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Stereoselective Synthesis of Chiral Amino Allenes by Organocopper-Mediated *anti*-S_N2'-Substitution Reaction of Chiral Ethynylaziridines

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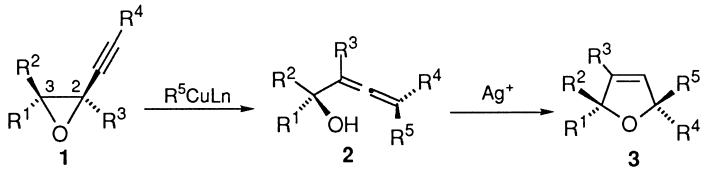
Abstract—Chiral *N*-protected amino allenes have been synthesized from 3-alkyl-2-ethynylaziridines via organocopper-mediated reactions. Treatment of enantiomerically pure (2*R*,3*S*)-2,3-*trans*-3-alkyl-2-ethynylaziridines with RCu(CN)M (M=Li or MgX) in THF at −78°C affords exclusively the expected (*S*,*S*)-amino allenes in high yields in a regio- and stereoselective manner. On the other hand, (2*S*,3*S*)-2,3-*cis*-3-alkyl-2-ethynylaziridines give stereoisomeric (*S*,*R*)-amino allenes in comparable high yields.

The stereochemical course of organocopper-mediated S_N2' substitution of propargylic compounds has been well documented.[1,2] Propargylic ethers,[3a] thio ethers,[3b] esters,[4] and sulfonates[5] usually undergo highly stereoselective *anti*-facial reactions; i.e. the S_N2' displacement generally proceeds *anti* to the leaving group (*anti*-S_N2' reactions). The organocopper-mediated ring-opening reaction of propargylic epoxides also affords the corresponding hydroxy allenes in a highly regio- and *anti*-S_N2'-selective manner.[6] The hydroxy allenes have been used as key intermediates in various subsequent chemical transformations.[7] Recently, Marshall and co-workers elegantly demonstrated that the hydroxy allenes could be cyclized to 2,5-dihydrofurans, important structural units of poly ether antibiotics [8] and various polyene mycotoxins,[9] in a highly regio- and stereo-selective manner (Scheme 1).[10] Interestingly, it has been reported by Alexakis et al. that the S_N2' displacement of the propargylic epoxides or ethers can lead to either *anti* or *syn* products, depending on the reaction conditions or copper reagents used.[3,11]

On the other hand, amino allenes, the aza-analogs of hydroxy allenes, are also an important class of molecules with highly reactive chemical properties due to their cumulated double bonds.[12] Allenic compounds bearing a nitrogen functionality separated from the allenic carbon atom by one,[13] three,[14] and four[15] carbon atoms are attractive substrates for constructing five- and six-membered azaheterocycles.[13d,14a–e,15,16]

Recently, highly strained compounds like azacyclopropanes[17] and azacyclobutanes[14d,18,19] have been successfully synthesized from amino allenes via palladium-catalyzed cyclization reactions. However, except for a few cases,[13g,i] a scan of the literature has revealed a surprising paucity of methods that facilitate the synthesis of chiral



Scheme 1.

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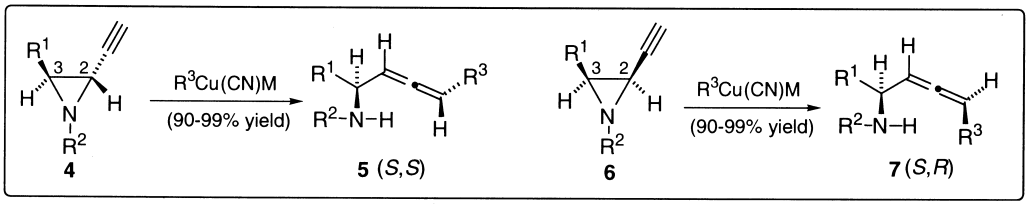


Scheme 2. Synthesis of amino allenes via an organocopper-mediated reaction; abbreviations: M=Li or MgBr; R^1=alkyl; R^2=arylsulfonyl; R^3=alkyl or tri-*n*-butylstannyl.

internal allenes bearing a nitrogen functionality separated from the allenic carbon atom only by one carbon atom.

In connection with a program directed towards the reaction of chiral amino allenes, we required a reliable procedure for the synthesis of internal amino allenes like **5** and **7** with high optical purity (Scheme 2). It is of considerable interest to determine whether chiral ethynylaziridines can be transformed diastereoselectively into chiral amino allenes. We wish to report a highly efficient ring-opening reaction of chiral 2,3-*trans*- and 2,3-*cis*-ethynylaziridines **4** and **6**[20] affording the corresponding (*S*,*S*)- and (*S*,*R*)-amino allenes **5** and **7** in both excellent isolated yields and high diastereoisomeric purities as illustrated in Scheme 2.[21]

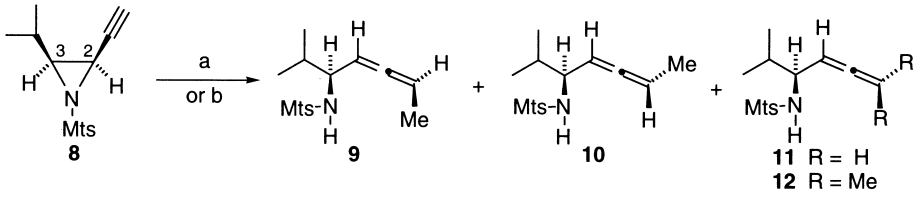
Results and Discussion

The requisite *N*-arylsulfonylated 2,3-*trans*- and 2,3-*cis*-3-alkyl-2-ethynylaziridines **8**, **16**, **20**–**25**, ***ent*-8**, ***ent*-16**, **34**–**37** with high optical purities for the present study were prepared in a straightforward manner from natural α-amino acids following our recently published procedures.[20] It is well known that the reactivity of NH-aziridines towards nucleophilic reagents is relatively low: hence, activation by the introduction of a strong electron-withdrawing protective group on the nitrogen atom of the aziridine is required. 2,4,6-Trimethylbenzenesulfonyl (Mts) or 4-methoxy-2,3,6-trimethylbenzenesulfonyl (Mtr) serves as an effective activating group. In addition, the Mts or Mtr group can withstand a wide range of chemical manipulations and yet be removed by the use of Yajima's protocol.[22]

Except for a few exceptional cases,[11] it has been well-documented that treatment of propargylic oxiranes with Gilman-type reagents afford the expected allenyl alcohols via an *anti*-S_N2' pathway.[6b,7,10b,c] Accordingly, we initiated our study to determine the scope of the organocopper-mediated ring-opening reaction using 2,3-*cis*-2-ethynylaziridine **8** with some organocopper reagents as shown in Scheme 3 and Table 1. The reaction of **8** in THF with Gilman-type reagent, $Me_2CuLi{\cdot}3LiI$, afforded a separable mixture of **9** (an *anti*-S_N2' product), **10** (a *syn*-S_N2' product), and **11** (a reduction product) in favor of the unexpected product **11** (entry 1, Table 1). In a similar manner, exposure of **8** to $Me_2CuLi{\cdot}LiCN{\cdot}2LiBr{\cdot}2LiCl$[23] yielded a mixture of **9**, **10**, and the dimethylated compound **12** (entry 2, Table 1).

Claeson and Olsson had previously reported that certain allenes were racemized by treatment with organocuprates.[24] However, this was not to be the present case since exposure of the chiral allene **9** or **10** to $Me_2CuLi{\cdot}LiCN{\cdot}2LiCl$ completely recovered the starting allene **9** or **10** unchanged. In the reactions of certain propargylic epoxides[11] with organocopper reagents, it has been frequently documented that small changes in the reaction conditions (solvents and organocopper reagents) and substrate structure can alter the course of reactions. Although it was not surprising that the reaction of **8** with $Me_2CuLi{\cdot}3LiI$ yielded a large amount of a reduction product **11** as the major product, the occurrence of the dimethylated product **12** by the reaction of **8** with $Me_2CuLi{\cdot}LiCN{\cdot}2LiBr{\cdot}2LiCl$ is an unprecedented striking example. For reasons we cannot explain, classical Gilman-type organocuprates and $R_2CuLi{\cdot}LiCN{\cdot}2LiCl$ gave mixtures containing little, if any, of the expected product **9** (Scheme 3).

After considerable experimentation, it was found that organocyanocuprates, $RCu(CN)M{\cdot}nLiX$ (M=Li or MgBr, X=Cl or Br), are the reagent of choice for the ring-opening reactions, giving excellent isolated yields of the corresponding *anti*-S_N2' products (Scheme 4). Typically, reaction of the aziridine **8** with $MeCu(CN)Li{\cdot}LiBr{\cdot}2LiCl$ in THF at −78°C for 3 h yielded the expected diastereomerically pure amino allene **9** (an *anti*-S_N2' product) as the single isomer in 93% isolated yield (entry 3, Table 1). While we cannot conclusively rule out the presence of trace quantities of isomeric- or reduction-products, the (*S*,*R*) product **9** was the only one detected by HPLC analysis. Similarly, exposure of **8** to *i*-PrCu(CN)MgBr·2LiCl, *n*-BuCu(CN)Li·2LiCl, and *n*-$Bu_3SnCu(CN)Li{\cdot}2LiCl$ yields the corresponding ring-opened products **13**, **14**, and **15** in high yields (entries 4–6, Table 1). The 2,3-*trans*-isomer **16** also gave exclusively the *anti*-S_N2' products **10**, **17**, **18**, and **19** (Scheme 4 and entries 7–10, Table 1).



Scheme 3. Reagents and abbreviations: a=$Me_2CuLi{\cdot}3Lil$; b=$Me_2CuLiCN{\cdot}2LiBr{\cdot}2LiCl$; Mts=2,4,6-trimethylbenzenesulfonyl.

Table 1. Reactions of some 2-ethynylaziridines with organocopper reagents (all reactions were carried out in THF at −78°C using 4 equiv. of the organocopper reagent)

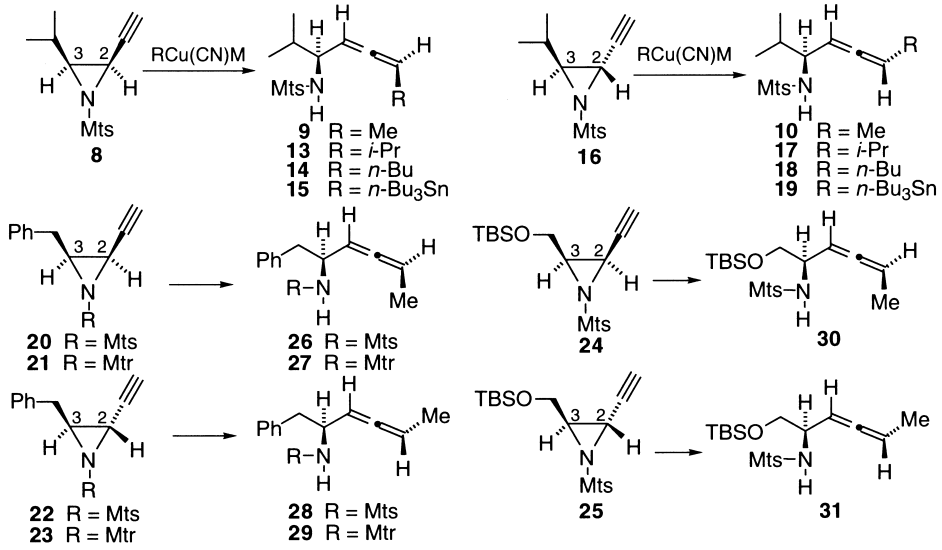
Entry	Substrate	Reagent	Reaction time (h)	Product(s)	Abs. config.	$[\alpha]_D$[a]	Ratio[b]	Yield (%)[c]
1	**8**	$Me_2CuLi{\cdot}3LiI$	0.5	**9**+**10**+**11**			**9**:**10**:**11**=25:2:73	78
2	**8**	$Me_2CuLi{\cdot}LiCN{\cdot}2LiBr{\cdot}2LiCl$	0.5	**9**+**10**+**12**			**9**:**10**:**12** 45:18:37	72
3	**8**	MeCu(CN)Li·LiBr·2LiCl	3.0	**9**	(*S*,*R*)	−73	**9**=100	93
4	**8**	*i*-PrCu(CN)MgCl·2LiCl	0.5	**13**	(*S*,*R*)	−102	**13**=100	99
5	**8**	*n*-BuCu(CN)Li·2LiCl	0.5	**14**	(*S*,*R*)	−108	**14**=100	97
6	**8**	$Bu_3SnCu(CN)Li{\cdot}2LiCl$	0.5	**15**	(*S*,*R*)	−236	**15**=100	90
7	**16**	MeCu(CN)Li·LiBr·2LiCl	0.5	**10**	(*S*,*S*)	+36	**10**=100	98
8	**16**	*i*-PrCu(CN)MgCl·2LiCl	0.5	**17**	(*S*,*S*)	+86	**17**=100	98
9	**16**	*n*-BuCu(CN)Li·2LiCl	0.5	**18**	(*S*,*S*)	+77	**18**=100	99
10	**16**	$Bu_3SnCu(CN)Li{\cdot}2LiCl$	0.5	**19**	(*S*,*S*)	+183	**19**=100	92
11	**20**	MeCu(CN)Li·LiBr·2LiCl	2	**26**	(*S*,*R*)	−63	**26**=100	96
12	**21**	MeCu(CN)Li·2LiCl	6	**27**	(*S*,*R*)	−73	**27**=100	99
13	**22**	MeCu(CN)Li·LiBr·2LiCl	0.5	**28**	(*S*,*S*)	+25	**28**=100	99
14	**23**	MeCu(CN)Li·2LiCl	0.5	**29**	(*S*,*S*)	+9	**29**=100	97
15	**24**	MeCu(CN)Li·2LiCl	[d]	**30**	(*R*,*R*)	−41	**30**=100	99
16	**25**	MeCu(CN)Li·2LiCl	0.5	**31**	(*R*,*S*)	+27	**31**=100	98
17	***ent*-8**	MeCu(CN)Li·LiBr·2LiCl	1.2	***ent*-9**	(*R*,*S*)	+77	***ent*-9**=100	88
18	***ent*-8**	EtCu(CN)MgBr·2LiCl	0.7	**32**	(*R*,*S*)	+99	**32**=**100**	89
19	***ent*-16**	MeCu(CN)Li·2LiCl	0.5	***ent*-10**	(*R*,*R*)	−38	***ent*-10**=100	90
20	***ent*-16**	EtCu(CN)MgBr·2LiCl	0.7	**33**	(*R*,*R*)	−64	**33**=100	97

[a] Optical rotations were measured in chloroform.
[b] Ratios were determined by isolation or HPLC.
[c] Isolated yields.
[d] −78°C (1 h) then −78°C to −20°C (1 h).

As shown in Scheme 4 and Table 1 (entries 11–16), the 2,3-*cis*- and *trans*-aziridines (**20** and **21**) and (**22** and **23**) prepared from (*S*)-phenylalanine as well as 2,3-*cis*- and *trans*-aziridines **24** and **25** synthesized from (*S*)-serine also gave the corresponding amino allenes in good yields by treatment with methylcyanocuprate. Thus, the described methodology involving the organocyanocuprate-mediated reaction clearly has several advantages over other methods in terms of mildness, selectivity, efficiency and convenience.

Although the absolute configuration listed in Table 1 of all the amino allenes synthesized could be deduced from the well-established organocyanocuprate-mediated *anti*-S_N2' pathway, the unambiguous structure assignment for **28** rested on X-ray analysis.[25] The X-ray data are consistent with a net *anti*-S_N2' substitution reaction. As can be seen from Fig. 1, in the solid-state, the phenyl ring of the benzyl group was folded over the allenic group. Such folding has also been reported for various compounds involving a benzyl group and a carbon–carbon double bond[26] and it has been suggested that the folded conformation would be stabilized by intramolecular dipole–dipole interactions generally referred to as π-stacking.

Mitochondrial monoamine oxidase (MAO) is a flavin-linked enzyme that is responsible for the oxidative inactivation of the transmitter amines.[27] An allenic amine **34** is a typical known irreversible inhibitor of MAO.[28] For the purpose of synthesis of bioactive compounds, the amino allenes ***ent*-9**, ***ent*-10**, **32**, and **33** have also been synthesized in high yields and diastereoisomeric purities from the



Scheme 4. Abbreviations: Mts=2,4,6-trimethylbenzenesulfonyl; Mtr=4-methoxy-2,4,6-trimethylbenzenesulfonyl. For organocopper reagents, see Table 1.

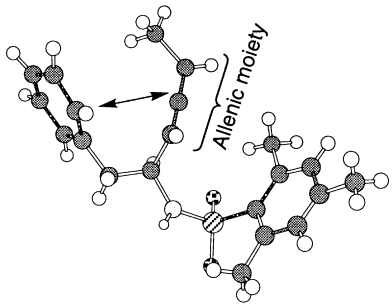


Figure 1. Solid-state conformation of **28**.

corresponding ethynylaziridines ***ent*-8** and ***ent*-16** (Scheme 5; entries 17–20, Table 1).

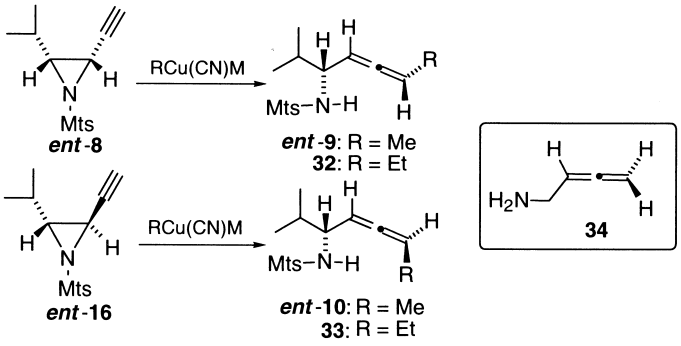
It has been shown by Alexakis, Normant and co-workers that some propargylic epoxides react with copper(I)-catalyzed Grignard reagents to afford α-allenic alcohols. The reaction has been reported to be highly diastereoselective and its stereochemical outcome (*syn*- or *anti*-isomer) has been fully controlled. In an attempt to study those factors which influence the product distribution, we briefly examined the effects of reaction condition parameters on the composition of products. The reaction of two aziridines **8** and **16** with *n*-BuMgCl was investigated under otherwise identical conditions to those reported by Alexakis[11b] (Scheme 6). The two reactions shown in Scheme 6 yielded in each case a mixture of two S_N2' products in favor of the *anti*-S_N2' product. In view of the low *syn*-S_N2' diastereoselectivity, this aspect of the study was not pursued further (Scheme 6).

Next, we examined the ring-opening reaction of alkynylaziridines **34**–**37** bearing a methoxycarbonyl or trimethylsilyl functionality on the terminal sp carbon atom (Schemes 7 and 8). Considerable difference was observed between the reactions of 2,3-*cis*- and 2,3-*trans*-aziridines with methylcyanocuprate.

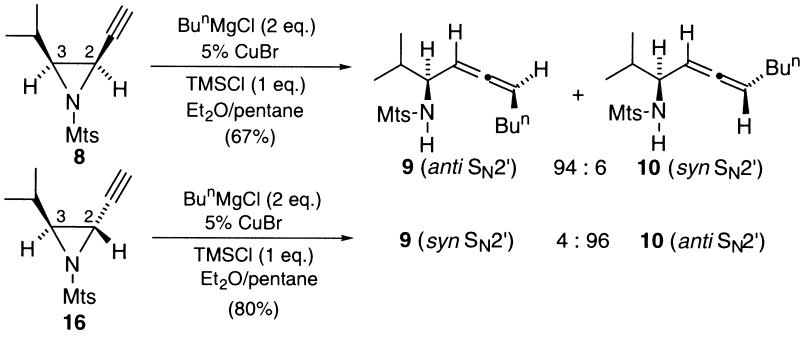
Thus, whereas treatment of 2,3-*cis*-aziridine **34** bearing a methoxycarbonyl group with MeCu(CN)Li gave a mixture of three products **38** (an *anti*-S_N2' product), **39** (a *syn*-S_N2' product), and **40** in variable ratios, exposure of 2,3-*cis*-aziridine **35** having a trimethylsilyl group to MeCu(CN)Li afforded a mixture of two products **41** and **42** (Scheme 7). It should be clearly noted that the reaction of **35** with methylcyanocuprate was very slow at −78°C and did not proceed to completion. Consequently, the reaction mixture was allowed to warm to 0°C and stirred for 1.5 h.

On the other hand, as shown in Scheme 8, 2,3-*trans*-aziridines **36** and **37** afford exclusively the *anti*-S_N2' products **39** and **43**, respectively, in high yields and high diastereomeric purities. Reaction time of 30 min at −78 to −20°C was sufficient for complete conversion of the 2,3-*trans*-alkynylaziridine **37** into the amino allene **43**.

Finally, we examined ring-opening reactions of ethynyl azacyclobutanes **44** and **45** under a number of different conditions and with a number of organocopper reagents in hopes of synthesizing amino allenes. In both cases, we obtained substantial amounts of the unchanged starting materials; however, there was no sign in any of these experiments of any quantities of the expected amino allenes. There



Scheme 5.



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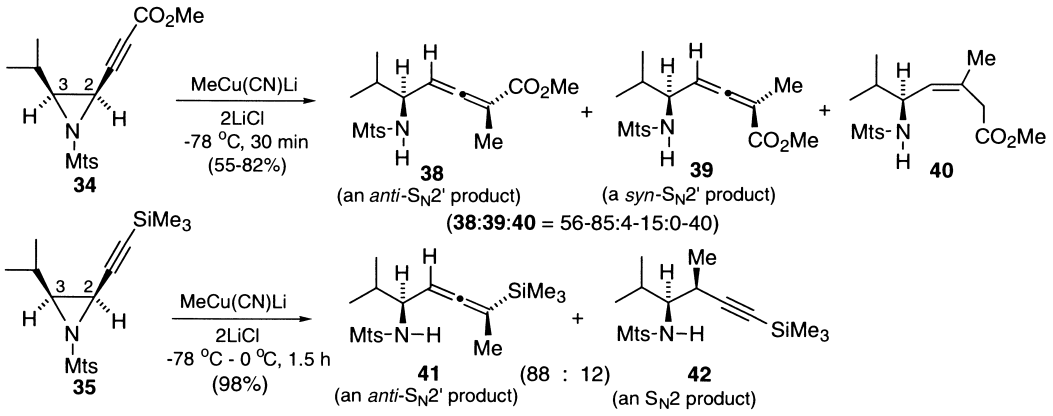
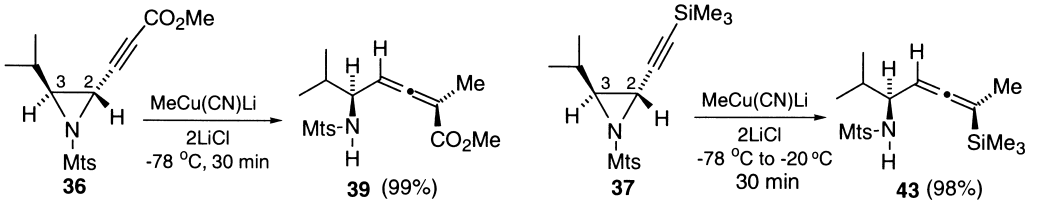
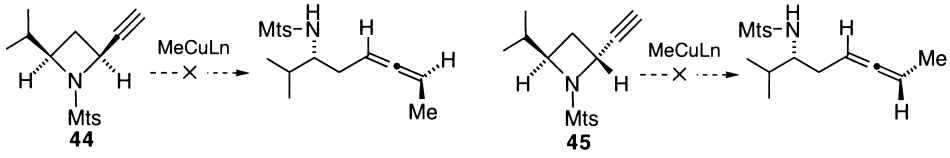


Scheme 7.



Scheme 8.



Scheme 9.

is, therefore, little hope of using *N*-protected ethynyl azacyclobutanes for amino allene formation (Scheme 9).

In summary, chiral amino allenes with high optical purity have been synthesized from (2*R*,3*S*)-2,3-*cis*- or (2*S*,3*S*)-2,3-*trans*-2-ethynylaziridines via organocopper-mediated reactions. Work on synthetic transformations of amino allenes thus obtained is in progress and will be reported elsewhere in due course.

Experimental

General methods

All reactions were carried out under a positive pressure of argon, and glassware and syringes were dried in an electric oven at 100°C prior to use. Melting points are uncorrected. Nominal (LRMS) and exact mass (HRMS) spectra were recorded on a JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. ^{1}H NMR spectra (270 or 300 MHz) were recorded in $CDCl_3$ unless otherwise specified. Chemical shifts are reported in parts per million downfield from internal Me_4Si (s=singlet, d=doublet, dd =double doublet, ddd=doublet of double doublet, t=triplet, m=multiplet). Optical rotations were measured in $CHCl_3$ with a JASCO DIP-360 digital polarimeter. For flash chromatography, silica gel 60 H (silica gel for thin-layer chromatography, Merck) or silica gel 60 (finer than 230 mesh, Merck) was employed. For HPLC, μ-bondasphere-C18 (3.9×150 mm, Merck) was employed.

General procedure for RCu(CN)Li·*n*LiX-mediated ring-opening reaction of 3-alkyl-2-ethynylaziridines (Table 1, entry 3–20). Synthesis of (5*S*,a*R*)-6-methyl-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-2,3-heptadiene (9) (Table 1, entry 3) from the aziridine (8). To a stirred solution of CuCN (71.6 mg, 0.8 mmol) and LiCl (67.7 mg, 1.6 mmol) in dry THF (1 mL) under argon was added by syringe MeLi·LiBr (1.5 M solution in Et_2O; 0.53 mL, 0.8 mmol) at −78°C, and the mixture was stirred for 10 min with warming to 0°C. The aziridine **8** (58.3 mg, 0.2 mmol) in dry THF (0.5 mL) was added to the above stirred reagent at −78°C, and the stirring was continued for 3 h followed by quenching with a solution of 1:1 saturated NH_4Cl–28% NH_4OH (2 mL). The mixture was extracted with Et_2O and the extract was washed with water and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane/EtOAc (5:1) gave the title compound **9** (57 mg, 93% yield) as colorless crystals from *n*-hexane. Mp 63°C. $[\alpha]_D^{22}=-73.4$ (c=0.638, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.81 (d, J=6.5 Hz, 3H), 0.86 (d, J=7.0 Hz, 3H),

1.56 (dd, J=7.0, 3.0 Hz, 3H), 1.75–1.87 (m, 1H), 2.29 (s, 3H), 2.64 (s, 6H), 3.53–3.62 (m, 1H), 4.55 (d, J=8.1 Hz, 1H), 4.83–4.91 (m, 1H), 5.02–5.13 (m, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.3, 18.1, 18.3, 21.1, 23.3, 33.2, 58.0, 89.4, 90.2, 132.1, 135.0, 139.1, 142.1, 203.9. LRMS (FAB) m/z, 308 (MH^+), 306, 264, 254, 200, 183, 167, 119 (base peak), 109, 91. HRMS (FAB) m/z, calcd for $C_{17}H_{26}NO_2S$ (MH^+) 308.1684; found: 308.1679.

(5*S*,a*S*)-6-Methyl-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)-amino]-2,3-heptadiene (10) (Table 1, entry 7). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **16** (1.02 g, 3.5 mmol) was converted into the title compound **10** (1.05 g, 98% yield) by treatment with MeCu(CN)-Li·LiBr·2LiCl at −78°C for 30 min. Compound **10**: colorless crystals from cold *n*-hexane. Mp 36°C. $[\alpha]_D^{23}$=+35.8 (c=1.68, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.84 (d, J=6.8 Hz, 3H), 0.86 (d, J=7.0 Hz, 3H), 1.56 (dd, J=6.8, 3.2 Hz, 3H), 1.75–1.89 (m, 1H), 2.29 (s, 3H), 2.64 (s, 6H), 3.54–3.61 (m, 1H), 4.59 (d, J=8.4 Hz, 1H), 4.87–4.96 (m, 1H), 5.02–5.14 (m, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.4, 18.0, 18.2, 21.1, 23.4, 33.3, 57.5, 89.9, 90.3, 132.1, 135.0, 139.0, 142.1, 203.5. LRMS (FAB) m/z, 308 (MH^+), 306, 264, 254, 200, 183, 167, 119 (base peak), 109, 91. HRMS (FAB) m/z, calcd for $C_{17}H_{26}NO_2S$ (MH^+) 308.1684; found: 308.1687.

Reaction of 2-ethynylaziridine (8) with Me_2CuLi·3LiI (Table 1, entry 1). (4*S*)-5-Methyl-4-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-1,2-hexadiene (11). To a stirred suspension of CuI (152 mg, 0.8 mmol) in dry THF (1 mL) under argon was added by syringe MeLi·LiI (0.90 M solution in Et_2O; 1.78 mL, 1.6 mmol) at −78°C, and the mixture was stirred for 10 min with warming to 0°C. The aziridine **8** (58.3 mg, 0.2 mmol) in THF (0.5 mL) was added to the above stirred reagent at −78°C, and the stirring was continued for 30 min followed by quenching with a solution of 1:1 saturated NH_4Cl–28% NH_4OH (2 mL). The mixture was extracted with Et_2O and the extract was washed with water and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane/EtOAc (8:1) gave a mixture of amino allenes **9**, **10**, and **11** (48 mg, 78% combined yield; **9**:**10**:**11**=25:2:73, HPLC). Further purification by flash chromatography over silica gel with *n*-hexane/EtOAc (15:1) gave the title compound **11** (35 mg) in a pure form. Compound **11**: colorless crystals from *n*-hexane. Mp 61°C. $[\alpha]_D^{30}$=−3.44 (c=0.524, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.84 (d, J=6.8 Hz, 3H), 0.88 (d, J=7.0 Hz, 3H), 1.75–1.87 (m, 1H), 2.30 (s, 3H), 2.63 (s, 6H), 3.56–3.66 (m, 1H), 4.57 (d, J=8.6 Hz, 1H), 4.63 (dd, J=6.8, 2.7 Hz, 2H), 4.93 (dt, J=6.8, 6.8 Hz, 1H), 6.94 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.2, 18.3, 21.1, 23.4, 33.4, 57.6, 78.1, 90.1, 132.1, 135.0, 139.1, 142.2, 207.4. Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90; N, 4.77. Found: C, 65.27; H, 7.84; N, 4.69.

Reaction of 2-ethynylaziridine (8) with $Me_2Cu(CN)$-Li_2·2LiBr·2LiCl (Table 1, entry 2). (5*S*)-2,6-Dimethyl-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-2,3-heptadiene (12). To a stirred solution of CuCN (107 mg, 1.2 mmol) and LiCl (102 mg, 2.4 mmol) in dry THF (1 mL) under argon was added by syringe MeLi·LiBr (1.5 M solution in Et_2O; 1.6 mL, 2.4 mmol) at −78°C, and the mixture was stirred for 10 min with warming to 0°C. The aziridine **8** (87.4 mg, 0.3 mmol) in dry THF (0.5 mL) was added dropwise to the above stirred reagent at −78°C, and the stirring was continued for 30 min followed by quenching with a solution of 1:1 saturated NH_4Cl–28% NH_4OH (2 mL). The mixture was extracted with Et_2O and the extract was washed with water and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane/EtOAc (8:1) gave a mixture of amino allenes **9**, **10**, and **12** (66 mg, 72% combined yield; **9**:**10**:**12**=45:18:37, HPLC). Further purification by flash chromatography over silica gel with *n*-hexane/EtOAc (15:1) gave the title compound **12** (24 mg) in a pure form. Compound **12**: colorless oil. $[\alpha]_D^{33}$=−35.0 (c=0.078, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.81 (d, J=6.8 Hz, 3H), 0.85 (d, J=7.0 Hz, 3H), 1.61 (d, J=3.0 Hz, 6H), 1.80–1.88 (m, 1H), 2.29 (s, 3H), 2.64 (s, 6H), 3.53 (ddd, J=7.8, 5.7, 4.6 Hz, 1H), 4.54 (d, J=7.8 Hz, 1H), 4.80–4.85 (m, 1H), 6.93 (s, 2H). LRMS (FAB) m/z, 322 (MH^+), 321, 278, 254, 183, 138, 123, 119 (base peak), 69, 55, 43, 41. HRMS (FAB) m/z, calcd for $C_{18}H_{28}NO_2S$ (MH^+) 322.1841; found: 322.1835.

(6*S*,a*R*)-2,7-Dimethyl-6-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-3,4-octadiene (13) (Table 1, entry 4). By a procedure similar to that described for the preparation of the amino allene **9** from **8**, the aziridine **8** (87.4 mg, 0.3 mmol) was converted into the title compound **13** (100 mg, 99% yield) by treatment with *i*-PrCu(CN)MgCl·2LiCl at −78°C for 30 min. Compound **13**: colorless oil; $[\alpha]_D^{30}$=−102 (c=1.04, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.84 (d, J=6.8 Hz, 3H), 0.87 (d, J=7.0 Hz, 3H), 0.957 (d, J=7.0 Hz, 3H), 0.961 (d, J=6.5 Hz, 3H), 1.78–1.95 (m, 1H), 2.14–2.28 (m, 1H), 2.29 (s, 3H), 2.63 (s, 6H), 3.57–3.65 (m, 1H), 4.58 (d, J=7.8 Hz, 1H), 5.05 (ddd, J=6.2, 5.4, 3.0 Hz, 1H), 5.12 (ddd, J=6.2, 6.2, 3.2 Hz, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.0, 18.3, 21.1, 22.69, 22.73, 23.5, 28.3, 33.4, 57.2, 91.2, 103.3, 132.1, 135.0, 139.0, 142.0, 200.7. LRMS (FAB) m/z, 336 (MH^+), 334, 292, 254, 200, 183, 152, 137, 119 (base peak), 95. HRMS (FAB) m/z, calcd for $C_{19}H_{30}NO_2S$ (MH^+) 336.1997; found: 336.1991.

(3*S*,a*R*)-2-Methyl-3-[*N*-(2,4,6-trimethylbenzenesulfonyl)-amino]-4,5-decadiene (14) (Table 1, entry 5). By a procedure similar to that described for the preparation of the amino allene **9** from **8**, the aziridine **8** (291 mg, 1 mmol) was converted into the title compound **14** (338 mg, 97% yield) by treatment with *n*-BuCu(CN)Li·2LiCl at −78°C for 30 min. Compound **14**: colorless oil; $[\alpha]32_D$=−108 (c=0.871, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (d, J=7.0 Hz, 3H), 0.86 (d, J=7.0 Hz, 3H), 0.89 (t, J=7.0 Hz, 3H), 1.27–1.38 (m, 4H), 1.76–1.88 (m, 1H), 1.86–1.95 (m, 2H), 2.29 (s, 3H), 2.63 (s, 6H), 3.56–3.63 (m, 1H), 4.60 (d, J=8.4 Hz, 1H), 4.92–4.99 (m, 1H), 5.10 (tdd, J=6.8, 6.8, 3.0 Hz, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.1, 18.0, 18.2, 21.1, 22.4, 23.4, 28.7, 31.6, 33.3, 57.3, 90.8, 95.6, 132.1, 135.0, 139.0, 142.0, 202.4. LRMS (FAB) m/z, 350 (MH^+), 348, 306, 254, 200, 183, 151, 119 (base peak), 95, 69. HRMS (FAB) m/z, calcd for $C_{20}H_{32}NO_2S$ (MH^+) 350.2154; found: 350.2160.

Reaction of 2-ethynylaziridine (8) with *n*-$Bu_3SuCu(CN)$-Li·2LiCl (Table 1, entry 6). (4*S*,a*R*)-5-Methyl-1-tributylstannyl-4-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-1,2-hexadiene (15). To a stirred solution of *n*-Bu_3SnH (0.323 mL, 1.2 mmol) in dry THF (1 mL) under argon was added LDA [0.5 M solution in *n*-hexane/THF (2:1); 2.4 mL, 1.2 mmol] at −78°C, and the mixture was stirred for 20 min at 0°C. A solution of CuCN (107 mg, 1.2 mmol) and LiCl (102 mg, 2.4 mmol) in dry THF (1.5 mL) was added dropwise to the above mixture at −78°C, and the mixture was stirred for 5 min with warming to 0°C. To the resulting dark red reagent, the aziridine **8** (87.3 mg, 0.3 mmol) in dry THF (0.5 mL) was added at −78°C with stirring, and the stirring was continued for 30 min followed by quenching with a solution of 1:1 saturated NH_4Cl–28% NH_4OH (5 mL). The mixture was extracted with Et_2O and the extract was washed with water and dried over $MgSO_4$. Usual workup followed by flash chromatography over silica gel with *n*-hexane/EtOAc (7:1) gave the title compound **15** (157 mg, 90% yield) as a colorless oil. $[\alpha]_D^{26}=-236$ (c=0.868, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.79–0.98 (m, 21H), 1.23–1.60 (m, 12H), 1.78–1.90 (m, 1H), 2.29 (s, 3H), 2.64 (s, 6H), 3.56–3.66 (m, 1H), 4.46–4.57 (m, 2H), 5.05–5.15 (m, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 10.7, 13.9, 18.2, 18.4, 21.1, 23.5, 27.4, 29.1, 33.3, 56.6, 80.8, 81.3, 132.1, 135.2, 139.0, 142.0, 205.4. LRMS (FAB) *m*/*z*, 582 $(M-H)^-$, 580, 578, 292, 290, 252, 248, 199 (base peak), 198, 183, 153, 64. HRMS (FAB) *m*/*z*, calcd for $C_{28}H_{48}NO_2SSn$ $(M-H)^-$ 582.2427; found: 582.2430.

(6*S*,a*S*)-2,7-Dimethyl-6-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-3,4-octadiene (17) (Table 1, entry 8). By a procedure similar to that described for the preparation of the amino allene **9** from **8**, the aziridine **16** (87.4 mg, 0.3 mmol) was converted into the title compound **17** (99 mg, 98% yield) by treatment with *i*-PrCu(CN)MgCl·2LiCl at −78°C for 30 min. Compound **17**: colorless crystals from cold *n*-hexane. Mp 47°C. $[\alpha]_D^{33}=+85.8$ (c=0.613, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.79 (d, J=7.0 Hz, 3H), 0.88 (d, J=7.0 Hz, 3H), 0.93 (d, J=7.0 Hz, 3H), 0.96 (d, J=6.8 Hz, 3H), 1.69–1.86 (m, 1H), 2.16–2.27 (m, 1H), 2.30 (s, 3H), 2.63 (s, 6H), 3.54–3.62 (m, 1H), 4.53 (d, J=8.1 Hz, 1H), 4.95 (ddd, J=6.2, 6.2, 3.0 Hz, 1H), 5.01 (ddd, J=6.2, 6.2, 3.0 Hz, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 18.3, 18.5, 21.1, 22.6, 23.3, 28.2, 33.3, 58.7, 91.7, 101.7, 132.1, 135.2, 139.0, 142.0, 201.7. LRMS (FAB) *m*/*z*, 336 (MH^+), 334, 292, 254, 200, 183, 152, 137, 119 (base peak), 95. HRMS (FAB) *m*/*z*, calcd for $C_{19}H_{30}NO_2S$ (MH^+) 336.1997; found: 336.2003.

(3*S*,a*S*)-2-Methyl-3-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-4,5-decadiene (18) (Table 1, entry 9). By a procedure similar to that described for the preparation of the amino allene **9** from **8**, the aziridine **16** (437 mg, 1.5 mmol) was converted into the title compound **18** (521 mg, 99% yield) by treatment with *n*-BuCu(CN)Li·2LiCl at −78°C for 30 min. Compound **18**: colorless oil; $[\alpha]_D^{31}=+76.6$ (c=1.13, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.82 (d, J=6.5 Hz, 3H), 0.84–0.88 (m, 3H), 0.88 (d, J=7.0 Hz, 3H), 1.25–1.32 (m, 4H), 1.73–1.87 (m, 1H), 1.85–1.95 (m, 2H), 2.29 (s, 3H), 2.63 (s, 6H), 3.52–3.61 (m, 1H), 4.58 (d, J=7.8 Hz, 1H), 4.84–4.92 (m, 1H), 5.01 (tdd, J=7.0, 7.0, 2.4 Hz, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.0, 18.1, 18.5, 21.1, 22.3, 23.3, 28.5, 31.4, 33.3, 58.4, 90.3, 94.4, 132.0, 135.1, 139.0, 142.0, 203.1. LRMS (FAB) *m*/*z*, 350 (MH^+), 348, 306, 254, 200, 183, 166, 151, 119 (base peak), 95, 69. HRMS (FAB) *m*/*z*, calcd for $C_{20}H_{32}NO_2S$ (MH^+) 350.2154; found: 350.2150.

(4*S*,a*S*)-5-Methyl-1-tributylstannyl-4-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-1,2-hexadiene (19) (Table 1, entry 10). By a procedure identical with that described for the preparation of the amino allene **15** from **8**, the aziridine **16** (87.3 mg, 0.3 mmol) was converted into the title compound **19** (160 mg, 92% yield) by treatment with *n*-$Bu_3SnCu(CN)Li·2LiCl$ at=−78°C for 30 min. Compound **19**: colorless oil; $[\alpha]_D^{28}=+183$ (c=0.552, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.77–0.97 (m, 21H), 1.21–1.52 (m, 12H), 1.69–1.83 (m, 1H), 2.29 (s, 3H), 2.63 (s, 6H), 3.48–3.59 (m, 1H), 4.25–4.42 (m, 1H), 4.44 (d, J=8.4 Hz, 1H), 4.67–4.76 (m, 1H), 6.92 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 10.6, 13.9, 18.3, 18.7, 21.1, 23.3, 27.4, 29.1, 33.6, 59.6, 77.9, 78.9, 132.0, 135.3, 139.1, 141.9, 206.3. LRMS (FAB) *m*/*z*, 582 $(M-H)^-$, 580, 578, 292, 290, 252, 248, 199, 198 (base peak), 183, 153, 64. HRMS (FAB) *m*/*z*, calcd for $C_{28}H_{48}NO_2SSn$ $(M-H)^-$ 582.2427; found: 582.2423.

(5*S*,a*R*)-5-[*N*-(2,4,6-Trimethylbenzenesulfonyl)amino]-6-phenyl-2,3-hexadiene (26) (Table 1, entry 11). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **20** (1.1 g, 3.24 mmol) was converted into the title compound **26** (1.1 g, 96% yield) by treatment with MeCu(CN)-Li·LiBr·2LiCl at −78°C for 2 h. Compound **26**: colorless oil. $[\alpha]_D^{28}=-63.2$ (c=0.155, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.51 (dd, J=7.0, 3.5 Hz, 3H), 2.28 (s, 3H), 2.55 (s, 6H), 2.84–2.87 (m, 2H), 3.87–3.98 (m, 1H), 4.57 (d, J=7.3 Hz, 1H), 5.00–5.17 (m, 2H), 6.89 (s, 2H), 7.04–7.12 (m, 2H), 7.15–7.25 (m, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.2, 21.1, 23.2, 42.5, 53.1, 90.4, 92.3, 126.8, 128.6, 129.8, 132.1, 134.3, 136.9, 139.2, 142.2, 203.2. LRMS (FAB) *m*/*z*, 356 (MH^+), 302, 264, 200, 183, 157, 129, 119 (base peak), 91. HRMS (FAB) *m*/*z*, calcd for $C_{21}H_{26}NO_2S$ (MH^+) 356.1684; found: 356.1689.

(5*S*,a*R*)-5-[*N*-(4-Methoxy-2,3,6-trimethylbenzenesulfonyl)amino]-6-phenyl-2,3-hexadiene (27) (Table 1, entry 12). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **21** (739 mg, 2 mmol) was converted into the title compound **27** (766 mg, 99% yield) by treatment with MeCu(CN)Li·2LiCl at −78°C for 6 h. Compound **27**: colorless needles from *n*-hexane/Et_2O (4:1). mp 92°C; $[\alpha]_D^{26}=-73.0$ (c=1.34, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.53 (dd, J=7.0, 3.2 Hz, 3H), 2.08 (s, 3H), 2.37 (s, 3H), 2.65 (s, 3H), 2.82 (dd, J=13.5, 6.5 Hz, 1H), 2.86 (dd, J=13.5, 6.5 Hz, 1H), 3.84 (s, 3H), 3.85–3.96 (m, 1H), 4.55 (d, J=7.0 Hz, 1H), 5.03–5.19 (m, 2H), 6.54 (s, 1H), 7.02–7.09 (m, 2H), 7.12–7.22 (m, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 12.2, 14.2, 18.1, 24.7, 42.4, 53.2, 55.7, 90.2, 92.6, 112.1, 125.3, 126.8, 128.5, 129.4, 129.7, 137.0, 138.9, 139.1, 159.4, 203.3. Anal. Calcd for $C_{22}H_{27}NO_3S$: C, 68.54; H, 7.06; N, 3.63. Found: C, 68.33; H, 7.00; N, 3.60.

(5*S*,a*S*)-5-[*N*-(2,4,6-Trimethylbenzenesulfonyl)amino]-6-phenyl-2,3-hexadiene (28) (Table 1, entry 13). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **22** (1.02 g, 3 mmol) was converted into the title compound **28** (1.06 g, 99% yield) by treatment with MeCu(CN)Li·LiBr·2LiCl at −78°C for 30 min. Compound **28**: colorless needles from *n*-hexane/Et_2O (1:1). Mp 96°C; $[\alpha]_D^{26}$=+24.8 (*c*=0.895, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.52 (dd, *J*=7.3, 3.2 Hz, 3H), 2.28 (s, 3H), 2.55 (s, 6H), 2.82 (dd, *J*=13.5, 7.3 Hz, 1H), 2.86 (dd, *J*=13.5, 6.2 Hz, 1H), 3.87–3.98 (m, 1H), 4.57 (d, *J*=7.3 Hz, 1H), 4.96–5.01 (m, 1H), 5.13 (qdd, *J*=7.3, 7.3, 2.7 Hz, 1H), 6.88 (s, 2H), 7.04–7.09 (m, 2H), 7.15–7.25 (m, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.2, 21.1, 23.2, 42.7, 53.6, 90.2, 92.3, 126.9, 128.6, 129.7, 132.1, 134.3, 137.0, 139.2, 142.2, 203.3. Anal. Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09; N, 3.94. Found: C, 70.69; H, 7.07; N, 3.80.

(5*S*,a*S*)-5-[*N*-(4-Methoxy-2,3,6-trimethylbenzenesulfonyl)amino]-6-phenyl-2,3-hexadiene (29) (Table 1, entry 14). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **23** (924 mg, 2.5 mmol) was converted into the title compound **29** (933 mg, 97% yield) by treatment with MeCu(CN)Li·2LiCl at −78°C for 30 min. Compound **29**: colorless oil. $[\alpha]_D^{27}$=+9.43 (*c*=1.08, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 1.54 (dd, *J*=7.0, 3.5 Hz, 3H), 2.08 (s, 3H), 2.38 (s, 3H), 2.64 (s, 3H), 2.76–2.88 (m, 2H), 3.84 (s, 3H), 3.85–3.96 (m, 1H), 4.55 (d, *J*=6.8 Hz, 1H), 5.01–5.10 (m, 1H), 5.14 (qdd, *J*=7.0, 7.0, 2.7 Hz, 1H), 6.54 (s, 1H), 7.02–7.09 (m, 2H), 7.12–7.22 (m, 3H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 12.2, 14.2, 18.0, 24.7, 42.6, 53.6, 55.7, 90.0, 92.5, 112.1, 125.2, 126.8, 128.5, 129.4, 129.6, 137.1, 139.0, 139.1, 159.4, 203.4. LRMS (FAB) *m*/*z*, 386 (MH^+), 332, 294 (base peak), 230, 213, 197, 157, 149, 119, 91. HRMS (FAB) *m*/*z*, calcd for $C_{22}H_{28}NO_3S$ (MH^+) 386.1790; found: 386.1796.

(5*R*,a*R*)-6-(*tert*-Butyldimethylsiloxy)-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-2,3-hexadiene (30) (Table 1, entry 15). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **24** (78.7 mg, 0.2 mmol) was converted into the title compound **30** (81 mg, 99% yield) by treatment with MeCu(CN)Li·2LiCl at −78°C for 1 h and an additional 1 h with warming to −20°C. Compound **30**: colorless oil. $[\alpha]_D^{26}$=−40.7 (*c*=0.961, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.02 (s, 6H), 0.87 (s, 9H), 1.57 (dd, *J*=7.0, 3.2 Hz, 3H), 2.29 (s, 3H), 2.64 (s, 6H), 3.51–3.60 (m, 2H), 3.66–3.76 (m, 1H), 4.97–5.13 (m, 3H), 6.94 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −5.3, 14.1 18.5, 21.1, 23.2, 26.0, 54.1, 65.9, 89.2, 90.1, 132.1, 134.6, 139.1, 142.2, 203.9. LRMS (FAB) *m*/*z*, 410 (MH^+), 408, 352, 314, 298, 264, 256, 211, 119, 79, 75, 73 (base peak). HRMS (FAB) *m*/*z*, calcd for $C_{21}H_{36}NO_3SSi$ (MH^+) 410.2185; found: 410.2186.

(5*R*,a*S*)-6-(*tert*-Butyldimethylsiloxy)-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-2,3-hexadiene (31) (Table 1, entry 16). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **25** (78.7 mg, 0.2 mmol) was converted into the title compound **31** (80 mg, 98% yield) by treatment with MeCu(CN)Li·2LiCl at −78°C for 30 min. Compound **31**: colorless oil. $[\alpha]_D^{24}$=+27.1 (*c*=0.784, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.87 (s, 9H), 1.57 (dd, *J*=6.8, 3.2 Hz, 1H), 2.29 (s, 3H), 2.63 (s, 6H), 3.55 (dd, *J*=9.7, 5.1 Hz, 1H), 3.58 (dd, *J*=9.7, 5.1 Hz, 1H), 3.66–3.75 (m, 1H), 4.95–5.03 (m, 1H), 5.05 (d, *J*=6.5 Hz, 1H), 5.06–5.17 (m, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ −5.34, −5.30, 14.3, 18.5, 21.1, 23.2, 26.0, 54.2, 66.1, 89.1, 89.8, 132.1, 134.6, 139.2, 142.2, 204.0. LRMS (FAB) *m*/*z*, 410 (MH^+), 408, 352, 314, 298, 264, 256, 211 (base peak), 119, 79, 75, 73. HRMS (FAB) *m*/*z*, calcd for $C_{21}H_{36}NO_3SSi$ (MH^+) 410.2185; found: 410.2177.

(6*R*,a*S*)-7-Methyl-6-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-3,4-octadiene (32) (Table 1, entry 18). By a procedure similar to that described for the preparation of the amino allene **9** from **8**, the aziridine ***ent*-8** (100 mg, 0.34 mmol) was converted into the title compound **32** (98 mg, 89% yield) by treatment with EtCu(CN)MgBr·2LiCl at −78°C for 42 min. Compound **32**: colorless oil. $[\alpha]_D^{25}$=+98.5 (*c*=0.644, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.84 (d, *J*=6.8 Hz, 3H), 0.87 (d, *J*=6.8 Hz, 3H), 0.95 (t, *J*=7.3 Hz, 3H), 1.79–1.99 (m, 3H), 2.29 (s, 3H), 2.63 (s, 6H), 3.56–3.64 (m, 1H), 4.57 (d, *J*=8.1 Hz, 1H), 4.97–5.04 (m, 1H), 5.12–5.21 (m, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.6, 17.9, 18.2, 21.0, 22.0, 23.4, 33.3, 57.2, 91.5, 95.0, 132.0, 134.9, 138.9, 142.0, 202.0. LRMS (FAB) *m*/*z*, 322 (MH^+), 278, 254, 123, 119 (base peak). HRMS (FAB) *m*/*z*, calcd for $C_{18}H_{28}NO_2S$ (MH^+) 322.1841; found: 322.1843.

(6*R*,a*R*)-7-Methyl-6-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-3,4-octadiene (33) (Table 1, entry 20). By a procedure similar to that described for the preparation of the amino allene **9** from **8**, the aziridine ***ent*-16** (100 mg, 0.34 mmol) was converted into the title compound **33** (107 mg, 97% yield) by treatment with EtCu(CN)MgBr·2LiCl at −78°C for 42 min. Compound **33**: colorless oil. $[\alpha]_D^{25}$=−63.9 (*c*=0.545, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.81 (d, *J*=6.8 Hz, 3H), 0.87 (d, *J*=6.8 Hz, 3H), 0.93 (t, *J*=7.3 Hz, 3H), 1.74–1.86 (m, 1H), 1.87–1.99 (m, 2H), 2.29 (s, 3H), 2.64 (s, 6H), 3.54–3.62 (m, 1H), 4.60 (d, *J*=8.1 Hz, 1H), 4.89–4.96 (m, 1H), 5.06–5.14 (m, 1H), 6.93 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.5, 18.1, 18.4, 21.1, 21.9, 23.3, 33.2, 58.3, 91.2, 96.2, 132.0, 135.0, 139.0, 142.0, 202.7. LRMS (FAB) *m*/*z*, 322 (MH^+), 278, 254, 123 (base peak), 119. HRMS (FAB) *m*/*z*, calcd for $C_{18}H_{28}NO_2S$ (MH^+) 322.1841; found: 322.1837.

Methyl (5*S*,a*S*)-2,6-Dimethyl-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-2,3-heptadienoate (38), its (5*S*,a*R*) isomer (39), and methyl (5*S*,3*Z*)-3,6-dimethyl-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-3-heptenoate (40) from the aziridine (34). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **34** (70 mg, 0.2 mmol) was converted into the title compound **38** (28 mg, 38% yield), **39** (2 mg, 3% yield), and **40** (20 mg, 27% yield) by treatment with MeCu(CN)-Li·2LiCl at −78°C for 30 min. Compound **38**: colorless oil. $[\alpha]_D^{25}$=+20.5 (*c*=2.22, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (d, *J*=7.0 Hz, 3H), 0.92 (d, *J*=6.8 Hz, 3H), 1.72 (d, *J*=3.0 Hz, 3H), 1.79–1.97 (m, 1H), 2.29 (s, 3H),

2.64 (s, 6H), 3.64 (ddd, *J*=8.4, 7.6, 5.4 Hz, 1H), 3.67 (s, 3H), 4.73 (d, *J*=8.4 Hz, 1H), 5.27 (dq, *J*=7.6, 3.0 Hz, 1H), 6.95 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.8, 18.2, 18.5, 21.1, 23.3, 33.4, 52.3, 58.1, 93.9, 97.8, 132.2, 134.6, 139.1, 142.4, 167.7, 209.4. LRMS (FAB) *m/z*, 366 (MH^+), 334, 322, 254, 183, 167 (base peak), 147, 119, 107, 73. HRMS (FAB) *m/z*, calcd for $C_{19}H_{28}NO_4S$ (MH^+) 366.1739; found: 366.1736. Compound **39**: colorless oil. $[\alpha]_D^{23}=-150$ (*c*=0.136, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.83 (d, *J*=7.0 Hz, 3H), 0.88 (d, *J*=7.0 Hz, 3H), 1.76 (d, *J*=3.0 Hz, 3H), 1.81–1.93 (m, 1H), 2.29 (s, 3H), 2.63 (s, 6H), 3.72 (d, *J*=0.5 Hz, 3H), 3.72–3.81 (m, 1H), 4.57–4.64 (m, 1H), 5.43 (dq, *J*=4.6, 3.0 Hz, 1H), 6.94 (s, 2H). ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.9, 17.8, 18.2, 21.1, 23.3, 33.3, 52.4, 57.0, 95.4, 99.6, 132.1, 134.7, 139.0, 142.3, 167.8, 209.1. LRMS (FAB) *m/z*, 366 (MH^+), 334, 322, 254, 183, 167 (base peak), 135, 119, 107, 91, 73. HRMS (FAB) *m/z*, calcd for $C_{19}H_{28}NO_4S$ (MH^+) 366.1739; found: 366.1742. Compound **40**: colorless oil. $[\alpha]_D^{24}=+85.0$ (*c*=0.528, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (d, *J*=6.8 Hz, 3H), 0.85 (d, *J*=6.8 Hz, 3H), 1.57 (d, *J*=1.4 Hz, 3H), 1.63–1.77 (m, 1H), 2.29 (s, 3H), 2.55 (d, *J*=15.2 Hz, 1H), 2.61 (s, 6H), 3.04 (d, *J*=15.2 Hz, 1H), 3.63 (s, 3H), 3.76 (ddd, *J*=9.8, 6.8, 5.6 Hz, 1H), 4.43 (d, *J*=6.8 Hz, 1H), 4.97 (dq, *J*=9.8, 1.4 Hz, 1H), 6.92 (s, 2H). LRMS (FAB) *m/z*, 368 (MH^+), 324, 169 (base peak), 137, 119, 109, 95. HRMS (FAB) *m/z*, calcd for $C_{19}H_{30}NO_4S$ (MH^+) 368.1895; found: 368.1890.

(5*S*,a*S*)-6-Methyl-2-trimethylsilyl-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-2,3-heptadiene (41) and (4*S*,3*S*)-3,5-dimethyl-1-trimethylsilyl-4-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-1-hexyne (42) from the aziridine (35). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **35** (51 mg, 0.14 mmol) was converted into the title compound **41** (46 mg, 87% yield) and **42** (6 mg, 11% yield), by treatment with MeCu(CN)Li·2LiCl for 1.5 h (−78 to 0°C). Compound **41**: colorless oil. $[\alpha]_D^{26}=+52.5$ (*c*=0.976, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.77 (d, *J*=7.0 Hz, 3H), 0.84 (d, *J*=6.8 Hz, 3H), 1.56 (d, *J*=2.7 Hz, 3H), 1.68–1.84 (m, 1H), 2.28 (s, 3H), 2.64 (s, 6H), 3.59 (ddd, *J*=7.8, 6.5, 4.6 Hz, 1H), 4.43 (d, *J*=7.8 Hz, 1H), 4.65 (dq, *J*=6.5, 2.7 Hz, 1H), 6.93 (s, 2H). LRMS (FAB) *m/z*, 380 (MH^+), 364, 344, 272, 256, 197, 196, 119, 73 (base peak). HRMS (FAB) *m/z*, calcd for $C_{20}H_{34}NO_2SSi$ (MH^+) 380.2079; found: 380.2068. Compound **42**: colorless crystals from *n*-hexane. Mp 117°C; $[\alpha]_D^{22}=-67.6$ (*c*= 0.352, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.75 (d, *J*=6.8 Hz, 3H), 0.90 (d, *J*=6.8 Hz, 3H), 1.08 (d, *J*=7.1 Hz, 3H), 2.03–2.13 (m, 1H), 2.29 (s, 3H), 2.48 (qd, *J*=7.1, 6.9 Hz, 1H), 2.66 (s, 6H), 3.08 (ddd, *J*=9.8, 6.9, 2.8 Hz, 1H), 4.68 (d, *J*=9.8 Hz, 1H), 6.94 (s, 2H). LRMS (FAB) *m/z*, 380 (MH^+), 364, 292, 254 (base peak), 183, 119, 73. HRMS (FAB) *m/z*, calcd for $C_{20}H_{34}NO_2SSi$ (MH^+) 380.2079; found: 380.2074.

(5*S*,a*R*)-6-Methyl-2-trimethylsilyl-5-[*N*-(2,4,6-trimethylbenzenesulfonyl)amino]-2,3-heptadiene (43). By a procedure identical with that described for the preparation of the amino allene **9** from **8**, the aziridine **37** (55 mg, 0.15 mmol) was converted into the title compound **43** (56 mg, 98% yield), by treatment with MeCu(CN)Li·2LiCl for 30 min (−78 to −20°C). Compound **43**: colorless oil. $[\alpha]_D^{21}=-124$ (*c*=0.953, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.79 (d, *J*=7.0 Hz, 3H), 0.84 (d, *J*=7.0 Hz, 3H), 1.60 (d, *J*=3.0 Hz, 3H), 1.78–1.90 (m, 1H), 2.29 (s, 3H), 2.64 (s, 6H), 3.64 (ddd, *J*=8.1, 5.1, 4.6 Hz, 1H), 4.44 (d, *J*=8.1 Hz, 1H), 4.71 (dq, *J*=5.1, 3.0 Hz, 1H), 6.93 (s, 2H). LRMS (FAB) *m/z*, 380 (MH^+), 364, 344, 272, 256, 196, 154, 119, 73 (base peak). HRMS (FAB) *m/z*, calcd for $C_{20}H_{34}NO_2SSi$ (MH^+) 380.2079; found: 380.2080.

(2*S*,4*R*)-2-Ethynyl-4-isopropyl-*N*-(2,4,6-trimethylbenzenesulfonyl)azetidine (44). Colorless needles from *n*-hexane/Et_2O (4:1). Mp 101°C; $[\alpha]_D^{30}=-23.4$ (*c*=1.32, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.73 (d, *J*=7.0 Hz, 3H), 0.83 (d, *J*=7.0 Hz, 3H), 1.66–1.75 (m, 1H), 2.08 (ddd, *J*=11.0, 8.0, 8.0 Hz, 1H), 2.30 (s, 3H), 2.31 (d, *J*=2.0 Hz, 1H), 2.42 (ddd, *J*=11.0, 9.0, 9.0 Hz, 1H), 2.69 (s, 6H), 4.17 (ddd, *J*=9.0, 8.0, 5.0 Hz, 1H), 4.67 (ddd, *J*=9.0, 8.0, 2.0 Hz, 1H), 6.92–6.93 (m, 2H). Anal. Calcd for $C_{17}H_{23}NO_2S$: C, 66.85; H, 7.59; N, 4.59. Found: C, 66.84; H, 7.43; N, 4.38.

(2*R*,4*R*)-2-Ethynyl-4-isopropyl-*N*-(2,4,6-trimethylbenzenesulfonyl)azetidine (45). Colorless crystals from *n*-hexane/Et_2O (5:1). Mp 92–94°C; $[\alpha]_D^{28}=+109$ (*c*=1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.64 (d, *J*=6.5 Hz, 3H), 0.68 (d, *J*=6.5 Hz, 3H), 1.59–1.67 (m, 1H), 2.07 (ddd, *J*=10.5, 8.0, 3.5 Hz, 1H), 2.29 (s, 3H), 2.35 (ddd, *J*=10.5, 8.0, 8.0 Hz, 1H), 2.60 (d, *J*=2.0 Hz, 1H), 2.64 (s, 6H), 4.58–4.63 (m, 2H), 6.91 (s, 2H). Anal. Calcd for $C_{17}H_{23}NO_2S$: C, 66.85; H, 7.59; N, 4.59. Found: C, 66.75; H, 7.38; N, 4.39.

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