allyltrifluoroborates additional to those described in our original study,[8] further illustrate the scope of the enantioselective rhodium-catalyzed allylboration of cyclic imines. In particular, these studies highlight the strong preference for C–C bond formation to occur at the more highly substituted end of the allyl fragment of the trifluoroborate, regardless of the position of the boron atom (e.g. compare Schemes 5, 8, and 9, along with products **13d** and **13h** in Table 2 with Schemes 1B and 6). Finally, the utility of the allylation products was demonstrated by representative transformations.

All commercially available reagents were used as received. Anhydrous dioxane was purchased from Sigma-Aldrich and used without further purification. Anhydrous THF, toluene, and CH_2Cl_2 were obtained by passage through activated alumina columns using a solvent purification system. Flash column chromatography was carried out using silica gel (Fisher Scientific 60Å particle size 35-70 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IRAffinity-1 instrument. ^{1}H NMR spectra were recorded on a Bruker AVA500 (500 MHz) or a Bruker AVA400 (400 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$ at 7.27 ppm, CD_3CN at 1.94 ppm, CD_3OD at 3.31 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), app (apparent), br (broad), m (multiplet). Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Proton-decoupled ^{13}C NMR spectra were recorded on a Bruker AVA500 (125.8 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm, CD_3CN at 118.26 ppm, CD_3OD at 49.0 ppm). Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. Proton-decoupled ^{19}F NMR spectra were recorded on a Bruker AVA400 (376 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of $CFCl_3$, using residual protonated solvent as internal standard ($CFCl_3$ at 376.38 MHz with respect to tetramethylsilane at 400.00 MHz). High-resolution mass spectra were recorded using electrospray ionization (ESI): or electron impact (EI): techniques on a Finnigan MAT 900 XLT spectrometer. Optical rotations were performed on an Optical Activity POLAAR 20 polarimeter. Chiral HPLC analysis was performed on an Agilent 1100 instrument using 4.6 x 250 mm columns. Authentic racemic samples of products for chiral HPLC assay determinations were obtained using $[Rh(cod)Cl]_2$ (2.5 mol%) as an achiral precatalyst. Chiral diene *ent*-**1** was prepared as described previously.[14] Imines **1**,[8] **4a**,[20] **4b**,[21] **4c**,[13c] **6**,[22] and **12**[23] were prepared according to previously described procedures. Potassium allyltrifluoroborates **2c**[24] and **2d**[8] were prepared as described previously.

Preparation of Potassium Allyltrifluoroborates: General Procedure A

Following a slight modification of the procedure of Lennox and Lloyd-Jones,[25] to a solution of the appropriate allylboronic acid pinacol ester (1.0 equiv) in MeOH (2 mL/mmol) and MeCN (2 mL/mmol) at room temperature was added a solution of KF (4.0 equiv) in H_2O (0.1 mL/mmol), and the mixture was stirred for 5 min until complete dissolution occurred. To this solution was added a solution of L-(+)-tartaric acid (2.05 equiv) in THF (1.5 mL/mmol of allylboronic acid pinacol ester) dropwise, and the resulting mixture was stirred at room temperature for 1 h. MeCN (5 mL/mmol of allylboronic acid pinacol ester) was added and the reaction was stirred for an additional 5 min before being filtered and concentrated *in vacuo* to leave a mixture of the potassium allyltrifluoroborate and pinacol. This residue was heated under reduced pressure to remove pinacol to leave the potassium allyltrifluoroborate as a white solid.

Potassium (*E*)-3-phenylprop-2-en-1-yltrifluoroborate (2e)[26]

The title compound was prepared according to General Procedure A from the corresponding allylboronic acid pinacol ester[27] (488 mg, 2.00 mmol), KF (0.46 g, 8.00 mmol), and L-(+)-tartaric acid (0.62 g, 4.13 mmol) to give a white solid (327 mg, 73%) that displayed spectroscopic data consistent with those reported previously.[26]

Potassium 2-methallyltrifluoroborate (2f)

The title compound was prepared according to General Procedure A from the corresponding allylboronic acid pinacol ester[28] (478

mg, 2.63 mmol), KF (0.61 g, 10.5 mmol), and L-(+)-tartaric acid (0.81 g, 5.38 mmol) to give a white solid (248 mg, 58%).

^{1}H NMR (400 MHz CD_3CN): δ = 4.34 (s, 1 H), 4.32 (s, 1 H), 1.69 (s, 3 H), 1.14 (br s, 2 H).

^{13}C NMR (100.6 MHz, CD_3CN): δ = 116.5, 110.3, 25.0, the carbon adjacent to the boron was not observed.

^{19}F NMR (376 MHz, CD_3CN): δ = –152.4.

(±)-Potassium α-methylallyltrifluoroborate (2g)
The title compound was prepared according to General Procedure A from the corresponding allylboronic acid pinacol ester[28] (910 mg, 5.00 mmol), KF (1.16 g, 20.0 mmol), and L-(+)-tartaric acid (1.54 g, 10.3 mmol) to give a white solid (570 mg, 70%).

^{1}H NMR (400 MHz, CD_3CN): δ = 6.04 (ddd, *J* = 17.3, 10.3, 6.9 Hz, 1 H), 4.66 (d, *J* = 17.3 Hz, 1 H), 4.60 (d, *J* = 10.3 Hz, 1 H), 1.14 (br s, 1 H), 0.85 (d, *J* = 6.7 Hz, 3 H).

^{13}C NMR (100.6 MHz, CD_3CN): δ = 110.9, 107.0, 25.1, 14.4.

^{19}F NMR (376 MHz, CD_3CN): δ = –146.5.

Potassium 1-cyclohex-2-enyltrifluoroborate (2h)[26]
The title compound was prepared according to General Procedure A from the corresponding allylboronic acid pinacol ester[29] (416 mg, 2.00 mmol), KF (0.46 g, 8.00 mmol) and L-(+)-tartaric acid (0.62 g, 4.13 mmol) to give a white solid (290 mg, 78%) that displayed spectroscopic data consistent with those reported previously.[26]

Potassium α,α-dimethylallyltrifluoroborate (2i)
The title compound was prepared according to General Procedure A from the corresponding allylboronic acid pinacol ester[28] (550 mg, 2.80 mmol), KF (0.65 g, 11.2 mmol), and L-(+)-tartaric acid (0.86 g, 5.74 mmol) to give a white solid (330 mg, 67%).

^{1}H NMR (400 MHz, CD_3CN): δ = 6.07-6.00 (m, 1 H), 4.61-4.55 (m, 2 H), 0.79 (s, 6 H).

^{13}C (100.6 MHz, CD_3CN): δ = 111.1, 105.1, 23.7 (2 × CH_3), the quaternary carbon adjacent to the boron was not observed.

^{19}F NMR (376 MHz, CD_3CN): δ = –151.3.

Rh-Catalyzed Allylation of Imines: General Procedure B
A vial containing the appropriate cyclic imine (0.30 mmol) and the appropriate potassium allyltrifluoroborate (0.45 mmol) was sealed and flushed with N_2 before anhydrous THF (3 mL) was added. To this solution was added a stock solution of the rhodium–chiral diene complex [Rh(*ent*-**L1**)Cl]$_2$ (10.0 mM in anhydrous dioxane, 0.45 mL, 0.0045 mmol = 3 mol% Rh) followed by MeOH (60 μL, 1.50 mmol), and the resulting mixture was heated to 55 °C for 15 h. The reaction was cooled to room temperature, filtered through a short plug of silica using EtOAc as eluent, and concentrated *in vacuo*. Purification of the residue by column chromatography gave the allylated product.

Rh-Catalyzed Allylation of Imines: General Procedure C
A vial containing the appropriate cyclic imine (0.30 mmol) and the appropriate potassium allyltrifluoroborate (0.45 mmol) was sealed and flushed with N_2 before anhydrous toluene (3 mL) was added. To this solution was added a stock solution of the rhodium–chiral diene complex [Rh(*ent*-**L1**)Cl]$_2$ (10.0 mM in anhydrous dioxane, 0.45 mL, 0.0045 mmol = 3 mol% Rh) followed by *i*-PrOH (115 μL, 1.50 mmol), and the resulting mixture was heated to 55 °C for 15 h. The reaction was cooled to room temperature, filtered through a short plug of silica using EtOAc as eluent, and concentrated *in vacuo*. Purification of the residue by column chromatography gave the allylated product.

(*S*)-3-Methyl-3-(prop-2-en-1-yl)-2,3-dihydro-[1,2]-benzothiazole-1,1-dioxide (5a)
The title compound was prepared according to General Procedure B from imine **4a** (54 mg, 0.30 mmol) and allyltrifluoroborate **2c** (66 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a yellow oil (38 mg, 57%).

R_f = 0.32 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –54.2 (*c* 0.70, $CHCl_3$).

IR (neat): 3250 (NH), 1373, 1271, 1254, 1148, 1121, 1049, 916, 770, 760 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.8 Hz, 1 H), 7.64 (td, *J* = 7.7, 1.1 Hz, 1 H), 7.53 (td, *J* = 7.7, 1.0 Hz, 1 H), 7.39 (d, *J* = 7.8 Hz, 1 H), 5.68 (dddd, *J* = 17.0, 10.3, 7.9, 6.7 Hz, 1 H), 5.24-5.17 (m, 2 H), 4.65 (br s, 1 H), 2.71 (dd, *J* = 14.1, 7.1 Hz, 1 H), 2.60 (dd, *J* = 14.1, 7.9 Hz, 1 H), 1.64 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 144.6, 135.7, 133.3, 131.7, 129.2, 123.0, 121.3, 121.2, 62.9, 45.7, 27.8.

HRMS (ESI): Exact mass calcd for $C_{11}H_{14}NO_2S$ $[M+H]^+$: 224.0740, found: 224.0735.

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 17.8 min, t_r (minor) = 24.0 min; 96% ee.

(*S*)-3-Butyl-3-(prop-2-en-1-yl)-2,3-dihydro-[1,2]-benzothiazole-1,1-dioxide (5b)
The title compound was prepared according to General Procedure B from imine **4b** (67 mg, 0.30 mmol) and allyltrifluoroborate **2c** (66 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a yellow oil (51 mg, 64%).

R_f = 0.45 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –30.3 (*c* 1.45, $CHCl_3$).

IR (neat): 3281 (NH), 1466, 1375, 1271, 1153, 1132, 1034, 930, 766, 683 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.7 Hz, 1 H), 7.64 (td, *J* = 7.7, 1.1 Hz, 1 H), 7.53 (td, *J* = 7.7, 1.0 Hz, 1 H), 7.35 (d, *J* = 7.8 Hz, 1 H), 5.63 (dddd, *J* = 17.1, 10.2, 7.6, 7.0 Hz, 1 H), 5.20-5.14 (m, 2 H), 4.54 (s, 1 H), 2.70-2.60 (m, 2 H), 1.93-1.87 (m, 2 H), 1.45-1.36 (m, 1 H), 1.32-1.23 (m, 2 H), 1.01-0.97 (m, 1 H), 0.85 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 142.9, 136.0, 133.2, 131.6, 129.3, 123.3, 121.5, 121.1, 66.3, 45.1, 40.0, 25.7, 22.6, 13.8.

HRMS (ESI): Exact mass calcd for $C_{14}H_{20}NO_2S$ $[M+H]^+$: 266.1209, found: 266.1205.

HPLC: Chiralpak AD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 24.7 min, t_r (minor) = 29.2 min; 96% ee.

(*S*)-Ethyl 5-methyl-1,1-dioxo-3-(prop-2-en-1-yl)-2,3-dihydro-[1,2]-benzothiazole-3-carboxylate (5c)
The title compound was prepared according to General Procedure B from imine **4c** (76 mg, 0.30 mmol) and allyltrifluoroborate **2c** (66 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a colorless oil (49 mg, 55%).

R_f = 0.35 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –22.4 (*c* 0.90, $CHCl_3$).

IR (neat): 3258 (NH), 1722 (C=O), 1261, 1231, 1182, 1144, 1134, 1040, 702, 660 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 1 H), 7.51 (s, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 5.77 (dddd, *J* = 16.9, 10.2, 7.8, 6.4 Hz, 1 H), 5.69 (s, 1 H), 5.23-5.17 (m, 2 H), 4.36-4.26 (m, 2 H), 2.96 (dd, *J* = 13.9, 7.8 Hz, 1 H), 2.71 (dd, *J* = 13.9, 6.4 Hz, 1 H), 2.49 (s, 3 H), 1.34 (3H, t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 169.5, 144.6, 138.0, 132.7, 131.4, 131.0, 125.1, 121.1, 120.7, 68.5, 63.4, 44.6, 21.8, 14.1.

HRMS (ESI): Exact mass calcd for $C_{14}H_{18}NO_4S$ $[M+H]^+$: 296.0951, found: 296.0951.

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (minor) = 13.9 min, t_r (major) = 18.4 min; 21% ee.

4-(Prop-2-en-1-yl)-4-(trifluoromethyl)-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dione (7)

The title compound was prepared according to General Procedure B from imine **6** (75 mg, 0.30 mmol) and allyltrifluoroborate **2c** and was purified by column chromatography (10% EtOAc/hexane) to give a yellow solid (75 mg, 85%).

R_f = 0.30 (10% EtOAc/hexane).

m.p. 76-77°C (CH_2Cl_2/hexane).

IR (neat): 3285 (NH), 1614, 1489, 1454, 1435, 1377, 1260, 1180, 856, 762 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.0 Hz, 1 H), 7.48 (dt, *J* = 7.5, 5.4 Hz, 1 H), 7.34 (td, *J* = 8.0, 1.2 Hz, 1 H), 7.16 (dd, *J* = 8.2, 1.1 Hz, 1 H), 5.61-5.53 (m, 1 H), 5.41-5.36 (m, 2 H), 5.13 (s, 1 H), 3.05 (dd, *J* = 14.5, 6.5 Hz, 1 H), 2.85 (dd, *J* = 14.5, 8.0 Hz, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 150.8, 131.5, 128.4, 127.0 (q, *J* = 2.6 Hz), 126.5, 124.3 (q, *J* = 286.3 Hz), 124.2, 120.0, 117.9, 65.8 (q, *J* = 29.1 Hz), 41.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.7.

HRMS (ESI): Exact mass calcd for $C_{11}H_{11}F_3NO_3S$ $[M+H]^+$: 294.0406, found: 294.0408.

To facilitate determination of enantiomeric excess, **7** was converted into the primary alcohol **7a** resulting from a hydroboration–oxidation sequence of the terminal alkene, according to the following procedure:

4-(Trifluoromethyl)-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dione (7a)

To a solution of the alkene **7** (66 mg, 0.23 mmol) in THF (3 mL) at 0 °C was added 9-BBN (0.5 M in THF, 1.37 mL, 0.68 mmol) over 2 min. The mixture was warmed to room temperature over 1 h and then stirred for a further 23 h. The reaction was cooled to 0 °C and 3 M NaOH (1 mL) and H_2O_2 (30 wt.% in H_2O, 2 mL) were added successively. The resulting mixture was stirred for 1 h at room temperature, diluted with H_2O (20 mL), acidified with 2 M HCl, and extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (60% EtOAc/hexane) gave the *alcohol* **7a** (61 mg, 86%) as a colorless gum.

R_f = 0.41 (60% EtOAc/hexane).

IR (neat): 3288 (OH and NH), 2924, 1454, 1375, 1177, 1159, 1115, 1055, 856, 762 cm^{-1}.

^{1}H NMR (CD_3OD, 500 MHz): δ = 7.61 (d, *J* = 8.0 Hz, 1 H), 7.55-7.52 (m, 1 H), 7.41-7.38 (m, 1 H), 7.19 (dd, *J* = 8.2, 1.2 Hz, 1 H), 3.60-3.52 (m, 2 H), 2.45-2.39 (m, 1 H), 2.14-2.08 (m, 1 H), 1.76-1.68 (m, 1 H), 1.38-1.26 (m, 1 H).

^{13}C NMR (125.8 MHz, CD_3OD): δ = 152.9, 132.5, 125.0 (q, *J* = 286.0 Hz), 127.4, 126.4 (q, *J* = 286.0 Hz), 120.7, 119.9, 68.1 (q, *J* = 28.6 Hz), 62.0, 33.1, 26.6.

^{19}F NMR (CD_3OD): δ = –78.0.

HRMS (ESI): Exact mass calcd for $C_{11}H_{12}F_3NO_4SNa$ $[M+Na]^+$: 334.0331, found: 334.0331.

HPLC: Chiralpak AD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min 280 nm, 25 °C); t_r = 19.3 min, 29.0 min; 0% ee.

(*S*)-3-Methyl-3-[(*S*)-1-hex-1-en-3-yl]-2,3-dihydro-[1,2]-benzothiazole-1,1-dioxide (8a)

The title compound was prepared according to General Procedure B from imine **4a** (54 mg, 0.30 mmol) and allyltrifluoroborate **2d** (86 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a yellow oil (38 mg, 48%).

R_f = 0.38 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –23.3 (*c* 0.60, $CHCl_3$).

IR (neat): 3219 (NH), 1389, 1377, 1271, 1238, 1153, 1134, 918, 770, 719 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.8 Hz, 1 H), 7.62 (td, *J* = 7.8, 1.1 Hz, 1 H), 7.52 (td, *J* = 7.7, 0.9 Hz, 1 H), 7.37 (d, *J* = 7.9 Hz, 1 H), 5.59 (app dt, *J* = 17.0, 10.1 Hz, 1 H), 5.09 (dd, *J* = 10.3, 1.8 Hz, 1 H), 4.99 (dd, *J* = 17.1, 1.7 Hz, 1 H), 4.61 (s, 1 H), 2.43-2.37 (m, 1 H), 1.70-1.64 (m, 1 H), 1.63 (s, 3 H), 1.46-1.35 (m, 1 H), 1.30-1.21 (m, 1 H), 1.20-1.10 (m, 1 H), 0.88 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 143.6, 136.8, 134.8, 132.9, 129.2, 124.0, 121.4, 119.8, 65.9, 53.7, 30.8, 26.0, 20.6, 13.9.

HRMS (ESI): Exact mass calcd for $C_{14}H_{20}NO_2S$ $[M+H]^+$: 266.1209, found: 266.1208.

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 11.6 min, t_r (minor) = 18.6 min; 98% ee.

(*S*)-3-Methyl-3-[(*R*)-1-phenylprop-2-en-1-yl]-2,3-dihydro-[1,2]-benzothiazole-1,1-dione (8b)

The title compound was prepared according to General Procedure B from imine **4a** (54 mg, 0.30 mmol) and allyltrifluoroborate **2e** (100 mg, 0.45 mmol) and was purified by column chromatography (20% EtOAc/hexane) to give a gum that solidified on standing to give a white solid (77 mg, 86%).

R_f = 0.26 (30% EtOAc/hexane).

m.p. 78-79 °C (EtOAc/hexane).

$[\alpha]_D^{20}$ –88.6 (*c* 3.70, $CHCl_3$).

IR (neat): 3233 (NH), 1389, 1373, 1275, 1153, 1132, 930, 891, 756, 708 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.7 Hz, 1 H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.53 (td, *J* = 7.5, 1.0 Hz, 1 H), 7.39-7.27 (m, 5 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 6.17 (ddd, *J* = 17.0, 10.2, 9.1 Hz, 1 H), 5.03 (dd, *J* = 10.2, 1.2 Hz, 1 H), 4.95 (ddd, *J* = 17.0, 1.4, 1.0 Hz, 1 H), 4.52 (s, 1 H), 3.69 (d, *J* = 9.0 Hz, 1 H), 1.51 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 143.0, 139.1, 135.9, 135.0, 133.0, 129.3, 129.3 (2 × CH), 128.6 (2 × CH), 127.6, 123.8, 121.4, 119.2, 66.0, 59.6, 27.1.

HRMS (ESI): Exact mass calcd for $C_{17}H_{18}NO_2S$ $[M+H]^+$: 300.1053, found: 300.1051.

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 22.4 min, t_r (minor) = 32.8 min; 91% ee.

(*S*)-3-Methyl-3-(2-methylprop-2-en-1-yl)-2,3-dihydro-[1,2]-benzothiazole-1,1-dione (8c)

The title compound was prepared according to General Procedure B from imine **4a** (54 mg, 0.30 mmol) and allyltrifluoroborate **2f** (73 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a yellow gum (40 mg, 56%).

R_f = 0.31 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –61.8 (*c* 0.55, $CHCl_3$).

IR (neat): 3273 (NH), 1369, 1277, 1263, 1163, 1150, 1128, 1057, 893, 758 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74 (t, *J* = 14.1 Hz, 1 H), 7.64 (td, *J* = 7.7, 0.9 Hz, 1 H), 7.53 (td, *J* = 7.6, 0.6 Hz, 1 H), 7.43 (d, *J* = 7.8 Hz, 1 H), 5.02-5.01 (m, 1 H), 4.84 (s, 1 H), 4.75 (s, 1 H), 2.74 (d, *J* = 13.9 Hz, 1 H), 2.59 (d, *J* = 13.9 Hz, 1 H), 1.65 (s, 3 H), 1.57 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 145.4, 140.6, 135.4, 133.1, 129.2, 123.2, 121.4, 117.8 , 62.5, 48.9, 29.0, 23.9.

HRMS (ESI): Exact mass calcd for $C_{12}H_{16}NO_2S$ $[M+H]^+$: 238.0896, found: 238.0893.

HPLC: Chiralpak AD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 20.6 min, t_r (minor) = 25.6 min; 98% ee.

(*S*)-3-Methyl-3-[(*S*)-but-3-en-1-yl)-2,3-dihydro-[1,2]-benzothiazole-1,1-dione (8d) and (*S*)-3-methyl-3-[(*R*)-but-3-en-1-yl)-2,3-dihydro-[1,2]-benzothiazole-1,1-dione (11)

General Procedure B was followed using imine **4a (**54 mg, 0.30 mmol) and allyltrifluoroborate **2g** (73 mg, 0.45 mmol). Purification by column chromatography (10% EtOAc/hexane) gave the *allylated product* **8d** as white solid (47 mg 66%) followed by *allylated product* **11** as a white solid (17 mg 24%). Recrystallization of **8d** and **11** from Et_2O gave colorless crystals, which enabled the stereochemistry of **8d** to be determined by X-ray crystallography.

Data for **8d**:

R_f = 0.33 (30% EtOAc/hexane).

m.p. 72-74 °C (Et_2O).

$[\alpha]_D^{20}$ –67.8 (*c* 1.15, $CHCl_3$).

IR (neat): 3250 (NH), 1267, 1234, 1157, 1134, 1125, 891, 766, 718, 586 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.8, 1 H), 7.62 (td, *J* = 7.8, 1.1 Hz, 1 H), 7.52 (td, *J* = 7.8, 0.9 Hz, 1 H), 7.37 (d, *J* = 5.7 Hz, 1 H), 5.71 (ddd, *J* = 16.6, 11.0, 7.9 Hz, 1 H), 5.08-5.02 (m, 2 H), 4.64 (s, 1 H), 2.74-2.67 (m, 1 H), 1.63 (s, 3 H) 1.17 (d, *J* = 6.9 Hz, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 143.8, 138.1, 135.2, 133.0, 129.2, 123.7, 121.4, 117.9, 65.9, 47.0, 26.0, 14.6.

HRMS (ESI): Exact mass calcd for $C_{12}H_{16}NO_2S$ $[M+H]^+$: 238.0896, found: 238.0898.

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 15.0 min, t_r (minor) = 22.5 min; 98% ee.

Data for **11**:

R_f = 0.29 (30% EtOAc/hexane).

m.p. 134-136 °C (Et_2O).

$[\alpha]_D^{20}$ –65.2 (*c* 0.50, $CHCl_3$).

IR (neat): 3283 (NH), 1366, 1273, 1234, 1177, 1152, 1134, 934, 764, 590 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.8 Hz, 1 H), 7.66 (td, *J* = 7.8, 1.1 Hz, 1 H), 7.55 (td, *J* = 7.8, 0.9 Hz, 1 H), 7.37 (d, *J* = 7.9 Hz, 1 H), 5.85 (ddd, *J* = 17.1, 10.3, 8.4 Hz, 1 H), 5.24 (dd, *J* = 10.3, 1.0 Hz, 1 H), 5.22-5.17 (m, 1 H), 4.33 (s, 1 H), 2.67-2.61 (m, 1 H), 1.62 (s, 3 H), 0.87 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 143.7, 138.2, 135.2, 133.3, 129.3, 123.2, 121.5, 118.1, 66.0, 47.3, 27.7, 15.0.

HRMS (ESI): Exact mass calcd for $C_{12}H_{16}NO_2S$ $[M+H]^+$: 238.0896, found: 238.0897.

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 13.6 min, t_r (minor) = 22.2 min; 98% ee.

(*S*)-4-[(*R*)-1-phenylprop-2-en-1-yl]-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dioxide (13a)

The title compound was prepared according to General Procedure C from imine **1** (55 mg, 0.30 mmol) and allyltrifluoroborate **2e** (101 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a yellow oil (81 mg, 90%).

R_f = 0.50 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –85.0 (*c* 0.80, $CHCl_3$).

IR (neat): 3273 (NH), 1414, 1364, 1321, 1165, 1103, 874, 822, 756, 696 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42-7.37 (m, 2 H), 7.35-7.31 (m, 4 H), 7.12 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.08-7.05 (m, 2 H), 6.04 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1 H), 5.34 (dt, *J* = 10.4, 1.3 Hz, 1 H), 5.16-5.12 (m, 1 H), 5.11 (dt, *J* = 17.3, 1.3 Hz, 1 H), 4.75 (d, *J* = 7.4 Hz, 1 H) 4.24 (dd, *J* = 13.3, 6.6 Hz, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 151.5, 138.6, 134.8, 129.7, 129.0 (2 × CH), 128.6 (2 × CH), 127.7, 126.9, 125.3, 121.5, 121.1, 119.2, 60.2, 52.5.

HRMS (ESI): Exact mass calcd for $C_{16}H_{16}NO_3S$ $[M+H]^+$: 302.0845, found: 302.0846.

HPLC: Chiralpak AD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 13.8 min, t_r (minor) = 15.8 min; 95% ee.

(*S*)-4-(2-Methylprop-2-en-1-yl)-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dioxide (13b)

The title compound was prepared according to General Procedure C from imine **1** (55 mg, 0.30 mmol) and allyltrifluoroborate **2f** (73 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a colorless oil (47 mg 65%).

R_f = 0.56 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –45.2 (*c* 0.85, $CHCl_3$).

IR (neat): 3273 (NH), 1406, 1360, 1188, 1165, 1103, 891, 816, 758, 675 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.30 (m, 1 H), 7.28-7.26 (m, 1 H), 7.24-7.20 (m, 1 H), 7.04 (dd, *J* = 8.2, 1.1 Hz, 1 H), 5.01 (d, *J* = 0.5 Hz, 1 H), 4.96 (app td, *J* = 8.6, 4.7 Hz, 1 H), 4.91 (s, 1 H), 4.63 (d, *J* = 7.8 Hz, 1 H), 2.88 (dd, *J* = 14.5, 4.7 Hz, 1 H), 2.69 (ddd, *J* = 14.5, 9.2, 0.7 Hz, 1 H), 1.76 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 151.0, 139.9, 129.5, 126.3, 125.4, 122.4, 119.1, 116.2, 54.4, 42.6, 22.0.

HRMS (ESI): Exact mass calcd for $C_{11}H_{13}NO_3S$ [M+Na]+: 262.0508, found: 262.0509.

HPLC: Chiralpak AD-H column (95:5 hexane:*i*-PrOH, 0.8 mL/min, 280 nm, 25 °C); t_r (major) = 20.2 min, t_r (minor) = 23.3 min; 79% ee.

(*S*)-4-[(*R*)-Cyclohex-2-en-1-yl]-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dioxide (13c)

The title compound was prepared according to General Procedure B from imine **1** (55 mg, 0.30 mmol) and allyltrifluoroborate **2h** (85 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a 10:1 inseparable mixture of diastereomers as a white solid (29 mg, 36%). Recrystallization of a small sample of **13c** from Et_2O gave colorless crystals that were suitable for X-ray crystallography.

R_f = 0.54 (30% EtOAc/hexane).

m.p. 128-130 °C (Et_2O).

$[\alpha]_D^{20}$ –38.4 (*c* 1.25, $CHCl_3$).

IR (neat): 3273 (NH), 1408, 1369, 1184, 1171, 1161, 878, 826, 766, 719 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 1 H), 7.25-7.22 (m, 2 H), 7.06-7.04 (m, 1 H), 6.04-5.99 (m, 1 H), 5.62-5.58 (m, 1 H), 4.90 (dd, *J* = 6.4, 5.0 Hz, 1 H), 4.54 (d, *J* = 6.2 Hz, 1 H), 3.13-3.06 (m, 1 H), 2.08-2.00 (m, 2 H), 1.82-1.75 (m, 1 H), 1.59-1.49 (m, 2 H), 1.27-1.18 (m, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 151.6, 132.3, 129.3, 126.6, 126.3, 125.5, 121.4, 119.2, 60.1, 39.0, 24.9, 22.2, 21.4.

HRMS (ESI): Exact mass calcd for $C_{13}H_{16}NO_3S$ $[M+H]^+$: 266.0845, found: 266.0846.

HPLC: Chiralcel OD-H column (95:5 hexane:*i*-PrOH, 0.8 mL/min, 254 nm, 25 °C); t_r (major) = 14.2 min, t_r (minor) = 24.2 min; 93% ee.

(*S*)-(2-Methylbut-3-en-2-yl)-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dioxide (13d)[8]

The title compound was prepared according to General Procedure C from imine **1** (55 mg, 0.30 mmol) and allyltrifluoroborate **2i** (79 mg, 0.45 mmol) and was purified by column chromatography (20% EtOAc/hexane) to give a yellow oil (54 mg, 71%) that displayed spectroscopic data consistent with those reported previously.[8]

R_f = 0.54 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –60.0 (*c* 0.50, $CHCl_3$).

HPLC: Chiralpak AD-H column (95:5 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 13.9 min, t_r (minor) = 25.1 min; 90% ee.

(*S*)-3-Methyl-4-phenyl-3[(*R*)-1-phenylprop-2-en-1-yl]-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (13e)

The title compound was prepared according to General Procedure B from imine **12** (62 mg, 0.30 mmol) and allyltrifluoroborate **2e** (101 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a colorless gum (84 mg, 86%).

R_f = 0.26 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ +52.7 (*c* 2.20, $CHCl_3$).

IR (neat): 3242 (NH), 1558, 1315, 1175, 1146, 995, 820, 710, 689, 652 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12-8.08 (m, 2 H), 7.70-7.65 (m, 1 H), 7.59-7.54 (m, 2 H), 7.42-7.38 (m, 4 H), 7.35-7.31 (m, 1 H), 6.24 (ddd, *J* = 17.0, 10.1, 9.4 Hz, 1 H), 5.03 (dd, *J* = 10.2, 1.2 Hz, 1 H), 4.97 (d, *J* = 17.0 Hz, 1 H), 4.48 (s, 1 H), 3.88 (d, *J* = 9.3 Hz, 1 H), 1.67 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 181.0, 138.1, 134.4, 133.7, 130.2 (2 × CH), 129.4 (2 × CH), 129.3, 129.1 (2 × CH), 128.9 (2 × CH), 128.0, 119.5, 75.9, 57.2, 26.1.

HRMS (ESI): Exact mass calcd for $C_{18}H_{19}N_2O_2S$ $[M+H]^+$: 327.1162, found: 327.1160.

HPLC: Chiralpak AD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 254 nm, 25 °C); t_r (major) = 23.9 min, t_r (minor) 25.2 min; 95% ee.

(*S*)-3-Methyl-3-(2-methylprop-2-en-1-yl)-4-phenyl-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (13f)

The title compound was prepared according to General Procedure B from imine **12** (62 mg, 0.30 mmol) and allyltrifluoroborate (73 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a yellow oil (71 mg, 90%).

R_f = 0.26 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –25.0 (*c* 0.80, $CHCl_3$).

IR (neat): 3300 (NH), 1553, 1294, 1175, 1144, 907, 824, 783, 692, 654 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.07 (dd, *J* = 8.5, 1.2 Hz, 2 H), 7.67-7.62 (m, 1 H), 7.57-7.52 (m, 2 H), 5.08-5.04 (m, 1 H), 4.87 (s, 1 H), 4.74 (s, 1 H), 2.98 (d, *J* = 14.5 Hz, 1 H), 2.73 (dd, *J* = 14.5, 0.6 Hz, 1 H), 1.84 (s, 3 H), 1.67 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 182.3, 139.5, 133.8 , 130.2 (2 × CH), 129.2 (2 × CH), 128.9, 118.6, 71.6, 46.7, 27.5, 23.4.

HRMS (ESI): Exact mass calcd for $C_{13}H_{17}N_2O_2S$ $[M+H]^+$: 265.1005, found: 265.1000.

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 254 nm, 25 °C); t_r (major) = 16.1 min, t_r (minor) = 19.2 min; 97% ee.

(*S*)-3-Methyl-3-(2-methylbut-3-en-2-yl)-4-phenyl-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (13 H)[8]

The title compound was prepared according to General Procedure B from imine **12** (62 mg, 0.30 mmol) and allyltrifluoroborate **2i** (79 mg, 0.45 mmol) and was purified by column chromatography (10% EtOAc/hexane) to give a yellow solid (72 mg, 87%) that displayed spectroscopic data consistent with those reported previously.[8]

R_f = 0.25 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ +40.7 (*c* 1.40, $CHCl_3$).

HPLC: Chiralpak AD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 22.1 min, t_r (minor) = 29.2 min; 91% ee.

(*S*)-4-[(*S*)-But-3-en-2-yl]-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dioxide (*ent*-3a)[8] and (*S*)-4-[(*R*)-but-3-en-2-yl]-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dioxide (*ent*-3b)[8]

General Procedure B was followed using imine **1** (55 mg, 0.30 mmol) and allyltrifluoroborate **2g** (73 mg, 0.45 mmol). Purification by column chromatography (20% EtOAc/hexane) gave a 2:1 inseparable mixture of the allylated products *ent*-**3a** and *ent*-**3b** as a yellow oil (43 mg, 60%) that displayed spectroscopic data consistent with those reported previously.[8]

R_f = 0.52 (30% EtOAc/hexane).

Data for *ent*-**3a**:

HPLC: Chiralpak AD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 225 nm, 25 °C); t_r (major) = 18.5 min, t_r (minor) = 38.6 min; 93% ee.

Data for *ent*-**3b**:

HPLC: Chiralpak AD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 225 nm, 25 °C); t_r (major) = 21.7 min, t_r (minor) = 43.0 min; 97% ee.

3(*S*)-3-[(*S*)-But-3-en-2-yl]-3-methyl-4-phenyl-2,3-dihydro-[1,2,5]-thiadiazole 1,1-dioxide (13i)[8] and 3(*S*)-3-[(*R*)-but-3-en-2-yl]-3-methyl-4-phenyl-2,3-dihydro-[1,2,5]-thiadiazole-1,1-dioxide (13j)[8]

General Procedure B was followed using imine **12** (62 mg, 0.30 mmol) and allyltrifluoroborate **2g** (73 mg, 0.45 mmol). Purification by column chromatography (10% EtOAc/hexane) gave the allylated product **13j** as a yellow oil (13 mg, 16%) followed by the allylated product **13i** as a yellow oil (38 mg, 48%) that displayed spectroscopic data consistent with those reported previously.[8] Both **13i** and **13j** were contaminated with small quantities (<10%) of each other.

Data for **13i**:

R_f = 0.22 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ +23.0 (*c* 1.00, $CHCl_3$).

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 254 nm, 25 °C); t_r (major) = 13.0 min, t_r (minor) = 22.2 min; 97% ee.

Data for **13j**:

R_f = 0.30 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ +16.6 (*c* 0.30, $CHCl_3$).

HPLC: Chiralcel OD-H column (90:10 hexane:*i*-PrOH, 0.8 mL/min, 254 nm, 25 °C); t_r (major) = 11.0 min, t_r (minor) = 17.3 min; 91% ee.

tert-Butyl _N_-[(_R_)-1-(2-hydroxyphenyl)but-3-en-1-yl]carbamate (17)

To a solution of allylation product **16**[8] in THF (1 mL) at room temperature was added $LiAlH_4$ (1.0 M in THF, 0.37 mL, 0.37 mmol) over 1 min at room temperature. The mixture was heated at 60 °C for 15 h, allowed to cool to temperature, and then cooled with an ice bath. The reaction was quenched carefully with EtOAc (1 mL), followed by the addition of EtOH (1 mL) and H_2O (2 mL). To the resulting turbid mixture was added Boc_2O (81 mg, 0.37 mmol) in one portion and the resulting mixture was stirred at room temperature for 1 h. The reaction was diluted with EtOAc (20 mL) and acidified with 2 M HCl until the aqueous layer became clear. The aqueous layer was separated and extracted with EtOAc (2 × 20 mL). The combined organic layers were dried (MgSO4), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (6:1 hexane:Et_2O→2:1 hexane:Et_2O) gave the *carbamate* **17** as a colorless oil (28 mg, 85%).

R_f = 0.54 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ +45.2 (*c* 1.15, $CHCl_3$).

IR (neat): 3310 (OH), 2925, 1680, 1502, 1456, 1367, 1170, 1043, 918, 860, 750 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.50 (br s, 1 H), 7.16-7.07 (m, 2 H), 6.88-6.80 (m, 2 H), 5.75 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1 H), 5.27 (br s, 1 H), 5.13 (dd, *J* = 17.2, 1.0 Hz, 1 H), 5.09 (d, *J* = 10.4 Hz, 1 H), 4.89 (br s, 1 H), 2.62 (t, *J* = 7.0 Hz, 2 H), 1.47 (s, 9H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 157.0, 154.7, 134.6, 128.5, 127.9, 126.6, 119.8, 117.8, 117.0, 80.7, 48.9, 38.6, 28.4 (3 × CH_3).

HRMS (EI): Exact mass calcd for $C_{15}H_{22}O_3N$ $[M+H]^+$: 264.1594, found: 264.1599.

HPLC: Chiralpak AS-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 230 nm, 25 °C); t_r (major) = 23.1 min, t_r (minor) = 30.6 min; 93% ee.

(_S_)-4-(3-Hydroxypropyl)-3,4-dihydro-[1,2,3]-benzoxathiazine-2,2-dioxide (18)

To a solution of the alkene **16** (prepared as described previously[8] by the reaction of imine 1 with potassium allyltrifluoroborate, but using chiral diene *ent*-**L1**) (225 mg, 1.00 mmol) in THF (3 mL) at 0 °C was added 9-BBN (0.5 M in THF, 6.0 mL, 3.0 mmol) over 2 min. The mixture was warmed to room temperature over 1 h and then stirred for a further 23 h. The reaction was cooled to 0 °C and 3 M NaOH (3 mL) and H_2O_2 (30 wt.% in H_2O, 6 mL) were added successively. The resulting mixture was stirred for 1 h at room temperature, diluted with H_2O (20 mL), acidified with 2 M HCl, and extracted with EtOAc (3 × 40 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (80% EtOAc/hexane) gave the *alcohol* **18** as a white solid (182 mg, 75%).

m.p. 112-113°C (CH_2Cl_2).

R_f = 0.36 (80% EtOAc/hexane).

$[\alpha]_D^{20}$ –36.7 (*c* 0.49, $CHCl_3$).

IR (neat): 3255 (OH), 2880, 1485, 1452, 1425, 1371, 1175, 1107, 883, 760 cm^{-1}.

^1H NMR (500 MHz, CD_3OD): δ = 7.40 (d, *J* = 7.8 Hz, 1 H), 7.36 (ddd, *J* = 8.3, 4.5, 1.1 Hz, 1 H), 7.24 (td, *J* = 1.6, 1.2 Hz, 1 H), 7.02 (dd, *J* = 8.2, 1.2 Hz, 1 H), 4.70 (dd, *J* = 10.9, 3.8 Hz, 1 H), 3.70-3.61 (m, 2 H), 2.26-2.18 (m, 1 H), 2.03-1.95 (m, 1 H), 1.90-1.82 (m, 1 H), 1.76-1.67 (m, 1 H).

^{13}C NMR (125.8 MHz, CD_3OD): δ = 152.8, 130.2, 127.9, 126.1, 125.0, 119.3, 62.3, 57.9, 31.3, 29.6.

HRMS (ESI): Exact mass calcd for $C_{10}H_{14}NO_4S$ $[M+H]^+$: 244.0638, found: 244.0640.

(_S_)-8-Oxa-7λ^6-thia-6-azatricyclo[7.4.0.0^{2,6}]trideca-1(9),10,12-triene-7,7-dioxide (19)

To a solution of the alcohol **18** (61 mg, 0.25 mmol) and PPh_3 (85 mg, 0.33 mmol) in CH_2Cl_2 (4 mL) at 0 °C was added a solution of DEAD (53 mg, 0.30 mmol) in CH_2Cl_2 (1 mL). The mixture was allowed to warm to room temperature over 1 h and then stirred for an additional 9 h. The reaction was quenched with EtOH (1 mL) and concentrated *in vacuo*. Purification of the residue by column chromatography (60% EtOAc/hexane) gave the product (56 mg, >95%) as a white solid.

m.p. 85-86 °C (EtOAc/hexane).

R_f = 0.57 (60% EtOAc/hexane).

$[\alpha]_D^{20}$ –125.0 (*c* 0.40, $CHCl_3$).

IR (neat): 2982, 1485, 1450, 1392, 1206, 1175, 1103, 1005, 856, 758 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.30 (dddd, *J* = 8.1, 7.3, 1.7, 0.8 Hz, 1 H), 7.21 (td, *J* = 7.5, 1.2 Hz, 1 H), 7.15 (dt, *J* = 7.5, 1.0 Hz, 1 H), 7.01 (dd, *J* = 8.2, 1.2 Hz, 1 H), 5.20 (dd, *J* = 7.4, 2.5 Hz, 1 H), 3.61-3.56 (m, 1 H), 3.51 (ddd, *J* = 10.1, 8.6, 5.8 Hz, 1 H), 2.59 (ddd, *J* = 16.5, 12.8, 7.7 Hz, 1 H), 2.30-2.24 (m, 1 H), 2.07-1.99 (m, 1 H), 1.92-1.83 (m, 1 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 151.0, 129.1, 126.6, 125.6, 122.5, 118.8, 62.7, 49.7, 34.0, 23.4.

HRMS (EI): Exact mass calcd for $C_{10}H_{12}NO_3S$ $[M+H]^+$: 226.0532, found: 226.0529.

HPLC: Chiralpak AD-H column (95:5 hexane:*i*-PrOH, 0.8 mL/min, 280 nm, 25 °C); t_r (minor) = 18.6 min, t_r (major) = 20.2 min; 92% ee.

tert-Butyl-_N_-[(_S_)-4-hydroxy-1-(2-hydroxyphenyl)butyl] carbamate (20)

To a solution of the cyclic sulfamate **18** (100 mg, 0.41 mmol) in THF (2 mL) at room temperature was added $LiAlH_4$ (2.0 M in THF, 0.62 mL, 1.24 mmol) dropwise over 4 min. The mixture was heated at 60 °C for 2 h, allowed to cool to room temperature, and then cooled with an ice bath. The reaction was quenched carefully with EtOAc (2 mL), followed by the addition of EtOH (2 mL) and H_2O (2 mL). To the resulting turbid mixture was added Boc_2O (268 mg, 1.24 mmol) in one portion and the resulting mixture was stirred at room temperature for 1 h. The reaction was diluted with EtOAc (40 mL) and acidified with 2 M HCl until the aqueous layer became clear. The aqueous layer was separated and extracted with EtOAc (2 × 40 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (80% EtOAc/hexane) gave the *carbamate* **20** (87 mg, 75%) as a colorless gum.

R_f = 0.42 (80% EtOAc/hexane).

$[\alpha]_D^{20}$ –33.6 (*c* 0.24, $CHCl_3$).

IR (neat): 3305 (OH and NH), 2980, 1680 (C=O), 1502, 1456, 1367, 1292, 1253, 1165, 752, 742 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.28 (br s, 1 H), 7.18 (dd, *J* = 12.1, 4.5 Hz, 2 H), 6.93 (d, *J* = 7.8 Hz, 1 H), 6.90 (dt, *J* = 7.5, 1.1 Hz, 1 H), 5.13 (s, 1 H), 4.86 (d, *J* = 6.9 Hz, 1 H), 3.72 (dt, *J* = 6.2, 0.9 Hz, 2 H), 2.06-1.95 (m, 2 H), 1.73-1.58 (m, 2 H), 1.45 (s, 9H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 157.3, 154.9, 128.8, 128.4, 126.3, 120.3, 117.8, 80.8, 62.3, 49.0, 30.6, 29.5, 28.3 (3 × CH_3).

HRMS (ESI): Exact mass calcd for $C_{15}H_{24}NO_4$ $[M+H]^+$: 282.1700, found: 282.1696.

***tert*-Butyl *N*-[(*S*)-2,3,4,5-tetrahydro-1-benzoxepin-5-yl] carbamate (21)**

To a solution of the alcohol **20** (68 mg, 0.24 mmol) and PPh_3 (82 mg, 0.31 mmol) in CH_2Cl_2 (4 mL) at 0 °C was added a solution of DEAD (51 mg, 0.29 mmol) in CH_2Cl_2 (1 mL). The mixture was allowed to warm to room temperature over 1 h and then stirred for an additional 9 h. The reaction was quenched with EtOH (1 mL) and concentrated *in vacuo*. Purification of the residue by column chromatography (20% EtOAc/hexane) gave the *tetrahydrobenzoxepine* **21** as a white solid (43 mg, 68%).

m.p. 105-106°C (CH_2Cl_2/hexane).

R_f = 0.40 (20% EtOAc/hexane).

$[\alpha]_D^{20}$ –40.0 (*c* 0.15, $CHCl_3$).

IR (neat): 3300 (NH), 2976, 2930, 1713 (C=O), 1450, 1366, 1236, 1224, 1170, 760 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.28-7.26 (m, 1 H), 7.20 (td, *J* = 7.7, 1.7 Hz, 1 H), 7.05 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.01 (dd, *J* = 7.5, 1.3 Hz, 1 H), 5.29 (d, *J* = 7.8 Hz, 1 H), 4.91 (t, *J* = 7.1 Hz, 1 H), 4.30 (app d, *J* = 11.9 Hz, 1 H), 3.75 (app t, *J* = 11.2 Hz, 1 H), 2.30-2.10 (m, 2 H), 1.88-1.81 (m, 1 H), 1.79-1.72 (m, 1 H), 1.44 (s, 9H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 159.3, 155.0, 135.5, 129.3, 128.9, 124.2, 122.0, 79.3, 73.8 , 53.9, 30.8, 28.4 (3 × CH_3), 26.7.

HRMS (ESI): Exact mass calcd for $C_{15}H_{22}NO_3$ $[M+H]^+$: 264.1594, found: 264.1595.

HPLC: Chiralpak AD-H column (98:2 hexane:*i*-PrOH, 0.8 mL/min, 280 nm, 25 °C); t_r (major) = 12.5 min, t_r (minor) = 15.6 min; 90% ee.

(3*S*,4*R*)-3-Methyl-4-phenyl-3-(prop-2-en-1-yl)-[1,2,5]-thiadiazolidine-1,1-dioxide (24)

To a solution of the imine **23** (prepared as described previously[8] by the reaction of imine **12** with allyltrifluoroborate **2c**, but using chiral diene *ent*-**L1**) (200 mg, 0.80 mmol) in THF (32 mL) at –20 °C was added DIBAL (1.0 M in THF, 3.2 mL, 3.2 mmol) over 2 min. The mixture was warmed gradually to room temperature over 2 h and stirred for a further 13 h. The reaction was quenched carefully with 1 M HCl solution until the pH value of the mixture reached 3. The mixture was diluted with H_2O (20 mL) and EtOAc (30 mL), and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 × 30 mL), and the combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (33% EtOAc/hexane) gave the *cyclic sulfamide* **24** as a colorless amorphous solid (182 mg, 90%).

R_f = 0.26 (30% EtOAc/hexane).

$[\alpha]_D^{20}$ –75.8 (*c* 0.42, CH_3OH).

IR (neat): 3271 (NH), 2980, 1454, 1381, 1312, 1265, 1157, 922, 741, 702 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.43-7.36 (m, 5 H), 5.67 (dddd, *J* = 17.1, 10.2, 7.8, 7.0 Hz, 1 H), 5.21-5.19 (m, 1 H), 5.14 (ddd, *J* = 17.1, 3.0, 1.3 Hz, 1 H), 4.90 (d, *J* = 5.1 Hz, 1 H), 4.82 (d, *J* = 5.1 Hz, 1 H), 4.60 (s, 1 H), 2.49 (dd, *J* = 13.7, 7.9 Hz, 1 H), 1.59 (dd, *J* = 13.7, 6.9 Hz, 1 H), 1.43 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 134.1, 131.9, 128.9, 128.8 (2 × CH), 127.3 (2 × CH), 121.2, 70.0, 65.0, 39.7, 24.2.

HRMS (EI): Exact mass calcd for $C_{12}H_{16}N_2O_2S$ $[M]^+$: 252.0927, found: 252.0928.

HPLC: Chiralcel OD-H column (80:20 hexane:*i*-PrOH, 0.8 mL/min, 211 nm, 25 °C); t_r (major) = 13.9 min, t_r (minor) = 28.1 min; 97% ee.

(1*R*,2*S*)-2-Methyl-1-phenyl-4-butene-1,2-diamine (25)

A solution of cyclic sulfamide **24** (101 mg, 0.40 mmol) and ethylenediamine (267 µL, 4.00 mmol) in dioxane (6 mL) was stirred at 100 °C for 15 h. The reaction was cooled to room temperature and concentrated *in vacuo*. To the residue was added a 1.25 M solution of HCl in MeOH (2 mL) and the resulting solution was stirred at room temperature for 2 h before being concentrated *in vacuo*. The residue was dissolved in H_2O (10 mL) and washed with EtOAc (2 × 10 mL). The organic layers were discarded and the aqueous phase was basified with 3 M NaOH (2 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to leave the *diamine* **25** (67 mg, 88%) as a pale yellow oil.

R_f = 0.15 (EtOAc).

$[\alpha]_D^{20}$ –30.0 (*c* 0.20, MeOH).

IR (neat): 3400 (NH), 2964, 1638, 1603, 1492, 1452, 1373, 999, 914, 704 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.39-7.31 (m, 5 H), 5.89 (ddt, *J* = 17.5, 10.2, 7.4 Hz, 1 H), 5.12 (ddt, *J* = 10.2, 2.0, 0.9 Hz, 1 H), 5.08 (ddt, *J* = 17.0, 2.3, 1.4 Hz, 1 H), 3.82 (s, 1 H), 2.13-2.03 (m, 2 H), 1.65 (br s, 4 H), 1.09 (s, 3 H).

^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 142.6, 134.3, 128.3 (2 × CH), 127.9 (2 × CH), 127.2, 118.3, 64.2, 54.7, 44.0, 24.7.

HRMS (EI): Exact mass calcd for $C_{12}H_{18}N_2$ $[M]^+$: 190.1465, found: 190.1465.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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