Supplementary Information

Highly Diastereoselective Addition of Alkoxyethynyl Aluminium Reagents to N-tert-Butylsulfinyl Aldimines

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Reactions were generally carried out under argon in oven-dried glassware. Standard inert atmosphere techniques were used in handling all air and moisture sensitive reagents. Dry THF was obtained by filtration through activated molecular sieves and dry CH₂Cl₂ by filtration through activated aluminium oxide. Thin-layer chromatography was performed on (0.2 mm) silica sheets, which were visualized under ultraviolet light and by heating the plate after treatment with phosphomolybdic acid in ethanol, a p-anisaldehyde staining solution (80 mL of 95% ethanol, 2.9 mL of sulfuric acid, 0.86 mL of acetic acid, 2.1 mL of p-anisaldehyde), ninhydrin in ethanol, ceric ammonium molybdate in ethanol, or basic, aqueous KMnO₄. Silica gel (0.040-0.063 mm) was employed for flash column chromatography. A Fourier transform infrared spectrometer was used to record IR spectra. ¹H NMR and ¹³C NMR spectra were recorded on either an AV 300, 400, or 500 MHz apparatus. All shifts for ¹H spectra were referenced to the residual solvent peak and are reported in ppm. When ambiguous, proton and carbon assignments were established through COSY, HMQC, and/or DEPT experiments. Mass spectra were recorded using either DCI (ammonia/isobutane 63/37), EI, or ESI techniques. HRMS were recorded on an Orbitrap apparatus (ESI). Microanalyses were performed by the microanalysis service of the DCM.

General procedure: To a solution of dichloroenol ether (4 eq) in dry THF (0.3 M) at –80 °C was added dropwise a solution of n-BuLi (2.5 M/hexane, 7.8 eq). The reaction mixture was allowed to warm to –20 °C over 45 min and cooled to –80 °C. A solution of Me₂AlCl (0.9 M in heptane, 4 eq) was then added dropwise and the solution stirred for 30 minutes at –80 °C. A solution of sulfinylimine (1a-i, 1 eq) in dry THF (0.3 M) was then added dropwise via a cannula, and the flask containing the imine was washed twice with dry THF. The reaction mixture was placed at 0 °C for 3-6 h. After complete disappearance of the starting material (TLC: pentane/EtOAc, 65:35), the reaction was cooled to –80 °C and quenched with NaHCO₃ and diluted with EtOAc. The organic phase was washed several times with Rochelle salt, water and brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure (bath temperature kept below 30 °C). The residue was purified by flash chromatography (SiO₂/2.5% Et₃N) to afford the N-tert-butanesulfinamides (2a-i).
(S,S\(^*\))-N-(3-(tert-Butoxy)-1-phenylprop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (2a). Sulfinylimine 1a (63 mg, 0.3 mmol) and O-tertbutyl-1,2-dichloroenolether (201 mg, 1.2 mmol) afforded 85 mg (92\%, dr > 98:2) of sulfinamide 2a as a white solid: m.p. 84-86 °C (decomp); IR (neat) 2254, 3034 cm\(^{-1}\); \(^1\)H NMR(400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.50-7.47 (m, 2H), 7.37-7.23 (m, 3H), 5.25 (d, \(J = 6.1\) Hz, 1H), 3.50 (d, \(J = 6.1\) Hz, 1H), 1.42 (s, 9H), 1.19 (s, 9H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 141.1, 128.7, 128.2, 127.9, 92.4, 87.2, 56.4, 51.5, 40.8, 27.5, 22.9; MS (ESI) \(m/z\) [M+H]\(^{+}\) 308.1; HRMS (FT, ESI) calcd for C\(_{17}\)H\(_{25}\)NNaO\(_2\)S: 330.14982. Found: 330.15012.

(S,S\(^*\))-N-(3-(Cyclohexyloxy)-1-phenylprop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (2a'). Sulfinylimine 1a (720 mg, 3.44 mol) and O-cyclohexyl-1,2-dichloroenolether (0.653g, 13.6 mmol) afforded 1.02g (89\%, dr > 98:2) of sulfinamide 2a': m.p. 89-91 °C (decomp); \([\alpha]\)\(^{20}\) \(+28.0\) (c = 1, CHCl\(_3\)); IR (neat) 2272, 3212 cm\(^{-1}\); \(^1\)H NMR(400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.52-7.46 (m, 2H), 7.38-7.24 (m, 3H), 5.24 (d, \(J = 5.7\) Hz, 1H), 5.00-4.20 (m, 1H), 3.52 (d, \(J = 5.7\) Hz, 1H), 2.02-1.90 (m, 2H), 1.81-1.68 (m, 2H), 1.68-1.55 (m, 2H), 1.55-1.44 (m, 1H), 1.39-1.22 (m, 3H), 1.19 (s, 9H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 141.0, 128.8, 128.2, 128.0, 94.4, 87.0, 56.4, 51.2, 38.9, 22.9, 31.3, 25.4, 23.4; MS (ESI) \(m/z\) [M+H]\(^{+}\) 334.2; HRMS (FT, ESI) calcd for C\(_{19}\)H\(_{27}\)NNaO\(_2\)S: 356.16547. Found: 356.16589.

(S,S\(^*\))-N-(3-(tert-Butoxy)-1-(4-methoxyphenyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide (2b). Sulfinylimine 1b (68 mg, 0.28 mmol) and O-tertbutyl-1,2-dichloroenolether (201 mg, 1.2 mmol) afforded 74 mg (77\%, dr > 98:2) of sulfinamide 2b isolated as a white solid: m.p. 82-84 °C (decomp); IR (neat) 2257, 3197 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.39 (d, \(J = 8.7\) Hz, 2H), 6.83 (d, \(J = 8.7\) Hz, 2H), 5.18 (d, \(J = 5.9\) Hz, 1H), 3.77 (s, 3H), 3.47 (d, \(J = 5.9\) Hz, 1H), 1.39 (s, 9H), 1.17 (s, 9H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 159.5, 133.2, 129.1, 114.0, 92.1, 87.0, 56.3,
55.5, 50.8, 40.9, 27.4, 22.8; MS (ESI) m/z [M+H]+ 338.2; HRMS (FT, ESI) calcd for C_{18}H_{27}NNaO_{3}S: 360.16039. Found: 360.16092.

\[(S^*,S^*)-N-(1-(4-Bromophenyl)-3-(tert-butoxy)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide\] (2c). Sulfinylimine 1c (86.6 mg, 0.3 mmol) and O-tert-butyl-1,2-dichloroenolether (219 mg, 1.3 mmol) afforded 106 mg (91%, dr = 96:4) of sulfinamide 2c as a yellow pale solid: m.p. 86-88 °C (decomp); IR (neat) 2264, 3141 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.46 (d, \(J = 8.5\) Hz, 2H), 7.36 (d, \(J = 8.5\) Hz, 2H), 5.20 (d, \(J = 5.7\) Hz, 1H), 3.50 (d, \(J = 5.7\) Hz, 1H), 1.40 (s, 9H), 1.19 (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm) 140.3, 131.9, 129.7, 122.2, 92.6, 87.5, 56.5, 50.8, 40.4, 27.4, 22.9; MS (ESI) m/z [M-H]– 385.9; HRMS (FT, ESI) calcd for C_{17}H_{24}BrNNaO_{2}S: 408.06033. Found: 408.06138.

\[(S^*,S^*)-N-(3-(tert-Butoxy)-1-(4-nitrophenyl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide\] (2d). Sulfinylimine 1d (88.2 mg, 0.34 mmol) and O-tert-butyl-1,2-dichloroenolether (222.9 mg, 1.33 mmol) afforded 110 mg (90 %, dr = 97:3) of sulfinamide 2d as a yellow pale solid: m.p. 83-85 °C (decomp); IR (neat) 2261, 3122 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) (ppm) 8.17- 8.14 (m, 2H), 7.67 -7.62 (m, 2H), 5.32 (d, \(J = 5.5\) Hz, 1H), 3.62 (d, \(J = 5.5\) Hz, 1H), 1.38 (s, 9H), 1.18 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm) 148.3, 147.8, 128.8, 124.0, 93.3, 87.9, 56.6, 50.7, 39.8, 27.4, 22.8; MS (ESI) m/z [M+H]+ 353.2; HRMS (FT, ESI) calcd for C_{17}H_{24}N_{2}NaO_{4}S: 375.13490. Found: 375.13522.

\[(S^*,S^*)-N-(3-(tert-Butoxy)-1-(furan-2-yl)prop-2-yn-1-yl)-2-methylpropane-2-sulfinamide\] (2e). Sulfinylimine 1e (56.8 mg, 0.29 mmol) and O-tert-butyl-1,2-dichloroenolether (205 mg, 1.22 mmol) afforded 72 mg (85%, dr = 95:5) of sulfinamide 2e as a yellow pale solid: m.p. 61-63 °C; IR (neat) 2268, 3151 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.36 (ps t, \(J = 1.9\) Hz, 1H), 6.31 (dd, \(J = 3.1, 1.9\) Hz, 1H), 5.28 (d, \(J = 6.4\) Hz, 1H), 3.49 (d, \(J = 6.4\) Hz, 1H), 1.43 (s,
9H), 1.20 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 153.6, 142.8, 110.5, 107.7, 91.2, 87.4, 56.5, 45.8, 38.4, 27.4, 22.7; MS (ESI) $m/z$ [M+H]$^+$ 298.2; HRMS (FT, ESI) calcd for C$_{15}$H$_{23}$NNaO$_3$S: 320.12909. Found: 320.12941.

(S$_S^*$,S$_S^*$)-N-(3-(tert-Butoxy)hept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (2f). Sulfinylimine 1f (56.3 mg, 0.3 mmol) and O-tertbutyl-1,2-dichloroenolether (204 mg, 1.2 mmol) afforded 70 mg (83%, dr = 93:7) of sulfinamide 2f as a white solid: m.p. 39-40 °C; IR (neat) 2257, 3027 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 4.02 (td, $J = 7.2$, 5.9 Hz, 1H), 3.14 (d, $J = 5.9$ Hz, 1H), 1.71-1.54 (m, 2H), 1.45-1.23 (m, 4H), 1.37 (s, 9H), 1.18 (s, 9H), 0.87 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 90.4, 86.5, 56.1, 48.1, 41.6, 37.9, 28.2, 27.4, 22.9, 22.6, 14.3; MS (ESI) $m/z$ [M+H]$^+$ 288.2; HRMS (FT, ESI) calcd for C$_{15}$H$_{29}$NNaO$_2$S: 310.18112. Found: 310.18133.

(S$_S^*$,S$_S^*$)-N-(3-(tert-Butoxy)-4-methylpent-1-yn-3-yl)-2-methylpropane-2-sulfinamide (2g). Sulfinylimine 1g (58.5 mg, 0.33 mmol) and O-tertbutyl-1,2-dichloroenolether (214 mg, 1.27 mmol) afforded 98 mg (83%, dr = 94:6) of sulfinamide 2g as a colourless oil: IR (neat) 2255, 3200 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm) 3.91 (dd, $J = 6.1$, 4.9 Hz, 1H), 3.11 (d, $J = 6.4$ Hz, 1H), 1.85 (dhept., $J = 6.7$, 4.9 Hz, 1H), 1.36 (s, 9H), 1.17 (s, 9H), 0.93 (d, $J = 6.7$ Hz, 3H), 0.92 (d, $J = 6.7$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ (ppm) 91.0, 86.4, 56.2, 54.0, 39.6, 34.2, 27.4, 22.9, 19.4, 17.6; MS (ESI) $m/z$ [M+H]$^+$ 274.2; HRMS (FT, ESI) calcd for C$_{14}$H$_{27}$NNaO$_2$S: 296.16547. Found: 296.16575.

(S$_S^*$,S$_S^*$)-N-(3-(tert-Butoxy)-4,4-dimethylpent-1-yn-3-yl)-2-methylpropane-2-sulfinamide (2h). Sulfinylimine 1h (56.2 mg, 0.3 mmol) and O-tertbutyl-1,2-dichloroenolether (211 mg, 1.26 mmol) afforded 71 mg (83%, dr = 95:5) of sulfinamide 2h as a white solid: m.p. 90-92 °C (decomp); IR (neat) 2255, 3207 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 3.67 (d, $J = 8.9$ Hz, 1H), 3.01 (d, $J = 8.9$ Hz, 1H), 1.38 (s, 9H), 1.20 (s, 9H), 0.95 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm) 91.2, 86.4,
59.0, 56.7, 40.4, 36.8, 27.5, 26.5, 23.1; MS (ESI) m/z [M+H]^+ 288.2; HRMS (FT, ESI) calcd for C_{15}H_{29}NNaO_{2}S: 310.18112. Found: 310.18137.
**↑Crude Product**

**↓Isolated**

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HN

S

O

t
Bu

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2b

Crude Product

Isolated
**Crude Product**

![Crude Product](image1)

**Isolated**

![Isolated](image2)

**300 MHz**  
**CDCl₃**  
**vech92b 1 1 I:\serco\cverrier Charlie RMN**

**400 MHz**  
**CDCl₃**  
**vech92b2 1 1 I:\serco\cverrier Charlie RMN**