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Novel Synthesis of Arylnaphthalene Lignans via Pd-Catalyzed [2+2+2] Cocyclization of Aryne and Diyne: Total Syntheses of Taiwanins C and E

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General.

All manipulations were performed under an argon atmosphere unless otherwise mentioned. All solvents and reagents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (Merck, 70-230 mesh), and flash chromatography was performed on silica gel 60 (Merck, 230-400 mesh).

Preparation of Substrates.

General Procedure for Coupling of Carboxylic Acid 5 with Propargylic Alcohol.

To a solution of 3-(benzo[*d*][1,3]dioxol-5-yl)propiolic acid (**5**), the corresponding propargylic alcohol (1.5-2.0 equiv. to **5**), and DMAP (0.3 equiv. to **5**) in CH_2Cl_2 (5 mL per 1.0 mmol of 5) was added DCC (1.5 equiv. to **5**) at 0 °C, and the mixture was stirred at room temperature for an appropriate time. The mixture was diluted with CH_2Cl_2, and the solution was washed with 5% HCl aq., sat. $NaHCO_3$ aq., and brine, and dried. After removal of the solvent, the residue was purified by column chromatography on silica gel to give the corresponding diyne.

Prop-2-ynyl 3-(benzo[*d*][1,3]dioxol-5-yl)propiolate (3a).

According to the General Procedure, the crude product, which was prepared from **5** (2.21 g, 12 mmol), propargyl alcohol (**6a**) (1.4 mL, 24 mmol), DMAP (0.43 g, 3.4 mmol), and DCC (3.65 g, 18 mmol) in CH_2Cl_2 (55 mL) at room temperature for 4 h, was purified by flash column chromatography on silica gel (hexane/AcOEt=12/1) to give **3a** (2.36 g, 89%) as an off-white solid. IR (neat) 3268, 2214, 2133, 1716 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 1.6, 7.9 Hz, 1 H), 7.01 (d, *J* = 1.6 Hz, 1 H), 6.80 (d, *J* = 7.9 Hz, 1 H), 6.03 (s, 2 H), 4.81 (d, *J* = 2.6 Hz, 2 H), 2.54 (t, *J* = 2.6 Hz, 1 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 53.1, 75.7, 76.8, 78.8, 88.2, 101.7, 108.7, 112.1, 112.5, 129.0, 47.5, 150.1, 153.0; EI-LRMS *m/z* 228 (M^+), 173, 146; EI-HRMS calcd for $C_{13}H_8O_4$ 228.0422, found 228.0418.

Methyl 4-[3-(benzo[*d*][1,3]dioxol-5-yl)propioloyloxy]but-2-ynoate (3b).

According to the General Procedure, the crude product, which was prepared from **5** (200 mg, 1.1 mmol), the propargylic alcohol **6b** (181 mg, 1.6 mmol), DMAP (39 mg, 0.32 mmol), and DCC (326 mg, 1.6 mmol) in CH_2Cl_2 (5 mL) at room temperature for 20 min, was purified by column chromatography on silica gel (hexane/AcOEt=3/1) to give **3b** (258 mg, 86%) as an off-white solid. IR (neat) 2210, 1717, 1602 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 1.6, 8.1 Hz, 1 H), 7.01 (d, *J* = 1.6 Hz, 1 H), 6.82 (d, *J* = 8.1 Hz, 1 H), 6.03 (s, 2 H), 4.92 (s, 2 H), 3.80 (s, 3 H); EI-LRMS *m/z* 286 (M^+), 271, 173; EI-HRMS calcd for $C_{15}H_{10}O_6$ 286.0477, found 286.0476.

4-*tert*-Butyldimethylsilyloxy-but-2-ynyl 3-(benzo[*d*][1,3]dioxol-5-yl)propiolate (7).

According to the General Procedure, the crude product, which was prepared from **5** (82 mg, 0.42 mmol), the propargylic alcohol **6c** (132 mg, 0.66 mmol), DMAP (15 mg, 0.12 mmol), and DCC (133 mg, 0.64 mmol) in CH_2Cl_2 (2 mL) at room temperature for 1.5 h, was purified by column chromatography on silica gel (hexane/AcOEt=4/1) to give **7** (195 mg, 100%) as a colorless oil. IR (nujol) 2212, 1715, 1602 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 1.6, 7.9 Hz, 1 H), 7.01 (d, *J* = 1.6 Hz, 1 H), 6.80 (d, *J* = 7.9 Hz, 1 H), 6.02 (s, 2 H), 4.85 (t, *J* = 2.0 Hz, 2 H), 4.37 (t, *J* = 2.0 Hz, 2 H), 0.91 (s, 9 H), 0.12 (s, 6 H); EI-LRMS *m/z* 372 (M^+), 329, 315, 241, 173; EI-HRMS calcd for $C_{20}H_{24}O_5Si$ (M^+) 372.1393, found 372.1380.

4-Hydroxybut-2-ynyl 3-(benzo[*d*][1,3]dioxol-5-yl)propiolate.

To a solution of **7** (273 mg, 0.73 mmol) in CH_3CN (3.4 mL) was added HF-CH_3CN solution (prepared by mixing conc. HF aq. with CH_3CN (ratio of 1:9), 0.9 mL) at 0 °C, and the mixture was stirred at room temperature for 2 h. To the solution was added sat. $NaHCO_3$ aqueous solution, and the solution was extracted with Et_2O. The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/AcOEt=3/2) to give the corresponding alcohol (179 mg, 94%) as a colorless solid. IR (nujol) 3517, 2211, 1681 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 1.6, 8.3 Hz, 1 H), 7.01 (d, *J* = 1.6 Hz, 1 H), 6.81 (d, *J* = 8.3 Hz, 1 H), 6.03 (s, 2 H), 4.86 (t, *J* = 1.6 Hz, 2 H), 4.33 (dt, *J* = 1.6, 6.3 Hz, 2 H), 1.58 (t, *J* = 6.3 Hz, 1 H); EI-LRMS *m/z* 258 (M^+), 241, 173; EI-HRMS calcd for $C_{14}H_{10}O_5$ (M^+) 258.0528, found 258.0534.

3-Formylprop-2-ynyl 3-(benzo[*d*][1,3]dioxol-5-yl)propiolate (3c).

To a solution of the above alcohol (86 mg, 0.33 mmol) in CH_2Cl_2 (1.6 mL) were added MS4A (643 mg) and PCC (214 mg, 0.99 mmol) at 0 °C, and the mixture was stirred at the same temperature for 1.5 h. The mixture was dilute with Et_2O, and filtered through a pad of Florisil. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (hexane/AcOEt=3/1) to give **3c** (57 mg, 67%) as a yellowish oil. IR (nujol) 2907, 2209, 1714, 1673, 1602 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 9.25 (s, 1 H), 7.21 (dd, *J* = 1.6, 7.9 Hz, 1 H), 7.02 (d, *J* = 1.6 Hz, 1 H), 6.82 (d, *J* = 7.9 Hz, 1 H), 6.03 (s, 2 H), 4.99 (s, 2 H); EI-LRMS *m/z* 256 (M^+), 227, 199; EI-HRMS calcd for $C_{14}H_8O_5$ (M^+) 256.0371, found 256.0363.

***N*-Methoxy-*N*-methyl-4-(tetrahydro-2*H*-pyran-2-yloxy)but-2-ynamide (10).**

A solution of **8** (100 mg, 0.71 mmol), **9** (137 mg, 1.1 mmol), $PdCl_2(CH_3CN)_2$ (5.8 mg, 0.02 mmol), PPh_3 (30 mg, 0.11 mmol), and CuI (15 mg, 0.077 mmol) in Et_3N (3.6 mL) was stirred at 90 °C for 2 h. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (hexane/AcOEt=8/1~2/1) to give **10** (98 mg, 61%) as a colorless oil. IR (neat) 2240, 1644 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.84 (s, 1 H), 4.44 (s, 2 H), 3.88-3.80 (m, 1 H), 3.78 (s, 3 H), 3.58-3.50 (m, 1 H), 3.24 (s, 3 H), 1.90-1.55 (m, 6 H); EI-LRMS *m/z* 227 (M^+), 167, 127; EI-HRMS calcd for $C_{11}H_{17}NO_4$ 227.1157, found 227.1156.

4-Hydroxy-*N*-methoxy-*N*-methylbut-2-ynamide (6d).

To a solution of **10** (949 mg, 4.2 mmol) in MeOH (11 mL) was added *p*-TsOH (80 mg, 0.42 mmol), and the mixture was stirred at room temperature for 2 h. To the mixture was added sat. $NaHCO_3$ aq., and the solution was concentrated. The solution was extracted with CH_2Cl_2 and the organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/AcOEt=1/2) to give **6d** (429 mg, 81%) as a colorless oil. IR (neat) 3395, 2239, 1639 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 4.45 (s, 2 H), 3.79 (s, 3 H), 3.24 (s, 3 H), 2.78 (bs, 1 H); EI-LRMS *m/z* 143 (M^+), 83; EI-HRMS calcd for $C_6H_9NO_3$ 143.0582, found 143.0576.

3-(*N*-Methoxy-*N*-methylcarbamoyl)prop-2-ynyl 3-(benzo[*d*][1,3]dioxol-5-yl)propiolate (3d).

According to the General Procedure, the crude product, which was prepared from **5** (405 mg, 2.1 mmol), the propargylic alcohol **6d** (358 mg, 2.5 mmol), DMAP (77 mg, 0.63 mmol), and DCC (676 mg, 3.3 mmol) in CH_2Cl_2 (15 mL) at room temperature for 20 min, was purified by flash column chromatography on silica gel (hexane/AcOEt=2/1) to give **3d** (576 mg, 86%) as a yellowish solid. IR (neat) 2210, 1714, 1644 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 1.6, 8.1 Hz, 1 H), 7.01 (d, *J* = 1.6 Hz, 1 H), 6.81 (d, *J* = 8.1 Hz, 1 H), 6.03 (s, 2 H), 4.96 (s, 2 H), 3.79 (s, 3 H), 3.24 (s, 3 H); EI-LRMS *m/z* 315 (M^+), 284, 255, 183; EI-HRMS calcd for $C_{16}H_{13}NO_6$ 315.0743, found 315.0731.

5-Bromobenzo[*d*][1,3]dioxol-6-yl trifluoromethanesulfonate (4b).

To a solution of 6-bromobenzo[*d*][1,3]dioxol-5-ol (**11**) (876 mg, 4.0 mmol) in THF (17 mL) was added hexamethyldisilazane (1.3 mL, 6.2 mmol), and the mixture was refluxed with stirring for 3 h. The mixture was concentrated in *vacuo*, and the residual crude **12** was dissolved in THF (17 mL). To the mixture was added BuLi (1.65 M hexane solution, 2.6 mL, 4.3 mmol) at -100 °C, and the temperature of the mixture was raised to -80 °C for 20 min. The mixture was again cooled to -100 °C, and Et_2O (17 mL) and trifluoromethanesulfonic anhydride (0.88 mL, 5.2 mmol) were added to the mixture. The temperature of the mixture was again raised to -80 °C for 20 min, and the reaction mixture was quenched with sat. $NaHCO_3$ aq. at the same temperature, and the mixture was slowly warmed to room temperature. The solution was extracted with Et_2O, and the organic layer was washed with brine, dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (hexane/AcOEt=30/1) to give **4b** (1.15 g, 83% from **11**) as a purplish oil. IR (neat) 1330, 1142 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.88 (s, 1 H),

6.84 (s, 1 H), 6.03 (s, 2 H), 0.33 (s, 9 H); EI-LRMS *m/z* 342 (M^+), 327, 194; EI-HRMS calcd for $C_{11}H_{13}O_5F_3SSi$ 342.0205, found 342.0197. Anal. Calcd for $C_{11}H_{13}O_5F_3SSi$: C, 38.59; H, 3.83. Found: C, 38.58; H, 3.83.

Spectral Data for Products of the [2+2+2] Cocyclization.

9-(Benzo[*d*][1,3]dioxol-5-yl)naphtho[2,3-*c*]furan-1(3*H*)-one (1a-a): IR (nujol) 1760, 1635 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 1 H), 7.89 (s, 1 H), 7.89 (d, *J* = 8.3 Hz, 1 H), 7.64 (dd, *J* =7.1, 8.3 Hz, 1 H), 7.50 (dd, *J* = 7.1, 8.3 Hz, 1 H), 6.98 (d, *J* = 7.9 Hz, 1 H), 6.86-6.82 (m, 2 H), 6.08 (d, *J* = 6.7 Hz, 1 H), 6.08 (d, *J* = 6.7 Hz, 1 H), 5.45 (s, 2 H); EI-LRMS *m/z* 304 (M^+), 275; EI-HRMS calcd for $C_{19}H_{12}O_4$ 304.0735, found 304.0737.

Methyl 9-(benzo[*d*][1,3]dioxol-5-yl)-1,3-dihydro-1-oxonaphtho[2,3-*c*]furan-4-carboxylate (1b-a): IR (nujol) 1770, 1717 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 9.10 (d, *J* = 8.7 Hz, 1 H), 7.93 (d, *J* = 7.9 Hz, 1 H), 7.81-7.75 (m, 1 H), 7.59-7.53 (m, 1 H), 6.99 (d, *J* = 7.9 Hz, 1 H), 6.84-6.83 (m, 2H), 6.09 (d, *J* = 6.3 Hz, 2 H), 5.64 (s, 2 H), 4.10 (s, 3 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 52.5, 70.1, 101.4, 108.3, 110.5, 115.3, 120.2, 123.6, 126.1, 127.0, 127.4, 128.8, 130.5, 133.9, 134.3, 144.6, 146.7, 147.6, 148.1, 166.3, 168.9; EI-LRMS *m/z* 362 (M^+), 348, 331; EI-HRMS calcd for $C_{21}H_{12}O_4$ 362.0790, found 362.0779.

9-(benzo[*d*][1,3]dioxol-5-yl)-1-oxo-1,3-dihydronaphtho[2,3-*c*]furan-4-carbaldehyde (1c-a): IR (neat) 2926, 1679, 1672 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ11.16 (s, 1 H), 8.84 (d, *J* = 8.6 Hz, 1 H), 8.03 (d, *J* = 8.6 Hz, 1 H), 7.90 (t, *J* = 7.9, 8.6 Hz, 1 H), 7.62 (dd, *J* = 7.9, 8.6 Hz, 1 H), 7.00 (d, *J* = 7.9 Hz, 1 H), 6.85-6.82 (m, 2 H), 6.11 (s, 1 H), 6.09 (s, 1 H), 5.77 (s, 2 H); E-LRMS m/z 332 (M^+), 303; EI-HRMS calcd for $C_{20}H_{12}O_5$ 332.0684, found 332.0691.

9-(Benzo[*d*][1,3]dioxol-5-yl)-1,3-dihydro-*N*-methoxy-*N*-methyl-1-oxonaphtho[2,3-*c*]furan-4-carboxamide (1d-a): IR (neat) 1768, 1646 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.7 Hz, 1 H), 7.93 (d, *J* = 8.3 Hz, 1 H), 7.69 (t, *J* = 7.5 Hz, 1 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 6.97 (d, *J* = 7.5 Hz, 1 H), 6.89-6.79 (m, 2 H), 6.08 (s, 1 H), 6.05 (s, 1 H), 5.43 (s, 2 H), 3.55 (s, 3 H), 3.39 (s, 3 H); EI-LRMS *m/z* 391 (M^+), 331; EI-HRMS calcd for $C_{22}H_{17}NO_6$ 391.1056, found 391.1065.

10-(benzo[*d*][1,3]dioxol-5-yl)-*N*-methoxy-*N*-methyl-1,3,6,8-tetrahydro-1-oxo-2,6,8-trioxa-indeno[5,6-*f*]inden-4-carboxamide (1d-b): IR (neat) 1762, 1653 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.26 (s, 1 H), 7.25 (s, 1H), 6.97 (d, *J* = 7.9 Hz, 1 H), 6.83-6.74 (m, 2 H), 6,10-6.06 (m, 4 H), 5.35 (s, 2 H), 3.51 (s, 3 H), 3.43 (s, 3 H); EI-LRMS *m/z* 435 (M^+), 375; EI-HRMS calcd for $C_{23}H_{17}NO_8$ 435.0954, found 435.0942.

Transformation of 1d-b into Taiwanins C and E.

Reduction of 1d-b with DIBAL-H producing 15a and 15b (Scheme 7).

To a solution of **1d-b** (40 mg, 0.09 mmol) in CH_2Cl_2 (1 mL) was DIBAL-H (1.0 M toluene solution, 0.1 mL, 0.01 mmol) at -78 °C, and the mixture was stirred at the same temperature for 4 h. To the solution was added an additional DIBAL-H (0.1 mL, 0.01 mmol) at the same temperature, and the mixture was stirred for 1.5 h. To the mixture were successively added MeOH (0.03 mL) and sat. potassium sodium tartrate aqueous solution at -78 °C, and the solution was warmed to room temperature. The solution was extracted with Et_2O, and the organic layer was washed with brine, dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O=30/1~8/1) to give **15a** (6 mg, 17%) and **15b** (23 mg, 67%). Spectral data of **15a**: IR (nujol) 2901, 1753, 1673 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 9.89 (s, 1 H), 8.52 (s, 1 H), 7.08 (s, 1 H), 7.00 (d, *J* = 7.9 Hz, 1 H), 6.87 (d, *J* = 2.0 Hz, 1 H), 6.84 (dd, *J* = 7.9, 2.0 Hz, 1 H), 6.15 (s, 2 H), 6.13 (d, *J* = 5.3 Hz, 1 H), 6.13 (d, *J* =5.3 Hz, 1 H), 5.67 (s, 2 H); EI-LRMS *m/z* 376 (M^+), 347, 319; EI-HRMS calcd for $C_{21}H_{12}O_7$ 376.0583, found 376.0591. Spectral data of **15b**: IR (neat) 3382, 2922, 1673 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 9.84 (s, 1 H), 7.42 (s, 1 H), 7.01 (s, 1 H), 6.96 (d, *J* = 7.3 Hz, 1 H), 6.84 (d, *J* = 1.3 Hz, 1 H), 6.82 (s, 1 H), 6.79 (d, *J* = 1.3, 7.3 Hz, 1 H), 6.11-6.08 (m, 4 H), 5.70-5.61 (m, 1 H), 5.44 (dd, *J* = 4.6, 15.2 Hz, 1 H), 3.31 (s, 1 H); EI-LRMS *m/z* 360 (M^+-OH-1), 332 (M^+-OH-CHO); EI-HRMS calcd for $C_{21}H_{12}O_6$ (M^+-OH-1) 360.0634, found 360.0626.

1,3,7,9-tetrahydro-5-(benzo[*d*][1,3]dioxol-5-yl)-4-carbomethoxy-1-oxo-2,7,9-trioxa-indeno[5,6-*e*]indene (16).

To a solution of **1d-b** (320 mg, 0.74 mmol) in CH_2Cl_2 (7 mL) were successively added MeOH (7 mL) and NaH (88 mg, 60% dispersion in mineral oil, 2.2 mmol) at 0 °C, and the mixture was stirred at room temperature for 5 h. To the mixture was added sat. NH_4Cl aq. at 0 °C, and the solution was evaporated in order to remove MeOH. The resultant aqueous layer was extracted with AcOEt,

and the organic layer was washed with brine, dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O=45/1) to give **16** (236 mg, 78%) as a colorless solid. IR (neat) 1732, 1703 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 8.51 (s, 1 H), 6.98 (s, 1 H), 6.94 (d, *J* = 7.9 Hz, 1 H), 6.74 (d, *J* = 1.6 Hz, 1 H), 6.71 (dd, *J* = 1.6, 7.9 Hz, 1 H), 6.12 (s, 2 H), 6.08 (d, *J* = 2.8 Hz, 1 H), 6.08 (d, *J* = 2.8 Hz, 1 H), 5.54 (d, *J* = 3.2 Hz, 2 H), 3.69 (s, 3 H); EI-LRMS *m/z* 406 (M^+), 374, 346; EI-HRMS calcd for $C_{22}H_{14}O_8$ (M^+) 406.0688, found 406.0692.

1,3,7,9-tetrahydro-5-(benzo[*d*][1,3]dioxol-5-yl)-4-carbomethoxy-1-hydroxy-2,7,9-trioxa-indeno [5,6-*e*]indene (17).

To a solution of **16** (26 mg, 0.064 mmol) in CH_2Cl_2 (1.6 mL) was added DIBAL-H (1.0 M toluene solution, 0.076 mL, 0.076 mmol) at -78 °C, and the mixture was stirred at the same temperature for 2 h. To the mixture were successively added MeOH (0.03 mL) and sat. potassium sodium tartrate aqueous solution at -78 °C, and the solution was warmed to room temperature. The solution was extracted with Et_2O, and the organic layer was washed with brine, dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O=50/1~6/1) to give **17** (16 mg, 63%) as a colorless solid along with the starting material **16** (3 mg, 12%). IR (neat) 3381, 1706 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.39 (s, 1 H), 6.95 (s, 1 H), 6.90 (d, *J* = 7.9 Hz, 1 H), 6.87-6.84 (m, 1 H), 6.73 (d, *J* = 7.9 Hz, 1 H), 6.69-6.63 (m, 1 H), 6.06 (s, 1 H), 5.60-5.50 (m, 1 H), 5.30 (m, 1 H), 3.63 (s, 3 H), 3.09 (d, *J* = 7.9 Hz, 1 H); EI-LRMS *m/z* 408 (M^+), 390, 376; EI-HRMS calcd for $C_{22}H_{16}O_8$ (M^+) 408.0845, found 408.0850.

1,3,6,8-tetrahydro-4-(benzo[d][1,3]dioxol-5-yl)-10-hydroxymethyl-3-oxo-2,6,8-trioxa-indeno[5, 6-*f*]indene (19).

To a solution of **17** (124 mg, 0.30 mmol) in MeOH/THF (8 mL/8 mL) was added $NaBH_4$ (59 mg, 1.5 mmol) at 0 °C, and the mixture was stirred at room temperature for 4 h. To the mixture was added again $NaBH_4$ (59 mg, 1.5 mmol) at 0 °C, and the mixture was stirred at room temperature for 15 h. Then, to the mixture was added again $NaBH_4$ (22 mg, 0.60 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. To the mixture was added 5% HCl aq. at 0 °C, then the mixture was evaporated in order to remove MeOH and THF. The resultant aqueous layer was extracted with CH_2Cl_2, and the organic layer was washed with sat. $NaHCO_3$ aq., brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O=9/2) to give **19** (109 mg, 95%) as a colorless solid. IR (neat) 3438, 1751 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ7.47 (s, 1 H), 7.13 (s, 1 H), 6.95 (d, *J* = 7.5 Hz, 1 H),

6.77-6.73 (m, 2 H), 6.10 (s, 2 H), 6.07 (d, J = 6.9 Hz, 1 H), 6.07 (d, J = 6.9 Hz, 1 H), 5.53 (s, 2 H), 5.16 (s, 2 H); EI-LRMS *m/z* 378 (M^+), 349; EI-HRMS calcd for $C_{21}H_{14}O_7$ (M^+) 378.0740, found 378.0741.

1,3,6,8-tetrahydro-4-(benzo[d][1,3]dioxol-5-yl)-10-formyl-3-oxo-2,6,8-trioxa-indeno[5,6-f]indene (13).

To a solution of **19** (109 mg, 0.29 mmol) in CH_2Cl_2 (4 mL) were added MS4A (545 mg) and PCC (186 mg, 0.86 mmol) at 0 °C, and the mixture was stirred at the same temperature for 1.5 h. The mixture was dilute with Et_2O, and filtered through a pad of Florisil. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O=50/1) to give **13** (96 mg, 89%) as a yellowish solid. IR (neat) 2907, 1757, 1682 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 10.9 (s, 1 H), 8.16 (s, 1 H), 7.22 (s, 1 H), 6.99 (d, J = 7.3 Hz, 1 H), 6.80 (s, 1 H), 6.79 (d, J = 7.3 Hz, 1 H), 6.17 (s, 2 H), 6.09 (d, J = 6.6 Hz, 2 H), 5.70 (s, 1 H); EI-LRMS *m/z* 376 (M^+), 358, 347; EI-HRMS calcd for $C_{21}H_{12}O_7$ (M^+) 376.0583, found 376.0584.

Synthesis of Taiwanin C from 13.

To a solution of **13** (14 mg, 0.037 mmol) in C_2H_5CN (2 mL) was added $RhCl(PPh_3)_3$ (48 mg, 0.052 mmol) was added, and the mixture was refluxed for 2 h. The reaction mixture was cooled to 0 °C, and EtOH was added to the solution. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O=60/1) to Taiwanin C (8 mg, 64%) as a colorless solid, whose spectral data were identical with those previously reported by Padwa et al. [*J. Org. Chem.* **1996**, *61*, 3706].

Synthesis of Taiwanin E from 13.

To a solution of **13** (64 mg, 0.17 mmol) in CH_2Cl_2 (4.2 mL) was added *m*CPBA (8234 mg, 1.4 mmol) at 0 °C, and the mixture was stirred at room temperature for 1 h. The mixture was diluted with Et_2O. The solution was successively washed with 10% $Na_2S_2O_3$ aq., sat. $NaHCO_3$ aq., and brine, and dried over Na_2SO_4. After removal of the solvent, the crude formate was dissolved in MeOH (7 mL), and K_2CO_3 (35 mg, 0.25 mmol) was added to the solution. The mixture was stirred at room temperature for 30 min, and the mixture was diluted with Et_2O, and filtered. The filtrate was washed with brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O=30/1) to give Taiwanin E (54 mg, 88% from **13**) as a colorless solid, whose spectral data were identical with those previously reported by Iwasaki et al. [*J. Org. Chem.* **1995**, *60*, 4585].