

# Supporting Information

## Sugar thiourea catalyzed highly enantioselective Michael addition of 2-hydroxy-1,4-naphthoquinone to $\beta$ -nitroalkenes

B. V. Subba Reddy,\*S. Madhusudana Reddy and Manisha Swain

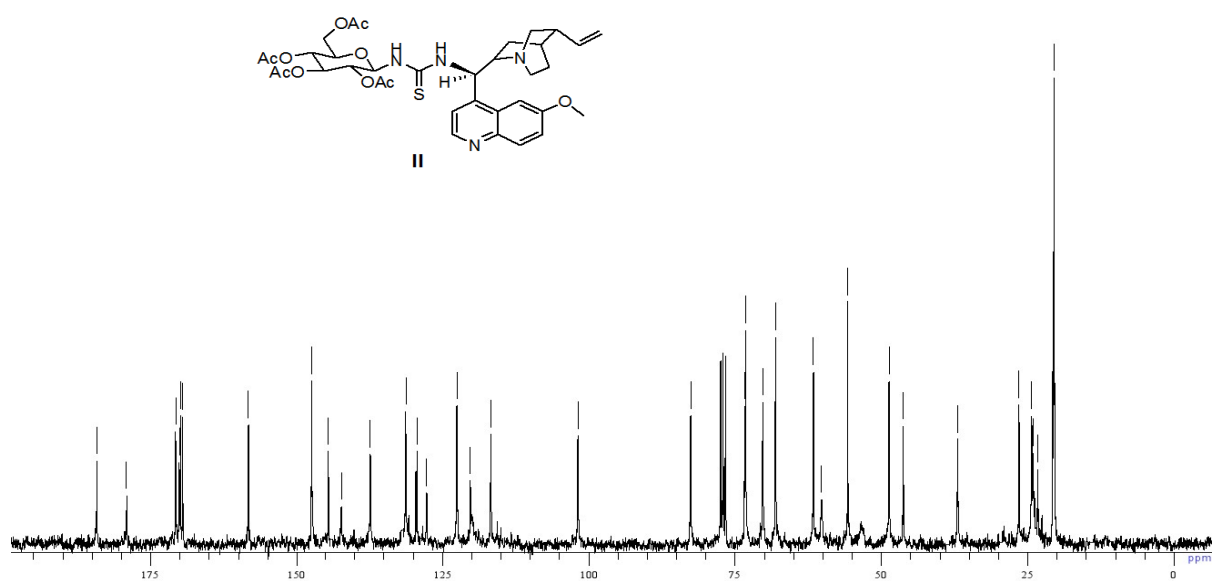
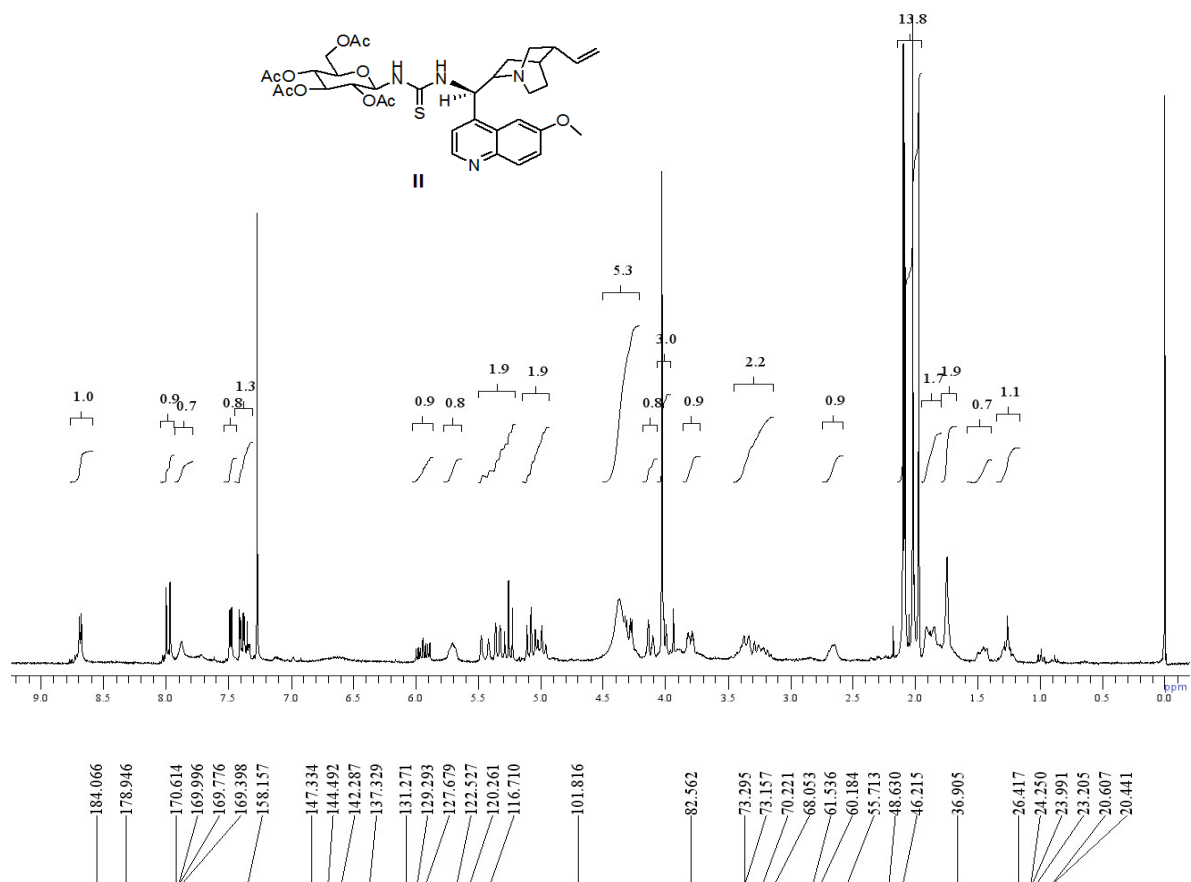
*Natural Product Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad, Andhra Pradesh, India, 500 007.E-mail:basireddy@iict.res.in; Fax: 91-40-27160512.*

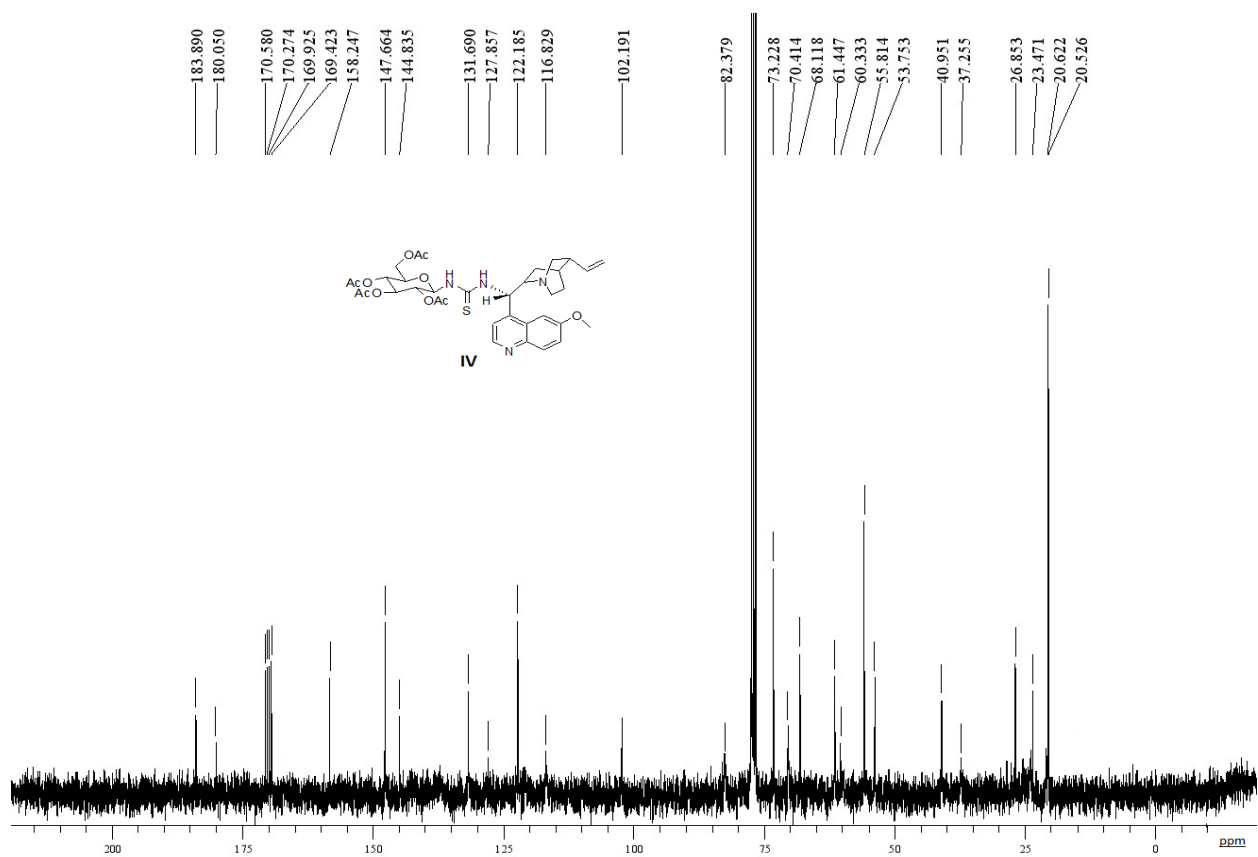
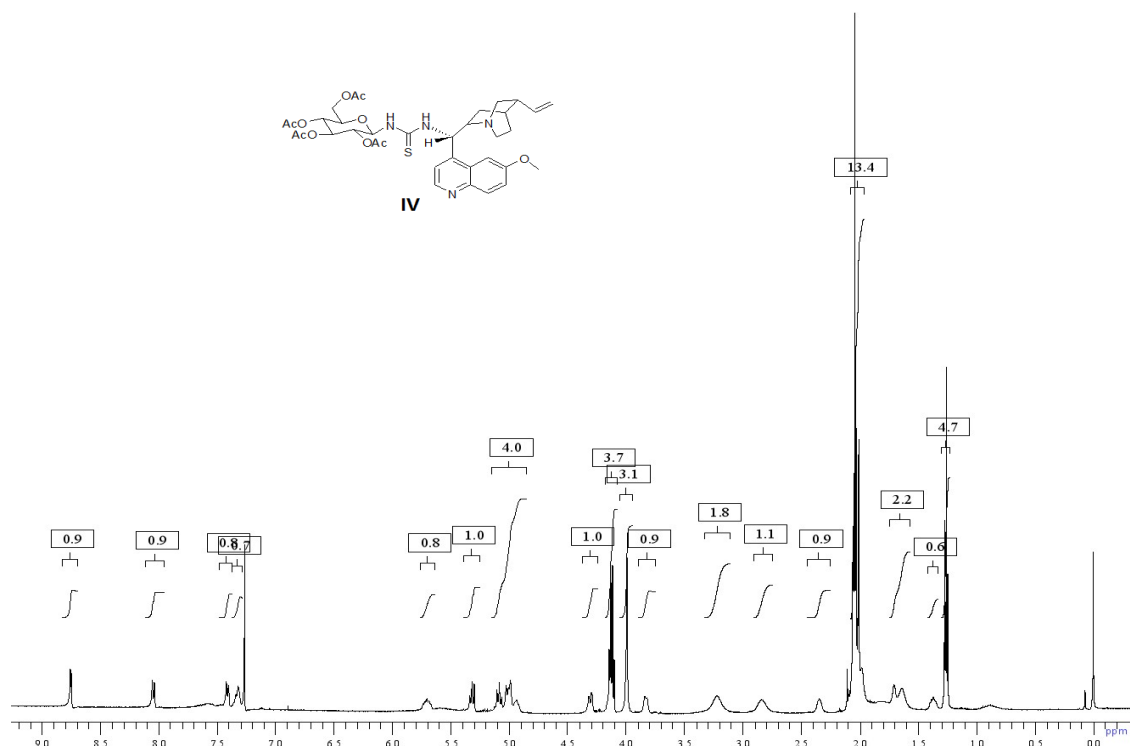
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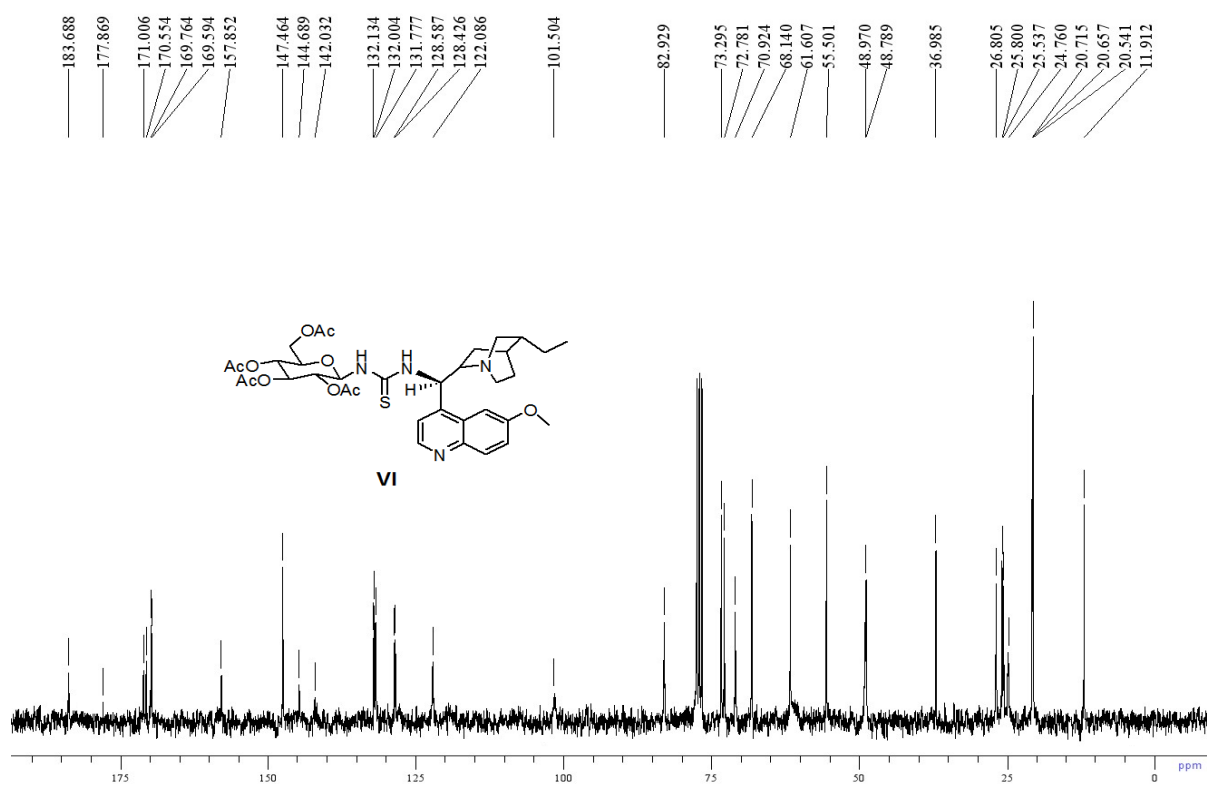
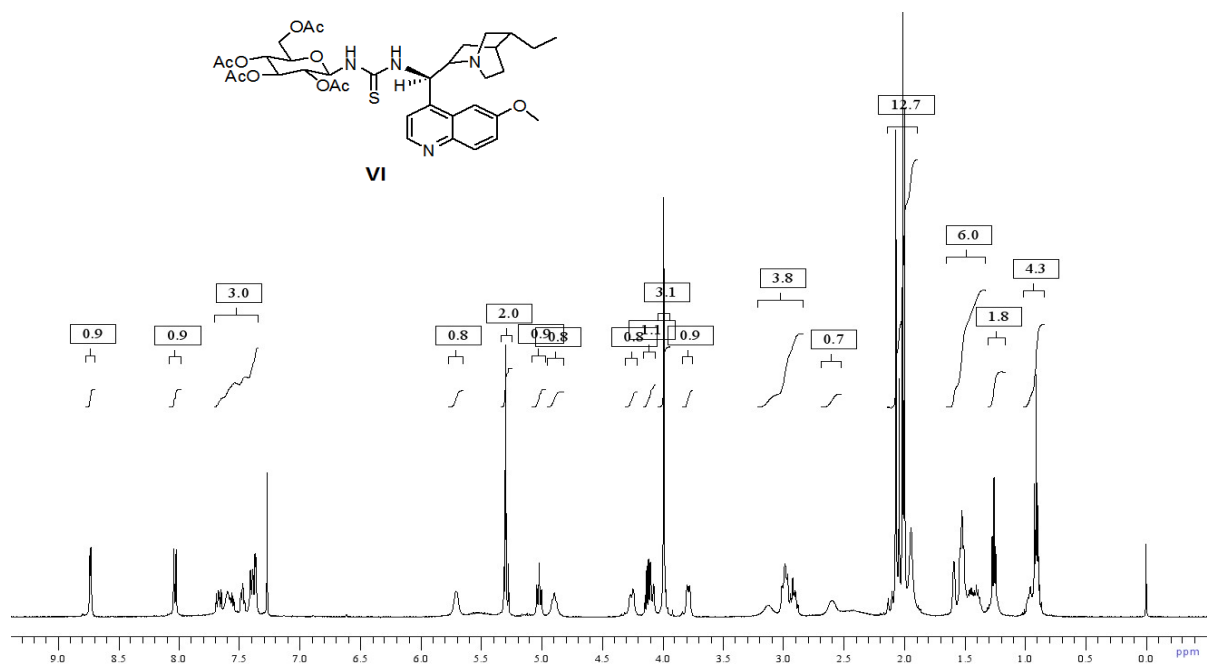
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2. Copy of NMR Spectra of ligands.....	(S3)
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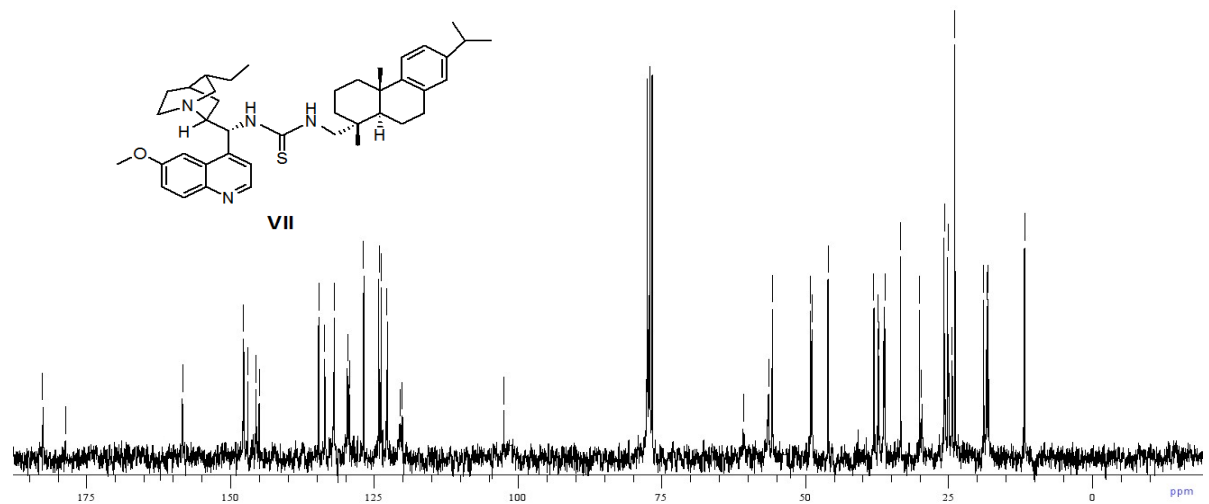
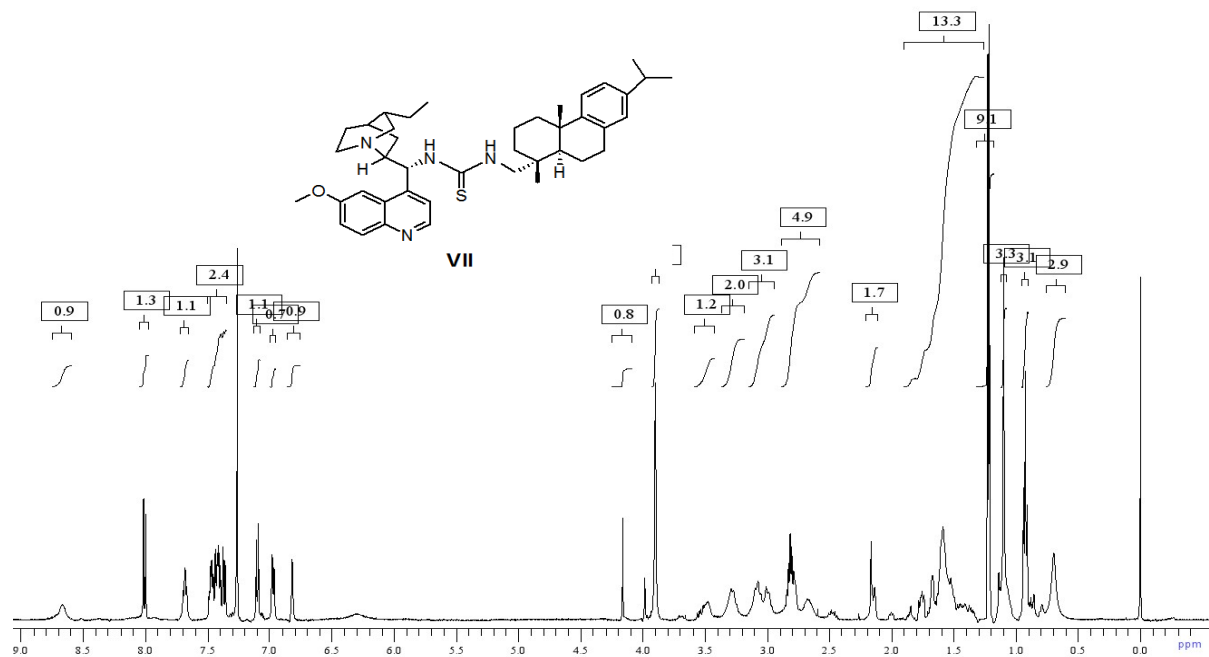
## General Remarks.

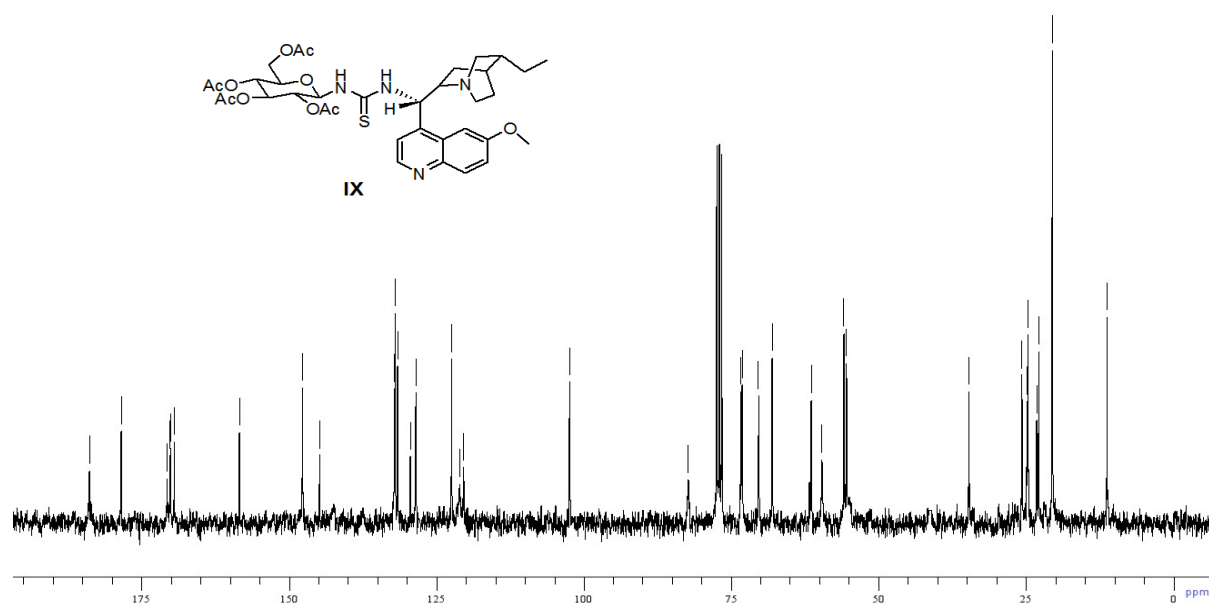
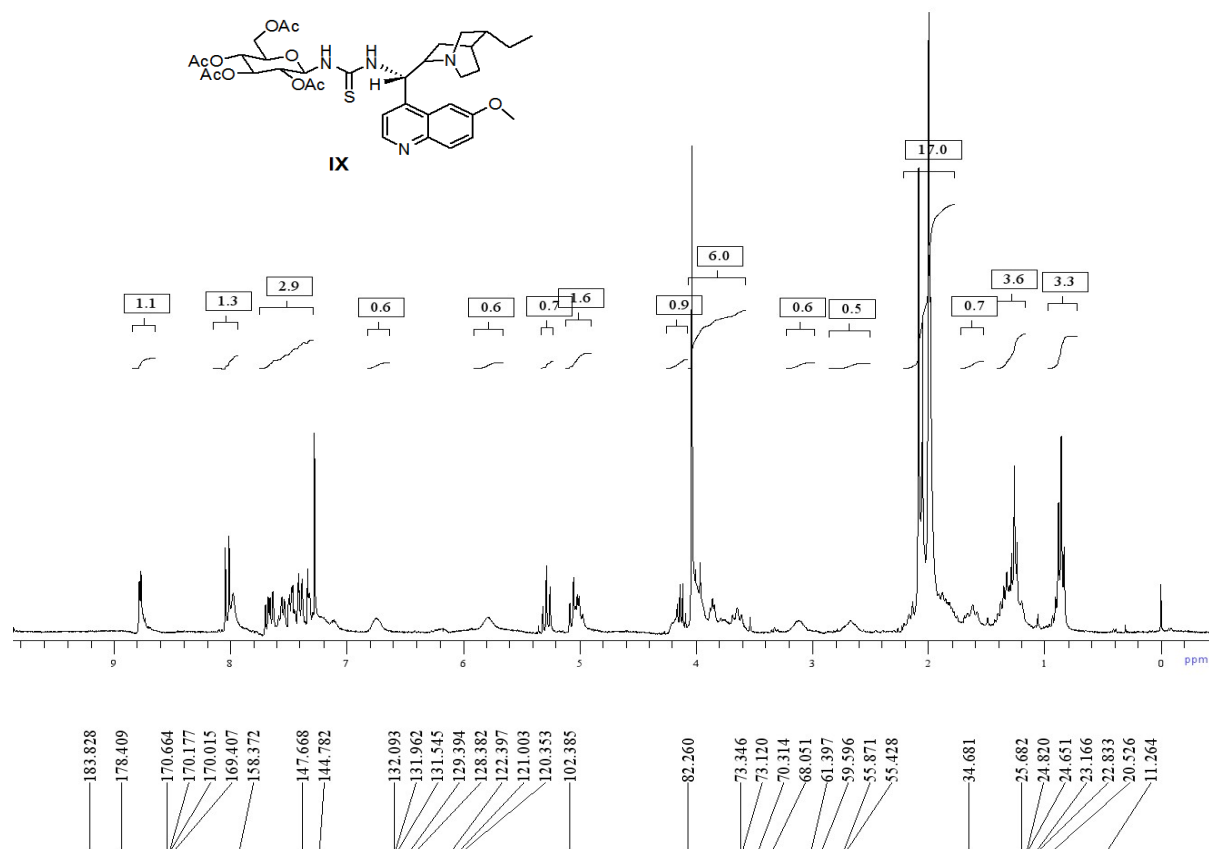
All reactions were carried out under nitrogen atmosphere. Commercial reagents were used as received, unless otherwise stated.  $^1\text{H}$  NMR were recorded on a 300 MHz or 500 MHz spectrometer using  $\text{CDCl}_3$  and  $\text{DMSO-D}_6$  as solvent.  $^{13}\text{C}$  NMR were recorded on 75 MHz and 125 MHz spectrometer using  $\text{CDCl}_3$  and  $\text{DMSO-D}_6$ . TMS was used as reference for  $^1\text{H}$  NMR analysis and  $\text{CDCl}_3$  used as reference for  $^{13}\text{C}$  NMR analysis. All the compounds were purified by column chromatography on silica gel (60-120 mesh) using hexane - ethyl acetate mixtures as eluent. Mass analysis was carried out using ESI mass spectrometer. Infrared (IR) spectra were recorded on a FT-IR spectrometer. Optical rotations were measured using a Rudolph (Digipol 781 M6U) polarimeter. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiracel OJ-H and AS-H columns. The absolute configurations of new compounds were determined by analogy.

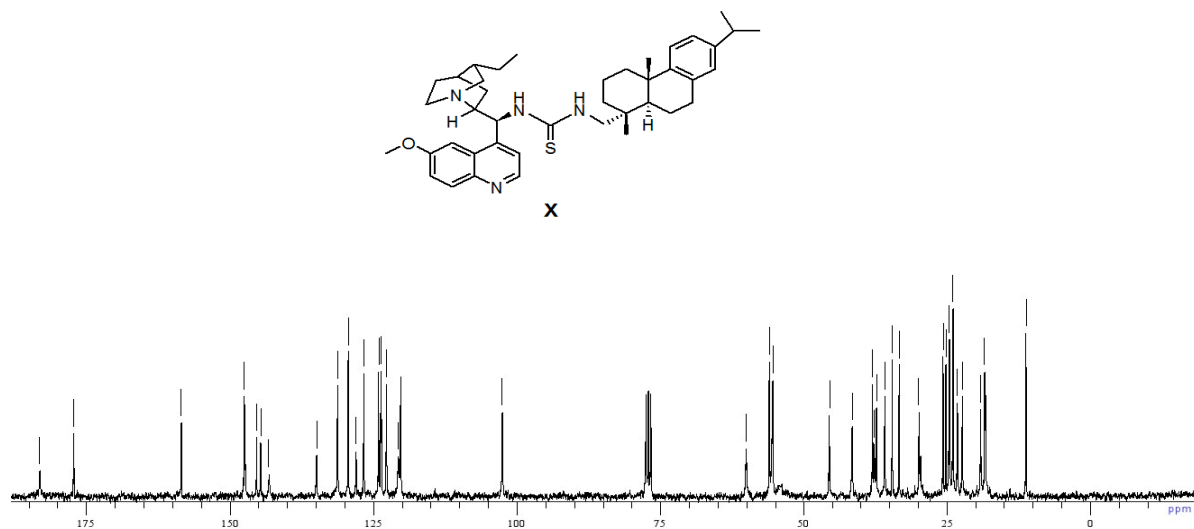
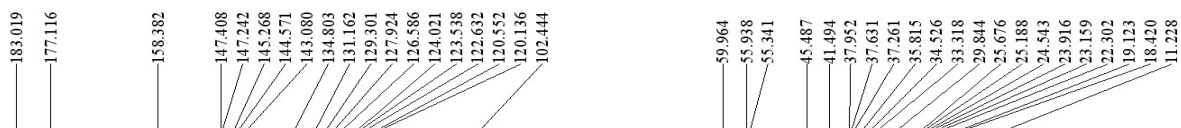
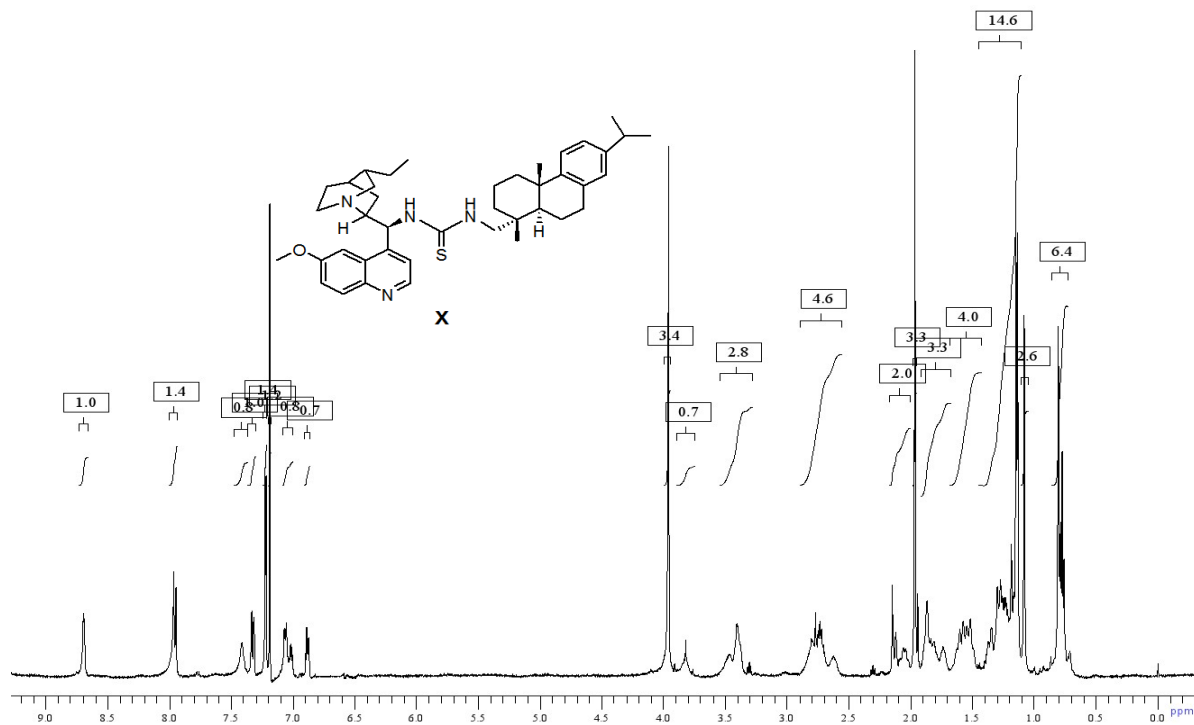




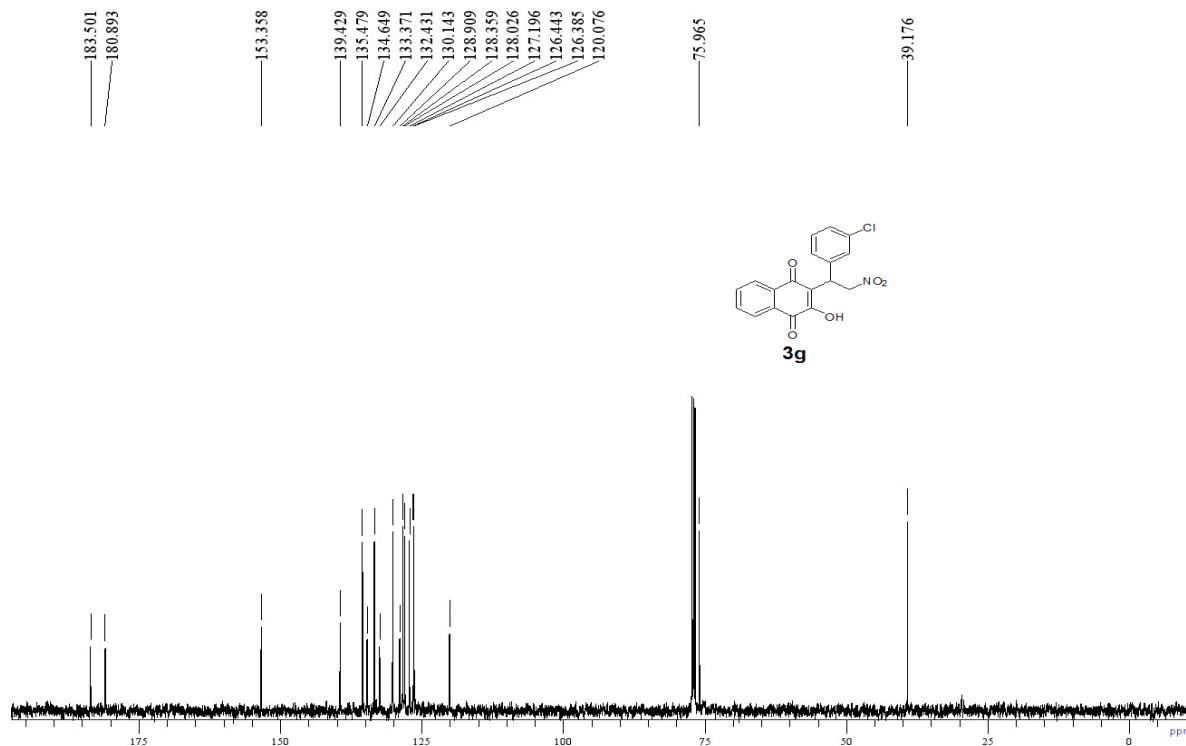
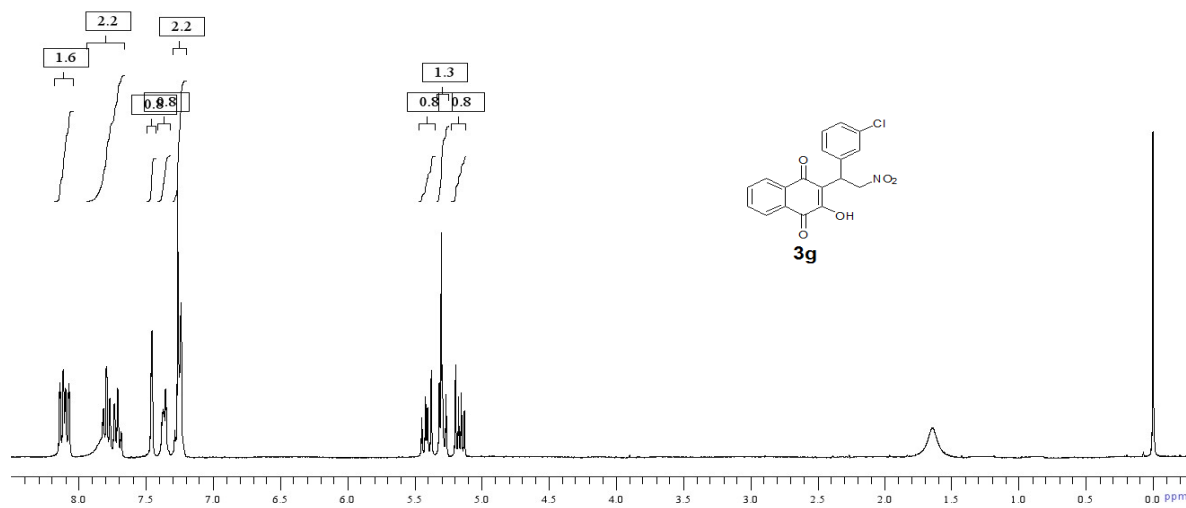


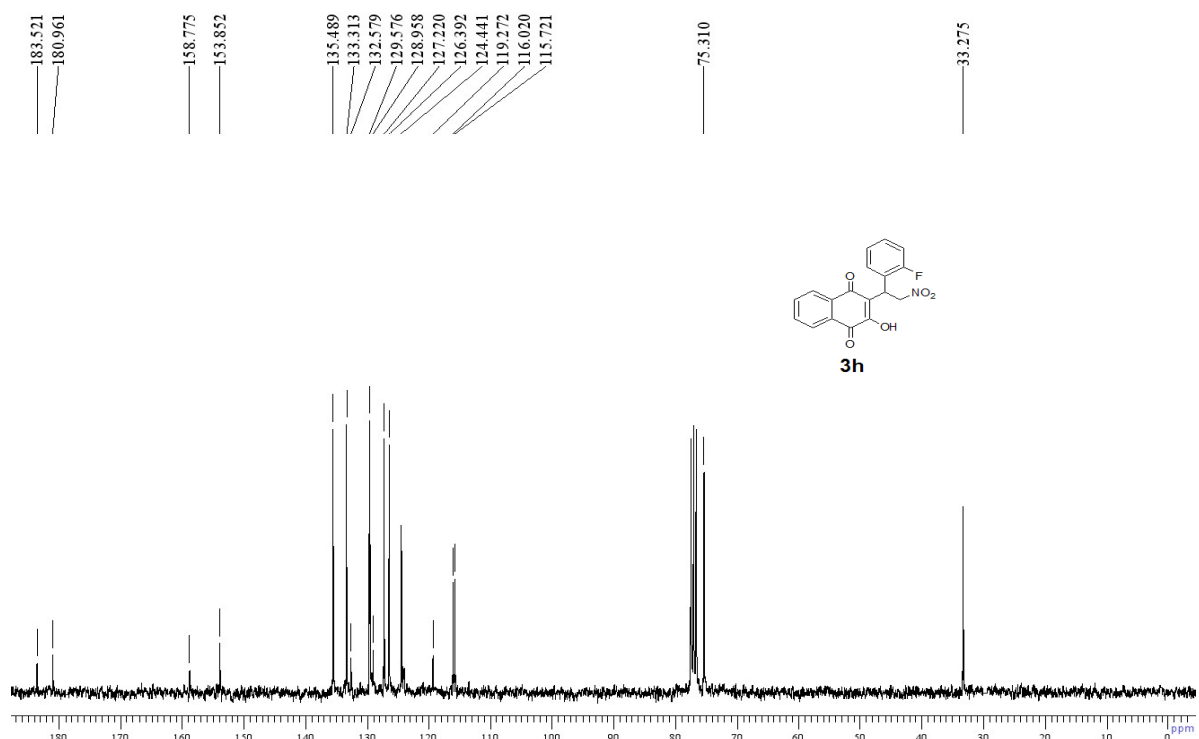
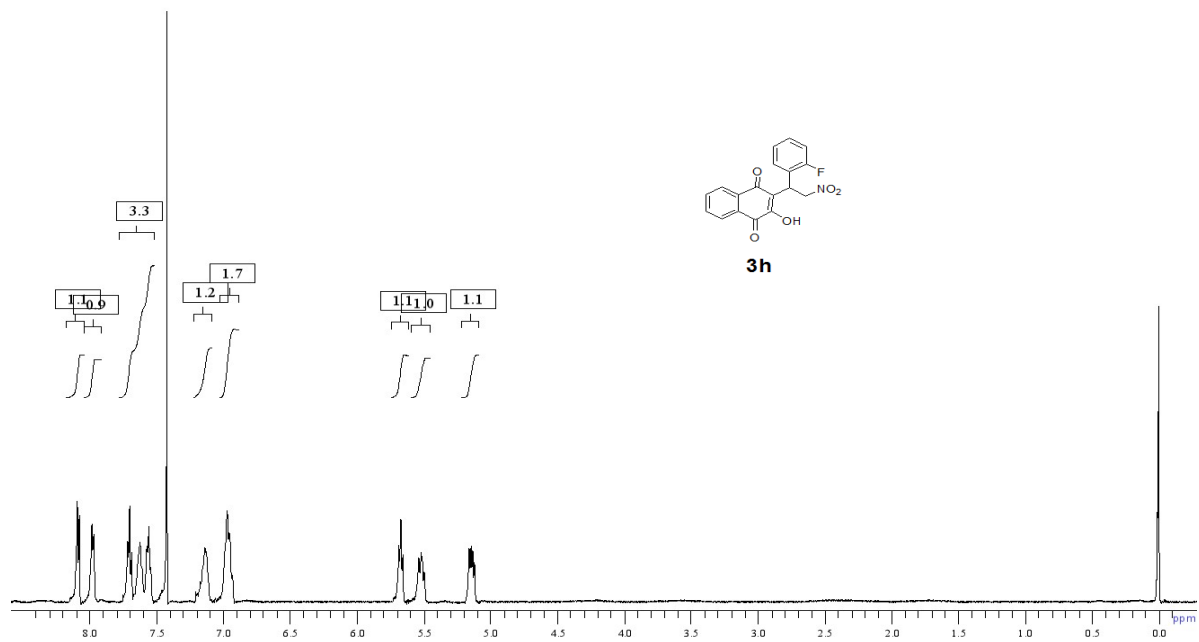


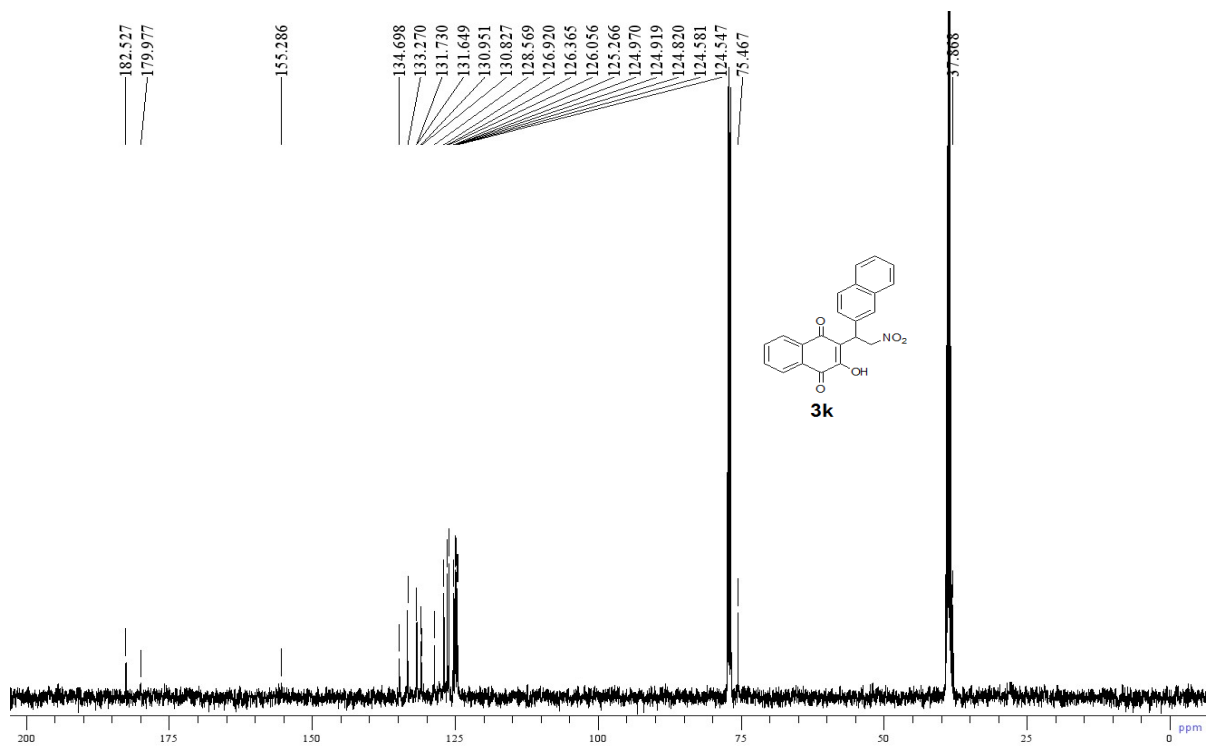
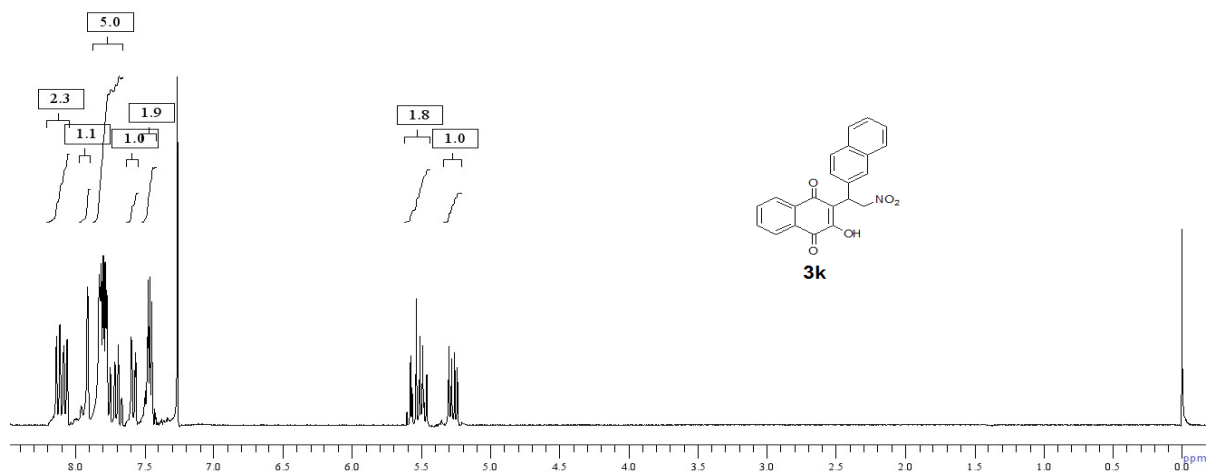


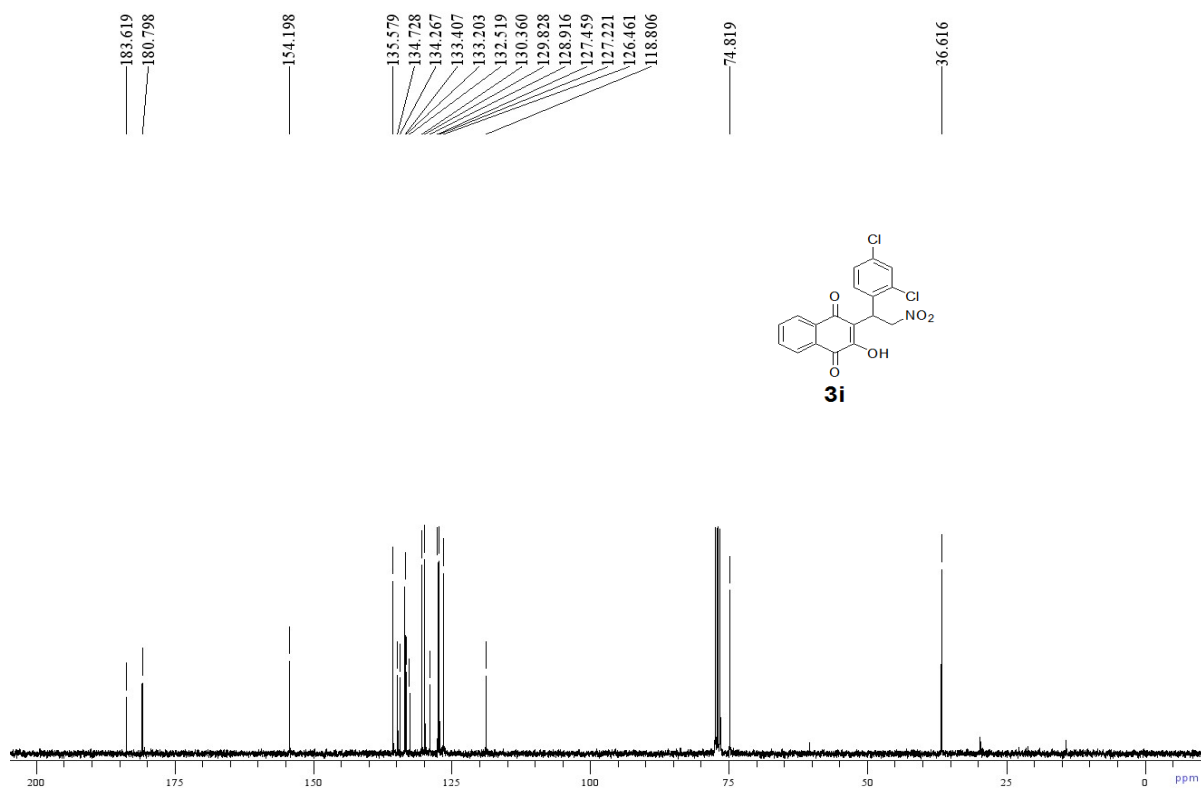
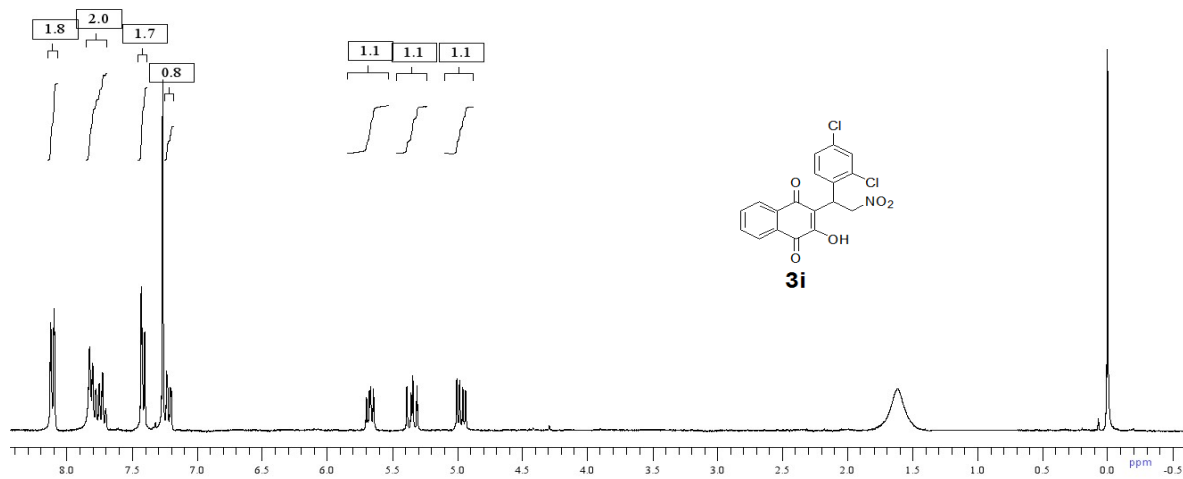


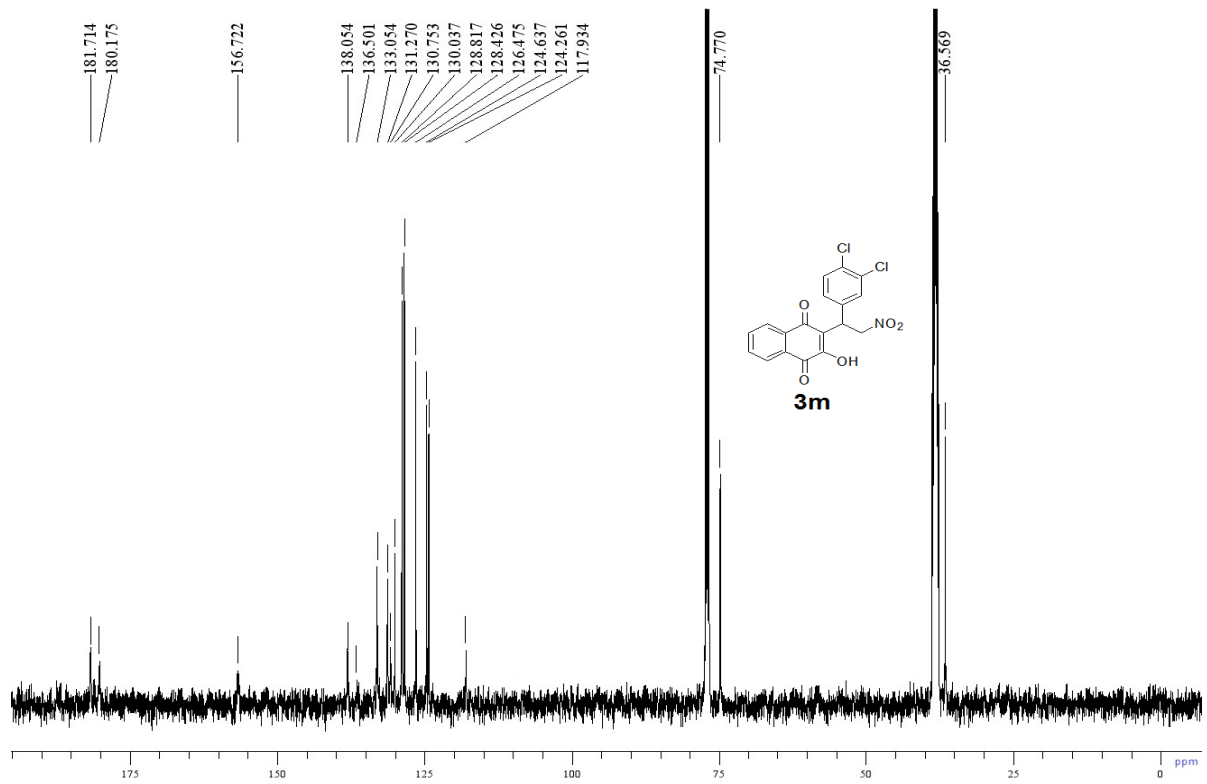
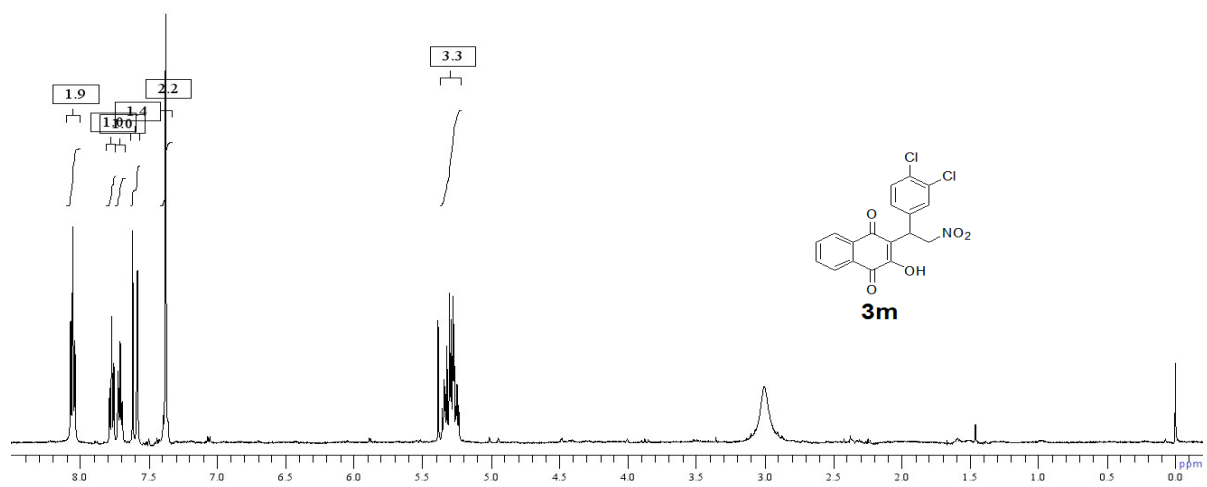


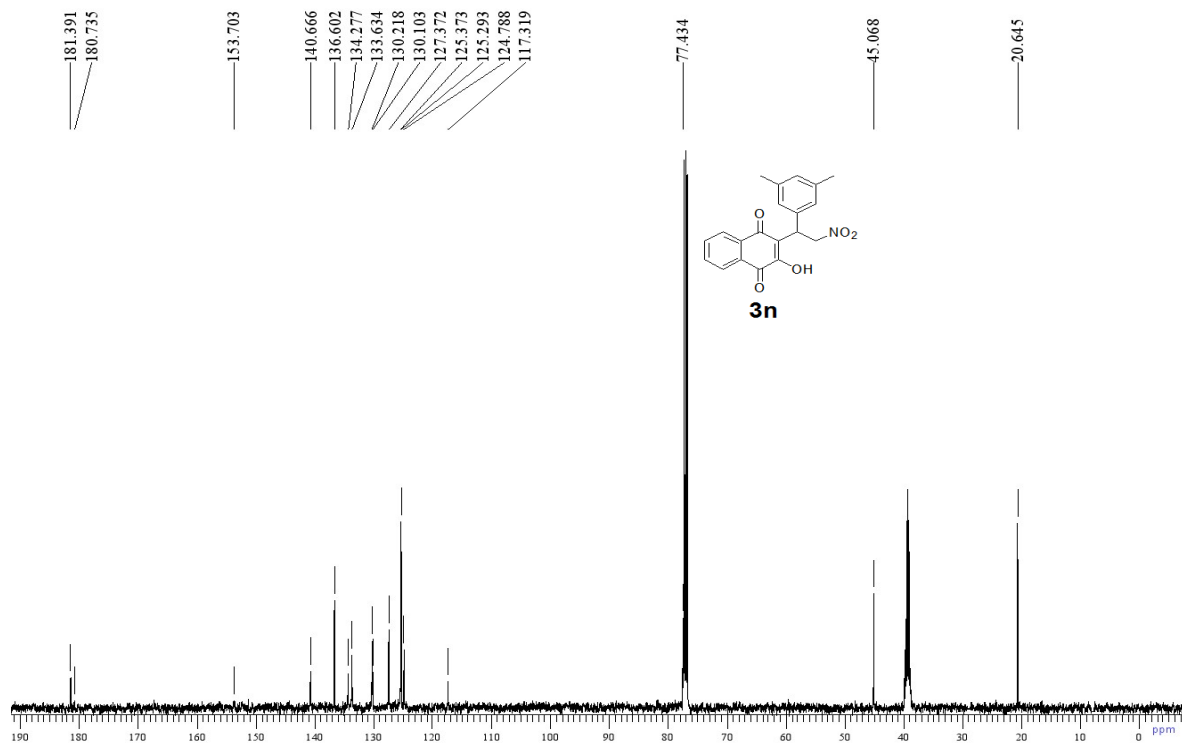
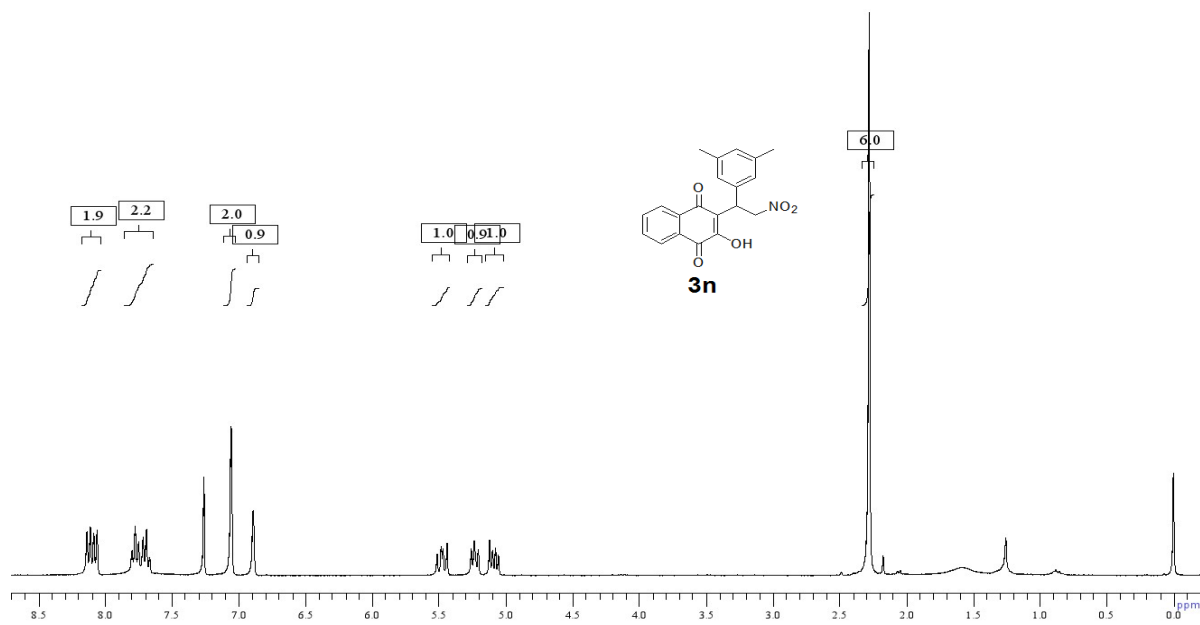


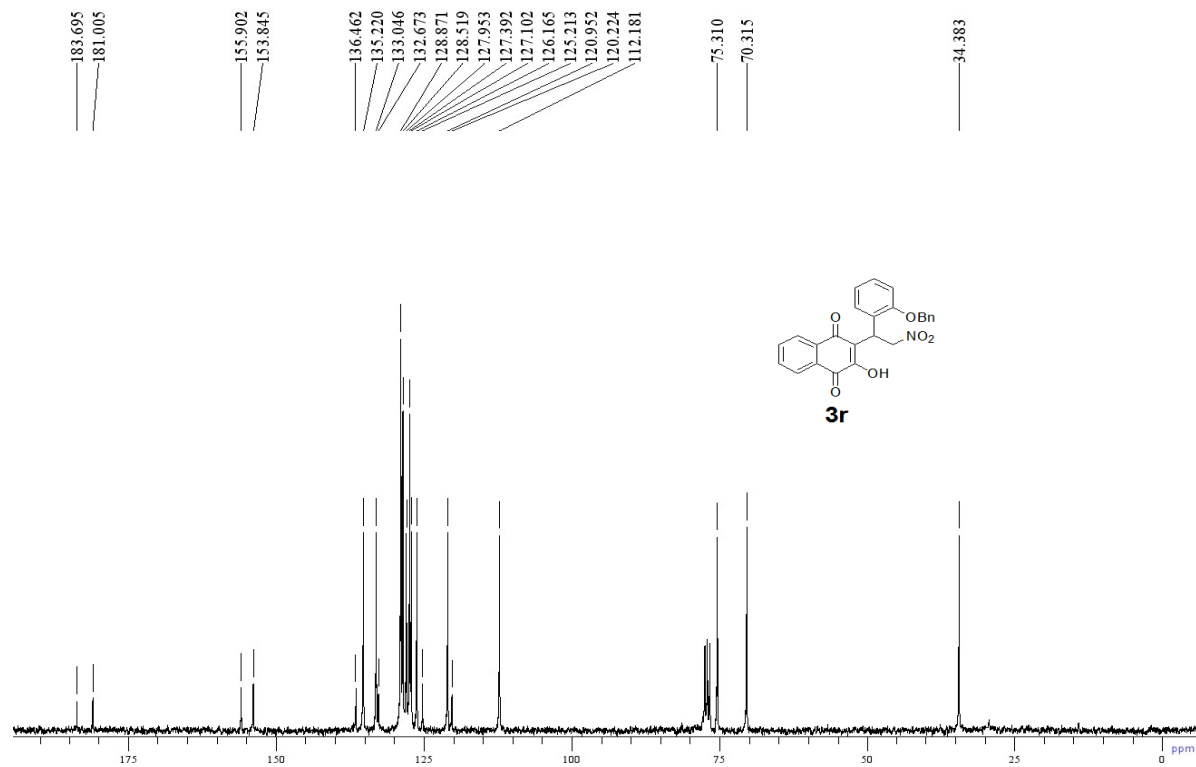
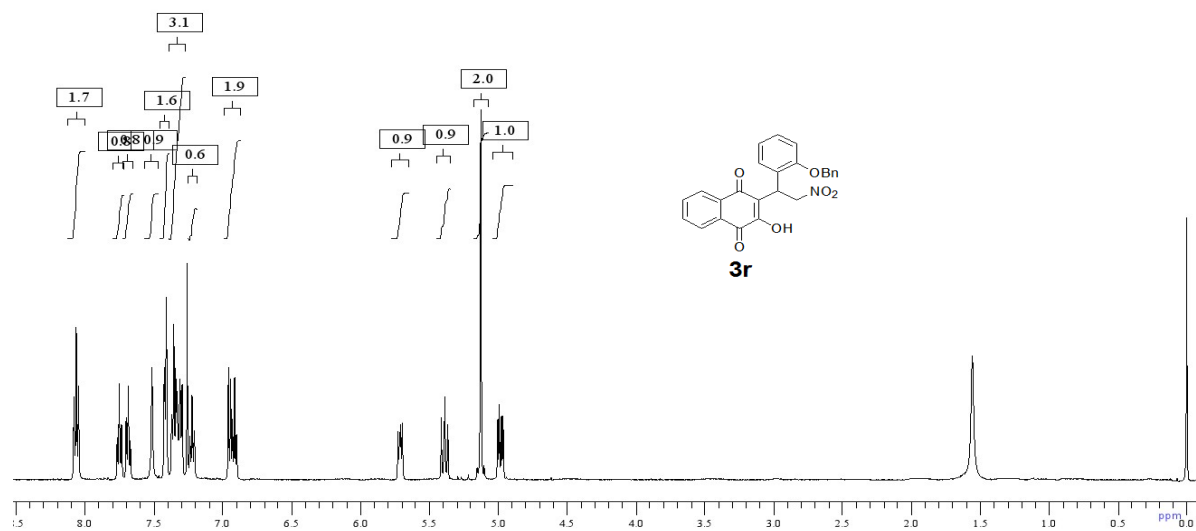




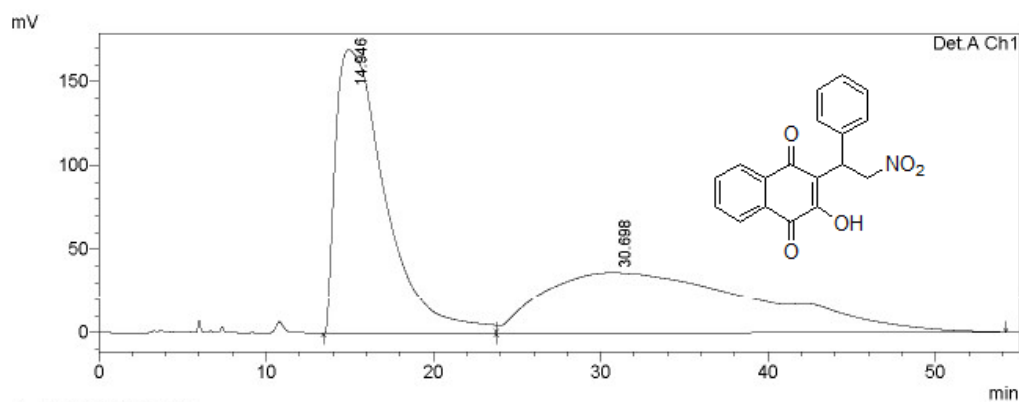








**2-hydroxy-3-(2-nitro-1-phenylethyl) naphthalene-1,4-dione(3a)**

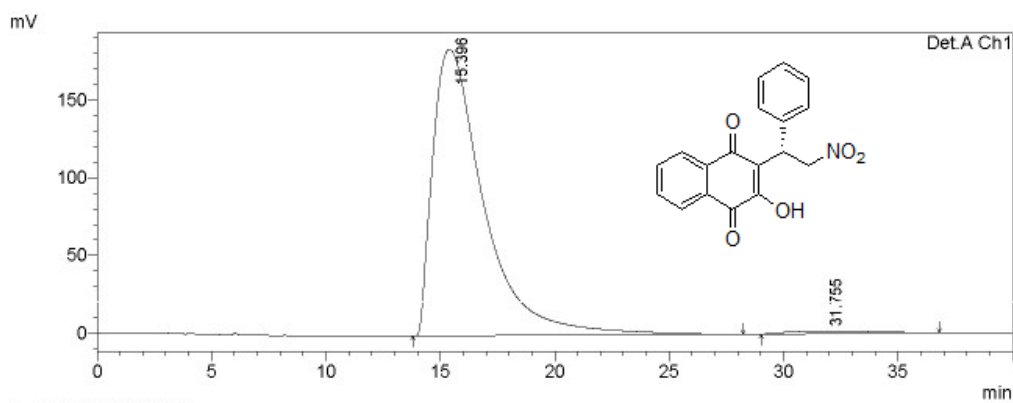


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.946	34884086	169162	51.659	82.414
2	30.698	32643614	36096	48.341	17.586
Total		67527700	205259	100.000	100.000



1 Det.A Ch1/254nm

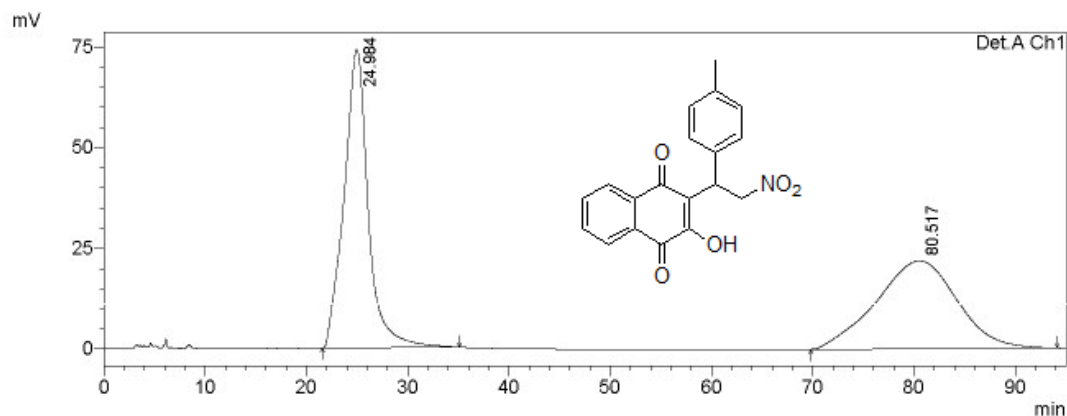
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.396	28810127	184378	98.465	99.130
2	31.755	449020	1618	1.535	0.870
Total		29259147	185996	100.000	100.000



### 2-hydroxy-3-(2-nitro-1-p-tolyloethyl)naphthalene-1,4-dione(3b)

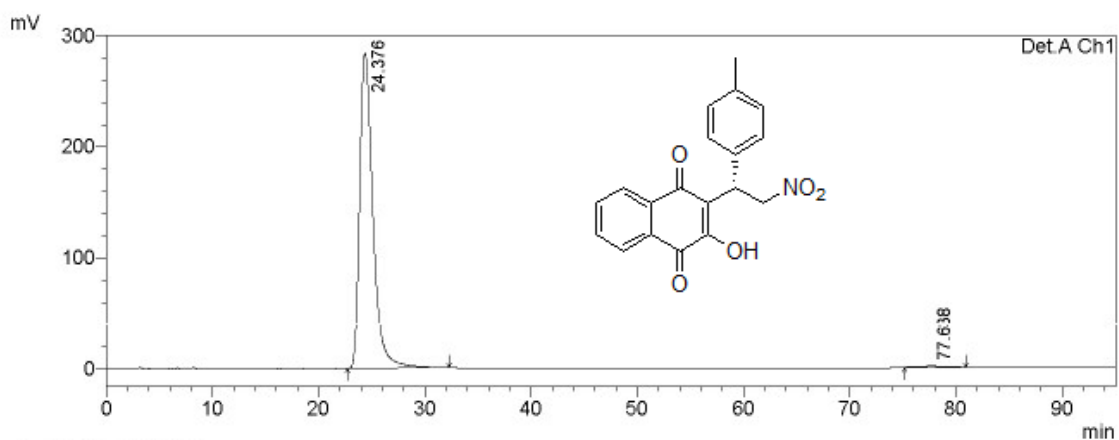


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.984	12328123	74165	50.245	77.113
2	80.517	12208035	22012	49.755	22.887
Total		24536159	96177	100.000	100.000



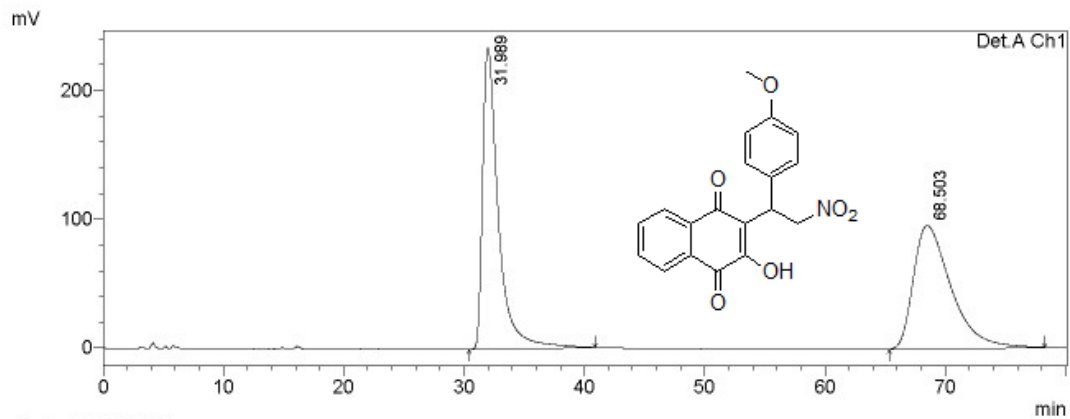
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.376	24601812	283821	99.200	99.673
2	77.638	198491	931	0.800	0.327
Total		24800303	284752	100.000	100.000

### 2-hydroxy-3-(1-(4-methoxyphenyl)-2-nitroethyl)naphthalene-1,4-dione(3c)

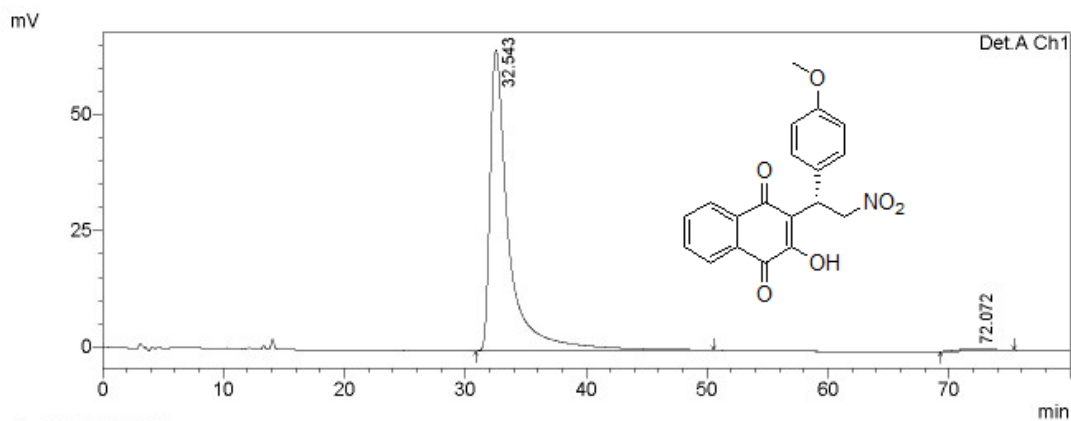


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.989	21233825	233757	50.566	70.965
2	68.503	20758744	95639	49.434	29.035
Total		41992569	329396	100.000	100.000



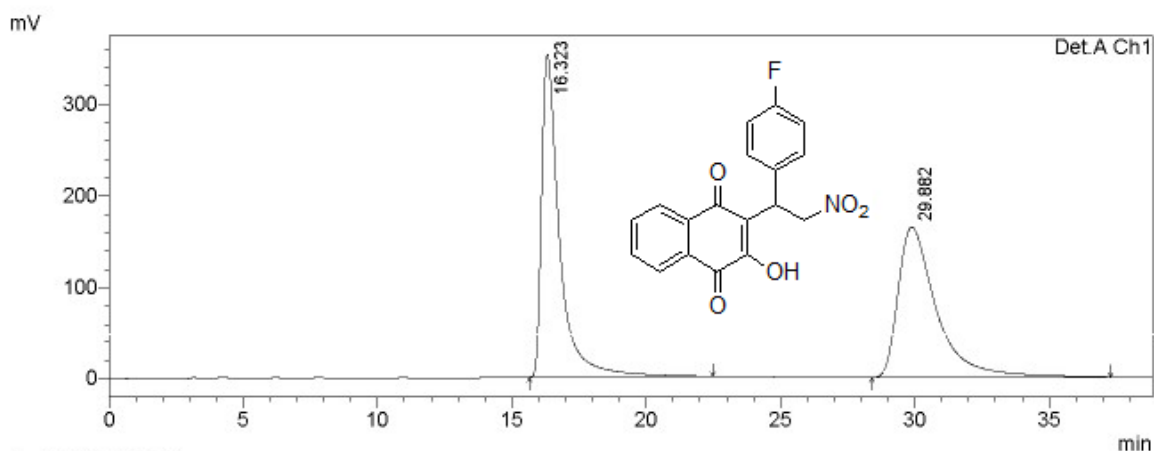
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.543	6996264	64720	98.663	99.285
2	72.072	94789	466	1.337	0.715
Total		7091053	65186	100.000	100.000

### 2-(1-(4-fluorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3d)

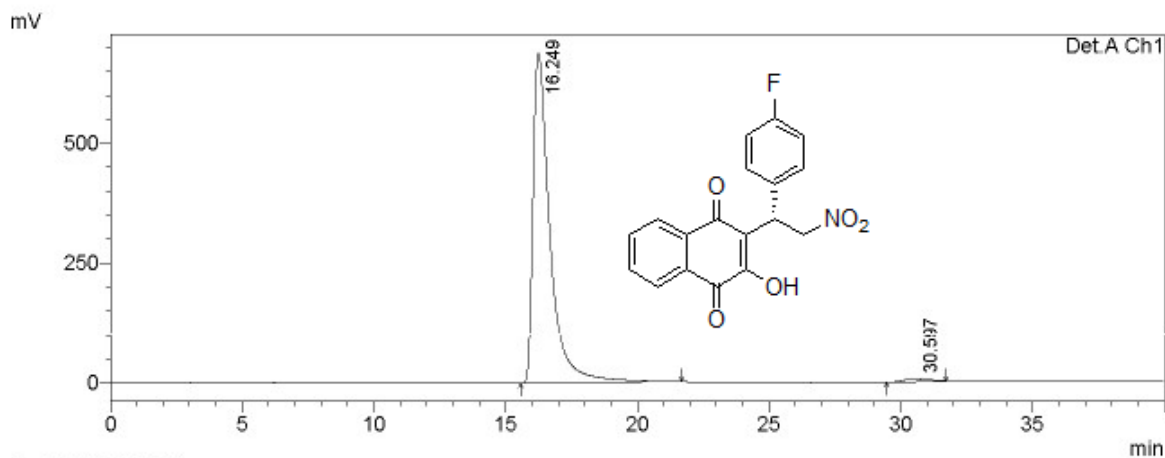


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.323	16464943	352586	50.140	68.160
2	29.882	16373299	164706	49.860	31.840
Total		32838241	517293	100.000	100.000



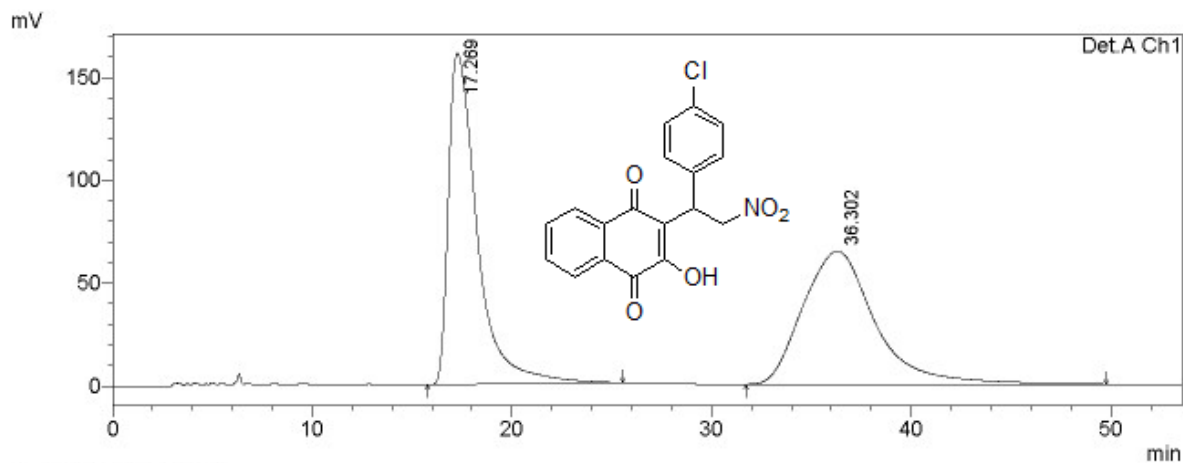
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.249	30842933	687657	98.628	99.155
2	30.597	429011	5862	1.372	0.845
Total		31271945	693519	100.000	100.000

## 2-(1-(4-chlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3e)

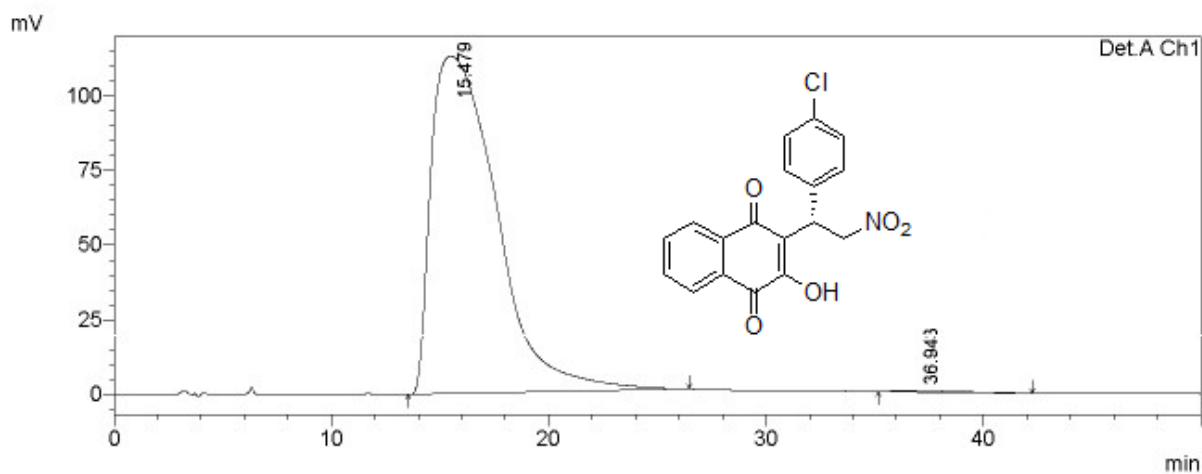


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.269	16223474	161149	49.946	71.332
2	36.302	16258822	64766	50.054	28.668
Total		32482296	225915	100.000	100.000



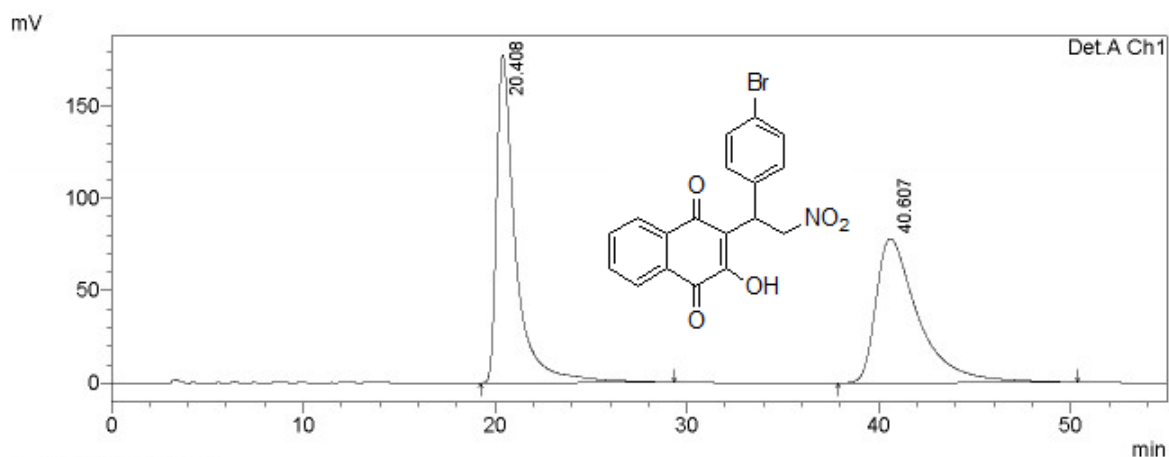
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.479	23828274	113209	99.689	99.647
2	36.943	74275	401	0.311	0.353
Total		23902549	113610	100.000	100.000

### 2-(1-(4-bromophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3f)

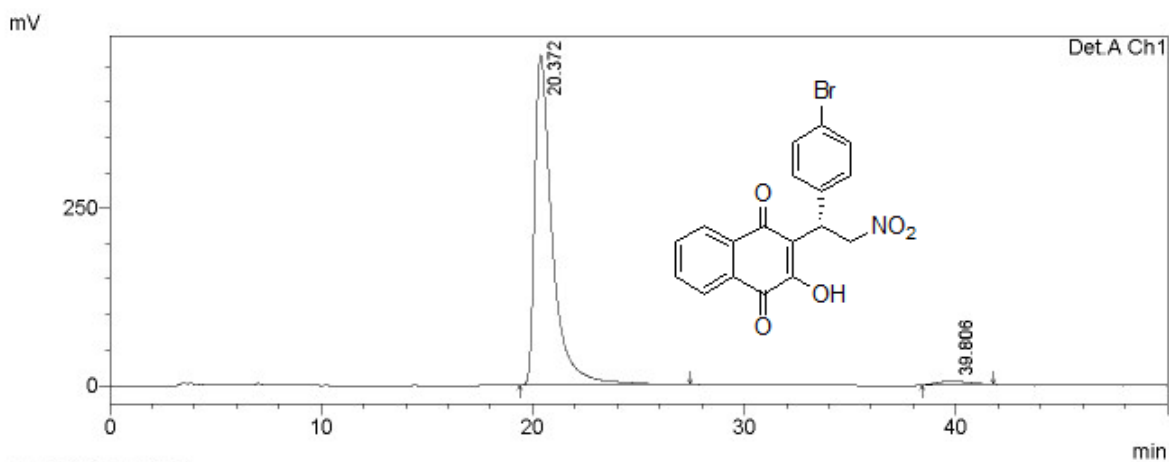


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.408	12195114	177723	50.534	69.502
2	40.607	11937353	77984	49.466	30.498
Total		24132467	255707	100.000	100.000



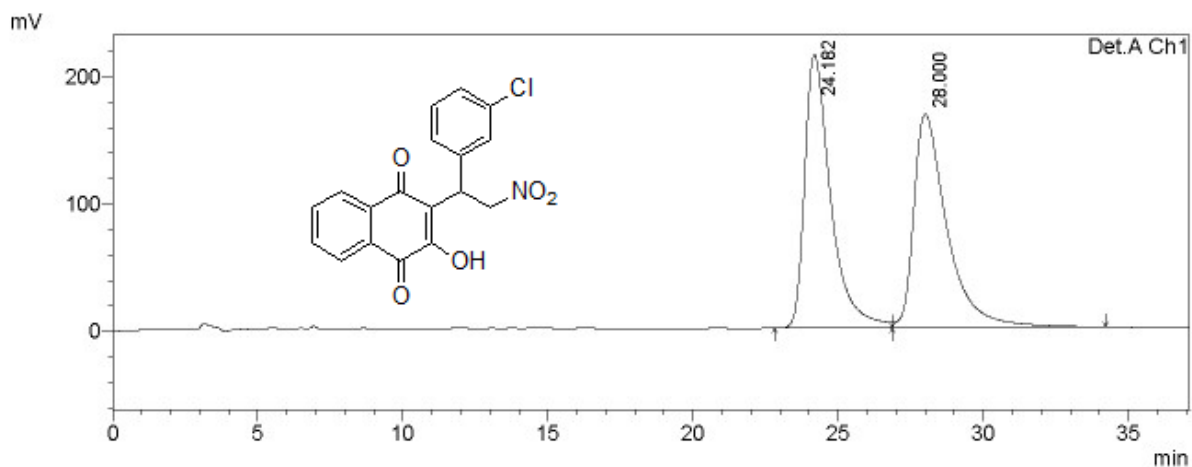
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.372	26932963	465995	98.049	98.943
2	39.806	535931	4980	1.951	1.057
Total		27468894	470975	100.000	100.000

### 2-(1-(3-chlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3g)

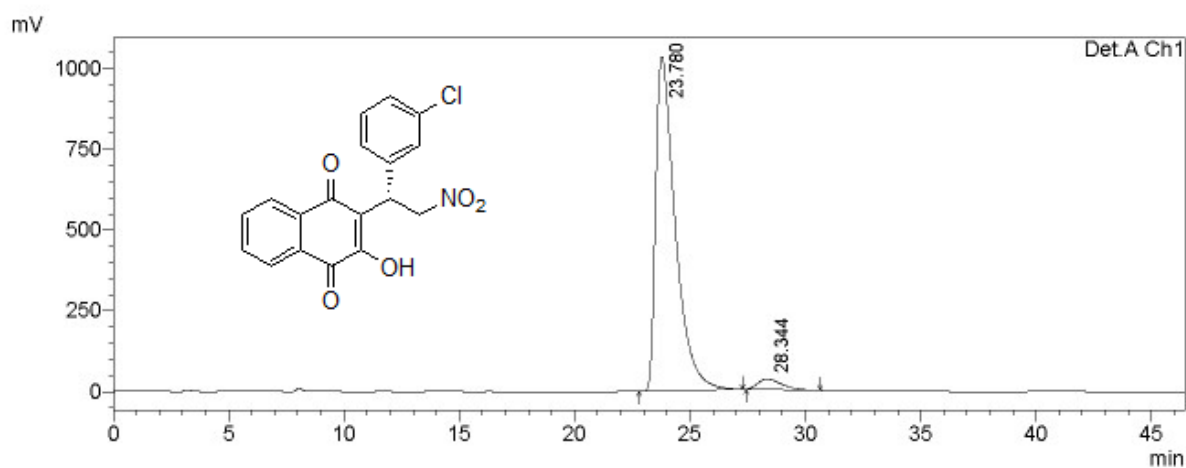


1 Det.A Ch1/254nm

PeakTable

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



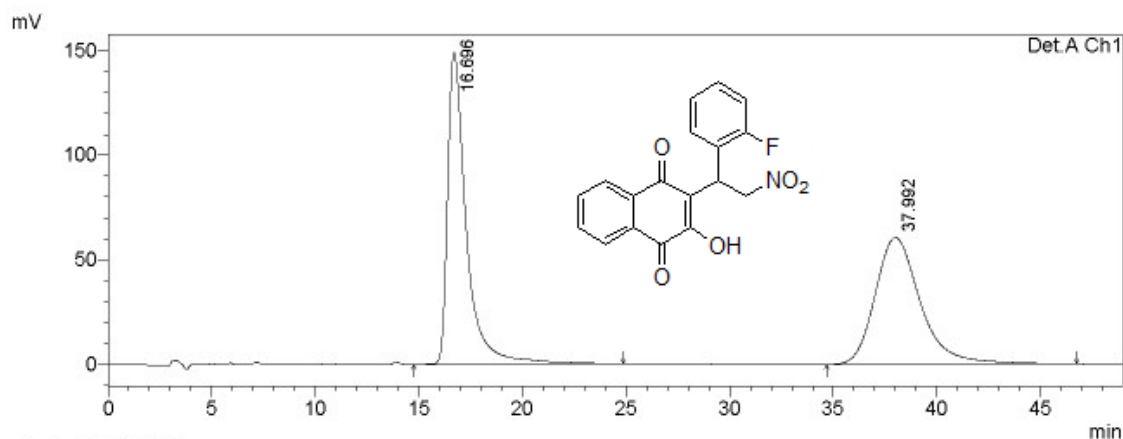
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.780	61267441	1035216	96.324	96.957
2	28.344	2338349	32490	3.676	3.043
Total		63605790	1067707	100.000	100.000

### 2-(1-(2-fluorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3h)

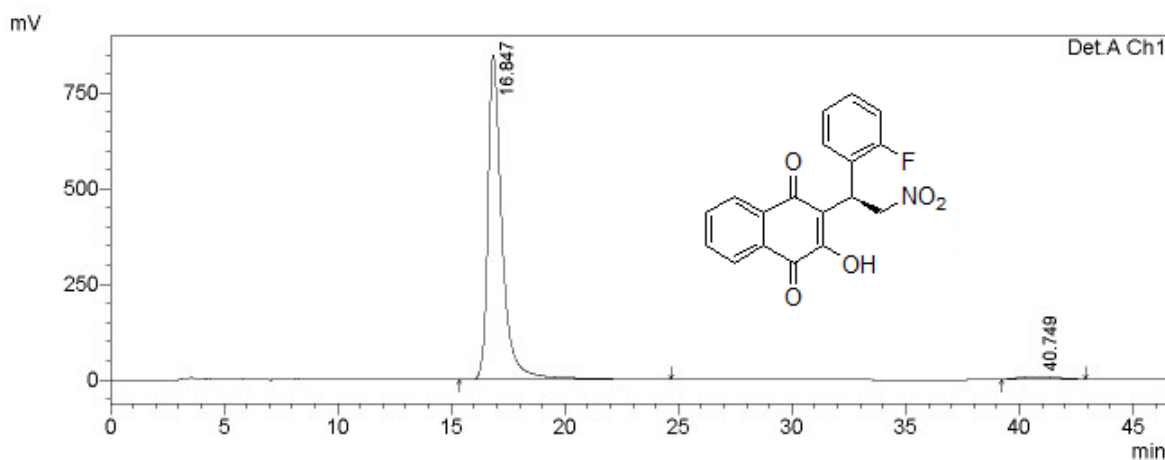


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.696	9389216	148939	50.494	71.166
2	37.992	9205430	60346	49.506	28.834
Total		18594646	209285	100.000	100.000



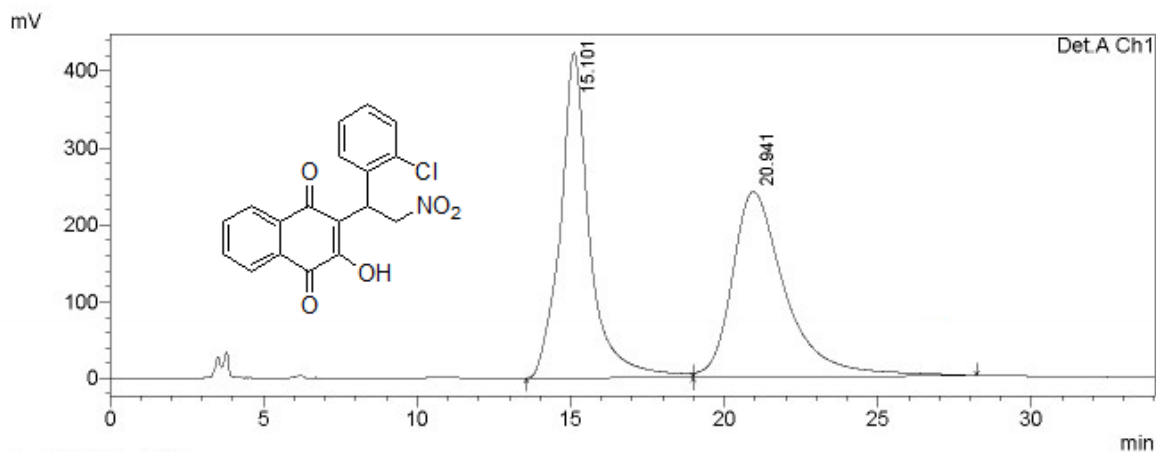
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.847	36703377	849391	97.857	99.172
2	40.749	803600	7092	2.143	0.828
Total		37506976	856483	100.000	100.000

## 2-(1-(2-chlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3i)

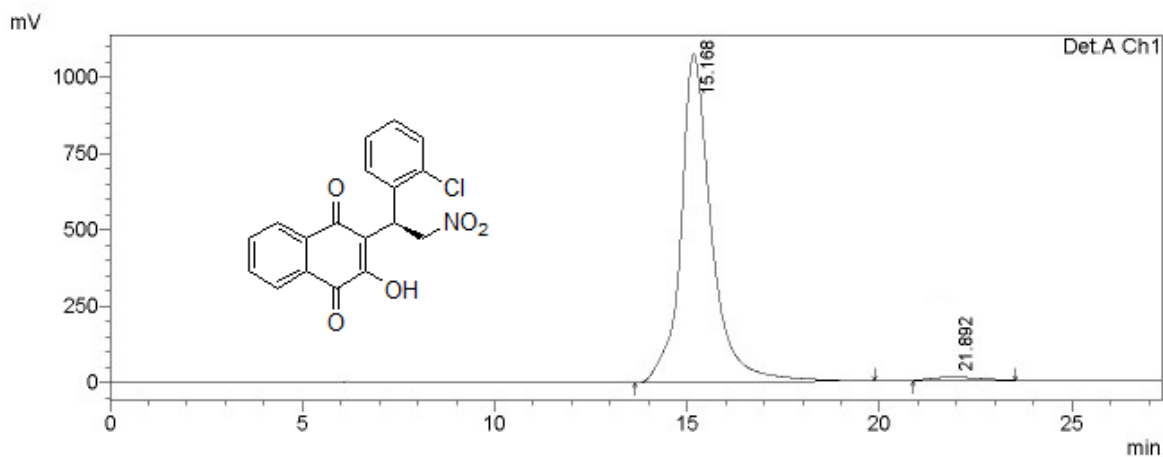


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.101	28158641	422664	49.244	63.684
2	20.941	29022822	241030	50.756	36.316
Total		57181464	663694	100.000	100.000



1 Det.A Ch1/254nm

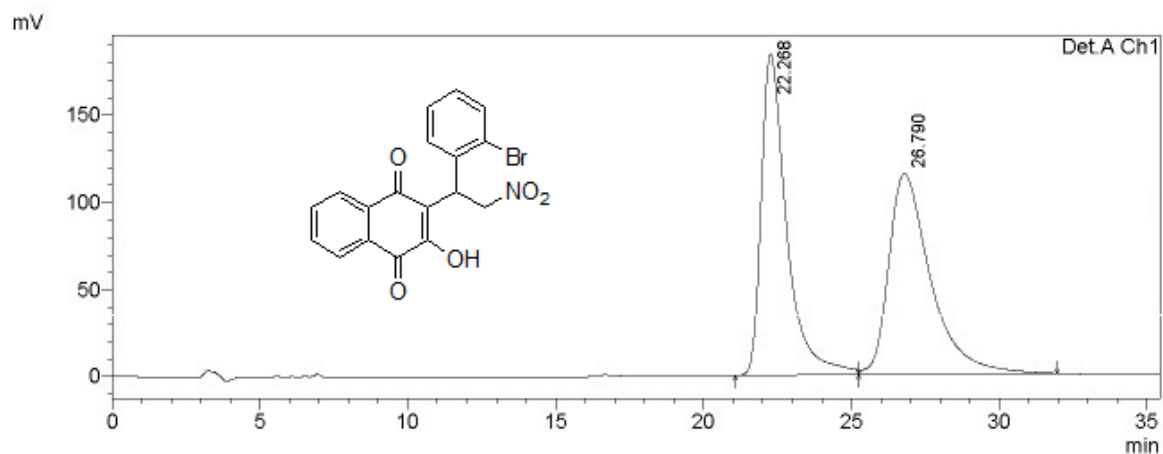
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.168	59692306	1075643	98.482	99.039
2	21.892	919995	10441	1.518	0.961
Total		60612301	1086085	100.000	100.000



### 2-(1-(2-bromophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3j)

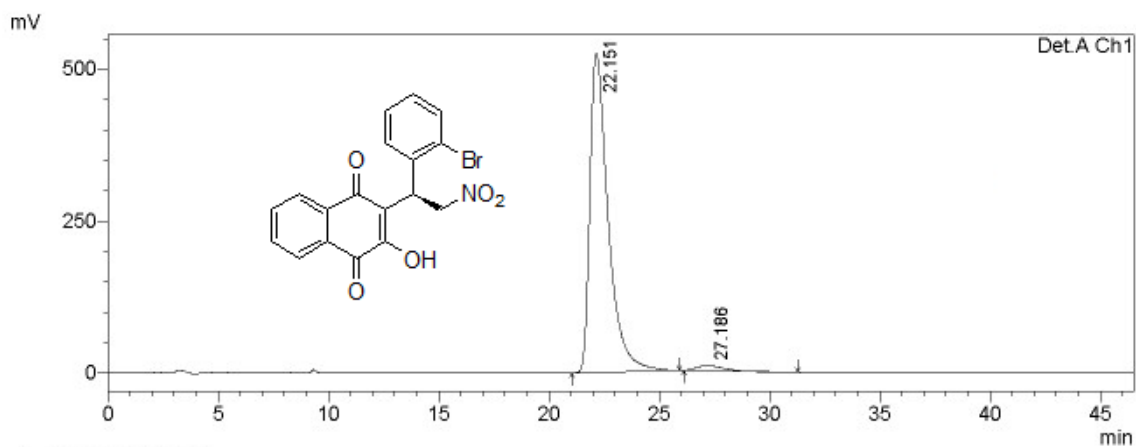


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.268	11038178	184512	49.188	61.518
2	26.790	11402402	115422	50.812	38.482
Total		22440580	299933	100.000	100.000



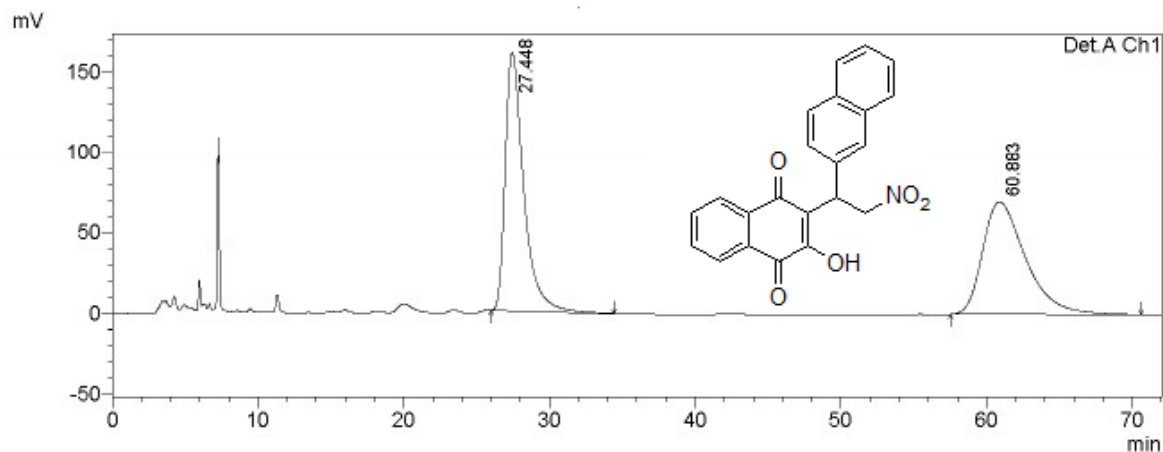
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.151	30233880	525671	97.637	98.389
2	27.186	731730	8605	2.363	1.611
Total		30965609	534276	100.000	100.000

### 2-hydroxy-3-(1-(naphthalen-2-yl)-2-nitroethyl)naphthalene-1,4-dione(3k)

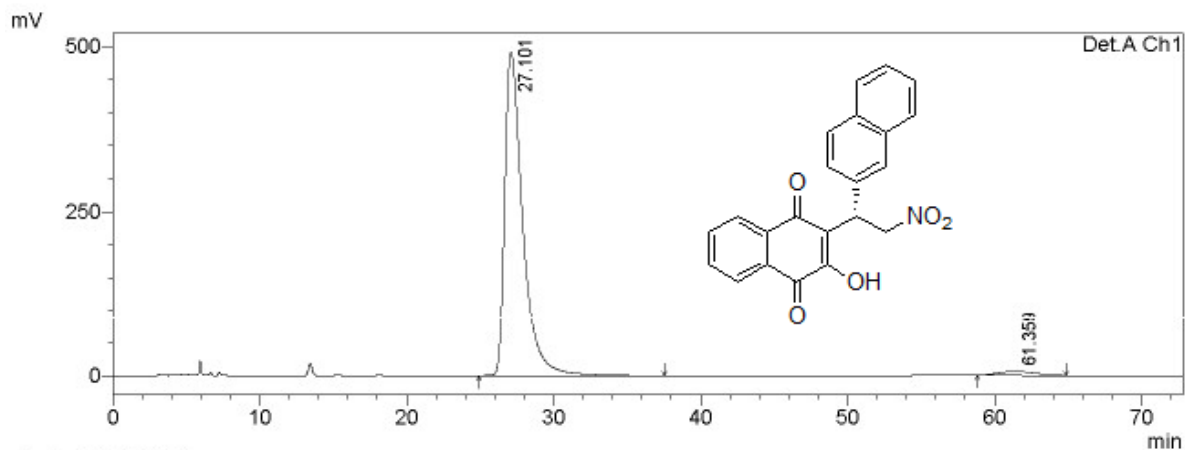


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.448	14076910	160267	49.592	69.673
2	60.883	14308276	69759	50.408	30.327
Total		28385186	230026	100.000	100.000



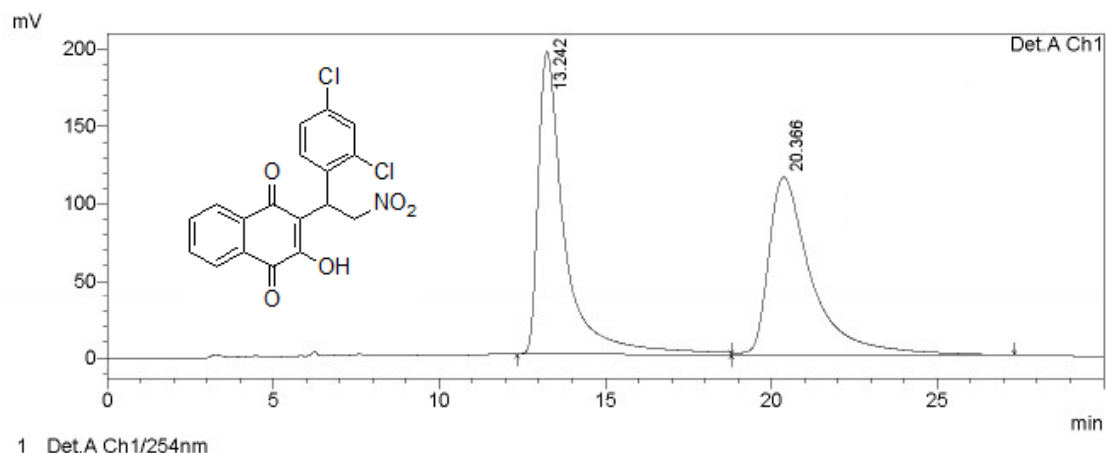
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.101	42089913	492512	97.499	98.784
2	61.359	1079889	6064	2.501	1.216
Total		43169802	498576	100.000	100.000

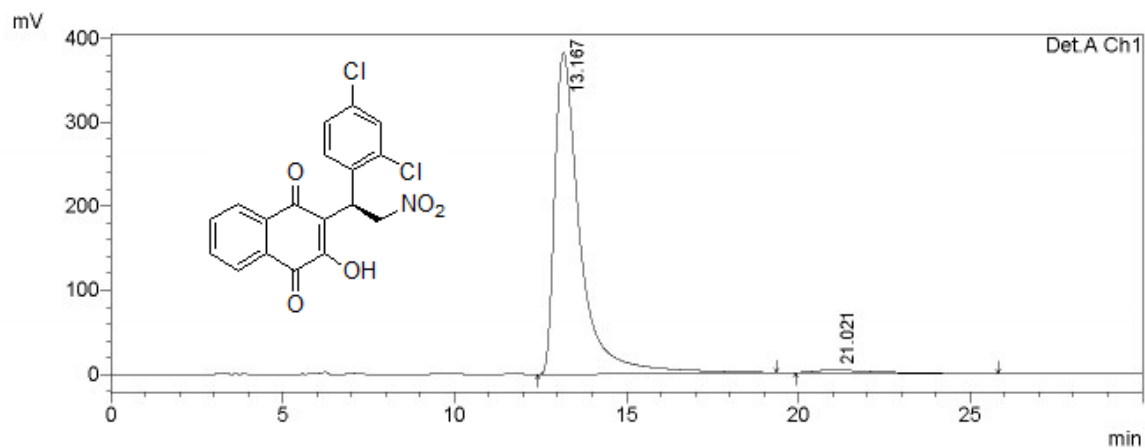
## 2-(1-(2,4-dichlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3I)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.242	10801413	196114	51.047	62.972
2	20.366	10358254	115318	48.953	37.028
Total		21159667	311433	100.000	100.000

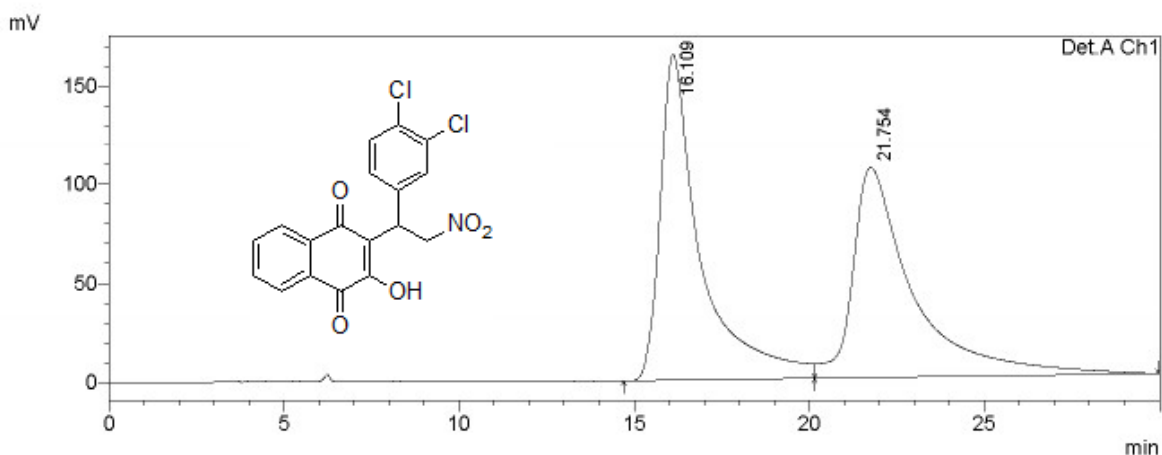


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.167	19662800	382901	98.011	99.136
2	21.021	399066	3337	1.989	0.864
Total		20061866	386238	100.000	100.000

## 2-(1-(3,4-dichlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3m)

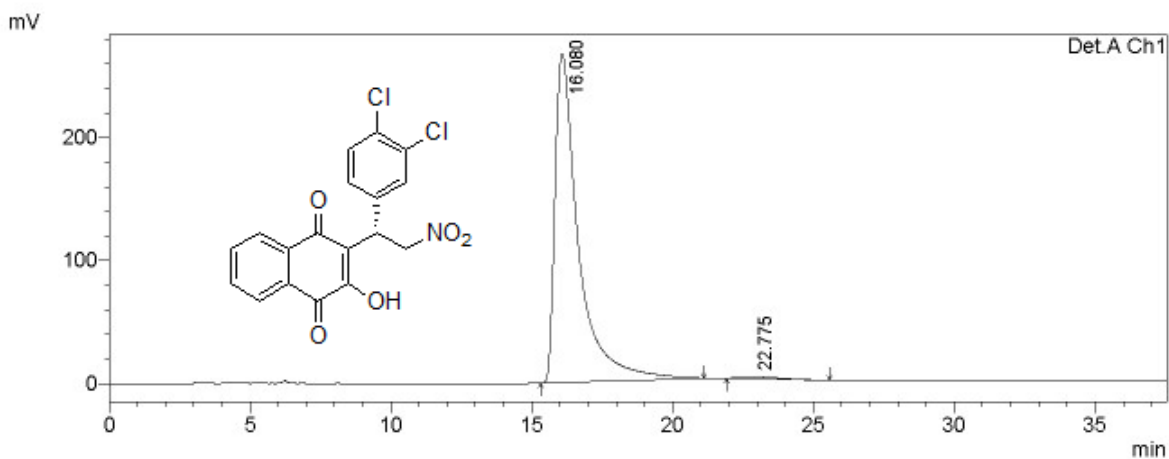


1 Det.A Ch1/254nm

PeakTable

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



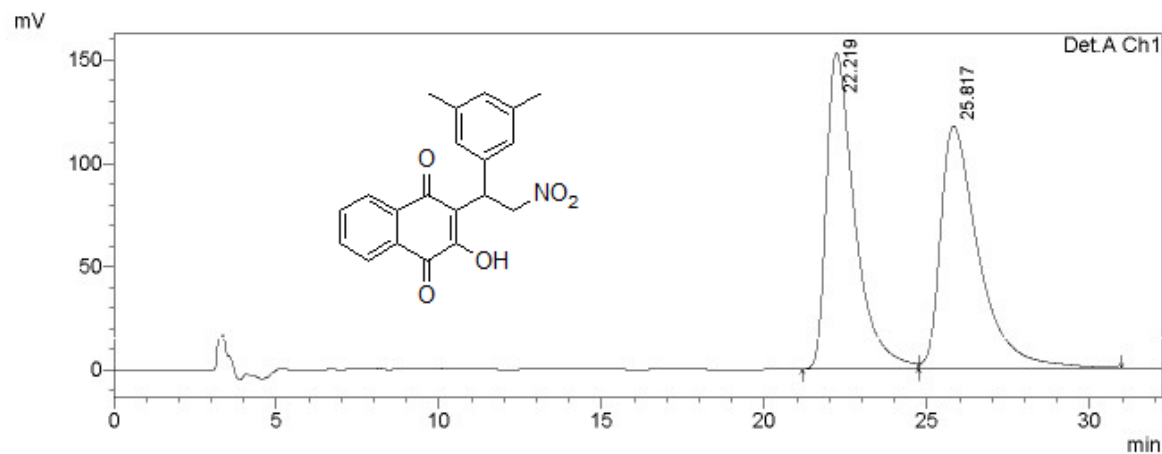
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.080	15568186	267697	98.818	99.319
2	22.775	186138	1834	1.182	0.681
Total		15754324	269531	100.000	100.000

## 2-(1-(3,5-dimethylphenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3n)

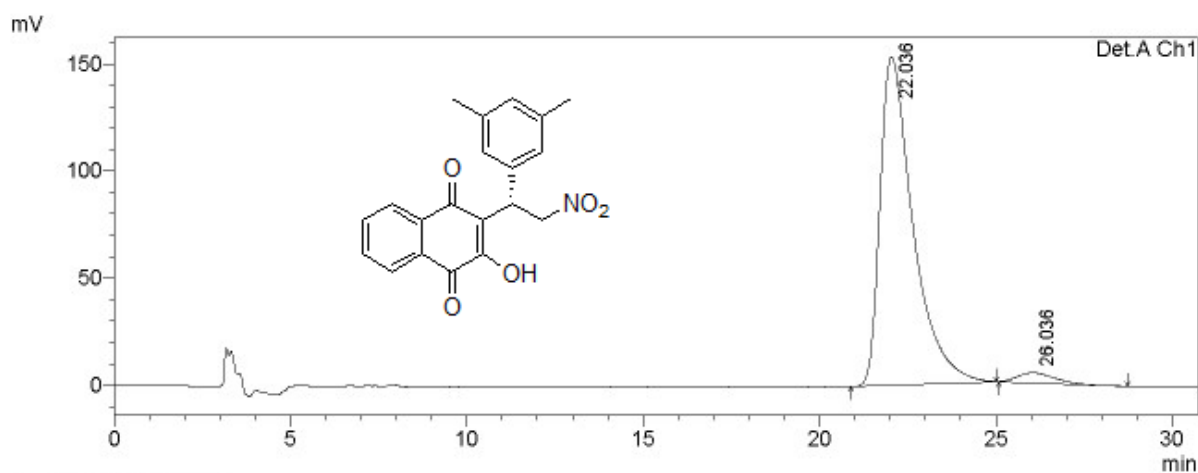


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.219	9252657	153153	49.222	56.585
2	25.817	9545332	117506	50.778	43.415
Total		18797989	270659	100.000	100.000



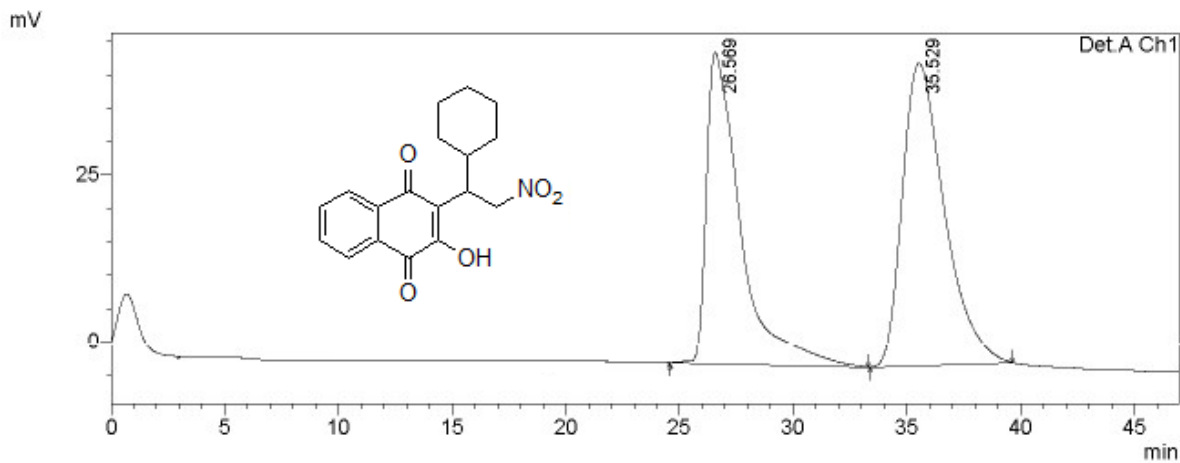
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.036	9931583	153111	96.848	97.052
2	26.036	323261	4650	3.152	2.948
Total		10254844	157762	100.000	100.000

**2-(1-cyclohexyl-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3o)**

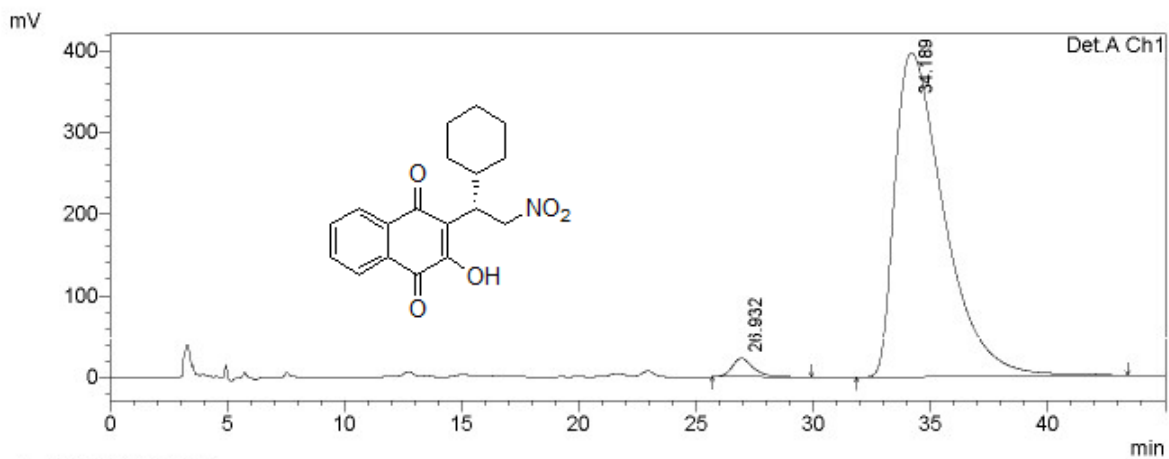


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.569	4860745	46807	45.365	50.732
2	35.529	5854063	45456	54.635	49.268
Total		10714808	92264	100.000	100.000



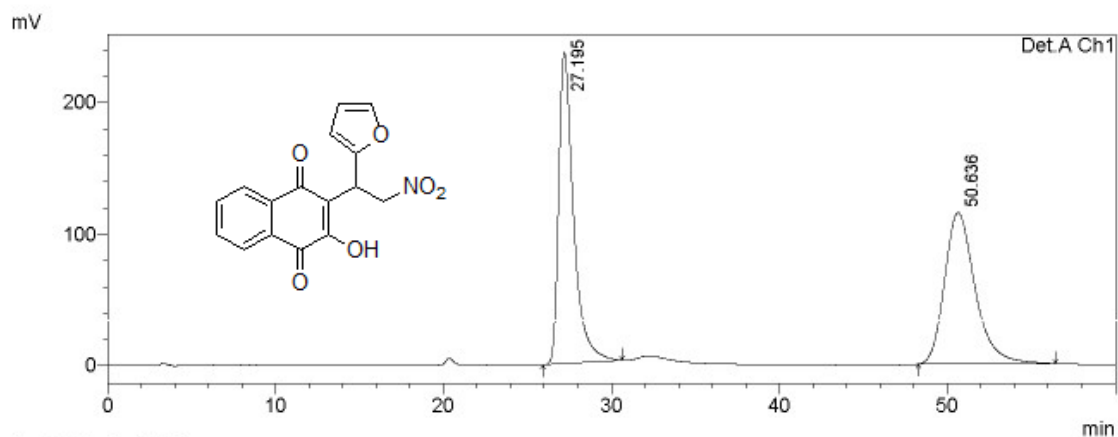
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.932	1446497	22845	2.422	5.437
2	34.189	58266394	397357	97.578	94.563
Total		59712891	420202	100.000	100.000

### 2-(1-(furan-2-yl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3p)

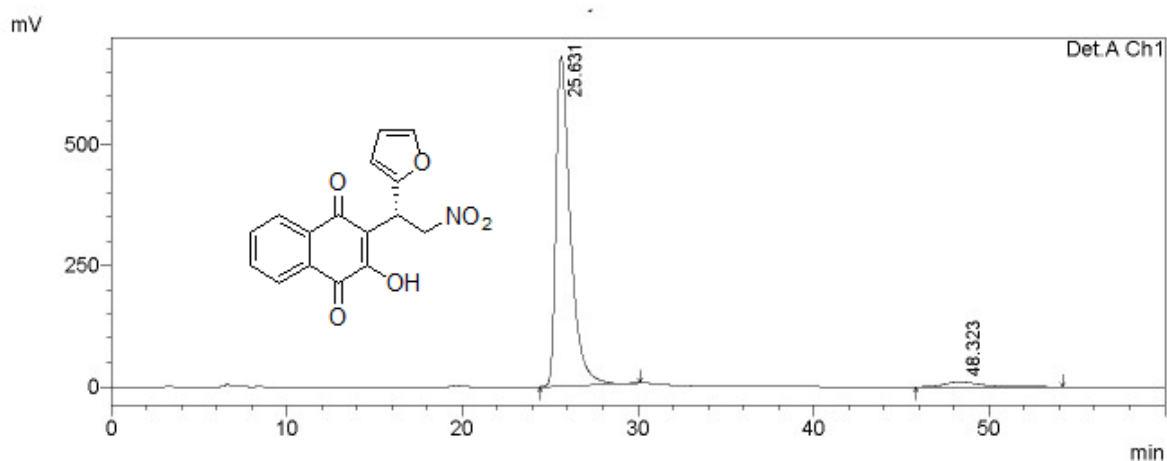


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.195	14600870	236948	49.979	67.254
2	50.636	14613210	115371	50.021	32.746
Total		29214080	352319	100.000	100.000



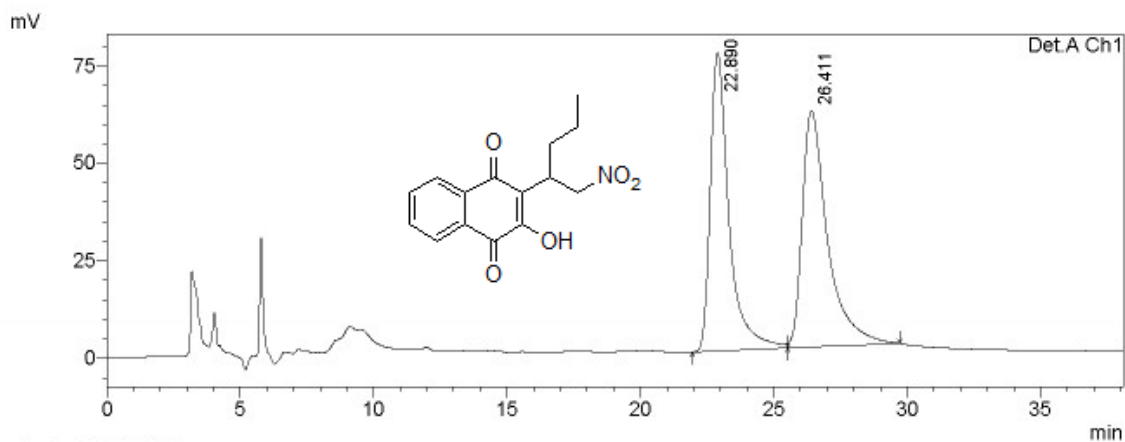
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.631	38557072	680857	96.346	98.487
2	48.323	1462149	10461	3.654	1.513
Total		40019221	691318	100.000	100.000

### 2-hydroxy-3-(1-nitropentan-2-yl)naphthalene-1,4-dione(3q)

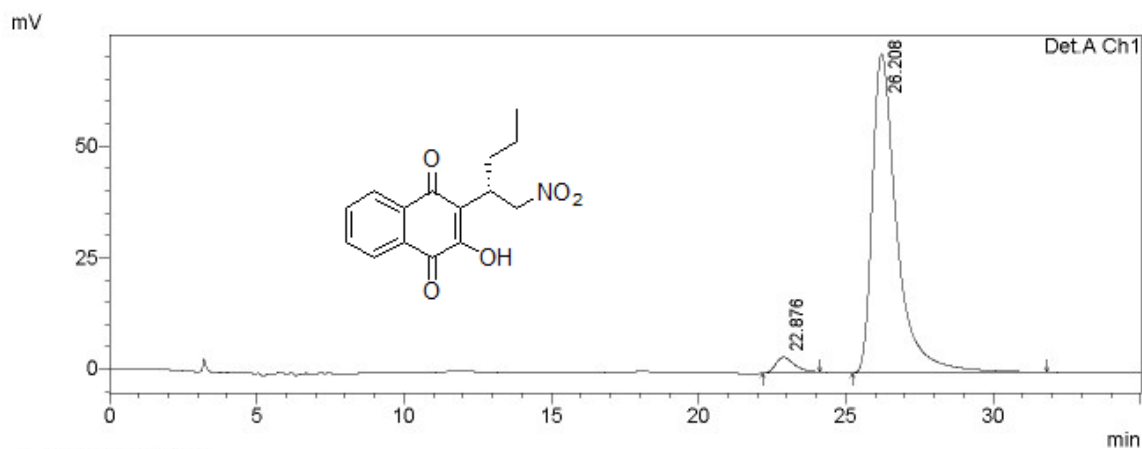


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.890	3719758	76606	48.166	55.772
2	26.411	4003070	60750	51.834	44.228
Total		7722828	137356	100.000	100.000



1 Det.A Ch1/254nm

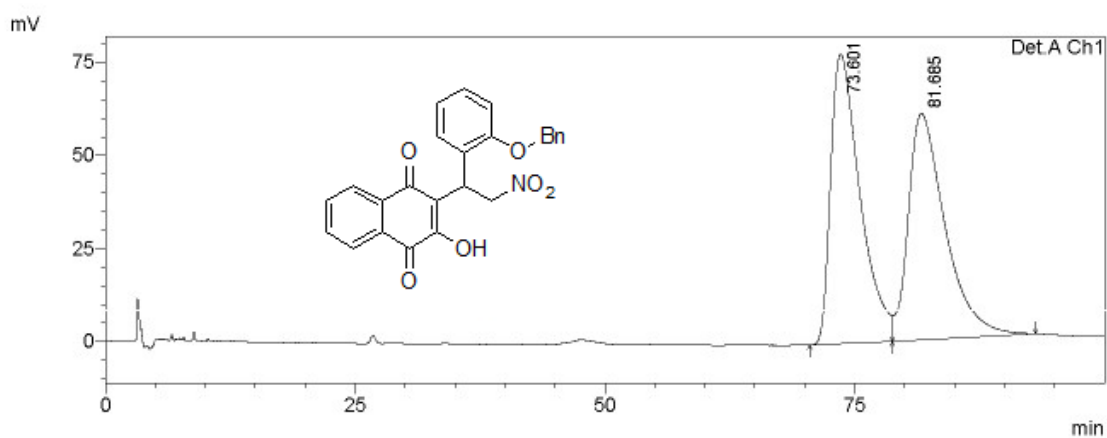
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.876	156233	3501	3.616	4.658
2	26.208	4163820	71655	96.384	95.342
Total		4320053	75156	100.000	100.000



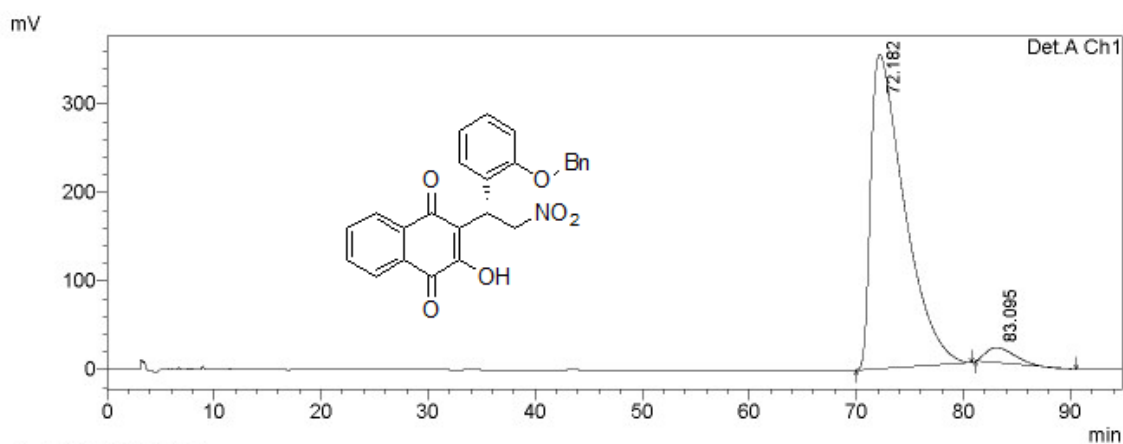
## 2-(1-(2-(benzyloxy)phenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione(3r)



1 Det.A Ch1/254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	73.601	15943143	77743	50.411	56.126
2	81.685	15683435	60772	49.589	43.874
Total		31626577	138515	100.000	100.000

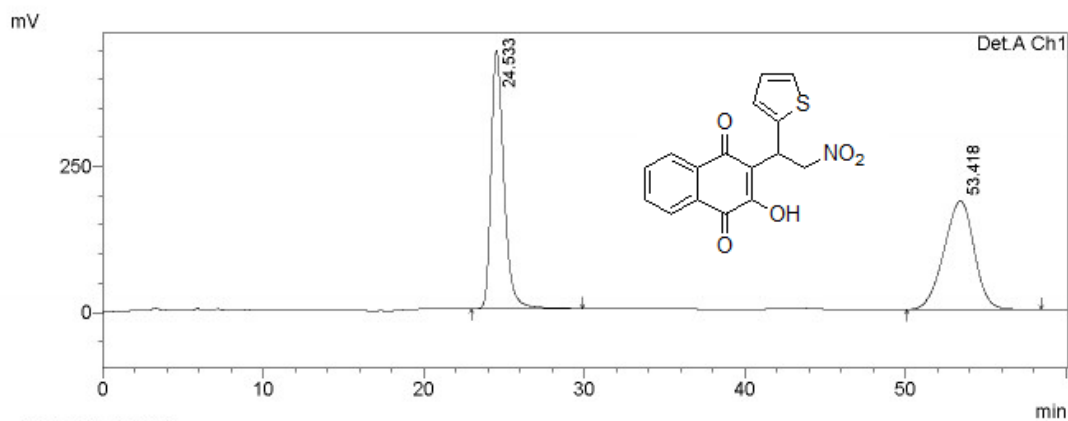


1 Det.A Ch1/254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	72.182	77268519	355200	96.290	95.509
2	83.095	2976940	16701	3.710	4.491
Total		80245460	371901	100.000	100.000

### 2-hydroxy-3-(2-nitro-1-(thiophen-2-yl)ethyl)naphthalene-1,4-dione(3s)

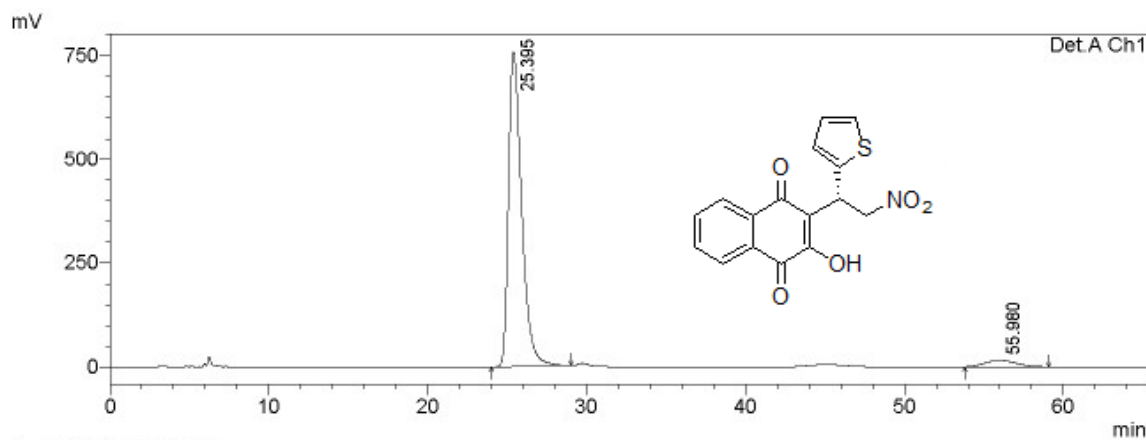


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.533	24486442	443239	50.109	70.432
2	53.418	24379847	186080	49.891	29.568
Total		48866289	629319	100.000	100.000



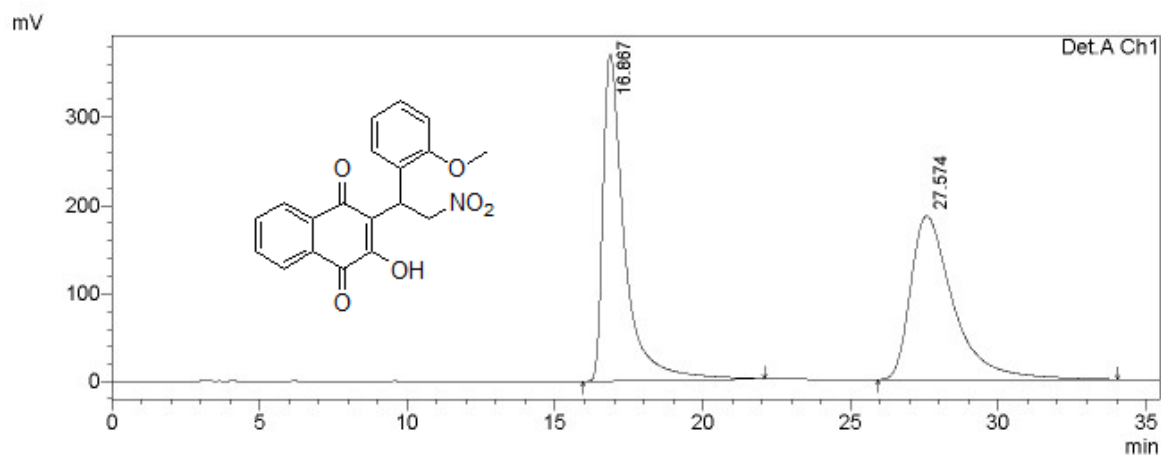
1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.395	43545454	757450	95.354	97.995
2	55.980	2121847	15497	4.646	2.005
Total		45667301	772947	100.000	100.000

## 2-hydroxy-3-(1-(2-methoxyphenyl)-2-nitroethyl)naphthalene-1,4-dione(3t)

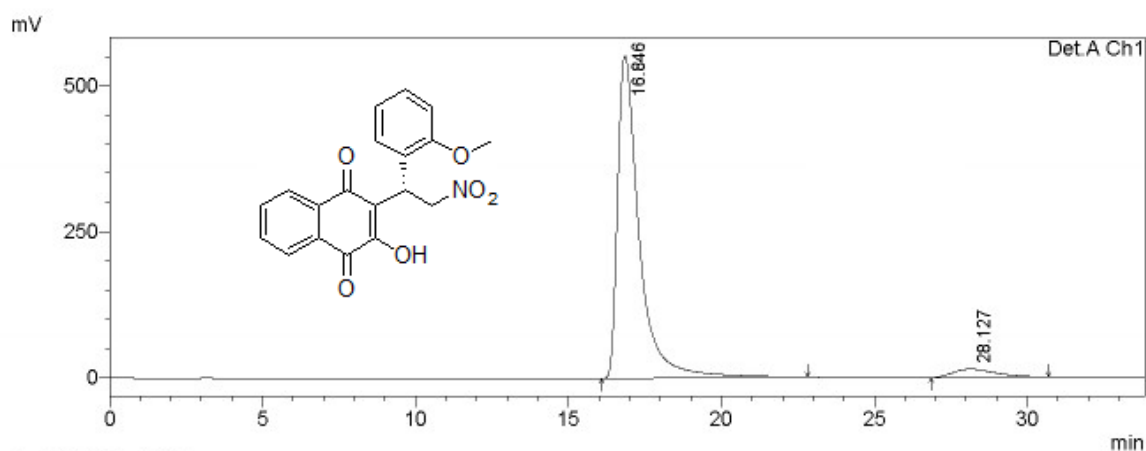


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.867	18814354	370885	50.084	66.572
2	27.574	18751286	186231	49.916	33.428
Total		37565639	557116	100.000	100.000



1 Det.A Ch1/254nm

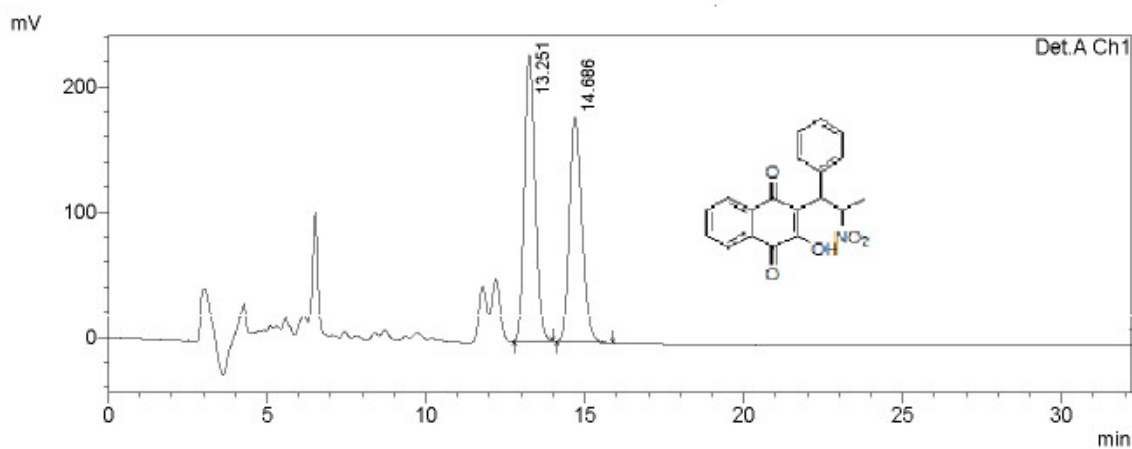
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.846	27156264	551780	95.082	97.476
2	28.127	1404679	14285	4.918	2.524
Total		28560943	566066	100.000	100.000

## 2-hydroxy-3-(2-nitro-1-phenylpropyl)naphthalene-1,4-dione(3u)

### <Chromatogram>



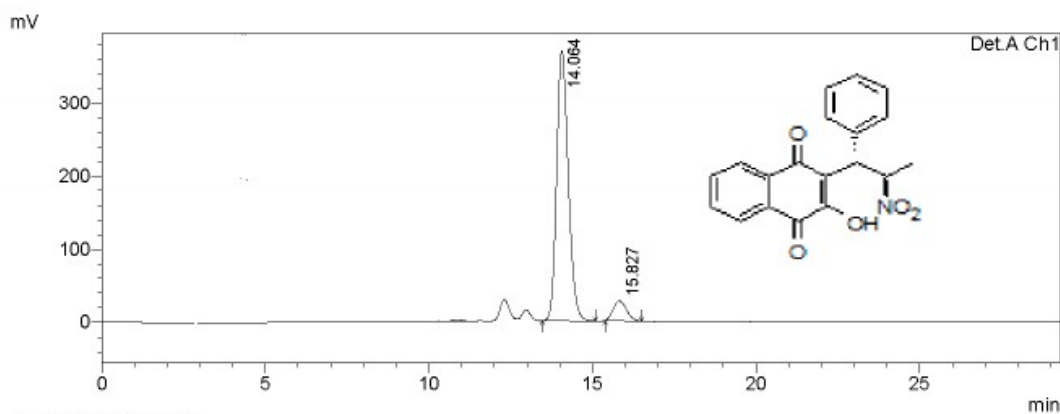
1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.251	5320995	228503	52.114	56.086
2	14.686	4889365	178916	47.886	43.914
Total		10210360	407419	100.000	100.000

### <Chromatogram>



1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.064	9208540	369242	92.789	93.316
2	15.827	715650	26450	7.211	6.684
Total		9924190	395692	100.000	100.000