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Chiral Aminated α-Methylenebenzocycloalkenes from *o*-Bromoaryl Aldehydes and Ketones

Juan Alberto Sirvent,[a] Francisco Foubelo,*[a] and Miguel Yus*[a]

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Chiral *tert*-butylsulfinyl imines **3**, which are easily prepared from the corresponding bromo carbonyl compounds **1** and *tert*-butanesulfinamide (**2**), undergo a diastereoselective allylation by using indium metal and allyl bromide to give the corresponding homoallyl sulfinylamines **4**. Treatment of compounds **4** with a catalytic amount of palladium acetate and triphenylphosphane gives *exo*-methylene-substituted-sulfinylamino)benzocycloalkenes **5** (five- to seven-membered rings) that are easily deprotected with hydrochloric acid to give chiral primary amines **6**.

Introduction

Chiral sulfinyl imines have become important starting materials for the syntheses of different enantiomerically pure nitrogen-containing compounds through enantio- and diastereoselective additions to prochiral C–N double bonds.[1] Thus, the syntheses of a wide range of chiral amine derivatives can be achieved by using this methodology.[2] In the last few years, we have studied the indium-promoted diastereoselective allylation of *N*-*tert*-butylsulfinyl aldimines[3] and ketimines[4] as well as its application to the syntheses of different natural alkaloids such as (+)-isosolenopsin,[3f] (–)- and (+)-aphanorphine,[3h] (+)-coniine,[3k] (–)-pelleterine,[3k] and 5-*epi*-(+)-cermizine C[3k] as well as to the formal syntheses of (–)-cermizine C, (+)-lasubine II, (+)-allosedridine,[3k] and tetraponerines T3 and T4.[3l] Herein, we describe the indium-promoted allylation[5] of chiral sulfinyl imines that are derived from 2-bromoaryl- or heteroaryl-substituted aldehydes and ketones followed by a cyclization under Heck-type conditions to afford chiral protected aminated α-methylene-benzocycloalkenes.

Results and Discussion

The starting *tert*-butylsulfinyl imines **3** were easily prepared[6] in tetrahydrofuran (THF) by the reaction of brominated carbonyl compound **1** with commercially available enantiomerically pure (*S*)-*tert*-butanesulfinamide (**2**) in the presence of titanium tetraethoxide at 23 and 76 °C for aldehydes and ketones, respectively (see Scheme 1). The reaction worked well with results independent of the electronic effects of the aromatic ring (compare compounds **3a**–**3d**), and the reaction worked efficiently for both electron-poor and electron-rich heterocycles (compare compounds **3e** and **3f**). In all cases, the *E* configuration was obtained after purification by column chromatography with the exception of compound **3j**, for which an *E*/*Z* mixture of 3:2 was isolated.

Once compounds **3** were prepared, we proceeded with their allylation under standard conditions,[3a] that is, treatment with allyl bromide in the presence of indium metal at 65 °C. Thus, the corresponding products **4** were obtained with almost total diastereoselectivity in most cases, and the attack of the intermediate allylindium occurred on the *Re* face of the imine with the *S* configuration at the sulfur atom (see Scheme 2). We observed this behavior as well with other types of indium-promoted allylations of sulfinyl imides. The diastereomeric ratios were easily determined by ^{1}H NMR analysis of the crude reaction mixtures through the comparison of the integrals of the *t*Bu group and the N–H for each of the diastereoisomers. (The largest chemical shift difference was always observed for the diastereomeric signals of the N–H). In all cases, the yields were good with the exception of compound **4j**. We do not have any explanation for this, but the congestion around the C–N double bond could play an important role. Importantly, the diastereomeric ratio for compound **4j** was in agreement with the *E*/*Z* isomeric ratio of the starting imine **3j**.

In fact, a one-pot transformation[3f,3j] from **1**→**4** was also possible with comparable yields, but the process was

[a] Departamento de Química Orgánica, Facultad de Ciencias and Instituto de Síntesis Orgánica (ISO), Universidad de Alicante, Apdo. 99, 03080 Alicante, Spain
Fax: +34-965903549
E-mail: foubelo@ua.es; yus@ua.es
Homepage: http://iso.ua.es/es/personal/director-iso.html

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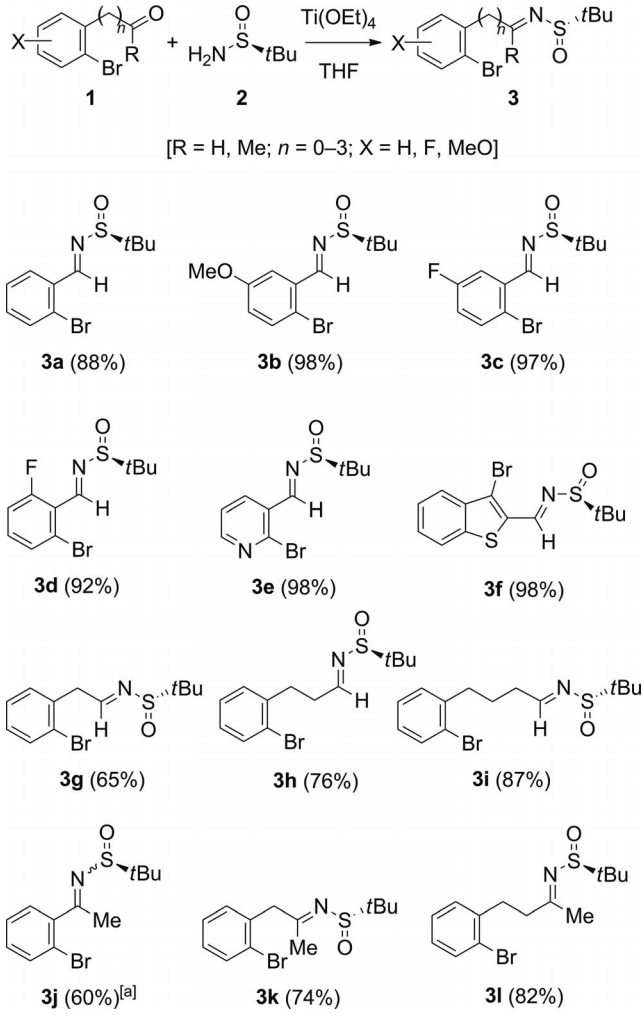
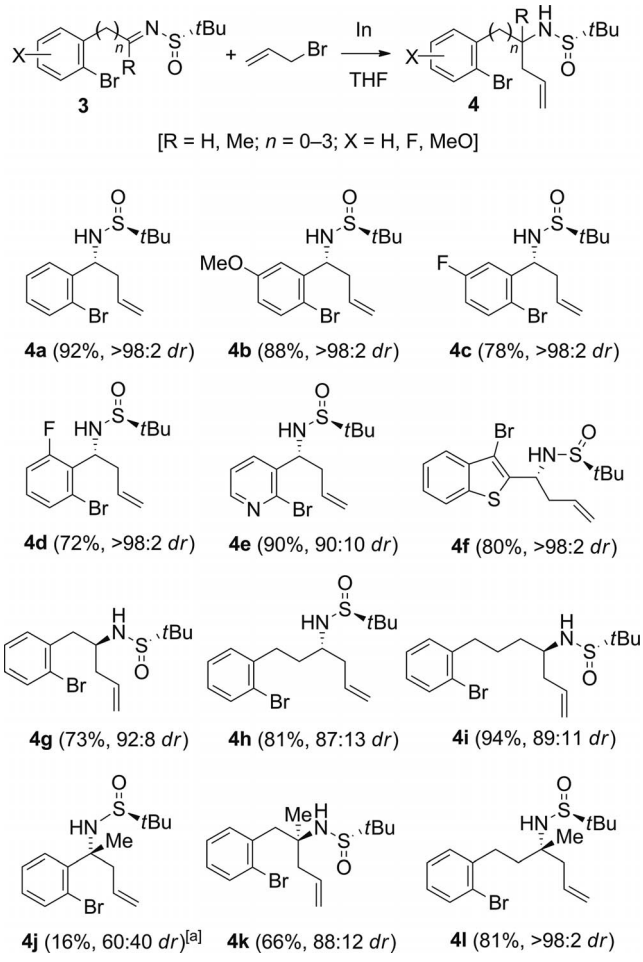


Scheme 1. Preparation of (*S*)-sulfinyl imines **3**. [a] A mixture (*E*/*Z*, 3:2) was obtained.



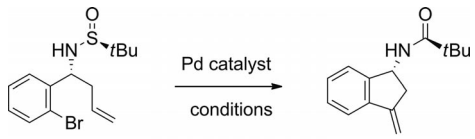
Scheme 2. Preparation of homoallylamine derivatives **4**. [a] A diastereomeric mixture (3:2) was obtained.

not as clean as the two-step process, and the purification of the corresponding product **4** was more difficult.

In the last part of this study, we carried out a Heck-type reaction of compounds **4** under palladium catalysis. For a model reaction, we optimized the cyclization of compound **4a** by performing the reaction under different conditions (see Table 1). Using different loadings of palladium acetate at around 80 °C, we realized that the best combination was with THF and tetrabutylammonium acetate (TBAA) under ligand-free conditions (see Table 1, Entries 1–5). Triphenylphosphane was effective as an additive, and after investigating different solvents and bases (see Table 1, Entries 6–13), we found that complete conversion was achieved by using triphenylphosphane as the additive and TBAA as the base with a reasonable catalyst loading at 90 °C for 20 h (see Table 1, Entry 13). Different additives such as titanium tetraethoxide and iron trichloride gave worse results (see Table 1, Entries 14–16). Finally, the use of palladium(0) catalysts such as $Pd(PPh_3)_4$ and $Pd(dba)_3$ without an additive (see Table 1, Entry 17) or with a different additives (see Table 1, Entries 18–20) did not improve the previous best results.

Once the best conditions to perform the Heck cyclization were established (see Table 1, Entry 13), we applied the procedure to all compounds **4**, and the expected methylene carbocycles **5** were obtained in variable yields (see Scheme 3). Starting from both aldehyde (to give **5a**–**5h**) and ketone (to give **5j**–**5l**) derivatives, the reaction successfully provided five- (i.e., **5a**–**5f** and **5j**), six- (i.e., **5g** and **5k**), and seven-membered rings (i.e., **5h** and **5l**), but it failed to provide eight-membered rings (i.e., **5i**). Importantly, in the case of compound **5b′**, which contained an electron-donating substituent on the aromatic ring, the best result was obtained with 14% loading of the palladium catalyst, otherwise the reaction did not progress. Surprisingly, the only isolated product in this case was *endo* derivative **5b′**. In the presence of the excess amount of palladium, it seems that an isomerization takes place from the *exo* isomer to the thermodynamically more stable *endo* isomer. This probably occurs by the reaction of the initially formed *exo* product

Table 1. Optimization of the preparation of compound **5**.



4a **5a**

Entry	*T* [°C]	*t* [h][a]	Catalyst [%]	Additive [%]	Base [equiv.]	Solvent	Conversion [%][b]
1	80	8	$Pd(OAc)_2$ (17)	–	Et_3N (6)	THF	0
2	80	16	$Pd(OAc)_2$ (10)	–	K_2CO_3 (6)	THF	72
3	80–100	15	$Pd(OAc)_2$ (2)	–	K_2CO_3 (2.5)	DMF[c]	0
4	80	15	$Pd(OAc)_2$ (3)	–	K_2CO_3 (6)	DMF[c]	60
5	90	17	$Pd(OAc)_2$ (4)	–	TBAA (3)	THF	75
6	80	72	$Pd(OAc)_2$ (10)	PPh_3 (40)	K_2CO_3 (6)	MeCN	53
7	80	24	$Pd(OAc)_2$ (20)	PPh_3 (45)	K_2CO_3 (6)	MeCN	65
8	80	48	$Pd(OAc)_2$ (20)	PPh_3 (50)	K_2CO_3 (6)	MeCN[d]	98
9	80	40	$Pd(OAc)_2$ (5)	PPh_3 (20)	K_2CO_3 (6)	THF	80
10	100	3	$Pd(OAc)_2$ (5)	PPh_3 (20)	NaOAc (3.5)	EtOH/H_2O[e]	0
11	90	72	$Pd(OAc)_2$ (2)	PPh_3 (4)	TBAA (2)	THF/H_2O[f]	60
12	90	21	$Pd(OAc)_2$ (2)	PPh_3 (8)	TBAA (1.5)	THF	81
13	90	20	$Pd(OAc)_2$ (4)	PPh_3 (16)	TBAA (1.5)	THF	100
14	80	24	$Pd(OAc)_2$ (5)	$Ti(OEt)_4$ (100)	–	THF	0
15	80	24	$Pd(OAc)_2$ (5)	$Ti(OEt)_4$ (100)	K_2CO_3 (4)	THF	30
16	80	24	$Pd(OAc)_2$ (5)	$FeCl_3$ (110)[g]	K_2CO_3 (6)	THF	50
17[h]	100	24	$Pd(PPh_3)_4$ (10)	–	K_2CO_3 (6)	THF/H_2O[i]	90
18[h]	80	20	$Pd(PPh_3)_4$ (5)	$InCl_3$ (119)	K_2CO_3 (6)	THF/H_2O[d]	95[j]
19	80	48	$Pd(PPh_3)_4$ (5)	CuI (120)	K_2CO_3 (6)	MeCN	10
20	80	16	$Pd_2(dba)_3$[k] (2)	PPh_3	K_2CO_3 (6)	THF	50

[a] Reaction time until progress of the reaction no longer observed. [b] Conversion deduced from the ^1H NMR spectrum, unless otherwise stated. [c] *N*,*N*-dimethylformamide. [d] Deoxygenated. [e] Ratio is 1:1. [f] Ratio is 20:1. [g] 20% of PPh_3 was also added. [h] Starting material **4g** was used in this run. [i] Ratio is 10:1. [j] Partial isomerization of the double bond took place under these reaction conditions to give an *exo*/*endo* ratio of 38:62. [k] Palladium(0) dibenzylideneacetone.

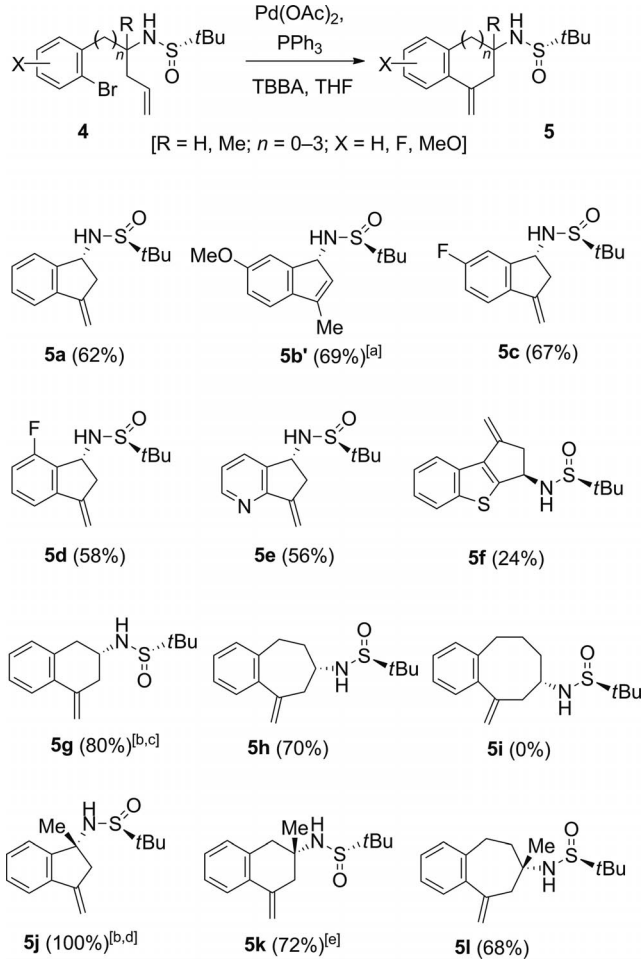
with the palladium hydride that is formed after a β-elimination of the Pd intermediate.[7] A 3:1 mixture of diastereomers for starting material **4j** (after enrichment by column chromatography from the 3:2 mixture obtained from the allylation reaction) was used to give a mixture of four diastereomers. The configurations of these compounds have not yet been assigned, but the *exo* olefins are the major components in the mixture (see Scheme 4). The *exo*/*endo* isomerization was also observed for the six-membered carbocycles **5g** (*exo*/*endo*, 1.4:1) and **5k** (*exo*/*endo*, 3.6:1).

Compound **5a** was then used to investigate the possibility of obtaining the deprotected amines, and treatment with a 6 M solution of hydrochloric acid gave the expected primary amine **6a** (see Scheme 5).

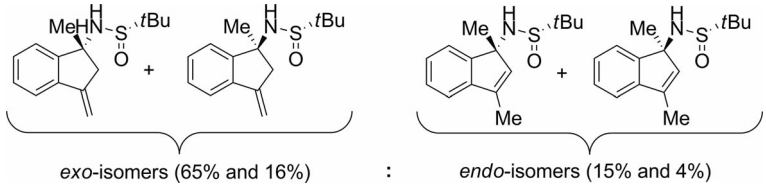
Also, with regard to preparing compounds **5**, we assayed a one-pot version of this process to obtain **5a** from the corresponding imine **3a** and even directly from aldehyde **1a**. Although there was good conversion (in MeCN or THF) of imine **3a**, it did not afford a clean reaction mixture. When we started from aldehyde **1a**, we were unable to isolate the expected final product **5a**.

To demonstrate that the corresponding enantiomers of compounds **3**–**5** can also be prepared by using *ent*-**2** as the chiral auxiliary, we performed the series of reactions that were used to obtain **5a**. Thus, *ent*-**5a** was isolated with similar results as those of its enantiomer but with the opposite optical rotation, that is, $[\alpha]_D^{20}$ = +21 (*c* = 1.0, CH_2Cl_2) for **5a** and $[\alpha]_D^{20}$ = –23 (*c* = 1.0, CH_2Cl_2) for *ent*-**5a** (see Scheme 6).

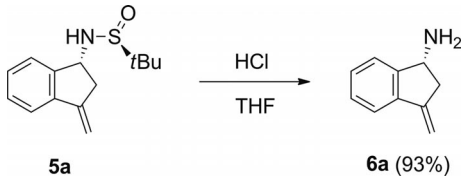
In the final part of this study, we explored the use of substituted allylic bromides to prepare compounds **4** and **5**, and for this purpose, we started from imine **3a**. Its reaction with methallyl, prenyl, and cyclohex-2-enyl bromides gave the expected compounds **4m**–**4o** (see Scheme 7). The reaction proceeded with high selectivity for the prenyl bromide to yield **4n** as the only regioisomer. Remarkably, in the case of cyclohex-2-enyl bromide, a single diastereomer was obtained after column purification, and the relative *anti* configuration was assigned on the basis of our experience with the indium-promoted addition of cyclohex-2-enyl bromide to the *N*-*tert*-butylsulfinyl imine of 3-phenylpropanal.[3f] By using the established optimal conditions, the final Heck-type reaction of these compounds afforded good results for compounds **5n** and **5o**, but fail to provide compound **5m**. Unfortunately, a mixture of three isomers was obtained in the case of **5o** (see Scheme 7).



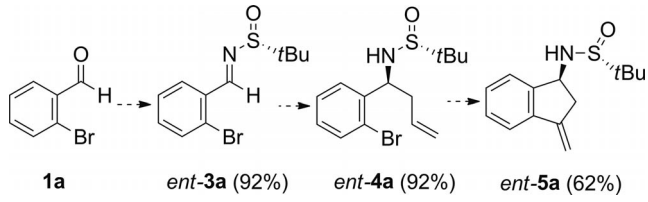
Scheme 3. Preparation of methylene-substituted carbocyles. [a] 14% of $Pd(OAc)_2$ was used. [b] Conversion. [c] An *exo*/*endo* ratio of 1.4:1 was obtained. [d] A mixture of four diastereomers was obtained (see text and Scheme 4). [e] An *exo*/*endo* ratio of 3.6:1 was obtained.



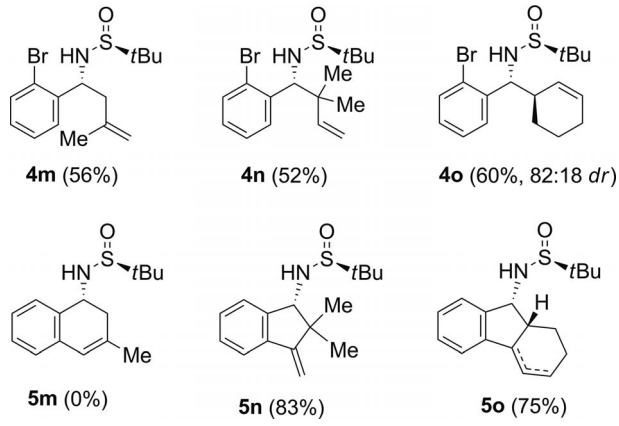
Scheme 4. Mixture of diastereomers for **5j**.



Scheme 5. Deprotection of compound **5a**.



Scheme 6. Reactions for the preparation of *ent*-**5a**.



Scheme 7. Compounds **4m**–**4o** and **5m**–**5o**.

Conclusions

The indium-promoted allylation of chiral *tert*-butylsulfinyl imines, which were derived from brominated aldehydes and ketones, followed by a palladium acetate-catalyzed Heck-type reaction yielded chiral aminated methylenebenzocycloalkenes through a two-step process. In the formation of six-membered rings, we observed the partial isomerization from the *exo* to the *endo* double bond. Finally, the cyclization, which successfully afforded five-, six-, and seven-membered rings, failed to yield the corresponding cyclooctene-derived product.

Experimental Section

General Methods: All reactions that required anhydrous conditions were performed in oven-dried glassware under argon. Unless other-

wise indicated, all commercially available chemicals were purchased from Across or Aldrich and were used without purification. The *N*-*tert*-butanesulfinamides (S_S and R_S) were a gift from Medalchemy (>99%*ee* by chiral HPLC on a Chiracel AS column; *n*-hexane/*i*PrOH, 90:10; 1.2 mL/min; λ = 222 nm). TLC was performed on Merck silica gel 60 F_{254} with aluminum plates and visualized by using phosphomolybdic acid (PMA) stain. Chromatographic purification was performed by flash chromatography with Merck silica gel 60 (0.040–0.063 mm) and *n*-hexane/AcOEt as the eluent. IR spectra were recorded (film) with a Nicolet Impact 510 P-FT Spectrometer. Melting points were recorded in open-glass capillary tubes with an OptiMelt (Stanford Research Systems) apparatus. Gas chromatographic analyses (GLC) were recorded with a Hewlett–Packard HP-5890 instrument equipped with a flame ionization detector (FID) and a 12 m capillary column (0.2 mm diam., 0.33 μm film thickness) with nitrogen (2 mL/min) as the carrier gas [injector temp. 275 °C, detector temp. 300 °C, column temp. 60 °C (3 min) and 60–270 °C (15 °C/min), P = 40 kPa as routine working conditions]. The ^{1}H NMR spectroscopic data were recorded with a Bruker AC-300 spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. The data is reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), unresolved, or br. s (broad signal); coupling constant(s) in Hz; and integration. The ^{13}C NMR spectroscopic data were recorded by ^{1}H decoupling with a Bruker 75 MHz spectrometer, and DEPT-135 experiments were performed to assign CH, CH_2, and CH_3. Optical rotations were measured with a Perkin–Elmer 341 polarimeter (concentration is given in g/100 mL, solvent). HRMS (EI) were recorded with a Finnigan MAT 95S. The starting bromoaryl carbonyl compounds **1a**–**1f**, **1k**, and **1j** were commercially available. Compound **1g**[8] was prepared by the oxidation of commercially available *o*-bromobenzyl alcohol with Dess–Martin periodinane. Compounds **1h**, **1i**,[9] and **1l**[10] were prepared from *o*-bromoiodobenzene through a palladium-catalyzed coupling reaction with allyl alcohol, but-3-en-1-ol, and but-3-en-2-ol, respectively.

General Procedure for the Synthesis of *N*-*tert*-Butylsulfinyl Imines 3: To a solution of *tert*-butanesulfinamide (**2**, 0.605 g, 5 mmol) and the corresponding carbonyl compound **1** (4.5 mmol) in dry THF (20 mL) under argon at 23 °C was slowly added titanium tetraethoxide (2.005 g, 1.885 mL, 9 mmol). The reaction mixture was stirred at the same temperature for 12 h for aldehydes and at 76 °C for 5 h for ketones. The resulting mixture was hydrolyzed with brine (30 mL), and the solution was extracted with ethyl acetate (3 × 15 mL). The combined organic extracts were dried with anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to yield pure compounds **3**. Imines **3a**,[11] **3g**,[12] **3h**,[12] and **3j**[13] were characterized by comparing their physical and spectroscopic data with those reported in the literature. The physical, spectroscopic, and analytical data for the remaining imines **3** are below.

(*S*,*E*)-*N*-(2-Bromo-5-methoxybenzylidene)-*tert*-butanesulfinamide (3b): The representative procedure was followed by using 2-bromo-5-methoxybenzaldehyde (222 mg, 1.0 mmol) and (S_S)-*tert*-butanesulfinamide (**2**, 133 mg, 1.1 mmol). Purification by column chromatography (hexane/AcOEt, 10:1) yielded **3b** (313 mg, 98%) as a yellow oil; R_f = 0.63 (hexane/AcOEt, 2:1). $[\alpha]_D^{20}$ = +133 (c = 1.06, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.93 (s, 1 H), 7.56 (d, J = 3.1 Hz, 1 H), 7.52 (d, J = 8.8 Hz, 1 H), 6.94 (dd, J = 8.8, 3.2 Hz, 1 H), 3.84 (s, 3 H), 1.28 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.2 (CH), 159.1 (C), 134.4 (CH), 133.4 (C), 120.3 (CH), 117.2 (C), 113.7 (CH), 58.1 (C), 55.7 (CH_3), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2959, 1597, 1466, 1085, 1015 cm^{-1}. LRMS (EI): *m*/*z* (%) = 213 (98), 211 (100), 198 (36), 196 (37), 170 (34), 168 (34), 117 (14), 89 (12), 88 (12), 75 (10), 63 (11), 62 (14). HRMS (EI): calcd. for $C_8H_6{}^{79}BrNO$ [M – $C_4H_{10}OS$]$^+$ 210.9633; found 210.9638.

(*S*,*E*)-*N*-(2-Bromo-5-fluorobenzylidene)-*tert*-butanesulfinamide (3c): The representative procedure was followed by using 2-bromo-5-fluorobenzaldehyde (211 mg, 1.0 mmol) and (S_S)-*tert*-butanesulfinamide (**2**, 133 mg, 1.1 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 10:1) yielded **3c** (297 mg, 97%) as a white solid; m.p. 56–58 °C. R_f = 0.71 (hexane/AcOEt, 2:1). $[\alpha]_D^{20}$ = +211 (c = 1.03, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.92 (d, J = 2.2 Hz, 1 H), 7.75 (dd, J = 9.1, 3.1 Hz, 1 H), 7.62 (dd, J = 8.8, 5.0 Hz, 1 H), 7.10 (ddd, J = 8.8, 7.6, 3.1 Hz, 1 H), 1.29 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.0 (d, J = 248.4 Hz, C), 161.5 (CH), 135.1 (d, J = 7.6 Hz, CH), 134.5 (d, J = 7.4 Hz, C), 120.8 (d, J = 23.2 Hz, CH), 120.6 (C), 116.2 (d, J = 24.0 Hz, CH), 58.4 (C), 22.9 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3067, 1592, 1461, 1255, 1084 cm^{-1}. LRMS (EI): *m*/*z* (%) = 251 (17), 249 (16), 170 (38), 149 (13), 94 (10), 85 (12), 71 (19), 70 (14), 69 (12), 57 (100), 55 (12), 43 (45), 41 (24). HRMS (EI): calcd. for $C_7H_5{}^{79}BrFNOS$ [M – C_4H_8]$^+$ 248.9259; found 248.9256.

(*S*,*E*)-*N*-(2-Bromo-6-fluorobenzylidene)-*tert*-butanesulfinamide (3d): The representative procedure was followed by using 2-bromo-6-fluorobenzaldehyde (211 mg, 1.0 mmol) and (S_S)-*tert*-butanesulfinamide (**2**, 133 mg, 1.1 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 12:1) yielded **3d** (281 mg, 92%) as a yellow oil; R_f = 0.65 (hexane/AcOEt, 2:1). $[\alpha]_D^{20}$ = +132 (c = 1.05, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84 (s, 1 H), 7.49 (d, J = 8.1 Hz, 1 H), 7.32 (td, J = 8.2, 5.6 Hz, 1 H), 7.18–7.11 (m, 1 H), 1.30 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 161.8 (d, J = 262.8 Hz, C), 158.4 (CH), 133.3 (d, J = 9.9 Hz, CH), 129.7 (d, J = 3.6 Hz, CH), 125.4 (C), 122.5 (d, J = 11.2 Hz, C), 116.1 (d, J = 22.1 Hz, CH), 58.1 (C), 22.66 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 1597, 1562, 1455, 1083, 895 cm^{-1}. LRMS (EI): *m*/*z* (%) = 201 (97), 199 (100), 120 (75), 100 (30), 93 (13), 75 (13). HRMS (EI): calcd. for $C_7H_3{}^{79}BrFN$ [M – $C_4H_{10}OS$]$^+$ 198.9433; found 198.9446.

(*S*,*E*)-*N*-[(2-Bromopyridin-3-yl)methylene]-*tert*-butanesulfinamide (3e): The representative procedure was followed by using 2-bromo-3-pyridinecarbaldehyde (387 mg, 2.0 mmol) and (S_S)-*tert*-butanesulfinamide (**2**, 270 mg, 2.2 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 5:1) yielded **3e** (566 mg, 98%) as a white solid; m.p. 43–46 °C. R_f = 0.40 (hexane/AcOEt, 2:1). $[\alpha]_D^{20}$ = +150 (c = 1.14, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.92 (s, 1 H), 8.49 (dd, J = 4.7, 2.0 Hz, 1 H), 8.31 (dd, J = 7.7, 2.0 Hz, 1 H), 7.40 (ddd, J = 7.7, 4.7, 0.6 Hz, 1 H), 1.29 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.1 (CH), 152.9 (CH), 144.9 (C), 137.7 (CH), 130.5 (C), 123.3 (CH), 58.5 (C), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2866, 1589, 1572, 1387, 1335, 1080, 1048 cm^{-1}. LRMS (EI): *m*/*z* (%) = 184 (31), 182 (32), 103 (100), 76 (42), 75 (18), 51 (13). HRMS (EI): calcd. for $C_6H_3{}^{79}BrN_2$ [M – $C_4H_{10}OS$]$^+$ 181.9480; found 181.9498.

(*S*,*E*)-*N*-[(3-Bromobenzo[*b*]thiophen-2-yl)methylene]-*tert*-butanesulfinamide (3f): The representative procedure was followed by using 3-bromobenzothiophene-2-carbaldehyde (507 mg, 2.0 mmol) and (S_S)-*tert*-butanesulfinamide (**2**, 267 mg, 2.2 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 12:1) yielded **3f** (692 mg, 98%) as a yellow solid; m.p. 112–114 °C. R_f = 0.66 (hexane/AcOEt, 2:1). $[\alpha]_D^{20}$ = +115 (c = 1.01, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.90 (m, 1 H), 7.84–7.79 (m, 1 H), 7.52–7.45 (m, 2 H), 1.29 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8 (CH), 139.8 (C), 138.5 (C), 134.9 (C), 128.4 (CH), 125.8 (CH), 124.7 (CH), 123.0 (CH), 116.4 (C), 58.6 (C), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2865, 1572, 1083, 730 cm^{-1}. LRMS (EI): *m*/*z* (%) = 241 (5), 240 (11), 239 (100), 238 (12), 237 (98), 158 (23), 114 (34).

HRMS (EI) calcd. for $C_9H_4{}^{79}BrNS$ [M – $C_4H_{10}OS$]$^+$ 236.9248; found 236.9253.

(*S*,*E*)-*N*-[4-(2-Bromophenyl)butylidene]-*tert*-butanesulfinamide (3i): The representative procedure was followed by using 4-(2′-bromophenyl)butyraldehyde (550 mg, 2.46 mmol) and (S_S)-*tert*-butanesulfinamide (**2**, 363 mg, 3.0 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 7:1) yielded **3i** (700 mg, 87%) as a yellow oil; R_f = 0.52 (hexane/AcOEt, 2:1). $[\alpha]_D^{20}$ = +150 (*c* = 1.14, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (t, *J* = 4.5 Hz, 1 H), 7.53 (dd, *J* = 7.7, 1.1 Hz, 1 H), 7.28–7.17 (m, 2 H), 7.07 (ddd, *J* = 8.0, 6.5, 2.6 Hz, 1 H), 2.86–2.76 (m, 2 H), 2.60 (td, *J* = 7.4, 4.5 Hz, 2 H), 2.04–1.91 (m, 2 H), 1.20 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.1 (CH), 140.8 (C), 133.0 (CH), 130.5 (CH), 127.9 (CH), 127.6 (CH), 124.5 (C), 56.7 (C), 35.7 (CH_2), 35.6 (CH_2), 25.6 (CH_2), 22.5 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2865, 1621, 1471, 1084, 749 cm^{-1}. LRMS (EI): *m*/*z* (%) = 225 (30), 223 (31), 185 (18), 184 (18), 183 (19), 182 (17), 171 (96), 170 (10), 169 (100), 144 (39), 116 (11), 115 (11), 104 (11), 103 (13), 91 (14), 90 (27), 89 (27), 77 (16), 63 (14), 51 (12). HRMS (EI): calcd. for $C_{10}H_{10}{}^{79}BrN$ [M – $C_4H_{10}OS$]$^+$ 222.9997; found 223.0007.

(*S*,*E*)-*N*-[1-(2-Bromophenyl)propan-2-ylidene]-*tert*-butanesulfinamide (3k): The representative procedure was followed by using 2′-bromophenylacetone (430 mg, 2.0 mmol) and (S_S)-*tert*-butanesulfinamide (**2**, 267 mg, 2.2 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 8:1) yielded **3k** (459 mg, 74%) as a yellow oil; R_f = 0.59 (hexane/AcOEt, 2:1). $[\alpha]_D^{20}$ = +68 (*c* = 1.06, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.0, 0.9 Hz, 1 H), 7.29–7.17 (m, 2 H), 7.15–7.07 (m, 1 H), 3.85 (s, 2 H), 2.39 (s, 3 H), 1.09 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 181.9 (C), 136.1 (C), 132.8 (CH), 131.8 (CH), 128.7 (CH), 127.5 (CH), 125.2 (C), 56.9 (C), 49.6 (CH_2), 22.9 (CH_3), 22.2 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2854, 1626, 1074, 749 cm^{-1}. LRMS (EI): *m*/*z* (%) = 261 (31), 259 (29), 181 (10), 180 (100), 171 (18), 169 (19), 162 (10), 138 (14), 132 (18), 131 (15), 90 (28), 89 (21), 57 (45), 44 (16), 41 (15). HRMS (EI): calcd. for $C_9H_{10}{}^{79}BrN$ [M – C_4H_8OS]$^+$ 210.9997; found 211.0023.

(*S*,*E*)-*N*-[4-(2-Bromophenyl)butan-2-ylidene]-*tert*-butanesulfinamide (3l): The representative procedure was followed by using 4-(2′-bromophenyl)-2-butanone (355 mg, 1.56 mmol) and (S_S)-*tert*-butanesulfinamide (**2**, 219 mg, 1.8 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 7:1) yielded **3l** (422 mg, 82%) as a yellow oil; R_f = 0.33 (hexane/AcOEt, 2:1). $[\alpha]_D^{20}$ = +97 (*c* = 1.12, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.9 Hz, 1 H), 7.26–7.18 (m, 2 H), 7.12–7.03 (m, 1 H), 3.07–2.99 (m, 2 H), 2.77–2.68 (m, 2 H), 2.36 (s, 3 H), 1.24 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.0 (C), 140.3 (C), 133.0 (CH), 130.4 (CH), 128.1 (CH), 127.7 (CH), 124.5 (C), 56.6 (C), 43.1 (CH_2), 32.2 (CH_2), 23.3 (CH_3), 22.3 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 1624, 1360, 1071, 750 cm^{-1}. LRMS (EI): *m*/*z* (%) = 226 (4), 224 (5), 212 (5), 210 (6), 171 (11), 169 (10), 147 (13), 146 (100), 131 (15), 130 (13), 77 (15), 70 (10). HRMS (EI): calcd. for $C_{10}H_{12}{}^{79}BrNOS$ [M – C_4H_8]$^+$ 272.9823; found 272.9829.

General Procedure for the Allylation of *N*-*tert*-Butylsulfinyl Imines 3. Synthesis of Homoallylamine Derivatives 4: A mixture of *N*-*tert*-butylsulfinyl imine **3** (1.0 mmol), allyl bromide (166 mg, 0.132 mL, 1.5 mmol), and indium (144 mg, 1.25 mmol) in dry THF (3 mL) was stirred for 6 h at 65 °C. Then, the resulting mixture was hydrolyzed with H_2O (5 mL), and the solution was extracted with AcOEt (3 × 5 mL). The combined organic phases were washed with brine (3 × 10 mL), dried with anhydrous $MgSO_4$, and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/AcOEt) to yield products **4**. The yields and the physical and spectroscopic data follow.

(S_S,1*R*)-1-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)but-3-en-1-amine (4a): The representative procedure was followed by using imine **3a** (288 mg, 1 mmol), indium (143 mg, 1.25 mmol), and allyl bromide (0.131 mL, 1.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **4a** (303 mg, 92%) as a colorless oil; R_f = 0.48 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +110 (*c* = 1.1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, *J* = 8.0, 1.1 Hz, 1 H), 7.39 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.31 (td, *J* = 7.5, 1.0 Hz, 1 H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1 H), 5.83–5.70 (m, 1 H), 5.24–5.16 (m, 2 H), 4.98 (ddd, *J* = 8.1, 4.9, 3.1 Hz, 1 H), 3.72 (d, *J* = 2.4 Hz, 1 H), 3.72 (d, *J* = 2.4 Hz, 1 H), 2.75–2.65 (m, 1 H), 2.50–2.39 (m, 1 H), 1.21 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.9 (C), 133.9 (CH), 133.2 (CH), 129.0 (CH), 128.8 (CH), 127.5 (CH), 123.6 (C), 119.7 (CH_2), 56.0 (C), 56.0 (CH), 41.7 (CH_2), 22.7 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3213, 1470, 1438, 1054, 1022, 913, 754 cm^{-1}. LRMS (EI): *m*/*z* (%) = 233 (55), 231 (54), 194 (17), 184 (17), 182 (17), 152 (100), 134 (16), 130 (18), 129 (10), 116 (11), 115 (10), 103 (10), 102 (13), 91 (14), 77 (16). HRMS (EI): calcd. for $C_7H_6{}^{79}BrNOS$ [M – C_7H_{14}]$^+$ 230.9353; found 230.9361.

(R_S,1*S*)-1-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)but-3-en-1-amine (*ent*-4a): The representative procedure was followed by using imine *ent*-**3a** (288 mg, 1 mmol), indium (143 mg, 1.25 mmol), and allyl bromide (0.131 mL, 1.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded *ent*-**4a** (303 mg, 92%) as a colorless oil. The physical and spectroscopic data were the same as the data for **4a**. $[\alpha]_D^{20}$ = –103 (*c* = 1.11, CH_2Cl_2).

(S_S,1*R*)-1-(2-Bromo-5-methoxyphenyl)-*N*-(*tert*-butylsulfinyl)but-3-en-1-amine (4b): The representative procedure was followed by using imine **3b** (160 mg, 0.5 mmol), indium (74 mg, 0.64 mmol), and allyl bromide (0.090 mL, 1.0 mmol). Purification by column chromatography (hexane/AcOEt, 3:1) yielded **4b** (154 mg, 88%) as a yellow oil; R_f = 0.31 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +135 (*c* = 1.11, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 8.8 Hz, 1 H), 6.97 (d, *J* = 3.1 Hz, 1 H), 6.70 (dd, *J* = 8.8, 3.1 Hz, 1 H), 5.86–5.69 (m, 1 H), 5.26–5.16 (m, 1 H), 4.91 (ddd, *J* = 8.0, 4.8, 2.9 Hz, 1 H), 3.77 (s, 3 H), 3.71 (d, *J* = 2.7 Hz, 1 H), 2.76–2.63 (m, 1 H), 2.48–2.33 (m, 1 H), 1.23 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.1 (C), 142.0 (C), 134.0 (CH), 133.8 (CH), 119.7 (CH_2), 114.6 (CH), 114.6 (CH), 113.8 (C), 56.02 (C), 55.97, 55.5, 41.7 (CH_2), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3215, 2957, 1594, 1571, 1469, 1048, 1015 cm^{-1}. LRMS (EI): *m*/*z* (%) = 305 (4), 303 (4), 263 (19), 261 (19), 224 (67), 215 (14), 214 (28), 113 (16), 212 (25), 184 (10), 183 (18), 182 (100), 166 (14), 164 (11), 160 (16), 91 (16), 63 (13). HRMS (EI): calcd. for $C_8H_8{}^{79}BrNO_2S$ [M – C_7H_{14}]$^+$ 260.9459; found 260.9477.

(S_S,1*R*)-1-(2-Bromo-5-fluorophenyl)-*N*-(*tert*-butylsulfinyl)but-3-en-1-amine (4c): The representative procedure was followed by using imine **3c** (214 mg, 0.7 mmol), indium (92 mg, 0.8 mmol), and allyl bromide (0.090 mL, 1.0 mmol). Purification by column chromatography (hexane/AcOEt, 3:1) yielded **4c** (190 mg, 78%) as a colorless oil; R_f = 0.45 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +118 (*c* = 1.1, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 8.8, 5.3 Hz, 1 H), 7.13 (dd, *J* = 9.8, 3.1 Hz, 1 H), 6.88 (ddd, *J* = 8.7, 7.8, 3.1 Hz, 1 H), 5.84–5.69 (m, 1 H), 5.26–5.17 (m, 2 H), 4.98–4.89 (m, 1 H), 3.74 (d, *J* = 2.1 Hz, 1 H), 2.75–2.63 (m, 1 H), 2.46–2.32 (m, 1 H), 1.23 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.2 (d, *J* = 246.5 Hz, C), 143.3 (d, *J* = 6.7 Hz, CH), 134.4 (d, *J* = 7.7 Hz, C), 133.5 (CH), 120.2 (CH_2), 117.4 (C), 116.3 (d, *J* = 22.6 Hz, ArCH), 115.9 (d, *J* = 24.0 Hz, CH), 56.2 (C), 55.7 (CH), 41.5 (CH_2), 22.7 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3215, 1466, 1053, 1027, 809 cm^{-1}.

LRMS (EI): *m*/*z* (%) = 251 (43), 249 (43), 212 (26), 203 (12), 202 (16), 201 (15), 200 (14), 171 (10), 170 (100), 152 (14), 148 (18), 134 (10), 122 (12), 121 (14), 95 (12), 94 (10), 91 (11). HRMS (EI): calcd. for $C_7H_5{}^{79}BrFNOS$ [M – C_4H_8]$^+$ 248.9259; found 248.9254.

(S_S,1*R*)-1-(2-Bromo-6-fluorophenyl)-*N*-(*tert*-butylsulfinyl)but-3-en-1-amine (4d): The representative procedure was followed by using imine **3d** (214 mg, 0.7 mmol), indium (92 mg, 0.8 mmol), and allyl bromide (0.090 mL, 1.0 mmol). Purification by column chromatography (hexane/AcOEt, 3:1) yielded **4d** (178 mg, 73%) as a white solid; m.p. 67–70 °C. R_f = 0.44 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +37 (*c* = 1.04, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (dt, *J* = 7.9, 1.1 Hz, 1 H); 7.11 (td, *J* = 8.1, 5.9 Hz, 1 H), 7.01 (ddd, *J* = 10.7, 8.3, 1.1 Hz, 1 H), 5.83–5.65 (m, 1 H), 5.17–5.03 (m, 3 H), 3.98 (d, *J* = 6.9 Hz, 1 H), 2.92–2.66 (m, 2 H), 1.14 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.6 (d, *J* = 247.8 Hz, C), 133.5 (CH), 129.8 (d, *J* = 9.7 Hz, CH), 129.2 (C), 129.1 (CH), 124.1 (C), 119.0 (CH_2), 115.7 (d, *J* = 23.1 Hz, CH), 58.3 (CH), 56.1 (C), 40.6 (CH_2), 22.5 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3320, 1453, 1439, 1234, 1187, 1058 cm^{-1}. LRMS (EI): *m*/*z* (%) = 251 (60), 249 (59), 202 (18), 200 (17), 171 (10), 170 (100), 152 (14), 148 (13), 134 (10), 122 (10), 95 (10), 75 (10). HRMS (EI): calcd. for $C_7H_5{}^{79}BrFNOS$ [M – C_7H_{14}]$^+$ 248.9259; found 248.9266.

(S_S,1*R*)-1-(2-Bromopyridin-3-yl)-*N*-(*tert*-butylsulfinyl)but-3-en-1-amine (4e): The representative procedure was followed by using imine **3e** (434 mg, 1.5 mmol), indium (215 mg, 1.87 mmol), and allyl bromide (0.202 mL, 2.25 mmol). Purification by column chromatography (hexane/AcOEt, 2:1) yielded **4e** (478 mg, 90%) as a yellow oil; R_f = 0.22 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +111 (*c* = 0.97, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.30 (dd, *J* = 4.7, 2.0 Hz, 1 H), 7.70 (ddd, *J* = 7.7, 2.0, 0.3 Hz, 1 H), 7.28 (ddd, *J* = 7.7, 4.7, 0.3 Hz, 1 H), 5.83–5.68 (m, 1 H), 5.23–5.17 (m, 2 H), 4.95 (ddd, *J* = 8.0, 5.0, 3.0 Hz, 1 H), 3.81 (d, *J* = 2.3 Hz, 1 H), 2.81–2.70 (m, 1 H), 2.54–2.42 (m, 1 H), 1.23 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.1 (CH), 143.2 (C), 138.4 (C), 137.3 (CH), 133.2 (CH), 123.0 (CH), 120.4 (CH_2), 56.4 (C), 55.6 (CH), 41.2 (CH_2), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3204, 1559, 1402, 1045 cm^{-1}. LRMS (EI): *m*/*z* (%) = 234 (100), 233 (10), 232 (97), 195 (11), 186 (13), 184 (14), 153 (91), 131 (13), 130 (47), 117 (12), 105 (83), 104 (23), 103 (28), 91 (14), 78 (43), 77 (27), 76 (19), 52 (11), 51 (26). HRMS (EI): calcd. for $C_9H_{11}{}^{79}BrN_2OS$ [M – C_4H_8]$^+$ 273.9775; found 273.9760.

(S_S,1*R*)-1-(3-Bromobenzo[*b*]thiophen-2-yl)-*N*-(*tert*-butylsulfinyl)but-3-en-1-amine (4f): The representative procedure was followed by using imine **3f** (344 mg, 1.0 mmol), indium (140 mg, 1.22 mmol), and allyl bromide (0.135 mL, 1.5 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 3:1) yielded **4f** (336 mg, 80%) as a mixture (*dr* 93:7) and as a yellow oil; R_f = 0.44 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +102 (*c* = 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (t, *J* = 8.7 Hz, 2 H), 7.44 (td, *J* = 7.6, 1.0 Hz, 1 H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1 H), 5.89–5.77 (m, 1 H), 5.29–5.26 (m, 1 H), 5.26–5.20 (m, 1 H), 5.14 (ddd, *J* = 7.9, 5.4, 2.2 Hz, 1 H), 3.82 (d, *J* = 1.6 Hz, 1 H), 2.83–2.74 (m, 1 H), 2.66–2.56 (m, 1 H), 1.24 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.9 (C), 138.3 (C), 137.5 (C), 133.2 (CH), 125.5 (CH), 125.2 (CH), 123.1 (CH), 122.6 (CH), 120.3 (CH_2), 106.4 (C), 56.4 (C), 53.1 (CH), 42.2 (CH_2), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3204, 2867, 1436, 1053, 752 cm^{-1}. LRMS (EI): *m*/*z* (%) = 331 (11), 329 (10), 289 (29), 287 (27), 282 (25), 280 (24), 251 (16), 250 (84), 242 (12), 241 (100), 240 (33), 239 (100), 238 (22), 214 (13), 212 (13), 208 (39), 187 (17), 186 (27), 185 (18), 172 (38), 171 (14), 159 (26), 133 (10), 132 (11), 115 (10), 89 (21). HRMS (EI): calcd. for $C_{12}H_{12}{}^{79}BrNOS_2$ [M – C_4H_8]$^+$ 328.9544; found 328.9536.

(S_S,2*R*)-1-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)pent-4-en-2-amine (4g): The representative procedure was followed by using imine **3g** (453 mg, 1.5 mmol), indium (207 mg, 1.8 mmol), and allyl bromide (0.180 mL, 2.0 mmol). Purification by column chromatography (hexane/AcOEt, 3:1) yielded **4g** (378 mg, 73%) as a yellow solid; m.p. 38–48 °C. R_f = 0.32 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +9 (*c* = 1.08, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.5 Hz, 1 H), 7.25–7.21 (m, 2 H), 7.11–7.03 (m, 1 H), 5.93–5.79 (m, 1 H), 5.25–5.18 (m, 2 H), 3.72–3.63 (m, 1 H), 3.34 (d, *J* = 6.9 Hz, 1 H), 2.95 (dd, *J* = 7.2, 5.5 Hz, 2 H), 2.48 (t, *J* = 6.7 Hz, 2 H), 1.06 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.3 (C), 133.9 (CH), 133.0 (CH), 132.0 (CH), 128.3 (CH), 127.4 (CH), 125.2 (C), 119.5 (CH_2), 56.2 (CH), 56.0 (C), 41.8 (CH_2), 40.7 (CH_2), 22.6 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3216, 1736, 1472, 1045, 1024, 912, 749 cm^{-1}. LRMS (EI): *m*/*z* (%) = 247 (3), 245 (3), 208 (9), 184 (8), 182 (8), 171 (11), 169 (11), 118 (100), 91 (11), 90 (11), 89 (10). HRMS (EI): calcd. for $C_8H_8{}^{79}BrNOS$ [M – C_7H_{14}]$^+$ 244.9510; found 244.9510.

(S_S,3*S*)-1-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)hex-5-en-3-amine (4h): The representative procedure was followed by using imine **3h** (221 mg, 0.7 mmol), indium (100 mg, 0.87 mmol), and allyl bromide (0.090 mL, 1.0 mmol). Purification by column chromatography (hexane/AcOEt, 5:2) yielded **4h** (202 mg, 81%) as a colorless oil; R_f = 0.34 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +43 (*c* = 0.95, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.9 Hz, 1 H), 7.26–7.19 (m, 2 H), 7.09–7.03 (m, 1 H), 5.87–5.75 (m, 1 H), 5.22–5.15 (m, 2 H), 3.46–3.37 (m, 1 H), 3.33 (d, *J* = 6.6 Hz, 1 H), 2.89 (ddd, *J* = 13.5, 11.1, 5.1 Hz, 1 H), 2.73 (ddd, *J* = 13.5, 11.1, 5.7 Hz, 1 H), 2.55–2.39 (m, 2 H), 1.91–1.70 (m, 2 H), 1.25 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.3 (ArC), 134.0 (CH), 133.0 (CH), 130.4 (CH), 127.9 (CH), 127.7 (CH), 124.5 (ArC), 119.4 (CH_2), 56.1 (C), 55.1 (CH), 40.7 (CH_2), 35.5 (CH_2), 32.7 (CH_2), 22.9 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3215, 1471, 1439, 1052, 1022, 749 cm^{-1}. LRMS (EI): *m*/*z* (%) = 261 (29), 259 (29), 222 (46), 197 (37), 195 (37), 172 (16), 171 (97), 169 (100), 132 (39), 118 (23), 117 (49), 115 (10), 104 (12), 103 (14), 102 (15), 91 (24), 90 (28), 89 (17), 77 (26), 70 (21). HRMS (EI): calcd. for $C_9H_{10}{}^{79}BrNOS$ [M – C_7H_{14}]$^+$ 258.9666; found 258.9697.

(S_S,4*R*)-7-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)hept-1-en-4-amine (4i): The representative procedure was followed by using imine **3i** (300 mg, 0.91 mmol), indium (131 mg, 1.14 mmol), and allyl bromide (0.123 mL, 1.37 mmol). Purification by column chromatography (hexane/AcOEt, 2:1) yielded **4i** (318 mg, 94%) as a colorless oil; R_f = 0.44 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +40 (*c* = 1.06, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.50 (m, 1 H), 7.26–7.16 (m, 1 H), 7.10–7.01 (m, 1 H), 5.86–5.70 (m, 1 H), 5.20–5.11 (m, 2 H), 3.41–3.31 (m, 1 H), 3.22 (d, *J* = 6.0 Hz, 1 H), 2.72 (t, *J* = 7.6 Hz, 2 H), 2.46–2.38 (m, 1 H), 2.37–2.27 (m, 1 H), 1.80–1.51 (m, 4 H), 1.20 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 141.5 (C), 134.2 (CH), 132.9 (CH), 130.4 (CH), 127.7 (CH), 127.5 (CH), 124.5 (C), 119.1 (CH_2), 55.9 (C), 54.7 (CH), 40.5 (CH_2), 36.2 (CH_2), 34.7 (CH_2), 25.9 (CH_2), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3217, 1471, 913, 750 cm^{-1}. LRMS (EI): *m*/*z* (%) = 317 (20), 315 (19), 275 (11), 273 (11), 224 (10), 211 (29), 209 (30), 171 (25), 169 (25), 146 (12), 132 (11), 131 (100), 130 (18), 118 (24), 115 (16), 104 (29), 103 (18), 102 (15), 91 (40), 90 (21), 89 (16), 77 (25), 70 (14), 56 (15), 55 (10). HRMS (EI): calcd. for $C_{13}H_{18}{}^{79}BrNOS$ [M – C_4H_8]$^+$ 315.0292; found 315.0293.

(S_S,2*R*)-2-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)pent-4-en-2-amine (4j): The representative procedure was followed by using imine **3j** (242 mg, 0.8 mmol), indium (115 mg, 1.0 mmol), and allyl bromide (0.108 mL, 1.2 mmol). Purification by column chromatography

(hexane/AcOEt, 3:1) yielded **4j** (44 mg, 16%, diastereomeric mixture, 3:1) as a yellow oil; R_f = 0.43 (hexane/AcOEt, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$, major isomer): δ = 7.62 (ddd, J = 7.9, 1.4 Hz, 1 H), 7.49 (dd, J = 8.0, 1.6 Hz, 1 H), 7.31–7.25 (m, 1 H), 7.11 (ddd, J = 7.4, 6.5, 1.7 Hz, 1 H), 5.53–5.40 (m, 1 H), 5.18–5.09 (m, 1 H), 5.07–5.00 (m, 1 H), 4.58 (s, 1 H), 3.20 (dd, J = 13.9, 7.3 Hz, 1 H), 3.13 (dd, J = 13.9, 7.2 Hz, 1 H), 1.89 (s, 3 H), 1.23 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, major isomer): δ = 142.5 (C), 136.0 (CH), 133.5 (CH), 129.05 (CH), 128.97 (CH), 127.5 (CH), 121.7 (C), 119.6 (CH_2), 61.1 (C), 56.4 (C), 45.4 (CH_2), 26.3 (CH_3), 23.0 (CH_3) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer): δ = 7.60 (dd, J = 8.3, 1.3 Hz, 1 H), 7.52 (dd, J = 8.0, 1.6 Hz, 1 H), 7.32–7.25 (m, 1 H), 7.13–7.07 (m, 1 H), 5.53–5.40 (m, 1 H), 5.18–5.09 (m, 1 H), 5.08–5.00 (m, 1 H), 4.94 (s, 1 H), 3.02 (dd, J = 14.0, 7.2 Hz, 1 H), 2.93 (dd, J = 13.9, 7.3 Hz, 1 H), 1.83 (s, 3 H), 1.25 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$, minor isomer): δ = 142.7 (C), 135.7 (CH), 133.2 (CH), 129.4 (CH), 127.6 (CH), 122.0 (C), 118.9 (CH), 60.9 (C), 56.3 (C), 45.1 (CH_2), 26.4 (CH_3), 22.9 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3217, 1638, 1462, 1427, 1061, 1016 cm^{-1}. LRMS (EI): m/z (%) = 274 (15), 272 (14), 247 (17), 245 (17), 208 (56), 184 (11), 182 (11), 167 (10), 166 (100), 144 (17), 130 (22), 129 (16), 115 (10), 103 (11), 102 (15), 91 (12). HRMS (EI): calcd. for $C_{10}H_{11}{}^{79}$BrNOS [M – C_4H_8]$^+$ 271.9745; found 271.9752.

(S_S,2R)-1-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)-2-methylpent-4-en-2-amine (4k): The representative procedure was followed by using imine **3k** (316 mg, 1.0 mmol), indium (143 mg, 1.25 mmol), and allyl bromide (0.135 mL, 1.5 mmol). Purification by column chromatography (hexane/AcOEt, 3:1) yielded **4k** (237 mg, 66%) as a colorless oil; R_f = 0.51 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = –20 (c = 1.04, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, J = 7.9 Hz, 1 H), 7.39 (dd, J = 7.7, 1.5 Hz, 1 H), 7.24 (t, J = 7.3 Hz, 1 H), 7.08 (td, J = 7.7, 1.6 Hz, 1 H), 6.06–5.89 (m, 1 H), 5.26 (s, 1 H), 5.24–5.18 (m, 1 H), 3.60 (s, 1 H), 3.19 (d, J = 13.8 Hz, 1 H), 2.93 (d, J = 13.8 Hz, 1 H), 2.57 (d, J = 7.4 Hz, 2 H), 1.29 (s, 3 H), 1.11 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.1 (C), 133.5 (CH), 133.1 (CH), 132.8 (CH), 128.3 (CH), 127.1 (CH), 126.5 (C), 120.0 (CH_2), 59.0 (C), 56.1 (C), 47.5 (CH_2), 45.8 (CH_2), 25.0 (CH_3), 22.7 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3222, 1436, 1048, 915, 747 cm^{-1}. LRMS (EI): m/z (%) = 171 (5), 169 (5), 134 (5), 133 (7), 132 (100), 116 (6), 114 (6), 91 (6), 90 (11), 89 (8), 84 (6). HRMS (EI): calcd. for $C_7H_6{}^{79}$Br [M – C_9H_{18}NOS]$^+$ 168.9653; found 168.9658.

(S_S,3S)-1-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)-3-methylhex-5-en-3-amine (4l): The representative procedure was followed by using imine **3l** (369 mg, 1.11 mmol), indium (160 mg, 1.4 mmol), and allyl bromide (0.151 mL, 1.68 mmol). Purification by column chromatography (*n*-hexane/AcOEt, 1:1) yielded **4l** (302 mg, 81%) as a yellow oil; R_f = 0.47 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +43 (c = 1.03, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.8 Hz, 1 H), 7.26–7.21 (m, 2 H), 7.10–7.00 (m, 1 H), 5.97–5.78 (m, 1 H), 5.25–5.09 (m, 2 H), 3.38 (s, 1 H), 2.94–2.64 (m, 2 H), 2.53–2.36 (m, 2 H), 1.84–1.72 (m, 2 H), 1.40 (s, 3 H), 1.24 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.5 (C), 133.3 (CH), 132.9 (CH), 130.6 (CH), 127.8 (CH), 127.8 (CH), 124.4 (C), 119.8 (CH_2), 57.6 (C), 56.1 (C), 46.8 (CH_2), 41.5 (CH_2), 30.7 (CH_2), 25.7 (CH_3), 22.9 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3222, 1637, 1471, 1053, 1023, 748 cm^{-1}. LRMS (EI): m/z (%) = 317 (2) [M – 56 (^{81}Br)]$^+$, 315 (2), 302 (2), 300 (2), 275 (23), 273 (22), 236 (45), 226 (4), 224 (5), 211 (4), 209 (4), 194 (7), 171 (49), 169 (50), 146 (61), 133 (17), 132 (100), 131 (11), 116 (16), 104 (16), 103 (12), 91 (27), 90 (24), 89 (15), 84 (42), 77 (22), 55 (11). HRMS (EI): calcd. for $C_{13}H_{18}{}^{79}$BrNOS [M – C_4H_8]$^+$ 315.0292; found 315.0320.

(S_S,1R)-1-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)-3-methylbut-3-en-1-amine (4m): The representative procedure was followed by using imine **3a** (288 mg, 1.0 mmol), indium (143 mg, 1.25 mmol), and 3-bromo-2-methylpropene (0.156 mL, 1.5 mmol). Purification by column chromatography (hexane/AcOEt, 3:1) yielded **4m** (220 mg, 64%) as a white solid; m.p. 76–78 °C. R_f = 0.52 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +165 (c = 1.02, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (dd, J = 8.0, 1.2 Hz, 1 H), 7.48 (dd, J = 7.8, 1.6 Hz, 1 H), 7.30 (td, J = 7.5, 1.0 Hz, 1 H), 7.13 (td, J = 7.8, 1.7 Hz, 1 H), 5.00 (dd, J = 11.1, 3.8 Hz, 1 H), 4.96 (s, 1 H), 4.88 (s, 1 H), 3.72 (s, 1 H), 2.62 (dd, J = 13.7, 3.7 Hz, 1 H), 2.23 (dd, J = 13.8, 10.6 Hz, 1 H), 1.86 (s, 3 H), 1.22 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.3 (C), 141.4 (C), 133.2 (CH), 128.9 (CH), 128.7 (CH), 127.6 (CH), 123.5 (C), 115.3 (CH_2), 55.9 (C), 53.4 (CH), 46.1 (CH_2), 22.7 (CH_3), 21.5 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3296, 1648, 1567, 1465, 1060, 755 cm^{-1}. LRMS (EI): m/z (%) = 233 (53), 231 (52), 225 (5), 223 (6), 184 (15), 182 (14), 153 (89), 152 (100), 144 (14), 134 (14), 129 (13), 77 (12). HRMS (EI): calcd. for $C_{11}H_{14}{}^{79}$BrNOS [M – C_4H_8]$^+$ 286.9979; found 286.9997.

(S_S,1R)-1-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)-2,2-dimethylbut-3-en-1-amine (4n): The representative procedure was followed by using imine **3a** (242 mg, 0.84 mmol), indium (115 mg, 1.0 mmol), and 3,3-dimethylallyl bromide (0.110 mL, 1.2 mmol). Purification by column chromatography (hexane/AcOEt, 5:1) yielded **4n** (156 mg, 52%) as a yellow oil; R_f = 0.52 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +108 (c = 1.05, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (dd, J = 8.0, 1.2 Hz, 1 H), 7.33 (dd, J = 7.9, 2.0 Hz, 1 H), 7.28 (td, J = 7.5, 1.2 Hz, 1 H), 7.13 (ddd, J = 8.0, 7.0, 2.0 Hz, 1 H), 5.98 (dd, J = 17.5, 10.7 Hz, 1 H), 5.24 (dd, J = 10.7, 1.1 Hz, 1 H), 5.17 (dd, J = 17.5, 1.1 Hz, 1 H), 4.90 (d, J = 2.3 Hz, 1 H), 3.74 (d, J = 1.6 Hz, 1 H), 1.14 (s, 9 H), 1.11 (s, 3 H), 1.03 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.5 (CH), 138.2 (C), 133.1 (CH), 131.1 (CH), 129.0 (CH), 126.7 (CH), 126.2 (C), 115.0 (CH_2), 61.8 (CH), 55.8 (C), 43.1 (C), 25.8 (CH_3), 22.7 (CH_3), 20.5 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3276, 1636, 1467, 1068, 1020 cm^{-1}. LRMS (EI): m/z (%) = 306 (11), 304 (11), 233 (66), 231 (65), 207 (17), 186 (64), 185 (14), 184 (83), 183 (11), 182 (17), 153 (10), 152 (100), 144 (10), 136 (20), 134 (12), 104 (12), 103 (10), 102 (15), 77 (17), 69 (10), 57 (28), 55 (12). HRMS (EI): calcd. for $C_7H_6{}^{79}$BrNOS [M – C_9H_{18}]$^+$ 232.9333; found 232.9328.

(S_S,1R,1′R)-(2-Bromophenyl)-*N*-(*tert*-butylsulfinyl)(cyclohex-2-en-1-yl)methanamine (4o): The representative procedure was followed by using imine **3a** (288 mg, 1 mmol), indium (143 mg, 1.25 mmol), and 3-bromocyclohexene (0.155 mL, 1.5 mmol). Purification by column chromatography (hexane/AcOEt, 4:1) yielded **4o** (110 mg, 60%) as a white solid; m.p. 114–117 °C. R_f = 0.50 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +150 (c = 0.93, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (dd, J = 7.9, 1.2 Hz, 1 H), 7.40 (dd, J = 7.8, 1.8 Hz, 1 H), 7.31 (td, J = 7.5, 1.1 Hz, 1 H), 7.12 (td, J = 7.4, 1.8 Hz, 1 H), 6.02–5.87 (m, 1 H), 5.55 (d, J = 10.0 Hz, 1 H), 4.75 (t, J = 4.4 Hz, 1 H), 3.64 (d, J = 4.3 Hz, 1 H), 2.73–2.60 (m, 1 H), 2.07–1.94 (m, 2 H), 1.93–1.75 (m, 2 H), 1.69–1.40 (m, 2 H), 1.20 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.4 (C), 133.2 (CH), 132.7 (CH), 129.2 (CH), 128.7 (CH), 127.2 (CH), 124.4 (CH), 123.5 (C), 61.4 (CH), 56.0 (C), 41.0 (CH), 27.0 (CH_2), 25.2 (CH_2), 22.8 (CH_3), 21.7 (CH_2) ppm. IR (ATR): $\tilde{\nu}$ = 3248, 1469, 1049, 1036 cm^{-1}. LRMS (EI): m/z (%) = 251 (12), 249 (12), 234 (45), 233 (77), 232 (23), 231 (74), 186 (21), 185 (11), 184 (43), 183 (9), 182 (23), 171 (18), 170 (32), 169 (16), 153 (11), 152 (100), 142 (10), 141 (10), 136 (16), 134 (14), 129 (11), 128 (12), 115 (11), 104 (11), 102 (13), 81 (20), 79 (11), 77 (22), 67 (13). HRMS (EI): calcd. for $C_{13}H_{16}{}^{79}$BrNOS [M – C_4H_8]$^+$ 313.0136; found 313.0101.

General Procedure for the Intramolecular Heck Reaction of Homoallylamine Derivatives 4. Synthesis of Methylene Carbocycles 5: A

mixture of homoallylamine derivative **4** (0.5 mmol), PPh_3 (0.1 mmol, 26.2 mg), $Pd(OAc)_2$ (0.025 mmol, 5.6 mg) and *n*-Bu_4NOAc (0.8 mmol, 242 mg) in dry THF (3 mL) was stirred at 90 °C under Ar for 16 h in a high-pressure tube. Then, the resulting mixture was hydrolyzed with H_2O (5 mL), and the solution was extracted with AcOEt (3 × 15 mL). The combined organic phases were dried with anhydrous $MgSO_4$ and evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/AcOEt) to yield products **5**. The yields and the physical and spectroscopic data follow.

(S_S,1*R*)-*N*-(*tert*-Butylsulfinyl)-3-methylene-2,3-dihydro-1*H*-inden-1-amine (5a): The representative procedure was followed by using sulfinamide **4a** (165 mg, 0.5 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (21 mg, 0.08 mmol), and TBAA (242 mg, 0.8 mmol). Purification by column chromatography (hexane/acetone, 4:1) yielded **5a** (77 mg, 62%) as a white solid; m.p. 77–81 °C. R_f = 0.34 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +21 (*c* = 1.00, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.49 (m, 1 H), 7.44–7.38 (m, 1 H), 7.35–7.28 (m, 2 H), 5.50 (t, *J* = 2.4 Hz, 1 H), 5.10 (t, *J* = 2.0 Hz, 1 H), 4.89 (ddd, *J* = 10.3, 7.9, 5.1 Hz, 1 H), 3.42 (d, *J* = 9.9 Hz, 1 H), 3.38 (ddt, *J* = 17.0, 7.9, 1.9 Hz, 1 H), 2.79 (ddt, *J* = 17.0, 5.0, 2.5 Hz, 1 H), 1.26 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.4 (C), 145.9 (C), 140.5 (C), 128.9 (CH), 128.8 (CH), 125.5 (CH), 120.8 (CH), 104.6 (CH_2), 59.8 (CH), 56.3 (C), 42.7 (CH_2), 22.9 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3166, 1643, 1041, 859, 754 cm^{-1}. LRMS (EI): *m*/*z* (%) = 191 (17), 145 (25), 144 (61), 143 (52), 130 (53), 129 (73), 128 (100), 127 (28), 116 (21), 115 (69), 103 (14), 102 (12), 89 (14), 77 (20), 75 (11), 65 (11), 64 (14), 63 (32), 56 (32), 55 (14), 51 (26). HRMS (EI): calcd. for $C_{10}H_9NOS$ [M – C_4H_{10}]$^+$ 191.0405; found 191.0405.

(R_S,1*S*)-*N*-(*tert*-Butylsulfinyl)-3-methylene-2,3-dihydro-1*H*-inden-1-amine (*ent*-5a): The representative procedure was followed by using sulfinamide *ent*-**4a** (165 mg, 0.5 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (21 mg, 0.08 mmol), and TBAA (242 mg, 0.8 mmol). Purification by column chromatography (hexane/acetone, 4:1) yielded *ent*-**5a** (77 mg, 62%) as a white solid. The physical and spectroscopic data were the same as the data for **5a**. $[\alpha]_D^{20}$ = –23 (*c* = 1.00, CH_2Cl_2).

(S_S,1*R*)-*N*-(*tert*-Butylsulfinyl)-6-methoxy-3-methyl-1*H*-inden-1-amine (5b′): The representative procedure was followed by using sulfinamide **4b** (116 mg, 0.32 mmol), $Pd(OAc)_2$ (9.0 mg, 0.0432 mmol, 14 mol-%), PPh_3 (42 mg, 0.16 mmol), and TBAA (293 mg, 0.97 mmol). Purification by column chromatography (hexane/acetone, 3:1) yielded **5b′** (62 mg, 69%) as a brown solid; m.p. 88–96 °C. R_f = 0.31 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = –124 (*c* = 0.94, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 8.2 Hz, 1 H), 7.04 (*J* = 2.4 Hz, 1 H), 6.85 (dd, *J* = 8.2, 2.4 Hz, 1 H), 6.18–6.16 (m, 1 H), 4.76 (d, *J* = 10.2 Hz, 1 H), 3.83 (s, 3 H), 3.24 (d, *J* = 10.2 Hz, 1 H), 2.07 (t, *J* = 1.8 Hz, 3 H), 1.26 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.9 (C), 147.4 (C), 140.9 (C), 137.4 (C), 130.7 (CH), 119.8 (CH), 112.7 (CH), 111.1 (CH), 63.1 (CH_3), 56.4 (C), 55.8 (CH), 22.9 (CH_3), 13.1 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3191, 1612, 1480, 1274, 1049, 1030, 822 cm^{-1}. LRMS (EI): *m*/*z* (%) = 207 (15), 175 (10), 174 (18), 173 (100), 172 (21), 160 (17), 158 (31), 144 (12), 143 (15), 130 (27), 115 (15), 103 (21), 77 (14), 57 (11). HRMS (EI): calcd. for $C_{15}H_{21}NO_2S$ 279.1293; found 279.1294.

(S_S,1*R*)-*N*-(*tert*-Butylsulfinyl)-6-fluoro-3-methylene-2,3-dihydro-1*H*-inden-1-amine (5c): The representative procedure was followed by using sulfinamide **4c** (210 mg, 0.6 mmol), $Pd(OAc)_2$ (5.4 mg, 0.024 mmol), PPh_3 (26 mg, 0.1 mmol), and TBAA (302 mg, 1.0 mmol). Purification by column chromatography (hexane/AcOEt, 2:1) yielded **5d** (107 mg, 67%) as a brown solid; m.p. 94–98 °C. R_f = 0.38 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +31 (*c* = 1.01, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (dd, *J* = 8.4, 5.1 Hz, 1 H), 7.08–7.03 (m, 1 H), 7.00 (*J* = 8.5, 2.4 Hz, 1 H), 5.41 (t, *J* = 2.3 Hz, 1 H), 5.0 (t, *J* = 1.8 Hz, 1 H), 4.84 (ddd, *J* = 9.8, 8.3, 5.7 Hz, 1 H), 3.40 (ddt, *J* = 17.0, 8.0, 1.9 Hz, 1 H), 3.38 (d, *J* = 8.3 Hz, 1 H), 2.80 (ddt, *J* = 17.0, 5.2, 2.5 Hz, 1 H), 1.27 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5 (d, *J* = 248.1 Hz, C), 148.1 (d, *J* = 7.7 Hz, C), 145.2 (C), 136.5 (d, *J* = 2.4 Hz, C), 122.3 (d, *J* = 8.9 Hz, CH), 116.4 (d, *J* = 23.4 Hz, CH), 112.0 (d, *J* = 22.5 Hz, CH), 104.1 (CH_2), 59.5 (CH), 56.4 (C), 43.1 (CH_2), 22.9 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3189, 1646, 1480, 1046, 1032, 862 cm^{-1}. LRMS (EI): *m*/*z* (%) = 209 (18), 163 (24), 162 (59) [M – 105]$^+$, 161 (55), 148 (56), 147 (67), 146 (100), 145 (13), 134 (21), 133 (78), 127 (20), 121 (10), 120 (10), 107 (12). HRMS (EI): calcd. for $C_{10}H_8FNOS$ [M – C_4H_8]$^+$ 209.0311; found 209.0321.

(S_S,1*R*)-*N*-(*tert*-Butylsulfinyl)-7-fluoro-3-methylene-2,3-dihydro-1*H*-inden-1-amine (5d): The representative procedure was followed by using sulfinamide **4d** (210 mg, 0.6 mmol), $Pd(OAc)_2$ (5.4 mg, 0.024 mmol), PPh_3 (26 mg, 0.1 mmol), and TBAA (302 mg, 1.0 mmol). Purification by column chromatography (hexane/AcOEt, 2:1) yielded **5d** (93 mg, 58%) as a white solid; m.p. 70–75 °C. R_f = 0.32 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +22 (*c* = 1.02, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31 (t, *J* = 3.8 Hz, 1 H), 7.30 (t, *J* = 3.4 Hz, 1 H), 7.00–6.90 (m, 1 H), 5.57 (t, *J* = 2.4 Hz, 1 H), 5.16 (t, *J* = 1.6 Hz, 1 H), 5.07 (ddd, *J* = 9.8, 8.1, 3.0 Hz, 1 H), 3.36 (d, *J* = 10.2 Hz, 1 H), 3.33 (ddd, *J* = 17.5, 8.0, 2.4 Hz, 1 H), 2.93 (ddd, *J* = 17.5, 5.0, 2.1 Hz, 1 H), 1.22 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4 (d, *J* = 251.6 Hz, C), 146.0 (d, *J* = 2.1 Hz, C), 143.9 (d, *J* = 4.9 Hz, C), 131.8 (C), 130.9 (d, *J* = 7.2 Hz, CH), 116.6 (d, *J* = 3.6 Hz, CH), 115.5 (d, *J* = 20.1 Hz, CH), 106.4 (CH_2), 57.7 (CH), 56.3 (C), 41.9 (CH_2), 22.6 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3138, 1583, 1473, 1239, 1029 cm^{-1}. LRMS (EI): *m*/*z* (%) = 209 (14), 163 (19), 162 (45), 161 (38), 149 (9), 148 (68), 147 (75), 146 (100), 145 (12), 134 (17), 133 (91), 128 (10), 127 (21), 120 (10), 115 (9), 107 (11). HRMS (EI): calcd. for $C_{10}H_8FNOS$ [M – C_4H_{10}]$^+$ 209.0311; found 209.0315.

(S_S,5*R*)-*N*-(*tert*-Butylsulfinyl)-7-methylene-6,7-dihydro-5*H*-cyclopenta[*b*]pyridin-5-amine (5e): The representative procedure was followed by using sulfinamide **4e** (200 mg, 0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol), PPh_3 (31 mg, 0.12 mmol), and TBAA (302 mg, 1.0 mmol). Purification by column chromatography (hexane/acetone, 3:1) yielded **5e** (84 mg, 56%) as an orange oil; R_f = 0.25 (AcOEt). $[\alpha]_D^{20}$ = –2 (*c* = 1.0, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 4.8 Hz, 1 H), 7.73 (ddd, *J* = 7.7, 1.4, 1.0 Hz, 1 H), 7.19 (dd, *J* = 7.7, 4.8 Hz, 1 H), 6.01 (t, *J* = 2.05 Hz, 1 H), 5.21 (t, *J* = 2.0 Hz, 1 H), 4.89 (td, *J* = 8.9, 4.8 Hz, 1 H), 3.63 (d, *J* = 9.6 Hz, 1 H), 3.41 (ddt, *J* = 17.3, 8.1, 2.1 Hz, 1 H), 2.83 (ddt, *J* = 17.3, 5.0, 2.6 Hz, 1 H), 1.25 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4 (C), 150.6 (CH), 145.0 (C), 139.1 (C), 133.8 (CH), 123.2 (CH), 108.2 (CH_2), 57.2 (CH), 56.4 (C), 40.6 (CH_2), 22.8, (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3179, 1437, 1069, 722 cm^{-1}. LRMS (EI): *m*/*z* (%) = 192 (14), 146 (24), 145 (62), 144 (50), 143 (23), 131 (52), 130 (100), 129 (56), 128 (10), 118 (11), 117 (22), 116 (10), 104 (10), 103 (13), 90 (10), 89 (12), 77 (17), 63 (16), 56 (17), 51 (14). HRMS (EI): calcd. for $C_9H_8N_2OS$ [M – C_4H_{10}]$^+$ 192.0357; found 192.0378.

(S_S,3*R*)-*N*-(*tert*-Butylsulfinyl)-1-methylene-2,3-dihydro-1*H*-benzo[*b*]-cyclopenta[*d*]thiophen-3-amine (5f): The representative procedure was followed by using the sulfinamide **4f** (170 mg, 0.44 mmol), $Pd(OAc)_2$ (4.4 mg, 0.0198 mmol), PPh_3 (21 mg, 0.08 mmol), and TBAA (242 mg, 0.8 mmol). Purification by column chromatog-

raphy (hexane/acetone, 6:1) yielded **5f** (32 mg, 24%) as a white solid; m.p. 110–118 °C. R_f = 0.35 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +36 (c = 1.01, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.7 Hz, 1 H), 7.80 (ddd, J = 8.0, 1.1, 0.7 Hz, 1 H), 7.43 (ddd, J = 7.9, 7.2, 1.2 Hz, 1 H), 7.36 (ddd, J = 8.0, 7.2, 1.3 Hz, 1 H), 5.47 (t, J = 2.2 Hz, 1 H), 5.11 (ddd, J = 9.7, 7.6, 3.4 Hz, 1 H), 5.07 (t, J = 1.8 Hz, 1 H), 3.70 (ddt, J = 16.7, 7.5, 1.9 Hz, 1 H), 3.57 (d, J = 9.4 Hz, 1 H), 3.16 (ddt, J = 16.7, 3.4, 2.1 Hz, 1 H), 1.24 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.7 (C), 145.8 (C), 142.6 (C), 141.0 (C), 132.6 (C), 125.2 (CH), 125.1 (CH), 123.9 (CH), 122.8 (CH), 103.2 (CH_2), 57.9 (CH), 56.5 (C), 46.8 (CH_2), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3152, 1634, 1034, 734 cm^{-1}. LRMS (EI): m/z (%) = 207 (25), 202 (10), 201 (50), 200 (77), 199 (100), 198 (12), 186 (35), 185 (17), 184 (38), 172 (20), 171 (42), 139 (10), 115 (10). HRMS (EI): calcd. for $C_{12}H_{11}NOS_2$ [M – C_4H_8]$^+$ 249.0282; found 249.0310.

(S_S,2R)-*N*-(*tert*-Butylsulfinyl)-4-methylene-1,2,3,4-tetrahydronaphthalen-2-amine (5g): The representative procedure was followed by using sulfinamide **4g** (51 mg, 0.15 mmol), $Pd(OAc)_2$ (1.3 mg, 0.006 mmol), PPh_3 (6.3 mg, 0.024 mmol), and TBAA (68 mg, 0.225 mmol). The conversion after 14 h was 80%, and the ^{1}H NMR spectroscopic data of the crude material also showed a mixture of isomers (*exo*/*endo*, 10:7). Purification by column chromatography (hexane/acetone, 5:1) yielded **5g** (18 mg, 45% overall yield). It was possible to isolate 5 mg of the pure *exo* isomer as a yellow oil. R_f = 0.32 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +21 (c = 0.5, CH_2Cl_2). Data for *exo* isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.61 (m, 1 H), 7.23–7.15 (m, 2 H), 7.13–7.06 (m, 1 H), 5.61 (s, 1 H), 5.08 (s, 1 H), 3.90–3.78 (m, 1 H), 3.32 (d, J = 5.8 Hz, 1 H), 3.17 (dd, J = 16.4, 4.5 Hz, 1 H), 2.96–2.80 (m, 2 H), 2.64 (dd, J = 13.9, 8.4 Hz, 1 H), 1.15 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1 (C), 134.1 (C), 134.0 (C), 129.7 (CH), 128.3 (CH), 126.6 (CH), 124.1 (CH), 111.3 (CH_2), 55.8 (C), 51.2 (CH), 41.0 (CH_2), 37.9 (CH_2), 22.7 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3201, 1629, 1052, 734 cm^{-1}. LRMS (EI): m/z (%) = 144 (20), 143 (100), 142 (22), 129 (19), 128 (34), 115 (14). HRMS (EI): calcd. for $C_{11}H_{11}NOS$ [M – C_4H_{10}]$^+$ 205.0561; found 205.0570.

(S_S,7S)-*N*-(*tert*-Butylsulfinyl)-5-methylene-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-amine (5h): The representative procedure was followed by using sulfinamide **4h** (116 mg, 0.32 mmol), $Pd(OAc)_2$ (3.6 mg, 0.016 mmol), PPh_3 (16.8 mg, 0.064 mmol), and TBAA (145 mg, 0.48 mmol). Purification by column chromatography (hexane/acetone, 5:1) yielded **5h** (62 mg, 70%) as a white solid; m.p. 78–84 °C. R_f = 0.33 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +54 (c = 0.71, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.25–7.13 (m, 3 H), 7.12–7.06 (m, 1 H), 5.25–5.22 (m, 1 H), 5.18 (d, J = 2.0 Hz, 1 H), 3.79–3.64 (m, 1 H), 3.51 (s, 1 H), 2.95–2.74 (m, 2 H), 2.73–2.48 (m, 2 H), 2.16–1.98 (m, 1 H), 1.94–1.65 (m, 1 H), 1.23 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.7 (C), 143.2 (C), 139.4 (C), 129.2 (CH), 128.3 (CH), 127.5 (CH), 126.5 (CH), 117.5 (CH_2), 55.8 (CH), 55.8 (C), 44.1 (CH_2), 34.3 (CH_2), 31.0 (CH_2), 22.7 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3222, 1716, 1241, 1027, 751 cm^{-1}. LRMS (EI): m/z (%) = 221 (13), 158 (21), 157 (100), 143 (12), 142 (13), 141 (11), 131 (35), 130 (14), 129 (53), 128 (24), 116 (13), 115 (26), 91 (25). HRMS (EI): calcd. for $C_{12}H_{15}NOS$ [M – C_4H_8]$^+$ 221.0874; found 221.0884.

(S_S,1R)-*N*-(*tert*-Butylsulfinyl)-1-methyl-3-methylene-2,3-dihydro-1*H*-inden-1-amine (5j): The representative procedure was followed by using sulfinamide **4j** (30 mg, 0.087 mmol, diastereomeric mixture, 3:1) $Pd(OAc)_2$ (0.974 mg, 0.0043 mmol), PPh_3 (4.6 mg, 0.0174 mmol), and TBAA (42 mg, 0.14 mmol). The ^{1}H NMR spectroscopic data of the crude product showed a mixture of four different products [major diastereoisomers: *exo*-**5j*a*** (52%) and *endo*-**5j*b*** (22%); minor diastereoisomers: *exo*-**5j*c*** (25%) and *endo*-**5j*d*** (1%)]. Purification by column chromatography (hexane/acetone, 6:1) yielded **5j** (17 mg, 74%). It was possible to enrich the proportion of **5j*a*** as a mixture of **5j*a*** (75%), **5j*b*** (5%), and **5j*c*** (20%) as a yellow oil; R_f = 0.26 (hexane/AcOEt, 1:1). Data for **5j*a***: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.49 (m, 1 H), 7.38–7.34 (m, 1 H), 7.32–7.28 (m, 2 H), 5.50 (t, J = 2.4 Hz, 1 H), 5.09 (t, J = 1.9 Hz, 1 H), 3.44 (br. s, 1 H), 3.19 (dt, J = 16.4, 2.4 Hz, 1 H), 2.95 (dt, J = 16.4, 1.9 Hz, 1 H), 1.60 (s, 1 H), 1.20 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.3 (C), 146.0 (C), 139.7 (C), 129.0 (CH), 128.7 (CH), 123.8 (CH), 120.8 (CH), 104.7 (CH_2), 64.0 (C), 55.8 (C), 49.2 (CH_2), 28.2 (CH_3), 22.7 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3202, 1645, 1472, 1364, 1049, 756 cm^{-1}. LRMS (EI): m/z (%) = 207 (3), 167 (11), 145 (10), 144 (59), 143 (20), 142 (29), 141 (32), 130 (12), 129 (100), 128 (59), 127 (21), 115 (20), 71 (10), 63 (15), 56 (12). HRMS (EI): calcd. for $C_{11}H_{11}NOS$ [M – C_4H_{10}]$^+$ 205.0561; found 205.0568.

(S_S,2R)-*N*-(*tert*-Butylsulfinyl)-2-methyl-4-methylene-1,2,3,4-tetrahydronaphthalen-2-amine (5k): The representative procedure was followed by using sulfinamide **4k** (101 mg, 0.28 mmol), $Pd(OAc)_2$ (2.5 mg, 0.0112 mmol), PPh_3 (11.7 mg, 0.045 mmol), and TBAA (127 mg, 0.42 mmol). The ^{1}H NMR spectroscopic data showed the crude product as a mixture (*exo*/*endo*, 78:22, 91% conversion). Purification by column chromatography (hexane/acetone, 5:1) yielded **5k** (38 mg, 49%, *exo* product) as a white solid; m.p. 91–99 °C. R_f = 0.22 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +46 (c = 0.98, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.62 (m, 1 H), 7.22–7.13 (m, 2 H), 7.11–7.03 (m, 1 H), 5.62 (d, J = 0.8 Hz, 1 H), 5.04 (d, J = 0.8 Hz, 1 H), 3.24 (s, 1 H), 3.12 (d, J = 16.6 Hz, 1 H), 2.93 (d, J = 16.6 Hz, 1 H), 2.71–2.58 (m, 2 H), 1.46 (s, 3 H), 1.00 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 140.5 (C), 134.3 (C), 133.6 (C), 129.7 (CH), 128.2 (CH), 126.5 (CH), 123.8 (CH), 110.9 (CH_2), 55.8 (C), 54.5 (C), 47.1 (CH_2), 43.4 (CH_2), 28.4 (CH_3), 22.5 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3213, 1628, 1455, 1051 cm^{-1}. LRMS (EI): m/z (%) = 158 (24), 157 (100), 156 (11), 143 (21), 142 (21), 141 (10), 128 (13), 115 (11). HRMS (EI): calcd. for $C_{12}H_{15}NOS$ [M – C_4H_8]$^+$ 221.0874; found 221.0898.

(S_S,7R)-*N*-(*tert*-Butylsulfinyl)-7-methyl-5-methylene-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-7-amine (5l): The representative procedure was followed by using sulfinamide **4e** (186 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PPh_3 (26 mg, 0.1 mmol), and TBAA (272 mg, 0.9 mmol). Purification by column chromatography (hexane/acetone, 5:1) yielded **5e** (99 mg, 68%) as a yellow oil; R_f = 0.30 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +19 (c = 0.98, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28–7.23 (m, 1 H), 7.18–7.14 (m, 2 H), 7.11–7.06 (m, 1 H), 5.27 (s, 1 H), 5.23 (s, 1 H), 3.64 (s, 1 H), 2.87 (dd, J = 15.4, 10.4 Hz, 1 H), 2.69 (dd, J = 15.4, 10.4 Hz, 1 H), 2.67 (d, J = 13.0 Hz, 1 H), 2.50 (d, J = 12.9 Hz, 1 H), 1.92 (dd, J = 13.5, 9.5 Hz, 1 H), 1.81 (dd, J = 13.5, 9.5 Hz, 1 H), 1.48 (s, 3 H), 1.22 (s, 9 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.1 (C), 142.7 (C), 139.5 (C), 129.4 (CH), 128.2 (CH), 127.4 (CH), 126.4 (CH), 118.0 (CH_2), 57.2 (C), 55.9 (C), 49.6 (CH_2), 40.2 (CH_2), 30.4 (CH_2), 22.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3216, 1626, 1050, 913 cm^{-1}. LRMS (EI): m/z (%) = 235 (4), 172 (34), 171 (100), 143 (27), 141 (11), 131 (44), 130 (16), 129 (40), 128 (27), 116 (11), 115 (25), 91 (23). HRMS (EI): calcd. for $C_{13}H_{15}NOS$ [M – C_4H_{10}]$^+$ 233.0874; found 233.0880.

(S_S,1R)-*N*-(*tert*-Butylsulfinyl)-2,2-dimethyl-3-methylene-2,2-dihydro-1*H*-inden-1-amine (5n): The representative procedure was followed by using sulfinamide **4n** (40 mg, 0.11 mmol), $Pd(OAc)_2$ (1.23 mg, 0.0055 mmol), PPh_3 (5.8 mg, 0.0022 mmol), and TBAA

(50 mg, 0.165 mmol). Purification by column chromatography (hexane/AcOEt, 5:1) yielded **5n** (25 mg, 83%) as a yellow oil; R_f = 0.53 (hexane/AcOEt, 1:1). $[\alpha]_D^{20}$ = +17 (c = 0.82, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.46 (m, 1 H), 7.36–7.26 (m, 3 H), 5.49 (s, 1 H), 5.02 (s, 1 H), 4.51 (d, J = 11.1 Hz, 1 H), 3.66 (d, J = 11.0 Hz, 1 H), 1.48 (s, 3 H), 1.33 (s, 9 H), 1.09 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.6 (C), 143.5 (C), 139.0 (C), 128.9 (CH), 128.6 (CH), 124.8 (CH), 121.2 (CH), 102.9 (CH_2), 70.7 (CH), 56.7 (C), 47.8 (C), 25.1 (CH_3), 25.0 (CH_3), 23.1 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3238, 1713, 1639, 1603, 1464, 1059 cm^{-1}. LRMS (EI): m/z (%) = 219 (37), 173 (20), 172 (11), 171 (24), 170 (36), 160 (43), 159 (17), 158 (84), 157 (31), 156 (100), 155 (23), 154 (10), 144 (16), 143 (60), 142 (28), 141 (59), 130 (25), 129 (33), 128 (54), 127 (17), 116 (14), 115 (40). HRMS (EI): calcd. for $C_{12}H_{13}NOS$ [M – C_4H_{10}]$^+$ 219.0718; found 219.0718.

Compound 5o: The representative procedure was followed by using sulfinamide **4o** (37 mg, 0.1 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol), PPh_3 (5.2 mg, 0.02 mmol), and TBAA (45 mg, 0.15 mmol). The ^{1}H NMR spectroscopic data of the crude material showed a very complex mixture of isomers that could not be purified. Conversion of the starting material was completed. Column chromatography (hexane/acetone, 4:1) was applied to the crude product to obtain **5o** (22 mg, 75%) as a brown oil; R_f = 0.50 (hexane/AcOEt, 1:1). The ^{1}H and ^{13}C NMR spectroscopic data are included in the Supporting Information. IR (ATR): $\tilde{\nu}$ = 3226, 2922, 1663, 1457, 1062, 748 cm^{-1}. LRMS (EI): m/z (%) = 233 (13), 184 (9), 170 (30), 169 (100), 168 (15), 167 (14), 156 (11), 142 (25), 141 (43), 130 (10), 129 (15), 128 (18), 115 (16). HRMS (EI): calcd. for $C_{13}H_{13}NOS$ [M – C_4H_{10}]$^+$ 231.0718; found 231.0721.

Desulfinylation of Compound 5a. Synthesis of (*R*)-3-Methylene-2,3-dihydro-1*H*-inden-1-amine (6a): To a solution of **5a** (70 mg, 0.28 mmol) in dry THF (1 mL) at 0 °C was added HCl (6 M solution, 0.33 mL). The mixture was stirred at room temperature for 1 h. Then, it was cooled to 0 °C, and NaOH (2 M solution, 5 mL) was added. The mixture was diluted with AcOEt (10 mL), and the organic phase was separated. The aqueous phase was extracted with AcOEt (2 × 15 mL). Then, the organic phases were collected, washed with NaOH (2 M solution, 10 mL) and H_2O (10 mL), dried with anhydrous $MgSO_4$, and evaporated (15 Torr) to yield free amine **6a** (38 mg, 93%) as a yellow oil; R_f = 0.26 (CH_2Cl_2/MeOH, 9:1). $[\alpha]_D^{20}$ = +10.4 (c = 0.99, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.46 (m, 1 H), 7.41–7.36 (m, 1 H), 7.32–7.24 (m, 2 H), 5.47 (t, J = 2.4 Hz, 1 H), 5.06 (t, J = 2.0 Hz, 1 H), 4.40 (dd, J = 7.6, 5.2 Hz, 1 H), 3.18 (ddt, J = 16.4, 7.7, 1.9 Hz, 1 H), 2.49–2.40 (m, 1 H), 2.04 (s, 2 H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.5 (C), 147.3 (C), 140.1 (C), 128.9 (CH), 127.9 (CH), 124.4 (CH), 120.7 (CH), 103.7 (CH_2), 54.6 (CH), 43.6 (CH_2) ppm. IR (ATR): $\tilde{\nu}$ = 3351, 3281, 1642, 867 cm^{-1}. LRMS (EI): m/z (%) = 145 (42), 144 (100), 143 (13), 130 (25), 129 (10), 128 (19), 127 (14), 115 (12). HRMS (EI): calcd. for $C_{10}H_{11}N$ 145.0891; found 145.0878.

Supporting Information (see footnote on the first page of this article): Spectroscopic data for imines **3a**, **3g**, **3h**, and **3j** and copies of the ^{1}H and ^{13}C NMR spectra of imines **3**, homoallylamine derivatives **4**, and compounds **5** and **6a**.

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