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The sulfinyl moiety in Lewis base-promoted allylations

J. Robin Fulton [a], Lamin M. Kamara [a], Simon C. Morton [b], Gareth J. Rowlands [c,*]

[a] Chemistry Division, Department of Chemistry and Biochemistry, University of Sussex, Falmer BN1 9QJ, UK
[b] AstraZeneca R&D Charnwood, Process Research and Development, Bakewell Road, Loughborough, Leicestershire LE11 5RH, UK
[c] Institute of Fundamental Sciences – Chemistry, Massey University, Private Bag 11 222, Palmerston North, New Zealand

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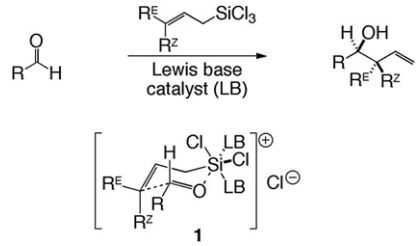
ABSTRACT

By employing Senanayake's oxathiazolidine-2-oxide reagent, a collection of sulfinamides was prepared and provided the first examples of sulfinamides promoting the allylation of benzaldehyde and *N*-benzoylhydrazones with allyltrichlorosilane. The optimum sulfinamide-derived Lewis base promoter displays comparable activity to the best sulfinyl-based Lewis bases reported. The use of bis-sulfoxides is also discussed.

1. Introduction

Lewis acid catalysis is still the dominant form of catalysis in organic chemistry; Lewis base-mediated processes are less comprehensively studied even though they offer catalysts with increased stability and the potential to catalyse a more diverse selection of reactions.[1,2] One aspect of Lewis base catalysis that has attracted appreciable attention is the allylation/crotylation of aldehydes and hydrazones with trichlorosilanes (Scheme 1).[3–7] A range of chiral Lewis bases have been introduced as catalysts for this transformation including phosphoramides,[3,5,6,8] phosphine oxides,[9] *N*-oxides[10] and formamides.[11] All these reagents are thought to interact with the silane to give a penta- or hexa-coordinate hypervalent silicate that enhances both the nucleophilicity of the allyl moiety and the electrophilicity of the silicon atom. The major attraction of this methodology is its high diastereospecificity in crotylations, which is postulated to arise due to the closed transition state **1**. The relative scarcity of Lewis base catalysts compared to the vast number of ligands for Lewis acid catalysis means there is a need to increase the repertoire of potential Lewis base catalysts.



Scheme 1. Lewis base-mediated crotylation.

The sulfinyl moiety has yet to be fully exploited in this arena even though it has good donor properties, is readily prepared and the chirality of sulfur is in close proximity to all the components of the reaction. We, along with two other groups, introduced chiral sulfoxides as Lewis basic organocatalysts for allylation[12–14] and subsequently, other groups have reported the use of sulfinyl derivatives in similar reactions.[15–18] Unfortunately, none of the sulfoxides investigated have proven entirely satisfactory; none show catalytic turnover,[19] and the allylation of aldehydes proceeds with only moderate enantioselectivity. In this paper we outline our preliminary attempts to ameliorate this situation with bis-sulfoxides and report the first use of monodentate sulfinamides as promoters for the Lewis base-mediated allylation of both aldehydes and *N*-benzoylhydrazones.

During detailed analysis of the mechanism of chiral phosphoramide-catalysed allylation, Denmark revealed that the reaction follows second order kinetics in the monodentate phosphoramide catalyst (such as **1**; Scheme 1) and hence proposed that bidentate promoters should be superior.[2,5,6,20] This drove us to investigate bidentate sulfinyl oxazoline promoters **2**

* Corresponding author. Fax: +64 6 350 5682.
E-mail address: g.j.rowlands@massey.ac.nz (G.J. Rowlands).

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(Fig. 1);[14] these were encouraging, giving homoallylic alcohols in good yield with moderate enantioselectivity but they were far from perfect. They displayed no catalytic turnover, requiring excess reagent to achieve acceptable yields and, more worryingly, decomposed under the reaction conditions. The results indicated that the enantioselectivity of the allylation was controlled by the sulfinyl moiety and that the oxazoline moiety was not only unnecessary but was detrimental to the promoter's stability. Therefore, we decided to replace it with a second sulfoxide group in order to maintain the bidentate nature of the promoters (**3**; Fig. 1). This research was undertaken before the publication of Fernández and Khiar's report on the activity of bis-sulfoxides in the allylation of hydrazones.[16,21]

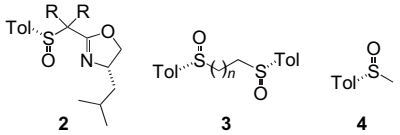


Figure 1. Sulfoxide-derived Lewis base promoters.

2. Results and discussion

2.1. Sulfoxide-derived Lewis base promoters

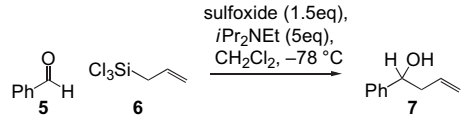
Our initial targets were the bis-sulfoxides **3** (n=1 to 3; Fig. 1).[21] The methyl-linked promoter (**3**; n=0) was not prepared as it was felt that the relatively acidic methylene position (pK_a approximately 18.2 in DMSO) would encourage deoxygenation by the Pummerer reaction. The ethyl-linked bis-sulfoxide (**3**; n=1) was prepared according to a literature procedure by copper(II)-mediated oxidative dimerisation of the (*R*)-methyl toluenesulfoxide **4**.[22] Bis-sulfoxides with a longer linker proved harder to synthesise; the most direct route, formation of a bis-Grignard reagent from a suitable dihalide and reaction with Andersen's sulfinate, (1*R*,2*S*,5*R*)-(+)-menthyl (*S*)-*p*-toluenesulfinate, failed. Reversal of the coupling partners with the anion of **4** displacing a suitable leaving group from the linker was also tried with equally unsatisfactory results.

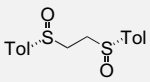
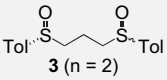
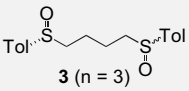
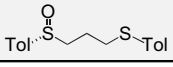
Finally, a convoluted, stepwise synthesis permitted a limited number of sulfoxides **3** to be prepared. The synthesis was based on the elaboration of **4**, thus one stereocentre was fixed. Unfortunately, the second was introduced by non-selective oxidation giving rise to a mixture of the desired enantiomer and the achiral *meso* diastereoisomer. Although separation of the diastereoisomers was impossible, we believed that the mixture would provide satisfactory preliminary results, as the unwanted diastereoisomer would only promote non-selective allylation and not preferential formation of the opposite enantiomer of homoallylic alcohol.

Since Kobayashi's[7] and Denmark's[3] seminal work in the early 1990s, the addition of allyltrichlorosilane to benzaldehyde has been extensively studied and is now considered as a benchmark reaction for understanding the potential of new Lewis base promoters. In order to ascertain the efficacy of the new sulfoxides **3** their activity was compared with methyl derivative **4**, the optimum sulfoxide for the allylation of benzaldehyde **5** with allyltrichlorosilane **6** (Table 1).[13]

All reactions were performed under identical conditions; 1 equiv of sulfoxide and 5 equiv of ethyldiisopropylamine in dichloromethane at −78 °C. Initial studies required the development of a method to evaluate the efficiency of the promoters simply and rapidly that did not rely on chiral chromatography or derivatisation; the yields were determined from the NMR spectra of the crude reaction mixture using 2,3,5,6-tetrachloronitrobenzene as an internal standard whilst the enantiomeric excess was ascertained using chiral solvating agent, (*S*)-*tert*-butylphenylphosphinothioic acid (TBPTA).[23] The spectra of a 1:2 mixture of (*S*)-TBPTA/alcohol **7** collected at −10 °C with proton decoupling displays a separate singlet for the benzylic proton of each enantiomer; (*R*)-**7** is at δ 4.76 ppm and (*S*)-**7** is at δ 4.74 ppm.

Table 1
Bis-sulfoxide-mediated allylation of benzaldehyde



Entry	Sulfoxide	Yield (%)	(*S*)-**7**/(*R*)-**7**
1	 **4**	27	77:23
2	 **3** (n = 1)	0	—
3	 **3** (n = 2)	3	70:30
4	 **3** (n = 3)	2	—
5		17	73:27

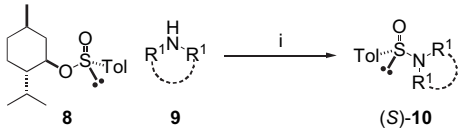
The results of the allylation are displayed in Table 1 and are disappointing with none of the novel sulfoxides competing with **4** (Table 1; Entry 1). The mixed sulfoxide sulfide gave the best results forming (*S*)-**7** in 46% ee (Table 1; Entry 5). This is comparable with the selectivity of **4** under the same reaction conditions. The bis-sulfoxide **3** (n=2) gave comparable enantioselectivity to both **4** and the mixed sulfoxide sulfide but was considerably less reactive (Table 1; Entry 3). Surprisingly, ethyl bis-sulfoxide **3** (n=1) gave pitiful results; this in stark contrast to the results of Fernández, who showed that **3** (n=1) was a competent promoter for the allylation of *N*-benzoylhydrazones.[16] The activity of the mixed sulfoxide sulfide (Table 1; Entry 5) compared to the bis-sulfoxides is far more intriguing; it appears that under our reaction conditions the second sulfoxide moiety impedes allylation, with all the bis-sulfoxides giving poor results. Ultimately, whilst these results are far from comprehensive they suggest that bis-sulfoxides show no substantial improvements over mono-sulfoxides; they show no catalytic turnover, reduced reactivity and, at best, comparable enantioselectivity.

Whilst more research needs to be performed in order to understand these systems, we felt that the sulfoxides did not offer sufficient potential to continue their pursuit; we had not improved enantioselectivity over existing sulfoxide promoters and we were still no closer to obtaining catalytic turnover. Therefore, we turned our attention to the study of sulfinamides as potential Lewis base catalysts.

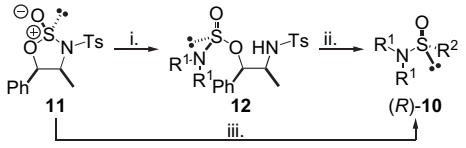
2.2. Sulfinamide-derived Lewis base promoters

Sulfinamides proffer several advantages over sulfoxides; firstly, their synthesis is simpler, permitting facile access to greater structural diversity and secondly, the amine moiety increases their donor ability and hence their reactivity. Earlier observations had confirmed this latter supposition, with simple sulfinamides reacting faster than the sulfoxides.[14,24] The studies reported here represent the first examples of sulfinamides being employed as Lewis base promoters for the allylation of aldehydes and hydrazones.

S-Toluene sulfinamides **10** were synthesised by treating Andersen's sulfinate, (1*R*,2*S*,5*R*)-(+)-menthyl (*S*)-*p*-toluenesulfinate **8**, with secondary amine (**9**)-derived lithium amides (Scheme 2; Table 2). A more flexible route employing Senanayake's *N*-sulfonyl-1,2,3-oxathiazolidine-2-oxide **11** as the source of the stereogenic S–O moiety,[25] permitted access to a wider range of promoters (Scheme 3; Table 2). Nucleophilic addition of a metal amide to the sulfur resulted in ring opening of **11** to give amino sulfites **12**. Treatment of **12** with 2 equiv of Grignard reagent furnished the desired sulfinamides **10**. A simple 'one-pot' procedure furnished the sulfinamides directly from **11** and circumvented the need to isolate **12**; reaction of 1 equiv of metal amide with **11** was followed by the addition of a single equivalent of Grignard reagent to give **10** in moderate yield. Curiously, reversal of the order of addition of the nucleophiles led to poor yields of sulfinamides for no discernable reason; Grignard-mediated ring opening proceeded in good yield but, in our hands, the addition of the amine moiety was unsatisfactory.



Scheme 2. Preparation of toluene sulfinamides **10**: LDA, THF, −78 °C.



Scheme 3. General synthesis of sulfinamides **10**: (i) **9**, *n*-BuLi, THF, −78 °C, 12 h; (ii) R^2MgCl, Et_2O, 0 °C, 12 h; (iii) **9**, *n*-BuLi, THF, −78 °C, 12 h then R^2MgCl, Et_2O, 0 °C, 12 h.

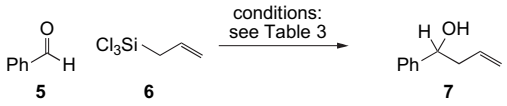
Table 2
Preparation of sulfinamides

Sulfinamide	R^1	R^2	Yield (%)	Ref.[a]
(*S*)-**10a**[b]	Et	Tol	77	26,27
(*S*)-**10b**[b]	*i*-Pr	Tol	96	26
(*S*)-**10c**[b]	C_4H_8O	Tol	24	28
(*R*)-**10d**[c]	C_4H_8O	Ph	26	29,30
(*R*)-**10e**[c]	C_4H_8O	Et	27	31
(*R*)-**10f**[c]	C_4H_8O	*i*-Pr	58	32
(*R*)-**10g**[c]	C_4H_8O	*t*-Bu	51	29
(*R*)-**10h**[c]	Et	Ph	52	29,33
(*R*)-**10i**[c]	Et	*i*-Pr	52	32
(*R*)-**10j**[c]	Et	*t*-Bu	55	34
(*R*)-**10k**[c]	Et	*i*-Bu	49	—
(*R*)-**10l**[c]	Pr	*i*-Bu	87	—
(*R*)-**10m**[c]	*i*-Pr	Ph	95	33,35

[a] All racemic sulfonamides (except **10k** and **10l**) are known compounds. Enantiomerically pure **10a**, **10b**, **10c**, **10h** and **10m** have been reported; full data has not been reported on any of the compounds and all compounds were made by alternative routes to that described in this paper.
[b] Synthesised according to Scheme 2.
[c] Synthesised according to Scheme 3.

Optimisation of the allylation of benzaldehyde employed the readily obtained (*S*)-**10a**. The reaction could be performed in either dichloromethane or acetonitrile with little change in efficiency (Table 3; Entries 1 and 2 vs 3 and 4); the use of dichloromethane at −78 °C was judged to be more practicable. The reaction was appreciably faster than the corresponding sulfoxide-promoted process with high yields being obtained in two hours compared to a minimum of six hours for the sulfoxides. Reactions in the absence of ethyldiisopropylamine gave racemic homoallylic alcohol (Table 3; Entries 1 and 3). The sulfinamide promoters racemise in the absence of amine base and this process clearly occurs faster than the allylation thus giving rise to a non-stereoselective reaction. The addition of base effectively stops the racemisation, with (*S*)-**10a** recovered from Entries 2 and 4 showing only a slight reduction in enantiopurity as measured by optical rotation. Addition of 2-methyl-2-butene, which has been reported to prevent decomposition of sulfoxide promoters,[12] failed to suppress racemisation (Table 3; Entry 5).

Table 3
Optimisation of the sulfinamide-promoted allylation of benzaldehyde



Entry	Sulfinamide (equiv)	Solvent (M)	EtN-*i*-Pr_2 (equiv)	Yield (%)	(*S*)-**7**/(*R*)-**7**[a]
1[b,c]	(*S*)-**10a** (3.0)	CH_2Cl_2 (0.3)	—	86	51:49
2[b,c]	(*S*)-**10a** (3.0)	CH_2Cl_2 (0.3)	2.1	86	59:41
3[d,e]	(*S*)-**10a** (1.5)	MeCN (0.6)	—	93	51:49
4[d,e]	(*S*)-**10a** (1.5)	MeCN (0.6)	2.5	86	61:39
5[d,e]	(*S*)-**10a** (1.5)	MeCN (0.6)	—[g]	58	51:49
6[b,c]	(*R*)-**10h** (3.0)	CH_2Cl_2 (0.6)	5.0	97	35:65
7[b,f]	(*R*)-**10g** (3.0)	MeCN	—	42	59:41
8[b,c]	(*R*)-**10i** (3.0)	CH_2Cl_2 (0.6)	5.0	89	48:52
9[b,c]	(*R*)-**10k** (3.0)	CH_2Cl_2 (0.6)	5.0	99	75:25
10[b,c]	(*R*)-**10l** (3.0)	CH_2Cl_2 (0.6)	5.0	93	75:25

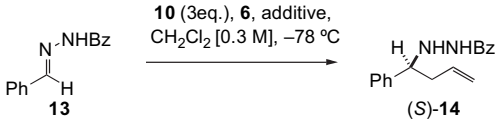
[a] Determined by HPLC—Chiralcel OD 0.46 cm×25 cm, hexane/2-propanol (9:1) flow rate 1 mL min^{-1}, t_R 8.21 min, t_S 9.07 min.
[b] 2.1 equiv of **6**.
[c] −78 °C.
[d] 2.5 equiv of **6**.
[e] −45 °C.
[f] rt.
[g] 2.5 equiv of 2-methyl-2-butene used instead of EtN-*i*-Pr_2.

Altering the structure of the sulfinamide permitted the stereoselectivity to be improved. Interestingly, alkyl sulfinamides gave the opposite enantioselectivity to *S*-aryl promoters (Table 3; Entry 6 vs 7–10); this reversal is not observed in the sulfinamide-promoted allylation of benzoylhydrazones (see below). The poor performance of isopropyl analogue (*R*)-**10i** was very surprising (Table 3; Entry 8); Fernández has reported that isopropyl *sulfoxides* are excellent promoters in the reaction of benzoyl hydrazones.[15,16] Considering both the isobutyl and the *tert*-butyl derivatives gave meaningful enantioselectivities, its non-selectivity in this reaction is inexplicable. The *tert*-butyl derivative (*R*)-**10g** was less active than the other promoters, requiring the reactions to be performed at room temperature to obtain satisfactory yields (Table 3; Entry 7). Curiously, whilst the bulk of the *tert*-butyl group hinders the reaction it protects the sulfinyl moiety from racemisation with **7** being formed in 18% ee *without* the addition of amine base. The isobutyl sulfinamides (*R*)-**10k** and (*R*)-**10l** surpassed all other promoters, giving homoallylic alcohol **7** in excellent yield and respectable enantioselectivity (Table 3; Entries 9 and 10). It is assumed that (*R*)-**10k** and (*R*)-**10l** offer a good compromise between the bulky *tert*-butyl group and aryl substituents. Alterations to the amine moiety had little effect on either reactivity or selectivity.

The sulfinamide promoters are far superior to the bis-sulfoxides and are the most effective sulfur-based promoters yet reported for the allylation of *aldehydes*. More impressive results have been published for the allylation of *N*-acylhydrazones with sulfur-based promoters than for the corresponding reactions with aldehydes.[12,15–17] Believing that this is caused by the *substrate* and not the promoter, we decided to investigate the activity of the sulfinamides in the allylation of hydrazones.

Initial optimisation of the reaction conditions and sulfinamide structure involved the allylation of the benzoylhydrazone of benzaldehyde **13** (Table 4). In all cases, an excess of sulfinamide was required to obtain a satisfactory yield; the best results were

Table 4
Optimisation of the sulfinamide-mediated allylation of *N*-benzoylhydrazone **13**



Entry	Reagent	**6** (equiv)	*i*-Pr_2NEt (equiv)	Yield (%)	(*R*)-**14**/(*S*)-**14**[a]
1[b,c]	(*S*)-**10a**	5.0	5.0	95	47:53
2[c]	(*S*)-**10a**	5.0	5.0	99	40:60
3	(*S*)-**10a**	5.0	—	53	44:56
4	(*S*)-**10a**	1.0	5.0	75	37:63
5	(*S*)-**10a**	2.1	5.0	85	35:65
6[c]	(*S*)-**10c**	5.0	5.0	97	48:52
7	(*S*)-**10b**	1.0	5.0	74	51:49
8	(*R*)-**10d**	2.1	2.1	80	57:43
9	(*R*)-**10e**	2.1	2.1	96	55:45
10	(*R*)-**10f**	2.1	2.1	93	72:28
11	(*R*)-**10g**	2.1	2.1	71	58:42
12	(*R*)-**10h**	2.1	2.1	83	63:37
13	(*R*)-**10i**	2.1	5.0	91	80:20
14	(*R*)-**10j**	2.1	5.0	92	54:46
15	(*R*)-**10k**	2.1	5.0	98	92:8

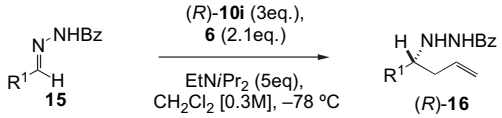
[a] Determined by HPLC—Chiralcel OD, 0.46 cm×25 cm, hexane/2-propanol (9:1), flow 1 mL/min, t_R 10.41 min, t_S 12.58 min.
[b] Reaction run at 0.1 M.
[c] additional 2.1 equiv of 2-methyl-2-butene.

obtained with 3 equiv. As observed by Kobayashi[12] and Fernández,[16] the concentration of the reaction was important; simply increasing the concentration from 0.1 M to 0.3 M resulted in an increase in selectivity from 6% to 20% ee (Table 4; Entries 1 and 2). As with the allylation of benzaldehyde the presence of an excess of ethyldiisopropylamine was essential for enantioselectivity; in its absence the sulfinamide catalysts undergo racemisation (Table 4; Entry 3 vs 2). Five equivalents of ethyldiisopropylamine proved to be the optimum amount. As expected, reducing the ratio of allyltrichlorosilane (Table 4; Entries 4–7) to Lewis base so that there was an excess of sulfinamide resulted a slower but more stereoselective reaction.

The structure of the sulfinamide was altered in order to improve the enantioselectivity. The amine portion of the promoter appears to be sensitive to steric hindrance; replacing the diethylamine moiety with the bulkier diisopropylamine group (Table 4; Entry 7) resulted in a complete loss in selectivity. This is in keeping with previous findings that show sulfoxide-based catalysts do not tolerate bulk near the sulfinyl moiety.[12,14–16] The conformationally restrained morpholine moiety displays similar activity to the diethylamine group although there is a minor drop in enantioselectivity (Table 4; Entries 8–11 vs 12–14). More dramatic results were obtained by varying the carbon substituent. As might be expected, minor alteration to the aryl group has little effect (Table 4; Entries 6 vs 8 and 8 vs 12) but substituting an alkyl group for the aryl group was more promising. Curiously, unlike the aldehyde series the change from aryl to alkyl did not result in a reversal of stereoselectivity. The small ethyl group gave poor enantioselectivity (Table 4; Entry 9) whilst appending too large a group, such as a *tert*-butyl moiety, reduces the activity and erodes selectivity (Table 4; Entries 11 and 14). The isopropyl substituent offers a good balance, contributing sufficient bulk to induce selectivity whilst maintaining reactivity and furnished **14** with promising enantioselectivity for both the morpholine and diethylamine series (Table 4; Entries 10 and 13). This is in agreement with Fernández who has previously noted the superior effect of the isopropyl group[15] but is sharp contrast to the results form the allylation of aldehydes. The best result was achieved with the final sulfinamide synthesised (**10k**; Table 4; Entry 15). This sulfinamide was prepared as we speculated that moving the bulk away from the active centre would result in a better promoter; full studies on this promoter were curtailed due to the development of a more successful catalyst system.[36]

We briefly ascertained the sulfinamide's efficiency in the allylation of a range of benzoylhydrazones (Table 5). The promoter readily induces the allylation of all the hydrazones **15** tested but with erratic results. The poor selectivity for the allylation of the isobutyraldehyde derivative was disappointing considering its success in Fernández's study; the subtle differences between the sulfinamide and sulfoxide promoters are intriguing.

Table 5
Sulfinamide-mediated allylation of *N*-benzoylhydrazones



Entry	R^1	Yield (%)	(*R*)-**16**/(*S*)-**16**[a]
1	Ph	91	80:20
2	*p*-Cl-C_6H_4	97	80:20
3	*p*-Br-C_6H_4	96	77:23
4	*p*-NO_2-C_6H_4	98	49:51
5	*p*-MeO-C_6H_4	72	70:30
6	*i*-Pr	90	46:54

[a] Determined by HPLC—Chiralcel OD, 0.46 cm×25 cm, hexane/2-propanol (9:1), flow 1 mL/min.

Comparing the efficacy of sulfinamides in the Lewis base-catalysed allylation of acylhydrazones and aldehydes uncovers a number of subtle differences. The reactions of the hydrazones are generally more efficient, occurring faster and giving higher yields and enantioselectivities. Furthermore, allylations performed by the same promoter give the *opposite* configuration of homoallylic alcohol and homoallylic hydrazine. These differences can be explained by invoking the transition states **17** and **18** (Fig. 2). Aldehydes presumably react via a chair-like transition state in which the aldehyde adopts the pseudo-equatorial position **17**. Benzoylhydrazones are potentially bidentate substrates with both the benzoyl carbonyl and the imine-like nitrogen able to coordinate to the silicon, generating a more defined transition state **18**. This activation of the silane *without* addition of a Lewis base could account for the increased activity; Kobayashi has reported that acylhydrazones show a more pronounced background reaction than aldehydes.[37] This transition state forces the hydrazone substituent into the pseudo-axial position and accounts for the reversal in selectivity. It could also explain the higher selectivity; positioning the substituent in the pseudo-axial position offers greater potential for pseudo-1,3-diaxial interaction between the substrate and the Lewis base.

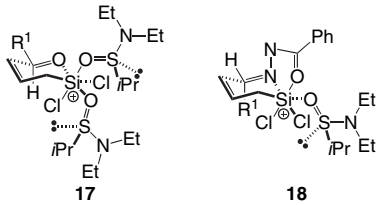


Figure 2. Possible transition states.

Other curious differences include the reversal in stereoselectivity observed when changing from an aromatic sulfinamide to an alkyl-substituted sulfinamide in the aldehyde series, an effect that is not observed in the hydrazone series. Additionally, whilst the *iso*propyl-substituted sulfinamide furnishes high enantioselectivities in the allylation of hydrazones it gives almost racemic

material during the allylation of aldehydes. Yet in both series the isobutyl derivative **10k** gave the best results; in the case of the allylation of the *N*-benzoylhydrazone, **13** (98% yield and 84% ee) compares favourably with the best sulfur-based Lewis base promoters yet reported.[16] All these results show that the allylation of aldehydes and hydrazones should be considered quite different reactions and that catalysts capable of promoting one reaction will not necessarily be good at promoting the other.

Whilst the results of the sulfinamide-promoted allylation of benzoylhydrazones are far more impressive than our results for the allylation of aldehydes, they still suffer from one major drawback compared to other Lewis base catalysts; there is no catalytic turnover. This is particularly interesting considering Sun et al. have shown that simple sulfinamides and bis-sulfinamides catalyse the trichlorosilane-mediated reduction of ketimines with as little as 0.2 equiv.[38] Furthermore, a recent publication purports that catalytic turnover can be obtained with bis-sulfoxides in allylation reactions.[19] At present, it is unclear why our sulfinamides bind irreversibly under the reaction conditions and thus inhibit turnover whilst these two reports do not suffer this problem.

3. Conclusion

In conclusion, we have shown that both bis-sulfoxides and mono-sulfinamides can be employed as Lewis base promoters for the allylation of benzaldehyde and *N*-benzoylhydrazones. The bis-sulfoxides appear to be of limited value, displaying both low enantioselectivity and no catalytic turnover. The sulfinamides are more promising; modification of Senanayake's chemistry has allowed rapid entry in to a range of sulfinamides and this has facilitated the development of new sulfinamide promoters for the Lewis base-catalysed allylation. The allylation proceeds in excellent yields and good enantioselectivities. Our best sulfinamide-based promoter compares favourably with the best sulfur-derived Lewis base catalysts yet reported. The results are more favourable than those found for the allylation of aldehydes suggesting subtle differences in these seemingly similar reactions.

4. Experimental

4.1. General

Unless otherwise stated reactions were performed under a dry nitrogen atmosphere. Reagents were used directly as obtained from commercial suppliers (Sigma–Aldrich, Fluka, Lancaster, Fisher) or purified according to standard procedures.[39] Chromatography refers to flash column chromatography on Fisher Matrex silica gel 60 (35–70 μm) or Merck Kieselgel 60 (230–400 mesh). NMR spectra were recorded on a Bruker DPX300FT spectrometer at ambient probe temperature, or on Varian unity INOVA-300, 400 or 500 Fourier transform spectrometers using either TMS as an internal standard or residual isotopic solvent as an internal reference. Infrared spectra were recorded on a Perkin–Elmer SpectrumOne FTIR Spectrophotometer. Mass spectra were recorded on KRATOS MS80F and MS25 double focussing spectrometers or carried out by the EPSRC Central Mass Spectrometry Service at Swansea. Data was also recorded on a Bruker Daltonics, FT Apex III, ESI, Hewlett Packard 5973 Mass Selective Detector (electron impact ionisation) connected to a Hewlett Packard 6890 Series GC System. Low-resolution electron impact (EI) mass spectra were recorded using a Fisons Autospect instrument. Liquid chromatography mass spectrometry data was collected on a Waters 2790 HPLC, 996 Photo Diode Array Detector and MicroMass ZMD single quadrupole mass spectrometer with Z-spray interface using electrospray ionisation with Pos/Neg switching. Melting points were recorded on a Büchi B-545 or on a Gallenkkamp Melting Point Apparatus and are uncorrected. Optical rotations were measured using a Perkin–Elmer 241 Polarimeter.

4.2. General procedure A: ring-opening *N*-tosyl-1,2,3-oxathiazolidine-2-oxide 11 with amines

This procedure was a modification of Senanayake's methodology.[25]

n-BuLi (2.5 M in Et_2O; 1.05 equiv) was added dropwise to a solution of amine (1.05 equiv) in THF (0.7 M) at 0 °C. The reaction was stirred for 1 h at 0 °C and then added slowly to a solution of (2*R*,4*S*,5*R*)-4-methyl-5-phenyl-*N*-tosyl-1,2,3-oxathiazolidine-2-oxide **11** (1.0 equiv) in THF (1 M) at −78 °C. The mixture was stirred for 3 h, and then warmed to rt overnight. The reaction was added to saturated $NaHCO_3$ aqueous solution and extracted with EtOAc (×3). The combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated to afford the crude sulfinate, which was purified by chromatography (1:1 EtOAc/hexane) to afford the sulfinamic acid (e.g. **12d**).

*4.2.1. (S)-Morpholinesulfinamic acid (1R,2S)-1-phenyl-2-[(toluenesulfonyl)amino]propyl ester **12d**.* General procedure A was performed on a 16.0 mmol scale of *N*-tosyl-1,2,3-oxathiazolidine-2-oxide **11** to give **12d** as a white crystalline solid (5.26 g, 75%); mp 90–92 °C; $[\alpha]_D$ −55.9 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3584, 3270, 2970, 1599, 1452, 1332, 1164, 932, 737; δ_H (300 MHz, $CDCl_3$) 7.82 (2H, d, *J*=8.1 Hz, H-2′, H-6′-Tol), 7.37–7.22 (5H, m, ArH), 7.17 (2H, d, *J*=7.0 Hz, H-2″, H-6″-Ph), 5.46 (1H, d, *J*=9.0 Hz, H-1), 3.71–3.22 (4H, m, 2×H-2‴, 2×H-3‴), 3.57–3.52 (1H, m, H-2), 3.28–2.98 (4H, m, 2×H-1‴, 2×H-4‴), 2.44 (3H, s, CH_3-Tol), 0.95 (3H, d, *J*=6.8 Hz, CH_3); δ_C ($CDCl_3$, 75 MHz) 143.8, 138.5, 138.5, 138.1, 130.2, 129.0, 128.7, 127.6, 126.3, 79.7, 66.5, 54.9, 41.6, 21.0, 15.1; HRMS (EI) found: $[M+Na]^+$ 461.1175. $C_{20}H_{26}N_2O_5S_2Na$ requires $[M+Na]^+$ 461.1164.

*4.2.2. (S)-Diethylsulfinamic acid (1R,2S)-1-phenyl-2-[(toluenesulfonyl)-amino]propyl ester **12h**.* General procedure A was performed on a 5.7 mmol scale of *N*-tosyl-1,2,3-oxathiazolidine-2-oxide **11** to give **12h** as an oil (1.31 g, 55%); $[\alpha]_D$ −10.3 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3270, 2854, 1599, 1463, 1378, 1163, 1091, 815, 723, 666; δ_H (300 MHz, $CDCl_3$) 7.63 (2H, d, *J*=8.3 Hz, H-2′, H-6′), 7.05–7.00 (5H, m, Ph), 6.87 (2H, d, *J*=8.1 Hz, H- 3′, H-5′), 4.54 (1H, d, *J*=2.3 Hz, H-1), 3.36–3.31 (1H, m, H-2), 3.00 (4H, q, *J*=7.2 Hz, 2×H-1‴, 2×H-3‴), 2.22 (3H, s, CH_3-Tol), 0.94 (6H, t, *J*=7.2 Hz, 2×CH_3), 0.71 (3H, d, *J*=6.8 Hz, CH_3); δ_C ($CDCl_3$, 75 MHz) 143.7, 138.7, 130.1, 128.8, 128.3, 127.6, 126.5, 126.2, 78.9, 54.9, 37.0, 21.9, 15.1, 14.3; HRMS (EI) found: $[M+Na]^+$ 447.1383. $C_{20}H_{28}N_2O_4S_2Na$ requires $[M+Na]^+$ 447.1371.

*4.2.3. (S)-Dipropylsulfinamic acid (1R,2S)-1-phenyl-2-[(toluenesulfonyl)amino]propyl ester **12l**.* General procedure A was performed on a 54.27 mmol scale of *N*-tosyl-1,2,3-oxathiazolidine-2-oxide **11** to give **12l** as an oil (15.90 g, 65%); $[\alpha]_D$ −11.3 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3253, 2965, 1737, 1599, 1452, 1333, 1242, 1161, 1091, 984, 947, 863, 815, 739, 663, 701, 515; δ_H (300 MHz, $CDCl_3$) 7.60 (2H, d, *J*=7.9 Hz, H-2′, H-6′), 7.10–7.03 (5H, m, ArH), 6.84 (2H, d, *J*=6.8 Hz, H-2″, H-6″-Ph), 5.52 (1H, s, H-1), 3.30 (1H, d, *J*=6.4 Hz, H-2), 2.89–2.63 (4H, m, H-1‴, H-4‴), 2.18 (3H, s, CH_3-Tol), 1.38–1.21 (4H, m, 2×H-2‴, 2×H-5‴), 0.70 (3H, d, *J*=6.6 Hz, CH_3), 0.64 (6H, t, *J*=7.4 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 143.7, 138.7, 138.3, 130.1, 128.8, 128.3, 127.6, 126.2, 78.8, 54.9, 45.3, 21.9, 21.4, 15.3, 11.9; HRMS (EI) found: $[M+Na]^+$ 475.1685. $C_{22}H_{32}N_2O_4S_2Na$ requires $[M+Na]^+$ 475.1696.

*4.2.4. (S)-Diisopropylsulfinamic acid (1R,2S)-1-phenyl-2-[(toluenesulfonyl)amino]propyl ester **12m**.* General procedure A was performed on a 24.22 mmol scale of *N*-tosyl-1,2,3-oxathiazolidine-

2-oxide **11** to give **12m** as an oil (8.04 g, 73%); $[\alpha]_D$ −7.3 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3234, 3064, 2976, 2935, 1599, 1496, 1453, 1380, 1334, 1185, 1164, 1107, 1000, 944, 816, 738, 703, 666; δ_H (300 MHz, $CDCl_3$) 7.80 (2H, d, *J*=8.3 Hz, H-2′, H-6′), 7.21–7.19 (5H, m, ArH), 7.00 (2H, d, *J*=7.2 Hz, H-2″, H-6″-Ph), 5.94 (1H, d, *J*=8.5 Hz, H-1), 3.94 (2H, septet, *J*=6.9 Hz, H-2‴, H-5‴), 3.45–3.39 (1H, m, H-2), 2.37 (3H, s, CH_3-Tol), 1.26–1.05 (12H, m, 4×CH_3 of *i*-Pr), 0.90 (3H, d, *J*=6.8 Hz, CH_3); δ_C ($CDCl_3$, 75 MHz) 143.6, 138.9, 138.6, 130.1, 128.7, 128.2, 127.7, 126.0, 79.2, 54.8, 44.0, 23.6, 22.0, 14.6; HRMS (EI) found: $[M+Na]^+$ 475.1669. $C_{22}H_{32}N_2O_4S_2Na$ requires $[M+Na]^+$ 475.1696.

4.3. General procedure B: synthesis of sulfinamides from Andersen's sulfinate

^{n}BuLi (2.5 M in hexane; 1.05 equiv) was added dropwise to a solution of amine (1.05 equiv) in THF (0.5 M) at 0 °C. The mixture was stirred for 1 h and was added slowly to a solution of (1*R*,2*S*,5*R*)-(+)-menthyl (*S*)-*p*-toluenesulfinate **8** (1.0 equiv) in THF (1.1 M) at −78 °C. The mixture was stirred for 3 h and was warmed to rt overnight. The reaction was poured into saturated aqueous $NaHCO_3$ solution and extracted with EtOAc. The combined organic phases were washed with brine, dried (Na_2SO_4) and concentrated to afford the crude product, which was purified by chromatography (eluent 1:3 EtOAc/hexane) to afford the desired compound.

4.3.1. (S)-N,N-Diethyl-p-toluenesulfinamide ***10a***[26,27]. General procedure B was performed on a 17.05 mmol scale of sulfinate **8** using diethylamine to give (*S*)-*N*,*N*-diethyl-*p*-toluenesulfinamide (**10a**) as an oil (2.76 g, 77%); $[\alpha]_D$ +77.3 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3052, 2974, 2872, 1596, 1490, 1381, 1175, 1087, 1009, 898, 814, 734; δ_H (300 MHz, $CDCl_3$) 7.31 (2H, d, *J*=8.1 Hz, H-2, H-6), 7.07 (2H, d, *J*=7.9 Hz, H-3, H-5), 2.90 (4H, q, *J*=7.2 Hz, 2×H-1′, 2×H-3′), 2.20 (3H, s, CH_3-Tol), 0.91 (6H, t, *J*=7.2 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 141.5, 141.2, 129.8, 126.6, 42.3, 21.7, 14.8; LRMS: *m*/*z* 211 $[M]^+$, 139, 72.

4.3.2. (S)-4-N,N-Diisopropyl-p-toluenesulfinamide ***10b***[26]. General procedure B was performed on a 2.82 mmol scale of sulfinate **8** using diisopropylamine to give (*S*)-4-*N*,*N*-diisopropyl-*p*-toluenesulfinamide (**10b**) as an oil (647 mg, 96%); $[\alpha]_D$ +77.6 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 2855, 1595, 1491, 1459, 1365, 1304, 1176, 1122, 1057, 1018, 949, 868, 817, 666; δ_H (300 MHz, $CDCl_3$) 7.44 (2H, d, *J*=8.1 Hz, H-2, H-6), 7.21 (2H, d, *J*=7.9 Hz, H-3, H-5), 3.48 (2H, septet, *J*=6.8 Hz, H-2′, H-5′), 2.33 (3H, s, CH_3-Tol), 1.34 (6H, d, *J*=6.8 Hz, 2×CH_3), 1.03 (6H, d, *J*=6.8 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 141.9 (C_{Ar}), 140.7 (C_{Ar}), 129.3 (CH_{Ar}), 126.9 (CH_{Ar}), 46.9 (CH), 24.3 (CH_3), 21.7 (CH_3); LRMS: *m*/*z* 239 $[M]^+$, 148, 91.

4.3.3. (S)-4-(p-Toluenesulfinyl)morpholine ***10c***[28]. General procedure B was performed on a 13.58 mmol scale of sulfinate **8** using morpholine to give (*S*)-4-(*p*-toluenesulfinyl)morpholine (**10c**) as an oil (730 mg, 24%); mp 108–110 °C; $[\alpha]_D$ −2.6 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 2955, 2853, 1592, 1451, 1377, 1285, 1259, 1110, 1088, 1068, 1019, 905, 819, 709, 695; δ_H (300 MHz, $CDCl_3$) 7.43 (2H, d, *J*=8.1 Hz, H-2, H-6), 7.23 (2H, d, *J*=8.1 Hz, H-3, H-5), 3.67–3.56 (4H, m, 2×H-2′, 2×H-6), 3.08–3.00 (2H, m, 2×H-5), 2.99–2.75 (2H, m, 2×H-3), 2.31 (3H, s, CH_3-Tol); δ_C ($CDCl_3$, 75 MHz) 141.9, 139.5, 130.0, 126.5, 67.3, 46.1, 21.8; LRMS: *m*/*z* 255 $[M]^+$, 139, 86.

4.4. General procedure C: synthesis of sulfinamides from sulfinamic acid derivatives

Grignard reagent (3.0 M in Et_2O; 2.1 equiv) was added dropwise to a solution of sulfinamic acid (**12**) (1.0 equiv) in Et_2O (0.1 M) at 0 °C. The mixture was stirred for 1 h and was warmed to rt overnight. The reaction was poured into saturated aqueous $NaHCO_3$ solution and extracted with EtOAc. The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated to afford the crude sulfinamide, which was purified by chromatography (eluent 1:1 EtOAc/hexane to 100% EtOAc gradient) to afford the product.

4.4.1. (R)-4-(Phenylsulfinyl)morpholine ***10d***[29,30]. General procedure C was performed on a 2.65 mmol scale of morpholinesulfinamic acid (**12d**) using phenylmagnesium bromide to give (*R*)-4-(phenylsulfinyl)morpholine (**10d**) as a crystalline solid (208 mg, 37%); mp=84–86 °C; $[\alpha]_D$ −75.8 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3055, 2859, 1445, 1266, 1113, 922, 738; δ_H (300 MHz, $CDCl_3$) 7.54–7.44 (2H, M, H-2, H-6), 7.32–7.21 (3H, m, H-3, H-4, H-5), 3.58–3.37 (4H, m, 2×H-2′, 2×H-3′), 3.01–2.84 (2H, m, 2×H-1′), 2.77–2.64 (2H, m, 2×H-4′); δ_C ($CDCl_3$, 75 MHz) 142.7, 131.7, 129.3, 67.3, 46.2; HRMS (EI) found: $[M+Na]^+$ 234.0559. $C_{10}H_{13}NO_2SNa$ requires $[M+Na]^+$ 234.0547.

4.4.2. (R)-4-(Ethylsulfinyl)morpholine ***10e***[31]. General procedure C was performed on a 3.79 mmol scale of sulfinamic acid derivative **12d** using ethylmagnesium chloride to give (*R*)-4-(ethylsulfinyl)morpholine (**10e**) as an oil (0.24 g, 38%); $[\alpha]_D$ −12.5 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 2923, 2856, 2762, 2498, 1955, 1721, 1646, 1455, 1379, 1290, 1259, 1156, 1025, 920, 846, 753, 697; δ_H (300 MHz, $CDCl_3$) 3.78–3.71 (4H, m, 2×H-2′, 2×H-3′), 3.19–3.01 (4H, m, 2×H-1′, 2×H-4′), 2.77 (2H, q, *J*=7.6 Hz, 2×H-1), 1.18 (3H, t, *J*=7.6 Hz, CH_3); δ_C ($CDCl_3$, 75 MHz) 67.2, 46.0, 45.1, 8.3; LRMS: *m*/*z* 163 $[M]^+$, 134, 86, 77.

4.4.3. (R)-4-(Isopropylsulfinyl)morpholine ***10f***[32]. General procedure C was performed on a 2.40 mmol scale of sulfinamic acid derivative **12d** using isopropylmagnesium chloride to give (*R*)-4-(isopropylsulfinyl)morpholine (**10f**) as an oil (0.34 g, 81%); $[\alpha]_D$ −80.1 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3053, 2971, 2504, 1645, 1368, 1266, 1162, 1113, 1045, 924, 738, 703; δ_H (300 MHz, $CDCl_3$) 3.71 (4H, t, *J*=4.3 Hz, 2×H-2′, 2×H-6′), 3.15–3.02 (4H, m, 2×H-3′, 2×H-5′), 2.88 (1H, septet, *J*=7.0 Hz, H-2), 1.25 (3H, d, *J*=7.0 Hz, CH_3), 1.09 (3H, d, *J*=7.0 Hz, CH_3); δ_C ($CDCl_3$, 75 MHz) 67.3, 51.2, 46.5, 17.3; LRMS: *m*/*z* 177 $[M]^+$, 134, 43.

4.4.4. (R)-4-(tert-Butylsulfinyl)morpholine ***10g***[29]. General procedure C was performed on a 3.15 mmol scale of sulfinamic acid derivative **12d** using *tert*-butylmagnesium chloride to give (*R*)-4-(*tert*-butylsulfinyl)morpholine (**10g**) as a white crystalline solid (0.43 g, 72%); mp=78–80 °C; $[\alpha]_D$ −14.5 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3055, 2986, 2306, 1422, 1267, 1112, 1071, 913, 896, 739; δ_H (300 MHz, $CDCl_3$) 3.68–3.56 (4H, m, 2×H-2′, 2×H-3′), 3.15–3.00 (4H, m, 2×H-1′, 2×H-4′), 1.13 (9H, s, *t*-Bu); δ_C ($CDCl_3$, 75 MHz) 67.1, 58.6, 47.3, 23.0; HRMS (EI) found: $[M+Na]^+$ 214.0872. $C_8H_{17}NO_2SNa$ requires $[M+Na]^+$ 214.0864.

4.4.5. (R)-N,N-Diethylbenzenesulfinamide ***10h***[29,33]. General procedure C was performed on a 1.75 mmol scale of sulfinamic acid derivative **12h** using phenylmagnesium chloride to give (*R*)-*N*,*N*-diethylbenzenesulfinamide (**10h**) as an oil (0.32 g, 94%); $[\alpha]_D$ −88.1 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3163, 3061, 2931, 2872, 1599, 1445, 1380, 1289, 1167, 1060, 1009, 900, 690, 665; δ_H (300 MHz, $CDCl_3$) 7.58 (2H, d, *J*=6.2 Hz, CH_{Ar}), 7.41 (3H, d, *J*=7.2 Hz, CH_{Ar}), 3.16 (4H, q, *J*=7.2 Hz, 2×CH_2), 1.05 (6H, t, *J*=7.2 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 130.9, 128.8, 126.7, 42.4, 14.8; LRMS: *m*/*z* 197 $[M]^+$, 72, 125.

4.4.6. (R)-N,N-Diethylisopropylsulfinamide ***10i***[32]. General procedure C was performed on a 3.89 mmol scale of sulfinamic acid derivative **12h** using isopropylmagnesium chloride to give (*R*)-*N*,*N*-diethylisopropylsulfinamide (**10i**) as an oil (0.59 g, 93%); $[\alpha]_D$ −29.6 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 2967, 2870, 1605, 1464, 1381, 1289, 1241, 1175, 1072, 1010, 895, 782, 665; δ_H (300 MHz, $CDCl_3$) 3.23 (2H, dq, *J*=14.5, 7.3 Hz, 2×H-1′), 3.03 (2H, dq, *J*=14.2, 7.1 Hz, 2×H-3′), 2.80

(1H, septet, J=6.9 Hz, H-2), 1.27 (3H, d, J=7.0 Hz, CH_3), 1.16 (3H, t, J=7.2 Hz, CH_3), 1.11 (6H, d, J=6.9 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 52.3, 42.3, 30.1, 17.2, 15.1; HRMS (EI) found: $[M+Na]^+$ 186.0923. $C_7H_{17}NOSNa$ requires $[M+Na]^+$ 186.0924.

4.4.7. (R)-N,N-Diethylisobutylsulfinamide ***10k***. General procedure C was performed on a 10.6 mmol scale of sulfinamic acid derivative **12h** using isobutylmagnesium chloride to give (*R*)-*N*,*N*-diethylisobutylsulfinamide (**10k**) as an oil (1.70 g, 90%); $[\alpha]_D$ −10.9 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3019, 2966, 2400, 1521, 1216, 1038, 929, 755; δ_H (300 MHz, $CDCl_3$) 3.28–3.18 (2H, m, H-1′), 3.05–2.96 (2H, m, H-3′), 2.62–2.52 (2H, m, H-1), 1.96 (1H, septet, J=6.3 Hz, H-2), 1.12 (6H, t, J=6.5 Hz, 2×CH_3), 0.96 (6H, d, J=6.0 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 62.9, 42.2, 25.1, 22.8, 5.1; HRMS (EI) found: $[M+Na]^+$ 200.1080. $C_8H_{19}NOSNa$ requires $[M+Na]^+$ 200.1076.

4.4.8. (R)-N,N-Dipropylisobutylsulfinamide ***10l***. General procedure C was performed on a 9.10 mmol scale of sulfinamic acid derivative **12l** using isobutylmagnesium chloride to give (*R*)-*N*,*N*-dipropylisobutylsulfinamide (**10l**) as brown oil (1.50 g, 87%); $[\alpha]_D$ −6.5 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 3019, 2966, 2876, 2400, 1522, 1466, 1216, 1039, 929, 763; δ_H (300 MHz, $CDCl_3$) 2.92–2.84 (2H, m, CH_2N), 2.75–2.58 (2H, m, CH_2N), 2.39–2.25 (2H, m, CH_2S), 1.84–1.58 (1H, m, CH), 1.40–1.17 (4H, m, 4×CH_2), 0.77 (6H, d, J=6.6 Hz, 2×CH_3), 0.65 (6H, t, J=7.3 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 63.1, 50.3, 25.0, 22.8, 21.4, 11.8; HRMS (EI) found: $[M+Na]^+$ 228.1393. $C_{10}H_{23}NOSNa$ requires $[M+Na]^+$ 228.1386.

4.4.9. (R)-N,N-Diisopropylbenzenesulfinamide ***10m***[33,35]. General procedure C was performed on a 3.32 mmol scale of sulfinamic acid derivative **12m** using phenylmagnesium chloride to give (*R*)-*N*,*N*-diisopropylbenzenesulfinamide (**10m**) as a white solid (0.71 g, 95%); mp=58–60 °C; $[\alpha]_D$ −86.9 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 2966, 1596, 1459, 1388, 1365, 1304, 1176, 1122, 1055, 1018, 949, 868, 817, 708, 640, 620, 557; δ_H (300 MHz, $CDCl_3$) 7.67–7.57 (2H, m, CH_{Ar}), 7.43–7.34 (3H, m, CH_{Ar}), 3.48 (2H, septet, J=6.8 Hz, 2×CH), 1.35 (6H, d, J=6.8 Hz, 2×CH_3), 1.03 (6H, d, J=6.8 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 130.5, 128.5, 127.3, 47.0, 24.1; HRMS (EI) found: $[M+Na]^+$ 248.1080. $C_{12}H_{19}NOSNa$ requires $[M+Na]^+$ 248.1077.

4.5. (*R*)-*N*,*N*-Diethyl-*tert*-butylsulfinamide 10j:[34] one-pot procedure

n-BuLi (1.5 M in hexane; 5.10 mL, 7.65 mmol, 1.05 equiv) was added dropwise to a solution of diethylamine (0.79 mL, 7.65 mmol, 1.05 equiv) in THF (25.5 mL) at 0 °C. The mixture was stirred for 1 h and was added slowly to a solution of (2*R*,4*S*,5*R*)-4-methyl-5-phenyl-*N*-tosyl-1,2,3-oxathiazolidine-2-oxide **11** (2.44 g, 6.95 mmol, 1.0 equiv) in THF (23.2 mL) at −78 °C. The mixture was stirred for 3 h and was warmed to rt overnight. When all starting material had been consumed, *tert*-butylmagnesium chloride (2.0 M in Et_2O; 7.30 mL, 14.60 mmol, 2.1 equiv) was added dropwise to the reaction and stirred at rt overnight. The reaction was poured into saturated aqueous $NaHCO_3$ solution (10 mL) and extracted with EtOAc (3×30 mL). The combined organic phases were washed with brine (40 mL), dried (Na_2SO_4) and concentrated to afford the crude sulfinamide, which was purified by chromatography (1:1 EtOAc/hexane to 1:0 EtOAc/hexane gradient) to afford the desired compound **10j** (0.68 mg, 55%); $[\alpha]_D$ +25.0 (*c* 1, $CHCl_3$); υ_{max} (thin film/cm^{-1}) 2972, 1635, 1455, 1380, 1289, 1166, 1062, 1003, 922, 889, 785, 646, 592, 526; δ_H (300 MHz, $CDCl_3$) 3.12 (2H, dq, J=14.5, 7.3 Hz, 2×H-1′), 2.91 (2H, dq, J=14.2, 7.1 Hz, 2×H-3′), 1.10 (9H, s, *t*-Bu), 1.07 (6H, t, J=7.2 Hz, 2×CH_3); δ_C ($CDCl_3$, 75 MHz) 57.7, 42.1, 23.6, 14.4; HRMS (EI) found: $[M+Na]^+$ 200.1080. $C_8H_{19}NOSNa$ requires $[M+Na]^+$ 200.1069.

4.6. Sulfinamide-mediated allylation of benzaldehyde: (1*S*)-1-Phenyl-3-buten-1-ol 7

To a solution of (*R*)-*N*,*N*-diethyl-2-propanesulfinamide **10i** (0.12 g, 0.74 mmol, 3.0 equiv) and diisopropylethylamine (0.21 mL, 1.25 mmol, 5.0 equiv) in CH_2Cl_2 (0.83 mL) was added allyltrichlorosilane (0.074 mL, 0.52 mmol, 2.1 equiv) dropwise at −78 °C. The mixture was stirred for 15 min, benzaldehyde (0.03 mL, 0.25 mmol, 1.0 equiv) was added to the reaction and stirred for 18 h at −78 °C. Saturated aqueous $NaHCO_3$ solution (20 mL) and CH_2Cl_2 (40) were added to the reaction and warmed to rt for 15 min. The two layers separated and the organic phase washed with brine (25 mL), dried ($MgSO_4$) and concentrated to afford the crude, which was purified by chromatography (1:4 EtOAc/hexane) to afford the desired product **7** (0.41 g, 98%). (*S*)-*N*,*N*-diethyl-2-propanesulfinamide **10i** was recovered in 90% yield. (1*S*)-1-Phenyl-3-buten-1-ol **11** was isolated as a clear oil; δ_H (300 MHz, $CDCl_3$) 7.34 (2H, d, J=4.2 Hz, ArH), 7.28 (3H, m, ArH), 5.80 (1H, m, CH alkene), 5.15 (2H, m, CH_2 alkene), 4.72 (1H, dd, J=7.2, 5.7 Hz, ArCH), 2.50 (2H, m, CH_2), 2.15 (1H, bs, OH). Data in agreement with literature.[13]

4.7. General procedure D: allylation of *N*-benzoylhydrazones

To a solution of sulfinamide (3.0 equiv) and diisopropylethylamine (5.0 equiv) in CH_2Cl_2 (0.3 M) was added allyltrichlorosilane (2.1 equiv) dropwise at −78 °C. The mixture was stirred for 15 min prior to the addition of *N*-benzoylhydrazone (1.0 equiv) (all *N*-benzoylhydrazones were prepared according to the procedure of Kobayashi[36]). The reaction was stirred at −78 °C until completion. Saturated aqueous $NaHCO_3$ solution and CH_2Cl_2 were added to the reaction and it was warmed to rt for 15 min. The layers were separated and the organic phase washed with brine, dried ($MgSO_4$) and concentrated. The residue was purified by chromatography (1:4 EtOAc/hexane) to afford the desired product. The sulfinamide could be recovered in approximately 90% yield. All data in agreement with the literature.[36]

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