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SYNTHETIC STUDY OF AFRITOXINONE A: STEREOSELECTIVE CONSTRUCTION OF FUROPYRANONE MOIETY

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Dedicated to Professor Isao Kuwajima on the occasion of his 77th birthday

Abstract – Stereoselective construction of the furopyranone moiety of the natural product afritoxinone A was demonstrated. This synthetic methodology features (i) stereoselective 1,4-addition of a tricyclic ring system, (ii) oxidative cleavage of the diol, followed by hydration of the resulting dialdehyde group, and (iii) acetalization via cationic cyclization of the pyranediol with the *tert*-butyl ester tether.

Afritoxinones A (**1**) and B (**2**) were isolated from the liquid culture of *Diplodia africane*, a fungal pathogen responsible for branch dieback of Phoenician junipers in Italy.[1] In addition, structurally related

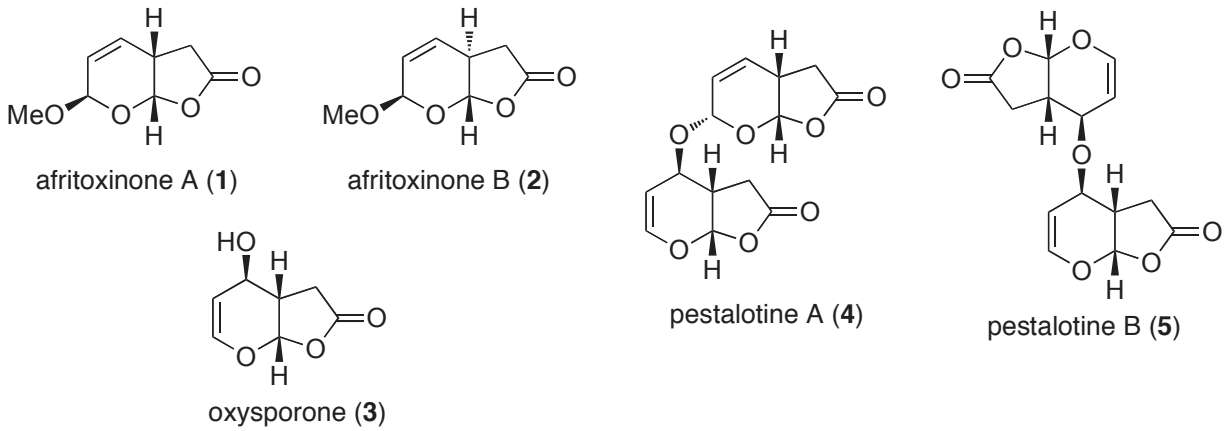
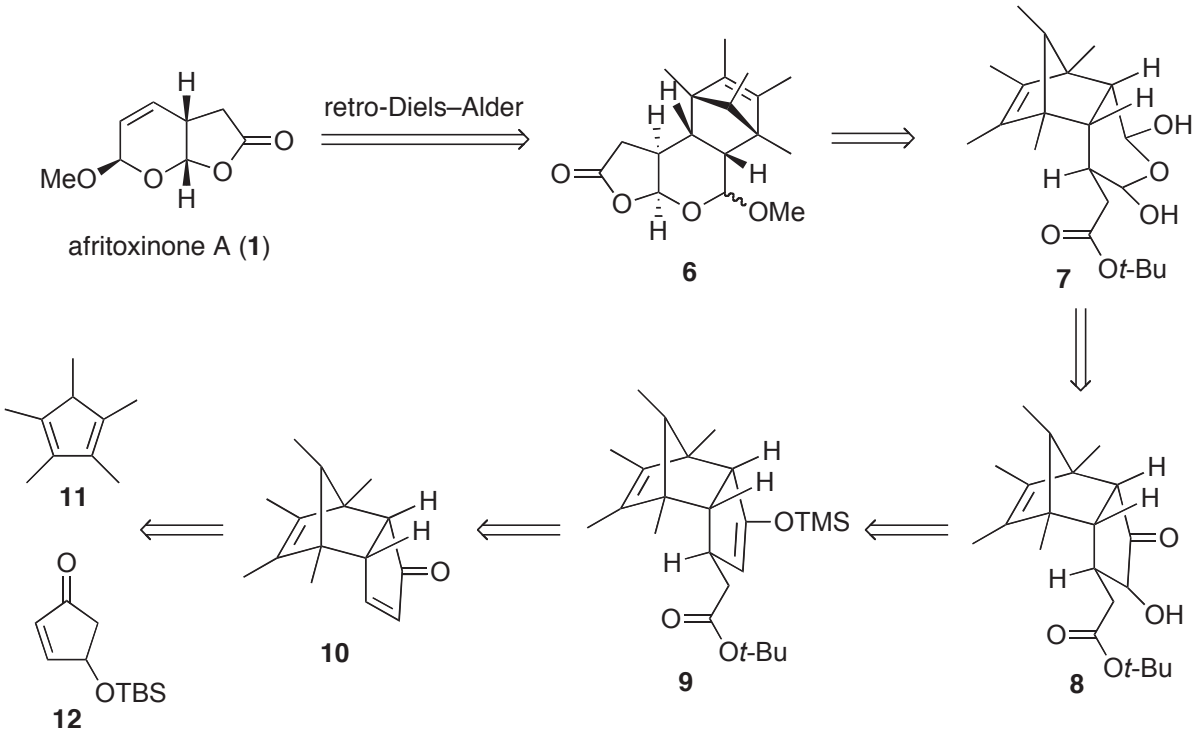


Figure 1. Structures of afritoxinone A (**1**), B (**2**), and related compounds

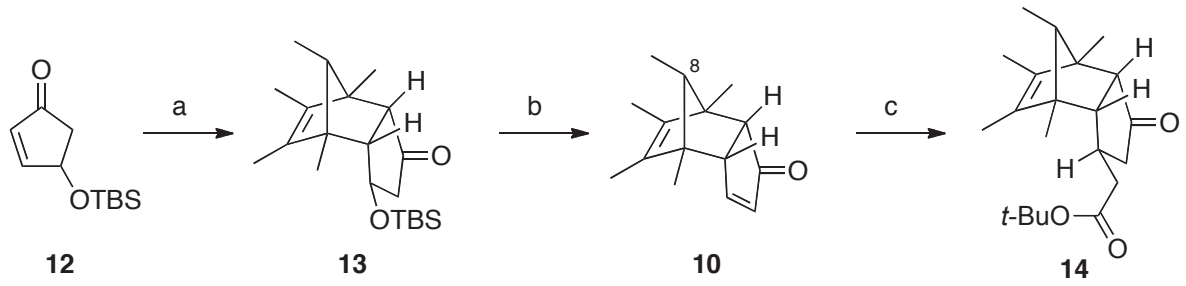
natural products, oxysporone (**3**),[2-4] pestalotines A (**4**), and B (**5**),[5] were isolated from *Pestalotiopsis sp*. HC02. These natural compounds contain a dihydrofuropyranone moiety in their structures, and possess phytotoxic activity. Although these structures are very simple, their total synthesis has not been reported to date. Furthermore, only a few reports on the construction of the perhydrofuropyranone skeleton, e.g., ring opening of cyclopropanated derivatives,[6-9] lactonization via single electron transfer protocol,[10] $TiCl_4$ mediated combination of pyruvate ester and dihydropyran,[11] and the enzymatic Baeyer–Villiger oxidation,[12] are known. In this report, we describe the stereoselective construction of the dihydrofuropyranone moiety toward the total synthesis of natural product afritoxinone A (**1**).

Our synthetic plan for afritoxinone A (**1**), based on Diels–Alder/retro-Diels–Alder reaction concepts[13] to construct the chiral carbons stereoselectively, is outlined in Scheme 1. The target natural product would be obtained by construction of the olefin group in the dihydrofuropyranone skeleton using the retro-Diels–Alder reaction of tetracyclic compound **6**. Tetracyclic compound **6** would be constructed by the cationic dehydrocyclization of pyrandiol **7** having a *tert*-butyl ester moiety. Pyrandiol **7** would be synthesized by Rubottom oxidation of silyl enol ether **9**, and reduction of the carbonyl group of the resulting α-hydroxy ketone **8**, followed by oxidative cleavage of the diol group. The silyl enol ether **9** would be obtained by stereoselective introduction of the β-ketoester of tricyclic enone **10** from the concave face of the tricyclic ring system. Tricyclic compound **10** would be prepared from the known silyloxy enone **12** and pentamethylcyclopentadiene (**11**).



Scheme 1. Synthetic strategy for afritoxinone A (**1**)

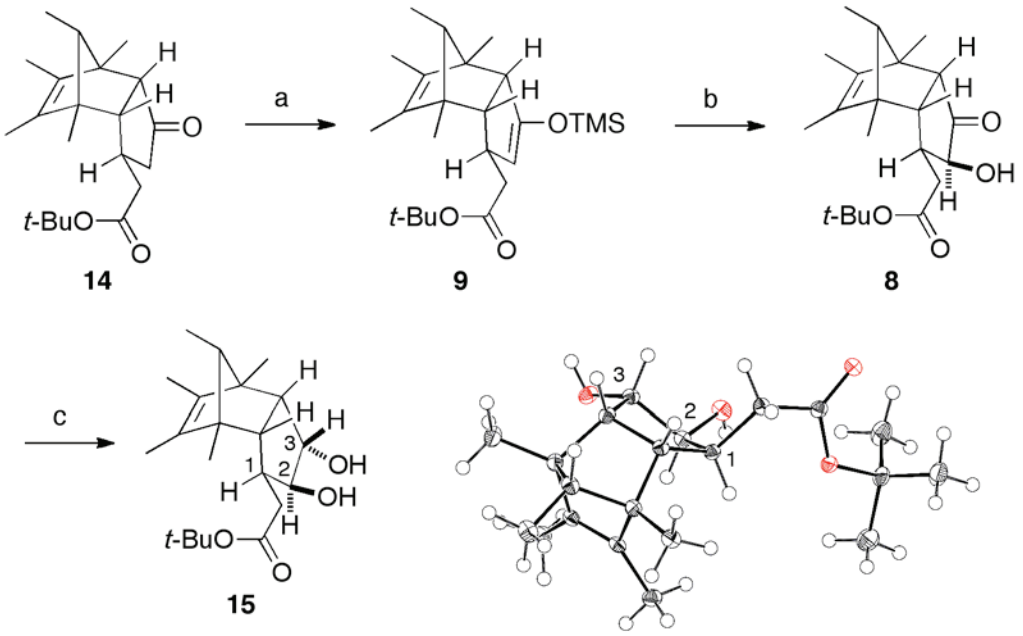
The investigation began by preparing tricyclic enone derivative **10**[15] as shown in Scheme 2. Diels–Alder reaction of the known cyclopentenone **12**,[16] prepared from furfuryl alcohol in two steps, with 1,2,3,4,5-pentamethylcyclopentadiene (**11**) in refluxing toluene gave tricyclic adduct **13** in 66% yield. Treatment of **13** with tetra-*n*-butylammonium fluoride afforded the tricyclic enone **10** as a mixture of two diastereoisomers (dr = 10:1) at C8 position in 95% yield. Stereoselective 1,4-addition reaction[17] of the tricyclic enone **10** was achieved by use of TMSOTf as a Lewis acid and Reformatsky reagent, prepared from *tert*-butyl bromoacetate and Zn powder, to yield alkylated ketone **14** as a single isomer at the β position. Although the stereochemistry at the β position of **14** was not confirmed at this stage, it is assumed to be that depicted in Scheme 2.



Scheme 2. Synthesis of the 1,4-adduct **14**. Reagents and Conditions: a) 1,2,3,4,5-pentamethylcyclopentadiene (**11**), toluene, reflux, 3 h, 66%; b) TBAF, THF, rt, 2 h, 95%; c) *tert*-butyl bromoacetate, Zn, TMSOTf, THF, –78 °C, 2 h, 92%.

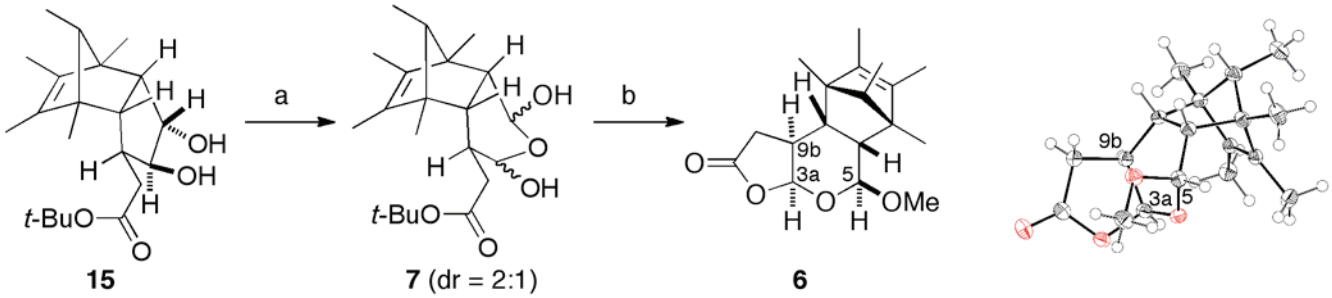
Introduction of the hydroxyl group at the α position of the carbonyl group, carried out in a two-step operation, involved formation of a silyl enol ether (63%), followed by Rubottom oxidation[18] of the resulting silyl enol ether to give α-hydroxy ketone **8** in 56% yield as shown in Scheme 3. Although assignment of the stereochemistry of the asymmetric carbon at the carbonyl α position was not performed, it was proposed that the hydroxyl group approached the convex side since mCPBA approached the double bond from the convex side. Reduction of the carbonyl group in **8** gave diol **15** in 95% yield. X-ray crystallographic analysis of diol **15**[19] indicated that the stereochemistry of the newly constructed asymmetric carbon was 1*R**,2*R**,3*S** as depicted in Scheme 3. These results indicate that the three reactions, nucleophilic attack of Reformatsky reagent to the β position of enone **10**, Rubottom oxidation with mCPBA of the silyl enol ether **9**, and hydride reduction of ketone **8** with $NaBH_4$, occurred from the concave side.

With the diol derivative in hand, our attention turned to the construction of the furopyranone moiety. Oxidative glycol cleavage of the 1,2-dihydroxyl moiety in **15** with sodium periodate in THF–H_2O afforded tetrahydropyranediol derivative **7** as a mixture of two diastereoisomers, which was a hydrated



Scheme 3. Synthesis of diol **15** and ORTEP drawing of **15**. Reagents and Conditions: a) LHMDS, TMSCl, THF, –78 °C, 0.5 h, 63%; b) *m*CPBA, CH_2Cl_2, 0 °C, 1 h, 56%; c) $NaBH_4$, MeOH, 0 °C, 0.5 h, 95%.

compound of the dialdehyde produced by glycol cleavage. Construction of the target furopyranone skeleton was accomplished by dehydrocondensation of **7** under acidic conditions in MeOH to give the tetracyclic furopyranone derivative **6** in 85% yield as a single diastereoisomer. The stereochemistry of tetracyclic compound **6** was determined by X-ray crystallographic analysis as depicted in Scheme 4.[20] The relative configuration between C3a and C9b of tetracyclic compound **6** is *cis*, which is identical to that of afritoxinone A (**1**).



Scheme 4. Synthesis of tetracyclic compound **6**. Reagents and Conditions: a) $NaIO_4$, THF–H_2O, rt, 3 h, 75% (dr = 2:1); b) TsOH, MeOH, rt, 0.5 h, 85%.

Finally, completion of our project by reconstruction of the olefin group and epimerization at C5 position was attempt. Unfortunately, cleavage of the pentamethylcyclopentadiene ring for deprotection of the

protected double bond by retro-Diels–Alder reaction under several conditions [heated solvent (e.g., xylene, diphenylether) with/without a diene compound (e.g., maleic anhydride)] did not proceed.[21] Thus, our main goal, the total synthesis of afritoxinone A (**1**), could not be completed.

In conclusion, we demonstrated the stereoselective construction of the furopyranone moiety in the natural product afritoxinone A (**1**). This synthetic methodology involving stereoselective 1,4-addition of Reformatsky reagent with the tricyclic enone, oxidative cleavage of the diol, and acetalization of the pyranediol with the *tert*-butyl ester tether under acidic conditions is a useful method for the stereoselective synthesis of natural products afritoxinones and pestalotines having the furopyranone skeleton. Synthetic projects of these natural products are now in progress in our laboratory.

EXPERIMENTAL

(3a*R**,4*R**,7*R**,7a*S**,8*R**)-3-(*tert*-Butyldimethylsilyloxy)-4,5,6,7,8-pentamethyl-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-methanoinden-1-one (**13**):

A solution of the enone **12** (5.00 g, 23.5 mmol) and 1,2,3,4,5-pentamethylcyclopentadiene (**11**) (7.6 mL, 6.41 g, 47.1 mmol) in toluene (78 mL) was refluxed for 3 h. After the solvent was removed in vacuo, the resulted residue was purified by silica gel column chromatography (hexane–AcOEt, 15:1) to give **13** (5.41 g, 66%) as pale yellow oil.

IR (neat) 2953, 1731, 1471, 1454, 1378, 1252, 1161, 1093, 1056, 926, 835, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.03 (3H, s), 0.06 (3H, s), 0.52 (3H, d, *J* = 6.4 Hz), 0.86 (9H, s), 1.18 (3H, s), 1.19 (3H, s), 1.37–1.43 (4H, m), 1.56 (3H, s), 1.90–2.04 (2H, m), 2.55–2.61 (2H, m), 4.02 (1H, dd, *J* = 5.9, 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ –4.7 (2C), 7.0, 11.2, 12.1, 14.5, 14.5, 17.9, 25.7 (3C), 50.5, 55.9, 58.4, 59.2, 62.2, 64.6, 68.9, 132.6, 134.0, 219.8. HRESIMS calcd for $C_{21}H_{37}O_2Si$ $[M+H]^+$ 349.2563, found 349.2567.

(3a*R**,4*S**,7*R**,7a*S**,8*R**)-4,5,6,7,8-Pentamethyl-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-1-one (**10**):

To a solution of the adduct **13** (5.41 g, 15.5 mmol) in THF (155 mL) was added tetra-*n*-butylammonium fluoride (1.0 M in THF solution, 18.6 mL, 18.6 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. After the reaction mixture was quenched by addition with water, the mixture was extracted with AcOEt. The combined organic layer was washed with brine, dried over $MgSO_4$, and the solvent was removed. The resulted residue was purified by silica gel column chromatography (hexane–AcOEt, 20:1) to give **10**[15] (3.19 g, 95%) as pale yellow oil.

IR (neat) 2954, 2925, 2868, 1696, 1439, 1377, 1184, 1162, 1066, 912, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.59 (3H, d, *J* = 6.4 Hz), 1.15 (3H, s), 1.24 (3H, s), 1.34 (3H, s), 1.44 (3H, s), 1.62 (1H, q, *J* =

6.4 Hz), 2.33 (1H, d, *J* = 5.3 Hz), 3.08 (1H, ddd, *J* = 5.3, 2.6, 1.4 Hz), 5.88 (1H, dd, *J* = 5.7, 1.4 Hz), 7.39 (1H, dd, *J* = 5.7, 2.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.1, 11.1, 11.2, 14.5, 14.7, 56.0, 56.5, 57.1, 57.2, 65.8, 131.3, 132.6, 136.3, 163.1, 210.5. HRESIMS calcd for $C_{15}H_{21}O$ $[M+H]^+$ 217.1592, found 217.1597.

tert-Butyl 2-((1*R**,3a*S**,4*R**,7*S**,7a*R**,8*R**)-4,5,6,7,8-pentamethyl-3-oxo-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-methanoinden-1-yl)acetate (**14**):

To a suspention of Reformatsky reagent, prepared from *tert*-butyl bromoacetate (1.36 mL, 1.80 g, 9.25 mmol) and zinc dust (605 mg, 9.25 mmol) in THF (10 mL), were added dropwise a solution of enone **10** (500 mg, 2.31 mmol) in THF (23 mL) and trimethylsilyl trifluoromethanesulfonate (1.67 mL, 2.05 g, 9.25 mmol) at –78 °C. After stirring for 2 h at –78 °C, the reaction was quenched by addition of saturated $NaHCO_3$ aqueous solution, and the mixture was extracted with AcOEt, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the resulted residue was purified by silica gel column chromatography (hexane–AcOEt, 15:1) to give **14** (677 mg, 92%) as colorless oil.

IR (neat) 2954, 2927, 2871, 1732, 1454, 1367, 1254, 1154, 1073, 951, 845 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.52 (3H, d, *J* = 6.4 Hz), 1.13 (3H, s), 1.20 (3H, s), 1.37 (1H, q, *J* = 6.4 Hz), 1.42–1.46 (12H, m), 1.63 (3H, s), 1.78–1.84 (1H, m), 1.98–2.05 (1H, m), 2.16–2.22 (2H, m), 2.24–2.27 (2H, m), 2.49 (1H, br d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.2, 11.3, 12.3, 14.3, 14.5, 28.0 (3C), 30.7, 43.7, 46.1, 56.8, 57.0, 58.7, 59.7, 64.4, 80.6, 133.3, 133.9, 171.4, 220.8. HRESIMS calcd for $C_{21}H_{32}O_3Na$ $[M+Na]^+$ 355.2249, found 355.2253.

tert-Butyl 2-((1*R**,3a*S**,4*R**,7*S**,7a*R**,8*R**)-4,5,6,7,8-pentamethyl-3-(trimethylsilyloxy)-3a,4,7,7a-tetrahydro-1*H*-4,7-methanoinden-1-yl)acetate (**9**):

To a solution of ketone **14** (4.12 g, 12.4 mmol) in THF (62 mL) was added LHMDS (1.0 M in THF, 24.8 mL, 24.8 mmol) at –78 °C, and stirred for 0.5 h at –78 °C. To this mixture was added dropwise trimethylsilylchloride (2.35 mL, 2.02 g, 18.6 mmol) at –78 °C, and stirred for 0.5 h at the same temperature. The reaction was quenched by addition of saturated $NaHCO_3$ aqueous solution, and the mixture was extracted with AcOEt, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the resulted residue was purified by silica gel column chromatography (hexane–AcOEt, 10:1) to give **9** (3.18 g, 63%) as colorless oil.

IR (neat) 2961, 1731, 1639, 1456, 1367, 1324, 1253, 1213, 1146 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6) δ 0.14 (9H, s), 0.65 (3H, d, *J* = 6.4 Hz), 1.11 (3H, s), 1.16 (1H, q, *J* = 6.4 Hz), 1.27 (3H, s), 1.41 (9H, s), 1.64 (3H, s), 1.66 (3H, s), 1.96 (1H, dd, *J* = 8.4, 2.4 Hz), 2.16–2.19 (2H, m), 2.54–2.60 (1H, m), 2.73 (1H, ddd, *J* = 8.4, 2.9, 1.1 Hz), 4.48–4.50 (1H, m); ^{13}C NMR (100 MHz, C_6D_6) δ –0.2 (3C), 8.2, 11.7, 13.0, 14.9,

15.4, 28.2 (3C), 39.1, 45.2, 56.0, 56.2, 57.4, 59.5, 63.7, 79.3, 107.0, 131.9, 134.1, 156.8, 171.8. HRESIMS calcd for $C_{24}H_{40}O_3NaSi$ $[M+Na]^+$ 427.2644, found 427.2642.

tert-Butyl 2-((1*R**,2*R**,3a*S**,4*R**,7*S**,7a*R**,8*R**)-2-hydroxy-4,5,6,7,8-pentamethyl-3-oxo-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-methanoinden-1-yl)acetate (**8**):

To a solution of silyl enol ether **9** (50.0 mg, 0.124 mmol) in CH_2Cl_2 (1 mL) was added $NaHCO_3$ (32.3 mg, 0.384 mmol) and *m*-chloroperbenzoic acid (29.7 mg, 0.133 mmol) at 0 °C, and the mixture was stirred at the same temperature. After stirring for 1 h, the reaction was quenched by addition of saturated $NaHCO_3$ aqueous solution, and the mixture was extracted with $CHCl_3$, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the resulted residue was purified by silica gel column chromatography (hexane–AcOEt, 10:1) to give **8** (23.9 mg, 56%) as colorless oil.

IR (neat) 3444, 2955, 2928, 2871, 1738, 1732, 1715, 1454, 1392, 1379, 1367, 1334, 1256, 1150, 1087 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.52 (3H, d, *J* = 6.4 Hz), 1.13 (3H, s), 1.15 (3H, s), 1.36 (3H, s), 1.37–1.42 (10H, m, including 9H, s, at δ 1.40), 1.63 (3H, s), 1.99 (1H, dd, *J* = 15.7, 8.0 Hz), 2.22 (1H, d, *J* = 8.8 Hz), 2.36 (1H, dd, *J* = 15.7, 5.6 Hz), 2.46–2.59 (3H, m), 3.51 (1H, d, *J* = 9.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.6, 11.2, 12.3, 14.2, 14.6, 28.0 (3C), 34.4, 36.7, 54.5, 56.8 (2C), 59.2, 64.5, 76.6, 80.6, 134.1, 134.8, 172.5, 218.7. HRESIMS calcd for $C_{21}H_{32}O_4Na$ $[M+Na]^+$ 371.2198, found 371.2213.

tert-Butyl 2-((1*R**,2*R**,3*S**,3a*S**,4*R**,7*S**,7a*R**,8*R**)-2,3-dihydroxy-4,5,6,7,8-pentamethyl-2,3,3a,4,7,7a-hexahydro-1*H*-4,7-methanoinden-1-yl)acetate (**15**):

To a solution of α-hydroxy ketone **8** (379 mg, 1.09 mmol) in MeOH (10 mL) was added sodium borohydride (49.4 mg, 1.31 mmol) at 0 °C, and the mixture was stirred for 0.5 h at the same temperature. After the mixture was quenched by addition of saturated $NaHCO_3$ aqueous solution, and the mixture was extracted with Et_2O, washed with brine, and dried over $MgSO_4$. After the solvent was removed in vacuo, the resulted residue was purified by silica gel column chromatography (hexane–AcOEt, 2:1) to give **15** (364 mg, 95%) as colorless prism.

Mp 132–134 °C (benzene–hexane); IR (KBr) 3390, 2951, 2924, 2870, 1732, 1704, 1449, 1368, 1256, 1155, 1114, 1098, 1069, 1029 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 0.58 (3H, d, *J* = 6.4 Hz), 1.09 (3H, s), 1.15 (1H, q, *J* = 6.4 Hz), 1.19 (3H, s), 1.27–1.33 (1H, br s), 1.40 (9H, s), 1.42–1.48 (1H, br s), 1.56 (3H, s), 1.74 (3H, s), 1.86–2.00 (2H, m), 2.13 (1H, dd, *J* = 9.1, 9.0 Hz), 2.17–2.23 (1H, m), 2.63 (1H, dd, *J* = 15.4, 6.4 Hz), 3.53 (1H, dd, *J* = 8.7, 7.5 Hz), 3.85 (1H, dd, *J* = 9.0, 8.7 Hz); ^{13}C NMR (100 MHz, C_6D_6) δ 7.8, 12.1, 12.7, 15.2, 16.2, 28.2 (3C), 36.9, 37.6, 52.7, 56.4, 56.5, 58.2, 64.8, 78.7, 79.8, 79.9, 134.1, 136.3, 173.5.

HRESIMS calcd for $C_{21}H_{35}O_4$ $[M+H]^+$ 351.2535, found 351.2535.

tert-Butyl 2-((4*R**,4a*R**,5*S**,8*R**,8a*S**,9*R**)-1,3-dihydroxy-5,6,7,8,9-pentamethyl-3,4,4a,5,8,8a-hexahydro-1*H*-5,8-methanoisochromen-4-yl)acetate (**7**):

To a solution of **15** (364 mg, 1.04 mmol) in THF–H_2O (2:1, 15 mL) was added sodium periodate (444 mg, 2.08 mmol) at 0 °C, and the mixture was stirred for 3 h at room temperature. After the reaction mixture was diluted with H_2O, the mixture was extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (hexane–AcOEt, 1:1) to give **7** (287 mg, 75%, mixture of two diastereomers, dr = 2:1) as colorless oil.

IR (neat) 3425, 2957, 2929, 2873, 1728, 1448, 1367, 1154, 1021 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, major isomer) δ 0.55 (3H, d, *J* = 6.4 Hz), 1.12 (3H, s), 1.14 (3H, s), 1.35 (1H, q, *J* = 6.4 Hz), 1.44 (9H, s), 1.59–1.70 (7H, m, including 3H, s, at δ 1.60, and 3H, s, at δ 1.62), 1.85–2.06 (2H, m), 2.23 (1H, dd, *J* = 15.9, 8.4 Hz), 2.69 (1H, dd, *J* = 15.9, 2.3 Hz), 3.16 (1H, d, *J* = 6.1 Hz), 3.72 (1H, d, *J* = 5.4 Hz), 4.78 (1H, dd, *J* = 7.8, 6.1 Hz), 5.01 (1H, dd, *J* = 8.6, 5.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, major isomer) δ 7.5, 12.2, 12.5, 14.9, 16.0, 28.1 (3C), 38.1, 38.9, 48.6, 53.8, 54.6, 56.3, 62.3, 80.7, 92.9, 96.1, 133.8, 134.4, 172.6. HRESIMS calcd for $C_{21}H_{34}O_5Na$ $[M+Na]^+$ 389.2304, found 389.2299.

(3a*R**,5*R**5a*S**,6*R**,9*R**,9a*R**,9b*R**,10*R**)-5-Methoxy-6,7,8,9,10-pentamethyl-5,5a,6,9,9a,9b-hexahydro-1*H*-6,9-methanofuro[2,3-*c*]isochromen-2(3a*H*)-one (**6**):

To a solution of **7** (287 mg, 0.783 mmol) in MeOH (8 mL) was added *p*-toluenesulfonic acid monohydrate (46.8 mg, 0.246 mmol) at room temperature, and the mixture was stirred for 0.5 h at the same temperature. After the solvent was removed in vacuo, the resulting residue was purified by silica gel column chromatography (hexane–AcOEt, 5:1) to give **6** (205 mg, 85%) as colorless needle.

Mp 125–127 °C (benzene–hexane); IR (KBr) 2955, 2917, 2870, 1785, 1448, 1380, 1366, 1333, 1262, 1188, 1116, 1058, 982, 957 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 0.47 (3H, d, *J* = 6.4 Hz), 0.70 (3H, s), 0.82 (3H, s), 0.91 (1H, q, *J* = 6.4 Hz), 1.26 (3H, s), 1.44 (3H, s), 1.56 (1H, d, *J* = 10.1 Hz), 1.78 (1H, d, *J* = 10.1 Hz), 1.80 (1H, ddd, *J* = 10.9, 10.1, 7.8 Hz), 2.09 (1H, dd, *J* = 17.6, 10.9 Hz), 2.67 (1H, dd, *J* = 17.6, 10.1 Hz), 3.28 (3H, s), 4.46 (1H, s), 4.98 (1H, d, *J* = 7.8 Hz); ^{13}C NMR (150 MHz, C_6D_6) δ 7.3, 12.0, 12.2, 13.3, 14.0, 29.2, 35.9, 45.4, 46.6, 55.1, 55.5, 55.8, 63.0, 97.6, 98.0, 131.3, 135.0, 174.8. HRESIMS calcd for $C_{18}H_{26}O_4Na$ $[M+Na]^+$ 329.1729, found 329.1724.

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19. CCDC 1004142 contains the supplementary crystallographic data of **15** for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
20. CCDC 1006210 contains the supplementary crystallographic data of **6** for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
21. In most cases, the starting material **6** was recovered. The retro-Diels–Alder reaction of the diol **15** was also attempted in the same conditions. These examinations resulted in decomposition of **15**.