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Synthesis of (±)-15-Deoxy-$\Delta^{12,14}$-prostaglandin J_2 and Δ^{12}-Prostaglandin J_2 15-Acetate Methyl Esters

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Abstract—A new synthetic approach to 15-deoxy-$\Delta^{12,14}$-prostaglandin J_2 and related compounds starting from Corey (±)-lactone diol has been developed. The key stage of this approach includes synthesis of a prostaglandin derivative possessing leaving groups in positions *9*, *13*, and *15* and their subsequent elimination by the action of an organic base.

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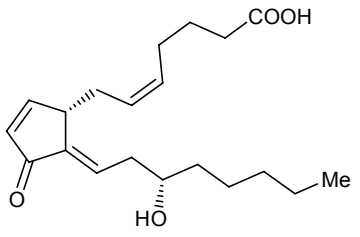
Among cyclopentenone prostaglandins (PG), of particular interest are products of albumin-catalyzed dehydration of prostaglandin D_2 (PGD_2), highly electrophilic Δ^{12}-PGJ_2 (**1**) and 15-deoxy-$\Delta^{12,14}$-PGJ_2 (**2**) [1]. Unlike other prostaglandins, compounds **1** and **2** contain cross-conjugated di- and triene fragments that are responsible for their biological properties [2, 3]. The anticarcinogenic activity of Δ^{12}-PGJ_2 (**1**) and Δ^{7}-PGA_1 is related to their ability to be reversibly transferred through cell membranes and inside cells. These compounds inhibit cellular processes via covalent binding to nuclear proteins [4]. Another important representative of diene prostaglandins, 15-deoxy-$\Delta^{12,14}$-PGJ_2 (**2**), is known as a selective ligand for $PPAR_\gamma$ (peroxisome proliferator-activated receptor γ), a member of nuclear receptors that directly regulate gene transcription and are responsible for triggering of inflammation, apoptosis, virus replication inhibition, etc. [5–7]. There are many publications on the biological properties of 15-deoxy-$\Delta^{12,14}$-PGJ_2; however, only a few syntheses of compounds **1** and **2** have been reported [8–11]. In particular, a procedure for their preparation from $PGF_{2\alpha}$ was patented [12].

In this article we describe a new synthetic approach to structures related to **1** and **2**. Here, the key stage is the synthesis of differently protected prostaglandin F derivatives **3** where the R^1 group protecting the C^{11}–OH group can be selectively removed without involving the other protecting groups. Naturally, the protecting groups R^2–R^4 should be readily leaving groups, such as acetate, toluenesulfonate, methanesulfonate, carbonate, etc. In the next stage, ketone **4** obtained by oxidation of the C^{11}–OH group should undergo stepwise decomposition, eventually leading to target prostaglandin **5** (Scheme 1).

One compound like **3** was synthesized using standard methods of the prostaglandin chemistry [13]. The starting compound was Corey (±)-lactone diol **6** [14]. Lactone **8** was obtained according to the previ-



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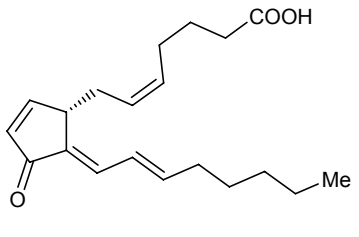

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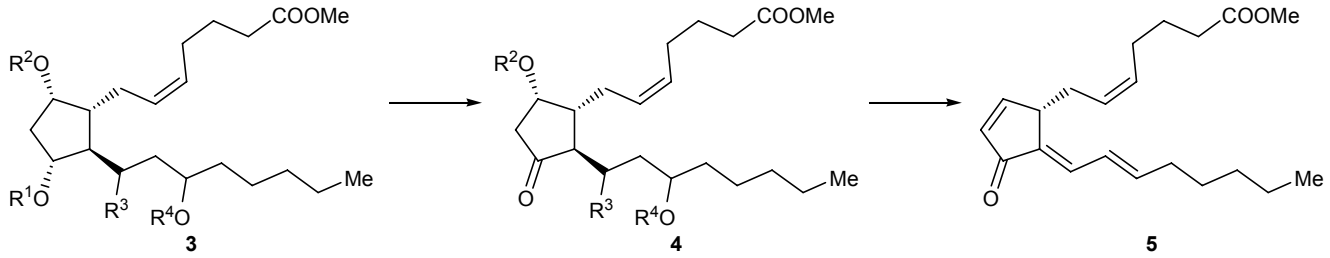
ously tested scheme [15] via selective protection of the primary hydroxy group in diol **6** with *tert*-butyldiphenylsilyl group, followed by protection of the secondary hydroxy group in **7** by tetrahydropyran-2-yl (THP) moiety (Scheme 2). Lactone **8** was then used to build up the upper prostaglandin chain according to Wittig. For this purpose, compound **8** was preliminarily reduced to lactol **9**, and the latter was subjected to olefination with the phosphonium ylide generated from triphenylphosphine and 5-bromopentanoic acid. Crude hydroxy acid **10** was alkylated with diazomethane, and hydroxy ester **11** was acetylated to obtain acetoxy ester **12**. Attempted purification of acid **10** by silica gel column chromatography was accompanied by removal of the THP protection with formation of dihydroxy acid **13**. Presumably, intramolecular assistance of the "free" carboxy group favors hydrolysis of the THP ether moiety. For identification purpose, dihydroxy acid **13** was methylated, and ester **14** was acetylated; as a result, diacetate **15** was isolated.

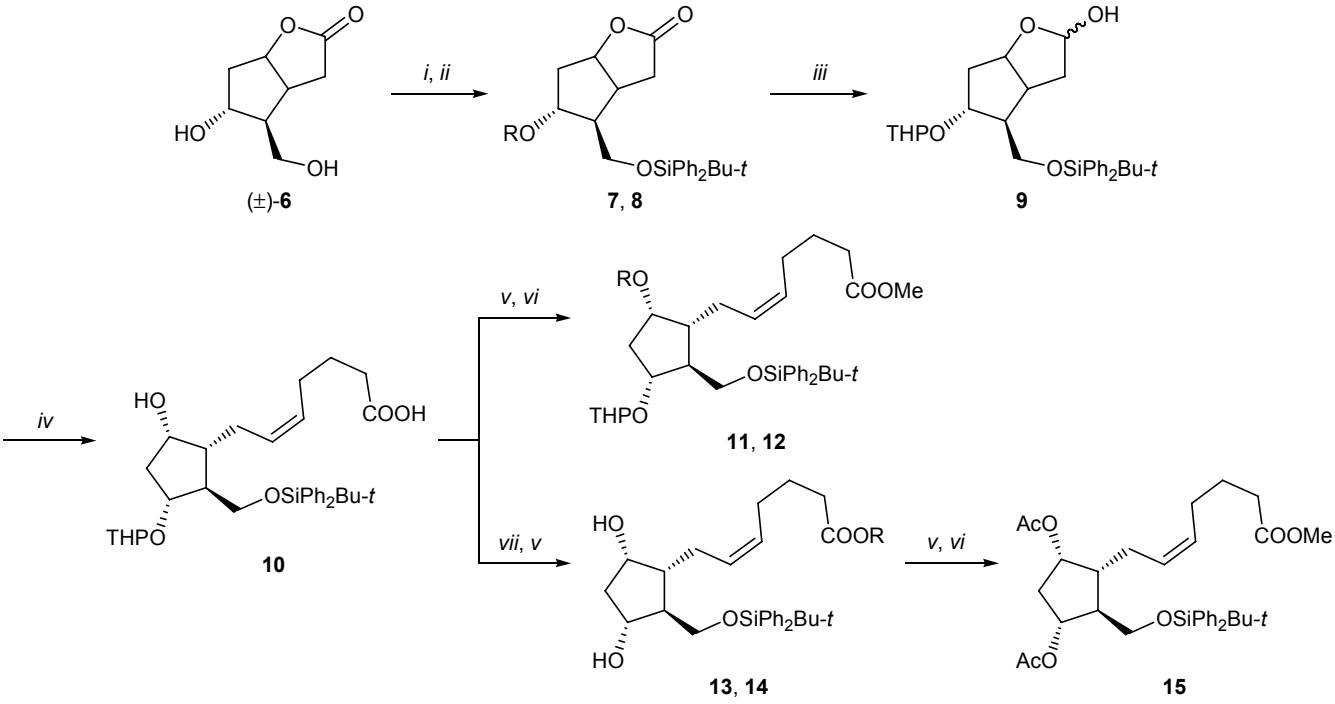
The construction of the lower side chain (ω-chain) was started from selective desilylation of **12** by the action of tetrabutylammonium fluoride. Alcohol **16** thus obtained was oxidized with Collins reagent to unstable aldehyde **17** whose chromatographic purification (as well as storage) was accompanied by formation of small amounts of aldehyde **18** and isomeric compounds. The condensation of **17** with dimethyl 2-oxoheptylphosphonate smoothly afforded 80% of enone **19** (Scheme 3). It seemed reasonable to use enone **19**

Scheme 1.



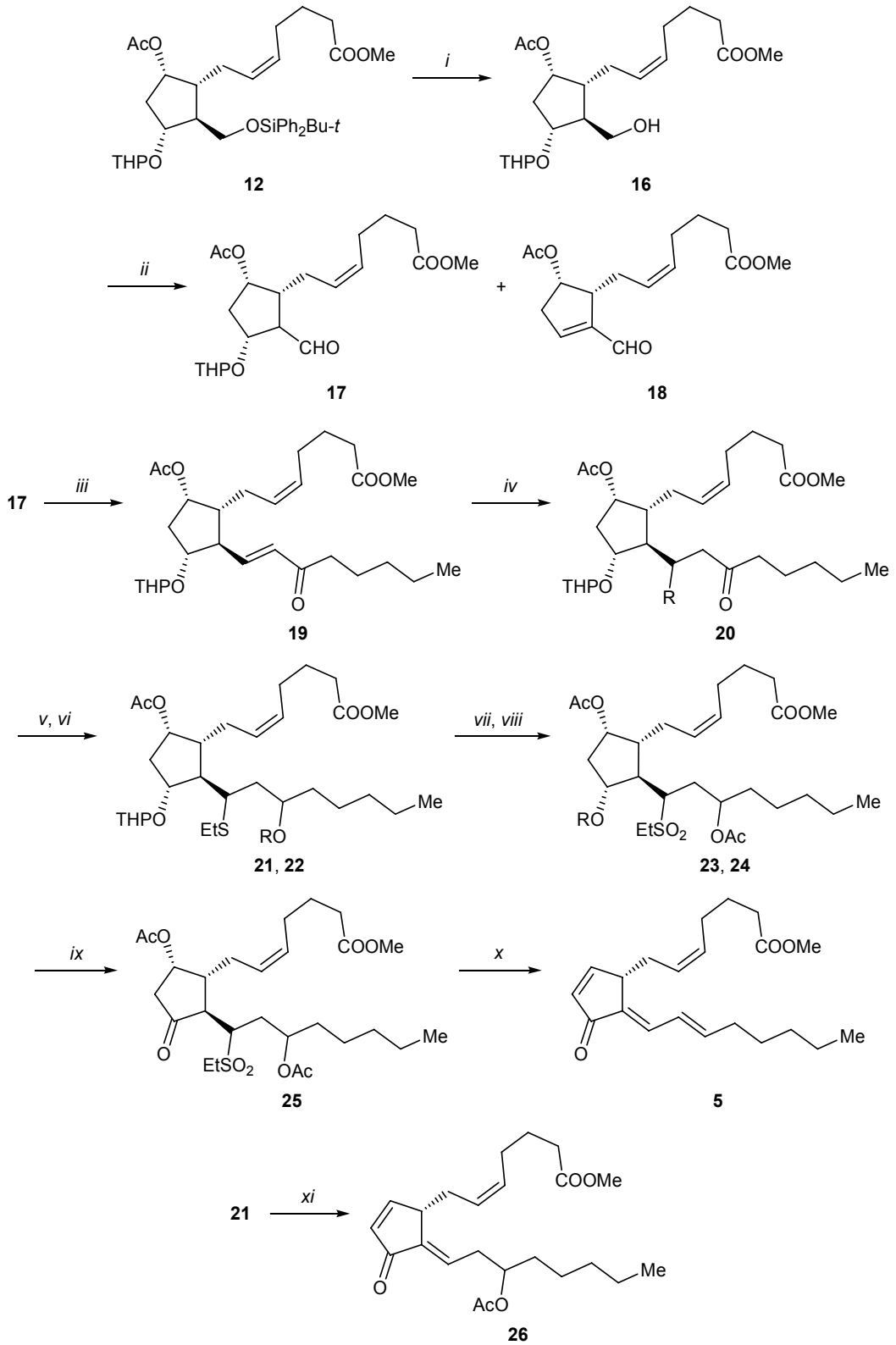
R^1–R^4 are protecting groups (see text).

Scheme 2.



7, **11**, **13**, R = H; **8**, R = THP; **12**, R = Ac; **14**, R = Me; *i*: *t*-$BuPh_2SiCl$ (1.2 equiv), imidazole, CH_2Cl_2; *ii*: dihydropyran, CH_2Cl_2, pyridine–TsOH; *iii*: *i*-Bu_2AlH, CH_2Cl_2, –70°C; *iv*: $Br^-Ph_3P^+(CH_2)_4CO_2H$, Me_6Si_2NNa, THF; *v*: CH_2N_2; *vi*: Ac_2O–pyridine; *vii*: SiO_2.

Scheme 3.



i: Bu_4NF, THF; *ii*: $CrO_3 \cdot 2\,Py$, CH_2Cl_2; *iii*: $(MeO)_2P(O)CH_2C(O)C_5H_{11}$, NaOH–$H_2O$, CH_2Cl_2, $Bu_4N^+Br^-$; *iv*: EtSH, THF, NaH; *v*: $NaBH_4$, MeOH, 0°C; *vi*: Ac_2O–pyridine; *vii*: 30% H_2O_2–$(NH_4)_6Mo_7O_{24} \cdot 7H_2O$; *viii*: 30% AcOH, 60°C; *ix*: PCC, CH_2Cl_2; *x*: DBU, PhH, 20°C; *xi*: H_2CrO_4–Me_2CO–H_2O; **20**, R = EtS; **21**, **24**, R = Ac; **22**, R = H; **23**, R = THP.

as building block for the introduction of C^{13}-leaving group via Michael reaction.

Taking into account the ease of base-catalyzed addition of thiols to enones, enone **19** was brought into 1,4-conjugate addition reaction with ethanethiol in THF. The reaction was catalyzed by sodium hydride, and it rapidly produced adduct **20** in a high yield. In the next step, the substituents on C^{13} and C^{15} in **20** were converted into readily leaving groups. The simplest and most convenient version involved transformation of the sulfide moiety into sulfone and of the oxo group into acetate. For this purpose, ketone **20** was reduced to alcohol **21** in high yield with $NaBH_4$ in methanol at 0°C, and alcohol **21** was acylated and oxidized with H_2O_2 in the presence of Mo(VI) salt to obtain sulfone **23**. Removal of the THP protection from **23**, followed by oxidation of alcohol **24** with pyridinium chlorochromate gave ketone **25**. We failed to deprotect the latter under acidic conditions. Ketone **25** remained unchanged after heating for 30 min in boiling benzene containing an equivalent amount of benzoic acid, but it was smoothly converted into compound **5** in benzene in the presence of DBU at room temperature. The progress of the reaction was monitored by TLC, and we thus succeeded in detecting two by-products whose structure was not determined because of too small amount of the isolated samples. An apparently chemorational version involving generation *in situ* of the 11-hydroxy function and sulfonyl group on C^{13} directly from THP ether **22** via oxidation with Jones reagent was successful only partly, and Δ^{12}-PGJ_2 derivative **26** was isolated in a moderate yield.

In summary, we have developed a synthetic approach to (±)-15-deoxy-$\Delta^{12,14}$-prostaglandin J_2 methyl ester on the basis of accessible building blocks that are conventional for prostaglandin chemistry, Corey lactone diol **5** and 15-oxoprostadienoic acid derivative **19**. The proposed approach can be implemented in a chiral version and is adaptable for the synthesis of analogs.

EXPERIMENTAL

The IR spectra were recorded from thin films on a Shimadzu IR Prestige-21 spectrometer. The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively, using the solvent signals ($CHCl_3$) as reference. The mass spectra (electron impact, 70 eV) were obtained on a Thermo Finnigan MAT 95XP instrument (ion source temperature 200°C, batch inlet probe temperature 60–280°C at a rate of 22 deg/min). Analytical TLC was performed on Sorbfil plates (Russia).

(±)-(3a*R,4*S**,5*R**,6a*S**)-4-{[*tert*-Butyl(diphenyl)silyloxy]methyl}-5-hydroxyhexahydro-2*H*-cyclopenta[*b*]furan-2-one (7).** Imidazole, 3.1 g (45.6 mmol), was added under stirring to a suspension of 3.57 g (20.7 mmol) of racemic lactone diol (±)-**6** in 150 mL of anhydrous methylene chloride, a solution of 6.26 g (22.77 mmol) of *tert*-butyl(chloro)diphenylsilane in 50 mL of anhydrous methylene chloride was slowly added, and the mixture was stirred for 6 h until compound **6** disappeared (TLC). The organic phase was washed with water and brine and evaporated under reduced pressure, and the residue was purified by silica gel chromatography using petroleum ether–ethyl acetate (4:1) as eluent. Yield 5 g (85%), colorless crystals, mp 92–97°C, R_f 0.22 (petroleum ether–ethyl acetate, 7:3). IR spectrum, ν, cm^{-1}: 3456, 3070, 1749, 1458, 1375, 1357, 1114, 1033, 707. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 s (9H, *t*-BuSi), 1.98 m (2H, 4-H, *endo*-6-H), 2.10 br.s (1H, OH), 2.40 m (2H, *endo*-3-H, *exo*-6-H), 2.58 m (1H, 3a-H), 2.69 d.d (1H, *exo*-3-H, J = 17.7, 9.9 Hz), 3.61 d.d (1H, CH_2O, J = 10.5, 6.7 Hz), 3.71 d.d (1H, CH_2O, J = 10.5, 5.2 Hz), 4.17 m (1H, 5-H), 4.87 t.d (1H, 6a-H, J = 6.9, 2.9 Hz), 7.42 m (6H, Ph), 7.63 d (4H, Ph, J = 6.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.06 (Si**C**Me_3), 26.80 (SiC**Me**$_3$), 35.21 (C^3), 39.34 (C^{3a}), 40.54 (C^6), 55.30 (C^4), 64.18 (CH_2O), 74.95 (C^5), 83.65 (C^{6a}), 127.78 (C^m), 129.90 (C^p), 132.79 (C^i), 135.44 (C^o), 177.20 (C^2). Mass spectrum, *m*/*z* (I_{rel}, %): 411 (20.6) $[M + H]^+$, 393 (5.9) $[M - H_2O]^+$, 365 (82.4), 333 (100) $[M - PhH]^+$. Calculated: M 410.58.

(±)-(3a*R,4*S**,5*R**,6a*S**)-4-{[*tert*-Butyl(diphenyl)silyloxy]methyl}-5-(tetrahydro-2*H*-pyran-2-yloxy)hexahydro-2*H*-cyclopenta[*b*]furan-2-one (8).** Freshly distilled dihydropyran, 2.2 g (26.18 mmol), was added dropwise under stirring to a solution of 5 g (17.45 mmol) of alcohol **7** in 60 mL of anhydrous methylene chloride, 0.49 g of pyridinium *p*-toluenesulfonate was then added, and the mixture was stirred until the reaction was complete (TLC). The mixture was washed with water and brine and evaporated under reduced pressure, and the residue was purified by chromatography. Yield 6.2 g (95%), colorless oily material, R_f 0.75 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 2938, 2932, 1774, 1472, 1428, 1112. ^1H NMR spectrum ($CDCl_3$), δ, ppm (mixture of diastereoisomers at a ratio of 1:1): 1.05 s (9H, *t*-Bu), 2.75 m (2H, 3-H), 3.40–3.90 m (4H, CH_2O), 4.10 m and 4.25 m (0.5H each, 5-H), 4.55 m and 4.65 m (0.5H

each, 2′-H), 4.90 m (6a-H), 7.40 m (6H) and 7.70 m (4H) (C_6H_5). ^{13}C NMR spectrum, ($CDCl_3$), δ_C, ppm: 19.10 (Si**C**Me_3), 19.26 ($C^{4'}$), 25.36 ($C^{5'}$), 26.79 (SiC**Me**$_3$), 30.50 and 30.68 ($C^{3'}$), 35.48 and 35.78 (C^3), 36.32 and 39.19 (C^6), 38.81 and 39.65 (C^{3a}), 54.20 and 55.37 (C^4), 62.07 (CH_2OSi), 63.01 and 63.88 ($C^{6'}$), 77.13 and 79.47 (C^5), 84.07 and 84.48 (C^{6a}), 95.52 and 98.58 ($C^{2'}$); 127.74, 129.84, 133.02, 135.48 (C_6H_5); 177.03 and 177.35 (C^2).

Methyl (±)-(5*Z*)-7-[(1*R,2*S**,3*R**,5*S**)-2-{[*tert*-butyl(diphenyl)silyloxy]methyl}-5-hydroxy-3-(tetrahydro-2*H*-pyran-2-yloxy)cyclopentyl]hept-5-enoate (11).** A solution of 6.2 g (12.5 mmol) of lactone **8** in 250 mL of anhydrous methylene chloride was cooled to –78°C, a solution of 8.7 mL (43.8 mmol) of *i*-Bu_2AlH in 30 mL of methylene chloride was added dropwise under stirring in an argon atmosphere, the mixture was stirred for 45 min at –78°C, 8.6 mL of methanol was added dropwise, and the mixture was allowed to gradually warm up to room temperature. Water, 50 mL, was then added, the mixture was stirred for 2 h, the precipitate was filtered off and washed with methylene chloride (3×10 mL), and the filtrate was combined with the washings, dried over $MgSO_4$, and evaporated on a rotary evaporator. The residue was treated with 30 mL of anhydrous benzene, the mixture was evaporated, and the residue was dried under reduced pressure (1 mm) for 30 min to isolate 5.9 g of colorless oily lactol **9** which was used in the next step without additional purification.

Sodium hexamethyldisilazide, 20.2 g (110 mmol), was added in portions under stirring at 0°C in an argon atmosphere to a suspension of 24.38 g (55 mmol) of triphenylphosphonium 5-bromopentanoate in 90 mL of anhydrous THF, and the mixture was allowed to warm up to room temperature and stirred for 0.5 h more. A solution of 5.9 g (11.9 mmol) of lactol **9** (see above) in 30 mL of THF was added to the red–orange solution of phosphonium ylide, and the mixture was stirred for 1 h. A solution of 1 g of potassium carbonate in 60 mL of water, 35 mL of diethyl ether, 35 mL of ethyl acetate, and 70 mL of benzene were then added, and the mixture was thoroughly stirred and allowed to settle down. The aqueous layer was extracted with diethyl ether–ethyl acetate (1:1, 3×50 mL), and the extracts were combined with the organic phase and washed with water (3×50 mL). The aqueous fractions were combined, cooled to 3–5°C, and acidified to pH ~6 with a saturated solution of sodium hydrogen sulfate under stirring. Acid **10** was extracted from the aqueous phase into ethyl acetate (3×50 mL), and the extract was washed with water (20 mL) and brine (30 mL), dried over $MgSO_4$, and evaporated on a rotary evaporator. The residue (crude acid **10**) was treated with excess diazomethane in diethyl ether, and methyl ester **11** was isolated by silica gel column chromatography. Yield 5.3 g (75%, calculated on lactol **9**), colorless viscous oily material, R_f 0.7 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 3527, 2933, 1739, 1429, 1113, 703, 565. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 s and 0.94 s (9H, *t*-Bu), 2.20 m (2H), 3.30–3.40 m (2H), 3.45 d.d (1H, *J* = 5.1, 10.2 Hz) and 3.60 d.d (1H, *J* = 4.1, 10.3 Hz) (CH_2OSi), 3.54 s (3H, OCH_3), 3.70 m (1.5H) and 3.80 m (0.5H), 4.00 m (2H, 5″-H), 4.25 m (1H, 3′-H), 4.59 m (0.5H) and 4.63 m (0.5H) (2″-H), 5.20–5.35 m (2H, CH=CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.17 and 19.78 ($C^{4''}$, Si**C**Me_3), 24.77 (C^3), 25.30 ($C^{5''}$), 26.50 (C^7), 27.04 (C^6), 26.77 (SiC**Me**$_3$), 30.66 and 31.20 ($C^{3''}$), 33.39 (C^2), 39.25 and 40.85 ($C^{4'}$), 46.53 and 46.75 ($C^{2'}$), 51.30 (OCH_3), 52.47 and 52.89 ($C^{1'}$), 61.99 and 63.94 (CH_2OSi), 63.94 and 64.57 ($C^{6''}$), 74.79 and 75.01 ($C^{5'}$), 79.72 and 80.87 ($C^{3'}$), 96.54 and 97.56 ($C^{2''}$), 127.59, 129.14 and 129.45, 129.60, 133.35 and 133.40 (C^i), 135.50 (CH=CH, C_6H_5), 174.01 (C=O).

Methyl (±)-(5*Z*)-7-{(1*R,2*S**,3*R**,5*S**)-5-acetoxy-2-[*tert*-butyl(diphenyl)silyloxymethyl]-3-(tetrahydro-2*H*-pyran-2-yloxy)cyclopentyl}hept-5-enoate (12).** Freshly distilled acetic anhydride, 4.8 mL (51 mmol), was added dropwise under stirring at 0°C to a solution of 5 g (8.4 mmol) of compound **11** and 0.07 g (0.56 mmol) of 4-dimethylaminopyridine (DMAP) in 40 mL of anhydrous pyridine. When the reaction was complete (TLC), the mixture was diluted with 50 mL of water and extracted with methylene chloride (3×40 mL). The extract was washed with water (2×20 mL) and brine (20 mL), dried over $MgSO_4$, and evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Yield 4.44 g (83%), oily material, R_f 0.65 (petroleum ether–ethyl acetate, 7:3). IR spectrum, ν, cm^{-1}: 2933, 2856, 1732, 1427, 1373, 1244, 1111, 1022, 704. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.05 s (9H, *t*-Bu), 2.03 s (3H, CH_3), 2.20 t (2H, 2-H, *J* = 7.5 Hz), 3.64 s (OCH_3), 3.65–3.90 m (4H), 4.10 m and 4.30 m (0.5H each, 3′-H), 4.45 m and 4.55 m (0.5H each, 2″-H), 5.09 m (1H, 5′-H), 5.33 m (2H, CH=CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.35 and 19.54 ($C^{4''}$, Si**C**Me_3), 21.33 (CH_3), 24.81 (C^3), 25.47($C^{5''}$), 26.62 (C^4), 25.71 (C^7), 26.92 (SiC**Me**$_3$), 31.11 ($C^{3''}$), 33.47 (C^2), 37.85 and 39.61 ($C^{4'}$), 42.55

and 43.27 ($C^{1'}$), 51.45 (OCH_3), 52.12 ($C^{2'}$), 62.26 (CH_2OSi), 62.86 ($C^{6''}$), 75.19 and 79.04 ($C^{3'}$), 76.18 and 76.36 ($C^{5'}$), 97.02 and 99.80 ($C^{2''}$), 127.67, 129.73 and 129.64, 133.47 and 133.55, 135.65 (C_6H_5), 128.74, 128.79 and 129.47, 129.73 (CH=CH), 170.76 and 170.91 (Me**C**O), 173.97 (**C**O_2Me).

Methyl (±)-(5*Z*)-7-{(1*R,2*S**,3*R**,5*S**)-3,5-diacetoxy-2-[*tert*-butyl(diphenyl)silyloxymethyl]cyclopentyl}]hept-5-enoate (15).** Chromatographic purification of a sample of hydroxy acid **10** on silica gel was accompanied by removal of the THP protecting group with formation of dihydroxy acid **13** which was identified as oily diacetoxy ester **15**, R_f 0.6 (petroleum ether–ethyl acetate, 7:3). IR spectrum, ν, cm^{-1}: 2953, 2932, 1735, 1466, 1428, 1240, 1112, 1106, 703. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.03 s (9H, *t*-Bu), 1.95 s and 2.08 s (3H each, OAc), 2.28 t (2H, CH_2, J = 7.6 Hz), 3.62 s (3H, OCH_3), 5.10 br.s (1H, 5′-H), 5.20 br.s (1H, 3′-H), 5.35 m (2H, CH=CH), 7.30 m (6H) and 7.65 m (4H) (C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.31 (Si**C**Me_3), 21.18 and 21.25 (**Me**CO), 24.75 (C^3), 25.60 (C^7), 26.68 (C^4), 26.86 (SiC**Me**$_3$), 33.43 (C^2), 38.97 ($C^{4'}$), 43.42 ($C^{1'}$), 51.50 (OMe, $C^{2'}$), 62.12 (CH_2OSi), 76.05 ($C^{3'}$, $C^{5'}$), 127.72, 129.75, 133.23, 133.38, 135.60, 135.64 (C_6H_5), 128.34, 129.00 (CH=CH), 170.58 and 170.68 (Me**C**O), 173.94 (**C**O_2Me).

Methyl (±)-(5*Z*)-7-[(1*R,2*S**,3*R**,5*S**)-5-acetoxy-2-hydroxymethyl-3-(tetrahydro-2*H*-pyran-2-yloxy)-cyclopentyl]hept-5-enoate (16).** A solution of 4 g (6.28 mmol) of silyl ether **12** in 50 mL of THF was cooled to 0°C, 12.65 mL of a 1 M solution of tetrabutylammonium fluoride in THF was added over a period of 3 min, and the mixture was stirred until the reaction was complete (TLC). The mixture was diluted with 100 mL of ethyl acetate, washed with water (3 × 50 mL) and brine (30 mL), dried over $MgSO_4$, and evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Yield 2.13 g (85%), colorless oily material, R_f 0.65 (petroleum ether–ethyl acetate, 7:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.03 s (3H, CH_3), 2.30 m (2H), 3.65 s (3H, OCH_3), 4.10 m (0.6H) and 4.35 m (0.4H) (3′-H), 4.55 m (0.4H) and 4.70 m (0.6H) (OCHO), 5.30 m (0.4H) and 5.60 m (0.6H) (5′-H), 5.35 m (2H, CH=CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.51 and 20.08 ($C^{4''}$), 21.04 (CH_3), 24.52 (C^3), 25.05 and 25.18 ($C^{5''}$), 25.41 and 25.53 (C^7), 26.34 (C^4), 30.72 and 31.02 ($C^{3''}$), 33.18 (C^2), 38.09 and 39.24 ($C^{4'}$), 43.09 and 43.42 ($C^{1'}$), 51.33 and 51.45 ($C^{2'}$), 51.38 (OCH_3), 62.35 and 62.56 ($C^{6''}$), 62.89 and 63.52 (CH_2OSi), 74.99 and 75.22 ($C^{3'}$), 78.92 and 79.04 ($C^{5'}$), 98.53 and 99.09 ($C^{2''}$), 128.17, 128.86 and 129.55 (CH=CH), 170.68 (Me**C**O), 173.94 and 174.00 (**C**O_2Me).

Methyl (±)-(5Z)-7-[(1*R,2*R**,3*R**,5*S**)-5-acetoxy-3-(tetrahydro-2*H*-pyran-2-yloxy)-2-formylcyclopentyl]hept-5-enoate (17).** A solution of 2 g (5 mmol) of alcohol **16** in 50 mL of anhydrous methylene chloride was cooled to 0°C, a solution of the CrO_3–pyridine complex prepared from 3.62 g (36.2 mmol) of chromium(VI) oxide and 56.8 mL of anhydrous pyridine in 50 mL of anhydrous methylene chloride was added in one portion, and the mixture was stirred for 1 h and filtered through 30 cm^3 of silica gel. The sorbent was washed with methylene chloride (3 × 30 mL), and the washings were combined with the filtrate and evaporated under reduced pressure. Yield 1.8 g (90%), colorless oily substance, R_f 0.6 (petroleum ether–ethyl acetate, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.00 s (3H, OAc), 2.25 t (2H, 2-H, J = 7.1 Hz), 3.60 s (3H, OCH_3), 4.45 m (1H, 3′-H), 4.50 br.s and 4.55 br.s (1H, 2″-H), 5.05 m (1H, 5′-H), 5.25–5.40 m (2H, CH=CH), 9.80 d (1H, CHO, J = 2.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.06 (CH_3), 51.35 (OCH_3), 98.38 and 99.13 ($C^{2''}$), 127.37; 127.54, 130.43, 130.62 (CH=CH); 170.12 and 170.37 (Me**C**O), 173.78 (**C**O_2Me), 201.86 and 202.38 (CHO).

Methyl (±)-(5*Z*)-7-[(5*S)-5-acetoxy-2-formylcyclopent-2-en-1-yl]hept-5-enoate (18)** was isolated as by-product in the chromatographic purification of aldehyde **17**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.98 s (3H, OAc), 3.60 s (3H, OCH_3), 6.75 br.s (1H, 3′-H), 9.65 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 127.84 and 129.84 (CH=CH), 147.50 ($C^{2'}$), 149.05 ($C^{3'}$), 189.15 (CHO).

Methyl (±)-(5*Z*,9α,11α,13*E*)-9-acetoxy-15-oxo-11-(tetrahydro-2*H*-pyran-2-yloxy)prosta-5,13-dien-1-oate (19). Aldehyde **17**, 1.8 g (4.54 mmol), was dissolved in 100 mL of anhydrous methylene chloride, 1 g (4.54 mmol) of dimethyl 2-oxoheptylphosphonate, 0.05 g of tetraethylammonium bromide, and 0.4 mL of 50% aqueous sodium hydroxide were added under vigorous stirring, and the mixture was stirred until the reaction was complete (6 h, TLC). The mixture was washed with water (2 × 30 mL) and brine (20 mL), dried over $MgSO_4$, and evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Yield 1.79 g (80%), colorless oily material, R_f 0.7 (petroleum ether–ethyl acetate, 1:1).

IR spectrum, ν, cm^{-1}: 2950, 2934, 1735, 1700, 1680 w, 1620, 1242. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (3H, CH_3, J = 6.9 Hz), 2.00 s and 2.01 s (3H, OAc), 2.22 t (2H, CH_2, J = 6.9 Hz), 2.50 t (2H, CH_2, J = 7.1 Hz), 3.60 s (3H, OCH_3), 4.05 m (1H, 11-H), 4.50 br.s (0.5H) and 4.55 br.s (0.5H, 2″-H), 5.00 br.s (1H, 9-H), 5.30 m (2H, CH=CH), 6.18 d.t (1H, 14-H, J = 1.7, 15.9 Hz), 6.68 m (1H, 13-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.88 and 14.14 (CH_3), 19.01 and 19.60 ($C^{4''}$), 21.18 and 21.19 (**Me**CO), 22.43 (C^{19}), 23.92 and 23.95 (C^{17}), 24.62 (C^3), 25.02 and 25.07 ($C^{5''}$), 25.27 and 25.33 (C^7), 26.55 (C^4), 30.66 (C^{18}), 31.40 and 31.42 ($C^{3''}$), 33.32 (C^8), 38.47 and 40.12 (C^{10}), 40.23 and 40.42 (C^{16}), 47.30 and 47.37 (C^8), 51.42 (OCH_3), 52.99 and 53.54 (C^{12}), 61.69 and 62.68 ($C^{6''}$), 74.18 and 74.48 (C^9), 78.78 and 81.02 (C^{11}), 96.61 and 99.18 ($C^{2''}$), 127.71 and 127.73 (C^6), 130.03 (C^{14}), 131.56 and 131.77 (C^5), 146.95 (C^{13}), 170.43 and 170.53 (Me**C**O), 173.82 (C^1), 200.28 and 200.42 (C^{15}).

Methyl (±)-(5*Z*,9α,11α)-9-acetoxy-15-oxo-13-ethylsulfanyl-11-(tetrahydro-2*H*-pyran-2-yloxy)-prost-5-en-1-oate (20). Sodium hydride, 0.04 g, was added under stirring in an argon atmosphere to a solution of 1.44 g (2.92 mmol) of enone **19** and 0.27 g (4.17 mmol) of ethanethiol in 40 mL of anhydrous THF. The mixture was stirred for 30 min, 80 mL of a saturated aqueous solution of ammonium chloride was added, and the mixture was extracted with methylene chloride (3×40 mL). The extract was dried over $MgSO_4$ and evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Yield 1.54 g (95%), colorless oily material, R_f 0.6 (petroleum ether–ethyl acetate, 7:3), a mixture of diastereoisomers. IR spectrum, ν, cm^{-1}: 2952, 2929, 1735, 1714, 1680, 1373, 1244, 1027. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (3H, CH_3, J = 6.4 Hz), 1.20 t (3H, CH_3, J = 6.4 Hz), 1.96 s and 1.98 s (3H, OAc), 3.60 s (3H, OCH_3), 4.40 m and 4.55 m (0.5H each, 2″-H), 5.0 m (1H, 9-H), 5.35 br.s (2H, CH=CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.91 (CH_3), 15.03 (CH_3), 31.37 and 31.44 (C^{18}), 33.51 (C^2), 51.47 (OCH_3), 94.64, 97.64, 100.18 ($C^{2''}$), 170.34, 170.79, 170.88 (Me**C**O), 173.96 (**C**O_2Me), 208.75, 209.44, 209.76, 210.09 (C^{15}).

Methyl (±)-(5*Z*,9α,11α)-9-acetoxy-13-ethylsulfanyl-15-hydroxy-11-(tetrahydro-2*H*-pyran-2-yloxy)-prost-5-en-1-oate (21). Sodium tetrahydridoborate, 0.2 g (5.2 mmol), was added in portions under stirring over a period of 1 h to a solution of 1.5 g (2.7 mmol) of ketone **20** in 20 mL of methanol. When the reaction was complete, 40 mL of water was added, methanol was distilled off, and the mixture was extracted with methylene chloride (4×30 mL). The combined extracts were washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Yield 1.35 g (90%), colorless oily material, R_f 0.45 (petroleum ether–ethyl acetate, 7:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t (3H, CH_3, J = 6.4 Hz), 1.25 t (3H, CH_3, J = 7.3 Hz), 2.30 t (2H, CH_2, J = 7.5 Hz), 2.55 q (2H, CH_2S, J = 6.8 Hz), 3.00 m (1H), 3.45 m (1H, 15-H), 3.65 s (3H, OCH_3), 3.75–3.95 m (2.5H, CH_2O and 0.5H, 11-H), 4.20 m (0.5H, 11-H), 4.50 br.s and 4.60 br.s (0.5H each, 2″-H), 5.05 m (1H, 9-H), 5.35 br.s (2H, CH=CH). ^{13}C NMR spectrum, ($CDCl_3$), δ_C, ppm: 14.02 (CH_3), 17.72 and 14.87 (CH_3), 19.91 ($C^{4''}$), 21.22 (CH_3), 22.60 (C^{19}), 24.76 (C^3), 25.36 (SCH_2), 26.68 (C^4), 31.05 and 31.29 ($C^{3''}$), 31.94 (C^{18}), 33.45 (C^2), 37.56 and 39.11 (C^{16}), 41.23 and 43.18 (C^{10}), 44.38 and 43.10 (C^{13}), 43.18 and 44.65 (C^8), 51.44 (OCH_3), 51.90 and 51.79 (C^{12}), 62.86 and 63.20 ($C^{6''}$), 69.48 and 63.20 (C^{15}), 75.00, 75.41 and 75.67 (C^9), 80.12 and 81.13 (C^{11}), 99.08 and 99.52 ($C^{2''}$), 128.07, 128.31, 129.67 and 129.88 (CH=CH), 170.46 and 170.64 (Me**C**O), 173.93 (C^1).

Methyl (±)-(5*Z*,9α,11α)-9,15-diacetoxy-13-ethylsulfanyl-11-(tetrahydro-2*H*-pyran-2-yloxy)prost-5-en-1-oate (22). A solution of 1.35 g (2.43 mmol) of alcohol **21** and 30 mg of 4-(dimethylamino)pyridine in 10 mL of anhydrous pyridine was cooled to 0°C, 1.42 mL (14.8 mmol) of acetic anhydride was added dropwise under stirring, and the mixture was allowed to warm up to room temperature and stirred for 3 h. The mixture was cooled again to 5°C, diluted with 20 mL of water, and extracted with methylene chloride (5×20 mL), the extract was washed with brine (20 mL) and evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Yield 1.42 g (98%), colorless oily material, R_f 0.6 (petroleum ether–ethyl acetate, 7:3). IR spectrum, ν, cm^{-1}: 2942, 2862, 1736, 1453, 1436, 1373, 1302, 1241. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (3H, CH_3, J = 6.5 Hz), 1.20 t (3H, CH_3, J = 7.1 Hz), 1.90 s and 2.00 s (OAc), 2.25 t (2H, CH_2, J = 7.5 Hz), 2.50 q (2H, CH_2S, J = 7.1 Hz), 2.70 m (1H), 3.40 m (1H), 3.60 s (3H, OCH_3), 3.70– 4.25 m (3H), 4.20 br.s and 4.30 br.s (0.5H each, 11-H), 4.40 br.s and 4.50 br.s (0.5H each, OCHO), 5.00 m (1H, 15-H), 5.15 m (1H, 9-H), 5.40 m (2H, CH=CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.97 (CH_3), 14.87 (CH_3), 19.73 and 20.17 ($C^{4''}$), 21.13 and 21.31 (CH_3), 22.48 (C^{19}), 24.78 (C^3, C^{17}), 25.46

($C^{5''}$), 26.06 (C^{7}), 26.58 (C^{4}), 31.23 and 31.31 ($C^{3''}$), 31.74 and 31.80 (C^{18}), 33.47 (C^{2}), 34.82 (C^{16}), 37.22 (C^{14}), 39.21, 40.03 and 40.35 (C^{10}), 42.60 and 42.97 (C^{13}), 44.41 and 45.01 (C^{8}), 51.30 (OCH_3), 51.40 (C^{12}), 62.54 and 63.35 ($C^{6''}$), 71.90 and 72.22 (C^{15}), 75.36 and 75.75 (C^{9}), 75.75 and 81.01 (C^{11}), 96.86 and 100.14 ($C^{2''}$), 128.41 and 129.67 (CH=CH), 170.53, 170.58, 170.79 and 170.93 (Me**C**O), 173.89 (C^{1}).

Methyl (±)-(5*Z*,9α,11α)-9,15-diacetoxy-13-ethanesulfonyl-11-(tetrahydro-2*H*-pyran-2-yloxy)-prost-5-en-1-oate (23). A solution of 0.125 g of $(NH_4)_6Mo_7O_{24}\cdot H_2O$ in 40 mL of methanol was cooled to 0°C, 3 mL of 30% hydrogen peroxide was added, and the mixture was stirred for 1 h. A solution of 1.4 g (2.34 mmol) of compound **22** in 10 mL of methanol was then added, the mixture was stirred for 3 h at 0°C, 2.8 g of Na_2SO_3 was added, and the mixture was allowed to warm up to room temperature and stirred for 2 h more. The mixture was diluted with 200 mL of methylene chloride and filtered through a Schott filter, the precipitate was washed on a filter with 30 mL of methylene chloride, the filtrate was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Yield 1.08 g (73%), colorless oily substance, R_f 0.6 (petroleum ether–ethyl acetate, 1:1). IR spectrum, ν, cm^{-1}: 2942, 2862, 1736, 1455, 1436, 1373, 1302, 1241, 1034, 730. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (3H, CH_3, J = 6.6 Hz), 1.30 t and 1.34 t (3H, CH_3, J = 7.4 Hz), 2.04 s and 2.05 s (OAc), 2.07 s (OAc), 2.30 t (2H, CH_2, J = 7.1 Hz), 3.00 m (2H, SO_2CH_2), 3.65 s (3H, OCH_3), 3.80 m (1H, 13-H), 4.40–4.70 m (2H, 2″-H, 11-H), 5.00–5.10 m (2H, 9-H, 15-H), 5.35 m (2H, CH=CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 6.19 and 6.36 (CH_3), 13.90 (CH_3), 19.97 and 20.59 ($C^{4''}$), 22.37 (C^{19}), 24.68 (C^{3}, C^{14}, C^{17}), 25.30 and 25.47 ($C^{5''}$), 25.32 (C^{7}), 26.55 (C^{5}), 31.21 and 31.34 ($C^{3''}$), 31.55 and 31.65 (C^{18}), 33.80 (C^{2}), 34.79 and 34.91 (C^{16}), 36.80 and 39.47 (C^{10}), 43.33 and 44.11 (C^{8}), 46.86 (CH_2SO_2), 48.48 and 48.91 (C^{13}), 51.38 (OCH_3), 55.37 and 55.68 (C^{12}), 62.96 and 63.94 ($C^{6''}$), 71.25 and 71.45 (C^{15}), 74.22 and 75.05 (C^{9}), 76.25 and 80.36 (C^{11}), 97.77 and 100.57 ($C^{2''}$), 127.69, 127.81, 127.87, 130.03, 130.08, 130.20 (CH=CH), 170.26, 170.41, 170.52, 170.72 (Me**C**O), 173.88 (C^{1}).

Methyl (±)-(5*Z*,9α,11α)-9,15-diacetoxy-11-hydroxy-13-(ethanesulfonyl)prost-5-en-1-oate (24). A solution of 1.08 g (1.71 mmol) of THP ether **23** in 70 mL of 60% acetic acid was heated for 1 h at 60°C. The mixture was evaporated under reduced pressure, the residue was diluted with 150 mL of water, and the product was extracted into ethyl acetate (3×50 mL). The combined extracts were washed with an aqueous solution of sodium hydrogen carbonate and with water, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography. Yield 0.8 g (86%), R_f 0.3 (petroleum ether–ethyl acetate, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t (3H, CH_3, J = 6.5 Hz); 2.04 s, 2.05 s, 2.06 s, 2.10 s, and 2.11 s (6H, OAc); 2.13 t (2H, 2-H, J = 7.3 Hz), 3.65 s (3H, OCH_3), 4.30 m (1H), 4.70 m (0.5H), 4.94 m (0.4H), 5.00–5.20 m (2H), 5.30–5.50 m (2H, CH=CH).

Methyl (±)-(5*Z*,9α)-9,15-diacetoxy-11-oxo-13-(ethanesulfonyl)prost-5-en-1-oate (25). Pyridinium chlorochromate, 6.14 g (28.5 mmol), was added under stirring to a solution of 0.8 g (1.47 mmol) of alcohol **24** in 120 mL of anhydrous methylene chloride. When the reaction was complete (6 h, TLC), the mixture was filtered through 50 cm^3 of silica gel, the filtrate was evaporated under reduced pressure, and the residue was purified by silica gel chromatography. Yield 0.69 g (86%), colorless oily material, R_f 0.3 (petroleum ether–ethyl acetate, 7:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (3H, CH_3, J = 7.1 Hz), 1.20–1.30 m (8H), 1.38 t (3H, CH_3, J = 7.5 Hz), 1.50–1.60 m (4H), 1.96 s, 2.08 s, 2.09 s (OAc), 2.30 t (2H, CH_2, J = 6.5 Hz), 2.90–3.15 m (2H, SO_2CH_2), 3.65 s (3H, OCH_3), 3.80 br.s (1H), 4.90 m (1H, 15-H), 5.10 br.s (1H, 9-H), 5.40 m (2H, CH=CH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 6.24 and 6.59 (CH_3), 13.90 and 13.98 (CH_3), 20.97, 21.01, 21.13, 21.20, 21.31 (**Me**CO), 22.47 (C^{19}), 24.71, 24.76 and 24.81 (C^{3}, C^{17}), 26.59 and 26.64 (C^{7}), 26.81 and 26.83 (C^{4}), 31.57 and 31.62 (C^{18}), 32.74 and 33.13 (C^{14}), 33.44 and 33.48 (C^{2}), 34.74 and 34.85 (C^{16}), 37.75 and 43.31 (C^{10}), 43.29 and 45.38 (C^{8}), 46.39 and 46.52 (CH_2SO_2), 49.15 and 49.37 (C^{13}), 51.50 (OCH_3), 56.30 (C^{12}), 70.31, 70.54, 71.35 and 71.42 (C^{15}), 76.17 and 77.96 (C^{9}), 126.17 and 127.18 (C^{6}), 130.69 and 131.42 (C^{5}), 170.27, 170.52, 170.56, 170.86 and 171.46 (Me**C**O), 173.91 and 173.96 (C^{1}), 212.76 (C^{11}).

(±)-15-Deoxy-$\Delta^{12,14}$-prostaglandin J_2 methyl ester (5). 1,8-Diazabicyclo[5.4.0]undec-7-ene, 0.2 g (1.3 mmol), was added to a solution of 0.65 g (1.19 mmol) of ketone **25** in 100 mL of benzene, and the mixture was stirred for 2 h. The mixture was filtered through 20 cm^3 of silica gel, the sorbent was washed with ethyl acetate (3×50 mL), the filtrate was combined with the washings and evaporated under reduced pressure, and the residue was subjected to

silica gel chromatography. Yield 0.126 g (32%), yellowish waxy material, R_f 0.55 (petroleum ether–ethyl acetate, 7:3). IR spectrum, ν, cm^{-1}: 2954, 2928, 2856, 1738, 1695, 1634. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.89 t (3H, CH_3, J = 7.0 Hz), 1.25–1.33 m (4H, 18-H, 19-H), 1.45 quint (2H, 17-H, J = 7.2 Hz), 1.65 quint (2H, 3-H, J = 7.5 Hz), 2.20 q (2H, 3-H, J = 7.3 Hz), 2.23 q (2H, 16-H, J = 7.3 Hz), 2.28 t (2H, 2-H, J = 7.5 Hz), 2.60 d.t (1H, 7-H), 3.58 m (1H, 8-H), 3.65 s (3H, OCH_3), 5.33–5.39 m (1H, 6-H), 5.43–5.48 m (1H, 5-H), 6.25 d.t (1H, 15-H, J = 6.9, 14.9 Hz), 6.32 d.d (1H, 14-H, J = 11.4, 15.0 Hz), 6.36 d.d (1H, 10-H, J = 1.8, 6.1 Hz), 7.50 d (1H, 13-H, J = 11.3 Hz), 7.47 d.d (1H, 9-H, J = 1.9, 6.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.05, 22.51, 24.72, 26.69, 28.50, 30.76, 31.45, 33.43, 33.50, 43.51, 51.56, 125.67, 125.99, 131.50, 131.72, 135.06 (C^{12}), 135.38, 146.96, 160.69, 173.94, 197.43. Mass spectrum, m/z (I_{rel}, %): 330.3 (90) $[M + H]^+$, 299 (10) $[M - OCH_3]^+$, 259 (100) $[M - C_5H_{11}]^+$. Calculated: M 330.46.

Methyl (5*Z*,9*E*)-15-acetoxy-11-oxoprosta-5,9,12-trien-1-oate (26). Tetrahydropyranyl ether **22**, 80 mg (0.13 mmol) was oxidized with 20 equiv of Jones reagent in aqueous acetone at 20°C (6 h). Excess oxidant was decomposed by adding 1.25 mL of propan-2-ol, the mixture was evaporated under reduced pressure, the residue was treated with 5 mL of water and extracted with methylene chloride (4× 5 mL), the combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure, and the residue was subjected to silica gel chromatography. Yield 10 mg (20%), oily material, R_f 0.7 (petroleum ether–ethyl acetate, 1:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.85 t (3H, CH_3, J = 6.9 Hz), 1.25 m (6H), 1.50–1.80 m (4H), 2.01 s and 2.05 s (3H, OAc), 2.25 m (2H), 2.50–2.70 m (2H), 3.45 m (1H), 3.65 s (3H, OCH_3), 4.95 m (1H, 15-H), 5.30–5.50 m (2H, CH=CH), 6.35 d.d (1H, 10-H, J = 1.7, 6.0 Hz), 6.45 t (1H, 13-H, J = 7.6 Hz), 7.50 d.d (1H, 9-H, J = 1.8, 6.0 Hz).

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