Enantioselective Michael /Hemiketalization of 5-hydroxy-2- methyl-4*H*-pyran-4-one to β,γ-unsaturated α-keto esters catalyzed by a bifunctional rosin-indane amine thiourea catalyst.

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1. General Remarks.

All the solvents were purchased from commercial source and dried prior to use. All the enantioselective Michael reactions were performed in an oven-dried Schlenk flask under an inert atmosphere of argon. All products were purified by column chromatography on silica gel 60-120 mesh using a mixture of ethylacetate-hexane as eluents. Progress of the reaction was monitored by Thin Layer Chromatography. ^{1}H NMR spectra were recorded in $CDCl_3$ using 300 MHz or 500 MHz spectrometers. ^{13}C NMR spectra were recorded in $CDCl_3$ using 75 MHz and 125 MHz NMR spectrometers. The chemical shifts (δ) were reported in parts per million (ppm) with respect to TMS as an internal standard. The coupling constants (J) are quoted in Hertz (Hz). Mass spectra were recorded on mass spectrometer by Electrospray ionization (ESI) technique. HPLC analysis was carried out in a Shimadzu LC-20 using chiral columns. A mixture of hexane-isopropyl alcohol was used as eluent. Optical rotations of the products were recorded on Digipol-781 M6U Polarimeter.

2. X ray crystallographic data for 3i and 5c

X-ray data for the compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method [1]. Preliminary lattice parameters and orientation matrices were obtained from four sets of frames.

Integration and scaling of intensity data were accomplished using SAINT program [1]. The structure was solved by direct methods using SHELXS97 [2] and refinement was carried out by full-matrix least-squares technique using SHELXL97 [2]. Anisotropic displacement parameters were included for all non-hydrogen atoms. Atoms O4/O5/C21/C22 of the ester group of 3i are disordered over two positions and the site-occupancy factors were refined to 0.664(10) and 0.336(10), respectively. The anisotropic displacement parameters of these disordered eater group were restrained to be similar (SIMU instruction in SHELXL97; Sheldrick, 2008). The O-bound H atom of 3i and 5c was located in difference Fourier maps and their positions and isotropic displacement parameters were refined. All other H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å and U_{iso}(H) = 1.5U_{eq}(C) for methyl H or 1.2U_{eq}(c) for other H atoms]. The methyl groups were allowed to rotate but not to tip. . In the absence of significant anomalous scattering efforts, Friedel pairs were merged in 3i.

However, the absolute configuration of the 5c was confirmed by unambiguous refinement of the absolute structure parameter (Flack & Bernardinelli, 2000).

3. Preparation of starting materials.

Ketoesters were prepared according to the reported literatures[3] .

a) General procedure for the preparation of 2-methyl-5-hydroxypyran-4-(1*H*)-one[4] (1)

Kojic acid (1 mmol) was dissolved in thionyl chloride (20 mmol) and the solution was stirred at room temperature for 30 minutes, precipitate was formed. The solid content was filtered and washed with hexane to give white solid (chlorokojic acid, 98% yield). The obtained white solid was added to 5 ml of distilled water and heated to 50°C with stirring. Zinc dust (3 mmol) was added followed by the dropwise addition of concentrated hydrochloric acid (56.1 mL) over 1 h with vigorous stirring maintaining the temperature between 70 and 80°C. The reaction mixture was stirred for a further 3h at 70°C. The excess zinc was removed by hot filtration, and the filtrate was extracted with CH_2Cl_2. The organic extracts were dried over anhydrous sodium sulfate, solvent was evaporated under reduced pressure and the residue was purified through column chromatography on silica gel (Hexane/EtOAc = 40/60) to give white solid (2-Methyl-5-hydroxypyran-4(1H)-one, 74% of yield).

(b) General procedure for the preparation of 2-(*tert*-butyldimethylsilanyloxy- methyl)-5-hydroxypyrane-4-one[5] (4a)

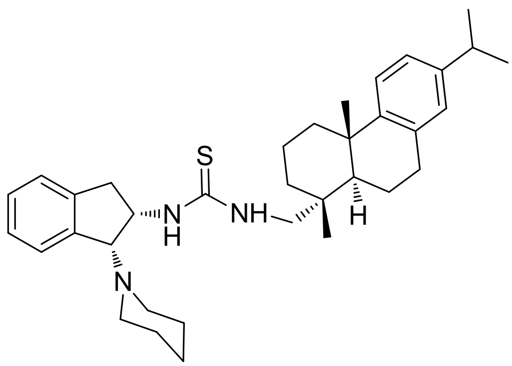
To a stirred solution of kojic acid (5 mmol) in 25 ml CH_2Cl_2, triethylamine (10 mmol) and DMAP (2 mg) were added. Then tert-butyl dimethylsilyl chloride (10 mmol) was added at 0°C, and the reaction mixture was stirred at the same temperature for 1 hr. The obtained reaction mixture was washed with water, extracted with ethyl acetate and the organic layer was dried over sodium sulfate. After removal of solvent the residue was used without further purification. To the above obtained residue was added 30% fomic acid/chloroform solution (25/25 ml) and the mixture was stirred for 1hour. After the completion of the reaction, Water (50ml) was added, extracted with chloroform and the obtained organic layer was dried with sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified through column chromatography on silica gel (Hexane/EtOAc = 80/20) to give 2-(tert-butyldimethylsilanyloxymethyl)-5-hydroxypyrane-4-one (White solid, 94% of yield).

(c) General procedure for the preparation of 2-((4-chlorophenylthio)-methyl)-5-hydroxy-4*H*-pyran-4-one[6] (4c)

To a stirred solution of chlorokojic acid (3 mmol) and triethylamine (4 mmol) in THF (10 mL) under N_2 was added 4-chlorobenzenethiol (3.3 mmol). The reaction mixture was stirred for 10 h at room temperature, after which THF was evaporated in vacuo. The residue was extracted with ethyl acetate and washed with water. The organic layer was dried over anhydrous sodium sulfate, solvent was evaporated under reduced pressure and the residue was purified through column chromatography on silica gel (Hexane/EtOAc = 3/7) to give white solid (2-((4-chlorophenylthio)methyl)-5-hydroxy-4H-pyran-4-one, 75% yield).

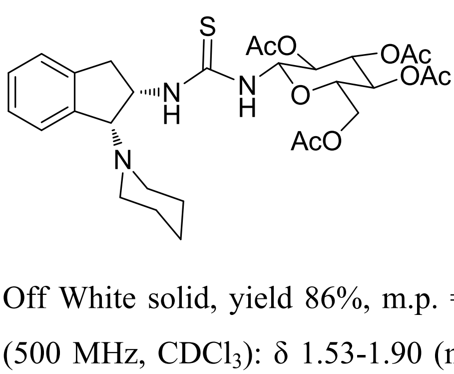
4. Spectral data of thiourea catalysts.

Ligand III



White solid, yield 85%, m.p. = 132-134 ^{0}C, $[\alpha]_D^{28}$ = -86.9 (c = 0.5, in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 3H), 1.15-1.27 (m, 9H), 1.29-1.50 (m, 4H), 1.53-1.89 (m, 9H), 2.33 (d, J = 13.0 Hz, 1H) 2.45-2.61 (m, 4H), 2.77-3.01 (m, 4H), 3.01- 3.21 (m, 1H), 3.50 (brs, 1H, NH), 6..33 (brs, 1H, NH), 6.92 (s, 1H), 7.00 (d, J = 7.9 Hz, 1H), 7.16-7.30 (m, 5H), 7.38 (d, J = 6.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.7, 18.4, 19.3, 23.9, 24.0, 25.2, 30.0, 33.4, 37.4, 38.2, 38.4, 50.7, 73.2, 123.7, 124.3, 125.0, 126.8, 127.4, 129.1, 134.8, 145.6, 147.1, 182.9. IR (KBr): υ 3273, 2928, 2857, 1545, 1453, 1376, 1269, 1114, 886, 752 cm^{-1}; MS (ESI) m/z 544 $[M+H]^+$; HRMS (ESI): Exact mass calcd for $C_{35}H_{50}N_3S$ 544.37200. Found: 544.37236

Ligand VIII



Off White solid, yield 86%, m.p. = 101-103 ^{0}C, $[\alpha]_D^{28}$ = -40.8 (c = 0.25, in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.53-1.90 (m, 6H), 2.01-2.11 (m, 12H), 2.56-2.75 (s, 4H), 2.93 (dd, J =

8.9, 15.9 Hz, 1H), 3.20 (dd, J = 7.9, 15.9 Hz, 1H), 3.52 (q, J = 7.9, 15.9 Hz, 1H) 3.93 (d, J = 8.9 Hz, 1H), 4.14 (d, J = 10.9 Hz, 1H), 4.37 (dd, J = 3.9, 11.9 Hz, 1H), 5.00 (t, J = 4.9 Hz, 1H), 5.07-5.17 (m, 2H), 5.37-5.44 (m, 1H), 6.10 (t, J = 8.9 Hz, 1H), 6.53 (d, J = 4.9 Hz, 1H), 7.20-7.34 (m, 4H), 10.48 (d, J = 7.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.6, 20.7, 24.2, 25.8, 26.3, 50.6, 61.7, 62.4, 68.2, 71.7, 72.9, 73.9, 74.6, 84.8, 123.7, 125.4, 127.5, 129.1, 138.0, 141.0, 169.6, 169.8, 170.5. IR (KBr): υ 3354, 2937, 1752, 1541, 1373, 1373, 1225, 1038, 909, 752 cm^{-1}; MS (ESI) m/z 606 [M+H]$^+$; HRMS (ESI): Exact mass calcd for $C_{29}H_{40}O_9N_3S$ 606.24798. Found: 606.24919.

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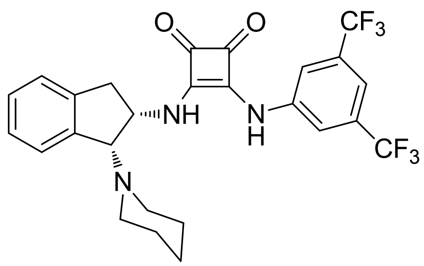
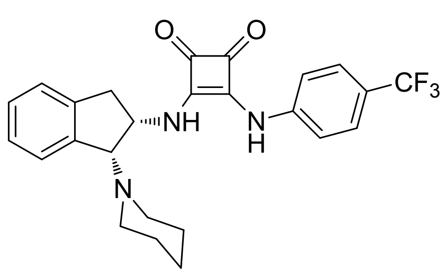


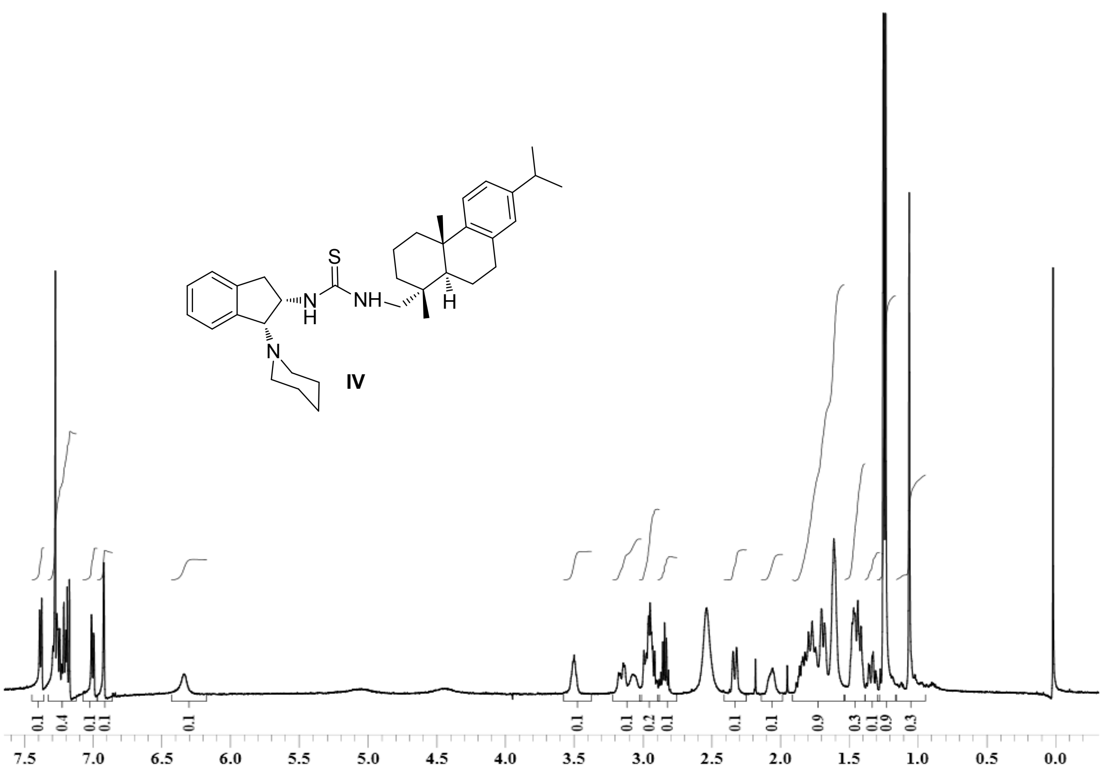
White solid, yield 74%, m.p. = 290-292 ^{0}C, $[\alpha]_D^{28}$ = -73.5 (c = 0.5, in $CHCl_3$). ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.40-1.76 (m, 6H), 2.56-2.80 (m, 4H), 3.43-3.28 (m, 3H), 5.83 (brs, 1H), 7.37-7.08 (m, 4H), 7.41 (s, 1H), 8. 16-7.84 (m, 2H), 8.04 (m, 3H), 9.86 (brs, NH, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.2, 24.9, 30.3, 50.4, 59.2, 74.1, 113.7, 116.8, 122.9, 123.9, 125.0, 125.9, 127.4, 130.9, 131.3, 138.8, 139.8, 140.1, 161.7, 168.4, 179.4, 183.2; IR (KBr): υ 3257, 2939, 1793, 1686, 1606, 1560, 1442, 1379, 1279, 1177, 1133, 883, 745 cm^{-1}; MS (ESI) m/z 524 [M+H]$^+$; HRMS (ESI): Exact mass calcd for $C_{26}H_{24}F_6N_3O_2$ 524.17672. Found: 524.17600.

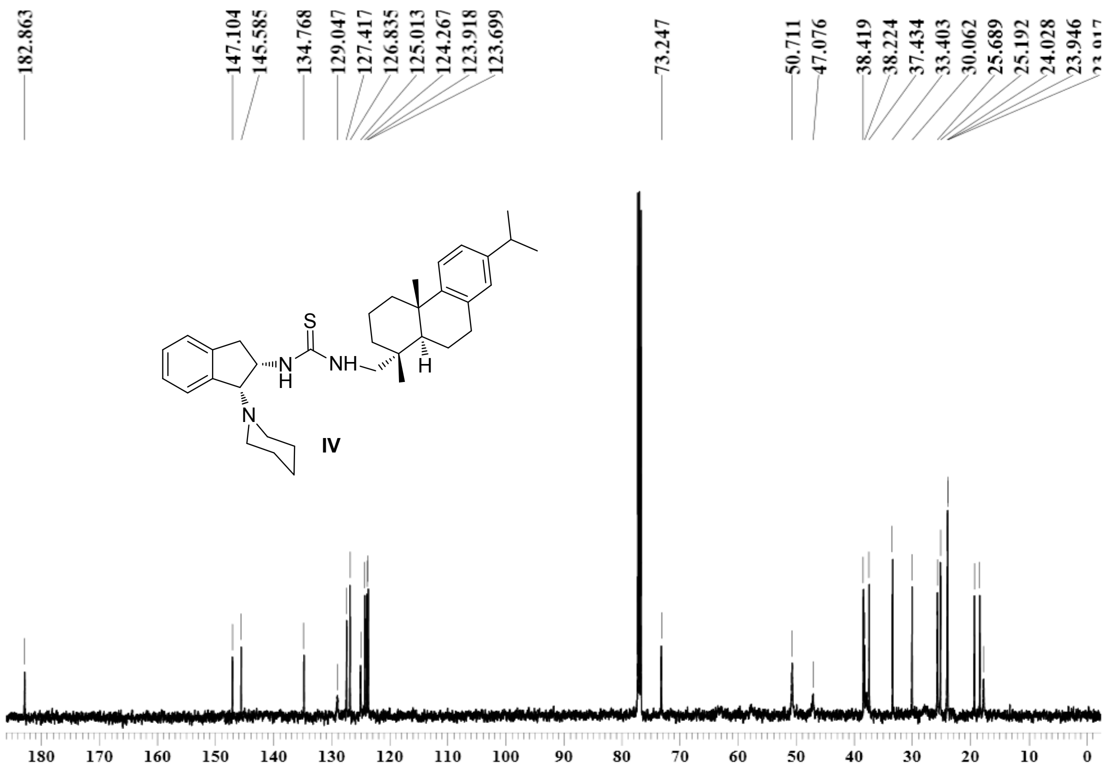
Ligand VII



White solid, yield 71%, m.p. = 270-272 ^{0}C, $[\alpha]_D^{28}$ = -71.2 (*c* = 0.5, in $CHCl_3$). ^{1}H NMR (300 MHz, DMSO-D_6): δ 1.37-1.77 (m, 6H), 2.48-2.77 (m, 4H), 2.91-2.38 (m, 3H), 5.75-5.91 (m, 1H), 7.14-7.38 (m, 3H), 7.49-7.74 (m, 5H), 7.92 (d, *J* = 8.3 Hz, 1H), 9.51 (brs, NH, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.9, 24.6, 30.0, 50.0, 58.8, 73.8, 116.5, 122.7, 123.6, 125.0, 125.6, 127.0, 138.5, 139.7, 141.1, 161.9, 167.9, 178.9, 182.9; IR (KBr): υ 3167, 2933, 1795, 1682, 1613 1554, 1446, 1323, 1118, 1015, 840, 748, 671 cm^{-1}; MS (ESI) *m/z* 456 $[M+H]^+$; HRMS (ESI): Exact mass calcd for $C_{25}H_{25}F_3N_3O_2$ 456.18934. Found: 456.18833.

4. Copy of ^{1}H NMR and ^{13}C NMR of ligands.

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47.076
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38.224
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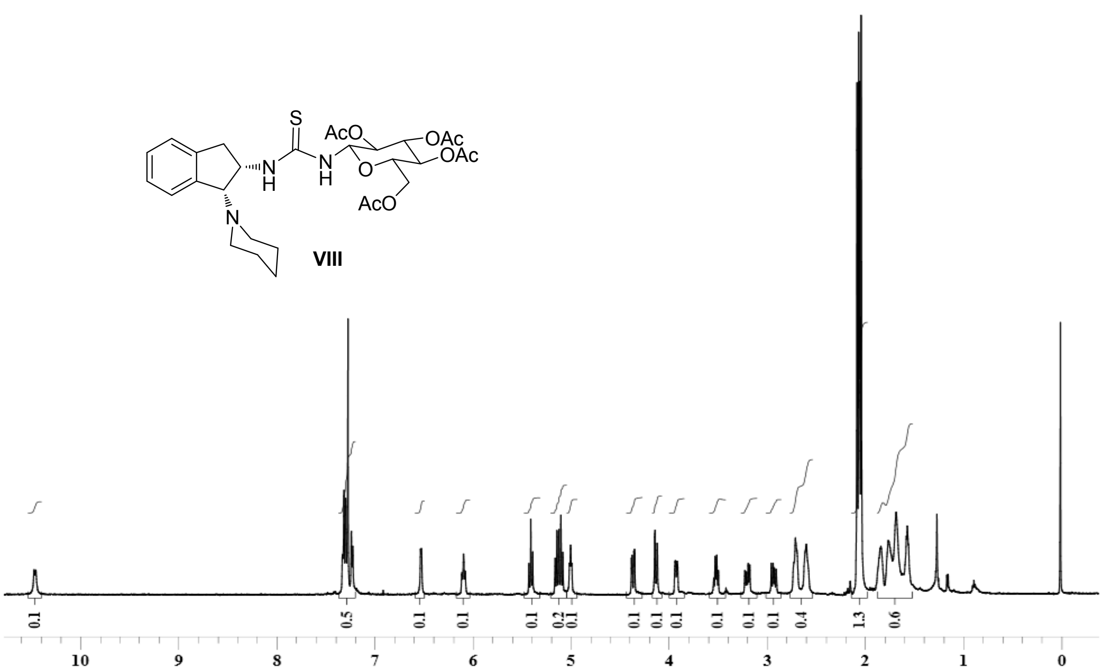
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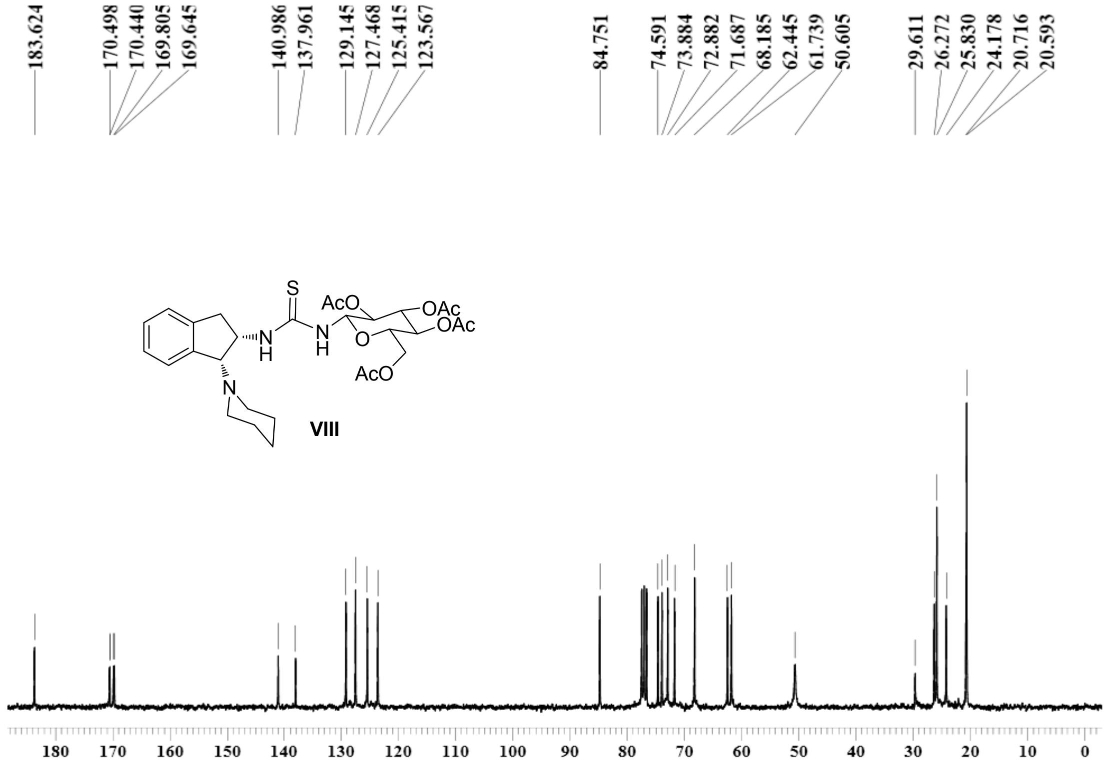
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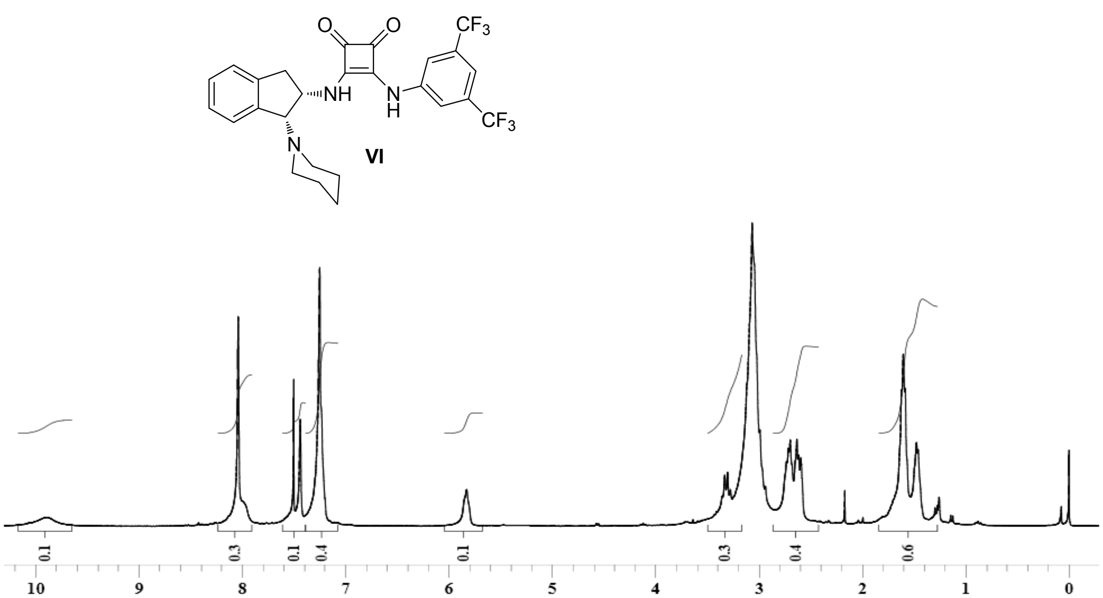
VIII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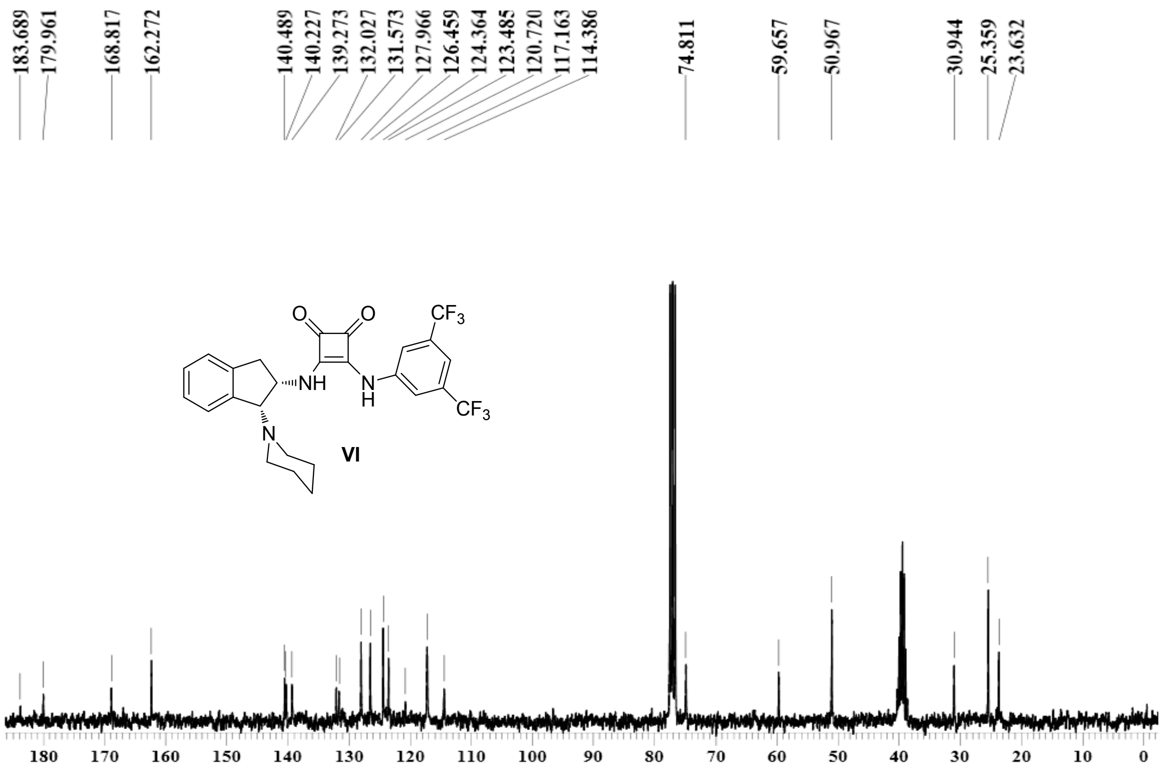
VI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50.967
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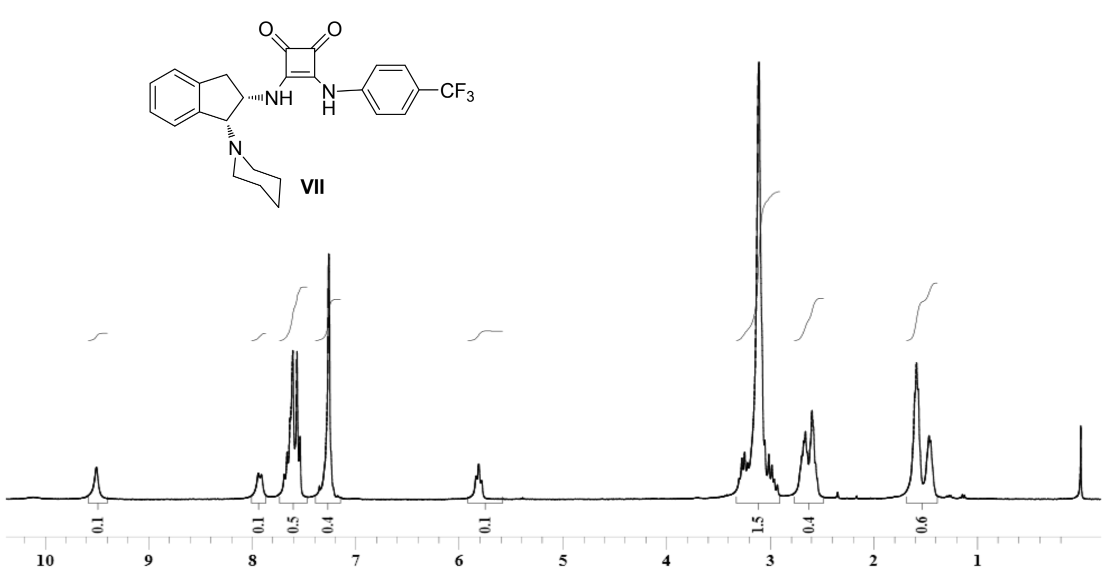
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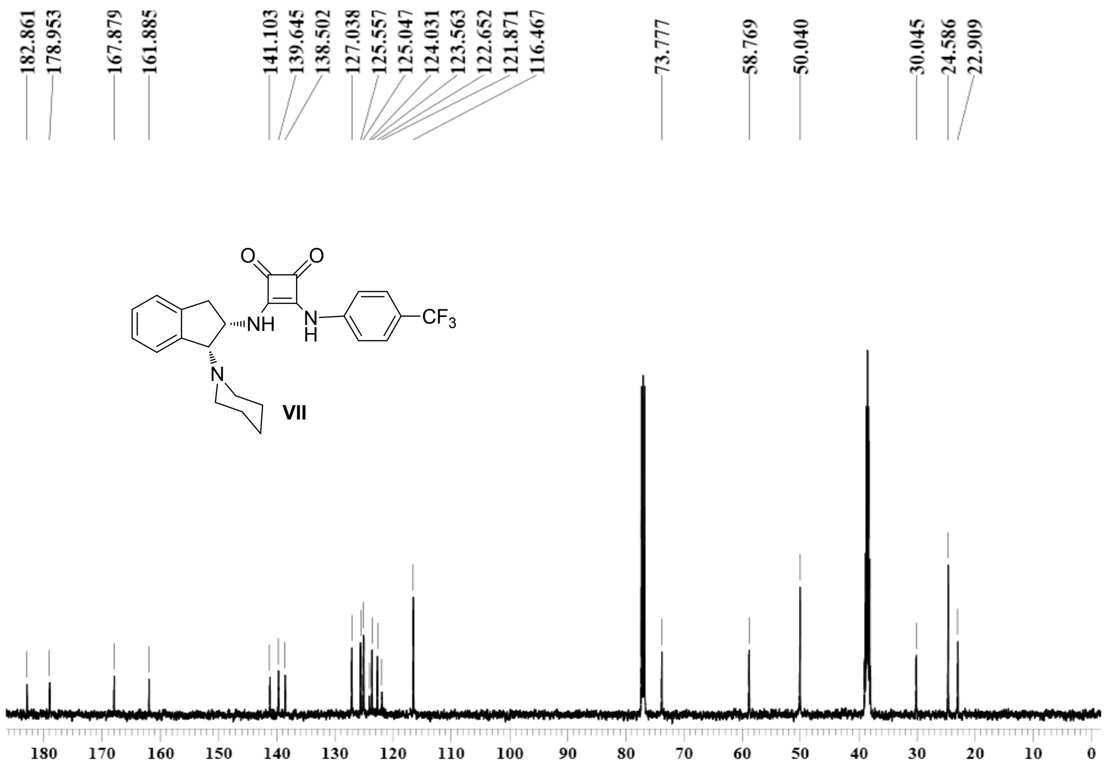

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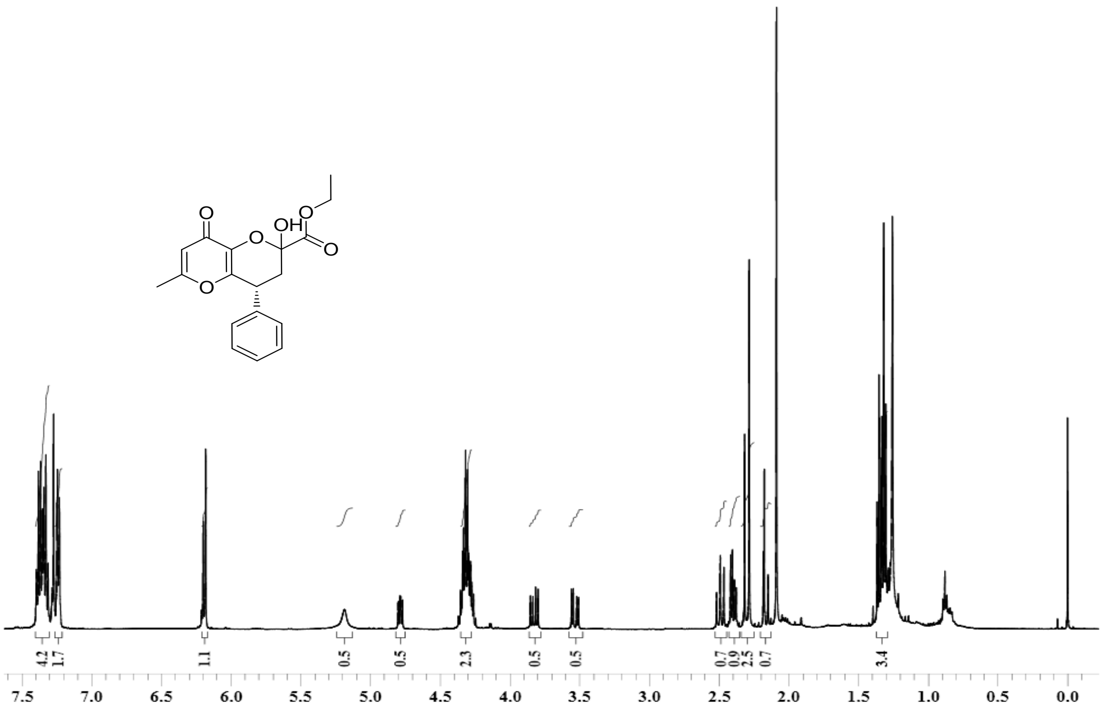

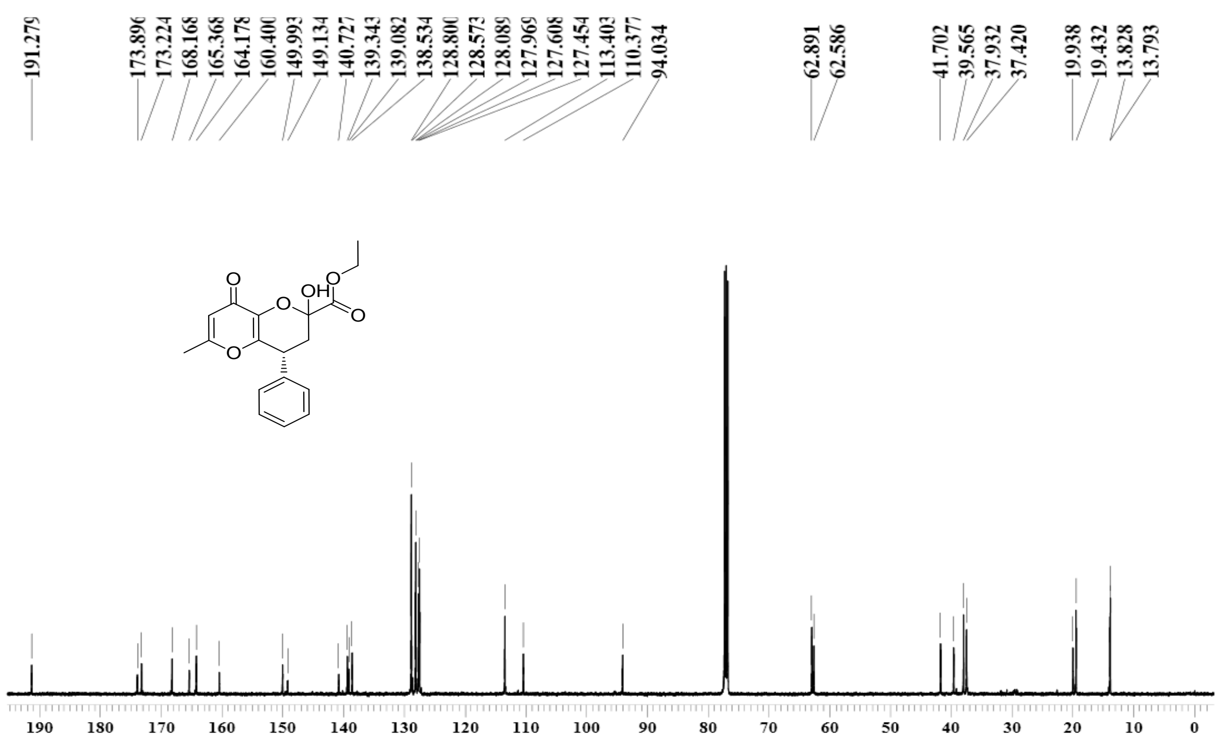

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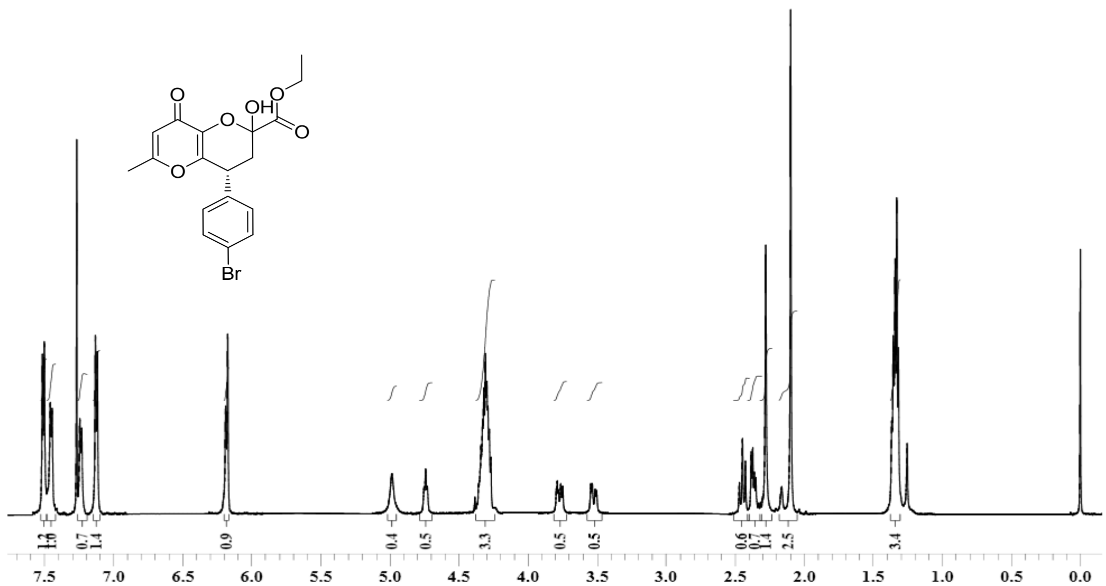

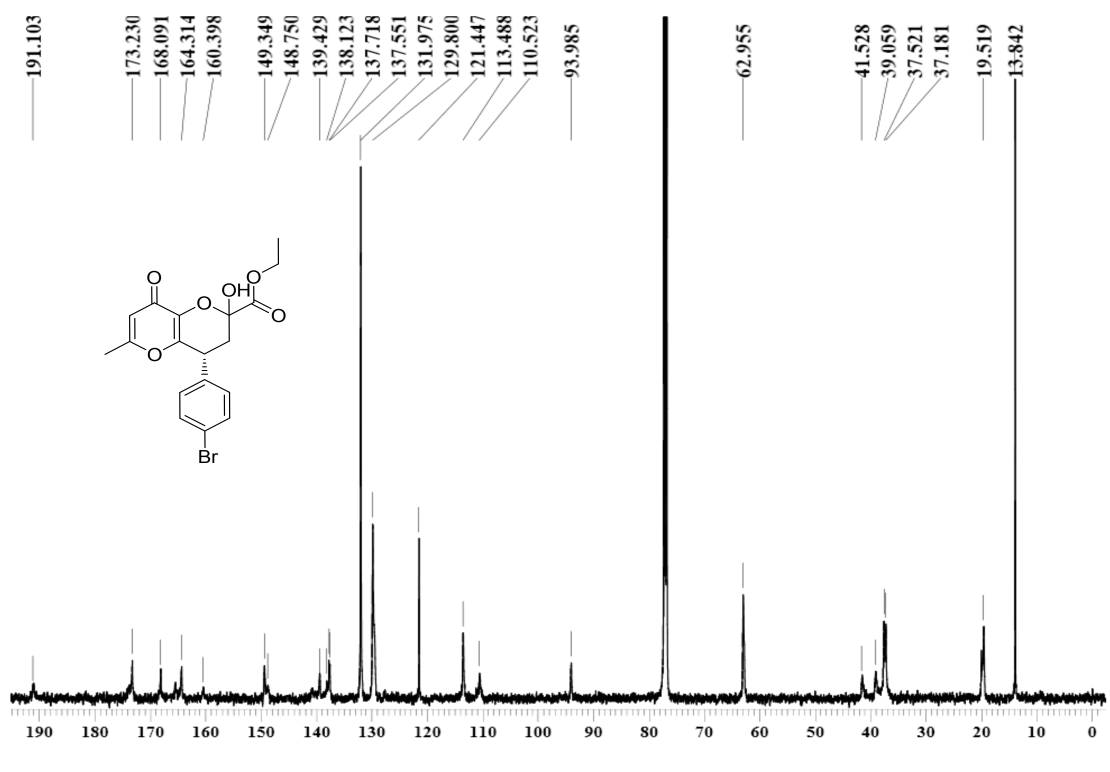

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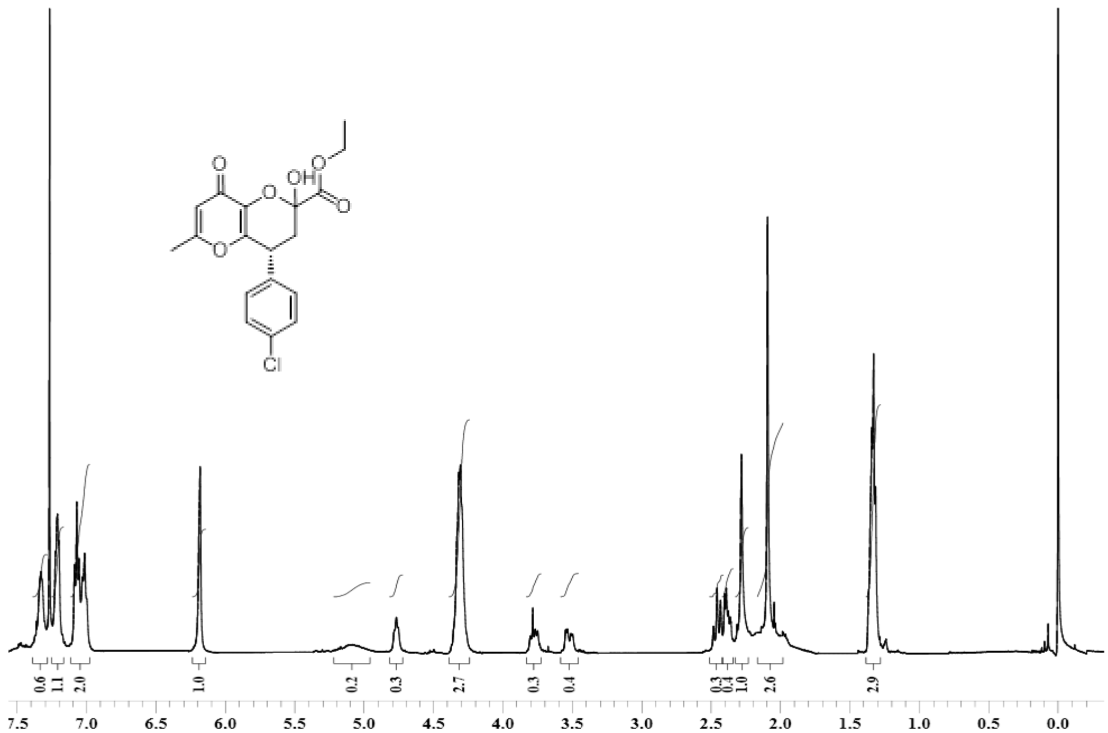

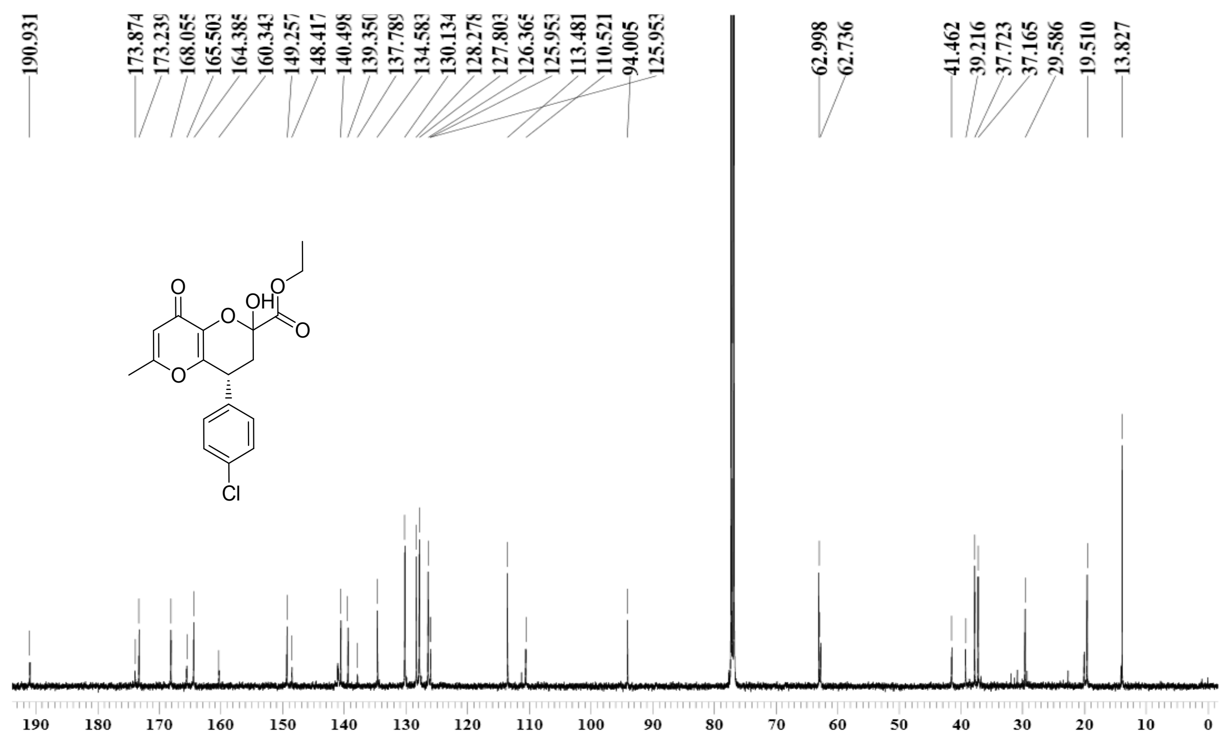

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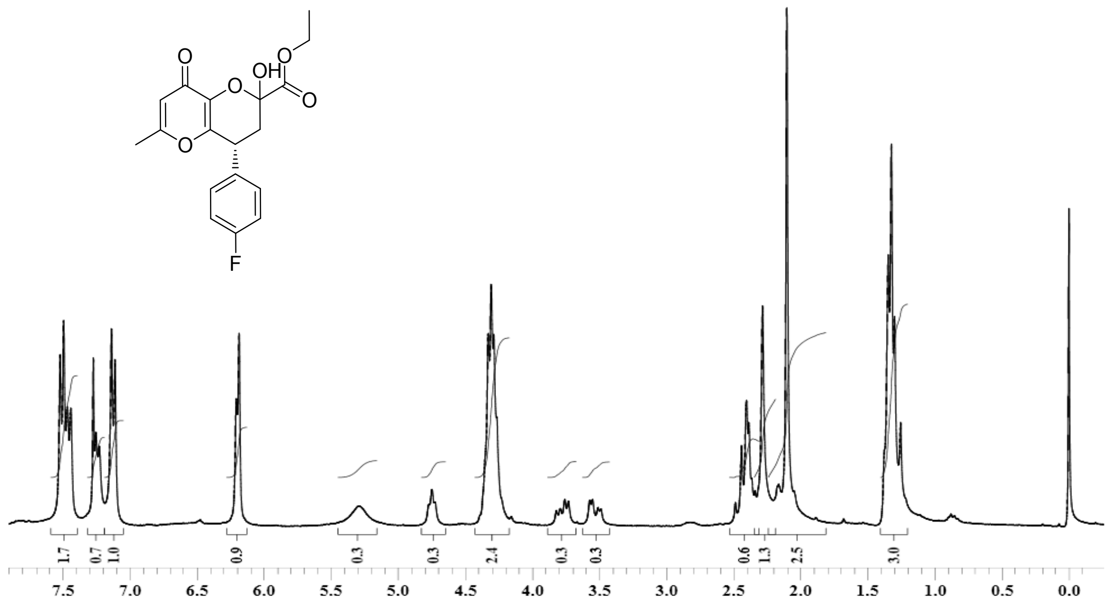

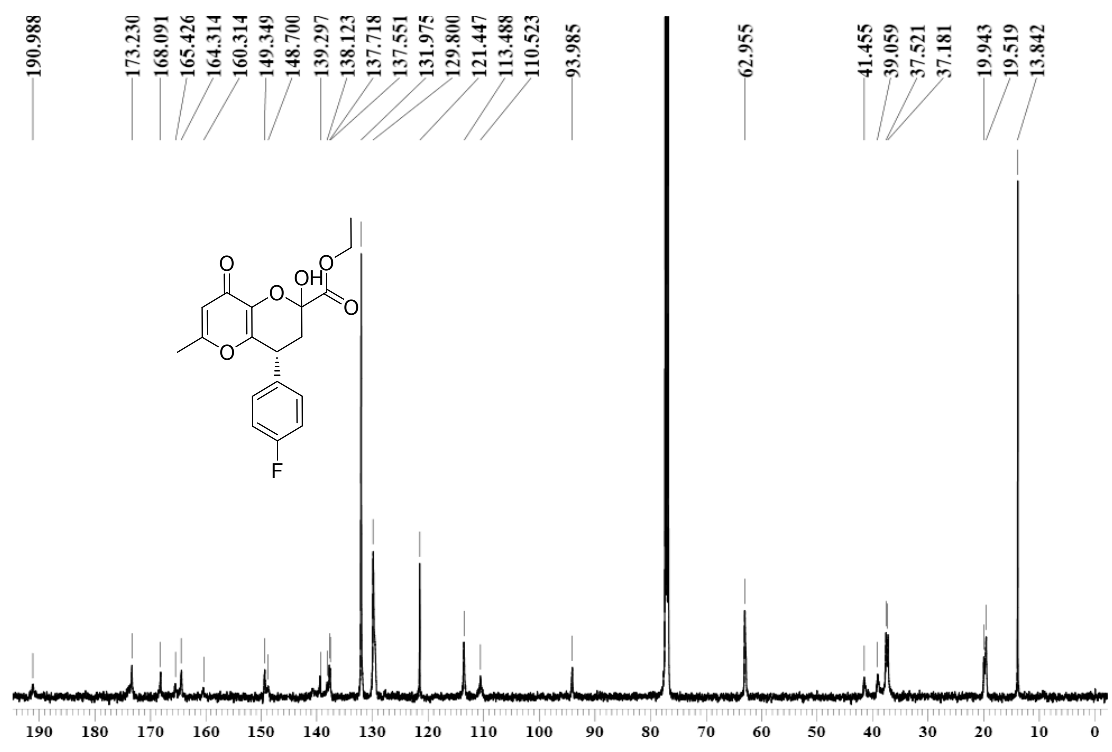

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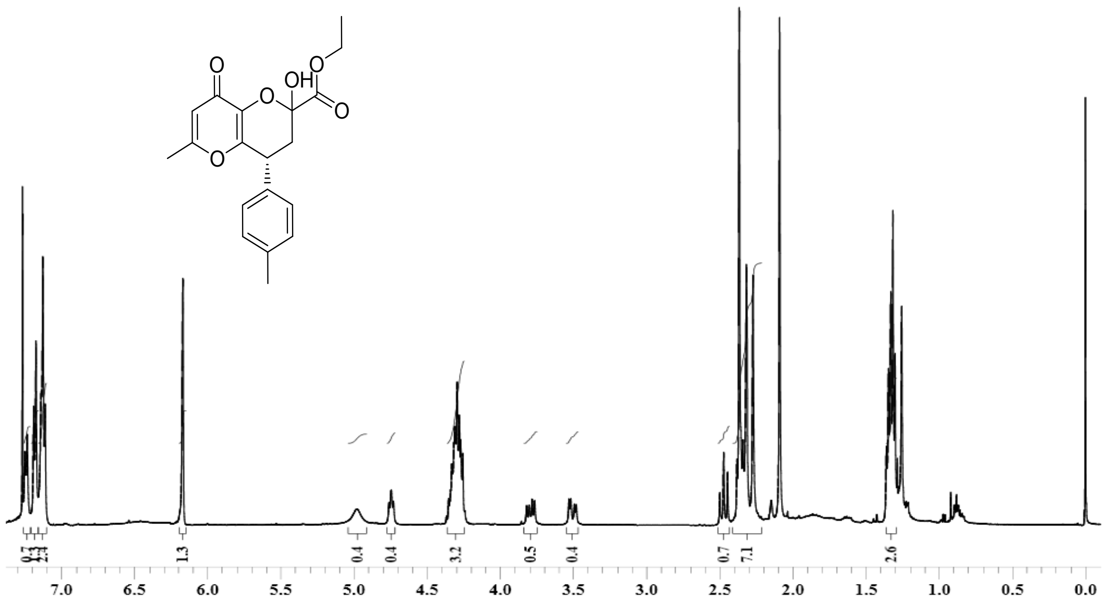

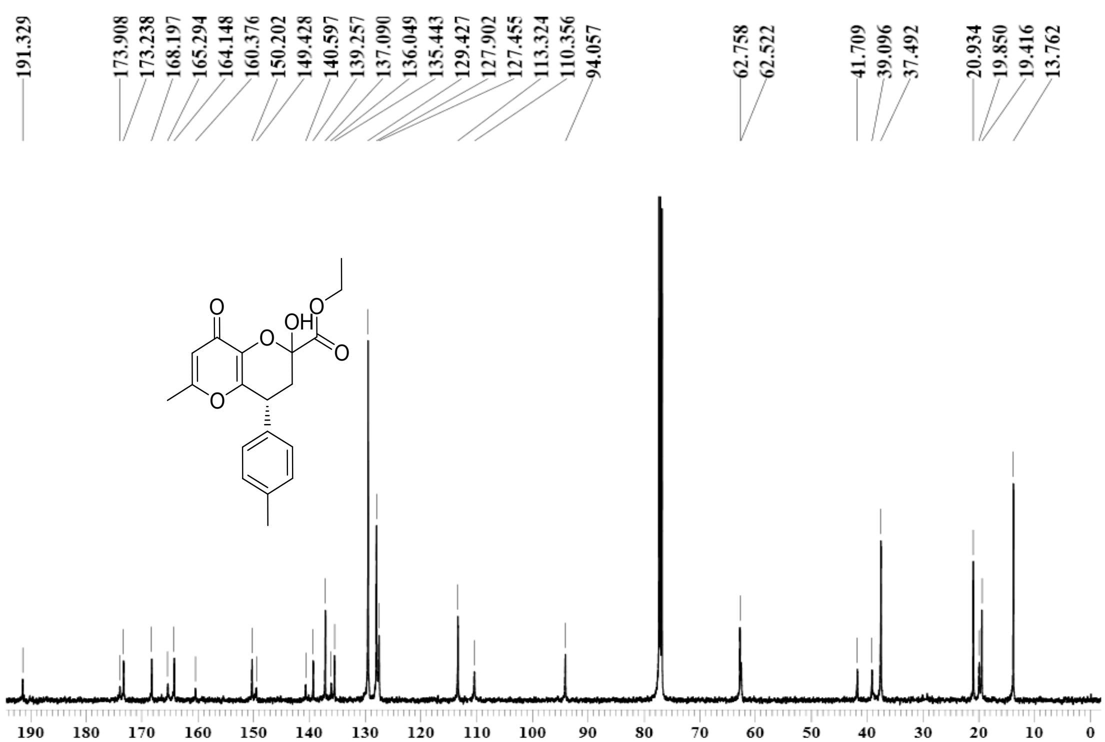

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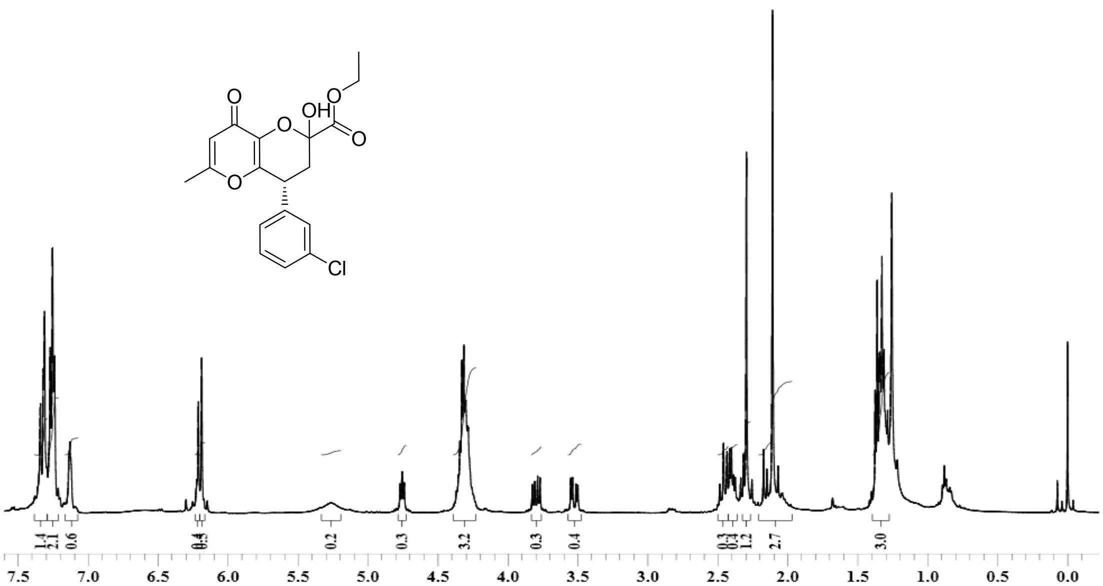

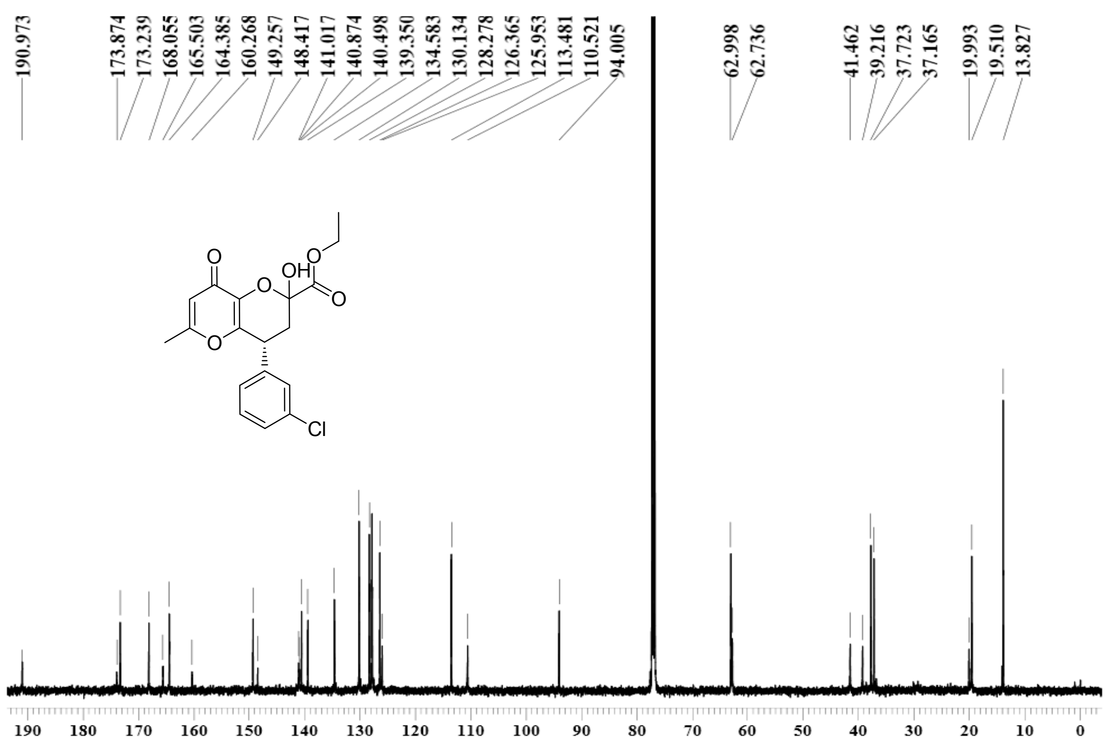

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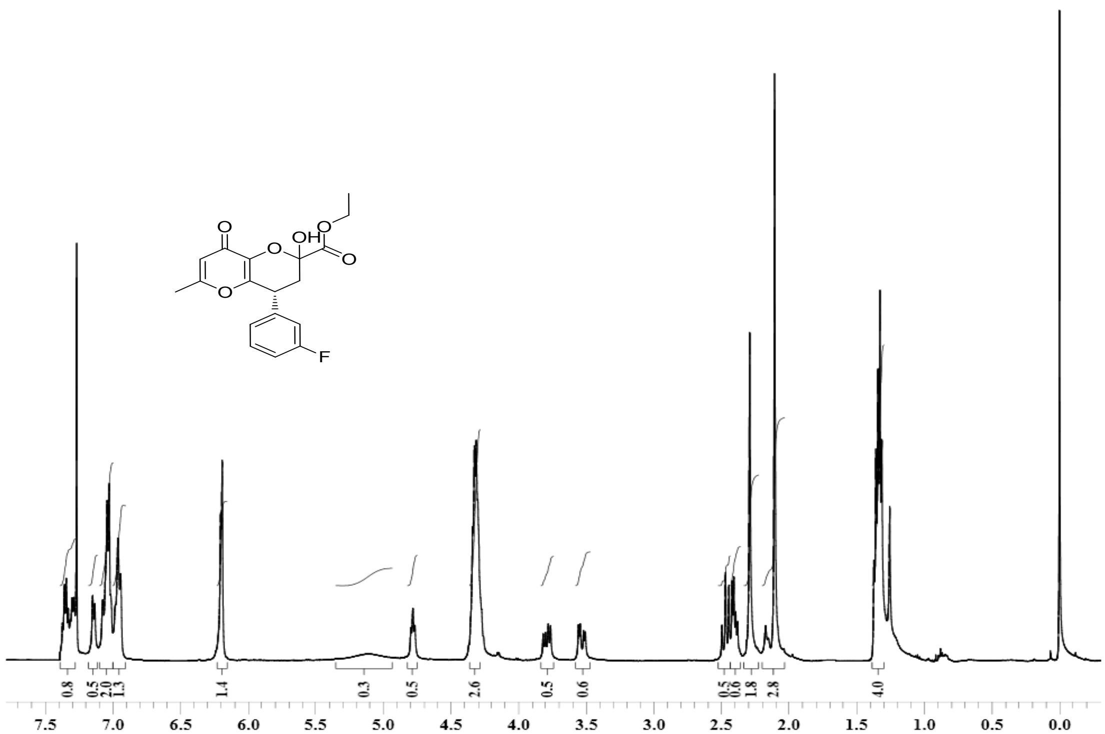

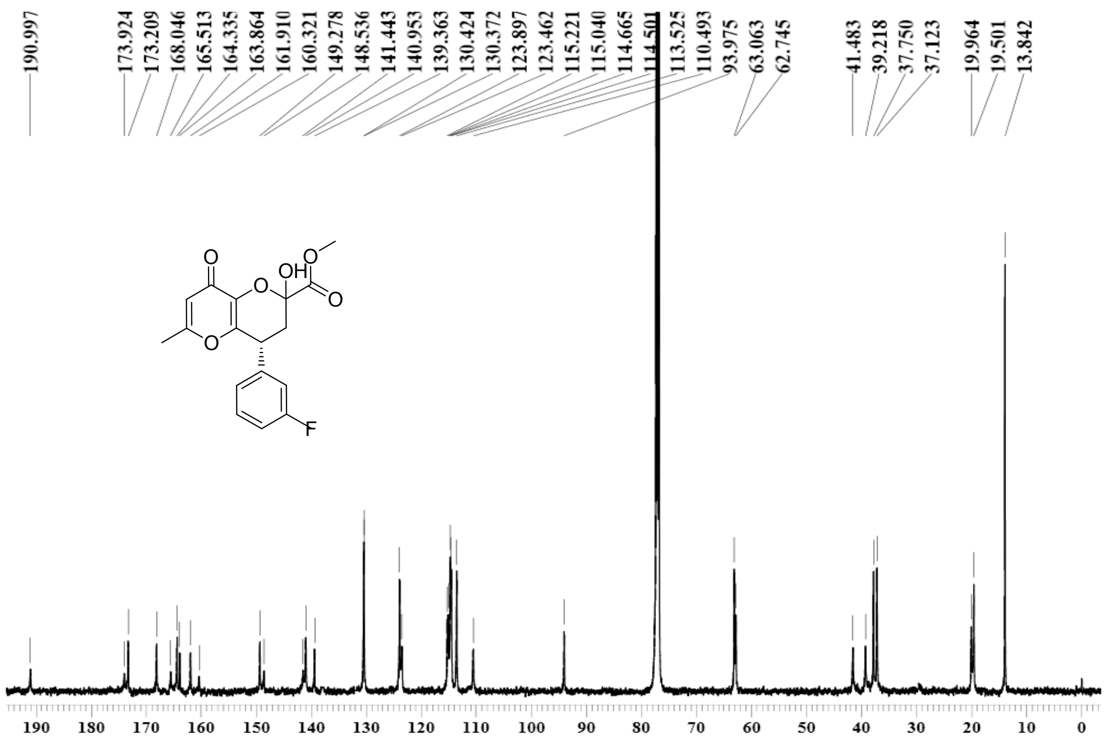

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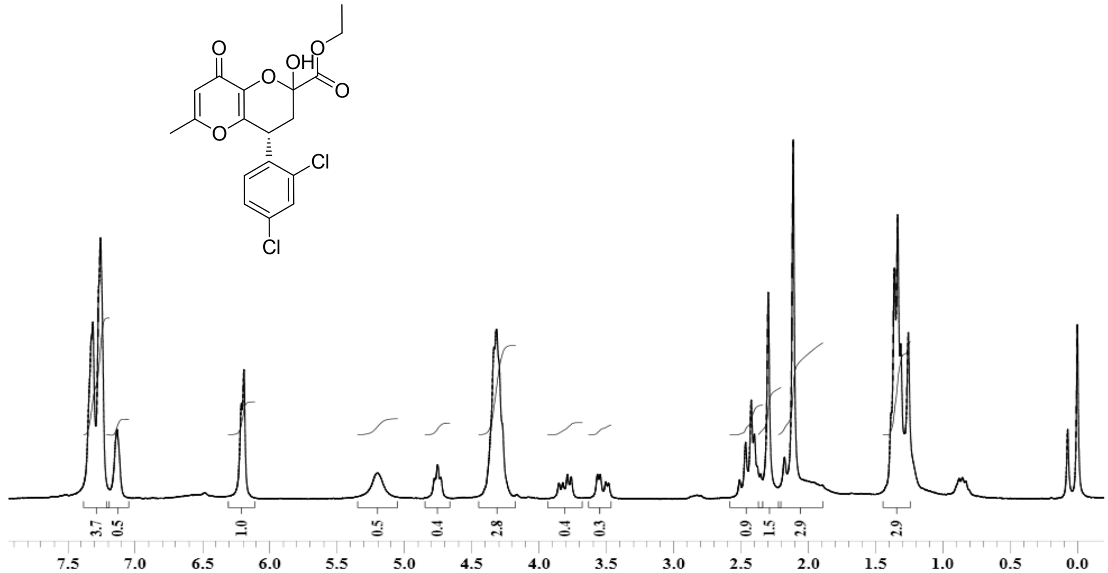

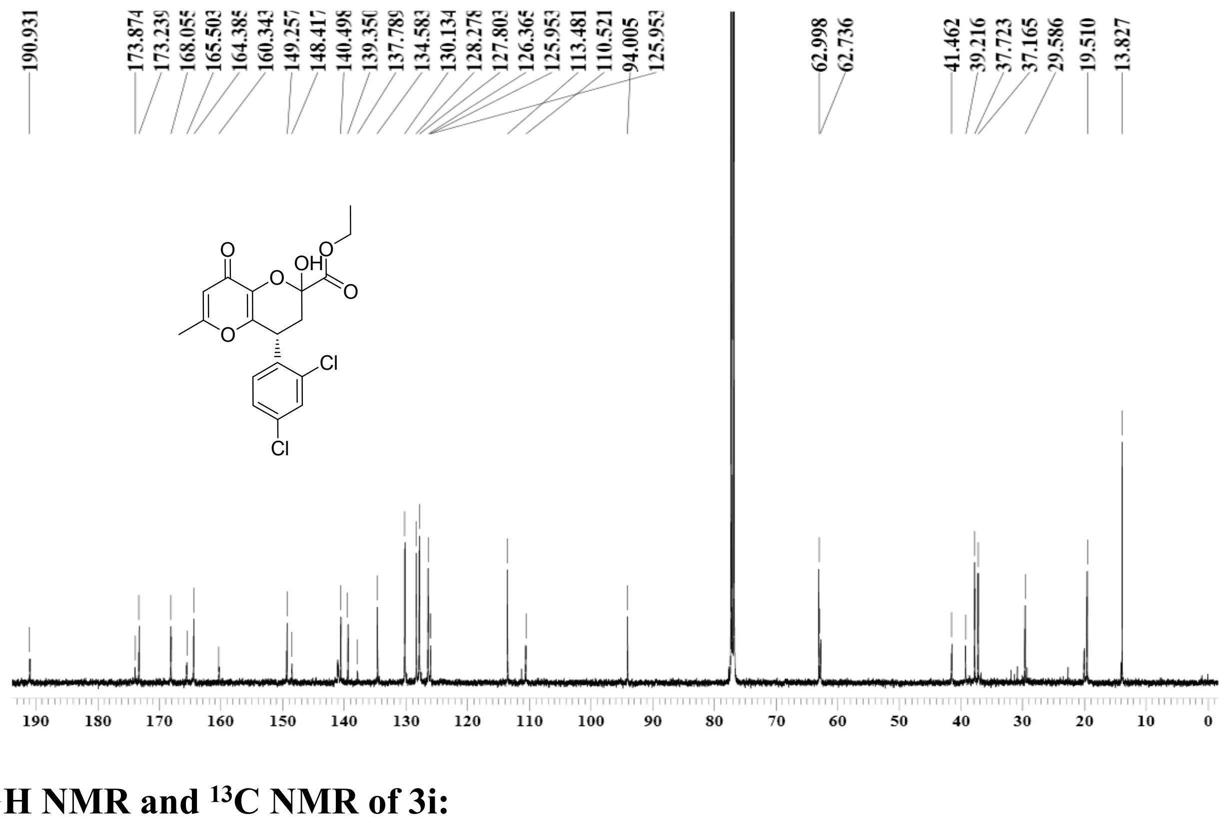

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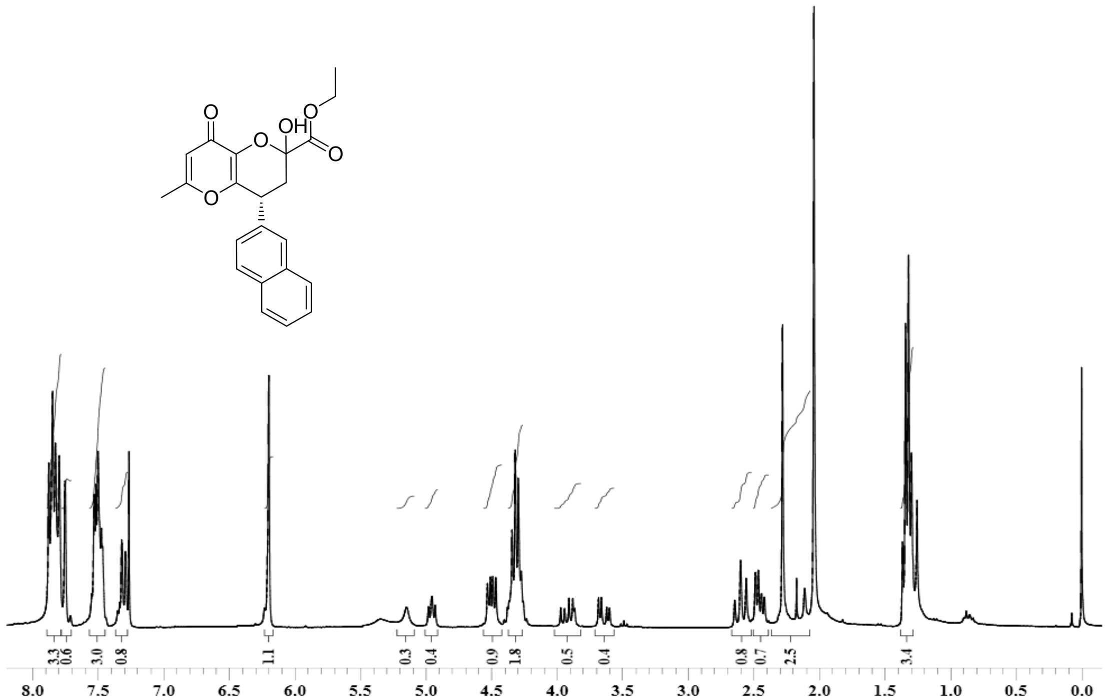

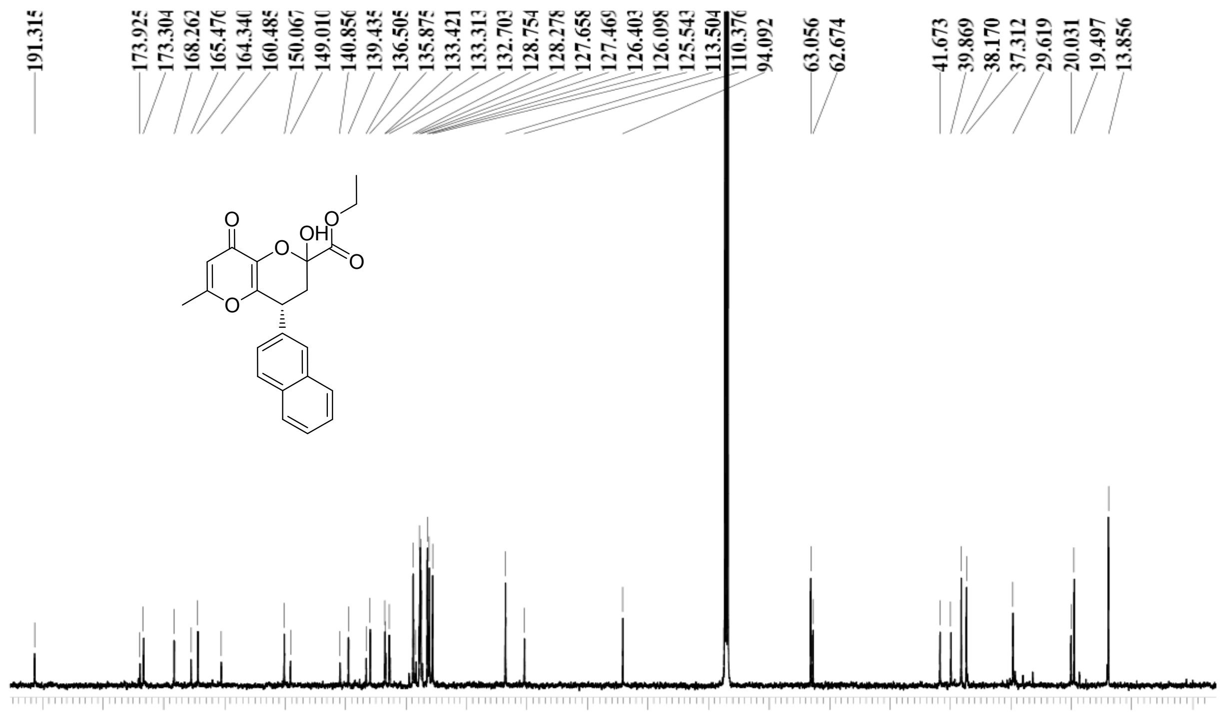

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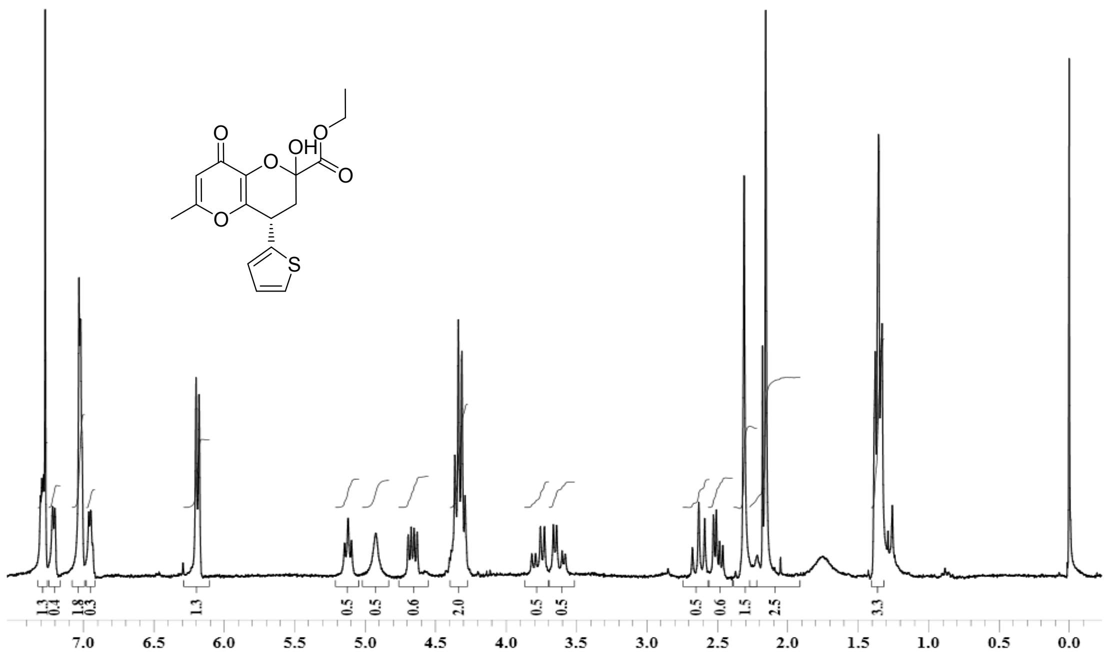

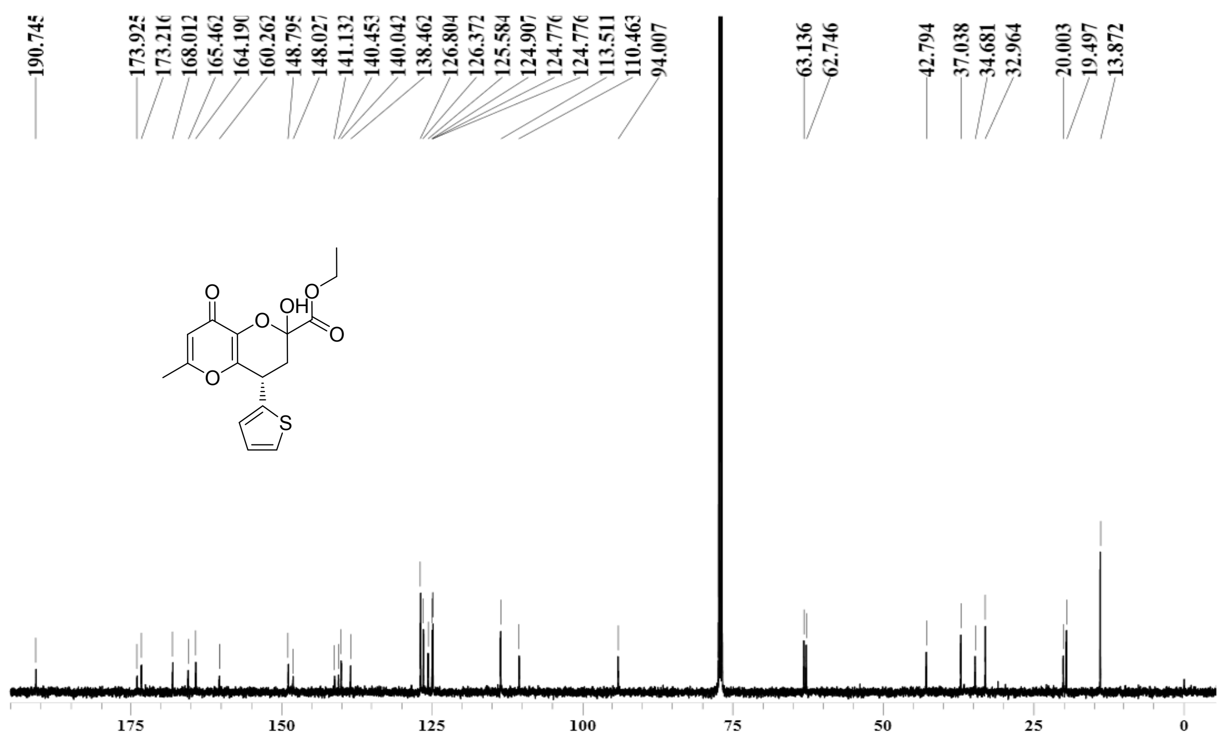

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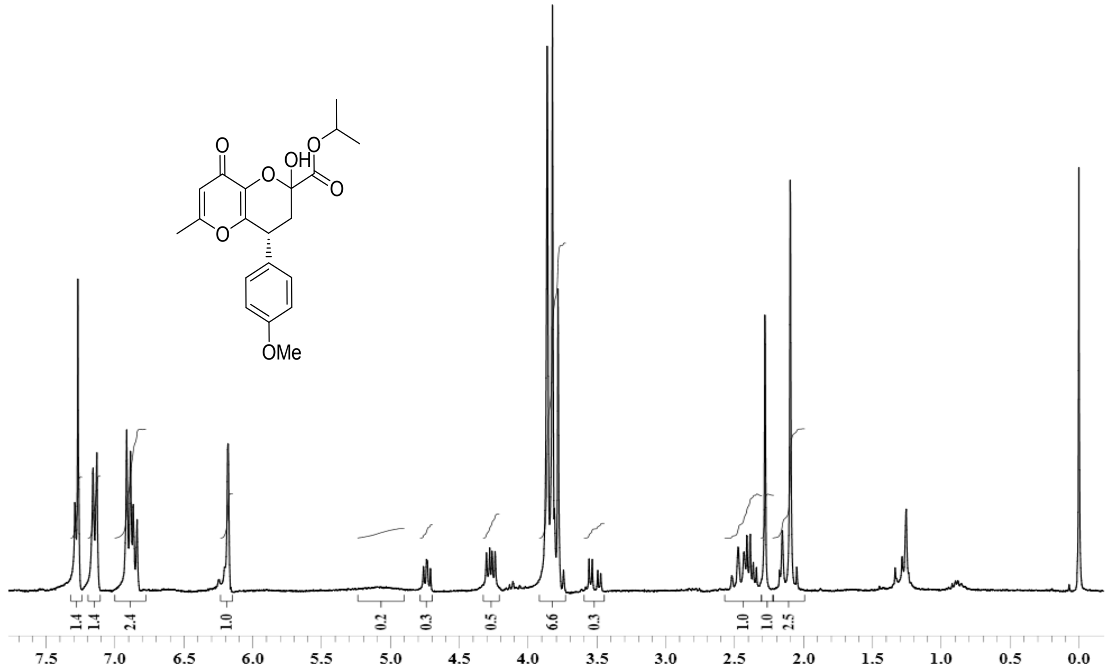

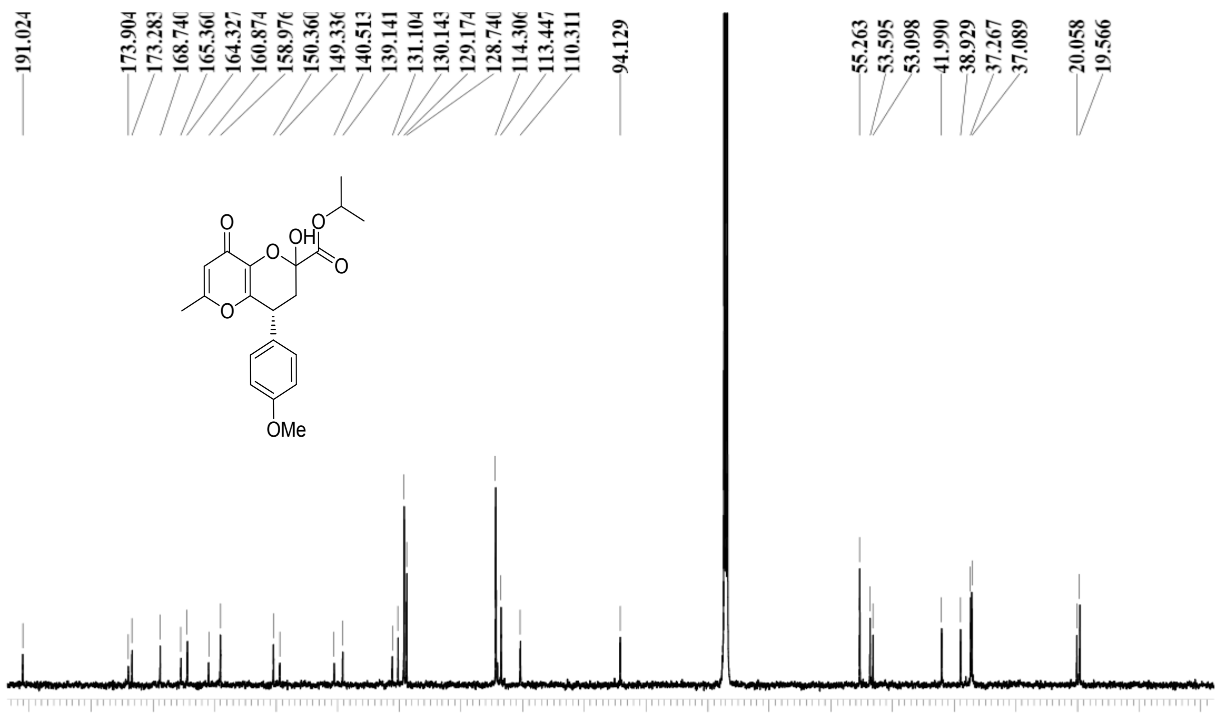

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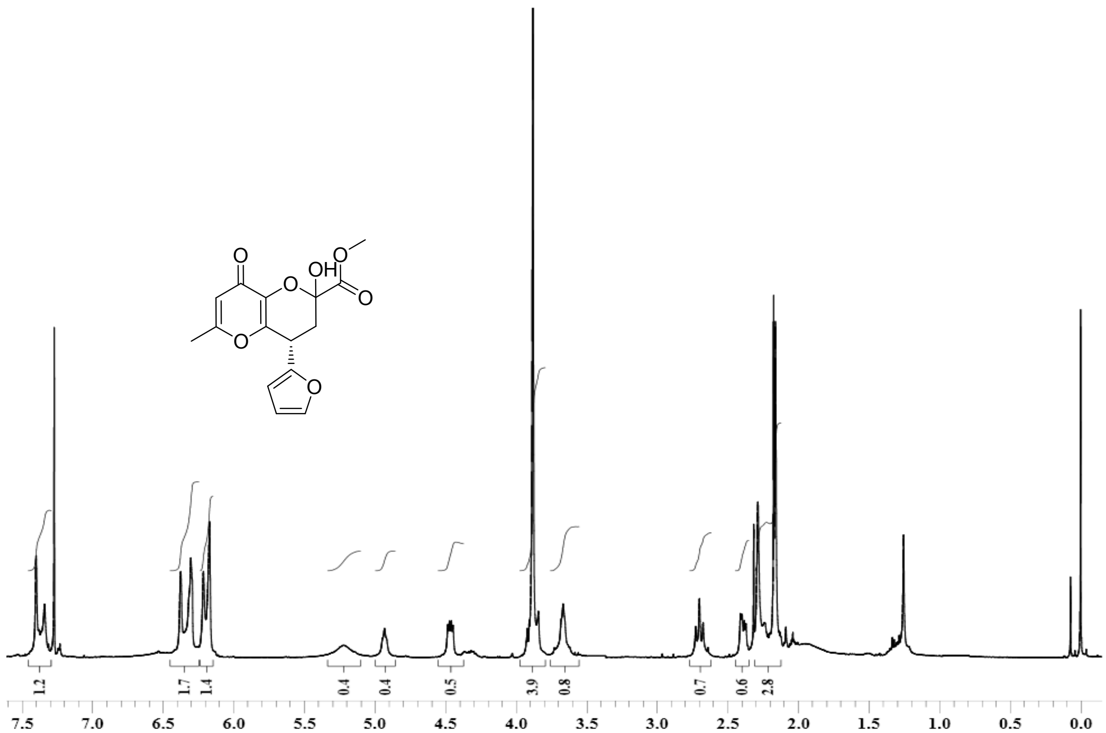
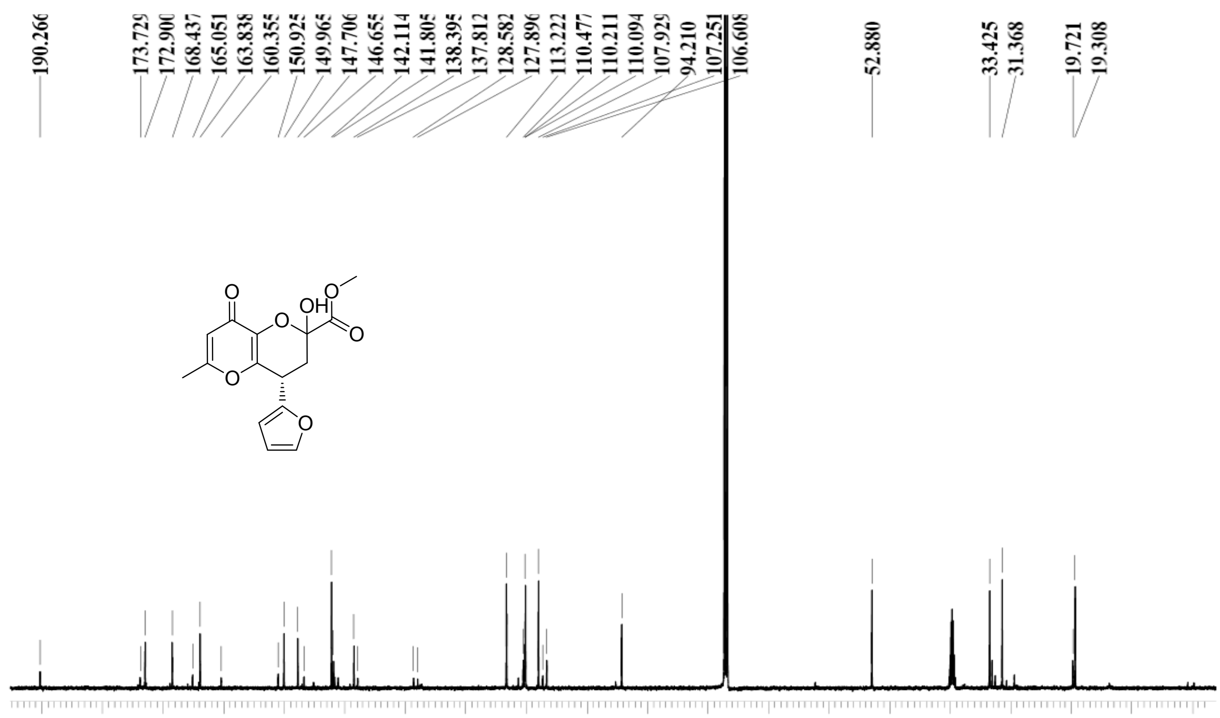
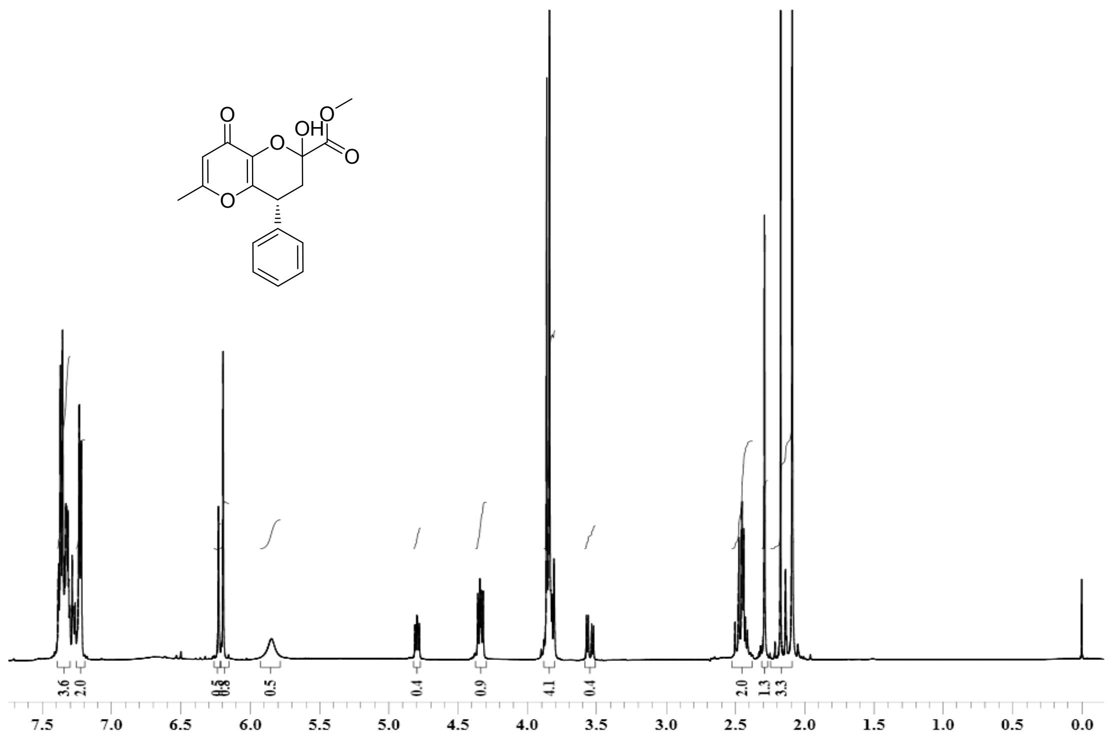
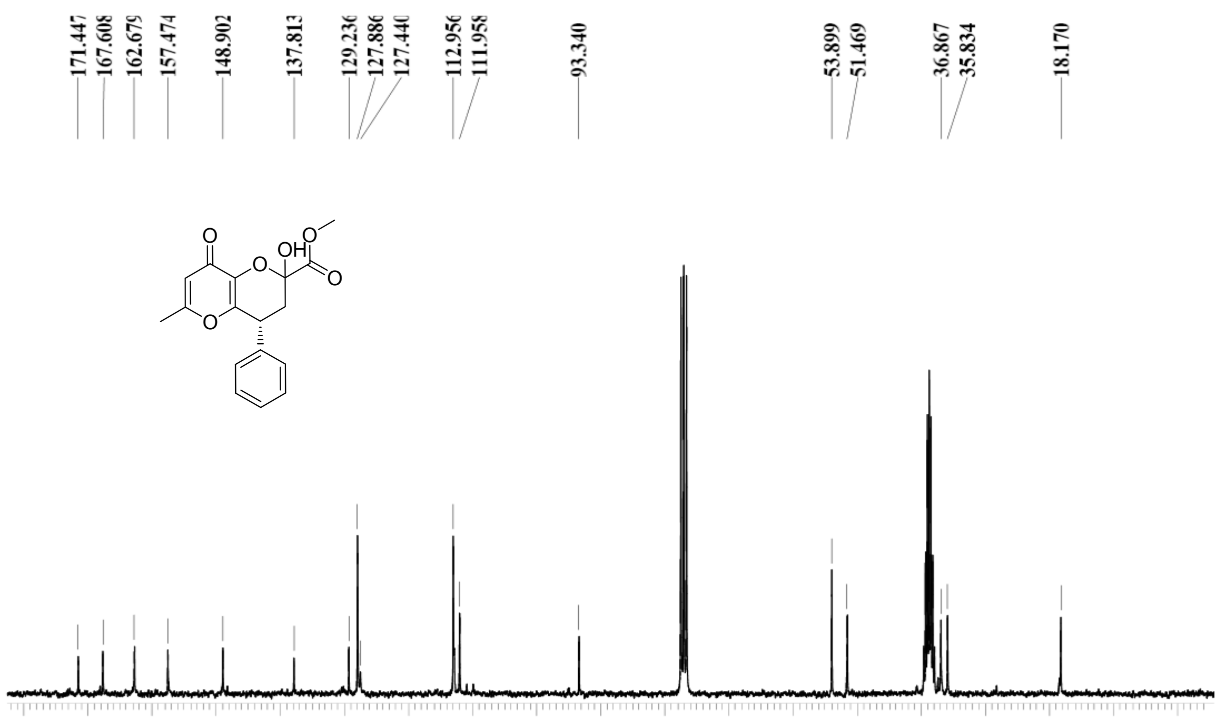


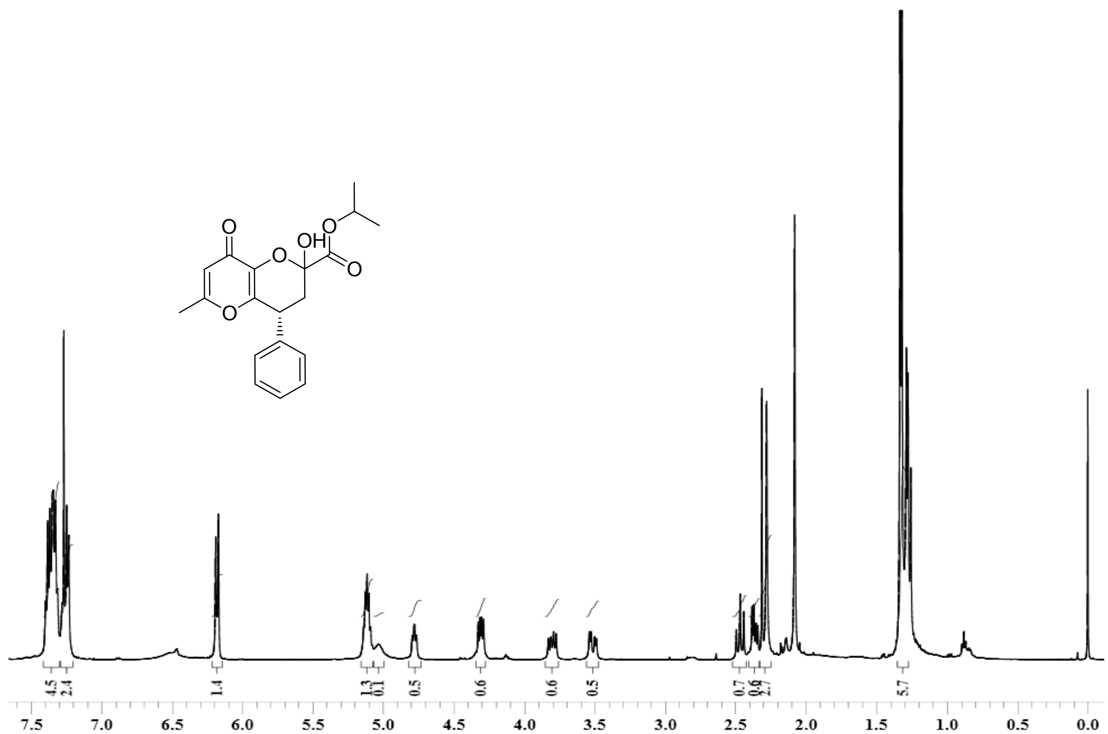


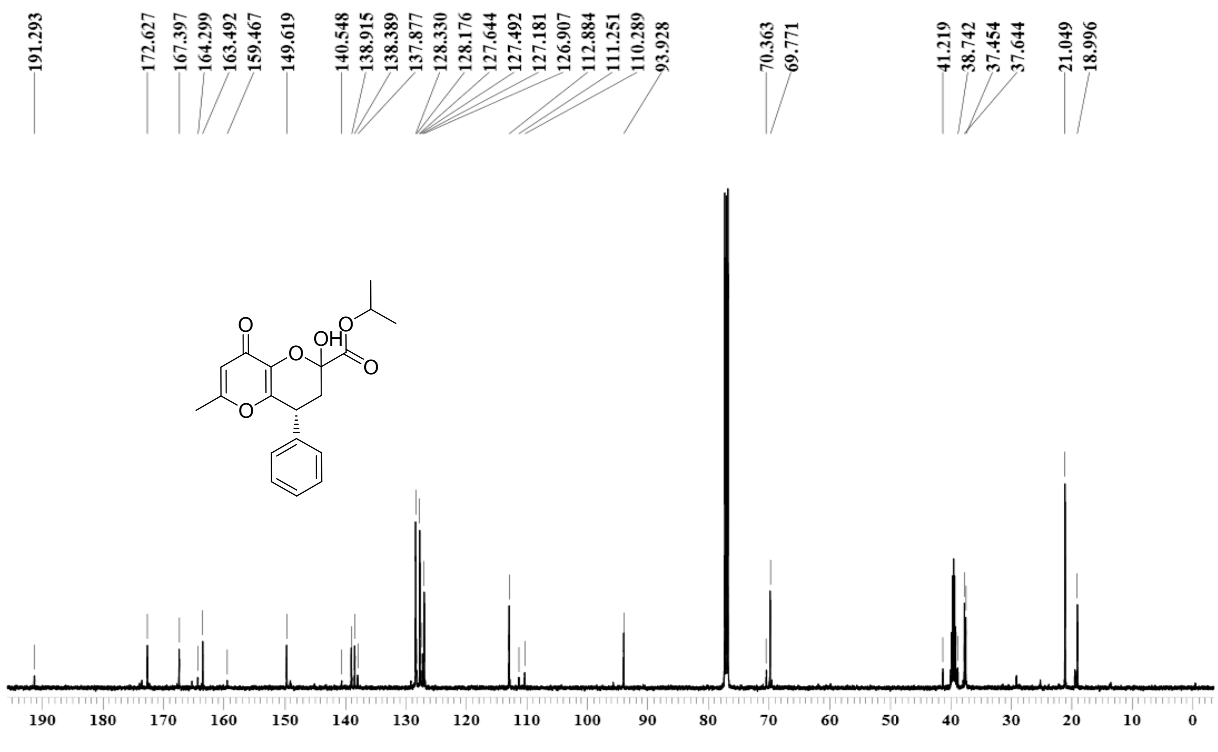
[1]H NMR and [13]C NMR of 3m:



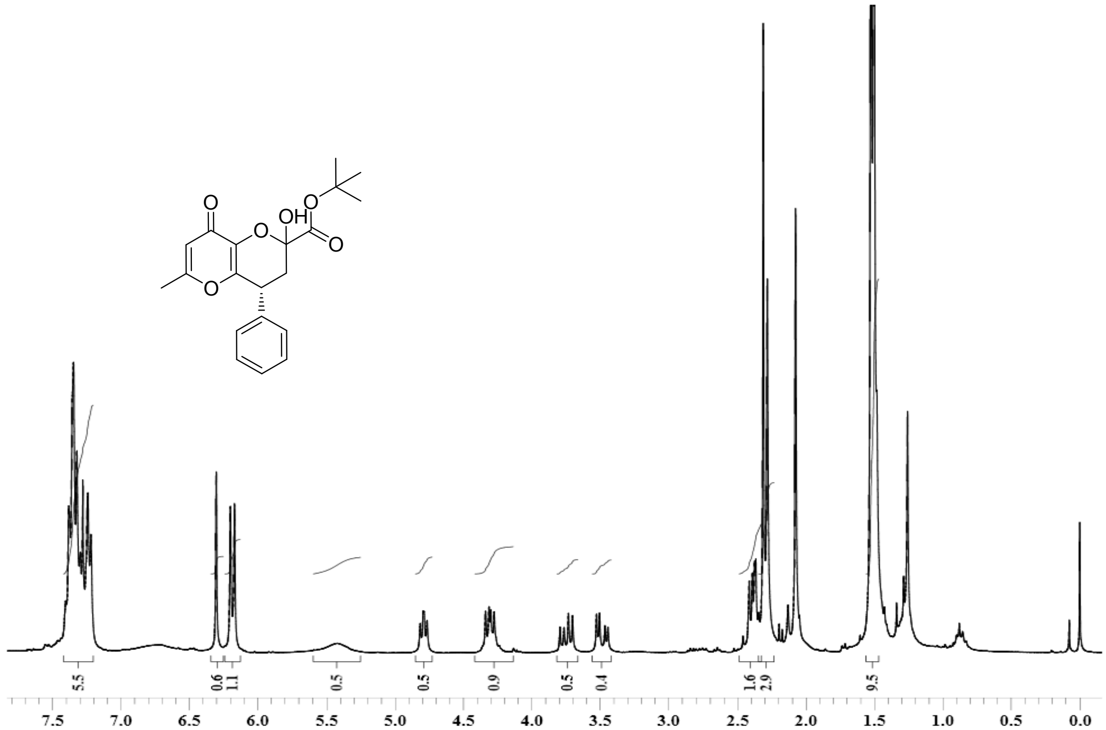


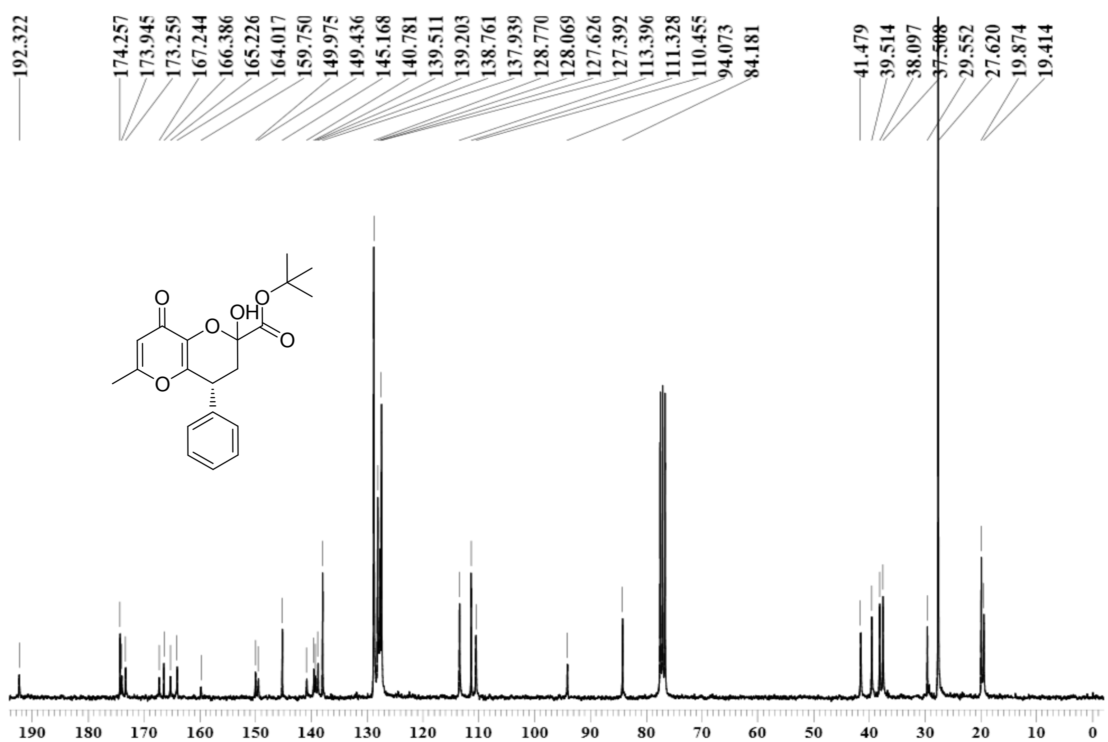
^{1}H NMR and ^{13}C NMR of 3n:



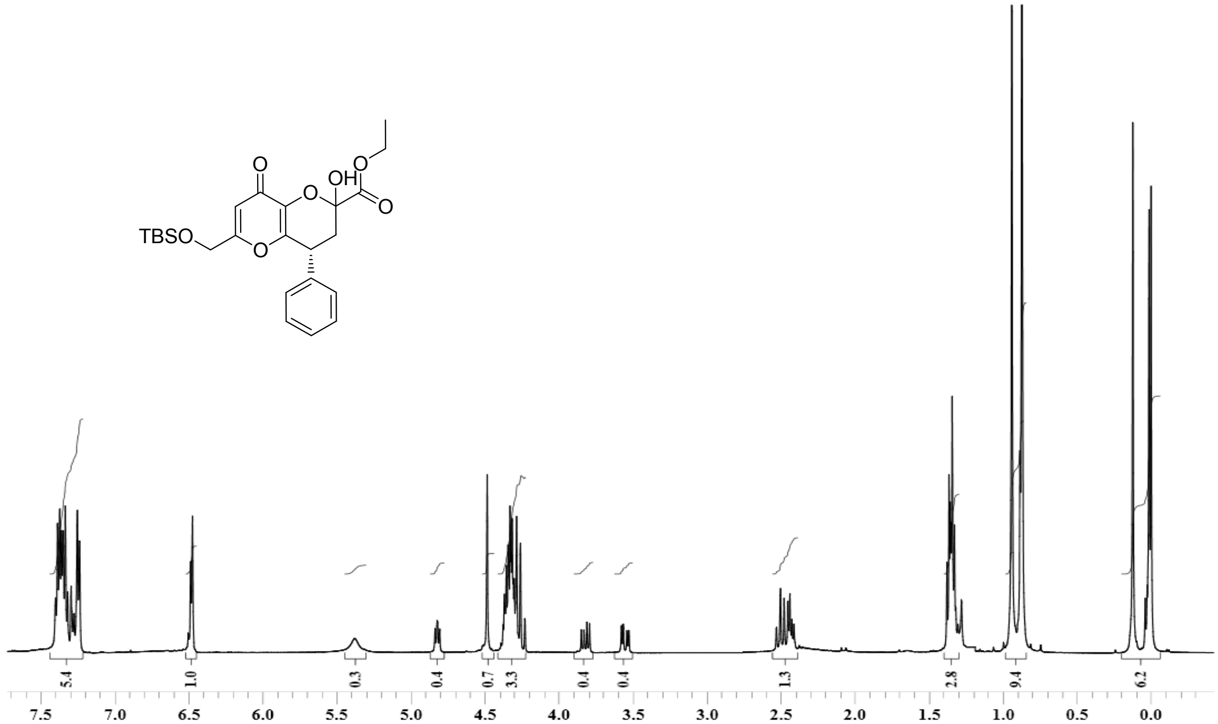


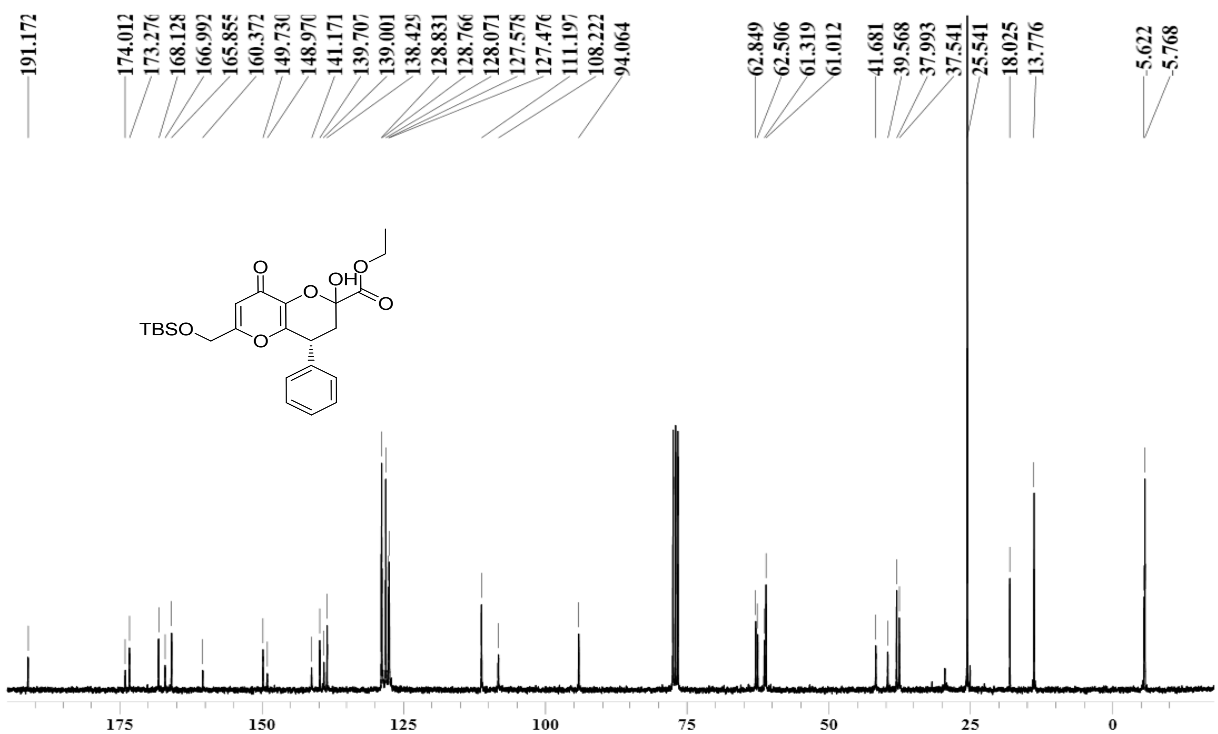
^{1}H NMR and ^{13}C NMR of 3o:


O
OH
O
O
O
O
5.5
0.6
1.1
0.5
0.5
0.9
0.5
0.4
1.6
2.9
9.5
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

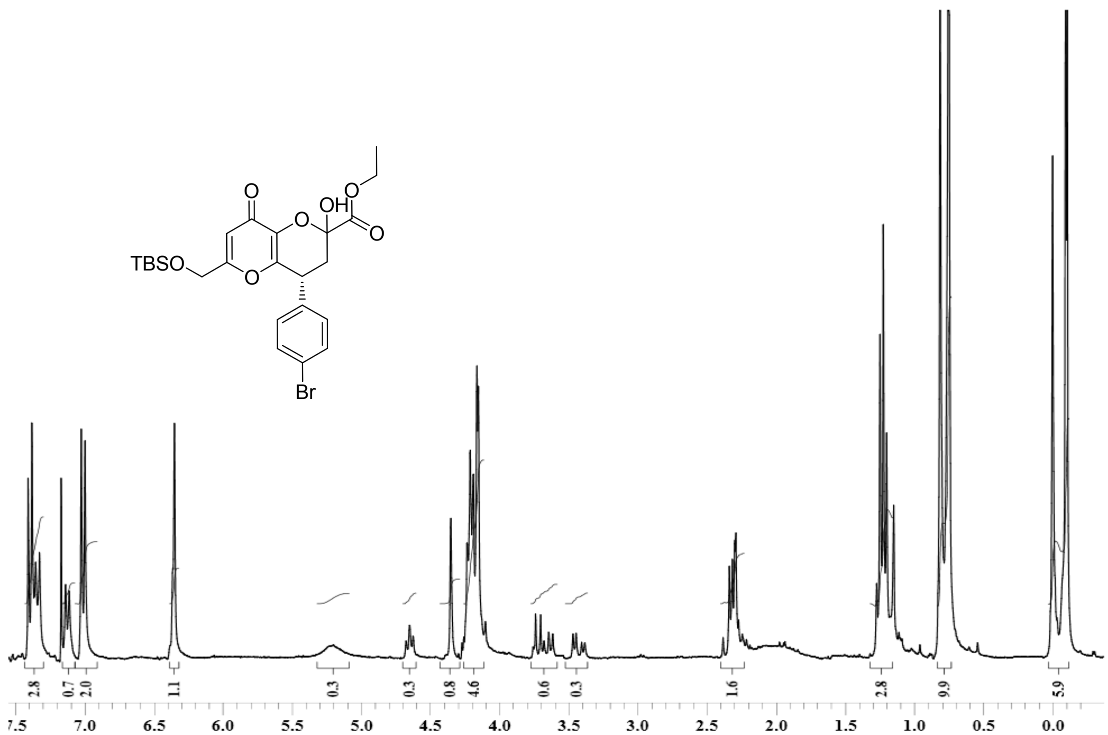

192.322
174.257
173.945
173.259
167.244
166.386
165.226
164.017
159.750
149.975
149.436
145.168
140.781
139.511
139.203
138.761
137.939
128.770
128.069
127.626
127.392
113.396
111.328
110.455
94.073
84.181
41.479
39.514
38.097
37.508
29.552
27.620
19.874
19.414
O
OH
O
O
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

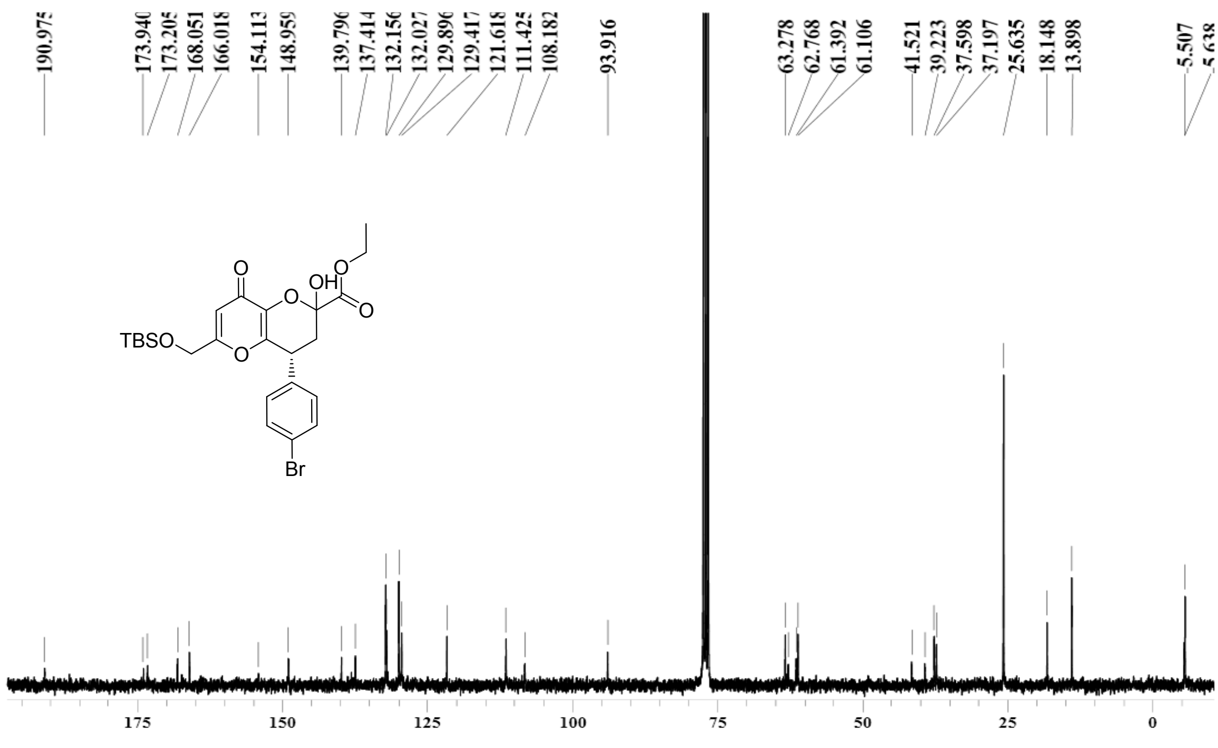
^{1}H NMR and ^{13}C NMR of 5a:



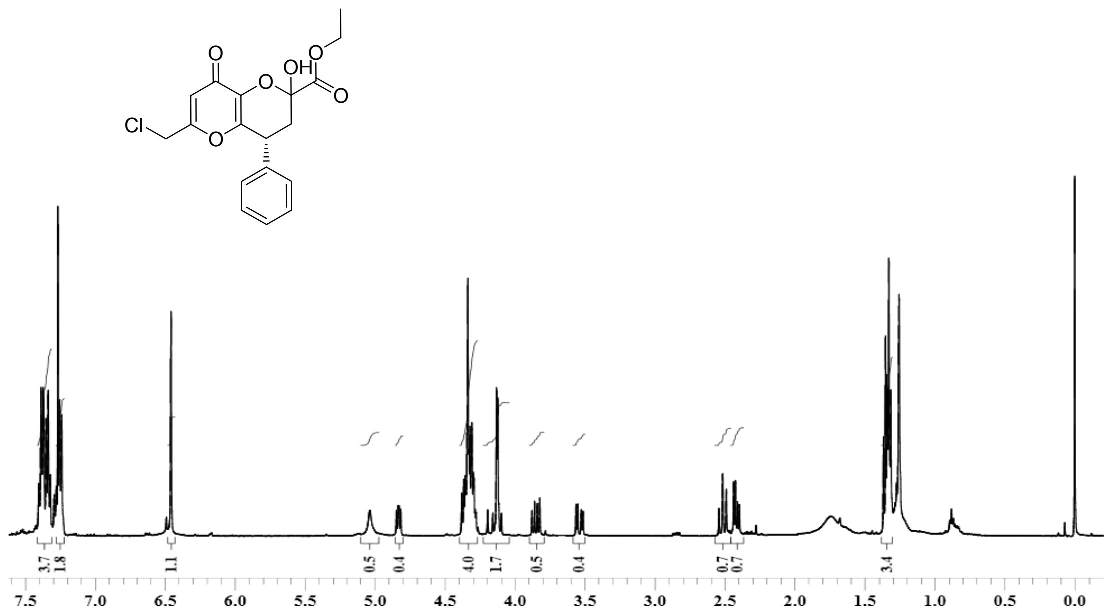


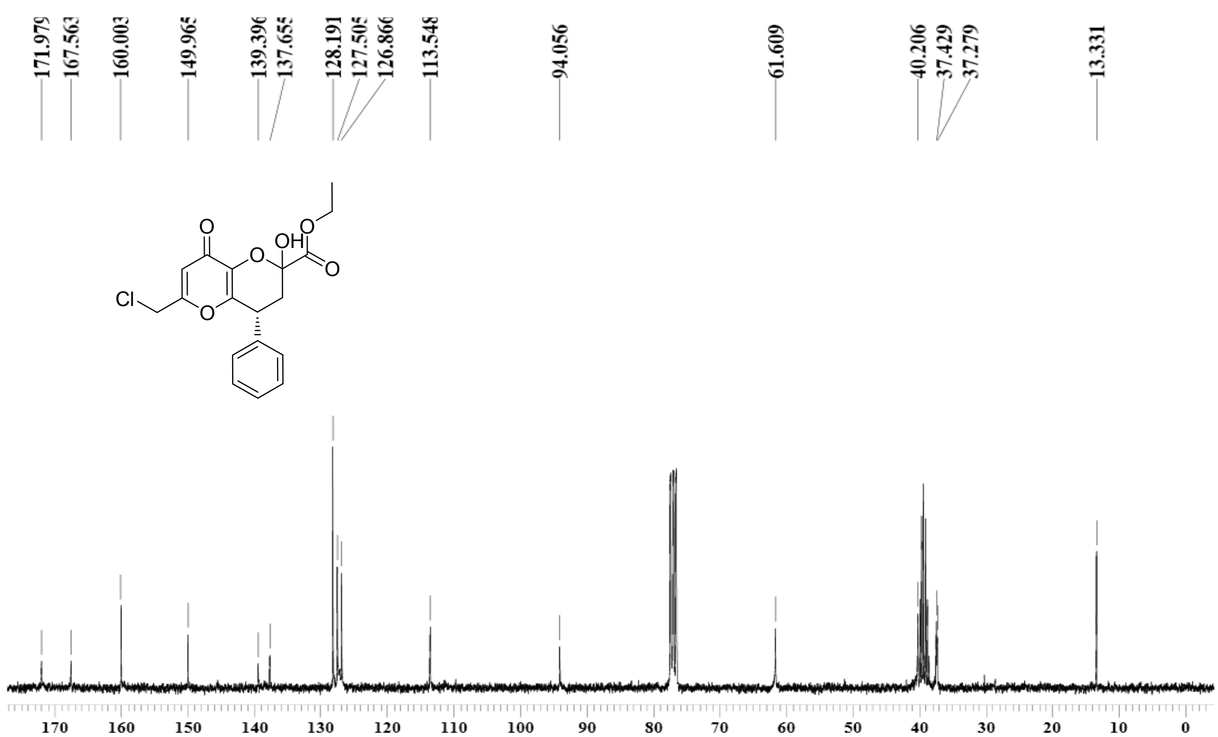
^{1}H NMR and ^{13}C NMR of 5b:



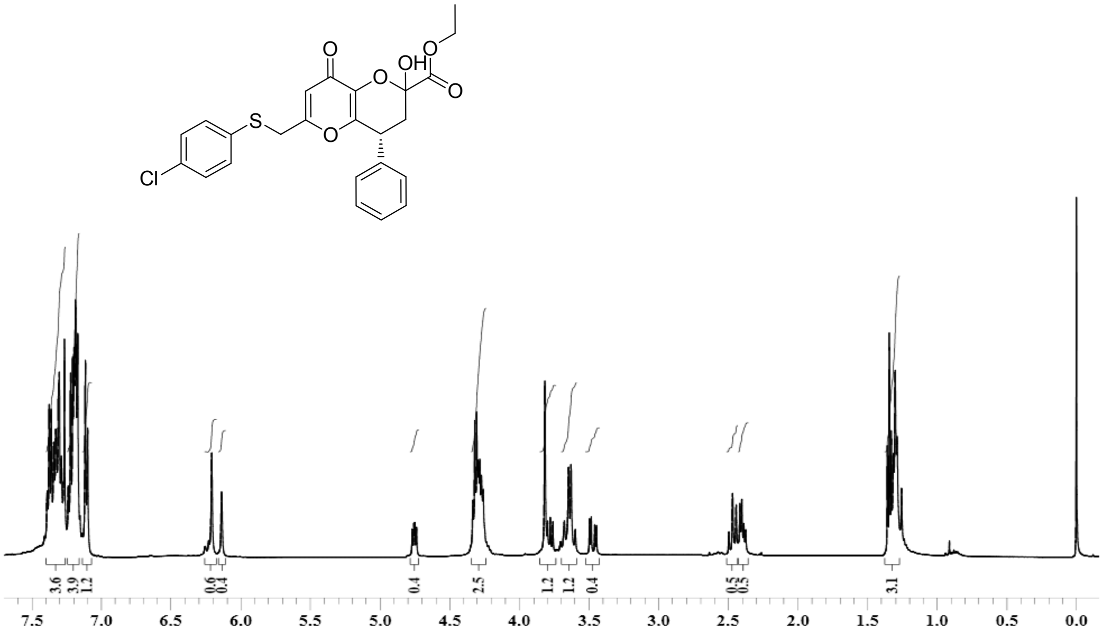


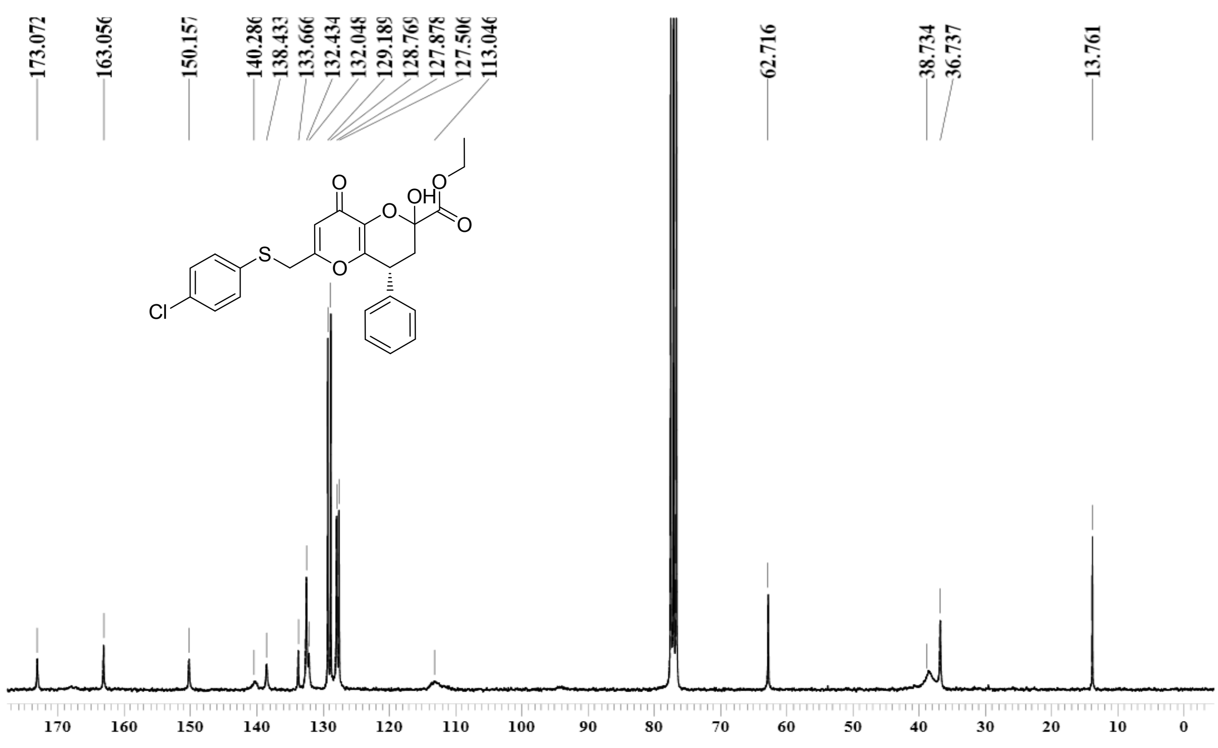
[1]H NMR and [13]C NMR of 5c:


O
OH
O
O
O
Cl
O
3.7 1.8 1.1 0.5 0.4 4.0 1.7 0.5 0.4 0.7 0.7 3.4
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

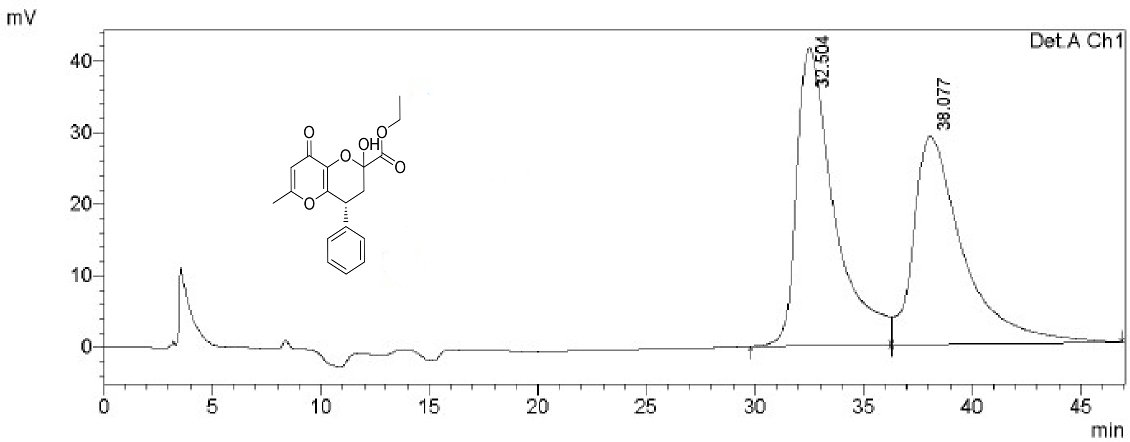

171.979
167.563
160.003
149.965
139.396
137.655
128.191
127.505
126.866
113.548
94.056
61.609
40.206
37.429
37.279
13.331
O
OH
O
O
O
Cl
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

^{1}H NMR and ^{13}C NMR of 5d:





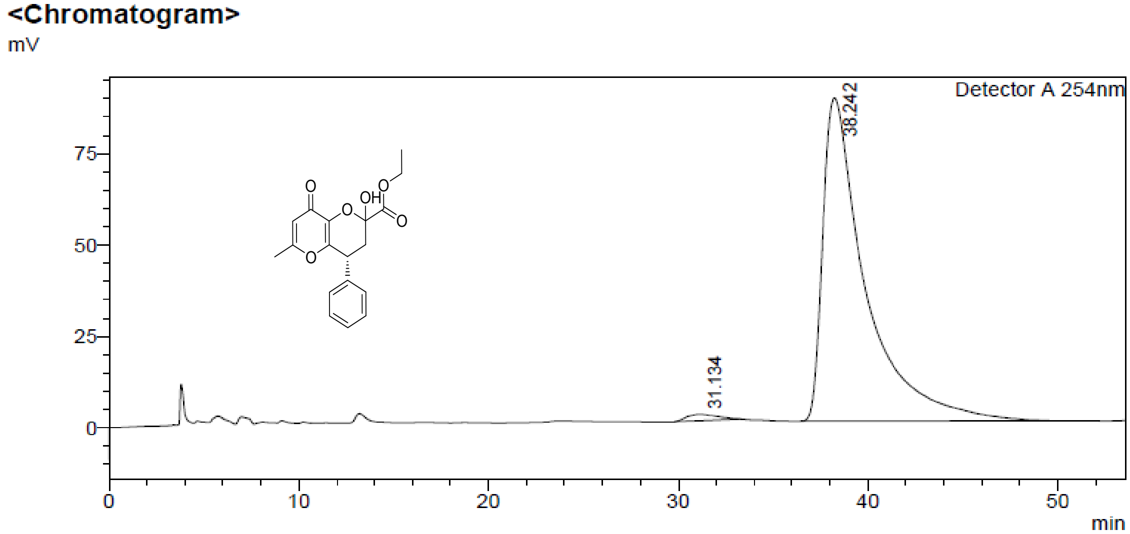
3a:



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.504	5012038	41584	52.046	58.877
2	38.077	4618052	29045	47.954	41.123
Total		9630090	70630	100.000	100.000

<Chromatogram>



Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	31.134	195318	1710	1.395	1.898
2	38.242	13810026	88397	98.605	98.102
Total		14005344	90107	100.000	100.000

3b:

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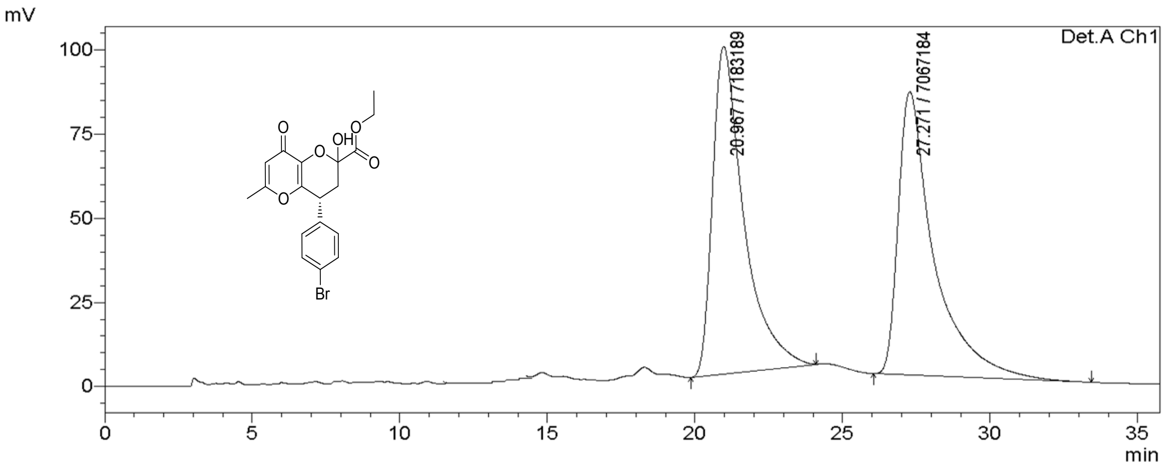
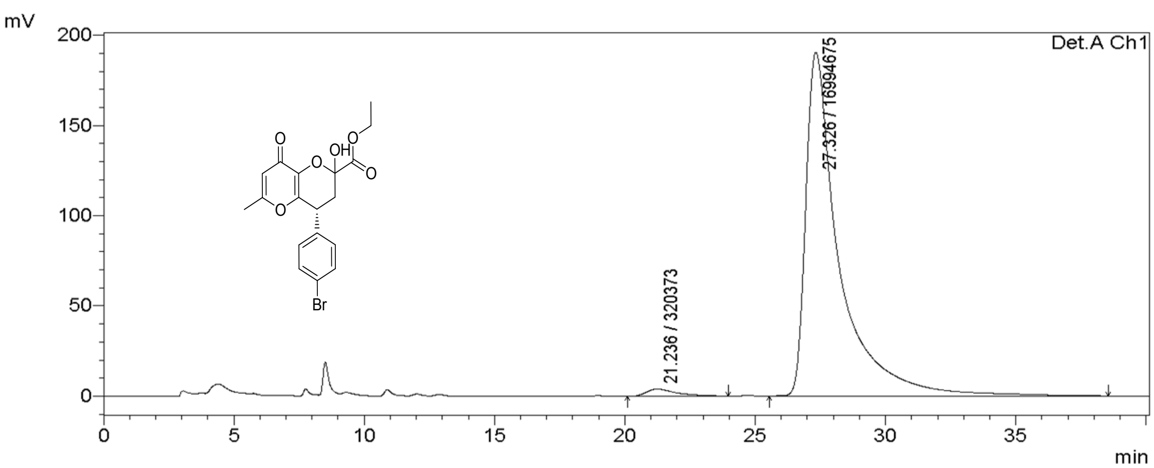


Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.967	7183189	97253	50.407	53.626
2	27.271	7067184	84100	49.593	46.374
Total		14250373	181352	100.000	100.000

<Chromatogram>



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.236	320373	3995	1.850	2.054
2	27.326	16994675	190517	98.150	97.946
Total		17315048	194513	100.000	100.000

3c:

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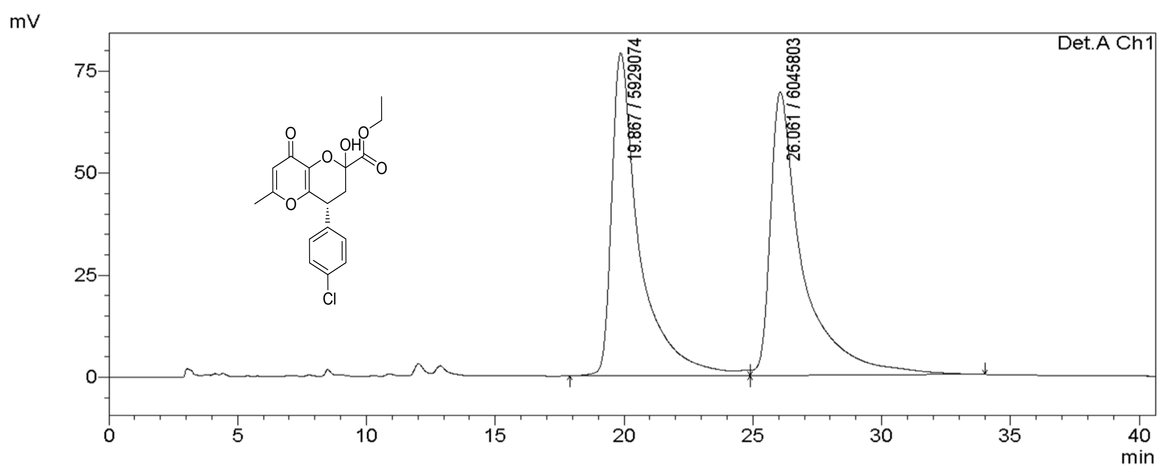

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.867	5929074	79242	49.513	53.314
2	26.061	6045803	69391	50.487	46.686
Total		11974878	148633	100.000	100.000

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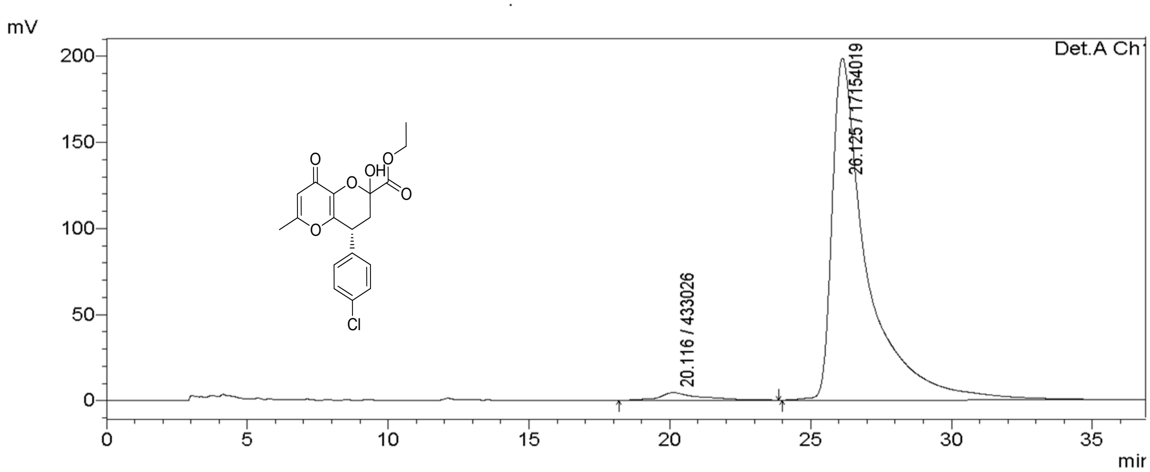

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.116	433026	4425	2.462	2.179
2	26.125	17154019	198628	97.538	97.821
Total		17587044	203053	100.000	100.000

3d:

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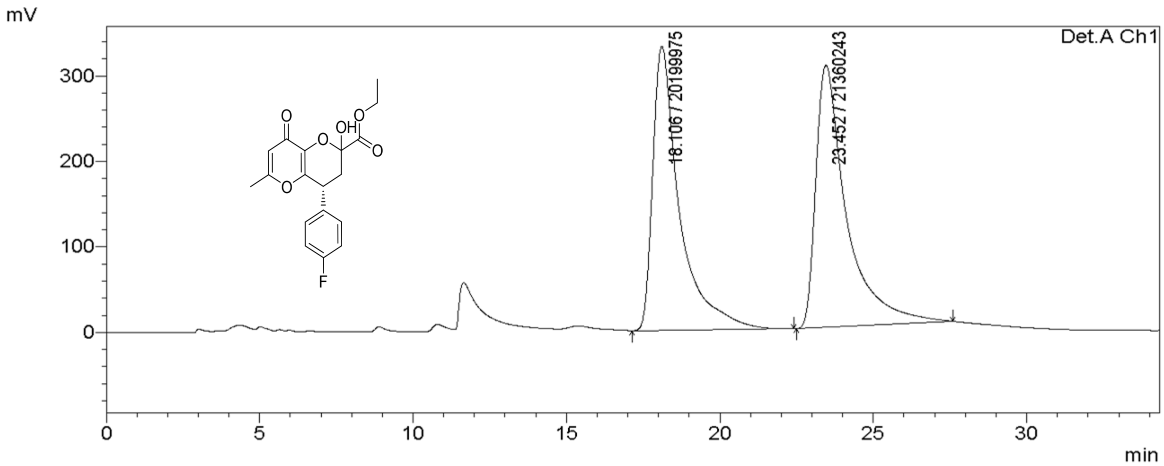

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.106	20199975	332274	48.604	52.011
2	23.452	21360243	306574	51.396	47.989
Total		41560218	638848	100.000	100.000

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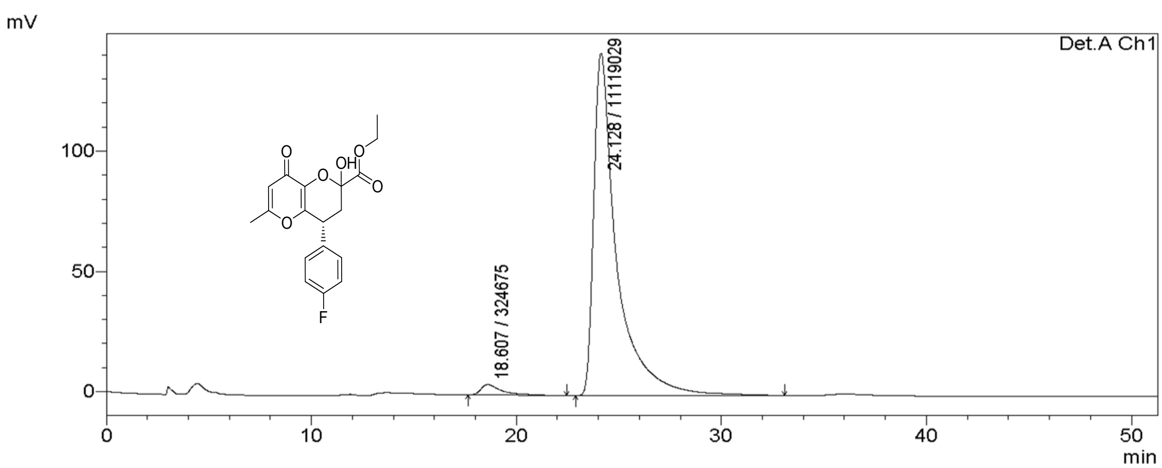
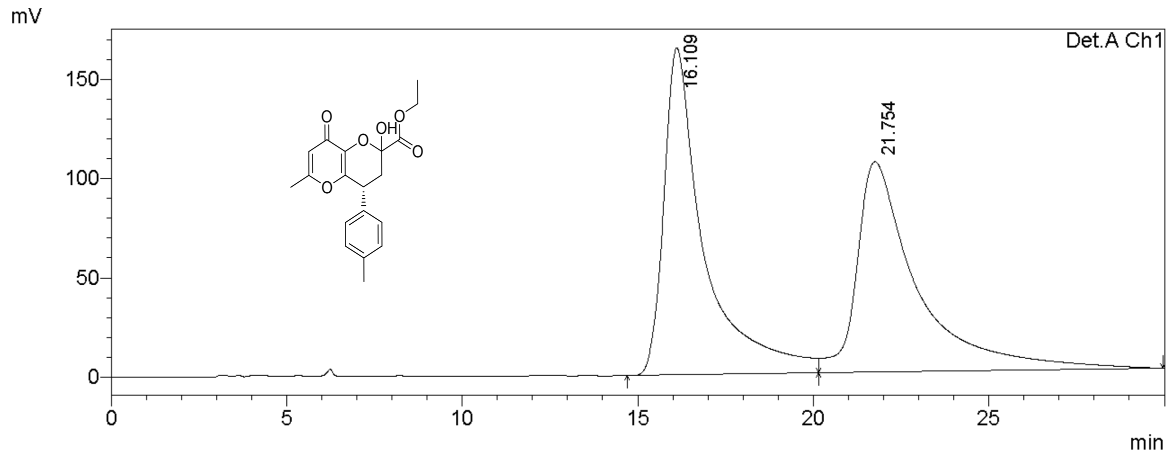


Detector A Ch1 254nm

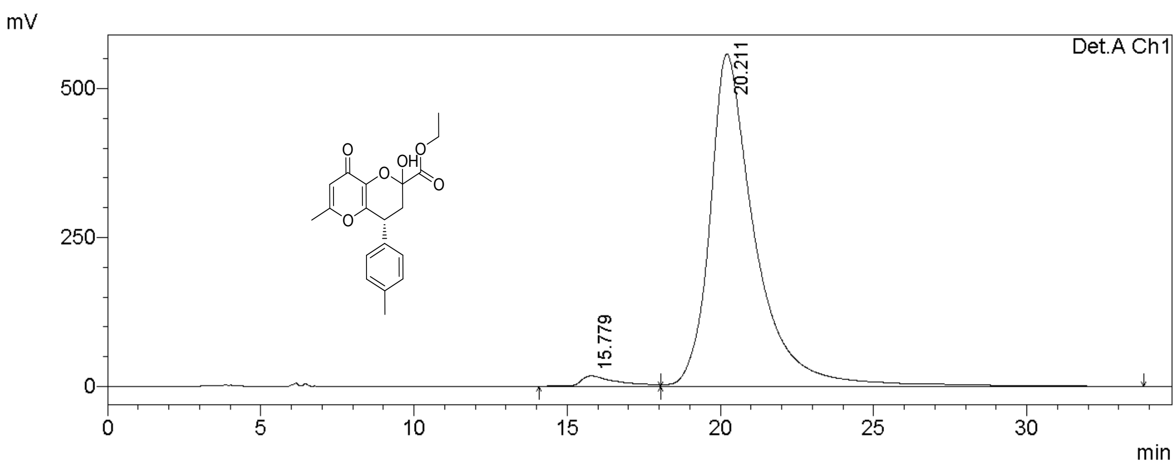
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.607	324675	4416	2.837	3.006
2	24.128	11119029	142473	97.163	96.994
Total		11443704	146889	100.000	100.000

3e:



Detector A Ch1 254nm

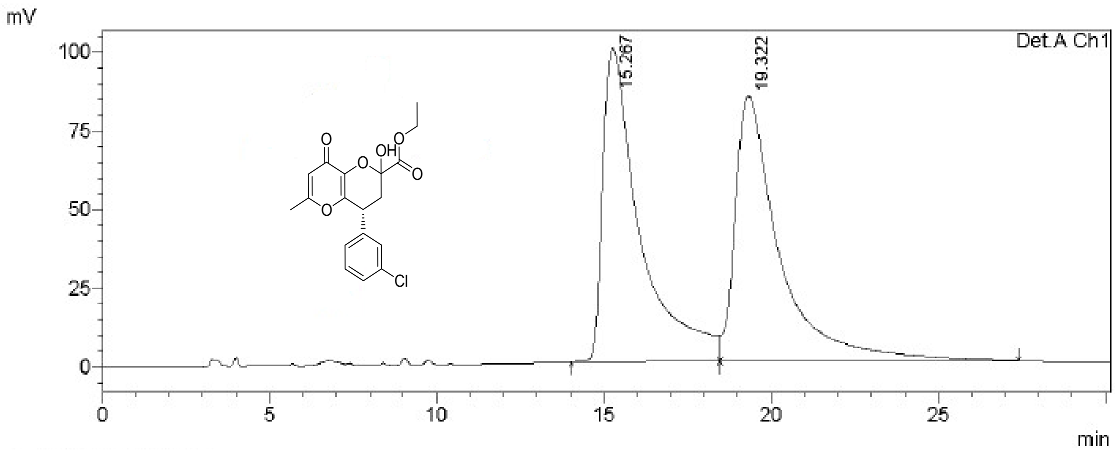
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.109	13174754	164773	50.764	60.832
2	21.754	12778122	106092	49.236	39.168
Total		25952876	270865	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.779	1379185	17233	2.354	2.996
2	20.211	57209755	557978	97.646	97.004
Total		58588940	575211	100.000	100.000

3f:



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.267	7717414	99502	49.833	54.202
2	19.322	7769106	84075	50.167	45.798
Total		15486521	183577	100.000	100.000

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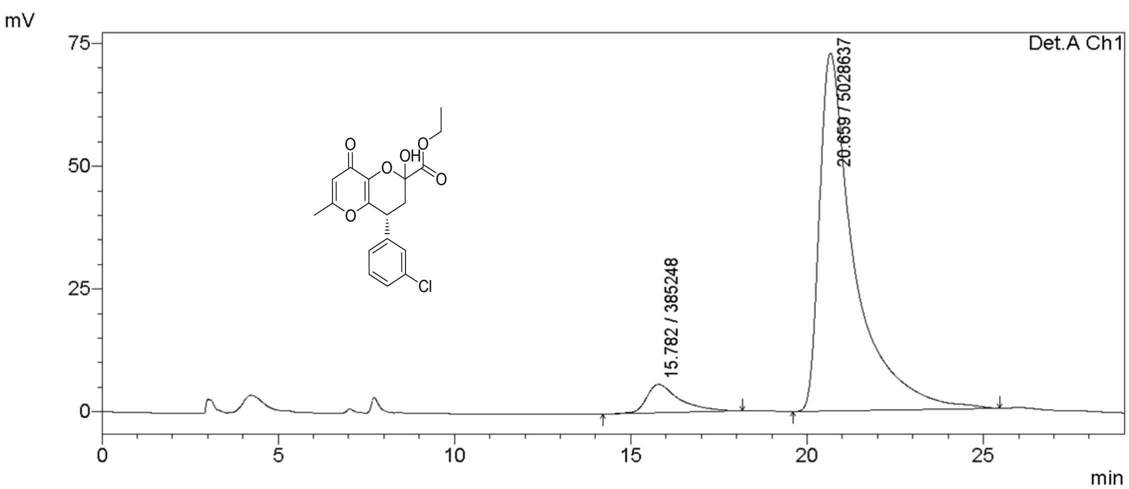

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.782	385248	5840	7.116	7.419
2	20.659	5028637	72878	92.884	92.581
Total		5413885	78718	100.000	100.000

3g:

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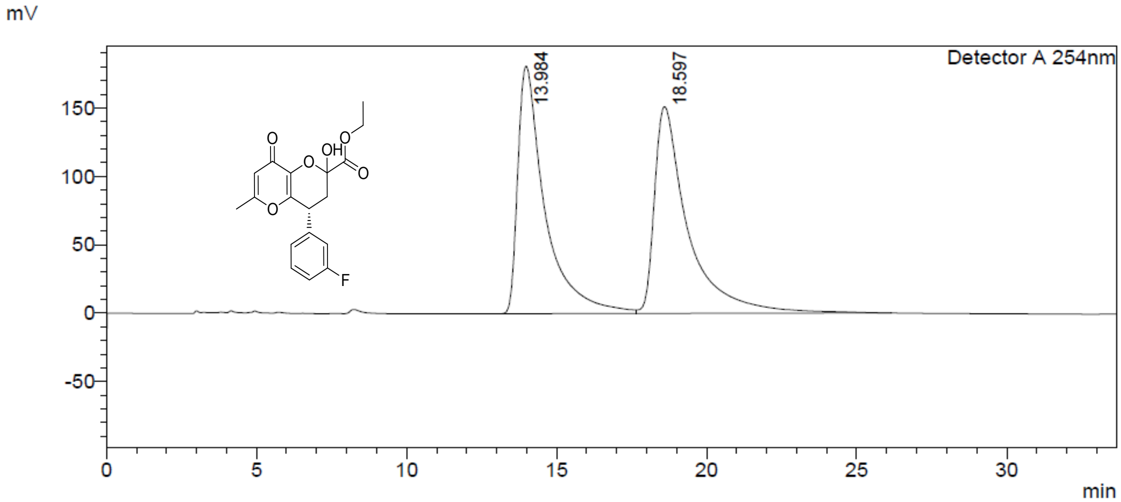

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	13.984	11410011	180874	49.203	54.471
2	18.597	11779458	151184	50.797	45.529
Total		23189469	332058	100.000	100.000

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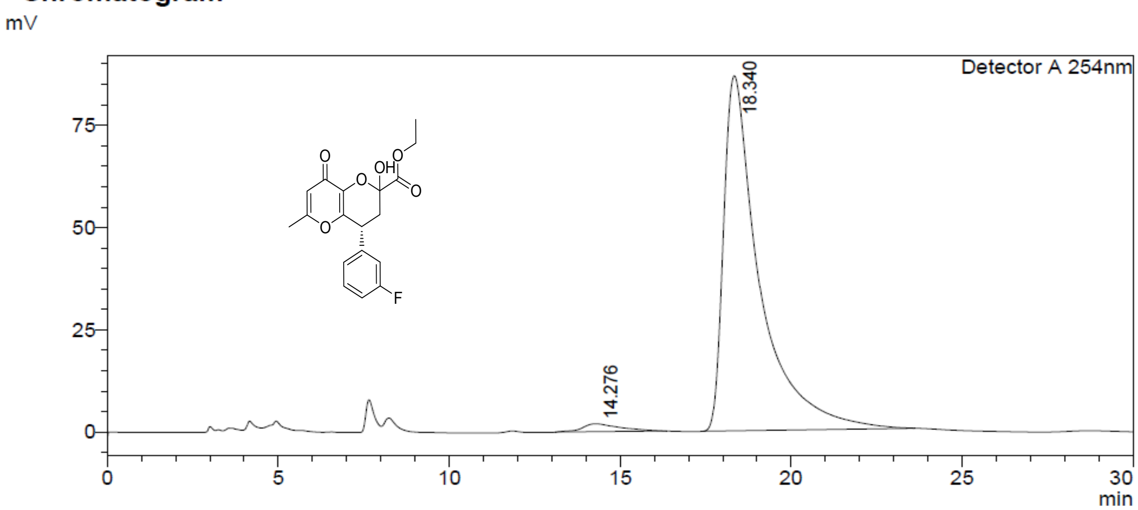

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	14.276	149927	1949	2.295	2.197
2	18.340	6383308	86762	97.705	97.803
Total		6533235	88712	100.000	100.000

3h:

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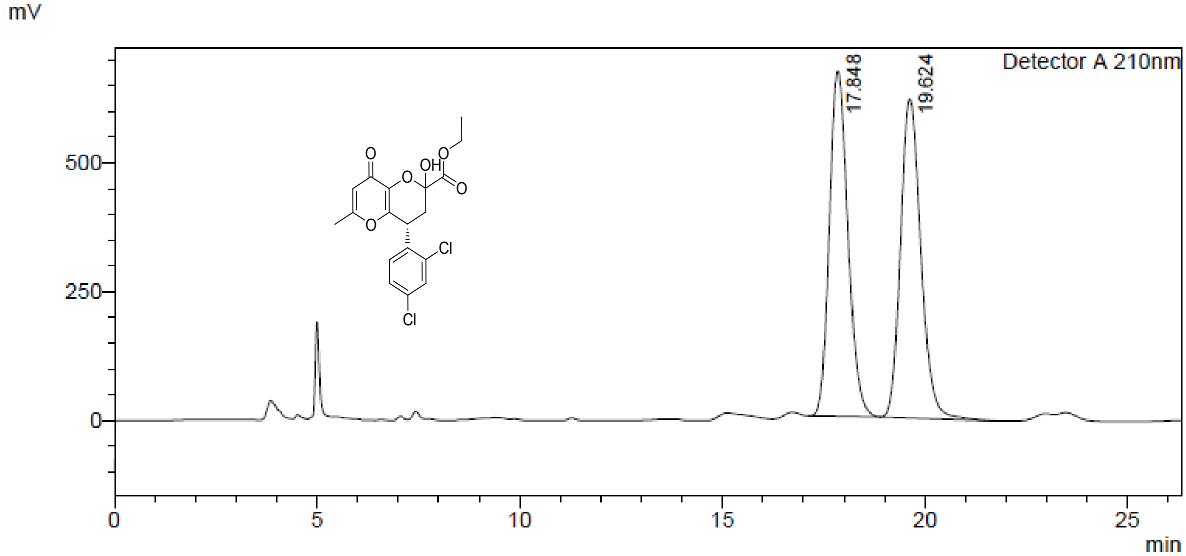
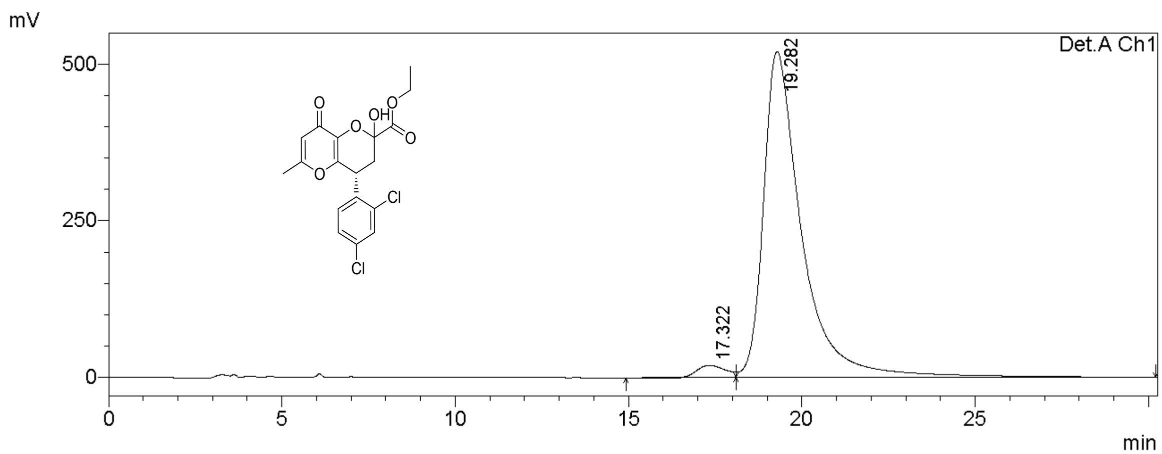


Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.848	21376383	670582	49.629	51.972
2	19.624	21695881	619684	50.371	48.028
Total		43072265	1290266	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.322	1178552	19655	2.849	3.644
2	19.282	40194115	519774	97.151	96.356
Total		41372667	539429	100.000	100.000

3i:

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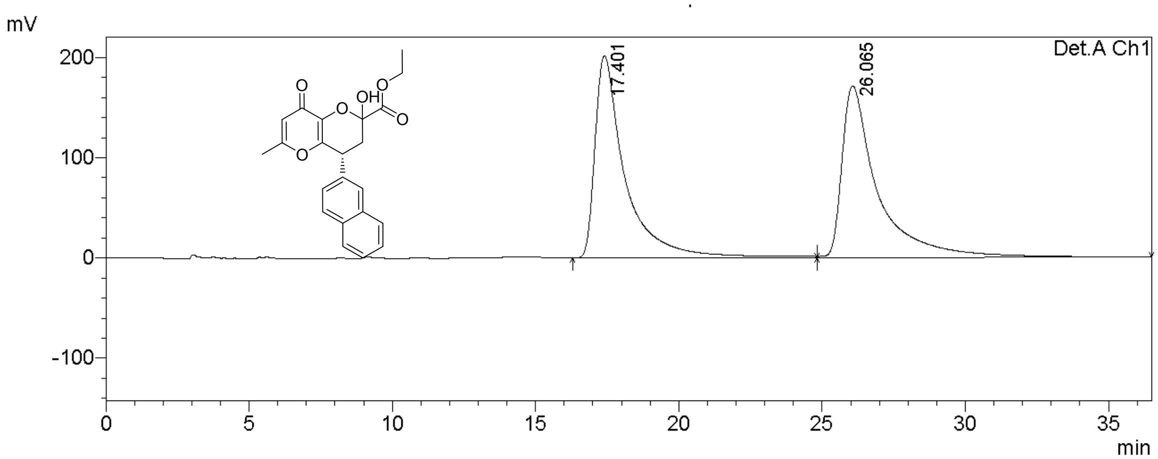

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.401	14750146	201647	49.711	54.072
2	26.065	14921450	171276	50.289	45.928
Total		29671596	372923	100.000	100.000

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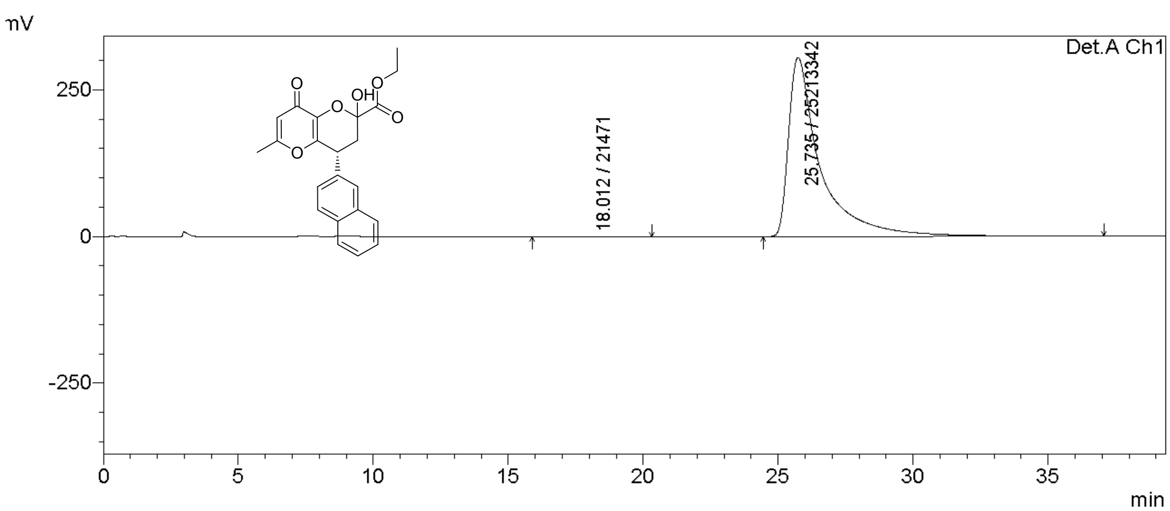

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.012	21471	151	0.085	0.049
2	25.735	25213342	305599	99.915	99.951
Total		25234813	305749	100.000	100.000

3j:

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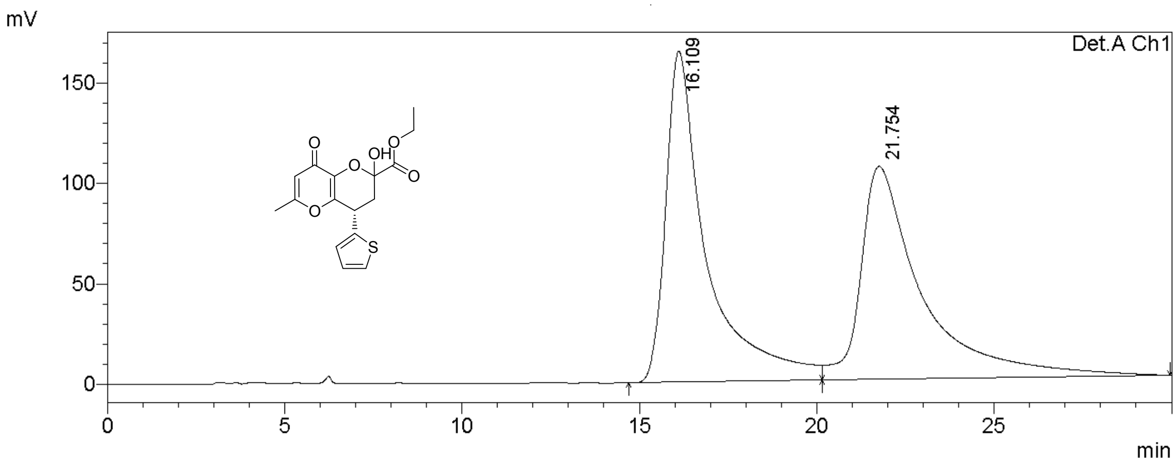

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.109	13174754	164773	50.764	60.832
2	21.754	12778122	106092	49.236	39.168
Total		25952876	270865	100.000	100.000

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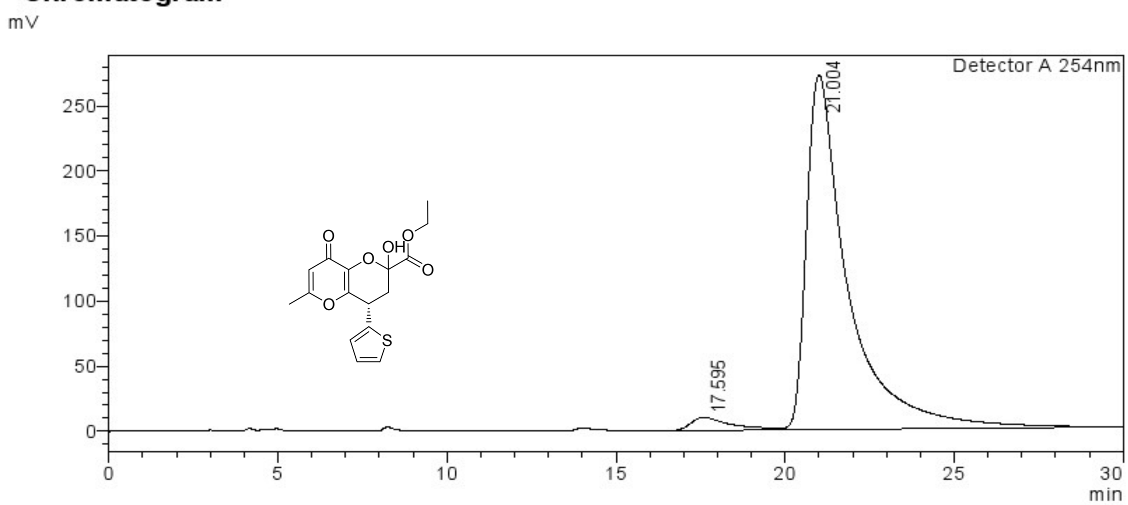
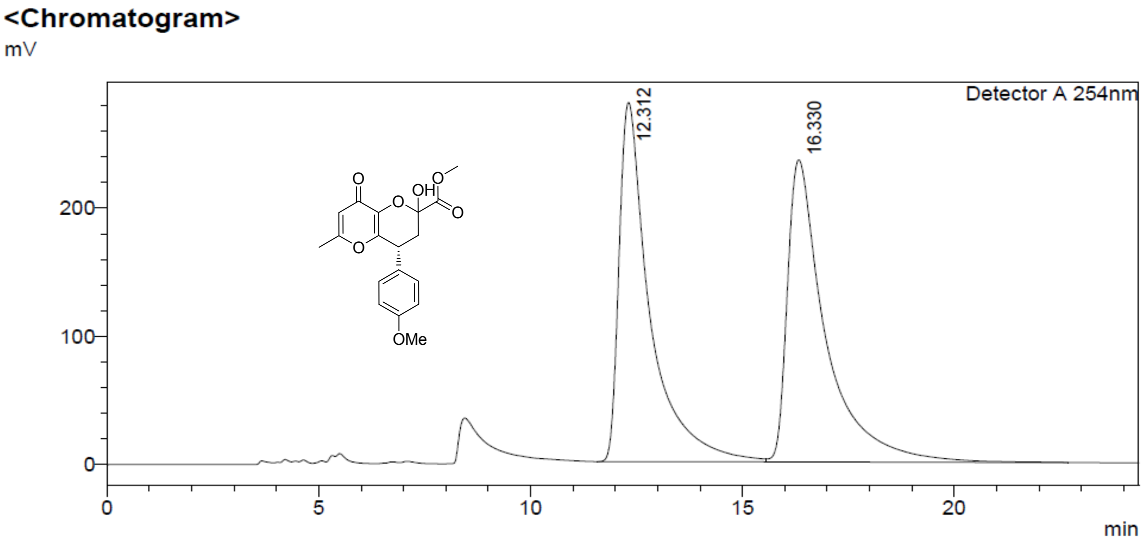


Detector A 254nm

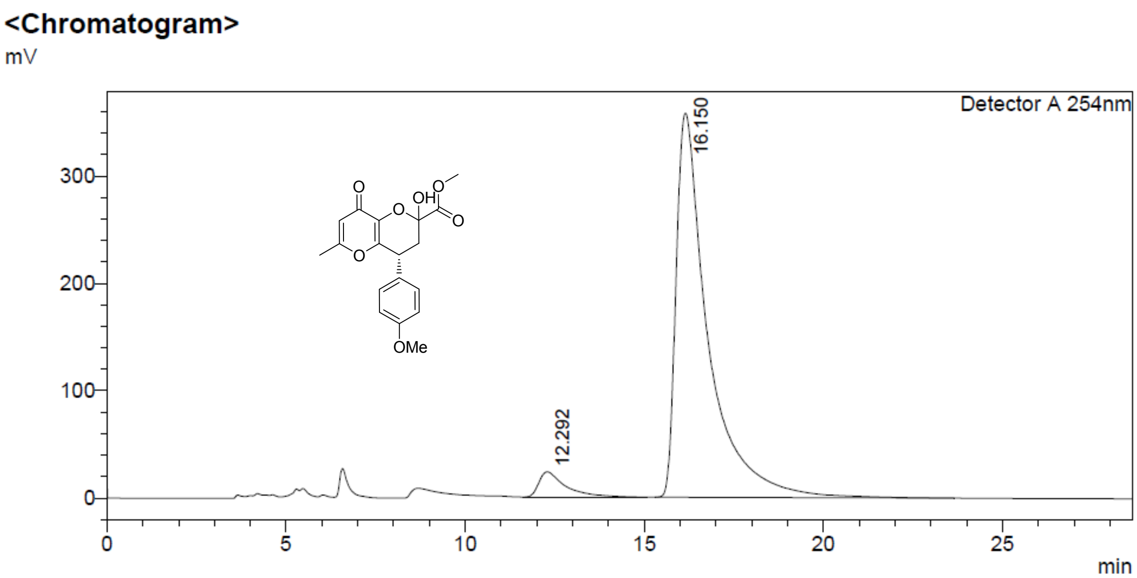
Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.595	794854	9808	3.306	3.478
2	21.004	23250222	272231	96.694	96.522
Total		24045076	282038	100.000	100.000

3k:



Detector A 254nm

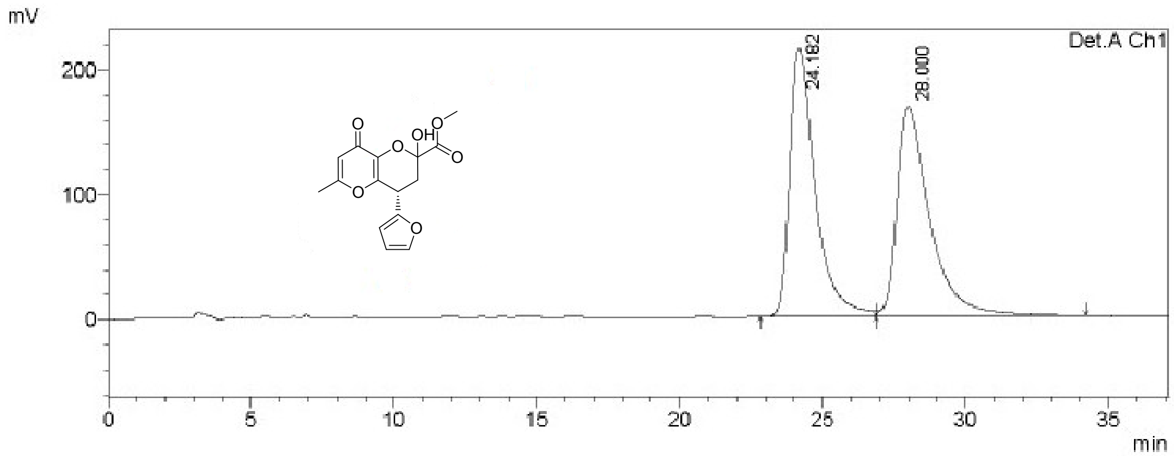
Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.312	14198658	280186	48.912	54.312
2	16.330	14830461	235700	51.088	45.688
Total		29029118	515886	100.000	100.000



Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.292	1233254	23582	5.269	6.184
2	16.150	22171495	357737	94.731	93.816
Total		23404749	381319	100.000	100.000

3l:



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.182	13403761	215132	49.968	56.145
2	28.000	13420755	168039	50.032	43.855
Total		26824516	383170	100.000	100.000

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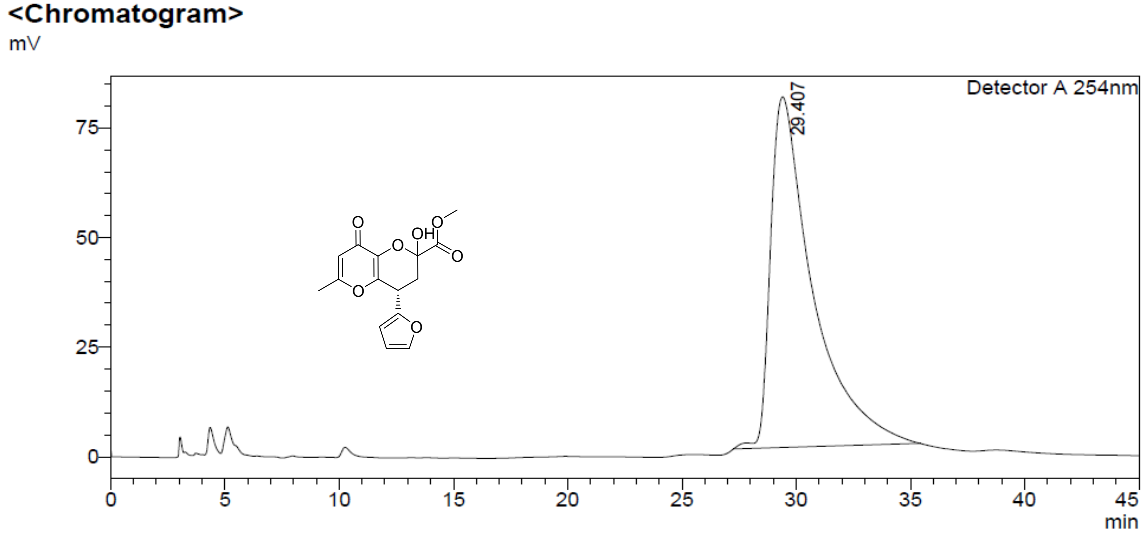

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	29.407	10278999	79952	100.000	100.000
Total		10278999	79952	100.000	100.000

3m:

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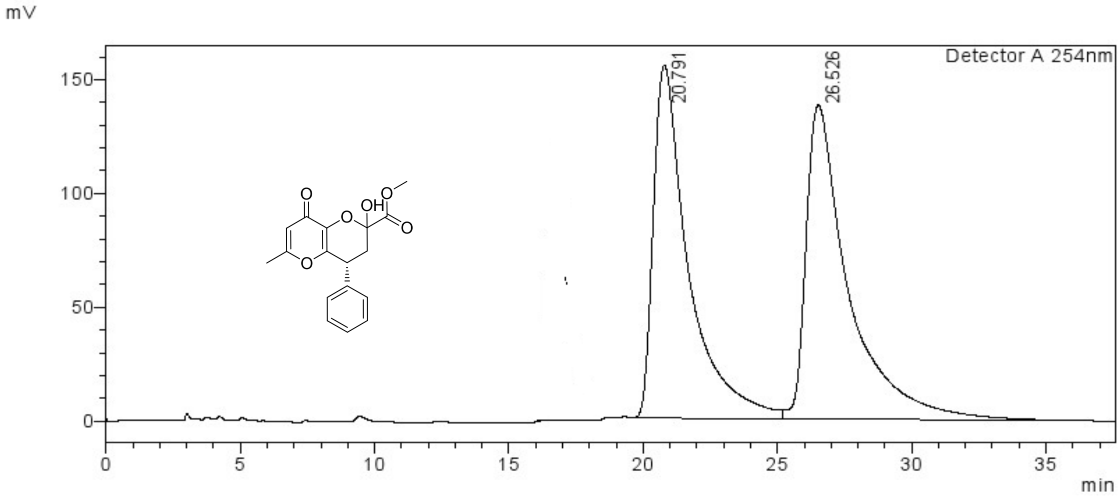

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.791	14028782	155030	48.157	52.922
2	26.526	15102477	137910	51.843	47.078
Total		29131259	292939	100.000	100.000

Detector A 254nm

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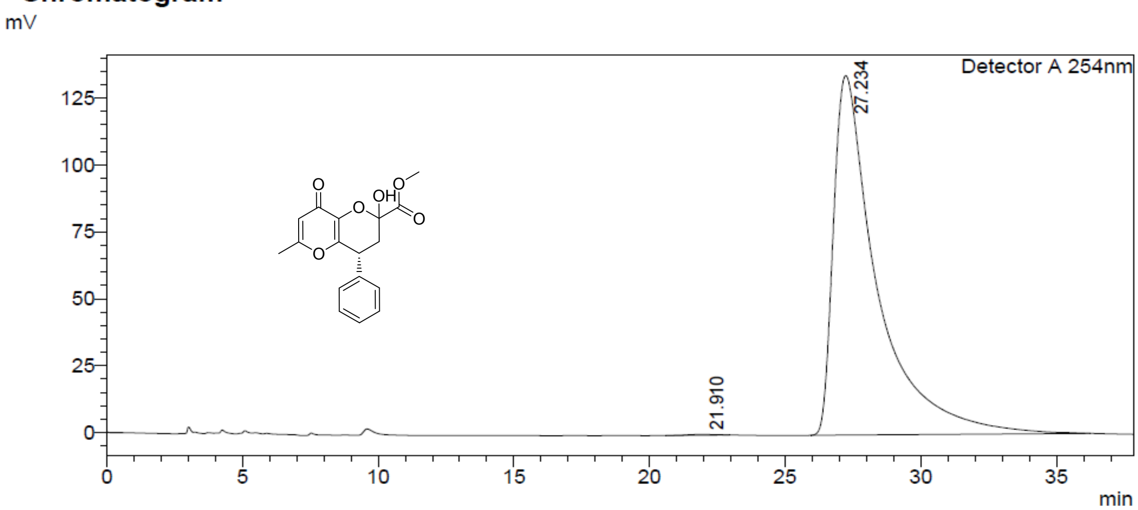

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	21.910	17338	256	0.115	0.191
2	27.234	15056393	134236	99.885	99.809
Total		15073731	134493	100.000	100.000

3n:

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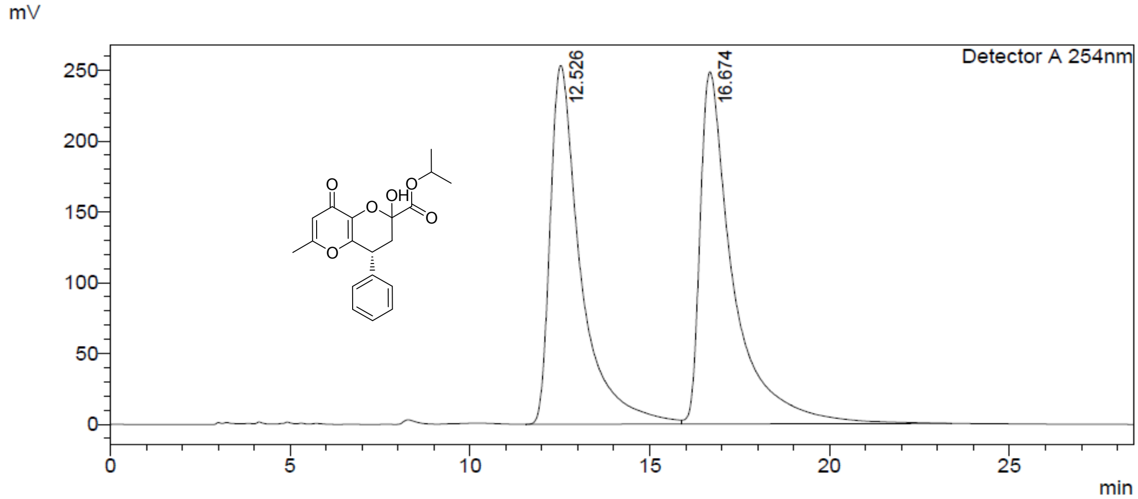

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	12.526	14932263	253295	48.414	50.462
2	16.674	15910679	248660	51.586	49.538
Total		30842941	501955	100.000	100.000

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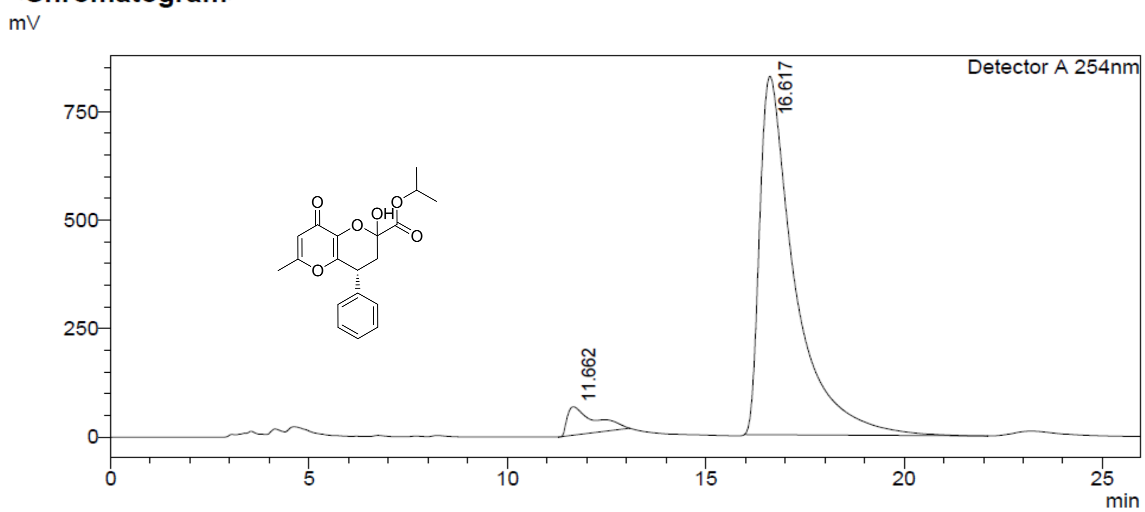
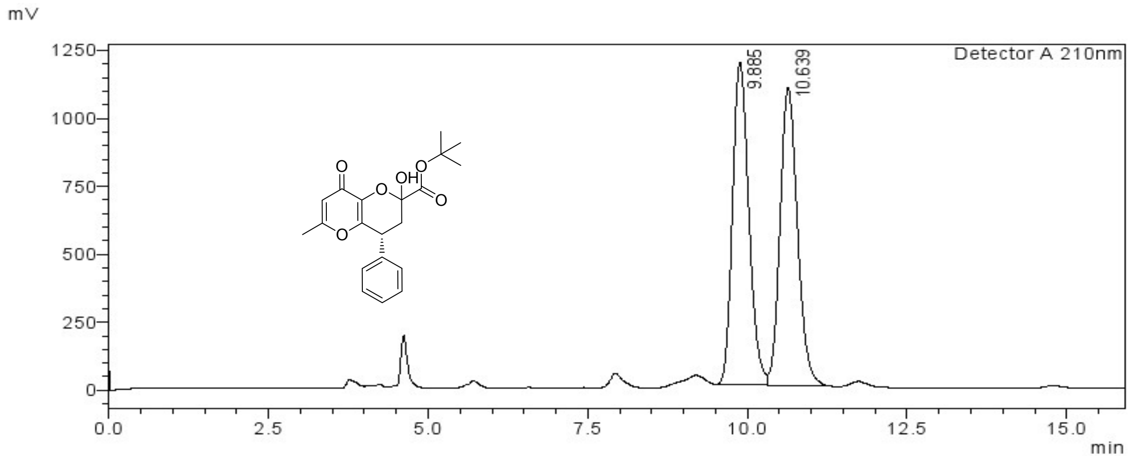


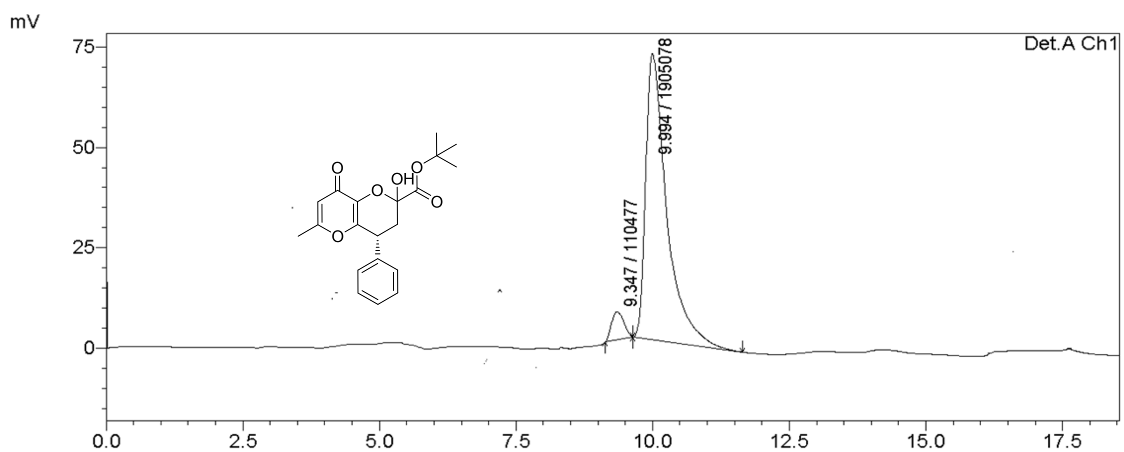
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	11.662	3142545	65697	5.805	7.369
2	16.617	50988145	825841	94.195	92.631
Total		54130690	891538	100.000	100.000

3o:



Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.885	21116991	1186104	50.377	51.988
2	10.639	20801320	1095377	49.623	48.012
Total		41918311	2281481	100.000	100.000



Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.347	110477	7074	5.481	9.021
2	9.994	1905078	71339	94.519	90.979
Total		2015555	78413	100.000	100.000

5a:

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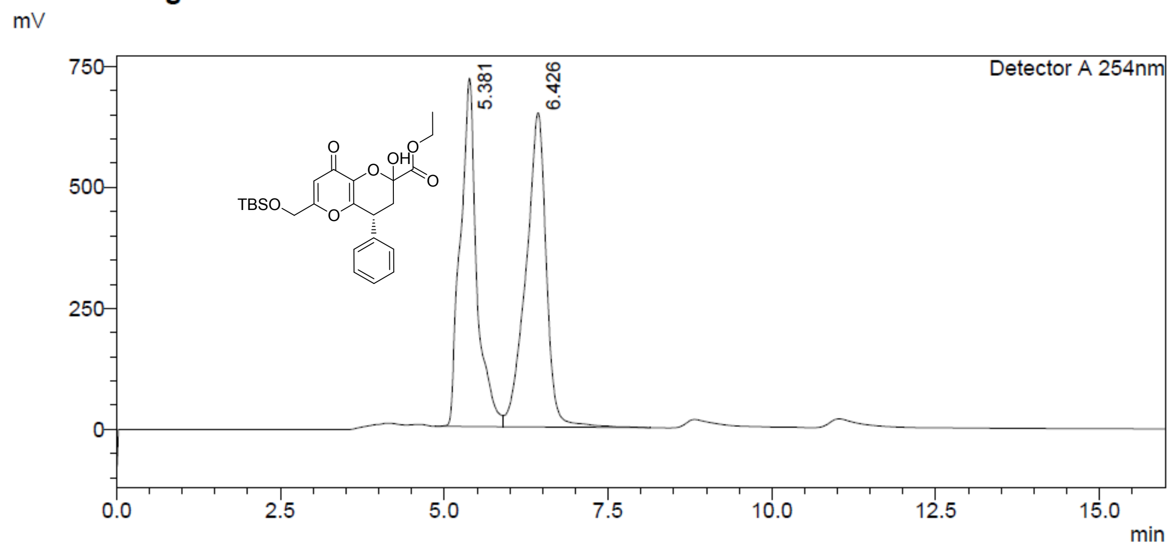
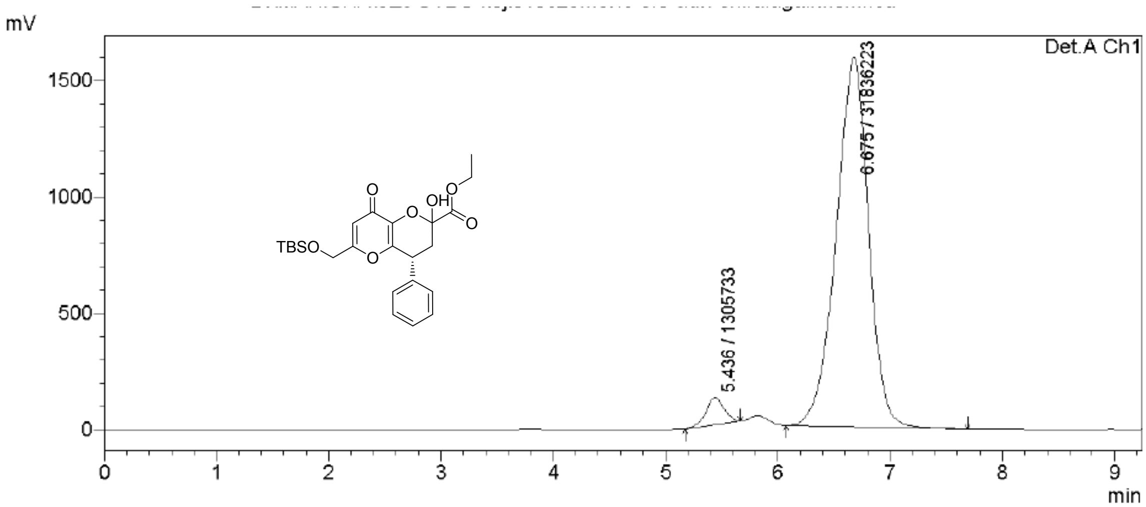


Peak#	Ret. Time	Area	Height	Area%	Height%
1	5.381	12598812	719349	47.279	52.585
2	6.426	14048942	648627	52.721	47.415
Total		26647755	1367976	100.000	100.000

Detector A 254nm



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.436	1305733	114996	3.940	6.754
2	6.675	31836223	1587531	96.060	93.246
Total		33141956	1702526	100.000	100.000

5b:

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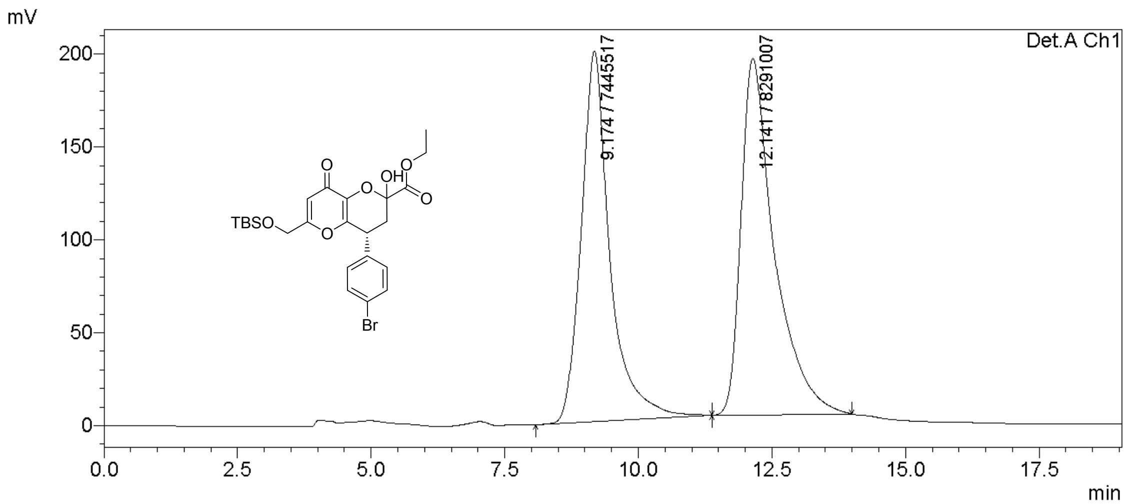

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.174	7445517	199708	47.314	50.978
2	12.141	8291007	192045	52.686	49.022
Total		15736524	391753	100.000	100.000

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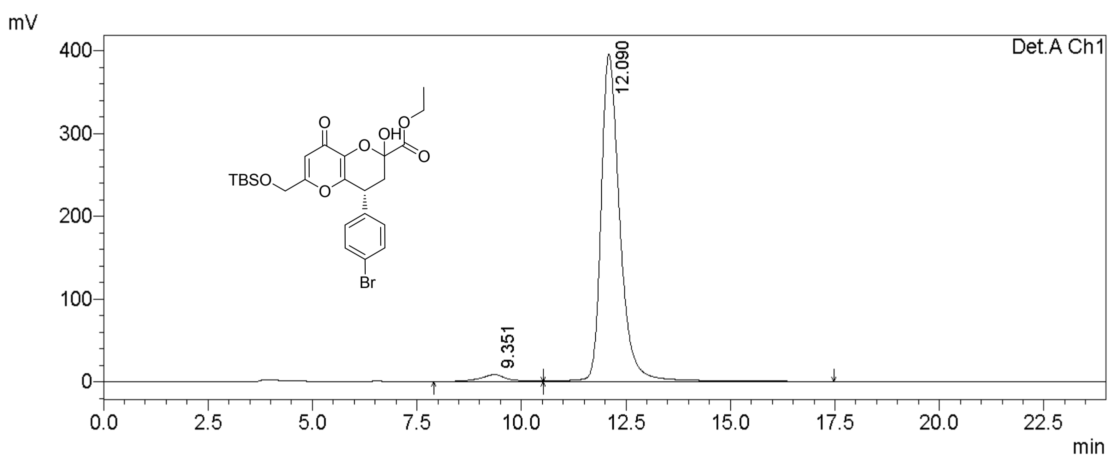
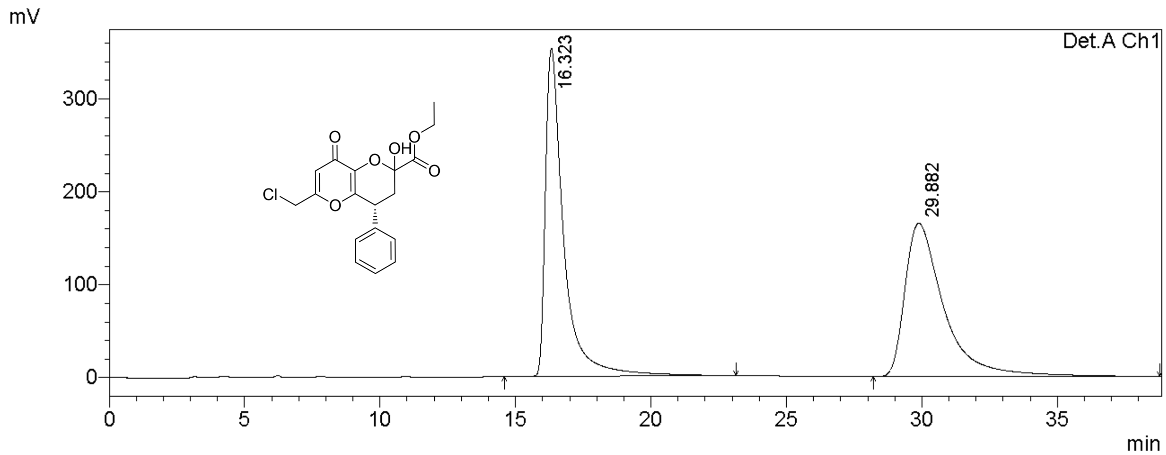


Detector A Ch1 254nm

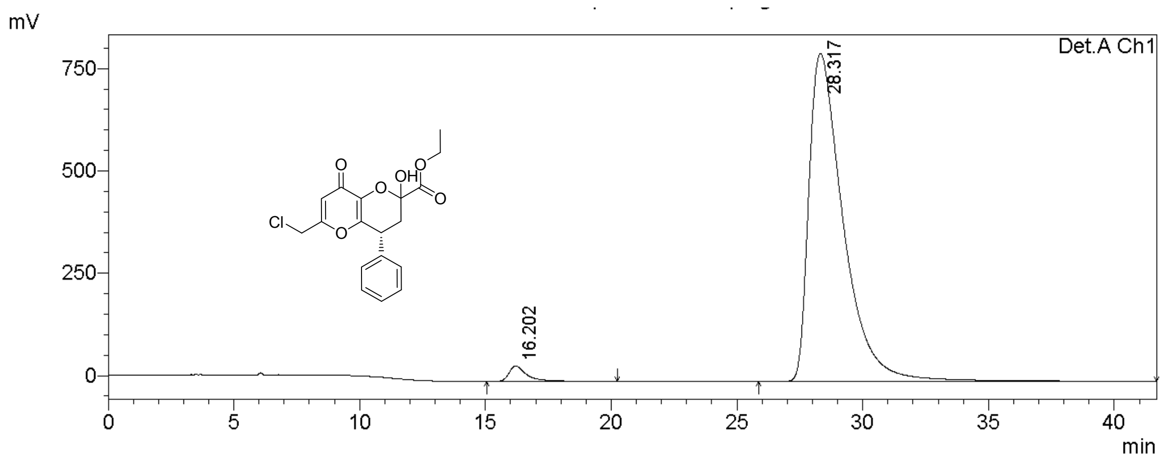
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.351	407070	8553	3.180	2.114
2	12.090	12392411	396065	96.820	97.886
Total		12799481	404619	100.000	100.000

5c:



Detector A Ch1 254nm

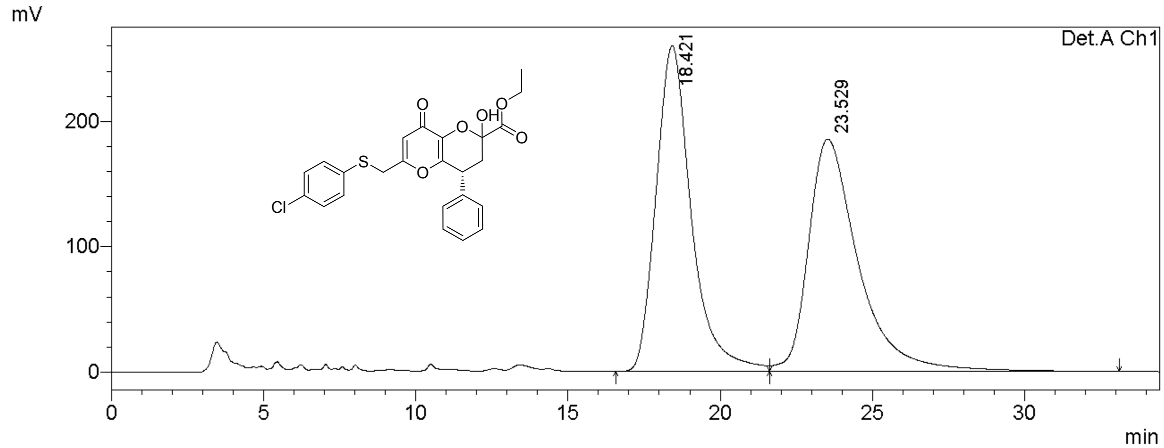
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.323	16712099	353251	50.213	68.175
2	29.882	16570184	164901	49.787	31.825
Total		33282284	518153	100.000	100.000



Detector A Ch1 254nm

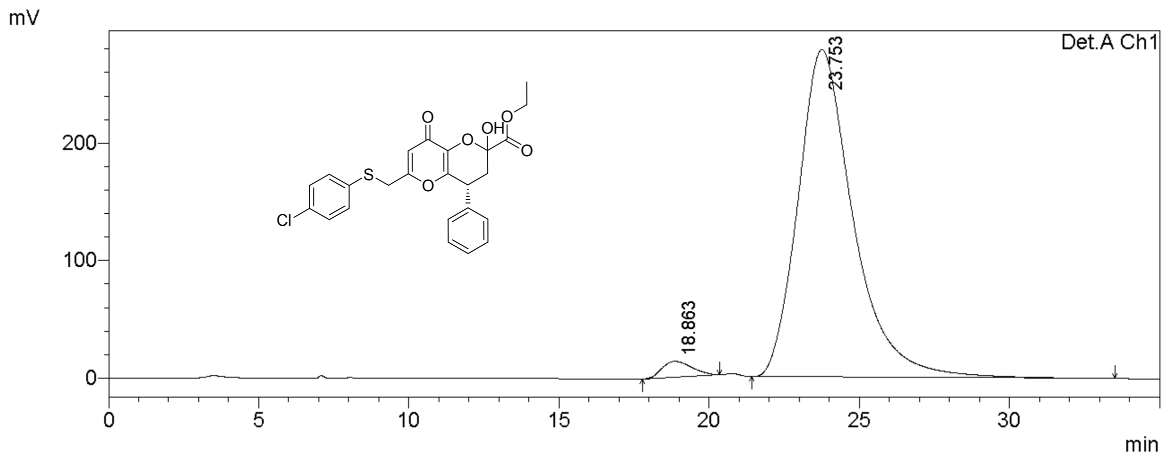
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.202	1902596	37884	2.428	4.513
2	28.317	76466802	801508	97.572	95.487
Total		78369399	839392	100.000	100.000

5d:



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.421	20977030	259891	49.809	58.373
2	23.529	21137741	185336	50.191	41.627
Total		42114771	445226	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.863	938678	13581	2.562	4.644
2	23.753	35697256	278846	97.438	95.356
Total		36635935	292426	100.000	100.000

8. References.

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