Synthesis of New Aromatic (C17−C20)-Locked Side-Chain Analogues of Calcitriol (1α,25-Dihydroxyvitamin D_3)[†,1]

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The synthesis of four new analogues of calcitriol (1α,25-$(OH)_2$-D_3) possessing aromatic and conjugated double bond units at the side chain are described. The triene system is introduced using the Lythgoe−Hoffmann La Roche convergent Wittig−Horner approach. The key steps in the preparation of the requisite upper fragments are the introduction of the side chain with the *E*-conjugated aromatic system and its photochemical conversion to the *Z* counterpart.

Introduction

1α,25-Dihydroxyvitamin D_3[2] [**1**, 1α,25-$(OH)_2$-D_3, calcitriol], the hormonally active form of vitamin D_3 (**2**, cholecalciferol), besides its important role in calcium homeostasis,[2a] also promotes cell differentiation and inhibits cell proliferation of various tumor cells, a fact that suggests its possible use in the treatment of cancer.[3] Unfortunately, the therapeutic value of 1α,25-$(OH)_2$-D_3 as an antitumor agent found serious limitations due to its potent calcemic effects.[2n,o,p] For this reason, there is continued and increasing interest aimed at the rational design of new analogues of 1α,25-$(OH)_2$-D_3 with selective biological functions as possible drugs for medical use. However, the incomplete understanding of the conformation or conformations that the hydroxylated side chain of 1α,25-$(OH)_2$-D_3 adopt upon binding to its receptor (VDR) or receptors (VDRs)[4] has led to the synthesis of numerous side-chain modified analogues of which only a few have been identified as promising drugs for the treatment of certain cancers[2n,p] and psoriasis.[5]

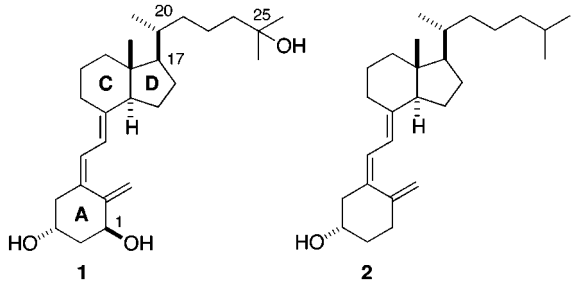

Figure 1.

As part of our efforts to understand the side-chain conformation of calcitriol in its bioactive form, we recently reported[6,7] the synthesis and conformational analysis of four side-chain analogues of 1α,25-$(OH)_2$-D_3. The four compounds in question incorporate conformationally locked units in the form of a double bond or a cyclopropane ring at C17−C20.[8] Here we report the synthesis of four new analogues in which the side chain features both an aromatic ring at C20 and a conjugated double bond at C17−C20.[9,10]

[†] This paper is dedicated to the memory of Prof. Pascual Teresa.

(1)) This work was taken in part from the doctoral thesis of Ana Isabel Fernández Gacio (1999, University of Santiago de Compostela).

(2) For reviews on the chemistry and/or biochemistry of vitamin D, see: (a) Norman, A. W. *Vitamin D the Calcium Homeostatic Steroid Hormone*; Academic Press: New York, 1979. (b) DeLuca, H. F.; Paaren, H. E.; Schnoes, H. K. *Top. Curr. Chem.* **1979**, *83*, 1. (c) Pardo, R.; Santelli, M. *Bull. Soc. Chim. Fr.* **1985**, 98. (d) Jones, G., guest Ed. *Steroids* **1987**, *49*, 1. (e) Ikekawa, N. *Med. Res. Rev.* **1987**, *7*, 333. (f) Quinkert, G. Vitamin D Active Compounds. Part I. *Synform* **1985**, *3*, 41. Part II. *Ibid*. **1986**, *4*, 131. Part III. *Ibid*. **1987**, *5*, 1. (g) Ostrem, V. K.; DeLuca, H. F. *Steroids* **1987**, *49*, 73. (h) Wilson, S. R.; Yasmin, A. Stereoselective Synthesis of Vitamin D. In *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1992; Vol. 10, p 43. (i) Calverley, M. J.; Jones, G. *Antitumor Steroids*; Blikenstaff, R. T., Ed.; Academic Press: New York, 1992. (j) Uskokovic, M. R. *Bioorg. Med. Chem. Lett.* **1993**, *3*, 1783. (k) Dai, H.; Posner, G. H. *Synthesis* **1994**, 1383. (l) Schmalz, H.-G. *Nachr. Chem. Technol. Lab.* **1994**, *42*, 397. (m) Zhu, G.-D.; Okamura, W. H. *Chem. Rev.* **1995**, *95*, 1877. (n) Bouillon, R.; Okamura, W. H.; Norman, A. W. Structure−Function Relationships in the Vitamin D Endocrine System. *Endocr. Rev.* **1995**, *16*, 200. (o) *Vitamin D: Chemistry, Biology and Clinical Applications of the Steroid Hormone*; Norman, A. W., Bouillon, R., Thomasset, M., Eds.; Vitamin D Workshop, Inc.: Riverside, CA, 1997. (p) Feldman, D.; Glorieux, F. H.; Pike, J. W. *Vitamin D*; Academic Press: San Diego, 1997.

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(5) (a) Calcipotriol, an analogue of 1α,25-$(OH)_2$-D_3, has been commercialized under the name of Dovonex by Leo Pharmaceuticals for the local treatment of psoriasis. Binderup, L.; Kragballe, K. *Rev. Contemp. Pharmacother.* **1992**, *3*, 357. (b) For Vitamin D analogues in the treatment of psoriasis, see: Kragballe K. *J. Cell. Biochem.* **1992**, *49*, 46.

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(7) The binding affinities of these analogues to VDR in vitro have been presented at the GESA meeting (Obernai, Alsace, May 1999). As compared with the natural hormone 1α,25-$(OH)_2$-D_3 (100%), the analogue with *Z* stereochemistry binds more efficiently to VDR (190%) and is more effective at promoting cell differentiation (HL-60 cells) (300%) than the natural hormone. The corresponding cyclopropanic derivative of the above *Z* olefinic analogue does not bind significantly to VDR (<1%) but induces cell differentiation (HL-60 cells) (1000%) better than the natural hormone. The *E* olefinic analogue binds poorly (5%) to VDR but is as effective (100%) as the natural hormone at promoting cell differentiation (HL-60).

(8) For conformational analysis of nonlocked side-chain analogues of 1α,25-$(OH)_2$-D_3, see: Yamada, S.; Yamamoto, K.; Masuno, H.; Ohta, M. *J. Med. Chem.* **1998**, *41*, 1467 and references therein.

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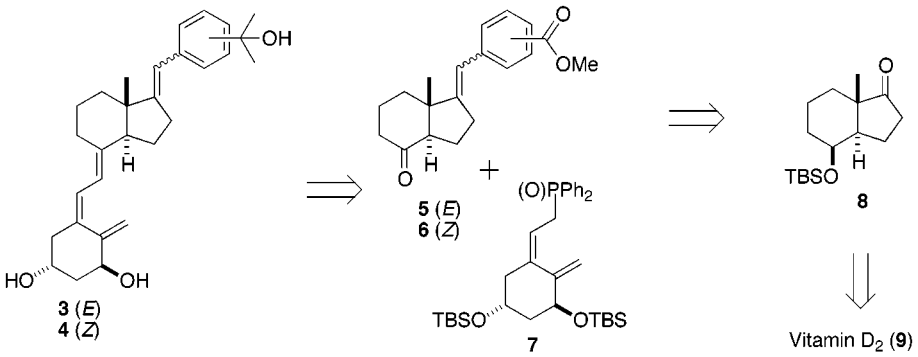
Scheme 1

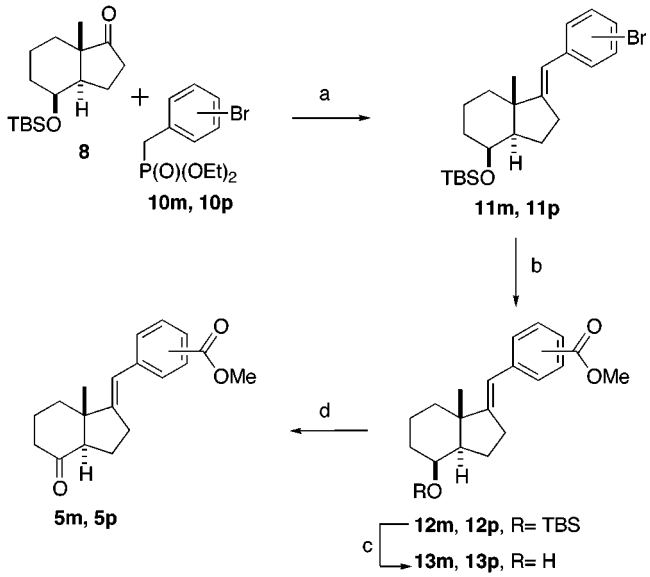


Results and Discussion

General Synthetic Approach. The synthesis of analogues **3** (*E* configuration at C20) and **4** (*Z* configuration at C20) (Scheme 1) follows the mild convergent Wittig−Horner approach originally developed by Lythgoe and later improved by the Hoffmann La Roche group.[2m,11] In this route, **5** or **6** is coupled with the anion of phosphine oxide **7** to provide, after alkylation and deprotection, analogues **3** or **4**, respectively. Ketone **8** (TBS = Si*t*-BuMe$_2$), which is readily prepared by degradation of vitamin D$_2$, serves as the key compound to synthesize the upper fragments **5** and **6**. The key steps are the introduction of aromatic units in the upper fragments, especially in the case of **6**. This route allows the incorporation of organic residues at C25 in the last steps of the synthesis.

Synthesis of Analogues 3. The synthesis of the corresponding upper fragments **5** is shown in Scheme 2. The known ketone **8**, readily prepared from vitamin D$_2$,[12] was separately treated with potassium carbanions of phosphonates **10**[13] to give the *E* olefins **11** (∼70%) and the corresponding *Z*-isomers (∼12%). The *E*/*Z* stereochemistry of these compounds was established by ^{1}H NMR NOE experiments and by comparison of their ^{1}H NMR spectra with those of similar compounds.[14] Palladium-catalyzed carbomethoxylation of bromides **11** in MeOH/DMSO under an atmosphere of CO provided the desired esters **12** (∼85%).[15] Cleavage of the silyl ether protecting groups to give alcohols **13** was followed by PDC oxidation to afford the desired ketones **5** (∼88% over the two steps).

Scheme 2[a]



[a] m = *meta*-series, p = *para*-series. (a) KH, THF, Δ (**11m**, 69%; **11p**, 70%); (b) CO, Pd(OAc)$_2$, Et$_3$N, dppp, MeOH, DMSO, Δ (**12m**, 86%, **12p**, 80%); (c) (HF, MeCN (**13m**, 92%; **13p**, 96%); (d) PDC, CH_2Cl_2 (**5m**, 95%; **5p**, 91%).

Scheme 3 shows the remaining steps leading to analogues **3**. Treatment of the phosphine oxide **7**[2m,16] with butyllithium followed by reaction of the resulting anion with ketones **5** according to known procedures,[11] provided the protected vitamin D analogues **14** (∼91%) with a methoxycarbonyl group at C25 for further functionalization. Treatment of esters **14** with methyllithium and subsequent removal of the silyl groups with tetrabutylammonium fluoride afforded the desired vitamin D analogues **3** (∼80% over the two steps, ∼33% overall yield from ketone **8**, seven steps).

Synthesis of Analogues 4. The introduction of the C17−C20 *Z* double bond proved to be more challenging than anticipated. Initial efforts to introduce the *Z* geometry by reaction of the ylide prepared from phosphonium salt **16** (KO*t*-Bu or NaH) with ketone **8** resulted in the recovery of starting material, presumably for steric reasons (Scheme 4). Attempts to isomerize olefin **12** to **19** by employing the Vedejs protocol[17,18] were unsuccessful due to difficulties in isolating epoxide **18**.

(9) For the synthesis and biological evaluation of side-chain analogues of 1α,25-(OH)$_2$-D$_3$ with aromatic units at C22, see Figadère, B.; Norman, A. W.; Henry, H. L.; Koeffler H. P.; Zhou, J.−Y.; Okamura, W. H. *J. Med. Chem.* **1991**, *34*, 2452.

(10) For other analogues of 1α,25-(OH)$_2$-D$_3$, possesing a double bond at C17−C20, see: Bretting, C.; Hansen, C. M.; Anderson, N. R. *Vitamin D, A Pluripotent Steroid Hormone: Structural Studies, Molecular Endocrinology and Clinical Applications*; Norman, A. W., Bouillon, R., Thomasset, M., Eds.; Walter de Gruyter: Berlin, 1994; pp 73−74.

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(15) Initial attempts to functionalize bromide **11** through its anion to give ester **12** using different electrophiles [MeOAc, AcCl, MeOC(O)Cl] resulted in poor yields (25−65%) due to extensive protonation.

(16) Compound **7** was prepared as per Mouriño, A.; Torneiro, M.; Vitale, C.; Fernández, S.; Pérez-Sestelo, J.; Annè, S.; Gregorio, C. *Tetrahedron Lett.* **1997**, *38*, 4713.

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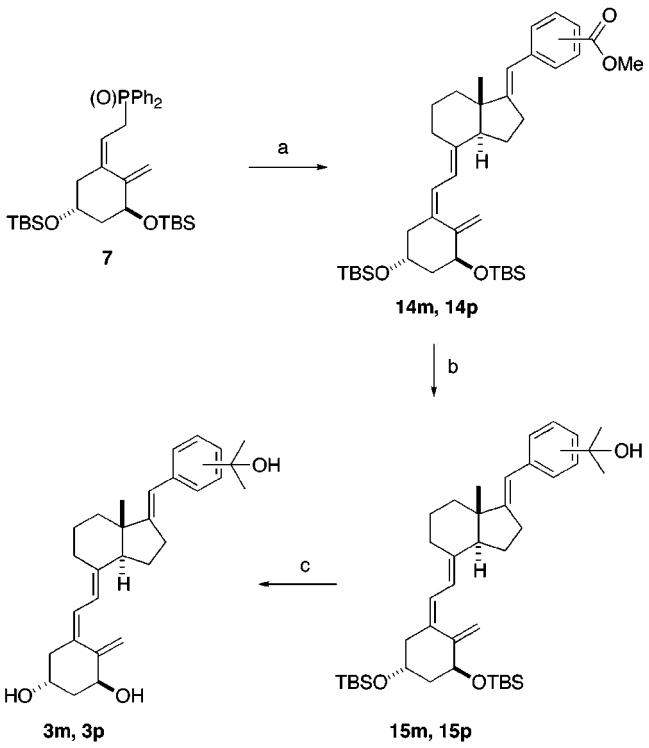
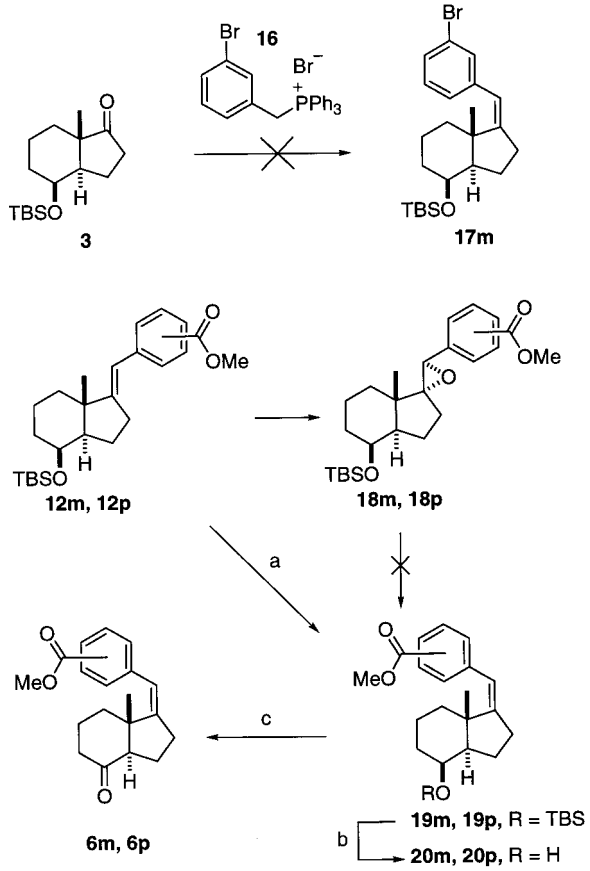
(18) This procedure has been successfully used in these laboratories for the introduction of olefinic side chains (ref 14).

Scheme 3[a]



[a] *n*-BuLi, THF, −78 °C; **5m** or **5p** (**14m**, 94%; **14p**, 89%); (b) MeLi, THF, −78 °C (**15m**, 90%; **15p**, 95%); (c) *n*-Bu_4NF, THF (**3m**, 90%; **3p**, 80%).

Scheme 4[a]



[a] (a) *hν*, THF (**19m**, 75%; **19p**, 78%); (b) HF, MeCN (**20m**, 94%; **20p**, 92%); (c) PDC, CH_2Cl_2 (**6m**, 97%; **6b**, 96%).

At this point we decided to explore photochemical isomerization as an alternative strategy to obtain the *Z* analogues. After much experimentation we were pleased to find that direct irradiation (THF, medium pressure-Hg, Pyrex reactor, 90 min) of (*E*)-ester **12** proceeded cleanly to provide a separable 4:1 mixture of the desired (*Z*)-ester **19** (∼75%) and starting material (17%).[19,20] Desilylation and oxidation afforded ketones **6** (∼96%), which were required for the Wittig−Horner coupling.

The remaning steps to vitamin D analogues **4** are depicted in Scheme 5 and are similar to those described for the preparation of vitamin D analogues **3** (two steps, overall yield from ketone **8**, 28%).

Biological Evaluation. The new analogues failed to bind significantly to the calf thymus vitamin D receptor (VDR) in in vitro competitive binding assay (RCI assay).[21] The RCIs values of **3m**, **3p**, and **4p** were all <1, whereas the RCI value for **4m** was 1.5 as compared for the reference compound 1α,25-$(OH)_2$-D_3. This poor binding in relation to structurally related analogues[6,7] may be attributed to steric hindrance by the aromatic unit.

Promotion of cell differentiation (in HL-60 human leukemia cells) and intestinal Ca absorption (in CaCo cells) have so far been tested only in the case of **4m**.[22,2n] This analogue proved to be as active as the natural hormone 1α,25-$(OH)_2$-D_3 regarding cell differentiation and was found to not stimulate the Ca-transport.

The results of broader biological screening of compounds **3m**, **3p**, **4m**, and **4p** will be reported in due course. Small samples of these analogues are available upon request for further biological evaluation.

In summary, we used the Lythgoe-Hoffmann La Roche approach to synthesize four new analogues of the hormone 1α,25-$(OH)_2$-D_3 with partially locked side chains (seven to eight steps, overall yield ∼30%). Key steps of the synthesis are the stereoselective installation of the *E* and *Z* olefinic side-chain fragments and the photochemical step to isomerize *E* double bonds to *Z* double bonds. This route allows the easy preparation of related vitamin D analogues by simple funcionalization at C25 in the last steps of the synthesis.

Experimental Section

General Methods. All reactions involving oxygen- or moisture-sensitive compounds were carried out under a dry argon atmosphere. Reaction temperatures refer to external bath temperatures. All dry solvents were distilled under argon immediately prior to use. Tetrahydrofuran (THF), ether (Et_2O), and benzene were distilled from Na/benzophenone. Dichloromethane (CH_2Cl_2) was distilled from P_2O_5. Absolute methanol and ethanol were distilled from Mg/I_2. Pyridine was distilled from KOH and CaH_2. Hexane, diisopropylamine (*i*-Pr_2NH), and triethylamine (Et_3N) were distilled from CaH_2.

(19) Irradiation of (*E*)-bromide **11** produces a 4:1 mixture of *Z*- and *E*-bromides with significant amounts of the corresponding protonated compounds. Difficulties were encountered in separating the *Z*- and *E*-bromides by chromatography, and this led us to carry out the photochemical experiments on the (*E*)-esters **12**.

(20) Attempts to improve the Z/E ratio (4:1) of isomers using various triplet sensitizers (acetophenone, fluorenone, anthracene, tetracene) were unsuccessful.

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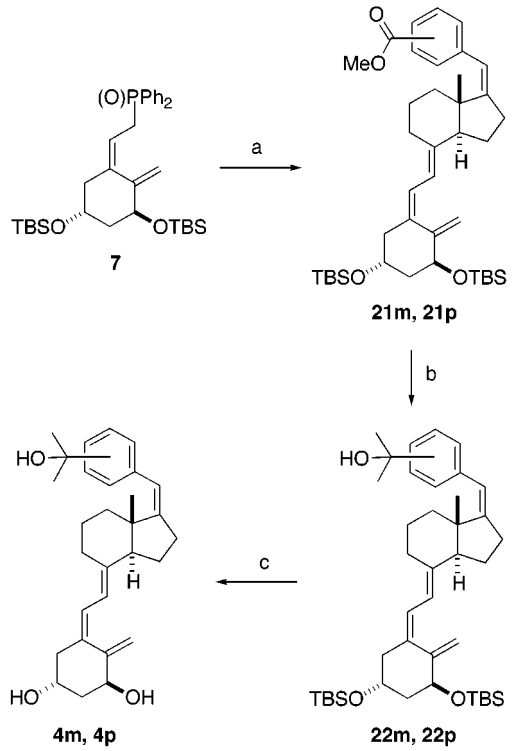
(22) The differentiation was expressed as the maturation parameter nitroblue tetrazolium reduction. The cells were cultured in serum free medium (i.e., without vitamin D binding protein).

Scheme 5[a]



[a] (a) *n*-BuLi, THF, −78 °C; **6m** or **6p** (**21m**, 94%; **21p**, 82%); (b) MeLi, THF, −78 °C (**22m**, 98%; **22p**, 93%); (c) *n*-Bu_4NF, THF (**4m**, 85%; **4p**, 85%).

Dimethyl sulfoxide (DMSO) was stored over 4 Å molecular sieves. KH was purified by successive washes with hexane and THF, evaporation of the solvents, and drying of the resulting solid in vacuo. Dppp [1,3-bis-(diphenylphoshino)propane] was purchased from Aldrich and used without further purification. Liquid reagents or solutions of reagents were added by syringe or cannula. Photochemical reactions were performed with a Hanovia lamp (450 W) of medium mercury pressure in a Pyrex glass reactor. Organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated using a rotary evaporator at aspirator pressure (20−30 mmHg). Reactions were monitored by thin-layer chromatography (TLC) using aluminum-backed Merck 60 silica gel plates (0.2 mm thickness). After viewing with ultraviolet illumination at 254 nm, the plates were visualized by immersion in a solution of phosphomolybdic acid in MeOH (5%), followed by heating. Flash column chromatography was performed with Merck 60 (230−400 mesh) silica gel. All NMR spectra were measured using solutions in $CDCl_3$ unless otherwise stated. Chemical shifts are reported on the δ scale (ppm) downfield from tetramethylsilane ($\delta = 0.0$) using the residual solvent signal as an internal standard: 7.26 (^{1}H), 77.0 triplet (^{13}C). All coupling constants are measured in hertz (Hz). Distortionless enhancement by polarization transfer (DEPT) was used to assign carbon types. Unless otherwise stated, mass spectra were measured using electron-impact ionization at 70 eV. Melting points (open capillary tubes) are uncorrected.

8*β*-*tert*-Butyldimethylsilyloxy-(17*E*)-[1-(3-bromophenyl)-methylidene]-de-A,B-androstane (11m). A solution of ketone **8** (1.88 g, 6.65 mmol) and diethyl 3-bromobenzylphosphonate **10m** (7.15 g, 23.28 mmol) in dry THF (40 mL) was added by cannula to a suspension of KH (0.85 g, 21.2 mmol) in dry THF (20 mL). The mixture was refluxed for 4 h and the reaction quenched with HCl (5%). The mixture was washed with water, dried, filtered, and concentrated in vacuo. The residue, an *E*/*Z* mixture (4:1), was purified by flash chromatography (hexanes) to give 0.34 g of **11m** [12%, $R_f = 0.7$ (hexanes), colorless oil] and 1.97 g of **17m** [69%, $R_f = 0.63$ (hexanes), colorless oil]. ^{1}H NMR: 7.47 (1 H, m), 7.20 (3 H, m), 5.94 (1 H, s), 4.13 (1 H, m), 2.74−2.47 (3 H, m), 1.20 (1 H, s), 0.92 (9 H, s), 0.06 (6 H, 2 s). ^{13}C NMR: 157.0 (C), 141.0 (C), 131.1 (CH), 129.7 (CH), 128.4 (CH), 126.8 (CH), 122.0 (C), 115.3 (CH), 69.2 (CH), 50.5 (CH), 45.0 (C), 36.8 (CH_2), 34.6 (CH_2), 28.3 (CH_2), 25.8 (3 CH_3), 24.1 (CH_2), 21.6 (CH_3), 18.0 (C), 17.6 (CH_2), −4.8 (CH_3), −5.2 (CH_3). MS [*m*/*e*, (%)]: 436 (MH^+, 35), 435 (MH^+, 39), 379 [$M^+ - C(CH_3)_3$, 45], 303 ($M^+ -$ OTBS, 100). Anal. Calcd for $C_{23}H_{35}OBrSi$: C, 63.57; H, 8.13; found: C, 63.52; H, 8.19.

(17*E*)-[8*β*-(*tert*-Butyldimethylsilyloxy)-1-(4-bromophenyl)methylidene]-de-A,B-androstane (11p). Procedure as above. **11p** [13%, $R_f = 0.7$ (hexanes), colorless oil] and 2.1 g of **17p** [70%, $R_f = 0.6$ (hexanes), colorless oil].

8*β*-*tert*-Butyldimethylsilyloxy-(17*E*)-{1-[3-(methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstane (12m). Et_3N (185 μL, 1.44 mmol), dppp (131 mg, 0.32 mmol), and $Pd(OAc)_2$ (65 mg, 0.29 mmol) were added to a solution of **11m** (628 mg, 1.44 mmol) in DMSO (30 mL) and MeOH (10 mL). The resulting suspension was purged with CO and stirred at 80 °C in a CO atmosphere (balloon pressure). After 12 h of stirring, H_2O was added, and the aqueous portion was extracted with EtOAc. The combined organic fractions were dried, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (hexanes) to give 512 mg of **12m** [86%, $R_f = 0.33$ (3% Et_2O/hexanes), colorless oil]. ^{1}H NMR: 8.01 (1 H, s), 7.82 (1 H, d, $J = 7.69$ Hz), 7.48 (1 H, d, $J = 7.87$ Hz), 7.34 (1 H, t, $J = 7.69$ Hz, H−Ar), 6.03 (1 H, s, H-20), 4.09 (1 H, m), 3.89 (3 H, s), 2.80−2.48 (2 H, m), 1.12 (3 H, s), 0.93 (9 H, s), 0.05 (6 H, s). ^{13}C NMR: 167.0 (C), 157.2 (C), 138.9 (C), 132.3 (CH), 129.8 (C), 129.2 (CH), 128.0 (CH), 126.4 (CH), 115.4 (CH), 69.0 (CH), 51.8 (CH_3), 50.3 (CH), 45.0 (C), 36.7 (CH_2), 34.5 (CH_2), 28.2 (CH_2), 25.7 (3 CH_3), 23.9 (CH_2), 21.5 (CH_3), 17.9 (CH_2), 17.5 (C), −4.9 (CH_3), −5.26 (CH_3). MS [*m*/*e*, (%)]: 437 ($M^+ + Na$, 19), 415 (MH^+, 100), 383 ($M^+ -$ OMe, 56), 357[$M^+ - C(CH_3)_3$, 35], 283 ($M^+ -$ OTBS, 77). HRMS: calcd for $C_{25}H_{39}O_3Si$: 415.2668; found: 415.2667. UV (EtOH) λ_{max} 254 nm; λ_{min} 228 nm.

8*β*-*tert*-Butyldimethylsilyloxy-(17*E*)-{1-[4-(methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstane (12p). Procedure as above. **12p** [80%, $R_f = 0.31$ (3% Et_2O/hexanes), white solid, mp 82−84 °C].

(17*E*)-{1-[3-(Methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstan-8*β*-ol (13m). An aqueous solution of HF (48%, 60 drops) was added dropwise to a solution of **12m** (440 mg, 1.06 mmol) in acetonitrile (15 mL). The resulting heterogeneous mixture was stirred at room temperature for 3 h and then treated with saturated aqueous $NaHCO_3$. The aqueous portion was extracted with Et_2O. The combined organic fractions were dried, filtered, and concentrated in vacuo. Flash chromatography (35% Et_2O/hexanes) afforded 294 mg of **13m** [92%, $R_f = 0.32$ (50% Et_2O/hexanes), colorless oil]. ^{1}H NMR: 7.92 (1 H, s), 7.75 (1 H, d, $J = 7.7$ Hz), 7.42 (1 H, d, $J = 7.8$ Hz), 7.29 (1 H, dd, $J = 7.7, 7.7$ Hz), 5.98 (1 H, s), 4.13 (1 H, m), 3.83 (3 H, s), 2.78 (1 H, m), 2.46 (1 H, m), 1.07 (3 H, s). ^{13}C NMR: 167.3 (C═O), 156.7 (C), 138.8 (C), 132.5 (CH), 129.9 (C), 129.2 (CH), 128.1 (CH), 126.6 (CH), 115.8 (CH), 68.9 (CH), 52.1 (CH), 50.0 (CH_3), 44.8 (C), 36.5 (CH_2), 33.8 (CH_2), 28.2 (CH_2), 23.5 (CH_2), 21.2 (CH_3), 17.4 (CH_2). MS [FAB, *m*/*e*, (%)]: 322 ($M^+ - H + Na$, 100), 283 ($M^+ -$ OH, 44), 251 ($MH^+ - CO_2Me$, 21). HRMS: calcd for $C_{19}H_{25}O_3$: 301.1804; found: 301.1803.

(17*E*)-{1-[4-(Methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstan-8*β*-ol (13p). Procedure as above. **13p** [96%, $R_f = 0.32$ (40% Et_2O/hexanes), colorless oil].

(17*E*)-{1-[3-(Methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstan-8-one (5m). PDC (221 mg, 0.59 mmol) was added to a solution of **13m** (117 mg, 0.39 mmol) in CH_2Cl_2 (20 mL). After being stirred 8 h, the resulting suspension was filtered through Celite and concentrated. The resulting residue was purified by flash chromatography (20% Et_2O/hexanes) to afford 111 mg of pure **5m** [95%, $R_f = 0.34$ (40% Et_2O/hexanes), white solid, mp 65−67 °C]. ^{1}H NMR: 7.97 (1 H, s), 7.83 (1 H, d, $J = 7.6$ Hz), 7.47 (1 H, d, $J = 7.81$ Hz), 7.36 (1 H, dd, $J = 7.68, 7.81$ Hz), 6.16 (1 H, s), 3.89 (3 H, s), 2.81−2.52 (3 H, m, H-14, 2 H-16), 0.83 (3 H, s, Me-18). ^{13}C NMR: 210.8 (C), 166.9

(C), 153.6 (C), 138.0 (C), 132.4 (CH), 130.0 (C), 129.2 (CH), 128.2 (CH), 127.0 (CH), 117.5 (CH), 58.9 (CH), 52.0 (CH_3), 51.9 (C), 40.9 (CH_2), 35.0 (CH_2), 27.9 (CH_2), 23.5 (CH_2), 20.4 (CH_2), 19.5 (CH_3). Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.47; H, 7.38; found: C, 76.24; H, 7.59.

(17*E*)-{1-[4-(Methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstan-8-one (5p). Procedure as above. **5p** [91%, R_f = 0.4 (40% Et_2O/hexanes), white solid, mp 102−103 °C].

(17*E*)-1α-*tert*-Butyldimethylsilyloxy-20-[3-(methyloxycarbonyl)phenyl]-17,20-didehydro-21,22,23,24,25,26,27-heptanorvitamin D_3 *tert*-butyldimethylsilyl ether (14m). A solution of *n*-BuLi (2.25 M in hexanes, 190 μL, 0.428 mmol) was added dropwise by syringe to a solution of the phosphine oxide **7** (277 mg, 0.476 mmol) in THF (6 mL) at −78 °C. The resulting deep red solution was stirred at −78 °C for 1 h followed by the slow addition of a solution of ketone **5m** (71 mg, 0.238 mmol) in THF (3 mL). The red solution was stirred in the dark at −78 °C for 4 h and then warmed to −40 °C over 2 h. The reaction was quenched with H_2O. The mixture was extracted with Et_2O, and the combined organic fractions were washed with brine, dried, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (2−80% Et_2O/hexanes) to give 146 mg of pure **14m** [94%, R_f = 0.6 (10% Et_2O/hexanes), colorless oil]. ^{1}H NMR (CD_2Cl_2, 250 MHz, δ): 8.01 (1 H, s,), 7.80 (1 H, d, *J* = 7.7 Hz), 7.53 (1 H, d, *J* = 7.69 Hz), 7.37 (1 H, dd, *J* = 7.7, 7.69 Hz), 6.30, 6.14 (2 H, AB, *J* = 11.1 Hz), 6.16 (1 H, s), 5.23 (1 H, broad s), 4.90 (1 H, broad s), 4.42 (1 H, m), 4.22 (1 H, m), 3.89 (3 H, s), 2.77−2.52−2.18 (3 H, m), 0.91 (9 H, s), 0.90 (9 H, s), 0.76 (3 H, s), 0.10 (6 H, s), 0.09 (6 H, s). ^{13}C NMR (CD_2Cl_2, 62.83 MHz, δ): 167.8 (C), 157.5 (C), 149.3 (C), 140.8 (C), 139.8 (C), 136.6 (C), 133.2 (CH), 131.0 (C), 130.0 (CH), 129.1 (CH), 127.4 (CH), 123.7 (CH), 119.4 (CH), 117.8 (CH), 112.0 (CH_2), 72.8 (CH), 68.4 (CH), 54.7 (CH), 52.7 (CH_3), 49.3 (C), 46.8 (CH_2), 45.7 (CH_2), 37.5 (CH_2), 29.7 (2 CH_2), 26.5 (6 CH_3), 24.1 (2 CH_2), 19.6 (CH_3), 19.0 (C), 18.8 (C), −4.10 (CH_3). MS [FAB, *m*/*e*, (%)]: 663 (MH^+, 7), 661 (M^+ − H, 7). HRMS: calcd for $C_{40}H_{63}O_4Si_2$: 663.4265; found: 663.4268.

(17*E*)-1α-*tert*-Butyldimethylsilyloxy-20-[4-(methyloxycarbonyl)phenyl]-17,20-didehydro-21,22,23,24,25,26,27-heptanorvitamin D_3 *tert*-butyldimethylsilyl ether (14p). Procedure as above. **14p** [89%, R_f = 0.83 (20% EtOAc/hexanes), colorless oil].

(17*E*)-1α-*tert*-Butyldimethylsilyloxy-20-[3-(dimethylhydroxymethyl)phenyl]-17,20-didehydro-21,22,23,24,25,-26,27-heptanorvitamin D_3 *tert*-butyldimethylsilyl ether (15m). A solution of MeLi (1.5 M in Et_2O, 0.32 mL, 0.485 mmol) was added by syringe to a solution of **14m** (64 mg, 0.097 mmol) in THF (10 mL) at −78 °C. After 45 min, the reaction was quenched with H_2O. The mixture was extracted with EtOAc. The combined organic fractions were washed with HCl (5%) and H_2O, dried, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (20−40% Et_2O/hexanes) to give 58 mg of pure **15m** [90%, R_f = 0.58 (20% EtOAc/hexanes), colorless oil]. ^{1}H NMR (MeOD, 250 MHz, δ): 7.49 (1 H, s), 7.28 (3 H, m), 6.33, 6.18 (2 H, AB, *J* = 11.2 Hz), 6.17 (1 H, s), 5.27 (1 H, broad s), 4.90 (1 H, broad s), 4.49 (1 H, m, H-1), 4.29 (1 H, m, H-3), 2.88 (1 H, m), 1.57 (6 H, s), 0.94 (18 H, s), 0.80 (3 H, s), 0.14 (6 H, s), 0.13 (6 H, 2 s). ^{13}C NMR (MeOD, 62.83 MHz, δ): 155.5 (C), 150.6 (C), 150.0 (C), 141.3 (C), 139.6 (C), 136.8 (C), 128.9 (CH), 127.3 (CH), 125.7 (CH), 124.2 (CH), 123.1 (CH), 119.6 (CH), 119.6 (CH), 111.9 (CH_2), 73.4 (CH), 72.9 (C), 68.9 (CH), 55.3 (CH), 47.2 (CH_2), 46.1 (CH_2), 38.0 (CH_2), 32.0 (2 CH_3), 30.0 (CH_2), 29.7 (CH_2), 26.5 (3 CH_3), 26.4 (3 CH_3), 24.5 (CH_2), 24.4 (CH_2), 19.6 (CH_3), 19.2 (C), 19.0 (C), −4.2 (CH_3), −4.4 (CH_3), −4.5 (CH_3), −4.7 (CH_3). MS [FAB, *m*/*e*, (%)]: 686 (MH^+ + Na, 44), 663 (MH^+, 44), 661 (M^+ − H, 52), 645 (M^+ − OH, 38), 531 (M^+ − OTBS, 31). HRMS: calcd for $C_{41}H_{67}O_3Si_2$: 663.4629; found: 663.4630.

(17*E*)-1α-*tert*-Butyldimethylsilyloxy-20-[4-(dimethylhydroxymethyl)phenyl]-17,20-didehydro-21,22,23,24,25,-26,27-heptanorvitamin D_3 *tert*-butyldimethylsilyl ether (15p). Procedure as above. **15p** [95%, R_f = 0.52 (20% EtOAc/hexanes), colorless oil].

(17*E*)-1α-20-[3-(Dimethylhydroxymethyl)phenyl]-17,-20-didehydro-21,22,23,24,25,26,27-heptanorvitamin D_3 (3m). A solution of TBAF (1.11 M in THF, 0.53 mL, 0.59 mmol) was added by syringe to a solution of **15m** (39 mg, 0.059 mmol) in THF (3 mL). After the mixture was stirred at room temperature for 26 h in the dark, a solution of NH_4Cl was added, and the resulting mixture was extracted with Et_2O. The combined organic extracts were dried, filtered, and concentrated in vacuo to give a residue that was purified by flash chromatography (80−100% Et_2O/hexanes) to afford 23 mg of pure vitamin D analogue **3m** [90%, R_f = 0.55 (100% EtOAc/hexanes), white solid, mp 100 °C (dec)]. ^{1}H NMR (MeOD, 300 MHz, δ): 7.49 (1 H, s), 7.28 (3 H, m), 6.39, 6.21 (2 H, AB, *J* = 11.1 Hz), 6.17 (1 H, s), 5.35 (1 H, broad s), 4.97 (1 H, broad s), 4.41 (1 H, m), 4.17 (1 H, m), 2.89 (1 H, m), 1.57 (6 H, s), 0.80 (3 H, s). ^{13}C NMR (MeOD, 75.40 MHz, δ): 156.0 (C), 151.0 (C), 150.2 (C), 142.2 (C), 140.0 (C), 136.7 (C), 129.3 (CH), 127.7 (CH), 126.1 (CH), 125.1 (CH), 123.5 (CH), 120.0 (CH), 119.9 (CH), 112.5 (CH_2), 73.4 (C), 71.9 (CH), 67.8 (CH), 55.8 (CH), 46.6 (CH_2), 44.1 (CH_2), 38.4 (CH_2), 32.4 (2 CH_3), 30.5 (CH_2), 30.1 (CH_2), 24.9 (2 CH_2), 19.8 (CH_3). MS [*m*/*e*, (%)]: 434 (M^+, 7), 416 (M^+ − H_2O, 48), 398 (M^+ − 2 H_2O, 96), 111 (100). HRMS: calcd for $C_{29}H_{38}O_3$: 434.2821; found: 434.2801.

(17*E*)-1α-20-[4-(Dimethylhydroxymethyl)phenyl]-17,-20-didehydro-21,22,23,24,25,26, 27-heptanorvitamin D_3 (3p). Procedure as above. **3p** [80%, R_f = 0.25 (80% EtOAc/hexanes), white solid, mp 122 °C (dec)]. ^{1}H NMR (MeOD, 300 MHz): 7.45 (2 H, d, *J* = 8.3 Hz), 7.31 (2 H, d, *J* = 8.3 Hz), 6.39, 6.22 (2 H, AB, *J* = 11.1 Hz), 6.13 (1 H, s), 5.35 (1 H, broad s), 4.96 (1 H, broad s), 4.41 (1 H, m), 4.17 (1 H, m), 1.56 (6 H, s), 0.80 (3 H, s). ^{13}C NMR (MeOD, 75.40 MHz): 155.4 (C), 149.8 (C), 148.2 (C), 141.8 (C), 138.1 (C), 136.3 (C), 129.0 (2 CH), 125.4 (2 CH), 124.7 (CH), 119.5 (CH), 118.9 (CH), 112.1 (CH_2), 72.8 (C), 71.5 (CH), 67.4 (CH), 55.4 (CH), 49.8 (C), 46.1 (CH_2), 43.7 (CH_2), 38.0 (CH_2), 31.8 (2 CH_3), 30.0 (CH_2), 26.7 (CH_2), 24.5 (2 CH_2), 19.4 (CH_3). UV (*i*-PrOH) λ_{max} (ε) 260 nm (44.000). MS [*m*/*e*, (%)]: 434 (M^+, 51), 416 (M^+ − H_2O, 78), 398 (M^+ − 2 H_2O, 62). HRMS: calcd for $C_{29}H_{38}O_3$: 434.2821; found: 434.2831.

8β-*tert*-Butyldimethylsilyloxy-(17*Z*)-{1-[3-(methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstane (19m). A solution of **12m** (24 mg, 0.06 mmol) in THF (10 mL) was irradiated during 1 h 30 min and then concentrated. The residue, which consisted of a 4:1 *Z*/*E* mixture, was purified by flash chromatography (1% Et_2O/hexanes) to give 18 mg of **19m** [75%, R_{fZ} = 0.37 (3% Et_2O/hexanes), colorless oil]. 4 mg of the starting ester **12m** was recovered (16%). ^{1}H NMR: 7.82 (2 H, broad s), 7.31 (2 H, m), 6.17 (1 H, s), 4.03 (1 H, m), 3.88 (3 H, s), 2.63 (1 H, m), 2.32 (1 H, m), 1.25 (3 H, s), 0.87 (9 H, s), 0.00 (3 H, s), −0.02 (3 H, s).^{13}C NMR: 167.2 (C), 155.3 (C), 139.2 (C), 133.8 (CH), 130.4 (CH), 129.2 (C), 127.3 (CH), 127.0 (CH), 117.8 (CH), 69.6 (CH), 52.5 (CH), 51.9 (CH_3), 44.5 (C), 37.2 (CH_2), 34.2 (CH_2), 31.0 (CH_2), 25.7 (3 CH_3), 23.0 (CH_2), 20.7 (CH_3), 17.9 (C), 17.5 (CH_2), −4.9 (CH_3), −5.2 (CH_3). MS [FAB, *m*/*e*, (%)]: 437 (M^+ + Na, 19), 415 (MH^+, 100), 383 (M^+ − OMe, 44), 357 [M^+ − $C(CH_3)_3$, 26], 283 (M^+ − OTBS, 62). HRMS: calcd for $C_{25}H_{39}O_3Si$: 415.2668; found: 415.2662. UV (EtOH) λ_{max} 248 nm; λ_{min} 228 nm.

8β-*tert*-Butyldimethylsilyloxy-(17*Z*)-{1-[4-(methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstane (19p). Procedure as above. **19p** [78%, R_{fZ} = 0.36 (3% Et_2O/hexanes), white solid, mp 71−72 °C]. Ester **12p** was recovered (18%).

(17*Z*)-{1-[3-(Methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstan-8β-ol (20m). Similar procedure to **13m** and **13p**. **20m** [94%, R_f = 0.38 (50% Et_2O/hexanes), colorless oil]. ^{1}H NMR: 7.87−7.84 (2 H, m), 7.36−7.26 (2 H, m), 6.22 (1 H, s), 4.13 (1 H, m), 3.91 (3 H, s), 2.69−2.39 (3 H, m), 1.28 (3 H, s). ^{13}C NMR: 167.3 (C), 154.6 (C), 139.1 (C), 133.8 (CH), 130.4 (CH), 129.3 (C), 127.5 (CH), 127.1 (CH), 118.2 (CH), 69.5 (CH), 52.1 (CH_3), 44.2 (C), 37.1 (CH_2), 33.5 (CH_2), 30.9 (CH_2), 22.5 (CH_2), 20.4 (CH_3), 17.3 (CH_2). MS [FAB, *m*/*e*, (%)]: 322 (M^+ − H + Na, 100), 301 (MH^+, 85), 283 (M^+ − OH, 95), 269 (M^+ − OMe, 36), 251 (MH^+ − CO_2Me, 21). HRMS: calcd for $C_{19}H_{25}O_3$: 301.1804; found: 301.1802.

(17*Z*)-{1-[4-(Methyloxycarbonyl)phenyl]methylidene}-

de-A,B-androstan-8*β*-ol (20p). Procedure as above. **20p** [107 mg, 92%, R_f = 0.37 (40% Et_2O/hexanes), white solid, mp 122 °C].

(17*Z*)-{1-[3-(Methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstan-8-one (6m). Procedure as **5m** and **5p**. **6m** [97%, R_f = 0.34 (40% Et_2O/hexanes)]. ^{1}H NMR: 7.91−7.85 (2 H, m), 7.35 (2 H, m), 6.36 (1 H, s), 3.92 (3 H, s), 2.38−2.76 (3 H, m, H-14), 0.98 (3 H, s). ^{13}C NMR: 211.2 (C), 167.1 (C), 152.3 (C), 138.6 (C), 133.5 (CH), 130.2 (CH), 129.6 (C), 127.8 (CH), 127.5 (CH), 120.0 (CH), 61.4 (CH), 52.1 (CH_3), 50.8 (C), 40.9 (CH_2), 35.5 (CH_2), 30.8 (CH_2), 23.6 (CH_2), 19.5 (CH_2), 19.4 (CH_3). MS [FAB, *m*/*e*, (%)]: 321 (M^+ + Na, 54), 299 (MH^+, 100), 283 (M^+ − CH_3, 25), 267 (M^+ − OMe, 74), 237 (37). HRMS: calcd for $C_{19}H_{23}O_3$: 299.1647; found: 299.1643.

(17*Z*)-{1-[4-(Methyloxycarbonyl)phenyl]methylidene}-de-A,B-androstan-8-one (6p). Procedure as above. **6p** [37 mg, 96%, R_f = 0.5 (40% Et_2O/hexanes), white solid, mp 91−93 °C].

(17*Z*)-1α-*tert*-Butyldimethylsilyloxy-20-[3-(methyloxycarbonyl)phenyl]-17,20-didehydro-21,22,23,24,25,26,27-heptanorvitamin D_3 *tert*-butyldimethylsilyl ether (21m). Procedure as for **14m** and **14p**. **21m** [94%, R_f = 0.67 (10% Et_2O/hexanes), colorless oil]. ^{1}H NMR (CD_2Cl_2, 250 MHz, δ): 7.82 (2 H, m), 7.33 (2 H, m), 6.33 (1 H, s), 6.24, 6.10 (2 H, AB, J = 11.2 Hz), 5.22 (1 H, broad s), 4.87 (1 H, broad s), 4.40 (1 H, m), 4.18 (1 H, m), 3.87 (3 H, s), 0.90 (9 H, s), 0.87 (9 H, s), 0.87 (3 H, s), 0.09 (6 H, s), 0.06 (6 H, s). ^{13}C NMR (CD_2Cl_2, 62.83 MHz, δ): 167.8 (C=O), 155.6 (C), 149.3 (C), 140.8 (C), 140.1 (C), 136.5 (C), 134.4 (CH), 131.0 (CH), 130.3 (C), 128.3 (CH), 127.8 (CH), 123.7 (CH), 120.2 (CH), 119.5 (CH), 112.0 (CH_2), 72.8 (CH), 68.4 (CH), 57.1 (CH), 52.7 (CH_3), 48.0 (C), 46.8 (CH_2), 45.7 (CH_2), 37.7 (CH_2), 32.2 (CH_2), 29.4 (CH_2), 26.4 (6 CH_3), 24.0 (CH_2), 23.1 (CH_2), 19.3 (CH_3), 19.0 (C), 18.8 (C), −4.1 (CH_3), −4.2 (CH_3), −4.3 (CH_3), −4.4 (CH_3). MS [FAB, *m*/*e*, (%)]: 663 (MH^+, 14), 661 (M^+ − H, 13), 531 (M^+ − OTBS, 6). HRMS: calcd for $C_{40}H_{63}O_4Si_2$: 663.4265; found: 663.4263.

(17*Z*)-1α-*tert*-Butyldimethylsilyloxy-20-[4-(methyloxycarbonyl)phenyl]-17,20-didehydro-21,22,23,24,25,26,27-heptanorvitamin D_3 *tert*-butyldimethylsilyl ether (21p). Procedure as above. **21p** [82%, R_f = 0.88 (20% EtOAc/hexanes), colorless oil].

(17*Z*)-1α-*tert*-Butyldimethylsilyloxy-20-[3-(dimethylhydroxymethyl)phenyl]-17,20-didehydro-21,22,23,24,25,26,-27-heptanorvitamin D_3 *tert*-butyldimethylsilyl ether (22m). Procedure as for **15m** and **15p**. **22m** [98%, R_f = 0.54 (20% EtOAc/hexanes), oil]. ^{1}H NMR (MeOD, 250 MHz, δ): 7.35 (1 H, d, J = 7.9 Hz), 7.32 (1 H, s), 7.23 (1 H, t, J = 7.5 Hz), 7.04 (1 H, d, J = 7.4 Hz), 6.39 (1 H, s), 6.28, 6.16 (2 H, AB, J = 11.0 Hz), 5.26 (1 H, broad s), 4.90 (1 H, broad s), 4.49 (1 H, m), 4.28 (1 H, m), 2.73 (1 H, m), 2.20 (2 H, m), 1.56 [3 H, s], 1.55 [3 H, s], 0.95 (9 H, s), 0.94 (3 H, s), 0.93 (9 H, s), 0.15 (6 H, s), 0.12 (6 H, s). ^{13}C NMR (MeOD, 62.83 MHz, δ): 154.3 (C), 149.9 (2 C), 141.3 (C), 139.7 (C), 136.7 (C), 128.2 (CH), 126.7 (CH), 124.2 (CH), 123.2 (CH), 122.2 (CH), 119.9 (CH), 112.0 (CH_2), 73.4 (CH), 72.8 (C), 68.9 (CH), 57.7 (CH), 47.2 (CH_2), 46.1 (CH_2), 38.1 (CH_2), 32.3 (CH_2), 32.0 (CH_3), 31.9 (CH_3), 29.8 (CH_2), 26.5 (3 CH_3), 26.4 (3 CH_3), 24.3 (CH_2), 23.6 (CH_2), 19.3 (CH_3), 19.2 (C), 19.0 (C), −4.2 (CH_3), −4.4 (CH_3), −4.5 (CH_3), −4.7 (CH_3). HRMS: calcd for $C_{41}H_{67}O_3Si_2$: 663.4629; found: 663.4624.

(17*Z*)-1α-*tert*-Butyldimethylsilyloxy-20-[4-(dimethylhydroxymethyl)phenyl]-17,20-didehydro-21,22,23,24,25,26,-27-heptanorvitamin D_3 *tert*-butyldimethylsilyl Ether (22p). Procedure as above. **22p** [93%, R_f = 0.53 (20% EtOAc/hexanes), colorless oil].

(17*Z*)-1α-20-[3-(Dimethylhydroxymethyl)phenyl]-17,-20-didehydro-21,22,23,24,25,26, 27-heptanorvitamin D_3 (4m). Procedure as for **3m** and **3p**. **4m** [85%, R_f = 0.27 (80% EtOAc/hexanes), white solid, mp 92 °C (dec)]. ^{1}H NMR (MeOD, 300 MHz, δ): 7.34 (1 H, d, J = 7.5 Hz), 7.33 (1 H, s), 7.23 (1 H, t, J = 7.5 Hz), 7.04 (1 H, d, J = 7.4 Hz, H−Ar), 6.39 (1 H, s), 6.34, 6.19 (2 H, AB, J = 11.2 Hz), 5.36 (1 H, broad s), 4.96 (1 H, broad s), 4.41 (1 H, m), 4.17 (1 H, m), 1.56 [3 H, s], 1.55 [3 H, s], 0.96 (3 H, s). ^{13}C NMR (MeOD, 75.40 MHz, δ): 154.4 (C), 149.9 (C), 149.8 (C), 141.8 (C), 139.8 (C), 136.2 (C), 128.2 (CH), 126.8 (CH), 124.7 (CH), 123.2 (CH), 122.2 (CH), 119.7 (CH), 112.1 (CH_2), 72.8 (CH), 71.4 (CH), 67.4 (CH), 57.7 (CH), 48.4 (C), 46.1 (CH_2), 43.7 (CH_2), 38.1 (CH_2), 32.2 (CH_2), 32.0 (CH_3), 31.9 (CH_3), 29.8 (CH_2), 24.3 (CH_2), 23.5 (CH_2), 19.1 (CH_3). MS [*m*/*e*, (%)]: 434 (M^+, 32), 416 (M^+ − H_2O, 88), 398 (M^+ − $2H_2O$, 73). Anal. Calcd for $C_{29}O_3H_{38}$: C, 80.13; H, 8.82; found: C, 80.40; H, 8.74. UV (*i*-PrOH) λ_{max} (ϵ) 260 nm (25000).

(17*Z*)-1α-20-[4-(Dimethylhydroxymethyl)phenyl]-17,-20-didehydro-21,22,23,24,25,26, 27-heptanorvitamin D_3 (4p). Procedure as above. **4p** [85%, R_f = 0.5 (100% Et_2O), white solid, mp 110 °C (dec)]. ^{1}H NMR (MeOD, 300 MHz): 7.44 (2 H, d, J = 8.26 Hz), 7.18 (2 H, d, J = 8.07 Hz), 6.38 (1 H, s), 6.37, 6.22 (2 H, AB, J = 11.2 Hz), 5.39 (1 H, broad s), 4.99 (1 H, broad s), 4.44 (1 H, m), 4.20 (1 H, m), 2.88 (1 H, m), 1.60 (6 H, s), 0.98 (3 H, s). ^{13}C NMR (MeOD, 75.40 MHz): 154.4 (C), 149.8 (C), 148.6 (C), 141.8 (C), 138.3 (C), 136.2 (C), 129.9 (CH), 124.8 (CH), 124.7 (CH), 121.7 (CH), 119.7 (CH), 112.1 (CH_2), 72.9 (C), 71.4 (CH), 67.4 (CH), 57.7 (CH), 46.1 (CH_2), 43.7 (CH_2), 38.1 (CH_2), 32.3 (CH_2), 31.9 (CH_3), 31.9 (CH_3), 29.8 (CH_2), 24.3 (CH_2), 23.5 (CH_2), 19.0 (CH_3). MS [*m*/*e*, (%)]: 434 (M^+, 11), 416 (M^+ − H_2O, 67), 398 (M^+ − $2H_2O$, 100), 380 (M^+ − $3H_2O$, 44). HRMS: calcd for $C_{29}H_{38}O_3$: 434.2821; found: 434.2848. UV (*i*-PrOH) λ_{max} (ϵ) 260 nm (20000).

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Supporting Information Available: ^{1}H and ^{13}C NMR (including DEPT) spectra of all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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