**Asymmetric Synthesis of α,α -Dibranched Propargylamines by Acetylide
Additions to *N-tert*-Butanesulfinyl Ketimines**

Supporting Information

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General Methods. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without purification. THF was distilled under N₂ from sodium/benzophenone and *i*-Pr₂EtN, CH₂Cl₂, pyridine, toluene, Et₂O, and CH₃OH were distilled under N₂ over CaH₂ immediately prior to use. 1-Pentyne and ethynylbenzene were distilled prior to use. All reactions were carried out in flame-dried glassware under an inert N₂ atmosphere. Unless otherwise specified, all spectra were obtained in CDCl₃ and chemical shifts are reported in ppm relative to internal solvent. Coupling constants are reported in Hz. Compounds **1a**, **1b**, **1g**, and **1h** were synthesized as previously reported.¹ The ¹H and ¹³C NMR of these products matched the published spectra.

General Procedure A: Synthesis of *tert*-butanesulfinyl ketimines. According to a modified literature procedure,¹ a 0.5 M THF solution of Ti(OEt)₄ (4 equiv) with (*S*)-*tert*-butanesulfinamide (1-2 equiv) and ketone (1 equiv) was prepared and the solution was heated to reflux. The solution was stirred for 20-40 h, and the mixture was cooled immediately upon completion. Once at room temperature, the mixture was poured into an equal volume of saturated aq. NaHCO₃ with rapid stirring. The resulting suspension was filtered through a plug of celite, and the filter cake was washed with EtOAc. The filtrate was transferred to a separatory funnel where the organic layer was washed with brine. The brine layer was extracted once with EtOAc, and the combined organic portions were dried (Na₂SO₄), filtered, and concentrated.

(*S*)-(+)-*N*-(1-Cyclohexyl-ethylidene)-2-methylpropanesulfinamide (1c). Procedure A was followed with a mixture of 2.90 g of (*S*)-*tert*-butanesulfinamide (23.9 mmol), 3.30 mL of 1-cyclohexyl-ethanone (23.9 mmol), and 21.8 g of Ti(OEt)₄ (95.6 mmol) in 191 mL of THF to

¹ Liu, G.; Cogan, D. A.; Owens, T.; Tang, T. P.; Ellman, J. A. *J. Org. Chem.* **1999**, *64*, 1278-1284.

afford *N*-sulfinyl ketimine **1c** (4.53 g, 83%) as a pale yellow oil after purification by silica gel chromatography (hexane/EtOAc = 1:1): $[\alpha]_D^{20} = +124.7$ (*c* 1.0, CHCl₃); IR 1071, 1187, 1361, 1449, 1619, 2851, 2922 cm⁻¹; ¹H NMR (400 MHz) δ 1.08-1.34 (m, 5H), 1.18 (s, 9H), 1.60-1.85 (m, 5H), 2.14-2.22 (m, 1H), 2.26 (s, 3H); ¹³C NMR (100 MHz) δ 21.4, 22.1, 25.8, 29.9, 30.0, 51.1, 56.3, 188.4. Anal. Calcd for C₁₂H₂₃NOS: C, 62.83; H, 10.11; N, 6.11. Found: C, 62.63; H, 10.41; N, 6.16.

(S)-(+)-*N*-(1-Cyclohexyl-propylidene)-2-methylpropanesulfinamide (1f). Procedure A was followed with a mixture of 0.909 g of (*S*)-*tert*-butanesulfinamide (7.50 mmol), 0.77 mL of 1-cyclohexyl-propanone (5.0 mmol), and 4.56 g of Ti(OEt)₄ (20.0 mmol) in 40 mL of THF to afford *N*-sulfinyl ketimine **1f** (0.73 g, 83%) as a pale yellow oil after HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min): $[\alpha]_D^{20} = +129.2$ (*c* 1.0, CHCl₃); IR 1075, 1188, 1360, 1450, 1619, 2854, 2928 cm⁻¹; ¹H NMR (400 MHz) δ 1.00-1.20 (m, 4H), 1.21 (s, 9H), 1.23-1.40 (m, 4H), 1.62-1.85 (m, 5H), 2.22-2.43 (m, 1.5H), 2.60-2.73 (m, 1.5H); ¹³C NMR (100 MHz) δ 11.9, 22.3, 25.9, 26.0, 26.1, 28.3, 30.58, 30.64, 48.7, 56.3, 192.5. Anal. Calcd for C₁₃H₂₅NOS: C, 64.15; H, 10.35; N, 5.75. Found: C, 64.07; H, 10.70; N, 5.80.

Synthesis of *N*-methoxy-*N*-methyl amides. According to a modified literature procedure,² to a 0.2 M solution of 4-methylcyclohexanecarboxylic acid (3.00 g, 21.1 mmol, 1 equiv) in 106 mL of CH₂Cl₂ was added *N,O*-dimethylhydroxylamine hydrochloride (2.06 g, 21.1 mmol, 1 equiv), 1-hydroxybenzotriazole (3.55 g, 23.2 mmol, 1.1 equiv), and *i*-Pr₂EtN (3.68 mL, 21.1 mmol, 1 equiv). The solution was stirred until homogeneous, then *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (4.45 g, 23.2 mmol, 1.1 equiv) was

² Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, 22, 3815-3818.

added, and the solution was stirred for 20 h. The solution was poured into 200 mL of H₂O with rapid stirring. After transfer to a separatory funnel, the aqueous layer was removed and the solution was washed with 200 mL of brine. The resulting solution was dried with MgSO₄, filtered, and concentrated. HPFC purification (hexane/*tert*-butyl methyl ether = 92:8 for 7 min, 92:8 to 34:66 over 72 min) provided pure *trans*-isomer (1.05 g, 27%) and *cis*-isomer (1.43 g, 37%) as pale yellow oils:

***N*-Methoxy-*N*-methyl 2-(*trans*-4-methylcyclohexyl)propionamide:** IR 970, 1176, 1449, 1658, 2865, 2924 cm⁻¹; ¹H NMR (400 MHz) δ 0.85 (d, *J* = 6.8, 3H), 0.85-0.99 (m, 2H), 1.28-1.40 (m, 1H), 1.40-1.55 (m, 2H), 1.68-1.77 (m, 4H), 2.50-2.63 (m, 1H), 3.13 (s, 3H), 3.65 (s, 3H); ¹³C NMR (100 MHz) δ 22.6, 28.9, 31.9, 32.1, 34.4, 40.0, 61.4, 177.5. Anal. Calcd for C₁₀H₁₉NO₂: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.81; H, 10.61; N, 7.56.

***N*-Methoxy-*N*-methyl 2-(*cis*-4-methylcyclohexyl)propionamide:** IR 999, 1175, 1449, 1659, 2850, 2923 cm⁻¹; ¹H NMR (400 MHz) δ 0.92 (d, *J* = 7.2, 3H), 1.42-1.54 (m, 6H), 1.66-1.78 (m, 3H), 2.62-2.71 (m, 1H), 3.12 (s, 3H), 3.63 (s, 3H); ¹³C NMR (100 MHz) δ 18.8, 24.4, 28.2, 30.9, 32.1, 38.3, 61.2, 177.3. Anal. Calcd for C₁₀H₁₉NO₂: C, 64.83; H, 10.34; N, 7.56. Found: C, 64.58; H, 10.58; N, 7.52.

(*S*)-(+)-*N*-[1-(*trans*-4-Methyl-cyclohexyl)-1-ethylidene]-2-methylpropanesulfonamide (1d). To a 0.1 M solution of *N*-methoxy-*N*-methyl 2-(*trans*-4-methylcyclohexyl)propionamide (2.30 g, 12.4 mmol, 1 equiv) in 125 mL of THF cooled in an ice-water bath was added dropwise with stirring CH₃MgBr (8.7 mL, 26 mmol, 2.1 equiv) as a 3.0 M solution in Et₂O. Stirring was continued for 2 h, and then the solution was allowed to warm to room temperature and poured into 250 mL of 5% (v/v) HCl/CH₃OH with rapid stirring. The solution was diluted with 500 mL

of CH₂Cl₂ and then poured into 200 mL of brine. The mixture was filtered through a plug of Celite, eluting with CH₂Cl₂, and transferred to a separatory funnel. The aqueous layer was removed, and the organic layer was washed with 400 mL of brine. The resulting solution was dried with Na₂SO₄, filtered, and concentrated. The product was filtered through a plug of silica, eluting with 1:9 Et₂O/pentane, and concentrated. The resulting ketone was carried on directly to the *N*-sulfinyl ketimine formation, following Procedure A with a mixture of 2.25 g of (*S*)-*tert*-butanesulfinamide (18.6 mmol) and 11.3 g of Ti(OEt)₄ (49.6 mmol) in 100 mL of THF. HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min) to afford *N*-sulfinyl ketimine **1d** (2.48 g, 82%) as a pale yellow oil: $[\alpha]_D^{20} = +111.1$ (*c* 1.0, CHCl₃); IR 1074, 1193, 1361, 1449, 1619, 2866, 2924 cm⁻¹; ¹H NMR (400 MHz) δ 0.82 (d, *J* = 6.8, 3H), 0.84-0.95 (m, 2H), 1.16 (s, 9H), 1.22-1.33 (m, 3H), 1.66-1.74 (m, 2H), 1.76-1.84 (m, 2H), 2.06-2.15 (m, 1H), 2.24 (s, 3H); ¹³C NMR (100 MHz) δ 21.4, 22.0, 22.3, 29.7, 30.0, 32.1, 34.48, 34.51, 50.9, 56.2, 188.3. Anal. Calcd for C₁₃H₂₅NOS: C, 64.15; H, 10.35; N, 5.75. Found: C, 63.76; H, 10.65; N, 5.94.

(S)-(+)-*N*-[1-(*cis*-4-Methyl-cyclohexyl)-1-ethylidine]-2-methylpropanesulfinamide

(1e). To a 0.1 M solution of *N*-methoxy-*N*-methyl 2-(*cis*-4-methylcyclohexyl)propionamide (0.926 g, 5.00 mmol, 1 equiv) in 50 mL of THF cooled in an ice-water bath was added dropwise with stirring CH₃MgBr (3.5 mL, 11 mmol, 2.1 equiv) as a 3.0 M solution in Et₂O. Stirring was continued for 2 h, and then the solution was allowed to warm to room temperature and poured into 100 mL of 5% (v/v) HCl/CH₃OH with rapid stirring. The solution was diluted with 200 mL of CH₂Cl₂ and then poured into 200 mL of brine. The mixture was filtered through a plug of Celite, eluting with CH₂Cl₂, and transferred to a separatory funnel. The aqueous layer was

removed, and the organic layer was washed with 200 mL of brine. The resulting solution was dried with Na₂SO₄, filtered, and concentrated. The product was filtered through a plug of silica, eluting with 1:9 Et₂O/pentane, and concentrated. The resulting ketone was carried on directly to *N*-sulfinyl ketimine formation, following Procedure A with a mixture of 0.909 g of (*S*)-*tert*-butanesulfinamide (7.50 mmol) and 4.56 g of Ti(OEt)₄ (20.0 mmol) in 40 mL of THF. HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min) to afford *N*-sulfinyl ketimine **1e** (0.952 g, 78%) as a pale yellow oil: $[\alpha]_D^{20} = +127.2$ (*c* 1.0, CHCl₃); IR 1073, 1187, 1361, 1456, 1616, 2865, 2924 cm⁻¹; ¹H NMR (400 MHz) δ 0.87 (d, *J* = 6.8, 3H), 1.20 (s, 9H), 1.28-1.40 (m, 2H), 1.44-1.59 (m, 4H), 1.63-1.81 (m, 3H), 2.27 (s, 3H), 2.28-2.34 (m, 1H); ¹³C NMR (100 MHz) δ 19.6, 21.6, 22.1, 25.4, 25.5, 29.1, 30.98, 31.02, 48.9, 56.2, 188.2. Anal. Calcd for C₁₃H₂₅NOS: C, 64.15; H, 10.35; N, 5.75. Found: C, 63.89; H, 10.73; N, 5.83.

General Procedure B: Synthesis of propargyl sulfinamides. To a 0.85 M solution of alkynyllithium (3.0-3.5 equiv) in toluene at -78 °C was added butyllithium (2.2 equiv) as a solution in hexanes. The resulting solution was stirred for ca. 15 min before a stirred -78 °C toluene solution of *N*-sulfinyl ketimine **1** (1.0 equiv, 0.35 M) and Me₃Al (1.2 equiv) was slowly added via cannula. Stirring was continued at -78 °C for 2 h, and then the solution was allowed to warm to rt over 4 h. Stirring was continued at rt for 10-30 h before the mixture was cooled in an ice-water bath. Saturated aq. Na₂SO₄ was added dropwise until gas was no longer evolved upon addition. The slurry was filtered and the filter cake was rinsed with EtOAc. The filtrate was dried (Na₂SO₄), filtered, and concentrated. The diastereomeric ratio was determined by HPLC or by NMR with hexamethylbenzene as an external standard. If the starting *N*-sulfinyl ketimine was not fully reacted, the crude material was dissolved in CH₃OH and a 1 M aq. solution of

CH₃CO₂H (2:1 ratio) was added and the solution was stirred at rt for 8-12 h to hydrolyze the *N*-sulfinyl ketimine. The resulting slurry was then concentrated to remove the CH₃OH, and brine was added. The slurry was then extracted three times with ethyl acetate, dried with Na₂SO₄, filtered, and concentrated. Chromatography afforded the diastereomerically pure propargyl sulfinamides **2**.

(Ss, S)-(+)-N-(1-Isopropyl-1-methyl-hex-2-ynyl)-2-methylpropanesulfinamide (2a).

Procedure B was followed with a mixture of 0.30 mL of 1-pentyne (3.0 mmol), 1.0 mL of butyllithium (2.2 mmol, 2.2 M in hexanes), 0.189 g of *N*-sulfinyl ketimine **1a** (1.00 mmol), and 0.12 mL of Me₃Al (1.2 mmol) in 7 mL total volume of toluene. HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min) provided propargyl sulfinamide **2a** (0.182 g, 71%) as a pale yellow oil: $[\alpha]_D^{20} = +67.4$ (*c* 1.0, CHCl₃); IR 1052, 1364, 1464, 2245, 2961, 3212 cm⁻¹; ¹H NMR (400 MHz) δ 0.96 (t, *J* = 7.0, 3H), 0.99 (d, *J* = 6.8, 3H), 1.01 (d, *J* = 6.8, 3H), 1.18 (s, 9H), 1.41 (s, 3H), 1.51 (app. sextet, *J* = 7.0, 2H), 1.82-1.90 (m, 1H), 2.17 (t, *J* = 7.0, 2H), 3.19 (s, 1H); ¹³C NMR (100 MHz) δ 13.4, 17.4, 17.9, 20.6, 22.2, 22.5, 26.0, 38.6, 55.8, 57.3, 82.3, 85.2. Anal. Calcd for C₁₄H₂₇NOS: C, 65.32; H, 10.57; N, 5.44. Found: C, 65.33; H, 10.76; N, 5.53.

(Ss, S)-(+)-N-(1-Isopropyl-1-methyl-3-phenyl-prop-2-ynyl)-2-methylpropanesulfinamide (2b). Procedure B was followed with a mixture of 0.33 mL of ethynylbenzene (3.0 mmol), 1.0 mL of butyllithium (2.2 mmol, 2.2 M in hexanes), 0.189 g of *N*-sulfinyl ketimine **1a** (1.00 mmol), and 0.12 mL of Me₃Al (1.2 mmol) in 7 mL total volume of toluene. HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min)

provided propargyl sulfinamide **2b** (0.215 g, 74%) as a pale yellow oil: $[\alpha]_D^{20} = +79.7$ (c 1.0, CHCl_3); IR 691, 755, 1054, 2961, 3210 cm^{-1} ; ^1H NMR (400 MHz) δ 1.08 (d, $J = 6.8$, 3H), 1.12 (d, $J = 6.8$, 3H), 1.23 (s, 9H), 1.54 (s, 3H), 2.02 (septet, $J = 6.8$, 1H), 3.35 (s, 1H), 7.25-7.31 (m, 3H), 7.42-7.48 (m, 2H); ^{13}C NMR (100 MHz) δ 17.3, 17.9, 22.5, 25.4, 38.6, 56.0, 57.6, 84.9, 91.6, 122.9, 128.05, 128.11, 131.7. Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{NOS}$: C, 70.06; H, 8.65; N, 4.81. Found: C, 70.07; H, 8.61; N, 4.79.

(Ss, *S*)-(+)-*N*-(1-*tert*-Butyl-1-methyl-3-trimethylsilanyl-prop-2-ynyl)-2-methylpropanesulfinamide (**2d**). Procedure B was followed with a mixture of 0.42 mL of (trimethylsilyl)ethyne (3.0 mmol), 1.0 mL of butyllithium (2.2 mmol, 2.2 M in hexanes), 0.203 g of *N*-sulfinyl ketimine **1b** (1.00 mmol), and 0.12 mL of Me_3Al (1.2 mmol) in 7 mL total volume of toluene. HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min) provided propargyl sulfinamide **2d** (0.244 g, 81%) as a white solid: mp 85-86 °C; $[\alpha]_D^{20} = +57.0$ (c 1.0, CHCl_3); IR 757, 839, 856, 1013, 1250, 2173, 2957, 3131 cm^{-1} ; ^1H NMR (400 MHz) δ 0.15 (s, 9H), 1.03 (s, 9H), 1.19 (s, 9H), 1.46 (s, 3H), 3.23 (s, 1H); ^{13}C NMR (100 MHz) δ -0.1, 22.6, 23.2, 25.2, 38.4, 56.2, 59.7, 89.2, 108.3. Anal. Calcd for $\text{C}_{15}\text{H}_{31}\text{NOSSi}$: C, 59.74; H, 10.36; N, 4.64. Found: C, 59.79; H, 10.67; N, 4.76.

(Ss, *S*)-(+)-*N*-(1-Cyclohexyl-1-methyl-3-trimethylsilanyl-prop-2-ynyl)-2-methylpropanesulfinamide (**2e**). Procedure B was followed with a mixture of 5.80 mL of (trimethylsilyl)ethyne (41.7 mmol), 21.2 mL of butyllithium (26.3 mmol, 1.24 M in hexanes), 2.73 g of *N*-sulfinyl ketimine **1c** (11.9 mmol), and 1.37 mL of Me_3Al (14.3 mmol) in 74 mL total volume of toluene. Purification by silica gel chromatography (hexane/EtOAc = 5:1) provided

propargyl sulfinamide **2e** (2.84 g, 73%) as a white solid: mp 72-74 °C; $[\alpha]_D^{20} = +48.4$ (c 1.0, CHCl₃); IR 758, 838, 861, 1011, 1248, 2174, 2922, 3104 cm⁻¹; ¹H NMR (400 MHz) δ 0.13 (s, 9H), 0.98-1.27 (m, 5H), 1.17 (s, 9H), 1.39 (s, 3H), 1.49-1.57 (m, 1H), 1.62-1.67 (m, 1H), 1.74-1.81 (m, 2H), 1.86-1.98 (m, 2H), 3.19 (s, 1H); ¹³C NMR (100 MHz) δ -0.1, 22.5, 25.8, 26.3, 27.0, 27.9, 48.1, 55.9, 57.4, 89.0, 108.3. Anal. Calcd for C₁₇H₃₃NOSSi: C, 62.33; H, 10.15; N, 4.28. Found: C, 62.54; H, 10.37; N, 4.41.

(Ss, S)-(+)-*N*-[1-Methyl-1-(*trans*-4-methyl-cyclohexyl)-3-trimethylsilanyl-prop-2-ynyl]-2-methylpropanesulfinamide (**2f**). Procedure B was followed with a mixture of 1.7 mL of (trimethylsilyl)ethyne (12 mmol), 4.3 mL of butyllithium (9.0 mmol, 2.1 M in hexanes), 1.0 g of *N*-sulfinyl ketimine **1d** (4.1 mmol), and 0.47 mL of Me₃Al (4.9 mmol) in 32 mL total volume of toluene. HPFC purification (hexane/EtOAc = 94:6 for 7 min, 94:6 to 50:50 over 108 min) provided propargyl sulfinamide **2f** (1.1 g, 80%) as a white solid: mp 75-79 °C; $[\alpha]_D^{20} = +40.9$ (c 1.0, CHCl₃); IR 759, 839, 879, 1014, 1026, 1249, 2176, 2918, 3098 cm⁻¹; ¹H NMR (400 MHz) δ 0.15 (s, 9H), 0.86 (d, $J = 6.4$, 3H), 0.88-0.97 (m, 2H), 1.06-1.17 (m, 2H), 1.19 (s, 9H), 1.23-1.33 (m, 1H), 1.42 (s, 3H), 1.46-1.54 (m, 1H), 1.71-1.77 (m, 2H), 1.85-1.98 (m, 2H), 3.22 (s, 1H); ¹³C NMR (100 MHz) δ -0.1, 22.4, 22.5, 26.0, 26.9, 27.8, 32.6, 34.88, 34.91, 47.8, 56.0, 57.4, 89.0, 108.3. Anal. Calcd for C₁₈H₃₅NOSSi: C, 63.28; H, 10.33; N, 4.10. Found: C, 63.45; H, 10.03; N, 4.45.

(Ss, S)-(+)-*N*-[1-Methyl-1-(*cis*-4-methyl-cyclohexyl)-3-trimethylsilanyl-prop-2-ynyl]-2-methylpropanesulfinamide (**2g**). Procedure B was followed with a mixture of 1.7 mL of (trimethylsilyl)ethyne (12 mmol), 4.3 mL of butyllithium (9.0 mmol, 2.1 M in hexanes), 1.0 g of

N-sulfinyl ketimine **1e** (4.1 mmol), and 0.47 mL of Me₃Al (4.9 mmol) in 32 mL total volume of toluene. HPFC purification (hexane/EtOAc = 94:6 for 7 min, 94:6 to 50:50 over 108 min) provided propargyl sulfinamide **2g** (1.2 g, 85%) as a white solid: mp 117-119 °C; $[\alpha]_D^{20} = +43.0$ (*c* 1.0, CHCl₃); IR 758, 837, 864, 1010, 1249, 2173, 2942, 3136 cm⁻¹; ¹H NMR (400 MHz) δ 0.15 (s, 9H), 0.93 (d, *J* = 7.2, 3H), 1.19 (s, 9H), 1.30-1.71 (m, 9H), 1.44 (s, 3H), 1.88-1.96 (m, 1H), 3.25 (s, 1H); ¹³C NMR (100 MHz) δ -0.1, 17.2, 21.0, 21.6, 22.5, 26.3, 26.6, 31.50, 31.53, 48.14, 56.0, 57.6, 89.0, 108.1. Anal. Calcd for C₁₈H₃₅NOSSi: C, 63.28; H, 10.33; N, 4.10. Found: C, 63.52; H, 10.67; N, 4.50.

(Ss, **S**)-(+)-*N*-(1-Cyclohexyl-1-ethyl-3-trimethylsilyl-prop-2-ynyl)-2-methylpropanesulfinamide (**2h**). Procedure B was followed with a mixture of 0.42 mL of (trimethylsilyl)ethyne (3.0 mmol), 1.0 mL of butyllithium (2.2 mmol, 2.2 M in hexanes), 0.243 g of *N*-sulfinyl ketimine **1f** (1.00 mmol), and 0.12 mL of Me₃Al (1.2 mmol) in 7 mL total volume of toluene. HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min) provided propargyl sulfinamide **2h** (0.274 g, 80%) as a white solid: mp 74-77 °C; $[\alpha]_D^{20} = +30.8$ (*c* 1.0, CHCl₃); IR 759, 839, 1011, 1248, 2170, 2924, 3132 cm⁻¹; ¹H NMR (400 MHz) δ 0.12 (s, 9H), 0.96 (t, *J* = 7.2, 3H), 1.00-1.14 (m, 3H), 1.16 (s, 9H), 1.18-1.25 (m, 2H), 1.53-1.70 (m, 4H), 1.71-1.79 (m, 2H), 1.85-1.91 (m, 2H), 3.12 (s, 1H); ¹³C NMR (100 MHz) δ -0.1, 8.71, 22.6, 26.4, 26.5, 27.0, 27.6, 30.5, 46.3, 56.3, 62.3, 90.9, 106.6. Anal. Calcd for C₁₈H₃₅NOSSi: C, 63.28; H, 10.33; N, 4.10. Found: C, 62.96; H, 10.50; N, 4.00.

(Ss, **S**)-(+)-*N*-(1-Butyl-1-methyl-3-trimethylsilyl-prop-2-ynyl)-2-methylpropanesulfinamide (**2i**). Procedure B was followed with a mixture of 0.42 mL of

(trimethylsilyl)ethyne (3.0 mmol), 1.0 mL of butyllithium (2.2 mmol, 2.2 M in hexanes), 0.203 g of *N*-sulfinyl ketimine **1g** (1.00 mmol), and 0.12 mL of Me₃Al (1.2 mmol) in 7 mL total volume of toluene. After hydrolysis of the remaining *tert*-butanesulfinyl ketimine, HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min) provided propargyl sulfinamide **2i** (0.140 g, 46%) as a white solid: mp 71-74 °C; $[\alpha]_D^{20} = +50.6$ (*c* 1.0, CHCl₃); IR 759, 839, 858, 1059, 1248, 2173, 2956, 3195 cm⁻¹; ¹H NMR (400 MHz) δ 0.14 (s, 9H), 0.90 (t, *J* = 7.2, 3H), 1.18 (s, 9H), 1.25-1.45 (m, 4H), 1.47 (s, 3H), 1.62-1.80 (m, 2H), 3.19 (s, 1H); ¹³C NMR (100 MHz) δ -0.1, 14.0, 22.5, 22.7, 26.7, 29.1, 42.9, 54.4, 55.9, 88.3, 108.5. Anal. Calcd for C₁₅H₃₁NOSSi: C, 59.74; H, 10.36; N, 4.64. Found: C, 59.46; H, 10.50; N, 4.73.

(Ss, **S**)-(+)-*N*-(1-Methyl-1-phenyl-3-trimethylsilanyl-prop-2-ynyl)-2-methylpropanesulfinamide (**2j**). Procedure B was followed with a mixture of 0.15 mL of (trimethylsilyl)ethyne (1.0 mmol), 0.36 mL of butyllithium (0.79 mmol, 2.2 M in hexanes), 0.080 g of *N*-sulfinyl ketimine **1h** (0.36 mmol), and 0.041 mL of Me₃Al (0.43 mmol) in 2.4 mL total volume of toluene. Product yield (20%) was determined by NMR analysis using hexamethylbenzene as an external standard. After hydrolysis of the remaining *tert*-butanesulfinyl ketimine, HPFC purification (hexane/EtOAc = 94:6 for 3 min, 94:6 to 50:50 over 30 min) provided propargyl sulfinamide **2j** as a white solid: 74-77 °C; $[\alpha]_D^{20} = +35.7$ (*c* 1.0, CHCl₃); IR 696, 760, 840, 1031, 1042, 1249, 2174, 2958, 3192 cm⁻¹; ¹H NMR (400 MHz) δ 0.22 (s, 9H), 1.22 (s, 9H), 1.82 (s, 3H), 3.56 (s, 1H), 7.27-7.32 (m, 1H), 7.32-7.38 (m, 2H), 7.64-7.68 (m, 2H); ¹³C NMR (100 MHz) δ -0.2, 22.5, 32.1, 56.2, 56.7, 91.0, 107.6, 126.1, 127.9, 128.4, 143.5. Anal. Calcd for C₁₇H₂₇NOSSi: C, 63.50; H, 8.46; N, 4.36. Found: C, 63.28; H, 8.52; N, 4.39.