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Regulation of Diastereoselectivity in the Carbocyclization of Allenyl (*S*)-*N*-*tert*-Butylsulfinimines through a Three-Component Assembly

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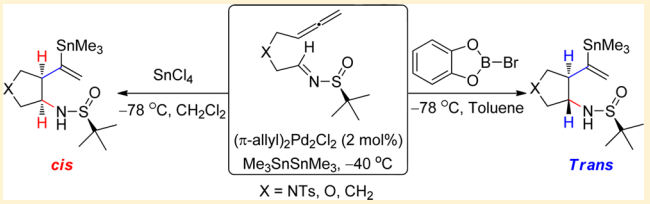
Supporting Information

ABSTRACT: Allenyl sulfinimines can be stereoselectively cyclized with hexamethylditin under palladium catalysis conditions followed by a selection of additives for an activated transmetalation. Reactivity and diastereoselectivity for the cyclization strongly depend on the characteristics of additives. A highly diastereoselective synthesis of five-membered rings is achieved from the reaction of the corresponding allenyl (*S*)-*N*-*tert*-butylsulfinimies through the following sequence. After the distannylation of the allenyl group with hexamethylditin catalyzed by the Pd complex, stereochemical routes are additive dependent: addition of $SnCl_4$ affords a *cis* ring exclusively, whereas a *trans* ring is formed predominantly by the introduction of *B*-bromocatecholborane. Extension of the methodology to the synthesis of six-membered *cis* rings is achieved by using *B*-bromocatecholborane. Stereochemical relationships of products were unambiguously deduced by X-ray crystallography.



INTRODUCTION

During the past few decades, substantial progress has been made for a variety of cyclization methods mediated by transition-metal catalysis.[1] Nonetheless, only a limited number of methods exist to establish both *cis* and *trans* rings selectively through transition-metal catalysis, despite their plentiful synthetic potential.[2] We describe herein our inverstigation into the carbocyclization of allenyl sulfinimines through a three-component assembly of allenyl, sulfiniminyl, and stannyl functionalities with regulation of stereochemical routes to construct *cis* or *trans* rings selectively, as depicted in Figure 1.

Structurally unique allene functionalities have been utilized as useful substrates and have played important roles in a variety of chemical transformations.[3] For example, many advances in cyclization using allenyl moieties mediated by transition metals have been made through a variety of synthetic strategies.[4] As part of our continuing efforts to utilize the allenyl functionality,[5] we disclosed our discoveries of synthetic methods for the synthesis of cyclic compounds from allenyl carbonyls and hydrazones by using transition-metal catalysis.[6] The major advantage of methods involving the use of an allenyl functionality for transition-metal catalysis is efficient conversion to an activated nucleophile in the presence of a reactive carbonyl equivalent. The characteristic features of our approaches in terms of structural aspects of products have encouraged us to carry out more investigations for designing an asymmetric version from **1** to **2**, which would expand the utility of the method. Furthermore, synthetic applications can be foreseen for the products to give a variety of bioactive substances, including structures appearing in Figure 1.[7]

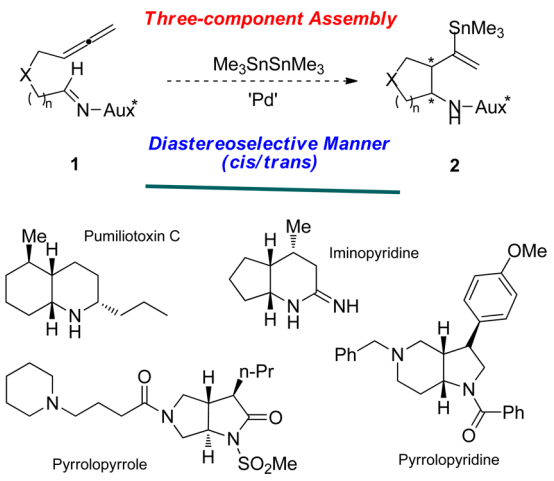


Figure 1. General cyclization strategy and examples of potential applications.

Asymmetric nucleophilic addition to imine functionalities to form chiral amines is one of the most fundamental reaction types in synthetic chemistry.[8] However, the lack of data concerning intramolecular versions in the construction of cyclic amine systems involving the use of transition-metal catalysts surprised us,[9] in view of the expected similarity of such a system to the well-defined cycloisomerization reactions with carbonyls.[10] We wish to report our discovery of a remarkable additive effect by a simple selection of transmetalating reagents for **5** to regulate *cis* or *trans* stereochemical routes for the conversion of **3** to **4**, which allows the reaction to proceed in good yield with high levels of diastereoselectivity (Scheme 1).

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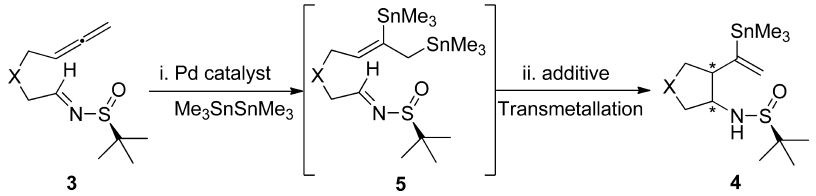
Scheme 1. Cyclization Pathway



RESULTS AND DISCUSSION

With this issue in mind, several allenyl (*S*)-*N*-*tert*-butylsulfinimines **3** were prepared according to the literature procedure,[11] and our investigations began with **3a** (X = N-SO_2Tol) as a model substrate under conditions similar to those previously employed for the carbocyclization.[6] The choice of the chiral *N*-*tert*-butylsulfinimines **3** was based on the reliability in terms of availability, the capability of π-facial stereoselectivity, and the efficacy of the addition with a variety of nucleophiles.[12] Initial attempts to cyclize **3a** with $Me_3SnSnMe_3$ in the presence of $(\pi\text{-allyl})_2Pd_2Cl_2$ (2 mol %) at −40 °C for 3 h in CH_2Cl_2 indicated that the conversion to the cyclized **4a** could not be realized, presumably due to the lack of reactivity of the sulfinimine moiety. Afterward, this weak point paved the way for an opportunity to find additives for the regulation of stereochemical routes.

We subsequently speculated that the activation of the intermediate **5** might require an additional transmetalating reagent to enhance nucleophilic addition to the sulfinimine part.[13] After surveying numerous conditions with potent Lewis acids, we found that $TiCl_4$ could be a useful additive in the cyclization. Initial experiments on the distannylation of **3a** followed by addition of $TiCl_4$ (1.1 equiv) at −78 °C for 5 h in CH_2Cl_2 afforded encouraging but marginal results. Although the cyclized product **4a** was produced during the reaction as the major component along with another unidentified diasteromer in a ratio of 9:1, the problem of low chemical yield (41%) remained to be solved.

We were delighted to find that $SnCl_4$ could be a more effective reagent in terms of diastereoselectivity and chemical yield (single diastereomer, 78% yield), as shown in Scheme 2. During the orienting experiments, key findings emerged as follows (Table 1, entries 2−7): (1) the use of 1.5 equiv of $SnCl_4$ proved to be most effective for the cyclization in terms of chemical yields, (2) the reaction performed at −78 °C in CH_2Cl_2 resulted in the best chemical yields in comparison with other solvents such as toluene and CH_3CH_2CN, and (3) the stereochemical relationship for *cis*-**4a** was deduced by X-ray crystallographic analysis. With the notion that this approach might lead to a general and efficient method for the synthesis of **4**, we set out to explore other substrates to produce structurally varying products. Indeed, the method turned out to be successful with **3b,c** in forming exclusively the cyclic products **4b,c**, respectively, in moderate to good yields, as shown in Scheme 2.

Scheme 2. *cis*-Selective Carbocyclization of 3

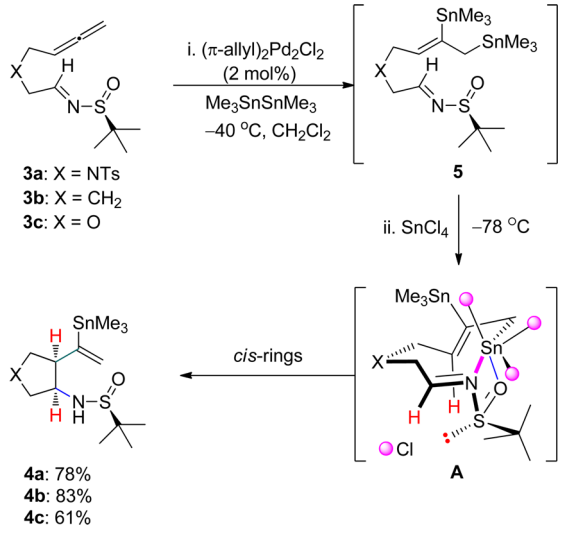


Table 1. Additive Effect for the Cyclization of 3a[a]

entry	additive[b]	solvent	major product	dr	yield, %[c]
1	none	CH_2Cl_2			NA[d]
2	$TiCl_4$	CH_2Cl_2	*cis*-**4a**	91:9[e]	41
3	$TiCl_4$	toluene	*cis*-**4a**	93:7[e]	23
4	$Ti(OiPr)_2Cl_2$	CH_2Cl_2	*cis*-**4a**	91:9[e]	21
5	$SnCl_4$	CH_2Cl_2	*cis*-**4a**	**4a** only	78
6	$SnCl_4$	toluene	*cis*-**4a**	**4a** only	54
7	$SnCl_4$	$EtCN_2$	*cis*-**4a**	**4a** only	26
8	CB-Br[f]	CH_2Cl_2	*trans*-**6a**	86:14[g]	57
9	CB-Br	toluene	*trans*-**6a**	97:3[g]	74
10	Me_2BBr	toluene	*trans*-**6a**	95:5[g]	33

[a]After the distannylation of **3a** as described in Scheme 1, additive was added at −78 °C and the reaction was performed for 1−5 h. [b]Use of 1.1−1.5 equiv. [c]Isolated and purified yield. [d]No cyclized products. [e]Stereochemically unidentified minor product. [f]CB = catecholboryl. [g]**6a**:**4a**.

Stereochemical model **A** in Scheme 2 could illustrate a possible stereochemical route for the *cis* product. From a mechanistic perspective, two major functions for the stereoselectivity in the course of cyclization are immediately discernible: transmetalation and the chelation effect. After the distannylation of an allenyl group, the resulting allylic stannane must be transmetalated by $SnCl_4$ to give the more reactive allylic trichlorostannane and subsequently an intramolecular allylic addition to the sulfinimine as depicted in **A**. The enhanced reactivity can be explained by assuming that the tight chelation of allylic tin with a sulfinyl moiety in a hexacoordinate array could result in the extent of LUMO decrease for the sulfinimine part[14] as well as HOMO increase for the trichlorostannyl part similar to the Lewis base catalyzed carbonyl addition.[15] Obtainment of the products can be accounted for by the intervention of the pseudopericyclic transannular model **A** with minimum steric interactions and optimal orbital interactions, which lead to the only reaction pathway to the product, as illustrated in Scheme 2.

In an effort to expand the scope of chemical transformation in the synthesis of *cis*-**4**, we focused on the design of a reaction

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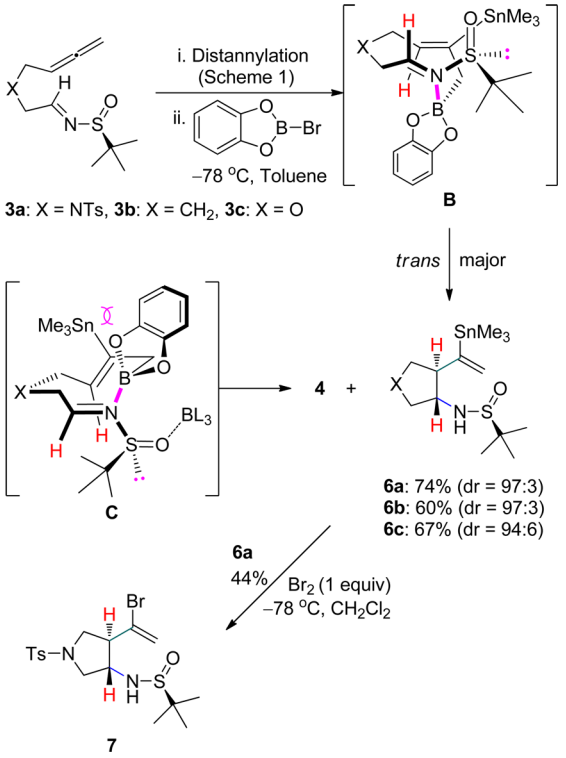
pathway to afford *trans*-**6** as a result of a reversal of diastereoselectivity on the basis of transannular stereochemical model **B**, as depicted in Scheme 3.

Scheme 3. *trans*-Selective Carbocyclization of 3

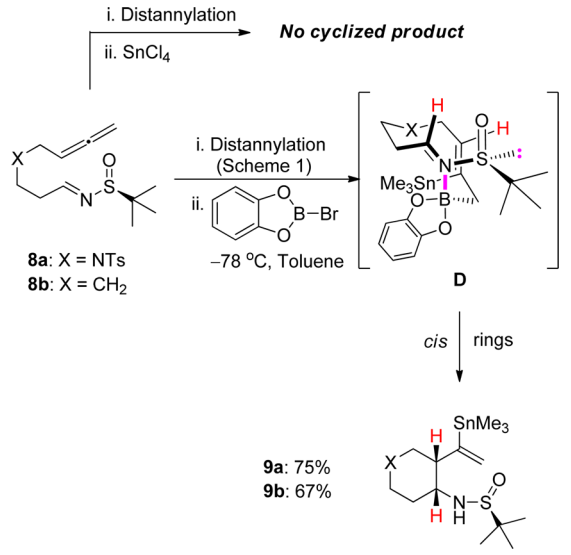


We reasoned that if model **A**, assembled from the allyltin species with a sulfinyl moiety, was possible only with 6-coordination, then it might be possible to reverse π-facial selectivity with 4-coordinating species such as borane substances via the model **B** in a predictable fashion. The key to this prediction is difficulty of assembling model **C** for a *cis* product under 4-coordination due to a severe steric interaction between the existing stannyl group and the tetrahedral borane system in the intramolecular allylic transfer reaction, as illustrated in Scheme 3.

Indeed, after surveying the reaction conditions (Table 1, entries 8–10), a reversal of diastereoselectivity was realized by replacement of $SnCl_4$ to *B*-bromocatecholborane. We observed several crucial factors as follows: (1) *B*-bromocatecholborane proved to be the most effective promoter for the cyclization in comparison with Me_2BBr and 9-BBN-Br, (2) the reaction performed at −78 °C in toluene resulted in the best chemical yield (74% yield) and diastereoselectivity (**6a:4a**, 97:3 dr) in comparison to that in CH_2Cl_2 (57%, 86:14 dr), (3) the scope of the reaction was extended to the allenyl sulfinimines **3b,c** in forming the corresponding **6b,c**, with high levels of diastereoselectivity, and (4) the relative stereochemistry was confirmed by X-ray crystallography after the conversion of **6a** with Br_2 (1 equiv) to **7**. It is worthy of note that the coordination of the sulfinyl unit with borane species in the stereochemical model **C** must be crucial in promoting the reaction to afford the unexpected minor product *cis*-**4**, as illustrated in Scheme 3.[12,16]

In light of the above results for the diastereoselective synthesis of *cis*-**4** and *trans*-**6**, we next turned our attention to the application of this approach to achieve the synthesis of six-membered rings. However, all attempts to cyclize **8a** under various conditions with $SnCl_4$ turned out to be unpromising. Fortunately, the reaction of **8a** under similar conditions with *B*-bromocatecholborane resulted in the formation of **9a** as a single diastereomer in 75% yield, as shown in Scheme 4.

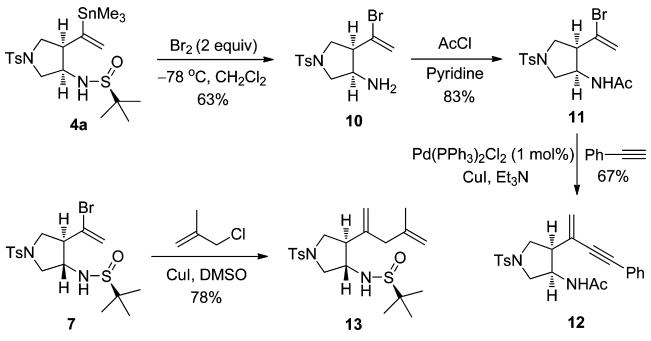
Scheme 4. Extension of the Method to Six-Membered Rings



Carbocyclization must take place through the stereochemical model **D**, which could be the only reaction pathway to the product. In addition, the method was successful with **8b** and afforded product **9b** in high purity. The stereochemical relationship of **9a** was also confirmed by X-ray analysis.

The products *cis*-**4** and *trans*-**6** are readily amenable to further chemical conversion to useful synthetic intermediates by the functional group transformations of vinylstannane. For example, the bromovinylic amine **10** was obtained in 63% yield by the treatment of **4a** with Br_2 (2 equiv) at −78 °C. Acetylation of **10** with acyl chloride in the presence of pyridine afforded **11**. Vinyl bromides can be converted to various useful substances. For example, the Sonogashira reaction of **11** with phenylacetylene provided **12** in 67% yield.[17] The copper-catalyzed coupling reaction of **7** with 2-methylallyl chloride was also effective in affording **13** in 78% yield, as shown in Scheme 5.[18]

Scheme 5. Synthetic Manipulations of Products



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CONCLUSION

In summary, readily available allenyl (*S*)-*N*-*tert*-butylsulfinimines **3** with hexamethylditin have been shown to undergo a diastereoselective carbocylization through a three-component assembly, providing a five-membered *cis*- or *trans*-ring system. This highly stereoselective transformation involves the distannylation of an allene unit with hexamethylditin by palladium catalyst, the transmetalation of the allylic trimethystannyl moiety to more reactive trichlorostannyl or catecholboryl species, and subsequently an intramolecular allylic transfer reaction with a chiral sulfinimine. Diastereoselectivity for five-membered *cis* or *trans* rings was determined by the characteristic feature of transmetalating reagents: 6-coordinating tin for the *cis* ring and 4-coordinating boron for the *trans* ring. The cyclizations are very effective for a series of allenyl sulfinimines, providing enantiomerically enriched carbocycles and heterocycles, which promise to be synthetically useful.

EXPERIMENTAL SECTION

General Methods. Unless otherwise stated, all reactions were run in flame-dried glassware under an atmosphere of nitrogen or argon using dry, deoxygenated solvents. Tetrahydrofuran (THF) was dried by refluxing over sodium/benzophenone ketyl until a permanent purple coloration appeared and distilled prior to use. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 prior to use. Solvents were also purified by passage through an alumina column under argon. All liquid reagents were distilled properly prior to use, unless otherwise indicated. Purification was conducted by flash column chromatography on silica gel (230−400 mesh), with a mixture of hexane and ethyl acetate as eluent, unless otherwise stated. All reactions were monitored by thin-layer chromatography carried out on Merck silica gel plate (60 F_{254}) using UV light as the visualizing agent and ethanolic anisaldehyde solution and heat as the developing agent. Silica gel (230−400 mesh) was used for column chromatography. The reported yields are for chromatographically pure isolated products. ^{1}H NMR spectra were recorded in $CDCl_3$ as a solvent with TMS or residual chloroform as the internal standard (δ 7.26 ppm). ^{13}C NMR spectra were measured in $CDCl_3$ as a solvent and are reported related to $CHCl_3$ (δ 77.16 ppm). Optical rotations were measured at ambient temperature. All X-ray data were collected at our departmental X-ray facility.

General Procedure for the Synthesis of Allenyl Sulfinimines: (+)-(*S*)-*N*-(Buta-2,3-dienyl)-*N*-{2-(*tert*-butylsulfinylimino)ethyl}-4-methylbenzenesulfonamide (3a). A solution of $Ti(OEt)_4$ (0.6 mL. 0.654 g, 2.86 mmol), diglyme (0.14 mL, 0.98 mmol), and allenyl aldehyde (0.37 g, 1.39 mmol) in THF (4 mL) was prepared under a nitrogen atmosphere. Then, (*S*)-*tert*-butanesulfinamide (0.17 g, 1.4 mmol) in THF (1 mL) was added and the reaction mixture was heated to reflux. Conversion was checked by TLC and the mixture cooled immediately upon completion. Once at room temperature, the mixture was poured into an equal volume of water while rapidly stirring. The resulting suspension was filtered through a plug of Celite and the filter cake was washed with EtOAc. The filtrate was transferred to a separatory funnel where the organic layer was washed with brine. The brine layer was extracted once with a small volume of EtOAc, and the combined organic portions dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by SiO_2 column chromatography to give **3a** (0.425 g, 1.15 mmol, 83%) as a pale yellow solid: TLC, R_f = 0.3 (2/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +127.2° (*c* 0.2, $CHCl_3$); IR (film) 3053, 2983, 2926, 1954, 1624, 1345, 1265, 1160, 1091 cm^{-1}; ^{1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (s, 9H), 2.40 (s, 3H), 3.87−3.94 (m, 2H), 4.23 (dd, 2H, *J* = 3.3, 8.4 Hz), 4.68−4.72 (m, 2H), 4.89−4.98 (m, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.90 (t, *J* = 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 22.6, 47.7, 50.7, 57.4, 77.0, 85.7, 127.5, 130.1, 136.9, 144.0, 165.1, 210.0. Anal. Calcd for $C_{17}H_{24}N_2O_3S_2$: C, 55.41; H, 6.56; N, 7.60. Found: C, 55.24; H, 6.63; N, 7.44.

(+)-(*S*)-*N*-(Hepta-5,6-dienylidene)-2-methylpropane-2-sulfinamide (3b). Compound **3b** (0.52 g, 2.44 mmol, 81% yield) was prepared from the corresponding allenyl aldehyde (0.33 g, 3.0 mmol) as a pale yellow oil according to the above general procedure for **3a**: TLC, R_f = 0.37 (3/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +295.6° (*c* 0.2, $CHCl_3$); IR (film) 2955, 2360, 1955, 1621, 1362, 1082 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16 (s, 9H), 1.73 (m, 2H), 2.05 (m, 2H), 2.54 (ddd, *J* = 7.4, 7.4, 4.5 Hz, 2H), 4.66 (m, 2H), 5.06 (tt, *J* = 6.6, 6.6 Hz, 2H), 8.04 (t, *J* = 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.3, 24.7, 27.5, 35.3, 56.4, 75.2, 89.0, 169.1, 208.6. Anal. Calcd for $C_{11}H_{19}NOS$: C, 61.93; H, 8.98; N, 6.57. Found: C, 61.88; H, 9.11; N, 6.63.

(+)-(*S*)-*N*-{2-(Buta-2,3-dienyloxy)ethylidene}-2-methylpropane-2-sulfinamide (3c). Compound **3c** (0.46 g, 2.13 mmol, 77% yield) was prepared from the corresponding allenyl aldehyde (0.31 g, 2.76 mmol) as a pale yellow oil according to the above general procedure for **3a**: TLC, R_f = 0.51 (1/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +263.3° (*c* 0.2, $CHCl_3$); IR (film) 2926, 1955, 1632, 1456, 1363, 1242, 1082 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17 (s, 9H), 4.12 (m, 2H), 4.39 (dd, *J* = 3.3, 1.5 Hz, 2H), 4.80 (m, 2H), 5.23 (tt, *J* = 6.9, 6.9 Hz, 1H), 8.07 (t, *J* = 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6, 57.3, 69.4, 71.1, 76.3, 87.3, 166.9, 209.9. Anal. Calcd for $C_{10}H_{17}NO_2S$: C, 55.78; H, 7.96; N, 6.51. Found: C, 55.64; H, 8,02; N, 6.43.

General Procedure for the Cyclization of *cis* Five-Membered Rings: (+)-(*S*)-2-Methyl-*N*-[(3*R*,4*R*)-1-tosyl-4-{1-(trimethylstannyl)vinyl}pyrrolidin-3-yl]propane-2-sulfinamide (4a). A flame-dried flask containing allenyl sulfinimine **3a** (154 mg, 0.42 mmol) was charged with freshly dried CH_2Cl_2 (2 mL) followed by (π-allyl)$_2$PdCl$_2$ (3.06 mg, 2 mol %) diluted in CH_2Cl_2 (0.5 mL). The resulting mixture was cooled to −40 °C. To this mixture was added dropwise hexamethyldistannane (180 mg, 0.55 mmol) in CH_2Cl_2 (1.5 mL) over 10 min along the wall of the flask while the temperature was kept below −40 °C. After addition, the solution was stirred for an additional 1 h at −40 °C. Conversion was checked by TLC, and the mixture was then cooled to −78 °C immediately upon completion of the reaction. To this reaction mixture was added precooled $SnCl_4$ (165 mg, 0.63 mmol) in CH_2Cl_2 (1 mL) over 10 min along the wall of the flask while the temperature was kept below −78 °C. After the reaction mixture was stirred for 2 h at −78 °C, aqueous $NaHCO_3$ (2 mL) was added, and then the mixture was diluted with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (5 mL). After the combined organic solution was dried over anhydrous Na_2SO_4, the solvents were removed under reduced pressure. Column chromatography (3/1 hexanes/EtOAc) afforded **4a** (175 mg, 0.33 mmol, 78%) as a white solid: TLC, R_f = 0.37 (1/1 hexanes/EtOAc); mp 96 °C, $[\alpha]^{20}_D$ = +65.6° (*c* 0.4, $CHCl_3$); IR (film) 3292, 2895, 2357, 1331, 1158, 1065, 1015 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20 (s, 9H, J^{119}_{Sn-H} = 54.7 Hz, J^{117}_{Sn-H} = 52.4 Hz), 1.00 (s, 9H), 2.41 (s, 3H), 3.08−3.14 (m, 1H), 3.22 (bs, 1H), 3.42−3.5 (m, 4H), 3.87 (m, 1H), 5.53 (dd, *J* = 1.5, 1.5 Hz, 1H, J_{Sn-H} = 68.3 Hz), 5.73 (dd, *J* = 1.5, 1.5 Hz, 1H, J_{Sn-H} = 137.1 Hz), 7.31 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −8.7, 21.8, 22.6, 48.3, 51.5, 53.1, 53.2, 56.1, 127.6, 129.5, 130.0, 134.6, 143.7, 150.0. Anal. Calcd for $C_{20}H_{34}N_2O_3S_2Sn$: C, 45.04; H, 6.43; N, 5.25. Found: C, 45.13; H, 6.44; N, 5.08. For X-ray crystallography, see the Supporting Information.

(+)-(*S*)-2-Methyl-*N*-[(1*S*,2*R*)-2-{1-(trimethylstannyl)vinyl}-cyclopentyl]propane-2-sulfinamide (4b). Compound **4b** (167 mg, 0.44 mmol, 83% yield) was prepared from **3b** (112 mg, 0.53 mmol) as a pale yellow amorphous solid according to the above general procedure for **4a**: TLC, R_f = 0.35 (3/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +184.9° (*c* 0.2, $CHCl_3$); IR (film) 3280, 2954, 1454, 1363, 1075 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9H, J^{119}_{Sn-H} = 54.0 Hz, J^{117}_{Sn-H} = 51.8 Hz), 1.14 (s, 9H), 1.62−2.04 (m, 6H), 2.86 (m, 1H), 3.20 (s, 1H), 3.75 (m, 1H), 5.46 (dd, *J* = 1.8, 1.8 Hz, 1H, J_{Sn-H} = 72.7 Hz), 5.80 (dd, *J* = 1.8, 1.8 Hz, 1H, J_{Sn-H} = 148.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −8.8, 21.5, 22.9, 25.7, 31.4, 54.2, 55.0, 55.6, 127.2, 154.1. Anal. Calcd for $C_{14}H_{29}NOSSn$: C, 44.47; H, 7.73; N, 3.70. Found: C, 44.44; H, 7.89; N, 3.51.

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(−)-(*S*)-2-Methyl-*N*-[(3*R*,4*S*)-4-{1-(trimethylstannyl)vinyl}-tetrahydrofuran-3-yl]propane-2-sulfinamide (4c). Compound **4c** (118 mg, 0.31 mmol, 61% yield) was prepared from **3c** (110 mg, 0.51 mmol) as a pale yellow amorphous solid according to the above general procedure for **4a**: TLC, R_f = 0.24 (1/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = −4.1° (*c* 0.5, $CHCl_3$); IR (film) 3209, 2915, 1642, 1364, 1271, 1053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H, J^{119}_{Sn-H} = 54.2 Hz, J^{117}_{Sn-H} = 52.0 Hz), 1.20 (s, 9H), 2.93 (ddd, *J* = 6.9, 6.9, 6.9 Hz, 1H), 3.22 (d, *J* = 7.8 Hz, 1H), 3.58−3.74 (m, 3H), 3.97−4.17 (m, 2H), 5.29 (dd, *J* = 1.8, 1.8 Hz, 1H, J_{Sn-H} = 67.9 Hz), 5.79 (dd, *J* = 1.8, 1.8 Hz, 1H, J_{Sn-H} = 141.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −8.3, 22.9, 56.2, 58.1, 62.3, 72.2, 74.1, 127.7, 152.7. Anal. Calcd for $C_{13}H_{27}NO_2SSn$: C, 41.07; H, 7.16; N, 3.68. Found: C, 41.17; H, 6.98; N, 3.27.

General Procedure for the Cyclization of *trans* Five-Membered Rings: (+)-(*S*)-2-Methyl-*N*-[(3*S*,4*R*)-1-tosyl-4-{1-(trimethylstannyl)vinyl}pyrrolidin-3-yl]propane-2-sulfinamide (6a). A flame-dried flask containing allenyl sulfinimine **3a** (168 mg, 0.46 mmol) was charged with dry toluene (2 mL) followed by (π-allyl)$_2PdCl_2$ (3.4 mg, 2 mol %) diluted in toluene (0.5 mL). The resulting mixture was cooled to −40 °C. To this mixture was added dropwise hexamethyldistannane (196 mg, 0.60 mmol) in toluene (1.5 mL) over 10 min along the wall of the flask while the temperature was kept below −40 °C. After addition, the solution was stirred for an additional 2 h at −40 °C. Reaction progress was monitored by TLC, and the mixture was then cooled to −78 °C immediately upon completion of the reaction. To this reaction mixture was added dropwise *B*-bromocatecholborane (147 mg, 0.74 mmol) in toluene (1.5 mL) over 15 min along the wall of the flask while the temperature was kept below −78 °C. After the reaction mixture was stirred for 2 h at −78 °C, aqueous $NaHCO_3$ (3 mL) was added, and then the mixture was diluted with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (5 mL). After the combined organic solution was dried over anhydrous Na_2SO_4, the solvents were removed under reduced pressure. A ^1H NMR spectrum of crude products indicated the formation of **6a** along with **4a** in a ratio of 97:3. Final purification was effected by flash column chromatography (3/1 hexanes/EtOAc) to afford **6a** (182 mg, 0.34 mmol, 74%) as a pale yellow amorphous solid: TLC, R_f = 0.3 (1/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +45.9° (*c* 0.2, $CHCl_3$); IR (film) 3270, 2957, 2233, 1346, 1164, 1069, 1014 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 9H, J^{119}_{Sn-H} = 54.3 Hz, J^{117}_{Sn-H} = 51.0 Hz), 1.08 (s, 9H), 2.41 (s, 3H), 2.77 (ddd, *J* = 7.8, 7.8, 7.8 Hz, 1H), 2.96−3.11 (m, 3H), 3.39−3.47 (m, 2H), 3.70 (dd, *J* = 10.5, 6.9 Hz, 1H), 5.24 (dd, *J* = 1.8, 1.8 Hz, 1H, J_{Sn-H} = 66.6 Hz), 5.69 (dd, *J* = 1.8, 1.8 Hz, 1H, J_{Sn-H} = 138.6 Hz), 7.32 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −8.3, 21.8, 22.7, 51.1, 53.7, 56.1, 56.3, 60.2, 127.9, 128.9, 130.1, 133.1, 144.0, 151.7. Anal. Calcd for $C_{20}H_{34}N_2O_3S_2Sn$: C, 45.04; H, 6.43; N, 5.25. Found: C, 44.88; H, 6.51; N, 5.11.

(+)-(*S*)-2-Methyl-*N*-[(1*R*,2*R*)-2-{1-(trimethylstannyl)vinyl}-cyclopentyl]propane-2-sulfinamide (6b). Compound **6b** (127 mg, 0.33 mmol, 60% yield) was prepared from **3b** (120 mg, 0.56 mmol) as a pale yellow oil according to the above general procedure for **6a**: TLC, R_f = 0.15 (1/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +14.5° (*c* 0.2, $CHCl_3$); IR (film) 3218, 2956, 2869, 1469, 1363, 1055 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 9H, J^{119}_{Sn-H} = 53.7 Hz, J^{117}_{Sn-H} = 51.6 Hz), 1.17 (s, 9H), 1.34−1.91 (m, 5H), 2.20 (m, 1H), 2.49 (ddd, *J* = 9.0, 9.0, 9.0 Hz, 1H), 3.02 (d, 7.5 Hz, 1H), 3.38 (m, 1H), 5.18 (dd, *J* = 1.5, 1.5 Hz, 1H, J_{Sn-H} = 70.1 Hz), 5.69 (dd, *J* = 1.5, 1.5 Hz, 1H, J_{Sn-H} = 152.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −8.0, 22.3, 23.0, 31.5, 34.5, 56.3, 59.6, 63.1, 126.3, 157.2. Anal. Calcd for $C_{14}H_{29}NOSSn$: C, 44.47; H, 7.73; N, 3.70. Found: C, 44.51; H, 7.69; N, 3.54.

(−)-(*S*)-2-Methyl-*N*-[(3*S*,4*S*)-4-{1-(trimethylstannyl)vinyl}-tetrahydrofuran-3-yl]propane-2-sulfinamide (6c). Compound **6c** (119 mg, 0.31 mmol, 67% yield) was prepared from **3c** (100 mg, 0.47 mmol) as a pale yellow oil according to the above general procedure for **6a**: TLC, R_f = 0.3 (1/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = −9.5° (*c* 0.2, $CHCl_3$); IR (film) 3079, 2590, 1474, 1291, 1058 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H, J^{119}_{Sn-H} = 53.9 Hz, J^{117}_{Sn-H} = 51.7 Hz), 1.18 (s, 9H), 3.21 (m, 2H), 3.82−3.89 (m, 3H), 4.01−4.08 (m, 2H), 5.47 (dd, *J* = 1.8, 1.8 Hz, 1H, J_{Sn-H} = 73.0 Hz), 5.76 (dd, *J* = 1.8, 1.8 Hz, 1H, J_{Sn-H} = 146.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −8.2, 23.2, 53.7, 56.8, 58.5, 70.8, 74.2, 129.2, 151.5. Anal. Calcd for $C_{13}H_{27}NO_2SSn$: C, 41.07; H, 7.16; N, 3.68. Found: C, 40.95; H, 7.21; N, 3.45.

Bromination of Vinyl Stannyl Group in 6a: (*S*)-*N*-{(3*S*,4*R*)-4-(1-Bromovinyl)-1-tosylpyrrolidin-3-yl}-2-methylpropane-2-sulfinamide (7). To a solution of **6a** (128 mg, 0.24 mmol) in CH_2Cl_2 (3 mL) at −78 °C was slowly added bromine solution (12.5 mg, 0.24 mmol, used freshly prepared 0.5 M in CH_2Cl_2). After it was stirred for 1 h, the mixture was quenched with 10% Na_2CO_3 and then extracted with CH_2Cl_2 (2×). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (3/1 hexanes/EtOAc and then EtOAc only) to give **7** (50.6 mg, 0.11 mmol, 44%) along with recovered **6a** (18 mg, 14%), and desulfinylated product (13 mg, 0.04 mmol, 16%). Compound **7** was recrystallized with a mixture of ether and hexane to give needlelike crystals: TLC, R_f = 0.25 (1/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +6.4° (*c* 0.3, $CHCl_3$); IR (film) 3404, 2924, 1629, 1207, 1109, 1041 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.15 (s, 9H), 2.45 (s, 3H), 2.89 (dd, *J* = 8.1, 8.1 Hz, 1H), 3.14−3.29 (m, 2H), 3.54 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.70−3.84 (m, 2H), 5.55 (d, *J* = 2.1 Hz, 1H), 5.75 (d, *J* = 2.1 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 22.6, 50.1, 53.2, 55.1, 56.4, 59.2, 76.8, 120.9, 127.9, 130.1, 130.4, 144.2. We could not obtain elemental analysis data at this time due to a shortage of sample. For X-ray crystallography, see the Supporting Information.

(+)-(*S*)-*N*-(Buta-2,3-dienyl)-*N*-{3-(*tert*-butylsulfinylimino)-propyl}-4-methylbenzenesulfonamide (8a). Compound **8a** (0.285 g, 0.75 mmol, 75% yield) was prepared from the corresponding allenyl aldehyde (0.28 g, 1.0 mmol) as a yellow oil according to the above general procedure for **3a**: TLC, R_f = 0.43 (2/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +75.4° (*c* 0.2, $CHCl_3$); IR (film) 2980, 2925, 2359, 1954, 1623, 1160, 1085 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (s, 9H), 2.42 (s, 3H), 2.80−2.86 (m, 2H), 3.48 (t, *J* = 7.2 Hz, 2H), 3.83−3.87 (m, 2H), 4.69−4.73 (m, 2H), 4.92 (tt, *J* = 6.9, 6.9 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 8.03 (t, *J* = 3.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 22.6, 35.7, 43.4, 47.7, 57.0, 76.8, 86.1, 127.5, 130.1, 136.8, 143.9, 166.7, 209.8. Anal. Calcd for $C_{18}H_{26}N_2O_3S_2$: C, 56.51; H, 6.85; N, 7.32. Found: C, 56.67; H, 6.77; N, 7.47.

(+)-(*S*)-2-Methyl-*N*-(octa-6,7-dienylidene)propane-2-sulfinamide (8b). Compound **8b** (0.38 g, 1.67 mmol, 71% yield) was prepared from the corresponding allenyl aldehyde (0.29 g, 2.33 mmol) as a pale yellow oil according to the above general procedure for **3a**: TLC, R_f = 0.4 (4:1 hexanes/EtOAc); $[\alpha]^{20}_D$ = +299.6° (*c* 0.2, $CHCl_3$); IR (film) 2928, 2861, 1955, 1621, 1455, 1362, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.17 (s, 9H), 1.44−1.52 (m, 2H), 1.60−1.70 (m, 2H), 1.97−2.05 (m, 2H), 2.51 (m, 2H), 4.64 (m, 2H), 5.07 (tt, *J* = 6.9, 6.9 Hz, 1H), 8.04 (t, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6, 25.1, 28.1, 28.8, 36.2, 56.8, 75.2, 89.8, 169.8, 208.8. Anal. Calcd for $C_{11}H_{21}NOS$: C, 63.39; H, 9.31; N, 6.16. Found: C, 63.44; H, 9.50; N, 6.08.

General Procedure for *cis* Six-Membered Rings: (+)-(*S*)-2-Methyl-*N*-[(3*S*,4*R*)-1-tosyl-3-{1-(trimethylstannyl)vinyl}-piperidin-4-yl]propane-2-sulfinamide (9a). A flame-dried flask containing allenyl sulfinimine **8a** (156 mg, 0.41 mmol) was charged with dry toluene (2 mL) followed by (π-allyl)$_2PdCl_2$ (3.0 mg, 2 mol %) diluted in toluene (0.5 mL). The resulting mixture was cooled to −40 °C. To this mixture was added dropwise hexamethyldistannane (175 mg, 0.53 mmol) in toluene (1.5 mL) over 10 min along the wall of the flask while the temperature was kept below −40 °C. After addition, the solution was stirred for an additional 2 h at −40 °C. The reaction progress was monitored by TLC, and the mixture was then cooled to −78 °C immediately upon completion of the reaction. To this reaction mixture was added dropwise *B*-bromocatecholborane (124 mg, 0.62 mmol) in toluene (1.5 mL) over 15 min along the wall of the flask while the temperature was kept below −78 °C. After the reaction mixture was stirred for 2 h at −78 °C, aqueous $NaHCO_3$ (3 mL) was added, and the mixture was then diluted with EtOAc (10

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mL). The aqueous layer was extracted with EtOAc (5 mL). After drying combined organic solution was dried over anhydrous Na_2SO_4, the solvents were removed under reduced pressure. Final purification was effected by flash column chromatography (3/1 hexanes/EtOAc) to afford **9a** (168 mg, 0.31 mmol, 75%) as a white solid: TLC, R_f = 0.22 (1/1 hexanes/EtOAc); mp 113−115 °C, $[\alpha]^{20}_D$ = +17.9° (*c* 0.2, $CHCl_3$); IR (film) 3053, 2983, 2924, 1420, 1343, 1271, 1165, 1062 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.18 (s, 9H, J^{119}_{Sn-H} = 54.1 Hz, J^{117}_{Sn-H} = 51.8 Hz), 1.10 (s, 9H), 1.94−2.21 (m, 2H), 2.44 (s, 3H), 2.74−2.91 (m, 3H), 3.16 (d, *J* = 6.9 Hz, 1H), 3.35−3.46 (m, 3H), 5.40 (dd, *J* = 1.2, 1.2 Hz, 1H, J_{Sn-H} = 73.3 Hz), 5.58 (dd, *J* = 1.2, 1.2 Hz, 1H, J_{Sn-H} = 148.4 Hz), 7.33 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −8.2, 21.8, 22.9, 31.6, 42.0, 45.8, 47.9, 52.5, 57.0, 127.5, 127.9, 130.1, 133.4, 144.0, 154.2. Anal. Calcd for $C_{21}H_{36}N_2O_3S_2Sn$: C, 46.08; H, 6.63; N, 5.12. Found: C, 46.18; H, 6.54; N, 5.11. For X-ray crystallography, see the Supporting Information.

(−)-(*S*)-2-Methyl-*N*-[(1*R*,2*S*)-2-{1-(trimethylstannyl)vinyl}-cyclohexyl]propane-2-sulfinamide (9b). Compound **9b** (123 mg, 0.31 mmol, 67% yield) was prepared from **8b** (95 mg, 0.47 mmol) as a pale yellow oil according to the above general procedure for **9a**: TLC, R_f = 0.67 (1/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = −34.7° (*c* 0.2, $CHCl_3$); IR (film) 2927, 2856, 1450, 1363, 1063 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.13 (s, 9H, J^{119}_{Sn-H} = 53.3 Hz, J^{117}_{Sn-H} = 52.2 Hz), 1.16 (s, 9H), 1.43−1.68 (m, 6H), 1.80 (m, 1H), 2.15 (m, 1H), 2.38 (m, 1H), 3.31 (d, *J* = 8.1 Hz, 1H), 3.58 (m, 1H), 5.27 (t, *J* = 1.5, 1.5 Hz, 1H, J_{Sn-H} = 77.4 Hz), 5.60 (t, *J* = 1.5, 1.5 Hz, 1H, J_{Sn-H} = 158.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ −8.6, 20.4, 23.3, 25.1, 25.8, 33.6, 49.5, 55.2, 56.9, 125.0, 157.9. Anal. Calcd for $C_{15}H_{31}NOSSn$: C, 45.94; H, 7.97; N, 3.57. Found: C, 46.11; H, 7.89; N, 3.53.

(+)-(3*R*,4*R*)-4-(1-Bromovinyl)-1-tosylpyrrolidin-3-amine (10). To a solution of **4a** (140 mg, 0.26 mmol) in CH_2Cl_2 (4 mL) at −78 °C was slowly added bromine solution (27.5 mg, 0.53 mmol, used freshly prepared 0.5 M in CH_2Cl_2). After it was stirred for 2 h at −78 °C, the mixture was quenched with 10% Na_2CO_3 and then extracted with CH_2Cl_2 (2×). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (1/2 hexanes/EtOAc and then EtOAc only) to give **10** (56.5 mg, 0.16 mmol, 63%) as a yellow oil: TLC, R_f = 0.18 (1:2 hexanes/EtOAc); $[\alpha]^{20}_D$ = +17.5° (*c* 0.2, $CHCl_3$); IR (film) 3379, 2927, 2387, 2283, 1538, 1348, 1162 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.97 (m, 1H), 3.25 (dd, *J* = 1.2, 9.9 Hz, 1H), 3.37 (dd, *J* = 9.9, 9.9 Hz, 1H), 3.47−3.58 (m, 2H), 3.69−3.71 (m, 1H), 5.57 (dd, *J* = 2.7, 1.2 Hz, 1H), 5.65 (dd, *J* = 2.7, 1.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 47.7, 53.1, 53.4, 55.2, 119.7 127.6, 128.6, 130, 133.8, 143.9. Anal. Calcd for $C_{13}H_{17}BrN_2O_2S$: C, 45.22; H, 4.96; N, 8.11. Found: C, 45.13; H, 5.18; N, 8.33.

(+)-*N*-{(3*R*,4*R*)-4-(1-Bromovinyl)-1-tosylpyrrolidin-3-yl}-acetamide (11). A flame-dried flask containing **10** (45 mg, 0.13 mmol) was charged with dry CH_2Cl_2 (3 mL) followed by Et_3N (21 mg, 0.2 mmol). After the mixture was cooled to 0 °C, acetyl chloride (13 mg, 0.18 mmol) diluted in CH_2Cl_2 (2 mL) was added. After it was stirred for an additional 1 h at 0 °C, the solution was warmed to room temperature and stirred overnight. The mixture was quenched with 5 N HCl and then saturated NH_4OH, and then it was extracted with CH_2Cl_2 (2×). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (1/1 hexanes/EtOAc) to give **11** (42 mg, 0.11 mmol, 83%) as a yellow oil: TLC, R_f = 0.51 (EtOAc only); $[\alpha]^{20}_D$ = +11.6° (*c* 0.2, $CHCl_3$); IR (film) 3369, 3054, 2925, 1675, 1346, 1265, 1165, 1093 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.87 (s, 3H), 2.45 (s, 3H), 3.23 (ddd, *J* = 7.5, 7.2, 7.5 Hz, 1H), 3.40−3.57 (m, 4H), 4.57 (m, 1H), 5.38 (d, *J* = 7.5 Hz, 1H), 5.65 (dd, *J* = 1.2, 1.2 Hz, 1H), 5.69 (dd, *J* = 1.2, 1.2 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.72 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 23.5, 49.7, 50.2, 51.2, 53.1, 121.0, 127.9, 128.5, 130.3, 133.4, 144.4, 170.3. Anal. Calcd for $C_{15}H_{19}BrN_2O_3S$: C, 46.52; H, 4.94; N, 7.23. Found: C, 46.68; H, 5.09; N, 7.35.

(−)-*N*-{(3*R*,4*R*)-4-(4-Phenylbut-1-en-3-yn-2-yl)-1-tosylpyrrolidin-3-yl}acetamide (12). A mixture of **11** (48 mg, 0.12 mmol), phenylacetylene (26 mg, 0.25 mmol), $Pd(PPh_3)_2Cl_2$ (1 mg, 1 mol %), CuI (1 mg, 0.005 mmol), and Et_3N (1 mL) in THF (4 mL) was stirred at 50 °C for 16 h under nitrogen. After the reaction mixture was cooled to room temperature, the crude product was concentrated under reduced pressure. Final purification was effected by flash column chromatography (1/1 hexanes/EtOAc) to afford **12** (34 mg, 0.08 mmol, 67%) as a yellow oil: TLC, R_f = 0.27 (1/2 hexanes/EtOAc); $[\alpha]^{20}_D$ = −4.1° (*c* 0.4, $CHCl_3$); IR (film) 3275, 3055, 2960, 2925, 2854, 1734, 1670, 1263, 1161, 1091, 1027 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.80 (s, 3H), 2.40 (s, 3H), 3.11 (dd, *J* = 14.7, 7.5 Hz, 1H), 3.39−3.63 (m, 4H), 4.51 (m, 1H), 5.41 (s,1H), 5.57 (d, *J* = 7.5 Hz, 1H), 5.62 (s, 1H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.37 (m, 5H), 7.74 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 23.4, 46.9, 49.8, 51.9, 53.2, 76.7, 87.6, 92.2, 120.9, 122.1, 125.7, 127, 127.7, 128.7, 129.1, 131.7, 144.0, 170.0. Anal. Calcd for $C_{23}H_{24}N_2O_3S$: C, 67.62; H, 5.92; N, 6.86. Found: C, 67.68; H, 5.89; N, 7.01..

(−)-(*S*)-2-Methyl-*N*-{(3*S*,4*R*)-4-(4-methylpenta-1,4-dien-2-yl)-1-tosylpyrrolidin-3-yl}propane-2-sulfinamide (13). A flame-dried flask was charged with CuI (5.5 mg, 0.029 mmol) and **7** (30 mg, 0.056 mmol) in THF (1 mL). To the mixture was added 3-chloro-2-methylpropene (10 mg, 0.11 mmol) dissolved in DMSO (1.5 mL) under a nitrogen atmosphere. After it was stirred for 2 h, the resulting mixture was quenched with NH_4OH aqueous solution and dried over anhydrous Na_2SO_4. The crude product was concentrated under reduced pressure and was purified by SiO_2 column chromatography to give **13** (18 mg, 0.042 mmol, 75%) as a pale yellow oil: TLC, R_f = 0.33 (1/1 hexanes/EtOAc); $[\alpha]^{20}_D$ = −7.90° (*c* 0.2, $CHCl_3$); IR (film) 3277, 2928, 1465, 1345, 1160, 1059, 677 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.02 (s, 9H), 1.63 (s, 3H), 2.41 (s, 3H), 2.73 (s, 2H), 2.82 (ddd, *J* = 10.5, 6.3, 5.1 Hz, 1H), 3.14 (bs, 1H), 3.34−3.56 (m, 4H), 3.91 (dd, *J* = 4.2, 4.2 Hz, 1H), 4.73 (s, 1H), 4.82 (s, 1H), 4.90 (s, 1H), 5.16 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 21.9, 22.5, 45.4, 46.9, 48.4, 52.1, 53.8, 56.0, 113.9, 116.1, 127.5, 129.9, 134.7, 141.4, 141.9, 143.6. Anal. Calcd for $C_{21}H_{32}N_2O_3S_2$: C, 59.40; H, 7.60; N, 6.60. Found: C, 59.61; H, 7.55; N, 6.44.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and tables giving crystallographic data for **4a, 7**, and **9a** and figures giving ^1H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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