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A Versatile Route to (*E*)- and (*Z*)-2-Hydroxy-3,4-unsaturated Disubstituted Sulfilimines and Their Haloamidation Reaction

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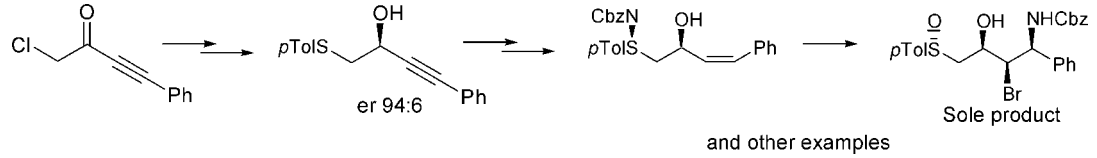

α-Chloro ynones have been reduced using Noyori's Ru catalyst to furnish α-chloro propargylic alcohols with excellent enantioselectivity. These have been used as a common precursor for the preparation of (*E*)- and (*Z*)-2-hydroxy-3,4-unsaturated disubstituted sulfilimines. The latter serve as precursors for the highly regio- and stereoselective preparation of bromo carbamates.

Introduction

Vicinal haloamines,[1] obtained by the addition of amine and halogen moieties across carbon−carbon double bonds, are useful building blocks in organic synthesis[2] and medicinal chemistry.[3] Halo amines have been obtained by (a) aminohalogenation[1a,4] via an aziridinium intermediate followed by attack of a halogen nucleophile or (b) haloamination[5] which involves a source of halonium ion and nitrogen nucleophiles.

We had reported a novel stereoselective method of preparation of bromo sulfonamides by haloamidation[6] of alkenes using *N*-Ts-sulfilimines as intramolecular nucleophiles (Figure 1).

The drawbacks with the reported methodology were that (i) the *cis*-disubstituted alkenes were accessible by a multistep sequence of reactions,[7] (ii) the *N*-Ts group in the product could be removed only using harsh reaction conditions which is not ideal for a substrate with sensitive functional groups, and (iii) it only provided access to racemic products. Subsequently, we reported a route to optically active 2-siloxy-3,4-unsaturated sulfilimines from the corresponding sulfoxides using *N*-sulfinylbenzylcarbamate[8] (CbzNSO), Burgess reagent,[9a] and their stereoselective conversion to bromo carbamates (Figure 2).[9b]

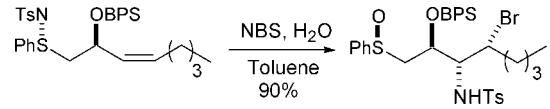

FIGURE 1. Preparation of bromo sulfonamide.

This methodology also suffered from the drawback of having to protect the β-hydroxy group of the sulfoxide and allowed ready preparation of *trans*-disubstituted alkenes.[10] We felt that a more direct route to both (*E*)- and (*Z*)-3,4-

[†] Lab of X-ray Crystallography.

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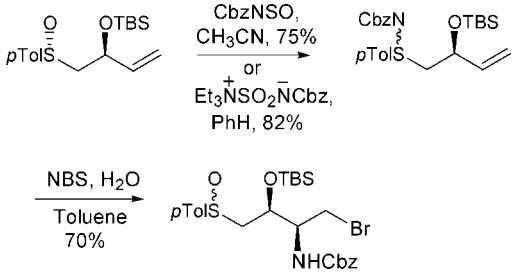


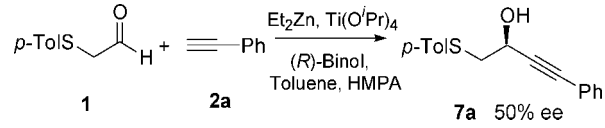
FIGURE 2. Preparation of bromo carbamate.

disubstituted-2-hydroxy sulfilimines was essential for a wide application of our methodology. Toward this goal, we disclose herein a versatile route to both *cis*- and *trans*-disubstituted β-hydroxy sulfilimines from a common intermediate and their regio- and stereoselective conversion to bromo carbamates.

Results and Discussion

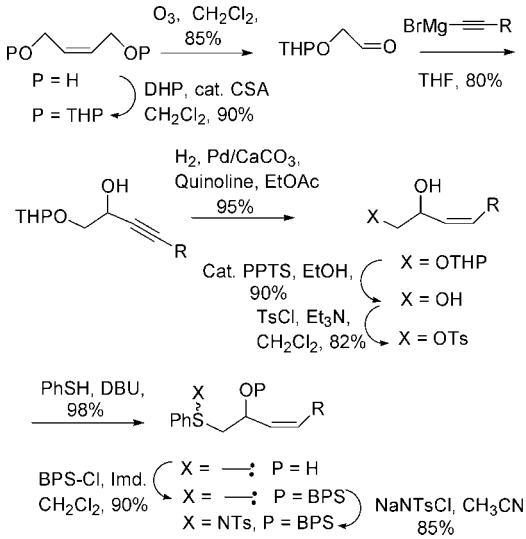
Optically active propargylic alcohols were reasoned to be suitable precursors to both *cis*- and *trans*-allylic alcohols. Thus, we initially considered preparing propargyl alcohols by introducing chirality simultaneously with carbon−carbon bond formation. Using Pu's protocol,[11] we could prepare propargyl alcohol **7a** from phenyl acetylene **2a** and *p*-tolythio acetaldehyde[12] **1** in only moderate enantiomeric excess Scheme 1.[13]

SCHEME 1. Enantioselective Preparation of Propargyl Alcohol

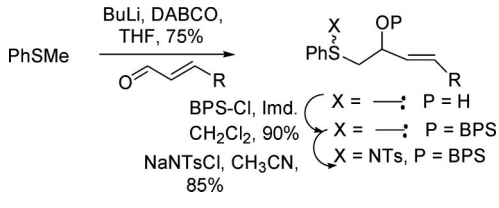


We therefore considered catalytic asymmetric reduction of ynones **4**.[14] Commercially available Weinreb amide **3** on reaction with lithium acetylides derived from alkynes **2a**−**d** afforded ynone **4** after the reaction mixture was quenched with aq HCl.[15] Chiral Rh hydrogenation catalysts have been reported to efficiently convert α-halogenated ketones to optically active alcohols though in moderate ee.[16] Ikariya and co-workers have reported highly efficient asymmetric transfer hydrogenation of α-chloro acetophenones using a well-defined chiral Rh complex.[17] The catalyst, however, when used for the reduction of α-chloro ketones possessing conjugated double or triple bonds, gave the corresponding products with only moderate ee ranging from 58−68%. The ynone **4a** has been reduced by Ikariya via transfer hydrogenation using the Rh catalyst under optimized conditions to afford propargylic alcohol **6a** in 68% ee. In this context, it was very pleasing to note that the transfer hydrogenation of ketones **4** using 2.5 mol % of Noyori's catalyst,[18] CpRuCl[(*S*,*S*)-Tsdpen] **5**, in the presence of formic acid−triethylamine azeotrope in dichloromethane as solvent at rt furnished propargylic alcohols **6** in good yield (70−80%) and enantioselectivity[19] (er 94−97 to **6**−**3**), Scheme 2. To the best of our knowledge, the conditions reported herein for the enantioselective transfer hydrogenation of α-chloro ynones afford the corresponding propargylic alcohols with the highest enantioselectivity reported to date. A mixture of formic acid/triethylamine was found to be an optimal hydrogen source as no reduction was observed using 2-propanol. The catalyst

(7) The *cis*-alkenes were obtained in nine steps from *cis*-2-butene-1,4-diol as depicted below.



The *trans* alkenes were obtained in only three steps as illustrated below.



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(10) The β-hydroxy γ,δ-*cis*-alkenes cannot be derived from the reaction of *cis* esters with the lithio anion of aryl methyl sulfoxide followed by reduction of the resulting β-keto sulfoxides since the *cis* ester undergoes isomerization to the *trans* ester. The alternative reaction of acetylenic esters with lithio anion of aryl methyl sulfoxide followed by reduction of the resulting ynones suffers from poor stereoselectivity; see: Sanchez-Obregon, R.; Ortiz, B.; Walls, F.; Yuste, F.; Garcia Ruano, J. L. *Tetrahedron: Asymmetry* **1999**, *10*, 947–955.

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(12) *p*-Tolylthio acetaldehyde was obtained by IBX oxidation of *p*-tolylthio ethanol.

(13) In future, with an efficient catalyst becoming available for the preparation of propargylic alcohols, by the direct reaction of aldehydes and alkynes, we can prepare optically active sulfilimines with excellent enantioselectivity readily in only three steps.

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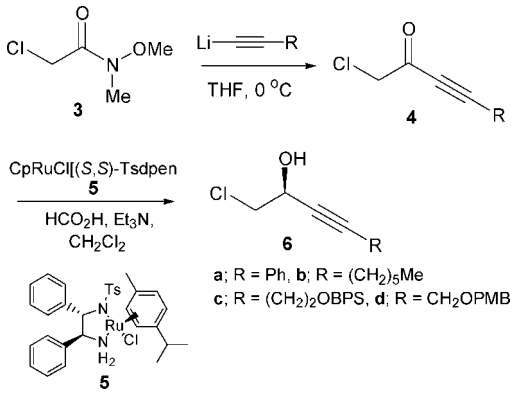
(19) The enantioselectivity was determined by chiral HPLC; see the Supporting Information. The *S* configuration was assigned on the basis of literature precedent.

SCHEME 2. Enantioselective Transfer Hydrogenation of Prochiral α-Chloro Ynones

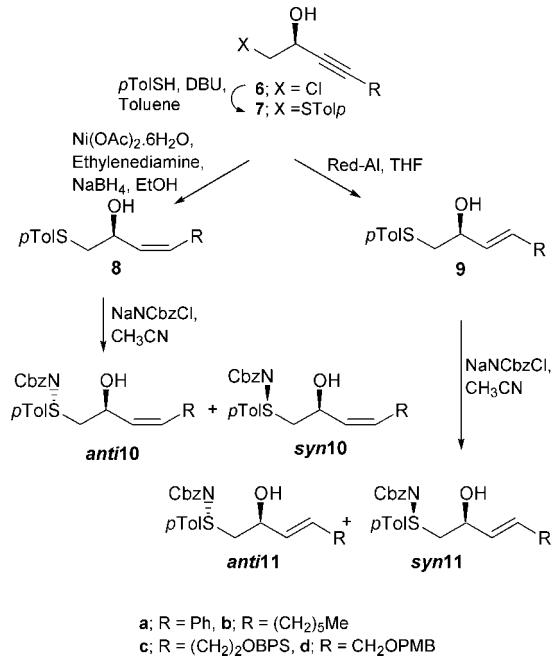


was prepared in situ, and dichloromethane was found to be the solvent of choice.[20]

Incidentally, the chloropropargylic alcohols are useful synthons and can be converted directly or via the corresponding epoxides into chiral α-functionalized alkynes,[21a,b] heterocycles,[21c,d] and allenes[21e,f] and subjected to nucleophilic displacement.[21g] Proceeding further, the chlorine was displaced by treatment of **6** with *p*-thiocresol in the presence of DBU in toluene to furnish sulfide **7**. Reduction of the triple bond using nickel boride[22] and Red-Al[23] afforded cleanly *cis*- and *trans*-allylic alcohols **8** and **9**, respectively. Further treatment of the sulfide with *N*-chloro-*N*-sodiobenzylcarbamate (NaNCbzCl) in acetonitrile as the solvent yielded an equimolar mixture of separable *anti*- and *syn*-sulfilimines,[24] Scheme 3. Diastereoselective imination using a chiral metal complex would furnish either *anti*- or *syn*-sulfilimines selectively if not exclusively.[25] It is noteworthy that selective oxidation of sulfides **8** and **9** using sodium metaperiodate or *m*-chloroperoxybenzoic acid at low temperatures would afford the corresponding β-hydroxy-γ,δ-disubstituted sulfoxides.

Having prepared the unsaturated sulfilimines, their regio- and stereoselective bromoamidation was next investigated, Table 1. An inspection of Table 1 reveals that the intramolecular transfer of the *N*-Cbz group from sulfur to carbon is highly regioselective affording 5-*exo* opening products in all cases except the styrene derivatives **10a** and **11a** which afford 6-*endo* opening products, both modes of opening being in accordance with Markovnikov's rule. The *anti*- and *syn*-sulfilimines behave stereoconvergently (compare entries 1,2, 3,4, etc.) to afford bromocarbamates with identical configuration at carbon but differing at sulfur, which was proven by oxidation of the sulfinyl moiety in the products individually to an identical sulfone. This therefore avoids the necessity of having to prepare diastereomerically pure *anti*- or

SCHEME 3. Preparation of *cis*- and *trans*-β-Hydroxy Sulfilimines



syn-β-hydroxy sulfilimines or, if prepared as a mixture, to separate them. The reaction is general and proceeds under mild reaction conditions. The reaction probably proceeds via the reversibly formed π-complex of the bromonium ion with the alkenes (*anti*,*cis* and *syn*,*trans* chosen for illustration) which on intramolecular attack by the sulfilimine group via 6-*endo* or 5-*exo* pathways would furnish intermediates **I** and **III** or **II** and **IV**, respectively, which then upon hydrolysis by attack of water at sulfur would yield the bromo carbamate sulfoxide with an inversion of sulfur configuration, Figure 3.

The outcome of electrophile-induced addition to allylic π-systems is determined by a delicate balance between steric, viz. minimization of A1,3 strain[26] and the stereoelectronic effect[27] of the allylic hydroxy (siloxy) group.[28] An electron-withdrawing allylic hydroxyl (siloxy) at the equatorial position of an intermediate (for instance **I**/ **II**) is better aligned for σ^* C−O orbital interaction with the π-system,[29] which results in a decrease in the rate through it. The rate-retarding effect[30] is avoided when the allylic hydroxyl (siloxy) is orthogonal to the π-system (for instance, intermediates **III**/**IV**). Sulfilimine ***anti*11a** probably reacts via twist-chair **VI**, favored for stereoelectronic and steric reasons, instead of chair intermediate **V**, which suffers from diaxial interactions between OH and *p*-Tol substituents, to furnish product ***syn*13**. The reaction via chair intermediate **VII**, favored by steric but disfavored by stereoelectronic effects, which would have afforded product ***syn*13X**, was not observed. Previously, it has been practically observed[6] that the silyl ether protected *N*-Ts sulfilimine **4d***a* related to

(20) The hydrogenation in EtOAc as the solvent afforded the alcohol in poor yield. The substrate to catalyst ratio (25:1) was found to be optimal. With a higher substrate to catalyst ratio (100:1) side reactions were observed.

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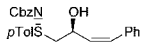
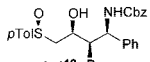
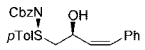
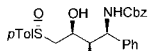
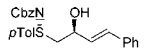
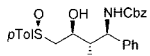
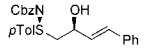
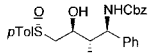
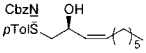
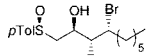
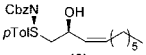
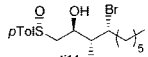
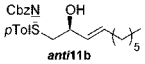
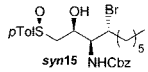
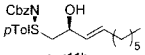
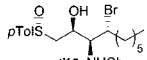
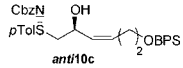
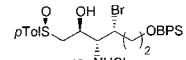
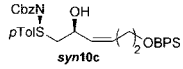
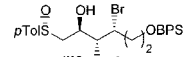
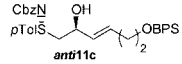
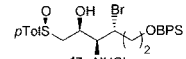
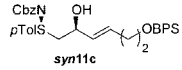
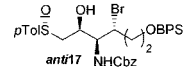
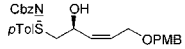
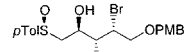
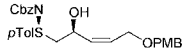
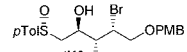
TABLE 1. Regio- and Stereoselective Preparation of Bromocarbamates[a]

Entry	Sulfilimine	Bromocarbamate[b]	Yield,[c] (dr)[d]
1	 ***anti*10a**	 ***syn*12**	76% (>95:<5)
2	 ***syn*10a**	 ***anti*12**	78% (>95:<5)
3	 ***anti*11a**	 ***syn*13**	78% (>95:<5)
4	 ***syn*11a**	 ***anti*13**	80% (>95:<5)
5	 ***anti*10b**	 ***syn*14**	76% (>95:<5)
6	 ***syn*10b**	 ***anti*14**	80 (>95:<5)
7	 ***anti*11b**	 ***syn*15**	82% (>95:<5)
8	 ***syn*11b**	 ***anti*15**	80% (75:25)[e]
9	 ***anti*10c**	 ***syn*16**	76% (>95:<5)
10	 ***syn*10c**	 ***anti*16**	75% (>95:<5)
11	 ***anti*11c**	 ***syn*17**	85% (>95:<5)
12	 ***syn*11c**	 ***anti*17**	82% (85:15)[e]
13	 ***anti*10d**	 ***syn*18**	74% (>95:<5)
14	 ***syn*10d**	 ***anti*18**	80% (>95:<5)

[a] All reactions were done using 0.5 mmol of the sulfilimine in the presence of 1.2 equiv of NBS and 1.5 equiv of water in toluene (0.2 M) at rt. [b] The structure of the sole or major product depicted. [c] Yield refers to isolated yields. [d] Diastereoselectivity (at C3 relative to C2) is based on ^{1}H NMR of the crude reaction mixture. [e] The isomers were inseparable; structures could be unambiguously assigned to the major products only.

anti*11a** afforded two products in a 3:1 ratio. The major product **5d*s probably is formed via intermediate **VI** which suffers from a severe gauche interaction between the bulky OBPS group and Br atom. This guache interaction is avoided in intermediate **VII**, which affords **5d*sX***. This probably explains for the erosion of selectivity observed in the case of **4d*a***, Figure 4.

Alkene ***syn*10b** probably reacts via intermediate **VIII** to furnish ***anti*14** as the sole product. The intermediate **IX**, which is expected to furnish ***anti*14X**, is favored for stereoelectronic reasons but disfavored by A1,3 strain. The related silyl-protected *N*-Ts sulfilimine **4c*s*** affords a 2:1 mixture of products.[6] The major product **5c*a*** probably is formed through intermediate **VIII** and the minor product via **IX**. The interactions between OBPS and Br observed in intermediate **VIII** are avoided in **IX**, Figure 5.

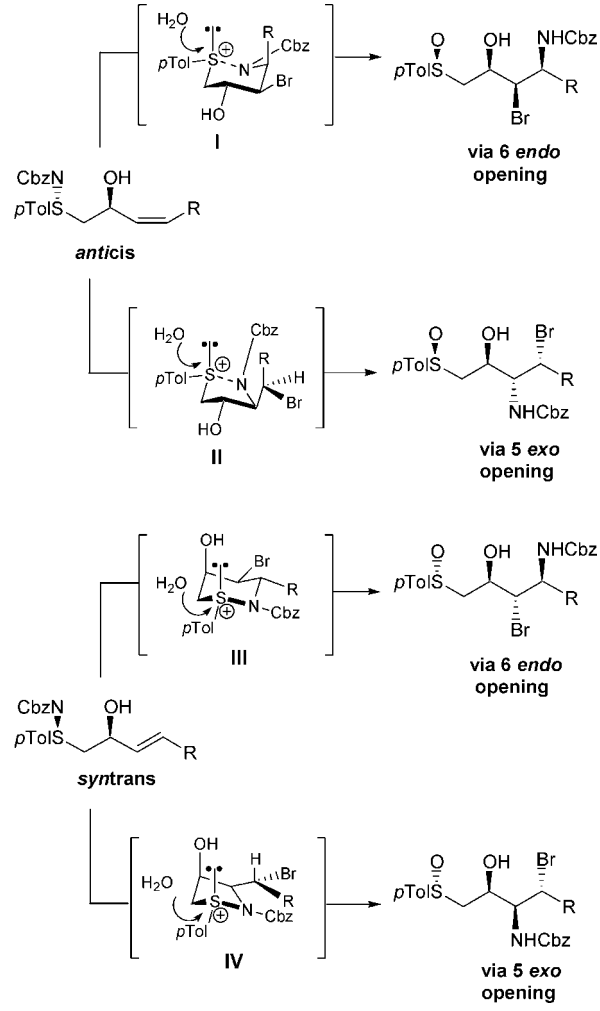


FIGURE 3. Probable reaction pathway.

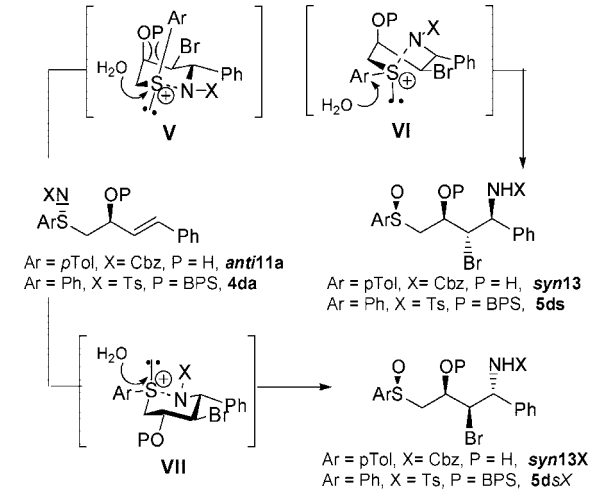


FIGURE 4. Probable reaction pathway.

The structure of ***anti*13** was unambiguously assigned by X-ray crystallography.[31] The structure of ***anti*12** was assigned by debromination using *n*-tributyltin hydride to afford an amino alcohol derivative which was identical to the debrominated product obtained from ***anti*13**.[31] The structure of ***syn*15** was confirmed by debromination and relating it to a known com-

(31) See the Supporting Information.

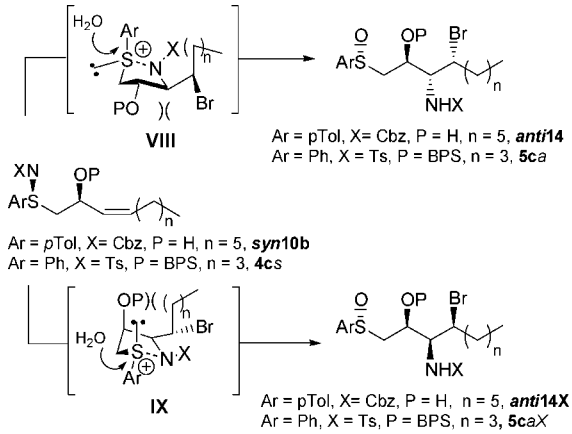


FIGURE 5. Probable reaction pathway.

pound.[8] Bromo carbamate ***anti*18** was debrominated and further converted to an acetonide. The NOE studies on the acetonide confirm the structure assigned to ***anti*18**.[31] The structures were assigned to products **14**, **16**, and **17** by analogy.

In conclusion, we have described a highly enantioselective preparation of α-chloropropargylic alcohols (useful synthons) by transfer hydrogenation using Noyori's catalyst and the preparation of *γ*,*δ*-*cis*- and *trans*-disubstituted *β*-hydroxysulfilimines from a common precursor by a straightforward sequence of reactions in few steps from readily available starting materials. The sulfilimines have been shown to be excellent intramolecular nucleophiles for the preparation of bromo carbamates regio- and stereoselectively. The products possess functional group handles for further manipulation and should serve as key intermediates for natural product synthesis and other bioactive molecules. In comparison to our earlier methodology using *N*-Ts sulfilimine, the methodology described herein has several advantages, in particular the stereoconvergent behavior of the diastereomeric sulfilimines, better stereoselectivity of bromo carbamate formation, and the nitrogen protecting group that can be removed under mild conditions.

Experimental Section

General Procedure for the Preparation of Propargyl Alcohol 6 by Transfer Hydrogenation. To a solution of the ynone **4** (1 equiv) in DCM (0.83 M) were added formic acid (8 equiv) and triethylamine (3.2 equiv) followed by Ru catalyst **5** (2.5 mol %) at once and the mixture stirred at rt until TLC examination revealed completion (2−3.5 h). The reaction mixture was diluted with EtOAc, washed successively with water and brine, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude product, which was purified by column chromatography to afford the propargyl alcohol **6**.

Alcohol 6a. Following the general procedure, ynone **4a** (1.78 g, 10 mmol) afforded the crude product, which was purified by column chromatography using 10% EtOAc/petroleum ether (v/v) to afford the propargyl alcohol **6a** (1.35 g, 7.5 mmol) in 75% yield as a gummy liquid, er 94:6 (column: Eurocel 01; mobile phase: 10% 2-propanol in hexane; flow rate: 1 mL/min). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.5−7.4 (m, 2H), 7.3−7.2 (m, 3H), 4.8 (q, J = 6.0 Hz, 1H), 3.8 (dd, J = 11.1, 4.3 Hz, 1H), 3.7 (dd, J = 11.1, 6.2 Hz, 1H), 2.4 (d, J = 6.0 Hz, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.3, 131.8, 128.8, 128.3, 86.3, 85.9, 63.0, 49.0. $[\alpha]_D^{25} = -7.5$ (c 1.0, $CHCl_3$). MS (FAB): 181 $[M + H]^+$.

Alcohol 6b. Similarly, ynone **4b** (1.86 g, 10 mmol) was hydrogenated over a period of 2.5 h to afford a crude product, which was purified by column chromatography using 10% EtOAc/petroleum ether (v/v) to afford the propargyl alcohol **6b** (1.5 g, 8 mmol) in 80% yield as a gummy liquid, er 94:6 (column: Chiralpack AD-H; mobile phase: 20% EtOH in hexane; flow rate: 1 mL/min). IR (KBr): 3376, 2928, 1697, 1385, 1035 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.6−4.5 (m, 1H), 3.7 (dd, J = 10.6, 3.8 Hz, 1H), 3.6 (dd, J = 10.6, 6.8 Hz, 1H), 2.2 (dt, J = 1.5, 6.8 Hz, 2H), 1.6−1.1 (m, 8H), 0.9 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 87.6, 77.2, 62.7, 49.5, 31.2, 28.4, 28.3, 22.5, 18.6, 14.0. $[\alpha]_D^{25} = -5.0$ (c 0.5, $CHCl_3$). MS (FAB): 189 $[M + H]^+$. HRMS (FAB): m/z calcd for $C_{10}H_{18}OCl$ 189.1041, found 189.1044.

Alcohol 6c. Similarly, ynone **4c** (3.8 g, 10 mmol) was hydrogenated over a period of 3.5 h to afford a crude compound which was purified by column chromatography using 8% EtOAc/petroleum ether (v/v) to afford the propargyl alcohol **6c** (2.8 g, 7.3 mmol) in 73% yield as a gummy liquid, er 98:2 (column: OD-H; mobile phase: 2% 2-propanol in hexane; flow rate: 1 mL/min). IR (KBr): 3422, 2925, 2275, 1645, 1064 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.7−7.6 (m, 4H), 7.5−7.3 (m, 6H), 4.6−4.4 (m, 1H), 3.8 (t, J = 6.6 Hz, 2H), 3.6 (dd, J = 11.1, 4.4 Hz, 1H), 3.5 (dd, J = 11.1, 6.6 Hz, 1H), 2.5 (dt, J = 1.5, 6.6 Hz, 2H), 2.1 (d, J = 5.9 Hz, 1H, OH), 1.1 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.5, 133.4, 129.7, 127.7, 84.5, 78.4, 62.6, 62.1, 49.2, 26.7, 22.8, 19.2. $[\alpha]_D^{25} = -6.0$ (c 2.0, $CHCl_3$). MS (ESI): 409 $[M + Na]^+$. HRMS (ESI): m/z calcd for $C_{22}H_{27}O_2NaSiCl$ 409.1366, found 409.1370.

Alcohol 6d. Similarly, ynone **4d** (2.5 g, 10 mmol) was hydrogenated over a period of 3 h to afford a crude compound which was purified by column chromatography using 15% EtOAc/petroleum ether (v/v) to afford the propargyl alcohol **6d** (1.8 g, 7.0 mmol) in 70% yield as a gummy liquid, er 93:7 (column: Eurocel 01; mobile phase: 10% 2-propanol in hexane; flow rate: 1 mL/min). IR (KBr): 3416, 2926, 2360, 1650, 1560, 1394, 1067 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.2 (d, J = 9.1 Hz, 2H), 6.8 (d, J = 9.1 Hz, 2H), 4.6−4.5 (m, 1H), 4.5 (s, 2H), 4.1 (s, 2H), 3.8 (s, 3H), 3.7−3.6 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4, 129.8, 128.6, 113.8, 83.7, 82.4, 71.3, 62.5, 56.8, 55.2, 48.8. $[\alpha]_D^{25} = -32.0$ (c 2.0, $CHCl_3$). MS (ESI): 277 $[M + Na]^+$. HRMS (ESI): m/z calcd for $C_{13}H_{15}O_3NaCl$ 277.0607, found 277.0614.

General Procedure for Preparation of Sulfilimines 10 and 11. To a stirred suspension of NaNCbzCl (5 equiv) in dry acetonitrile (2 M) at rt was added a solution of the sulfide (1 equiv) in dry acetonitrile (0.4 M) and the mixture stirred until TLC examination revealed completion (2−3 h). The reaction mixture was diluted with EtOAc, washed with water and brine, and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to afford the crude product, which was purified by column chromatography to afford the sulfilimine as a 1:1 mixture of *syn* and *anti* isomers. The *anti* isomer eluted first during column chromatography.

Sulfilimine 10a. To a stirred suspension of NaNCbzCl (1 g, 5 mmol) in dry acetonitrile (3 mL) at rt was added a solution of sulfide **8a** (270 mg, 1 mmol) in dry acetonitrile (2 mL). After 3 h, the reaction mixture was diluted with EtOAc (25 mL), washed with water (2 × 10 mL) and brine (10 mL), and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to afford the sulfilimine **10a** (352 mg, 0.84 mmol) as a 1:1 mixture of *syn* and *anti* isomers in a combined yield of 84%. Data for ***anti*10a**. Gummy liquid. IR (KBr): 3351, 2927, 1719, 1611, 1334, 1051 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6 (d, J = 8.7 Hz, 2H), 7.5−7.1 (m, 12H), 6.5 (d, J = 11.7 Hz, 1H), 5.7 (dd, J = 11.7, 8.9 Hz, 1H), 5.2−5.1 (br s, 1H-OH), 5.1−5.0 (m, 3H), 3.2 (dd, J = 13.0, 9.6 Hz, 1H), 3.0 (dd, J = 13.0, 2.1 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0, 143.0, 137.1, 135.6, 132.1, 130.5, 130.4, 129.9, 128.5, 128.3, 128.2, 127.9, 127.6, 127.4, 126.6, 67.8, 63.0, 57.0, 21.4. $[\alpha]_D^{25} = -16.5$ (c 0.75, $CHCl_3$). MS (ESI): 420 $[M + H]^+$. HRMS (ESI): m/z calcd for $C_{25}H_{26}NO_3S$ 420.1633, found 420.1642. Data for **syn10a**. Gummy liquid. IR (KBr): 3351, 2927, 1719, 1611, 1334, 1051 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6 (d, J = 8.3 Hz,

2H), 7.3−7.1 (m, 10H), 7.1−7.0 (m, 2H), 6.5 (d, J = 11.5 Hz, 1H), 5.6 (dd, J = 11.5, 8.7 Hz, 1H), 5.1 (dd, J = 12.5 Hz, 1H), 4.9 (dd, J = 12.5 Hz, 1H), 4.8 (dt, J = 1.5, 8.7 Hz, 1H), 3.4 (dd, J = 13.0, 9.6 Hz, 1H), 3.0 (dd, J = 13.0, 2.3 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.2, 143.6, 137.0, 135.6, 132.5, 131.0, 130.7, 130.5, 128.5, 128.2, 128.0, 127.7, 127.5, 127.0, 124.1, 67.8, 64.0, 56.9, 21.5. $[\alpha]_D^{25}$ = +25.3 (c 0.75, $CHCl_3$). MS (ESI): 420 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{25}H_{26}NO_3S$ 420.1633, found 420.1637.

Sulfilimine 10b. Similarly sulfide **8b** (278 mg, 1 mmol) was reacted with NaNCbzCl (1 g, 5 mmol) over 2.5 h period to afford the crude product, which was purified by column chromatography using 35% EtOAc/petroleum ether (v/v) to afford the sulfilimine **10b** (363 mg, 0.85 mmol) as a 1:1 mixture of *syn* and *anti* isomers in a combined yield of 85%. Data for **anti10b**. Gummy liquid. IR (KBr): 3424, 2924, 1638, 1520, 1335, 1060 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7 (d, J = 7.5 Hz, 2H), 7.4−7.1 (m, 7H), 5.5−5.3 (m, 2H), 5.2 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.8−4.7 (m, 1H), 4.7 (d, J = 6.8 Hz, 1H, OH), 3.1 (dd, J = 12.8, 10.6 Hz, 1H), 2.8 (dd, J = 12.8, 2.3 Hz, 1H), 2.4 (s, 3H), 1.9−1.7 (m, 2H), 1.4−1.1 (m, 8H), 0.9 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0, 142.0, 139.3, 133.5, 130.7, 130.1, 129.6, 128.5, 128.2, 128.1, 124.0, 66.9, 64.9, 62.9, 31.6, 29.7, 29.4, 28.9, 22.6, 21.4, 14.0. $[\alpha]_D^{25}$ = −15.0 (c 0.5, $CHCl_3$). MS (ESI): 428 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{25}H_{34}NO_3S$ 428.2259, found 428.2250. Data for **syn10b**. Gummy liquid. IR (KBr): 3424, 2924, 1638, 1520, 1335, 1060 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7 (d, J = 8.3 Hz, 2H), 7.4−7.1 (m, 7H), 5.6−5.3 (m, 2H), 5.2 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.9−4.8 (m, 1H), 3.4 (dd, J = 12.8, 9.8 Hz, 1H), 2.9 (dd, J = 12.8, 2.3 Hz, 1H), 2.4 (s, 3H), 2.1−1.9 (m, 2H), 1.4−1.1 (m, 8H), 0.9 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5, 143.3, 137.4, 134.4, 132.0, 130.6, 129.0, 128.2, 127.9, 127.6, 126.9, 67.7, 63.9, 57.7, 31.6, 29.3, 28.8, 27.8, 22.5, 21.4, 14.0. $[\alpha]_D^{25}$ = +20.0 (c 0.5, $CHCl_3$). MS (ESI): 428 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{25}H_{34}NO_3S$ 428.2259, found 428.2249.

Sulfilimine 10c. Similarly sulfide **8c** (476 mg, 1 mmol) was reacted with NaNCbzCl (1 g, 5 mmol) over a 3 h period to afford the crude product, which was purified by column chromatography using 30% EtOAc/petroleum ether (v/v) to furnish the sulfilimine **10c** (531 mg, 0.85 mmol) as a 1:1 mixture of *syn* and *anti* isomers in a combined yield of 85%. Data for **anti10c**. Gummy liquid. IR (KBr): 3276, 2924, 1566, 1504, 1346, 1113, 849 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7−7.6 (m, 6H), 7.4−7.2 (m, 13H), 5.6−5.4 (m, 2H), 5.1 (s, 2H), 4.8−4.7 (m, 1H), 4.7 (d, J = 7.0 Hz, 1H-OH), 3.7−3.5 (m, 2H), 3.0 (dd, J = 12.8, 9.8 Hz, 1H), 2.9 (dd, J = 12.8, 2.5 Hz, 1H), 2.4 (s, 3H), 2.3−2.1 (m, 2H), 1.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 143.1, 137.4, 135.7, 133.7, 130.7, 130.4, 130.2, 129.8, 128.7, 128.4, 128.2, 127.8, 126.8, 124.2, 68.0, 67.1, 63.1, 58.4, 31.2, 27.0, 21.5, 19.3. $[\alpha]_D^{25}$ = −8.0 (c 1.0, $CHCl_3$). MS (ESI): 626 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{37}H_{44}NO_4SiS$ 626.2760, found 626.2750. Data for ***syn*10c**. Gummy liquid. IR (KBr): 3276, 2924, 1566, 1504, 1346, 1113, 849 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7−7.6 (m, 6H), 7.5−7.2 (m, 13H), 5.7−5.4 (m, 2H), 5.1 (dd, J = 12.5 Hz, 1H), 5.0 (dd, J = 12.5 Hz, 1H), 4.7−4.6 (m, 1H), 3.6 (t, J = 6.6 Hz, 2H), 3.4 (dd, J = 12.5, 9.6 Hz, 1H), 2.9 (dd, J = 12.5, 2.9 Hz, 1H), 2.4 (s, 3H), 2.3 (q, J = 5.1 Hz, 2H), 1.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.4, 143.3, 137.2, 135.5, 133.3, 131.7, 131.0, 130.5, 130.0, 129.7, 128.2, 127.9, 127.7, 127.6, 126.9, 67.6, 63.8, 62.9, 57.0, 31.0, 27.1, 21.4, 19.1. $[\alpha]_D^{25}$ = +44.5 (c 1.0, $CHCl_3$). MS (ESI): 626 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{37}H_{44}NO_4SiS$ 626.2760, found 626.2748.

Sulfilimine 10d. Similarly sulfide **8d** (344 mg, 1 mmol) was reacted with NaNCbzCl (1 g, 5 mmol) over a 3 h period to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to furnish the sulfilimine **10d** (404 mg, 0.82 mmol) as a 1:1 mixture of *syn* and *anti* isomers in a combined yield of 82%. Data for **anti10d**. Gummy liquid. IR (KBr): 3446, 2928, 1636, 1258, 776 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6 (d, J = 8.3 Hz, 2H), 7.4−7.2 (m, 9H), 6.9 (d, J = 8.7 Hz, 2H), 5.7−5.6 (m, 2H), 5.1 (dd, J = 12.5 Hz, 1H), 5.0 (dd, J = 12.5 Hz, 1H), 4.9−4.8 (m, 1H), 4.3 (ABq, J = 11.3 Hz, 2H), 4.0−3.9 (m, 2H), 3.8 (s, 3H), 3.1 (dd, J = 12.8, 9.8 Hz, 1H), 3.0 (dd, J = 12.8, 2.3 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.1, 159.2, 143.0, 137.1, 132.0, 130.5, 129.8, 129.4, 129.3, 128.4, 128.2, 127.9, 127.7, 126.7, 113.8, 72.2, 67.8, 65.6, 63.0, 58.3, 55.2, 21.4. $[\alpha]_D^{25}$ = −12.0 (c 1.0, $CHCl_3$). MS (ESI): 494 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{28}H_{32}NO_5S$ 494.2001, found 494.1995. Data for **syn10d**. Gummy liquid. IR (KBr): 3446, 2928, 1636, 1258, 776 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6 (d, J = 7.6 Hz, 2H), 7.4−7.2 (m, 9H), 6.9 (d, J = 8.3 Hz, 2H), 5.7−5.6 (m, 2H), 5.1 (dd, J = 12.8 Hz, 1H), 5.0 (dd, J = 12.8 Hz, 1H), 4.8−4.7 (m, 1H), 4.4 (s, 2H), 4.0 (t, J = 4.5 Hz, 2H), 3.8 (s, 3H), 3.3 (dd, J = 12.8, 9.1 Hz, 1H), 3.0 (dd, J = 12.8, 2.3 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5, 159.4, 143.3, 137.3, 132.8, 131.7, 130.7, 130.6, 129.5, 129.3, 128.3, 128.0, 127.7, 126.8, 113.9, 72.4, 67.7, 65.8, 64.6, 57.1, 55.3, 21.5; $[\alpha]_D^{25}$ = +10.0 (c 1.0, $CHCl_3$). MS (ESI): 494 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{28}H_{32}NO_5S$ 494.2001, found 494.1992.

Sulfilimine 11a. Similarly sulfide **9a** (270 mg, 1 mmol) was reacted with NaNCbzCl (1 g, 5 mmol) over a 2.5 h period to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to furnish the sulfilimine **11a** (356 mg, 0.85 mmol) as a 1:1 mixture of *syn* and *anti* isomers in a combined yield of 85%. Data for **anti11a**. Gummy liquid. IR (KBr): 3351, 2927, 1719, 1611, 1334, 1051 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.7 (d, J = 8.3 Hz, 2H), 7.4−7.2 (m, 12H), 6.7 (d, J = 15.9 Hz, 1H), 6.1 (dd, J = 15.9, 6.0 Hz, 1H), 5.1 (s, 2H), 4.8 (q, J = 6.0 Hz), 3.2−3.1 (m, 2H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 143.3, 137.2, 136.1, 131.8, 131.4, 130.7, 128.6, 128.3, 128.1, 128.0, 127.7, 126.8, 126.6, 124.0, 68.0, 66.9, 58.9, 21.5. $[\alpha]_D^{25}$ = −19.5 (c 1.0, $CHCl_3$). MS (ESI): 420 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{25}H_{26}NO_3S$ 420.1633, found 420.1645; Data for **syn11a**. Gummy liquid. IR (KBr): 3351, 2927, 1719, 1611, 1334, 1051 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7 (d, J = 7.6 Hz, 2H), 7.4−7.2 (m, 12H), 6.7 (d, J = 15.9 Hz, 1H), 6.1 (dd, J = 15.9, 6.0 Hz, 1H), 5.1 (s, 2H), 4.7−4.6 (m, 1H), 3.4 (dd, J = 12.8, 9.0 Hz, 1H), 3.1 (dd, J = 12.8, 3.0 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5, 143.4, 137.1, 135.9, 131.9, 131.5, 130.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.6, 126.8, 126.6, 68.2, 67.7, 57.3, 21.4. $[\alpha]_D^{25}$ = +64.0 (c 1.0, $CHCl_3$). MS (ESI): 420 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{25}H_{26}NO_3S$ 420.1633, found 420.1643.

Sulfilimine 11b. Similarly, sulfide **9b** (278 mg, 1 mmol) was reacted with NaNCbzCl (1 g, 5 mmol) over a 2 h period to afford the crude product, which was purified by column chromatography using 35% EtOAc/petroleum ether (v/v) to furnish the sulfilimine **11b** (350 mg, 0.82 mmol) as a 1:1 mixture of *syn* and *anti* isomers in a combined yield of 82%; Data for ***anti*11b**. IR (KBr): 3424, 2924, 1638, 1520, 1335, 1060 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.7 (d, J = 8.1 Hz, 2H), 7.5−7.1 (m, 7H), 5.8−5.6 (m, 1H), 5.4 (dd, J = 15.4, 5.9 Hz,. 1H), 5.1 (s, 2H), 4.7 (d, J = 5.9 Hz, 1H-OH), 4.5−4.4 (q, J = 6.6 Hz, 1H), 3.1−2.9 (m, 2H), 2.4 (s, 3H), 2.0 (q, J = 6.6 Hz, 2H), 1.4−1.1 (m, 8H), 0.9 (t, J = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.6, 143.2, 134.2, 130.6, 128.7, 128.5, 128.4, 128.3, 128.0, 127.7, 126.8, 68.0, 66.8, 59.1, 32.1, 31.6, 28.8, 28.7, 22.5, 21.4, 14.0. $[\alpha]_D^{25}$ = −35.0 (c 0.6, $CHCl_3$). MS (ESI): 428 [M + H]$^+$. HRMS (ESI): m/z calcd for $C_{25}H_{34}NO_3S$ 428.2259, found 428.2252. Data for **syn11b**. Gummy liquid. IR (KBr): 3424, 2924, 1638, 1520, 1335, 1060 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.6 (d, J = 8.3 Hz, 2H), 7.3−7.1 (m, 7H), 5.7−5.6 (m, 1H), 5.3 (dd, J = 15.1, 6.0 Hz, 1H), 5.1 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.4−4.3 (m, 1H), 3.3 (dd, J = 12.8, 9.1 Hz, 1H), 2.9 (dd, J = 12.8, 3.0 Hz, 1H), 2.4 (s, 3H), 1.9 (q, J = 6.8 Hz, 2H), 1.4−1.1 (m, 8H), 0.9 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1, 143.4, 134.5, 130.7, 129.0, 128.6, 128.5, 128.3, 128.0, 127.7, 127.0, 68.5, 67.8, 57.3, 32.1, 31.6, 29.7, 28.8, 22.6, 21.5, 14.1. $[\alpha]_D^{25}$ = +85.0 (c 1.2, $CHCl_3$). MS (ESI):

428 $[M + H]^+$. HRMS (ESI): *m/z* calcd for $C_{25}H_{34}NO_3S$ 428.2259, found 428.2255.

Sulfilimine 11c. Similarly, sulfide **9c** (476 mg, 1 mmol) was reacted with NaNCbzCl (1 g, 5 mmol) over a 3 h period to afford the crude product, which was purified by column chromatography using 30% EtOAc/petroleum ether (v/v) to furnish the sulfilimine **11c** (512 mg, 0.82 mmol) as a 1:1 mixture of *syn* and *anti* isomers in a combined yield of 82%. Data for **anti11c**. Gummy liquid. IR (KBr): 3276, 2924, 1566, 1504, 1346, 1113, 849 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.7−7.6 (m, 6H), 7.5−7.2 (m, 13H), 5.8−5.6 (m, 1H), 5.4 (dd, J = 15.6, 6.3 Hz, 1H), 5.1 (s, 2H), 4.7 (d, J = 7.0 Hz, 1H-OH), 4.5 (q, J = 6.3 Hz, 1H), 3.7 (t, J = 6.3 Hz, 2H), 3.0 (d, J = 6.3 Hz, 2H), 2.4 (s, 3H), 2.3 (q, J = 7.0 Hz, 2H). 1.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 142.9, 137.0, 135.3, 133.6, 130.7, 130.4, 129.9, 129.4, 128.5, 128.3, 128.1, 127.8, 127.5, 126.6, 67.7, 66.4, 63.0, 58.8, 35.3, 26.7, 21.2, 19.0. $[\alpha]_D^{25} = -9.5$ (*c* 1.0, $CHCl_3$). MS (ESI): 626 $[M + H]^+$. HRMS (ESI): *m/z* calcd for $C_{37}H_{44}NO_4SiS$ 626.2760, found 626.2755. Data for **syn11c**. Gummy liquid. IR (KBr): 3276, 2924, 1566, 1504, 1346, 1113, 849 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.8−7.6 (m, 6H), 7.5−7.2 (m, 13H), 5.8−5.7 (m, 1H), 5.5 (dd, J = 15.1, 6.0 Hz, 1H), 5.1 (dd, J = 12.8, 1H), 5.0 (dd, J = 12.8, 1H), 4.5−4.4 (m, 1H), 3.7 (t, J = 6.0 Hz, 2H), 3.3 (dd, J = 12.8, 9.8 Hz, 1H), 3.0 (dd, J = 12.8, 1.5 Hz, 1H), 2.4 (s, 3H), 2.3 (q, J = 6.0 Hz, 2H), 1.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.4, 143.5, 137.2, 135.5, 133.8, 131.6, 131.1, 130.6, 129.6, 128.5, 128.3, 128.0, 127.6, 126.9, 68.4, 67.8, 63.1, 57.2, 35.5, 26.8, 21.5, 19.2. $[\alpha]_D^{25} = +38.0$ (*c* 1.5, $CHCl_3$). MS (ESI): 626 $[M + H]^+$. HRMS (ESI): *m/z* calcd for $C_{37}H_{44}NO_4SiS$ 626.2760, found 626.2753.

Sulfilimine 11d. Silmilarly, sulfide **9d** (344 mg, 1 mmol) was reacted with NaNCbzCl (1 g, 5 mmol) over a 2.5 h period to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to furnish the sulfilimine **11d** (394 mg, 0.8 mmol) as a 1:1 mixture of *syn* and *anti* isomers in a combined yield of 80%. Data for **anti11d**. Gummy liquid. IR (KBr): 3446, 2928, 1636, 1258, 776 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.7 (d, J = 8.3 Hz, 2H), 7.5−7.2 (m, 9H), 6.8 (d, J = 9.1 Hz, 2H), 5.9 (td, J = 5.3, 15.1 Hz, 1H), 5.7 (dd, J = 15.1, 5.3 Hz, 1H), 5.1 (s, 2H), 4.6 (q, J = 6.0 Hz, 1H), 4.4 (s, 2H), 3.9 (d, J = 5.3 Hz, 2H), 3.8 (s, 3H), 3.1−3.0 (m, 2H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.8, 160.2, 137.1, 136.0, 132.2, 130.8, 130.7, 129.3, 128.6, 128.3, 128.1, 127.7, 126.7, 113.8, 72.1, 69.3, 68.0, 66.3, 58.6, 55.3, 21.5. $[\alpha]_D^{25} = -10.0$ (*c* 0.5, $CHCl_3$). MS (ESI): 494 $[M + H]^+$. HRMS (ESI): *m/z* calcd for $C_{28}H_{32}NO_5S$ 494.2001, found 494.1987. Data for **syn11d**. Gummy liquid. IR (KBr): 3446, 2928, 1636, 1258, 776 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.7 (d, J = 8.3 Hz, 2H), 7.4−7.1 (m, 9H), 6.8 (d, J = 8.3 Hz, 2H), 5.9 (td, J = 5.3, 15.1 Hz, 1H), 5.7 (dd, J = 15.1, 5.3 Hz, 1H), 5.1 (dd, J = 12.8 Hz, 1H), 5.0 (dd, J = 12.8 Hz, 1H), 4.5−4.4 (m, 1H), 4.4 (s, 2H), 3.9 (d, J = 4.5 Hz, 2H), 3.8 (s, 3H), 3.3 (dd, J = 12.8, 9.1 Hz, 1H), 3.0 (dd, J = 12.8, 3.0 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5, 160.3, 143.5, 139.8, 137.2, 131.3, 130.7, 130.1, 129.6, 129.4, 128.3, 128.0, 127.7, 126.8, 113.8, 72.2, 69.3, 67.9, 67.8, 60.0, 55.3, 21.5; $[\alpha]_D^{25} = +13.0$ (*c* 0.5, $CHCl_3$). MS (ESI): 494 $[M + H]^+$. HRMS (ESI): *m/z* calcd for $C_{28}H_{32}NO_5S$ 494.2001, found 494.1990.

General Procedure for the Preparation of Bromo Carbamates. To a solution of sulfilimine (1 equiv) in toluene (0.25 M) was added water (1.5 equiv) followed by freshly recrystallized NBS (1.2 equiv) and the mixture stirred at rt for 30 min. The reaction mixture was then diluted with EtOAc, washed with saturated aq $NaHCO_3$, water, and brine, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to afford the crude product, which was purified by column chromatography to afford bromo carbamate.

Bromo Carbamate *syn*12. Following the general procedure, sulfilimine **anti10a** (257 mg, 0.5 mmol) afforded the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to afford bromo carbamate ***syn*12** (195 mg, 0.38 mmol) in 76% yield as a white solid. Mp:130−132 °C. IR (KBr): 3453, 2925, 1742, 1539, 1239, 950 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.5 (d, J = 8.1 Hz, 2H), 7.4−7.2 (m, 12H), 5.8 (s, 1H), 5.4 (d, J = 10.0 Hz, 1H), 5.1 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.7−4.6 (br s, 1H-OH), 4.4 (m, 1H), 3.8 (dt, J = 10.2, 2.1 Hz, 1H), 3.0−2.9 (m, 2H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.1, 142.3, 138.6, 136.0, 130.2, 128.9, 128.8, 128.5, 128.3, 128.1, 127.9, 124.0, 70.7, 67.1, 60.1, 58.8, 55.3, 21.5. $[\alpha]_D^{25} = +50.0$ (*c* 0.8, $CHCl_3$). MS (ESI): 538 $[M + Na]^+$. HRMS (ESI): *m/z* calcd for $C_{25}H_{26}NO_4NaSBr$ 538.0663, found 538.0651.

Bromo Carbamate *anti*12. Similarly, sulfilimine **syn10a** (257 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to furnish bromo carbamate **anti12** (200 mg, 0.39 mmol) in 78% yield as a white solid. Mp: 174−176 °C. IR (KBr): 3453, 2925, 1742, 1539, 1239, 950 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.5−7.2 (m, 14H), 5.7 (s, 1H), 5.1 (d, J = 10.4 Hz, 1H), 5.1 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.8 (d, J = 3.2 Hz, OH), 4.2 (t, J = 9.6 Hz, 1H), 3.9 (dt, J = 2.5, 10.2 Hz, 1H), 3.2 (dd, J = 14.0, 9.4 Hz, 1H), 2.7 (dd, J = 14.0, 1.1 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 156.1, 141.9, 140.5, 139.4, 137.1, 129.8, 128.3, 128.2, 127.9, 127.5, 127.1, 123.6, 65.5, 65.1, 61.9, 60.8, 56.4, 20.8. $[\alpha]_D^{25} = -10.0$ (*c* 0.4, $CHCl_3$). MS (ESI): 538 $[M + Na]^+$. HRMS (ESI): *m/z* calcd for $C_{25}H_{26}NO_4NaSBr$ 538.0663, found 538.0655.

Bromo Carbamate *syn*13. Similarly sulfilimine ***anti*11a** (210 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to furnish to afford bromo carbamate ***syn*13** (200 mg, 0.39 mmol) in 78% yield as a white solid. Mp: 80−82 °C. IR (KBr): 3453, 2925, 1742, 1539, 1239, 950 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.5−7.2 (m, 14H), 6.3 (d, J = 8.9 Hz, 1H), 5.2 (m, 3H), 4.5 (d, J = 3.4 Hz, OH), 4.4−4.2 (m, 2H), 3.1 (dd, J = 13.2, 3.0 Hz, 1H), 2.8 (dd, J = 13.2, 4.9 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4, 142.2, 139.3, 135.5, 130.2, 129.0, 128.5, 128.3, 128.1, 127.0, 124.0, 67.3, 65.8, 61.4, 60.3, 59.5, 21.6. $[\alpha]_D^{25} = +25.0$ (*c* 0.4, $CHCl_3$). MS (ESI): 538 $[M + Na]^+$. HRMS (ESI): *m/z* calcd for $C_{25}H_{26}NO_4NaSBr$ 538.0663, found 538.0652.

Bromo Carbamate *anti*13. Similarly, sulfilimine **syn11a** (210 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to furnish bromo carbamate **anti13** (206 mg, 0.4 mmol) in 80% yield as a white solid. Mp: 74−76 °C. IR (KBr): 3453, 2925, 1742, 1539, 1239, 950 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.5−7.2 (m, 14H), 5.9 (d, J = 8.8 Hz, 1H), 5.4 (t, J = 9.1 Hz, 1H), 5.1 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.6 (t, J = 7.2 Hz, 1H), 4.1 (dd, J = 9.1, 7.2 Hz, 1H), 3.2−3.0 (m, 2H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.3, 142.0, 138.4, 137.2, 136.1, 130.1, 128.5, 128.2, 128.1, 127.9, 124.1, 68.1, 67.1, 61.3, 58.8, 55.3, 21.4. $[\alpha]_D^{25} = -6.0$ (*c* 0.5, $CHCl_3$). MS (ESI): 538 $[M + Na]^+$. HRMS (ESI): *m/z* calcd for $C_{25}H_{26}NO_4NaSBr$ 538.0663, found 538.0658.

Bromo Carbamate *syn*14. Similarly sulfilimine ***anti*10b** (214 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 35% EtOAc/petroleum ether (v/v) to furnish bromo carbamate **syn14** (199 mg, 0.38 mmol) in 76% yield as a white solid. Mp: 122−124 °C. IR (KBr): 3383, 2960, 1678, 1518, 1284 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.4 (d, J = 7.6 Hz, 2H), 7.4−7.2 (m, 7H), 5.2−5.0 (m, 3H), 4.7 (t, J = 7.6 Hz, 1H), 4.5−4.4 (br s, OH), 4.4−4.3 (m, 1H), 3.6 (t, J = 9.8 Hz, 1H), 3.0−2.8 (m, 2H), 2.4 (s, 3H), 1.9−1.6 (m, 3H), 1.6−1.1 (m, 7H), 0.9 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4, 142.1, 140.4, 136.1, 130.2, 128.5, 128.3, 128.0, 124.0, 70.6, 67.2, 58.9, 58.2, 57.7, 36.3, 31.5, 29.6, 28.5, 22.4, 21.4, 13.9. $[\alpha]_D^{25} = +35$ (*c* 0.6, $CHCl_3$). MS (ESI): 546 $[M + Na]^+$. HRMS (ESI): *m/z* calcd for $C_{25}H_{34}NO_4NaSBr$ 546.1289, found 546.1281.

Bromo Carbamate *anti*14. Similarly, sulfilimine **syn10b** (214 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford

the crude product, which was purified by column chromatography using 35% EtOAc/petroleum ether (v/v) to furnish bromo carbamate **anti14** (209 mg, 0.4 mmol) in 80% yield as a white solid. Mp: 158−160 °C. IR (KBr) 3383, 2960, 1678, 1518, 1284 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.4 (d, J = 8.3 Hz, 2H), 7.4−7.2 (m, 7H), 5.1 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.8 (d, J = 9.8 Hz, 1H), 4.7−4.6 (m, 2H, H + OH), 4.0 (t, J = 9.8 Hz, 1H), 3.7 (t, J = 9.8 Hz, 1H), 3.1 (dd, J = 13.6, 9.1 Hz, 1H), 2.7 (d, J = 13.6 Hz, 1H), 2.4 (s, 3H), 1.9−1.7 (m, 2H), 1.6−1.1 (m, 8H), 0.9 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4, 141.7, 138.8, 136.1, 130.1, 128.5, 128.3, 128.0, 124.0, 68.7, 67.2, 58.0, 57.97, 57.7, 36.3, 31.5, 29.6, 28.5, 27.5, 22.5, 21.4, 13.9. $[\alpha]_D^{25}$ = −12.0 (c 0.3, $CHCl_3$). MS (ESI): 546 $[M + Na]^+$. HRMS (ESI): m/z calcd for $C_{25}H_{34}NO_4NaSBr$ 546.1289, found 546.1282.

Bromo Carbamate *syn*15. Similarly, sulfilimine ***anti*11b** (214 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 35% EtOAc/petroleum ether (v/v) to furnish bromo carbamate **syn15** (214 mg, 0.41 mmol) in 82% yield as a white solid. Mp: 145−147 °C. IR (KBr): 3383, 2960, 1678, 1518, 1284 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.5 (d, J = 8.1 Hz, 2H), 7.4−7.2 (m, 7H), 5.4 (d, J = 10.0 Hz, 1H), 5.1 (m, 3H), 4.4−4.3 (br s, OH), 4.1 (dt, J = 2.3, 9.4 Hz, 1H), 3.9 (t, J = 10.0 Hz, 1H), 2.9 (dd, J = 13.2, 9.8 Hz, 1H), 2.8 (dd, J = 13.2, 1.5 Hz, 1H), 2.4 (s, 3H), 2.0−1.5 (m, 3H), 1.5−1.1 (m, 7H), 0.9 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2, 142.2, 139.9, 130.2, 128.5, 128.1, 127.8, 124.0, 123.8, 68.2, 67.0, 60.1, 59.7, 55.5, 34.4, 31.6, 28.6, 27.3, 22.5, 21.4, 14.0. $[\alpha]_D^{25}$ = +40 (c 0.75, $CHCl_3$). MS (ESI): 546 $[M + Na]^+$. HRMS (ESI): m/z calcd for $C_{25}H_{34}NO_4NaSBr$ 546.1289, found 546.1277.

Bromo Carbamate *anti*15. Similarly, sulfilimine **syn11b** (214 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 35% EtOAc/petroleum ether (v/v) to furnish bromo carbamate ***anti*15** (209 mg, 0.4 mmol) as a 3:1 mixture of inseparable isomers in a combined yield of 80% yield. White solid. ^1H NMR of major isomer (300 MHz, $CDCl_3$): δ 7.5 (d, J = 8.1 Hz, 2H), 7.4−7.2 (m, 7H), 5.4 (d, J = 10.2 Hz, 1H), 5.2−4.8 (m, 4H), 4.0 (dt, J = 3.0, 9.4 Hz, 1H), 3.6 (t, J = 9.6 Hz, 1H), 3.2−3.1 (m, 1H), 2.6 (dd, J = 13.6, 1.5 Hz, 1H), 2.4 (s, 3H), 1.9−1.5 (m, 3H), 1.5−1.1 (m, 7H), 0.9 (t, J = 7.0 Hz, 3H). ^1H NMR of minor isomer (300 MHz, $CDCl_3$): δ 7.4 (d, J = 8.1 Hz, 2H), 7.4−7.2 (m, 7H), 5.2−4.8 (m, 4H), 4.4−4.1 (m, 3H), 3.2−3.1 (m, 1H), 2.8 (dd, J = 0.9, 13.2 Hz, 1H) 2.4 (s, 3H), 1.9−1.5 (m, 3H), 1.5−1.1 (m, 7H), 0.9 (t, J = 7.0 Hz, 3H). MS (ESI): 546 $[M + Na]^+$.

Bromo Carbamate *syn*16. Similarly, sulfilimine **anti10c** (313 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 30% EtOAc/petroleum ether (v/v) to furnish bromo carbamate **syn16** (274 mg, 0.38 mmol) in 76% yield as a gummy liquid. IR (KBr): 3429, 2925, 2859, 1741, 1606, 1108 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.7−7.6 (m, 6H), 7.5−7.2 (m, 13H), 5.1−5.0 (m, 3H), 4.5 (t, J = 6.8 Hz, 1H), 4.4−4.3 (m, 1H), 3.8 (t, J = 5.3 Hz, 2H), 3.6 (t, J = 9.8 Hz, 1H), 2.9 (d, J = 5.3 Hz, 2H), 2.4 (s, 3H), 2.1−1.9 (m, 2H), 1.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.2, 142.4, 140.4, 135.73, 135.66, 133.8, 130.4, 129.8, 128.7, 128.5, 128.2, 127.8, 124.1, 70.7, 67.4, 67.1, 61.1, 58.9, 54.2, 39.1, 26.9, 21.6, 19.3. $[\alpha]_D^{25}$ = +24.0 (c 0.5, $CHCl_3$). MS (ESI): 722 $[M + H]^+$. HRMS (ESI): m/z calcd for $C_{37}H_{44}NO_5NaSiSBr$ 744.1790, found 744.1781.

Bromo Carbamate *anti*16. Similarly sulfilimine **syn10c** (313 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 30% EtOAc/petroleum ether (v/v) to furnish bromo carbamate **anti16** (270 mg, 0.38 mmol) in 75% yield as a white solid. Mp: 108−110 °C. IR (KBr): 3429, 2925, 2859, 1741, 1606, 1108 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 7.7−7.6 (m, 6H), 7.5−7.2 (m, 13H), 5.1 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.7 (d, J = 10.3 Hz, 1H), 4.4−4.3 (m, 2H, 1H + OH), 4.0 (t, J = 9.6 Hz, 1H), 3.9−3.6 (m, 3H), 3.2 (dd, J = 14.0, 9.6 Hz, 1H), 2.6 (d, J = 14.0 Hz, 1H), 2.5 (s, 3H), 2.1−1.9 (m, 2H), 1.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4, 141.8, 139.0, 136.1, 135.7, 133.5, 130.3, 129.8, 128.7, 128.5, 128.2, 127.8, 124.1, 68.4, 67.3, 61.1, 58.9, 58.3, 54.7, 39.1, 26.9, 21.6, 19.3. $[\alpha]_D^{25}$ = −11.0 (c 0.5, $CHCl_3$). MS (ESI): 722 $[M + H]^+$. HRMS (ESI): m/z calcd for $C_{37}H_{44}NO_5NaSiSBr$ 744.1790, found 744.1787.

Bromo Carbamate *syn*17. Similarly, sulfilimine **anti11c** (313 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 30% EtOAc/petroleum ether (v/v) to furnish bromo carbamate ***syn*17** (306 mg, 0.43 mmol) in 85% yield as a gummy liquid. IR (KBr): 3429, 2925, 2859, 1741, 1606, 1108 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.7−7.6 (m, 6H), 7.5−7.2 (m, 13H), 5.3 (d, J = 10.1 Hz, 1H), 5.0 (m, 3H), 4.5−4.3 (m, H + OH), 3.9−3.7 (m, 3H), 2.9 (dd, J = 13.2, 9.8 Hz, 1H), 2.7 (dd, J = 13.2, 2.4 Hz, 1H), 2.4 (s, 3H), 1.9−1.7 (m, 2H), 1.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4, 142.7, 142.2, 140.4, 135.7, 135.6, 133.6, 130.4, 129.8, 128.7, 128.3, 127.8, 124.0, 68.4, 67.3, 67.1, 61.5, 60.2, 51.7, 37.4, 27.0, 21.6, 19.3. $[\alpha]_D^{25}$ = +45 (c 1.0, $CHCl_3$). MS (ESI): 722 $[M + H]^+$. HRMS (ESI): m/z calcd for $C_{37}H_{44}NO_5NaSiSBr$ 744.1790, found 744.1785.

Bromo Carbamate *anti*17. Similarly, sulfilimine ***syn*11c** (313 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 30% EtOAc/petroleum ether (v/v) to furnish bromo carbamate ***anti*17** (296 mg, 0.41 mmol) as a 6:1 mixture of inseparable isomers in a combined yield of 82% yield as a gummy liquid. ^1H NMR of major isomer (300 MHz, $CDCl_3$): δ 7.6−7.5 (m, 6H), 7.5−7.2 (m, 13H), 5.4 (d, J = 9.8 Hz, 1H), 5.2−5.0 (m, 2H), 5.0−4.9 (br s, OH), 4.7 (d, J = 9.1 Hz, 1H), 4.3 (t, J = 9.1 Hz, 1H), 3.9−3.7 (m, 2H), 3.6 (t, J = 9.1 Hz, 1H), 3.2−3.0 (m, 1H), 2.5 (d, J = 12.8 Hz, 1H), 2.4 (s, 3H), 2.3−2.1 (m, 1H), 1.9−1.7 (m, 1H), 1.0 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 141.9, 138.4, 135.6, 135.5, 133.4, 130.2, 129.6, 128.5, 128.2, 127.9, 127.6, 124.1, 67.2, 65.9, 61.4, 59.7, 58.3, 52.0, 37.4, 26.8, 21.4, 19.2. ^1H NMR of minor isomer (300 MHz, $CDCl_3$): δ 7.6−7.5 (m, 6H), 7.5−7.2 (m, 13H), 5.5 (d, J = 11.3 Hz, 1H), 5.2−5.0 (m, 2H), 4.6 (d, J = 9.1 Hz, 1H), 4.5−4.4 (m, 1H), 4.2−4.0 (m, 1H), 3.9−3.7 (m, 2H), 3.2−3.0 (m, 2H), 2.7 (dd, J = 13.6, 2.3 Hz, 1H), 2.4 (s, 6H), 2.3−2.1 (m, 1H), 1.9−1.7 (m, 1H), 1.0 (s, 9H). MS (ESI): 722 $[M + H]^+$.

Bromo Carbamate *syn*18. Similarly, sulfilimine **anti10d** (247 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to furnish bromo carbamate **syn18** (218 mg, 0.37 mmol) in 74% yield as a white solid. Mp: 142−144 °C. IR (neat): 3416, 2924, 2854, 1705, 1404 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.5 (d, J = 8.1 Hz, 2H), 7.4−7.1 (m, 9H), 6.9 (d, J = 8.5 Hz, 2H), 5.2−5.0 (m, 3H), 4.8 (t, J = 6.4 Hz, 1H), 4.5 (br s, 1H), 4.4−4.3 (m, 3H), 4.0 (t, J = 9.6 Hz, 1H), 3.8 (s, 3H), 3.7−3.5 (m, 2H), 3.0−2.9 (m, 2H), 2.4 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 156.0, 142.2, 133.1, 132.3, 130.1, 129.5, 129.3, 128.5, 128.2, 128.0, 123.9, 113.7, 72.8, 70.6, 70.2, 67.3, 58.8, 55.2, 54.8, 52.3, 21.5. $[\alpha]_D^{25}$ = +22.0 (c 0.4, $CHCl_3$). MS (ESI): 612 $[M + Na]^+$. HRMS (ESI): m/z calcd for $C_{28}H_{32}NO_6NaSBr$ 612.1031, found 612.1032.

Bromo Carbamate *anti*18. Similarly, sulfilimine ***syn*10d** (247 mg, 0.5 mmol) was reacted with NBS (106 mg, 0.6 mmol) to afford the crude product, which was purified by column chromatography using 40% EtOAc/petroleum ether (v/v) to furnish bromo carbamate ***anti*18** (236 mg, 0.4 mmol) in 80% yield as a white solid. Mp: 181−183 °C. IR (neat): 3416, 2924, 2854, 1705, 1404 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.4 (d, J = 8.1 Hz, 2H), 7.4−7.2 (m, 9H), 6.9 (d, J = 8.7 Hz, 2H), 5.1 (dd, J = 12.1 Hz, 1H), 5.0 (dd, J = 12.1 Hz, 1H), 4.9 (d, J = 8.9 Hz, 1H), 4.8 (t, J = 7.0 Hz, 1H), 4.4 (s, 2H), 4.2−4.0 (m, 2H), 3.8 (s, 3H), 3.7−3.5 (m, 2H), 3.1 (dd, J = 13.8, 8.7 Hz, 1H), 2.7 (dd, J = 13.8, 1.5 Hz, 1H), 2.4 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.1, 156.0, 141.6, 138.8, 136.1, 130.1, 129.6, 129.4, 128.0, 128.4, 127.9, 124.0, 113.7, 72.8, 70.8, 67.0, 60.5, 60.4, 55.2, 54.6, 53.3, 21.4. $[\alpha]_D^{25}$ = −8.0 (c 0.4,

$CHCl_3$). MS (ESI): 612 $[M + Na]^+$. HRMS (ESI): *m*/*z* calcd for $C_{28}H_{32}NO_6NaSBr$ 612.1031, found 612.1035.

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Supporting Information Available: Experimental details for the preparation of ynones **4**, sulfide **7**, *cis*-alkenes **8**, *trans*-alkenes **9**, debromination products from ***anti*13**, ***syn*15**, and sulfones from bromo carbamates including data and X-ray structure of ***anti*13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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