Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supplementary Data

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

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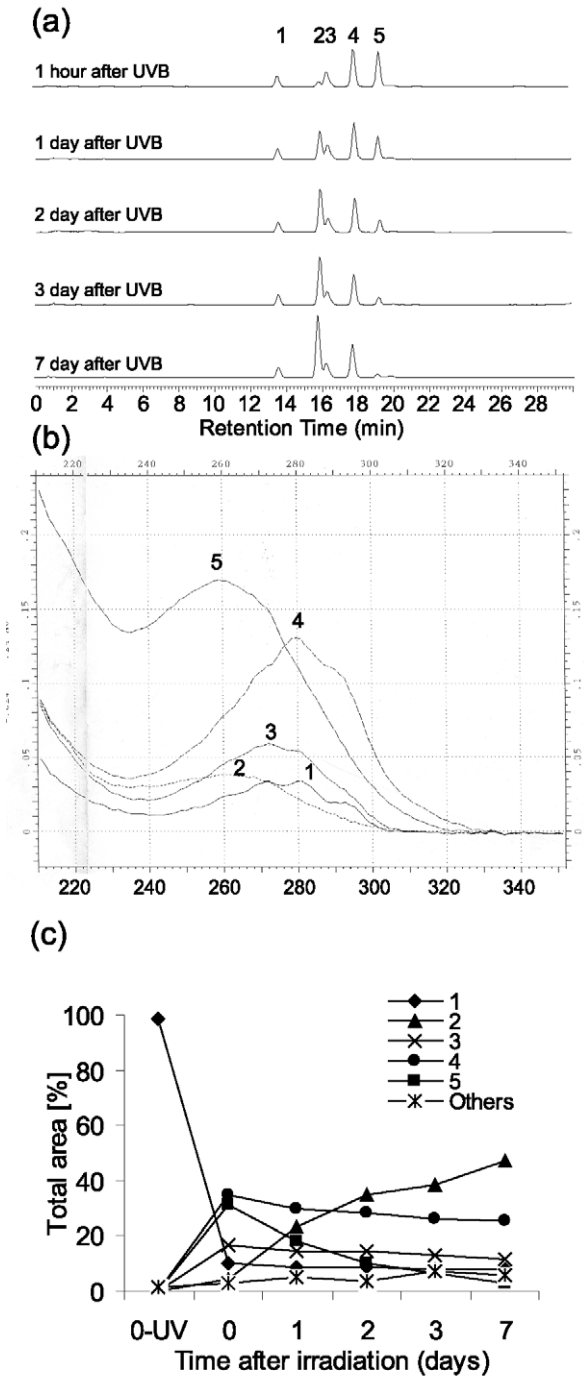

Fig. S1. UV- driven photolysis of 3β-hydroxyandrosta-5,7-diene (5b) and time dependent isomerization of products.

(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.

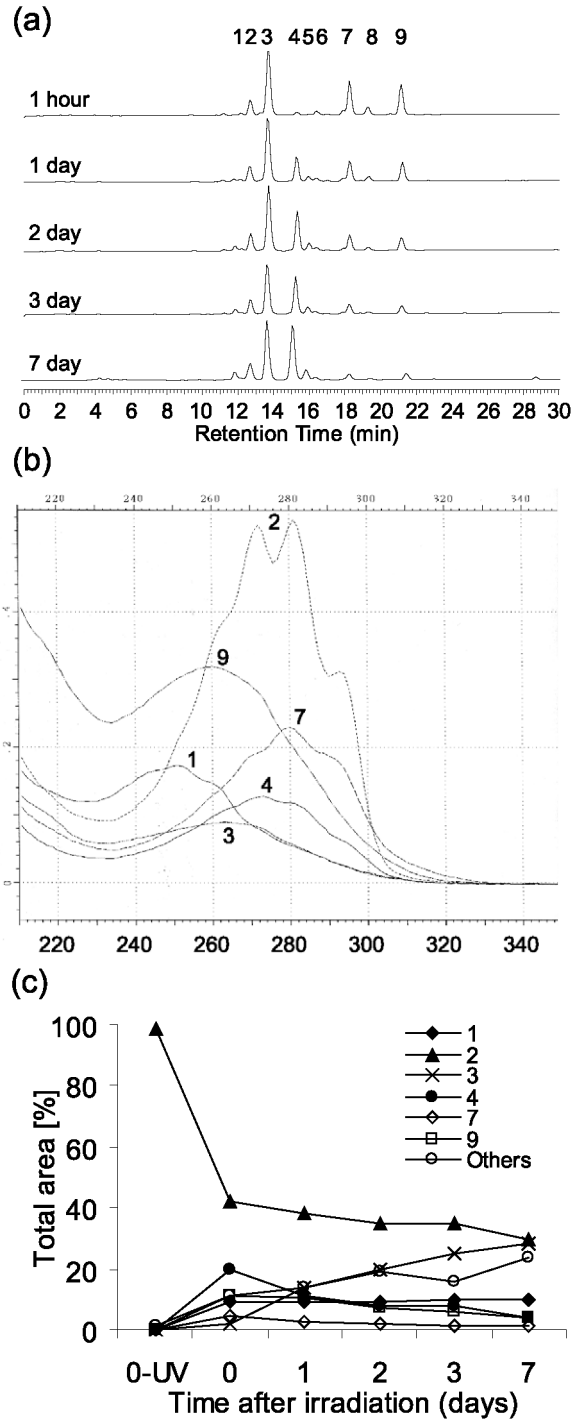

Fig. S2. The UV- driven photolysis of 3β,17 β -hydroxypregna-5,7-dien-20-one (5a) and time dependent isomerization of products.

(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.

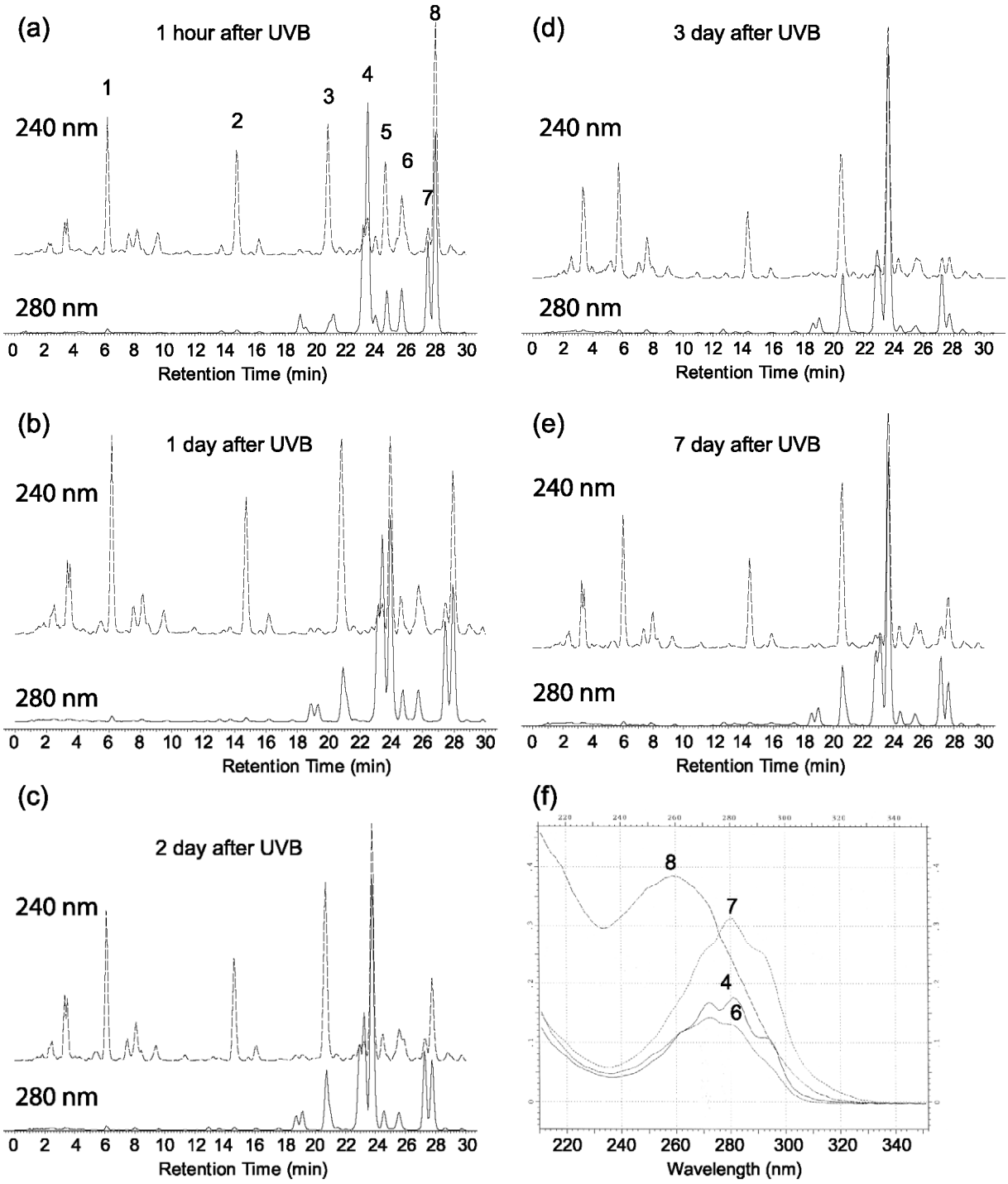

Fig. S3. UVB driven photolysis of 3β,20-dihydroxypregna-5,7-diene (4b).

(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.

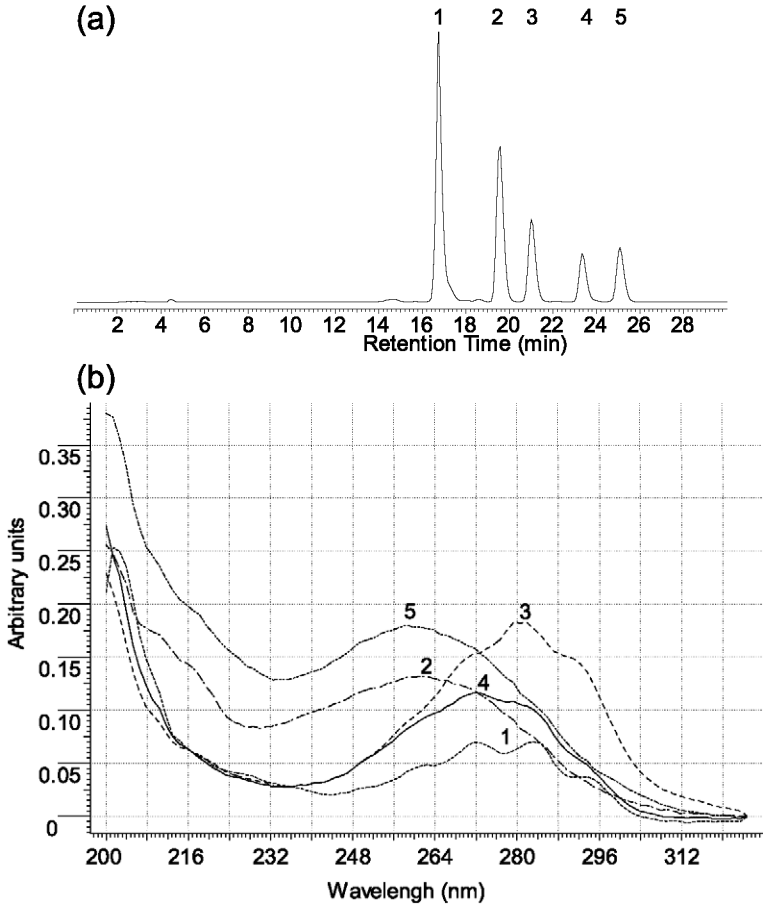

Fig. S4. UVB- driven photolysis of 3β,17-dihydroxyandrosta-5,7-diene (4a).

(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.

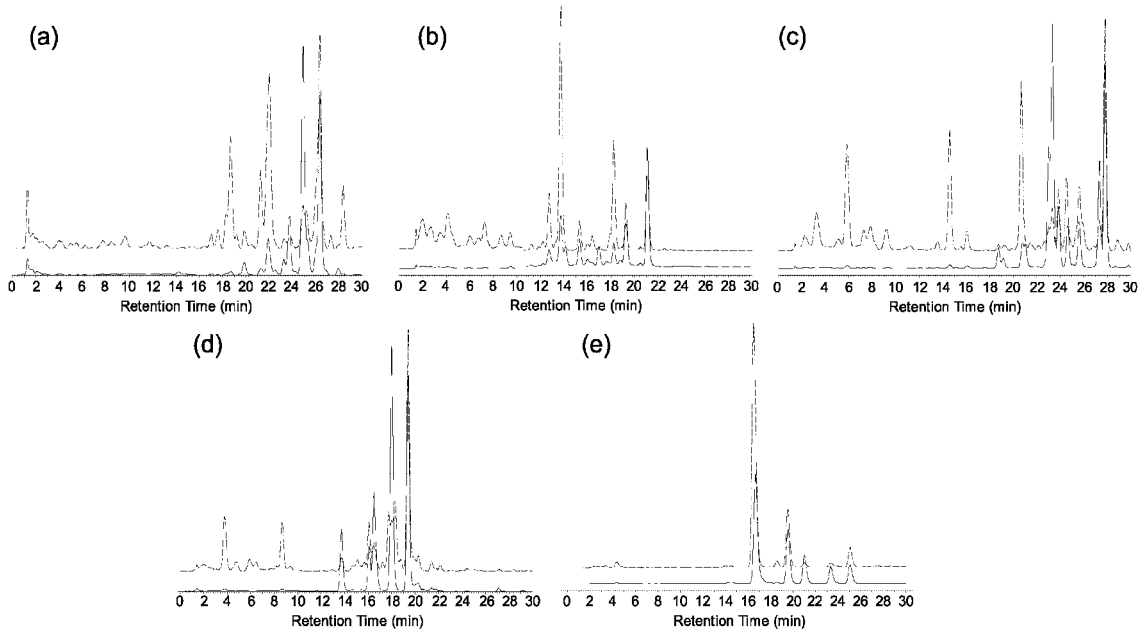

Fig.S5. Comparison of UVB- driven photolysis of androsta- and pregna-5,7-dienes.

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.

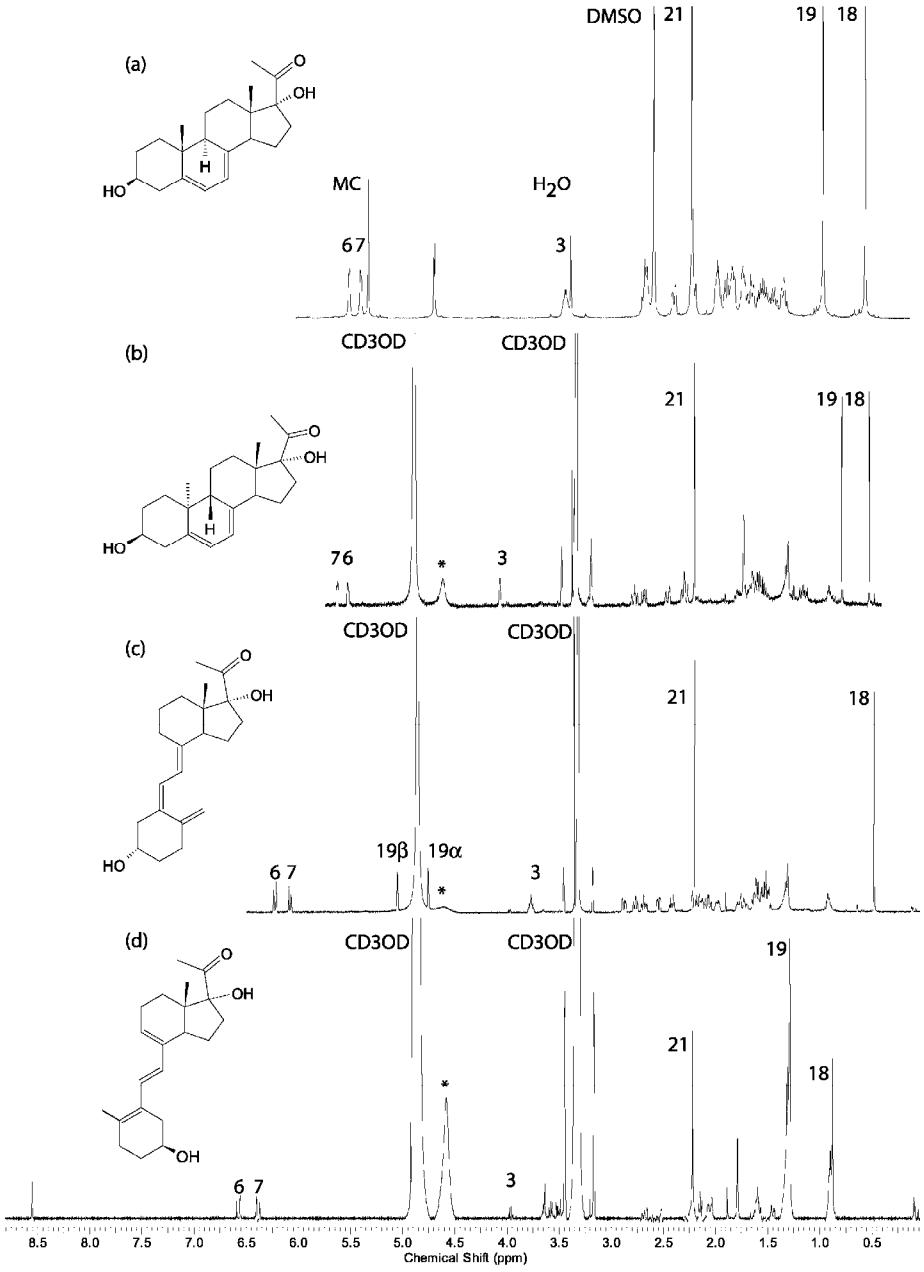

Fig. S6. Proton NMR spectra of androsta- and pregna-5,7-dienes and main products of their irradiation with 5a as an example.

(a) 3β,17α-dihydroxypregna-5,7-dien-20-one (**5a**), (b) 3β,17α-dihydoxy-9β,10α-pregna-5,7-dien-20-one (**5a-L**) (c) *5Z,7E*-3β,17α-dihydroxy-9,10-secopregna-5,7,10(19)trien-20-one (**5a-D**) (d) 6*E*-3β,17α-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 (*).

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

Solvent	CDCl3	CDCl3	CDCl3	CDCl3	CDCl3	CD3OD
	3c	**5c**	**5a**	**4b**	**5b**	**4a**
1 CH_2	α 1.337	α 1.31	α 1.31*	α 1.31*	α 1.38	α 1.28
	β 1.89	β 1.90	β 1.90*	β 1.90	β 1.91	β 1.83
2 CH_2	α 1.942	α 1.92	α 1.92*	α 1.92	α 1.94	α 1.8-2.20
	β 1.583	β 1.54	β 1.54*	β 1.54*	β 1.52	β 1.46
3 CH	4.71	3.65	3.64	3.64	3.66	3.51
4 CH_2	α 2.51	α 2.48	2.48	α 2.41	α 2.51	α 2.41
	β 2.364	β 2.31	2.31	β 2.29	β 2.31	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	α 1.7	α 1.7*	α 1.7-1.8	α 1.75	α 1.68
	β 1.788	β 1.7	β 1.7*	β 1.7-1.8	β 1.75	β 1.68
12 CH_2	α 1.518	α 1.49	α 1.49*	α 1.49*	α 1.37	α 1.18
	β 2.114	β 2.12	β 2.12*	β 2.18	β 1.94	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	α 1.82	α 1.82*	α 1.82*	α 2.1	α 1.8-2.0
	β 1.543	β 1.51	β 1.51*	β 1.51*	β 1.79	β 1.72
16 CH_2	α 1.765	α 1.76	α 2.61	α 1.76*	α 2.20	α 1.55
	β 2.21	β 2.22	2.70	β 2.22*	β 2.54	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]

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	α 2.11	α 2.11*	α 2.11	α2.17	α2.12
			β 2.41	β 2.41	β 2.41*	β 2.41	β2.42	β2.41
2 CH_2	35.5	36.372	α 1.93	α 1.97	α 1.97*	α 1.97	α1.97*	α1.97
			β 1.68	β 1.68	β 1.68*	β 1.54	β 1.54*	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	α 2.53	α 2.53*	α 2.55	α 2.59	α 2.54
			β 2.30	β 2.19	β 2.19*	β 2.20	β 2.24	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 CH2	29.05	29.573	2.85	2.87	CH 5.35	2.87	2.94	2.89
			1.72	1.5		1.56	1.67*	1.67
11 CH_2	23.3	23.938	α 1.77	α 1.75	α 1.75*	α 1.68	α 1.71*	α 1.71
			β 1.77	β 1.75	β 1.75*	β 1.67	β 1.53*	β 1.53
12 CH_2	39.75	38.457	α 1.56	α 1.50	α 1.50*	α 1.34	α 1.24*	α 1.24
			β 2.05	β 2.06	β 2.06	β 1.52	β1.86*	β1.86
14 CH	56.7	51.882	2.12	2.14	2.14*	2.02	β2.47	β 1.99
15 CH_2	22.46	22.045	α 1.61	α 1.6	α 1.6*	α 1.50	α 1.45*	α 1.45
			β 1.61	β 1.6	β 1.6*	β 1.50	β 1.64*	β 1.64
16 CH_2	22.61	29.979	α 1.7	α 1.68	α 1.68*	α 1.63	α 1.46*	α 1.46
			β 2.17	β 2.76	β 2.76*	β 2.17	β 2.47	β 2.06
17 CH	64.25	82.799	2.7	N/A	N/A	1.51	N/A	3.74
18 CH3	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	α 4.75	CH_3 1.79	α 4.74	4.82	4.75
			β 5.06	β 5.05	N/A	β 5.04	5.1	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 determinated

N/A – Not applicable (ternary carbons)

Table S3. ^{1}H 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 determinated
N/A – Not applicable (ternary carbons)

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.