

Supporting Data

Synthesis and photo-conversion of androsta- and pregna-5,7-dienes to vitamin D3-like derivatives.

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Contents:

S2-S8 Figures S1-7

S9-S11 Tables S1-3

S12 Literature

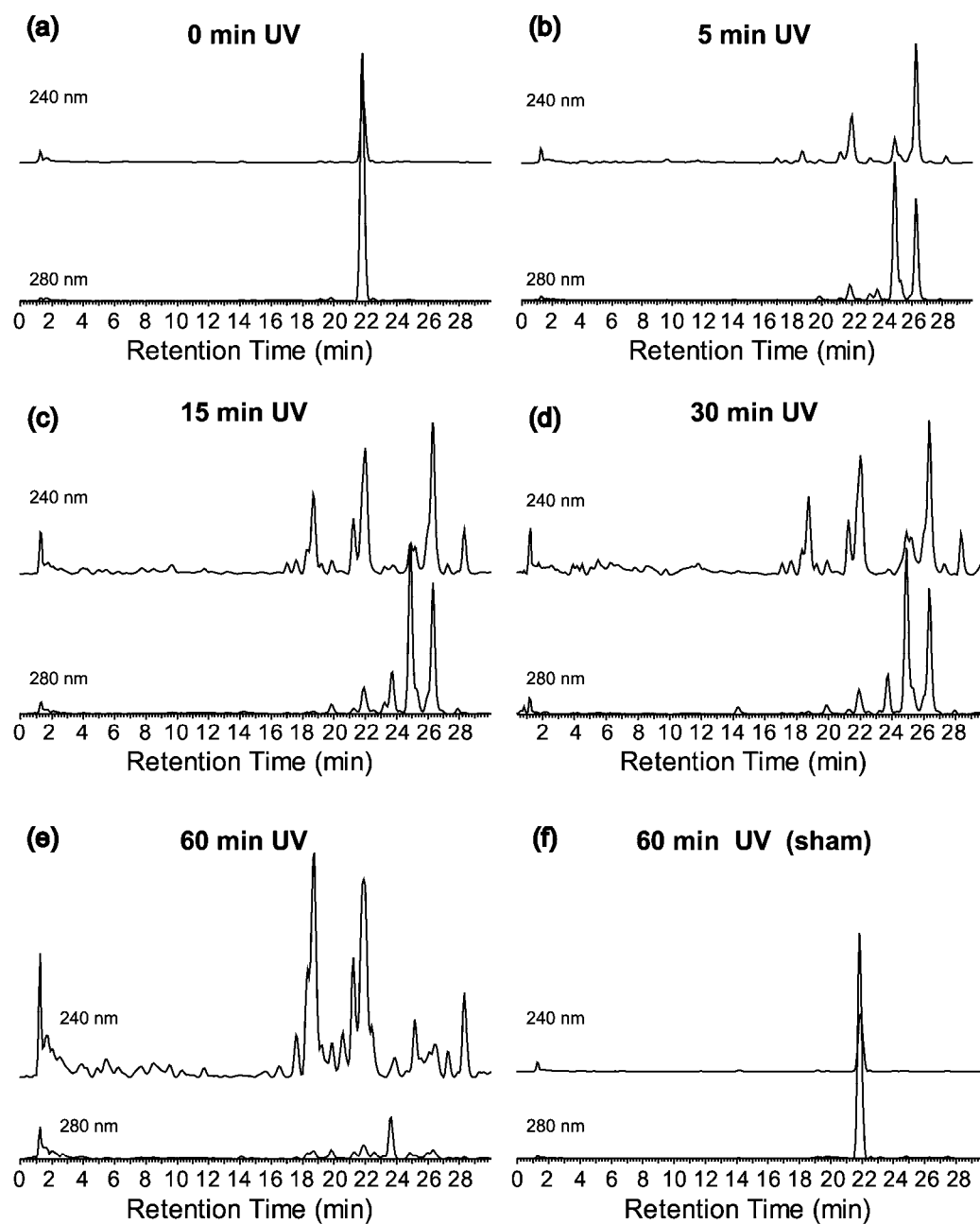


Fig. S1. UVB dose dependent photolysis of 3 β -hydroxypregna-5,7-diene-20-one (**5c**).

RP-HPLC separation of **5c** irradiation products after treatment with UVB for 0 minutes (a), 5 (b), 15 (c), 30 (d), 60 (e). The sample was incubated in the dark, at room temperature (20°C) for 1 hour and subjected to RP-HPLC (f). Sham irradiation: (sham) the sample was covered with aluminum foil and subjected to UV for 60 min. The UV spectra for RP-HPLC were recorded at 240 nm (upper chromatogram) or 280 nm (lower chromatogram).

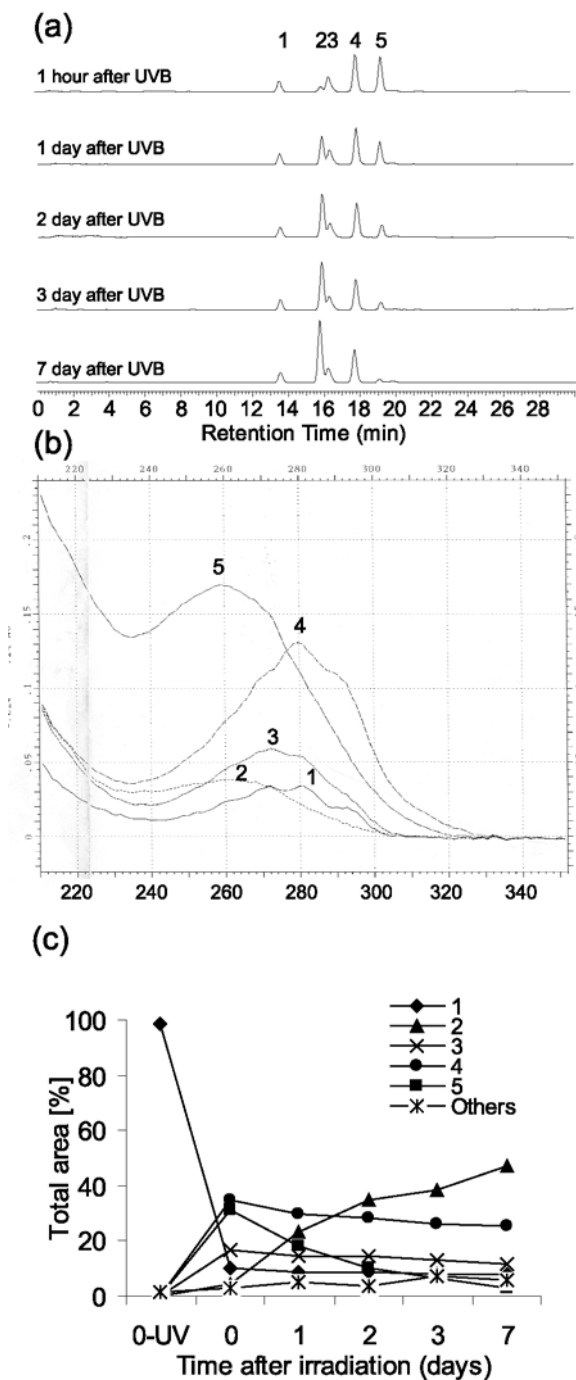


Fig. S2. UV- driven photolysis of 3 β -hydroxyandrosta-5,7-diene (5b) and time dependent isomerization of products.

(a) RP-HPLC separation of 5b irradiation products after treatment with UVB for 15 minutes. The sample was incubated in the dark, at room temperature (20°C) for 1 hour or 1, 2, 3, or 7 days after irradiation. (b) Representative UV spectra of irradiated samples. (1 - **5b**, 2- **5b-D**, 3 - **5b-L**, 4 - **5b-T**, 5 - **5b-pD**). (c) The changes in relative amount of substrate and products during incubation after irradiation at 20°C. The changes are expressed as a ratio of total area under the selected peak to the total area of peaks in percent. The UV spectra for RP-HPLC (Panel a) were measured at 280 nm.

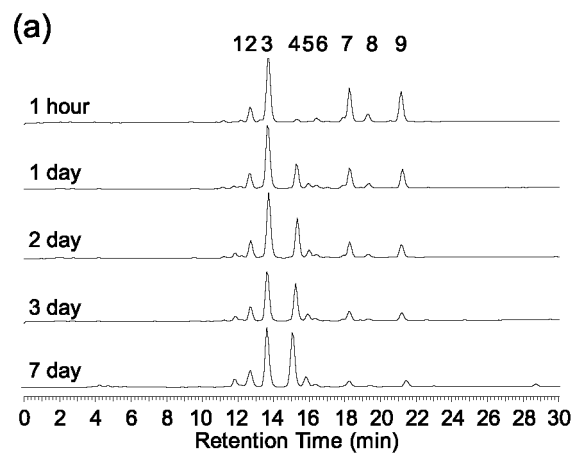
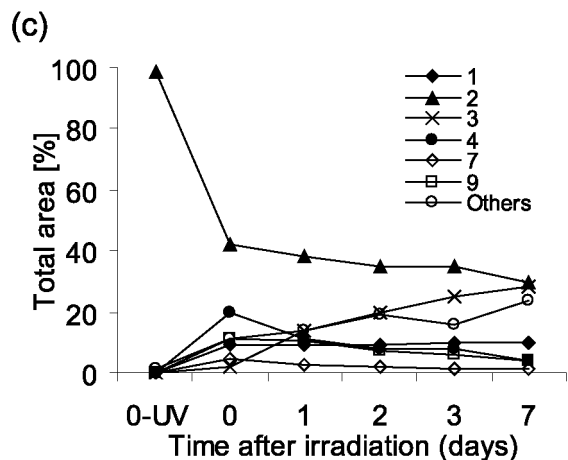
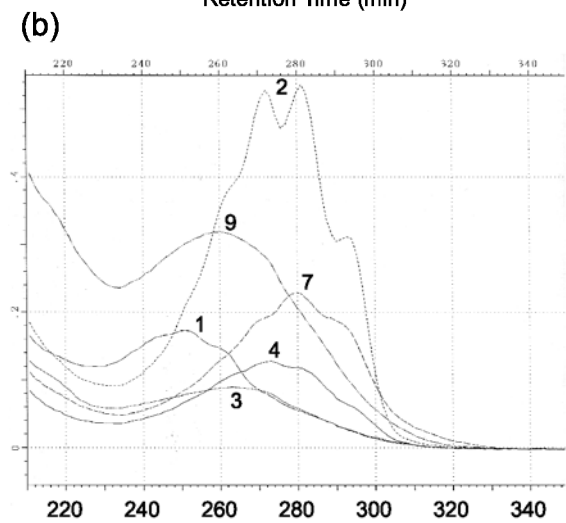


Fig. S3. The UV- driven photolysis of 3 β ,17 β -hydroxypregna-5,7-dien-20-one (**5a**) and time dependent isomerization of products.

(a) RF-HPLC separation of **5a** irradiation products after treatment with UVB for 15 minutes. The sample was incubated in the dark, at room temperature (20°C) for 1 hour or 1, 2, 3, or 7 days after irradiation. (b) Representative UV spectra of irradiated samples. (1 - **5a-iT**, 2- **5a**, 3- **5a-D**, 4 - **5a-L**, 7 - **5a-T**, 9 - **5a-pD**). (c) The changes in relative amount of substrate and products during incubation after irradiation at 20°C. The changes are expressed as a ratio of total area under the selected peak to the total area of peaks in percent. The UV spectra for RP-HPLC (Panel a) were measured at 280 nm.



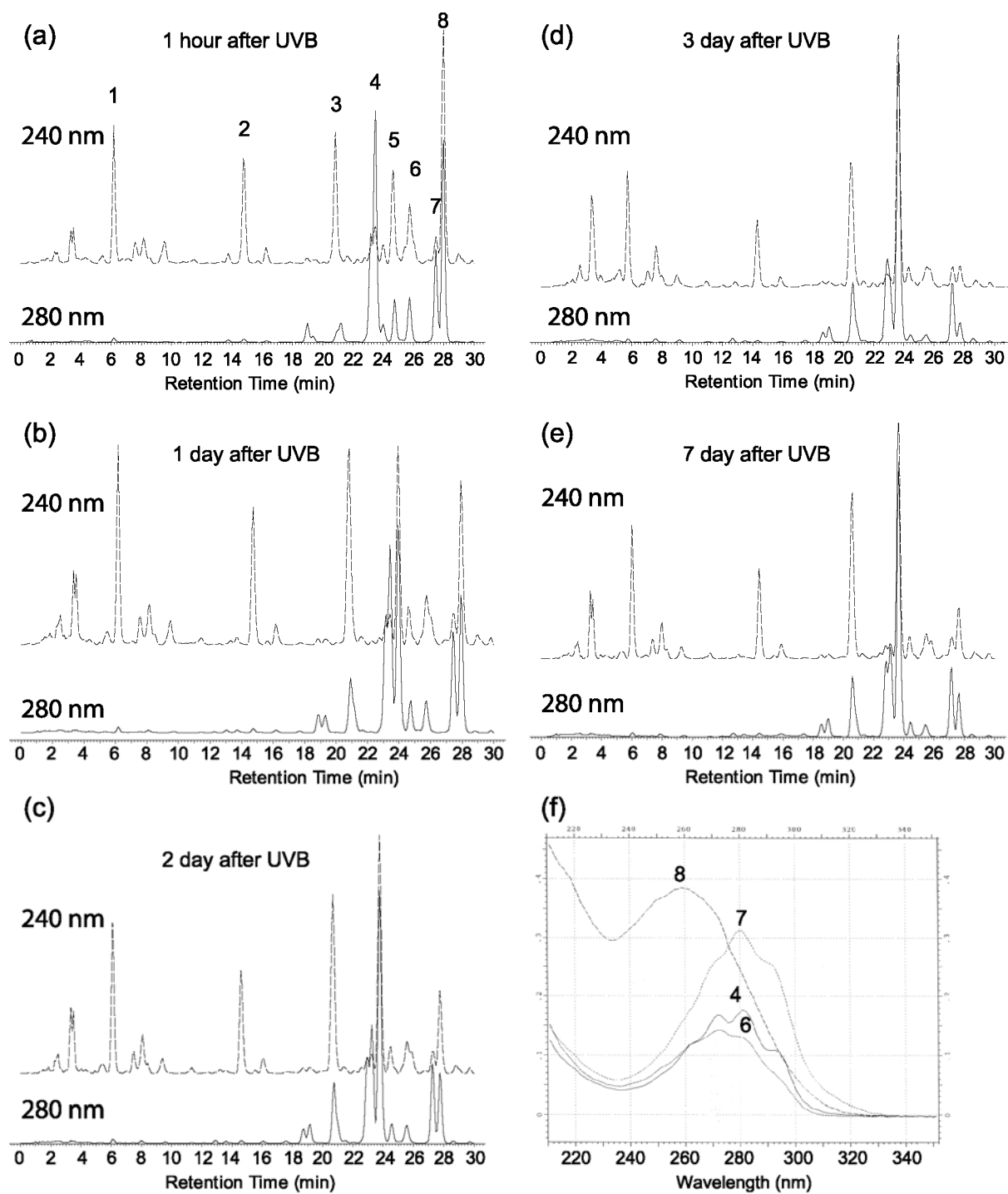


Fig. S4. UVB driven photolysis of 3β,20-dihydroxypregna-5,7-diene (4b).

(a) RP-HPLC separation of **4a** irradiation products after treatment with UVB for 15 minutes and incubation for 1 hour (a), 1 (b), 2 (c), 3 (d) and 7 (e) days in the dark, at room temperature (20°C). (b) Representative UV spectra of irradiated samples. (4 – **4b**, 6- **4b-L**, 7 – **4b-T**, 8 – **4b-pD**). The UV spectra for RP-HPLC (Panel a-e) were measured at 240 nm upper trace and 280 lower trace.

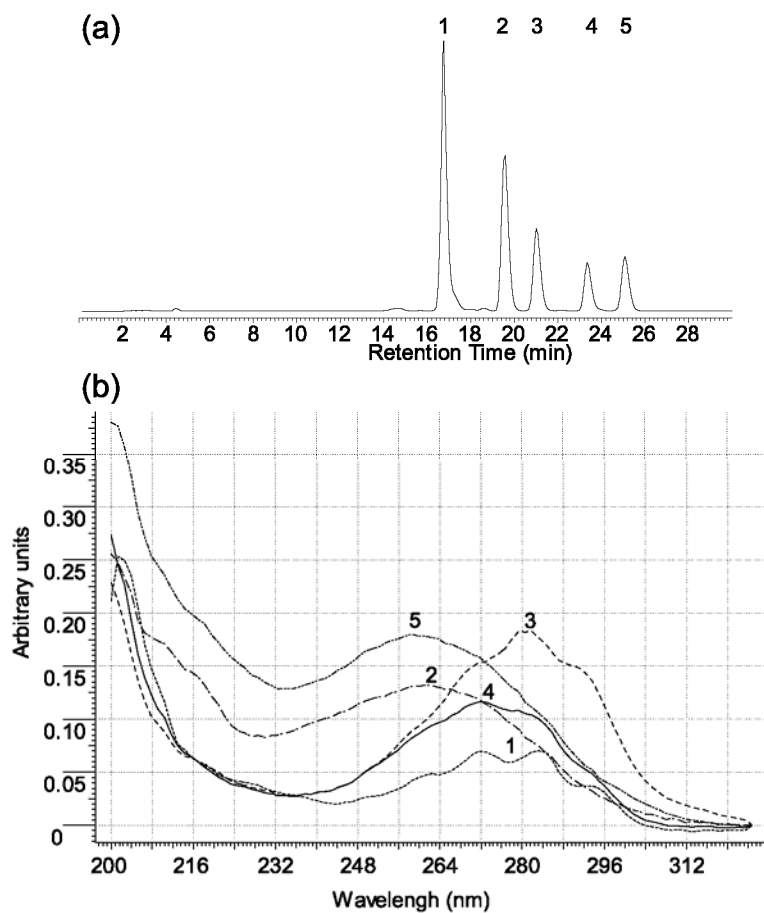


Fig. S5. UVB- driven photolysis of 3 β ,17-dihydroxyandrosta-5,7-diene (**4a**).

(a) RP-HPLC separation of **4a** irradiation products after treatment with UVB for 15 minutes and incubation for 4 days in the dark, at room temperature (20°C).
(b) Representative UV spectra of irradiated samples. (1 – **4a**, 2- **4a-D**, 3 - **4a-T**, 4 – **4a-L**, 5 – **4a-pD**). The UV spectra for RP-HPLC (Panel a) were measured at 280 nm.

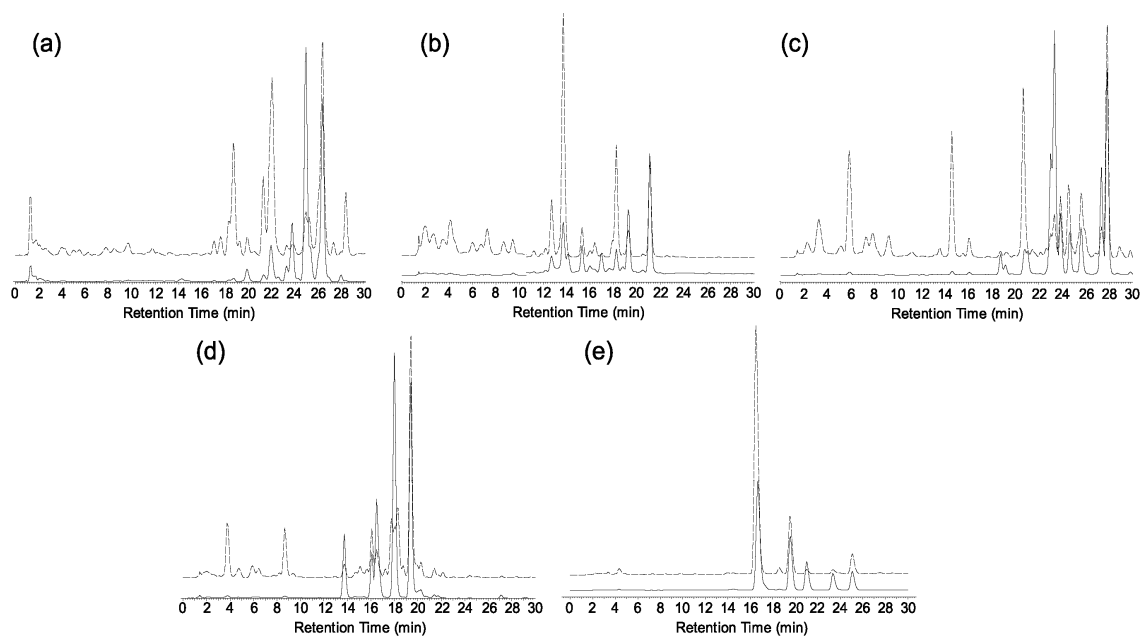


Fig.S6. Comparison of UVB- driven photolysis of androsta- and pregna-5,7-dienes.

RP-HPLC separation of **5c** (a), **5a** (b), **4b** (c), **5b** (d) and **4a** (e) irradiation products after treatment with UVB for 15 minutes. The UV spectra for RF-HPLC (Panel a-e) were measured at 240 nm upper trace and 280 lower trace.

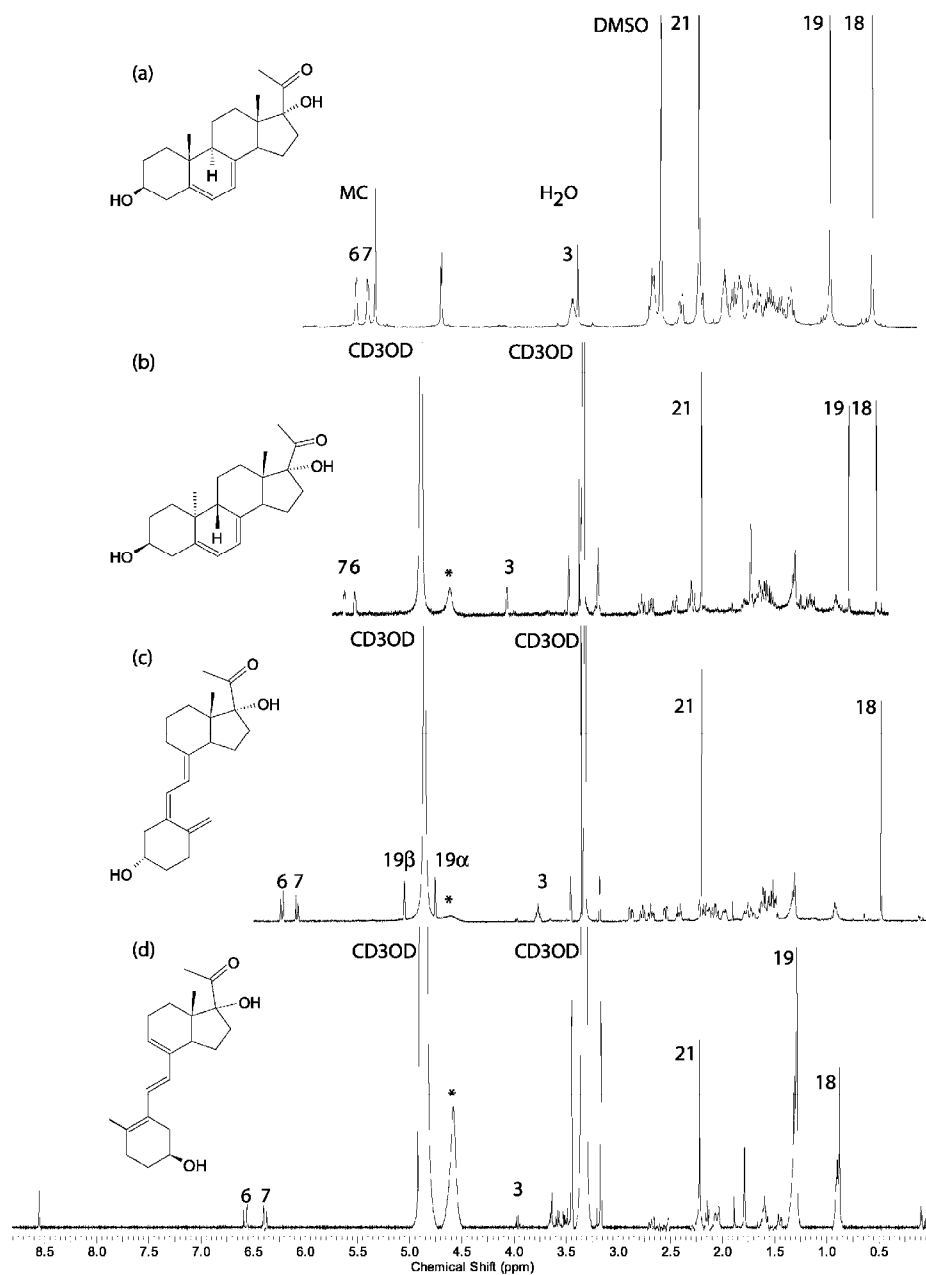


Fig. S7. Proton NMR spectra of androsta- and pregna-5,7-dienes and main products of their irradiation with **5a** as an example.

(a) 3 β ,17 α -dihydroxypregna-5,7-dien-20-one (**5a**), (b) 3 β ,17 α -dihydroxy-9 β ,10 α -pregna-5,7-dien-20-one (**5a-L**) (c) 5*Z*,7*E*-3 β ,17 α -dihydroxy-9,10-secopregna-5,7,10(19)trien-20-one (**5a-D**) (d) 6*E*-3 β ,17 α -dihydroxy-9,10-secopregna-5(10),6,8-trien-20-one (**5a-T**). The main peaks used for structural identification of compounds are marked by number of carbon. Impurities and solvents are described or marked with a star (*).

Short side-chain 5,7-dienes and their D-like derivatives

Table S1. ¹H NMR chemical shifts of steroidal-5,7-dienes

Solvent	CDCl ₃ 3c	CDCl ₃ 5c	CDCl ₃ 5a	CDCl ₃ 4b	CDCl ₃ 5b	CD ₃ OD 4a
1 CH ₂	α 1.337 β 1.89	α 1.31 β 1.90	α 1.31* β 1.90*	α 1.31* β 1.90	α 1.38 β 1.91	α 1.28 β 1.83
2 CH ₂	α 1.942 β 1.583	α 1.92 β 1.54	α 1.92* β 1.54*	α 1.92 β 1.54*	α 1.94 β 1.52	α 1.8-2.20 β 1.46
3 CH	4.71	3.65	3.64	3.64	3.66	3.51
4 CH ₂	α 2.51 β 2.364	α 2.48 β 2.31	2.48 2.31	α 2.41 β 2.29	α 2.51 β 2.31	α 2.41 β 2.24
6 CH	5.58	5.58	5.58	5.58	5.63	5.55
7 CH	5.42	5.43	5.45	5.42	5.56	5.37
9 CH	2.03	2.02	2.02*	2.02*	2.07	1.91
11 CH ₂	α 1.712 β 1.788	α 1.7 β 1.7	α 1.7* β 1.7*	α 1.7-1.8 β 1.7-1.8	α 1.75 β 1.75	α 1.68 β 1.68
12 CH ₂	α 1.518 β 2.114	α 1.49 β 2.12	α 1.49* β 2.12*	α 1.49* β 2.18	α 1.37 β 1.94	α 1.18 β 1.8-2.0
14 CH	2.047	2.05	2.05	2.05	2.2	1.8-2.0
15 CH ₂	α 1.827 β 1.543	α 1.82 β 1.51	α 1.82* β 1.51*	α 1.82* β 1.51*	α 2.1 β 1.79	α 1.8-2.0 β 1.72
16 CH ₂	α 1.765 β 2.21	α 1.76 β 2.22	α 2.61 2.70	α 1.76* β 2.22*	α 2.20 β 2.54	α 1.55 β 1.8-2.0
17 CH	2.632	2.63	C	2.17	C	3.69
18 CH ₃	0.582	0.58	0.69	0.77	0.83	0.68
19 CH ₃	0.947	0.95	0.78	0.7	0.98	0.96
20 C				3.75 CH		
21 CH ₃	2.148	2.16	2.29	1.17		
3β-Ac CH ₃	2.044					

* Chemical shifts based on similar structures presented in this manuscript or previously published data.¹

Short side-chain 5,7-dienes and their D-like derivatives

Table S2. ¹³C and ¹H NMR chemical shifts of vitamin D-like compounds and T-like (5aD) compound.

	¹³ C 5c-D	¹³ C 4a-D	¹ H 5c-D	¹ H 5a-D	¹ H 5a-T	¹ H 4b-D	¹ H 5b-D	¹ H 4a-D
1 CH ₂	23.12	33.333	α 2.12 β 2.41	α 2.11 β 2.41	α 2.11* β 2.41*	α 2.11 β 2.41	α 2.17 β 2.42	α 2.12 β 2.41
2 CH ₂	35.5	36.372	α 1.93 β 1.68	α 1.97 β 1.68	α 1.97* β 1.68*	α 1.97 β 1.54	α 1.97* β 1.54*	α 1.97 β 1.54
3 CH -OH	69.99	70.345	3.96	3.76	3.86	3.76	3.8	3.77
4 CH ₂	46.5	46.806	α 2.58 β 2.30	α 2.53 β 2.19	α 2.53* β 2.19*	α 2.55 β 2.20	α 2.59 β 2.24	α 2.54 β 2.19
6 CH	122.2	122.282	6.22	6.23	6.58	6.22	6.27	6.23
7 CH	118.98	118.73	6.06	6.08	6.39	6.02	6.19	6.04
9 CH ₂	29.05	29.573	2.85 1.72	2.87 1.5	CH 5.35	2.87 1.56	2.94 1.67*	2.89 1.67
11 CH ₂	23.3	23.938	α 1.77 β 1.77	α 1.75 β 1.75	α 1.75* β 1.75*	α 1.68 β 1.67	α 1.71* β 1.53*	α 1.71 β 1.53
12 CH ₂	39.75	38.457	α 1.56 β 2.05	α 1.50 β 2.06	α 1.50* β 2.06	α 1.34 β 1.52	α 1.24* β 1.86*	α 1.24 β 1.86
14 CH	56.7	51.882	2.12	2.14	2.14*	2.02	β 2.47	β 1.99
15 CH ₂	22.46	22.045	α 1.61 β 1.61	α 1.6 β 1.6	α 1.6* β 1.6*	α 1.50 β 1.50	α 1.45* β 1.64*	α 1.45 β 1.64
16 CH ₂	22.61	29.979	α 1.7 β 2.17	α 1.68 β 2.76	α 1.68* β 2.76*	α 1.63 β 2.17	α 1.46* β 2.47	α 1.46 β 2.06
17 CH	64.25	82.799	2.7	N/A	N/A	1.51	N/A	3.74
18 CH ₃	13.04	11.348	0.51	0.46	0.883	0.61	0.75	0.58
19 CH ₂	113.7	112.492	α 4.81 β 5.06	α 4.75 β 5.05	CH ₃ 1.79 N/A	α 4.74 β 5.04	4.82 5.1	4.75 5.04
20 C	ND	ND	N/A	N/A	ND	3.62	N/A	N/A
21-CH ₃	31.47		2.143	2.223	2.23	1.12	N/A	N/A

* Chemical shifts based on similar structures.

ND – Not determined

N/A – Not applicable (ternary carbons)

Short side-chain 5,7-dienes and their D-like derivatives

Table S3. ¹H NMR chemical shifts of L-like compounds

	5a-L	4b-L	4a-L
1 CH ₂	α 1.31*	α 1.31*	α 1.296
	β 1.90*	β 1.90*	β 1.771
2 CH ₂	α 1.92*	α 1.92*	α 1.711
	β 1.54*	β 1.54*	β 1.616
3 CH	4.03	4.03	4.033
4 CH ₂	α 2.44	α 2.44	α 2.43
	β 2.28	β 2.35	β 2.264
6 CH	5.584	5.57	5.423
7 CH	5.488	5.42	5.58
9 CH	2.02*	2.02*	2.34
11 CH ₂	α 1.7-1.8*	α 1.7-1.8*	α 1.49
	β 1.7-1.8*	β 1.7-1.8*	β 1.49
12 CH ₂	α 1.49*	α 1.49*	α 1.51
	β 2.18*	β 2.18*	β 1.91
14 CH	2.05*	2.05*	2.48
15 CH ₂	α 1.82*	α 1.82*	α 1.667
	β 1.51*	β 1.51*	β 1.575
16 CH ₂	α 2.68	α 1.76*	α 1.501
	β 2.76	β 2.22*	β 2.083
17 CH	N/A	2.17*	3.833
18 CH ₃	0.517	0.77	0.691
19 CH ₃	0.777	0.7	0.754
20 C	N/A	3.65 CH	
21 CH ₃	2.183	1.13	

* Chemical shifts based on similar structures

ND – Not determined

N/A – Not applicable (ternary carbons)

Short side-chain 5,7-dienes and their D-like derivatives

1. A. U. Siddiqui, W. K. Wilson, S. Swaminathan and G. J. Schroepfer, Jr., Efficient preparation of steroidal 5,7-dienes of high purity, *Chemistry and physics of lipids*, 1992, **63**, 115-129.