Supplementary Material

Highly efficient, solvent-free esterification of testosterone promoted by a recyclable polymer-supported tosylic acid catalyst under microwave irradiation

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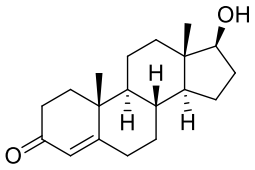
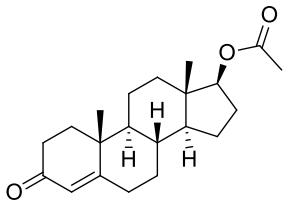
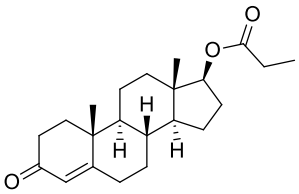
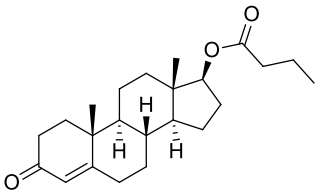
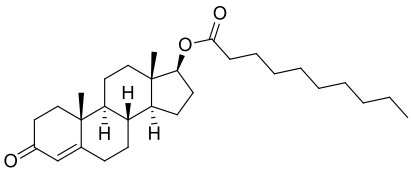
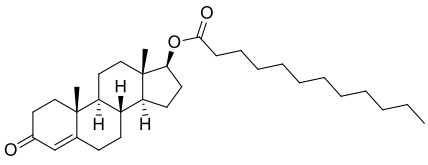
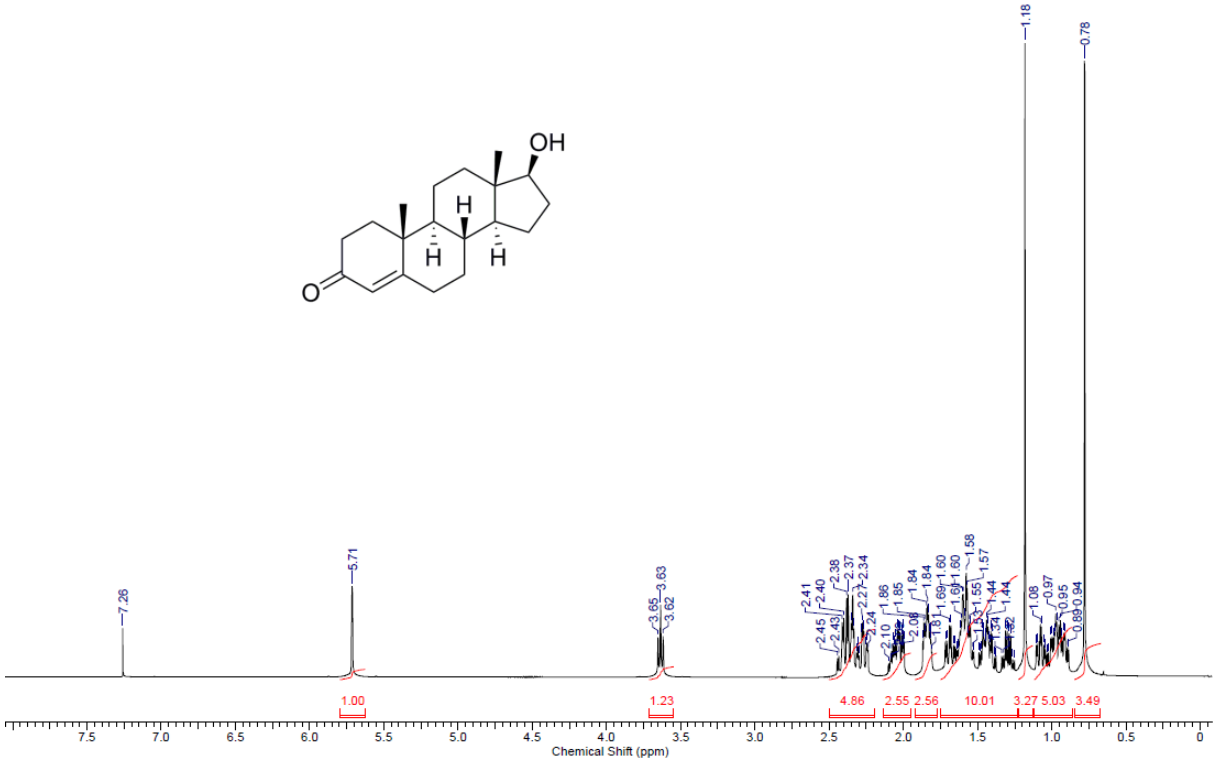
Table S1. Analytical HPLC conditions of different testosterone esters by Chiralcel OD-H (Daicel) column

Compound	Ratio of *n*-hexane to 2-propanol[a]	Retention time [min]
	85:15	12.482
	90:10	18.810
	95:5	40.468
	85:15	12.792
	90:10	16.736
	95:5	26.785
	85:15	11.618
	85:15	10.752
	85:15	8.715
	85:15	8.372

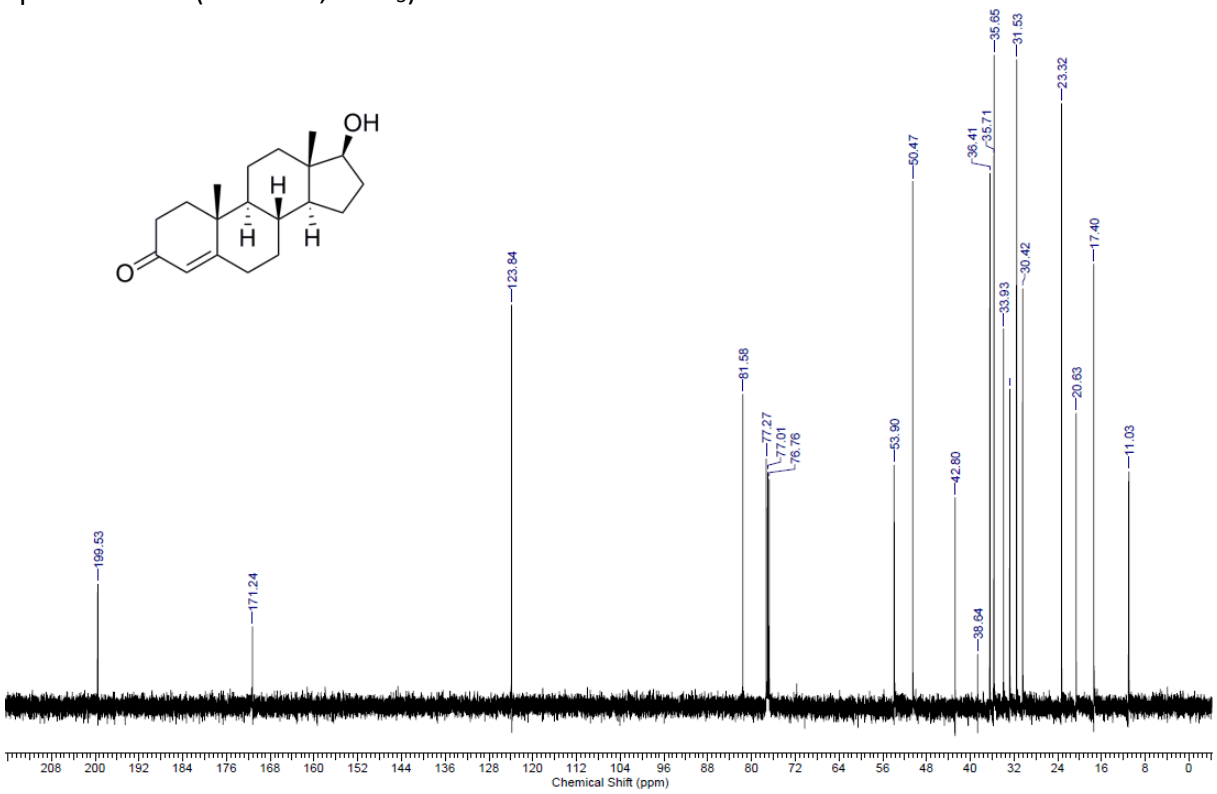
[a] The samples were carried out at 254 nm and 30 °C. The elution velocity was set at 0.8 mL/min.

Testosterone (1):

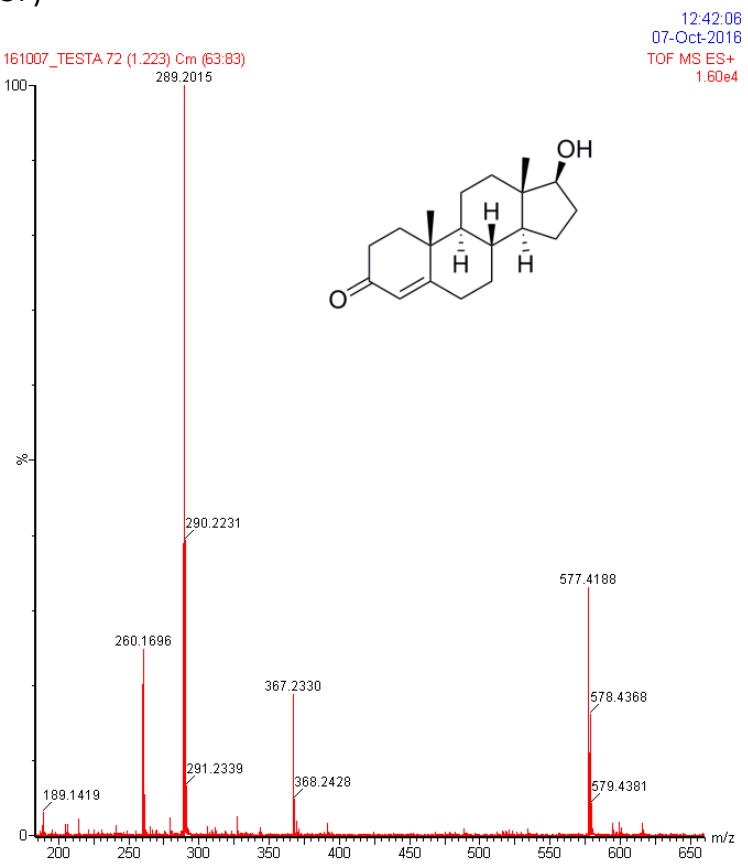
^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$)



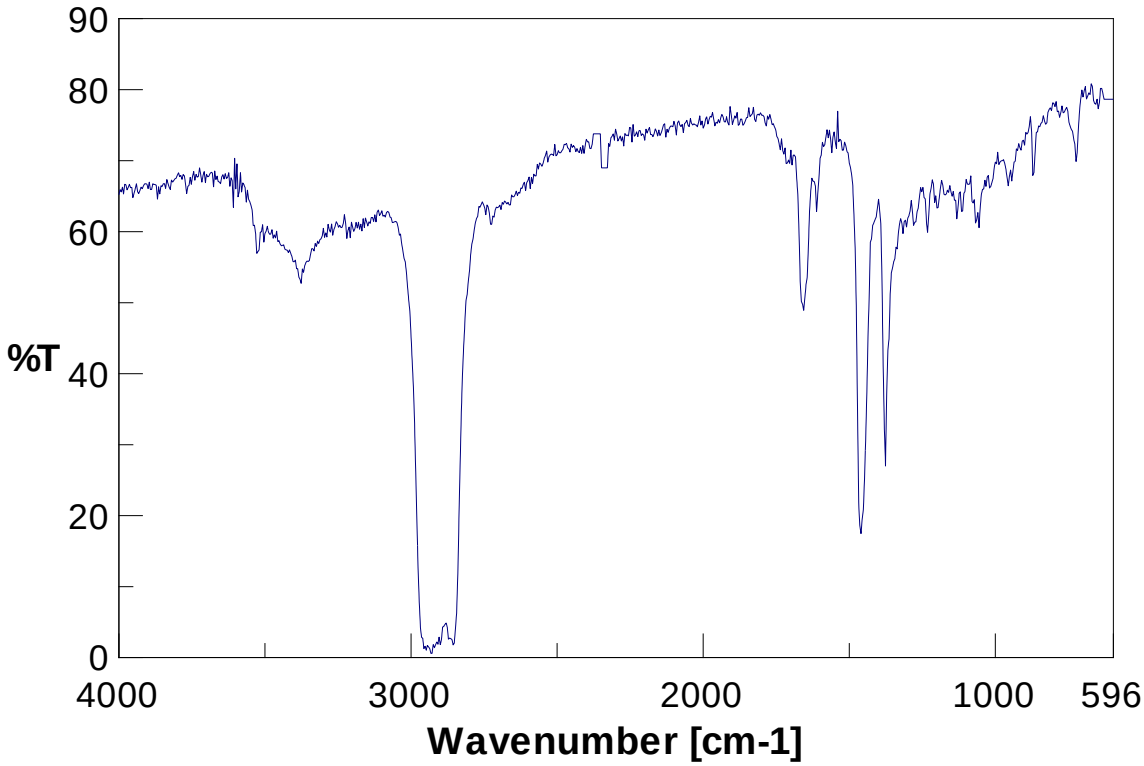
^{13}C NMR spectrum of **1** (126 MHz, $CDCl_3$)



HRMS spectrum of **1** (ESI-TOF)

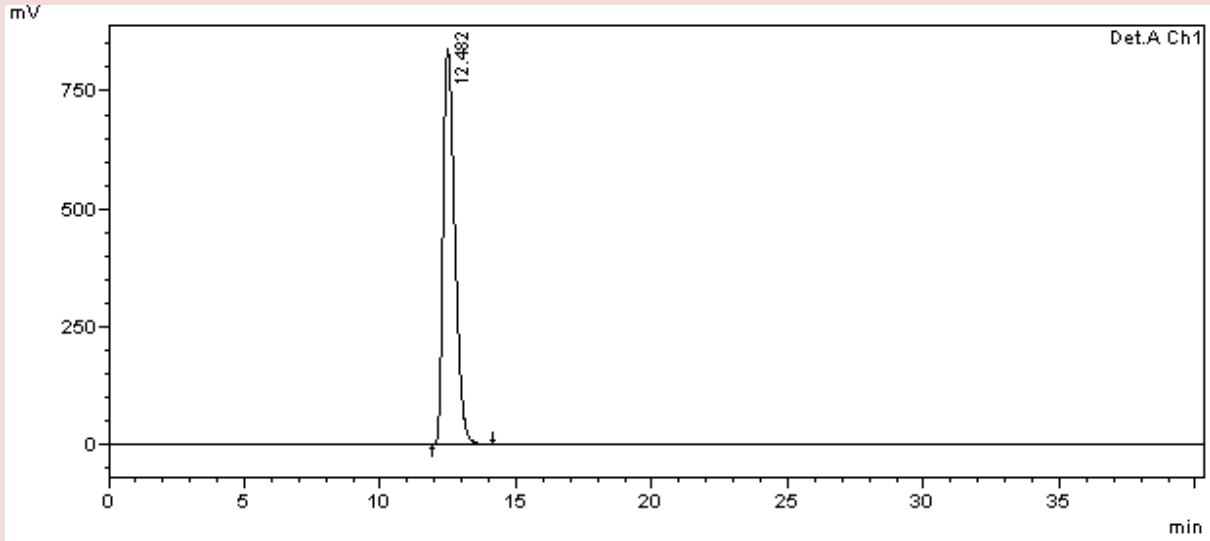


IR spectrum of **1** (Mineral oil, Nujol)



HPLC chromatogram of **1**

HPLC conditions: *n*-hexane-2-ProH (85:15, v/v); f=0.8 mL/min; λ=254 nm; *p*=3.3 MPa

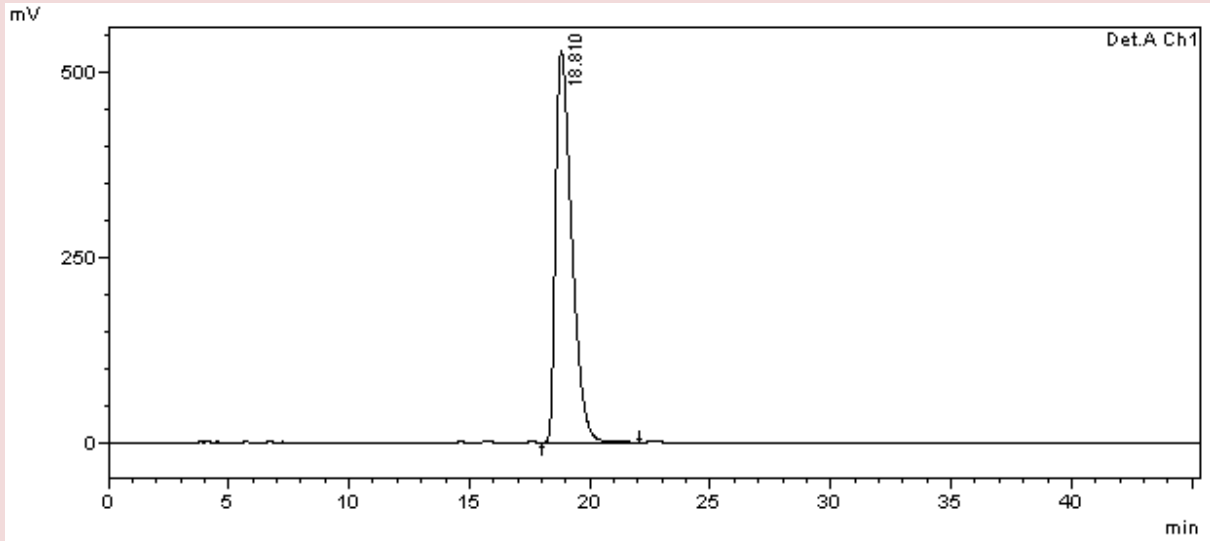


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.482	25085069	838158	100.000	100.000
Total		25085069	838158	100.000	100.000

HPLC conditions: *n*-hexane-2-ProH (90:10, v/v); f=0.8 mL/min; λ=254 nm; *p*=3.2 MPa

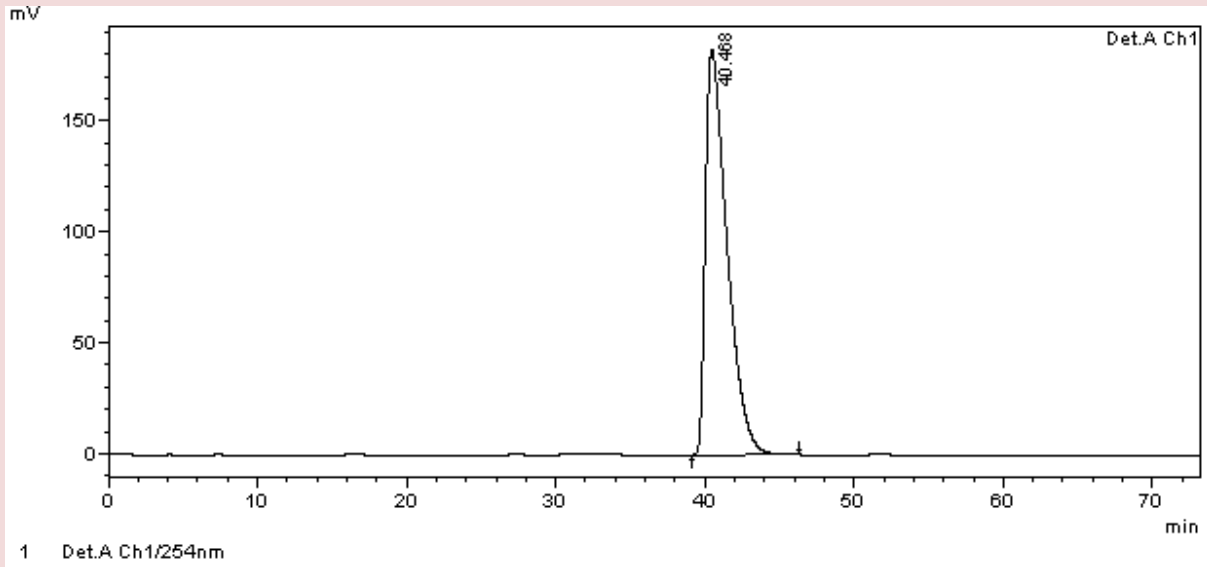


Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.810	24678063	528516	100.000	100.000
Total		24678063	528516	100.000	100.000

HPLC conditions: *n*-hexane-2-ProH (95:5, v/v); f=0.8 mL/min; λ=254 nm; *p*=3.0 MPa



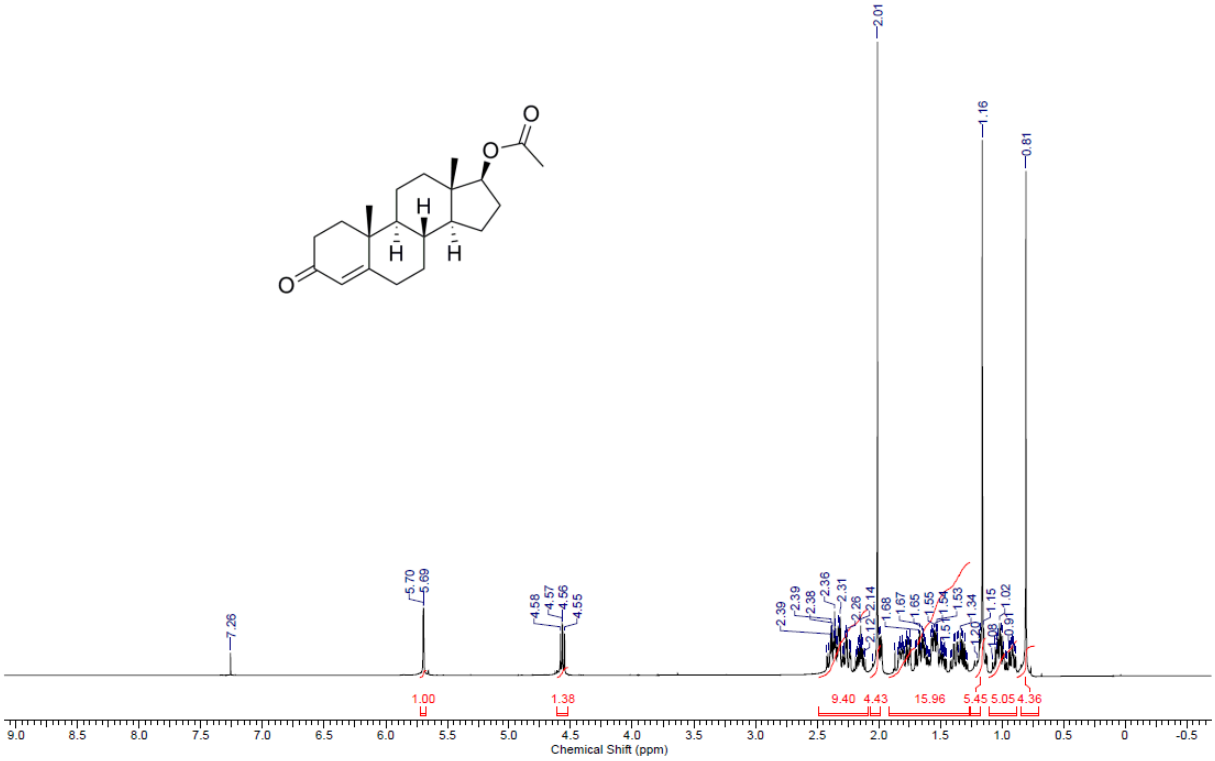
Peak Table

Detector A Ch1 254nm

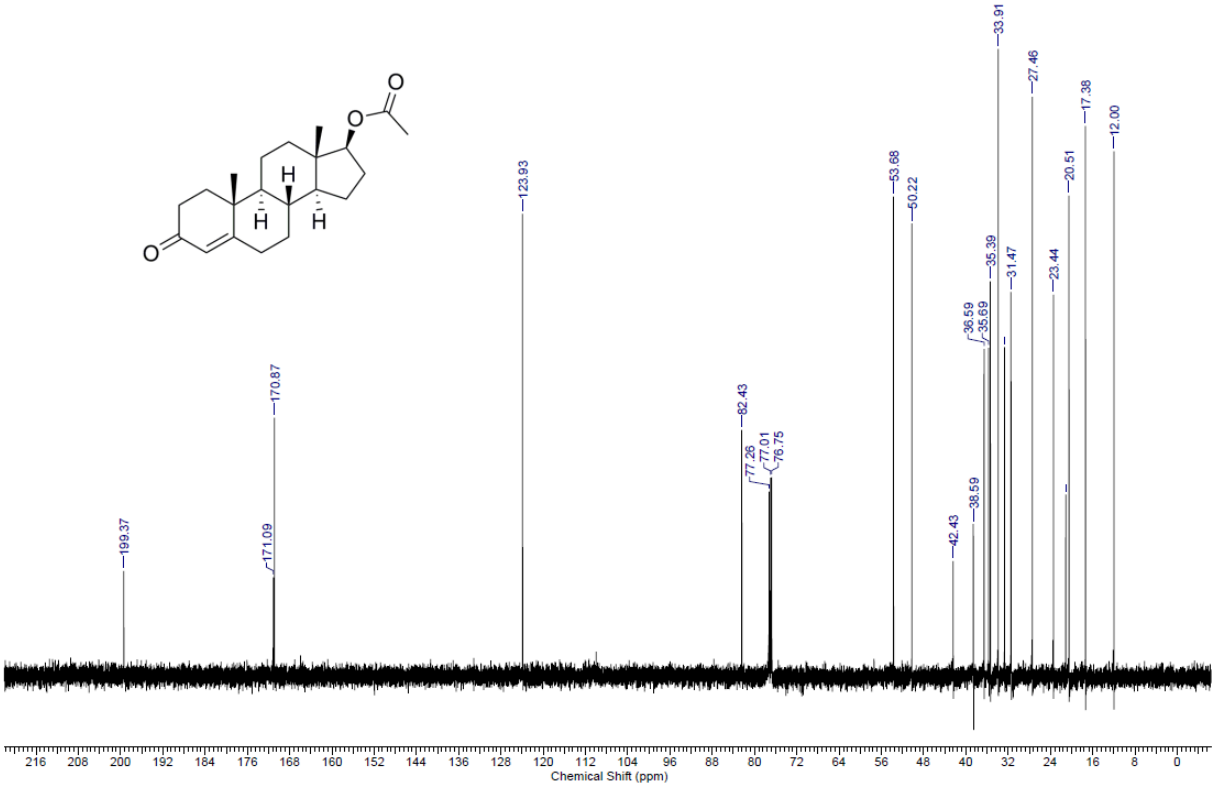
Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.468	18423378	182495	100.000	100.000
Total		18423378	182495	100.000	100.000

Testosterone acetate (2a):

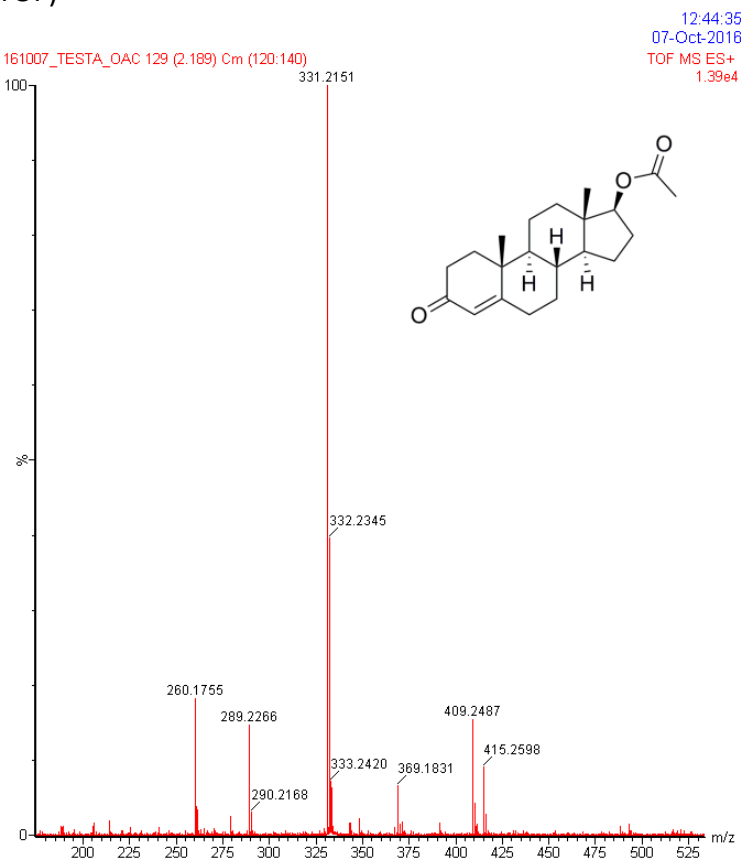
^{1}H NMR spectrum of **2a** (500 MHz, $CDCl_3$)



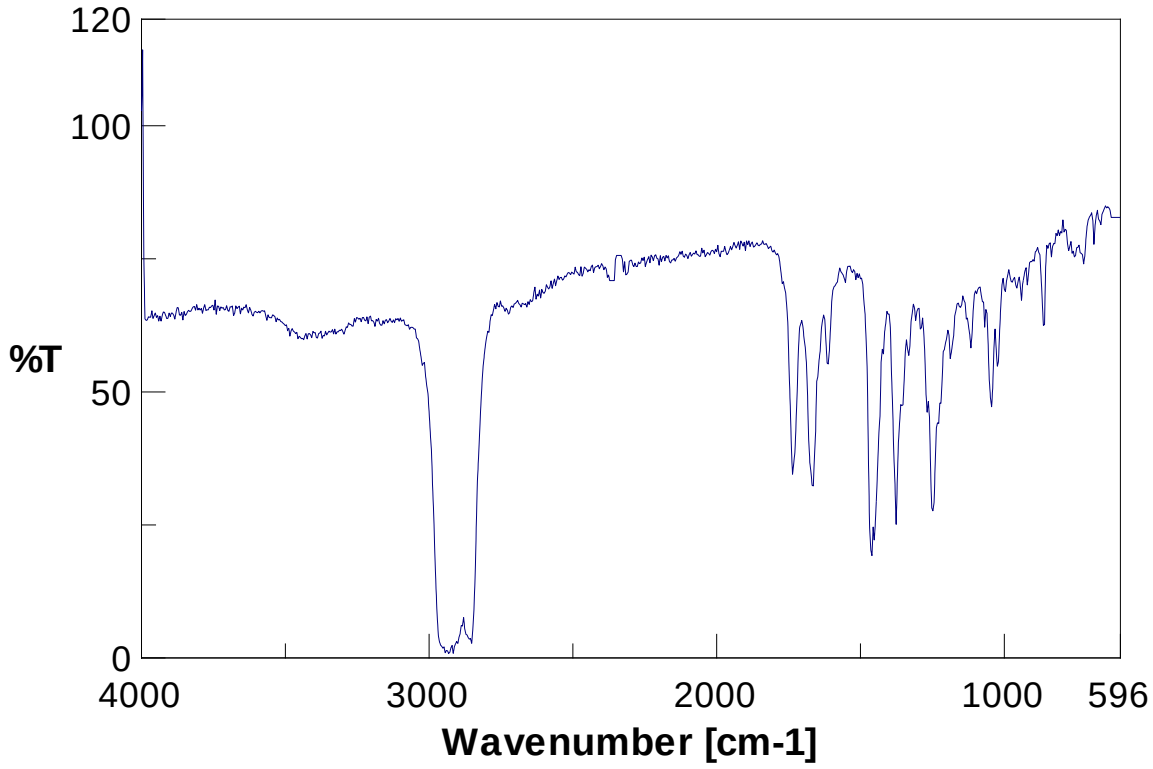
^{13}C NMR spectrum of **2a** (126 MHz, $CDCl_3$)



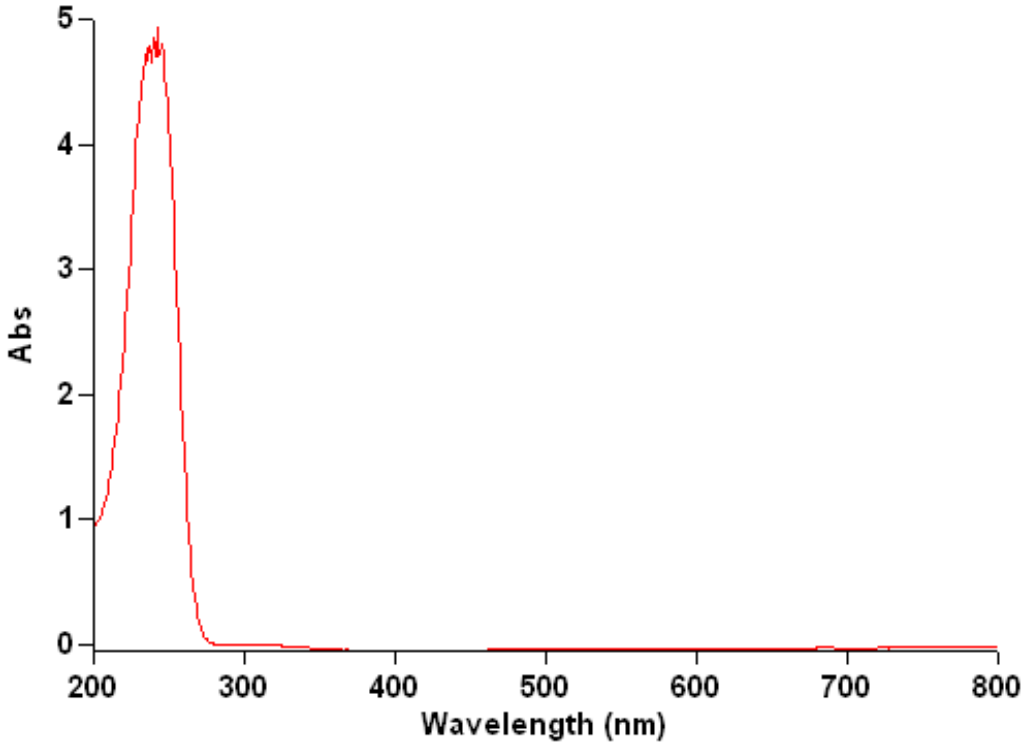
HRMS spectrum of **2a** (ESI-TOF)



IR spectrum of **2a** (Mineral oil, Nujol)



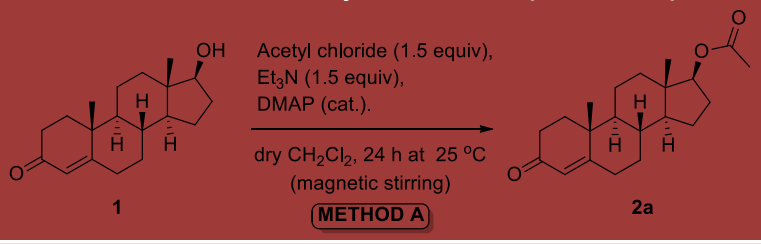
UV/VIS spectrum of **2a** (EtOH)

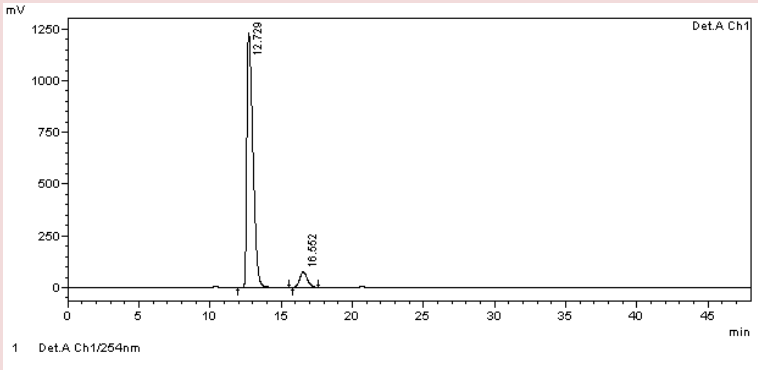


Wavelength (nm)	Abs
245.00	4.807
242.00	4.928
240.00	4.850
237.00	4.781
235.00	4.776

HPLC chromatograms of **2a**

2a (93% purity) obtained after DMAP-catalyzed reaction (Method A).



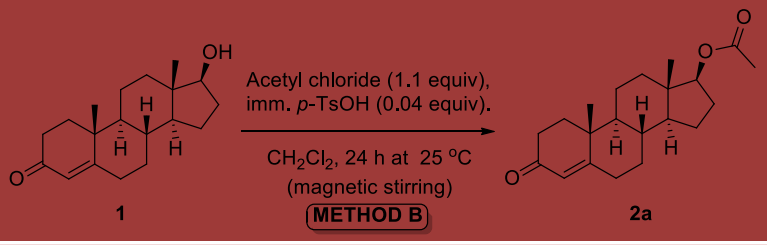


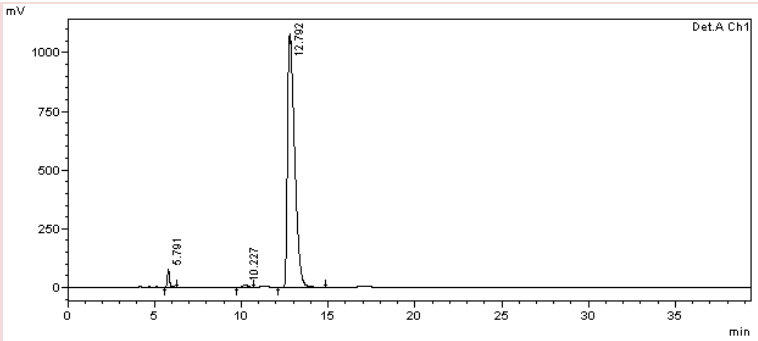
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.729	36629718	1230498	92.897	94.317
2	16.552	2800746	74147	7.103	5.683
Total		39430465	1304646	100.000	100.000

2a (97% purity) obtained after TsOH-catalyzed reaction (normal mode) (Method B).



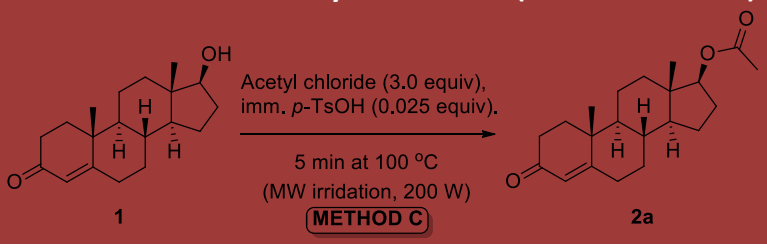


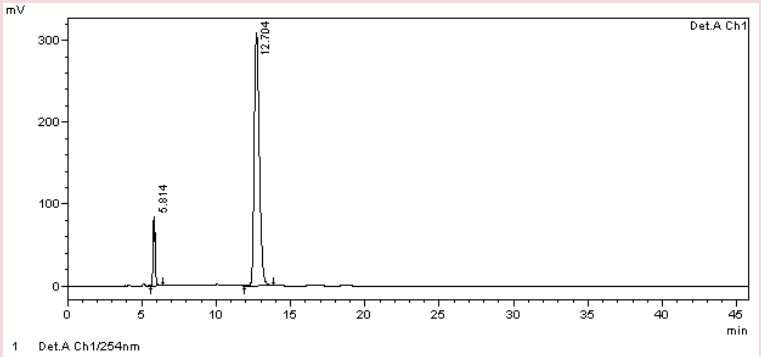
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.791	667321	74828	2.115	6.417
2	10.227	222011	11501	0.703	0.986
3	12.792	30668987	1079727	97.182	92.596
Total		31558319	1166057	100.000	100.000

2a (91% purity) obtained after TsOH-catalyzed reaction (5 min MW mode) (Method C).



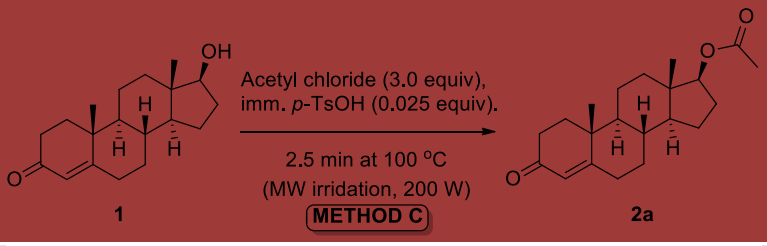


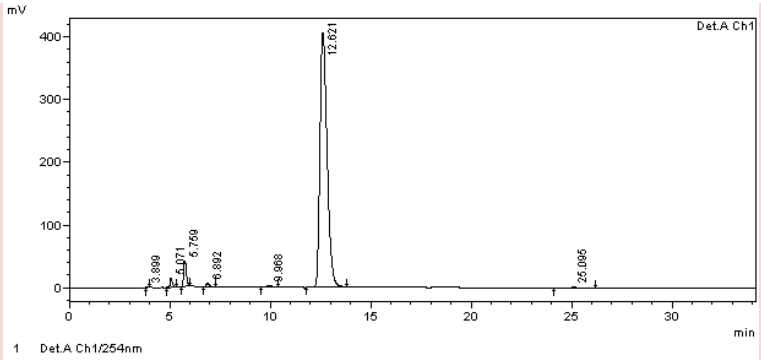
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.814	760808	84380	9.370	21.447
2	12.704	7358941	309063	90.630	78.553
Total		8119749	393443	100.000	100.000

2a (94% purity) obtained after TsOH-catalyzed reac. (2.5 min MW mode) (Method C).





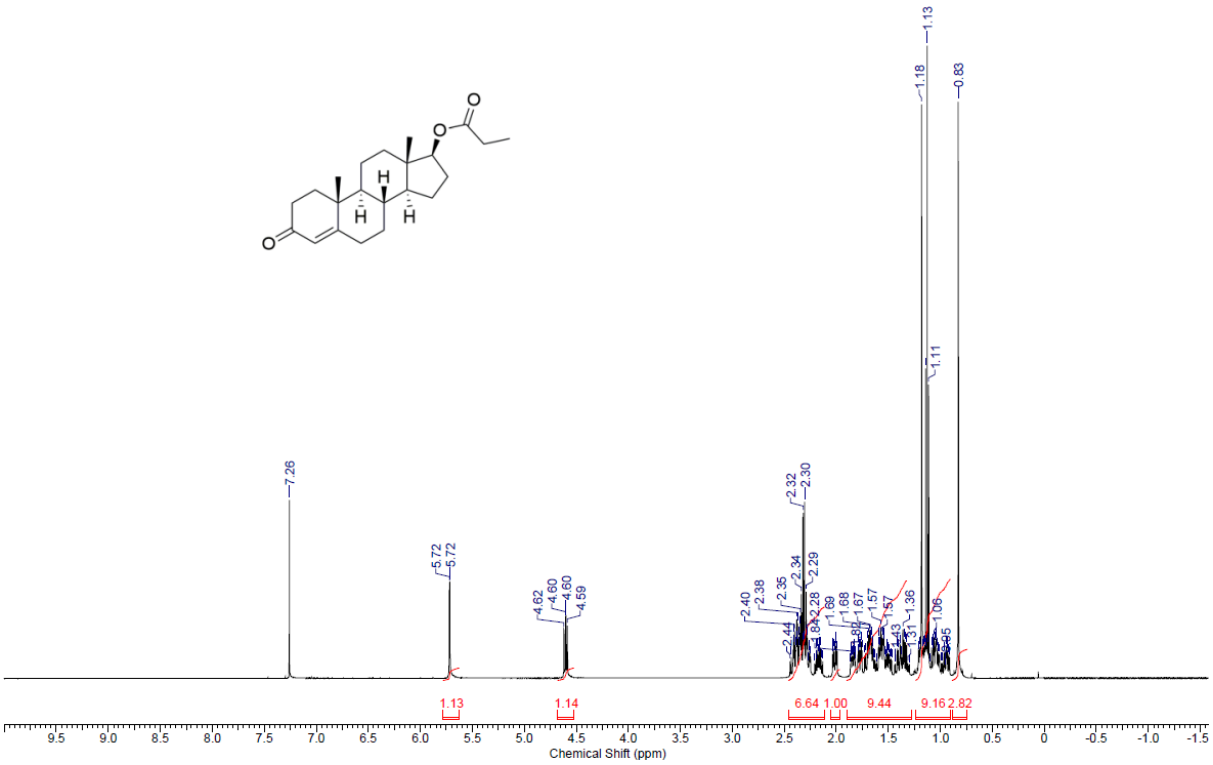
Peak Table

Detector A Ch1 254nm

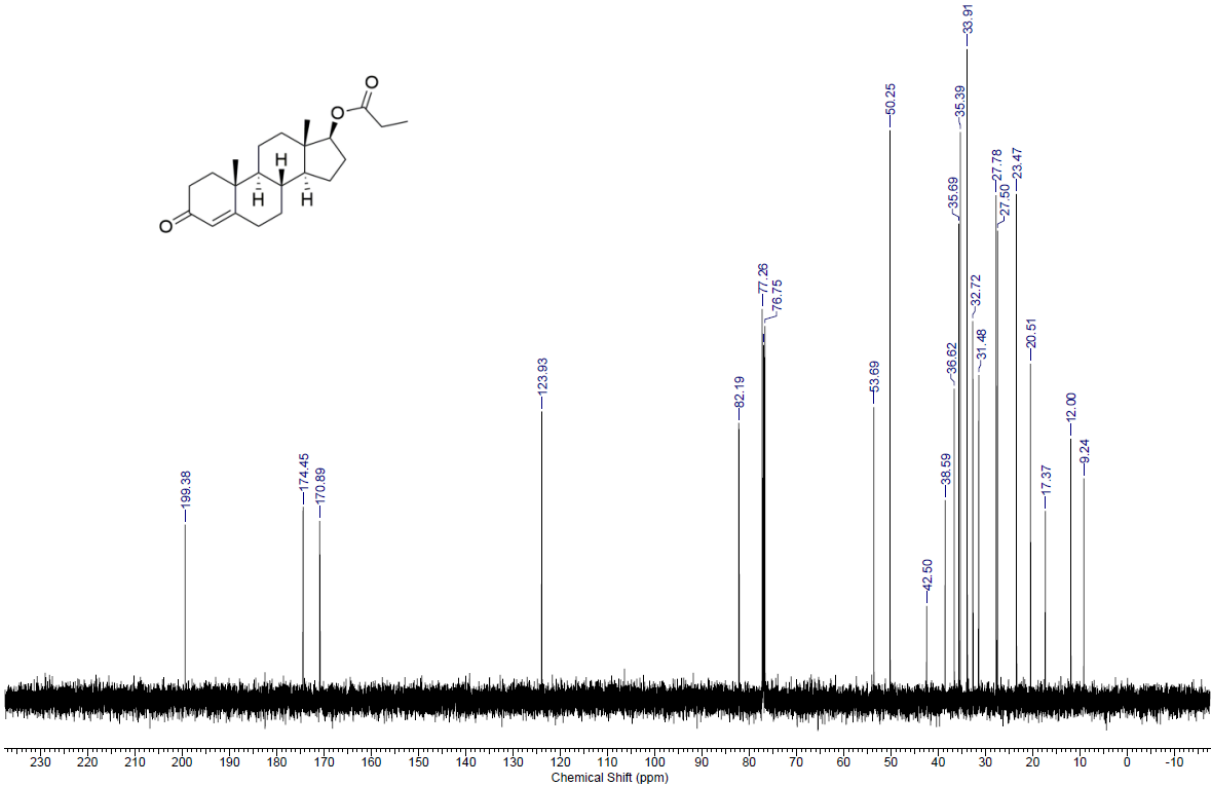
Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.899	8914	1137	0.083	0.241
2	5.071	116917	14779	1.090	3.136
3	5.759	386433	41286	3.604	8.760
4	6.892	75861	6183	0.708	1.312
5	9.968	40935	1986	0.382	0.422
6	12.621	10059230	405301	93.819	86.002
7	25.095	33681	599	0.314	0.127
Total		10721972	471271	100.000	100.000

Testosterone propionate (2b):

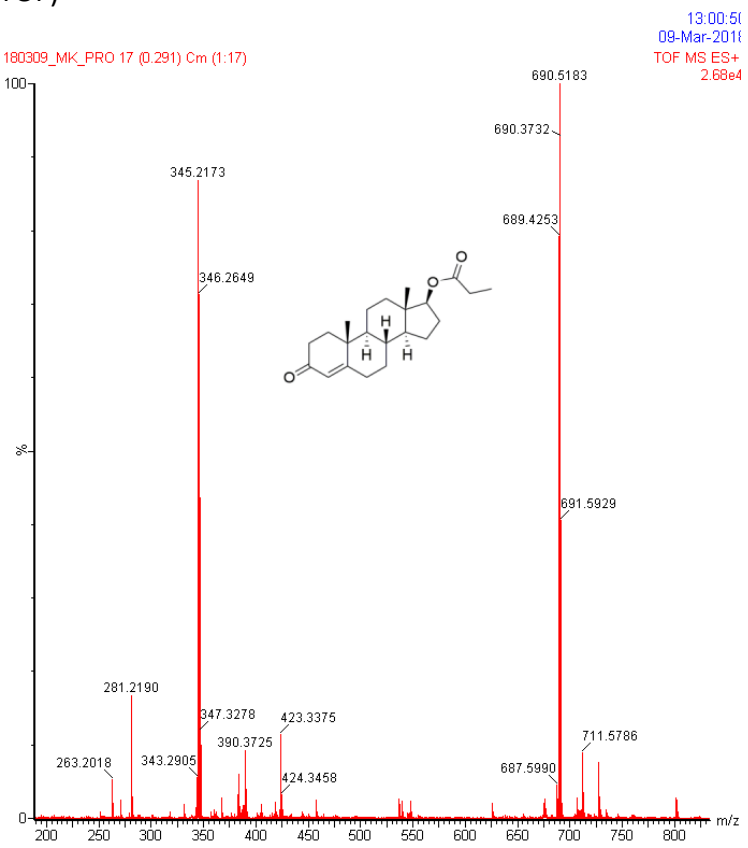
^{1}H NMR spectrum of **2b** (500 MHz, $CDCl_3$)



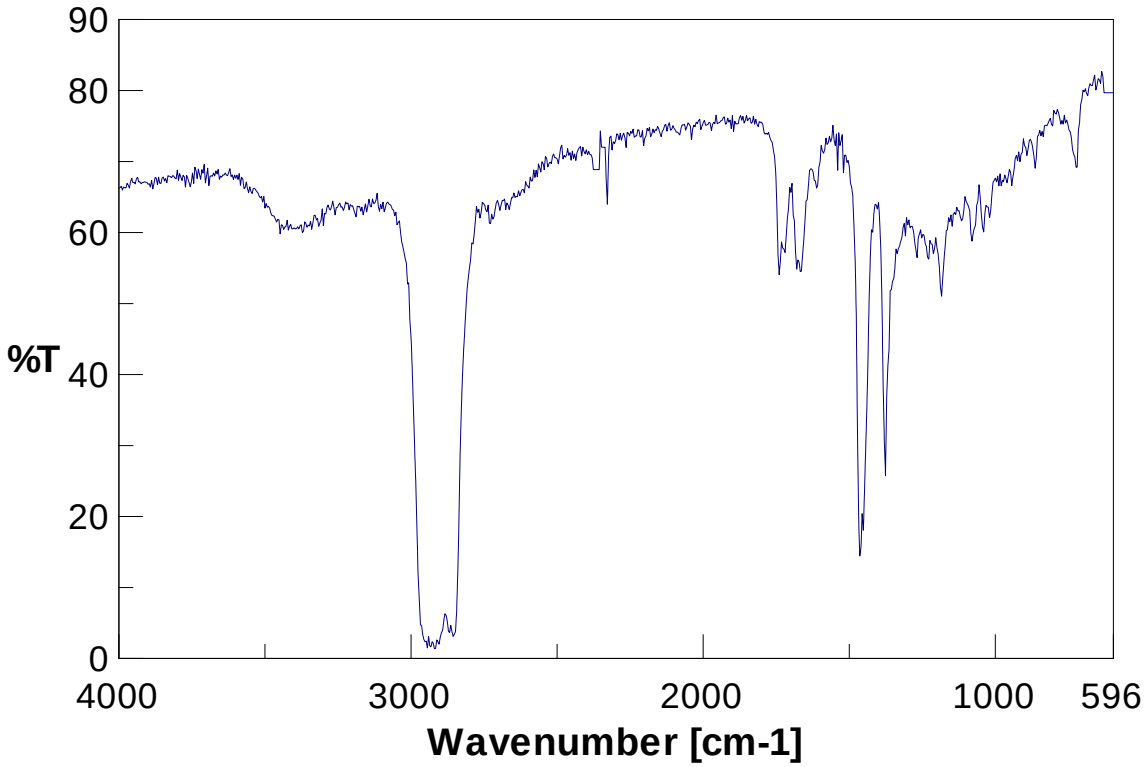
^{13}C NMR spectrum of **2b** (126 MHz, $CDCl_3$)



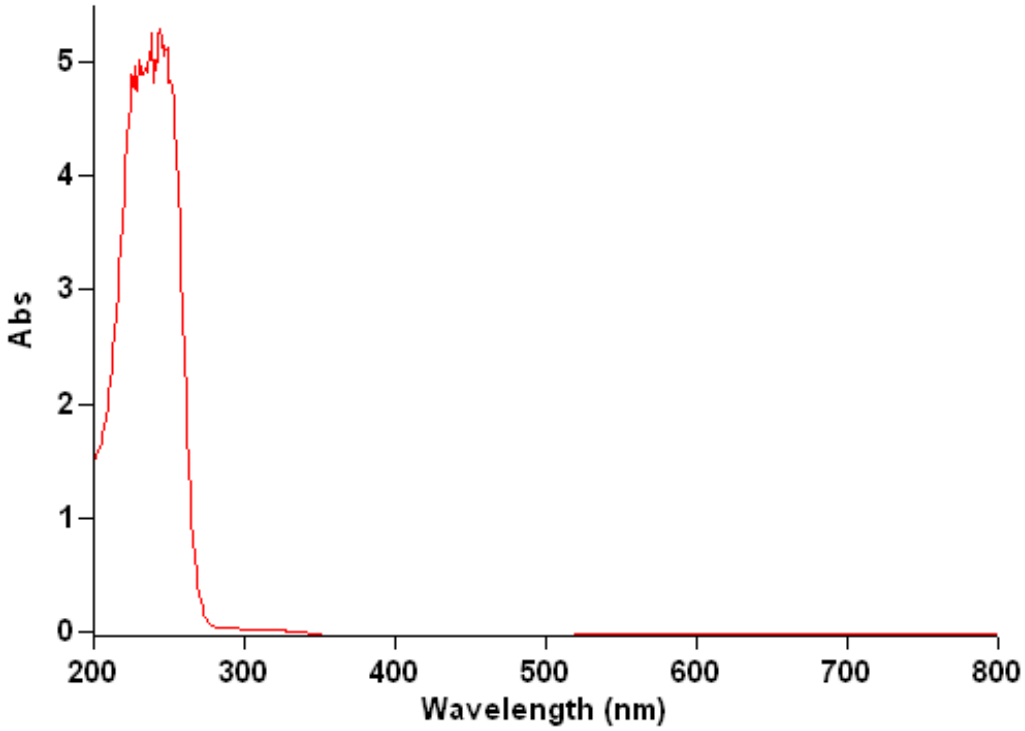
HRMS spectrum of **2b** (ESI-TOF)



IR spectrum of **2b** (Mineral oil, Nujol)



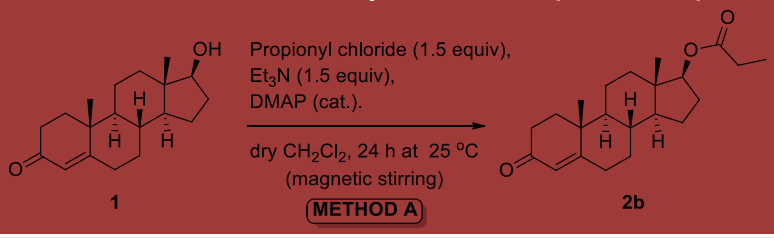
UV/VIS spectrum of **2b** (EtOH)

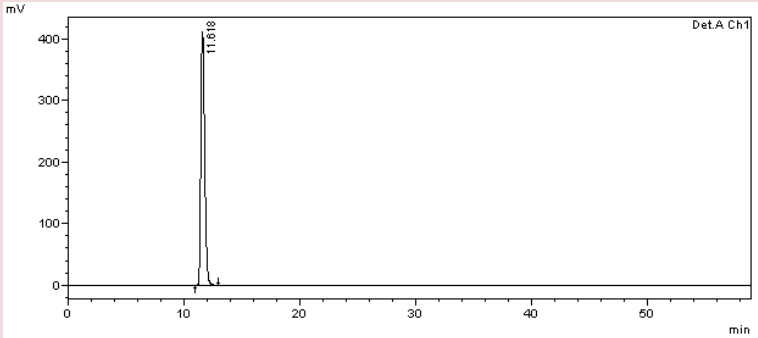


Wavelength (nm)	Abs
251.00	4.840
249.00	5.128
247.00	5.145
244.00	5.288
239.00	5.238
237.00	5.088
235.00	4.961
230.00	5.007
227.00	4.960
225.00	4.886

HPLC chromatograms of **2b**

2b (>99% purity) obtained after DMAP-catalyzed reaction (Method A).



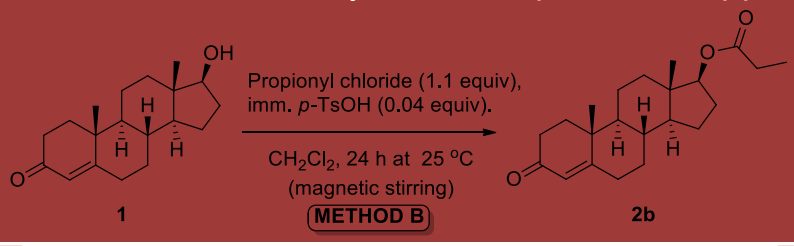


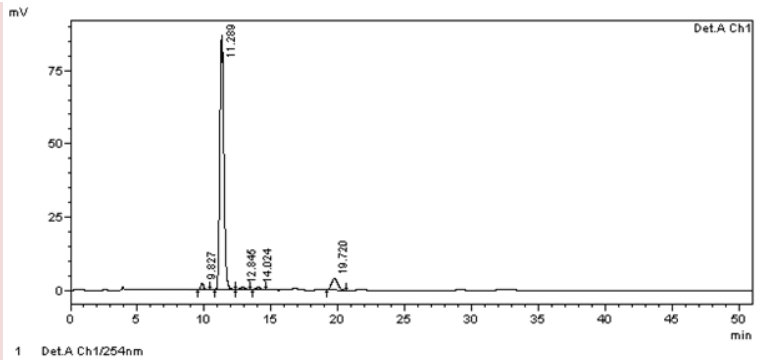
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.618	9448055	410932	100.000	100.000
Total		9448055	410932	100.000	100.000

2b (90% purity) obtained after TsOH-catalyzed reaction (normal mode) (Method B).



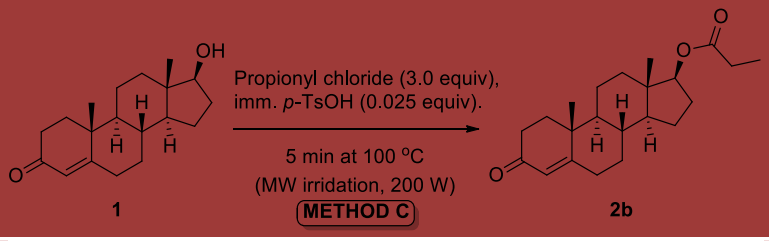


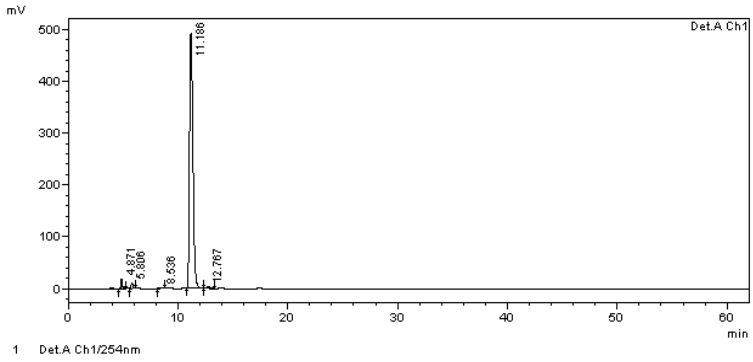
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.827	34927	2378	1.742	2.497
2	11.289	1795232	86835	89.539	91.203
3	12.845	22319	908	1.113	0.954
4	14.024	22571	986	1.126	1.036
5	19.720	129915	4104	6.480	4.310
Total		2004964	95211	100.000	100.000

2b (97% purity) obtained after TsOH-catalyzed reaction (5 min MW mode) (Method C).



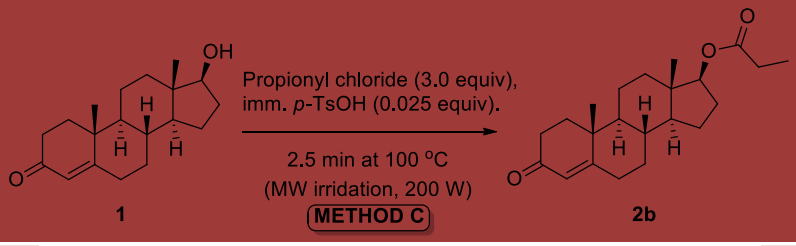


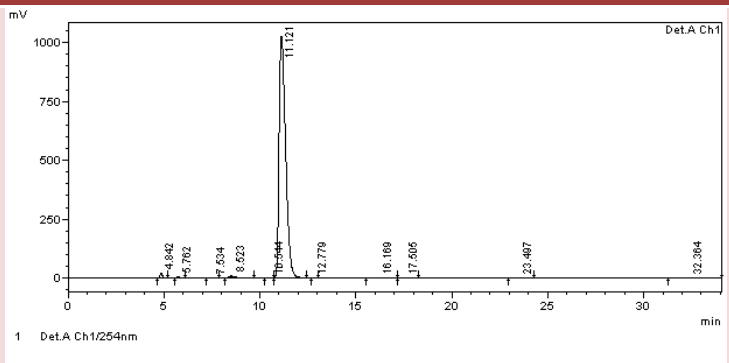
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.871	139687	19042	1.284	3.610
2	5.806	107053	11733	0.984	2.224
3	8.536	35058	2159	0.322	0.409
4	11.186	10523952	491606	96.735	93.188
5	12.767	73462	3005	0.675	0.570
Total		10879213	527545	100.000	100.000

2b (98% purity) obtained after TsOH-catalyzed reac. (2.5 min MW mode) (Method C).





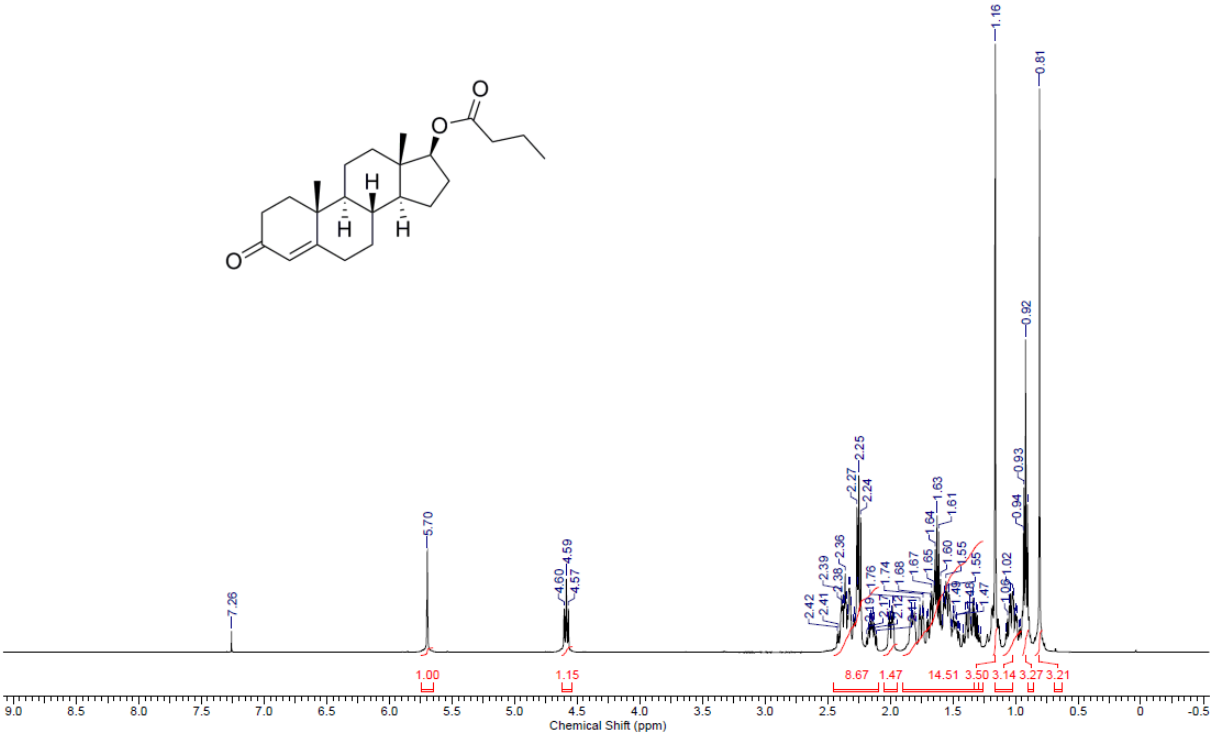
Peak Table

Detector A Ch1 254nm

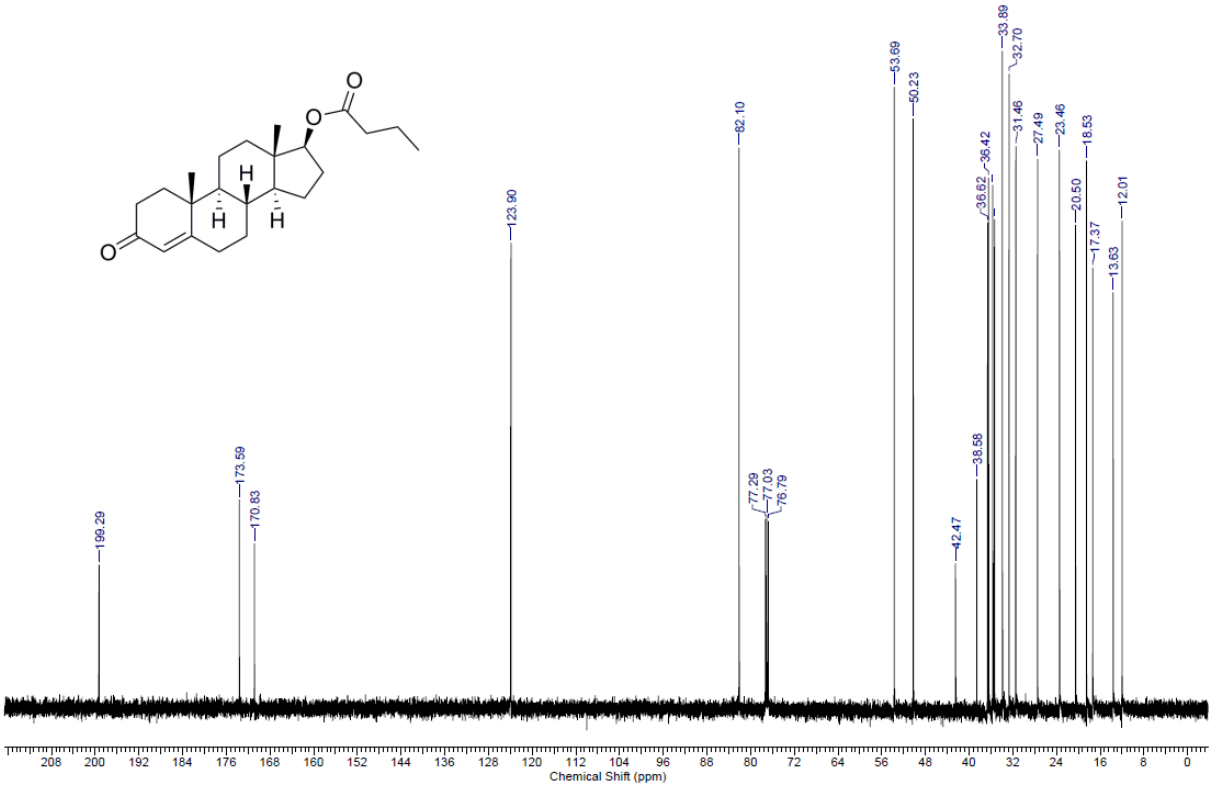
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.842	169959	22128	0.687	2.081
2	5.762	53014	5456	0.214	0.513
3	7.534	16959	954	0.069	0.090
4	8.523	187199	7441	0.757	0.700
5	10.544	21376	1395	0.086	0.131
6	11.121	24166564	1023830	97.728	96.269
7	12.779	4758	336	0.019	0.032
8	16.169	41404	795	0.167	0.075
9	17.505	14032	384	0.057	0.036
10	23.497	5732	147	0.023	0.014
11	32.364	47349	649	0.191	0.061
Total		24728346	1063513	100.000	100.000

Testosterone butanoate (2c):

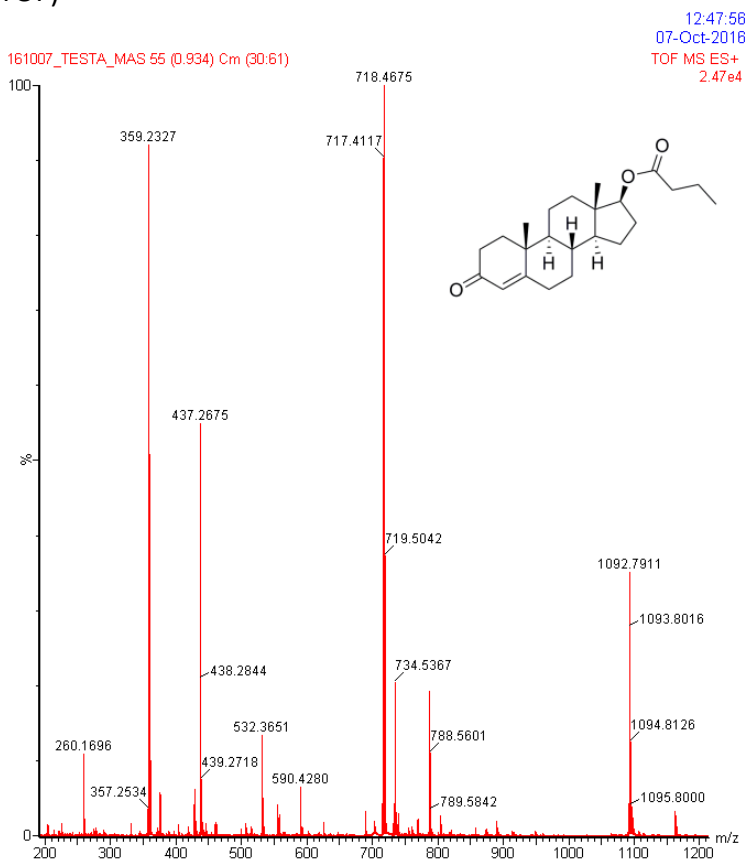
^{1}H NMR Spectrum of **2c** (500 MHz, $CDCl_3$)



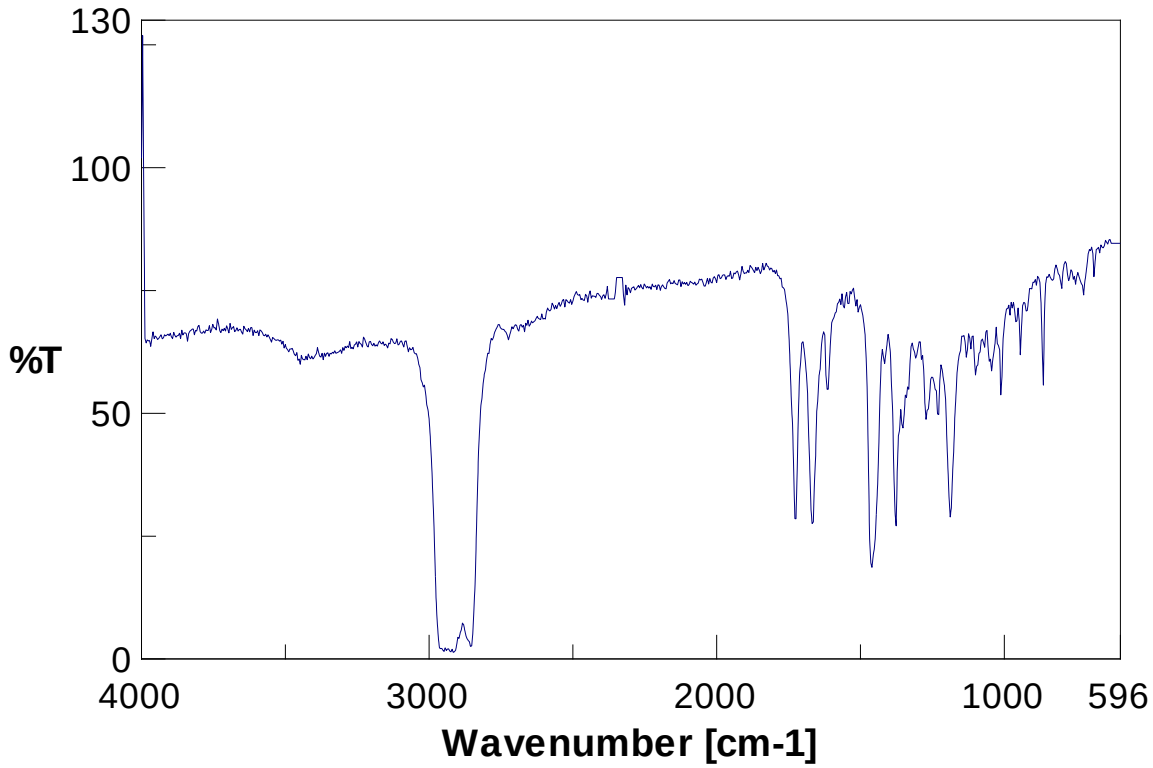
^{13}C NMR Spectrum of **2c** (126 MHz, $CDCl_3$)



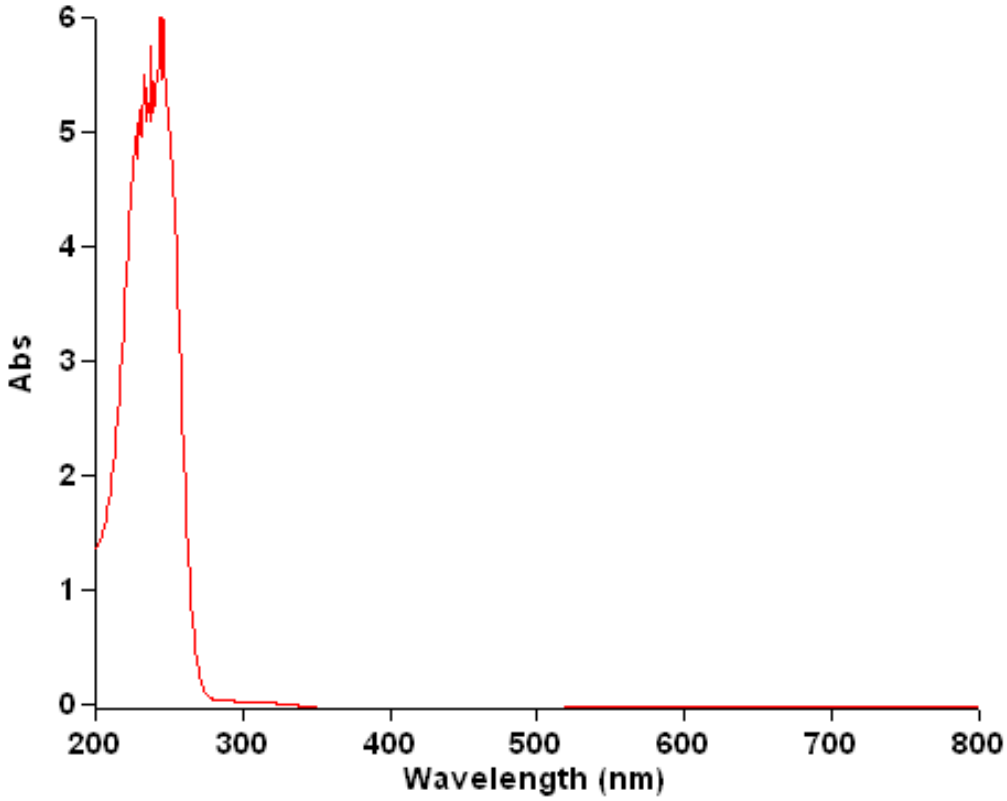
HRMS spectrum of **2c** (ESI-TOF)



IR spectrum of **2c** (Mineral oil, Nujol)



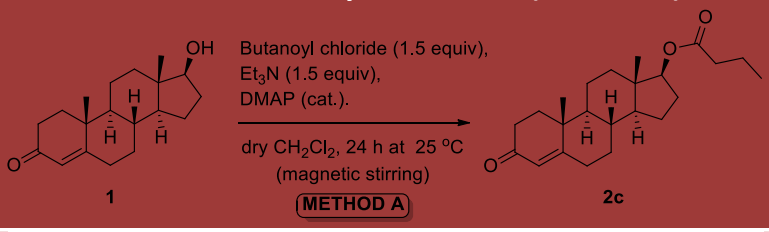
UV/VIS spectrum of **2c** (EtOH)

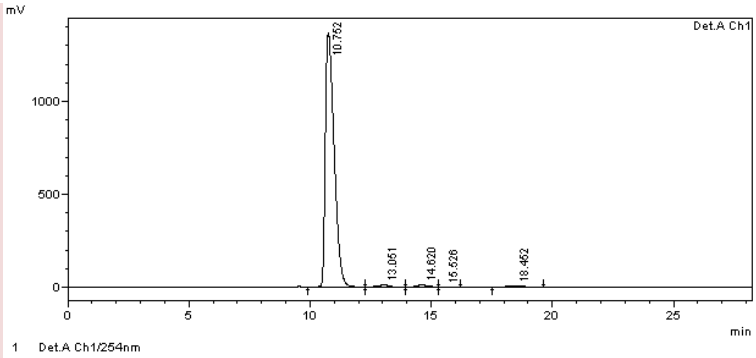


Wavelength (nm)	Abs
246.00	10.000
244.00	6.084
238.00	5.754
236.00	5.259
233.00	5.509
231.00	5.227
228.00	5.068

HPLC chromatograms of **2c**

2c (97% purity) obtained after DMAP-catalyzed reaction (Method A).



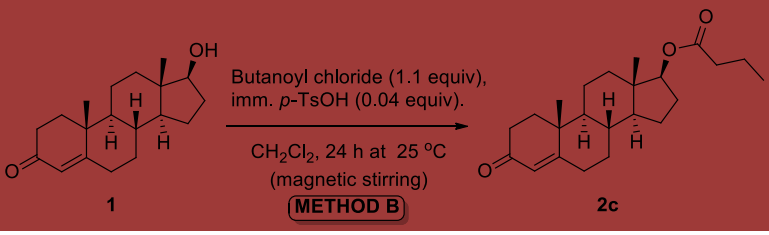


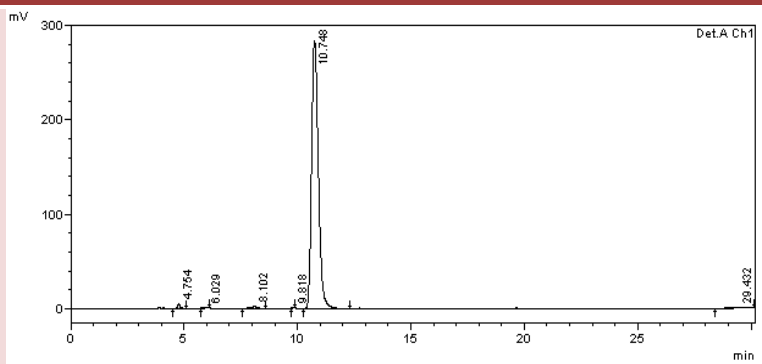
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.752	34315491	1367447	96.883	97.674
2	13.051	365030	12443	1.031	0.889
3	14.620	352364	10733	0.995	0.767
4	15.526	33985	1063	0.096	0.076
5	18.452	352809	8330	0.996	0.595
Total		35419678	1400016	100.000	100.000

2c (98% purity) obtained after TsOH-catalyzed reaction (normal mode) (Method B).



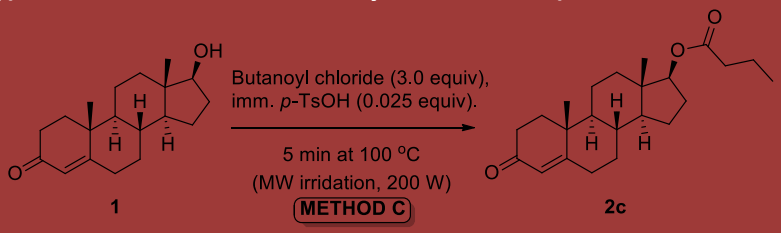


Peak Table

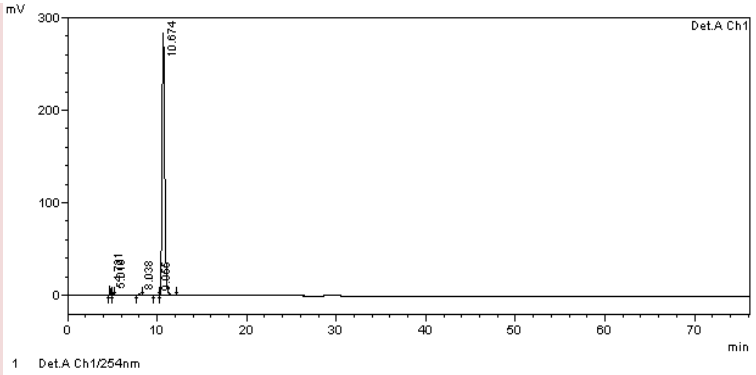
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.754	39159	5018	0.656	1.715
2	6.029	5722	337	0.096	0.115
3	8.102	38700	2252	0.648	0.770
4	9.818	1722	242	0.029	0.083
5	10.748	5825988	283640	97.589	96.935
6	29.432	58624	1119	0.982	0.382
Total		5969914	292608	100.000	100.000

2c (98% purity) obtained after TsOH-catalyzed reaction (5 min MW mode) (Method C).



1 2c

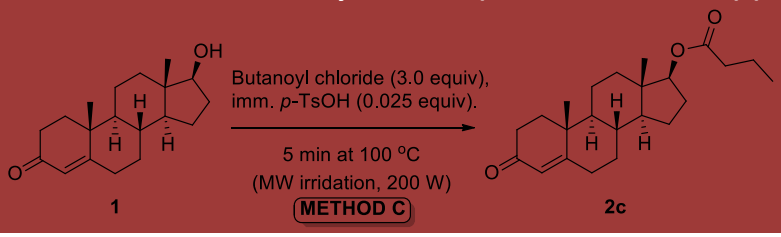


Peak Table

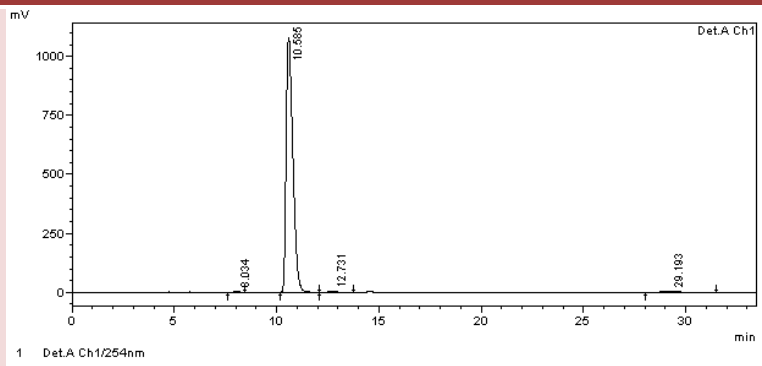
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.721	71619	10117	1.196	3.396
2	5.019	23039	2667	0.385	0.895
3	8.038	19829	1339	0.331	0.449
4	9.955	10095	535	0.169	0.180
5	10.674	5861965	283264	97.919	95.080
Total		5986548	297922	100.000	100.000

2c (98% purity) obtained after TsOH-catalyzed reac. (2.5 min MW mode) (Method C).



1 2c



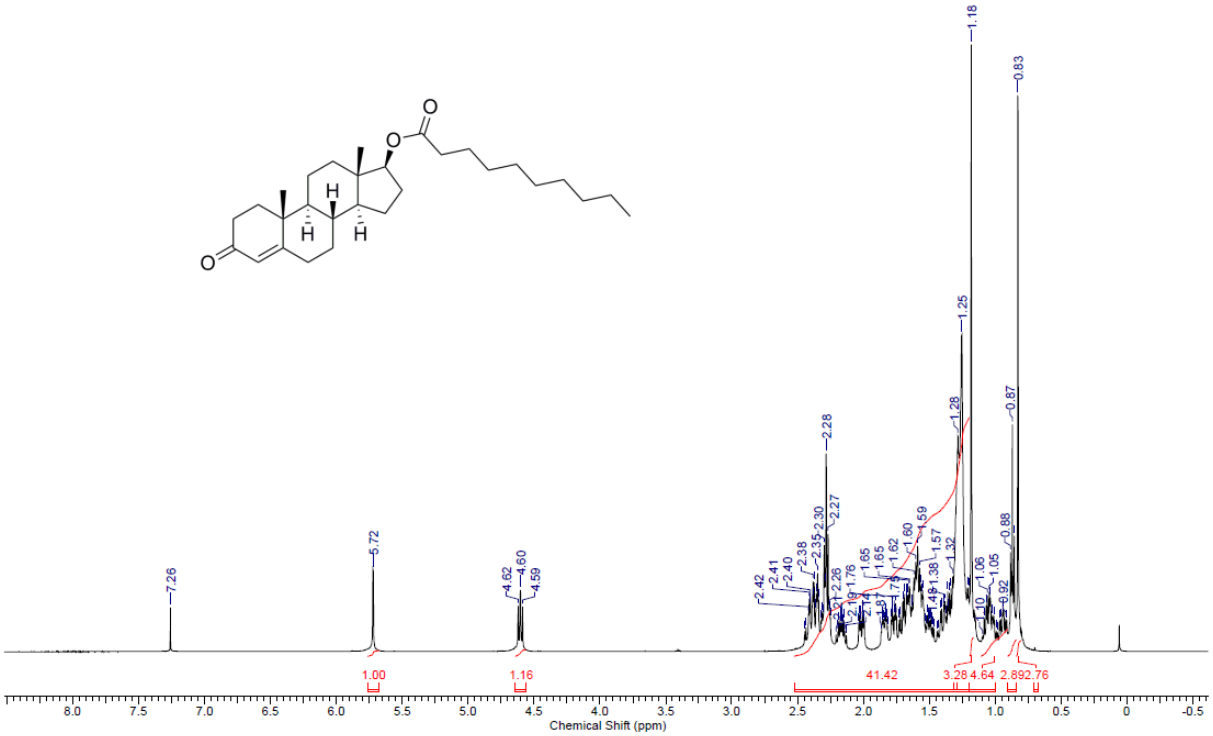
Peak Table

Detector A Ch1 254nm

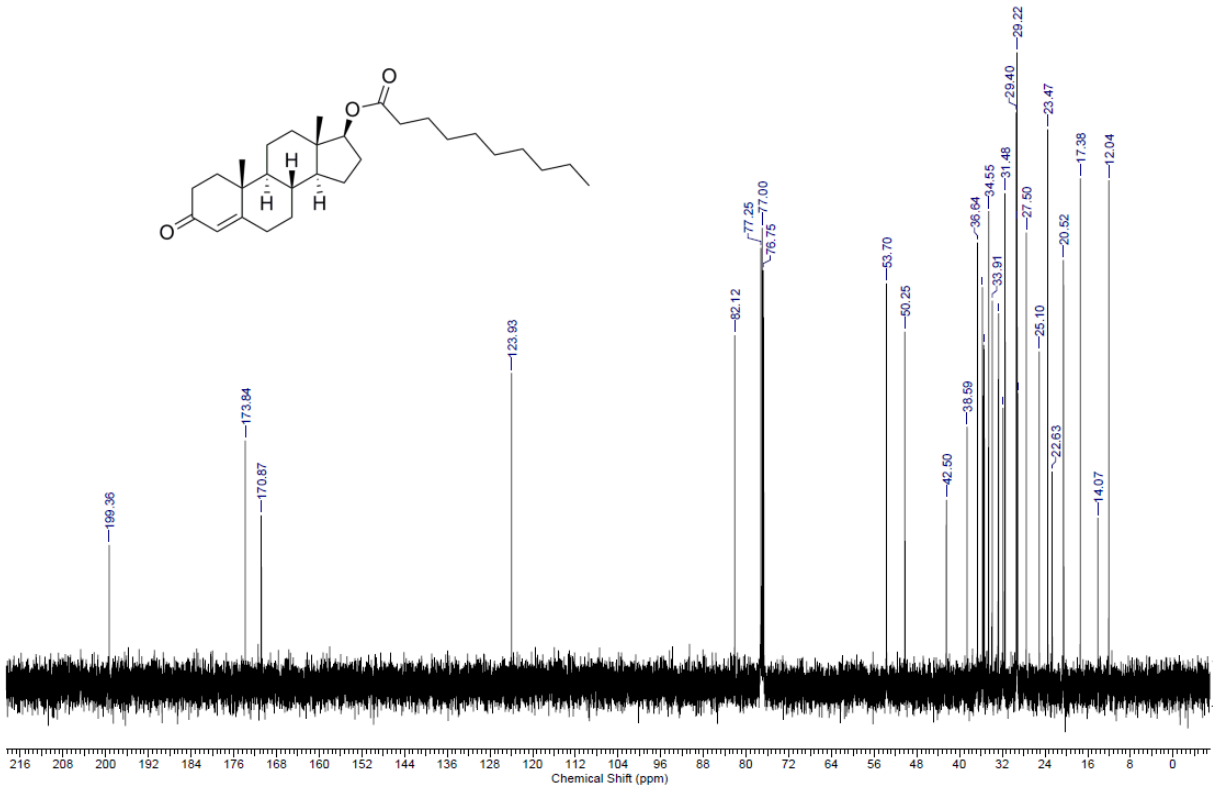
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.034	98248	6448	0.391	0.590
2	10.585	24655355	1077645	98.055	98.634
3	12.731	125225	4615	0.498	0.422
4	29.193	265645	3858	1.056	0.353
Total		25144474	1092566	100.000	100.000

Testosterone decanoate (2d):

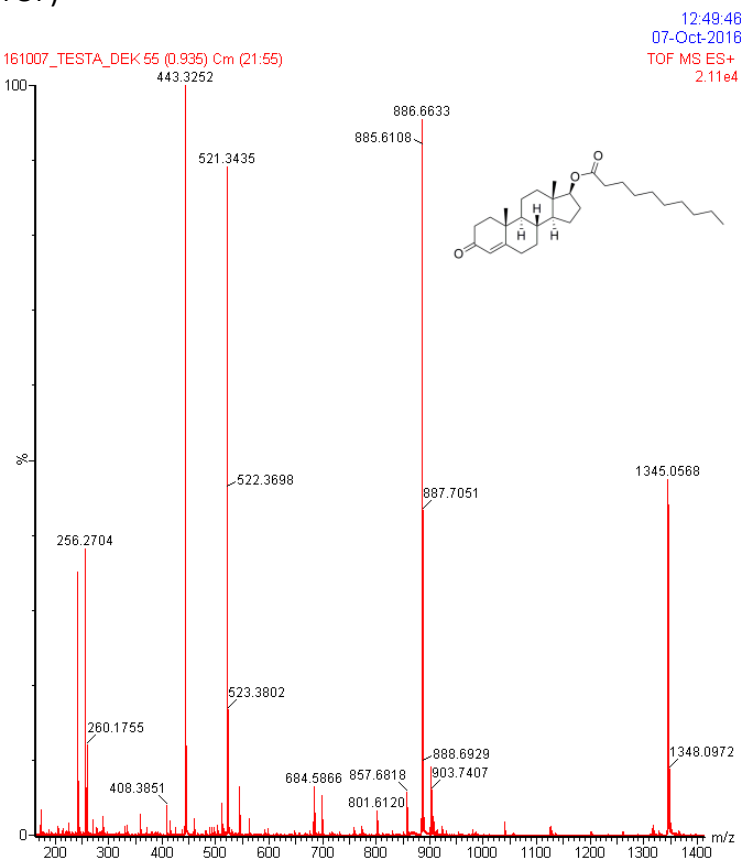
^{1}H NMR spectrum of **2d** (500 MHz, $CDCl_3$)



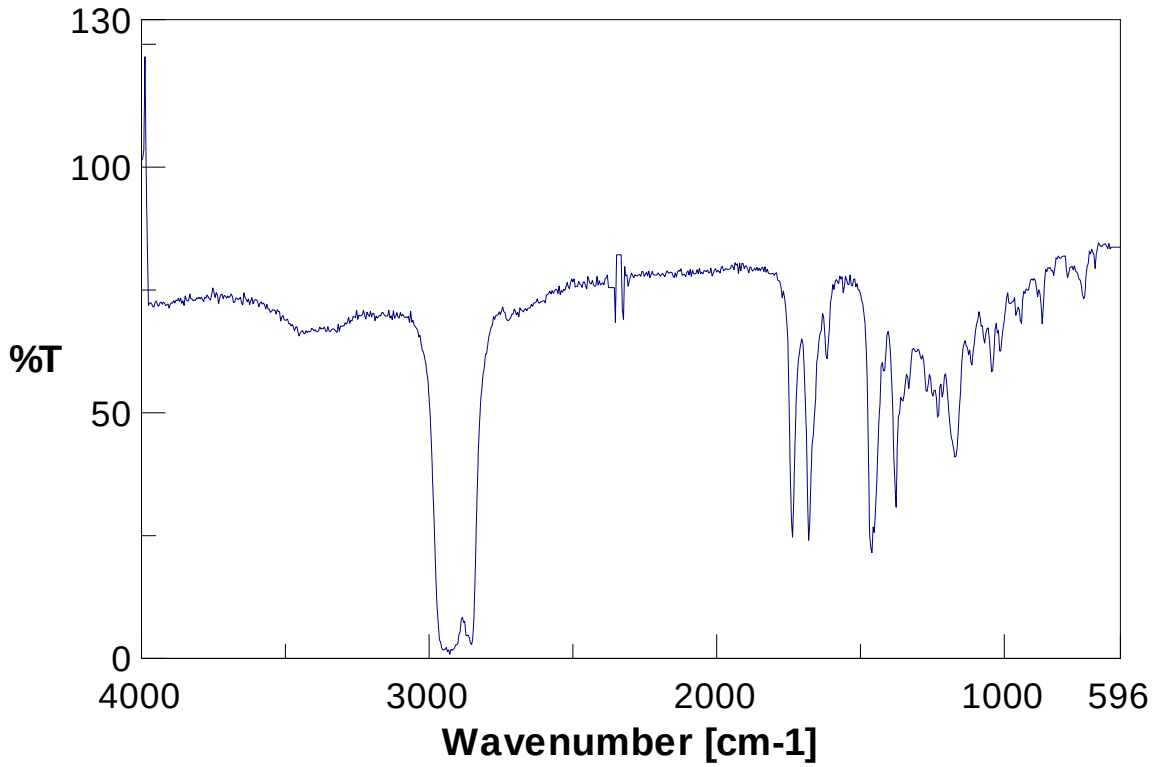
^{13}C NMR spectrum of **2d** (126 MHz, $CDCl_3$)



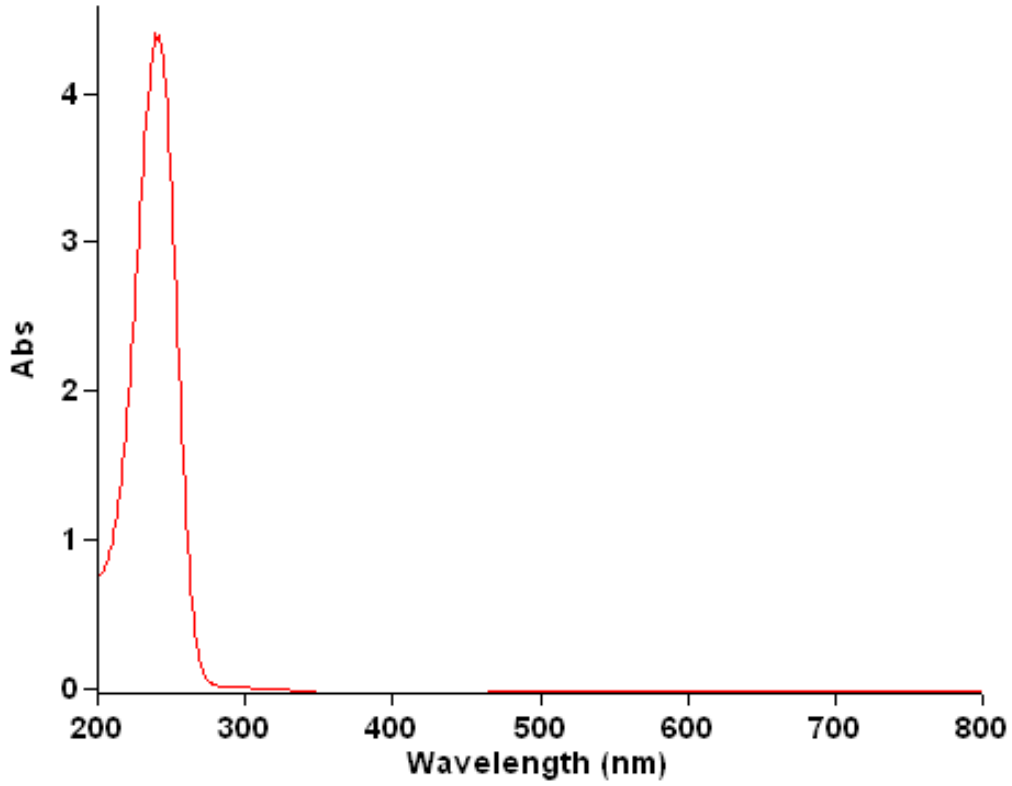
HRMS spectrum of **2d** (ESI-TOF)



IR spectrum of **2d** (Mineral oil, Nujol)



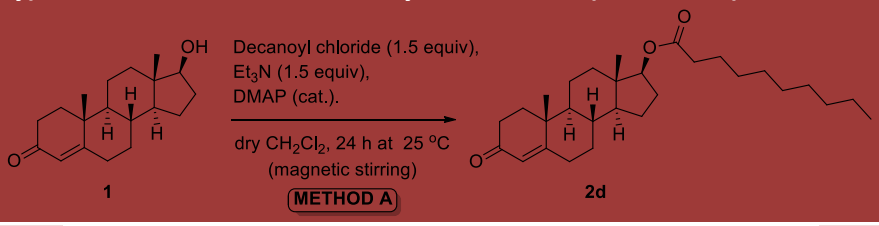
UV/VIS spectrum of **2d** (EtOH)

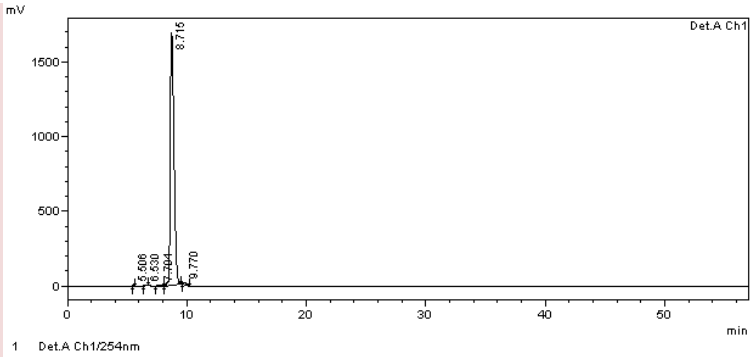


Wavelength (nm)	Abs
241.00	4.401
239.00	4.407

HPLC chromatograms of **2d**

2d (99% purity) obtained after DMAP-catalyzed reaction (Method A).



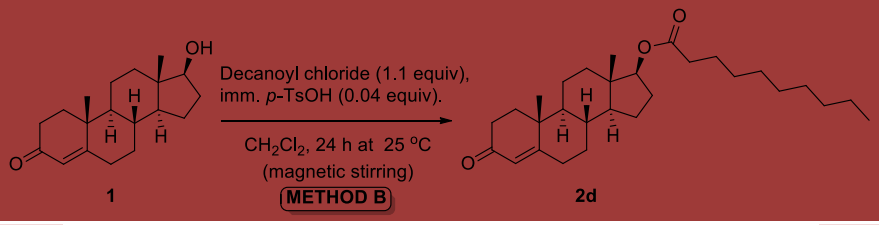


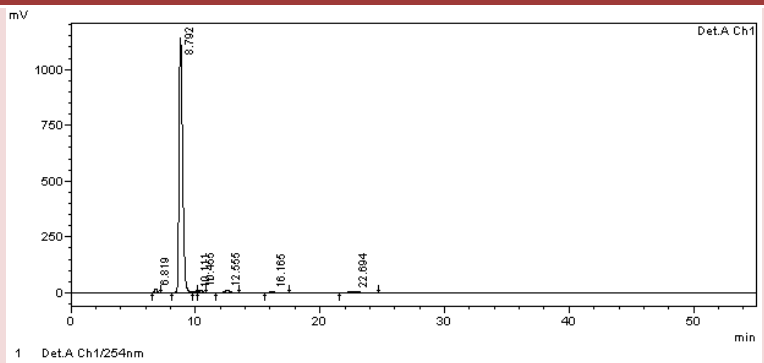
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.506	21557	3579	0.058	0.209
2	6.530	65601	6130	0.178	0.358
3	7.704	121722	6153	0.330	0.359
4	8.715	36501794	1687629	98.949	98.513
5	9.770	178695	9620	0.484	0.562
Total		36889370	1713111	100.000	100.000

2d (95% purity) obtained after TsOH-catalyzed reaction (normal mode) (Method B).



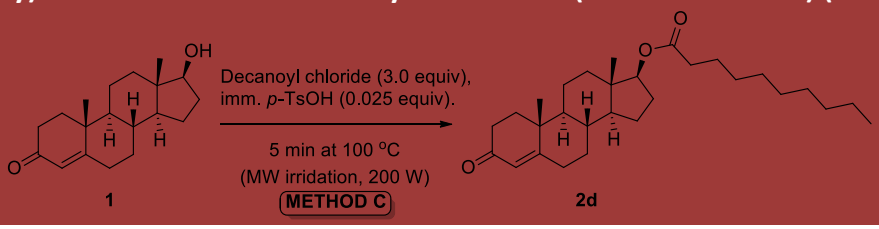


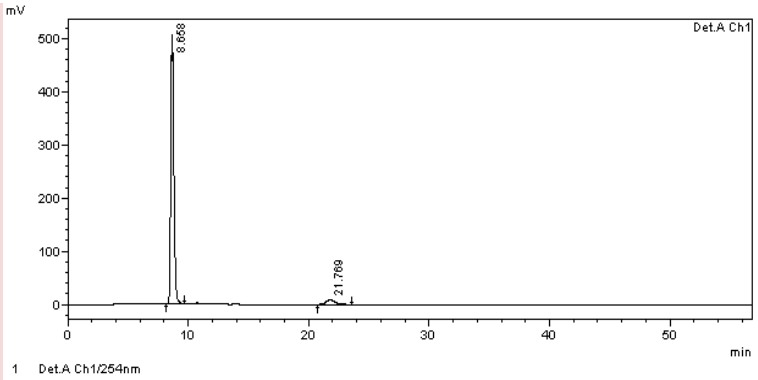
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.819	201538	15375	0.841	1.297
2	8.792	22854463	1139804	95.404	96.158
3	10.111	47575	3251	0.199	0.274
4	10.455	150429	7818	0.628	0.660
5	12.555	299052	10978	1.248	0.926
6	16.165	97512	2972	0.407	0.251
7	22.694	304888	5149	1.273	0.434
Total		23955455	1185347	100.000	100.000

2d (95% purity) obtained after TsOH-catalyzed reaction (5 min MW mode) (Method C).



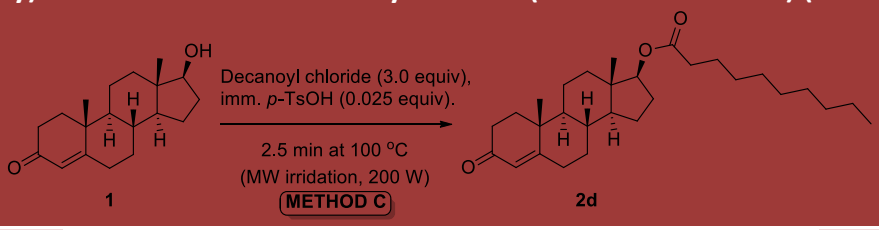


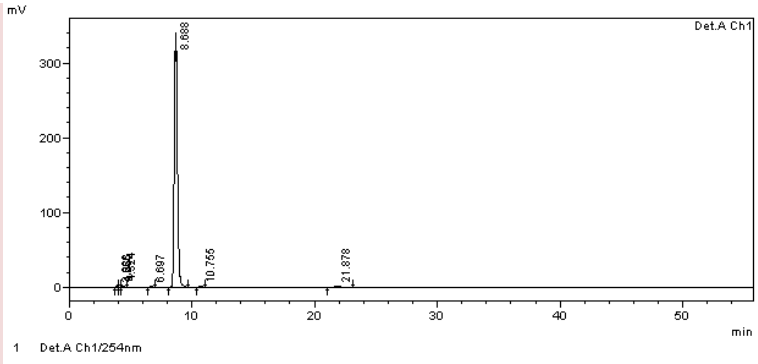
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.658	9053597	506821	95.162	98.359
2	21.769	460319	8454	4.838	1.641
Total		9513917	515275	100.000	100.000

2d (98% purity) obtained after TsOH-catalyzed reac. (2.5 min MW mode) (Method C).





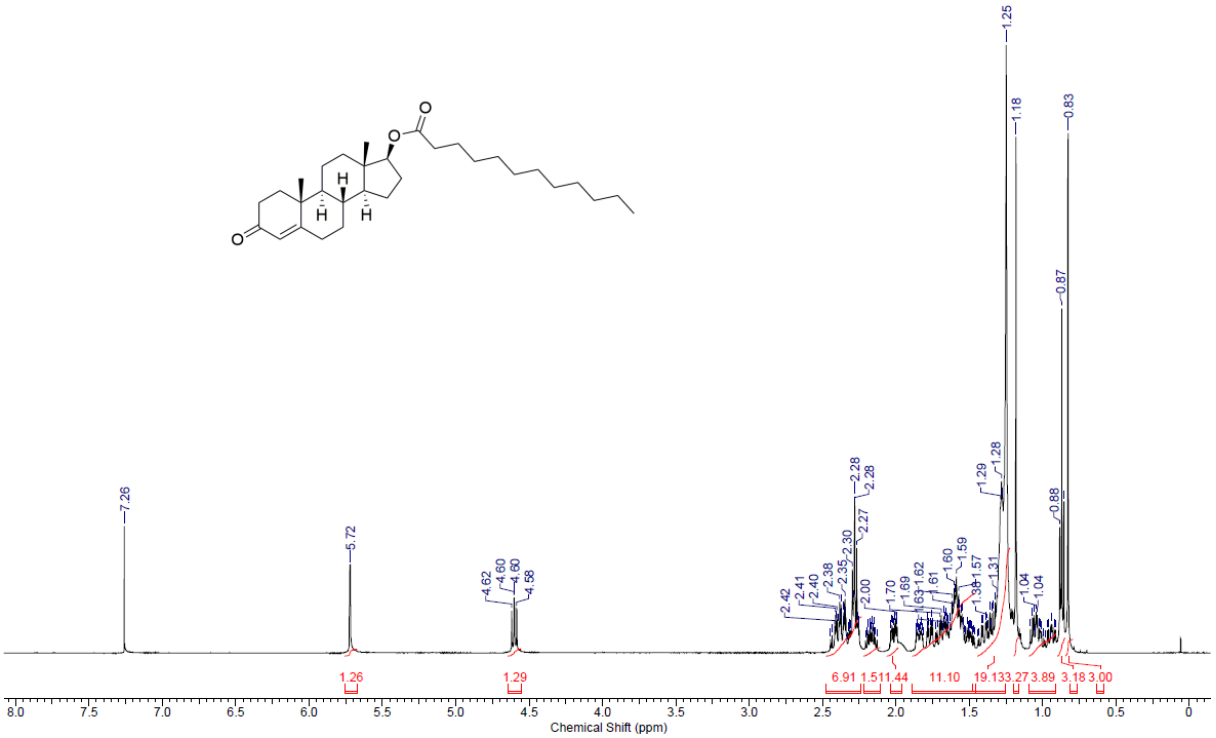
Peak Table

Detector A Ch1 254nm

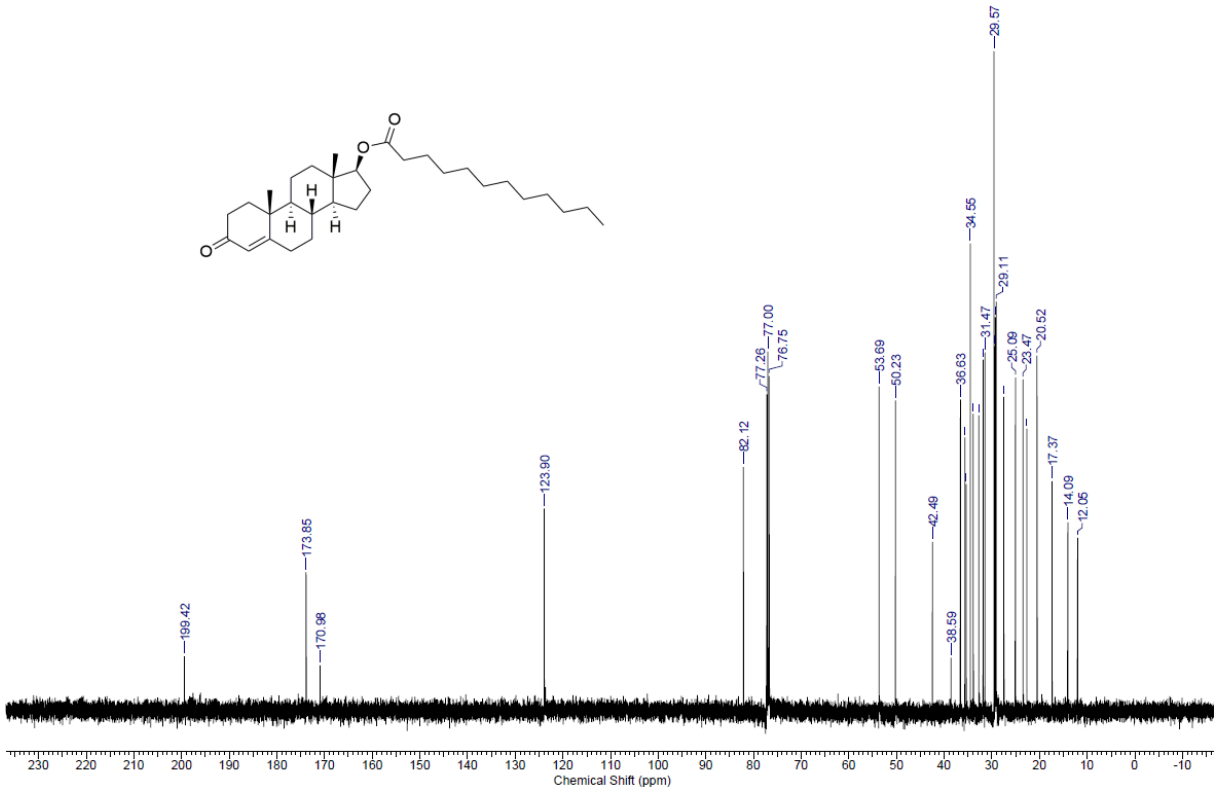
Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.888	5758	630	0.094	0.182
2	4.065	3314	415	0.054	0.120
3	4.324	25463	2257	0.417	0.652
4	6.697	16802	1290	0.275	0.372
5	8.688	6004714	340156	98.298	98.239
6	10.755	13949	807	0.228	0.233
7	21.878	38670	700	0.633	0.202
Total		6108670	346255	100.000	100.000

Testosterone laurate (2e):

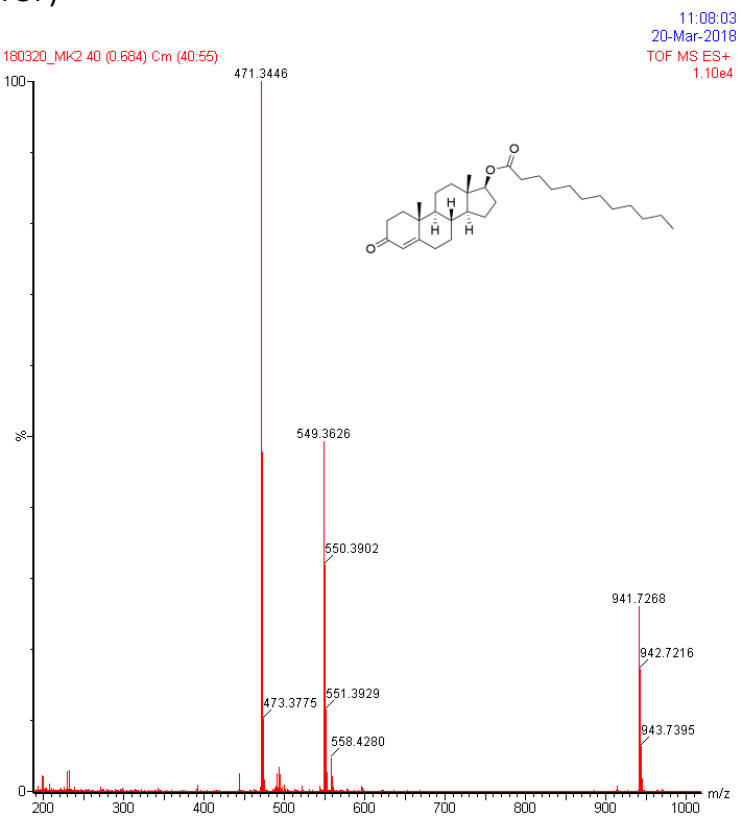
^{1}H NMR Spectrum of **2e** (500 MHz, $CDCl_3$)



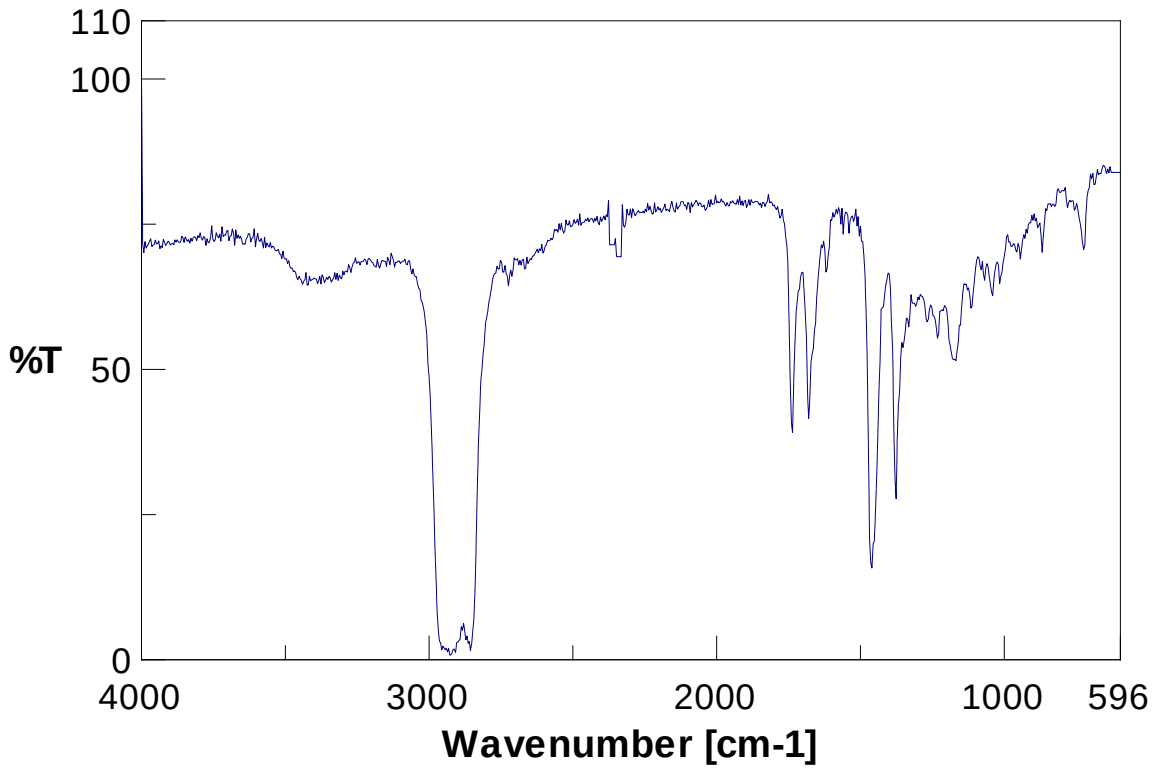
^{13}C NMR Spectrum of **2e** (126 MHz, $CDCl_3$)



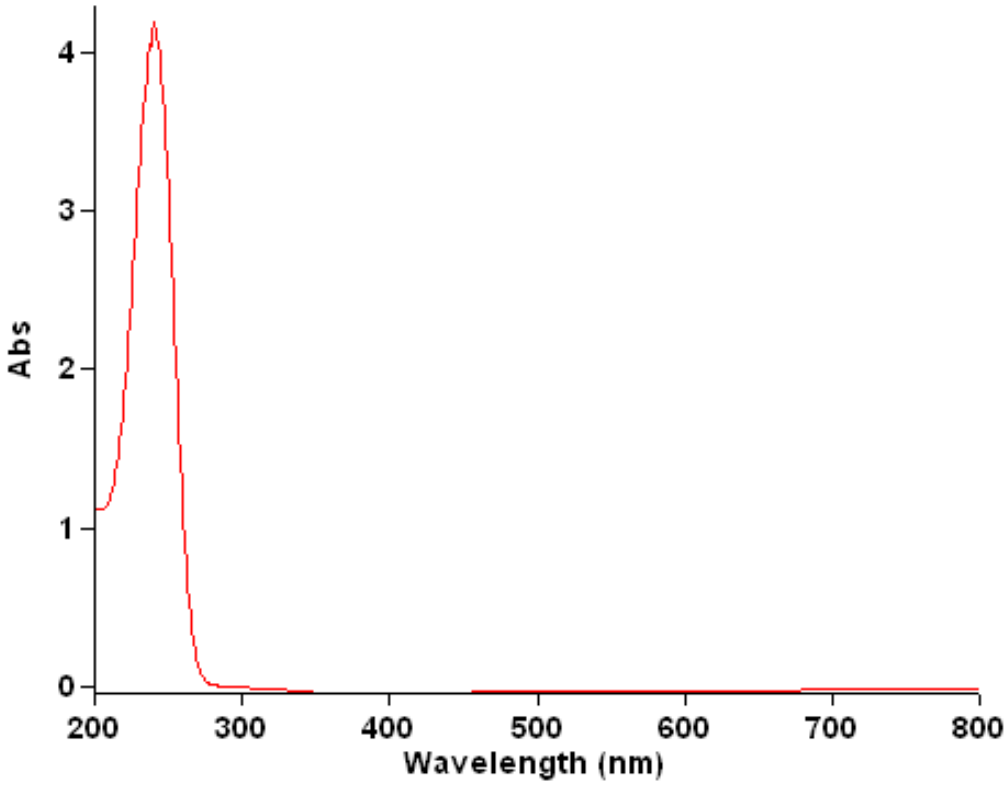
HRMS spectrum of **2e** (ESI-TOF)



IR spectrum of **2e** (Mineral oil, Nujol)



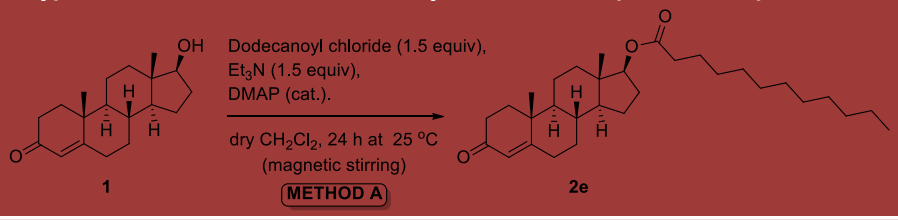
UV/VIS spectrum of **2e** (EtOH)

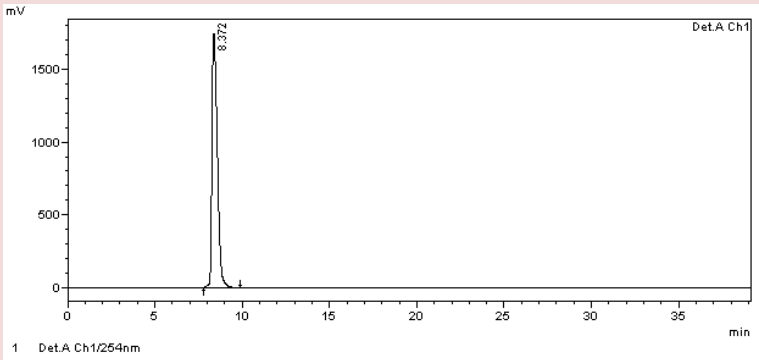


Wavelength (nm)	Abs
240.00	4.193

HPLC chromatograms of **2e**

2e (>99% purity) obtained after DMAP-catalyzed reaction (Method A).



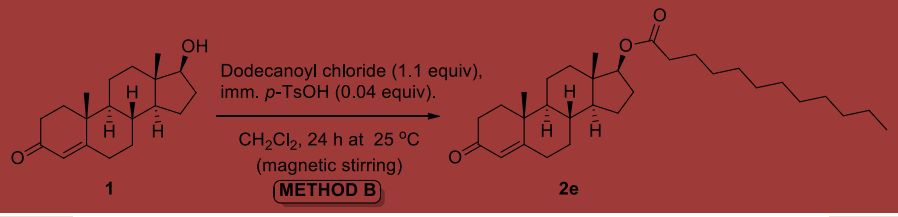


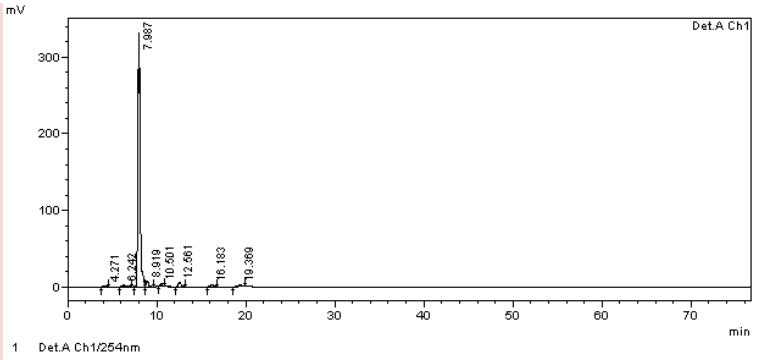
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.372	37519200	1740497	100.000	100.000
Total		37519200	1740497	100.000	100.000

2e (91% purity) obtained after TsOH-catalyzed reaction (normal mode) (Method B).



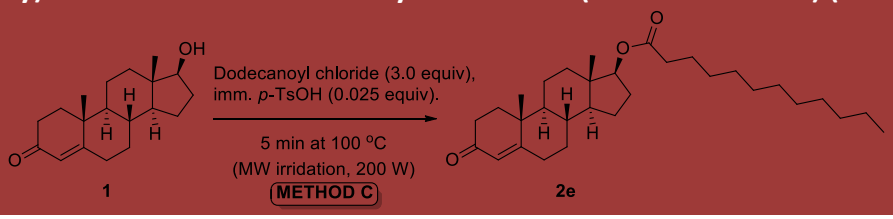


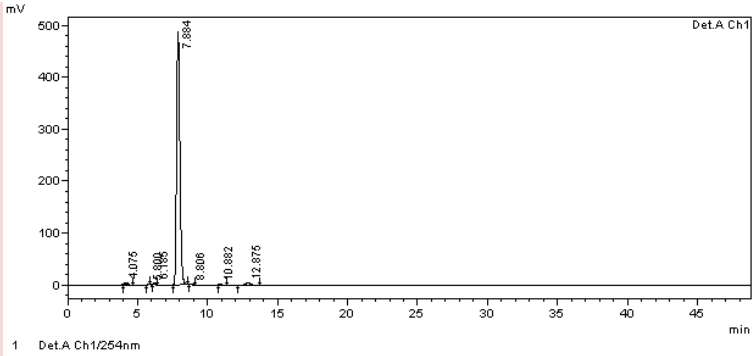
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.271	19628	1267	0.311	0.355
2	6.242	57239	2432	0.907	0.681
3	7.987	5755413	331270	91.179	92.779
4	8.919	155516	8008	2.464	2.243
5	10.501	70491	4481	1.117	1.255
6	12.561	133577	5993	2.116	1.678
7	16.183	57714	2052	0.914	0.575
8	19.369	62632	1551	0.992	0.434
Total		6312211	357053	100.000	100.000

2e (97% purity) obtained after TsOH-catalyzed reaction (5 min MW mode) (Method C).



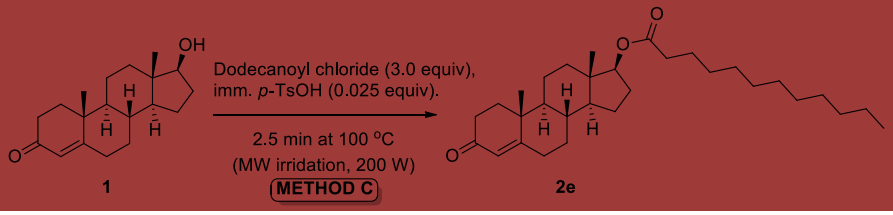


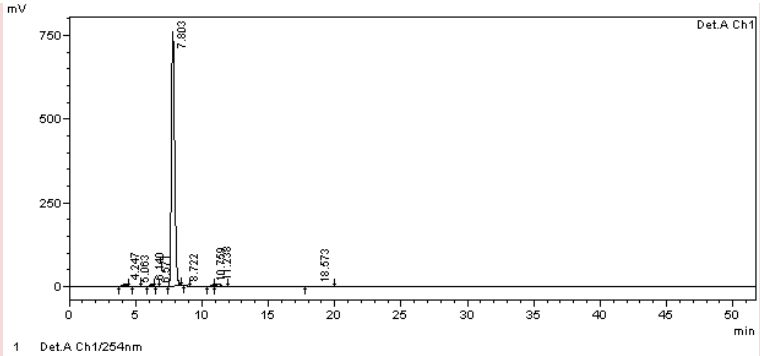
Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.075	48090	3691	0.590	0.737
2	5.800	6027	712	0.074	0.142
3	6.185	34554	3166	0.424	0.633
4	7.884	7936997	487063	97.376	97.320
5	8.806	12291	918	0.151	0.183
6	10.882	3865	339	0.047	0.068
7	12.875	109070	4590	1.338	0.917
Total		8150894	500478	100.000	100.000

2e (97% purity) obtained after TsOH-catalyzed reac. (2.5 min MW mode) (Method C).





Peak Table

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.247	91460	5303	0.694	0.677
2	5.063	9280	476	0.070	0.061
3	6.140	67876	5423	0.515	0.692
4	6.571	3339	366	0.025	0.047
5	7.803	12735496	759843	96.697	97.023
6	8.722	20527	1515	0.156	0.193
7	10.759	25937	1490	0.197	0.190
8	11.238	154838	7487	1.176	0.956
9	18.573	61740	1259	0.469	0.161
Total		13170493	783161	100.000	100.000