Kinetic Resolution in Asymmetric Epoxidation using Iminium Salt Organocatalysis

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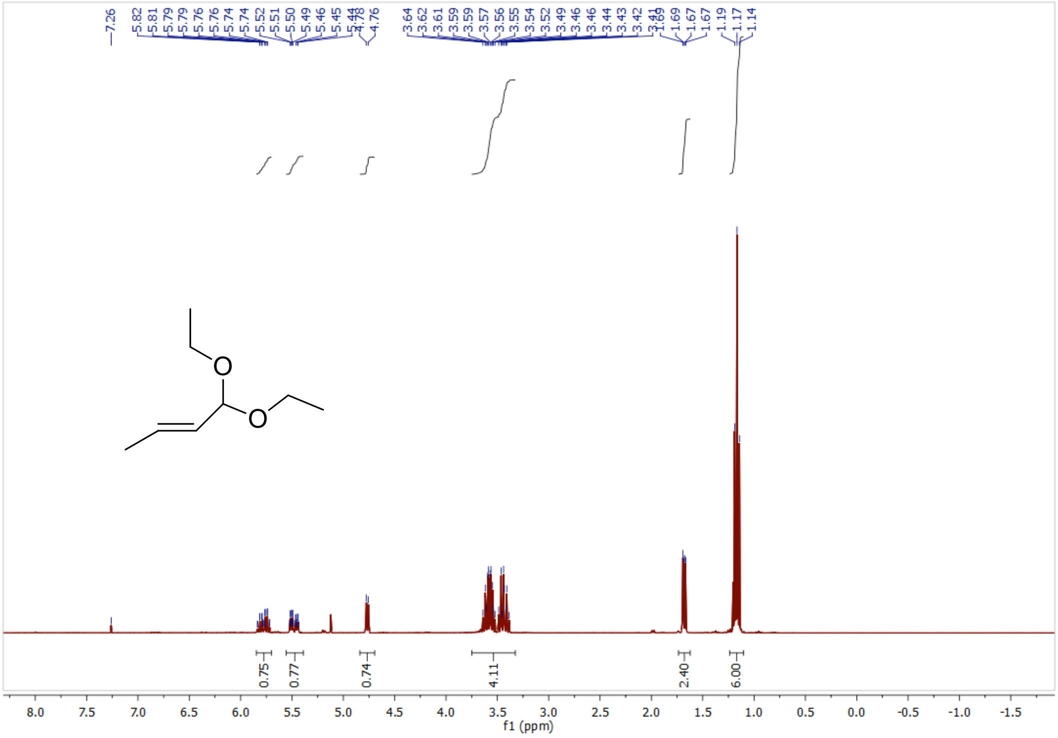
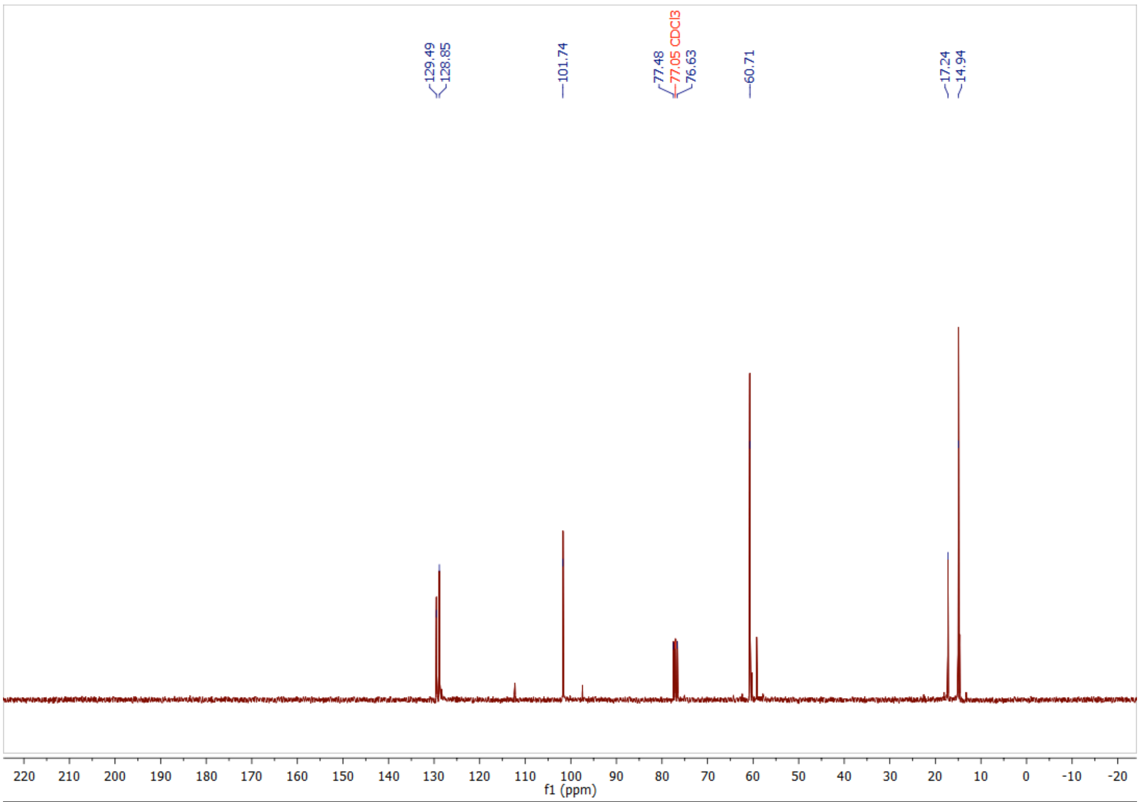
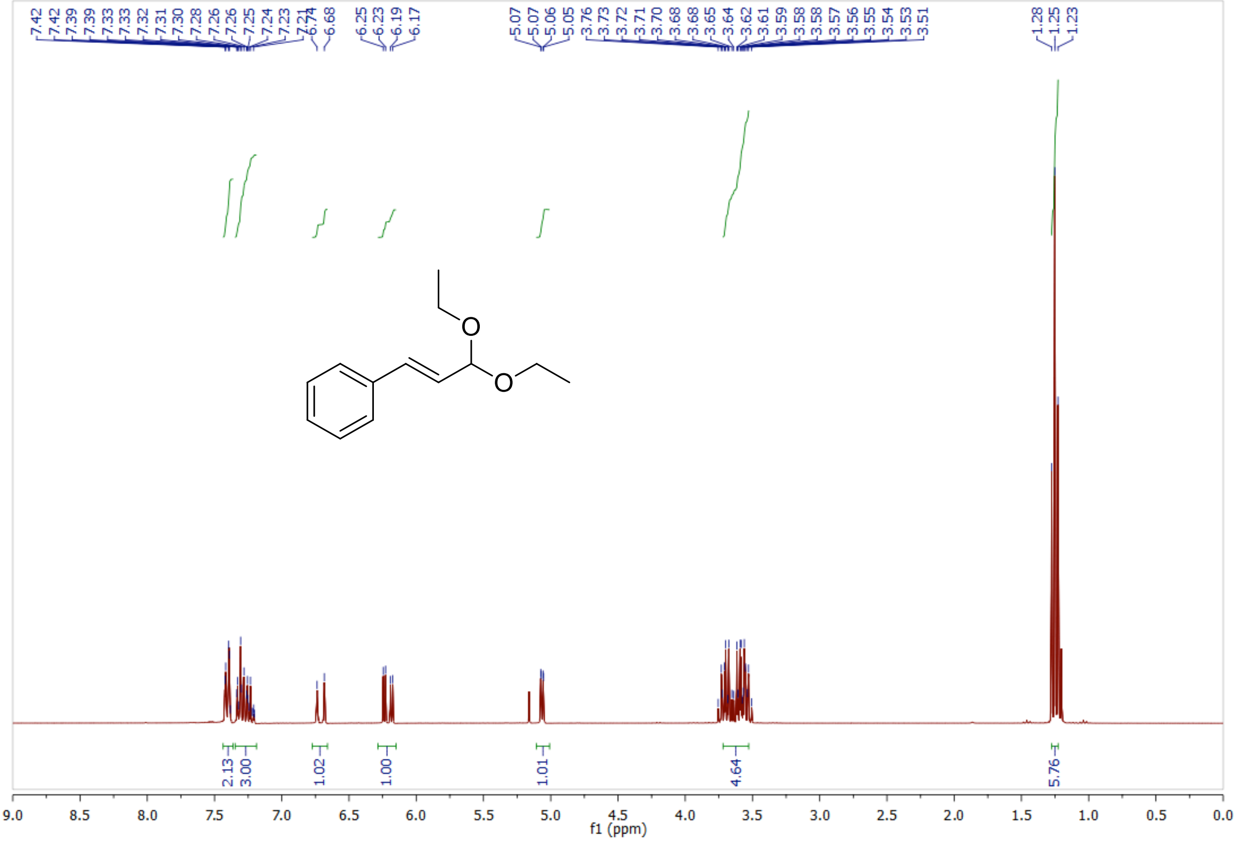
Supporting information

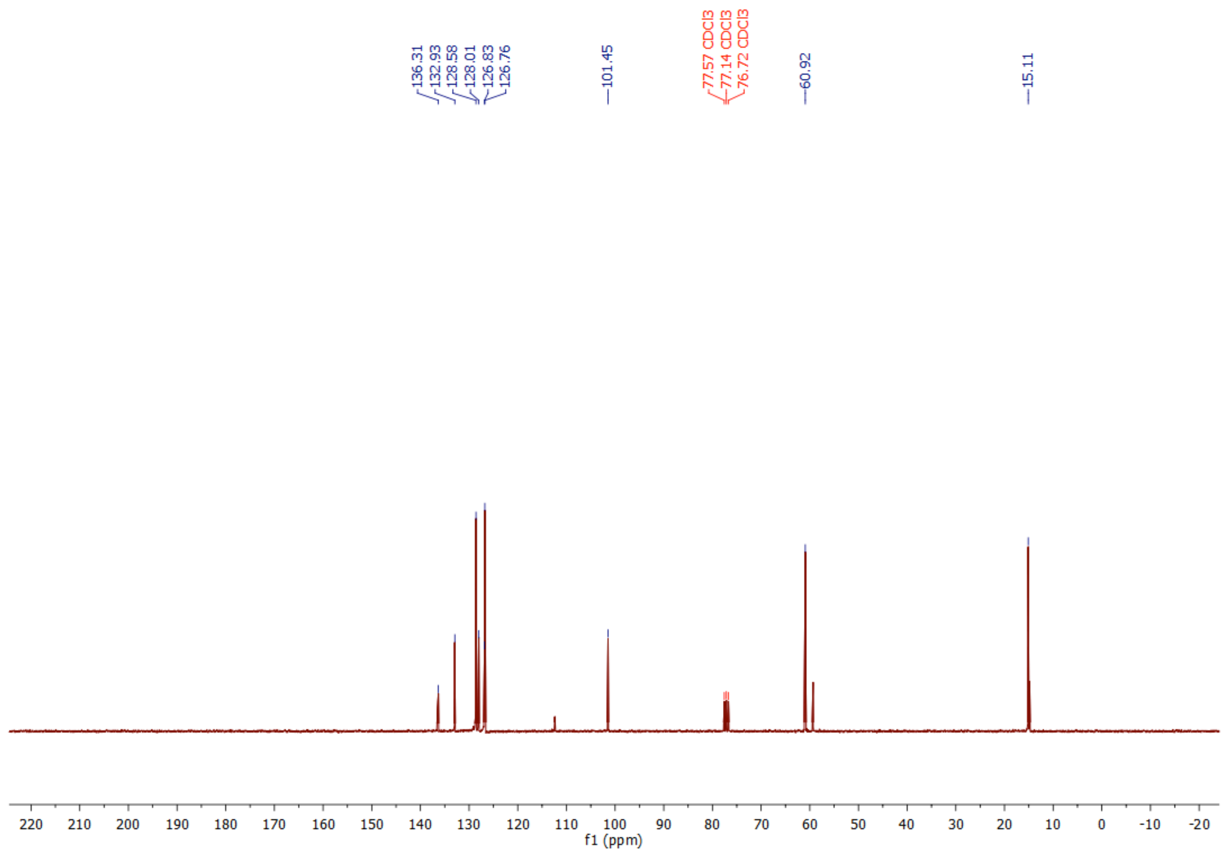
1,1-diethyoxybut-2-ene (9)



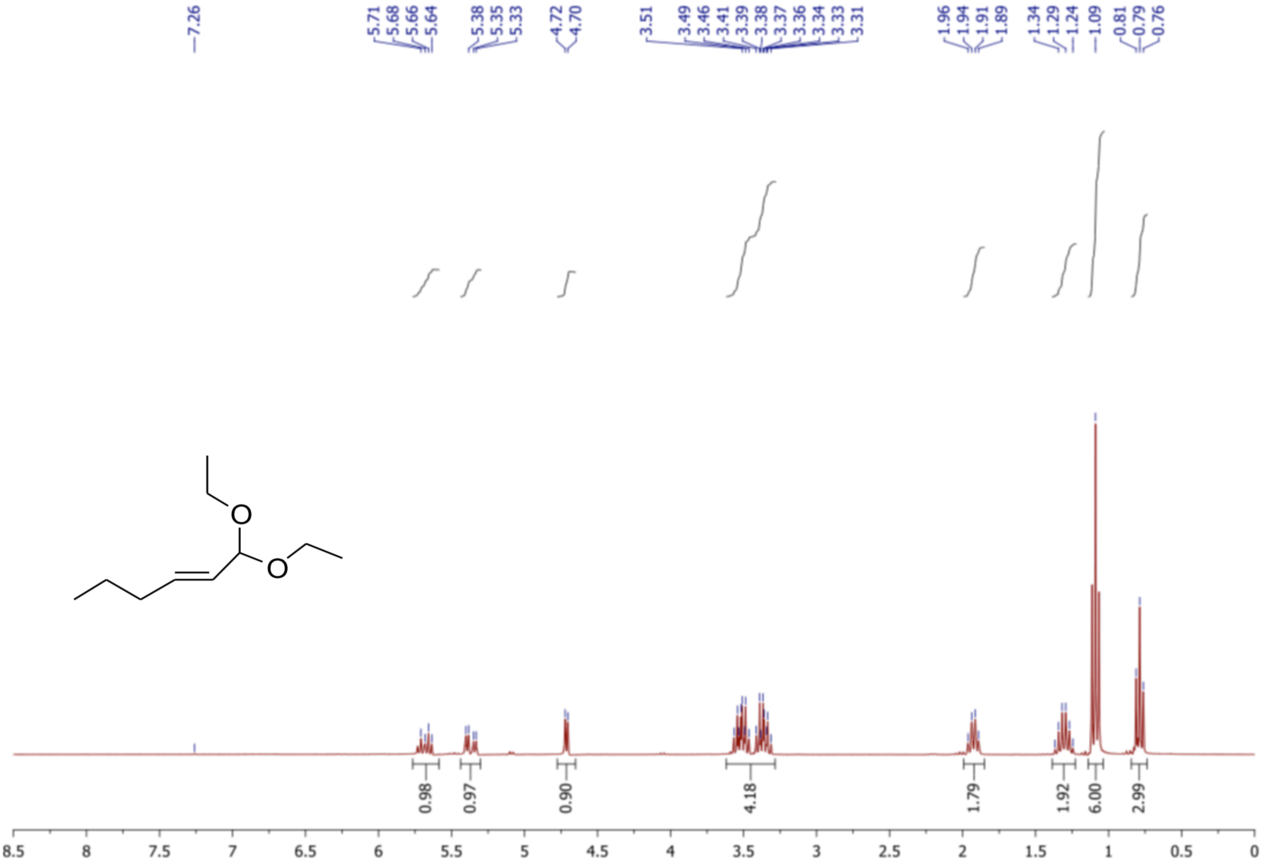


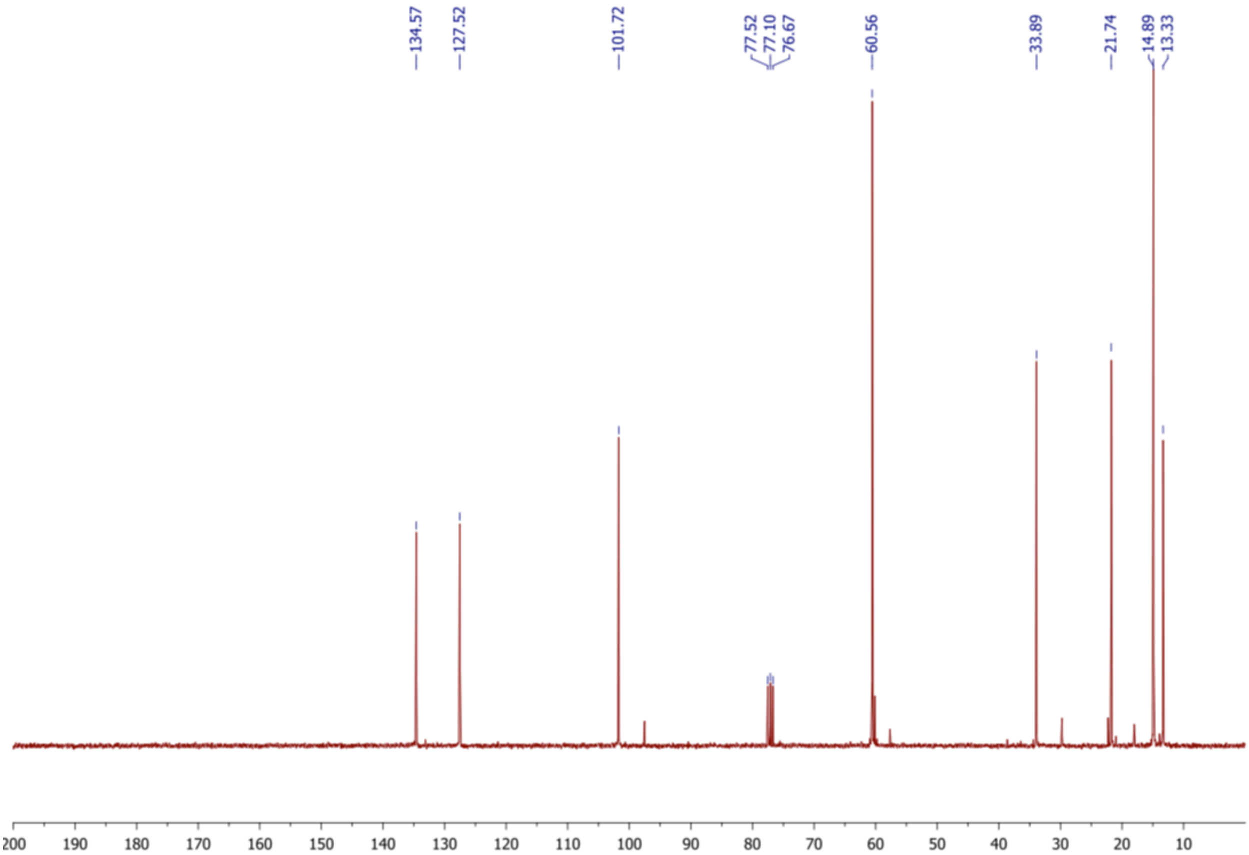
(3,3-diethoxyprop-1-enyl)benzene (10)



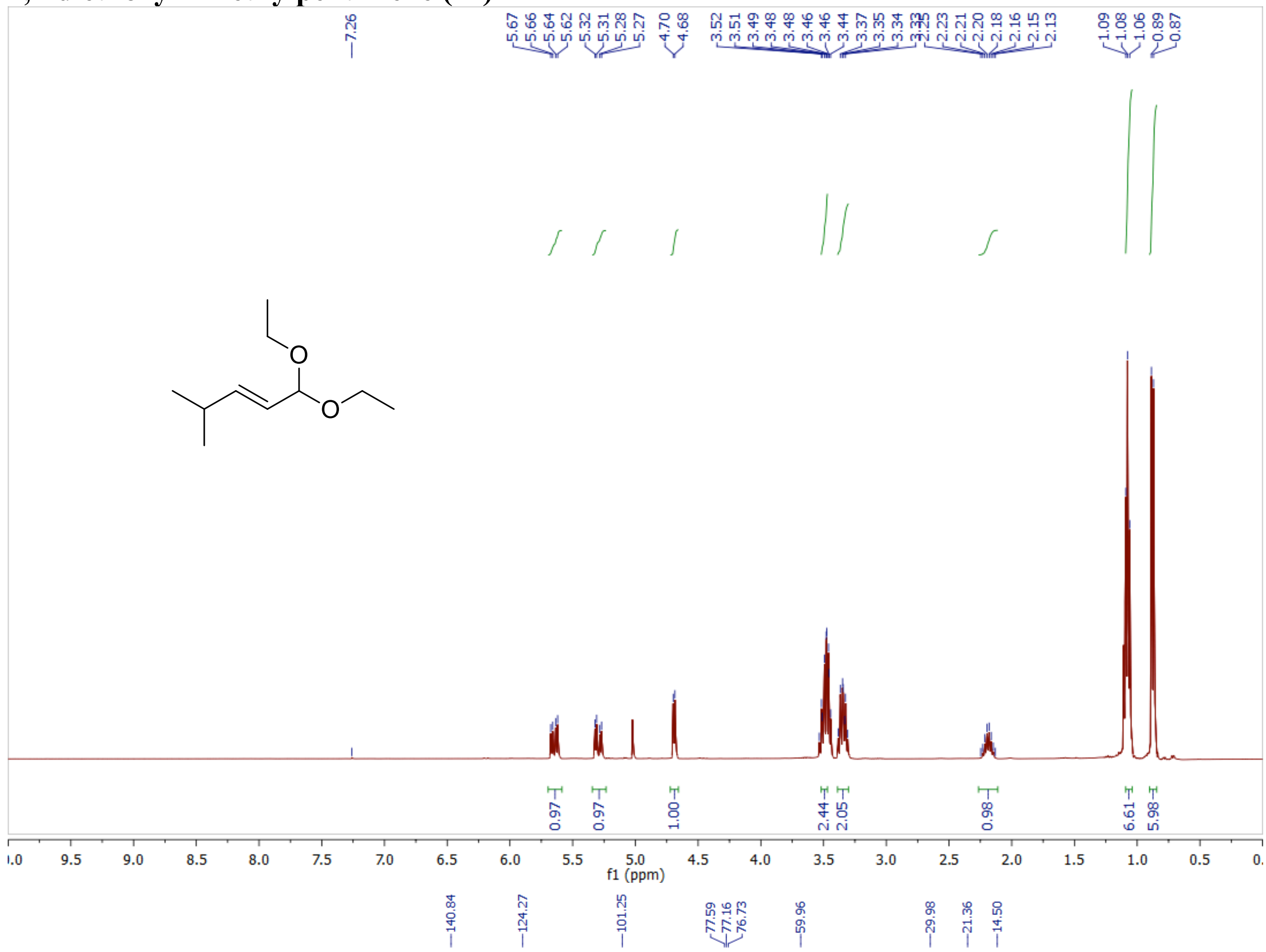


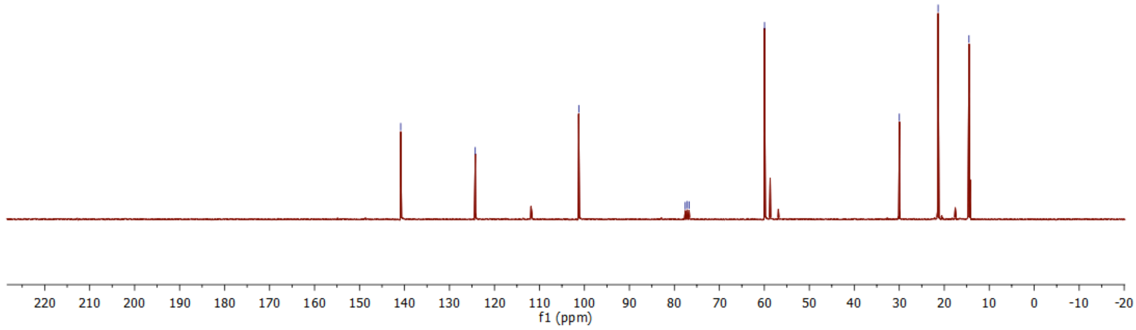
1,1-diethoxyhex-2-ene (11)



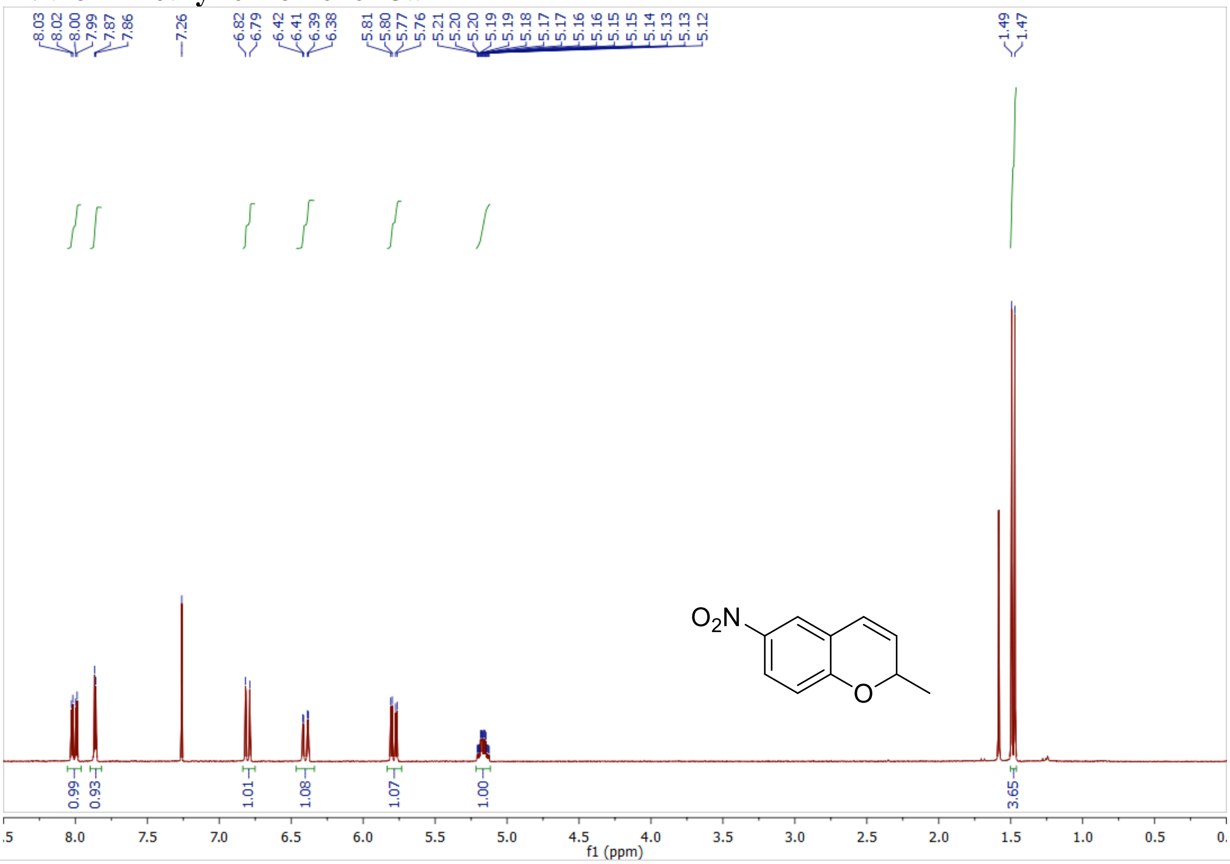


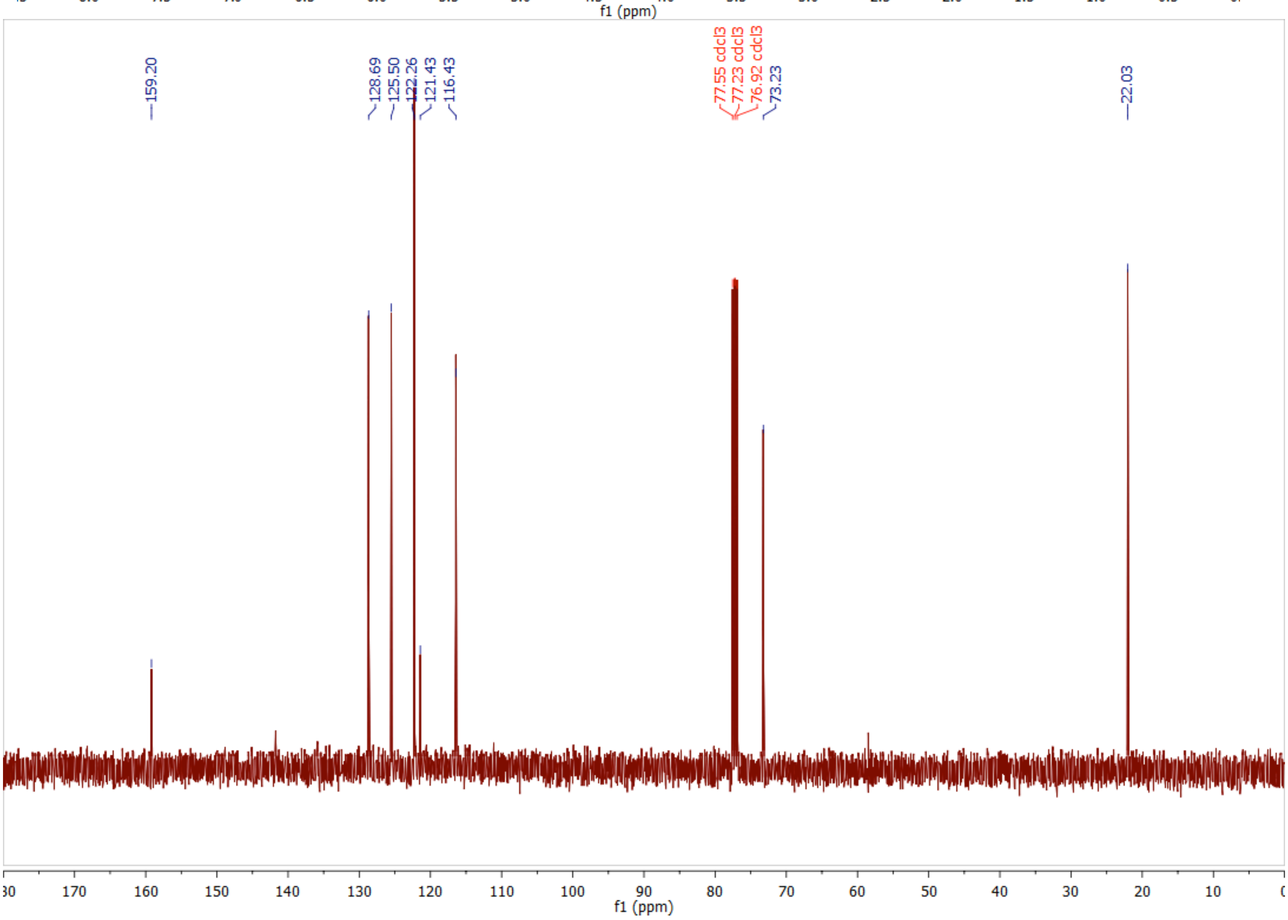
1,1-diethoxy-4-methylpent-2-ene (12)





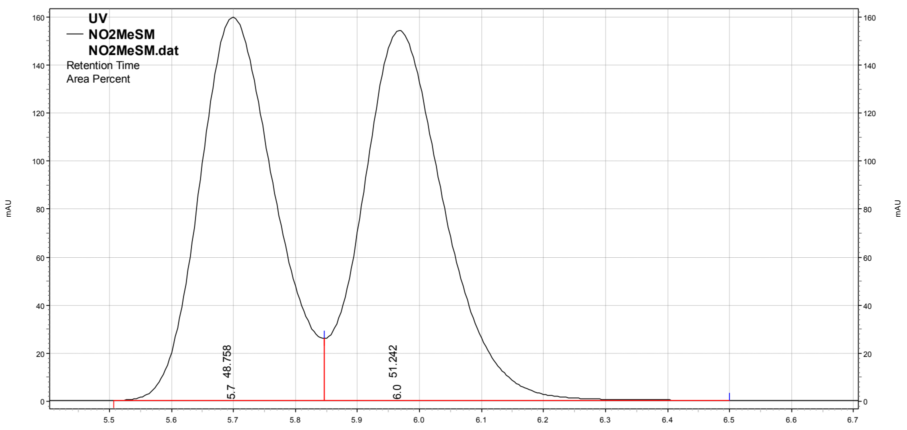
6-Nitro-2-methyl-chromene 13a





Area % Report for racemic 6-Nitro-2-methyl-chromene 13a

Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\alkene SM traces\NO2MeSM.dat
Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\untitled.met

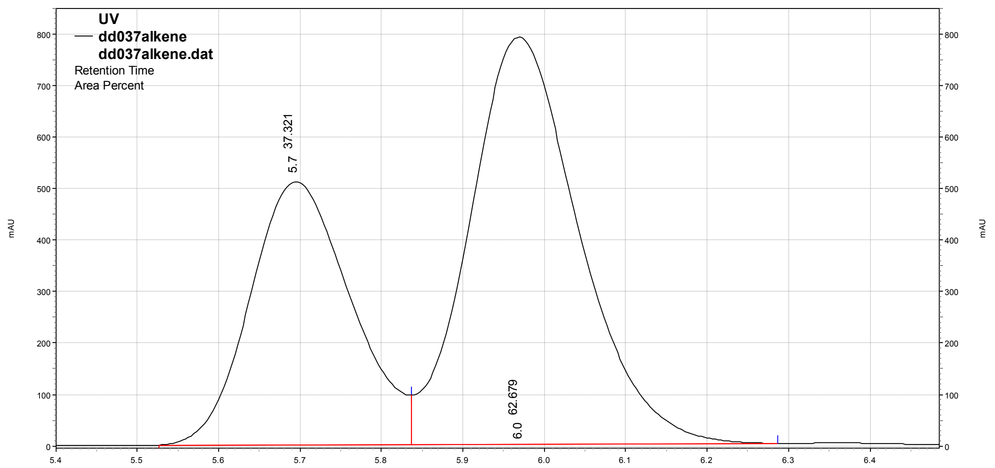


UV Results

Retention Time	Area	Area %	Height	Height %
5.700	5372313	48.76	637791	50.86
5.967	5646074	51.24	616152	49.14
Total	11018387	100	1253943	100

Area % Report for enantioenriched 6-Nitro-2-methyl-chromene 13a

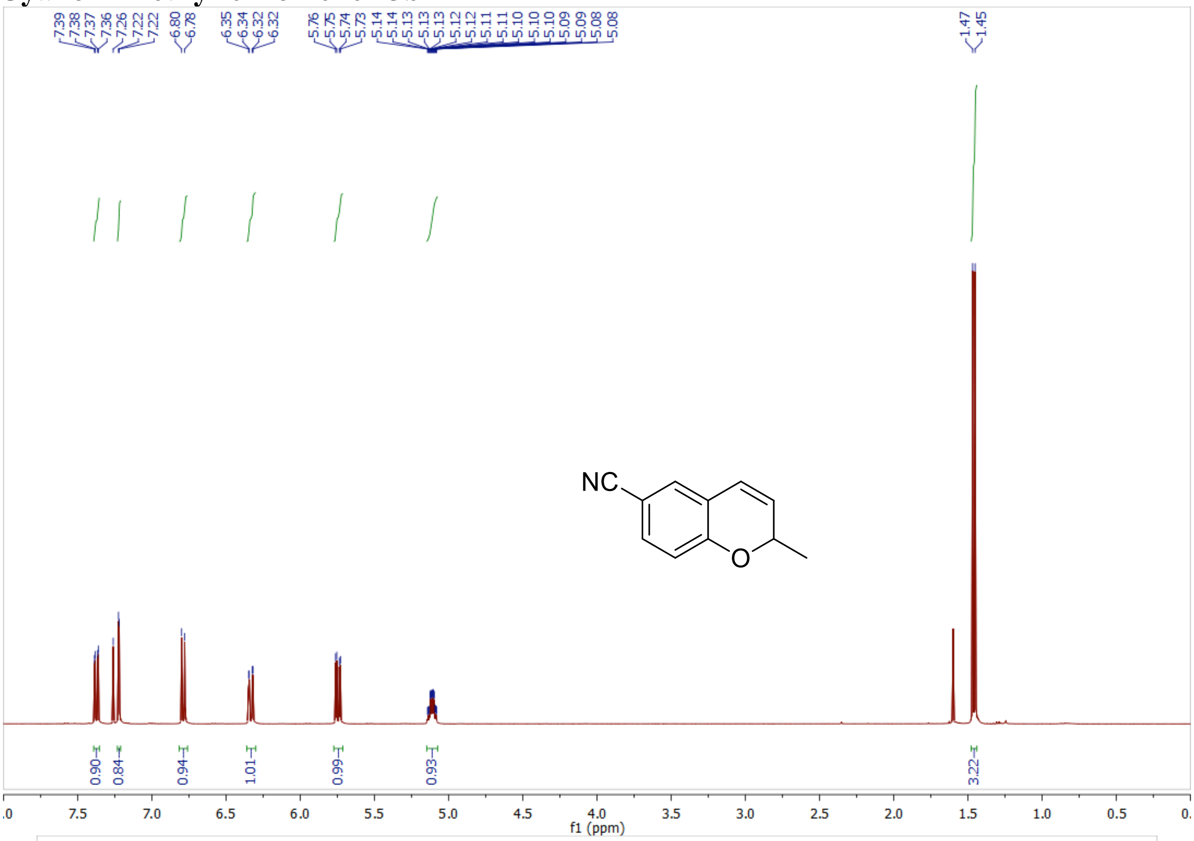
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\dd037alkene.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10 30min.met

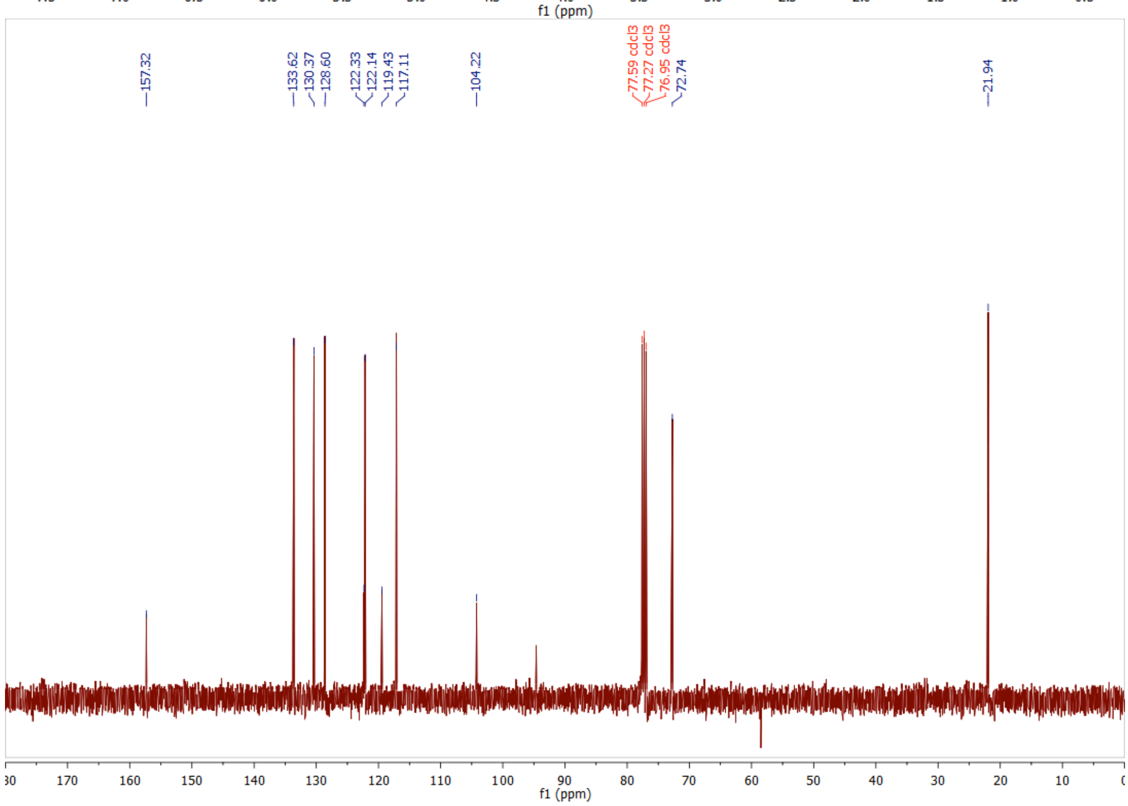


UV Results

Retention Time	Area	Area %	Height	Height %
5.693	17536346	37.32	2042197	39.27
5.970	29451699	62.68	3158232	60.73
		ee=25.36		
Totals	46988045	100	5200429	100

6-Cyano-2-methyl-chromene 13b

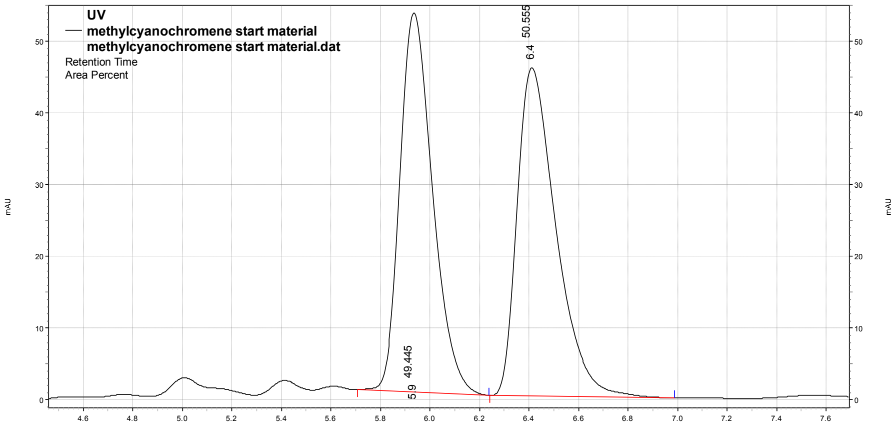




Area % Report for racemic 6-Cyano-2-methyl-chromene 13b

Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\d\methylcyanochromene start material.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90:10, 30 min, 1ml

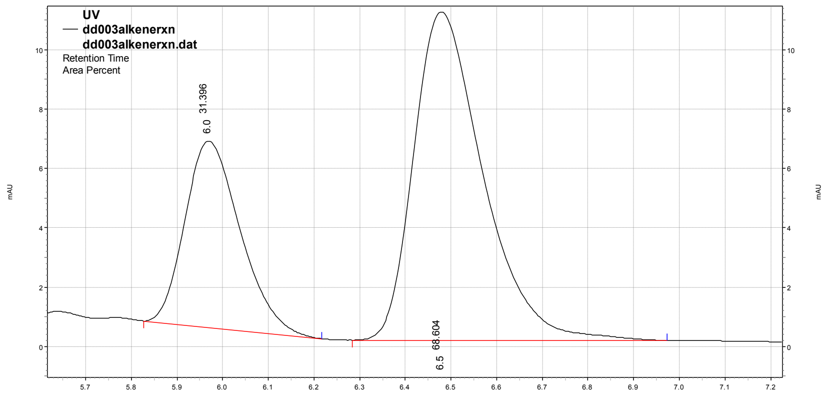


UV Results

Retention Time	Area	Area %	Height	Height %
5.937	1939947	49.45	211629	53.62
6.413	1983485	50.55	183058	46.38
Totals	3923432	100.00	394687	100.00

Area % Report for enantioenriched 6-Cyano-2-methyl-chromene 13b

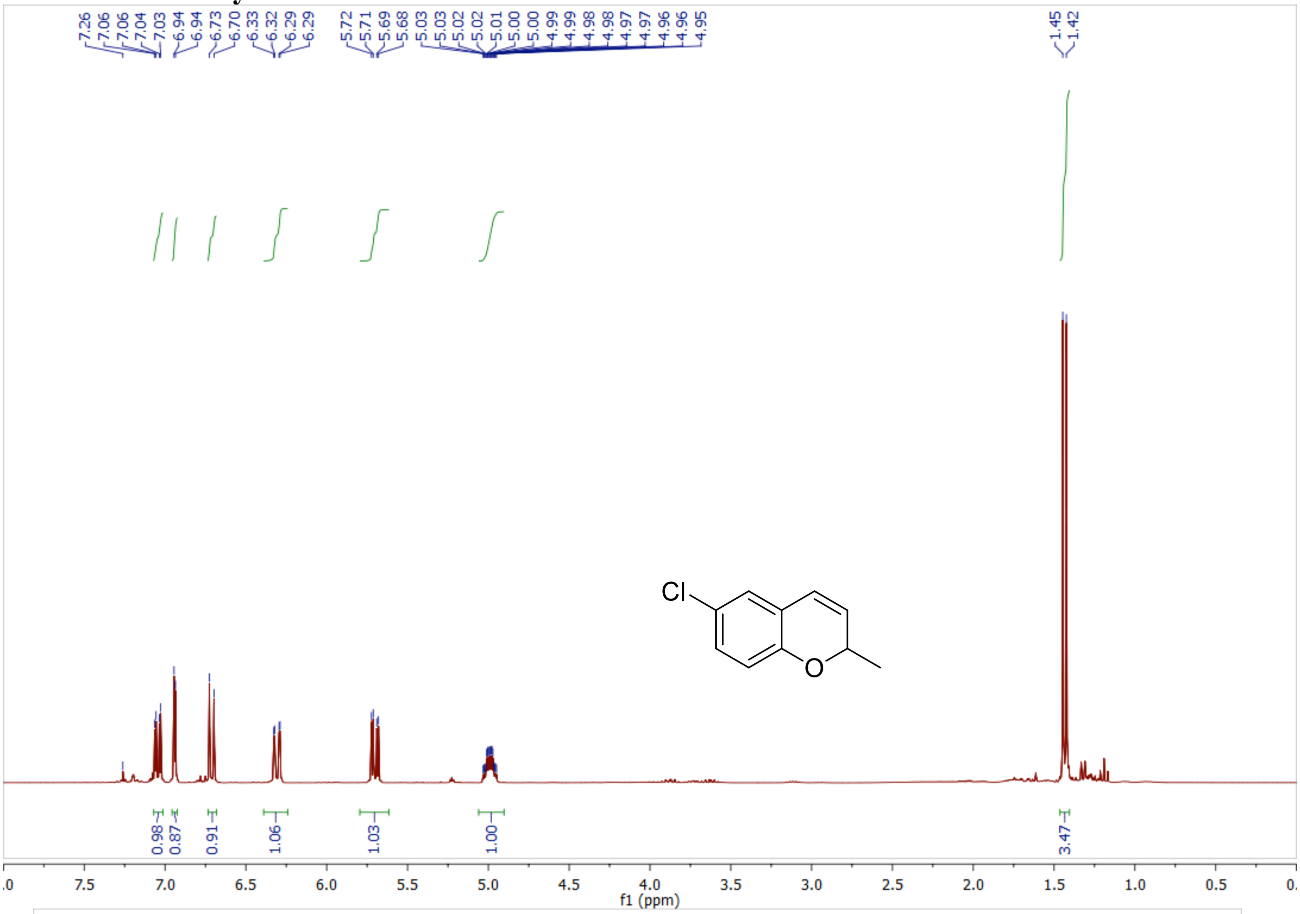
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd003alkenerxn.dat

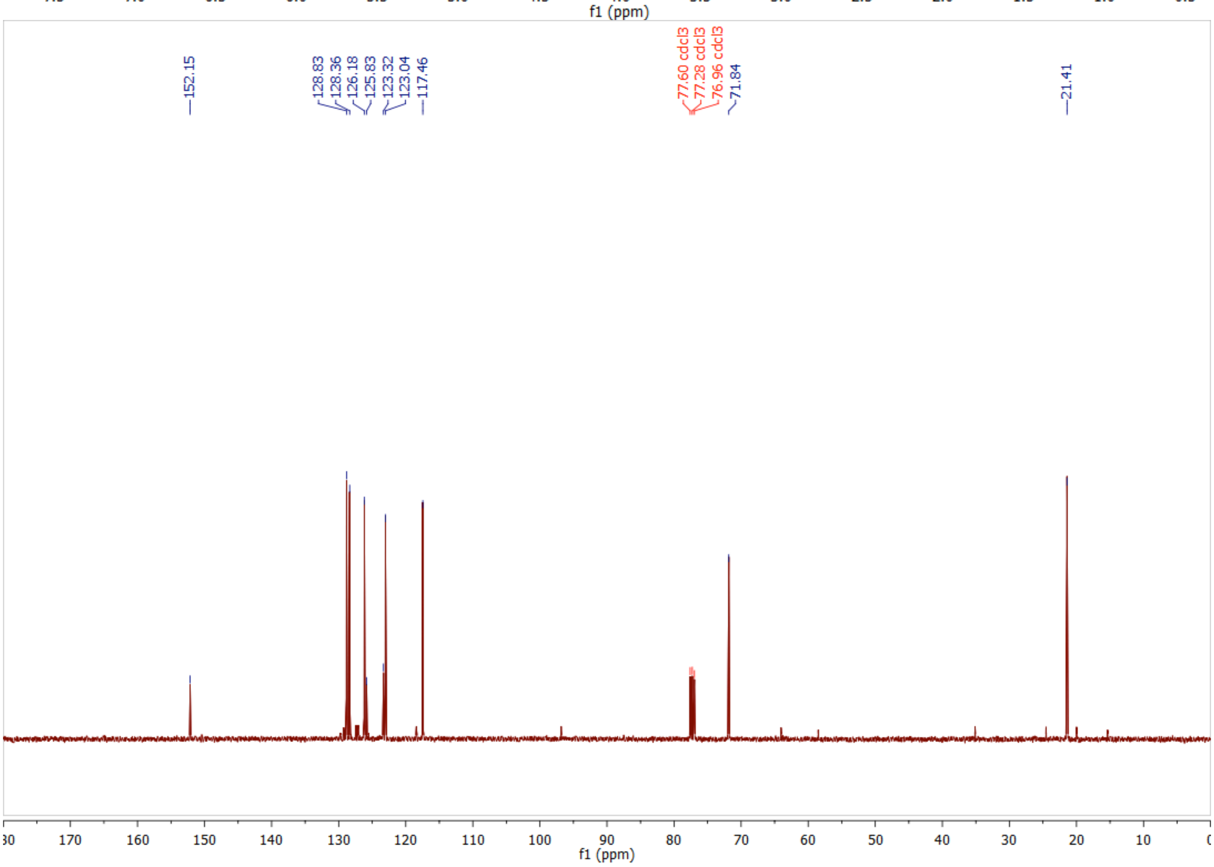


UV Results

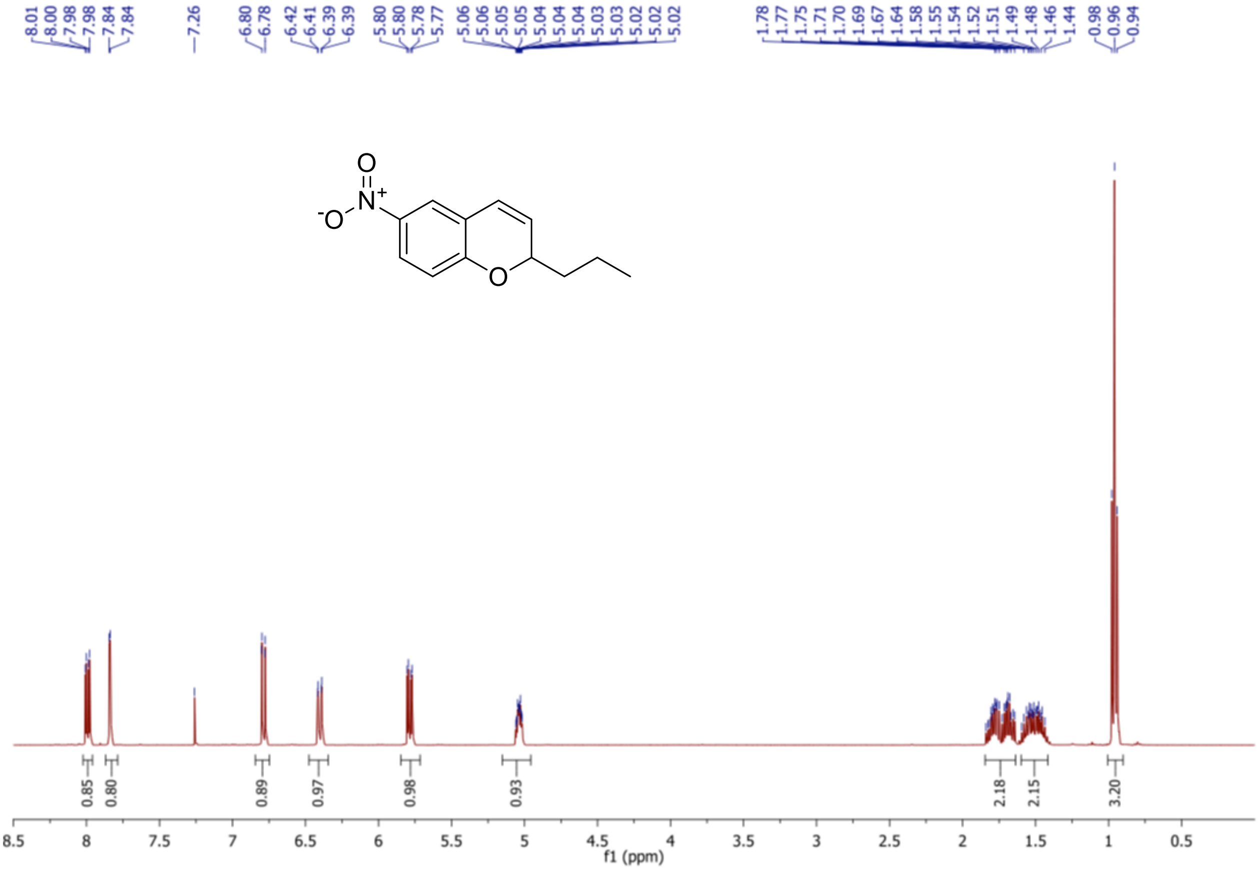
Retention Time	Area	Area %	Height	Height %
5.970	212816	31.40	25128	36.22
6.480	465036	68.60	44246	63.78
Totals	677852	100.00	69374	100.00

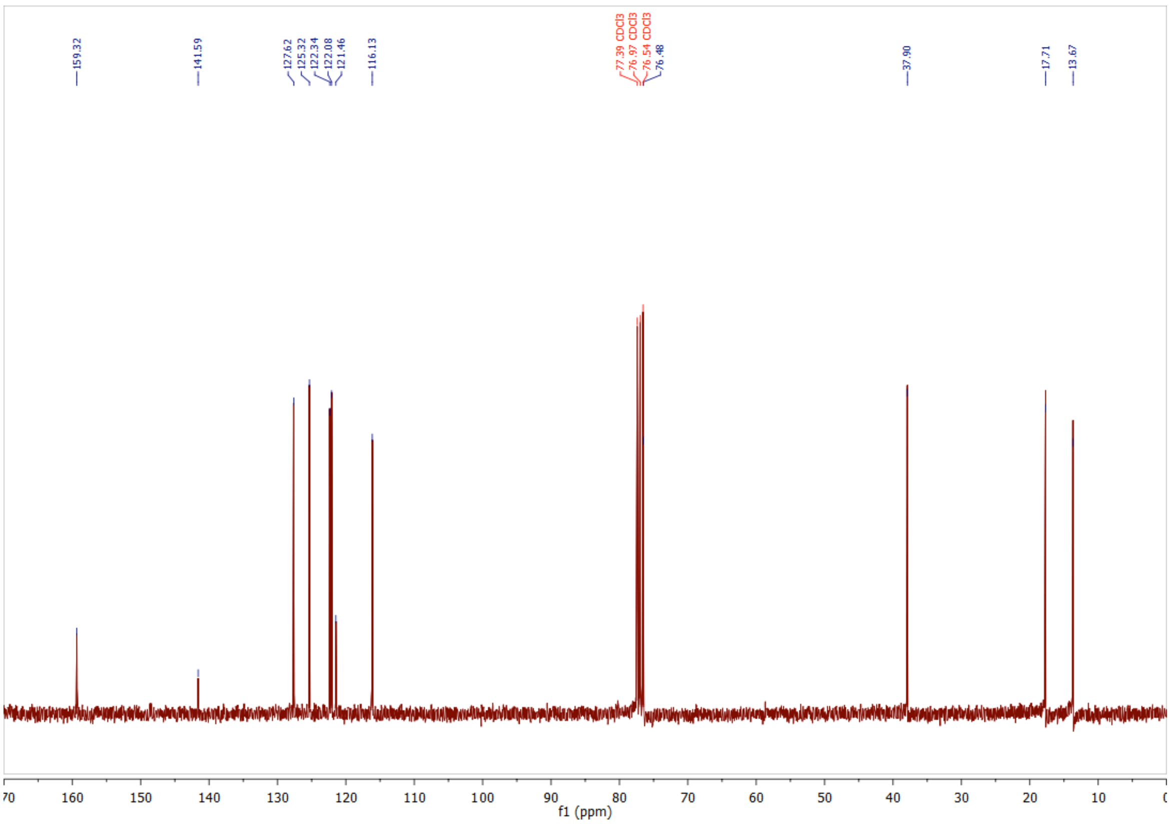
6-Chloro-2-methyl-chromene 13c



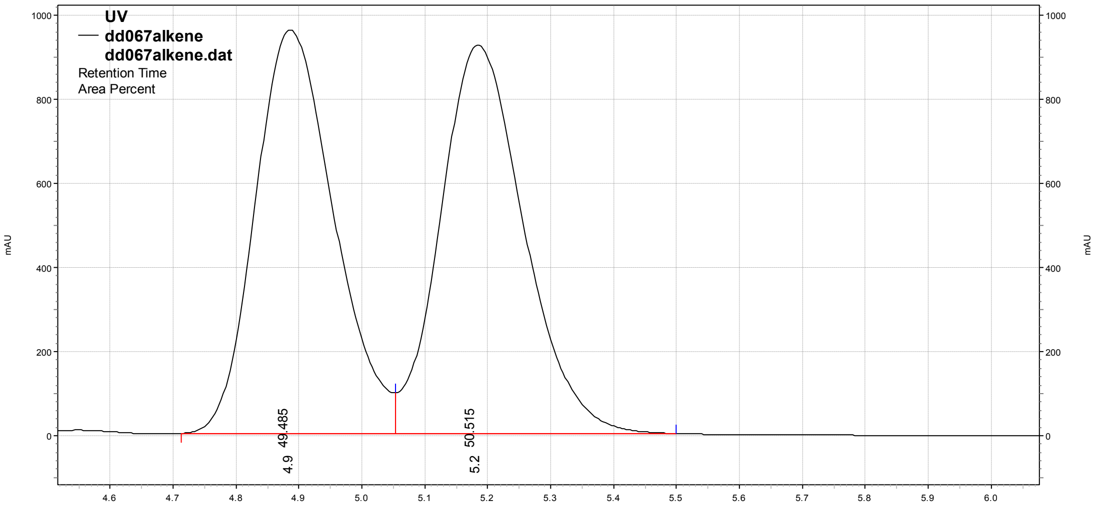


6-Nitro-2-propyl-chromene 14a:





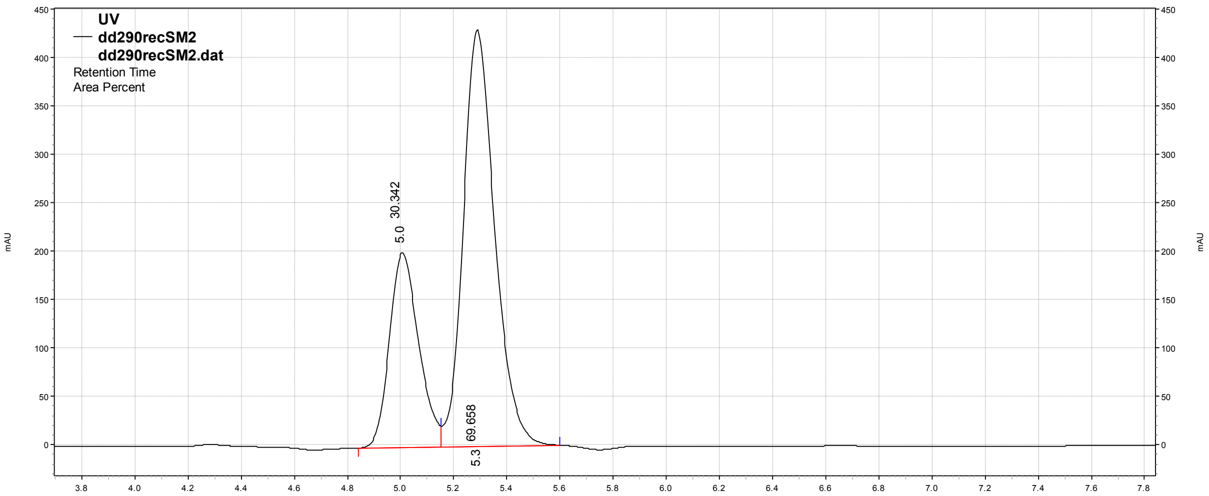
Area % Report for racemic 6-Nitro-2-propyl-chromene 14a:
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd067alkene.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10 30min.met



UV Results

Retention Time	Area	Area %	Height	Height %
4.887	33466619	49.49	3842139	50.96
5.183	34162933	50.51	3697575	49.04
Totals	67629552	100.00	7539714	100.00

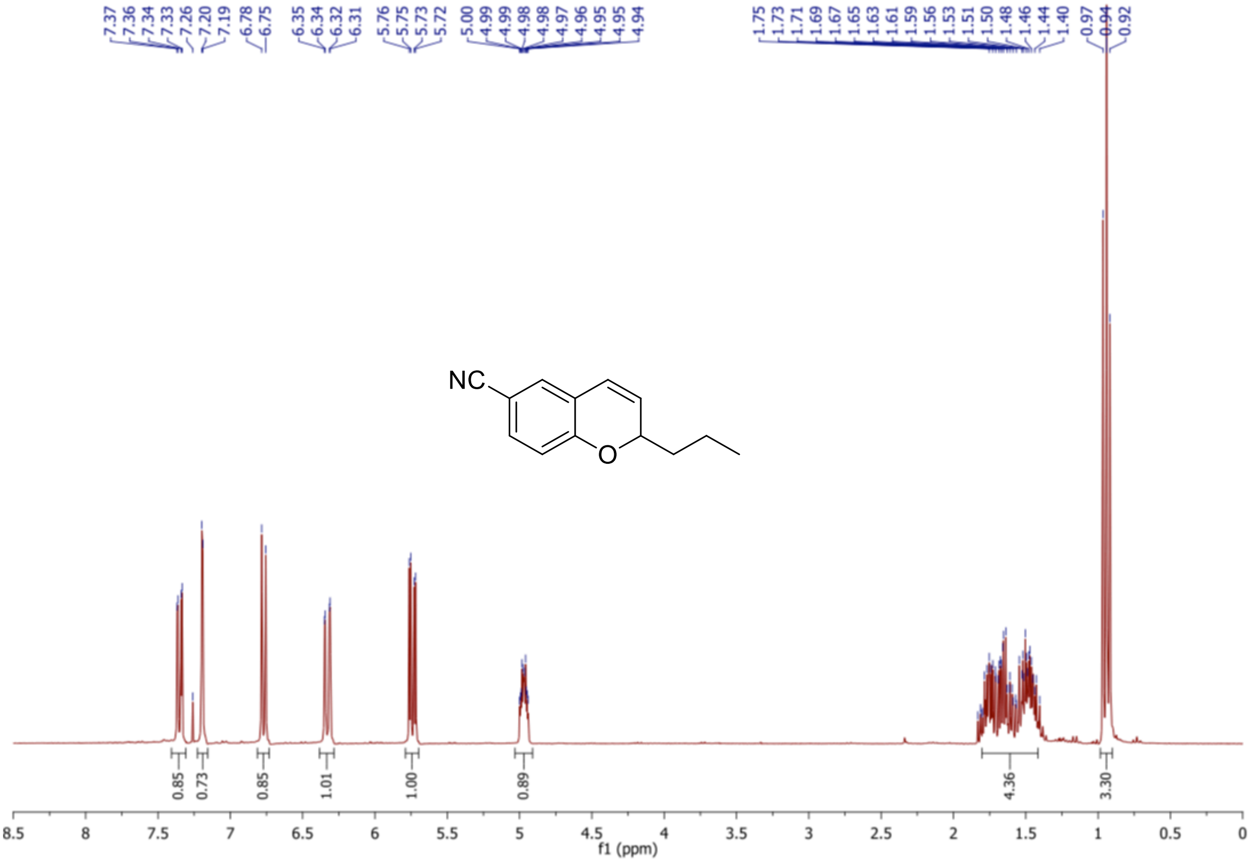
Area % Report for enantioenriched 6-Nitro-2-propyl-chromene 14a:
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd290recSM2.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10 30min.met

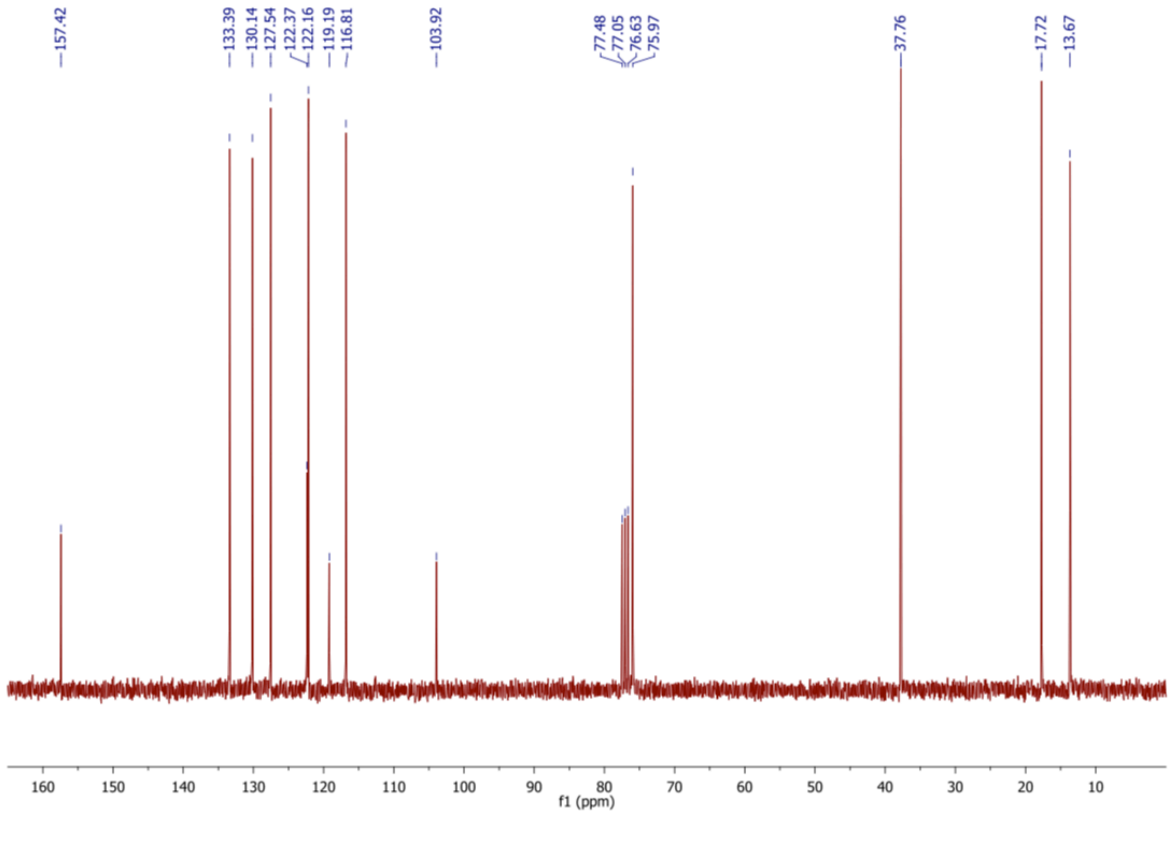


UV Results

Retention Time	Area	Area %	Height	Height %
5.007	6174048	30.34	804376	31.84
5.290	14173968	69.66	1721780	68.16
Totals	20348016	100.00	2526156	100.00

6-Cyano-2-propyl-chromene 14b

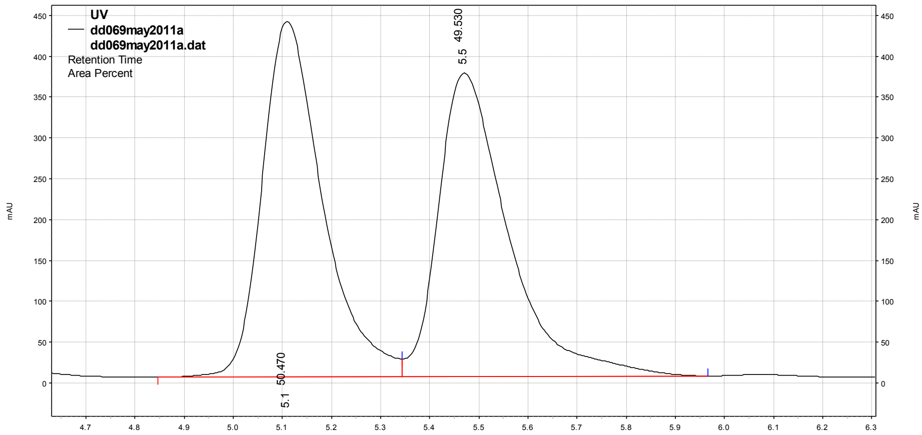




Area % Report for racemic 6-Cyano-2-propyl-chromene 14b

Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\dd069may2011a.dat

Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\90.10 30min.met



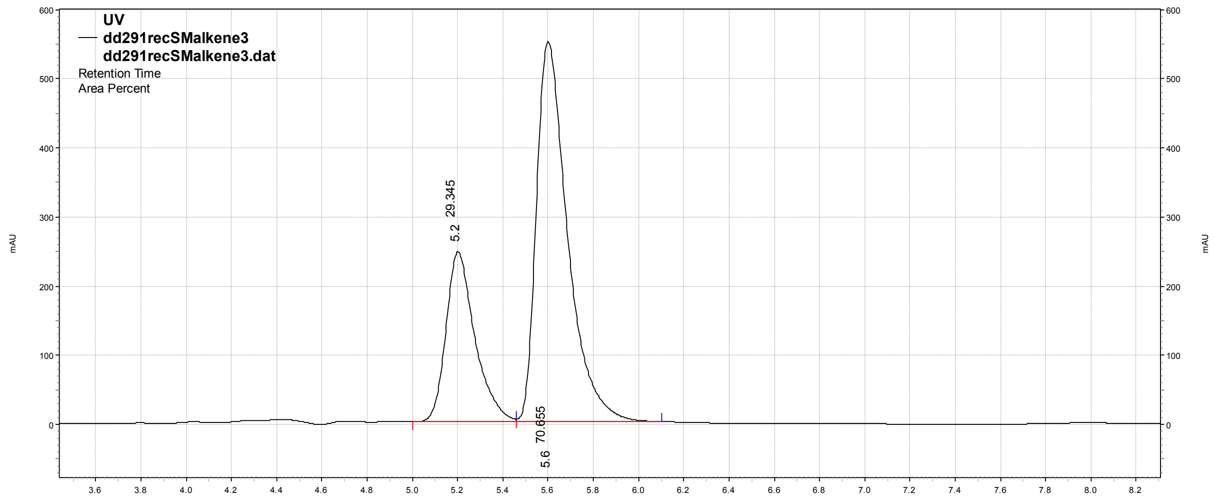
UV Results

Retention Time	Area	Area %	Height	Height %
5.110	14914823	50.47	1740913	53.94
5.470	14637053	49.53	1486569	46.06
Totals	29551876	100.00	3227482	100.00

Area % Report for enantioenriched 6-Cyano-2-propyl-chromene 14b

Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd291recSMalkene3.dat

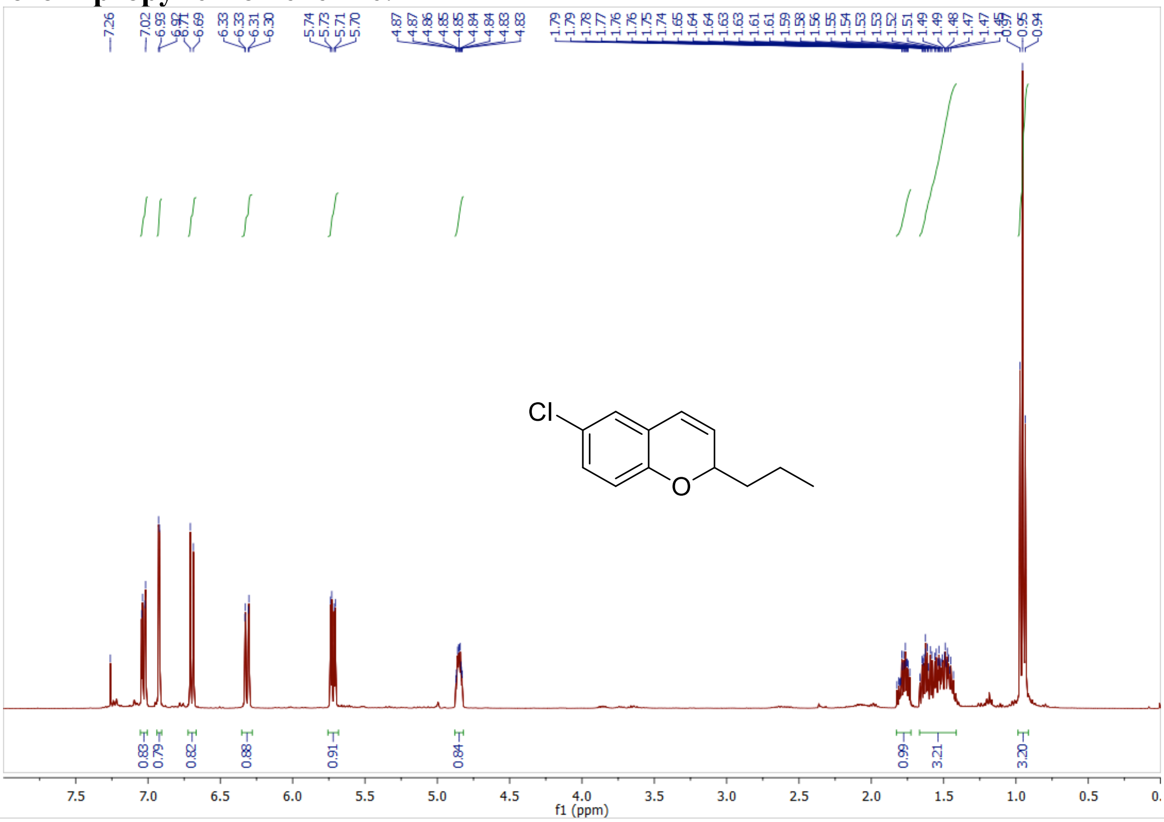
Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\90.10 30min 1mL.met

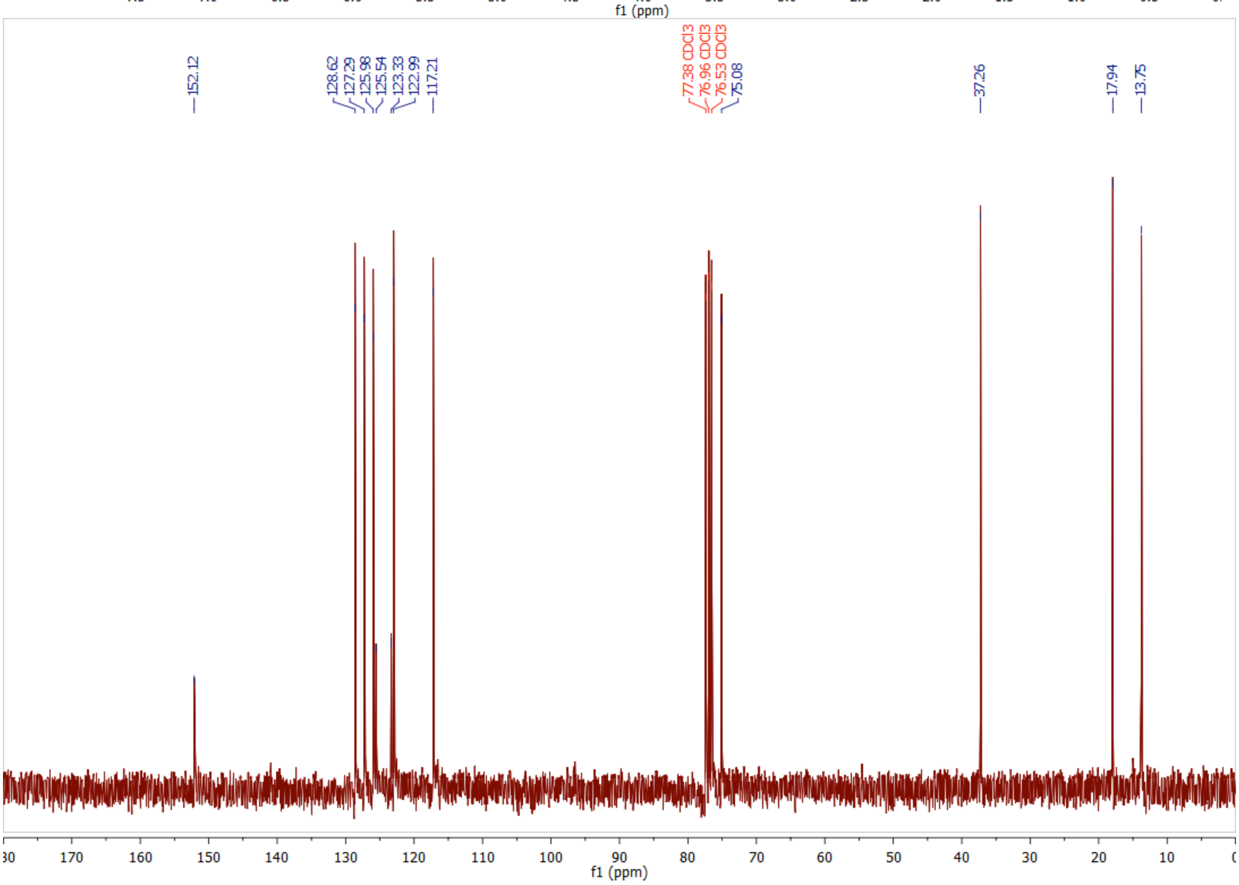


UV Results

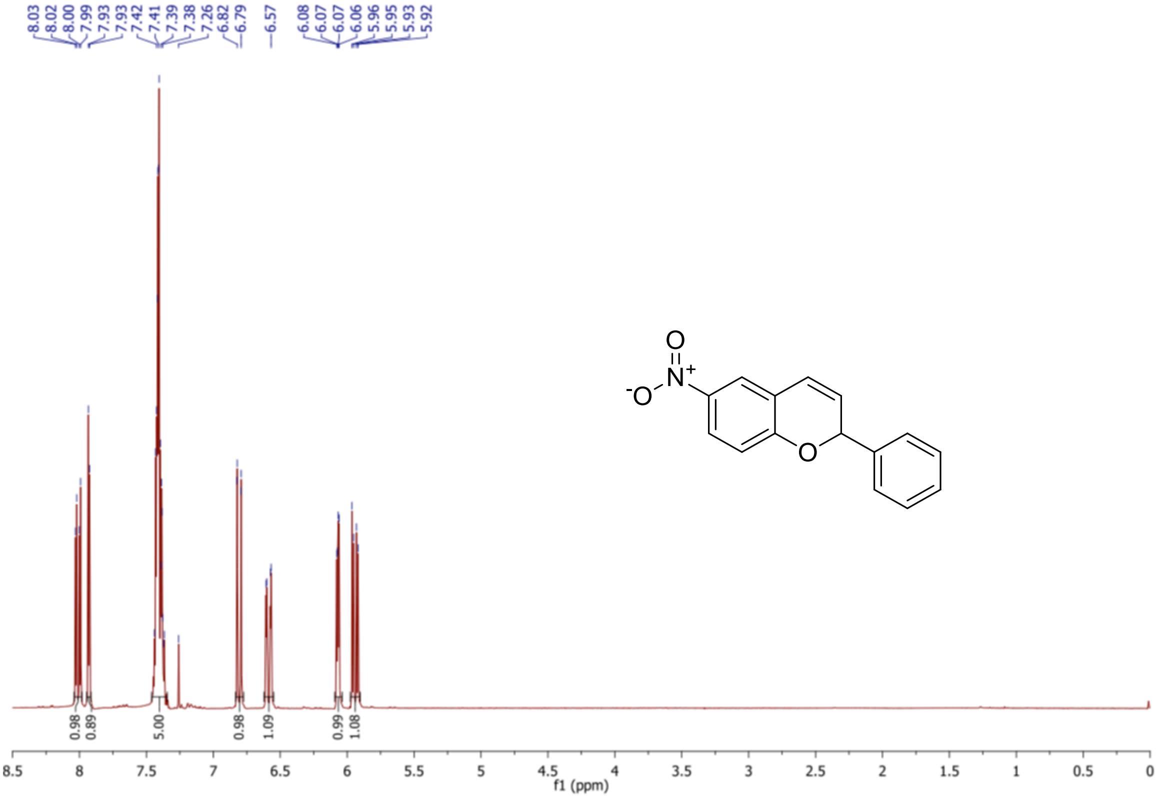
Retention Time	Area	Area %	Height	Height %
5.200	8735061	29.35	983030	30.90
5.600	21031639	70.65	2198768	69.10
Totals	29766700	100.00	3181798	100.00

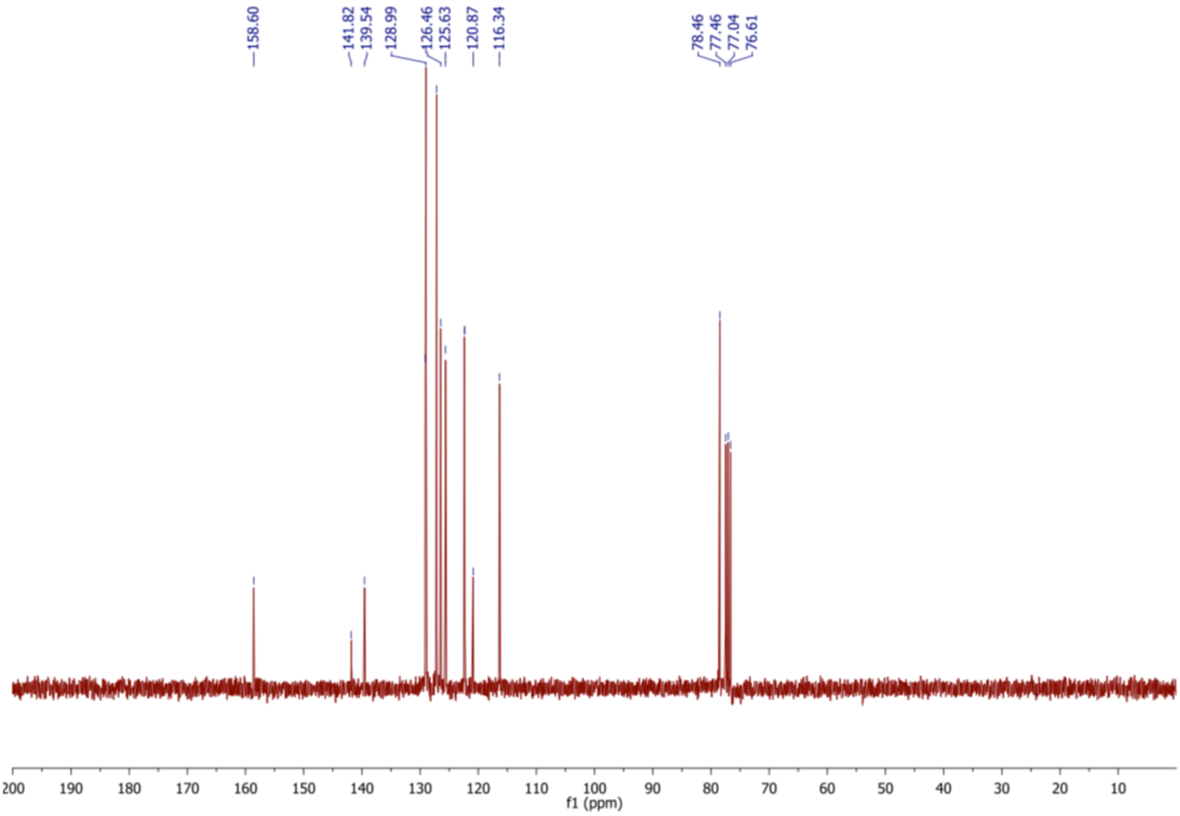
6-Chloro-2-propyl-chromene 14c:



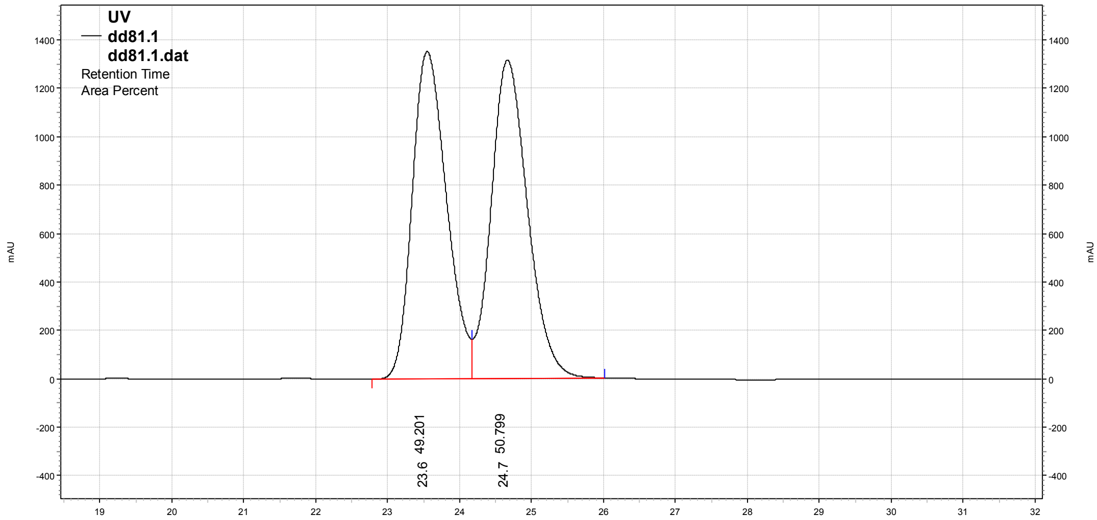


6-Nitro-2-phenyl-chromene 15a





Area % Report for racemic 6-Nitro-2-phenyl-chromene 15a
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\dd81.1.dat
Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\95.5 0.5ml 80min.met

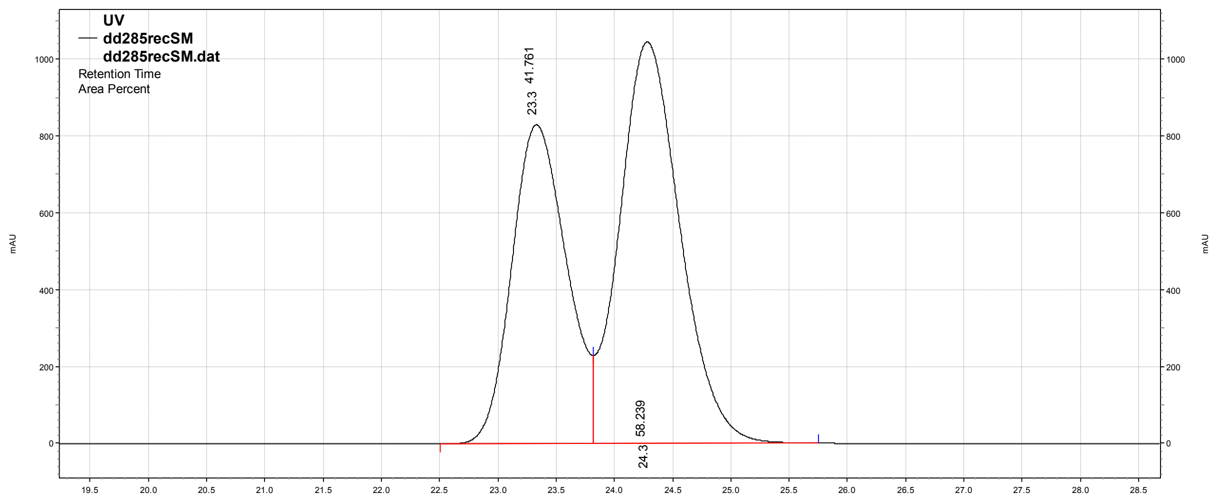


UV Results

Retention Time	Area	Area %	Height	Height %
23.550	180174362	49.20	5413004	50.69
24.663	186029264	50.80	5264712	49.31

Totals	366203626	100.00	10677716	100.00

Area % Report for enantioenriched 6-Nitro-2-phenyl-chromene 15a
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd285recSM.dat
Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\95.5 0.5ml 80min.met

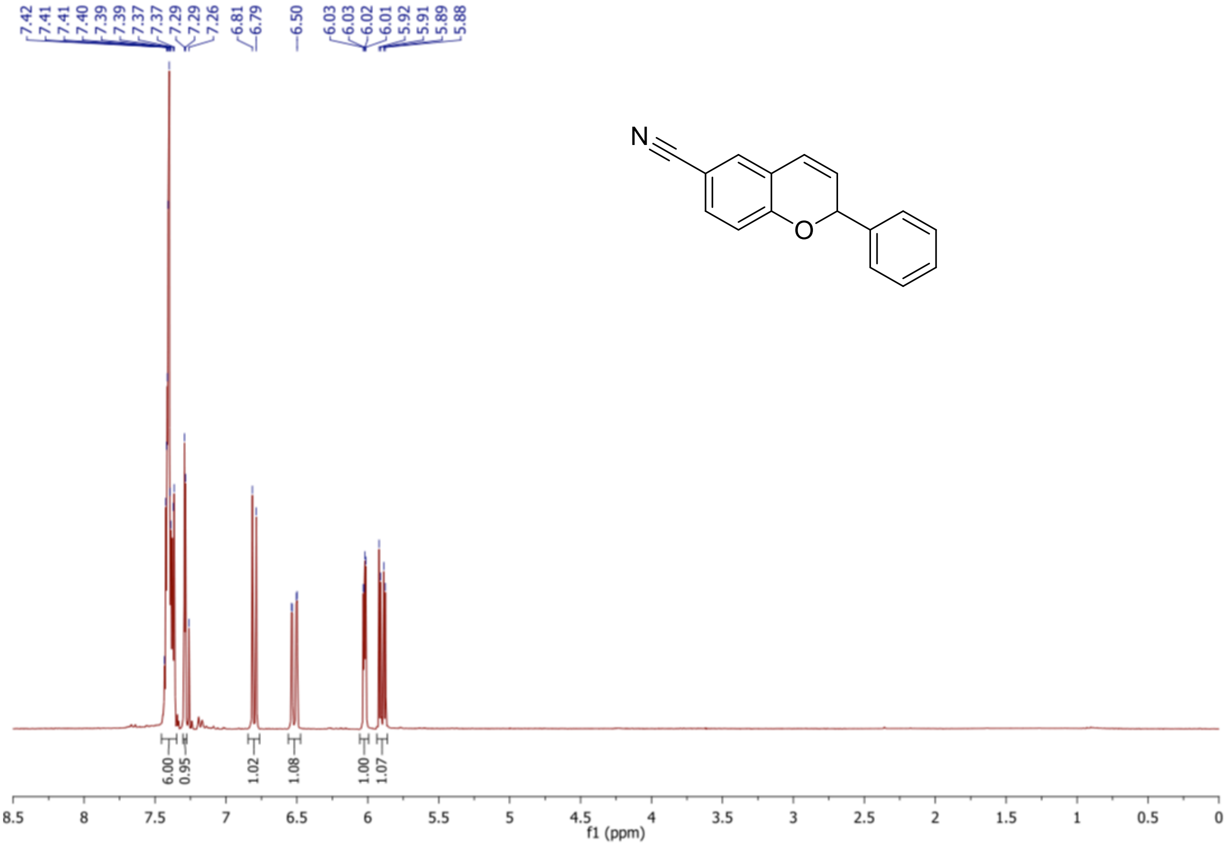


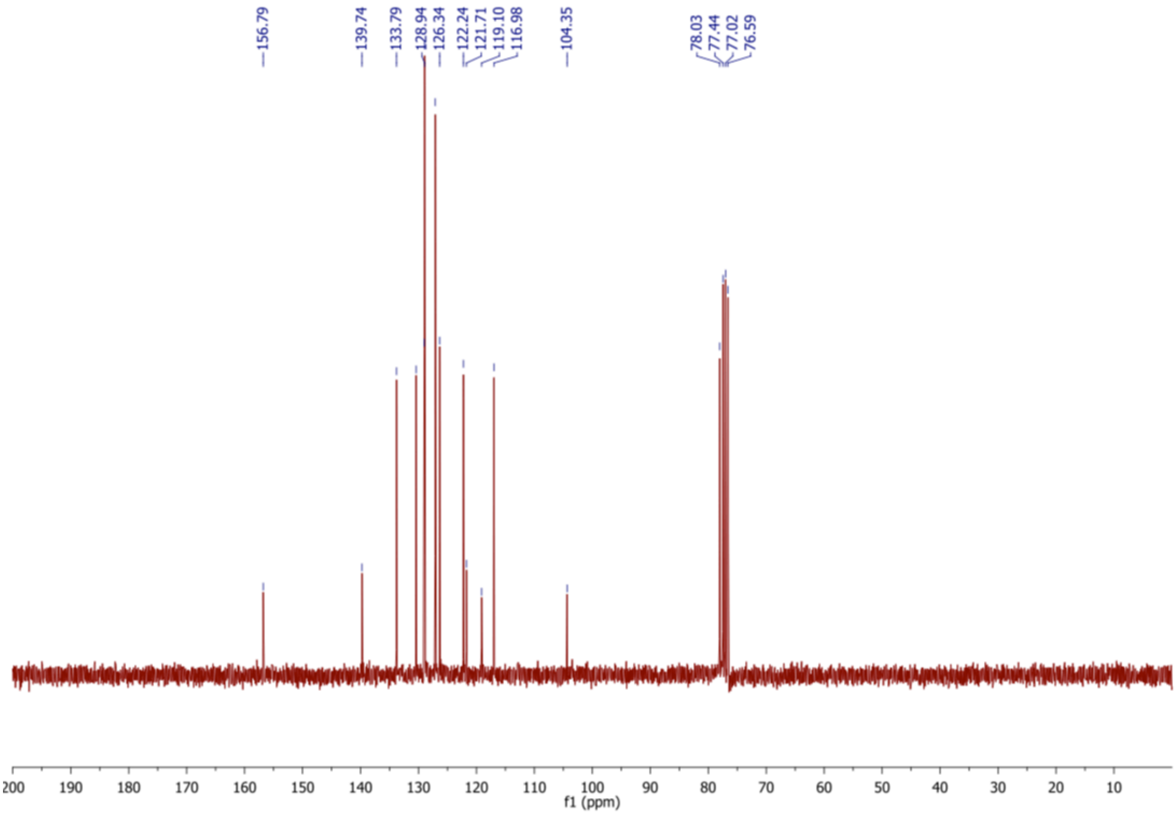
UV Results

Retention Time	Area	Area %	Height	Height %
23.330	108893727	41.76	3320800	44.27
24.283	151858843	58.24	4180011	55.73

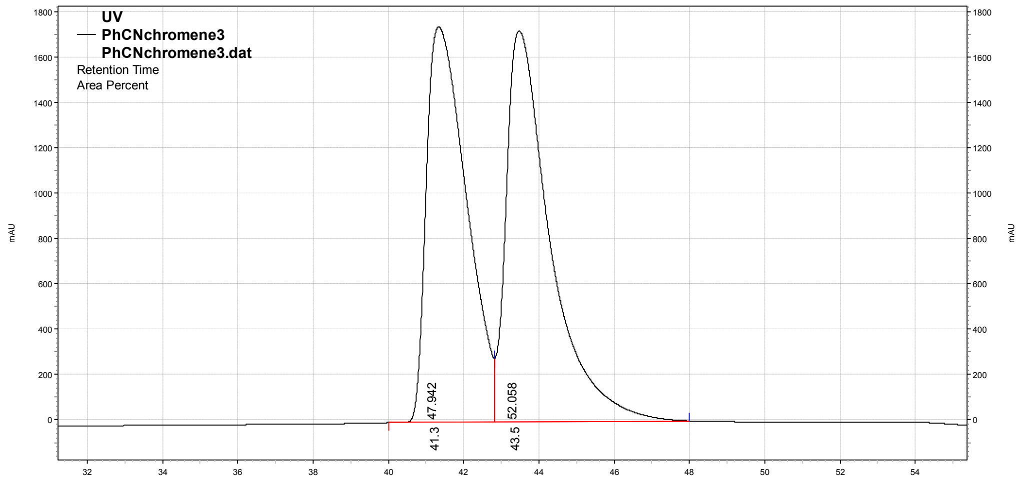
Totals	260752570	100.00	7500811	100.00

6-Cyano-2-phenyl-chromene 15b





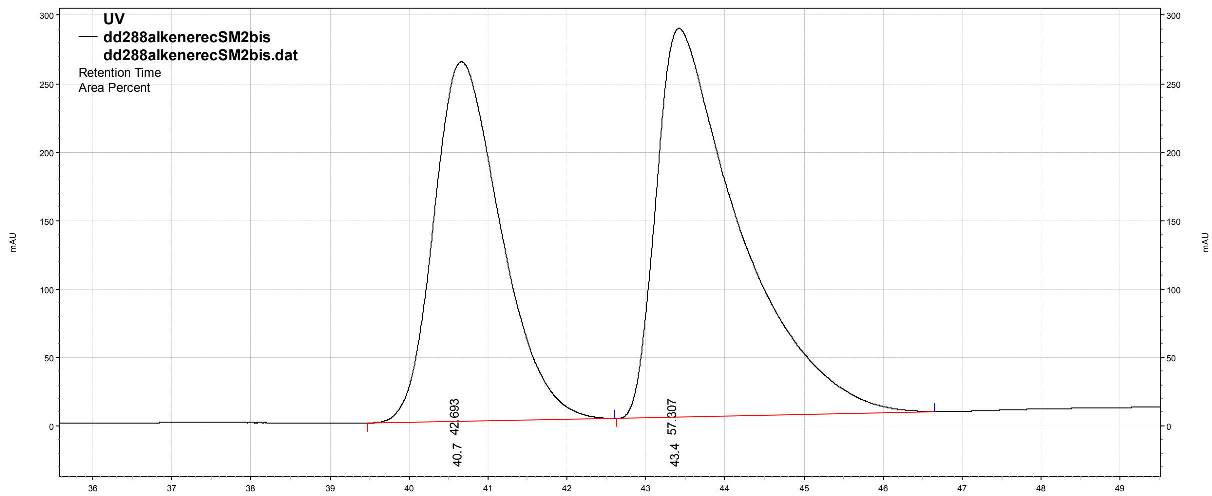
Area % Report for racemic 6-Cyano-2-phenyl-chromene 15b
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\PhCNchromene3.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Dave\method\230nm\99.5.0.5.met



UV Results

Retention Time	Area	Area %	Height	Height %
41.337	514307753	47.94	6969959	50.28
43.470	558463298	52.06	6891331	49.72
Totals	1072771051	100.00	13861290	100.00

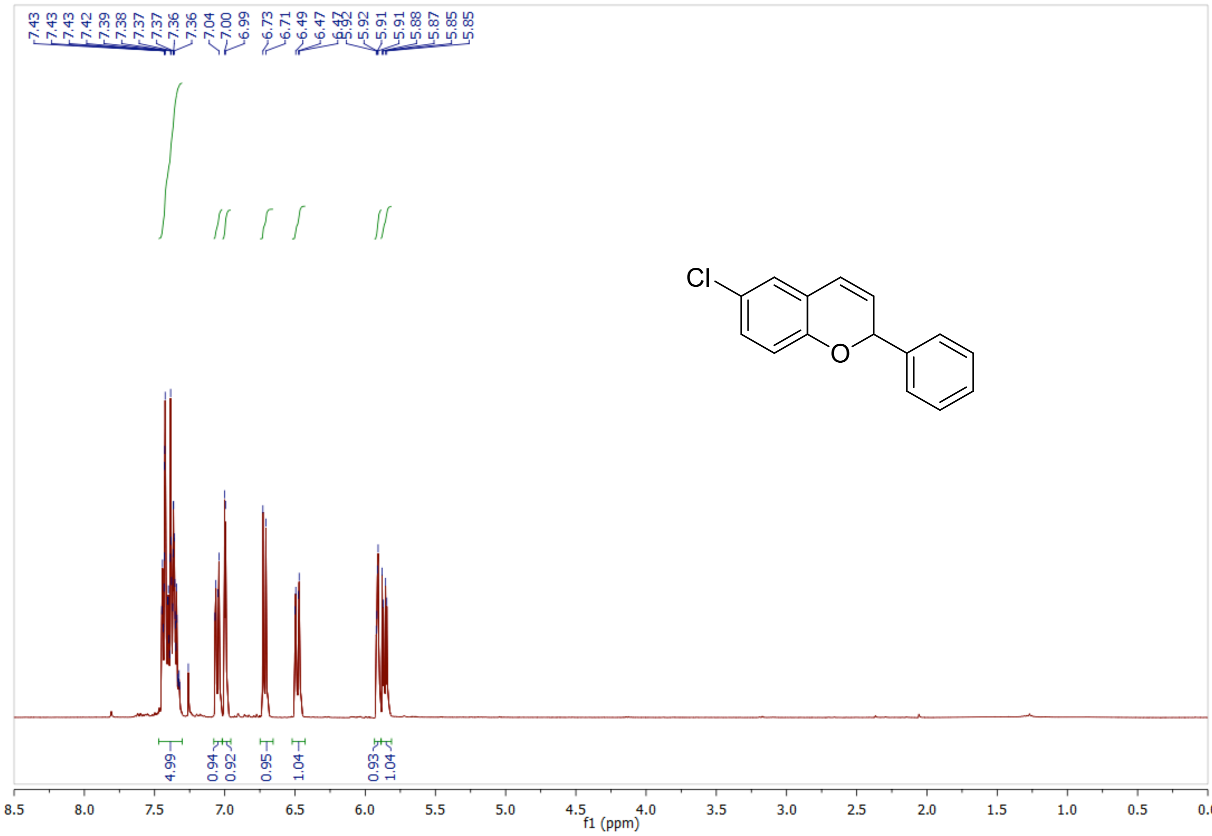
Area % Report for enantioenriched 6-Cyano-2-phenyl-chromene 15b
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd288alkenerecSM2bis.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Dave\method\230nm\99.5.0.5.met

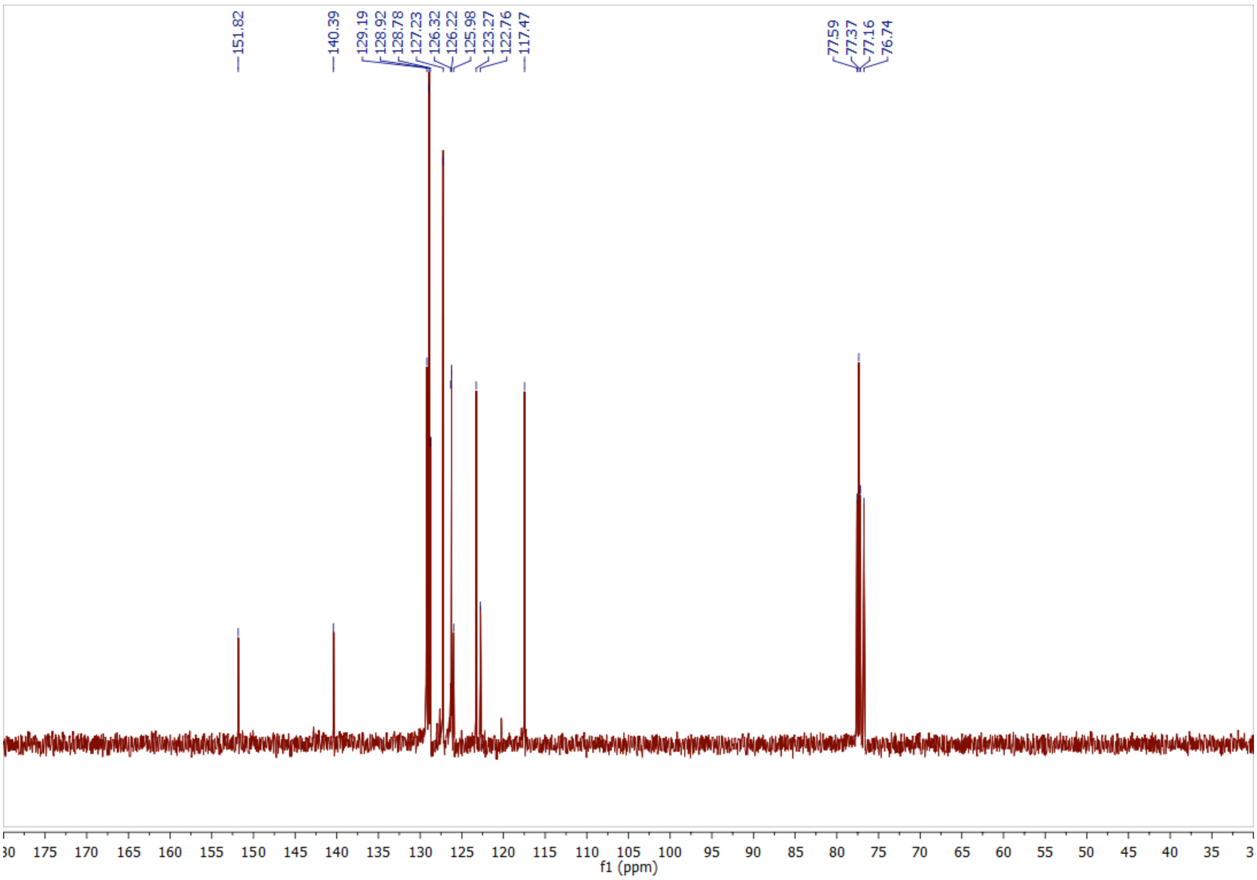


UV Results

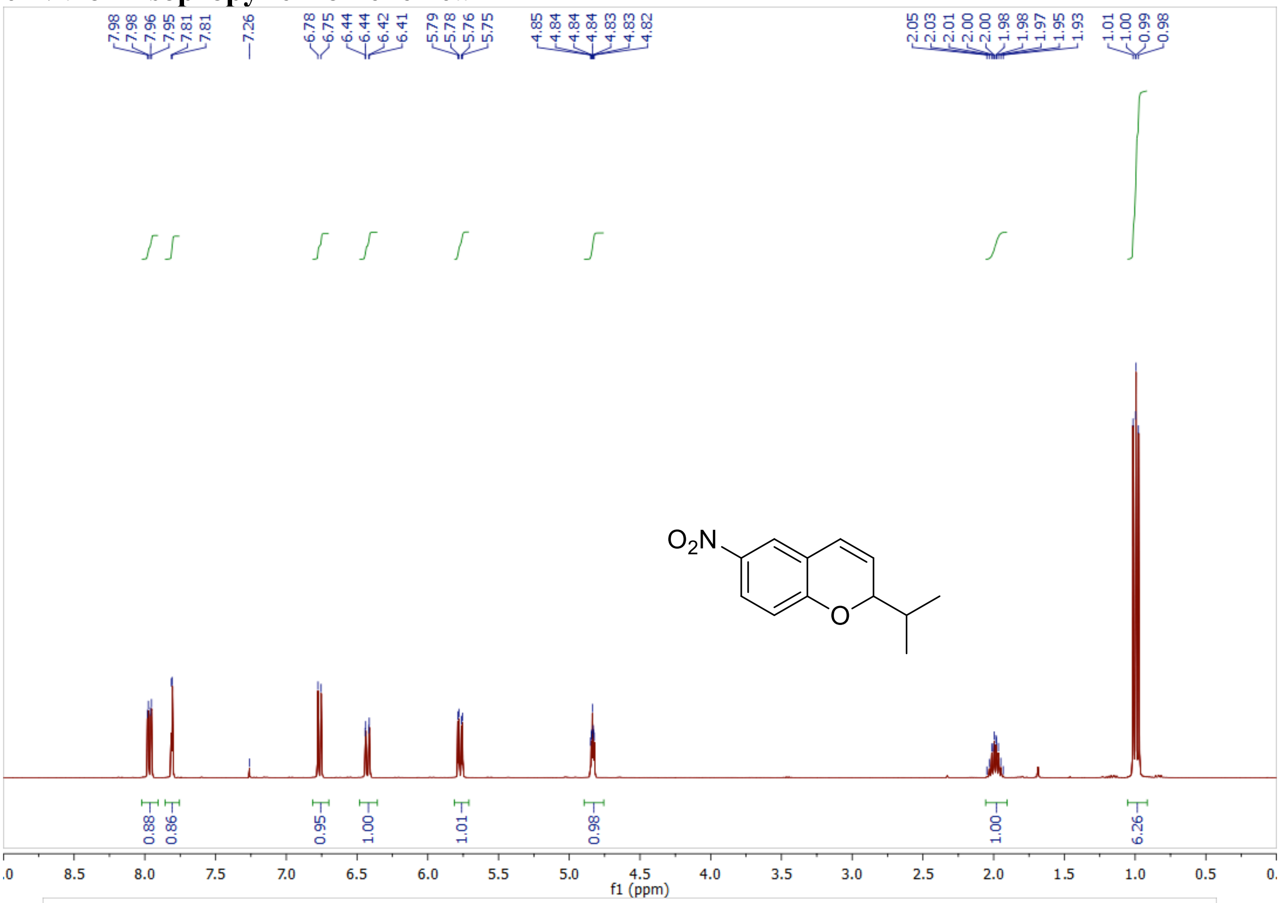
Retention Time	Area	Area %	Height	Height %
40.663	62108870	42.69	1051182	48.05
43.417	83370682	57.31	1136548	51.95
Totals	145479552	100.00	2187730	100.00

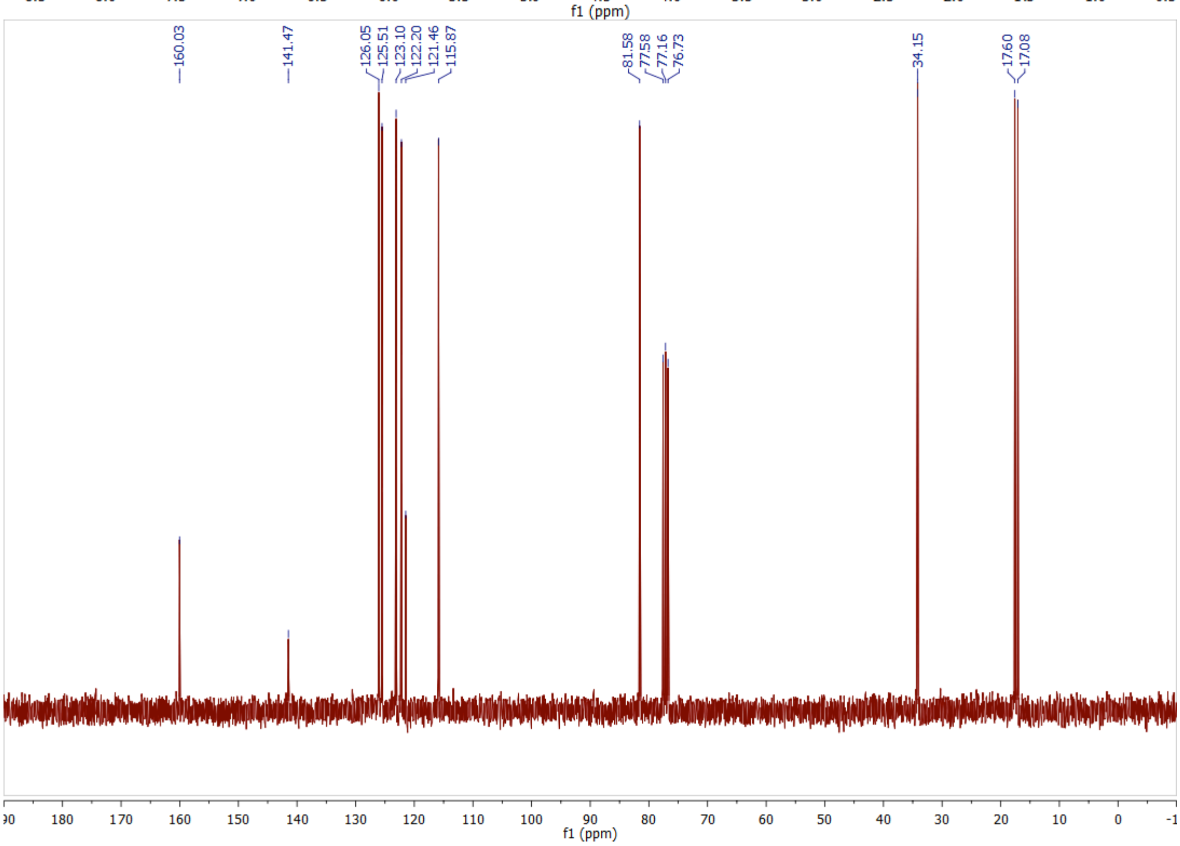
6-Chloro-2-phenyl-chromene 15c





6-Nitro-2-isopropyl-chromene 16a

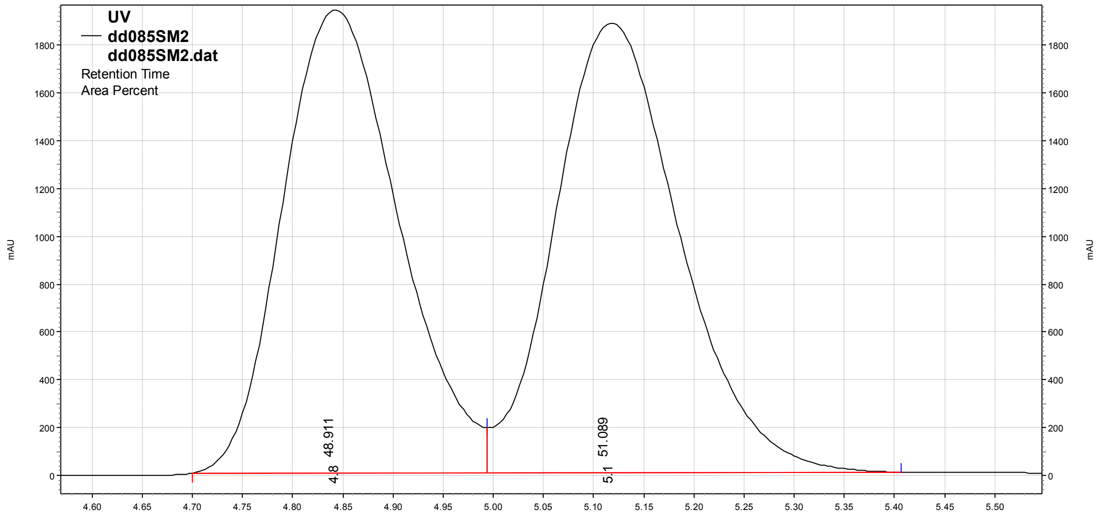




Area % Report for racemic 6-Nitro-2-isopropyl-chromene 16a

Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd085SM2.dat

Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10.1h.met



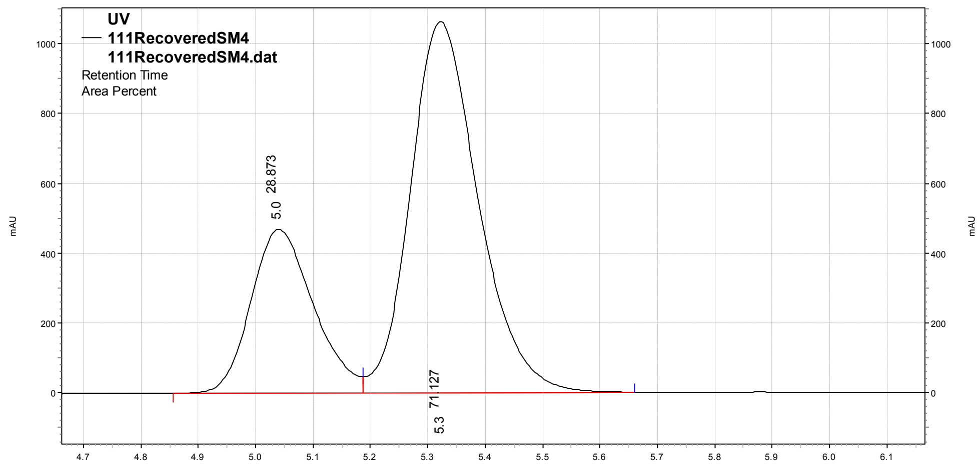
UV Results

Retention Time	Area	Area %	Height	Height %
4.843	62471583	48.91	7745176	50.73
5.117	65252560	51.09	7521949	49.27
Totals	127724143	100.00	15267125	100.00

Area % Report for enantioenriched 6-Nitro-2-isopropyl-chromene 16a.

Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\111RecoveredSM4.dat

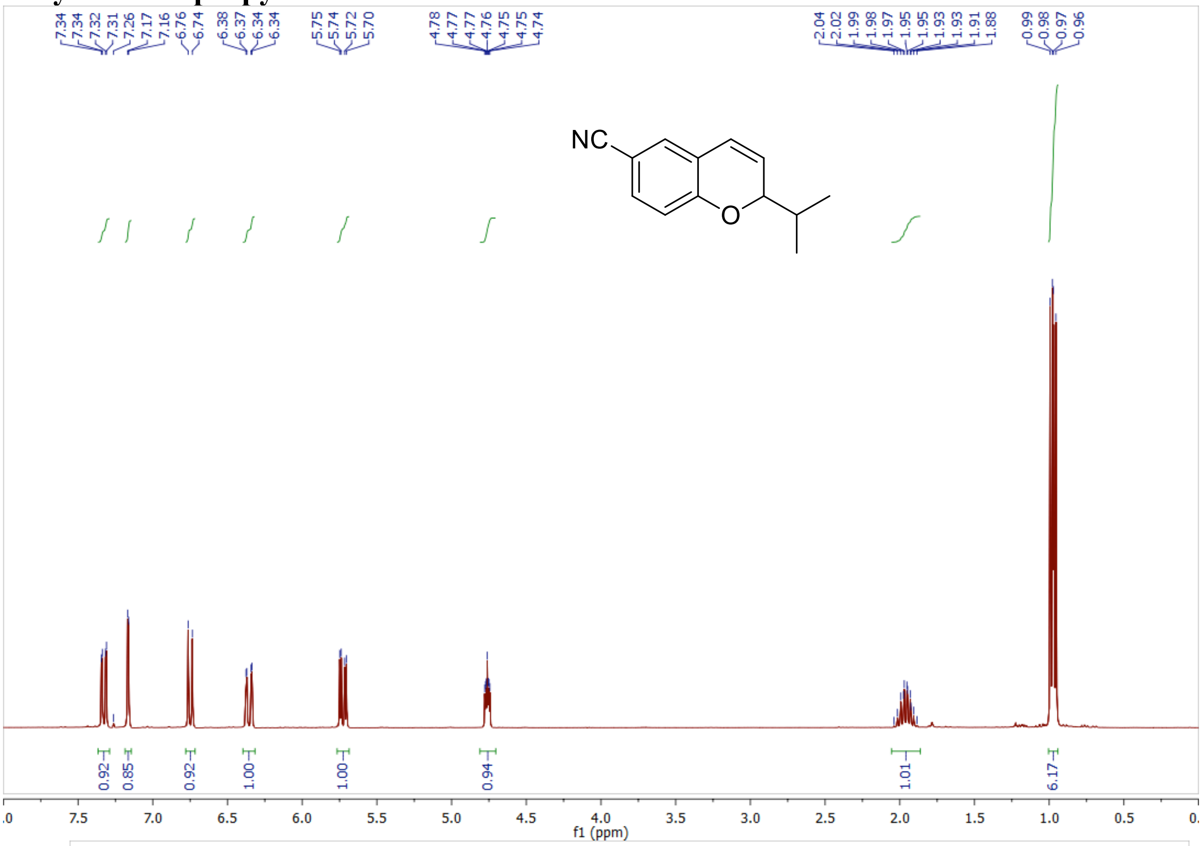
Method: C:\EZChrom Elite\Enterprise\Projects\Dave\method\90.10.1h.met

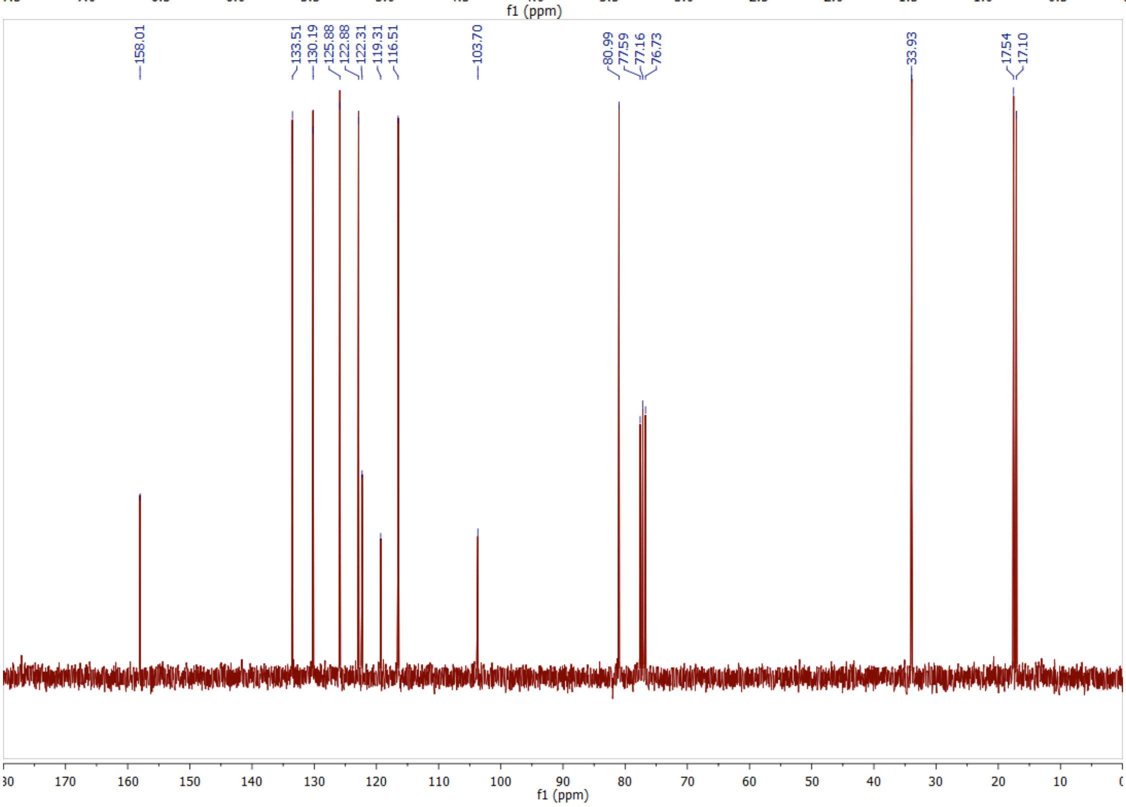


UV Results

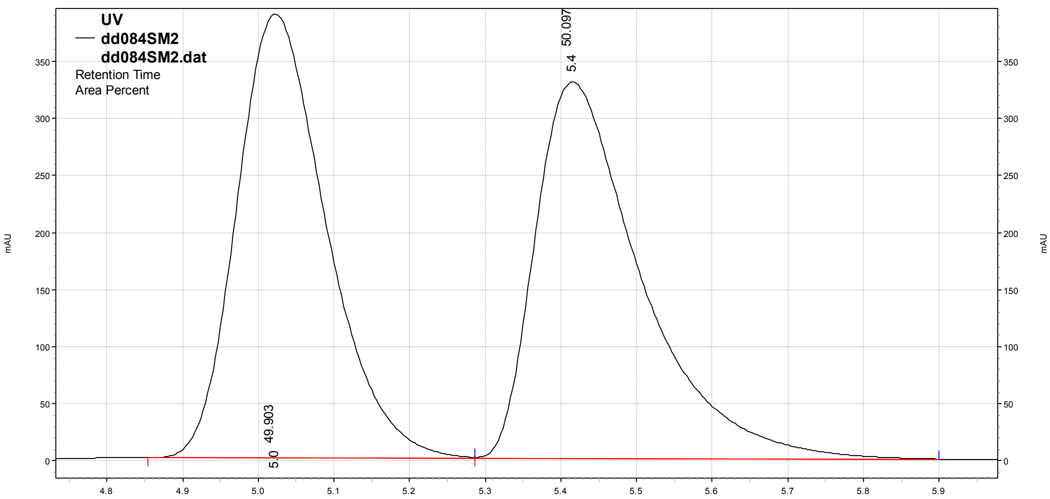
Retention Time	Area	Area %	Height	Height %
5.040	14166670	28.87	1870886	30.56
5.323	34899561	71.13	4250643	69.44
		ee= 42.26		
Totals	49066231	100.00	6121529	100.00

6-Cyano-2-isopropyl-chromene 16b





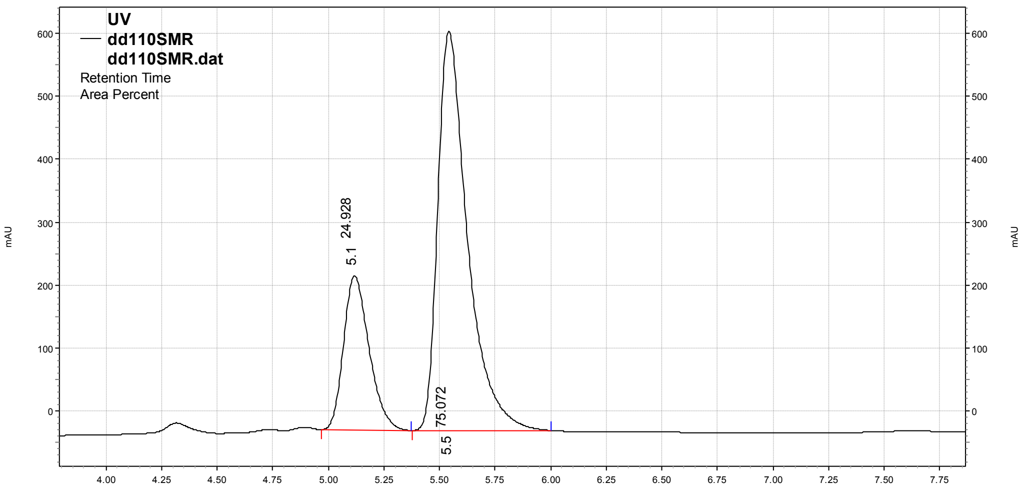
Area % Report for racemic 6-Cyano-2-isopropyl-chromene 16b
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd084SM2.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10.1h.met



UV Results

Retention Time	Area	Area %	Height	Height %
5.023	12826528	49.90	1555434	54.11
5.417	12876177	50.10	1319204	45.89
Totals	25702705	100.00	2874638	100.00

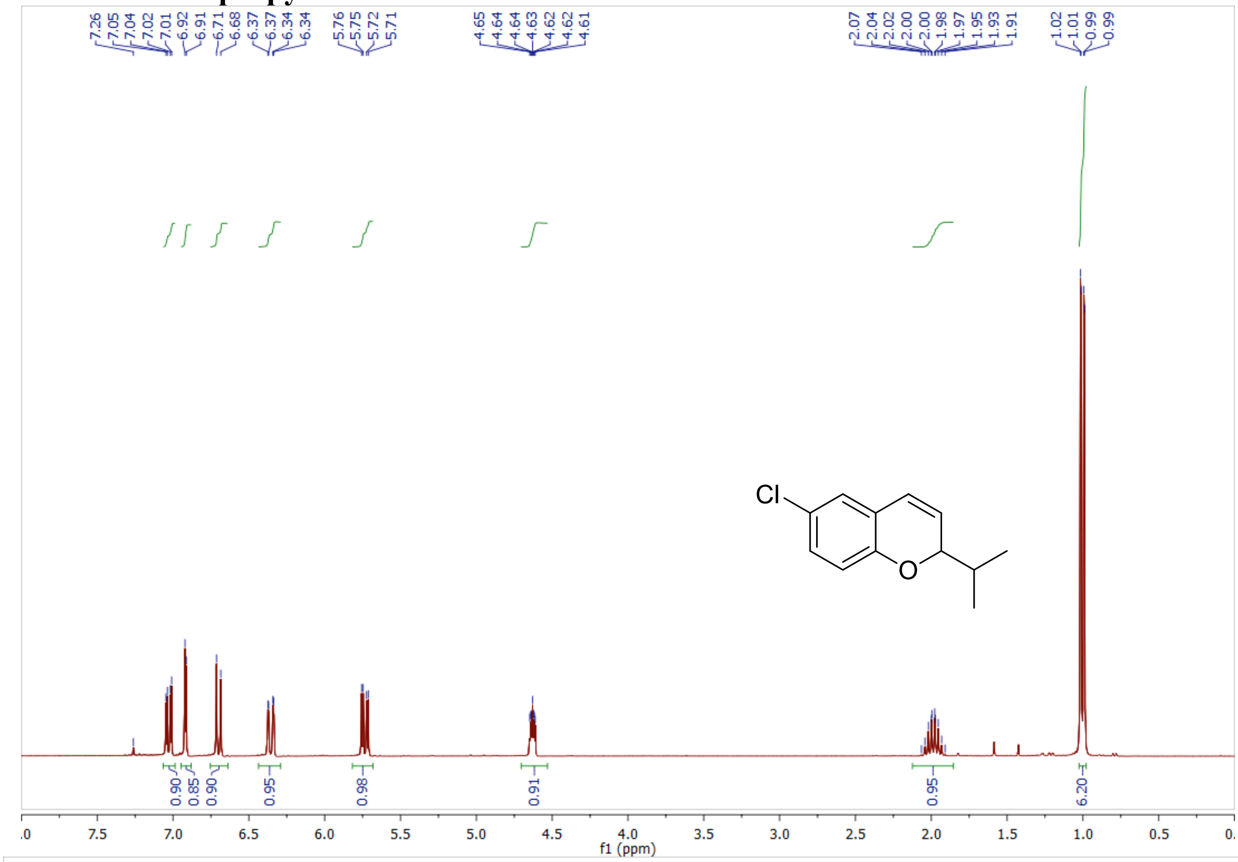
Area % Report for enantioenriched 6-Cyano-2-isopropyl-chromene 16b
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd110SMR.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Dave\method\90.10.1h.met

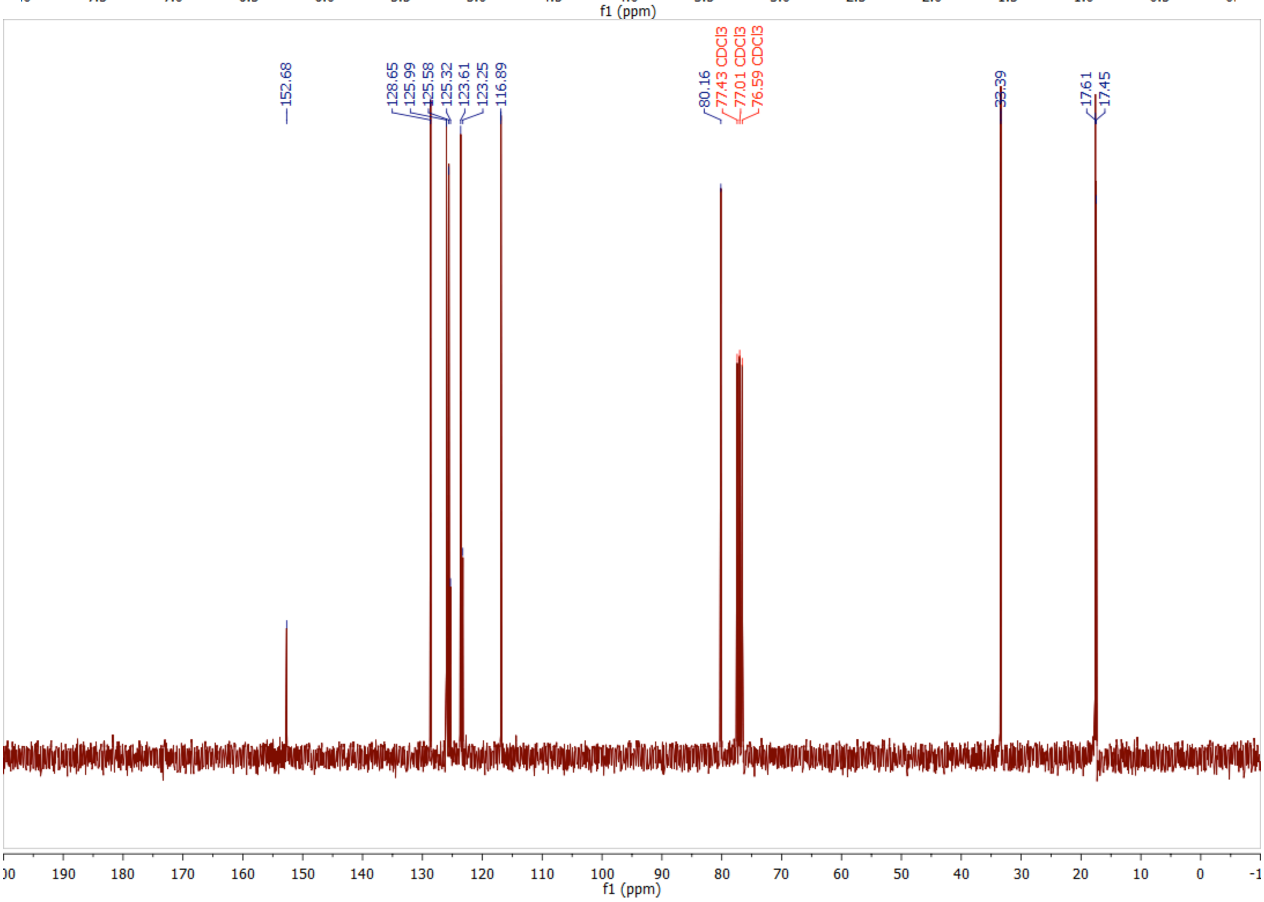


UV Results

Retention Time	Area	Area %	Height	Height %
5.117	7847582	24.93	979532	27.86
5.543	23633357	75.07	2535759	72.14
		ee= 50.14		
Totals	31480939	100.00	3515291	100.00

6-Chloro-2-isopropyl-chromene 16c

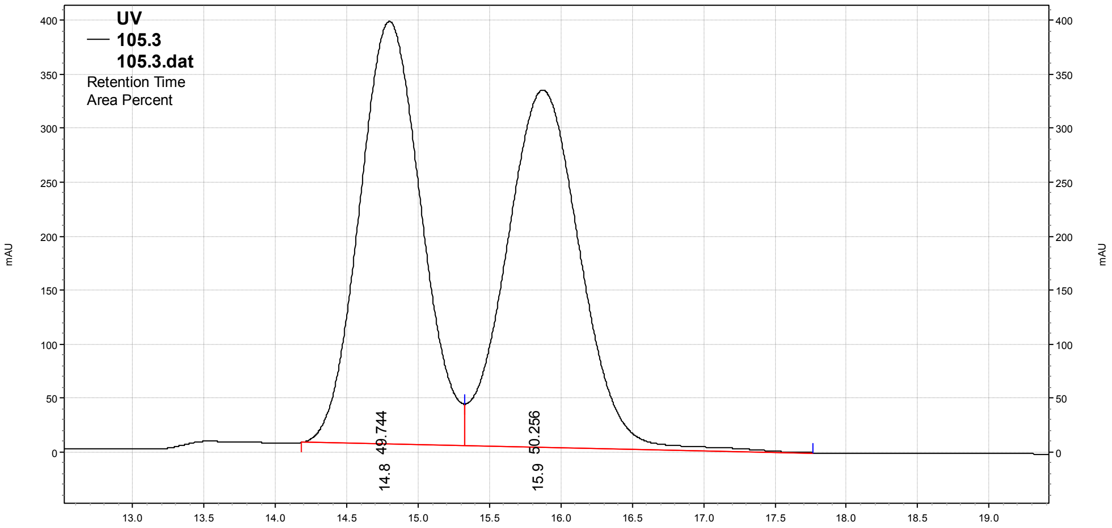




Area % Report

Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\105.3.dat

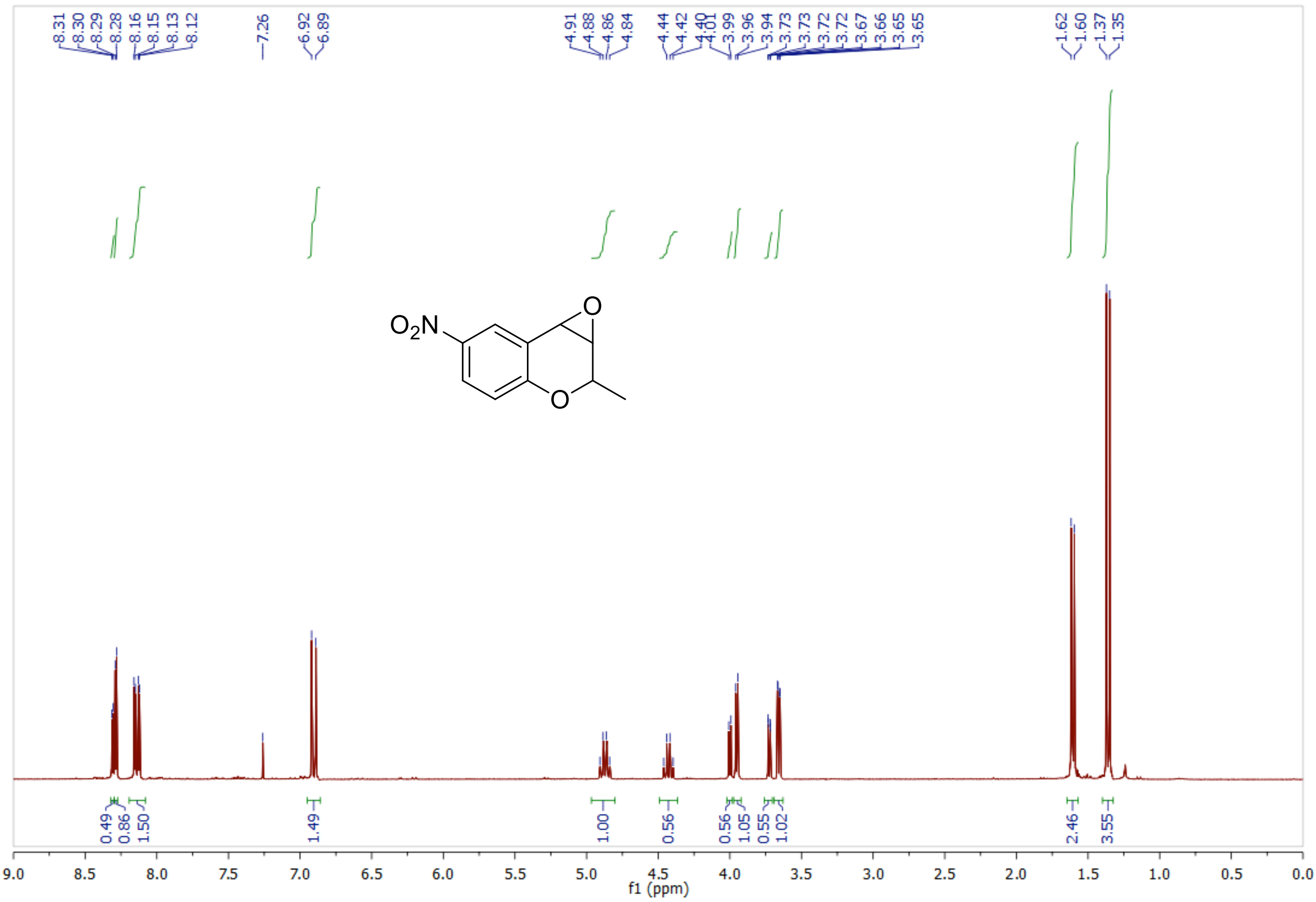
Method: C:\EZChrom Elite\Enterprise\Projects\Dave\method\99.9.0.1.0.25ml.met

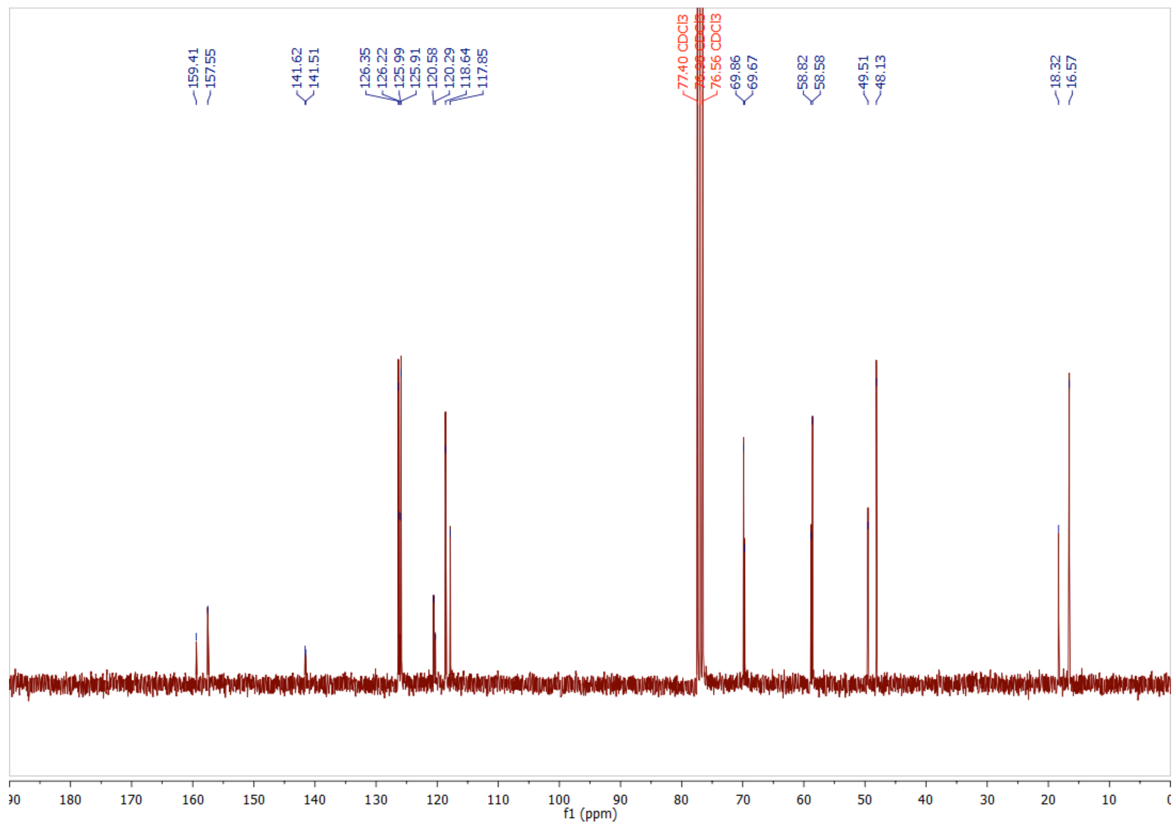


UV Results

Retention Time	Area	Area %	Height	Height %
14.800	47194770	49.74	1566402	54.19
15.873	47680866	50.26	1323970	45.81
Totals	94875636	100.00	2890372	100.00

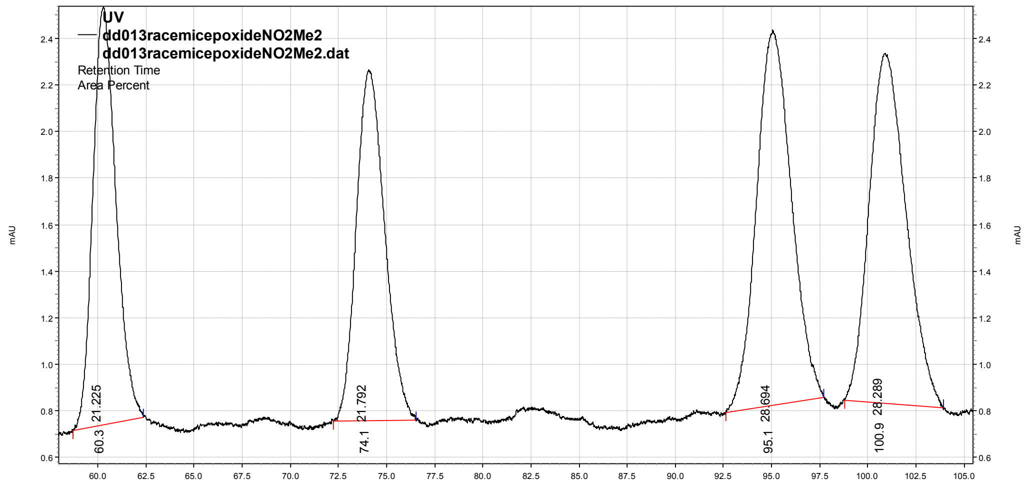
6-Nitro-2-methyl-chromene epoxide (±)-17a





Racemic HPLC trace: 6-nitro-2-methyl-3,4-epoxy-chromene (±)-17a

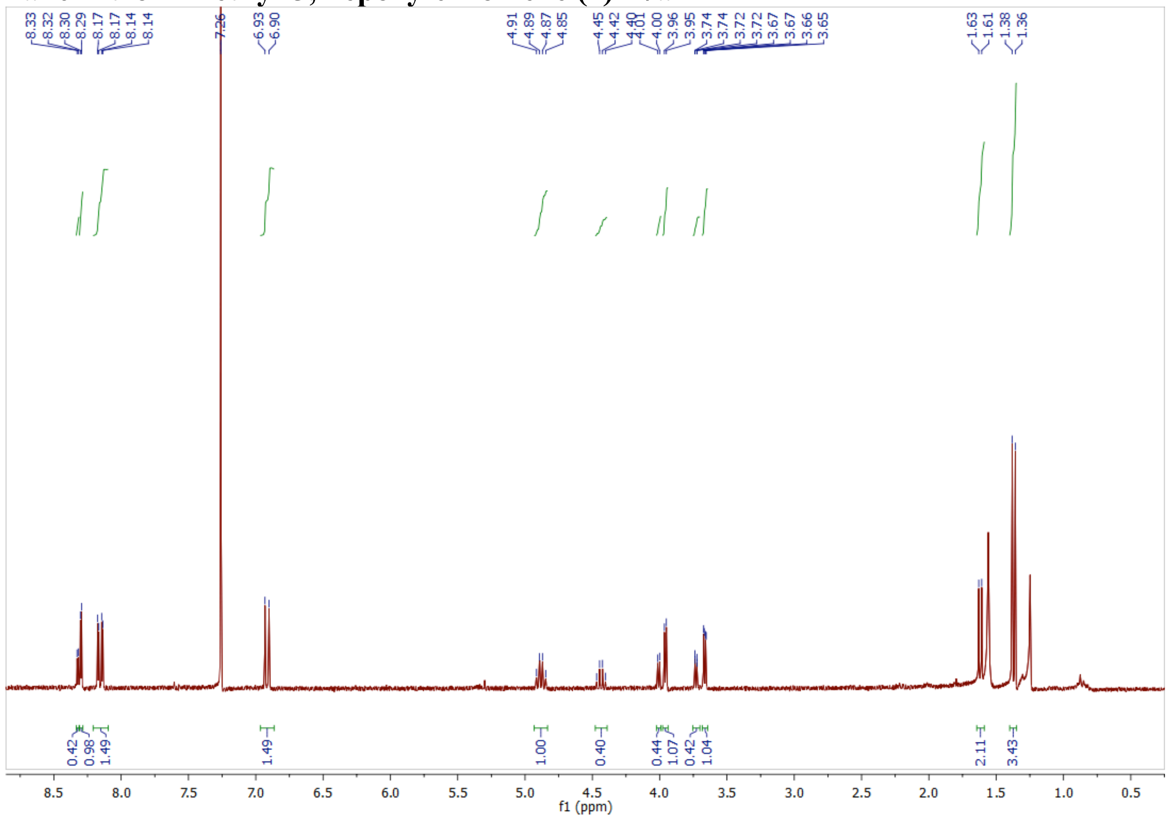
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\dd013racemicepoxideNO2Me2.dat
Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\untitled.met



UV Results

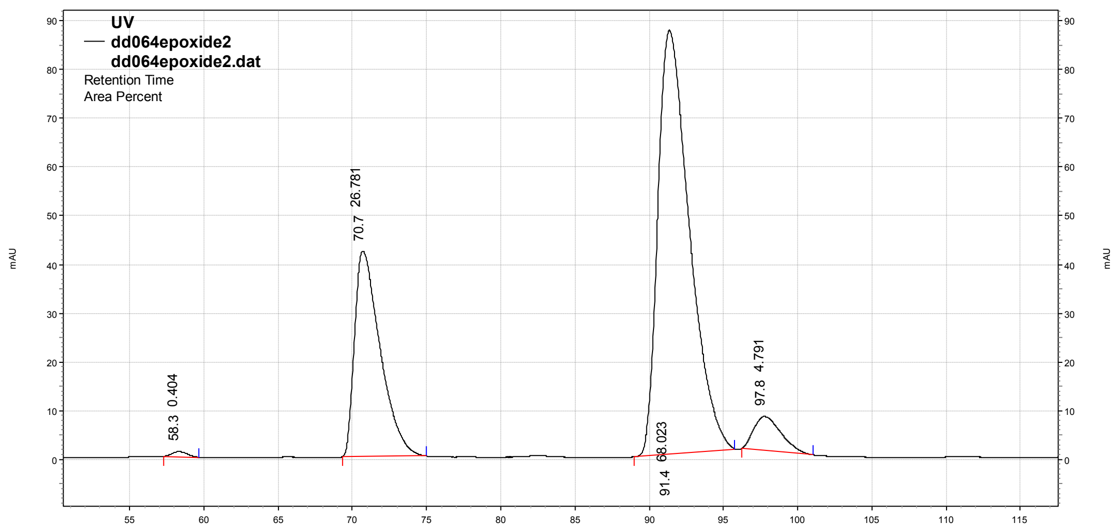
Retention Time	Area	Area %	Height	Height %
60.307	601894	21.22	7187	27.98
74.090	617977	21.79	6032	23.48
95.060	813716	28.69	6452	25.12
100.870	802221	28.29	6016	23.42
Totals	2835808	100	25687	100

Chiral 6-nitro-2-methyl-3,4-epoxy-chromene (–)-17a



Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd064epoxide2.dat

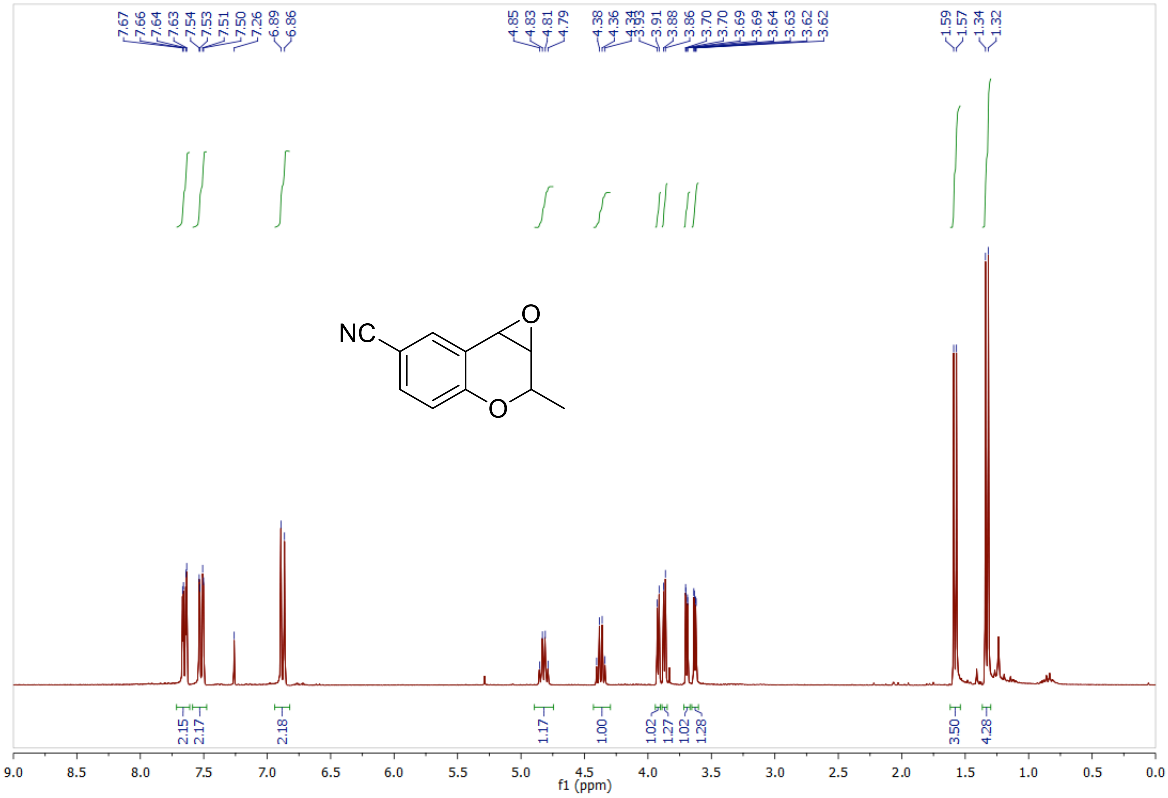
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\99.5 0.5 0.5ml 3 hours MeCN chrom.met

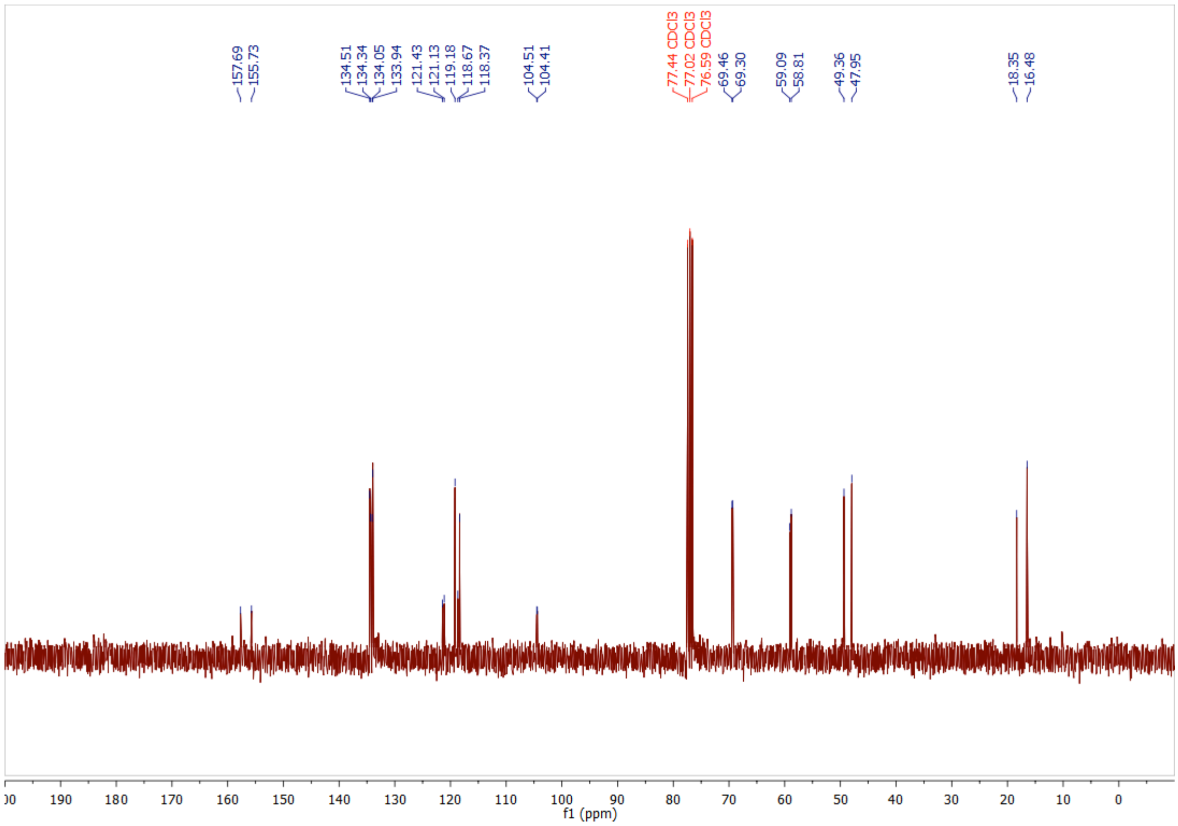


UV Results

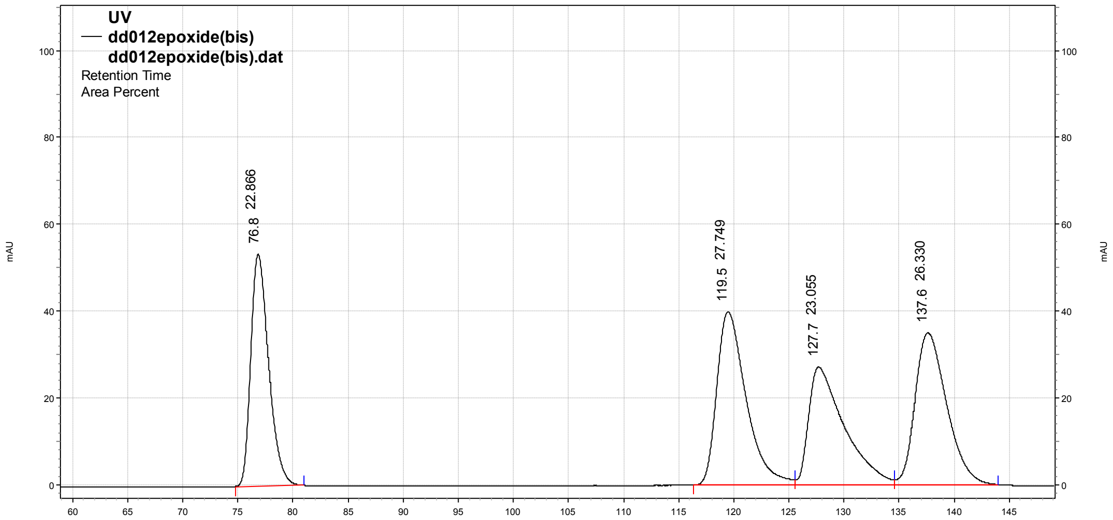
Retention Time	Area	Area %	Height	Height %
58.287	305798	0.40	4236	0.77
70.713	20257880	26.78	168758	30.74
Minor dia.		ee = 97.06		
91.357	51454852	68.02	348064	63.39
97.753	3624319	4.79	28015	5.10
Major dia.		ee = 86.84		
Totals	75642849	100.00	549073	100.00

Racemic 6-Cyano-2-methyl-chromene epoxide (±)-17b





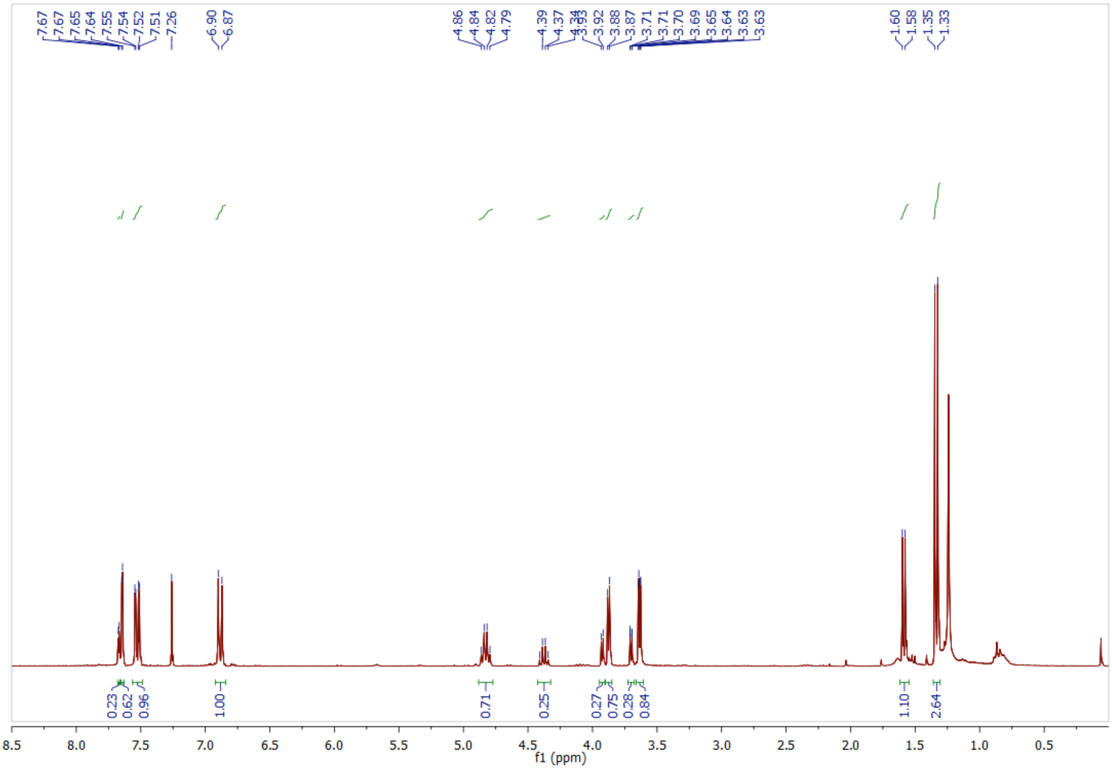
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\dd012epoxide(bis).dat
Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\untitled.met



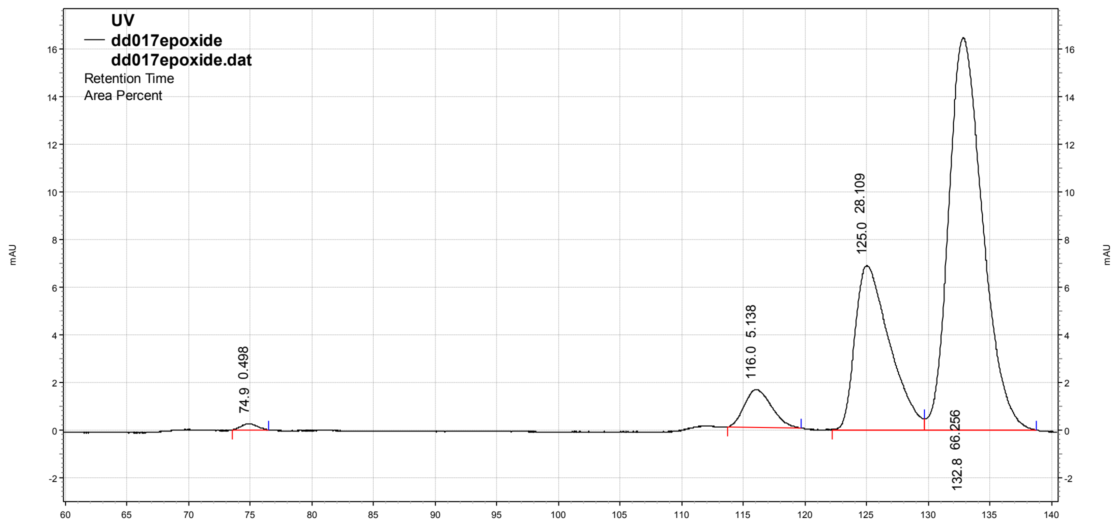
UV Results

Retention Time	Area	Area %	Height	Height %
76.817	24233994	22.87	213438	34.33
119.490	29409374	27.75	159788	25.70
127.700	24434049	23.05	108516	17.45
137.623	27905105	26.33	140040	22.52
Totals	105982522	100.00	621782	100.00

Chiral 6-cyano-2-methyl-3,4-epoxy-chromene (–)-17b



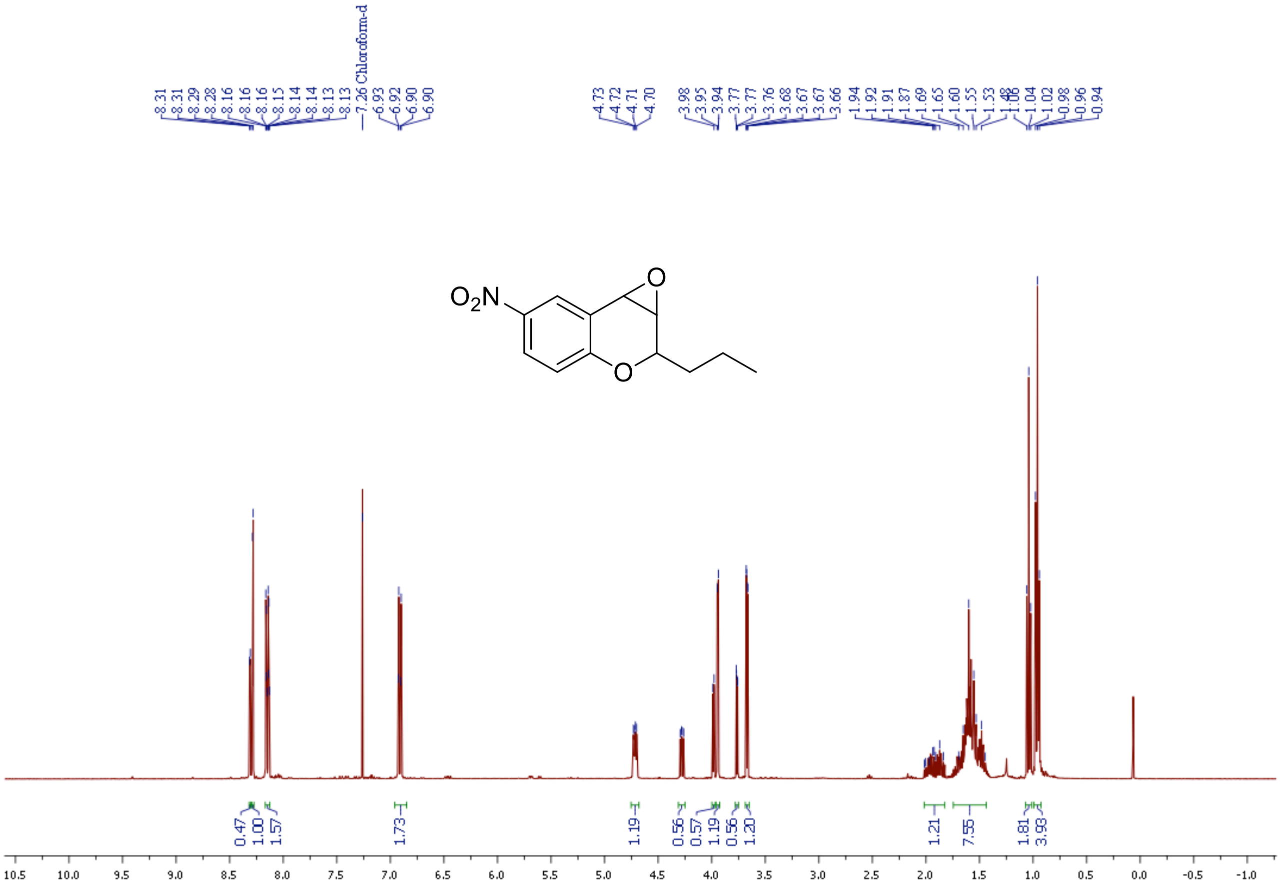
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd017b\epoxide\dd017epoxide.dat
Method: C:\EZChrom Elite\Enterprise\Projects\ben\Method\untitled.met

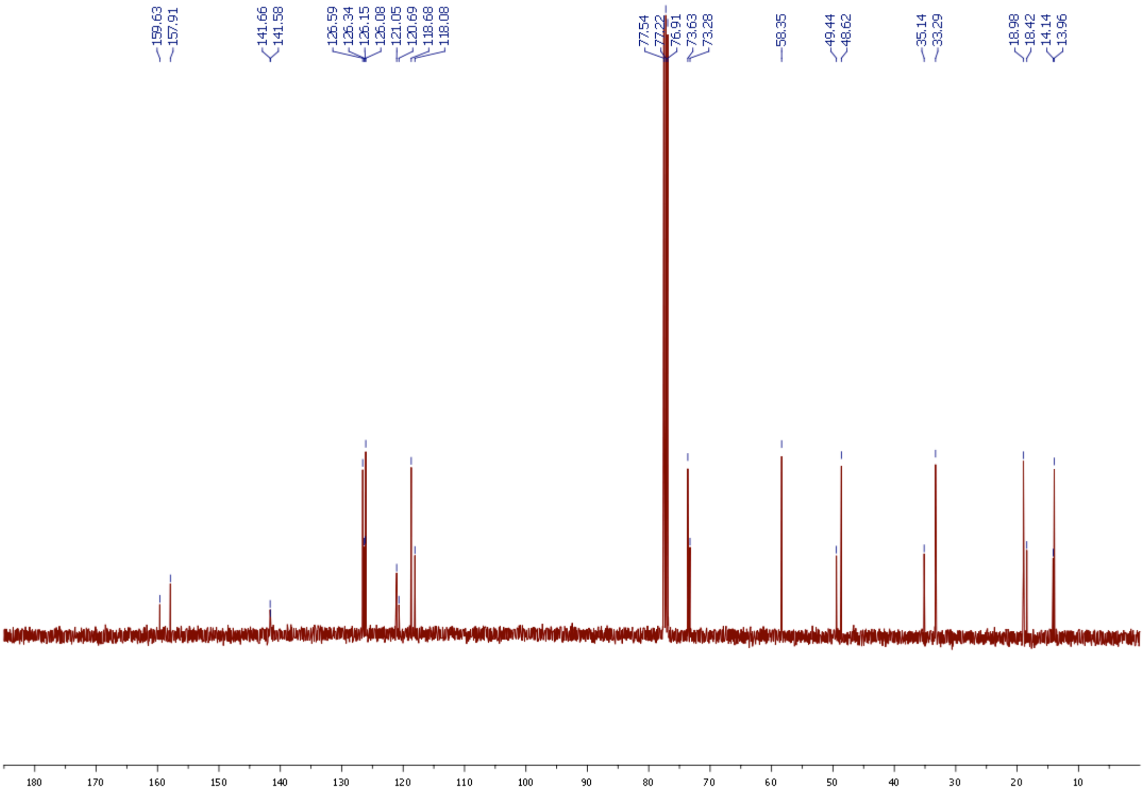


UV Results

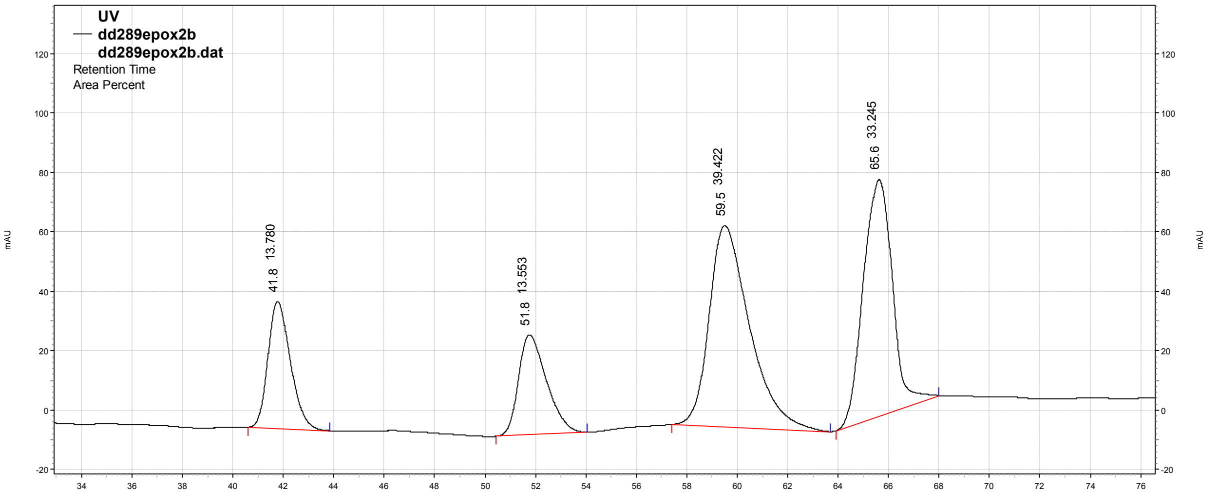
Retention Time	Area	Area %	Height	Height %
74.877	95192	0.50	1076	1.07
116.040	983013	5.14	6381	6.32
125.013	5377924	28.11	27606	27.33
132.813	12676530	66.26	65949	65.29
Minor dia.		ee= 96.51		
Major dia.		ee= 85.60		
Totals	19132659	100	101012	100

Racemic 6-nitro-2-propyl-3,4-epoxy-chromene (±)-18a





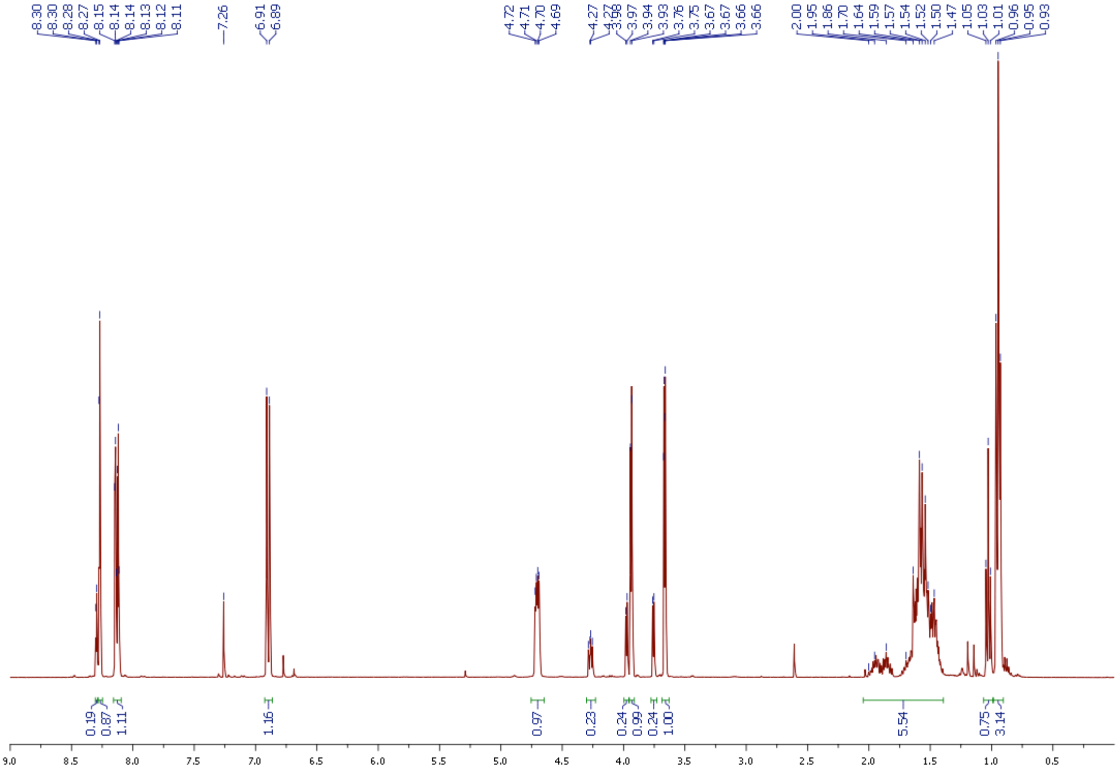
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd289epox2b.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\99.5 0.5 0.5ml 3 hours MeCN chrom.met
Acquired: 28/11/2011 13:06:43
Printed: 01/12/2011 16:03:44



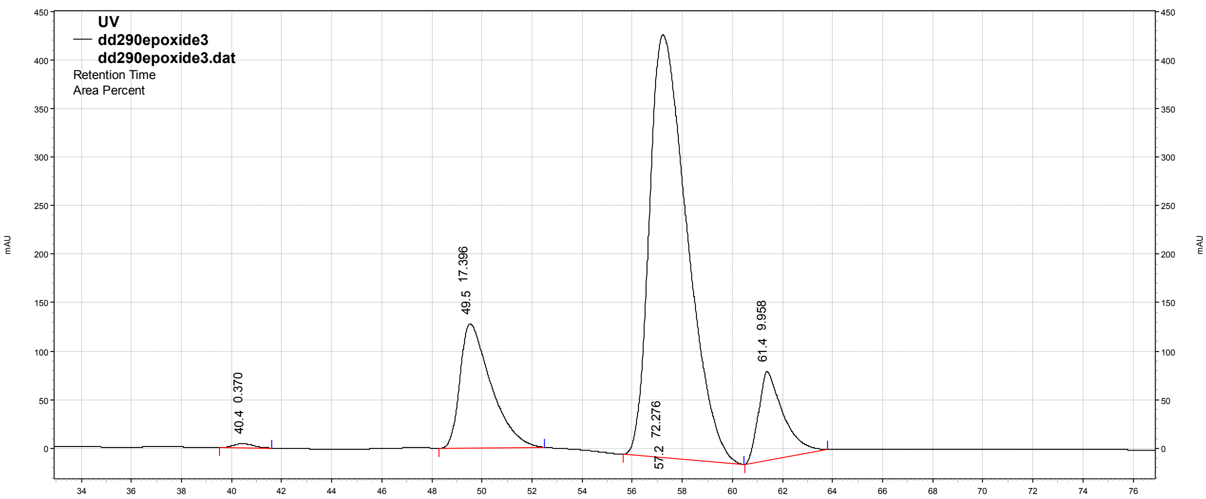
UV Results

Retention Time	Area	Area %	Height	Height %
41.770	10569320	13.78	170539	19.07
51.760	10395150	13.55	134643	15.05
59.503	30236509	39.42	270732	30.27
65.630	25498951	33.25	318554	35.61
Totals	76699930	100.00	894468	100.00

Enantioenriched 6-nitro-2-propyl-3,4-epoxy-chromene (–)-18a



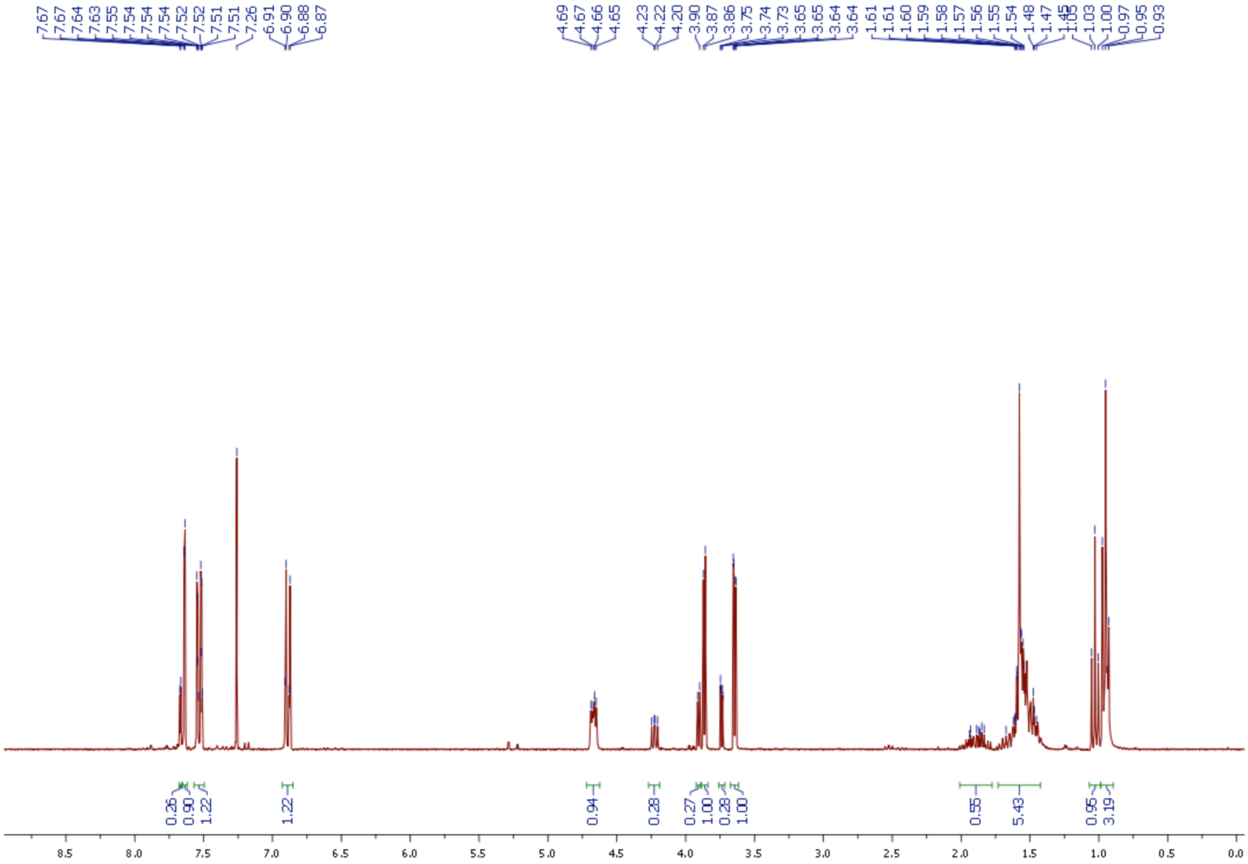
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd290epoxide3.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\99.5 0.5 0.5ml 3 hours MeCN chrom.met

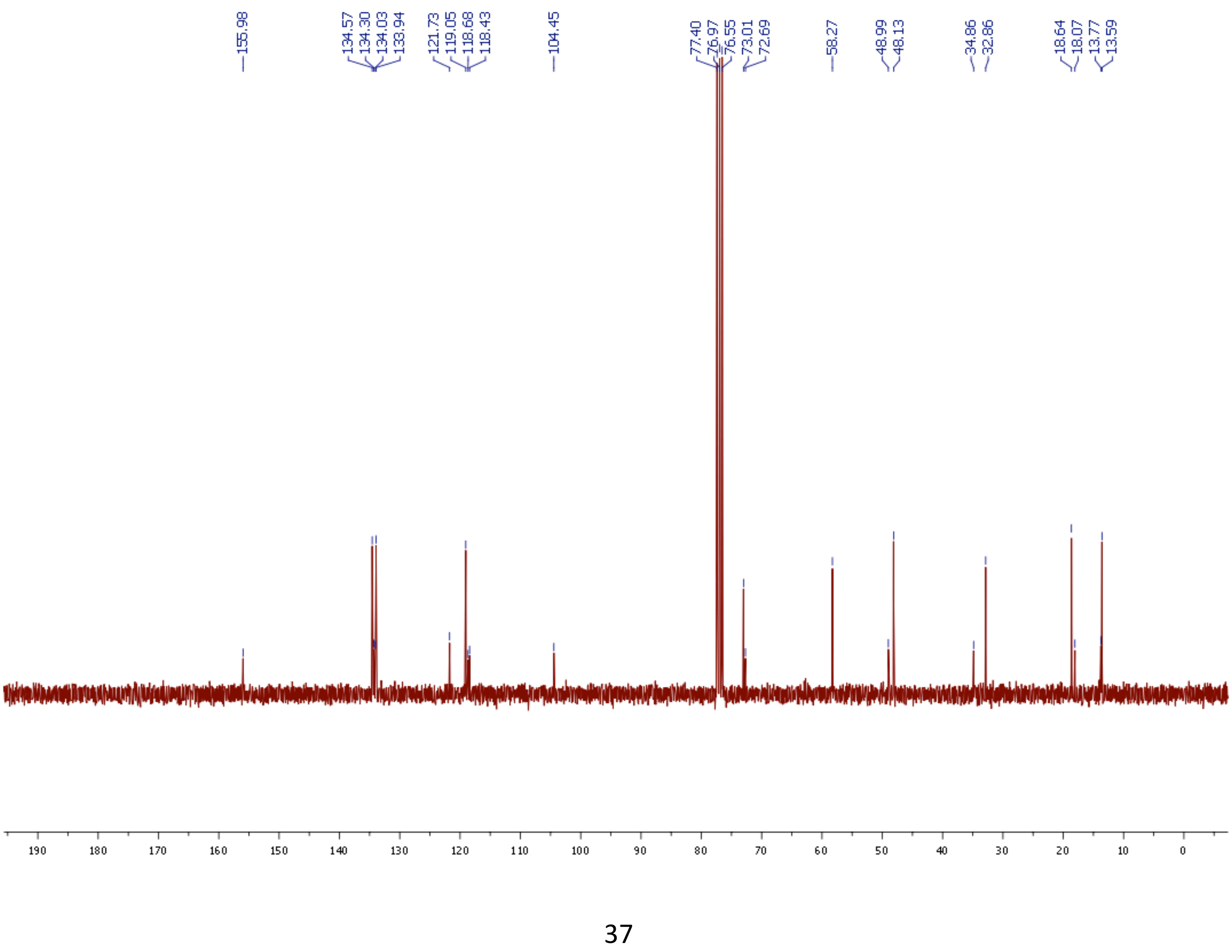


UV Results

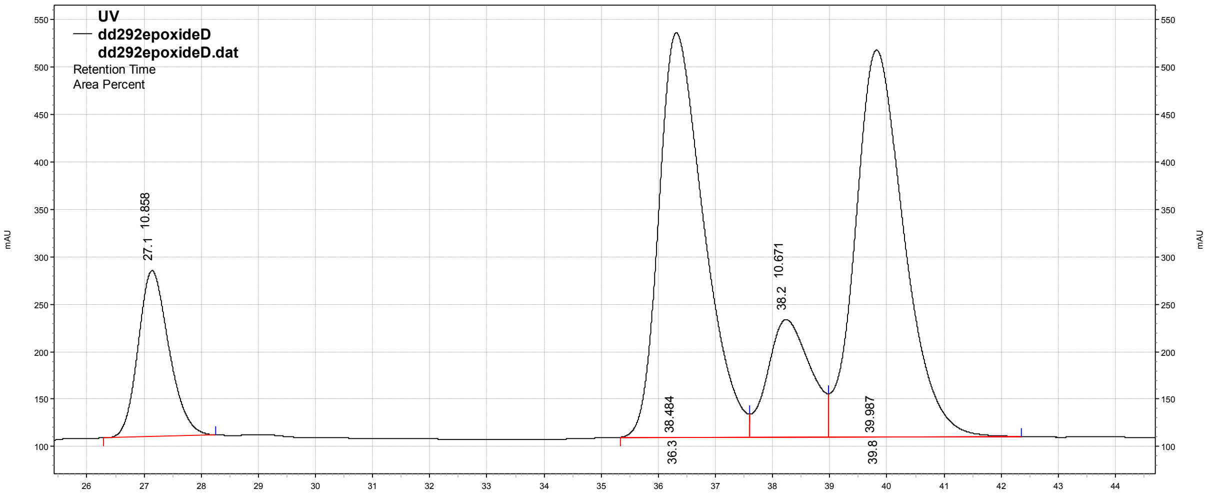
Retention Time	Area	Area %	Height	Height %
40.447	934073	0.37	17161	0.65
49.523	43870223	17.40	511300	19.39
57.230	182266625	72.28	1742542	66.09
61.390	25111807	9.96	365731	13.87
Totals	252182728	100.00	2636734	100.00

6-Cyano-2-propyl-chromene epoxide
Racemic 6-cyano-2-propyl-chromene epoxide (±)-18b





Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd292epoxideD.dat
Method: C:\EZChrom Elite\Enterprise\Projects\ben\111111.met

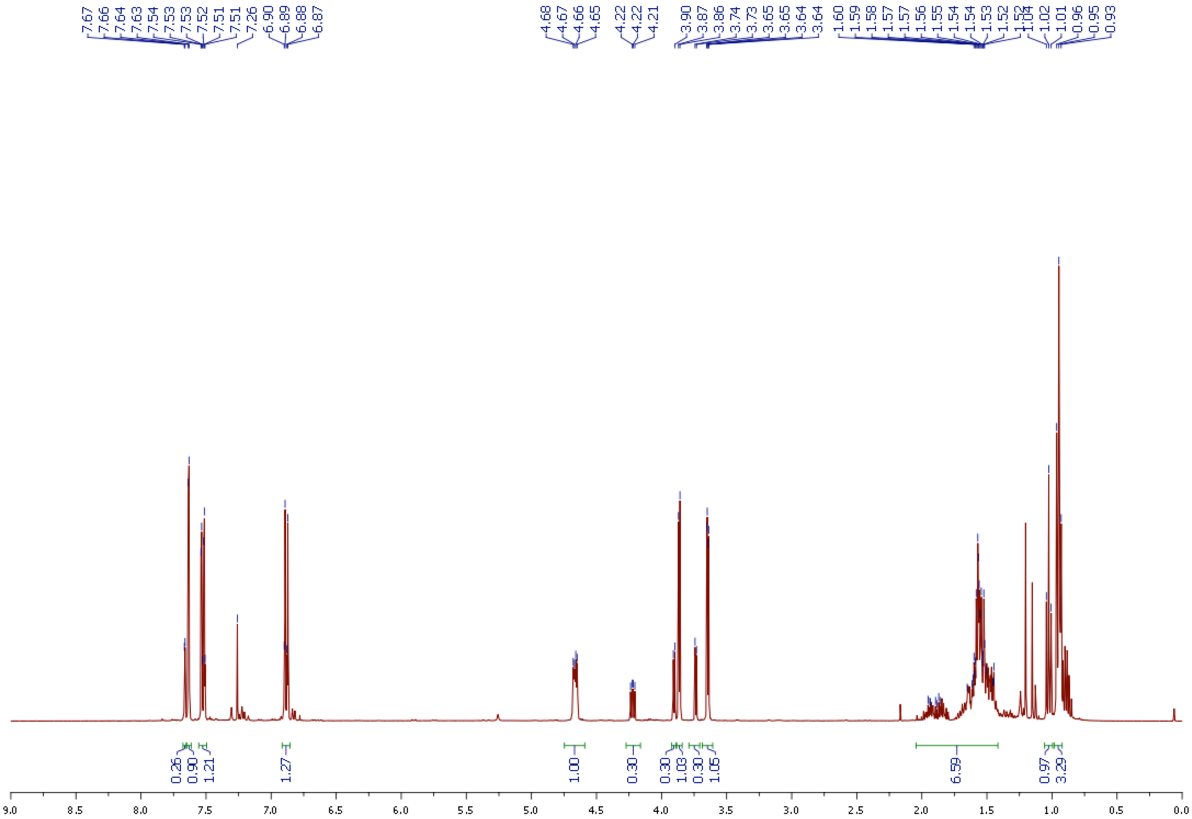


UV Results

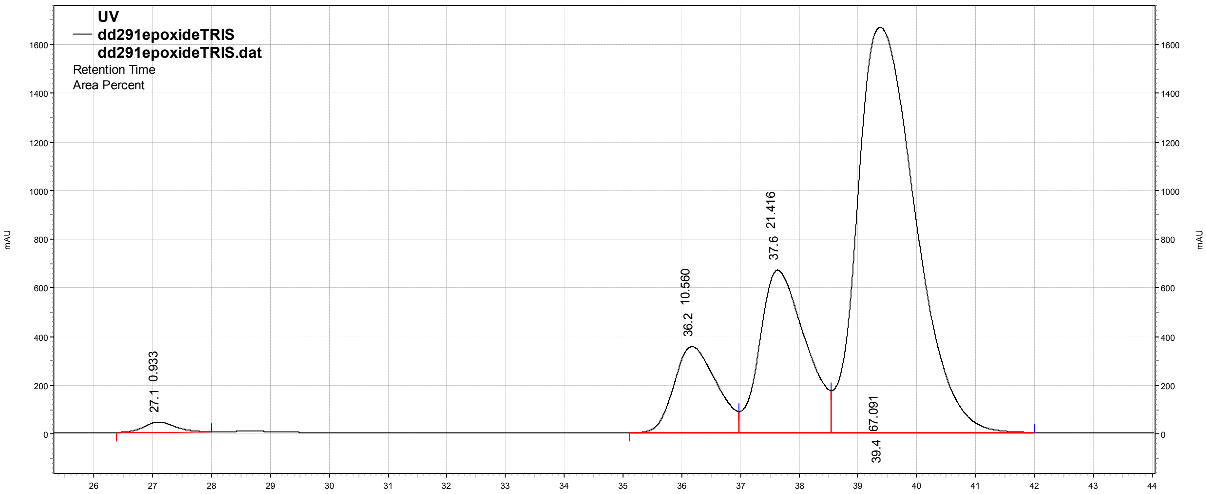
Retention Time	Area	Area %	Height	Height %
27.140	26258489	10.86	700342	15.45
36.317	93068512	38.48	1705381	37.63
38.237	25805385	10.67	494970	10.92
39.820	96704505	39.99	1631842	36.00

Totals				
	241836891	100.00	4532535	100.00

Enantioenriched 6-cyano-2-propyl-chromene epoxide (–)-18b



Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd291epoxideTRIS.dat
Method: C:\EZChrom Elite\Enterprise\Projects\ben\111111.met

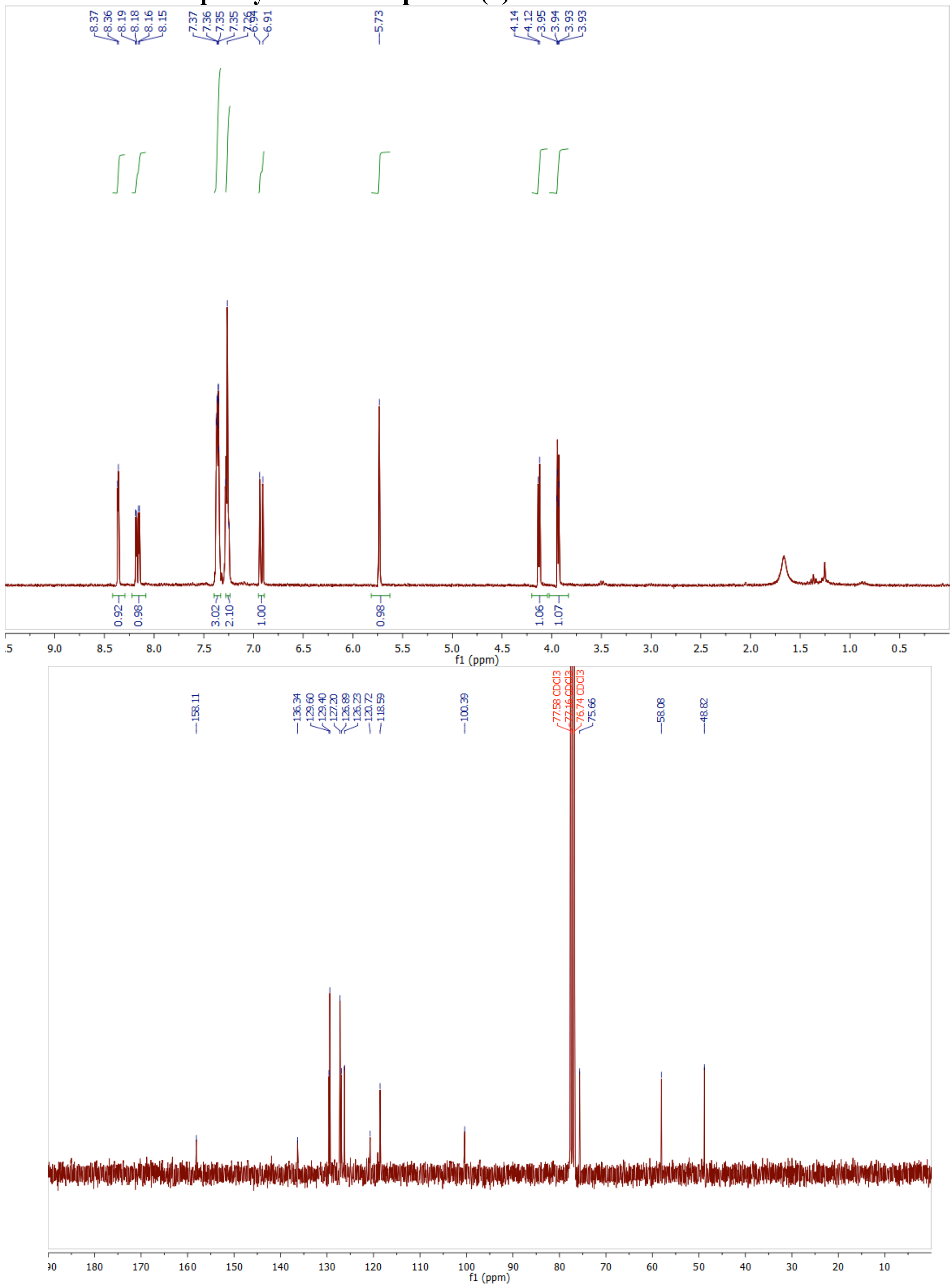


UV Results

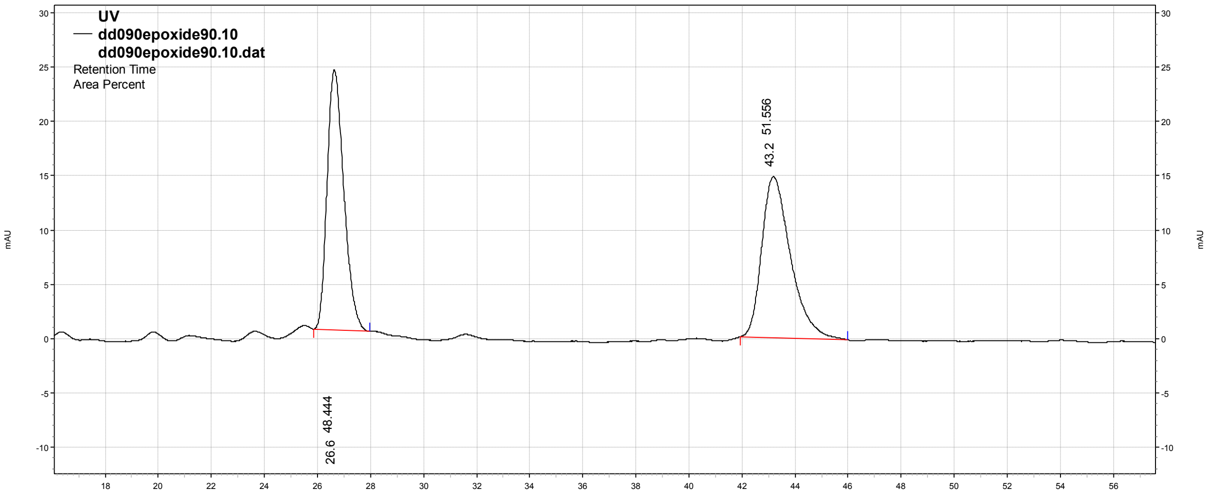
Retention Time	Area	Area %	Height	Height %
27.100	6337632	0.93	169392	1.55
36.173	71698121	10.56	1419259	12.99
37.633	145407113	21.42	2675394	24.48
39.380	455535817	67.09	6662958	60.98
Totals	678978683	100.00	10927003	100.00

6-Nitro-2-phenyl chromene epoxide

Racemic 6-nitro-2-phenyl chromene epoxide (±)-19a



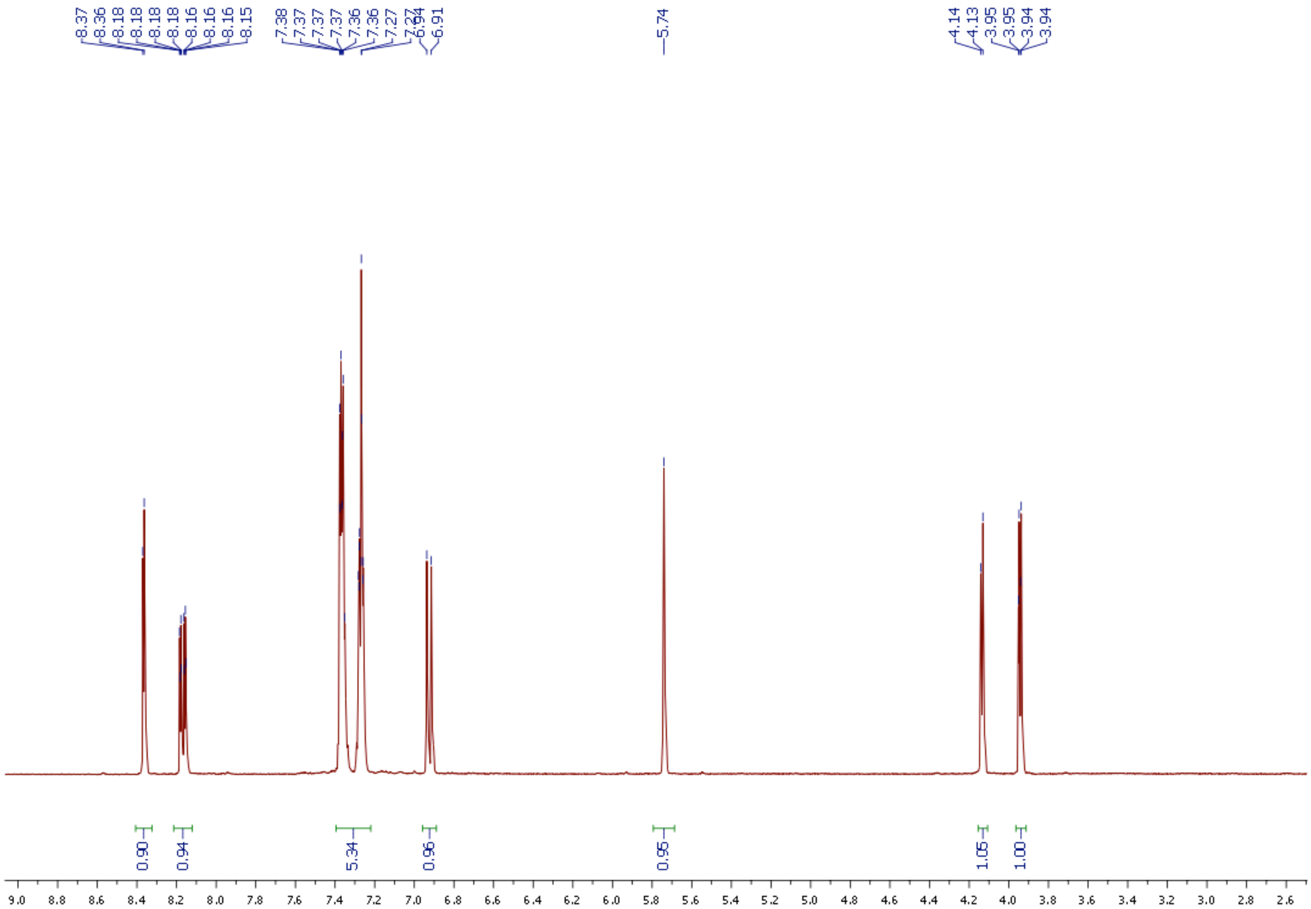
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd090epoxide90.10.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10.1h.met



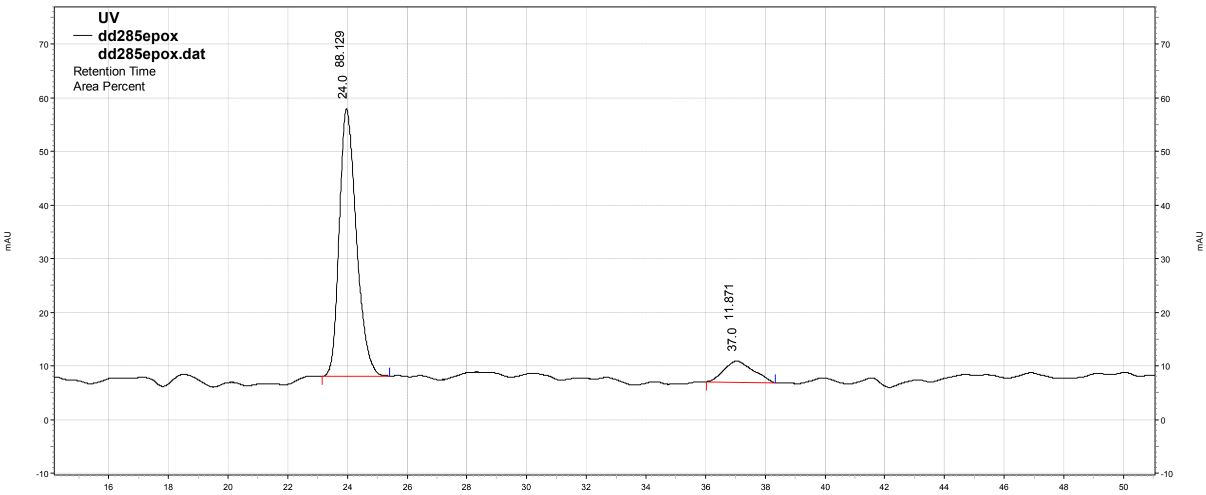
UV Results

Retention Time	Area	Area %	Height	Height %
26.633	4211728	48.44	95882	61.75
43.183	4482307	51.56	59382	38.25
Totals	8694035	100.00	155264	100.00

Enantioenriched 6-nitro-2-phenyl chromene (+)-19a



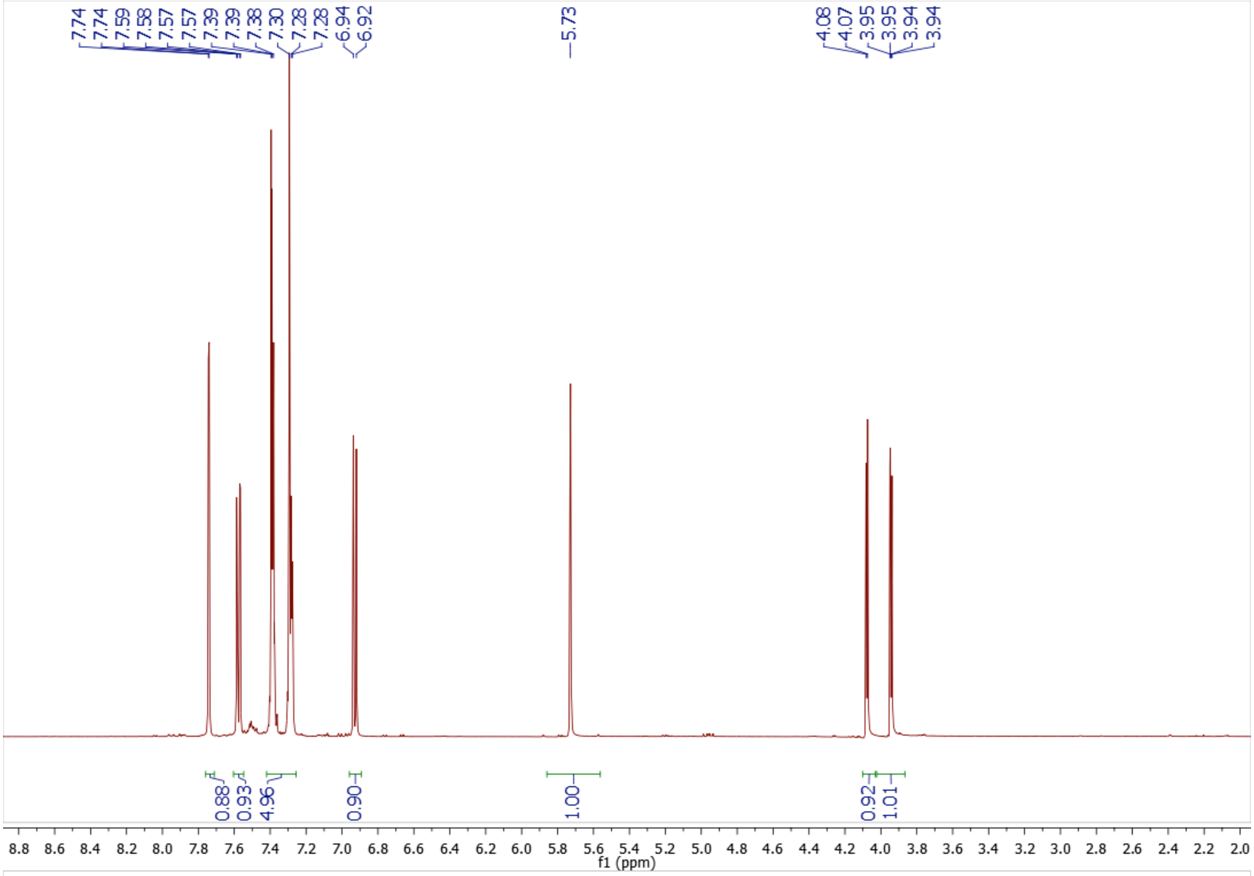
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd285epox.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10.1h.met

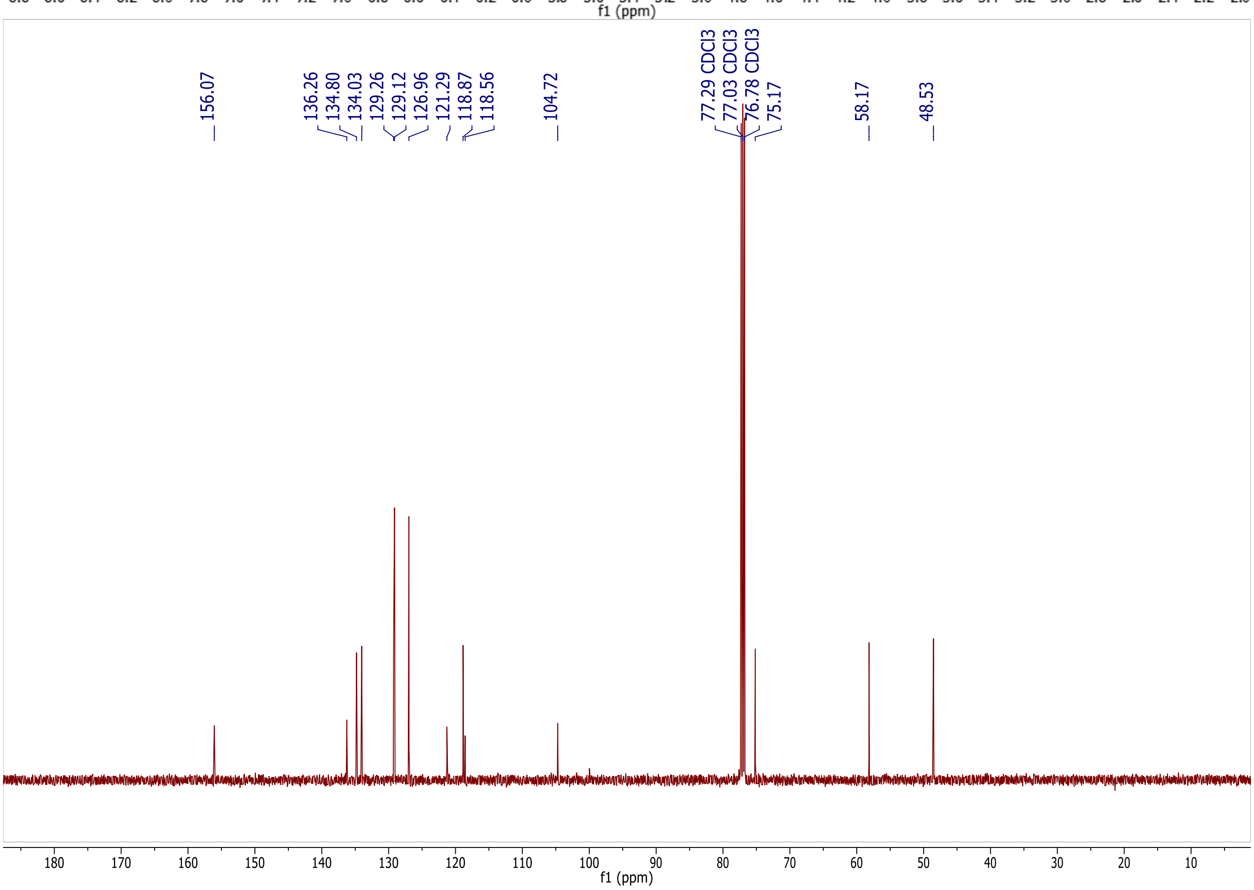


UV Results

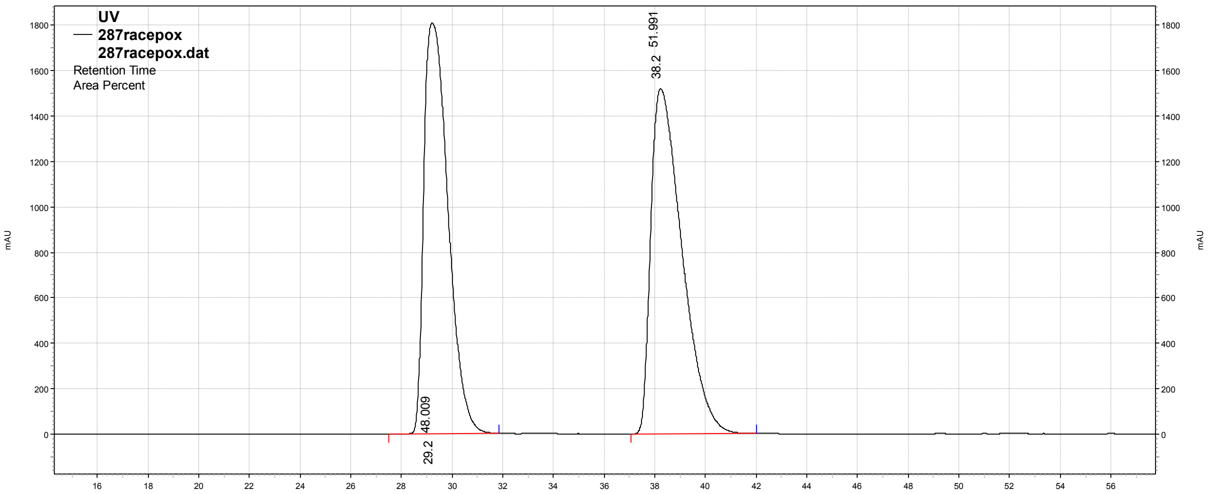
Retention Time	Area	Area %	Height	Height %
23.970	7937828	88.13	199409	92.73
37.013	1069212	11.87	15623	7.27
Totals	9007040	100.00	215032	100.00

6-Cyano-2-phenyl-chromene epoxide
Racemic 6-cyano-2-phenyl-3,4-epoxy-chromene (±)-19b





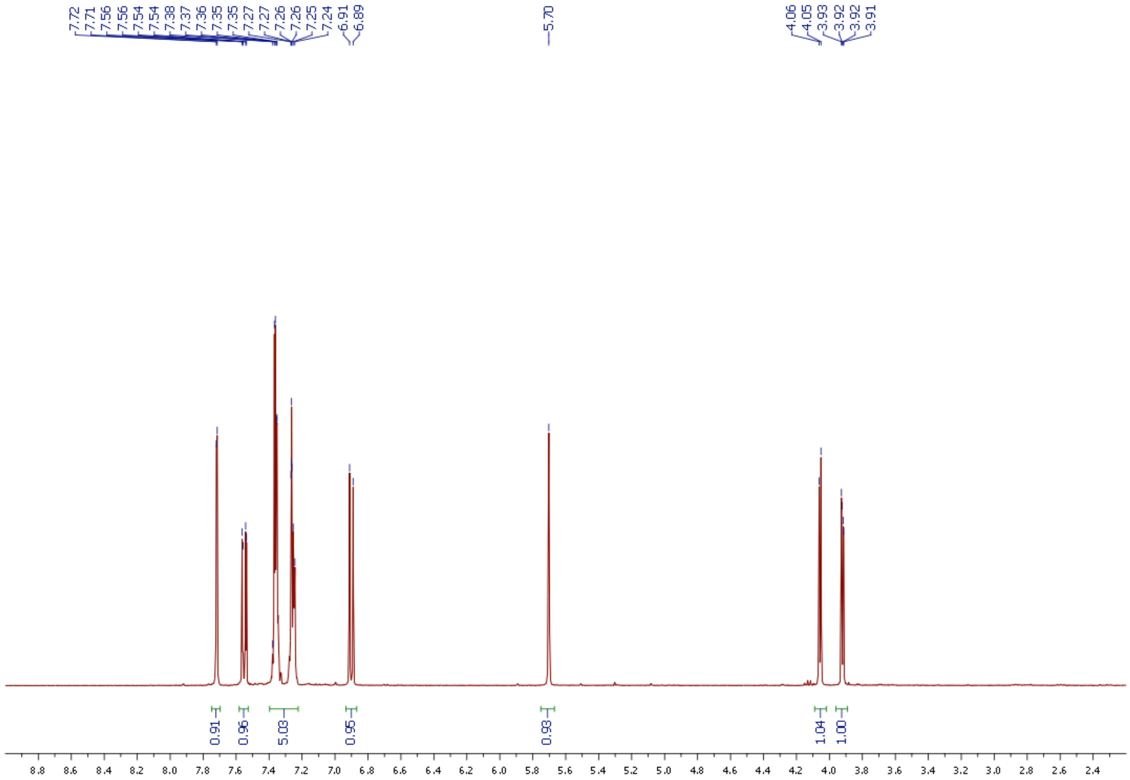
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\287racepox.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10 1mL 60min.met



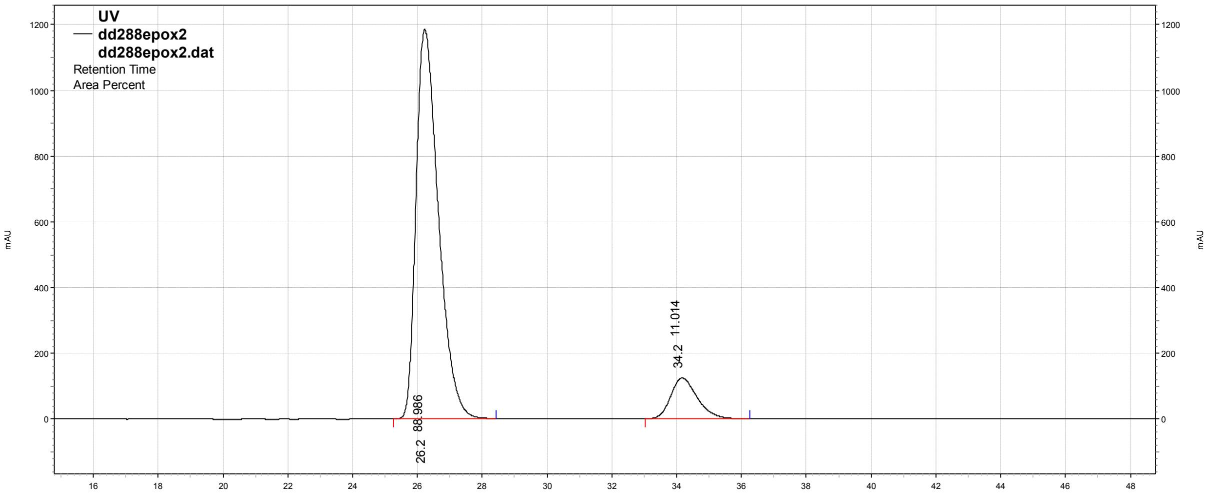
UV Results

Retention Time	Area	Area %	Height	Height %
29.213	479698387	48.01	7228572	54.34
38.227	519477371	51.99	6072709	45.66
Totals	999175758	100.00	13301281	100.00

Enantioenriched 6-cyano-2-phenyl-3,4-epoxy-chromene (+)-19b



Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\paper2011\dd288epox2.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\90.10.1h.met



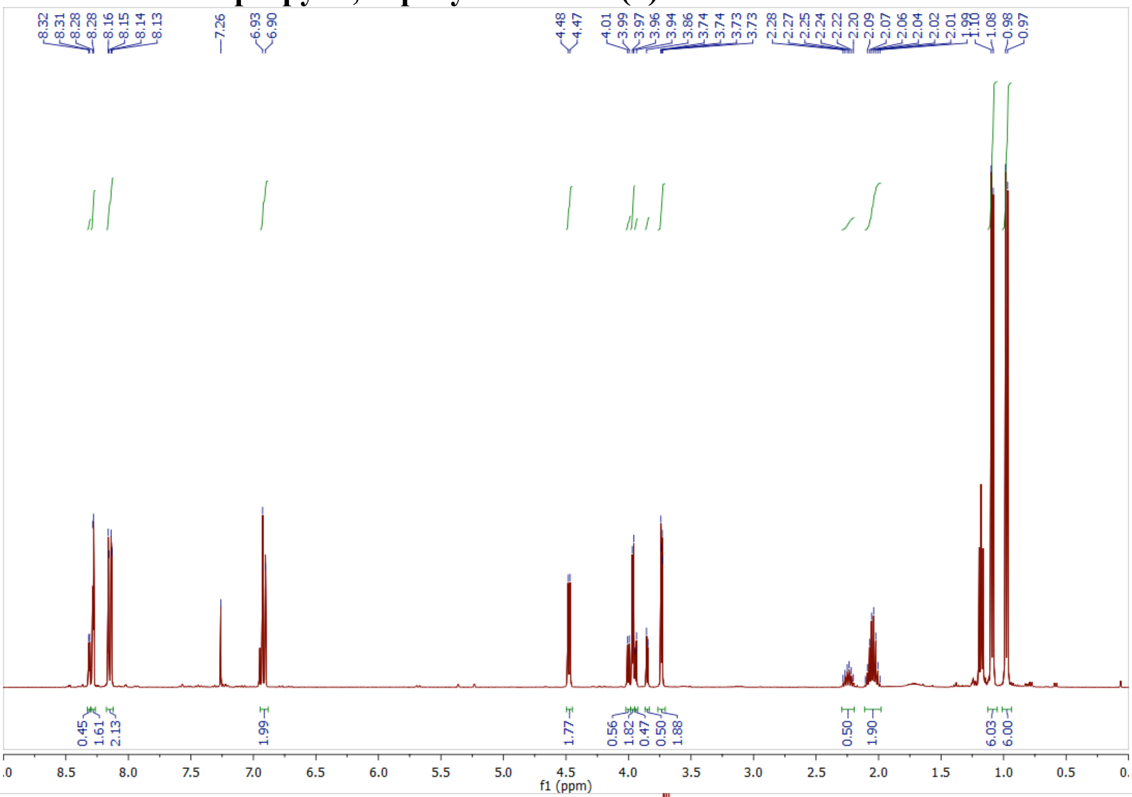
UV Results

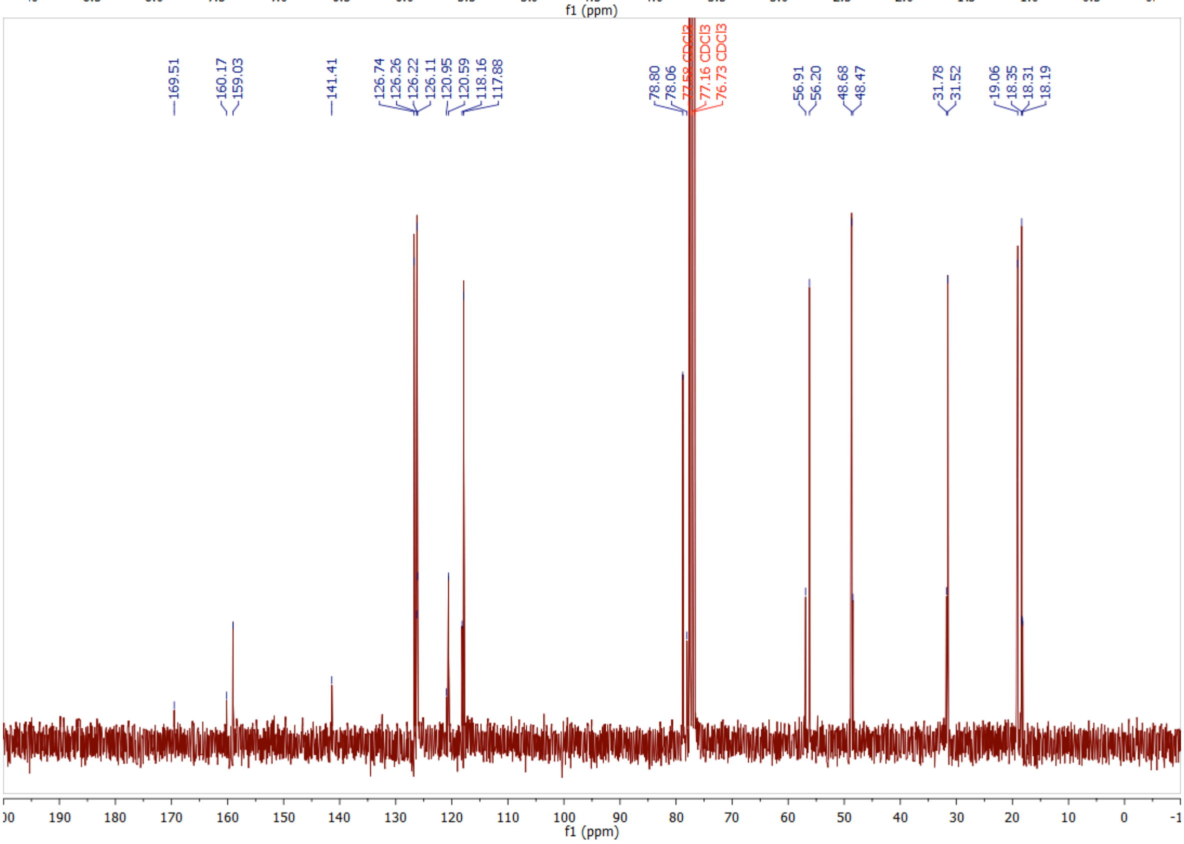
Retention Time	Area	Area %	Height	Height %
26.227	227664852	88.99	4739603	90.55
34.170	28179676	11.01	494739	9.45

Totals				
	255844528	100.00	5234342	100.00

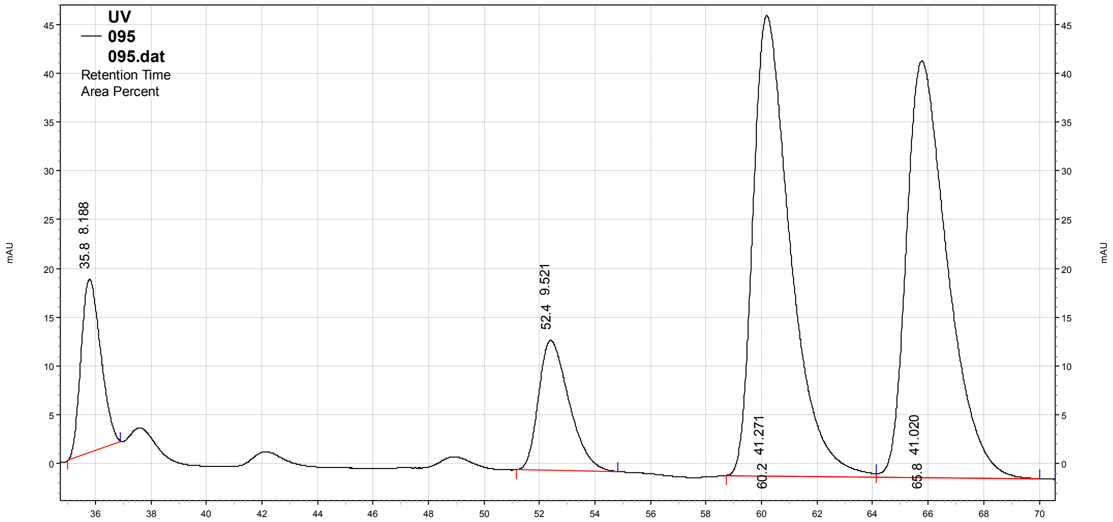
6-Nitro-2-isopropyl-chromene epoxide

Racemic 6-nitro-2-isopropyl-3,4-epoxy-chromene (±)-20a





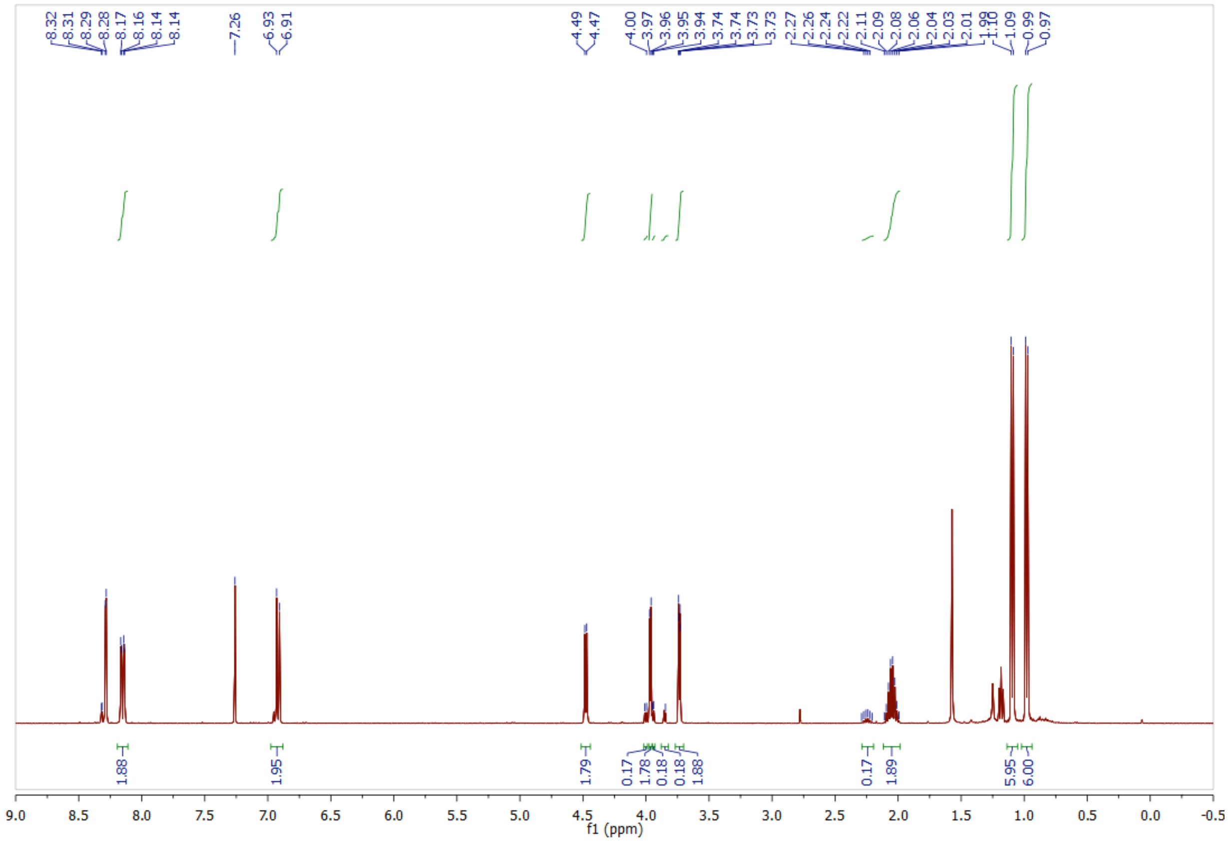
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\095.dat
Method: C:\EZChrom Elite\Enterprise\Projects\yohan\Method\99.5 0.5 0.5ml 3 hours MeCN chrom.met



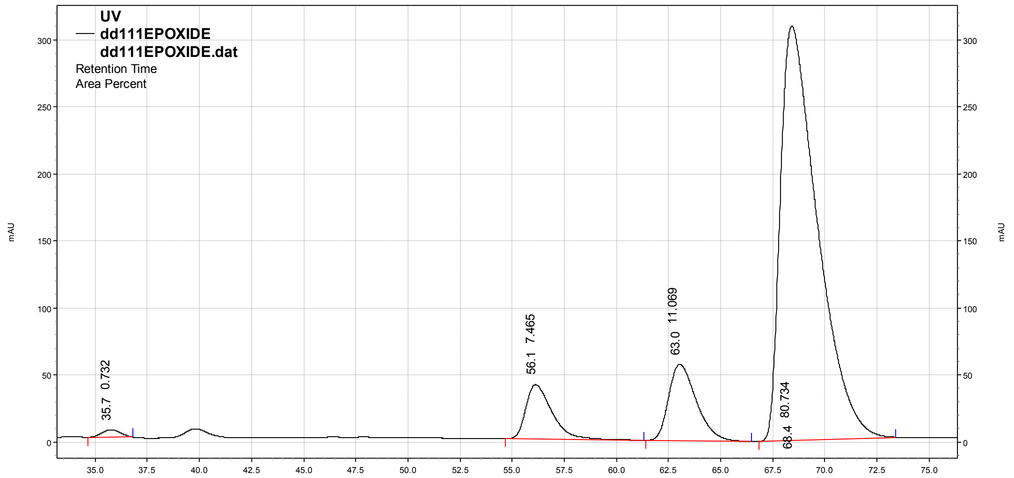
UV Results

Retention Time	Area	Area %	Height	Height %
35.783	3499657	8.19	70992	14.68
52.393	4069103	9.52	53301	11.02
60.190	17639496	41.27	188488	38.99
65.777	17532004	41.02	170695	35.31
Totals	42740260	100.00	483476	100.00

Chiral 6-nitro-2-isopropyl-3,4-epoxy-chromene (–)-20a



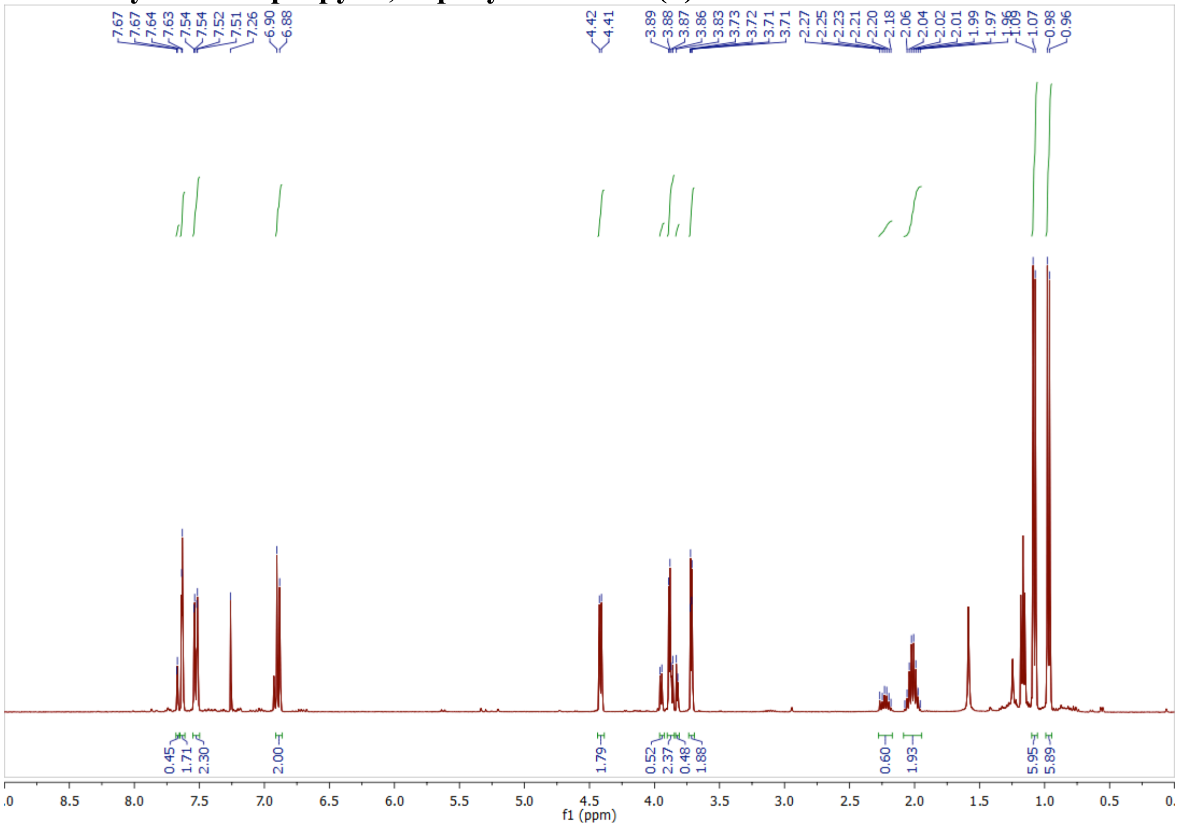
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd111EPOXIDE.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Dave\method\99.5 0.5 0.5ml 3 hours MeCN chrom.met

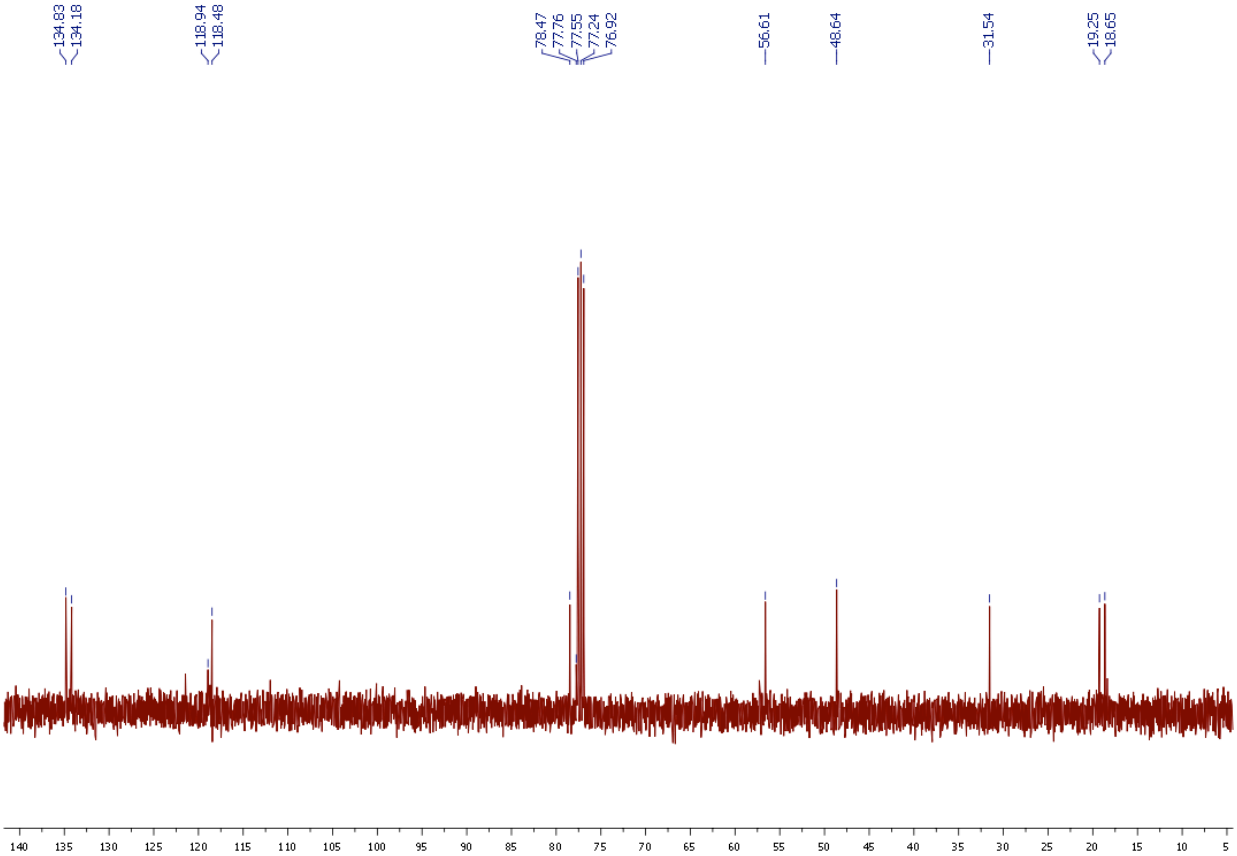


UV Results

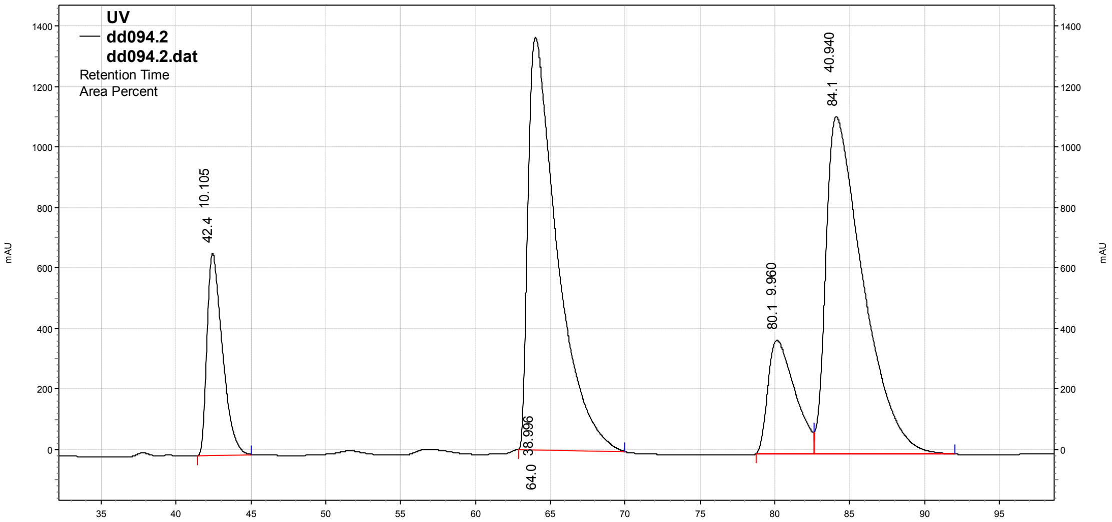
Retention Time	Area	Area %	Height	Height %
35.743	1385180	0.73	22378	1.36
56.130	14124369	7.46	162183	9.84
Minor dia.		ee=82.17		
63.047	20944908	11.07	227670	13.81
68.417	152763467	80.73	1236305	74.99
Major dia.		ee=75.88		
Totals	189217924	100.00	1648536	100.00

6-Cyano-2-isopropyl-chromene epoxide
Racemic 6-cyano-2-isopropyl-3,4-epoxy-chromene (±)-20b





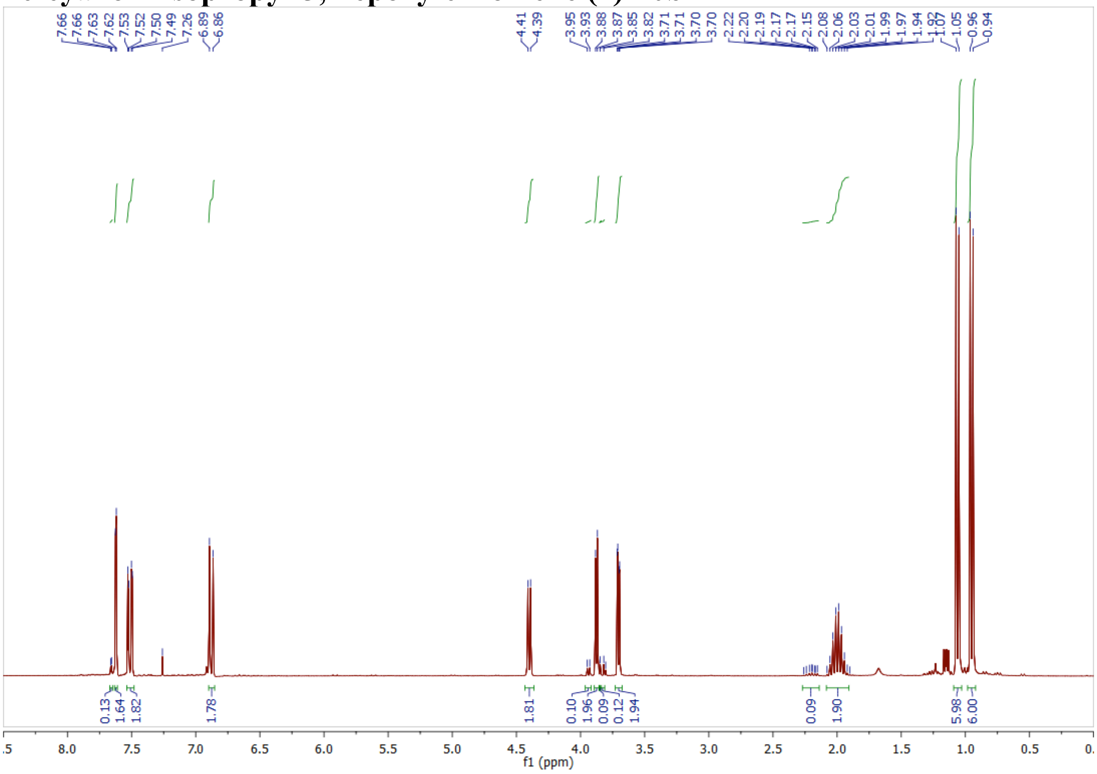
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd094.2.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Dave\method\99.5 0.5 0.5ml 3 hours MeCN chrom.met



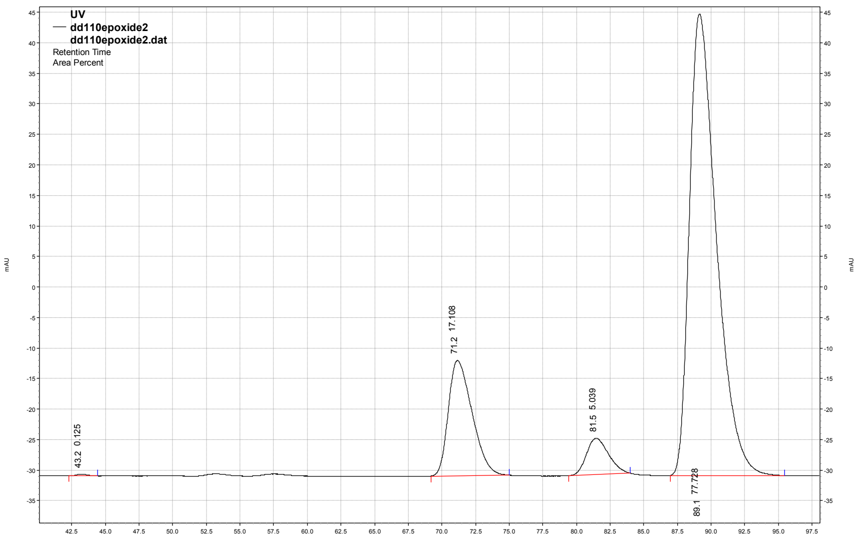
UV Results

Retention Time	Area	Area %	Height	Height %
42.440	190699438	10.10	2671724	18.95
64.013	735938851	39.00	5454226	38.69
80.140	187967029	9.96	1504738	10.68
84.103	772625826	40.94	4465081	31.68
Totals	1887231144	100.00	14095769	100.00

Chiral 6-cyano-2-isopropyl-3,4-epoxy-chromene (–)-20b



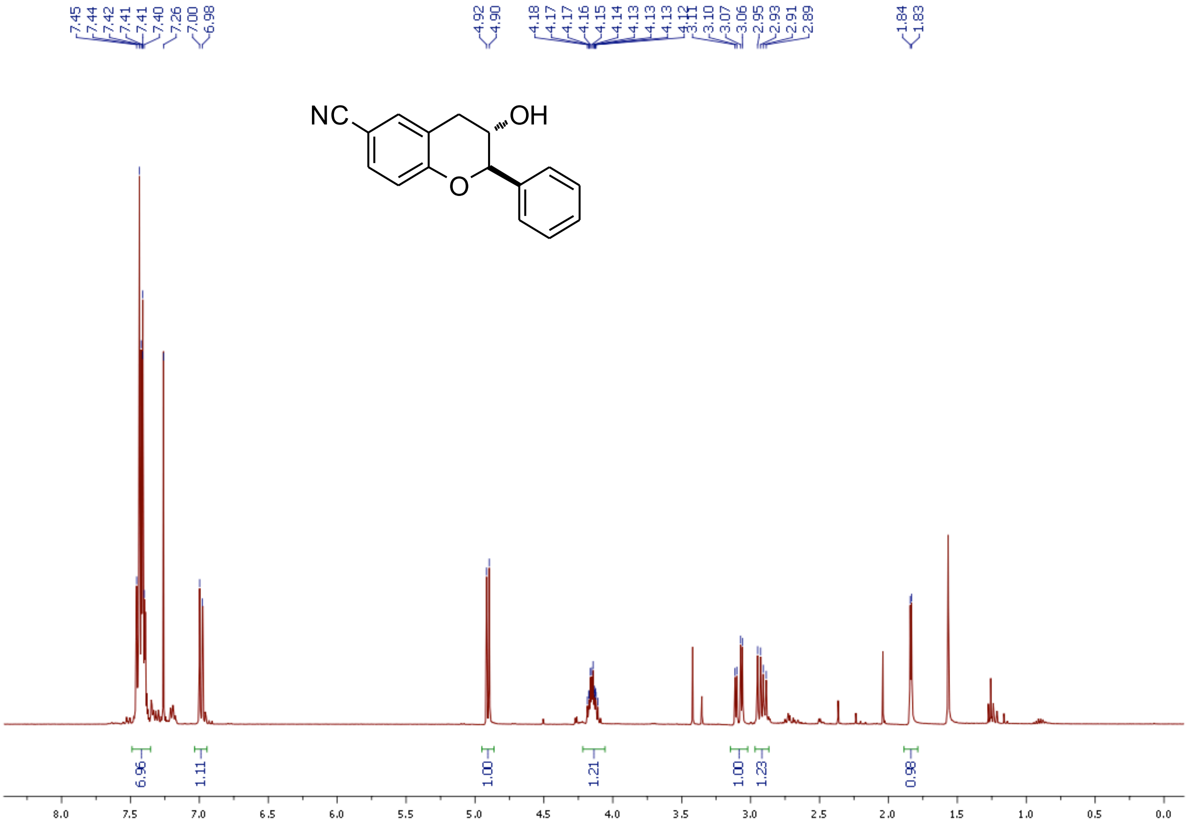
Data File: C:\EZChrom Elite\Enterprise\Projects\Dave\1st year phd\dd110epoxide2.dat
Method: C:\EZChrom Elite\Enterprise\Projects\Dave\method\99.5 0.5 0.5ml 3 hours MeCN chrom.met

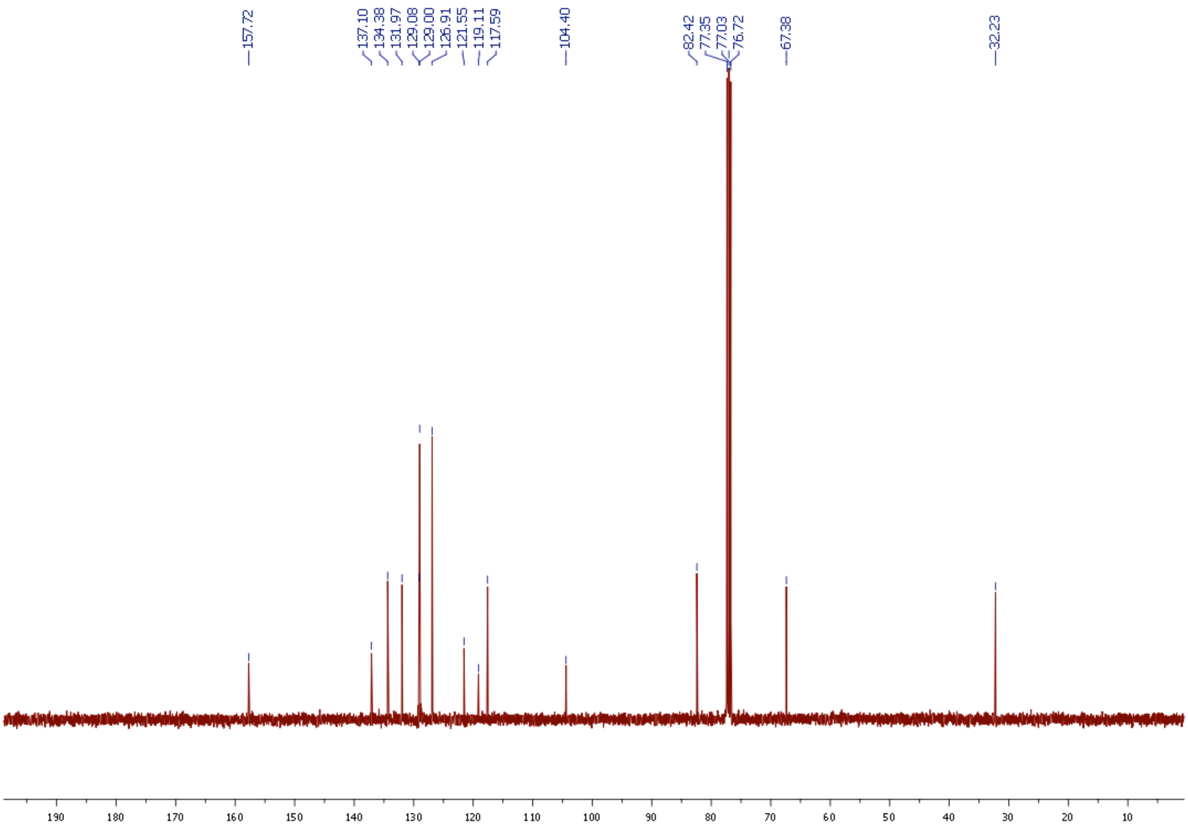


UV Results

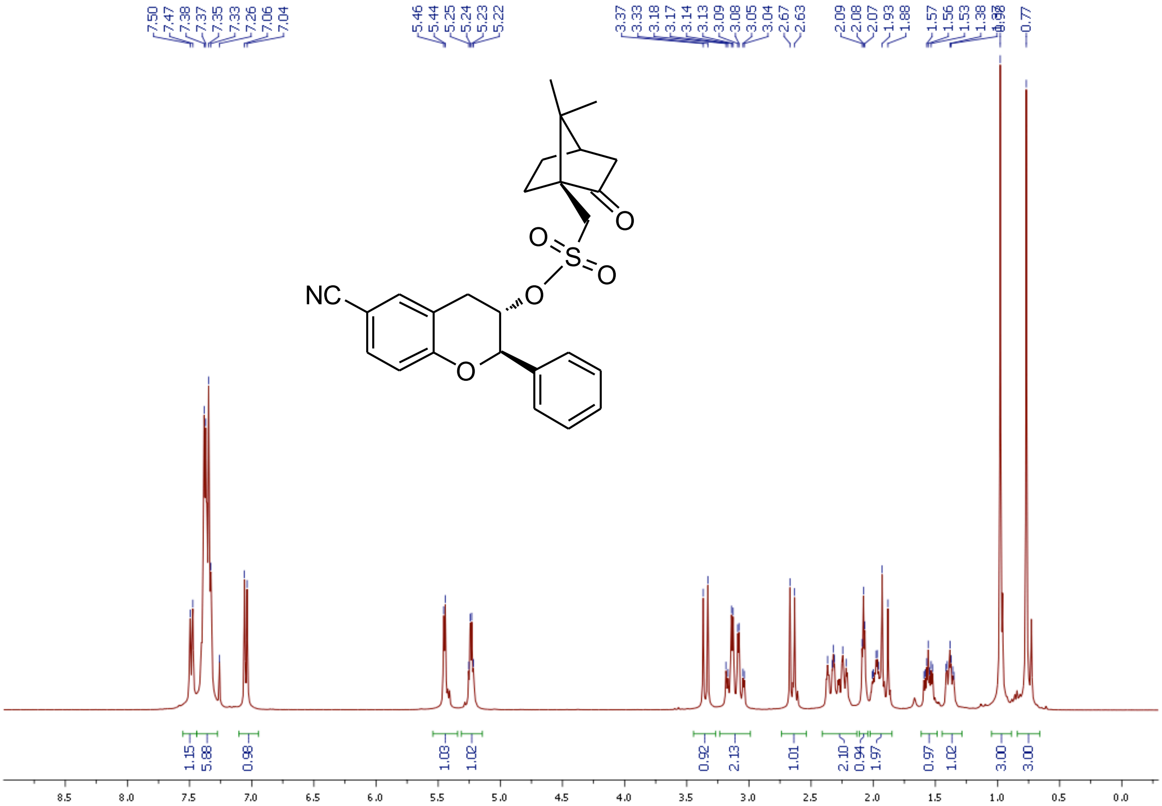
Retention Time	Area	Area %	Height	Height %
43.173	67588	0.12	1184	0.29
71.150	9270749	17.11	75500	18.73
81.470	2730918	5.04	23856	5.92
89.147	42121596	77.73	302562	75.06
Totals	54190851	100.00	403102	100.00

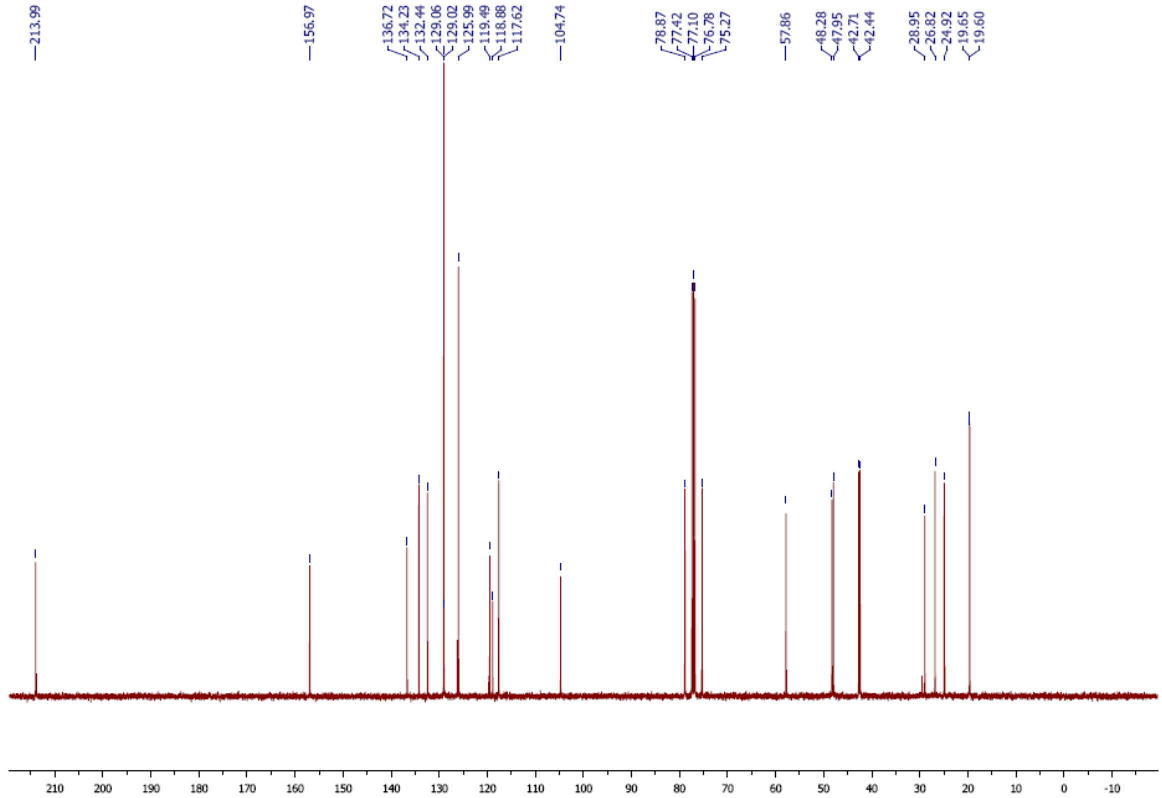
Alcohol (+)-23

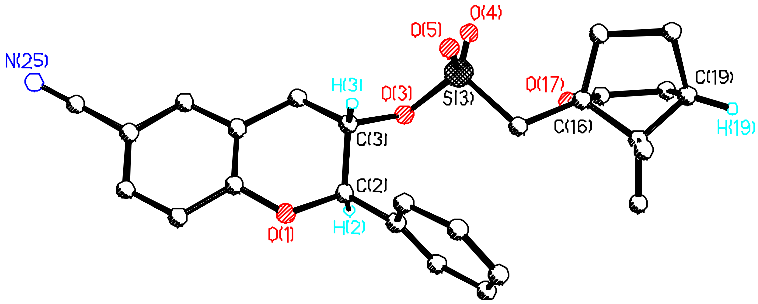




(10*S*)-Camphorsulfonyl ester (+)-24







Single crystal X-Ray structure of sulfonyl ester 24