Supporting Informations

Palladium-Catalyzed Tandem Cyclization of Allenyl-Aldehydes and -Ketones with Aryl Iodides and $\text{Bu}_3\text{SnSnBu}_3$

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General. All reagents were obtained from commercial sources and used without further purification unless stated otherwise. THF was distilled from sodium-benzophenone under N_2 . IR spectra were recorded on a FT-IR spectrometer. ^1H NMR were conducted at 500 MHz in CDCl_3 , and chemical shifts are reported δ units relative to the tetramethylsilane (TMS) signal at 0.00 ppm. Coupling constants (J) are reported in Hz. For thin-layer chromatography (TLC), Merck precoated plates (silica gel 60 F₂₅₄, 0.25 mm) were used. Silica gel 60 (TA792685, 230-400 mesh) from Merck was used for column chromatography. The reported yields are for chromatographically pure isolated products.

4-(1-Phenyl-vinyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ol (*cis*-3a**):** A white solid: mp 120 °C; TLC, SiO_2 , EtOAc / hexanes 1 : 2, R_f = 0.41; IR (KBr) ν 3575, 3056, 2984, 1428, 1339, 1266, 1161, 740; ^1H NMR (500 MHz, CDCl_3) δ 2.43 (s, 3H), 3.27 (m, 1H), 3.38 (dd, 1H, J = 11.5, 0.6 Hz), 3.40 (dd, 1H, J = 11.4, 9.0 Hz), 3.60 (dd, 1H, J = 11.5, 4.2 Hz), 3.74 (dd, 1H, J = 9.0, 7.0 Hz), 4.16 (dd, 1H, J = 7.0, 4.6 Hz), 5.05 (t, 1H, J = 1.5 Hz), 5.45 (dd, 1H, J = 1.5, 0.7), 7.29 (m, 2H), 7.31 (m, 2H), 7.33 (m, 1H), 7.35 (d, 2H, J = 8.3), 7.76 (d, 2H, J = 8.3); ^{13}C NMR (125 MHz, CDCl_3) δ 143.9, 143.7, 140.9, 134.5, 130.1, 129.1, 128.6, 127.9, 126.5, 116.5, 70.8, 56.2, 49.1, 48.9, 21.9; HRMS calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$ 343.1242 found 343.1229. (*trans*-**3a**): TLC, SiO_2 , EtOAc / hexanes 1 : 2, R_f = 0.39; IR (neat) ν 3594, 3057, 2984, 1428, 1340, 1266, 1160, 740; ^1H NMR (500 MHz, CDCl_3) δ 2.44 (s, 3H), 3.16 (m, 1H), 3.22 (dd, 1H, J = 10.8, 4.1 Hz), 3.22 (dd, 1H, J = 10.1, 5.8 Hz), 3.60 (dd, 1H, J = 10.8, 5.5 Hz), 3.65 (dd, 1H, J = 10.1, 7.6 Hz), 4.17 (m, 1H), 5.06 (d, 1H, J = 1.2 Hz), 5.31 (s, 1H), 7.31 (m, 2H), 7.33 (d, 2H, J = 8.3), 7.34 (m, 2H), 7.35 (d, 2H, J = 8.3); ^{13}C NMR (125 MHz, CDCl_3) δ 146.3, 143.7, 140.7, 133.7, 129.7, 128.5, 128.0, 127.6, 126.4, 113.4, 74.2, 54.1, 50.7, 50.6, 21.6; HRMS calcd for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$ 343.1242 found 343.1253.

4-[1-(4-Methoxy-phenyl)vinyl]-1-(toluene-4-sulfonyl)pyrrolidin-3-ol (*cis-3b*): TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.21; IR (neat) ν 3575, 3056, 2984, 1606, 1511, 1427, 1339, 1261, 1166, 748; ¹H NMR (500 MHz, CDCl₃) δ 2.43 (s, 3H), 3.25 (m, 1H), 3.37 (m, 2H), 3.61 (dd, 1H, *J* = 11.4, 4.0 Hz), 3.72 (dd, 1H, *J* = 9.2, 7.0 Hz), 3.80 (s, 3H), 4.17 (m, 1H), 5.0 (d, 1H, *J* = 1.5 Hz), 5.40 (s, 1H), 6.85 (d, 2H, *J* = 8.8 Hz), 7.23 (d, 2H, *J* = 8.8 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 7.76 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 160.0, 144.0, 142.9, 134.4, 133.3, 130.2, 128.0, 127.7, 115.1, 114.4, 70.8, 56.3, 55.7, 49.0, 48.9, 22.0; HRMS calcd for C₂₀H₂₃NO₄S 373.1348 found 373.1335. (*trans-3b*): TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.19; IR (neat) ν 3580, 3056, 2983, 1606, 1510, 1426, 1340, 1262, 1166, 740; ¹H NMR (500 MHz, CDCl₃) δ 2.45 (s, 3H), 3.13 (m, 1H), 3.21 (dd, 1H, *J* = 11.0, 4.0 Hz), 3.30 (dd, 1H, *J* = 10.3, 5.5 Hz), 3.62 (m, 2H), 3.80 (s, 3H), 4.16 (m, 1H), 4.96 (d, 1H, *J* = 1.5 Hz), 5.24 (s, 1H), 6.85 (d, 2H, *J* = 8.8 Hz), 7.23 (d, 2H, *J* = 8.8 Hz), 7.33 (d, 2H, *J* = 8.4 Hz), 7.72 (d, 2H, *J* = 8.4 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 160.0, 144.0, 142.9, 134.4, 133.2, 130.2, 128.0, 127.7, 115.1, 114.5, 70.8, 56.2, 55.7, 49.0, 48.9, 22.0; HRMS calcd for C₂₀H₂₃NO₄S 373.1348 found 373.1346.

4-(1-Thiophen-2-yl-vinyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ol (*cis-3c*): TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.18; IR (neat) ν 3577, 3056, 2984, 1425, 1341, 1161, 740; ¹H NMR (500 MHz, CDCl₃) δ 2.44 (s, 3H), 3.24 (m, 1H), 3.41 (m, 2H), 3.67 (ddd, 1H, *J* = 11.7, 4.4, 1.5 Hz), 3.70 (dd, 1H, *J* = 9.2, 7.0 Hz), 4.36 (m, 1H), 5.0 (d, 1H, *J* = 1.1 Hz), 5.64 (s, 1H), 6.99 (m, 2H), 7.21 (dd, 1H, *J* = 5.1, 1.1 Hz), 7.34 (d, 2H, *J* = 8.1 Hz), 7.77 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 144.1, 144.0, 136.1, 134.4, 130.2, 128.1, 128.0, 125.6, 124.1, 114.6, 71.0, 56.1, 49.2, 48.6, 22.0; HRMS calcd for C₁₇H₁₉NO₃S₂ 349.0806 found 349.0818. (*trans-3c*): TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.16; IR (neat) ν 3566, 3057, 2930, 1422, 1340, 1265, 1160, 740; ¹H NMR (500 MHz, CDCl₃) δ 2.44 (s, 3H), 3.15 (m, 1H), 3.41 (m, 2H), 3.60 (m, 2H), 4.26 (m, 1H), 4.93 (s, 1H), 5.45 (s, 1H), 6.99 (m, 2H), 7.18 (d, 1H, *J* = 5.1 Hz), 7.34 (d, 2H, *J* = 8.1 Hz), 7.77 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 144.1, 144.0, 136.1, 134.3, 130.2, 128.0, 127.9, 125.5, 124.1, 114.6, 71.0, 56.1, 49.1, 48.6, 22.0; HRMS calcd for C₁₇H₁₉NO₃S₂ 349.0806 found 349.0804.

3-Hydroxy-4-(1-phenyl-vinyl)cyclopentane-1,1-dicarboxylic acid ethyl ester (*cis-3d*): TLC, SiO₂, EtOAc / hexanes 1 : 3, R_f = 0.38; IR (neat) ν 3573, 3057, 2986, 1728, 1438, 1265, 1181, 739; ¹H NMR (500 MHz, CDCl₃) δ 1.27 (t, 6H, *J* = 7.3 Hz),

2.52 (m, 3H), 2.67 (t, 1H, $J = 13.2$ Hz), 3.23 (m, 1H), 4.14 (m, 1H), 4.22 (q, 4H, $J = 7.3$ Hz), 5.24 (s, 1H), 5.47 (s, 1H), 7.33 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.9, 172.6, 146.1, 141.8, 128.7, 128.0, 126.5, 115.4, 72.6, 61.9, 58.2, 50.1, 42.2, 35.3, 14.2; HRMS calcd for $\text{C}_{19}\text{H}_{24}\text{O}_5$ 332.1624 found 332.1620. (*trans*-**3d**): TLC, SiO_2 , EtOAc / hexanes 1 : 3, $R_f = 0.36$; IR (neat) ν 3591, 3056, 2985, 1728, 1431, 1431, 1265, 1185, 741; ^1H NMR (500 MHz, CDCl_3) δ 1.23 (t, 3H, $J = 7.0$ Hz), 1.27 (t, 3H, $J = 7.0$ Hz), 2.09 (dd, 1H, $J = 13.9, 10.3$ Hz), 2.23 (dd, 1H, $J = 14.3, 6.2$ Hz), 2.69 (dd, 1H, $J = 14.3, 7.0$ Hz), 2.71 (dd, 1H, $J = 13.9, 7.7$ Hz), 3.11 (m, 1H), 4.18 (m, 1H), 4.23 (q, 4H, $J = 7.0$ Hz), 5.2 (s, 1H), 5.3 (s, 1H), 7.34 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.9, 172.5, 149.2, 141.9, 128.6, 127.8, 126.9, 112.7, 76.5, 62.1, 61.9, 52.1, 41.3, 37.9, 14.2; HRMS calcd for $\text{C}_{19}\text{H}_{24}\text{O}_5$ 332.1624 found 332.1624.

3-Methyl-4-(1-phenyl-vinyl)-1-(toluene-4-sulfonyl)pyrrolidin-3-ol (*cis*-**3e**): A white solid: mp 102 °C; TLC, SiO_2 , EtOAc / hexanes 1 : 2, $R_f = 0.35$; IR (KBr) ν 3579, 3056, 2985, 1427, 1265, 740; ^1H NMR (500 MHz, CDCl_3) δ 0.94 (s, 3H), 2.45 (s, 3H), 3.18 (dd, 1H, $J = 11.4, 7.3$ Hz), 3.36 (d, 1H, $J = 11$ Hz), 3.45 (m, 1H), 3.75 (dd, 1H, $J = 9.5, 7.3$ Hz), 5.15 (s, 1H), 5.47 (s, 1H), 7.31 (m, 7H), 7.77 (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 144.1, 143.7, 142.6, 134.4, 129.9, 128.8, 128.2, 127.8, 126.7, 116.9, 77.5, 60.8, 52.1, 51.5, 25.1, 21.8; HRMS calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_3\text{S}$ 357.1399 found 357.1392. (*trans*-**3e**): TLC, SiO_2 , EtOAc / hexanes 1 : 2, $R_f = 0.33$; IR (neat) ν 3583, 3056, 2985, 1427, 1265, 741; ^1H NMR (500 MHz, CDCl_3) δ 0.97 (s, 3H), 2.46 (s, 3H), 3.29 (m, 2H), 3.39 (d, 1H, $J = 10.6$ Hz), 3.51 (dd, 1H, $J = 9.9, 6.6$ Hz), 3.77 (dd, 1H, $J = 9.9, 7.7$ Hz), 5.03 (s, 1H), 5.32 (s, 1H), 7.31 (m, 7H), 7.77 (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 146.6, 143.7, 142.0, 134.0, 129.8, 128.6, 127.9, 127.6, 126.8, 114.8, 79.1, 59.3, 52.2, 51.5, 22.5, 21.6; HRMS calcd for $\text{C}_{20}\text{H}_{23}\text{NO}_3\text{S}$ 357.1399 found 357.1398.

3-Hydroxy-3-methyl-4-(1-thiophen-2-yl-vinyl)cyclopentane-1,1-dicarboxylic acid diethyl ester (*cis*-**3f**): TLC, SiO_2 , EtOAc / hexanes 1 : 2, $R_f = 0.39$; IR (neat) ν 3464, 3056, 2985, 1728, 1424, 1264, 1194, 742; ^1H NMR (500 MHz, CDCl_3) δ 1.17 (s, 3H), 1.27 (m, 6H), 2.42 (d, 1H, $J = 14.3$ Hz), 2.52 (dd, 1H, $J = 13.2, 7.3$ Hz), 2.64 (d, 1H, $J = 14.3$ Hz), 2.75 (dd, 1H, $J = 13.2, 12.8$ Hz), 3.15 (dd, 1H, $J = 12.8, 7.3$ Hz), 4.22 (m, 4H), 5.28 (s, 1H), 5.70 (s, 1H), 6.97 (dd, 1H, $J = 5.1, 3.7$ Hz), 7.08 (dd, 1H, $J = 3.7, 1.1$ Hz), 7.18 (dd, 1H, $J = 5.1, 1.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 173.2, 172.9, 146.8, 139.1, 127.8, 125.1, 124.3, 114.2, 79.1, 62.1, 57.3, 53.3, 48.4, 38.7, 26.8, 14.4; HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3\text{S}$ 265.0773. found: 265.0783.

3-(1-Phenyl-vinyl)-1-(toluene-4-sulfonyl)piperidin-4-ol (*cis*-**3g**): A white solid: mp 134 °C; TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.40; IR (KBr) ν 3577, 3056, 2986, 1428, 1340, 1265, 1162, 910, 740; ¹H NMR (500 MHz, CDCl₃) δ 1.86 (m, 2H), 2.44 (s, 3H), 2.65 (m, 1H), 2.72 (t, 1H, *J* = 11.4 Hz), 3.07 (m, 1H), 3.63 (m, 1H), 3.77 (m, 2H), 4.91 (d, 1H, *J* = 1.1 Hz), 5.38 (s, 1H), 7.32 (m, 7H), 7.69 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 148.0, 143.7, 140.8, 133.6, 129.9, 128.8, 128.3, 127.8, 126.7, 114.5, 63.6, 45.0, 44.1, 40.8, 31.5, 21.7; HRMS calcd for C₂₀H₂₃NO₃S 357.1399 found 357.1398. (*trans*-**3g**): TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.15; IR (neat) ν 3588, 3056, 2985, 1427, 1342, 1265, 1163, 741; ¹H NMR (500 MHz, CDCl₃) δ 1.73 (m, 1H), 2.07 (m, 1H), 2.26 (dd, 1H, *J* = 12.1, 11.0 Hz), 2.44 (s, 3H), 2.48 (ddd, 1H, *J* = 12.1, 12.1, 2.9 Hz), 2.77 (ddd, 1H, *J* = 10.3, 10.3, 4.0 Hz), 3.63 (m, 1H), 3.82 (m, 2H), 5.16 (s, 1H), 5.46 (s, 1H), 7.33 (m, 7H), 7.62 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 147.4, 143.8, 141.5, 133.8, 130.0, 128.8, 128.2, 127.8, 126.7, 114.9, 71.4, 50.2, 49.2, 45.1, 32.6, 21.8; HRMS calcd for C₂₀H₂₃NO₃S 357.1399 found 357.1397.

3-(1-Thiophen-2-yl-vinyl)-1-(toluene-4-sulfonyl)piperidin-4-ol(*cis*-**3h**): A white solid: mp 116 °C; TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.35; IR (KBr) ν 3579, 3056, 2986, 1427, 1343, 1265, 1163, 741; ¹H NMR (500 MHz, CDCl₃) δ 1.92 (m, 2H), 2.44 (s, 3H), 2.67 (m, 1H), 2.74 (t, 1H, *J* = 11.4 Hz), 3.05 (m, 1H), 3.65 (m, 1H), 3.70 (m, 1H), 4.00 (m, 1H), 4.80 (s, 1H), 5.54 (s, 1H), 6.99 (dd, 1H, *J* = 5.1, 3.7 Hz) 7.01 (dd, 1H, *J* = 3.7, 1.1 Hz), 7.21 (dd, 1H, *J* = 5.1, 1.1 Hz), 7.34 (d, 2H, *J* = 8.1 Hz), 7.68 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 143.8, 143.7, 140.5, 133.5, 129.9, 127.7, 127.6, 125.2, 123.9, 112.4, 64.0, 45.3, 43.9, 40.8, 31.4, 21.6; HRMS calcd for C₁₈H₂₁NO₃S₂ 363.0963 found 363.0966. (*trans*-**3h**): TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.1; IR (neat) ν 3587, 3056, 2985, 1427, 1341, 1265, 1163, 741; ¹H NMR (500 MHz, CDCl₃) δ 1.78 (m, 1H), 2.10 (m, 1H), 2.26 (dd, 1H, *J* = 12.1, 11.4 Hz), 2.44 (s, 3H), 2.47 (m, 1H), 2.84 (ddd, 1H, *J* = 10.3, 10.3, 3.7 Hz), 3.69 (ddd, 1H, *J* = 10.3, 10.3, 4.4 Hz), 3.90 (m, 2H), 5.05 (s, 1H), 5.62 (s, 1H), 7.01 (dd, 1H, *J* = 5.1, 3.7 Hz), 7.13 (dd, 1H, *J* = 3.7, 1.1 Hz), 7.22 (dd, 1H, *J* = 5.1, 1.1 Hz), 7.33 (d, 2H, *J* = 8.1 Hz), 7.64 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 144.3, 144.1, 140.2, 134.0, 130.2, 128.2, 128.0, 125.6, 124.6, 112.6, 71.3, 50.5, 49.4, 45.3, 32.8, 21.9; HRMS calcd for C₁₈H₂₁NO₃S₂ 363.0963 found 363.0966.

4-Hydroxy-3-(1-phenyl-vinyl)cyclohexane-1,1-dicarboxylic acid ethyl ester (*cis*-**3i**): TLC, SiO₂, EtOAc / hexanes 1 : 3, R_f = 0.42; IR (neat) ν 3578, 3056, 2985,

1728, 1430, 1265, 740; ^1H NMR (500 MHz, CDCl_3) δ 1.26 (t, 3H, $J = 7.0$ Hz), 1.30 (t, 3H, $J = 7.0$ Hz), 1.65 (m, 1H), 1.91 (m, 1H), 2.21 (m, 4H), 2.95 (m, 1H), 3.68 (m, 1H), 4.20 (q, 2H, $J = 7.0$ Hz), 4.27 (q, 2H, $J = 7.0$ Hz), 5.16 (s, 1H), 5.42 (s, 1H), 7.31 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.5, 171.6, 150.7, 141.9, 128.9, 128.2, 127.1, 114.6, 65.0, 61.9, 61.7, 55.6, 43.0, 29.3, 29.1, 24.9, 14.6, 14.5; HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{O}_5$ 346.1780 found 346.1781. (*trans*-**3i**): TLC, SiO_2 , EtOAc / hexanes 1 : 3, $R_f = 0.27$; IR (neat) ν 3576, 3056, 2983, 1728, 1433, 1264, 741; ^1H NMR (500 MHz, CDCl_3) δ 1.21 (t, 3H, $J = 7.0$ Hz), 1.26 (t, 3H, $J = 7.0$ Hz), 1.52 (m, 1H), 1.61 (m, 1H), 1.87 (m, 1H), 2.10 (m, 1H), 2.47 (m, 1H), 2.52 (m, 1H), 2.72 (m, 1H), 3.76 (m, 1H), 4.13 (q, 2H, $J = 7.0$ Hz), 4.25 (q, 2H, $J = 7.0$ Hz), 5.25 (s, 1H), 5.47 (s, 1H), 7.32 (m, 3H), 7.45 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.5, 171.7, 150.0, 141.7, 128.4, 127.7, 126.5, 113.2, 72.0, 61.6, 61.4, 47.6, 37.1, 30.7, 29.8, 29.7, 14.1, 14.0; HRMS calcd for $\text{C}_{20}\text{H}_{26}\text{O}_5$ 346.1780 found 346.1786.

3-(1-Thiophen-2-yl-vinyl)tetrahydro-pyran-4-ol (*cis*-**3j**): TLC, SiO_2 , EtOAc / hexanes 1 : 2, $R_f = 0.41$; IR (neat) ν 3573, 3444, 3055, 2959, 1614, 1426, 1264, 1093, 740; ^1H NMR (500 MHz, CDCl_3) δ 1.82 (m, 2H), 1.95 (m, 1H), 3.04 (m, 1H), 3.80 (m, 3H), 3.90 (t, 1H, $J = 11.0$ Hz), 4.11 (m, 1H), 4.86 (s, 1H), 5.57 (s, 1H), 7.00 (dd, 1H, $J = 5.1, 3.7$ Hz), 7.01 (d, 1H, $J = 3.7$ Hz), 7.20 (d, 1H, $J = 5.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 144.7, 140.6, 128.0, 125.3, 124.0, 112.7, 65.6, 64.7, 63.0, 46.0, 32.7; HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$ 210.0715 found 210.0723. (*trans*-**3j**): TLC, SiO_2 , EtOAc / hexanes 1 : 2, $R_f = 0.29$; IR (neat) ν 3587, 3405, 3057, 2982, 1425, 1266, 1077, 740; ^1H NMR (500 MHz, CDCl_3) δ 1.76 (m, 1H), 2.05 (m, 1H), 2.81 (ddd, 1H, $J = 10.3, 10.3, 4.4$ Hz), 3.22 (t, 3H, $J = 11.4$ Hz), 3.51 (ddd, 1H, $J = 12.1, 12.1, 2.2$ Hz), 3.95 (m, 1H), 4.02 (m, 1H), 4.08 (m, 1H), 5.12 (s, 1H), 5.64 (s, 1H), 7.00 (dd, 1H, $J = 5.1, 3.7$ Hz), 7.16 (dd, 1H, $J = 3.7, 1.1$ Hz), 7.21 (dd, 1H, $J = 5.1, 1.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 145.5, 139.7, 128.0, 125.4, 124.3, 112.5, 71.7, 71.3, 67.3, 51.3, 34.6; HRMS calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$ 210.0715 found 210.0716.

***N*-[3-(4-Methoxy-phenyl)-4-tributylstannanyl-but-2-enyl]-4-methyl-*N*-(3-oxo-butyl)benzenesulfonamide (4a)**: TLC, SiO_2 , EtOAc / hexanes 1 : 2, $R_f = 0.52$; IR (neat) ν 3056, 2981, 1427, 1264, 1160, 742; ^1H NMR (500 MHz, CDCl_3) δ 0.64 (m, 6H), 0.83 (t, 9H, $J = 7.3$ Hz), 1.22 (m, 14H), 2.01 (s, 3H), 2.42 (s, 3H), 2.45 (t, 2H, $J = 7.7$ Hz), 3.20 (t, 2H, $J = 7.7$ Hz), 3.75 (d, 2H, $J = 7.0$ Hz), 3.79 (s, 3H), 5.00 (t, 1H, $J = 7.0$ Hz), 6.82 (d, 2H, $J = 8.8$ Hz), 6.97 (d, 2H, $J = 8.8$ Hz), 7.27 (d, 2H, $J = 8.1$ Hz), 7.67 (d, 2H, $J = 8.1$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 270.1, 159.0, 147.1, 143.3,

137.2, 133.1, 130.0, 129.5, 127.4, 115.4, 113.8, 55.5, 46.6, 42.8, 41.7, 30.4, 29.2, 29.1, 27.6, 21.8, 14.0, 9.7; HRMS calcd for C₃₄H₅₃NO₄SSn: 689.2717. found: 689.2715.

3-[1-(4-Methoxy-phenyl)vinyl]-4-methyl-1-(toluene-4-sulfonyl)piperidin-4-ol

(*cis*-**3k**): TLC, SiO₂, EtOAc / hexanes 1 : 2, R_f = 0.37; IR (neat) ν 3577, 3056, 2983, 1426, 1262, 1169, 901, 740; ¹H NMR (500 MHz, CDCl₃) δ 0.93 (s, 3H), 1.76 (m, 2H), 2.44 (s, 3H), 2.69 (m, 2H), 2.96 (dd, 1H, *J* = 12.1, 4.0 Hz), 3.66 (m, 1H), 3.71 (ddd, 1H, *J* = 11.4, 4.0, 1.8 Hz), 3.81 (s, 3H), 4.94 (s, 1H), 5.35 (s, 1H), 6.87 (m, 2H), 7.30 (m, 2H), 7.34 (d, 2H, *J* = 8.1 Hz), 7.68 (d, 2H, *J* = 8.1 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 159.5, 147.5, 143.6, 136.1, 133.7, 129.9, 127.8, 127.4, 114.2, 114.0, 68.6, 48.9, 47.1, 42.4, 38.3, 29.8, 29.7, 21.7; HRMS calcd for C₂₂H₂₇NO₄S 401.1661 found 401.1663.

2-(3-Oxo-butyl)-2-(3-phenyl-4-tributylstannanyl-but-2-enyl)malonic acid diethyl ester (4b): TLC, SiO₂, EtOAc / hexanes 1 : 3, R_f = 0.55; IR (neat) ν 3056, 2958, 2924, 1725, 1451, 1368, 1266, 1191, 740; ¹H NMR (500 MHz, CDCl₃) δ 0.72 (m, 6H), 0.84 (t, 9H, *J* = 7.3 Hz), 1.21 (m, 8H), 1.25 (t, 6H, *J* = 7.3 Hz), 1.34 (m, 6H), 2.13 (s, 3H), 2.20 (t, 2H, *J* = 7.7 Hz), 2.49 (t, 2H, *J* = 7.7 Hz), 2.72 (d, 2H, *J* = 7.0 Hz), 4.19 (q, 4H, *J* = 7.3 Hz), 5.18 (t, 1H, *J* = 7.0 Hz), 7.26 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 207.6, 171.5, 144.3, 144.0, 128.5, 127.2, 126.5, 115.3, 61.6, 57.1, 39.2, 33.4, 30.1, 29.3, 29.2, 27.6, 27.0, 14.3, 14.1, 10.0; HRMS calcd for C₃₃H₅₄O₅Sn: 648.2993. found: 648.2987.

4-Hydroxy-4-methyl-3-(1-phenyl-vinyl)cyclohexane-1,1-dicarboxylic acid ethyl ester (*cis*-3l**)**: TLC, SiO₂, EtOAc / hexanes 1 : 3, R_f = 0.47; IR (neat) ν 3580, 3056, 2984, 1727, 1430, 1264, 901, 741; ¹H NMR (500 MHz, CDCl₃) δ 0.90 (s, 3H), 1.26 (t, 3H, *J* = 7.0 Hz), 1.29 (t, 3H, *J* = 7.0 Hz), 1.5 (ddd, 1H, *J* = 13.9, 12.1, 6.2 Hz), 1.75 (ddd, 1H, *J* = 13.9, 3.7, 3.3 Hz), 2.20 (m, 2H), 2.27 (t, 1H, *J* = 13.2 Hz), 2.36 (m, 1H), 2.91 (dd, 1H, *J* = 13.2, 3.3 Hz), 4.19 (q, 2H, *J* = 7.0 Hz), 4.29 (q, 2H, *J* = 7.0 Hz), 5.26 (s, 1H), 5.42 (s, 1H), 7.33 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 172.0, 171.3, 150.9, 144.7, 128.5, 127.4, 126.2, 115.0, 69.6, 61.4, 61.3, 55.4, 46.8, 36.5, 33.4, 29.9, 26.4, 14.2, 14.1; HRMS calcd for C₂₁H₂₈O₅ 360.1937 found 360.1937.

Supplementary materials for 3a

NMR spectra and calculations

All NMR measurements were performed on a Bruker Avance 400 spectrometer system (9.4 T) at a temperature of 298K. The NMR spectra of ^1H NMR, ^{13}C NMR, DEPT, *J-Resolved*, COSY, HMQC, HMBC, and NOESY were collected in CHCl_3 -d with TMS as an internal reference. The concentration of the samples was 50 mM. For ^1H -NMR analysis, 16 transients were acquired with a 1 sec relaxation delay using 32K data points. The 90° pulse was 10.0 μsec with a spectral width of 3378Hz. ^{13}C NMR and DEPT spectra were obtained for a spectral width of 20964Hz, collecting 64K data points. The 90° pulse was 10.4 μsec . Two-dimensional spectra were acquired with 2048 data points for t_2 and 256 for t_1 increments. All calculations were performed using MSI software (San Diego, U.S.A.) on a Silicon Graphics O2 workstation. The potentials were arranged using a consistent-valence force field and the calculation was performed for 500 ps. Among 500 calculated structures, ten structures with the lowest total energy were superimposed and used for analysis.

Result

The complete assignments of the ^1H and ^{13}C NMR data of **cis-3a** and **trans-3a** are listed in Tables 1 and 2, respectively. Conformations of ring juncture protons, H3 and H4, of two compounds are *cis* and/or *trans*. In order to determine the conformation, H3 and H4 as well as one of vinyl protons, H6a, were investigated. As shown in Fig. 1, while the nOe crosspeak between H6a and H3 is not observed in the NOESY spectrum of **cis-3a**, it is observed in that of **trans-3a**. But the nOe crosspeak between H6a and H4 is observed in both compounds. The observations are summarized in Table 3.

In the case of *cis* conformation (Fig. 2a), the distances of H6a and H3, and H6a and H4 calculated by molecular modeling are 4.55Å and 3.68Å, respectively. In the case of *trans* conformation (Fig. 2b), those are 3.96Å and 2.57Å. These calculated values are summarized in Table 4. A comparison of the nOe crosspeaks and the distances calculated by molecular modeling results that **cis-3a** has *cis* conformation of ring juncture protons and **trans-3a**, *trans* conformation.

In order to confirm the result, the relationship between coupling constants and the Karplus equation was used. The coupling constant between H3 and H4 obtained from the J-resolved spectrum of **cis-3a** is 4.6 Hz. The dihedral angle determined based on the Karplus equation is 40.5° . While the angle of the *cis* conformer calculated by molecular modeling is 43.4° , the angle of the *trans* conformer is 175.7° . Therefore, the conformation of ring juncture protons of **cis-3a** is *cis*.

Fig. 1. NOESY spectra showing ring juncture protons, H3 and H4, and vinyl proton, H6a. (top : *cis*-**3a**, bottom : *trans*-**3a**)

Table 3. NOE crosspeaks observed among ring juncture protons and vinyl proton.

compound	nOe crosspeak	
	H6a /H3	H6a /H4
<i>cis</i> - 3a	not observed	observed
<i>trans</i> - 3a	observed	observed

Fig. 2. Cis and trans conformations of ring juncture protons obtained from the molecular modeling calculation. (left : *cis* conformer, right : *trans* conformer)

Table 4. The distances among ring juncture protons and vinyl proton calculated by molecular modeling.

conformation	calculated distance (Å)	
	H6a /H3	H6a /H4
<i>cis</i> (204.7 kcal)	4.55	3.68
<i>trans</i> (203.4 kcal)	2.57	3.96

Table 1. The complete assignments of the ^1H and ^{13}C NMR data of *cis*-**3a**.

δ of ^{13}C	CHn	δ of ^1H	assignment
21.9	q	2.43(s)	7'
48.9	t	3.40(dd 9.0, 11.4)	2
49.1	d	3.74(dd 9.0, 7.0)	4
56.2	t	3.27(m)	4
		3.38(dd 0.6, 11.5)	1
70.8	d	3.60(dd 4.2, 11.5)	3
		4.16(dd 4.6, 7.0)	3
116.5	t	5.05(t, 1.5)	6a
		5.45(dd 0.7, 1.5)	6b
126.5	d	7.29(m)	c
127.9	d	7.76(d 8.3)	2', 6'
128.6	d	7.33(m)	d
129.1	d	7.31(m)	b
130.1	d	7.35(d 8.3)	3', 5'
134.5	s	-	1'
140.9	s	-	5
143.7	s	-	a
143.9	s	-	4'

Table 1. The complete assignments of the ^1H and ^{13}C NMR data of *trans*-**3a**.

δ of ^{13}C	CHn	δ of ^1H	assignment
21.6	q	2.44(s)	7'
50.6	d	3.16(m)	4
50.7	t	3.22(dd 5.8, 10.1)	1
		3.65(dd 7.6, 10.1)	1
54.1	t	3.22(dd 4.1, 10.8)	2
		3.60(dd 5.5, 10.8)	2
74.2	d	4.17(m)	3
		5.06(d 1.2)	6a
113.4	t	5.31(s)	6b
126.4	d	7.33(m)	c
127.6	d	7.73(d 8.3)	2', 6'
128.0	d	7.34(m)	d
128.5	d	7.31(m)	b
129.7	d	7.35(d 8.3)	3', 5'
133.7	s	-	1'
140.7	s	-	a
143.7	s	-	4'
146.3	s	-	5

X-ray crystallographic data

Table 1. Crystal data and structure refinement for **cis-3a**

Identification code	cis-3a
Empirical formula	C ₃₈ H ₄₂ N ₂ O ₆ S ₂
Formula weight	686.86
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	?, ?
Unit cell dimensions	a = 12.136(2) Å alpha = 65.951(12) deg. b = 12.7389(17) Å beta = 81.600(14) deg. c = 13.752(2) Å gamma = 65.106(9) deg.
Volume	1760.2(5) Å ³
Z, Calculated density	2, 1.296 Mg/m ³
Absorption coefficient	0.200 mm ⁻¹
F(000)	728
Crystal size	? x ? x ? mm
Theta range for data collection	1.91 to 25.00 deg.
Limiting indices	-14 ≤ h ≤ 0, -13 ≤ k ≤ 12, -16 ≤ l ≤ 16
Reflections collected / unique	6251 / 5946 [R(int) = 0.0213]
Completeness to theta = 25.00	96.1 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5946 / 0 / 560
Goodness-of-fit on F ²	1.031
Final R indices [I > 2sigma(I)]	R1 = 0.0463, wR2 = 0.1135
R indices (all data)	R1 = 0.0636, wR2 = 0.1253
Extinction coefficient	0.0031(7)
Largest diff. peak and hole	0.251 and -0.247 e.Å ⁻³

Table 2. Crystal data and structure refinement for **cis-3h**

Identification code	cis-3h
Empirical formula	C ₁₈ H ₂₁ N O ₃ S ₂
Formula weight	363.48
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	?, ?
Unit cell dimensions	a = 17.9792(11) Å alpha = 90 deg. b = 5.7605(5) Å beta = 90 deg. c = 17.0233(12) Å gamma = 90 deg.
Volume	1763.1(2) Å ³
Z, Calculated density	4, 1.369 Mg/m ³
Absorption coefficient	0.318 mm ⁻¹
F(000)	768
Crystal size	? x ? x ? mm
Theta range for data collection	2.27 to 25.00 deg.
Limiting indices	0 ≤ h ≤ 21, 0 ≤ k ≤ 6, 0 ≤ l ≤ 20
Reflections collected / unique	1483 / 1483 [R(int) = 0.0000]
Completeness to theta = 25.00	91.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1483 / 1 / 260
Goodness-of-fit on F ²	1.058
Final R indices [I > 2σ(I)]	R ₁ = 0.0528, wR ₂ = 0.1303
R indices (all data)	R ₁ = 0.0625, wR ₂ = 0.1444
Absolute structure parameter	-0.2(2)
Extinction coefficient	0.0059(17)
Largest diff. peak and hole	0.302 and -0.298 e.Å ⁻³