

Highly enantioselective synthesis of Warfarin and its analogs catalysed by primary amine-phosphinamide bifunctional catalysts

Juan Dong and Da-Ming Du*

*School of Chemical Engineering and Environment, Beijing Institute of Technology,
Beijing 100081, People's Republic of China*

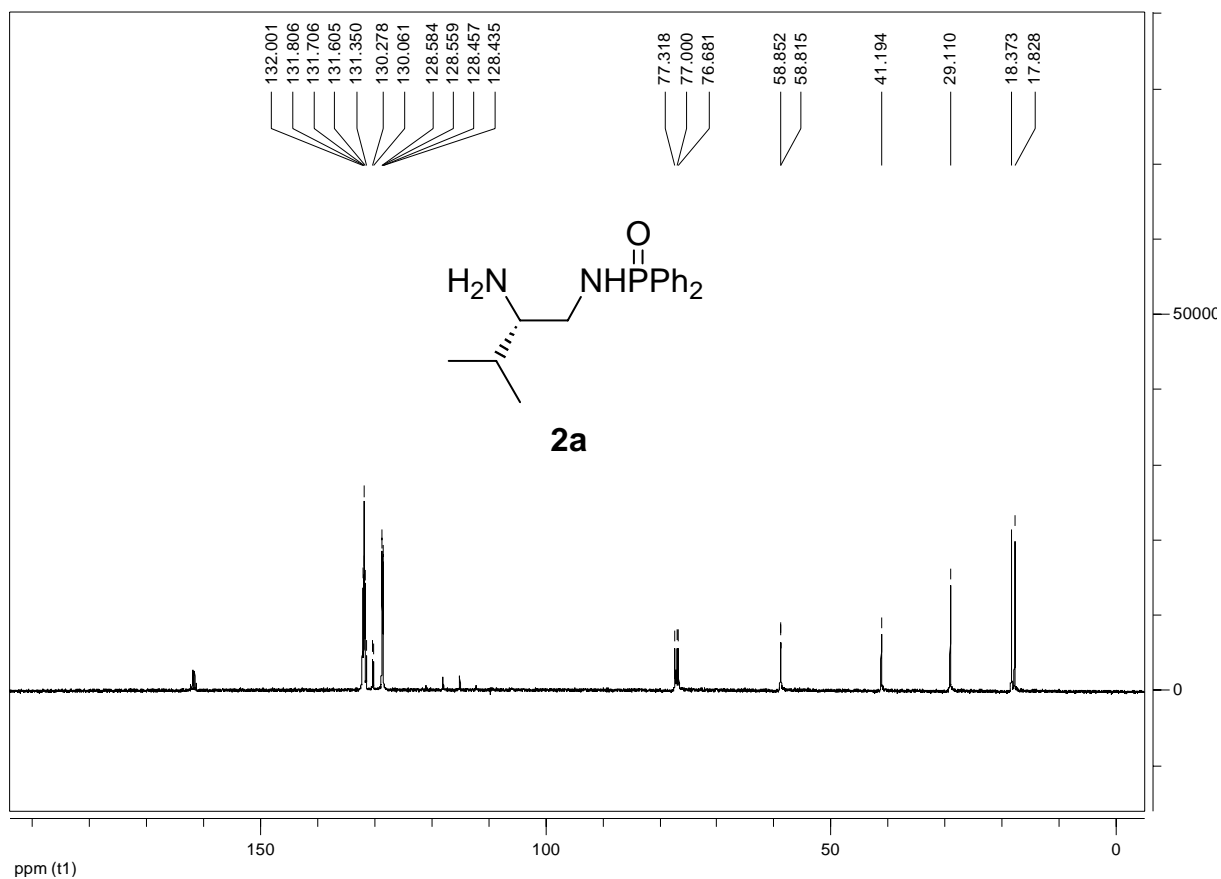
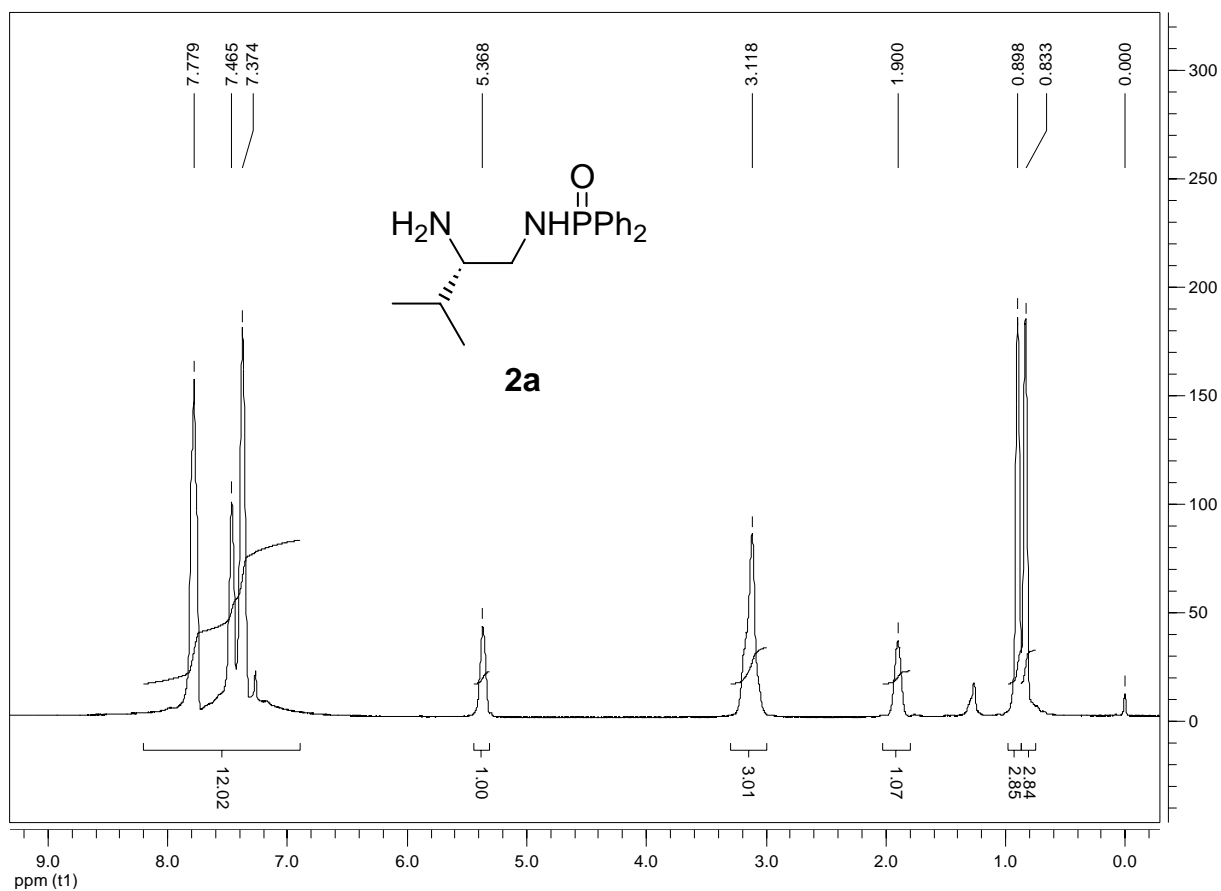
dudm@bit.edu.cn

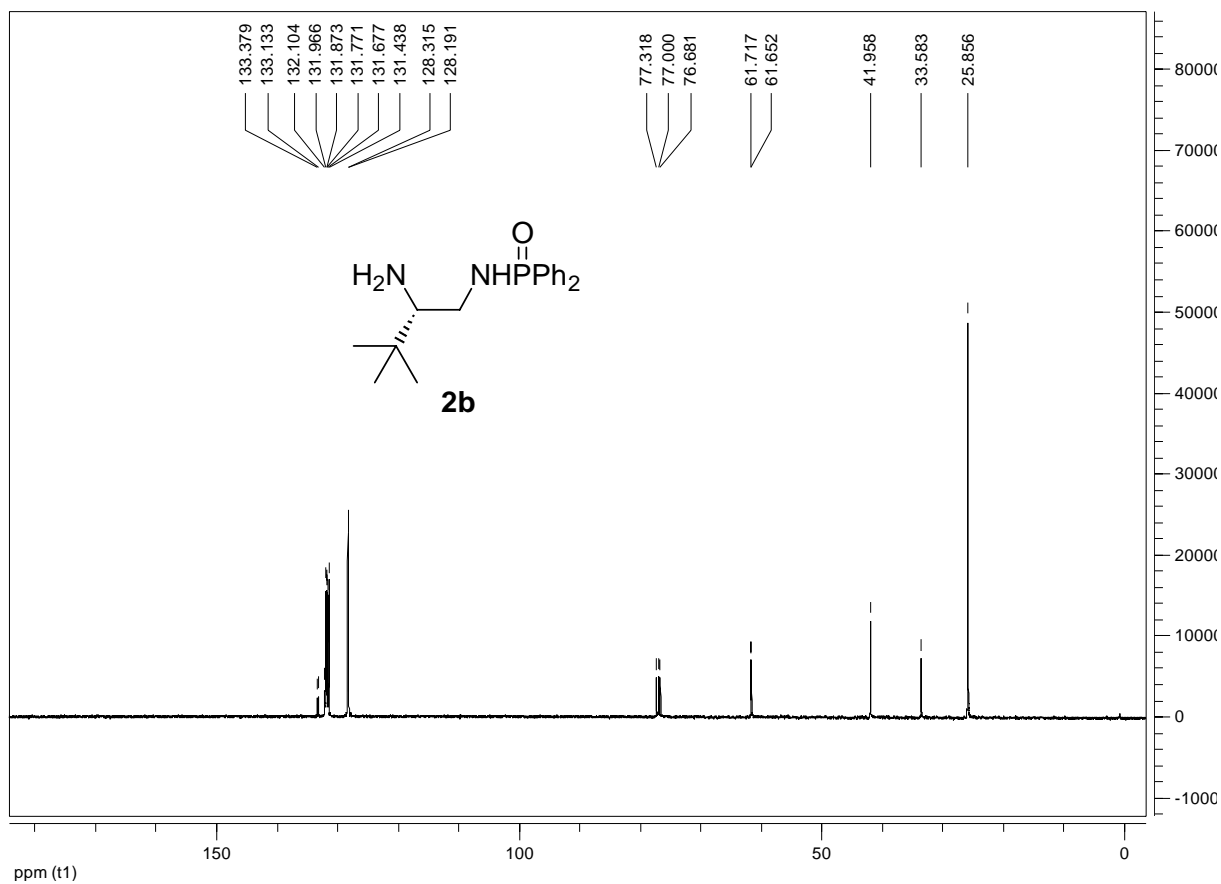
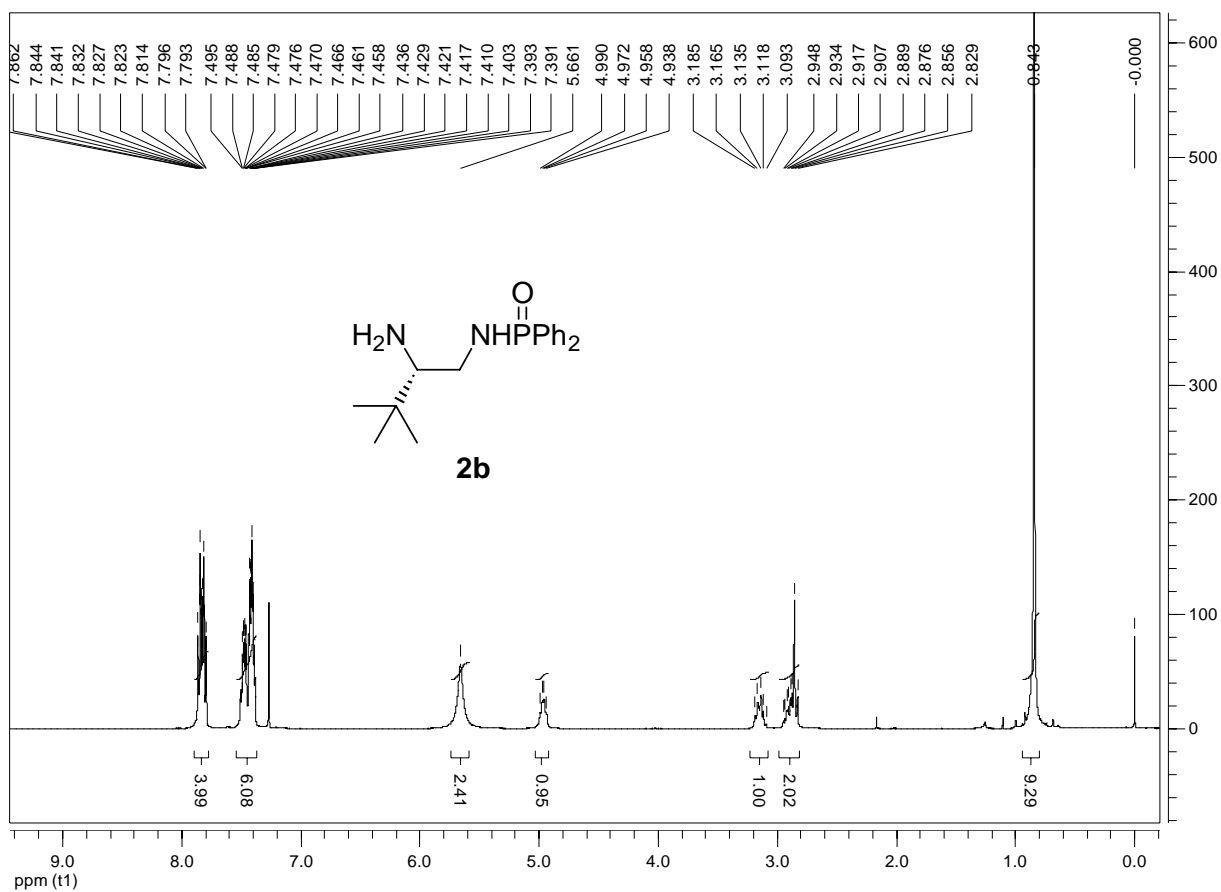
Supporting Information

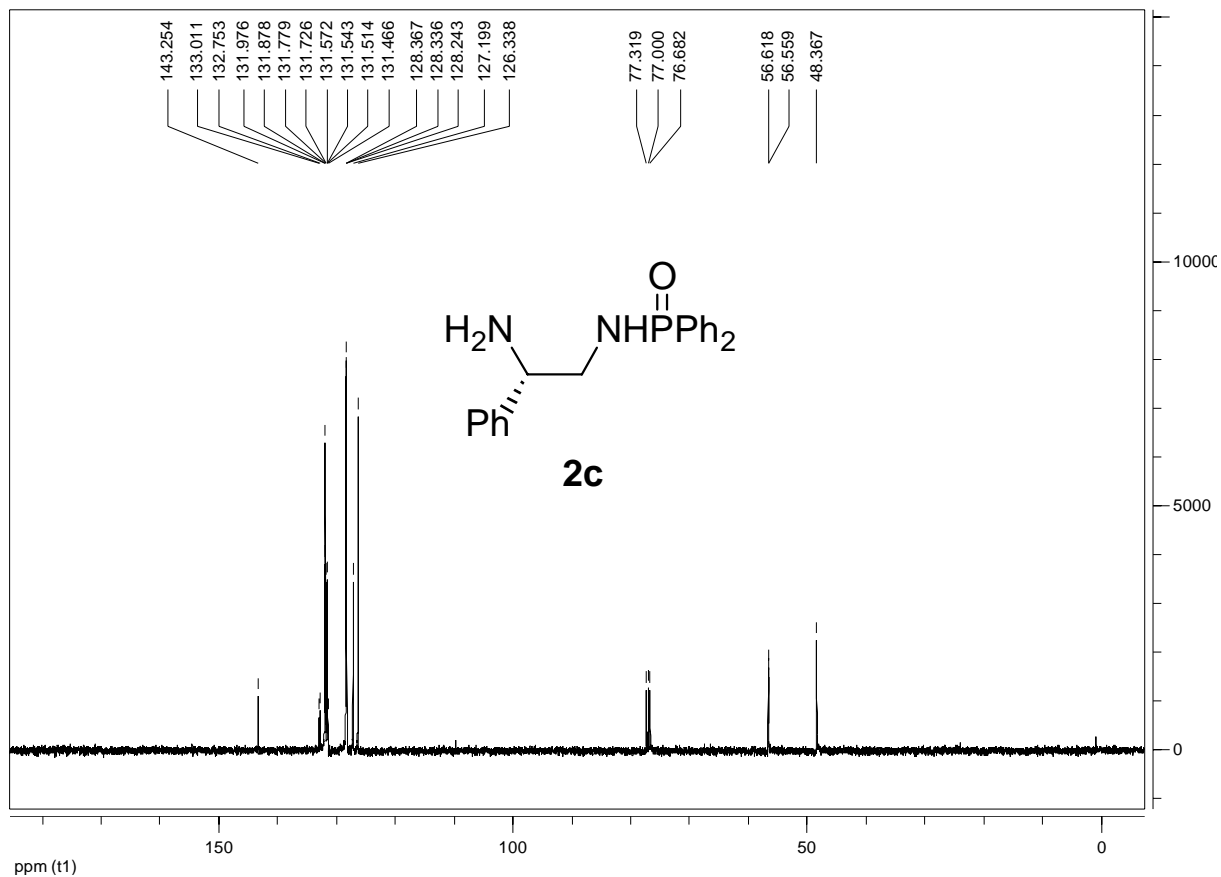
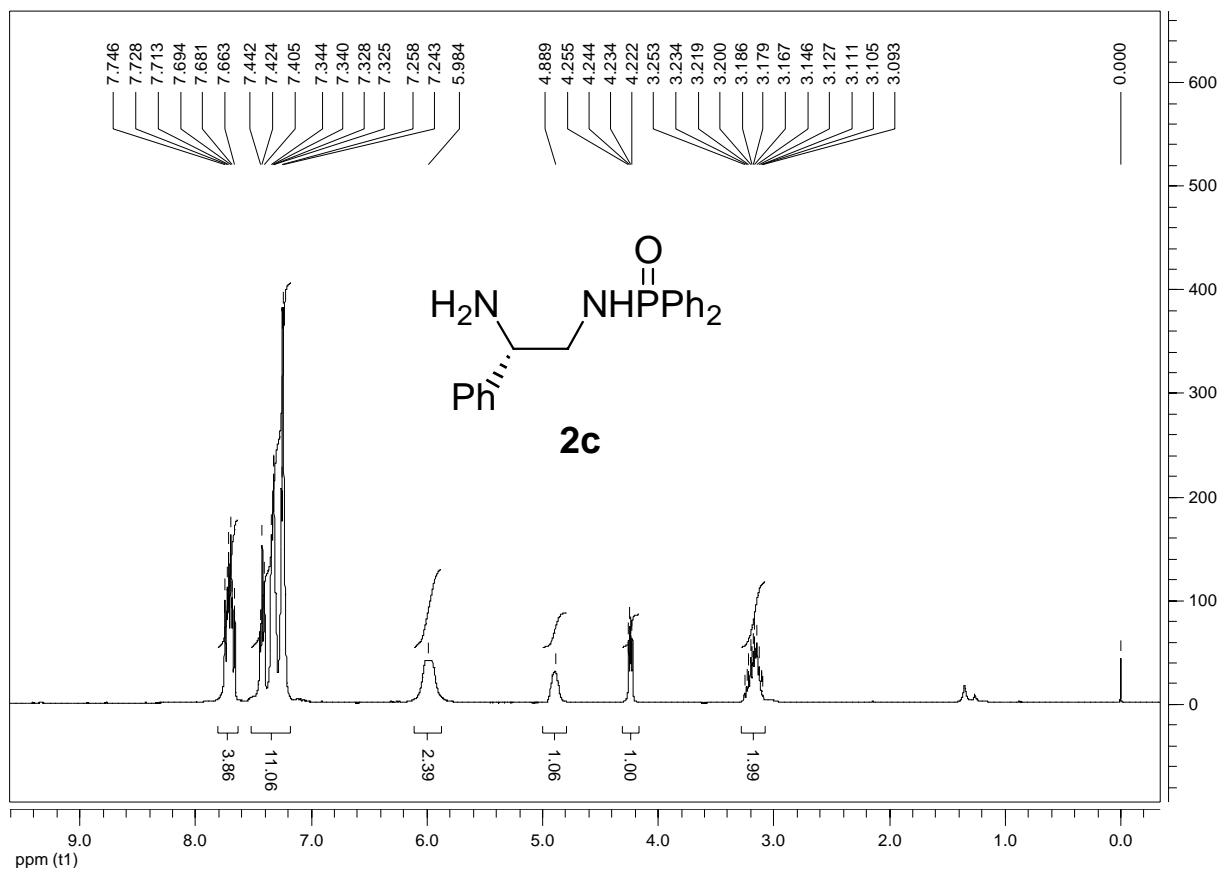
Contents

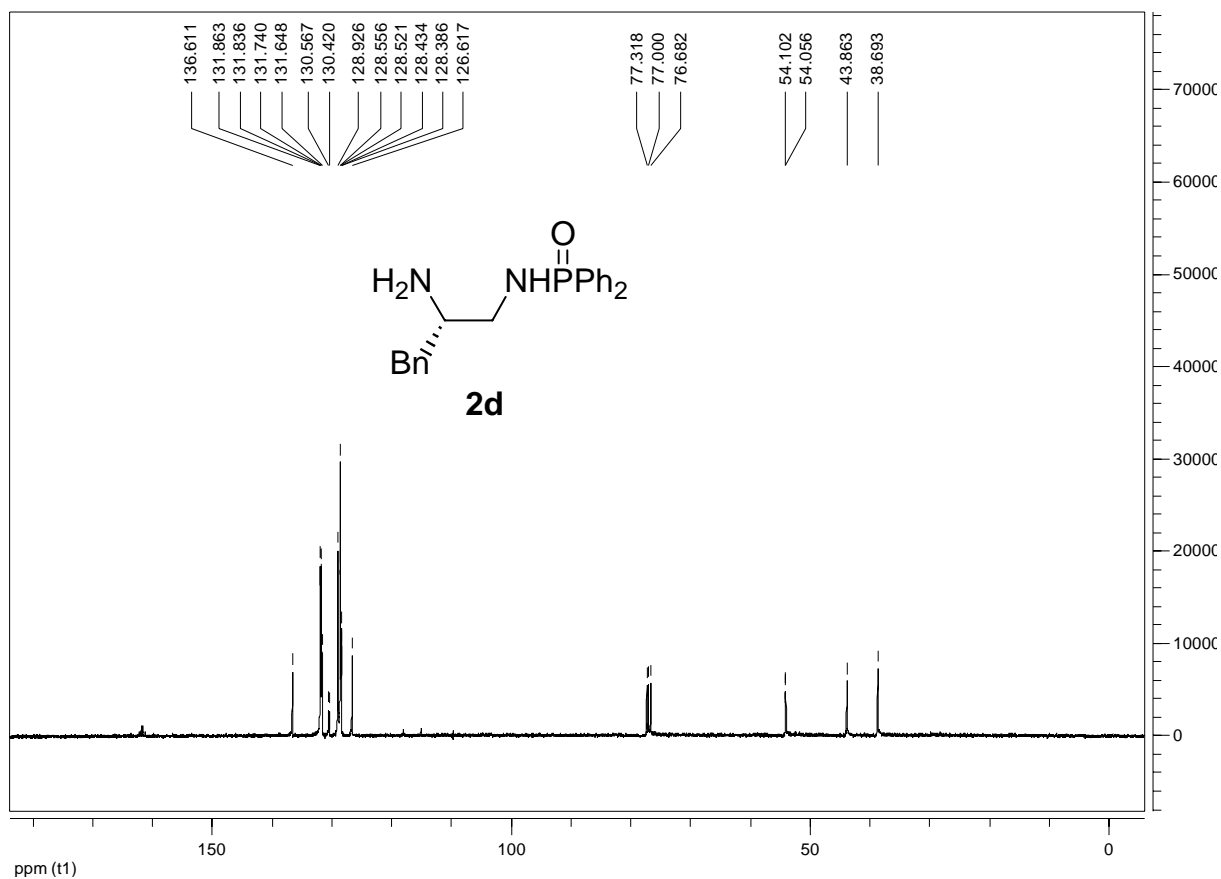
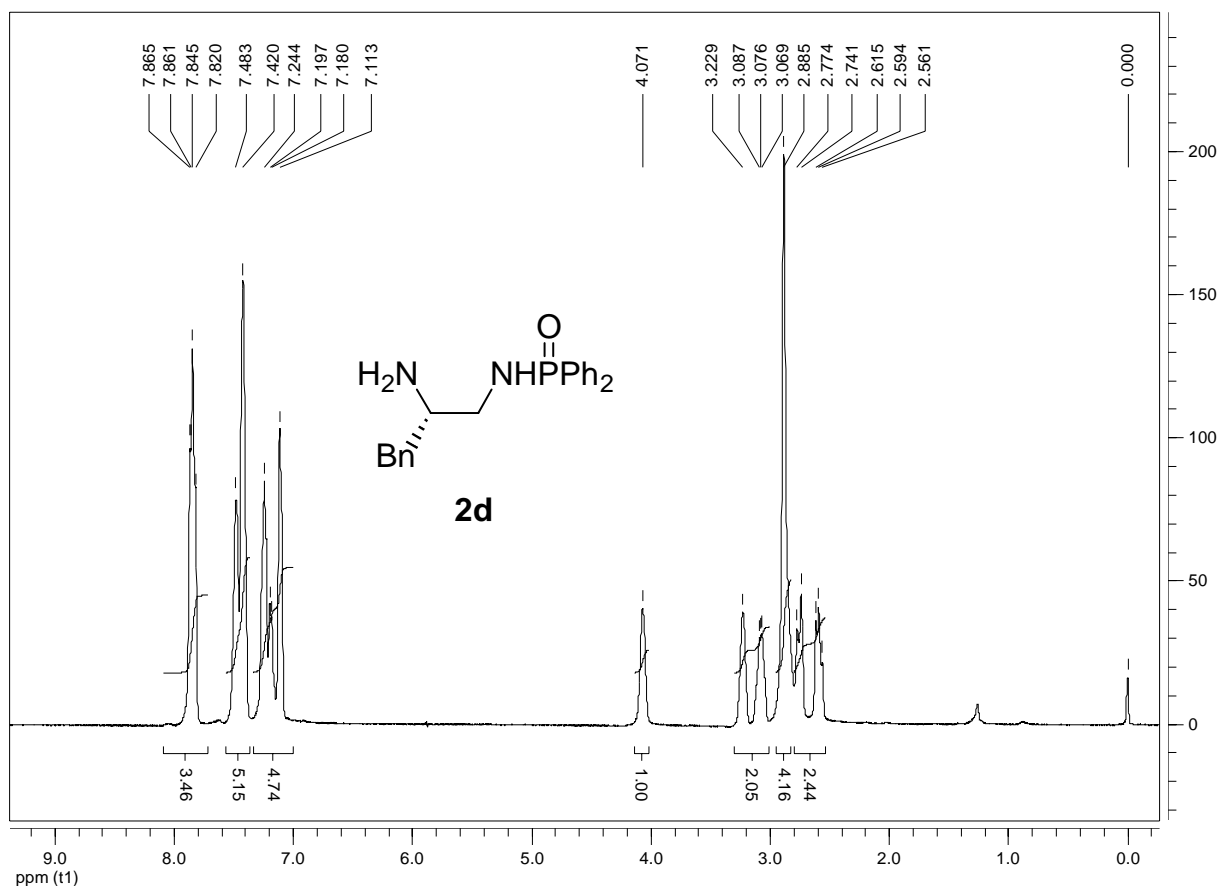
Copies of ^1H and ^{13}C NMR spectra of new compounds.....	S1
Copies of HPLC chromatographs of Michael addition products.....	S7

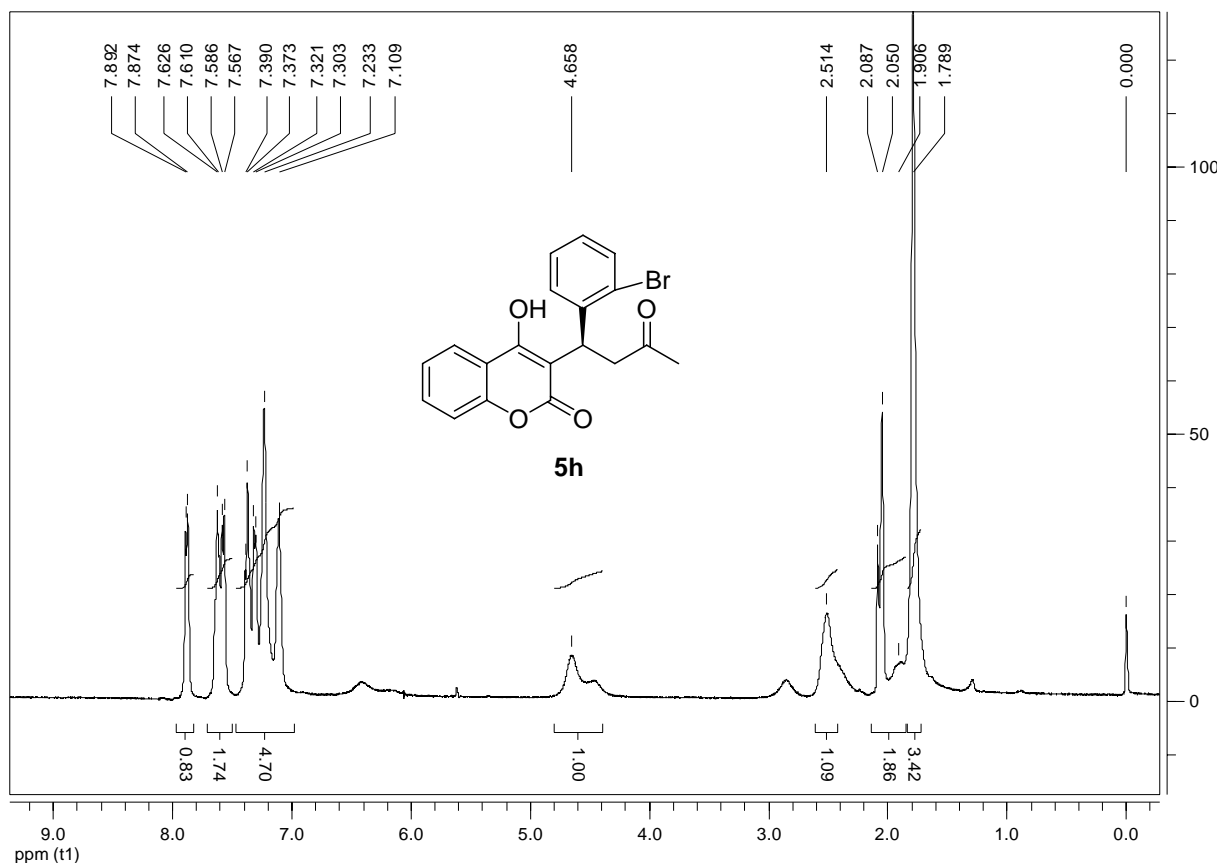
Copies of ^1H and ^{13}C NMR spectra of new compounds



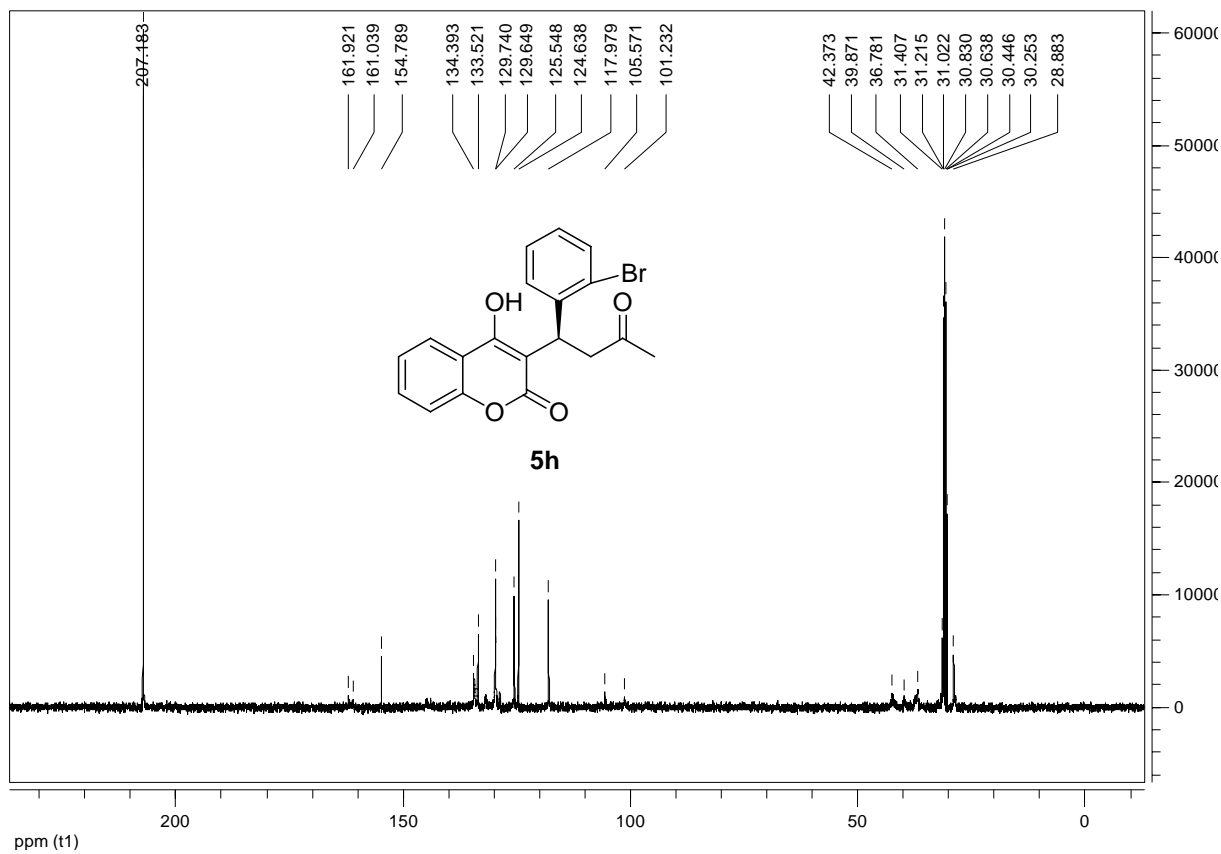


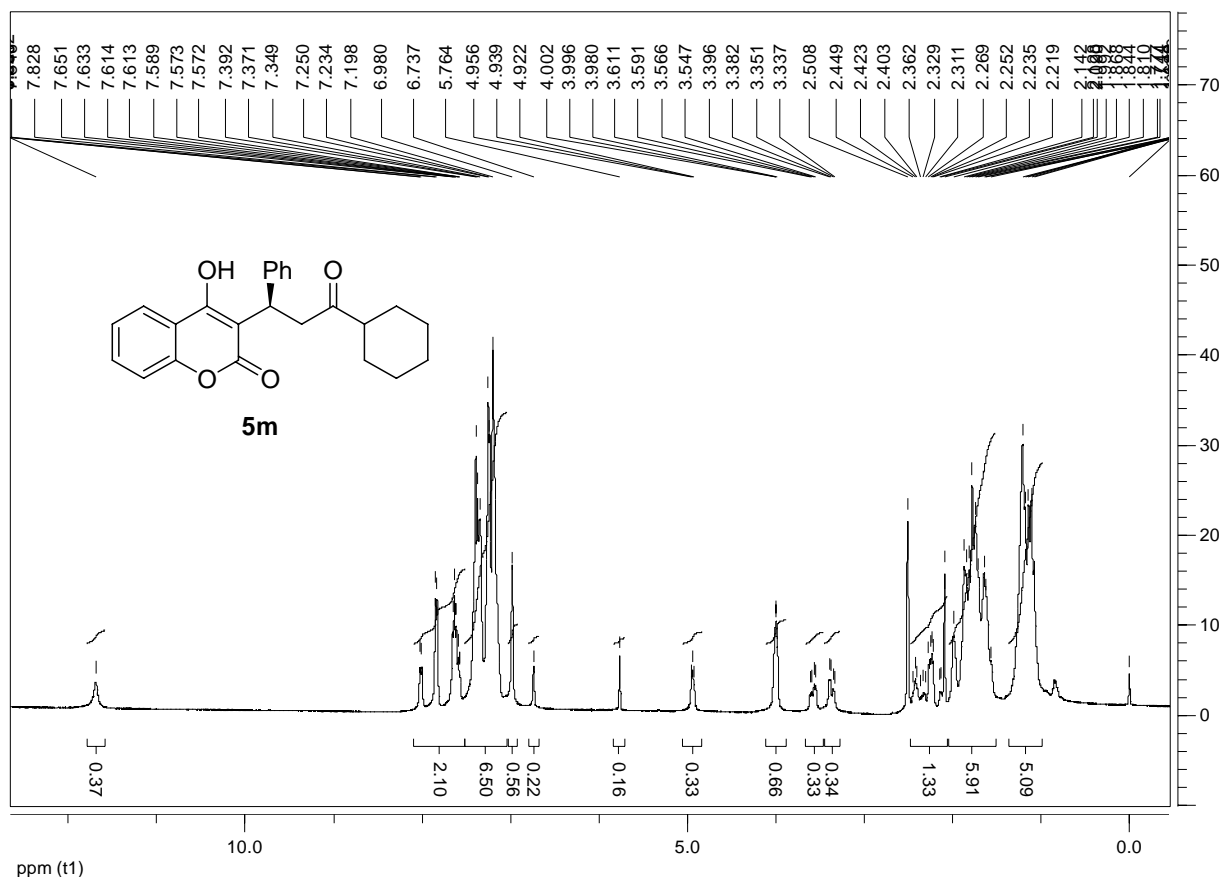




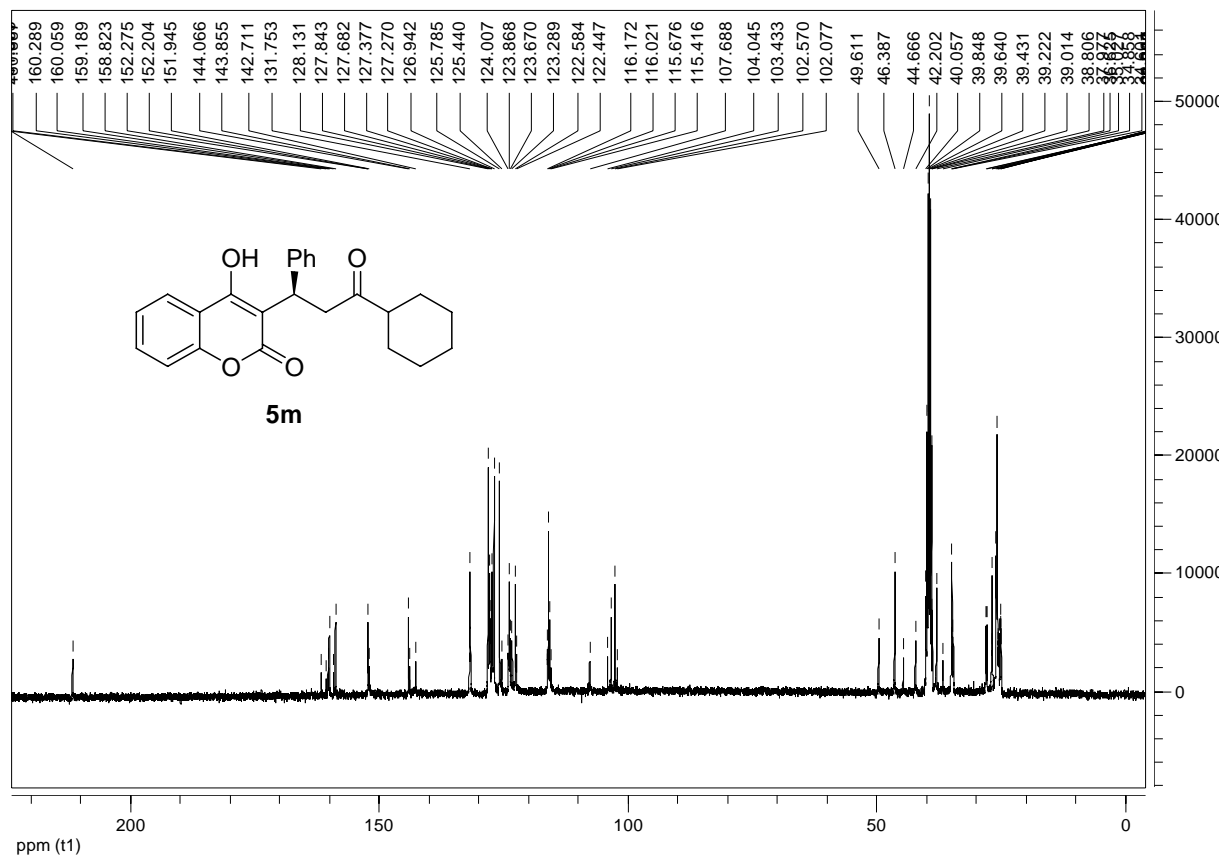


(The product was found to exist as pseudodiastereomeric hemiketal form in solution)



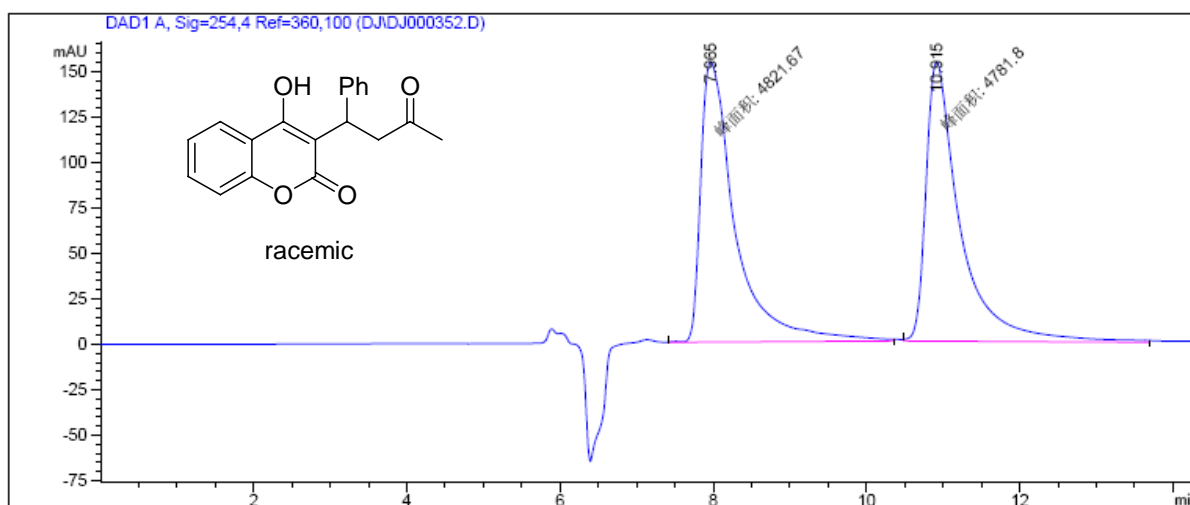


(The product was found to exist in rapid equilibrium with a pseudodiastereomeric hemiketal form in solution)

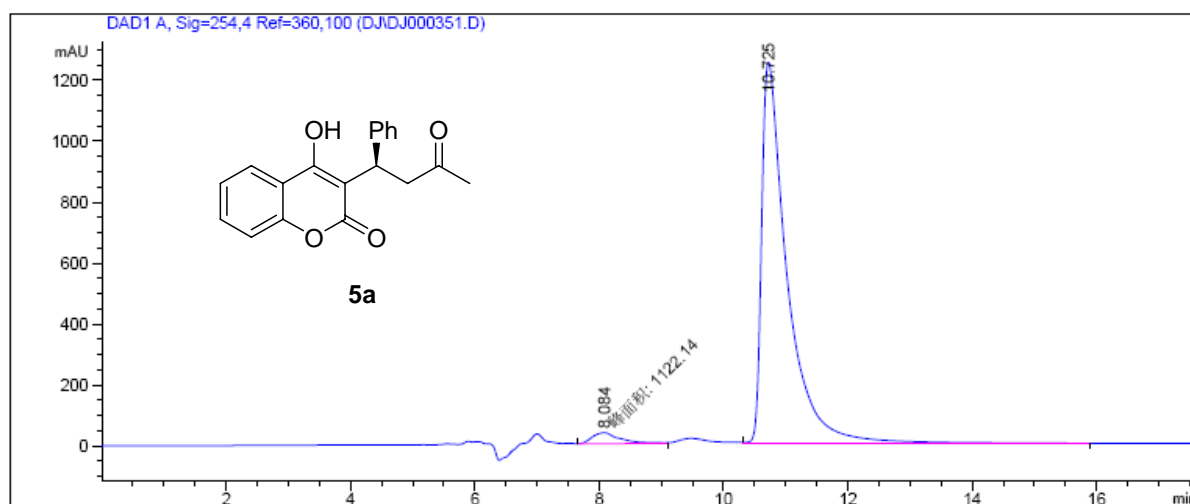


Copies of HPLC chromatographs of Michael addition products

4-Hydroxy-3-(3-oxo-1-phenylbutyl)-chromen-2-one (5a):

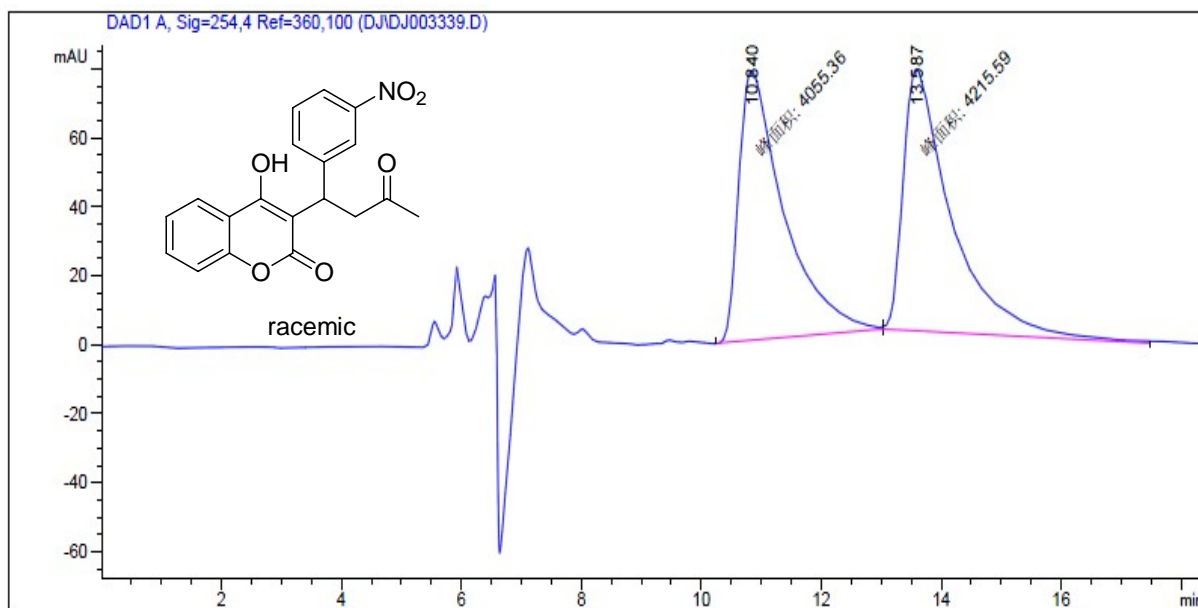


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.965	MM	0.5218	4821.66602	154.02078	50.2076
2	10.915	MM	0.5193	4781.80176	153.46213	49.7924

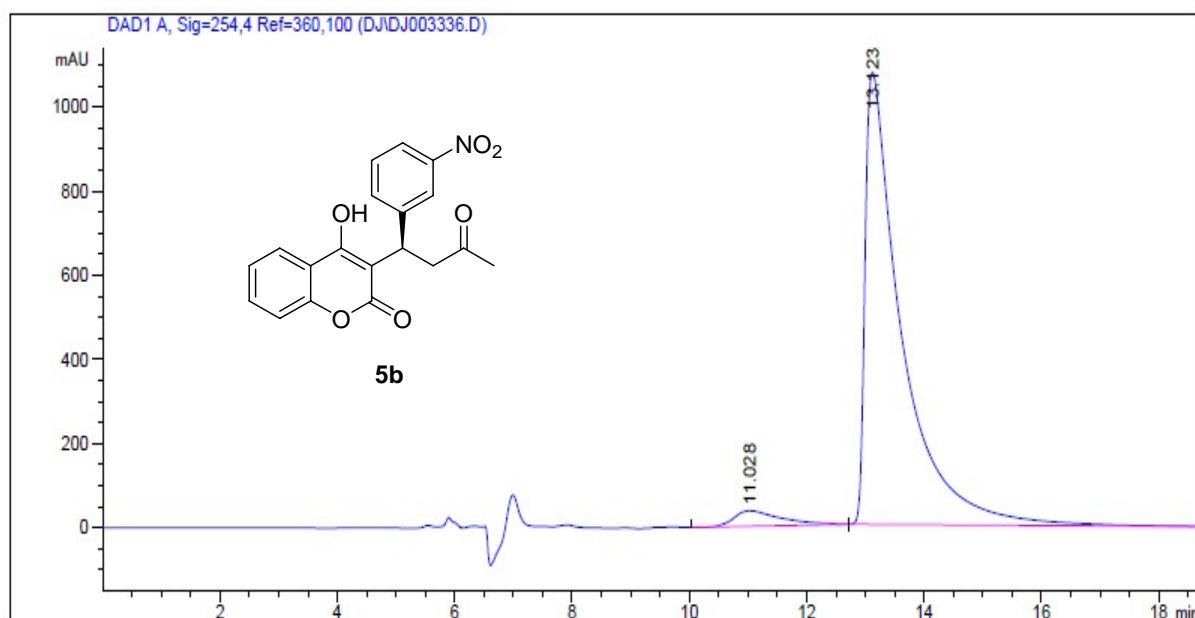


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.084	MM	0.5145	1122.13745	36.35252	3.0403
2	10.725	VB S	0.4098	3.57861e4	1250.87280	96.9597

4-Hydroxy-3-[1-(3-nitro-phenyl)-3-oxo-butyl]-chromen-2-one (5b):

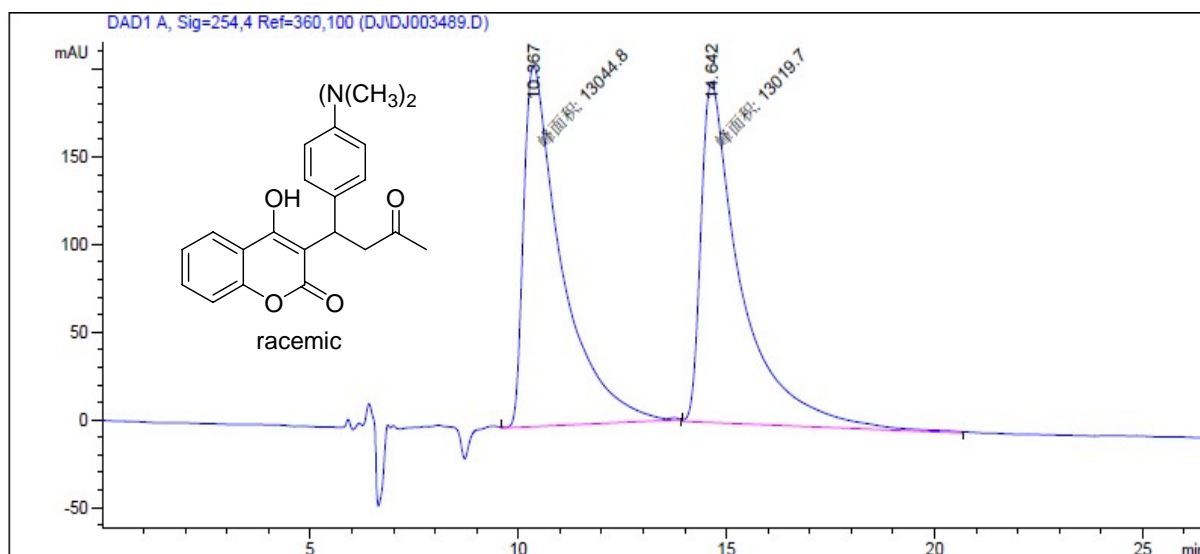


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.840	MM	0.8663	4055.36426	78.01944	49.0314
2	13.587	MM	0.9261	4215.59424	75.86870	50.9686

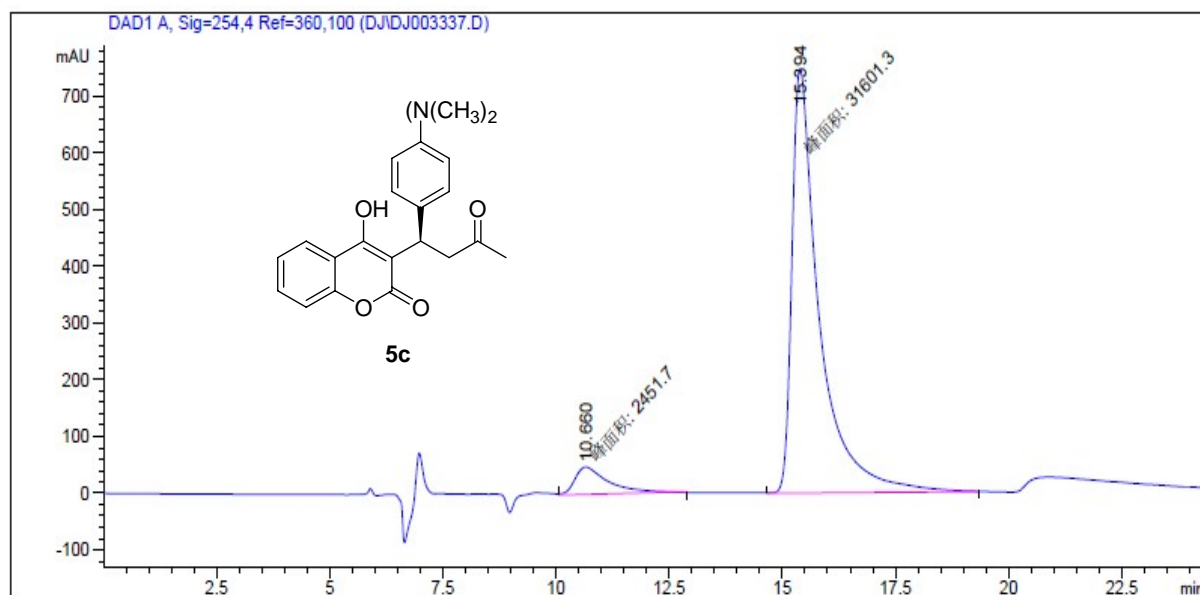


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.028	VB S	0.7872	2055.39063	37.05040	4.2474
2	13.123	BBA	0.6032	4.63368e4	1074.30090	95.7526

4-Hydroxy-3-[1-(4-dimethylamino-phenyl)-3-oxo-butyl]-chromen-2-one (5c):

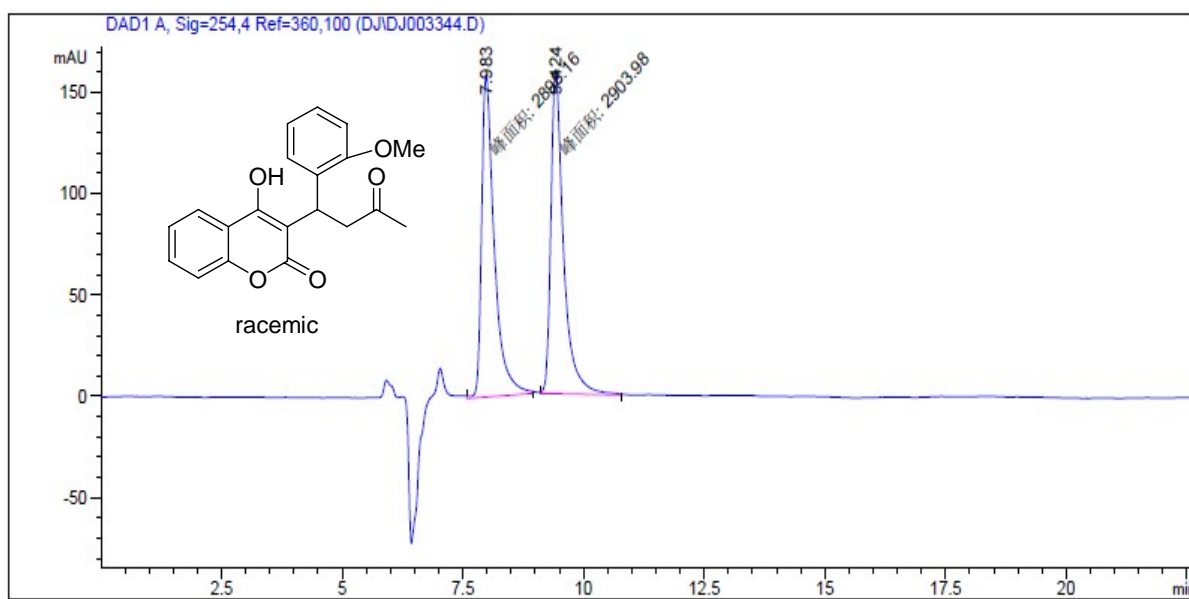


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.367	MM	1.0553	1.30448e4	206.02795	50.0481
2	14.642	MM	1.1161	1.30197e4	194.42818	49.9519

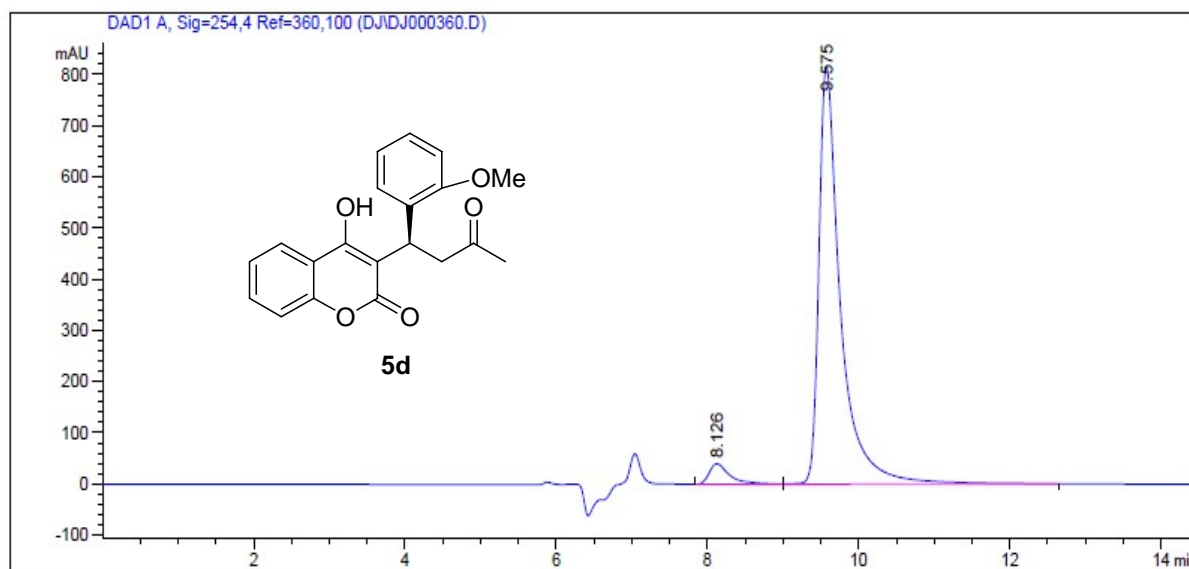


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.660	MM	0.8496	2451.70239	48.09386	7.1997
2	15.394	MM	0.7039	3.16013e4	748.27222	92.8003

4-Hydroxy-3-[1-(2-methoxy-phenyl)-3-oxo-butyl]-chromen-2-one (5d):

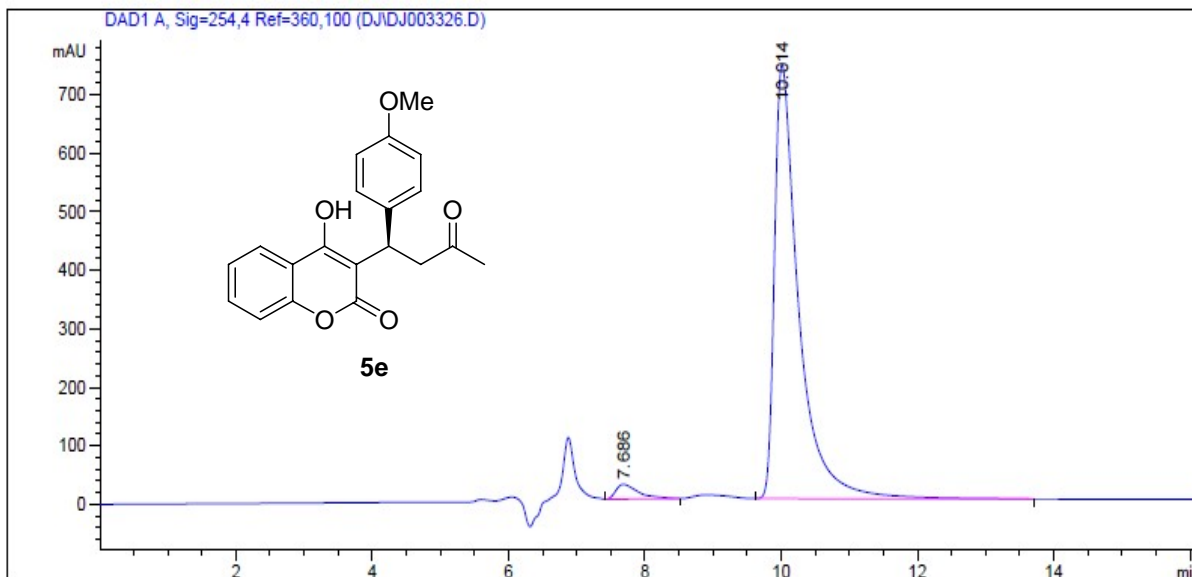
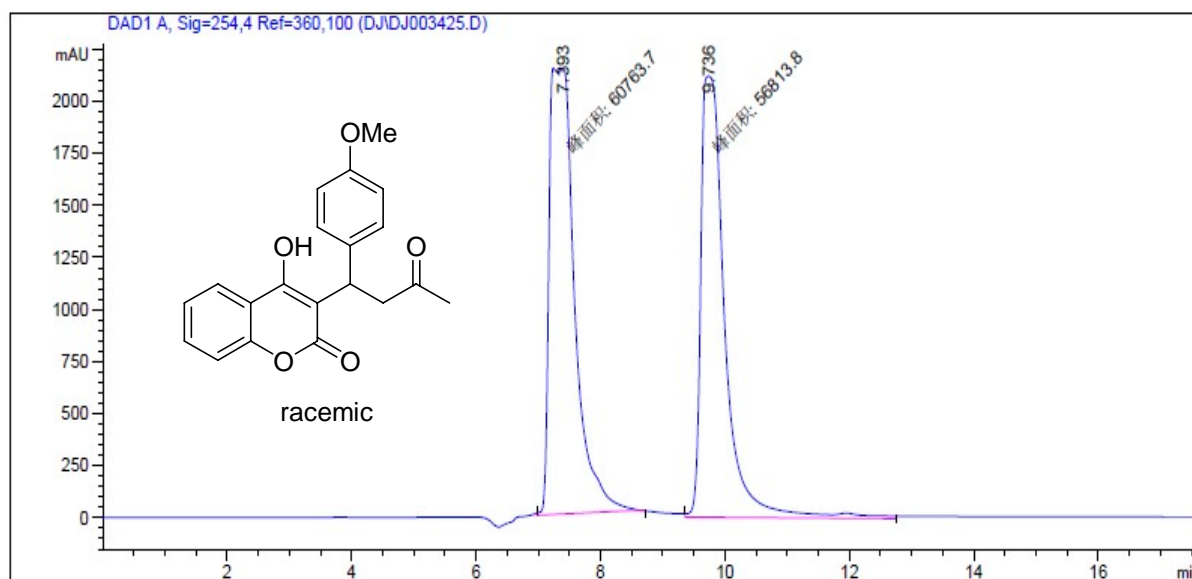


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.983	MM	0.3030	2898.16284	159.41415	49.9498
2	9.424	MM	0.3027	2903.98291	159.87947	50.0502

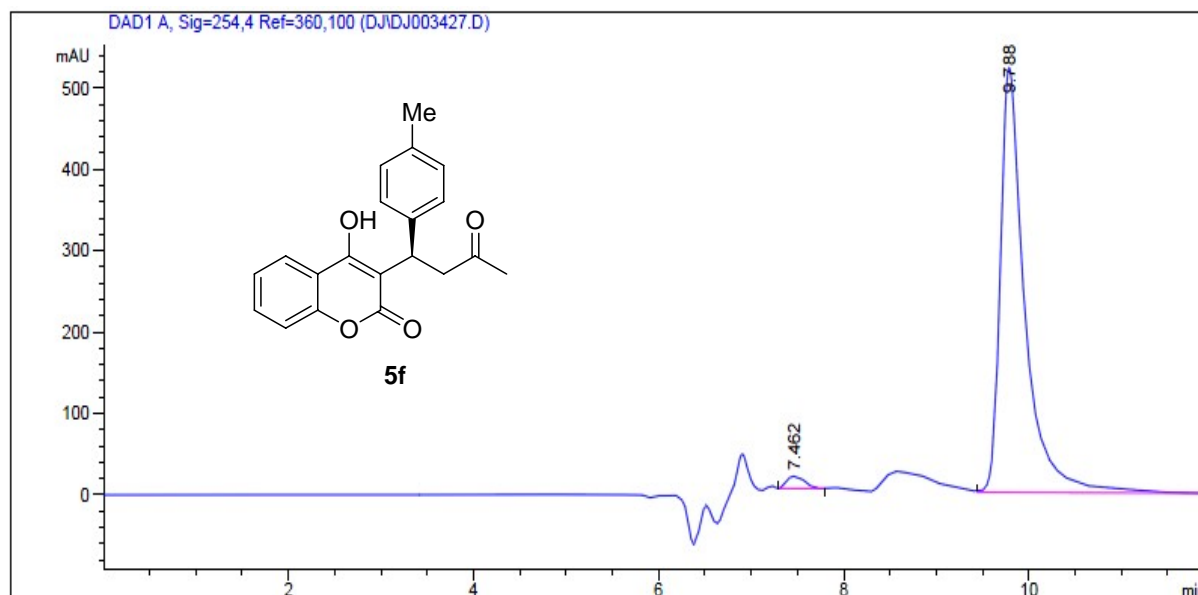
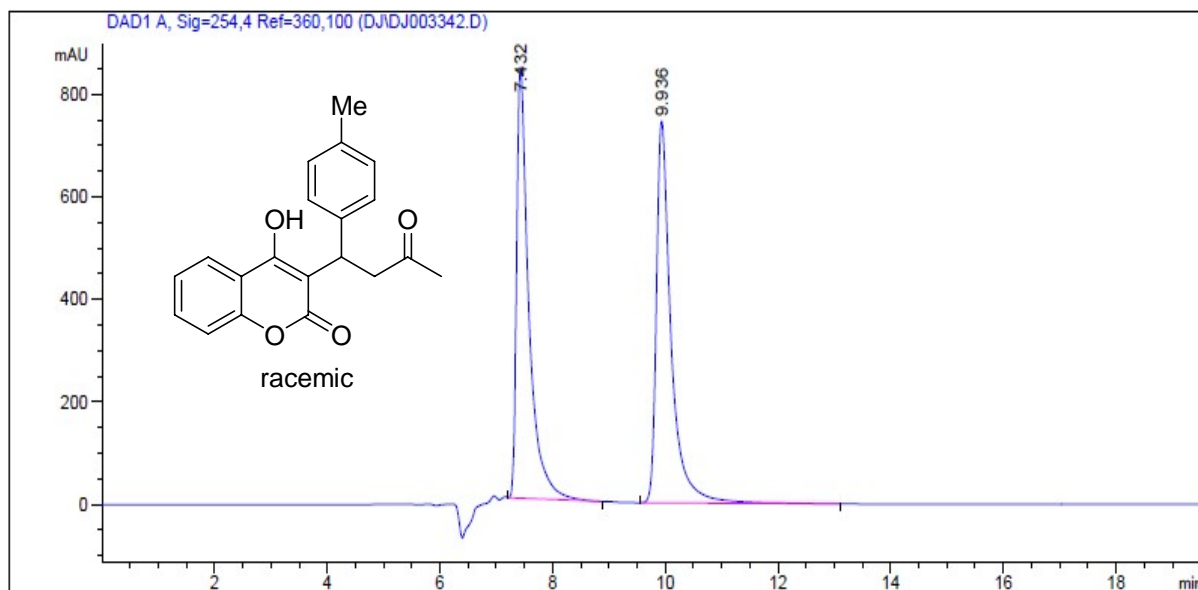


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.126	BV	0.2802	753.12573	39.90929	4.4362
2	9.575	VB S	0.2881	1.62236e4	815.50171	95.5638

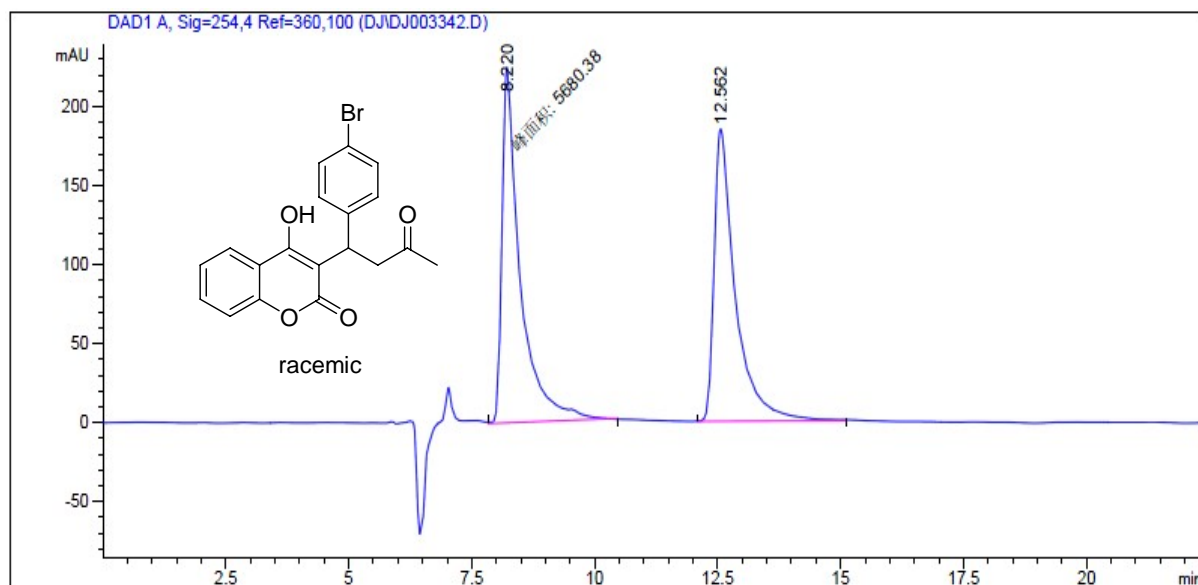
4-Hydroxy-3-[1-(4-methoxy-phenyl)-3-oxo-butyl]-chromen-2-one (5e):



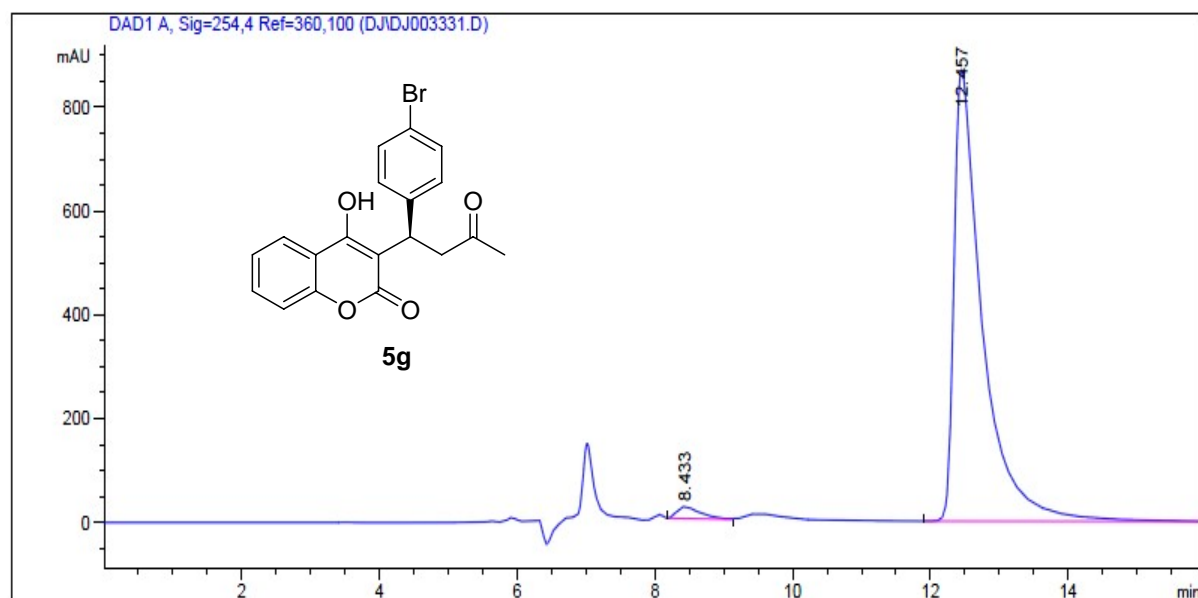
4-Hydroxy-3-[1-(4-methyl-phenyl)-3-oxo-butyl]-chromen-2-one (5f):



3-[1-(4-Bromo-phenyl)-3-oxo-butyl]-4-hydroxychromen-2-one (5g):

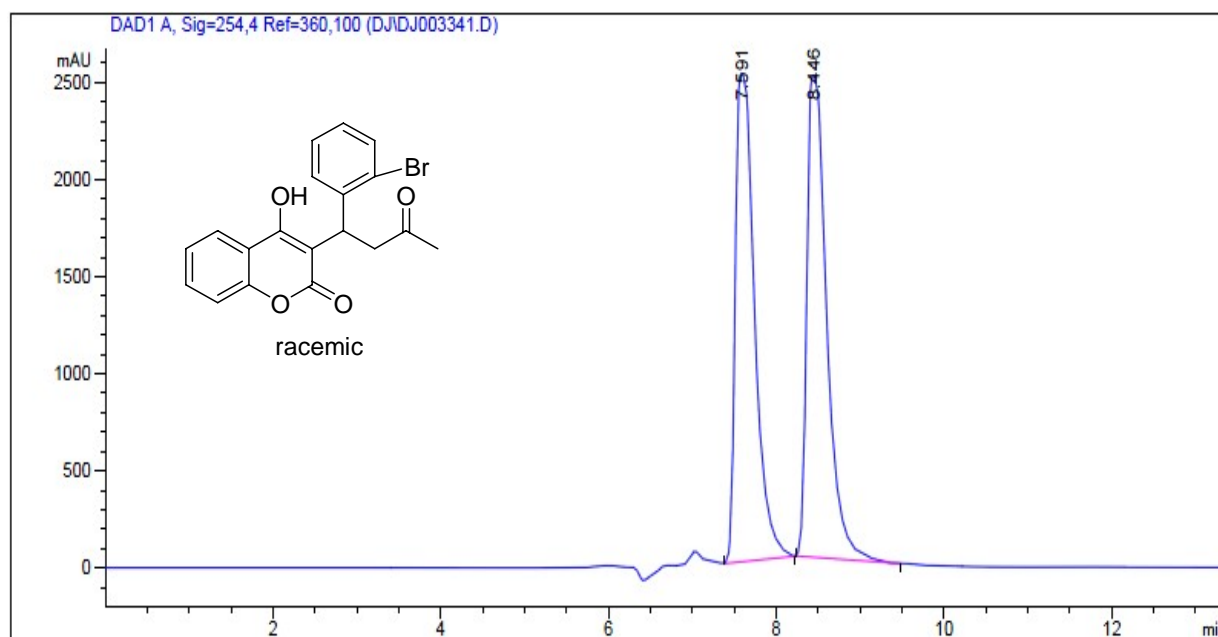


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.220	MM	0.4200	5680.38135	225.38715	50.8748
2	12.562	BB	0.4261	5485.03760	184.88409	49.1252

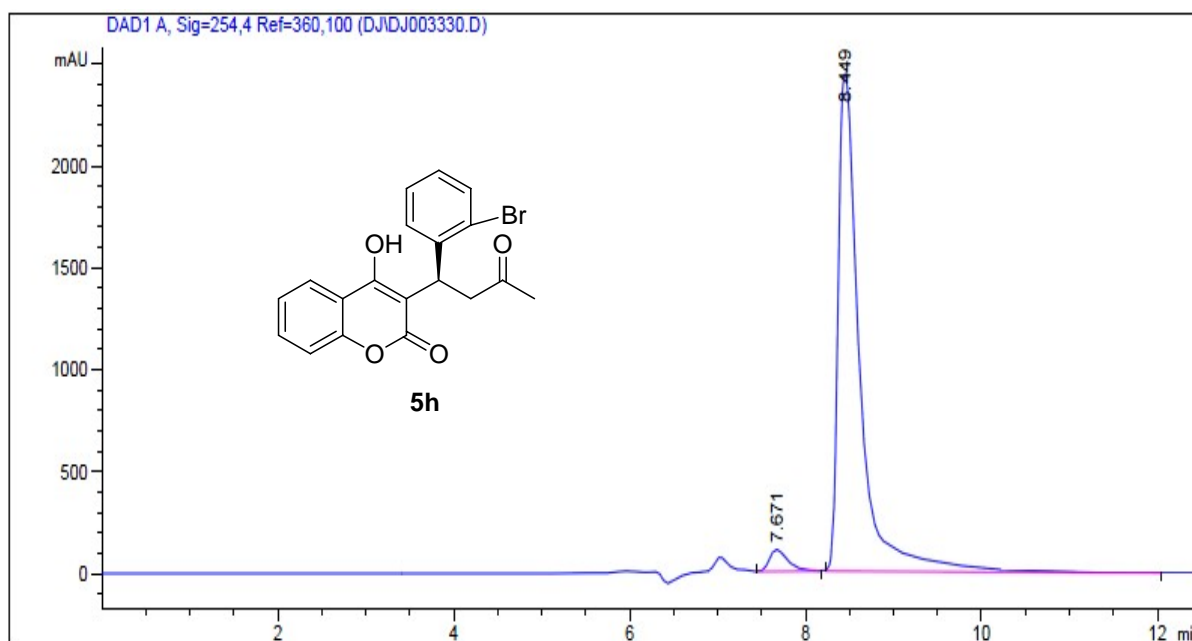


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.433	BV	0.3479	526.71191	22.94009	2.0801
2	12.457	VBAS	0.4091	2.47946e4	868.50403	97.9199

3-[1-(2-Bromo-phenyl)-3-oxo-butyl]-4-hydroxychromen-2-one (5h):

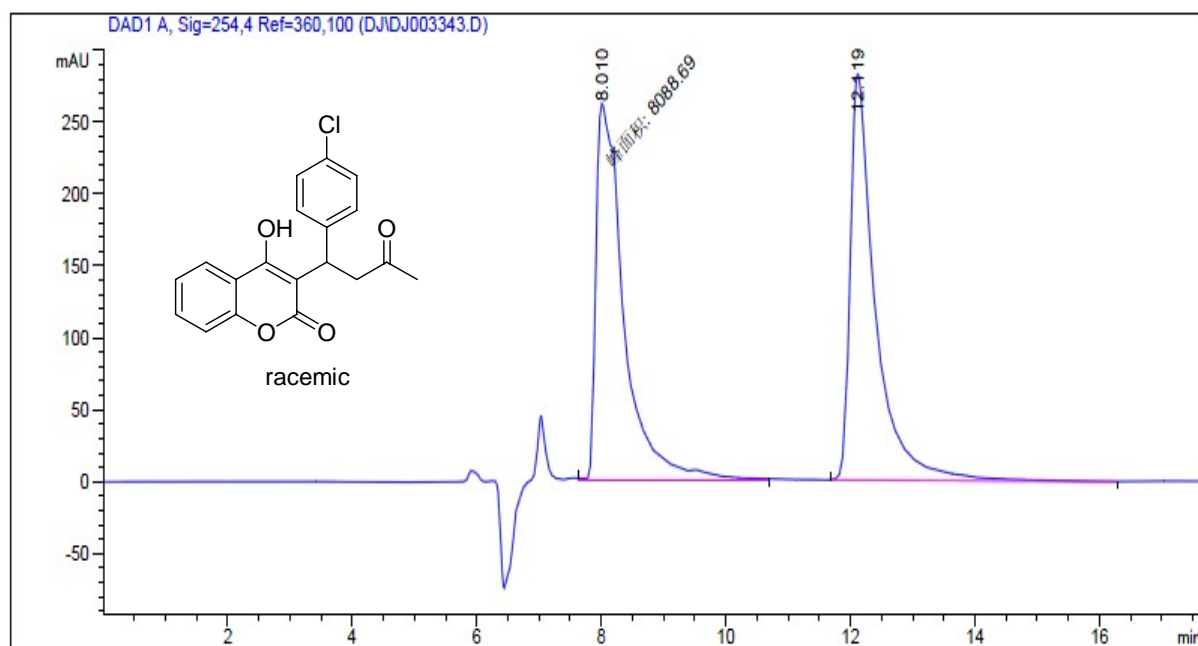


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.591	BB S	0.2445	3.97685e4	2514.23560	49.3838
2	8.446	BV	0.2557	4.07609e4	2481.18555	50.6162

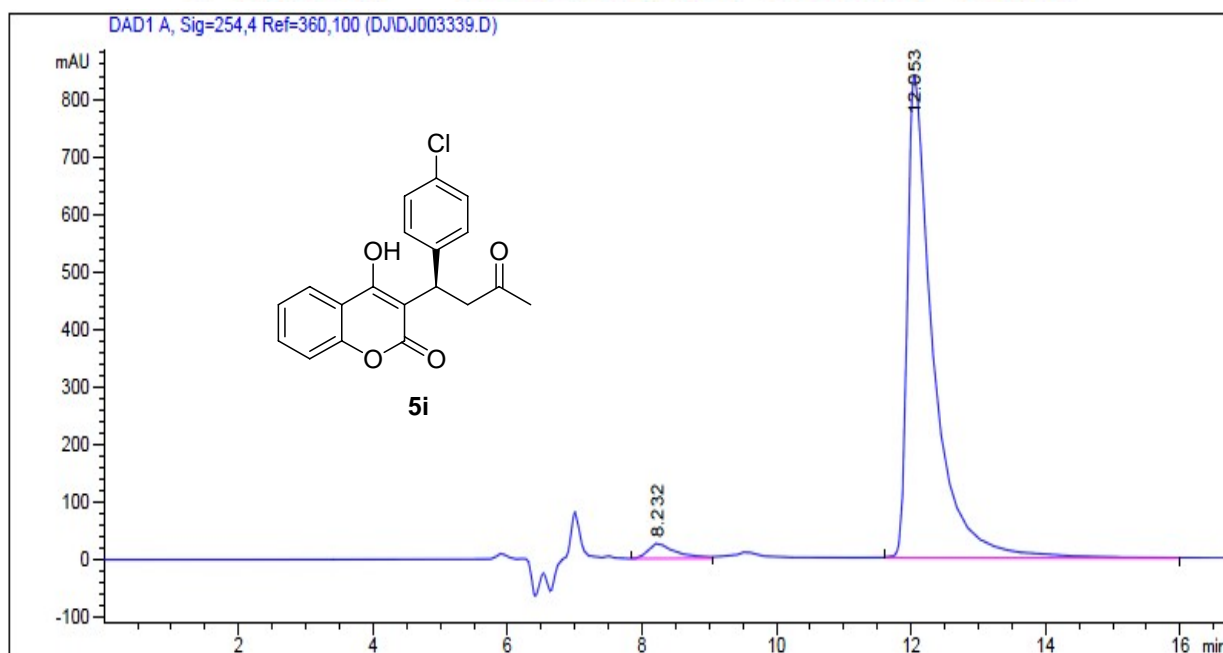


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.671	BB S	0.2194	1554.54028	108.35823	3.6186
2	8.449	BB S	0.2501	4.14054e4	2438.73022	96.3814

3-[1-(4-Chloro-phenyl)-3-oxo-butyl]-4-hydroxychromen-2-one (5i):

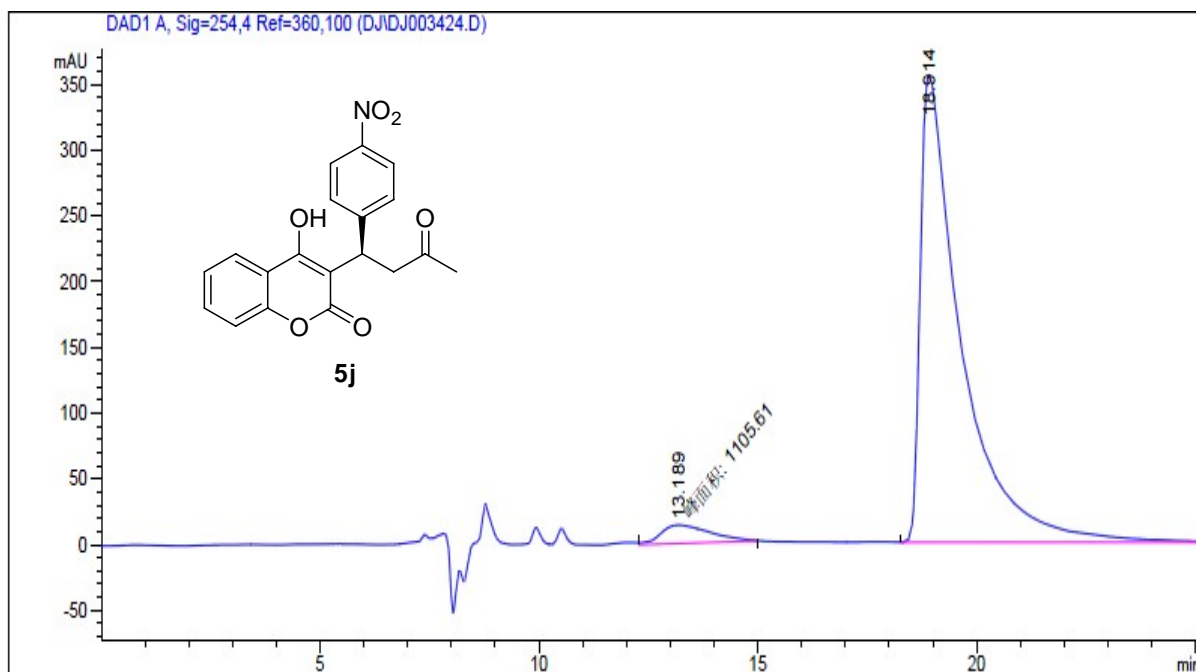
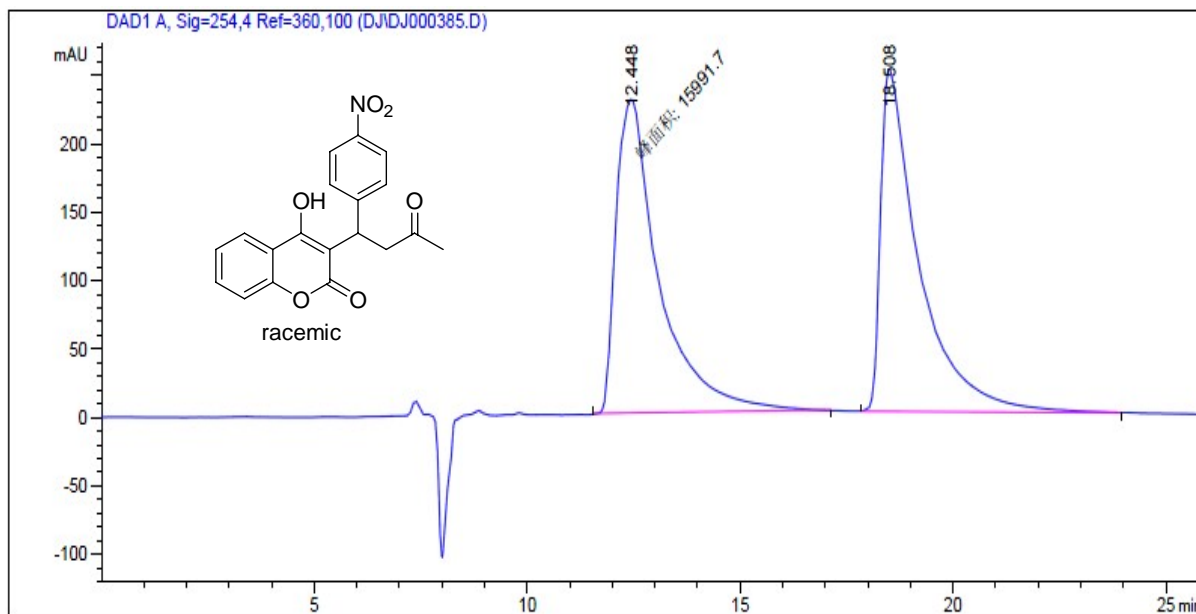


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.010	MM	0.5156	8088.69238	261.46130	50.6580
2	12.119	BV	0.3981	7878.54883	281.85455	49.3420

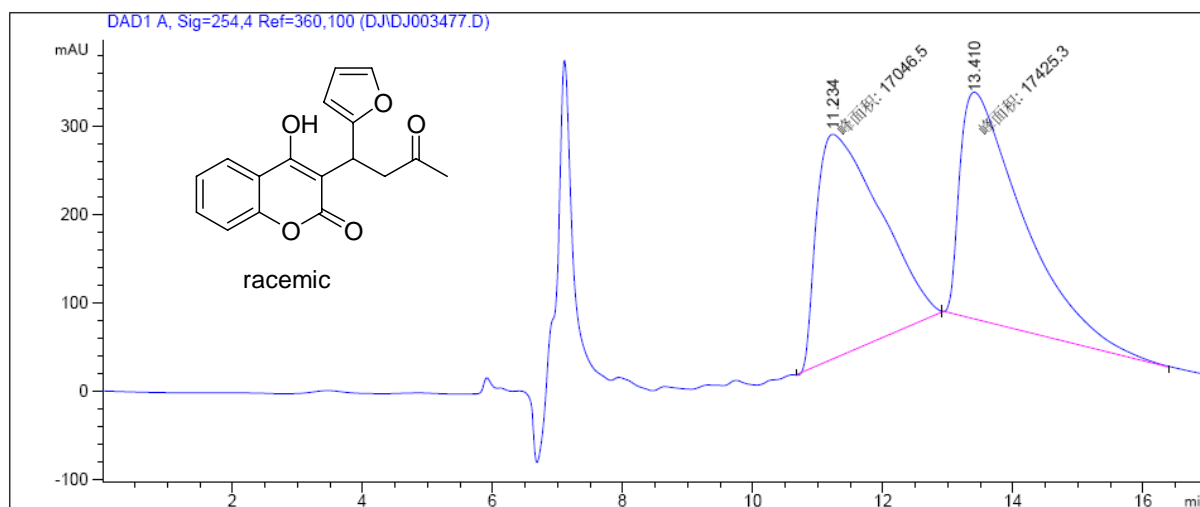


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.232	BV	0.3785	721.34540	26.42527	3.1620
2	12.053	VV	0.3758	2.20913e4	837.25836	96.8380

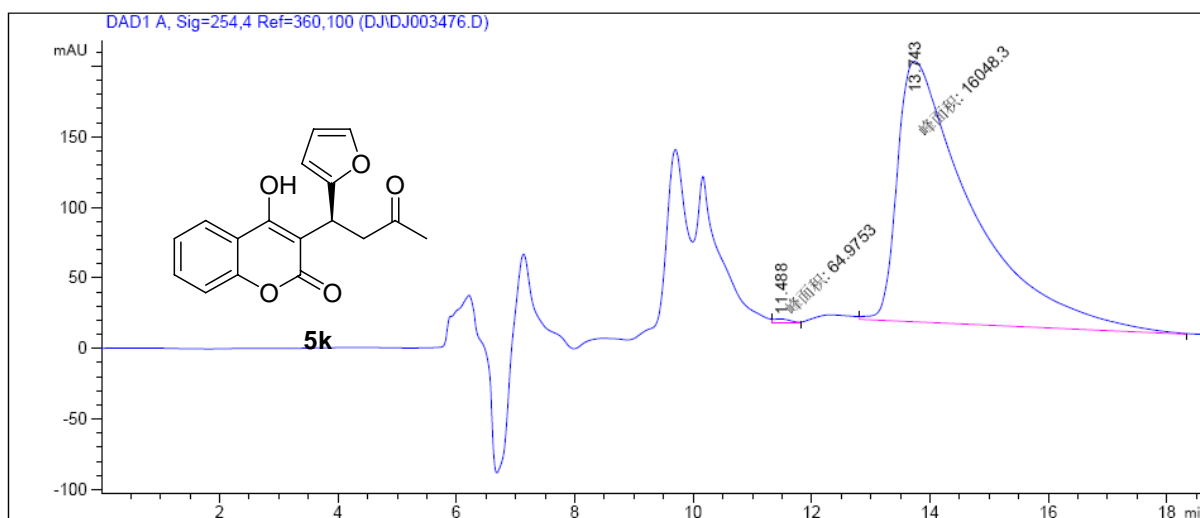
4-Hydroxy-3-[1-(4-nitro-phenyl)-3-oxo-butyl]-chromen-2-one (5j):



3-(1-Furan-2-yl-3-oxo-butyl)-4-hydroxy-chromen-2-one (5k):

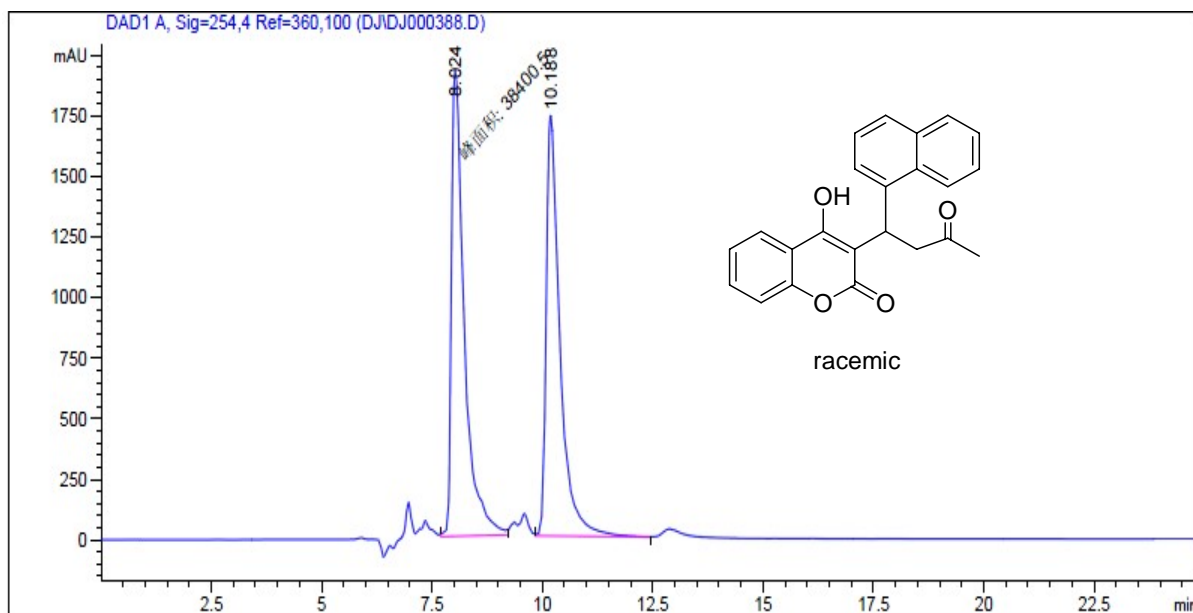


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.234	MM	1.1169	1.70465e4	254.36360	49.4506
2	13.410	MM	1.1317	1.74253e4	256.61481	50.5494

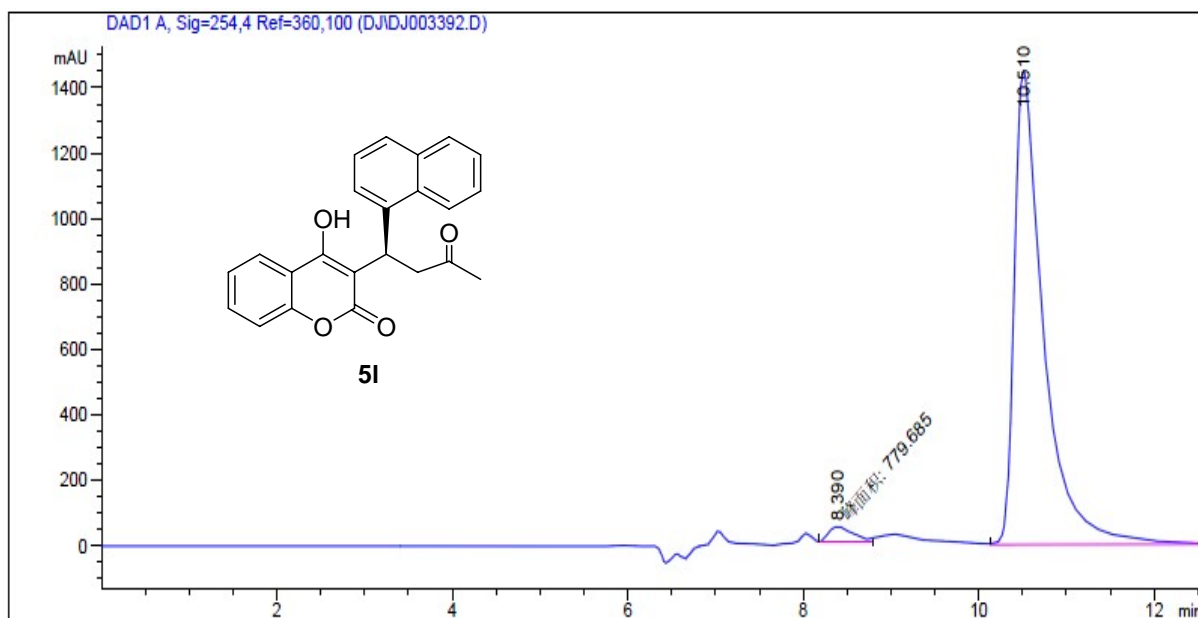


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.488	MM	0.3457	64.97527	3.13292	0.4032
2	13.743	MM	1.4486	1.60483e4	184.63850	99.5968

4-Hydroxy-3-(1-naphthalen-1-yl-3-oxo-butyl)-chromen-2-one(5I):

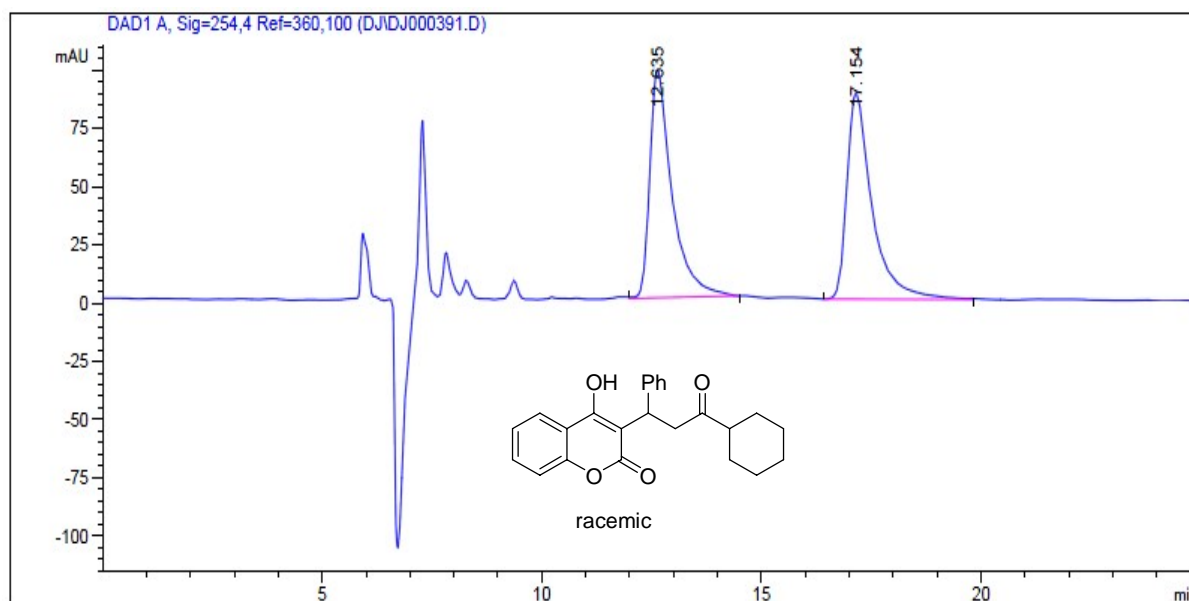


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.024	MM	0.3322	3.84005e4	1926.36816	50.7631
2	10.188	VB S	0.3146	3.72460e4	1734.09729	49.2369

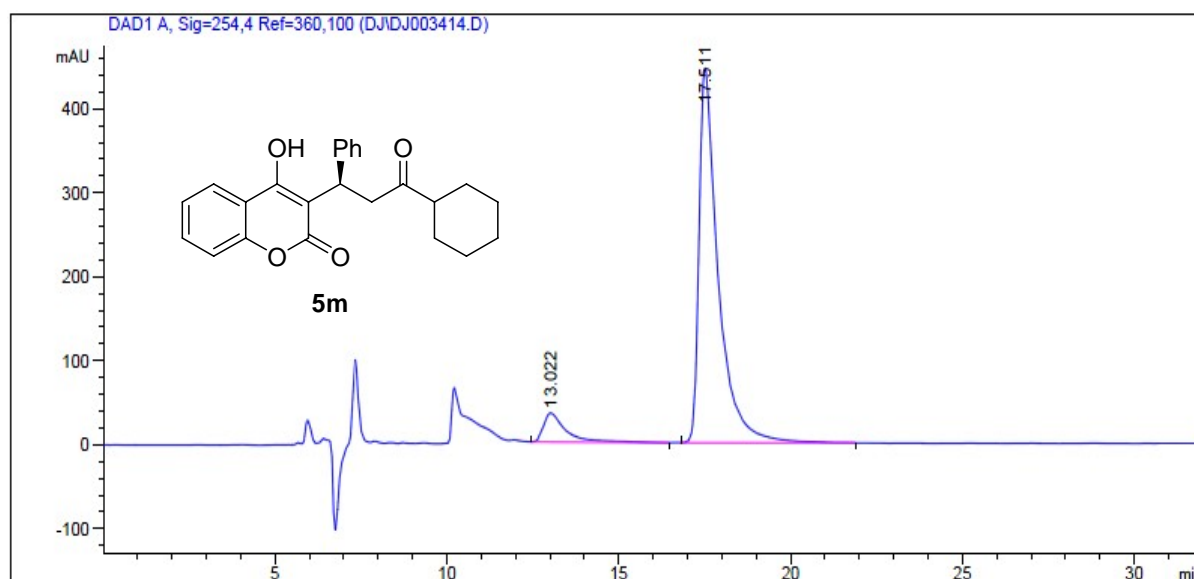


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.390	MM	0.2940	779.68451	44.19642	2.2863
2	10.510	VBAS	0.3367	3.33228e4	1446.94714	97.7137

4-Hydroxy-3-(4-cyclohexyl-3-oxo-1-phenyl-butyl)-chromen-2-one (5m):



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.635	VB S	0.5108	3410.50122	97.80566	49.4006
2	17.154	VB	0.5736	3493.25708	89.05994	50.5994



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.022	BB	0.6517	1554.87292	34.37627	8.3181
2	17.511	BB	0.5570	1.71377e4	445.27176	91.6819