Supporting Information

Convergent Synthesis of the E'FGH Ring Fragment of Ciguatoxin 1B via an Acetylene Cobalt Complex Strategy

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SCHEME S1. Synthesis of H ring-aldehyde **20** (part I)

Reagents, conditions, and yields. (a) 2-PrOH, $\text{BF}_3 \cdot \text{OEt}_2$, CH_2Cl_2 ; (b) Et_3N , MeOH, H_2O , 84% in two steps; (c) TBSCl, imid., DMF, 100%; (d) Ac_2O , DMSO, 97%; (e) PPh_3MeBr , $n\text{-BuLi}$, THF, 81%; (f) Li, liq. NH_3 , EtOH, 79%; (g) AD-mix- β , MeSO_2NH_2 , $t\text{-BuOH}$, H_2O , 74%; (h) BzCl , Py, CH_2CH_2 , 94%; (i) TBAF, THF, 86%; (j) I_2 , PPh_3 , imid., Et_2O , CH_3CN , 100%; (k) NaCN , DMSO, 88%; (l) 1,3-propanedithiol, $\text{BF}_3 \cdot \text{OEt}_2$, CH_2CH_2 then $\text{Me}_2\text{C}(\text{OMe})_2$, CSA, 78%; (m) K_2CO_3 , MeOH, 77%; (n) TESCl, imid., DMF, 100%; (o) MeI, NaHCO_3 , CH_3CN , H_2O , rt, 2d, 83%. (ref. S2)

ref. S1) Another conditions preparing S3, see: Prevost, N.; Rouessac, F. *Tetrahedron Lett.* **1997**, 38, 4215.

S2) Takano, S.; Hatakeyama, S.; Ogasawara, K. *J. Chem. Soc. Chem. Commun.* **1977**, 68.

SCHEME S2. Synthesis of H ring-aldehyde **20** (part II)

Reagents, conditions, and yields. (a) vinylmagnesium bromide, THF, -78°C , 87%; (b) TBAF, THF; (c) Ac_2O , Py, CH_2Cl_2 , DMAP, 100% in two steps; (d) $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$, $n\text{-Bu}_3\text{P}$, HCO_2H , Et_3N , THF, 85%; (e) O_2 , PdCl_2 , CuCl, DMF, H_2O , 98%; (f) $\text{BF}_3 \cdot \text{OEt}_2$, CH_3CN , 88%; (g) TiCl_4 , Et_3SiH , CH_2Cl_2 , 0°C , 100% (ref. S3); (h) K_2CO_3 , MeOH; (i) $\text{PhCH}(\text{OMe})_2$, CSA, CH_2Cl_2 , 86% in two steps; (j) DIBAL, CH_2Cl_2 , -78°C , 95%; (k) NaBH_4 , MeOH, 0°C , 99%; (l) $\text{PhCH}(\text{OMe})_2$, CSA, CH_2Cl_2 , 86%; (m) TMSCl, Et_3N , DMAP, CH_2Cl_2 , 97%; (n) DIBAL, toluene, -78°C to -10°C , 90%; (o) IBX, Py, DMSO, 91%.

ref. S3) Kotsuki, H.; Ushio, Y.; Kadota, I.; Ochi, M. *Chem. Lett.* **1988**, 927.

Experimental Section

General Methods: Infrared spectra (IR) were recorded on a FT/IR spectrophotometer and are reported in wave number (cm^{-1}). ^1H NMR spectra were measured at 600 MHz, 400 MHz or 300 MHz. Measured in CDCl_3 , chemical shifts are reported in ppm using tetramethylsilane ($\delta = 0.00$ ppm) as an internal standard. Measured in $\text{C}_5\text{D}_5\text{N}$, chemical shifts are reported in ppm using the solvent resonance as an internal standard ($\text{C}_5\text{HD}_4\text{N}$: $\delta = 7.19$ ppm). Data are reported as follows; chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, sep = septet, br = broadened, m = multiplet), coupling constant(s), and assignment, respectively. ^{13}C NMR spectra were measured at 150 MHz, 100 MHz, or 75 MHz. Chemical shifts are reported in ppm using the solvent resonance as internal standards (CDCl_3 : $\delta = 77.0$ ppm, $\text{C}_5\text{D}_5\text{N}$: $\delta = 135.5$ ppm). 2D NMR (COSY, NOESY, HMQC, HMBC) were measured at 600 MHz or 400 MHz. MS and MS/MS spectra were measured utilizing a Q-TOF mass spectrometer equipped with a Z-spray type ESI source and are reported in m/z . High resolution mass spectra (HRMS) are reported in m/z . Elemental analyses were performed by Mr. Kitamura in Analytical Laboratory at School of Bioagricultural Sciences, Nagoya University. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated glass plates 60F₂₅₄ using UV light as visualizing agent and *p*-anisaldehyde solution and heated as developing agents. Silica gel 60 (particle size 0.063-0.2 mm ASTM) and silica gel 60 N (spherical, neutral, particle size 0.063-0.2 mm) were used for open-column chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on 0.5 mm silica gel plates (60F₂₅₄, Art 1.05774). Dry THF was distilled from potassium metal with benzophenone under N_2 atmosphere. Dry CH_2Cl_2 was distilled from CaH_2 under N_2 atmosphere. Pyridine and Et_3N were dried over anhydrous KOH. $\text{BF}_3 \cdot \text{OEt}_2$ was distilled from CaH_2 . All other commercially available reagents were used as received.

The data for compound **5**, **7**, **9**, **10**, **17**, **18**, **19** were reported in our previous paper, see: Takai, S.; Isobe, M. *Org. Lett.* **2002**, *4*, 1183-1186.

Diol **S1** (Supporting Information)

To a solution of tri-*O*-acetyl-D-glucal (200 g, 0.735 mol) and 2-propanol (112 ml, 1.47 mol) in dry CH₂Cl₂ (2.0 l) was added dropwise BF₃•OEt₂ (46.4 ml, 0.367 mol) at 0 °C under N₂ atmosphere. After stirring for 50 min at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo to give a crude **diacetate**.

To a solution of the crude **diacetate** in MeOH (1.5 l) were added H₂O (300 ml) and Et₃N (300 ml). After stirring for 5.5 h at rt, the reaction mixture was concentrated in vacuo, and crystallized (hexane/ether) to give diol **S1** (116.5g, 84% in two steps).

Diol **S1**. Mp. 98-100 °C. IR (KBr) $\nu_{\max}$ 3392, 2970, 2937, 2900, 1439, 1386, 1326, 1096, 1029, 947, 819, 794 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.18 (3H, d, *J* = 6.0 Hz), 1.24 (3H, d, *J* = 6.0 Hz), 2.23 (1H, br-s), 2.40 (1H, br-s), 3.75 (1H, dt, *J* = 9.0, 4.5 Hz), 3.86 (2H, m), 3.98 (1H, sep, *J* = 6.0 Hz), 4.21 (1H, t, *J* = 4.5 Hz), 5.09 (1H, br-s), 5.73 (1H, dt, *J* = 10, 2.5 Hz), 5.96 (1H, br-d, *J* = 10 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 21.8, 23.6, 62.8, 64.3, 70.4, 71.2, 92.5, 127.0, 133.2. $[\alpha]_D^{23} +74.1^\circ$ (c 1.00, CHCl₃). Anal. Calcd for C₉H₁₆O₄: C, 57.43; H, 8.57. Found: C, 57.26; H, 8.48.

Alcohol **S2**

To a solution of diol **S1** (20.4 g, 0.108 mol) and imidazole (22.1 g, 0.324 mol) in DMF (1.0 l) was added TBSCl (19.6 g, 0.13 mol) at 0 °C under N₂ atmosphere. After stirring for 30 min at 0 °C, the reaction mixture was poured into NaHCO₃ aq. and extracted with ether. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give alcohol **S2** (32.8 g, 100%).

Alcohol **S2**. IR (KBr) $\nu_{\max}$ 3448, 2959, 2931, 2887, 2859, 1473, 1385, 1256, 1131, 1087, 1031, 837, 778 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 0.10 (6H, s), 0.90 (9H, s), 1.16 (3H, d, *J* = 6.0 Hz), 1.23 (3H, d, *J* = 6.0 Hz), 2.80 (1H, d, *J* = 4.0 Hz), 3.77 (2H, m), 3.88 (1H, m), 3.95 (1H, sep, *J* = 6.0 Hz), 4.16 (1H, m), 5.04 (1H, m), 5.73 (1H, dt, *J* = 10.5, 2.5 Hz), 5.96 (1H, dt, *J* = 10.5, 1.0 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ -5.67, -5.62, 18.2, 21.9, 23.7, 25.8, 65.5, 67.2, 69.9, 70.1, 92.4, 126.5, 132.6. $[\alpha]_D^{23} +26.6^\circ$ (c 3.12, CHCl₃). Anal. Calcd for C₁₅H₃₀O₄Si: C, 59.56; H, 10.00. Found: C, 59.57; H, 9.98.

Enone **S3**

To a solution of alcohol **S2** (32.8 g, 0.108 mol) in DMSO (600 ml) was added Ac₂O (400 ml). After stirring for 11.5 h at rt, the reaction mixture was poured into an ice-cold water and extracted with ether. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give enone **S3** (31.58 g, 97%).

Enone **S3**. IR (KBr) $\nu_{\max}$ 2958, 2931, 2885, 2859, 1698, 1473, 1384, 1319, 1255, 1135, 1091, 1065, 1035, 917, 837, 778 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 0.05 (3H, s), 0.07 (3H, s), 0.87 (9H, s), 1.21

(3H, d, $J = 6.0$ Hz), 1.26 (3H, d, $J = 6.0$ Hz), 3.98 (1H, dd, $J = 11.5, 5.5$ Hz), 4.07 (1H, sep, $J = 6.0$ Hz), 4.08 (1H, dd, $J = 11.5, 2.5$ Hz), 4.49 (1H, dd, $J = 5.5, 2.5$ Hz), 5.40 (1H, d, $J = 3.5$ Hz), 6.08 (1H, d, $J = 10.5$ Hz), 6.84 (1H, dt, $J = 10.5, 3.5$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ -5.51, -5.47, 18.2, 21.8, 23.2, 25.7, 62.5, 71.0, 76.0, 91.4, 127.9, 144.7, 195.2. $[\alpha]_{\text{D}}^{23} -7.8^\circ$ (c 0.77, CHCl_3). Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_4\text{Si}$: C, 59.96; H, 9.39. Found: C, 59.96; H, 9.53.

Diene S4

To a solution of methylenetriphenylphosphorane (31.1 mmol), which was prepared by addition of *n*-BuLi (19.4 ml, 31.1 mol) to a stirred slurry of PPh_3MeBr (11.1 g, 31.1 mmol) in 150 ml of dry THF at -78°C under N_2 atmosphere followed by stirring for 30 min at rt, was added dropwise enone **S3** (6.23 g, 20.7 mmol) in dry THF (50 ml) at -78°C under N_2 atmosphere. After stirring for 2 h at -78°C and for 30 min at rt, the reaction mixture was poured into NH_4Cl aq. at 0°C and extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to give diene **S4** (5.0 g, 81%).

Diene **S4**. IR (KBr) ν_{max} 2958, 2930, 2886, 2859, 1608, 1473, 1382, 1317, 1256, 1172, 1127, 1094, 1028, 839, 776 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.09 (6H, s), 0.90 (9H, s), 1.18 (3H, d, $J = 6.0$ Hz), 1.26 (3H, d, $J = 6.0$ Hz), 3.83 (1H, dd, $J = 11.0, 6.5$ Hz), 4.03 (1H, dd, $J = 11.0, 4.5$ Hz), 4.06 (1H, sep, $J = 6.0$ Hz), 4.55 (1H, m), 4.98 (1H, m), 5.11 (1H, m), 5.18 (1H, d, $J = 3.5$ Hz), 5.60 (1H, m), 6.26 (1H, d, $J = 10.0$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ -5.5, -5.4, 18.2, 21.7, 23.6, 25.8, 64.1, 69.0, 69.3, 92.2, 112.2, 126.1, 130.2, 139.8. $[\alpha]_{\text{D}}^{23} -63.8^\circ$ (c 2.13, CHCl_3). Anal. Calcd for $\text{C}_{16}\text{H}_{30}\text{O}_3\text{Si}$: C, 64.38; H, 10.13. Found: C, 64.38; H, 10.13.

Diol S6

To a solution of diene **S4** (14.0 g, 46.9 mmol) in liquid NH_3 (423 ml) and EtOH (47 ml) was added lithium (1.54 g, 220 mmol) at refluxing temperature. After stirring for 30 min, NH_4Cl powder was added to the reaction mixture, which was then concentrated in vacuo. The residue was dissolved in water and extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to give olefin **S5** (11.2 g, 79%).

To a solution of olefin **S5** (6.68 g, 22.2 mmol) in *tert*-butanol (110 ml) and water (110 ml) were added AD-mix- β (31.12 g) and methanesulfonamide (2.1 g) at 0°C . After stirring for 25.5 h at rt, the reaction mixture was poured into an ice-cold water and extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to give diol **S6** (5.53 g, 74%).

Diol **S6**. IR (KBr) ν_{max} 3424, 2931, 2858, 1473, 1380, 1257, 1129, 1022, 839, 777 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.09 (6H, s), 0.90 (9H, s), 1.11 (3H, d, $J = 6.0$ Hz), 1.15 (3H, d, $J = 6.0$ Hz), 1.30 (3H, s), 1.86 (2H, m), 3.54 (1H, dd, $J = 4.0, 3.0$ Hz), 3.63 (1H, dd, $J = 10.5, 6.0$ Hz), 3.86 (1H, sep, $J = 6.0$ Hz), 3.88 (1H, dd, $J = 11.5, 3.0$ Hz), 4.02 (1H, dd, $J = 11.5, 4.0$ Hz), 5.01 (1H, dd, $J = 3.5, 1.5$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ -5.7, -5.6, 18.1, 21.0, 21.2, 23.2, 25.7, 35.4, 63.7, 68.2, 69.3, 72.2, 72.3, 95.3. $[\alpha]_{\text{D}}^{26} 87.9^\circ$ (c 2.22, CHCl_3). Anal. Calcd for $\text{C}_{16}\text{H}_{34}\text{O}_5\text{Si}$: C, 57.45; H, 10.24. Found: C, 57.17; H, 10.29.

Benzoate **S7**

To a solution of diol **S6** (2.94 g, 8.79 mmol) and pyridine (3.6 ml, 36.3 mmol) in dry CH₂Cl₂ (45 ml) was added BzCl (1.53 ml, 13.2 mmol) at rt. After stirring for 7 h at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give benzoate **S7** (3.6 g, 94%).

Benzoate **S7**. IR (KBr) $\nu_{\max}$ 3484, 2956, 2931, 2857, 1723, 1275, 1113, 1029, 838, 778, 712 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 0.12 (3H, s), 0.13 (3H, s), 0.92 (9H, s), 1.15 (3H, d, J = 6.5 Hz), 1.20 (3H, d, J = 6.5 Hz), 1.29 (3H, s), 1.96 (1H, ddd, J = 12.5, 5.0, 1.0 Hz), 2.31 (1H, dt, J = 12.5, 4.0 Hz), 3.71 (2H, m), 3.92 (1H, sep, J = 6.5 Hz), 3.94 (1H, dd, J = 11.5, 2.5 Hz), 4.07 (1H, dd, J = 11.5, 4.0 Hz), 5.13 (1H, dd, J = 4.0, 1.0 Hz), 5.30 (1H, dd, J = 12.5, 5.0 Hz), 7.10-8.11 (5H, m). ¹³C NMR (CDCl₃, 75 MHz) δ -5.7, -5.6, 18.2, 21.3, 23.3, 25.8, 31.9, 63.6, 68.6, 72.0, 72.5, 72.7, 95.2, 128.4, 129.9, 130.3, 133.1, 166.2. $[\alpha]_D^{26}$ +91.2° (c 5.15, CHCl₃). Anal. Calcd for C₂₃H₃₈O₆Si: C, 62.98; H, 8.73. Found: C, 62.87; H, 8.95.

Diol **S8**

To a solution of benzoate **S7** (1.12 g, 2.55 mmol) in THF (25 ml) was added 1.0 M TBAF in THF (3 ml, 3 mmol) at 0 °C. After stirring for 5 min at 0 °C, the reaction mixture was poured into NH₄Cl aq. at 0 °C and extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give diol **S8** (710 mg, 86%).

Diol **S8**. IR (KBr) $\nu_{\max}$ 3437, 2975, 2935, 1720, 1451, 1382, 1277, 1113, 1027, 714 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.17 (3H, d, J = 6.0 Hz), 1.22 (3H, d, J = 6.0 Hz), 1.29 (3H, s), 2.03 (1H, ddd, J = 12.5, 5.0, 1.0 Hz), 2.25 (1H, dt, J = 12.5, 4.0 Hz), 3.71 (1H, dd, J = 5.0, 3.0 Hz), 3.88 (1H, dd, J = 12.0, 3.0 Hz), 3.89 (1H, sep, J = 6.0 Hz), 4.08 (1H, dd, J = 12.0, 5.0 Hz), 5.18 (1H, dd, J = 4.0, 1.0 Hz), 5.35 (1H, dd, J = 12.5, 5.0 Hz), 7.42-8.10 (5H, m). ¹³C NMR (CDCl₃, 75 MHz) δ 21.2, 21.3, 23.3, 32.0, 61.8, 69.0, 72.06, 72.13, 72.6, 95.1, 128.5, 129.8, 130.0, 133.3, 165.9. $[\alpha]_D^{26}$ +112.7° (c 3.27, CHCl₃). Anal. Calcd for C₁₇H₂₄O₆: C, 62.95; H, 7.46. Found: C, 62.94; H, 7.46.

Iodide **S9**

To a solution of diol **S8** (710 mg, 2.19 mmol) in ether (15 ml) and CH₃CN (5 ml) were added imidazole (298 mg, 4.38 mmol) and triphenylphosphine (861 mg, 3.28 mmol) and iodine (833 mg, 3.28 mmol) at 0 °C. After stirring for 10 min at 0 °C and for 20 h at rt, the reaction mixture was poured into Na₂SO₃ aq. at 0 °C and extracted with ether. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give iodide **S9** (950 mg, 100%).

Iodide **S9**. IR (KBr) $\nu_{\max}$ 3510, 2974, 2931, 1721, 1452, 1382, 1274, 1113, 1026, 712 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.16 (3H, d, J = 6.0 Hz), 1.25 (3H, s), 1.26 (3H, d, J = 6.0 Hz), 2.05 (1H, ddd, J = 11.5, 6.5, 1.0 Hz), 2.12 (1H, dt, J = 11.5, 4.0 Hz), 2.18 (1H, br-s), 3.34 (1H, t, J = 10.5 Hz), 3.51 (1H, dd, J = 10.5, 2.5 Hz), 3.98 (1H, dd, J = 10.5, 2.5 Hz), 4.16 (1H, sep, J = 6.0 Hz), 5.18 (1H, dd, J = 4.0, 1.0 Hz), 5.33 (1H, dd, J = 11.5, 6.5 Hz), 7.42-8.10 (5H, m). ¹³C NMR (CDCl₃, 75 MHz) δ 2.4, 20.6,

20.8, 23.1, 31.9, 68.1, 71.7, 71.8, 74.3, 93.9, 128.5, 129.76, 129.84, 133.3, 165.8. $[\alpha]_{\text{D}}^{26} +80.2^\circ$ (*c* 4.07, CHCl₃). Anal. Calcd for C₁₇H₂₃IO₅: C, 47.02; H, 5.34. Found: C, 46.95; H, 5.46.

Nitrile **S10**

To a solution of iodide **S9** (1.46 g, 3.36 mmol) in DMSO (34 ml) was added NaCN (198 mg, 4.04 mmol) at rt. After stirring for 12.5 h at 60 °C, to the reaction mixture was added NaCN (82 mg, 1.67 mmol) and stirring for 4 h. Then the reaction mixture was poured into NH₄Cl aq. at 0 °C in draft chamber and extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give nitrile **S10** (984 mg, 88%).

Nitrile **S10**. IR (KBr) ν_{max} 3503, 2976, 2936, 2256, 1720, 1452, 1383, 1275, 1113, 1037, 714 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 1.17 (3H, d, *J* = 6.0 Hz), 1.20 (3H, s), 1.28 (3H, d, *J* = 6.0 Hz), 2.05 (1H, ddd, *J* = 11.5, 5.5, 1.5 Hz), 2.13 (1H, dt, *J* = 11.5, 3.5 Hz), 2.27 (1H, br-d, *J* = 3.0 Hz), 2.67 (1H, dd, *J* = 17.0, 4.0 Hz), 3.51 (1H, dd, *J* = 17.0, 9.5 Hz), 4.01 (1H, sep, *J* = 6.0 Hz), 4.12 (1H, dd, *J* = 9.5, 4.0 Hz), 5.13 (1H, dd, *J* = 3.5, 1.5 Hz), 5.38 (1H, dd, *J* = 11.5, 5.5 Hz), 7.42-8.10 (5H, m). ¹³C NMR (CDCl₃, 75 MHz) δ 17.9, 20.7, 21.1, 23.2, 31.8, 69.3, 69.8, 70.7, 71.8, 94.8, 117.9, 128.5, 129.66, 129.73, 133.4, 165.7. $[\alpha]_{\text{D}}^{26} +95.1^\circ$ (*c* 3.08, CHCl₃). Anal. Calcd for C₁₈H₂₃NO₅: C, 64.85; H, 6.95. Found: C, 64.77; H, 7.08.

TES-Dithiane **S11**

To a solution of nitrile **S10** (3.77 g, 11.3 mmol) and 1,3-propanedithiol (1.25 ml, 12.5 mmol, 1.1 equiv.) in CH₂Cl₂ (110 ml) was added BF₃•OEt₂ (2.87 ml, 0.2 M) at 0 °C. After stirring for 40 min at 0 °C, to the reaction mixture was added 2,2-dimethoxypropane (20.9 ml, 169.9 mmol) and CSA (330 mg), then stirring for 4 h at rt. Then the reaction mixture was poured into NaHCO₃ aq. at 0 °C and extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give an **acetone** (3.74 g, 78%).

To a solution of the **acetone** (3.74 g, 8.87 mmol) in MeOH (90 ml) was added K₂CO₃ (1.23 g, 8.90 mmol, 1.0 equiv.) at rt. After stirring for 1.5 h at rt, the reaction mixture was poured into NH₄Cl aq. at 0 °C and extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give an **alcohol** (2.16 g, 77%).

To a solution of the **alcohol** (6.81 g, 21.5 mmol) and imidazole (5.84 g, 85.8 mmol) in DMF (110 ml) was added TESCl (7.2 ml, 42.9 mmol) at rt. After stirring for 3 h 35 min at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to give TES-dithiane **S11** (9.56 g, 100%).

TES-Dithiane **S11**. IR (KBr) ν_{max} 2985, 2956, 2879, 2254, 1376, 1242, 1218, 1100, 1003, 742 cm⁻¹. ¹H NMR (300 MHz, CDCl₃) δ 0.67 (6H, q, *J* = 8.0 Hz), 1.00 (9H, t, *J* = 8.0 Hz), 1.08 (3H, s), 1.37 (3H, s), 1.44 (3H, s), 1.80 (1H, m), 1.90 (1H, m), 2.10 (1H, m), 2.16 (1H, m), 2.52 (1H, dd, *J* = 16.5, 9.5 Hz), 2.66 (1H, dd, *J* = 16.5, 3.0 Hz), 2.89 (4H, m), 4.03 (1H, t, *J* = 6.0 Hz), 4.14 (1H, dd, *J* = 9.5, 3.0 Hz), 4.20 (1H, t, *J* = 7.5 Hz). ¹³C NMR (CDCl₃, 75 MHz) δ 5.3, 6.8, 14.8, 20.3, 25.8, 26.6, 28.4, 29.5, 29.6,

38.9, 43.3, 74.7, 79.0, 83.5, 108.7, 117.5. $[\alpha]_D^{26} +21.9^\circ$ (c 2.01, CHCl_3). Anal. Calcd for $\text{C}_{20}\text{H}_{37}\text{NO}_3\text{S}_2\text{Si}$: C, 55.64; H, 8.64; N, 3.24. Found: C, 56.01; H, 8.97; N, 3.26.

Aldehyde **S12**

To a solution of TES-dithiane **S11** (150 mg, 0.34 mmol) in CH_3CN (3.0 ml) and water (0.75 ml) were added NaHCO_3 (565 mg, 6.73 mmol) and MeI (0.42 ml, 6.73 mmol) at rt. After stirring for 10 h 40 min at rt, the reaction mixture was poured into an ice-cold water and extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to give aldehyde **S12** (95 mg, 83%).

Aldehyde **S12**. IR (KBr) ν_{max} 2958, 2879, 2255, 1725, 1377, 1223, 1104, 1002, 746 cm^{-1} . ^1H NMR (300 MHz, CDCl_3) δ 0.60 (6H, q, $J = 8.0$ Hz), 0.93 (9H, t, $J = 8.0$ Hz), 1.07 (3H, s), 1.30 (3H, s), 1.39 (3H, s), 2.52 (1H, dd, $J = 17.0, 9.5$ Hz), 2.53 (1H, ddd, $J = 16.5, 5.5, 2.0$ Hz), 2.65 (1H, dd, $J = 17.0, 3.0$ Hz), 2.16 (1H, ddd, $J = 16.5, 5.5, 2.0$ Hz), 4.10 (1H, dd $J = 9.5, 3.0$ Hz), 4.21 (1H, t, $J = 5.5$ Hz), 9.71 (1H, t, $J = 2.0$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ 4.8, 6.7, 14.9, 20.1, 26.7, 28.3, 47.8, 73.3, 78.9, 83.0, 109.1, 117.3, 199.5. HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{32}\text{NO}_4\text{Si}$ $[\text{M}+\text{H}]^+$ 342.2101, found 342.2075. $[\alpha]_D^{26} +24.1^\circ$ (c 1.28, CHCl_3).

Olefin **S14**

To a solution of **S12** (544 mg, 1.53 mmol) in dry THF (7.7 ml) was added 1.0 M vinyl magnesium bromide in THF (2.3 ml, 2.30 mmol) at -78°C under N_2 atmosphere. After stirring for 20 min at -78°C , the reaction mixture was poured into NH_4Cl aq. at 0°C and then extracted with ether. The combined organic layer was washed with brine and dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to afford an **allyl alcohol** (510 mg, 87%).

To a solution of the **allyl alcohol** (131 mg, 0.34 mmol) in THF (3.4 ml) was added 1.0 M TBAF in THF (0.51 ml, 0.51 mmol) at 0°C . After stirring for 30 min at rt, the reaction mixture was poured into NH_4Cl aq. at 0°C and then extracted with AcOEt. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo to give a crude **diol**.

To a solution of the crude **diol** in CH_2Cl_2 (3.4 ml) were added pyridine (0.4 ml), Ac_2O (0.2 ml) and DMAP (20 mg). After stirring for 16 h at rt, the reaction mixture was concentrated to give a crude oil. The residue was purified by SiO_2 to afford diacetate **S13** (116 mg, 100% in two steps) as a colorless oil.

To a solution of $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (30 mg, 0.029 mmol) in dry THF (6 ml) was added tri-*n*-butyl phosphine (0.029 ml, 0.12 mmol) at rt under N_2 atmosphere. After stirring for 3 min at rt, Et_3N (0.81 ml, 5.80 mmol), formic acid (0.16 ml, 4.35 mmol) and diacetate **S13** was added to the reaction mixture. After stirring for 30 min at 60°C , the reaction mixture was poured into H_2O at 0°C and then extracted with ether. The combined organic layer was washed with brine and dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to afford Olefin **S14** (348 mg, 85%) as a colorless oil.

Olefin **S14**. IR (KBr) ν_{max} 3079, 2989, 2938, 2256, 1742, 1643, 1458, 1377, 1232, 1100, 1029, 998, 919, 845 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 1.18 (3H, s), 1.37 (3H, s), 1.44 (3H, s), 1.63 (1H, dddd, $J = 14.0, 10.0, 8.0, 6.5$ Hz), 1.79 (1H, dddd, $J = 14.0, 9.0, 7.0, 3.0$ Hz), 2.03-2.10 (2H, m), 2.11 (3H, s),

2.51 (1H, dd, $J = 16.5, 5.0$ Hz), 2.59 (1H, dd, $J = 16.5, 8.0$ Hz), 4.19 (1H, dd, $J = 8.0, 5.0$ Hz), 4.98 (1H, dd, $J = 10.0, 3.0$ Hz), 4.99 (1H, dm, $J = 10.0$ Hz), 5.03 (1H, ddt, $J = 17.0, 1.5, 1.5$ Hz), 5.78 (1H, ddt, $J = 17.0, 10.0, 6.5$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 16.9, 19.9, 21.1, 26.7, 28.4, 29.4, 30.1, 76.7, 76.7, 82.6, 109.0, 115.4, 116.8, 137.3, 170.3. ESI Q-TOF MS calcd for $\text{C}_{15}\text{H}_{23}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$ 304.152, found 304.134. $[\alpha]_{\text{D}}^{24}$ 32.3° (c 1.08, CHCl_3). Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_4$ C, 64.03; H, 8.24; N, 4.98. Found: C, 63.93; H, 8.30; N, 5.21.

Ketone S15

To a solution of Olefin **S14** (338 mg, 1.2 mmol) in DMF (11 ml) and H_2O (1 ml) were added palladium (II) chloride (11 ml, 0.060 mmol) and copper (I) chloride (12 mg, 0.12 mmol). After stirring for 32 h at rt under oxygen atmosphere, the reaction mixture was extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to afford Ketone **S15** (348 mg, 98%) as a colorless oil.

Ketone **S15**. IR (KBr) ν_{max} 2990, 2942, 2256, 1740, 1717, 1419, 1376, 1236, 1101, 1063, 1025, 998, 938, 900, 847, 633, 600, 534, 521, 448 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 1.19 (3H, s), 1.38 (3H, s), 1.44 (3H, s), 1.75 (1H, dddd, $J = 14.0, 10.0, 8.0, 6.0$ Hz), 2.05 (1H, dddd, $J = 14.0, 8.0, 7.5, 3.0$ Hz), 2.11 (3H, s), 2.13 (3H, s), 2.46 (1H, ddd, $J = 18.0, 8.0, 6.0$ Hz), 2.52 (1H, ddd, $J = 18.0, 8.0, 7.5$ Hz), 2.54 (1H, dd, $J = 17.0, 5.0$ Hz), 2.61 (1H, dd, $J = 17.0, 8.0$ Hz), 4.16 (1H, dd, $J = 8.0, 5.0$ Hz), 4.89 (1H, dd, $J = 10.0, 3.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 16.8, 19.8, 21.0, 23.9, 26.6, 28.4, 29.9, 39.7, 76.7, 82.5, 109.0, 116.8, 170.4, 207.1. ESI Q-TOF MS calcd for $\text{C}_{15}\text{H}_{23}\text{NNaO}_5$ $[\text{M}+\text{Na}]^+$ 320.147, found 320.130. $[\alpha]_{\text{D}}^{24}$ 23.4° (c 1.85, CHCl_3). Anal. Calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_5$ C, 60.59; H, 7.80; N, 4.71. Found: C, 60.59; H, 7.79; N, 4.72.

Anhydro S16

To a solution of Ketone **S15** (348 mg, 1.18 mmol) in CH_3CN (12 ml, dehydrated) was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.79 M in 1,2-dichloroethane, 1.94 ml, 1.53 mmol). After stirring for 18 h at 50 °C, the reaction mixture was poured into NaHCO_3 aq. at 0 °C and then extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to afford anhydro **S16** (249 mg, 88%) as white crystals.

Anhydro **S16**. Mp 87.5-88.3 °C. IR (KBr) ν_{max} 2993, 2941, 2253, 1740, 1449, 1376, 1257, 1240, 1207, 1121, 1058, 1037, 908, 833 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 1.28 (3H, s), 1.52 (3H, s), 1.57-1.65 (1H, m), 1.72-1.79 (1H, m), 1.77-1.83 (1H, m), 2.03-2.12 (1H, m), 2.14 (3H, s), 2.45 (1H, ddd, $J = 16.5, 6.0$ Hz), 2.53 (1H, dd, $J = 16.5, 5.5$ Hz), 4.13 (1H, dd, $J = 6.0, 5.5$ Hz), 4.70 (1H, dd, $J = 4.5, 2.0$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 16.4, 21.1, 22.1, 23.4, 24.6, 30.4, 69.4, 75.6, 82.5, 108.8, 117.0, 170.5. ESI Q-TOF MS calcd for $\text{C}_{12}\text{H}_{17}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$ 262.106, found 262.101. $[\alpha]_{\text{D}}^{24}$ 66.6° (c 0.38, CHCl_3). Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{NO}_4$ C, 60.24; H, 7.16; N, 5.85. Found: C, 60.26; H, 7.12; N, 5.66.

Alcohol **S17**

To a solution of anhydro **S16** (148 mg, 0.62 mmol) and Et₃SiH (0.30 ml, 1.86 mmol) in CH₂Cl₂ (6.2 ml) was added TiCl₄ (0.14 ml, 0.63 mmol) at 0 °C under N₂ atmosphere. After stirring for 20 min at 0 °C, the reaction mixture was poured into a 1:1 mixture of NaHCO₃ aq. and potassium sodium tartrate aq. After stirring for 1 h at rt, the reaction mixture was extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to afford alcohol **S17** (149 mg, 100%) as a colorless oil.

Alcohol **S17**. IR (KBr) $\nu_{\max}$ 3484, 2975, 2939, 2880, 2252, 1740, 1380, 1248, 1145, 1109, 1076, 1046, 994 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 1.14 (3H, d, *J* = 6.0 Hz), 1.21 (3H, s), 1.31-1.42 (1H, m), 1.63-1.68 (1H, m), 1.67-1.74 (1H, m), 1.97-2.04 (1H, m), 2.06 (3H, s), 2.58 (1H, dd, *J* = 17.0, 5.0 Hz), 2.63 (1H, dd, *J* = 17.0, 7.5 Hz), 3.04 (1H, d, *J* = 9.0 Hz), 3.67 (1H, ddd, *J* = 9.0, 7.5, 5.0 Hz), 3.70 (1H, dqd, *J* = 12.0, 6.0, 2.0 Hz), 5.04 (1H, dd, *J* = 11.5, 5.0 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ 14.4, 20.3, 21.2, 21.4, 24.6, 32.2, 66.7, 69.6, 70.7, 76.1, 118.5, 170.6. ESI Q-TOF MS calcd for C₁₂H₁₉NNaO₄ [M+Na]⁺ 264.121, found 264.105. [α]_D²⁴ 19.3° (*c* 1.00, CHCl₃). Anal. Calcd for C₁₂H₁₉NO₄ C, 59.73; H, 7.94; N, 5.81. Found: C, 59.73; H, 8.12; N, 5.63.

Benzylidene acetal **S18**

To a solution of alcohol **S17** (109 mg, 0.45 mmol) in MeOH (2.3 ml) was added K₂CO₃ (19 mg, 0.14 mmol). After stirring for 20 min at rt, the reaction mixture was poured into NH₄Cl aq. at 0 °C and then extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo to give a crude **diol**.

To a solution of the crude **diol** in CH₂Cl₂ (4.5 ml) were added PhCH(OMe)₂ (0.102 ml, 0.70 mmol) and CSA (10 mg, 0.045 mmol). After stirring for 2 h at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and then extracted with CH₂Cl₂. The combined organic layer was washed with brine and dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to afford benzylidene acetal **S18** (102 mg, 86% in two steps) as white crystals.

Benzylidene acetal **S18**. Mp 113.0-113.6 °C. IR (KBr) $\nu_{\max}$ 2939, 2882, 2253, 1458, 1386, 1212, 1150, 1105, 1023, 956, 748, 698 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 1.11 (3H, d, *J* = 6.0 Hz), 1.30-1.44 (1H, m), 1.60 (3H, s), 1.76-1.82 (1H, m), 1.80-1.89 (2H, m), 2.94 (1H, dd, *J* = 17.5, 4.5 Hz), 3.10 (1H, dd, *J* = 17.5, 10.5 Hz), 3.77 (1H, *J* = 9.0, 7.0 Hz), 3.86 (1H, dqd, *J* = 12.0, 6.0, 2.5 Hz), 4.21 (1H, dd, *J* = 10.5, 4.5 Hz), 5.83 (1H, s), 7.31-7.51 (5H, m). ¹³C NMR (CDCl₃, 100 MHz) δ 15.0, 17.2, 21.7, 23.8, 33.2, 66.5, 70.3, 74.4, 77.7, 96.6, 117.7, 126.2, 128.3, 129.1, 137.1. ESI Q-TOF MS calcd for C₁₇H₂₁NNaO₃ [M+Na]⁺ 310.142, found 310.170. [α]_D²⁶ 92.8° (*c* 1.20, CHCl₃). Anal. Calcd for C₁₇H₂₁NO₃: C, 71.06; H, 7.37; N, 4.87. Found: C, 71.06; H, 7.744; N, 4.92.

Secondary alcohol **S19**

To a solution of benzylidene acetal **S18** (105 mg, 0.37 mmol) in dry CH₂Cl₂ (3.7 ml) was added dropwise 1.01 M DIBAL in toluene (0.54 ml, 0.55 mmol) at -78 °C under N₂ atmosphere. After stirring for 1 h at -78 °C, 2-PrOH (1.6 ml), silica gel (3 g) and AcOEt (10 ml) were added into the reaction mixture at -78 °C. After

stirring for 1 h at rt, the reaction mixture was passed through SuperCel[®] and concentrated to give a crude oil, which was purified by SiO₂ to afford an **aldehyde** (101 mg, 95%) as a colorless oil.

To a solution of the **aldehyde** (73 mg, 0.25 mmol) in MeOH (2.5 ml) was added NaBH₄ (19 mg, 0.50 mmol) at 0 °C. After stirring for 20 min at 0 °C, the reaction mixture were added 2-PrOH (1.6 ml), silica gel (3 g) and AcOEt (10 ml) at -78 °C. After stirring for 1 h at rt, the reaction mixture was poured into NH₄Cl aq. at 0 °C and then extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to afford a **primary alcohol** (72 mg, 99%) as a colorless oil.

To a solution of the **primary alcohol** (167 mg, 0.57 mmol) in CH₂Cl₂ (2.5 ml) were added PhCH(OMe)₂ (0.13 ml, 0.856 mmol) and CSA (26 mg, 0.11 mmol). After stirring for 12 h at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and then extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to afford secondary alcohol **S19** (144 mg, 86%).

Secondary alcohol **S19**. IR (KBr) $\nu_{\max}$ 3537, 2973, 2939, 2868, 1456, 1373, 1309, 1216, 1118, 1100, 1085, 1023, 990, 760, 699 cm⁻¹. ¹H NMR (CDCl₃, 600 MHz) δ 1.09 (3H, d, *J* = 6.0 Hz), 1.18-1.27 (1H, m), 1.37 (3H, s), 1.56-1.62 (1H, m), 1.60-1.66 (1H, m), 1.75 (1H, dm, *J* = 13.0 Hz), 1.83-1.88 (1H, m), 2.08 (1H, dddd, *J* = 13.0, 11.5, 11.5, 5.0 Hz), 3.20 (1H, s), 3.70 (1H, dqd, *J* = 12.0, 6.0, 1.5 Hz), 3.89 (1H, dd, *J* = 11.5, 2.0 Hz), 3.94 (1H, dd, *J* = 11.0, 5.0 Hz), 3.96 (1H, ddd, *J* = 11.5, 11.5, 2.5 Hz), 4.36 (1H, dd, *J* = 11.5, 5.0 Hz), 5.48 (1H, s), 7.31-7.44 (5H, m). ¹³C NMR (CDCl₃, 150 MHz) δ 15.6, 21.7, 24.6, 27.0, 32.5, 65.6, 67.3, 67.7, 75.6, 85.5, 102.0, 125.8, 128.4, 129.0, 138.3. ESI Q-TOF MS calcd for C₁₇H₂₄NaO₄ [M+Na]⁺ 315.157, found 315.156. $[\alpha]_D^{26}$ 31.3° (*c* 1.20, CHCl₃). Anal. Calcd for C₁₇H₂₄O₄: C, 69.84; H, 8.27. Found: C, 69.87; H, 8.13.

Primary alcohol S20

To a solution of secondary alcohol **S19** (184 mg, 0.63 mmol) in CH₂Cl₂ (6.3 ml) were added Et₃N (0.35 ml, 2.52 mmol), TMSCl (0.16 ml, 1.26 mmol) and DMAP (15 mg, 0.126 mmol) at 0 °C. After stirring for 10 min at 0 °C, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and then extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to afford a **TMS-ether** (222 mg, 97%) as white crystals.

To a solution of the **TMS-ether** (31 mg, 0.085 mmol) in toluene (0.85 ml, dehydrated) was added dropwise 1.01 M DIBAL in toluene (0.84 ml, 0.85 mmol) at -78 °C under N₂ atmosphere. The reaction mixture was gradually warm up to -10 °C over 2.5 h and stirred for 4 h at -10 °C. To the reaction mixture were added 2-PrOH (1.6 ml), silica gel (3 g) and AcOEt (10 ml) at -78 °C. After stirring for 1 h at rt, the reaction mixture was passed through SuperCel[®] and concentrated to give a crude oil, which was purified by SiO₂ to afford primary alcohol **S20** (28 mg, 90%) as a colorless oil.

Primary alcohol **S20**. IR (KBr) $\nu_{\max}$ 3425, 2943, 2872, 1944, 1869, 1809, 1734, 1455, 1381, 1252, 1101, 993, 970, 903, 863, 841, 748, 734, 697 cm⁻¹. ¹H NMR (CDCl₃, 600 MHz) δ 0.08 (9H, s), 1.13 (3H, d, *J* = 6.0 Hz), 1.16 (3H, s), 1.35 (1H, dddd, *J* = 13.5, 13.0, 12.0, 4.5 Hz), 1.59-1.64 (1H, m), 1.64-1.71 (1H, m), 1.79-1.84 (1H, m), 1.86-1.96 (2H, m), 3.47 (1H, br-d, *J* = 8.0 Hz), 3.51-3.61 (1H, m), 3.68 (1H, t, *J*

= 5.0 Hz), 3.71 (1H, dqd, J = 12.0, 6.0, 2.5 Hz), 3.77-3.82 (1H, m), 4.14 (1H, dd, J = 11.0, 5.0 Hz), 4.58 (1H, d, J = 11.5 Hz), 4.62 (1H, d, J = 11.5 Hz), 7.25-7.39 (5H, m). ^{13}C NMR (CDCl_3 , 150 MHz) δ 0.9, 14.0, 21.5, 28.9, 30.5, 32.4, 58.5, 66.2, 68.6, 72.5, 80.1, 127.4, 127.7, 128.3, 138.9. ESI Q-TOF MS calcd for $\text{C}_{20}\text{H}_{34}\text{NaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$ 389.212, found 389.215. $[\alpha]_{\text{D}}^{25}$ -20.6° (c 0.60, CHCl_3). Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_4\text{Si}$: C, 65.53; H, 9.35. Found: C, 65.65; H, 9.33.

H ring-aldehyde **20**

To a solution of primary alcohol **S20** (23 mg, 0.063 mmol) in DMSO (1 ml) were added pyridine (51 μl , 0.63 mmol) and IBX (26 mg, 0.094 mmol). After stirring for 3 h at rt, the reaction mixture was diluted with H_2O (5 ml) at 0 °C. The resulting emulsion was passed through SuperCel® and washed with ether. The filtrate was extracted with ether and concentrated in vacuo. The residue was purified by SiO_2 to afford H ring-aldehyde **20** (21 mg, 91%) as a colorless oil.

H ring-aldehyde **20**. IR (KBr) ν_{max} 2942, 2870, 1719, 1456, 1375, 1252, 1101, 1028, 992, 903, 842, 747, 698 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 0.10 (9H, s), 1.09 (3H, d, J = 6.0 Hz), 1.12 (3H, s), 1.25-1.35 (1H, m), 1.58-1.64 (1H, m), 1.63-1.71 (1H, m), 1.78-1.86 (1H, m), 2.62-2.65 (2H, m), 3.63 (1H, dqd, J = 12.0, 6.0, 2.5 Hz), 3.92 (1H, t, J = 5.0 Hz), 4.12 (1H, dd, J = 11.0, 5.0 Hz), 4.65 (1H, d, J = 11.5 Hz), 4.70 (1H, d, J = 11.5 Hz), 7.22-7.41 (5H, m), 9.80 (1H, t, J = 2.5 Hz). ^{13}C NMR (CDCl_3 , 100 MHz) δ 0.9, 14.0, 21.5, 28.9, 32.7, 43.6, 66.0, 68.7, 73.0, 79.3, 79.5, 127.5, 127.7, 128.3, 138.6, 202.3. ESI Q-TOF MS calcd for $\text{C}_{20}\text{H}_{32}\text{NaO}_4\text{Si}$ $[\text{M}+\text{Na}]^+$ 387.197, found 387.194. $[\alpha]_{\text{D}}^{27}$ -18.1° (c 1.00, CHCl_3). Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{O}_4\text{Si}$: C, 65.89; H, 8.85. Found: C, 65.88; H, 8.57.

Hydroxy-vinylsilane **6** (Main Text)

To a solution of cobalt complex **7** (34 mg, 0.040 mmol) in 1,2-dichloroethane (4 ml) were added Et_3SiH (0.063 ml, 0.40 mmol) and bistrimethylsilylacetylene (0.18 ml, 0.79 mmol). Additional Et_3SiH (0.063 ml x 4, 1.60 mmol) was added until cobalt complex **12** was consumed. After stirring for 4 h at 65 °C under N_2 atmosphere, the reaction mixture was concentrated to give a crude oil, which was purified by SiO_2 to afford a vinylsilane (22 mg, 81%).

To a solution of the vinylsilane (22 mg, 0.032 mmol) in MeOH (1 ml) was added K_2CO_3 (5 mg, 0.036 mmol). After stirring for 3 h at rt, the reaction mixture was poured into NH_4Cl aq. at 0 °C and then extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by PTLC to afford hydroxy-vinylsilane **6** (20 mg, 95%).

Hydroxy-vinylsilane **6**. IR (KBr) ν_{max} 3447, 2950, 2873, 1637, 1455, 1374, 1327, 1264, 1208, 1091, 1074, 1013, 748, 734, 698 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 0.57 (6H, q, J = 7.5 Hz), 0.91 (9H, t, J = 7.5 Hz), 1.27-1.38 (1H, m), 1.36-1.45 (1H, m), 1.44-1.53 (1H, m), 1.51-1.57 (2H, m), 1.67-1.77 (2H, m), 1.94-2.03 (2H, m), 2.05-2.16 (2H, m), 2.56-2.77 (1H, br), 3.04 (1H, ddd, J = 9.5, 4.0, 4.0 Hz), 3.06 (1H, s), 3.21 (1H, ddd, J = 9.5, 4.5, 4.5 Hz), 3.23 (1H, ddd, J = 11.0, 7.5, 3.0 Hz), 3.39 (1H, dd, J = 10.0, 4.5 Hz), 3.41 (1H, dd, J = 9.5, 3.5 Hz), 3.49 (1H, dd, J = 10.0, 6.0 Hz), 3.57 (1H, dddd, J = 11.0, 6.0, 4.5, 2.0 Hz), 3.69 (1H, ddd, J = 10.0, 9.5, 4.5 Hz), 3.82 (1H, ddm, J = 11.0, 4.0 Hz), 3.92 (1H, ddd, J = 9.0, 3.5, 3.0 Hz), 4.01 (1H, br-ddm, J = 7.5, 7.5 Hz), 4.53 (1H, d, J = 12.0 Hz), 4.54 (1H, d, J = 11.5 Hz),

4.57 (1H, d, $J = 12.0$ Hz), 4.74 (1H, d, $J = 11.5$ Hz), 5.65 (1H, ddd, $J = 11.0, 10.5, 5.5$ Hz), 5.77 (1H, d, $J = 7.5$ Hz), 6.09 (1H, d, $J = 11.0$ Hz), 7.25-7.38 (10H, m). ^{13}C NMR (CDCl_3 , 100 MHz) δ 3.2, 7.4, 25.4, 27.8, 28.0, 29.2, 29.6, 36.3, 67.8, 69.6, 71.3, 72.5, 73.0, 73.4, 74.2, 74.6, 74.9, 84.7, 95.8, 127.4, 127.6, 127.6, 127.7, 128.3, 128.4, 139.1, 140.6, 151.6. $[\alpha]_{\text{D}}^{27} -105.9^\circ$ (c 0.11, CHCl_3). Anal. Calcd for $\text{C}_{39}\text{H}_{56}\text{O}_6\text{Si}$: C, 72.18; H, 8.70. Found: C, 72.19; H, 8.81.

Bromide 15

To a solution of the hydroxy-vinylsilane **6** (17 mg, 0.026 mmol) in CH_2Cl_2 (2.6 ml) was added TBCO (32 mg, 0.079 mmol) at 0°C . After stirring for 1.5 h at 0°C under N_2 atmosphere in the dark, the reaction mixture was poured into 1N-NaOH aq. at 0°C and then extracted with CH_2Cl_2 . The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to afford an bromide **15** (19 mg, 100%).

Bromide **15**. IR (KBr) ν_{max} 2926, 2855, 1735, 1647, 1456, 1376, 1097, 1076, 1003, 733, 697 cm^{-1} . ^1H NMR (CDCl_3 , 600 MHz) δ 0.66 (6H, q, $J = 7.5$ Hz), 0.92 (9H, t, $J = 7.5$ Hz), 1.38-1.44 (1H, m), 1.43-1.49 (1H, m), 1.47-1.58 (1H, m), 1.64 (1H, dm, $J = 14.0$ Hz), 1.74 (1H, dddddd, $J = 14.0, 13.5, 12.5, 5.0, 4.5$ Hz), 1.83 (1H, dm, $J = 13.0$ Hz), 1.88 (1H, ddd, $J = 16.0, 11.5, 6.0$ Hz), 2.06 (1H, ddd, $J = 13.0, 4.5, 1.0$ Hz), 2.07-2.12 (1H, m), 2.18 (1H, dd, $J = 16.0, 9.0$ Hz), 2.84 (1H, ddd, $J = 16.0, 8.5, 8.0$ Hz), 3.18 (1H, dd, $J = 9.0, 9.0$ Hz), 3.21 (1H, ddd, $J = 9.5, 9.0, 4.0$ Hz), 3.34 (1H, ddd, $J = 12.5, 11.5, 2.5$ Hz), 3.48 (1H, dd, $J = 10.0, 5.0$ Hz), 3.49 (1H, ddd, $J = 10.5, 9.0, 8.5$ Hz), 3.59 (1H, dd, $J = 10.0, 4.5$ Hz), 3.59-3.63 (1H, m), 3.61-3.67 (1H, m), 3.89 (1H, dd, $J = 11.5, 4.5$ Hz), 4.08 (1H, ddd, $J = 10.5, 10.5, 4.5$ Hz), 4.58 (2H, s), 4.67 (1H, d, $J = 12.0$ Hz), 4.74 (1H, dm, $J = 8.5$ Hz), 4.77 (1H, ddd, $J = 6.0, 5.0, 1.0$ Hz), 4.85 (1H, dm, $J = 2.0$ Hz), 4.85 (1H, d, $J = 12.0$ Hz), 5.67 (1H, dd, $J = 5.0, 2.0$ Hz), 7.24-7.36 (10H, m). ^{13}C NMR (CDCl_3 , 150 MHz) δ 4.5, 7.8, 25.1, 27.9, 29.7, 30.7, 37.1, 37.6, 47.8, 68.1, 69.7, 69.8, 71.6, 72.7, 73.0, 73.4, 73.7, 74.6, 74.7, 76.6, 84.5, 127.5, 127.6, 127.8, 128.3, 128.4, 137.5, 138.4, 138.8. HRMS (FAB) calcd for $\text{C}_{39}\text{H}_{56}\text{BrO}_6\text{Si}$ $[\text{M}+\text{H}]^+$ 727.3030, found 727.3032. $[\alpha]_{\text{D}}^{27} +51.6^\circ$ (c 0.70, CHCl_3).

E'FH ring 22

To a solution of E' ring-enyne **9** (25 mg, 0.105 mmol), which was dried in advance with benzene-azeotrope, in dry THF (1 ml) was added dropwise 1.59 M *n*-BuLi in Hexane (0.060 ml, 0.096 mmol) at -78°C under N_2 atmosphere. After stirring for 30 min at -78°C , a solution of H ring-aldehyde **20** (25 mg, 0.069 mmol), which was dried in advance with benzene-azeotrope, in dry THF (1 ml) was added to the reaction mixture. After stirring for 30 min at -78°C , the reaction mixture was poured into NH_4Cl aq. at 0°C and then extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by SiO_2 to afford an propargyl alcohol (30 mg, 73%) as a colorless oil, recovered E' ring-enyne **9** (10 mg, 40%) and recovered H ring-aldehyde **20** (4 mg, 16%).

To a solution of the propargyl alcohol (30 mg, 0.050 mmol) in MeOH (0.5 ml) was added K_2CO_3 (35 mg, 0.249 mmol). After stirring for 6 h at rt, the reaction mixture was poured into NH_4Cl aq. at 0°C and then

extracted with ether. The combined organic layer was washed with brine, dried over Na₂SO₄ and concentrated in vacuo to give a crude **diol**, which was purified by short SiO₂ and used in next step.

To a solution of the **diol** in CH₂Cl₂ (1 ml) were added pyridine (0.2 ml), Ac₂O (0.1 ml) and DMAP (5 mg). After stirring for 10 h at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and then extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by short SiO₂ to afford a crude **diacetate**.

To a solution of the crude **diacetate** in MeOH (1 ml) was added PPTS (10 mg). After stirring for 1.5 h at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and then extracted with AcOEt. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by short SiO₂ to afford a crude **alcohol**.

To a solution of the crude **alcohol** in dry CH₂Cl₂ (1 ml) was added a solution of Co₂(CO)₈ (34 mg, 0.10 mmol) in dry CH₂Cl₂ (1 ml) at 0 °C under N₂ atmosphere. After stirring for 1 h at rt, the solvent was concentrated. The residue was purified by SiO₂ to afford acetylene cobalt complex **22** (37 mg, 90% in four steps) as a reddish brown oil.

To a solution of acetylene cobalt complex **21** (31 mg, 0.037 mmol) in dry CH₂Cl₂ (7.5 ml) was added a TsOH•H₂O (13 mg, 0.075 mmol) at 0 °C under N₂ atmosphere. After stirring for 1 h at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and then extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by SiO₂ to afford E'FH ring **22** (25 mg, 86%) as a reddish brown oil.

E'FH ring **22**. IR (KBr) $\nu_{\max}$ 2935, 2854, 2089, 2050, 2025, 1744, 1560, 1457, 1374, 1240, 1095, 1044, 736, 661, 515, 497 cm⁻¹. ¹H NMR (CDCl₃, 600 MHz) δ 1.12 (3H, d, *J* = 6.0 Hz), 1.30 (3H, s), 1.31-1.40 (1H, m), 1.39-1.49 (1H, m), 1.53-1.56 (2H, m), 1.59-1.63 (1H, m), 1.63-1.68 (1H, m), 1.80-1.84 (1H, m), 1.88 (1H, ddd, *J* = 14.5, 10.5, 1.5 Hz), 1.99 (3H, s), 2.05-2.09 (1H, m), 2.18 (1H, ddd, *J* = 14.5, 10.0, 1.0 Hz), 2.32 (1H, ddd, *J* = 13.0, 7.5, 5.0 Hz), 2.68 (1H, ddm, *J* = 13.0, 9.5 Hz), 3.17-3.22 (1H, m), 3.31 (1H, ddd, *J* = 12.0, 12.0, 2.0 Hz), 3.31-3.34 (1H, m), 3.62 (1H, dd, *J* = 10.0, 1.5 Hz), 3.71 (1H, dqd, *J* = 12.0, 6.0, 2.0 Hz), 3.84 (1H, dm, *J* = 12.0 Hz), 4.64 (1H, d, *J* = 12.0 Hz), 4.84 (1H, dd, *J* = 10.5, 1.0 Hz), 4.85 (1H, d, *J* = 12.0 Hz), 4.99 (1H, dd, *J* = 11.0, 5.0 Hz), 5.86 (1H, ddd, *J* = 10.5, 9.5, 7.5 Hz), 6.73 (1H, d, *J* = 10.5 Hz), 7.20-7.32 (5H, m). ¹³C NMR (CDCl₃, 100 MHz) δ 13.6, 21.4, 21.6, 25.2, 25.5, 29.3, 29.9, 32.4, 39.0, 65.7, 67.9, 71.4, 73.4, 73.8, 77.5, 78.2, 80.1, 81.5, 86.9, 100.5, 127.1, 127.2, 128.2, 130.6, 139.5, 169.9, 196.2, 199.3, 199.8. HRMS (FAB) calcd for C₃₅H₃₉Co₂O₁₂ [M+H]⁺ 769.1105, found 769.1098. [α]_D²⁷ -560.9° (*c* 0.02, CHCl₃).

Acetylene cobalt complex **24**

To a solution of acetylene cobalt complex **21** (2.6 mg, 0.0031 mmol) in dry CH₂Cl₂ (0.6 ml) was added BF₃•OEt₂ (0.20 M in 1,2-dichloroethane, 0.015 ml, 0.0031 mmol) at 0 °C under N₂ atmosphere. After stirring for 6 min at 0 °C and for 8 min at rt, the reaction mixture was poured into NaHCO₃ aq. at 0 °C and then extracted with CH₂Cl₂. The combined organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by PTLC to afford E'FH' ring **22** (1.2 mg, 50%) and acetylene cobalt complex **24** (0.7 mg, 33%).

Acetylene cobalt complex **24**. IR (KBr) $\nu_{\max}$ 3504, 2935, 2853, 2086, 2047, 2017, 1744, 1718, 1560, 1457, 1374, 1243, 1095, 1045, 522 cm^{-1} . ^1H NMR (CDCl_3 , 600 MHz) δ 1.12 (3H, d, $J = 6.0$ Hz), 1.18 (3H, s), 1.34-1.40 (1H, m), 1.39-1.46 (1H, m), 1.62-1.71 (2H, m), 1.67-1.69 (2H, m), 1.79-1.86 (1H, m), 1.86-1.93 (1H, m), 1.96-2.00 (1H, m), 2.04 (3H, s), 2.07-2.11 (1H, m), 2.32 (1H, dddd, $J = 15.5, 9.0, 6.0, 1.5$ Hz), 2.77 (1H, d, $J = 5.5$ Hz), 2.90 (1H, ddm, $J = 15.5, 8.0$ Hz), 3.00 (1H, ddd, $J = 15.0, 11.5, 5.5$ Hz), 3.07 (1H, d, $J = 7.5$ Hz), 3.08 (1H, ddd, $J = 9.0, 9.0, 3.0$ Hz), 3.32 (1H, ddd, $J = 11.0, 11.0, 4.0$ Hz), 3.33-3.38 (1H, m), 3.42 (1H, ddd, $J = 10.5, 7.5, 2.5$ Hz), 3.46 (1H, ddd, $J = 15.0, 11.5, 4.0$ Hz), 3.70 (1H, dqd, $J = 12.0, 6.0, 2.0$ Hz), 3.90 (1H, dm, $J = 11.5$ Hz), 5.04 (1H, dd, $J = 11.0, 5.0$ Hz), 5.94 (1H, ddd, $J = 10.5, 8.0, 6.0$ Hz), 6.44 (1H, d, $J = 10.5$ Hz). ^{13}C NMR (CDCl_3 , 150 MHz) δ 13.4, 21.3, 21.6, 24.9, 25.7, 32.3, 32.4, 32.7, 33.2, 66.2, 67.7, 70.5, 70.7, 74.3, 81.8, 85.7, 99.2, 127.2, 131.4, 170.6, 200.1, 206.6. HRMS (FAB) calcd for $\text{C}_{28}\text{H}_{35}\text{Co}_2\text{O}_{12}$ $[\text{M}+\text{H}]^+$ 681.0792, found 681.0814. $[\alpha]_{\text{D}}^{27} +22.0^\circ$ (c 0.02, CHCl_3).

Ketone **25** (Conjugate enone **26** and Diene **27**)

In a PORTABLE REACTOR (TVS-N2 type, TAIATSU TECHNO[®] CORPORATION, Japan) was placed a solution of acetylene cobalt complex **22** (9.0 mg, 0.012 mmol) in hexane (12 ml). After stirring for 9 h at 65 $^\circ\text{C}$ under 100 kg/cm^2 H_2 atmosphere, the pressure was reduced to ambient pressure at rt. The reaction mixture was passed through SuperCel[®] and concentrated to give a crude oil, which was purified by PTLC to afford ketone **25** (2.7 mg, 46%), conjugate enone **26** (0.4 mg, 7%), and diene **27** (0.7 mg, 12%).

Ketone **25**. IR (KBr) $\nu_{\max}$ 3030, 2936, 2854, 1741, 1717, 1447, 1374, 1241, 1094, 1033, 993, 749, 737, 698, 620 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 1.11 (3H, d, $J = 6.0$ Hz), 1.25-1.33 (1H, m), 1.28 (3H, s), 1.29-1.40 (1H, m), 1.36-1.54 (2H, m), 1.57-1.63 (1H, m), 1.61-1.67 (1H, m), 1.79-1.83 (2H, m), 1.91 (3H, s), 1.96-2.03 (2H, m), 2.22 (1H, ddd, $J = 13.5, 6.0, 3.0$ Hz), 2.58 (1H, dd, $J = 10.5, 7.0$ Hz), 2.97 (1H, dd, $J = 13.5, 10.5, 4.0$ Hz), 2.98 (1H, ddd, $J = 13.0, 8.0, 4.0$ Hz), 3.29 (1H, ddd, $J = 11.5, 11.5, 3.0$ Hz), 3.31 (1H, ddd, $J = 8.0, 4.0, 3.0$ Hz), 3.52-3.55 (1H, m), 3.68 (1H, dqd, $J = 11.5, 6.0, 2.0$ Hz), 3.83 (1H, ddm, $J = 11.5, 4.5$ Hz), 3.94 (1H, dd, $J = 6.5, 5.5$ Hz), 3.97 (1H, dd, $J = 10.5, 10.5$ Hz), 4.57 (1H, d, $J = 11.5$ Hz), 4.71 (1H, d, $J = 11.5$ Hz), 4.97 (1H, dd, $J = 11.0, 5.0$ Hz), 5.64 (1H, ddd, $J = 10.5, 10.5, 7.0$ Hz), 5.71 (1H, ddd, $J = 10.5, 10.5, 6.0$ Hz), 7.22-7.36 (5H, m). ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.0, 21.3, 21.8, 25.3, 25.5, 28.7, 29.4, 32.4, 32.9, 36.8, 65.8, 68.2, 70.6, 72.9, 75.0, 78.2, 78.8, 80.4, 82.1, 124.7, 127.3, 127.5, 128.2, 128.7, 139.0, 170.0, 211.8. HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{41}\text{O}_7$ $[\text{M}+\text{H}]^+$ 501.2852, found 501.2859. $[\alpha]_{\text{D}}^{27} +189.8^\circ$ (c 0.29, CHCl_3).

Conjugate enone **26**. IR (KBr) $\nu_{\max}$ 2933, 2852, 1740, 1653, 1457, 1374, 1242, 1093, 1035, 736, 699 cm^{-1} . ^1H NMR (CDCl_3 , 600 MHz) δ 1.11 (3H, d, $J = 6.0$ Hz), 1.25 (3H, s), 1.34 (1H, dddd, $J = 13.5, 13.5, 11.5, 4.5$ Hz), 1.43 (1H, dddd, $J = 13.5, 13.5, 11.5, 4.5$ Hz), 1.48-1.57 (2H, m), 1.55-1.60 (1H, m), 1.58-1.62 (1H, m), 1.60-1.65 (1H, m), 1.67 (1H, ddd, $J = 14.5, 9.5, 3.0$ Hz), 1.89-1.94 (1H, m), 1.94 (3H, s), 1.97-2.03 (1H, m), 2.69 (1H, dd, $J = 13.5, 5.5$ Hz), 2.74 (1H, ddd, $J = 13.5, 9.5, 7.5$ Hz), 2.80 (1H, br-dd, $J = 13.5, 9.5$ Hz), 3.06 (1H, br-dd, $J = 13.5, 3.0$ Hz), 3.09 (1H, ddd, $J = 10.5, 9.0, 4.5$ Hz), 3.23 (1H, ddd, $J = 9.5, 7.5, 2.5$ Hz), 3.31 (1H, ddd, $J = 11.5, 11.5, 2.5$ Hz), 3.50 (1H, dd, $J = 9.5, 2.5$ Hz), 3.67 (1H, dqd, $J = 11.5, 6.5, 2.5$ Hz), 3.84 (1H, ddm, $J = 11.5, 4.5$ Hz), 3.95 (1H, dddd, $J = 10.0, 5.5, 3.0, 3.0$

Hz), 4.59 (1H, d, $J = 11.5$ Hz), 4.77 (1H, d, $J = 11.5$ Hz), 4.86 (1H, dd, $J = 11.0, 5.5$ Hz), 6.05 (1H, d, $J = 12.0$ Hz), 6.32 (1H, ddd, $J = 12.0, 9.5, 9.5$ Hz), 7.25-7.35 (5H, m). ^{13}C NMR (CDCl_3 , 150 MHz) δ 13.4, 21.4, 21.8, 25.3, 25.7, 30.8, 32.4, 36.8, 50.0, 65.6, 68.0, 70.9, 73.8, 75.2, 78.5, 79.8, 81.6, 127.3, 127.7, 128.3, 134.4, 139.2, 139.8, 170.1, 202.3. HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{41}\text{O}_7$ $[\text{M}+\text{H}]^+$ 501.2852, found 501.2851. $[\alpha]_{\text{D}}^{27} +104.8^\circ$ (c 0.06, CHCl_3).

Diene **27**. IR (KBr) ν_{max} 2934, 2851, 1743, 1456, 1374, 1243, 1143, 1091, 1046, 1030, 993, 737, 698 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 1.11 (3H, d, $J = 6.0$ Hz), 1.25 (3H, s), 1.34-1.41 (1H, m), 1.38-1.47 (1H, m), 1.48-1.58 (2H, m), 1.57-1.68 (2H, m), 1.77 (1H, ddd, $J = 15.0, 9.0, 3.0$ Hz), 1.86 (1H, ddd, $J = 15.0, 10.0, 2.5$ Hz), 1.93 (3H, s), 1.96-2.03 (1H, m), 2.00-2.10 (1H, m), 2.14-2.21 (1H, m), 2.76 (1H, ddd, $J = 14.0, 11.0, 3.5$ Hz), 3.08 (1H, ddd, $J = 9.5, 4.0, 3.5$ Hz), 3.15 (1H, ddd, $J = 10.5, 9.5, 4.0$ Hz), 3.27 (1H, ddd, $J = 11.5, 11.5, 3.0$ Hz), 3.53 (1H, dd, $J = 9.0, 2.5$ Hz), 3.68 (1H, dqd, $J = 9.5, 6.0, 2.0$ Hz), 3.84 (1H, dddd, $J = 11.5, 4.5, 1.5, 1.5$ Hz), 3.92 (1H, ddd, $J = 10.0, 7.5, 3.0$ Hz), 4.57 (1H, d, $J = 11.5$ Hz), 4.64 (1H, d, $J = 11.5$ Hz), 5.05 (1H, dd, $J = 11.0, 5.0$ Hz), 5.60 (1H, ddd, $J = 11.5, 7.5, 2.0$ Hz), 5.76 (1H, dddd, $J = 11.5, 11.0, 6.0, 2.0$ Hz), 5.95 (1H, dm, $J = 11.5$ Hz), 5.98 (1H, dm, $J = 11.5$ Hz), 7.24-7.35 (5H, m). ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.6, 21.3, 21.8, 25.0, 26.2, 31.8, 32.5, 33.1, 37.2, 65.8, 67.9, 70.8, 72.3, 78.1, 78.9, 80.2, 80.5, 81.0, 127.4, 127.8, 128.3, 129.6, 129.8, 130.1, 135.1, 139.1, 170.0. HRMS (FAB) calcd for $\text{C}_{29}\text{H}_{41}\text{O}_6$ $[\text{M}+\text{H}]^+$ 485.2903, found 485.2917. $[\alpha]_{\text{D}}^{27} -45.1^\circ$ (c 0.10, CHCl_3).

E'FGH ring 28

To a solution of ketone **25** (4.0 mg, 0.0080 mmol) in MeOH (0.8 ml) was added K_2CO_3 (11 mg, 0.080 mmol). After stirring for 7 h at rt, the reaction mixture was poured into NH_4Cl aq. at 0°C and then extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by PTLC to afford a **hydroxy-ketone** (3.6 mg, 97%).

To a solution of the **hydroxy-ketone** (3.0 mg, 0.0065 mmol) and Et_3SiH (0.052 ml, 0.33 mmol) in dry CH_3CN (1.3 ml) was added $\text{BF}_3\cdot\text{OEt}_2$ (0.79 M in 1,2-dichloroethane, 0.083 ml, 0.065 mmol) at -15°C under N_2 atmosphere. After stirring for 10 min at 0°C and for 30 min at rt, the reaction mixture was poured into NaHCO_3 aq. at 0°C and then extracted with ether. The combined organic layer was washed with brine, dried over Na_2SO_4 , and concentrated in vacuo. The residue was purified by PTLC to afford E'FGH ring **28** (2.1 mg, 72%).

E'FGH ring **28**. IR (KBr) ν_{max} 2930, 2850, 1734, 1456, 1381, 1340, 1141, 1089, 966, 735, 697 cm^{-1} . ^1H NMR (pyridine- d_5 , 600 MHz, -20°C , major conformer) δ 1.07 (3H, d, $J = 5.5$ Hz), 1.12-1.21 (1H, m), 1.40-1.46 (2H, m), 1.41 (3H, s), 1.44-1.50 (2H, m), 1.67-1.72 (1H, m), 1.72-1.77 (1H, m), 1.98-2.03 (1H, m), 2.10-2.15 (1H, m), 2.13-2.18 (1H, m), 2.27-2.32 (1H, m), 2.32-2.38 (1H, m), 2.82-2.88 (1H, m), 2.91-2.98 (1H, m), 3.12 (1H, dd, $J = 11.5, 11.5$ Hz), 3.15-3.19 (1H, m), 3.18 (1H, dd, $J = 11.0, 4.5$ Hz), 3.25 (1H, dd, $J = 9.0, 5.0$ Hz), 3.50-3.57 (2H, m), 3.72-3.76 (1H, m), 3.77 (1H, br-dd, $J = 11.5, 3.5$ Hz), 3.83 (1H, dd, $J = 7.5, 5.5$ Hz), 4.76 (1H, d, $J = 12.0$ Hz), 4.97 (1H, d, $J = 12.0$ Hz), 5.81-5.88 (2H, m), 7.28-7.61 (5H, m, aromatic). ^1H NMR (CDCl_3 , 400 MHz, -20°C , a 1:1 mixture of DOWN and UP conformers) δ 1.16 (3Hx1/2, d, $J = 6.0$ Hz), 1.17 (3Hx1/2, d, $J = 6.0$ Hz), 1.26 (3Hx1/2, s), 1.27 (3Hx1/2,

s), 1.27-1.33 (1H, m), 1.40-1.51 (1H, m), 1.60-1.70 (2H, m), 1.70-1.82 (2H, m), 1.70-1.82 (1H, m), 2.04-2.10 (1H, m), 2.08-2.12 (1H, m), 2.10-2.15 (1Hx1/2, m), 2.12-2.23 (2H, m), 2.20-2.25 (1Hx1/2, m), 2.68-2.75 (1Hx1/2, m), 2.74-2.80 (1Hx1/2, m), 2.78-2.83 (1Hx1/2, m), 2.85-2.98 (1Hx1/2, m), 3.00 (1Hx1/2, dd, $J = 10.0, 10.0$ Hz), 3.15-3.19 (3Hx1/2, m), 3.22-3.29 (1Hx1/2, m), 3.30-3.40 (1H, m), 3.34-3.45 (3Hx1/2, m), 3.61-3.69 (1H, m), 3.65-3.71 (1Hx1/2, m), 3.68-3.72 (1Hx1/2, m), 3.70-3.80 (1H, m), 3.90 (1H, dm, $J = 11.5$ Hz), 4.14 (1Hx1/2, d, $J = 12.0$ Hz), 4.17 (1Hx1/2, d, $J = 12.0$ Hz), 4.30 (1Hx1/2, d, $J = 12.0$ Hz), 4.33 (1Hx1/2, d, $J = 12.0$ Hz), 5.68-5.79 (2H, m), 7.30-7.44 (5H, m). ^{13}C NMR (pyridine- d_5 , 150 MHz, -20 °C, major conformer) δ 11.4, 21.9, 26.2, 27.3, 31.2, 32.5, 32.6, 33.5, 39.7, 64.7, 68.0, 73.3, 80.8, 81.1, 81.4, 82.3, 82.9, 83.1, 85.6, 127.5, 127.9, 128.5, 128.6, 128.7, 140.3. HRMS (FAB) calcd for $\text{C}_{27}\text{H}_{38}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$ 465.2617, found 465.2628. $[\alpha]_{\text{D}}^{27}$ -4.19° (c 0.10, CHCl_3).

The parameters of conformer **A**, **B**, **C** and **D** calcd by Macromodel (in kJ/mol).

Conformer	A	B	C	D
Total Energy	57.54	62.81	55.92	76.29
Stretch	13.44	13.67	13.62	14.16
Bend	57.20	58.15	50.27	51.94
Prop Torsion	67.15	67.67	73.10	14.30
Improp Torsion	0.03	0.03	0.03	0.03
Electrostatic	-206.15	-205.92	-204.29	-202.05
Cross Terms	5.21	5.52	5.18	5.47
van der Waals	120.66	123.69	118.01	132.44
Solvation	0.00	0.00	0.00	0.00

The parameters of conformer **X** and **Y** calcd by Macromodel (in kJ/mol).

conformer	X	Y
Total Energy	96.62	92.16
Stretch	15.32	15.05
Bend	58.66	57.92
Prop Torsion	85.26	84.75
Improp Torsion	0.03	0.03
Electrostatic	-178.77	-178.19
Cross Terms	5.98	5.66
van der Waals	110.15	106.95
Solvation	0.00	0.00

Solvent: CDCl₃
Ambient temperature
GEMINI 300 "varian"

PULSE SEQUENCE
Pulse 35.0 degrees
Acq. time 1.697 sec
Width 18857.7 Hz
384 repetitions

OBSERVE C13, 75.4233443 MHz
DECOUPLE H1, 299.9549185 MHz
Power 30 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 10 minutes

exp1 std1h

SAMPLE DEC. & VT
 date Apr 24 01 dfrq 299.945
 solvent CDCl3 dn H1
 file exp dof -10000.0
 ACQUISITION dm nnn
 sfrq 299.955 dmm c
 tn H1 dmf 200
 at 3.748
 np 33728 wtfile
 sw 4499.3 proc ft
 fb 2250 fn not used
 bs 15
 pw 6.0 werr react
 d1 0.252 wexp autolist('ent~
 tuf 149.3 erJ', 'h1_process_v~
 nt 15 962')
 ct 15 wbs
 alock n wnt
 gain not used

FLAGS
 il n
 in n
 dp y

DISPLAY
 sp -60.0
 wp 3119.5
 vs 1630
 sc 0
 wc 400
 hzmm 7.00
 is 8103.19
 rfl 596.2
 rfp 0
 th 2
 ins 1.000
 a1 cdc ph

Solvent: CDCl₃
Ambient temperature
GEMINI-300 "varian"

PULSE SEQUENCE
Pulse 35.0 degrees
Acq. time 1.697 sec
Width 18857.7 Hz
48 repetitions

OBSERVE C13, 75.4233469 MHz
DECOUPLE H1, 299.9549165 MHz
Power 30 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 minute

exp1 stdin

SAMPLE DEC. & VT
date Dec 21 01 dfrq 299.945
solvent CDCl3 dn H1
file exp dsf -10000.0
ACQUISITION dn nnn
sfrq 299.955 dnm c
tn H1 dnf 200
at 3.748 PROCESSING
np 33726 wtfile
sw 4499.3 proc ft
fb 2250 fn not used
bs 16
pw 3.0 warr react
d1 0.252 wexp autolist('ent'
tof 149.3 enj', 'h1_process_u'
nt 16 1082')
ct 16 wds
alock n wnt
gain not used

FLAGS

il n
in n
dp y

DISPLAY

sp -60.0
wp 3119.5
vs 1289
sc 0
wc 400
hzmm 7.80
is 4843.59
rfl 2771.6
rfo 2171.7
tn 2
ins 1.000
ai cdc ph

Solvent: CDCl₃
Ambient temperature
GEMINI-300 "varian"

PULSE SEQUENCE
Pulse 35.0 degrees
Acq. time 1.697 sec
Width 18957.7 Hz
16 repetitions

OBSERVE C13, 75.4233529 MHz
DECOUPLE H1, 299.9549185 MHz
Power 30 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 minute

exp1 std1h

SAMPLE DEC. & VT
date May 5 01 dfrq 299.945
solvent CDC13 dn H1
file exp dof -10000.0
ACQUISITION dm nnn
sfrq 299.955 dmm c
tn H1 dmf 200
at 3.748 PROCESSING
np 33728 wfile
sw 4499.3 proc ft
fb 2250 fn not used
bs 16
pw 6.0 werr react
d1 0.252 wexp autolist('ent'
tof 149.3 erJ', 'h1_process_u'
nt 16 968')
t 16 wbs
alock n wnt
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -60.0
wp 3119.5
vs 945
sc 0
wc 400
hzmm 7.80
is 4538.47
rfl 2771.6
rfp 2171.7
th 2
ins 1.000
ai cdc ph

Solvent: CDCl₃
Ambient temperature
GEMINI-300 "varian"

PULSE SEQUENCE

Pulse 35.0 degrees
Acq. time 1.697 sec
Width 18857.7 Hz
32 repetitions

OBSERVE C13, 75.4233501 MHz

DECOUPLE H1, 299.9549185 MHz

Power 30 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 65536

Total time 1 minute

ST9079 1H CDCL3

Current Data Parameters

NAME shige400-3
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters

Date 500000
Time 11.28
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 Hz
DW 500000.0 usec
RG 715
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SFO1 400.1368000 MHz
SWH 6410.26 Hz
TD 32768
NS 16
DS 2

F2 - Processing parameters

SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ST9079 13C CDCL3

Current Data Parameters
 NAME shige400-3
 EXPNO 12
 PROCNO 2

F2 - Acquisition Parameters
 Date 500000
 Time 11.28
 PULPROG zgpgdc
 SOLVENT CDCL3
 AQ 1.4418120 sec
 FIDRES 0.346791 Hz
 DW 500000.0 usec
 RG 22800
 NUCLEUS 13C
 DI2 0.0000200 sec
 DL5 23.00 dB
 P31 100.0 usec
 D1 0.6000000 sec
 P0 3.9 usec
 DE 27.5 usec
 SFO1 100.6239300 MHz
 SWH 22727.27 Hz
 TD 65536
 NS 14533
 DS 2
 D11 0.0300000 sec

F2 - Processing parameters
 SI 32768
 SF 100.6138717 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.00

ST9107-1 1H CDCL3

S16

Current Data Parameters
NAME shige400-3
EXPNO 70
PROCNO 1

F2 - Acquisition Parameters
Date_ 701225
Time 17.28
INSTRUM ARX400
PROBHD 5 mm QNP 1H
PULPROG zg0
TD 32768
SOLVENT CDCL3
NS 16
DS 2
SWH 6410.256 Hz
FIDRES 0.195625 Hz
AQ 2.5559540 sec
RG 1024
DW 78.000 usec
DE 97.50 usec
TE 300.0 K

F2 - Processing parameters
SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ST9107-1 13C CDCL3

Current Data Parameters
 NAME shige400-3
 EXPNO 75
 PROCNO 2

F2 - Acquisition Parameters
 Date 500000
 Time 11.28
 PULPROG zg0dc
 SOLVENT CDCL3
 AQ 1.3762760 sec
 FIDRES 0.363304 Hz
 DW 500000.0 usec
 RG 22800
 NUCLEUS 13C
 D12 0.0000200 sec
 DL5 23.00 dB
 P31 100.0 usec
 D1 0.6000000 sec
 P0 3.9 usec
 DE 26.2 usec
 SF01 100.6239300 MHz
 SWH 23809.52 Hz
 TD 65536
 NS 4453
 DS 2
 D11 0.0300000 sec

F2 - Processing parameters
 SI 32768
 SF 100.6138714 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.00

ST9112 1H CDCL3

Current Data Parameter
NAME shige400-3
EXPNO 80
PROCNO 1

F2 - Acquisition Parameter
Date 710106
Time 21.56
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 Hz
DW 78.0 usec
RG 1024
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SFO1 400.1368000 MHz
SWH 6410.26 Hz
TD 32768
NS 32
DS 2

F2 - Processing parameter
SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 34.20 cm
F1P 8.500 ppm
F1 3401.14 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.27778 Hz
HZCM 111.14845 Hz

ST9112 13C CDCL3

Current Data Parameter
 NAME shige400-3
 EXPNO 83
 PROCNO 2

F2 - Acquisition Parameter
 Date 710107
 Time 13.52
 PULPROG zgpg30
 SOLVENT CDCL3
 AQ 1.3762760 sec
 FIDRES 0.363304 Hz
 DW 21.0 usec
 RG 22800
 NUCLEUS 13C
 D12 0.0000200 sec
 DL5 23.00 dB
 P31 100.0 usec
 D1 0.6000000 sec
 P0 3.9 usec
 DE 26.3 usec
 SFO1 100.6239300 MHz
 SWH 23809.52 Hz
 TD 65536
 NS 18447
 DS 2
 D11 0.0300000 sec

F2 - Processing parameter
 SI 32768
 SF 100.6138714 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameter
 CX 33.90 cm
 F1P 218.294 ppm
 F1 21963.37 Hz
 F2P -18.349 ppm
 F2 -1846.15 Hz
 PPMCM 6.98061 Hz
 HZCM 702.34583 Hz

ST10069-1 1H CDCL3

Current Data Parameter
NAME shige400-3
EXPNO 160
PROCNO 1

F2 - Acquisition Parameter
Date_ 710324
Time 4.16
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 Hz
DW 78.0 usec
RG 360
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SFO1 400.1368000 MHz
SWH 6410.26 Hz
TD 32768
NS 16
DS 2

F2 - Processing parameter
SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameter
CX 34.20 cm
F1P 8.500 ppm
F1 3401.14 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.27778 Hz
HZCM 111.14845 Hz

ST10069-1 13C CDCL3

Current Data Parameter.
 NAME shige400-3
 EXPNO 163
 PROCNO 2

F2 - Acquisition Param.
 Date 710324
 Time 13.08
 PULPROG zg0dc
 SOLVENT CDCL3
 AQ 1.4418120 sec
 FIDRES 0.346791 Hz
 DW 22.0 usec
 RG 22800
 NUCLEUS 13C
 D12 0.0000200 sec
 DL5 23.00 dB
 P31 100.0 usec
 D1 0.6000000 sec
 P0 3.9 usec
 DE 27.5 usec
 SFO1 100.6239300 MHz
 SWH 22727.27 Hz
 TD 65536
 NS 7134
 DS 2
 D11 0.0300000 sec

F2 - Processing parameter.
 SI 32768
 SF 100.6138766 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameter:
 CX 33.90 cm
 FIP 210.000 ppm
 F1 21128.92 Hz
 F2P -10.000 ppm
 F2 -1006.14 Hz
 PPMCM 6.48968 Hz
 HZCM 652.95135 Hz

ST10073-1 1H CDCL3

Current Data Parameter.
 NAME shige600-1
 EXPNO 140
 PROCNO 1

F2 - Acquisition Parameter
 Date_ 1020319
 Time 7.45
 INSTRUM AMX260
 PROBHD 5 mm Dual
 PULPROG zg0
 TD 32768
 SOLVENT CDCL3
 NS 16
 DS 2
 SWH 8474.576 Hz
 FIDRES 0.258624 Hz
 AQ 1.9333620 sec
 RG 1024
 DW 59.000 usec
 DE 84.29 usec
 TE 300.0 K
 HL1 2 dB
 D1 1.00000000 sec
 P0 4.10 usec
 DE 84.29 usec
 SFO1 600.1400600 MHz
 NUCLEUS 1H

F2 - Processing parameter
 SI 16384
 SF 600.1364600 MHz
 WDW EM
 SSB 0
 LB 0.10 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 33.80 cm
 F1P 8.500 ppm
 F1 5101.16 Hz
 F2P -1.000 ppm
 F2 -600.14 Hz
 PPMCM 0.28107 Hz
 HZCM 168.67741 Hz

ST10073-1 13C CDCL3

S19

Current Data Parameter:
 NAME shige600-1
 EXPNO 142
 PROCNO 2

F2 - Acquisition Param
 Date_ 1020319
 Time 8.52
 INSTRUM AMX260
 PROBHD 5 mm Dual
 PULPROG zg0dc
 TD 65536
 SOLVENT CDCL₃
 NS 2000
 DS 2
 SWH 35714.285 Hz
 FIDRES 0.544957 Hz
 AQ 0.9175540 sec
 RG 32768
 DW 14.000 usec
 DE 20.00 usec
 TE 300.0 K
 D11 0.0300000 sec
 CPDPRG waltz16
 P31 100.00 usec
 S2 25 dB
 HL1 90 dB
 D1 1.00000000 sec
 P0 5.00 usec
 DE 20.00 usec
 SFO1 150.9195300 MHz
 NUCLEUS 13C

F2 - Processing param
 SI 65536
 SF 150.9044303 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameter:
 CX 33.90 cm
 F1P 210.000 ppm
 F1 31689.93 Hz
 F2P -10.000 ppm
 F2 -1509.04 Hz
 PPMCM 6.48968 Hz
 HZCM 979.32074 Hz

Current Data Parameters
NAME shige400-3
EXPNO 180
PROCNO 1

F2 - Acquisition Parameters
Date 710328
Time 18.25
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 Hz
DW 78.0 usec
RG 715
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SF01 400.1368000 MHz
SWH 6410.26 Hz
TD 32768
NS 16
DS 2

F2 - Processing parameters
SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 34.40 cm
F1P 11.000 ppm
F1 4401.48 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.34884 ppm/ci
HZCM 139.58175 Hz/cm

ST10080 13C CDCL3

20

Current Data Parameter:
NAME shige400-3
EXPNO 185
PROCNO 2

F2 - Acquisition Parameter:
Date 710329
Time 18.55
PULPROG zg0dc
SOLVENT CDCL₃
AQ 1.4418120 sec
FTDRES 0.346791
DW 22.0 usec
RG 22800
NUCLEUS 13C
D12 0.0000200 sec
DL5 23.00 dB
P31 100.0 usec
D1 0.6000000 sec
P0 3.9 usec
DE 27.5 usec
SFO1 100.6239300 MHz
SWH 22727.27 Hz
TD 65536
NS 400
DS 2
D11 0.0300000 sec

F2 - Processing parameter:
SI 32768
SF 100.6138724 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

1D NMR plot parameter:
CX 33.90 cm
F1P 210.000 ppm
F1 21128.92 Hz
F2P -10.000 ppm
F2 -1006.14 Hz
PPMCM 6.48968
HZCM 652.95135

ST10129 1H CDCL3

Current Data Parameters
 NAME shige400-3
 EXPNO 220
 PROCNO 1

F2 - Acquisition Parameters
 Date 500000
 Time 11.28
 PULPROG zg0
 SOLVENT CDCL3
 AQ 2.5559239 sec
 FIDRES 0.195625 Hz
 DW 500000.0 usec
 RG 256
 NUCLEUS 1H
 D1 1.0000000 sec
 P0 3.0 usec
 DE 97.5 usec
 SFO1 400.1368000 MHz
 SWH 6410.26 Hz
 TD 32768
 NS 16
 DS 2

F2 - Processing parameters
 SI 16384
 SF 400.1344000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

ST10129 13C CDCL3

142.588
142.232

109.418
109.300
100.895
97.025
81.730
81.632
80.489
80.438
80.102
80.054
77.317
77.000
76.682
76.091
72.651
67.690
60.047
59.587
33.189
33.051
31.325
29.837
25.517
25.213
24.554
20.604
20.264
15.283

Current Data Parameters
NAME shige400-3
EXPNO 221
PROCNO 2

F2 - Acquisition Parameters
Date 500000
Time 11.28
PULPROG zg0dc
SOLVENT CDCL3
AQ 1.4418120 sec
FIDRES 0.346791 Hz
DW 500000.0 usec
RG 22800
NUCLEUS 13C
D12 0.0000200 sec
DL5 23.00 dB
P31 100.0 usec
D1 0.6000000 sec
P0 3.9 usec
DE 27.5 usec
SF01 100.6239300 MHz
SWH 22727.27 Hz
TD 65536
NS 400
DS 2
D11 0.0300000 sec

F2 - Processing parameters
SI 32768
SF 100.6138738 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

exp1 std1h

SAMPLE DEC. & VT
date Nov 20 00 dfrq 299.945
solvent CDC13 dn H1
file exp dof -10000.0
ACQUISITION dm nnn
sfrq 299.955 dmm c
tn H1 dmf 200
at 3.748
np 33728 wtfile
sw 4499.3 proc ft
fb 2250 fn not used
bs 16
pw 3.0 werr react
d1 0.252 wexp autolist('ent'
tof 149.3 erJ', 'h1_process_u'
nt 16 878')
ct 16 wbs
alock n wnt
gain not used
FLAGS
il n
in n
dp y
DISPLAY
sp -60.0
wp 3119.5
vs 10020
sc 0
wc 400
hzmm 7.80
is 13938.53
rfl 615.3
rfp 0
th 22
ins 1.000
a1 cdc ph

DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 minutes

ST7015 1H CDCL3

Current Data Parameters

NAME 2D
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters

Date 710126
Time 1.19
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 Hz
DW 78.0 usec
RG 1024
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SF01 400.1368000 MHz
SWH 6410.26 Hz
TD 32768
NS 64
DS 2

F2 - Processing parameters

SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 32.20 cm
F1P 11.000 cm
F1 4401.48 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.37267 ppm/cm
HZCM 149.11841 Hz/cm

ST7015 13 C CDCL3

Current Data Parameters

NAME 2D
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters

Date 710126
Time 4.10
PULPROG zg0dc
SOLVENT CDCL3
AQ 1.4418120 sec
FIDRES 0.346791 Hz
DW 22.0 usec
RG 22800
NUCLEUS 13C
D12 0.0000200 sec
DL5 23.00 dB
P31 100.0 u
D1 0.6000000 sec
P0 3.9 usec
DE 27.5 usec
SF01 100.6239300 MHz
SWH 22727.27 Hz
TD 65536
NS 2000
DS 2
D11 0.0300000 sec

F2 - Processing parameters

SI 32768
SF 100.6138700 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 32.00 cm
F1P 212.929 ppm
F1 21423.64 Hz
F2P -12.957 ppm
F2 -1303.63 Hz
PPMCM 7.05894 ppm/cm
HZCM 710.22729 Hz/cm

ST7010 1H CDCL3

Current Data Parameters
NAME 20
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date 710126
Time 23.35
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 Hz
DQ 78.0 usec
RG 715
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SFO1 400.1368000 MHz
SWH 6410.26 Hz
TD 32768
NS 32
DS 0

F2 - Processing parameters
SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameters
CX 34.40 cm
F1P 8.000 cm
F1 3201.08 cm
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.23256 ppm/cm
HZCM 93.05450 Hz/cm

Chemical structure of compound **6** is shown above the spectrum. The structure is a complex polycyclic molecule featuring a central eight-membered ring with a double bond and a SiEt_3 group. It is substituted with a OBn group, a HO group, and a CH_2OBn group. The spectrum displays the following chemical shifts (ppm):

Chemical Shift (ppm)
151.56
140.59
139.10
128.35
128.25
127.68
127.60
127.55
127.36
95.76
84.68
77.32
77.00
76.69
74.90
74.61
74.15
73.39
72.98
72.54
71.25
69.61
67.61
36.32
29.58
29.18
27.99
27.80
25.36
7.36
3.21

```

F2 - Acquisition Parameters
Date          710127
Time          11.39
PULPROG       zgpgdc
SOLVENT       CDCL3
AQ            1.4418120 sec
FIDRES        0.346791 Hz
DW            22.0 usec
RG            22800
NUCLEUS        13C
D12            0.0000200 sec
DL5            23.00 dB
P31            100.0 u
D1            0.6000000 sec
P0             3.9 usec
DE            27.5 usec
SF01          100.6239300 MHz
SWH           22727.27 Hz
TD            65536
NS            4000
DS            2
D11           0.0300000 sec

```

```
F2 - Processing parameters
SI                32768
SF              100.6143610 MHz
WDW                EM
SSB                0
LB                3.00 Hz
GB                0
PC                1.00
```

```

1D NMR plot parameters
CX              33.80 cm
F1P            190.116 ppm
F1             19128.38 Hz
F2P            -10.000 ppm
F2            -1006.14 Hz
PPMCM          5.92058 ppm/cm
HZCM           595.69580 Hz/cm

```

ST7038 1H CDCL3

Current Data Parameters

NAME sig600
EXPNO 70
PROCNO 1

F2 - Acquisition Parameters

Date_ 20010211
Time 8.45
INSTRUM AMX2600
PROBHD 5 mm Dual 19
PULPROG zg0
TD 32768
SOLVENT CDCL3
NS 64
DS 0
SWH 8474.576 Hz
FIDRES 0.258624 Hz
AQ 1.9333620 sec
RG 512
DW 59.000 usec
DE 84.29 usec
TE 300.0 K
HL1 1 dB
D1 1.00000000 sec
P0 4.10 usec
DE 84.29 usec
SFO1 600.1400600 MHz
NUCLEUS 1H

F2 - Processing parameters

SI 16384
SF 600.1364600 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

ST7038 13C CDCL3

146.469
138.821
138.421
137.451
128.352
128.288
127.834
127.571
127.454

84.516
77.213
77.001
76.789
76.624
74.713
74.579
73.720
73.416
72.987
72.662
71.552
69.781
69.701
68.110
47.775
37.563
37.057
30.658
29.669
27.922
25.056

7.746
7.484
4.522
4.360

Current Data Parameters

NAME sig600
EXPNO 71
PROCNO 2

F2 - Acquisition Parameters

Date_ 20010211
Time 8.58
INSTRUM AMX2600
PROBHD 5 mm Dual 19
PULPROG zg0dc
TD 65536
SOLVENT CDCL3
NS 20830
DS 2
SWH 35714.285 Hz
FIDRES 0.544957 Hz
AQ 0.9175540 sec
RG 16384
DW 14.000 usec
DE 20.00 usec
TE 300.0 K

F2 - Processing parameters

SI 65536
SF 150.9044265 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

Current Data Parameters
 NAME shige400-2
 EXPNO 390
 PROCNO 1

F2 - Acquisition Parameters
 Date 701026
 Time 13.24
 PULPROG zg0
 SOLVENT CDCL3
 AQ 2.5559239 sec
 FIDRES 0.195625 Hz
 DW 78.0 usec
 RG 1024
 NUCLEUS 1H
 D1 1.0000000 sec
 P0 3.0 usec
 DE 97.5 usec
 SF01 400.1368000 MHz
 SWH 6410.26 Hz
 TD 32768
 NS 16
 DS 2

F2 - Processing parameters
 SI 16384
 SF 400.1344000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 34.20 cm
 F1P 8.500 ppm
 F1 3401.14 Hz
 F2P -1.000 ppm
 F2 -400.13 Hz
 PPMCM 0.27778 ppm/cm
 HZCM 111.14845 Hz/cm

ST-9008 13C CDCL3

Current Data Parameters

NAME shige400-2
EXPNO 395
PROCNO 2

F2 - Acquisition Parameters

Date 701027
Time 2.33
PULPROG zg0dc
SOLVENT CDCL3
AQ 1.3762760 sec
FIDRES 0.363304 Hz
DQ 21.0 usec
RG 22800
NUCLEUS 13C
D12 0.0000200 sec
DL5 23.00 dB
P31 100.0 usec
D1 0.6000000 sec
P0 3.9 usec
DE 26.3 usec
SF01 100.6239300 MHz
SMH 23809.52 Hz
TD 65536
NS 6924
DS 2
D11 0.0300000 sec

F2 - Processing parameters

SI 32768
SF 100.6138714 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 33.90 cm
F1P 218.294 ppm
F1 21963.37 Hz
F2P -18.349 ppm
F2 -1846.15 Hz
PPMCM 6.98061 ppm/cm
HZCM 702.34583 Hz/cm

Current Data Parameters
 NAME shige400-2
 EXPNO 460
 PROCNO 1

F2 - Acquisition Parameters
 Date 701105
 Time 15.09
 PULPROG zg0
 SOLVENT CDCL3
 AQ 2.5559239 sec
 FIDRES 0.195625 Hz
 DW 78.0 usec
 RG 1024
 NUCLEUS 1H
 D1 1.0000000 sec
 P0 3.0 usec
 DE 97.5 usec
 SF01 400.1368000 MHz
 SWH 6410.26 Hz
 TD 32768
 NS 341
 DS 2

F2 - Processing parameters
 SI 16384
 SF 400.1344000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 34.50 cm
 F1P 8.500 ppm
 F1 3401.14
 F2P -1.000 ppm
 F2 -400.13 Hz
 PPMCM 0.27536 ppm/cm
 HZCM 110.18194 Hz/cm

Current Data Parameters

NAME shige400-2
EXPNO 462
PROCNO 2

F2 - Acquisition Parameters

Date 701106
Time 2.40
PULPROG zg0dc
SOLVENT CDCL3
AQ 1.4418120 sec
FIDRES 0.346791 Hz
DQ 22.0 usec
RG 22800
NUCLEUS 13C
D12 0.0000200 sec
OL5 23.00 dB
P31 100.0 usec
D1 0.6000000 sec
P0 3.9 usec
DE 27.5 usec
SF01 100.6239300 MHz
SWH 22727.27 Hz
TD 65536
NS 15879
DS 2
D11 0.0300000 sec

F2 - Processing parameters

SI 32768
SF 100.6138717 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 34.00 cm
F1P 212.912 ppm
F1 21421.92 Hz
F2P -12.974 ppm
F2 -1305.35 Hz
PPMCM 6.64371 ppm/cm
HZCM 668.44916 Hz/cm

19

Current Data Parameters
 NAME shige400-2
 EXPNO 453
 PROCNO 1

F2 - Acquisition Parameters
 Date 701106
 Time 3.11
 PULPROG zg0
 SOLVENT CDCL3
 AQ 2.5559239 sec
 FIDRES 0.195625 Hz
 DW 78.0 usec
 RG 1024
 NUCLEUS 1H
 D1 1.0000000 sec
 P0 3.0 usec
 DE 97.5 usec
 SF01 400.1368000 MHz
 SWH 6410.26 Hz
 TD 32768
 NS 16
 DS 2

F2 - Processing parameters
 SI 16384
 SF 400.1344000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 34.30 cm
 F1P 8.500 ppm
 F1 3401.14
 F2P -1.000 ppm
 F2 -400.13 Hz
 PPMCM 0.27697 ppm/cm
 HZCM 110.82440 Hz/cm

Current Data Parameters

NAME shige400-2
EXPNO 452
PROCNO 2

F2 - Acquisition Parameters

Date 701103
Time 10.01
PULPROG zg0dc
SOLVENT CDCL3
AQ 1.4418120 sec
FIDRES 0.346791 Hz
DW 22.0 usec
RG 22800
NUCLEUS 13C
D12 0.0000200 sec
DL5 23.00 dB
P31 100.0 u
D1 0.6000000 sec
P0 3.9 usec
DE 27.5 usec
SF01 100.6239300 MHz
SWH 22727.27 Hz
TD 65536
NS 2070
DS 2
D11 0.0300000 sec

F2 - Processing parameters

SI 32768
SF 100.6138724 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

1D NMR plot parameters

CX 33.80 cm
F1P 212.905 ppm
F1 21421.22 Hz
F2P -12.981 ppm
F2 -1306.05 Hz
PPMCM 6.68302 ppm/cm
HZCM 672.40454 Hz/cm

ST9012 1H CDCL3 300K

5

broadening in CDCl₃ at 27 °C

Current Data Parameters

NAME shige600-1
EXPNO 69
PROCNO 1

F2 - Acquisition Parameters

Date_ 20011023
Time 4.02
INSTRUM AMX2600
PROBHD 5 mm Dual 19
PULPROG zg0
TD 32768
SOLVENT CDCL3
NS 1
DS 0
SWH 8474.576 Hz
FIDRES 0.258624 Hz
AQ 1.9333620 sec
RG 512
DW 59.000 usec
DE 84.29 usec
TE 300.0 K
HL1 1 dB
D1 1.00000000 sec
P0 4.10 usec
DE 84.29 usec
SFO1 600.1400600 MHz
NUCLEUS 1H

F2 - Processing parameters

SI 16384
SF 600.1364600 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

ST9012_1H_CDCL3_253K

5

DOWN : UP = 2 : 1
in CDCl₃ at -20 °C

Current Data Parameters

NAME shige600-1
EXPNO 66
PROCNO 1

F2 - Acquisition Parameters

Date_ 20011023
Time 2.34
INSTRUM AMX2600
PROBHD 5 mm Dual 19
PULPROG zg0
TD 32768
SOLVENT CDCL3
NS 16
DS 0
SWH 5747.126 Hz
FIDRES 0.175388 Hz
AQ 2.8508661 sec
RG 512
DW 87.000 usec
DE 108.75 usec
TE 300.0 K

F2 - Processing parameters

SI 16384
SF 600.1364600 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

Chemical structure of compound **5** is shown above the spectrum. The structure is a complex polycyclic molecule with multiple ether and ester groups.

13C NMR Spectrum (ppm):

- 138.283
- 137.842
- 128.341
- 128.239
- 127.906
- 127.613
- 127.543
- 127.403
- 87.400
- 86.630
- 86.491
- 86.157
- 82.766
- 82.475
- 81.476
- 80.778
- 79.565
- 78.436
- 78.323
- 77.847
- 77.211
- 76.999
- 76.787
- 76.399
- 76.129
- 73.119
- 72.346
- 71.008
- 70.723
- 68.354
- 67.984
- 39.064
- 38.967
- 35.467
- 33.960
- 32.886
- 32.333
- 31.609
- 31.242
- 30.143
- 29.693
- 27.480

Current Data Parameters
NAME shige600-1
EXPNO 73
PROCNO 2

Date_	20011028
Time	13.19
INSTRUM	AMX2600
PROBHD	5 mm Dual 19
PULPROG	zgdc
TD	65536
SOLVENT	CDCL3
NS	1804
DS	2
SWH	35714.285 Hz
FIDRES	0.544957 Hz
AQ	0.9175540 sec
RG	16384
DW	14.000 usec
DE	20.00 usec
TE	300.0 K
D11	0.0300000 sec
CPDPRG	waltz16
P31	100.00 usec
S2	21 dB
HL1	90 dB
D1	1.00000000 sec
P0	5.00 usec
DE	20.00 usec
SFO1	150.9195300 MHz
NUCLEUS	13C

<i>SI</i>	65536
<i>SF</i>	150.9044597 MHz
<i>WDW</i>	EM
<i>SSB</i>	0
<i>LB</i>	3.00 Hz
<i>GB</i>	0
<i>PC</i>	1.00

ST9012 HOM2DJ CDCL3 253K 021225

Current Data Parameters

NAME shige600-1
EXPNO 211
PROCNO 2

F2 - Acquisition Parameters

PULPROG jres
TD 1024
NS 32
DS 4
SWH 5434.78 Hz
AQ 0.0942580 sec
RG 256
DW 92.000 usec
DE 131.43 usec
PHP 1
QNP 1
P1 7.80 usec
HL1 2 dB
D1 2.00000000 sec
D0 0.0000030 sec
P2 15.6 usec
DE 131.43 usec
SFO1 600.1388605 MHz
NUCLEUS 1H
IN0 0.00714286 sec

F1 - Acquisition parameters

ND0 2
TD 300
SFO1 600.1389 MHz
FIDRES 0.233333 Hz
SW 0.117 ppm
FnMODE undefined

F2 - Processing parameters

SI 1024
SF 600.1364600 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters

SI 1024
MC2 QF
SF 600.1388605 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0

22

Current Data Parameters
 NAME shige400-3
 EXPNO 230
 PROCNO 1

F2 - Acquisition Parameters
 Date 710511
 Time 20.10
 PULPROG zg0
 SOLVENT CDCL3
 AQ 2.5559239 sec
 FIDRES 0.195625 Hz
 DW 78.0 usec
 RG 1024
 NUCLEUS 1H
 D1 1.0000000 sec
 P0 3.0 usec
 DE 97.5 usec
 SF01 400.1368000 MHz
 SWH 6410.26 Hz
 TD 32768
 NS 16
 DS 2

F2 - Processing parameters
 SI 16384
 SF 400.1344000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 34.40 cm
 F1P 8.500 ppm
 F1 3401.14 Hz
 F2P -1.000 ppm
 F2 -400.13 Hz
 PPMCM 0.27616 ppm/cm
 HZCM 110.50223 Hz/cm

ST10146 13C CDCL3

199.856
199.332
196.188

169.949

139.453

130.608

128.222

127.225

127.140

100.530

86.915

81.510

80.091

78.235

77.472

77.321

77.003

76.685

73.775

73.425

71.354

67.908

65.709

39.036

32.411

29.880

29.281

25.515

25.156

24.559

21.630

21.386

13.718

13.613

22

Current Data Parameter

NAME shige400-3
EXPNO 232
PROCNO 2

F2 - Acquisition Parameter

Date 710512
Time 0.41
PULPROG zgpgdc
SOLVENT CDCL3
AQ 1.4418120 sec
FIDRES 0.346791 Hz
DW 22.0 usec
RG 22800
NUCLEUS 13C
D12 0.0000200 sec
DL5 23.00 dB
P31 100.0 usec
D1 0.6000000 sec
P0 3.9 usec
DE 27.5 usec
SFO1 100.6239300 MHz
SWH 22727.27 Hz
TD 65536
NS 1178
DS 2
D11 0.0300000 sec

F2 - Processing parameter

SI 32768
SF 100.6138717 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00

1D NMR plot parameter

CX 33.90 cm
F1P 210.000 ppm
F1 21128.91 Hz
F2P -10.000 ppm
F2 -1006.14 Hz
PPMCM 6.48968 Hz
HZCM 652.95135 Hz

ST10137-2 1H CDCL3

24

Current Data Parameter
NAME shige600-1
EXPNO 160
PROCNO 1

F2 - Acquisition Parameter
Date_ 1020501
Time 17.22
INSTRUM AMX260
PROBHD 5 mm Dual
PULPROG zg0
TD 32768
SOLVENT CDCL3
NS 104
DS 2
SWH 8474.576 Hz
FIDRES 0.258624 Hz
AQ 1.9333620 sec
RG 8192
DW 59.000 usec
DE 84.29 usec
TE 300.0 K
HL1 2 dB
D1 1.00000000 sec
P0 4.10 usec
DE 84.29 usec
SFO1 600.1400600 MHz
NUCLEUS 1H

F2 - Processing parameter
SI 16384
SF 600.1364600 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameter
CX 33.80 cm
F1P 8.500 ppm
F1 5101.16 Hz
F2P -1.000 ppm
F2 -600.14 Hz
PPMCM 0.28107 Hz
HZCM 168.67741 Hz

ST10137-2 13C CDCL3

24

Current Data Parameter
 NAME shige600-1
 EXPNO 162
 PROCNO 2

F2 - Acquisition Param
 Date_ 1020501
 Time 20.44
 INSTRUM AMX260
 PROBHD 5 mm Dual
 PULPROG zg0dc
 TD 65536
 SOLVENT CDCL3
 NS 16154
 DS 2
 SWH 35714.285 Hz
 FIDRES 0.544957 Hz
 AQ 0.9175540 sec
 RG 32768
 DW 14.000 usec
 DE 20.00 usec
 TE 300.0 K
 D11 0.0300000 sec
 CPDPRG waltz16
 P31 100.00 usec
 S2 25 dB
 HL1 90 dB
 D1 1.00000000 sec
 P0 5.00 usec
 DE 20.00 usec
 SFO1 150.9195300 MHz
 NUCLEUS 13C

F2 - Processing parameter
 SI 65536
 SF 150.9044275 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 0.90

1D NMR plot parameters
 CX 33.90 cm
 FIP 218.414 ppm
 F1 32959.61 Hz
 F2P -10.000 ppm
 F2 -1509.05 Hz
 PPMCM 6.73787 Hz
 HZCM 1016.77435 Hz

ST10158-2 1H CDCL3

25

Current Data Parameter:
NAME shige400-3
EXPNO 240
PROCNO 1

F2 - Acquisition Parameter:
Date_ 710523
Time 6.47
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 Hz
DW 78.0 usec
RG 2048
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SFO1 400.1368000 MHz
SWH 6410.26 Hz
TD 32768
NS 64
DS 2

F2 - Processing parameter:
SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameter:
CX 34.20 cm
F1P 8.500 ppm
F1 3401.14 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.27778 Hz
HZCM 111.14845 Hz

Chemical structure of compound **25** is shown above the spectrum. The structure is a complex polycyclic molecule featuring a central eight-membered ring with a double bond, fused to a six-membered ring containing an oxygen atom. It also includes a side chain with a benzyl ether group (OBn), a methyl group (Me), and an acetoxy group (AcO). Stereochemistry is indicated with wedges and dashes.

The ¹³C NMR spectrum (CDCl₃) displays the following chemical shifts (ppm):

Chemical Shift (ppm)
211.838
169.950
139.017
128.651
128.210
127.491
127.260
124.650
82.106
80.427
78.759
78.172
77.317
76.999
76.682
75.004
72.906
70.567
68.150
65.766
36.745
32.945
32.399
29.362
28.732
25.497
25.258
21.749
21.316
14.019

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

ID NMR plot parameters:
CX 33.90 cm
F1P 212.912 ppm
F1 21421.92 Hz
F2P -12.974 ppn
F2 -1305.35 Hz
PPMCM 6.66331 l
HZCM 670.42102 l

ST10163-3 1H CDCL3

Current Data Parameter

NAME shige600-1
EXPNO 170
PROCNO 1

F2 - Acquisition Parameter

Date_ 1020518
Time 15.41
INSTRUM AMX260
PROBHD 5 mm Dual
PULPROG zg0
TD 32768
SOLVENT CDCL3
NS 32
DS 2
SWH 8474.576 Hz
FIDRES 0.258624 Hz
AQ 1.9333620 sec
RG 1024
DW 59.000 usec
DE 84.29 usec
TE 300.0 K
HL1 2 dB
D1 1.00000000 sec
P0 4.10 usec
DE 84.29 usec
SFO1 600.1400600 MHz
NUCLEUS 1H

F2 - Processing parameter

SI 16384
SF 600.1364600 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

1D NMR plot parameter

CX 33.80 cm
F1P 8.500 ppm
F1 5101.16 Hz
F2P -1.000 ppm
F2 -600.14 Hz
PPMCM 0.28107 Hz
HZCM 168.67741 Hz

ST10163-3 13C CDCL3

Current Data Parameter
 NAME shige600-1
 EXPNO 172
 PROCNO 2

F2 - Acquisition Parameter
 Date_ 20020518
 Time 17.17
 INSTRUM AMX260
 PROBHD 5 mm Dual
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCL3
 NS 23459
 DS 2
 SWH 35714.285 Hz
 FIDRES 0.544957 Hz
 AQ 0.9175540 sec
 RG 32768
 DW 14.000 usec
 DE 20.00 usec
 TE 300.0 K
 D11 0.0300000 sec
 CPDPRG waltz16
 P31 75.00 usec
 S2 25 dB
 HL1 90 dB
 D1 1.0000000 sec
 P0 7.00 usec
 DE 20.00 usec
 SFO1 150.9195300 MHz
 NUCLEUS 13C

F2 - Processing parameter
 SI 65536
 SF 150.9044275 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.20

ST10163-1 1H CDCL3

27

Current Data Parameter.
NAME shige400-3
EXPNO 250
PROCNO 1

F2 - Acquisition Param
Date 710524
Time 2.58
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 1
DW 78.0 usec
RG 2860
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SFO1 400.1368000 1
SWH 6410.26 Hz
TD 32768
NS 32
DS 2

F2 - Processing param
SI 16384
SF 400.1344000 M
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

1D NMR plot parameter:
CX 34.20 cm
F1P 8.500 ppm
F1 3401.14 Hz
F2P -1.000 ppm
F2 -400.13 Hz
PPMCM 0.27778 1
HZCM 111.14845 1

ST10163-1 13C CDCL3

27

Current Data Parameter:
 NAME shige400-3
 EXPNO 253
 PROCNO 2

F2 - Acquisition Param
 Date 710524
 Time 18.12
 PULPROG zgpgdc
 SOLVENT CDCL3
 AQ 1.4418120 sec
 FIDRES 0.346791 Hz
 DW 22.0 usec
 RG 22800
 NUCLEUS 13C
 D12 0.0000200 sec
 DL5 23.00 dB
 P31 100.0 usec
 D1 0.6000000 sec
 P0 3.9 usec
 DE 27.5 usec
 SFO1 100.6239300 MHz
 SWH 22727.27 Hz
 TD 65536
 NS 18330
 DS 2
 D11 0.0300000 sec

F2 - Processing parameter
 SI 32768
 SF 100.6138710 MHz
 WDW EM
 SSB 0
 LB 3.00 Hz
 GB 0
 PC 1.00

1D NMR plot parameter:
 CX 33.90 cm
 FIP 210.000 ppm
 F1 21128.91 Hz
 F2P -10.000 ppm
 F2 -1006.14 Hz
 PPMCM 6.48968 Hz
 HZCM 652.95135 Hz

ST10167 1H CDCL3 253K

UP : DOWN = 1 : 1
in CDCl₃ at -20 °C

Current Data Parameters

NAME shige400-3
EXPNO 270
PROCNO 1

F2 - Acquisition Parameters

Date 500000
Time 11.28
PULPROG zg0
SOLVENT CDCL3
AQ 2.5559239 sec
FIDRES 0.195625 Hz
DW 500000.0 usec
RG 5700
NUCLEUS 1H
D1 1.0000000 sec
P0 3.0 usec
DE 97.5 usec
SFO1 400.1368000 MHz
SWH 6410.26 Hz
TD 32768
NS 64
DS 2

F2 - Processing parameters

SI 16384
SF 400.1344000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

ST10169-1 1H Py-d5 300K

28

broadening in Py-d₅ at 27 °C

Current Data Parameter

NAME shige600-1
EXPNO 180
PROCNO 1

F2 - Acquisition Param

Date_ 20020524
Time 8.20
INSTRUM AMX260
PROBHD 5 mm Dual
PULPROG zg0
TD 32768
SOLVENT CDCL₃
NS 16
DS 2
SWH 8474.576 Hz
FIDRES 0.258624 Hz
AQ 1.9333620 sec
RG 512
DW 59.000 usec
DE 84.29 usec
TE 300.0 K

F2 - Processing param

SI 16384
SF 600.1364600 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

ST10169-1 1H Py-d5 253K

UP : DOWN = 3.5 : 1
in Py-*d*₅ at -20 °C

Current Data Parameters
NAME shige600-1
EXPNO 220
PROCNO 2

F2 - Acquisition Parameters
Date_ 701225
Time 16.20
INSTRUM AMX26
PROBHD 5 mm Dual
PULPROG zg0
TD 32768
SOLVENT CDCl
NS 16
DS 2
SWH 6329.114 Hz
FIDRES 0.193149
AQ 2.5887220 sec
RG 512
DW 79.000 usec
DE 98.75 usec
TE 253.0 K

F2 - Processing parameters
SI 16384
SF 600.1362377 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

Chemical structure of compound **28** is shown above the spectrum. The structure is a complex polycyclic molecule with multiple stereocenters and functional groups, including a benzyl ether (OBn) and a methyl group (Me).

The ¹³C NMR spectrum displays the following chemical shifts (ppm):

- 149.903, 149.724, 149.544, 140.257, 135.667, 135.502, 135.338, 135.145, 128.670, 128.584, 128.502, 127.889, 127.508, 123.619, 123.454, 123.289, 123.088
- 86.681, 85.636, 83.102, 82.912, 82.324, 81.411, 81.051, 80.835, 79.909, 78.557, 73.328, 67.966, 64.693
- 39.716, 33.472, 32.576, 32.499, 31.196, 29.902, 27.303, 26.237, 21.918, 11.434

1D NMR plot parameters:	
CX	33.80 cm
F1P	41.630 ppm
F1	6282.15 Hz
F2P	9.458 ppm
F2	1427.24 Hz
PPMCM	0.951841
HZCM	143.63641

ST10169-1 HOM2DJ Py-d5 253K

Current Data Parameters
NAME shige600-1
EXPNO 221
PROCNO 2

F2 - Acquisition Parameters
Date_ 701225
Time 16.37
INSTRUM AMX2600
PROBHD 5 mm Dual 19
PULPROG jres
TD 1024
SOLVENT Pyr
NS 32
DS 4
SWH 6329.114 Hz
FIDRES 6.180775 Hz
AQ 0.0809460 sec
RG 256
DW 79.000 usec
DE 112.86 usec
TE 253.0 K

F1 - Acquisition parameters
ND0 2
TD 300
SFO1 600.1393 MHz
FIDRES 0.233333 Hz
SW 0.117 ppm
FnMODE undefined

F2 - Processing parameters
SI 1024
SF 600.1362370 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 QF
SF 600.1393023 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0