Influence of HMPA on the Stereochemical Outcome of the Addition of a Racemic Allenylzinc onto Enantiopure N-*tert*-Butanesulfinimines: Stereoselective Access to Enantiopure *cis*-Ethynylaziridines**

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Abstract: In the presence of 60 equivalents of HMPA, the condensation of the racemic allenylzinc derived from 1-chloro-3-trimethylsilylpropyne onto enantiopure non-α-branched N-*tert*-butanesulfinimines was proven to give access to the corresponding *cis*-ethynylaziridines as the major products. The good *cis* selectivity observed presumably resulted from a high kinetic resolution with the allenylzinc being partially configurationally labile with respect to the time scale defined by the rate of the reaction. Both single crystal X-ray analysis and semiempirical calculations conducted at the MM2 and AM1 levels of theory proved that the reaction certainly occurred through a preferred synclinal transition state in a supra- or antarafacial S_E2' process. In all cases, chromatographic purification over silica gel allowed the *cis*-ethynyl-N-*tert*-butanesulfinylaziridines to be obtained as diastereo- and enantiomerically pure compounds ($dr > 98{:}2$ and $ee > 99\,\%$).

Keywords: allenylzinc · chiral resolution · conformation analysis · diastereoselectivity · transition states

Introduction

Despite their great synthetic potential, relatively little investigation has been undertaken so far on both the synthesis and the reactivity of alkynylaziridines. However, in the past ten years, few syntheses have been reported in the literature.[1] Regarding enantiopure alkynylaziridines, only three methods have been described. Dai's group has first 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*).[2] Shortly after, Ibuka and co-workers disclosed two multi-step syntheses from (*S*)-α-amino acids.[3] The key steps of these syntheses were a dehydrobromination reaction of 2-(1-bromovinyl)aziridine intermediates and an aziridine ring closure of amino alcohols bearing an ethynyl group under Mitsunobu conditions, respectively. More recently, Tanaka and co-workers have developed a highly stereoselective synthesis of ethynylaziridines from (*S*)-α-amino acids via the intramolecular amination of chiral bromoallene intermediates.[4] In both Ibuka's and Tanaka's works, *trans*- and *cis*-alkynylaziridines could be obtained in enantiomerically pure forms (*ee* > 98 %). However, neither *trans*- nor *cis*-alkynylaziridines could be prepared selectively since both had to be isolated from stereoisomeric mixtures (at different steps of the syntheses) by chromatographic separations. Moreover, the field of application of this method still remains quite restricted because of the limitation in the starting materials available, that is (*S*)-α-amino acids.

As part of our general interest to prepare ethynylaziridines,[5] we have very recently disclosed a straightforward access to enantiopure *trans*-N-*tert*-butanesulfinylaziridines through the condensation of the racemic allenylzinc **1**, derived from 1-chloro-3-trimethylsilylpropyne, onto the corresponding enantiopure *E* sulfinimines (R_S)-**2** (Scheme 1).

In all cases, the high stereoselectivity was assumed to be due to a good kinetic resolution of racemic allenylzinc **1** (which could be regarded as partially configurationally stable at the time scale defined by the rate of the reaction), the matched pair (a*S*)-**1**/(R_S)-**2** reacting much faster than the mismatched pair (a*R*)-**1**/(R_S)-**2**. This resolution was reasonably postulated to result from the chelate type transition state **TS-1** in which the zinc atom of racemic allenylzinc **1** is coordinated by both the nitrogen and the oxygen atoms of the imine in a four-membered metallacycle.[6]

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[**] Propargylic Carbenoids, Part 6; for Part 5 see ref. [5a].

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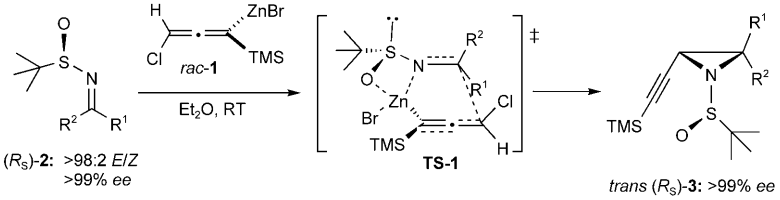


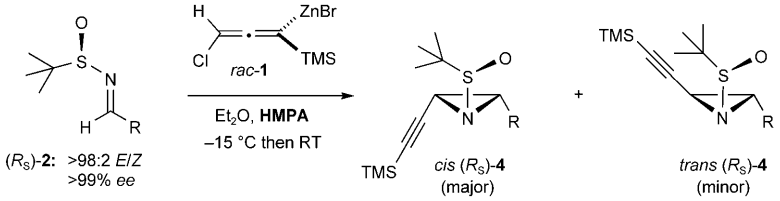
Scheme 1. Synthesis of enantiopure *trans* N-*tert*-butanesulfinylaziridines.[6]

Thus, our method was proven to be valuable for the stereoselective synthesis of enantiopure *trans*-ethynyl-N-*tert*-butanesulfinylaziridines. We then decided to expand its field of application to the synthesis of the enantiopure *cis* compounds, and we report herein our recent results about this topic.

Results and Discussion

Reaction of racemic allenylzinc 1 in the presence of HMPA (eight equivalents): Under the assumption that the coordination of the zinc was responsible for the formation of the chelate transition state **TS-1**, we first reasoned that using a Lewis acid could have some influence on the stereoselective outcome of the reaction. Indeed, because of the coordination of the Lewis acid by both the nitrogen and oxygen atoms of the imine, the formation of the chelate transition state **TS-1** could perhaps be prevented. Under these conditions, we even envisioned the formation of *cis*-ethynylaziridines as major products through an open transition state with reference to our previous works on the addition of racemic allenylzinc **1** onto N-sulfonylimines or aromatic aldehydes.[5a–c] Unfortunately, in preliminary works, the pre-coordination of N-*tert*-butanesulfinimines by $ZnBr_2$ or $BF_3{\cdot}Et_2O$ in CH_2Cl_2 or MAD [methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide)][7] in toluene was proven to afford the *trans* aziridines as major products. These results could be explained by a decoordination of the Lewis acid which allows the subsequent coordination of the allenylzinc species to take place; this leads to the *trans* isomer through **TS-1**. On the other hand, the use of $TiCl_4$ in CH_2Cl_2 only led to unindentified by-products.

We proceeded under the assumption that HMPA (i.e., hexamethylphosphoric triamide) would be able to coordinate the zinc atom of reagent **1** as observed for various metal ions[8] and more particularly for lithium.[9] We could then envisioned a switching of the stereoselectivity as previously observed in the cyclopropanation reaction of telluronium allylides with α,β-unsaturated esters and amides.[10] On this assumption, we decided to examine the reaction of enantiopure *E* (*S*)-N-*tert*-butanesulfinimines (R_S)-**2a–i**, readily prepared in good yields from enantiopure (*S*)-(+)-N-*tert*-butanesulfinamide according to Ellman's procedure,[11] with racemic allenylzinc **1** in the presence of HMPA (Scheme 2).



Scheme 2. Reaction of racemic allenylzinc **1** onto enantiopure N-*tert*-butanesulfinimines (R_S)-**2a–i** in the presence of HMPA.

In a typical procedure, sulfinimines (R_S)-**2a–i** were reacted in Et_2O with six equivalents of racemic allenylzinc **1** in the presence of HMPA. At first, eight equivalents of HMPA were used, that is 1.3 equivalents with respect to reagent **1** (Table 1).

These conditions allowed the reaction with non-α-branched imines (R_S)-**2a–h** to be complete (Table 1, entries 1–10). Although after 30 min of stirring at −15 °C no starting imine was detected by TLC, the reaction mixture needed to be stirred overnight at room temperature to reach the end of the aziridine ring closure from the α-chloro N-zincated sulfinamide intermediates. On the other hand, no reaction occurred with the α-branched imine (R_S)-**2i**

Table 1. Addition of racemic allenylzinc **1** onto enantiopure N-*tert*-butanesulfinimines (R_S)-**2a–i** in the presence of 8 equiv HMPA (Scheme 2).

	Imine	R	Equiv *rac*-**1**	Aziridine	*cis*/*trans*[a]	*dr* (*cis*)[a]
1	(R_S)-**2a**	Me	6.0	(R_S)-**4a**	86:14	>98:2
2	(R_S)-**2b**	Pr	1.0	(R_S)-**4b**	51:49[b]	>98:2
3	*rac*-**2b**	Pr	3.0	*rac*-**4b**	78:22	>98:2
4	(R_S)-**2b**	Pr	6.0	(R_S)-**4b**	75:25	>98:2
5	(R_S)-**2c**	heptyl	6.0	(R_S)-**4c**	57:43	>98:2
6	(R_S)-**2d**	(*E*)-crotyl[c]	6.0	(R_S)-**4d**	79:21	>98:2
7	(R_S)-**2e**	(*E*)-1-heptenyl	6.0	(R_S)-**4e**	56:44	>98:2
8	(R_S)-**2f**	(*E*)-cinnamyl	6.0	(R_S)-**4f**	85:15	>98:2
9	(R_S)-**2g**	2-phenylethyl	6.0	(R_S)-**4g**	53:47	>98:2
10	(R_S)-**2h**	1-heptynyl	6.0	(R_S)-**4h**	62:38	>98:2
11	(R_S)-**2i**	*c*-hex	6.0	(R_S)-**4i**	–[d]	–[d]

[a] Selectivities were measured by ^1H NMR at 400 MHz on the crude reaction mixtures. [b] 36% of the starting imine was recovered. [c] As a mixture of the *E* and *Z* isomers in a 95:5 ratio. [d] No reaction.

(Table 1, entry 11). As expected, HMPA had a dramatic influence on the stereochemical outcome of the reaction since the corresponding aziridines (R_S)-**4a–h** were obtained as *cis*/*trans* isomeric mixtures with fair to high selectivities in favor of the *cis* isomers (Table 1, entries 1 and 4–10). Overall these selectivites were assigned by ^{1}H NMR at 400 MHz allowing the differentiation of the *trans* and *cis* isomers on the crude reaction mixtures. Moreover, single *cis* isomers were observed, as seen by ^{1}H NMR at 400 MHz, indicating that the N-*tert*-butanesulfinyl auxiliary had fully played the role of a good chiral directing group. However, to our great surprise, the *cis*-aziridines (R_S)-**4a–h** were different from those obtained, as minor products, when performing the reaction without HMPA.[6] The absolute stereochemistry of the *cis*-aziridines (R_S)-**4a–h** was unambiguously deduced to be (R_S,2*R*,3*S*) from the single-crystal X-ray analysis of aziridine (R_S)-**4f** (Figure 1).[12]

When running the reaction between imine (R_S)-**2b** and only one equivalent of racemic allenylzinc **1**, 36% of the starting imine were recovered while an equimolar mixture of *cis*- and *trans* aziridines was obtained (Table 1, entry 2). This result could be explained by the configurational stability of allenylzinc **1** with respect to the time scale defined by the reaction rate under these conditions and strongly suggests that each enantiomer of **1** gave only one isomer (*cis* or *trans*). Furthermore, since the reaction of six equivalents of racemic allenylzinc with imine (R_S)-**2b** led to a *cis*/*trans* ratio very close to that obtained with racemic imine **2b** (Table 1, entries 3 versus 4), we could reasonably postulated that almost the highest kinetic resolution was attained under these conditions.[13]

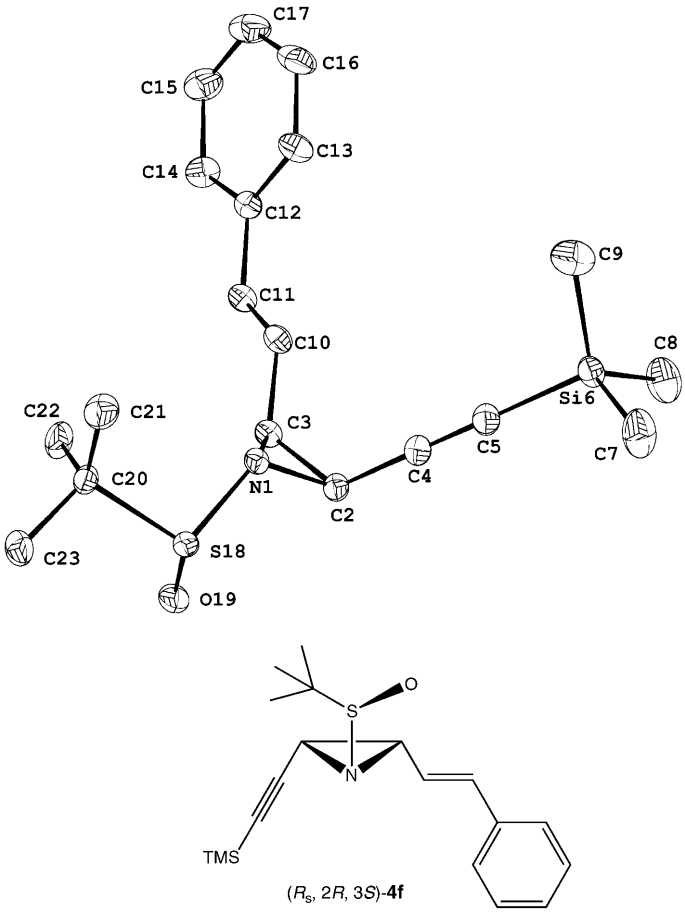


Figure 1. ORTEP drawing of *cis*-aziridine (R_S)-**4f**.

Reaction of racemic allenylzinc 1 in the presence of HMPA (60 equivalents): The amount of HMPA was also shown to have an influence on the level of the stereoselectivity of the addition of racemic allenylzinc **1** onto N-*tert*-butanesulfinimines (R_S)-**2a–h**. Indeed, using larger amounts of HMPA allowed the stereoselectivity to be improved in all cases. In fact, the best results were obtained with 60 equivalents of HMPA, that is 10 equivalents with respect to allenylzinc **1** (entries 1 and 3–9, Table 2).

All imines (R_S)-**2a–h** gave the corresponding aziridines (R_S)-**4a–h** with better *cis*/*trans* ratios, ranging from 71:29 to 89:11. Moreover, aziridines (R_S)-**4a–h** could be isolated in good yields (50 to 64%) as diastereo- and enantiopure compounds (*dr* > 98:2 and *ee* > 99%) by flash chromatography on silica gel.

When carrying out the reaction between imine (R_S)-**2b** and only one equivalent of racemic allenylzinc **1**, 55% of the starting imine was recovered while a 66:34 *cis*/*trans* ratio was obtained (Table 2, entry 2). This result, significantly different from 50:50 (obtained in the presence of 8 equiv HMPA, see above), could be explained by the partial configurational lability of allenylzinc **1** with respect to the time scale defined by the reaction rate under these conditions. Thus, everything proceeded as planned though the rate of racemization of allenylzinc **1** were higher in the presence of 60 equivalents of HMPA than in the presence of eight equivalents. This apparent faster racemization of **1** could well explained the in-

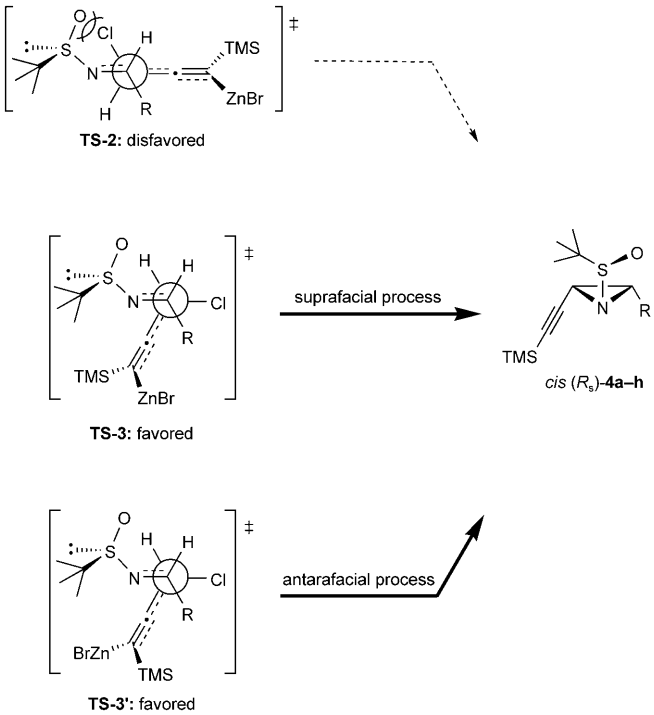
Table 2. Addition of six equivalents of racemic allenylzinc **1** onto enantiopure N-*tert*-butanesulfinimines (R_S)-**2a–h** in the presence of 60 equiv HMPA (Scheme 2).

Entry	Imine	R	Aziridine	*cis*/*trans*[a]	*dr* (*cis*)[a]	Yield [%][b]
1	(R_S)-**2a**	Me	(R_S)-**4a**	89:11	>98:2	64
2	(R_S)-**2b**	Pr	(R_S)-**4b**	66:34[c]	>98:2	[d]
3	(R_S)-**2b**	Pr	(R_S)-**4b**	84:16	>98:2	54
4	(R_S)-**2c**	heptyl	(R_S)-**4c**	78:22	>98:2	56
5	(R_S)-**2d**	(*E*)-crotyl[e]	(R_S)-**4d**	84:16	>98:2	55
6	(R_S)-**2e**	(*E*)-1-heptenyl	(R_S)-**4e**	71:29	>98:2	62
7	(R_S)-**2f**	(*E*)-cinnamyl	(R_S)-**4f**	87:13	>98:2	56
8	(R_S)-**2g**	2-phenylethyl	(R_S)-**4g**	71:29	>98:2	50
9	(R_S)-**2h**	1-heptynyl	(R_S)-**4h**	73:27	>98:2	60

[a] Selectivities were measured by ^{1}H NMR at 400 MHz on the crude reaction mixtures. [b] Yields in the purified major *cis* isomers. [c] Reaction carried out with 1 equiv racemic allenylzinc **1**; 55% of the starting imine was recovered. [d] Not determined. [e] As a mixture of the *E* and *Z* isomers in a 95:5 ratio.

creasing of the *cis*/*trans* ratio when using 60 equivalents of HMPA.[13]

Conformation of N-*tert*-butanesulfinimines and possible transition states: The absolute stereochemistry (R_S,2*R*,3*S*) of the *cis* aziridines could be explained not only by an antiperiplanar transition state **TS-2**, with reference to N-sulfonylimines and aromatic aldehydes,[5a] but also by a synclinal transition state **TS-3** (Scheme 3). However, because of steric interactions between the chlorine and the oxygen of the N-*tert*-butanesulfinyl group in **TS-2**, the synclinal transition state **TS-3** would certainly be preferred. It is noteworthy that **TS-3**, which corresponds to a suprafacial S_E2' process, could alternatively be replaced with **TS-3′** corresponding to an antarafacial S_E2' process (Scheme 3).



Scheme 3. Postulated synclinal transition states **TS-3** and **TS-3′** for the formation of *cis*-aziridines (R_S)-**4a–h**.

The structures of these transition states were supported by both semiempirical MM2 and AM1 calculations[14] which clearly indicated that the conformation **C-1** (Figure 2) is the most stable conformation of the imine. For instance, in the case of imine (R_S)-**4f**, MM2 calculations have shown that the conformation **C-1** is preferred by 5.23 kJ mol^{-1} relative to the **C-2** one (Figure 2). A similar trend was observed by AM1 calculations since the heat of formation of the **C-1** conformation was determined to be lower by 24.34 kJ mol^{-1} than the **C-2** one. It is noteworthy that the **C-2** conformation has been previously assumed to be the reactive conformation through the coordination of the zinc, when performing the reaction without HMPA, as depicted in Scheme 1.

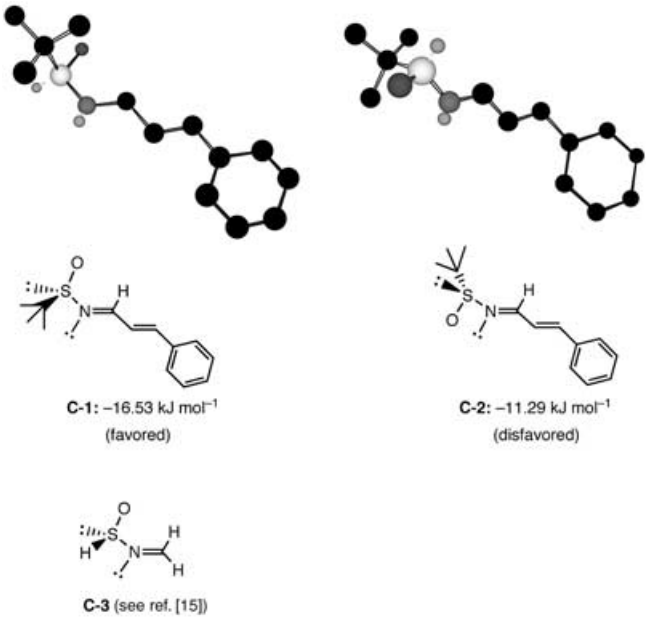


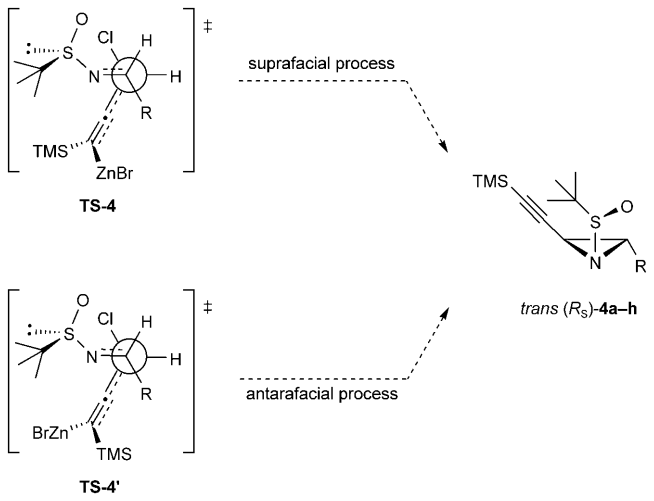
Figure 2. MM2 calculations on the conformation of sulfinimine (R_S)-**4f**.

These semiempirical calculations are fully in accordance with previous theoretical works by Bharatam's group.[15] Indeed, this group has carried out calculations using ab initio and density functional (DFT) methods at the MP2-(full)/6-31+G* level to study the conformational preferences of the simplest sulfinimine H(O)S-N=CH_2. Then, it has been shown that this sulfinimine prefers to adopt the conformation **C-3**, in which the S−O bond and the lone pair on the nitrogen atom are antiperiplanar, mainly as a result of an important $n_N \rightarrow \sigma^*_{S-O}$ negative hyperconjugative interaction. In addition, these theoretical calculations strongly suggested that the conformation of sulfinimines is blocked because of a high S–N rotational barrier (41.30 kJ mol^{-1}).

Like the major *cis*-aziridines (R_S)-**4a–h**, the minor *trans* isomers (R_S)-**4a–h** were formed as single diastereomers. The latter were different from those, that is (R_S)-**3**, which had been previously obtained as the major compounds in the absence of HMPA.[6] As a consequence, the stereochemistry of the *trans*-aziridines (R_S)-**4a–h** could be unambiguously assigned to (R_S,2*S*,3*S*). By analogy with **TS-3** and **TS-3′**, only the synclinal transition states **TS-4** and **TS-4′** could reasonably be evoked to explain the formation of *trans*-aziridines (R_S)-**4a–h** (Scheme 4).

Moreover, as each enantiomer of allenylzinc **1** gives only one isomer (*cis* or *trans*), it could be assumed that *trans*- and *cis* aziridines are obtained through the same supra- or antarafacial processes. In other words, two competitive synclinal transition states **TS-3**/**TS-4** or **TS-3′**/**TS-4′** could be evoked to explain our results (Figure 3).

Thus, the synclinal transition states **TS-3/3′** and **TS-4/4′**, in which allenylzinc **1** approaches onto the less hindered face of the imine (the *Re* face), that is opposite to the very bulky *tert*-butyl substituent at the sulfur center, correspond to the matched and mismatched situations, respectively. These



Scheme 4. Postulated synclinal transition states **TS-4** and **TS-4′** for the formation of *trans*-aziridines (R_S)-**4a**–**h**.

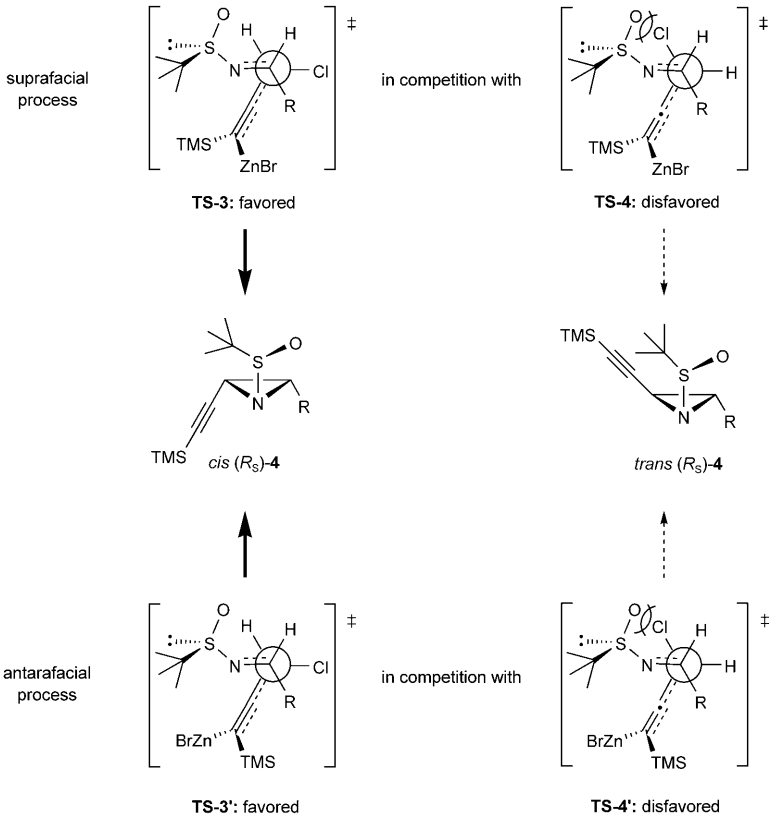


Figure 3. Origin of the *cis* selectivity in the additon of racemic allenylzinc **1** onto enantiopure imines (R_S)-**2a**–**h** in the presence of HMPA.

competitive transition states allow the decreasing of the *cis*/*trans* ratio to be explained when the substituent R on the imine becomes bulkier and bulkier. Indeed, the bulkier is the substituent R on the imine, the higher are the steric interactions with the chlorine atom in the synclinal transition states **TS-3/3′**. On the other hand, the bulkiness of R should have only little influence on the synclinal transition states **TS-4/4′** since the allenyl moiety can be regarded as very little hindered (see Figure 3). Then, making the substituent R bulkier and bulkier should render **TS-3/3′** less favored relative to **TS-4/4′** leading to a drop in the *cis* selectivity. Moreover, with the very bulky α-branched sulfinimine (R_S)-**2i** (Table 1, entry 11) no reaction occurred at all, neither through **TS-3/3′** nor **TS-4/4′**. This is in agreement with our previously works which have shown that such an imine exhibited a low reactivity towards allenylzinc **1** even through the chelate transition state.

Variable temperature NMR experiments on *trans* aziridines: Surprisingly, all *trans*-aziridines (R_S)-**4a**–**h** exhibited many broad signals by ^{1}H NMR at 400 MHz at room temperature in $CDCl_3$ or C_6D_6. More striking, in all ^{13}C NMR spectra, several signals were missing. For instance, in the case of *trans*-aziridine (R_S)-**4g**, the two aziridinyl hydrogens and the four hydrogens of the -$(CH_2)_2$- group were not distinguishable by ^{1}H NMR at 20 °C in $CDCl_3$ giving two broad signals between 2.90–2.63 and 2.15–2.07 ppm, respectively (Figure 4a). For the same compound, only four carbons, out of the thirteen non-equivalent carbons of the molecule, gave signals by ^{13}C NMR at 20 °C in $CDCl_3$ (Figure 5a)!

NMR experiments at low temperature were then performed. The ^{1}H NMR spectrum of *trans*-aziridine (R_S)-**4g** obtained at −20 °C in $CDCl_3$ exhibited two sets of signals among which two trimethylsilyl and two *tert*-butyl groups were discernible. Moreover, two doublets with coupling constants of 3.8 and 3.3 Hz were distinctly observed at 2.93 and 2.70 ppm, respectively. These two doublets correspond to two different propargylic aziridinyl hydrogens; this suggests the presence of two invertomers, with a *trans* stereochemistry for the aziridine ring, in a 64:36 ratio (Figure 4b). This experiment showed that the critical temperature (T_c) was between 0 and −10 °C and allowed a barrier of interconversion of about 54 kJ mol^{-1} to be determined.

Similarly, in the ^{13}C NMR spectrum of *trans*-aziridine (R_S)-**4g** recorded at −50 °C in $CDCl_3$, twenty-five carbons were observed and more particularly four acetylenic carbons. This was again in agreement with a mixture of two in-

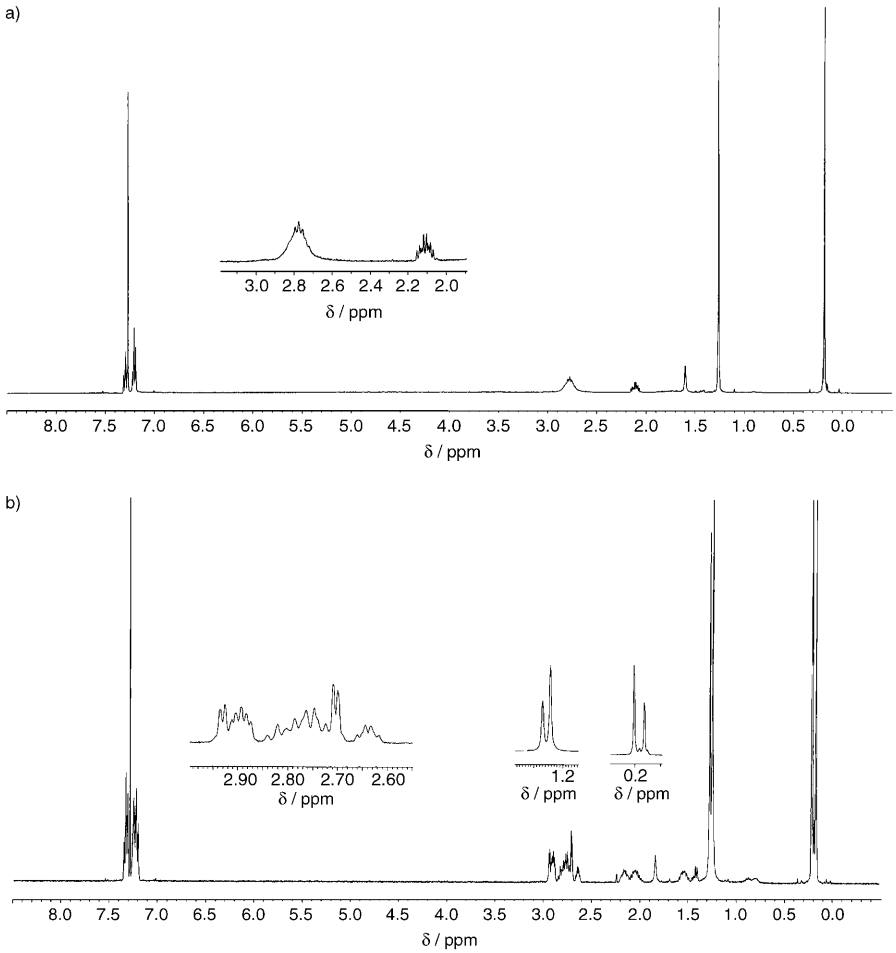


Figure 4. a) ^{1}H NMR spectrum of *trans*-aziridine (R_S)-**4g** in $CDCl_3$ at 20 °C. b) ^{1}H NMR spectrum of *trans*-aziridine (R_S)-**4g** in $CDCl_3$ at −20 °C.

vertomers (Figure 5b). At last, when running the ^{13}C NMR experiment in $CDCl_3$ at 40 °C, nine carbons were discernible. At this temperature, the equilibrium between the two invertomers was making faster so that only one set of signals was observed. However, four carbons were still missing (Figure 5c).

Thus, we reasoned that all *trans*-aziridines (R_S)-**4a–h** were obtained as mixtures of the two possible (R_N) and (S_N) invertomers in slow equilibrium with respect to the time scale defined by the NMR rate at 20 °C in $CDCl_3$ or C_6D_6 (Scheme 5).

Conclusion

In summary, HMPA was proven to have a dramatic influence on the stereochemical outcome of the condensation of racemic allenylzinc **1** onto enantiopure non-α-branched N-*tert*-butanesulfinimines (R_S)-**2**. Performing the reaction in the presence of 60 equivalents of HMPA in Et_2O allowed the corresponding *cis*-ethynylaziridines (R_S)-**4** to be formed as the major compounds with good to high selectivities (*cis*/*trans* ratios ranging from 71:29 to 89:11). The *cis* selectivity was postulated to result from a high kinetic resolution through a synclinal transition state in a supra- or antarafacial S_E2' process which has been supported by semiempirical AM1 and MM2 calculations. Furthermore, after chromatographic separation over silica gel, (R_S,2*R*,3*S*) *cis*-ethynyl-N-*tert*-butanesulfinylaziridines (R_S)-**4** were obtained as diastereo- and enantiomerically pure products (>98:2 *dr* and >99% *ee*).

Experimental Section

General remarks: Experiments involving organometallic compounds were carried out in dried glassware under a positive pressure of dry nitrogen. Liquid nitrogen was used as a cryoscopic fluid. A four neck round-bottom flask equipped with an internal thermometer, a septum cap, a nitrogen or argon inlet and a mechanic stirring was used. Et_2O was freshly distilled from sodium/benzophenone prior to use. Zinc bromide (98%) was purchased from Aldrich. It was melted under dry nitrogen and, immediately after cooling down to room temperature, was dissolved in anhydrous Et_2O. Commercial *n*BuLi was titrated with an 1 M solution of *s*BuOH in toluene in the presence of 2,2′-dichinolyl. All other reagents and solvents were of commercial quality and were used without purification. Flash column chromatographic separations were carried out over Merck silica gel 60 (0.015–0.040 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are reported in ppm relative to an internal standard of residual chloroform (7.27 ppm for ^{1}H NMR and 77.1 ppm for ^{13}C NMR) or benzene (7.15 ppm for ^{1}H NMR and 128.6 ppm for ^{13}C NMR). IR spectra were recorded with a ATRD Bruker Tensor 27 spectrophotometer. Melting points were not corrected and were measured with a Stuart Scientific melting point apparatus SMP3 (1 C). MS and HRMS were performed by the Service de Spectrométrie de Masse de l'Ecole Normale Supérieure (Paris).

General procedure 1—Synthesis of enantiopure N-*tert*-butanesulfinimines (R_S)-2: Ellman's procedure[11] was followed starting from enantiopure N-*tert*-butanesulfinamide (R_S)-**2** (>99% *ee*). The spectral data of imines (R_S)-**2b**,**d** were identical to those reported in the literature.[6] Under a nitrogen atmosphere, a stirred suspension of (R_S)-(+)-*tert*-butanesulfinamide (>99% *ee*, 605 mg, 5.00 mmol), aldehyde (1.5 to 7.0 equiv), PPTS (65 mg, 0.25 mmol) and anhydrous $MgSO_4$ (3.00 g, 25.00 mmol) in CH_2Cl_2 (8 mL) was stirred 24 h at room temperature. The mixture was filtered over a pad Celite and concentrated in vacuo. The residual oil was purified by flash chromatography over silica gel yielding enantiopure *E*-sulfinimine (R_S)-**2**.

(R_S,*E*)-(−)-*N*-Ethylidene-*tert*-butanesulfinamide [(R_S)-2a]: GP 1 was followed with acetaldehyde (2.0 mL, 35.0 mmol). Flash chromatography (CH_2Cl_2) over silica gel yielded enantiopure sulfinimine (R_S)-**2a** as a

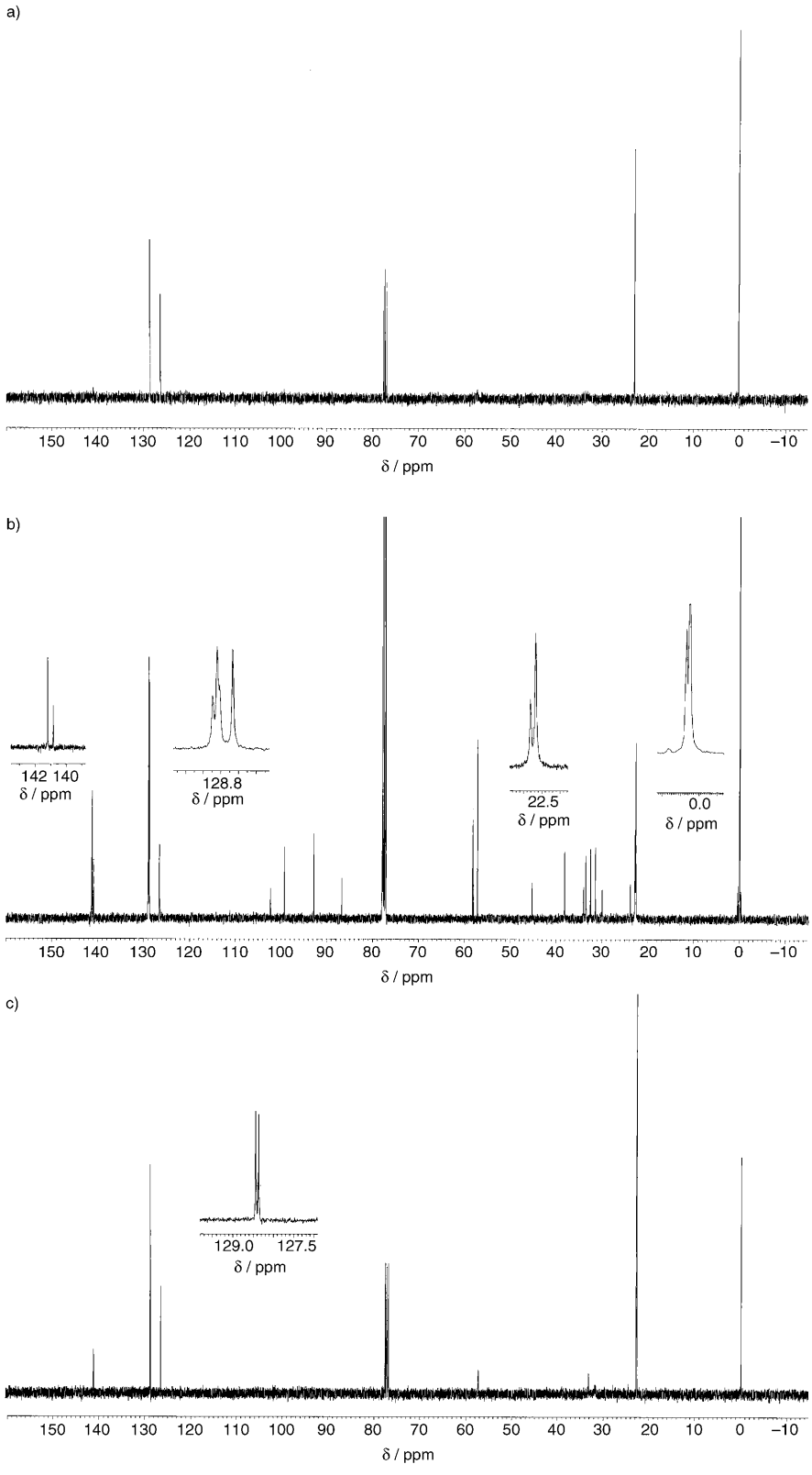


Figure 5. a) ^{13}C NMR spectrum of *trans*-aziridine (R_S)-**4g** in $CDCl_3$ at a) 20 °C; b) −50 °C; c) 40 °C.

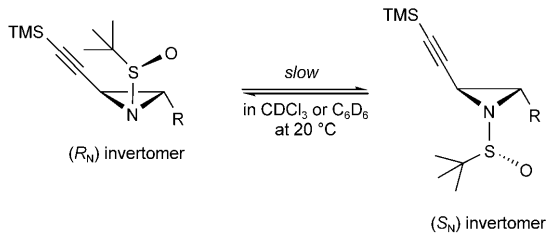
yellow oil (430 mg, 2.93 mmol, *E*/*Z* 97:3, 59 %). $[\alpha]_D$ = −207.1 (*c* = 1.20, $CHCl_3$, 20 °C); ^1H NMR ($CDCl_3$): δ = 9.79 (q, *J* = 3.0 Hz, 1H *Z* isomer), 8.09 (q, *J* = 5.2 Hz, 1H *E* isomer), 2.24 (d, *J* = 6.1 Hz, 3H *E* isomer), 2.21 (d, *J* = 2.6 Hz, 3H *Z* isomer), 1.20 (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 166.3, 50.9, 22.8, 22.5; IR (ATR Diamand): $\tilde{\nu}$ = 2960 (w), 2925 (w), 2868 (w), 1626 (m), 1078 cm^{-1} (s); MS (CI, NH_3): *m*/*z*: 165 [*M*+NH_4^+], 148 [*M*+H^+].

(R_S,*E*)-(−)-*N*-Octylidene-*tert*-butanesulfinamide [(R_S)-2c]: GP 1 was followed with octanal (1.20 mL, 7.50 mmol). Flash chromatography over silica gel (5→25 % Et_2O/pentane) yielded sulfinimine (R_S)-**2c** (784 mg, 3.39 mmol, 68 %) as a yellow oil. $[\alpha]_D$ = −180.9 (*c* = 0.96, $CHCl_3$, 20 °C); ^1H NMR ($CDCl_3$): δ = 8.07 (t, *J* = 4.8 Hz, 1H), 2.55–2.49 (m, 2H), 1.67–1.59 (m, 2H), 1.40–1.24 (m, 8H), 1.20 (s, 9H), 089 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 169.7, 56.4, 36.1, 31.7, 29.2, 29.0, 25.5, 22.6, 22.3, 14.1; IR (ATR Diamand): $\tilde{\nu}$ = 2955 (w), 2925 (w), 2856 (w), 1621 (m), 1085 cm^{-1} (s); MS (CI, NH_3): *m*/*z*: 232 [*M*+H^+].

(R_S,*E*,*E*)-(−)-*N*-(2-Octenyl)idene-*tert*-butanesulfinamide [(R_S)-2e]: GP 1 was followed with technical (*E*)-2-octenal (1.50 mL, 10.00 mmol). Flash chromatography over silica gel (5→20 % Et_2O/pentane) yielded sulfinimine (R_S)-**2e** (933 mg, 4.07 mmol, *E*/*Z* 98:2, 82 %) as a pale yellow oil. $[\alpha]_D$ = −428.3 (*c* = 0.92, $CHCl_3$, 20 °C); ^1H NMR ($CDCl_3$): δ = 8.62 (d, *J* = 8.8 Hz, 1H *Z* isomer), 8.20 (d, *J* = 9.1 Hz, 1H *E* isomer), 6.56 (td, *J* = 6.6, 15.4 Hz, 1H), 6.44 (tdd, *J* = 1.3, 9.1, 15.4 Hz, 1H), 2.30 (q, *J* = 7.0 Hz, 2H), 1.55–1.49 (m, 2H), 1.36–1.32 (m, 4H), 1.22 (s, 9H), 0.92 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ = 164.1, 151.7, 128.6, 57.0, 32.9, 31.2, 27.8, 22.3, 13.9; IR (ATR Diamand): $\tilde{\nu}$ = 2957 (w), 2926 (w), 2859 (w), 1639 (m), 1580 (s), 1080 cm^{-1} (s); MS (CI, NH_3): *m*/*z*: 247 [*M*+NH_4^+], 230 [*M*+H^+].

(R_S,*E*,*E*)-(−)-*N*-(3-Phenylpropenyl)-idene-*tert*-butanesulfinamide [(R_S)-2f]: GP 1 was followed with (*E*)-cinnamaldehyde (1.26 mL, 10.00 mmol). Flash chromatography over silica gel (10→40 % Et_2O/pentane) yielded sulfinimine (R_S)-**2f** (1.00 g, 4.26 mmol, 85 %) as a yellow solid. M.p. 56–58 °C; $[\alpha]_D$ = −344.1 (*c* = 0.92, $CHCl_3$, 20 °C); ^1H NMR ($CDCl_3$): δ = 8.40 (d, *J* = 9.1 Hz, 1H), 7.58–7.56 (m, 2H), 7.45–7.40 (m, 3H), 7.26 (d, *J* = 15.7 Hz, 1H), 7.11 (dd, *J* = 9.1, 15.7 Hz, 1H), 1.26 (s, 9H); ^{13}C NMR ($CDCl_3$): δ = 163.8, 146.4, 135.0, 130.2, 130.0, 127.9, 125.5, 57.6, 22.5; IR (ATR Diamand): $\tilde{\nu}$ = 3056 (w), 2963 (w), 2927 (w), 2866 (w), 1625 (m), 1597 (s), 1579 (s), 1099 cm^{-1} (s); MS (CI, NH_3): *m*/*z*: 236 [*M*+H^+].

(R_S,*E*)-(−)-*N*-(3-Phenylpropyl)idene-*tert*-butanesulfinamide [(R_S)-2g]: GP 1 was followed with 3-phenylpropionaldehyde (0.66 mL, 7.50 mmol). Flash chromatography over silica gel (10→30 % Et_2O/pentane) yielded sulfinimine (R_S)-**2g** (1.07 g, 4.51 mmol,



Scheme 5. Slow equilibrium between the two *trans* invertomers.

90%) as a colorless oil. $[\alpha]_D = -207.1$ ($c = 1.20$, $CHCl_3$, 20°C); ^1H NMR ($CDCl_3$): $\delta = 8.12$ (t, $J = 4.2$ Hz, 1H), 7.31–7.28 (m, 2H), 7.26–7.19 (m, 3H), 3.00–2.97 (m, 2H), 2.90–2.85 (m, 2H), 1.14 (s, 9H); ^{13}C NMR ($CDCl_3$): $\delta = 168.5$, 140.3, 128.5, 128.3, 126.3, 56.5, 37.4, 31.4, 22.3; IR (ATR Diamand): $\tilde{\nu} = 3061$ (w), 3027 (w), 2958 (w), 2924 (w), 1621 (m), 1079 cm^{-1} (s); MS (CI, NH_3): m/z: 255 $[M+NH_4^+]$, 238 $[M+H^+]$.

(R_S,*E*)-(−)-*N*-(2-Octynyl)idene-*tert*-butanesulfinamide [(R_S)-2h]: GP 1 was followed with 2-octynal (1.42 mL, 10.00 mmol). Flash chromatography over silica gel (5→25% Et_2O/pentane) yielded sulfinimine (R_S)-**2h** (969 mg, 4.27 mmol, 86%) as a yellow oil. $[\alpha]_D = -260.8$ ($c = 1.03$, $CHCl_3$, 20°C); ^1H NMR ($CDCl_3$): $\delta = 7.88$ (t, $J = 1.8$ Hz, 1H), 2.47 (td, $J = 1.8$, 7.0 Hz, 2H), 1.70–1.60 (m, 2H), 1.46–1.33 (m, 4H), 1.25 (s, 9H), 093 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 148.3$, 103.6, 77.7, 57.8, 31.0, 27.5, 22.4, 22.0, 19.7, 13.8; IR (ATR Diamand): $\tilde{\nu} = 2929$ (m), 2862 (w), 2216 (s), 1565 (s), 1086 cm^{-1} (s); MS (CI, NH_3): m/z: 245 $[M+NH_4^+]$, 228 $[M+H^+]$.

General procedure 2—Addition of racemic allenylzinc 1 onto pure *E* enantiopure *N*-*tert*-butanesulfinimines (R_S)-2: Under a nitrogen atmosphere, to a solution of 1-chloro-3-trimethylsilylpropyne (0.48 mL, 3.00 mmol) in anhydrous Et_2O (24 mL) were successively added at −95°C, TMEDA (0.46 mL, 3.00 mmol) and *n*BuLi (2.15 M solution in hexanes, 1.20 mL, 3.00 mmol). After 5 min of stirring at −95°C, to the yellow mixture was added dropwise a solution of $ZnBr_2$ (1.0 M in Et_2O, 3.00 mL, 3.00 mmol). The resulting white slurry mixture was warmed to −15°C at which temperature HMPA (5.25 mL, 30.00 mmol) and the sulfinimine (R_S)-**2** (0.50 mmol) in anhydrous Et_2O (2 mL) were successively added. The mixture was stirred at −15°C for 30 min and then warmed to room temperature. After being stirred overnight at this temperature, the solution was quenched by 1 M HCl (25 mL). The layers were separated and the aqueous one extracted with Et_2O (3×25 mL). The combined organic layers were successively washed with 1 M HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL), water (2×10 mL) and brine (10 mL). The resulting organic layer was then dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residual oil was purified by flash chromatography yielding enantiopure *cis*- and *trans*-aziridines (R_S)-**4**.

Addition of 1 onto Sulfinimine (R_S)-2a: GP 2 was followed with sulfinimine (R_S)-**2a** (74 mg, 0.50 mmol). Flash chromatography over silica gel (5→20% Et_2O/pentane) yielded major *cis*- and minor *trans*-aziridines (R_S)-**4a**.

(R_S,2*R*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-methyl-2-trimethylsilylethynylaziridine [*cis*-(R_S)-4a]: Obtained as a yellow solid (83 mg, 0.32 mmol, 64%). M.p. <20°C; $[\alpha]_D = -248.7$ ($c = 1.10$, $CHCl_3$, 20°C); ^1H NMR ($CDCl_3$, 20°C): $\delta = 2.87$–2.81 (m, 1H), 2.72 (d, $J = 6.8$ Hz, 1H), 1.37 (d, $J = 5.8$ Hz, 3H), 1.25 (s, 9H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): $\delta = 100.6$, 88.7, 56.9, 31.1, 28.3, 22.7, 13.2, −0.1; IR (ATR Diamand): $\tilde{\nu} = 2960$ (w), 2929 (w), 2901 (w), 2869 (w), 2176 (w), 1250 (m), 1081 (s), 835 (s), 759 cm^{-1} (m); HRMS: m/z: calcd for $C_{12}H_{24}NOSSi$: 258.1348; found: 258.1340 $[M+H^+]$.

(R_S,2*S*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-methyl-2-trimethylsilylethynylaziridine [*trans*-(R_S)-4a]: Obtained as a pale yellow solid (19 mg, 0.07 mmol, 14%). M.p. 54–56°C; $[\alpha]_D = -97.1$ ($c = 1.25$, $CHCl_3$, 20°C); ^1H NMR ($CDCl_3$, 20°C): $\delta = 2.95$–2.60 (m, 2H), 1.42–1.27 (m, 3H), 1.25 (s, 9H), 0.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): $\delta = 22.8$, 0.0 (missing six carbons); IR (ATR Diamand): $\tilde{\nu} = 3002$ (w), 2960 (w), 2924 (w), 2899 (w), 2865 (w), 2184 (w), 2161 (w), 1247 (m), 1076 (s), 836 (s), 760 cm^{-1} (m); HRMS: m/z: calcd for $C_{12}H_{24}NOSSi$: 258.1348; found: 258.1346 $[M+H^+]$.

Addition of 1 onto sulfinimine (R_S)-2b: GP 2 was followed with sulfinimine (R_S)-**2b** (88 mg, 0.50 mmol). Flash chromatography over silica gel (5→20% Et_2O/pentane) yielded major *cis*- and minor *trans*-aziridines (R_S)-**4b**.

(R_S,2*R*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-propyl-2-trimethylsilylethynylaziridine [*cis*-(R_S)-4b]: Obtained as a yellow oil (77 mg, 0.27 mmol, 54%). $[\alpha]_D = -206.3$ ($c = 1.16$, $CHCl_3$, 20°C); ^1H NMR (C_6D_6, 20°C): $\delta = 2.89$–2.85 (m, 1H), 2.78 (d, $J = 6.8$ Hz, 1H), 1.73–1.66 (m, 2H), 1.48–1.27 (m, 2H), 1.03 (s, 9H), 0.87 (t, $J = 7.3$ Hz, 3H), 0.08 (s, 9H); ^{13}C NMR (C_6D_6, 20°C): $\delta = 102.4$, 89.0, 57.0, 36.1, 31.4, 29.0, 23.1, 20.6, 14.7, 0.4; IR (ATR Diamand): $\tilde{\nu} = 2959$ (m), 2174 (w), 1250 (m), 1082 (s), 839 (s), 759 cm^{-1} (m); HRMS: m/z: calcd for $C_{14}H_{28}NOSSi$: 286.1661; found: 286.1665 $[M+H^+]$.

(R_S,2*S*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-propyl-2-trimethylsilylethynylaziridine [*trans*-(R_S)-4b]: Obtained as a yellow oil (17 mg, 0.06 mmol, 12%). $[\alpha]_D = -115.5$ ($c = 1.16$, $CHCl_3$, 20°C); ^1H NMR ($CDCl_3$, 20°C): $\delta = 2.80$–2.72 (m, 2H), 1.81–1.74 (m, 1H), 1.57–1.40 (m, 3H), 1.26 (s, 9H), 0.98 (t, $J = 7.3$ Hz, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): $\delta = 22.6$, 13.8, −0.2 (missing seven carbons); IR (ATR Diamand): $\tilde{\nu} = 2959$ (m), 272 (w), 2175 (w), 1249 (m), 1080 (s), 840 (s), 759 cm^{-1} (m); HRMS: m/z: calcd for $C_{14}H_{28}NOSSi$: 286.1661; found: 286.1667 $[M+H^+]$.

Addition of racemic allenylzinc 1 onto sulfinimine (R_S)-2c: GP 2 was followed with sulfinimine (R_S)-**2c** (116 mg, 0.50 mmol). Flash chromatography over silica gel (5→20% Et_2O/pentane) yielded major *cis*- and minor *trans*-aziridines (R_S)-**4c**.

(R_S,2*R*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-heptyl-2-trimethylsilylethynylaziridine [*cis*-(R_S)-4c]: Obtained as a yellow oil (96 mg, 0.28 mmol, 56%). $[\alpha]_D = -136.6$ ($c = 1.06$, $CHCl_3$, 20°C); ^1H NMR (C_6D_6, 20°C): $\delta = 2.94$–2.88 (m, 1H), 2.80 (d, $J = 6.6$ Hz, 1H), 1.79–1.72 (m, 2H), 1.51–1.17 (m, 10H), 1.04 (s, 9H), 0.90 (t, $J = 6.8$ Hz, 3H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): $\delta = 101.0$, 88.7, 57.1, 35.9, 32.0, 29.7, 29.4, 28.6, 28.3, 26.5, 22.9, 20.6, 14.3, 0.0; IR (ATR Diamand): $\tilde{\nu} = 2957$ (m), 2925 (w), 2857 (w), 2173 (w), 1249 (m), 1083 (s), 840 (s), 759 cm^{-1} (m); HRMS: m/z: calcd for $C_{18}H_{36}NOSSi$: 342.2287; found: 342.2281 $[M+H^+]$.

(R_S,2*S*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-heptyl-2-trimethylsilylethynylaziridine [*trans*-(R_S)-4c]: Obtained as a yellow oil (27 mg, 0.08 mmol, 16%). $[\alpha]_D = -82.2$ ($c = 1.23$, $CHCl_3$, 20°C); ^1H NMR ($CDCl_3$, 20°C): $\delta = 2.90$–2.62 (m, 2H), 1.81–1.76 (m, 1H), 1.51–1.28 (m, 11H), 1.27 (s, 9H), 0.89 (t, $J = 6.9$ Hz, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): $\delta = 32.0$, 29.5, 29.4, 22.9, 22.8, 14.3, 0.1 (missing seven carbons); IR (ATR Diamand): $\tilde{\nu} = 2957$ (m), 2926 (m), 2857 (m), 2176 (w), 1249 (m), 1081 (s), 840 (s), 759 cm^{-1} (m); HRMS: m/z: calcd for $C_{18}H_{36}NOSSi$: 342.2287; found: 342.2288 $[M+H^+]$.

Addition of 1 onto sulfinimine (R_S)-2d: GP 2 was followed with sulfinimine (R_S)-**2d** (86 mg, 0.50 mmol). Flash chromatography over silica gel (5→20% Et_2O/pentane) yielded major *cis*- and minor *trans*-aziridines (R_S)-**4d**.

[(R_S,2*R*,3*S*)-(*E*)]-(−)-*N*-*tert*-Butanesulfinyl-3-(1-propenyl)-2-trimethylsilylethynylaziridine [*cis*-(R_S)-4d]: Obtained as a yellow oil (77 mg, 0.27 mmol, 55%). $[\alpha]_D = -112.9$ ($c = 1.01$, $CHCl_3$, 20°C); ^1H NMR ($CDCl_3$, 20°C): $\delta = 5.93$ (qd, $J = 6.6$, 15.1 Hz, 1H), 5.42 (ddq, $J = 1.8$, 8.8, 15.1 Hz, 1H), 3.24 (dd, $J = 6.8$, 8.8 Hz, 1H), 2.86 (d, $J = 6.8$ Hz, 1H), 1.81 (dd, $J = 1.8$, 6.6 Hz, 3H), 1.23 (s, 9H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): $\delta = 133.2$, 124.5, 100.5, 89.1, 57.4, 36.4, 28.7, 22.9, 18.2, −0.2; IR (ATR Diamand): $\tilde{\nu} = 2959$ (w), 2901 (w), 2868 (w), 2180 (w), 1250 (m), 1082 (s), 840 (s), 759 cm^{-1} (m); HRMS: m/z: calcd for $C_{14}H_{26}NOSSi$: 284.1504; found: 284.1500 $[M+H^+]$.

[(R_S,2*S*,3*S*)-(*E*)]-(−)-*N*-*tert*-Butanesulfinyl-3-(1-propenyl)-2-trimethylsilylethynylaziridine [*trans*-(R_S)-4d]: Obtained as a yellow solid as a mixture of two invertomers in a 93:7 ratio (19 mg, 0.07 mmol, 13%). M.p. 41–43°C; $[\alpha]_D = -131.9$ ($c = 1.23$, $CHCl_3$, 20°C); ^1H NMR ($CDCl_3$, 20°C): $\delta = 6.02$–5.93 (m, 1H), 5.50–5.03 (m, 1H), 3.19–2.81 (m, 2H), 1.85 (dd, $J = 1.8$, 6.8 Hz, 3H minor invertomer), 1.76 (dd, $J = 1.5$, 6.4 Hz, 3H for the major invertomer), 1.27 (s, 9H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): $\delta = 23.0$, 18.3, 0.0 (missing seven carbons); IR (ATR Diamand):

$\tilde{\nu}$ = 2958 (w), 2173 (w), 1249 (m), 1078 (s), 840 (s), 759 cm^{-1} (m); HRMS: *m*/*z*: calcd for $C_{14}H_{26}NOSSi$: 284.1504; found: 284.1507 [*M*+H$^+$].

Addition of 1 onto sulfinimine (R_S)-2e: GP 2 was followed with sulfinimine (R_S)-**2e** (115 mg, 0.50 mmol). Flash chromatography over silica gel (5→15% Et_2O/pentane) yielded major *cis*- and minor *trans*-aziridines (R_S)-**4e**.

[(R_S,2*R*,3*S*)-(*E*)]-(−)-*N*-*tert*-Butanesulfinyl-3-(1-heptenyl)-2-trimethylsilylethynylaziridine [*cis*-(R_S)-4e]: Obtained as a yellow oil (105 mg, 0.31 mmol, 62%). $[\alpha]_D$ = −60.9 (*c* = 1.08, $CHCl_3$, 20°C); ^{1}H NMR ($CDCl_3$, 20°C): δ = 5.93 (td, *J* = 6.8, 15.7 Hz, 1H), 5.38 (ddt, *J* = 1.3, 8.9, 15.7 Hz, 1H), 3.24 (dd, *J* = 6.6, 8.9 Hz, 1H), 2.86 (d, *J* = 6.6 Hz, 1H), 2.11 (qd, *J* = 1.3, 6.6 Hz, 2H), 1.45–1.37 (m, 2H), 1.33–1.26 (m, 4H), 1.22 (s, 9H), 0.90 (t, *J* = 6.8 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): δ = 138.8, 123.2, 100.6, 89.0, 57.4, 36.6, 32.5, 31.3, 28.8, 28.6, 22.9, 22.5, 14.1, −0.1; IR (ATR Diamand): $\tilde{\nu}$ = 2957 (m), 2926 (m), 2858 (w), 2174 (w), 1731 (w), 1666 (w), 1250 (m), 1082 (s), 841 (s), 759 cm^{-1} (m); HRMS: *m*/*z*: calcd for $C_{18}H_{34}NOSSi$: 340.2130; dound: 340.2134 [*M*+H$^+$].

[(R_S,2*S*,3*S*)-(*E*)]-(−)-*N*-*tert*-Butanesulfinyl-3-(1-heptenyl)-2-trimethylsilylethynylaziridine [*trans*-(R_S)-4e]: Obtained as a yellow oil (35 mg, 0.11 mmol, 21%). $[\alpha]_D$ = −95.7 (*c* = 1.05, $CHCl_3$, 20°C); ^{1}H NMR ($CDCl_3$, 20°C): δ = 6.02–5.88 (m, 1H), 5.45–4.90 (m, 1H), 3.33–2.71 (m, 2H), 2.07 (q, *J* = 6.8 Hz, 2H), 1.40–1.17 (m, 17H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): δ = 31.3, 30.4, 28.7, 22.8, 22,5, 14.1, −0.1 (missing seven carbons); IR (ATR Diamand): $\tilde{\nu}$ = 2957 (m), 2926 (m), 2858 (w), 2177 (w), 1730 (w), 1249 (m), 1078 (s), 841 (s), 760 cm^{-1} (m); HRMS: *m*/*z*: calcd for $C_{18}H_{34}NOSSi$: 340.2130; found: 340.2127 [*M*+H$^+$].

Addition of 1 onto sulfinimine (R_S)-2f: GP 2 was followed with sulfinimine (R_S)-**2f** (118 mg, 0.50 mmol). Flash chromatography over silica gel (5→20% Et_2O/pentane) yielded major *cis*- and minor *trans*-aziridines (R_S)-**4f**.

[(R_S,2*R*,3*S*)-(*E*)]-(+)-*N*-*tert*-Butanesulfinyl-3-(2-phenylethenyl)-2-trimethylsilylethynylaziridine [*cis*-(R_S)-4f]: Obtained as a pale yellow solid (96 mg, 0.28 mmol, 56%). M.p. 116–120°C (decomp); $[\alpha]_D$ = +15.9 (*c* = 1.10, $CHCl_3$, 20°C); ^{1}H NMR ($CDCl_3$, 20°C): δ = 7.44–7.38 (m, 2H), 7.38–7.29 (m, 3H), 6.82 (d, *J* = 16.2 Hz, 1H), 6.17 (dd, *J* = 8.8, 16.2 Hz, 1H), 3.44 (dd, *J* = 6.6, 8.8 Hz, 1H), 2.99 (d, *J* = 6.6 Hz, 1H), 1.26 (s, 9H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): δ = 136.3, 136.2, 128.7, 128.2, 126.5, 123.0, 100.3, 89.5, 57.6, 36.8, 29.3, 22.9, −0.1; IR (ATR Diamand): $\tilde{\nu}$ = 3034 (w), 2984 (w), 2954 (w), 2898 (w), 2867 (w), 2167 (w), 1655 (w), 1598 (w), 1578 (w), 1250 (m), 1077 (s), 841 (s), 758 cm^{-1} (m); HRMS: *m*/*z*: calcd for $C_{19}H_{28}NOSSi$: 346.1661; found: 346.1667 [*M*+H$^+$].

[(R_S,2*S*,3*S*)-(*E*)]-(−)-*N*-*tert*-Butanesulfinyl-3-(2-phenylethenyl)-2-trimethylsilylethynylaziridine [*trans*-(R_S)-4f]: Obtained as a pale yellow solid (26 mg, 0.08 mmol, 15%). M.p. 113–116°C (decomp); $[\alpha]_D$ = −231.3 (*c* = 1.01, $CHCl_3$, 20°C); ^{1}H NMR (C_6D_6, 20°C): δ = 7.40–7.28 (m, 5H), 6.83 (br d, *J* = 15.7 Hz, 1H), 6.30–5.77 (m, 1H), 3.60–2.87 (m, 2H), 1.28 (s, 9H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): δ = 136.2, 128.9, 128.4, 126.8, 23.0, 0.1 (missing seven carbons); IR (ATR Diamand): $\tilde{\nu}$ = 3027 (w), 2957 (w), 2169 (w), 1598 (w), 1578 (w), 1250 (m), 1071 (s), 839 (s), 758 cm^{-1} (m); HRMS: *m*/*z*: calcd for $C_{19}H_{28}NOSSi$: 346.1661; found: 346.1663 [*M*+H$^+$].

Addition of 1 onto sulfinimine (R_S)-2g: GP 2 was followed with sulfinimine (R_S)-**2g** (119 mg, 0.50 mmol). Flash chromatography over silica gel (5→20% Et_2O/pentane) yielded major *cis*- and minor *trans*-aziridines (R_S)-**4g**.

(R_S,2*R*,3*S*)-(−)-N-tert-Butanesulfinyl-3-(2-phenylethyl)-2-trimethylsilylethynylaziridine [*cis*-(R_S)-4g]: Obtained as a pale yellow solid (86 mg, 0.25 mmol, 50%). M.p. 54–56°C; $[\alpha]_D$ = −129.9 (*c* = 0.91, $CHCl_3$, 20°C); ^{1}H NMR (C_6D_6, 20°C): δ = 7.19–7.05 (m, 5H), 2.95–2.89 (m, 1H), 2.78 (d, *J* = 6.6 Hz, 1H), 2.76–2.70 (m, 1H), 2.53–2.46 (m, 1H), 2.07–1.95 (m, 2H), 0.99 (s, 9H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$, 20°C): δ = 141.2, 128.5, 128.3, 126.1, 100.5, 88.8, 57.0, 35.2, 32.6, 30.7, 28.1, 22.6, −0.1; IR (ATR Diamand): $\tilde{\nu}$ = 3028 (w), 2961 (w), 2927 (w), 2864 (w), 2171 (w), 1603 (w), 1249 (m), 1080 (s), 836 (s), 762 cm^{-1} (m); HRMS: *m*/*z*: calcd for $C_{19}H_{30}NOSSi$: 348.1817; found: 348.1821 [*M*+H$^+$].

(R_S,2*S*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-(2-phenylethyl)-2-trimethylsilylethynylaziridine [*trans*-(R_S)-4g]: Obtained as a white solid (35 mg, 0.10 mmol, 20%). M.p. 103–106°C; $[\alpha]_D$ = −118.7 (*c* = 0.90, $CHCl_3$, 20°C).

^{1}H NMR ($CDCl_3$):

at +20°C: δ = 7.33–7.27 (m, 2H), 7.27–7.18 (m, 3H), 2.90–2.63 (m, 5H), 2.15–2.07 (m, 1H), 1.26 (s, 9H), 0.18 (s, 9H);

at −20°C (as a mixture of two invertomers 64:36): δ = 7.33–7.27 (m, 2H, major and minor invertomers), 7.27–7.18 (m, 3H, major and minor invertomers), 2.93 (d, *J* = 3.8 Hz, 1H minor invertomer), 2.91–2.87 (m, 2H minor invertomer), 2.84–2.72 (m, 2H major invertomer), 2.70 (d, *J* = 3.3 Hz, 1H major invertomer), 2.69–2.60 (m, 1H, minor invertomer), 2.19–2.14 (m, 1H, major invertomer), 2.13–1.98 (m, 1H, major invertomer), 1.58–1.43 (m, 1H, major invertomer), 1.45–1.40 (m, 1H minor invertomer), 1.27(s, 9H, minor invertomer), 1.25 (s, 9H, major invertomer), 0.18 (s, 9H, major invertomer), 0.15 (s, 9H, minor invertomer);

^{13}C NMR ($CDCl_3$):

at +20°C: δ = 128.7, 128.6, 126.4, 28.8, 0.0 (missing eight carbons);

at +40°C: δ = 140.8, 128.4, 128.3, 126.1, 57.0, 33.0, 31.6, 22.6, −0.3 (missing four carbons);

at −50°C (as a mixture of two invertomers): δ = 141.2 (major invertomer), 140.9 (minor invertomer), 128.9 (minor invertomer), 128.84 (major invertomer), 128.81 (minor invertomer), 128.6 (major and minor invertomers), 126.4 (major invertomer), 102.3 (minor invertomer), 99.3 (major invertomer), 92.8 (major invertomer), 86.7 (minor invertomer), 58.2 (minor invertomer), 57.1 (major invertomer), 45.3 (minor invertomer), 38.2 (major invertomer), 34.0 (minor invertomer), 33.6 (major invertomer), 32.5 (major invertomer), 31.5 (major invertomer), 30.0 (minor invertomer), 23.9 (minor invertomer), 22.9 (minor invertomer), 22.7 (major invertomer), 0.1 (minor invertomer), 0.0 (major invertomer);

IR (ATR Diamand): $\tilde{\nu}$ = 3058 (w), 3025 (w), 3001 (w), 2959 (w), 2922 (w), 2860 (w), 2177 (w), 1601 (w), 1250 (m), 1080 (s), 836 (s), 758 cm^{-1} (m); HRMS: *m*/*z*: calcd for $C_{19}H_{30}NOSSi$: 348.1817; found: 348.1820 [*M*+H$^+$].

Addition of 1 onto sulfinimine (R_S)-2h: GP 2 was followed with sulfinimine (R_S)-**2h** (114 mg, 0.50 mmol). Flash chromatography over silica gel (5→10% Et_2O/pentane) yielded major *cis*- and minor *trans*-aziridines (R_S)-**4h**.

(R_S,2*R*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-(1-heptynyl)-2-trimethylsilylethynylaziridine [*cis*-(R_S)-4h]: Obtained as a pale yellow oil (101 mg, 0.30 mmol, 60%). $[\alpha]_D$ = −129.7 (*c* = 1.03, $CHCl_3$, 20°C); ^{1}H NMR (C_6D_6, 20°C): δ = 3.51 (td, *J* = 1.8, 6.3 Hz, 1H), 2.80 (d, *J* = 6.3 Hz, 1H), 2.02 (dt, *J* = 1.8, 7.1 Hz, 2H), 1.41–1.34 (m, *J* = 6.6 Hz, 2H), 1.28–1.14 (m, 4H), 1.07 (s, 9H), 0.82 (t, *J* = 7.1 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (C_6D_6, 20°C): δ = 101.5, 89.7, 85.5, 75.2, 58.0, 31.7, 29.8, 29.2, 26.6, 23.2, 23.0, 19.6, 14.7, 0.4; IR (ATR Diamand): $\tilde{\nu}$ = 2957 (m), 2931 (w), 2862 (w), 2240 (w), 2170 (w), 1250 (m), 840 (s), 760 (m) cm^{-1}; HRMS: *m*/*z*: calcd for $C_{18}H_{32}NOSSi$: 338.1974; found: 338.1975 [*M*+H$^+$].

(R_S,2*S*,3*S*)-(−)-*N*-*tert*-Butanesulfinyl-3-(1-heptynyl)-2-trimethylsilylethynylaziridine [*trans*-(R_S)-4h]: Obtained as a yellow oil (46 mg, 0.14 mmol, 27%). $[\alpha]_D$ = −110.2 (*c* = 1.11, $CHCl_3$, 20°C); ^{1}H NMR (C_6D_6, 20°C): δ = 3.31–2.98 (m, 2H), 2.21–2.19 (m, 2H), 1.54–1.40 (m, 2H), 1.38–1.30 (m, 3H), 1.29 (s, 9H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (C_6D_6, 20°C): δ = 66.6, 57.7, 30.9, 28.1, 22.7, 22.1, 18.7, 14.0, 0.0 (missing five carbons); IR (ATR Diamand): $\tilde{\nu}$ = 2957 (m), 2931 (w), 2862 (w), 2240 (w), 2170 (w), 1250 (m), 840 (s), 760 (m) cm^{-1}; HRMS: *m*/*z*: calcd for $C_{18}H_{32}NOSSi$: 338.1974; found: 338.1980 [*M*+H$^+$].

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