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General Procedure. All experiments dealing with air- and moisture-sensitive compounds were conducted under an atmosphere of dry argon. Ethereal solvents were distilled from benzophenone ketyl immediately before use. Dichloromethane was distilled successively from P_2O_5 and CaH_2, and stored over 4Å molecular sieves. For shin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. For flash column chromatography, silica gel 60 K070-WH (70-230 mesh) from Katayama Chemical or silica gel 60 (Art 7734, 70-230 mesh) from Merck was used. Silica gel preparative TLC (PTLC) was performed on Merck silica gel 60 PF_{254} (Art 7747). Melting point (mp) determinations were performed by using a Yanako MP-S3 instrument and are uncorrected. ^1H NMR and ^{13}C NMR were measured on a JEOL JNM GX-400, a JNM alpha-400, a JNM lambda-300, or a JNM lambda-400 spectrometer. Infrared (IR) spectra were recorded on a Jasco IRA-202 or a Perkin Elmer 1600 FTIR spectrometer. High resolution mass spectra (HRMS) were obtained with a Hitachi M-80 or a JEOL JMS AX505HA spectrometer. Optical rotations ($[\alpha]_D$) were measured on a Jasco DIP-360 or a DIP-1000 polarimeter.

Synthesis of phenol 12: To a mixture of phenol **11**[15] (2.97 g, 12.2 mmol) and paraformaldehyde (0.555 g) in CH_2Cl_2 (25 mL) was slowly added Et_2AlCl (1.8 mL, 14 mmol, neat) at 0 °C. After stirring for 30 min, the reaction mixture was warmed to room temperature, and the stirring was continued for 17 h. The reaction was quenched by adding 2 M HCl, and the products were extracted with EtOAc. The combined organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 6/4) to give phenol **12** (3.28 g, 98%) as a colorless solid; mp 101–103 °C; ^1H NMR ($CDCl_3$) δ 2.19 (s, 3 H), 2.75 (t, 1 H, J = 5.9 Hz), 3.76 (s, 3 H), 4.68 (d, 2 H, J = 5.9 Hz), 4.96 (s, 2 H), 6.20 (s, 1 H), 6.58 (s, 1 H), 7.28–7.42 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 9.4, 60.7, 62.1, 70.8, 107.8, 120.0, 123.6, 127.2, 127.7, 128.4, 137.4, 141.5, 146.0, 150.4; IR (neat) 3460, 3270, 2950, 1610, 1500, 1455, 1430, 1390, 1350, 1240, 1190, 920, 900, 750 cm^{-1}; Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 69.95; H, 6.79.

Synthesis of alcohol 13: A mixture of phenol **12** (12.3 g, 44.9 mmol) and K_2CO_3 (25.4 g, 184 mmol) and CH_3I (14 mL, 225 mmol) in acetone (230 mL) was heated at 60 °C for 9 h. After cooling to 0 °C, the reaction was quenched by adding saturated aqueous NH_4Cl, and the mixture was extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in

vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 6/4) to give alcohol **13** (11.9 g, 92%) as a colorless oil, which solidified in refrigerator; mp 52–53 °C; ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3 H), 2.34–2.52 (broad, 1 H), 3.81 (s, 3 H), 3.84 (s, 3 H), 4.64 (d, 2 H, J = 5.1 Hz), 5.01 (s, 2 H), 6.67 (s, 1 H), 7.29–7.43 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 9.04, 60.2, 60.9, 61.2, 70.3, 106.8, 120.8, 127.1, 127.7, 128.4, 131.3, 137.3, 144.9, 151.7, 153.3; IR (neat) 3430, 2950, 1610, 1590, 1490, 1465, 1415, 1335, 1245, 1190, 1130, 1100 cm^{-1}; Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.54; H, 7.17.

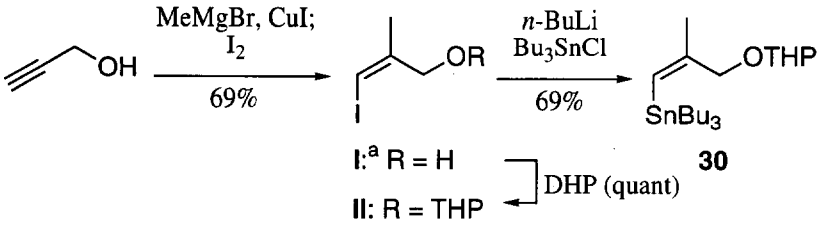
Syntheis of iodo alcohol 14: To a mixture of alcohol **13** (4.03 g, 14.0 mmol) and silver(I) trifluoroacetate (6.18 g, 28.0 mmol) in $CHCl_3$ (60 mL) was added a solution of I_2 (5.33 g, 21.0 mmol) in $CHCl_3$ (90 mL) with stirring at 0 °C. After stirring for 1 h, the mixture was filtered through a Celite pad, which was washed with $CHCl_3$. To the filtrate was added aqueous saturated $Na_2S_2O_3$, and the mixture was extracted with $CHCl_3$. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 3/1) to give iodo alcohol **14** (5.47 g, 94%) as a colorless oil, which solidified in refrigerator; mp 70–72 °C; ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 2.52 (s, 1 H), 3.83 (s, 3 H), 3.83 (s, 3 H), 4.84 (d, 2 H, J = 7.9 Hz), 4.86 (s, 2 H), 7.33–7.57 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 60.1, 61.5, 64.6, 74.3, 92.1, 126.5, 128.05, 128.12, 128.4, 134.9, 136.6, 148.7, 152.5, 153.0; IR (neat) 3450, 2940, 1500, 1450, 1405, 1370, 1315, 1260, 1245, 1190, 1105, 1090, 1025, 1005 cm^{-1}; Anal. Calcd for $C_{17}H_{19}O_4I$: C, 49.29; H, 4.62. Found: C, 49.15; H, 4.63.

Synthesis of aldehyde 15: A mixed suspension of iodo alcohol **14** (1.64 g, 3.96 mmol), pyridine (190 mg, 2.40 mmol) and PDC (2.39 g, 6.36 mmol) in CH_2Cl_2 (25 mL) was vigorously stirred for 41 h. An additional amount of PDC (0.596 g, 1.59 mmol) was added, and the stirring was continued for 6 h. After diluting with hexane, the mixture was filtered through a Celite pad, and washed with Et_2O. The filtrate was concentrated in vacuo, and the residue was purified by flash column chromatography (hexane/EtOAc = 9/1) to give aldehyde **15** (1.50 g, 92%) as a yellow oil, which solidified in refrigerator; mp 35–38 °C; ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 3.87 (s, 3 H), 3.92 (s, 3 H), 4.88 (s, 2 H), 7.35–7.59 (m, 5 H), 10.15 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.5, 60.5, 62.3, 74.6, 88.2, 128.2, 128.4, 128.6, 128.9, 132.6, 136.4, 152.4, 153.1, 153.7, 192.5; IR (neat) 2950, 1695, 1570, 1550, 1460, 1370, 1310, 1250, 1105, 1090 cm^{-1}; Anal. Calcd for $C_{17}H_{17}O_4I$: C, 49.53; H, 4.16. Found: C, 49.24; H, 4.11.

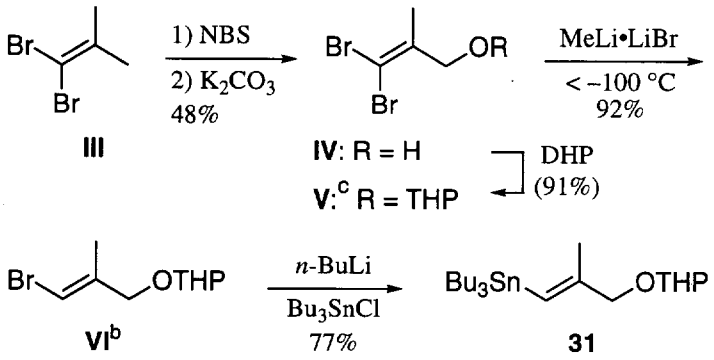
Synthesis of methyl ester 17: To a solution of phosphonate **16**[19] (1.35 g, 5.27 mmol) in THF (10 mL) was added *n*-BuLi (3.2 mL, 1.66 M hexane solution, 5.3 mmol) at 0 °C, and the mixture was stirred for 10 min. After cooling to –78 °C, a solution of aldehyde **15** (1.41 g, 3.41 mmol) in THF (10 mL) was added, and the temperature was gradually raised to room temperature for 1.5 h. The reaction was quenched by adding saturated aqueous NH_4Cl, and the products were extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give crude ketene dithioacetal (2.58 g). To a solution of the crude material in MeOH (20 mL) was added $AgNO_3$ (1.87 g, 11.0 mmol), and the mixture was heated at 60 °C for 1 h. After cooling to room temperature, the mixture was filtered through a Celite pad, and washed with EtOAc. The filtrate was azeotropically evaporated with toluene to remove MeOH, and the residue was dissolved in EtOAc and washed with brine. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatography (hexane/EtOAc = 85/15) to give methyl ester **17** (1.48 g, 95%, 2 steps) as a pale yellow oil; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H), 3.72 (s, 3 H), 3.81 (s, 3 H), 3.82 (s, 3 H), 3.96 (s, 2 H), 4.85 (s, 2 H), 7.32–7.57 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 10.8, 40.6, 52.0, 60.0, 60.5, 74.2, 93.4, 125.7, 128.0, 128.1, 128.4, 130.2, 136.8, 148.4, 152.1, 152.9, 171.2; IR (neat) 2950, 1745, 1460, 1410, 1380, 1320, 1240, 1170, 1110, 1090, 1030, 1005 cm^{-1}; Anal. Calcd for $C_{19}H_{21}O_5I$: C, 50.02; H, 4.64. Found: C, 50.06; H, 4.83.

Syntheses of Vinyl Anion Precursors: The vinylstannanes **30**, **31**, and **32** were synthesized according to the following schemes (Scheme A–C).

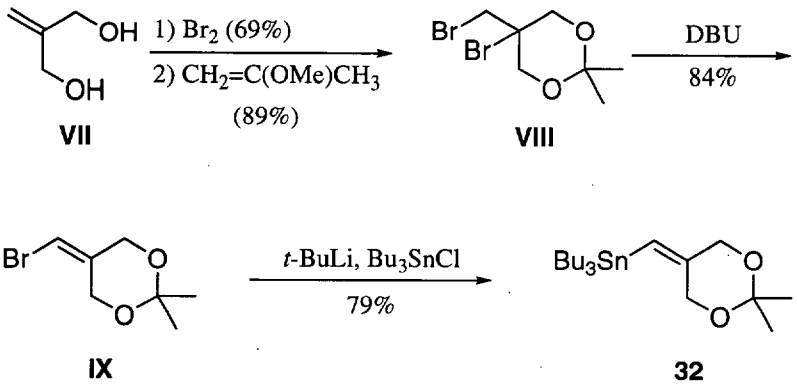
Scheme A Precursor for Furaquinocin A



Scheme B Precursor for Furaquinocin B[b]



Scheme C Precursor for Furaquinocin H



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Synthesis of (Z)-vinylstannane 30. *(i) iodination*: To a suspension of CuI (1.26 g, 6.63 mmol) and propargyl alcohol (3.68 g, 65.7 mmol) in Et_2O (50 mL) was added a solution of MeMgBr (1.31 M in Et_2O, 151 mL, 198 mmol) for 2 h at –20 °C, and the mixture was gradually warmed to 25 °C for 12 h. This mixture was chilled to 0 °C, to which was added a solution of I_2 (33.4 g, 131 mmol) in Et_2O (150 mL), and the stirring was continued at 25 °C for 24 h. The mixture was poured into crushed ice, and filtered through a Celite pad. The organic layer was separated and successively washed with saturated aq. $Na_2S_2O_3$, saturated aq. Na_2SO_4, and dried (Na_2SO_4) and concentrated in vacuo. Bulb-to-bulb distillation (110–125 °C, 25 mmHg) gave alcohol **I** (8.81 g, 68%) as colorless oil. The spectroscopic properties (^{1}H NMR, IR) of **I** were consistent with those reported in the literature.[a]

(ii) THP protection: A mixture of alcohol **I** (5.67 g, 28.6 mmol), 3,4-dihydro-2*H*-pyran (4.82 g, 57.3 mmol), and *p*-TsOH•H_2O (273 mg, 1.44 mmol) was stirred for 2 days. After diluting with Et_2O, the mixture was washed with 2 M NaOH, saturated aq. NH_4Cl, brine, then dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by flash column chromatograpy (hexane, then hexane/EtOAc = 95/5) to give THP ether **II** (8.07 g, quantitative) as a colorless oil.

(iii) stannylation: To a solution of THP ether **II** (2.00 g, 7.09 mmol) in THF (20 mL) was added *n*-BuLi (1.6 M in hexane, 6.7 mL, 10.7 mmol) at –78 °C. After stirring for 3 h, a solution of Bu_3SnCl (3.25 g, 9.98 mmol) in THF (5 mL) was added to this mixture, and stirring was continued for 4 h at –78 °C. The reaction was quenched by adding pH 7 phosphate buffer, and the products were extracted with hexane (×3). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by fractional distillation to give vinylstannane **30** (2.17 g, 69%) as a colorless oil: bp 135–150 °C, 0.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J = 7.1 Hz, 9 H), 1.23–1.85 (m, 24 H), 1.95 (d, J = 1.3 Hz, 3 H), 3.81 (d, J = 11.3 Hz, 1 H), 3.86–3.96 (m, 2 H), 4.16 (d, J = 11.3 Hz, 1 H), 4.60 (t, J = 3.5 Hz, 1 H), 5.72 (q, J = 1.3 Hz, 1 H) (^{1}H–Sn coupling was observed as satellite peaks at 5.61, 5.83); ^{13}C NMR ($CDCl_3$) δ 10.3 (^{13}C–Sn coupling was observed as satellite peaks at 8.1 and 12.6), 13.7, 19.5, 24.4, 25.5, 27.4, 29.2, 30.7, 62.2, 73.1, 98.0, 127.3, 151.3; IR (neat) 2950, 5920, 2870, 2850, 1610, 1460, 1380, 1340, 1200, 1130, 1120, 1080, 1020, 870 cm^{-1}; Anal. Calcd for $C_{21}H_{42}O_2Sn$: C, 56.65; H, 9.51. Found: C, 56.79; H, 9.60.

Synthesis of (E)-vinylstannane 31. *(i) vinyl bromide VI*:[b] A solution of dibromide **V**[c] (2.82 g, 8.98 mmol) in Et_2O (25 mL) and hexane (50 mL) was chilled to ca. –110 °C (liq. N_2–THF bath was used).

To this solution was slowly added a solution of MeLi•LiBr (1.5 M in Et_2O, 7.2 mL, 10.8 mmol) below –100 °C for 15 min, and the mixture was stirred for 5 min. The reaction was stopeed by adding MeOH (5 mL), and the mixture was gradually warmed to 0 °C. After adding H_2O, the products were extracted with Et_2O (×5), and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. Bulb-to-bulb distillation (105–110 °C, 9 mmHg) gave vinyl bromide **VI** (1.95 g, 92%) as colorless oil. The spectroscopic properties of **VI** were consistent with those reported in the literature.[b]

(ii) stannylation: To a solution of bromide **VI** (1.37 g, 5.83 mmol) in DME (36 mL) and THF (18 mL) was added *t*-BuLi (1.6 M pentane solution, 8.0 mL, 13 mmol) at –78 °C, and stirred for 1 h. To the resulting solution was added a solution of Bu_3SnCl (2.08 g, 6.40 mmol) in THF (5 mL), and after stirring for 1 h, the temperature was gradually raised to 25 °C. The reaction was quenched by adding pH 7 phosphate buffer, and the product was extracted with hexane (×3). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was fractionally distillated to give vinylstannane **31** (1.99 g, 77%) as colorless oil: bp 96–104 °C (0.08 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.4 Hz, 9 H), 1.24–1.96 (m, 24 H), 1.77 (s, 3 H), 3.44–3.55 (m, 1 H), 3.85–3.94 (m, 1 H), 3.97 (d, J = 13.0 Hz, 1 H), 4.18 (d, J = 13.0 Hz, 1 H), 4.63 (t, J = 3.5 Hz, 1 H), 5.82 (s, 1 H) (^{1}H–Sn coupling was observed as satellite peaks at 5.71, 5.94); ^{13}C NMR ($CDCl_3$) δ 7.7, 10.0, 10.3, 13.7, 19.5, 21.7, 25.5, 27.3, 29.2, 30.6, 62.2, 73.1, 97.4, 123.9, 150.3; IR (neat) 2930, 2850, 1620, 1460, 1380, 1200, 1080, 1020 cm^{-1}; Anal. Calcd for $C_{21}H_{42}O_2Sn$: C, 56.65; H, 9.51. Found: C, 56.59; H, 9.62.

Synthesis of vinylstannane 32. *(i) bromination*: To a solution of 2-methylene-1,3-propanediol **VII** (4.01 g, 45.6 mmol) in CH_2Cl_2 (50 mL) was added a solution of Br_2 (7.64 g, 47.8 mmol) in CH_2Cl_2 (20 mL) at –78 °C for 40 min. After stirring for 15 min, the resulting mixture was diluted with 1,2-dichloromethane (50 mL) at 0 °C, and the volatile material was evaporated in vacuo. The residue was recrystallized (CH_2Cl_2–EtOH) to give dibromodiol (7.81 g, 69%) as colorless needles; mp 99–100 °C; ^{1}H NMR (acetone-d_6) δ 3.92 (d, J = 6.0 Hz, 4 H), 3.99 (s, 2 H), 4.42 (t, J = 6.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 37.0, 65.9, 74.7; IR (KBr) 3240, 2970, 1450, 1210, 1070, 1050, 950 cm^{-1}; Anal. Calcd for $C_4H_8Br_2O_2$: C, 19.38; H, 3.25. Found: C, 19.12; H, 3.01.

(ii) protection: A solution of the above diol (3.85 g, 15.5 mmol), pyridinium *p*-toluenesulfonate (196 mg, 0.780 mmol), and 2-methoxypropene (3.36 g, 46.7 mmol) in DMF (16 mL) was stirred for 20 min at 25 °C. After cooling to 0 °C, the reaction was quenched by adding saturated $NaHCO_3$, and the products were extracted with Et_2O (×5). The combined organic extracts were successively washed with H_2O and brine, dried (Na_2SO_4), and concentrated in vacuo. Bulb-to-bulb distillation (120–135 °C, oven temperature; 11 mmHg) to give acetonide **VIII** (3.99 g, 89%) as a colorless oil; ^1H NMR (C_6D_6) δ 1.07 (s, 3 H), 1.18 (s, 3 H), 3 67 (s, 2 H), 3.82 (d, J = 11.4 Hz, 2 H), 3.89 (d, J = 11.4 Hz, 2 H); ^{13}C NMR (C_6D_6) δ 19.4, 27.2, 38.5, 59.2, 67.6, 98.9; IR (neat) 3500, 2970, 2870, 1800, 1450, 1380, 1120, 1010, 850 cm^{-1}; Anal. Calcd for $C_7H_{12}Br_2O_2$: C, 29.44; H, 4.38. Found: C, 29.19; H, 4.20.

(iii) elimination of HBr: A solution of acetonide **VIII** (3.15 g, 10.9 mmol) and DBU (6.67 g, 43.9 mmol) in benzene (22 mL) was refluxed for 30 min. After cooling to 0 °C, saturated aqueous NH_4Cl was added to this mixture, and the products were extracted with hexane (×5). The combined organic extracts were successively washed with saturated aqueous NH_4Cl, saturated aqueous $NaHCO_3$, brine, then dried (Na_2SO_4), and concentrated in vacuo. Bulb-to-bulb distillation (90–105 °C, oven temperature, 21 mmHg) gave vinyl bromide **IX** (1.91 g, 85%) as colorless oil: ^1H NMR (C_6D_6) δ 1.18 (s, 3 H), 1.25 (s, 3 H), 3.78 (s, 2 H), 4.27 (s, 2 H), 5.35 (s, 1 H); ^{13}C NMR (C_6D_6) δ 24.0, 61.9, 62.6, 99.1, 99.5, 139.7; IR (neat) 2990, 2850, 1650, 1450, 1380, 1220, 1090, 1040, 830 cm^{-1}; Anal. Calcd for $C_7H_{11}O_2Br$: C, 40.60; H, 5.35. Found: C, 40.45; H, 5.20.

(iv) stannylation: To a solution of bromide **IX** (317 mg, 1.53 mmol) in Et_2O (6 mL) was added *t*-BuLi (1.62 M in pentane, 2.1 mL, 3.4 mmol) at –78 °C. After stirring for 45 min, to this mixture was added a solution of Bu_3SnCl (548 mg, 1.68 mmol) in Et_2O (2 mL), and the stirring was continued for 2.5 h at –78 °C. The reaction was quenched by adding MeOH (2 mL), and pH 7 phosphate buffer was added to this mixture. The products were extracted with Et_2O (×5), and combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was distilled (bulb-to-bulb, 105–120 °C, oven temperature, 0.25 mmHg) to give vinylstannane **32** (503 mg, 79%) as a colorless oil: ^1H NMR ($CDCl_3$) δ 0.85–0.94 (m, 9 H), 1.23–1.54 (m, 18 H), 1.42 (s, 6 H), 4.26 (s, 2 H), 4.31 (s, 2 H), 5.62 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.0, 13.6, 24.0, 27.2, 29.1, 65.3, 66.5, 98.5, 120.2,

150.6; IR (neat) 2960, 2850, 1460, 1380, 1220, 1090, 840 cm^{-1}; Anal. Calcd for $C_{19}H_{38}O_2Sn$: C, 55.50; H, 9.31. Found: C, 55.60; H, 9.49.

Total Synthesis of (–)-Furaquinocin A

Synthesis of silyl ether 34a: A mixture of alcohol **33a** (39.3 mg, 57.7 μmol) and *p*-TsOH•H_2O (1.2 mg, 6.3 μmol) in EtOH (3 mL) was heated at 75 °C for 11 h. After cooling to 0 °C, the reaction was quenched by adding saturated aqueous $NaHCO_3$, and the products were extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The crude material (45 mg) was dissolved in CH_2Cl_2 (2 mL), to which was added Et_3N (61.0 mg, 0.604 mmol) and TBSOTf (77.6 mg, 0.294 mmol) at –78 °C, and the mixture was stirred for 1.5 h at –78 °C. The reaction was quenched by adding pH 7 phosphate buffer, and the products were extracted with EtOAc. The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 85/15) to give silyl ether **34a** (34.9 mg, 82%) as a pale yellow oil; ^1H NMR ($CDCl_3$) δ –0.08 (s, 3 H), –0.04 (s, 3 H), 0.40 (s, 3 H), 0.41 (s, 3 H), 0.80 (s, 9 H), 1.07 (s, 9 H), 1.55 (s, 3 H), 1.68 (d, J = 6.6 Hz, 3 H), 1.74 (s, 3 H), 2.13–2.22 (m, 1 H), 2.29 (s, 3 H), 2.35–2.46 (m, 1 H), 3.74–3.80 (m, 1 H), 3.93 (s, 6 H), 3.88 (d, J = 11.3 Hz, 1 H), 4.11 (d, J = 11.3 Hz, 1 H), 4.53 (q, J = 6.6 Hz, 1 H), 4.76 (d, J = 10.0 Hz, 1 H), 4.92 (d, J = 10.0 Hz, 1 H), 5.24 (t, J = 7.2 Hz, 1 H), 7.05 (s, 1 H), 7.32–7.60 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ –5.5, –5.4, –3.8, –3.7, 9.5, 14.4, 18.3, 18.6, 21.4, 22.0, 25.8, 26.2, 31.6, 51.7, 60.5, 60.5, 61.6, 75.1, 76.5, 90.0, 100.6, 110.0, 117.9, 120.9, 124.8, 127.8, 128.2, 128.7, 130.3, 137.6, 137.8, 142.5, 148.1, 148.9, 151.7, 156.4; IR (neat) 3570, 2930, 2860, 1630, 1590, 1570, 1450, 1390, 1320, 1250, 1100, 1050, 840 cm^{-1}; $[\alpha]_D^{27}$ –30.9 (*c* 1.15, $CHCl_3$); HRMS *m/z* 736.4174 (736.4190 calcd for $C_{42}H_{64}O_7Si_2$, M^+).

Synthesis of quinone 35a: A mixture of silyl ether **34a** (15.1 mg, 20.5 μmol), 1,4-cyclohexadiene (0.2 mL) 10% Pd-C (15 mg) in EtOH (2 mL) was heated at 40 °C for 30 min. After cooling to room temperature, the mixture was filtered through a Celite pad, which was washed with EtOAc. The filtrate was concentrated in vacuo to give crude naphthol (15 mg), which was dissolved in CH_2Cl_2 (2 mL). To the solution was added *t*-BuOH (0.2 mL), pH 7 phosphate buffer (0.4 mL) and the mixture was cooled at 0 °C. DDQ (9.3 mg, 41 μmol) was added to the mixture, and which was stirred for 5 min. The reaction was quenched by adding pH 7 phosphate buffer, and the products were extracted with EtOAc (×5). The combined organic extracts were washed with brine, dried (Na_2SO_4), and

concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to give quinone **35a** (10.9 mg, 84%) as a bright yellow oil; ^{1}H NMR ($CDCl_3$) δ –0.02 (s, 3 H), –0.01 (s, 3 H), 0.38 (s, 3 H), 0.39 (s, 3 H), 0.81 (s, 9 H), 1.03 (s, 9 H), 1.51 (s, 3 H), 1.74 (d, *J* = 6.7 Hz, 3 H), 1.75 (s, 3 H), 2.05 (s, 3 H), 2.07–2.12 (m, 1 H), 2.33–2.44 (m, 1 H), 2.43 (d, *J* = 3.1 Hz, 1 H), 3.69–3.76 (m, 1 H), 3.82 (d, *J* = 11.2 Hz, 1 H), 4.01 (s, 3 H), 4.11 (d, *J* = 11.2 Hz, 1 H), 4.56 (q, *J* = 6.7 Hz, 1 H), 5.20 (t, *J* = 7.9 Hz, 1 H), 7.15 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ –5.5, –5.4, –3.7, –3.6, 9.3, 14.4, 18.3, 18.5, 20.7, 22.3, 25.9, 26.0, 31.7, 51.0, 60.7, 61.6, 74.4, 91.5, 109.7, 110.8, 124.4, 128.8, 133.4, 133.5, 138.6, 156.7, 156.9, 162.5, 180.7, 183.7; IR (neat) 3510, 2940, 2860, 1660, 1650, 1620, 1590, 1470, 1390, 1290, 1260, 1170, 1100, 1050, 840 cm^{-1}; $[\alpha]^{24}_D$ +13.3 (*c* 1.04, $CHCl_3$); HRMS *m/z* 630.3425 (630.3408 calcd for $C_{34}H_{54}O_7Si_2$, M^+).

Total Synthesis of (–)-Furaquinocin B

Synthesis of silyl ether 34b: A mixture of alcohol **33b** (25.4 mg, 37.4 μmol) and 1 M H_2SO_4 (2.5 mL) in DME (10 mL) was heated at 75 °C for 2.5 h. After cooling to 0 °C, the reaction was quenched by adding saturated aqueous $NaHCO_3$, and the products were extracted with EtOAc (×5). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The crude material (30 mg) was dissolved in CH_2Cl_2 (2 mL), to which was added Et_3N (38 mg, 0.38 mmol) and TBSOTf (49 mg, 0.19 mmol) at –78 °C. After stirred for 30 min, the reaction was quenched by adding pH 7 phosphate buffer, and the products were extracted with Et_2O (×5). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 85/15) to give silyl ether **34b** (19.3 mg, 70%) as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ –0.08 (s, 3 H), –0.05 (s, 3 H), 0.40 (s, 3 H), 0.41 (s, 3 H), 0.80 (s, 9 H), 1.07 (s, 9 H), 1.56 (s, 3 H), 1.68 (d, *J* = 6.6 Hz, 3 H), 1.74 (s, 3 H), 2.15–2.46 (m, 2 H), 2.29 (s, 3 H), 3.75–3.80 (m, 1 H), 3.88 (d, *J* = 11.3 Hz, 1 H), 3.93 (s, 6 H), 4.11 (d, *J* = 11.3 Hz, 1 H), 4.53 (d, *J* = 6.6 Hz, 1 H), 4.76 (d, *J* = 10.0 Hz, 1 H), 4.92 (d, *J* = 10.0 Hz, 1 H), 5.24 (t, *J* = 7.2 Hz, 1 H), 7.05 (s, 1 H), 7.34–7.60 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ –5.5, –5.4, –3.8, –3.7, 9.5, 14.4, 18.3, 18.6, 21.4, 22.0, 25.8, 26.2, 31.6, 51.7, 60.5, 60.6, 61.6, 75.1, 76.5, 90.0, 100.6, 110.0, 117.9, 120.9, 124.8, 127.8, 128.2, 128.7, 130.3, 137.6, 137.8, 142.5, 148.1, 148.9, 151.7, 156.4; IR (neat) 3520, 2930, 2860, 1630, 1570, 1390, 1320, 1250, 1100, 1050, 840 cm^{-1}; $[\alpha]^{24}_D$ –21.9 (*c* 1.15, $CHCl_3$); HRMS *m/z* 736.4182 (736.4190 calcd for $C_{42}H_{64}O_7Si_2$, M^+).

Synthesis of quinone 35b: A mixture of silyl ether **34b** (46.6 mg, 63.3 μmol), 1,4-cyclohexadiene (51 mg, 0.638 mmol), 10% Pd–C (47 mg) in EtOH (3 mL) was heated at 45 °C for 20 min. After cooling to room temperature, the mixture was filtered through a Celite pad, which was washed with EtOAc. The filtrate was concentrated in vacuo to give crude naphthol (50 mg), which was dissolved in CH_2Cl_2 (6 mL). To the solution was added *t*-BuOH (0.8 mL), pH 7 phosphate buffer (1.6 mL) and the mixture was cooled at 0 °C. A solution of DDQ (17.2 mg, 75.7 μmol) in CH_2Cl_2 (2 mL) was added to the mixture, and which was stirred for 10 min. The reaction was diluted by adding saturated aqueous $NaHCO_3$, and the products were extracted with EtOAc (×5). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 8/2) to give quinone **35b** (32.8 mg, 82%) as a bright yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6 H), 0.37 (s, 3 H), 0.39 (s, 3 H), 0.88 (s, 9 H), 1.03 (s, 9 H), 1.26 (s, 1 H), 1.52 (s, 6 H), 1.73 (d, J = 7.0 Hz, 3 H), 2.04 (s, 3 H), 2.10–2.18 (m, 1 H), 2.32–2.42 (m, 1 H), 3.79–3.84 (m, 1 H), 3.98 (s, 2 H), 4.02 (s, 3 H), 4.56 (q, J = 7.0 Hz, 1 H), 5.35 (t, J = 6.9 Hz, 1 H), 7.16 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ –5.3, –3.7, –3.6, 9.3, 13.8, 14.3, 18.4, 18.5, 20.6, 25.9, 26.0, 31.4, 50.8, 60.7, 68.1, 75.1, 91.4, 109.8, 110.9, 120.1, 128.5, 133.5, 133.6, 138.7, 156.8, 157.0, 162.4, 180.7, 183.8; IR (neat) 3510, 2930, 2860, 1650, 1590, 1470, 1390, 1290, 1170, 1060, 840 cm^{-1}; $[\alpha]_D^{28}$ –17 (*c* 0.76, $CHCl_3$); HRMS *m/z* 630.3395 (630.3408 calcd for $C_{34}H_{54}O_7Si_2$, M^+).

Total Synthesis of (–)-Furaquinocin H

Synthesis of silyl ether 34h: A mixture of alcohol **33h** (95.8 mg, 0.147 mmol) and *p*-TsOH•H_2O (5.6 mg, 29 μmol) in EtOH (7 mL) was gently refluxed for 5 h. After cooling to 0 °C, the reaction was quenched by adding saturated aqueous $NaHCO_3$, and the products were extracted with EtOAc (×5). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The crude material (100 mg) was dissolved in CH_2Cl_2 (1 mL), to which was added Et_3N (150 mg, 1.49 mmol) and TBSOTf (195 mg, 0.739 mmol) at –78 °C. After stirring for 30 min, the reaction was quenched by adding pH 7 phosphate buffer, and the products were extracted with EtOAc (×5). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (benzene/Et_2O = 95/5) to give silyl ether **34h** (92.8 mg, 73%) as a pale yellow oil; ^{1}H NMR ($CDCl_3$) δ –0.06 (s, 3 H), –0.10 (s, 3 H), 0.001 (s, 3 H), 0.02 (s, 3 H), 0.39 (s, 3 H), 0.41 (s, 3 H), 0.77 (s, 9 H), 0.88 (s, 9 H), 1.06 (s, 9 H), 1.58 (s, 3 H), 1.69 (d, J = 6.9 Hz, 3 H),

2.05–2.19 (m, 1 H), 2.29 (s, 3 H), 2.44–2.58 (m, 1 H), 3.78–3.83 (m, 1 H), 3.93 (s, 6 H), 3.97 (s, 1 H), 4.06–4.16 (m, 4 H), 4.52 (q, J = 6.9 Hz, 1 H), 4.76 (d, J = 10.1 Hz, 1 H), 4.92 (d, J = 10.1 Hz, 1 H), 5.51 (t, J = 7.9 Hz, 1 H), 7.04 (s, 1 H), 7.31–7.60 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ –5.6, –5.5, –5.4, –5.3, –3.8, –3.6, 9.5, 14.6, 18.2, 18.3, 18.6, 21.7, 25.8, 25.9, 26.2, 31.3, 51.6, 58.0, 60.5, 60.6, 65.1, 74.7, 76.5, 89.9, 100.5, 110.0, 118.3, 120.8, 125.3, 127.8, 128.2, 128.7, 130.3, 137.8, 140.6, 142.6, 148.2, 148.8, 151.7, 156.4; IR (neat) 3480, 2960, 2860, 1630, 1590, 1570, 1460, 1390, 1250, 1120, 1050, 840 cm^{-1}; $[\alpha]_D^{26}$ –3.1 (*c* 0.95, $CHCl_3$); HRMS *m/z* 867.5093 (867.5082 calcd for $C_{48}H_{79}O_8Si_3$, M^++1).

Synthesis of quinone 35h: A mixture of silyl ether **34h** (14.9 mg, 17.2 μmol), 1,4-cyclohexadiene (0.2 mL) 10% Pd–C (15 mg) in EtOH (2 mL) was heated at 35 °C for 2 h. After cooling to room temperature, the mixture was filtered through a Celite pad, which was washed with EtOAc. The filtrate was concentrated in vacuo to give crude naphthol (15 mg), which was dissolved in CH_2Cl_2 (1 mL). To the solution wase buffer (0.2 mL) and the mixture was cooled at 0 °C. DDQ (7.8 mg, 34 μmol) was added to the mixture, and which was stirred for 15 min. After adding pH 7 phosphate buffer, the products were extracted with Et_2O (×5). The combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (benzene/Et_2O = 8/2) to give quinone **35h** (11.0 mg, 84%) as a bright yellow oil; ^{1}H NMR ($CDCl_3$) δ –0.08 (s, 3 H), –0.05 (s, 3 H), 0.00 (s, 3 H), 0.004 (s, 3 H), 0.34 (s, 3 H), 0.36 (s, 3 H), 0.77 (s, 9 H), 0.85 (s, 9 H), 1.00 (s, 9 H), 1.51 (s, 3 H), 1.72 (d, J = 6.8 Hz, 3 H), 2.02 (s, 3 H), 2.05–2.15 (m, 1 H), 2.39–2.52 (m, 1 H), 2.59 (s, 1 H), 3.70–3.75 (m, 1 H), 3.86 (d, J = 11.2 Hz, 1 H), 3.99 (s, 3 H), 4.05 (d, J = 11.2 Hz, 1 H), 4.06–4.13 (m, 2 H), 4.54 (q, J = 6.8 Hz, 1 H), 5.45 (dd, J_1 = 5.9, J_2 = 10.0 Hz, 1 H), 7.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ –5.6, –5.5, –5.4, –5.3, –3.7, –3.6, 9.3, 14.5, 18.2, 18.3, 18.5, 20.9, 25.82, 25.88, 25.95, 31.3, 50.9, 57.9, 60.7, 65.0, 73.9, 91.4, 109.6, 110.8, 124.5, 128.9, 133.4, 133.5, 141.4, 156.7, 156.8, 162.5, 180.7, 183.7; IR (neat) 3510, 2930, 2860, 1670, 1590, 1470, 1390, 1290, 1260, 1060, 840 cm^{-1}; $[\alpha]^{25}_D$ +16 (*c* 0.95, $CHCl_3$); HRMS *m/z* 761.4294 (761.4300 calcd for $C_{40}H_{69}O_8Si_3$, M^++1).