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Palladium-Catalyzed Regio- and Diastereoselective Tandem Silastannylation/Allylation of Allene-Aldehydes and Allene-Ketones: Synthesis of *cis*-Cyclopentanols and Cyclohexanols **

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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. ^{1}H 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 F_{254}, 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.

***N*-Buta-2,3-dienyl-*N*-(2-oxoethyl)toluene-4-sulfonamide (1a).**
A mixture of propargyl *p*-tosylamide (2 g, 9.1 mmol), K_2CO_3 (3.8 g, 27.2 mmol), bromoacetaldehyde dimethylacetal(1.8 g, 10.9 mmol), and DMF (50 mL) was heated at 100 °C for 10 h. The mixture was cooled to 25 °C and poured into ice. The resulting solution was extracted with a portion of EtOAc. The combined organic extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and residue was purified by silica gel column chromatography (EtOAc/hexanes 1 : 2) to give 1-(1,1-dimethoxyhex-5-yne-3-sulfonyl)-4-methylbenzene (2.4 g, 85%). A suspension of 1-(1,1-dimethoxyhex-5-yne-3-sulfonyl)-4-methylbenzene (2.3 g, 7.7 mmol), cuprous bromide (552 mg, 3.9 mmol), paraformaldehyde (600 mg, 19.3 mmol) and diisopropylamine (2.2 mL, 15.4 mmol) in dioxane (50 mL) was gently heated at reflux and stirred for 12 h, cooled to room temperature, and filtered through a Celite pad. The dark-brown filtrate was concentrated *in vacuo* to a gummy residue and then diluted with 30 mL of water followed by addition of 50 mL of ether and acidified with 6 N hydrochloric acid to pH 2. The ether-water layers were decanted from any residues, the ether layer was separated, and the aqueous solution was extracted with ether (5×20 mL). The ether extracts were combined and washed with a small portion of water until was reached to pH 6.5. The organic layer was then washed with brine, dried over $MgSO_4$ and concentrated. The crude product was separated by silca gel column chromatography (EtOAc : hexanes 1 : 2) to give 1-(1,1-dimethoxyhepta-5,6-diene-3-sulfonyl)-4-methylbenzene (1.6 g, 68%). (Crabbe reaction: Crabbe, F.; Nassim, B.; Robert-Lopes, M-T. Org. Synth. Coll. VII, 276-277) A solution of acetal (1.5 g, 4.8 mmol) in trifluoroacetic acid : $CHCl_3$: H_2O (1 : 2 : 1) was stirred at 0 °C for 90 min. The mixture was diluted with CH_2Cl_2 and washed with 10% aqueous $NaHCO_3$ solution. Workup as usual gave a residue, which was purified by silica gel column chromatography (EtOAc/hexanes 1:2) to give **1a** (968 mg, 78%). A white solid: mp 49

°C; TLC, SiO_2, EtOAc / hexanes 1 : 2, R_f = 0.39; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.44 (s, 3H), 3.82 (d, 2H, *J* = 1.5 Hz), 3.84 (dt, 2H, *J* = 7.0, 2.4 Hz), 4.74 (dt, 2H, *J* = 6.8, 2.4 Hz), 5.01 (tt, 1H, *J* = 7.0, 6.8 Hz), 7.38 (d, 2H, *J* = 8.2 Hz), 7.70 (d, 2H, *J* = 8.2 Hz), 9.63 (t, 1H, *J* = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.9, 199.1, 144.8, 136.2, 130.7, 128.1, 86.0, 77.5, 56.8, 49.5, 22.3; HRMS calcd for $C_{13}H_{15}NO_3S$: 265.0773. found: 265.0783.

Buta-2,3-dienyl-(2-oxoethyl)carbamic acid *tert*-butyl ester (1b) This compound was readily prepared from 2-aminoethanol in six steps; (1) $(Boc)_2O$ (1 equiv), MeOH, 2 h. (2) TBDMSCl, imidazole, CH_2Cl_2, 3 h.(3) propargyl bromide (1 equiv), NaH, DMF, rt, 1 h. (4) Bu_4NF, CH_2Cl_2, rt, 2 h. (5) Crabbe reaction (6) Swern oxidation (28% overall yield). A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.32; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.41 (s, 9H), 3.85 (m, 4H), 4.73 (dt, 2H, *J* = 6.5, 2.9 Hz), 5.05 (m, 1H), 9.51 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 209.9, 199.8, 155.5, 87.5, 81.6, 77.3, 57.3, 47.6, 28.9; HRMS calcd for $C_{11}H_{17}NO_3$: 211.1208. found: 211.1201.

***N*-Buta-2,3-dienyl-*N*-(3-oxopropyl)toluene-4-sulfonamide (4a)** This compound was readily prepared from propargyl-*p*-tosylamide in four steps; (1) (3-bromo-propoxy)-*tert*-butyl-dimethyl-silane (1.2 equiv), K_2CO_3, DMF, 100 °C, 12 h. (2) Bu_4NF, CH_2Cl_2, rt, 2 h. (3) Crabbe reaction (4) Swern oxidation (33% overall yield). A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 1, R_f = 0.61; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.44 (s, 3H), 3.82 (d, 2H, *J* = 1.5 Hz), 3.84 (dt, 2H, *J* = 7.0, 2.4 Hz), 4.74 (dt, 2H, *J* = 6.8, 2.4 Hz), 5.01 (tt, 1H, *J* = 7.0, 6.8 Hz), 7.38 (d, 2H, *J* = 8.2 Hz), 7.70 (d, 2H, *J* = 8.2 Hz), 9.63 (t, 1H, *J* = 1.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.9, 199.5, 144.8, 136.2, 130.7, 128.1, 86.0, 77.5, 56.8, 49.5, 22.3; HRMS calcd for $C_{14}H_{17}NO_3S$: 279.0929. found: 279.0933.

Buta-2,3-dienyl-(2-oxopropyl)carbamic acid *tert*-butyl ester (4b) This compound was readily prepared from 3-amino-1-propanol as described in the case of **1b** (25% overall yield). A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.50; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.43 (s, 9H), 2.68 (td, 2H, *J* = 6.2, 1.8 Hz), 3.52 (t, 2H, *J* = 6.2 Hz), 3.81 (br, 2H), 4.76 (dt, 2H, *J* = 6.5, 2.9 Hz), 5.09 (m, 1H), 9.51 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 209.4, 201.8, 155.9, 88.0, 80.8, 77.2, 47.5, 44.0, 41.7, 28.9; HRMS calcd for $C_{12}H_{19}NO_3$: 225.1365. found: 225.1363.

2-Buta-2,3-dienyl-2-(2-oxoethyl)malonic acid diethyl ester (1c)
To a solution of diethyl malonate (3 g, 18.7mmol) in THF (50 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 750 mg) and stirred at rt. After 1 h, bromoacetaldehyde dimethylacetal (3.8 g, 2.2 mmol) was added, and the reaction was heated at reflux for 3 day and cooled to room temperature. The reaction was then quenched with saturated aqueous NH_4Cl (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (EtOAc/hexane 1 : 5) to give 2-(2,2-dimethyloxy-ethyl)malonic acid diethyl ester (3.8 g, 83%). To a solution of 2-(2,2-

dimethyloxyethyl)malonic acid diethyl ester (3 g, 12.1 mmol) in THF(50 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 532 mg) and stirred at rt. After 1 h, propargyl bromide (1.58 g, 13.3 mmol) was added, and the reaction was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (EtOAc/hexane 1 : 5) to give 2-(2,2-dimethyloxyethyl)-2-prop-2-ynylmalonic acid diethyl ester (3.18 g, 92%). **1c** was prepared from 2-(2,2-dimethyloxyethyl)-2-prop-2-ynylmalonic acid diethyl ester by the Crabbe reaction and deprotection of acetal (overally yield for two steps; 65%) and described as the above. **1c :** A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.35; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.21 (t, 6H, *J* = 7.0 Hz), 2.67 (dt, 2H, *J* = 7.9, 2.6 Hz), 2.95 (d, 2H, *J* = 1.5 Hz), 4.17 (q, 4H, *J* = 7.0 Hz), 4.63 (dt, 2H, *J* = 6.8, 2.6 Hz), 4.94 (tt, 1H, *J* = 7.9, 6.8 Hz), 9.68 (t, 1H, *J* = 1.5 Hz);. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.9, 199.5, 170.4, 84.8, 75.6, 62.6, 55.7, 46.7, 34.1, 14.6; HRMS calcd for $C_{13}H_{18}O_5$: 254.1154. found: 254.1179.

Allene-ketones **1d**, **4e** were readily prepared from **1a**, **4a** in two steps; (1) MeMgBr (1.1 equiv), THF, 0 °C, 1 h. (2) PCC, CH_2Cl_2. (72% and 78% overall yields, respectively)

***N*-Buta-2,3-dienyl-*N*-(2-oxopropyl)toluene-4-sulfonamide (1d)**
A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.21 (s, 3H), 2.43 (s, 3H), 3.83 (dt, 2H, *J* = 7.3, 2.4 Hz), 3.94 (s, 2H), 4.71 (dt, 2H, *J* = 6.8, 2.4 Hz), 4.97 (tt, 1H, *J* = 7.0, 6.8 Hz), 7.32 (d, 2H, *J* = 8.2 Hz), 7.70 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.6, 204.8, 144.4, 136.9, 130.4, 128.1, 86.0, 77.2, 56.5, 48.8, 27.8, 22.2; HRMS calcd for $C_{14}H_{17}NO_3S$: 279.0929. found: 279.0927.

***N*-Buta-2,3-dienyl-*N*-(3-oxobutyl))toluene-4-sulfonamide (4e)**
a colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.16 (s, 3H), 2.43 (s, 3H), 2.85 (t, 2H, *J* = 7.3 Hz), 3.38 (t, 2H, *J* = 7.3 Hz), 3.84 (dt, 2H, *J* = 7.0, 2.6 Hz), 4.71 (dt, 2H, *J* = 6.8, 2.6 Hz), 4.91 (tt, 1H, *J* = 7.0, 6.8 Hz), 7.31 (d, 2H, *J* = 8.2 Hz), 7.69 (d, 2H, *J* = 8.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 209.8, 207.2, 143.9, 137.0, 130.2, 127.8, 86.4, 76.8, 48.3, 43.8, 42.7, 30.6, 20.9; HRMS calcd for $C_{15}H_{19}NO_3S$: 293.1086. found: 293.1082.

2-Buta-2,3-dienyl-2-(2-oxopropyl)malonic acid diethyl ester (1e)
To a solution of 2-buta-2,3-dienyl-malonic acid diethyl ester (200 mg, 0.94 mmol) in THF (5 mL) at 0 °C was added NaH (60% dispersion in mineral oil, 42 mg). After 1 h, bromoaceton (141 mg, 10.3 mmol) was added, and the reaction was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and residue was purified by silica gel column chromatography (EtOAc/hexane 1 : 5) to give **1e** (179 mg, 71%). A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 5, R_f = 0.24; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.22 (t, 6H, *J* = 7.0 Hz), 2.13 (s, 3H), 2.71 (dt, 2H, *J* = 7.9, 2.6 Hz), 3.15 (s, 1H), 4.17 (q, 4H, *J* = 7.0 Hz), 4.64 (dt, 2H, *J* = 6.8, 2.6 Hz), 4.93 (tt, 1H, *J* = 7.9, 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.4, 205.9, 170.6, 85.1, 75.2, 62.2, 55.7, 45.9, 33.0, 30.8, 14.4; HRMS calcd for $C_{14}H_{20}O_5$: 268.1311. found: 268.1309.

2-Buta-2,3-dienyl-2-(3-oxopropyl)malonic acid diethyl ester (4c)
A solution of 2-Buta-2,3-dienylmalonic acid diethyl ester (250 mg, 1.18 mmol), NaOEt (8.2 mg, 0.12 mmol). acrolein (72,7 mg, 1.29 mmol), and EtOH (3 mL) was stirred at room temperature for 2 h. The solvent was evaporated in vacuo and the residue was purified by silica gel column chromatography (EtOAc/hexane 1 : 5) to give **4c** (206 mg, 65%). A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 5, R_f = 0.23; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.26 (t, 6H, *J* = 7.0 Hz), 2.24(t, 2H, *J* = 7.9 Hz), 2.49 (td, 2H, *J* = 7.9, 1.2 Hz), 2.62 (dt, 2H, *J* = 7.9, 2.6 Hz), 4.19 (q, 2H, *J* = 7.0 Hz), 4.20 (q, 2H, *J* = 7.0 Hz), 4.68 (dt, 2H, *J* = 6.8, 2.6 Hz), 4.96 (tt, 1H, *J* = 7.9, 6.8 Hz). 9.75 (t, 1H, *J* = 1.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.1, 200.9, 170.6, 84.1, 74.9, 62.0, 55.8, 32.8, 29.2, 27.3, 14.1; HRMS calcd for $C_{14}H_{20}O_5$: 268.1311. found: 268.1300.

2-Buta-2,3-dienyl-2-(3-oxobutyl)malonic acid diethyl ester (4f) was prepared from 2-buta-2,3-dienylmalonic acid diethyl ester by the conjugate addition to the methyl vinyl ketone as described on the case of acrolein (78% yield). A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 5, R_f = 0.26; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.18 (t, 6H, *J* = 7.0 Hz), 2.06(s, 3H), 2.10 (t, 2H, *J* = 7.9 Hz), 2.39 (t, 2H, *J* = 7.9 Hz), 2.52 (dt, 2H, *J* = 7.9, 2.6 Hz), 4.10 (t, 2H, *J* = 7.0 Hz), 4.11 (t, 2H, *J* = 7.0 Hz), 4.59 (dt, 2H, *J* = 6.8, 2.6 Hz), 4.89 (tt, 1H, *J* = 7.9, 6.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.4, 207.3, 170.9, 84.5, 75.0, 61.6, 57.0, 38.9, 33.3, 30.0, 26.7, 14.4; HRMS calcd for $C_{15}H_{22}O_5$: 282.1467. found: 282.1459.

3-Buta-2,3-dienyloxypropionaldehyde (4d)
To a stirred suspension of NaH (415 mg of a 60% suspension in mineral oil, 10.4 mmol) in THF (20 mL) at 0 °C was added dropwise a solution of 1,3-propandiol (3 mL, 41.5 mmol) in THF (10 mL) and stirred at room temperature for 1 h. The propargyl bromide (80 wt. % solution in toluene) (1.1 mL, 9.45 mmol) was added dropwise, and the mixture stirred room temperature for 12 h. The reaction was quenched with water (20 mL). Most of the organic solvents were evaporated, and the aqueous residue was extracted with ether (50 mL). The organic layer was washed with water. Concentration and silica gel column chromatographic separation gave 3-prop-2-ynyloxypropan-1-ol (1.1 g, 80%). **4d** was prepared from 3-prop-2-ynyloxypropan-1-ol by the Crabbe reaction and Swern oxidation (53% in two steps). A colorless oil; TLC, SiO_2, EtOAc / hexanes 1 : 3, R_f = 0.42; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.66 (td, 2H, *J* = 6.2, 1.8 Hz), 3.78 (t, 2H, *J* = 6.2 Hz), 4.01 (dt, 2H, *J* = 6.8, 2.4 Hz), 4.78 (dt, 2H, *J* = 6.8, 2.4 Hz), 5.20 (tt, 1H, *J* = 6.7 Hz), 9.78 (t, 1H, *J* = 1.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.0, 201.7, 88.1, 76.5, 69.6, 67.6, 64.1, 44.5; HRMS calcd for $C_7H_{10}O_2$ 126.0681. found: 126.0684.

Typical procedure for the cyclization of allene-aldehydes and allene-ketones

1-(Toluene-4-sulfonyl)-4-(1-trimethylsilanylvinyl)pyrrolidin-3-ol (3a)
To a stirred solution of allene-aldehyde **1a** (100 ml, 0.38 mmol), $Me_3SiSnBu_3$ (6.9 mg, 5 mol%), and (π-allyl)$_2$$Pd_2Cl_2$ (5 mol %) in THF (3 mL) was added trimethyl(tributylstannyl)silane 2 (150 mg, 0.41 mmol). The reaction mixture was stirred

room temperature for 10 min and THF was evaporated *in vacuo*. The crude product was separated by column chromatography (hexane : ethyl acetate = 2 : 1) to afford the cyclized product **3a** (91 mg, 71%). A white solid: mp 95 °C; TLC, SiO_2, EtOAc / hexane 1 :2, R_f = 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.00 (s, 9H), 2.35 (s, 3H), 2.89 (m, 1H), 3.29 (dd, 1H, *J* = 9.3, 11.3 Hz), 3.35 (d, 1H, *J* = 11.5 Hz), 3.40 (dd, 1H, *J* = 7.2, 9.3 Hz), 4.05 (m, 1H), 5.59 (d, 2H, *J* = 1.3 Hz), 7.25 (d, 2H, *J* = 8.0 Hz), 7.68 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.9, 145.0, 135.7, 131.2, 129.7, 129.1, 72.2, 57.7, 50.1, 49.8, 23.1, 0.0; HRMS calcd for $C_{16}H_{25}NO_3SSi$: 339.1324. found: 339.1366.

3-Hydroxy-4-(1-trimethylsilanylvinyl)pyrrolidin-1-carboxylic acid *tert*-butyl ester (3b)

A colorless oil; TLC, SiO_2, EtOAc / hexane 1 : 3, R_f = 0.38; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.14 (s, 9H), 1.46 (s, 9H), 2.99 (m, 1H), 3.41-3.61 (m, 4H), 4.16 (m, 1H), 5.72 (s, 1H), 5.82 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.4, 147.7, 128.7, 80.0, 71.6, 55.0, 48.5, 46.5, 29.2, -0.8; HRMS calcd for $C_{14}H_{27}NO_3SSi$: 285.1760. found: 285.1766.

3-Hydroxy-4-(1-trimethylsilanylvinyl)cyclipentan-1,1-dicarboxylic acid diethyl ester (3c)

A colorless oil; TLC, SiO_2, EtOAc / hexane 1 : 3, R_f = 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.10 (s, 9H), 1.22 (t, 3H, *J* = 7.0 Hz), 1.23 (t, 3H, *J* = 7.0 Hz), 2.19 (dd, 1H, *J* = 13.2, 7.0 Hz), 2.51 (m, 2H), 2.63 (dd, 1H, *J* = 13.2, 12.9 Hz), 2.83 (m, 1H), 4.11 (m, 1H), 4.17 (q, 2H, *J* = 7.0 Hz), 4.18 (q, 2H, *J* = 7.0 Hz), 5.64 (dd, 1H, *J* = 2.1, 0.9 Hz), 5.80 (dd, 1H, *J* = 2.1, 2.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 174.1, 173.9, 150.3, 128.4, 74.0, 63.0, 59.2, 51.3, 43.7, 36.2, 15.4, 0.0; HRMS calcd for $C_{16}H_{28}O_5Si$: 328.1706. found:328.1718.

3-Methyl-1-(toluene-4-sulfonyl)-4-(1-trimethylsilanylvinyl)pyrrolidin-3-ol (3d)

A colorless oil; TLC, SiO_2, EtOAc / hexane 1 :2, R_f = 0.42; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.11 (s, 9H), 1.16 (s, 3H), 2.43 (s, 3H), 2.67 (dd, 1H, *J* = 10.9, 7.6 Hz), 3.28 (dd, 1H, *J* = 10.9, 9.7 Hz), 3.33 (d, 1H, *J* = 10.9 Hz), 3.42 (d, 1H, *J* = 10.9 Hz), 3.52 (dd, 1H, *J* = 9.7, 7.6 Hz), 5.68 (d, 1H, *J* = 2.0 Hz), 5.81 (d, 1H, *J* = 2.0 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 7.74 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 148.0, 144.1, 135.0, 130.4, 130.3, 128.2, 78.0, 61.4, 53.3, 52.0, 25.8, 22.2, -0.4; HRMS calcd for $C_{17}H_{27}NO_3SSi$: 353.1481. found: 353.1488.

3-Hydroxy-3-methyl-4-(1-trimethylsilanylvinyl)cyclopentan-1,1-dicarboxylic acid diethyl ester (3e)

A colorless oil; TLC, SiO_2, EtOAc / hexane 1 : 5, R_f = 0.31; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.10 (s, 9H), 1.20 (m, 6H), 2.29 (d, 1H, *J* = 14.4 Hz), 2.38 (dd, 1H, *J* = 12.6, 7.6 Hz), 2.52 (dd, 1H, *J* = 13.2, 12.6 Hz), 2.57 (d, 1H, *J* = 14.4 Hz), 2.64 (dd, 1H, *J* = 13.2, 7.6 Hz), 4.19 (m, 1H), 5.67 (d, 1H, *J* = 2.6 Hz), 5.80 5.99 (d, 1H, *J* = 2.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 173.3, 150.3, 129.0, 79.7, 62.0, 57.4, 53.2, 48.9, 40.3, 26.8, 14.4, -0.4; HRMS calcd for $C_{17}H_{30}O_5Si$: 342.1863. found: 342.1865.

1-(Toluene-4-sulfonyl)-3-(1-trimethylsilanylvinyl)piperidine-4-ol (5a)
A white solid: mp 88 °C; TLC, SiO_2, EtOAc / hexane 1 : 2, R_f = 0.40; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.11 (s, 9H), 1.92 (m, 2H), 2.44 (s, 3H), 2.58 (m, 1H), 2.67 (m, 2H), 2.46 (m, 1H), 3.60 (m, 1H), 3.79 (m, 1H), 5.52 (d, 1H, *J* = 2.0 Hz), 5.58 (d, 1H, *J* = 2.0 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 7.65 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 152.3, 144.2, 134.1, 130.4, 128.3, 127.0. 64.4, 44.9, 44.5, 41.1, 31.7, 22.2, -0.7; HRMS calcd for $C_{17}H_{27}NO_3SSi$: 353.1481. found: 353.1431.

4-Hydroxy-3-(1-trimethylsilanylvinyl)piperidine-1-carboxylic acid *tert*-butyl ester (5b)
A colorless oil; TLC, SiO_2, EtOAc / hexane 1 : 3, R_f = 0.54; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.11 (s, 9H), 1.45 (s, 9H), 1.68 (m, 2H), 1.85 (ddd, 1H, *J* = 13.8, 6.5, 2.9 Hz), 2.46 (m, 1H), 3.00-3.20 (m, 2H), 3.80-3.96 (m, 2H), 5.60 (dd, 1H, *J* = 2.1, 0.6 Hz), 5.67 (dd, 1H, *J* = 2.1, 1.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 155.6, 152.8, 126.8, 80.1, 65.5, 45.3, 43.0, 42.1, 38.7, 32.1, 29.2, -0.7; HRMS calcd for $C_{15}H_{29}NO_3SSi$: 299.1917. found: 299.1915.

4-Hydroxy-3-(1-trimethylsilanylvinyl)cyclohexane-1,1-dicarboxylic acid diethyl ester (5c)
A white solid: mp 83 °C; TLC, SiO_2, EtOAc / hexane 1 : 4, R_f = 0.30; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.10 (s, 9H), 1.23 (t, 3H, *J* = 7.0 Hz), 1.25 (t, 3H, *J* = 7.0 Hz), 1.68 (m, 1H), 1.96 (m, 2H), 2.04 (m, 1H), 2.13 (m, 1H), 2.19 (dd, 1H, *J* = 13.2, 13.2 Hz), 2.54 (m, 1H), 3.72 (m, 1H), 4.15 (q, 2H, *J* = 7.0 Hz), 4.21 (q, 2H, *J* = 7.0 Hz), 5.61 (s, 1H), 5.73 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.8, 171.8, 154.3, 126.4, 65.8, 61.8, 55.9, 42.5, 29.5, 29.2, 25.0, 14.8, -0.7; HRMS calcd for $C_{17}H_{30}O_5Si$: 342.1863. found: 342.1860.

3-(1-Trimethylsilanylvinyl)tetrahydropyran-4-ol (5d)
A colorless oil; TLC, SiO_2, EtOAc / hexane 1 : 3, R_f = 0.44; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.12 (s, 9H), 1.81 (m, 1H), 1.90 (m, 1H), 2.70 (m, 1H), 3.57 (dd, 1H, *J* = 11.2, 4.11 Hz), 3.70-3.87 (m, 3H), 3.93 (m, 1H), 5.61 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 152.1, 127.0, 66.0, 64.8, 62.9, 45.3, 32.8, -0.9; HRMS calcd for $C_{10}H_{20}O_2Si$: 200.1233. found: 200.1234.

4-Methyl-1-(Toluene-4-sulfonyl)-3-(1-trimethylsilanylvinyl)piperidine-4-ol (5e)
A colorless oil; TLC, SiO_2, EtOAc / hexane 1 : 3, R_f = 0.45; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.11 (s, 9H), 1.10 (s, 3H),), 1.67 (ddd, 1H, *J* = 13.9, 3.2, 2.6 Hz), 1.76 (ddd, 1H, *J* = 13.9, 4.7, 1.5 Hz), 2.43 (s, 3H), 2.48 (dd, 1H, *J* = 11.7, 3.8 Hz), 2.57 (dd, 1H, *J* = 11.7, 11.4 Hz), 2.68 (ddd, 1H, *J* = 12.6, 12.0, 3.2 Hz), 3.36 (ddd, 1H, *J* = 11.4, 3.8, 2.1 Hz), 3.63 (dddd, 1H, *J* = 11.4, 4.7, 2.6, 2.1 Hz), 5.68 (d, 1H, *J* = 2.0 Hz), 5.81 (d, 1H, *J* = 2.0 Hz), 7.33 (d, 2H, *J* = 8.0 Hz), 7.74 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 152.8, 144.5, 135.1, 131.0, 129.1, 128.8, 70.2, 48.8, 48.4, 43.3, 39.8, 30.7, 27.7, 0.0; HRMS calcd for $C_{18}H_{29}NO_3SSi$: 367.1637. found: 367.1622.

4-Hydroxy-4-methyl-3-(1-trimethylsilanylvinyl)cyclohexane-1,1-dicarboxylic acid diethyl ester (5f)

A colorless oil; TLC, SiO_2, EtOAc / hexane 1 : 3, R_f = 0.53; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.08 (s, 9H), 1.05 (s, 3H), 1.22 (m, 6H), 1.54 (ddd, 1H, *J* = 13.5, 13.5, 5.0 Hz), 1.66 (m, 1H), 1.98 (ddd, 1H, *J* = 13.5, 3.5, 2.4 Hz), 2.12 (m, 3H), 2.31 (dd, 1H, *J* = 13.2, 3.2 Hz), 4.15 (m, 4H), 5.57 (d, 1H, *J* = 2.4 Hz), 5.94 (d, 1H, *J* = 2.4 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.4, 171.6, 154.7, 127.2, 70.5, 61.6, 55.7, 45.2, 37.2, 34.0, 30.2, 26.7, 14.4, -0.9; HRMS calcd for $C_{18}H_{32}O_5Si$: 356.2019. found: 356.2021.

2-(3-Oxobutyl)-2-(4-tributylstannyl-3-trimethylsilanylbut-2-enyl)malonic acid diethyl ester (6)

A colorless oil; TLC, SiO_2, EtOAc / hexane 1 : 3, R_f = 0.77; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.00 (s, 9H), 0.86 (s, 15H), 1.24 (t, 6H, *J* = 7.0 Hz), 1.30 (m, 6H), 1.48 (m, 6H), 2.11 (s, 3H), 2.15 (m, 4H), 2.45 (t, 2H, *J* = 7.9 Hz), 2.53 (d, 2H, *J* = 6.5 Hz), 4.16 (q, 4H, *J* = 7.0 Hz), 5.24 (t, 1H, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 208.3, 171.7, 145.3, 126.0, 61.7, 56.8, 39.3, 33.0, 31.5, 30.4, 29.5, 27.9, 27.1, 14.6, 14.2, 10.4, -1.2; HRMS calcd for $C_{30}H_{58}O_5SiSn$: 644.3076. found: 644.3008.

NMR spectra and calculations of 3a

All NMR measurements were performed on a Bruker Avance 400 spectrometer system (9.4 T) at a temperature of 298K. The NMR spectra of ^{1}H NMR, ^{13}C NMR, DEPT, 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 ^{1}H-NMR analysis, 16 transients were acquired with a 1 sec relaxation delay using 32K data points. The 90^o pulse was 9.7 μsec with a spectral width of 4,000 Hz. ^{13}C NMR and DEPT spectra were obtained for a spectral width of 8,000 Hz, collecting 64K data points. The 90 ^{o} pulse was 9.6 μsec. Two-dimensional spectra were acquired with 2048 data points for t2 and 256 for t1 increments. All calculations were performed using MSI software (San Diego, U.S.A.) on a Silicon Graphics INDY R4400 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.

Results

The structure and nomenclature of 3a are shown in Fig. 1. In order to confirm the conformation between two junction protons, H3 and H4, theoretical structures of *cis* and *trans* conformers were calculated using molecular modeling. In addition, several NMR experiments were carried out. Total energy of *cis* conformer was 116.3 kcal/mol and that of *trans*, 115.8 kcal/mol, so that both conformers could exist. While the distance between H3 and H4 obtained from the calculated *cis* conformer was 2.4A, that from *trans* conformer was 3.0A. According to the following equation, the distance between H3 and H4 was obtained from nOe data.

$$(V_{sample})^{2/3} = \eta_{sample}\,,$$

$$\frac{\eta_{reference}}{\eta_{sample}} = \frac{r_{sample}^{6}}{r_{reference}^{6}}$$

where the reference was nOe between H2a and H2e, and the sample was nOe between H3 and H4. Because the distance between H2a and H2e is known as 1.8A, the distance between H3 and H4 obtained based on nOe is 2.1A which is closer to the distance calculated in *cis* conformer than that in *trans* conformer. Therefore, the conformation of 3a is *cis*.

In order to clarify this conclusion, another approach was introduced. While the calculated distance between H3 and H6 in *cis* conformer was 4.6A, that in *trans* was 2.1A. When the distance was 2.1A, nOe could be observed, but the NOESY experiments carried out at the several different conditions did not show nOe between H3 and H6 (Fig. 2). Therefore, the conformation of **3a** was decided to be *cis*.

Fig. 1. The structure and nomenclature of **3a**.

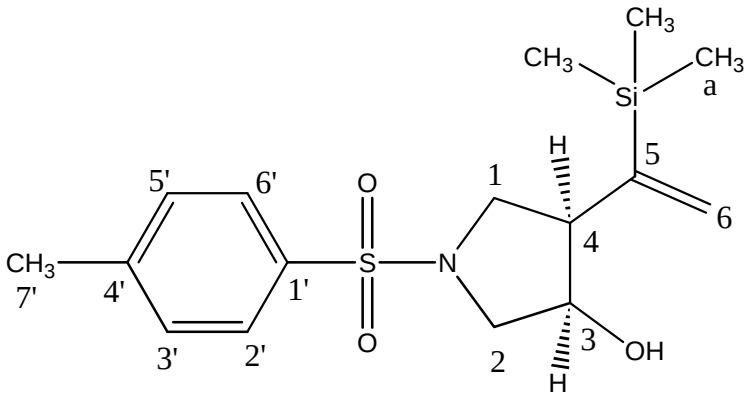
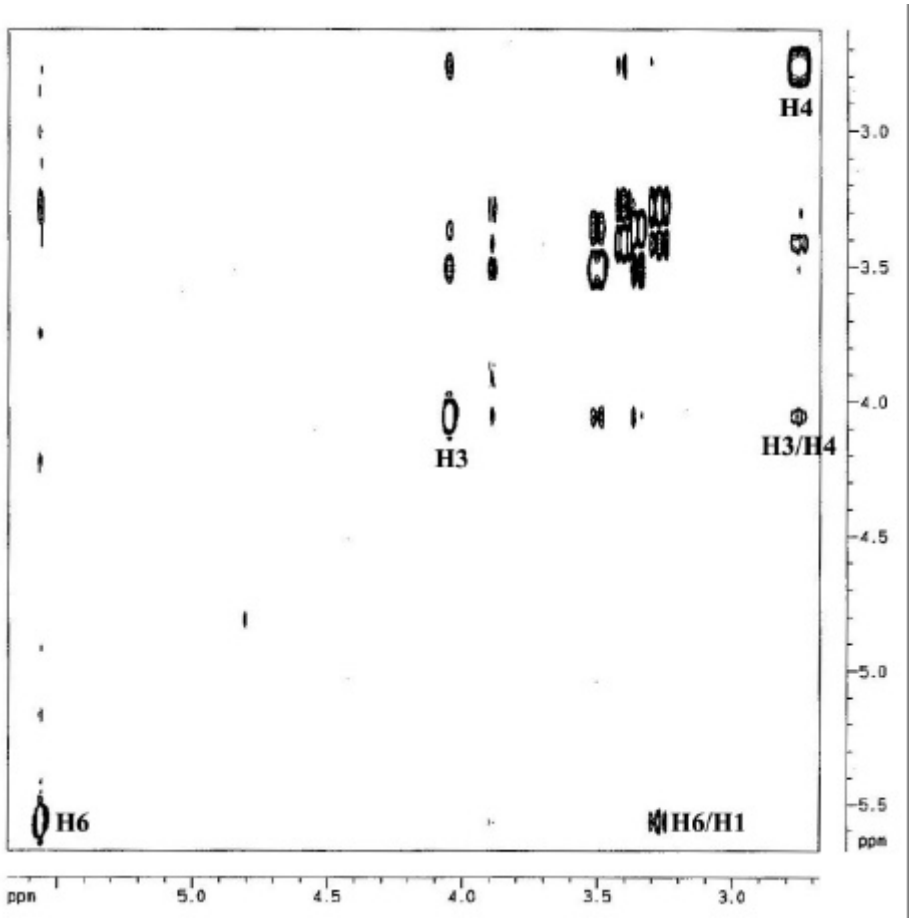


Fig. 2. The NOESY spectrum of **3a.**


H4
H3
H3/H4
H6
H6/H1
3.0
3.5
4.0
4.5
5.0
5.5
ppm
ppm
5.0
4.5
4.0
3.5
3.0

X-ray Structure Analysis 5d

Table 1. Crystal data and structure refinement for **5d**.

Identification code	**5d**
Empirical formula	C10 H20 O2 Si
Formula weight	200.35
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P-1(No.2)
Unit cell dimensions	a = 6.117(3) A alpha = 101.176(9) deg.
	b = 9.546(4) A beta = 106.402(8) deg.
	c = 10.589(5) A gamma = 93.797(9) deg.
Volume	577.0(5) A^3
Z, Calculated density	2, 1.153 Mg/m^3
Absorption coefficient	0.174 mm^-1
F(000)	220
Crystal size	0.25 x 0.18 x 0.10 mm
Theta range for data collection	2.06 to 28.32 deg.
Limiting indices	-8<=h<=7, -12<=k<=10, -14<=l<=10
Reflections collected / unique	3724 / 2607 [R(int) = 0.0302]
Completeness to theta = 28.32	90.6 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2607 / 0 / 198
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0543, wR2 = 0.1484
R indices (all data)	R1 = 0.0660, wR2 = 0.1593
Largest diff. peak and hole	0.448 and -0.472 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **5d**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	2654(3)	3570(2)	2225(2)	38(1)
C(2)	3901(3)	3731(2)	1206(2)	50(1)
O(3)	5903(2)	4745(2)	1800(2)	55(1)
C(4)	5330(4)	6136(2)	2247(3)	54(1)
C(5)	4157(4)	6140(2)	3294(3)	56(1)
C(6)	2034(3)	5039(2)	2799(2)	42(1)
C(7)	597(3)	2427(2)	1672(2)	38(1)

Si(8)	-149(1)	1379(1)	2832(1)	45(1)
O(9)	414(2)	5541(2)	1818(2)	54(1)
C(71)	-688(4)	2181(3)	392(2)	55(1)
C(81)	-786(5)	2597(3)	4232(3)	61(1)
C(82)	2296(6)	437(4)	3542(4)	77(1)
C(83)	-2694(5)	39(3)	1922(4)	73(1)

Table 3. Bond lengths [A] and angles [deg] for **5d**.

C(1)-C(7)	1.507(2)
C(1)-C(2)	1.511(3)
C(1)-C(6)	1.532(2)
C(2)-O(3)	1.416(2)
O(3)-C(4)	1.422(3)
C(4)-C(5)	1.480(3)
C(5)-C(6)	1.512(3)
C(6)-O(9)	1.401(2)
C(7)-C(71)	1.327(3)
C(7)-Si(8)	1.8574(19)
Si(8)-C(83)	1.843(3)
Si(8)-C(82)	1.848(3)
Si(8)-C(81)	1.849(2)
C(7)-C(1)-C(2)	113.19(16)
C(7)-C(1)-C(6)	112.35(14)
C(2)-C(1)-C(6)	109.36(15)
O(3)-C(2)-C(1)	110.93(17)
C(2)-O(3)-C(4)	110.82(14)
O(3)-C(4)-C(5)	111.26(18)
C(4)-C(5)-C(6)	111.57(19)
O(9)-C(6)-C(5)	106.71(17)
O(9)-C(6)-C(1)	112.01(15)
C(5)-C(6)-C(1)	109.49(16)
C(71)-C(7)-C(1)	121.23(18)
C(71)-C(7)-Si(8)	120.20(15)
C(1)-C(7)-Si(8)	118.56(13)
C(83)-Si(8)-C(82)	109.06(17)
C(83)-Si(8)-C(81)	108.69(14)
C(82)-Si(8)-C(81)	108.92(16)
C(83)-Si(8)-C(7)	110.46(13)
C(82)-Si(8)-C(7)	109.59(12)
C(81)-Si(8)-C(7)	110.09(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **5d**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	35(1)	35(1)	43(1)	8(1)	12(1)	4(1)
C(2)	42(1)	47(1)	63(1)	4(1)	26(1)	3(1)
O(3)	36(1)	49(1)	85(1)	15(1)	27(1)	5(1)
C(4)	41(1)	43(1)	81(2)	19(1)	19(1)	0(1)
C(5)	50(1)	46(1)	64(1)	0(1)	16(1)	-7(1)
C(6)	44(1)	39(1)	45(1)	2(1)	21(1)	-1(1)
C(7)	38(1)	34(1)	42(1)	3(1)	14(1)	4(1)
Si(8)	46(1)	38(1)	53(1)	9(1)	21(1)	1(1)
O(9)	36(1)	46(1)	87(1)	21(1)	23(1)	9(1)
C(71)	52(1)	56(1)	48(1)	4(1)	10(1)	-9(1)
C(81)	70(2)	63(2)	55(1)	11(1)	32(1)	0(1)
C(82)	75(2)	77(2)	100(2)	48(2)	35(2)	28(2)
C(83)	75(2)	51(1)	87(2)	-1(1)	34(2)	-20(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **5d**.

	x	y	z	U(eq)
H(1)	3800(30)	3300(20)	3000(20)	39(5)
H(2A)	2950(40)	3980(30)	450(30)	64(7)
H(2B)	4460(40)	2770(30)	910(20)	61(6)
H(4A)	6770(40)	6770(30)	2620(20)	65(7)
H(4B)	4340(40)	6430(20)	1530(20)	48(6)
H(5A)	5150(50)	5850(30)	3940(30)	78(9)
H(5B)	3580(40)	7170(30)	3490(30)	73(7)
H(6)	1430(30)	4990(20)	3510(20)	37(5)
H(9)	-730(50)	5110(30)	1710(30)	69(8)
H(71A)	-2030(40)	1510(30)	20(30)	67(7)
H(71B)	-230(40)	2660(30)	-260(30)	71(7)
H(81A)	-1280(50)	2060(30)	4720(30)	78(8)
H(81B)	-1900(50)	3110(30)	3850(30)	87(9)
H(81C)	490(60)	3150(40)	4820(40)	97(10)
H(82A)	2410(50)	-400(40)	2770(40)	102(10)
H(82B)	3750(70)	980(40)	3850(40)	129(14)
H(82C)	2100(60)	60(50)	4290(50)	146(15)
H(83A)	-3180(60)	-420(40)	2490(40)	102(11)
H(83B)	-4380(60)	490(40)	1600(30)	119(12)
H(83C)	-2450(50)	-560(40)	1290(40)	97(11)