Supporting Information

Synthesis of 7,6-Spirocyclic Imine with Butenolide Ring Provides Evidence for the Relative Configuration of Marine Toxin 13-desMe Spirolide C

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**General Procedures**

All reactions sensitive to air or moisture were performed under argon atmosphere with dry glassware unless otherwise noted in particular. The dehydrated solvents, dichloromethane (DCM), tetrahydrofuran (THF), toluene, N,N-dimethylformamide (DMF) were purchased from Kanto Chemical Co. Inc. or Wako Pure Chemical Industries Ltd. and were used without further dehydration. All other chemicals were purchased from local vendors, and used as supplied unless otherwise stated. Thin-layer chromatography (TLC) of E. Merck silica gel 60 F254 pre-coated plates (0.25-mm thickness) was used for the reaction analyses. For column chromatography, Kanto silica gel 60N (spherical, 100-210 μm or 40-50 μm) was used. Optical rotations were recorded on a JASCO P-1010 polarimeter. IR spectra were recorded on a JASCO FT-IR-300E Fourier transform infrared spectrometer. ¹H- and ¹³C-NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer, a JEOL JNM-ECA500 spectrometer and a Bruker AVANCE 700. Chemical shifts are reported in ppm from tetramethylsilane (TMS) with reference to internal residual solvent [¹H NMR, CHCl₃ (7.24), CD₂HOD (3.30), C₆D₆ (7.16); ¹³C NMR, CDCl₃ (77.16), CD₂OD (49.00), C₆D₆ (128.06)] The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, brd = broad doublet. High resolution mass spectra (HRMS) were recorded on a Thermo Scientific LTQ-Orbitrap XL mass spectrometer.
Experimental Procedures

Desired-\textit{exo} (7\textit{R},29\textit{R}) vinyl silatrane derivative 7\textsuperscript{[1]}

To a solution of the $\alpha$-methylene-$\varepsilon$-lactam 6 (398 mg, 1.39 mmol) and silatrane dienyne 5 (464 mg, 1.66 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (8.7 mL, 0.15 M) was added $\text{Mg(OTf)}_2$ (224 mg, 0.69 mmol). After being stirred at 110 °C for 24 h, the mixture was concentrated under reduced pressure. Purification by flash silica gel column chromatography (hexane/EtOAc = 2/1 to 1/4) afforded the desired-\textit{exo} DA adduct 7 (623 mg, 1.10 mmol, 79\%) as a slightly yellow solid, which is same as previously reported compound.

$R_f = 0.51$ (silica gel, EtOAc); $[\alpha]_D^{16} +40.8$ (c 0.07, CHCl$_3$); $^1$H NMR (C$_6$D$_6$, 500MHz): $\delta$ 7.44 (2H, d, $J = 7.5$ Hz), 7.11 (2H, t, $J = 7.5$ Hz), 7.05 (1H, t, $J = 7.5$ Hz), 5.24 1H, d, $J = 13.0$ Hz), 5.20 (1H, d, $J = 13.0$ Hz), 4.26 (1H, brs), 3.86 (2H, d, $J = 3.5$, 15.0 Hz ), 3.54 (1H, dd, $J = 3.0$, 15.0 Hz ), 3.35 (6H, t, $J = 5.5$ Hz ), 2.79 (1H, d, $J = 18.5$ Hz), 2.69 (1H, d, $J = 18.5$ Hz), 2.53 (3H, s), 2.04 (1H, d, $J = 14.5$ Hz), 1.92 (6H, t, $J = 5.5$ Hz), 1.87 (1H, m), 1.75 (2H, m),1.48 (3H, d, $J = 2.5$ Hz), 1.29 (1H, dd, $J = 11.0$, 14.5 Hz), 0.94 (3H, d, $J = 6.5$ Hz), 0.89 (1H, m), 0.81 (3H, d, $J = 6.5$ Hz); $^{13}$C NMR (C$_6$D$_6$, 125 MHz): $\delta$ 176.9, 156.8, 139.2, 137.0, 131.0, 128.5, 127.9, 127.3, 80.6, 77.4, 68.2, 58.7, 51.5, 51.4, 49.2, 43.3, 40.2, 36.2, 32.0, 30.2, 27.8, 23.8, 20.8, 17.9, 3.5; IR (neat) 2960, 2917, 2871, 1706, 1455, 1375, 1268, 1201, 1124, 1101, 771, 605, 590, 464, 455, 447, 418, 408 cm$^{-1}$; HRMS (ESIMS): m/z calcd for C$_{31}$H$_{42}$N$_2$O$_6$SiNa [M+Na]$^+$ 589.2710, found 589.2703.

5-silatrane $N$-Ts Lactam 4
To a solution of N-Cbz lactam 7 (0.116 g, 0.200 mmol) in EtOAc (8.0 mL) was added 4% Pd/C (en) (109 mg, 0.041 mmol) and injected H₂ gas. After being stirred at room temperature for 18 h, the reaction mixture was filtrated thorough Celite with EtOAc and concentrated under reduced pressure. The residue was used in the next step without further purification. To a solution of crude lactam 7A in DCM (4.0 mL) was added 1.5 M LDA (1.3 mL, 2.0 mmol) at 0 ºC slowly. After being stirred at 0 ºC for 20 min., TsCl (57 mg, 0.30 mmol) was added at 0 ºC. The resulting mixture was stirred under room temperature for 19 h. After cooling to room temperature, the reaction mixture was quenched with saturated NaHCO₃ solution and was stirred at room temperature for 15 min. The aqueous layer was extracted with DCM, and the organic layer was washed by brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by flash silica gel column chromatography (hexane/EtOAc = 1/1 to 0/1) afforded the N-Ts lactam 7 (90.6 mg, 0.154 mmol, 77%) as an orange solid.

Rₜ = 0.48 (silica gel, EtOAc); [α]D₉ +86.5 (c 0.12, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 7.81 (2H, d, J = 8.0 Hz), 7.22 (2H, d, J = 8.0 Hz), 5.47 (1H, dq, J = 6.5, 10.0 Hz), 5.01 (1H, t, J = 10.0 Hz), 4.22 (1H, d, J = 15.5 Hz), 3.83 (2H, m), 3.72 (6H, t, J = 5.5 Hz), 2.76 (6H, m), 2.38 (3H, s), 2.16 (2H, br), 1.67 (1H, m), 1.65 (3H, s), 1.62 (1H, m), 1.53 (3H, dd, J = 0.5, 6.5 Hz), 1.36-1.28 (4H, m), 1.09 (3H, d, J = 5.5 Hz), 0.92 (3H, d, J = 6.0 Hz); ¹³C NMR (CDCl₃, 125 MHz): δ 176.2, 143.6, 141.8, 137.3, 129.7, 129.6, 128.9, 128.7, 127.5, 58.8, 51.7, 50.7, 48.2, 45.7, 40.5, 36.8, 35.3, 32.8, 26.7, 22.6, 21.7, 21.2, 20.6, 17.7, 13.6; IR (neat) 2962, 2927, 1685, 1457, 1345, 1214, 1184, 1165, 1078, 1057, 1034, 811, 763, 730, 706, 660, 579, 545 cm⁻¹; HRMS (ESIMS): m/z calcd for C₃₀H₄₄N₂O₆SNa [M+Na]⁺ 611.2587, found 611.2589.

5-Iodide N-Ts lactam 8:

To a solution of 5-silatrane N-Ts lactam 4 (0.158 g, 0.269 mmol) in dry THF (5.4 mL) was added N-iodosuccinimide (91 mg, 0.40 mmol) and stirred at room temperature for 30 min. The reaction mixture was quenched with aqueous sodium thiosulfate at room temperature and extracted with DCM three times.
The organic layer was washed by brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by open silica gel column chromatography (hexane/EtOAc = hexane to 3/1) afforded the vinyl iodide 8 (0.145 g, 0.268 mmol, quant.) as a light yellow solid.

Rₚ = 0.57 (silica gel, hexane/EtOAc = 3/1); [α]₀ evolved +174.6 (c 0.17, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 7.82 (2H, d, J = 8.5 Hz), 7.28 (2H, d, J = 8.5 Hz), 5.62 (1H, dq, J = 7.0, 11.0 Hz), 5.03 (1H, td, J = 1.5, 10.5 Hz), 4.13 (1H, dd, J = 3.5, 16.0 Hz), 4.00 (1H, dd, J = 3.5, 16.0 Hz), 3.69 (1H, d, J = 11.0 Hz), 2.42 (3H, s), 2.40 (1H, m), 2.03 (1H, m), 1.74 (3H, t, J = 2.0 Hz), 1.68 (1H, m), 1.65 (1H, m), 1.64 (3H, dd, J = 1.5, 7.0 Hz), 1.33 (2H, m), 1.26 (1H, m), 1.23 (1H, m), 1.12 (3H, d, J = 7.0 Hz), 0.92 (3H, d, J = 6.5 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 175.1, 144.5, 138.8, 136.2, 129.3, 129.0, 128.4, 127.9, 95.2, 50.5, 49.0, 45.6, 40.5, 40.3, 38.7, 35.4, 32.6, 28.3, 21.9, 21.3, 18.0, 13.6; IR (neat) 2961, 2926, 2875, 1686, 1344, 1166, 1080, 1060, 754, 661, 580, 545 cm⁻¹; HRMS (ESIMS): m/z calcd for C₂₄H₃₂I₃NO₃SNa [M+Na]⁺ 564.1045, found 564.1039.

5-vinyl N-Ts lactam 3:

To a solution of vinyl iodide 8 (0.145 g, 0.268 mmol) in DMF (13.5 mL, Freeze-Pump-Thaw) was added LiCl (0.114 g, 2.70 mmol), Pd(PPh₃)₄ (0.062 g, 0.054 mmol) and tributylvinyltin (139 μL, 0.480 mmol). After being stirred at 80 °C for 1 h, the reaction mixture was quenched by water and extracted with Et₂O. The organic layer was washed by brine and dried with anhydrous Na₂SO₄, filtrated and concentrated under reduced pressure. Purification by flash silica gel column chromatography (hexane/EtOAc = 10/1) afforded the 5-vinyl product 3 (0.115 g, 0.261 mmol, 97%) as a white solid.

Rₚ = 0.26 (hexane/EtOAc = 10/1); [α]₀ evolved +97.8 (c 0.23, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 7.81 (2H, d, J = 8.0 Hz), 7.22 (2H, d, J = 8.5 Hz), 6.59 (1H, dd, J = 11.0, 17.5 Hz), 5.60 (1H, dq, J = 7.0, 10.5 Hz), 5.01 (1H, td, J = 1.5, 11.0 Hz), 4.85 (1H, d, J = 11.0 Hz), 4.81 (1H, d, J = 17.5 Hz) 4.16 (1H, dd, J = 3.0, 15.5...
Hz), 4.03 (1H, dd, J = 2.5, 15.5 Hz), 3.61 (1H, d, J = 11.0 Hz), 2.39 (1H, m), 2.37 (3H, s), 2.00 (1H, m), 1.72 (1H, m), 1.71 (3H, s), 1.65 (2H, m), 1.64 (3H, d, J = 1.5, 7.0 Hz), 1.32-1.27 (3H, m), 1.11 (3H, d, J = 6.5 Hz), 0.91 (3H, d, J = 6.0 Hz); 13C NMR (CDCl3, 125 MHz) δ 175.6, 144.1, 136.6, 134.8, 134.2, 129.3, 129.0, 128.9, 127.5, 126.3, 110.6, 50.3, 49.0, 45.3, 40.5, 40.1, 35.4, 30.2, 22.4, 21.7, 21.2, 18.0, 17.7, 13.7; IR (neat) 2957, 2925, 1687, 1344, 1185, 1166, 1077, 1068, 707, 660, 583, 544 cm⁻¹; HRMS (ESIMS): m/z calcd for C26H35NO3SNa [M+Na]+ 464.2235, found 464.2229.

Aldehyde 9

To a solution of 5-vinyl lactam 3 (25.0 mg, 0.057 mmol) in THF (1.4 mL) and water (1.4 mL) was added 4% OsO₄ (10 μL, 0.0017 mmol) and NaIO₄ (24.0 mg, 0.110 mol) at 0 °C. After being stirred at 0 °C for 2 h, the reaction mixture was quenched by aqueous sodium thiosulfate. The aqueous layer was extracted with EtOAc, and the organic layer was washed by aqueous sodium thiosulfate and brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by open silica gel column chromatography (hexane/EtOAc = 2/1) afforded the aldehyde 9 (17.7 mg, 0.040 mmol, 70%) as a white solid.

Rf = 0.43 (hexane/EtOAc = 2/1); [α]D²⁷ +148.7 (c 0.06, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 9.85 (1H, s), 7.78 (2H, d, J = 8.0 Hz), 7.21 (2H, d, J = 8.0 Hz), 5.74 (1H, dq, J = 7.0, 10.5 Hz), 5.00 (1H, td, J = 1.5, 11.0 Hz), 4.23 (1H, dd, J = 2.0, 16.0 Hz), 3.95 (1H, dd, J = 3.0, 15.5 Hz), 3.57 (1H, d, J = 11.0 Hz), 2.39 (3H, s), 2.06 (1H, m), 2.03 (3H, s), 2.01 (1H, m), 1.75-1.64 (3H, m), 1.68 (3H, dd, J = 1.5, 7.0 Hz), 1.33 (1H, m), 1.24 (2H, m), 1.13 (3H, d, J = 7.0 Hz), 0.93 (3H, d, J = 6.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 190.4, 175.1, 157.8, 144.9, 135.9, 130.2, 129.9, 129.0, 127.6, 50.6, 48.5, 47.5, 40.5, 40.0, 35.2, 28.5, 21.7, 21.3, 20.1, 17.7, 17.0, 14.3, 13.7; IR (neat) 2960, 2926, 1684, 1664, 1346, 1167, 1080, 661, 581, 544 cm⁻¹; HRMS (ESIMS): m/z calcd for C26H33NO3SNa [M+Na]+ 466.2028, found 466.2037.
To a solution of aldehyde 9 (50.4 mg, 0.114 mmol) in THF (5.5 mL) was added vinyl Grignard reagent (1.0 M, 0.45 mL, 0.45 mmol) at -78 °C. After being stirred at -78 °C for 1 h, the reaction mixture was quenched by saturated aqueous NH₄Cl at 0 °C. The resulting mixture was extracted with Et₂O. The organic layer was washed by brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Without purification, to this crude solution in DMF (2.2 mL) was added imidazole (111.9 mg, 1.644 mmol) and TBSCI (82.8 mg, 0.549 mmol) at 0 °C. After being stirred at room temperature for 24 h., the reaction mixture was quenched by saturated aqueous NH₄Cl, and the resulting mixture was extracted with EtOAc. The organic layer was washed by brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by open silica gel column chromatography (hexane/EtOAc = 6/1) afforded the silyl ethers 10 (62.6 mg, 0.107 mmol, 94% over 2 steps) as a colorless oil as a mixture of two diastereomers (epimeric at C5 position, dr = 1:1.1).

Rf = 0.76 (hexane/EtOAc = 2/1); IR (neat) 2954, 2927, 2856, 1686, 1349, 1251, 1167, 1081, 1063, 1031, 854, 836, 774, 660, 582 cm⁻¹; HRMS (ESIMS): m/z calcd for C₃₅H₆₀NO₄SiNa [M+Na]⁺ 608.3206, found 608.3197.

**Allyl alcohols 2**

(1) NEt₃, TFAA  
DCM, rt., 30 min.

(2) SmI₂, THF  
-78 °C, 1 h

(3) TBAF, THF  
rt., 20 h, 68% (4 steps)

2a (39%)  
2b (29%)
To a solution of N-Ts lactam 10 (0.197 g, 0.337 mmol) in THF (11.3 mL) was added methyl lithium solution (1.2 M, 5.6 mL, 6.8 mmol) at -78 °C. After being stirred at -78 °C for 5 min., the reaction mixture was warmed to room temperature. After being stirred at room temperature for 1 h, the reaction mixture was quenched by saturated aqueous NH₄Cl at 0 °C and extracted with Et₂O. The organic layer was washed by brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Without further purification, to a solution of the N-Ts amine 10A at 0 ºC was added NEt₃ (236 μL, 1.70 mmol) and TFAA (240 μL, 1.70 mmol) [2]. After stirring at room temperature for 30 min., the reaction mixture was concentrated under reduced pressure. To a solution of intermediate in THF (1.7 mL) was added SmI₂ (0.1 M in THF, 16.6 mL, 1.66 mmol) at -78 °C. After stirring at -78 °C for 1 h, the reaction mixture was filtrated through open silica gel with EtOAc and concentrated under reduced pressure. Without further purification, the trifluoracetamide and TBAF (1.0 M, 4.1 mL, 4.1 mmol) in dry THF (11.3 mL) was stirred at room temperature for 12 h, and the reaction mixture was quenched by saturated aqueous NH₄Cl at 0 °C, and the resulting mixture was extracted with Et₂O. The organic layer was washed by brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by open silica gel column chromatography with a very small amount of NEt₃ (hexane to hexane/EtOAc = 3/1 to 2/1 to 1/1) afforded the allyl alcohol 2a (56.9 mg, 0.133 mmol, 39%) as a slightly yellow oil and the allyl alcohol 2b (42.4 mg, 0.0988 mmol, 29%) as a slightly yellow oil, respectively.

**2a:** R_f = 0.23 (hexane/EtOAc = 2/1); [α]_D²⁷ +106.6 (c 0.05, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 6.56 (1H, br), 5.73 (1H, ddd, J = 3.0, 10.5, 17.5 Hz), 5.62 (1H, dq, J = 6.5, 11.0 Hz), 5.16 (1H, dt, J = 2.0, 17.0 Hz), 5.14 (1H, tq, J = 1.5, 11.0 Hz), 5.08 (1H, dt, J = 2.0, 10.5 Hz), 5.05 (1H, m), 3.52 (1H, d, J = 11.0 Hz), 3.26 (1H, m), 3.01 (1H, dt, J = 5.0, 13.5 Hz), 2.59 (1H, br), 2.24 (1H, dd, J = 8.0, 18.5 Hz), 2.12 (3H, s), 2.02 (1H, m), 1.90 (1H, m), 1.74 (3H, dd, J = 1.5, 6.5 Hz), 1.65 (3H, t, J = 2.0 Hz), 1.50 (2H, m), 1.33 (2H, m), 1.25 (1H, m), 0.77 (3H, d, J = 7.0 Hz), 0.67 (3H, d, J = 7.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 213.9, 138.5, 132.1, 130.2, 129.2, 126.4, 114.3, 71.3, 54.2, 44.3, 42.3, 41.7, 35.8, 28.0, 26.9, 26.0, 20.8, 17.9, 15.3, 14.0, 13.7, 11.9; IR (neat) 3329, 2965, 2934, 1711, 1560, 1459, 1388, 1365, 1358, 1209, 1185, 1161, 1028, 995, 927, 747, 727, 707, 472, 457 cm⁻¹; HRMS (ESIMS): m/z calcd for C₂₂H₃₄F₃NO₃Na [M+Na]⁺ 452.2388, found 452.2386.

**2b:** R_f = 0.11 (hexane/EtOAc = 2/1); [α]_D²⁷ +81.0 (c 0.05, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 6.70 (1H, br), 5.77 (1H, ddd, J = 4.5, 10.5, 17.0 Hz), 5.60 (1H, dq, J = 7.0, 11.0 Hz), 5.18 (1H, dt, J = 1.5, 17.0 Hz), 5.11 (1H, tq, J = 1.5, 11.0 Hz), 5.09-5.07 (2H, m), 3.54 (1H, d, J = 11.0 Hz), 3.26 (1H, m), 3.01 (1H,
dt, \( J = 5.0, 13.5 \text{ Hz} \), 2.85 (1H, br), 2.18 (3H, s), 2.14 (1H, m), 2.00 (2H, m), 1.74 (3H, dd, \( J = 2.0, 7.0 \text{ Hz} \)), 1.64 (3H, t, \( J = 1.5 \text{ Hz} \)), 1.53-1.36 (3H, m), 1.26 (1H, m), 0.77 (3H, d, \( J = 7.0 \text{ Hz} \)), 0.67 (3H, d, \( J = 7.0 \text{ Hz} \)); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \( \delta \) 214.2, 138.5, 129.5, 126.3, 114.1, 71.4, 54.4, 44.3, 42.2, 41.8, 35.7, 27.8, 26.9, 26.1, 20.8, 17.8, 15.3, 13.7, 11.8; IR (neat) 3342, 2971, 2936, 1711, 1699, 1365, 1217, 1206, 1159, 994, 925, 773, 669 cm\(^{-1}\); HRMS (ESIMS): m/z calcd for C\(_{23}\)H\(_{34}\)F\(_3\)NO\(_3\)Na [M+Na]\(^{+}\) 452.2388, found 452.2386.

### Allyl esters 11

To a solution of the allyl alcohol 2a (6.6 mg, 0.015 mmol) in DCM (0.50 mL) at 0 °C was added NEt\(_3\) (41.5 μL, 0.299 mmol) and methacryloyl chloride (9.5 μL, 0.10 mmol). After stirring at 0 °C for 2 h, the reaction mixture was warmed to room temperature and stirred for 1 h. Then additional NEt\(_3\) (41.5 μL, 0.299 mmol) and methacryloyl chloride (9.5 μL, 0.10 mmol) were added at 0 °C. After being stirred at room temperature for 1 h., the reaction mixture was quenched by saturated aqueous NH\(_4\)Cl at 0 °C, and the resulting mixture was extracted with DCM. The organic layer was washed by brine, dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. Purification by open silica gel column chromatography with a very small amount of NEt\(_3\) (hexane to hexane/EtOAc = 3/1) afforded the allyl ester 11a (6.5 mg, 0.013 mmol, 87%) as a colorless oil.

**11a:** \( R_f = 0.52 \) (hexane/EtOAc = 2/1); \([\alpha]_D^{27} +105.0 \) (c 0.12, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \( \delta \) 6.52 (1H, br), 6.10 (1H, s), 6.09 (1H, m), 5.67 (1H, ddd, \( J = 4.5, 10.5, 17.0 \text{ Hz} \)), 5.63 (1H, dq, \( J = 7.0, 11.0 \text{ Hz} \)), 5.55 (1H, 5, \( J = 1.5 \text{ Hz} \)), 5.13-5.08 (2H, m), 5.07 (1H, dt, \( J = 1.5, 12.5 \text{ Hz} \)), 3.52 (1H, d, \( J = 11.0 \text{ Hz} \)), 3.25 (1H, m), 3.02 (1H, dt, \( J = 5.5, 13.5 \text{ Hz} \)), 2.12 (3H, s), 2.08-1.98 (3H, m), 1.95 (3H, s), 1.74 (3H, dd, \( J = 1.5, 7.0 \text{ Hz} \)), 1.70 (3H, t, 2.0 Hz), 1.64 (1H, m), 1.51-1.42 (3H, m), 0.83 (1H, m), 0.77 (3H, d, \( J = 7.0 \text{ Hz} \)), 0.66 (3H, d, \( J = 7.0 \text{ Hz} \)); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \( \delta \) 213.7, 166.3, 136.7, 134.7, 133.8, 128.9, 127.1, 126.8,
125.6, 115.6, 73.9, 54.2, 44.3, 42.5, 41.7, 35.9, 29.9, 28.2, 26.6, 26.0, 21.7, 18.5, 18.3, 15.4, 13.7, 11.9; IR (neat) 3335, 2973, 2942, 2892, 1712, 1562, 1458, 1387, 1209, 1183, 1160, 934, 757, 727, 668 cm\(^{-1}\); HRMS (ESIMS): m/z calcd for C\(_{27}\)H\(_{38}\)F\(_3\)NO\(_4\)Na [M+Na]+ 520.2651, found 520.2647.

**11b:** In the same manner as that described above, the allyl ester 11b (4.9 mg, 0.010 mmol, 83%) was obtained from 5a (5.1 mg, 0.012 mmol); \(R_2 = 0.52\) (hexane/EtOAc = 2/1); \([\alpha]_D^{27} +84.0\) (c 0.05, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 6.52 (1H, br), 6.08 (1H, s), 6.04 (1H, m), 5.76 (1H, ddd, \(J = 5.0, 10.5, 17.0\) Hz), 5.64 (1H, dq, \(J = 7.0, 11.0\) Hz), 5.54 (1H, 5, \(J = 5.0\) Hz), 5.16 (1H, dt, \(J = 1.5, 18.5\) Hz), 5.14 (1H, dt, \(J = 1.5, 10.5\) Hz), 5.10 (1h, tq, \(J = 1.5, 11.0\) Hz), 3.48 (1H, d, \(J = 11.0\) Hz), 3.25 (1H, m), 3.04 (1H, dt, m), 2.12 (3H, s), 2.08-1.98 (3H, m), 1.93 (3H, s), 1.76 (3H, dd, \(J = 1.5, 7.0\) Hz), 1.71 (3H, s), 1.51-1.44 (4H, m), 0.84 (1H, m), 0.77 (3H, d, \(J = 7.0\) Hz), 0.67 (3H, d, \(J = 7.0\) Hz); \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 213.2, 166.2, 136.5, 134.8, 133.6, 129.3, 127.5, 126.7, 125.5, 115.7, 74.1, 54.2, 44.3, 43.4, 41.8, 36.3, 29.7, 28.4, 26.2, 26.1, 21.8, 18.5, 18.3, 15.5, 13.8, 12.0; IR (neat) 3324, 2966, 2933, 1714, 1220, 1183, 1158, 935, 781 cm\(^{-1}\); HRMS (ESIMS): m/z calcd for C\(_{27}\)H\(_{38}\)F\(_3\)NO\(_4\)Na [M+Na]+ 520.2651, found 520.2649.

**Butenolides 12**

![Butenolides 12](image)

To a solution of the allylic ester 11a (6.5 mg, 0.013 mmol) in CICH\(_2\)CH\(_2\)Cl (440 \(\mu\)L) was added Grubbs 1\(^{\text{st}}\) catalyst (2.1 mg, 0.0026 mmol) at room temperature. After stirring at 90 °C for 2 h, additional Grubbs 1\(^{\text{st}}\) catalyst (2.1 mg, 0.0026 mmol) were added. Moreover, after being stirred at 90 °C for 2.5 h., additional Grubbs 1\(^{\text{st}}\) catalyst (2.1 mg, 0.0026 mmol) were added again. After being stirred at 90 °C for 1.5 h, the reaction mixture was evaporated under reduced pressure. Purification by open silica gel column chromatography (hexane to hexane/EtOAc = 4/1 to 2/1) afforded 12a (2.6 mg, 0.0056 mmol, 43%) as a colorless oil.
**12a:** $R_f = 0.12$ (hexane/EtOAc = 2/1); $\left[\alpha\right]_D^{27} = +106.0$ (c 0.05, CHCl$_3$); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 6.77 (1H, 5, $J = 1.5$ Hz), 6.43 (1H, br), 5.73 (1H, t, $J = 1.5$ Hz), 5.68 (1H, dq, $J = 7.0$, 11.0 Hz), 5.12 (1H, tq, $J = 1.5$, 11.0 Hz), 3.57 (1H, d, $J = 11.0$ Hz), 3.26 (1H, m), 3.02 (1H, dt, $J = 5.0$, 13.5 Hz), 2.13 (3H, s), 1.94 (1H, m), 1.91 (3H, t, $J = 2.0$ Hz), 1.76 (3H, s), 1.75 (3H, dd, $J = 2.0$, 7.0 Hz), 1.67 (2H, m), 1.56 (1H, m), 1.48-1.41 (2H, m), 0.87-0.83 (2H, m), 0.78 (3H, d, $J = 7.0$ Hz); $^13$C NMR (CDCl$_3$, 125 MHz) $\delta$ 213.6, 174.7, 157.4, 147.7, 136.7, 130.6, 128.5, 123.8, 79.7, 54.3, 44.3, 42.4, 35.9, 29.9, 28.1, 26.5, 25.9, 20.7, 18.0, 15.2, 13.8, 11.8, 10.8; IR (neat) 3341, 2966, 2933, 2860, 1759, 1715, 1560, 1459, 1366, 1212, 1179, 1163, 1107, 1044, 955, 727, 421 cm$^{-1}$; HRMS (ESIMS): m/z calcd for C$_{25}$H$_{34}$F$_3$NO$_4$Na [M+Na]$^+$ 492.2338, found 492.2340.

**12b:** In the same manner as that described above, the butenolide 12b (3.6 mg, 0.0077 mmol, 77%) was obtained from 11b (4.9 mg, 0.0099 mmol); $R_f = 0.24$ (hexane/EtOAc = 2/1); $\left[\alpha\right]_D^{27} = +82.8$ (c 0.05, CHCl$_3$); $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 6.79 (1H, 5, $J = 1.5$ Hz), 6.55 (1H, br), 5.72 (1H, t, $J = 1.5$ Hz), 5.64 (1H, dq, $J = 7.0$, 11.0 Hz), 5.05 (1H, tq, $J = 1.5$, 11.0 Hz), 3.64 (1H, d, $J = 11.0$ Hz), 3.28 (1H, m), 2.98 (1H, dt, $J = 5.0$, 13.5 Hz), 2.17 (3H, s), 1.96 (1H, m), 1.91 (3H, t, $J = 2.0$ Hz), 1.75 (3H, dd, $J = 2.0$, 7.0 Hz), 1.73 (3H, s), 1.60 (2H, m), 1.52 (1H, m), 1.48-1.36 (2H, m), 0.88-0.78 (2H, m), 0.77 (3H, d, $J = 7.0$ Hz), 0.66 (3H, d, $J = 7.0$ Hz); $^13$C NMR (CDCl$_3$, 125 MHz) $\delta$ 213.7, 174.5, 157.5, 147.4, 135.5, 130.1, 129.0, 126.9, 123.6, 80.0, 54.2, 44.3, 41.9, 41.7, 35.5, 27.9, 27.6, 26.9, 26.1, 20.2, 18.0, 15.2, 13.7, 11.8, 10.7; IR (neat) 3340, 2966, 2946, 2860, 1746, 1723, 1440, 1366, 1230, 1177, 955, 722, 410 cm$^{-1}$; HRMS (ESIMS): m/z calcd for C$_{25}$H$_{34}$F$_3$NO$_4$Na [M+Na]$^+$ 492.2338, found 492.2342.

**N-Boc amines 13**

To a solution of the trifluoroacetamide 12a (6.0 mg, 0.013 mmol) in DCM (1.6 mL) was added NEt$_3$ (32 μL, 0.23 mmol), DMAP (1.9 mg, 0.016 mmol) and (Boc)$_2$O (19.9 mg, 0.0911 mmol) at 0 °C$^{[3]}$. After stirring at room temperature for 1.5 h, hydrazine hydrate (18 μL, 0.59 mmol) was added at room
After being stirred at room temperature for 20 min., the cloudy reaction mixture was quenched by saturated aqueous NH₄Cl at 0 °C, and the resulting mixture was extracted with DCM. The organic layer was washed by brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure. Purification by open silica gel column chromatography (hexane/EtOAc = 2/1) afforded the N-Boc amine 13a (4.4 mg, 0.0093 mmol, 72%) as a colorless oil.

13a: Rf = 0.46 (hexane/EtOAc = 1/1); [α]D²⁷ +94.2 (c 0.055, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 6.76 (1H, 5, J = 1.5 Hz), 6.72 (1H, br), 5.67 (1H, dq, J = 7.0, 11.0 Hz), 5.12 (1H, tq, J = 1.5, 11.0 Hz), 4.46 (1H, br), 3.47 (1H, d, J = 11.0 Hz), 2.92 (2H, m), 2.10 (3H, s), 1.97 (1H, m), 1.91 (3H, t, J = 1.5 Hz), 1.88 (1H, m), 1.79 (3H, dd, J = 2.0, 7.0 Hz), 1.77 (3H, s), 1.55 (2H, m), 1.44 (9H, s), 1.29-1.22 (2H, m), 0.89-0.80 (2H, m), 0.73 (3H, d, J = 7.0 Hz), 0.64 (3H, d, J = 7.0 Hz); ¹³C NMR (CDCl₃, 125 MHz) δ 221.6, 168.5, 156.2, 147.8, 136.5, 130.4, 128.9, 127.0, 124.1, 79.7, 54.1, 43.3, 42.1, 37.7, 29.9, 28.6, 25.6, 22.9, 20.7, 18.1, 15.4, 14.3, 14.1, 12.0, 10.8; IR (neat) 3395, 2970, 2935, 2850, 1754, 1707, 1524, 1458, 1392, 1368, 1279, 1254, 1176, 1099, 1045, 957, 868, 786, 700, 413 cm⁻¹; HRMS (ESIMS): m/z calcd for C₂₈H₄₃NO₅Na [M+Na]⁺ 496.3039, found 496.3038.

13b: In the same manner as that described above, the N-Boc amine 13b (10.0 mg, 0.0211 mmol, 66%) was obtained from 12b (15.0 mg, 0.0320 mmol); Rf = 0.55 (hexane/EtOAc = 1/1); [α]D²⁷ +74.2 (c 0.055, CHCl₃); ¹H NMR (CDCl₃, 500 MHz): δ 6.79 (1H, 5, J = 1.5 Hz), 6.72 (1H, br), 5.63 (1H, dq, J = 7.0, 11.0 Hz), 5.06 (1H, tq, J = 1.5, 11.0 Hz), 4.49 (1H, br), 3.52 (1H, d, J = 10.5 Hz), 2.92 (2H, m), 2.13 (3H, s), 1.97 (1H, m), 1.92 (3H, t, J = 1.5 Hz), 1.87 (1H, m), 1.79 (3H, dd, J = 1.5, 7.0 Hz), 1.75 (3H, s), 1.50 (2H, m), 1.44 (9H, s), 1.36-1.29 (2H, m), 0.89-0.80 (2H, m), 0.72 (3H, d, J = 7.0 Hz), 0.64 (3H, d, J = 7.0 Hz) ¹³C NMR (CDCl₃, 125 MHz) δ 222.3, 174.9, 155.9, 147.35, 135.5, 12301, 1294, 126.6, 123.8, 80.1, 54.0, 45.0, 43.0, 42.2, 37.2, 28.6, 26.6, 25.8, 20.3, 18.0, 15.4, 14.1, 12.0, 10.8; IR (neat) 3388, 2982, 2928, 2853, 1755, 1701, 1536, 1279, 1260, 1045, 791, 755 cm⁻¹; HRMS (ESIMS): m/z calcd for C₂₈H₄₃NO₅Na [M+Na]⁺ 496.3039, found 496.3035.
Spirocyclic imines 1

To a solution of the Boc amine 13a (1.8 mg, 0.0038 mmol) in toluene (0.65 mL) was added TFA (1.5 μL, 0.019 mmol). After stirring at 40 °C for 1 h, additional TFA (3.0 μL, 0.038 mmol) was added at the same temperature. And then, after being stirred at 120 °C for 2.5 h., the solvent was evaporated and residue was dried under high vacuum to afforded 1a (1.3 mg, 0.0037 mmol, quant.) as a yellow solid.

1a: Rf = 0.55 (CHCl3/MeOH = 6/1); [α]D25 +129.6 (c 0.05, CHCl3); 1H NMR (CD3OD, 500 MHz): δ 7.14 (1H, t, J = 1.5 Hz), 5.97 (1H, br), 5.88 (1H, dq, J = 7.0, 11.0 Hz), 5.25 (1H, t, J = 11.0 Hz), 4.07 (1H, dd, J = 5.0, 13.5 Hz), 3.77 (1H, d, J = 10.5 Hz), 3.47 (1H, dd, J = 2.5, 13.5 Hz), 3.22 (3H, s), 2.20 (1H, m), 1.95 (1H, m), 1.91 (3H, t, J = 2.0 Hz), 1.85 (3H, dd, J = 1.5, 6.5 Hz), 1.79 (1H, m), 1.77 (3H, s), 1.75 (1H, m), 1.72 (1H, m), 1.57 (1H, br), 1.29 (1H, m), 1.08 (3H, d, J = 7.0 Hz), 1.03 (3H, d, J = 6.5 Hz); 13C NMR (CD3OD, 175 MHz) δ 202.4, 176.8, 149.5, 133.9, 131.2, 130.7, 128.0, 126.3, 82.0, 52.6, 50.4, 46.7, 45.3, 39.0, 38.2, 36.4, 31.0, 20.8, 20.3, 18.5, 17.1, 14.4, 10.5; IR (neat) 3019, 2966, 2933, 2857, 1756, 1680, 1464, 1384, 1192, 1190, 1136, 1110, 1042, 796, 755, 719, 663 cm⁻¹; HRMS (ESIMS): m/z calcd for C23H34NO2 [M+H]+ 356.2584, found 356.2588, m/z calcd for C23H33NO2Na [M+Na]+ 378.2409, found 378.2407.

1b: In the same manner as that described above, the spirocyclic imine 1b (0.8 mg, 0.002 mmol, quant.) was obtained from 13b (1.1 mg, 0.002 mmol); Rf = 0.55 (CHCl3/MeOH = 6/1); [α]D25 +90.4 (c 0.05, CHCl3); 1H NMR (CD3OD, 500 MHz): δ 7.15 (1H, br), 5.99 (1H, br), 5.86 (1H, dq, J = 7.0, 11.0 Hz), 5.25 (1H, t, J = 11.0 Hz), 4.03 (1H, dd, J = 4.0, 14.0 Hz), 3.80 (1H, d, J = 11.0 Hz), 3.54 (1H, dd, J = 3.5, 14.0 Hz), 3.22 (3H, s), 1.98-1.93 (2H, m), 1.92 (2H, m), 1.91 (3H, t, J = 2.0 Hz), 1.86 (3H, dd, J = 1.5, 6.5 Hz), 1.83 (3H, s), 1.75 (1H, m), 1.69 (1H, m), 1.59 (1H, m), 1.32 (1H, m), 1.08 (3H, d, J = 7.0 Hz), 1.01 (3H, d, J = 7.0 Hz); 13C NMR (CD3OD, 175 MHz) δ 202.5, 176.7, 150.1, 136.1, 131.4, 130.3, 128.1, 126.2, 81.3, 52.9, 50.1, 46.4, 45.3, 39.1, 38.9, 36.4, 30.8, 30.6, 21.0, 20.9, 18.4, 17.7, 14.3, 10.5; IR (neat) 2968, 2928, 2862, 1757, 1681, 1201, 1137, 1045, 756 cm⁻¹; HRMS (ESIMS): m/z calcd for C23H33NO2Na [M+Na]+ 378.2409, found 378.2409.
Design of 7,6-spirocyclic imine derivative

A computational study showed that the dimethylated 7-membered spirocyclic imine ring and the C7 olefin substituent are necessary to strictly reproduce the original environment around C4 position as shown in below. Conformational search was performed using MacroModel and the force field used in these calculation was OPLS3e. The MCMM method was used and a 50 kJ/mol cutoff was applied.

Lowest energy structure

<13-desMe-SPX C>

<1a: diMe, C7-olefin> ➔ Desired conformation

<1a': didesMe, C7-olefin> ➔ Undesired

<1a'': diMe, C7-acetylene> ➔ Undesired
Selective Diels-Alder Reaction

1. Investigation of solvent effect

In order to improve the face selectivity and the reactivity, we investigated the solvent effect (entry 3-7). As a result, 1,2-dichloroethane was found to dramatically improve the reactivity despite it didn’t affect the face selectivity (entry 7). This is considered to be due to the high solubility of 1,2-dichloroethane for 2-silatrane dienyne 5.

2. Chelating effect of Mg(OTf)₂

In order to obtain the experimental evidence of chelating effect by magnesium catalyst, we compared $^{13}$C NMR spectra of lactam 6 with or without Mg(OTf)₂ in d4-Cl CD₂CD₂Cl [4]. As a result, the chemical shifts of C1 and C10 positions in the complex-lactam 6 with Mg(OTf)₂ were shifted downfield by 3.3 and 1.7 ppm, respectively, compared to those of free lactam 6. In addition, the downfield shift for α-carbon (C2)
and upfield shift for β-carbon (C6, C7, C11) were also observed. These key differences of chemical shifts clearly suggested the magnesium coordination toward carboxyl groups (C1 and C10) of lactam 6.

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[a] δH_{free} = δ_{free} - δ_{complex}

[b] Chemical shifts of 6’ (complex) were assigned by HSQC and HMBC measurements in d6-CDCl3CDCl3.

3. Plausible reaction mechanism

Since the chelating effect of magnesium has been revealed, the stable conformation of lactam 6’ with Mg(OTf)2 was then investigated by a NOESY measurement. The obtained NOE correlations indicated that the Diels-Alder reaction occurred selectively on the favorable side due to the steric hindrance between the acetylene moiety of diene and the 3-axial-hydrogen group (shown in red) of dienophile.
Absolute Configuration of Allyl Alcohol 2b

1. Synthesis of MTPA esters 2b’

MTPA esters 2b’: To a solution of 2b (1.0 mg, 0.0023 mmol) in DCM (116 μL) at 0 °C was added NEt₃ (3 μL, 0.002 mmol), DMAP (0.4 mg, 0.007 mmol), and (S)-MTPA chloride (1.3 μL, 0.0070 mmol). After the mixture was stirred for 20 min. at room temperature, the solvent was evaporated. Flash column chromatography (hexane/EtOAc = 3/1) furnished the MTPA ester (R)-2b’ (1.2 mg, 0.0019 mmol) as a yellow oil.

(S)- 2b’: In the same manner as that described above, the MTPA ester (S)-2b’ (1.4 mg, 0.0022 mmol) was obtained from 2b (1.0 mg, 0.0023 mmol) by using (R)-MTPA chloride.

2. Structural determination by modified Mosher’s method

The absolute configuration at the C4 position of the allyl alcohol 2b could be confirmed as R judging from the differences in the chemical shifts between MTPA esters (S)-2b’ and (R)-2b’.
Structural Determination

1. Comparison of key NOE correlations of natural 13-desMe-SPX C and 13,19-didesMe-SPX C with synthetic spiroimine unis 1a and 1b

![Structural diagram]

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<tr>
<th>C#</th>
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<th>13,19-didesMe-SPX C [^{[b]}] NOEs</th>
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<th>1b (4R) NOEs</th>
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[^{[a]}] Spectra were recorded using CD_{3}OD as solvent and chemical shifts were referred to CH_{3}OH = 3.30 ppm (^{1}H).
[^{[b]}] Data taken from (7).
[^{[c]}] Data taken from (8).
[^{[d]}] Intensity of the NOE(ROE)s are very weak.

Three critical NOE correlations are shown in green color. From the results of NOESY measurement, the conformation of the cyclohexene ring moiety of the synthesized compounds is almost consistent with that of the natural product.
(4S)-Spirocyclic Imine (1a)
<H7-H34a, H8-H31, H33b-H34b>

(4R)-Spirocyclic Imine (1b)
<H7-H34a, H8-H31, H33b-H34b>
2. Comparison of $^1$H NMR chemical shifts of natural 13-desMe-SPX C with synthetic spiroimine units 1a and 1b

![Chemical structures](image)

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<th>1b (4R)</th>
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[a] Spectra were recorded using CD$_2$OD as solvent and chemical shifts were referred to CHD$_2$OH = 3.30 ppm ($^1$H). [b] Data taken ref.(5). [c] $\Delta\delta = \delta_{\text{13-desMe-SPX C}} - \delta_{\text{1}}$
3. Comparison of $^{13}$C NMR chemical shifts of natural 13-desMe-SPX C with synthetic spiroimine units 1a and 1b

![Chemical Structures](image)

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[a] Spectra were recorded using CD$_3$OD as solvent and chemical shifts were referred to $^{13}$CD$_3$OD = 49.0 ppm ($^{13}$C). [b] Data taken ref.(6). [c] $\Delta \delta = \delta_{13\text{desMe-SPX C}} - \delta_{1}$
4. Comparison of key $^1$H NMR chemical shifts of natural 13-desMe-SPX C with synthetic spiroimine unis 1a and 1b

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<td>1.77</td>
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[a] Spectra were recorded using CD$_3$OD as solvent and chemical shifts were referred to CHD$_2$OH = 3.30 ppm ($^1$H). [b] Data reported by Wright group. [c] $\Delta^\delta = ^\delta_{13\text{desMe}-\text{SPX C}} - ^\delta_{1}$

$^1$H NMR data (CD$_3$OD)
5. Comparison of key $^{13}$C NMR chemical shifts of natural 13-desMe-SPX C with synthetic spiroimine units 1a and 1b

![13-desMe-SPX C](image)

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[a] Spectra were recorded using CD$_3$OD as solvent and chemical shifts were referred to $^{13}$CD$_3$OD = 49.0 ppm ($^{13}$C). [b] Data taken ref. (5). [c] $\Delta\delta = \delta$13desMe-SPX C – $\delta$1

![13C NMR data in CD$_3$OD](image)
6. Comparison of $^1$H NMR chemical shifts of natural 13,19-didesMe-SPX C with synthetic spiroimine units 1a and 1b

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[a] Spectra were recorded using CD$_2$OD as solvent and chemical shifts were referred to CHD$_2$OH = 3.30 ppm ($^1$H). [b] Data taken ref (6). [c] $\Delta\delta = 13,19$-didesMe-SPX C – $\delta^1$
7. Comparison of $^{13}$C NMR chemical shifts of natural 13,19-didesMe-SPX C with synthetic spiroimine units 1a and 1b

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[a] Spectra were recorded using CD$_2$OD as solvent and chemical shifts were referred to $^{13}$CD$_2$OD = 49.0 ppm ($^{13}$C). [b] Data taken ref.(8). [c] $\Delta\delta = \delta_{13,19\text{-didesMe-SPX C}} - \delta_{1}.$
8. Comparison of key $^1$H and $^{13}$C NMR chemical shifts of natural 13,19-didesMe-SPX C with synthetic spiroimine units 1a and 1b

![Diagram of 13,19-didesMe-SPX C and 1a and 1b](image)

**1$^1$H NMR data in CD$_3$OD**

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**1$^{13}$C NMR data in CD$_3$OD**

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</table>
9. Conformational analysis of γ-butenolide ring of compounds 1a and 1b

Strong NOE correlation between H4 and H37 showed that 1a had conformation A (gauche+) or B (gauche-). Additionally, the NOE correlations of H3/H35a and H3/H37 were observed, but that of H4/H35a was not observed, indicating that a spiroimine unit 1a (4S) had a conformation A (gauche+). This result was also supported by the calculation showing that a conformation A (gauche+) is the lowest energy structure as shown in left figure. As with 1a, the NOE correlation between H4 and H37 was strongly observed in 1b. Further, judging from the result of the conformational search and other observed correlations (H3/H37, H3/H35b and H4/H35a), 1b was found to have conformation D (eclipsed) as the most stable conformation. These conformational searches were performed using a MacroModel. The OPLS3e and the MCMM (Torsional Sampling) were used for these calculation as the force field and the method, respectively.
References


Copies of $^1$H, $^{13}$C NMR Spectra
<table>
<thead>
<tr>
<th>X : parts per Million : Proton</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.0  10.0  9.0  8.0  7.0  6.0  5.0  4.0  3.0  2.0  1.0  0.0 -1.0</td>
</tr>
<tr>
<td>7.447  7.432  7.132  7.116  7.101  7.022  5.262  5.248  5.222  5.203  5.178  5.153  4.262  3.837  3.358  3.347  2.754  2.699  2.539  1.930  1.919  1.485  1.480  1.096  1.001  0.931  0.890  0.883  0.877  0.815  0.802</td>
</tr>
</tbody>
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**Comment:** single_pulse

**Data Format:** 1D REAL

**Dim Size:** 26214

**Dim Units:** [ppm]

**Dimensions:** X

**Filename:** KM-6-122-F2__proton-1-10

**Author:** Murata

**Experiment:** proton.jsp

**Sample Id:** KM-6-122-F2'

**Solvent:** BENZENE-D6

**Actual Start Time:** 2-MAR-2017 14:07:02

**Revision Time:** 17-OCT-2019 14:00:06

**Comment:** single_pulse

**Data Format:** 1D REAL

**Dim Size:** 26214

**Dim Units:** [ppm]

**Dimensions:** X

**Site:** ECA 500

**Spectrometer:** JNM-ECA500

**Field Strength:** 11.7473579[T] (500[MHz])

**X_Acq_Duration:** 3.49175808[s]

**X_Acq_Time:** 3.49175808[s]

**X_Angle:** 45[deg]

**X_Atn:** 4.5[dB]

**X_Pulse:** 3.2[us]

**Irr_Mode:** Off

**Tri_Mode:** Off

**Dante_Presat:** FALSE

**Initial_Wait:** 1[s]

**Phase:** [0, 90, 270, 180, 180, 27]

**Repetition_Time:** 8.49175808[s]

**Relaxation_Delay:** 5[s]

**Irr_Offset:** 5.0[ppm]

**Tri_Offset:** 5.0[ppm]

**Clipped:** FALSE

**Scans:** 8

**Total_Scans:** 8

**Temp_Get:** 25[dC]

**X_90_Width:** 6.4[us]

**X_Acq_Time:** 3.49175808[s]

**X_Angle:** 45[deg]

**X_Atn:** 4.5[dB]

**X_Pulse:** 3.2[us]

**Irr_Mode:** Off

**Tri_Mode:** Off

**Dante_Presat:** FALSE

**Initial_Wait:** 1[s]

**Phase:** [0, 90, 270, 180, 180, 27]

**Repetition_Time:** 8.49175808[s]
Filename          = KM-9-183-F1_proton-1-8.jd
Author            = Murata
Experiment        = proton.jxp
Sample_Id         = KM-9-183-F1
Solvant           = CHLOROFORM-D
Actual_Start_Time = 9-MAR-2019 09:01:34
Revision_Time     = 16-OCT-2019 14:38:30
Comment           = single_pulse
Data_Format       = 1D REAL
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 6.98351616[s]
X_Domain          = 1H
X_Sweep           = 9.3843438[kHz]
X_Sweep_Clipped   = 7.50750751[kkHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8
Relaxation_Delay  = 5[s]
Recov_Gain        = 30
Temp_Get          = 32.4[dC]
X_90_Width        = 13.1[us]
X_Acq_Time        = 6.98351616[s]
X_Angle           = 45[deg]
X_Atn             = 4[db]
X_Pulse           = 6.55[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 11.98351616[s]

X : parts per Million : Proton
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
X : parts per Million : Proton
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 ... Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 11.98351616[s]
**Filename** = KM-10-51-F1_carbon-1-8.jd  
**Author** = Murata  
**Experiment** = carbon_jxp  
**Sample_Id** = KM-10-51-F1  
**Solvant** = CHLOROFORM-D  
**Actual_Start_Time** = 11-APR-2019 19:16:34  
**Revision_Time** = 16-OCT-2019 11:02:46  
**Comment** = single pulse decoupled ga  
**Data_Format** = 1D COMPLEX  
**Dim_Size** = 26214  
**Dim_Title** = Carbon13  
**Dim_Units** = [ppm]  
**Dimensions** = X  
**Site** = ECA 500  
**Spectrometer** = JNM-ECA500  
**Field_Strength** = 11.7473579 [T] (500 [MHz])  
**X_Acq_Duration** = 0.83361792 [s]  
**X_Domain** = 13C  
**X_Freq** = 125.76529768 [MHz]  
**X_Offset** = 100 [ppm]  
**X_Points** = 32768  
**X_Prescans** = 4  
**X_Resolution** = 1.19950086 [Hz]  
**X_Sweep** = 31.46540888 [kHz]  
**X_Sweep_Clipped** = 31.46540888 [kHz]  
**Irr_Domain** = Proton  
**Irr_Freq** = 500.15991521 [MHz]  
**Irr_Offset** = 5.0 [ppm]  
**Irr_Pwidth** = 92 [us]  
**Decoupling** = TRUE  
**Noe** = TRUE  
**Noe_Time** = 2 [s]  
**Noe_delay** = 2 [s]  
**Recvr_Gain** = 52  
**Temp_Get** = 25 [°C]  
**X_90_Width** = 22 [us]  
**X_Acq_Time** = 0.83361792 [s]  
**X_Angle** = 30 [deg]  
**X_Atn** = 7 [dB]  
**X_Pulse** = 7.33333333 [us]  
**Irr_Atn_Dec** = 27.65 [dB]  
**Irr_Atn_No** = 27.65 [dB]  
**Irr_Noise** = WALTZ  
**Irr_Pwidth** = 92 [us]  
**Decoupling** = TRUE  
**Initial_Wait** = 1 [s]  
**Noe_Time** = 2 [s]  
**Repetition_Time** = 2.83361792 [s]
10 (dr = 1:1.1)
Filename          = KM-10-83-F2(SI)_proton-1-
Author            = Murata
Experiment        = proton.jsp
Sample_Id         = KM-10-83-F2(SI)
Solvant           = CHLOROFORM-D
Actual_Start_Time = 28-APR-2019 20:30:23
Revision_Time     = 17-OCT-2019 15:24:47
Comment           = single_pulse
Data_Format       = 1D REAL
Dim_Size          = 52429
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR
Field_Strength    = 11.7473579 [T] (500 [MHz])
X_Acq_Duration    = 6.98351616 [s]
X_Domain          = 1H
X_Gain            = 6.98351616 [MHz]
X_Offset          = 5.0 [ppm]
X_Resolution      = 0.14319434 [Hz]
X_Sweep           = 9.38438438 [kHz]
Irr_Domain        = Proton
Irr_Offset        = 5.0 [ppm]
Tri_Domain        = Proton
Tri_Offset        = 5.0 [ppm]
Clipped           = FALSE
Scans             = 100
Total_Scans       = 100
Relaxation_Delay  = 5 [s]
Recov_Gain        = 44
Temp_Get          = 25 [dC]
X_90_Width        = 1.03 [us]
X_Acq_Time        = 6.98351616 [s]
X_Angle           = 45 [deg]
X_Pulse           = 6.55 [us]
Irr_Mode          = OFF
Tri_Mode          = OFF
Dante_Presat      = FALSE
Initial_Wait      = 1 [s]
Repetition_Time   = 11.98351616 [s]
Filename          = KM-10-95-F2(SI)_proton-1
Author            = Murata
Experiment        = proton.jxp
Sample_Id         = KM-10-95-F2(SI)
Solvent           = CHLOROFORM-D
Actual_Start_Time = 13-MAY-2019 22:40:05
Comment           = single_pulse
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Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 6.98351616[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 65536
X_Prescans        = 1
X_Resolution      = 0.14319434[kHz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
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Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 16
Total_Scans       = 16
Relaxation_Delay  = 5[s]
Recov_Gain        = 46
Temp_Get          = 25[dC]
X_90_Width        = 13.1[us]
X_Acq_Time        = 6.98351616[s]
X_Angle           = 45[deg]
X_Atn             = 4[db]
X_Pulse           = 6.55[us]
Irr_Mode          = OFF
Tri_Mode          = OFF
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 11.98351616[s]
Filename          = KM-10-95-F2(SI)_carbon-1-
Author            = Murata
Experiment        = carbon.jxp
Sample_Id         = KM-10-95-F2(SI)
Solvent           = CHLOROFORM-D
Actual_Start_Time = 13-MAY-2019 22:44:29
Revision_Time     = 16-OCT-2019 13:07:18
Comment           = single pulse decoupled ga
Data_Format       = 1D REAL
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.44654088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 12000
Total_Scans       = 12000
Relaxation_Delay  = 2[s]
Recvr_Gain        = 60
Temp_Get          = 24.9[dC]
X_90_Width        = 11.6[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 10[db]
X_Pulse           = 3.86666667[us]
Irr_Atn_Dec       = 20.5[db]
Irr_Atn_Noe       = 20.5[db]
Irr_Noise         = WALTZ
Irr_Width         = 92[us]
Decoupling        = TRUE
Initial_Wait      = 2[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 2.83361792[s]
Filename          = KM-10-97-Fl(SI)_carbon-1-
Author            = Murata
Experiment        = carbon.jxp
Sample_Id         = KM-10-97-Fl(SI)
Solvent           = CHLOROFORM-D
Actual_Start_Time = 14-MAY-2019 21:25:59
Revision_Time     = 16-OCT-2019 13:16:29
Comment           = single pulse decoupled ga
Data_Format       = 1D REAL
Dim_Size          = 26214
Dim_Title         = Carbon13
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = DELTA2_NMR
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 0.83361792[s]
X_Domain          = 13C
X_Freq            = 125.76529768[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescan         = 4
X_Resolution      = 1.19959034[Hz]
X_Sweep           = 39.3081761[kHz]
X_Sweep_Clipped   = 31.4464088[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Irr_Clipped       = FALSE
Scans             = 14000
Total_Scans       = 14000
Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 25[°C]
X_90_Width        = 11.6[us]
X_Acq_Time        = 0.83361792[s]
X_Angle           = 30[deg]
X_Atn             = 10[dB]
X_Pulse           = 3.86666667[us]
Irr_Atn_Dec       = 20.5[db]
Irr_Atn_Noise     = 20.5[db]
Irr_Noise         = WALTZ
Irr_Pwidth        = 92[us]
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
SepWait_Time      = 2.83361792[s]
X : parts per Million : Proton

Filename          = KM-10-Imine(R)-CD3OD_prot
Author            = Murata
Experiment        = proton.jsp
Sample_Id         = KM-10-Imine(R)-CD3OD
Solvent           = METHANOL-D4
Actual_Start_Time = 8-JUL-2019 21:27:05
Revision_Time     = 16-OCT-2019 22:57:45
Comment           = single_pulse
Data_Format       = 1D REAL
Dim_Size          = 26214
Dim_Title         = Proton
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECA 500
Spectrometer      = JNM-ECA500
Field_Strength    = 11.7473579[T] (500[MHz])
X_Acq_Duration    = 3.49175808[s]
X_Domain          = 1H
X_Freq            = 500.15991521[MHz]
X_Offset          = 5.0[ppm]
X_Points          = 32768
X_Prescans        = 1
X_Resolution      = 0.28638868[kHz]
X_Sweep           = 9.38438438[kHz]
X_Sweep_Clipped   = 7.50750751[kHz]
Irr_Domain        = Proton
Irr_Freq          = 500.15991521[MHz]
Irr_Offset        = 5.0[ppm]
Tri_Domain        = Proton
Tri_Freq          = 500.15991521[MHz]
Tri_Offset        = 5.0[ppm]
Clipped           = FALSE
Scans             = 50
Total_Scans       = 50
Relaxation_Delay  = 5[s]
Recov_Gain        = 44
Temp_Get          = 25.3[dC]
X_90_Width        = 7.3[us]
X_Acq_Time        = 3.49175808[s]
X_Angle           = 45[deg]
X_Atn             = 4.5[dB]
X_Pulse           = 3.65[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Preset      = FALSE
Initial_Wait      = 1[s]
Phase             = [0, 90, 270, 180, 180, 27]
Repetition_Time   = 8.49175808[s]