Supporting Information

An NHC-Catalyzed, Stereoselective α-Functionalization of α,β-Unsaturated Carboxylic Acids through In Situ Activation

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1. General methods

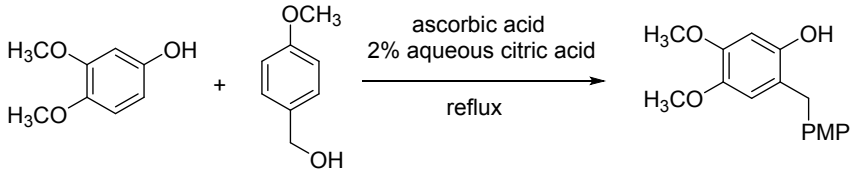
Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}**.** ^{1}H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in $CDCl_3$ (100 MHz**,** ^{13}C NMR) or DMSO-d_6 with chemical shift (δ) given in ppm relative to TMS as internal standard. High-resolution mass spectra (HRMS) were obtained on a micrOTOF-Q Ⅱ HRMS/MS instrument (Bruker).

1.1 Syntheses of NHC precursors

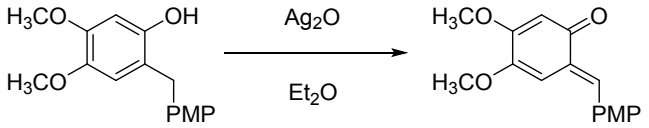
These precatalysts were prepared according to the known reports[1].

1.2 Syntheses of *o*-quinone methides

The *o*-quinone methide and vinyl *o*-quinone methide were synthesized according to Jurd's procedure.[2] Synthesis procedure for 3,4-dimethoxy-6-(4-methoxyphenylmethylidene)cyclohexa-2,4-dien-1-one.



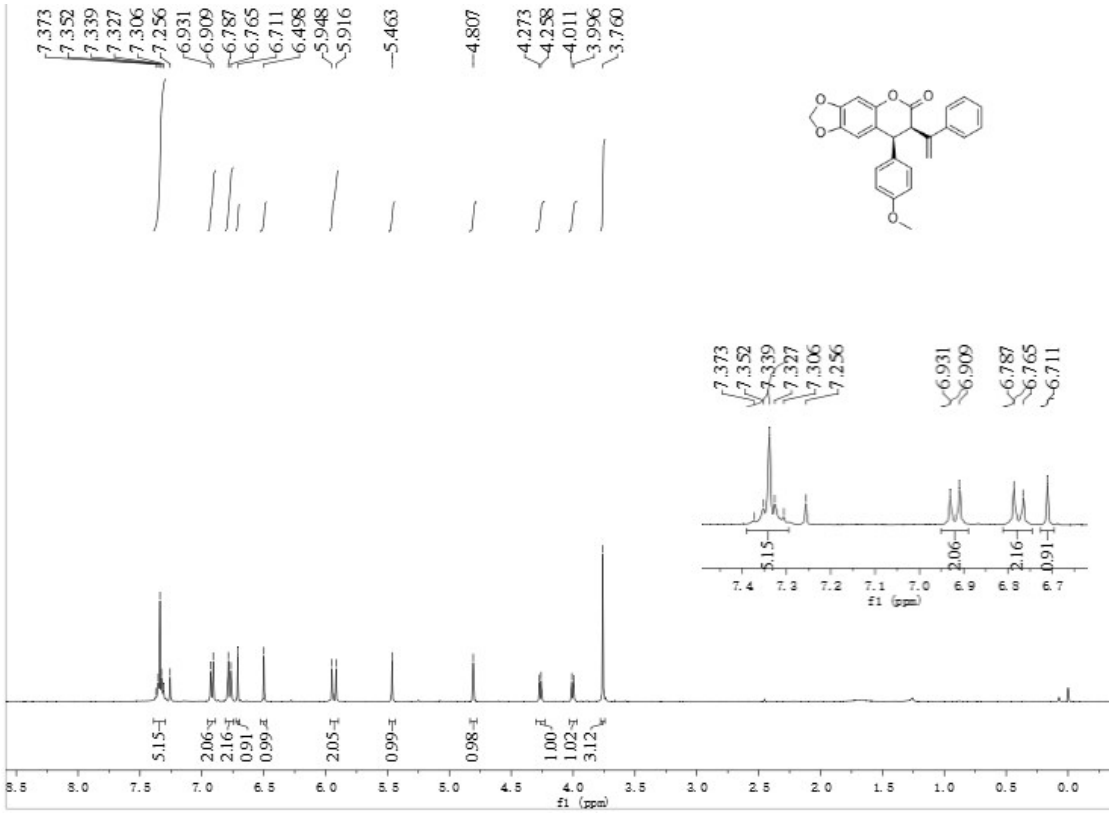
According to Jurd's method[2]: A suspension of 3,4-dimethoxyphenol (3.08 g, 20.0 mmol) and alcohol (1 eq. 20 mmol) in 2% aqueous citric acid (100 mL) containing ascorbic acid (1.0 g, 5.6 mmol) was heated under reflux for over 17 hours. On cooling, the oily product crystallized. After a crude recrystallization from benzene, yellowish solid directly used in the next step.



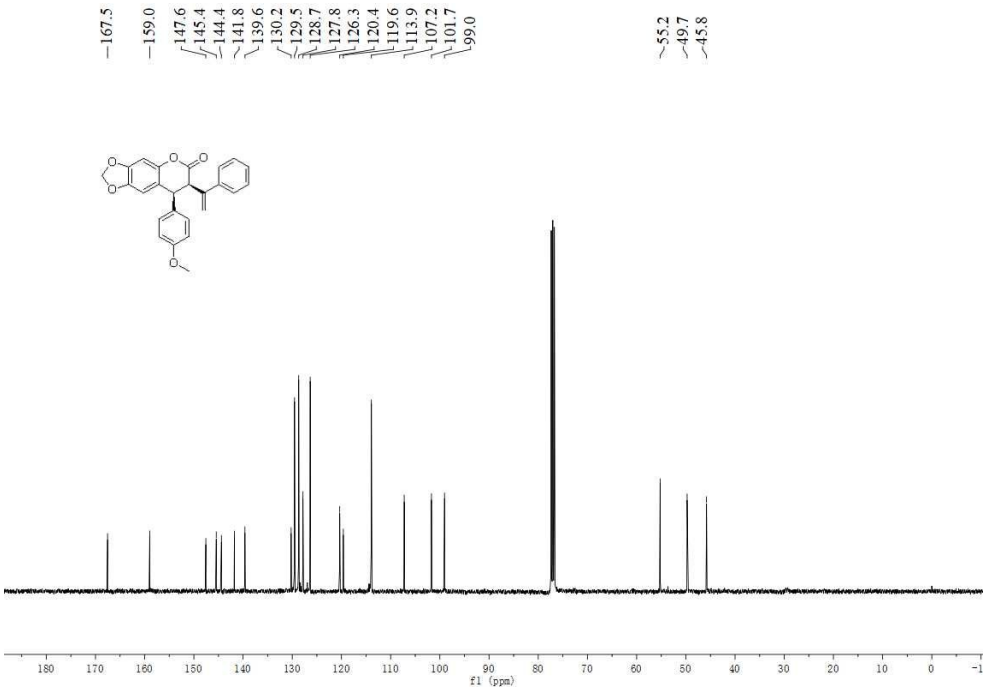
Modified Jurd's synthesis of o-quinone methide[3]. A solution of 4,5-dimethoxy-2-(4-methoxybenzyl)phenol (1.0 g) in ether (50 mL) was added silver oxide (1.5 g) then stirred overnight. The solution was filtered, then concentrated to 20 mL, cooled, and red crystals were collected (0.47 g). The product is acid and heat sensitive.1.3 Preparation of racemic products.

2. ^{1}H NMR and ^{13}C NMR Spectra

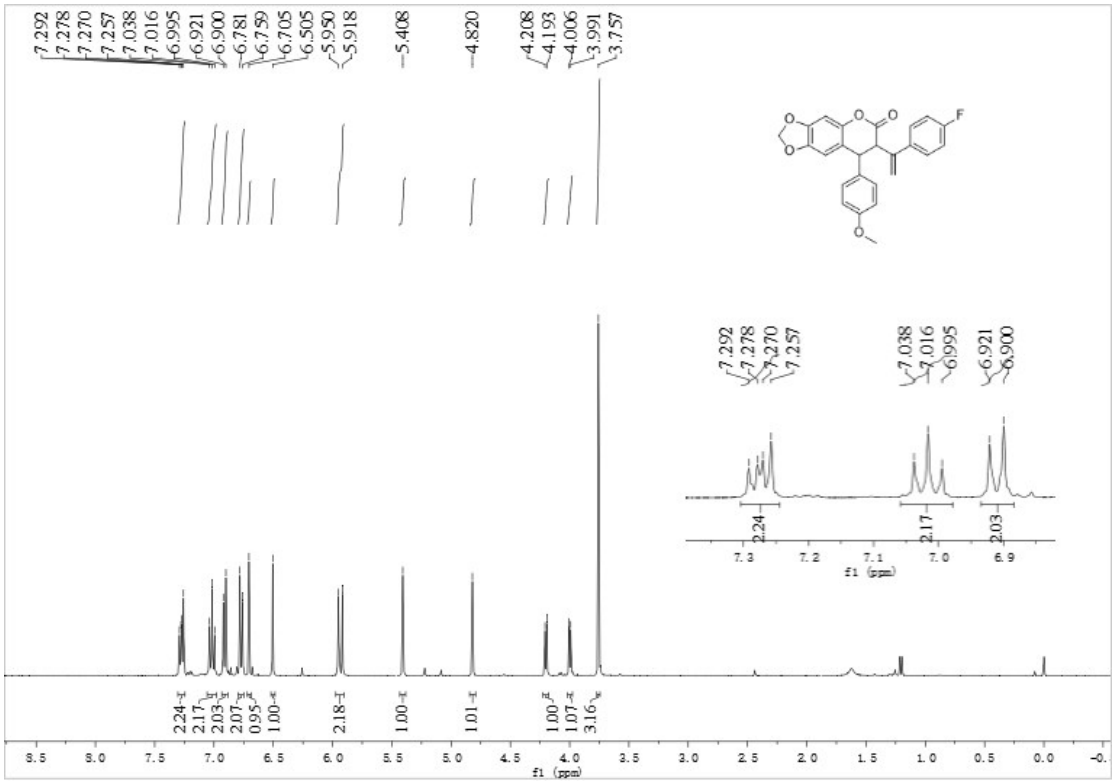
^{1}H NMR Spectrum of Compound (**3a**)



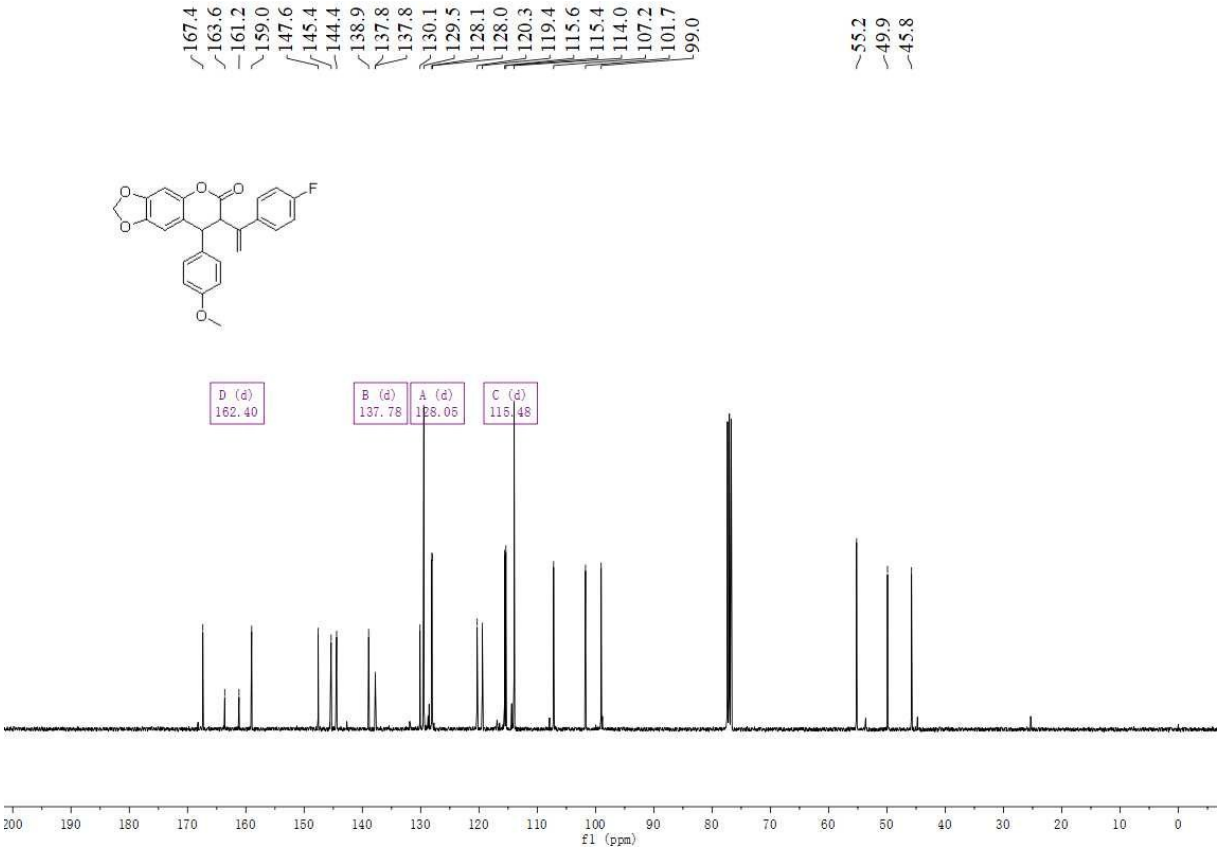
^{13}C NMR Spectrum of Compound (**3a**)



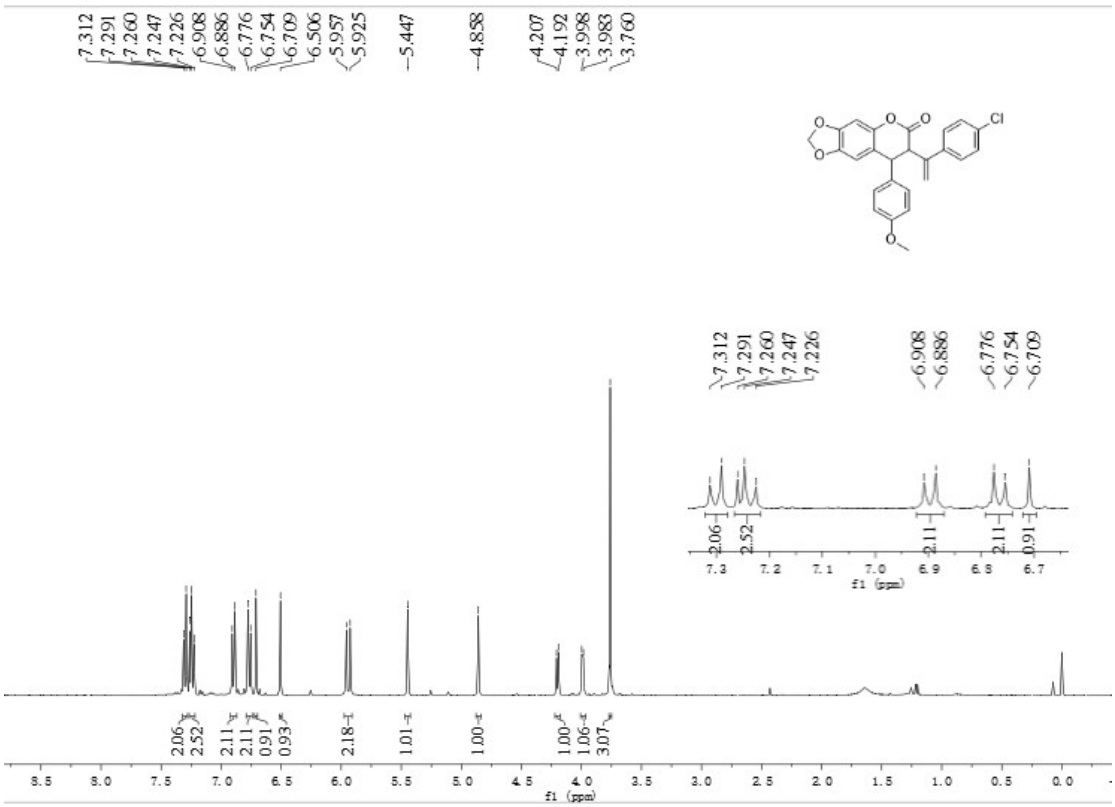
^{1}H NMR Spectrum of Compound (**3b**)



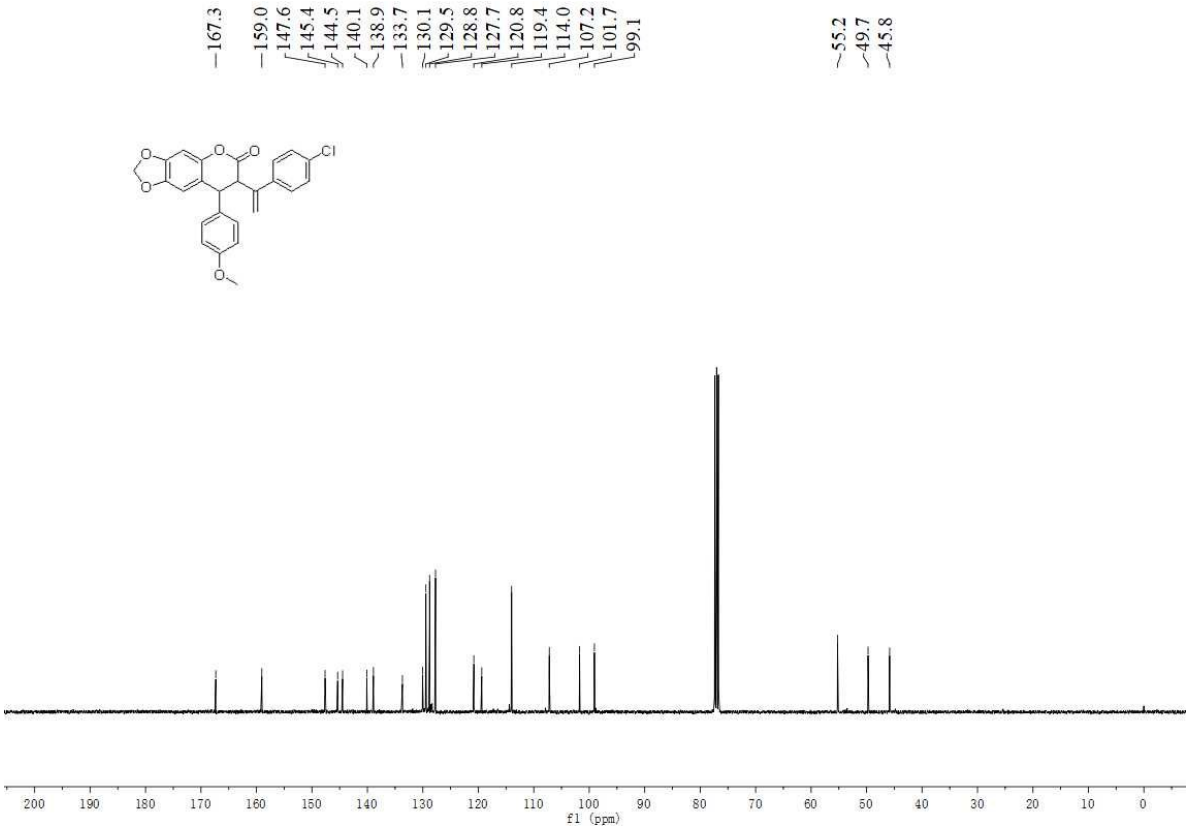
^{13}C NMR Spectrum of Compound (**3b**)



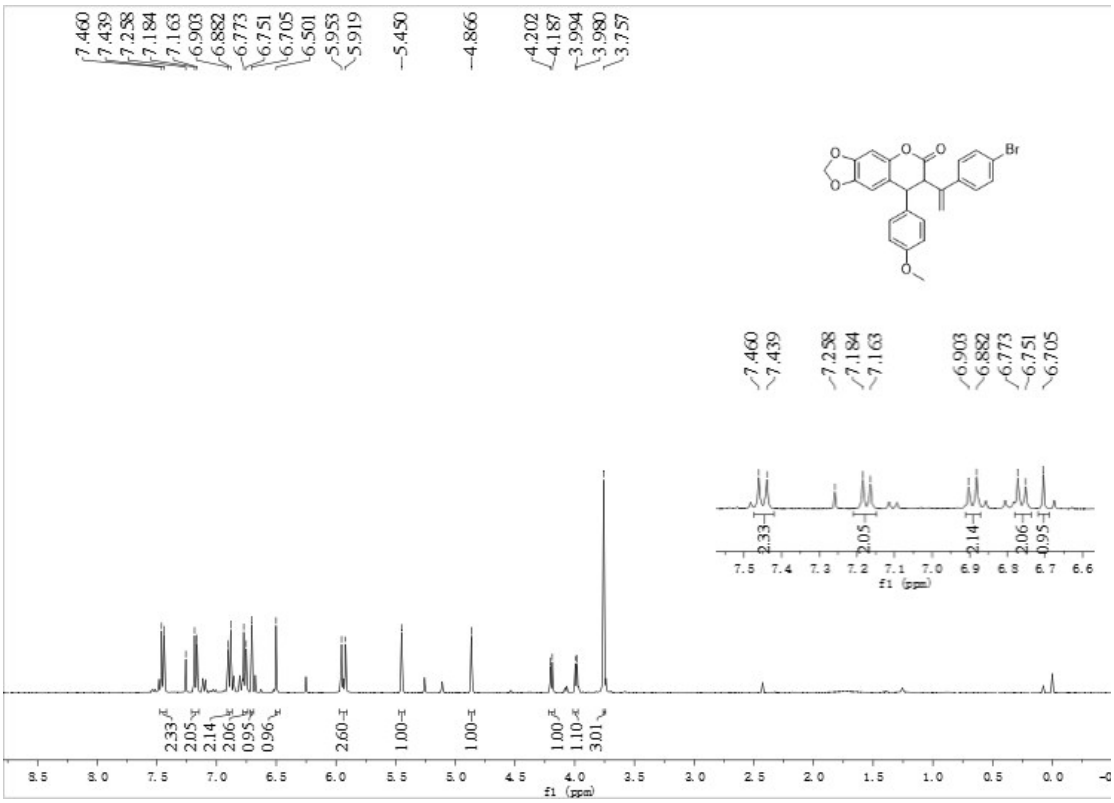
^{1}H NMR Spectrum of Compound (**3c**)



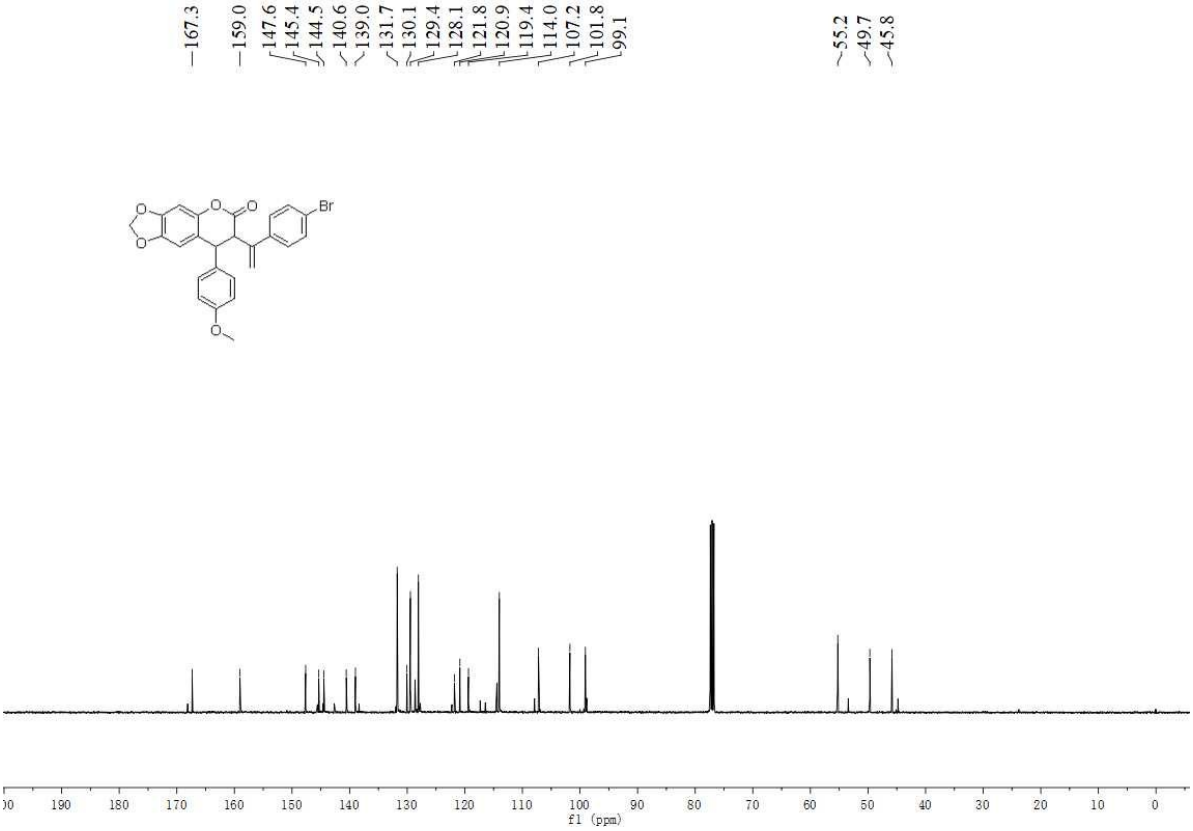
^{13}C NMR Spectrum of Compound (**3c**)



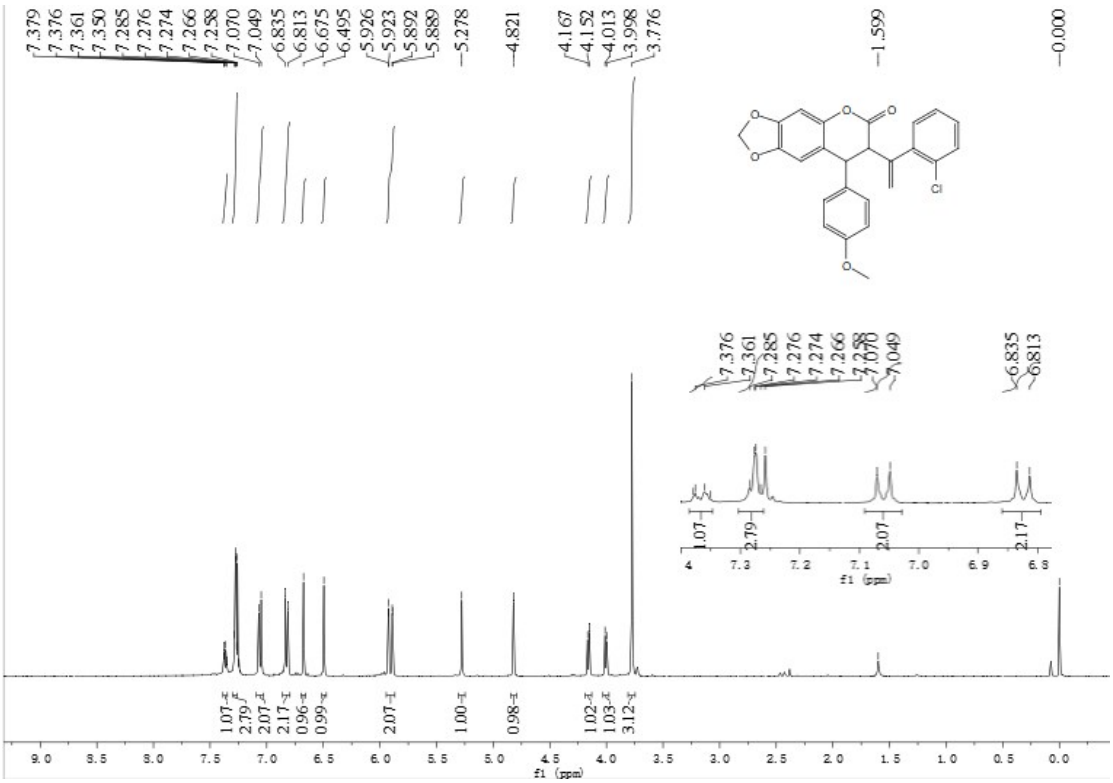
^{1}H NMR Spectrum of Compound (**3d**)



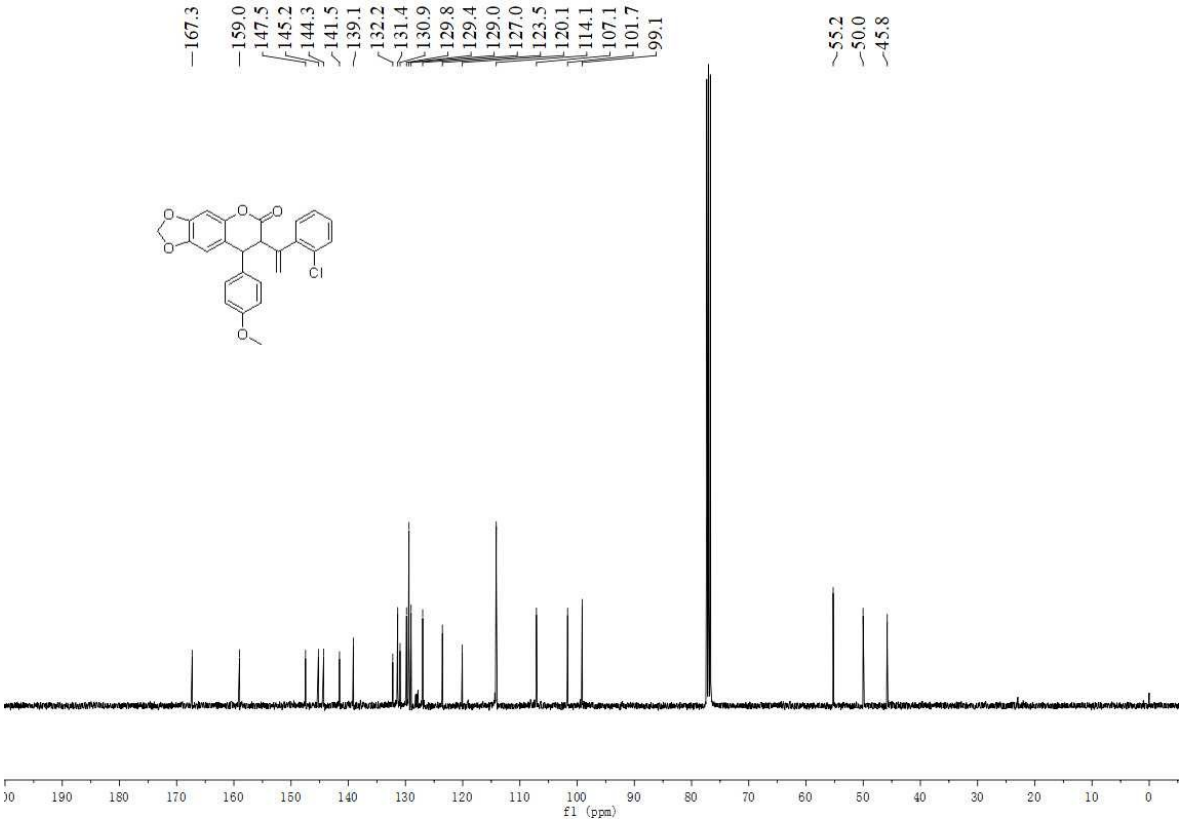
^{13}C NMR Spectrum of Compound (**3d**)



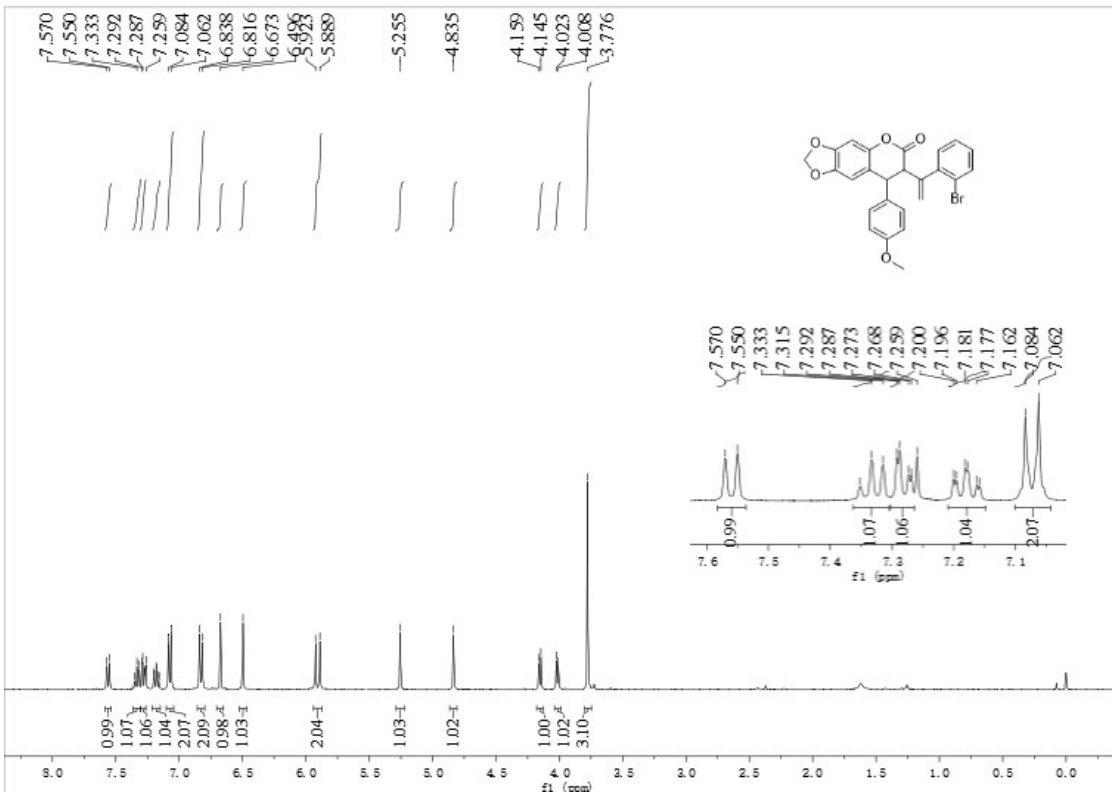
^{1}H NMR Spectrum of Compound (**3e**)



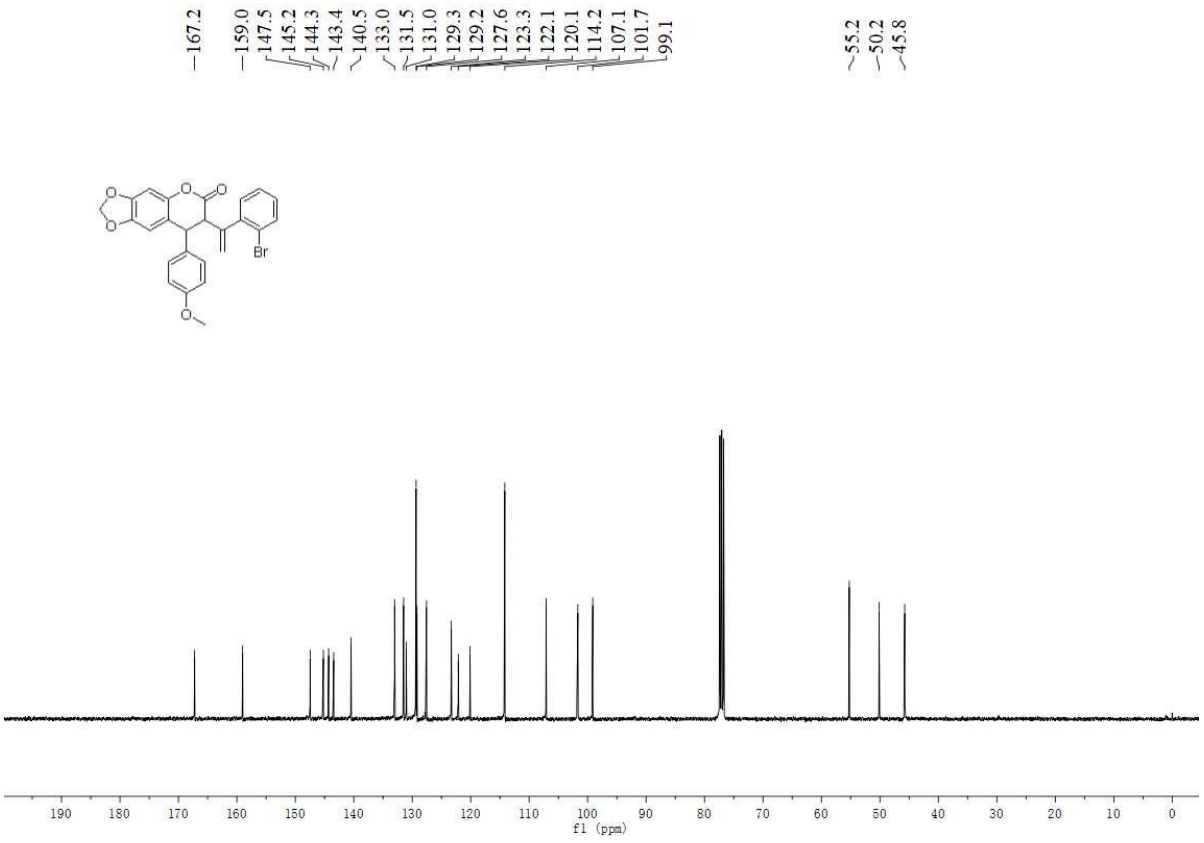
^{13}C NMR Spectrum of Compound (**3e**)



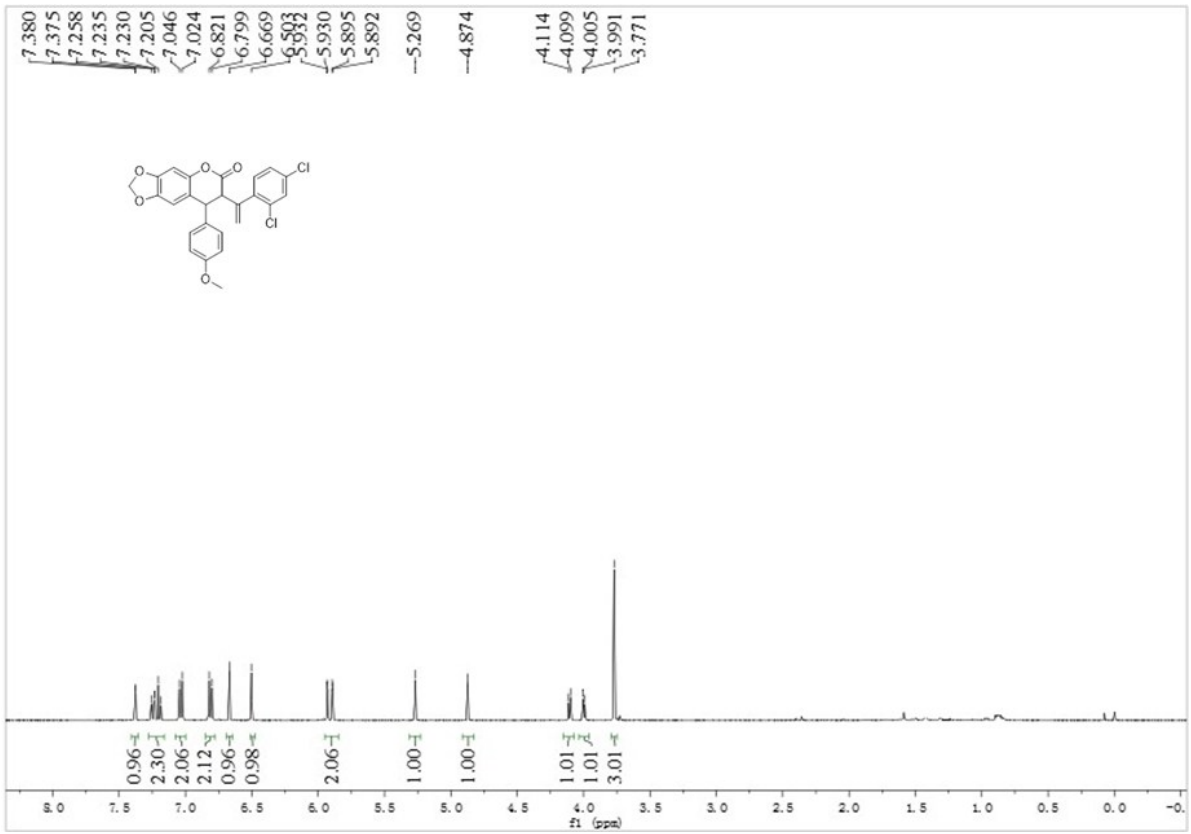
^{1}H NMR Spectrum of Compound (**3f**)



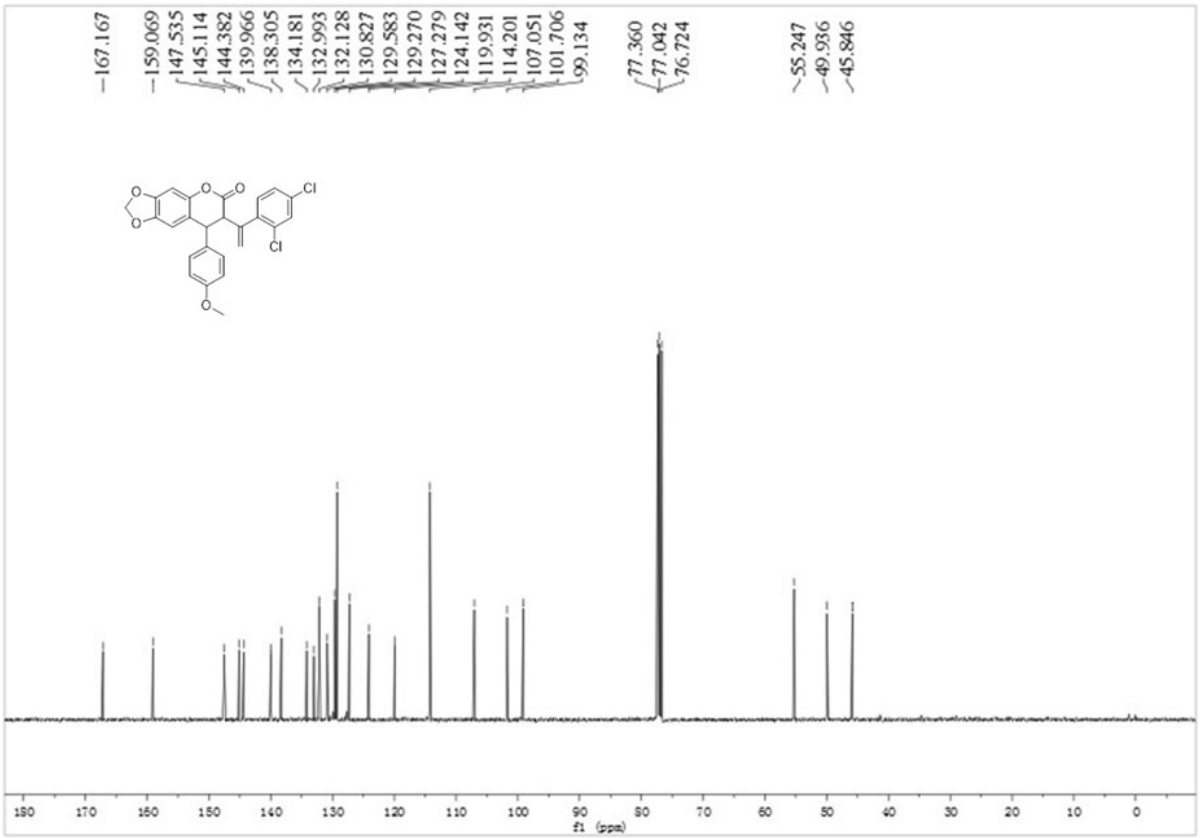
^{13}C NMR Spectrum of Compound (**3f**)



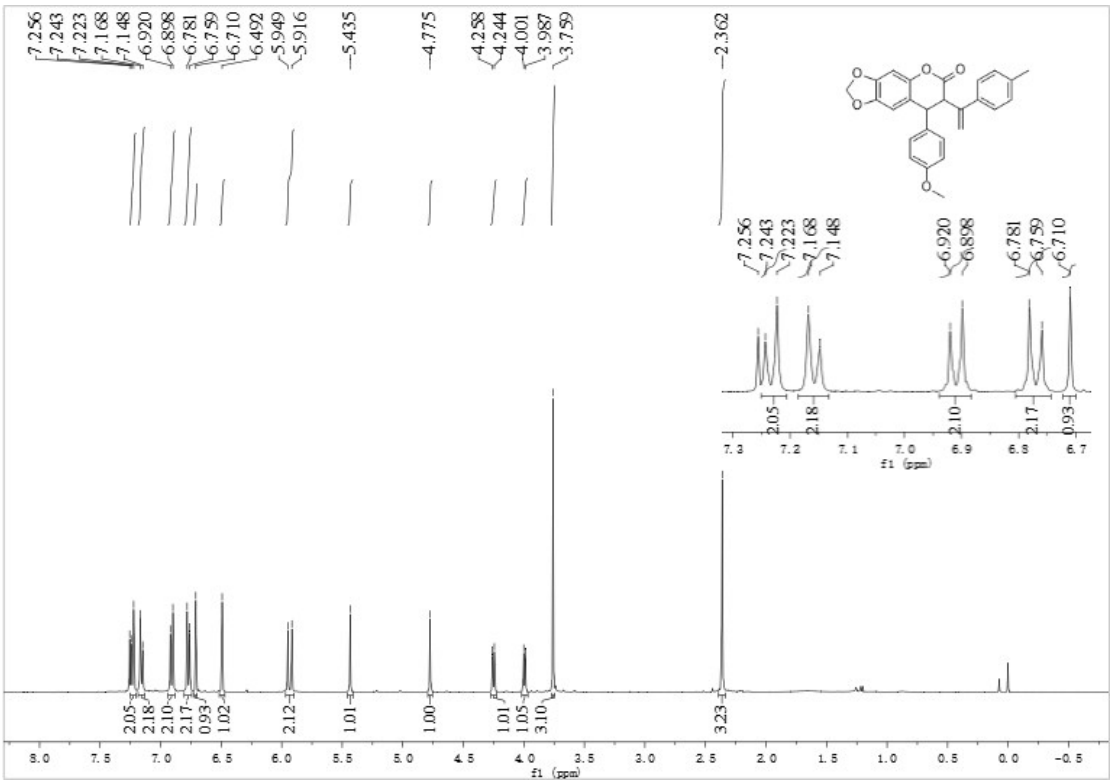
^{1}H NMR Spectrum of Compound (**3g**)



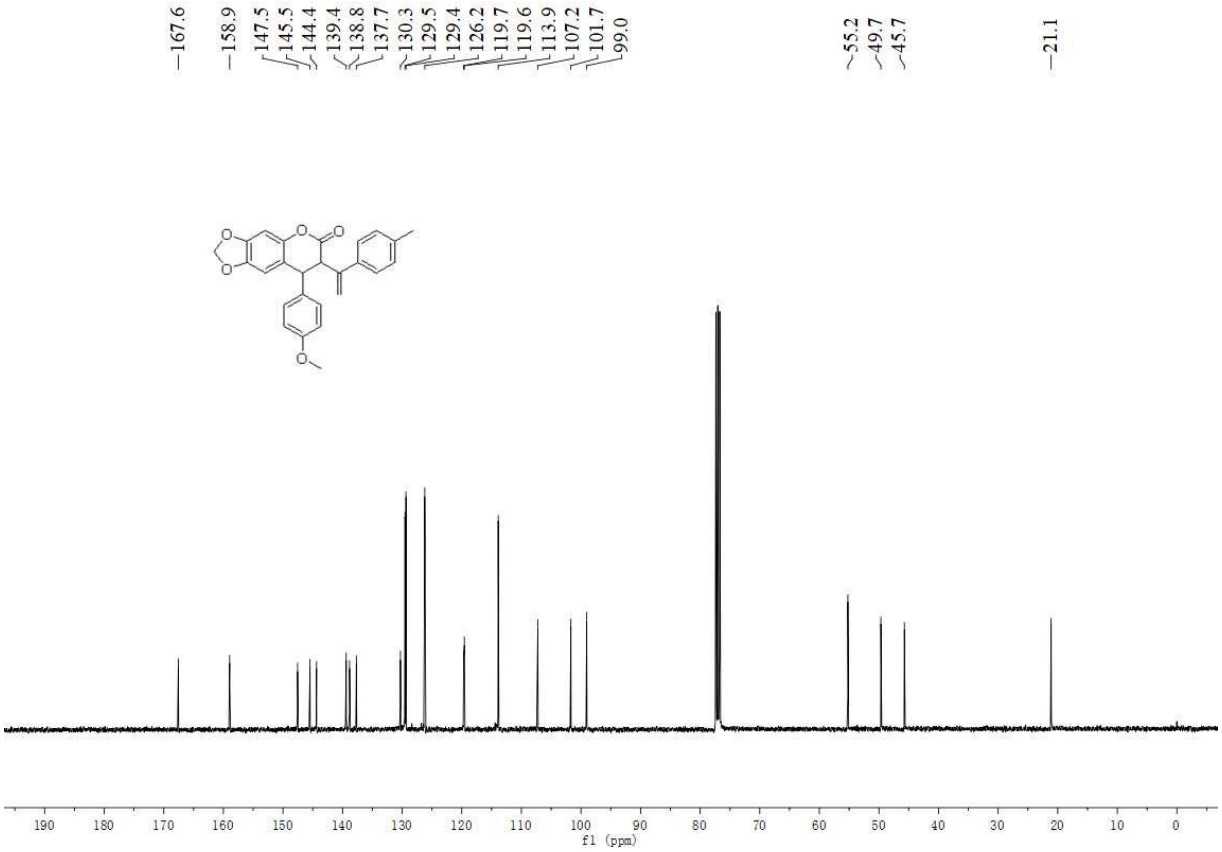
^{13}C NMR Spectrum of Compound (**3g**)



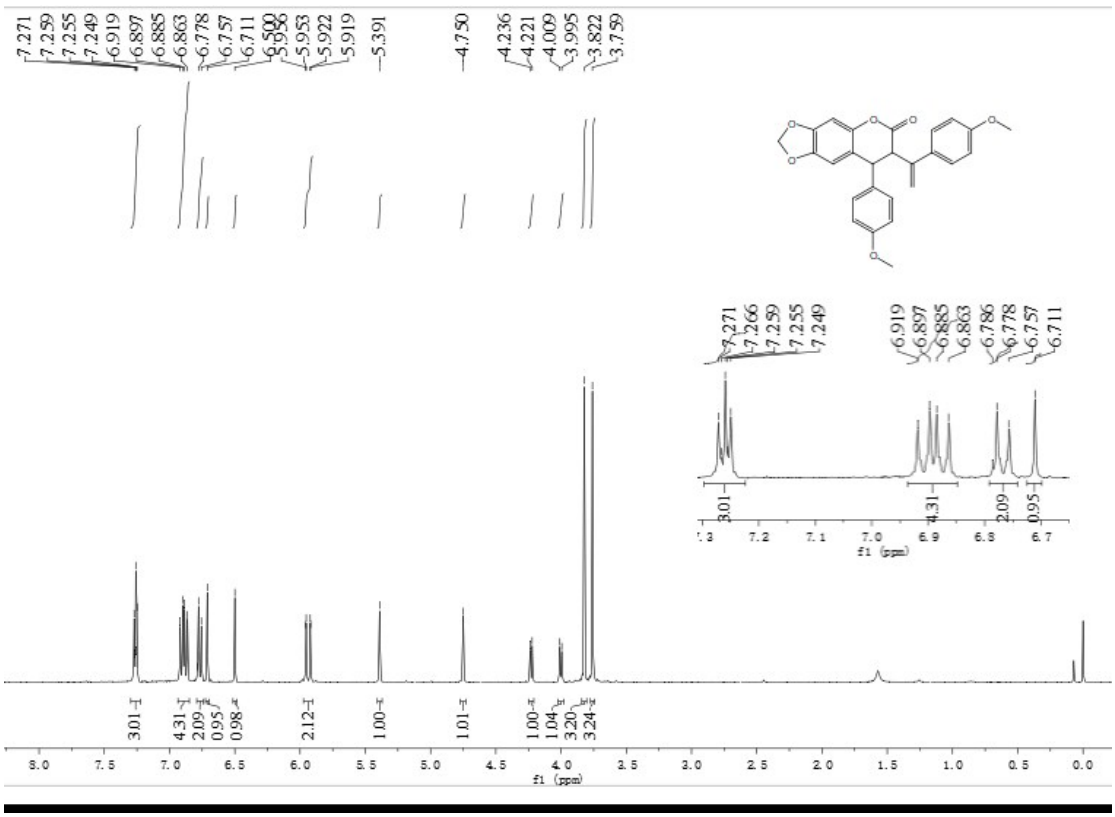
^{1}H NMR Spectrum of Compound (**3h**)



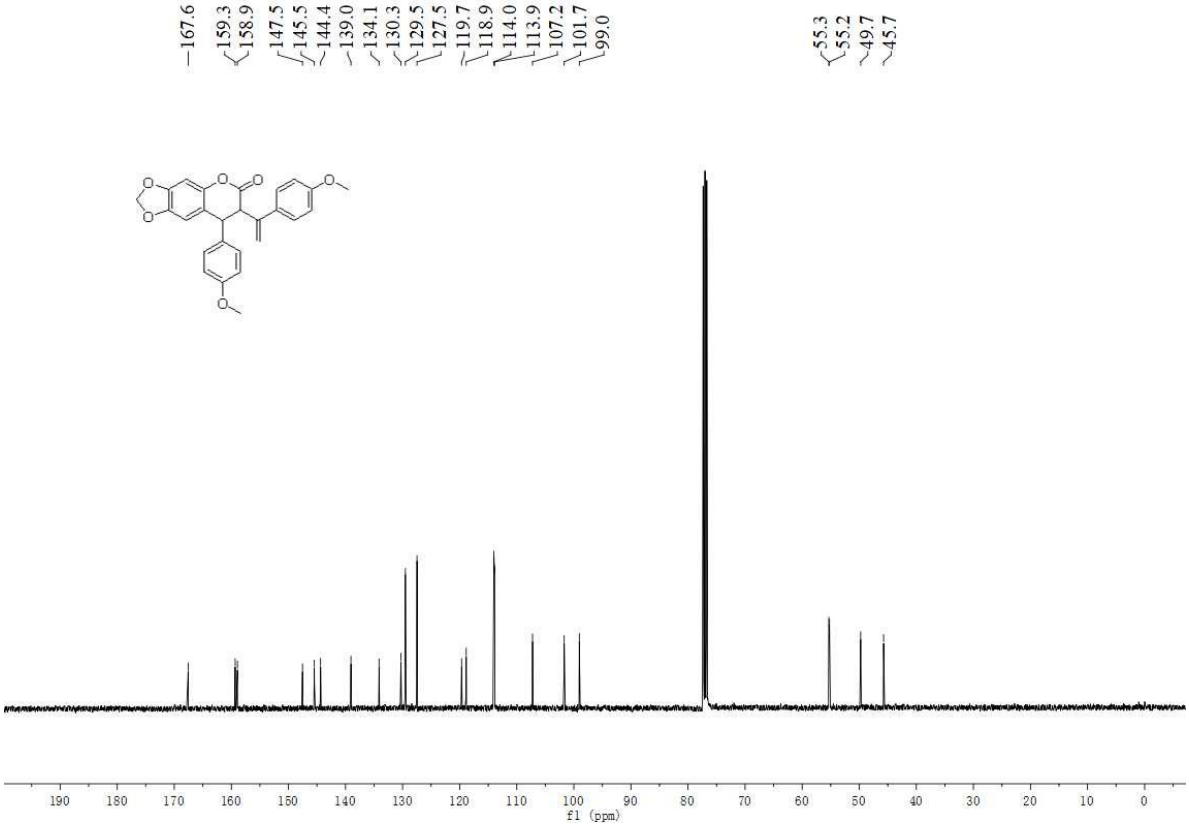
^{13}C NMR Spectrum of Compound (**3h**)



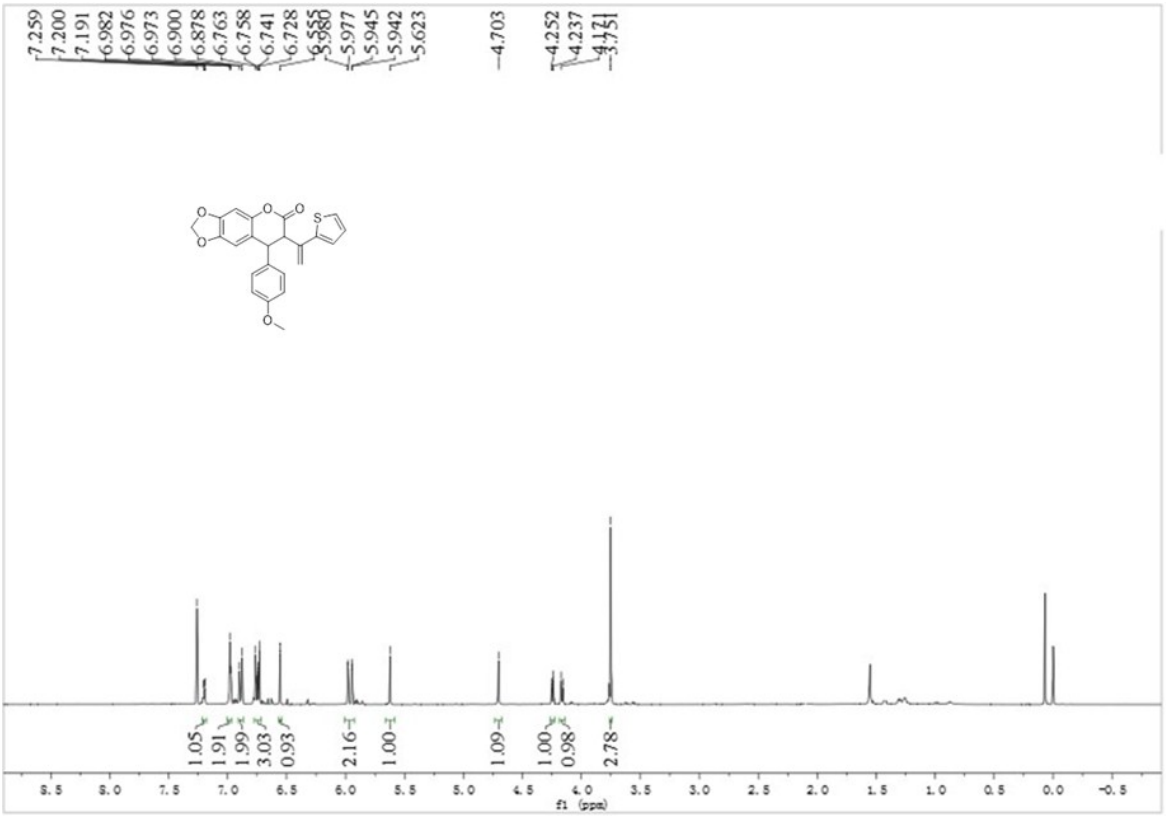
^{1}H NMR Spectrum of Compound (**3i**)



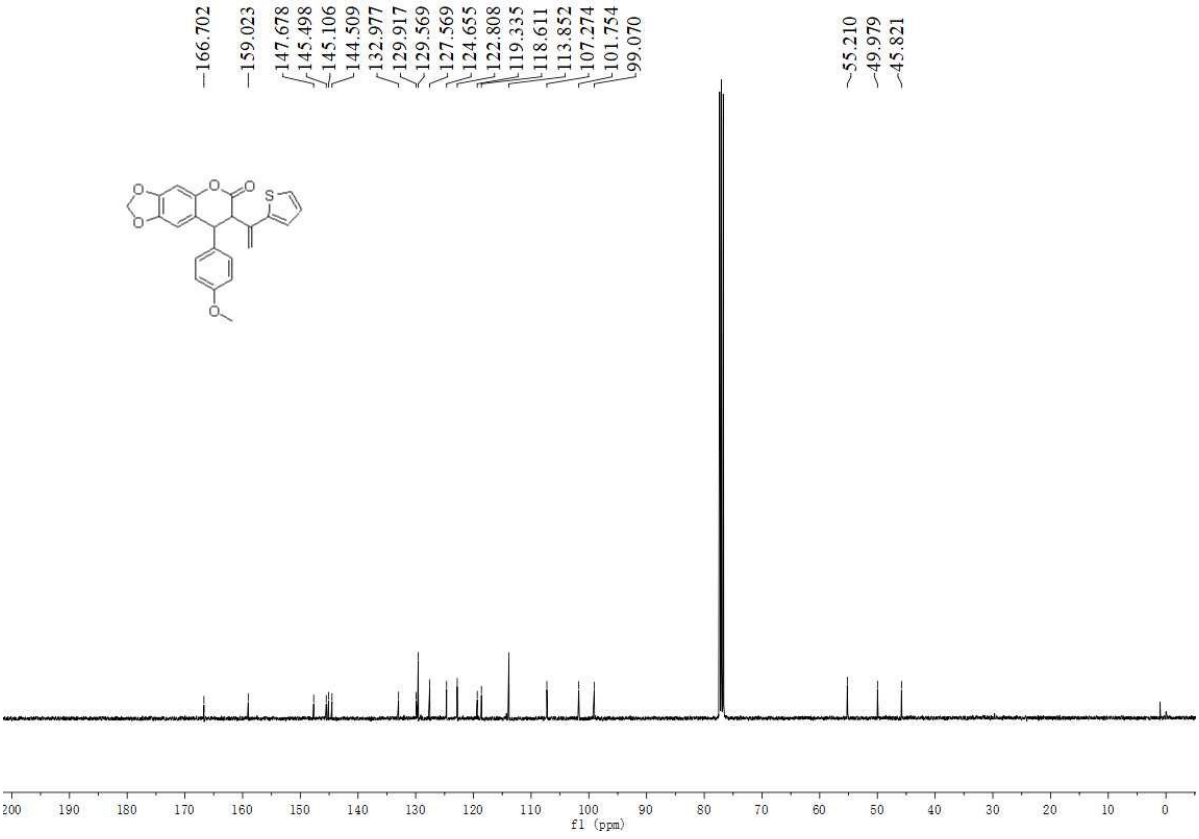
^{13}C NMR Spectrum of Compound (**3i**)



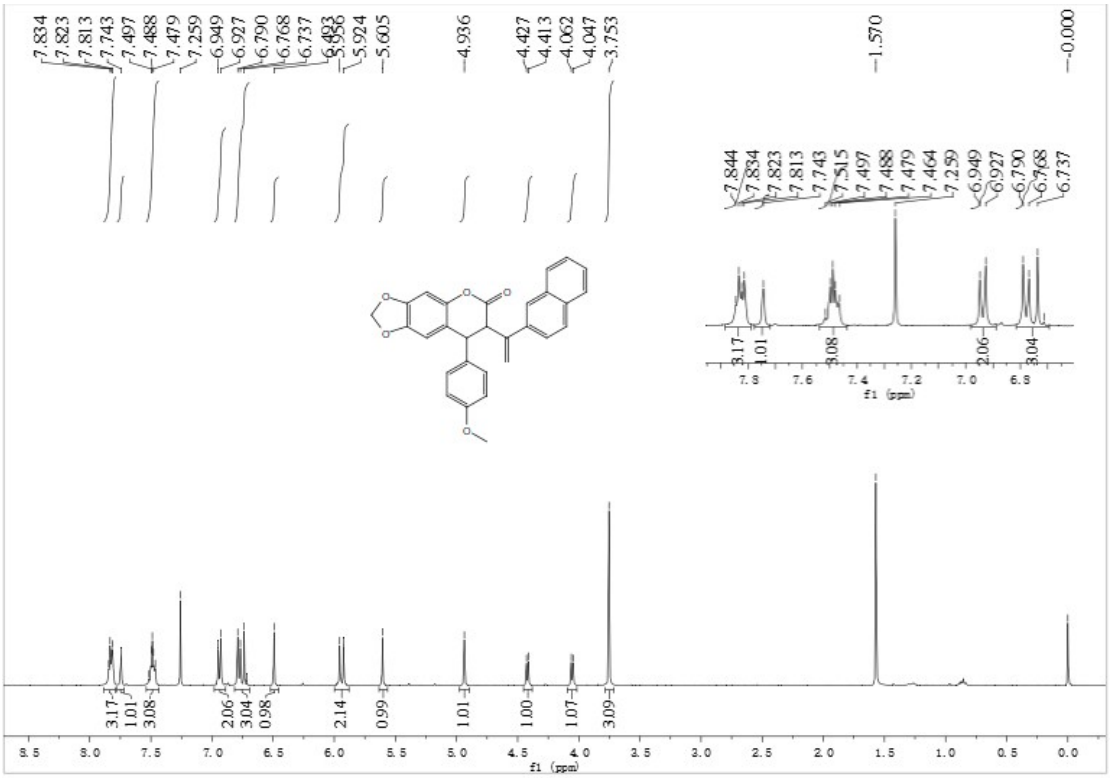
^{1}H NMR Spectrum of Compound (**3j**)



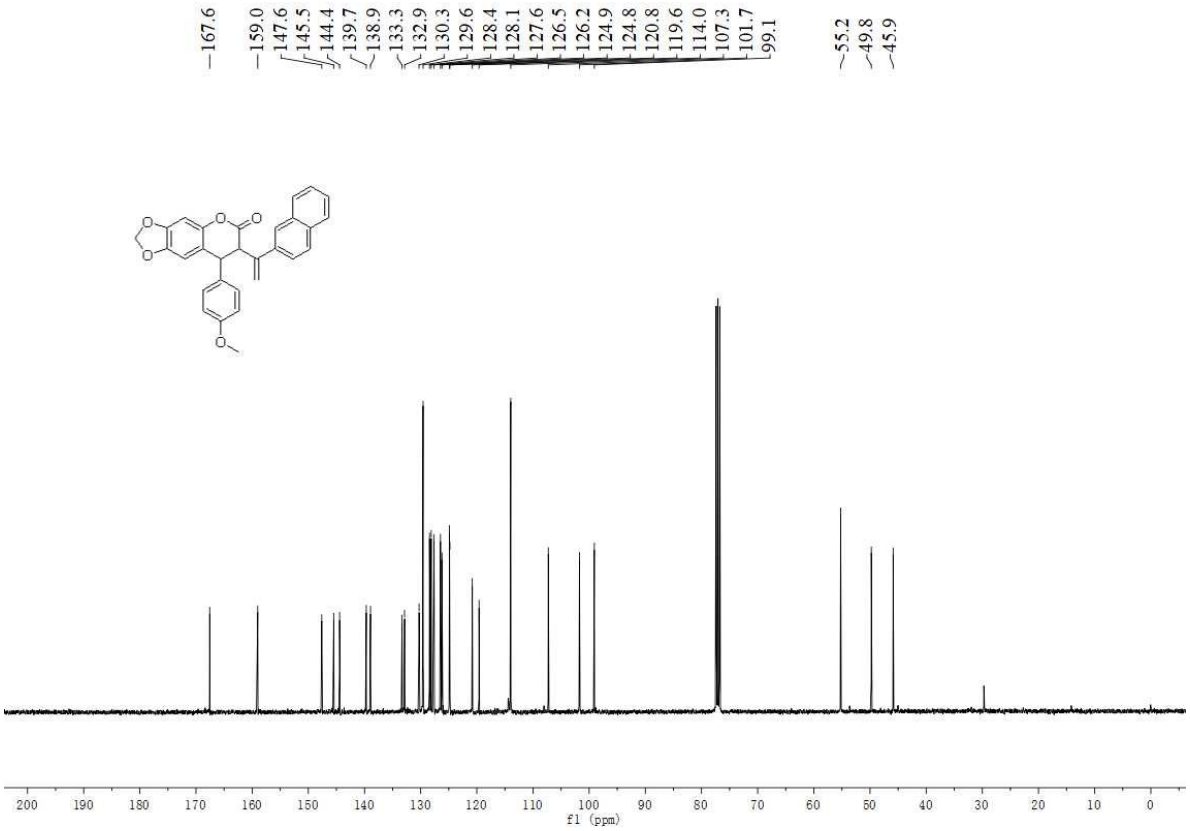
^{13}C NMR Spectrum of Compound (**3j**)



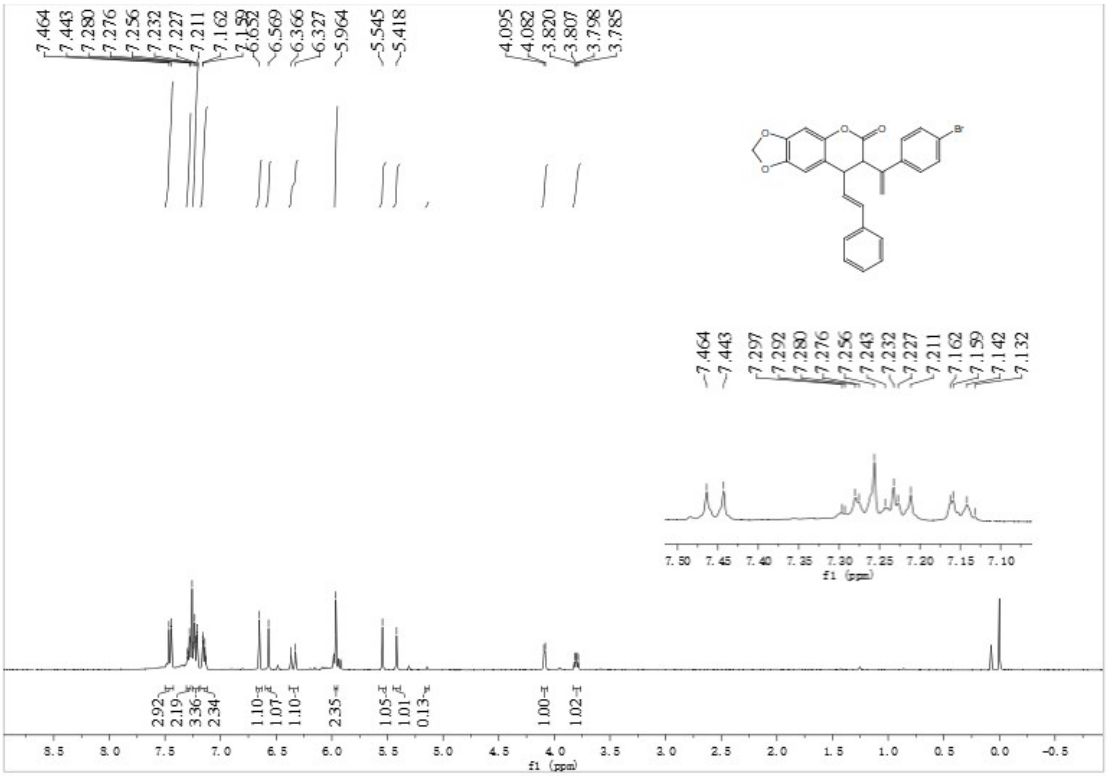
^{1}H NMR Spectrum of Compound (**3k**)



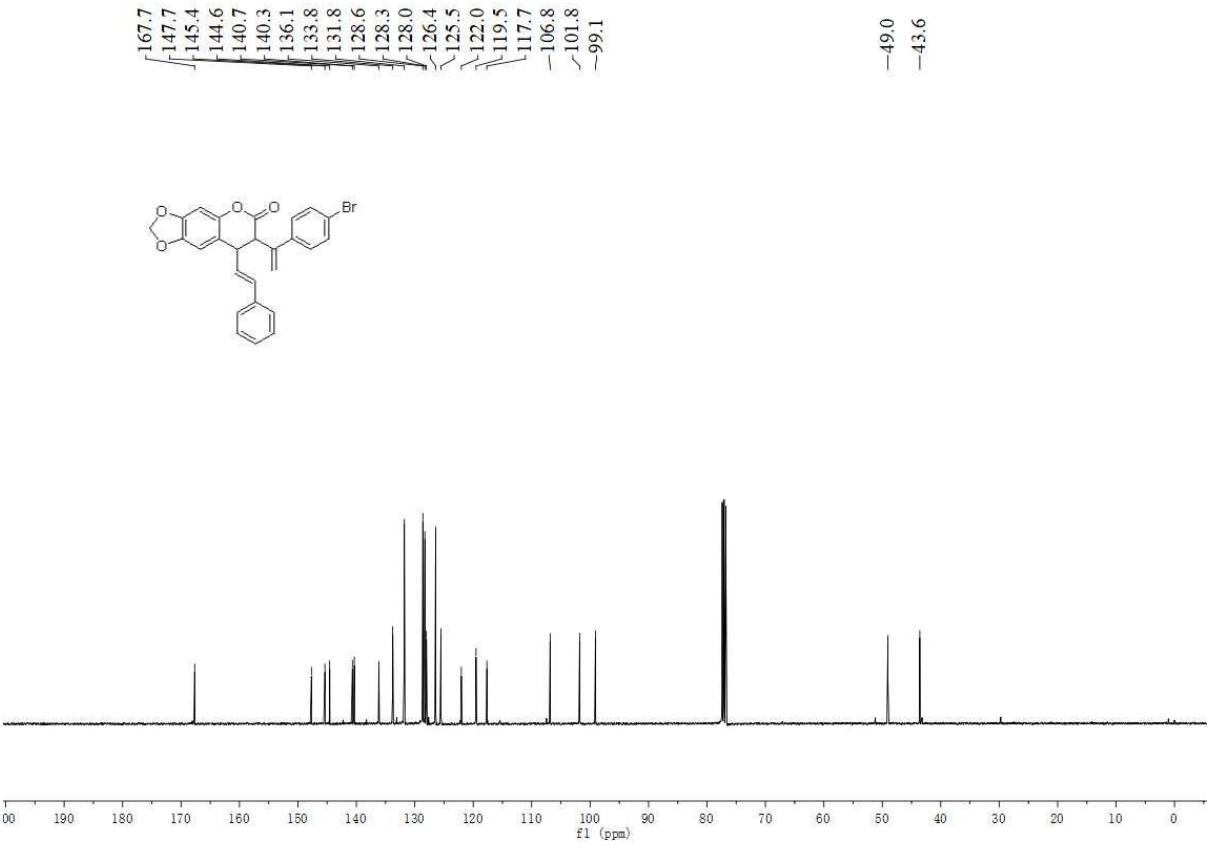
^{13}C NMR Spectrum of Compound (**3k**)



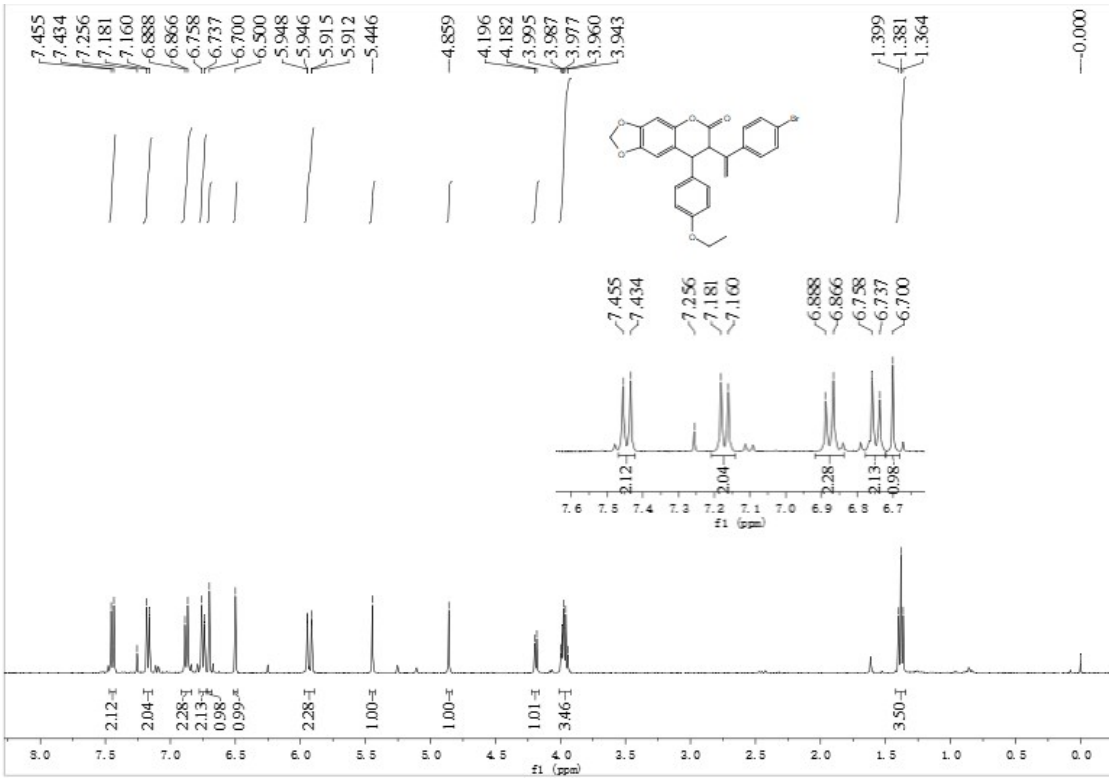
^{1}H NMR Spectrum of Compound (**3l**)



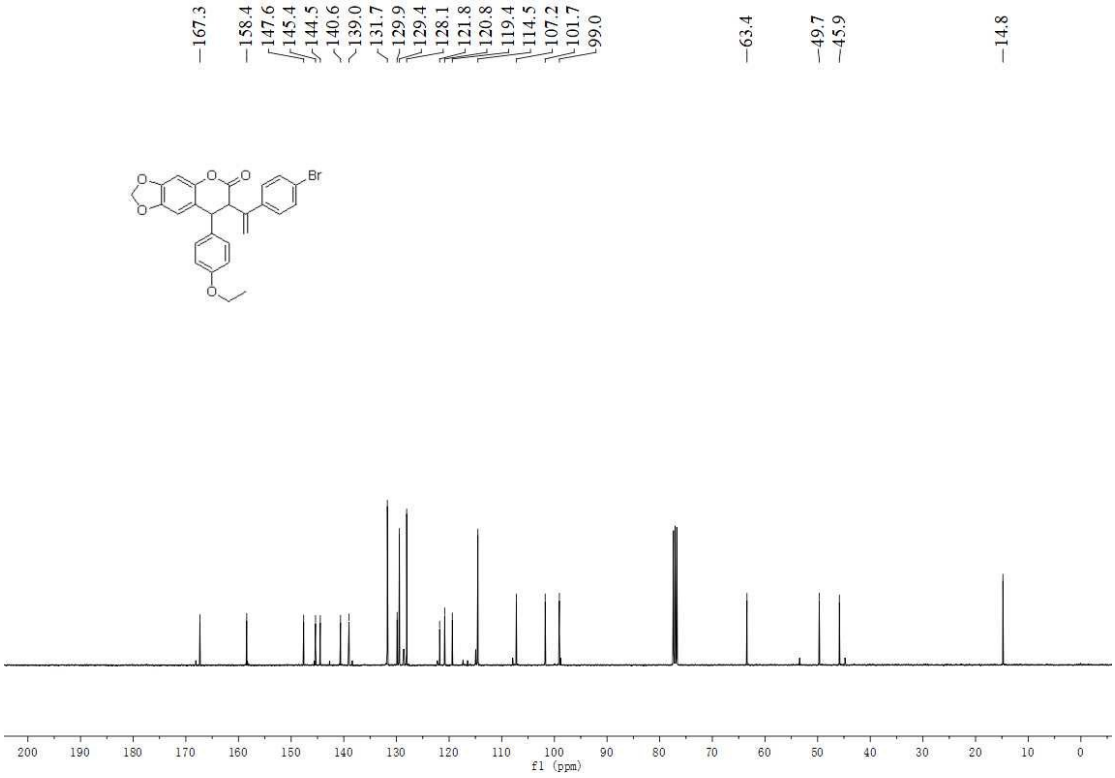
^{13}C NMR Spectrum of Compound (**3l**)



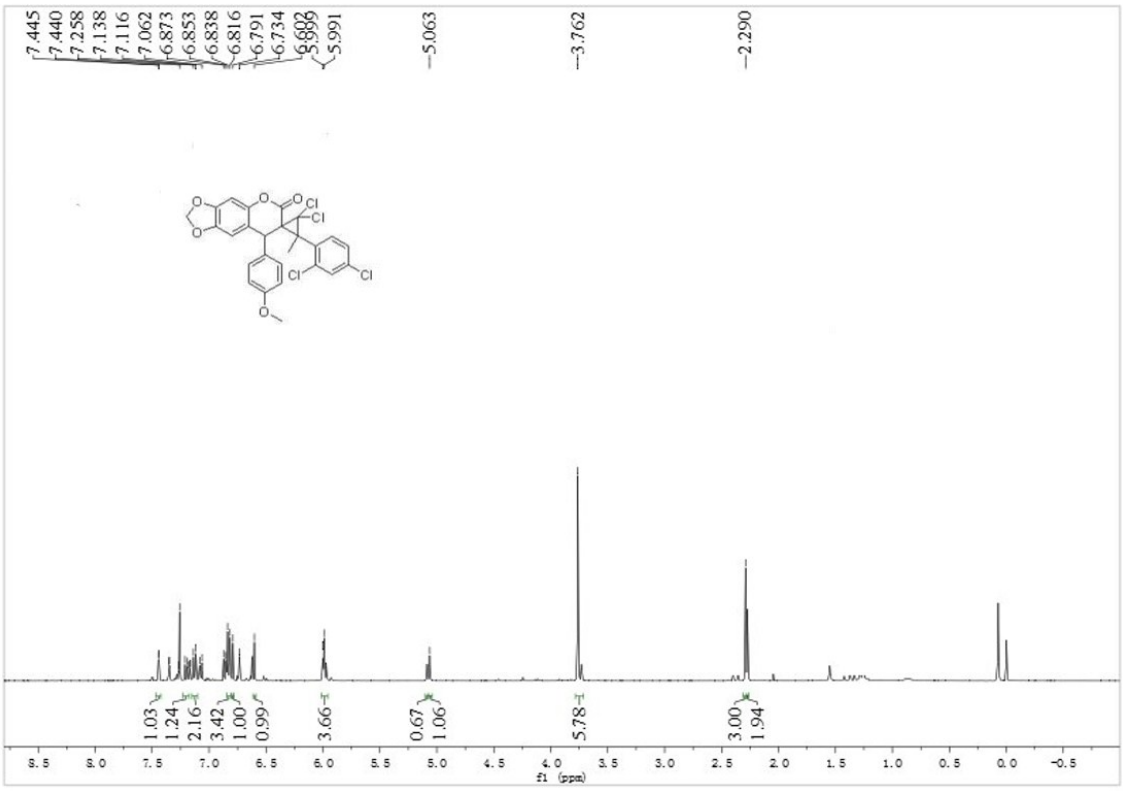
^{1}H NMR Spectrum of Compound (**3m**)



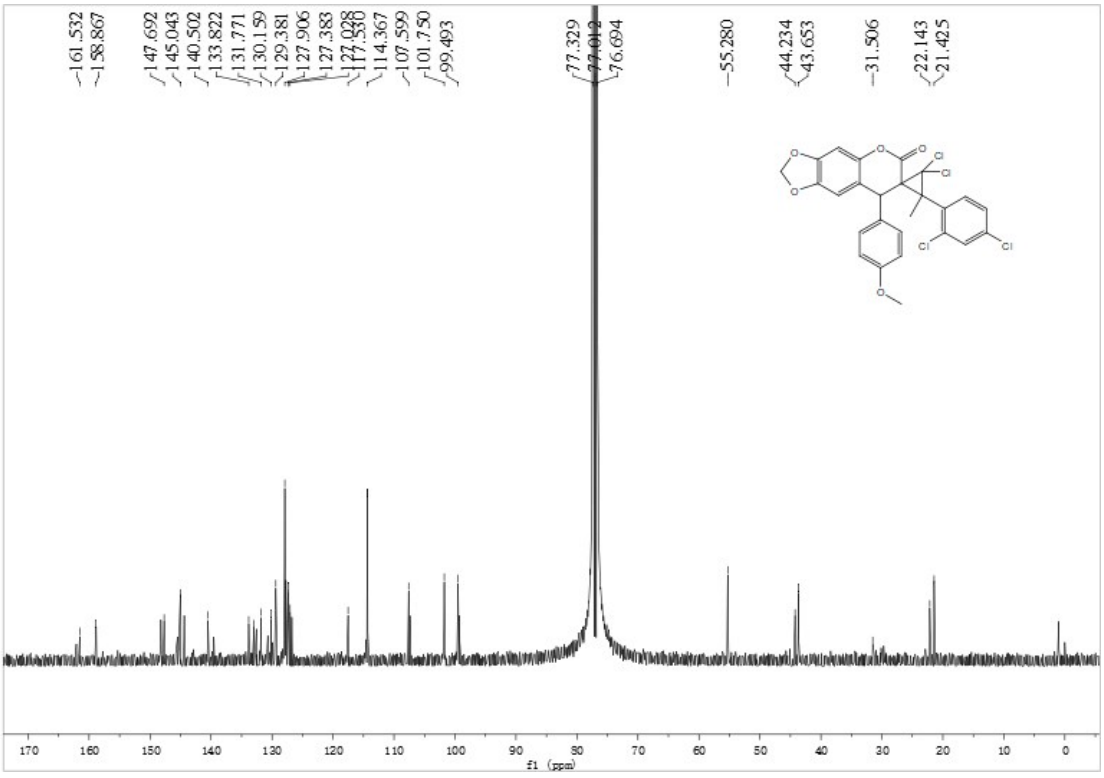
^{13}C NMR Spectrum of Compound (**3m**)



^{1}H NMR Spectrum of Compound (**3g'**)



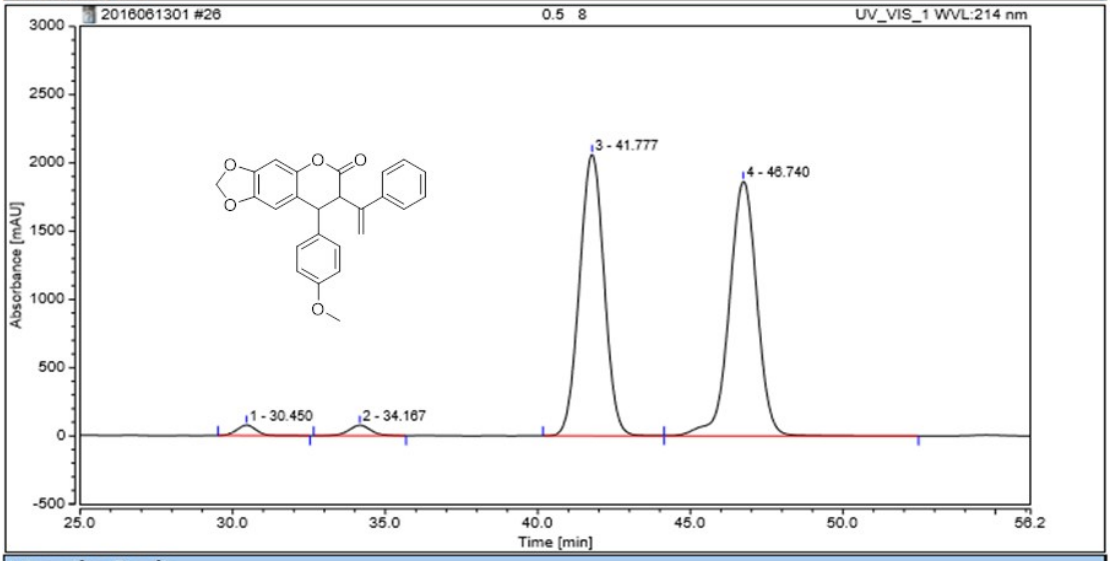
^{13}C NMR Spectrum of Compound (**3g'**)



3. HPLC Spectra

3a

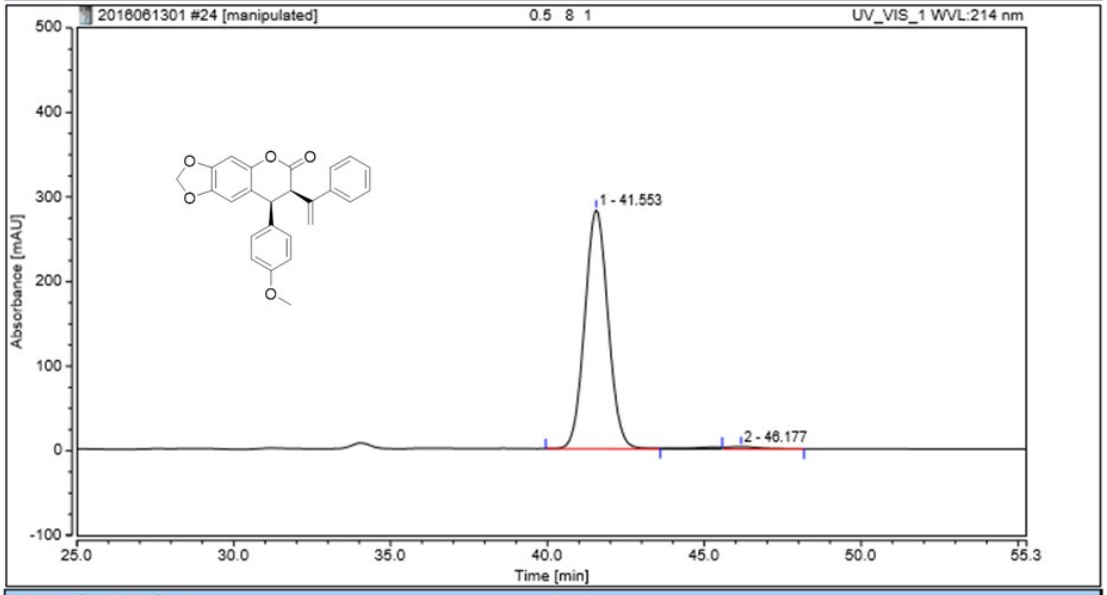
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.450	57.790	76.778	1.44	1.88	n.a.
2		34.167	65.658	76.486	1.64	1.87	n.a.
3		41.777	1925.705	2062.135	48.12	50.52	n.a.
4		46.740	1953.092	1866.585	48.80	45.73	n.a.
Total:			**4002.245**	**4081.984**	**100.00**	**100.00**	

Chromatogram



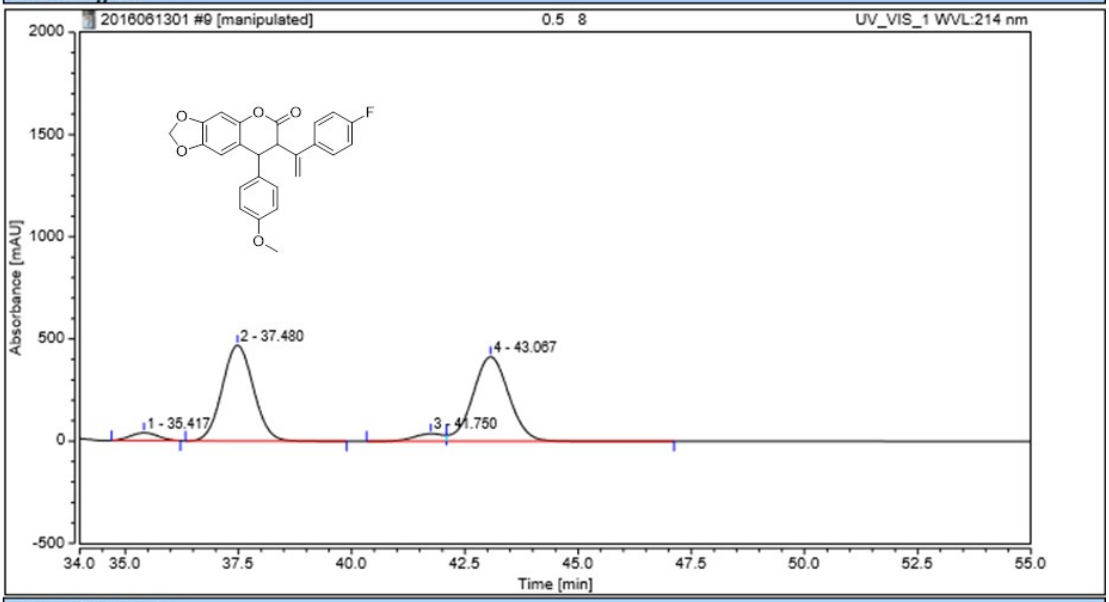
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		41.553	242.514	282.299	98.84	99.11	n.a.
2		46.177	2.852	2.524	1.16	0.89	n.a.
Total:			**245.367**	**284.823**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 46.2 min, t (major) = 41.6 min].

3b

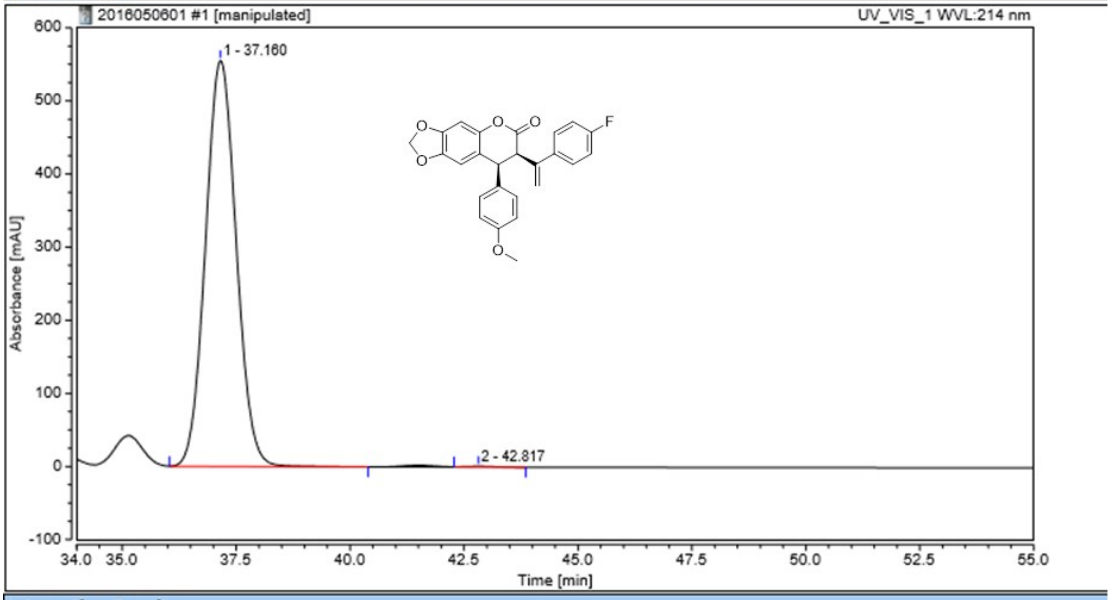
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		35.417	27.261	38.374	3.36	4.01	n.a.
2		37.480	375.095	467.684	46.17	48.92	n.a.
3		41.750	27.361	36.506	3.37	3.82	n.a.
4		43.067	382.617	413.363	47.10	43.24	n.a.
Total:			**812.333**	**955.927**	**100.00**	**100.00**	

Chromatogram

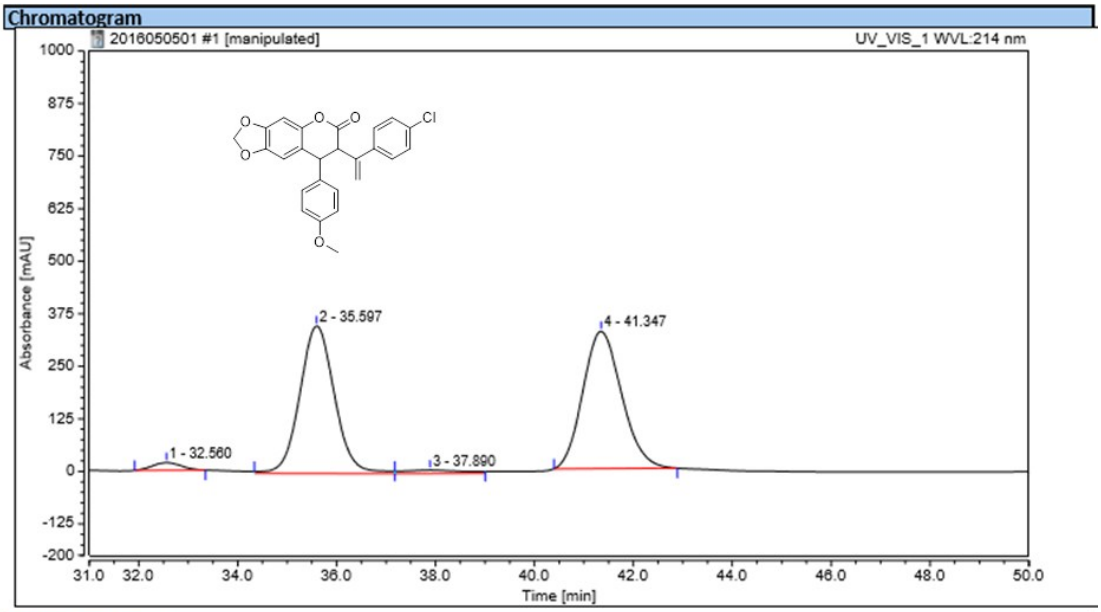


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		37.160	433.149	555.309	99.79	99.81	n.a.
2		42.817	0.897	1.059	0.21	0.19	n.a.
Total:			**434.046**	**556.367**	**100.00**	**100.00**	

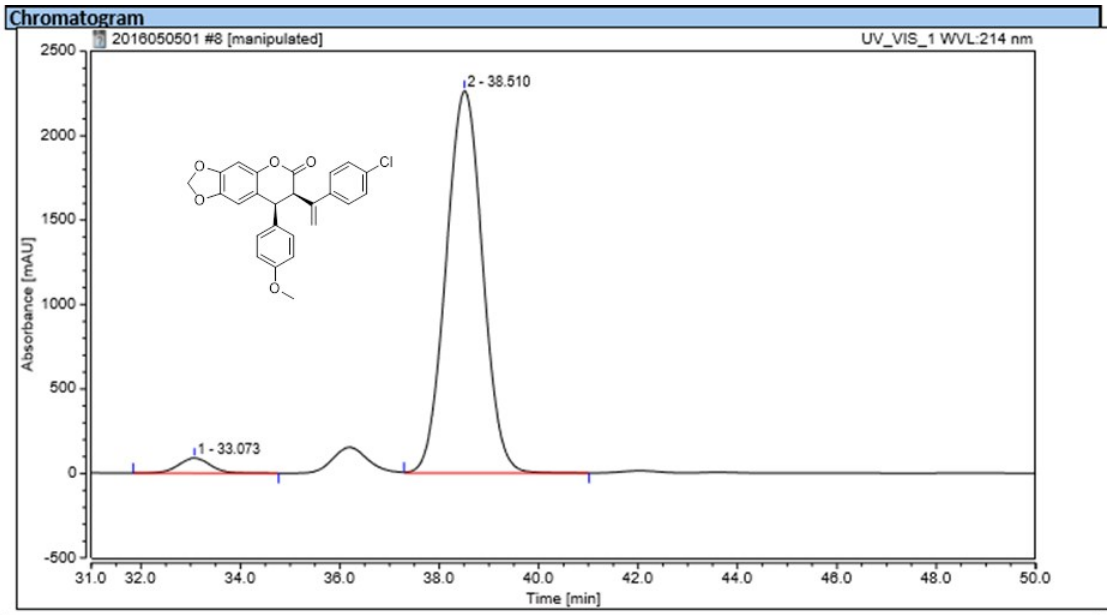
HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 42.8 min, t (major) = 37.2 min].

3c



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32.560	12.078	17.987	1.99	2.56	n.a.
2		35.597	286.276	351.111	47.19	49.88	n.a.
3		37.890	11.763	8.413	1.94	1.20	n.a.
4		41.347	296.560	326.410	48.88	46.37	n.a.
Total:			**606.677**	**703.921**	**100.00**	**100.00**	



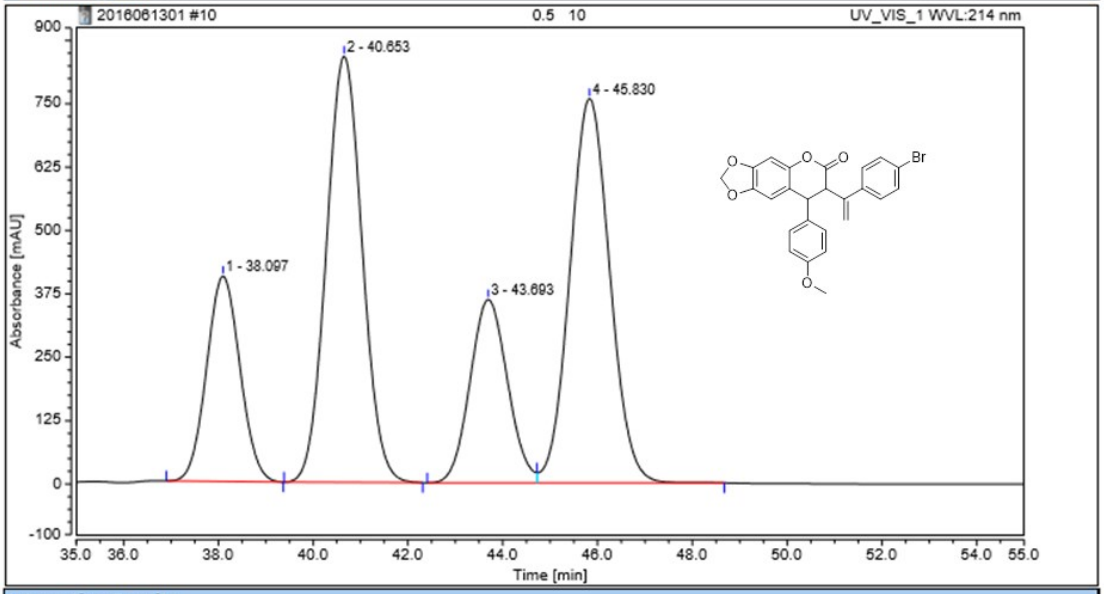
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		33.073	66.284	88.803	3.33	3.77	n.a.
2		38.510	1927.006	2264.355	96.67	96.23	n.a.
Total:			**1993.290**	**2353.157**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8,λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 33.1 min, t (major) = 38.5 min].

3d

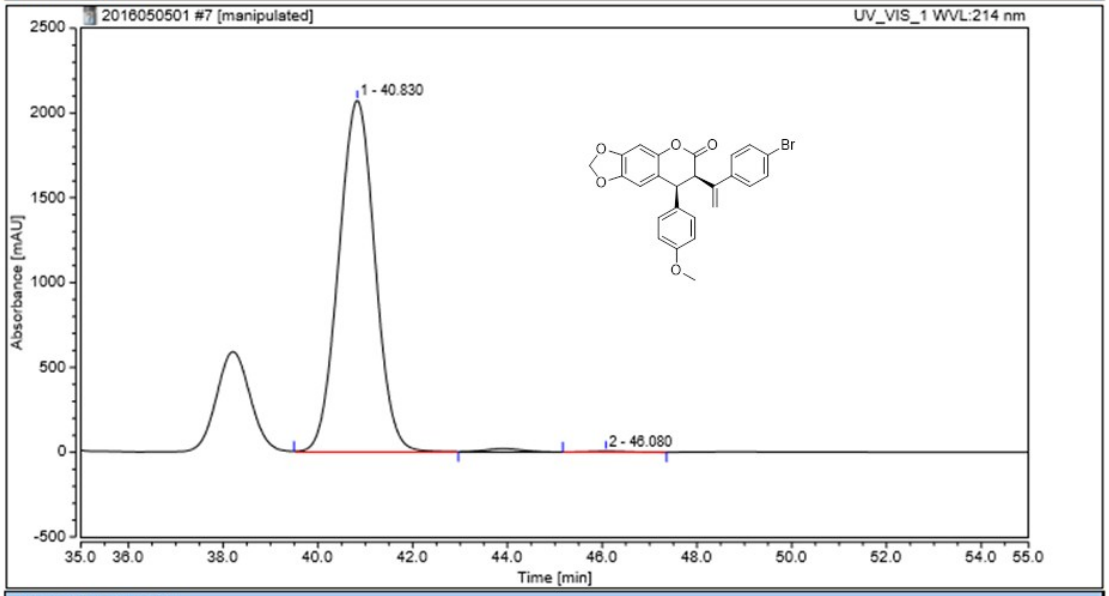
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		38.097	330.903	405.034	15.48	17.12	n.a.
2		40.653	736.421	841.130	34.45	35.55	n.a.
3		43.693	330.807	361.437	15.48	15.28	n.a.
4		45.830	739.238	758.350	34.59	32.05	n.a.
Total:			**2137.369**	**2365.951**	**100.00**	**100.00**	

Chromatogram



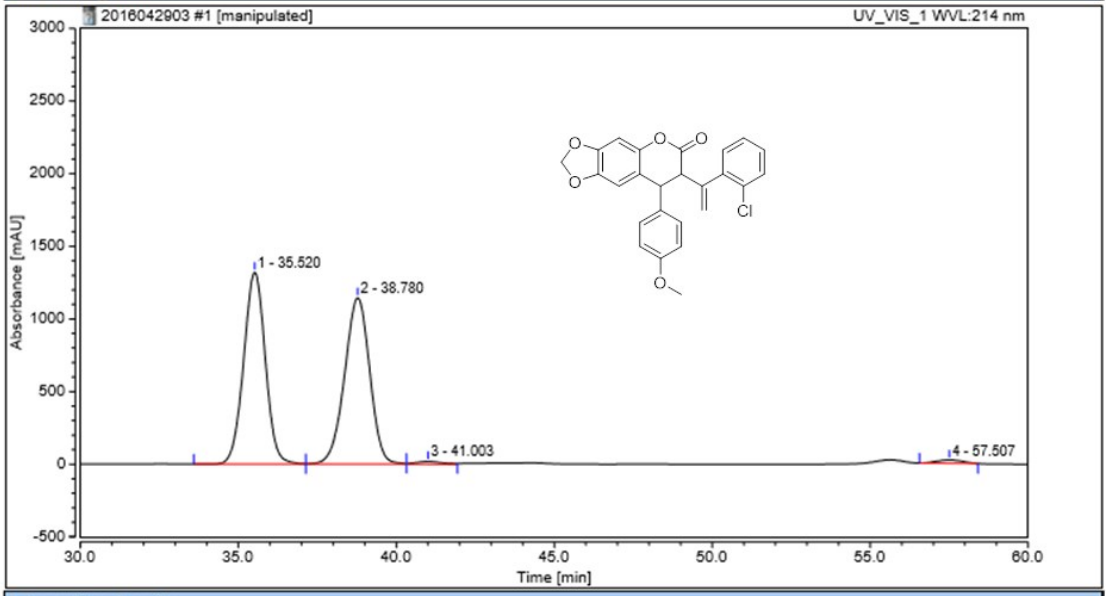
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		40.830	1833.677	2071.763	99.74	99.77	n.a.
2		46.080	4.702	4.836	0.26	0.23	n.a.
Total:			**1838.379**	**2076.599**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 46.1 min, t (major) = 40.8 min].

3e

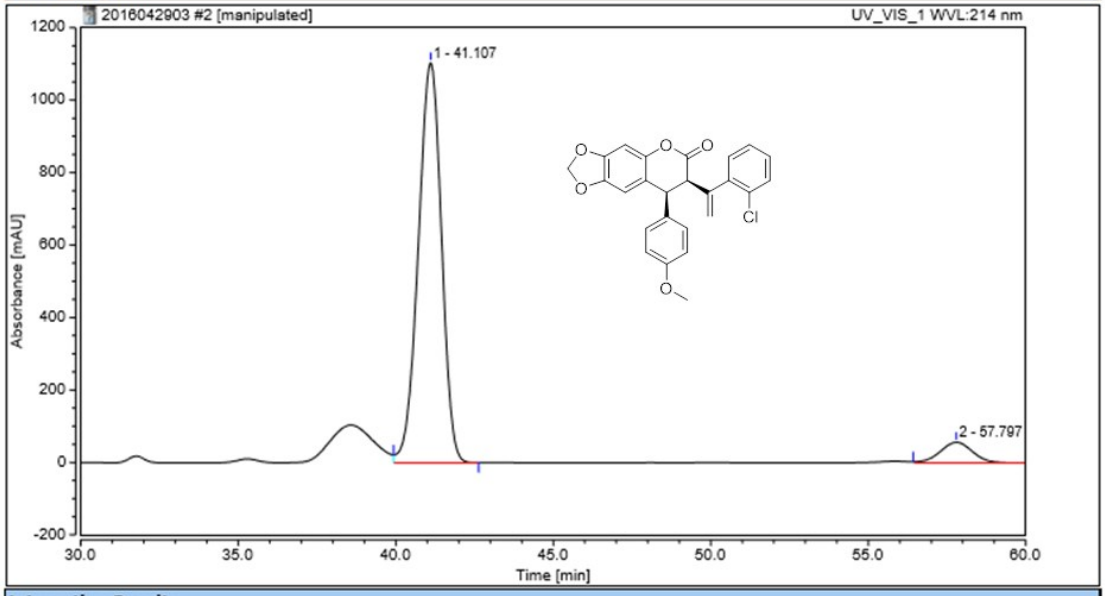
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		35.520	1052.321	1321.637	48.90	52.68	n.a.
2		38.780	1059.677	1145.565	49.24	45.66	n.a.
3		41.003	17.892	18.220	0.83	0.73	n.a.
4		57.507	22.036	23.269	1.02	0.93	n.a.
Total:			**2151.925**	**2508.692**	**100.00**	**100.00**	

Chromatogram



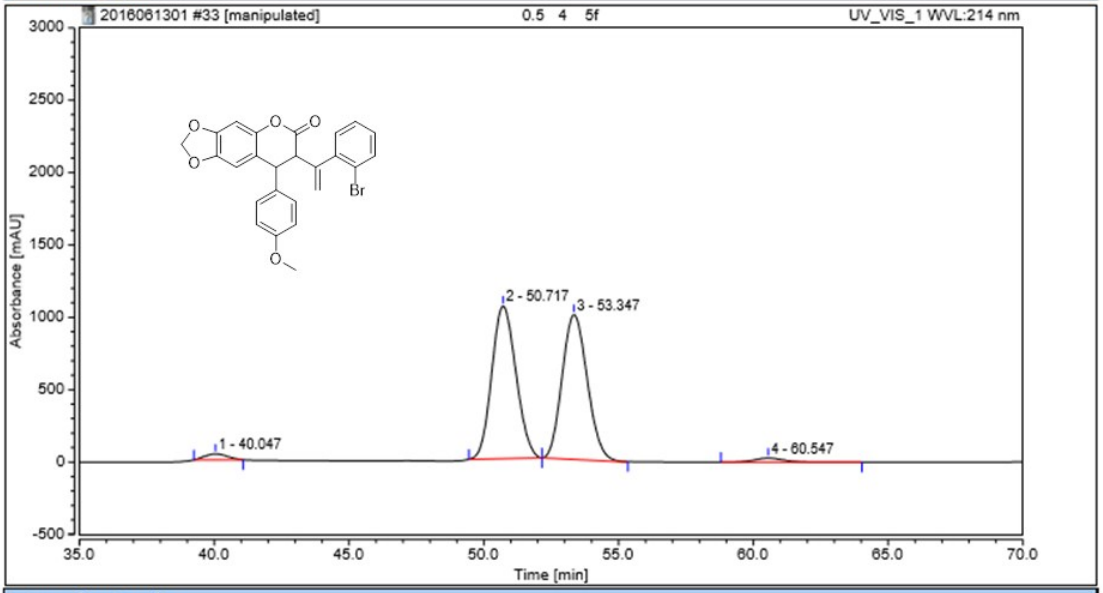
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		41.107	942.303	1105.101	93.29	95.12	n.a.
2		57.797	67.778	56.752	6.71	4.88	n.a.
Total:			**1010.081**	**1161.853**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 57.8 min, t (major) = 41.1 min].

3f

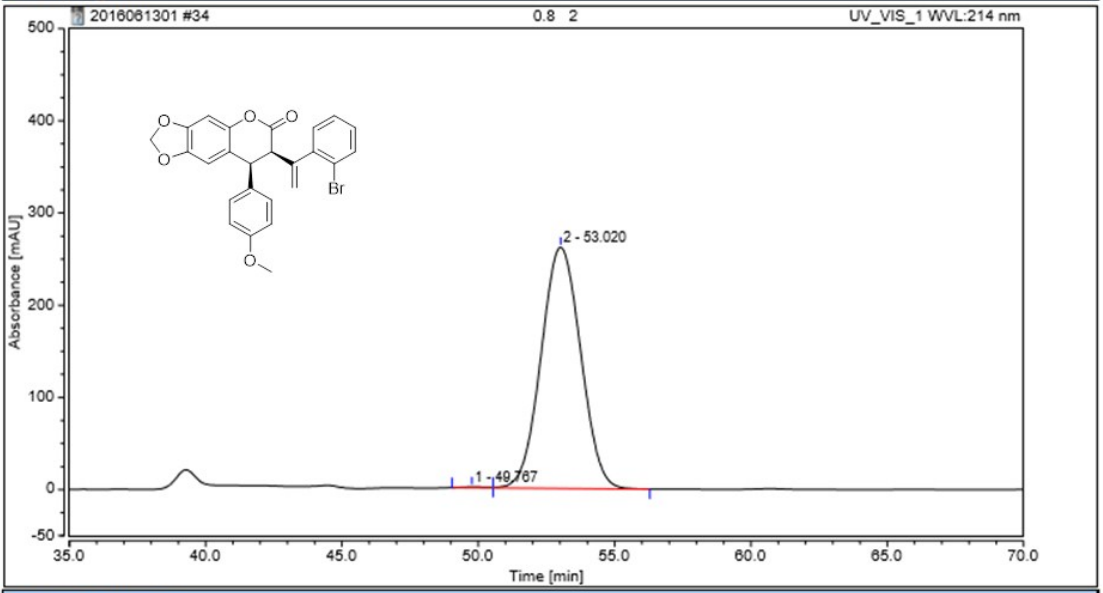
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		40.047	39.445	40.262	1.75	1.90	n.a.
2		50.717	1098.022	1054.938	48.66	49.66	n.a.
3		53.347	1083.303	1001.068	48.01	47.12	n.a.
4		60.547	35.547	28.156	1.58	1.33	n.a.
Total:			**2256.318**	**2124.424**	**100.00**	**100.00**	

Chromatogram

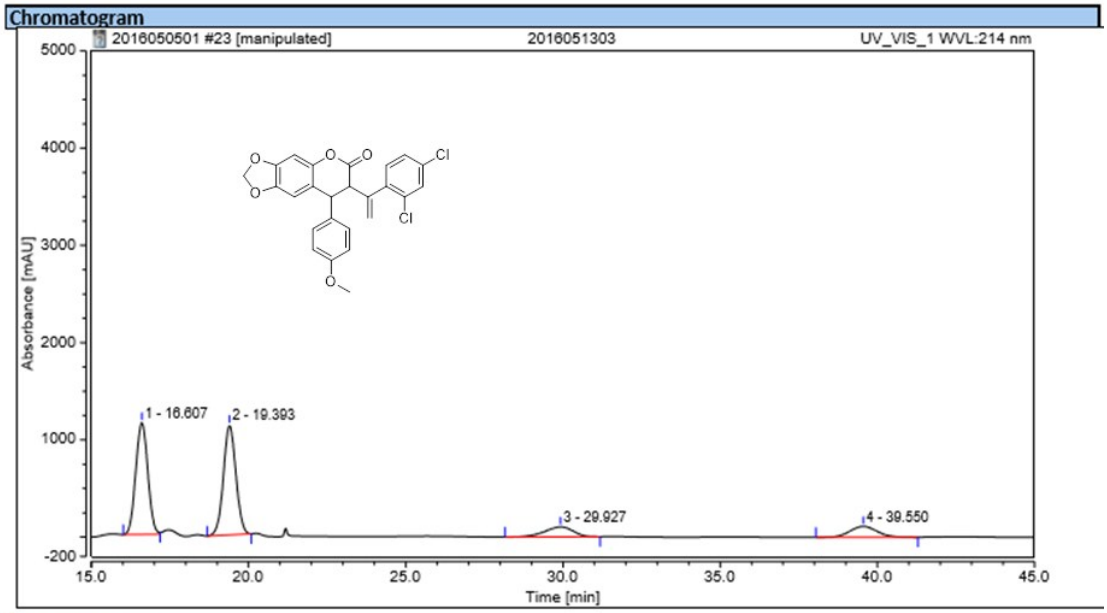


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		49.767	1.000	0.876	0.23	0.33	n.a.
2		53.020	440.064	261.530	99.77	99.67	n.a.
Total:			**441.064**	**262.406**	**100.00**	**100.00**	

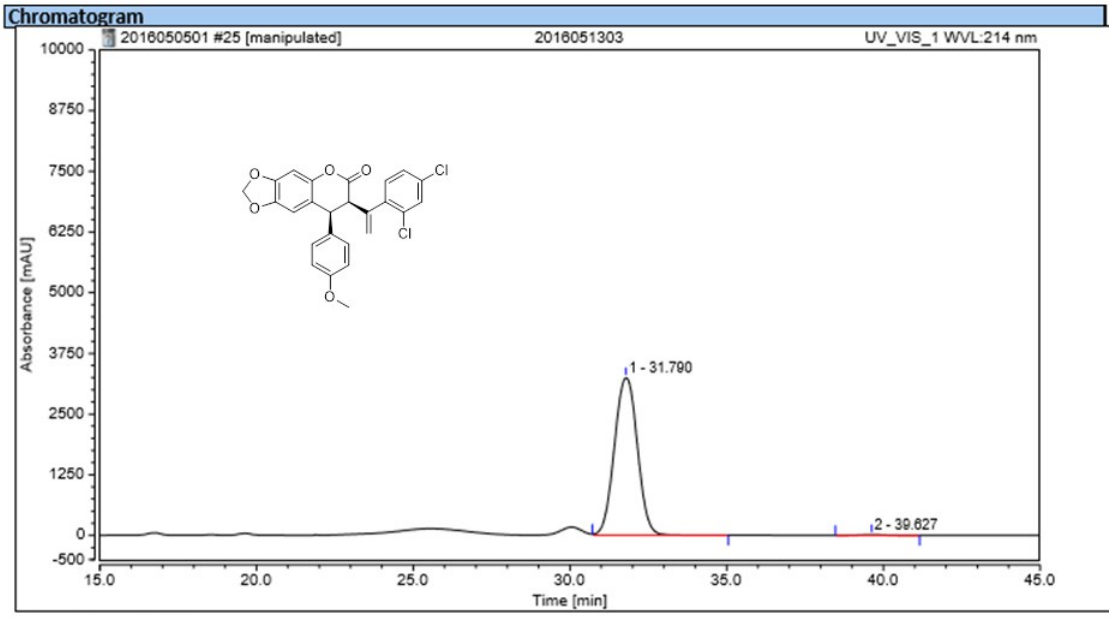
HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL. min^{-1}, T = 30 ^{o}C, t (minor) = 49.8 min, t (major) = 53.0 min].

3g



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.607	513.978	1150.871	41.11	46.20	n.a.
2		19.393	518.837	1127.405	41.49	45.26	n.a.
3		29.927	106.546	101.384	8.52	4.07	n.a.
4		39.550	111.005	111.543	8.88	4.48	n.a.
Total:			**1250.367**	**2491.203**	**100.00**	**100.00**	

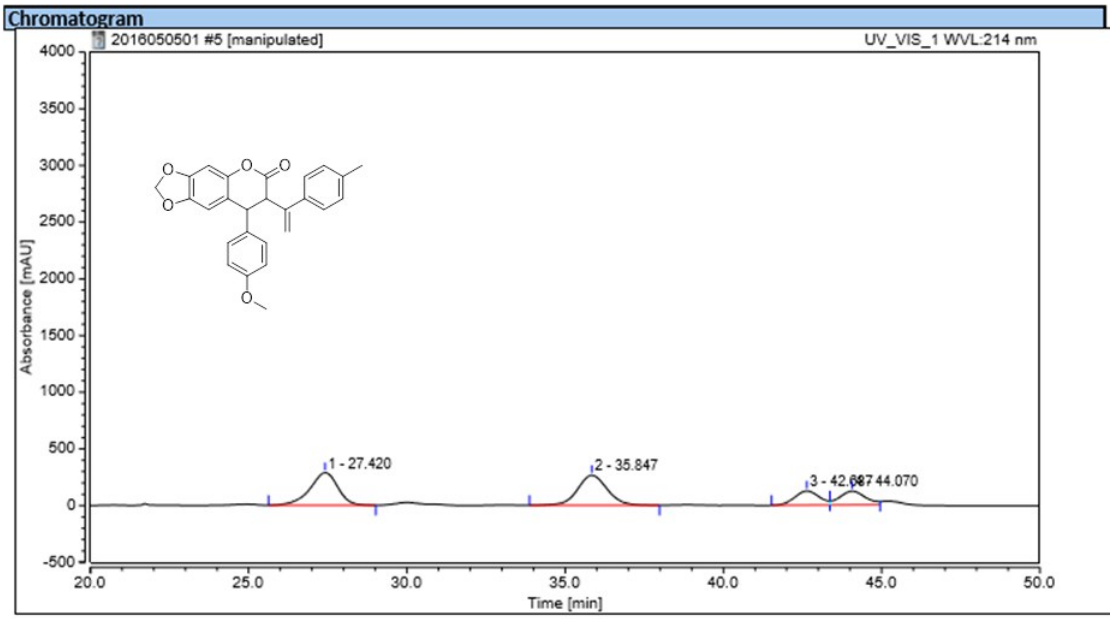


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		31.790	2761.293	3247.000	99.49	99.51	n.a.
2		39.627	14.082	15.875	0.51	0.49	n.a.
Total:			**2775.375**	**3262.875**	**100.00**	**100.00**	

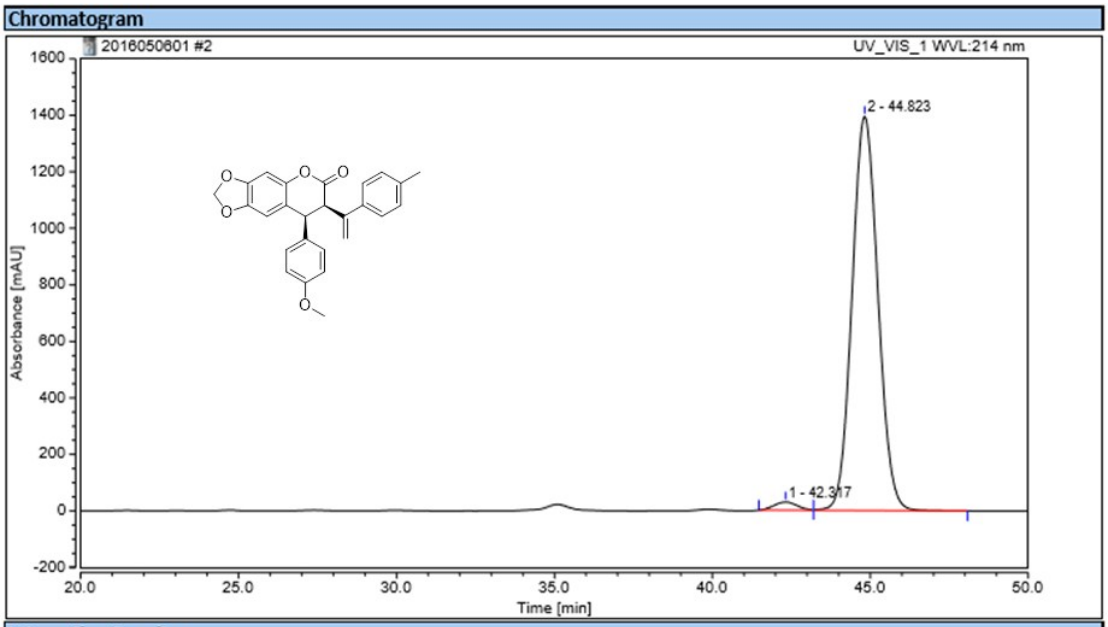
HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 39.6 min, t (major) = 31.8 min].

3h



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		27.420	293.682	287.182	36.22	35.98	n.a.
2		35.847	287.602	264.758	35.47	33.17	n.a.
3		42.637	112.984	124.636	13.94	15.62	n.a.
4		44.070	116.518	121.582	14.37	15.23	n.a.
Total:			**810.786**	**798.159**	**100.00**	**100.00**	



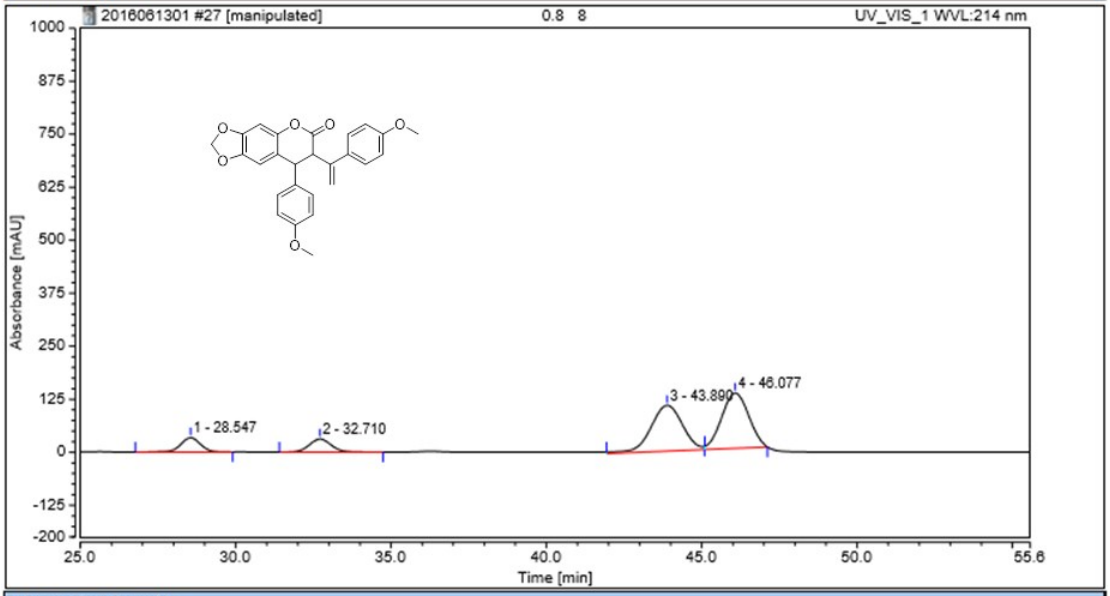
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		42.317	24.786	28.978	1.84	2.03	n.a.
2		44.823	1323.284	1395.185	98.16	97.97	n.a.
Total:			**1348.070**	**1424.164**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 ^{o}C, t (minor) = 42.3 min, t (major) = 44.8 min].

3i

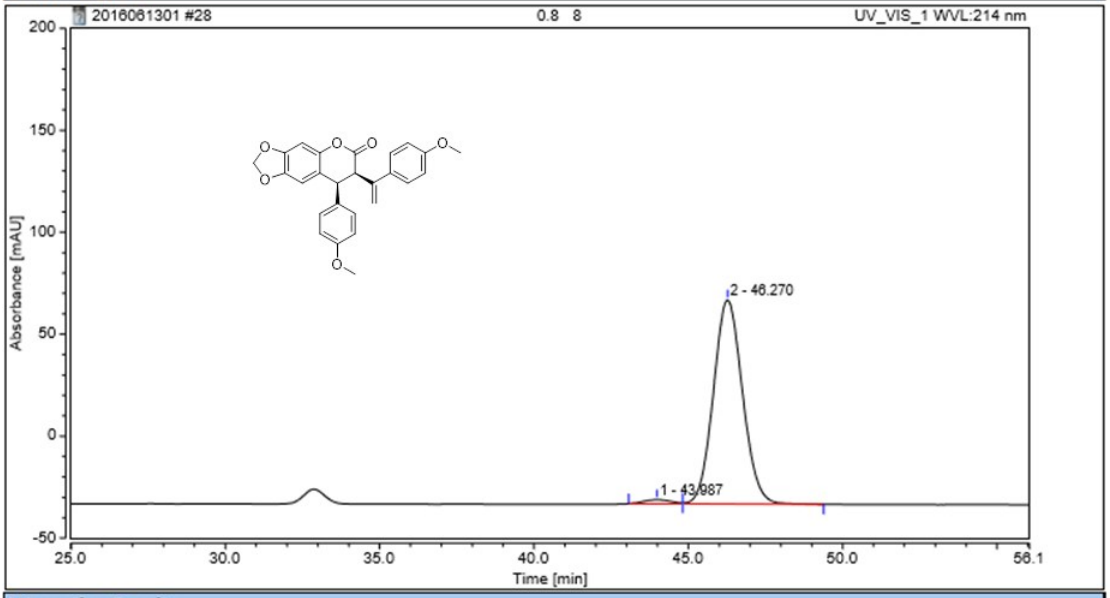
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		28.547	24.760	33.656	8.03	11.12	n.a.
2		32.710	24.859	30.693	8.06	10.15	n.a.
3		43.890	127.139	107.873	41.24	35.66	n.a.
4		46.077	131.555	130.320	42.67	43.07	n.a.
Total:			**308.314**	**302.543**	**100.00**	**100.00**	

Chromatogram



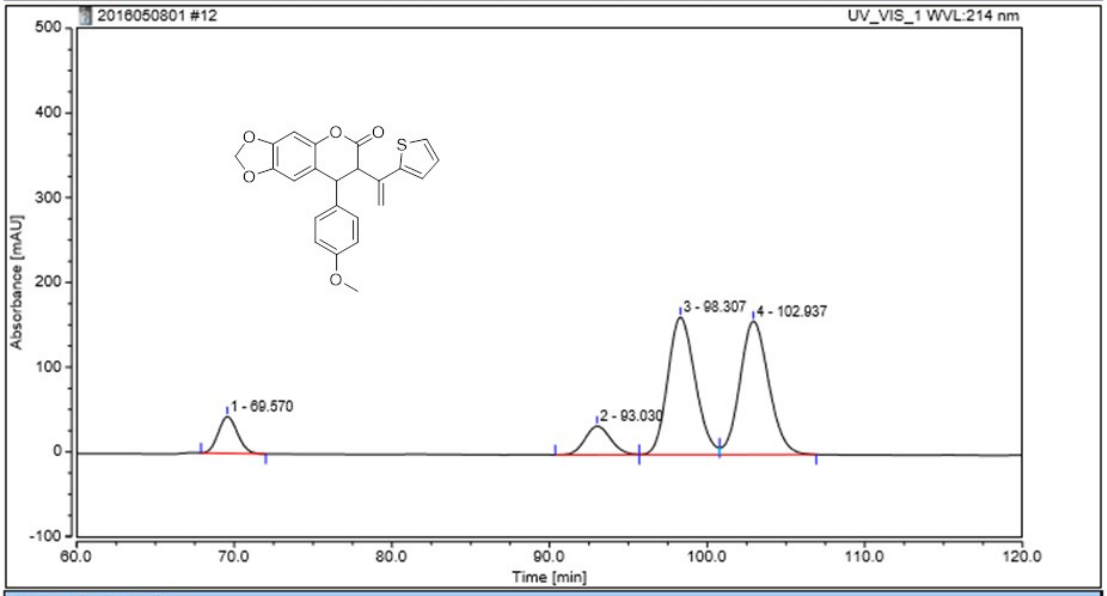
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		43.987	1.972	1.980	1.77	1.94	n.a.
2		46.270	109.531	100.036	98.23	98.06	n.a.
Total:			**111.503**	**102.015**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T= 30 °C, t (minor) = 44.0 min, t (major) = 46.3 min].

3j

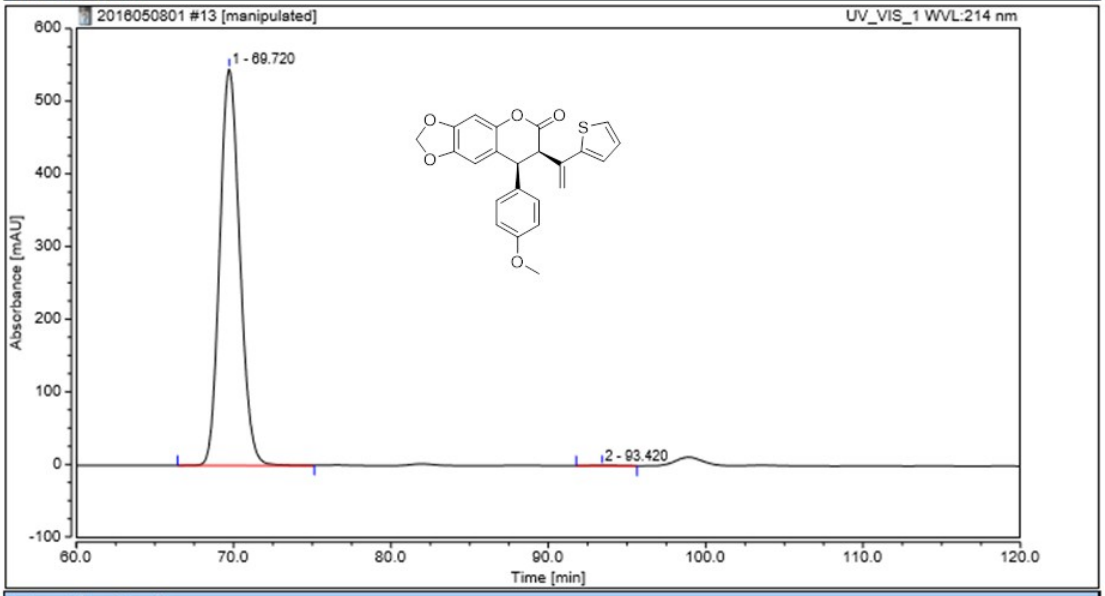
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		69.570	60.970	43.125	7.75	10.87	n.a.
2		93.030	64.024	33.854	8.14	8.54	n.a.
3		98.307	327.730	162.200	41.66	40.90	n.a.
4		102.937	334.045	157.381	42.46	39.69	n.a.
Total:			**786.769**	**396.560**	**100.00**	**100.00**	

Chromatogram



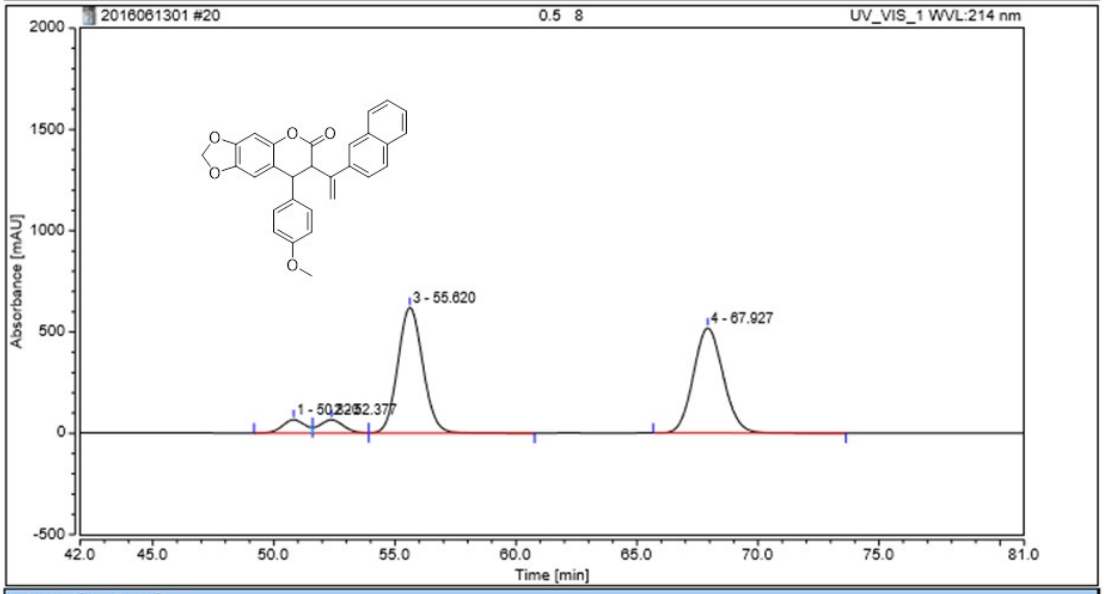
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		69.720	805.367	546.149	99.87	99.89	n.a.
2		93.420	1.039	0.623	0.13	0.11	n.a.
Total:			**806.406**	**546.772**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 93.4 min, t (major) = 69.7 min].

3k

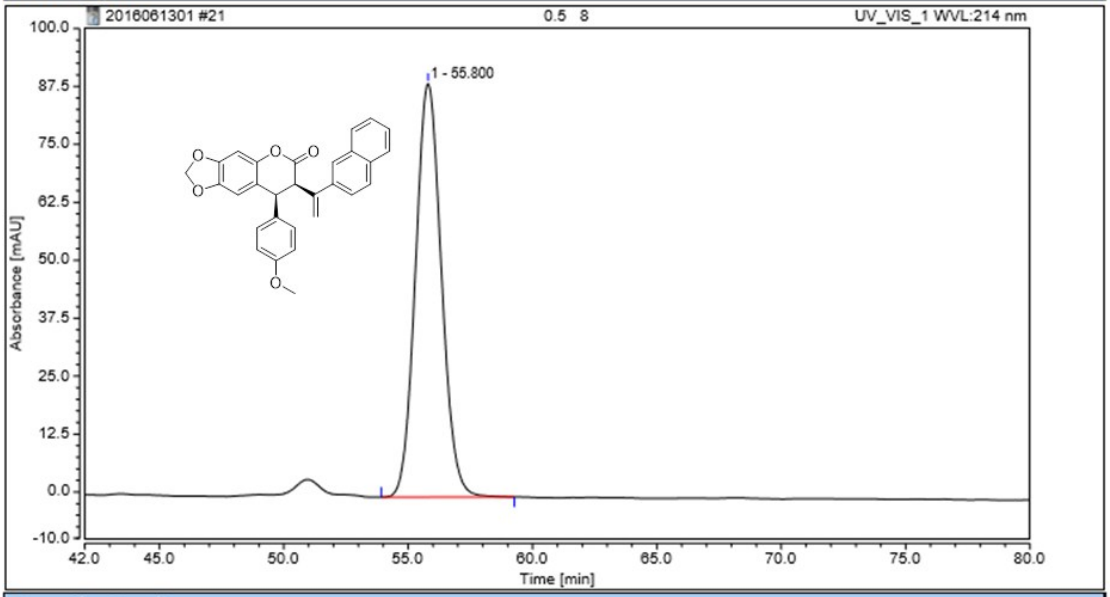
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		50.820	70.260	65.115	4.31	5.13	n.a.
2		52.377	74.020	65.120	4.54	5.14	n.a.
3		55.620	743.355	619.856	45.59	48.88	n.a.
4		67.927	742.944	518.037	45.56	40.85	n.a.
Total:			**1630.579**	**1268.128**	**100.00**	**100.00**	

Chromatogram



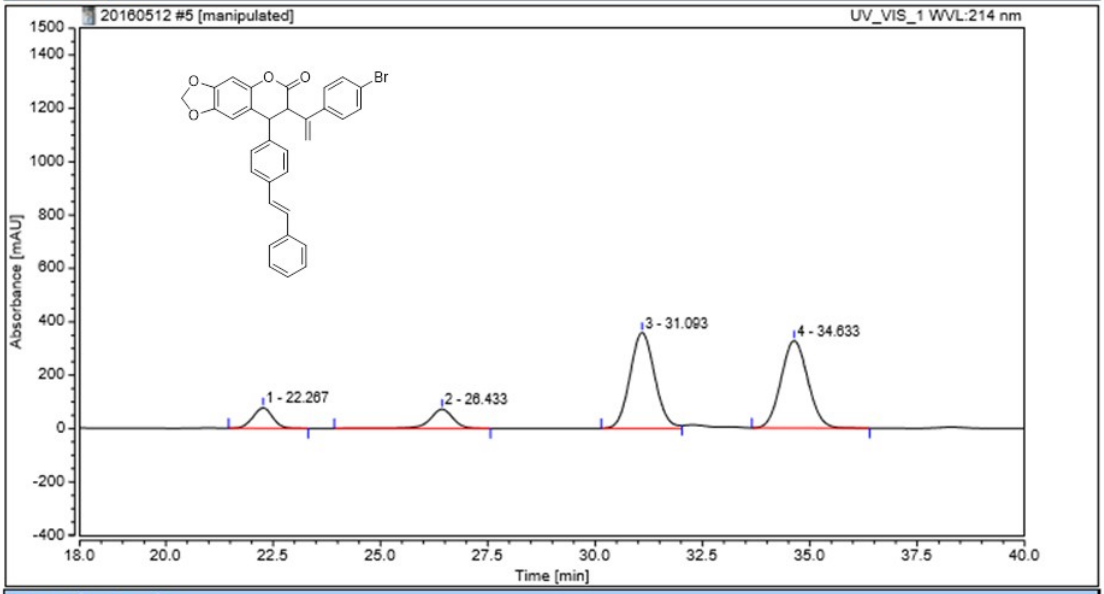
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		55.800	108.052	89.263	100.00	100.00	n.a.
Total:			**108.052**	**89.263**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 68.0 min, t (major) = 55.8 min].

3l

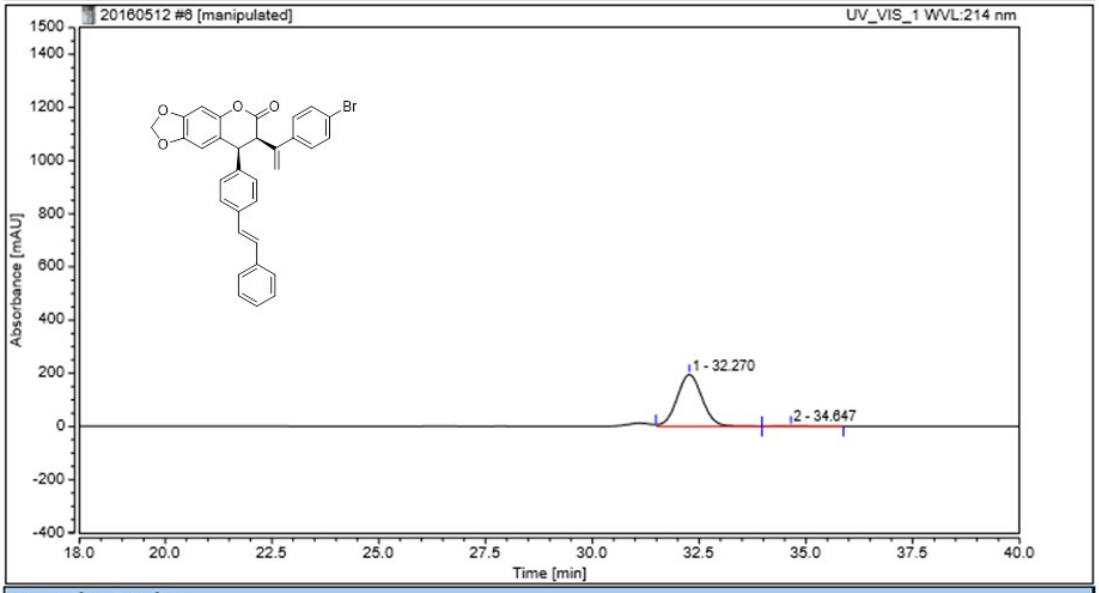
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		22.267	40.654	76.700	7.24	9.19	n.a.
2		26.433	44.114	71.696	7.85	8.59	n.a.
3		31.093	240.690	359.113	42.84	43.02	n.a.
4		34.633	236.369	327.242	42.07	39.20	n.a.
Total:			**561.827**	**834.751**	**100.00**	**100.00**	

Chromatogram

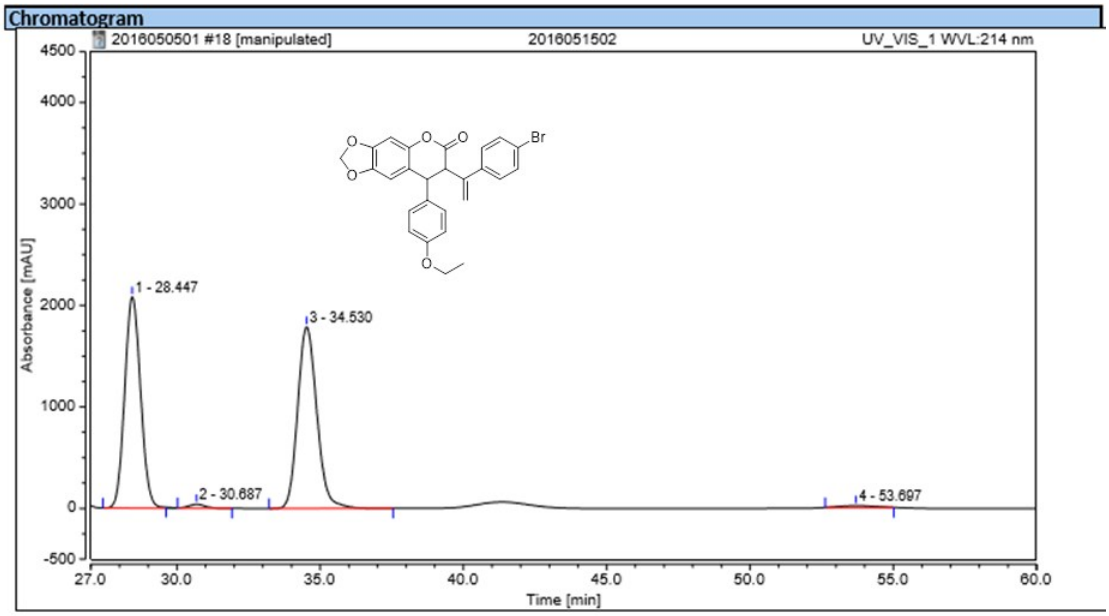


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32.270	132.493	194.590	99.43	99.50	n.a.
2		34.647	0.762	0.973	0.57	0.50	n.a.
Total:			**133.255**	**195.564**	**100.00**	**100.00**	

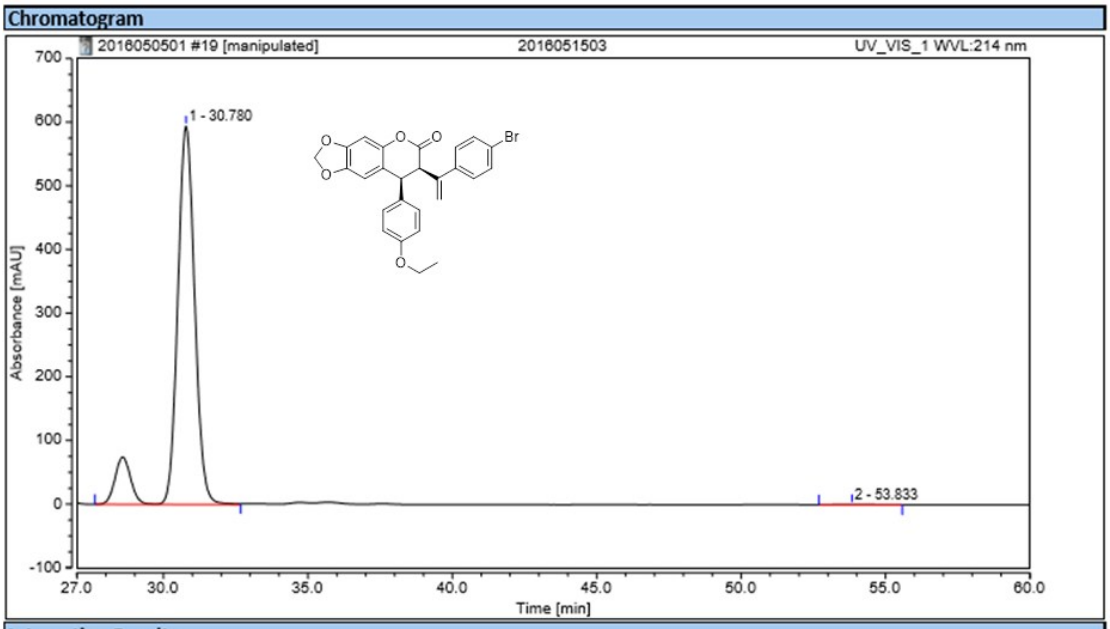
HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL·min^{-1}, T = 30 °C, t (minor) = 34.6 min, t (major) = 32.3 min].

3m



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		28.447	1337.092	2083.239	48.21	52.99	n.a.
2		30.687	25.970	38.748	0.94	0.99	n.a.
3		34.530	1385.956	1791.967	49.97	45.58	n.a.
4		53.697	24.475	17.667	0.88	0.45	n.a.
Total:			**2773.493**	**3931.621**	**100.00**	**100.00**	



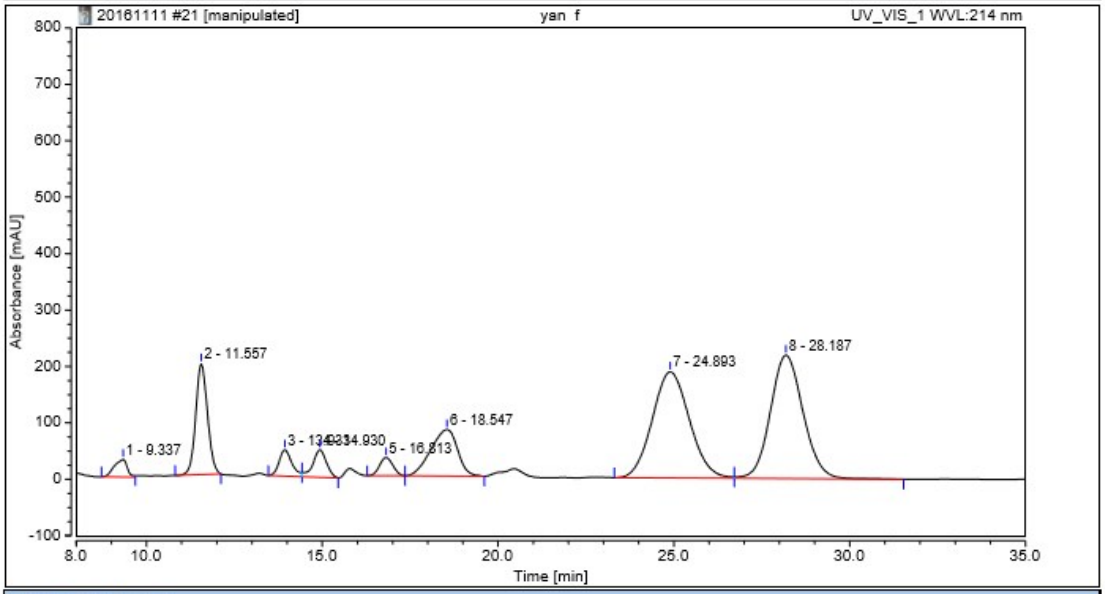
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		30.780	446.492	594.556	99.87	99.92	n.a.
2		53.833	0.595	0.460	0.13	0.08	n.a.
Total:			**447.087**	**595.016**	**100.00**	**100.00**	

HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 92/8, λ = 254 nm, v = 0.5 mL.min^{-1}, T = 30 ^{o}C, t (minor) = 53.7 min, t (major) = 30.8 min].

3g'

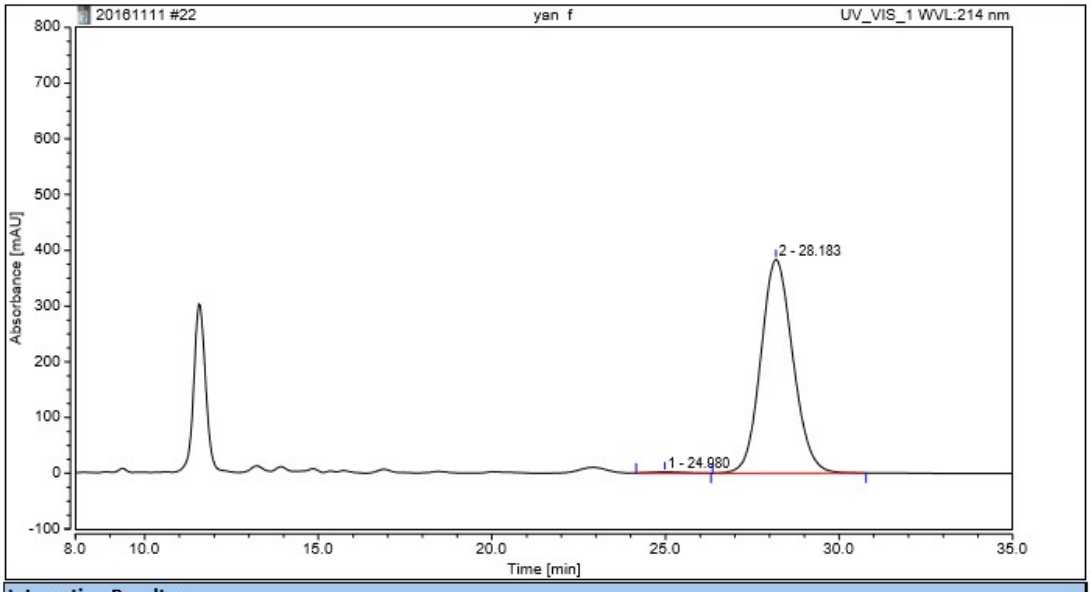
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.337	13.326	31.371	1.95	3.72	n.a.
2		11.557	76.438	196.309	11.17	23.26	n.a.
3		13.933	19.396	46.382	2.84	5.50	n.a.
4		14.930	21.637	48.661	3.16	5.77	n.a.
5		16.813	14.095	32.038	2.06	3.80	n.a.
6		18.547	72.484	82.310	10.60	9.75	n.a.
7		24.893	230.607	187.945	33.71	22.27	n.a.
8		28.187	236.143	218.856	34.52	25.93	n.a.
Total:			**684.126**	**843.871**	**100.00**	**100.00**	

Chromatogram



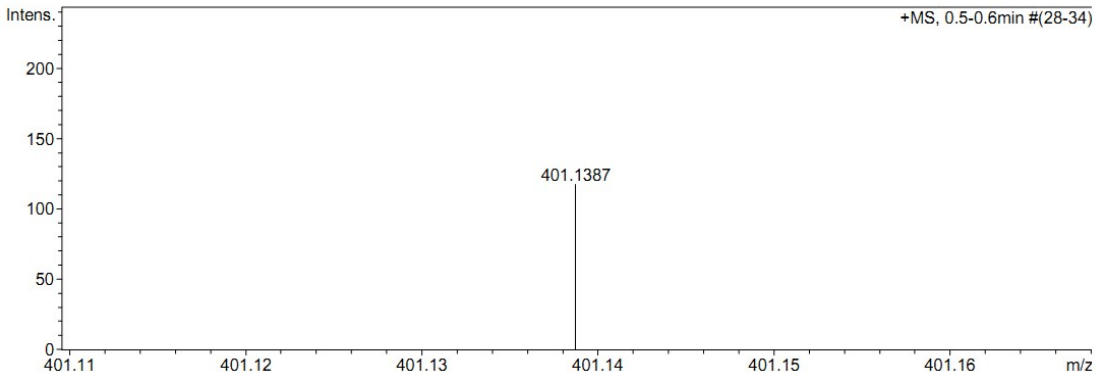
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		24.980	1.922	1.869	0.47	0.49	n.a.
2		28.183	410.166	383.002	99.53	99.51	n.a.
Total:			**412.088**	**384.872**	**100.00**	**100.00**	

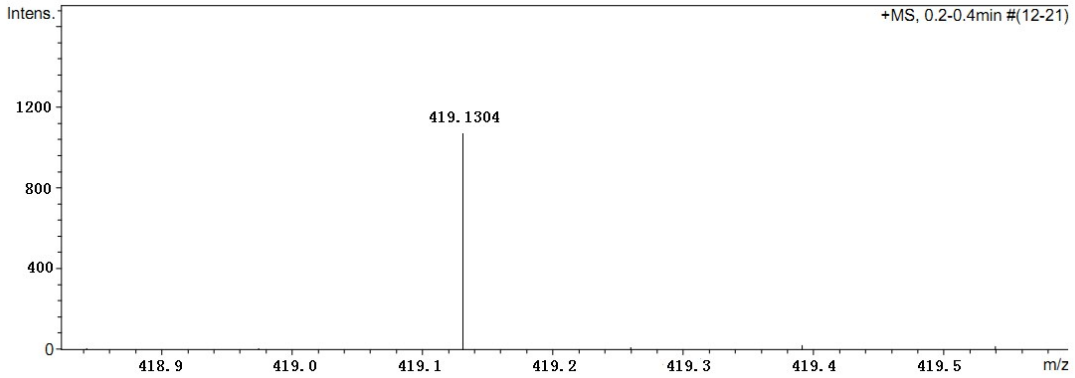
HPLC [Daicel Chiralpak IC, *n*-hexane/isopropanol = 93/7, λ = 254 nm, v = 0.6 mL·min^{-1}, T = 30 ^{o}C, t (minor) = 25.0 min, t (major) = 28.2 min].

4. HRMS Spectra

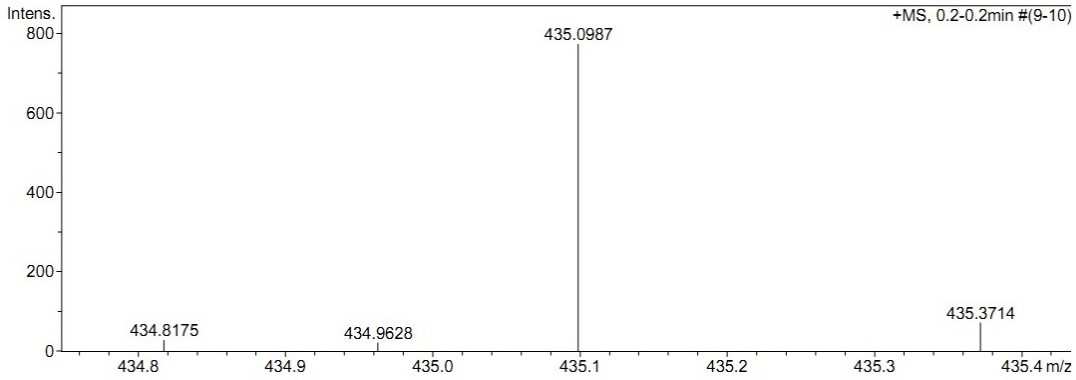
3a


Intens.
+MS, 0.5-0.6min #(28-34)
200
150
401.1387
100
50
0
401.11
401.12
401.13
401.14
401.15
401.16
m/z

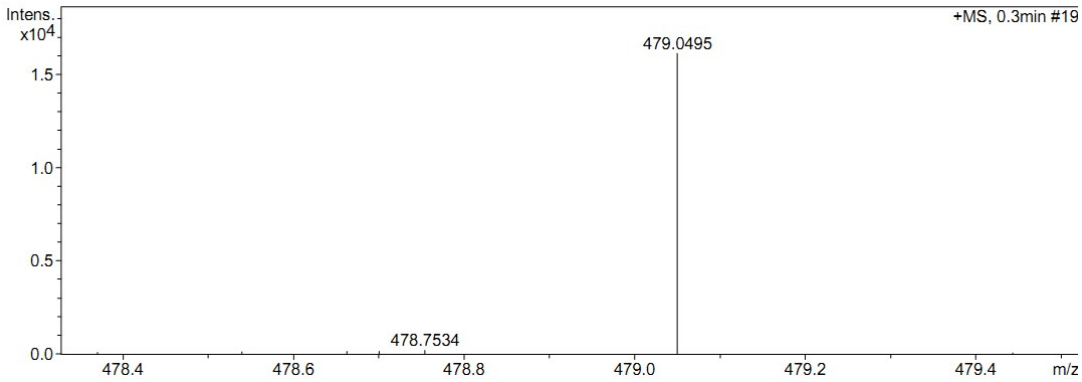
3b


Intens.
+MS, 0.2-0.4min #(12-21)
1200
419.1304
800
400
0
418.9
419.0
419.1
419.2
419.3
419.4
419.5
m/z

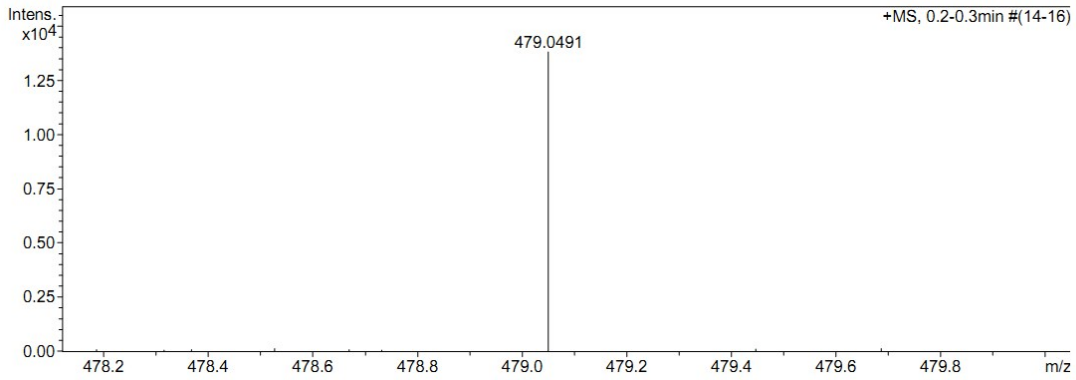
3c


Intens.
+MS, 0.2-0.2min #(9-10)
800
435.0987
600
400
200
434.8175
434.9628
435.3714
0
434.8
434.9
435.0
435.1
435.2
435.3
435.4 m/z

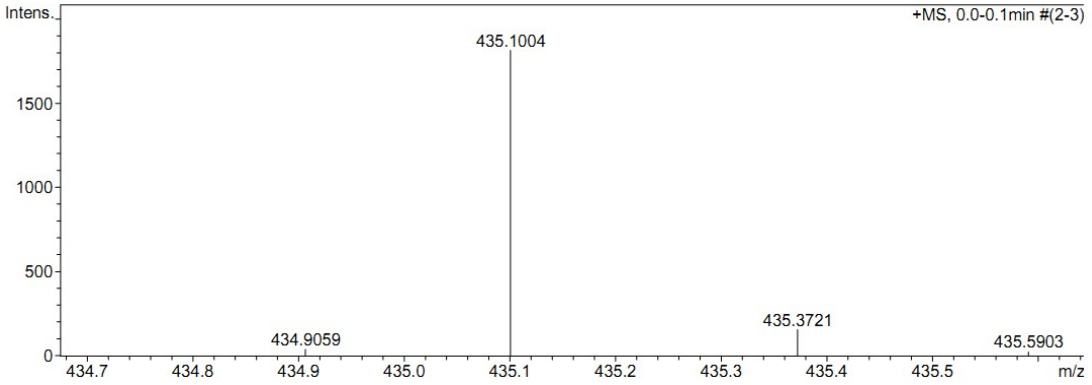
3d


Intens.
+MS, 0.3min #19
x10^4
1.5
479.0495
1.0
0.5
478.7534
0.0
478.4
478.6
478.8
479.0
479.2
479.4
m/z

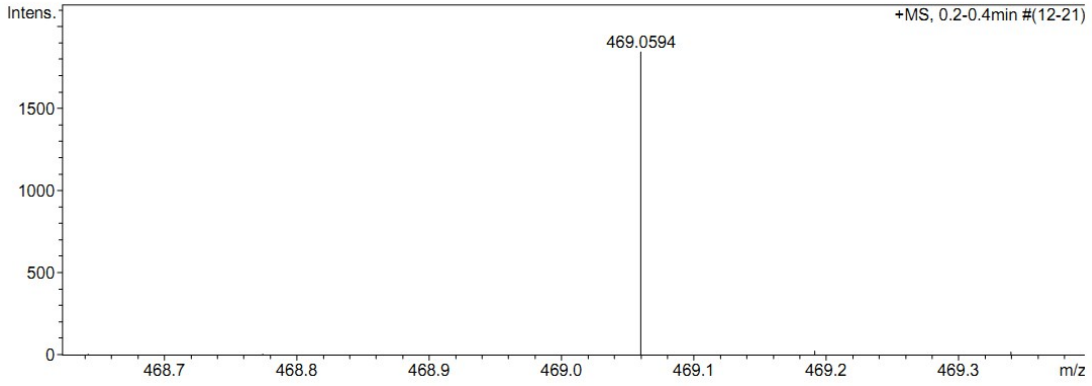
3e


Intens.
x10^4
+MS, 0.2-0.3min #(14-16)
479.0491
1.25
1.00
0.75
0.50
0.25
0.00
478.2
478.4
478.6
478.8
479.0
479.2
479.4
479.6
479.8
m/z

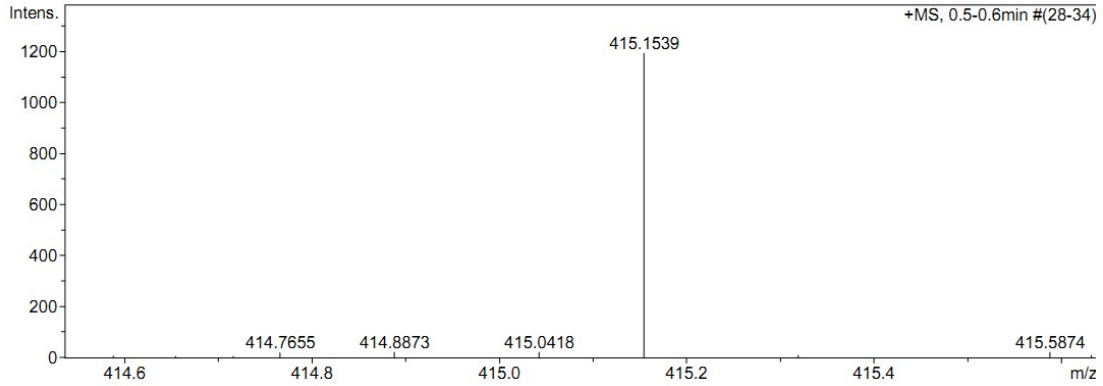
3f


Intens.
+MS, 0.0-0.1min #(2-3)
435.1004
1500
1000
500
0
434.9059
435.3721
435.5903
434.7
434.8
434.9
435.0
435.1
435.2
435.3
435.4
435.5
m/z

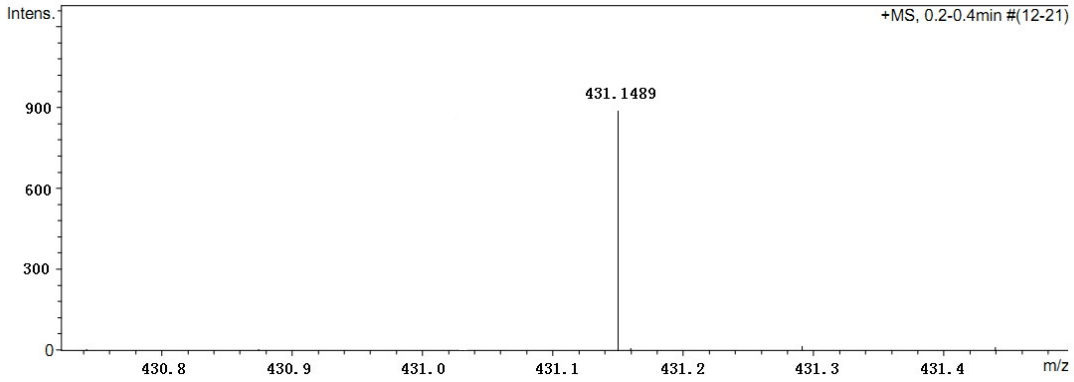
3g


Intens.
+MS, 0.2-0.4min #(12-21)
469.0594
1500
1000
500
0
468.7
468.8
468.9
469.0
469.1
469.2
469.3
m/z

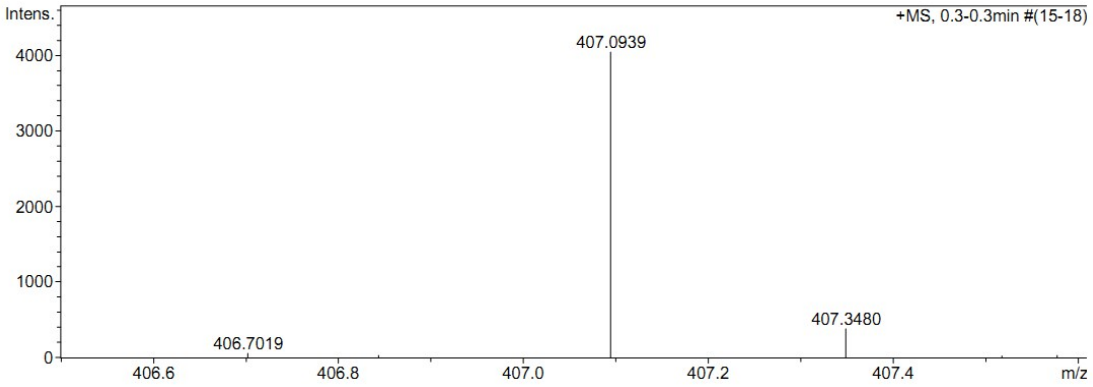
3h


Intens.
+MS, 0.5-0.6min #(28-34)
415.1539
1200
1000
800
600
400
200
0
414.7655
414.8873
415.0418
415.5874
414.6
414.8
415.0
415.2
415.4
m/z

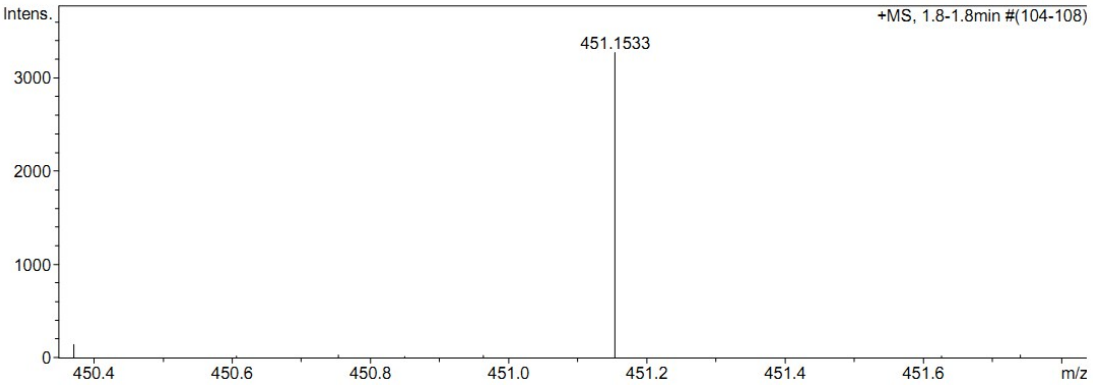
3i


Intens.
+MS, 0.2-0.4min #(12-21)
431.1489
900
600
300
0
430.8
430.9
431.0
431.1
431.2
431.3
431.4
m/z

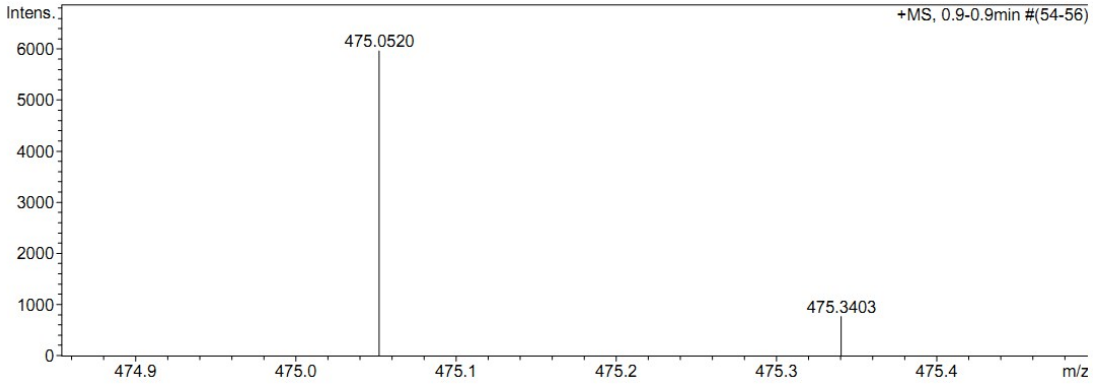
3j


Intens.
+MS, 0.3-0.3min #(15-18)
407.0939
4000
3000
2000
1000
0
406.7019
407.3480
406.6
406.8
407.0
407.2
407.4
m/z

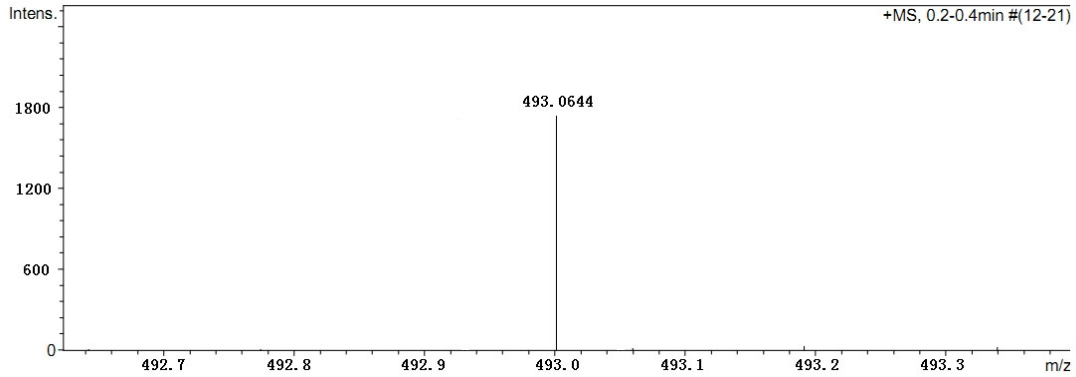
3k


Intens.
+MS, 1.8-1.8min #(104-108)
451.1533
3000
2000
1000
0
450.4
450.6
450.8
451.0
451.2
451.4
451.6
m/z

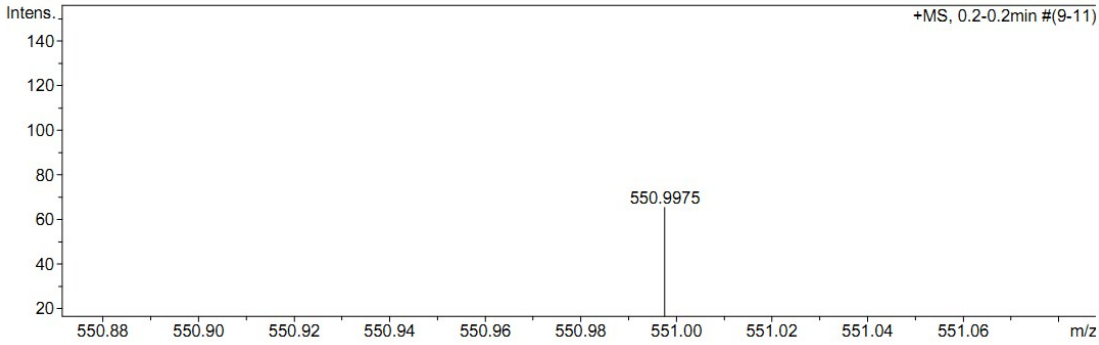
3l


Intens.
+MS, 0.9-0.9min #(54-56)
475.0520
6000
5000
4000
3000
2000
1000
0
475.3403
474.9
475.0
475.1
475.2
475.3
475.4
m/z

3m

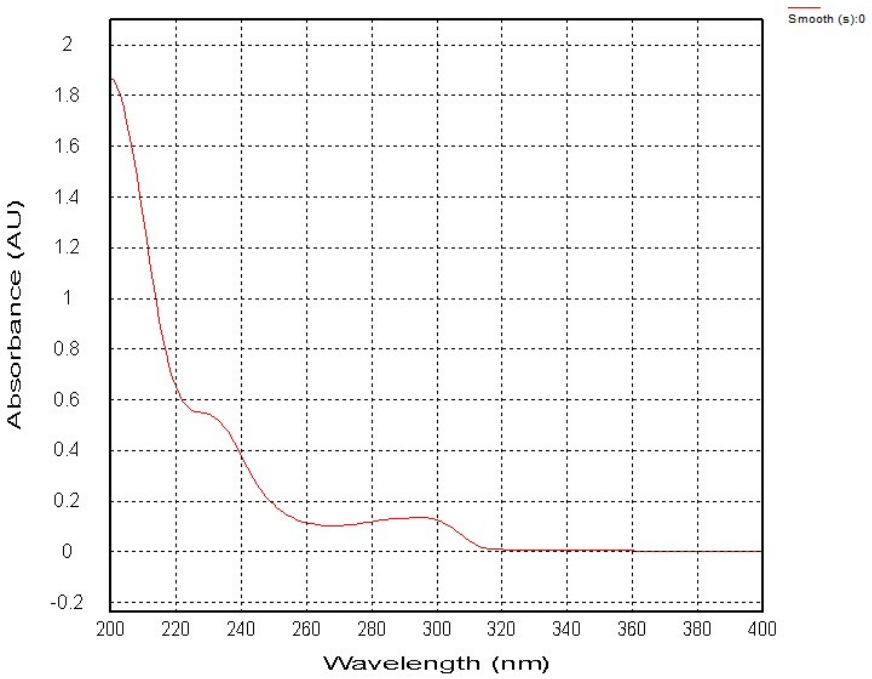

Intens.
+MS, 0.2-0.4min #(12-21)
493.0644
1800
1200
600
0
492.7
492.8
492.9
493.0
493.1
493.2
493.3
m/z

3g'

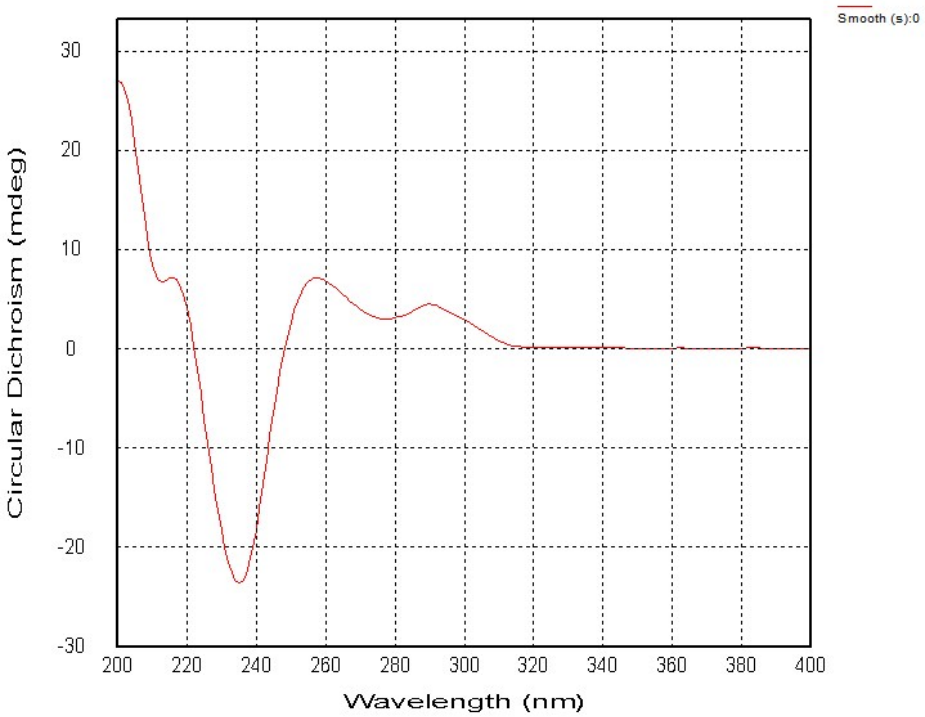

Intens.
+MS, 0.2-0.2min #(9-11)
550.9975
140
120
100
80
60
40
20
550.88
550.90
550.92
550.94
550.96
550.98
551.00
551.02
551.04
551.06
m/z

5. Determination of stereochemistry of compound 3g

5.1 UV & CD spectrum of 3g



UV of **3g**



CD of **3g**

ProBinaryX

Attributes :

- Time Stamp :Tue Feb 19 13:31:36 2019

- File ID : {491FDE7B-2E1B-4ad6-85FB-5AEFEACE71BC}
- Is CFR Compliant : false
- Original data has not been modified.

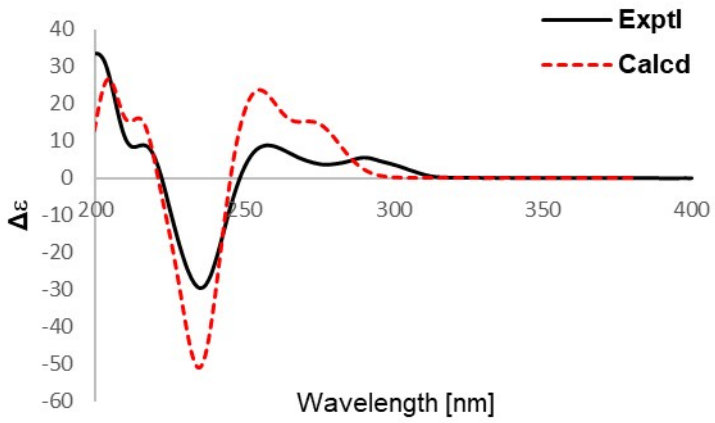
Remarks:

- User: CD
- Date: 2019/02/19
- Instrument: 0547
- DetectorType: LAAPD
- DichOS Calibration Correction Curve: 0547/2
- HV (CDDC channel): 335.754 v
- Time per point: 0.25 s
- Description: 3g
- Concentration: 0.0115 mg/mL CH_3OH
- Pathlength: 1 mm
- Temperature: ---- C

Settings:

- Time-per-point: 0.25s (25us x 10000)
- SE
- Wavelength: 200nm - 400nm
- Step Size: 1nm
- Bandwidth: 1nm
- 3 repeats in set.
- -iter option selected

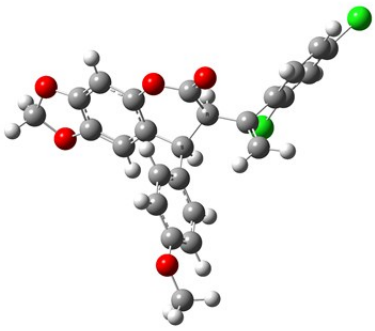
5.2 Comparison of the result of DFT calculation and CD analysis of 3g



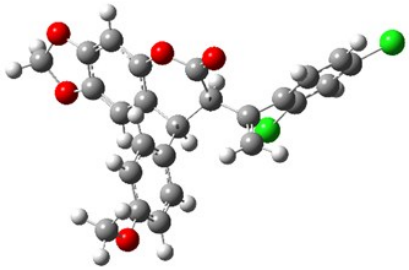
Computational method for ECD of compound 3g

The CONFLEX[4,5] searches based on molecular mechanics with MMFF94S force fields were performed for compounds of (7*R*, 8*S*)-**3g**, which gave 24 stable conformers, respectively. Selected conformers (7) with distributions higher than 1%

were further optimized by the density functional theory method at the B3LYP/6-31G* level in Gaussian 09 program package,[6] which gave 2 conformers (**3ga** & **3gb**) matched with the ROESY data. The optimized geometries were further checked by frequency calculation and resulted in no imaginary frequencies. The ECD was calculated using TD-DFT-B3LYP/6-31G(d,p) of theory on B3LYP/6-31G(d) optimized geometries through the IEFPCM model (in MeOH), respectively. The overall calculated ECD curve was generated using SpecDis 1.60[7] with σ=0.16 ev, UV shift -20 nm, respectively.



3ga (51.35%)



3gb (48.65%)

Standard orientation of **3ga** at B3LYP-6-31G(g) level in gas:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.861699	-3.590747	0.416257
2	6	0	2.991353	-2.996006	-0.828017
3	6	0	2.360610	-1.830664	-1.136239
4	6	0	1.564089	-1.232657	-0.143269
5	6	0	1.453338	-1.843710	1.083372
6	6	0	2.098206	-3.044255	1.402732
7	8	0	3.576540	-4.738780	0.435909
8	6	0	4.312183	-4.772906	-0.766842
9	8	0	3.788944	-3.772465	-1.606728
10	6	0	0.818194	0.066278	-0.392819
11	6	0	-0.491914	-0.015117	0.441191
12	6	0	-0.205482	-0.337330	1.898847
13	8	0	0.729268	-1.279846	2.106867
14	6	0	1.711142	1.286203	-0.197759
15	6	0	1.861804	2.200209	-1.223126
16	6	0	2.675209	3.322943	-1.100279

17	6	0	3.359889	3.542079	0.081163
18	6	0	3.226009	2.627283	1.125638
19	6	0	2.423586	1.519791	0.982779
20	6	0	-1.514690	1.108113	0.314401
21	6	0	-2.940794	0.664481	0.172932
22	6	0	-1.247526	2.396089	0.418468
23	6	0	-3.475023	0.159569	-1.007082
24	6	0	-4.795878	-0.239332	-1.107931
25	6	0	-5.607202	-0.138174	0.004764
26	6	0	-5.116531	0.351076	1.199808
27	6	0	-3.792479	0.744334	1.271748
28	17	0	-7.270785	-0.638287	-0.109594
29	17	0	-2.485920	0.025557	-2.441447
30	8	0	-0.756471	0.133301	2.830760
31	8	0	4.171557	4.590415	0.318215
32	6	0	4.366927	5.555594	-0.675980
33	1	0	2.465300	-1.377841	-2.104376
34	1	0	1.985535	-3.488809	2.371881
35	1	0	5.354527	-4.567129	-0.558378
36	1	0	4.193992	-5.737305	-1.233762
37	1	0	0.498447	0.072254	-1.426495
38	1	0	-0.970354	-0.920299	0.074027
39	1	0	1.329729	2.054895	-2.147082
40	1	0	2.756453	4.001243	-1.927206
41	1	0	3.767357	2.804859	2.036047
42	1	0	2.357956	0.829474	1.804081
43	1	0	-2.035888	3.123340	0.341481
44	1	0	-0.260790	2.774934	0.590789
45	1	0	-5.180435	-0.615337	-2.035103
46	1	0	-5.754701	0.420244	2.059713
47	1	0	-3.394662	1.108857	2.199550
48	1	0	5.045432	6.284543	-0.259403
49	1	0	4.811172	5.122901	-1.566181
50	1	0	3.435884	6.045697	-0.940622

Standard orientation of **3gb** at B3LYP-6-31G(g) level in gas:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.823711	3.548850	0.562634
2	6	0	-2.919665	3.068232	-0.732820
3	6	0	-2.291425	1.926442	-1.123874

4	6	0	-1.533716	1.232458	-0.163680
5	6	0	-1.455645	1.731316	1.115192
6	6	0	-2.097787	2.907200	1.519895
7	8	0	-3.526789	4.700031	0.662233
8	6	0	-4.220107	4.852873	-0.556450
9	8	0	-3.683636	3.920892	-1.463949
10	6	0	-0.791903	-0.048150	-0.503221
11	6	0	0.494260	-0.050573	0.371016
12	6	0	0.162505	0.138149	1.842191
13	8	0	-0.770539	1.068643	2.106067
14	6	0	-1.697749	-1.273480	-0.436229
15	6	0	-2.451450	-1.592044	0.682544
16	6	0	-3.272222	-2.711306	0.716886
17	6	0	-3.363009	-3.534536	-0.395197
18	6	0	-2.625310	-3.222432	-1.532459
19	6	0	-1.810069	-2.111209	-1.544731
20	6	0	1.517344	-1.163142	0.172910
21	6	0	2.948612	-0.716037	0.125708
22	6	0	1.243737	-2.453553	0.140222
23	6	0	3.524608	-0.099947	-0.979554
24	6	0	4.849108	0.299289	-0.994931
25	6	0	5.621072	0.083857	0.129467
26	6	0	5.088122	-0.518485	1.252564
27	6	0	3.761443	-0.909277	1.239687
28	17	0	7.288771	0.583292	0.122466
29	17	0	2.586204	0.180669	-2.426554
30	8	0	0.675911	-0.424513	2.744136
31	8	0	-4.128916	-4.640039	-0.471029
32	6	0	-4.902107	-5.027241	0.629681
33	1	0	-2.369413	1.562949	-2.131395
34	1	0	-2.011026	3.263267	2.527513
35	1	0	-5.271960	4.648494	-0.401340
36	1	0	-4.071574	5.852346	-0.932115
37	1	0	-0.443283	0.031107	-1.524532
38	1	0	0.986363	0.881330	0.102194
39	1	0	-2.418452	-0.968324	1.557379
40	1	0	-3.830955	-2.917564	1.608783
41	1	0	-2.705420	-3.862568	-2.391209
42	1	0	-1.241369	-1.895966	-2.432462
43	1	0	2.032697	-3.174150	0.019595
44	1	0	0.250652	-2.841990	0.238293
45	1	0	5.266553	0.762817	-1.866593
46	1	0	5.695950	-0.676174	2.122715
47	1	0	3.330892	-1.361604	2.112591

48	1	0	-5.417009	-5.928684	0.333731
49	1	0	-4.282336	-5.238400	1.494620
50	1	0	-5.632743	-4.267874	0.887374

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