

Supporting Information

Enantioselective Michael addition of 2-hydroxy-1,4-naphthoquinone and 1,3-dicarbonyls to nitroalkenes catalyzed by a novel bifunctional rosin-derived indane amine thiourea catalyst

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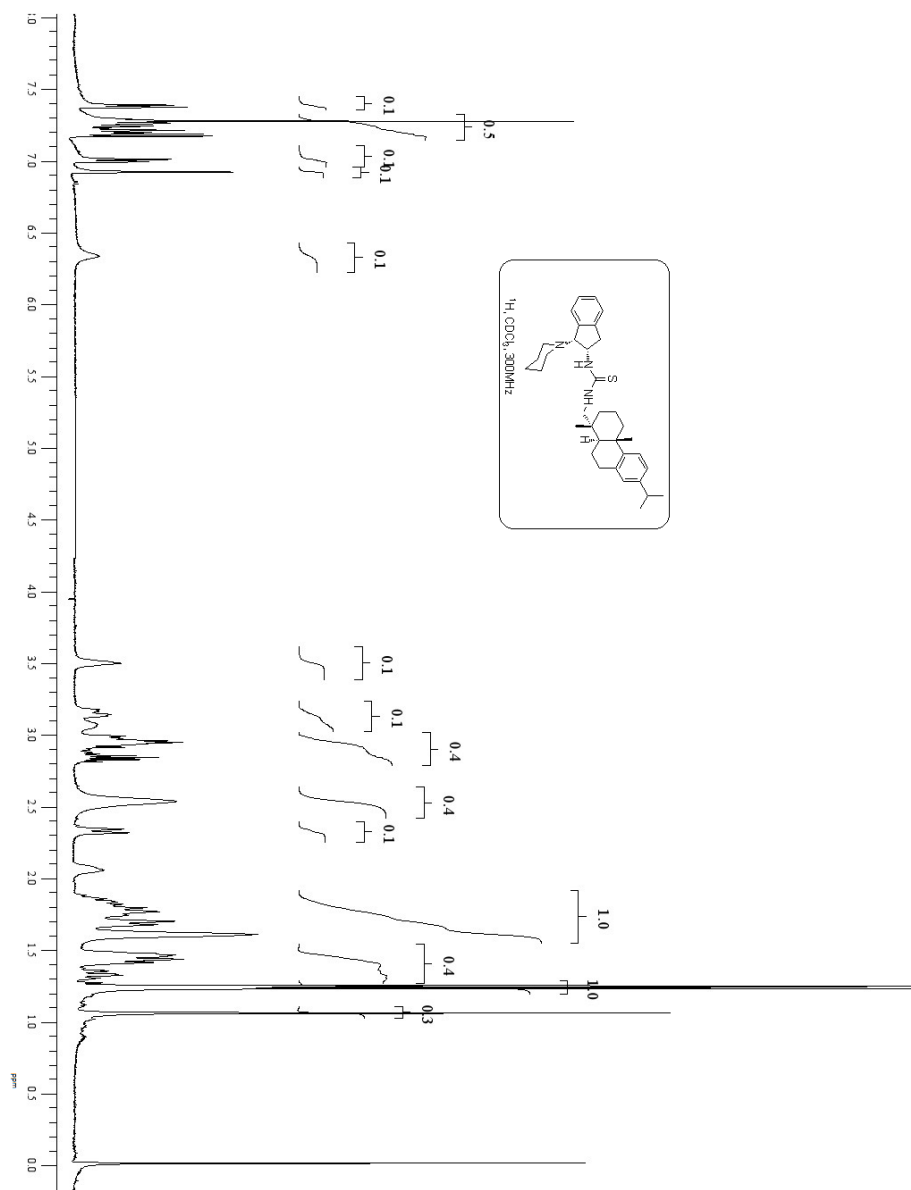
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4. HPLC Data of the products (3a-3v), (7a-7k) and (9a-9c)	S20-S53

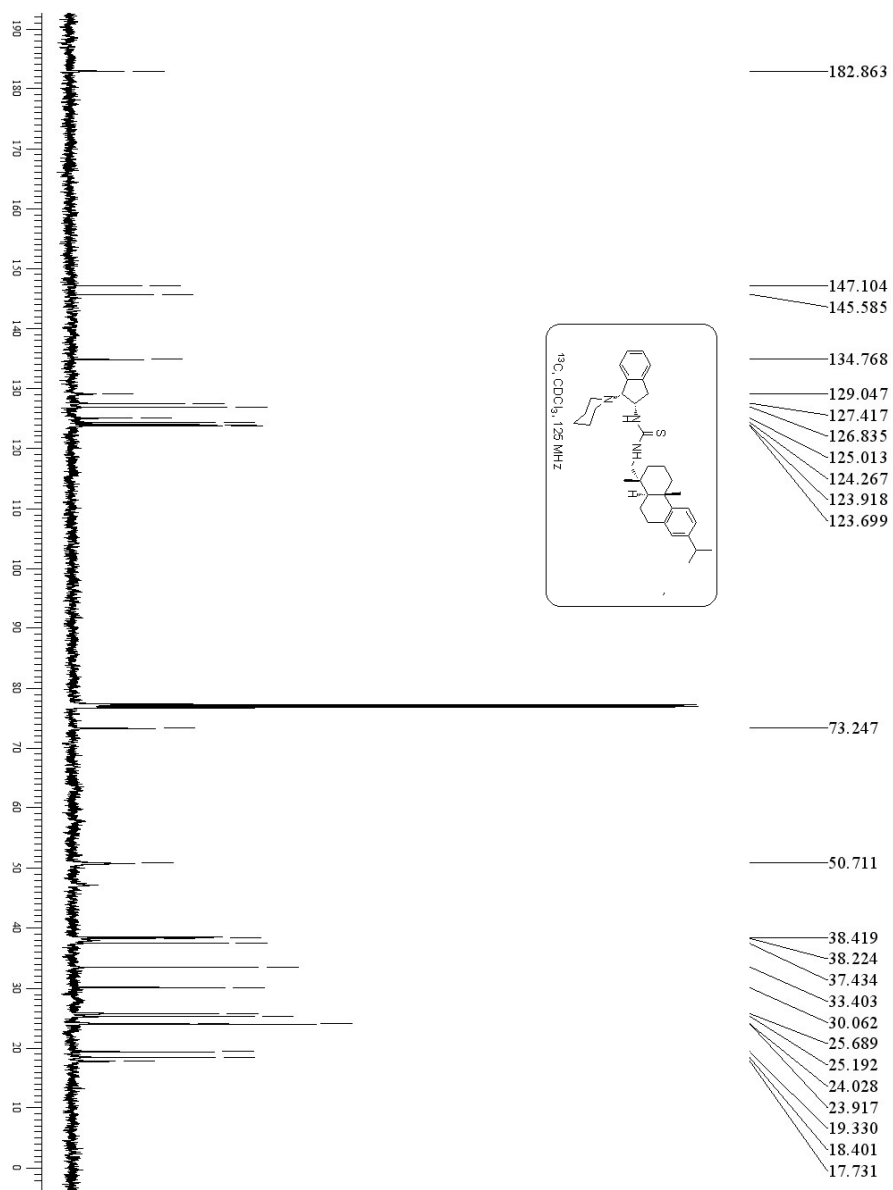
General Remarks

The solvent dichloromethane was dried according to a standard literature procedure. The reactions were performed in oven-dried single necked round bottom tube under an argon atmosphere. Glass syringes were used to transfer the solvent. The products were purified by column chromatography on silica gel of 60–120 or 100-200 mesh. Thin layer chromatographic plates were visualized by the ultraviolet light and/or by exposure to iodine vapours and/or by exposure to methanolic acidic solution of *p*-anisaldehyde followed by heating (<1 min) on a hot plate (~250 °C). Organic solutions were concentrated on rotary evaporator at 35–40 °C. IR spectra were recorded on FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using 300, 400, 500 or 600 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) or Atmospheric pressure chemical ionization (APCI) technique.

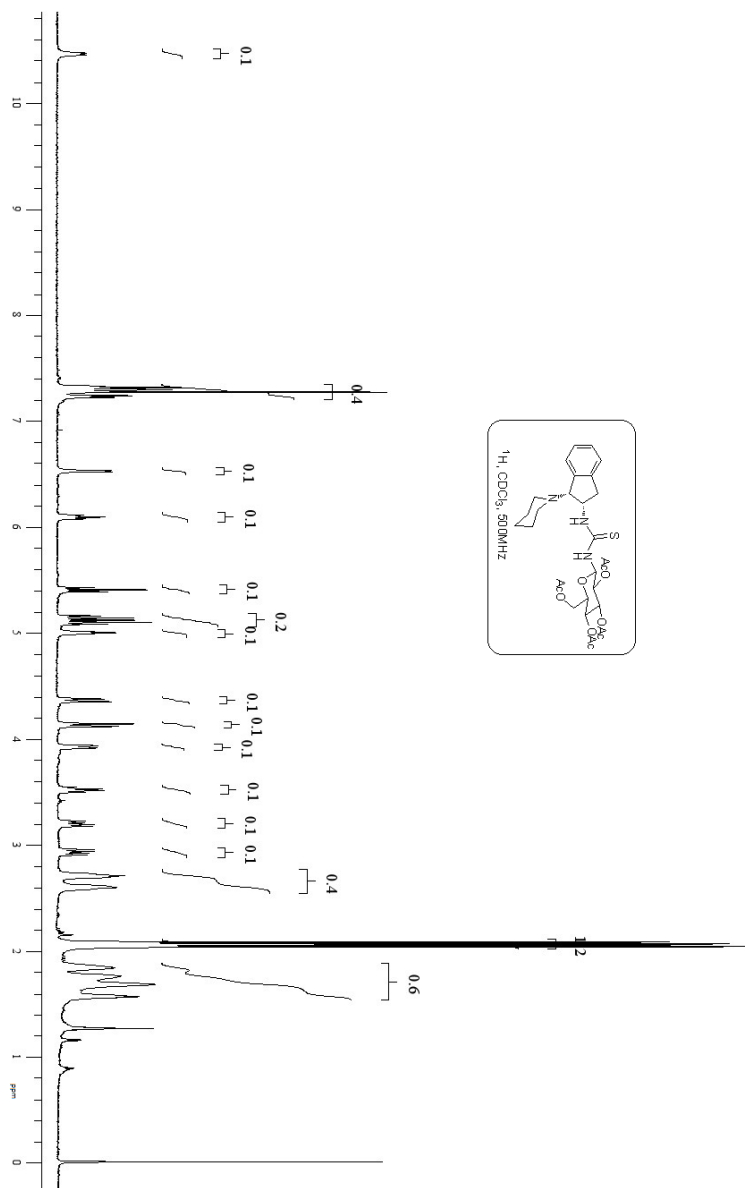
2. Copies of ^1H and ^{13}C NMR spectra of Catalysts:

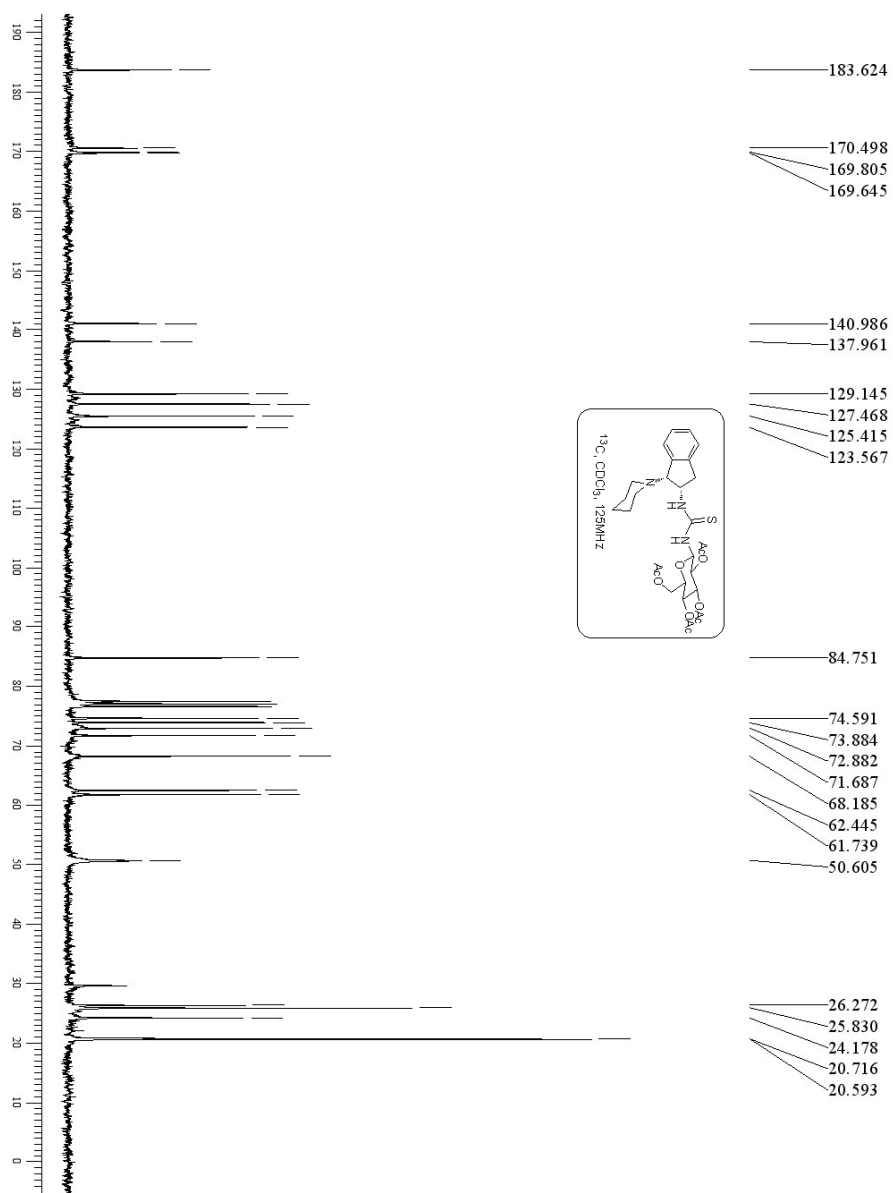
^1H and ^{13}C spectra of Ligand **III**



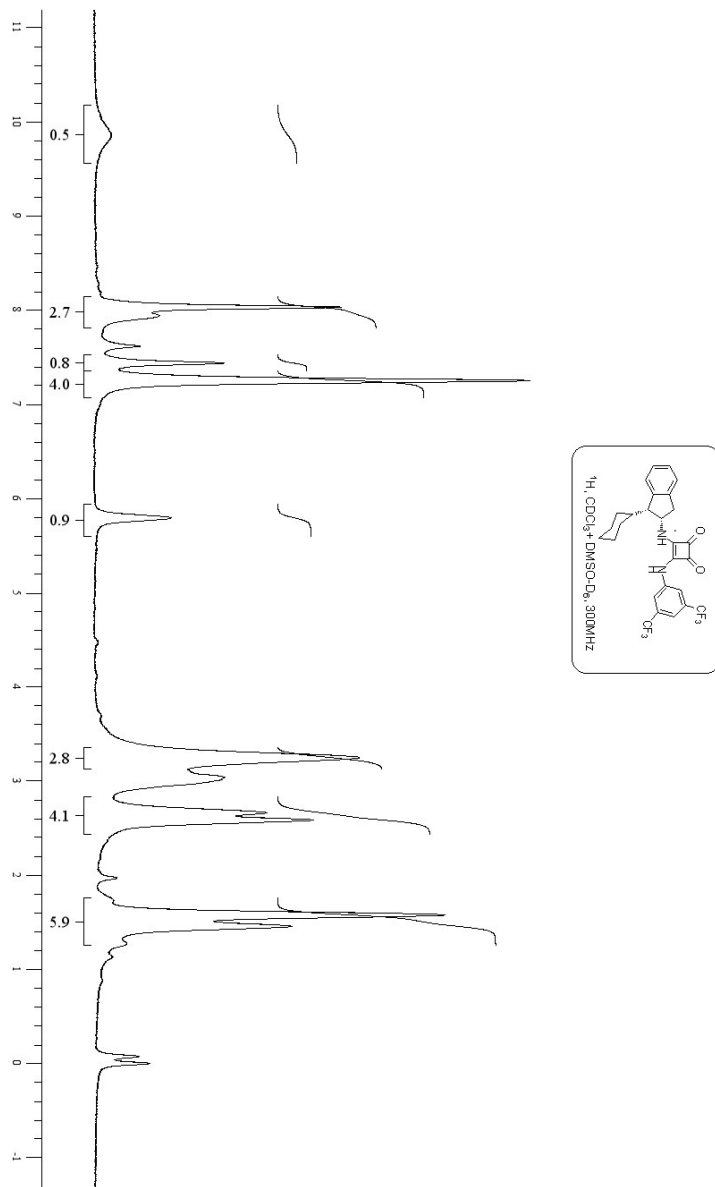


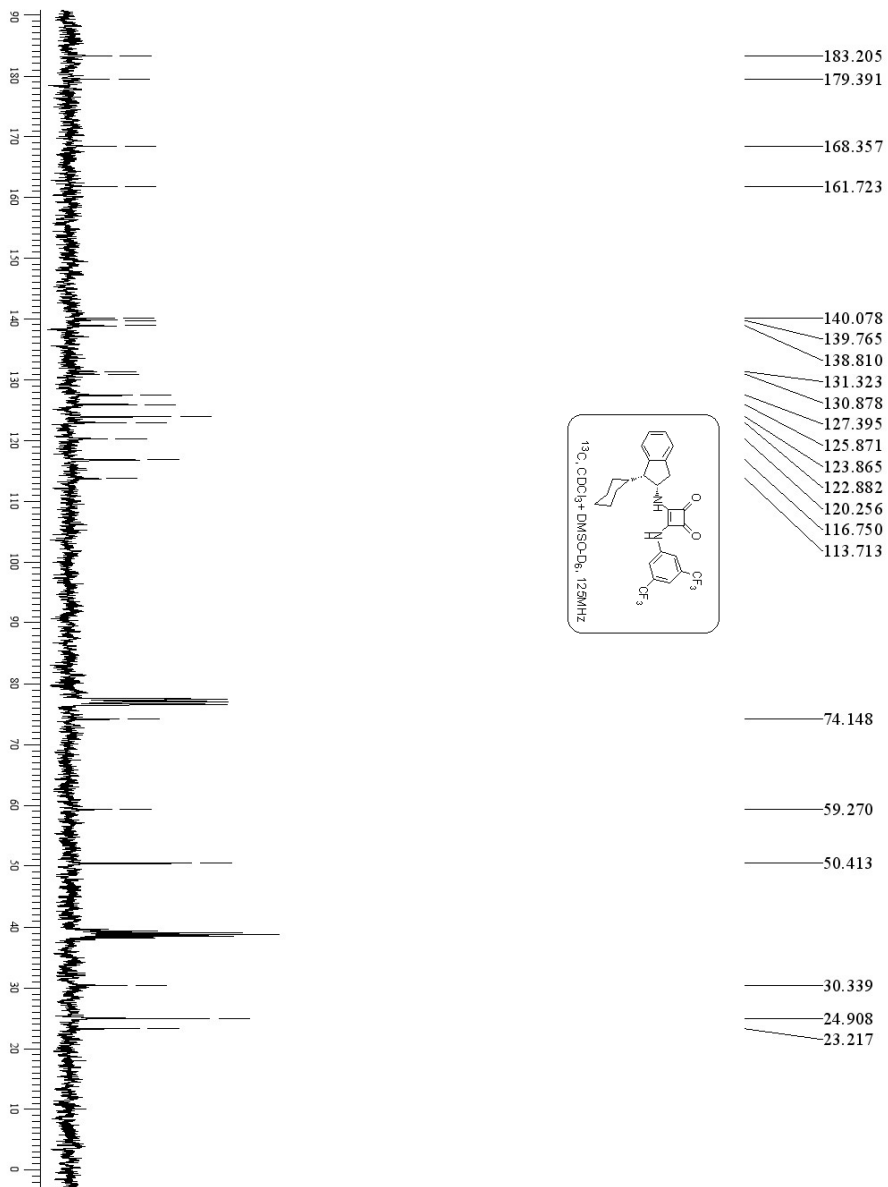
^1H and ^{13}C spectra of Ligand VI



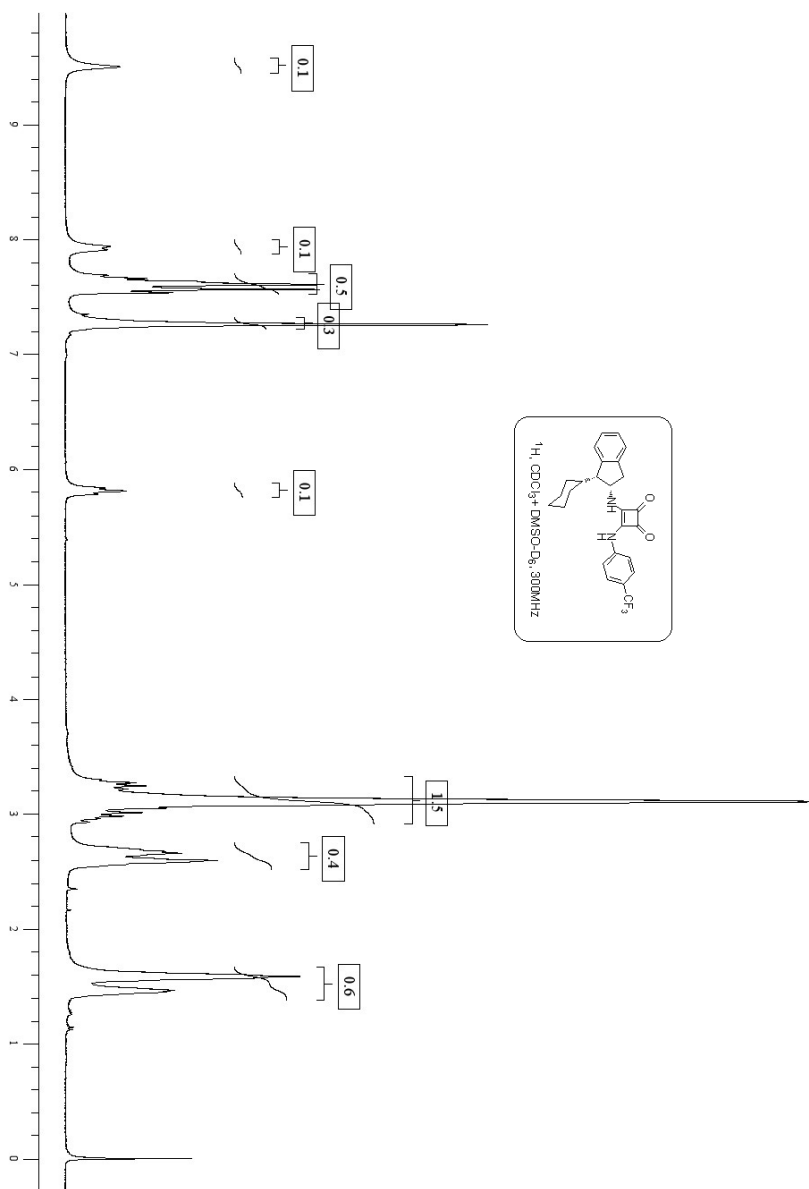


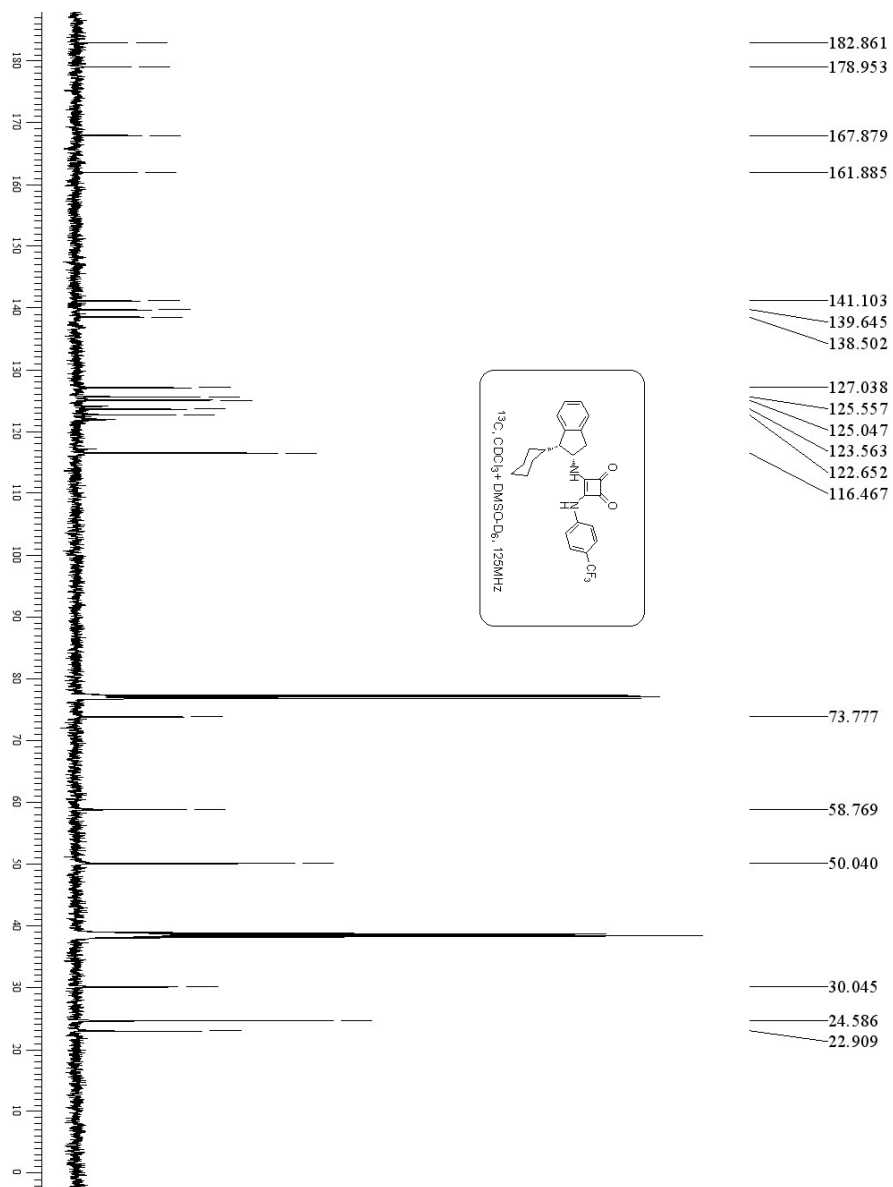
^1H and ^{13}C spectra of Ligand V



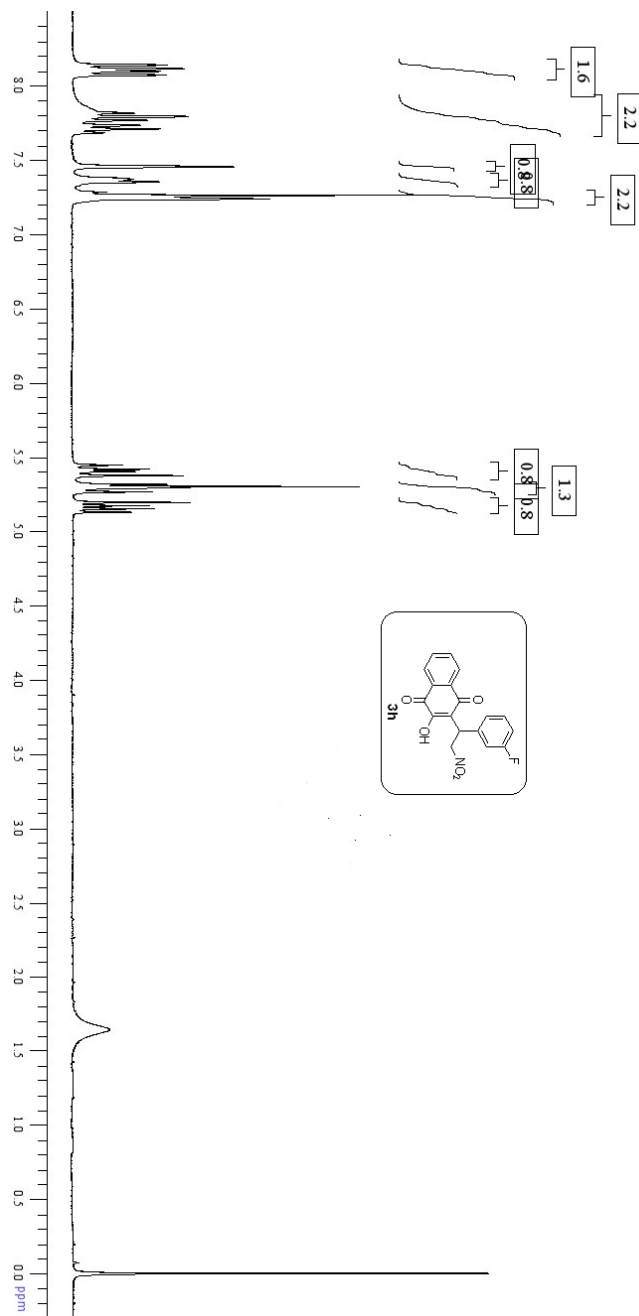


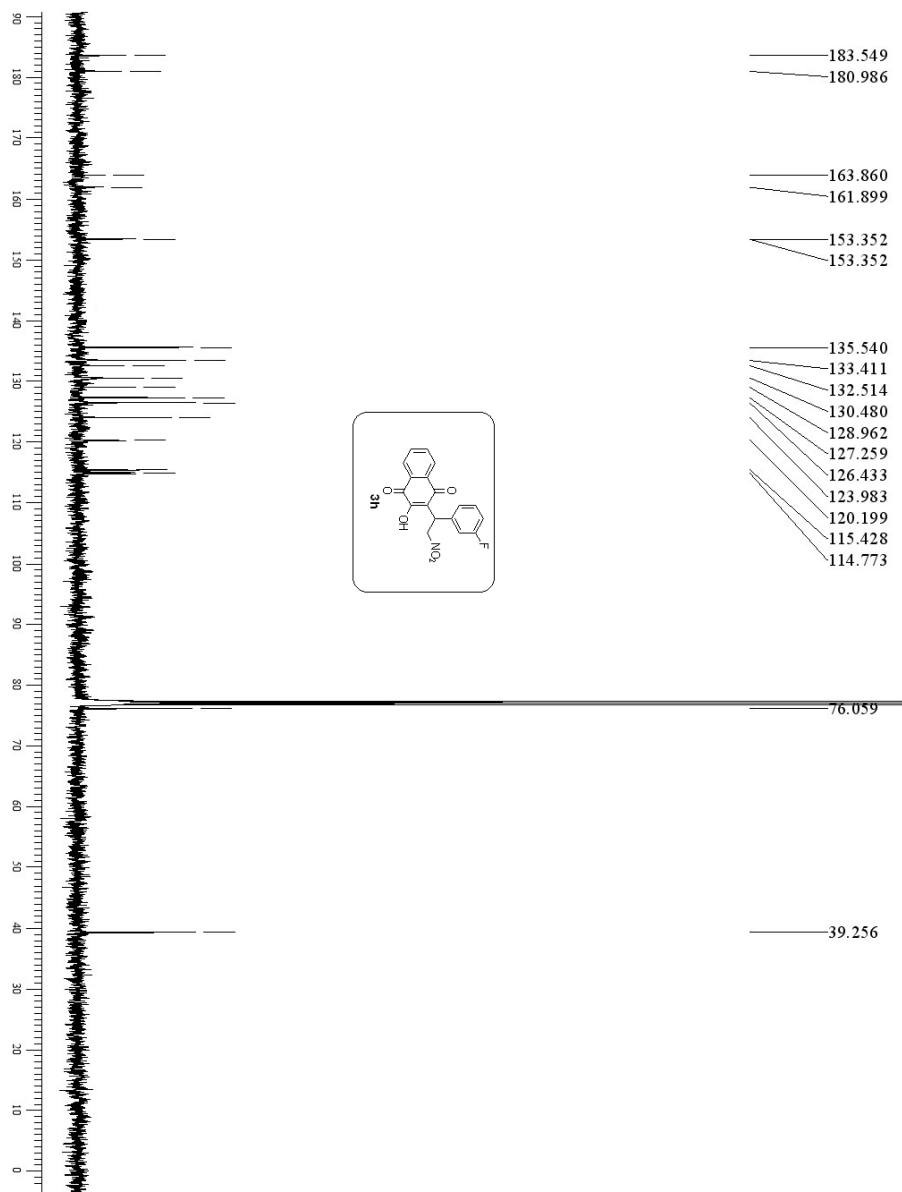
^1H and ^{13}C spectra of Ligand VI

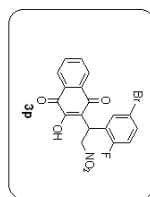
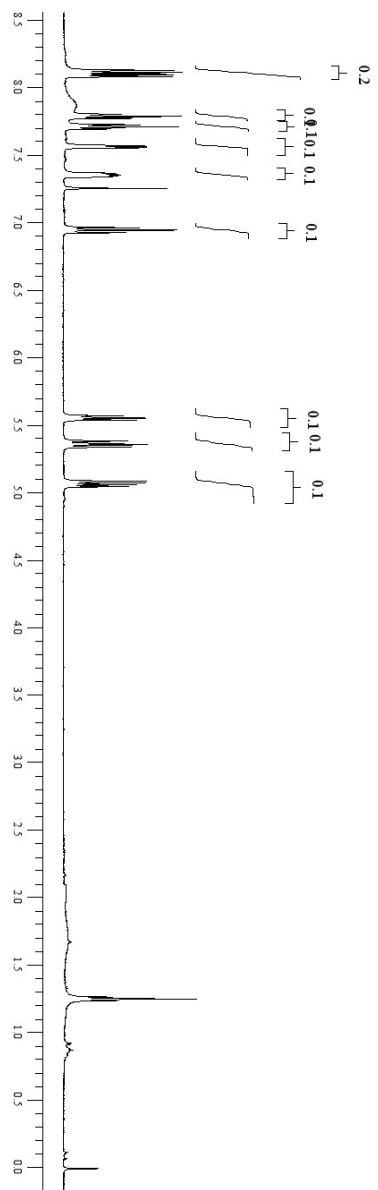


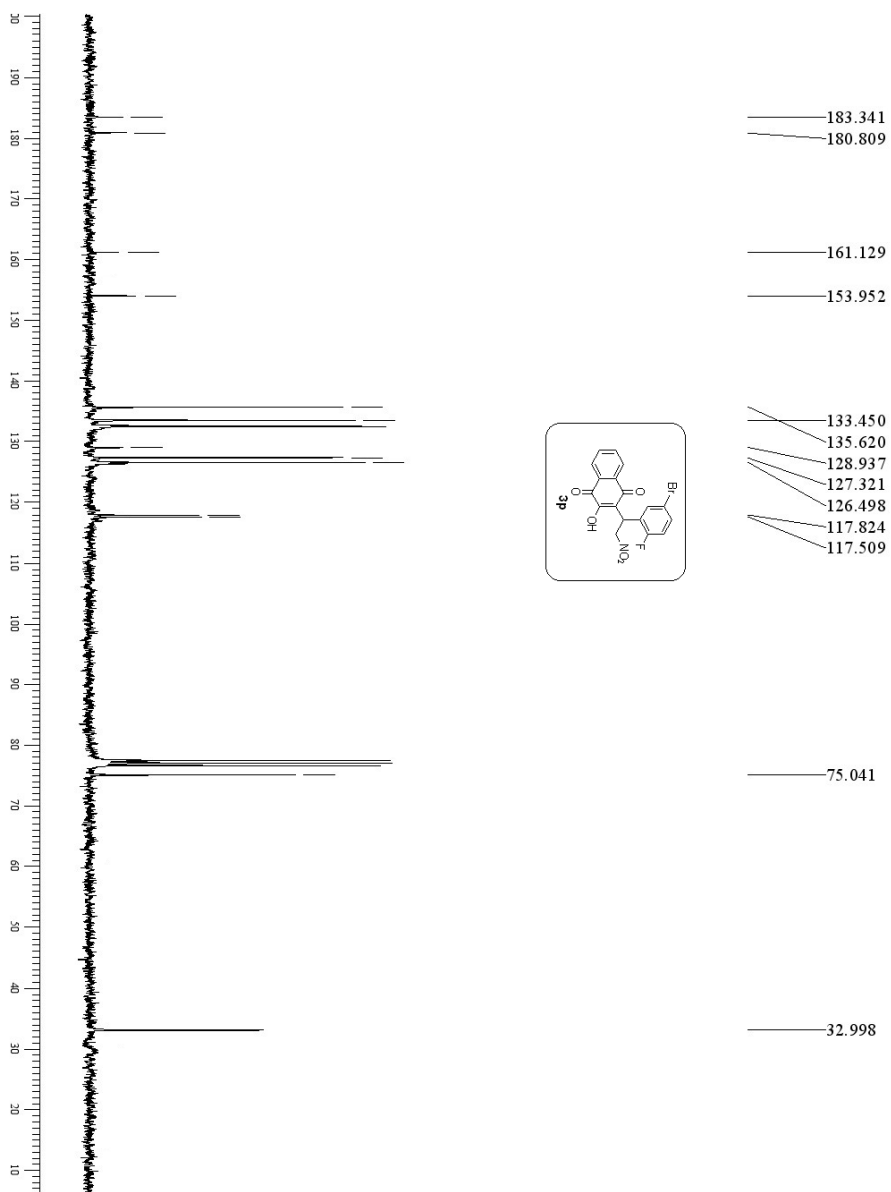


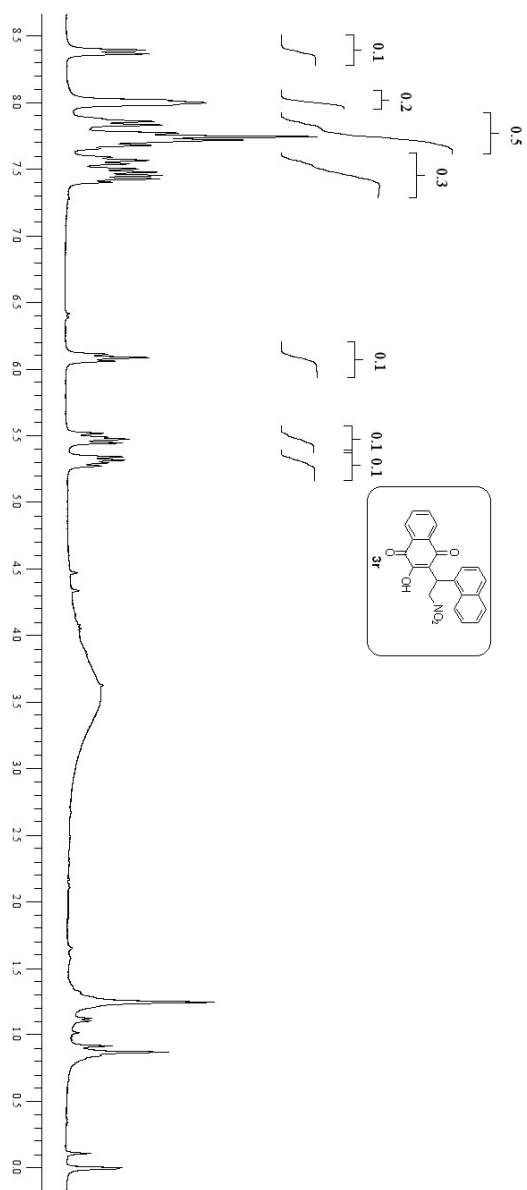
^1H and ^{13}C Spectra of Compounds:

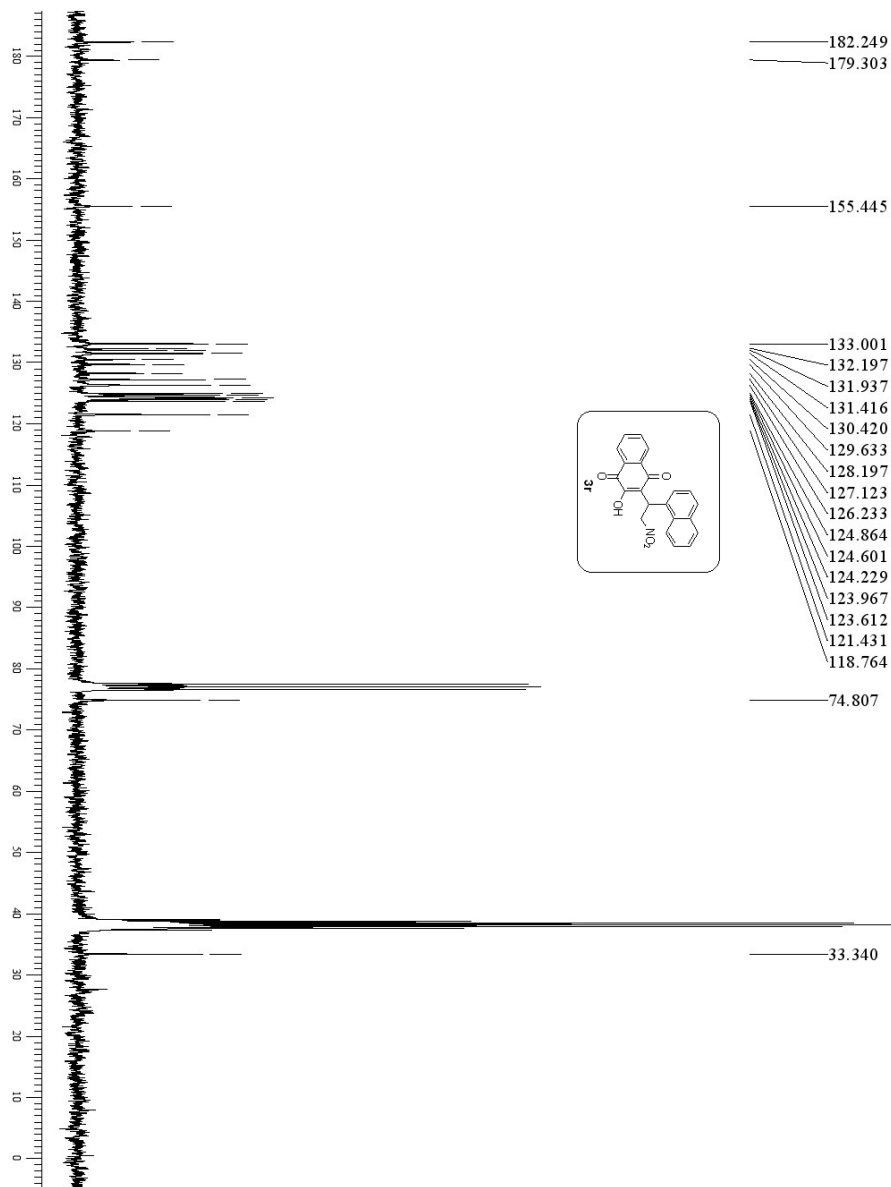


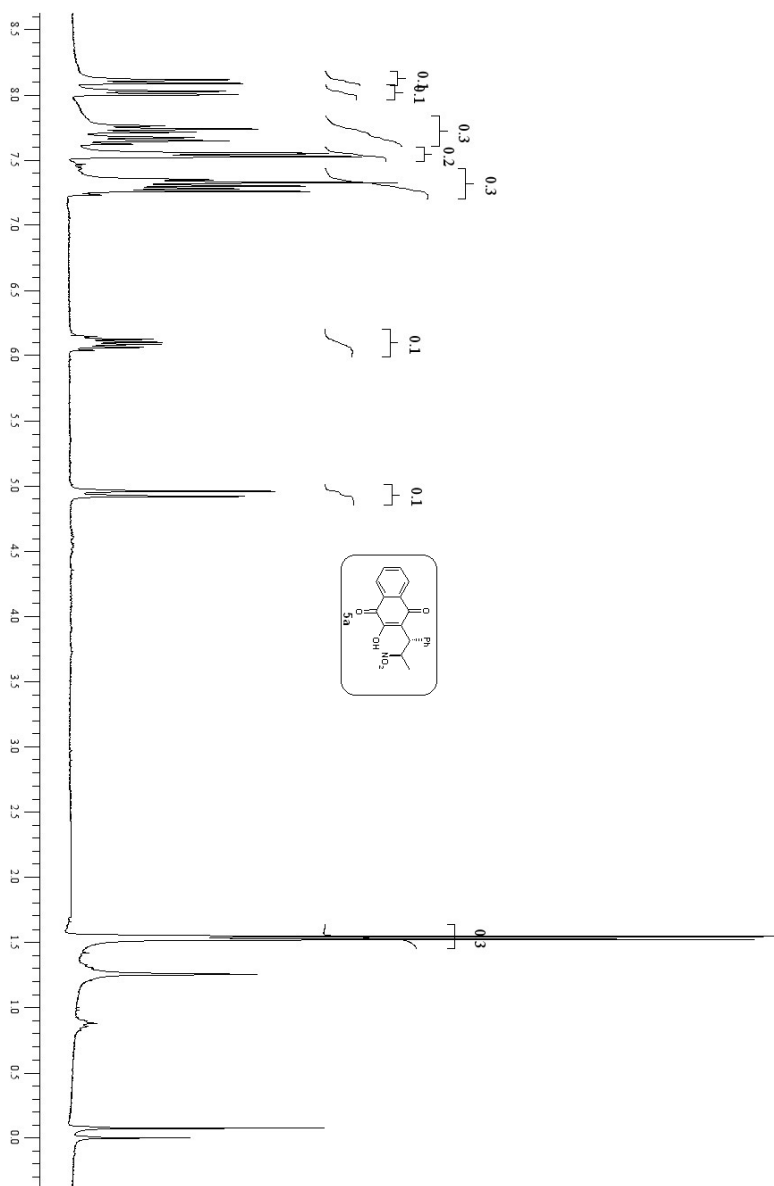


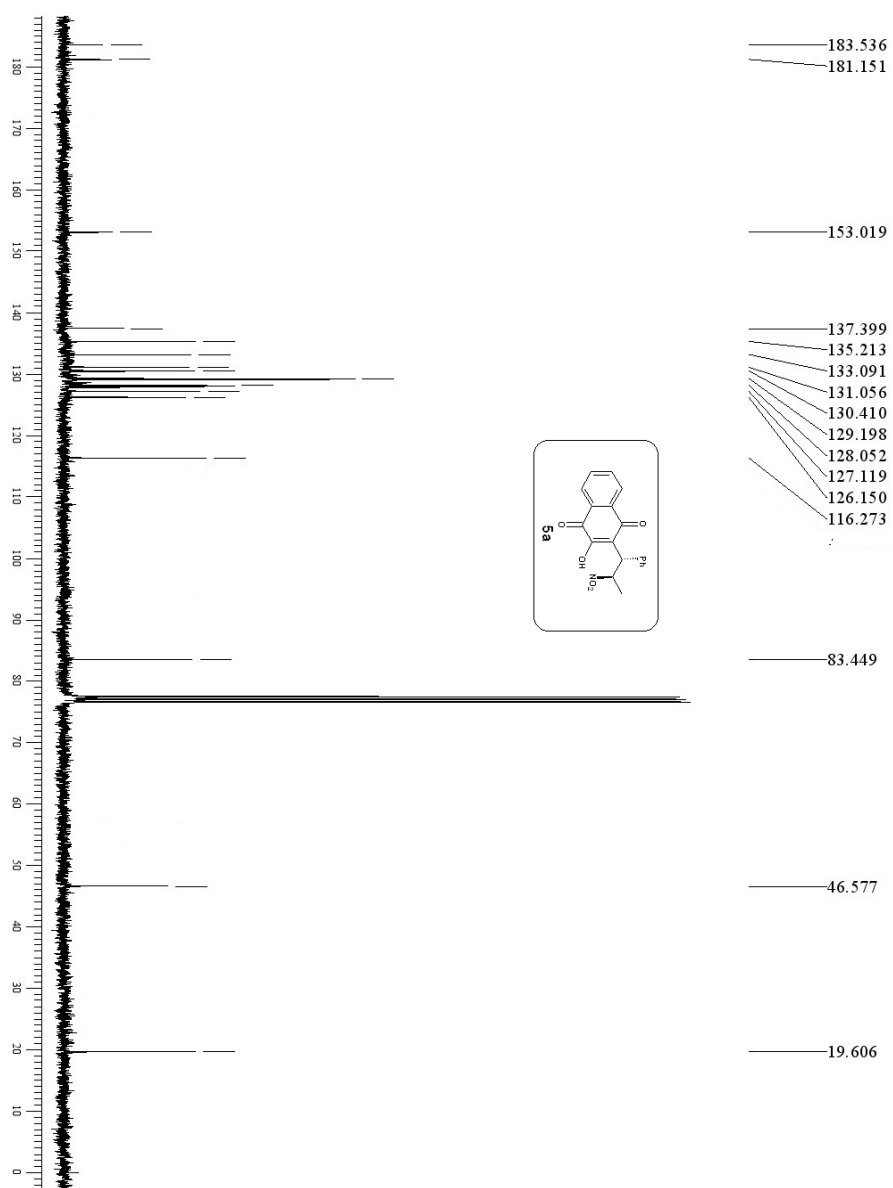


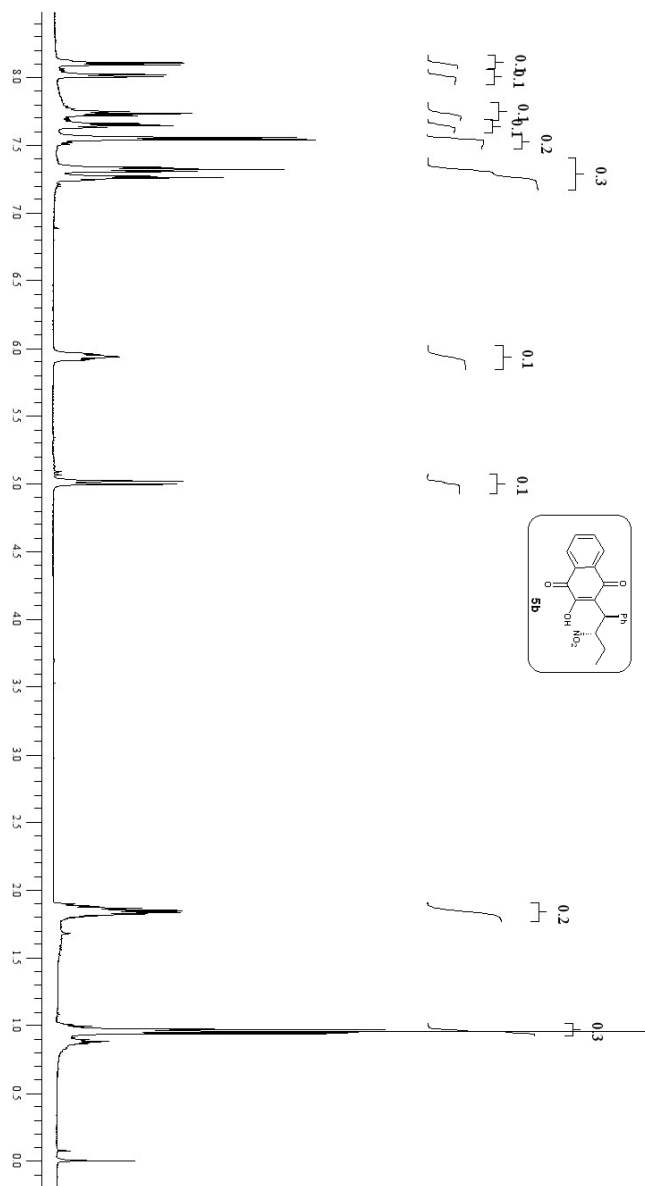




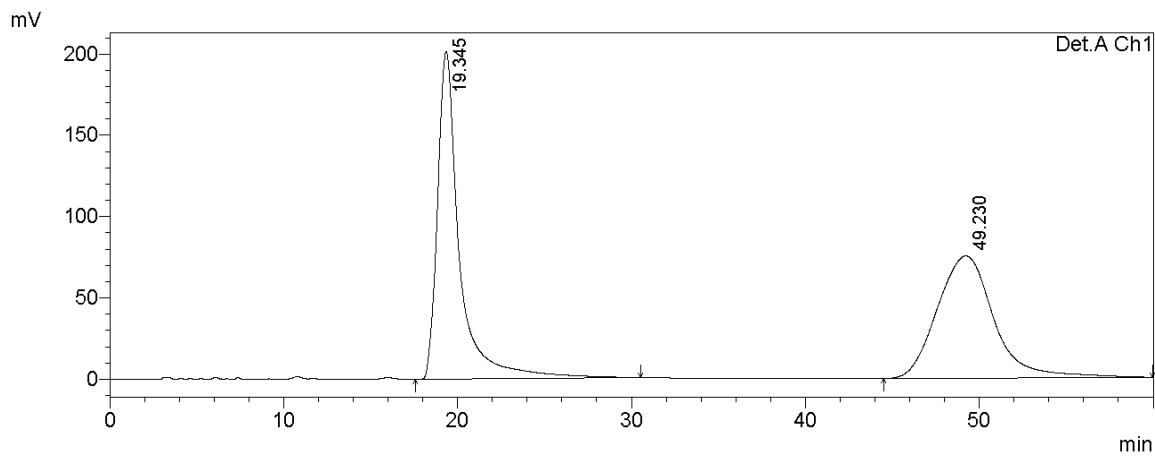






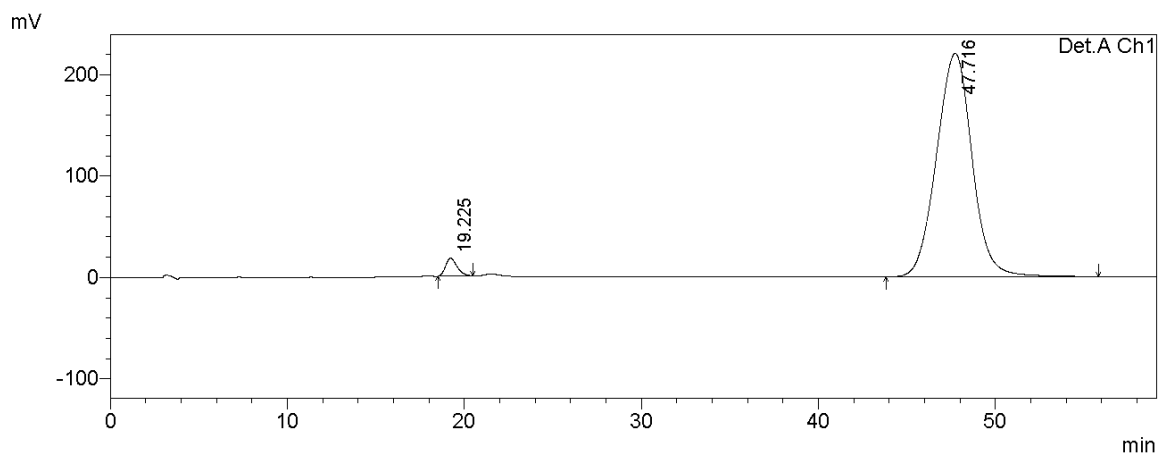


(R)-2-Hydroxy-3-(2-nitro-1-phenylethyl)naphthalene-1,4-dione (3a)



Detector A Ch1 254nm

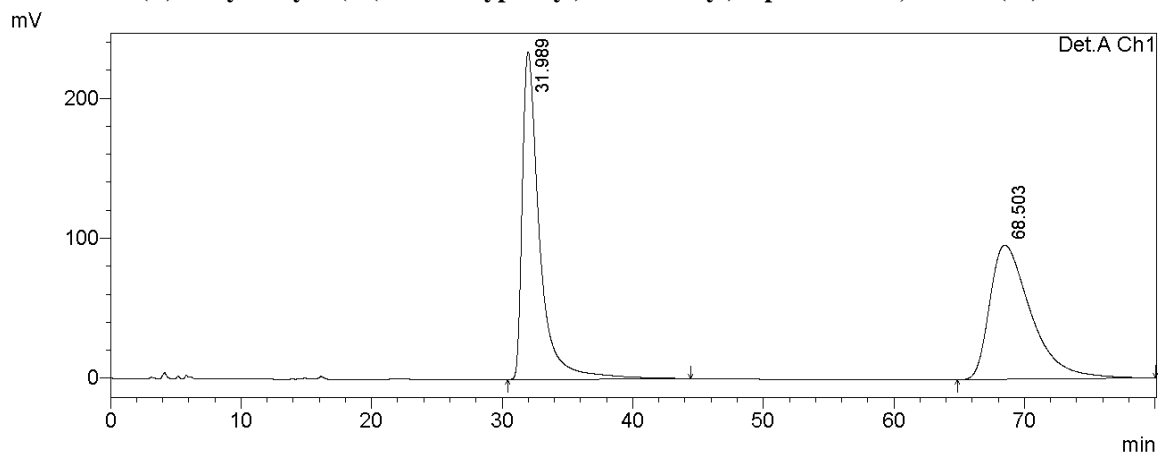
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.345	17662369	201435	50.904	72.843
2	49.230	17035216	75097	49.096	27.157
Total		34697585	276532	100.000	100.000



Detector A Ch1 254nm

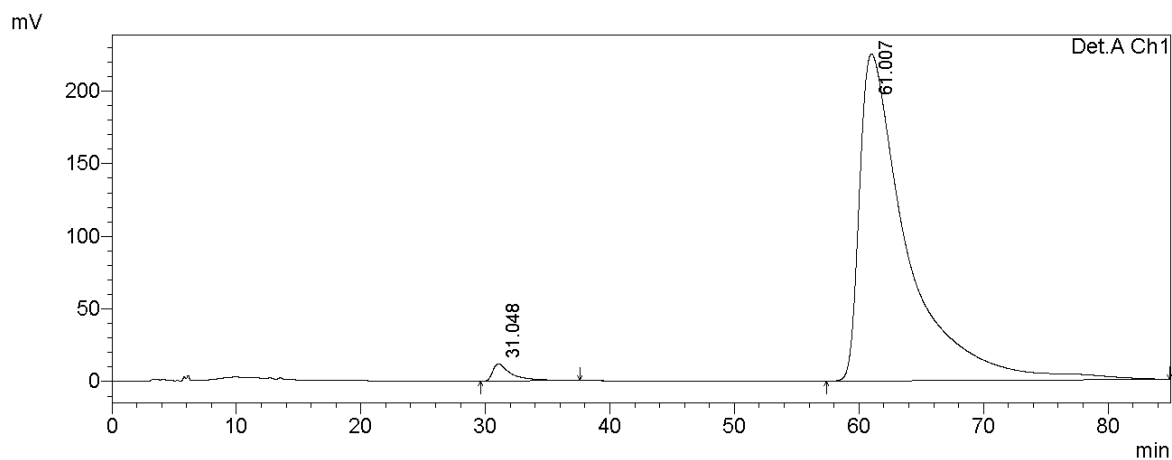
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.225	788829	17563	2.502	7.381
2	47.716	30742675	220398	97.498	92.619
Total		31531503	237960	100.000	100.000

(R)-2-Hydroxy-3-(1-(4-methoxyphenyl)-2-nitroethyl)naphthalene-1,4-dione (3c)



Detector A Ch1 254nm

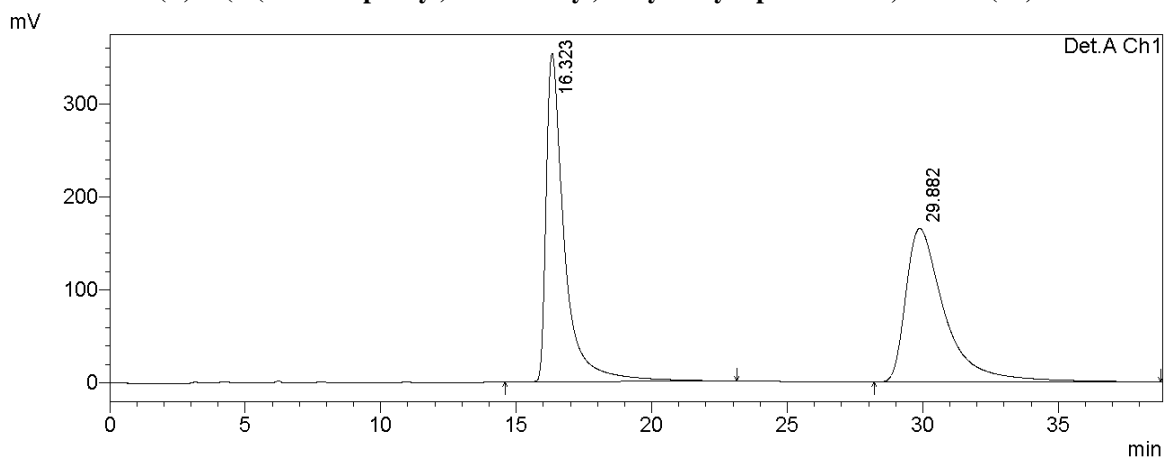
Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.989	21600776	233891	50.564	70.909
2	68.503	21118854	95954	49.436	29.091
Total		42719629	329844	100.000	100.000



Detector A Ch1 254nm

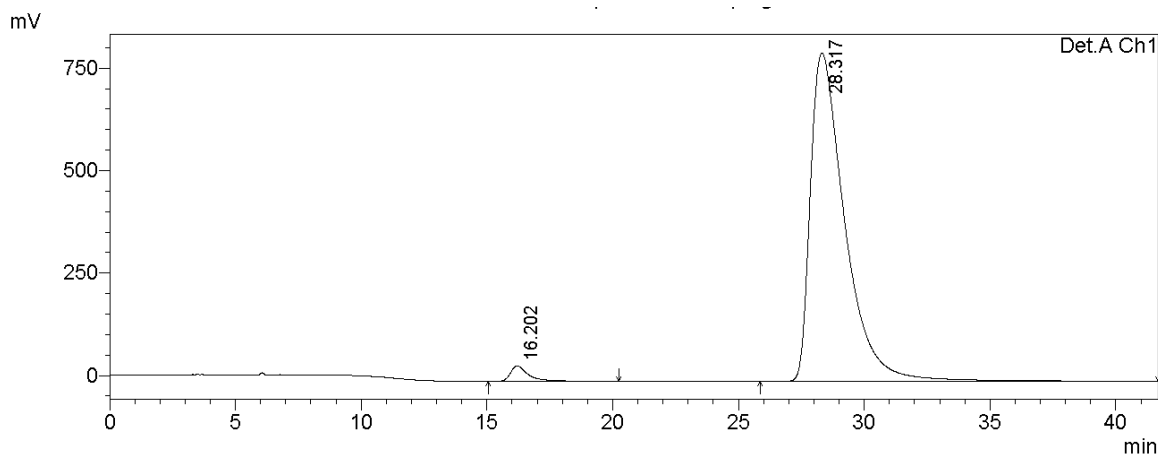
Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.048	1291961	11937	2.112	5.033
2	61.007	59878490	225256	97.888	94.967
Total		61170451	237193	100.000	100.000

(R)-2-(1-(4-Fluorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3d)



Detector A Ch1 254nm

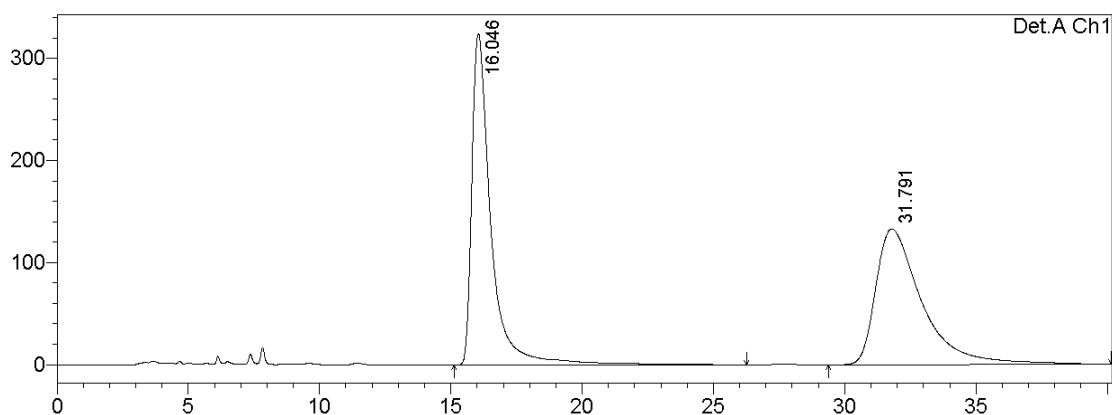
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.323	16712099	353251	50.213	68.175
2	29.882	16570184	164901	49.787	31.825
Total		33282284	518153	100.000	100.000



Detector A Ch1 254nm

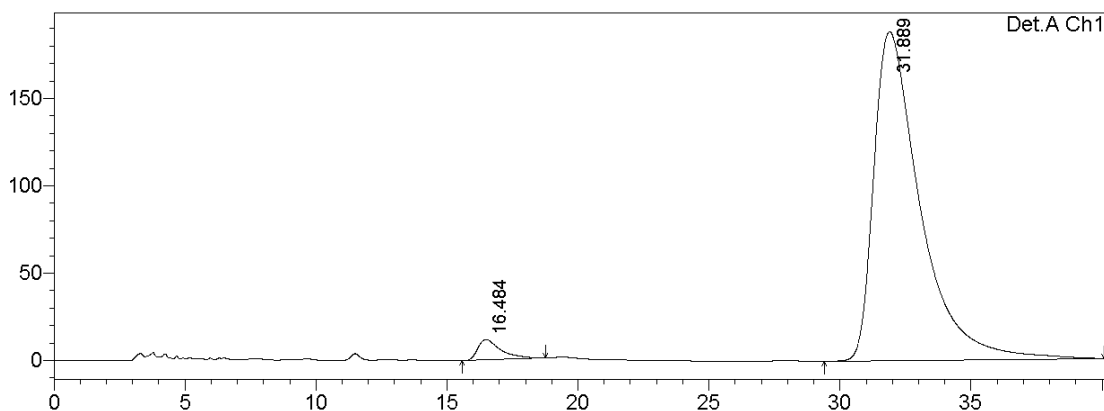
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.202	1902596	37884	2.428	4.513
2	28.317	76466802	801508	97.572	95.487
Total		78369399	839392	100.000	100.000

(R)-2-(1-(4-Chlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3e)



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.046	16495437	324806	50.312	70.955
2	31.791	16290996	132958	49.688	29.045
Total		32786433	457764	100.000	100.000

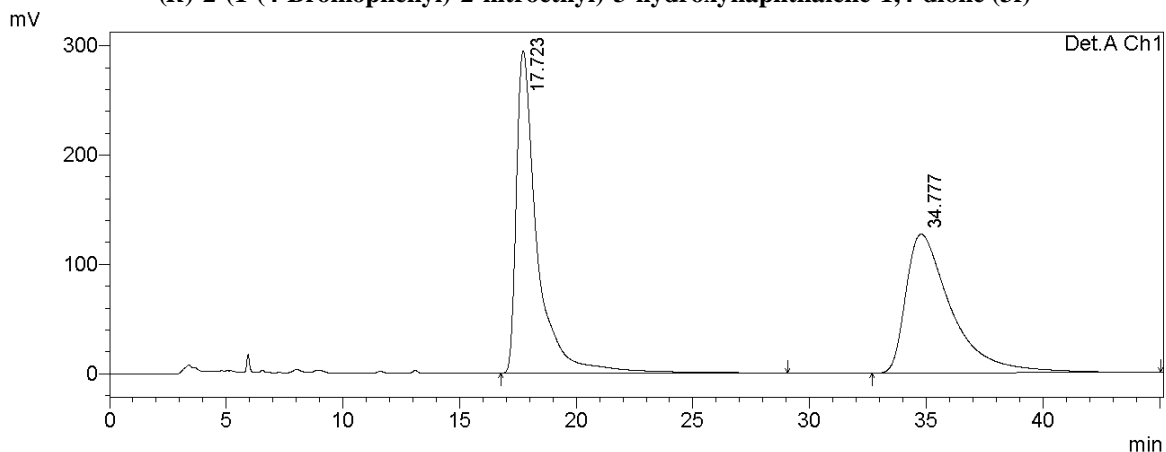


PeakTable

Detector A Ch1 254nm

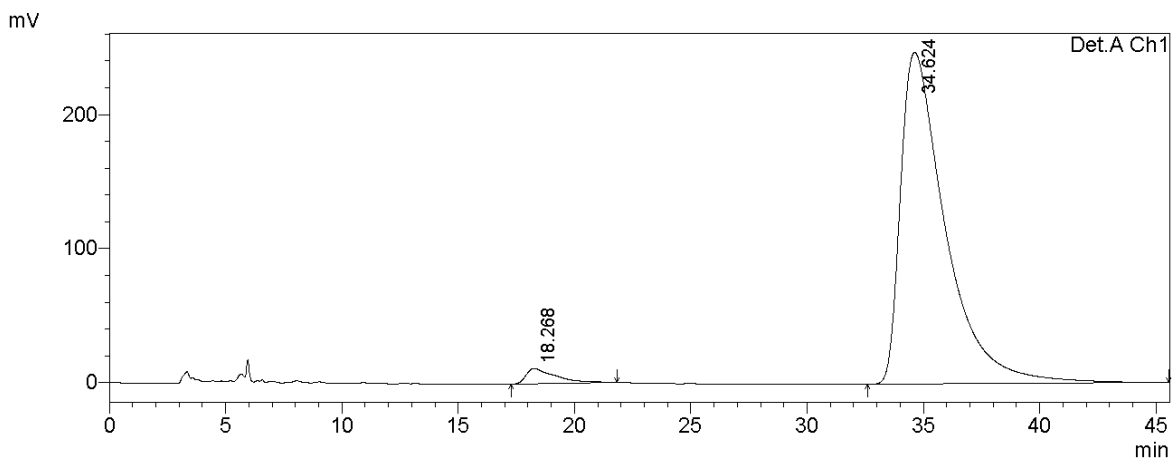
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.484	733265	11828	3.062	5.910
2	31.889	23212845	188325	96.938	94.090
Total		23946110	200153	100.000	100.000

(R)-2-(1-(4-Bromophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3f)



Detector A Ch1 254nm

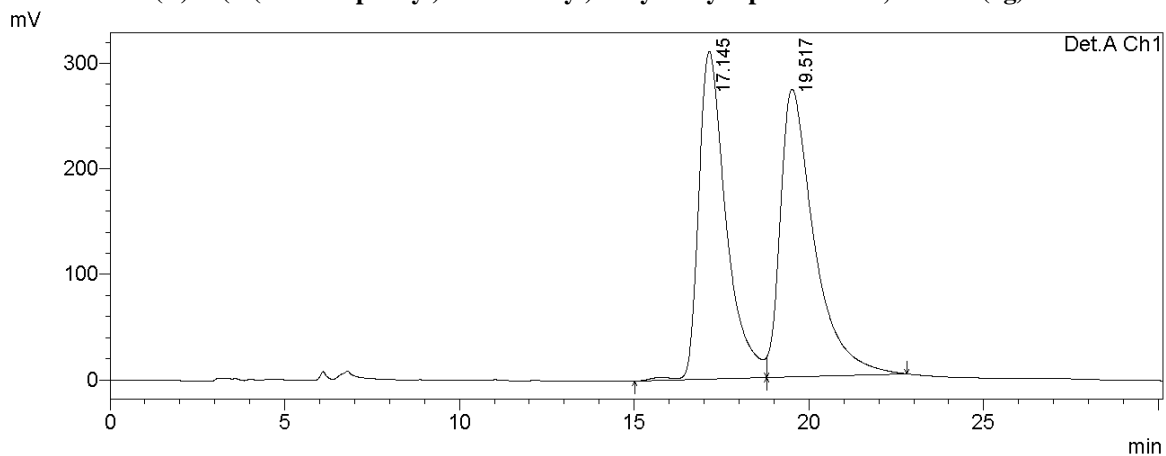
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.723	18365647	295124	51.428	69.861
2	34.777	17345931	127323	48.572	30.139
Total		35711578	422448	100.000	100.000



Detector A Ch1 254nm

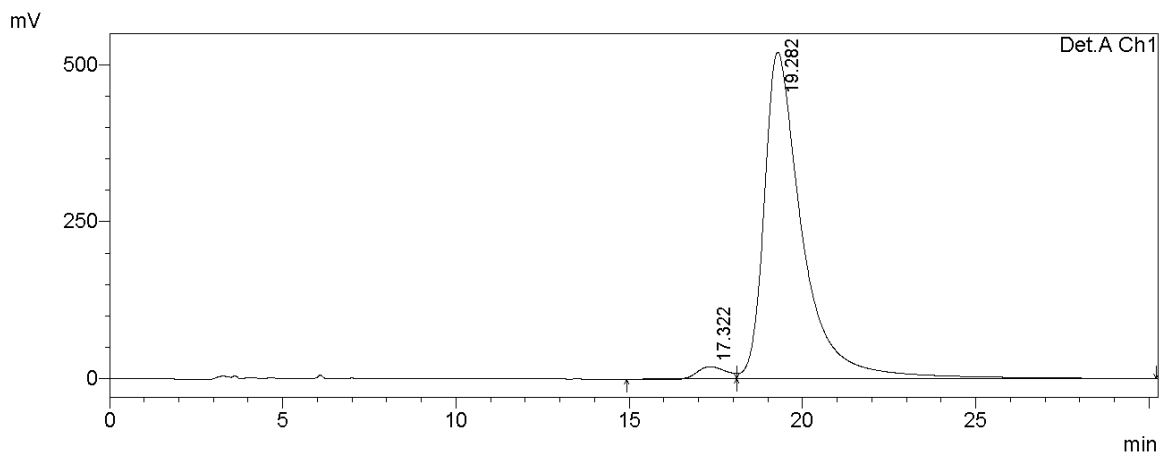
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.268	1010170	11394	2.944	4.402
2	34.624	33299762	247416	97.056	95.598
Total		34309931	258810	100.000	100.000

(R)-2-(1-(3-Chlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3g)



Detector A Ch1 254nm

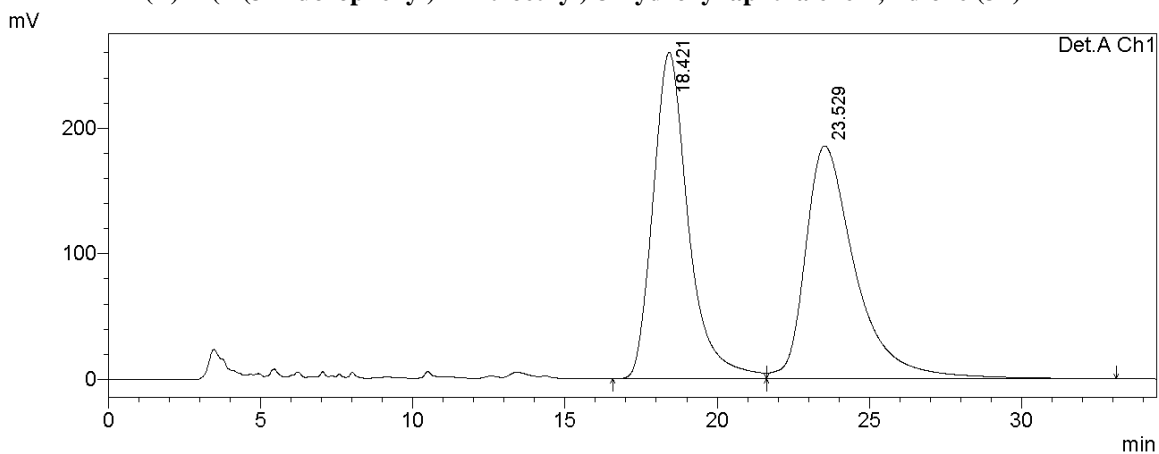
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.145	16941584	310582	47.935	53.238
2	19.517	18401321	272807	52.065	46.762
Total		35342904	583388	100.000	100.000



Detector A Ch1 254nm

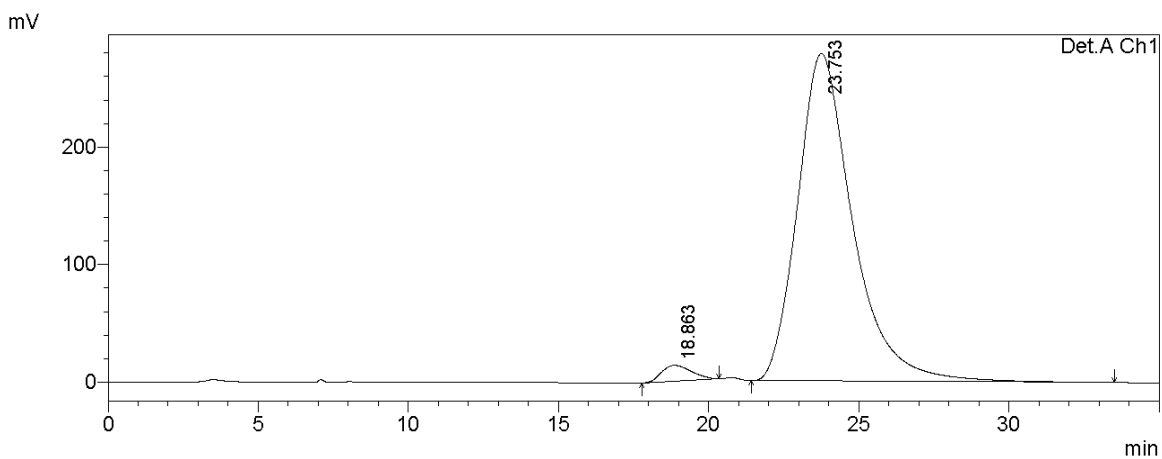
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.322	1178552	19655	2.849	3.644
2	19.282	40194115	519774	97.151	96.356
Total		41372667	539429	100.000	100.000

(R)-2-(1-(3-Fluorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3h)



Detector A Ch1 254nm

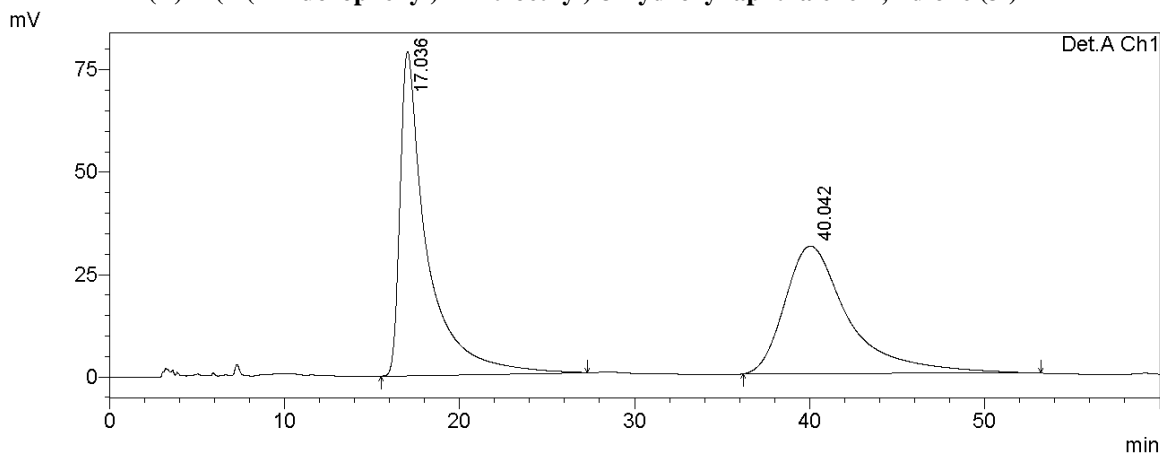
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.421	20977030	259891	49.809	58.373
2	23.529	21137741	185336	50.191	41.627
Total		42114771	445226	100.000	100.000



Detector A Ch1 254nm

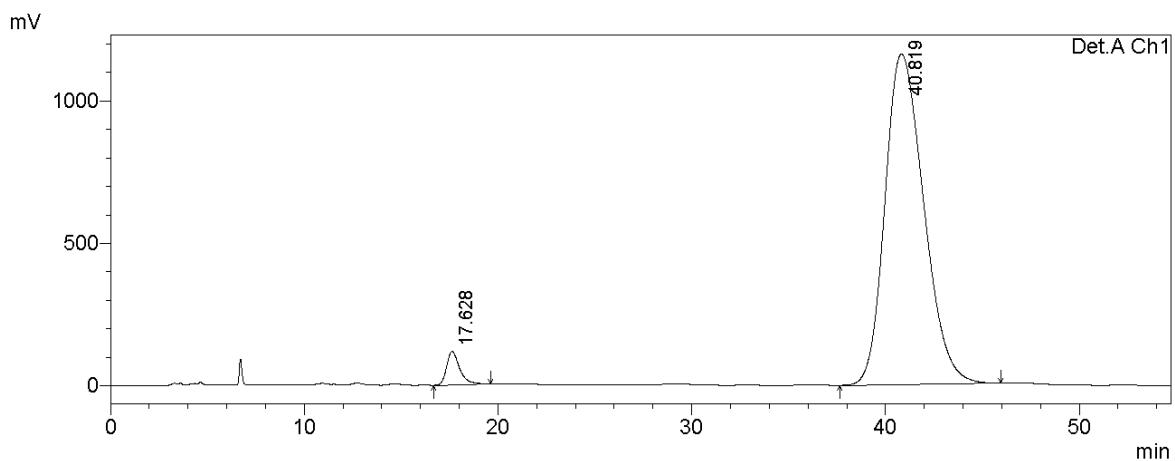
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.863	938678	13581	2.562	4.644
2	23.753	35697256	278846	97.438	95.356
Total		36635935	292426	100.000	100.000

(R)-2-(1-(2-Fluorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3i)



Detector A Ch1 254nm

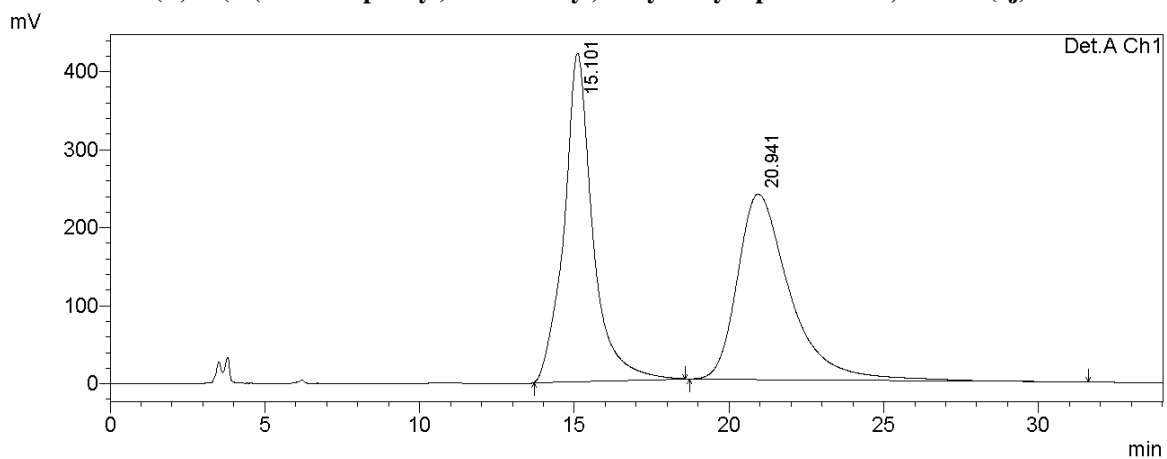
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.036	8452239	79152	51.576	71.732
2	40.042	7935676	31192	48.424	28.268
Total		16387915	110344	100.000	100.000



Detector A Ch1 254nm

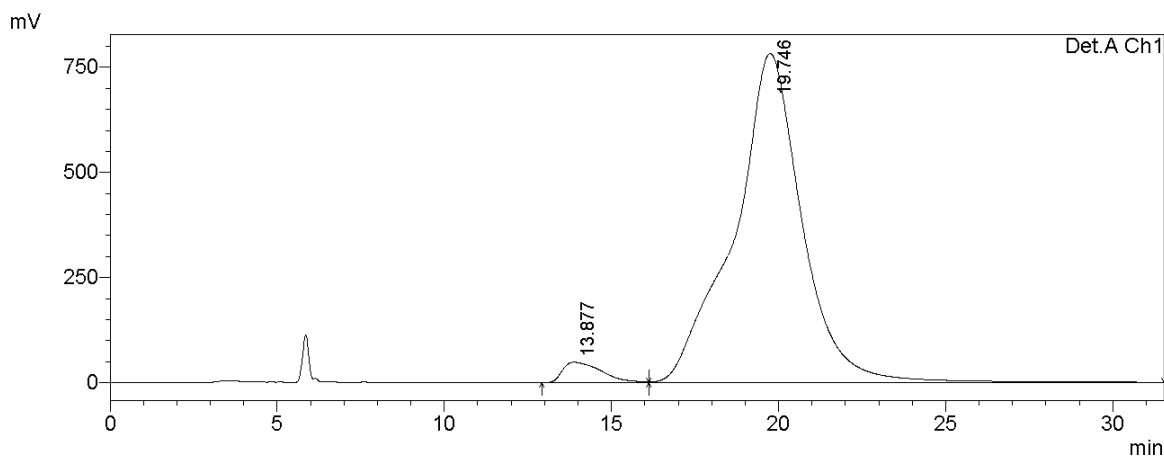
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.628	5507586	117613	3.301	9.201
2	40.819	161345163	1160678	96.699	90.799
Total		166852749	1278291	100.000	100.000

(R)-2-(1-(2-Chlorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3j)



Detector A Ch1 254nm

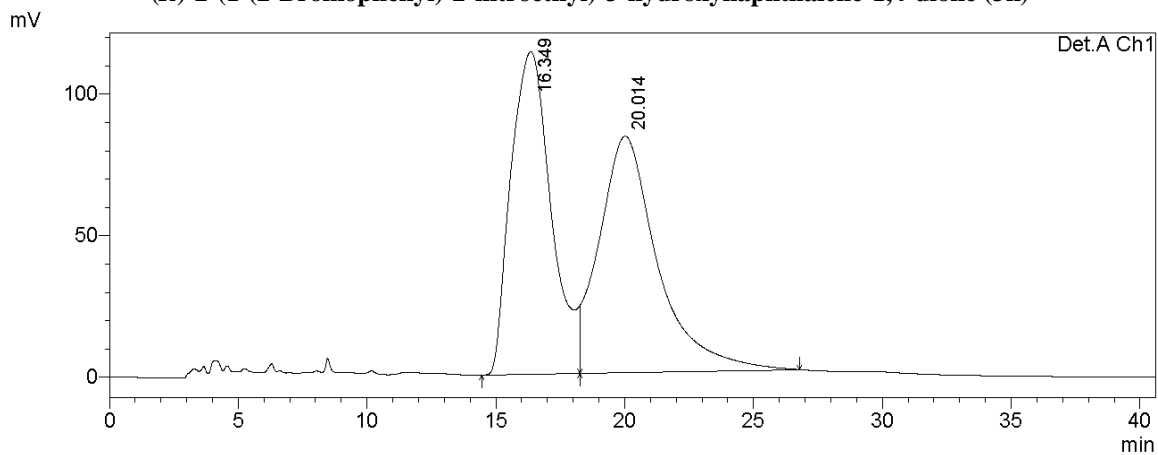
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.101	27136213	420343	49.253	63.895
2	20.941	27959128	237520	50.747	36.105
Total		55095341	657863	100.000	100.000



Detector A Ch1 254nm

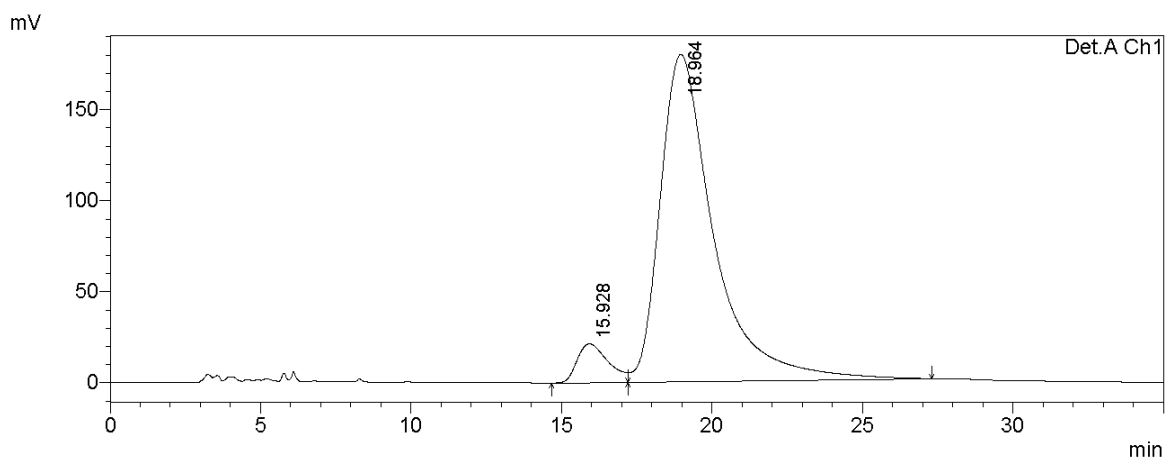
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.877	3870453	48292	3.386	5.812
2	19.746	110433094	782636	96.614	94.188
Total		114303547	830928	100.000	100.000

(R)-2-(1-(2-Bromophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3k)



Detector A Ch1 254nm

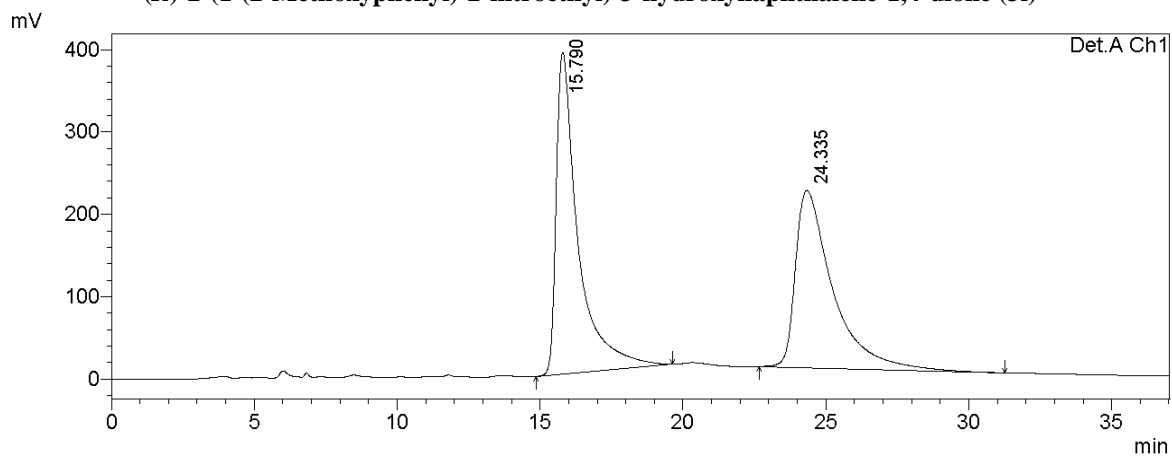
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.349	12430718	114048	48.535	57.717
2	20.014	13181372	83552	51.465	42.283
Total		25612090	197600	100.000	100.000



Detector A Ch1 254nm

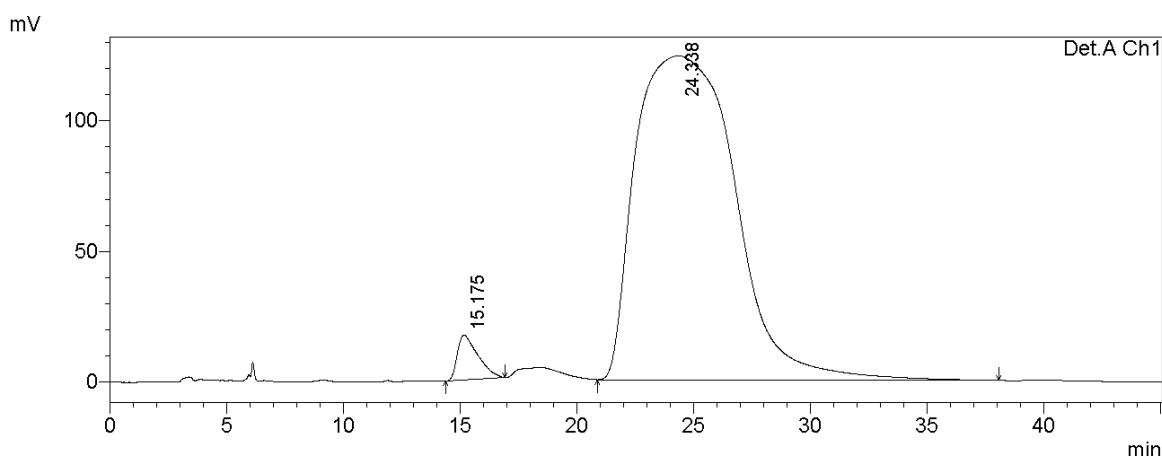
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.928	1527456	21250	6.416	10.575
2	18.964	22278611	179703	93.584	89.425
Total		23806067	200953	100.000	100.000

(R)-2-(1-(2-Methoxyphenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3I)



Detector A Ch1 254nm

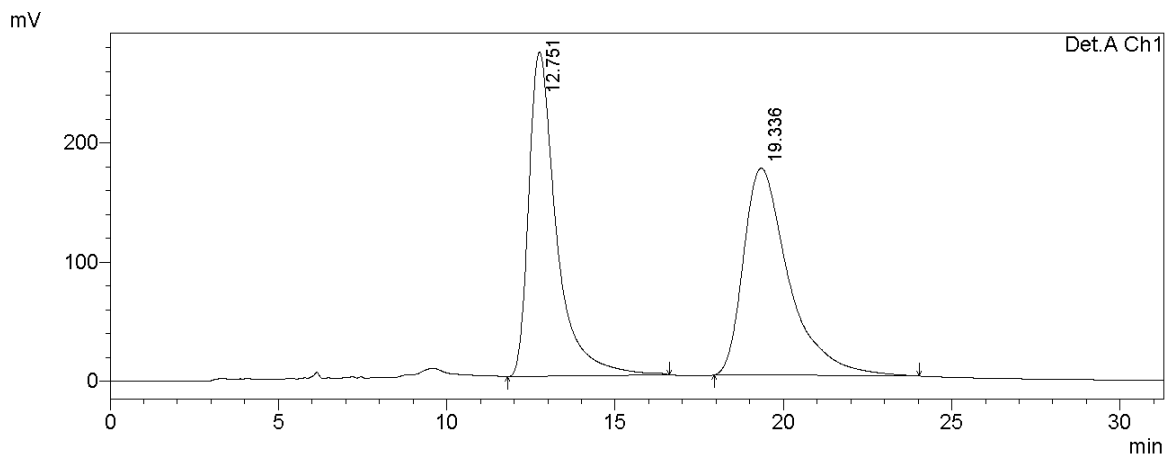
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.790	20857004	390975	51.622	64.471
2	24.335	19546447	215457	48.378	35.529
Total		40403451	606431	100.000	100.000



Detector A Ch1 254nm

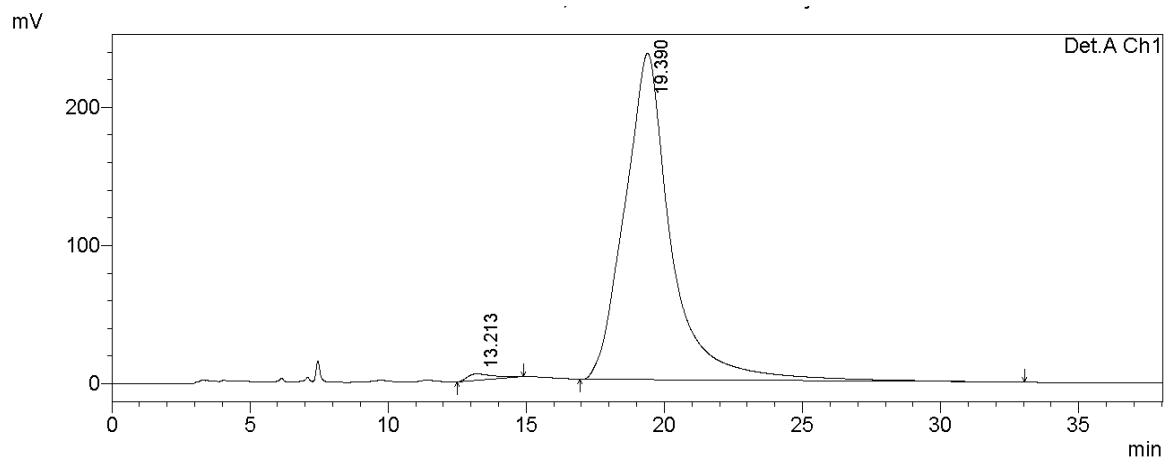
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.175	1059797	17233	2.802	12.214
2	24.338	36758065	123865	97.198	87.786
Total		37817862	141098	100.000	100.000

(R)-2-(1-(2,4-Dichlorophenyl)-2-nitroethyl)-3-hydroxy naphthalene-1,4-dione (3m)



Detector A Ch1 254nm

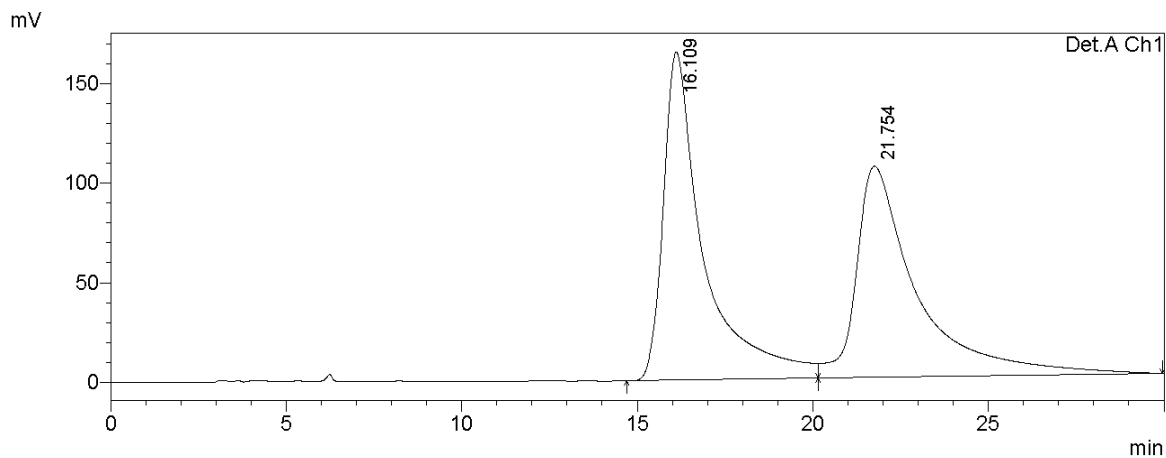
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.751	15586951	272454	48.869	61.048
2	19.336	16308154	173842	51.131	38.952
Total		31895105	446296	100.000	100.000



Detector A Ch1 254nm

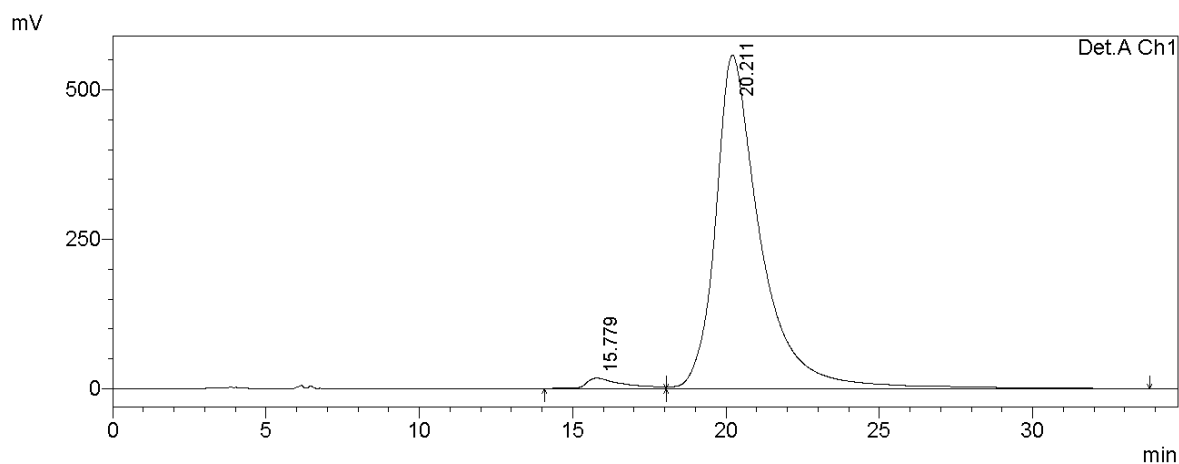
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.213	299763	4645	1.070	1.927
2	19.390	27722208	236440	98.930	98.073
Total		28021971	241085	100.000	100.000

(R)-2-(1-(3,4-Dichlorophenyl)-2-nitroethyl)-3-hydroxy naphthalene-1,4-dione (3n)



Detector A Ch1 254nm

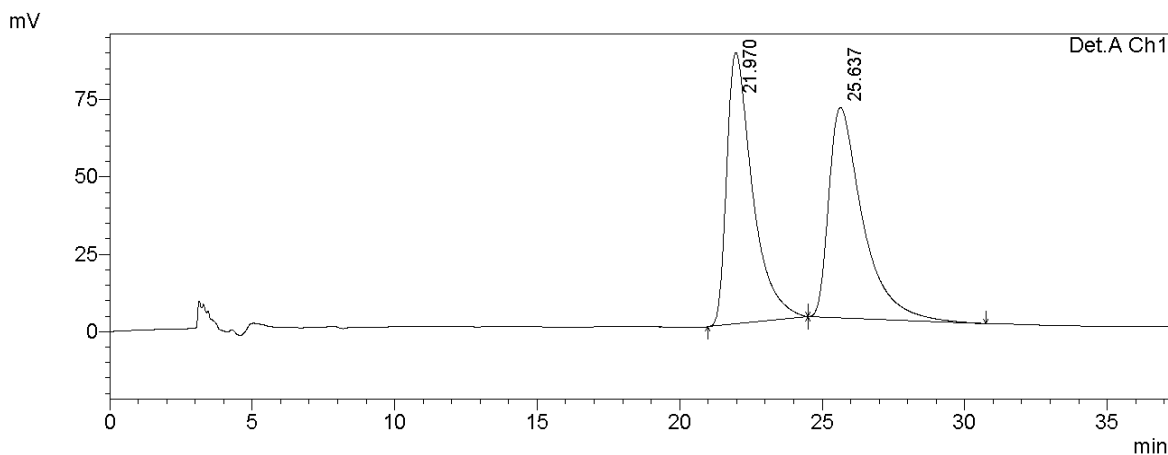
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.109	13174754	164773	50.764	60.832
2	21.754	12778122	106092	49.236	39.168
Total		25952876	270865	100.000	100.000



Detector A Ch1 254nm

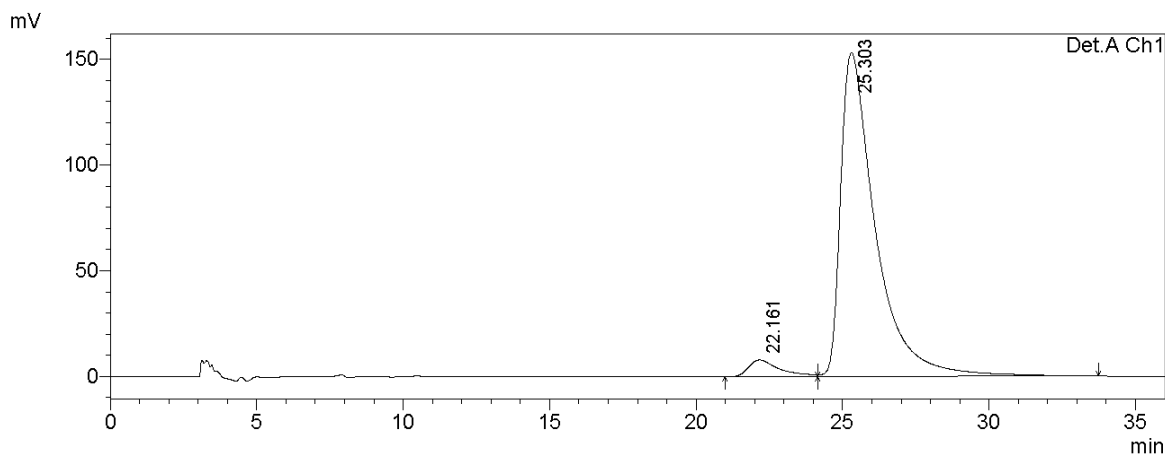
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.779	1379185	17233	2.354	2.996
2	20.211	57209755	557978	97.646	97.004
Total		58588940	575211	100.000	100.000

(R)-2-(1-(3,5-Dimethylphenyl)-2-nitroethyl)-3-hydroxy naphthalene-1,4-dione (3o)



Detector A Ch1 254nm

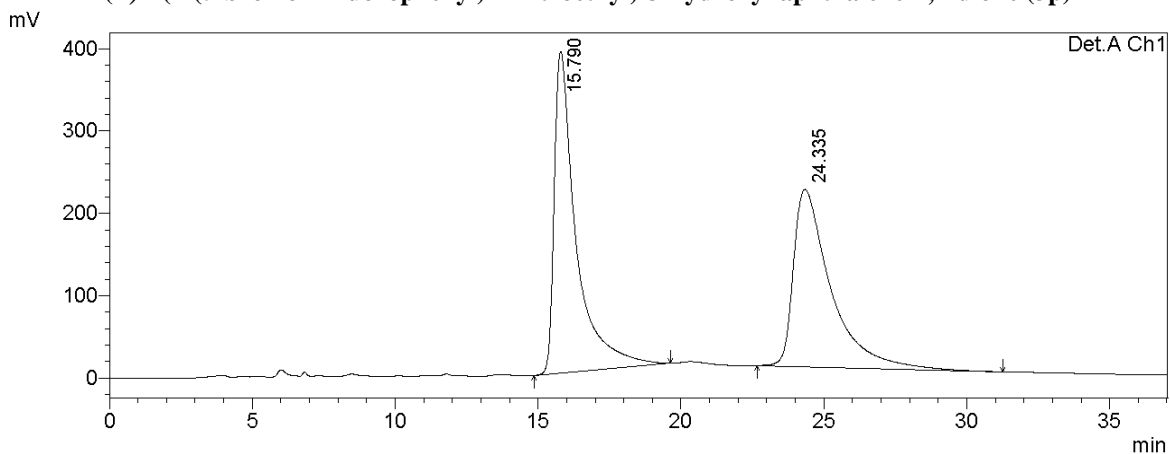
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.970	5539139	87668	49.652	56.337
2	25.637	5616708	67946	50.348	43.663
Total		11155847	155613	100.000	100.000



Detector A Ch1 254nm

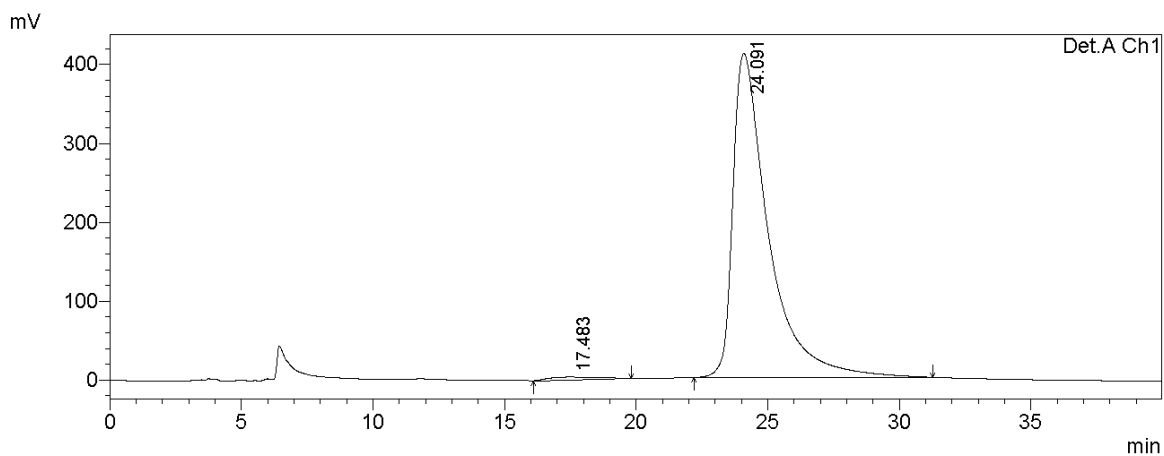
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.161	594352	7982	4.469	4.951
2	25.303	12704599	153235	95.531	95.049
Total		13298952	161217	100.000	100.000

(R)-2-(1-(5-bromo-2-fluorophenyl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3p)



Detector A Ch1 254nm

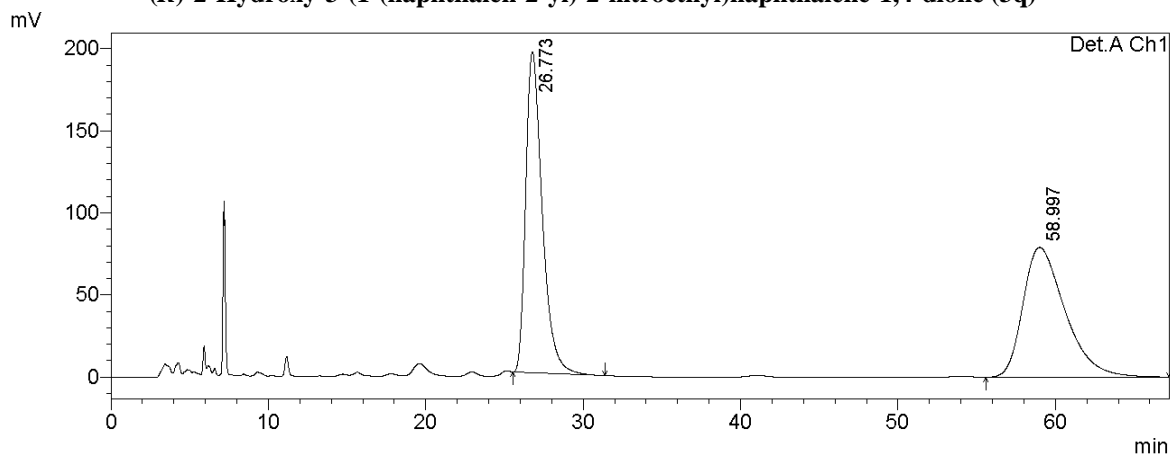
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.790	20857004	390975	51.622	64.471
2	24.335	19546447	215457	48.378	35.529
Total		40403451	606431	100.000	100.000



Detector A Ch1 254nm

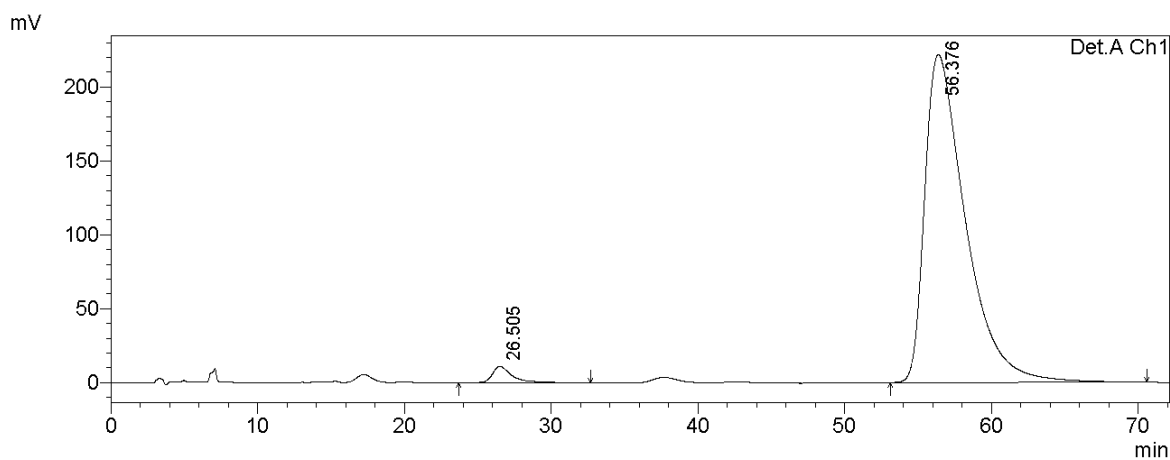
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.483	430700	3429	1.103	0.827
2	24.091	38602659	411026	98.897	99.173
Total		39033360	414456	100.000	100.000

(R)-2-Hydroxy-3-(1-(naphthalen-2-yl)-2-nitroethyl)naphthalene-1,4-dione (3q)



Detector A Ch1 254nm

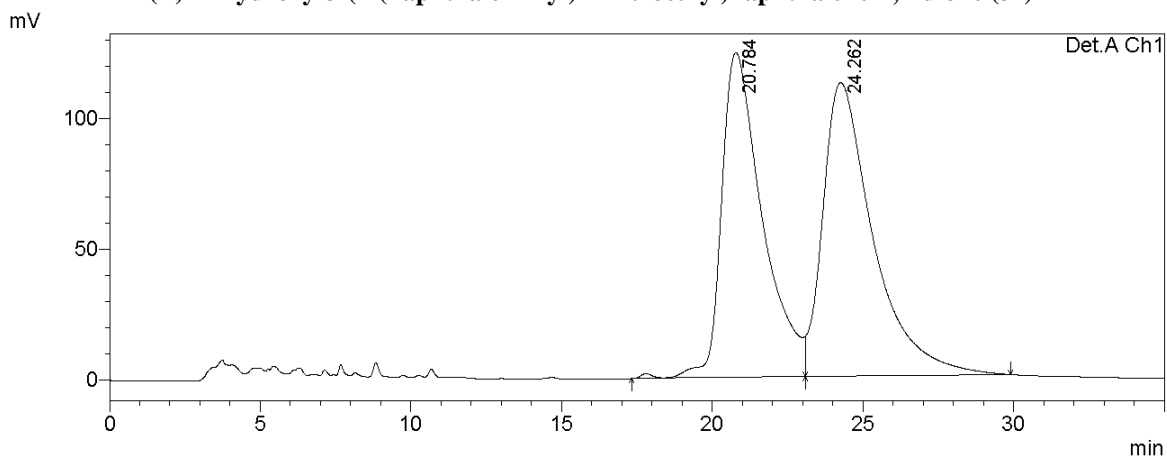
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.773	14295990	195558	49.336	71.223
2	58.997	14680910	79012	50.664	28.777
Total		28976899	274569	100.000	100.000



Detector A Ch1 254nm

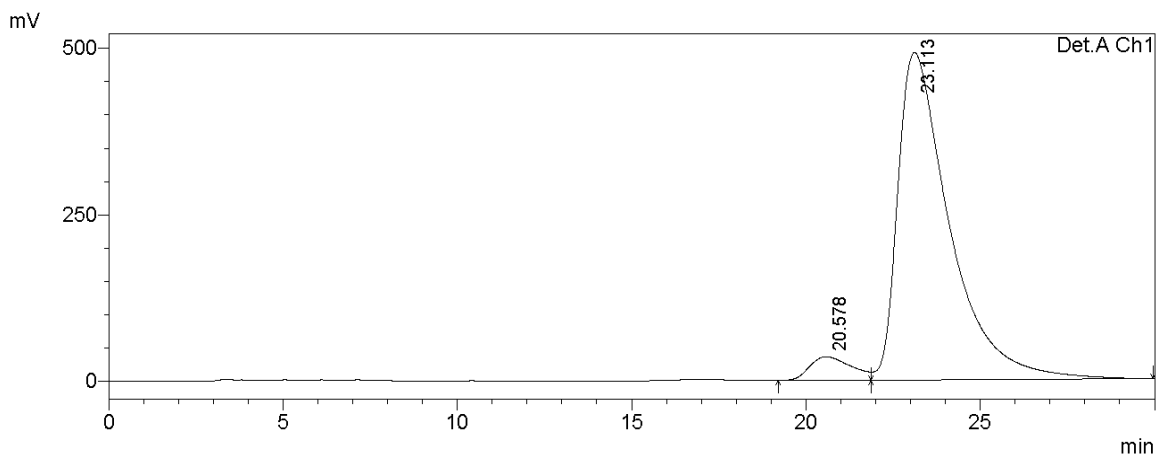
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.505	1118605	11212	2.546	4.811
2	56.376	42819353	221824	97.454	95.189
Total		43937958	233036	100.000	100.000

(R)-2-Hydroxy-3-(1-(naphthalen-1-yl)-2-nitroethyl)naphthalene-1,4-dione (3r)



Detector A Ch1 254nm

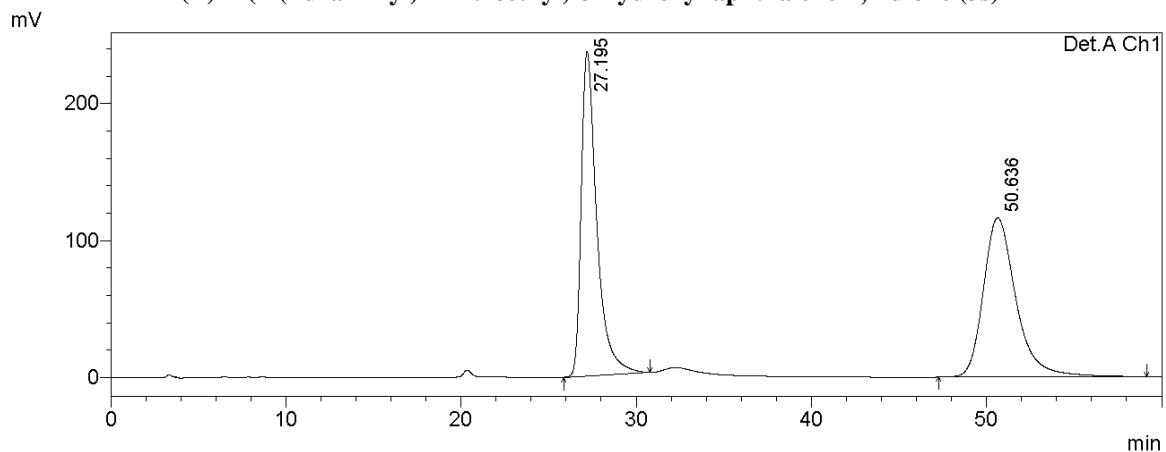
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.784	11726836	124215	47.400	52.500
2	24.262	13013237	112384	52.600	47.500
Total		24740073	236599	100.000	100.000



Detector A Ch1 254nm

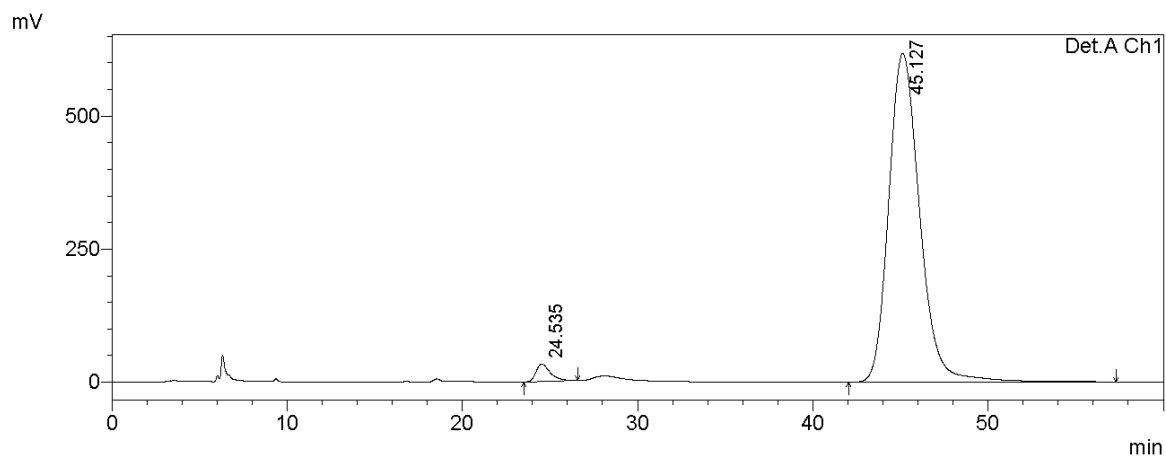
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.578	2920927	35142	5.420	6.666
2	23.113	50966085	492010	94.580	93.334
Total		53887012	527152	100.000	100.000

(R)-2-(1-(Furan-2-yl)-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3s)



Detector A Ch1 254nm

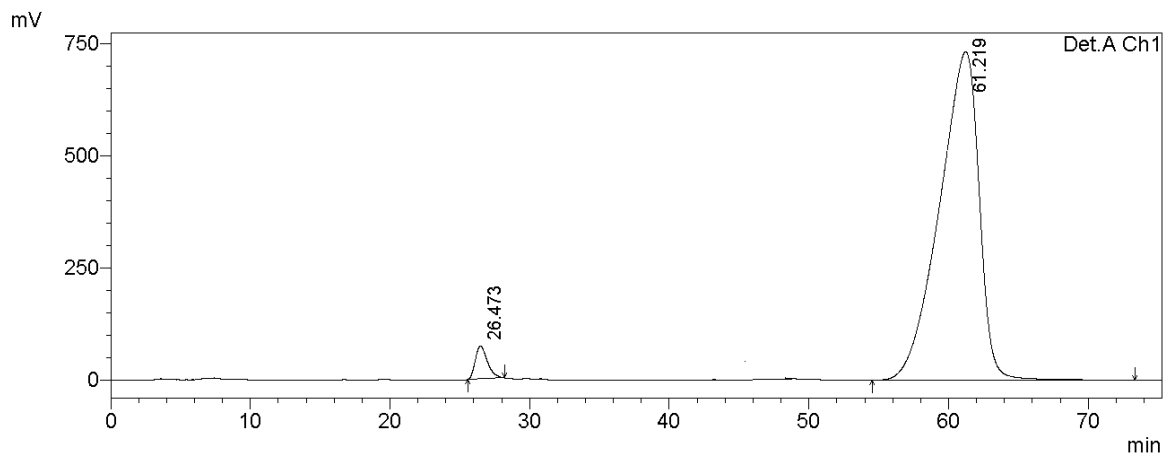
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.195	14632238	237010	49.233	67.099
2	50.636	15087905	116213	50.767	32.901
Total		29720143	353223	100.000	100.000



Detector A Ch1 254nm

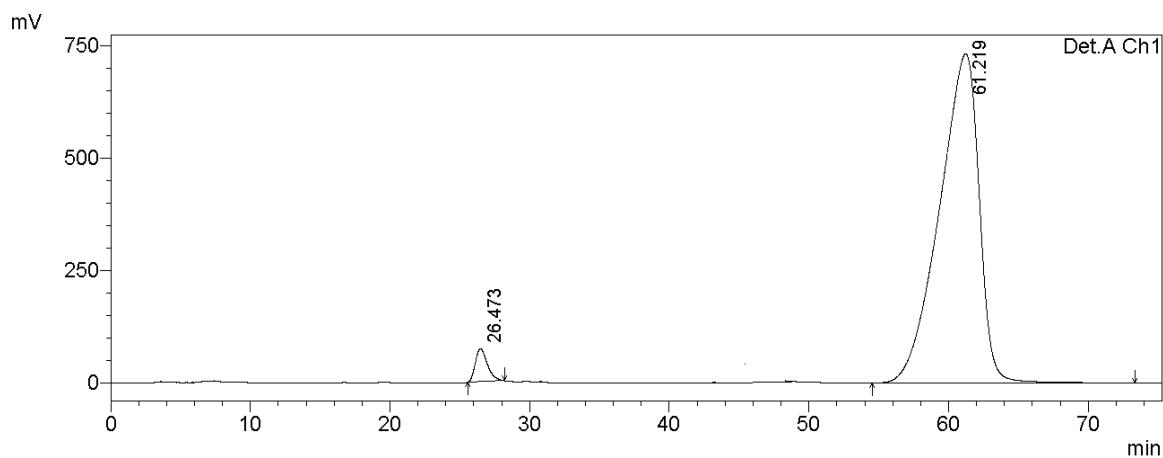
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.535	1858920	32684	2.387	5.027
2	45.127	76020666	617438	97.613	94.973
Total		77879586	650123	100.000	100.000

(R)-2-Hydroxy-3-(2-nitro-1-(thiophen-2-yl)ethyl)naphthalene-1,4-dione (3t)



Detector A Ch1 254nm

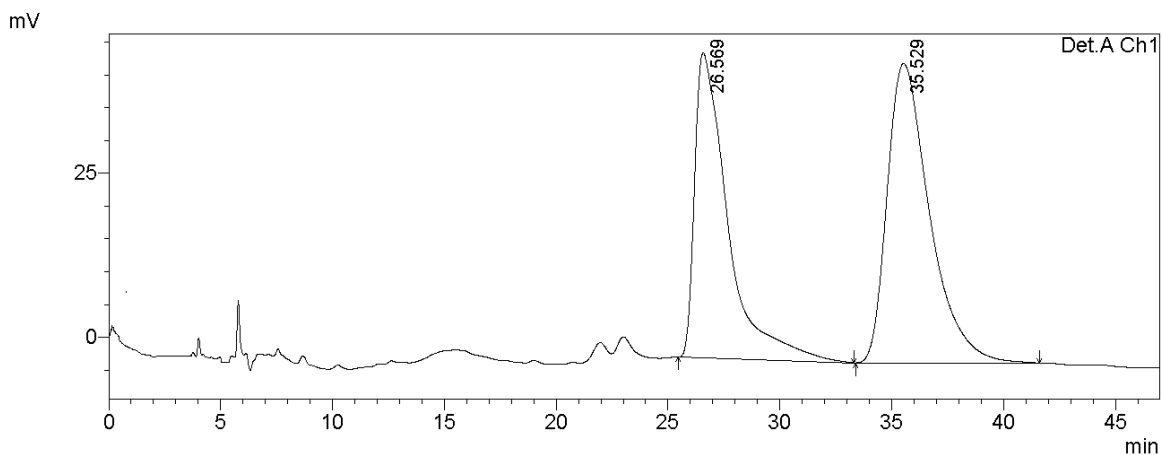
Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.433	23299838	398432	49.528	71.133
2	56.176	23744006	161688	50.472	28.867
Total		47043843	560121	100.000	100.000



Detector A Ch1 254nm

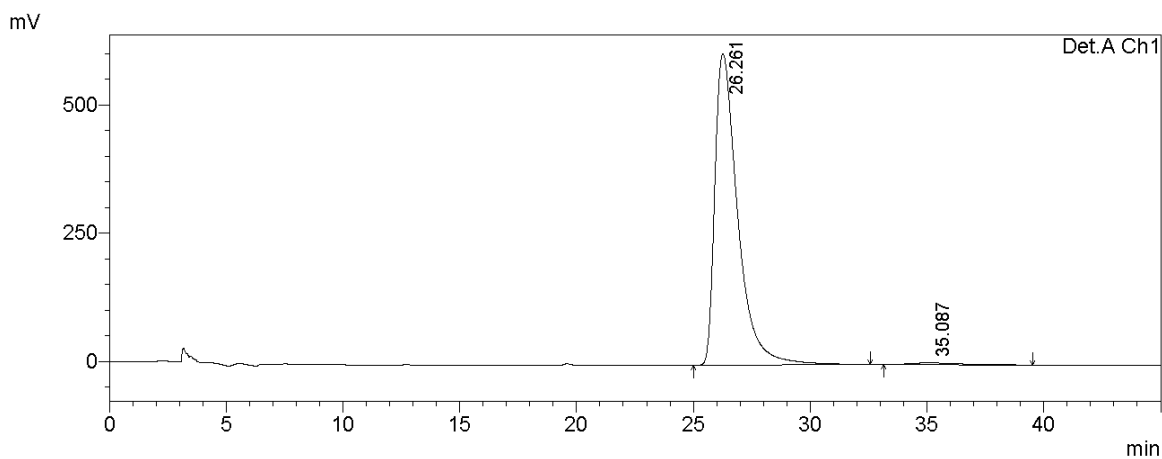
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.473	4404380	73141	2.954	9.079
2	61.219	144690645	732457	97.046	90.921
Total		149095025	805598	100.000	100.000

(S)-2-(1-Cyclohexyl-2-nitroethyl)-3-hydroxynaphthalene-1,4-dione (3u)



Detector A Ch1 254nm

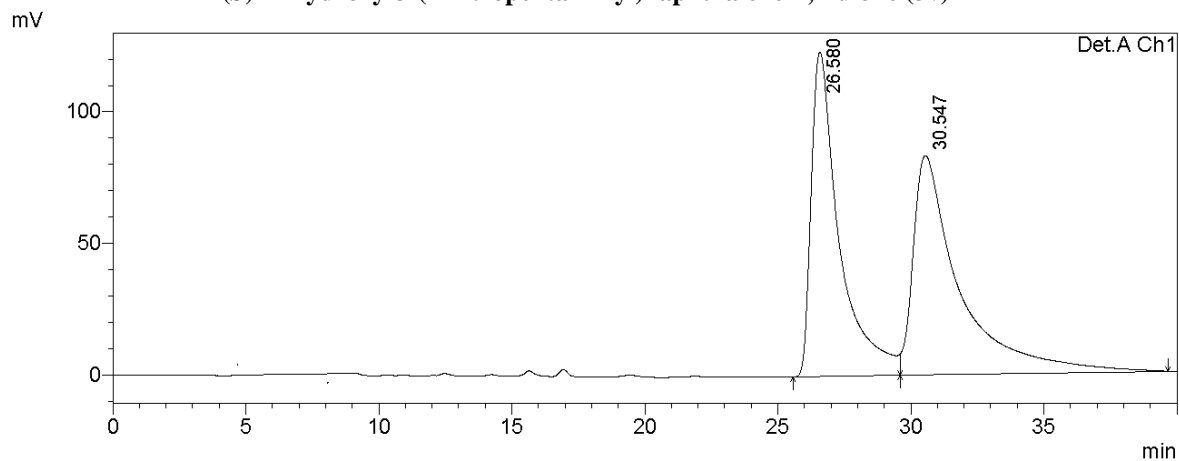
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.569	4802558	46619	44.413	50.503
2	35.529	6010759	45691	55.587	49.497
Total		10813317	92310	100.000	100.000



Detector A Ch1 254nm

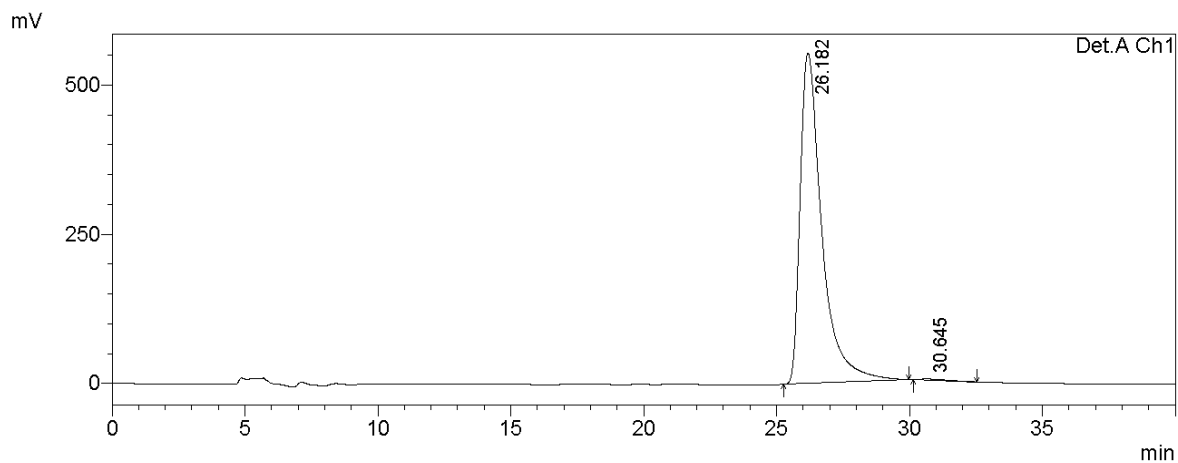
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.261	41415839	606387	98.732	99.413
2	35.087	531990	3583	1.268	0.587
Total		41947829	609970	100.000	100.000

(S)-2-Hydroxy-3-(1-nitropentan-2-yl)naphthalene-1,4-dione (3v)



Detector A Ch1 254nm

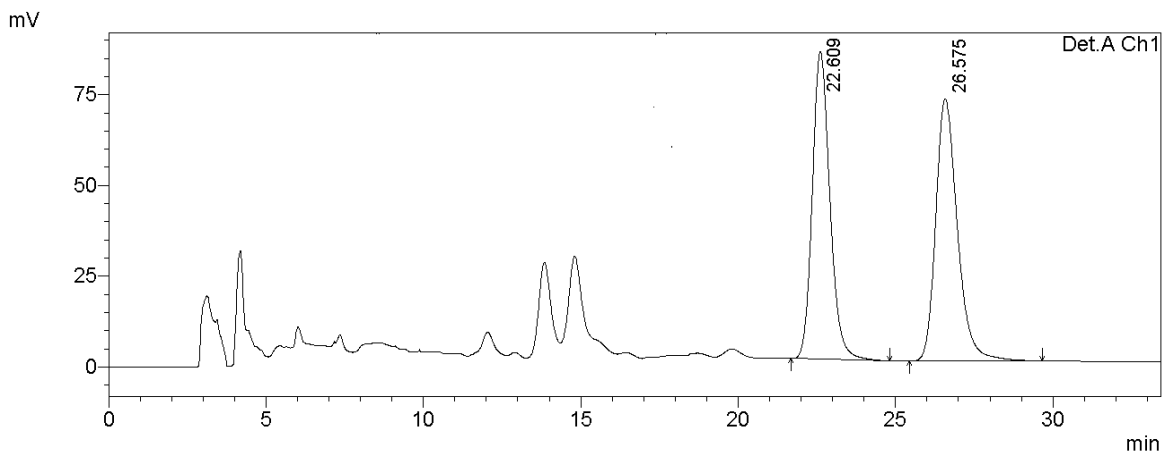
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.580	9038506	123331	47.093	59.665
2	30.547	10154558	83374	52.907	40.335
Total		19193064	206705	100.000	100.000



Detector A Ch1 254nm

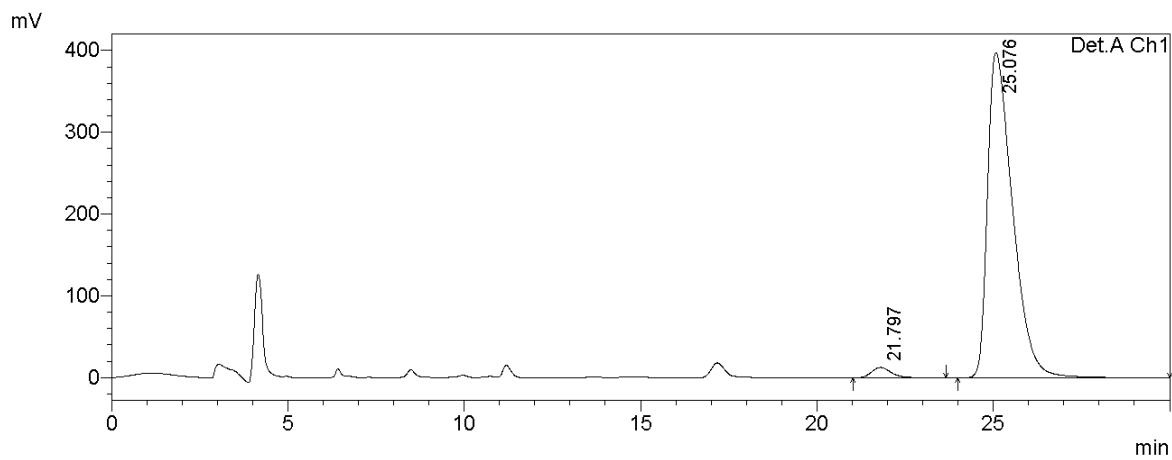
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.182	31435082	553306	99.621	99.708
2	30.645	119677	1619	0.379	0.292
Total		31554759	554925	100.000	100.000

2-Hydroxy-3-((1R,2S)-2-nitro-1-phenylpropyl)naphthalene-1,4-dione (5a)



Detector A Ch1 220nm

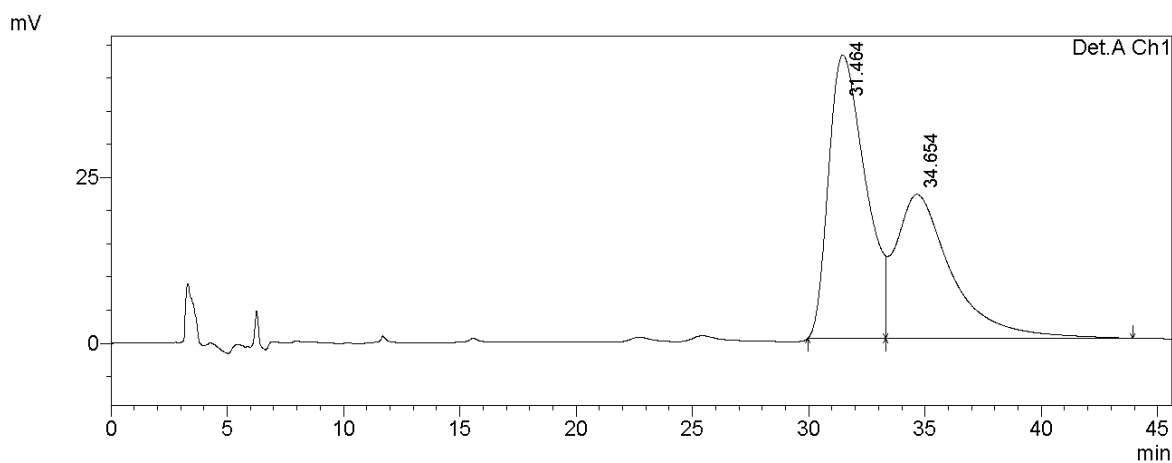
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.609	3300195	84745	48.860	53.995
2	26.575	3454245	72204	51.140	46.005
Total		6754439	156948	100.000	100.000



Detector A Ch1 220nm

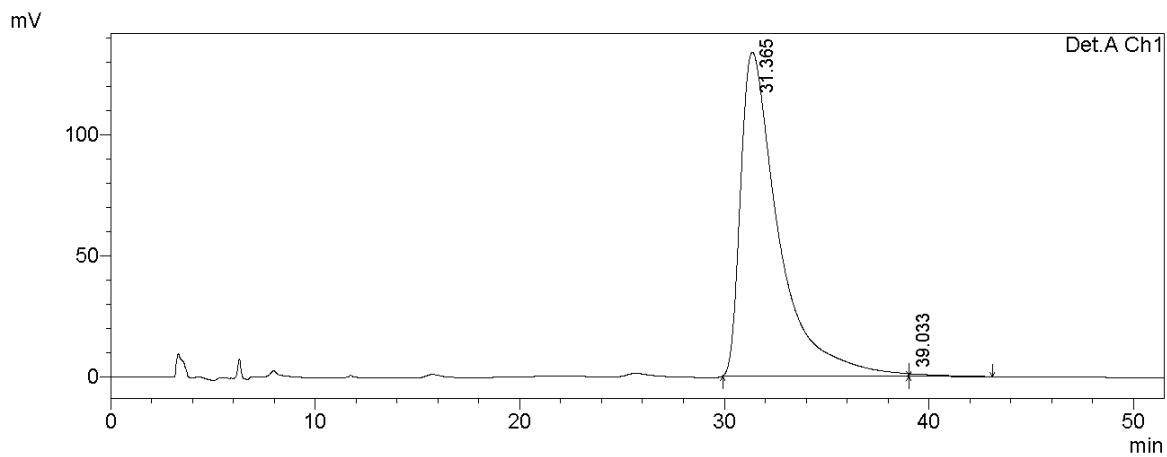
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.797	496452	12693	2.461	3.094
2	25.076	19678651	397538	97.539	96.906
Total		20175103	410231	100.000	100.000

2-hydroxy-3-((1R,2S)-2-nitro-1-phenylbutyl)naphthalene-1,4-dione (5b)



Detector A Ch1 254nm

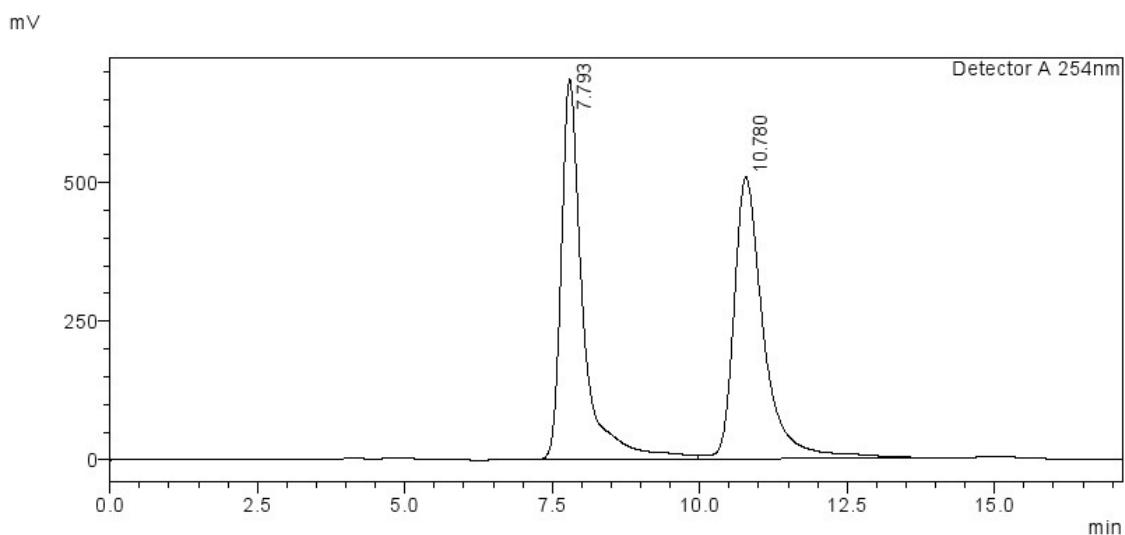
Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.464	4720975	42746	56.500	66.302
2	34.654	3634716	21726	43.500	33.698
Total		8355691	64472	100.000	100.000



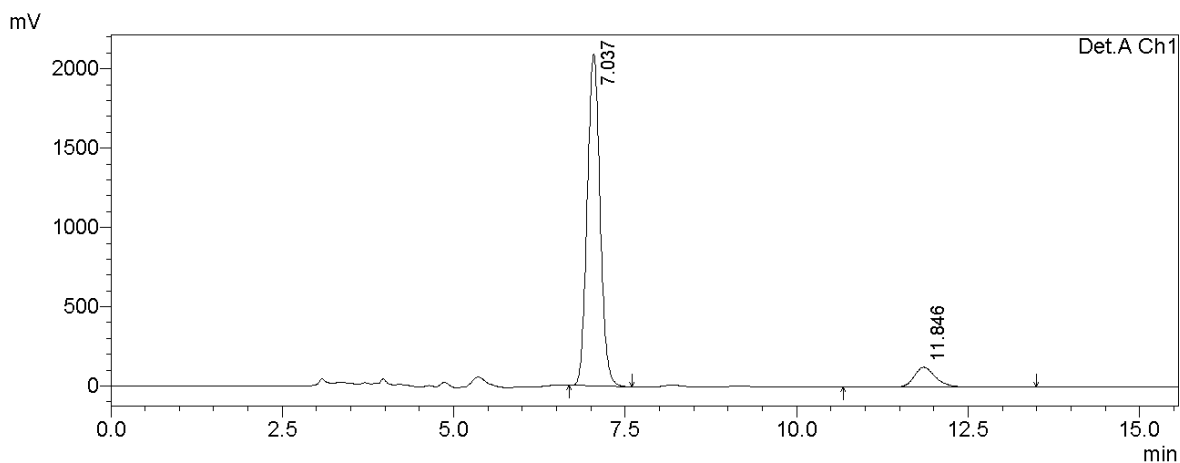
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.365	17282616	133587	99.397	99.156
2	39.033	104855	1138	0.603	0.844
Total		17387471	134724	100.000	100.000

(S)-3-[1-(4-Methylphenyl)-2-nitroethyl]pentane-2,4-dione (7b)



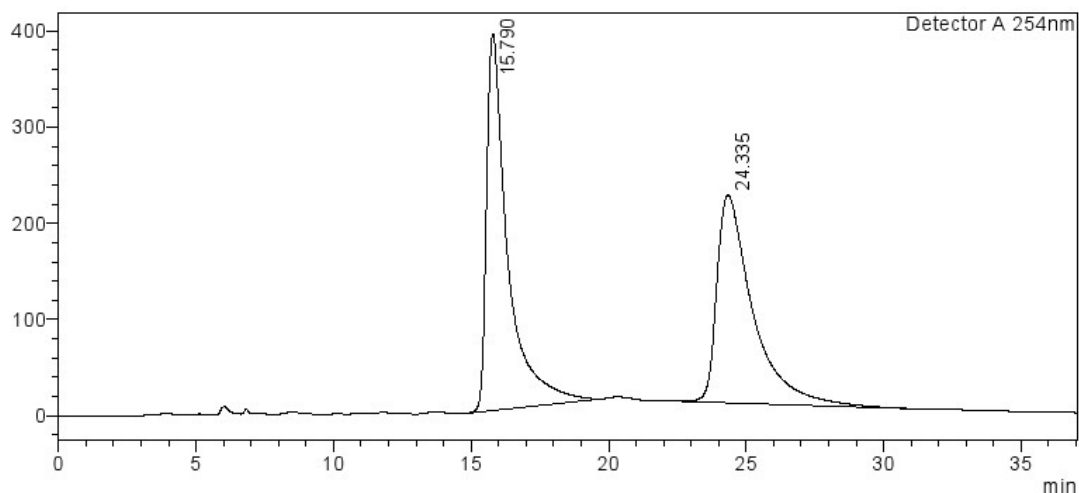
Peak#	Ret. Time	Area	Height	Area%
1	7.793	17552919	686447	49.606
2	10.780	17831759	507377	50.394
Total		35384678	1193825	100.000



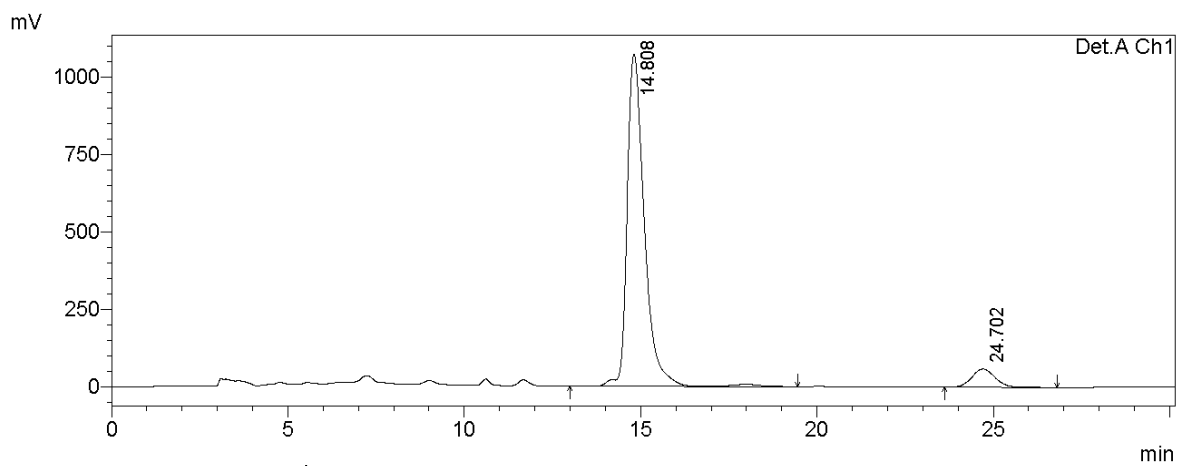
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.037	27393422	2092612	90.893	94.332
2	11.846	2744823	125743	9.107	5.668
Total		30138244	2218356	100.000	100.000

(S)-3-[1-(4-Bromophenyl)-2-nitroethyl]pentane-2,4-dione (7d)



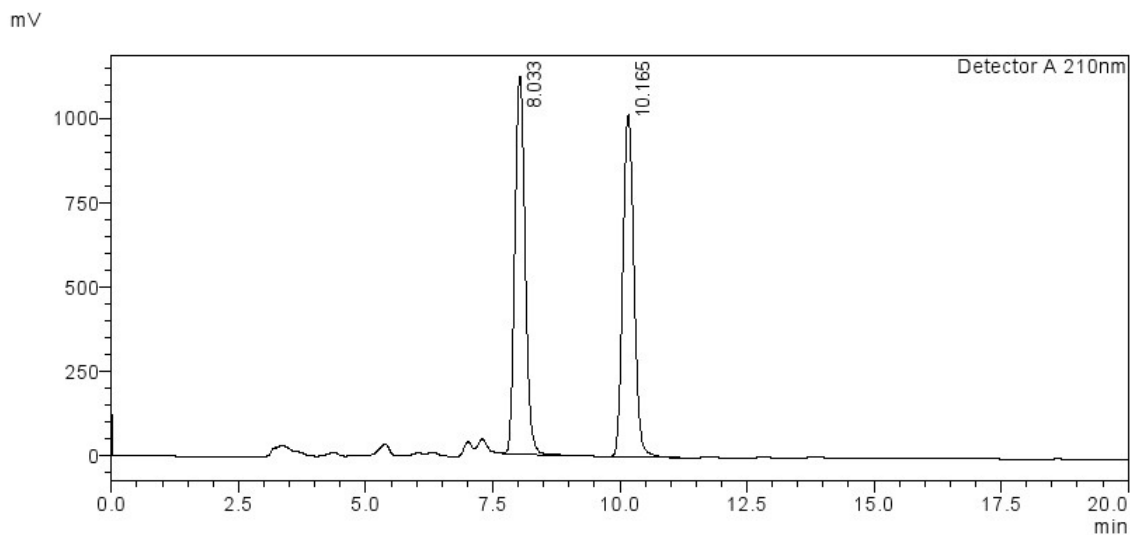
Peak#	Ret. Time	Area	Height	Area%
1	15.790	20857004	390975	51.622
2	24.335	19546447	215457	48.378
Total		40403451	606431	100.000



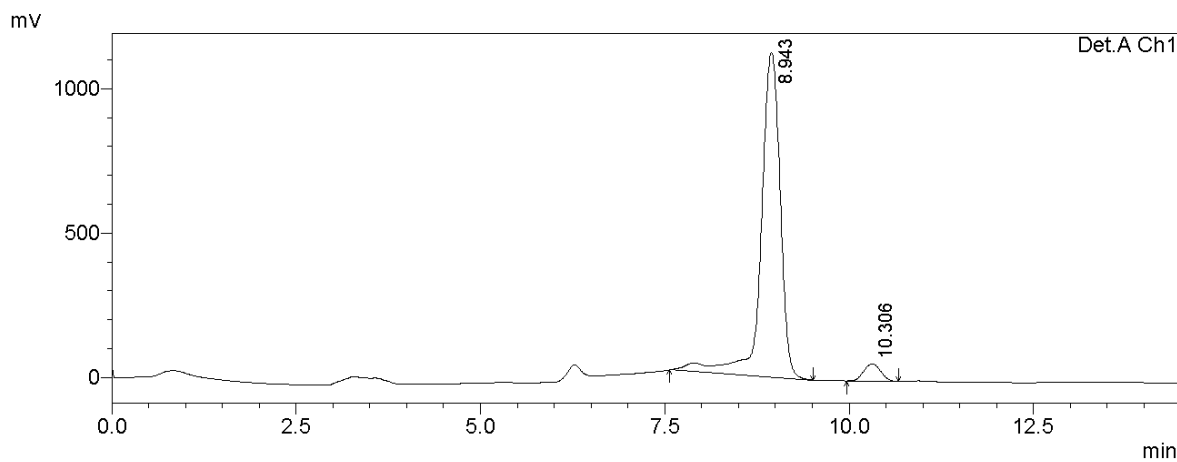
Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.808	36589952	1073383	93.246	94.829
2	24.702	2650213	58536	6.754	5.171
Total		39240165	1131919	100.000	100.000

(S)-3-[1-(Furan-2-yl)-2-nitroethyl]pentane-2,4-dione (7e)

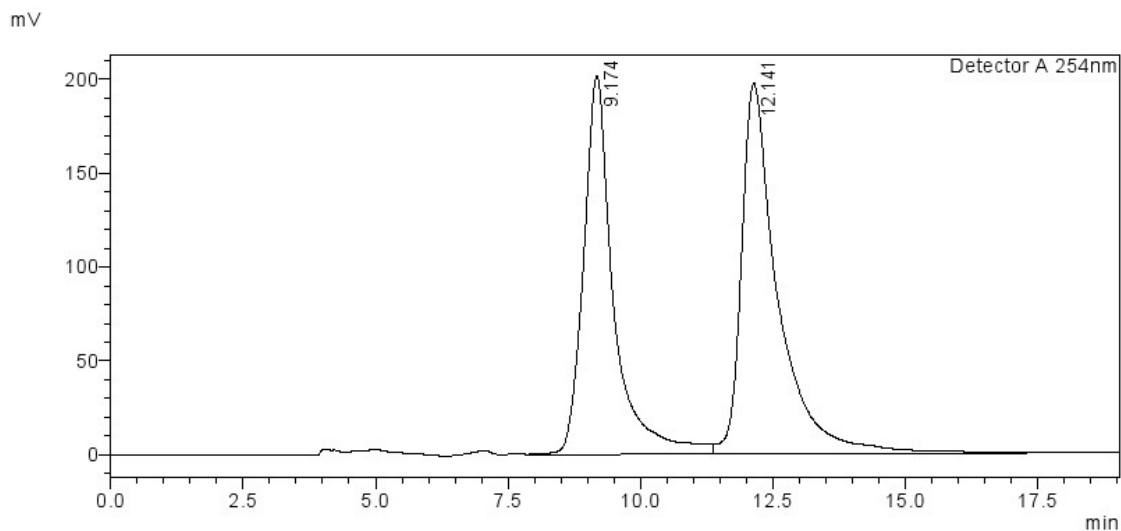


Peak#	Ret. Time	Area	Height	Conc.
1	8.033	15766517	1119028	50.254
2	10.165	15607239	1014896	49.746
Total		31373757	2133924	

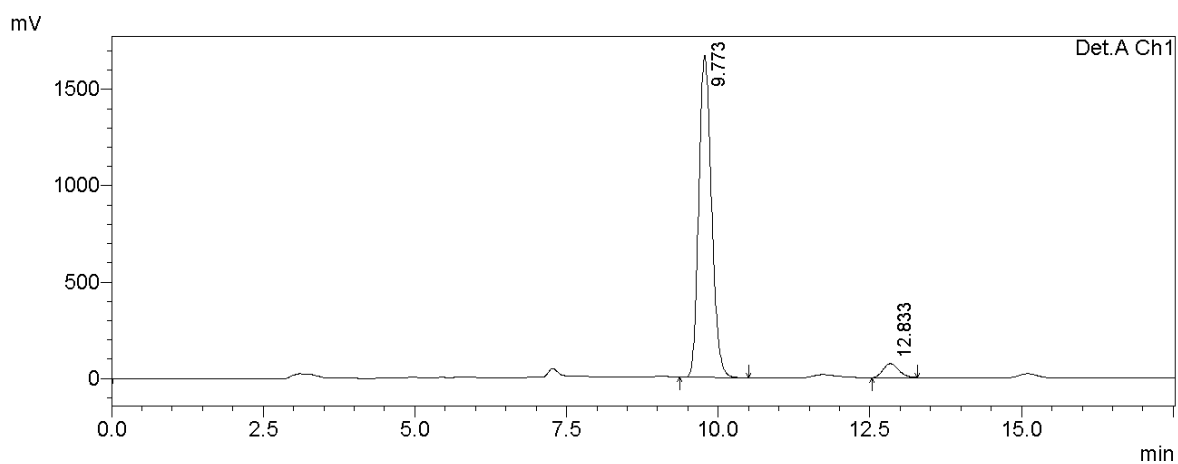


Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.943	20586553	1124989	95.499	94.928
2	10.306	970358	60105	4.501	5.072
Total		21556911	1185094	100.000	100.000

(S)-3-[1-(Thiophen-2-yl)-2-nitroethyl]pentane-2,4-dione(7f)



Peak#	Ret. Time	Area	Height	Area%
1	9.174	7960069	201483	45.742
2	12.141	9442192	197248	54.258
Total		17402261	398731	100.000

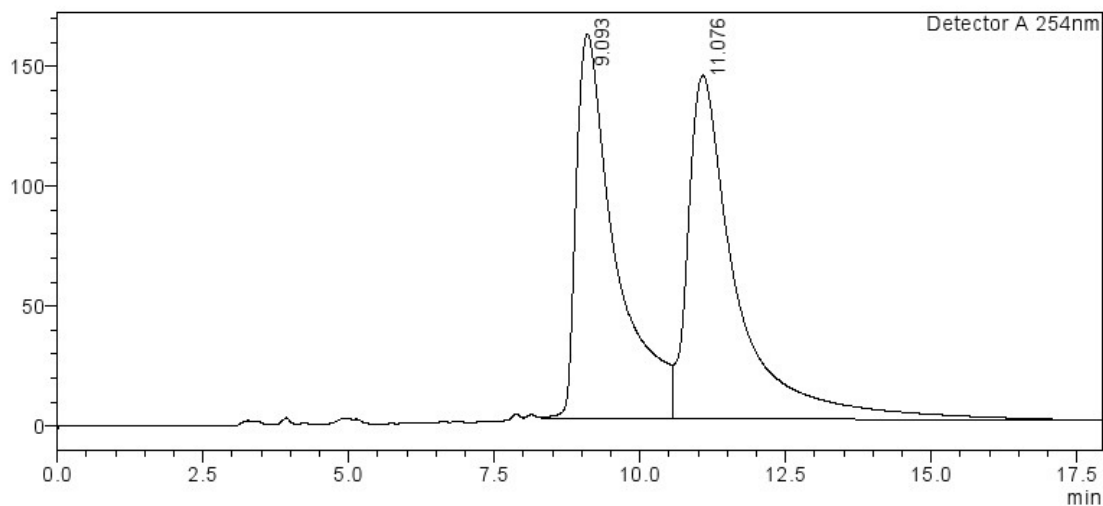


Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.773	24577069	1671969	95.020	95.837
2	12.833	1288060	72628	4.980	4.163
Total		25865129	1744597	100.000	100.000

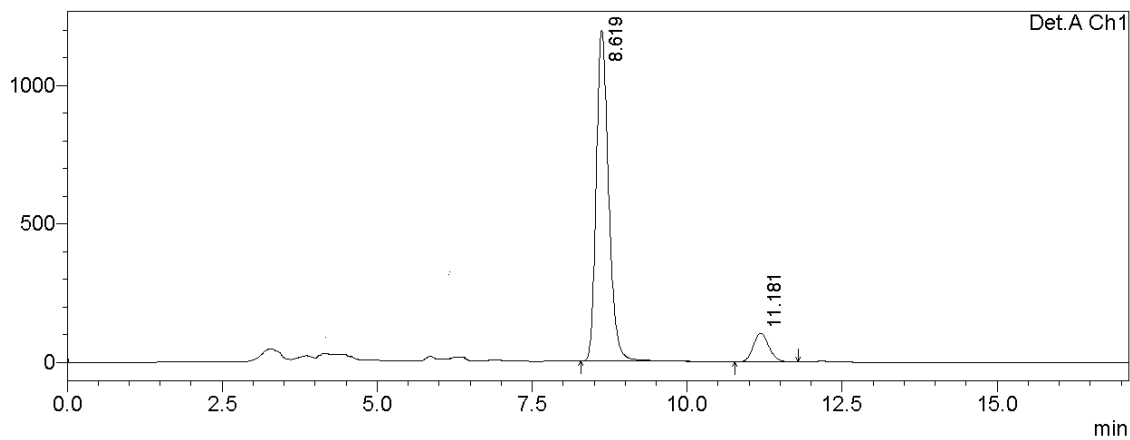
(S)-3-[1-(4-Benzyloxyphenyl)-2-nitroethyl]pentane-2,4-dione (7i)

mV



Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.093	7471877	160144	47.267	52.795
2	11.076	8336085	143189	52.733	47.205
Total		15807963	303334	100.000	100.000

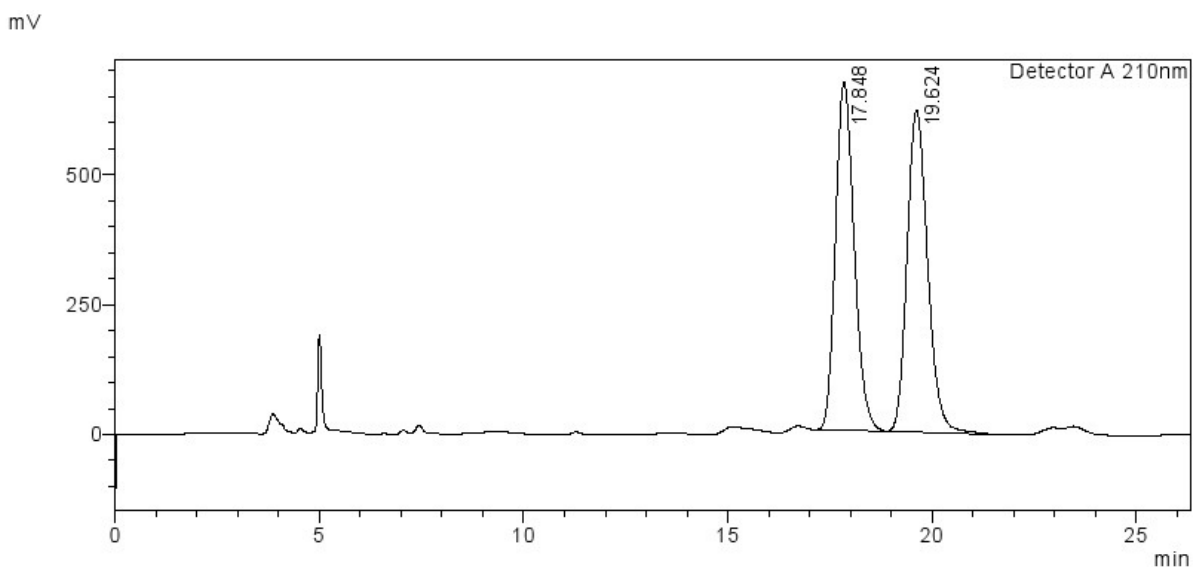
mV



Detector A Ch1 210nm

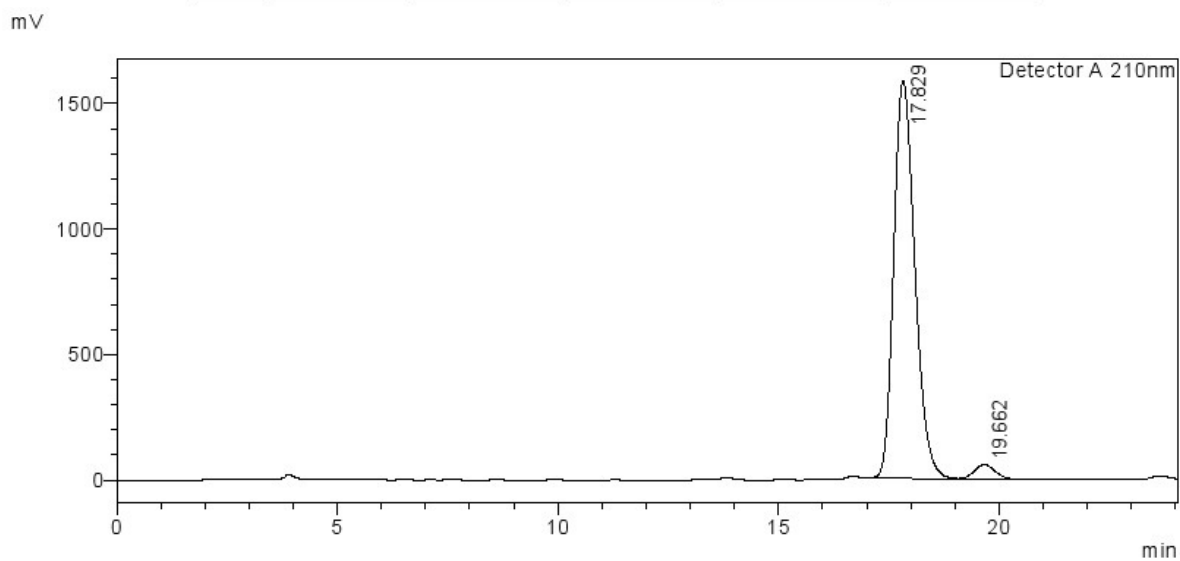
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.619	16793519	1195105	90.265	92.016
2	11.181	1811224	103702	9.735	7.984
Total		18604743	1298807	100.000	100.000

(S)-3-[1-(2-Benzoyloxyphenyl)-2-nitroethyl]pentane-2,4-dione(7j)



Detector A 210nm

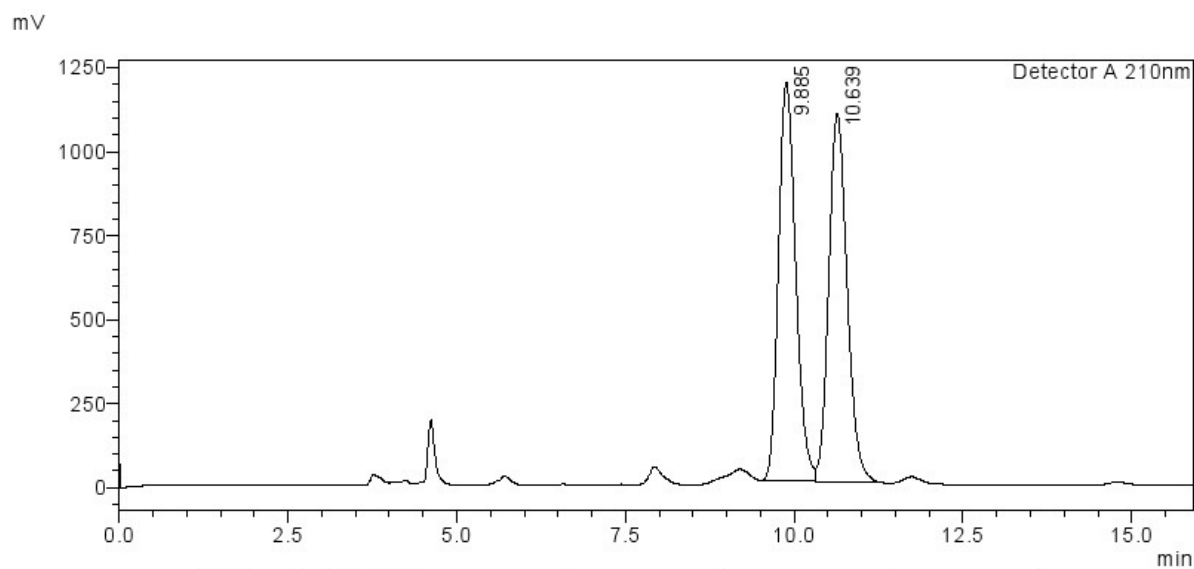
Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.848	21376383	670582	49.629	51.972
2	19.624	21695881	619684	50.371	48.028
Total		43072265	1290266	100.000	100.000



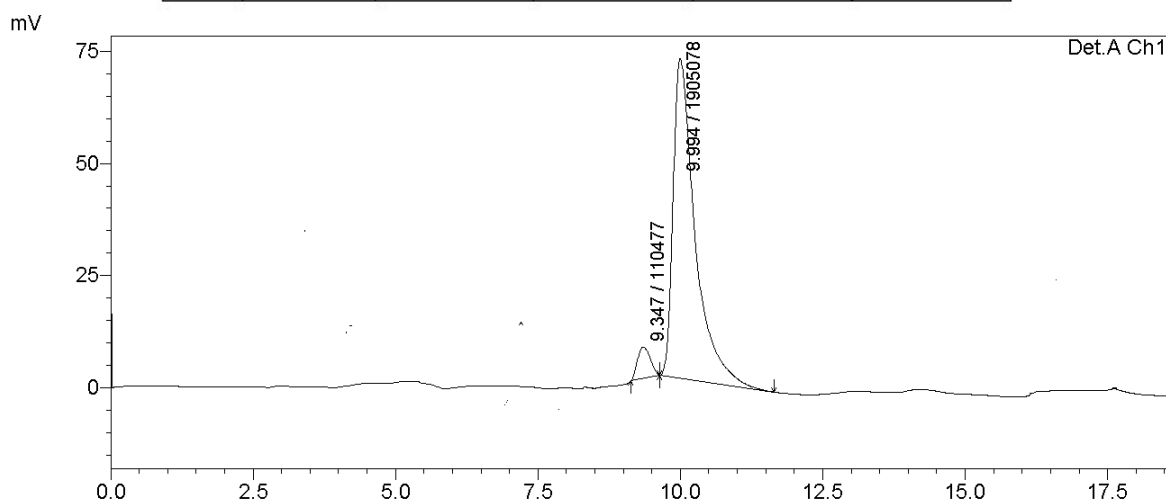
Detector A 210nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	17.829	52807450	1582702	96.482	96.485
2	19.662	1925661	57663	3.518	3.515
Total		54733112	1640365	100.000	100.000

3-(*R*)-3-methyl-1-nitrobutan-2-yl)pentane-2,4-dione (7k)



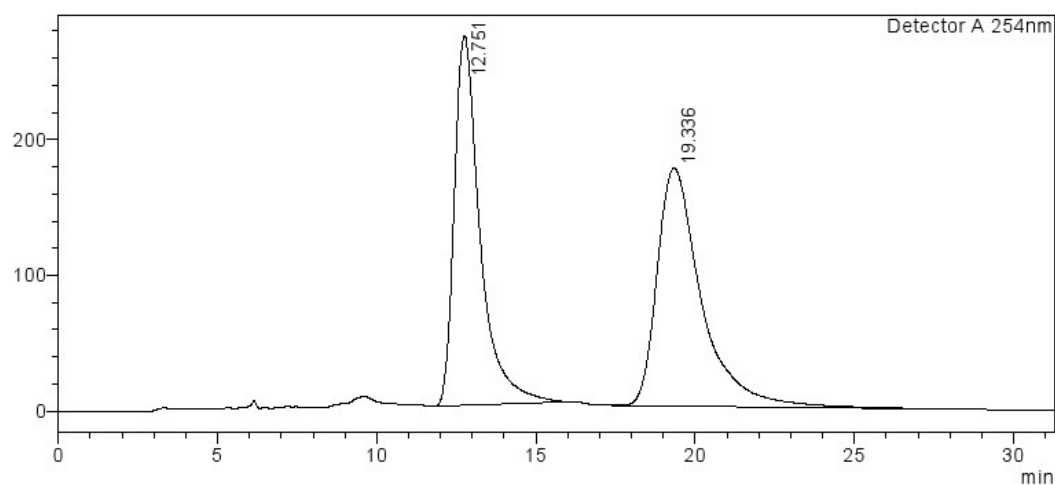
Peak#	Ret. Time	Area	Height	Area%	Height%
1	9.885	21116991	1186104	50.377	51.988
2	10.639	20801320	1095377	49.623	48.012
Total		41918311	2281481	100.000	100.000



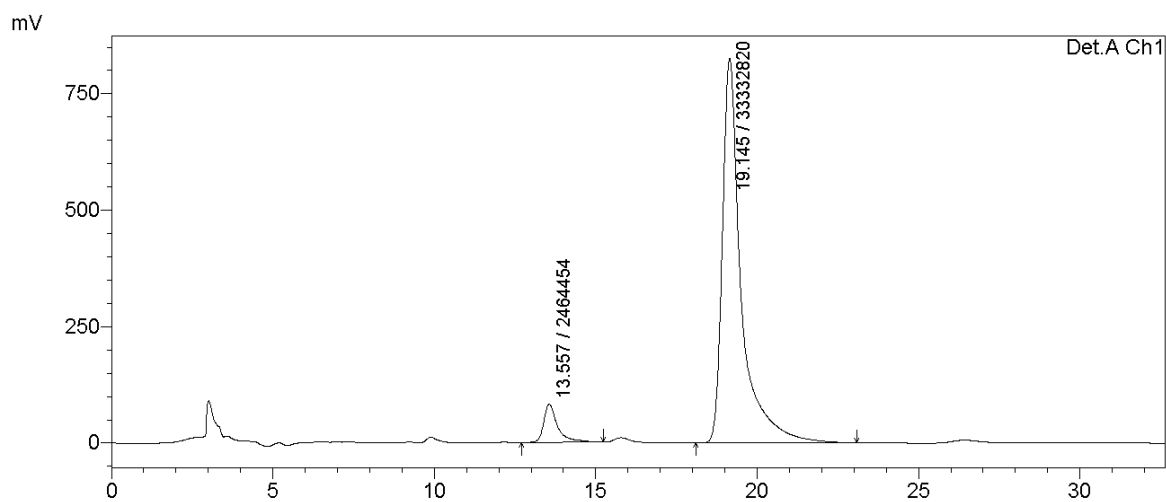
Detector A Ch1 210nm

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

Dimethyl (S)-2-(2-nitro-1-phenylethyl)malonate (9a)



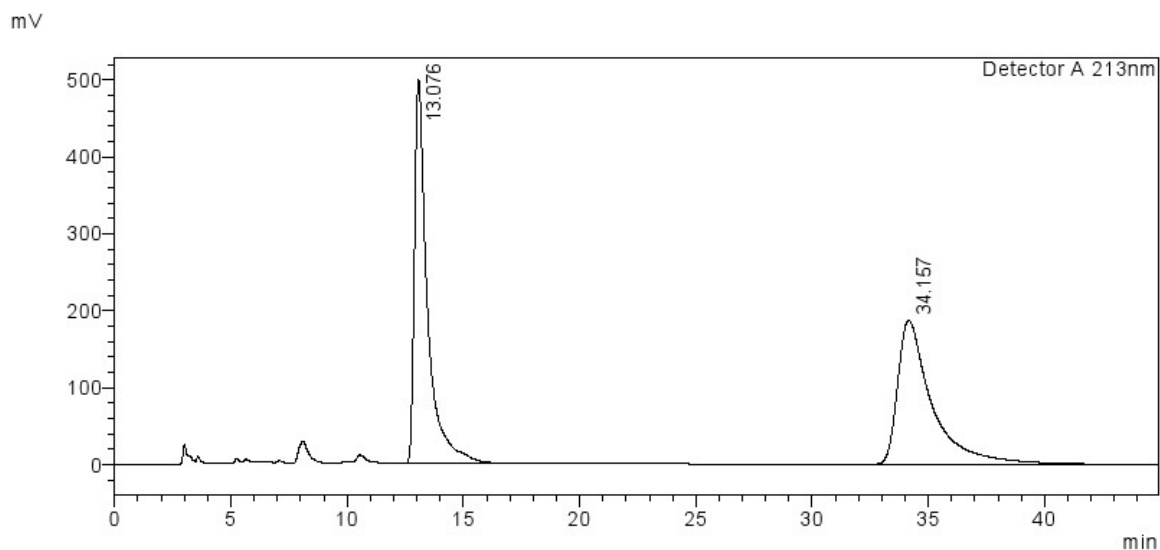
Peak#	Ret. Time	Area	Height	Area%
1	12.751	15321533	272064	47.470
2	19.336	16954813	175072	52.530
Total		32276346	447136	100.000



Detector A Ch1 210nm

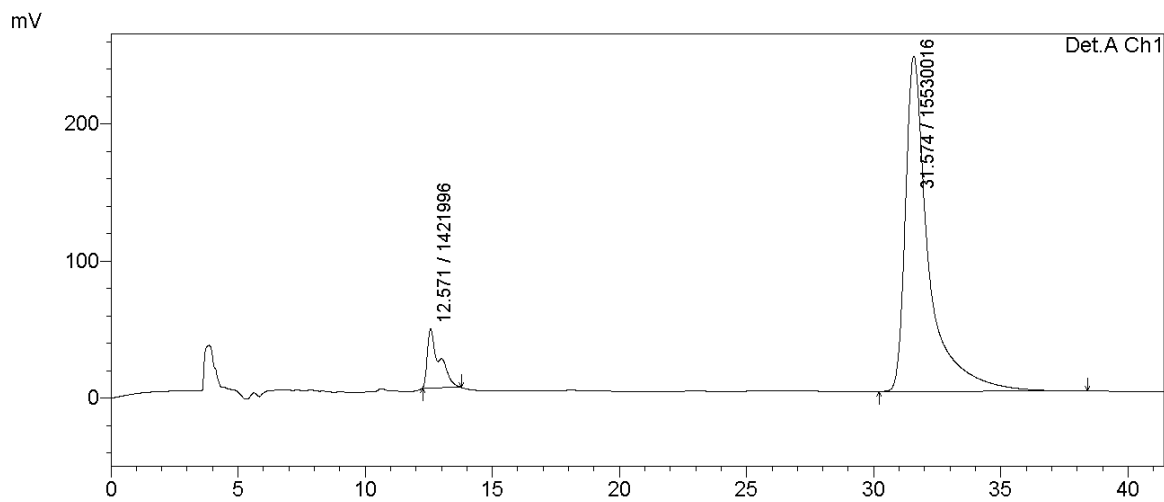
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.557	2464454	82557	6.884	9.087
2	19.145	33332820	825976	93.116	90.913
Total		35797274	908533	100.000	100.000

Diethyl (S)-2-(2-nitro-1-phenylethyl)malonate (9b)



Detector A 213nm

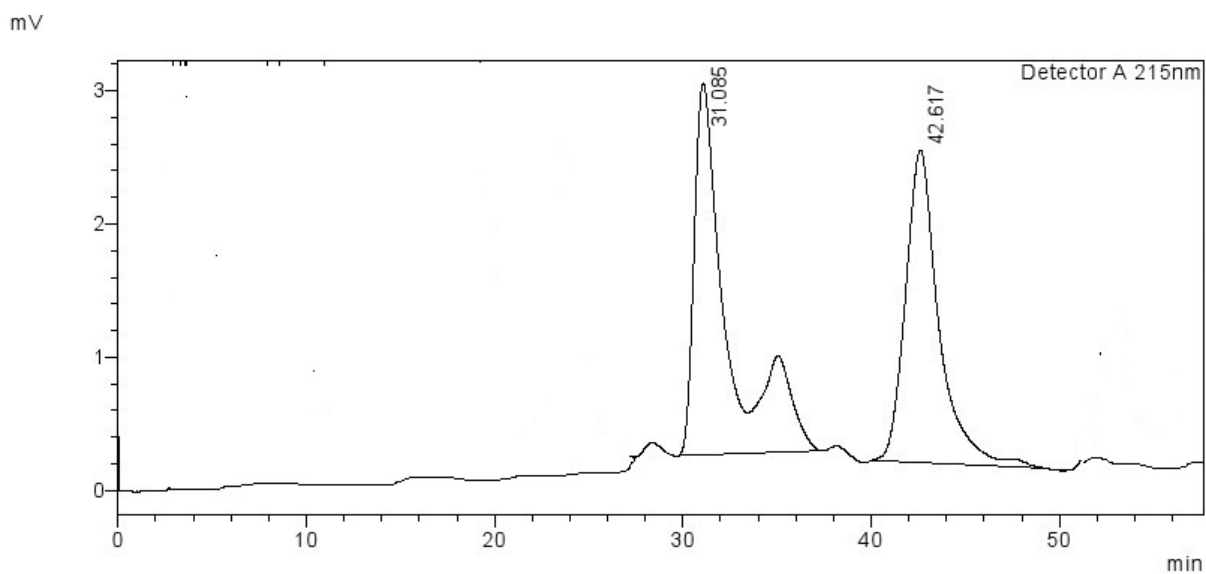
Peak#	Ret. Time	Area	Area%	Height%
1	13.076	19405417	50.284	72.739
2	34.157	19186324	49.716	27.261
Total		38591741	100.000	100.000



Detector A Ch1 213nm

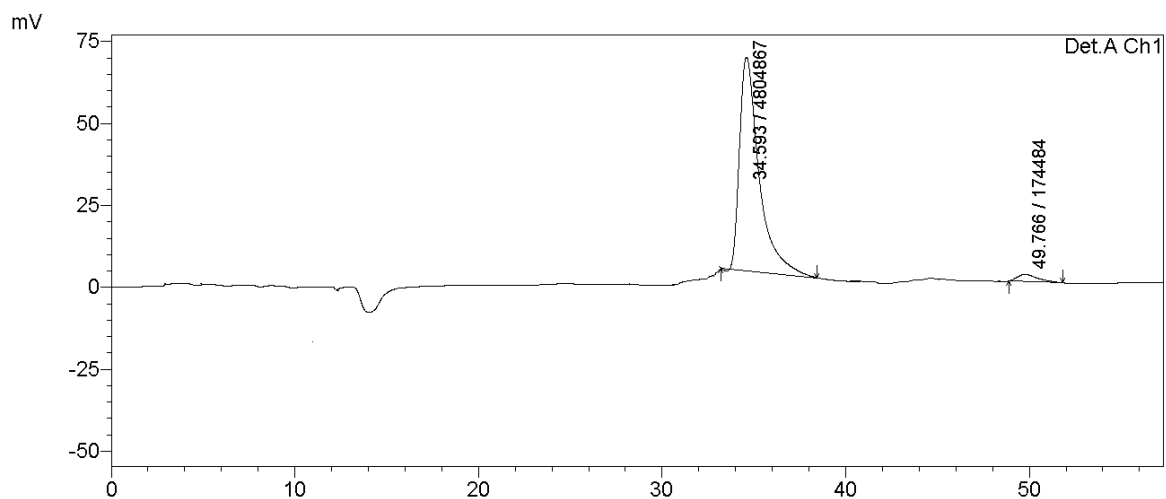
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.571	1421996	43115	8.388	14.981
2	31.574	15530016	244674	91.612	85.019
Total		16952012	287789	100.000	100.000

(S)-2-[(S)-2-nitro-1-phenylethyl]-1-phenylbutane-1,3-dione (9c):



Detector A 215nm

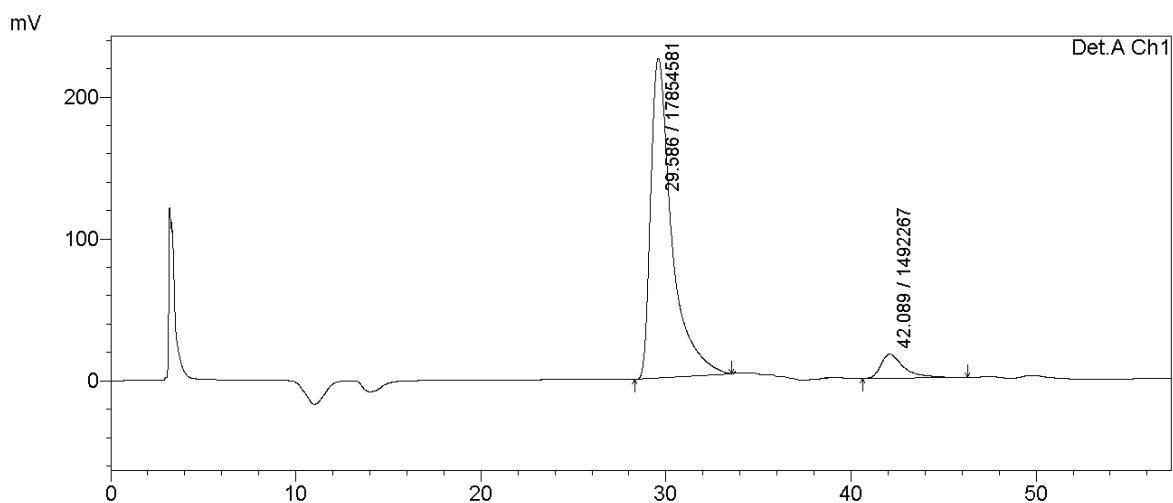
Peak#	Ret. Time	Area	Height	Area%	Height%
1	31.085	341819	2789	54.212	54.332
2	42.617	288701	2344	45.788	45.668
Total		630520	5133	100.000	100.000



Detector A Ch1 215nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.593	4804867	65144	96.496	96.777
2	49.766	174484	2169	3.504	3.223
Total		4979351	67314	100.000	100.000

(R)-2-[(S)-2-nitro-1-phenylethyl]-1-phenylbutane-1,3-dione:



Detector A Ch1 215nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.586	17854581	225514	92.287	93.021
2	42.089	1492267	16918	7.713	6.979
Total		19346848	242433	100.000	100.000