Supporting Information

Telluronium Salts Mediated Aziridination of Chiral N-tert-Butyl-sulfinylimines: Highly Stereoselective Synthesis of Optically Active Vinylaziridines

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General Information All reaction flasks were dried by flame. And all reactions were carried out under N₂ unless otherwise noted. All solvents were purified according to standard methods.

¹H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in chloroform-d₃. All signals are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration).

¹³C NMR spectra were recorded on a VARIAN Mercury 75 MHz spectrometer in chloroform-d₃. All signals are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

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Part I

Procedure for aziridination between telluronium salt and *N-tert*-Butylsulfinylimine in Table 1.

Entries 1-6, Table 1: To a suspension of telluronium salt (0.6 mmol, 1.5 equiv) in THF (8.0 mL) at -78 °C was added base (0.6 mmol, 1.5 equiv). After 20 min, *N-tert*-butylsulfinylimine (0.4 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Entries 7-8, Table 1: To a suspension of telluronium salt (0.6 mmol, 1.5 equiv) in toluene (8.0 mL) at -78 °C was added base (0.6 mmol, 1.5 equiv). After 20 min, *N-tert*-butylsulfinylimine (0.4 mmol, 1.0 equiv) in toluene (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Procedure for aziridination between telluronium salt and *N-tert*-butylsulfinylimine in Table 2.

Method A (Entries 1-3, Table 2): To a suspension of telluronium salt (0.6 mmol, 1.5 equiv) in THF (8.0 mL) at -78 °C was added base (0.6 mmol, 1.5 equiv) and then additive. After 20 min, *N-tert*-butylsulfinylimine (0.4 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Method B (Entry 4, Table 2): To a mixture of telluronium salt (0.6 mmol, 1.5 equiv) and LiBr (0.8 mmol, 2.0 equiv) in THF (8.0 mL) at -78 °C was added base (0.6 mmol, 1.5 equiv). After 20

min, *N-tert*-butylsulfinylimine (0.4 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Method B (Entry 5, Table 2): To a mixture of telluronium salt (0.6 mmol, 1.5 equiv) and MgBr₂ (0.8 mmol, 2.0 equiv) in THF (8.0 mL) at -78 °C was added base (0.76 mmol, 1.9 equiv). After 20 min, *N-tert*-butylsulfinylimine (0.4 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Method B (Entry 6, Table 2): To a mixture of telluronium salt (0.6 mmol, 1.5 equiv) and Ti(OEt)₄ (0.8 mmol, 2.0 equiv) in THF (8.0 mL) at -78 °C was added base (1.6 mmol, 4.0 equiv). After 20 min, *N-tert*-butylsulfinylimine (0.4 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Procedure for aziridination between telluronium salt and *N-tert*-butylsulfinylimine in Table 3 and Table 4.

Method A in Table 3 or Table 4: To a suspension of telluronium salt (0.6 mmol, 1.5 equiv) in THF (8.0 mL) at -78 °C was added base (0.6 mmol, 1.5 equiv). After 20 min, *N-tert*-butylsulfinylimine (0.4 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Method B in Table 3 or Table 4: To a mixture of telluronium salt (0.6 mmol, 1.5 equiv) and Ti(OEt)₄ (0.8 mmol, 2.0 equiv) in THF (8.0 mL) at -78 °C was added base (1.6 mmol, 4.0 equiv).

After 20 min, *N-tert*-butylsulfinylimine (0.4 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Procedure for aziridination between telluronium salt **1a and *N-tert*-butylsulfinylimine **2l** (Scheme 1).**

To a suspension of telluronium salt **1a** (0.6 mmol, 1.5 equiv) in THF (8.0 mL) at -78 °C was added LiHMDS (0.6 mmol, 1.5 equiv). After 20 min, imine **2l** (0.4 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise. The resulting suspension was stirred at -78 °C for further 4 h, warmed to rt in 1 h, passed through a short silica gel column (eluted with ethyl acetate). After concentration of the elution, the residue was purified by flash column chromatography to afford the desired product.

Part II

White solide. Mp 105-107°C. IR (thin film) ν/cm^{-1} 3502 (m), 2959 (m), 1600 (m), 1586 (m). MS (MALDI): 357.1 [M-BPh₄]. EA: Calcd. for C₃₈H₅₁BSiTe: C: 67.69%; H: 7.62%. Found: C: 67.60%; H: 7.60%. ¹H NMR (300 MHz, CDCl₃/TMS) δ 7.49 (s, 9H), 7.06 (t, J = 7.5 Hz, 7H), 6.91 (t, J = 7.2 Hz, 4H), 5.73 (d, J = 18.3 Hz, 1H), 5.38 (dt, J = 18.3, 7.5 Hz, 1H), 2.47 (d, J = 7.5 Hz, 2H), 2.01 (dd, J = 11.7, 7.2 Hz, 2H), 1.87 (dd, J = 11.7, 7.2 Hz, 2H), 1.72-1.39 (m, 2H), 0.88-0.85 (m, 12H), 0.09 (s, 9H). ¹³C NMR (75 MHz, CDCl₃/TMS) δ 164.4 (q, J = 48.6 Hz), 144.0, 136.2, 132.1, 126.0 (d, J = 2.9 Hz), 122.1, 35.4, 28.4, 26.5, 24.0, 23.9, -1.4.

(*E*)-*N*-((*E*)-2-Ethylhex-2-enylidene)-2-methylpropane-2-sulfinamide

Colorless oil. $[\alpha]_D^{+467}$ (c 0.92, CHCl₃). IR (thin film) ν/cm^{-1} 2963 (s), 2932 (m), 2872 (m), 1633 (m), 1579 (s), 1089 (m). MS (EI): m/z (% relative intensity) 230 (35) [M+H], 57 (100). HRMS (ESI): Calcd for C₁₂H₂₃NOS [M+Na]: 252.1391. Found: 252.1392. ¹H NMR (300 MHz, CDCl₃/TMS) δ 7.98 (s, 1H), 6.12 (t, J = 8.1 Hz, 1H), 2.43-2.25 (m, 2H), 2.21 (q, J = 7.2 Hz, 2H), 1.52-1.35 (m, 2H), 1.18 (s, 9H), 0.95 (t, J = 7.5 Hz, 3H), 0.87 (t, J = 7.5 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃/TMS) δ 165.9, 148.0, 140.9, 57.0, 30.5, 22.4, 22.1, 19.0, 13.8, 13.4.

(E)-1-(*tert*-Butylsulfinyl)-2-phenyl-3-(2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a clear pale-yellow oil. $[\alpha]_D^{+199}$ (c 0.89, CHCl_3). IR (thin film) ν/cm^{-1} 2955 (s), 2926 (m), 2866 (m), 1607 (m), 1455 (m), 1248 (m), 1081 (m). MS (EI): m/z (% relative intensity) 216 (3) $[\text{M} - ^t\text{BuSO}]$, 43 (100). HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{27}\text{NOSSi}$ $[\text{M} + \text{Na}]$: 344.1476. Found: 344.1475. ^1H NMR (300 MHz, CDCl_3/TMS) δ 7.34-7.26 (m, 5H), 6.11 (d, $J = 18.9$ Hz, 1H), 5.65 (dd, $J = 18.9, 7.2$ Hz, 1H), 3.95 (d, $J = 6.9$ Hz, 1H), 3.04 (t, $J = 6.9$ Hz, 1H), 1.23 (s, 9H), -0.05 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 138.2, 137.5, 134.1, 128.1, 127.4, 57.1, 43.5, 38.2, 22.8, -1.6.

(E)-1-(*tert*-Butylsulfinyl)-2-(4-chlorophenyl)-3-(2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a clear pale-yellow oil. $[\alpha]_D^{-5.6}$ (c 1.2, CHCl_3). IR (thin film) ν/cm^{-1} 2956 (s), 2926 (m), 2866 (m), 1614 (m), 1492 (m), 1248 (m), 1085 (s). MS (EI): m/z (% relative intensity) 355 (0.3) M^+ , 250 (42) $[\text{M} - ^t\text{BuSO}]$, 57 (100). HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{26}\text{ClNOSSi}$ $[\text{M} + \text{Na}]$: 378.1087. Found: 378.1085. ^1H NMR (300 MHz, CDCl_3/TMS) δ 7.38-7.26 (m, 4H), 6.15 (d, $J = 18.6$ Hz, 1H), 5.65 (dd, $J = 18.6, 7.2$ Hz, 1H), 3.94 (d, $J = 7.2$ Hz, 1H), 3.07 (t, $J = 7.2$ Hz, 1H), 1.25 (s, 9H), 0.01 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 138.0, 137.6, 133.3, 132.8, 129.4, 128.3, 57.1, 43.6, 37.6, 22.7, -1.6.

(*E*)-1-(*tert*-Butylsulfinyl)-2-(4-(trifluoromethyl)phenyl)-3-(2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a pale-yellow solid. Mp 69-71°C. $[\alpha]_D^{25} +5.4$ (c 1.0, CHCl₃). IR (thin film) ν/cm^{-1} 2957 (s), 2928 (m), 2866 (m), 1620 (m), 1364 (w), 1325 (s), 1067 (s). MS (EI): m/z (% relative intensity) 284 (31) [M- ^tBuSO], 57 (100). HRMS (ESI): Calcd for C₁₈H₂₆F₃NOSSi [M+Na]: 412.1347. Found: 412.1349. ¹H NMR (300 MHz, CDCl₃/TMS) δ 7.57 (ABd, J = 7.8 Hz, 2H), 7.44 (ABd, J = 7.8 Hz, 2H), 6.12 (d, J = 18.0 Hz, 1H), 5.58 (dd, J = 18.0, 6.9 Hz, 1H), 3.97 (d, J = 7.2 Hz, 1H), 3.08 (t, J = 6.9 Hz, 1H), 1.22 (s, 9H), -0.08 (s, 9H). ¹⁹F NMR δ -62.9. ¹³C NMR (75 MHz, CDCl₃/TMS) δ 138.5 (d, J = 1.8 Hz), 138.4, 137.2, 129.7 (q, J = 33 Hz), 128.4, 125.1 (q, J = 3.7 Hz), 122.2 (t, J = 272.9 Hz), 57.1, 43.6, 37.7, 22.7, -1.6.

(*E*)-1-(*tert*-Butylsulfinyl)-2-*p*-tolyl-3-(2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a pale-yellow oil. $[\alpha]_D^{25} +14.9$ (c 1.0, CHCl₃). IR (thin film) ν/cm^{-1} 2955 (s), 2925 (m), 2867 (m), 1615 (w), 1516 (m), 1083 (s). MS (EI): m/z (% relative intensity) 230 (54) [M- ^tBuSO], 73 (100). HRMS (ESI): Calcd for C₁₈H₂₉NOSSi [M+Na]: 358.1629. Found: 358.1631. ¹H NMR (300 MHz, CDCl₃/TMS) δ 7.25 (ABd, J = 7.5 Hz, 2H), 7.15 (ABd, J = 7.5 Hz, 2H), 6.14 (d, J = 18.6 Hz, 1H), 5.71 (dd, J = 18.6, 7.5 Hz, 1H), 3.94 (d, J = 6.9 Hz, 1H), 3.04 (t, J = 7.2 Hz, 1H), 2.37 (s, 3H), 1.25 (s, 9H), -0.02 (s, 9H). ¹³C NMR (75 MHz, CDCl₃/TMS) δ 138.4, 137.4, 137.1, 131.1, 128.8, 127.9, 57.0, 43.6, 38.1, 22.8, 21.1, -1.6.

(E)-1-(*tert*-Butylsulfinyl)-2-(naphthalen-1-yl)-3-(2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a pale-yellow oil. $[\alpha]_D -112.1$ (c 1.0, CHCl_3). IR (thin film) ν/cm^{-1} 2955 (s), 2926 (m), 2867 (m), 1608 (w), 1363 (m), 1083 (s). MS (EI): m/z (% relative intensity) 266 (78) $[\text{M} - ^t\text{BuSO}]$, 73 (100). HRMS (ESI): Calcd for $\text{C}_{21}\text{H}_{29}\text{NOSSi}$ $[\text{M} + \text{Na}]$: 394.1634. Found: 394.1631. ^1H NMR (300 MHz, CDCl_3/TMS) δ 8.11-8.08 (m, 1H), 7.81-7.78 (m, 1H), 7.71 (d, $J = 8.1$ Hz, 1H), 7.51 (d, $J = 7.2$ Hz, 1H), 7.47-7.35 (m, 3H), 6.00 (d, $J = 18.6$ Hz, 1H), 5.40 (dd, $J = 18.6, 7.2$ Hz, 1H), 4.51 (d, $J = 7.2$ Hz, 1H), 3.23 (t, $J = 7.2$ Hz, 1H), 1.25 (s, 9H), -0.28 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 137.9, 137.2, 133.3, 132.2, 129.9, 128.5, 127.8, 126.2, 125.8, 125.2, 124.8, 123.3, 57.1, 43.5, 36.7, 22.7, -1.8.

(E)-1-(*tert*-Butylsulfinyl)-2-(furan-2-yl)-3-(2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a pale-yellow oil. $[\alpha]_D +73.3$ (c 1.2, CHCl_3). IR (thin film) ν/cm^{-1} 2956 (s), 2926 (m), 2868 (m), 1608 (w), 1475 (m), 1083 (s). MS (EI): m/z (% relative intensity) 312 (1) $[\text{M} + \text{H}]$, 206 (2) $[\text{M} - ^t\text{BuSO}]$, 57 (100). HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{SSi}$ $[\text{M} + \text{Na}]$: 334.1265. Found: 334.1267. ^1H NMR (300 MHz, CDCl_3/TMS) δ 7.40 (d, $J = 1.5$ Hz, 1H), 6.38-6.36 (m, 1H), 6.28 (d, $J = 3.0$ Hz, 1H), 6.14 (d, $J = 18.6$ Hz, 1H), 5.94 (dd, $J = 18.6, 6.9$ Hz, 1H), 3.91 (d, $J = 6.9$ Hz, 1H), 3.04 (t, $J = 7.2$ Hz, 1H), 1.25 (s, 9H), 0.07 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 149.2, 142.5, 139.1, 137.4, 110.3, 109.2, 57.2, 42.9, 32.2, 22.7, -1.5..

(E)-1-(tert-Butylsulfinyl)-2-cyclohexyl-3-(2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 25/1) as a pale-yellow oil. $[\alpha]_D -34.0$ (c 0.89, CHCl_3). IR (thin film) ν/cm^{-1} 2956 (m), 2926 (s), 2852 (m), 1612 (w), 1450 (m), 1083 (m). MS (EI): m/z (% relative intensity) 328 (5) $[\text{M}+\text{H}]$, 222 (9) $[\text{M}-\text{t-BuSO}]$, 73 (100). HRMS (ESI): Calcd for $\text{C}_{17}\text{H}_{33}\text{NOSSi}$ $[\text{M}+\text{Na}]$: 350.1947. Found: 350.1944. ^1H NMR (300 MHz, CDCl_3/TMS) δ 6.08 (d, $J = 18.9$ Hz, 1H), 5.85 (dd, $J = 18.6, 7.2$ Hz, 1H), 3.20 (t, $J = 7.2$ Hz, 1H), 2.05 (t, $J = 8.1$ Hz, 1H), 1.90-1.86 (m, 1H), 1.77-1.31 (m, 6H), 1.25 (s, 9H), 1.15-0.85 (m, 4H), 0.07 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 139.1, 136.9, 56.7, 44.6, 37.8, 36.3, 30.7, 29.7, 26.2, 25.6, 25.5, 22.8, -1.4.

(E)-2-tert-Butyl-1-(tert-butylsulfinyl)-3-(2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 25/1) as a pale-yellow oil. $[\alpha]_D +11$ (c 0.89, CHCl_3). IR (thin film) ν/cm^{-1} 2956 (s), 2928 (m), 2868 (m), 1606 (w), 1479 (m), 1084 (m). MS (ESI): m/z 302.2 $[\text{M}+\text{H}]$. HRMS (ESI): Calcd for $\text{C}_{15}\text{H}_{31}\text{NOSSi}$ $[\text{M}+\text{Na}]$: 324.1789. Found: 324.1788. ^1H NMR (300 MHz, CDCl_3/TMS) δ 6.10 (d, $J = 18.6$ Hz, 1H), 5.98 (dd, $J = 18.6, 7.2$ Hz, 1H), 3.15 (t, $J = 7.5$ Hz, 1H), 2.05 (d, $J = 6.9$ Hz, 1H), 1.2 (s, 9H), 0.97 (s, 9H), 0.06 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 140.7, 136.6, 56.7, 48.5, 39.0, 31.8, 27.9, 22.8, -1.5.

1-(*tert*-Butylsulfinyl)-2-(*E*)-styryl-3-((*E*)-2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 25/1) as a pale-yellow oil. $[\alpha]_D^{+14.8}$ (c 0.9, CHCl₃). IR (thin film) ν/cm^{-1} 2955 (m), 2926 (m), 1611 (w), 1248 (m), 1080 (m), 839 (m). MS (EI): m/z (% relative intensity) 242 (100), 73 (58), 243 (25), 57 (18), 115 (17), 59 (10), 228 (9). HRMS (ESI) Calcd for C₁₉H₂₉NOSi⁺(M⁺+Na): 370.16308. Found: 370.16313. ¹H NMR (300 MHz, CDCl₃/TMS) δ 7.39-7.27 (m, 5H), 6.74 (d, J = 16.2 Hz, 1H), 6.16 (d, J = 16.8 Hz, 1H), 6.06-5.87 (m, 2H), 3.48 (dd, J = 8.4, 6.9 Hz, 1H), 2.99 (t, J = 6.9 Hz, 1H), 1.25 (s, 9H), 0.09 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) 139.1, 136.8, 136.3, 135.4, 128.6, 127.9, 126.3, 123.2, 57.1, 42.5, 37.9, 22.9, -1.4.

1-(*tert*-Butylsulfinyl)-2-((*E*)-1-phenylprop-1-en-2-yl)-3-((*E*)-2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a pale-yellow oil. $[\alpha]_D^{+9.3}$ (c 0.95, CHCl₃). IR (thin film) ν/cm^{-1} 3023 (m), 2955 (s), 2926 (m), 2867 (m), 1613 (m), 1363 (m), 1083 (m). MS (EI): m/z (% relative intensity) 256 (85) [M- ^tBuSO], 73 (100). HRMS (ESI): Calcd for C₂₀H₃₁NOSSi [M+Na]: 384.1792. Found: 384.1788. ¹H NMR (300 MHz, CDCl₃/TMS) δ 7.32-7.17 (m, 5H), 6.59 (s, 1H), 6.09 (d, J = 18.9 Hz, 1H), 5.81 (dd, J = 18.9, 7.2 Hz, 1H), 3.39 (d, J = 7.2 Hz, 1H), 2.90 (t, J = 7.2 Hz, 1H), 1.83 (s, 3H), 1.25 (s, 1H), -0.01 (s, 9H). ¹³C NMR (75 MHz, CDCl₃/TMS) δ 138.7, 137.1, 136.9, 130.9, 128.8, 128.2, 128.1, 126.5, 56.9, 42.7, 41.2, 22.6, 17.0, -1.5.

1-(*tert*-Butylsulfinyl)-2-((*E*)-hept-3-en-3-yl)-3-((*E*)-2-(trimethylsilyl)vinyl)aziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a pale-yellow oil. $[\alpha]_D^{+76.5}$ (c 0.95, CHCl_3). IR (thin film) ν/cm^{-1} 2958 (s), 2930 (m), 2872 (m), 1612 (m), 1362 (m), 1084 (m). MS (EI): m/z (% relative intensity) 236 (39) [$\text{M} - ^t\text{BuSO}$], 73 (100). HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{35}\text{NOSSi}$ [$\text{M} + \text{Na}$]: 364.2099. Found: 364.2101. ^1H NMR (300 MHz, CDCl_3/TMS) δ 6.97 (d, $J = 18.9$, 1H), 5.66 (dd, $J = 18.9$, 7.8 Hz, 1H), 5.42 (t, $J = 7.5$ Hz, 1H), 3.22 (d, $J = 7.5$ Hz, 1H), 2.77 (t, $J = 7.2$ Hz, 1H), 2.10-1.93 (m, 4H), 1.38-1.25 (m, 2H), 1.18 (s, 9H), 0.90-0.81 (m, 6H), -0.04 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 139.8, 135.9, 132.5, 127.4, 56.7, 42.8, 39.2, 29.1, 23.2, 22.9, 22.5, 13.7, 12.5, -1.6.

(*E*)-1-(*tert*-Butylsulfinyl)-2-methyl-2-phenyl-3-(2-(trimethylsilyl)vinyl)aziridine

For *trans* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a white solide. Mp 78-80°C. $[\alpha]_D -4.3$ (c 1.02, CHCl_3). IR (thin film) ν/cm^{-1} 2955 (s), 2925 (s), 2853 (m), 1616 (m), 1248 (m), 1092 (m). MS (ESI): m/z 336 [$\text{M} + \text{H}$]. HRMS (ESI): Calcd for $\text{C}_{18}\text{H}_{29}\text{NOSSi}$ [$\text{M} + \text{Na}$]: 358.1632. Found: 358.1631. ^1H NMR (300 MHz, CDCl_3/TMS) δ 7.54-7.50 (m, 2H), 7.38-7.31 (m, 3H), 6.23 (d, $J = 18.6$ Hz, 1H), 6.12 (dd, $J = 18.6$, 6.9 Hz, 1H), 3.25 (d, $J = 6.6$ Hz, 1H), 1.69 (s, 3H), 1.21 (s, 9H), 0.12 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 139.5, 139.1, 138.1, 128.8, 128.3, 128.1, 57.0, 52.2, 52.1, 22.5, 21.5, -1.4.

1-(*tert*-Butylsulfinyl)-2-phenyl-3-vinylaziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 20/1) as a clear pale-yellow oil. $[\alpha]_D^{17}$ (c 0.91, CHCl_3). IR (thin film) ν/cm^{-1} 2958 (sm), 2925 (s), 2855 (m), 1497 (m), 1082 (m). MS (EI): m/z (% relative intensity) 250 (6) $[\text{M}+\text{H}]$, 57 (100). HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_{19}\text{NOS}$ $[\text{M}+\text{Na}]$: 272.1081. Found: 272.1080. ^1H NMR (300 MHz, CDCl_3/TMS) δ 7.37-7.24 (m, 5H), 5.56-5.38 (m, 2H), 5.23-5.18 (m, 1H), 3.96 (d, $J = 6.9$ Hz, 1H), 3.02 (t, $J = 7.2$ Hz, 1H), 1.24 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 134.1, 131.4, 128.3, 127.9, 127.6, 120.7, 57.0, 42.0, 37.8, 22.8.

(*E*)-1-(*tert*-Butylsulfinyl)-2-phenyl-3-styrylaziridine

For *cis* isomer: isolated by flash column chromatography (eluant: petroleum ether/ethyl acetate = 15/1) as a clear pale-yellow oil. $[\alpha]_D^{+24}$ (c 0.9, CHCl_3). IR (thin film) ν/cm^{-1} 2957 (m), 2924 (s), 2854 (m), 1603 (m), 1452 (m), 1080 (m). MS (EI): m/z (% relative intensity) 220 (91) $[\text{M}-^t\text{BuSO}]$, 115 (100). HRMS (ESI): Calcd for $\text{C}_{20}\text{H}_{23}\text{NOS}$ $[\text{M}+\text{Na}]$: 348.1391. Found: 348.1393. ^1H NMR (300 MHz, CDCl_3/TMS) δ 7.43-7.18 (m, 10H), 6.74 (d, $J = 15.6$ Hz, 1H), 5.84 (dd, $J = 15.9, 8.4$ Hz, 1H), 4.04 (d, $J = 6.9$ Hz, 1H), 3.19 (t, $J = 7.2$ Hz, 1H), 1.25 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3/TMS) δ 136.3, 135.5, 134.2, 128.5, 128.4, 128.0, 127.8, 127.6, 126.3, 122.8, 57.1, 42.2, 38.3, 22.8.

Part III

Part IV

1) The stereochemical assignments for *cis*- and *trans*- isomers of 1,2-disubstituted aziridines are based on the proton coupling constants observed. In literature, some of the *trans*-isomers are known and so for these compounds (minor or a trace amount), it is easy to determine the relative configuration of the products just by comparison of the ^1H NMR with the known compounds. For the unknown compounds, the proton coupling constants of the *cis*-isomers prove larger than those of the corresponding *trans*-isomers (e.g., $J = 6.9 - 7.5$ Hz for *cis*-isomer vs $3.6 - 4.5$ Hz for *trans*-isomer, respectively).¹ By comparing coupling constants, the *cis/trans*-configurations could be assigned easily.

1 a) Li, A. H.; Dai, L. X.; Hou, X. L.; Chen, M. B. *J. Org. Chem.* **1996**, *61*, 4641. b) Wang, D. K.; Dai, L. X.; Hou, X. L. *Chem. Commun.* **1997**, 1231. c) Yang, X. F.; Zhang, M. J.; Hou, X. L.; Dai, L. X. *J. Org. Chem.* **2002**, *67*, 8097. d) Morton, D.; Pearson, D.; Field, R. A.; Stockman, R. A. *Org. Lett.* **2004**, *6*, 2377.

2) The determination of trisubstituted aziridine **3I**

As shown in the ^1H - ^1H NOESY spectrum of **3I**, there is a strong ^1H - ^1H correlation between protons **a** and **c** (protons on phenyl group) but a correlation between **a** and **b** is not observed. Also there observed a ^1H - ^1H correlation between **d/e** and **b** but no ^1H - ^1H correlations between **d/e** and **c**. So the relative of trisubstituted aziridine **3I** is assigned as follows: