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High Kinetic Resolution in the Addition of a Racemic Allenylzinc onto Enantiopure *N-tert*-Butanesulfinimines: Concise Synthesis of Enantiopure *trans*-2-Ethynylaziridines[1]

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Enantiopure *trans*-ethynyl *N-tert*-butanesulfinylaziridines (R_S)-**6** were prepared in good to excellent yields by the condensation of the racemic allenylzinc species **1** derived from 3-chloro-1-trimethylsilylpropyne onto the corresponding enantiopure *N-tert*-butanesulfinimines (R_S)-**5**. The absolute stereochemistry of enantiopure *N-tert*-butanesulfinylaziridines (R_S)-**6** was shown to be (R_S,2*R*,3*R*) and results from a chelate-type transition state in which the zinc atom of allenylzinc **1** is coordinated by both the nitogen and the oxygen atoms of the imine. Further removal of the *N-tert*-butanesulfinyl auxiliary of alkyl 3-substituted and 3,3-disubstituted ethynyl *N-tert*-butanesulfinylaziridines (R_S)-**6** could be achieved by treatment with HCl in MeOH affording the corresponding deprotected aziridines (2*R*,3*R*)-**9** and (2*R*)-**9** respectively as enantiomerically pure compounds.

Introduction

Aziridines and more particularly alkenyl- and alkynylaziridines constitute an interesting class of compounds as their high electrophilicity enables them to undergo stereoselective ring-opening reactions with a wide variety of nucleophiles. For instance, alkenylaziridines have proven to be valuable intermediates in carbon−carbon forming reactions such as metal-mediated S_N2' reactions[2] and opening aziridine ring rearrangements.[3] The cis−trans transition metal-mediated equilibration of alkenylaziridines has also been well-studied.[4] Recently, ethenylaziridines have been involved in the synthesis of chiral amino allenes (valuable intermediates in the synthesis of six- or five-membered azacyles[5]) with high optical purities by the organocopper-mediated *anti*-S_N2' substitution reaction.[6] More recently, those compounds have been used as chiral carbon nucleophiles in a stereoselective indium(I)-mediated reductive coupling reaction catalyzed by palladium(0) with aldehydes giving 1,3-amino alcohols with three stereocenters.[7] In contrast, despite their great synthetic potential, relatively little investigation has been undertaken so far on both the synthesis and the reactivity of alkynylaziridines in the literature.[8] Racemic alkynylaziridines have been previously prepared by the reaction of nitrenes or nitrene equivalents with enynes,[9] by the condensation of lithiated cinnamyl chloride onto imines[10] or from the corresponding alkynyloxiranes in a two-step procedure.[11] As regards the synthesis of enantiopure alkynylaziridines, only two methods have been described. Recently, Dai and co-workers have reported the synthesis of enantiopure *cis*-alkynylaziridines by the asymmetric aziridination of *N*-tosylimines with D-(+)-camphor derived sulfonium ylides in moderate to good enantioselectivities (14−85% ee).[12] Shortly afterward, Ibuka and co-workers disclosed two multistep syntheses from (*S*)-α-amino acids. The key steps of these syntheses were a dehydrobromination reaction of 2-(1-

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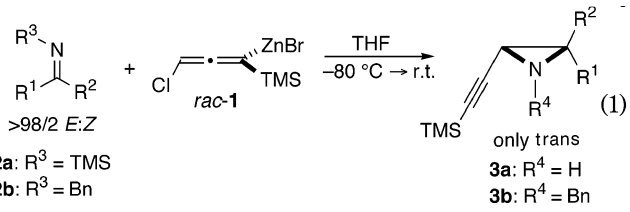
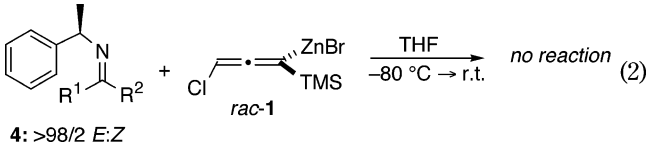
bromovinyl)aziridine intermediates and an aziridine ring closure of amino alcohols bearing an ethynyl group under Mitsunobu conditions, respectively.[13] More recently, Tanaka's group has developed a highly stereoselective synthesis of *cis*-ethynylaziridines from (*S*)-α-amino acids via the intramolecular amination of chiral bromoallene intermediates.[14] In both Ibuka's and Tanaka's works, *trans*- and *cis*-ethynylaziridines were obtained in enantiomerically pure forms (>98% ee). However, they could not be prepared selectively since they were isolated from stereoisomeric mixtures (at different steps of the syntheses) by chomatographic separations. Moreover, a limited number of aziridines could be obtained due to the limitation of the starting materials available.

Thus, when starting our study and to the best of our knowledge, no univocal and general synthesis of enantiopure *trans*-alkynylaziridines was reported in the literature so that an efficient and concise diastereo- and enantioselective access to such compounds still remained a challenge. With this aim in mind, we have recently described a stereoselective access to racemic 3-substituted *trans*-*N*-H and -*N*-benzyl 2-trimethylsilylethynylaziridines **3a** and **3b** by the reaction of racemic allenylzinc reagent **1** derived from 3-chloro-1-trimethylsilylpropyne with achiral *N*-trimethylsilyl- and *N*-benzylimines **2a** and **2b**, respectively (eq 1).[15]



In a continuation of this work, we have undertaken to develop a new synthesis of ethynylaziridines in a diastereo- and enantioselective manner. However, since allenylzinc **1** could not been prepared yet in an enantioenriched form, we have envisoned to use imines bearing a chiral auxiliary on the nitrogen atom. At first, we thought that the *N*-α-methylbenzyl substituent would play the role of a good chiral directing group since it has proved to induce high levels of stereoselectivity in some reactions such as the addition of organometallic reagents onto *N*-α-methylbenzylimines[16,17] and the carbocylization reaction of α-amino ester zinc enolates.[18] Unfortunately, in preliminary works we have found that *N*-α-methylbenzylimines **4**, easily prepared in the two enantiomeric forms from the cheap and commercially available (*R*)- and (*S*)-α-methylbenzylamines, do not react at all with allenylzinc **1** even overnight at room temperature, only products from the carbenoidic decomposition of **1** being observed (eq 2).



Facing the lack of reactivity of *N*-α-methylbenzylimines, we reasoned that the use of the presumed more reactive *N*-sulfinimines would allow us to reach our goal since both Davis'[19] and Ellman's[20] groups have carried out extensive studies on the stereoselective addition of organometallic reagents (including Grignard reagents, organolithiums, and enolates) to enantiomerically pure *N*-*p*-toluene- and *N*-*tert*-butanesulfinimines, respectively. We were particularly interested in Ellman's *N*-*tert*-butanesulfinimines since the *N*-*tert*-butanesulfinyl group has often provided enhanced diastereofacial selectivity compared to other *N*-sulfinyl auxiliaries such as the *N*-*p*-toluenesulfinyl group.[21] Furthermore, the *N*-*tert*-butanesulfinyl group has proven to be comparable in reactivity to a Boc group and in this context would play the dual role of a chiral directing and protecting group (it is easily removed under acidic conditions) for further transformations. Moreover, Ellman and others have shown that the *N*-*tert*-butanesulfinyl group induces high stereoselectivities in numerous nucleophile additions onto imines. For instance, the asymmetric syntheses of trifluoromethylated vicinal ethylenediamines,[22] 1,2- and 1,3-amino

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SCHEME 1

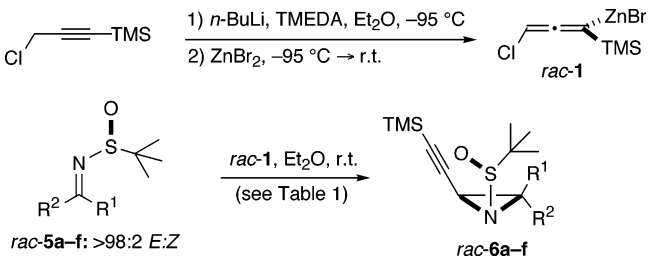


TABLE 1. Reaction of Racemic Allenylzinc 1 with Racemic *N-tert*-Butanesulfinimines 5a−f (Scheme 1)

entry	imine	R^1	R^2	equiv of **1**	aziridine	trans: cis[a]	dr[a,b]	yield[c] (%)
1	*rac*-**5a**	H	*n*-Pr	1.5	*rac*-**6a**	90:10	>98:2	70
2	*rac*-**5b**	H	crotyl[d]	3.0	*rac*-**6b**	94:6	>98:2	67
3	*rac*-**5c**	H	*i*-Pr	6.0	*rac*-**6c**	96:4	>98:2	64
4	*rac*-**5d**	H	*c*-hexyl	6.0	*rac*-**6d**	90:10	>98:2	56
5	*rac*-**5e**	H	Ph	6.0	*rac*-**6e**	91:9	>98:2	58
6	*rac*-**5f**	Me	Ph	6.0	*rac*-**6f**	91:9	>98:2	54

[a] Selectivities measured by ^{1}H NMR on the crude reaction mixtures. [b] dr values of the major isomers. [c] Isolated yields in purified major isomers. [d] The *E*:*Z* ratio of the C−C double bond of the starting imine was 95:5.

alcohols,[20c,23] α- and β-amino acid derivatives,[20d,f] nonracemic amines,[20e,24] α-aminoorganostannanes,[25] and *P*,*N*-sulfinyl iridium catalysts[26] have been recently reported in the literature. Thus, we reasoned that enantiopure *N-tert*-butanesulfinimines could give a straightforward access to the corresponding ethynylaziridines in diastereo- and enantiomerically pure forms through the reaction with allenylzinc **1**. We report herein our recent results about this topic.

Results and Discussion

Pure *E* racemic *N-tert*-butanesulfinimines **5a**−**f** were easily accessible in high yields (64−82%) from racemic *N-tert*-butanesulfinamide[27] according to Ellman's procedure.[20h,28] Their reaction with racemic allenylzinc **1**, generated by dropwise addition of *n*-BuLi to an equimolar mixture of 3-chloro-1-trimethylsilypropyne and TMEDA at −95 °C in Et_2O,[29,30] was examined (Scheme 1).

In all cases, racemic imines **5a**−**f** exhibited little reactivity with racemic **1** (much less reactivity than the corresponding *N*-trimethylsilyl- and *N*-benzyl ones) giving low conversions below 0 °C. Excesses of allenylzinc **1** needed to be used for a complete reaction at room temperature because of the competitive carbenoidic decomposition of this organometallic species. However, when performing the reaction in Et_2O at room temperature, racemic *trans*-ethynyl aziridines **6a**−**e** were obtained with excellent diastereoselectivities as determined by ^{1}H NMR (the cis isomers being characterized by greater coupling constants between the two aziridinyl protons than the trans isomers). Moreover, only single trans stereoisomers were detected by ^{1}H NMR (>98:2 dr).

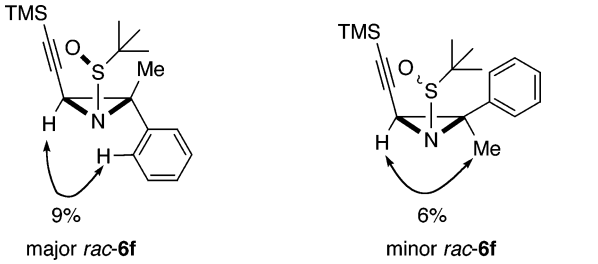


FIGURE 1. NOE experiments on racemic major and minor aziridines **6f**.

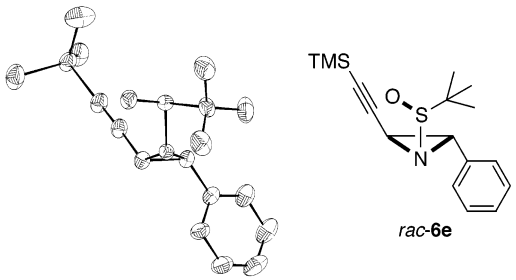
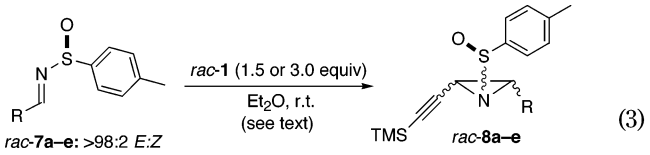


FIGURE 2. ORTEP drawing of racemic trans aziridine **6e**.

With aziridine **6f** containing a quaternary stereogenic carbon, the same trans stereochemistry for the major isomer was deduced from NOE experiments, while the minor isomer was shown to be cis (Figure 1).

The excellent trans diastereoselectivity observed in these reactions clearly indicated a high induction of the chiral *N-tert*-butanesulfinyl group of the imine on the stereochemical outcome of the reaction. After chromatography over silica gel, all racemic trans aziridines **6a**−**f** were isolated as diastereomerically pure compounds. Their stereochemistry was deduced from the single-crystal X-ray analysis[30] of racemic aziridine **6e** (Figure 2). On the other hand, the stereochemistry of the cis isomers could not be assigned.

The reaction was also examined with pure *E* racemic *N*-*p*-toluenesulfinimines **7a**−**e** readily available in high yields (85−94%) from racemic *N*-*p*-toluenesulfinamide according to Davis' procedure[32] (eq 3).



(3)

R = *n*-Pr (**7a**), crotyl (**7b**), *i*-Pr (**7c**), *c*-hexyl (**7d**), Ph (**7e**)

rac-**8a,b,e:** stereoisomeric mixtures
rac-**8c:** 56%, single isomer
rac-**8d:** 50%, single isomer

All these imines exhibited a much higher reactivity than racemic *N-tert*-butanesulfinimines **5a**−**f**. In most

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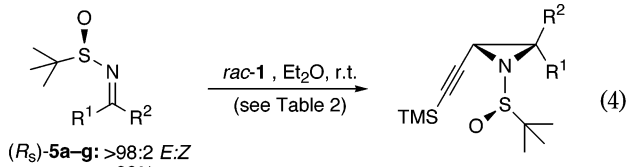
cases, smaller amounts of racemic allenylzinc reagent **1** were needed to achieve the completion of the reaction at room temperature, i.e., 1.5 and 3.0 equiv for imines **7a**,**b**,**e** and **7c**,**d**, respectively. Nevertheless, except with imines **7c** and **7d**, poor levels of diastereoselection were observed since complex stereoisomeric mixtures of trans and cis aziridines were obtained. The drop in selectivity with some sulfinimines **7** could presumably be attributed to an enhancement of their reactivity toward allenylzinc **1** so that no facial stereodifferentiation could take place. Unfortunately, lowering the temperature did not permit the stereoselectivity of the reaction to be improved. As mentioned above, sulfinimines **7c** and **7d** led to the corresponding *trans*-ethynyl *N*-*p*-toluenesulfinylaziridines **8c** and **8d** in 56% and 50% yield, respectively, as single stereoisomers (>98:2 trans:cis and >98:2 dr). The relative stereochemistry of the latter was reasonably postulated to be the same as that of *N*-*tert*-butanesulfinylaziridines **6a**−**f** [i.e. (*S**$_S$,2*S**,3*S**)].

Thus, our method proved to be valuable only for preparing a series of diastereomerically pure racemic *trans*-ethynyl *N*-*tert*-butanesulfinylaziridines. We have then undertaken its extension to the synthesis of enantioenriched *trans*-*N*-*tert*-butanesulfinylaziridines (R_S)-**6a**−**g**. Pure *E* enantiopure *N*-*tert*-butanesulfinimines (R_S)-**5a**−**g** were easily prepared in excellent yields (76−90%) from enantiopure *N*-*tert*-butanesulfinamide (>99% ee as determibed by chiral GC analysis on a Lipodex E capillary column) following the procedure reported by Ellman.[20h,28] Imines (R_S)-**5c**,**e**,**f** exhibited the same specific optical rotations as those reported in the literature [20h,28] so that they were considered to be enantiopure (>99% ee). By analogy, unknown imines (R_S)-**5a**,**b**,**d**,**g** were reasonably presumed to have the same optical purity. Since the procedure for the preparation of allenylzinc **1** allows only the formation of a racemic mixture we were confronted by the reaction between this racemic nucleophile **1** and enantiopure sulfinimines (R_S)-**5** (eq 4).



(R_S)-**5a–g:** >98:2 *E*:*Z* >99% ee

(R_S)-**6a–g:** >99% ee (4)

When carried out in Et_2O at room temperature with 1.5 equiv of racemic allenylzinc **1**, enantiopure imine (R_S)-**5a** gave a mixture of trans and cis aziridines (R_S)-**6a** with a selectivity of 79:21 in favor of the trans isomer (Table 2, entry 1). The trans:cis selectivity significantly deviated from that obtained when racemic imine **5a** was reacted with 1.5 equiv of racemic **1** (Table 2, entries 1 vs 2). In this context, according to Hoffmann's works on the configurational stability of organometallic reagents,[33,34]

TABLE 2. Reaction of Racemic 1 with *N*-*tert*-Butanesulfinimines (R_S)-5a−g (eq 4)

entry	imine	R^1	R^2	equiv of *rac*-**1**	aziridine	trans:cis[a]	dr[a,b]	yield[c] (%)
1	(R_S)-**5a**	H	*n*-Pr	1.5	(R_S)-**6a**	79:21	>98:2	*d*
2	*rac*-**5a**	H	*n*-Pr	1.5	*rac*-**6a**	90:10	>98:2	70
3	(R_S)-**5a**	H	*n*-Pr	6.0	(R_S)-**6a**	89:11	>98:2	61
4	(R_S)-**5b**[e]	H	crotyl	6.0	(R_S)-**6b**	90:10	>98:2	64
5	(R_S)-**5c**	H	*i*-Pr	6.0	(R_S)-**6c**	94:6	>98:2	69
6	(R_S)-**5d**	H	*c*-hexyl	6.0	(R_S)-**6d**	90:10	>98:2	58
7	(R_S)-**5e**	H	Ph	6.0	(R_S)-**6e**	86:14	>98:2	50
8	(R_S)-**5f**	Me	Ph	6.0	(R_S)-**6f**	90:10	>98:2	69
9	(R_S)-**5g**	*n*-pent	*n*-pent	6.0	(R_S)-**6g**		>98:2	87

[a] Selectivities measured by ^{1}H NMR on the crude reaction mixtures. [b] dr values of the major isomers. [c] Isolated yields in purified major isomers. [d] Not determined. [e] The *E*:*Z* ratio of the C−C double bond of the starting imine was 95:5.

allenylzinc **1** could be regarded as *at least partially configurationally stable with respect to the time scale defined by the reaction rate*. Under these conditions, as predicted by Hoffmann, using a large excess of racemic allenylzinc **1** (6 equiv) allowed the stereoselectivity to be improved up to a trans:cis ratio of 89:11, very close to the theorical upper 90:10 ratio obtained with the racemic imine **5a** (Table 2, entry 3).

The same condition reactions were applied to the other enantiopure *N*-*tert*-butanesulfinylaldimines and ketimines (R_S)-**5b**−**f**. After chromatography over silica gel, *trans*-ethynylaziridines (R_S)-**6a**−**f** were then isolated as diastereomerically (>98:2 dr) and enantiomerically (>99% ee) pure compounds in good isolated yields ranging from 50% to 69%. In all cases, enantiopure imines (R_S)-**5a**−**f** afforded the corresponding aziridines (R_S)-**6a**−**f** with trans:cis stereoselectivities close to those observed with the series of racemic aziridines **6a**−**f** (Table 2, entries 3−8).

The high trans selectivity could not reasonably be explained through a thermodynamical process since *cis*-sulfonylaziridines have been described to be thermodynamically favored.[4] In fact, overall these results strongly suggested that the *trans isomers* (R_S)-***6*** *could result from the matched* (R_S)-***5***/(*aS*)-***1*** *pairs* via the chelate type transition state **TS-1** analogous to those evoked by others in the addition of lithium or titanium enolates and of potassium dialkyl phosphites onto sulfinimines.[20c,f,31] Similarly, the *cis isomers* (R_S)-***6*** *could result from the mismatched* (R_S)-***5***/(*aR*)-***1*** *pairs* via the open transition state **TS-2** with reference to *N*-sulfonylimines[15b] and aromatic aldehydes[29] (Scheme 2). Under the same conditions, the symmetrical ketimine (R_S)-**5g** gave aziridine (R_S)-**6g** in excellent yield (87%) and as a single isomer (Table 2, entry 9). The stereochemical outcome of this reaction simply reflects a high facial selectivity since, in this particular case ($R^1 = R^2$ in Scheme 2), the notion of matched and mismatched pairs does not make any sense.

Having in hand an efficient method for preparing *trans*-ethynyl *N*-*tert*-butanesulfinylaziridines in highly diastereo- and enantioselective fashion, we have then undertaken their conversion into the corresponding *N*-H aziridines. The *N*-*tert*-butanesulfinyl auxiliary is described to be comparable in reactivity to the Boc group and to be easily removed under acidic conditions. However, in the case of 2-phosphonate *N*-*tert*-butanesulfinylaziridines it has been recently reported by Davis that no deprotection could occur without aziridine ring opening.[31a]

(32) Davis, F. A.; Zhang, Y.; Andemichael, Y.; Fang, T.; Fanelli, D. L.; Zhang, H. *J. Org. Chem*. **1999**, *64*, 1403−1406.

(33) (a) Hoffmann, R. W.; Julius, M.; Chemla, F.; Ruhland, T.; Frenzen, D. *Tetrahedron* **1994**, *50*, 6049−6060. (b) Hirsch, R.; Hoffmann, R. W. *Chem. Ber*. **1992**, *125*, 975−982.

(34) For a recent review on the configurational stability of enantioenriched organolithium reagents see: Basu, A.; Thayumanavan, S. *Angew. Chem.*, *Int. Ed.* **2002**, *41*, 716−738.

SCHEME 2. Origin of *trans*- and *cis*-*N*-*tert*-Butanesulfinylaziridines (R_S)-6

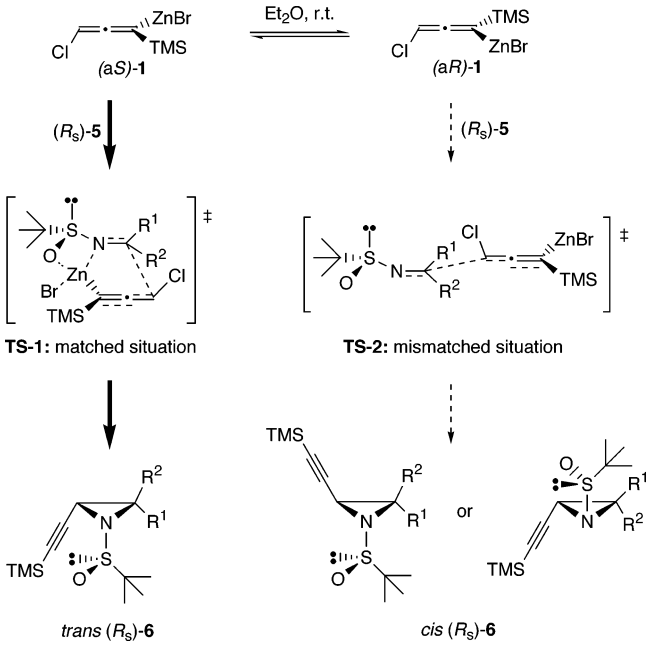
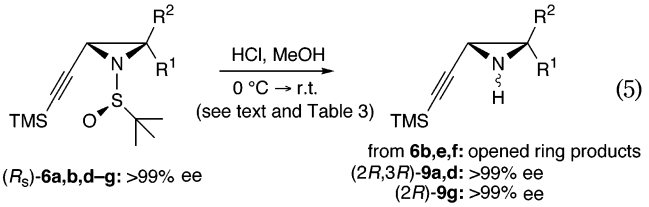


TABLE 3. Removal of the *N*-*tert*-Butanesulfinyl Auxiliary from (R_S)-6a,d,g (eq 5)

entry	sulfinyl-aziridine	R^1	R^2	product	invertomer - ratio[a]	yield - (%)
1	(R_S)-**6a**	H	*n*-Pr	(2*R*,3*R*)-**9a**	80:20	66[b]
2	(R_S)-**6d**	H	*c*-hexyl	(2*R*,3*R*)-**9d**	96:4	82[b]
3	(R_S)-**6g**	*n*-pent	*n*-pent	(2*R*)-**9g**	97:3	100[c]

[a] Invertomer ratios measured by ^{1}H NMR on the purified products. [b] Isolated yields in purified products. [c] No purification was necessary.

However, we have tried to deprotect trans aziridines (R_S)-**6a**,**b**,**d**−**g** by treatment with HCl (eq 5).



To our great delight and in contrast to the results previously reported by Davis, when performing the reaction with 5 equiv of HCl in MeOH, the deprotection could be achieved within 30 min at room temperature but only from alkyl 3-substituted and 3,3-disubstituted aziridines (R_S)-**6a**,**d** and (R_S)-**6g**, respectively (Table 3).

The corresponding *N*-H aziridine was accompanied by a small amount of opened aziridine ring products (about 15%) in the case of the little hindered trans aziridine (R_S)-**6a**. Deprotected aziridines were formed as single products from the more hindered trans aziridine (R_S)-**6d** and the alkyl 3,3-disubstituted (R_S)-**6g** one. Thus aziridines (2*R*,3*R*)-**9a**,**d** and (2*R*)-**9g** were isolated in good to excellent yields (ranging from 66% to 100%) as mixtures of the two possible invertomers in ratios depending upon the difference of steric hindrance between the two sides of the aziridine ring (Table 3, entry 1 vs entries 2 and 3). In the other cases, i.e., with *trans*-ethenyl and aromatic aziridines, (R_S)-**6b**,**e**,**f**, only products resulting from the aziridine ring opening reaction with MeOH were observed. With such substrates the formation of a stabilized allylic or benzylic carbocation, which underwent subsequent reaction with MeOH, would certainly be evoked to explain the aziridine ring opening reaction.

Conclusion

In summary, we have developed a concise and efficient synthesis of enantiopure *trans*-ethynyl *N*-*tert*-butanesulfinylaziridines by the condensation of the allenylzinc species derived from 3-chloro-1-trimethylsilylpropyne onto *N*-*tert*-butanesulfinylaldimines and ketimines at room temperature in Et_2O. The excellent stereoselectivity was shown to result from a high kinetic resolution in the reaction of the racemic allenylzinc with enantiopure *N*-*tert*-butanesulfinimines. This kinetic resolution was proven to be the consequence of the zinc being coordinated by both the oxygen and the nitrogen atoms of the sulfinimine in a chelate-type transititon state. The formation of certain enantiopure acetylenic *N*-H aziridines could also be achieved through deprotection under acidic conditions. The extension of this method to other γ-functionalized allenylzincs, in the aim of preparing nonracemic 1,2-amino alcohols or diamines for instance, and the synthetic use of 2-ethynylsulfinylaziridines are currently under investigation in our group and will be reported in due course.

Experimental Section

General. See the Supporting Information.

Preparation of Enantiopure *N*-*tert*-Butanesulfinimines (R_S)-5a−g. The literature procedure[20h,28] was followed. The ^{1}H and ^{13}C values and the specific optical rotations obtained for *N*-*tert*-butanesulfinimines (R_S)-**5c**,**e**,**f** correspond to those reported.

(R_S,*E*)-(−)-*N*-Butylidene-*tert*-butanesulfinamide, (R_S)-5a. The literature procedure[20h,28] was followed. Under a nitrogen atmosphere, a suspension of butyraldehyde (0.68 mL, 7.50 mmol), (R_S)-(+)-*tert*-butanesulfinamide (>99% ee by chiral GC analysis on a Lipodex E capillary column, 605 mg, 5.00 mmol), PPTS (65 mg, 0.25 mmol), and anhydrous $MgSO_4$ (3.00 g, 25.00 mmol) in CH_2Cl_2 (8 mL) was stirred for 24 h at room temperature. The mixture was filtered over a pad of Celite and concentrated in vacuo. The residual oil was purified by filtration over a pad of silica gel (eluant: CH_2Cl_2) yielding enantiopure *E* sulfinimine (R_S)-**5a** as a colorless oil (705 mg, 4.32 mmol, 87%). $[\alpha]_D$ −305.0 (*c* 0.94, $CHCl_3$, 20 °C); IR (ATR Diamand) 2873 (m), 1621 (w), 1082 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (1H, t, J = 4.8 Hz), 2.50 (2H, m), 1.67 (2H, m), 1.20 (9H, s), 0.99 (3H, t, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 56.8, 38.4, 22.7, 19.3, 14.2. Anal. Calcd for $C_8H_{17}NOS$: C, 54.81; H, 9.78; N, 7.99. Found: C, 54.75; H, 9.85; N, 7.89.

(R_S,*E*,*E*)-(−)-*N*-(But-2-enylidene)-*tert*-butanesulfinamide, (R_S)-5b. The literature procedure[20h,28] was followed as above from crotonaldehyde (95:5 *E*:*Z*, 0.62 mL, 7.50 mmol) yielding enantiopure *E* sulfinimine (R_S)-**5b** as a yellow oil (705 mg, 4.08 mmol, 82%). $[\alpha]_D$ −589.0 (*c* 0.94, $CHCl_3$, 20 °C); IR (ATR Diamand) 3034 (w), 1645 (s), 1580 (s), 1078 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (1H, d, J = 9.2 Hz), 6.58 (1H, qd, J = 15.4, 6.5 Hz), 6.46 (1H, qdd, J = 15.4, 9.2, 1.5 Hz), 1.99 (3H, dd, J = 6.5, 1.5 Hz), 1.22 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163, 146.5, 130.2, 57.0, 22.3, 18.8. Anal. Calcd for $C_8H_{15}NOS$: C, 55.45; H, 8.73; N, 8.08. Found: C, 55.22; H, 8.78; N, 8.01.

(R_S,*E*)-(−)-*N*-Cyclohexylmethylidene-*tert*-butanesulfinamide, (R_S)-5d. The literature procedure[20h,28] was followed as above from cyclohexanecarboxaldehyde (0.91 mL, 7.50 mmol) yielding enantiopure *E* sulfinimine (R_S)-**5d** as a colorless oil (946 mg, 4.40 mmol, 88%). $[\alpha]_D$ −232.5 (*c* 0.98, $CHCl_3$, 20 °C); IR (ATR Diamand) 1618 (s), 1083 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (1H, d, J = 4.6 Hz), 2.47 (1H, m), 1.92−1.68 (7H, m), 1.67−1.35 (3H, m), 1.20 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 56.8, 44.4, 29.7, 26.2, 25.7, 22.7. Anal. Calcd for $C_{11}H_{21}NOS$: C, 61.35; H, 9.83; N, 6.50. Found: C, 61.32; H, 9.85; N, 6.22.

(R_S)-(−)-*N*-α-Pentylhexylidene-*tert*-butanesulfinamide, (R_S)-5g. The literature procedure[20h,28] was followed. Under a nitrogen atmosphere, a stirred solution of 6-undecanone (1.13 mL, 5.50 mmol), (R_S)-(+)-*tert*-butanesulfinamide (>99% ee by chiral GC analysis on a Lipodex E capillary column, 605 mg, 5.00 mmol), and $Ti(OEt)_4$ (technical grade, 2.30 mL, 11.00 mmol) in THF (11 mL) was refluxed for 18 h. After cooling to room temperature, the solution was poured into vigorously stirred saturated aqueous NaCl (15 mL). The mixture was filtred over a pad of Celite and the solid rinced with AcOEt (4 × 30 mL). The organic layer was washed with brine and the resulting aqueous layer was extracted once with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was purified by flash chromatography (gradient eluant: 20−25% Et_2O in pentane) yielding enantiopure sulfinimine (R_S)-**5g** as a pale yellow oil (1.100 g, 4.03 mmol, 82%). $[\alpha]_D$ −132.8 (*c* 1.01, $CHCl_3$, 20 °C); IR (ATR Diamand) 1619 (s), 1075 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.64 (2H, m), 2.36 (2H, m), 1.55 (4H, m), 1.28 (8H, m), 1.19 (9H, s), 0.85 (6H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 56.1, 40.8, 36.4, 31.9, 31.3, 27.0, 25.2, 22.5, 22.3, 22.2, 13.9, 13.8. Anal. Calcd for $C_{15}H_{31}NOS$: C, 65.88; H, 11.43; N, 5.12. Found: C, 65.80; H, 11.56; N, 5.03.

Preparation of Racemic *N*-*p*-Toluenesulfinimines 7a−e. The literature procedure[32] was followed. The ^1H and ^{13}C spectral data obtained for racemic *N*-*p*-toluenesulfinimines **7a**−**c**,**e** correspond to those reported.

(S_S*,*E*)-*N*-Cyclohexylmethylidene-*p*-toluenesulfinamide, 7d. The literature procedure[32] was followed. Under a nirogen atmosphere, a solution of cyclohexanecarboxaldehyde (0.49 mL, 7.50 mmol), racemic *p*-toluenesulfinamide (621 mg, 4.00 mmol), and $Ti(OEt)_4$ (technical grade, 4.20 mL, 20.00 mmol) in CH_2Cl_2 (60 mL) was refluxed for 1 h. After cooling to 0 °C, the mixture was quenched with H_2O (60 mL) and filtred over a pad of Celite and the solid was rinced with CH_2Cl_2 (3 × 60 mL). The layers were separated and the aqueous layer was extracted once with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residual oil was purified by filtration over a pad of silica gel (eluant: CH_2Cl_2) yielding racemic *E* sulfinimine **7d** as a colorless oil (849 mg, 3.41 mmol, 85%). IR (ATR Diamand) 1615 (s), 1092 (s), 1072 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (1H, d, J = 4.4 Hz), 7.56 (2H, d, J = 8.1 Hz), 7.32 (2H, d, J = 8.1 Hz), 2.44 (1H, m), 2.42 (3H, s), 1.91−1.60 (5H, m), 1.37−1.27 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 142.1, 141.4, 129.7, 124.5, 43.6, 29.0, 25.8, 25.2, 21.3. Anal. Calcd for $C_{14}H_{19}NOS$: C, 67.43; H, 7.68; N, 5.62. Found: C, 67.31; H, 7.79; N, 5.50.

Preparation of Racemic Allenylzinc 1. Under a nitrogen atmosphere, TMEDA (0.15 mL, 1.0 mmol) and *n*-BuLi (2.1 M solution in hexanes, 0.48 mL, 1.0 mmol) were successively added to a solution of 1-chloro-3-trimethylsilylpropyne (0.16 mL, 1.0 mmol) in anhydrous Et_2O (13 mL) at −95 °C. After 5 min of stirring at −95 °C, a solution of $ZnBr_2$ (1.0 M in Et_2O, 1.0 mL, 1.0 mmol) was added dropwise to the yellow mixture. The resulting white slurry mixture was then warmed to room temperature and used immediately.

(R_S,2*R*,3*R*)-(−)-*N*-*tert*-Butanesulfinyl-3-propyl-2-trimethylsilylethynylaziridine, (R_S)-6a. Under a nitrogen atmosphere, a solution of enantiopure *E* sulfinimine (R_S)-**5a** (87 mg, 0.50 mmol) in anhydrous Et_2O (2 mL) was cannulated to a solution of racemic allenylzinc **1** (3.0 mmol) at room temperature. After being stirred for 4 h at room temperature, the solution was quenched by 30% aqueous NH_3:saturated aqueous NH_4Cl (1:2 solution). The layers were separated and the aqueous layer was extracted with Et_2O (3×). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residual oil was purified by flash chromatography (gradient eluant: 5−20% Et_2O in pentane) yielding enantiopure trans aziridine (R_S)-**6a** as a colorless oil (87 mg, 0.30 mmol, 61%). $[\alpha]_D$ −158.8 (*c* 1.02, $CHCl_3$, 20 °C); IR (ATR Diamand) 2175 (w), 1249 (m), 1099 (m), 840 (s), 759 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.76 (1H, d, J = 3.8 Hz), 2.57 (1H, td, J = 7.9, 3.8 Hz), 1.91 (1H, m), 1.51−1.37 (3H, m), 1.31 (9H, s), 0.98 (3H, t, J = 7.3 Hz), 0.20 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 100.7, 91.1, 57.2, 47.0, 33.1, 32.8, 22.8, 20.2, 14.2, 0.1. Anal. Calcd for $C_{14}H_{27}NOSSi$: C, 58.89; H, 9.53; N, 4.91. Found: C, 58.89; H, 9.49; N, 4.85.

[(R_S,2*R*,3*R*)-(*E*)]-(−)-*N*-*tert*-Butanesulfinyl-3-(prop-1-enyl)-2-trimethylsilylethynylaziridine, (R_S)-6b. The above procedure was followed with enantiopure *E* sulfinimine (R_S)-**5b** (86 mg, 0.50 mmol). Flash chromatography (gradient eluant: 5−20% Et_2O in pentane) yielded enantiopure trans aziridine (R_S)-**6b** as a colorless oil (90 mg, 0.32 mmol, 64%). $[\alpha]_D$ −99.8 (*c* 1.01, $CHCl_3$, 20 °C); IR (ATR Diamand) 2171 (w), 1249 (m), 1101 (m), 841 (s), 759 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (1H, qd, J = 15.4, 6.6 Hz), 5.24 (1H, ddd, J = 15.4, 8.3, 1.5 Hz), 3.02 (1H, dd, J = 8.3, 3.8 Hz), 2.88 (1H, d, J = 3.8 Hz), 1.69 (3H, dd, J = 6.6, 1.5 Hz), 1.22 (9H, s), 0.13 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6, 125.7, 99.6, 91.0, 57.1, 48.4, 33.4, 22.5, 17.9, −0.3; HRMS found 284.1498, $C_{14}H_{26}NOSSi$ [MH^+] requires 284.1504.

(R_S,2*R*,3*R*)-(−)-*N*-*tert*-Butanesulfinyl-3-isopropyl-2-trimethylsilylethynylaziridine, (R_S)-6c. The above procedure was followed with enantiopure *E* sulfinimine (R_S)-**5c** (87 mg, 0.50 mmol). Flash chromatography (eluant: 3% Et_2O in CH_2Cl_2) yielded enantiopure trans aziridine (R_S)-**6c** as a colorless oil (99 mg, 0.34 mmol, 69%). $[\alpha]_D$ −233.5 (*c* 1.08, $CHCl_3$, 20 °C); IR (ATR Diamand) 2176 (w), 1249 (m), 1049 (m), 840 (s), 759 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.81 (1H, d, J = 4.0 Hz), 2.53 (1H, dd, J = 6.8, 4.0 Hz), 1.85 (1H, m), 1.32 (9H, s), 1.09 (3H, d, J = 6.4 Hz), 0.92 (3H, d, J = 6.8 Hz), 0.19 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 100.4, 90.9, 56.8, 51.0, 30.1, 28.5, 22.6, 20.0, 17.9, −0.3. Anal. Calcd for $C_{14}H_{27}NOSSi$: C, 58.89; H, 9.53; N, 4.91. Found: C, 58.72; H, 9.72; N, 4.82.

(R_S,2*R*,3*R*)-(−)-*N*-*tert*-Butanesulfinyl-3-cyclohexyl-2-trimethylsilylethynylaziridine, (R_S)-6d. The above procedure was followed with enantiopure *E* sulfinimine (R_S)-**5d** (107 mg, 0.50 mmol). Flash chromatography (gradient eluant: 5−20% Et_2O in pentane) yielded enantiopure trans aziridine (R_S)-**6d** as a white solid (95 mg, 0.29 mmol, 58%). Mp (pentane) 70−71 °C. $[\alpha]_D$ −140.8 (*c* 0.99, $CHCl_3$, 20 °C); IR (ATR Diamand) 2183 (w), 1242 (m), 1106 (m), 839 (s), 764 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.82 (1H, d, J = 4.0 Hz), 2.53 (1H, dd, J = 6.3, 4.0 Hz), 1.95 (1H, m), 1.78−1.69 (4H, m), 1.49 (1H, m), 1.32 (9H, s), 1.28−1.08 (4H, m), 1.08−0.95 (m, 1H), 0.19 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 100.6, 90.9, 57.0, 50.4, 38.2, 30.8, 30.7, 28.9, 26.1, 25.7, 25.6, 22.7, −0.3. Anal. Calcd for $C_{17}H_{31}NOSSi$: C, 62.71; H, 9.60; N, 4.30. Found: C, 62.84; H, 9.61; N, 4.20.

(R_S,2*R*,3*R*)-(−)-*N*-*tert*-Butanesulfinyl-3-phenyl-2-trimethylsilylethynylaziridine, (R_S)-6e. The above procedure was followed with enantiopure *E* sulfinimine (R_S)-**5e** (104 mg, 0.50 mmol). Flash chromatography (gradient eluant: 5−20% Et_2O in pentane) yielded enantiopure trans aziridine (R_S)-**6e** as a white solid (80 mg, 0.251 mmol, 50%). Mp 124−127 °C dec. $[\alpha]_D$ −61.7 (*c* 0.95, $CHCl_3$, 20 °C); IR (ATR Diamand) 2183 (w), 1248 (m), 1083 (m), 839 (s), 761 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.33 (3H, m), 7.28−7.26 (2H, m), 3.46 (1H d, J = 3.5 Hz), 3.09 (1H, d, J = 3.5 Hz), 126 (9H, s), 0.24 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 128.8, 128.5,

126.3, 98.7, 92.6, 57.2, 47.6, 36.7, 22.5, −0.3. Anal. Calcd for $C_{17}H_{31}NOSSi$: C, 63.90; H, 7.89; N, 4.38. Found: C, 63.41; H, 8.16; N, 4.22.

(R_S,2*R*,3*R*)-(+)-*N*-*tert*-Butanesulfinyl-3-methyl-3-phenyl-2-trimethylsilylethynylaziridine, (R_S)-6f. The above procedure was followed with enantiopure *E* sulfinimine (R_S)-**5f** (111 mg, 0.50 mmol). Flash chromatography (gradient eluant: 5−20% Et_2O in pentane) yielded enantiopure trans aziridine (R_S)-**6f** as a white solid (115 mg, 0.34 mmol, 69%). Mp (pentane) 111−133 °C. $[\alpha]_D$ +15.7 (*c* 1.02, $CHCl_3$, 20 °C); IR (ATR Diamand) 2178 (w), 1246 (m), 1078 (m), 843 (s), 759 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53−7.50 (2H, m), 7.42−7.33 (3H, m), 3.24 (1H, s), 1.81 (3H, s), 1.29 (9H, s), 0.23 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 128.9, 128.5, 128.4, 99.7, 91.0, 57.4, 52.5, 38.0, 23.0, 22.4, −0.2; HRMS found 334.1661, $C_{18}H_{28}NOSSi$ [MH^+] requires 334.1667.

(R_S,2*R*)-(−)-*N*-*tert*-Butanesulfinyl-3,3-dipentyl-2-trimethylsilylethynylaziridine, (R_S)-6g. The above procedure was followed with enantiopure sulfinimine (R_S)-**5g** (136 mg, 0.50 mmol). Flash chromatography (gradient eluant: 5−20% Et_2O in pentane) yielded enantiopure aziridine (R_S)-**6g** as a yellow oil (167 mg, 0.43 mmol, 87%). $[\alpha]_D$ −77.3 (*c* 0.93, $CHCl_3$, 20 °C); IR (ATR Diamand) 2166 (w), 1249 (m), 1099 (m), 841 (s), 759 (m); ^1H NMR (400 MHz, $CDCl_3$) δ 2.67 (1H, s), 2.00 (1H, m), 1.69−1.33 (15H, m), 1.29 (9H, s), 0.91 (6H, m), 0.18 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 100.9, 89.2, 57.0, 53.2, 39.6, 32.3, 31.8, 31.5, 26.1, 24.4, 22.51, 22.49, 22.0, 14.1, 14.0, −0.2; HRMS found 384.2757, $C_{21}H_{42}NOSSi$ [MH^+] requires 384.2756.

(*S$_S$,2*S**,3*S**)-(±)-3-Isopropyl-*N*-*p*-toluenesulfinyl-2-trimethylsilylethynylaziridine, 8c.** Under a nitrogen atmosphere, a solution of racemic *E* sulfinimine **7c** (104 mg, 0.50 mmol) in anhydrous Et_2O (2 mL) was cannulated to a solution of racemic allenylzinc **1** (1.5 mmol) at room temperature. After being stirred for 1 h at room temperature, the solution was quenched by Na_2CO_3/$NaHCO_3$ buffer and diluted with H_2O. The layers were then separated and the aqueous layer was extracted with Et_2O (3×). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residual oil was purified by flash chromatography over silica gel (eluant: 3% Et_3N in 8% Et_2O/pentane) to yield racemic trans aziridine **8c** as a viscous colorless oil (89 mg, 0.28 mmol, 56%). IR (ATR Diamand) 2173 (w), 1597 (w), 1249 (m), 1102 (m), 840 (s), 731 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (2H, d, J = 8.4 Hz), 7.34 (2H, d, J = 8.4 Hz), 2.95 (1H, d, J = 4.0 Hz), 2.44 (3H, s), 2.24 (1H, dd, J = 7.6, 4.0 Hz), 1.32 (1H, m), 0.82 (3H, d, J = 6.8 Hz), 0.49 (3H, d, J = 6.8 Hz), 0.22 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.5, 129.8, 125.9, 99.5, 92.9, 50.5, 34.8, 30.5, 21.8, 19.3, 19.0, 0.0. Anal. Calcd for $C_{17}H_{25}NOSSi$: C, 63.90; H, 7.89; N, 4.38. Found: C, 63.48; H, 8.02; N, 4.07.

(*S$_S$,2*S**,3*S**)-(±)-3-Cyclohexyl-*N*-*p*-toluenesulfinyl-2-trimethylsilylethynylaziridine, 8d.** The above procedure was followed with racemic *E* sulfinimine **7d** (124 mg, 0.50 mmol). Flash chromatography (eluant: 3% Et_3N in 8% Et_2O/pentane) yielded racemic trans aziridine **8d** as a viscous pale yellow oil (90 mg, 0.25 mmol, 50%). IR (ATR Diamand) 3038 (w), 2174 (w), 1596 (w), 1248 (m), 1103 (m), 841 (s), 759 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (2H, d, J = 8.4 Hz), 7.31 (2H, d, J = 8.4 Hz), 2.94 (1H, d, J = 4.0 Hz), 2.44 (3H, s), 2.28 (1H, dd, ^3J = 7.6, 4.0 Hz), 1.70−1.48 (4H, m), 1.13−0.88 (6H, m), 0.59 (1H, m), 0.21 (9H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.6, 142.1, 129.5, 125.6, 99.4, 92.6, 49.2, 39.6, 34.3, 29.6, 29.3, 25.9, 25.5, 25.3, 21.6, −0.2. Anal. Calcd for $C_{20}H_{29}NOSSi$: C, 66.80; H, 8.13; N, 3.90. Found: C, 66.81; H, 8.30; N, 3.78.

(2*R*,3*R*)-(+)-3-Propyl-2-trimethylsilylethynylaziridine, (2*R*,3*R*)-9a. Under an argon atmosphere, to a stirred solution of enantiopure *trans*-*N*-sulfinylaziridine (R_S)-**6a** (142 mg, 0.50 mmol) in absolute MeOH (15 mL) was added at 0 °C HCl (1 M etheral solution, 2.50 mL, 2.50 mmol) and the resulting mixture was warmed to room temperature. After 30 min of stirring at this temperature, saturated aqueous $NaHCO_3$ (30 mL) was added, the layers were partitioned, and the aqueous layer was extracted with Et_2O (3×). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporated in vacuo to give a pale yellow oil. After purification by flash chromatography (eluant: 15% Et_2O in pentane), enantiopure *trans*-*N*-H aziridine (2*R*,3*R*)-**9a** was obtained as a yellow oil (59 mg, 0.33 mmol, 66%). Invertomer ratio: 80:20. $[\alpha]_D$ +63.3 (*c* 1.26 $CHCl_3$, 20 °C); IR (ATR Diamand) 2168 (m), 1249 (m), 836 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.26 (0.8H, br s), 2.07 (0.8H, br s: major invertomer), 1.76 (0.4H, br s: minor invertomer), 1.55−1.30 (5H, m), 0.97 (2.4H, t, J = 7.2 Hz: major invertomer), 0.61 (0.6H, br s: minor invertomer), 0.16 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.9, 84.6, 40.3, 35.3 (br), 25.4, 20.3, 13.8, −0.1; HRMS found 182.1366, $C_{10}H_{20}NSi$ [MH^+] requires 182.1365.

(2*R*,3*R*)-(+)-3-Cyclohexyl-2-trimethylsilylethynylaziridine, (2*R*,3*R*)-9d. The above procedure was followed with enantiopure *trans*-*N*-sulfinylaziridine (R_S)-**6d** (162 mg, 0.50 mmol). Flash chromatography (eluant: 15% Et_2O in pentane) yielded enantiopure *trans*-*N*-H aziridine (2*R*,3*R*)-**9d** as a yellow oil (89 mg, 0.41 mmol, 82%). Invertomer ratio: 96:4. $[\alpha]_D$ +84.4 (*c* 1.09 $CHCl_3$, 20 °C); IR (ATR Diamand) 3152 (m), 2161 (m), 837 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11−2.07 (2H, m), 1.87−1.67 (5H, m), 1.20−1.05 (5H, m), 0.86 (1H, m), 0.21 (0.36H, s: minor invertomer), 0.16 (8.64H, s: major invertomer), H on the nitrogen atom was not observed; ^{13}C NMR (100 MHz, $CDCl_3$) δ 106.2, 84.4, 45.7, 41.6, 30.6, 30.3, 26.3, 25.8, 25.7, 24.3, −0.1; HRMS found 222.1673, $C_{13}H_{24}Nsi$ [MH^+] requires 222.1678.

(2*R*)-(+)-3,3-Dipentyl-2-trimethylsilylethynylaziridine, (2*R*)-9g. The above procedure was followed with enantiopure *N*-sulfinylaziridine (R_S)-**6g** (96 mg, 0.25 mmol) yielding enantiopure *N*-H aziridine (2*R*)-**9g** as a white solid (70 mg, 0.25 mmol, 100%). Invertomer ratio: 97:3. Mp 87−89 °C. $[\alpha]_D$ +57.3 (*c* 1.10 $CHCl_3$, 20 °C); IR (ATR Diamand) 2165 (w), 1249 (m), 839 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (0.03H, br s: minor invertomer), 2.22 (0.97H, br s: major invertomer), 1.69 (1H, m), 1.37−1.28 (16H, m), 0.92 (3H, t, J = 6.8), 0.90 (3H, t, J = 7.1), 0.21 (0.27H, s: minor invertomer); 0.16 (8.73H, s: major invertomer), H on the nitrogen atom was not observed; ^{13}C NMR (100 MHz, $CDCl_3$) δ 104.4, 85.6, 45.3, 35.7, 34.2 (minor invertomer), 33.0 (minor invertomer), 32.1, 31.5 (minor invertomer), 30.3 (minor invertomer), 31.9, 25.5, 25.0, 22.7, 22.6, 14.1, 14.0, −0.1; HRMS found 280.2465, $C_{17}H_{34}NSi$ [MH^+] requires 280.2461.

Supporting Information Available: General methods and ^1H and ^{13}C NMR spectra for compounds (R_S)-**5a**,**b**,**d**,**g**, (R_S)-**6a**−**g**, *rac*-**7d**,**8c**,**d**, (2*R*,3*R*)-**9a**,**d**, and (2*R*)-**9g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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