

## Supporting Information

### Silylative Carbocyclization of Allenyl-Carbonyl Units with Et<sub>3</sub>SiH Catalyzed by Rhodium: *cis*-Stereoselective Synthesis of Homoallylic Cycloalkanols

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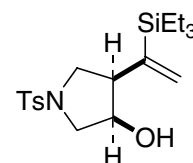
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**General:** All reactions were run in flame dried glassware under an atmosphere of nitrogen. Diethyl ether (Et<sub>2</sub>O) was dried by refluxing over sodium/benzophenone ketyl until a permanent purple coloration was presented, and distilled prior to use. Tetrahydrofuran (THF) was distilled from sodium-benzophenone under N<sub>2</sub>. Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was distilled from CaH<sub>2</sub> prior to use. All liquid reagents purchased from the Aldrich were distilled properly prior to use, unless otherwise indicated. Purification was conducted by flash column chromatography on silica gel (230-400 mesh), eluting with a mixture of hexane and ethyl acetate, unless otherwise stated. All reactions were monitored by thin layer chromatography carried out on Merck silica gel plate (60 F<sub>254</sub>) using UV light as visualizing agent and ethanolic anisaldehyde solution and heat as developing agent. Silica gel 60 (TA792685, 230-400 mesh) from Merck was used for column chromatography. The reported yields are for chromatographically pure isolated products. FT-IR spectra were recorded on a Nicolet 320. <sup>1</sup>H NMR spectra were recorded on a Varian Unity Inova at 500 MHz and a Bruker Avance 400 spectrometer in CDCl<sub>3</sub> as a solvent with TMS or residual chloroform as the internal standard. <sup>13</sup>C NMR spectra were measured on a Varian Unity Inova at 125 MHz in CDCl<sub>3</sub> as a solvent. EI-mass spectra were obtained on a VG-Instrument Trio 2000 system at 70 eV.

**1-(Toluene-4-sulfonyl)-4-(1-triethylsilanylvinyl)pyrrolidin-3-ol (2a):**

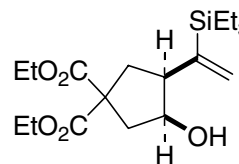
**Typical procedure.** A stainless steel autoclave was charged with the



allenyl-aldehyde **1a** (210 mg, 0.80 mmol), triethylsilane (186 mg, 1.60 mmol), and Rh(acac)(CO)<sub>2</sub> (2.0 mg, 1 mol %) in diethyl ether (5 mL). The system was flushed three times with CO (10 atm) and the autoclave was pressurized to 10 atm and the mixture was stirred at 70 °C for 8 h. The solution was then cooled and concentrated under reduced pressure to give crude products. Final purification was effected by column chromatography to give the cyclized product **2a** (226 mg, 0.59 mmol, 74%) as a white solid: mp 81 °C; TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 2, R<sub>f</sub> = 0.51; IR (film): 3511, 2947, 1637, 1332, 1156, 731 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.58 (m, 6H), 0.89 (t, 9H, *J* = 7.9 Hz), 2.43 (s, 3H), 2.79 (ddd, 1H, *J* = 3.7, 7.1, 11.6 Hz), 3.33 (dd, 1H, *J* = 9.4, 11.6 Hz), 3.43 (dd, 1H, *J* = 1.0, 11.5 Hz), 3.49 (dd, 1H, *J* = 7.1, 9.4 Hz), 3.59 (dd, 1H, *J* = 1.0, 4.1 Hz), 4.06 (ddd, 1H, *J* = 3.7, 4.1, 11.5 Hz), 5.63 (d, 1H, *J* = 2.0 Hz), 5.74 (d, 1H, *J* = 2.0 Hz), 7.32 (m, 2H), 7.74 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 3.1, 7.6, 22.0, 48.8, 56.5, 70.9, 127.9, 130.0, 130.1, 134.5, 143.7, 143.9; HRMS calcd for C<sub>19</sub>H<sub>31</sub>NO<sub>3</sub>SSi: 381.1794. found: 381.1796.

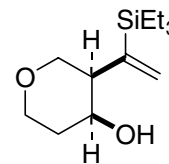
**3-Hydroxy-4-(1-triethylsilanylviny)cyclopentane-1,1-dicarboxylic acid diethyl ester (2b):**

A colorless oil: TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 3, R<sub>f</sub> = 0.51; IR (neat) 3545, 2951, 1729, 1458, 1258, 730 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.64 (m, 6H), 0.93 (t, 9H, *J* = 7.9 Hz), 1.25 (t, 3H, *J* = 7.0 Hz), 1.26 (t, 3H, *J* = 7.0 Hz), 2.19 (dd, 1H, *J* = 13.1, 6.4 Hz), 2.54 (m, 2H), 2.67 (dd, 1H, *J* = 13.1, 12.6 Hz), 2.83 (m, 1H), 4.07 (m, 1H), 4.19 (q, 2H, *J* = 7.0 Hz), 4.22 (q, 2H, *J* = 7.0 Hz), 5.67 (d, 1H, *J* = 2.3 Hz), 5.94 (d, 1H, *J* = 2.3 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 3.2, 7.7, 14.4, 35.3, 42.6, 50.2, 58.2, 61.9, 72.8, 128.9, 146.2, 172.8, 173.2; HRMS calcd for C<sub>19</sub>H<sub>31</sub>O<sub>5</sub>Si: 370.2176. found: 370.2182.



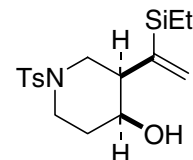
**3-(1-Triethylsilanylviny)tetrahydropyran-4-ol (2c):**

A colorless oil. TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 4, R<sub>f</sub> = 0.53; IR (neat) 3441, 2950, 1459, 1109, 728 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.60 (m, 6H), 0.92 (m, 9H), 1.68 (m, 1H), 1.82 (m, 2H), 2.36 (t, 1H, *J* = 7.6 Hz), 3.51 (t, 2H, *J* = 7.6 Hz), 3.78 (m, 2H), 4.14 (m, 1H), 5.37 (d, 1H, *J* = 2.9 Hz), 5.67 (d, 1H, *J* = 2.9 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 3.2, 7.7, 36.2, 44.3, 64.8, 68.3, 71.3, 127.6, 145.7; HRMS calcd for C<sub>13</sub>H<sub>26</sub>O<sub>2</sub>Si: 242.1702. found: 242.1713.

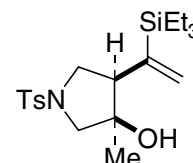


**1-(Toluene-4-sulfonyl)-3-(1-triethylsilanylviny)piperidin-4-ol (2d):**

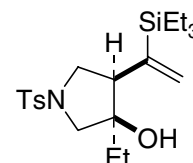
A colorless oil. TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 2, R<sub>f</sub> = 0.46; IR (neat) 3523, 2918, 2358, 1337, 1160, 729 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.62 (m, 6H), 0.93 (t, 9H, *J* = 7.9 Hz), 1.86 (m, 1H), 1.94 (dddd, 1H, *J* = 2.2, 3.4, 3.5, 13.9 Hz), 2.44 (s, 3H), 2.60-2.65 (m, 2H), 2.70 (dd, 1H, *J* = 10.3, 12.1 Hz), 3.46 (m, 1H), 3.60 (m, 1H), 3.76 (m, 1H), 5.55 (dd, 1H, *J* = 0.6, 1.9 Hz), 5.60 (m, 1H), 7.32 (dd, 2H, *J* = 0.7, 8.6 Hz), 7.66 (dd, 2H, *J* = 0.5, 8.6 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 2.9, 7.3, 21.5, 31.0, 40.4, 43.7, 44.3, 63.6, 127.5, 127.6, 129.7, 133.6, 143.4, 148.9; HRMS calcd for C<sub>20</sub>H<sub>33</sub>NO<sub>3</sub>SSi: 395.1950. found: 395.1948.

**3-Methyl-1-(toluene-4-sulfonyl)-4-(1-triethylsilanylviny)pyrrolidin-3-ol (2e):**

A colorless oil. TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 2, R<sub>f</sub> = 0.49. IR (neat) 3509, 2952, 1338, 1158, 727 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.58 (m, 6H), 0.89 (t, 9H, *J* = 7.8 Hz), 1.16 (s, 3H), 2.43 (s, 3H), 2.59 (dd, 1H, *J* = 7.5, 10.9 Hz), 3.27 (dd, 1H, *J* = 9.6, 10.9 Hz), 3.32 (d, 1H, *J* = 11.0 Hz), 3.42 (d, 1H, *J* = 11.0 Hz), 3.54 (dd, 1H, *J* = 7.5, 9.6 Hz), 5.65 (d, 1H, *J* = 2.0 Hz), 5.92 (d, 1H, *J* = 2.0 Hz), 7.33 (m, 2H), 7.74 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 3.3, 7.7, 22.0, 25.5, 51.1, 53.2, 61.2, 127.9, 130.0, 131.3, 134.5, 143.9, 144.5; HRMS calcd for C<sub>20</sub>H<sub>33</sub>NO<sub>3</sub>SSi: 395.1950. found: 395.1953.

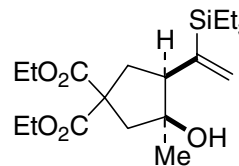
**3-Ethyl-1-(toluene-4-sulfonyl)-4-(1-triethylsilanylviny)pyrrolidin-3-ol (2f)**

A colorless oil. TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 3, R<sub>f</sub> = 0.44; IR (neat) 3499, 2952, 1634, 1339, 1159, 726 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.56 (m, 8H), 0.89 (m, 12 H), 2.44 (s, 3H), 2.60 (dd, 1H, *J* = 7.4, 10.8 Hz), 3.25 (dd, 1H, *J* = 9.6, 10.8 Hz), 3.35 (s, 2H), 3.54 (dd, 1H, *J* = 7.4, 9.6 Hz), 5.64 (d, 1H, *J* = 2.3 Hz), 5.93 (d, 1H, *J* = 2.3 Hz), 7.33 (d, 2H, *J* = 7.9 Hz), 7.74 (d, 2H, *J* = 7.9 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 3.7, 8.1, 22.4, 32.7, 50.9, 53.6, 59.4, 81.0, 128.3, 130.4, 131.7, 135.0, 144.2, 145.3; HRMS calcd for C<sub>21</sub>H<sub>35</sub>NO<sub>3</sub>SSi: 409.2107. found: 409.2096.



**3-Hydroxy-3-methyl-4-(1-triethylsilylvinyl)cyclopentane-1,1-dicarboxylic acid diethyl ester (2g)**

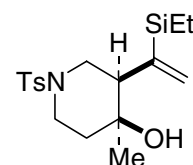
A colorless oil. TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 5, R<sub>f</sub> = 0.44; IR (neat) 3481, 2953, 1728, 1456, 1259, 727 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)



δ 0.63 (m, 6H), 0.93 (m, 9H), 1.22 (s, 3H), 1.25 (m, 6H), 2.30 (d, 1H, *J* = 14.3 Hz), 2.40 (m, 1H), 2.50 (m, 1H), 2.59 (m, 2H), 4.20 (m, 4H), 5.67 (d, 1H, *J* = 2.3 Hz), 6.14 (d, 1H, *J* = 2.3 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 3.4, 7.8, 14.4, 26.9, 40.5, 48.9, 52.3, 57.3, 62.0, 79.7, 130.2, 147.1, 173.2, 173.3; HRMS calcd for C<sub>20</sub>H<sub>33</sub>NO<sub>3</sub>SSi: 384.2332. found: 384.2319.

**4-Methyl-1-(toluene-3-sulfonyl)-3-(1-triethylsilylvinyl)piperidin-4-ol (2h)**

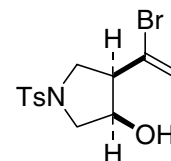
A colorless oil. TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 2, R<sub>f</sub> = 0.48; IR (neat)



3517, 2950, 1339, 1158, 728 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.63 (m, 6H), 0.95 (m, 9H), 1.18 (s, 3H), 2.43 (s, 3H), 1.68 (ddd, 1H, *J* = 2.3, 3.2, 13.8 Hz), 1.74 (md, 1H, *J* = 4.6 Hz), 2.42 (m, 1H), 2.57 (dd, 1H, *J* = 11.4, 11.8 Hz), 2.69 (ddd, 1H, *J* = 3.2, 11.5, 12.6 Hz), 3.37 (ddd, 1H, *J* = 2.0, 3.8, 11.4 Hz), 3.63 (dddd, 1H, *J* = 2.0, 2.3, 4.6, 11.5 Hz), 5.55 (d, 1H, *J* = 2.0 Hz), 5.89 (d, 1H, *J* = 2.0 Hz), 7.31 (m, 2H), 7.65 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 3.4, 7.8, 21.9, 29.8, 39.0, 42.5, 47.7, 69.6, 128.0, 129.3, 130.1, 134.3, 143.7, 149.1; HRMS calcd for C<sub>20</sub>H<sub>33</sub>NO<sub>3</sub>SSi: 409.2107. found: 409.2117.

**4-(1-Bromo-vinyl)-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (3a)**

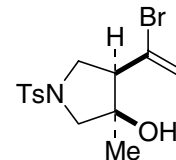
To a solution of **2a** (50 mg, 0.13 mmol) in 2 mL of CH<sub>2</sub>Cl<sub>2</sub> at -78 °C was added bromine (23.0 mg, 0.14 mmol). After 20min, the mixture was quenched with 10% Na<sub>2</sub>CO<sub>3</sub> and extracted with MC. The organic layer



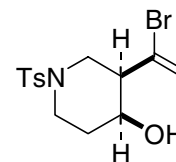
was dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The residue was added 2 mL of THF and added slowly 1 M solution in THF of TBAF (0.26 g, 0.26 mmol) for 10 min. After 40 min, the mixture was concentrated in vacuo. The crude product was purified by SiO<sub>2</sub> column chromatography to give a product **3a** (27.1 mg, 60%). TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 1, R<sub>f</sub> = 0.16. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.43 (s, 3H), 2.99 (m, 1H), 3.38 (dd, 2H, *J* = 9.2, 7.3 Hz), 3.61 (dd, 2H, *J* = 9.2, 11.2 Hz), 4.48 (m, 2H), 5.61 (dd, 1H, *J* = 2.7, 1.7 Hz), 5.69 (dd, 1H, *J* = 2.7, 1.3 Hz), 7.33 (d, 2H, *J* = 8.2 Hz), 7.74 (d, 2H, *J* = 8.2 Hz).

**4-(1-Bromo-vinyl)-3-methyl-1-(toluene-4-sulfonyl)-pyrrolidin-3-ol (3b)**

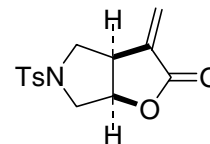
TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 2, R<sub>f</sub> = 0.24. IR (neat) 3504, 2970, 1624, 1598, 1337, 1159, 666 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.39 (s, 3H), 2.44 (s, 3H), 2.85 (dd, 1H, *J* = 10.4, 7.8 Hz), 3.27 (d, 1H, *J* = 11.0 Hz), 3.41 (d, 1H, *J* = 11.0 Hz), 3.64 (dd, 1H, *J* = 9.6, 7.8 Hz), 5.75 (s, 2H), 7.34 (d, 2H, *J* = 8.2 Hz), 7.74 (d, 2H, *J* = 8.2 Hz).

**3-(1-Bromo-vinyl)-1-(toluene-4-sulfonyl)-piperidin-4-ol (3c)**

TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 1, R<sub>f</sub> = 0.57. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.92 (m, 2H), 2.44 (s, 3H), 2.64 (m, 2H), 2.73 (m, 1H), 3.61 (m, 1H), 3.75 (m, 1H), 4.30 (m, 1H), 5.51 (dd, 1H, *J* = 2.6, 1.3 Hz), 5.67 (dd, 1H, *J* = 2.6, 0.7 Hz), 7.33 (d, 2H, *J* = 8.2 Hz), 7.66 (d, 2H, *J* = 8.2 Hz).

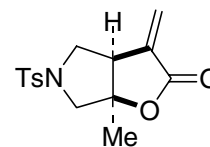
**3-Methylene-5-(toluene-4-sulfonyl)hexahydrofuro[2,3-*c*]pyrrol-2-one (4a)**

A 10 mL, two-necked flask equipped with reflux condenser, an argon inlet, a rubber septum, and a magnetic stirrer was charged with Ni(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (55.1 mg, 0.09 mmol) and **3a** (27.1 mg, 0.079 mmol). The system was alternatively evacuated and filled with argon three times *via* syringe was introduced 3 mL of dry THF, and Et<sub>3</sub>N (15.9 mg, 0.16 mmol) was added. The mixture was heated at reflux for 15 min, during which color changed from colorless to yellow. The mixture was cooled to room temperature, poured into 20 mL of Et<sub>2</sub>O, and washed with 0.2 mL of aqueous 3*N* HCl. The combined aqueous layers were extracted with Et<sub>2</sub>O, and then the combined organic layers were washed with saturated aqueous NaHCO<sub>3</sub> and saturated aqueous NaCl. The organic layers were dried anhydrous MgSO<sub>4</sub>, filtered and concentrated in vacuo. The crude product was purified by SiO<sub>2</sub> column chromatography to give a product **4a** (17.3 mg, 75%) as a white solid. mp. 115 °C; TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 1, R<sub>f</sub> = 0.48; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.45 (s, 3H), 3.07 (dd, 1H, *J* = 5.3, 11.7 Hz), 3.22 (dd, 1H, *J* = 10.0, 7.6 Hz), 3.37 (dd, 1H, *J* = 10.0, 2.9 Hz), 3.55 (m, 1H), 3.63 (dd, 1H, *J* = 0.6, 11.7 Hz), 4.97 (m, 1H), 5.77 (d, 1H, *J* = 2.4 Hz), 6.35 (d, 1H, *J* = 2.4 Hz), 7.36 (d, 2H, *J* = 8.2 Hz), 7.68 (d, 2H, *J* = 8.2 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.6, 145.2, 137.4, 132.1, 130.6, 128.7, 125.8, 79.7, 55.2, 54.7, 42.6, 22.3; HRMS calcd for C<sub>14</sub>H<sub>15</sub>NO<sub>4</sub>S: 293.0776. found: 293.0705.



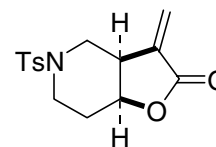
**6a-Methyl-3-methylene-5-(toluene-4-sulfonyl)hexahydrofuro[2,3-c]pyrrol-2-one (4b)**

A white solid. M.p. 156 °C; TLC, SiO<sub>2</sub>, EtOAc / hexanes 1 : 1, R<sub>f</sub> = 0.37; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.48 (s, 3H), 2.45 (s, 3H), 2.96 (d, 1H, *J* = 11.1 Hz), 3.14 (m, 1H), 3.27 (dd, 1H, *J* = 10.0, 3.5 Hz), 3.39 (dd, 1H, *J* = 10.0, 8.0 Hz), 3.56 (d, 1H, *J* = 11.1 Hz), 5.72 (d, 1H, *J* = 2.4 Hz), 6.33 (d, 1H, *J* = 2.4 Hz), 7.35 (d, 2H, *J* = 8.2 Hz), 7.67 (d, 2H, *J* = 8.2 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.7, 144.8, 138.3, 132.2, 130.3, 128.4, 125.5, 88.6, 59.0, 55.3, 48.7, 24.6, 22.0; HRMS calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>4</sub>S: 307.0878. found: 307.0883.



**3-Methylene-5-(toluene-4-sulfonyl)hexahydrofuro[3,2-c]pyridin-2-one (4c)**

A colorless oil. R<sub>f</sub> = 0.52 (EtOAc/hexane 1:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 2.13 (dt, 2H, *J* = 7.0, 4.4 Hz), 2.65 (m, 1H), 3.28 (m, 1H), 3.43 (m, 1H), 3.59 (ddd, 1H, *J* = 12.7, 6.5, 1.8 Hz), 4.54 (dd, 1H, *J* = 9.4, 3.8 Hz), 5.71 (d, 1H, *J* = 1.5 Hz), 6.25 (d, 1H, *J* = 1.5 Hz), 7.34 (d, 2H, *J* = 8.2 Hz), 7.62 (d, 2H, *J* = 8.2 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.1, 144.9, 137.7, 133.4, 130.7, 128.2, 124.0, 74.0, 46.3, 41.8, 40.0, 27.9, 22.3; HRMS calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>4</sub>S: 307.0878. found: 307.0863.



## Supplementary materials for 2a

### 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  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, *J*-Resolved, COSY, HMQC, HMBC, and NOESY were collected in  $\text{CHCl}_3\text{-d}$  with TMS as an internal reference. The concentration of the samples was 50 mM. For  $^1\text{H}$ -NMR analysis, 16 transients were acquired with a 1 sec relaxation delay using 32K data points. The  $90^\circ$  pulse was 9.7  $\mu\text{sec}$  with a spectral width of 3571 Hz.  $^{13}\text{C}$  NMR and DEPT spectra were obtained for a spectral width of 20500 Hz, collecting 64K data points. The  $90^\circ$  pulse was 9.8  $\mu\text{sec}$ . 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 50 ps. Among 50 calculated structures, ten structures with the lowest total energy were superimposed and used for analysis.

### Result

The structure of **2a** is shown in Fig. 1. In order to determine the configuration of ring juncture proton, the three dimensional structures of *cis* and *trans* isomers were obtained using the molecular modeling calculation. As shown in Fig. 2, while in the case of the *cis* isomer, the distances between H4 and H6b are closer than those between H4 and H6a, in the case of the *trans* isomer, the distances between H4 and H6a are closer than those between H4 and H6b. The distances calculated from molecular modeling are listed in Table 1. Fig. 3 shows 1D slice of the NOESY spectrum of **2a**, where H4 is saturated. The distance between H4 and H6a obtained based on the nOe signal is 2.74 Å, and that between H4 and H6b, 2.40 Å. That is, this result satisfies the *cis* configuration. Here, the distance between H1a and H1b is used as a reference, which is 1.8 Å. Therefore, **2a** has *cis* configuration of ring juncture proton. The assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **2a** listed in Tables 2.

Table 1. The distances of interested protons obtained from molecular modeling calculations.  
(The structures are shown in Fig. 2).

	Calculated distance (Å)	Calculated distance (Å)
	H4/H6a	H4/H6b
<i>cis1</i>	2.79	2.24
<i>cis2</i>	2.97	2.19
<i>trans1</i>	2.45	3.09
<i>trans2</i>	2.40	3.21

Table 2. The distances obtained from nOe crosspeaks of interested protons.

	Distance (Å)
H4/H6a	2.74
H4/H6b	2.40



Table 3. The complete assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **2a**.

$\delta_{^{13}\text{C}}$	of CHn	$\delta$ of $^1\text{H}$	assignment
2.7	t	0.58 (m)	a', c', e'
7.2	q	0.89 (t, 7.9)	b', d', f'
21.6	q	2.43	g
48.3	t	3.33 (dd, 9.4, 11.6) 3.49 (dd, 7.1, 9.4)	5
48.5	d	2.79 (ddd, 3.7, 7.1, 11.6)	3
56.0	t	3.43 (dd, 1.0, 11.5) 3.59 (ddd, 1.0, 4.1, 11.5)	6a 6b
70.5	d	4.06 (md, 3.7)	4
127.5	d	7.74 (m)	b, c
129.6	d	7.32 (m)	d, e
129.6	t	5.64 (dd, 0.9, 2.0) 5.74 (m)	1
134.1	s	-	f
143.3	s	-	2
143.4	s	-	a

Fig. 1. The structure of **2a**.

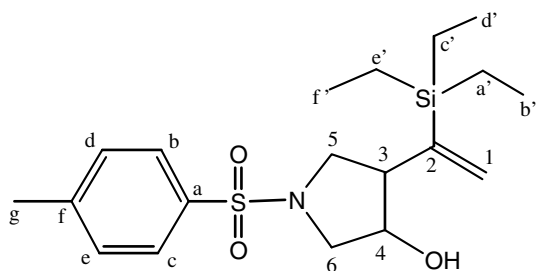




Fig. 2. The three dimensional structures of *cis* (left side) and *trans* (right side) isomers calculated by molecular modeling.

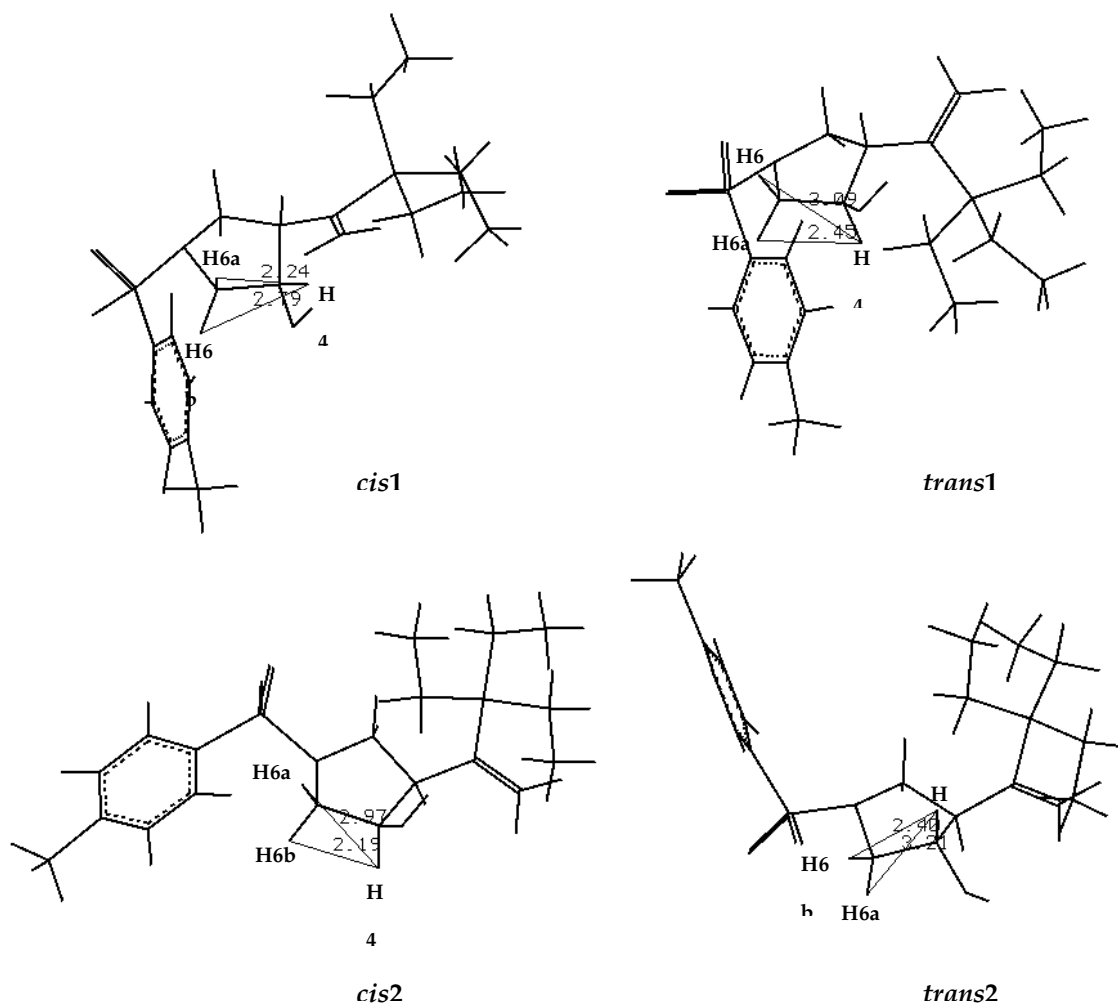
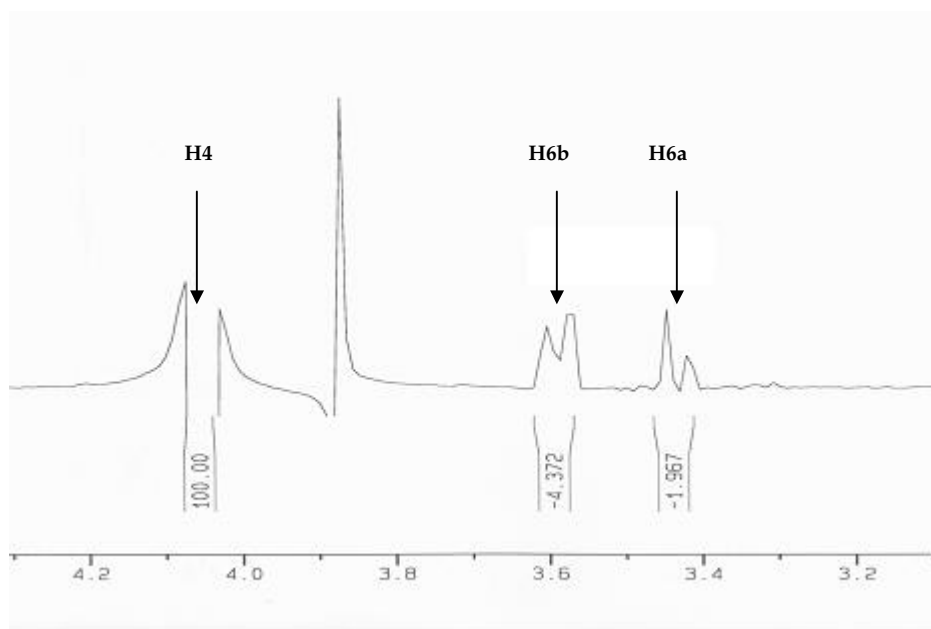


Fig. 3. 1D slice of the NOESY spectrum of **2a** (H4 is saturated).



## Supplementary materials for 2d

### 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  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, COSY, HMQC, HMBC, and NOESY were collected in  $\text{CHCl}_3\text{-d}$  with TMS as an internal reference. The concentration of the samples was 50 mM. For  $^1\text{H}$ -NMR analysis, 16 transients were acquired with a 1 sec relaxation delay using 32K data points. The  $90^\circ$  pulse was 9.7  $\mu\text{sec}$  with a spectral width of 4371Hz.  $^{13}\text{C}$  NMR and DEPT spectra were obtained for a spectral width of 18832Hz, collecting 64K data points. The  $90^\circ$  pulse was 9.8  $\mu\text{sec}$ . 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 50 ps. Among 50 calculated structures, ten structures with the lowest total energy were superimposed and used for analysis.

### Result

The structure of **2d** is shown in Fig. 1. The difference of the configuration of ring juncture protons makes several distances among protons near to them to show the difference. Based on the molecular modeling calculation, four isomers such as *cis1*, *cis2*, *trans1*, and *trans2*, can be considered (Fig. 2). Especially, four distances are investigated and they are listed in Table1. If the configuration of ring juncture protons of **2d** is *cis1*, a strong nOe signal between H4 and H7b should be observed. As shown in Fig. 3, however, it is not observed. Likewise, if the compound has the configuration of *trans1* or *trans2*, strong nOe signals among H3/H6a and H4/ H7a should be observed. But they are not shown. Only one nOe signal is observed among H3, H6a, H6b, H4, H7a, and H7b. That is H3/H6a. As a result, the compound has the configuration of *cis2*. The assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **2d** listed in Tables 2.

Table 1. The distances of interested protons obtained from molecular modeling calculations. (The structures are shown in Fig. 2).

Configuration	Calculated distance (Å)			
	H3/H6a	H3/H6b	H4/H7a	H4/H7b
<i>cis</i> 1(181kcal)	4.02	4.24	3.74	2.91
<i>cis</i> 2(181kcal)	2.64	3.70	4.46	4.01
<i>trans</i> 1(189kcal)	2.54	3.68	2.77	3.88
<i>trans</i> 2(190kcal)	2.55	3.71	2.57	3.79

Table 2. The assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **2d**.

$\delta$ of $^{13}\text{C}$	$\text{CH}_n$	$\delta$ of $^1\text{H}$	assignment
2.9	t	0.62 (m)	a', c', e'
7.3	q	0.93 (t, 7.9)	b', d', f'
21.5	q	2.44	g
31.0	t	1.86 (m) 1.94 (dddd, 2.2, 3.4, 3.5, 13.9)	6
40.4	t	2.60 (dm, 3.1) 3.60 (m)	7
43.7	t	2.70 (dd, 10.3, 12.1) 3.46 (m)	5
44.3	d	2.65 (m)	3
63.7	d	3.76 (m)	4
127.59	t	5.55 (dd, 0.6, 1.9) 5.60 (m)	1
127.65	d	7.66 (dd, 0.5, 8.6)	b', c'
129.7	d	7.32 (dd, 0.7, 8.6)	d', e'
133.6	s	-	a
143.5	s	-	f
149.9	s	-	2

Fig. 1. The structure of **2d**.

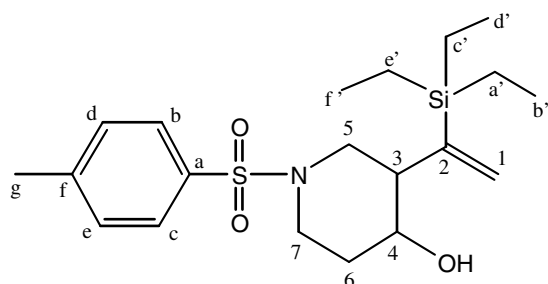


Fig. 2. The three dimensional structures of *cis* (left side) and *trans* (right side) isomers calculated by molecular modeling.

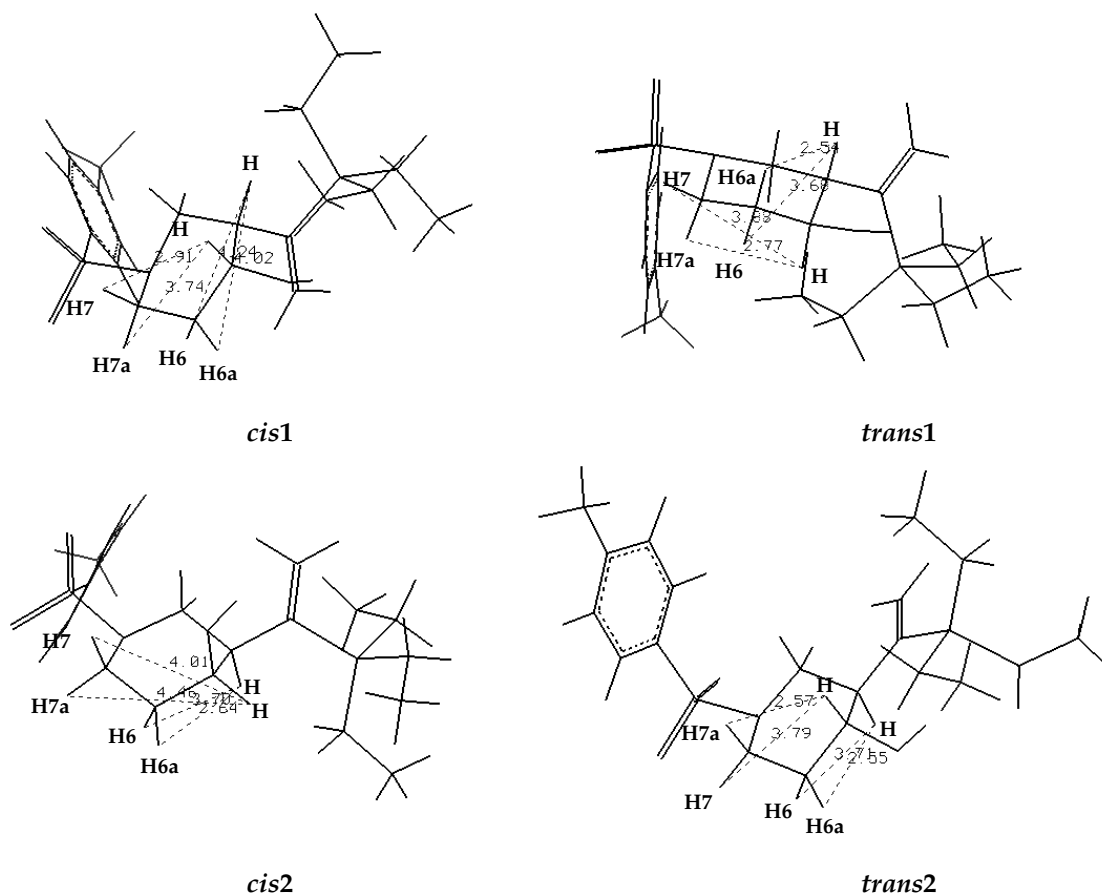
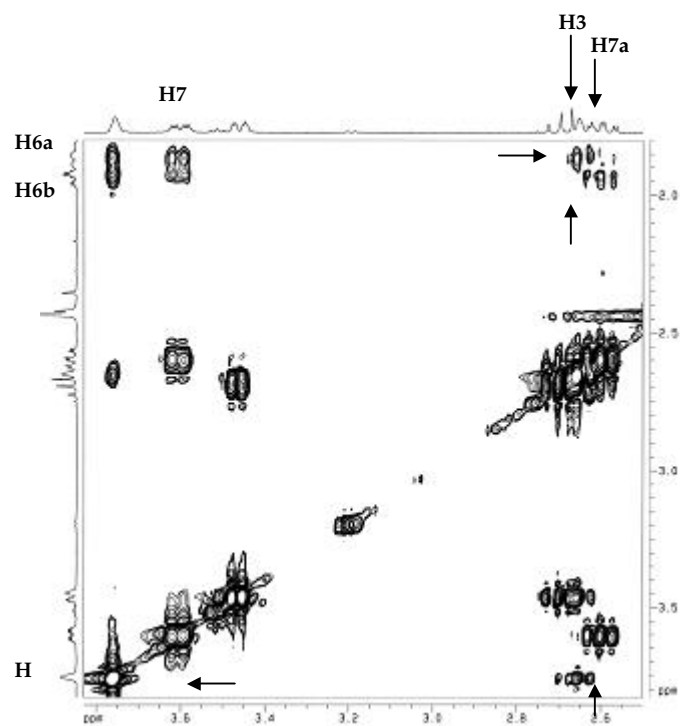


Fig. 3. The NOESY spectrum of **2d**.





## Supplementary materials for 2e

### 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  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, *J*-Resolved, COSY, HMQC, HMBC, and NOESY were collected in  $\text{CHCl}_3\text{-d}$  with TMS as an internal reference. The concentration of the samples was 50 mM. For  $^1\text{H}$ -NMR analysis, 16 transients were acquired with a 1 sec relaxation delay using 32K data points. The  $90^\circ$  pulse was 9.7  $\mu\text{sec}$  with a spectral width of 3434 Hz.  $^{13}\text{C}$  NMR and DEPT spectra were obtained for a spectral width of 19048 Hz, collecting 64K data points. The  $90^\circ$  pulse was 9.8  $\mu\text{sec}$ . 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 50 ps. Among 50 calculated structures, ten structures with the lowest total energy were superimposed and used for analysis.

### Result

The structure of **2e** is shown in Fig. 1. In order to determine the configuration of ring juncture proton, H3 and methyl group,  $7\text{CH}_3$ , the three dimensional structures of *cis* and *trans* isomers were obtained using the molecular modeling calculation. As shown in Fig. 2, the distances between H3 and H7 of *cis* isomers are closer than those of *trans* isomers. The distances obtained from molecular modeling calculations are listed in Table1. Fig. 3 shows 1D slice of the NOESY spectrum of **2e**, where H3 is saturated. The distance calculated based on the nOe signal is 2.52 Å (Table 2), which agrees with the value of *cis* isomer. Here, the distance between H1a and H1b is used as a reference, which is 1.8 Å. Therefore, **2e** has *cis* configuration of ring juncture proton, H3 and methyl group,  $7\text{CH}_3$ . The assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **2e** listed in Tables 2.

Table 1. The distances of interested protons obtained from molecular modeling calculations.  
(The structures are shown in Fig. 2).

	Calculated distance (Å)
	H3/H7
<i>cis1</i>	2.45
<i>cis2</i>	2.36
<i>trans1</i>	3.87
<i>trans2</i>	4.03

Table 2. The distances obtained from nOe crosspeaks of interested protons.

	Distance(Å)
H3/H7	2.52

Table 3. The complete assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **2e**.

$\delta_{^{13}\text{C}}$	of CHn	$\delta$ of $^1\text{H}$	assignment
2.9	t	0.57 (m)	a', c', e'
7.3	q	0.89 (t, 7.8)	b', d', f'
21.6	q	2.43	g
25.1	q	1.16	7
50.7	d	2.59 (dd, 7.5, 10.9)	3
52.8	t	3.27 (dd, 9.6, 10.9) 3.54 (dd, 7.5, 9.6)	5
60.8	t	3.32 (d, 11.0) 3.42 (d, 11.0)	6
76.7	s	-	4
127.5	d	7.74 (m)	b, c
129.6	d	7.33 (m)	d, e
130.9	t	5.65 (d, 2.0) 5.92 (d, 2.0)	1
134.1	s	-	a
143.4	s	-	f
144.2	s	-	2
		1.56	OH

Fig. 1. The structure of **2e**.

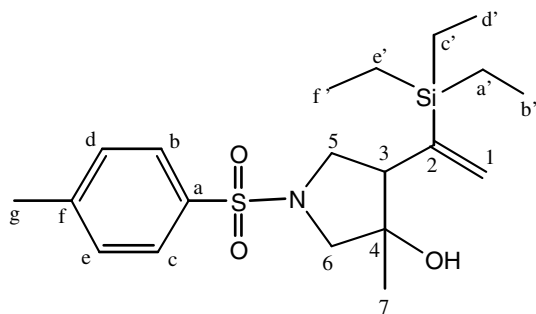


Fig. 2. The three dimensional structures of *cis* (left side) and *trans* (right side) isomers calculated by molecular modeling.

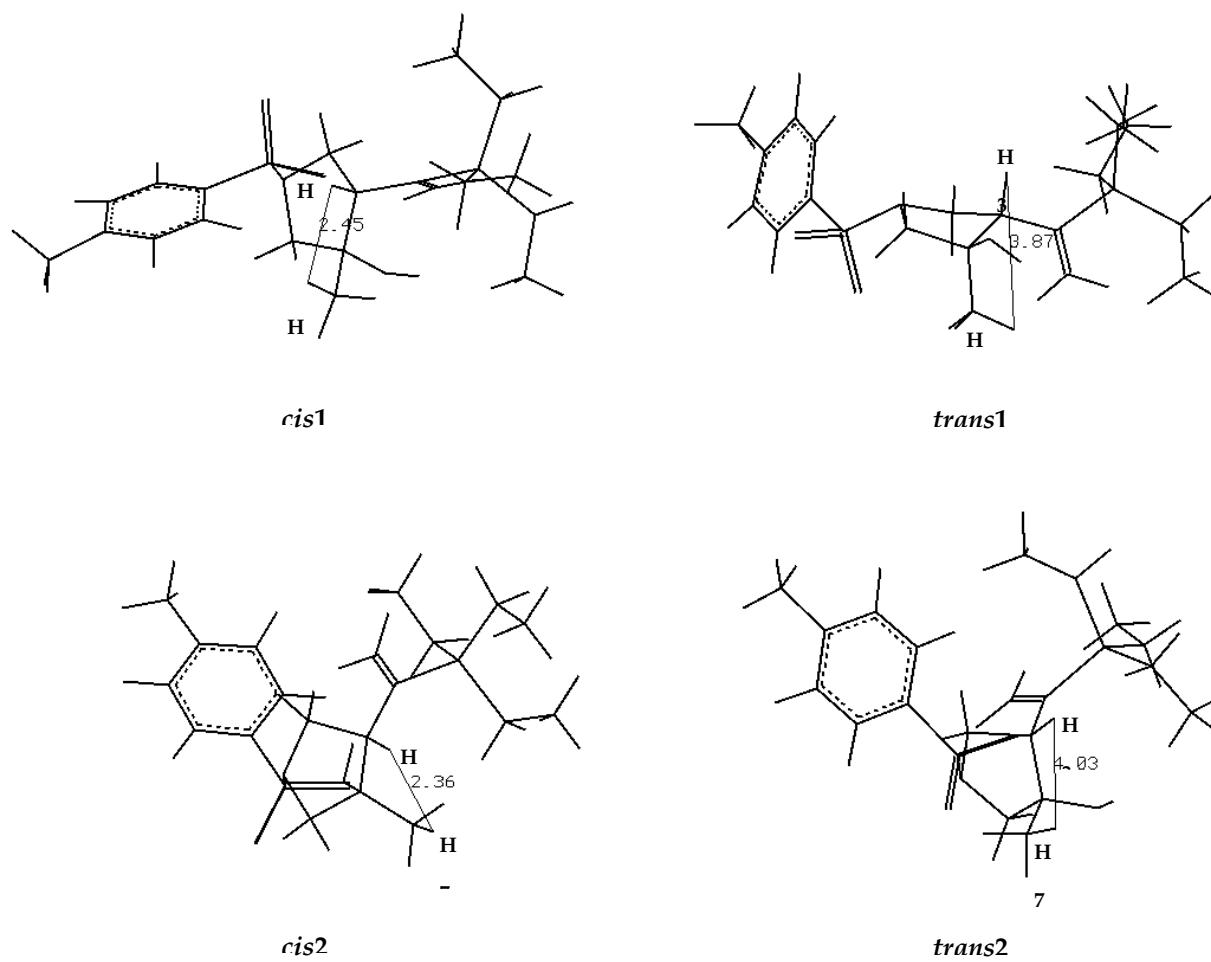
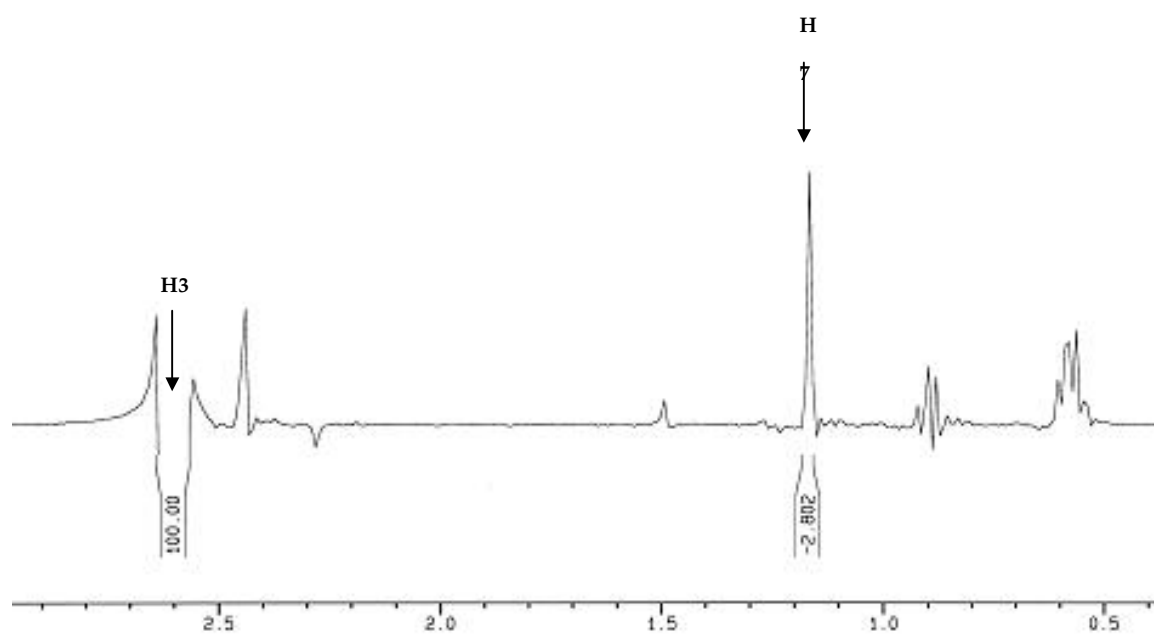


Fig. 3. 1D slice of the NOESY spectrum of **2e** (H3 is saturated).



## Supplementary materials for 2h

### 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  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, DEPT, *J*-Resolved, COSY, HMQC, HMBC, and NOESY were collected in  $\text{CHCl}_3$ -d with TMS as an internal reference. The concentration of the samples was 50 mM. For  $^1\text{H}$ -NMR analysis, 16 transients were acquired with a 1 sec relaxation delay using 32K data points. The  $90^\circ$  pulse was 9.7  $\mu\text{sec}$  with a spectral width of 3289Hz.  $^{13}\text{C}$  NMR and DEPT spectra were obtained for a spectral width of 19048Hz, collecting 64K data points. The  $90^\circ$  pulse was 9.8  $\mu\text{sec}$ . 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 50 ps. Among 50 calculated structures, ten structures with the lowest total energy were superimposed and used for analysis.

### Result

The structure of **2h** is shown in Fig. 1. In order to determine the configuration of ring juncture proton, H3 and methyl group,  $8\text{CH}_3$ , the three dimensional structures of *cis* and *trans* isomers were obtained using the molecular modeling calculation (Fig. 2) The distances between H3 and H6a, and H3 and H6b are listed in Table 1. While in the case of H3/H6a, four configurations are expected to show weak nOe or nothing, in the case of H3/H6b, *cis* isomers are expected to show strong nOe and *trans* isomers, weak nOe or nothing. The NOESY spectrum of **2h** is shown in Fig. 3. While the nOe signal of H3/H6a is not observed, that of H3/H6b is observed. As a result, the observation of nOe signals agrees with the case of *cis* isomers, so that the configuration between ring juncture proton, H3 and junction methyl group,  $8\text{CH}_3$  of **2h** should be *cis*. The assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **2h** are listed in Table 2.

Table 1. The distances of interested protons obtained from molecular modeling calculations.  
(The structures are shown in Fig. 2).

configuration	calculated distance (Å)	
	H3/H6a	H3/H6b
<i>cis</i> 1(181kcal)	3.78	2.70
<i>cis</i> 2(181kcal)	3.85	2.62
<i>trans</i> 1(189kcal)	4.42	4.09
<i>trans</i> 2(190kcal)	4.26	3.96

Table 2. The assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of **2h**.

$\delta_{^{13}\text{C}}$	of CHn	$\delta$ of $^1\text{H}$	assignment
2.9	t	0.63 (m)	a', c', e'
7.4	q	0.95 (m)	b', d', f'
21.5	q	2.43	g
29.4	q	1.18	8
38.6	t	1.68 (ddd, 2.3, 3.2, 13.8)	6a
		1.74 (md, 4.6)	6b
42.7	t	2.69 (ddd, 3.2, 11.5, 12.6)	7
		3.63 (dddd, 2.0, 2.3, 4.6, 11.5)	
46.9	t	2.57 (dd, 11.4, 11.8)	5
		3.37 (ddd, 2.0, 3.8, 11.4)	
47.3	d	2.42 (m)	3
69.2	s	-	4
127.6	d	7.65 (m)	b, c
128.9	t	5.55 (d, 2.3)	1
		5.89 (dd, 1.0, 2.3)	
129.6	d	7.31 (m)	d, e
133.9	s	-	a/f
143.3	s	-	a/f
148.7	s	-	2
		1.56	OH

Fig. 1. The structure of **2h**.

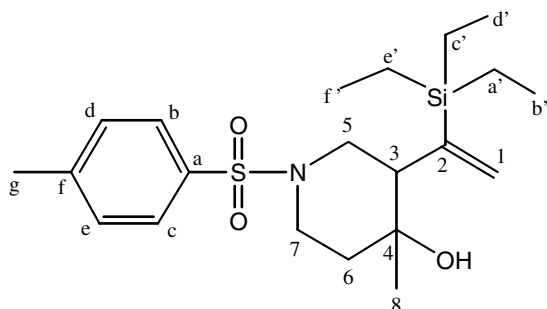


Fig. 2. The three dimensional structures of *cis* (left side) and *trans* (right side) isomers calculated by molecular modeling.

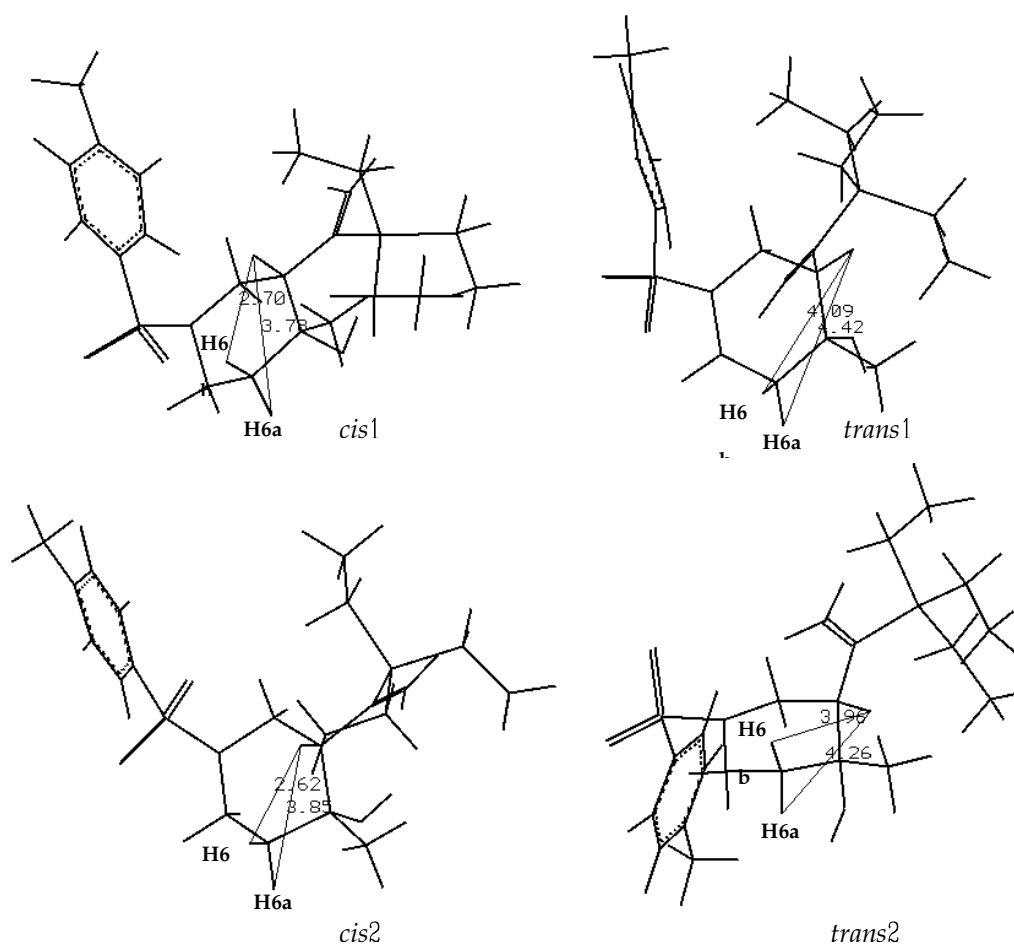
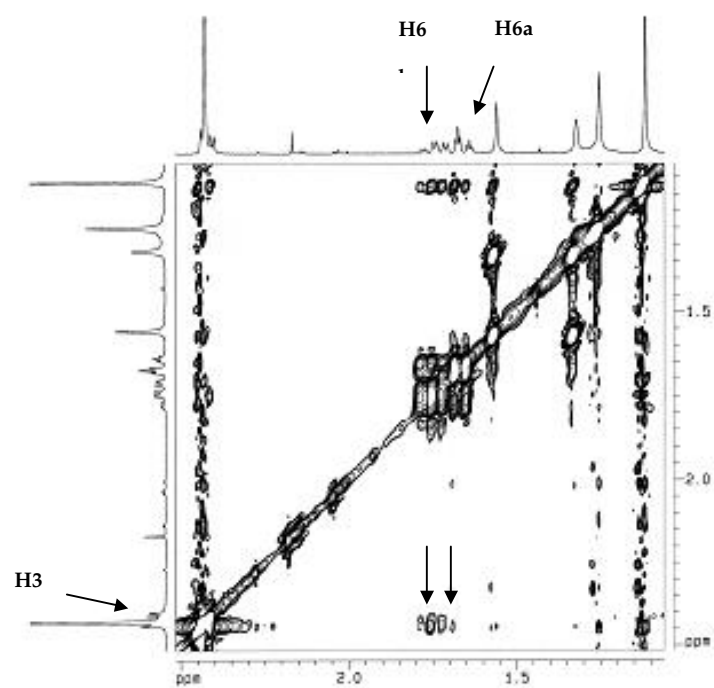




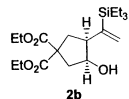
Fig. 3. The NOESY spectrum of **2h**.



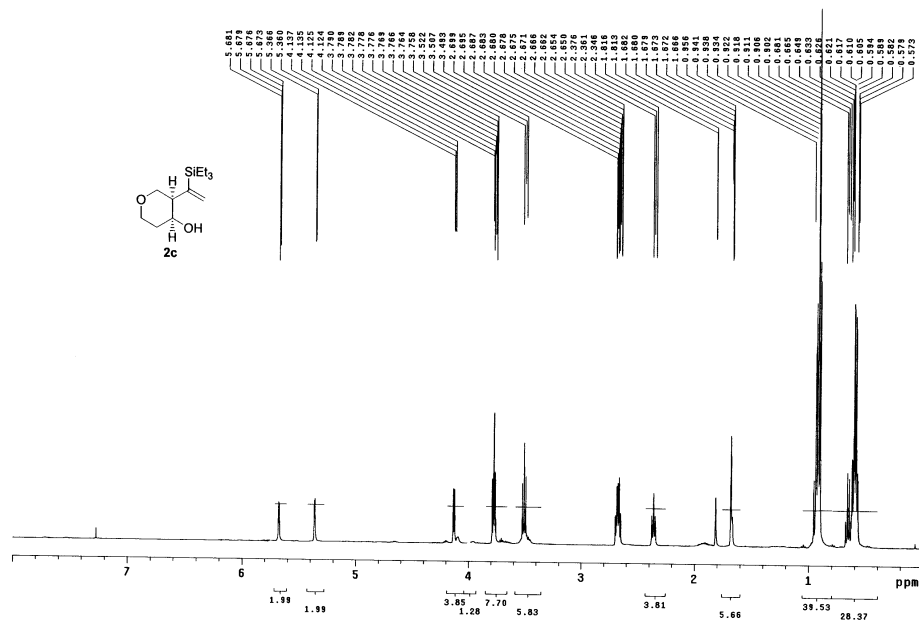
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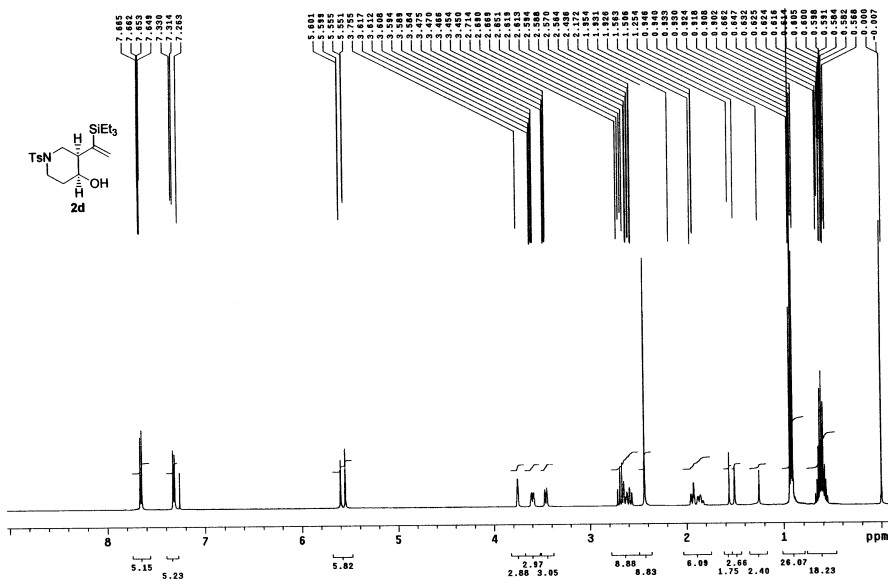
**Pulse Sequence:** s2pul



HYT03-2  
Pulse Sequence: s2pu1



HYT03-5  
Pulse Sequence: s2pu1



Chemical structure of compound 10: CC1(C)C(C(=C)Si(C)(C)C)C(O)C1N(C2=CC=CC=C2)S(=O)(=O)C3=CC=CC=C3

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 10. The spectrum shows peaks from 0 to 10 ppm. Key peaks include a broad singlet at 9.57 ppm (OH), a doublet at 7.74 ppm (TsN aromatic), a doublet at 7.32 ppm (TsN aromatic), a doublet at 6.15 ppm (H-3), a doublet at 5.64 ppm (H-2), a doublet at 3.01 ppm (H-1), a doublet at 2.60 ppm (H-4), a doublet at 1.05 ppm (methyl), and a doublet at 0.10 ppm (TMS). Integration values are provided below the baseline.

Chemical structure of compound **2f** is shown above the spectrum. The structure is a 4-toluenesulfonyl-2-methyl-2-vinyl-1,3-dioxolane derivative.

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound **2f** is displayed below the structure. The x-axis represents the chemical shift in ppm, ranging from 0 to 9. Integration values are provided below the baseline.

Chemical shift values (ppm) labeled above the spectrum: 7.744, 7.741, 7.728, 7.338, 7.323, 5.326, 5.322, 5.318, 5.314, 5.310, 3.272, 3.253, 3.251, 3.252, 2.865, 2.858, 2.856, 1.387, 1.375, 1.372, 1.279, 1.254, 1.251, 1.248, 1.011, 0.882, 0.880, 0.878, 0.876, 0.855, 0.853, 0.877, 0.877, 0.852, 0.852, 0.831, 0.831, 0.000.

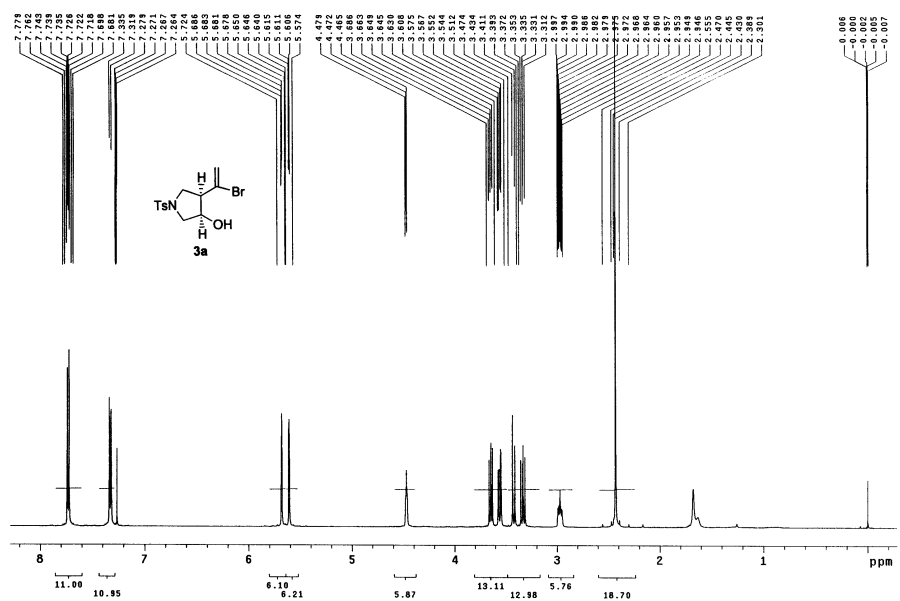
Integration values (from left to right): 4.96, 5.03, 2.78, 2.78, 2.96, 2.85, 5.75, 8.23, 2.74, 5.85, 33.41, 17.16.

Chemical structure of **2g** is shown in the top left corner. The structure is a cyclopentane ring with two ethyl ester groups (EtO<sub>2</sub>C) at positions 1 and 2, a methyl group (Me) at position 3, a hydroxyl group (OH) at position 4, and a trimethylsilyl group (SiEt<sub>3</sub>) at position 5. The stereochemistry is indicated with wedges and dashes.

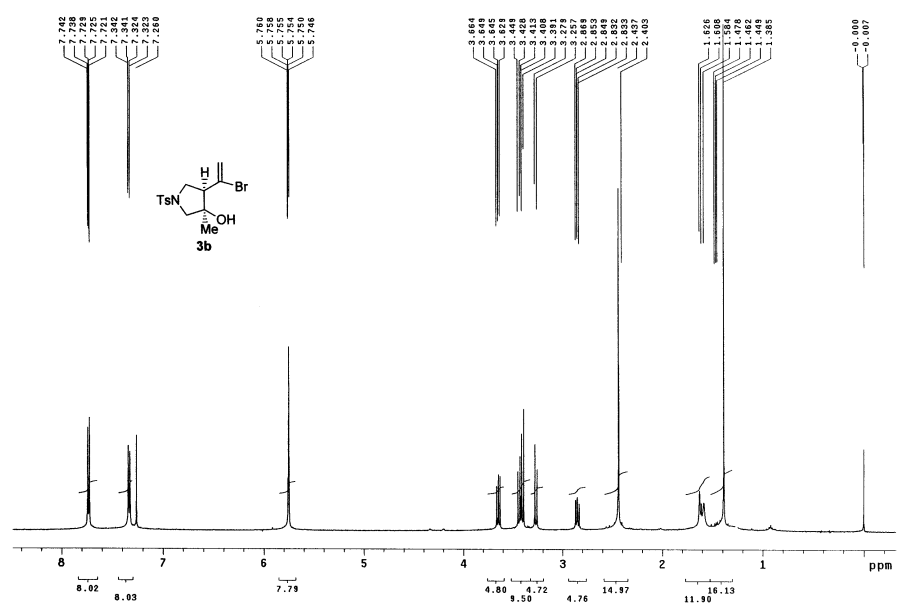
The <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) shows the following chemical shifts (ppm) and integration values:

- Chemical shifts (ppm): 7.132, 6.132, 5.669, 4.935, 4.925, 4.218, 4.205, 4.204, 4.200, 4.194, 4.180, 4.182, 4.171, 4.160, 4.158, 4.150, 4.148, 4.146, 4.144, 4.142, 4.140, 4.138, 4.136, 4.134, 4.132, 4.130, 4.128, 4.126, 4.124, 4.122, 4.120, 4.118, 4.116, 4.114, 4.112, 4.110, 4.108, 4.106, 4.104, 4.102, 4.100, 4.098, 4.096, 4.094, 4.092, 4.090, 4.088, 4.086, 4.084, 4.082, 4.080, 4.078, 4.076, 4.074, 4.072, 4.070, 4.068, 4.066, 4.064, 4.062, 4.060, 4.058, 4.056, 4.054, 4.052, 4.050, 4.048, 4.046, 4.044, 4.042, 4.040, 4.038, 4.036, 4.034, 4.032, 4.030, 4.028, 4.026, 4.024, 4.022, 4.020, 4.018, 4.016, 4.014, 4.012, 4.010, 4.008, 4.006, 4.004, 4.002, 4.000, 3.998, 3.996, 3.994, 3.992, 3.990, 3.988, 3.986, 3.984, 3.982, 3.980, 3.978, 3.976, 3.974, 3.972, 3.970, 3.968, 3.966, 3.964, 3.962, 3.960, 3.958, 3.956, 3.954, 3.952, 3.950, 3.948, 3.946, 3.944, 3.942, 3.940, 3.938, 3.936, 3.934, 3.932, 3.930, 3.928, 3.926, 3.924, 3.922, 3.920, 3.918, 3.916, 3.914, 3.912, 3.910, 3.908, 3.906, 3.904, 3.902, 3.900, 3.898, 3.896, 3.894, 3.892, 3.890, 3.888, 3.886, 3.884, 3.882, 3.880, 3.878, 3.876, 3.874, 3.872, 3.870, 3.868, 3.866, 3.864, 3.862, 3.860, 3.858, 3.856, 3.854, 3.852, 3.850, 3.848, 3.846, 3.844, 3.842, 3.840, 3.838, 3.836, 3.834, 3.832, 3.830, 3.828, 3.826, 3.824, 3.822, 3.820, 3.818, 3.816, 3.814, 3.812, 3.810, 3.808, 3.806, 3.804, 3.802, 3.800, 3.798, 3.796, 3.794, 3.792, 3.790, 3.788, 3.786, 3.784, 3.782, 3.780, 3.778, 3.776, 3.774, 3.772, 3.770, 3.768, 3.766, 3.764, 3.762, 3.760, 3.758, 3.756, 3.754, 3.752, 3.750, 3.748, 3.746, 3.744, 3.742, 3.740, 3.738, 3.736, 3.734, 3.732, 3.730, 3.728, 3.726, 3.724, 3.722, 3.720, 3.718, 3.716, 3.714, 3.712, 3.710, 3.708, 3.706, 3.704, 3.702, 3.700, 3.698, 3.696, 3.694, 3.692, 3.690, 3.688, 3.686, 3.684, 3.682, 3.680, 3.678, 3.676, 3.674, 3.672, 3.670, 3.668, 3.666, 3.664, 3.662, 3.660, 3.658, 3.656, 3.654, 3.652, 3.650, 3.648, 3.646, 3.644, 3.642, 3.640, 3.638, 3.636, 3.634, 3.632, 3.630, 3.628, 3.626, 3.624, 3.622, 3.620, 3.618, 3.616, 3.614, 3.612, 3.610, 3.608, 3.606, 3.604, 3.602, 3.600, 3.598, 3.596, 3.594, 3.592, 3.590, 3.588, 3.586, 3.584, 3.582, 3.580, 3.578, 3.576, 3.574, 3.572, 3.570, 3.568, 3.566, 3.564, 3.562, 3.560, 3.558, 3.556, 3.554, 3.552, 3.550, 3.548, 3.546, 3.544, 3.542, 3.540, 3.538, 3.536, 3.534, 3.532, 3.530, 3.528, 3.526, 3.524, 3.522, 3.520, 3.518, 3.516, 3.514, 3.512, 3.510, 3.508, 3.506, 3.504, 3.502, 3.500, 3.498, 3.496, 3.494, 3.492, 3.490, 3.488, 3.486, 3.484, 3.482, 3.480, 3.478, 3.476, 3.474, 3.472, 3.470, 3.468, 3.466, 3.464, 3.462, 3.460, 3.458, 3.456, 3.454, 3.452, 3.450, 3.448, 3.446, 3.444, 3.442, 3.440, 3.438, 3.436, 3.434, 3.432, 3.430, 3.428, 3.426, 3.424, 3.422, 3.420, 3.418, 3.416, 3.414, 3.412, 3.410, 3.408, 3.406, 3.404, 3.402, 3.400, 3.398, 3.396, 3.394, 3.392, 3.390, 3.388, 3.386, 3.384, 3.382, 3.380, 3.378, 3.376, 3.374, 3.372, 3.370, 3.368, 3.366, 3.364, 3.362, 3.360, 3.358, 3.356, 3.354, 3.352, 3.350, 3.348, 3.346, 3.344, 3.342, 3.340, 3.338, 3.336, 3.334, 3.332, 3.330, 3.328, 3.326, 3.324, 3.322, 3.320, 3.318, 3.316, 3.314, 3.312, 3.310, 3.308, 3.306, 3.304, 3.302, 3.300, 3.298, 3.296, 3.294, 3.292, 3.290, 3.288, 3.286, 3.284, 3.282, 3.280, 3.278, 3.276, 3.274, 3.272, 3.270, 3.268, 3.266, 3.264, 3.262, 3.260, 3.258, 3.256, 3.254, 3.252, 3.250, 3.248, 3.246, 3.244, 3.242, 3.240, 3.238, 3.236, 3.234, 3.232, 3.230, 3.228, 3.226, 3.224, 3.222, 3.220, 3.218, 3.216, 3.214, 3.212, 3.210, 3.208, 3.206, 3.204, 3.202, 3.200, 3.198, 3.196, 3.194, 3.192, 3.190, 3.188, 3.186, 3.184, 3.182, 3.180, 3.178, 3.176, 3.174, 3.172, 3.170, 3.168, 3.166, 3.164, 3.162, 3.160, 3.158, 3.156, 3.154, 3.152, 3.150, 3.148, 3.146, 3.144, 3.142, 3.140, 3.138, 3.136, 3.134, 3.132, 3.130, 3.128, 3.126, 3.124, 3.122, 3.120, 3.118, 3.116, 3.114, 3.112, 3.110, 3.108, 3.106, 3.104, 3.102, 3.100, 3.098, 3.096, 3.094,

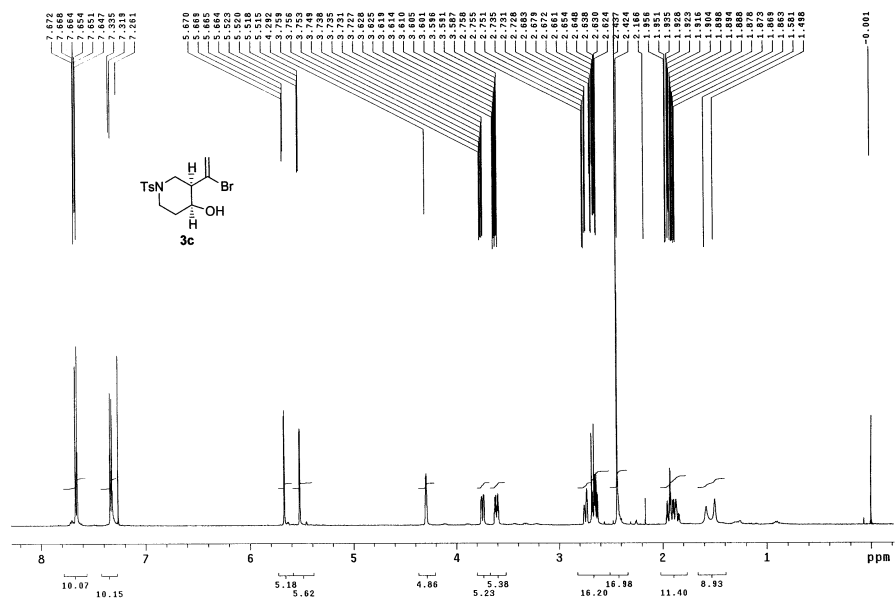
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Pulse Sequence: s2pu1



KWY-047A  
Pulse Sequence: s2pu1



KWY-045  
Pulse Sequence: s2pu1



KWY-029  
Pulse Sequence: s2pu1

