A Novel Synthesis of (±)-Prostaglandin B_1 Methyl Ester

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Five simple preparative methods of (±)-prostaglandin B_1 (PGB_1) methyl ester are described. All routes were started from a common intermediate, 7-(2-hydroxy-5-oxo-1-cyclopentenyl)heptanoic acid derived from cyclooctanone via two steps. The key reaction of these routes is a palladium-catalyzed vinylation. The methods provided other PGB_1 congeners and are applicable to synthesize 11-functionalized PG systems.

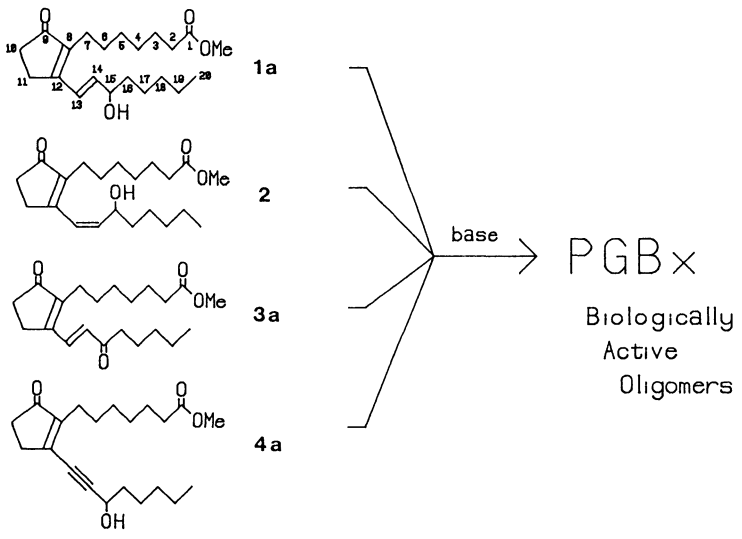
PGB_x[1] is an oligomeric mixture of prostaglandin B series, and has unique biological activities which are quite different from the ordinary prostaglandin activities. For example, it conserves oxidative phosphorylation in rat liver mitochondria in vitro and reverses the damaging effect of experimentally induced ischemia in heart and brain of monkey and dog in vivo.[1] 15-DehydroPGB_1 methyl ester (**3a**) is usually used as a monomer for the synthesis of PGB_x. Instead of **3a**, PGB_1 methyl ester (**1a**), 13, 14-cisPGB_1 methyl ester (**2**), and 13,14-dehydroPGB_1 methyl ester (**4a**) can also be used (Scheme 1). To elucidate structures and biological activities of the oligomers, it is necessary to prepare various PGB_x from some closely related monomers. Although the total syntheses of PGB_1 or its equivalents have already been known,[2-4] multi-step reactions and severe conditions are required in most of the cases. For the study of new biologically active features of PGB_x, it is important to develop a novel synthetic method by which enough amount of PGB_1 and the starting materials for PGB_x can be obtained in a few steps and in simple procedures.

As the preliminary investigation of a new short synthetic sequence to prepare (±)-PGB_1 methyl ester and its related compounds, we have already reported synthesis of 15-dehydroPGB_1 methyl ester (**3a**) via four steps.[5] We have also reported the synthetic methods to obtain the key intermediate **7** from commercially available cyclooctanone via two steps and to derive other synthons for prostaglandins from **7** (Scheme 2).[6]

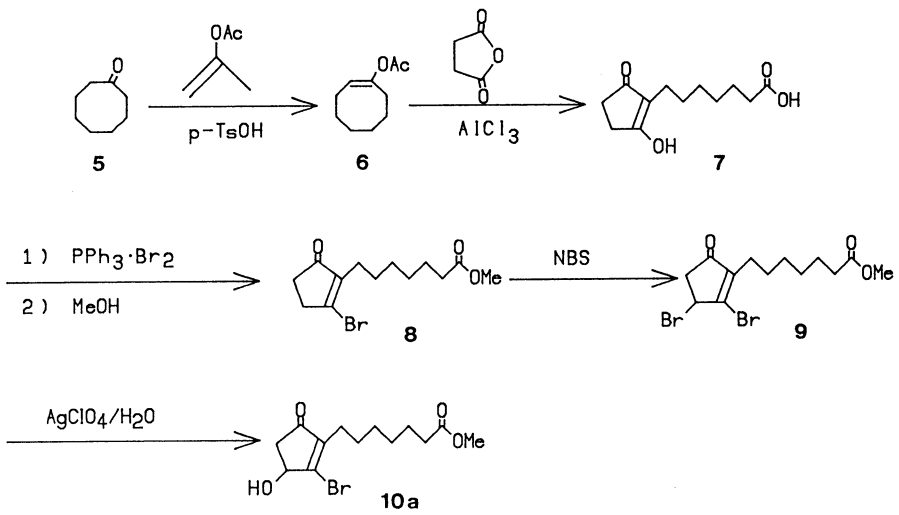
In this report, we describe the facile synthetic method to form a sort of PGB_1 methyl esters from the key intermediate **8** and its application to a 11-functionalized PG analogue in detail (Schemes 3 and 4).

The ω-chain moieties of PGB_1 methyl esters were successfully introduced to the synthetic intermediates **8** by applying the palladium-catalyzed vinylation reaction.[7] Coupling reaction of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**8**) with (±)-3-(*t*-butyldimethylsiloxy)-1-octene (**12b**) gave (±)-methyl 15-(*t*-butyldimethylsiloxy)-9-oxoprost-8(12),13-dienoate {(±)-15-(*t*-butyldimethylsiloxy)PGB_1 methyl ester} (**1b**) in a 92% yield. The reaction was catalyzed by a few molar percent of the mixture of palladium diacetate and triphenylphosphine (1: 2 mole ratio). Triethylamine was also added for trapping hydrogen bromide. Desilylation of **1b** with tetrabutylammonium fluoride gave (±)-PGB_1 methyl ester (**1a**) in a 96% yield.

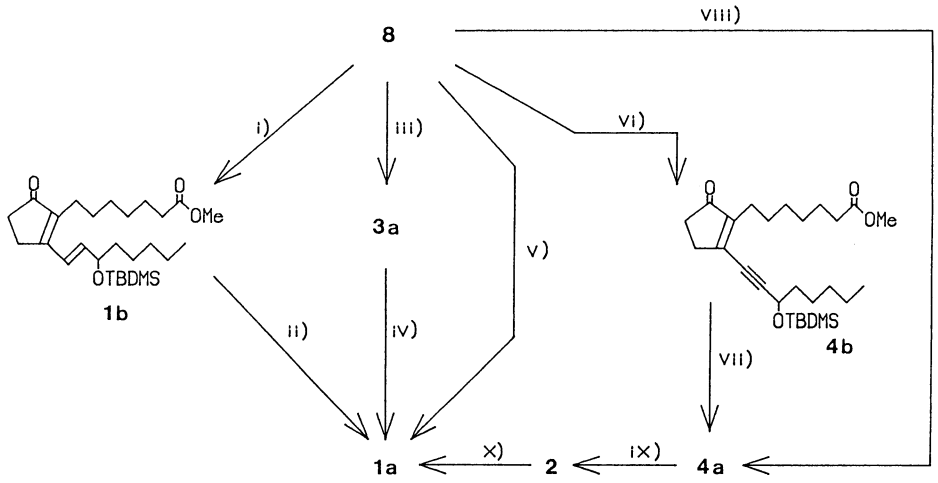
Coupling reaction of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**8**) with 1-octen-3-one (**12c**) gave 15-dehydroPGB_1 methyl ester (**3a**) in an 80% yield



Scheme 1.



Scheme 2.



Scheme. 3. i)[a] (±)-3-(*t*-Butyldimethylsiloxy)-1-octene (**12b**). ii) Bu_4NF/THF. iii)[a] 1-Octen-3-one (**12c**). iv) $NaBH_4/CH_3OH$. v)[a] (±)-1-Octen-3-ol (**12a**). vi)[a] (±)-3-(*t*-Butyldimethylsiloxy)-1-octyne (**13b**). vii) Bu_4NF/THF. viii)[a] (±)-1-Octyn-3-ol (**13a**). ix) H_2, Lindlar catalyst/CH_3CH_2OH. x) I_2/C_6H_{12}, $CHCl_3$. a) $Pd(OAc)_2 \cdot 2PPh_3$ and Et_3N were used.

and 15-dehydro-13,14-dihydroPGB$_1$ methyl ester (**3b**) as a by-product in a 3% yield. Compound **3a** was easily converted to **1a** by the reduction with sodium borohydride in a 78% yield.

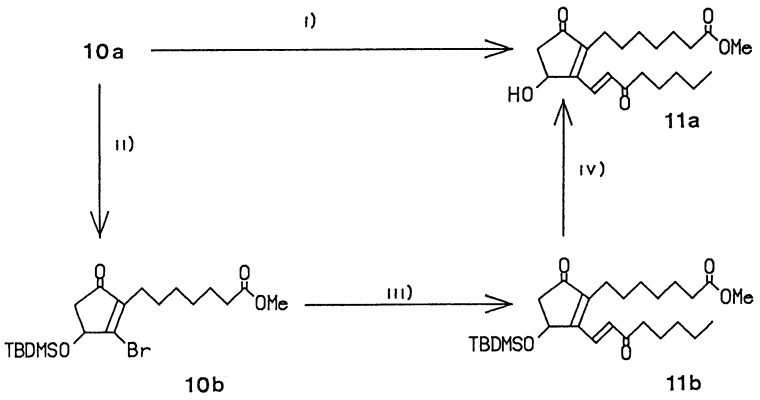
(±)-PGB$_1$ methyl ester (**1a**) could be obtained by the coupling reaction of **8** and (±)-1-octen-3-ol (**12a**) directly in a 42% yield. Under the reaction conditions, the double-bond isomer [15-dehydro-13,14-dihydro-PGB$_1$ methyl ester (**3b**)] and the oxidized compound [15-dehydroPGB$_1$ methyl ester (**3a**)] were obtained in 24 and 11% yields, respectively.

(±)-Methyl 15-(*t*-butyldimethylsiloxy)-9-oxoprost-8(12)-en-13-ynoate {(±)-15-(*t*-butyldimethylsiloxy)-13,14-dehydroPGB$_1$ methyl ester} (**4b**) was obtained from methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate (**8**) and (±)-3-(*t*-butyldimethylsiloxy)-1-octyne (**13b**) in a 50% yield (69% based on the consumed **8**). Desilylation of **4b** with tetrabutylammonium fluoride gave (±)-13,14-dehydroPGB$_1$ methyl ester (**4a**) in a 97% yield.

(±)-13,14-DehydroPGB$_1$ methyl ester (**4a**) was also obtained directly from **8** and (±)-1-octyn-3-ol (**13a**) in a 33% yield. In this case, 15-dehydroPGB$_1$ methyl ester (**3a**) was obtained in a 10% yield. The α,β-enone **3a** is an isomer of the β,γ-ynol **4a**.

Hydrogenolysis of (±)-13,14-dehydroPGB$_1$ methyl ester (**4a**) over Lindlar catalyst gave (±)-13,14-cisPGB$_1$ methyl ester (**2**) in an 89% yield. Any other isomeric compounds, such as (±)-8,12-dihydro-, (±)-13,14-dihydro-, and (±)-13,14-transPGB$_1$ methyl ester, were not detected in this reaction.

Double-bond isomerization of **2** was achieved with iodine in a 98% yield. That is, (±)-13,14-cisPGB$_1$ methyl ester (**2**) was converted to (±)-PGB$_1$ methyl



Scheme. 4. i)[a] 1-Octen-3-one (**12c**). ii) TBDMSCl, Et_3N, DMAP/CH_2Cl_2. iii)[a] 1-Octen-3-one (**12c**). iv) Bu_4NF/THF. a) $Pd(OAc)_2 \cdot 2PPh_3$ and Et_3N were used.

ester (**1a**) by treating with iodine in dark at 40 °C for 13 h. In this case, equilibrium was completely inclined to the trans isomer.

The synthetic strategy described above was also extended to the 11-functionalized PG systems (Scheme 4).

Reaction of (±)-methyl 7-(2-bromo-3-hydroxy-5-oxo-1-cyclopentenyl)heptanoate (**10a**) with 1-octen-3-one (**12c**) gave directly (±)-15-dehydro-11-hydroxyPGB_1 methyl ester (**11a**) in a 15% yield. Reaction of (±)-methyl 7-[2-bromo-3-(*t*-butyldimethylsiloxy)-5-oxo-1-cyclopentenyl]heptanoate (**10b**), which was derived from **10a**, and 1-octen-3-one (**12c**) gave (±)-11-(*t*-butyldimethylsiloxy)-15-dehydroPGB_1 methyl ester (**11b**) in a 76% yield. Desilylation of **11b** with tetrabutylammonium fluoride gave (±)-15-dehydro-11-hydroxy-PGB_1 methyl ester (**11a**) in a 49% yield.

Experimental

Instrumentation. The ^1H NMR spectra were measured with a Varian EM-390 (90 MHz) spectrometer. The chemical shifts are expressed in parts per million (ppm) (δ) downfield from tetramethylsilane. The infrared spectra were obtained using a JASCO IR-810 Spectrometer. The low-resolution mass spectra (MS) and the high-resolution mass spectra (HRMS) were determined on a JEOL D-300 Mass Spectrometer. The boiling points are uncorrected.

Materials and Substances. 1-Octen-3-one (**12c**)[8] was obtained from (±)-1-octen-3-ol (**12a**) by the Jones' oxidation. (±)-3-(*t*-Butyldimethylsiloxy)-1-octene (**12b**)[9] and (±)-3-(*t*-butyldimethylsiloxy)-1-octyne (**13b**)[10] were obtained from (±)-1-octen-3-ol (**12a**) and (±)-1-octyn-3-ol (**13a**), respectively with *t*-butylchlorodimethylsilane. Solvents were dried over Zeolite A-3 or A-4 when necessary.

(±)-15-(*t*-Butyldimethylsiloxy)PGB_1 Methyl Ester (1b). A mixture of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate [**8**; 119.5 mg (0.39 mmol)], (±)-3-(*t*-butyldimethylsiloxy)-1-octene [**12b**; 158.3 mg (0.65 mmol)], and triethylamine [72.0 mg (0.71 mmol)] with 8.5 mg of the palladium catalyst (a mixture of palladium diacetate and triphenylphosphine; 1 : 2 mole ratio) was heated to 100 °C in a reaction tube under Ar for 24 h. The reaction mixture was dissolved in 3 ml of ether and insoluble components were filtered off. After evaporation, the reaction mixture was separated by a medium-pressure silica-gel column chromatography (LiChroprep Si 60), and 167. 2 mg (92.0%) of **1b** was obtained. Starting material **8** (3.9 mg: 1.3%) was also recovered.

1b: ^1H NMR ($CDCl_3$) δ=6.69 (d, J=15 Hz, 1H), 6.13 (dd, J=15, 5.4 Hz, 1H), 4.25 (m, 1H), 3.55 (s, 3H), 2.1—2.7 (m, 8H), 1.15—1.75 (m, 16H), 0.90 (s, 9H), 0.75—1.0 (m, 3H), 0.06 (s, 3H) and 0.03 (s, 3H); IR (film) 2930, 2860, 1740, 1695, and 1640 cm^{-1}; Found: m/z 464.3340. Calcd for $C_{27}H_{48}O_4Si$: M, 464.3323.

15-DehydroPGB$_1$ Methyl Ester (3a).[2] A mixture of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate [**8**; 146.3 mg (0.48 mmol)], 1-octen-3-one [**12c**; 142.7 mg (1.15 mmol)], and triethylamine [156.4 mg (1.55 mmol)] with 5.6 mg of the palladium catalyst was heated to 100 °C in a reaction tube under Ar for 24 h. The reaction mixture was dissolved in 3 ml of ether and insoluble components were filtered off. After evaporation, separation with medium-pressure silica-gel column chromatography (LiChroprep Si 60) gave 133.0 mg (79.6%) of **3a** and 4.9 mg (2.6%) of 15-dehydro-13,14-dihydroPGB_1 methyl ester (**3b**).[3] Starting material **8** (9.8 mg: 6.7%) was also recovered.

3a: ^1H NMR ($CDCl_3$) δ=7.51 (d, J=16.5 Hz, 1H), 6.45 (d, J=16.5 Hz, 1H), 3.60 (s, 3H), 2.15—2.75 (m, 10H), 1.2—1.9 (m, 14H), and 0.90 (t, J=6 Hz, 3H); IR (film) 2930, 2850, 1735, 1705, and 1630 cm^{-1}.

3b: ^1H NMR ($CDCl_3$) δ=3.67 (s, 3H), 2.05—2.75 (m, 14H), 1.1—1.8 (m, 14H), and 0.89 (t, J=6.6 Hz, 3H); IR (film) 2930, 2860, 1740, 1720, 1700, and 1640 cm^{-1}.

(±)-15-(*t*-Butyldimethylsiloxy)-13,14-dehydroPGB$_1$ Methyl Ester (4b). A mixture of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate [**8**; 304.7 mg (1.01 mmol)], (±)-3-(*t*-butyldimethylsiloxy)-1-octyne [**13b**; 264.2 mg (1.10 mmol)], and triethylamine [106.7 mg, (1.06 mmol)] with 37.5 mg of the palladium catalyst was heated to 100 °C in a reaction tube under Ar for 23 h. Ether (3 ml) was added and filtrated. By medium-pressure silica-gel column chromatography (LiChroprep Si 60), 230.1 mg (49.5%) of **4b** was afforded. Compound **8** (88.0 mg: 28.9%) was recovered.

4b: Bp 122 °C/0.15 mmHg (1 mmHg=133.322 Pa); ^1H NMR ($CDCl_3$) δ=4.5 (t, J=6 Hz, 1H), 3.6 (s, 3H), 2.2—2.6 (m, 8H), 1.2—1.9 (m, 16H), 0.93 (s, 9H), 0.8—0.95 (m, 3H), and

0.16 (s, 6H); IR (film) 2950, 2930, 2860, 1740, 1705, and 1615 cm^{-1}; Found: C, 69.97; H, 10.04%. Calcd for $C_{27}H_{46}O_4Si$: C, 70.08; H, 10.02%.

(±)-13,14-DehydroPGB$_1$ Methyl Ester (4a).[2,4] a) To a solution of 0.37 g (0.80 mmol) of **4b** in 20 ml of THF was added 2 ml of 1 M (1 M=1 mol dm^{-3}) tetrabutylammonium fluoride in THF. The reaction mixture was stirred at room temperature for 2 h. To the resultant mixture was added 20 ml of ether. The ethereal layer was washed with equal volumes of water twice and brine, dried over anhydrous magnesium sulfate. After medium-pressure silica-gel column chromatography (LiChroprep Si 60), 0.27 g (97%) of (±)-13,14-dehydroPGB$_1$ methyl ester (**4a**) was obtained.

b) A mixture of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)-heptanoate [**8**; 62.0 mg (0.20 mmol)], (±)-1-octyn-3-ol [**13a**; 39.9 mg (0.32 mmol)], and triethylamine [26.0 mg (0.26 mmol)] with 2.0 mg of palladium diacetate and 4.6 mg of triphenylphosphine was heated to 100 °C in a reaction tube under Ar for 5 h. Ether (3 ml) was added and filtrated. Separation with medium-pressure silica-gel column chromatography (LiChroprep Si 60) gave 23.5 mg (33.0%) of **4a** and 7.0 mg (10%) of 15-dehydroPGB$_1$ methyl ester (**3a**). Starting material **8** (1.9 mg: 3%) was also recovered.

4a: ^{1}H NMR ($CDCl_3$) δ=4.6 (t, J=6 Hz, 1H), 3.6 (s, 3H), 2.2—2.8 (m, 8H), 1.2—1.9 (m, 16H), and 0.9 (t, J=6 Hz, 3H); IR (film) 3400, 1735, 1700, 1600, 1435, and 1360 cm^{-1}.

(±)-13,14-cisPGB$_1$ Methyl Ester (2).[2,4] Hydrogenolysis of 0.50 g (1.4 mmol) of (±)-13,14-dehydroPGB$_1$ methyl ester (**4a**) was achieved over Lindlar catalyst[11] in ethanol under atmospheric pressure. The reaction mixture was filtered and after removal of ethanol, ether (30 ml) was added. The resultant solution was washed with 20 ml of 0.1 M HCl three times, 20 ml of water three times and brine, and dried. Removal of solvents gave 0.45 g (89%) of (±)-13,14-cisPGB$_1$ methyl ester (**2**).

2: ^{1}H NMR ($CDCl_3$) δ=6.38 (d, J=12 Hz, 1H), 5.75 (dd, J=12, 9 Hz, 1H), 4.6 (m, 1H), 3.6 (s, 3H), 2.6—2.85 (m, 2H), 2.1—2.5 (m, 6H), 1.2—1.8 (m, 16H), and 0.9 (t, J=6 Hz, 3H); IR (film) 3400, 1730, 1690, 1620, 1585, 1330, and 1260 cm^{-1}.

(±)-PGB$_1$ Methyl Ester (1a).[2-4] a) To a solution of 142.0 mg of **1b** in 20 ml of THF and 2 ml of water was added 1 ml of 1 M tetrabutylammonium fluoride/THF solution. The reaction mixture was stirred at room temperature for 7 days and poured into 30 ml of water. The reaction mixture was extracted with 100 ml and then 50 ml of ether. Combined organic layer was washed with 50 ml of water twice and dried. After evaporation, the mixture was separated with medium-pressure silica-gel column chromatography, and 102.7 mg (95.9%) of (±)-PGB$_1$ methyl ester (**1a**) was obtained.

b) A solution of 20 mg of sodium borohydride in dry methanol (2 ml) was added dropwise at 0 °C to a solution of 98.1 mg (0.28 mmol) of 15-dehydroPGB$_1$ methyl ester (**3a**) in methanol (3 ml). After stirring for 15 min at 0 °C, 0.5 ml of acetone was added. The reaction mixture was poured into 5 ml of water and extracted with 5 ml of ether three times. Combined ethereal layer was washed with equal volumes of water three times and brine, and dried. After evaporation, separation with medium-pressure silica-gel column chromatography (LiChroprep Si 60) gave 76.2 mg (78%) of (±)-PGB$_1$ methyl ester (**1a**).

c) A mixture of methyl 7-(2-bromo-5-oxo-1-cyclopentenyl)heptanoate [**8**; 83.3 mg (0.28 mmol)], (±)-1-octen-3-ol [**12a**; 47.3 mg (0.37 mmol)], and triethylamine [42.1 mg (0.42 mmol)] with 1.4 mg of palladium diacetate and 3.6 mg of triphenylphosphine was heated to 100°C in a reaction tube under Ar for 22 h. Ether (3 ml) was added and filtrated. The reaction mixture was separated with medium-pressure silica-gel column chromatography (LiChroprep Si 60), and 40.1 mg (41.7%) of **1a**, 10.3 mg (10.8%) of 15-dehydroPGB$_1$ methyl ester (**3a**), and 22.6 mg (23.5%) of 15-dehydro-13,14-dihydroPGB$_1$ methyl ester (**3b**) were obtained. Starting material **8** (12.0 mg: 14.4%) was also recovered.

d) To a solution of 0.42 g (1.2 mmol) of (±)-13,14-cisPGB$_1$ methyl ester (**2**) in 2 ml of a solvent (cyclohexane : chloroform=20 : 1) was added 2 ml of iodine solution (0.5% w/v in the solvent described above) and allowed to stand in dark at 40 °C for 13 h. The reaction mixture was diluted with 20 ml of ether and washed with 10 ml of sodium thiosulfate three times and brine, and dried. Removal of solvents gave 0.41 g (98%) of (±)-PGB$_1$ methyl ester (**1a**).

1a: ^{1}H NMR ($CDCl_3$) δ=6.73 (d, J=16 Hz, 1H), 6.20 (dd, J=16.6 Hz, 1H), 4.3 (m, 1H), 3.6 (s, 3H), 2.5—2.7 (m, 2H), 2.2—2.5 (m, 6H), 1.2—1.7 (m, 16H), and 0.9 (t, J=6 Hz, 3H); IR (film) 3450, 1735, 1690, 1635, 1590, and 1370 cm^{-1}.

(±)-11-(*t*-Butyldimethylsiloxy)-15-dehydroPGB$_1$ Methyl Ester (11b). (±)-Methyl 7-(2-bromo-3-hydroxy-5-oxo-1-cyclopentenyl)heptanoate [**10a**: 0.50 g (1.6 mmol)] was silylated in dichloromethane by *t*-butylchlorodimethylsilane [0.69 g (4.6 mmol)] with triethylamine [0.51 g (5.1 mmol)] and 4-(dimethylamino)pyridine [40 mg (0.33 mmol)] to give (±)-methyl 7-[2-bromo-3-(*t*-butyldimethylsiloxy)-5-oxo-1-cyclopentenyl]heptanoate [**10b**; 0.62 g (91%)]; ^{1}H NMR ($CDCl_3$) δ=4.63 (dd, J=6, 3 Hz, 1H), 3.49 (s, 3H), 2.70 (dd, J=16.5, 6 Hz, 1H), 2.0—2.4 (m, 5H), 1.2—1.8 (m, 8H), 0.8 (s, 9H), 0.1 (s, 3H), and 0.06 (s, 3H); IR (film) 2950, 2940, 2860, 1740, 1720, and 1635 cm^{-1}; Found: m/z 377.0604, 375.0674. Calcd for $C_{15}H_{24}O_4BrSi$: M−C_4H_9, 377.0606, 375.0720. A mixture of (±)-methyl 7-[2-bromo-3-(*t*-butyldimethylsiloxy)-5-oxo-1-cyclopentenyl]heptanoate [**10b**; 439.6 mg (1.01 mmol)], 1-octen-3-one [**12c**; 143.6 mg (1.14 mmol)], and triethylamine [124.2 mg (1.23 mmol)] with 15.8 mg of the palladium catalyst was heated to 100 °C in a reaction tube under Ar for 80 h. Ether (3 ml) was added and filtrated. Separation by medium-pressure silica-gel column chromatography (LiChroprep Si 60) gave 370.0 mg (76.2%) of **11b**; ^{1}H NMR ($CDCl_3$) δ=7.45 (d, J=16.5 Hz, 1H), 6.78 (d, J=16.5 Hz, 1H), 5.11 (dd, J=3, 6 Hz, 1H), 3.71 (s, 3H), 2.0—2.9 (m, 8H), 1.2—1.9 (m, 14H), 1.0 (s, 9H), 0.9—1.1 (m), 0.33 (s, 3H), and 0.27 (s, 3H); IR (film) 2940, 2860, 1740, 1705, 1675, and 1590 cm^{-1}; MS m/z 478 (M^+), 447 (M−MeO), 421 (M−Bu+H), 389 (M−Bu−MeO); Found m/z 478.3132. Calcd for $C_{27}H_{46}O_5Si$: M, 478.3114.

(±)-15-Dehydro-11-hydroxyPGB$_1$ Methyl Ester (11a).[3] a) A mixture of (±)-methyl 7-(2-bromo-3-hydroxy-5-oxo-1-cyclopentenyl)heptanoate [**10a**; 75.8 mg (0.32 mmol)], (±)-1-octen-3-ol [**12a**; 42.4 mg (0.34 mmol)], and triethylamine [43.4 mg (0.43 mmol)] with 2.4 mg of the palladium catalyst was heated to 100 °C in a reaction tube under Ar for 48 h. Ether (3 ml) was added and filtrated. After purification with medium-pressure silica-gel column chromatography (LiChroprep Si 60), 13.2 mg (15.3%) of **11a** was obtained; ^{1}H NMR ($CDCl_3$) δ=7.39 (d, J=15 Hz, 1H), 6.89 (d, J=15 Hz, 1H), 5.05 (m, 1H), 3.60 (s, 3H), 2.15—3.0 (m, 8H), 1.1—1.9 (m, 14H), and 0.9 (t, J=6 Hz, 3H); IR (film) 3450, 2930, 2860, 1740, 1705, and 1590 cm^{-1}; MS m/z 364 (M^+), 346 (M−H_2O), 314 (M−H_2O−MeOH); Found: m/z 364.2239. Calcd for

$C_{21}H_{32}O_5$: M, 364.2247.

b) To a solution of 20.4 mg of (±)-11-(*t*-butyldimethylsiloxy)-15-dehydroPGB$_1$ methyl ester (**11b**) in 3 ml of THF was added 0.06 ml of 1 M tetrabutylammonium fluoride/THF solution, and the mixture was stirred at room temperature for 10 min. To the resultant mixture was added 10 ml of ether and water. The organic layer was washed with equal volumes of water and brine, and dried. After removal of solvents, silica-gel column chromatography gave 7.6 mg (50%) of (±)-15-dehydro-11-hydroxyPGB$_1$ methyl ester (**11a**).

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8) Beilstein IV, Band I, 3468.

9) Bp 76 °C/4 mmHg; ^{1}H NMR ($CDCl_3$) δ=5.73 (ddd, J=18, 12, 6 Hz, 1H), 4.8—5.2 (m, 2H), 4.0 (brq, J=4.5 Hz, 1H),1.2—1.7 (m, 8H), 0.9 (s, 9H), 0.85—1.15 (m, 3H), 0.07 (s, 3H), and 0.03 (s, 3H); IR (film) 2960, 2940, 2830, 1470, and 1460 cm^{-1}; Found: m/z 242.2091. Calcd for $C_{14}H_{30}OSi$: M, 242.2066.

10) Bp 77 °C/2.7 mmHg; ^{1}H NMR ($CDCl_3$) δ=4.40 (t of d, J=6, 3 Hz, 1H), 2.43 (d, J=3 Hz, 1H), 1.2—2.0 (m, 8H), 1.02 (s, 9H), 0.85—1.15 (m, 3H), 0.25 (s, 3H), and 0.20 (s, 3H): IR (film) 3320, 2960, 2940, 2860, 1750, 1475, and 1465 cm^{-1}; Found: m/z 240.1917. Calcd for $C_{14}H_{28}OSi$: M, 240.1910.

11) Lindlar catalyst was prepared from 35 mg of 5% palladium over barium sulfate and 18 mg of equinoline is 4 mol of methanol under hydrogen with stirring for 1.5 h.