

# Supporting Information for

## One-pot Asymmetric Synthesis of Spiro[dihydrofurocoumarin/pyroazolone] Scaffold by Michael Addition/I<sub>2</sub>-Mediated Cyclization Sequence

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Dan-Qian Xu<sup>\* a</sup>

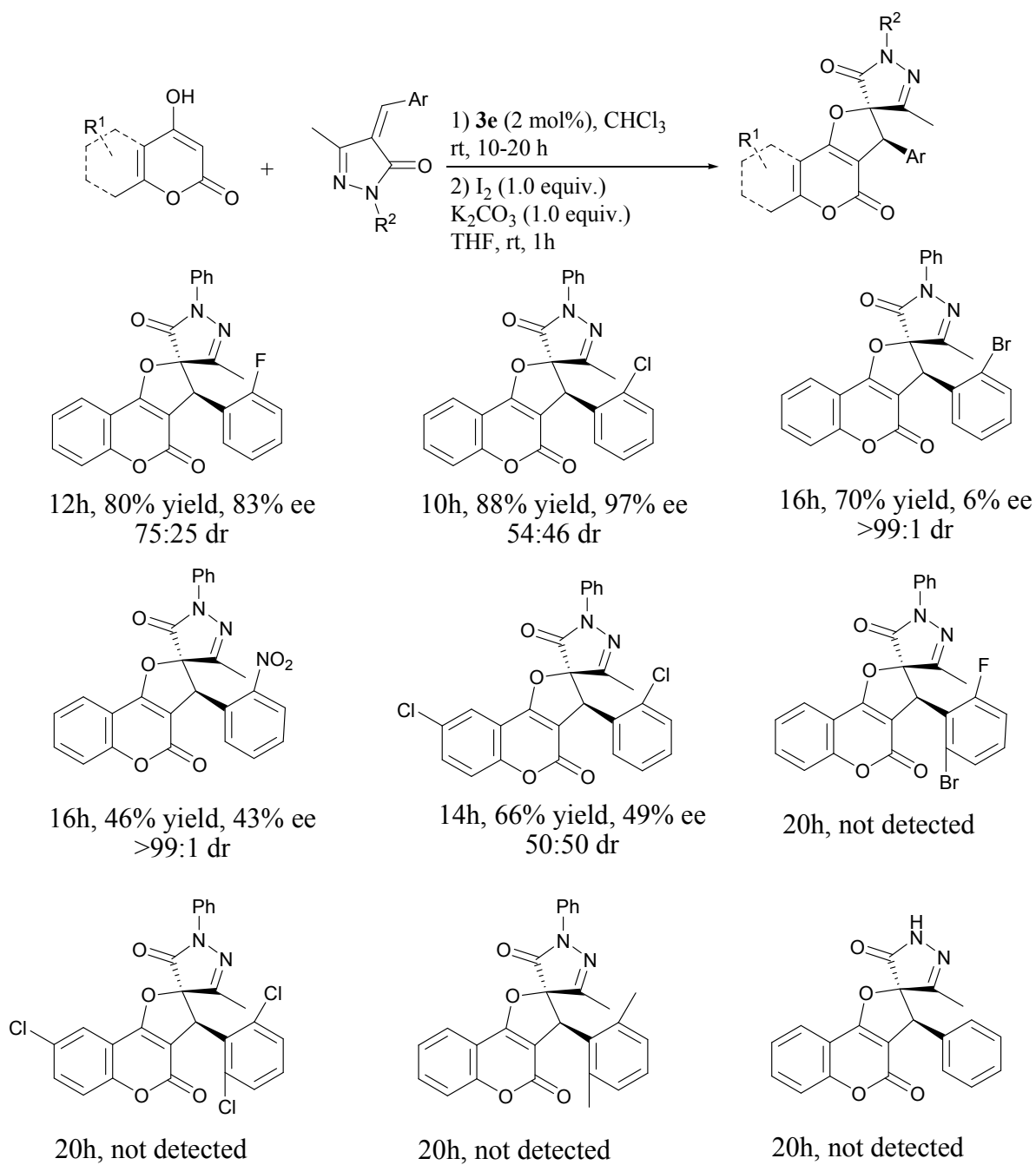
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## 1. Scheme S1.



## 2. ESI-MS spectra, high resolution mass data of intermediates A and B, and $^1\text{H}$ , $^{13}\text{C}$ NMR spectra, HPLC chromatograms of A.

### 2.1 ESI-MS spectra, high resolution mass data of intermediates A and B.

Figure S1. ESI-MS spectrum of A, after 8 h of the Michael reaction.

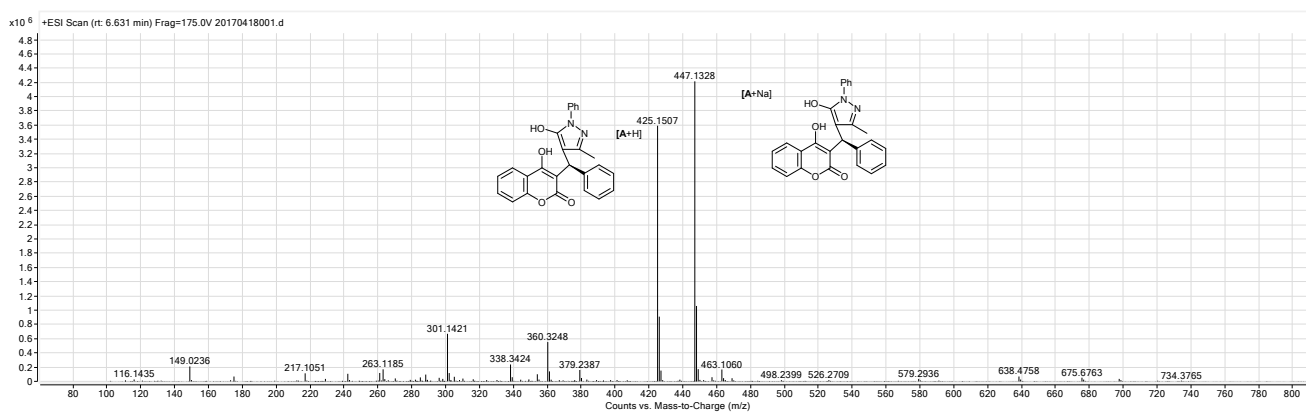


Figure S2. ESI-MS spectrum of B, after 0.2 h of the  $\text{I}_2$ -mediated cyclization reaction.

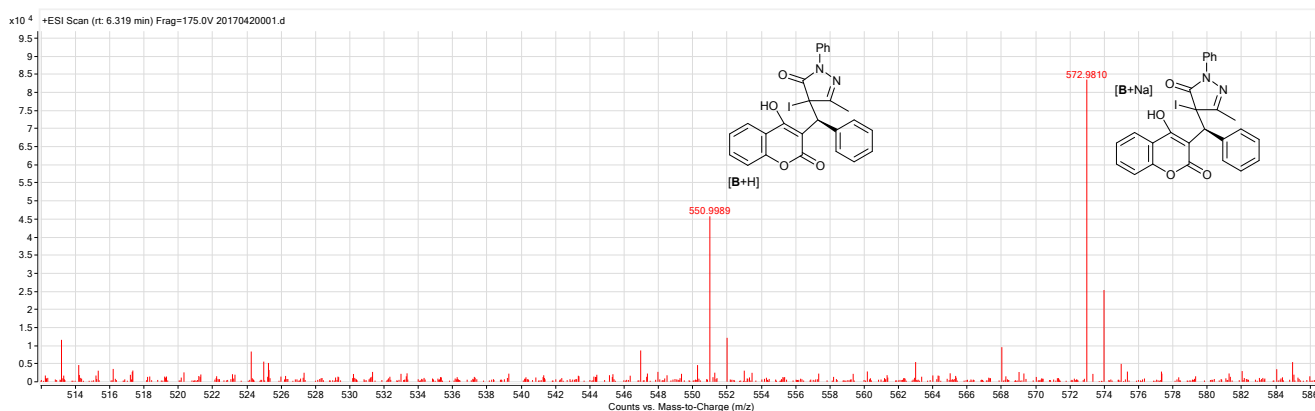
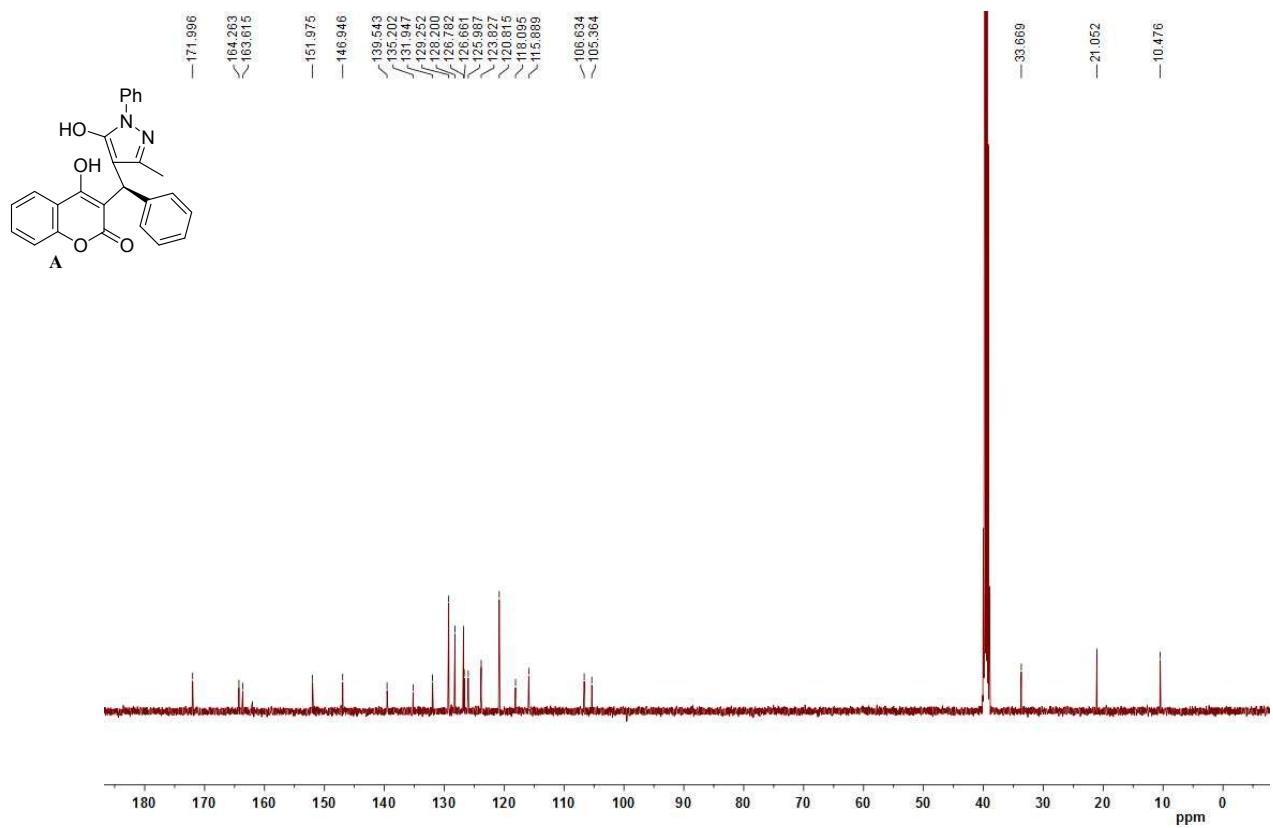
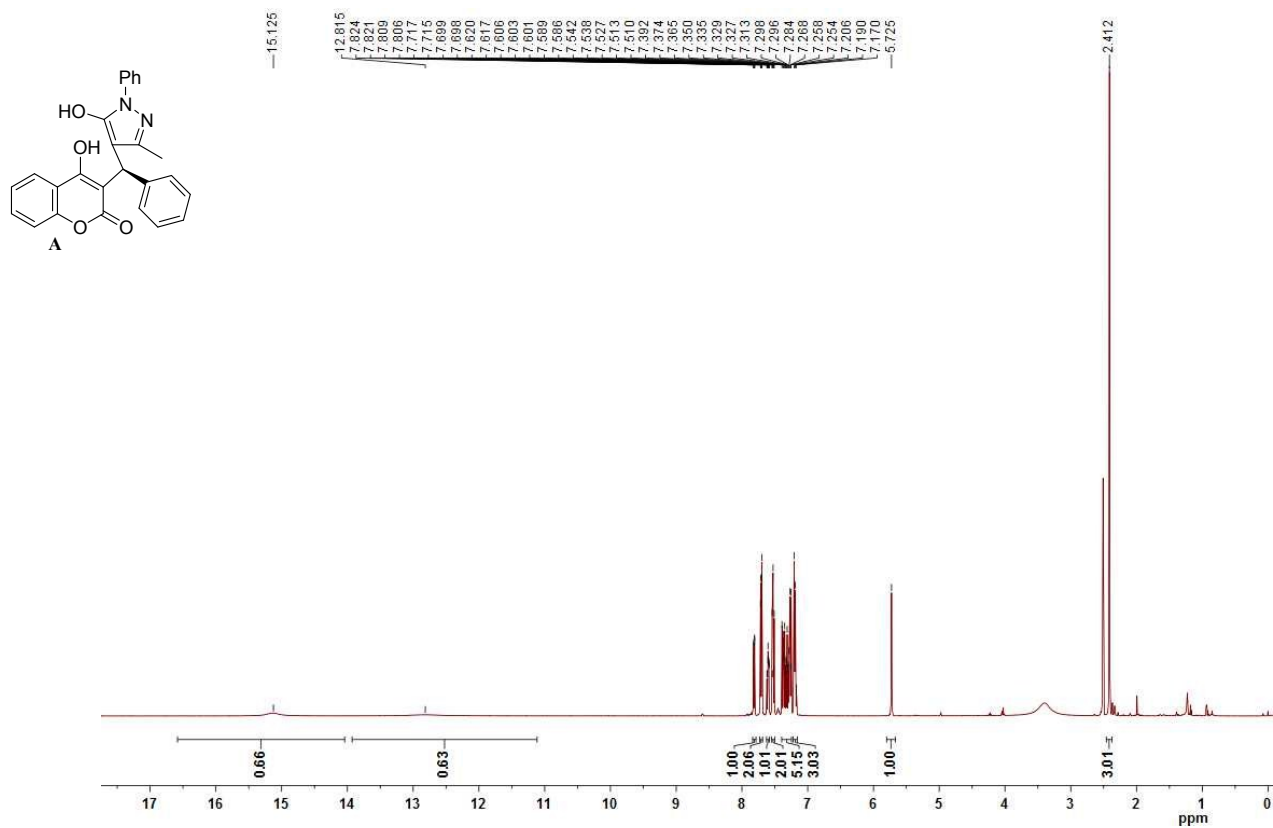


Table S1. High resolution mass data of detected intermediates A and B.

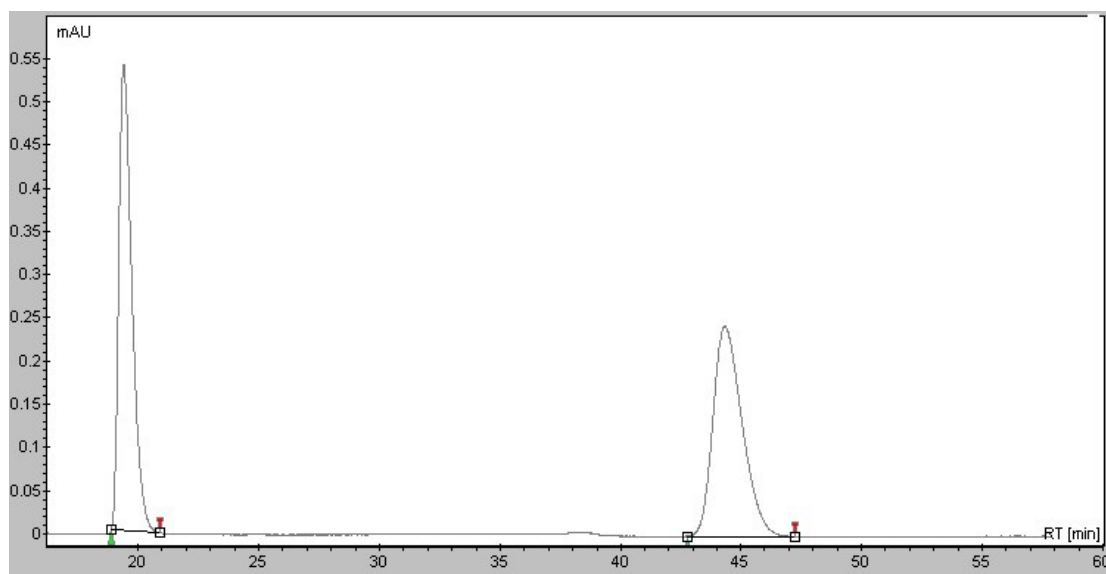
Species	Formula	Mass (measured)	Mass (calculated)	Error (ppm)
A	$\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_4$	424.1507	424.1501	1.4
B	$\text{C}_{26}\text{H}_{19}\text{IN}_2\text{O}_4$	549.9999	549.9986	2.4

## 2.2 $^1\text{H}$ , $^{13}\text{C}$ NMR spectra, and HPLC chromatograms of A.

### $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of A

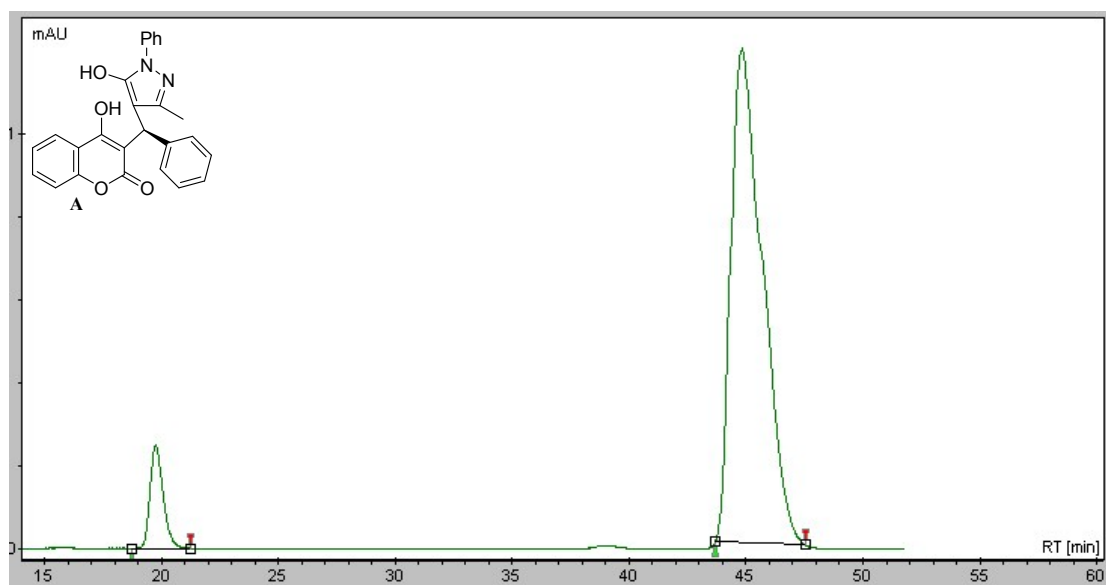


### HPLC chromatogram of A (racemic)



#	Start time[min]	Time[min]	End time[min]	Area%
1	18.872	19.385	20.888	49.975
2	42.744	44.317	47.261	50.025

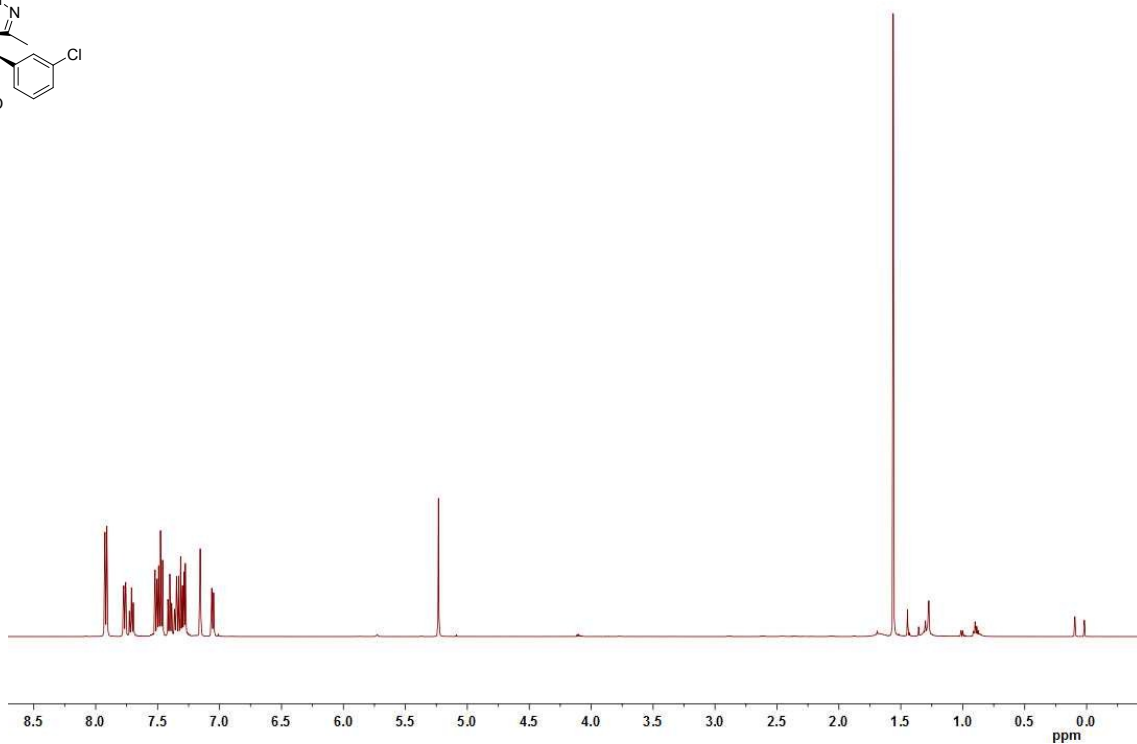
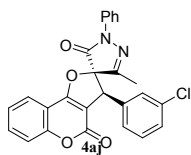
### HPLC chromatogram of A (chiral)



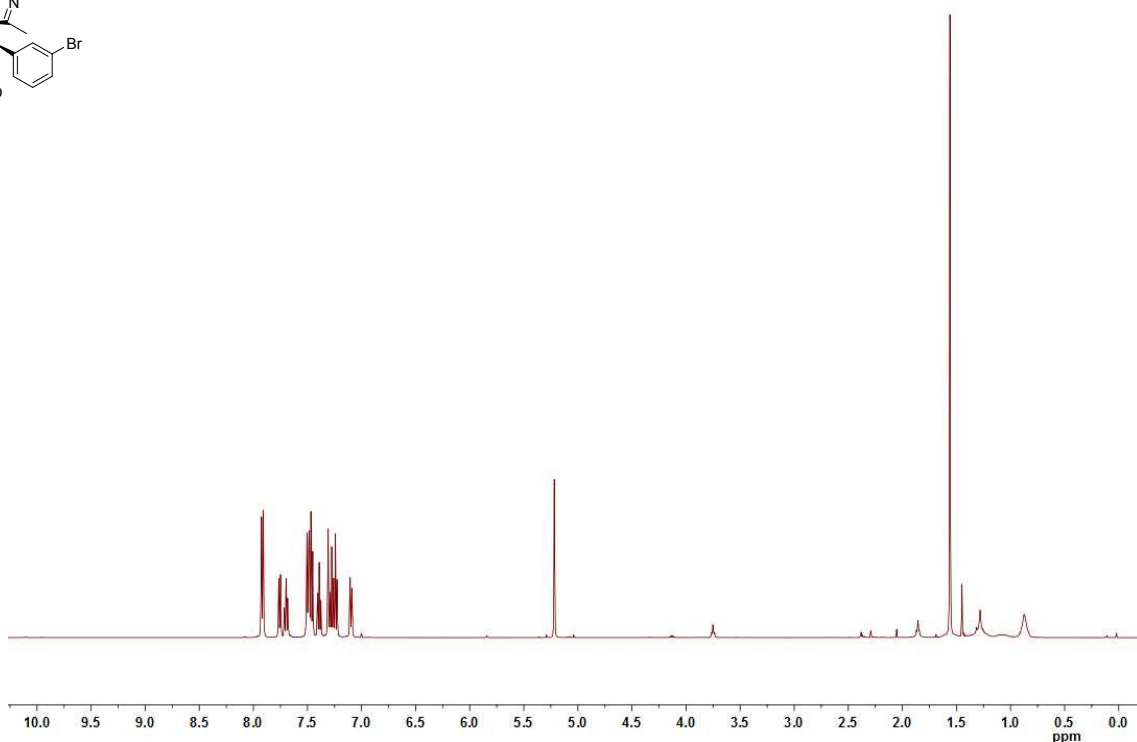
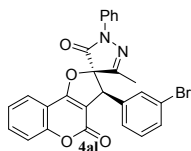
#	Start time[min]	Time[min]	End time[min]	Area%
1	18.748	19.745	21.272	7.947
2	43.697	44.810	47.519	92.053

### 3. $^1\text{H}$ spectra of crude compounds 4aj and 4al.

#### $^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ ) spectrum of crude compound 4aj

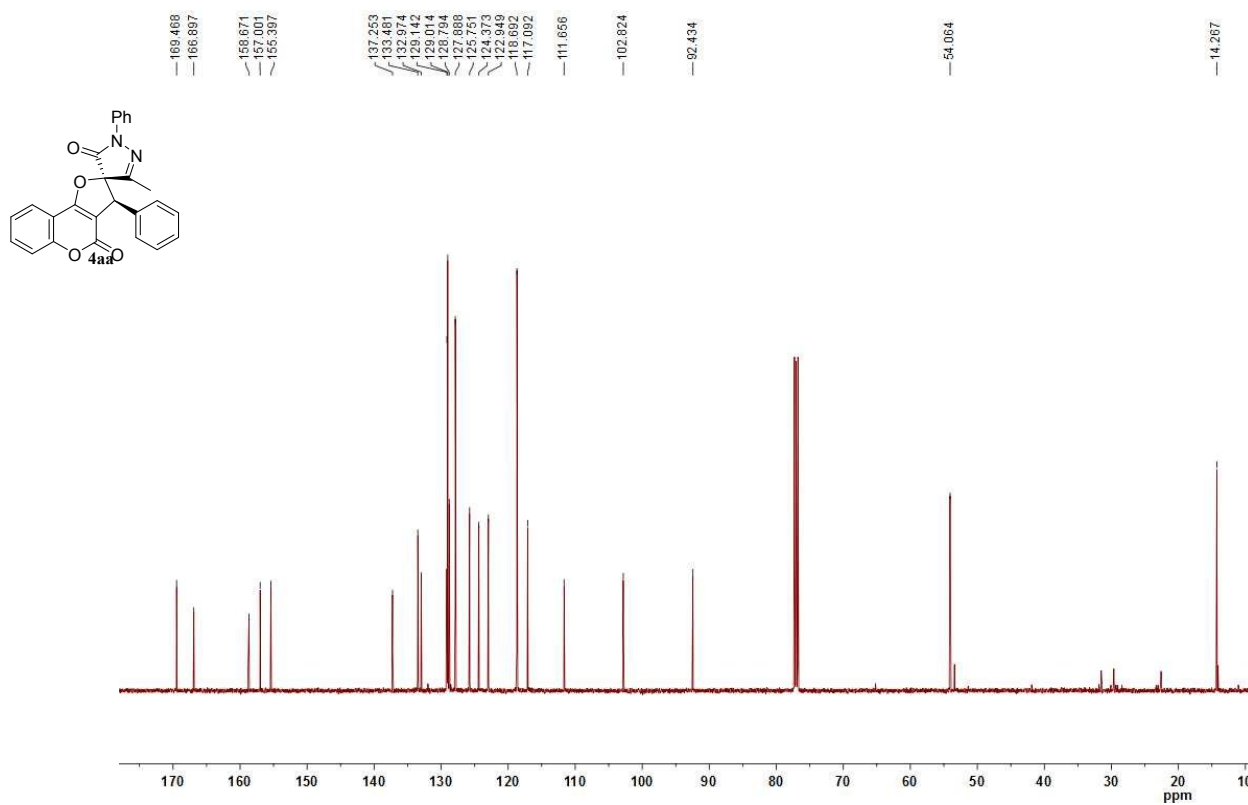
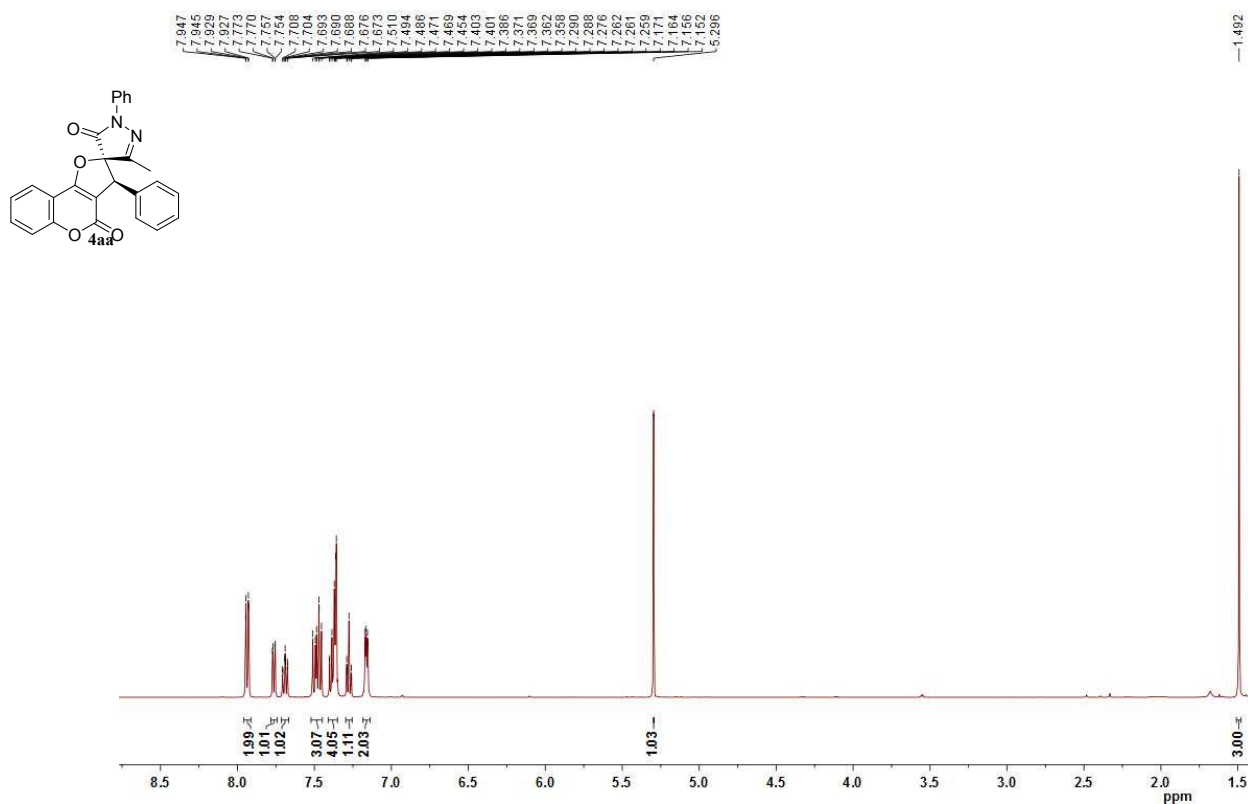


#### $^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ ) spectrum of crude compound 4al

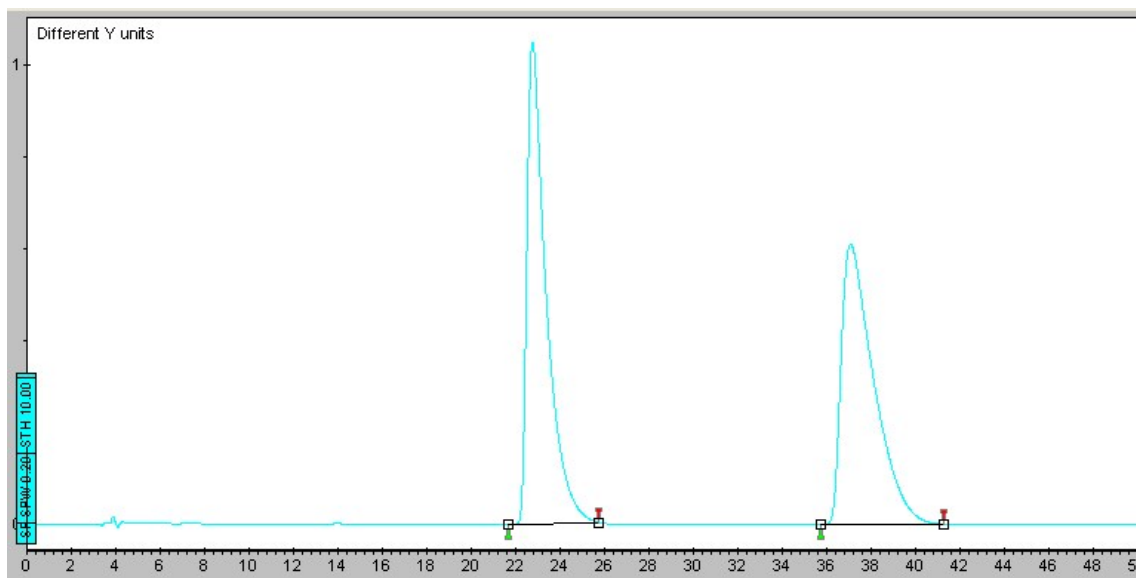


# 4. $^1\text{H}$ , $^{13}\text{C}$ NMR, and HPLC chromatograms of compounds 4aa-4ap, 4ba-4bk, and 5a-5e.

## $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of 4aa

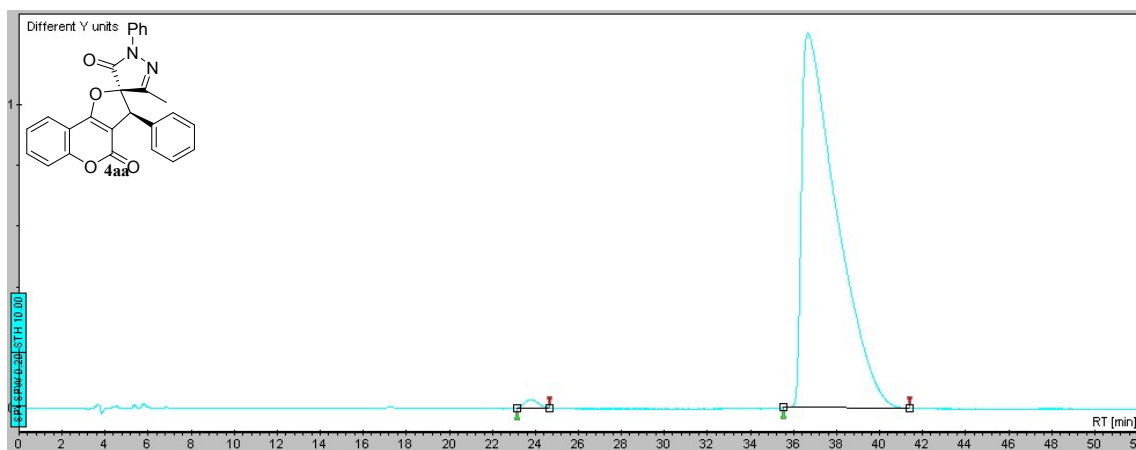


## HPLC chromatogram of 4aa (racemic)



	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	21.676	22.778	25.744	50.555
2	35.748	37.093	41.284	49.445

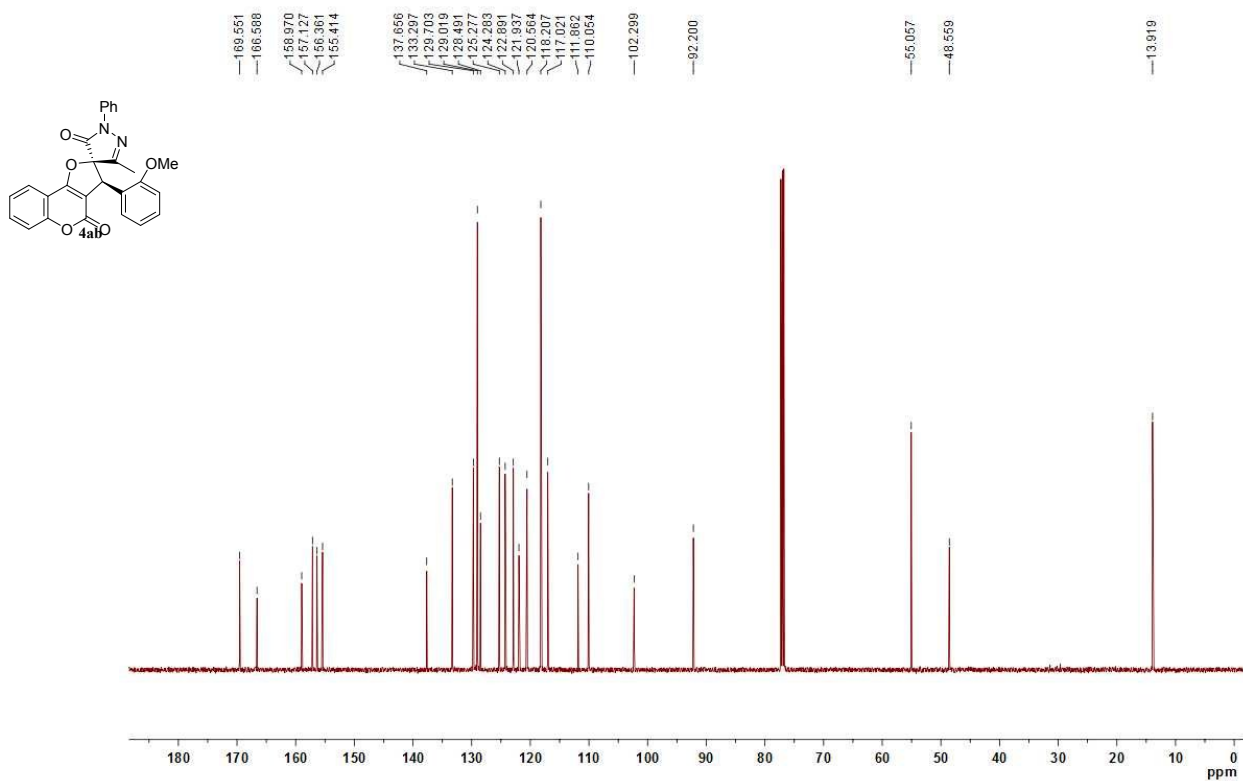
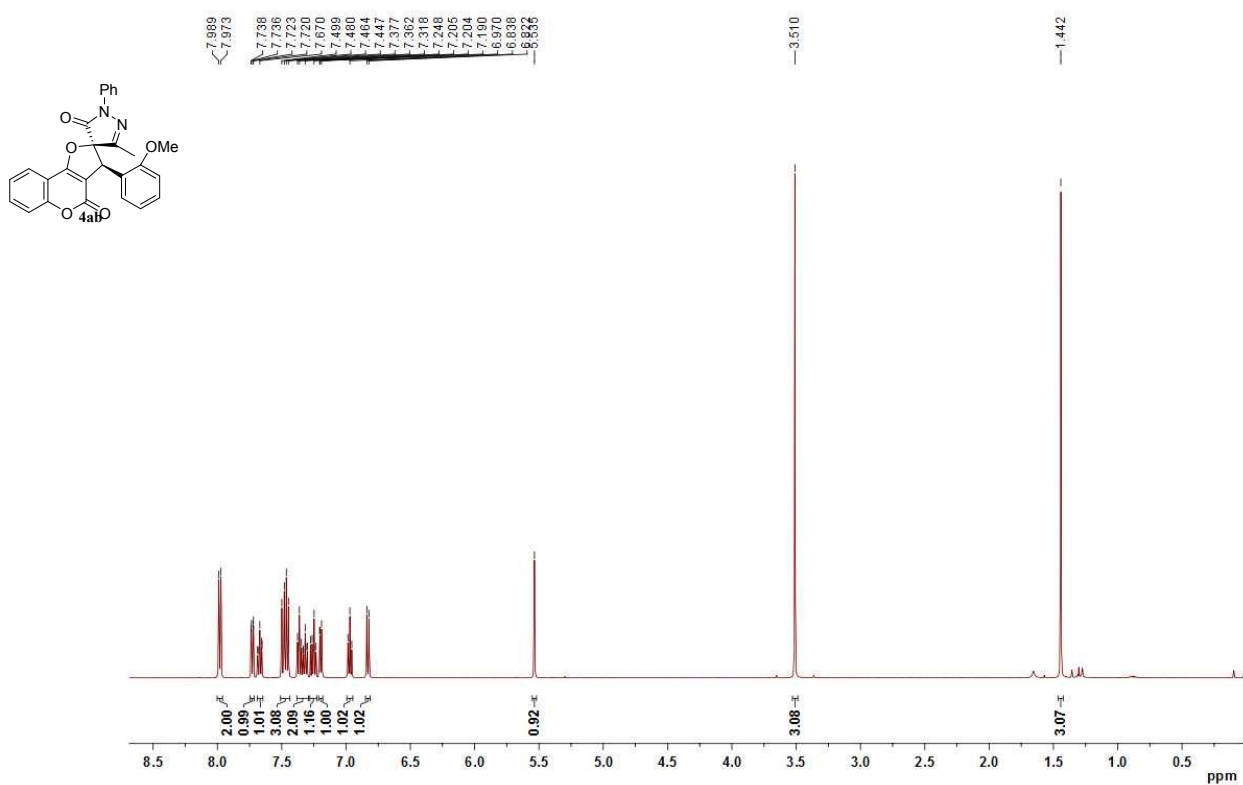
## HPLC chromatogram of 4aa (chiral)



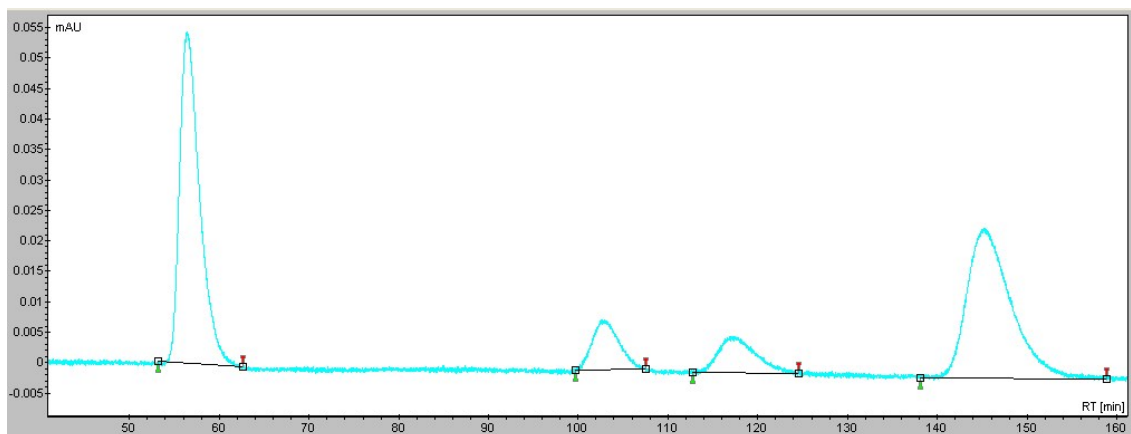
	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	23.147	23.772	24.654	0.867
2	35.527	36.651	41.395	99.133



# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ab

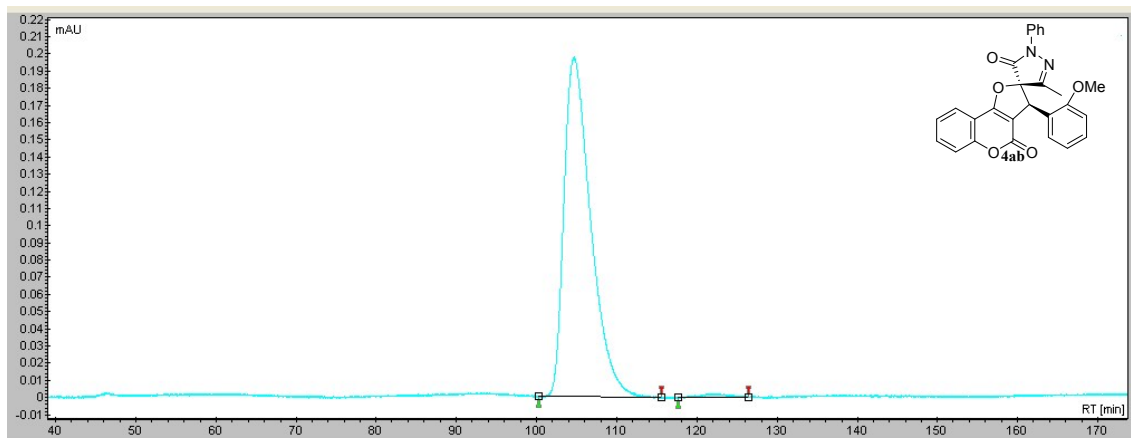


### HPLC chromatogram of 4ab (racemic)



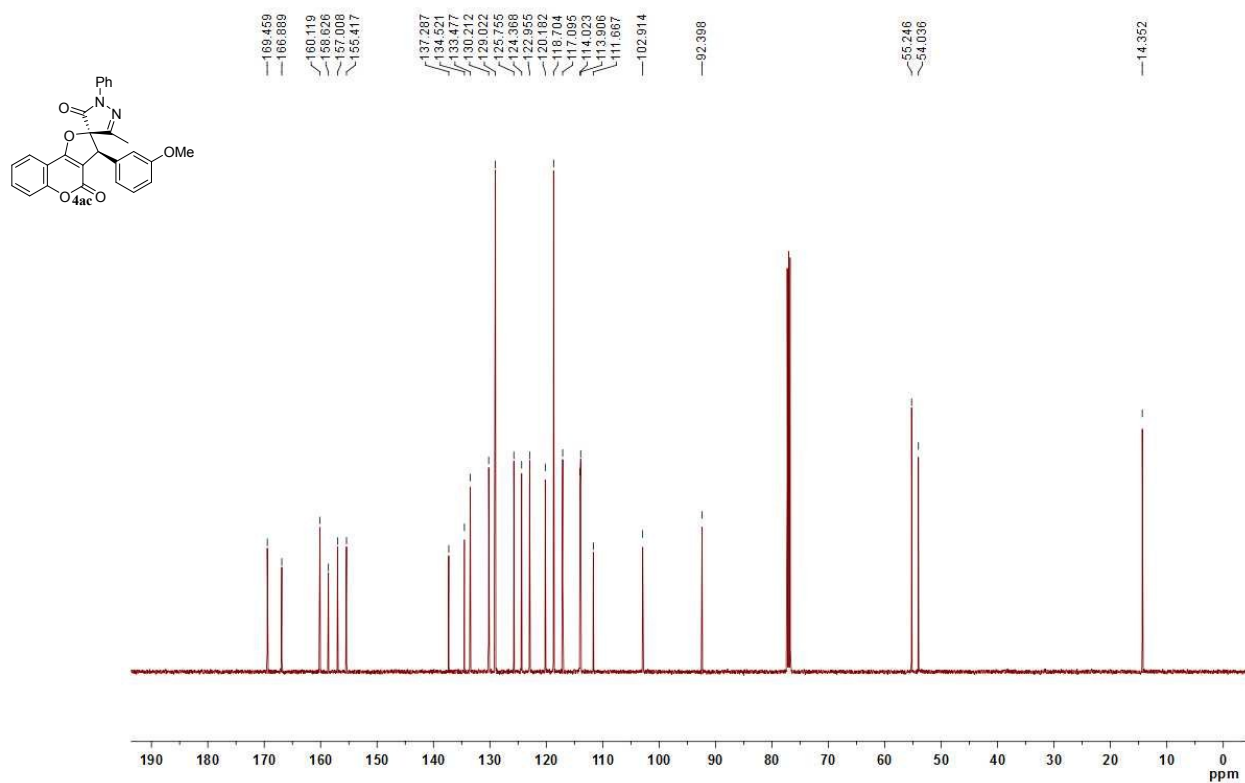
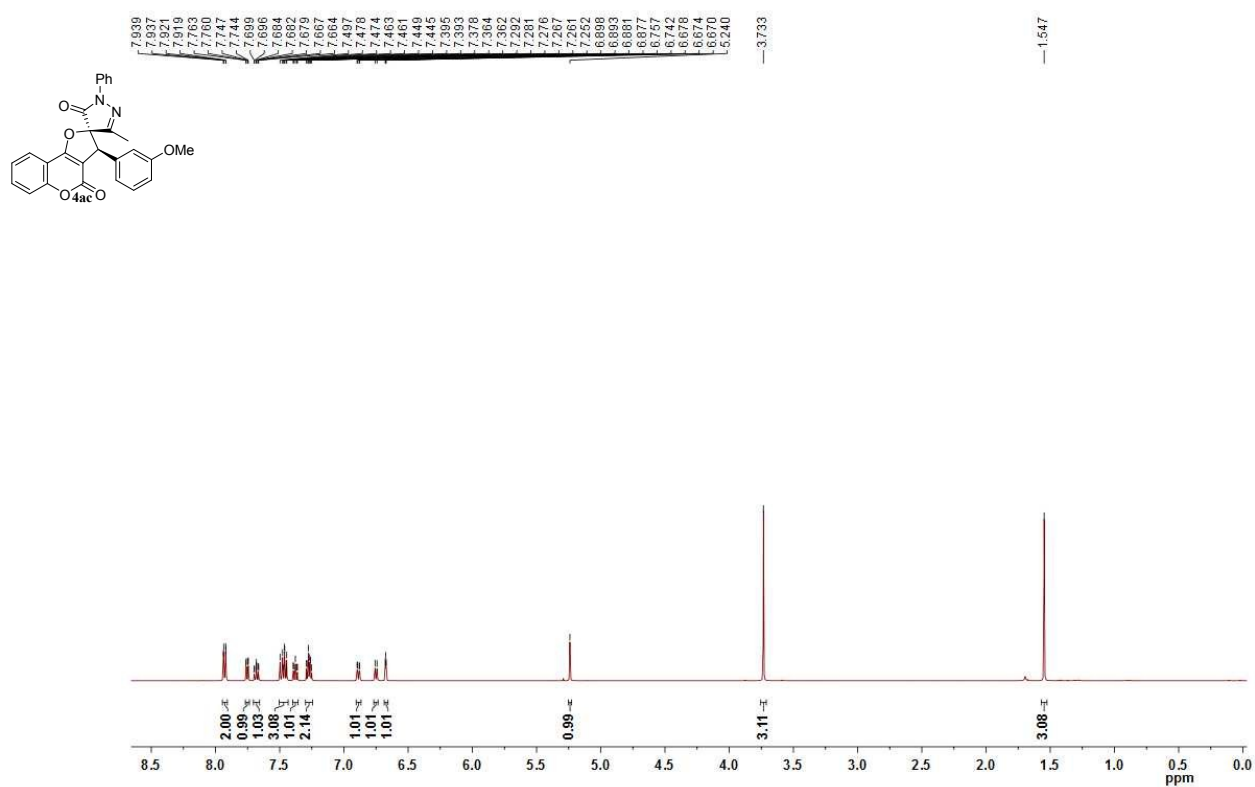
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	53.178	56.454	62.661	41.767
2	99.662	102.798	107.471	8.325
3	112.678	117.171	124.578	8.12
4	138.546	145.654	159.213	41.788

### HPLC chromatogram of 4ab (chiral)

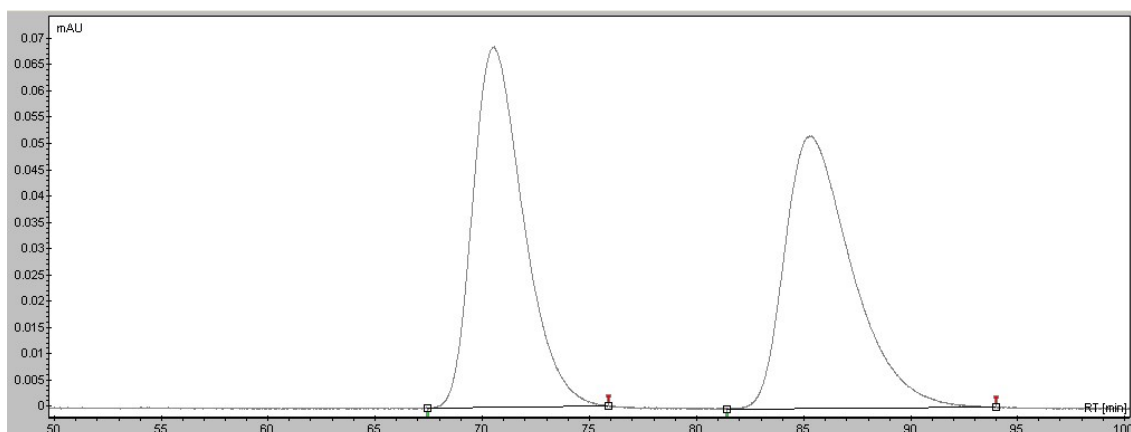


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	100.294	104.676	115.587	99.157
2	117.686	121.753	126.441	0.843

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ac

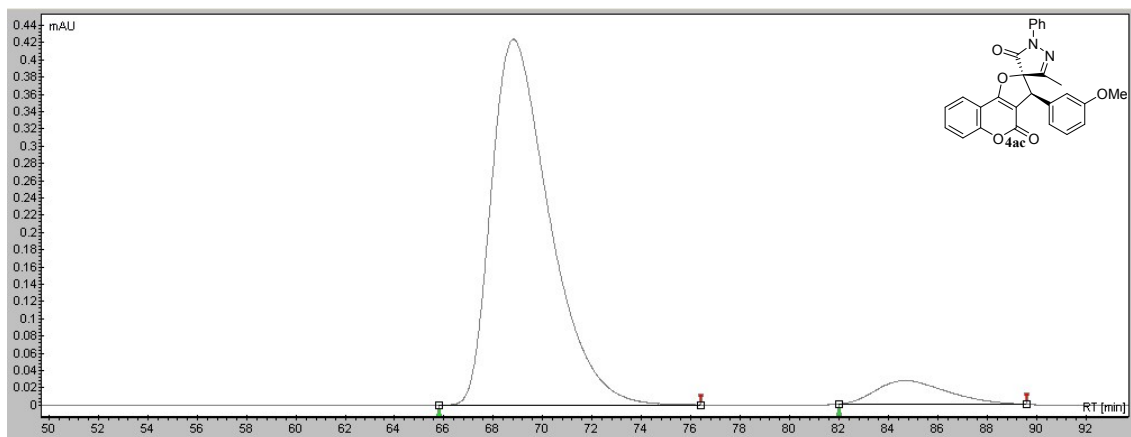


## HPLC chromatogram of 4ac (racemic)



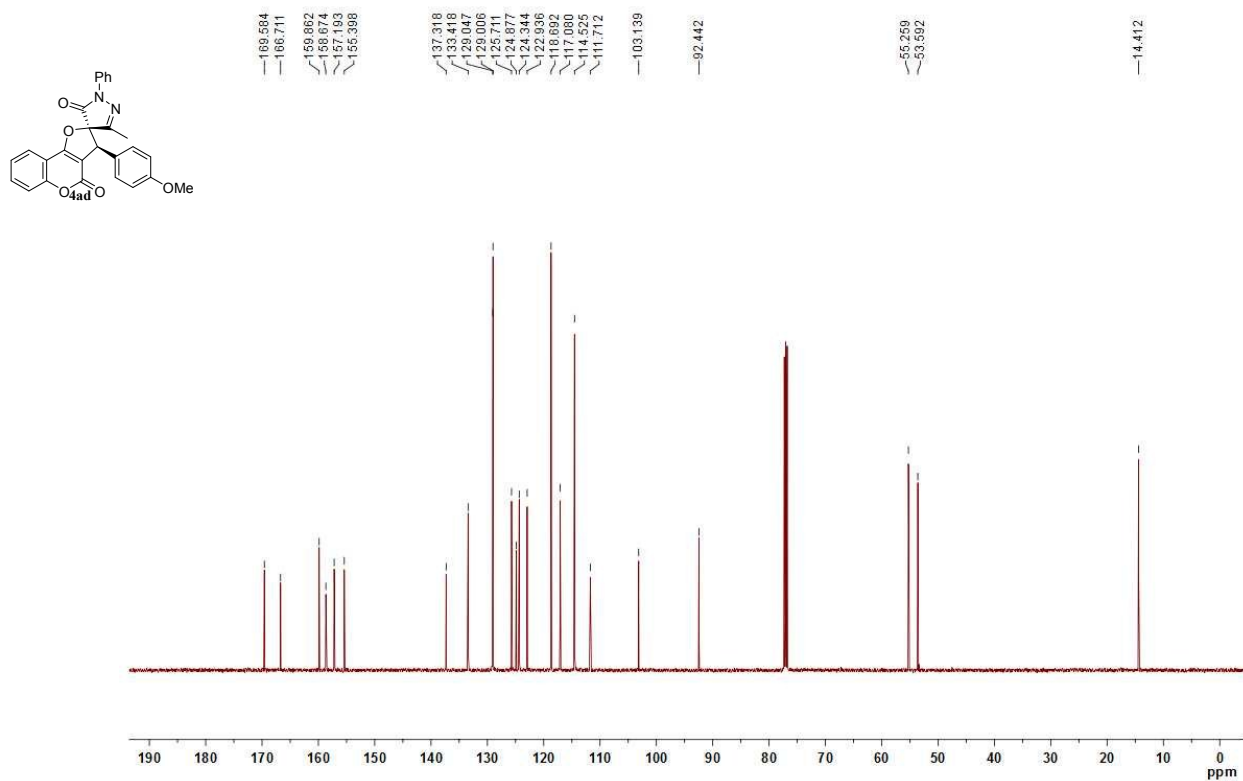
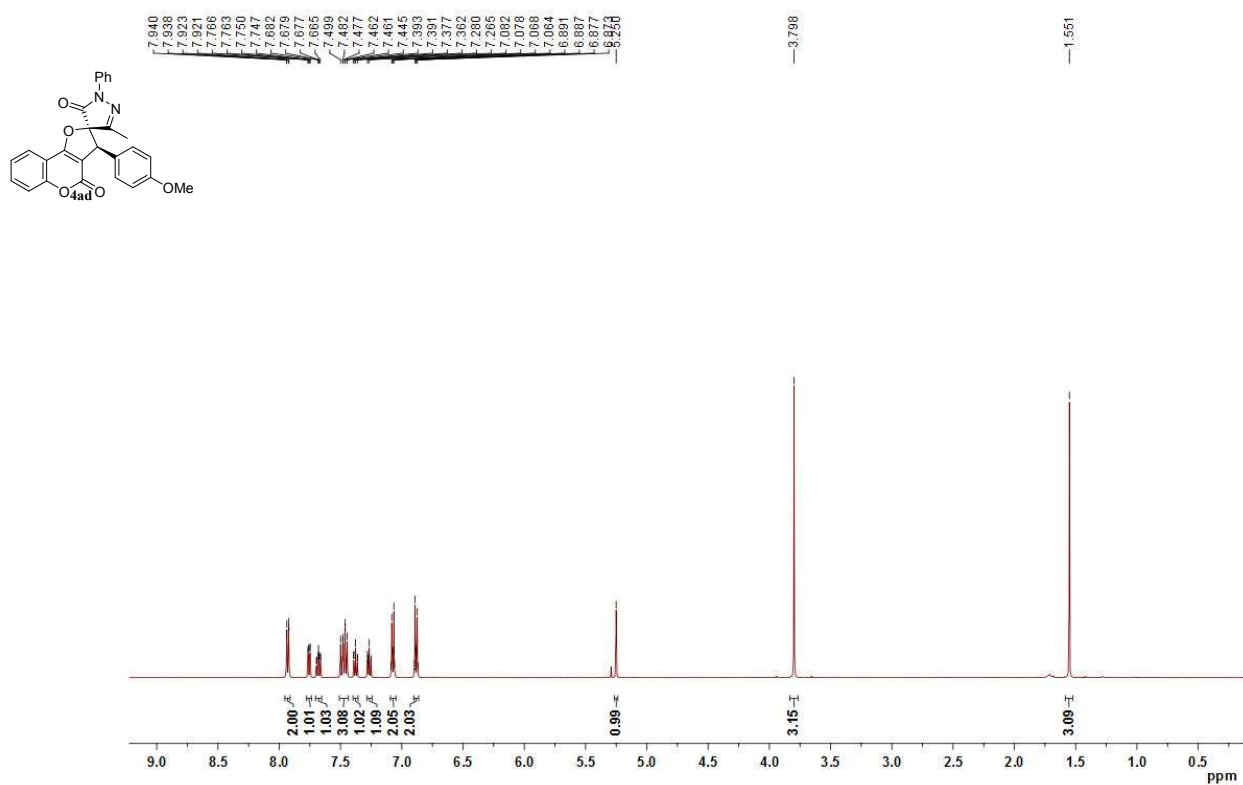
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	67.41	70.521	75.869	49.819
2	81.421	85.276	93.977	50.181

## HPLC chromatogram of 4ac (chiral)

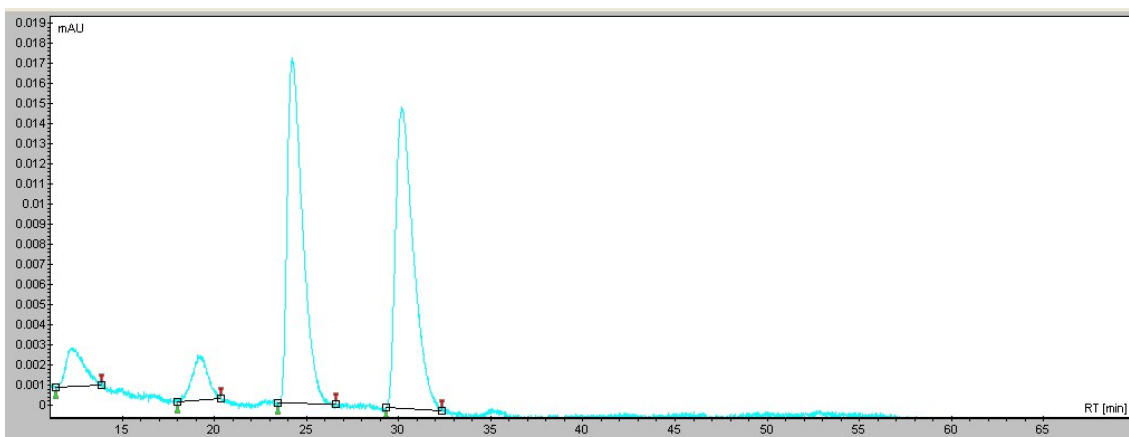


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	65.805	68.842	76.369	92.707
2	81.981	84.716	89.574	7.293

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ad

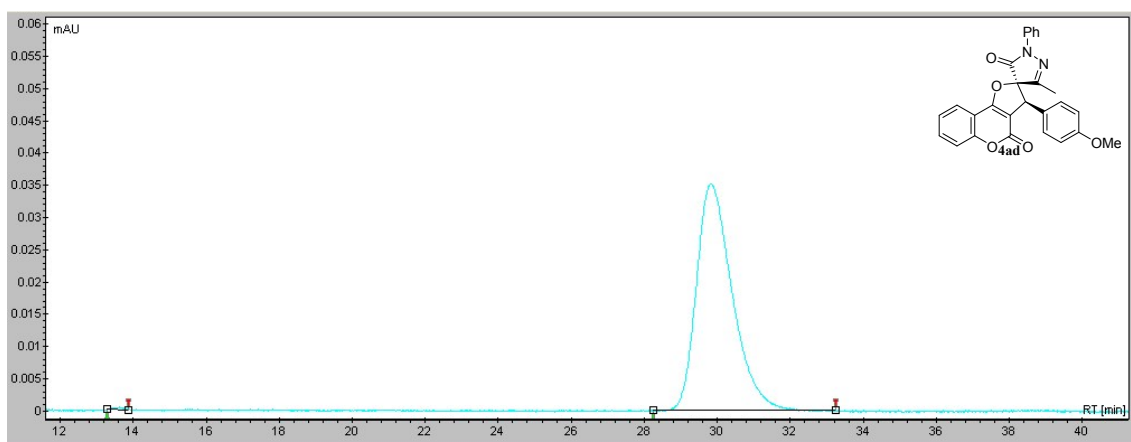


### HPLC chromatogram of 4ad (racemic)



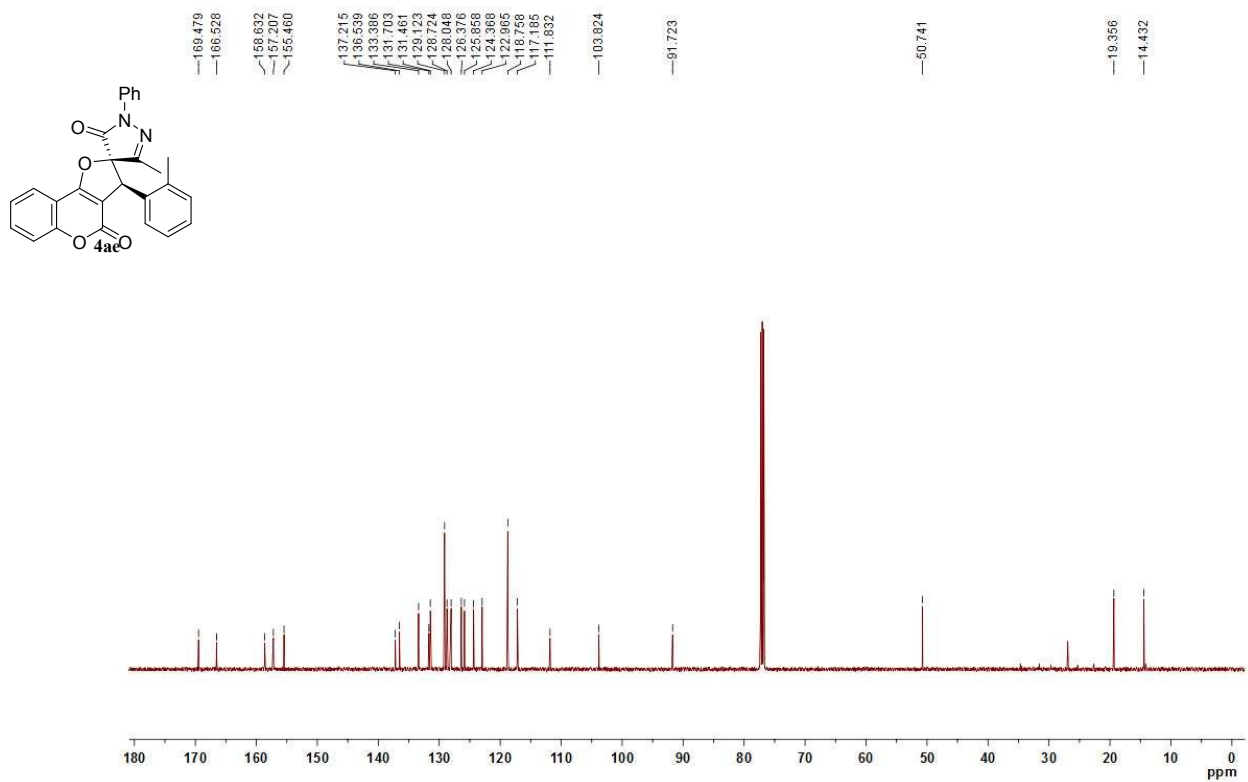
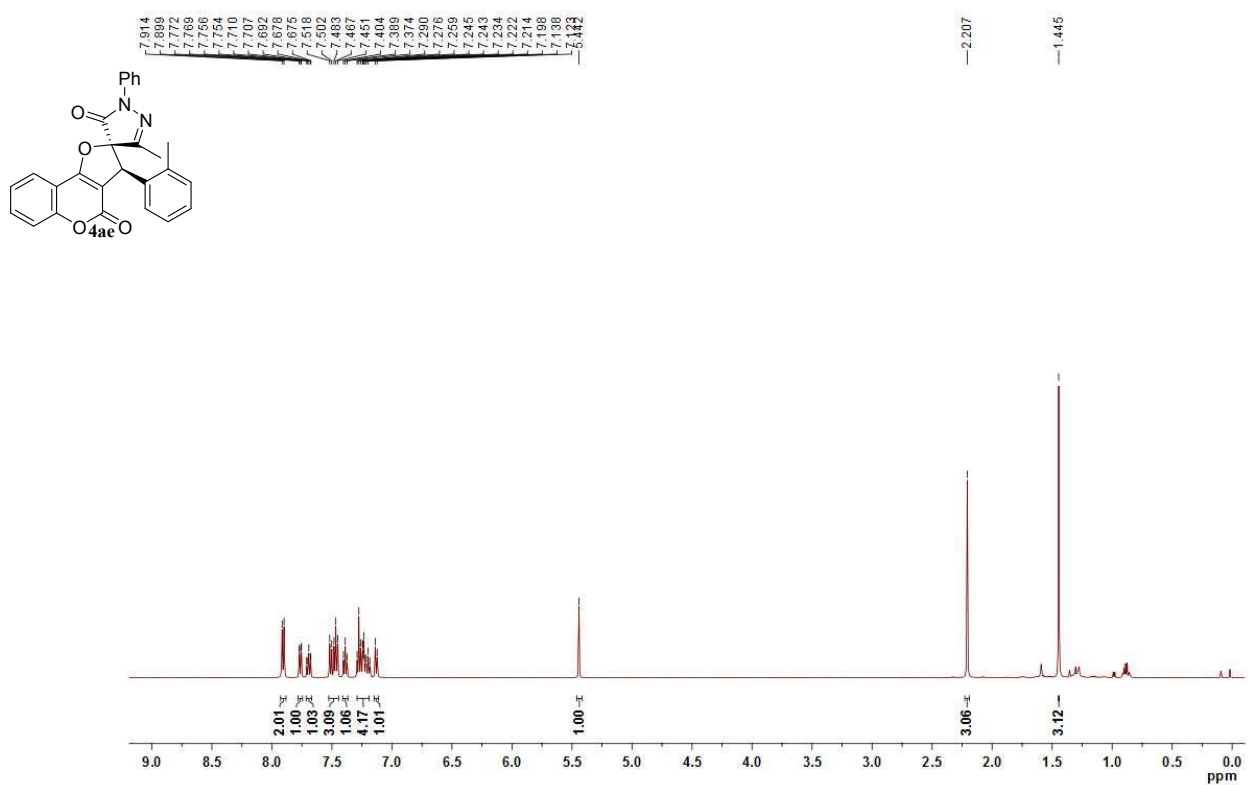
#	Start time[min]	Time[min]	End time[min]	Area%
1	11.386	12.239	13.869	5.817
2	17.988	19.199	20.35	5.832
3	23.439	24.225	26.588	43.578
4	29.313	30.184	32.342	44.773

### HPLC chromatogram of 4ad (chiral)

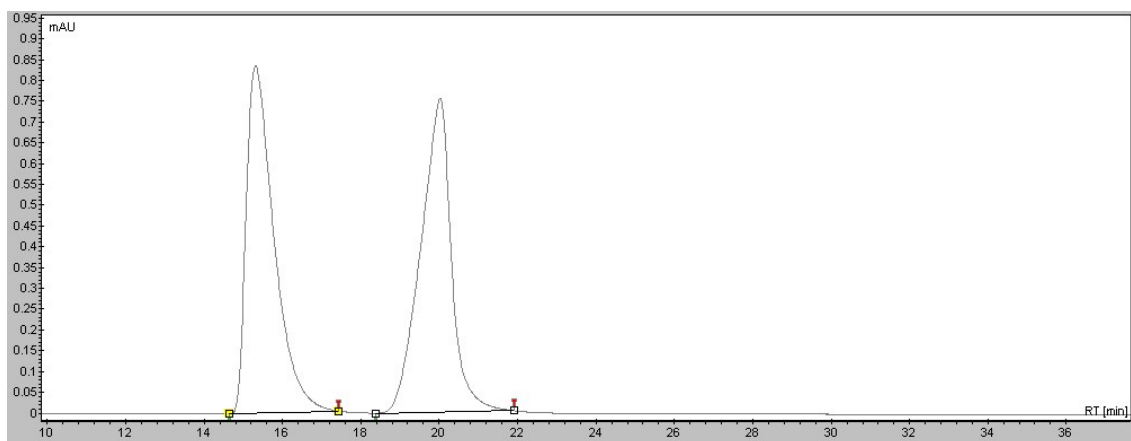


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	13.286	13.608	13.868	0.242
2	28.234	29.829	33.236	99.758

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ae

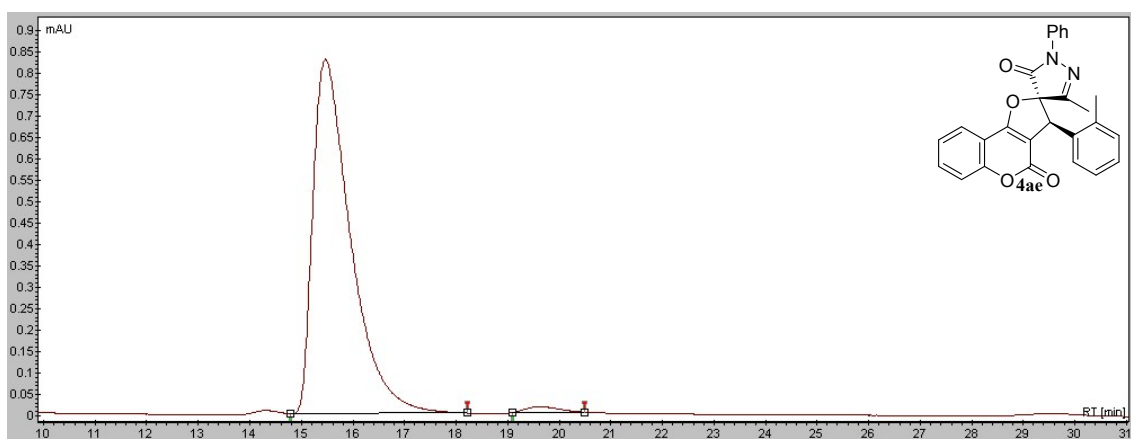


## HPLC chromatogram of 4ae (racemic)



#	Start time[min]	Time[min]	End time[min]	Area%
1	14.651	15.306	17.432	50.136
2	18.372	20.025	21.898	49.864

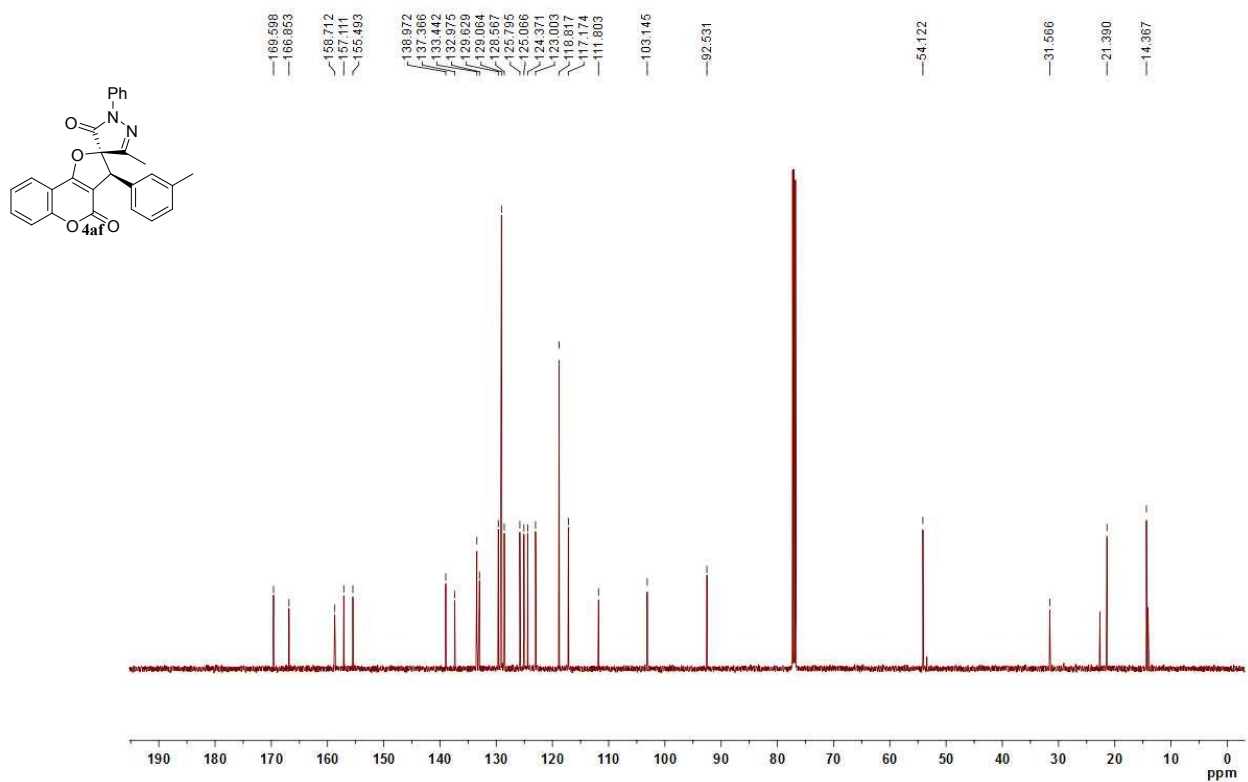
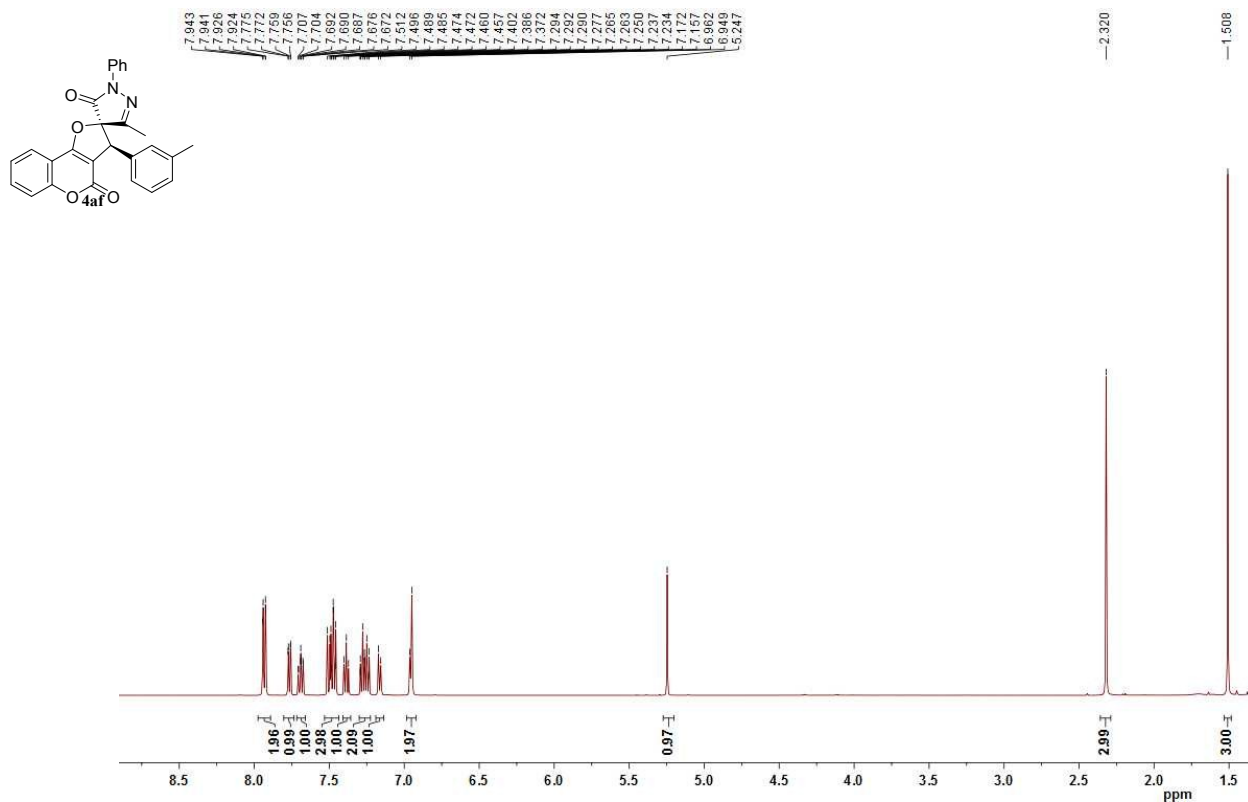
## HPLC chromatogram of 4ae (chiral)



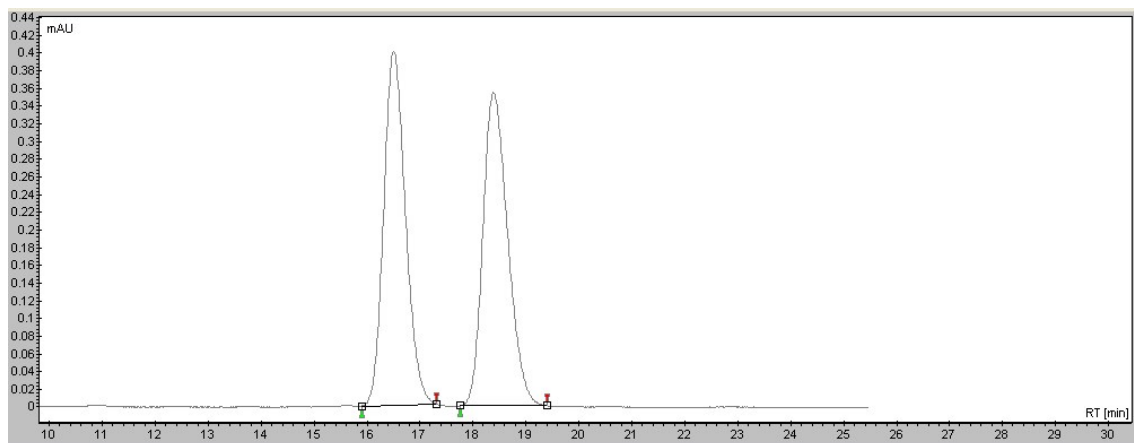
#	Start time[min]	Time[min]	End time[min]	Area%
1	14.785	15.466	18.224	98.663
2	19.097	19.625	20.483	1.337



# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4af

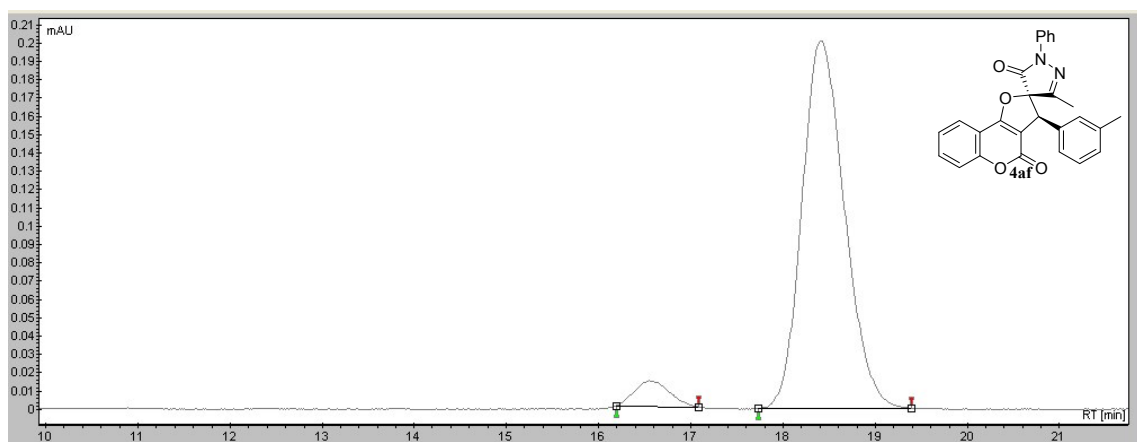


## HPLC chromatogram of 4af (racemic)



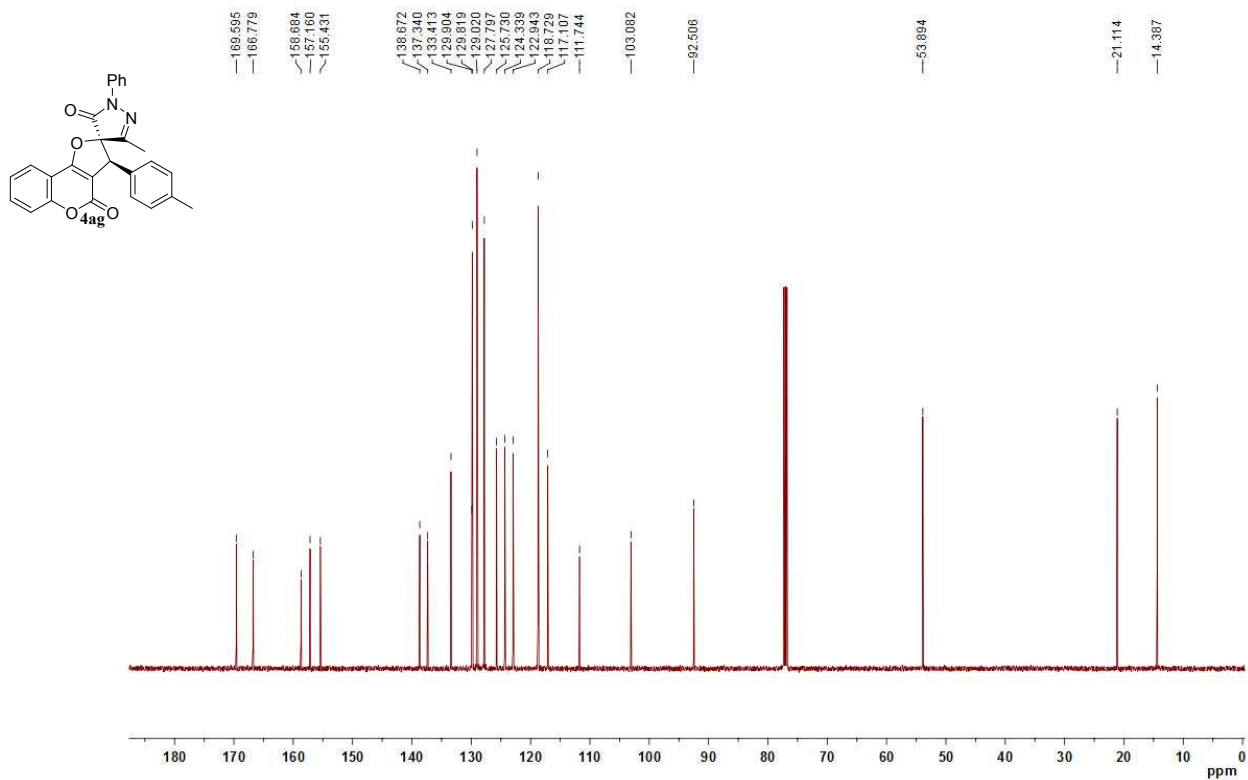
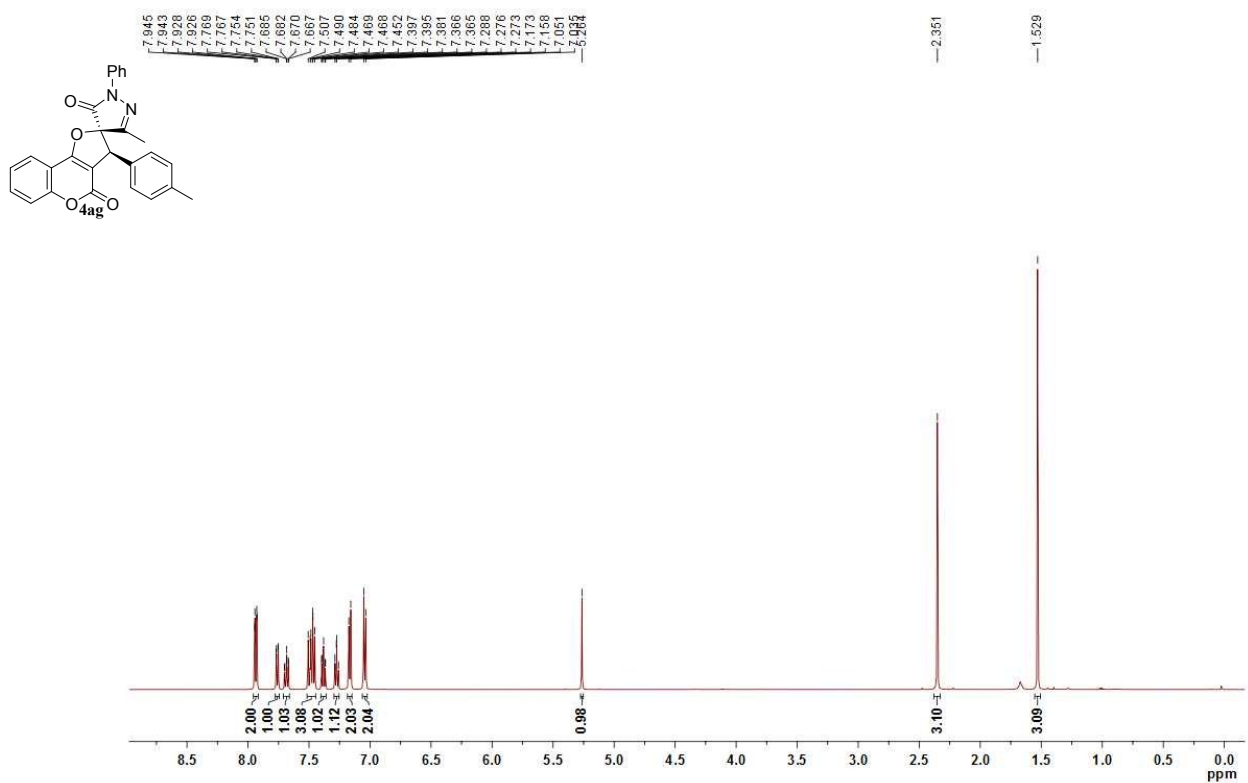
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	15.899	16.505	17.32	49.85
2	17.768	18.385	19.4	50.15

## HPLC chromatogram of 4af (chiral)

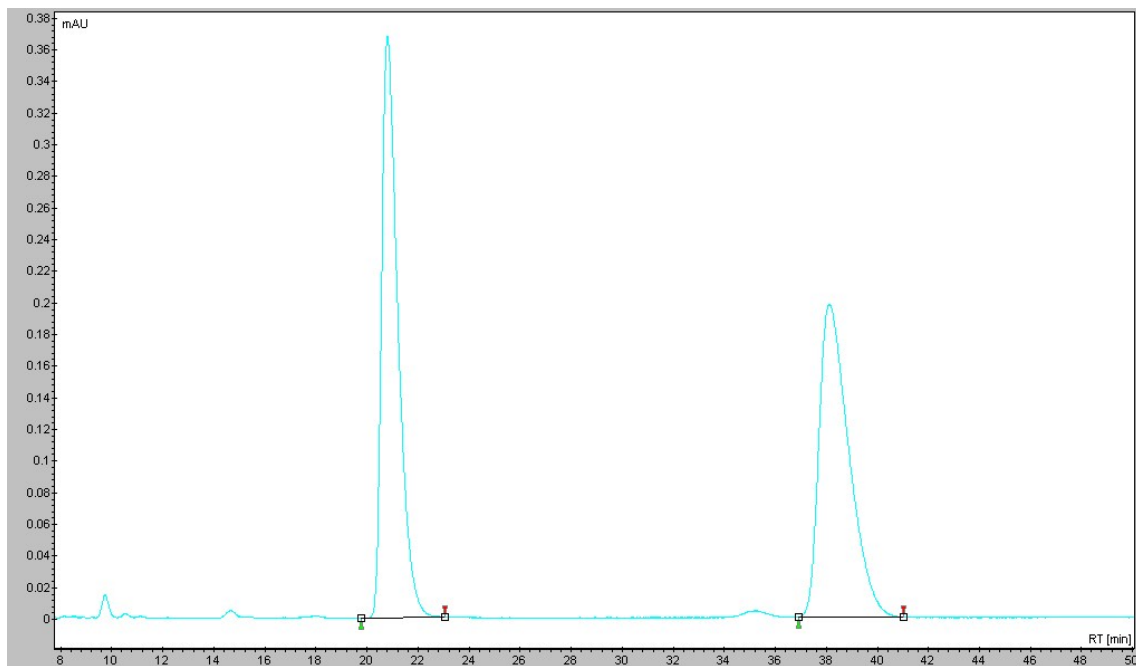


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	16.194	16.572	17.085	5.374
2	17.733	18.412	19.394	94.626

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ag

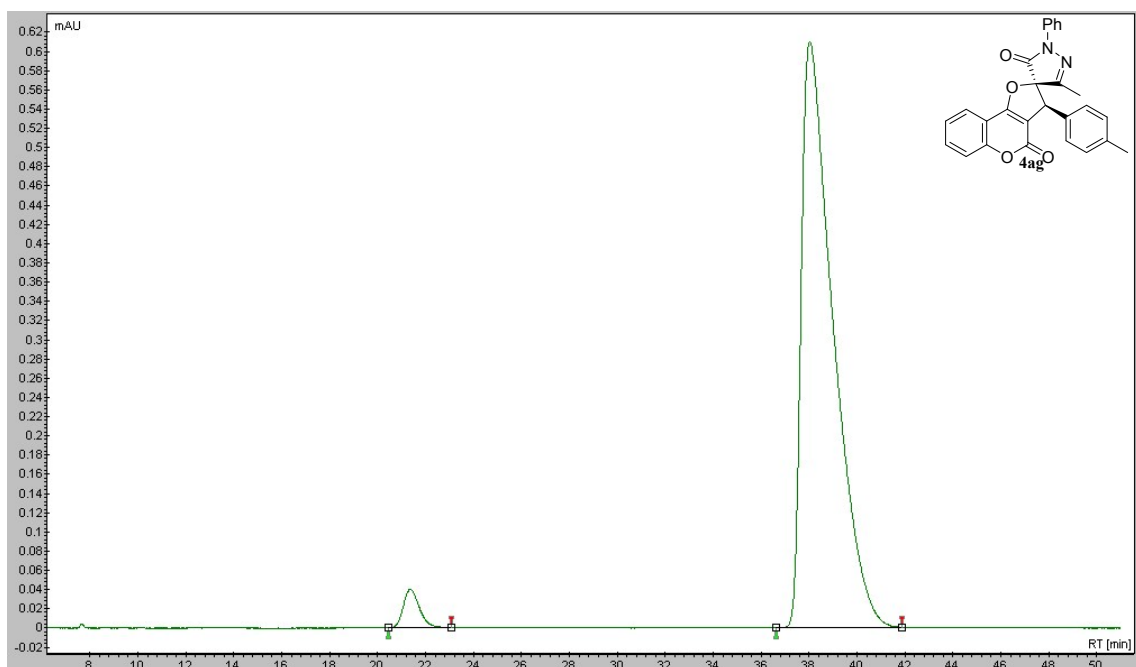


## HPLC chromatogram of 4ag (racemic)



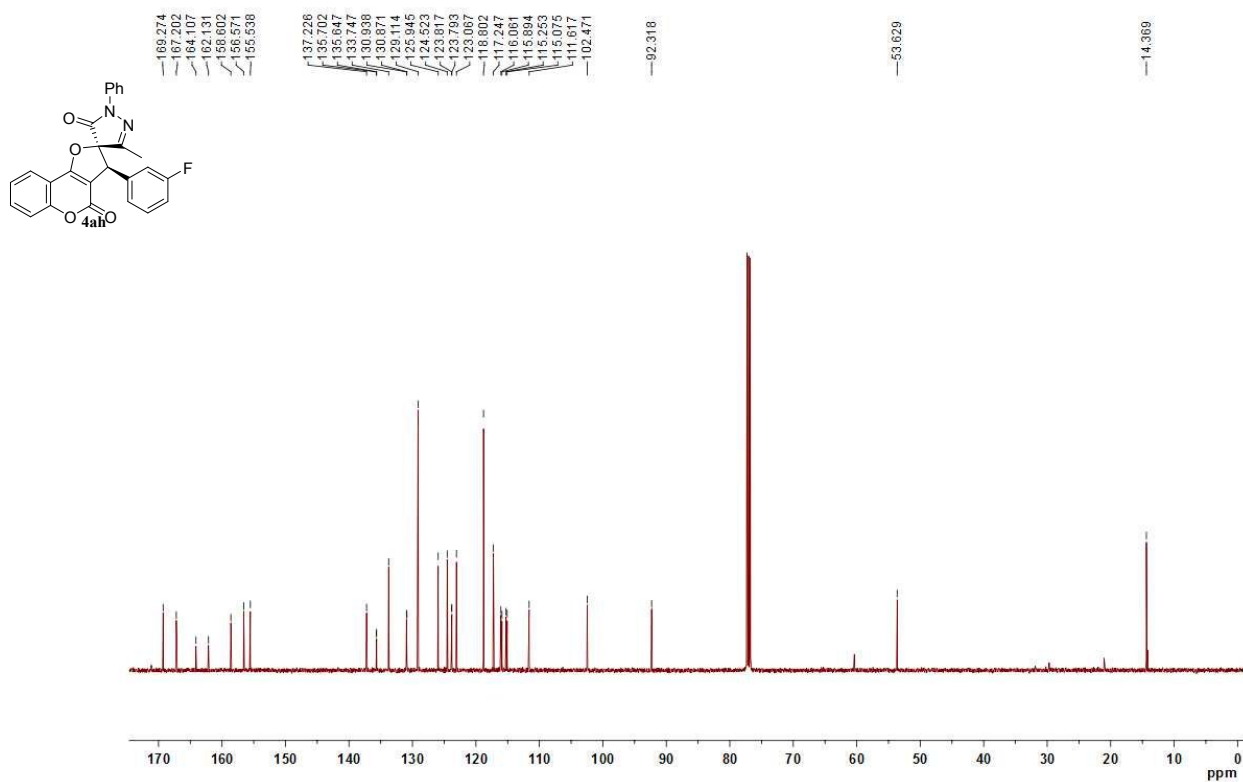
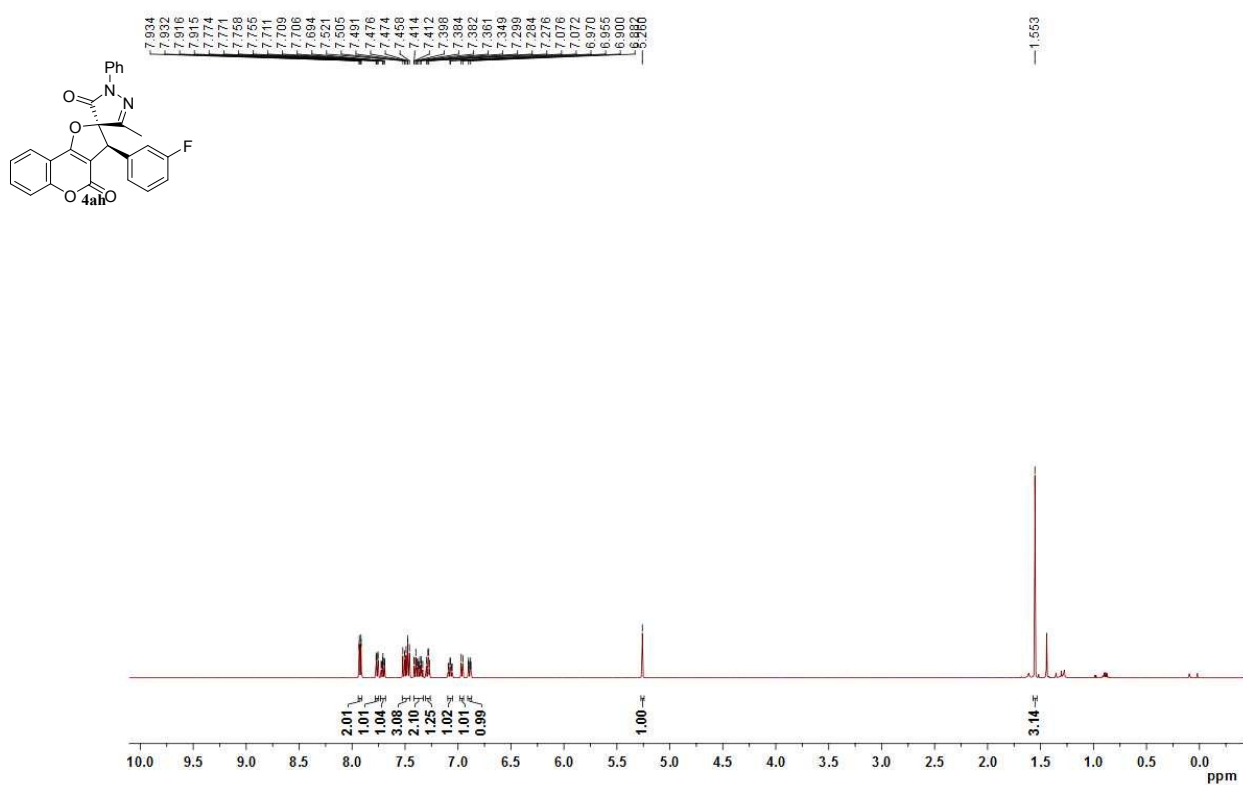
#	Start time[min]	Time[min]	End time[min]	Area%
1	19.797	20.798	23.066	50.594
2	36.918	38.117	41.020	49.406

## HPLC chromatogram of 4ag (chiral)

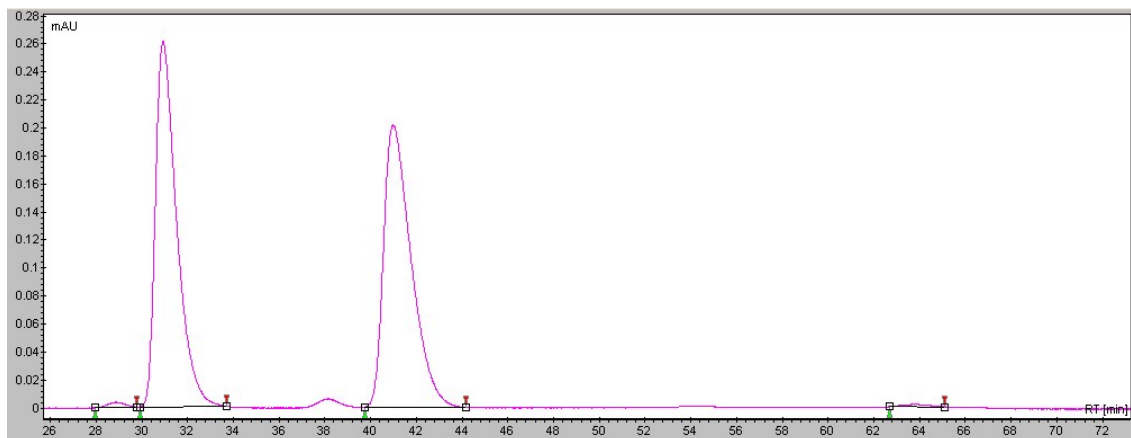


#	Start time[min]	Time[min]	End time[min]	Area%
1	20.447	21.357	23.082	3.183
2	36.626	38.024	41.896	96.817

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ah

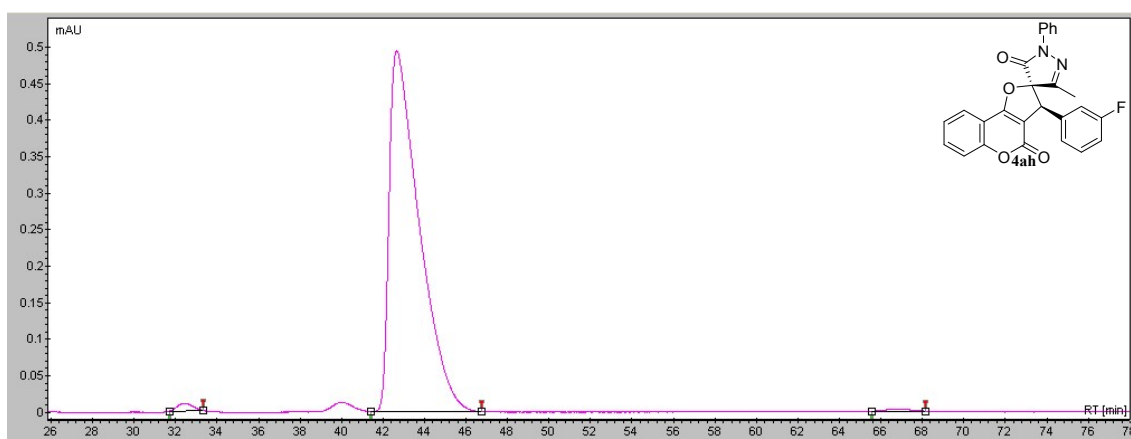


### HPLC chromatogram of 4ah (racemic)



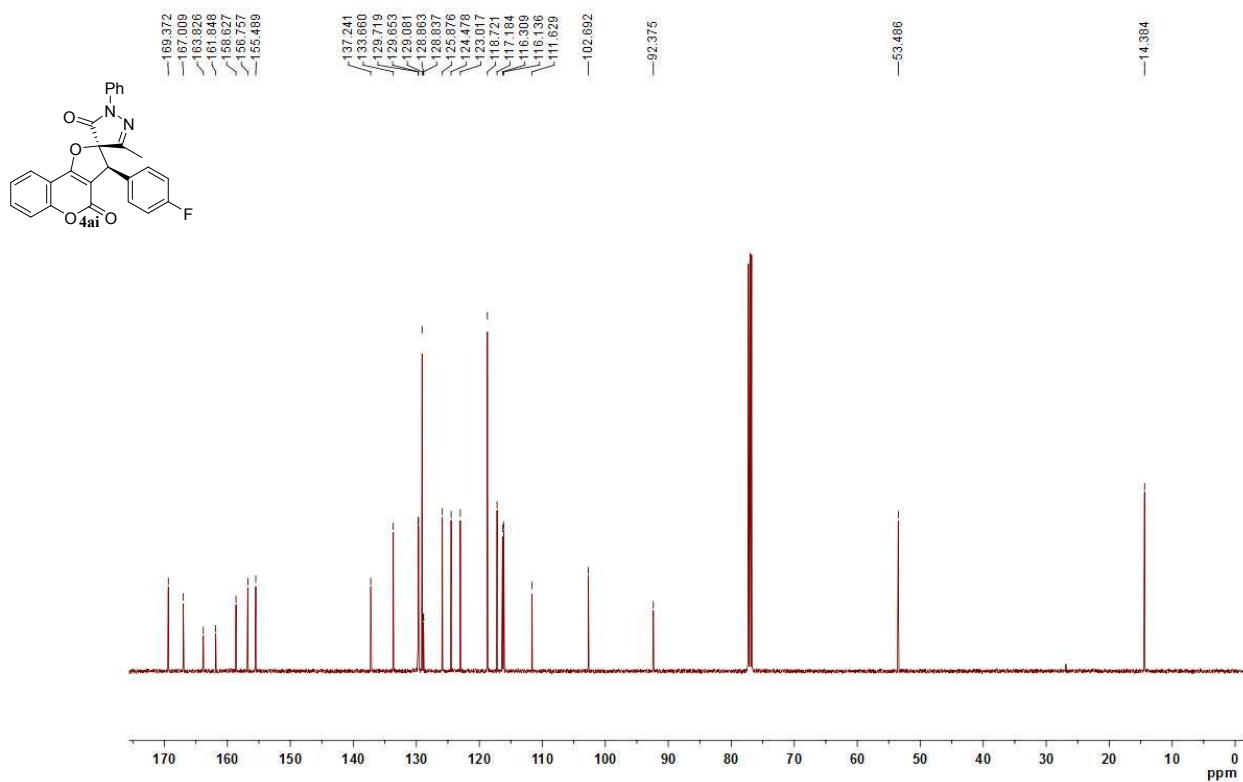
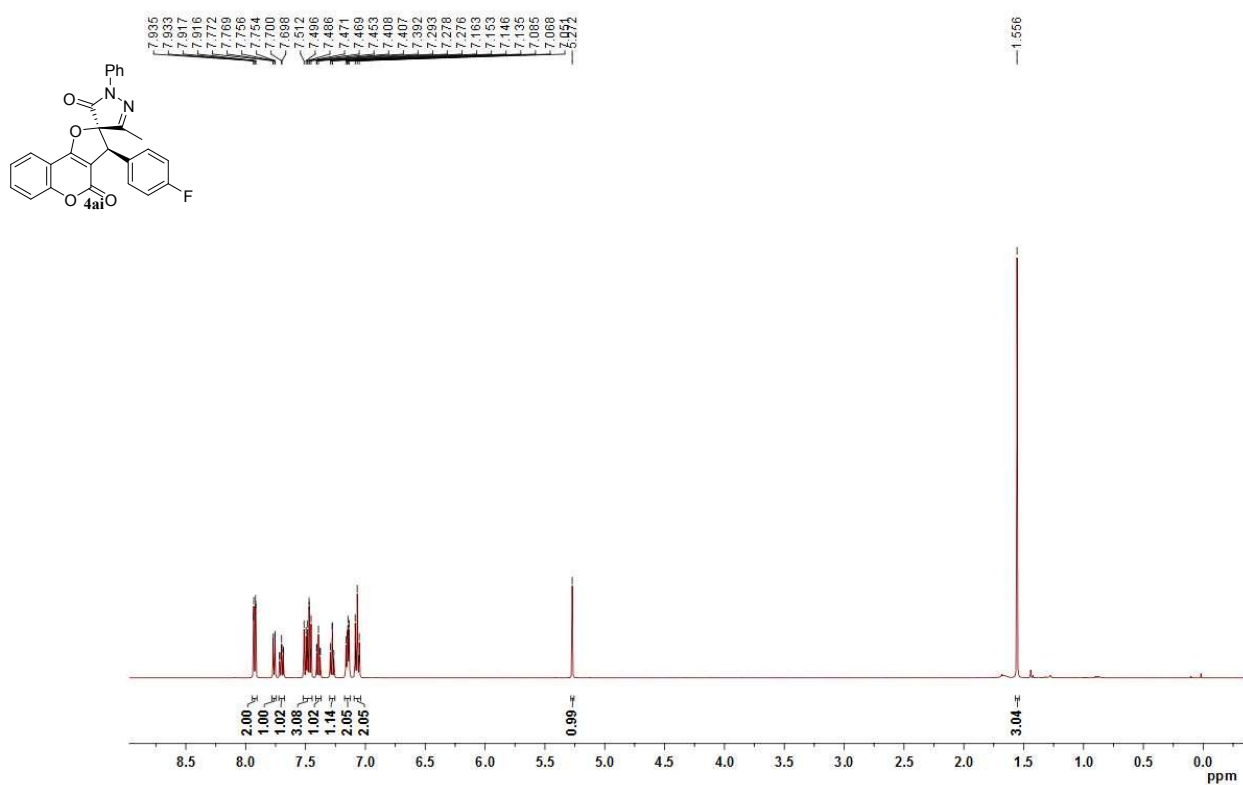
#	Start time[min]	Time[min]	End time[min]	Area%
1	27.937	28.856	29.781	0.542
2	29.918	30.922	33.687	49.46
3	39.74	40.985	44.169	49.578
4	62.67	63.817	65.106	0.42

### HPLC chromatogram of 4ah (chiral)

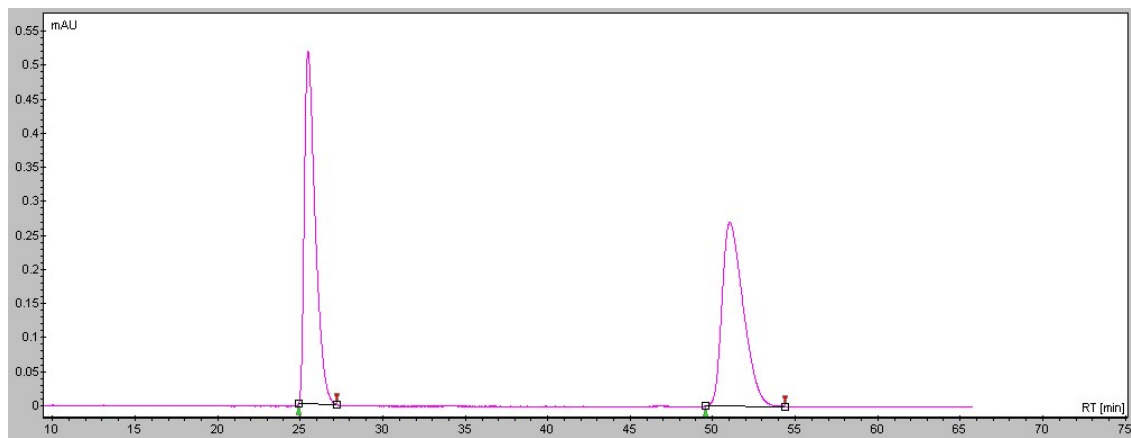


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	31.692	32.415	33.345	1.07
2	41.429	42.678	46.756	98.443
3	65.588	66.829	68.16	0.487

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ai

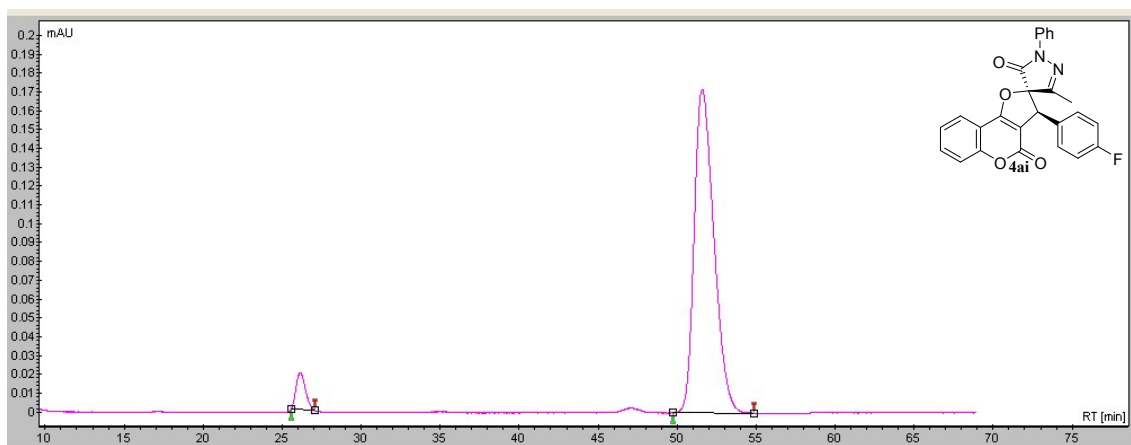


### HPLC chromatogram of 4ai (racemic)



#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	24.917	25.471	27.225	49.635
2	49.562	51.035	54.382	50.365

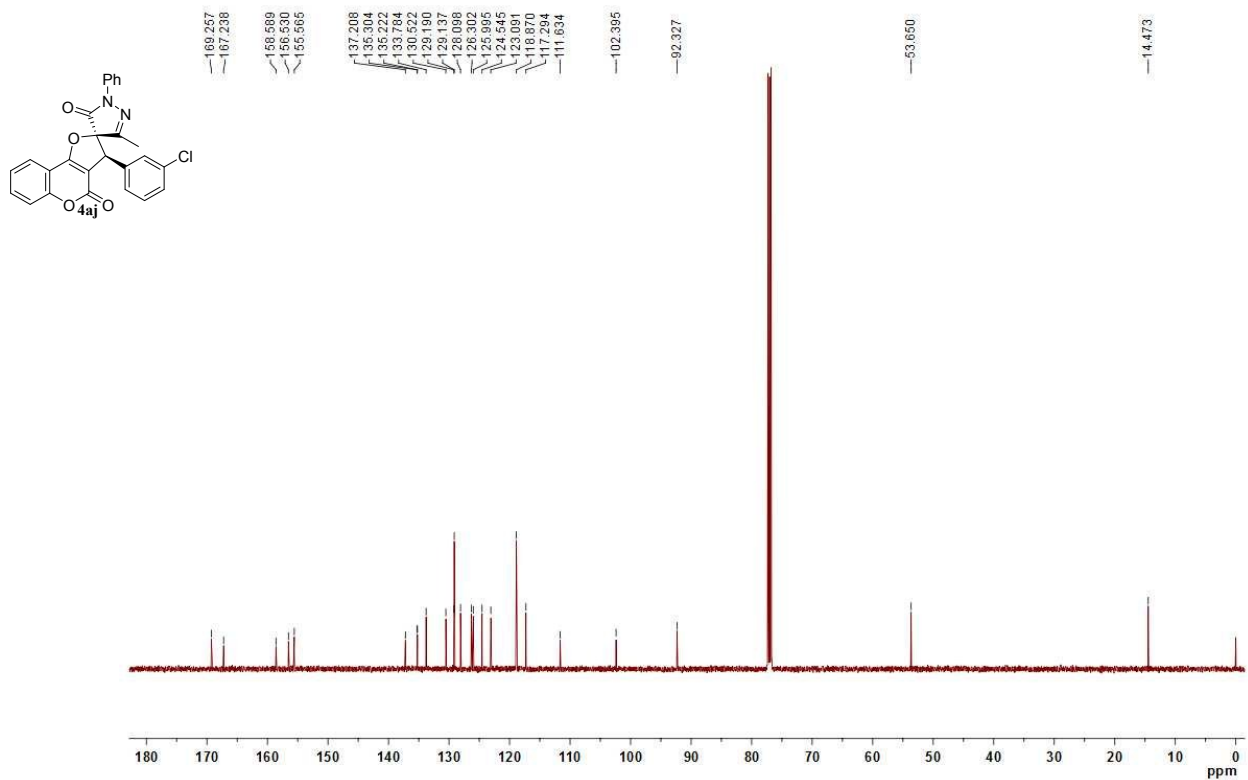
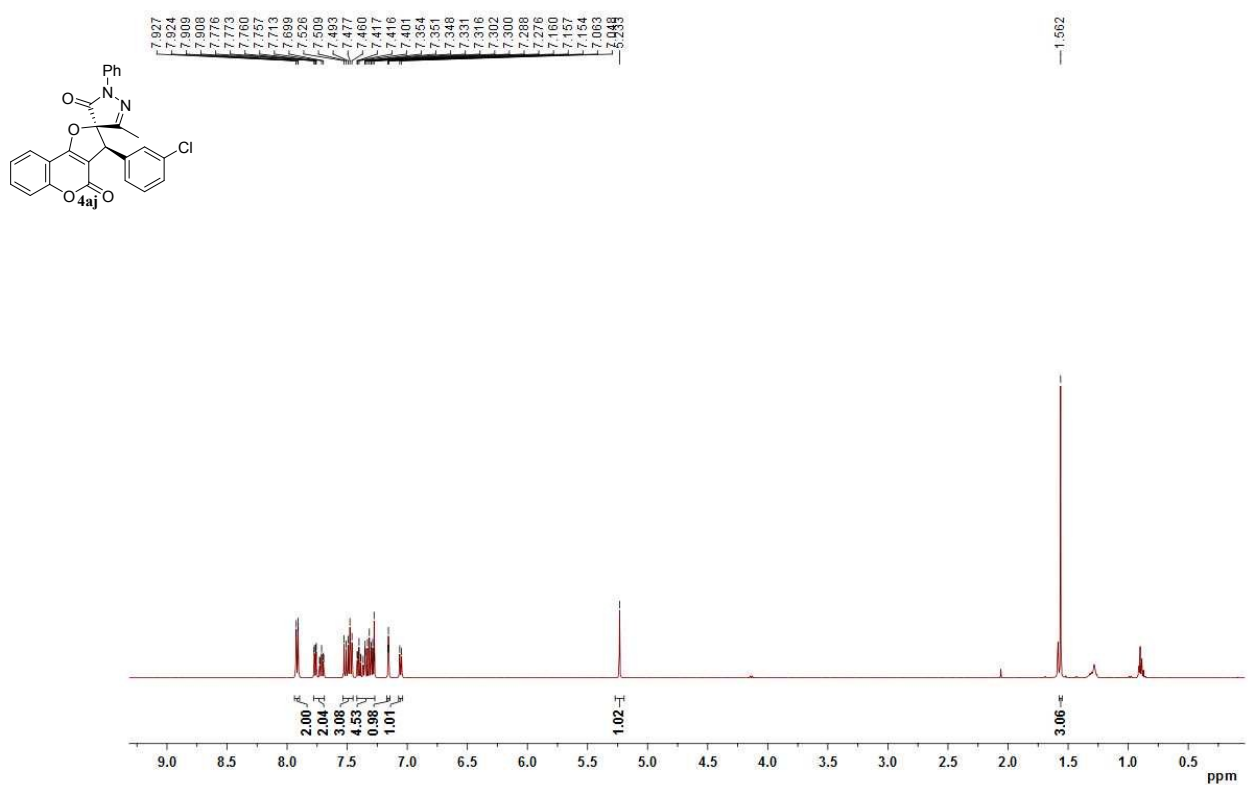
### HPLC chromatogram of 4ai (chiral)



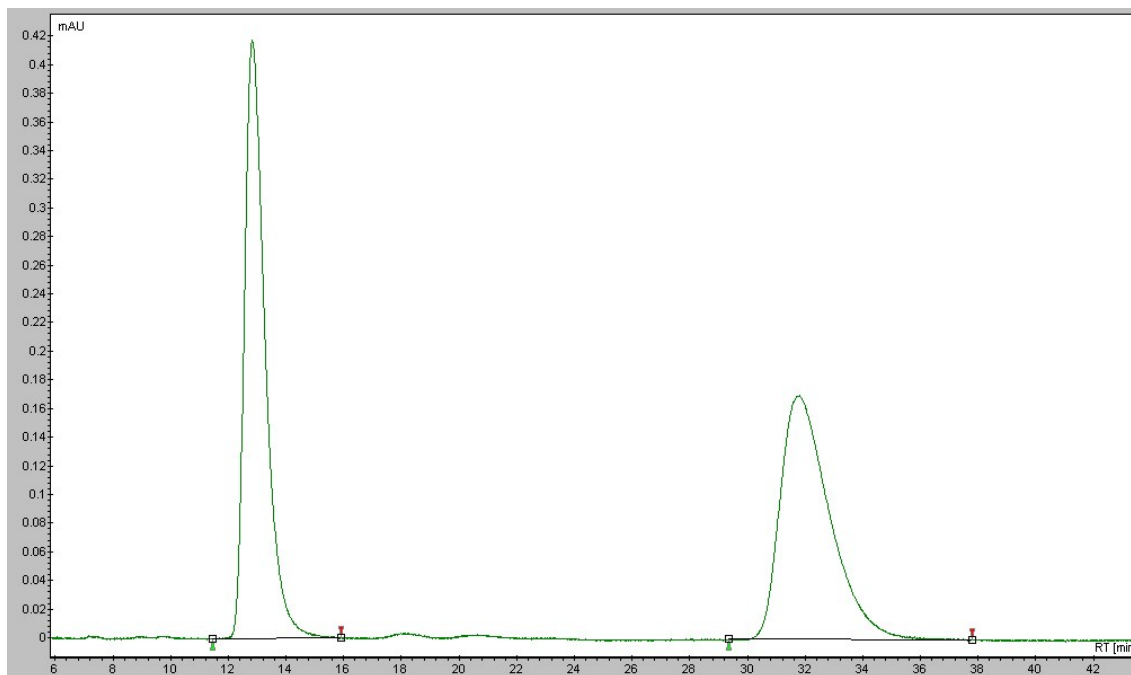
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	25.58	26.137	27.076	5.125
2	49.735	51.581	54.865	94.875



# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4aj

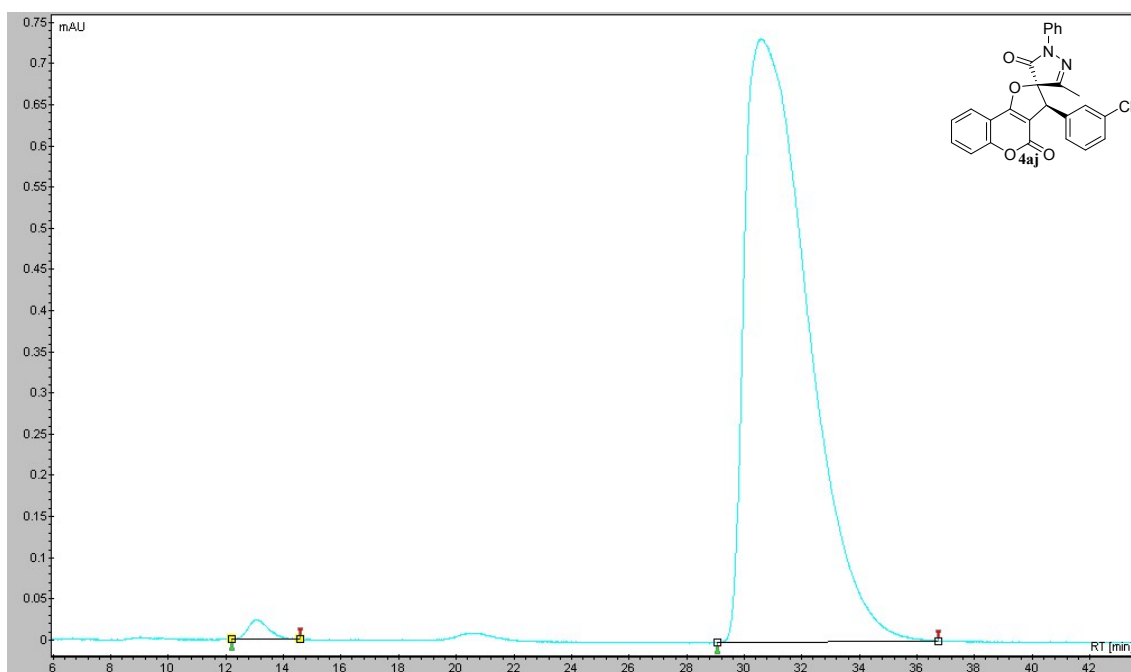


## HPLC chromatogram of 4aj (racemic)



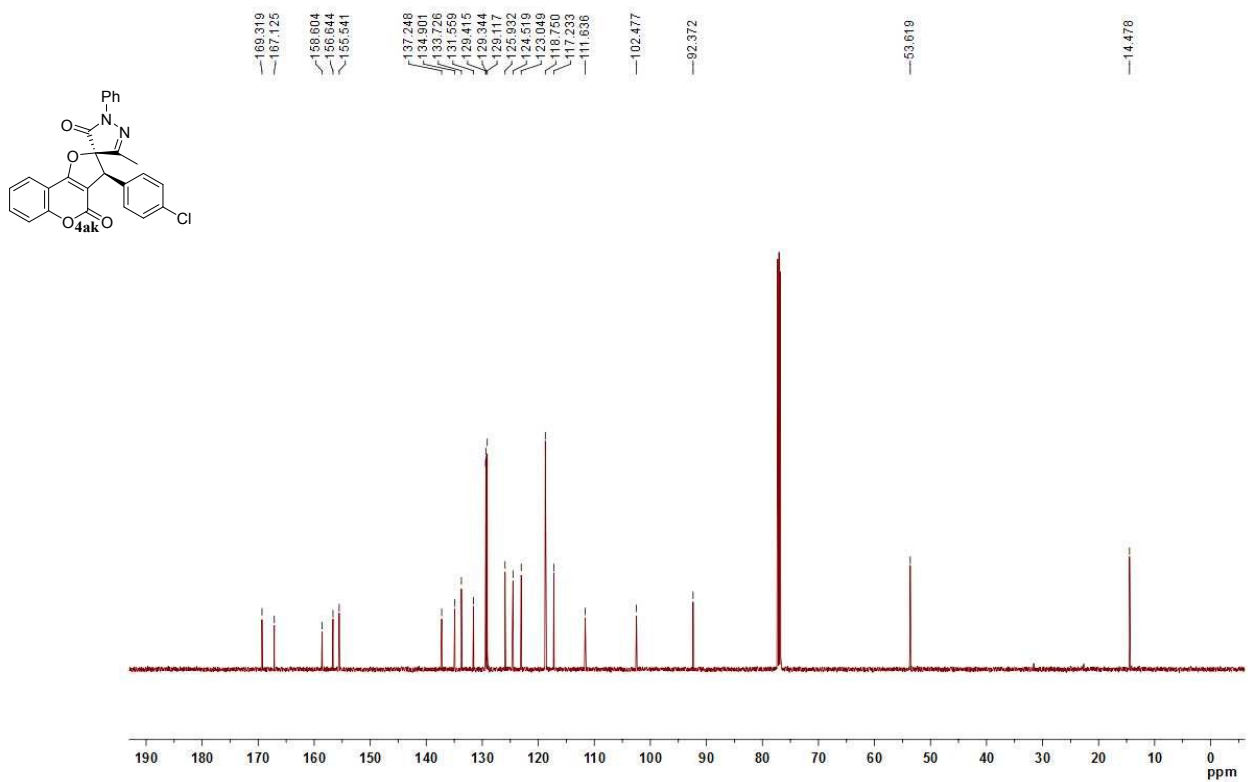
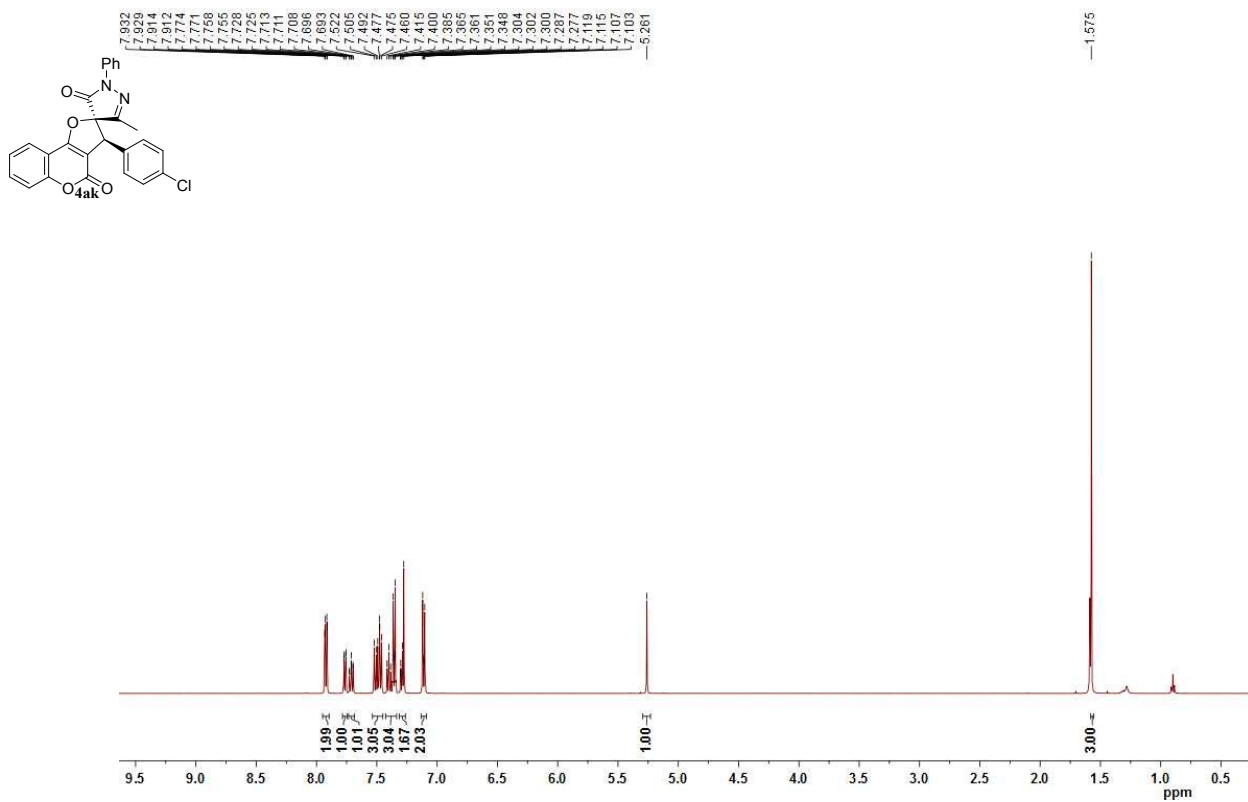
#	Start time[min]	Time[min]	End time[min]	Area%
1	11.462	12.839	15.897	50.536
2	29.353	31.784	37.775	49.464

## HPLC chromatogram of 4aj (chiral)

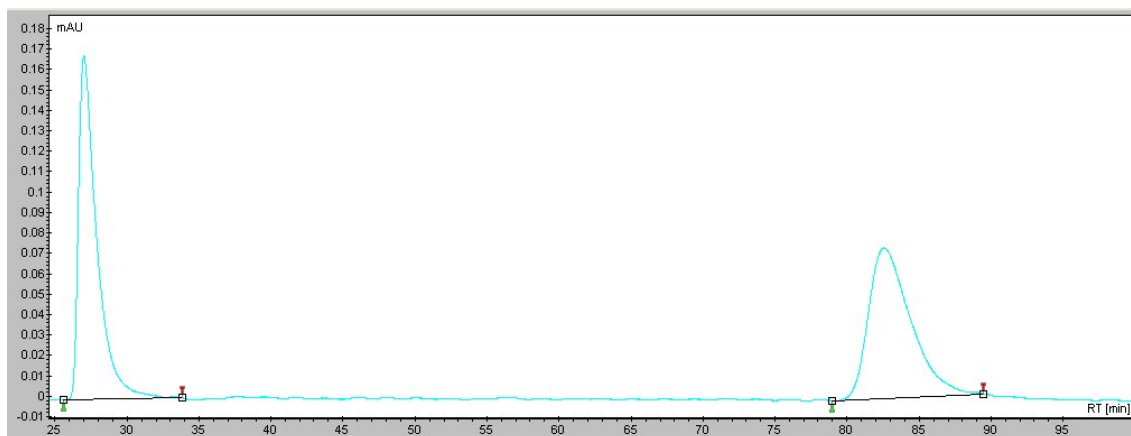


#	Start time[min]	Time[min]	End time[min]	Area%
1	12.207	13.066	14.581	1.072
2	29.049	30.598	36.735	98.928

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ak

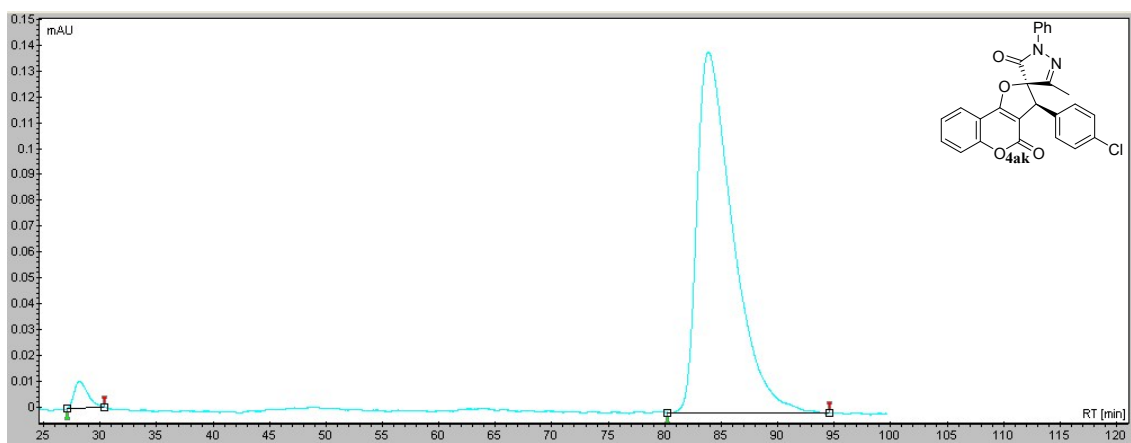


## HPLC chromatogram of 4ak (racemic)



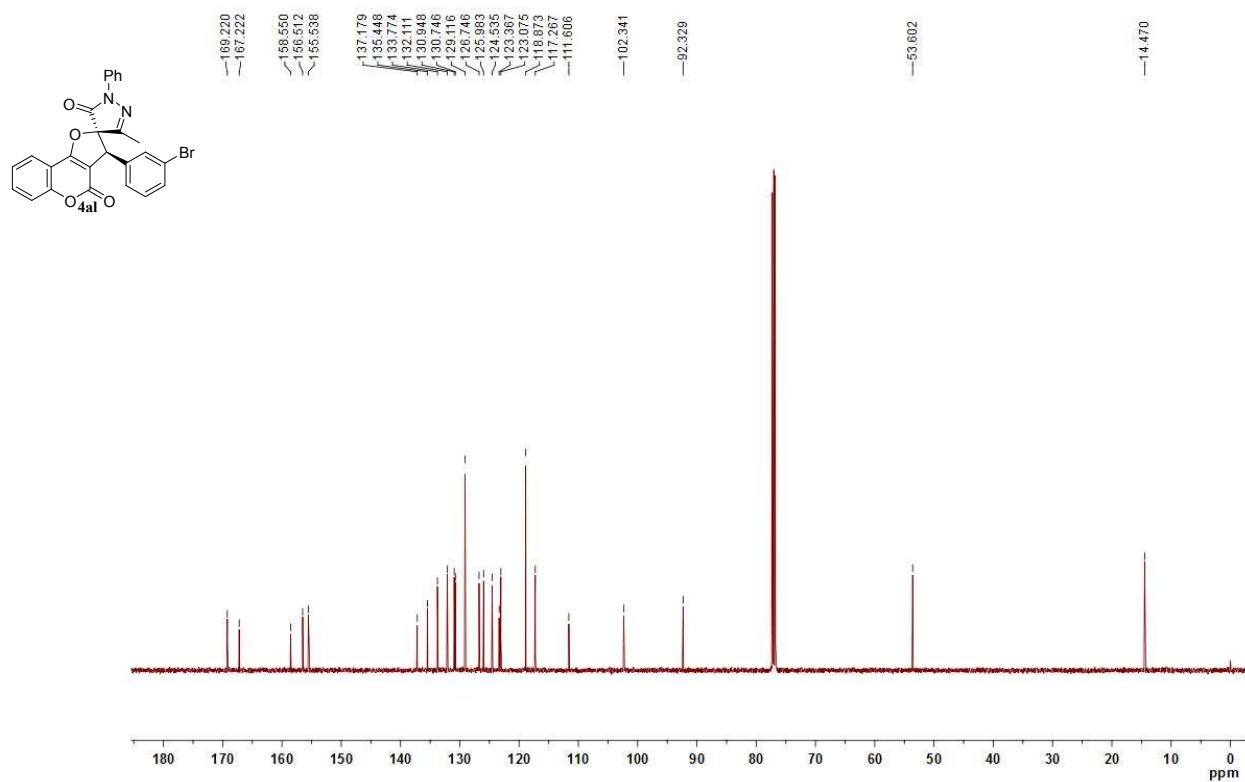
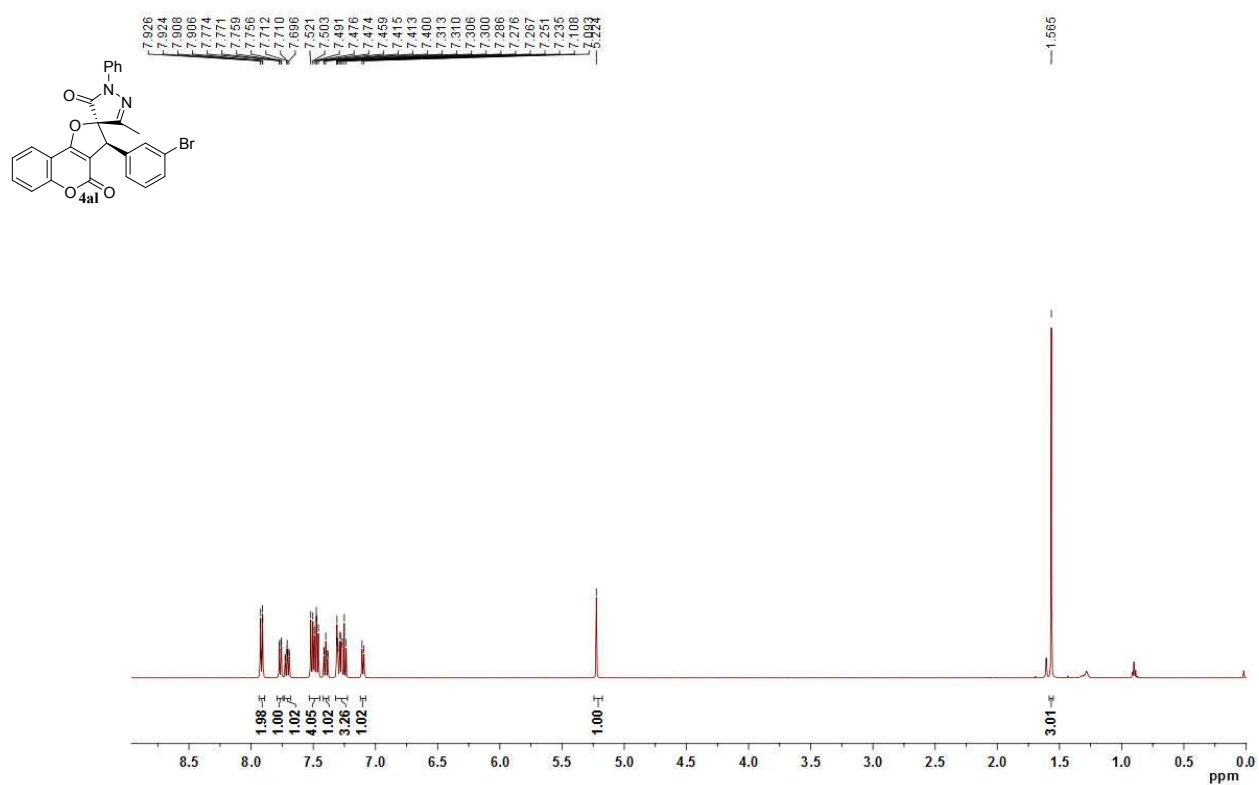
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	25.145	28.821	34.474	49.78
2	79.281	83.533	89.572	51.22

## HPLC chromatogram of 4ak (chiral)

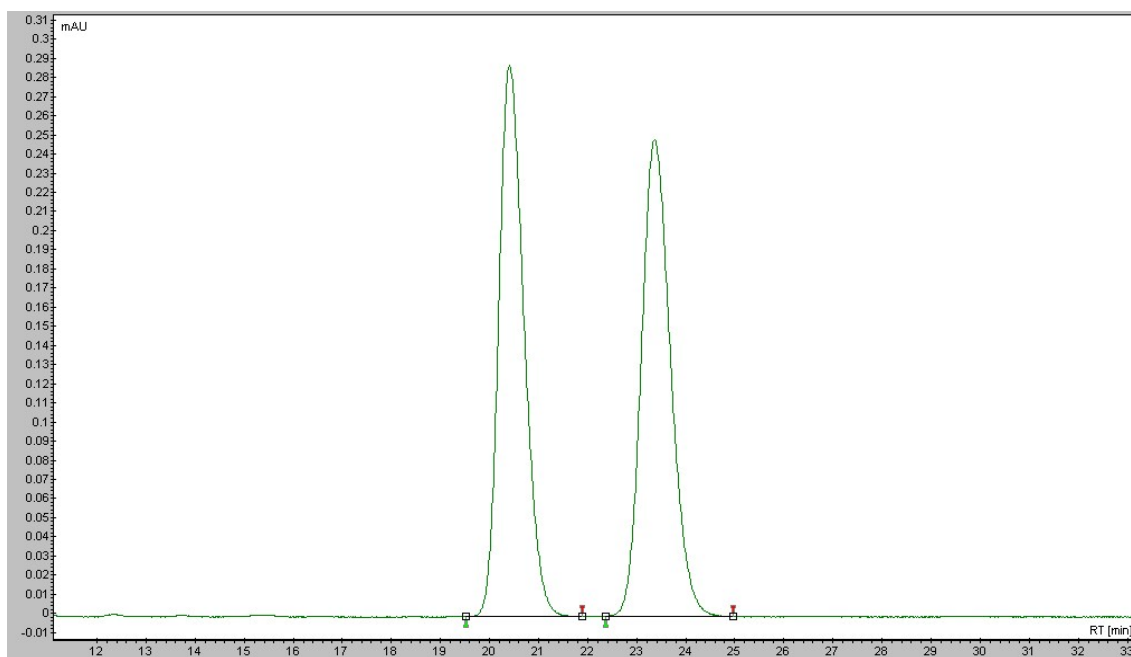


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	27.115	28.177	30.414	2.767
2	80.211	83.863	94.542	97.233

# $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of 4al

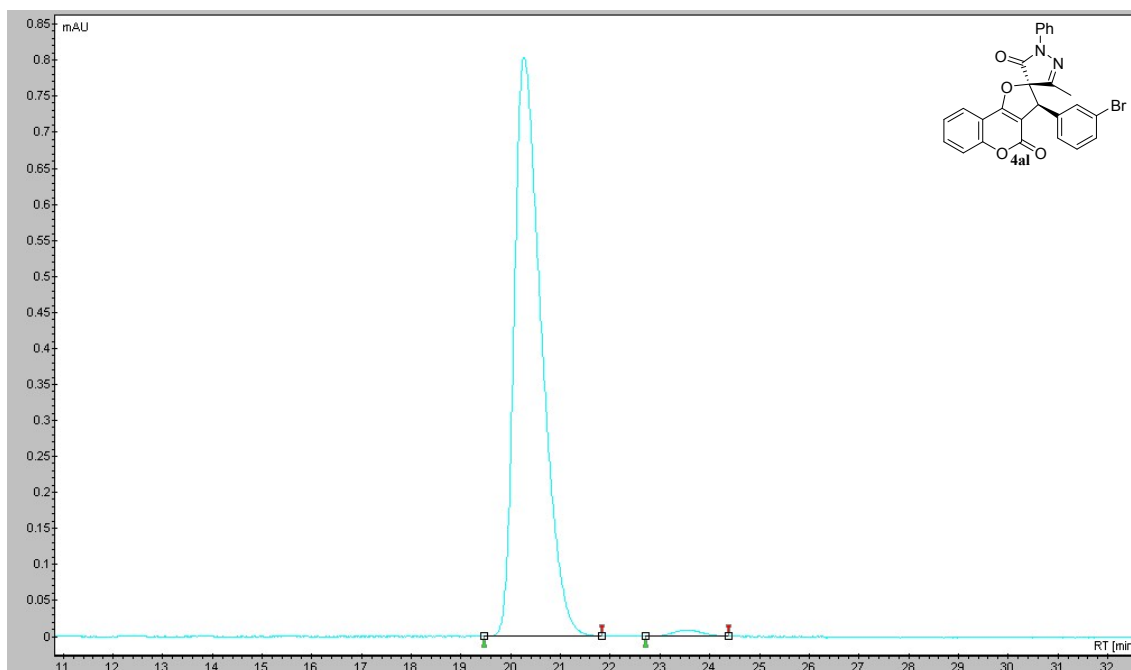


## HPLC chromatogram of 4al (racemic)



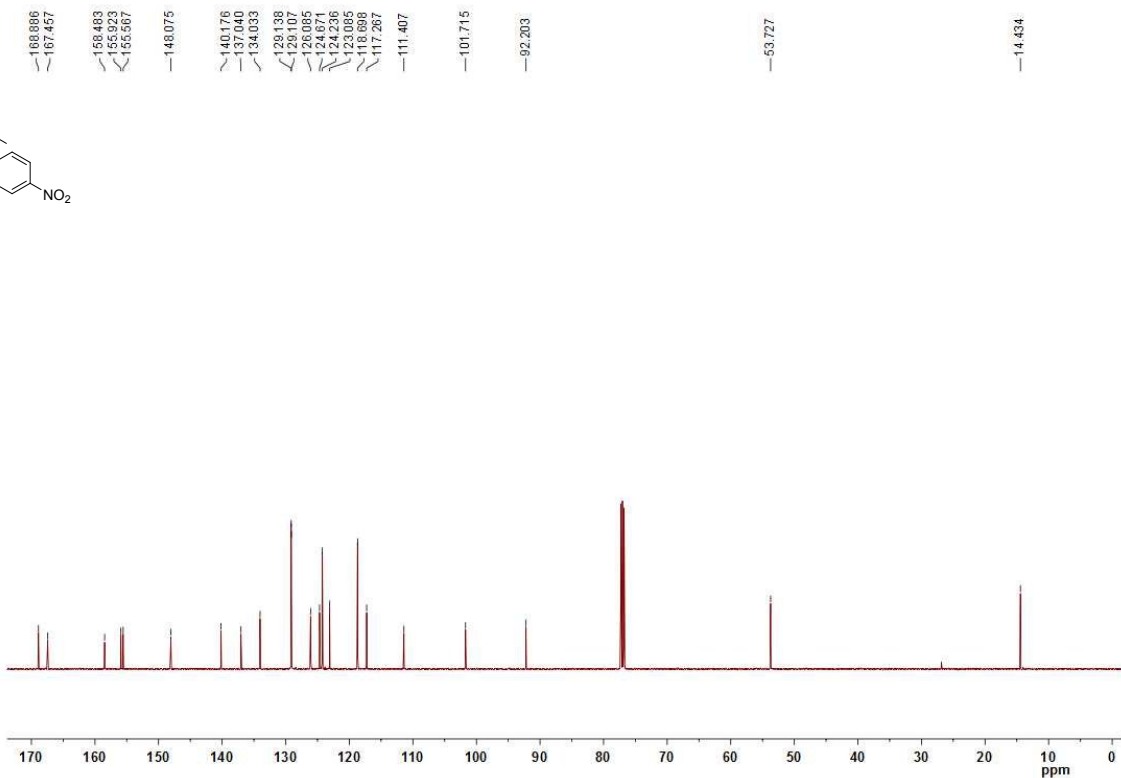
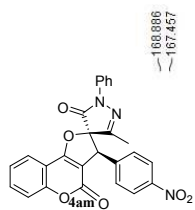
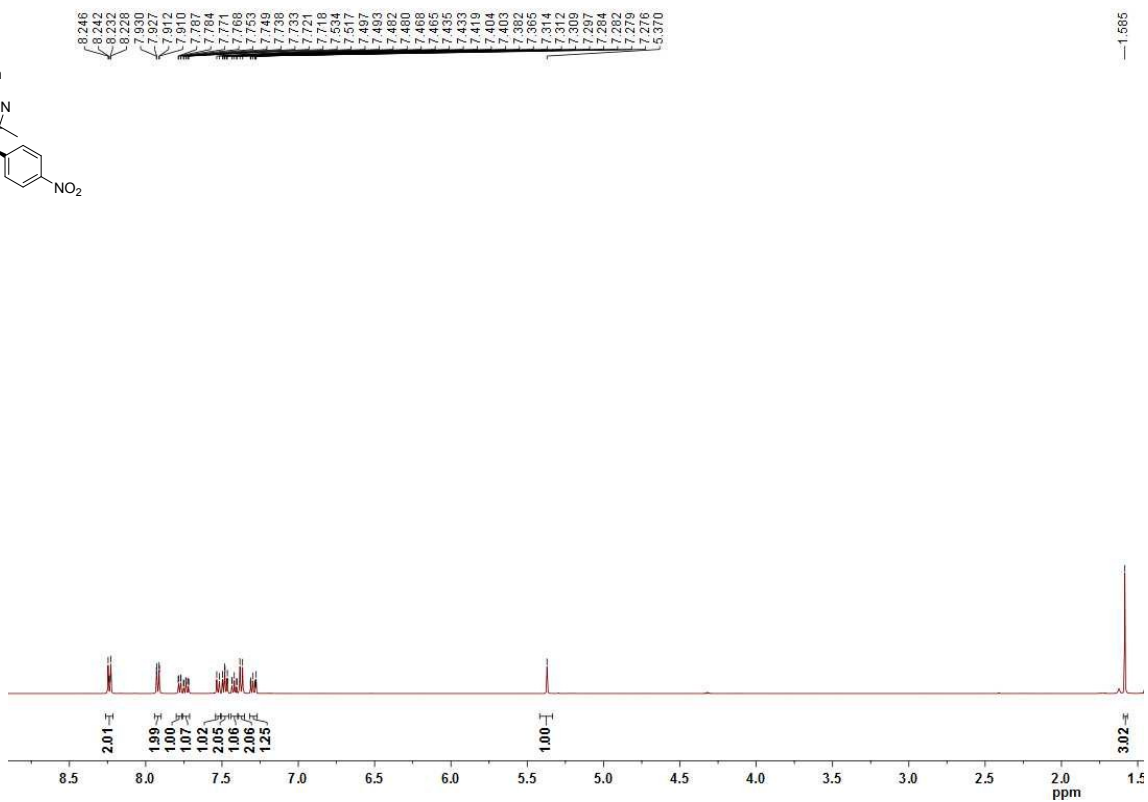
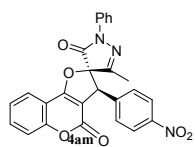
#	Start time[min]	Time[min]	End time[min]	Area%
1	19.524	20.412	21.881	49.979
2	22.374	23.372	24.977	50.021

## HPLC chromatogram of 4al (chiral)

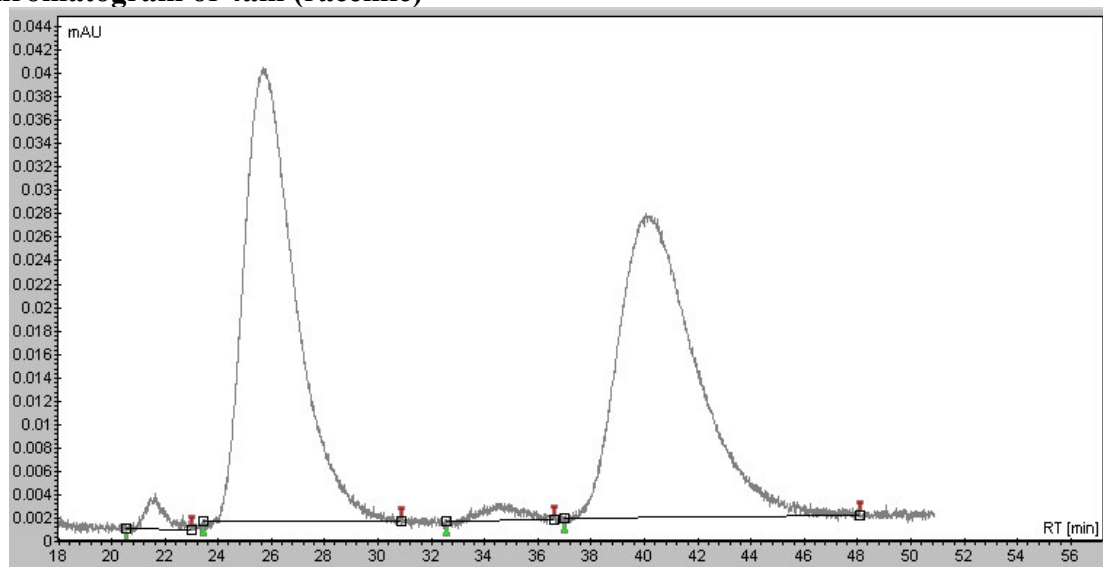


#	Start time[min]	Time[min]	End time[min]	Area%
1	19.464	20.265	21.825	98.803
2	22.702	23.545	24.389	1.197

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4am

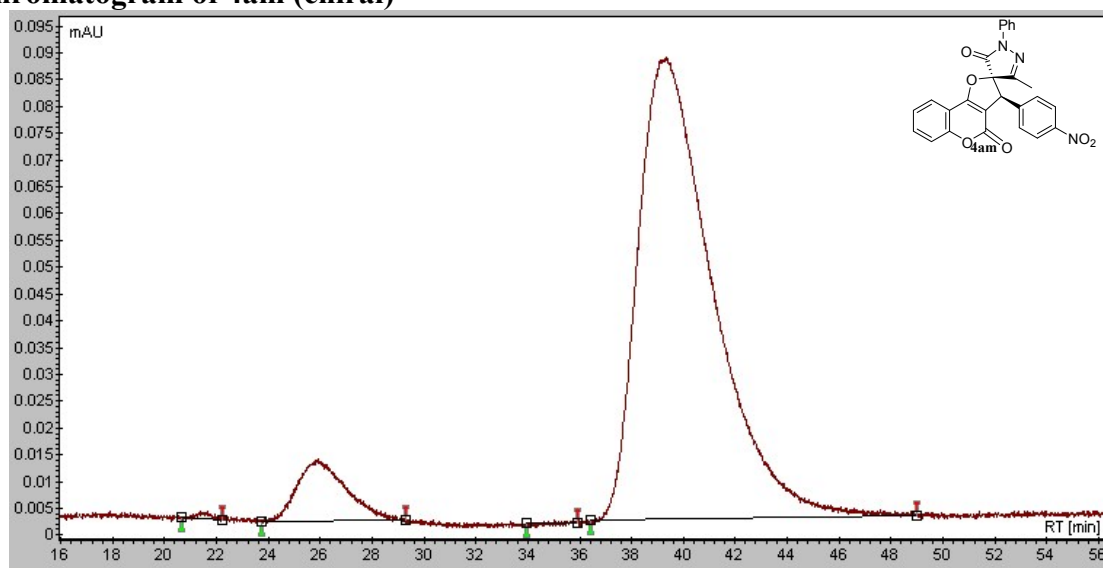


### HPLC chromatogram of 4am (racemic)



#	Start time[min]	Time[min]	End time[min]	Area%
1	20.545	21.598	23.025	1.275
2	23.45	25.705	30.888	48.608
3	32.589	34.637	36.627	1.143
4	36.981	40.104	48.104	48.974

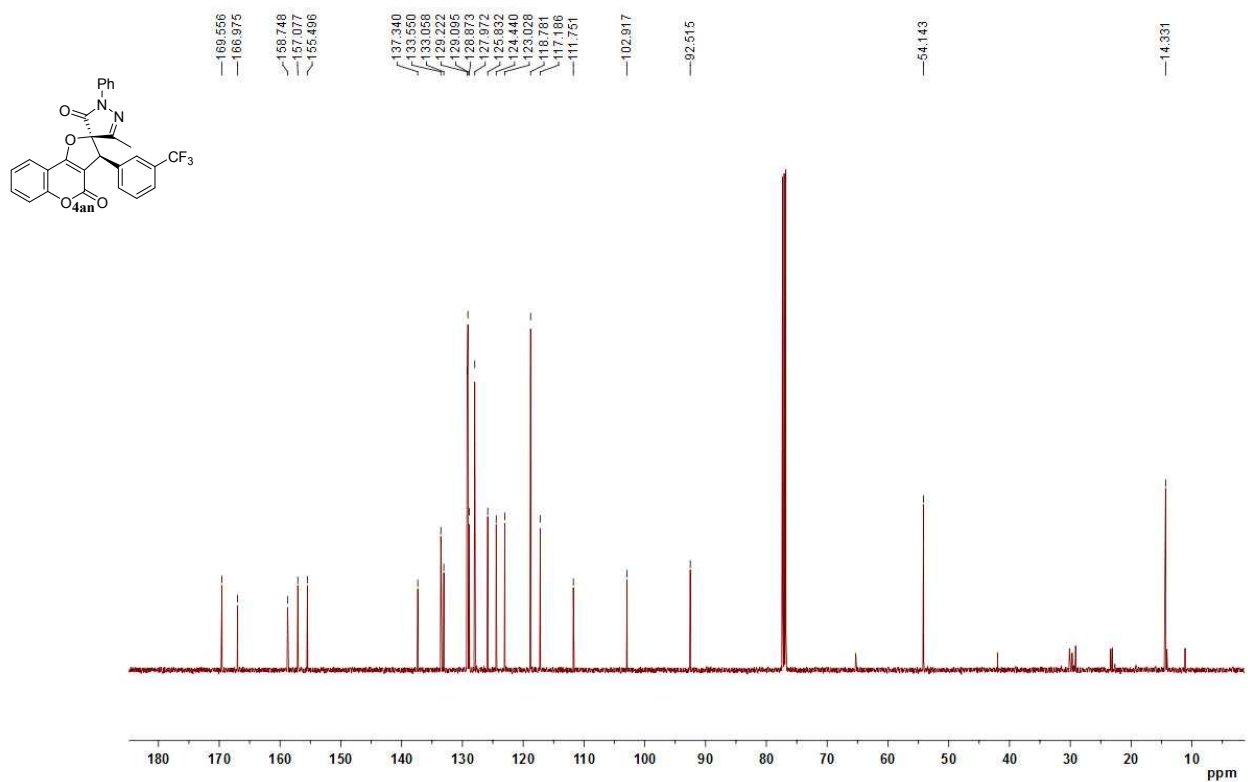
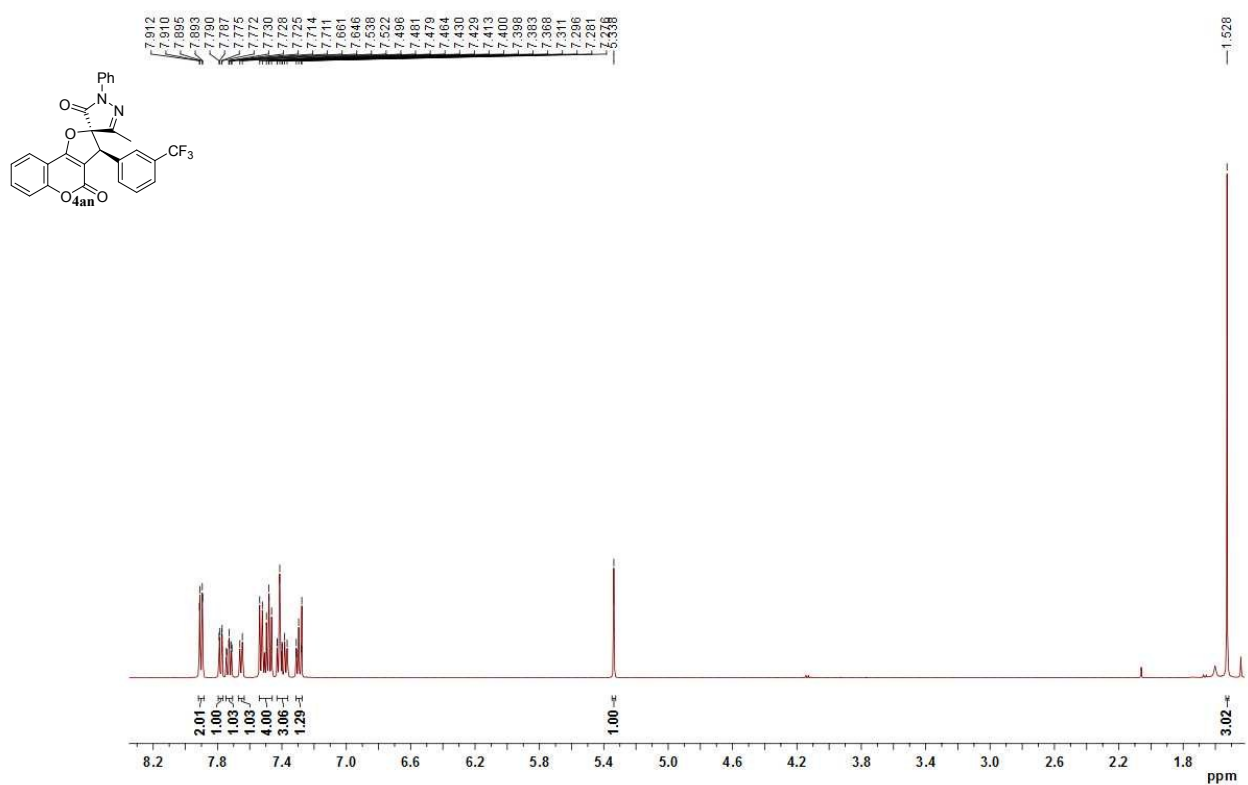
### HPLC chromatogram of 4am (chiral)



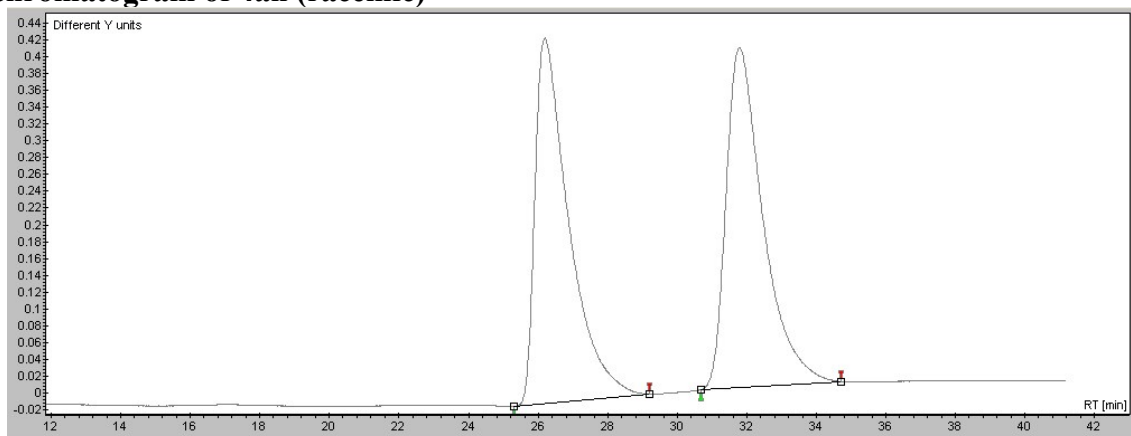
#	Start time[min]	Time[min]	End time[min]	Area%
1	20.672	21.598	22.237	0.214
2	23.719	25.865	29.32	7.956
3	33.932	33.944	35.908	0.075
4	36.402	39.264	49.003	91.755



# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4an

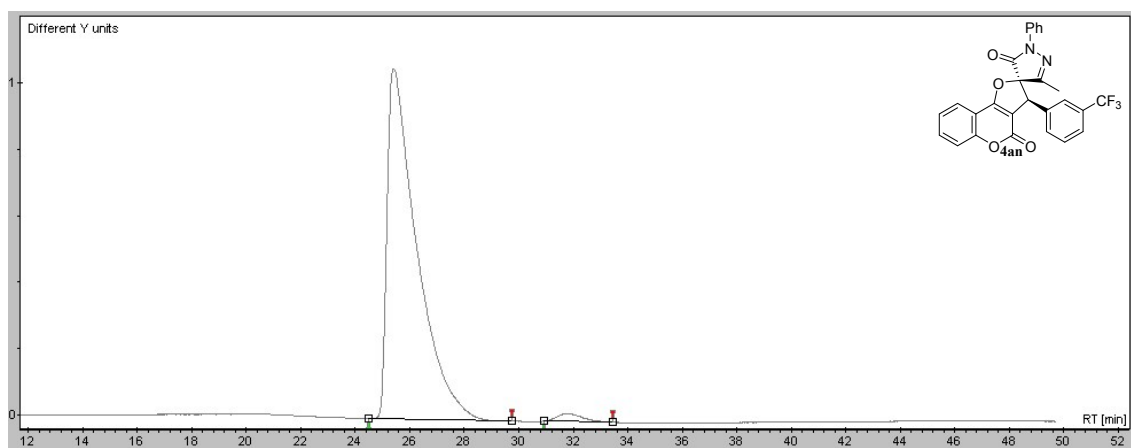


### HPLC chromatogram of 4an (racemic)



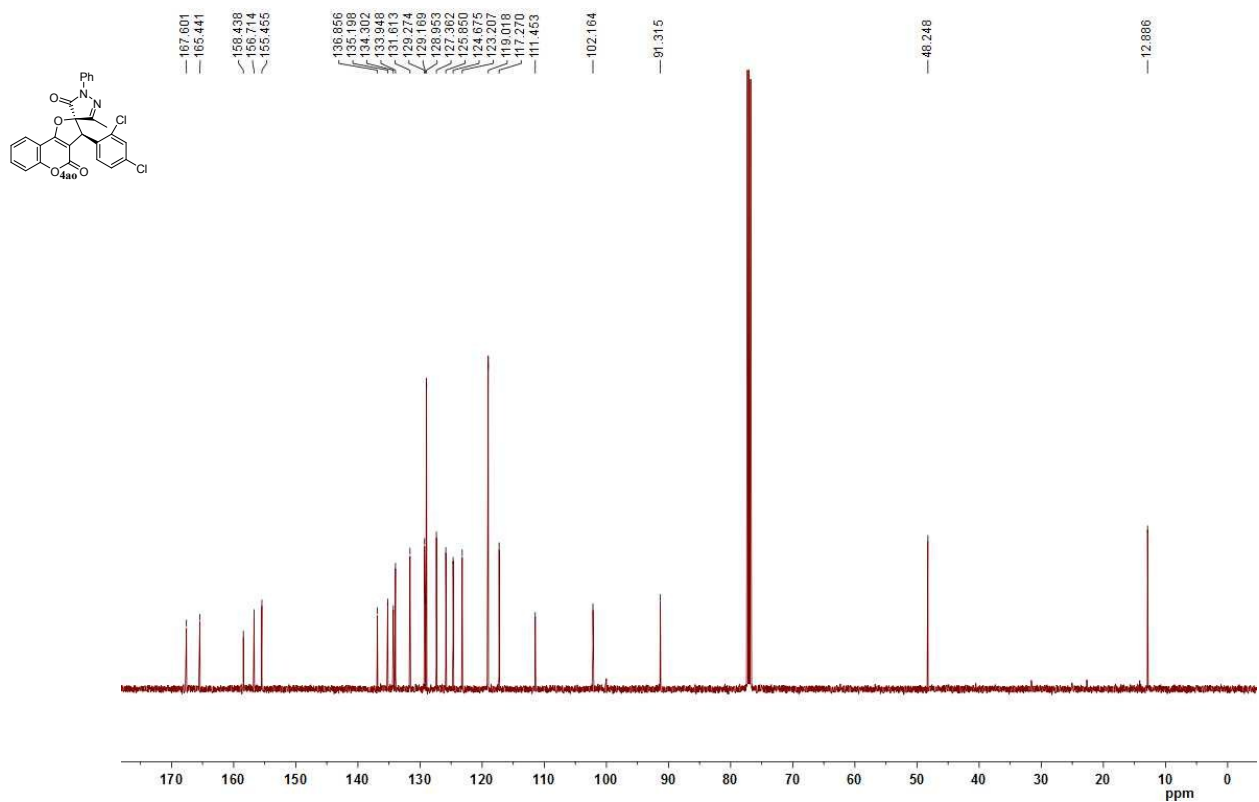
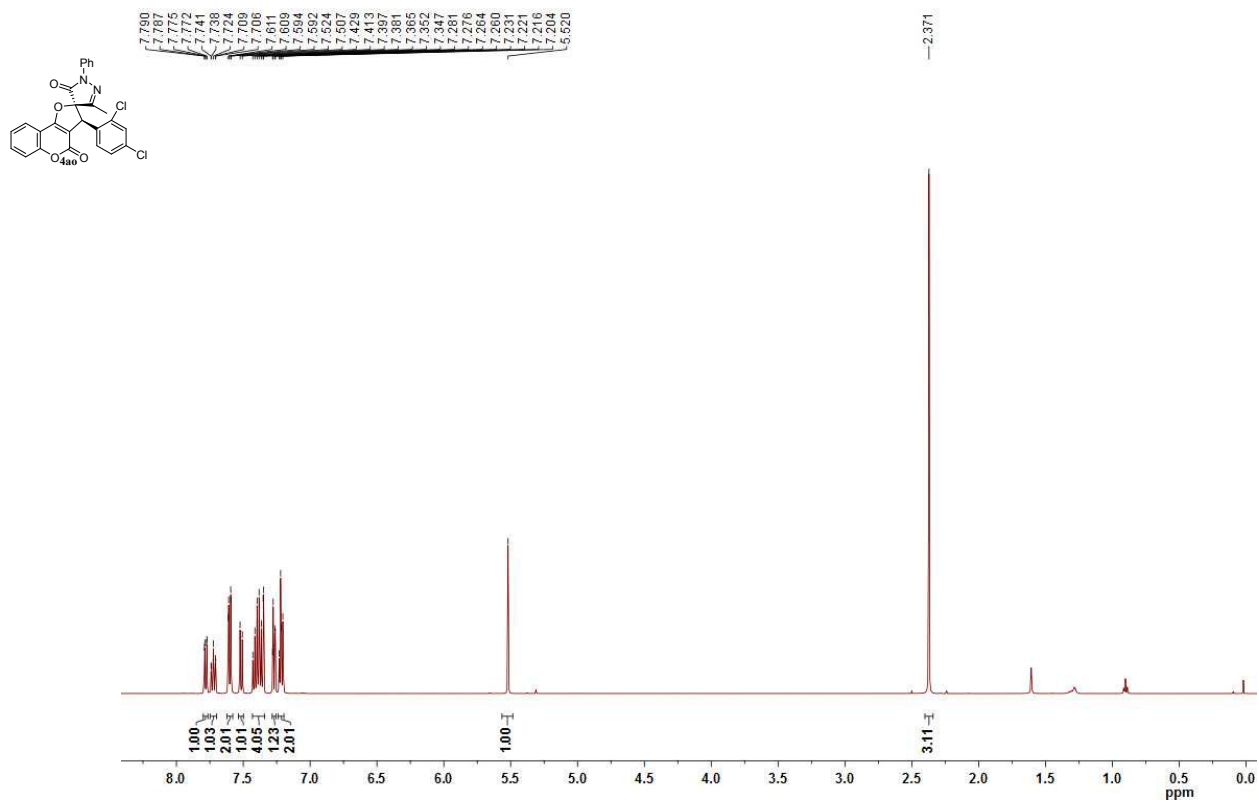
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	25.316	26.185	29.188	49.62
2	30.677	31.784	34.719	50.38

### HPLC chromatogram of 4an (chiral)

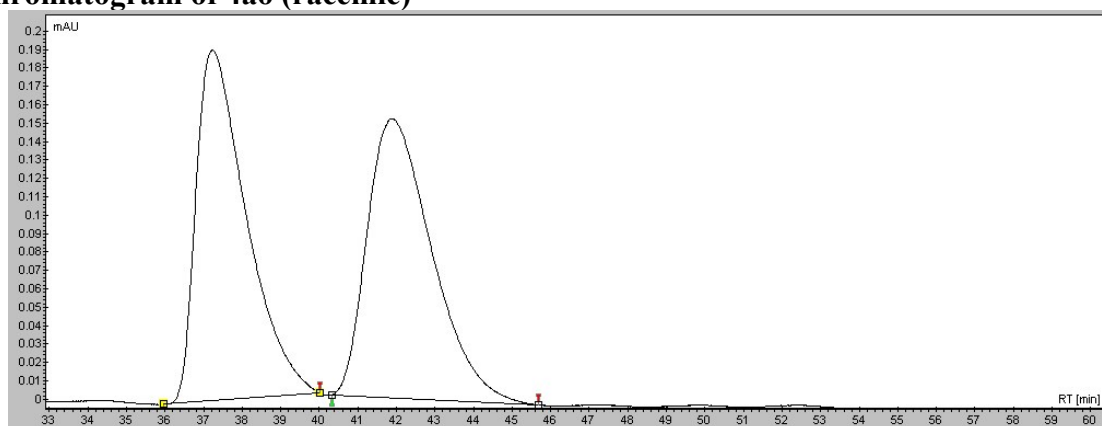


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	24.5	25.398	29.74	98.13
2	30.921	31.798	33.438	1.87

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ao

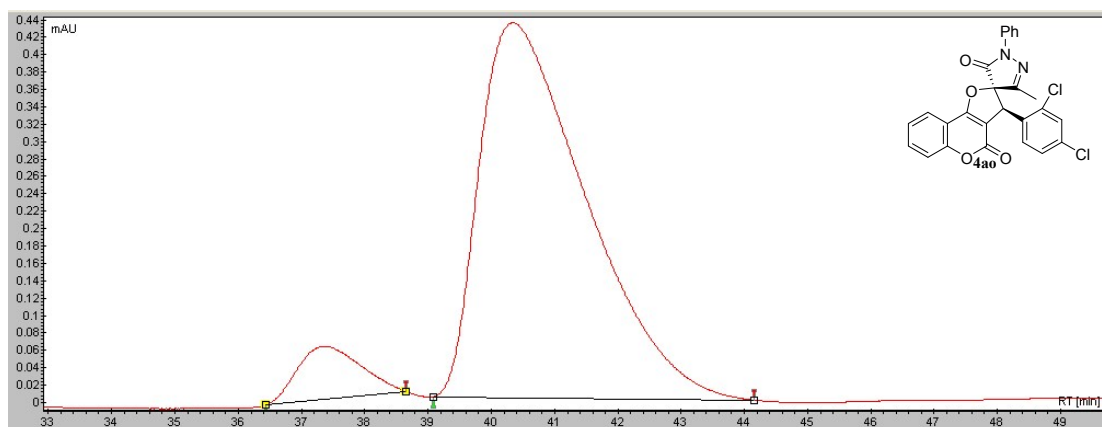


### HPLC chromatogram of 4ao (racemic)



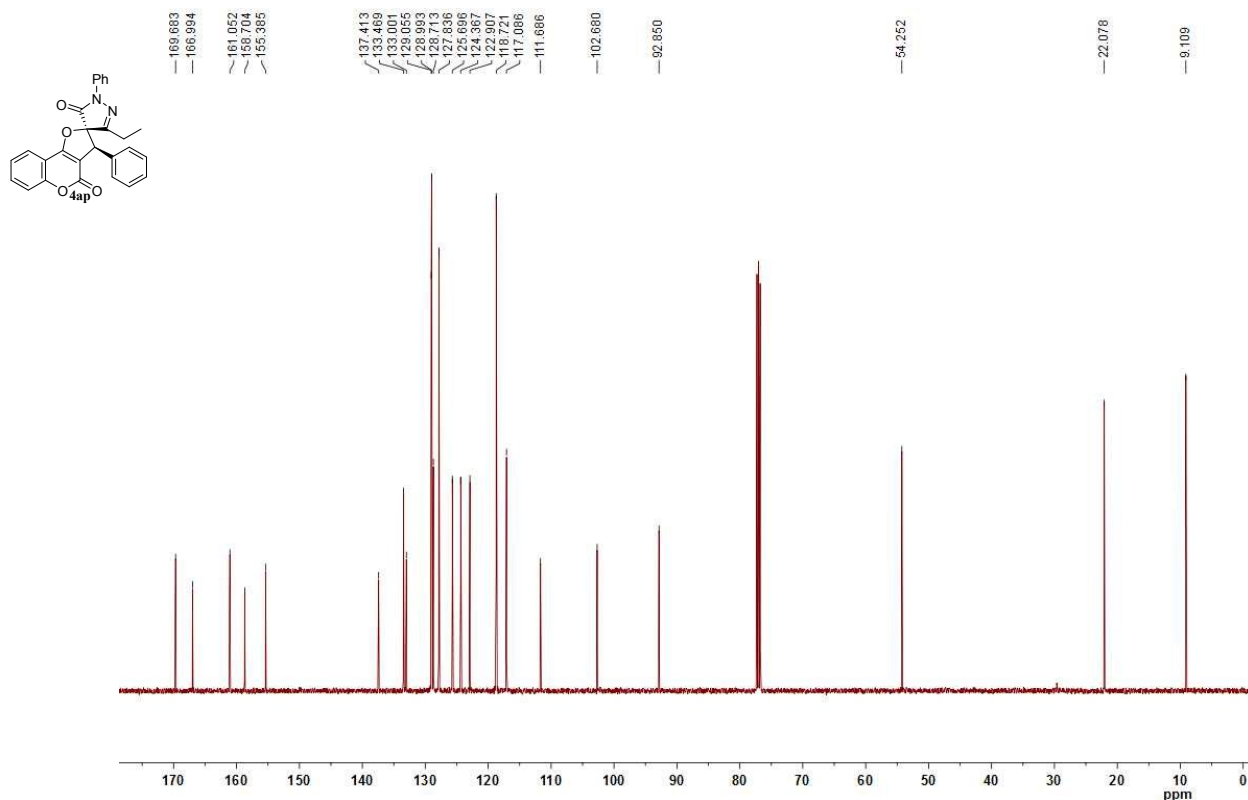
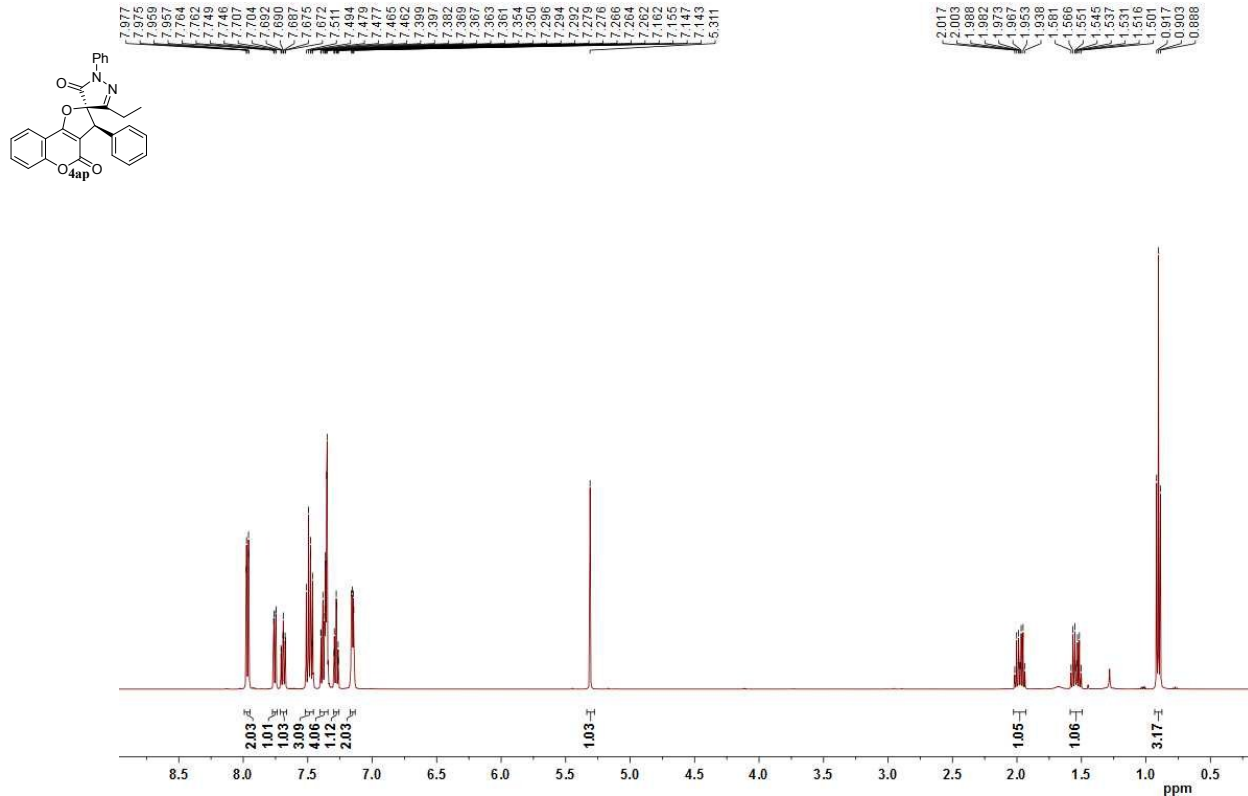
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	35.97	37.224	40.028	49.444
2	40.336	41.89	45.685	50.556

### HPLC chromatogram of 4ao (chiral)

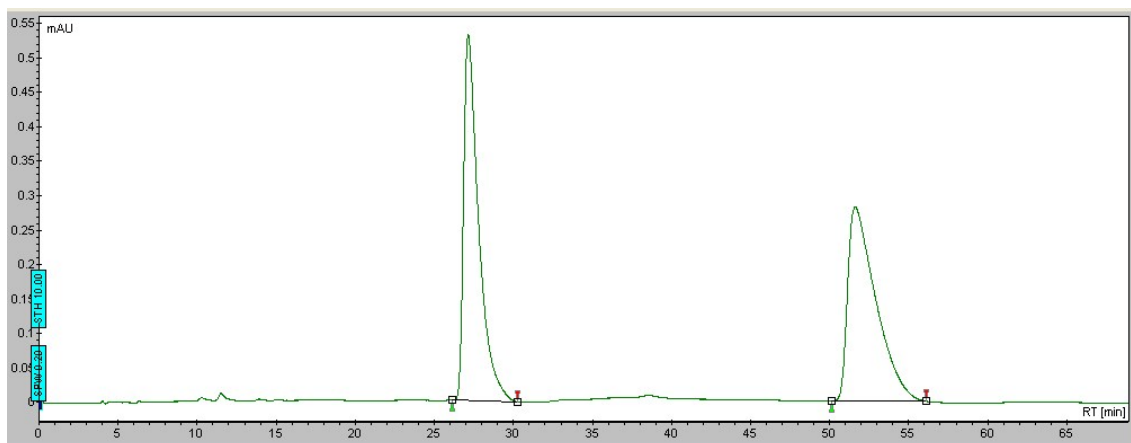


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	36.443	37.331	38.66	7.73
2	39.085	40.344	44.146	92.27

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ap

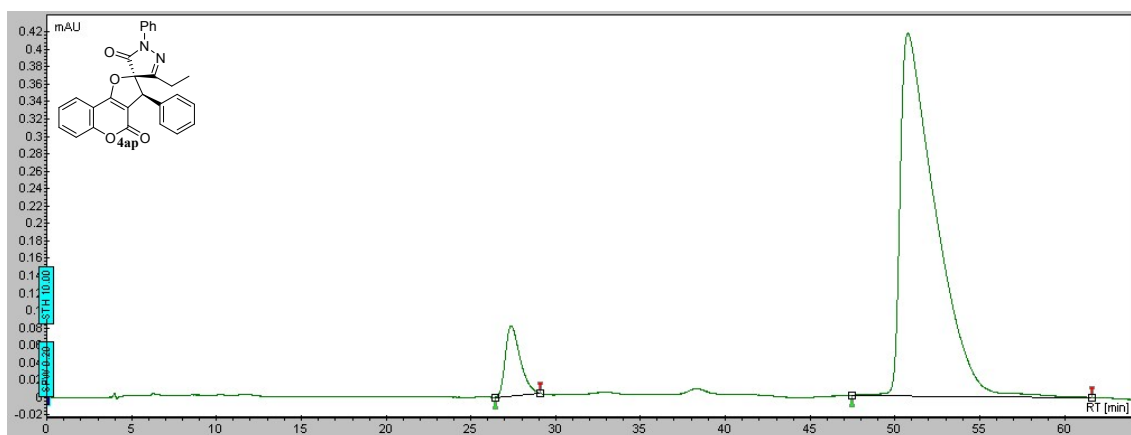


## HPLC chromatogram of 4ap (racemic)



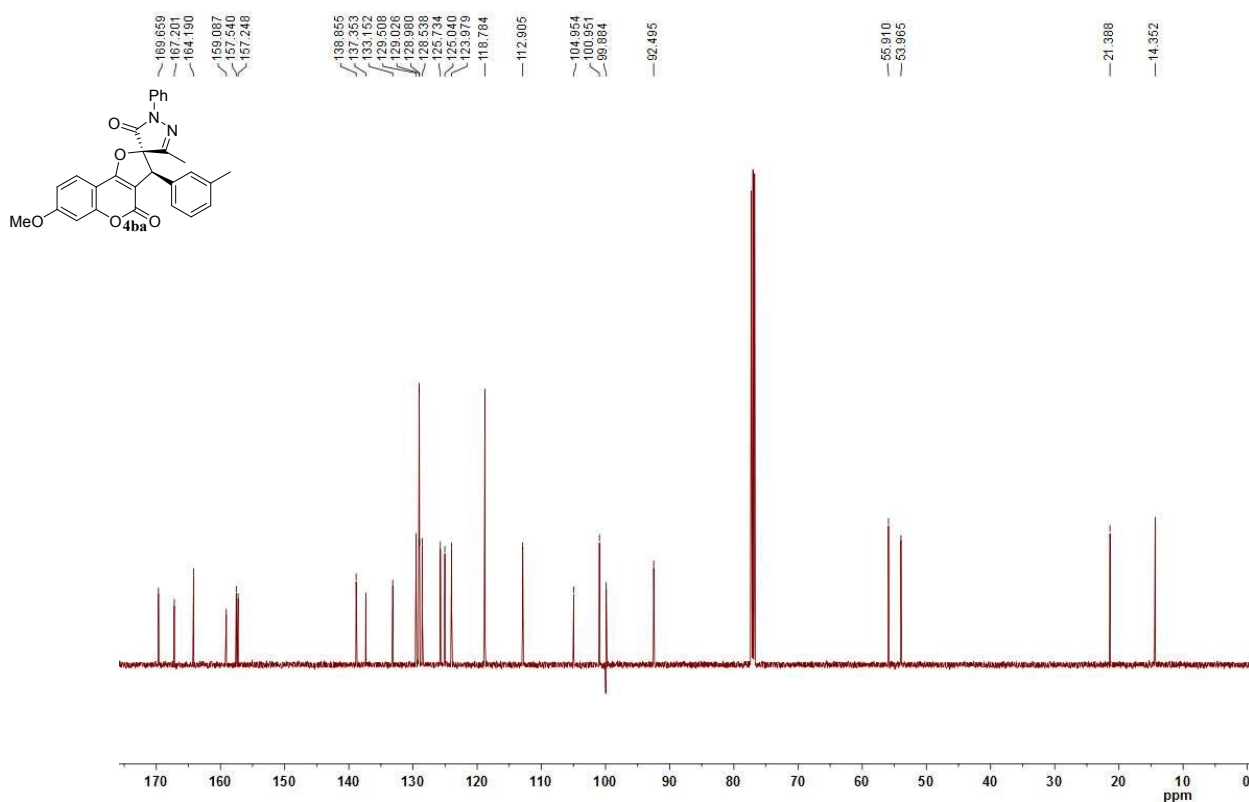
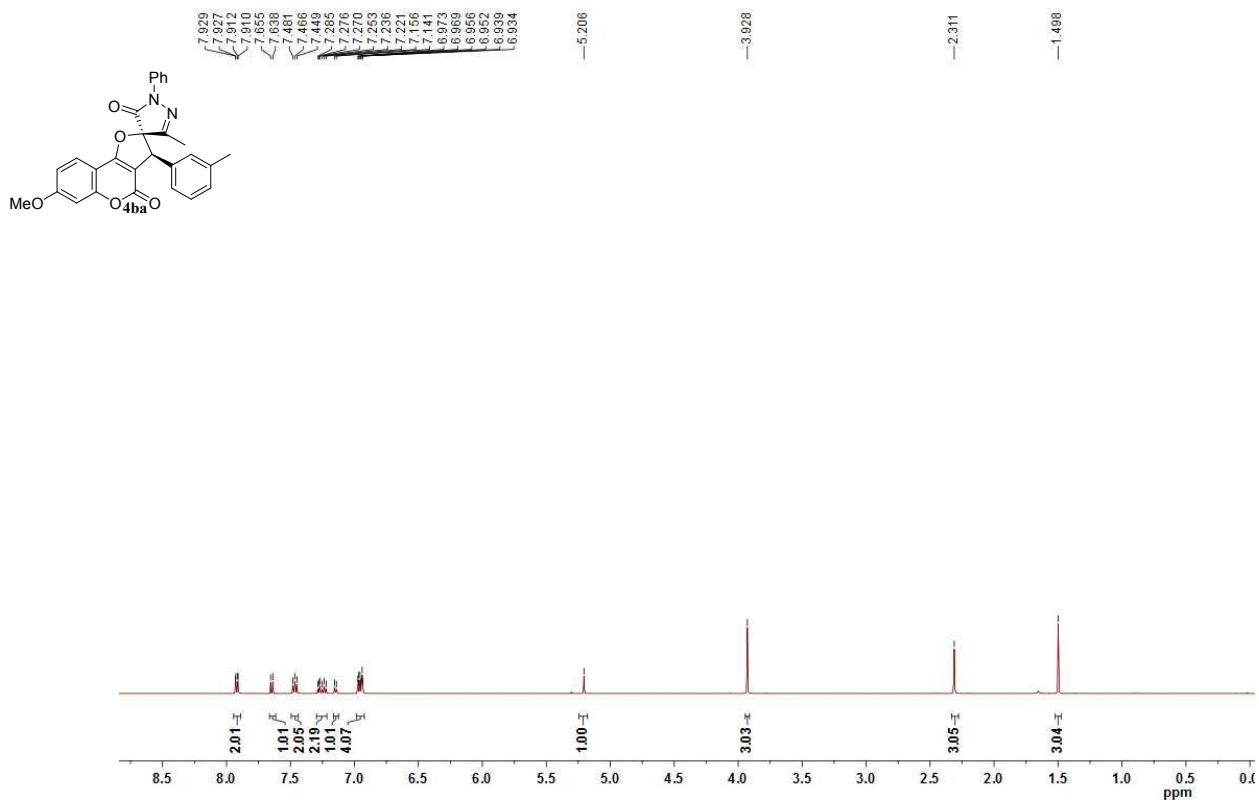
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	26.13	27.137	30.259	50.173
2	50.124	51.608	56.104	49.827

## HPLC chromatogram of 4ap (chiral)

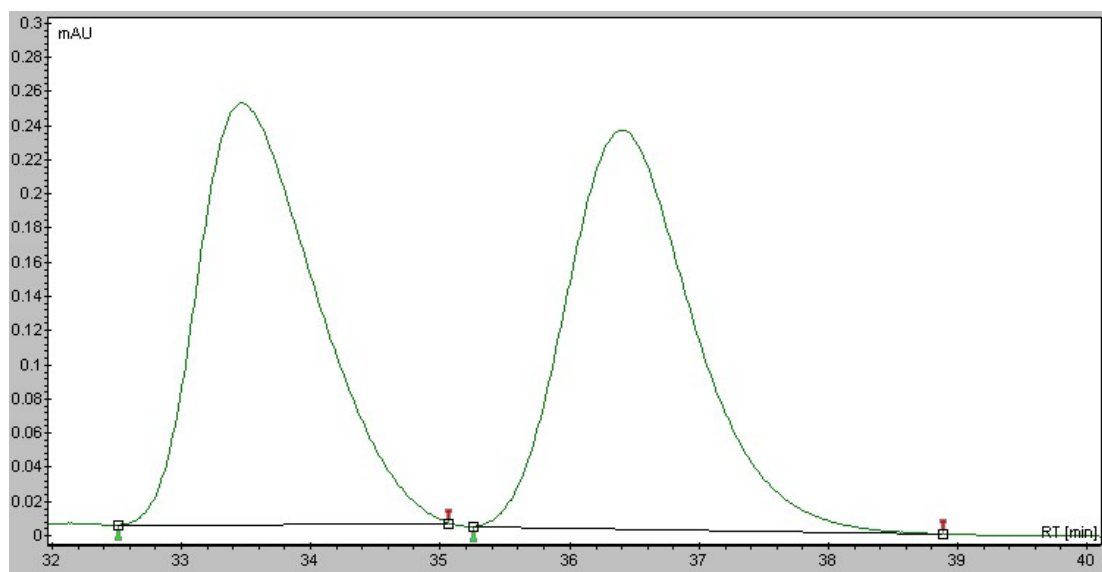


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	26.441	27.371	29.085	7.536
2	47.461	50.756	61.607	92.464

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4ba

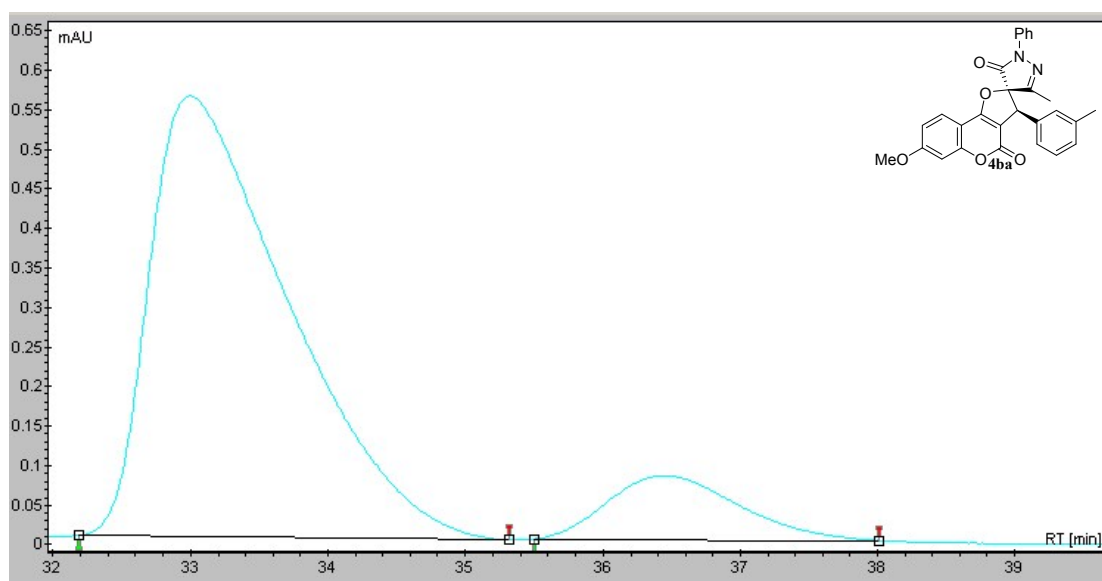


### HPLC chromatogram of 4ba (racemic)



#	Start time[min]	Time[min]	End time[min]	Area%
1	32.505	33.464	35.066	49.479
2	35.255	36.397	38.895	50.521

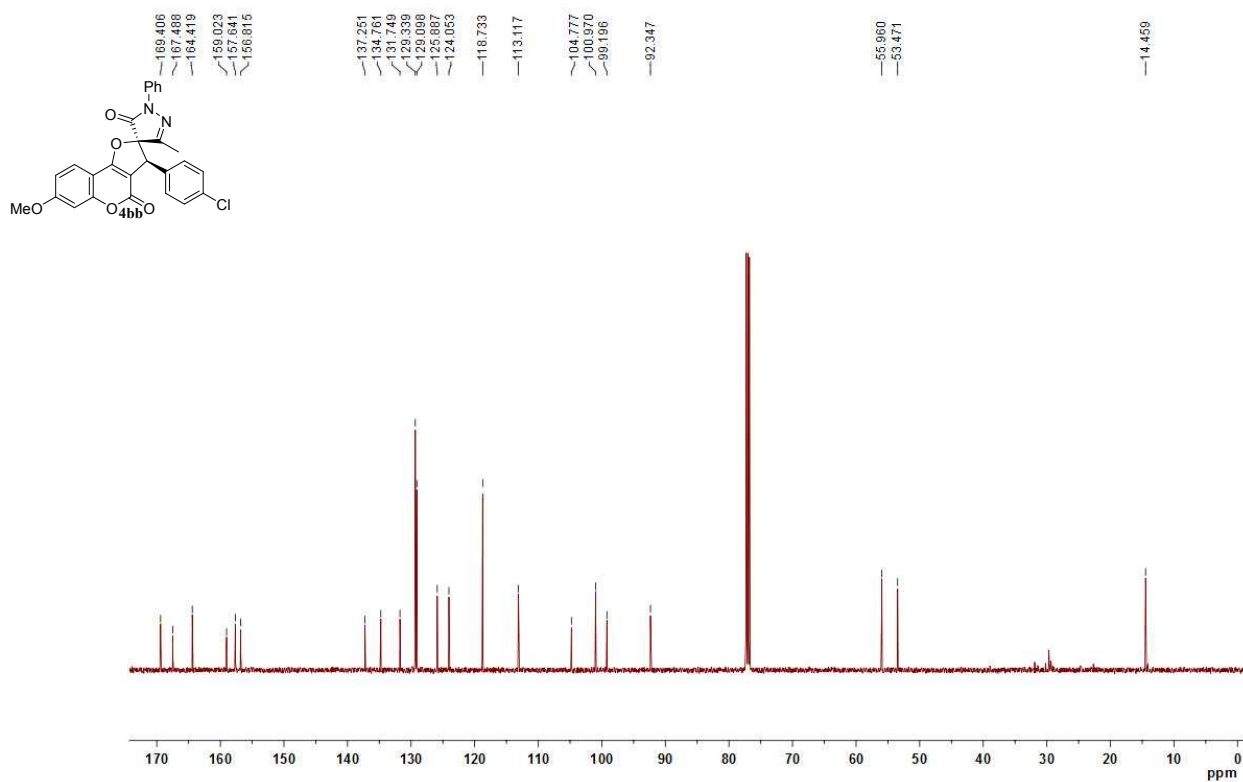
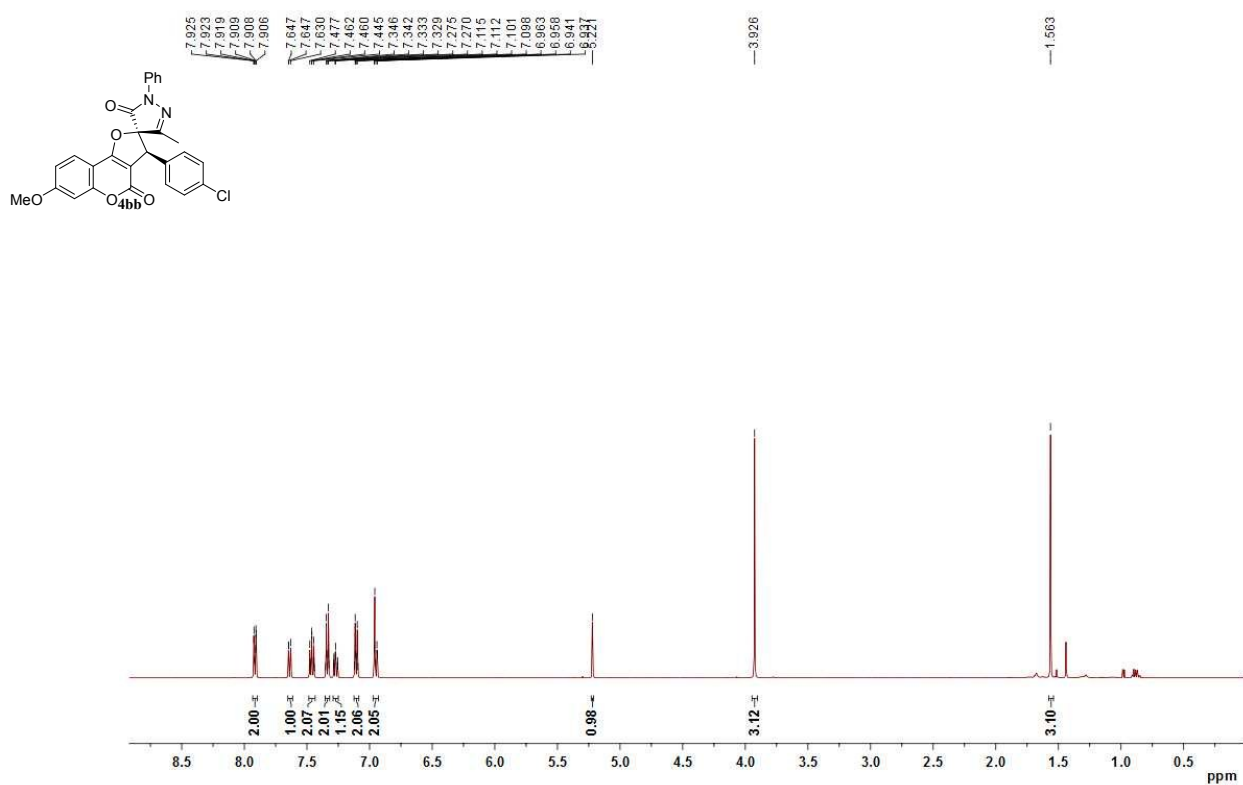
### HPLC chromatogram of 4ba (chiral)



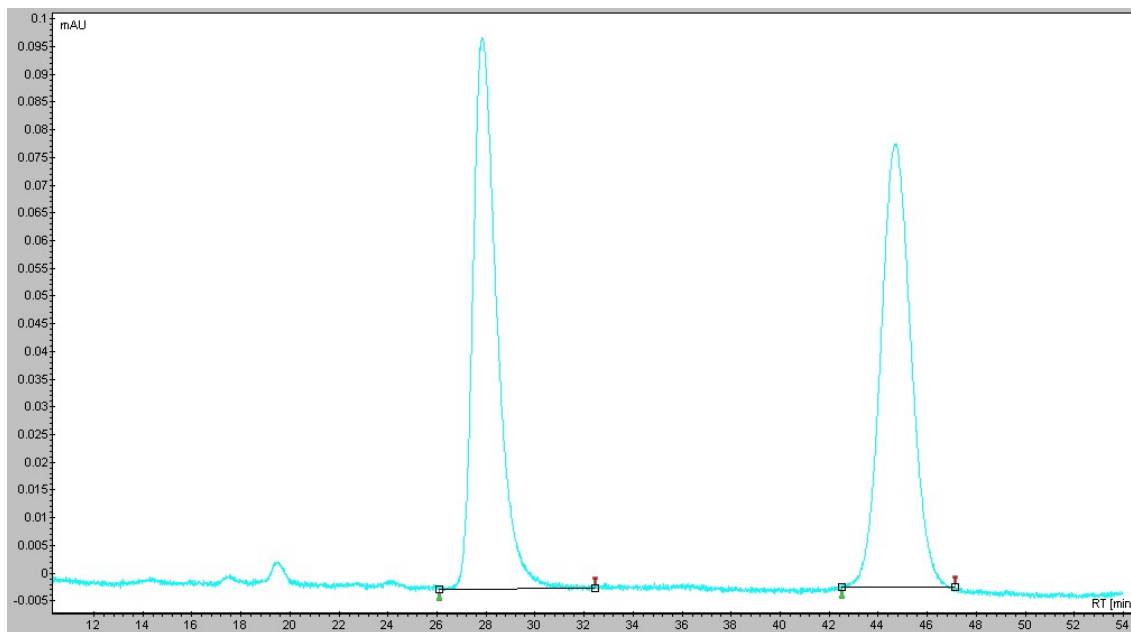
#	Start time[min]	Time[min]	End time[min]	Area%
1	32.184	32.998	35.316	88.045
2	35.501	36.451	38.01	11.955



# $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of 4bb

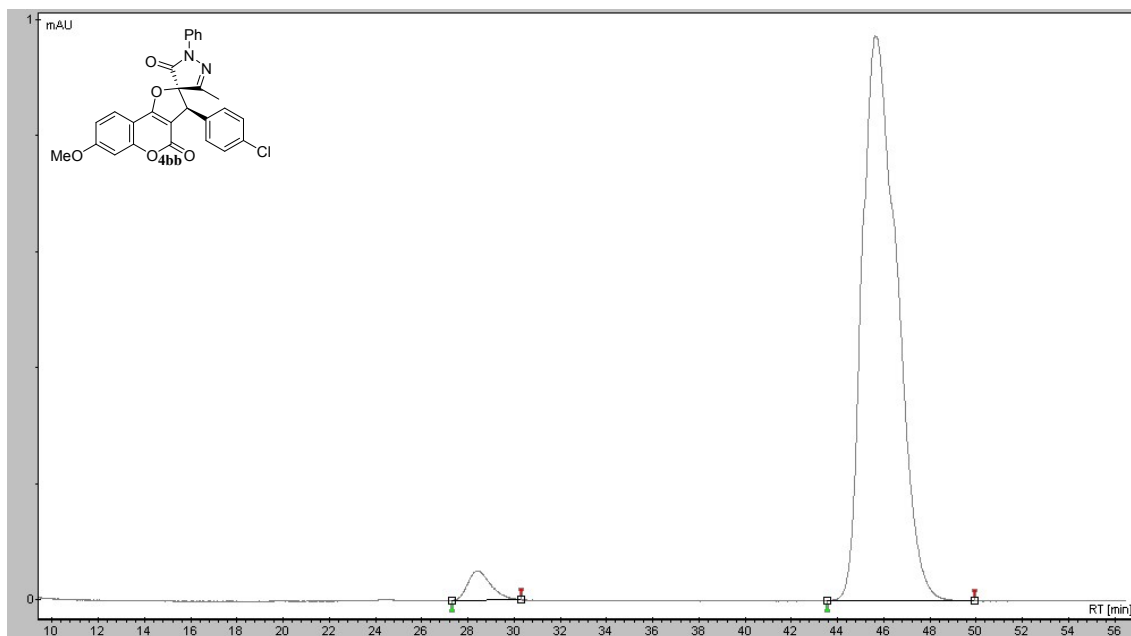


## HPLC chromatogram of 4bb (racemic)



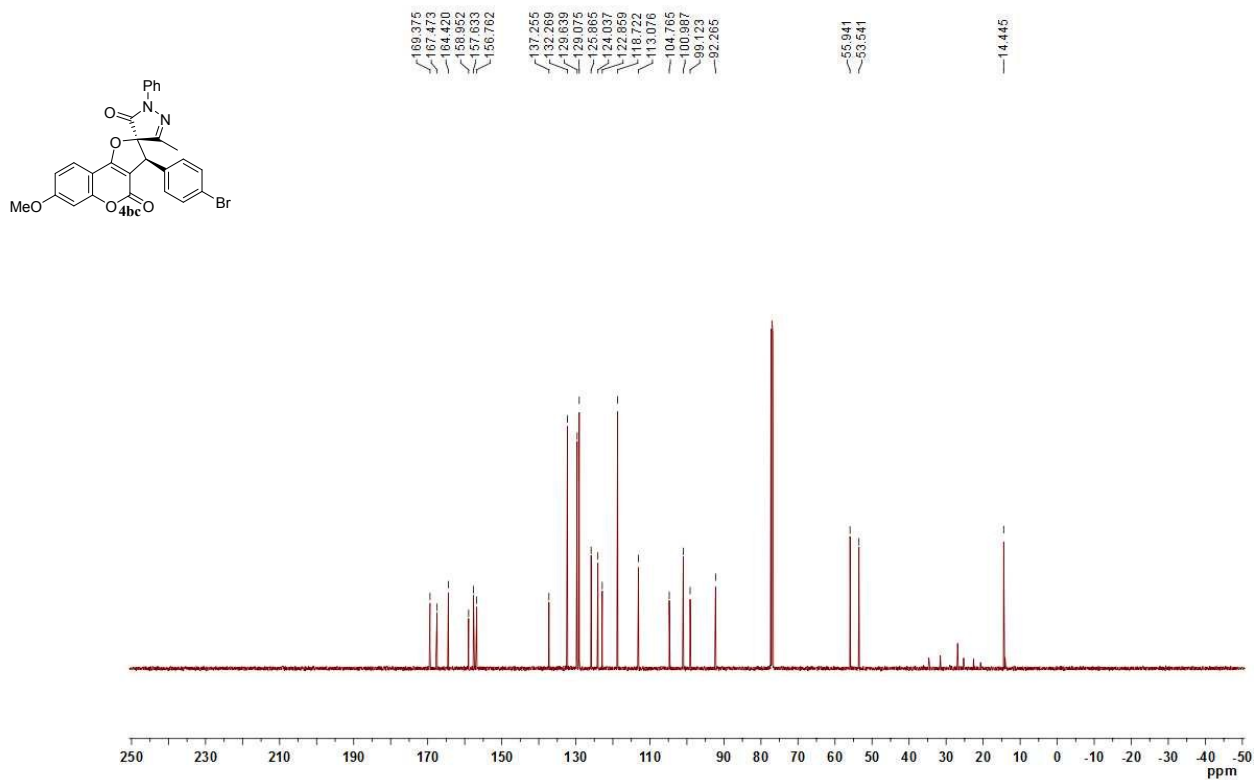
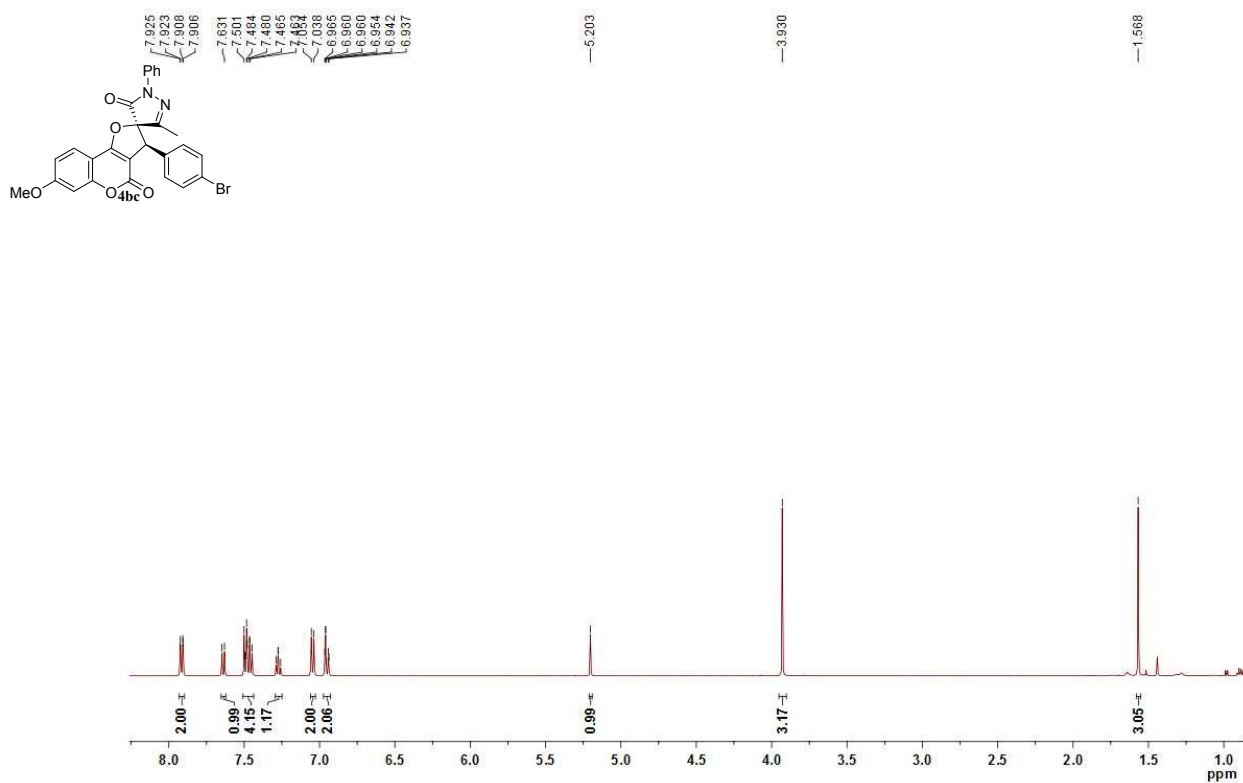
#	Start time[min]	Time[min]	End time[min]	Area%
1	26.101	27.851	32.459	49.775
2	42.498	44.703	47.127	50.225

## HPLC chromatogram of 4bb (chiral)

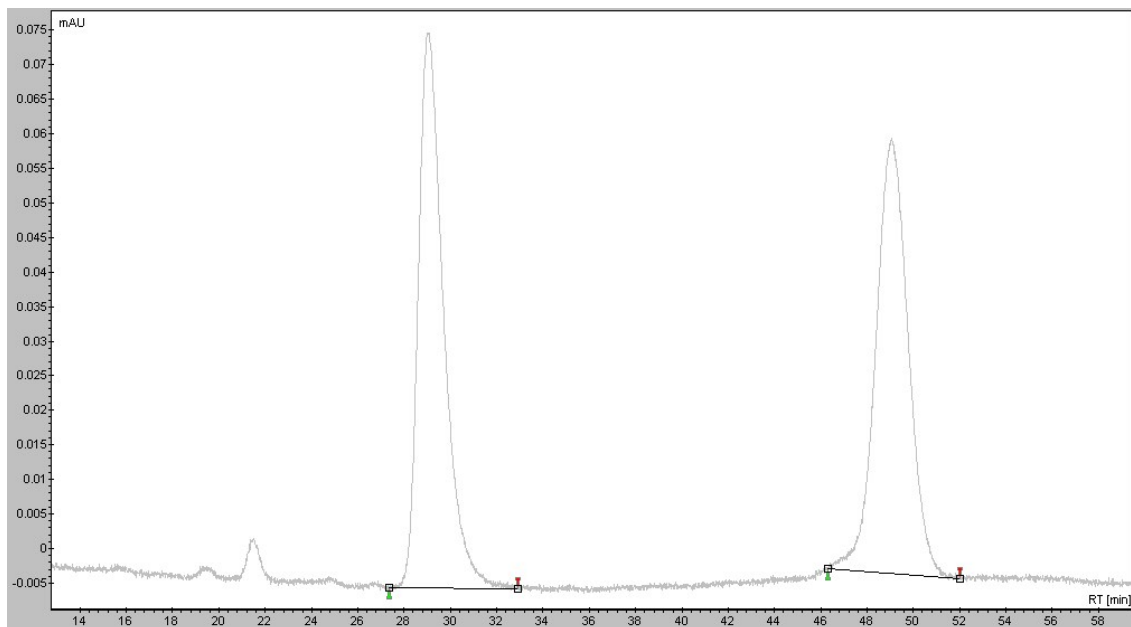


#	Start time[min]	Time[min]	End time[min]	Area%
1	27.313	28.411	30.289	3.317
2	43.537	45.597	49.957	96.683

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4bc

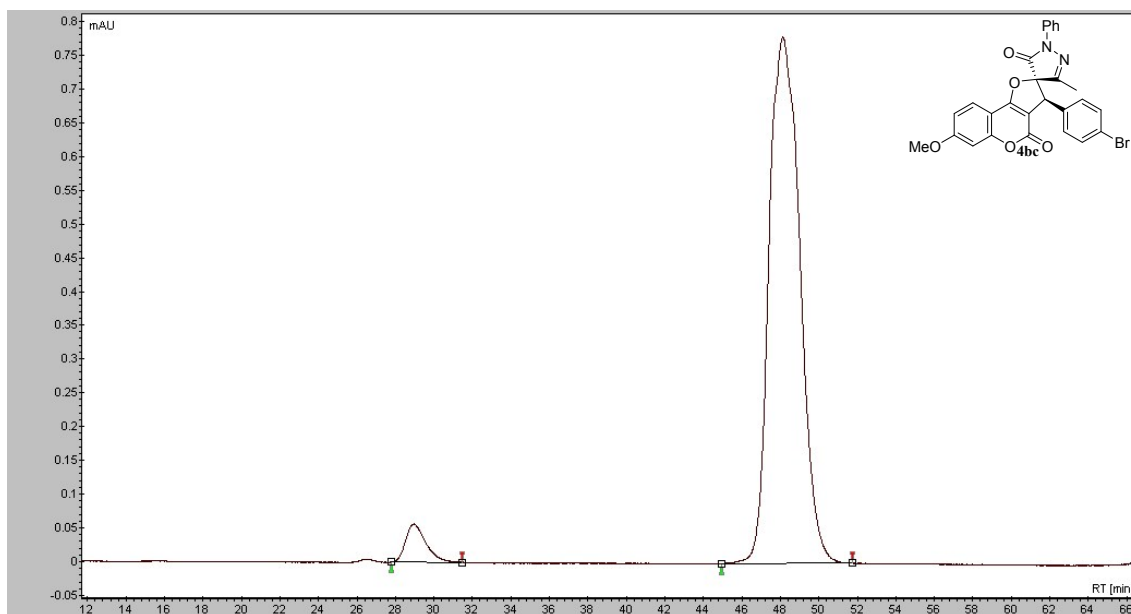


### HPLC chromatogram of 4bc (racemic)



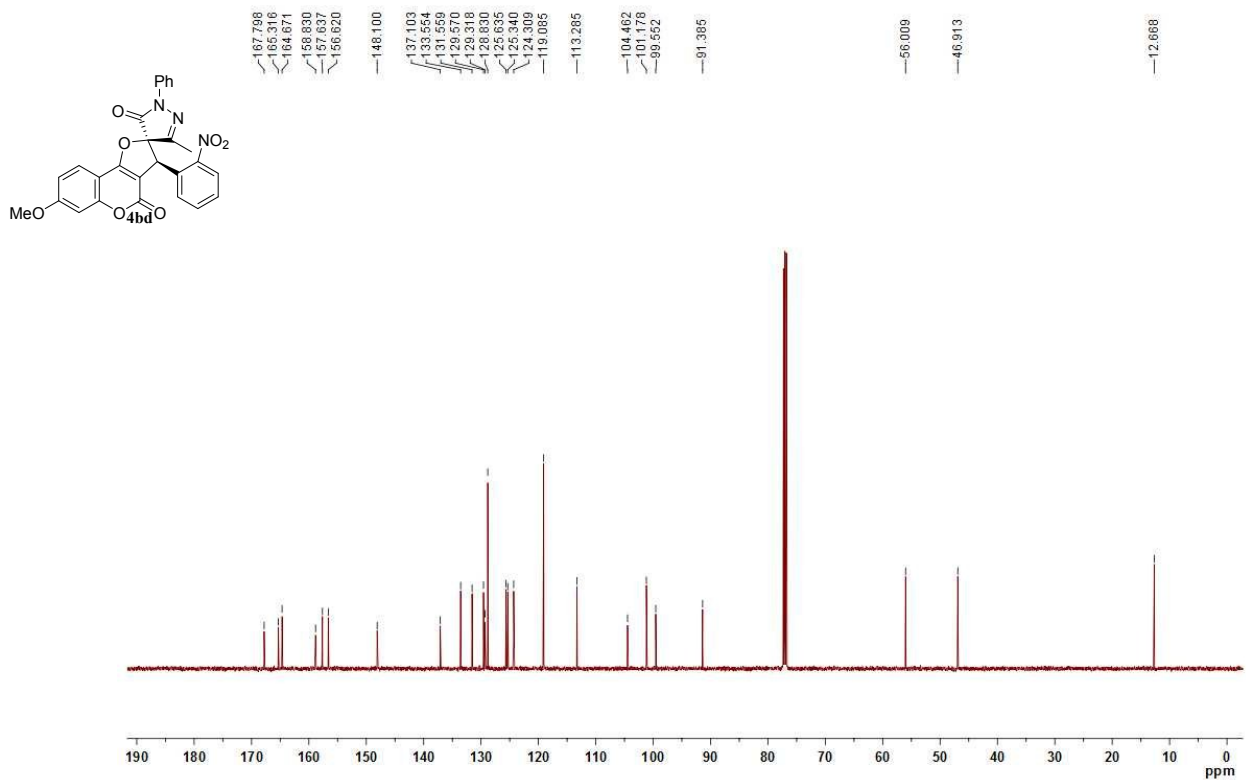
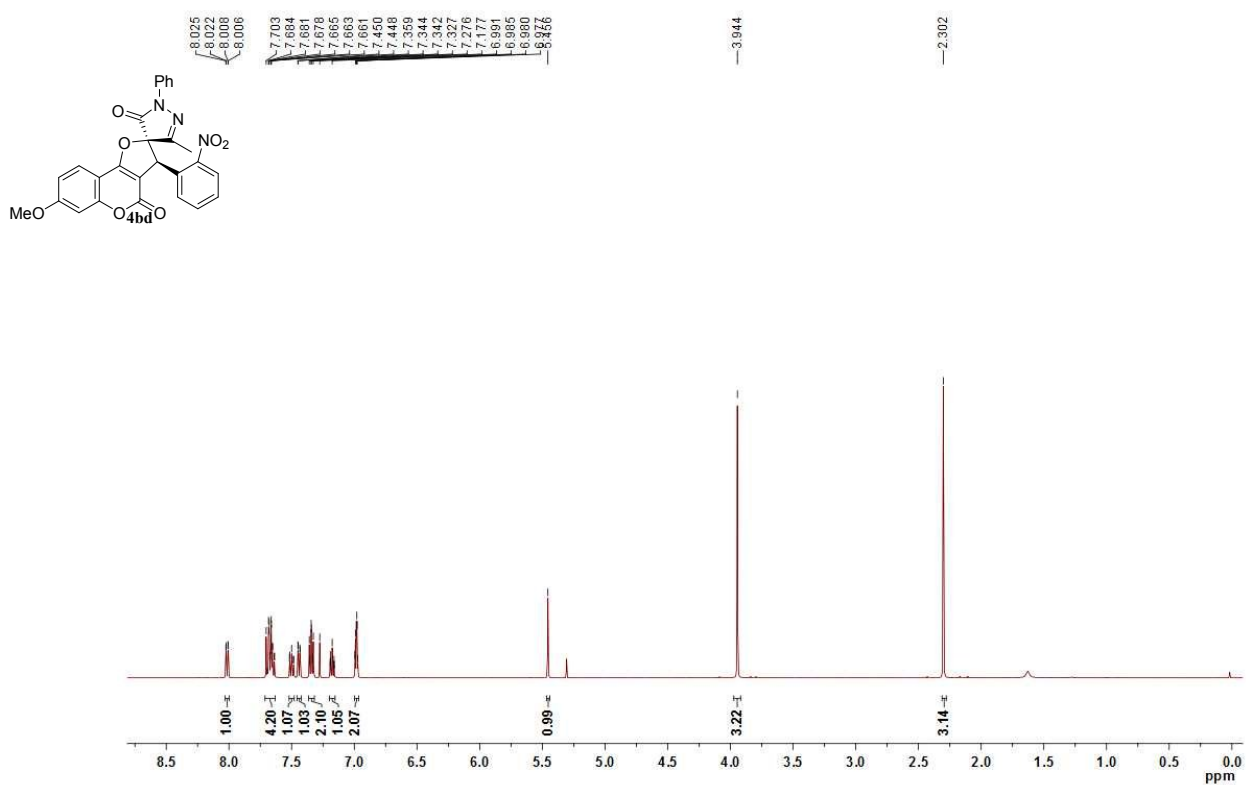
#	Start time[min]	Time[min]	End time[min]	Area%
1	27.382	29.038	32.920	49.985
2	46.300	49.063	52.025	50.015

### HPLC chromatogram of 4bc (chiral)

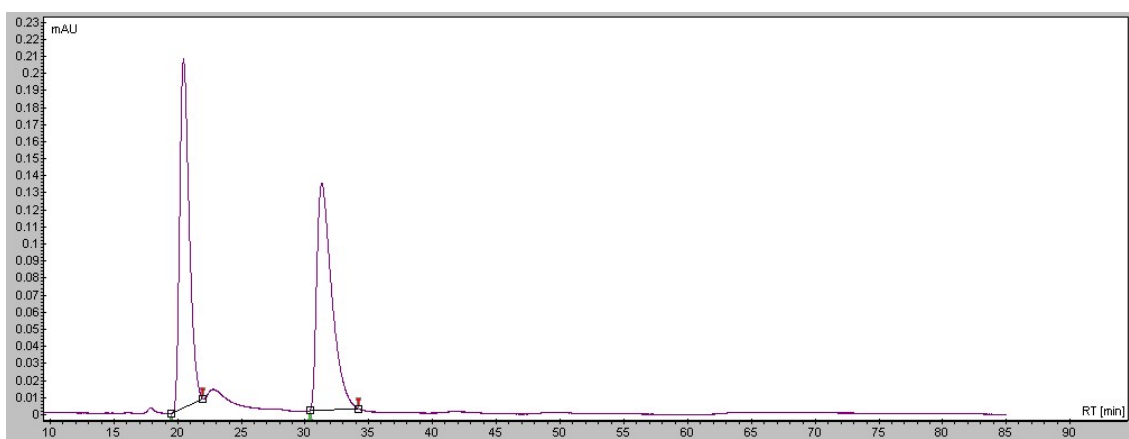


#	Start time[min]	Time[min]	End time[min]	Area%
1	27.692	28.963	31.110	4.494
2	44.991	48.116	52.170	95.506

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4bd

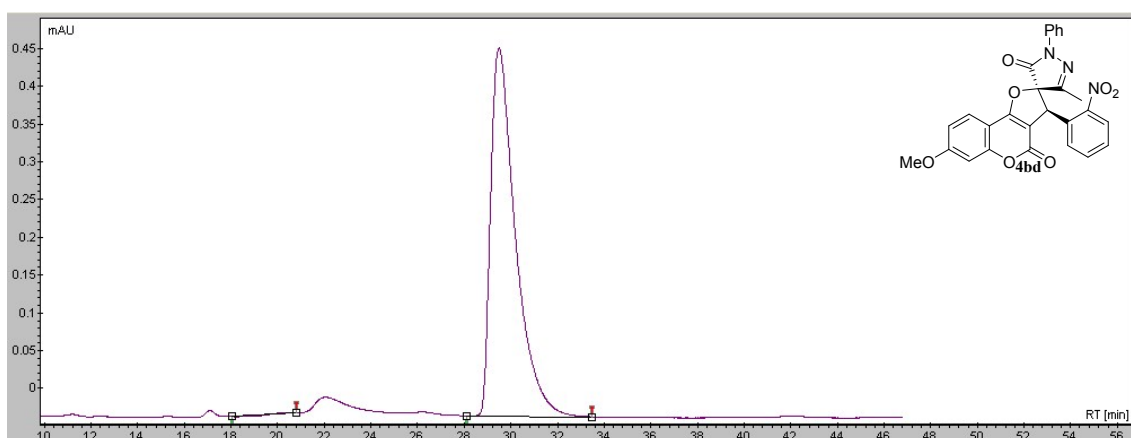


## HPLC chromatogram of 4bd (racemic)



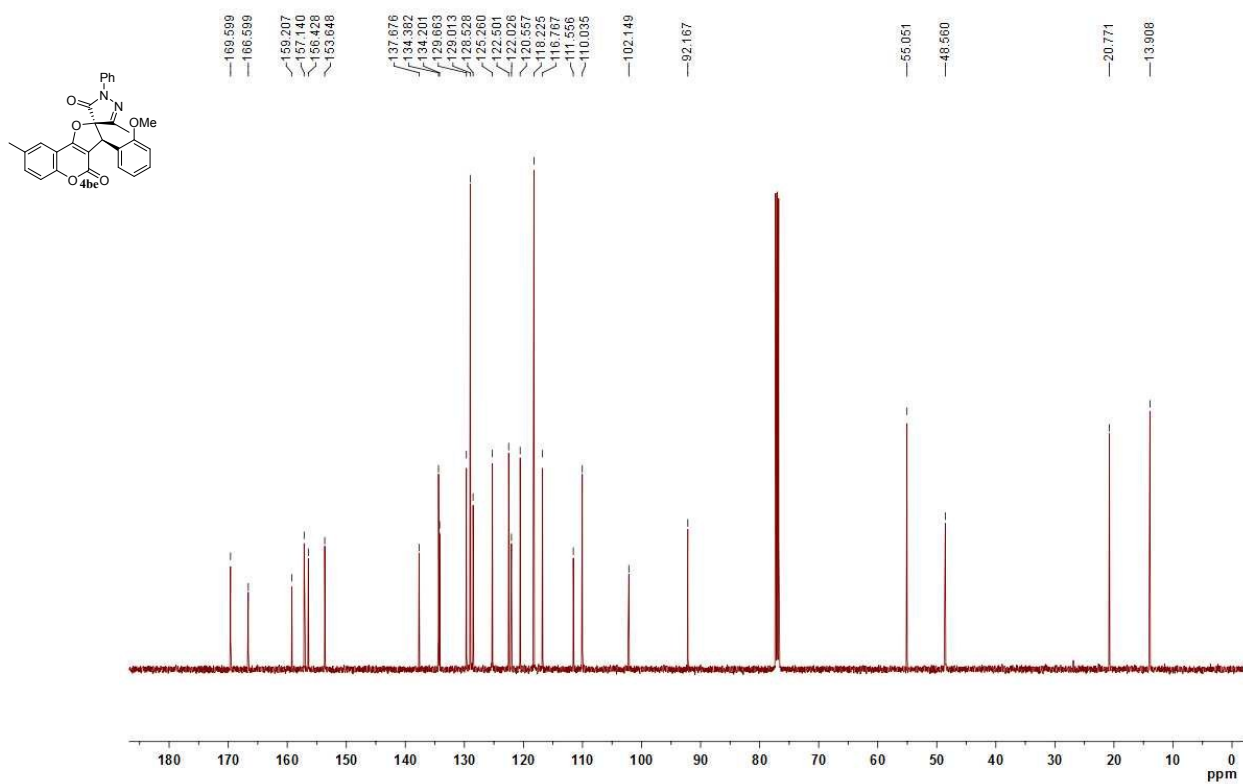
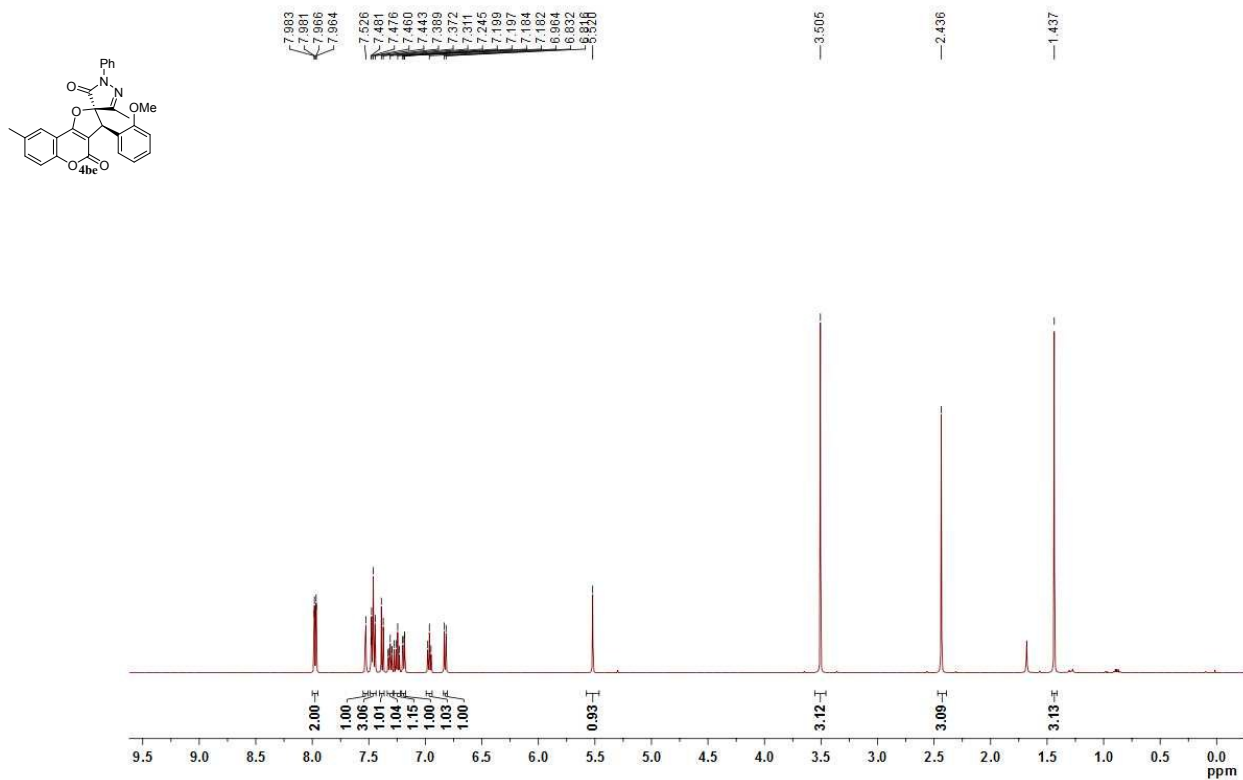
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	19.538	20.473	21.99	49.393
2	30.401	31.309	34.179	50.607

## HPLC chromatogram of 4bd (chiral)

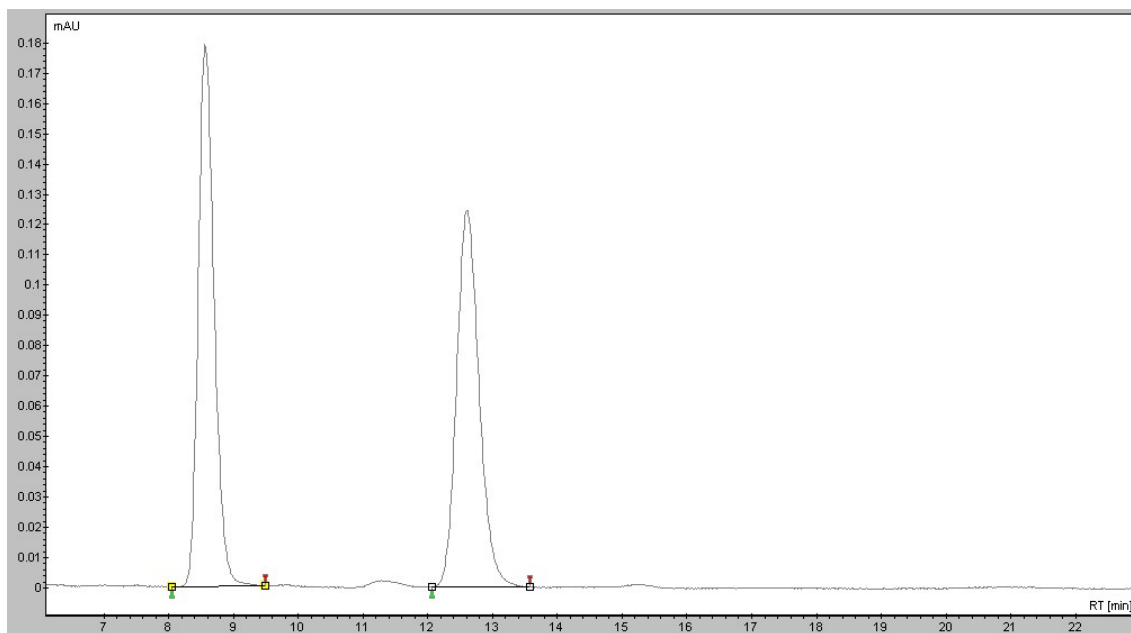


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	18.044	19.132	20.801	0.09
2	28.106	29.491	33.475	99.91

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4be

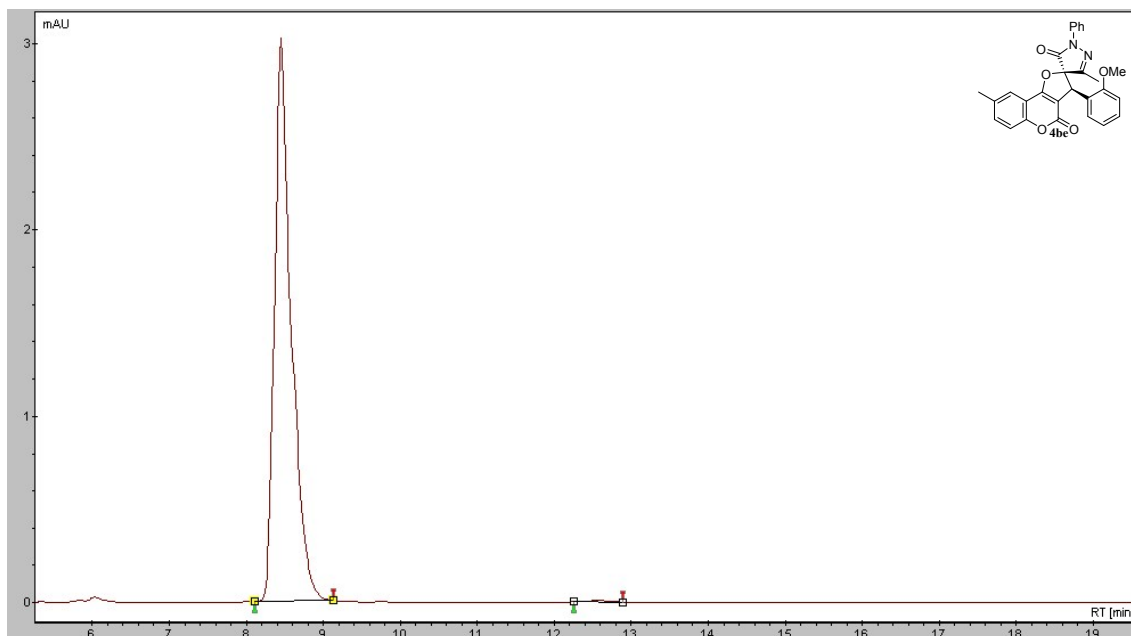


### HPLC chromatogram of 4be (racemic)



#	Start time[min]	Time[min]	End time[min]	Area%
1	8.052	8.559	9.498	50.418
2	12.061	12.599	13.573	49.582

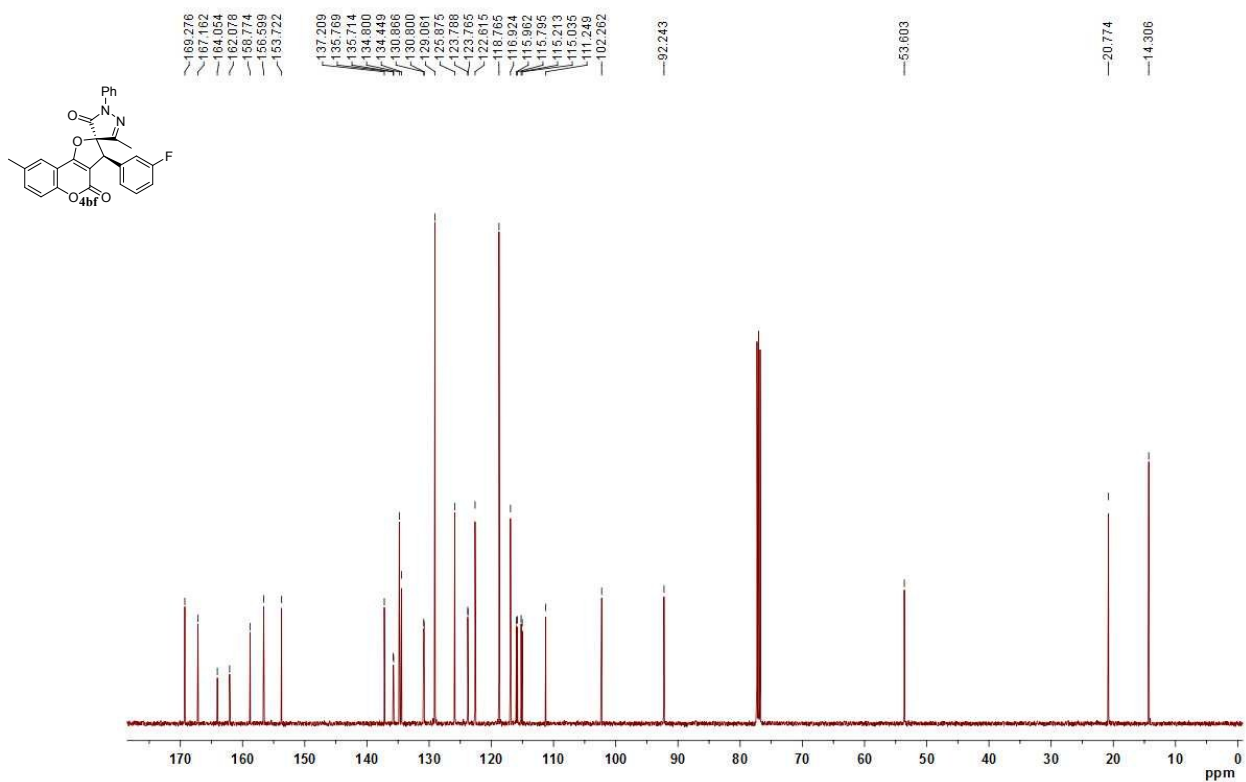
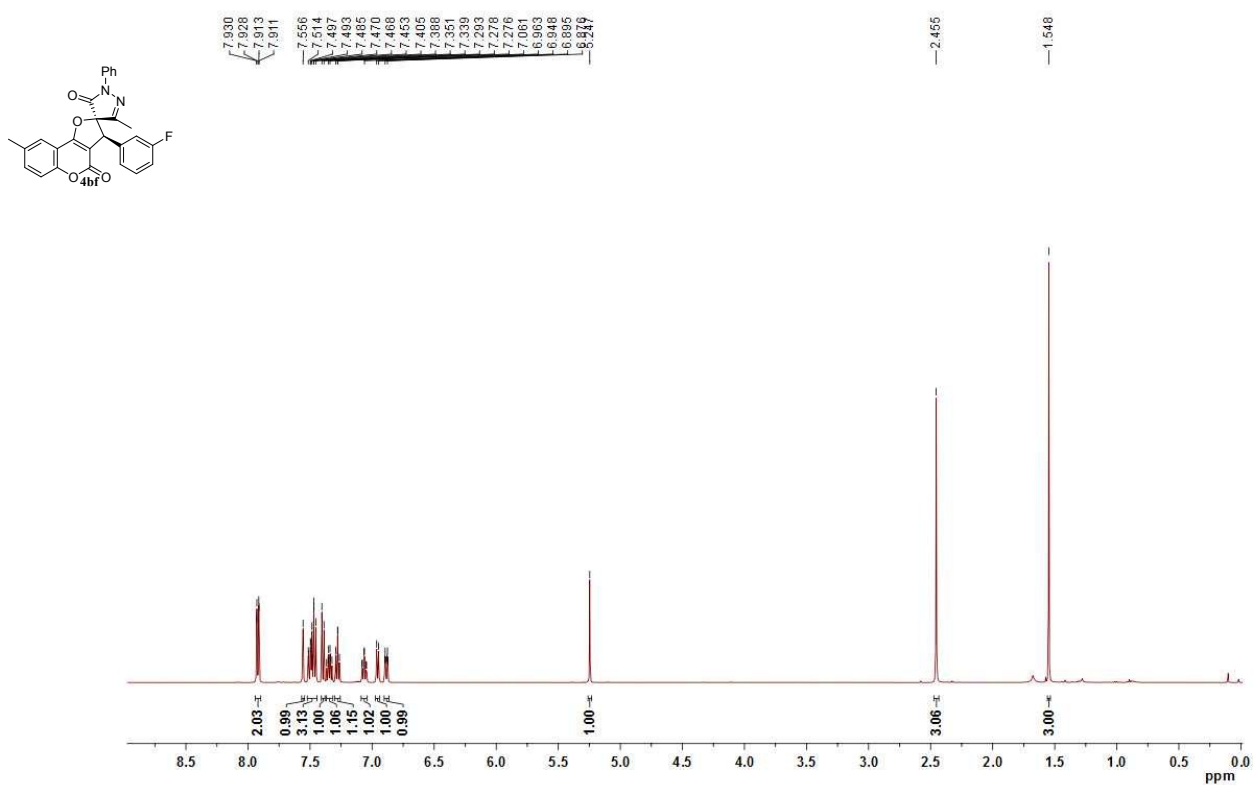
### HPLC chromatogram of 4be (chiral)



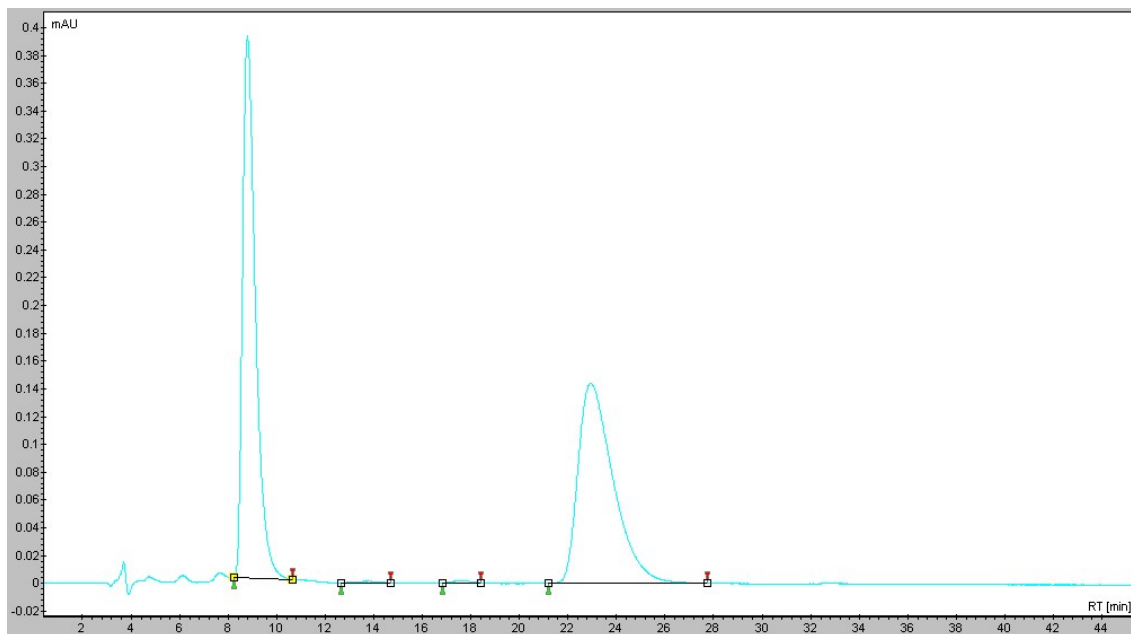
#	Start time[min]	Time[min]	End time[min]	Area%
1	8.116	8.453	9.130	99.692
2	12.255	12.572	12.572	0.308



# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4bf

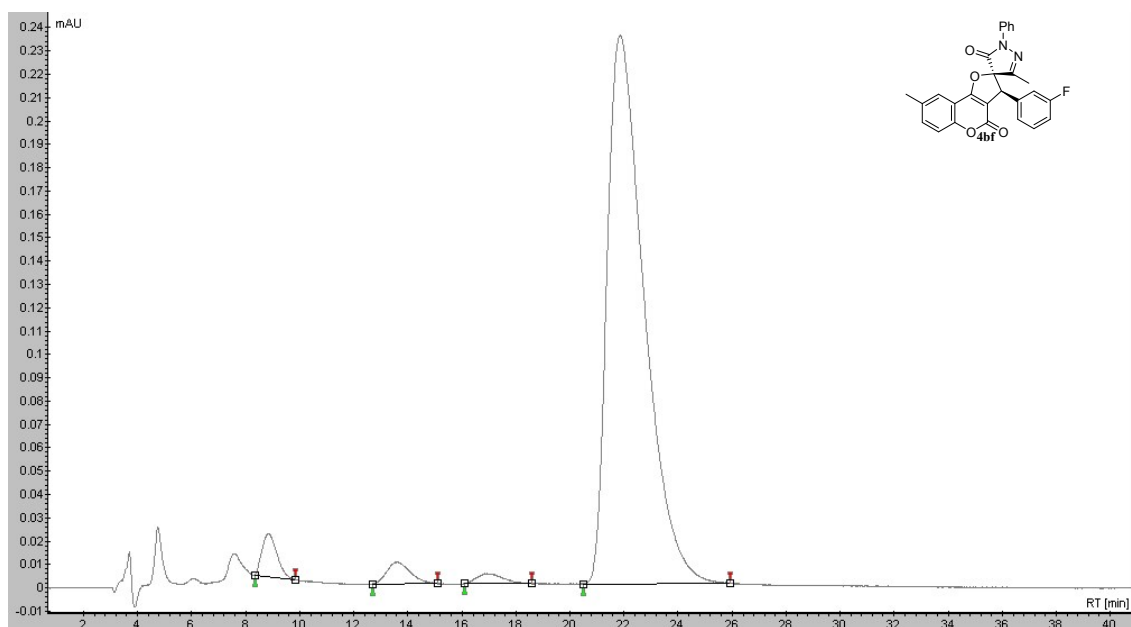


## HPLC chromatogram of 4bf (racemic)



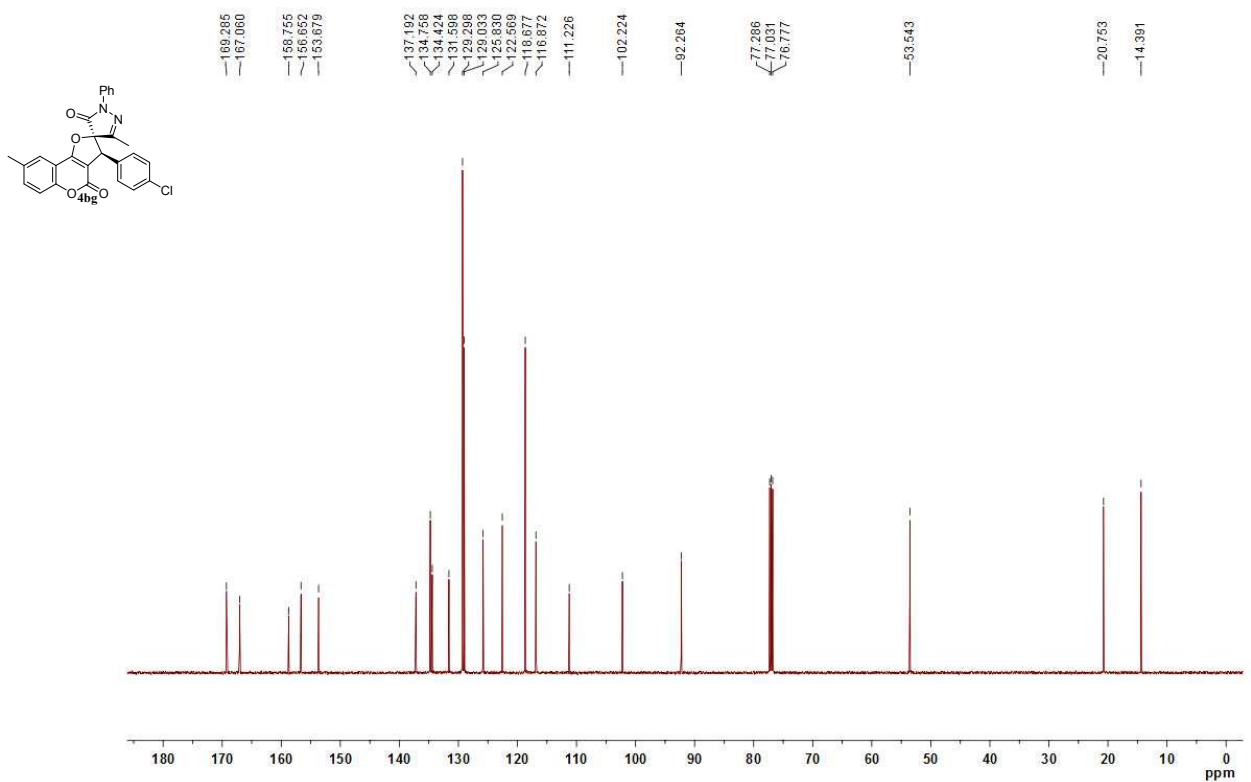
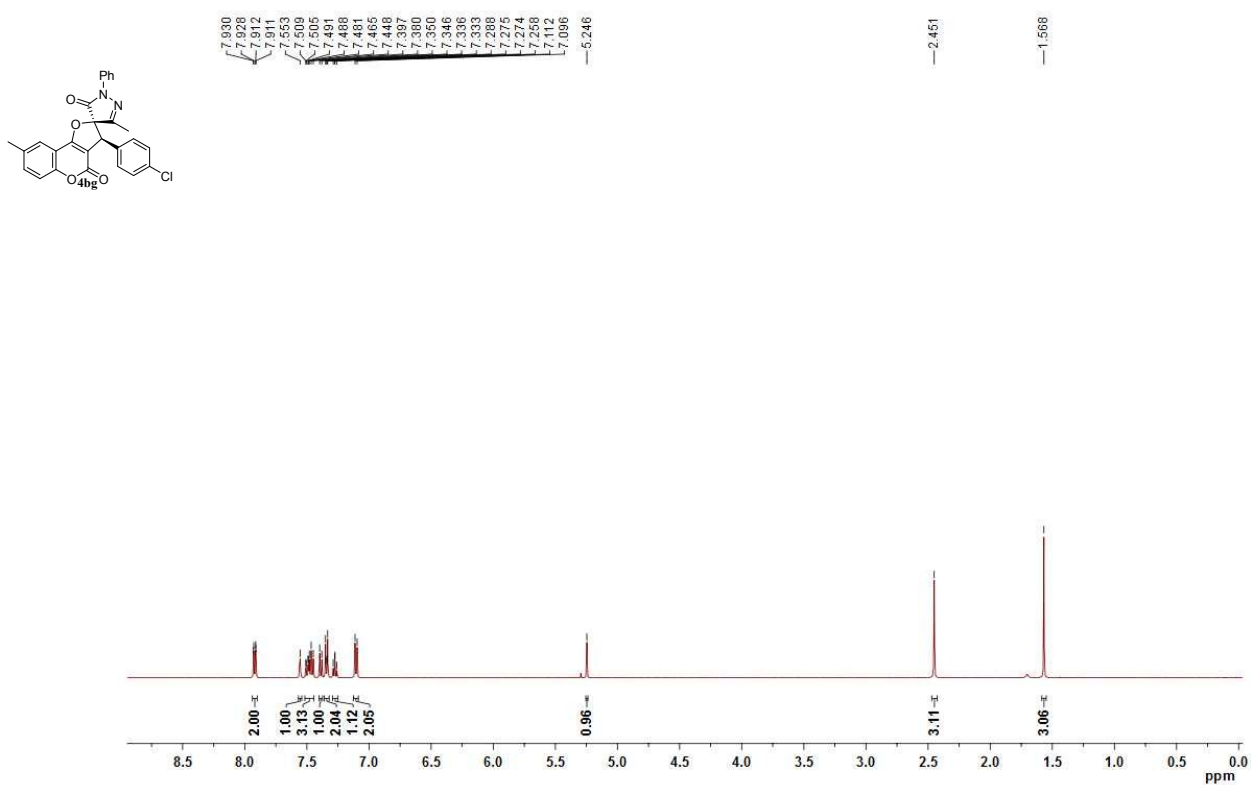
#	Start time[min]	Time[min]	End time[min]	Area%
1	8.244	8.797	10.638	49.767
2	12.657	13.782	14.700	0.251
3	16.836	17.554	18.414	0.256
4	21.210	22.965	27.725	49.727

## HPLC chromatogram of 4bf (chiral)

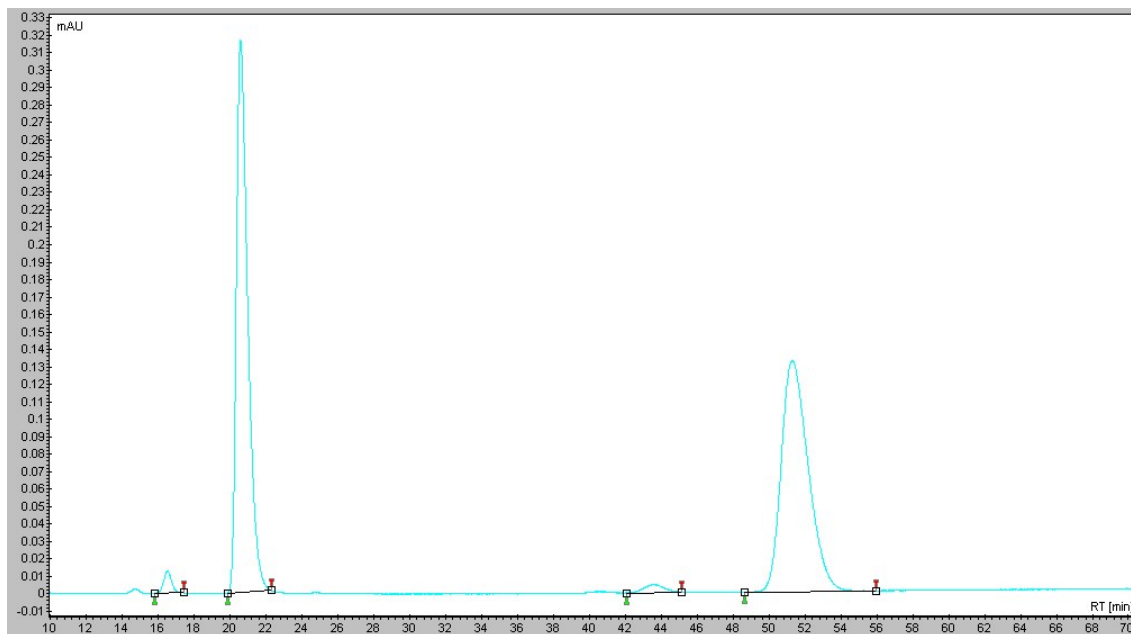


#	Start time[min]	Time[min]	End time[min]	Area%
1	8.333	8.839	9.856	2.957
2	12.690	13.599	15.101	2.342
3	16.116	16.972	18.612	1.188
4	20.516	21.865	25.930	93.513

# $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of 4bg

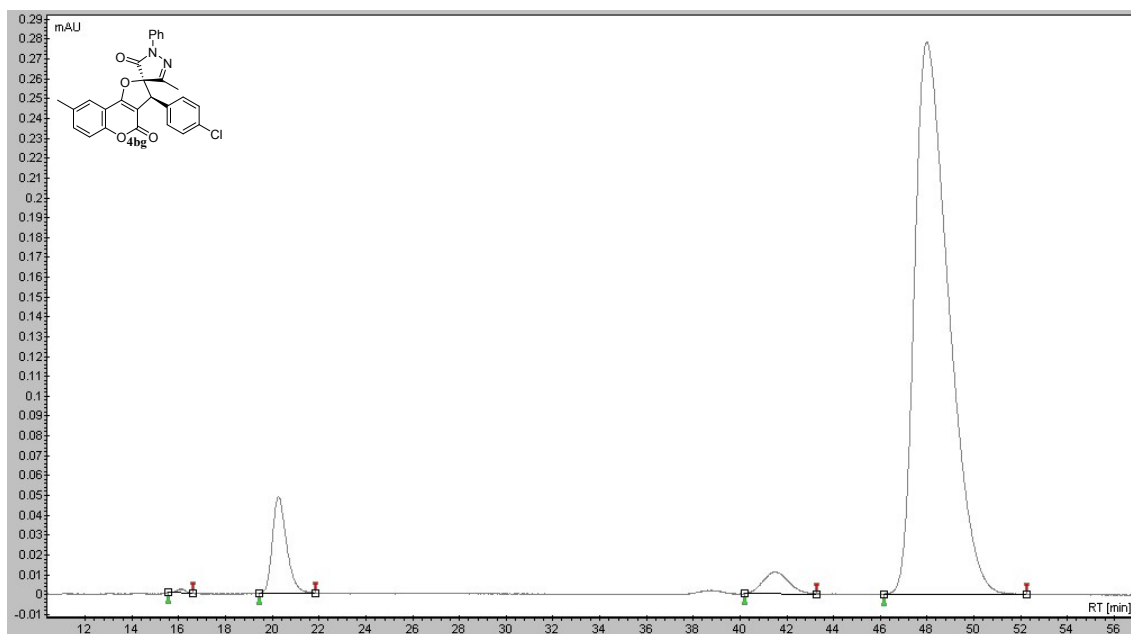


## HPLC chromatogram of 4bg (racemic)



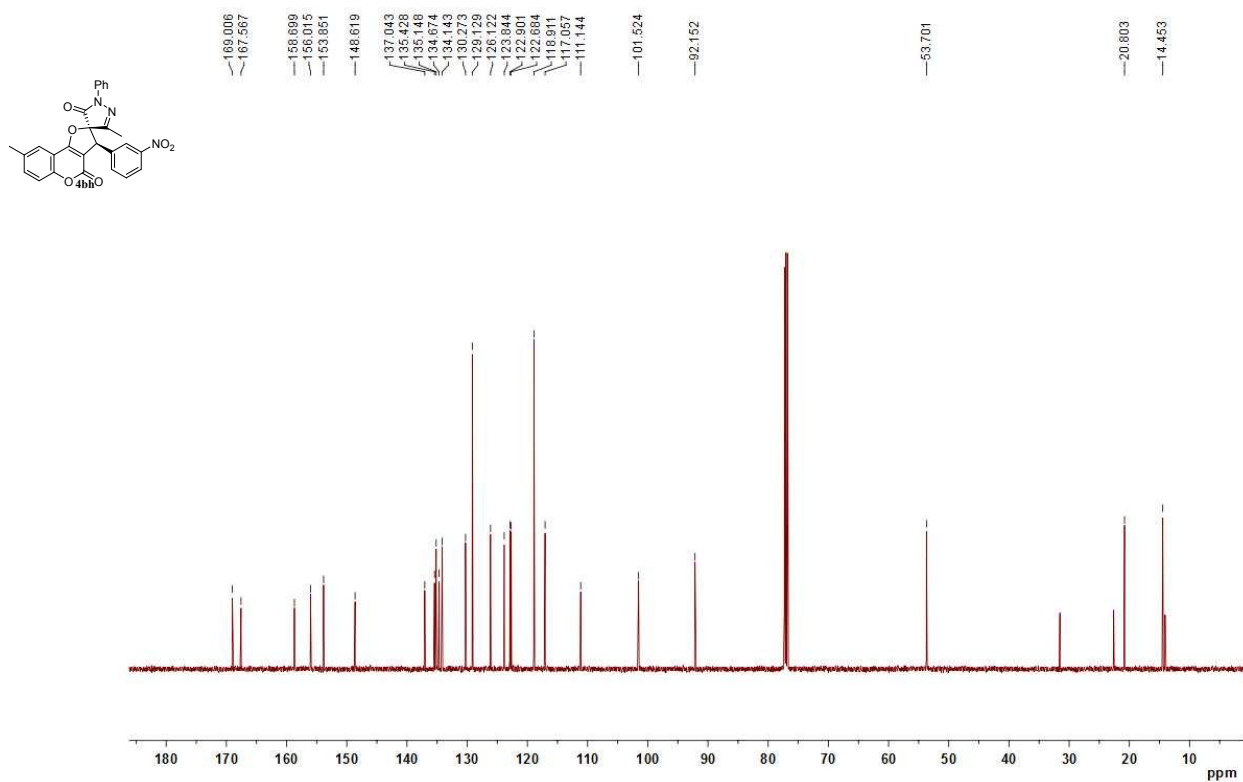
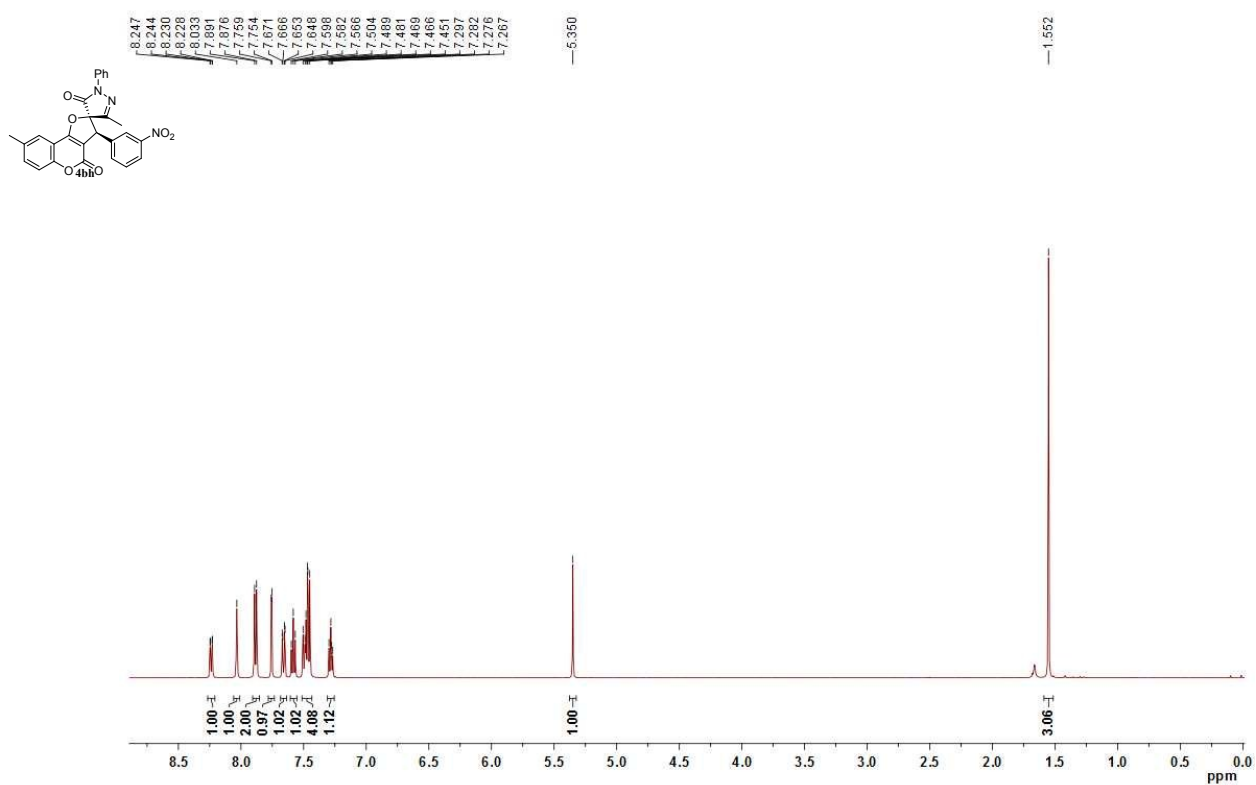
#	Start time[min]	Time[min]	End time[min]	Area%
1	15.793	16.501	17.418	1.373
2	19.855	20.566	22.291	48.934
3	42.056	43.544	45.124	1.287
4	48.644	51.302	55.954	48.407

## HPLC chromatogram of 4bg (chiral)

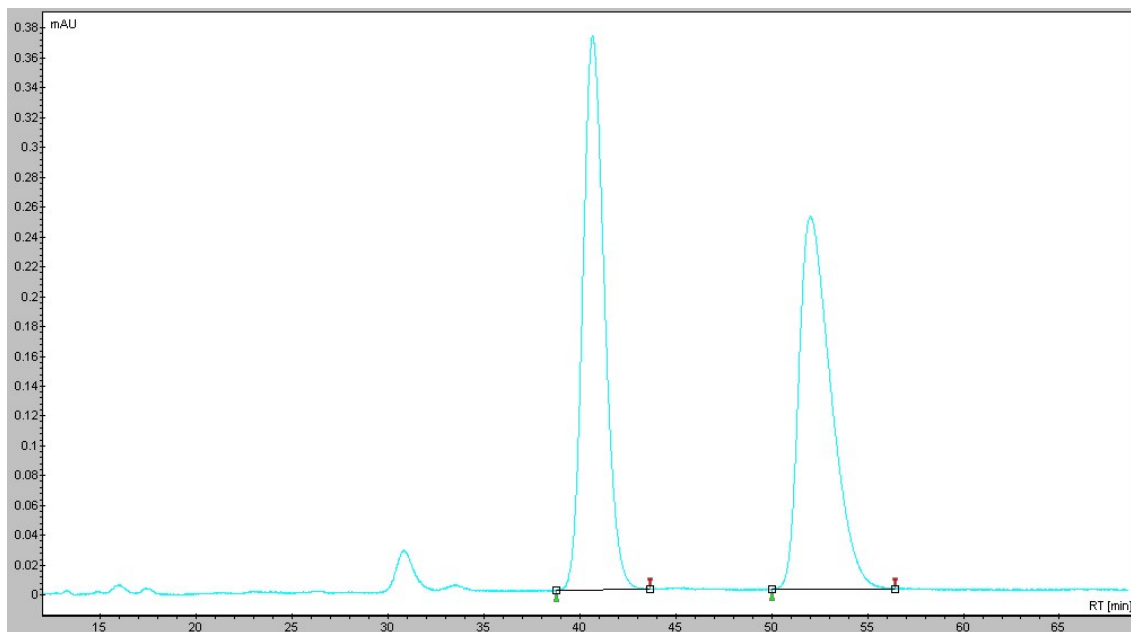


#	Start time[min]	Time[min]	End time[min]	Area%
1	15.542	16.092	16.601	0.166
2	19.427	20.265	21.841	6.596
3	40.209	41.504	43.270	2.706
4	46.154	47.983	52.277	90.531

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4bh

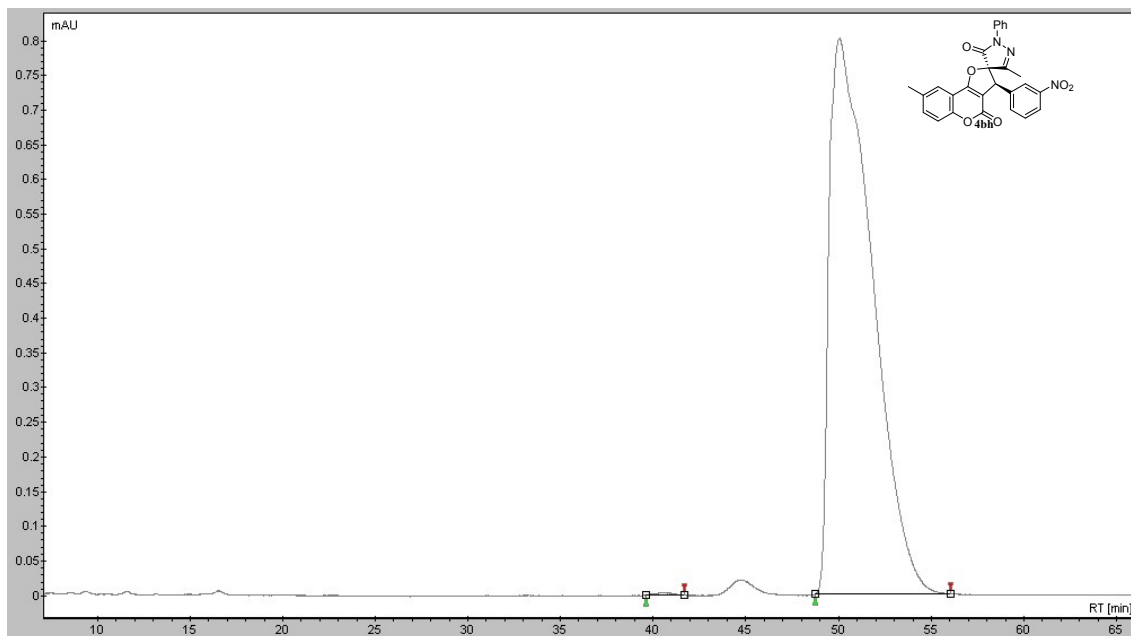


### HPLC chromatogram of 4bh (racemic)



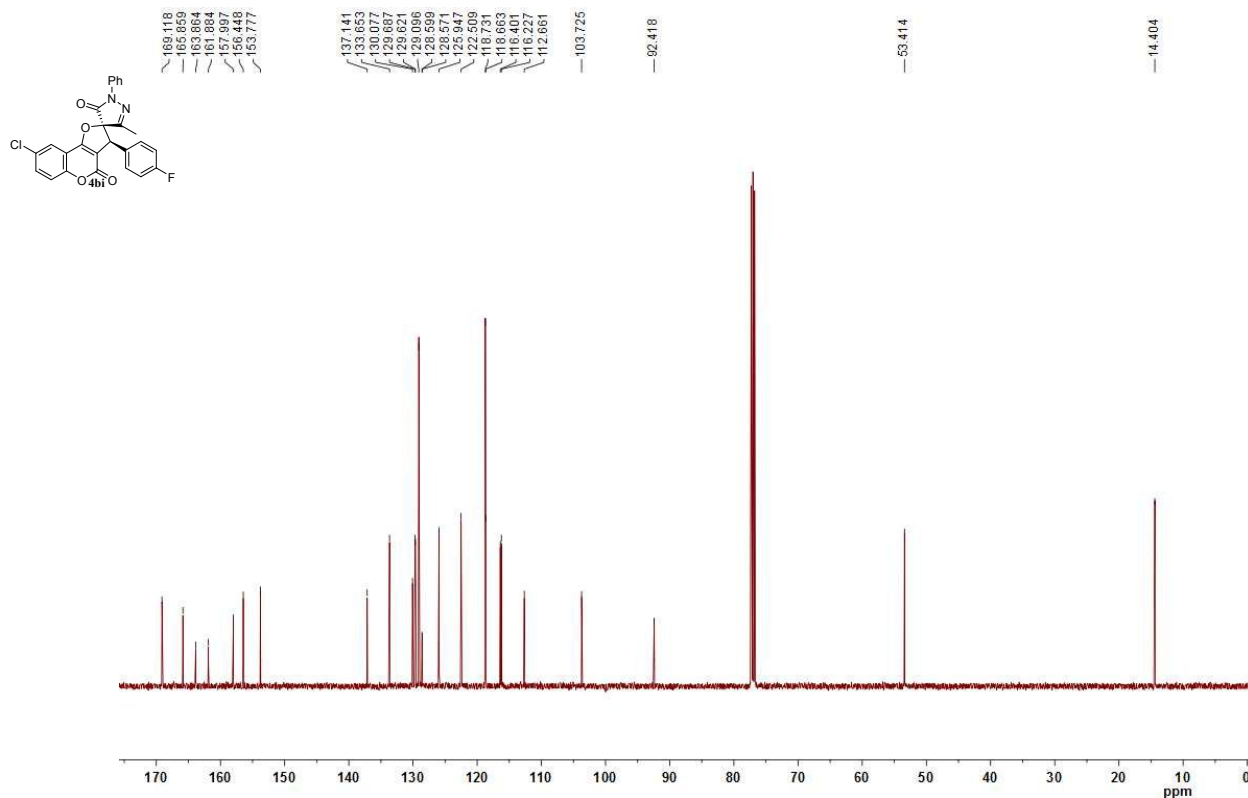
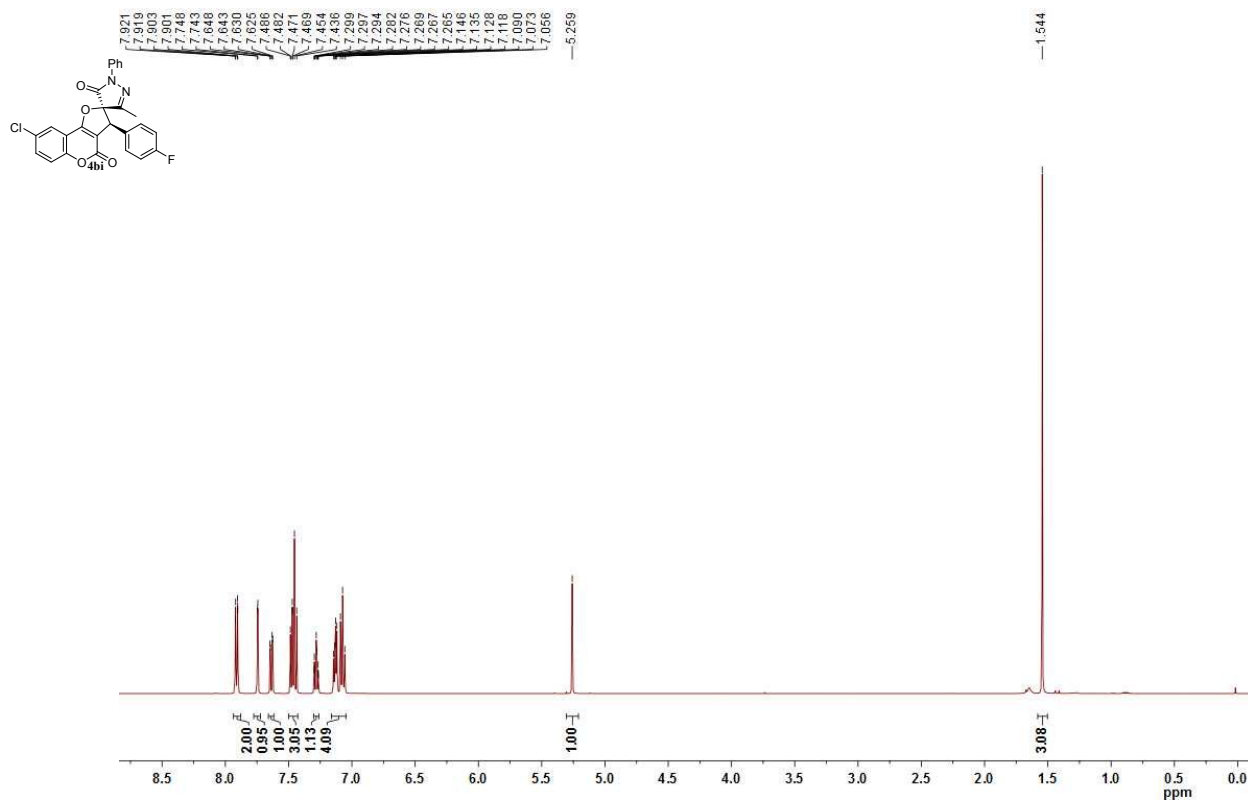
#	Start time[min]	Time[min]	End time[min]	Area%
1	38.772	40.639	43.663	50.074
2	50.042	52.021	56.422	49.926

### HPLC chromatogram of 4bh (chiral)

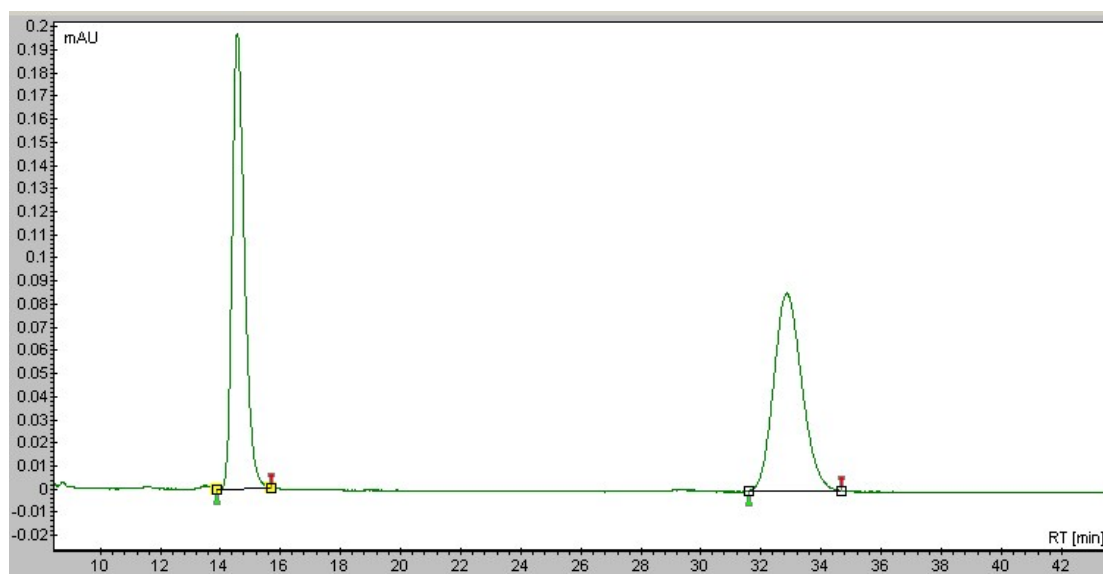


#	Start time[min]	Time[min]	End time[min]	Area%
1	39.607	40.572	41.684	0.200
2	48.747	50.062	56.086	99.800

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4bi

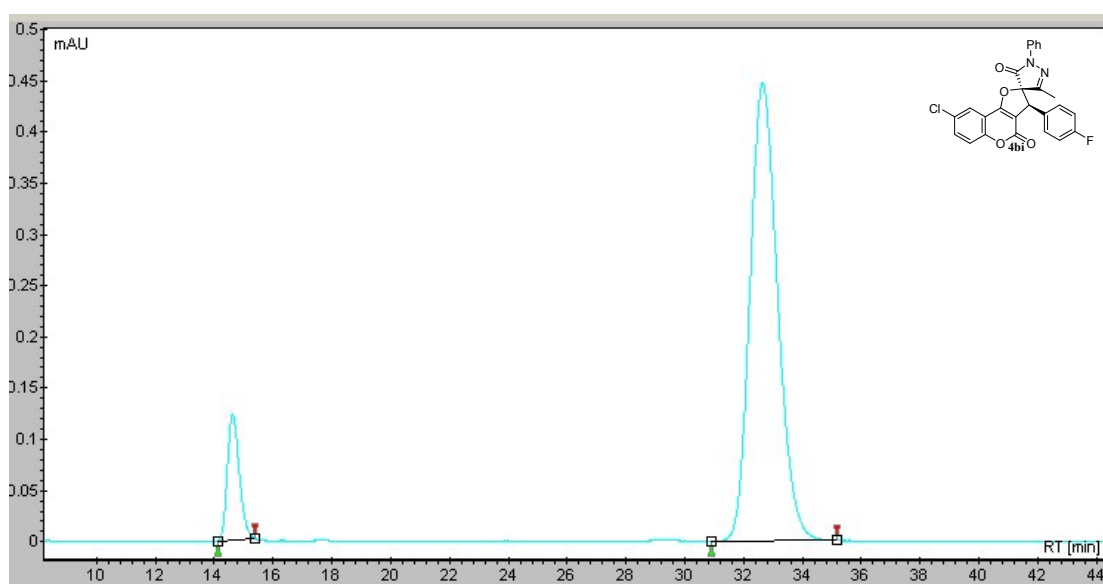


### HPLC chromatogram of 4bi (racemic)



#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	13.897	14.568	15.676	50.145
2	31.575	32.855	34.688	49.855

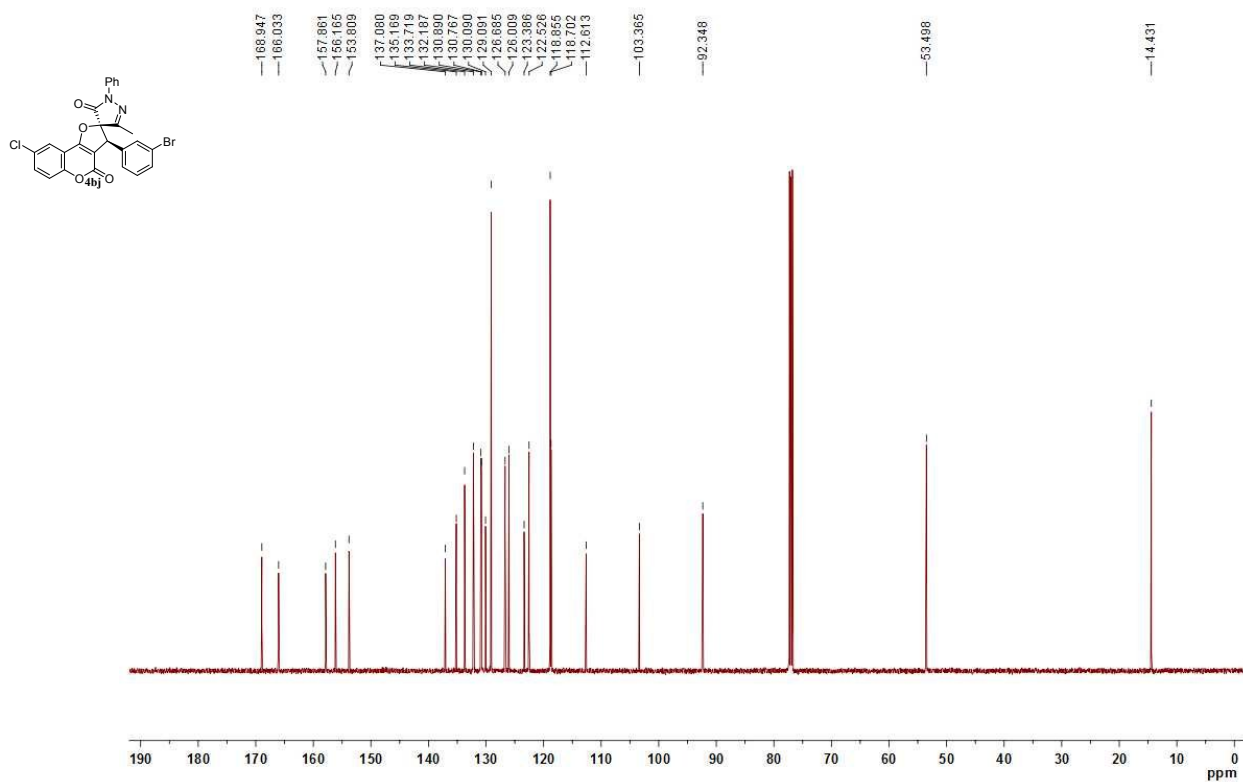
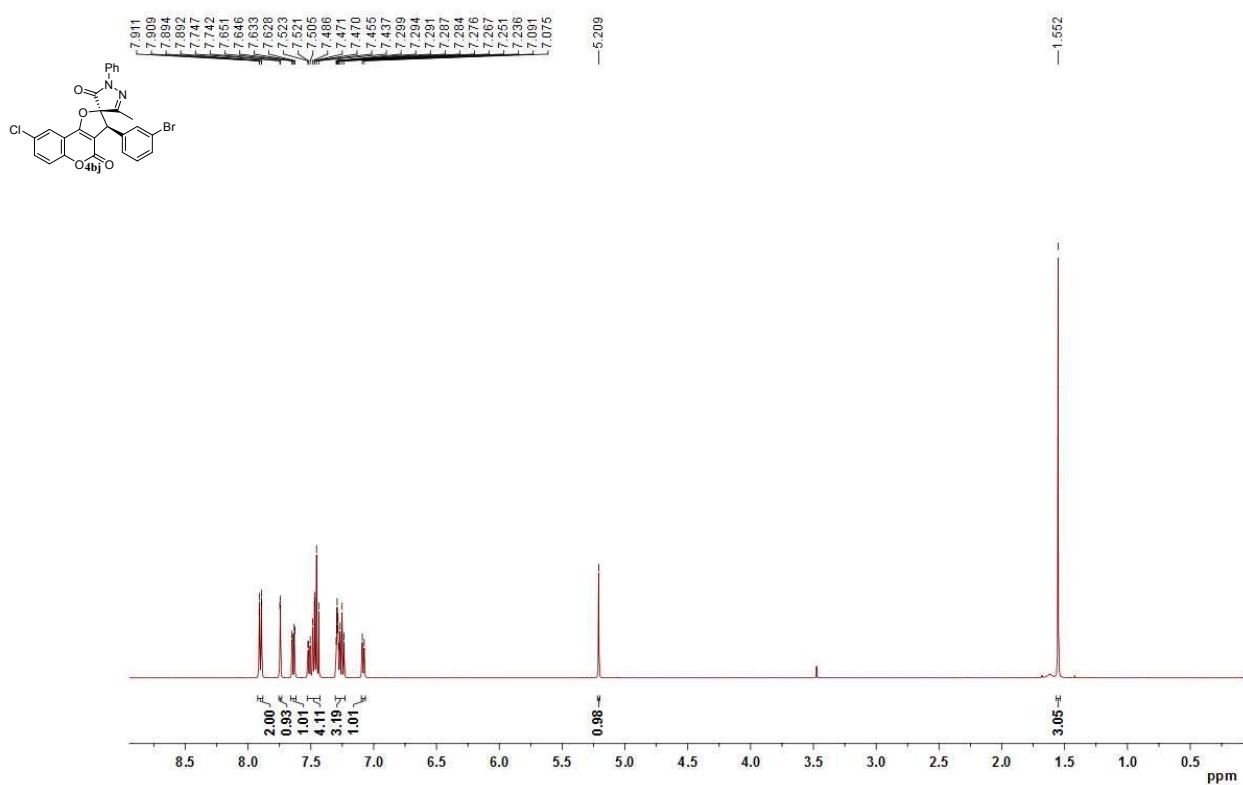
### HPLC chromatogram of 4bi (chiral)



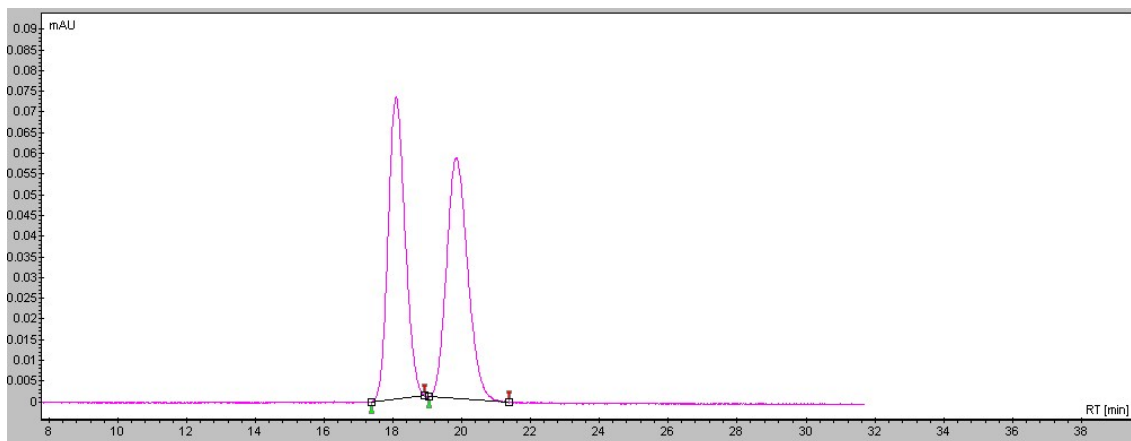
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	14.117	14.626	15.361	10.532
2	30.909	32.651	35.2	89.468



# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 4bj

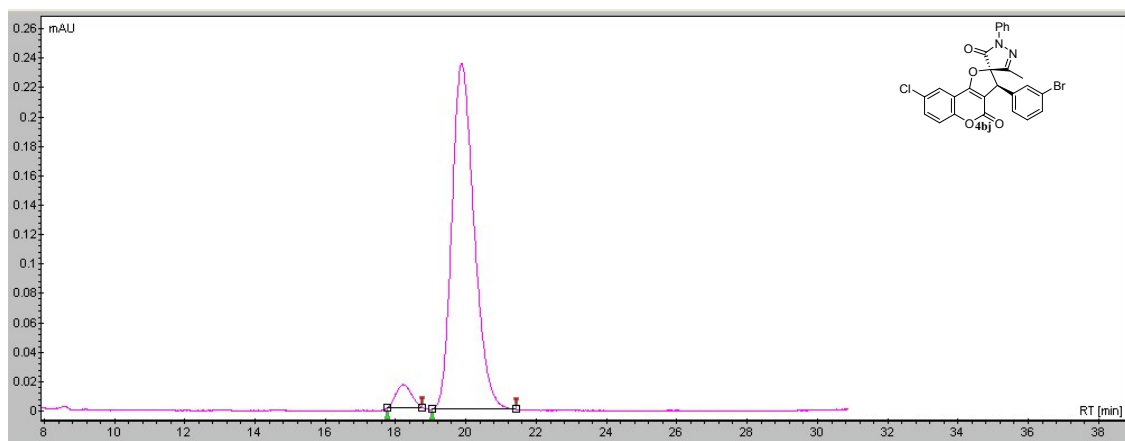


### HPLC chromatogram of 4bj (racemic)



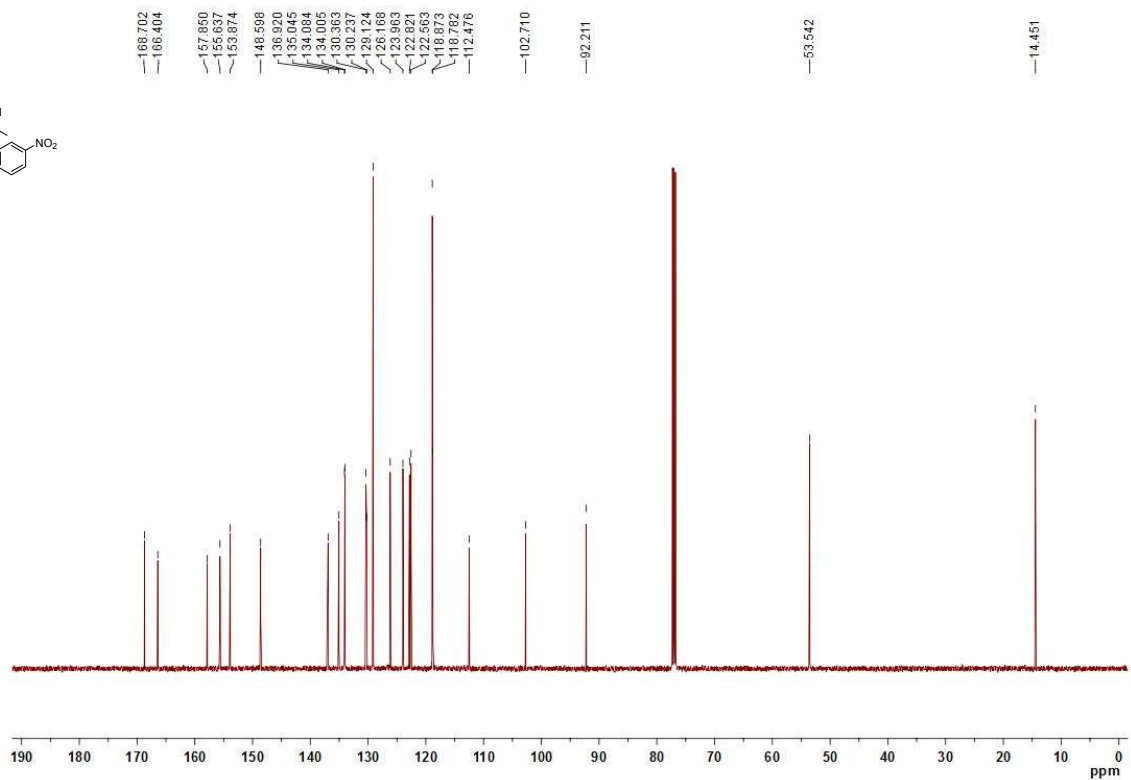
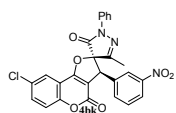
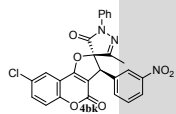
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	17.367	18.079	18.907	49.901
2	19.039	19.825	21.365	50.099

### HPLC chromatogram of 4bj (chiral)

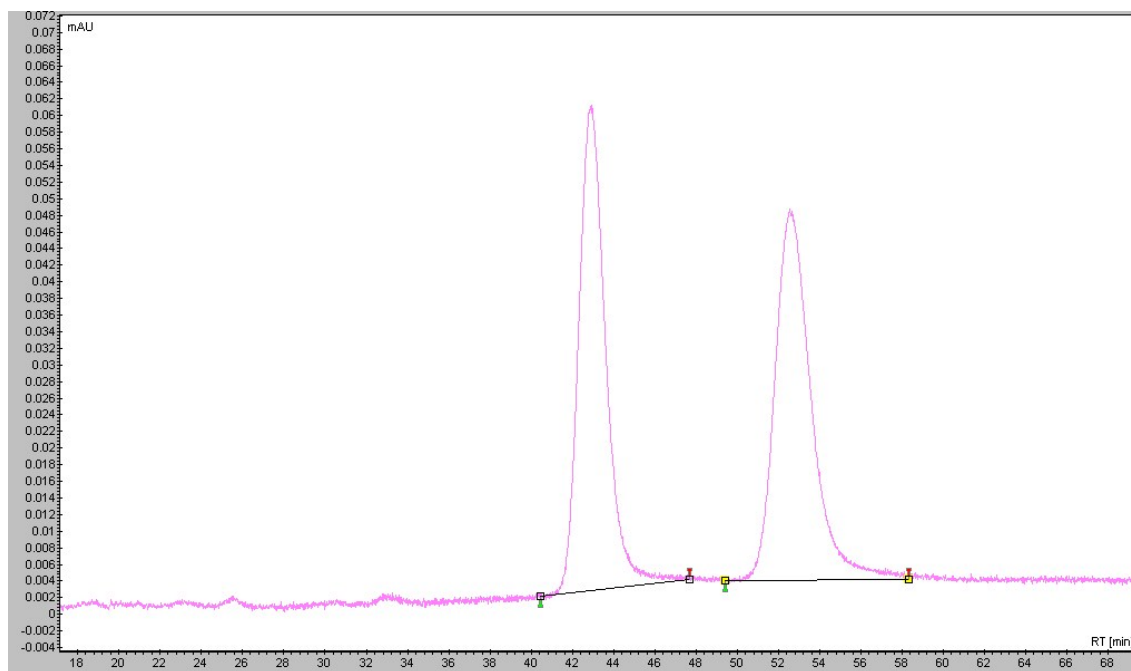


#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	17.761	18.212	18.75	4.461
2	19.037	19.879	21.428	95.539

# $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of 4bk

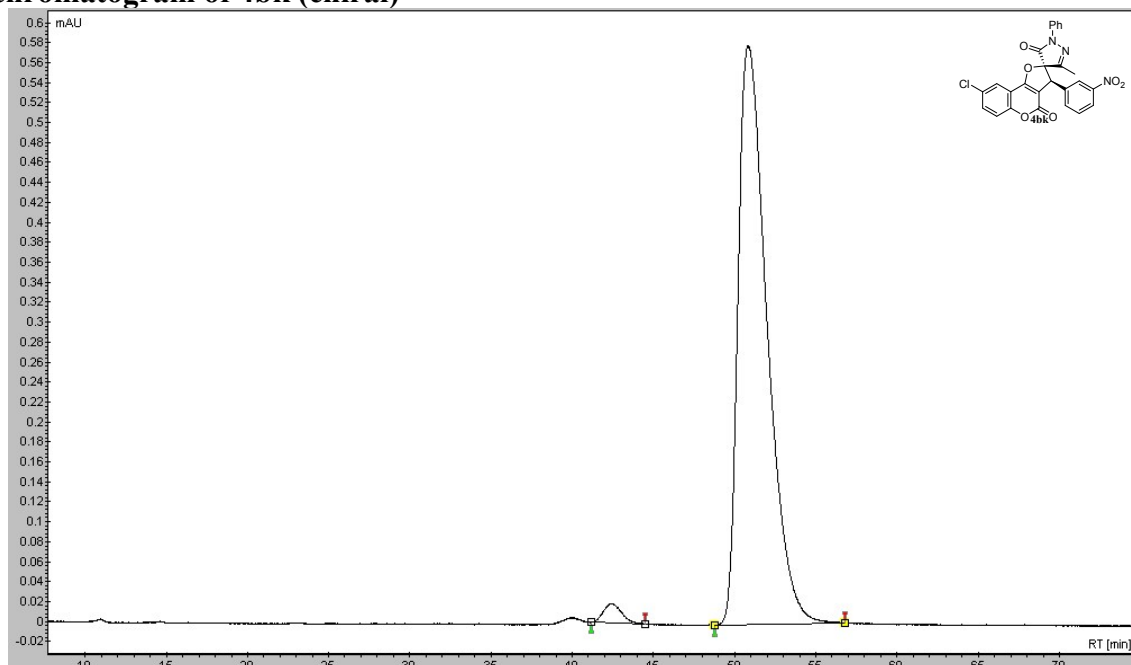


## HPLC chromatogram of 4bk (racemic)



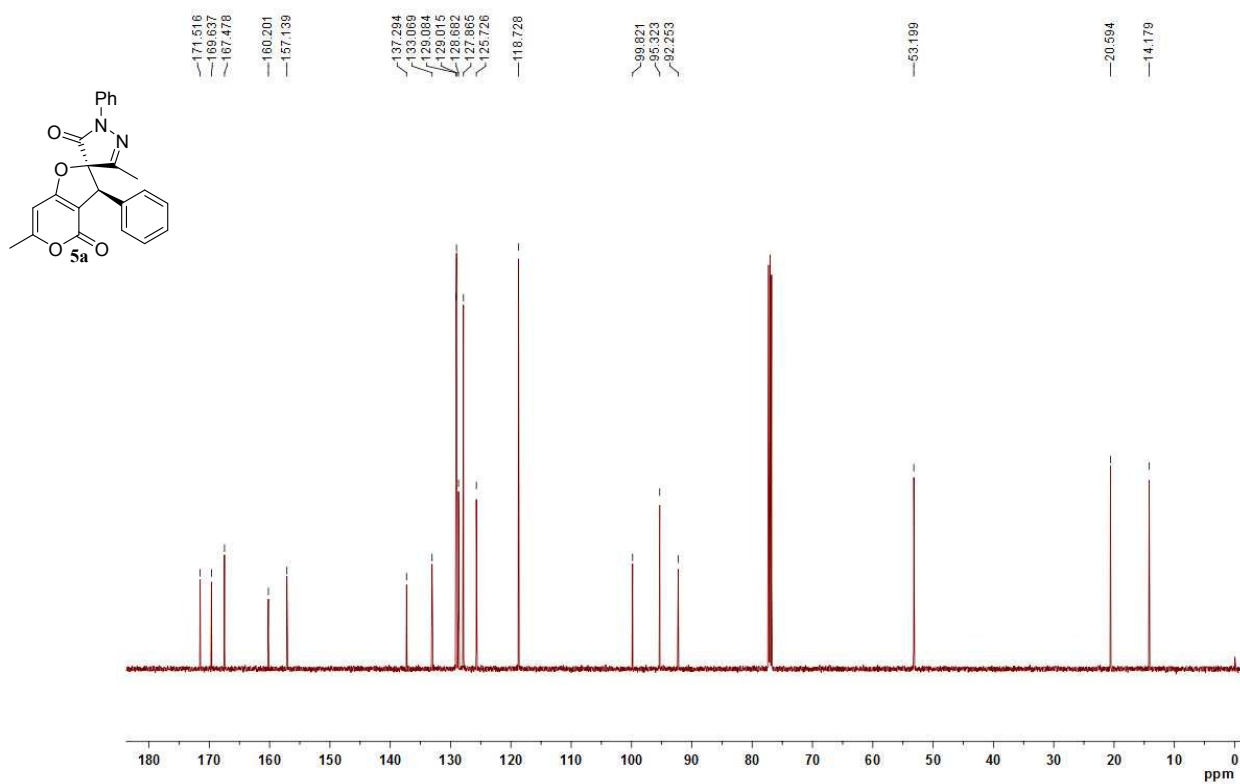
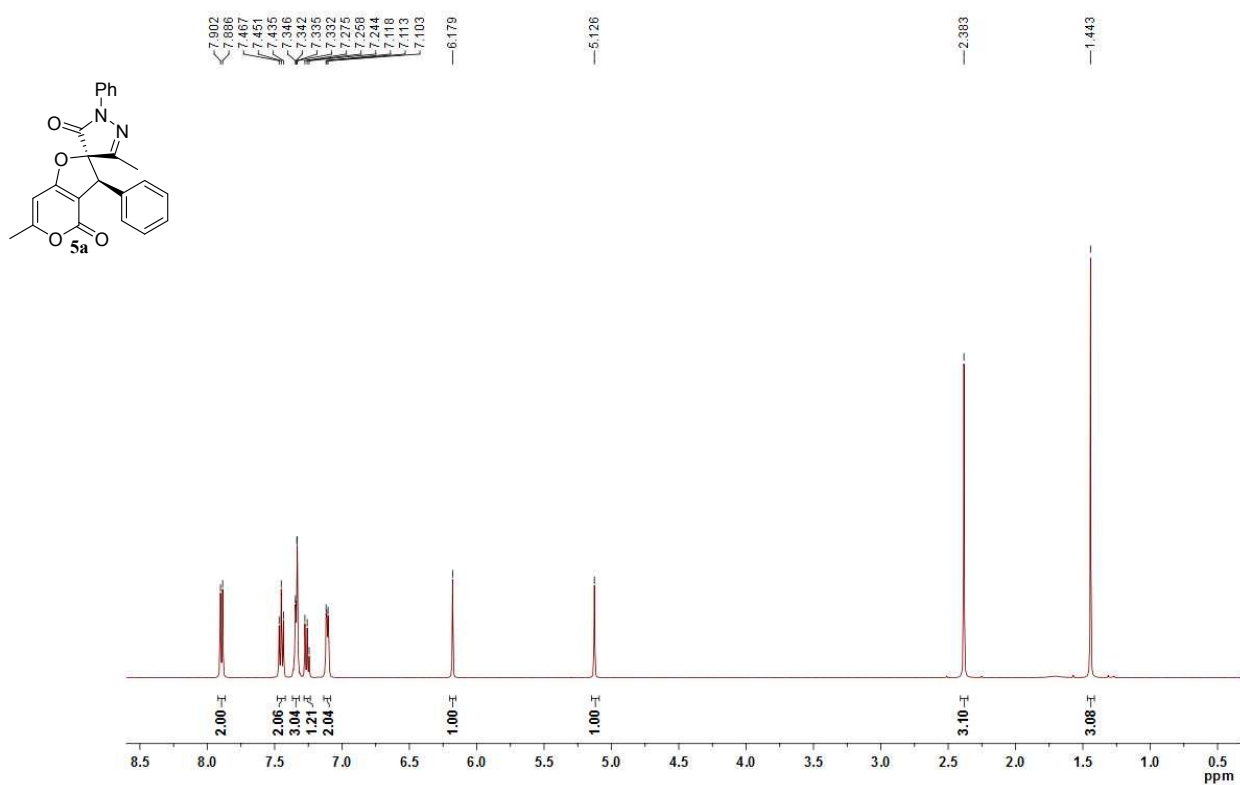
#	Start time[min]	Time[min]	End time[min]	Area%
1	40.473	42.905	47.700	49.293
2	49.435	52.581	58.324	50.707

## HPLC chromatogram of 4bk (chiral)

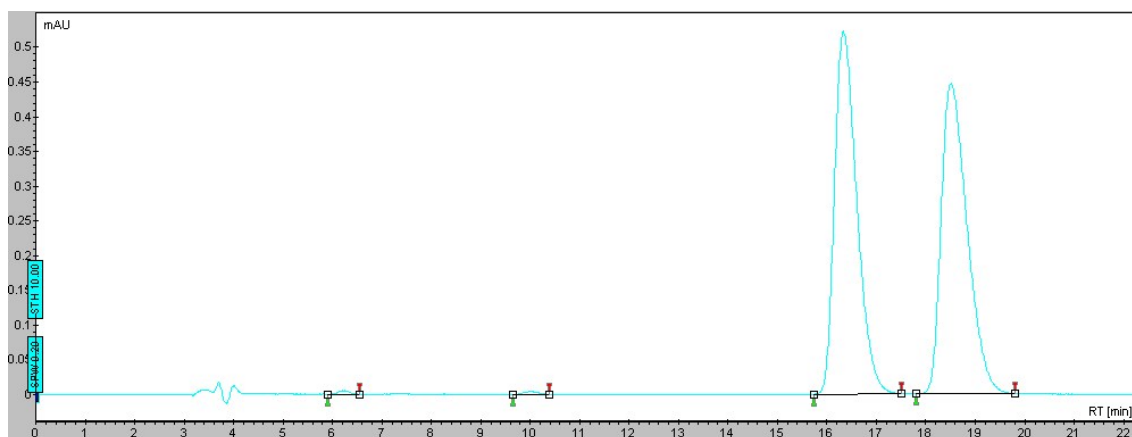


#	Start time[min]	Time[min]	End time[min]	Area%
1	41.150	42.478	44.455	2.059
2	48.762	50.795	56.767	97.941

# $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of 5a

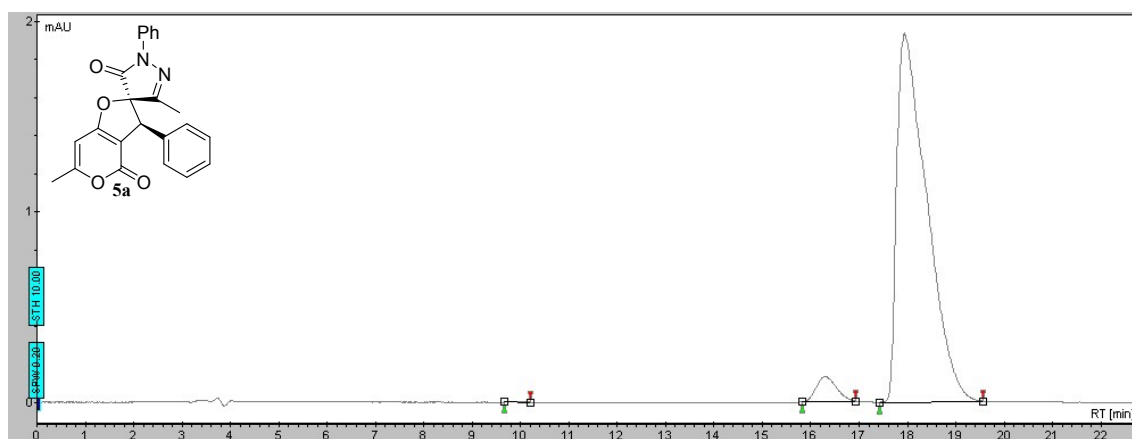


### HPLC chromatogram of 5a (racemic)



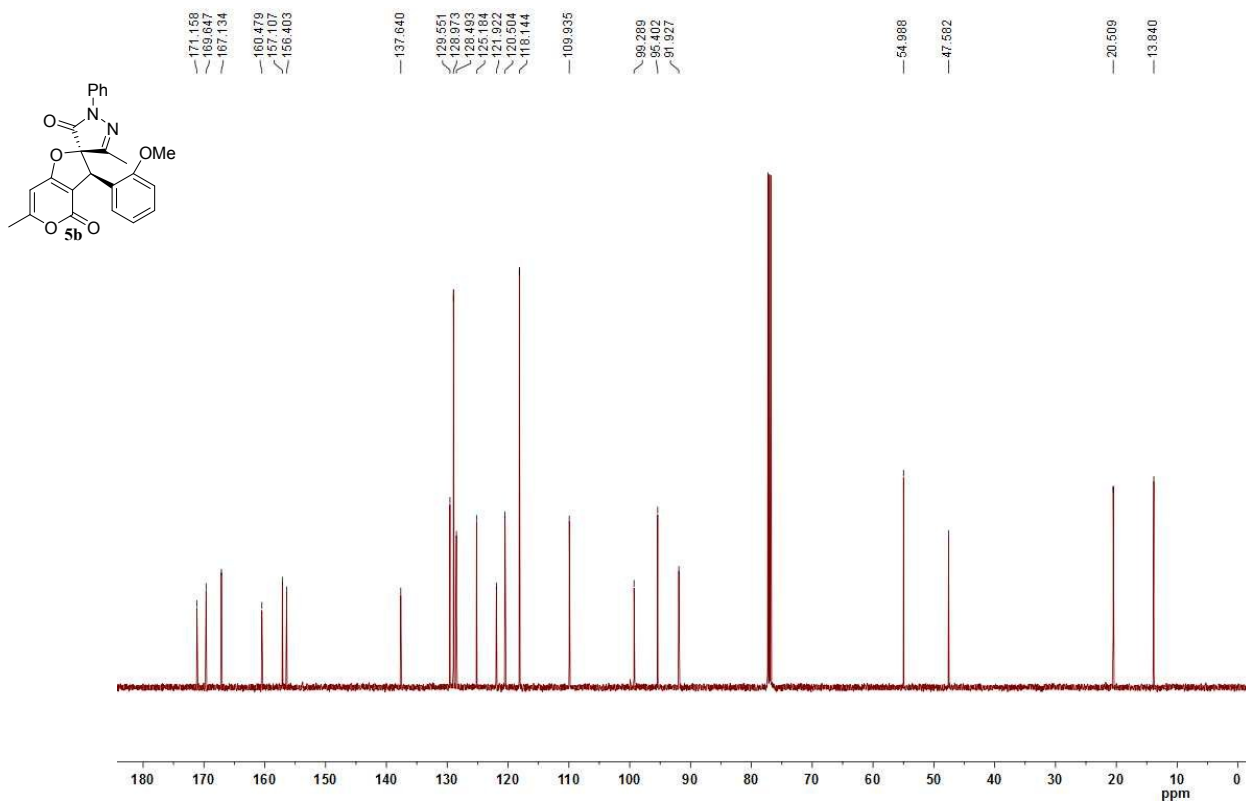
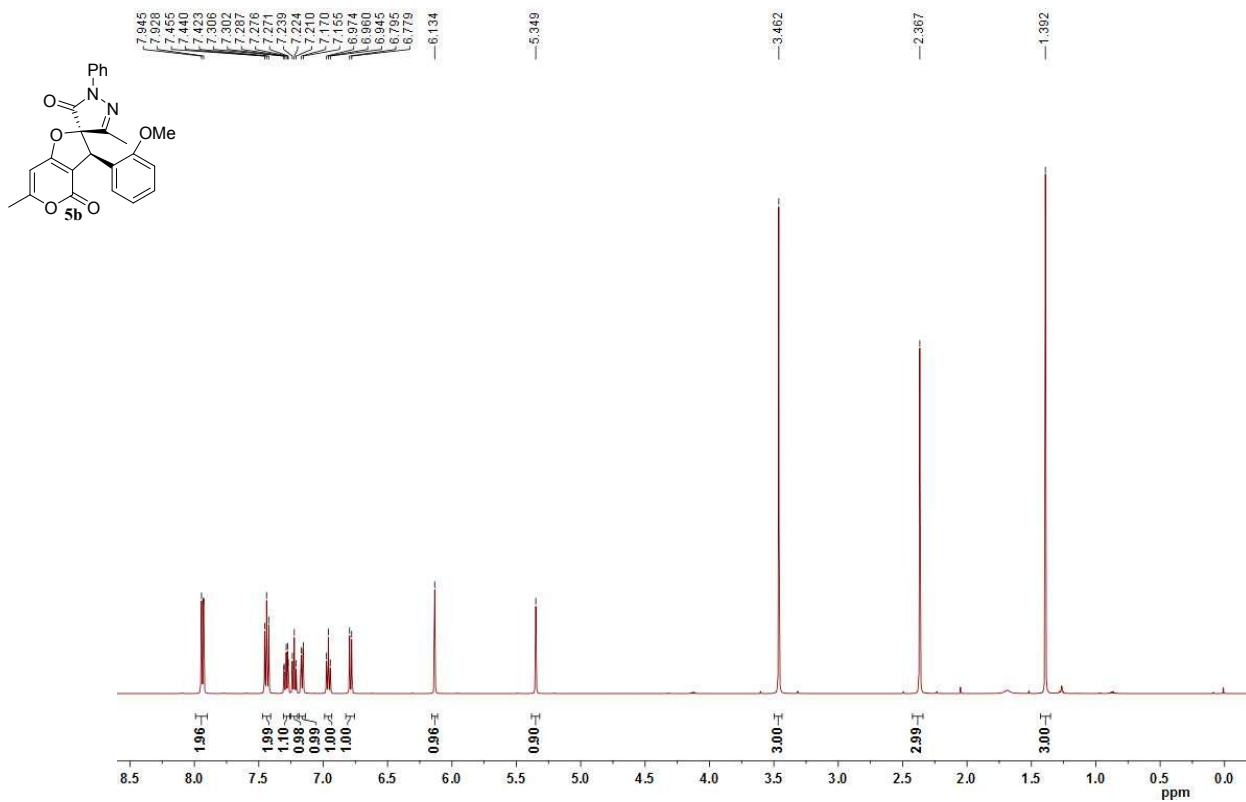
#	Start time[min]	Time[min]	End time[min]	Area%
1	5.905	6.213	6.548	0.24
2	9.65	9.999	10.385	0.239
3	15.738	16.332	17.507	49.822
4	17.806	18.505	19.805	49.7

### HPLC chromatogram of 5a (chiral)

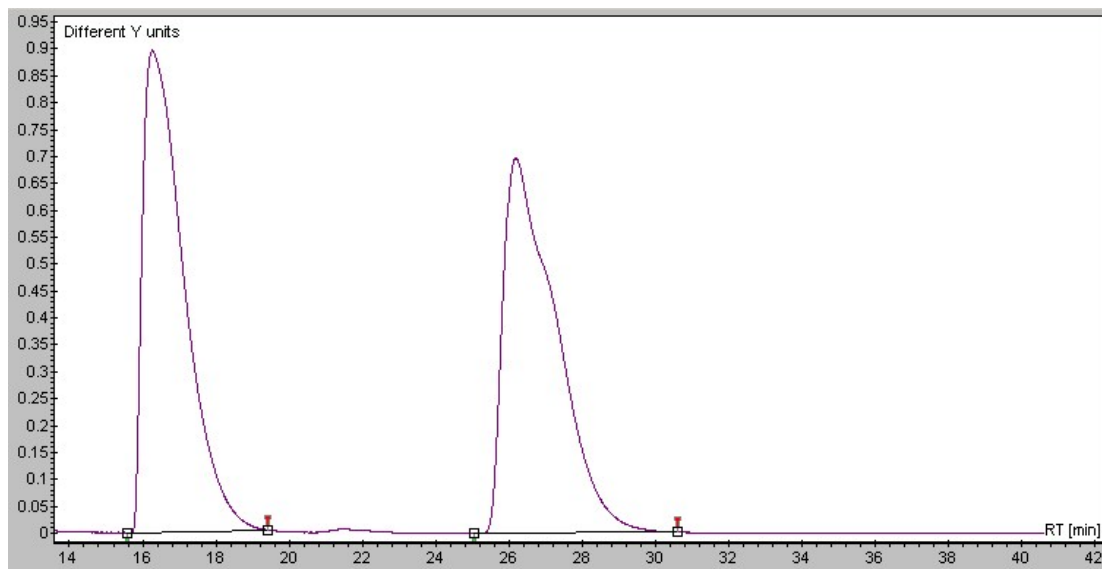


#	Start time[min]	Time[min]	End time[min]	Area%
1	9.664	9.879	10.204	0.026
2	15.824	16.292	16.929	4.363
3	17.423	17.932	19.562	95.611

# $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of 5b

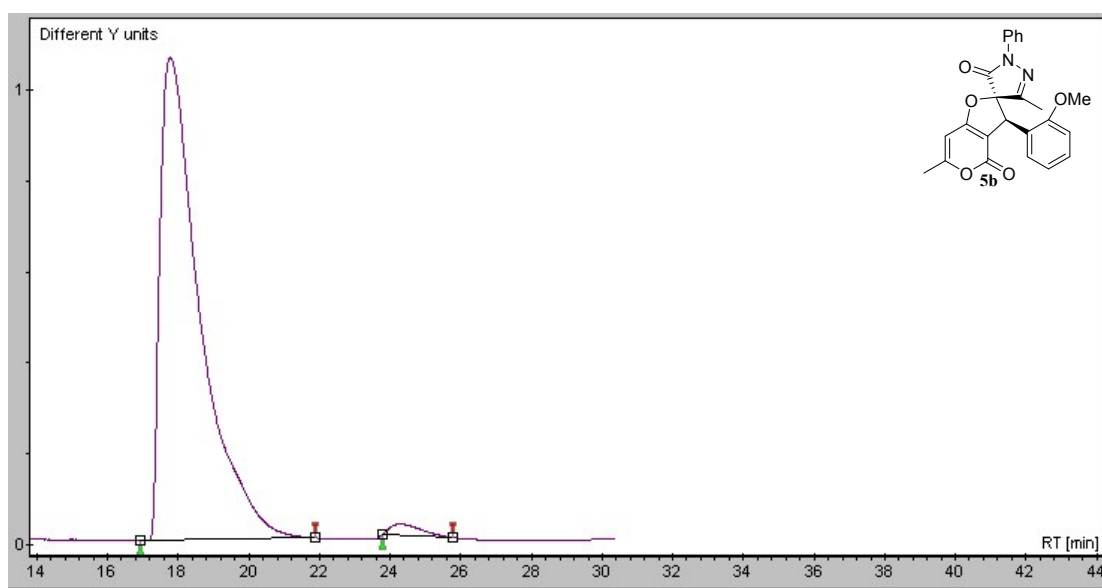


### HPLC chromatogram of 5b (racemic)



#	Start time[min]	Time[min]	End time[min]	Area%
1	15.56	16.252	19.408	50.314
2	25.066	26.185	30.611	49.686

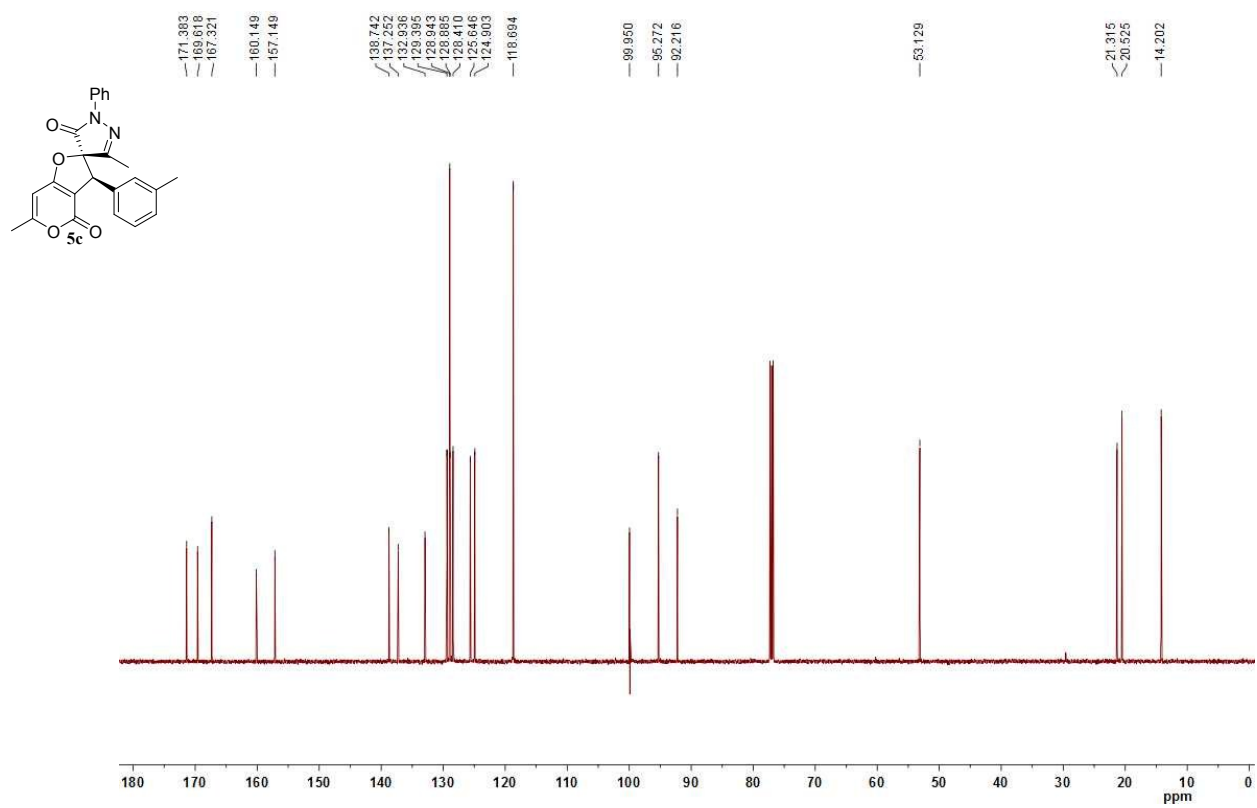
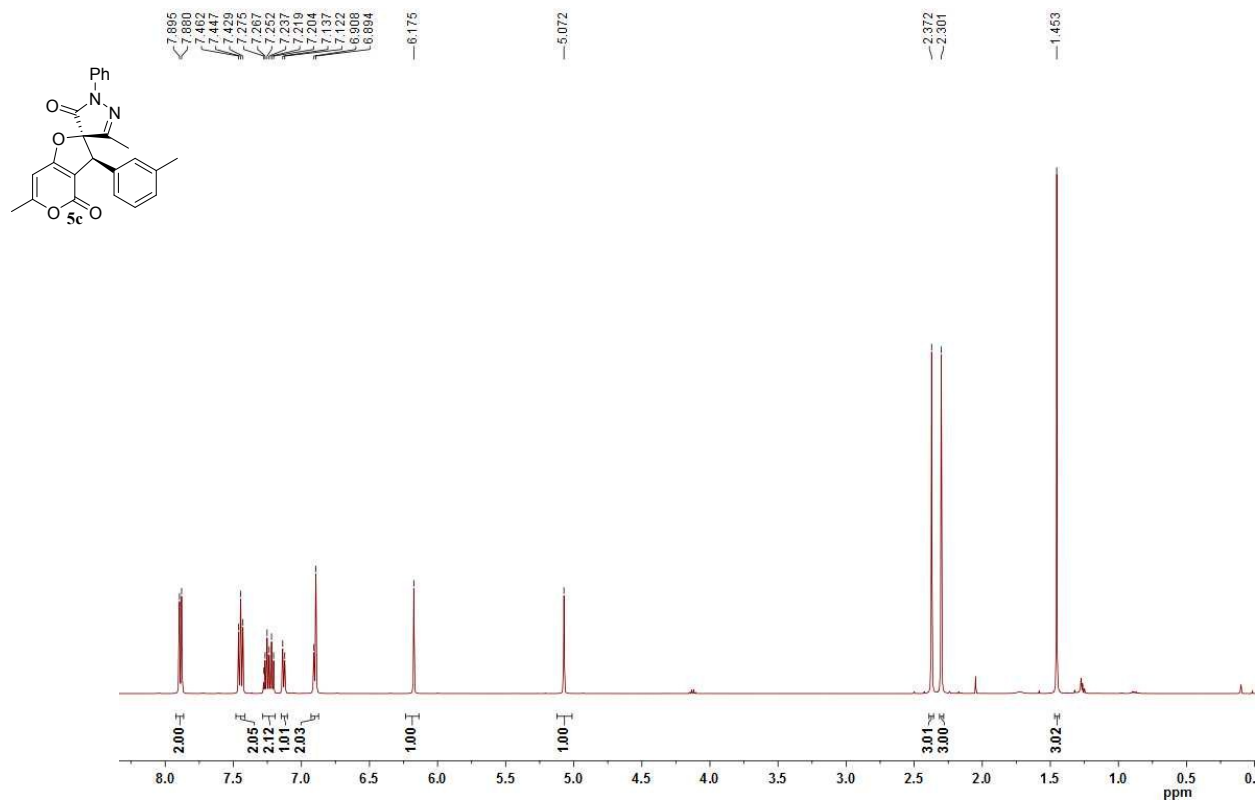
### HPLC chromatogram of 5b (chiral)



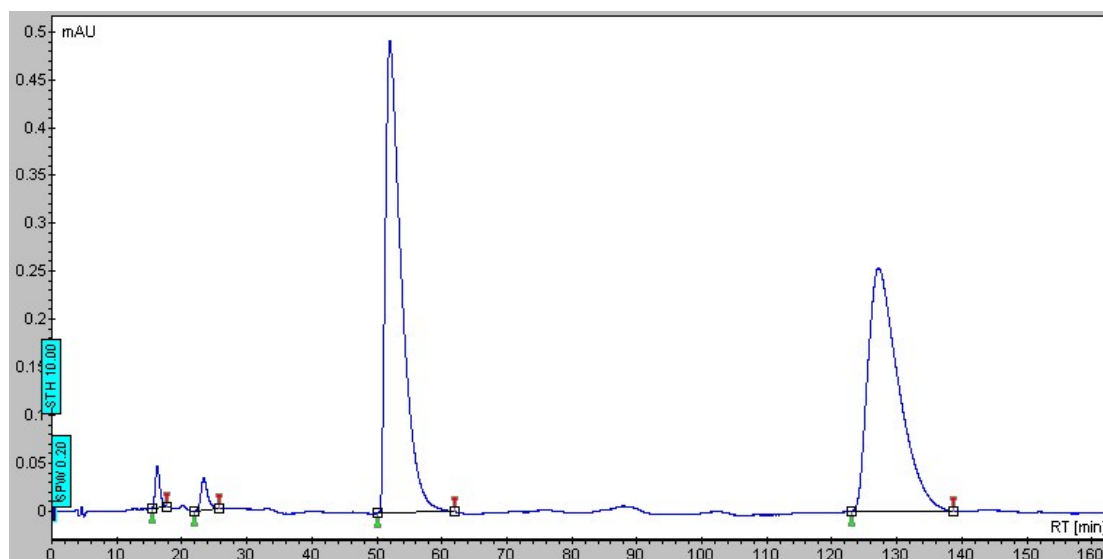
#	Start time[min]	Time[min]	End time[min]	Area%
1	16.929	17.772	21.88	98.221
2	23.785	24.305	25.774	1.779



# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 5c

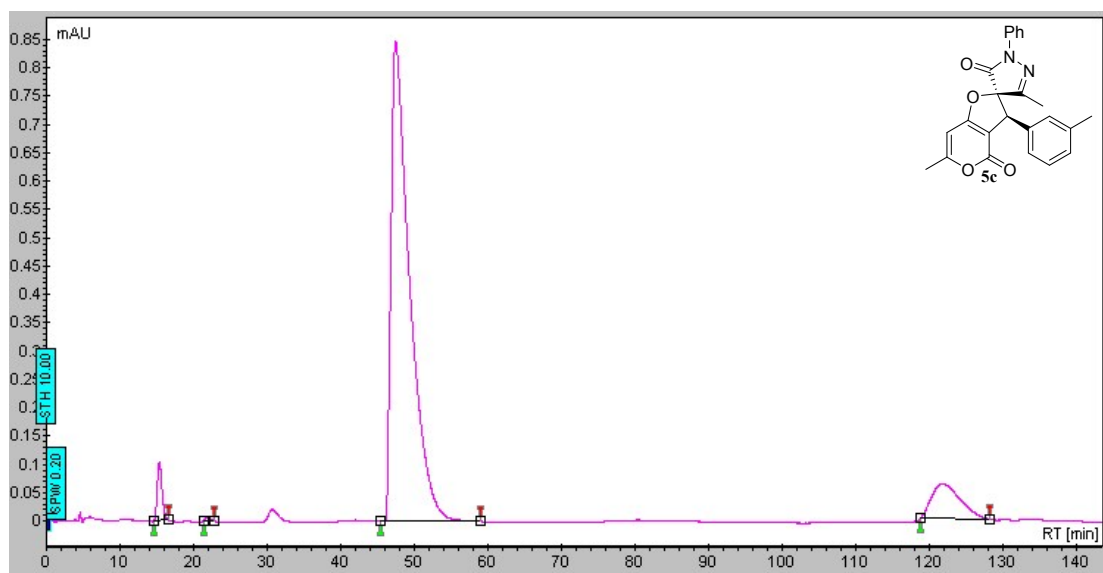


### HPLC chromatogram of 5c (racemic)



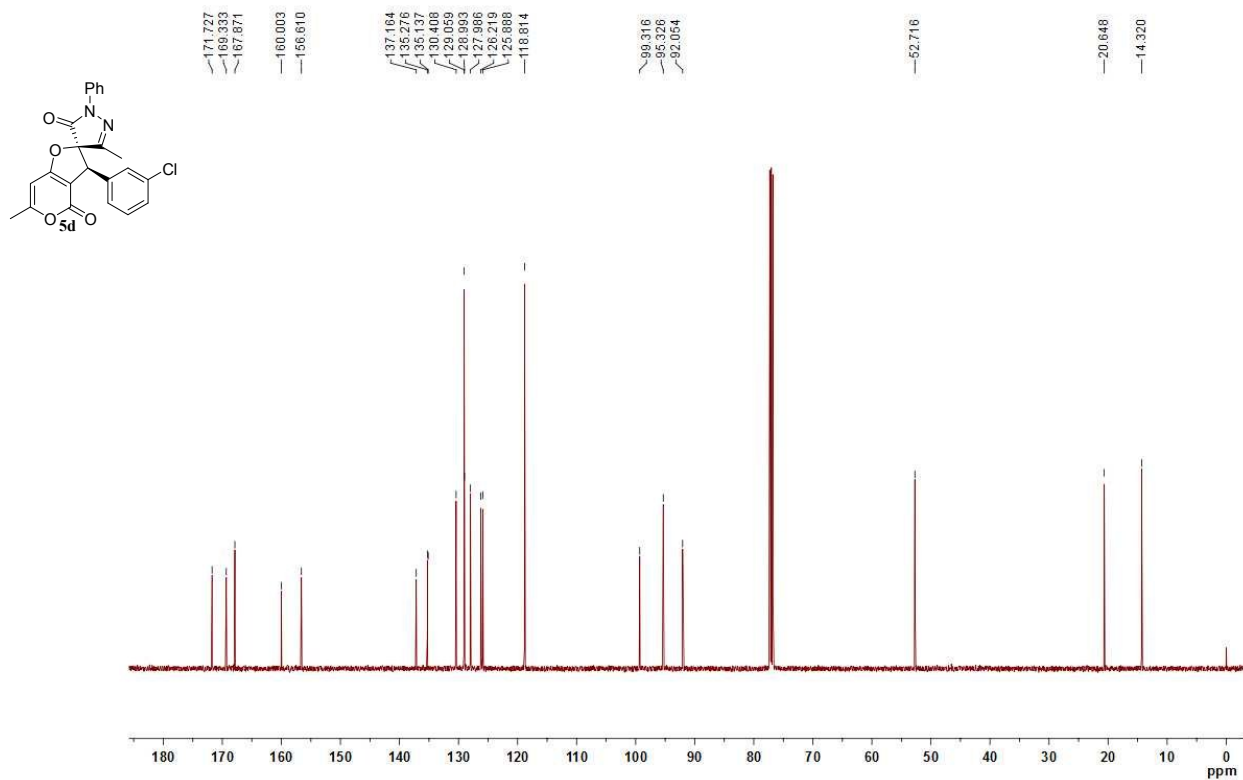
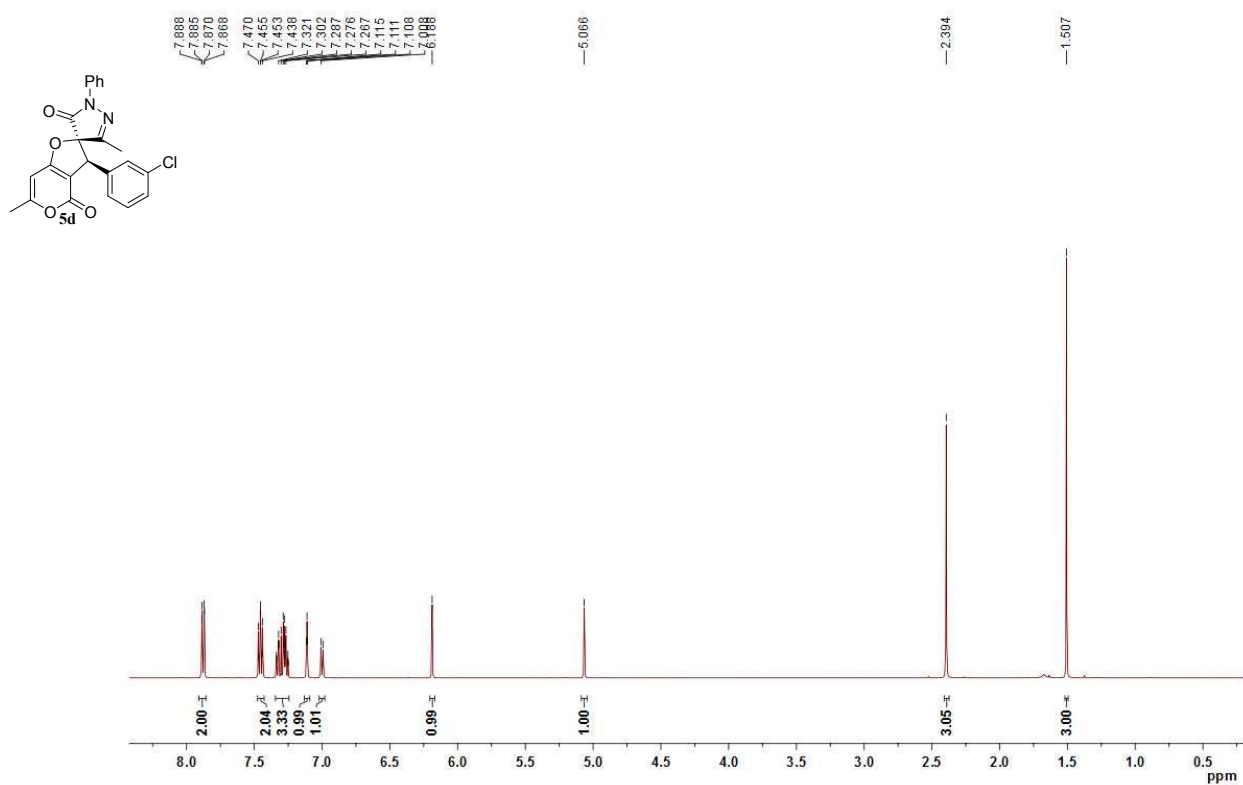
#	Start time[min]	Time[min]	End time[min]	Area%
1	15.435	16.225	17.672	1.225
2	21.923	23.365	25.725	1.324
3	50.109	52.005	61.965	49.319
4	123.035	127.188	138.694	48.132

### HPLC chromatogram of 5c (chiral)

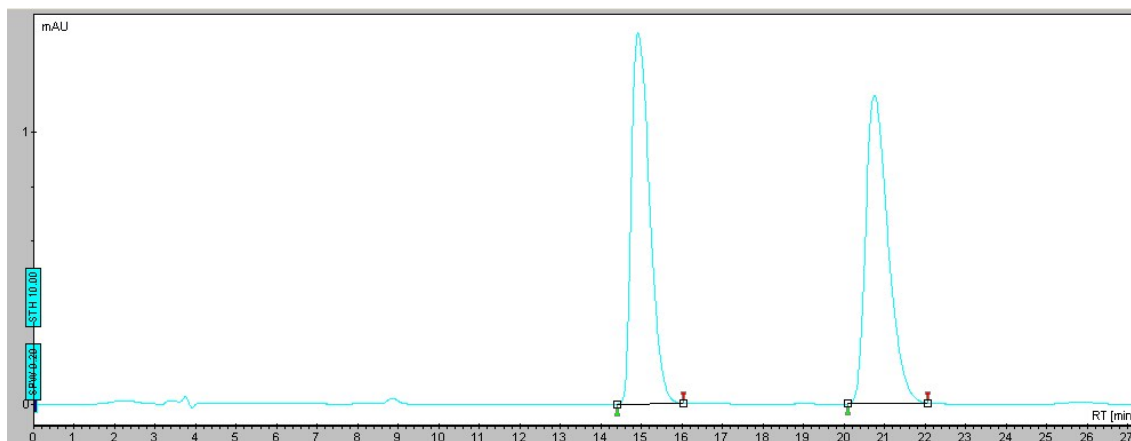


#	Start time[min]	Time[min]	End time[min]	Area%
1	14.591	15.332	16.589	2.752
2	21.386	21.913	22.785	0.166
3	45.37	47.409	58.962	87.239
4	118.723	121.753	128.117	9.843

# <sup>1</sup>H NMR, <sup>13</sup>C NMR spectra of 5d

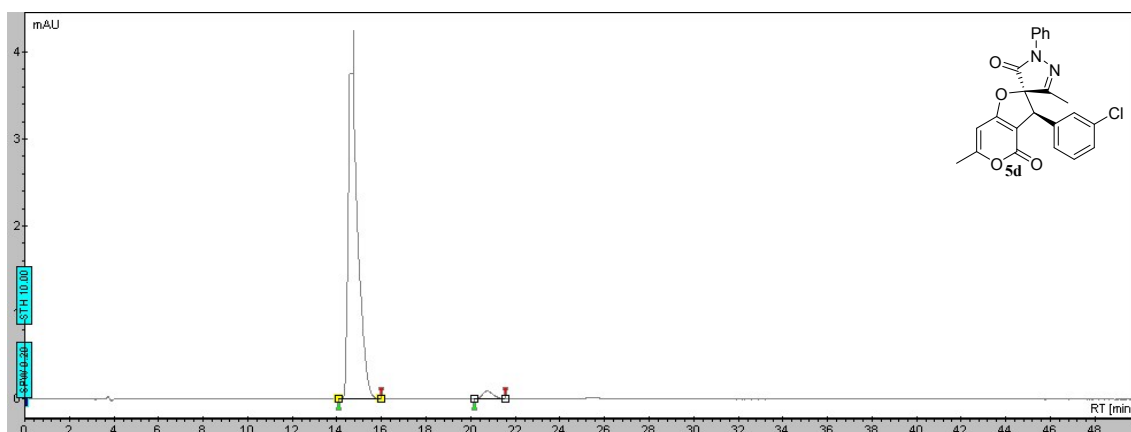


### HPLC chromatogram of 5d (racemic)



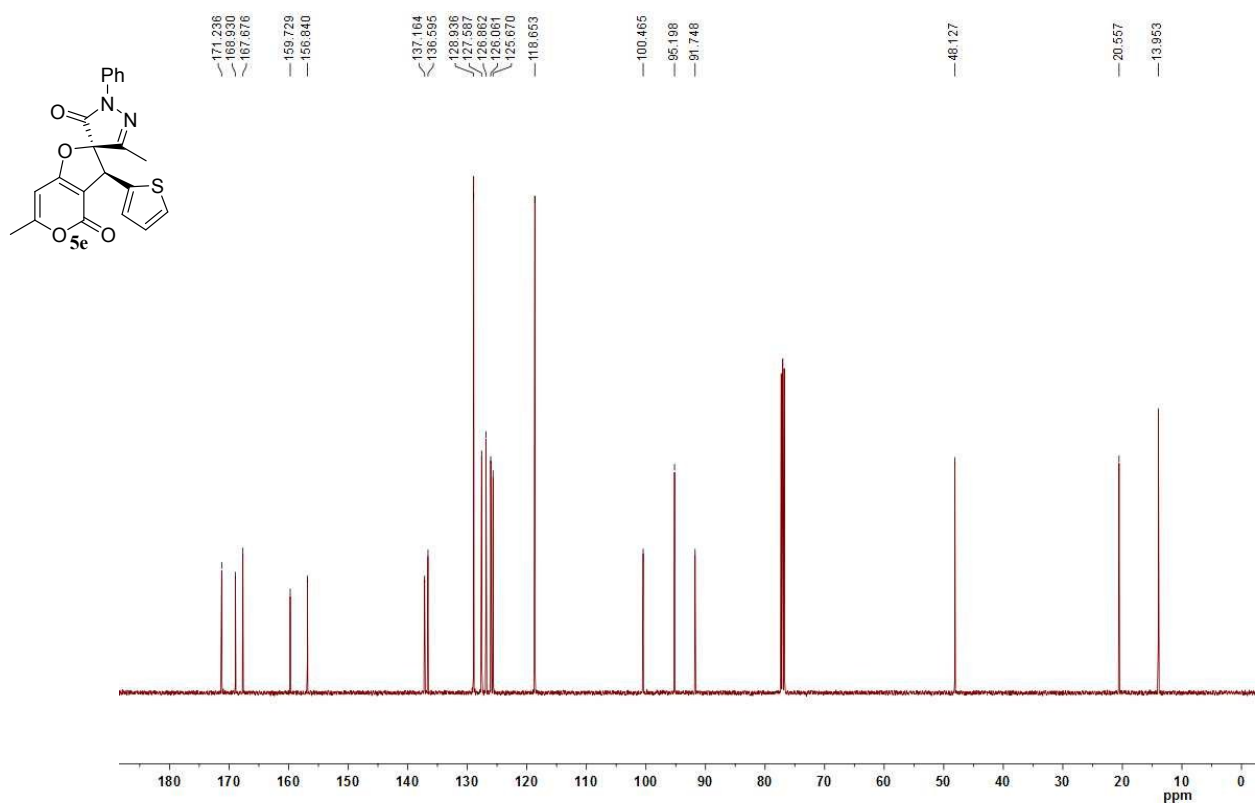
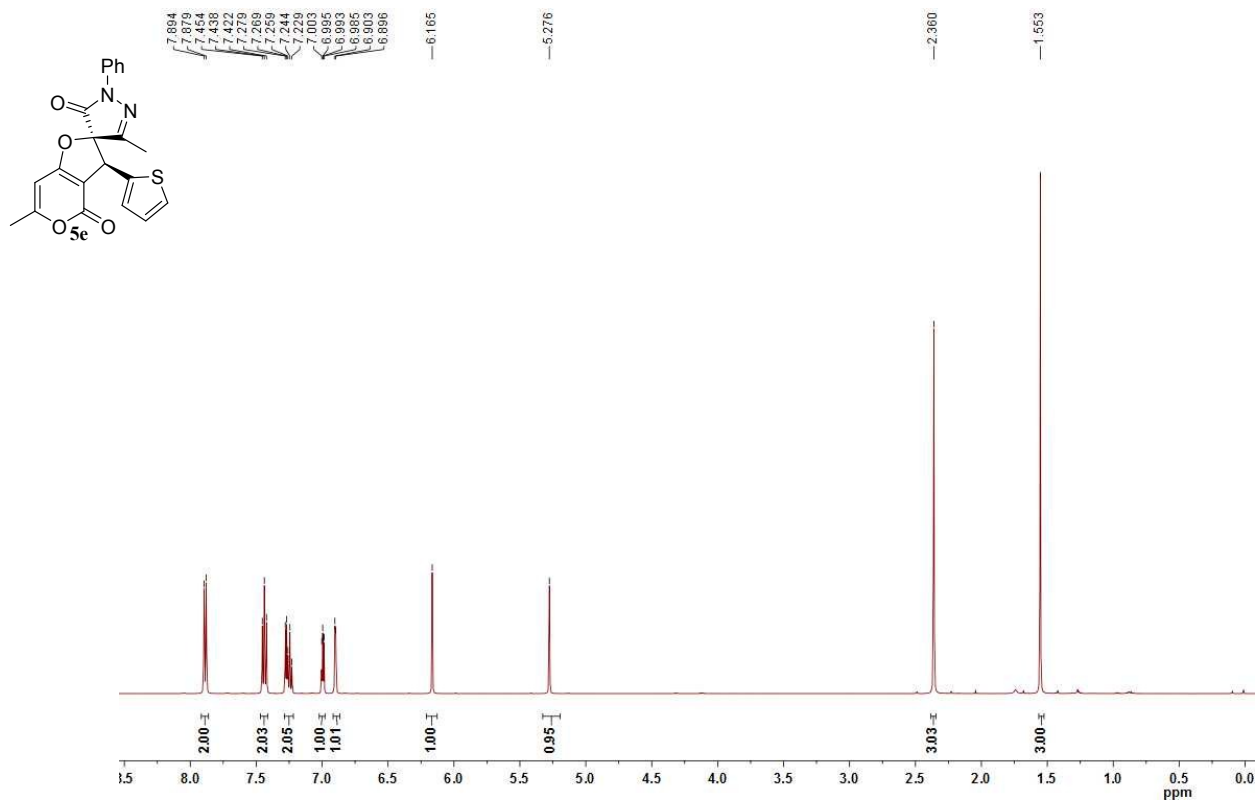
#	Start time[min]	Time[min]	End time[min]	Area%
1	14.401	14.919	16.035	49.462
2	20.094	20.745	22.066	50.538

### HPLC chromatogram of 5d (chiral)

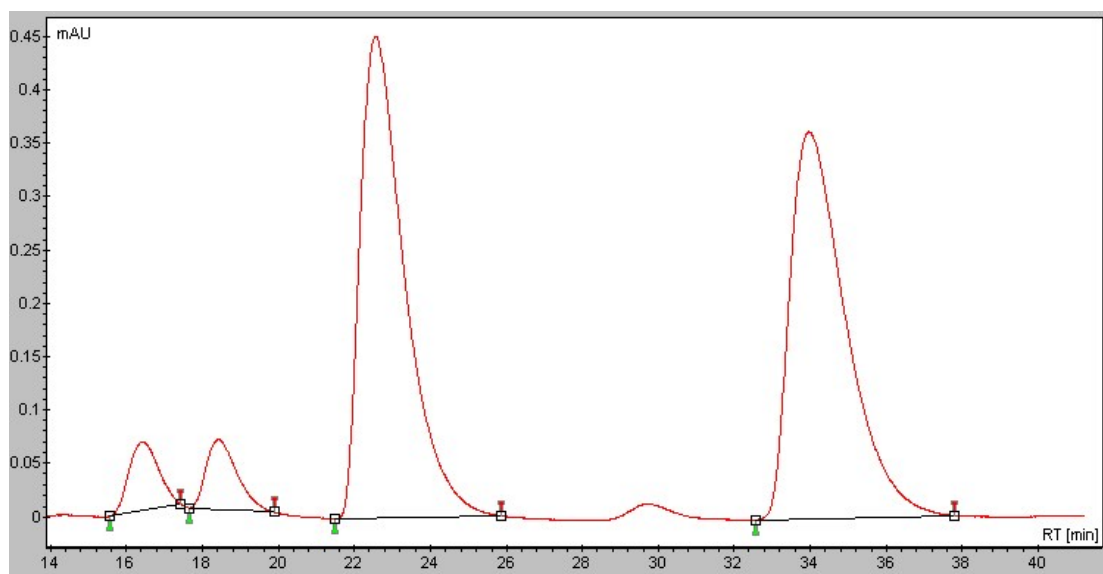


#	Start time[min]	Time[min]	End time[min]	Area%
1	14.079	14.746	15.987	97.344
2	20.164	20.745	21.556	2.656

# $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of 5e

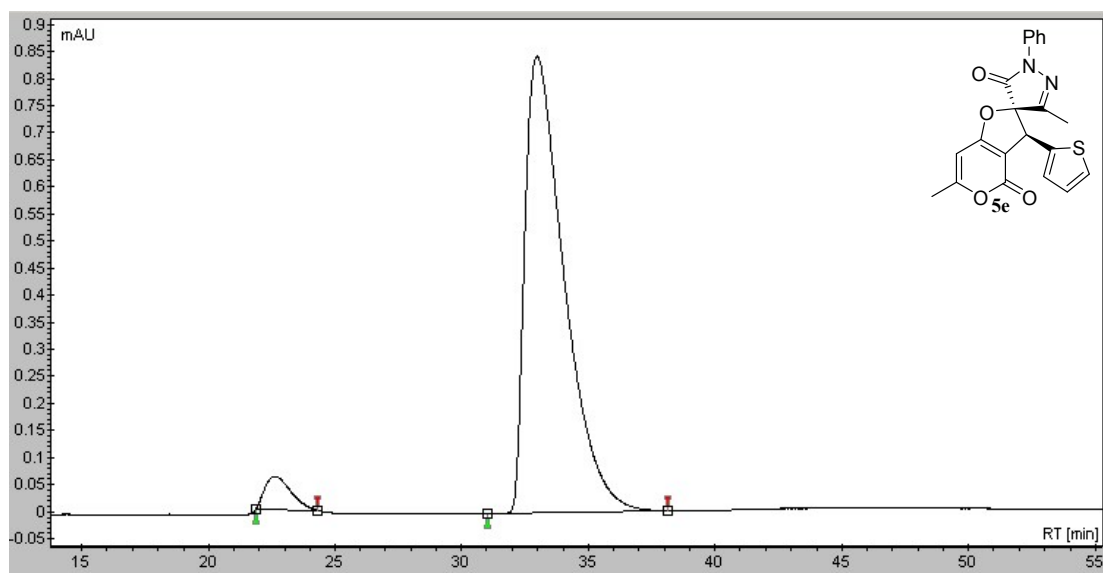


### HPLC chromatogram of 5e (racemic)



#	Start time[min]	Time[min]	End time[min]	Area%
1	15.571	16.412	17.409	4.254
2	17.639	18.425	19.88	4.548
3	21.489	22.558	25.855	45.516
4	32.577	33.958	37.806	45.682

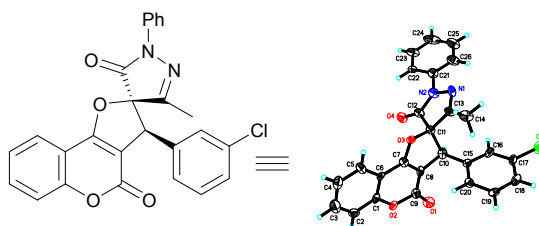
### HPLC chromatogram of 5e (chiral)



#	Start time[min]	Time[min]	End time[min]	Area%
1	21.896	22.625	24.329	4.549
2	31.02	32.998	38.144	95.451

## 5. X-ray crystal structure of compound 4aj, 4al and 4ap.

### 5.1 X-ray crystal structure of compound 4aj.

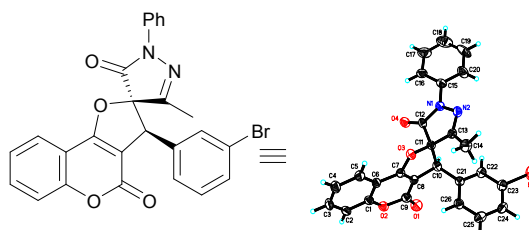


**Table S2.** Crystal data and structure refinement parameters of compound (4aj)

Parameter	Value
CCDC deposition number	1553767
Empirical formula	C <sub>26</sub> H <sub>17</sub> ClN <sub>2</sub> O <sub>4</sub>
Formula weight	456.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Cell dimensions	a = 8.624(3) Å    α = 90° b = 9.752(4) Å    β = 90° c = 26.737(10) Å    γ = 90°
Volume	2248.6(15) Å <sup>3</sup>
Z	4
Density (calculated)	1.350 Mg /m <sup>3</sup>
Absorption coefficient	0.206 mm <sup>-1</sup>
<i>F</i> <sub>000</sub>	944
Crystal size	0.200 × 0.140 × 0.080 mm <sup>3</sup>
Theta range for data collection	1.523 to 24.991°
Index ranges	-10 ≤ <i>h</i> ≤ 10 -11 ≤ <i>k</i> ≤ 11 -25 ≤ <i>l</i> ≤ 31
Reflections collected	11850
Independent reflections	3970 [ <i>R</i> <sub>(int)</sub> = 0.0890 ]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>

Data /restraints /parameters	3970 / 0 / 300
Goodness of fit on $F^2$	1.138
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.1238$ , $\omega R_2 = 0.2984$
$R$ indices (all data)	$R_1 = 0.1508$ , $\omega R_2 = 0.3136$
Absolute structure parameter	0.21(9)
Extinction coefficient	0.051(9)
Largest diff. peak and hole	0.589 and -0.541 e.Å <sup>-3</sup>

## 5.2 X-ray crystal structure of compound 4al.



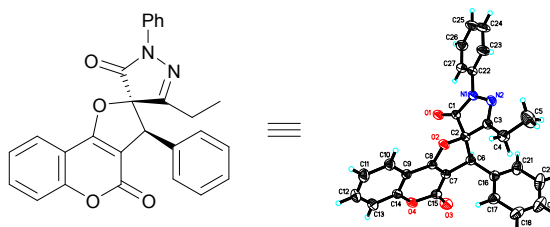
**Table S3.** Crystal data and structure refinement parameters of compound (4al)

Parameter	Value
CCDC deposition number	1509834
Empirical formula	C <sub>26</sub> H <sub>17</sub> BrN <sub>2</sub> O <sub>4</sub>
Formula weight	501.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21
Cell dimensions	$a = 8.743(2)$ Å $\alpha = 90^\circ$ $b = 9.675(3)$ Å $\beta = 94.291(6)^\circ$ $c = 15.147(3)$ Å $\gamma = 90^\circ$
Volume	1277.7(6) Å <sup>3</sup>
$Z$	2
Density (calculated)	1.524 Mg/m <sup>3</sup>
Absorption coefficient	1.855 mm <sup>-1</sup>
$F_{000}$	592
Crystal size	0.200 × 0.160 × 0.130 mm <sup>3</sup>
Theta range for data collection	2.336° to 24.998°



Index ranges	-10 ≤ <i>h</i> ≤ 10 -11 ≤ <i>k</i> ≤ 11 -18 ≤ <i>l</i> ≤ 13
Reflections collected	7093
Independent reflections	4277 [ <i>R</i> <sub>(int)</sub> = 0.0434 ]
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data /restraints /parameters	4277 / 1 / 326
Goodness of fit on <i>F</i> <sup>2</sup>	1.018
Final <i>R</i> indices [ <i>I</i> > 2σ ( <i>I</i> ) ]	<i>R</i> <sub>1</sub> = 0.0599, ω <i>R</i> <sub>2</sub> = 0.1321
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1018, ω <i>R</i> <sub>2</sub> = 0.1521
Extinction correction	n/a
Flack parameter	0.041(15)
Largest diff. peak and hole	0.419 and -0.310 e.Å <sup>-3</sup>

### 5.3 X-ray crystal structure of compound 4ap.



**Table S4.** Crystal data and structure refinement parameters of compound (**4aq**)

Parameter	Value
CCDC deposition number	1553766
Empirical formula	C <sub>27</sub> H <sub>20</sub> N <sub>2</sub> O <sub>4</sub>
Formula weight	436.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Cell dimensions	a = 8.3497(11) Å    α = 90° b = 9.7735(13) Å    β = 90°

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	$c = 27.653(4) \text{ \AA}$	$\gamma = 90^\circ$
Volume	2256.6(5) $\text{\AA}^3$	
$Z$	4	
Density (calculated)	1.285 Mg /m <sup>3</sup>	
Absorption coefficient	0.087 mm <sup>-1</sup>	
$F_{000}$	912	
Crystal size	0.200 × 0.160 × 0.120 mm <sup>3</sup>	
Theta range for data collection	2.210 to 25.495°	
Index ranges	-8 ≤ $h$ ≤ 10	
	-11 ≤ $k$ ≤ 11	
	-33 ≤ $l$ ≤ 30	
Reflections collected	12988	
Independent reflections	4193 [ $R_{\text{(int)}} = 0.0498$ ]	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data /restraints /parameters	4193 / 0 / 299	
Goodness of fit on $F^2$	1.020	
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0435$ , $\omega R_2 = 0.0934$	
$R$ indices (all data)	$R_1 = 0.0616$ , $\omega R_2 = 0.1012$	
Absolute structure parameter	-0.1(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.167 and -0.153 e. $\text{\AA}^{-3}$	

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