

Convergent Synthesis of the E'FGH' ring fragment of ciguatoxin 1B via an acetylene cobalt complex strategy

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Supporting Information

Iodide **7**

Iodide **7**. IR (KBr) ν_{\max} 2955, 2930, 2857, 1472, 1463, 1362, 1253, 1203, 838, 776 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 0.09 (3H, s, TBS), 0.12 (3H, s, TBS), 0.88 (9H, s, ^tBu), 1.49 (1H, m, H-3), 1.66 (2H, m, H-2), 2.03 (1H, m, H-3), 2.82 (1H, ddd $J = 8.5, 6.0, 3.0$ Hz, H-5), 3.33 (1H, dd, $J = 10.5, 6.0$ Hz, H-6), 3.41 (1H, m, H-4), 3.43 (1H, ddd, $J = 11.5, 7.5, 3.5$ Hz, H-1), 3.51 (1H, dd, $J = 10.5, 3.0$ Hz, H-6), 3.97 (1H, dm, $J = 11.5$ Hz, H-1). ^{13}C NMR (CDCl_3 , 75 MHz) δ -4.64, -4.00, 9.23, 17.78, 25.39, 25.68, 33.03, 67.94, 71.16, 80.78. ESI Q-TOF MS calcd for $\text{C}_{12}\text{H}_{25}\text{INaO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 379.057, found 379.065. $[\alpha]_{\text{D}}^{27} +59.3^\circ$ (c 0.86, CHCl_3). Anal. Calcd for $\text{C}_{12}\text{H}_{25}\text{IO}_2\text{Si}$: C, 40.45; H, 7.07. Found: C, 40.45; H, 7.22.

Nitrile **8**

To a solution of iodide **7** (3.38 g, 9.49 mmol) in dimethylsulfoxide (47 ml) was added sodium cyanide (697 mg, 14.2 mmol). After stirring for 2 h at 80 °C under nitrogen atmosphere, the reaction mixture was poured into ammonium chloride aq. at rt in draft and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ethyl acetate / hexane = 10 / 90) to afford nitrile **8** (2.31 g, 95%) as a colorless oil.

Nitrile **8**. IR (KBr) ν_{\max} 2955, 2931, 2859, 2251, 1472, 1363, 1254, 1134, 1127, 1101, 1050, 869, 839, 778, 670 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 0.09 (3H, s, TBS), 0.11 (3H, s, TBS), 0.88 (9H, s, ^tBu), 1.45 (1H, dddd, $J = 12.5, 12.5, 10.5, 4.5$ Hz, H-3), 1.60-1.79 (2H, m, H-2), 2.02-2.10 (1H, dm, $J = 12.5$ Hz, H-3), 2.58 (1H,

dd, $J = 16.5, 6.5$ Hz, H-6), 2.73 (1H, dd, $J = 16.5, 3.5$ Hz, H-6), 3.26 (1H, ddd $J = 9.0, 6.5, 3.5$ Hz, H-5), 3.36 (1H, ddd, $J = 11.5, 11.5, 3.5$ Hz, H-1), 3.44 (1H, ddd, $J = 10.5, 9.0, 4.5$ Hz, H-4), 3.94 (1H, dddd, $J = 11.5, 4.5, 2.0, 1.5$ Hz, H-1). ^{13}C NMR (CDCl_3 , 100 MHz) δ -4.89, -3.97, 17.79, 21.40, 25.14, 25.66, 33.44, 67.98, 70.14, 77.91, 117.51. ESI Q-TOF MS calcd for $\text{C}_{13}\text{H}_{25}\text{NNaO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 278.155, found 278.152. $[\alpha]_{\text{D}}^{27} +57.2^\circ$ (c 1.78, CHCl_3). Anal. Calcd for $\text{C}_{13}\text{H}_{25}\text{NO}_2\text{Si}$: C, 61.13; H, 9.87; N, 5.48. Found: C, 60.96; H, 10.25; N, 5.61.

Aldehyde 9

To a solution of nitrile **8** (1.42 g, 5.56 mmol) in dry toluene (28 ml) was added dropwise a solution of 1.0 M diisobutylaluminum hydride in hexane (7.23 ml, 7.23 mmol) at -78°C under nitrogen atmosphere. After stirring for 1 h at -78°C , the reaction mixture was added 10% acetic acid aq. (28 ml) at -78°C . After warming up to rt gradually, the reaction mixture was added ether (200 ml) and poured into a mixture of saturated sodium hydrogen carbonate aq. and saturated potassium sodium tartrate aq. (50 ml / 50 ml). After stirring for 1 h at rt, the reaction mixture was extracted with ether (x 3). The combined organic layer was washed with brine and then dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 10 / 90) to afford aldehyde **9** (836 mg, 58%) as a colorless oil

Aldehyde **9**. IR (KBr) ν_{max} 2956, 2931, 2858, 2728, 1731, 1473, 1363, 1260, 1129, 1101, 838, 777, 670 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 0.04 (3H, s, TBS), 0.05 (3H, s, TBS), 0.86 (9H, s, ^tBu), 1.38-1.52 (1H, m, H-3), 1.61-1.72 (2H, m, H-2), 1.98-2.08 (1H, m, H-3), 2.42 (1H, ddd, $J = 16.5, 9.0, 3.0$ Hz, H-6), 2.77 (1H, ddd, $J = 16.5, 4.0, 2.0$ Hz, H-6), 3.28-3.40 (1H, m, H-1 and H-4), 3.58 (1H, td, $J = 9.0, 4.0$ Hz, H-5), 3.85 (1H, dm, $J = 11.5$ Hz, H-1), 9.76 (1H, dd, $J = 3.0, 2.0$ Hz, $-\text{CHO}$). ^{13}C NMR (CDCl_3 , 75 MHz) δ -4.90, -4.11, 17.77, 25.39, 25.64, 33.32, 46.70, 67.81, 70.98, 78.19, 201.84. ESI Q-TOF MS calcd for $\text{C}_{13}\text{H}_{26}\text{NaO}_3\text{Si}$ $[\text{M}+\text{Na}]^+$ 281.155, found 281.161. $[\alpha]_{\text{D}}^{26} +43.4^\circ$ (c 0.85, CHCl_3). Anal. Calcd for $\text{C}_{13}\text{H}_{26}\text{O}_3\text{Si}$: C, 60.42; H, 10.14. Found: C, 60.36; H, 10.24.

Silyl Enyne 11

To a solution of 1,3-bis(triisopropylsilyl)propyne **10** (1.41 g, 4.00 mmol) in dist. tetrahydrofuran (15 ml) was added dropwise a solution of 1.50 M *n*-BuLi in hexane

(2.45 ml, 3.68 mmol) at -78 °C under nitrogen atmosphere. After stirring for 20 min at 0 °C, the reaction mixture was added dropwise a solution of aldehyde **9** (792 mg, 3.06 mmol) in dist. tetrahydrofuran (5 ml) at -78 °C. After stirring for 2 h at -78 °C, the reaction mixture was poured into saturated ammonium chloride aq. at 0 °C and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 2 / 98) to afford silyl enyne **11** (983 mg, 73%, *Z* : *E* = 4.9 : 1) as a colorless oil.

Silyl Enyne **11** (**Z-isomer**). IR (KBr) ν_{\max} 2943, 2892, 2866, 2148, 1464, 1252, 1130, 1100, 1036, 999, 883, 838, 776, 677 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 0.06 (6H, s, TBS), 0.88 (9H, s, ^tBu -TBS), 1.08 (18H, s, TIPS), 1.09 (3H, s, TIPS), 1.43 (1H, dddd, J = 16.0, 12.5, 6.5, 5.5 Hz, H-3), 1.63 (2H, m, H-2), 2.00 (1H, dm, J = 12.5 Hz, H-3), 2.52 (1H, dddd, J = 16.5, 8.5, 7.5, 1.5 Hz, H-6), 2.79 (1H, dddd, J = 16.5, 6.0, 3.5, 2.0 Hz, H-6), 3.18 (1H, ddd, J = 8.5, 8.5, 3.5 Hz, H-5), 3.31 (1H, m, H-1), 3.31 (1H, m, H-4), 3.87 (1H, dm, J = 11.5 Hz, H-1), 5.62 (1H, ddd, J = 11.0, 2.0, 1.5 Hz, H-8), 6.04 (1H, ddd, J = 11.0, 7.5, 6.0 Hz, H-7). ^{13}C NMR (CDCl_3 , 400 MHz) δ -4.63, -4.11, 11.33, 17.95, 18.68, 25.64, 25.85, 33.38, 33.61, 67.80, 71.46, 81.81, 95.41, 103.91, 110.85, 141.56. $[\alpha]_{\text{D}}^{22} +28.0^\circ$ (c 0.60, CHCl_3). ESI Q-TOF MS calcd for $\text{C}_{25}\text{H}_{49}\text{O}_2\text{Si}_2$ $[\text{M}+\text{H}]^+$ 437.327, found 437.338.

E' ring-enyne 12

To a solution of silyl enyne **11** (865 mg, 1.98 mmol) in tetrahydrofuran (10 ml) was added a solution of 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (15.8 ml, 15.8 mmol) at 0 °C. After stirring for 10 h at rt under nitrogen atmosphere, the reaction mixture was poured into saturated ammonium chloride aq. at 0 °C and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 50 / 50) to afford an alcohol (308 mg, 94%) as a colorless oil.

To a solution of the alcohol (98 mg, 0.59 mmol) in dichloromethane (3 ml) was added ethyl vinyl ether (0.56 ml, 5.90 mmol) and pyridinium *p*-toluenesulfonate (44 mg, 0.18 mmol). After stirring for 2 h at rt under nitrogen atmosphere, the reaction mixture was poured into saturated sodium hydrogen carbonate aq. at 0 °C and then extracted with dichloromethane (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was

purified by silica gel column chromatography (ether / hexane = 5 / 95) to afford E' ring-enyne **12** (137 mg, 97%) as a colorless oil.

E' ring-enyne **12** (**Z-isomer**). IR (KBr) ν_{\max} 3290, 2977, 2939, 2853, 1441, 1395, 1378, 1341, 1280, 1210, 1131, 1099, 1059, 1046, 949, 639 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 1.20 (3H, t, $J = 7.0$ Hz, EE), 1.31 (1/2x3H, d, $J = 5.5$ Hz, EE), 1.33 (1/2x3H, d, $J = 5.5$ Hz, EE), 1.34-1.56 (1H, m, H-3), 1.60-1.72 (2H, m, H-2), 2.14-2.30 (1H, m, H-3), 2.44-2.82 (2H, m, H-6), 3.08-3.11 (1H, m, acetylenic), 3.14-3.42 (3H, m, H-1,H-4 and H-5), 3.43-3.72 (2H, m, EE), 3.89 (1H, dm, $J = 12$ Hz, H-1), 4.75 (1/2x1H, q, $J = 5.5$ Hz, EE), 4.84 (1/2x1H, q, $J = 5.5$ Hz, EE), 5.55 (1H, dm, $J = 11.0$ Hz, H-8), 6.19 (1H, dm, $J = 11.0$ Hz, H-7). ESI Q-TOF MS calcd for $\text{C}_{14}\text{H}_{23}\text{O}_3$ $[\text{M}+\text{H}]^+$ 239.165, found 239.177.

Propargyl Alcohol 16

To a solution of silylacetylene **15** (620 mg, 1.22 mmol) in methanol (6 ml) was added K_2CO_3 (34 mg, 0.24 mmol). After stirring for 2 h at rt, the reaction mixture was poured into saturated ammonium chloride aq. at 0 °C and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ethyl acetate / hexane = 20 / 80) to afford an alcohol (475 mg, 99%).

To a solution of the alcohol (17.8 g, 45.3 mmol) in benzylchloride (110 ml) was added KOH powder (12.7 g, 226.5 mmol). After stirring for 2 h at 90 °C, the reaction mixture was poured into saturated ammonium chloride aq. at 0 °C slowly and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 6 / 94) to afford a benzyl ether (19.1 g, 87%) as a pale yellow oil.

To a solution of the benzyl ether (480 mg, 0.99 mmol), which was treatment with toluene azeotrope in advance, in dist. tetrahydrofuran (10 ml) was added a solution of *n*-BuLi (1.60 M in Hexane, 0.75 ml, 1.19 mmol) at -78 °C under nitrogen atmosphere. After stirring for 20 min at 0 °C, a solution of $(\text{HCHO})_n$ (149 mg, 4.96 mmol) in dist. tetrahydrofuran 5 ml was added. After stirring for 1 h at -78 °C and for 16 h at 0 °C, the reaction mixture was poured into saturated ammonium chloride aq. at 0 °C and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 5 / 95 to 25 / 75) to afford

SM (76 mg, 16%), formated-**16** (84 mg, 16%) and propargyl alcohol **16** (283 mg, 55%) as a pale yellow oil.

To a solution of **formated-16** (84 mg, 0.16 mmol) in MeOH (3 ml) was added K_2CO_3 (22 mg, 0.16 mmol). After stirring for 20 min at rt, the reaction mixture was poured into saturated ammonium chloride aq. at 0 °C and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 50 / 50) to afford propargyl alcohol **16** (80 mg, 100%) as a pale yellow oil.

Propargyl Alcohol **16**. IR (KBr) ν_{max} 3434, 3071, 3047, 2958, 2932, 2892, 2858, 1962, 1895, 1830, 1590, 1473, 1428, 1390, 1364, 1304, 1158, 1113, 1028, 822, 742, 701, 613, 513 cm^{-1} . 1H NMR ($CDCl_3$, 400 MHz) δ 1.08 (9H, s, tBu), 2.16 (1H, br-s, -OH), 3.37 (1H, dd $J = 10.0, 5.5$ Hz, H-6), 3.47 (1H, dd, $J = 10.0, 6.0$ Hz, H-6), 4.06 (2H, br-d, $J = 6.0$ Hz, propargylic), 4.26 (1H, dm, $J = 8.5$ Hz, H-1), 4.32-4.38 (2H, m, H-2 and H-5), 4.48 (1H, d, $J = 12.0$ Hz, $-OCH_2Ph$), 4.53 (1H, d, $J = 12.0$ Hz, $-OCH_2Ph$), 5.67 (2H, s, olefinic), 7.22-7.75 (15H, m, aromatic). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.32, 26.87, 51.08, 69.00, 70.19, 72.03, 73.47, 74.46, 84.04, 84.43, 127.42, 127.67, 127.77, 128.34, 129.74, 129.84, 130.26, 133.48, 133.62, 136.05, 136.16, 137.92. ESI Q-TOF MS calcd for $C_{32}H_{36}NaO_4Si$ $[M+Na]^+$ 535.228, found 535.228. $[\alpha]_D^{24}$ -53.3° (c 1.10, $CHCl_3$). Anal. Calcd for $C_{32}H_{36}O_4Si$: C, 74.96; H, 7.08. Found: C, 74.75; H, 7.38.

Allyl Alcohol **17**

To a solution of **16** (363 mg, 0.71 mmol) in dist. THF (7 ml) was added a solution of Red-Al® (65% in toluene, 0.43 ml, 1.42 mmol) at 0 °C. After stirring for 20 min at 0 °C and for 15 min at rt, 10% acetic acid aq. was added at 0 °C and then the reaction mixture was poured into a mixture of saturated sodium hydrogen carbonate aq. and saturated potassium sodium tartrate aq. (1vol./1vol.) at 0 °C. After stirring for 1 h at rt, the reaction mixture was extracted with ether (x 3). The combined organic layer was washed with water and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 30 / 70) to afford allyl alcohol **17** (344 mg, 0.67 mmol, 95%) as a colorless oil.

Allyl alcohol **17**. IR (KBr) ν_{max} 3448, 3071, 3032, 2931, 2858, 1473, 1428, 1390, 1363, 1310, 1111, 1091, 978, 862, 822, 741, 702, 612, 508 cm^{-1} . 1H NMR ($CDCl_3$,

300 MHz) δ 1.05 (9H, s, ^tBu), 1.26 (1H, br-s, -OH), 3.39 (1H, dd $J = 10.0, 5.0$ Hz, H-6), 3.45 (1H, dd, $J = 10.0, 6.0$ Hz, H-6), 3.92 (1H, ddd, $J = 8.5, 6.5, 1.0$ Hz, H-1), 3.99 (2H, br-m, H-3'), 4.17 (1H, dddd, $J = 8.5, 3.0, 1.5, 1.5$ Hz, H-2), 4.35 (1H, m, H-5), 4.51 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 4.55 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 5.56 (1H, ddt, $J = 15.5, 6.5, 1.5$ Hz, H-1'), 5.66 (1H, ddd, $J = 10.5, 1.5, 1.5$ Hz, *cis*-olefinic), 5.75 (1H, ddd, $J = 10.5, 2.0, 1.5$ Hz, *cis*-olefinic), 5.91 (1H, dtd, $J = 15.5, 5.5, 1.0$ Hz, H-2'), 7.22-7.69 (15H, m, aromatic). ¹³C NMR (CDCl₃, 75 MHz) δ 19.22, 26.83, 63.02, 69.11, 72.22, 73.36, 74.09, 79.17, 127.60, 127.74, 128.36, 129.04, 129.81, 130.83, 133.03, 133.54, 133.98, 136.05, 138.05. ESI Q-TOF MS calcd for C₃₂H₃₈KO₄Si [M+K]⁺ 553.218, found 553.217. $[\alpha]_D^{24} -82.7^\circ$ (*c* 1.05, CHCl₃). Anal. Calcd for C₃₂H₃₈O₄Si: C, 74.67; H, 7.44. Found: C, 74.68; H, 7.67.

β -Diol 19 and α -Diol 20

To a solution of allyl alcohol **17** (2.20 g, 4.27 mmol) in dist. dichloromethane (21 ml) were added *di*-sodium hydrogenphosphate (1.20 g, 8.55 mmol) and 80% *m*-chloroperbenzoic acid (1.03 g, 4.77 mmol) at 0 °C. After stirring for 14 h at rt under nitrogen atmosphere, the reaction mixture was poured into saturated sodium sulfite aq. and then extracted with dichloromethane (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 30 / 70) to afford a crude epoxy alcohol **18** (2.22 g) as a colorless oil.

To a solution of the crude epoxy alcohol **18** (2.22 g) in dist. toluene (21 ml) was added a solution of Red-Al[®] (65% in toluene, 2.5 ml, 8.55 mmol) at 0 °C. After stirring for 1.5 h at 0 °C, the reaction mixture was added 10% acetic acid aq. at 0 °C and then poured into a mixture of saturated sodium hydrogen carbonate aq. and saturated potassium sodium tartrate aq. (1vol./1vol.) at 0 °C. After stirring for 1 h at rt, the reaction mixture was extracted with ether (x 3). The combined organic layer was washed with water and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 30 / 70) to afford allyl alcohol **17** (126 mg, 6%) and a olefinic alcohol (1.92 g, 86% in two steps) as a colorless oil.

To a solution of the olefinic alcohol (3.30 g, 6.19 mmol) in ethanol (62 ml) were added sodium hydrogen carbonate (1.56 g, 18.6 mmol) and 10% palladium charcoal (620 mg). After stirring for 4 h at rt under hydrogen atmosphere, the reaction mixture was passed through SuperCel[®]. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 20 / 80) to afford β -diol **19** and α -diol **20** (total 3.31 g, 100%) as a colorless oil.

β -Diol **19**. IR (KBr) ν_{\max} 3444, 2929, 2857, 1968, 1890, 1831, 1735, 1455, 1428, 1363, 1111, 825, 742, 703, 612, 503 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 1.04 (9H, s, $t\text{Bu}$), 1.10-1.14 (1H, m, H-4), 1.44-1.56 (2H, m, H-3 and H-4), 1.68-1.86 (2H, m, H-2' and H-3), 1.92-2.15 (2H, br, -OH), 1.97 (1H, dddd, $J = 14.5, 8.0, 8.0, 5.0$ Hz, H-2'), 3.19 (1H, dd, $J = 9.0, 1.0$ Hz, H-1), 3.33 (1H, dd, $J = 10.0, 4.0$ Hz, H-6), 3.39 (1H, dd, $J = 10.0, 6.5$ Hz, H-6), 3.54-3.63 (1H, m, H-5), 3.72-3.82 (1H, m, H-2), 3.743.84 (2H, m, H-3'), 4.21 (1H, dd, $J = 8.0, 4.0$ Hz, H-1'), 4.48 (1H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}$), 4.53 (1H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}$), 7.23-7.74 (15H, m, aromatic). ^{13}C NMR (CDCl_3 , 75 MHz) δ 19.22, 26.87, 27.16, 32.47, 36.61, 60.68, 67.92, 68.50, 72.69, 73.24, 76.57, 83.43, 127.53, 127.68, 127.77, 128.40, 129.71, 129.89, 133.39, 134.44, 135.89, 138.11. ESI Q-TOF MS calcd for $\text{C}_{32}\text{H}_{42}\text{NaO}_5\text{Si}$ [$\text{M}+\text{Na}$] $^+$ 557.270, found 557.273. $[\alpha]_{\text{D}}^{25} -26.6^\circ$ (c 1.60, CHCl_3). Anal. Calcd for $\text{C}_{32}\text{H}_{42}\text{O}_5\text{Si}$: C, 71.87; H, 7.92. Found: C, 71.79; H, 7.86.

α -Diol **20**. IR (KBr) ν_{\max} 3424, 3071, 3032, 2932, 2893, 2859, 1968, 1890, 1831, 1773, 1467, 1455, 1428, 1363, 1317, 1112, 1084, 824, 742, 703, 613, 505 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) δ 1.03 (9H, s, $t\text{Bu}$), 1.02-1.12 (1H, m, H-4), 1.43-1.55 (2H, m, H-4 and H-2'), 1.67-1.75 (2H, m, H-3), 1.72-1.80 (1H, m, H-2'), 2.84 (1H, br-s, -OH), 3.09-3.27 (1H, br-m, -OH), 3.32 (1H, dd $J = 10.0, 4.0$ Hz, H-6), 3.38 (1H, dd, $J = 10.0, 6.0$ Hz, H-6), 3.41 (1H, dd, $J = 9.0, 4.5$ Hz, H-1), 3.48-3.58 (2H, m, H-1' and H-5), 3.67-3.82 (2H, m, H-3'), 4.18 (1H, ddd, $J = 9.0, 4.5, 4.0$ Hz, H-2), 4.46 (1H, d, $J = 16.5$ Hz, $-\text{OCH}_2\text{Ph}$), 4.51 (1H, d, $J = 16.5$ Hz, $-\text{OCH}_2\text{Ph}$), 7.25-7.71 (15H, m, aromatic). ^{13}C NMR (CDCl_3 , 100 MHz) δ 19.15, 26.89, 27.38, 32.85, 32.89, 61.24, 71.41, 72.37, 72.63, 73.29, 83.61, 127.52, 127.57, 127.63, 127.86, 128.36, 129.77, 130.04, 132.89, 134.13, 135.74, 135.81, 138.08. ESI Q-TOF MS calcd for $\text{C}_{32}\text{H}_{42}\text{NaO}_5\text{Si}$ [$\text{M}+\text{Na}$] $^+$ 557.270, found 557.267. $[\alpha]_{\text{D}}^{25} -36.1^\circ$ (c 0.64, CHCl_3). Anal. Calcd for $\text{C}_{32}\text{H}_{42}\text{O}_5\text{Si}$: C, 71.87; H, 7.92. Found: C, 71.79; H, 7.86.

Alcohol **21**

To a solution of β -diol **19** (380 mg, 0.71 mmol) in dichloromethane (3.5 ml) were added benzaldehyde dimethylacetal (0.21 ml, 1.42 mmol) and 10-comphorsulfonic acid (33 mg, 0.14 mmol) at rt. After stirring for 14 h, the reaction mixture was poured into saturated sodium hydrogen carbonate aq. at 0 $^\circ\text{C}$ and then extracted with dichloromethane (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by

silica gel column chromatography (ether / hexane = 10 / 90) to afford a benzylidene acetal (438 mg, 99%) as a colorless oil.

To the benzylidene acetal (590 mg, 0.95 mmol) in round flask was added dropwise a solution of 1.0 M $\text{BH}_3 \cdot \text{THF}$ in THF (9.5 ml, 9.47 mmol) at rt. After refluxing for 7 h, the reaction mixture was added methanol at 0 °C much carefully. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 15 / 85) to afford alcohol **21** (525 mg, 89%) as a colorless oil.

Alcohol **21**. IR (KBr) ν_{max} 3449, 3069, 3032, 2932, 2858, 1961, 1890, 1825, 1734, 1455, 1428, 1363, 1111, 1029, 825, 740, 703, 612, 503 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 1.02 (9H, s, $t\text{Bu}$), 1.08-1.22 (1H, m, H-4), 1.36-1.52 (2H, m, H-3 and H-4), 1.76-1.96 (2H, m, H-3 and H-2'), 2.04-2.16 (1H, m, H-2'), 3.05 (1H, br, -OH), 3.30 (1H, dd, $J = 9.5, 3.5$ Hz, H-6), 3.34 (1H, dd, $J = 9.0, 1.0$ Hz, H-1), 3.44 (1H, dd, $J = 9.5, 7.0$ Hz, H-6), 3.47-3.55 (1H, m, H-2), 3.59-3.69 (1H, m, H-5), 3.85 (1H, ddd, $J = 10.5, 7.5, 3.5$ Hz, H-3'), 4.02 (1H, ddd, $J = 10.5, 9.0, 4.5$ Hz, H-3'), 4.23 (1H, ddd, $J = 6.0, 4.5, 1.0$ Hz, H-1'), 4.37 (1H, d, $J = 11.5$ Hz, $-\text{OCH}_2\text{Ph}$), 4.45 (1H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}$), 4.50 (1H, d, $J = 11.5$ Hz, $-\text{OCH}_2\text{Ph}$), 4.56 (1H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}$), 7.18-7.70 (20H, m, aromatic). ^{13}C NMR (CDCl_3 , 75 MHz) δ 19.15, 26.93, 27.00, 32.86, 33.85, 58.46, 68.36, 71.82, 72.59, 73.21, 74.81, 77.14, 84.24, 127.33, 127.49, 127.57, 127.68, 127.77, 128.21, 128.36, 129.64, 129.74, 133.82, 134.76, 135.82, 135.89, 138.18, 139.02. ESI Q-TOF MS calcd for $\text{C}_{39}\text{H}_{49}\text{O}_5\text{Si}$ $[\text{M}+\text{H}]^+$ 625.335, found 625.370. $[\alpha]_{\text{D}}^{24} -11.9^\circ$ (c 1.13, CHCl_3). Anal. Calcd for $\text{C}_{39}\text{H}_{48}\text{O}_5\text{Si}$: C, 74.96; H, 7.74. Found: C, 74.96; H, 7.87.

Aldehyde **22**

To a solution of **21** (623 mg, 1.00 mmol) in DMSO (5 ml) was added IBX (419 mg, 1.50 mmol). After stirring for 5 h at rt, the reaction mixture was diluted with H_2O (10 ml). The resulting emulsion was passed through SuperCel[®] and washed with ether. The filtrate was extracted with ether (x 3). Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 20 / 80) to afford aldehyde **22** (569 mg, 92%) as a colorless oil.

Aldehyde **22**. IR (KBr) ν_{max} 3069, 3032, 2932, 2893, 2858, 1720, 1473, 1455, 1428, 1363, 1111, 1028, 825, 741, 703, 612, 509 cm^{-1} . ^1H NMR (CDCl_3 , 300 MHz) δ 1.05 (9H, s, $t\text{Bu}$), 1.10-1.26 (1H, m, H-4), 1.35-1.47 (1H, m, H-3), 1.48-1.57 (1H, m, H-4), 1.77-1.87 (1H, m, H-3), 2.67 (1H, ddd, $J = 16.5, 4.5, 3.5$ Hz, H-2'), 2.83 (1H, ddd, $J = 16.5, 6.0, 1.5$ Hz, H-2'), 3.29 (1H, dd, $J = 9.0, 2.0$ Hz, H-1), 3.28 (1H, m,

H-6), 3.40-3.51 (2H, m, H-5 and H-6), 4.03 (1H, ddd, $J = 10.5, 9.0, 4.5$ Hz, H-2), 4.41 (1H, d, $J = 11.5$ Hz, $-\text{OCH}_2\text{Ph}$), 4.45 (1H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}$), 4.51 (1H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}$), 4.52 (1H, d, $J = 11.5$ Hz, $-\text{OCH}_2\text{Ph}$), 4.53 (1H, ddd, $J = 6.0, 4.5, 2.0$ Hz, H-1'), 7.15-7.71 (20H, m, aromatic), 9.85 (1H, dd, $J = 2.5, 1.5$ Hz, H-3'). ^{13}C NMR (CDCl_3 , 75 MHz) δ 19.09, 26.90, 27.45, 32.82, 45.00, 68.12, 72.18, 72.64, 73.06, 73.24, 77.11, 84.20, 127.47, 127.53, 127.61, 127.63, 127.67, 128.24, 128.32, 129.64, 129.73, 133.76, 134.55, 135.78, 135.87, 138.32, 138.44, 201.80. ESI Q-TOF MS calcd for $\text{C}_{39}\text{H}_{46}\text{NaO}_5\text{Si}$ $[\text{M}+\text{Na}]^+$ 645.301, found 645.353. $[\alpha]_{\text{D}}^{24} -13.3^\circ$ (c 1.30, CHCl_3). Anal. Calcd for $\text{C}_{39}\text{H}_{46}\text{O}_5\text{Si}$: C, 75.20; H, 7.44. Found: C, 75.07; H, 7.66.

E'FH' ring 25

To a solution of E' ring-aldehyde **12** (603 mg, 2.53 mmol), which was treatment with toluene azeotrope in advance, in dist. tetrahydrofuran (25 ml) was added dropwise a solution of 1.59 M *n* BuLi in Hexane (1.59 ml, 2.53 mmol) at -78°C under nitrogen atmosphere. After stirring for 30 min at -78°C , a solution of aldehyde **22** (1.05 g, 1.69 mmol), which was treatment with toluene azeotrope in advance, in dist. tetrahydrofuran (7 ml) was added to the reaction mixture over 10min. After stirring for 35 min at -78°C , the reaction mixture was poured into saturated sodium hydrogen carbonate aq. at 0°C and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ethyl acetate / hexane = 5 / 95 to 20 / 80) to afford an propargyl alcohol (1.24 g, 86%) as a colorless oil, recovered E' ring-enyne **12** (258 mg, 43%) and recovered H' ring-aldehyde **22** (151 mg, 14%).

To a solution of the propargyl alcohol (250 mg, 0.29 mmol) in tetrahydrofuran (2.9 ml) was added 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (0.58 ml, 0.58 mmol) at 0°C . After stirring for 7 h at rt under nitrogen atmosphere, the reaction mixture was poured into saturated ammonium chloride aq. at 0°C and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude diol, which was used in next step without further purification.

To a solution of the crude diol in dichloromethane (4 ml) were added pyridine (0.5 ml), acetic anhydride (0.2 ml) and *N,N*-dimethylaminopyridine (10 mg). After stirring for 2 h at rt, the reaction mixture was poured into saturated sodium hydrogen carbonate aq. at 0°C and then extracted with dichloromethane (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the

solvent gave a crude oil, which was purified by silica gel column chromatography (ethyl acetate / hexane = 30 / 70) to afford diacetate **23** (201 mg, 98%) as a colorless oil.

To a solution of diacetate **23** (37 mg, 0.052 mmol) in methanol (2 ml) was added pyridinium *p*-toluenesulfonate (13 mg, 0.052 mmol). After stirring for 30 min at rt, the reaction mixture was poured into saturated sodium hydrogen carbonate aq. at 0 °C and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by short silica gel column chromatography to afford a crude alcohol.

To a solution of the crude alcohol in dry dichloromethane (2 ml) was added a solution of Co₂(CO)₈ (36 mg, 0.10 mmol) in dry dichloromethane (1 ml) at 0 °C under nitrogen atmosphere. After stirring for 1.5 h at rt, the solvent was concentrated. The residue was purified by silica gel column chromatography (ether / hexane = 40 / 60) to afford acetylene cobalt complex **24** (46 mg, 96% in two steps) as a reddish brown oil.

To a solution of acetylene cobalt complex **24** (71 mg, 0.077 mmol) in dry dichloromethane (7.7 ml) was added a solution of BF₃·OEt₂ (0.20 M in 1,2-dichloroethane, 0.39 ml, 0.077 mmol) at 0 °C under nitrogen atmosphere. After stirring for 10 min at 0 °C and for 30 min at rt, the reaction mixture was poured into saturated sodium hydrogen carbonate aq. at 0 °C and then extracted with dichloromethane (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by silica gel column chromatography (ether / hexane = 30 / 70) to afford E'FH' ring **25** (51 mg, 77%) as a reddish brown oil.

E'FH' ring **25**. IR (KBr) ν_{\max} 2931, 2855, 2361, 2090, 2051, 2026, 1741, 1560, 1456, 1373, 1239, 1095, 736, 698, 661, 518, 498 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 1.27-1.38 (1H, m, H-3), 1.42-1.60 (2H, m, H-2), 1.42-1.60 (2H, m, H-16 and H-17), 1.75-1.86 (1H, m, H-3 and H-17), 1.92 (3H, s, -OCOCH₃), 1.97 (1H, ddd, *J* = 14.5, 10.5, 3.5 Hz, H-12), 2.26-2.38 (3H, m, H-6, H-12 and H-16), 2.69 (1H, br-dd, *J* = 13.5, 9.5 Hz, H-6), 3.21 (1H, dd, *J* = 10.0, 4.5 Hz, H-4), 3.28 (1H, dd, *J* = 10.0, 4.0 Hz, H-5), 3.25-3.35 (1H, m, H-1), 3.40-3.47 (1H, m, H-6), 3.53-3.62 (3H, m, H-14, H-18 and H-19), 3.81-3.91 (2H, m, H-1 and H-13), 4.54 (2H, s, -OCH₂Ph), 4.59 (1H, d, *J* = 12.0 Hz, -OCH₂Ph), 4.67 (1H, d, *J* = 12.0 Hz, -OCH₂Ph), 4.79 (1H, dd, *J* = 11.5, 1.5 Hz, H-11), 4.91 (1H, ddd, *J* = 10.0, 9.5, 5.0 Hz, H-15), 5.86 (1H, ddd, *J* = 11.0, 9.5, 7.5 Hz, H-7), 6.76 (1H, d, *J* = 11.0 Hz, H-8), 7.22-7.34 (10H, m, aromatic). ¹³C NMR (CDCl₃, 100 MHz) δ 21.16, 25.56, 27.56, 29.19, 29.28, 29.87, 38.70, 67.92, 68.83, 71.72, 72.79, 73.48, 74.03, 74.64, 77.50, 78.13, 80.06, 80.61, 86.78, 99.72, 127.55, 127.62, 127.70, 128.34, 130.51, 130.70, 138.40, 138.64, 169.79, 199.41. ESI Q-TOF MS calcd for C₄₁H₄₃Co₂O₁₃ [M+H]⁺ 861.137, found 861.168. [α]_D²⁷ -916.0° (*c* 0.016, CHCl₃).

Ketone **26**, Conjugated Enone **27** and Diene **28**

To a PORTABLE REACTOR (TVS-N2 type, TAIATSU TECHNO® CORPORATION, Japan) was placed a solution of acetylene cobalt complex **25** (29 mg, 0.034 mmol) in benzene (17 ml). After stirring for 4.5 h at 65 °C under 100 kg/cm² hydrogen 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 preparative thin layer chromatography to afford SM (2.1 mg, 7%), diene **27** (2.9 mg, 15%), ketone **26** (7.3 mg, 37%) and conjugated enone **28** (0.7 mg, 4%).

Ketone **26**. IR (KBr) ν_{\max} 2931, 2858, 1738, 1716, 1455, 1372, 1240, 1092, 1038, 738, 699 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 1.27 (1H, dddd, $J = 12.0, 12.0, 11.0, 5.0$ Hz, H-3), 1.40-1.50 (2H, m, H-16 and 17), 1.47-1.53 (2H, m, H-2), 1.77 (1H, dm, $J = 8.5$ Hz, H-17), 1.87 (3H, s, -OCOCH₃), 1.91-1.96 (2H, m, H-12), 1.97-2.03 (1H, m, H-3), 2.20 (1H, ddd, $J = 13.5, 6.5, 3.0$ Hz, H-6), 2.29 (1H, ddd, $J = 8.0, 5.0, 3.0$ Hz, H-16), 2.56 (1H, dd, $J = 10.5, 7.0$ Hz, H-9), 2.97 (1H, ddd, $J = 13.5, 10.5, 3.5$ Hz, H-6), 2.97 (1H, ddd, $J = 11.0, 9.5, 4.0$ Hz, H-4), 3.27 (1H, ddd, $J = 9.5, 3.5, 3.0$ Hz, H-5), 3.28 (1H, ddd, $J = 11.5, 11.5, 3.0$ Hz, H-1), 3.43 (1H, dd, $J = 12.5, 7.5$ Hz, H-19), 3.50 (1H, dd, $J = 9.5, 2.5$ Hz, H-14), 3.55-3.60 (1H, m, H-18), 3.57 (1H, dd, $J = 12.5, 5.5$ Hz, H-19), 3.73 (1H, ddd, $J = 7.0, 5.5, 2.5$ Hz, H-13), 3.83 (1H, dm, $J = 11.5$ Hz, H-1), 3.87 (1H, dd, $J = 8.5, 5.5$ Hz, H-11), 3.97 (1H, dd, $J = 10.5, 10.5$ Hz, H-9), 4.51 (2H, s, -OCH₂Ph), 4.53 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 4.58 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 4.86 (1H, ddd, $J = 10.0, 9.5, 5.0$ Hz, H-15), 5.62 (1H, ddd, $J = 10.5, 10.5, 7.0$ Hz, H-8), 5.71 (1H, ddd, $J = 10.5, 10.5, 6.5$ Hz, H-7), 7.25-7.37 (10H, m, aromatic). ¹³C NMR (CDCl₃, 100 MHz) δ 21.13, 25.51, 27.36, 28.67, 29.11, 29.40, 32.76, 36.90, 68.15, 68.27, 71.41, 72.87, 73.43, 73.54, 75.20, 77.60, 78.83, 79.66, 82.16, 124.57, 127.63, 127.99, 128.32, 128.38, 128.69, 138.12, 138.30, 169.80, 211.48. ESI Q-TOF MS calcd for C₃₅H₄₄NaO₈ [M+Na]⁺ 615.293, found 615.284. $[\alpha]_{\text{D}}^{24} +118.7^\circ$ (c 0.30, CHCl₃).

Diene **28**. IR (KBr) ν_{\max} 2926, 2854, 1739, 1455, 1373, 1240, 1145, 1090, 1046, 738, 698 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 1.30-1.46 (3H, m, H-3, H-16 and 17), 1.45-1.55 (2H, m, H-2), 1.78 (1H, dm, $J = 7.5$ Hz, H-17), 1.89 (3H, s, -OCOCH₃), 1.90-1.95 (2H, m, H-12), 1.94-1.99 (1H, m, H-3), 2.22 (1H, br-ddd, $J = 13.5, 6.0, 4.0$ Hz, H-6), 2.30 (1H, ddd, $J = 8.5, 5.0, 3.0$ Hz, H-16), 2.74 (1H, ddd, $J = 13.5, 10.5, 3.5$ Hz, H-6), 3.07 (1H, ddd, $J = 9.5, 4.0, 3.5$ Hz, H-5), 3.20 (1H, ddd, $J = 10.5, 9.5, 4.0$ Hz, H-4), 3.25 (1H, ddd, $J = 11.5, 11.5, 3.0$ Hz, H-1), 3.39 (1H, dd, $J = 12.5, 7.5$ Hz, H-19), 3.50 (1H, dd, $J = 9.5, 2.5$ Hz, H-14), 3.55-3.60 (1H, m, H-18), 3.57 (1H, dd, $J = 12.5, 5.5$ Hz, H-19), 3.73 (1H, ddd, $J = 7.0, 5.5, 2.5$ Hz, H-13), 3.83 (1H, dm, $J = 11.5$ Hz, H-1), 3.87 (1H, dd, $J = 8.5, 5.5$ Hz, H-11), 3.97 (1H, dd, $J = 10.5, 10.5$ Hz, H-9), 4.51 (2H, s, -OCH₂Ph), 4.53 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 4.58 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 4.86 (1H, ddd, $J = 10.0, 9.5, 5.0$ Hz, H-15), 5.62 (1H, ddd, $J = 10.5, 10.5, 7.0$ Hz, H-8), 5.71 (1H, ddd, $J = 10.5, 10.5, 6.5$ Hz, H-7), 7.25-7.37 (10H, m, aromatic). ¹³C NMR (CDCl₃, 100 MHz) δ 21.13, 25.51, 27.36, 28.67, 29.11, 29.40, 32.76, 36.90, 68.15, 68.27, 71.41, 72.87, 73.43, 73.54, 75.20, 77.60, 78.83, 79.66, 82.16, 124.57, 127.63, 127.99, 128.32, 128.38, 128.69, 138.12, 138.30, 169.80, 211.48. ESI Q-TOF MS calcd for C₃₅H₄₄NaO₈ [M+Na]⁺ 615.293, found 615.284. $[\alpha]_{\text{D}}^{24} +118.7^\circ$ (c 0.30, CHCl₃).

= 10.0, 2.5 Hz, H-14), 3.43 (1H, dd, $J = 12.0, 7.0$ Hz, H-19), 3.53-3.58 (1H, m, H-18), 3.57 (1H, dd, $J = 12.0, 5.5$ Hz, H-19), 3.78 (1H, td, $J = 6.0, 2.5$ Hz, H-13), 3.83 (1H, dm, $J = 11.5$ Hz, H-1), 3.96 (1H, dt, $J = 7.0, 7.0$ Hz, H-11), 4.53 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 4.54 (2H, s, -OCH₂Ph), 4.58 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 4.90 (1H, ddd, $J = 10.0, 10.0, 5.0$ Hz, H-15), 5.58 (1H, dd, $J = 11.0, 7.0$ Hz, H-10), 5.79 (1H, ddd, $J = 11.0, 10.5, 6.0$ Hz, H-7), 5.97 (1H, br-d, $J = 11.0$ Hz, H-9), 6.01 (1H, br-d, $J = 11.0$ Hz, H-8), 7.25-7.39 (10H, m, aromatic). ¹³C NMR (CDCl₃, 100 MHz) δ 21.13, 26.10, 27.47, 29.07, 31.65, 33.23, 38.17, 67.90, 68.50, 71.15, 72.90, 73.40, 77.56, 78.83, 80.54, 80.74, 80.90, 127.59, 127.63, 127.94, 128.35, 129.46, 129.78, 130.27, 134.74, 138.35, 138.51, 169.80. ESI Q-TOF MS calcd for C₃₅H₄₄NaO₇ [M+Na]⁺ 599.298, found 599.302. $[\alpha]_D^{25} -74.6^\circ$ (c 0.25, CHCl₃). Anal. Calcd for C₃₅H₄₄O₇: C, 72.89; H, 7.69. Found: C, 72.88; H, 7.72.

Conjugated Enone **27**. IR (KBr) ν_{\max} 2928, 2855, 1737, 1653, 1455, 1373, 1241, 1093, 1040, 738, 699 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz) δ 1.29-1.40 (1H, m, H-3), 1.40-1.50 (2H, m, H-16 and 17), 1.46-1.58 (2H, m, H-2), 1.74-1.78 (1H, m, H-17), 1.80-1.94 (1H, m, H-3), 1.80-1.94 (2H, m, H-12), 1.88 (3H, s, -OCOCH₃), 2.25-2.31 (1H, m, H-16), 2.70 (1H, ddd, $J = 13.5, 9.5, 7.0$ Hz, H-6), 2.79 (1H, dd, $J = 13.5, 6.0$ Hz, H-10), 2.85-2.93 (1H, m, H-10), 2.90 (1H, br-ddd, $J = 13.5, 9.5, 2.0$ Hz, H-6), 3.07 (1H, ddd, $J = 10.5, 9.5, 4.5$ Hz, H-4), 3.23 (1H, ddd, $J = 9.5, 7.0, 2.0$ Hz, H-5), 3.28 (1H, ddd, $J = 11.5, 11.5, 3.0$ Hz, H-1), 3.43 (1H, dd, $J = 12.0, 3.5$ Hz, H-19), 3.44 (1H, dd, $J = 9.5, 2.5$ Hz, H-14), 3.52-3.58 (1H, m, H-18), 3.56 (1H, dd, $J = 12.0, 5.5$ Hz, H-19), 3.75 (1H, ddd, $J = 7.5, 4.5, 2.5$ Hz, H-13), 3.83 (1H, dm, $J = 11.5$ Hz, H-1), 3.94 (1H, ddt, $J = 7.5, 4.5, 2.5$ Hz, H-11), 4.53 (1H, d, $J = 11.5$ Hz, -OCH₂Ph), 4.53 (1H, $J = 12.0$ Hz, -OCH₂Ph), 4.56 (1H, d, $J = 11.5$ Hz, -OCH₂Ph), 4.57 (1H, d, $J = 12.0$ Hz, -OCH₂Ph), 4.85 (1H, ddd, $J = 10.0, 9.5, 5.0$ Hz, H-15), 6.11 (1H, d, $J = 12.0$ Hz, H-8), 6.32 (1H, dt, $J = 12.0, 9.5$ Hz, H-7), 7.26-7.38 (10H, m, aromatic). ¹³C NMR (CDCl₃, 100 MHz) δ 21.14, 25.58, 27.39, 29.10, 29.68, 30.67, 32.43, 37.18, 49.98, 67.99, 68.45, 71.91, 72.86, 73.43, 74.21, 76.25, 77.45, 80.25, 80.35, 127.59, 127.68, 127.93, 128.34, 128.37, 134.71, 138.33, 138.40, 139.74, 169.84, 202.29. ESI Q-TOF MS calcd for C₃₅H₄₄NaO₈ [M+Na]⁺ 615.293, found 615.290. $[\alpha]_D^{26} +16.8^\circ$ (c 0.12, CHCl₃).

E'FGH' ring 5

To a solution of ketone **26** (7.9 mg, 0.013 mmol) in methanol (1 ml) was added K₂CO₃ (3 mg, 0.022 mmol). After stirring for 3 h at rt, the reaction mixture was poured into saturated ammonium chloride aq. at 0 °C and then extracted with ether (x 3). The

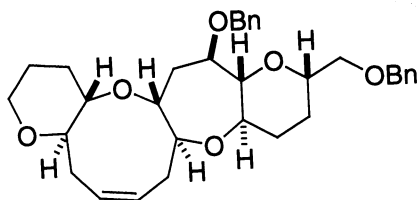
combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by preparative thin layer chromatography to afford a hydroxyketone (7.2 mg, 99%).

To a solution of the hydroxyketone (7.2 mg, 0.013 mmol) and triethylsilane (0.13 ml, 0.81 mmol) in dry acetonitrile (1.3 ml) was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.79 M in 1,2-dichloroethane, 0.1 ml, 0.079 mmol) at $-15\text{ }^\circ\text{C}$ under nitrogen atmosphere. After stirring for 20 min at $-15\text{ }^\circ\text{C}$ and for 30 min at rt, the reaction mixture was poured into saturated sodium hydrogen carbonate aq. at $0\text{ }^\circ\text{C}$ and then extracted with ether (x 3). The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Concentration of the solvent gave a crude oil, which was purified by preparative thin layer chromatography to afford E'FGH' ring **5** (4.0 mg, 57%) as a white solid.

E'FGH' ring **5**. Mp $113.0\text{-}113.5\text{ }^\circ\text{C}$. IR (KBr) ν_{max} 2931, 2863, 1455, 1118, 1097, 733, 695 cm^{-1} . ^1H NMR (CDCl_3 , 600 MHz, $-20\text{ }^\circ\text{C}$, a 2:1 mixture of DOWN and UP conformers) δ 1.40-1.47 (1H, m, H-17), 1.45-1.51 (1H, m, H-16), 1.49-1.56 (1H, m, H-3), 1.64-1.71 (2H, m, H-2), 1.70-1.75 (1H, m, H-17), 2.05 (1/3H, dd, $J = 13.5, 5.5$ Hz, H-9_{UP}), 2.07-2.12 (1/3H, m, H-6_{UP}), 2.07-2.12 (2x2/3H, m, H-6_{DOWN} and H-3_{DOWN}), 2.10-2.15 (1/3H, m, H-12_{UP}), 2.10-2.15 (2x2/3H, m, H-12_{DOWN}), 2.14-2.18 (1H, m, H-16), 2.18-2.22 (1/3H, m, H-3_{UP}), 2.25 (2/3H, dd, $J = 12.5, 5.5$ Hz, H-9_{DOWN}), 2.28 (1/3H, dd, $J = 14.0, 5.0$ Hz, H-12_{UP}), 2.75 (2/3H, ddd, $J = 12.5, 10.5, 9.5$ Hz, H-6_{DOWN}), 2.80 (2/3H, ddd, $J = 12.5, 9.5, 9.5$ Hz, H-9_{DOWN}), 2.92-2.96 (1/3H, m, H-9_{UP}), 2.94-2.98 (1/3H, m, H-6_{UP}), 3.00 (2/3H, dd, $J = 9.5, 9.5$ Hz, H-5_{DOWN}), 3.13 (2/3H, dd, $J = 9.5, 9.5$ Hz, H-10_{DOWN}), 3.17 (1H, ddd, $J = 9.5, 9.5, 4.0$ Hz, H-15), 3.25 (1/3H, ddd, $J = 10.5, 10.0, 4.5$ Hz, H-4_{UP}), 3.31 (1/3H, dd, $J = 10.0, 5.5$ Hz, H-5_{UP}), 3.32-3.38 (1H, m, H-1), 3.33 (2/3H, dd, $J = 9.5, 3.5$ Hz, H-14_{DOWN}), 3.40 (1/3H, dd, $J = 9.5, 4.0$ Hz, H-14_{UP}), 3.41 (2/3H, ddd, $J = 10.5, 9.5, 4.5$ Hz, H-4_{DOWN}), 3.46-3.49 (2H, m, H-19), 3.48-3.52 (1/3H, m, H-13_{UP}), 3.53-3.58 (1/3H, m, H-10_{UP}), 3.57-3.61 (1H, m, H-18), 3.71-3.74 (1/3H, m, H-11_{UP}), 3.71-3.74 (2/3H, m, H-13_{DOWN}), 3.82 (2/3H, ddd, $J = 9.5, 9.0, 2.5$ Hz, H-11_{DOWN}), 3.86-3.92 (1H, m, H-1), 4.60 (1/3H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}_{\text{UP}}$), 4.60 (2x2/3H, s, $-\text{OCH}_2\text{Ph}_{\text{DOWN}}$), 4.60 (2x1/3H, s, $-\text{OCH}_2\text{Ph}_{\text{UP}}$), 4.61 (2/3H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}_{\text{DOWN}}$), 4.68 (1/3H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}_{\text{UP}}$), 4.70 (2/3H, d, $J = 12.0$ Hz, $-\text{OCH}_2\text{Ph}_{\text{DOWN}}$), 5.71 (2/3H, ddd, $J = 11.0, 9.5, 5.5$ Hz, H-8_{DOWN}), 5.72 (2/3H, ddd, $J = 11.0, 10.5, 5.5$ Hz, H-7_{DOWN}), 5.80 (1/3H, ddd, $J = 11.0, 10.5, 5.5$ Hz, H-8_{UP}), 5.84 (1/3H, ddd, $J = 11.0, 10.5, 5.0$ Hz, H-7_{UP}), 7.29-7.40 (10H, m, aromatic). ^{13}C NMR (CDCl_3 , 150 MHz, at $-20\text{ }^\circ\text{C}$, a 2:1 mixture of DOWN and UP conformers) δ 25.59, 25.90, 27.36, 27.48, 29.40, 29.69, 30.14, 31.24, 31.35, 31.61, 32.33, 32.89, 33.96, 35.47, 38.97, 39.06, 67.98, 68.36, 70.72, 71.01, 72.35, 73.12, 76.13, 76.40, 77.85, 78.32, 78.44, 79.57, 80.78, 81.48, 82.48, 82.77, 86.16, 86.49, 86.55, 86.63, 87.40, 127.33, 127.37,

127.40, 127.54, 127.61, 127.91, 128.12, 128.24, 128.34, 128.94, 137.84, 138.28, 138.34. ESI Q-TOF MS calcd for $C_{33}H_{42}NaO_6$ $[M+Na]^+$ 557.288, found 557.285. $[\alpha]_D^{25} +21.7^\circ$ (*c* 0.32, $CHCl_3$). Anal. Calcd for $C_{33}H_{42}O_6$: C, 74.13; H, 7.92. Found: C, 73.96; H, 8.03.

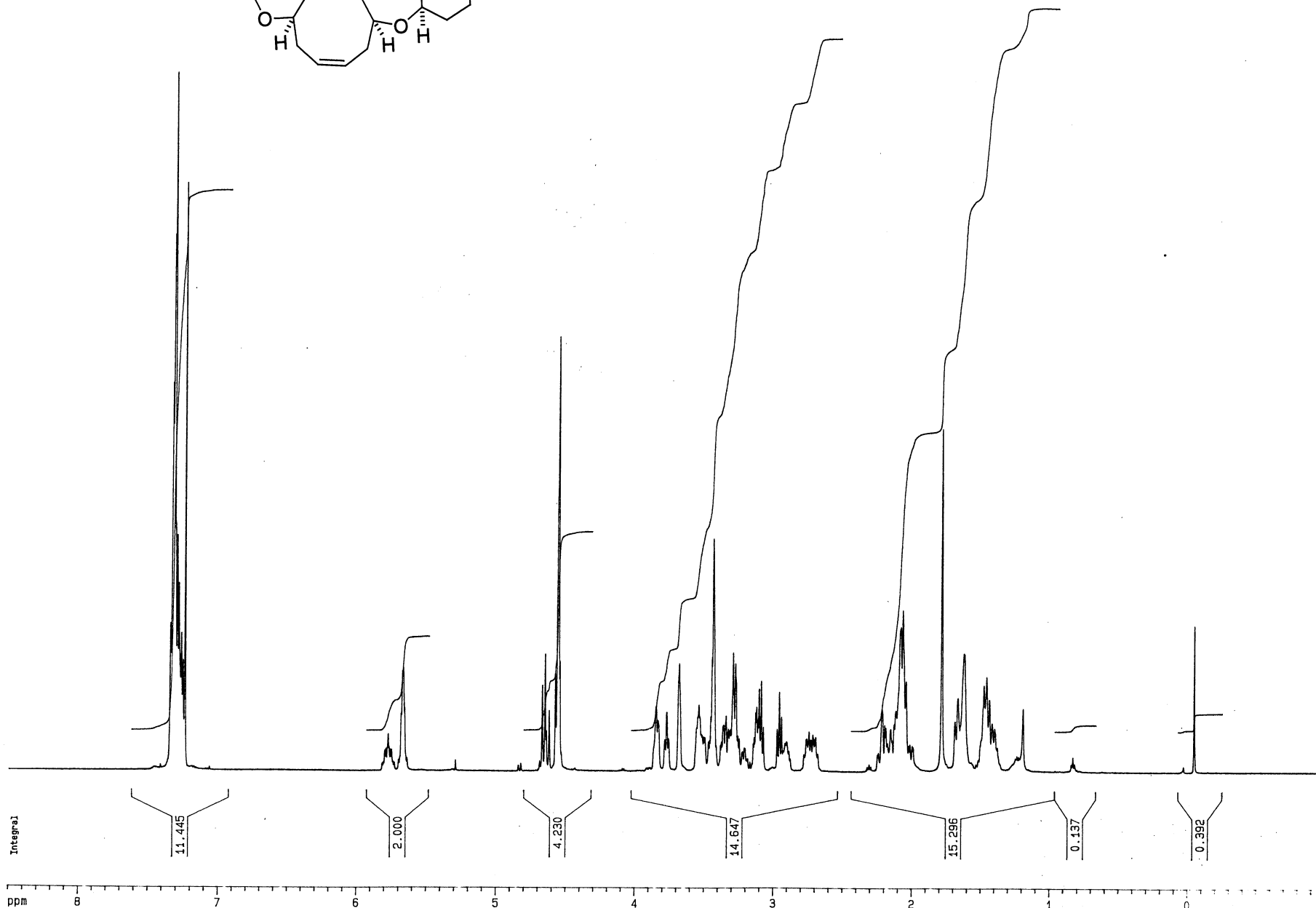
NAME shige600-1
 EXPNO 66
 PROCNO 1



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 SOLVENT CDCL3
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 DS 0
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 FIDRES 0.175388 Hz
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 RG 512
 DW 87.000 usec
 DE 108.75 usec
 TE 300.0 K

F2 - Processing parameters
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 GB 0
 PC 1.00

1D NMR plot parameters
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 F2P -1.000 ppm
 F2 -600.14 Hz
 PPMCM 0.28024 ppm/cm
 HZCM 168.17982 Hz/cm



ppm 8 7 6 5 4 3 2 1 0