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Indium-Promoted Diastereo- and Regioselective Propargylation of Chiral Sulfinylimines

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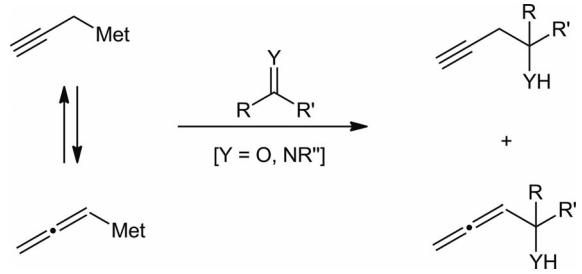
The reaction of different chiral imines **3** derived from aldehydes or ketones with the silylated propargyl bromide **4b** under sonication in the presence of indium metal led mainly or exclusively to the formation of protected homopropargylamines **5** in a diastereoselective manner. Of special interest are the ketimine derivatives because the new stereocenter has a quaternary configuration. The selective deprotection of the two protecting groups, the silicon and sulfinyl moieties, was easily achieved by conventional methodologies.

Introduction

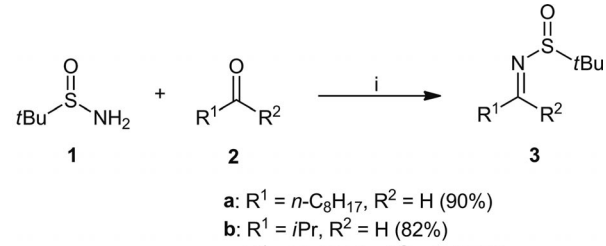
The addition of organometallic reagents to carbonyl compounds and their imines is one of the most useful and versatile methodologies for creating both a new carbon–carbon bond and also a new functionality, an alcohol or amine, respectively.[1] The enantio- and/or diastereoselective version of this process is of additional interest because at least one new stereogenic center is generated.[2] Moreover, when an allyl or propargyl organometallic reagent is used,[3] the process offers the possibility of further transformation of the unsaturation to form more carbon–carbon or carbon–heteroatom bonds.[4] However, in the case of propargylation, α- or γ-substitution (regioselectivity) also involves chemoselectivity because a propargyl or allenyl moiety can be alternatively produced, respectively (Scheme 1).[5] Continuing our studies of the diastereoselective Barbier-type addition of allyl halides to chiral sulfinylimines promoted by indium metal,[6] we report herein the regioselective propargylation of the same starting imines to give the expected chiral *N*-protected homopropargylic amines.[7,8]

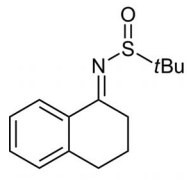


Scheme 1. Regio- and chemoselectivity in the addition of propargyl/allenyl metals to carbonyl compounds and imines.

Results and Discussion

The starting sulfinylimines[9] **3** were prepared according to the standard procedure described in the literature[10] by reaction of commercially available (*R*)- or (*S*)-*tert*-butanesulfinamide (**1**) with aldehydes or ketones **2** in the presence of titanium tetraethoxide in THF (Scheme 2).





3o

a: R^1 = *n*-C_8H_{17}, R^2 = H (90%)
b: R^1 = *i*Pr, R^2 = H (82%)
c: R^1 = $Ph(CH_2)_2$, R^2 = H (95%)
d: R^1 = $PhCH_2$, R^2 = H (78%)
e: R^1 = Ph, R^2 = H (86%)
f: R^1 = 4-$O_2NC_6H_4$, R^2 = H (75%)
g: R^1 = 4-HOC_6H_4, R^2 = H (67%)
h: R^1 = 2-$BrC_6H_4CH_2$, R^2 = H (65%)
i: R^1 = 2-BrC_6H_4, R^2 = H (94%)
j: R^1 = R^2 = Me (47%)
k: R^1 = Et, R^1 = Me (44%, *dr* 85:15)
l: R^1 = nC_5H_{11}, R^2 = Me (67%, *dr* 83:17)
m: R^1-R^2 = $(CH_2)_3CH$=CH (75%, *dr* 60:40)
n: R^1 = Ph, R^2 = Me (76%, *dr* >98:2)
o: (45%, *dr* >98:2)

Scheme 2. Synthesis of starting sulfinylimines. Reagents and conditions: i) $Ti(OEt)_4$ (2 equiv.), THF, 23 °C, 12 h (for aldehydes) or 66 °C, 5 h (for ketones).

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To optimize the reaction, we studied the propargylation of imine (*R*)-**3c** with propargyl bromides **4a** and **4b** under different reaction conditions. Thus, by using a slight excess of the imine in THF at 100 °C, the conversion was good, but a mixture of the corresponding compounds **5** and **6** was obtained (Table 1, entry 1). The addition of sodium iodide under aqueous conditions did not improve either the conversion or the selectivity (Table 1, entry 2). The use of a mixture of DMF/Et_2O as solvent gave good conversion but low selectivity (Table 1, entry 3). Better conversion but again low selectivity was obtained by using sonication with or without THF (Table 1, entries 4 and 5, respectively). We then studied the same reaction but with the bromide **4b**: In this case we found that sonication in THF gave quantitative conversion and selectivity, as well as high diastereoselectivity (Table 1, entry 6 and footnote [d]). Without sonication, and even under forcing conditions, the reaction did not proceed (Table 1, entry 7). Finally, and just for comparison, we carried out two experiments with bromide **4b** in which indium was replaced by zinc with or without sonication; low or complete conversion was obtained, but with low diastereomeric excess in the second case (Table 1, entries 8 and 9, and footnote [e]).

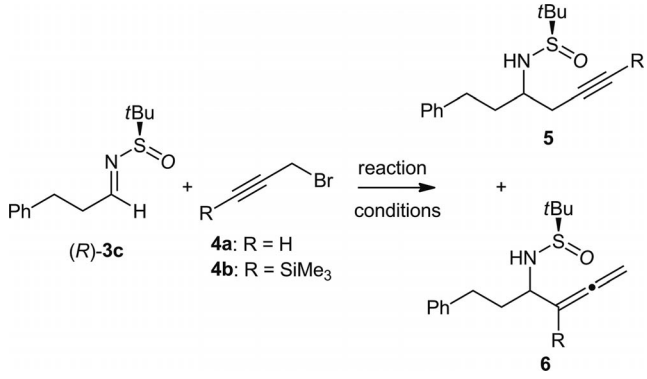
Having obtained the best conditions (Table 1, entry 6), we carried out the reactions of aldimines **3a**–**i** with the silylated compound **4b**, obtaining in general good diastereoselectivities and isolated yields. Purification by column chromatography afforded the major diastereomer in pure form, which in all cases present the stereochemistry shown in Table 2. Only for compounds **5a** and **5h** were small amounts of the corresponding allenes detected by ^{1}H NMR spectroscopy (Table 2, entries 1 and 8, respectively). The use of the enantiomer (*S*)-**3h** led to the formation of compound **5h** with the expected reversed configuration at both stereocenters (Table 2, entry 8). Finally, it is worthy noting that compound (*R*)-**3f** containing an electron-deficient aromatic ring was not reactive at all in the same process under similar reaction conditions (Table 2, entry 6).

In the second part of this study we considered the propargylation of ketimines **3j**–**o** under the same optimized reaction conditions shown in Tables 1 and 2. Ketimines **3k**–**m** were obtained as *E*/*Z* mixtures of diastereomers (see Scheme 2) and used in the reactions without further purification. This process is of additional synthetic interest because the newly created stereocenter is quaternary, these types of chiral compounds not being so readily accessible by conventional methodologies.[11] As expected, the diastereoselectivity was modest for the cyclohexenone derivative **5m**, and surprisingly poor for the acetophenone derivative **5n** (Table 3, entries 4 and 5, respectively). In the other cases, including the butanone derivative **5k**, the diastereoselectivity was excellent (Table 3, entries 2, 3, and 6). Finally, as was commented upon for compound **5h**, the opposite configuration at the new stereocenter was also observed in the case of imine (*S*)-**3n** (Table 3, entry 5).

From a mechanistic point of view, the formation of the propargylic product **5** is determined by the nature of the organoindium intermediate. Thus, the reaction of the starting bromide **4b** with indium metal initially gives the corresponding propargylic intermediate **I**, which, by metallotropic rearrangement, is in equilibrium with the allenylindium **II**. Owing to the well-known stabilization effect of the silicon atom on α-carbanions (d orbital interaction[12]), the most stable species is **II**, and considering that in allylindium intermediates γ addition is preferred over α addition,[13] transition state **IV** is preferred to **III**, so the final product **5** is mainly or exclusively obtained (Scheme 3).

Concerning the diastereoselectivity of the new stereocenter, the structure of compound **5** was assigned by comparing the ^{1}H NMR spectra of compounds (*R*)-**5b** and (*R*)-**5e** with those reported in the literature by Chemla and Ferreira[8b] with allenylzinc intermediates: We found that in our case the configuration of the new stereocenter is opposite to that previously described. Thus, we concluded that nucleophilic attack takes place in our case at the *Si* face for imines with the R_S configuration and at the *Re* face for imines with the S_S configuration. This conclusion shows that both methodologies (indium- or zinc-promoted propargylation) are complementary. In the case of the reaction

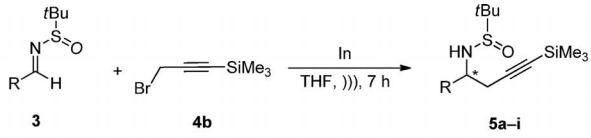
Table 1. Optimization of the reaction conditions;)))) = sonication.



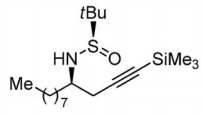
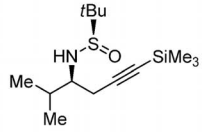
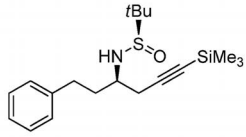
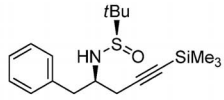
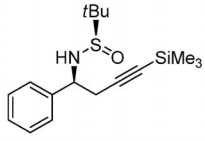
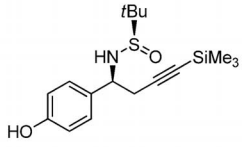
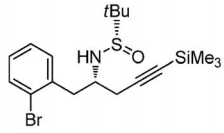
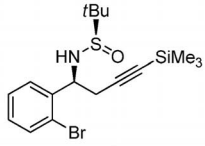
Entry	**4** (amount, equiv.)	Reaction conditions	Conv. [%][a]	Products **5/6** [%][b]
1	**4a** (1.2)	In (1.1 equiv.), THF, 100 °C, 20 h	82	48:34
2	**4a** (6)	In (6 equiv.), NaI (4 equiv.), THF/H_2O, 23 °C, 20 h	49	23:26
3	**4a** (2.5)	In (3.5 equiv.), DMF-Et_2O (1:1), 60 °C, 20 h	97 (68)[c]	49:48
4	**4a** (3.3)	In (3.3 equiv.), THF,))), 4.5 h	100	50:50
5	**4a** (3.3)	In (3.3 equiv.),))), 6 h	100	69:31
6	**4b** (3.3)	In (3.3 equiv.), THF,))), 7 h	100	100 (80)[c,d]/–
7	**4b** (3.3)	In (3.3 equiv.), THF, 60 °C, 7 h	<5	–
8	**4b** (3.3)	Zn (3.3 equiv.), THF,))), 7 h	25	25/–
9	**4b** (3.3)	Zn (3.3 equiv.), THF, 90 °C, 7 h	100	100[e]/–

[a] Based on the consumption of the starting material **3**. [b] Based on the ^{1}H NMR spectra of the crude products. [c] Isolated yield after column chromatography. [d] *dr* = 88:12 by ^{1}H NMR analysis of the reaction crude. [e] *dr* = 53:47 by ^{1}H NMR analysis of the reaction crude.

Table 2. Propargylation of aldimines **3**.



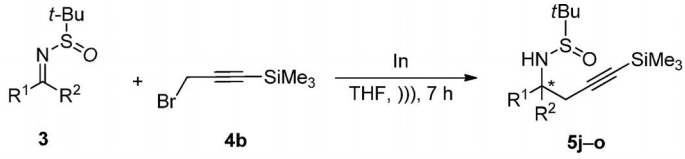
3 **4b** **5a–i**

Entry	Imines		Products			
	3	R	**5**	Structure[a]	*dr*[b]	Yield [%][c]
1	(*R*)-**3a**	$Me(CH_2)_7$	**5a**[d]		>98:2	57
2	(*R*)-**3b**	*i*Pr	**5b**		90:10	58
3	(*R*)-**3c**	$Ph(CH_2)_2$	**5c**		88:12	80
4	(*R*)-**3d**	$PhCH_2$	**5d**		>98:2	73
5	(*R*)-**3e**	Ph	**5e**		88:12	69
6	(*R*)-**3f**	$4\text{-}NO_2C_6H_4$	**5f**	–	–	–
7	(*R*)-**3g**	$4\text{-}HOC_6H_4$	**5g**		79:21	51
8	(*S*)-**3h**	$2\text{-}BrC_6H_4CH_2$	**5h**[e]		95:5	63
9	(*R*)-**3i**	$2\text{-}BrC_6H_4$	**5i**		97:3	71

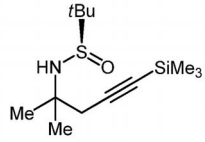
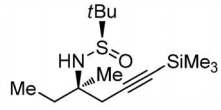
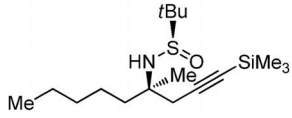
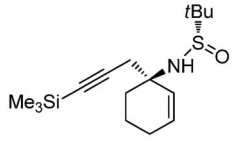
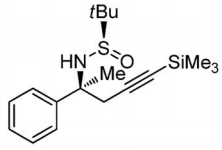
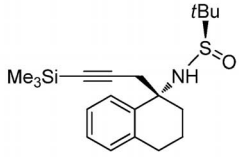
[a] Major diastereomer. [b] Diastereomeric ratio determined by ^{1}H NMR analysis of the reaction crude. [c] Isolated yield after column chromatography. [d] A 93:7 ratio of compound **5a** and the corresponding allene **6a** was revealed by ^{1}H NMR analysis of the reaction crude. [e] A 82:18 ratio of compound **5h** and the corresponding allene **6h** was revealed by ^{1}H NMR analysis of the reaction crude.

with zinc, transition state **V** has been proposed in which the zinc atom coordinates to only the nitrogen atom of the imine to form a six-membered ring in which the imine adopts the most stable *s-cis* conformation.[8a] In our case, we propose transition state **VI**, also involving a six-membered ring, but with the simultaneous coordination of the indium atom to both the nitrogen and oxygen atoms of the imine, so fixing a conformation in which nucleophilic attack takes place at the less hindered *Si* face for imines with the R_S configuration (Figure 1). However, and taking into account the diastereoselectivity found for ethyl methyl ketone and acetophenone derivatives **3k** and **3n** (Table 3, entries 2 and

Table 3. Propargylation of ketimines **3**.



3 **4b** **5j–o**

Entry	Imines		Products			
	3	R^1,R^2	**5**	Structure[a]	*dr*[b]	Yield [%][c]
1	(*R*)-**3j**	Me,Me	**5j**		–	47
2	(*R*)-**3k**	Et,Me	**5k**		>98:2	52
3	(*R*)-**3l**	$Me(CH_4)_4$, Me	**5l**		>98:2	63
4	(*S*)-**3m**	$(CH_2)_2CH{=}CH$	**5m**		75:25	67
5	(*R*)-**3n**	Ph,Me	**5n**		60:40	54
6	(*R*)-**3o**	–[d]	**5o**		>98:2	10

[a] Major diastereomer. [b] Diastereomeric ratio determined by ^{1}H NMR analysis of the reaction crude. [c] Isolated yield after column chromatography. [d] See Scheme 2.

5, respectively), in addition to steric interactions, a competing mechanism involving electronic effects could not be ruled out. It is worth noting that the diastereoselectivities obtained for homopropargylic amine derivatives **5k**–**m** (Table 3, entries 2–4) greatly exceed the *Z*/*E* isomeric ratio of the starting ketimines **3k**–**m** (Scheme 2). It seems that at the reaction temperature, one of the imine isomers preferentially undergoes propargylation concomitant with rapid imine isomer equilibration, leading to a dynamic kinetic resolution. Similar enhanced diastereoselectivities compared with the *E*/*Z* isomer ratios of the starting substrate have previously been observed for nucleophilic addition to *N*-*tert*-butanesulfinyl ketimines.[6l,10]

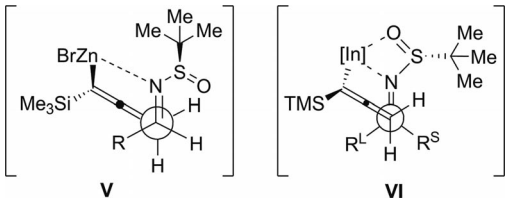
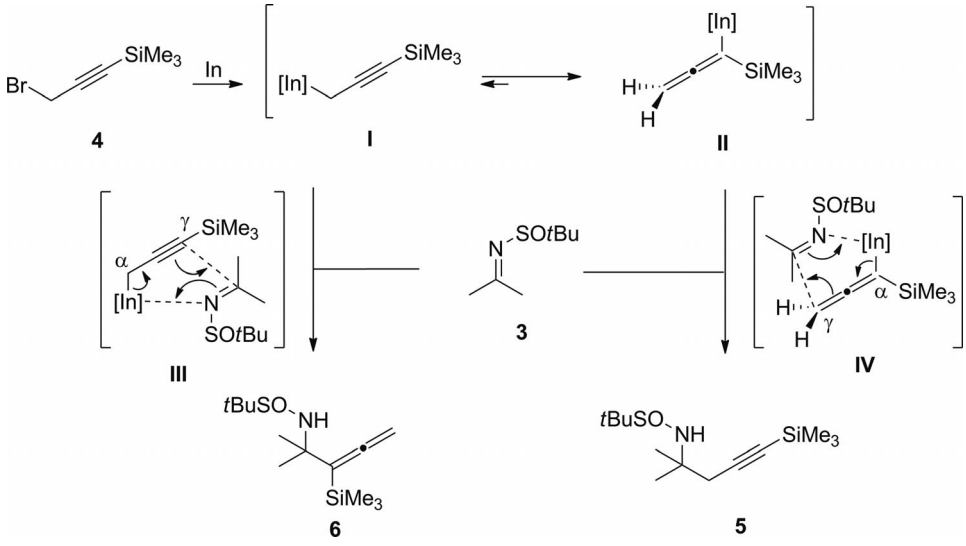
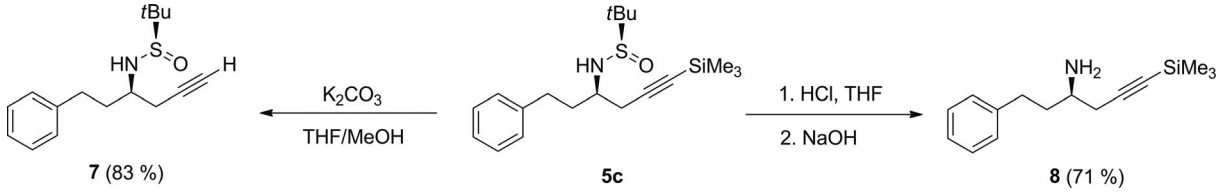


Figure 1. Transition states **V** and **VI**.

In the final part of this work we studied the orthogonal deprotection of the two protecting groups, the silicon and sulfinyl moieties. Thus, treatment of compound **5c** with potassium carbonate in THF/methanol gave exclusive desilylation to afford compound **7** in 83% yield. When the same starting material was treated successively with hydrogen



Scheme 3. Proposed mechanism for the propargylation of imines **4**.



Scheme 4. Selective deprotection of compound **5c**.

chloride and sodium hydroxide, desulfinylation occurred to give amine **8** as the only reaction product (Scheme 4).

Conclusions

From the results obtained in this study we can conclude that the indium-promoted propargylation of chiral aldimines and ketimines **3** with the silylated bromoalkyne **4b** is a versatile and useful methodology for preparing fully protected chiral homopropargylic amines in an enantiopure form. Selective deprotection of these compounds by conventional procedures allowed the preparation of the corresponding monoprotected compounds.

Experimental Section

General: All reactions requiring anhydrous conditions were performed in oven-dried glassware under argon. Unless otherwise indicated, all commercially available chemicals were purchased from Acros or Aldrich and used without purification. *N-tert*-Butanesulfinamides (S_S and R_S) were a gift of Medalchemy (>99% *ee* by chiral HPLC on a Chiracel AS column, 90:10 *n*-hexane/*i*PrOH, 1.2 mL/min, λ = 222 nm). TLC was performed on Merck silica gel 60 F_{254} using aluminium plates and visualized with phosphomolybdic acid (PMA) stain. Chromatographic purification was performed by flash chromatography using Merck silica gel 60 (0.040–0.063 mm) and *n*-hexane/EtOAc as eluent. IR spectra were measured (film) with a Nicolet Impact 510 P-FT spectrometer. Melting points were recorded with an OptiMelt (Stanford Research Systems) apparatus using open-glass capillaries. Gas chromatographic analyses (GLC) were determined 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) using nitrogen (2 mL/min) as carrier gas, $T_{injector}$ = 275 °C, $T_{detector}$ = 300 °C, T_{column} = 60 °C (3 min) and 60–270 °C (15 °C/min), P = 40 kPa as routine working conditions. ^{1}H NMR spectra were recorded with a Bruker AC-300 spectrometer using $CDCl_3$ as the solvent and TMS as internal standard. The data is reported as [s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br. s = broad signal, coupling constant(s) in Hz, integration]. ^{13}C NMR spectra were recorded with ^{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) spectra were recorded with a Finnigan MAT 95S spectrometer.

General Procedure for the Synthesis of *N-tert*-Butanesulfinylimines 3: Titanium tetraethoxide (2.2281 g, 2.095 mL, 10 mmol) was slowly added to a solution of *tert*-butanesulfinamide (**1**; 0.605 g, 5 mmol) and the corresponding carbonyl compound **2** (5.5 mmol) in dry THF (20 mL) under argon at 23 °C. The reaction mixture was stirred for 12 h at the same temperature for aldehydes **2a**–**i** and at 66 °C for 5 h for ketones **2j**–**o**. The resulting mixture was hydrolyzed with brine (30 mL), extracted with ethyl acetate (3 × 15 mL), dried with anhydrous $MgSO_4$, and the solvent evaporated (15 Torr). The residue was purified by column chromatography (sil-

ica gel, hexane/ethyl acetate) to yield pure compounds **3**. Yields are given in Scheme 2. Imines **3a**,[14] **3b**,[15] **3c**,[16] **3d**,[15] **3e**,[15] **3h**,[17] **3i**,[18] **3j**,[19] **3k**,[20] **3m**,[21] **3n**,[15] and **3o**[22] were characterized by comparison of their physical and spectroscopic data with those reported in the literature. The corresponding physical, spectroscopic, and analytical data for imines **3f**, **3g**,and **3l** follow.

(*R*)-*N*-(*tert*-Butylsulfinyl)-*N*-(*p*-nitrobenzylidene)amine [(*R*)-3f]: White solid; m.p. 112–113 °C (hexane/CH_2Cl_2). $[\alpha]_D^{23}$ = –47 (*c* = 1.0, CH_2Cl_2); R_f = 0.34 (hexane/EtOAc, 3:1). IR (KBr): $\tilde{\nu}$ = 3113, 3025, 2948, 2914, 2360, 2341, 1584, 1529, 1343, 1087 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.71 (s, 1 H), 8.35 (dt, *J* = 8.8, 2.1 Hz, 2 H), 8.08 (dt, *J* = 8.8, 2.1 Hz, 2 H), 1.32 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.4 (CH), 149.4, 138.5, 129.7, 123.8 (ArC), 58.1 (C), 22.3 (CH_3) ppm. MS (EI): *m*/*z* (%) = 148 (100) [M – *t*BuSOH]$^+$, 118 (16), 102 (100), 90 (27), 76 (22), 75 (40), 51 (25). HRMS (EI): calcd. for $C_7H_4N_2O_2$ [M – *t*BuSOH]$^+$ 148.0273; found 148.0280.

(*R*)-*N*-(*tert*-Butylsulfinyl)-*N*-(*p*-hydroxybenzylidene)amine [(*R*)-3g]: White solid; decomposition >208 °C. $[\alpha]_D^{23}$ = +15 (*c* = 1.36, CH_3OH); R_f = 0.14 (hexane/EtOAc, 3:1). IR (KBr): $\tilde{\nu}$ = 3230–3126, 2981, 2360, 2341, 1589, 1576, 1514, 1437, 1280, 1160, 1035 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.49 (s, 1 H), 7.77 (dt, *J* = 8.7, 2.4 Hz, 2 H), 6.94 (dt, *J* = 8.7, 2.4 Hz, 2 H), 6.14 (br. s, 1 H), 1.27 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.8 (CH), 159.7, 131.6, 126.8, 115.9 (ArC), 57.7 (C), 22.5 (CH_3) ppm. MS (EI): *m*/*z* (%) = 119 (100) [M – *t*BuSOH]$^+$, 91 (17), 64 (22). HRMS (EI): calcd. for C_7H_5NO [M – *t*BuSOH]$^+$ 119.0371; found 119.0382.

(R_S,*E*)-*N*-(*tert*-Butylsulfinyl)heptan-2-imine [(*R*)-3l]: Yellow oil. $[\alpha]_D^{20}$ = +144 (*c* = 1.07, CH_2Cl_2); R_f = 0.59 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 2955, 2928, 2862, 1622, 1457, 1362, 1187, 1074, 669 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.35–2.44 (m, 2 H), 2.31 (s, 3 H), 1.53–1.69 (m, 2 H), 1.26–1.38 (m, 4 H), 1.24 (s, 9 H), 0.89 (t, *J* = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 185.6 (C), 56.2 (C), 43.4, 31.3, 25.2 (CH_2), 23.0 (CH_3), 22.4 (CH_2), 22.1, 13.9 (CH_3) ppm. MS (EI): *m*/*z* (%) = 161 (58) [M – C_4H_8]$^+$, 112 (15), 105 (56), 97 (26), 96 (20), 89 (43), 82 (10), 70 (17), 64 (60), 58 (11), 57 (100), 56 (71), 55 (54), 54 (12), 53 (15), 50 (11). HRMS (EI): calcd. for $C_7H_{15}NOS$ [M – C_4H_8]$^+$ 161.0874; found 161.0886.

General Procedure for the Propargylation of *N*-*tert*-Butanesulfinylimines 3. Synthesis of Homopropargylamine Derivatives 5: A mixture of *N*-*tert*-butanesulfinyl imine **3** (0.5 mmol), 3-bromo-1-trimethylsilyl-1-propyne (**4b**; 313 mg, 0.275 mL, 1.65 mmol), and indium (189 mg, 1.65 mmol) was sonicated in dry THF (2 mL) for 7 h. Then the resulting mixture was hydrolyzed with H_2O (5 mL) and extracted with EtOAc (3× 15 mL). The organic phase was washed with brine (3× 10 mL), dried with anhydrous $MgSO_4$, and the solvent evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc) to yield products **5**. The yields are given in Table 2 and Table 3, the physical and spectroscopic data follow.

(4*R*,R_S)-*N*-(*tert*-Butylsulfinyl)-1-(trimethylsilyl)dodec-1-yn-4-amine (5a): Colorless oil. $[\alpha]_D^{20}$ = –11.4 (*c* = 1.16, CH_2Cl_2); R_f = 0.65 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3203, 2956, 2924, 2855, 2173, 1466, 1363, 1249, 1052, 840, 759, 648 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.58 (d, *J* = 7.7 Hz, 1 H), 3.38–3.27 (m, 1 H), 2.65 (dd, *J* = 16.8, 5.7 Hz, 1 H), 2.48 (dd, *J* = 16.8, 5.0 Hz, 1 H), 1.65–1.50 (m, 2 H), 1.39–1.24 (m, 12 H), 1.23 (s, 9 H), 0.88 (t, *J* = 6.8 Hz, 3 H), 0.15 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 102.8, 88.2, 55.9 (C), 54.4 (CH), 34.7, 31.8, 29.4, 29.3, 29.2, 27.9, 25.6 (CH_2), 22.7, 14.1, 0.04 (CH_3) ppm. MS (EI): *m*/*z* (%) = 301 (7) [M – C_4H_8]$^+$, 253 (29), 189 (26), 142 (12), 140 (25), 84 (13), 77 (11), 75 (16), 74 (10), 73 (100), 70 (24), 69 (13). HRMS (EI): calcd. for $C_{15}H_{31}NOSSi$ [M – C_4H_8]$^+$ 301.1896; found 301.1940.

(3*S*,R_S)-*N*-(*tert*-Butylsulfinyl)-2-methyl-6-(trimethylsilyl)hex-5-yn-3-amine (5b): White solid; m.p. 40–43 °C (hexane/CH_2Cl_2). $[\alpha]_D^{20}$ = –8.3 (*c* = 1.01, CH_2Cl_2); R_f = 0.60 (hexane/EtOAc, 1:1). IR (KBr): $\tilde{\nu}$ = 3449, 3263, 3123, 2959, 2929, 2898, 2870, 2174, 1473, 1466, 1429, 1366, 1248, 1008, 838, 758, 698, 646 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.61 (d, *J* = 8.0 Hz, 1 H), 3.17–3.06 (m, 1 H), 2.65 (dd, *J* = 17.0, 5.8 Hz, 1 H), 2.56 (dd, *J* = 17.0, 5.1 Hz, 1 H), 2.06–1.94 (m, 1 H), 1.24 (s, 9 H), 0.94 (d, *J* = 6.8 Hz, 3 H), 0.92 (d, *J* = 6.8 Hz, 3 H), 0.15 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 102.9, 88.2 (C), 59.8 (CH), 56.1 (C), 31.2 (CH), 25.0 (CH_2), 22.8, 18.8, 18.4, 0.03 (CH_3) ppm. MS (EI): *m*/*z* (%) = 231 (7) [M – C_4H_8]$^+$, 188 (10), 184 (16), 183 (100), 140 (33), 120 (23), 119 (65), 102 (17), 83 (10), 75 (23), 73 (85), 72 (19), 59 (11), 57 (67), 56 (33), 55 (10). HRMS (EI): calcd. for $C_{10}H_{21}NOSSi$ [M – C_4H_8]$^+$ 231.1113; found 231.1124.

(3*R*,R_S)-*N*-(*tert*-Butylsulfinyl)-1-phenyl-6-(trimethylsilyl)hex-5-yn-3-amine (5c): White solid; m.p. 51–52 °C (hexane/CH_2Cl_2). $[\alpha]_D^{20}$ = –16.1 (*c* = 1.01, CH_2Cl_2); R_f = 0.50 (hexane/EtOAc, 1:1). IR (KBr): $\tilde{\nu}$ = 3271, 2959, 2928, 2175, 1250, 1032, 838, 759, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.14 (m, 5 H), 3.65 (d, *J* = 8.1 Hz, 1 H), 3.45–3.31 (m, 1 H), 2.79–2.62 (m, 2 H), 2.71 (dd, *J* = 16.9, 5.9 Hz, 1 H), 2.53 (dd, *J* = 16.8, 4.6 Hz, 1 H), 2.01–1.87 (m, 2 H), 1.26 (s, 9 H), 0.16 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.4 (C), 128.5, 128.3, 126.0 (CH), 102.4, 88.4, 56.0 (C), 53.9 (CH), 36.6, 31.8, 28.0 (CH_2), 22.7, 0.04 (CH_3) ppm. MS (EI): *m*/*z* (%) = 293 (5) [M – 56]$^+$, 246 (13), 245 (58), 140 (13), 91 (99), 75 (16), 73 (100).

(2*R*,R_S)-*N*-(*tert*-Butylsulfinyl)-1-phenyl-5-(trimethylsilyl)pent-4-yn-2-amine (5d): Yellow oil. $[\alpha]_D^{20}$ = –21.1 (*c* = 1.06, CH_2Cl_2); R_f = 0.53 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3444, 3118, 3020, 2959, 2177, 1473, 1456, 1426, 1364, 1249, 1081, 1052, 1026, 1003, 839, 743, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.14 (m, 5 H), 3.70–3.57 (m, 2 H), 2.99 (dd, *J* = 13.6, 6.1 Hz, 1 H), 2.86 (dd, *J* = 13.6, 6.7 Hz, 1 H), 2.58 (dd, *J* = 16.9, 5.7 Hz, 1 H), 2.48 (dd, *J* = 16.9, 4.6 Hz, 1 H), 1.15 (s, 9 H), 0.19 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.6 (C), 129.5, 128.4, 126.6 (CH), 102.6, 88.7, 56.0 (C), 55.9 (CH), 40.9, 26.9 (CH_2), 22.5, 0.04 (CH_3) ppm. MS (EI): *m*/*z* (%) = 279 (1) [M – C_4H_8]$^+$, 231 (31), 188 (19), 167 (14), 140 (19), 104 (37), 98 (27), 91 (52), 75 (14), 73 (100), 71 (13). HRMS (EI): calcd. for $C_{14}H_{21}NOSiS$ [M – C_4H_8]$^+$ 279.1113; found 279.1161.

(1*S*,R_S)-*N*-(*tert*-Butylsulfinyl)-1-phenyl-4-(trimethylsilyl)but-3-yn-1-amine (5e): White solid; m.p. 80–82 °C (hexane/CH_2Cl_2). $[\alpha]_D^{20}$ = –133.1 (*c* = 1.00, CH_2Cl_2); R_f = 0.52 (hexane/EtOAc, 1:1). IR (KBr): $\tilde{\nu}$ = 3231, 3209, 2955, 2932, 2899, 2178, 1249, 1046, 1024, 837, 757, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.28 (m, 5 H), 4.56 (m, 1 H), 4.15 (br. s, 1 H), 2.74 (dd, *J* = 16.9, 5.1 Hz, 1 H), 2.64 (dd, *J* = 16.8, 8.3 Hz, 1 H), 1.24 (s, 9 H), 0.16 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4 (C), 128.5, 128.0, 127.5 (CH), 102.2, 89.1 (C), 56.5 (CH), 55.7 (C), 30.3 (CH_2), 22.6, 0.1 (CH_3) ppm. MS (EI): *m*/*z* (%) = 217 (22) [M – C_4H_8]$^+$, 202 (14), 153 (74), 144 (10), 136 (20), 129 (20), 128 (20), 77 (14), 75 (16), 74 (10), 73 (100).

(1*S*,R_S)-*N*-(*tert*-Butylsulfinyl)-1-(4-hydroxyphenyl)-4-(trimethylsilyl)but-3-yn-1-amine (5g): Colorless oil. $[\alpha]_D^{20}$ = –120.1 (*c* = 1.03, CH_2Cl_2); R_f = 0.31 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3206, 3114, 2958, 2899, 2179, 1616, 1600, 1517, 1458, 1248, 1170, 1021, 1006, 834, 763, 642 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43 (s, 1 H), 7.14 (d, *J* = 8.5 Hz, 2 H), 6.79 (d, *J* = 8.5 Hz, 2 H), 4.53–4.41 (m, 1 H), 4.29 (d, *J* = 1.7 Hz, 1 H), 2.68–2.59 (m, 2 H), 1.25 (s, 9 H),

0.16 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 130.6 (C), 128.8, 115.7 (CH), 102.5, 88.9 (C), 56.1 (CH), 55.8 (C), 30.1 (CH_2), 22.6, 0.07 (CH_3) ppm. MS (EI): *m*/*z* (%) = 281 (8) [M – C_4H_8]$^+$, 263 (10), 233 (11), 207 (16), 169 (52), 145 (16), 127 (13), 122 (11), 121 (56), 120 (31), 75 (14), 74 (10), 73 (100). HRMS (EI): calcd. for $C_{13}H_{17}NOSiS$ [M – C_4H_8 – H_2O]$^+$ 263.0795; found 263.0806.

(2*R*,*S*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-(2-bromophenyl)-5-(trimethylsilyl)-pent-4-yn-2-amine (5h): White solid; m.p. 104–105 °C (hexane/CH_2Cl_2). $[\alpha]_D^{20}$ = –14.6 (*c* = 1.00, CH_2Cl_2); R_f = 0.48 (hexane/EtOAc, 1:1). IR (KBr): $\tilde{\nu}$ = 3214, 2980, 2959, 2924, 2848, 2179, 1472, 1438, 1419, 1249, 1169, 1090, 1032, 1017, 837, 752, 659, 645 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 7.7 Hz, 1 H), 7.25–7.22 (m, 2 H), 7.12–6.93 (m, 1 H), 3.80–3.64 (m, 2 H), 3.14 (dd, *J* = 13.7, 7.1 Hz, 1 H), 3.01 (dd, *J* = 13.7, 5.9 Hz, 1 H), 2.73 (dd, *J* = 16.9, 5.5 Hz, 1 H), 2.58 (dd, *J* = 16.9, 3.8 Hz, 1 H), 1.09 (s, 9 H), 0.19 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.8 (C), 132.8, 131.7, 128.3, 127.4 (CH), 125.2, 102.3, 89.0, 56.0 (C), 55.4 (CH), 41.2, 27.8 (CH_2), 22.4, 0.07 (CH_3) ppm. MS (EI): *m*/*z* (%) = 311 (15) [M – C_4H_8SO]$^+$, 309 (16), 207 (11), 188 (16), 172 (12), 171 (12), 169 (12), 140 (19), 98 (22), 91 (13), 90 (11), 75 (14), 73 (100), 71 (11). HRMS (EI): calcd. for $C_{14}H_{20}NSi^{79}Br$ [M – C_4H_8SO]$^+$ 309.0548; found 309.0522.

(1*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-(2-bromophenyl)-4-(trimethylsilyl)-but-3-yn-1-amine (5i): Colorless oil. $[\alpha]_D^{20}$ = –111.7 (*c* = 1.06, CH_2Cl_2); R_f = 0.49 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3208, 2958, 2897, 2868, 2179, 1471, 1438, 1362, 1249, 1059, 1023, 840, 755, 643 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (dd, *J* = 8.0, 1.1 Hz, 1 H), 7.42 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.33–7.27 (m, 1 H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1 H), 5.04 (dt, *J* = 6.9, 4.8 Hz, 1 H), 4.23 (d, *J* = 4.2 Hz, 1 H), 2.90 (dd, *J* = 16.9, 5.1 Hz, 1 H), 2.66 (dd, *J* = 16.9, 6.9 Hz, 1 H), 1.25 (s, 9 H), 0.14 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.6 (C), 133.0, 129.2, 129.2, 127.2 (CH), 123.3, 101.4, 89.6, 56.0 (C), 55.3 (CH), 28.6 (CH_2), 22.6, 0.10 (CH_3) ppm. MS (EI): *m*/*z* (%) = 297 (15) [M – C_4H_8SO]$^+$, 295 (15), 233 (18), 231 (18), 184 (11), 152 (52), 128 (27), 77 (10), 75 (17), 74 (10), 73 (100). HRMS (EI): calcd. for $C_{13}H_{18}NSi^{79}Br$ [M – C_4H_8SO]$^+$ 295.0392; found 295.0392.

(*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-2-methyl-5-(trimethylsilyl)pent-4-yn-2-amine (5j): White solid; m.p. 44–47 °C (hexane/CH_2Cl_2). $[\alpha]_D^{20}$ = –59.1 (*c* = 1.06, CH_2Cl_2); R_f = 0.23 (hexane/EtOAc, 1:1). IR (KBr): $\tilde{\nu}$ = 3262, 2976, 2958, 2931, 2173, 1458, 1407, 1361, 1249, 1167, 1047, 933, 837, 758 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.52 (s, 1 H), 2.42 (s, 2 H), 1.41 (s, 3 H), 1.35 (s, 3 H), 1.21 (s, 9 H), 0.15 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 103.1, 88.1, 55.6, 54.6 (C), 35.6 (CH_2), 28.5, 28.1, 22.6, 0.03 (CH_3) ppm. MS (EI): *m*/*z* (%) = 217 (7) [M – C_4H_8]$^+$, 170 (11), 169 (72), 162 (16), 154 (35), 153 (13), 137 (20), 106 (39), 105 (86), 97 (18), 96 (12), 88 (22), 83 (12), 75 (20), 74 (12), 73 (100), 58 (15), 57 (70). HRMS (EI): calcd. for $C_9H_{19}NOSSi$ [M – C_4H_8]$^+$ 217.0957; found 217.0950.

(3*R*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-3-methyl-6-(trimethylsilyl)hex-5-yn-3-amine (5k): Yellow oil. $[\alpha]_D^{20}$ = –46.2 (*c* = 1.00, CH_2Cl_2); R_f = 0.43 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3218, 2961, 2901, 2881, 2173, 1457, 1406, 1379, 1362, 1249, 1161, 1053, 945, 923, 839, 759, 649 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56 (s, 1 H), 2.46 (s, 2 H), 1.69 (q, *J* = 7.4 Hz, 2 H), 1.35 (s, 3 H), 1.22 (s, 9 H), 0.90 (t, *J* = 7.4 Hz, 3 H), 0.15 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 103.2, 88.2, 57.1, 55.8 (C), 33.3, 33.1 (CH_2), 25.2, 22.7, 8.0, 0.0 (CH_3) ppm. MS (EI): *m*/*z* (%) = 231 (6) [M – C_4H_8]$^+$, 183 (55), 176 (11), 168 (19), 154 (13), 120 (56), 119 (75), 102 (13), 97 (11), 75 (17), 74 (16), 73 (100), 71 (27), 57 (29). HRMS (EI): calcd. for $C_{10}H_{21}NOSSi$ [M – C_4H_8]$^+$ 231.1113; found 231.1121.

(4*R*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-4-methyl-1-(trimethylsilyl)non-1-yn-4-amine (5l): Colorless oil. $[\alpha]_D^{20}$ = –42.5 (*c* = 1.02, CH_2Cl_2); R_f = 0.55 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3183, 2956, 2933, 2863, 2173, 1458, 1376, 1362, 1249, 1039, 934, 839, 759, 697, 654 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 1 H), 2.45 (d, *J* = 1.3 Hz, 2 H), 1.63 (t, *J* = 7.6 Hz, 2 H), 1.36 (s, 3 H), 1.33–1.24 (m, 6 H), 1.22 (s, 9 H), 0.89 (t, *J* = 6.8 Hz, 3 H), 0.15 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 103.2, 88.2, 57.0, 55.8 (C), 40.4, 33.6, 32.1 (CH_2), 25.8 (CH_3), 23.1 (CH_2), 22.7 (CH_3), 22.5 (CH_2), 14.0, 0.02 (CH_3) ppm. MS (EI): *m*/*z* (%) = 273 (5) [M – C_4H_8]$^+$, 225 (26), 161 (58), 154 (12), 137 (11), 112 (15), 105 (19), 97 (16), 75 (14), 74 (15), 73 (100), 57 (12), 55 (13). HRMS (EI): calcd. for $C_{13}H_{27}NOSSi$ [M – C_4H_8]$^+$ 273.1583; found 273.1576.

(1*S*,*S*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[3-(trimethylsilyl)prop-2-yn-1-yl]-cyclohex-2-en-1-amine (5m): Yellow oil. $[\alpha]_D^{20}$ = +69.8 (*c* = 1.00, CH_2Cl_2); R_f = 0.43 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3203, 3022, 2955, 2908, 2868, 2834, 2173, 1456, 1418, 1376, 1362, 1249, 1053, 839, 759, 731, 696, 646 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.96 (dt, *J* = 10.0, 3.6 Hz, 1 H), 5.78 (dd, *J* = 10.1, 0.8 Hz, 1 H), 3.82 (s, 1 H), 2.63 (d, *J* = 16.7 Hz, 1 H), 2.48 (d, *J* = 16.7 Hz, 1 H), 2.09–1.92 (m, 3 H), 1.78–1.56 (m, 3 H), 1.23 (s, 9 H), 0.15 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.8, 129.9 (CH), 102.7, 88.3, 55.8, 55.3 (C), 35.5, 34.2, 25.1 (CH_2), 22.7 (CH_3), 18.4 (CH_2), 0.0 (CH_3) ppm. MS (EI): *m*/*z* (%) = 255 (2) [M – C_4H_8]$^+$, 207 (17), 206 (13), 191 (25), 143 (94), 134 (19), 95 (30), 94 (17), 91 (15), 79 (17), 73 (100), 67 (25). HRMS (EI): calcd. for $C_{12}H_{21}NOSSi$ [M – C_4H_8]$^+$ 255.1113; found 255.1123.

(2*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-2-phenyl-5-(trimethylsilyl)pent-4-yn-2-amine (5n): Yellow oil. $[\alpha]_D^{20}$ = –64.7 (*c* = 1.91, CH_2Cl_2); R_f = 0.54 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3203, 3035, 2957, 2926, 2868, 2173, 1473, 1447, 1249, 1054, 839, 760, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.42 (m, 2 H), 7.39–7.23 (m, 3 H), 4.16 (s, 1 H), 2.88 (d, *J* = 16.7 Hz, 1 H), 2.65 (d, *J* = 16.7 Hz, 1 H), 1.88 (s, 3 H), 1.24 (s, 9 H), 0.12 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1 (C), 128.2, 127.4, 126.6 (CH), 102.7, 89.2, 59.6, 56.3 (C), 37.0 (CH_2), 27.1, 22.7, 0.09 (CH_3) ppm. MS (EI): *m*/*z* (%) = 279 (6) [M – C_4H_8]$^+$, 231 (13), 230 (15), 216 (12), 167 (82), 158 (19), 157 (12), 150 (23), 143 (13), 128 (28), 119 (36), 104 (40), 77 (17), 75 (14), 74 (12), 73 (100). HRMS (EI): calcd. for $C_{14}H_{21}NOSSi$ [M – C_4H_8]$^+$ 279.1113; found 279.1127.

(1*S*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-[3-(trimethylsilyl)prop-2-yn-1-yl]-1,2,3,4-tetrahydronaphthalen-1-amine (5o): Orange oil. $[\alpha]_D^{20}$ = –5.27 (*c* = 0.64, CH_2Cl_2); R_f = 0.31 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3208, 2954, 2868, 2174, 1451, 1362, 1249, 1050, 839, 758, 731, 654 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.59 (m, 1 H), 7.20 (dt, *J* = 4.8, 3.6 Hz, 2 H), 7.12–7.07 (m, 1 H), 3.93 (s, 1 H), 2.99 (d, *J* = 16.9 Hz, 1 H), 2.90–2.68 (m, 2 H), 2.78 (d, *J* = 16.9 Hz, 1 H), 2.30–2.13 (m, 2 H), 2.02–1.91 (m, 1 H), 1.90–1.78 (m, 1 H), 1.23 (s, 9 H), 0.10 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.2, 137.6 (C), 129.1, 128.2, 127.7, 125.9 (CH), 103.2, 88.7, 58.4, 56.3 (C), 37.2, 34.4, 29.7 (CH_2), 22.8 (CH_3), 19.3 (CH_2), 0.1 (CH_3) ppm. MS (EI): *m*/*z* (%) = 305 (2) [M – C_4H_8]$^+$, 257 (13), 256 (12), 241 (14), 193 (72), 184 (10), 167 (12), 146 (12), 145 (35), 144 (19), 141 (12), 130 (11), 117 (38), 116 (12), 115 (12), 75 (14), 74 (12), 73 (100). HRMS (EI): calcd. for $C_{16}H_{23}NOSSi$ [M – C_4H_8]$^+$ 305.1270; found 305.1302.

Desilylation of Compound 5c. Synthesis of (3*R*,*R*$_S$)-*N*-(*tert*-Butylsulfinyl)-1-phenylhex-5-yn-3-amine (7): A suspension of K_2CO_3 (5 mg, 0.036 mmol) in methanol (4 mL) was added dropwise to a solution of compound **5c** (175 mg, 0.5 mmol) in THF (4 mL). The

reaction mixture was stirred for 12 h at room temperature and then it was hydrolyzed with a 1 N NH_4Cl aqueous solution (8 mL) and extracted with methyl *tert*-butyl ether (3× 15 mL). The organic phase was dried with anhydrous $MgSO_4$ and the solvent evaporated (15 Torr). The residue was purified by column chromatography (silica gel, hexane/EtOAc, 2:1) to yield compound **7** as a yellow oil (139 mg, 0.41 mmol, 83% yield). $[\alpha]_D^{20}$ = –23.5 (*c* = 0.83, CH_2Cl_2); R_f = 0.20 (hexane/EtOAc, 1:1). IR (film): $\tilde{\nu}$ = 3219, 3061, 3025, 2978, 2948, 2864, 2111, 1602, 1495, 1455, 1363, 1175, 1054, 699 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.25 (m, 2 H), 7.24–7.14 (m, 3 H), 3.55 (d, *J* = 8.8 Hz, 1 H), 3.47–3.32 (m, 1 H), 2.82–2.61 (m, 3 H, CH_2), 2.56–2.44 (m, 1 H), 2.07 (t, *J* = 2.6 Hz, 1 H), 2.03–1.88 (m, 2 H), 1.26 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.3 (C), 128.5, 128.3, 126.0 (CH), 79.9, 71.7, 56.1 (C), 54.3 (CH), 36.7, 32.0, 26.7 (CH_2), 22.6 (CH_3) ppm. MS (EI): *m*/*z* (%) = 221 (1) $[M - C_4H_8]^+$, 157 (11), 132 (53), 117 (51), 116 (28), 101 (16), 98 (16), 92 (10), 91 (100), 77 (16), 68 (32), 67 (28), 65 (19). HRMS (EI): calcd. for $C_{12}H_{15}NOS$ $[M - C_4H_8]^+$ 221.0874; found 221.0877.

Desulfinylation of Compound 5c. Synthesis of (3*R*)-1-Phenyl-6-(trimethylsilyl)hex-5-yn-3-amine (8): A 6 M HCl aqueous solution (0.100 mL, 0.6 mmol) was added to a solution of compound **5c** (70 mg, 0.2 mmol) in THF (0.2 mL) at 0 °C. The reaction mixture was stirred at 0 °C until monitoring by TLC indicated that all the starting material had disappeared (1.5 h). The resulting mixture was then basified with a 1 M NaOH aqueous solution. The reaction mixture was extracted with EtOAc (2× 10 mL), the organic layer was washed first with a 1 M NaOH aqueous solution (5 mL) and then with H_2O (5 mL), dried with anhydrous $MgSO_4$, and finally the solvent was evaporated (15 Torr) to yield compound **8** as a yellow oil (35 mg, 0.14 mmol, 71% yield). $[\alpha]_D^{20}$ = +0.2 (*c* = 1.12, CH_2Cl_2); R_f = 0.32 (CH_2Cl_2/MeOH, 1:1). IR (film): $\tilde{\nu}$ = 3030, 2957, 2853, 2171, 1495, 1454, 1249, 1030, 838, 759, 698, 646 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33–7.24 (m, 2 H), 7.22–7.14 (m, 3 H), 2.98–2.85 (m, 1 H), 2.80–2.61 (m, 2 H), 2.41 (dd, *J* = 16.8, 4.9 Hz, 1 H), 2.27 (dd, *J* = 16.8, 7.0 Hz, 1 H), 1.90–1.63 (m, 4 H), 0.16 (s, 9 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.8 (C), 128.4, 128.3, 125.8 (CH), 104.1, 87.0 (C), 49.7 (CH), 38.4, 32.5, 29.3 (CH_2), 0.09 (CH_3) ppm. MS (EI): *m*/*z* (%) = 135 (11) $[M - (CH_3)_3SiC{\equiv}CCH_2]^+$, 134 (100), 117 (21), 91 (57). HRMS (EI): calcd. for $C_{15}H_{23}NSi$ $[M]^+$ 245.160; found 245.1593.

Supporting Information (see footnote on the first page of this article): Spectroscopic data for imines **3a**–**e**, **3h**–**k**, and **3m**–**o**, ^1H and ^{13}C NMR spectra of imines **3**, homopropargylic amine derivatives **5**, and compounds **7** and **8**.

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