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Stereoselective Total Synthesis of (±)-Peribysin E

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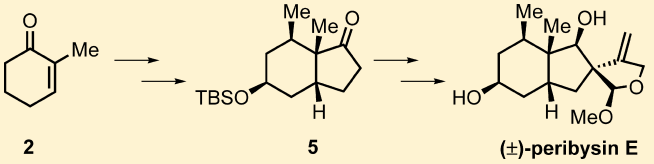
Supporting Information

ABSTRACT: Radical cyclization of iodoketone **3** afforded *cis*-hydrindanone **8**. Compound **8** was converted into key intermediate **5** via conventional transformations. Annulation of a spiro-lactal unit to **5** was pursued with three different approaches. In the first approach, radical cyclization of propargyl ester **17** provided spiro-lactone **18** with an undesired stereochemistry. Attempts to invert the stereochemistry at the spiro-center via retro-aldol and aldol condensation of compound **20** failed. In the second approach, key intermediate **5** was transformed into **23**. Acylation of compound **23** gave **24** as a single diastereomer with the desired stereochemistry but in low yield. NBS bromination of **24** followed by lactone formation gave **26** in low yield. Alternatively, allylic oxidation of **24** with SeO_2 followed by lactonization gave **26** also in low yield. Finally, a third approach employing a semipinacol-type rearrangement of epoxy-alcohol **33** gave aldehyde **34** with the desired stereochemistry. Treatment of compound **34** with HCl in MeOH effected spiro-lactal formation and provided (±)-peribysin E. The overall yield of our synthesis is 3.2% from 2-methylcyclohenen-1-one.



INTRODUCTION

Peribysin E (**1**) and related metabolites were isolated by Yamada and co-workers from a strain of *Periconia byssoides* OUPS-N133 originally separated from the sea hare, *Aplysia kurodai*.[1] These natural products, especially peribysin E (**1**), Figure 1, were reported to inhibit adhesion of leukemia HL-60 cells to human-umbilical-vein endothelial cells (HUVEC).[2] Because of its potent cell-adhesion inhibitory activity and its scarcity, peribysin E has become a target for total synthesis. Danishefsky and co-workers achieved the first total synthesis of both enantiomers of peribysin E and thereby reassigned the absolute configuration (shown as **1**). In their elegant synthesis, a Diels–Alder reaction followed by semipinacol-type ring contraction served to secure the stereochemistry of peribysin E (**1**).[3]

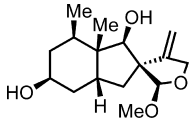


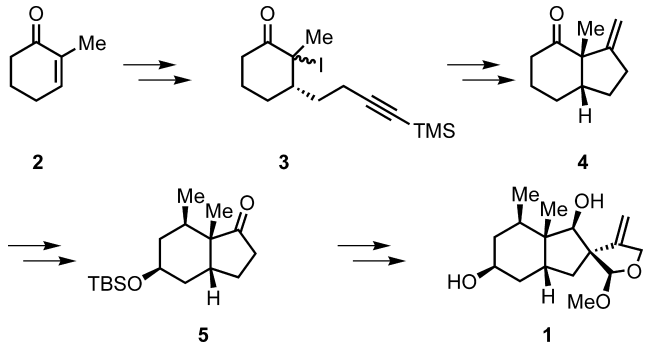
Figure 1. Structure of peribysin E.

In our laboratories, we developed a radical cyclization of α-iodoketones to prepare *cis*-hydrindanones.[4] This method was applied to total synthesis of various natural products.[5] We envisioned that our method would be also applicable for the total synthesis of peribysin E.

RESULTS AND DISCUSSION

Our synthetic planning was shown in Scheme 1. According to our method,[4] 2-methylcyclohexen-1-one (**2**)[6] could be converted into α-iodoketone **3** with an alkynyl side chain.

Scheme 1



Radical cyclization of **3** would give *cis*-hydrindanone **4**. After several conventional transformations, compound **4** could be converted into key intermediate **5**. The spiro-annulation of a β-methylene lactal unit to **5** could furnish peribysin E (**1**).

Our synthesis thus began with 2-methylcyclohexen-1-one (**2**), Scheme 2. CuI-mediated conjugate addition of 4-(trimethylsilyl)-3-butynylmagnesium chloride (**6**) to **2**, followed by trapping the resulting enolate with chlorotrimethylsilane, generated TMS-enol ether **7**. Treatment of **7** with a mixture of NaI and *m*-CPBA gave α-iodoketone **3**. Photolysis of α-iodoketone **3** with a sunlamp in the presence of hexamethylditin, followed by reduction with tributyltin hydride, gave compound **8**. Hydrodesilylation of compound **8** with trifluoroacetic acid followed by reduction with sodium borohydride cleanly afforded alcohol **9** as a single diastereomer. Dihydroxylation of the exocyclic double bond of **9** with OsO_4

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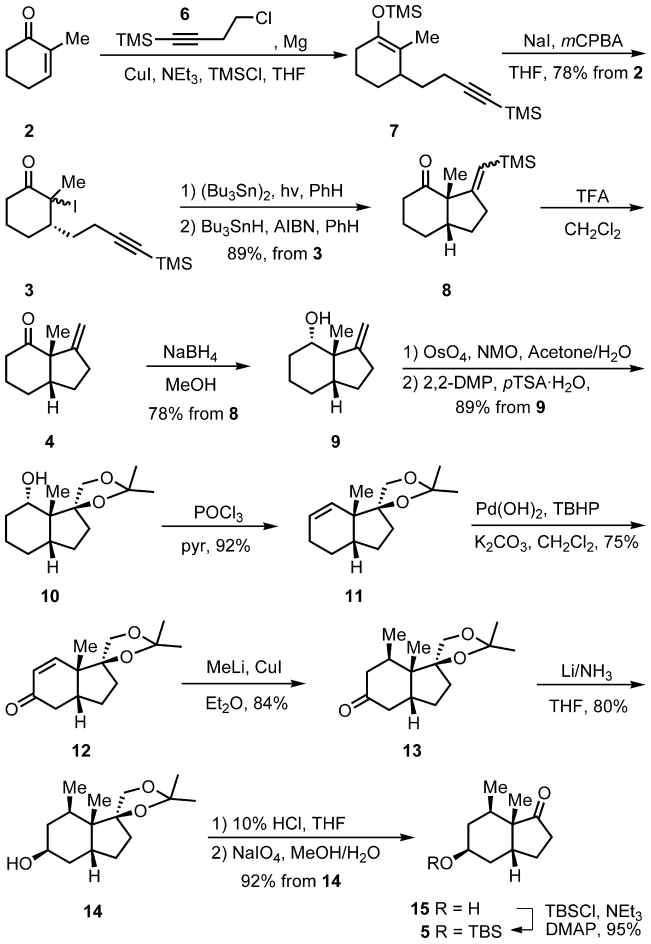
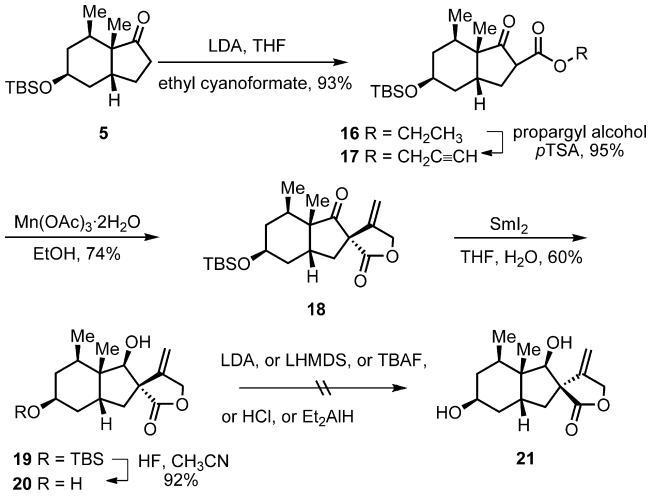
Scheme 2



and *N*-methylmorpholine-*N*-oxide, followed by treatment of the diol intermediate with 2,2-dimethyloxypropane, gave acetonide **10**. Dehydration of **10** with $POCl_3$ at 70 °C afforded compound **11**. Allylic oxidation of **11** with $Pd(OH)_2$ and *tert*-butyl hydroperoxide gave enone **12**.[7] CuI mediated conjugate addition of methyllithium to enone **12** afforded ketone **13** as a single diastereomer. Reduction of ketone **13** with $NaBH_4$, or DIBAL, or *L*-selectride gave a mixture of epimeric alcohols. The desired alcohol **14** was obtained only with Li/NH_3 reduction. Removal of the acetonide group in **14** followed by oxidative cleavage with $NaIO_4$ afforded ketone **15**. The stereochemistry of **15** was determined with single-crystal X-ray analysis.[8] Protection of the alcohol group in **15** with a *tert*-butyldimethylsilyl (TBS) group afforded the key hydrindanone **5**.

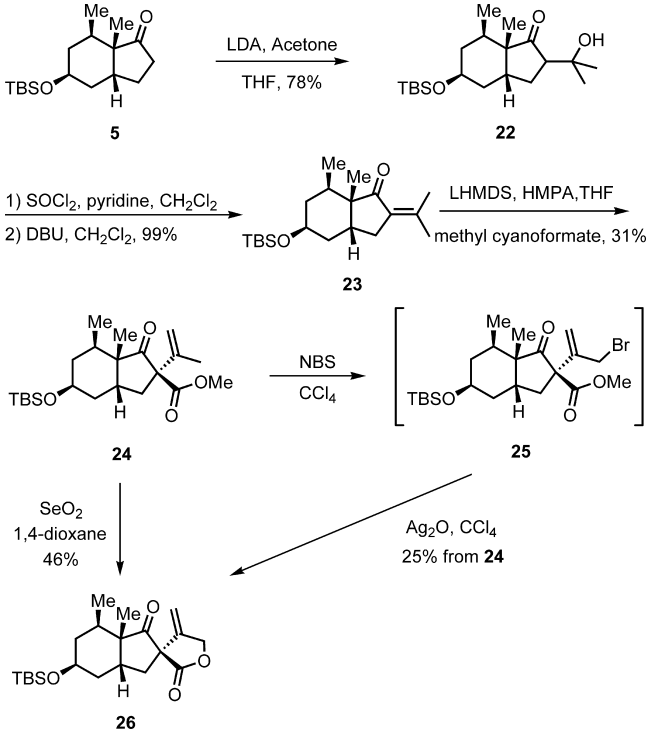
We then devoted our effort to stereoselective annulation of the spiro-lactal unit to hydrindanone **5**, Scheme 3. Compound **5** was first treated with lithium diisopropylamide and then ethyl cyanoformate to give ethyl ester **16**. Trans-esterification of **16** with propargyl alcohol in the presence of *p*-toluenesulfonic acid gave propargyl ester **17**. Treatment of **17** with manganese triacetate effected a radical cyclization to afford spiro compound **18**.[9] A single-crystal X-ray analysis indicated that **18** had the undesired stereochemistry at the spiro-center.[10] We then attempted a retro-aldol and aldol condensation according to Deprés' procedure to invert the undesired stereochemistry at the spiro-center.[9] Samarium(II) iodide reduction of **18**, followed by removal of the TBS group with 50% HF in

Scheme 3



acetonitrile, generated diol **20**.[11] Attempted retro-aldol and aldol reactions of **20** with several bases, such as TBAF, LDA, LHMDS, or with acids, such as HCl, Et_2AlH, failed to produce the desired compound **21**.

Scheme 4



We then tried an alternative route, Scheme 4. Compound **5** was treated with lithium diisopropylamide and then acetone to give *β*-hydroxy ketone **22**. Dehydration of **22** followed by isomerization of the double bond with DBU afforded enone **23**. Enone **23** was first deprotonated with lithium bis-(trimethylsilyl)amide and then acylated with methyl cyanoformate to afford exclusively keto-ester **24** but only in 31% yield. A single-crystal X-ray analysis indicated that **24** has the desired stereochemistry at the spiro-center.[12] Compound **24** was then brominated with NBS to give compound **25**.

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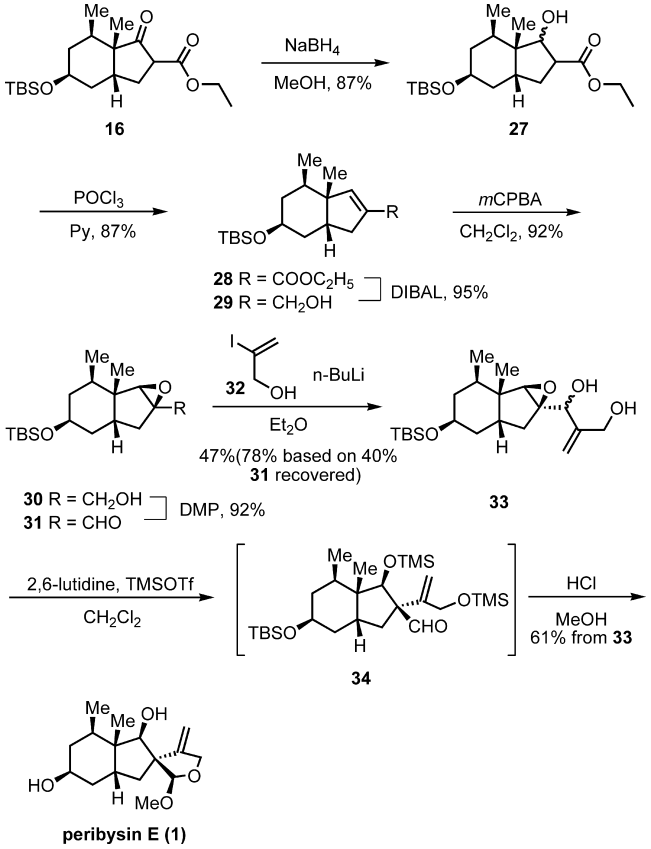
Treatment of crude **25** with silver(I) oxide gave compound **26** in low yield (25% in two steps from **24**).[13] Alternatively, allylic oxidation of **24** with SeO_2 in 1,4-dioxane at 85 °C followed by lactonization gave compound **26** in 46% yield. Our effort to optimize the yields of this second approach was not successful.

Scheme 5



We then decided to pursue a third approach using semipinacol-type rearrangement as the key step, Scheme 5. Reduction of ketone ester **16** with $NaBH_4$ gave compound **27**. Dehydration of **27** afforded α,β-unsaturated ester **28**. Reduction of the ester group in **28** with DIBAL gave allylic alcohol **29**. Stereoselective epoxidation of allylic alcohol **29** with *m*-CPBA gave compound **30**. Dess–Martin oxidation of alcohol **30** gave aldehyde **31**. Reaction of **31** with the dianion generated from 2-iodopropen-1-ol (**32**) and *n*-BuLi gave epoxy-alcohol **33**.[14] Treatment of **33** with 2,6-lutidine and TMSOTf effected a semipinacol-type rearrangement to afford the unstable intermediate **34**.[15] Treatment of **34** with HCl/MeOH successfully afforded (±)-peribysin E (**1**) with the correct stereochemistry. The ^1H and ^{13}C NMR spectra of our synthetic peribysin E agree satisfactorily with those reported by Danshefsky's group.

CONCLUSION

In summary, we achieved a stereoselective total synthesis of (±)-peribysin E via α-carbonyl radical cyclization and semipinacol-type rearrangement. Our synthesis provided (±)-peribysin E in 3.2% overall yield from 2-methylcyclohexen-1-one and is adaptable for preparation of analogues and derivatives of peribysin E for anticancer study.

EXPERIMENTAL SECTION

2-Iodo-2-methyl-3-[4-(trimethylsilyl)but-3-yn-1-yl]-cyclohexanone (3). To magnesium turnings (4.54 g, 181.56 mmol) suspended in anhydrous THF (10 mL), 1,2-dibromoethane (0.20 mL) was added. The reaction mixture was heated to reflux. A solution of 4-chloro-1-trimethylsilyl-1-butyne (16.05 g, 99.86 mmol) and 1,2-dibromoethane (0.10 mL) in THF (50 mL) was added dropwise over a period of 1 h. After an additional reflux for 2 h, the reaction mixture was cooled to −30 °C. CuI (12.97 g, 68.06 mmol) was added. To the resulting mixture, 2-methyl cyclohexen-1-one **2** (5.00 g, 45.39 mmol) in anhydrous THF (60 mL) was added dropwise. Chlorotrimethylsilane (11.46 mL, 90.78 mmol) and triethylamine (12.58 mL, 90.78 mmol) was then added. The reaction mixture was stirred at −30 °C for 16 h and then warmed up to room temperature. After filtration, water was added. The filtrate was extracted with ether (3 × 200 mL). The combined organic layer was washed with saturated NH_4Cl (100 mL) and brine (100 mL) and dried over $MgSO_4$. Concentration gave crude **7**. It was immediately used for the next reaction. To a solution of NaI (20.41 g, 136.17 mmol) and crude **7** in THF (250 mL) was added dropwise *m*-CPBA (70%, 23.50 g, 136.17 mmol) in THF (150 mL) at 0 °C. The reaction mixture was stirred for 3 h. Water was added. The mixture was extracted with ether (3 × 100 mL). The combined organic layer was washed with saturated $Na_2S_2O_3$ (150 mL), saturated $NaHCO_3$ (150 mL), and brine (150 mL) and dried over $MgSO_4$. Concentration and silica gel flash column chromatography (EtOAc/hexane, 1:50) afforded **3** (12.83 g, 78%) as a yellow oil. Data for the major diastereomer: IR (neat) ν 2956, 2864, 2174, 1706, 1443, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.52 (td, J = 14.4, 6.5 Hz, 1H), 2.44–2.31 (m, 2H), 2.32–2.18 (m, 1H), 2.04 (s, 3H), 2.03–1.95 (m, 1H), 1.95–1.81 (m, 2H), 1.59–1.36 (m, 3H), 0.43–0.33 (m, 1H), 0.10 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0 (C), 106.3 (C), 85.7 (C), 60.4 (C), 49.0 (CH), 35.7 (CH_2), 34.2 (CH_2), 28.7 (CH_2), 27.7 (CH_3), 24.8 (CH_2), 17.7 (CH_2), 0.0 (CH_3); HRMS (FAB) m/z calcd for $C_{14}H_{23}O$ Si I 362.0563, found 362.0559.

[3(*E* and *Z*),3a*S,7a*S**]-3a-Methyl-3-[(trimethylsilyl)-methylene]octahydro-4*H*-inden-4-one (8).** To a solution of **3** (23.73 g, 65.49 mmol) in anhydrous benzene (600 mL) was added $(Bu_3Sn)_2$ (6.55 mL, 13.09 mmol). The reaction mixture was heated to reflux and irradiated with a sunlamp for 2 h. The sunlamp was removed. AIBN (2.15 g, 13.09 mmol) and Bu_3SnH (19.35 mL, 72.04 mmol) were added. The reaction mixture was heated to reflux for 2 h. Concentration and silica gel flash column chromatography (EtOAc/hexane, 1:50) gave **8** (13.76 g, 89%) as a mixture of *E* and *Z* isomers (pale yellow oil). Data for the major isomer: IR (neat) ν 2951, 2930, 2864, 1705, 1608, 1246 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.40 (t, J = 2.1 Hz, 1H), 2.77– 2.64 (m, 1H), 2.56–2.45 (m, 2H), 2.29–2.18 (m, 1H), 2.12–2.02 (m, 1H), 1.98–1.77 (m, 2H), 1.69–1.53 (m, 2H), 1.52–1.39 (m, 2H), 1.15 (s, 3H), −0.01 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5 (C), 165.2 (C), 122.3 (CH), 60.9 (C), 54.0 (CH), 40.3 (CH_2), 35.1 (CH_2), 28.7 (CH_2), 28.5 (CH_2), 26.6 (CH_2), 22.6 (CH_3), 0.8 (CH_3); HRMS (EI) m/z calcd for $C_{14}H_{24}OSi$ 236.1596, found 236.1590.

(3a*S,7a*S**)-3a-Methyl-3-methyleneoctahydro-4*H*-inden-4-one (4).** To a solution of **8** (13.76 g, 58.29 mmol) in CH_2Cl_2 (300 mL) was added CF_3COOH (15.09 mL, 196.47 mmol) at 0 °C. The reaction mixture was stirred for 1 h and then neutralized with saturated $NaHCO_3$ (75 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layer was washed with brine (50 mL) and dried over $MgSO_4$. Concentration gave a crude product **4** as a pale yellow oil, which was used for the next reaction: IR (neat) ν 2928, 2864, 1702, 1648, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.89 (t, J = 2.1 Hz, 1H), 4.67 (t, J = 2.5 Hz, 1H), 2.61–2.42 (m, 2H), 2.41–2.32 (m, 1H), 2.31–2.23 (m, 1H), 2.14–2.05 (m, 1H), 1.96–1.84 (m, 2H), 1.76–1.67 (m, 1H), 1.63–1.50 (m, 2H), 1.49–1.37 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.9 (C), 155.5 (C), 107.3 (CH_2), 59.9 (C) 50.3 (CH), 38.7 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 28.1 (CH_2), 24.6 (CH_2), 23.4 (CH_3); HRMS (EI) m/z calcd for $C_{11}H_{16}O$ 164.1201, found 164.1201.

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(3a*S,4*S**,7a*S**)-3a-Methyl-3-methyleneoctahydro-1*H*-inden-4-ol (9).** To a solution of the crude product **4** in methanol (400 mL), $NaBH_4$ (4.95 g, 130.98 mmol) was added portionwise at 0 °C. After stirring for 0.5 h, water (50 mL) and CH_2Cl_2 (200 mL) were added. The organic layer was separated, washed with saturated $NaHCO_3$ (50 mL) and brine (30 mL), and dried over $MgSO_4$. Concentration and silica gel flash column chromatography (EtOAc/hexane, 1:50) furnished **9** (7.55 g, 78% from **8**) as a colorless oil: IR (neat) ν 3399, 2932, 2860, 1648, 1458 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.05 (ddd, J = 2.6, 1.9, 0.9 Hz, 1H), 4.94 (t, J = 2.3 Hz, 1H), 3.52 (dd, J = 4.1, 3.2 Hz, 1H), 2.51−2.29 (m, 2H), 1.92−1.68 (m, 5H), 1.66−1.46 (m, 4H), 1.31−1.19 (m, 1H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3 (C), 106.0 (CH_2), 75.3 (CH), 47.9 (C) 45.5 (CH), 32.5 (CH_2), 28.8 (CH_2), 28.3 (CH_2), 25.1 (CH_2), 24.7 (CH_3), 16.2 (CH_2); HRMS (EI) m/z calcd for $C_{11}H_{18}O$ 166.1358, found 166.1353.

(3a′*S,4*S**,7′*S**,7a′*R**)-2,2,7a′-Trimethyloctahydrospiro[1,3-dioxolane-4,1′-inden]-7′-ol (10).** To a mixture of *N*-methyl morpholine-*N*-oxide (42.80 mL, 182.64 mmol, 50% in water), water (18 mL), acetone (60 mL), and osmium tetroxide (0.05 M in *t*-butanol, 45.66 mL, 2.28 mmol) was added compound **9** (7.59 g, 45.66 mmol). The reaction mixture was stirred for 18 h at room temperature. A slurry of sodium hydrosulfite (1 g) and magnesium silicate (magnesol, 12 g) was added. The reaction mixture was filtered. Acetone was removed under vacuum. The resulting mixture was extracted with EtOAc (3 × 250 mL). The combined organic layer was washed with brine (100 mL) and dried over $MgSO_4$. Concentration gave a crude product, which was used for the next reaction. To a solution of the diol crude product in CH_2Cl_2 (220 mL) at room temperature was added 2,2-dimethoxypropane (22.40 mL, 182.64 mmol) and *p*-toluenesulfonic acid (3.48 g, 18.26 mmol). The reaction mixture was stirred for 1.5 h and quenched with saturated $NaHCO_3$ (30 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:10) gave alcohol **10** (9.77 g, 89%) as a white solid: mp 113−114 °C; IR (neat) ν 3460, 2986, 2936, 2863, 1461, 1246, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.06 (d, J = 9.0 Hz, 1H), 3.99 (d, J = 9.0 Hz, 1H), 3.57−3.48 (m, 1H), 2.21−2.08 (m, 1H), 2.06−1.91 (m, 2H), 1.88−1.63 (m, 4H), 1.61−1.42 (m, 3H), 1.38 (d, J = 0.5 Hz, 3H), 1.32 (d, J = 0.5 Hz, 3H), 1.30−1.20 (m, 2H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 108.2 (C), 94.1 (C), 72.0 (CH), 69.6 (CH_2), 48.1 (C), 42.8 (CH), 40.4 (CH_2), 31.5 (CH_2), 27.0 (CH_2), 26.7 (CH_3), 26.1 (CH_3), 24.2 (CH_2), 19.8 (CH_3), 14.5 (CH_2); HRMS (EI) m/z calcd for $C_{14}H_{24}O_3$ 240.1725, found 240.1717.

(3a′*S,4*S**,7a′*R**)-2,2,7a′-Trimethyl-2′,3′,3a′,4′,5′,7a′-hexahydrospiro[1,3-dioxolane-4,1′-indene] (11).** To a solution of the alcohol **10** (8.89 g, 36.99 mmol) in anhydrous pyridine (120 mL) at room temperature was added phosphorus oxychloride (22.40 mL, 182.64 mmol). The reaction mixture was stirred at 70 °C for 4 h and quenched with saturated $NaHCO_3$ (100 mL). The organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 200 mL). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:100) afforded the compound **11** (7.57 g, 92%) as a colorless oil: IR (neat) ν 2982, 2948, 2924, 1649, 1456, 1368, 1212 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.64 (ddd, J = 10.2, 5.0, 2.6 Hz, 1H), 5.23 (ddt, J = 10.2, 2.7, 1.4 Hz, 1H), 3.94 (d, J = 8.6 Hz, 1H), 3.71 (d, J = 8.7 Hz, 1H), 2.16−2.07 (m, 1H), 2.07−1.95 (m, 1H), 1.91−1.73 (m, 3H), 1.73−1.55 (m, 2H), 1.53− 1.44 (m, 1H), 1.38−1.32 (m, 1H), 1.38 (s, 3H), 1.32 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.0 (CH), 128.2 (CH), 108.7 (C), 92.3 (C), 68.7 (CH_2), 45.8 (C), 41.2 (CH), 36.5 (CH_2), 27.3 (CH_3), 26.3 (CH_3), 24.2 (CH_2), 22.6 (CH_2), 20.9 (CH_3), 20.6 (CH_2); HRMS (EI) m/z calcd for $C_{14}H_{22}O_2$ 222.1620, found 222.1620.

(3a′*R,4*S**,7a′*R**)-2,2,7a′-Trimethyl-2′,3′,3a′,7a′-tetrahydrospiro[1,3-dioxolane-4,1′-inden]-5′(4′*H*)-one (12).** To a mixture of 20% $Pd(OH)_2/C$(1.32 g, 1.88 mmol), K_2CO_3 (1.29 g, 9.39 mmol), CH_2Cl_2 (160 mL), and 70% *t*-BuOOH in water (12.89 mL, 93.9 mmol) was added compound **11** (8.35 g, 37.56 mmol). The reaction mixture was vigorously stirred at room temperature. After stirring for 24 h, a mixture of 20% $Pd(OH)_2/C$ (1.32 g, 1.88 mmol), K_2CO_3 (1.29 g, 9.39 mmol), and 70% *t*-BuOOH in water (12.89 mL, 93.9 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was then filtered through a short pad of silica gel. The short pad of silica gel was washed with CH_2Cl_2 (200 mL). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:10) afforded the enone **12** (6.66 g, 75%) as a pale yellow oil: IR (neat) ν 2983, 2938, 1678, 1457, 1237, 1237 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.37 (dd, J = 10.3, 2.0 Hz, 1H), 5.90 (dd, J = 10.3, 0.9 Hz, 1H), 4.09 (d, J = 8.9 Hz, 1H), 3.90 (d, J = 8.9 Hz, 1H), 2.58 (dd, J = 16.6, 4.8 Hz, 1H), 2.52−2.45 (m, 1H), 2.42 (ddd, J = 16.7, 2.8, 0.9 Hz, 1H), 2.12−2.00 (m, 1H), 1.96−1.88 (m, 1H), 1.67−1.56 (m, 1H), 1.40 (d, J = 0.6 Hz, 3H), 1.37 (d, J = 0.6 Hz, 3H), 1.37−1.27 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9 (C), 152.0 (CH), 129.5 (CH), 109.6 (C), 92.4 (C), 67.7 (CH_2), 48.0 (C), 41.6 (CH), 38.2 (CH_2), 37.0 (CH_2), 26.8 (CH_3), 26.3 (CH_3), 26.1 (CH_2), 17.7 (CH_3); HRMS (EI) m/z calcd for $C_{14}H_{20}O_3$ 236.1412, found 236.1409.

(3a′*R,4*S**,7′*R**,7a′*S**)-2,2,7′,7a′-Tetramethylhexahydrospiro[1,3-dioxolane-4,1′-inden]-5′(4′*H*)-one (13).** To a slurry of copper iodide (16.65 g, 87.39 mmol) in anhydrous Et_2O (100 mL) was added methyllithium (2.23 M in Et_2O/hexane, 78.38 mL, 174.79 mmol) dropwise at 0 °C. The reaction mixture was stirred for 60 min at 0 °C. A solution of the enone **12** (5.90 g, 24.97 mmol) in anhydrous Et_2O (60 mL) was added over 0.5 h. The reaction mixture was stirred for 1 h and then quenched with saturated NH_4Cl (100 mL). The reaction mixture was extracted with Et_2O (3 × 200 mL). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:20) afforded the ketone **13** (5.29 g, 84%) as a colorless oil: IR (neat) ν 2983, 2945, 2877, 1716, 1456, 1239, 1212 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.91 (d, J = 8.4 Hz, 1H), 3.79 (d, J = 8.4 Hz, 1H), 2.56−2.37 (m, 2H), 2.26−2.14 (m, 2H), 2.04 (ddd, J = 14.7, 4.2, 2.0 Hz, 1H), 2.01−1.91 (m, 2H), 1.91−1.78 (m, 2H), 1.41 (s, 3H), 1.31−1.22 (m, 4H), 1.09 (s, 3H), 0.84 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.9 (C), 107.7 (C), 93.6 (C), 69.0 (CH_2), 47.0 (CH), 46.8 (C), 46.4 (CH_2), 41.1 (CH_2), 34.9 (CH_2), 33.7 (CH), 28.0 (CH_3), 26.1 (CH_3), 25.6 (CH_2), 17.6 (CH_3), 12.3 (CH_3); HRMS (EI) m/z calcd for $C_{15}H_{24}O_3$ 252.1725, found 252.1731.

(3a′*R,4*S**,5′*S**,7′*R**,7a′*S**)-2,2,7′,7a′-Tetramethyloctahydrospiro[1,3-dioxolane-4,1′-inden]-5′-ol (14).** To a solution of ketone **13** (2.96 g, 11.73 mmol) in THF (100 mL) at −78 °C was added liquid ammonia (100 mL). Lithium (821 mg, 117.30 mmol) was added in small pieces. The reaction mixture was stirred at −78 °C for 1 h. Solid NH_4Cl (10 g) was added. Ammonia was allowed to evaporate. Water (80 mL) was added. The reaction mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:4) afforded the acetal alcohol **14** (2.39 g, 80%) as a colorless oil: IR (neat) ν 3399, 2982, 2927, 2878, 1465, 1240, 1214 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.89−3.79 (m, 2H), 3.78 (d, J = 8.4 Hz, 1H), 2.26 (tdd, J = 10.0, 5.0, 2.5 Hz, 1H), 2.02−1.91 (m, 1H), 1.87−1.71 (m, 3H), 1.63−1.56 (m, 1H), 1.42 (s, 3H), 1.40−1.31 (m, 1H), 1.56−1.45 (m, 3H), 1.24 (s, 3H), 1.21−1.09 (m, 1H), 0.91 (s, 3H), 0.75 (d, J = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 107.4 (C), 94.9 (C), 68.9 (CH_2), 66.7 (CH), 46.7 (C), 45.6 (CH), 41.3 (CH_2), 34.6 (CH_2), 33.7 (CH_2), 31.5 (CH), 28.3 (CH_3), 26.1 (CH_3), 24.1 (CH_2), 17.9 (CH_3), 11.8 (CH_3); HRMS (EI) m/z calcd for $C_{15}H_{26}O_3$ 254.1882, found 254.1872.

(3a*R,5*S**,7*R**,7a*S**)-5-Hydroxy-7,7a-dimethyloctahydro-1*H*-inden-1-one (15).** To acetal alcohol **14** (2.39 g, 9.40 mmol) was added a 2:1 mixture of MeOH/10% HCl (75 mL). The reaction mixture was stirred 1 h and then neutralized with saturated $NaHCO_3$. Solid $NaIO_4$ (4.02 g, 18.81 mmol) was added. The reaction mixture was stirred for 2 h and then filtered through a short pad of silica gel.

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The short pad of silica gel was washed with CH_2Cl_2 (150 mL). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:2) afforded the hydroxyl ketone **15** (1.58 g, 92%) as a white solid. Recrystallization from ether afforded colorless needles: mp 104−105 °C; IR (neat) ν 3410, 2960, 2925, 2876, 1730, 1464, 1277 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.92 (tt, J = 11.4, 4.6 Hz, 1H), 2.49−2.37 (m, 1H), 2.21−2.04 (m, 2H), 1.97 (ddt, J = 13.2, 4.4, 2.1 Hz, 1H), 1.89−1.79 (m, 2H), 1.79−1.70 (m, 1H), 1.70−1.46 (m, 3H), 1.19 (ABq, J = 12.1 Hz, 1H), 0.95 (s, 3H), 0.81 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.1 (C), 66.5 (CH), 49.6 (C), 45.2 (CH), 39.2 (CH_2), 36.0 (CH_2), 33.7 (CH_2), 28.9 (CH), 22.9 (CH_2), 15.3 (CH_3), 13.5 (CH_3); HRMS (EI) m/z calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1302.

(3a*R,5*S**,7*R**,7a*S**)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-7,7a-dimethyloctahydro-1*H*-inden-1-one (5).** To a solution of hydroxyl ketone **15** (1.10 g, 6.09 mmol) in anhydrous CH_2Cl_2 (60 mL) were added triethylamine (2.40 mL, 17.25 mmol), 4-(dimethylamino)-pyridine (372 mg, 3.05 mmol), and *tert*-butyldimethylsilyl chloride (1.83 g, 12.18 mmol). The reaction mixture was stirred for 12 h and then quenched with saturated $NaHCO_3$ (30 mL). The reaction mixture was diluted with CH_2Cl_2 (150 mL) and then washed with brine (50 mL). The organic layers was dried over $MgSO_4$ and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:50) afforded the ketone **5** (1.70 g, 94%) as a colorless oil: IR (neat) ν 2957, 2928, 2857, 1735, 1463, 1254 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (tt, J = 11.1, 4.5 Hz, 1H), 2.45−2.31 (m, 1H), 2.18−1.95 (m, 2H), 1.89−1.70 (m, 3H), 1.64−1.46 (m, 3H), 1.18 (td, J = 13.1, 11.1 Hz, 1H), 0.90 (s, 3H), 0.87−0.80 (m, 9H), 0.75 (d, J = 6.7 Hz, 3H), 0.01 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0 (C), 67.3 (CH), 49.6 (C), 45.3 (CH), 39.6 (CH_2), 35.9 (CH_2), 34.2 (CH_2), 29.0 (CH), 25.8 (CH_3), 22.9 (CH_2), 18.1 (C), 15.3 (CH_3), 13.5 (CH_3), −4.6 (CH_3), −4.7 (CH_3); HRMS (FAB) m/z calcd for $C_{17}H_{32}O_2Si$ 296.2172, found 296.2172.

Ethyl (3a*R,5*S**,7*R**,7a*S**)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-7,7a-dimethyl-1-oxooctahydro-1*H*-indene-2-carboxylate (16).** To a solution of diisopropylamine (0.20 mL, 1.41 mmol) in anhydrous THF (3 mL), was added *n*-BuLi (0.67 mL, 2.0 M solution in hexane, 1.35 mmol) at −78 °C, followed by addition of a solution of **5** (200 mg, 0.67 mmol) dissolved in anhydrous THF (3 mL). The reaction mixture was stirred for 1 h at −78 °C, and then ethyl cyanoformate (141 mg, 1.42 mmol) was added dropwise. After stirring for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ (20 mL) and then extracted with ether (3 × 50 mL). The combined organic layer was washed with brine (20 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:50) afforded the ketone ester **16** (229 mg, 93%) as a colorless oil: IR (neat) ν 2957, 2929, 2857, 1750, 1724, 1252 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.22−4.09 (m, 2H), 3.94−3.79 (m, 1H), 3.41 (dd, J = 9.9, 2.1 Hz, 0.3H), 3.14 (dd, J = 10.8, 8.8 Hz, 0.7H), 2.39−2.14 (m, 1H), 2.12−1.96 (m, 2H), 1.89−1.79 (m, 1H), 1.65−1.50 (m, 2H), 1.29−1.14 (m, 4H), 0.96 (s, 3H), 0.85 (s, 9H), 0.75 (d, J = 6.8 Hz, 3H), 0.04 (s, 1H), 0.02 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.7 (C), 169.9 (C), 67.0 (CH), 61.4 (CH_2), 54.1 (CH), 50.4 (C), 43.1 (CH), 39.6 (CH_2), 33.7 (CH_2), 28.0 (CH), 27.9 (CH_2), 25.8 (CH_3), 18.1 (C), 15.1 (CH_3), 14.1 (CH_3), 13.8 (CH_3), −4.6 (CH_3), −4.6 (CH_3); HRMS (ESI) (M + Na)$^+$ m/z calcd for $C_{20}H_{36}O_4SiNa$ 391.2281, found 391.2281.

Prop-2-yn-1-yl (3a*R,5*S**,7*R**,7a*S**)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-7,7a-dimethyl-1-oxooctahydro-1*H*-indene-2-carboxylate (17).** To a solution of the ketone ester **16** (487 mg, 1.32 mmol) in anhydrous benzene (12 mL) were added propargyl alcohol (1.57 mL, 26.42 mmol) and *p*-toluenesulfonic acid (25 mg, 0.13 mmol). The reaction mixture was stirred for 24 h at 105 °C, quenched with saturated $NaHCO_3$ (20 mL), and then extracted with Et_2O (3 × 50 mL). The combined organic layer was washed with brine (20 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:50) afforded the ketone ester **17** (474 mg, 95%) as a colorless oil: IR (neat) ν 3312, 2956, 2929, 2857, 2131, 1753, 1730, 1253 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.83−4.59 (m, 2H), 3.96−3.78 (m, 1H), 3.49 (dd, J = 10.0, 2.3 Hz, 0.3H), 3.21 (dd, J = 10.9, 8.9 Hz, 0.7H), 2.47−2.46 (m, 1H), 2.42−1.98 (m, 3H), 1.96−1.72 (m, 2H), 1.69−1.51 (m, 2H), 1.29−1.12 (m, 1H), 0.98 (s, 3H), 0.86 (s, 9H), 0.76 (m, 3H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7 (C), 174.6 (C), 145.4 (C), 106.9 (CH_2), 71.4 (CH_2), 66.4 (CH), 61.4 (C), 51.8 (C), 43.7 (CH), 39.5 (CH_2), 33.7 (CH_2), 33.6 (CH_2), 27.9 (CH), 25.8 (CH_3), 18.1 (C), 15.1 (CH_3), 14.5 (CH_3), −4.6 (CH_3), −4.7 (CH_3); HRMS (FAB) (M + H)$^+$ m/z calcd for $C_{21}H_{35}O_4Si$ 379.2305, found 379.2306.

(3*S,3a′*R**,5′*S**,7′*R**,7a′*S**)-5′-{[*tert*-Butyl(dimethyl)silyl]-oxy}-7′,7a′-dimethyl-4-methyleneoctahydrospiro[furan-3,2′-indene]-1′,2(3′*H*)-dione (18).** To a solution of $Mn(OAc)_3$ hydrate (666 mg, 2.49 mmol) in absolute ethanol (10 mL) was added dropwise a solution of **17** (376 mg, 0.99 mmol) in absolute ethanol (10 mL). The reaction mixture was stirred for 3 h and then diluted with ether (100 mL) and filtered through Celite. Concentration and silica gel flash column chromatography (EtOAc/hexane, 20:1) furnished **18** (278 mg, 74%) as a white solid. Recrystallization from ether afforded colorless needles: mp 110−111 °C; IR (neat) ν 2929, 2856, 2886, 1775, 1732, 1669, 1252 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.13−4.97 (m, 3H), 4.81−4.69 (m, 1H), 3.95 (tt, J = 11.2, 4.7 Hz, 1H), 2.65 (t, J = 13.6 Hz, 1H), 2.38−2.20 (m, 1H), 2.15−1.99 (m, 2H), 1.95−1.89 (m, 1H), 1.73−1.65 (m, 1H), 1.60 (ddd, J = 13.7, 11.3, 5.4 Hz, 1H), 1.22 (ABq, J = 12.2 Hz, 1H), 1.03 (s, 3H), 0.87 (s, 9H), 0.75 (d, J = 6.8 Hz, 3H), 0.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.0 (C), 169.2 (C), 75.2 (C), 66.9 (CH), 53.7 (CH), 52.9 (CH_2), 50.5 (C), 43.1 (CH), 39.6 (CH_2), 33.6 (CH_2), 28.1 (CH), 27.9 (CH_2), 25.8 (CH_3), 18.2 (C), 15.1 (CH_3), 13.8 (CH_3), −4.6 (CH_3), −4.6 (CH_3); HRMS (FAB) m/z calcd for $C_{21}H_{34}O_4Si$ 378.2226, found 378.2221.

(3*S,3a′*R**,5′*S**,7′*R**,7a′*S**)-5′-{[*tert*-Butyl(dimethyl)silyl]-oxy}-1′-hydroxy-7′,7a′-dimethyl-4-methylenedecahydrospiro-[furan-3,2′-inden]-2-one (19).** To a stirred solution of samarium (437 mg, 2.90 mmol) in anhydrous and degassed THF (6 mL) under argon was added 1,2-diiodomthane (0.18 mL, 2.20 mmol). The reaction mixture was stirred for 2 h. Degassed water (0.18 mL) was added. A solution of **18** (220 mg, 0.58 mmol) in anhydrous and degassed THF (3 mL) was added dropwise. After stirring for 1 h, the reaction mixture was extracted with ether (3 × 50 mL). The combined organic layer was washed with water (20 mL), saturated $NaHCO_3$ (10 mL), and brine (10 mL) and dried over $MgSO_4$. Concentration and silica gel flash column chromatography (EtOAc/hexane, 1:5) furnished alcohol **19** (132 mg, 60%) as a white solid: mp 124−125 °C; IR (neat) ν 3489, 2955, 2928, 2856, 1756, 1671, 1255 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.27 (t, J = 1.5 Hz, 1H), 5.20 (t, J = 1.9 Hz, 1H), 4.77 (dt, J = 12.6, 2.4 Hz, 1H), 4.68 (dt, J = 12.7, 1.8 Hz, 1H), 4.00 (d, J = 9.5 Hz, 1H), 3.87 (tt, J = 11.0, 4.6 Hz, 1H), 2.34 (dd, J = 14.2, 13.1 Hz, 1H), 2.21−2.12 (m, 1H), 1.92−1.83 (m, 1H), 1.83−1.76 (m, 3H), 1.66−1.59 (m, 1H), 1.53 (ddd, J = 13.6, 11.2, 5.3 Hz, 1H), 1.25 (q, J = 12.3 Hz, 1H), 0.90 (s, 3H), 0.85 (s, 9H), 0.82 (d, J = 6.7 Hz, 3H), 0.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9 (C), 146.0 (C), 109.2 (CH_2), 84.5 (CH), 71.3 (CH_2), 66.8 (CH), 57.1(C), 47.5 (C), 46.7 (CH), 40.3 (CH_2), 38.6 (CH_2), 33.9 (CH_2), 32.1 (CH), 25.9 (CH_3), 18.2 (C), 16.3 (CH_3), 14.5 (CH_3), −4.6 (CH_3), −4.7 (CH_3); HRMS (ESI) (M + Na)$^+$ m/z calcd for $C_{21}H_{36}O_4Si$ Na 403.2281, found 403.2274.

(1′*R,3*S**,3a′*R**,5′*S**,7′*R**,7a′*S**)-1′,5′-Dihydroxy-7′,7a′-dimethyl-4-methylenedecahydrospiro[furan-3,2′-inden]-2-one (20).** To a solution of alcohol **19** (132 mg, 0.35 mmol) in CH_3CN (4 mL) was added HF (0.5 mL, 50% aqueous solution). The reaction mixture was stirred for 0.5 h, quenched with saturated $NaHCO_3$ (2 mL), and extracted with ether (3 × 50 mL). The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$. Concentration and silica gel flash column chromatography (EtOAc/hexane, 1:1) furnished diol **20** (84 mg, 91%) as a white solid. Recrystallization from $CHCl_3$ afforded colorless crystals: mp 154−156 °C; IR (neat) ν 3412, 2958, 2925, 2856, 1754, 1672, 1275 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.27 (s, 1H), 5.19 (s, 1H), 4.76 (dt, J = 12.6, 2.3 Hz, 1H), 4.67 (dt, J = 12.8, 1.5 Hz, 1H), 3.98 (s, 1H), 3.92 (tt, J = 11.3, 4.5 Hz, 1H), 2.37−2.28 (m, 1H), 2.25−2.15 (m, 1H),

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2.03−1.95 (m, 2H), 1.95−1.84 (m, 2H), 1.82−1.68 (m, 2H), 1.48 (ddd, J = 13.2, 11.7, 5.1 Hz, 1H), 1.21 (ABq, J = 12.2 Hz, 1H), 0.89 (s, 3H), 0.83 (d, J = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.9 (C), 145.7 (C), 109.3 (CH_2), 84.2 (CH), 71.3 (CH_2), 66.0 (CH), 57.1 (C), 47.5 (C), 46.6 (CH), 40.0 (CH_2), 38.5 (CH_2), 33.1 (CH_2), 31.8 (CH), 16.3 (CH_3), 14.4 (CH_3); HRMS (FAB) $(M + H)^+$ m/z calcd for $C_{15}H_{23}O_4$ 267.1596, found 267.1599.

(3a*R,5*S**,7*R**,7a*S**)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-2-(1-hydroxy-1-methylethyl)-7,7a-dimethyloctahydro-1*H*-inden-1-one (22).** To a solution of diisopropylamine (0.12 mL, 0.83 mmol) in anhydrous THF (5 mL) was added *n*-BuLi (0.30 mL, 2.5 M solution in hexane, 0.76 mmol) at −78 °C. A solution of **5** (200 mg, 0.67 mmol) in anhydrous THF (2 mL) was then added. The reaction mixture was stirred for 1 h at −78 °C. Acetone (0.11 mL, 1.38 mmol) was then added dropwise. After stirring for 1 h, the reaction mixture was quenched with saturated NH_4Cl (10 mL) and then extracted with ether (3 × 50 mL). The combined organic layer was washed with brine (20 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:50) afforded the β-hydroxyl ketone **22** (188 mg, 78%) as a colorless oil: IR (neat) ν 3492, 2929, 2857, 1714, 1462, 1376, 1256 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.50 (s, 1H), 3.87 (tt, J = 11.0, 4.5 Hz, 1H), 2.58 (dd, J = 10.6, 3.0 Hz, 1H), 2.16−1.97 (m, 2H), 1.86−1.75 (m, 1H), 1.69−1.56 (m, 3H), 1.51 (ddd, J = 13.6, 11.1, 5.0 Hz, 1H), 1.22−1.13 (m, 4H), 1.04 (s, 3H), 0.91 (s, 4H), 0.86 (s, 9H), 0.75 (d, J = 6.7 Hz, 3H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 225.3 (C), 73.4 (C), 67.1 (CH), 53.8 (CH), 51.5 (C), 43.3 (CH), 39.3 (CH_2), 33.9 (CH_2), 30.6 (CH), 28.8 (CH_3), 26.8 (CH_2), 25.9 (CH_3), 25.3 (CH_3), 18.2 (C), 15.5 (CH_3), 12.9 (CH_3), −4.6 (CH_3), −4.6 (CH_3); HRMS (FAB) $(M - H)^+$ m/z calcd for $C_{20}H_{37}O_3Si$ 353.2512, found 353.2508.

(3a*R,5*S**,7*R**,7a*S**)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-7,7a-dimethyl-2-(1-methylethylidene)octahydro-1*H*-inden-1-one (23).** To a solution of β-hydroxyl ketone **22** (4.00 g, 11.29 mmol) and pyridine (4.10 mL, 50.81 mmol) in CH_2Cl_2 (220 mL), thionyl chloride (1.63 mL, 22.58 mmol) was added dropwise at 0 °C. The reaction mixture was stirred for 2 h and then neutralized with saturated $NaHCO_3$ (150 mL). The reaction mixture was extracted with Et_2O (3 × 300 mL). The combined organic layer was washed with brine (150 mL) and dried over $MgSO_4$. Concentration gave a crude product, which was used for the next reaction. To a solution of crude product in CH_2Cl_2 (110 mL) was added DBU (3.18 mL, 22.58 mmol) at room temperature. The reaction mixture was stirred for 12 h and then neutralized with saturated NH_4Cl (50 mL). The reaction mixture was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic layer was washed with brine (50 mL) and dried over $MgSO_4$. Concentration and silica gel flash column chromatography (EtOAc/hexane, 1:50) afforded the enone **22** (3.61 g, 99%) as a pale yellow oil: IR (neat) ν 2957, 2928, 2856, 1704, 1634, 1461, 1254 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (tt, J = 11.1, 4.5 Hz, 1H), 2.50−2.28 (m, 2H), 2.19 (s, 3H), 2.01−1.91 (m, 1H), 1.87−1.76 (m, 4H), 1.64−1.48 (m, 3H), 1.20 (ABq, J = 12.4 Hz, 1H), 0.95 (s, 3H), 0.87 (s, 9H), 0.77 (d, J = 6.7 Hz, 3H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.3 (C), 148.5 (C), 129.9 (C), 67.6 (CH), 51.0 (C), 41.6 (CH), 39.7 (CH_2), 34.2 (CH_2), 30.3 (CH), 30.2 (CH_2), 25.8 (CH_3), 24.4 (CH_3), 20.7 (CH_3), 18.2 (C), 15.7 (CH_3), 13.7 (CH_3), −4.6 (CH_3), −4.6 (CH_3); HRMS (FAB) m/z calcd for $C_{20}H_{36}O_2Si$ 336.2485, found 336.2479.

Methyl (2*R,3a*R**,5*S**,7*R**,7a*S**)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-2-isopropenyl-7,7a-dimethyl-1-oxooctahydro-1*H*-indene-2-carboxylate (24).** To a solution of enone **23** (1.00 g, 2.97 mmol) in anhydrous THF (5 mL) was added LHMDS (5.94 mL, 1.0 M solution in THF, 5.94 mmol) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C. HMPA (0.62 mL, 3.56 mmol) and methyl cyanoformate (1.23 mL, 14.85 mmol) were added dropwise. After stirring for 1 h, the reaction mixture was quenched with saturated $NaHCO_3$ (10 mL) and then extracted with ether (3 × 100 mL). The combined organic layer was washed with brine (50 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:50) afforded the compound **24** (360 mg, 31%) as a white solid. Recrystallization from ether afforded colorless needles: mp 97−99 °C; IR (neat) ν 2954, 2928, 2856, 1750, 1724, 1643, 1460, 1250 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (dd, J = 1.3, 0.7 Hz, 1H), 4.78 (s, 1H), 3.79 (tt, J = 11.0, 4.6 Hz, 1H), 3.65 (s, 3H), 2.48 (dd, J = 12.9, 6.8 Hz, 1H), 2.27−2.20 (m, 1H), 1.95 (t, J = 13.0 Hz, 1H), 1.83 (ddt, J = 6.7, 4.2, 1.9 Hz, 1H), 1.73 (d, J = 0.6 Hz, 3H), 1.68−1.47 (m, 3H), 1.18 (ABq, J = 12.5 Hz, 1H), 0.97 (s, 3H), 0.84 (s, 9H), 0.75 (d, J = 6.7 Hz, 3H), 0.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.0 (C), 170.5 (C) 143.5 (C), 112.5 (CH_2), 66.9 (CH), 66.1 (C), 52.9 (CH_3), 50.9 (C), 42.0 (CH), 39.6 (CH_2), 35.1 (CH_2), 33.5 (CH_2), 29.2 (CH), 25.8 (CH_3), 20.9 (CH_3), 18.1 (C), 15.2 (CH_3), 14.4 (CH_3), −4.6 (CH_3); HRMS (FAB) m/z calcd for $C_{22}H_{38}O_4Si$ 394.2539, found 394.2541.

(3*R,3a′*R**,5′*S**,7′*R**,7a′*S**)-5′-{[*tert*-Butyl(dimethyl)silyl]oxy}-7′,7a′-dimethyl-4-methyleneoctahydrospiro[furan-3,2′-indene]-1′,2(3′*H*)-dione (26).** To a solution of compound **24** (235 mg, 0.60 mmol) was added SeO_2 (265 mg, 2.38 mmol) in 1,4-dioxane (20 mL). The reaction mixture was stirred at 85 °C for 14 h and then concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:50) afforded the compound **26** (103 mg, 46%) as a colorless oil: IR (neat) ν 2927, 2856, 2856, 1776, 1733, 1670, 1462, 1254 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.18 (d, J = 1.6 Hz, 1H), 5.07 (dt, J = 12.6, 2.4 Hz, 1H), 5.03 (d, J = 1.5 Hz, 1H), 4.81 (dt, J = 12.5, 1.6 Hz, 1H), 3.88 (tt, J = 11.4, 4.4 Hz, 1H), 2.75−2.65 (m, 1H), 2.29 (dd, J = 13.4, 7.1 Hz, 1H), 2.08 (t, J = 13.3 Hz, 1H), 1.95−1.86 (m, 1H), 1.73−1.58 (m, 3H), 1.27 (ABq, J = 12.2 Hz, 1H), 1.04 (s, 3H), 0.88 (d, J = 2.9 Hz, 9H), 0.79 (d, J = 6.7 Hz, 3H), 0.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.1 (C), 174.5 (C), 144.3 (C), 107.7 (CH_2), 71.8 (CH_2), 66.8 (CH), 61.4 (C), 51.0 (C), 41.5 (CH), 39.6 (CH_2), 33.2 (CH_2), 33.0 (CH_2), 29.8 (CH), 25.8 (CH_3), 18.1 (C), 15.1 (CH_3), 14.2 (CH_3), −4.6 (CH_3); HRMS (FAB) $(M + H)^+$ m/z calcd for $C_{21}H_{35}O_4Si$ 379.2305, found 379.2302.

Ethyl (5*S,7*R**,7a*S**)-5-{[*tert*-Butyl(dimethyl)silyl]oxy}-1-hydroxy-7,7a-dimethyloctahydro-1*H*-indene-2-carboxylate (27).** To a solution of **16** (550 mg, 1.49 mmol) in MeOH (15 mL), $NaBH_4$ (113 mg, 2.99 mmol) was added portionwise at 0 °C. After stirring for 0.5 h, water (10 mL) and CH_2Cl_2 (30 mL) were added. The organic layer was separated, washed with saturated $NaHCO_3$ (10 mL) and brine (10 mL), and dried over $MgSO_4$. Concentration and silica gel flash column chromatography (hexane/EtOAc, 20:1) furnished hydroxyl ester **27** (482 mg, 87%) as a diastereomeric mixture (colorless oil). One diastereomer (R_f = 0.63) was isolated with silica gel flash column chromatography (EtOAc/hexane, 1:5): IR (neat) ν 3489, 2955, 2928, 2857, 1711, 1254 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, J = 7.1 Hz, 2H), 3.99−3.86 (m, 2H), 3.26 (d, J = 5.9 Hz, 1H), 2.96 (ddd, J = 10.1, 8.9, 7.3 Hz, 1H), 2.05−1.92 (m, 2H), 1.92−1.80 (m, 1H), 1.79−1.68 (m, 1H), 1.68−1.58 (m, 2H), 1.52−1.43 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.17 (td, J = 13.3, 8.7 Hz, 1H), 0.93 (s, 3H), 0.91 (d, J = 6.7 Hz, 3H), 0.85 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6 (C), 82.3 (CH), 67.1 (CH), 60.7 (CH_2), 45.5 (C), 45.2 (CH), 42.4 (CH), 40.3 (CH_2), 35.4 (CH_2), 31.8 (CH_2), 27.9 (CH), 25.9 (CH_3), 19.3 (CH_3), 18.2 (C), 17.7 (CH_3), 14.2 (CH_3), −4.6 (CH_3), −4.7 (CH_3); HRMS (ESI) $(M + Na)^+$ m/z calcd for $C_{20}H_{38}O_4SiNa$ 393.2437, found 393.2431. Another diastereomer (R_f = 0.45) was isolated with silica gel flash column chromatography (EtOAc/hexane, 1:5): IR (neat) ν 3489, 2956, 2928, 2857, 1717, 1254 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (q, J = 7.1 Hz, 2H), 3.88 (dd, J = 9.8, 3.9 Hz, 1H), 3.77 (tt, J = 11.1, 4.5 Hz, 1H), 2.89−2.77 (m, 1H), 2.32 (d, J = 3.9 Hz, 1H), 1.90−1.77 (m, 3H), 1.72−1.59 (m, 2H), 1.56−1.49 (m, 1H), 1.45−1.36 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.17 (ABq, J = 12.2 Hz, 1H), 1.01 (d, J = 6.6 Hz, 3H), 0.99 (s, 3H), 0.85 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0 (C), 85.5 (CH), 67.1 (CH), 60.7 (CH_2), 47.3 (CH), 44.1 (C), 43.6 (CH), 41.5 (CH_2), 34.0 (CH_2), 29.9 (CH), 27.5 (CH_2), 25.9 (CH_3), 18.3 (CH_3), 18.2 (C), 17.6 (CH_3), 14.3 (CH_3), −4.6 (CH_3); HRMS (ESI) $(M + Na)^+$ m/z calcd for $C_{20}H_{38}O_4SiNa$ 393.2437, found 393.2431.

Ethyl (3a*R,4*R**,6*S**,7a*R**)-6-{[*tert*-Butyl(dimethyl)silyl]oxy}-3a,4,7a-trimethyl-3a,4,5,6,7,7a-hexahydro-1*H*-indene-2-carboxylate (28).** To a stirred solution of the hydroxyl ester **27** (482 mg, 1.30 mmol) in anhydride pyridine (20 mL) at room temperature

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was added phosphorus oxychloride (798 mg, 5.21 mmol). The reaction mixture was stirred for 4 h at 70 °C and then quenched with saturated $NaHCO_3$ (25 mL). The reaction mixture was extracted with Et_2O (3 × 50 mL). The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:100) afforded the ester **28** (398 mg, 87%) as a colorless oil: IR (neat) ν 2956, 2927, 2856, 1715, 1626, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, J = 2.3 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.78 (tt, J = 10.8, 4.2 Hz, 1H), 2.55−2.39 (m, 2H), 2.19−2.08 (m, 1H), 1.89−1.78 (m, 1H), 1.55−1.44 (m, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.22−1.12 (m, 1H), 1.01 (s, 3H), 0.87 (s, 9H), 0.85 (d, J = 6.8 Hz, 3H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (C), 153.7 (CH), 133.8 (C), 68.6 (CH), 60.1 (CH_2), 48.7 (CH), 47.7 (C), 38.7 (CH_2), 35.5 (CH), 35.2 (CH_2), 34.3 (CH_2), 25.9 (CH_3), 18.2 (C), 17.1 (CH_3), 16.9 (CH_3), 14.2 (CH_3), −4.7 (CH_3); HRMS (ESI) $(M + Na)^+$ m/z calcd for $C_{20}H_{36}O_3SiNa$ 375.2331, found 375.2330.

((3a*S,4*R**,6*S**)-6-{[*tert*-Butyl(dimethyl)silyl]oxy}-3a,4-dimethyl-3a,4,5,6,7,7a-hexahydro-1*H*-inden-2-yl)methanol (29).** To a solution of the unsaturated ester **28** (330 mg, 0.94 mmol) in CH_2Cl_2 (10 mL) at −78 °C was added DIBAL (2.35 mL, 1 M in toluene) dropwise. The reaction mixture was stirred for 1 h and then quenched with acetone (3 mL). A saturated aqueous solution of Rochelle's salt (sodium potassium tartrate, 20 mL) was added. The reaction mixture was stirred for 30 min. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:10) afforded the allylic alcohol **29** (277 mg, 95%) as a colorless oil: IR (neat) ν 3360, 2956, 2926, 2856, 1645, 1255 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.66 (s, 1H), 4.09 (s, 2H), 3.76 (tt, J = 10.9, 4.3 Hz, 1H), 2.31−2.03 (m, 3H), 1.87−1.76 (m, 1H), 1.70 (s, 1H), 1.57−1.38 (m, 3H), 1.14 (td, J = 13.1, 10.8 Hz, 1H), 0.93 (s, 3H), 0.86 (s, 9H), 0.80 (d, J = 6.7 Hz, 3H), 0.03 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6 (C), 136.8 (CH), 69.1 (CH), 62.3 (CH_2), 48.4 (CH), 47.4 (C), 39.0 (CH_2), 36.4 (CH_2), 36.2 (CH), 34.7 (CH_2), 25.9 (CH_3), 18.3 (C), 17.7 (CH_3), 17.1 (CH_3), −4.6 (CH_3); HRMS (EI) m/z calcd for $C_{18}H_{34}O_2Si$ 310.2328, found 310.2325.

((1a*R,1b*S**,2*R**,4*S**,5a*S**,6a*R**)-4-{[*tert*-Butyl(dimethyl)silyl]oxy}-1b,2-dimethyloctahydro-6a*H*-indeno[1,2-*b*]oxiren-6a-yl)methanol (30).** To a solution of *m*-CPBA (70%, 370 mg, 2.14 mmol) in CH_2Cl_2 (3 mL) was added a solution of the allylic alcohol **29** (332 mg, 1.07 mmol) in CH_2Cl_2 (12 mL). The reaction mixture was stirred for 1 h at 0 °C and then quenched with saturated Na_2SO_3 (10 mL) and saturated $NaHCO_3$ (10 mL). The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:5) afforded the epoxide alcohol **30** (320 mg, 92%) as a colorless oil: IR (neat) ν 3438, 2927, 2856, 1459, 1254 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.88 (dd, J = 12.4, 3.1 Hz, 1H), 3.72 (dd, J = 12.4, 7.3 Hz, 1H), 3.63 (tt, J = 11.1, 4.3 Hz, 1H), 3.31 (s, 1H), 1.98−1.83 (m, 2H), 1.80−1.63 (m, 2H), 1.60−1.46 (m, 2H), 1.44−1.32 (m, 2H), 1.22−1.12 (m, 1H), 0.98 (s, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.85 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.1 (CH), 67.6 (CH), 65.8 (C), 61.8 (CH_2), 41.7 (C), 40.0 (CH), 39.7 (CH_2), 33.1 (CH_2), 32.2 (CH), 30.9 (CH_2), 25.9 (CH_3), 18.2 (C), 16.7 (CH_3), 13.8 (CH_3), −4.6 (CH_3); HRMS (ESI) $(M + Na)^+$ m/z calcd for $C_{18}H_{34}O_3SiNa$ 349.2175, found 349.2173.

(1a*R,1b*S**,2*R**,4*S**,5a*S**,6a*S**)-4-{[*tert*-Butyl(dimethyl)silyl]oxy}-1b,2-dimethyloctahydro-6a*H*-indeno[1,2-*b*]oxirene-6a-carbaldehyde (31).** To a solution of epoxide alcohol **30** (320 mg, 0.98 mmol) in anhydride CH_2Cl_2 (10 mL) was added Dess−Martin periodinane (6.50 mL, 1.96 mmol, 15 wt % in CH_2Cl_2). After stirring for 1 h, saturated $NaHCO_3$ (10 mL) and saturated $Na_2S_2O_3$ (10 mL) were added. After stirring for 0.5 h, the reaction mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with brine (25 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:30) afforded the epoxide alcohol **31** (292 mg, 92%) as a pale yellow oil: IR (neat) ν 2956, 2928, 2856, 1723, 1462, 1251 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 3.65 (tt, J = 11.1, 4.3 Hz, 1H), 3.60 (s, 1H), 2.05 (dd, J = 14.2, 11.5 Hz, 1H), 1.87 (dd, J = 14.2, 7.5 Hz, 1H), 1.76−1.67 (m, 2H), 1.54−1.47 (m, 1H), 1.45−1.28 (m, 2H), 1.23−1.11 (m, 1H), 1.04 (s, 3H), 0.89 (d, J = 6.8 Hz, 3H), 0.85 (s, 9H), 0.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6 (CH), 68.2 (CH), 67.7 (CH), 67.3 (C), 42.2 (C), 39.4 (CH_2), 39.2 (CH), 32.8 (CH_2), 31.7 (CH), 27.3 (CH_2), 25.8 (CH_3), 18.1 (C), 16.5 (CH_3), 14.1 (CH_3), −4.7 (CH_3); HRMS (FAB) $(M - H)^+$ m/z calcd for $C_{18}H_{31}O_3Si$ 323.2042, found 323.2048.

1-((1a*R,1b*S**,2*R**,4*S**,5a*S**,6a*R**)-4-{[*tert*-Butyl(dimethyl)silyl]oxy}-1b,2-dimethyloctahydro-6a*H*-indeno[1,2-*b*]oxiren-6a-yl)-2-methylenepropane-1,3-diol (33).** To a solution of *n*-BuLi (0.20 mL, 2.5 M solution in hexane, 0.48 mmol) in Et_2O (1.5 mL) at −78 °C was added iodo alcohol **32** (47 mg, 0.24 mmol) in Et_2O (1.5 mL) over a period of 0.5 h. A solution of aldehyde **31** (40 mg, 0.12 mmol) in Et_2O (1 mL) was added. The reaction mixture was stirred for 0.5 h and then quenched with saturated NH_4Cl (5 mL). The reaction mixture was extracted with EtOAc (3 × 15 mL). The combined organic layer was washed with brine (5 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:2) afforded the diol **33** (22 mg, 47%, 78% based on 40% **31** recovered) as a diastereomeric mixture (colorless oil). One diastereomer (R_f = 0.25) was isolated with silica gel flash column chromatography (EtOAc/hexane, 1:2): IR (neat) ν 3421, 2957, 2926, 2855, 1655, 1255 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.25 (d, J = 0.6 Hz, 1H), 5.14 (s, 1H), 4.48 (s, 1H), 4.24 (d, J = 13.4 Hz, 1H), 4.15 (d, J = 13.6 Hz, 1H), 3.61 (tt, J = 11.1, 4.4 Hz, 1H), 3.33 (s, 1H), 2.65 (s, 1H), 2.53 (s, 1H), 1.83 (dd, J = 12.2, 6.6 Hz, 1H), 1.76−1.60 (m, 3H), 1.54−1.46 (m, 1H), 1.44−1.28 (m, 2H), 1.21−1.12 (m, 1H), 0.98 (s, 3H), 0.90 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 0.6 Hz, 9H), 0.02 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5 (C), 114.7 (CH_2), 73.5 (CH), 68.1 (CH), 68.0 (CH), 67.3 (C), 63.9 (CH_2), 41.8 (C), 39.9 (CH), 39.6 (CH_2), 33.1 (CH_2), 32.1 (CH), 29.8 (CH_2), 25.9 (CH_3), 18.2 (C), 16.5 (CH_3), 13.7 (CH_3), −4.6 (CH_3); HRMS (ESI) $(M + Na)^+$ m/z calcd for $C_{21}H_{38}O_4SiNa$ 405.2437, found 405.2427. Another diastereomer (R_f = 0.19) was isolated with silica gel flash column chromatography (EtOAc/hexane, 1:2): IR (neat) ν 3440, 2957, 2856, 1653, 1256 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.20 (dd, J = 2.4, 1.2 Hz, 1H), 5.18 (d, J = 0.6 Hz, 1H), 4.40 (s, 1H), 4.33 (d, J = 13.3 Hz, 1H), 4.20 (d, J = 13.4 Hz, 1H), 3.62 (tt, J = 11.2, 4.4 Hz, 1H), 3.42 (s, 1H), 1.81−1.70 (m, 3H), 1.69−1.62 (m, 2H), 1.59−1.46 (m, 2H), 1.44−1.34 (m, 2H), 1.11−1.23 (m, 1H), 0.99 (s, 3H), 0.91 (d, J = 6.8 Hz, 3H), 0.85 (s, 9H), 0.02 (d, J = 1.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1 (C), 114.8 (CH_2), 73.0 (CH), 68.1 (CH), 67.3 (C), 67.2 (CH), 64.3 (CH_2), 41.8 (C), 40.2 (CH), 39.7 (CH_2), 33.1 (CH_2), 32.1 (CH), 30.8 (CH_2), 25.9 (CH_3), 18.2 (C), 16.7 (CH_3), 13.8 (CH_3), −4.6 (CH_3); HRMS (ESI) $(M + Na)^+$ m/z calcd for $C_{21}H_{38}O_4SiNa$ 405.2437, found 405.2431.

(±)-Peribysin E (1). To a solution of **33** (8.5 mg, 0.022 mmol) in anhydrous CH_2Cl_2 (2 mL) at 0 °C were added 2,6-lutidine (0.036 mL, 0.314 mmol) and TMSOTf (0.028 mL, 0.157 mmol). After stirring for 0.5 h, saturated $NaHCO_3$ (5 mL) was added. The reaction mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was washed with brine (10 mL) and dried over $MgSO_4$. Concentration gave the crude product **34**. To a solution of the crude product **34** in MeOH (3 mL) was added 35% HCl (0.02 mL). The reaction mixture was stirred for 0.5 h and then quenched with saturated $NaHCO_3$ (5 mL). The reaction mixture was extracted with EtOAc (3 × 10 mL). The combined organic layer was washed with brine (5 mL), dried over $MgSO_4$, and concentrated. Silica gel flash column chromatography (EtOAc/hexane, 1:2) afforded (±)-peribysin E (**1**) (3.8 mg, 61%) as a colorless oil: IR (neat) ν 3404, 2923, 2926, 2864, 1655, 1263 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.06 (s, 1H), 4.96 (t, J = 2.0 Hz, 1H), 4.92 (t, J = 2.5 Hz, 1H), 4.46 (dt, J = 13.0, 2.3 Hz, 1H), 4.38 (dt, J = 13.1, 2.2 Hz, 1H), 3.94−3.85 (m, 1H), 3.54 (d, J = 2.1 Hz, 1H), 3.36 (s, 3H), 2.13 (d, J = 2.7 Hz, 1H), 2.01−1.95 (m, 1H), 1.92 (ddt, J = 13.2, 4.5, 2.2 Hz, 1H), 1.87 (dd, J = 13.1, 6.0 Hz, 1H), 1.77−1.71 (m, 1H), 1.71−1.66 (m, 1H), 1.60−1.53 (m, 1H), 1.49 (ddd, J = 13.1, 11.5, 5.7 Hz, 1H), 1.34 (s, 1H), 1.30−1.19 (m, 1H), 0.91 (s, 3H), 0.84 (d, J =

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6.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.7 (C), 105.6 (CH), 103.1 (CH_2), 88.6 (CH), 69.0 (CH_2), 67.1 (CH), 60.8 (C), 55.1 (CH_3), 45.9 (CH), 40.0 (CH_2), 35.5 (CH), 34.3 (CH_2), 32.9 (CH_2), 16.1 (CH_3), 14.4 (CH_3); HRMS (ESI) $(M + Na)^+$ m/z calcd for $C_{16}H_{26}O_4Na$ 305.1729, found 305.1727.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for compounds **2**−**5**, **8**−**20**, **22**−**24**, **26**−**31**, **33**, and (±)-peribysin E (**1**) and crystallographic information (CIF files) for compounds **15**, **18**, **20**, and **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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