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An Approach to the Stereoselective Synthesis of Enantiopure Dihydropyrroles and Aziridines from a Common Sulfinyl-Sulfinamide Intermediate

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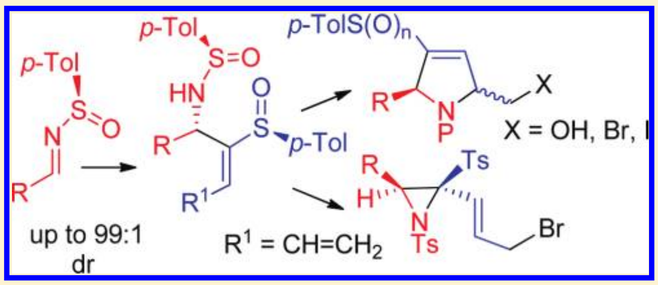
Supporting Information

ABSTRACT: The diastereoselective addition of lithiated vinyl sulfoxides to enantiopure sulfinimines provides direct access to a wide assortment of allylic sulfinamides in good yields and excellent selectivities. These adducts are key precursors to differently functionalized *cis*- and *trans*-dihydropyrroles. Modulation of the protecting group on nitrogen prior to cyclization has a significant impact on the stereochemical outcome, allowing for the selective preparation of 2,5-*cis*- or 2,5-*trans*-3-sulfinyl disubstituted dihydropyrroles from a common sulfinamide intermediate. Further research on halocyclization conditions has also yielded a stereoselective synthesis of trisubstituted vinyl aziridines from these chiral sulfinamides, simply by changing the halogenating agent.



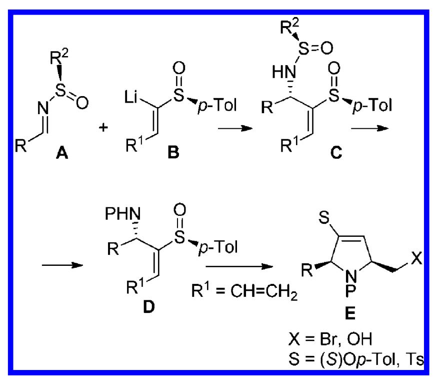
INTRODUCTION

Nitrogen heterocycles are versatile building blocks, and their use in organic synthesis has been extensively explored. In particular, dihydropyrroles constitute an interesting class because they allow for direct access to pyrroles and pyrrolidines.[1] Currently, there is growing interest focused on the synthesis of polysubstituted pyrrolidines, and the stereocontrolled entry to different diastereomers from a common starting material is regarded as an important synthetic challenge.[2] Additionally, very few efficient methods for obtaining enantiopure *trans*-2,5-disubstituted pyrrolidines have been reported.[3] Among the different strategies, one straightforward route to five-membered *N*-heterocycles is the amino cyclization of chiral γ,δ-unsaturated amines, and substantial research has been devoted to this subject.[4]

Similarly, enantiomerically pure aziridines are another important class of targets in organic chemistry for their many interesting applications and biological activities.[5] Aziridines can also be converted into functionalized α-substituted (O, N, S, P) amino derivatives or into other heterocycles.[6] In order to obtain these strained rings, several efficient approaches have been developed in recent years, mainly based on intramolecular substitution reactions of amines or transformations of imines and alkenes.[7] Most diastereoselective routes found in the literature lead to mono- and disubstituted aziridines, with the tri- and tetrasubstituted variants being less accessible. Moreover, vinyl aziridines are useful synthetic intermediates; however, problems associated with the control of regioselectivity and lability under acidic conditions could arise.[8]

As part of our continuing program in chiral sulfur chemistry,[9] we recently reported the synthesis of 3-sulfinyl and 3-sulfonyl *cis*-2,5-disubstituted dihydropyrroles **E** from chiral *N*-sulfinimines **A** (Scheme 1).[10] This route involves the diastereoselective

Scheme 1. Diastereoselective Synthesis of 2,5-*cis*-Dihydropyrroles



addition of lithiated vinyl and dienyl sulfoxides **B** to enantiopure sulfinimines **A**, a plausible alternative to the aza-Morita−Baylis−Hillman reaction (Aza-MBH).[11] Although nonracemic *N*-sulfinimines have proven to be efficient chiral auxiliaries for this reaction, the loss of selectivity for trisubstituted double bonds and the long reaction times are still drawbacks to be

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overcome. Our preliminary results showed poor stereocontrol for the addition of **B** to aldehydes and sulfonimines; however, the additional chiral sulfur of sulfinimines **A** provides a double diastereoselection scenario based on two chiral sulfur atoms that gives sulfinamides **C** with high stereoselectivity.

In this article, we will describe a full study of the development of this recent methodology: synthesis of new allylic sulfinamides **C** (different R, R^1, and R^2), preparation of a variety of *N*-protected amines **D**, and examination of the effect of the protecting group (P) on the cyclization step (R^1 = CH=CH_2). Furthermore, we have examined the synthesis of new enantiopure heterocycles under diverse cyclization conditions (MCPBA/CSA, TBATB, I_2, NIS, and NBS), and we have described some examples of their reactivity as it contributes to expanding the scope of the initial report.[10a]

■ RESULTS AND DISCUSSION

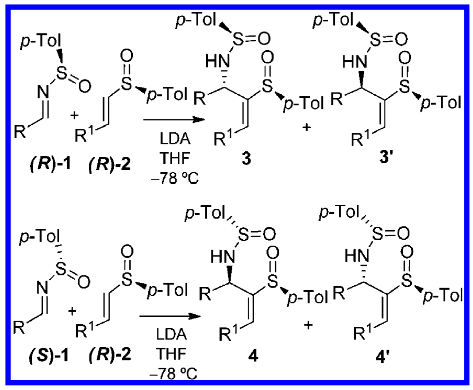
Synthesis of Enantiopure Sulfonamides. Our synthetic approach starts by submitting a number of optically pure sulfinimines **(*R*)-1** and **(*S*)-1**[12] to treatment with (R_S,*E*)-lithio vinyl sulfoxides (generated from **(*R*)-2** and LDA),[13] obtaining in all cases good to excellent yields (55–91%) and moderate to high diastereoselectivities of allylic sulfinamides **3** and **4** (Table 1).

The scope of the reaction was examined by varying not only the absolute configuration of the sulfinimine sulfur (*R* or *S*), but also the nature of the R group, including aryls, linear and branched alkyls, alkenyls, and quaternary centers from sulfinyl ketimines (Table 1, **(*R*)-1a–k**, **(*S*)-1a–n**). In addition, aryl, alkyl, and alkenyl substitutions at vinyl sulfoxide **(*R*)-2a–c** gave outstanding yields and selectivities (91:9–99:1) for the matched pair. These results highlight the crucial role of the absolute configuration of the sulfinimine in the process because both the yields and selectivities increased when aldimines **(*R*)-1** were employed (Table 1, entries 1, 2, 4, 6–10, and 13–16, matched pairs). Table 1 clearly illustrates the broad substrate scope under these general conditions. Also, with the aim of improving the outcome for the mismatched pair, bulkier mesityl sulfinimine **(*S*)-1g** was synthesized, and a slight increase in the selectivity to 85:15 was observed (compare Table 1 entries 11 and 12).

In contrast with these results, when sulfinyl ketimine **(*S*)-1l** was submitted to the addition of lithiated dienyl sulfoxide **(*R*)-2c**, we observed a high diastereoselectivity (1:99, **4n**:**4n′**, Table 1, entry 17), although a significant amount of starting material was also recovered, probably because of the competitive deprotonation of the ketimine. However, we did not find a similar result for the enantiomeric ketimine **(*R*)-1l**, as only complex crude mixtures containing starting material and various byproducts were obtained.[14] This observation suggests an inversion in the matched/mismatched pair for sulfinyl ketimines.[15] More electron-deficient sulfinyl ketimines **(*S*)-1m** and **(*S*)-1n** were employed and provided the same high diastereoselectivity. In the case of **(*S*)-1n**, a slight increase in reactivity was also observed (Table 1, entries 18 and 19).

As we described previously, the observed stereochemical outcome can be explained in terms of the preferred *S*-*cis* conformation of *N*-sulfinyl aldimine and through a rigid transition state in which lithium coordinates to the oxygens of both the sulfoxide and the sulfinimine (Figure 1). Thus, the two chiral sulfinyl groups are each positioned to influence the stereochemical outcome, providing the high selectivities.[10a] Hence, the nucleophilic addition takes place mostly anti to the *p*-tolyl group of the sulfinyl aldimine onto the *re*-face of **(*R*)-1** for the matched pair or the *si*-face of **(*S*)-1** for the mismatched pair. Interestingly, in terms of facial discrimination, sulfinimines behave similarly to the addition of α-sulfinyl carbanions,[15]

Table 1. Addition of Lithio Vinyl and Dienyl Sulfoxides to *N*-Sulfinimines (*R*)-1 and (*S*)-1



entry	1 (R)	2 (R^1)	3/4 (%)[a]	dr (3:3′/4:4′)[b]
1	**R-1a** (Ph)	**R-2a** (Ph)	**3a** (55)	99:1
2	**R-1a** (Ph)[c]	**R-2b** (^{n}Bu)	**3b** (90)	91:9
3	**S-1a** (Ph)[c]	**R-2b** (^{n}Bu)	**4b** (69)	82:18
4	**R-1a** (Ph)	**R-2c** (CH=CH_2)	**3c** (95)	99:1
5	**S-1a** (Ph)	**R-2c** (CH=CH_2)	**4c** (91)	87:13
6	**R-1b** (1-naphth)	**R-2c** (CH=CH_2)	**3d** (70)	99:1
7	**R-1c** (*p*-MeOC_6H_4)	**R-2c** (CH=CH_2)	**3e** (70)	99:1
8	**R-1d** (3,4-$(MeO)_2C_6H_3$)	**R-2c** (CH=CH_2)	**3f** (75)	99:1
9	**R-1e** (*p*-$CF_3C_6H_4$)	**R-2c** (CH=CH_2)	**3g** (86)	94:6
10	**R-1f** (^{i}Pr)	**R-2c** (CH=CH_2)	**3h** (93)	99:1
11	**S-1f** (^{i}Pr)	**R-2c** (CH=CH_2)	**4h** (69)	75:25
12	**S-1g** (^{i}Pr)[d]	**R-2c** (CH=CH_2)	**4i** (72)	85:15
13	**R-1h** (^{n}Bu)	**R-2c** (CH=CH_2)	**3j** (98)	99:1
14	**R-1i** (Cy)	**R-2c** (CH=CH_2)	**3k** (68)	99:1
15	**R-1j** ($Ph(CH_2)_2$)	**R-2c** (CH=CH_2)	**3l** (68)	99:1
16	**R-1k** (*E*-Ph(CH=CH))	**R-2c** (CH=CH_2)	**3m** (62)	99:1
17	**S-1l** (Ph, Me)[e]	**R-2c** (CH=CH_2)	**4n′** (50)[f]	1:99
18	**S-1m** (*p*-NO_2Ph, Me)[e]	**R-2c** (CH=CH_2)	**4o′** (51)[f]	1:99
19	**S-1n** (*p*-CNPh, Me)[e]	**R-2c** (CH=CH_2)	**4p′** (48)[f]	1:99

[a]Combined yield. [b]Ratio determined by ^{1}H NMR analysis. [c]3.0 equiv of LDA and **1** were employed. [d]**S-1g**: (+)-(*S*)-2,4,6-trimethyl-*N*-[(1*E*)-2-methylpropylidene] benzenesulfinamide. [e]A sulfinyl ketimine was employed as starting material. [f]Starting material ***R*-2c** was always recovered in these experiments (***S*-1l**: 40%, ***S*-1m**: 45%, ***S*-1n**: 35%).

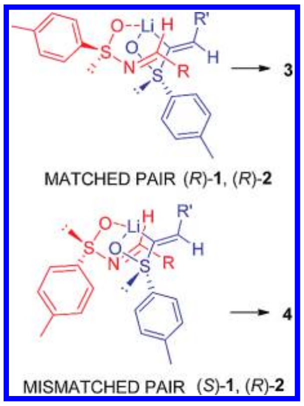
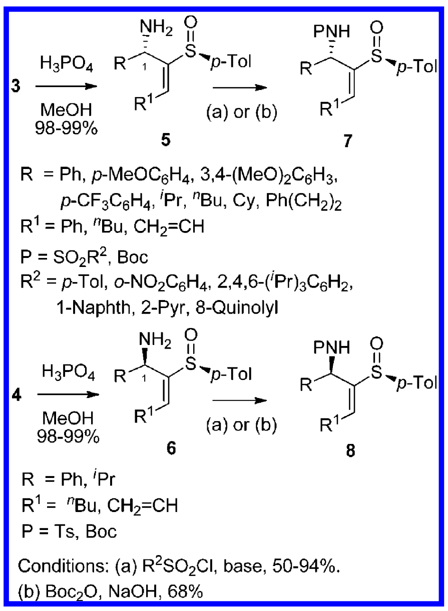


Figure 1. Stereochemical outcome of the addition of (*R*)-**2** to *N*-sulfinimines (*R*)-**1** and (*S*)-**1**.

vinylaluminum reagents,[11g] and α-imino enolates[9f] but opposite to Baylis–Hillman nucleophiles[11c,d] and other enolates.[10b]

Subsequent cleavage of sulfinamides **3** and **4** under acidic conditions[16] provided allylic amines **5** and **6**, respectively (Scheme 2). Also, desulfinylation of mixtures of **4h**:**4h′** to give

Scheme 2. Synthesis of Diastereomeric Amines 5 and 6 and Their Protected Derivatives 7 and 8

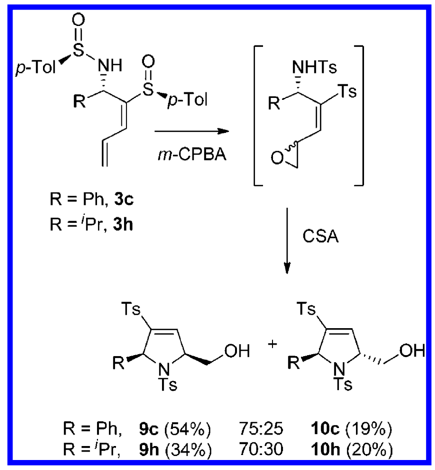


6h:**5h** (R = ^{i}Pr, R^1 = CH$_2$=CH) allowed us to establish that each pair of sulfinamides (**3**:**3′** and **4**:**4′**) were diastereomers at C-1. It should be noted that **5h** obtained by this method was identical to the amine obtained by desulfinylation of **3h**.

The major allylic amines **5** and **6** were further protected using different sulfonyl chlorides and Boc$_2$O to afford products **7** and **8** in good yields (Scheme 2). Our efforts to synthesize sulfonamides in a single step by selective oxidation of the sulfinamide in the presence of the sulfoxide moiety failed.[17]

Synthesis of *cis*- and *trans*-2,5-Substituted Dihydropyrroles. In order to obtain hydroxymethyl dihydropyrroles **9** and **10**, sulfinamides **3c** and **3h** were treated with *m*-CPBA[18] in toluene (Scheme 3). We observed a fast oxidation of both sulfinyl groups followed by slow epoxidation at the distal double bond. We determined that the epoxidation controls the selectivity of the process because the cyclization of isolated

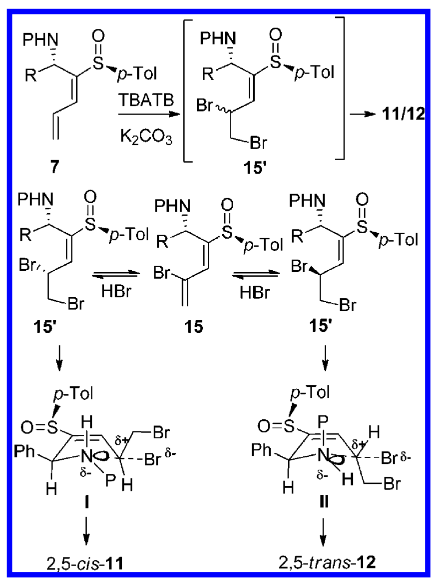
Scheme 3. One-Pot Preparation of Hydroxymethyl Dihydropyrroles 9 and 10 from 3



mixtures of oxiranes with camphorsulfonic acid (CSA) led to an identical ratio of cyclized products.[19] Nevertheless, in situ cyclization by reaction with a catalytic amount of CSA provided **9** and **10** in moderate yields and diastereoselectivities, with the 2,5-*cis* dihydropyrroles **9c** and **9h** being predominant. The stereochemical assignment was based on an X-ray analysis of the dihydropyrroles (see the Supporting Information).

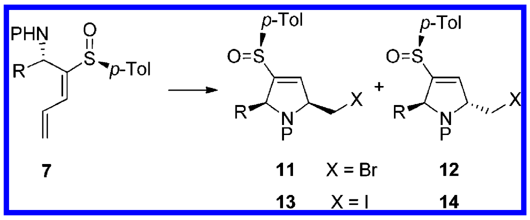
Hoping to preserve the sulfoxide moiety and after considerable experimentation, we attempted the halocyclization with tetrabutylammonium tribromide (TBATB) and K$_2$CO$_3$ (Scheme 4). In the cases of **3c**, **7a** (R = Ph, P = Boc), and **8a**,**b**

Scheme 4. Stereochemical Outcome for Bromomethyl Dihydropyrroles with TBATB



(R = Ph, P = Boc, Ts), complex mixtures were obtained. In contrast, we could obtain the desired 3-sulfinyl bromomethyl dihydropyrroles 2,5-*cis*-**11** and 2,5-*trans*-**12** by installing a more acidic sulfonamido group onto the nitrogen of diastereomers **7**.[20] Moreover, we were delighted to detect the formation of a major product 2,5-*cis*-**11** for aryl and alkyl *p*-tolylsulfonamides **7b**,**c**,**d** (Table 2, entries 1–3). The absolute configuration of the bromomethyl pyrroles was unequivocally assigned by X-ray analysis of **12a**.[10a] Interestingly, moderately fast disappearance

Table 2. Stereoselective Synthesis of 2,5-*cis*- and 2,5-*trans*-Halomethyl Dihydropyrroles



entry	compd	R	P	conditions[a]	ratio *cis:trans*	*cis* (%)	*trans* (%)
1	**7b**	Ph	Ts	TBATB/K_2CO_3 CH_2Cl_2	80:20	**11a** (56)	**12a** (15)
2	**7c**	^{i}Pr	Ts	TBATB/K_2CO_3 CH_2Cl_2	87:13	**11b** (48)	**12b** (9)
3	**7d**	^{n}Bu	Ts	TBATB/K_2CO_3 CH_2Cl_2	90:10	**11c** (57)	**12c**[b]
4	**7e**	Ph	*o*-$NO_2C_6H_4SO_2$	TBATB/K_2CO_3 CH_2Cl_2	80:20	**11d** (41)	**12d** (17)
5	**7f**	Ph	2,4,6-$^iPr_3C_6H_2SO_2$	TBATB/K_2CO_3 CH_2Cl_2	80:20	**11e** (49)	**12e** (8)
6	**7g**	Ph	8-quinolylSO_2	TBATB/K_2CO_3 CH_2Cl_2	20:80	**11f** (14)	**12f** (49)
7	**7h**	3,4-$(MeO)_2C_6H_3$	8-quinolylSO_2	TBATB/K_2CO_3 CH_2Cl_2	10:90	**11g** (9)	**12g** (65)
8	**7i**	^{i}Pr	8-quinolylSO_2	TBATB/K_2CO_3 CH_2Cl_2	56:44	**11h** (57)[c]	12h
9	**7j**	Ph	1-naphthSO_2	TBATB/K_2CO_3 CH_2Cl_2	78:22	**11i** (50)[c]	12i
10	**7k**	Ph	2-pyridylSO_2	TBATB/K_2CO_3 CH_2Cl_2	73:27	**11j** (46)	**12j** (16)
11	**7l**[d]	Ph/Me	Ts	TBATB/K_2CO_3 CH_2Cl_2	35:65	**11k**[b]	**12k**[e] (43)
12	**7b**	Ph	Ts	I_2/K_2CO_3 CH_3CN-H_2O	42:58	**13a** (23)	**14a** (43)
13	**7b**	Ph	Ts	NIS/K_2CO_3 CH_2Cl_2	56:44	**13a** (39)	**14a** (32)
14	**7b**	Ph	Ts	NIS/K_2CO_3 toluene	21:79	**13a** (8)	**14a** (65)

[a]Room temperature while stirring for 2−7 days was employed in all experiments. [b]Not isolated. [c]Combined yield of both isomers. [d]**7l** (*S*-configuration in C-2) was prepared from **4n′** in two steps. The sulfonamido moiety is attached to a quaternary center. [e]**12k** is assigned as (2*S*,5*R*).

of the starting material (1−2 days) does not provide the dihydropyrroles, but instead leads to mixtures of dibromo adducts (Scheme 4, **15′**). Then, these intermediates slowly cyclize (1−5 days) into the final products. Other solvents ($CHCl_3$, CH_3CN, THF), bases (Et_3N, DBU, KO^{t}Bu), and bromine sources (Br_2, $PhMe_3NBr_3$, $BnMe_3Br_3$, $DMAPHBr_3$) were tried to increase the reaction rate, but no significant improvements in rate, yield, or selectivity could be obtained.

At this point, the influence of the sulfonyl substituent on the cyclization step was explored, and thus we tested different sulfonamides **7e−g** (R = Ph, Table 2, entries 4−6). Although electronic and steric factors in **7e** and **7f** did not appreciably affect the ratio of **11** and **12**, the overall yield was slightly reduced. More surprising for us was the inversion in ratio observed upon changing from *p*-tolyl (**7b**) to 8-quinolyl sulfonamide (**7g** and **7h**), leading to the 2,5-*trans* isomers **12f** and **12g** as the major products (Table 2, entries 1 vs 6 and 7). The absolute configuration of the new stereogenic carbon and the configurational stability of the sulfinyl group under the reaction conditions were confirmed by X-ray crystallography of **12f**. Unfortunately, the effect of the 8-quinolyl sulfonamido group is limited to aromatic substrates (R = Ar), as the reaction with **7i** (R = ^{i}Pr) is virtually nonselective, providing a 56:44 *cis*:*trans* ratio (Table 2, entry 8). The unique behavior of the 8-quinolyl sulfonamido group is evidenced by the ratios found for **7j** (P = 1-naphthSO_2) and **7k** (P = 2-pyridylSO_2) because 2,5-*cis*-dihydropyrroles **11i** and **11j** were obtained as major products (Table 2, entries 9−10). The above results indicate that along with possible π-stacking effects (R = Ar/P = 8-quinolylSO_2), the position of the nitrogen in the quinoline ring could determine the diastereomeric outcome of the reaction. Sulfonamide **7l**, with an additional methyl group at the sulfonamido position (C-2, 2*S*), was also submitted to the bromocyclization reaction, giving a slightly lower yield of a 35:65 mixture of dihydropyrroles. The major product was tentatively assigned as 2,5-*trans*-**12k** (Ph trans to CH_2Br) by comparison of the ^1H NMR data with other compounds of the series (Table 2, entry 11).

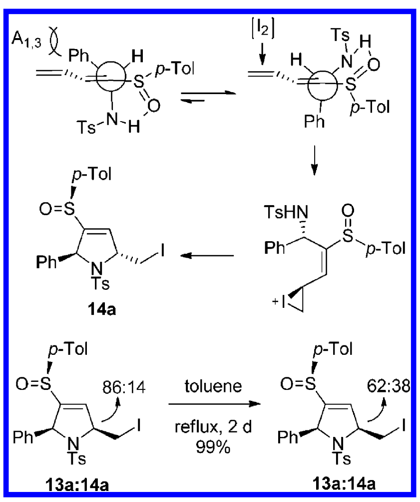
Finally, iodine was examined as an alternative halogen source in the synthesis of dihydropyrroles (Table 2, entries 12−14). Molecular iodine provides a modest selectivity for the 2,5-*trans*-**14a** (42:58) that is reversed toward 2,5-*cis*-**13a** by using NIS in CH_2Cl_2 (56:44). However, the nature of the solvent is crucial because changing to toluene resulted in a 21:79 mixture of iodomethyl dihydropyrroles **13a** and **14a**.

As mentioned above, when the bromocyclizations were quenched at short reaction times, primarily mixtures of dibromo intermediates **15′** were isolated in variable ratios (Scheme 4). Interestingly, we found that the diastereomeric ratios of these dibromo intermediates did not correspond to the final *cis*:*trans* ratios of the cyclized products (e.g., a 56:44 mixture of dibromo adducts from **7b** (R = Ph, P = Ts) led to an 80:20 mixture of **11a**:**12a**). This disparity between intermediates and products along with the isolation of trace amounts of vinyl bromide **15** led us to speculate about the possibility of equilibrium between dibromo diastereomers under the reaction conditions.[21] The nature of the sulfonamido group (P) would then determine which dibromo adduct cyclizes faster to the dihydropyrrole. Thus, although transition states **I** are favored from a steric point of view (Ph, P, CH_2Br in *anti* relative arrangement), it is possible that by modifying the nature of P, transition states **II** become more stabilized, thus providing 2,5-*trans*-**12** as the major product. In the latter case, *π*,*π*-stacking between the quinolyl and phenyl groups and chelation of K cations to both nitrogen atoms (quinoline and sulfonamide) could contribute to this outcome.

In addition, we have evidenced that TBATB has a relevant impact on the efficiency and rate of the cyclization as treatment of the dibromo intermediates (from **7b**) with K_2CO_3 gave only complex mixtures of products. Other bases such as DBU or DABCO produced only small amounts of **11** and **12**.

Alternatively, when **7b** was treated with I_2 or NIS iodomethyl pyrrolidines **13a** and **14a** were isolated. The best diastereoselectivity was achieved using NIS/K_2CO_3 in toluene (21:79) to provide 2,5-*trans*-**14a** as the major dihydropyrrole (Table 2, entry 14). Since diiodo intermediates were not detected under these conditions, a common iodonium mechanism could be operating in this case. Scheme 5 depicts the approach of iodine

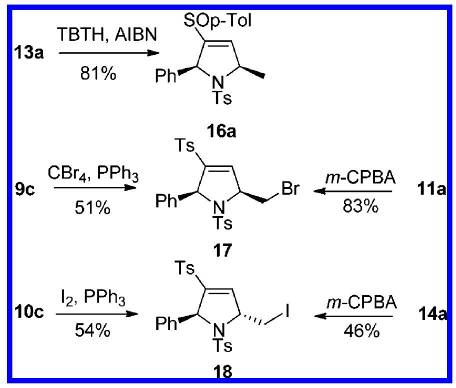
Scheme 5. Reaction Course for Iodocyclization



to the distal double bond. Coordination of the sulfoxide (oxygen) and the sulfonamide (proton) in a nonpolar solvent such as toluene could determine the reactive conformer of the substrate. A possible epimerization from *cis* (**13a**) to *trans* product (**14a**) under the reaction/isolation conditions is ruled out. Equilibration between the diastereoisomers only occurs after refluxing in toluene for 2 days, and the thermodynamic ratio for **13a**:**14a** was determined to be 62:38.[22] In addition, it should be mentioned that the pure heterocycles are stable and can be stored at room temperature without isomerization.

A thorough inspection of the [1]H NMR data of the dihydropyrroles shows, in general, a remarkable difference in the value of J_{H2-H5} values of the 2,5-*cis* (0−2.6 Hz) versus the 2,5-*trans* series (4.6−5.9 Hz). Also, the shifts of the methylene protons (CH_2X) are higher in the 2,5-*trans*- than in the 2,5-*cis*-dihydropyrroles ($\Delta\delta$ = 0.4−0.5 ppm for each methylenic proton). In addition, along with the X-ray analysis, some transformations were performed to extend the stereochemical assignments to the iodomethyl and the hydroxymethyl dihydropyrroles. Thus, treatment of *cis*-iodomethyl dihydropyrrole **13a** with tributyltin hydride/AIBN led to the 5-methyl pyrroline **16a** in good yield, and NOE experiments on this derivative confirmed a 2,5-*cis* arrangement (Scheme 6).

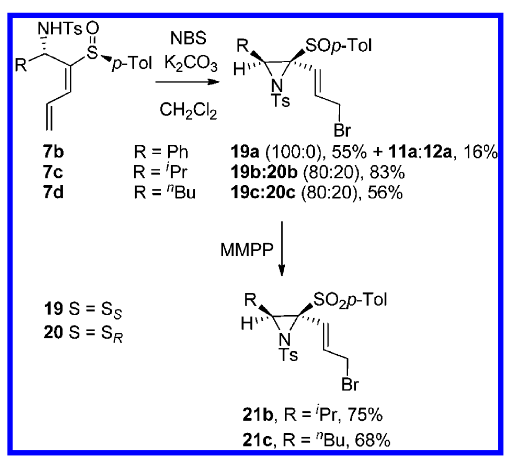
Scheme 6. Structural Correlation of Dihydropyrroles



Moreover, **11a** and **14a** were oxidized with *m*-CPBA to yield 3-sulfonyl dihydropyrroles **17** and **18** in moderate to good yields (Scheme 6), whereas reaction of hydroxymethyl dihydropyrroles **9c** and **10c** with CBr_4 and I_2, respectively, also led to the corresponding halocycloadducts **17** and **18**, thus correlating the stereochemistry of both the *cis* (**9**, **11**, **13**) and *trans* products (**10**, **12**, **14**).

Synthesis of *N*-Sulfinyl Aziridines. While probing the use of other halogenating reagents, we examined the reaction of sulfinyl sulfonamide **7b** with NBS/K_2CO_3 (Scheme 7). To our

Scheme 7. Diastereoselective Synthesis of Trisubstituted Aziridines



surprise, sulfinyl aziridine **19a** was isolated as a single diastereoisomer (55%) along with minor amounts of 2,5-*cis*- and

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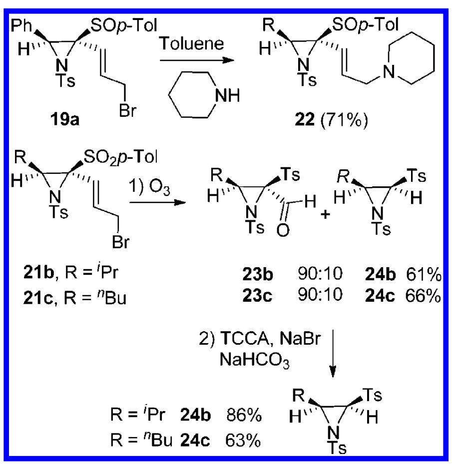
2,5-*trans*-dihydropyrroles **11a** and **12a** (45:55, 16%) (Scheme 7).[23] The relative configuration of the new stereogenic center was assigned by NOE experiments. Alkyl derivatives **7c** and **7d** were also submitted to the reaction conditions with *N*-bromosuccinimide; however, an 80:20 mixture of aziridines **19b,c** and **20b,c**, diastereomers at the sulfur atom, were isolated after chromatographic purification.[24] The epimerization at sulfur through the process was confirmed by oxidation of mixtures of **19** and **20** with magnesium monoperoxyphthalate (MMPP) to afford **21b** and **21c** as single diastereoisomers. The synthesis of sulfinyl vinyl aziridines under these conditions is a notable achievement; however, it should be mentioned that both the purity of the starting material and the source of NBS appear to be crucial requirements for the reaction to succeed.[25] The aziridine cyclization could be understood by the absence of an effective bromide source that would allow for the sulfonamide cyclization onto the bromonium intermediate at the distal double bond.[7i] Strict stereoelectronic requirements would lead primarily to the formation of the aziridine ring (S_N2' cyclization) as a single diastereoisomer along with small amounts of dihydropyrroles (S_N2 cyclization). Interestingly, the aziridine cyclization does not take place on the simple allylic sulfonamide **7a**, derived from **3a** where a single double bond instead of a diene moiety is present. Although sulfonamides are known to react with NBS to form N−Br compounds, we could not detect any sign of N−Br intermediates whose presence might slow down the rate of cyclization.[4c,26]

Seeking to explore the chemoselective transformations of these highly functionalized aziridines, we submitted **19a** to bromide displacement with piperidine to afford sulfinyl aziridine **22** in 71% yield (Scheme 8). Ozonolysis protocols were then

Scheme 8. Chemoselective Transformations of Trisubstituted Aziridines



attempted on sulfonyl aziridines **21b** and **21c** with the aim of transforming the allylic bromide into a carboxylic acid moiety. However, ozonolysis at room temperature in acetone/H_2O led to a 90:10 mixture of the aldehyde **23b** and 2,3-*cis*-ditosyl aziridine **24b**, produced by decarboxylation of the carboxylic acid (not shown). The value of 6.8 Hz for J_{H2-H3} in **24b** indicates that the stereochemistry of the aziridine is preserved.[27] The use of milder reaction conditions for **21c** by lowering the temperature (−78 °C) and quenching with SMe_2 did not influence the result. Mixtures of **23bc** and **24bc** were then fully oxidized with TCCA[28] (trichloroisocianuric acid) to afford ditosyl aziridines **24b** and **24c** as single isomers in good yields.

In conclusion, we have extended the scope of the methodology for the preparation of enantiopure 2-sulfinyl allylic sulfinamides from readily available sulfinimines and α-metalated vinyl and dienyl sulfoxides, evidencing the generality of the process that allows for the synthesis of allylic amines and sulfonamides for a broad number of substrates with high yields and diastereoselectivities. In addition, we have studied in depth different protocols for aminocyclizations to afford sulfinyl and sulfonyl dihydropyrroles. Importantly, we have found that the sulfonamido group has a significant influence on the stereochemical outcome of the bromocyclization, allowing for the selective preparation of 2,5-*cis*- or 2,5-*trans*-3-sulfinyl disubstituted dihydropyrroles from a common sulfinamide intermediate. On the other hand, a highly diastereoselective route for the synthesis of trisubstituted vinyl aziridines has been found using NBS as source of bromine. Further applications of these cyclizations to the synthesis of bioactive products are currently under exploration in our laboratory.

■ EXPERIMENTAL SECTION

1. Materials and Methods. ^1H and ^{13}C NMR spectra were recorded at 300, 400, or 500 MHz (^1H) using $CDCl_3$ as solvent and with the residual solvent signal as internal reference ($CDCl_3$, 7.24 and 77.0 ppm) unless otherwise noted. Optical rotations were measured at 20 °C in $CHCl_3$ solution using a sodium lamp. Low- and high-resolution mass spectra were recorded using the electronic impact technique with ionization energy of 70 eV or using the electrospray (ESI) chemical ionization techniques in its positive or negative modes. Vinyl and dienyl sulfoxides were prepared as *E*/*Z* mixtures that completely isomerized to the *E* isomer upon lithiation.[13] *N*-Sulfinimines[12] and (*S*)-2,4,6-trimethylbenzenesulfinamide[29] were prepared as described in the literature. Compounds **3b,c,h,j**, **5c,h**, **4b,c,h**, **6c,h**, **9c**, **10c**, **7b−d**, **8a**, **11a−c**, and **17** were already reported.[10a]

2. General Procedure for the Synthesis of Vinyl Sulfinamides. A round-bottomed flask was charged with THF (3.5 mL/mmol) and 2.1 equiv of freshly distilled *i*-Pr_2NH and cooled to −78 °C. To the above solution was added 2.0 equiv of *n*-BuLi, and the resulting LDA solution was stirred at this temperature. After 10 min, a solution of 1.0 equiv of a *Z*/*E* mixture of vinyl or dienyl sulfoxides in THF (2 mL/mmol), previously dried over 4 Å sieves, was added slowly dropwise (ca. 8 min/mmol of sulfoxide) to produce a pale yellow solution. After stirring for an additional 10 min at −78 °C, 2.0 equiv of *N*-sulfinimine in THF (2 mL/mmol) was added dropwise, and the resulting colorless solution was stirred at this temperature for 10 min. The reaction mixture was quenched with a saturated solution of NH_4Cl (2 mL/mmol) and H_2O (2 mL/mmol) and diluted with EtOAc (3 mL/mmol). The layers were separated, and the aqueous layer was extracted with EtOAc (3 times, 4 mL/mmol). The combined organic extracts were washed with a saturated solution of NaCl (4 mL/mmol), dried over Na_2SO_4, and concentrated under reduced pressure to give a crude product that was purified by column chromatography using the appropriate mixture of eluents. In most cases, recovery of the excess *N*-sulfinimine was straightforward.

2.1. Synthesis of (−)-(R)-N-[(1S,2E)-2-((S)-p-Tolylsulfinyl)-1,3-diphenyl-2-propen-1-yl]-4-methylbenzenesulfinamide, ***3a***. From an *E*/*Z* mixture of vinyl sulfoxides ***R*-2a** (59 mg, 0.24 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***R*-1a** (124 mg, 0.51 mmol, 2.0 equiv), following the general procedure, **3a** was obtained as a single isomer. Chromatographic purification (10−50% EtOAc/hex) gave **3a** (65 mg, 55%) as a colorless oil.

Data for **3a**: R_f 0.10 (40% EtOAc/hex); $[\alpha]^{20}_D$ −57.8 (*c* = 1.17); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 3 H), 2.34 (s, 3 H), 5.13 (d, 1 H, *J* = 6.3 Hz), 5.89 (d, 1 H, *J* = 6.3 Hz), 7.14−7.17 (m, 9 H), 7.27−7.36 (m, 6 H), 7.40 (dt, 2 H, *J* = 8.3, 1.8 Hz), 7.45 (dt, 2 H, *J* = 8.3, 1.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 21.4, 56.1, 125.4 (2 C), 126.2 (2 C), 126.8 (2 C), 127.6, 128.5 (2 C), 128.6, 128.7 (2 C), 129.0 (2 C), 129.4 (2 C), 129.9 (2 C), 133.4, 133.9, 138.5, 140.0, 141.1, 141.4, 142.1, 146.3; IR (film) 3191, 3056, 3020, 2920, 1594, 1492, 1448, 1400, 1176, 1085, 1051, 1014, 810, 752, 697 cm^{-1}; MS (ESI) 486 [M + 1]$^+$ (100%), 993 [2M + Na]$^+$. Anal. Calcd for $C_{29}H_{27}NO_2S_2$: C, 71.72; H, 5.60; N, 2.88; S, 13.20. Found: C, 71.85; H, 5.25; N, 2.47; S, 13.02.

*2.2. Synthesis of (−)-(R)-N-[(1S,2E)-2-((S)-p-Tolylsulfinyl)-1-(1-naphthyl)-2,4-pentadien-1-yl]-4-methylbenzenesulfinamide, **3d**.* From an *E*/*Z* mixture of dienyl sulfoxides (45 mg, 0.23 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***R*-1b** (184 mg, 0.46 mmol, 2.0 equiv), following the general procedure, **3d** was obtained as a single isomer. Chromatographic purification (20−50% EtOAc/hex) gave **3d** (78 mg, 70%) as a colorless oil.

Data for **3d**: R_f 0.21 (60% EtOAc/hex); $[\alpha]^{20}_D$ −32.6 (c = 1.23); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.10 (s, 3 H), 2.92 (s, 3 H), 4.52 (d, 1 H, J = 2.1 Hz), 5.70 (dd, 1 H, J = 9.7, 1.6 Hz), 5.80 (dd, 1 H, J = 16.3, 1.6 Hz), 6.40 (d, 1 H, J = 2.2 Hz), 6.71 (d, 2 H, J = 7.9 Hz), 6.96 (dt, 2 H, J = 8.2, 1.9 Hz), 7.13−7.24 (m, 4 H), 7.24−7.42 (m, 4 H), 7.54−7.64 (m, 4 H), 7.72 (dd, 1 H, J = 7.9, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 21.1, 21.2, 49.9, 122.1, 124.6, 125.0 (2 C), 125.2 (2 C), 125.5 (2 C), 126.3, 126.6, 128.5, 128.9 (2 C), 129.2, 129.3 (2 C), 130.0, 130.2, 132.1, 133.4, 134.1, 138.5, 141.1 (2 C), 141.5, 143.1; IR (film) 3050, 2949, 2924, 2849, 1594, 1491, 1458, 1376, 1085, 1049, 805, 776, 758 cm^{-1}; MS (ESI) 508 [M + Na]$^+$ (100%), 993 [2M + Na]$^+$; HRMS (ESI) m/z for $C_{29}H_{28}NO_2S_2$ [M + H]$^+$ calcd 486.1561, observed 486.1552.

*2.3. Synthesis of (−)-(R)-N-[(1S,2E)-1-(4-Methoxyphenyl)-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-4-methylbenzenesulfinamide, **3e**.* From an *E*/*Z* mixture of dienyl sulfoxides **2c** (92 mg, 0.476 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***R*-1d** (260 mg, 0.951 mmol, 2.0 equiv), following the general procedure, compound **3e** was obtained as a single diastereomer. Chromatographic purification (20−55% EtOAc/hex) provided **3e** (156 mg, 70%) as a white solid.

Data for **3e**: R_f 0.15 (50% EtOAc/hex); mp 155 °C; $[\alpha]^{20}_D$ −18.4 (c = 2.60); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.32 (s, 3 H), 2.37 (s, 3 H), 3.71 (s, 3 H), 4.51 (br d, 1 H, J = 4.9 Hz), 5.49 (dd, 1 H, J = 9.9, 1.4 Hz), 5.57 (d, 1 H, J = 4.6 Hz), 5.59 (dd, 1 H, J = 16.6, 1.5 Hz), 6.64 (m, 2 H), 6.78 (ddd, 1 H, J = 16.6, 11.2, 9.9 Hz), 6.98 (d, 1 H, J = 11.2 Hz), 7.00 (m, 2 H), 7.15 (m, 2 H), 7.23 (m, 2 H), 7.37 (m, 2 H), 7.53 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 21.5, 55.2, 55.3, 114.0 (2 C), 125.3 (2 C), 125.5, 126.1 (2 C), 129.6 (2 C), 129.9 (2 C), 130.5 (2 C), 130.7, 130.8, 132.9, 139.8, 141.8, 141.8, 142.0, 145.4, 159.2; IR (KBr) 3436, 3191, 2924, 1610, 1511, 1493, 1455, 1304, 1249, 1178, 1090, 1048, 1016, 931, 810, 705, 624, 533 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{28}NO_3S_2$ [M + H]$^+$ calcd 466.1511, observed 466.1532.

*2.4. Synthesis of (−)-(R)-N-[(1S,2E)-1-(3,4-Dimethoxyphenyl)-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-4-methylbenzenesulfinamide, **3f**.* From an *E*/*Z* mixture of dienyl sulfoxides **2c** (2.70 g, 14.2 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***R*-1d** (8.56 g, 28.3 mmol, 2.0 equiv), following the general procedure, compound **3f** was obtained as a single diastereomer. Chromatographic purification (20−55% EtOAc/hex) provided **3f** (5.27 g, 75%) as a white solid.

Data for **3f**: R_f 0.10 (50% EtOAc/hex); mp 71−73 °C; $[\alpha]^{20}_D$ −24.2 (c = 0.95); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.30 (s, 3 H), 2.36 (s, 3 H), 3.65 (s, 3 H), 3.78 (s, 3 H), 4.53 (br d, 1 H, J = 4.9 Hz), 5.47 (d, 1 H, J = 9.9), 5.57 (d, 1 H, J = 4.7 Hz), 5.60 (d, 1 H, J = 14.1 Hz), 6.51 (d, 1 H, J = 0.8 Hz), 6.60 (d, 1 H, J = 8.4 Hz), 6.69 (dm, 1 H, J = 8.2 Hz), 6.70−6.80 (m, 1 H), 7.01 (d, 1 H, J = 11.3 Hz), 7.13 (d, 2 H, J = 8.4 Hz), 7.22 (d, 2 H, J = 8.5 Hz), 7.36 (d, 2 H, J = 8.2 Hz), 7.52 (d, 2 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 27.1, 55.5, 55.9, 56.1, 110.6, 119.8, 125.5 (2 C), 125.8, 126.1 (2 C), 129.7 (2 C), 130.1 (2 C), 130.7, 131.4, 133.3, 140.1, 141.8, 142.0, 142.2, 145.5, 148.9, 149.1; IR (KBr) 3436, 2925, 2851, 1594, 1516, 1464, 1264, 1144, 1089, 1048, 1029, 810, 625 cm^{-1}; HRMS (ESI) m/z for $C_{27}H_{30}NO_4S_2$ [M + H]$^+$ calcd 496.1616, observed 496.1620.

*2.5. Synthesis of (−)-(R)-N-[(1S,2E)-2-((S)-p-Tolylsulfinyl)-1-(4-(trifluoromethyl)phenyl)-2,4-pentadien-1-yl)]-4-methylbenzenesulfinamide, **3g**.* From an *E*/*Z* mixture of dienyl sulfoxides **2c** (93 mg, 0.482 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***R*-1e** (300 mg, 0.964 mmol, 2.0 equiv), following the general procedure, compound **3g** was obtained as a 94:6 mixture of diastereomers. Chromatographic purification (20−50% EtOAc/hex) provided major diastereomer **3g** (208 mg, 86%) as a colorless oil.

Data for **3g**: R_f 0.2 (50% EtOAc/hex); $[\alpha]^{20}_D$ −74.7 (c = 2.00); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.26 (s, 3 H), 2.29 (s, 3 H), 5.24 (d, 1 H, J = 5.5 Hz), 5.53 (dd, 1 H, J = 9.8, 1.3 Hz), 5.61 (dd, 1 H, J = 16.5, 1.3 Hz), 5.73 (d, 1 H, J = 5.5 Hz), 6.77 (ddd, 1 H, J = 16.5, 11.3, 9.8 Hz), 6.95 (d, 1 H, J = 11.3 Hz), 7.03−7.14 (m, 6 H), 7.22−7.25 (m, 4 H), 7.45 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1, 48.6, 53.7, 125.0 (q, J = 3.8 Hz), 125.3 (2 C), 125.8 (2 C), 126.3, 127.3 (q, J = 272 Hz), 127.5 (2 C), 129.6 (2 C, q, J = 39 Hz), 129.4 (2 C), 129.8 (2 C), 129.9, 133.7, 139.3, 141.2, 141.6, 142.1, 142.7, 144.5; IR (film) 3648, 3173, 2925, 2870, 1618, 1595, 1445, 1416, 1380, 1326, 1265, 1164, 1068, 932, 838, 736, 704 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{25}F_3NO_2S_2$ [M + H]$^+$ calcd 504.1279, observed 504.1280.

*2.6. Synthesis of (+)-(S)-N-[(1R,2E)-1-Isopropyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-2,4,6-trimethylbenzenesulfinamide, **4i**, and (S)-N-[(1S,2E)-1-Isopropyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-2,4,6-trimethylbenzenesulfinamide, **4i′**.* From an *E*/*Z* mixture of dienyl sulfoxides **2c** (80 mg, 0.42 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***S*-1g** (208 mg, 0.88 mmol, 2.0 equiv), following the general procedure, an 85:15 mixture of **4i**:**4i′** was obtained. Chromatographic purification (10−50% EtOAc/hex) gave the mixture of isomers **4i**:**4i′** (128 mg, 72%) as a colorless oil. Crystallization (2:1 Et_2O/hex) of this fraction led to **4i** as a white solid (102 mg, 57%).

Data for **4i**: R_f 0.21 (40% EtOAc/hex); mp 118 °C; $[\alpha]^{20}_D$ +194.7 (c = 0.69); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.84 (d, 3 H, J = 6.6 Hz), 1.05 (d, 3 H, J = 6.6 Hz), 1.98 (m, 1 H), 2.25 (s, 3 H), 2.26 (s, 3 H), 2.31 (s, 6 H), 3.95 (d, 1 H, J = 6.8 Hz), 4.08 (dd, 1 H, J = 9.3, 7.2 Hz), 5.47 (d, 1 H, J = 10.0 Hz), 5.60 (d, 1 H, J = 16.6 Hz), 6.81 (m, 3 H), 7.00 (m, 3 H), 7.40 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.0 (2 C), 19.9, 20.0, 20.9, 21.3, 32.4, 60.3, 124.9, 125.5 (2 C), 127.2, 129.7 (2 C), 130.0, 130.4 (2 C), 132.3, 135.9, 138.4, 139.9, 140.2, 141.9, 145.6; IR (KBr) 3233, 2964, 2926, 2867, 1600, 1492, 1466, 1081, 1048, 927, 851, 810, 754, 664 cm^{-1}; MS (ESI) 430 [M + 1]$^+$ (100%), 452 [M + Na]$^+$, 881 [2M + Na]$^+$. Anal. Calcd for $C_{24}H_{31}NO_2S_2$: C, 67.09; H, 7.27; N, 3.26; S, 14.93. Found: C, 66.86; H, 7.04; N, 3.07; S, 14.81.

Partial data for **4i′**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.39 (br s, 1 H), 7.66 (d, 2 H, J = 8.3 Hz).

*2.7. Synthesis of (+)-(R)-N-[(1S,2E)-1-Cyclohexyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-4-methylbenzenesulfinamide, **3k**.* From an *E*/*Z* mixture of dienyl sulfoxides **2c** (463 mg, 2.41 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***R*-1i** (1.25 g, 4.81 mmol, 2.0 equiv), following the general procedure, compound **3k** was obtained as a single diastereomer. Chromatographic purification (25−50% EtOAc/hex) provided **3k** (729 mg, 69%) as a white solid.

Data for **3k**: R_f 0.15 (50% EtOAc/hex); mp 85 °C; $[\alpha]^{20}_D$ +71.6 (c = 1.90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.69−0.88 (m, 3 H), 0.91−1.04 (m, 2 H), 1.07−1.23 (m, 1 H), 1.44−1.69 (m, 4 H), 1.81 (br d, 1 H, J = 13.1 Hz), 2.36 (s, 3 H), 2.39 (s, 3 H), 4.03 (dd, 1 H, J = 9.2, 4.5 Hz), 4.18 (d, 1 H, J = 4.5 Hz), 5.46 (d, 1 H, J = 9.9 Hz), 5.56 (d, 1 H, J = 16.6 Hz), 6.66 (ddd, 1 H, J = 16.6, 11.2, 9.9 Hz), 6.96 (d, 1 H, J = 11.3 Hz), 7.24−7.28 (m, 4 H), 7.50 (br d, 2 H, J = 8.1 Hz), 7.57 (br d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 21.5, 25.8, 25.8, 25.9, 30.1, 30.5, 41.9, 58.6, 124.4, 125.3 (2 C), 126.5 (2 C), 129.5 (2 C), 130.0 (2 C), 130.5, 132.0, 139.9, 141.5, 142.2, 142.5, 144.8; IR (KBr) 3436, 2925, 2853, 1637, 1450, 1043, 811, 560 cm^{-1}; HRMS (ESI) m/z for $C_{25}H_{32}NO_2S_2$ [M + H]$^+$ calcd 442.1874, observed 442.1908.

*2.8. Synthesis of (+)-(R)-N-[(1S,2E)-1-Phenyl-4-((S)-p-tolylsulfinyl)-4,6-heptadien-3-yl]-4-methylbenzenesulfinamide, **3l**.* From an *E*/*Z* mixture of dienyl sulfoxides **2c** (106 mg, 0.553 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***R*-1j** (300 mg, 1.11 mmol, 2.0 equiv), following the general procedure, compound **3l** was obtained as a single diastereomer. Chromatographic purification (25−45% gradient EtOAc/hex) provided **3l** (174 mg, 68%) as a white solid.

Data for **3l**: R_f 0.20 (50% EtOAc/hex); mp 60 °C; $[\alpha]^{20}_D$ +18.8 (c = 1.30); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (q, 2 H, J = 7.6 Hz), 2.33 (s, 3 H), 2.37 (s, 3 H), 2.37−2.52 (m, 2 H), 4.27 (d, 1 H, J = 4.9 Hz), 4.48 (td, 1 H, J = 7.1, 4.9 Hz), 5.41 (d, 1 H, J = 10.0 Hz), 5.55 (d, 1 H,

J = 16.5 Hz), 6.44 (ddd, 1 H, J = 16.6, 11.3, 10.0 Hz), 6.90–6.93 (m, 3 H), 7.08–7.24 (m, 7 H), 7.46–7.49 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.21, 21.26, 31.9, 38.0, 52.5, 124.7, 125.1 (2 C), 125.9, 126.1 (2 C), 128.2 (2 C), 128.2 (2 C), 129.3 (2 C), 129.4, 129.8 (2 C), 129.9, 131.9, 140.1, 140.1, 141.3, 142.1, 145.6; IR (KBr) 3436, 3082, 3055, 3022, 2923, 1633, 1493, 1454, 1177, 1088, 1052, 1016, 935, 810, 752, 702, 624, 554, 508 cm^{-1}; HRMS (ESI) m/z for $C_{27}H_{30}NO_2S_2$ [M + H]$^+$ calcd 464.1718, observed 464.1712.

2.9. Synthesis of (−)-(R)-N-([3S,1E,4E)-1-Phenyl-4-((S)-p-tolylsulfinyl)-1,4,6-heptatrien-3-yl]-4-methylbenzenesulfinamide, 3m. From an E/Z mixture of dienyl sulfoxides **2c** (272 mg, 1.42 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***R*-1k** (763 mg, 2.83 mmol, 2.0 equiv), following the general procedure, compound **3m** was obtained as a single diastereomer. Chromatographic purification (0–50% EtOAc/hex) provided **3m** (408 mg, 62%) as a white solid.

Data for **3m**: R_f 0.25 (50% EtOAc/hex); mp 53 °C; $[\alpha]^{20}_D$ −1.4 (c = 0.70); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.23 (s, 3 H), 2.34 (s, 3 H), 4.17 (br s, 1 H), 5.28 (dd, 1 H, J = 7.5, 3.3 Hz), 5.52 (dd, 1 H, J = 15.7, 7.5 Hz), 5.58 (d, 1 H, J = 9.9 Hz), 5.69 (d, 1 H, 16.6 Hz), 6.13 (d, 1 H, J = 15.7 Hz), 6.83 (ddd, 1 H, J = 16.6, 11.2, 9.9 Hz), 6.92 (m, 2 H), 7.05 (d, 1 H, J = 11.3 Hz), 7.14–7.26 (m, 7 H), 7.51–7.57 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.32, 21.35, 53.4, 125.2 (2 C), 125.6, 126.3 (2 C), 126.4 (2 C), 126.7, 128.0, 128.3 (2 C), 129.5 (2 C), 130.0 (2 C), 130.2, 132.6, 133.0, 135.6, 139.8, 141.6, 141.8, 142.2, 144.2; IR (KBr) 3437, 3174, 3049, 3022, 2920, 2862, 1628, 1597, 1493, 1448, 1304, 1177, 1090, 1052, 1016, 987, 967, 930, 837, 809, 752, 695, 623, 594, 557, 511, 484 cm^{-1}; HRMS (ESI) m/z for $C_{27}H_{28}NO_2S_2$ [M + H]$^+$ calcd 462.1561, observed 462.1562.

2.10. Synthesis of (+)-(S)-N-[(2S,3E)-2-Phenyl-3-((S)-p-tolylsulfinyl)-3,5-hexadien-2-yl]-4-methylbenzenesulfinamide, 4n′. From an E/Z mixture of dienyl sulfoxides **2c** (200 mg, 1.04 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***S*-1l** (540 mg, 2.08 mmol, 2.0 equiv), following the general procedure, compound **4n′** was obtained as a single diastereomer (60%) along with 40% of starting material (ratio measured in the ^{1}H NMR of the crude). Chromatographic purification (0–50% gradient EtOAc/hex) provided **4n′** (234 mg, 50%) as a white solid.

Data for **4n′**: R_f 0.10 (50% EtOAc/hex); mp 135–137 °C; $[\alpha]^{20}_D$ −108 (c = 0.62); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.11 (s, 3 H), 2.41 (s, 6 H), 4.83 (brs, 1 H), 5.25 (dd, 1 H, J = 10.0, 1.5 Hz), 5.45 (dd, 1 H, J = 6.6, 0.9 Hz), 6.00–6.13 (m, 1 H), 7.01 (d, 1 H, J = 11.5 Hz), 7.20–7.36 (m, 9 H), 7.40 (d, 2 H, J = 8.3 Hz), 7.62 (d, 2 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 21.8, 30.5, 65.8, 125.2 (2 C), 125.9, 127.1 (2 C), 128.1 (2 C), 128.6, 128.9 (2 C), 129.8 (2 C), 130,1 (2 C), 130.4 (2 C), 132.4, 140.5, 141.8, 142.3, 142.4, 149.2; IR (KBr) 3436, 3191, 3054, 2926, 1595, 1494, 1445, 1191, 1078, 1060, 820, 811, 701 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{28}NO_2S_2$ [M + H]$^+$ calcd 450.1561, observed 450.1600.

2.11. Synthesis of (+)-(S)-N-[(2S,3E)-2-(4-Nitrophenyl)-3-((S)-p-tolylsulfinyl)-3,5-hexadien-2-yl]-4-methylbenzenesulfinamide, 4o′. From an E/Z mixture of dienyl sulfoxides (37 mg, 0.19 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***S*-1m** (116 mg, 0.38 mmol, 2.0 equiv), following the general procedure, compound **4o′** was obtained as a single diastereomer (55%) along with 45% of starting material (ratio measured in the ^{1}H NMR of the crude). Chromatographic purification (0–50% gradient EtOAc/hex) provided **4o′** (49 mg, 51%) as a yellow solid.

Data for **4o′**: R_f 0.10 (50% EtOAc/hex); mp 103–105 °C; $[\alpha]^{20}_D$ +57.9 (c = 1.60); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.11 (s, 3 H), 2.41 (s, 6 H), 4.83 (br s, 1 H), 5.25 (dd, 1 H, J = 10.0, 1.5 Hz), 5.45 (dd, 1 H, J = 6.6, 0.9 Hz), 6.00–6.13 (m, 1 H), 7.01 (d, 1 H, J = 11.5 Hz), 7.20–7.36 (m, 9 H), 7.40 (d, 2 H, J = 8.3 Hz), 7.62 (d, 2 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 21.5, 30.4, 65.5, 123.8 (2 C), 124.6 (2 C), 126.6 (2 C), 127.1, 128.7 (2 C), 129.6, 129.7 (2 C), 130.1 (2 C), 133.6, 139.7, 142.0 (2 C), 142.5, 147.4, 147.5, 150.1; IR (KBr) 3436, 2924, 1644, 1606, 1596, 1519, 1492, 1347, 1049, 855, 810 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{27}N_2O_4S_2$ [M + H]$^+$ calcd 495.1412, observed 495.1411. Anal. Calcd for $C_{26}H_{26}N_2O_4S_2$: C, 63.13; H, 5.30; N, 5.66; S, 12.97. Found: C, 63.01; H, 5.15; N, 5.75; S, 12.77.

2.12. Synthesis of (+)-N-[(2S,3E)-2-(4-Cyanophenyl)-3-((S)-p-tolylsulfinyl)-3,5-hexadien-2-yl]-4-methylbenzenesulfonamide, 4p′. From an E/Z mixture of dienyl sulfoxides **2c** (39 mg, 0.20 mmol, 1.0 equiv) with 2.0 equiv of LDA and sulfinimine ***S*-1n** (113 mg, 0.40 mmol, 2.0 equiv), following the general procedure, compound **4p′** was obtained as a single diastereomer (65%) along with 35% of starting material (ratio measured in the ^{1}H NMR of the crude). Chromatographic purification (0–50% gradient EtOAc/hex) provided **4p′** (46 mg, 48%) as a yellow solid.

Data for **4p′**: R_f 0.10 (50% EtOAc/hex); mp 140–142 °C; $[\alpha]^{20}_D$ +87.9 (c = 2.10); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.11 (s, 3 H), 2.45 (s, 6 H), 4.89 (br s, 1 H), 5.34 (dm, 1 H, J = 10.7 Hz), 5.52 (dm, 1 H, J = 15.9 Hz), 5.97–6.03 (m, 1 H), 7.03 (d, 1 H, J = 11.5 Hz), 7.26–7.29 (m, 9 H), 7.43 (d, 2 H, J = 9.1 Hz), 7.49 (d, 2 H, J = 8.9 Hz), 7.65 (d, 2 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 21.6, 30.2, 65.6, 112.1, 118.3, 124.9 (2 C), 125.3, 126.6 (2 C), 127.0, 128.5 (2 C), 129.7 (2 C), 130.3 (2 C), 132.4 (2 C), 133.7, 139.7, 141.9 (2 C), 142.4, 147.5, 148.2; IR (KBr) 3411, 2927, 2232, 1596, 1404, 1091, 929, 810, 669 cm^{-1}; HRMS (ESI) m/z for $C_{27}H_{27}N_2O_2S_2$ [M + H]$^+$ calcd 475.1514, observed 475.1516. Anal. Calcd for $C_{27}H_{26}N_2O_2S_2$: C, 68.32; H, 5.52; N, 5.90; S, 13.51. Found: C, 68.12; H, 5.75; N, 5.53; S, 13.32.

3. General Procedure for the Synthesis of Amines. To a solution of 1.0 equiv of N-sulfinamides **3** or **4** in MeOH (18 mL/mmol) was added 4.0 equiv of H_3PO_4 (85% aqueous solution). The mixture was stirred from 0 °C to rt until the disappearance of **3** or **4** (aliquots for TLC were neutralized with solid K_2CO_3). The solvent was evaporated, and the crude was diluted with water (10 mL/mmol). After basifying with solid K_2CO_3 to pH = 10–11, it was extracted with $CHCl_3$ (3 × 8 mL/mmol). The combined organic extracts were dried over Na_2SO_4 and concentrated under vacuum to afford the corresponding amines **5** or **6** that were purified by chromatography on silica gel using the appropriate mixture of eluents.

3.1. Synthesis of (−)-(1S,2E)-1,3-Diphenyl-2-((S)-p-tolylsulfinyl)-2-propen-1-amine, 5a. From sulfinamide **3a** (58 mg, 0.12 mmol, 1.0 equiv) and 4.0 equiv of H_3PO_4, according to the standard procedure (5 h), **5a** was obtained after purification by chromatography (40–80% Et_2O/CH_2Cl_2) as a white solid (36 mg, 87%).

Data for **5a**: R_f 0.21 (80% Et_2O/CH_2Cl_2 × 2); mp 125 °C; $[\alpha]^{20}_D$ −37.6 (c = 0.46); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.86 (br s, 2 H), 2.32 (s, 3 H), 5.25 (s, 1 H), 7.09–7.13 (m, 7 H), 7.25–7.37 (m, 7 H), 7.50 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 52.9, 125.7 (2 C), 126.6 (2 C), 127.0, 128.2 (2 C), 128.5 (3 C), 129.2 (2 C), 129.7 (2 C), 132.1, 134.1, 140.5 (2 C), 141.6, 150.0; IR (KBr) 3370, 3297, 3073, 3050, 3020, 2861, 1594, 1490, 1445, 1394, 1376, 1082, 1043, 931, 805, 753, 700, 640, 617, 505 cm^{-1}; MS (ESI) 717 [2M + Na]$^+$, 370 [M + Na]$^+$, 348 [M + 1]$^+$ (100%). Anal. Calcd for $C_{22}H_{21}NOS$: C, 76.04; H, 6.09; N, 4.03; S, 9.23. Found: C, 75.86; H, 5.88; N, 4.10; S, 8.95.

3.2. Synthesis of (−)-(1S,2E)-1-Phenyl-2-((S)-p-tolylsulfinyl)-2-hepten-1-amine, 5b. From **3b**[10a] (41 mg, 0.09 mmol, 1.0 equiv) and 4.0 equiv of H_3PO_4, according to the standard procedure (6 h), **5b** was obtained after purification by chromatography (30% Et_2O/CH_2Cl_2–Et_2O) as a colorless oil (29 mg, 99%).

Data for **5b**: R_f 0.07 (80% Et_2O/CH_2Cl_2); $[\alpha]^{20}_D$ −63.7 (c = 1.14); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.75 (t, 3 H, J = 7.1 Hz), 1.10–1.19 (m, 3 H), 1.23–1.30 (m, 1 H), 1.69 (s, 2 H), 1.91–2.11 (m, 2 H), 2.37 (s, 3 H), 4.82 (s, 1 H), 6.41 (t, 1 H, J = 7.6 Hz), 6.97–7.00 (m, 2 H), 7.10–7.16 (m, 3 H), 7.24 (d, 2 H, J = 7.9 Hz), 6.45 (d, 2 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.7, 21.4, 22.3, 28.4, 30.6, 51.3, 125.2 (2 C), 126.0 (2 C), 126.7, 128.1 (2 C), 129.8 (2 C), 138.1, 140.1, 141.4, 142.1, 148.4; IR (film) 3362, 3292, 3056, 3026, 2955, 2927, 2855, 1676, 1594, 1492, 1450, 1082, 1042, 809, 698 cm^{-1}; MS (ESI) 328 [M + 1]$^+$ (100%); HRMS (ESI) m/z for $C_{20}H_{26}NOS$ [M + H]$^+$ calcd 328.1735, observed 328.1753.

3.3. Synthesis of (+)-(1R,2E)-1-Phenyl-2-((S)-p-tolylsulfinyl)-2-hepten-1-amine, 6b. From **4b**[10a] (32 mg, 0.07 mmol, 1.0 equiv) and 4.0 equiv of H_3PO_4, according to the standard procedure (6 h), **6b** was obtained after purification by chromatography (30–60% Et_2O/CH_2Cl_2) as a colorless oil (19 mg, 84%).

Data for **6b**: R_f 0.21 (80% Et_2O/CH_2Cl_2); $[\alpha]^{20}_D$ +108.7 (c = 0.98); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.76 (t, 3 H, J = 7.1 Hz), 1.11–1.18

(m, 2 H), 1.21–1.36 (m, 2 H), 2.03–2.09 (m, 4 H), 2.38 (s, 3 H), 4.94 (s, 1 H), 6.46 (t, 1 H, *J* = 7.3 Hz), 7.15–7.28 (m, 5 H), 7.33 (m, 2 H), 7.52 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 13.7, 21.4, 22.3, 28.3, 30.5, 50.2, 125.1 (2 C), 126.3 (2 C), 126.7, 128.1 (2 C), 129.9 (2 C), 138.7, 140.7, 141.3, 142.5, 148.8; IR (film) 3368, 3292, 3056, 2927, 2855, 1597, 1493, 1450, 1161, 1082, 1042, 1014, 811 cm^{-1}; MS (ESI) 328 [M + 1]$^+$ (100%); HRMS (ESI) *m/z* for $C_{20}H_{26}NOS$ [M + H]$^+$ calcd 328.1735, observed 328.1740.

3.4. Synthesis of (+)-(1S,2E)-1-(4-Methoxyphenyl)-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-amine, ***5e***. From **3e** (24 mg, 0.052 mmol, 1.0 equiv) and 4.0 equiv of H_3PO_4, according to the standard procedure (6 h), amine **5e** was obtained after purification by chromatography (0–5% EtOH/CH_2Cl_2) as a colorless oil (13 mg, 76%).

Data for **5e**: R_f 0.25 (10% EtOH/CH_2Cl_2); $[\alpha]^{20}_D$ +25.3 (*c* = 1.80); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.60 (br s, 2 H), 2.34 (s, 3 H), 3.71 (s, 3 H), 4.86 (s, 1 H), 5.33 (dd, 1 H, *J* = 9.9, 1.6 Hz), 5.48 (dd, 1 H, *J* = 16.7, 1.6, Hz), 6.60 (ddd, 1 H, *J* = 16.7, 11.3, 9.9 Hz), 6.66 (m, 2 H), 6.90 (d, 1 H, *J* = 11.3 Hz), 6.95 (d, 2 H, *J* = 8.9 Hz), 7.19 (d, 2 H, *J* = 8.4 Hz), 7.42 (d, 2 H, *J* = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 51.5, 55.1, 113.6 (2 C), 124.4, 125.5 (2 C), 127.3 (2 C), 129.8 (2 C), 130.8, 132.3, 133.9, 139.9, 141.6, 149.5, 158.4; IR (film) 3369, 3291, 3000, 2926, 2836, 1608, 1510, 1492, 1463, 1417, 1303, 1249, 1177, 1113, 1081, 1036, 928, 835, 809, 735, 704 cm^{-1}; HRMS (ESI) *m/z* for $C_{19}H_{22}NO_2S$ [M + H]$^+$ calcd 328.1371, observed 328.1373.

3.5. Synthesis of (−)-(1S,2E)-1-(3,4-Dimethoxyphenyl)-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-amine, ***5f***. From **3f** (2.6 g, 5.25 mmol, 1.0 equiv) and 4.0 equiv of H_3PO_4, according to the standard procedure (2 h), amine **5f** was obtained after purification by chromatography (0–10% EtOH/Et_2O) as an orange oil (1.22 g, 65%).

Data for **5f**: R_f 0.20 (10% EtOH/Et_2O); $[\alpha]^{20}_D$ −8.7 (*c* = 0.58); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (br s, 2 H), 2.25 (s, 3 H), 3.52 (s, 3 H), 3.70 (s, 3 H), 4.83 (br s, 1 H), 5.24 (d, 1 H, *J* = 10.0 Hz), 5.41 (d, 1 H, *J* = 16.8 Hz), 6.56–6.66 (m, 3 H, H-4), 6.83 (m, 2 H), 6.83 (d, 1 H, *J* = 11.2 Hz), 7.11 (d, 2 H, *J* = 8.1 Hz), 7.35 (d, 2 H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.9, 51.2, 55.3, 55.5, 109.6, 110.8, 118.6, 124.0, 125.1 (2 C), 129.4 (2 C), 130.5, 132.1, 134.2, 140.0, 141.1, 147.8, 148.6, 149.7; IR (film) 3435, 2936, 1596, 1514, 1464, 1264, 1141, 1027, 810, 765 cm^{-1}; HRMS (ESI) *m/z* for $C_{20}H_{24}NO_3S$ [M + H]$^+$ calcd 358.1477, observed 358.1484.

3.6. Synthesis of (−)-(1S,2E)-2-((S)-p-Tolylsulfinyl)-1-(4-(trifluoromethyl)phenyl)-2,4-pentadien-1-amine, ***5g***. From **3g** (160 mg, 0.318 mmol, 1.0 equiv) and 4.0 equiv of H_3PO_4, according to the standard procedure (18 h), amine **5g** was obtained after purification by chromatography (0–5% EtOH/CH_2Cl_2) as an orange solid (92 mg, 79%).

Data for **5g**: R_f 0.25 (10% EtOH/CH_2Cl_2); mp 38 °C; $[\alpha]^{20}_D$ −10.5 (*c* = 1.30); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.67 (s, 2 H), 2.32 (s, 3 H), 5.01 (s, 1 H), 5.39 (ddd, 1 H, *J* = 10.0, 1.6, 0.7 Hz), 5.54 (ddd, 1 H, *J* = 16.7, 1.6, 0.8 Hz), 6.54 (ddd, 1 H, *J* = 16.7, 11.3, 10.0 Hz), 6.96 (dt, 1 H, *J* = 11.3, 0.7 Hz), 7.07–7.16 (m, 4 H), 7.31–7.39 (m, 4 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 51.7, 124.5 (q, *J* = 274 Hz), 125.5 (q, *J* = 3.5 Hz), 125.9 (2 C), 126.0, 126.9 (2 C), 129.5 (2 C, q, *J* = 37 Hz), 130.1 (2 C), 130.6, 133.6, 139.6, 142.1, 146.1, 149.1; IR (KBr) 3368, 3292, 3052, 2926, 2856, 2237, 1595, 1493, 1412, 1380, 1123, 1069, 1043, 1017, 929, 849, 756, 733 cm^{-1}; HRMS (ESI) *m/z* for $C_{19}H_{19}F_3NOS$ [M + H]$^+$ calcd 366.1139, observed 366.1140.

3.7. Synthesis of (+)-(1S,2E)-1-Cyclohexyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-amine, ***5k***. From **3k** (600 mg, 1.36 mmol, 1.0 equiv) and 5.0 equiv of H_3PO_4, according to the standard procedure (22 h), amine **5k** was obtained after purification by chromatography (0–5% EtOH/CH_2Cl_2) as an orange solid (346 mg, 84%).

Data for **5k**: R_f 0.30 (10% EtOH/CH_2Cl_2); mp 128 °C; $[\alpha]^{20}_D$ +328.3 (*c* = 1.43); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.65–0.85 (m, 2 H), 0.92–1.18 (m, 5 H), 1.29–1.44 (m, 1 H), 1.50–1.72 (m, 4 H), 1.91 (br d, 1 H, *J* = 12.2 Hz), 2.38 (s, 3 H), 3.05 (d, 1 H, *J* = 9.2 Hz), 5.41 (m, 1 H), 5.53 (m, 1 H), 6.91 (m, 1 H), 6.96 (d, 1 H, *J* = 11.3 Hz), 7.26 (d, 2 H, *J* = 8.6 Hz), 7.55 (d, 2 H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.9, 26.3, 26.4, 26.6, 30.6, 30.7, 43.8, 56.5, 123.6, 126.8 (2 C), 130.4 (2 C), 130.7, 131.9, 140.7, 142.6, 148.3; IR (KBr) 3436, 3376, 2954, 2806, 1592, 1493, 1448, 1399, 1307, 1262, 1209, 1181, 1084, 1041, 1016, 995, 928, 879, 788, 707 cm^{-1}; HRMS (ESI) *m/z* for $C_{18}H_{26}NOS$ [M + H]$^+$ calcd 304.1735, observed 304.1727.

3.8. Synthesis of (+)-(3S,4E)-1-Phenyl-4-((S)-p-tolylsulfinyl)-4,6-heptadien-3-amine, ***5l***. From **3l** (171 mg, 0.369 mmol, 1.0 equiv) and 4.0 equiv of H_3PO_4, according to the standard procedure (18 h), amine **5l** was obtained after purification by chromatography (0–5% EtOH/CH_2Cl_2) as an orange solid (93 mg, 77%).

Data for **5l**: R_f 0.35 (10% EtOH/CH_2Cl_2); mp < 30 °C; $[\alpha]^{20}_D$ +146.1 (*c* = 0.90); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (br s, 2 H), 1.44 (m, 1 H), 1.65 (m, 1 H), 2.33 (m, 1 H), 2.34 (s, 3 H), 2.47 (ddd, 1 H, *J* = 13.7, 10.0, 5.6 Hz), 3.64 (dd, 1 H, *J* = 8.2, 5.9 Hz), 5.37 (dd, 1 H, *J* = 9.8, 1.6 Hz), 5.49 (dd, 1 H, *J* = 16.4, 1.6 Hz), 6.75 (ddd, 1 H, *J* = 16.4, 11.3, 9.8 Hz), 6.85 (d, 1 H, *J* = 11.3 Hz), 6.92 (m, 2 H), 7.07–7.22 (m, 5 H), 7.45 (app d, 2 H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 32.8, 39.1, 49.4, 123.6, 125.8, 125.9, 128.2, 128.3, 129.8, 129.9, 130.1, 131.4, 140.7, 141.1, 141.7 (some peaks overlap); IR (KBr) 3435, 3055, 2922, 2856, 1630, 1596, 1454, 1398, 1302, 1209, 1178, 1043, 1015, 925, 810, 749, 700, 636, 624 cm^{-1}; HRMS (ESI) *m/z* for $C_{20}H_{24}NOS$ [M + H]$^+$ calcd 326.1573, observed 326.1588.

3.9. Synthesis of (+)-(2S,3E)-2-Phenyl-3-((S)-p-tolylsulfinyl)hexa-3,5-dien-2-amine, ***5n***. From **4n′** (408 mg, 0.91 mmol, 1.0 equiv) and 5.0 equiv of H_3PO_4, according to the standard procedure (48 h), amine **5n** was obtained after purification by chromatography (0–5% EtOH/CH_2Cl_2) as an orange oil (230 mg, 81%).

Data for **5n**: R_f 0.34 (4% EtOH/CH_2Cl_2); $[\alpha]^{20}_D$ +218.1 (*c* = 5.02); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.61 (br s, 2H, NH), 1.81 (s, 3 H), 2.41 (s, 3 H), 5.14 (ddd, 1 H, *J* = 9.8, 1.9, 0.4 Hz), 5.88 (ddd, 1 H, *J* = 15.6, 1.9, 0.7 Hz), 5.88 (ddd, 1 H, *J* = 16.6, 11.4, 9.9 Hz), 7.06–7.13 (m, 3 H), 7.20–7.70 (m, 5 H), 7.72 (d, 2 H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 29.7, 58.8, 123.6, 125.2 (2 C), 126.9 (2 C), 127.0, 128.7 (2 C), 129.8 (2 C), 129.9, 130.3, 141.5, 142.6, 148.1, 152.0; IR (film) 3435, 3056, 2924, 1597, 1492, 1445, 1318, 1302, 1084, 1041, 811, 702 cm^{-1}; HRMS (ESI) *m/z* for $C_{19}H_{22}NOS$ [M + H]$^+$ calcd 312.1422, observed 312.1413.

4. General Procedure for the Synthesis of Sulfonamides 7/8. To a solution of 1.0 equiv of amines **5** or **6** in anhydrous CH_2Cl_2 (3 mL/mmol) were added 1.3–3.0 equiv of RSO_2Cl and 2.7–3.5 equiv of Et_3N. The mixture was stirred from 0 °C to rt and monitored by TLC until completion. Then, it was hydrolyzed with a 50:50 mixture of a saturated aqueous solution of K_2CO_3 and H_2O (10 mL/mmol) and extracted with CH_2Cl_2 (3 × 10 mL/mmol). The combined organic phases were washed with a saturated solution of NaCl (10 mL/mmol), dried over Na_2SO_4, and filtered, and the solvent was evaporated under reduced pressure to give sulfonamides **7** or **8**, which were purified by chromatography on silica gel using the appropriate mixture of eluents.

Alternatively, **7l** was synthesized using Na_2CO_3 in CH_2Cl_2/H_2O as described in section **4.9**.

4.1. Synthesis of (+)-N-[(1R,2E)-2-((S)-p-Tolylsulfinyl)-1,3-diphenylprop-2-en-1-yl]-4-methylbenzenesulfonamide, ***7a***. From amine **5a** (28 mg, 0.08 mmol, 1.0 equiv), TsCl (23 mg, 0.12 mmol, 1.5 equiv), and Et_3N (30 μL, 0.20 mmol, 2.5 equiv), following the general procedure (24 h) and after chromatographic purification (10–50% EtOAc/hex), **7a** was obtained as a colorless oil (26 mg, 65%).

Data for **7a**: R_f 0.43 (60% EtOAc/hex); $[\alpha]^{20}_D$ +14.8 (*c* = 2.40); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 2.35 (s, 3 H, Me *p*-Tol), 2.36 (s, 3 H, Me *p*-Tol), 6.07 (d, 1 H, *J* = 9.3 Hz), 6.50 (dd, 1 H, *J* = 9.3, 1.5 Hz), 6.87 (s, 1 H, H-3), 7.04 (d, 2 H, *J* = 9.3 Hz), 7.12–7.16 (m, 5 H, ArH), 7.16–7.19 (m, 4 H, ArH), 7.31 (m, 3 H, ArH), 7.34–7.38 (m, 4 H, ArH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4 (2 C), 55.9, 126.0 (2 C), 126.8 (2 C), 127.0 (2 C), 127.6, 128.5 (2 C), 128.6 (2 C), 128.9 (2 C), 129.0, 129.2 (2 C), 130.0 (2 C), 133.4 (2 C), 137.6 (2 C), 139.5, 142.3, 142.9, 144.9; IR (film) 3271, 1597, 1493, 1450, 1332, 1160, 1086, 1056, 811, 756 cm^{-1}; HMRS (ESI) *m/z* for $C_{29}H_{27}NNaO_3S_2$ [M + Na]$^+$ calcd 524.1330, observed 524.1327.

4.2. Synthesis of (+)-N-[(1S,2E)-1-Phenyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-2-nitrobenzenesulfonamide, ***7e***. From amine **5c**[10a] (78 mg, 0.26 mmol, 1.0 equiv), 2-nitrobenzenesulfonyl chloride (76 mg, 0.34 mmol, 1.3 equiv), and Et_3N (0.07 mL, 0.52 mmol, 2.0 equiv), following the standard procedure (24 h) and after chromatographic purification (10−60% EtOAc/hex), **7e** was obtained as a colorless oil (94 mg, 74%).

Data for **7e**: R_f 0.25 (40% EtOAc/hex); $[\alpha]^{20}_D$ +19.5 (c = 1.10); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.32 (s, 3 H), 5.49 (d, 1 H, J = 9.8 Hz), 5.53 (d, 1 H, J = 15.6 Hz), 5.84 (d, 1 H, J = 8.1 Hz), 6.64 (ddd, 1 H, J = 15.7, 11.3, 9.8 Hz), 6.67 (d, 1 H, J = 10.8 Hz), 6.96 (d, 1 H, J = 8.3 Hz), 7.03−7.08 (m, 5 H), 7.14 (d, 2 H, J = 7.8 Hz), 7.32 (d, 2 H, J = 8.3 Hz), 7.55 (td, 1 H, J = 7.8, 1.2 Hz), 7.60 (td, 1 H, J = 7.6, 1.5 Hz), 7.78 (dd, 1 H, J = 7.8, 1.2 Hz), 7.81 (dd, 1 H, J = 7.8, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 56.1, 125.0, 125.3 (2 C), 126.8, 126.9 (2 C), 127.7, 128.4 (2 C), 129.6, 129.8 (2 C), 130.8, 132.5, 133.2, 134.2, 134.3, 137.4, 139.0, 141.8, 143.4, 147.4; IR (film) 3435, 1540, 1451, 1355, 1168, 1051, 742, 700, 591 cm^{-1}; MS (ESI) 483 [M + 1]$^+$ (100%), 987 [2M + Na]$^+$; HRMS (ESI) m/z for $C_{24}H_{22}N_2O_5S_2$ [M]$^+$ calcd 482.0970, observed 482.0965.

4.3. Synthesis of (+)-N-[(1S,2E)-1-Phenyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-2,4,6-triisopropylbenzenesulfonamide, ***7f***. From amine **5c**[10a] (74 mg, 0.25 mmol, 1.0 equiv), 2,4,6-triisopropylbenzenesulfonyl chloride (204 mg, 0.67 mmol, 2.7 equiv), and Et_3N (0.14 mL, 1.0 mmol, 4.0 equiv), following the standard procedure (48 h) and after chromatographic purification (10−40% EtOAc/hex), **7f** was obtained as a colorless oil (72 mg, 51%).

Data for **7f**: R_f 0.28 (30% EtOAc/hex); $[\alpha]^{20}_D$ +14.1 (c = 0.59); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.13 (t, 12 H, J = 6.8 Hz), 1.22 (d, 6 H, J = 6.8 Hz), 2.36 (s, 3 H), 2.85 (m, 1 H), 3.95 (m, 2 H), 5.40 (dd, 1 H, J = 10.0, 1.0 Hz), 5.44 (dd, 1 H, J = 16.6, 1.0 Hz), 5.85 (d, 1 H, J = 7.3 Hz), 6.14 (d, 1 H, J = 7.3 Hz), 6.43 (d, 1 H, J = 11.2 Hz), 6.55 (ddd, 1 H, J = 16.4, 11.0, 10.0 Hz), 6.99 (d, 2 H, J = 7.1 Hz), 7.05−7.12 (m, 5 H), 7.20 (d, 2 H, J = 7.8 Hz), 7.40 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.4, 23.6 (2 C), 24.7 (2 C), 24.8 (2 C), 29.8 (2 C), 34.1, 56.1, 123.5 (2 C), 125.9, 126.3 (2 C), 127.0 (2 C), 127.7, 128.4 (2 C), 129.5, 129.9 (2 C), 132.8, 133.9, 138.0, 139.2, 142.1, 144.4, 149.7, 152.6; IR (film) 3435, 2959, 2927, 1629, 1455, 1324, 1153, 1040, 667 cm^{-1}; MS (ESI) 564 [M + 1]$^+$ (100%), 1149 [2M + Na]$^+$; HRMS (ESI) m/z for $C_{33}H_{41}NO_3S_2$ [M]$^+$ calcd 563.2528, observed 563.2502.

4.4. Synthesis of (+)-N-[(1S,2E)-1-Phenyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-8-quinolinesulfonamide, ***7g***. From amine **5c**[10a] (97 mg, 0.33 mmol, 1.0 equiv), 8-quinolinesulfonyl chloride (96 mg, 0.42 mmol, 1.3 equiv), and Et_3N (0.09 mL, 0.65 mmol, 2.0 equiv), following the standard procedure (4 h) and after chromatographic purification (5−40% EtOAc/CH_2Cl_2), **7g** was obtained as a white solid (104 mg, 65%).

Data for **7g**: R_f 0.22 (60% EtOAc/hex); mp 195 °C; $[\alpha]^{20}_D$ +94.4 (c = 0.75); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.28 (s, 3 H), 5.35 (m, 1 H), 5.40 (m, 1 H), 5.68 (d, 1 H, J = 8.1 Hz), 6.57 (m, 1 H), 6.60 (d, 1 H, J = 11.0 Hz), 6.80−6.84 (m, 4 H), 6.88−6.91 (m, 1 H), 7.00 (d, 2 H, J = 8.1 Hz), 7.13 (d, 2 H, J = 8.1 Hz), 7.45 (d, 1 H, J = 9.5 Hz), 7.47 (dd, 1 H, J = 8.3, 4.4 Hz), 7.51 (dd, 1 H, J = 8.1, 7.51 Hz), 7.93 (dd, 1 H, J = 8.3, 1.5 Hz), 8.17 (dd, 1 H, J = 8.3, 1.7 Hz), 8.22 (dd, 1 H, J = 7.3, 1.5 Hz), 8.90 (dd, 1 H, J = 4.4, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 56.1, 122.1, 125.3, 125.5 (2 C), 126.8 (2 C), 127.3, 127.9 (2 C), 128.6, 129.5 (2 C), 129.9, 130.4, 132.4, 133.1, 136.6, 136.7, 137.6, 139.8, 141.4, 142.9, 144.5, 151.0 (2 C); IR (KBr) 3435, 1493, 1333, 1166, 1146, 1082, 1049, 790, 701 cm^{-1}; MS (ESI) 489 [M + 1]$^+$ (100%), 511 [M + Na]$^+$. Anal. Calcd for $C_{27}H_{24}N_2O_3S_2$: C, 66.37; H, 4.95; N, 5.73; S, 13.12. Found: C, 66.09; H, 5.20; N, 5.65; S, 12.98.

4.5. Synthesis of (−)-N-[(1S,2E)-1-Phenyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]naphthalene-1-sulfonamide, ***7j***. From amine **5c**[10a] (70 mg, 0.24 mmol, 1.0 equiv), 1-naphthalenesulfonyl chloride (70 mg, 0.31 mmol, 1.3 equiv), and Et_3N (67 μL, 0.48 mmol, 2.0 equiv), following the standard procedure (24 h) and after chromatographic purification (5−40% EtOAc/CH_2Cl_2), **7j** was obtained as a white solid (101 mg, 87%).

Data for **7j**: R_f 0.22 (40% EtOAc/hex); mp 76−78 °C; $[\alpha]^{20}_D$ −9.60 (c = 1.60); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.36 (s, 3 H), 5.30 (d, 1 H, J = 16.6 Hz), 5.36 (m, 1 H, J = 10.0 Hz), 5.80 (d, 1 H, J = 8.1 Hz), 6.04 (dd, 1 H, J = 11.0, 0.9 Hz), 6.52 (ddd, 1 H, J = 16.5, 11.0, 10.0 Hz), 6.88 (d, 1 H, J = 8.0 Hz), 7.03−7.14 (m, 9 H), 7.35 (t, 1 H, J = 7.8 Hz), 7.60 (td, 1 H, J = 7.1, 0.9 Hz), 7.67 (td, 1 H, J = 7.1, 1.3 Hz), 7.90 (d, 1 H, J = 7.8 Hz), 7.95 (d, 1 H, J = 8.1 Hz), 8.05 (dd, 1 H, J = 7.3, 1.2 Hz), 8.59 (d, 1 H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 56.9, 124.2, 124.9, 126.3, 126.4 (2 C), 127.1 (3 C), 127.9, 128.2, 128.6 (3 C), 129.1, 129.6, 129.7, 130.1, 133.5, 134.2, 134.4, 135.7, 137.2, 138.8, 142.4, 143.7 (2 C); IR (KBr) 3467, 3059, 2868, 1595, 1493, 1451, 1330, 1162, 1135, 1052, 805, 772 cm^{-1}; HRMS (ESI) m/z for $C_{28}H_{25}NO_3S_2$ [M]$^+$ calcd 487.1276, observed 487.1245. Anal. Calcd for $C_{28}H_{25}NO_3S_2$: C, 68.97; H, 5.17; N, 2.87; S, 13.15. Found: C, 68.75; H, 5.20; N, 2.65; S, 12.93.

4.6. Synthesis of (+)-N-[(1S,2E)-1-Phenyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]pyridine-2-sulfonamide, ***7k***. From amine **5c**[10a] (70 mg, 0.24 mmol, 1.0 equiv), 2-pyridinesulfonyl chloride (70 mg, 0.31 mmol, 1.3 equiv), and Et_3N (67 μL, 0.48 mmol, 2.0 equiv), following the standard procedure (20 h) and after chromatographic purification (5−60% EtOAc/CH_2Cl_2), **7k** was obtained as a white solid (84 mg, 80%).

Data for **7k**: R_f 0.22 (60% EtOAc/hex); mp 139−141 °C; $[\alpha]^{20}_D$ +107.4 (c = 3.80); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.35 (s, 3 H), 5.48 (d, 1 H, J = 16.8 Hz), 5.50 (m, 1 H, J = 9.5 Hz), 5.95 (d, 1 H, J = 8.5 Hz), 6.48 (d, 1 H, J = 11.7 Hz), 6.63 (d, 1 H, J = 10.0 Hz), 6.68 (ddd, 1 H, J = 16.3, 11.0, 10.0 Hz), 7.13−7.20 (m, 7 H), 7.33 (d, 2 H, J = 8.1 Hz), 7.60 (m, 1 H), 7.77 (m, 2 H), 8.54 (ddd, 1 H, J = 4.6, 2.3, 1.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 56.6, 121.9, 125.9 (2 C), 126.2, 126.5, 127.0 (2 C), 127.8, 128.6 (2 C), 130.0 (2 C), 133.4, 133.5, 137.7, 138.1, 139.5, 142.0, 144.0, 150.0, 157.9; IR (KBr) 3436, 3233, 2975, 1577, 1492, 1428, 1344, 1172, 1121, 1011, 954, 808, 782 cm^{-1}; HRMS (ESI) m/z for $C_{23}H_{22}N_2O_3S_2$ [M]$^+$ calcd 438.1072, observed 438.1059.

4.7. Synthesis of (+)-N-[(1S,2E)-1-(3,4-Dimethoxyphenyl)-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]quinoline-8-sulfonamide, ***7h***. From amine **5f** (1100 mg, 3.08 mmol, 1.0 equiv), 8-quinolinesulfonyl chloride (1050 mg, 4.62 mmol, 1.5 equiv), and Et_3N (1.50 mL, 10.78 mmol, 3.5 equiv), following the general procedure (20 h) and after chromatographic purification (25−40% EtOAc/hex), **7h** was obtained as a white solid (1569 mg, 93%).

Data for **7h**: R_f 0.20 (80% Et_2O/CH_2Cl_2); mp 68−70 °C; $[\alpha]^{20}_D$ +58.5 (c = 0.53); ^{1}H NMR ($CDCl_3$, 300 MHz)-COSY δ 2.29 (s, 3 H, Me *p*-Tol), 3.40 (s, 3 H, OMe), 3.68 (s, 3 H, OMe), 5.34 (d, 1 H, J = 9.8 Hz, H-5 *trans*), 5.38 (d, 1 H, J = 16.6 Hz, H-5 *cis*), 5.63 (d, 1 H, J = 8.1 Hz, H-1 HMBC(H−N)), 6.18 (s, 1 H, ArH), 6.28 (d, 1 H, J = 8.3 Hz, ArH), 6.39 (d, 1 H, J = 8.3 Hz, ArH), 6.55 (m, 1 H, H-4), 6.63 (d, 1 H, J = 11.2 Hz, H-3), 7.04 (d, 2 H, J = 8.1, ArH), 7.19 (d, 2 H, J = 8.1, ArH), 7.38 (br d, 1 H, J = 8.6 Hz, NH HMBC(H−N)), 7.46 (dd, 1 H, J = 8.1, 4.2 Hz, ArH), 7.49 (dd, 1 H, J = 7.3, 8.1 Hz, ArH), 7.93 (d, 1 H, J = 8.3 Hz, ArH), 8.16 (d, 1 H, J = 8.3 Hz, ArH), 8.21 (d, 1 H, J = 7.3 Hz, ArH), 8.90 (d, 1 H, J = 4.2 Hz, CH=N HMBC(H−N)); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 21.3, 55.4, 55.8, 56.2, 110.2, 110.4, 119.5, 122.0, 125.3, 125.5 (2 C), 128.6, 129.5 (2 C), 129.8, 130.0, 130.4 132.4, 132.9, 136.6, 137.0, 140.3, 141.4, 143.0, 144.8, 148.3, 148.6, 151.0 (2 C); IR (KBr) 3259, 2931, 1595, 1515, 1492, 1335, 1246, 1165, 1144, 1029, 911, 839, 810, 790, 762, 732 cm^{-1}; HRMS (ESI) m/z for $C_{29}H_{28}N_2O_5S_2$ [M]$^+$ calcd 548.1440, observed 548.1434.

4.8. Synthesis of (+)-N-[(1S,2E)-1-Isopropyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]quinoline-8-sulfonamide, ***7i***. From amine **5h**[10a] (125 mg, 0.48 mmol, 1.0 equiv), 8-quinolinesulfonyl chloride (141 mg, 0.62 mmol, 1.3 equiv), and Et_3N (1.34 mL, 0.96 mmol, 2.0 equiv), following the standard procedure (4 h) and after chromatographic purification (1−30% EtOH/CH_2Cl_2), **7i** was obtained as a solid (159 mg, 73%).

Data for **7i**: R_f 0.20 (5% EtOH/CH_2Cl_2); mp 49−51 °C; $[\alpha]^{20}_D$ +239 (c = 0.53); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.45 (d, 3 H, J = 6.6 Hz), 1.01 (d, 3 H, J = 6.6 Hz), 1.72 (m, 1 H), 2.28 (s, 3 H), 4.24 (t, 1 H, J = 8.8 Hz), 5.28 (d, 1 H, J = 16.6 Hz), 5.31 (d, 1 H, J = 9.8 Hz), 6.25 (d, 1 H, J = 11.5 Hz), 6.59 (ddd, 1 H, J = 16.6, 11.0, 10.0 Hz), 6.95 (d, 1 H, J = 8.8 Hz), 7.00 (d, 2 H, J = 8.1 Hz), 7.13 (d, 2 H, J = 8.1 Hz), 7.46 (dd, 1 H, J = 8.3, 7.3 Hz), 7.51 (dd, 1 H, J = 8.3, 4.2 Hz), 7.94 (dd, 1 H, J = 8.3, 1.5 Hz), 8.13 (dd, 1 H, J = 7.3, 1.5 Hz,), 8.21 (dd, 1 H, J = 8.3, 1.7 Hz), 9.02 (dd, 1 H, J = 8.3, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.2, 19.8, 21.4, 32.6, 59.2, 122.3, 124.3, 125.3, 125.9 (2 C), 128.7, 129.7 (2 C), 129.8, 130.1, 131.4, 132.8, 136.7 (2 C), 140.0, 141.9, 143.1, 144.7, 151.2; IR (KBr) 3268, 3063, 2960, 2937, 2873, 1596, 1568, 1494, 1172, 1045, 987, 833, 792, 719 cm^{-1}; HRMS (ESI) m/z for $C_{24}H_{26}N_2O_3S_2$ $[M]^+$ calcd 454.1385, observed 454.1394.

*4.9. Synthesis of (+)-N-[(2S,3E)-2-Phenyl-3-((S)-p-tolylsulfinyl)-3,5-hexadien-2-yl]-4-methylbenzenesulfonamide, **7l**.* Amine **5n** (25 mg, 0.084 mmol, 1.0 equiv), TsCl (19 mg, 0.1 mmol, 1.2 equiv), and Na_2CO_3 (19 mg, 0.18 mmol, 2.1 equiv) in 1 mL of CH_2Cl_2 and 1 mL of H_2O as solvents were stirred 4 days at room temperature. The organic layer was separated, washed with brine, and evaporated. After chromatographic purification (25−40% EtOAc/hex) **7l** was obtained as a yellow oil (25 mg, 63%).

Data for **7l**: R_f 0.30 (50% EtOAc/hex); $[\alpha]^{20}_D$ +1.3 (c = 1.30); ^1H NMR ($CDCl_3$, 300 MHz)-COSY δ 1.80 (s, 3 H, Me), 2.31 (s, 3 H, Me p-Tol), 2.45 (s, 3 H, Me p-Tol), 5.21 (dd, 1 H, J = 9.9, 1.5 Hz, H-6 *cis*), 5.42 (dd, 1 H, J = 16.7, 0.7 Hz, H-6 *trans*), 5.81 (ddd, 1 H, J = 16.7, 11.3, 9.9 Hz, H-5), 6.83 (d, 1 H, J = 11.3 Hz, H-4), 6.91 (d, 2 H, J = 8.0 Hz, ArH), 6.96−7.07 (m, 5 H, ArH), 7.13 (d, 2 H, J = 8.2 Hz, ArH), 7.36 (d, 2 H, J = 8.1 Hz, ArH), 7.46 (br s, 1 H, NH), 7.63 (d, 2 H, J = 8.1 Hz, ArH); 2D NOESY between H-5/H-6, H-4-ArH (sulfox), NH/ArH (Ts); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 21.4, 21.5, 26.0, 66.8, 125.8 (2 C), 126.5 (2C), 126.8, 127.2 (2 C), 127.4, 128.0 (2 C), 128.9 (2 C), 130.0, 130.1 (2 C), 136.4, 138.6, 139.1, 141.8, 142.0, 142.2, 147.2; IR (film) 3435, 3153, 2922, 1598, 1446, 1331, 1246, 1161, 1092, 1028, 911, 811, 702, 666 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{28}NO_3S_2$ $[M + H]^+$ calcd 466.1511, observed $[M + H]^+$ 466.1504.

*4.10. Synthesis of (+)-N-[(1S,2E)-1-(4-Methoxyphenyl)-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-4-methylbenzenesulfonamide, **7m**.* From amine **5e** (42 mg, 0.128 mmol, 1.0 equiv), TsCl (49 mg, 0.256 mmol, 2.0 equiv), and Et_3N (60 μL, 0.385 mmol, 3.0 equiv), following the general procedure (20 h) and after chromatographic purification (20−40% EtOAc/hex) **7m** was obtained as a white solid (59 mg, 96%).

Data for **7m**: R_f 0.25 (50% EtOAc/hex); mp 48 °C; $[\alpha]^{20}_D$ +27.8 (c = 2.80); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.36 (s, 3 H), 2.37 (s, 3 H), 3.72 (s, 3 H), 5.43 (d, 1 H, J = 10.8 Hz), 5.44 (d, 1 H, J = 15.8 Hz), 5.65 (d, 1 H, J = 7.8 Hz), 6.11 (d, 1 H, J = 7.7 Hz), 6.38 (d, 1 H, J = 11.2 Hz), 6.62 (ddd, 1 H, J = 10.8, 11.2, 15.8 Hz), 6.64 (app d, 2 H, J = 8.7 Hz), 6.96 (app d, 2 H, J = 8.7 Hz), 7.14 (app d, 2 H, J = 5.9 Hz), 7.17 (app d, 2 H, J = 5.9 Hz), 7.27 (app d, 2 H, J = 8.2 Hz), 7.54 (app d, 2 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.9, 22.0, 55.7, 56.2, 114.3 (2 C), 126.4 (2 C), 126.5 (2 C), 127.7 (2 C), 128.7 (2 C), 129.8 (2 C), 130.2, 130.3, 130.4, 133.5, 138.1, 139.6, 142.5, 143.5, 144.3, 159.6; IR (KBr) 3437, 2924, 2854, 1610, 1511, 1458, 1334, 1305, 1251, 1160, 1080, 1033, 927, 811, 705, 665, 624, 549 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{28}NO_4S_2$ $[M + H]^+$ calcd 482.1460, observed 482.1468.

*4.11. Synthesis of (+)-N-[(1S,2E)-2-((S)-p-Tolylsulfinyl)-1-(4-(trifluoromethyl)phenyl)-2,4-pentadien-1-yl]-4-methylbenzenesulfonamide, **7n**.* From amine **5g** (61 mg, 0.167 mmol, 1.0 equiv), TsCl (64 mg, 0.334 mmol, 2.0 equiv), and Et_3N (70 μL, 0.501 mmol, 3.0 equiv), following the general procedure (5 h) and after chromatographic purification (25−40% gradient EtOAc/hex), **7n** was obtained as a white solid (56 mg, 65%).

Data for **7n**: R_f 0.25 (50% EtOAc/hex); mp 68 °C; $[\alpha]^{20}_D$ +17.0 (c = 3.00); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 3 H), 2.36 (s, 3 H), 5.48 (br s, 1 H), 5.52 (dd, 1 H, J = 8.4, 1.5 Hz), 6.47 (d, 1 H, J = 11.2 Hz), 6.52−6.64 (m, 2 H), 7.12 (br d, 4 H, J = 7.7 Hz), 7.20 (m, 4 H), 7.31 (br d, 2 H, J = 8.1 Hz), 7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 21.9, 56.0, 124.2 (q, J = 272 Hz), 125.7 (2 C, q, J = 3.7 Hz), 126.3, 127.4, 127.6, 127.8, 129.7, 129.9, 130.2 (2 C, q, J = 33 Hz), 130.4, 134.5, 138.0, 139.2, 142.2 142.8, 143.3, 143.8 (some signals overlap); IR (KBr) 3435, 2927, 2868, 1620, 1597, 1493, 1450, 1419, 1327, 1163, 1123, 1069, 1018, 935, 868, 810, 706, 669, 549 cm^{-1}; HRMS (ESI) m/z for $C_{26}H_{25}F_3NO_3S_2$ $[M + H]^+$ calcd 520.1228, observed 520.1198.

*4.12. Synthesis of (+)-N-[(3S,4E)-1-Phenyl-4-((S)-p-tolylsulfinyl)-4,6-heptadien-3-yl]-4-methylbenzenesulfonamide, **7o**.* From amine **5l** (57 mg, 0.156 mmol, 1.0 equiv), TsCl (59 mg, 0.312 mmol, 2.0 equiv), and Et_3N (65 μL, 0.468 mmol, 3.0 equiv), following the general procedure (4 h) and after chromatographic purification (20−40% EtOAc/hex), **7o** was obtained as a white solid (74 mg, 99%).

Data for **7o**: R_f 0.25 (50% EtOAc/hex); mp 136 °C; $[\alpha]^{20}_D$ +74.4 (c = 1.80); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.73 (m, 1 H), 1.87 (m, 1 H), 2.34−2.57 (m, 2 H), 2.38 (s, 3 H), 2.39 (s, 3 H), 4.50 (td, 1 H, J = 6.5, 8.1 Hz), 5.35−5.46 (m, 2 H), 5.66 (d, 1 H, J = 7.9 Hz), 6.26−6.40 (m, 2 H), 6.92 (m, 2 H), 7.11−7.22 (m, 7 H), 7.39 (m, 2 H), 7.64 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 21.5, 31.9, 37.5, 52.3, 125.3, 126.0 (2 C), 126.1 (2 C), 127.2 (2 C), 128.3 (4 C), 128.4 (2 C), 129.4, 130.1, 132.2, 137.5, 139.4, 140.0, 142.4, 143.2, 144.1; IR (KBr) 3436, 3182, 3061, 3026, 2924, 2860, 1633, 1597, 1493, 1453, 1398, 1333, 1291, 1209, 1182, 1162, 1088, 1042, 1026, 1014, 994, 963, 949, 911, 886, 813, 751, 700, 668, 637, 619, 570, 549, 501 cm^{-1}; HRMS (ESI) m/z for $C_{27}H_{30}NO_3S_2$ $[M + H]^+$ calcd 480.1667, observed 480.1679.

*4.13. Synthesis of (+)-N-[(1S,2E)-1-Cyclohexyl-2-((S)-p-tolylsulfinyl)-2,4-pentadien-1-yl]-4-methylbenzenesulfonamide, **7p**.* From amine **5k** (88 mg, 0.290 mmol, 1.0 equiv), TsCl (111 mg, 0.580 mmol, 2.0 equiv), and Et_3N (120 μL, 0.870 mmol, 3.0 equiv), following the general procedure (4 h) and after chromatographic purification (20−40% EtOAc/hex), **7p** was obtained as a white solid (116 mg, 87%).

Data for **7p**: R_f 0.25 (50% EtOAc/hex); mp 58 °C; $[\alpha]^{20}_D$ +103.3 (c = 3.80); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.69−1.22 (m, 5 H), 1.46−1.75 (m, 5 H), 2.08 (app d, 1 H, J = 12.7 Hz), 2.37 (s, 6 H), 4.33 (t, 1 H, J = 9.5 Hz), 5.28 (d, 1 H, J = 16.6), 5.37 (d, 1 H, J = 10.3 Hz), 5.93 (d, 1 H, J = 11.0 Hz), 6.02 (d, 1 H, J = 8.9 Hz), 6.53 (ddd, 1 H, J = 16.6, 11.0, 10.3 Hz), 7.15 (app d, 2 H, J = 8.0 Hz), 7.17 (d, 2 H, J = 8.0 Hz), 7.26 (d, 2 H, J = 8.2 Hz), 7.57 (d, 2 H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.5, 21.5, 25.6, 25.7, 26.0, 30.1, 40.9, 58.9, 124.8, 126.6 (2 C), 127.0 (2 C), 129.2 (2 C), 129.8 (2 C), 129.9, 132.7, 138.3, 139.2, 142.6, 142.8, 142.8; IR (KBr) 3436, 2926, 2853, 1632, 1494, 1450, 1334, 1161, 1088, 1046, 931, 813, 668, 569, 551 cm^{-1}; HRMS (ESI) m/z for $C_{25}H_{32}NO_3S_2$ $[M + H]^+$ calcd 458.1824, observed 458.1813.

5. Synthesis of (+)-*tert*-Butyl *N*-[(1*R*,2*E*)-1-phenyl-2-((*S*)-*p*-tolylsulfinyl)-2,4-pentadien-1-yl] Carbamate, 8b. To amine **6c** (38 mg, 0.13 mmol, 1 equiv) in CH_2Cl_2 (20 mL/mmol) at 0 °C were added sequentially 1 N NaOH (0.3 + 0.3 + 0.2 mL, 6 equiv) and 0.5 M Boc_2O in CH_2Cl_2 (0.3 + 0.3 + 0.2 mL, 3.2 equiv). The mixture was stirred from 0 °C to rt (24 h) until disappearance of the starting material. Then, CH_2Cl_2 was evaporated under vacuum, and the residue was extracted with $CHCl_3$. The organic extracts were washed with brine, dried (Na_2SO_4), and evaporated under vacuum. After chromatographic purification (10−40% EtOAc/hex), **8b** was obtained as a white solid (40 mg, 79%).

Data for **8b**: R_f 0.28 (30% EtOAc/hex); mp 155 °C; $[\alpha]^{20}_D$ +181.6 (c = 0.64); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.35 (s, 9 H), 2.33 (s, 3 H), 5.22 (d, 1 H, J = 8.8 Hz), 5.43 (d, 1 H, J = 10.0 Hz), 5.60 (d, 1 H, J = 16.6 Hz), 5.93 (d, 1 H, J = 8.8 Hz), 6.51 (ddd, 1 H, J = 16.6, 10.8, 10.6 Hz), 7.03 (d, 3 H, J = 10.9 Hz), 7.15 (d, 5 H, J = 7.6 Hz), 7.38 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.3, 28.2 (3 C), 51.2, 79.8, 125.4 (2 C), 125.7, 126.1 (2 C), 127.1, 128.3 (2 C), 129.8 (2 C), 129.9, 133.5, 138.7, 139.3, 141.6, 145.3, 154.6; IR (KBr) 3427, 3337, 3020, 2973, 2920, 1709, 1629, 1508, 1491, 1450, 1365, 1282, 1249, 1170, 1082, 1049, 981, 937, 806 cm^{-1}; MS (ESI) 817 $[2M + Na]^+$ (100%), 420 $[M + Na]^+$. Anal. Calcd for $C_{23}H_{27}NO_3S$: C, 69.49; H, 6.85; N, 3.52; S, 8.07. Found: C, 69.71; H, 6.67; N, 3.76; S, 7.93.

6. General Procedure for the Synthesis of Hydroxymethyl 2-Sulfonyldihydropyrroles. To a solution of 1.0 equiv of **3** in toluene (10 mL/mmol) was added 3.5 equiv of solid m-CPBA (70%). The mixture was stirred until the disappearance by TLC of the bis-tosylated compound generated at the initial stage. Then, 0.2 equiv of CSA was added, and the reaction was stirred until no epoxides were observed by TLC. After that, the reaction was hydrolyzed with 1 M solution of $Na_2S_2O_4$ (5 mL/mmol) and extracted with EtOAc (3 × 5 mL/mmol). The organic phases were washed with saturated aqueous solution of $NaHCO_3$ (5 mL/mmol), H_2O (5 mL/mmol), and brine (5 mL/mmol).

It was dried over Na_2SO_4 and concentrated under reduced pressure to give a mixture of 2,5-*cis* **9** and 2,5-*trans*-dihydropyrroles **10**, which were separated by chromatography on silica gel using the appropriate mixture of eluents.

*6.1. Synthesis of (+)-N-[(1S,2E)-1-Isopropyl-2-[(4-methylphenyl)-sulfonyl]-3-[(2S)-2-oxiranyl]-2-propen-1-yl]-4-methylbenzenesulfonamide, (+)-[(2S,5S)-5-Isopropyl-1,4-bis[(4-methylphenyl)sulfonyl]-2,5-dihydro-1H-pyrrol-2-yl]methanol, **9h**, and (+)-[(2R,5S)-5-Isopropyl-1,4-bis[(4-methylphenyl)sulfonyl]-2,5-dihydro-1H-pyrrol-2-yl]methanol, **10h**.* From sulfinamide **3h**[10a] (70 mg, 0.2 mmol, 1.0 equiv), *m*-CPBA 70% (171 mg, 0.7 mmol, 3.5 equiv), and CSA (8 mg, 0.04 mmol, 0.2 equiv), following the standard procedure (7 days), a 70:30 *cis*:*trans* mixture of dihydropyrroles was obtained. After chromatographic purification (CH_2Cl_2-5% EtOAc/CH_2Cl_2), **9h** (26 mg, 34%, colorless oil) and **10h** (16 mg, 20%, white solid) were obtained. When quenching the reaction at shorter times (5−6 days), small amounts of a monoepoxide (10%) were obtained. Monoepoxide (8 mg) was further treated with CSA to afford **9h** as a single isomer (6 mg, 74%).

Data for *cis*-**9h**: R_f 0.29 (10% EtOAc/CH_2Cl_2); $[\alpha]^{20}_D$ +62.4 (*c* = 0.58); ^1H NMR ($CDCl_3$, 400 MHz)-COSY δ 0.81 (d, 3 H, *J* = 6.9 Hz, Me *i*-Pr), 1.11 (d, 3 H, *J* = 7.1 Hz, Me *i*-Pr), 2.25 (m, 1 H, CH *i*-Pr), 2.42 (s, 3 H, Me *p*-Tol), 2.49 (s, 3 H, Me *p*-Tol), 2.64 (dd, 1 H, *J* = 8.6, 2.9 Hz, OH), 3.67 (ddd, 1 H, *J* = 11.1, 8.8, 5.3 Hz, CH_2), 3.80 (ddd, 1 H, *J* = 11.1, 7.1, 3.1 Hz, CH_2), 4.33 (dddd, 1 H, *J* = 7.5, 5.1, 2.6, 1.1 Hz, H-2), 4.55 (dt, 1 H, *J* = 2.6, 1.2 Hz, H-5), 6.35 (dd, 1 H, *J* = 2.7, 1.3 Hz, H-3), 7.14 (dd, 2 H, *J* = 8.6, 0.6 Hz, ArH), 7.31 (dd, 2 H, *J* = 8.6, 0.5 Hz, ArH), 7.44 (dt, 2 H, *J* = 8.4, 2.0 Hz, ArH), 7.54 (dt, 2 H, *J* = 8.2, 2.2 Hz, ArH); 1D-NOE CH_2 (3.80 ppm)/2 Me *i*-Pr (2.6%); CH_2 (3.67 ppm)/Me *i*-Pr (0.81 ppm) (1.2%); Me *i*-Pr (0.81 ppm)/CH_2 (1.5%); ^{13}C NMR ($CDCl_3$, 125 MHz)-HSQC δ 17.1 (Me *i*-Pr), 20.2 (Me *i*-Pr), 21.7 (2 C, Me *p*-Tol), 31.5 (CH *i*-Pr), 64.4 (CH_2), 69.1 (C-2), 72.8 (C-5), 127.7 (2 C), 128.1 (2 C), 129.9 (2 C), 130.0 (2 C), 132.7, 135.8, 137.0, 137.1, 144.3, 145.2; IR (film) 3523, 2965, 2928, 1597, 1350, 1319, 1160, 1084, 757 cm^{-1}; MS (ESI) 450 $[M + H]^+$; HRMS (ESI) *m*/*z* for $C_{22}H_{27}NO_5S_2$ $[M]^+$ calcd 449.1331, observed 449.1325.

Data for *trans*-**10h**: R_f 0.39 (10% EtOAc/CH_2Cl_2); mp 165 °C $[\alpha]^{20}_D$ +51.3 (*c* = 0.76); ^1H NMR ($CDCl_3$, 400 MHz)-COSY δ 0.69 (d, 3 H, *J* = 6.9 Hz, Me *i*-Pr), 1.08 (d, 3 H, *J* = 7.3 Hz, Me *i*-Pr), 1.23 (br s, 1 H, OH), 2.41 (s, 3 H, Me *p*-Tol), 2.46 (s, 3 H, Me *p*-Tol), 2.57 (m, 1 H, CH *i*-Pr), 3.70 (dd, 1 H, *J* = 12.8, 3.1 Hz, CH_2), 4.06 (dd, 1 H, *J* = 12.8, 3.1 Hz, CH_2), 4.34 (ddt, 1 H, *J* = 4.9, 3.1, 1.6 Hz, H-2), 4.81 (ddd, 1 H, *J* = 4.9, 2.2, 0.9 Hz, H-5), 6.50 (dd, 1 H, *J* = 1.5, 0.9 Hz, H-3), 7.28 (dd, 2 H, *J* = 8.6, 0.5 Hz, ArH), 7.35 (dd, 2 H, *J* = 8.4, 0.6 Hz, ArH), 7.65 (dt, 2 H, *J* = 8.4, 2.0 Hz, ArH), 7.76 (dt, 2 H, *J* = 8.2, 2.0 Hz, ArH); 1D-NOE H-2/Me *i*-Pr (1.5%); Me *i*-Pr (1.08 ppm)/H-2 (0.1%); Me *i*-Pr (0.69 ppm)/H-2 (0.5%); ^{13}C NMR ($CDCl_3$, 100 MHz)-HSQC δ 16.5 (Me *i*-Pr), 18.1 (Me *i*-Pr), 21.5 (Me *p*-Tol), 21.7 (Me *p*-Tol), 32.3 (CH *i*-Pr), 62.5 (CH_2), 68.3 (C-2), 73.9 (C-5), 126.7 (2 C), 128.3 (2 C), 129.9 (2 C), 130.1 (2 C), 135.6, 137.2, 141.4, 143.4, 143.9, 145.3; IR (KBr) 3435, 2959, 2926, 1596, 1335, 1319, 1159, 1090, 812 cm^{-1}; MS (ESI) 450 $[M + H]^+$. Anal. Calcd for $C_{22}H_{27}NO_5S_2$: C, 58.77; H, 6.05; N, 3.12; S, 14.26. Found: C, 59.01; H, 6.12; N, 2.98; S, 14.05.

Data for monoepoxide: R_f 0.71 (10% EtOAc/CH_2Cl_2); $[\alpha]^{20}_D$ +79.2 (*c* = 0.80); ^1H NMR ($CDCl_3$, 300 MHz) δ 0.46 (d, 3 H, *J* = 6.6 Hz), 0.95 (d, 3 H, *J* = 6.6 Hz), 1.95 (m, 1 H), 2.40 (s, 3 H), 2.41 (m, 1 H), 2.42 (s, 3 H), 2.95 (dd, 1 H, *J* = 5.4, 4.1 Hz), 3.47 (ddd, 1 H, *J* = 7.8, 3.9, 2.4 Hz), 4.09 (t, 1 H, *J* = 10.4 Hz), 6.01 (d, 1 H, *J* = 8.3 Hz), 6.05 (m, 1 H), 7.25 (d, 2 H, *J* = 8.1 Hz, ArH), 7.29 (d, 2 H, *J* = 8.1 Hz), 7.66 (dt, 4 H, *J* = 8.5, 2.0 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.4, 19.9, 21.5, 21.7, 31.2, 47.4, 48.5, 59.1, 127.1 (2 C), 128.1 (2 C), 129.5 (2 C), 130.0 (2 C), 133.7, 137.3, 142.3, 143.4, 144.9, 145.0; IR (film) 3306, 2924, 1722, 1431, 1318, 1303, 1286, 1161, 1144, 1085, 814 cm^{-1}; MS (ESI) 450 $[M + H]^+$.

7. General Procedure for the Synthesis of Bromomethyl 3-Sulfinyl-2,5-dihydro-1*H*-pyrroles, 11 and 12. To a solution of sulfonamides **7** in anhydrous CH_2Cl_2 (7 mL/mmol) protected from light were added 2.0 equiv of solid tetrabutylammonium tribromide (TBATB) and 2.5 equiv of solid K_2CO_3 at rt. The mixture was stirred until the disappearance of **7** and no further evolution was detected by TLC. It was quenched with a 1 M solution of $Na_2S_2O_4$ (10 mL/mmol), extracted with CH_2Cl_2 (3 × 10 mL/mmol), washed with a saturated solution of NaCl (10 mL/mmol), dried over Na_2SO_4, and filtered, and the solvent was evaporated under reduced pressure to give a mixture of 2,5-*cis* **11** and 2,5-*trans*-dihydropyrroles **12**, which were separated by chromatography on silica gel using the appropriate mixture of eluents.

*7.1. Synthesis of (+)-(2S,5S)-5-(Bromomethyl)-1-[(2-nitrophenyl)-sulfonyl]-2-phenyl-3-((S)-tolylsulfinyl)-2,5-dihydro-1H-pyrrole, **11d**, and (+)-(2S,5R)-5-(Bromomethyl)-1-[(2-nitrophenyl)-sulfonyl]-2-phenyl-3-((S)-tolylsulfinyl)-2,5-dihydro-1H-pyrrole, **12d**.* From sulfonamide **7e** (25 mg, 0.05 mmol, 1.0 equiv), TBATB (50 mg, 0.1 mmol, 2.0 equiv), and K_2CO_3 (18 mg, 0.13 mmol, 2.5 equiv), following the standard procedure (6 days), a crude mixture of 80:20 *cis*:*trans* isomers was obtained, and after chromatographic purification (20−80% EtOAc/hex), **11d** (12 mg, 41%, colorless oil) and **12d** (5 mg, 17%, colorless oil) were obtained.

Data for *cis*-**11d**: R_f 0.27 (60% EtOAc/hex); $[\alpha]^{20}_D$ +102.7 (*c* = 0.44); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.40 (s, 3 H), 3.51 (dd, 1 H, *J* = 10.0, 9.0 Hz), 3.89 (dd, 1 H, *J* = 10.2, 3.8 Hz), 5.11 (ddt, 1 H, *J* = 9.0, 3.9, 2.2 Hz), 5.19 (t, 1 H, *J* = 1.9 Hz), 6.85 (t, 1 H, *J* = 1.9 Hz), 7.16−7.23 (m, 6 H), 7.25−7.27 (m, 3 H), 7.40 (ddd, 1 H, *J* = 7.8, 7.3, 1.2 Hz), 7.47 (dd, 1 H, *J* = 7.8, 1.2 Hz), 7.51 (dd, 1 H, *J* = 8.1, 1.2 Hz), 7.60 (ddd, 1 H, *J* = 7.8, 7.1, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC 21.6 (Me *p*-Tol), 33.9 (CH_2), 67.5 (C-5), 69.8 (C-2), 121.4, 125.3 (2 C), 128.5 (2 C), 128.9 (2 C), 129.3, 129.5, 130.3 (2 C), 130.4, 130.9, 131.4, 134.0 (2 C), 136.1, 137.5, 143.0, 149.6; IR (film) 2923, 1544, 1372, 1171, 1057, 756 cm^{-1}; MS (ESI) 561 $[M + H]^+$, 583 $[M + Na]^+$; HRMS (ESI) *m*/*z* for $C_{24}H_{22}BrN_2O_5S_2$ $[M + H]^+$ calcd 561.0154, observed 561.0133.

Data for *trans*-**12d**: R_f 0.38 (60% EtOAc/hex); $[\alpha]^{20}_D$ +180.6 (*c* = 0.33); ^1H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3 H), 3.80 (dd, 1 H, *J* = 10.7, 1.7 Hz), 4.23 (dd, 1 H, *J* = 10.9, 4.6 Hz), 5.13 (dd, 1 H, *J* = 5.1, 1.7 Hz), 5.65 (tt, 1 H, *J* = 4.6, 2.0 Hz), 6.62 (t, 1 H, *J* = 2.2 Hz), 6.75 (dd, 1 H, *J* = 8.1, 1.5 Hz), 6.91−7.21 (m, 6 H), 7.27−7.39 (m, 4 H), 7.44 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.6, 31.8, 68.0, 70.0, 123.4, 125.3, 126.7 (2 C), 128.6 (2 C), 128.9, 129.3 (2 C), 129.4, 130.3 (2 C), 131.0, 131.1, 132.6, 137.2, 142.9, 143.7, 150.3; IR (film) 2924, 1542, 1368, 1164, 1083, 1049, 758 cm^{-1}; MS (ESI) 561 $[M + H]^+$, 583 $[M + Na]^+$.

*7.2. Synthesis of (−)-(2S,5S)-5-(Bromomethyl)-2-phenyl-3-((S)-tolylsulfinyl)-1-[(2,4,6-triisopropylphenyl)sulfonyl]-2,5-dihydro-1H-pyrrole, **11e**, and (2S,5R)-5-(Bromomethyl)-2-phenyl-3-((S)-tolylsulfinyl)-1-[(2,4,6-triisopropylphenyl)sulfonyl]-2,5-dihydro-1H-pyrrole, **12e**.* From sulfonamide **7f** (20 mg, 0.04 mmol, 1.0 equiv), TBATB (34 mg, 0.07 mmol, 2.0 equiv), and K_2CO_3 (12 mg, 0.09 mmol, 2.5 equiv), following the standard procedure (6 days), a crude of 80:20 *cis*:*trans* isomers was obtained. Chromatographic purification (10−50% EtOAc/hex) gave **11e** (11 mg, 49%, colorless oil) and **12e** (2 mg, 8%, colorless oil).

Data for *cis*-**11e**: R_f 0.42 (40% EtOAc/hex); $[\alpha]^{20}_D$ −5.9 (*c* = 0.44); ^1H NMR ($CDCl_3$, 300 MHz)-COSY δ 0.90 (d, 6 H, *J* = 6.8 Hz, Me Ar × 2), 0.93 (d, 6 H, *J* = 6.8 Hz, Me Ar × 2), 1.18 (d, 6 H, *J* = 6.8 Hz, Me Ar × 2), 2.42 (s, 3 H, Me *p*-Tol), 2.81 (m, 1 H, CH Ar), 3.20 (m, 2 H, CH_2), 3.76 (m, 2 H, CH Ar × 2), 5.03 (t, 1 H, *J* = 1.7 Hz, H-2), 5.14 (ddt, 1 H, *J* = 7.8, 6.3, 1.9 Hz, H-5), 6.90 (m, 2 H, ArH), 6.97 (m, 3 H, ArH), 7.15−7.23 (m, 3 H, ArH), 7.26−7.35 (m, 4 H, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz)-HSQC 21.6 (Me *p*-Tol), 23.5 (Me Ar), 23.6 (Me Ar), 24.3 (2 C, Me Ar), 24.7 (2 C, Me Ar), 29.1 (2 C, Me Ar), 33.6 (CH_2), 34.2 (CH Ar), 66.2 (C-5), 68.8 (C-2), 124.0 (2 C), 126.0 (2 C), 128.5 (2 C), 128.6 (2 C), 128.8, 129.7, 130.4 (2 C), 130.6, 137.1, 137.4, 143.3, 149.6, 151.9 (2 C), 154.6; IR (film) 2961, 2927, 1599, 1457, 1314, 1260, 1152, 1084, 1057, 807, 679 cm^{-1}; MS (ESI) 642 $[M + H]^+$, 664 $[M + Na]^+$; HRMS (ESI) *m*/*z* for $C_{33}H_{41}BrNO_3S_2$ $[M + H]^+$ calcd 642.1711, observed 642.1730.

Partial data for *trans*-**12e**: R_f 0.27 (40% EtOAc/hex); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.05 (d, 6 H, *J* = 6.8 Hz), 1.13 (d, 12 H, *J* = 6.6 Hz), 2.43 (s, 3 H), 2.72 (m, 1 H), 3.76 (m, 2 H), 3.86 (dd, 1 H, *J* = 10.5, 2.4 Hz), 4.00 (dd, 1 H, *J* = 10.5, 6.2 Hz), 5.03 (dd, 1 H, *J* =

4.6, 2.2 Hz), 5.34 (m, 1 H), 6.73 (t, 1 H, J = 2.2 Hz), 6.77 (m, 3 H), 6.98 (m, 4 H), 7.26 (d, 1 H, J = 8.5 Hz), 7.36 (d, 2 H, J = 8.1 Hz).

7.3. Synthesis of (−)-8-[(2S,5R)-5-(Bromomethyl)-3-((S)-tolylsulfinyl)-2-phenyl-2,5-dihydro-1H-pyrrol-1-yl]sulfonylquinoline, ***12f****, and 8-[(2S,5S)-5-(Bromomethyl)-3-((S)-tolylsulfinyl)-2-phenyl-2,5-dihydro-1H-pyrrol-1-yl]sulfonylquinoline,* ***11f****.* From sulfonamide **7g** (48 mg, 0.10 mmol, 1.0 equiv), TBATB (95 mg, 0.20 mmol, 2.0 equiv), and K_2CO_3 (34 mg, 0.24 mmol, 2.5 equiv), following the standard procedure (7 days), an 80:20 mixture of **12f** and **11f** was obtained, and after chromatographic purification (CH_2Cl_2-10% EtOAc/CH_2Cl_2), **12f** (28 mg, 49%, white solid) and **11f** (8 mg, 14%, colorless oil) were obtained.

Data for **12f**: R_f 0.23 (5% EtOAc/CH_2Cl_2); mp 148 °C; $[\alpha]^{20}_D$ −26.1 (c = 0.72); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 2.42 (s, 3 H, Me p-Tol), 4.04 (dd, 1 H, J = 10.5, 2.1 Hz, CH_2), 4.32 (dd, 1 H, J = 10.3, 5.1 Hz, CH_2), 5.09 (dd, 1 H, J = 5.1, 2.0 Hz, H-2), 6.51−6.59 (br s, 4 H, ArH), 6.64 (ddt, 1 H, J = 5.1, 2.0 Hz, H-5), 6.69 (t, 1 H, J = 2.0 Hz, H-4), 6.82 (tt, 1 H, J = 7.3, 1.2 Hz, ArH), 7.01 (dd, 1 H, J = 8.1, 7.6 Hz, ArH), 7.26 (d, 2 H, J = 7.8 Hz, ArH), 7.37 (dt, 2 H, J = 8.1, 1.8 Hz, ArH), 7.44 (dd, 1 H, J = 7.6, 1.3 Hz, ArH), 7.52 (dd, 1 H, J = 8.3, 4.4 Hz, ArH), 7.70 (dd, 1 H, J = 8.1, 1.5 Hz, ArH), 8.14 (dd, 1 H, J = 8.1, 1.8 Hz, ArH), 9.04 (dd, 1 H, J = 4.2, 1.7 Hz, ArH); NOE-1D H-2/2 CH_2 (0.18%); CH_2 (4.32 ppm)/H-2 (0.27%); ^{13}C NMR ($CDCl_3$, 125 MHz)-HSQC δ 21.6 (Me p-Tol), 38.9 (CH_2), 68.0 (C-5), 69.5 (C-2), 121.8, 125.3, 126.4 (2 C), 127.5 (2 C), 128.3, 128.8, 130.1 (C-4), 130.2 (2 C), 131.2, 132.2, 133.1, 136.5, 137.3, 139.4, 143.4, 149.5, 150.8 (2 C) (some signals overlap); IR (KBr) 2961, 2927, 1599, 1457, 1314, 1260, 1152, 1084, 1057, 807, 679 cm^{-1}; MS (ESI) 567 [M + H]$^+$. Anal. Calcd for $C_{27}H_{23}BrN_2O_3S_2$: C, 57.14; H, 4.08; N, 4.94; S, 11.30. Found: C, 56.89; H, 4.00; N, 5.08; S, 11.46.

Partial data for the minor product **11f**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.59 (dd, 1 H, J = 10.2, 9.8 Hz), 4.13 (dd, 1 H, J = 9.8, 3.9 Hz), 5.45 (t, 1 H, J = 1.8 Hz), 5.52 (ddt, 1 H, J = 10.2, 3.9, 2.2 Hz), 8.00 (dd, 1 H, J = 8.3, 1.6 Hz), 8.22 (dd, 1 H, J = 8.5, 1.8 Hz), 8.36 (dd, 1 H, J = 7.6, 1.5 Hz), 8.54 (dd, 1 H, J = 4.1, 1.7 Hz).

7.4. Synthesis of (+)-2-[(2S,5S)-5-(Bromomethyl)-2-phenyl-3-((S)-p-tolylsulfinyl)-2,5-dihydro-1H-pyrrol-1-yl]sulfonylpyridine, ***11j****, and 2-[(2S,5R)-5-(Bromomethyl)-2-phenyl-3-((S)-p-tolylsulfinyl)-2,5-dihydro-1H-pyrrol-1-yl]sulfonylpyridine,* ***12j****.* From sulfonamide **7k** (41 mg, 0.097 mmol, 1.0 equiv), TBATB (52 mg, 0.11 mmol, 1.10 equiv), and K_2CO_3 (20 mg, 0.15 mmol, 1.5 equiv), following the standard procedure (7 days), a 73:27 mixture of 2,5-*cis* **11j** and 2,5-*trans* **12j** was obtained, and after chromatographic purification (CH_2Cl_2-10% EtOAc/CH_2Cl_2), **11j** (23 mg, 46%, white solid) and **12j** (8 mg, 16%, colorless oil) were obtained.

Data for 2,5-*cis* **11j**: R_f 0.30 (10% EtOAc/CH_2Cl_2); mp 154−156 °C; $[\alpha]^{20}_D$ +37.0 (c = 0.39); ^{1}H NMR ($CDCl_3$, 400 MHz)-COSY δ 2.43 (s, 3 H, Me p-Tol), 3.53 (t, 1 H, J = 9.9 Hz, CH_2), 4.01 (dd, 1 H, J = 9.7, 3.8 Hz, CH_2), 5.04 (ddt, 1 H, J = 10.1, 4.0, 2.2 Hz, H-5), 5.33 (t, 1 H, J = 2.0 Hz, H-2), 6.88 (t, 1 H, J = 1.8 Hz, H-4), 7.19−7.32 (m, 9 H, ArH), 7.44 (ddd, 1 H, J = 7.5, 4.7, 1.3 Hz, ArH), 7.69 (d, 1 H, J = 7.9 Hz, ArH), 7.77 (td, 1 H, J = 7.8, 1.6 Hz, ArH), 8.43 (dm, 1 H, J = 4.8 Hz, ArH); NOESY-2D H-5/2 CH_2; H-5/H-4; H-4/ArH. ^{13}C NMR ($CDCl_3$, 125 MHz)-HSQC δ 21.6 (Me p-Tol), 34.4 (CH_2), 68.2 (C-5), 70.7 (C-2), 123.1, 125.7 (2 C), 126.8, 128.3 (2 C), 128.8 (2 C), 129.0, 129.7 (C-4), 130.1 (2 C), 137.1, 137.8, 142.8, 149.4, 149.8 (2 C), 156.4; IR (KBr) 3082, 2923, 1580. 1425, 1343, 1171, 1129, 1060, 1050, 808, 744, 657, 607 cm^{-1}; HRMS (ESI) m/z for $C_{23}H_{22}BrN_2O_3S_2$ [M + H]$^+$ calcd 517.0255, observed 517.0221.

Partial data for the minor product 2,5-*trans* **12j**: R_f 0.10 (10% EtOAc/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz)-COSY δ 2.44 (s, 3 H, Me p-Tol), 3.98 (dd, 1 H, J = 10.4, 2.2 Hz, CH_2), 4.19 (dd, 1 H, J = 10.4, 5.5 Hz, CH_2), 5.90 (dd, 1 H, J = 5.1, 1.6 Hz, H-5), 5.90 (ddm, 1 H, J = 4.4, 2.0 Hz, H-5), 6.70 (t, 1 H, J = 1.8 Hz, H-4), 6.78 (dm, 2 H, J = 7.5 Hz, ArH), 6.91 (br t, 2 H, J = 7.5 Hz, ArH), 7.06 (tm, 1 H, J = 7.3 ArH), 7.23−7.32 (m, 5 H, ArH), 7.40 (d, 2 H, J = 8.2 Hz, ArH), 8.53 (dm, 1 H, J = 4.6 Hz, ArH); ^{13}C NMR ($CDCl_3$, 125 MHz)-HSQC δ 21.6 (Me p-Tol), 37.6 (CH_2), 68.4 (C-5), 70.0 (C-2), 121.1, 125.8, 126.2 (2 C), 128.0 (2 C), 128.7 (2 C), 129.4, 129.9 (C-4), 130.1 (2 C), 133.8, 137.1, 143.5, 149.3, 149.8 (2 C), 150.0, 159.2; HRMS (ESI) m/z for $C_{23}H_{22}BrN_2O_3S_2$ [M + 1]$^+$ calcd 517.0255, observed 517.0237.

7.5. Synthesis of (2S,5S)-5-(Bromomethyl)-1-(naphthalen-1-ylsulfonyl)-2-phenyl-3-((S)-p-tolylsulfinyl)-2,5-dihydro-1H-pyrrole, ***11i****, and (2S,5R)-5-(Bromomethyl)-1-(naphthalen-1-ylsulfonyl)-2-phenyl-3-((S)-p-tolylsulfinyl)-2,5-dihydro-1H-pyrrole,* ***12i****.* From sulfonamide **7j** (49 mg, 0.1 mmol, 1.0 equiv), TBATB (55 mg, 0.11 mmol, 1.10 equiv), and K_2CO_3 (20 mg, 0.15 mmol, 1.5 equiv), following the standard procedure (6 days), 50% (23 mg) of an inseparable 78:22 mixture of 2,5-*cis* **11i** and 2,5-*trans* **12i** was obtained.

Data for 2,5-*cis* **11i** from the mixture: R_f 0.40 (5% EtOAc/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3 H), 3.48 (t, 1 H, J = 9.3 Hz), 3.70 (dd, 1 H, J = 10.1, 3.5 Hz), 5.09 (m, 1 H), 5.16 (dm, 1 H, J = 9.0 Hz), 6.82 (t, 1 H, J = 2.0 Hz); HRMS (ESI) m/z for $C_{28}H_{25}BrNO_3S_2$ [M + H]$^+$ calcd 566.0459, observed 566.0476.

Data for the minor product 2,5-*trans* **12i** from the mixture: R_f 0.40 (5% EtOAc/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3 H, Me p-Tol), 4.13 (dd, 1 H, J = 10.4, 2.2 Hz, CH_2), 4.29 (dd, 1 H, J = 10.5, 5.9 Hz, CH_2), 5.08 (m, 1 H, H-2), 5.59 (ddm, 1 H, J = 5.3, 2.2 Hz, H-5), 6.51 (dm, 2 H, J = 8.3 Hz, ArH), 6.68 (t, 1 H, J = 2.1 Hz, H-4), 6.72 (br t, 2 H, J = 7.6 Hz, ArH).

7.6. Synthesis of (−)-8-[(2S,5R)-5-(Bromomethyl)-2-(3,4-dimethoxyphenyl)-3-((S)-p-tolylsulfinyl)-2,5-dihydro-1H-pyrrol-1-yl]sulfonylquinoline, ***12g****, and 8-[(2S,5S)-5-(Bromomethyl)-2-(3,4-dimethoxyphenyl)-3-((S)-p-tolylsulfinyl)-2,5-dihydro-1H-pyrrol-1-yl]sulfonylquinoline,* ***11g****.* From sulfonamide **7h** (45 mg, 0.082 mmol, 1.0 equiv), TBATB (80 mg, 0.164 mmol, 2.0 equiv), and K_2CO_3 (29 mg, 0.205 mmol, 1.5 equiv), following the standard procedure (7 days), a 90:10 mixture of 2,5-*trans* and 2,5-*cis* was obtained, and after chromatographic purification (CH_2Cl_2-10% EtOAc/CH_2Cl_2), **12g** (33 mg, 65%, yellow solid) and **11g** (5 mg, 9%, colorless oil) were obtained.

Data for 2,5-*trans* **12g**: R_f 0.20 (10% EtOAc/CH_2Cl_2); mp 98−100 °C; $[\alpha]^{20}_D$ −95.0 (c = 0.57); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.43 (s, 3 H), 2.92 (brs, 3 H), 3.73 (s, 3 H), 4.04 (dd, 1H, J = 10.4, 2.0 Hz), 4.33 (dd, 1 H, J = 10.4, 5.2 Hz), 5.06 (dd, 1 H, J = 5.0, 2.2 Hz), 5.76 (br s, 1 H), 6.34 (m, 2 H), 6.64 (ddm, 1 H, J = 4.2, 1.9 Hz), 6.71 (t, 1 H, J = 1.8 Hz), 7.07 (t, 1 H, J = 7.7 Hz), 7.27 (dm, 2 H, J = 8.5 Hz), 7.39 (dm, 2 H, J = 8.2 Hz), 7.52 (dd, 1 H, J = 3.1, 1.5 Hz), 7.55 (m, 1 H), 7.75 (dd, 1 H, J = 5.0, 1.4 Hz), 8.18 (dd, 1 H, J = 8.4, 2.2 Hz), 9.06 (dd, 1 H, J = 4.2, 1.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 39.1, 55.1, 55.9, 68.1, 69.3, 109.7, 121.8, 123.1, 125.0, 125.8, 126.4 (2 C), 128.4, 130.3 (3 C), 130.5, 132.0, 132.3, 136.8, 137.5, 139.4, 143.5, 148.1, 149.3, 149.5, 150.8 (2 C); IR (KBr) 3049, 2932, 1515, 1338, 1261, 1162, 1144, 790, 678 cm^{-1}; HRMS (ESI) m/z for $C_{29}H_{28}BrN_2O_5S_2$ [M + H]$^+$ calcd 627.0623, observed 627.0644.

Partial data for the minor product 2,5-*cis* **11g**: R_f = 0.30 (10% EtOAc/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 3 H), 3.74 (s, 3 H), 3.77 (dd, 1 H, J = 10.1, 8.9 Hz), 3.86 (s, 3 H), 4.15 (dd, 1 H, J = 10.1, 3.7 Hz), 5.47 (m, 1 H), 5.51 (dm, 1 H, J = 8.5 Hz), 6.65−6.78 (m, 4 H), 7.03 (m, 4 H), 7.46−7.55 (m, 2 H), 8.01 (dm, 1 H, J = 8.1 Hz), 8.23 (dm, 1 H, J = 8.4 Hz), 8.34 (dm, 1 H, J = 7.5 Hz), 8.60 (dm, 1 H, J = 4.2 Hz).

7.7. Synthesis of 8-[(2S,5S)-5-(Bromomethyl)-2-isopropyl-3-(p-tolylsulfinyl)-2,5-dihydro-1H-pyrrol-1-yl]sulfonylquinoline, ***11h****, and 8-[(2S,5R)-5-(Bromomethyl)-2-isopropyl-3-(p-tolylsulfinyl)-2,5-dihydro-1H-pyrrol-1-yl]sulfonylquinoline,* ***12h****.* From sulfonamide **7i** (25 mg, 0.055 mmol, 1.0 equiv), TBATB (53 mg, 0.11 mmol, 2.0 equiv), and K_2CO_3 (19 mg, 0.14 mmol, 2.5 equiv), following the standard procedure (7 days), a 56:44 mixture of *cis* and *trans* isomers was obtained. Chromatographic purification (1−10% EtOAc/CH_2Cl_2) gave the mixture of both compounds (16 mg, 57%, colorless oil).

Partial data for 2,5-*cis*-**11h**: R_f 0.15 (5% EtOAc/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94 (d, 3 H, J = 7.5 Hz), 1.06 (d, 3 H, J = 7.4 Hz), 2.27 (m, 1 H), 2.33 (s, 3 H), 3.44 (dd, 1 H, J = 11.2, 9.0 Hz), 4.04 (dd, 1 H, J = 9.2, 4.2 Hz), 4.21 (m, 1 H), 5.84 (ddm, 1 H, J = 11.5, 4.1 Hz), 6.80 (d, 2 H, J = 7.0 Hz), 6.85 (br s, 1 H), 6.92 (d, 2 H, J = 7.0 Hz), 7.50 (dd, 1 H, J = 8.3, 4.1 Hz), 7.55 (t, 1 H, J = 7.8 Hz), 8.03 (dd, 1 H, J = 8.1, 1.2 Hz), 8.25 (dd, 1 H, J = 8.3, 1.9 Hz), 8.35 (dd, 1 H, J = 7.4, 1.5 Hz), 8.64 (dd, 1 H, J = 4.2, 1.6 Hz); HRMS (ESI) m/z for $C_{24}H_{26}BrN_2O_3S_2$ [M + H]$^+$ calcd 533.0568, observed 533.0583.

Partial data for 2,5-*trans*-**12h**: R_f 0.10 (5% EtOAc/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.26 (d, 3 H, *J* = 7.4 Hz), 0.87 (d, 3 H, *J* = 7.4 Hz), 2.46 (m, 1 H), 2.47 (s, 3 H), 4.02 (dd, 1 H, *J* = 10.5, 2.5 Hz), 4.12 (m, 1 H), 4.80 (m, 1 H), 6.00 (m, 1 H), 6.69 (br s, 1 H), 7.30 (d, 2 H, *J* = 7.8 Hz), 7.48 (dd, 1 H, *J* = 8.3, 4.2 Hz), 7.60 (dd, 1 H, *J* = 8.0, 7.3 Hz), 7.66 (d, 2 H, *J* = 8.1 Hz), 8.01 (dd, 1 H, *J* = 8.3, 1.5 Hz), 8.23 (dd, 1 H, *J* = 8.6, 2.0 Hz), 8.43 (dd, 1 H, *J* = 7.6, 1.5 Hz), 8.75 (dm, 1 H, *J* = 1.9 Hz).

7.8. Synthesis of (2S,5S)-5-(Bromomethyl)-2-methyl-2-phenyl-3-(p-tolylsulfinyl)-1-(p-tolylsulfonyl)-2,5-dihydro-1H-pyrrole, 11k, and (+)-(2S,5R)-5-(Bromomethyl)-2-methyl-2-phenyl-3-(p-tolylsulfinyl)-1-(p-tolylsulfonyl)-2,5-dihydro-1H-pyrrole, 12k. From sulfonamide **7l** (30 mg, 0.06 mmol, 1.0 equiv), TBATB (58 mg, 0.12 mmol, 2.0 equiv), and K_2CO_3 (21 mg, 0.15 mmol, 2.5 equiv), following the standard procedure (3 days), a 35:65 mixture of *cis* and *trans* isomers was obtained. Chromatographic purification (10−50% EtOAc/hex) gave a pure fraction of the major isomer **12k** (14 mg, 43%, yellow solid).

Data for *trans*-**12k**: R_f 0.30 (40% EtOAc/hex); mp 111−113 °C; $[\alpha]^{20}_D$ +68.4 (*c* = 0.68); ^{1}H NMR ($CDCl_3$, 300 MHz)-COSY δ 1.63 (s, 3 H, Me), 2.33 (s, 3 H, Me *p*-Tol), 2.42 (s, 3 H, Me *p*-Tol), 3.84 (dd, 1 H, *J* = 10.3, 7.1 Hz, CH_2), 4.11 (dm, 1 H, *J* = 10.0 Hz, CH_2), 4.96 (dt, 1 H, *J* = 7.1, 2.7 Hz, H-5), 6.82 (d, 2 H, *J* = 8.3 Hz, ArH sulfoxide), 6.87 (d, 2 H, *J* = 2.4 Hz, H-4), 6.93 (d, 2 H, *J* = 7.2 Hz, ArH sulfoxide), 7.03−7.12 (m, 4 H, ArH, Ph), 7.21−7.28 (m, 3 H, ArH Ph, sulfonamide), 7.46 (d, 2 H, *J* = 8.0 Hz, ArH, sulfonamide); 1D NOESY between Me/H-Ph (7.03−7.12 ppm) (5%); CH_2 (3.84 ppm)/Me (1.8%); CH_2 (3.84 ppm)/H-5 (2%); CH_2 (3.84 ppm)/CH_2 (4.11 ppm) (21%); CH_2 (4.11 ppm)/H-5 (3.0%); CH_2 (4.11 ppm)/H-4 (0.5%); H-5/2 × CH_2 (3.5%); H-5/H-4 (3%); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 21.6, 26.8, 36.4, 65.8, 75.4, 126.7 (2 C), 126.8 (2 C), 128.1, 128.2 (2 C), 128.3, 129.0 (2 C), 130.2, 136.7, 136.8, 139.2, 142.8, 143.5, 154.0 (some signals overlap); IR (film) 2926, 1597, 1494, 1448, 1340, 1036 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{26}H_{27}BrNO_3S_2$ [M + H]$^+$ calcd 544.0616, observed 544.0606.

Partial data for the minor isomer **11k**: R_f 0.40 (40% EtOAc/hex); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.63 (s, 3 H, Me), 2.37 (s, 3 H, Me *p*-Tol), 2.39 (s, 3 H, Me *p*-Tol), 3.43 (dd, 1 H, *J* = 10.0, 8.5 Hz, CH_2), 4.11 (dd, 1 H, *J* = 10.3, 3.2 Hz, CH_2), 4.96 (dm, 1 H, *J* = 8.5 Hz, H-5), 6.78 (d, 1 H, *J* = 1.9 Hz, H-4), 7.12−7.39 (m, 13 H, ArH).

8. Synthesis of (+)-(2*S*,5*S*)-5-(Iodomethyl)-2-phenyl-3-((*S*)-tolylsulfinyl)-1-(*p*-tolylsulfonyl)-2,5-dihydro-1*H*-pyrrole, 13a, and (+)-(2*S*,5*R*)-5-(Iodomethyl)-2-phenyl-3-((*S*)-tolylsulfinyl)-1-(*p*-tolylsulfonyl)-2,5-dihydro-1*H*-pyrrole, 14a. To a solution of sulfonamide **7b**[10a] (43 mg, 0.10 mmol, 1.0 equiv) in a 10:1 mixture of CH_3CN/H_2O (10 mL/mmol) protected from light were added K_2CO_3 (40 mg, 0.29 mmol, 3.0 equiv) and I_2 (73 mg, 0.29 mmol, 3.0 equiv) at rt. The mixture was stirred until the disappearance of **7b** by TLC. Then, it was quenched with a saturated solution of $Na_2S_2O_4$ (10 mL/mmol), extracted with CH_2Cl_2 (3 × 10 mL/mmol), and washed with a saturated solution of NaCl (10 mL/mmol). It was dried over Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure to give a 42:58 mixture of 2,5-*cis* and 2,5-*trans* dihydropyrroles. Chromatographic purification (10−50% EtOAc/hex) gave *cis* (13 mg, 23%, colorless oil) and *trans* (25 mg, 43%, white solid).

Alternatively, a solution of **7b** (48 mg, 0.11 mmol, 1.0 equiv) in CH_2Cl_2 (7 mL/mmol) protected from light, with solid K_2CO_3 (88 mg, 0.64 mmol, 6.0 equiv) and NIS (105 mg, 0.48 mmol, 4.4 equiv), at rt was stirred for 4 days. A similar workup gave a crude mixture of 56:44 *cis*:*trans* isomers. Chromatographic purification (10−50% EtOAc/hex) gave *cis* (25 mg, 39%, colorless oil) and *trans* (20 mg, 32%, white solid).

Also, a solution of **7b** (19 mg, 0.04 mmol, 1.0 equiv) in toluene (14 mL/mmol) protected from light, with solid K_2CO_3 (26 mg, 0.19 mmol, 4.5 equiv) and NIS (26 mg, 0.19 mmol, 4.5 equiv), at rt was stirred for 4 days. A similar workup gave a crude mixture of 21:79 *cis*:*trans* isomers. Chromatographic purification (10−50% EtOAc/hex) gave *cis* (2 mg, 8%, colorless oil) and *trans* (15 mg, 65%, white solid).

Data for 2,5-*cis*-**13a**: R_f 0.24 (40% EtOAc/hex); $[\alpha]^{20}_D$ +76.4 (*c* = 0.47); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 2.40 (s, 3 H, Me *p*-Tol), 2.45 (s, 3 H, Me *p*-Tol), 3.21 (dd, 1 H, *J* = 10.5, 9.5 Hz, CH_2), 3.68 (dd, 1 H, *J* = 9.5, 3.9 Hz, CH_2), 4.74 (ddt, 1 H, *J* = 10.5, 3.9, 2.0 Hz, H-5), 4.86 (t, 1 H, *J* = 2.0 Hz, H-2), 6.80 (t, 1 H, *J* = 2.0 Hz, H-4), 7.11 (d, 2 H, *J* = 8.1 Hz, ArH), 7.17 (m, 4 H, ArH), 7.20 (d, 2 H, *J* = 7.8 Hz, ArH), 7.29 (m, 3 H, ArH), 7.34 (dt, 2 H, *J* = 8.3, 1.8 Hz, ArH); 1D-NOE (C_6D_6) between H-2/Ar−H (6.88−7.08 ppm) (6.2%); H-5/CH_2 (2.2%); CH_2 (3.55 ppm)/H-5 (2.1%); CH_2 (2.97 ppm)/Ar−H (6.88−7.08 ppm) (1.5%); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 7.7 (CH_2), 21.5 (2 C), 68.1, 70.2, 125.6 (2 C), 127.3 (2 C), 128.3 (2 C), 128.8 (2 C), 129.0, 129.7 (2 C), 130.2 (2 C), 130.7, 134.3, 137.1, 137.7, 142.9, 144.0, 149.4; IR (film) 3436, 3032, 2922, 1596, 1493, 1455, 1353, 1306, 1164, 1087, 1056, 865, 810, 756, 700, 667, 587, 549 cm^{-1}; MS (ESI) 578 [M + H]$^+$ (100%), 1177 [2M + Na]$^+$. Anal. Calcd for $C_{25}H_{24}INO_3S_2$: C, 51.99; H, 4.19; N, 2.43; S, 11.10. Found: C, 52.04; H, 4.31; N, 2.21; S, 11.01.

Data for 2,5-*trans*-**14a**: R_f 0.17 (40% EtOAc/hex); mp 205 °C; $[\alpha]^{20}_D$ +84.2 (*c* = 0.99); ^{1}H NMR-COSY ($CDCl_3$, 300 MHz) δ 2.28 (s, 3 H, Me *p*-Tol), 2.43 (s, 3 H, Me *p*-Tol), 3.83 (dd, 1 H, *J* = 10.2, 2.3 Hz, CH_2), 3.90 (dd, 1 H, *J* = 10.1, 6.1 Hz, CH_2), 4.80 (ddt, 1 H, *J* = 5.9, 2.0 Hz, H-5), 5.04 (dd, 1 H, *J* = 5.1, 1.5 Hz, H-2), 6.57 (t, 1 H, *J* = 1.7 Hz, H-4), 6.85 (m, 6 H, ArH), 7.06 (t, 2 H, *J* = 7.6 Hz, ArH), 7.22 (m, 1 H, ArH), 7.29 (d, 2 H, *J* = 7.8 Hz, ArH), 7.42 (d, 2 H, *J* = 7.8 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 12.9 (CH_2), 21.4 (Me *p*-Tol), 21.6 (Me *p*-Tol), 66.2 (C-5), 70.2 (C-2), 126.3 (2 C), 126.4 (2 C), 128.4 (2 C), 128.9, 129.0 (2 C), 129.5 (2 C), 130.3 (2 C), 130.5, 133.8, 137.2, 137.6, 142.7, 143.5, 150.6; IR (KBr) 3435, 2920, 1595, 1455, 1344, 1309, 1160, 1092, 1058, 814, 704, 675, 597, 549, 506 cm^{-1}; MS (ESI) 578 [M + H]$^+$ (100%), 1177 [2M + Na]$^+$. Anal. Calcd for $C_{25}H_{24}INO_3S_2$: C, 51.99; H, 4.19; N, 2.43; S, 11.10. Found: C, 52.13; H, 4.25; N, 2.37; S, 11.12.

9. Synthesis of (+)-(2*S*,5*R*)-5-Methyl-2-phenyl-3-((*S*)-*p*-tolylsulfinyl)-1-(*p*-tolylsulfonyl)-2,5-dihydro-1*H*-pyrrole, 16a. To a solution of **13a** (13 mg, 0.02 mmol, 1.0 equiv) in anhydrous toluene (10 mL/mmol) were added Bu_3SnH (0.007 mL, 0.02 mmol, 1.1 equiv) and AIBN (0.5 equiv). The solution was heated at 80 °C for 16 h. The solvent was removed under reduced pressure, and **16a** was obtained as a colorless oil (8 mg, 81%) after chromatography (10−40% EtOAc/hex).

Data for **16a**: R_f 0.12 (40% EtOAc/hex); $[\alpha]^{20}_D$ +129.1 (*c* = 0.33); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 1.53 (d, 3 H, *J* = 6.6 Hz, Me), 2.38 (s, 3 H, Me *p*-Tol), 2.45 (s, 3 H, Me *p*-Tol), 4.71 (qt, 1 H, *J* = 6.6, 2.1 Hz, H-5), 4.92 (t, 1 H, *J* = 1.7 Hz, H-2), 6.46 (t, 1 H, *J* = 2.0 Hz, H-4), 7.08 (d, 2 H, *J* = 8.1 Hz, ArH), 7.15 (m, 2 H, ArH), 7.21 (m, 4 H, ArH), 7.30 (m, 5 H, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 21.5 (Me *p*-Tol), 21.6 (Me *p*-Tol), 22.9 (Me), 63.6 (C-5), 69.3 (C-2), 125.7 (2 C), 127.2 (2 C), 128.1 (2 C), 128.7, 128.8 (2 C), 129.5 (2 C), 130.2 (2 C), 132.7, 135.3 (2 C), 137.9, 142.9, 143.4, 146.8; 1D-NOE between H-4/H-5 (1.7%); H-4/Me (1.1%); H-2/Ar−H (7.15−7.21 ppm) (5.2%); H-5/H-4 (2.0%); Me/Ar−H (1.2%); Me/H-4 (0.8%); Me/H-5 (2.0%), Me/Ph (7.15−7.21 ppm) (1.0%); IR (film) 3031, 2926, 1597, 1493, 1455, 1350, 1305, 1163, 1083, 1053, 1014, 810, 752, 699, 666, 607 cm^{-1}; MS (ESI) 452 [M + H]$^+$ (100%), 474 [M + Na]$^+$; HRMS (ESI) *m*/*z* for $C_{25}H_{26}NO_3S_2$ [M + H]$^+$ calcd 452.1354, observed 452.1322.

10. Synthesis of (+)-(2*S*,5*R*)-5-(Iodomethyl)-2-phenyl-1,3-bis(*p*-tolylsulfonyl)-2,5-dihydro-1*H*-pyrrole, 18. To a stirred solution of **10c**[10a] (5.0 mg, 0.01 mmol, 1.0 equiv), triphenylphosphine (11 mg, 0.04 mmol, 4.0 equiv), and imidazole (3 mg, 0.04 mmol, 4.0 equiv) in dry toluene (0.5 mL) was added iodine (8 mg, 0.03 mmol, 3.0 equiv), and the resulting mixture was refluxed for 2 h. After cooling, the solution was treated with saturated aqueous $NaHCO_3$ (10 mL/mmol), and after stirring for 10 min, it was diluted with EtOAc (10 mL/mmol). The phases were separated; the organic phase was washed with saturated aqueous $Na_2S_2O_4$ (2 × 10 mL/mmol) and dried over Na_2SO_4. Filtration, evaporation under reduced pressure, and further purification of the crude (10−40% EtOAc/hex) yielded the desired product **18** as a colorless oil (3.2 mg, 54%).

Alternatively, from dihydropyrrole **14a** (4 mg, 0.01 mmol, 1.0 equiv) and *m*-CPBA (5 mg, 0.02 mmol, 2.0 equiv) in CH_2Cl_2 (5 h at rt), and after an aqueous workup and chromatographic purification

(CH_2Cl_2-5% EtOAc/CH_2Cl_2), an identical product was obtained (2 mg, 46%).

Data for **18**: R_f 0.13 (20% EtOAc/hex); $[\alpha]^{20}_D$ +28.1 (c = 0.21); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 2.26 (s, 3 H, Me p-Tol), 2.33 (s, 3 H, Me p-Tol), 3.76 (dd, 1 H, J = 10.0, 7.4 Hz, CH_2), 3.95 (dd, 1 H, J = 10.0, 2.4 Hz, CH_2), 4.83 (ddt, 1 H, J = 7.4, 5.4, 2.4 Hz, H-5), 5.67 (dd, 1 H, J = 5.4, 1.2 Hz, H-2), 6.70 (d, 2 H, J = 6.6 Hz, ArH), 6.83–6.88 (m, 7 H, ArH), 7.03 (d, 2 H, J = 7.8 Hz, ArH), 7.08 (t, 1 H, J = 7.3 Hz, ArH), 7.29 (d, 2 H, J = 8.3 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 10.4 (CH_2), 21.4 (Me p-Tol), 21.6 (Me p-Tol), 66.0 (C-5), 70.8 (C-2), 121.7, 126.5 (2 C), 128.0 (2 C), 128.2 (2 C), 128.4, 129.0 (2 C), 129.4, 129.6 (2 C), 139.6 (some signals overlap); IR (film) 2923, 1735, 1596, 1456, 1326, 1156, 1088, 811, 759, 698 cm^{-1}; MS (ESI) 594 $[M + H]^+$, 616 $[M + Na]^+$; HRMS (ESI) m/z for $C_{25}H_{25}INO_4S_2$ $[M + H]^+$ calcd 594.0270, observed 594.0265.

11. General Procedure for the Synthesis of Sulfinyl Aziridines, 19. To a solution of sulfonamide **7** in CH_2Cl_2 (7 mL/mmol) protected from light were added 4.5–6.0 equiv of solid K_2CO_3 and 1.0–4.0 equiv of NBS (in fractions of 1.5 equiv of K_2CO_3 and 1.0 equiv of NBS) at rt. The mixture was stirred until the disappearance of **7** as monitored by TLC. It was quenched with a 1 M solution of $Na_2S_2O_4$ (20 mL/mmol), extracted with CH_2Cl_2 (3 × 15 mL/mmol), and washed with a saturated solution of NaCl (10 mL/mmol). Then, it was dried over Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure to give a crude product that was purified by chromatography on deactivated silica gel using the appropriate mixture of eluents.

*11.1. Synthesis of (−)-(2R,3S)-[2-((1E)-3-Bromo-1-propen-1-yl)-3-phenyl-2-((S)-p-tolylsulfinyl)-1-(p-tolylsulfonyl)]aziridine, **19a**.* From sulfonamide **7b**[10a] (86 mg, 0.19 mmol, 1.0 equiv), K_2CO_3 (120 mg, 0.87 mmol, 4.5 equiv), and NBS (102 mg, 0.57 mmol, 3.0 equiv), following the general procedure (2 days) and after chromatographic purification (10–50% EtOAc/hex), aziridine **19a** (55 mg, 55%) was obtained as a single diastereomer (colorless oil) with minor amounts of dihydropyrroles **11a**:**12a**, (45:55, 16 mg, 16%).

Data for **19a**: R_f 0.31 (40% EtOAc/hex); $[\alpha]^{20}_D$ −27.1 (c = 0.70); ^{1}H NMR ($CDCl_3$, 500 MHz)-selective decouplings δ 2.30 (s, 3 H, Me p-Tol), 2.43 (s, 3 H, Me p-Tol), 3.93 (m, 2 H, CH_2Br), 4.36 (s, 1 H, H-3), 5.88 (ddd, 1 H, J = 15.2, 8.6, 6.6 Hz, H-2′), 6.32 (d, 1 H, J = 15.4 Hz, H-1′), 6.67 (dd, 2 H, J = 6.6, 1.7 Hz, ArH), 7.05 (d, 2 H, J = 8.1 Hz, ArH), 7.25 (m, 2 H, ArH), 7.34 (m, 5 H, ArH), 7.91 (dt, 2 H, J = 8.3, 1.7 Hz, ArH); 1D-NOE between H-3/H-1′ (0.8%); H-3/H-2′ (2.6%); H-2′/H-3 (2.3%); H-1′/H-3 (0.5%); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 21.4 (Me p-Tol), 21.7 (Me p-Tol), 30.2 (CH_2), 50.1 (C-3), 71.2 (C-2), 120.0, 125.3 (2 C), 127.9 (3 C), 128.6 (2 C), 129.1, 129.4 (2 C), 129.8 (2 C), 130.4, 136.0, 136.1, 137.3 (2 C), 142.4, 145.0; IR (film) 3030, 2923, 1596, 1492, 1452, 1402, 1331, 1163, 1089, 1032, 811, 755, 700, 666 cm^{-1}; HRMS (ESI) m/z for $C_{25}H_{25}BrNO_3S_2$ $[M + H]^+$ calcd 530.0459, observed 530.0460.

*11.2. Synthesis of (2R,3S)-[2-((1E)-3-Bromo-1-propen-1-yl)-3-isopropyl-2-((S)-p-tolylsulfinyl)-1-(p-tolylsulfonyl)]aziridine, **19b**, and (2R,3S)-[2-((1E)-3-Bromo-1-propen-1-yl)-3-isopropyl-2-((R)-p-tolylsulfinyl)-1-(p-tolylsulfonyl)]aziridine, **20b**.* From sulfonamide **7c**[10a] (39 mg, 0.09 mmol, 1.0 equiv), K_2CO_3 (57 mg, 0.42 mmol, 4.5 equiv), and NBS (48 mg, 0.27 mmol, 3.0 equiv), following the general procedure (1.5 days), an 80:20 mixture of **19b** and **20b** was obtained. Chromatographic purification (10–50% EtOAc/hex, deactivated silica) yielded an 80:20 mixture of aziridines **19b** and **20b** (38 mg, 83%) as a colorless oil. Further purification on silica gel allowed us to isolate small amounts of both pure products; however, they were unstable under these conditions.

Data for **19b**: R_f 0.42 (5% EtOAc/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 300 MHz)-COSY δ 0.71 (d, 3 H, J = 6.6 Hz, Me i-Pr), 1.03 (d, 3 H, J = 6.8 Hz, Me i-Pr), 2.24 (m, 1 H, CH i-Pr), 2.41 (s, 3 H, Me p-Tol), 2.44 (s, 3 H, Me p-Tol), 2.90 (d, 1 H, J = 10.0 Hz, H-3), 3.82 (dd, 1 H, J = 10.5, 8.5 Hz, CH_2Br), 3.90 (dd, 1 H, J = 10.5, 6.1 Hz, CH_2Br), 5.84 (d, 1 H, J = 15.4 Hz, H-1′), 5.98 (ddd, 1 H, J = 14.9, 8.8, 6.1 Hz, H-2′), 7.28 (d, 2 H, J = 8.1 Hz, ArH), 7.32 (d, 2 H, J = 8.3 Hz, ArH), 7.58 (d, 2 H, J = 8.1 Hz, ArH), 7.86 (d, 2 H, J = 8.3 Hz, ArH); 1D-NOE between H-1′/CH_2 (2.6%); H-1′/H-3 (0.6%); H-2′/CH_2 (2.7%); H-2′/H-3 (1.8%); H-3/H-1′+H-2′ (1.5%); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 19.9, 21.0, 21.6, 21.7, 25.3, 30.0, 57.9, 68.9, 124.0, 125.4, 126.6 (2 C), 128.3 (2 C), 129.6 (2 C), 129.7 (2 C), 135.9, 137.0, 143.0, 144.8; MS (ESI) 1015 $[2M + 2 + Na]^+$ (100%), 527 $[M + MeOH]^+$.

Partial data for **20b**: R_f 0.52 (5% EtOAc/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 0.79 (d, 3 H, J = 6.8 Hz, Me i-Pr), 1.16 (d, 3 H, J = 6.8 Hz, Me i-Pr), 2.10 (m, 1 H, CH i-Pr), 2.42 (s, 3 H, Me p-Tol), 2.45 (s, 3 H, Me p-Tol), 2.92 (d, 1 H, J = 10.0 Hz, H-3), 3.90 (ddd, 1 H, J = 9.8, 8.1, 1.0 Hz, CH_2Br), 3.98 (ddd, 1 H, J = 10.8, 6.8, 1.2 Hz, CH_2Br), 5.64 (d, 1 H, J = 15.2 Hz, H-1′), 6.13 (ddd, 1 H, J = 14.9, 7.8, 6.8 Hz, H-2′), 7.28 (d, 2 H, J = 7.8 Hz, ArH), 7.32 (d, 2 H, J = 7.8 Hz, ArH), 7.50 (d, 2 H, J = 8.1 Hz, ArH), 7.73 (d, 2 H, J = 8.3 Hz, ArH); 1D-NOE between H-3/H-1′ (0.61%); H-3/H-2′ (0.85%); H-3/CH i-Pr (0.52%); H-3/Me (1.16 ppm) (1.7%); H-3/Me (0.79 ppm); 1.6%; H-1′/H-3: 0.14%; H-1′/CH_2 (1.6%); H-2′/H-3 (1.2%); H-2′/CH_2 (1.9%).

*11.3. Synthesis of (2R,3S)-[2-((1E)-3-Bromo-1-propen-1-yl)-3-butyl-2-((S)-p-tolylsulfinyl)-1-(p-tolylsulfonyl)]aziridine, **19c**, and (2R,3S)-[2-((1E)-3-Bromo-1-propen-1-yl)-3-butyl-2-((R)-p-tolylsulfinyl)-1-(p-tolylsulfonyl)]aziridine, **20c**.* From sulfonamide **7d** (42 mg, 0.10 mmol, 1.0 equiv), K_2CO_3 (100 mg, 0.72 mmol, 7.5 equiv), and NBS (95 mg, 0.54 mmol, 5.0 equiv), following the general procedure (5 days), an 80:20 mixture of **19c** and **20c** was obtained. Chromatographic purification (10–50% EtOAc/hex) yielded a fraction of 70:30 mixture of aziridines **19c** and **20c** (28 mg, 56%) as a colorless oil.

Data for major isomer **19c** from the mixture: R_f 0.35 (40% EtOAc/hex); ^{1}H NMR ($CDCl_3$, 300 MHz)-COSY δ 0.81 (d, 3 H, J = 7.0 Hz, Me n-Bu), 1.16–1.35 (m, 4 H, CH_2 n-Bu), 1.82 (q, 2 H, J = 6.8 Hz, CH_2 n-Bu), 2.40 (s, 3 H, Me p-Tol), 2.45 (s, 3 H, Me p-Tol), 3.22 (dd, 1 H, J = 7.6, 6.1 Hz, H-3), 3.77–3.90 (m, 2 H, CH_2Br), 5.86 (ddd, 1 H, J = 15.6, 7.8, 5.9 Hz, H-2′), 5.96 (d, 1 H, J = 15.6 Hz, H-1′), 7.30 (m, 4 H, ArH), 7.49 (d, 2 H, J = 8.3 Hz, ArH), 7.86 (d, 2 H, J = 8.3 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 13.8, 21.5, 21.7, 22.0, 27.0, 29.8 (CH_2 n-Bu), 30.2 (CH_2Br), 50.7 (C-3), 69.4 (C-2), 122.3 (C-1′), 125.8 (2 C), 128.1 (2 C), 129.6 (2 C), 129.8 (2 C), 136.2 (C-2′), 137.0, 137.8, 142.7, 144.8; IR (film) 2956, 2927, 1596, 1454, 1335, 1163, 1089, 1059, 811 cm^{-1}; HMRS (ESI) m/z for $C_{23}H_{28}BrNNaO_3S_2$ $[M + Na]^+$ calcd 532.0592, observed 532.0596.

Partial data for **20c** from the mixture: ^{1}H NMR ($CDCl_3$, 300 MHz)-COSY δ 2.42 (s, 3 H, Me p-Tol), 2.46 (s, 3 H, Me p-Tol), 3.89–4.01 (m, 2 H, CH_2Br), 5.64 (d, 1 H, J = 15.4 Hz, H-1′), 6.17 (m, 1 H, H-2′), 7.49 (d, 2 H, J = 8.3 Hz, ArH), 7.73 (d, 2 H, J = 8.3 Hz, ArH).

12. General Procedure for the Oxidation of Sulfinyl Aziridines with MMPP, 21. To a cold (0 °C) solution of aziridines **19** and **20** in MeOH (5 mL/mmol), solid MMPP was added, and after 5 min it was allowed to warm to rt. The reaction was stirred at this temperature until disappearance of the starting material (monitored by TLC). Then, it was quenched with saturated aqueous $NaHCO_3$ (0.3 mL/mmol), and the solvent was evaporated under reduced pressure. The crude was purified with deactivated silica gel to give sulfonyl aziridines **21** using the appropriate mixture of eluents.

*12.1. Synthesis of (−)-(2R,3S)-[2-((1E)-3-Bromo-1-propen-1-yl)-3-isopropyl-1,2-bis(p-tolylsulfonyl)]aziridine, **21b**.* From an 80:20 mixture of aziridines **19b**:**20b** (26 mg, 0.05 mmol, 1.0 equiv) and MMPP (49 mg, 0.08 mmol, 1.5 equiv), following the general procedure (18 h) and after chromatographic purification of the crude (10–40% EtOAc/hex), **21b** was obtained as a colorless oil (20 mg, 75%).

Data for **21b**: R_f 0.20 (20% EtOAc/hex); $[\alpha]^{20}_D$ −43.2 (c = 0.34); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 0.68 (d, 3 H, J = 6.6 Hz, Me i-Pr), 1.12 (d, 3 H, J = 6.8 Hz, Me i-Pr), 2.44 (m, 1 H, CH i-Pr), 2.45 (s, 6 H, Me p-Tol), 2.92 (d, 1 H, J = 10.3 Hz, H-3), 3.88 (m, 2 H, CH_2Br), 5.79 (d, 1 H, J = 15.2 Hz, H-1′), 6.21 (ddd, 1 H, J = 15.2, 8.1, 7.1 Hz, H-2′), 7.34 (t, 4 H, J = 7.7 Hz, ArH), 7.76 (dt, 2 H, J = 8.3, 1.7 Hz, ArH), 7.81 (dt, 2 H, J = 8.6, 1.9 Hz, ArH); 1D-NOE between H-1′/H-3 (0.25%); H-1′/CH_2 (2.3%); H-2′/CH_2 (2%); H-2′/H-3 (2%); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 19.8, 21.1, 21.7 (2 C), 26.0, 29.8 (CH_2), 59.1 (C-3), 67.6, 123.3, 125.6, 128.3 (4 C), 129.7 (4 C), 137.7 (2 C), 145.2, 145.6; IR (film) 2967, 2926, 1597, 1332, 1163, 1082, 965, 814, 745, 708, 677 cm^{-1}; MS (ESI) 1047 [2M + 2 + Na]$^+$, 512 [M + 1]$^+$; HRMS (ESI) *m*/*z* for $C_{22}H_{27}BrNO_4S_2$ [M + H]$^+$ calcd 512.0565, observed 512.0577.

*12.2. Synthesis of (−)-(2R,3S)-[2-((1E)-3-Bromo-1-propen-1-yl)-3-butyl-1,2-bis(p-tolylsulfonyl)]aziridine, **21c**.* From a 70:30 mixture of aziridines **19c**:**20c** (30 mg, 0.06 mmol, 1.0 equiv) and MMPP (54 mg, 0.088 mmol, 1.5 equiv), following the general procedure (17 h) and after chromatographic purification of the crude (10−40% EtOAc/hex), **21c** was obtained as a colorless oil (21 mg, 68%).

Data for **21c**: R_f 0.43 (70% Et_2O/hex); $[\alpha]^{20}_D$ −61.0 (*c* = 0.29); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.79 (t, 3 H, *J* = 7.0 Hz, Me *n*-Bu), 1.15−1.30 (m, 4 H, CH_2 *n*-Bu), 1.98 (m, 2 H, CH_2 *n*-Bu), 2.45 (s, 6 H, Me *p*-Tol), 3.21 (dd, 1 H, *J* = 8.3, 5.6 Hz, H-3), 3.83−3.90 (m, 2 H, CH_2Br), 5.84 (d, 1 H, *J* = 15.1 Hz, H-1′), 6.20 (ddd, 1 H, *J* = 15.1, 8.3, 6.8 Hz, H-2′), 7.33 (d, 4 H, *J* = 7.8 Hz, ArH), 7.74 (dt, 2 H, *J* = 8.3, 1.9 Hz, ArH), 7.81 (dt, 2 H, *J* = 8.3, 1.5 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz)-HSQC δ 13.8 (Me *n*-Bu), 21.7 (Me *p*-Tol), 21.8 (Me *p*-Tol), 22.1 (CH_2 *n*-Bu), 26.1 (CH_2 *n*-Bu), 29.7 (CH_2), 29.9 (CH_2), 52.4 (C-3), 67.2 (C-2), 123.2 (C-1′), 128.1 (2 C), 129.7 (6 C), 134.7, 135.8, 137.6 (C-2′), 145.0, 145.5; IR (film) 2958, 2928, 1597, 1455, 1332, 1163, 1083, 955, 814 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{23}H_{28}BrNNaO_4S_2$ [M + Na]$^+$ calcd 548.0541, observed 548.0536.

13. Synthesis of (−)-1-[(*E*)-3-[(2*R*,3*S*)-3-Phenyl-2-(*S*)-*p*-tolylsulfinyl-1-tolylsulfonylaziridin-2-yl]-2-propen-1-yl]piperidine, 22. To a solution of aziridine **19a** (39 mg, 0.07 mmol, 1.0 equiv) in toluene (0.7 mL) was added piperidine (2.0 equiv, 0.014 mL, 0.15 mmol), and it was stirred at rt until disappearance of the starting material by TLC (2 h). The solvent was evaporated under reduced pressure, and the crude was purified on deactivated silica (1−5% EtOH/CH_2Cl_2) to yield a pure fraction of aziridine **22** as a colorless oil (28 mg, 71%).

Data for **22**: R_f 0.14 (10% EtOH/CH_2Cl_2); $[\alpha]^{20}_D$ −34.8 (*c* = 0.99); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.43 (br s, 2 H), 1.59 (br s, 4 H), 2.20 (m, 2 H), 2.29 (s, 3 H), 2.42 (m, 2 H), 2.42 (s, 3 H), 3.08 (m, 2 H), 4.46 (s, 1 H), 5.82 (m, 1 H), 6.29 (d, 1 H, *J* = 15.6 Hz), 6.63 (dt, 2 H, *J* = 8.3, 1.7 Hz), 7.03 (d, 2 H, *J* = 8.1 Hz), 7.24−7.34 (m, 7 H), 7.90 (dt, 2 H, *J* = 8.3, 1.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.4, 21.7, 23.6, 25.2, 50.1 (2 C), 54.2 (2 C), 60.4, 72.6, 124.9 (2 C), 127.8 (4 C), 127.8 (2 C), 128.6 (2 C), 129.0, 129.2 (2 C), 129.8 (2 C), 130.6, 136.4 (2 C), 142.1, 144.9; IR (film) 2933, 1597, 1494, 1453, 1340, 1164, 1090, 1056, 908, 812, 752 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{30}H_{35}N_2O_3S_2$ [M + H]$^+$ calcd 535.2089, observed 535.2091.

14. Procedure for the Synthesis of Ditosyl Aziridines, 24. Step 1: Ozonolysis.

Procedure A: To a cold (0 °C) solution of aziridine **21** in a 95:5 acetone/H_2O solution (7 mL/mmol), O_2 was bubbled for 10 min, followed by a flow of O_3. The reaction was stirred at this temperature until disappearance of the starting material by TLC. The reaction was diluted with hexane (10 mL/mmol), quenched with a saturated solution of NaCl (10 mL/mmol), and extracted with EtOAc (3 × 10 mL/mmol). The combined organic phases were washed with a saturated solution of NaCl (10 mL/mmol), dried over Na_2SO_4, and filtered, and the solvent was evaporated under reduced pressure. The crude was analyzed by ^{1}H NMR and submitted to further oxidation.

Procedure B: To a cold (−78 °C) solution of aziridine **21** in CH_2Cl_2 (19 mL/mmol), O_2 was bubbled for 10 min, followed by a flow of O_3. The reaction was allowed to reach −50 °C and was stirred until the disappearance of the starting material by TLC. SMe_2 was added (5 equiv), and the reaction was warmed to rt. The solvent was evaporated under reduced pressure, and the crude was analyzed by ^{1}H NMR and submitted to further oxidation.

Step 2: Oxidation with TCCA.

To a solution of the above mixtures in acetone (10 mL/mmol), a 15% $NaHCO_3$ aqueous solution (30 mL/mmol) was added. The reaction was cooled to 0 °C, and solid trichloroisocianuric acid (TCCA, 10 equiv) and NaBr (0.2 equiv) were added. The reaction was then stirred at rt for 4−10 days. The reaction was quenched with ^{i}PrOH (0.6 mL/mmol), and the crude was filtered through Celite. Finally, the solvent was evaporated under reduced pressure, followed by purification on deactivated silica gel.

*14.1. Synthesis of (2S,3S)-3-Isopropyl-1,2-bis-(p-tolylsulfonyl)-aziridine-2-carbaldehyde, **23b**, and (+)-(2R,3S)-3-Isopropyl-1,2-bis-(p-tolylsulfonyl)aziridine, **24b**.* From sulfonamide **21b** (20 mg, 0.04 mmol, 1.0 equiv), following general procedure A for ozonolysis (50 min), a 90:10 mixture of **23b**:**24b** was obtained (10 mg, 61%). Oxidation of the mixture (9 days) using TCCA (70 mg, 0.3 mmol, 10 equiv), 15% $NaHCO_3$ aqueous solution (0.9 mL), and NaBr afforded a pure fraction of **24b** as a white oil (8.1 mg, 86%).

Data for **23b** from the mixture: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.91 (d, 3 H, *J* = 6.7 Hz, Me *i*-Pr), 1.12 (d, 3 H, *J* = 6.8 Hz, Me *i*-Pr), 2.45 (s, 3 H, Me *p*-Tol), 2.48 (s, 3 H, Me *p*-Tol), 2.52−2.60 (m, 1 H, CH *i*-Pr), 3.41 (d, 1 H, *J* = 10.0 Hz, H-3), 7.34 (d, 2 H, *J* = 9.0 Hz, ArH), 7.37 (d, 2 H, *J* = 8.9 Hz, ArH), 7.78 (dt, 2 H, *J* = 8.4, 1.8 Hz, ArH), 7.87 (dt, 2 H, *J* = 8.4, 1.8 Hz, ArH), 9.42 (s, 1 H, CHO).

Data for **24b**: R_f 0.25 (60% Et_2O/hex); $[\alpha]^{20}_D$ +52.6 (*c* = 0.81); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 0.92 (d, 3 H, *J* = 6.8 Hz, Me *i*-Pr), 1.13 (d, 3 H, *J* = 6.8 Hz, Me *i*-Pr), 2.37−2.48 (m, 1 H, CH *i*-Pr), 2.42 (s, 3 H, Me *p*-Tol), 2.44 (s, 3 H, Me *p*-Tol), 2.80 (dd, 1 H, *J* = 10.3, 6.8 Hz, H-3), 3.84 (d, 1 H, *J* = 6.8 Hz, H-2), 7.18 (d, 2 H, *J* = 7.8 Hz, ArH), 7.20 (d, 2 H, *J* = 7.8 Hz, ArH), 7.60 (dt, 2 H, *J* = 8.3, 1.9 Hz, ArH), 7.62 (dt, 2 H, *J* = 8.3, 1.9 Hz, ArH); 1D-NOE between H-3/H-2 (2.0%); H-2/H-3 (3.0%); ^{13}C NMR ($CDCl_3$, 125 MHz)-HSQC δ 19.7 (Me *i*-Pr), 21.2 (Me *i*-Pr), 21.7 (2 C, Me *p*-Tol), 26.2 (CH *i*-Pr), 53.0 (C-3), 57.4 (C-2), 128.3 (2 C), 128.4 (2 C), 129.6 (2 C), 129.8 (2 C), 133.6, 135.8, 145.2 (2 C); IR (film) 2969, 2928, 1597, 1466, 1336, 1303, 1162, 1086, 977, 891, 813, 759, 680 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{19}H_{27}N_2O_4S_2$ [M+NH_4]$^+$ calcd 411.1412, observed 411.1421.

*14.2. Synthesis of (2S,3S)-3-Butyl-1,2-bis-(p-tolylsulfonyl)-aziridine-2-carbaldehyde, **23c**, and (+)-(2R,3S)-3-Butyl-1,3-bis-(p-tolylsulfonyl)aziridine, **24c**.* From sulfonamide **21c** (15 mg, 0.03 mmol, 1.0 equiv), following general procedure B for ozonolysis (30 min), a 90:10 mixture of **23c**:**24c** was obtained (8 mg, 66%). Oxidation of the mixture (4 days) with TCCA (42 mg, 0.18 mmol, 10 equiv), 15% $NaHCO_3$ aqueous solution (0.54 mL), and NaBr afforded a pure fraction of **24c** as a colorless oil (4.6 mg, 63%).

Partial data for **23c**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.86 (m, 3 H, Me *n*-Bu), 1.30−1.39 (m, 4 H, CH_2 *n*-Bu), 1.99−2.19 (m, 2 H, CH_2 *n*-Bu), 2.42 (s, 3 H, Me *p*-Tol), 2.45 (s, 3 H, Me *p*-Tol), 3.08 (dd, 1 H, *J* = 12.9, 7.3 Hz, H-3), 7.32 (d, 2 H, *J* = 8.5 Hz, ArH), 7.36 (d, 2 H, *J* = 8.5 Hz, ArH), 7.78 (d, 2 H, *J* = 8.3 Hz, ArH), 7.86 (d, 2 H, *J* = 8.3 Hz, ArH), 9.43 (s, 1 H, CHO).

Data for **24c**: R_f 0.21 (50% Et_2O/hex); $[\alpha]^{20}_D$ +46.1 (*c* = 0.46); ^{1}H NMR ($CDCl_3$, 500 MHz)-COSY δ 0.86 (t, 3 H, *J* = 7.0 Hz, Me *n*-Bu), 1.30−1.39 (m, 4 H, CH_2 *n*-Bu), 1.95−2.06 (m, 2 H, CH_2 *n*-Bu), 2.42 (s, 3 H, Me *p*-Tol), 2.44 (s, 3 H, Me *p*-Tol), 3.08 (ddd, 1 H, *J* = 8.3, 6.8, 5.4 Hz, H-3), 3.82 (d, 1 H, *J* = 7.3 Hz, H-2), 7.18 (d, 2 H, *J* = 7.8 Hz, ArH), 7.21 (d, 2 H, *J* = 7.8 Hz, ArH), 7.61 (d, 4 H, *J* = 8.3 Hz, ArH); 1D-NOE between H-3/H-2 (2.8%); H-2/H-3 (2.9%); ^{13}C NMR ($CDCl_3$, 125 MHz)-HSQC δ 13.8 (Me *n*-Bu), 21.7 (2 C), 22.1, 25.9 (CH_2 *n*-Bu), 29.6 (CH_2 *n*-Bu), 46.7 (C-3), 57.1 (C-2), 128.3 (4 C), 129.7 (2 C), 129.8 (2 C), 133.7, 135.8, 145.2 (2 C); IR (film) 2958, 2927, 2860, 1597, 1456, 1335, 1162, 1086, 814, 717 cm^{-1}; HRMS (ESI) *m*/*z* for $C_{20}H_{29}N_2O_4S_2$ [M + NH_4]$^+$ calcd 425.1569, observed 425.1556.

■ ASSOCIATED CONTENT

Supporting Information

Spectral data (^{1}H NMR and ^{13}C NMR) for new compounds and X-ray data and structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Oxidizing agents such as *m*-CPBA, MMPP (magnesium monoperoxyphthalate), and PhIO at different temperatures and solvents were tested to afford mixtures of mono- and dioxidized products. Although PhIO showed some regioselectivity, it yielded mixtures of sulfonamides as epimers at the vinyl sulfoxide.
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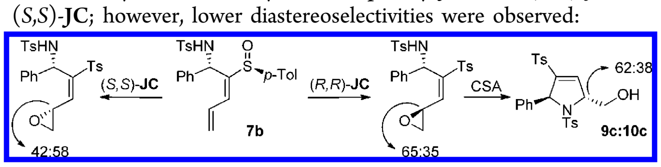
(19) We carried out Katsuki−Jacobsen epoxidation employing commercially available catalysts developed by Jacobsen (*R*,*R*)-**JC** and (*S*,*S*)-**JC**; however, lower diastereoselectivities were observed:



Some examples of the epoxidation of dienyl sulfoxides: (a) Fernández de la Pradilla, R.; Manzano, P.; Montero, C.; Priego, J.; Martínez-Ripoll, M.; Martínez-Cruz, L. A. *J. Org. Chem.* **2003**, *68*, 7755−7767. (b) Fernández de la Pradilla, R.; Castellanos, A. *Tetrahedron Lett.* **2007**, *48*, 6500−6504.
(20) Significant amounts of **8a,b** were obtained by addition of (*R*)-**2c** to sulfonimines. Although the failure of the halocyclization for **8a,b** is not fully understood, conformational differences between **7** and **8** could be involved.
(21) At this point, it is not clear to us if the equilibration between the dibromo adducts could take place through **15** followed by addition of bromide from TBATB or through an epibromonium type of mechanism.
(22) Refluxing the mixture over one week did not change this ratio.
(23) Experiments to optimize these transformations included the changing of solvents, temperature, and the presence or absence of light. 1,3-Dibromo-5,5-dimethylhydantoin as bromine source did not improve the yield of aziridine. Substitution of Ts for Ns at nitrogen did not improve the result. For a recent review on *N*-halo reagents, see: Veisi, H.; Ghorbani-Vaghei, R. *Tetrahedron* **2010**, *66*, 7445−7463.
(24) Epimerization of sulfinyl aziridines **19b** and **19c** mainly occurred upon purification on silica gel.
(25) Low conversions were found for the aziridination of other sulfonamides **7m−p** (R = $MeOC_6H_4$, $CF_3C_6H_4$, CH_2CH_2Ph, Cy). We suspect that the reagent (NBS) quality and the presence of traces amounts of impurities in the starting materials could play a role in the inconsistency of the results.
(26) Attempts to promote the presence of TsNBr species inhibited the cyclization. For related conditions, see: (a) Komeyana, K.; Morimoto, T.; Takaki, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 2938−2941. (b) Talluri, S. K.; Sudalai, A. *Org. Lett.* **2005**, *7*, 855−857.
(27) (a) Arroyo, Y.; Meana, A.; Sanz-Tejedor, M. A.; Alonso, I.; García Ruano, J. L. *Chem.—Eur. J.* **2010**, *16*, 9874−9883. (b) Midura, W.-H. *Tetrahedron Lett.* **2007**, *48*, 3907−3910.
(28) De Luca, L.; Giacomelli, G.; Masala, S.; Porcheddu, A. *J. Org. Chem.* **2003**, *68*, 4999−5001.
(29) Ramachandar, T.; Wu, Y.; Zhang, J.; Davis, F. A. *Org. Synth.* **2006**, *83*, 131−140.