Supporting Information for

Organocatalytic Chemo-, (*E/Z*)- and Enantioselective Formal Alkenylation of Indole-derived Hydroxylactams Using *o*-Hydroxystyrenes as A Source of An Alkenyl Group

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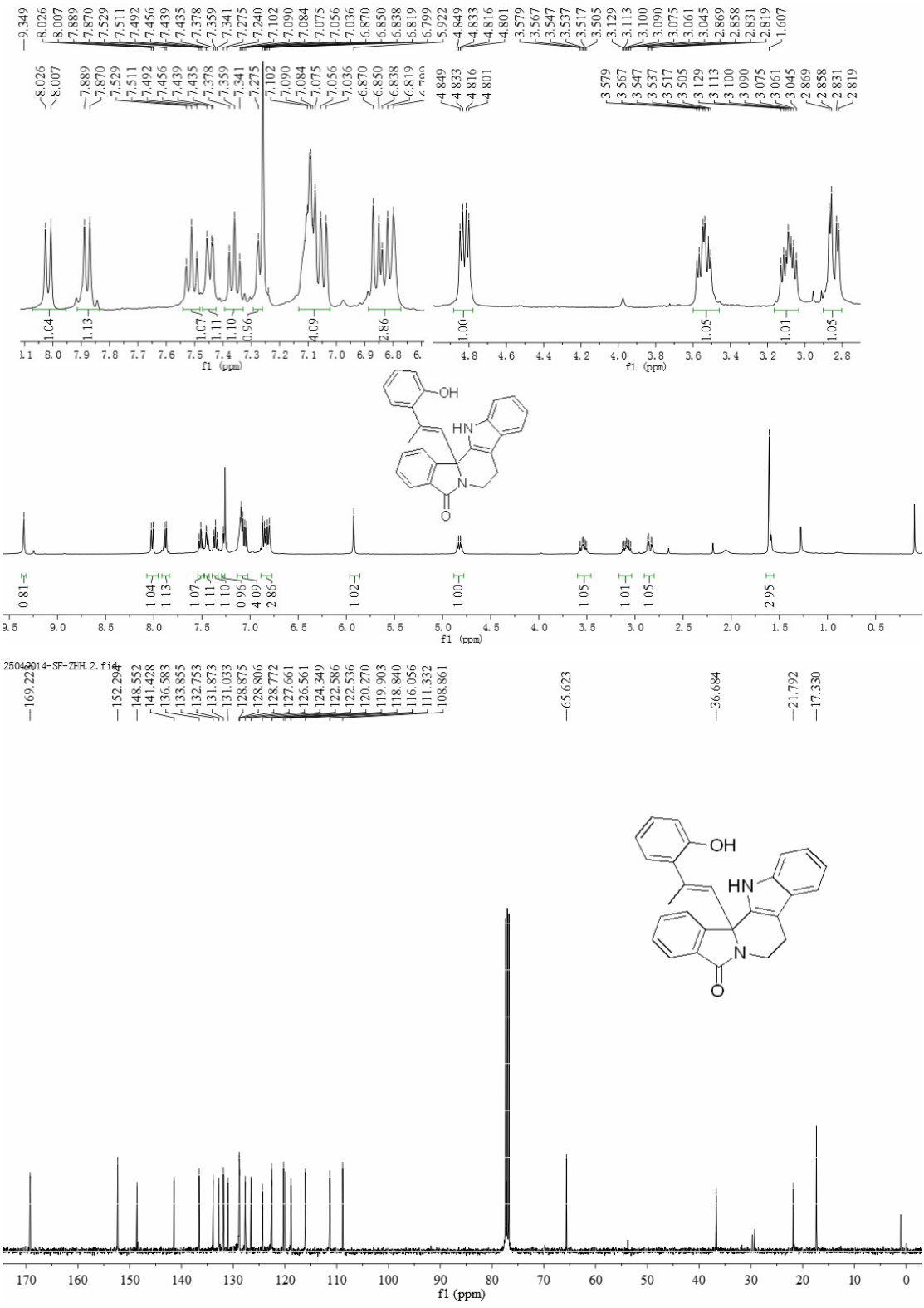
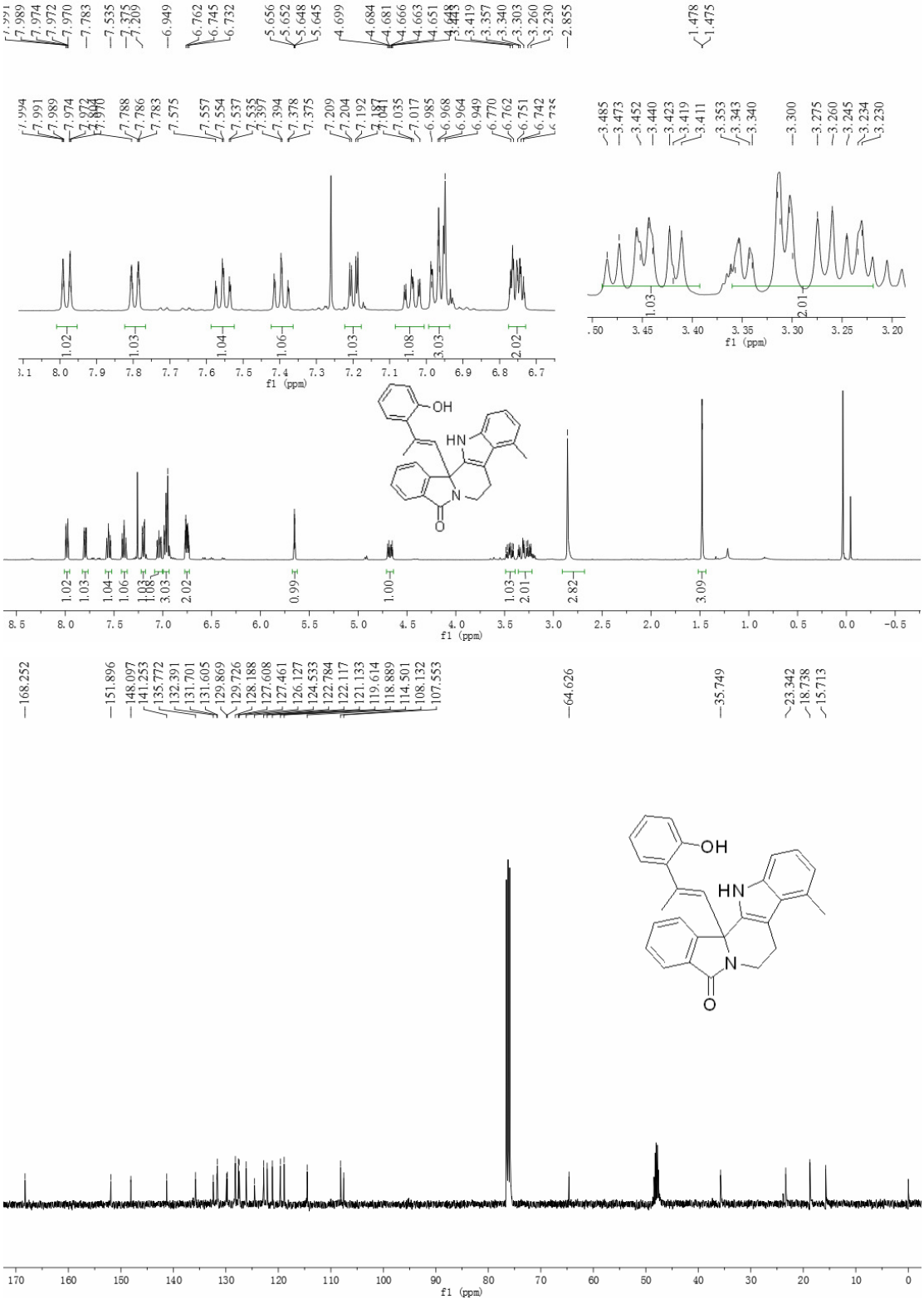
^{1}H and ^{13}C NMR spectra of products 3 and 8

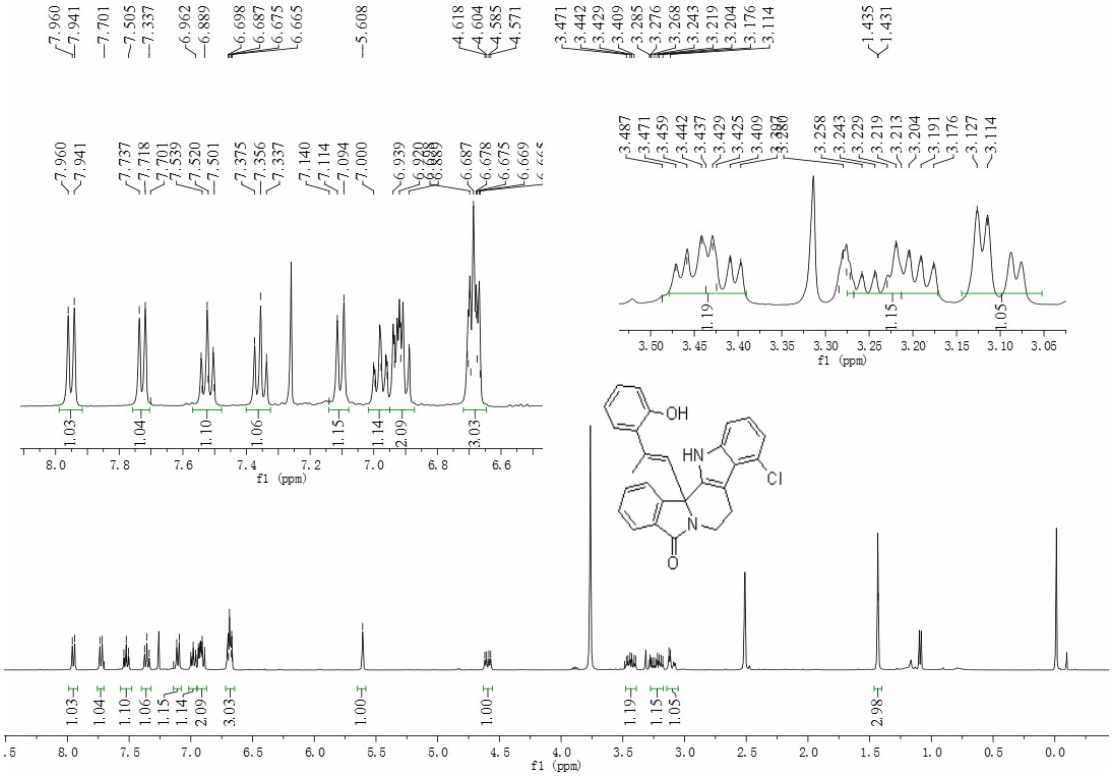
3aa:

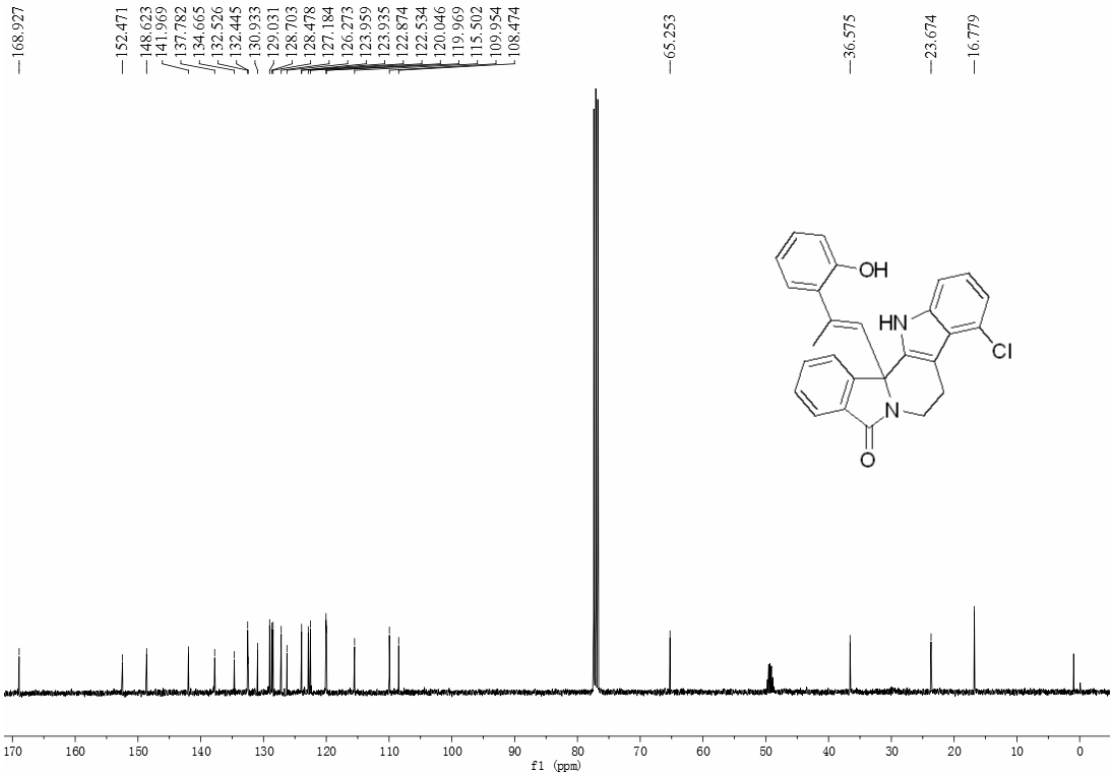


3ba: (inseparable chemoselective isomers, cr = 93:7)



3ca: (inseparable chemoselective isomers, cr = 93:7)





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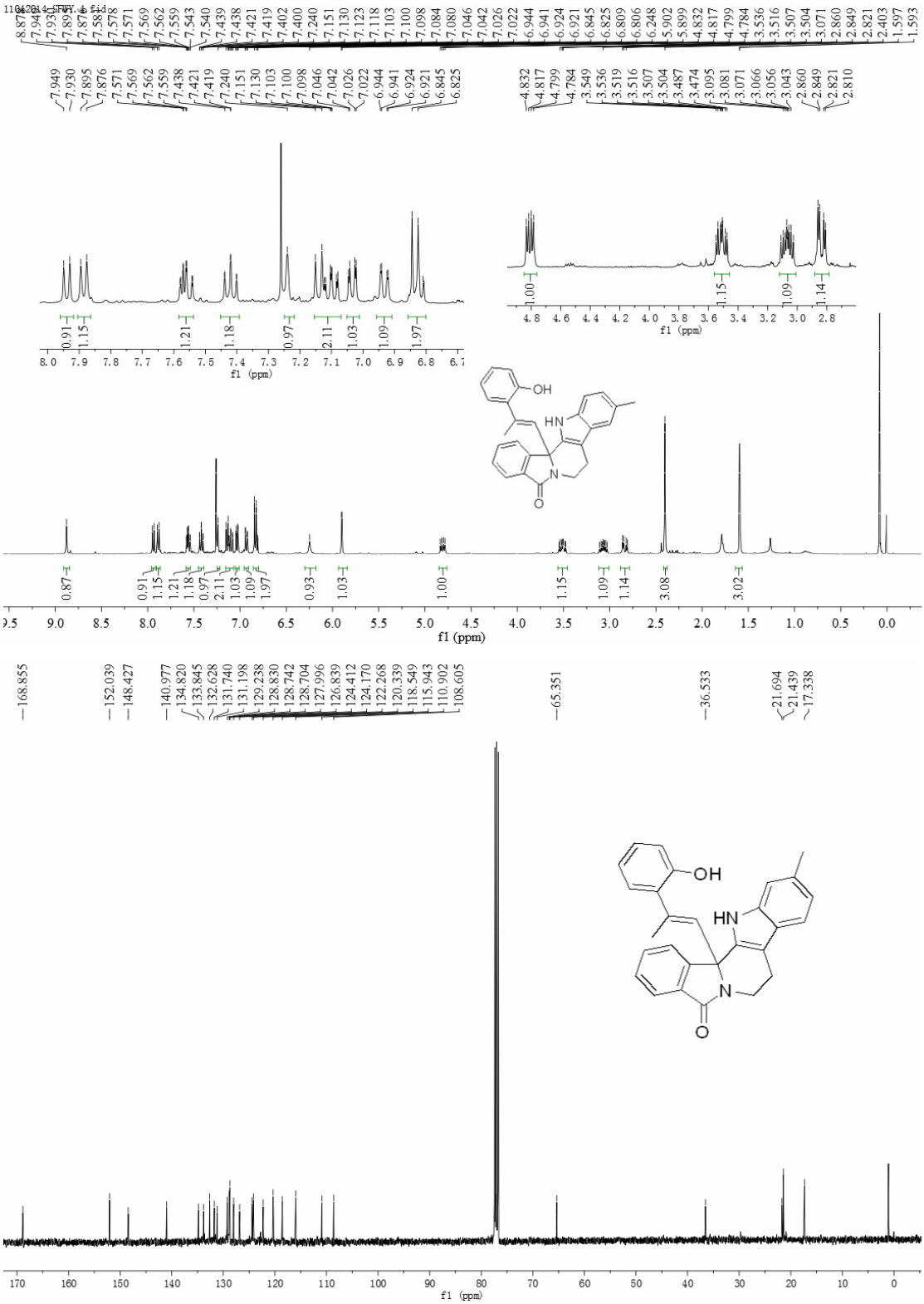

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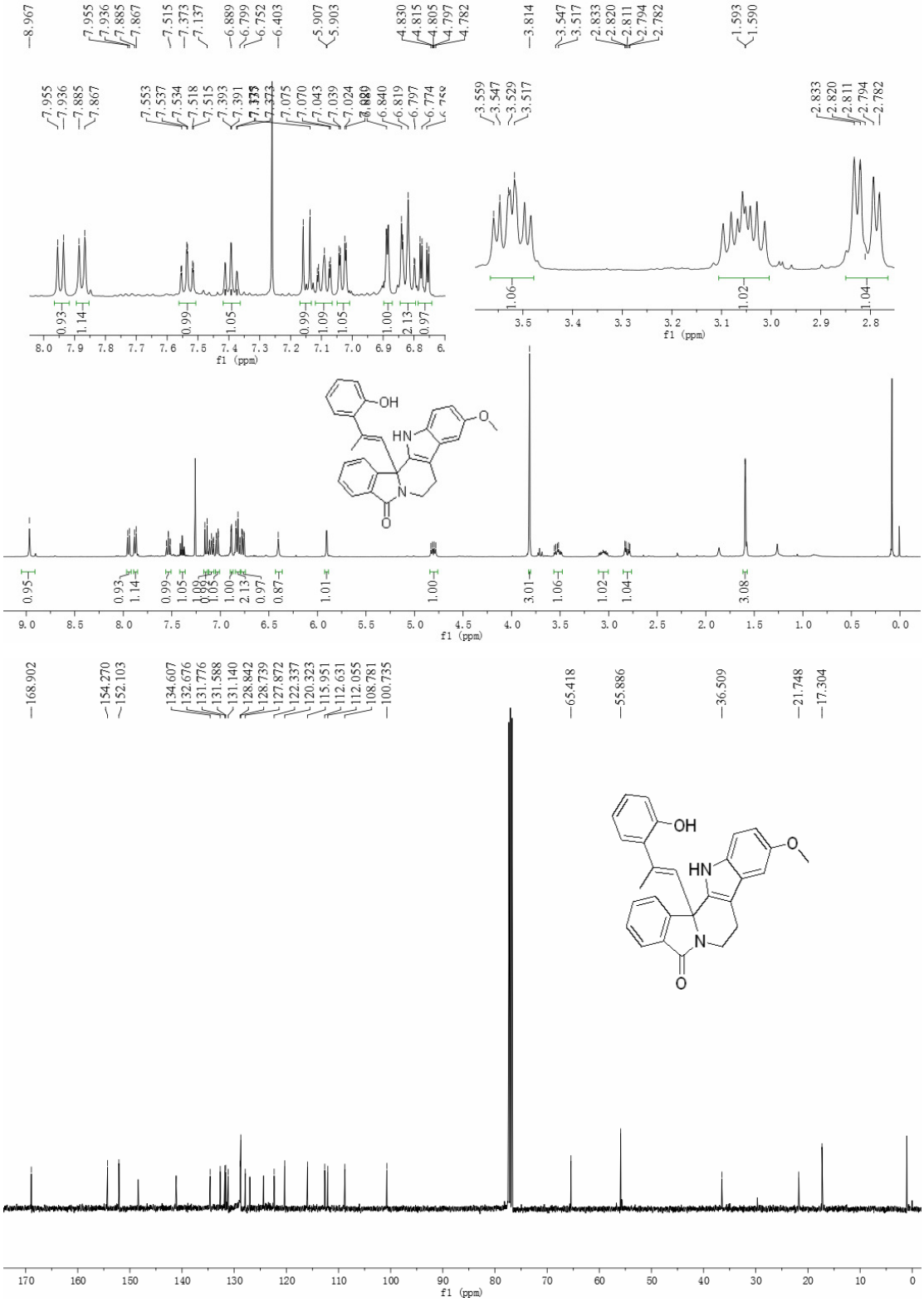

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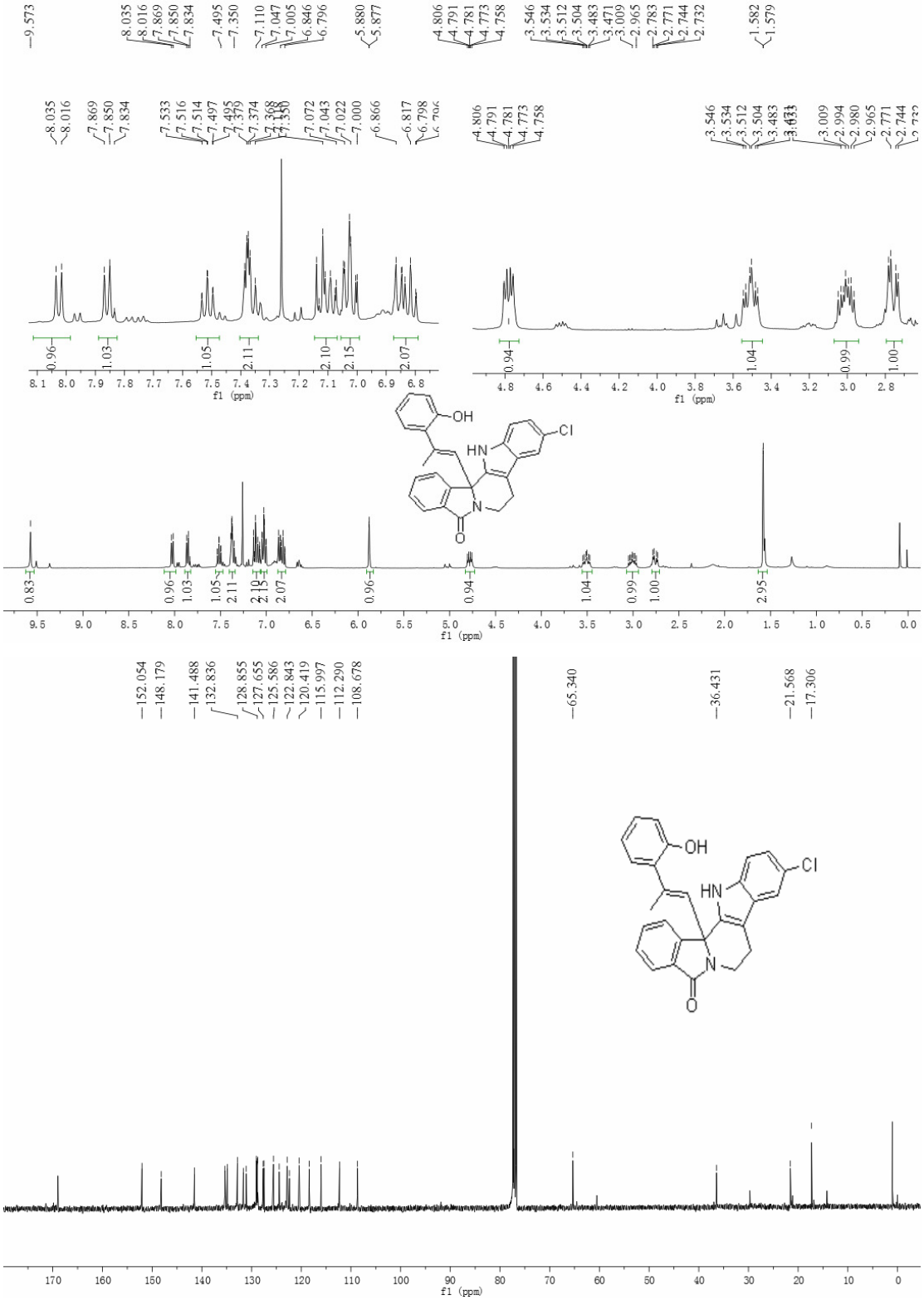

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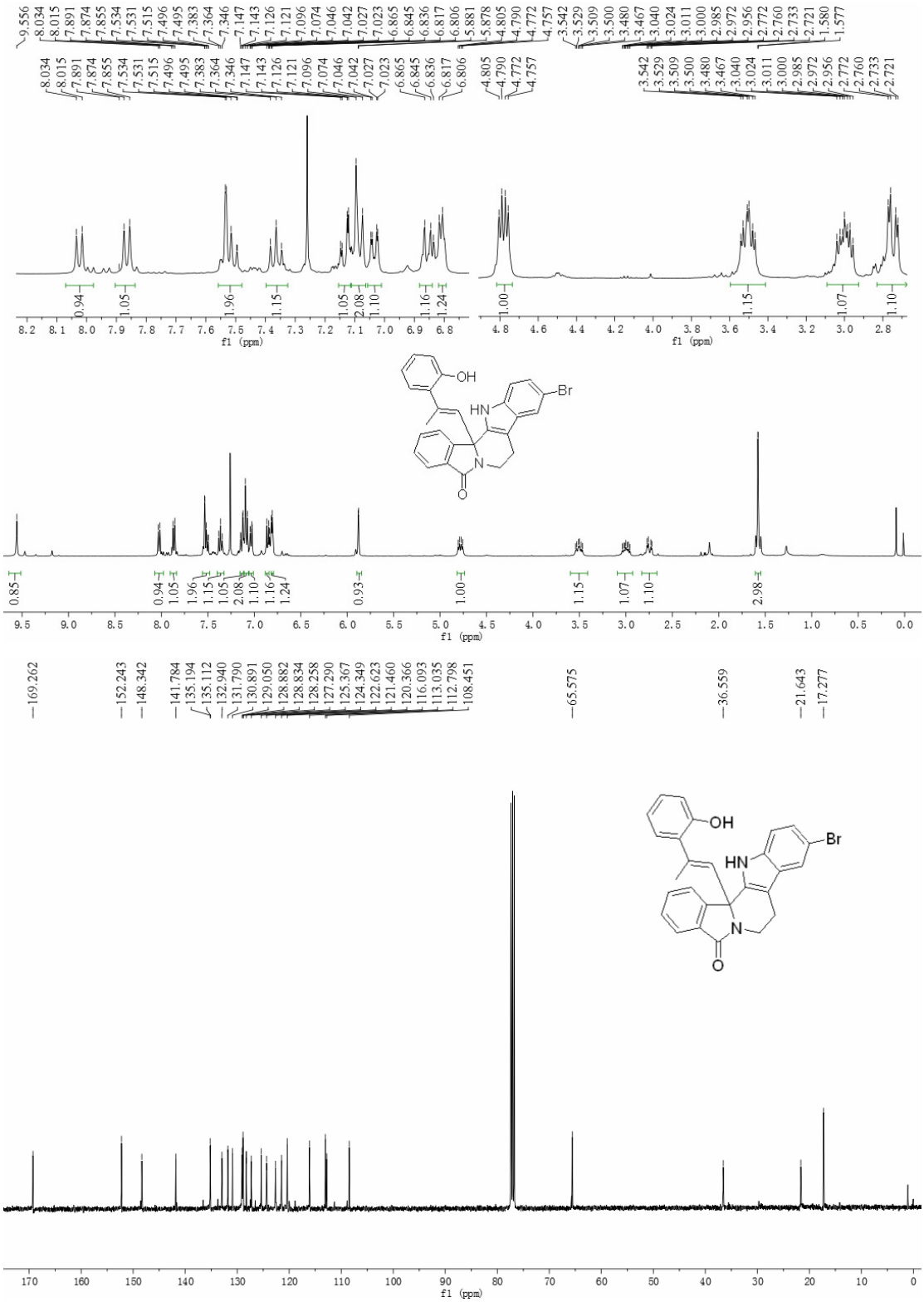

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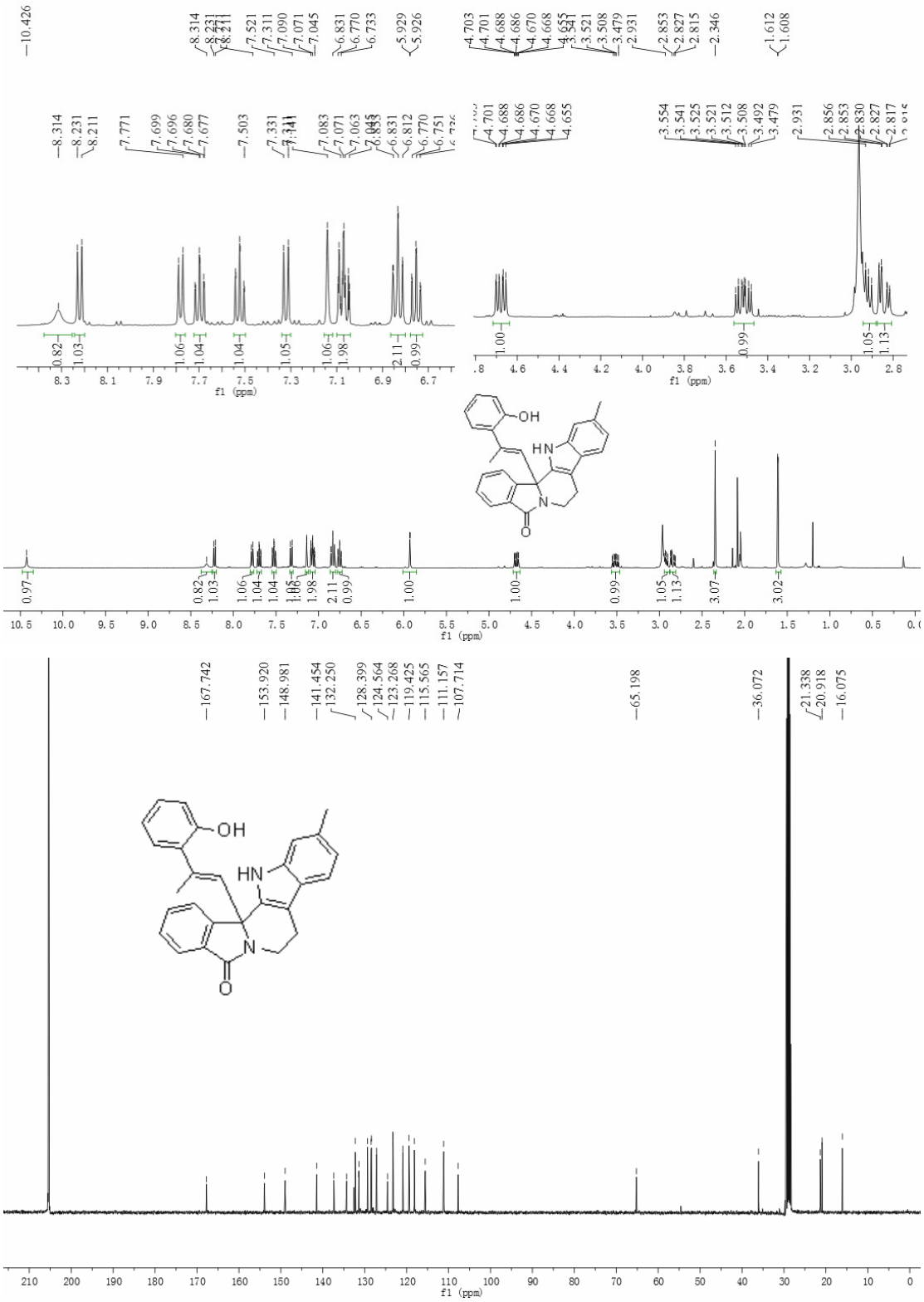
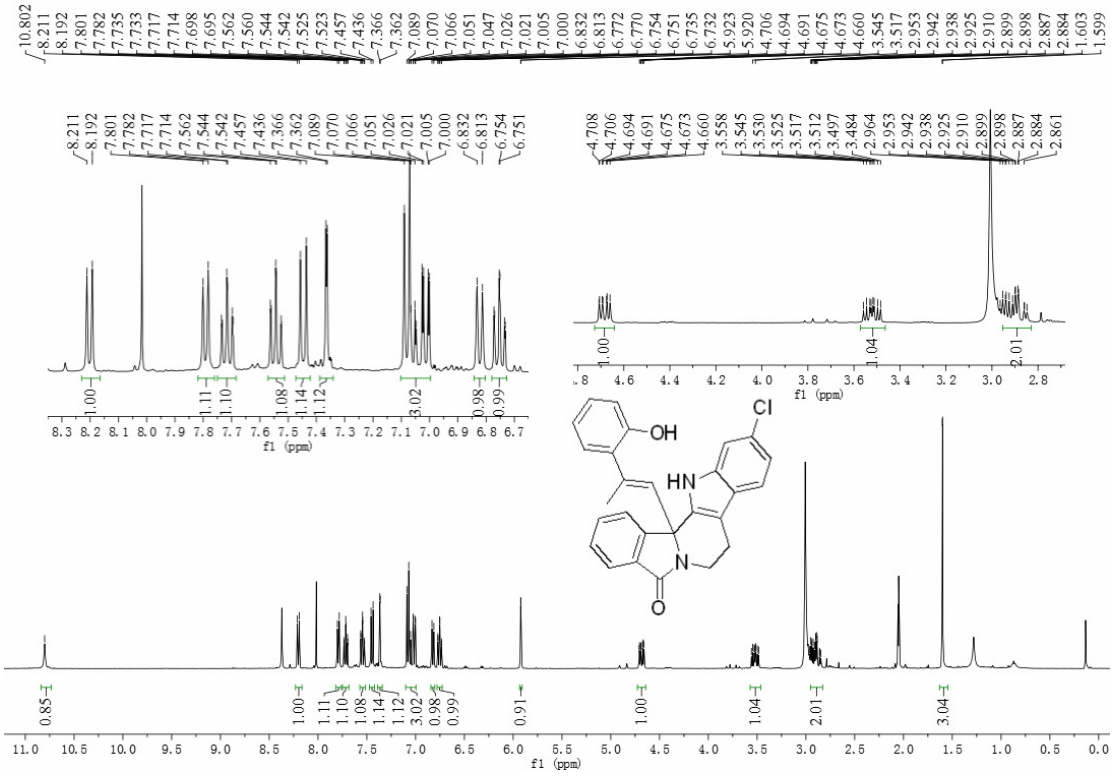
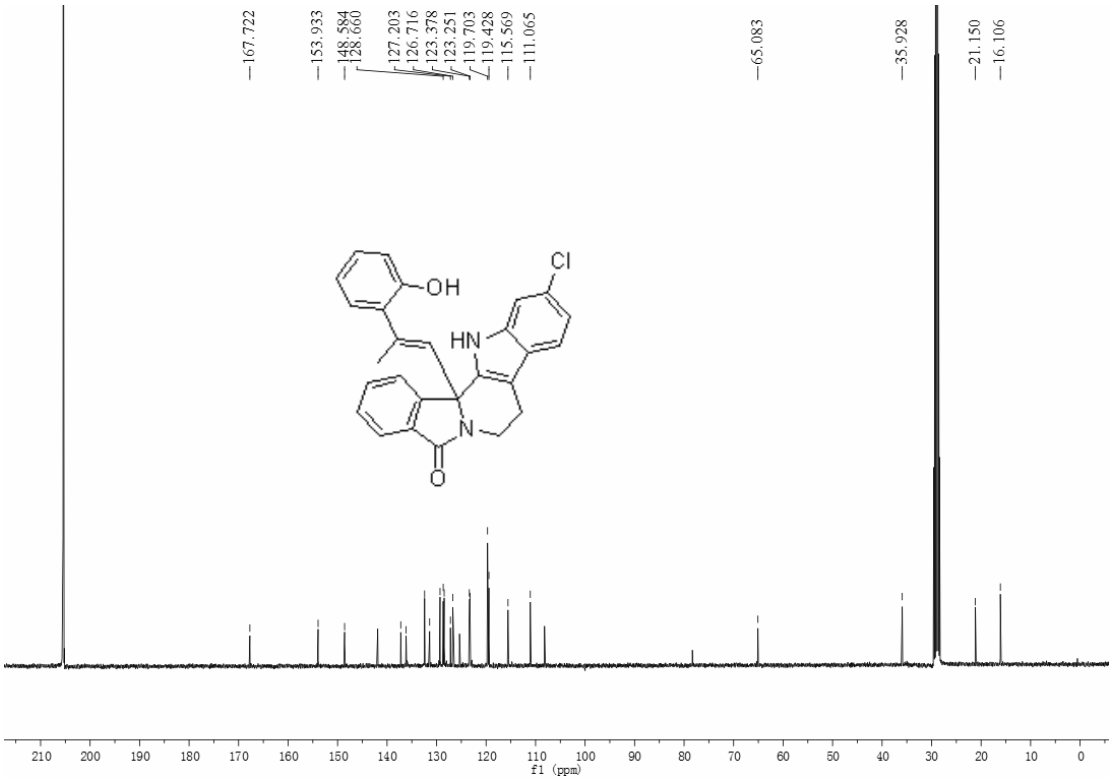


3ia: (inseparable chemoselective isomers, cr = 91:9)





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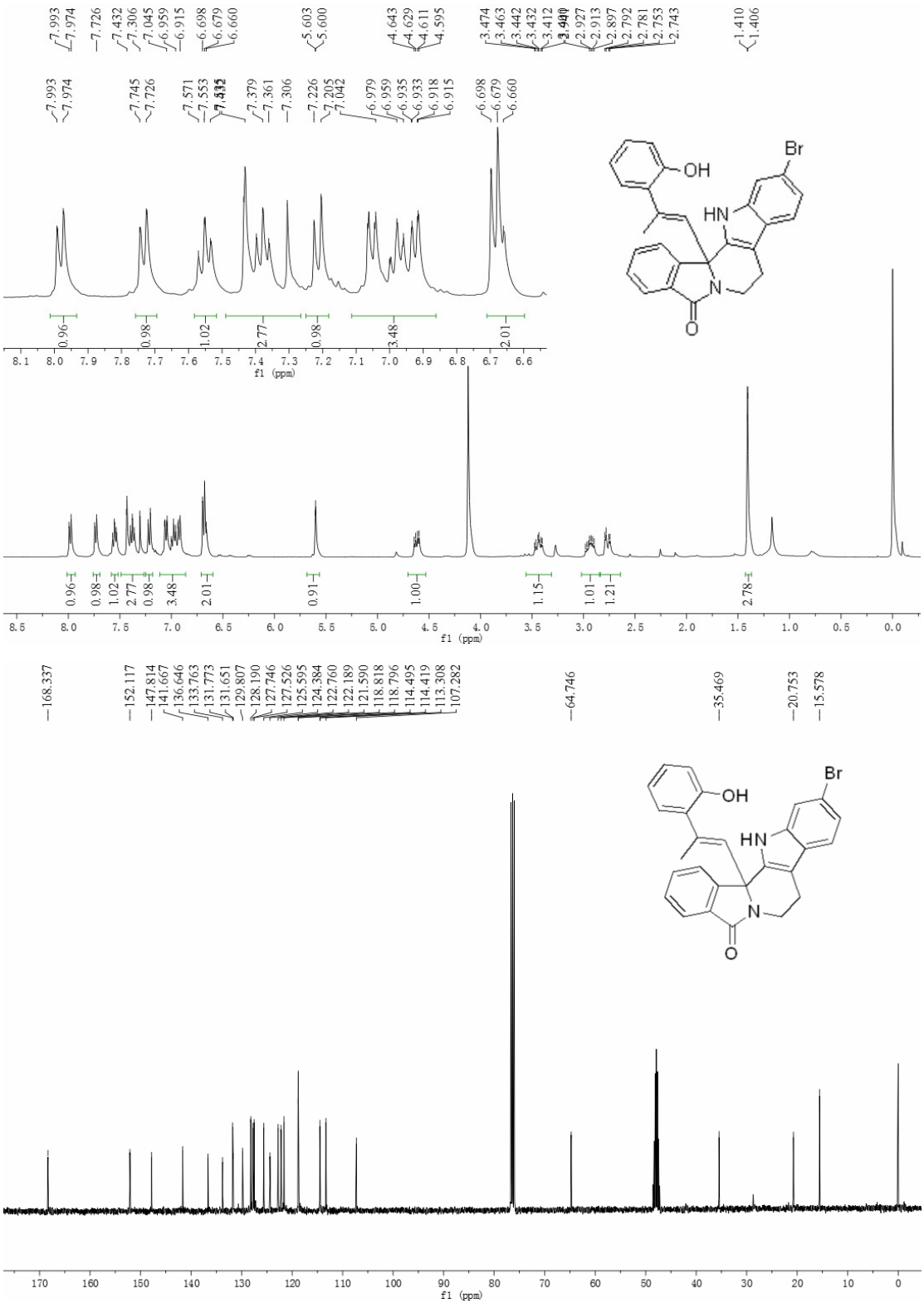

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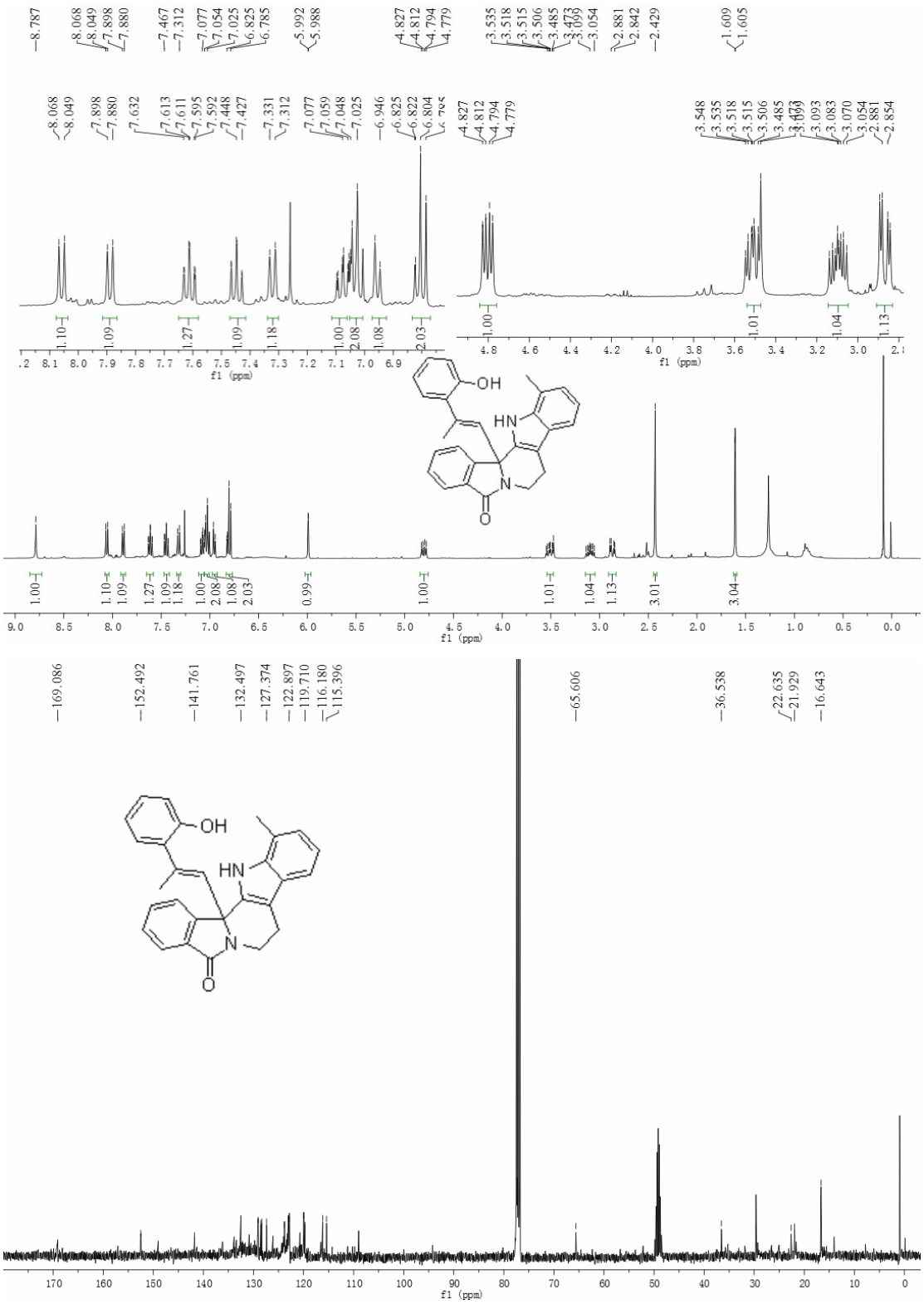

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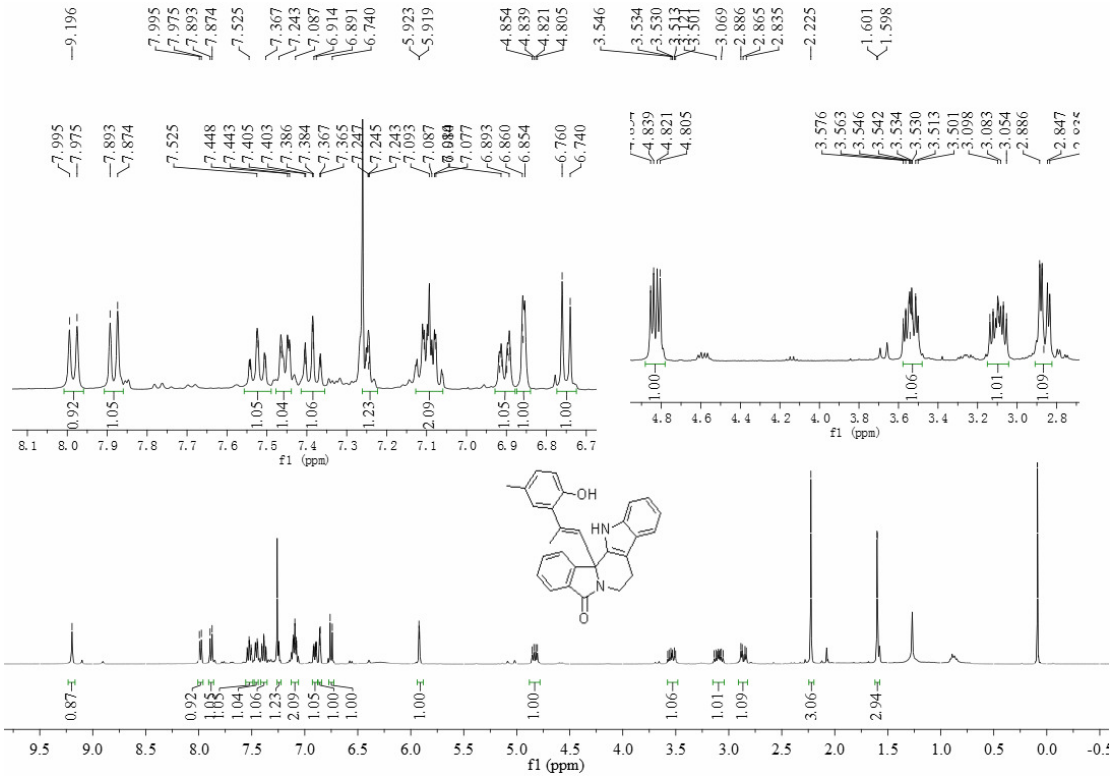

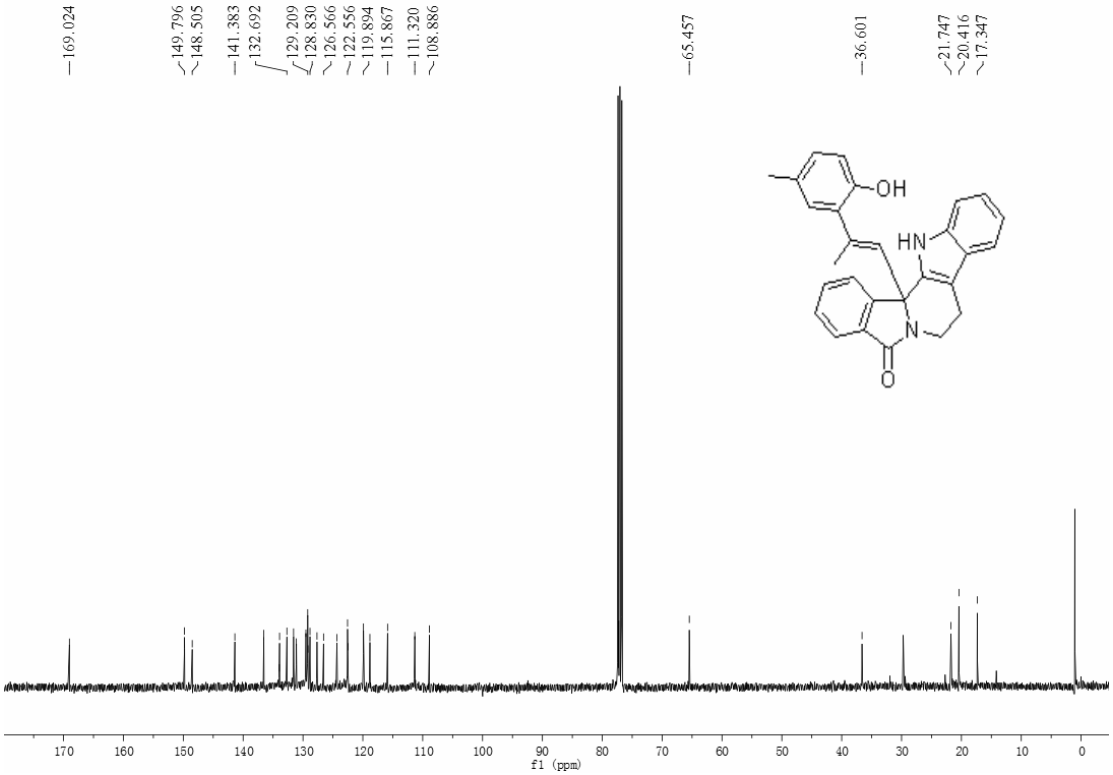

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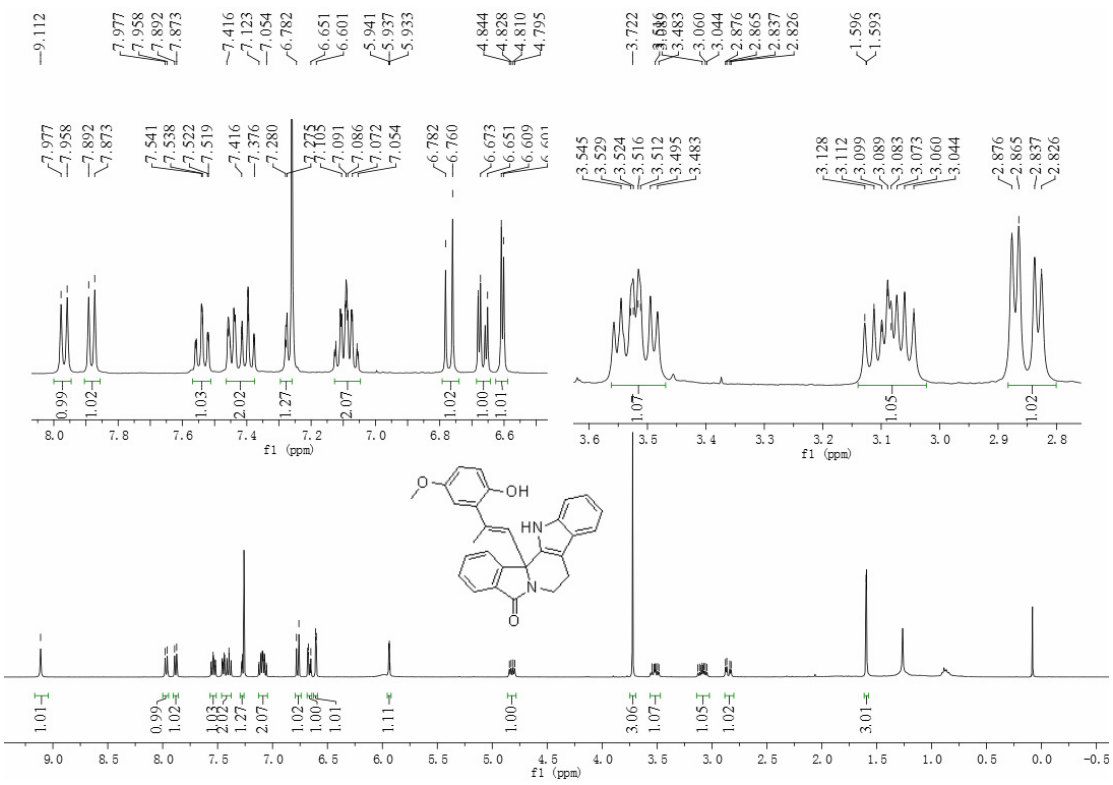
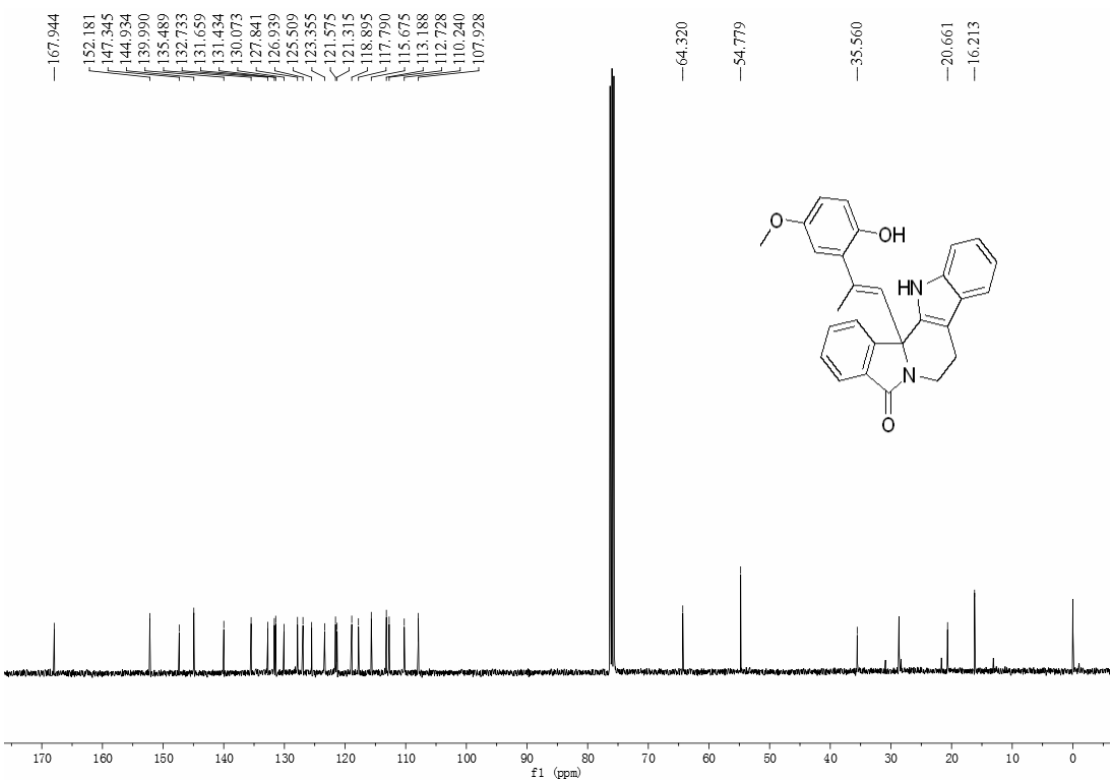
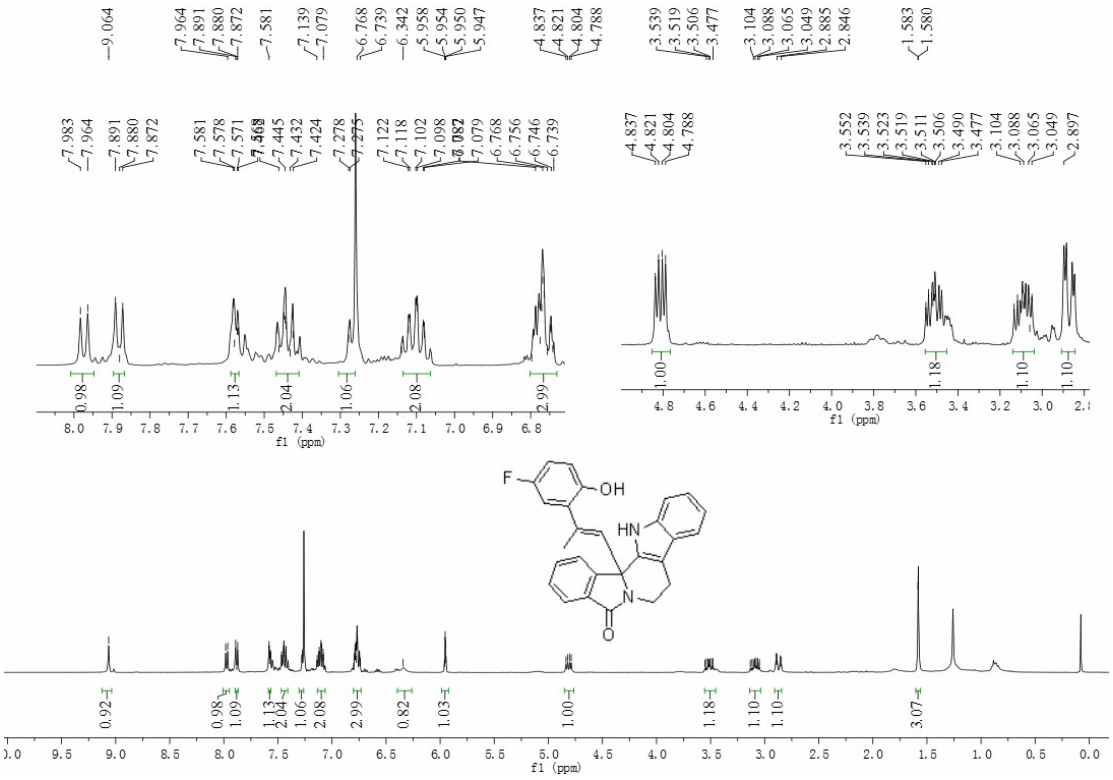
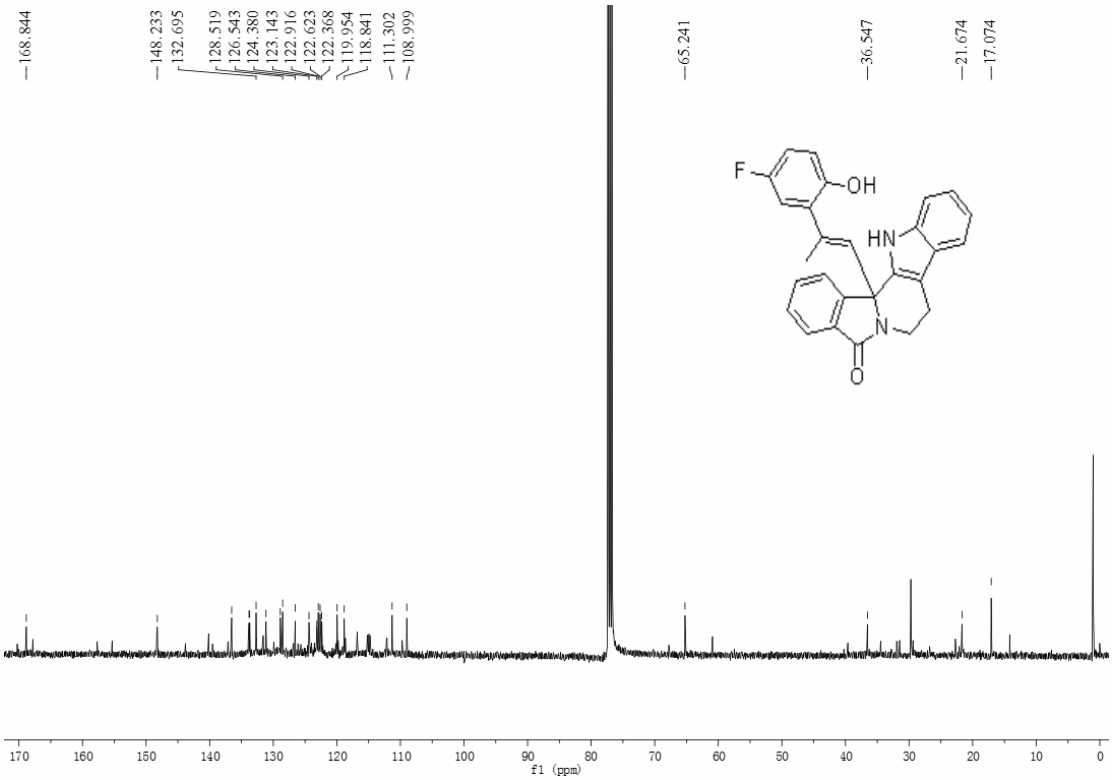

9.112
7.977
7.958
7.892
7.873
7.416
7.123
7.054
6.782
6.651
6.601
5.941
5.937
5.933
4.844
4.828
4.810
4.795
3.722
3.545
3.529
3.524
3.516
3.512
3.495
3.483
3.128
3.112
3.099
3.089
3.083
3.073
3.060
3.044
2.876
2.865
2.837
2.826
1.596
1.593
f1 (ppm)
OH
HN
O
N

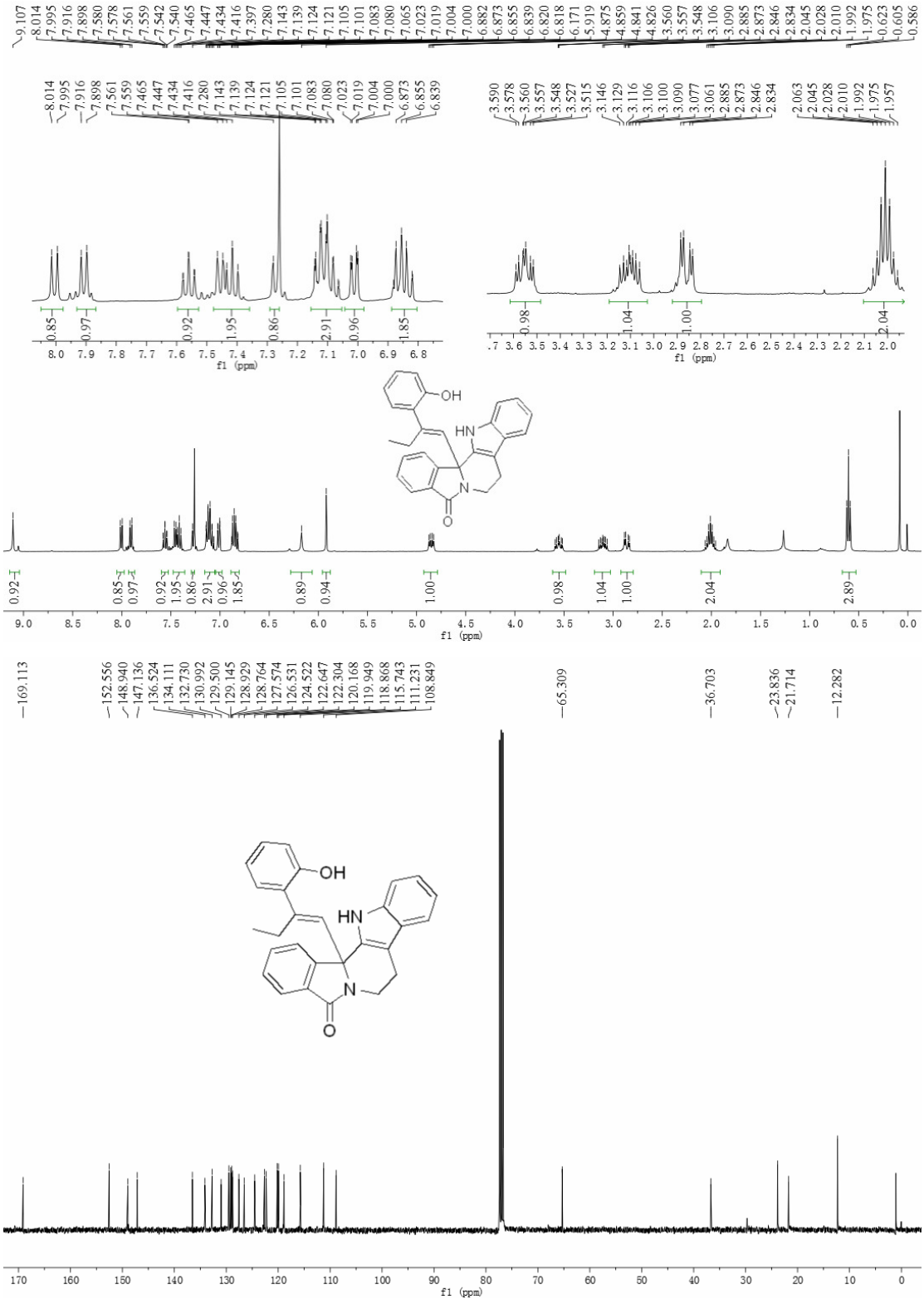

167.944
152.181
147.345
144.934
139.990
135.489
132.733
131.659
131.434
130.073
127.841
126.939
125.509
123.355
121.575
121.315
118.895
117.790
115.675
113.188
112.728
110.240
107.928
64.320
54.779
35.560
20.661
16.213
f1 (ppm)
OH
HN
O
N

3ad: (inseparable chemoselective isomers, cr = 84:16)

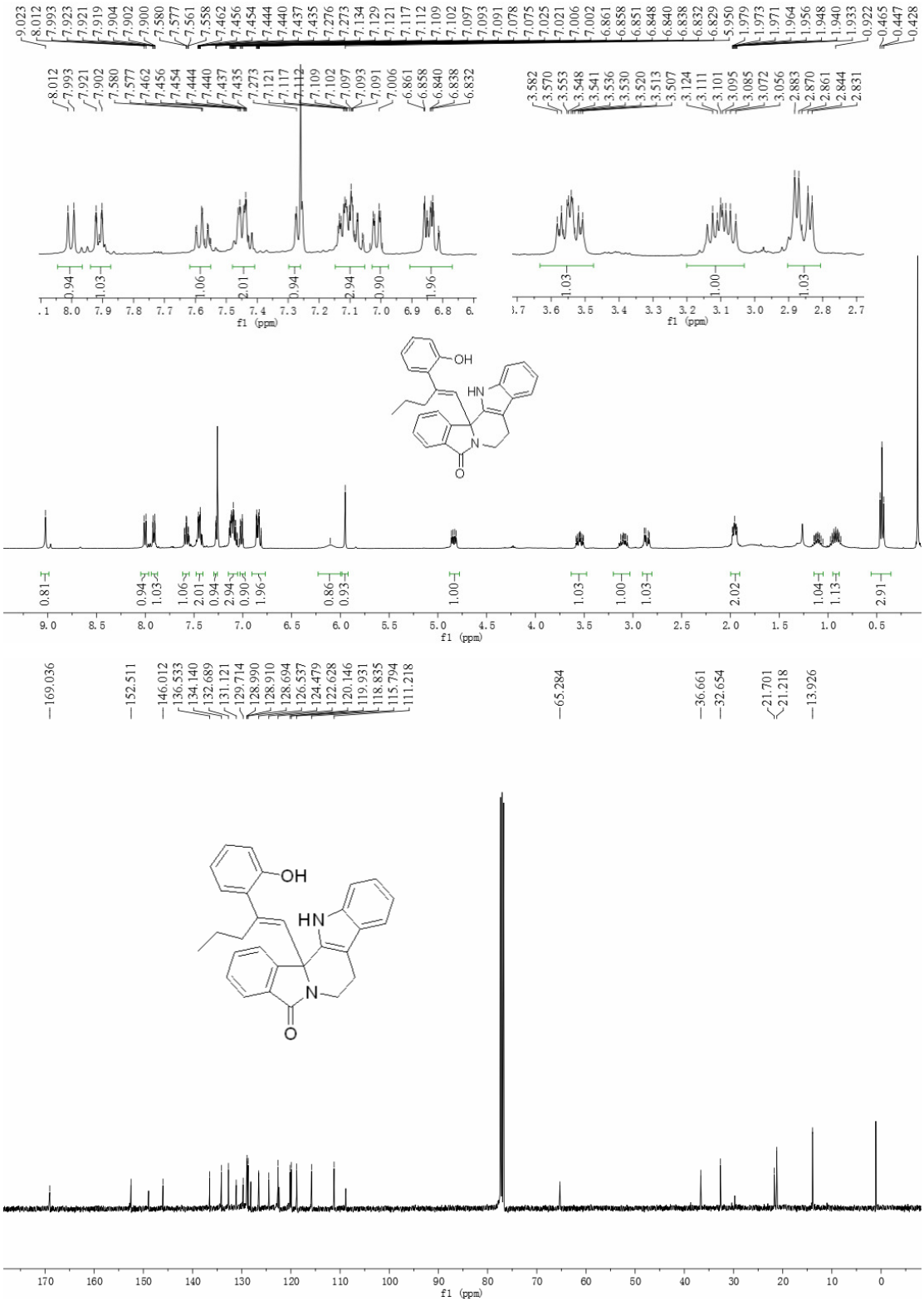




3ae:



3af: (inseparable chemoselective isomers, cr = 93:7)



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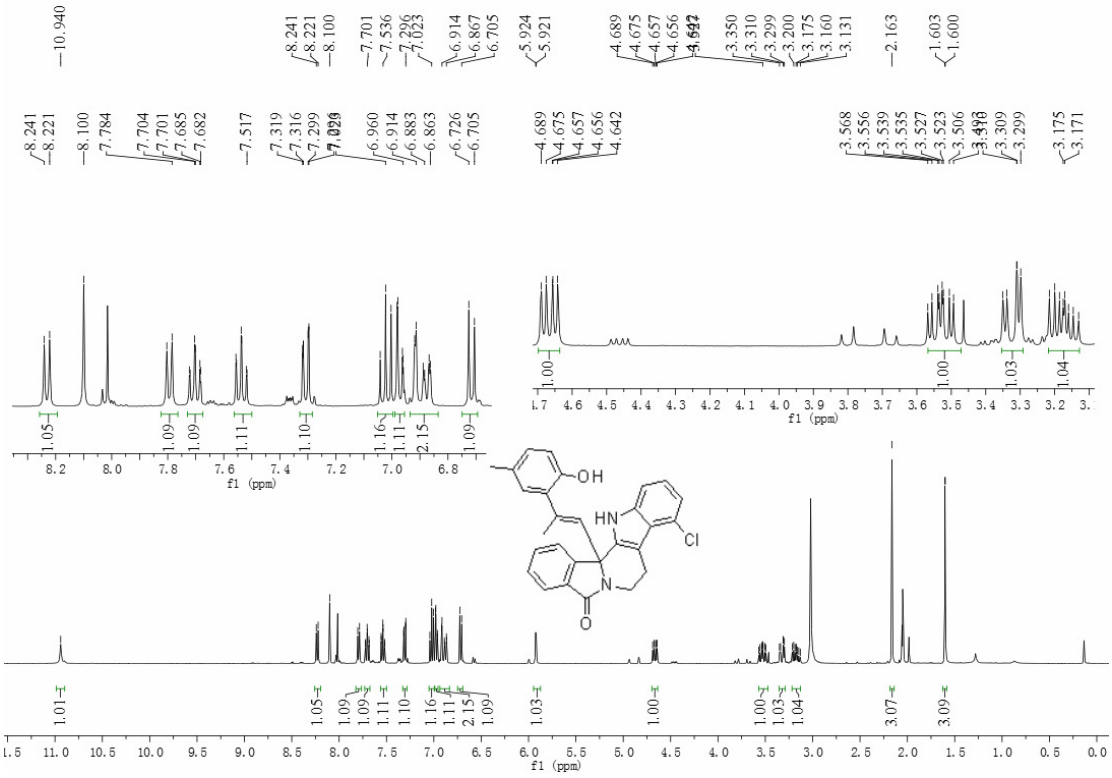
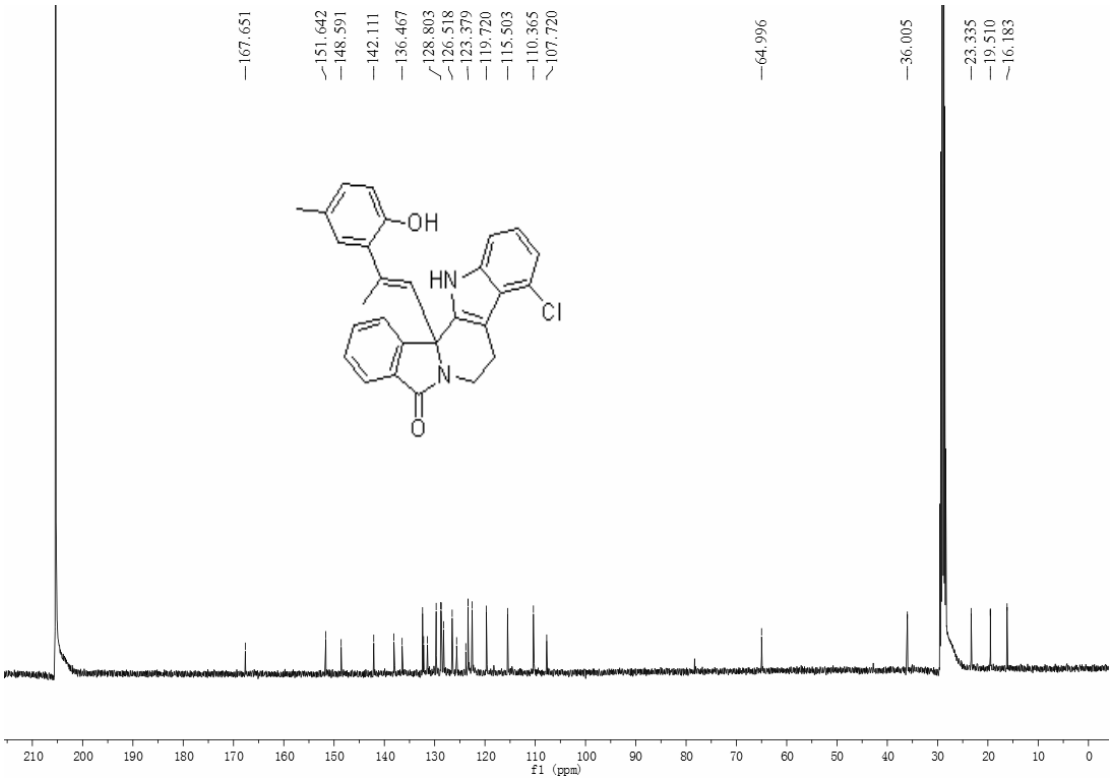
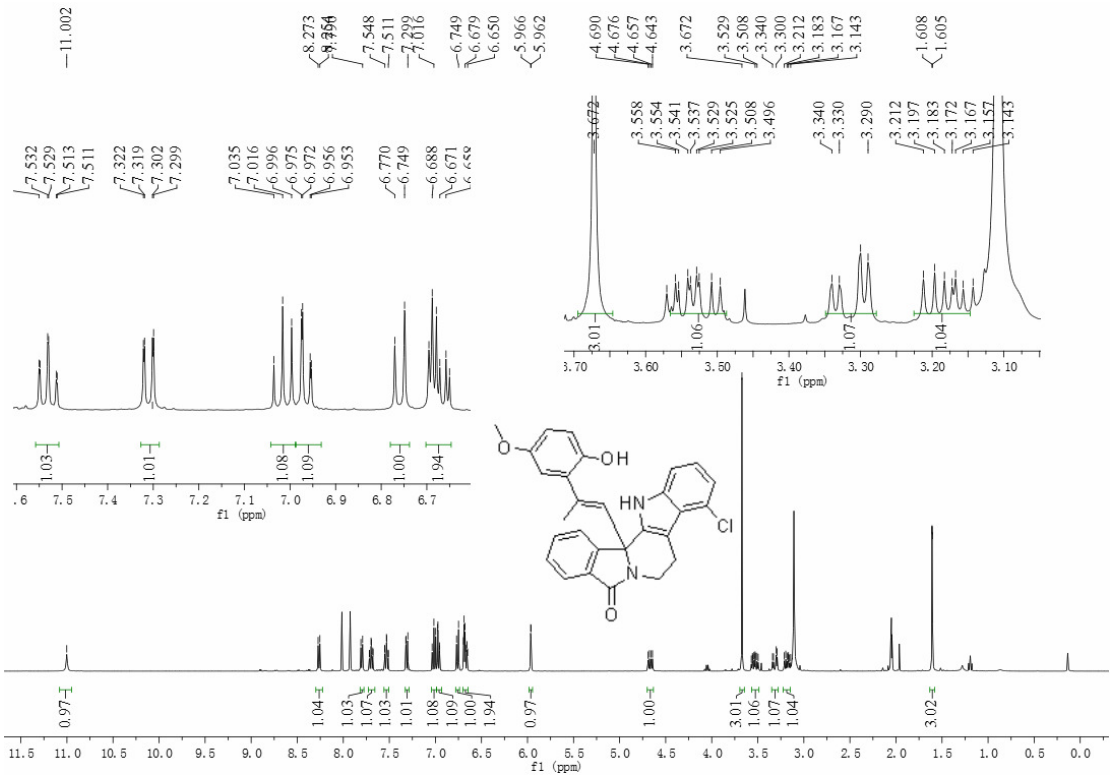




3cc:


11.002
8.273
8.256
7.548
7.532
7.529
7.513
7.511
7.322
7.319
7.302
7.299
7.035
7.016
6.996
6.975
6.972
6.956
6.953
6.770
6.749
6.688
6.671
5.966
5.962
4.690
4.676
4.657
4.643
3.672
3.558
3.554
3.541
3.537
3.529
3.525
3.508
3.496
3.340
3.330
3.290
3.212
3.197
3.183
3.172
3.167
3.157
3.143
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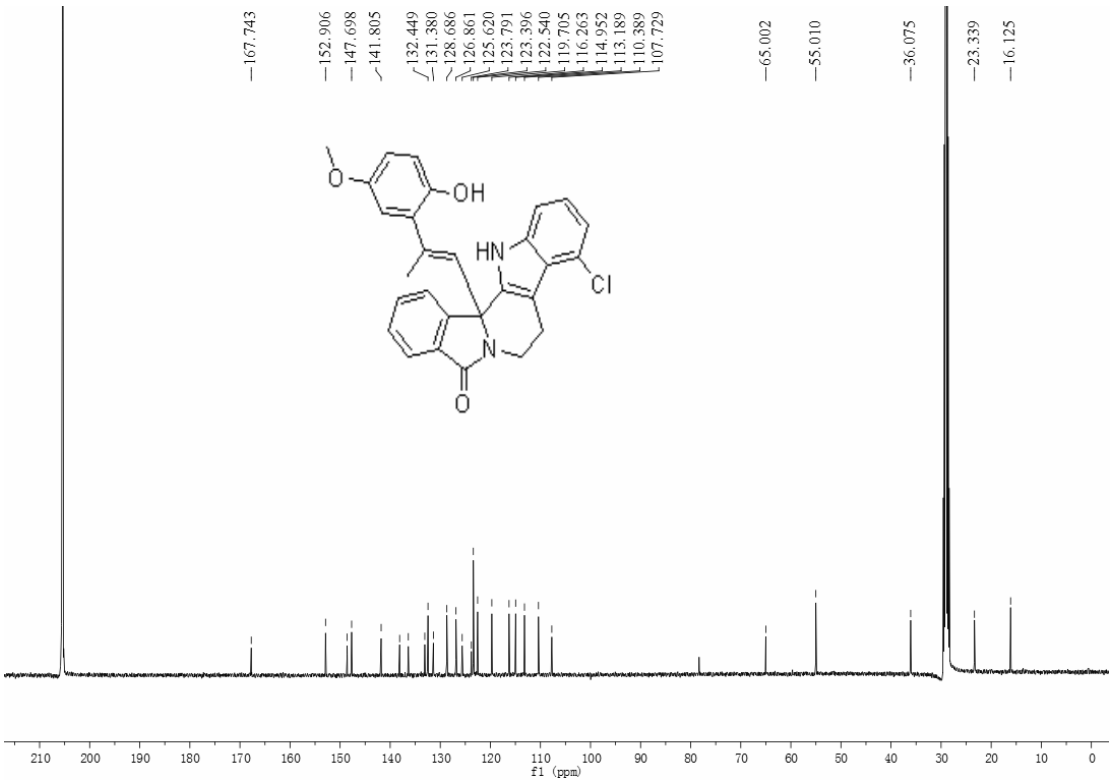
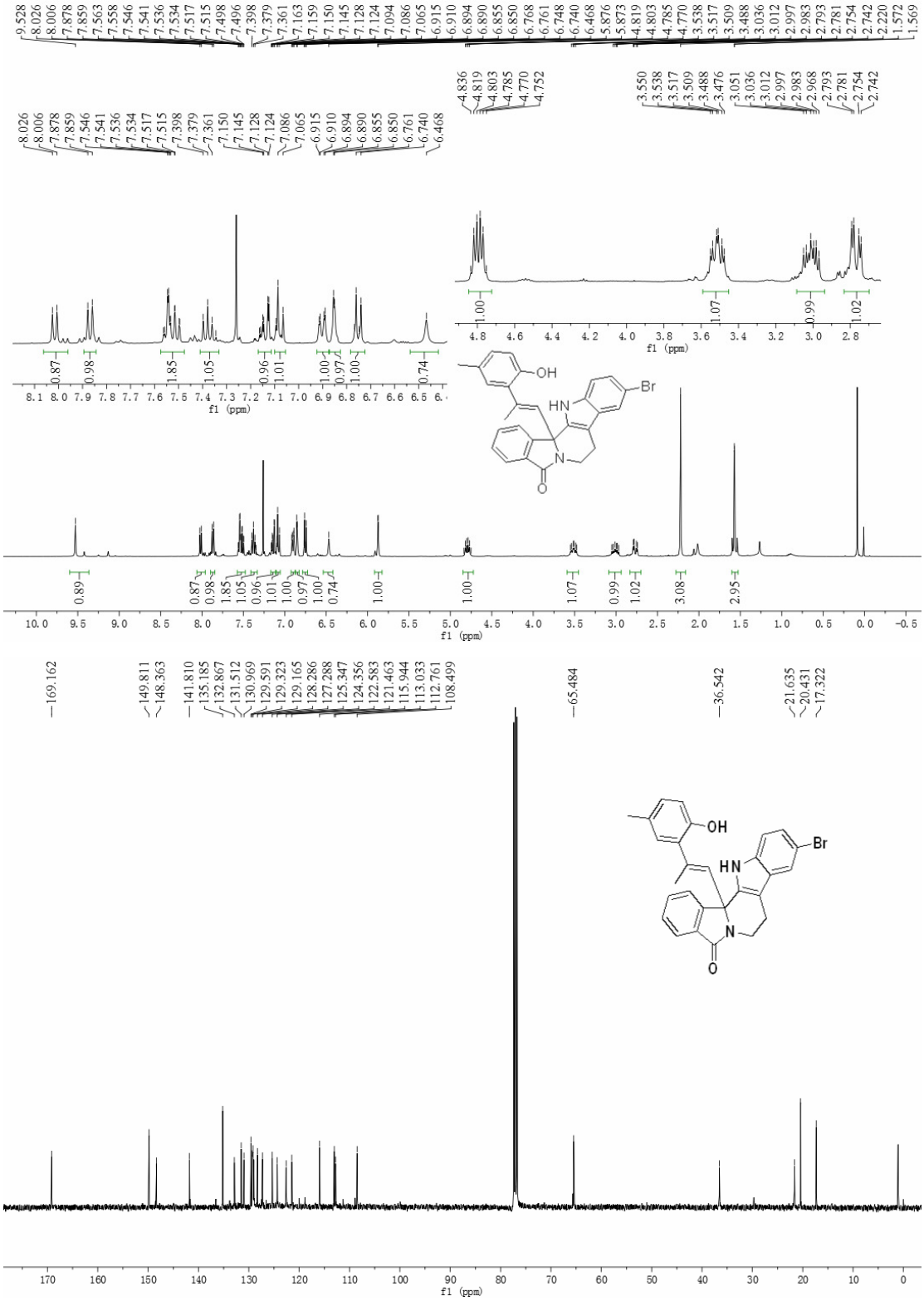
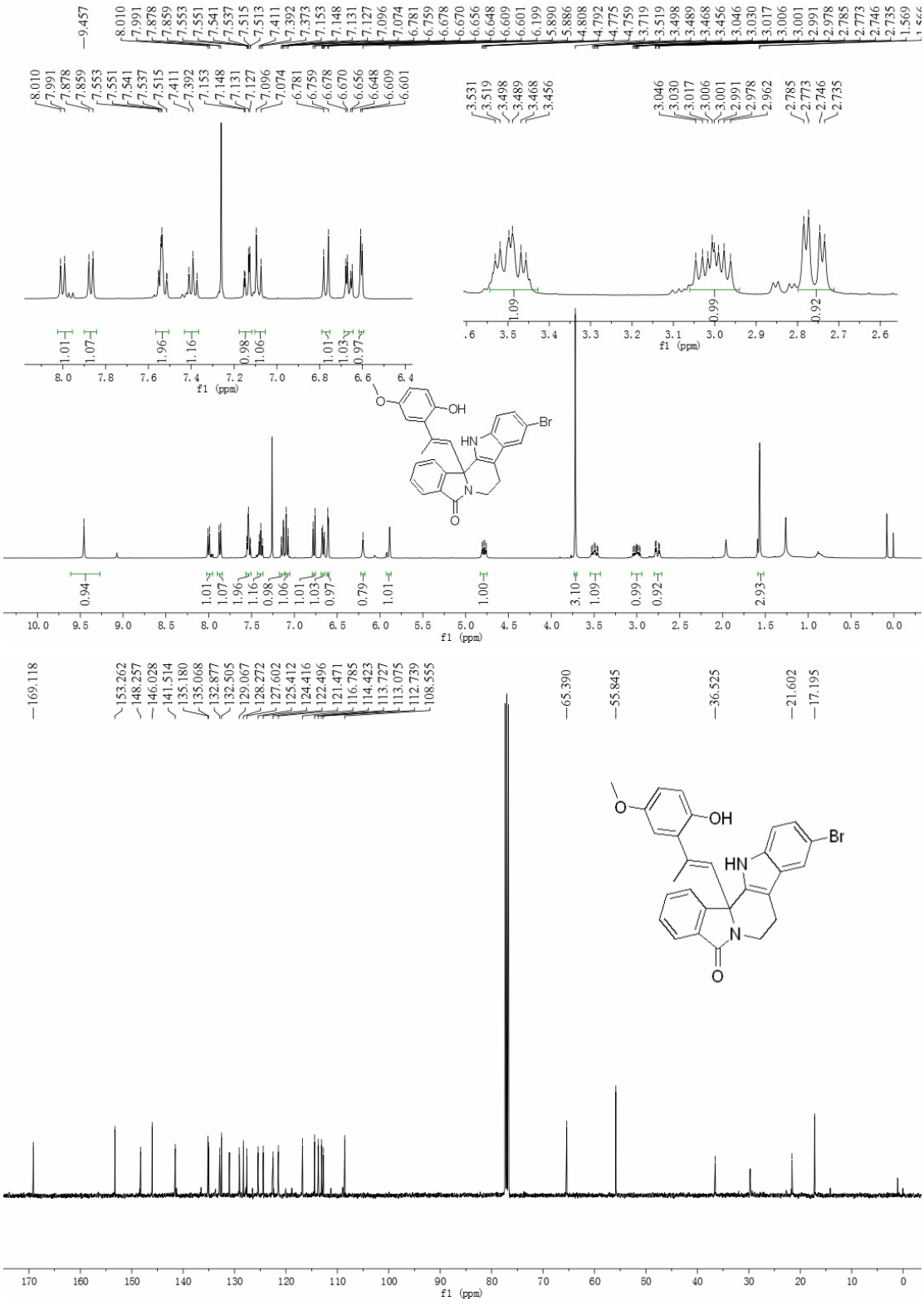
1.605
OH
HN
Cl
N
O
f1 (ppm)


167.743
152.906
147.698
141.805
132.449
131.380
128.686
126.861
125.620
123.791
123.396
122.540
119.705
116.263
114.952
113.189
110.389
107.729
65.002
55.010
36.075
23.339
16.125
OH
HN
Cl
N
O
f1 (ppm)

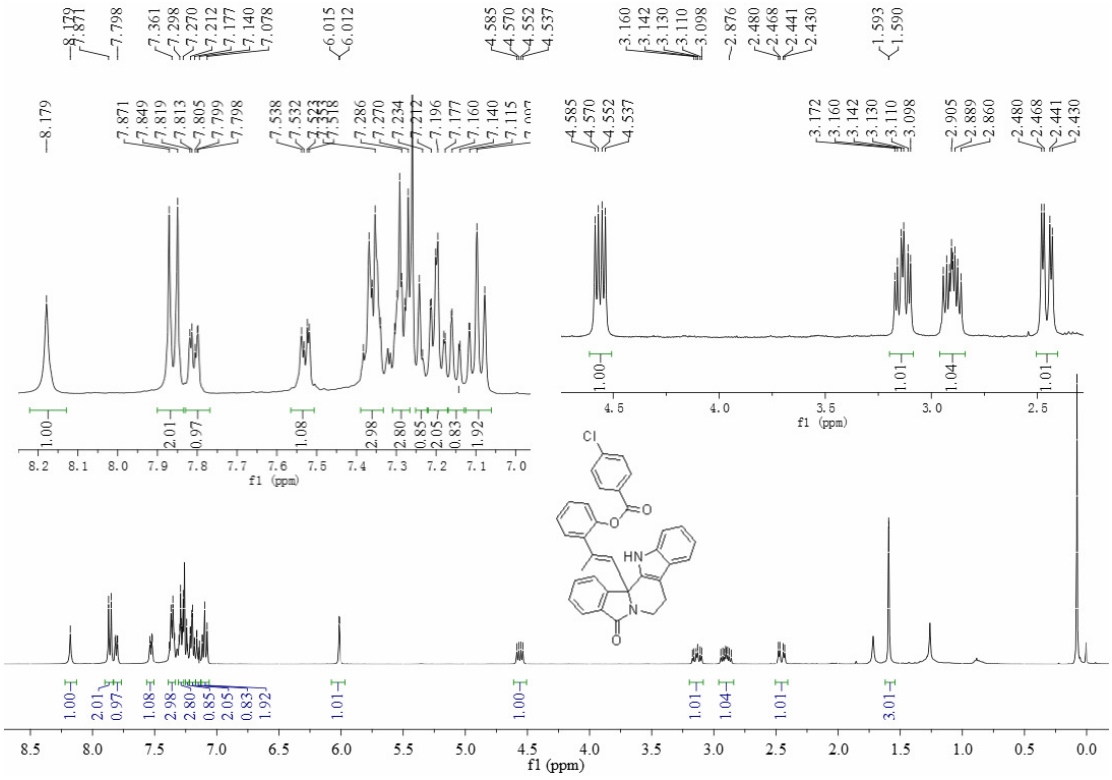
3gb: (inseparable chemoselective isomers, cr = 93:7)

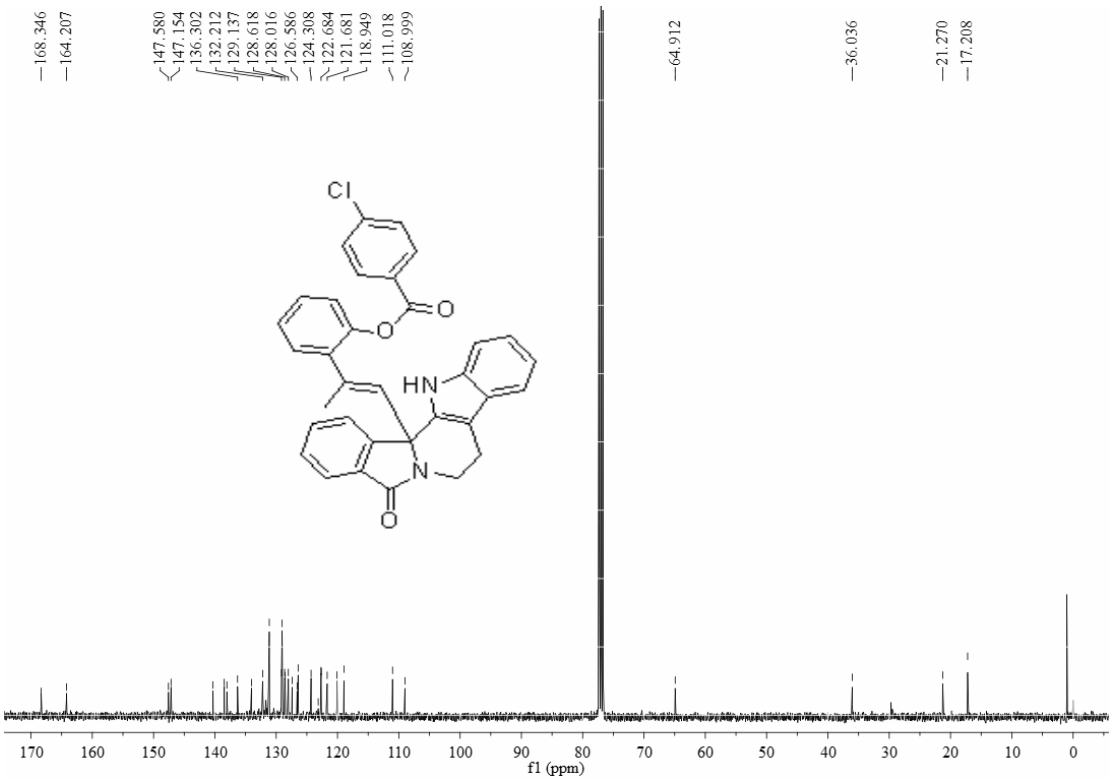


3gc: (inseparable chemoselective isomers, cr = 84:16)



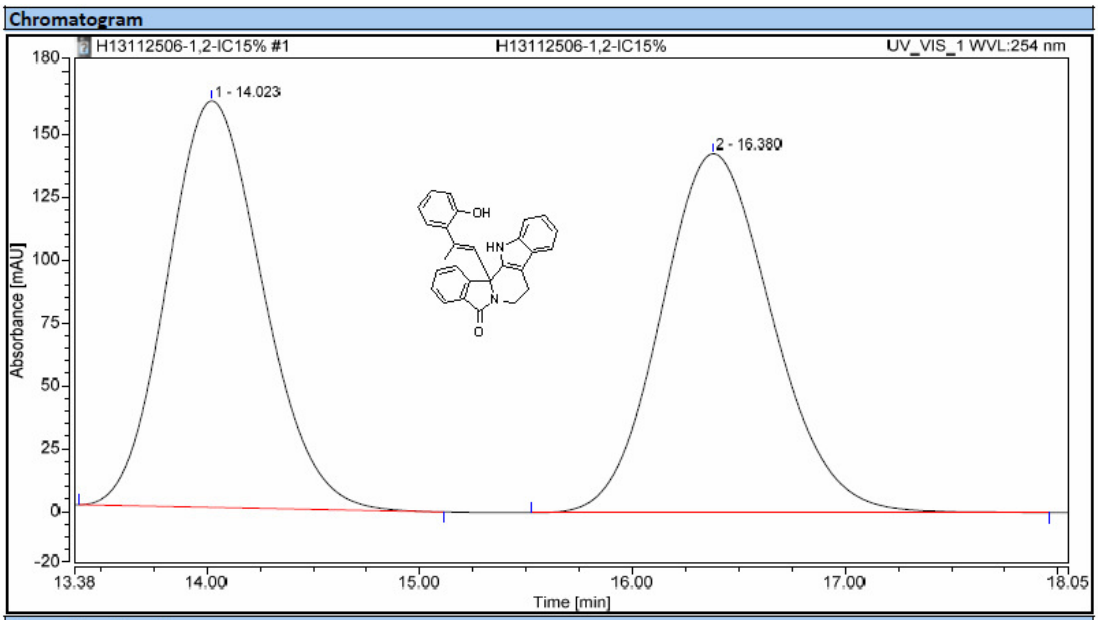
Compound 8:





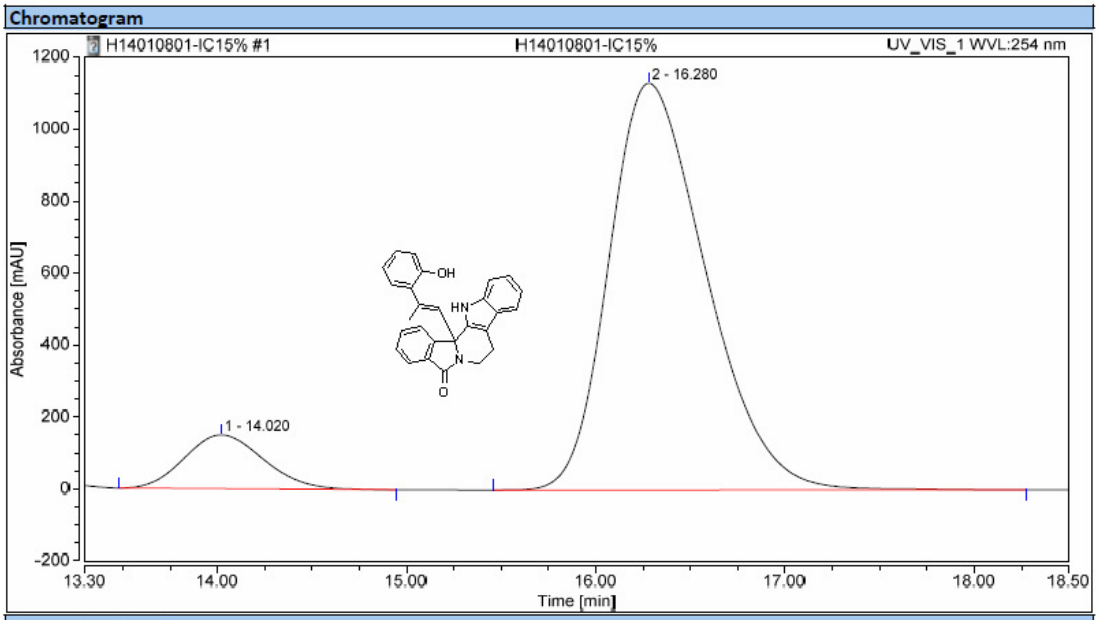
HPLC spectra of products 3 and 8

3aa:



Integration Results

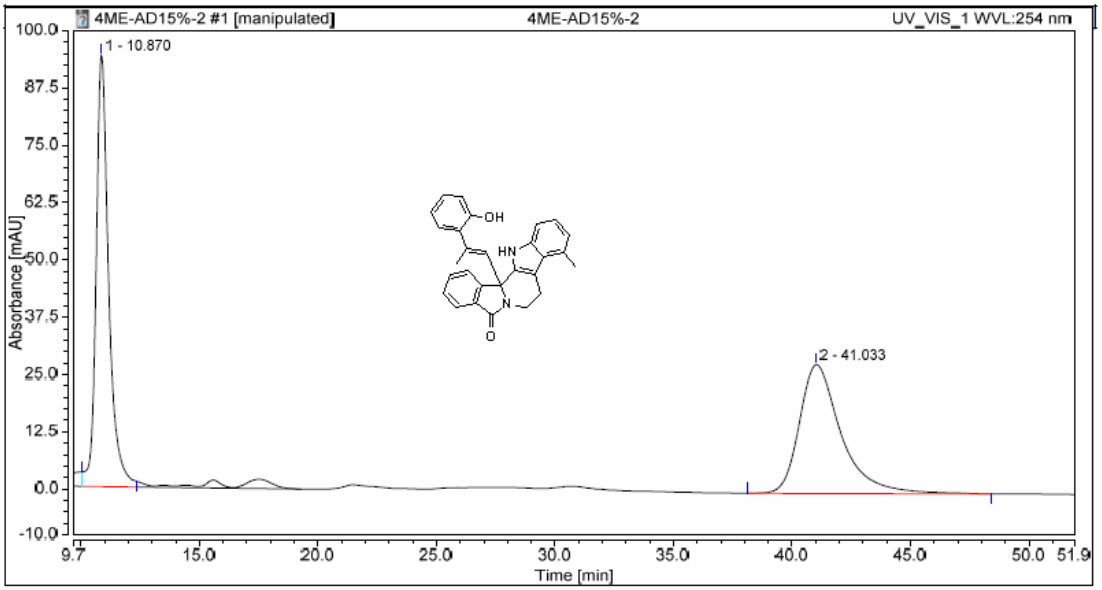
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.023	83.977	161.362	49.25	53.10	n.a.
2		16.380	86.538	142.543	50.75	46.90	n.a.
Total:			170.515	303.905	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.020	72.278	149.246	9.73	11.66	n.a.
2		16.280	670.359	1130.211	90.27	88.34	n.a.
Total:			742.637	1279.457	100.00	100.00	

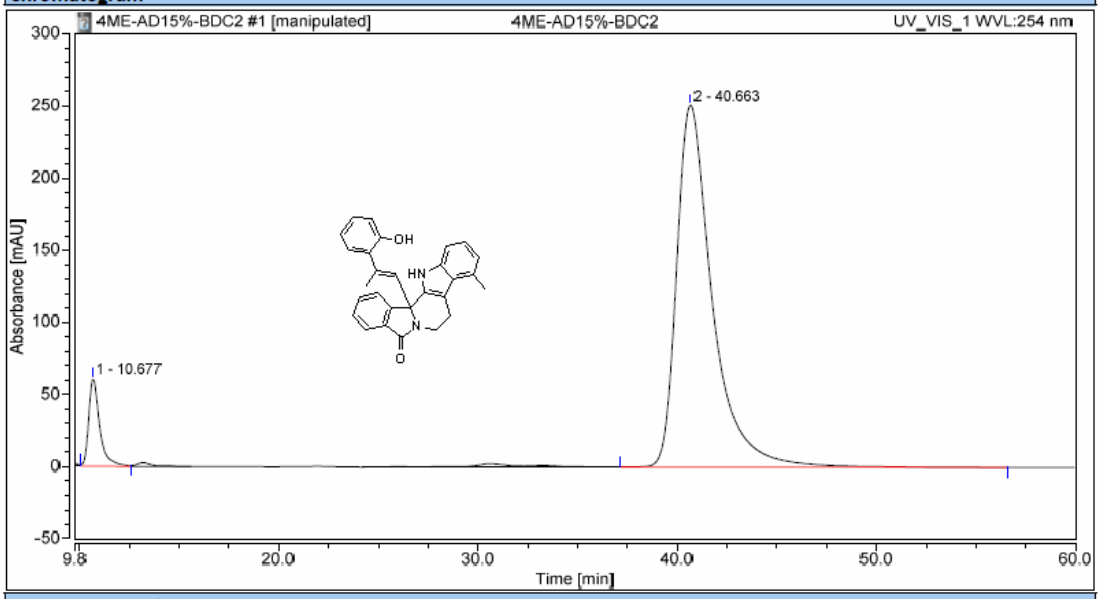
3ba:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.870	57.743	94.183	50.17	77.01	n.a.
2		41.033	57.344	28.111	49.83	22.99	n.a.
Total:			**115.087**	**122.294**	**100.00**	**100.00**	

Chromatogram

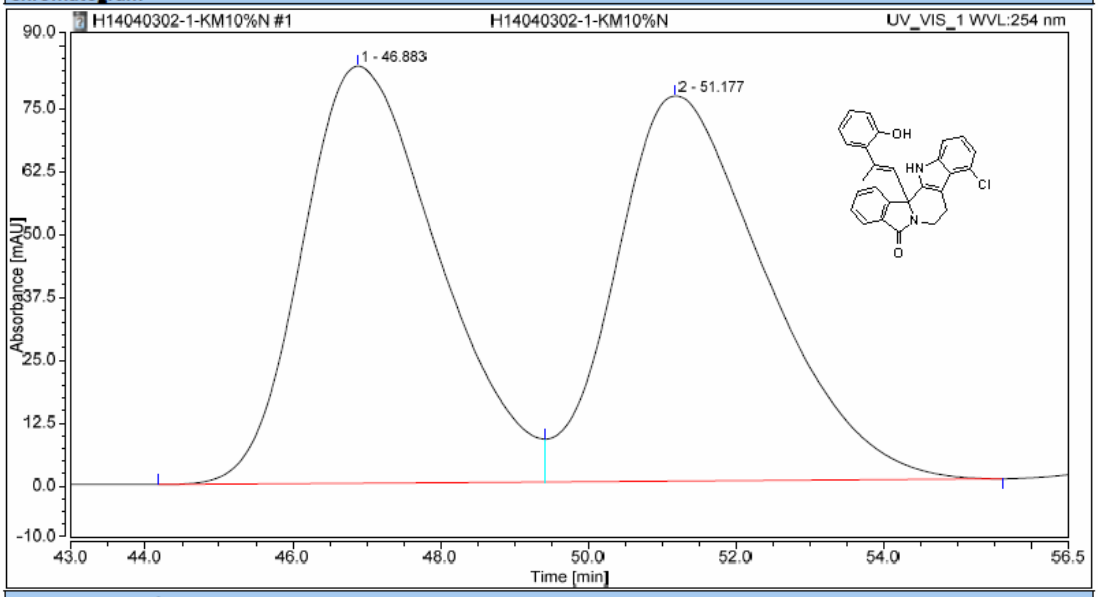


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.677	38.868	60.680	6.93	19.46	n.a.
2		40.663	521.846	251.099	93.07	80.54	n.a.
Total:			**560.714**	**311.779**	**100.00**	**100.00**	

3ca:

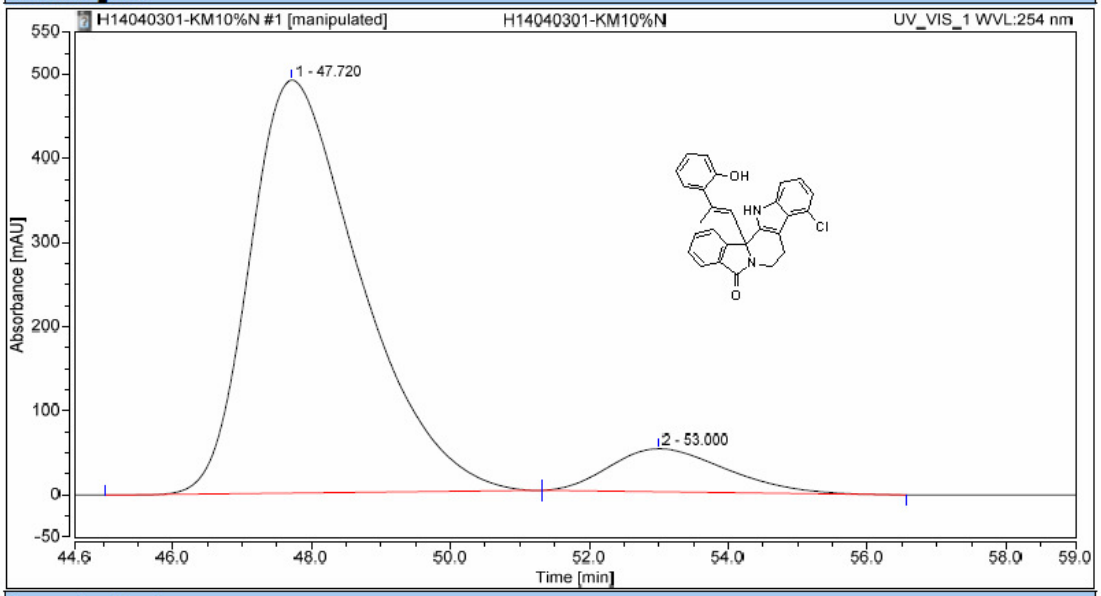
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		46.883	176.971	82.765	49.59	52.01	n.a.
2		51.177	179.913	76.378	50.41	47.99	n.a.
Total:			**356.884**	**159.143**	**100.00**	**100.00**	

Chromatogram

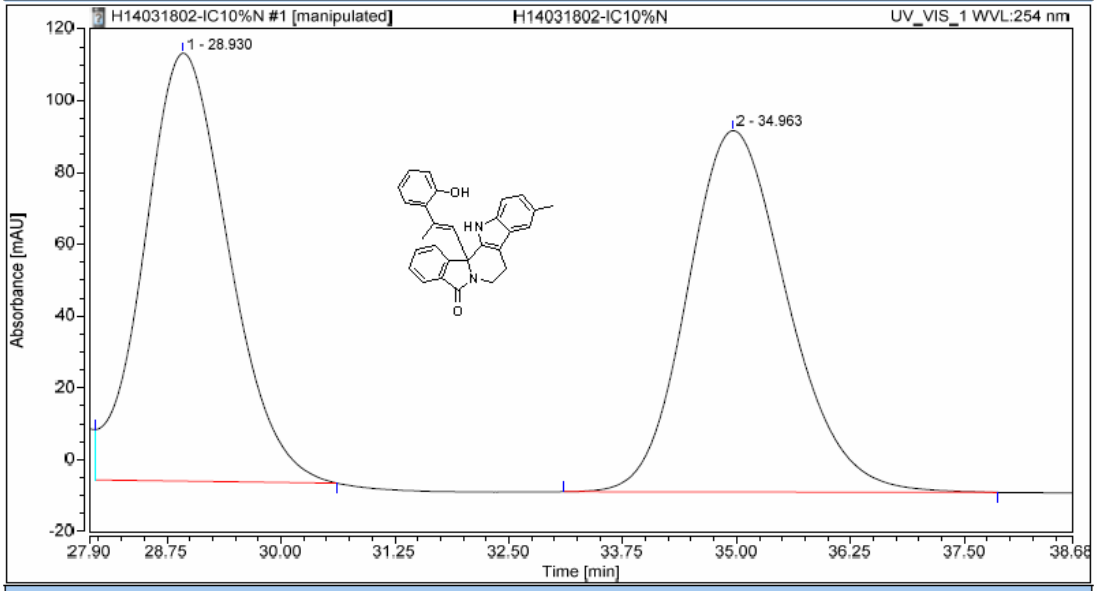


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		47.720	905.211	490.736	90.15	90.56	n.a.
2		53.000	98.926	51.170	9.85	9.44	n.a.
Total:			**1004.137**	**541.906**	**100.00**	**100.00**	

3da:

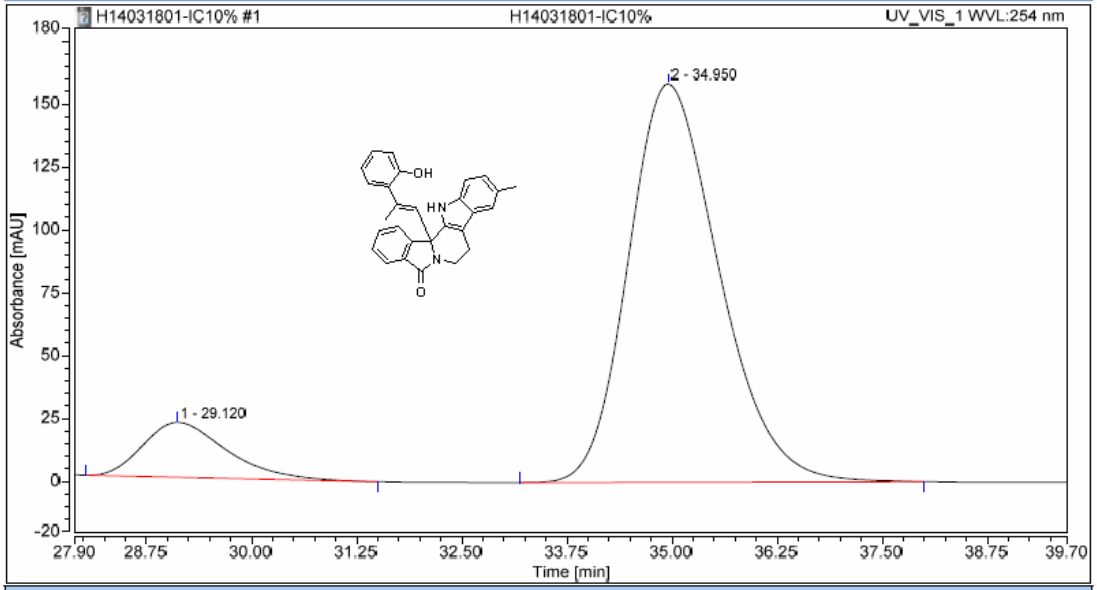
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		28.930	128.521	119.177	50.06	54.23	n.a.
2		34.963	128.210	100.595	49.94	45.77	n.a.
Total:			**256.731**	**219.772**	**100.00**	**100.00**	

Chromatogram

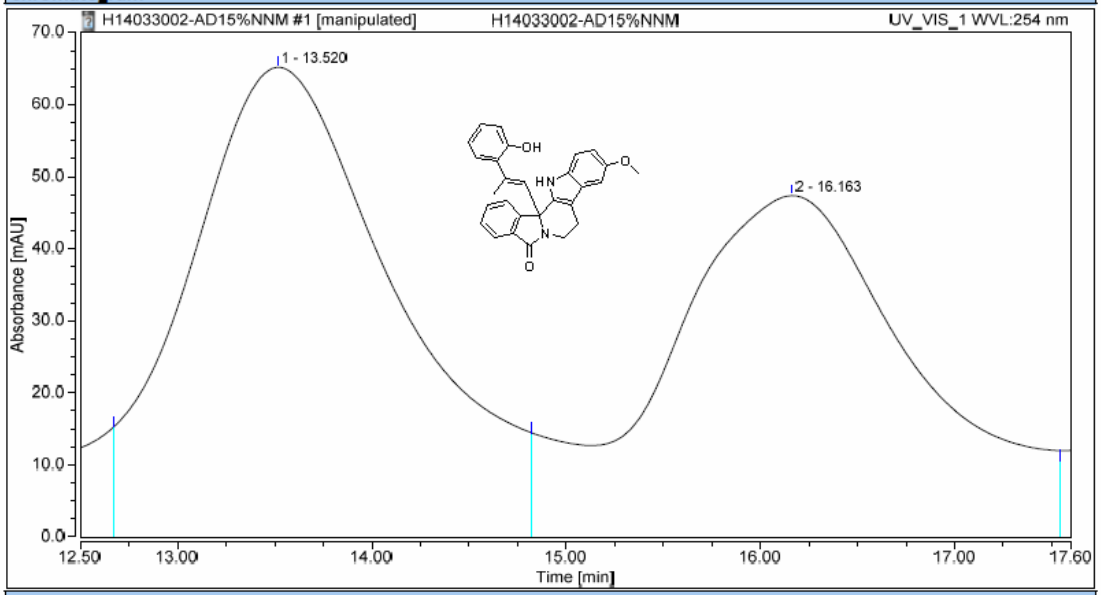


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		29.120	25.104	21.820	11.25	12.12	n.a.
2		34.950	198.114	158.159	88.75	87.88	n.a.
Total:			**223.218**	**179.979**	**100.00**	**100.00**	

3ea:

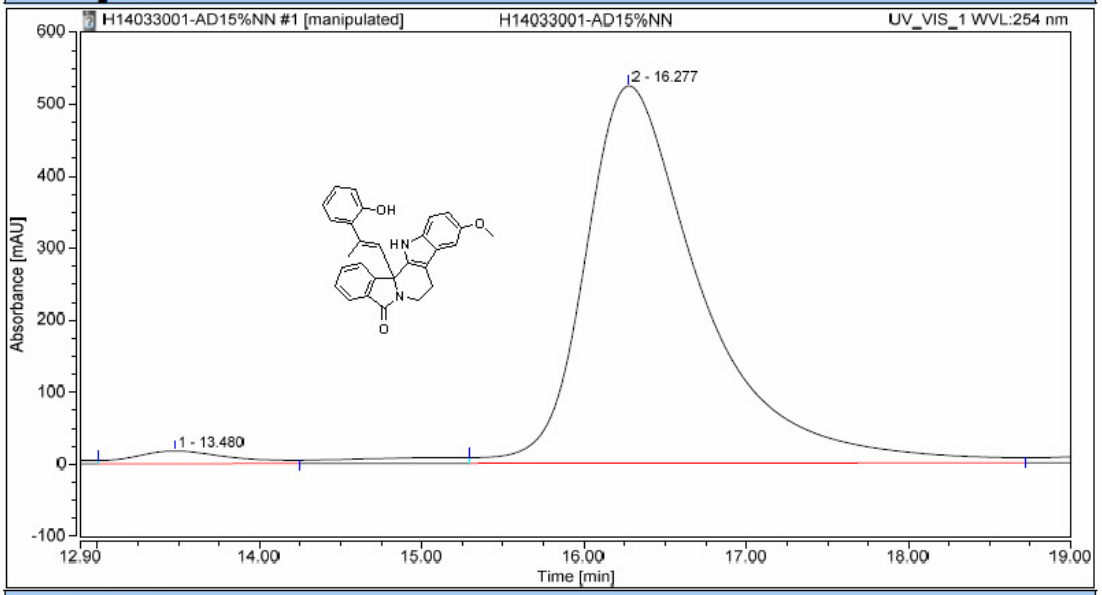
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.520	103.323	75.455	49.90	55.95	n.a.
2		16.163	103.741	59.401	50.10	44.05	n.a.
Total:			207.064	134.856	100.00	100.00	

Chromatogram

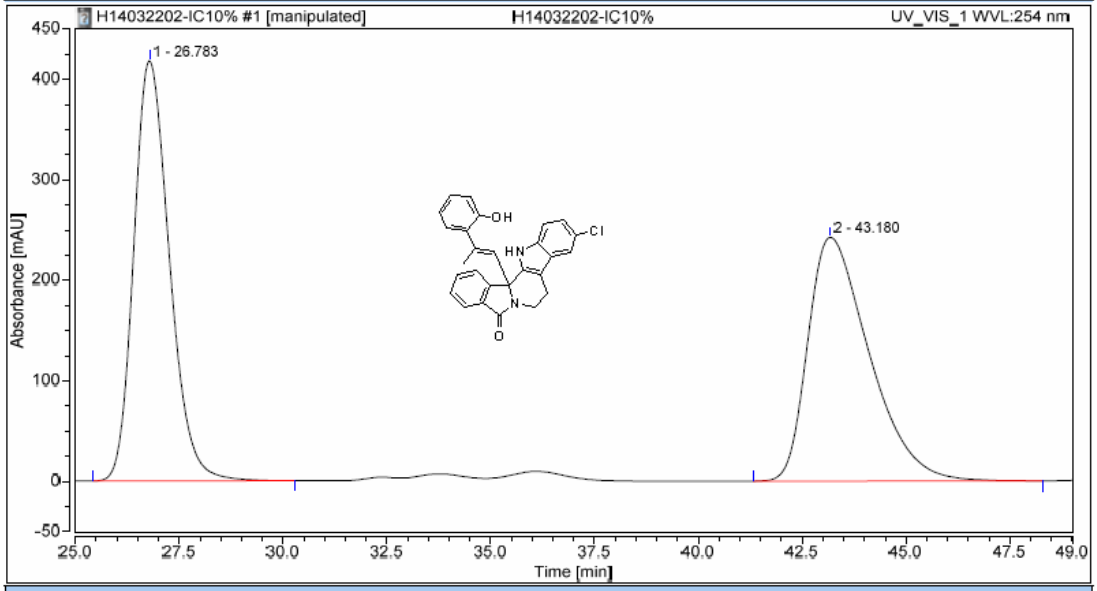


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.480	12.231	17.542	2.72	3.24	n.a.
2		16.277	437.956	523.693	97.28	96.76	n.a.
Total:			450.187	541.235	100.00	100.00	

3fa:

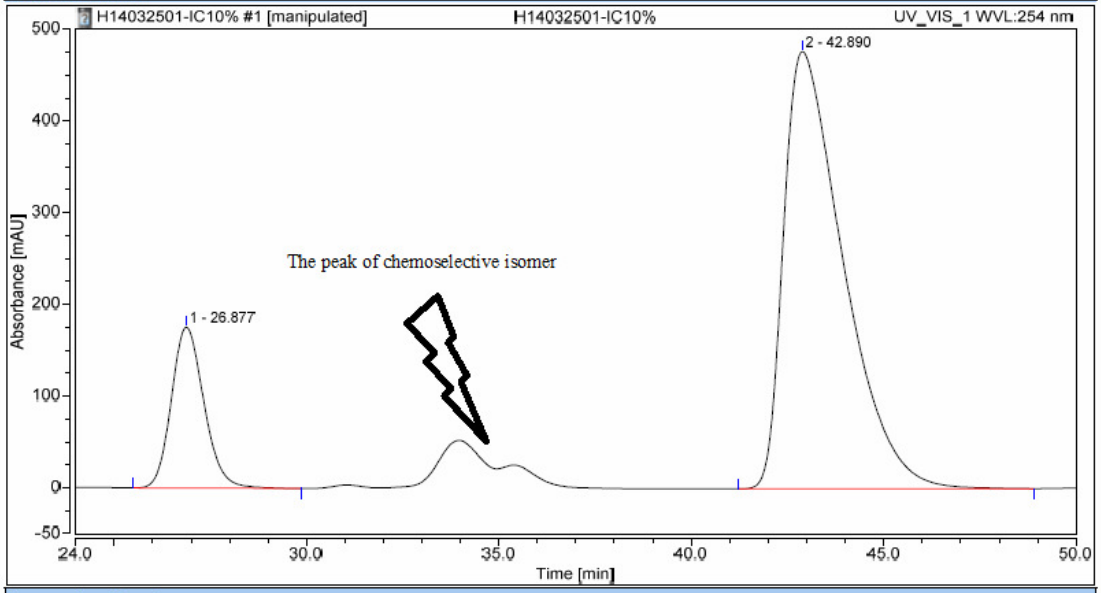
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.783	415.296	417.639	50.02	63.28	n.a.
2		43.180	414.998	242.385	49.98	36.72	n.a.
Total:			830.294	660.024	100.00	100.00	

Chromatogram

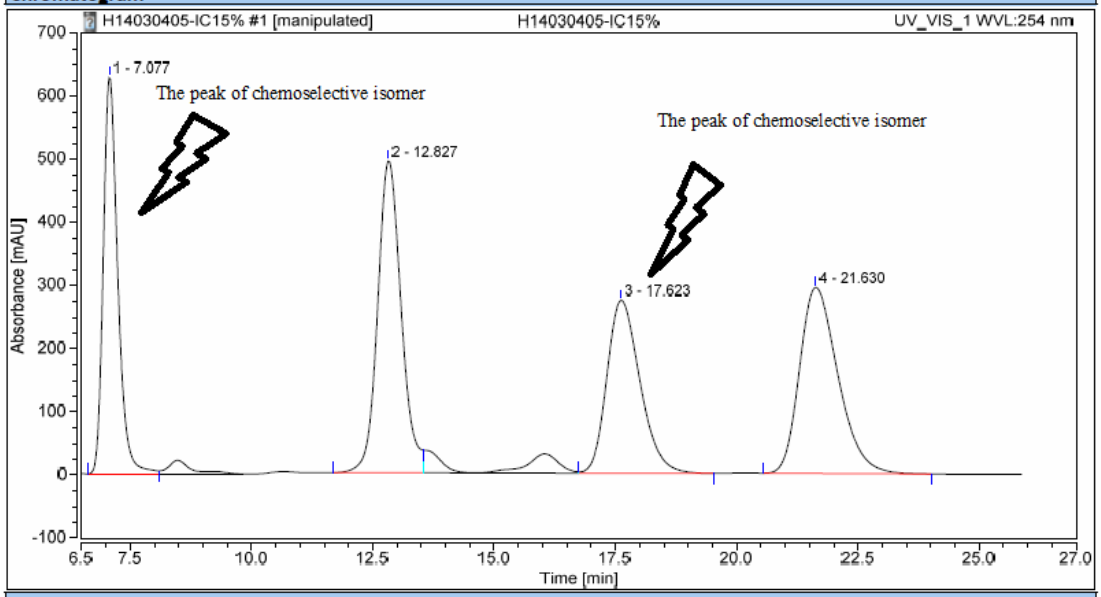


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		26.877	172.682	175.664	16.79	26.93	n.a.
2		42.890	855.977	476.739	83.21	73.07	n.a.
Total:			1028.658	652.403	100.00	100.00	

3ga:

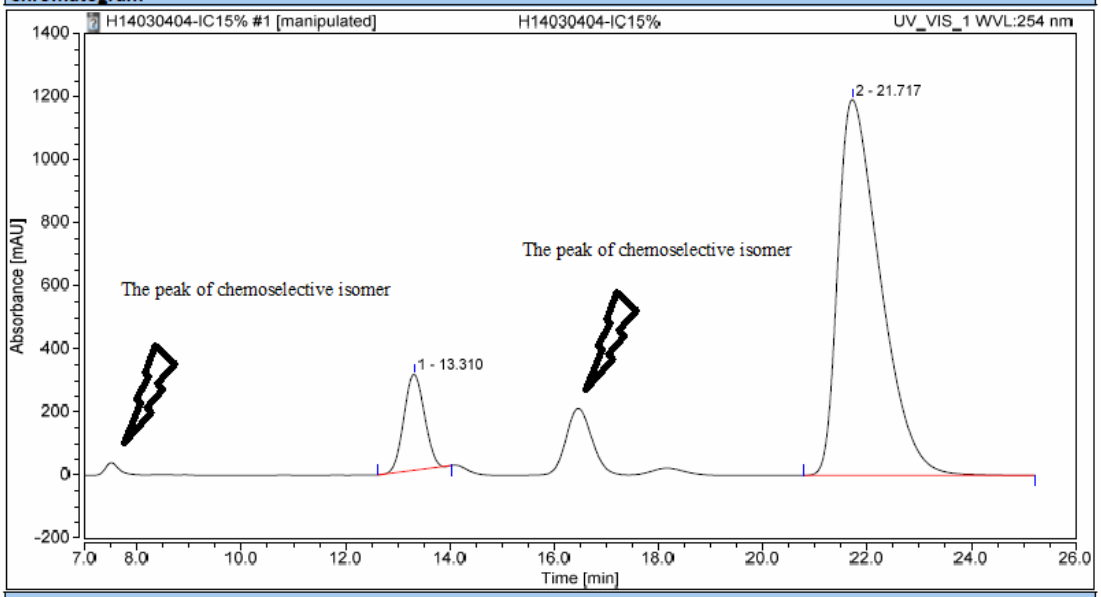
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.077	217.300	629.229	22.12	37.18	n.a.
2		12.827	277.571	494.302	28.26	29.21	n.a.
3		17.623	216.934	274.037	22.09	16.19	n.a.
4		21.630	270.423	294.953	27.53	17.43	n.a.
Total:			**982.228**	**1692.520**	**100.00**	**100.00**	

Chromatogram

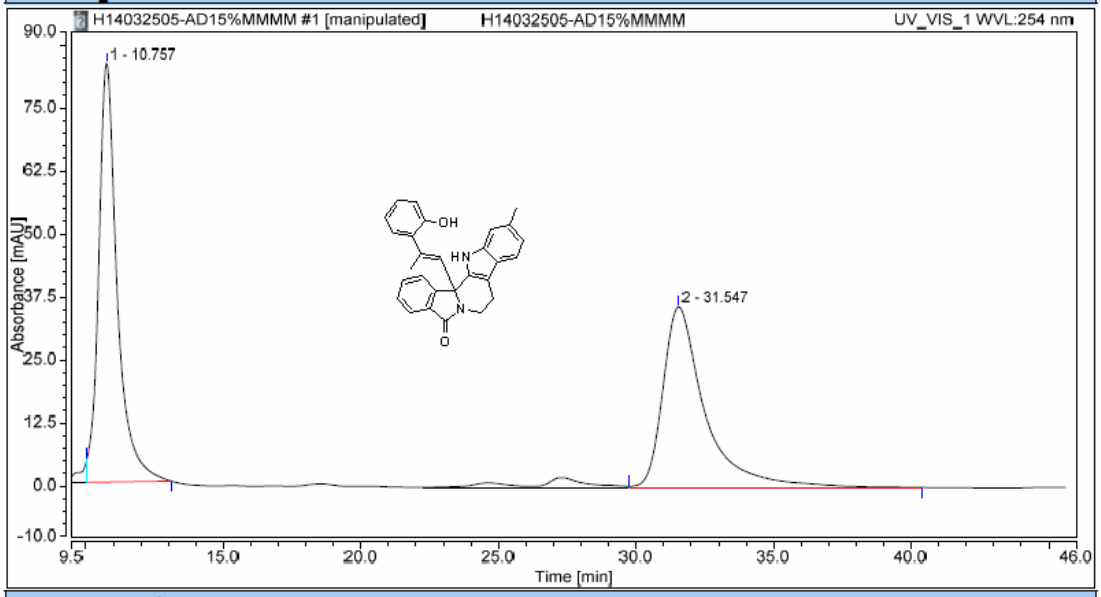


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.310	138.506	304.410	11.02	20.33	n.a.
2		21.717	1118.508	1193.233	88.98	79.67	n.a.
Total:			**1257.014**	**1497.643**	**100.00**	**100.00**	

3ha:

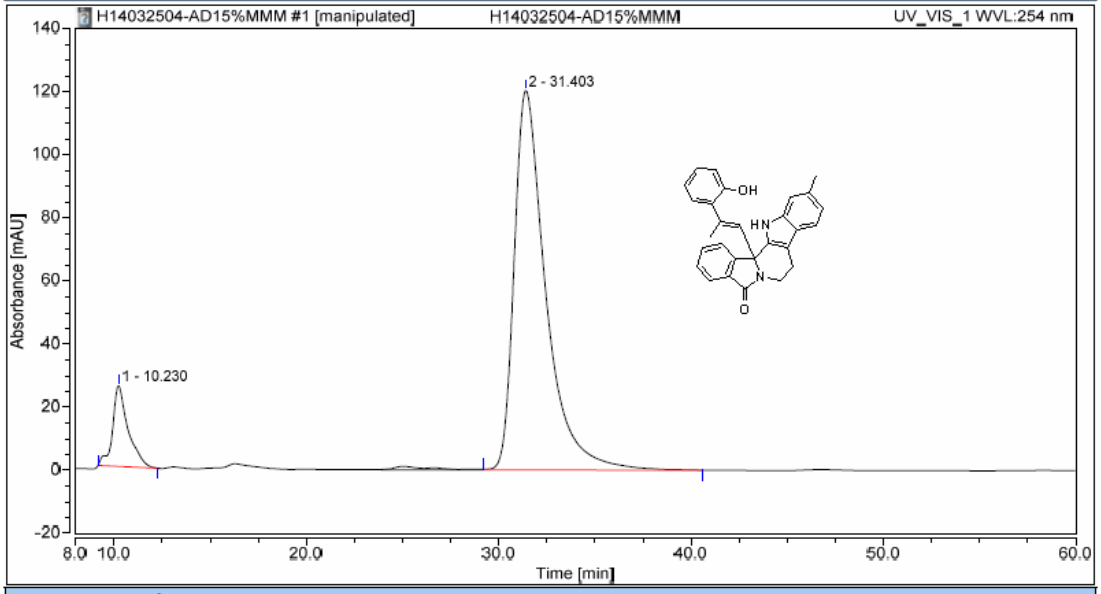
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.757	64.651	83.024	50.54	69.86	n.a.
2		31.547	63.257	35.818	49.46	30.14	n.a.
Total:			**127.908**	**118.842**	**100.00**	**100.00**	

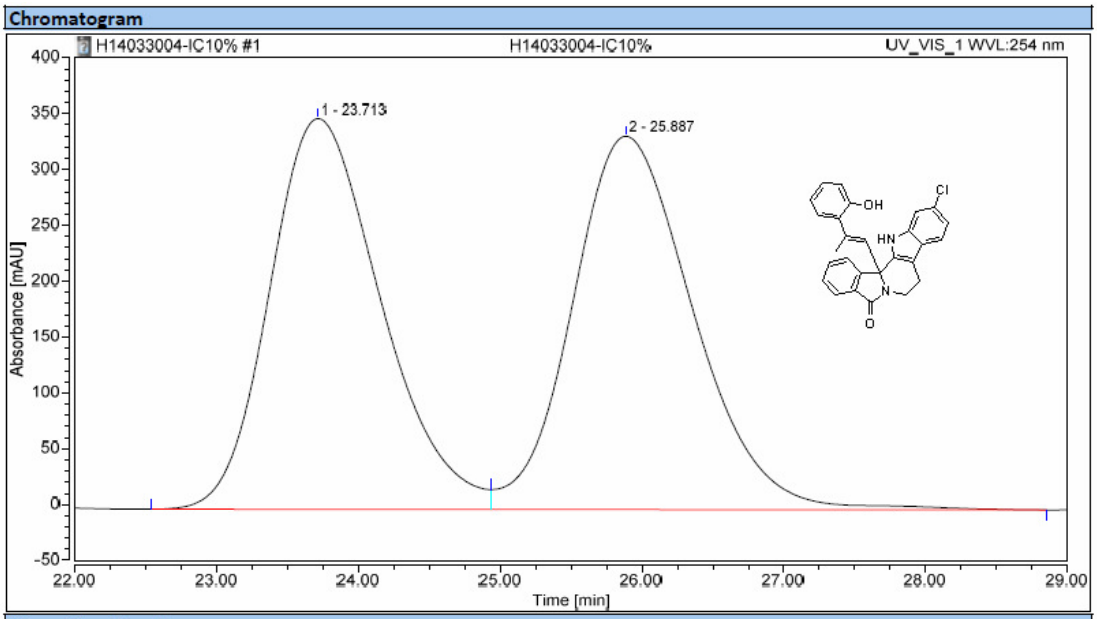
Chromatogram



Integration Results

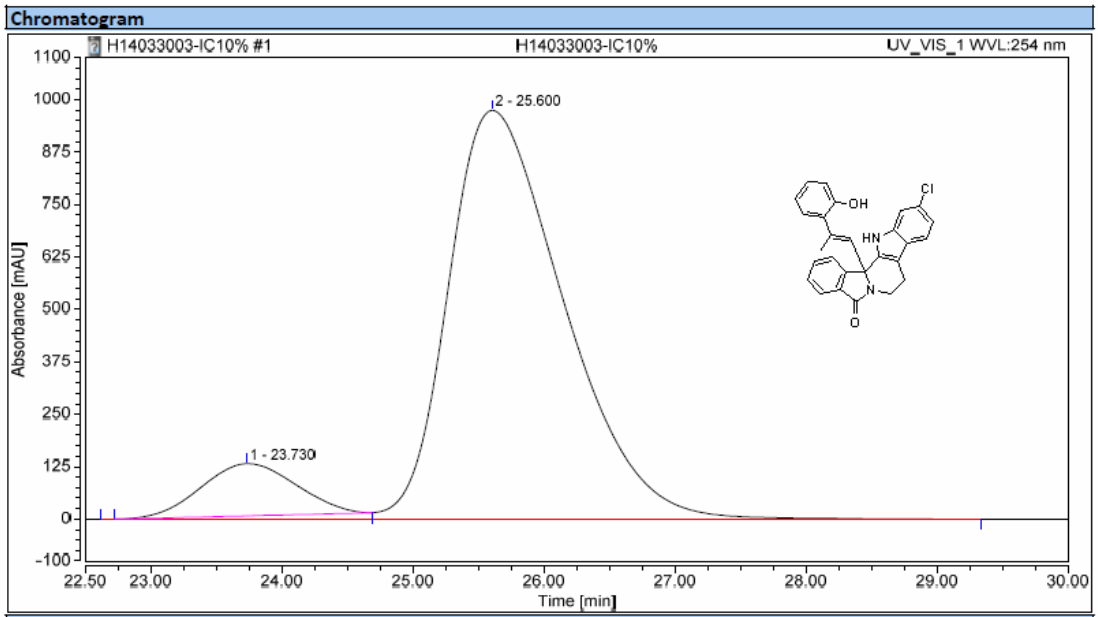
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.230	24.100	25.678	9.53	17.58	n.a.
2		31.403	228.787	120.369	90.47	82.42	n.a.
Total:			**252.887**	**146.047**	**100.00**	**100.00**	

3ia:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.713	317.533	349.724	49.06	51.14	n.a.
2		25.887	329.744	334.178	50.94	48.86	n.a.
Total:			**647.277**	**683.902**	**100.00**	**100.00**	

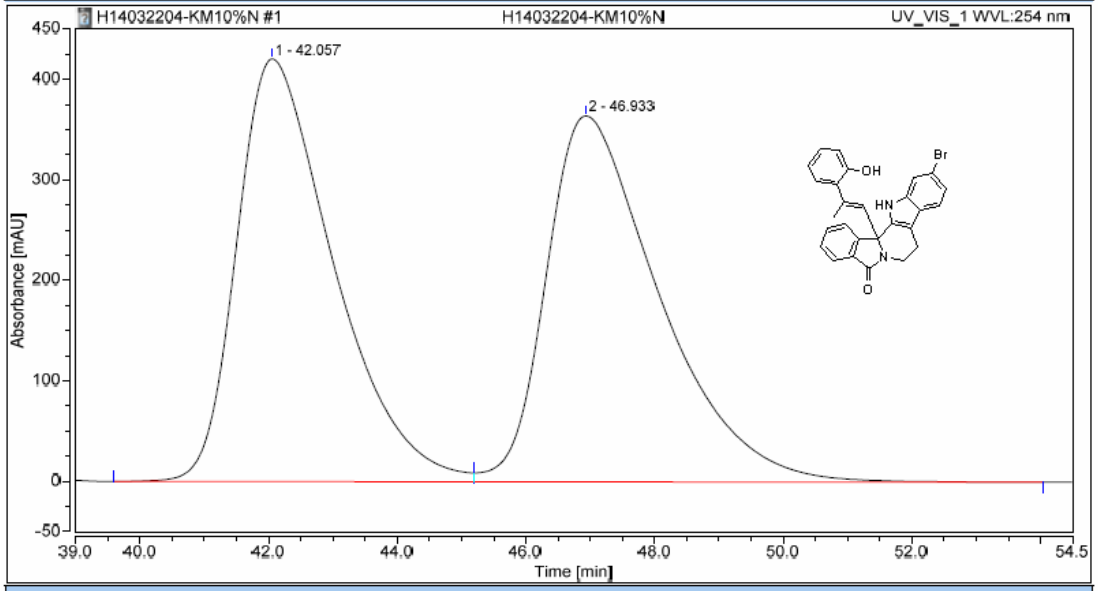


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		23.730	103.793	124.494	9.33	11.32	n.a.
2		25.600	1008.438	975.210	90.67	88.68	n.a.
Total:			**1112.231**	**1099.704**	**100.00**	**100.00**	

3ja:

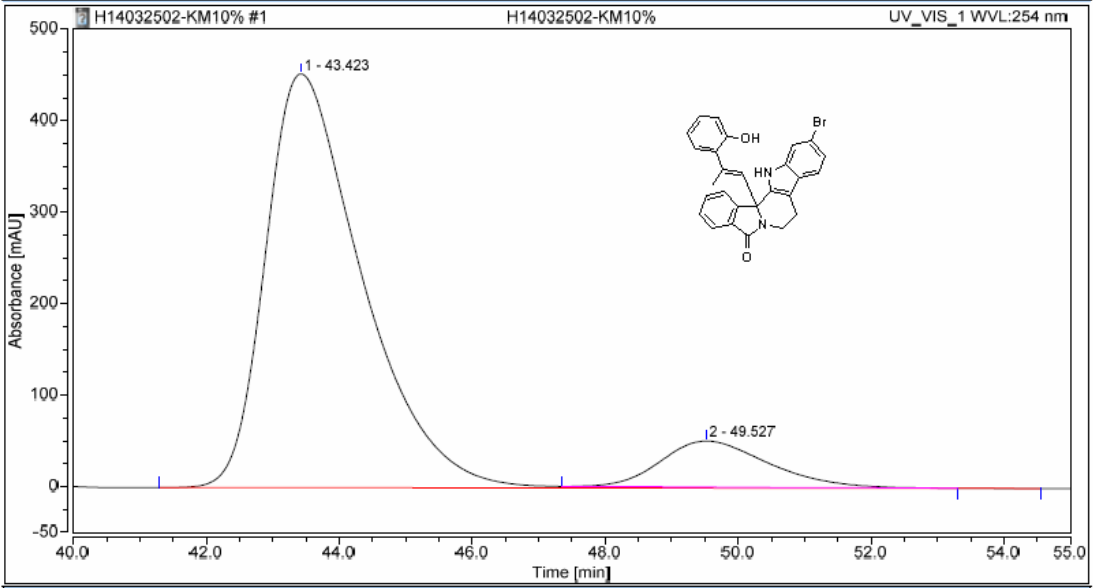
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		42.057	731.632	420.376	49.69	53.60	n.a.
2		46.933	740.783	363.943	50.31	46.40	n.a.
Total:			1472.415	784.319	100.00	100.00	

Chromatogram

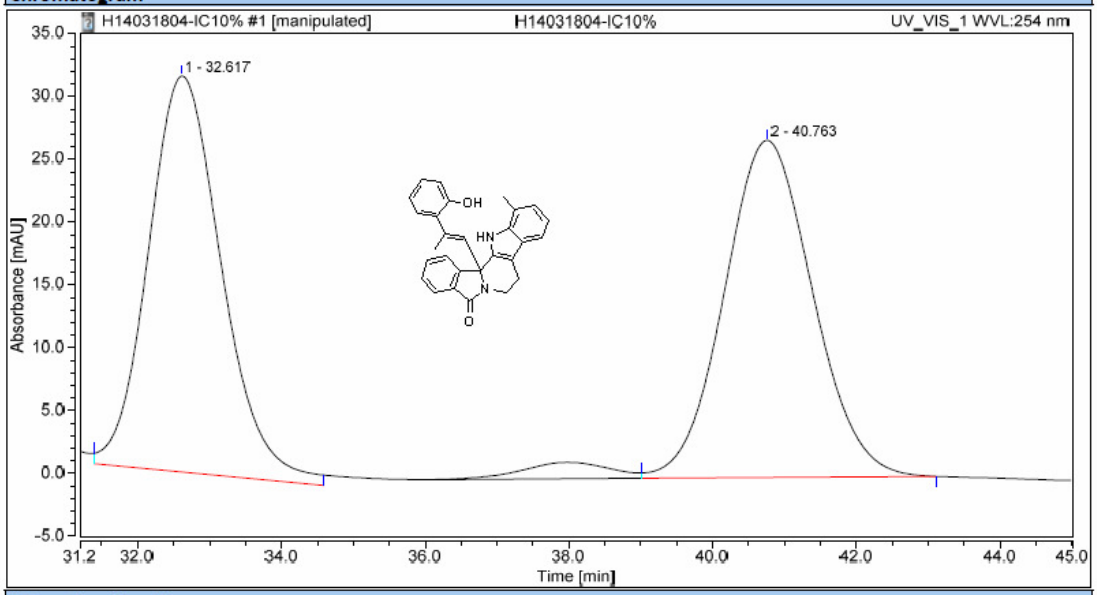


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		43.423	765.104	452.160	89.06	89.99	n.a.
2		49.527	93.979	50.293	10.94	10.01	n.a.
Total:			859.083	502.453	100.00	100.00	

3ka:

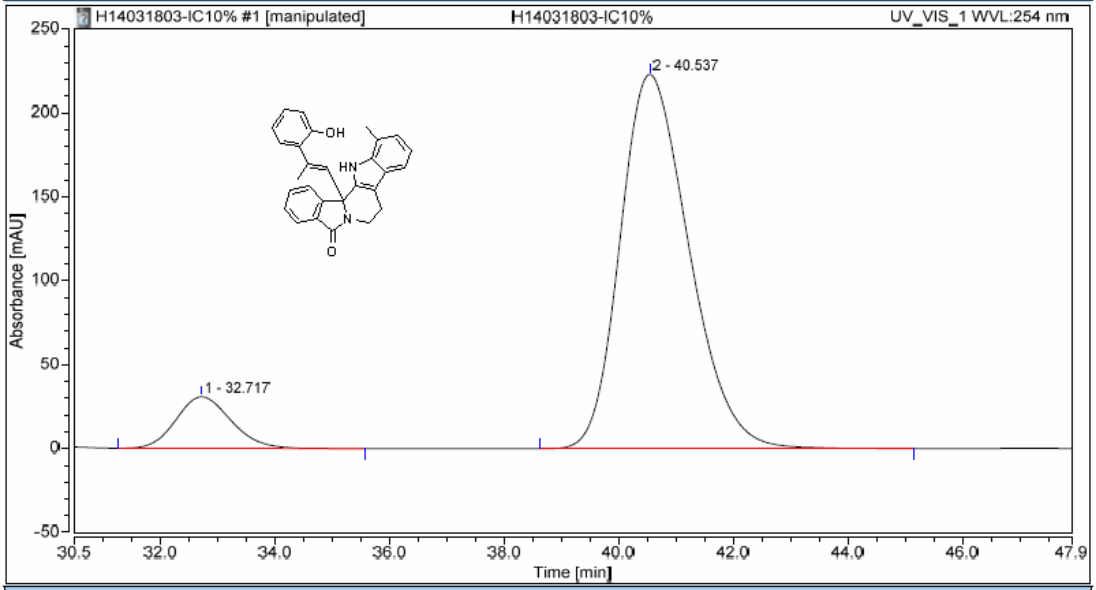
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32.617	37.163	31.517	49.31	54.02	n.a.
2		40.763	38.209	26.828	50.69	45.98	n.a.
Total:			75.373	58.345	100.00	100.00	

Chromatogram

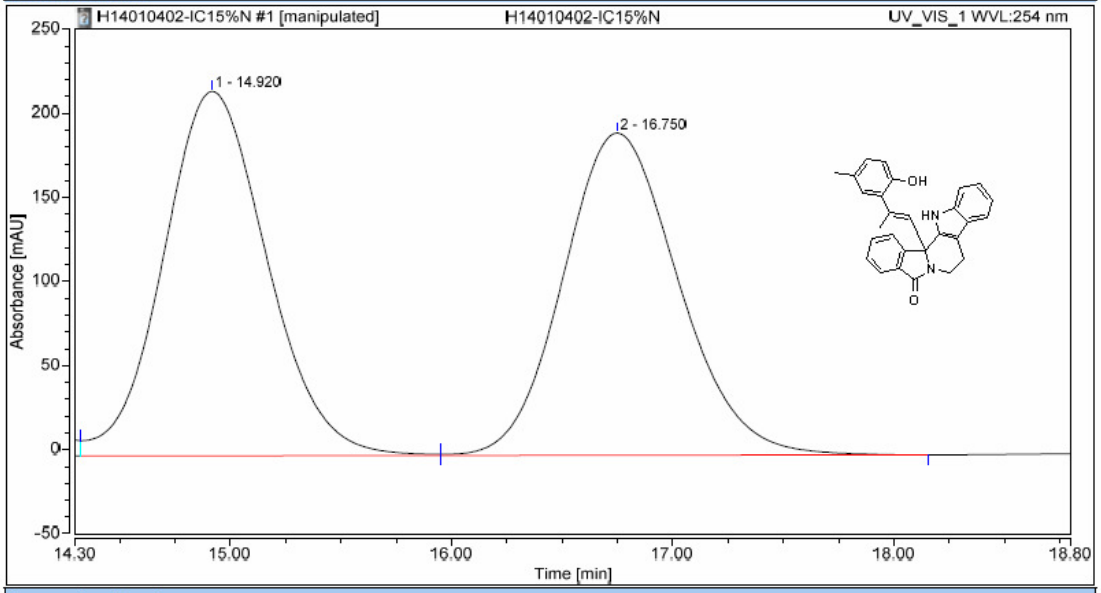


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		32.717	34.151	30.681	9.90	12.09	n.a.
2		40.537	310.664	223.174	90.10	87.91	n.a.
Total:			344.815	253.855	100.00	100.00	

3ab:

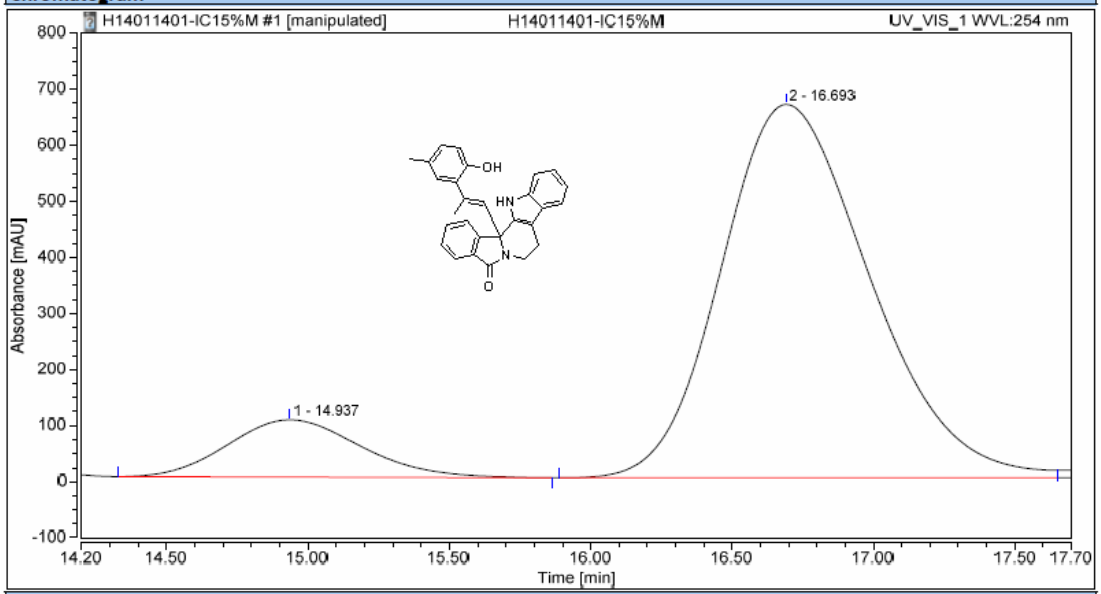
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.920	117.721	216.749	50.45	53.08	n.a.
2		16.750	115.621	191.615	49.55	46.92	n.a.
Total:			233.343	408.363	100.00	100.00	

Chromatogram

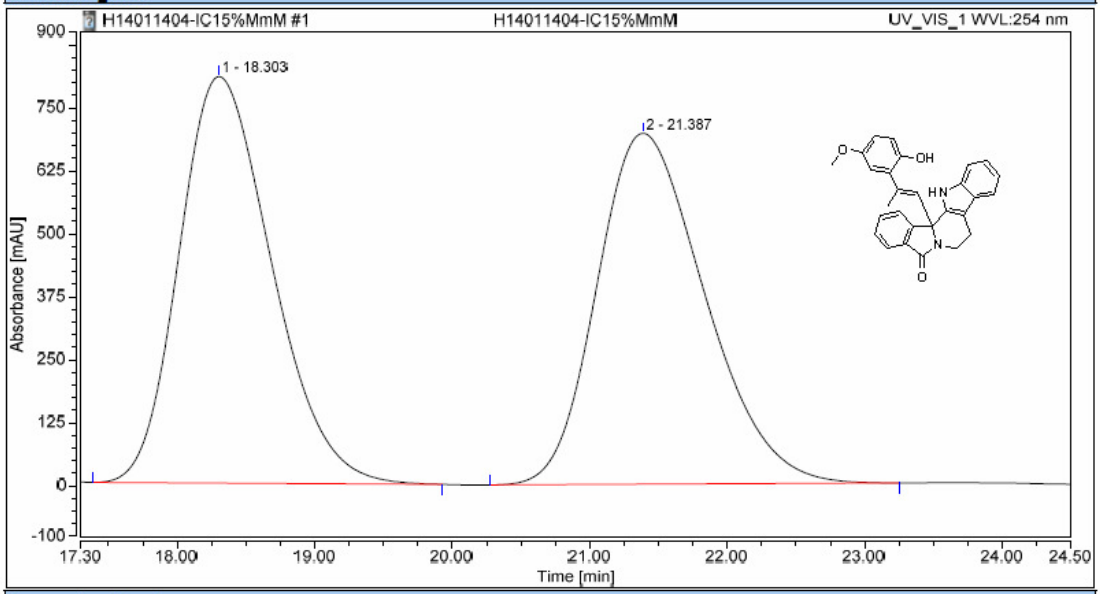


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.937	55.541	102.107	12.05	13.29	n.a.
2		16.693	405.519	665.923	87.95	86.71	n.a.
Total:			461.060	768.030	100.00	100.00	

3ac:

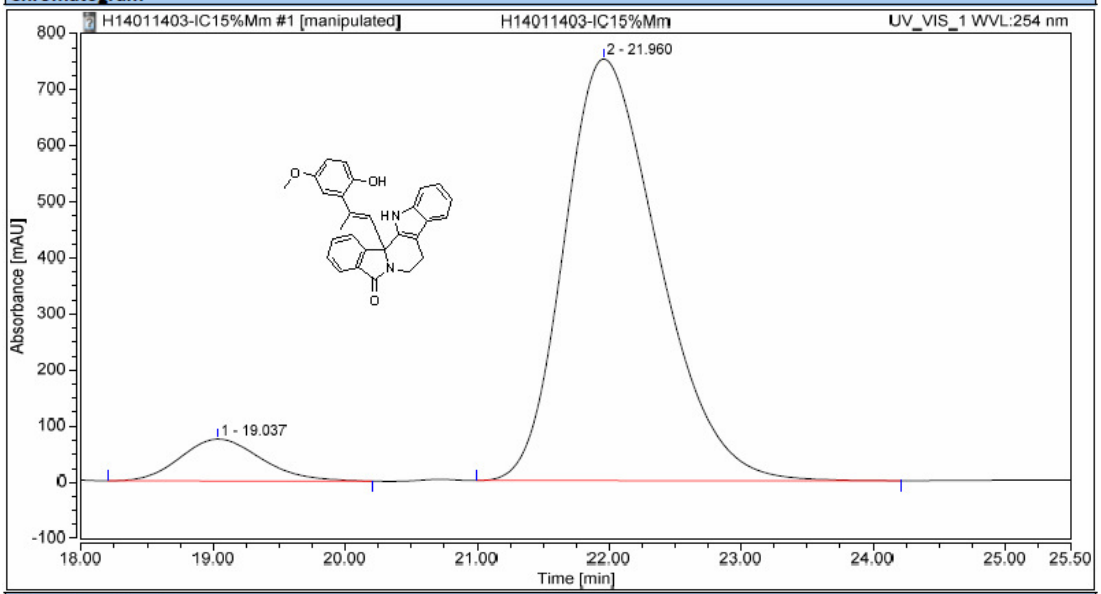
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.303	628.751	806.364	49.90	53.68	n.a.
2		21.387	631.305	695.932	50.10	46.32	n.a.
Total:			**1260.055**	**1502.296**	**100.00**	**100.00**	

Chromatogram

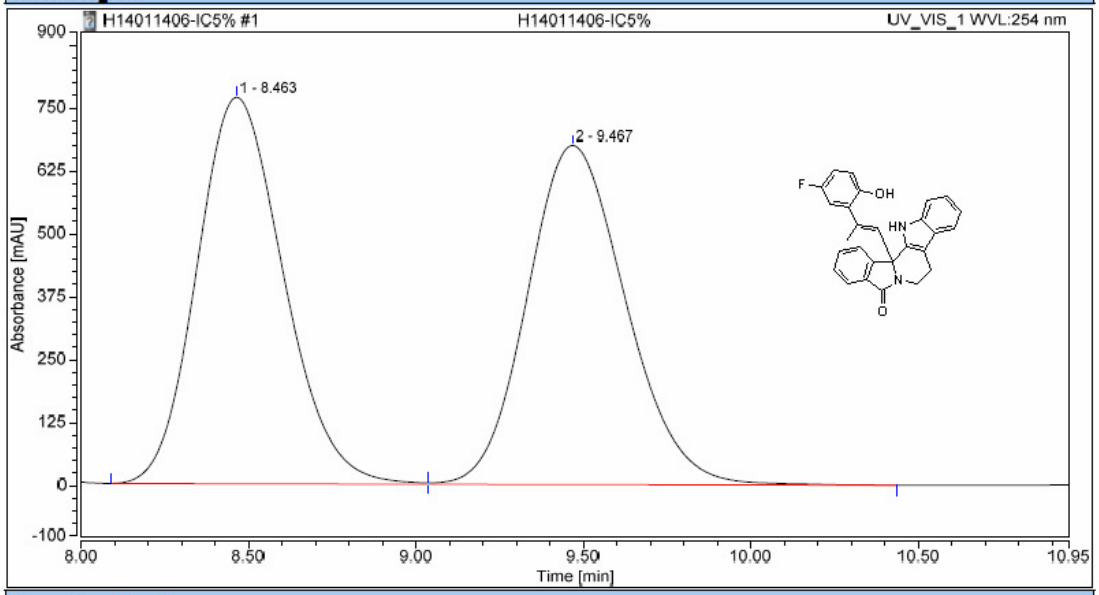


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		19.037	53.146	74.674	7.83	9.04	n.a.
2		21.960	625.468	751.653	92.17	90.96	n.a.
Total:			**678.614**	**826.327**	**100.00**	**100.00**	

3ad:

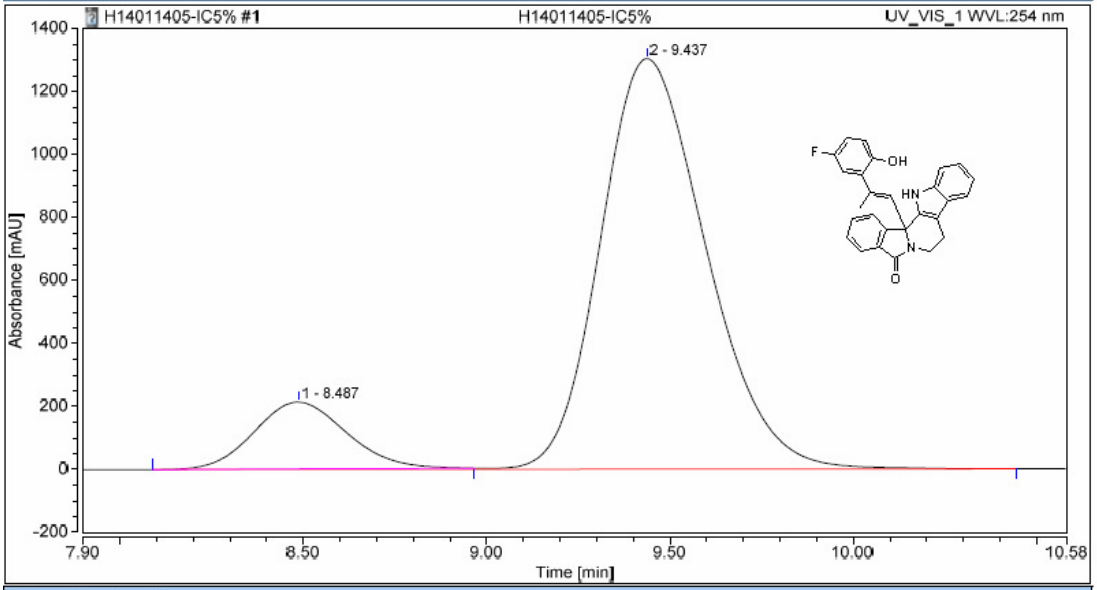
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.463	229.782	766.976	50.09	53.26	n.a.
2		9.467	228.942	673.014	49.91	46.74	n.a.
Total:			**458.724**	**1439.990**	**100.00**	**100.00**	

Chromatogram

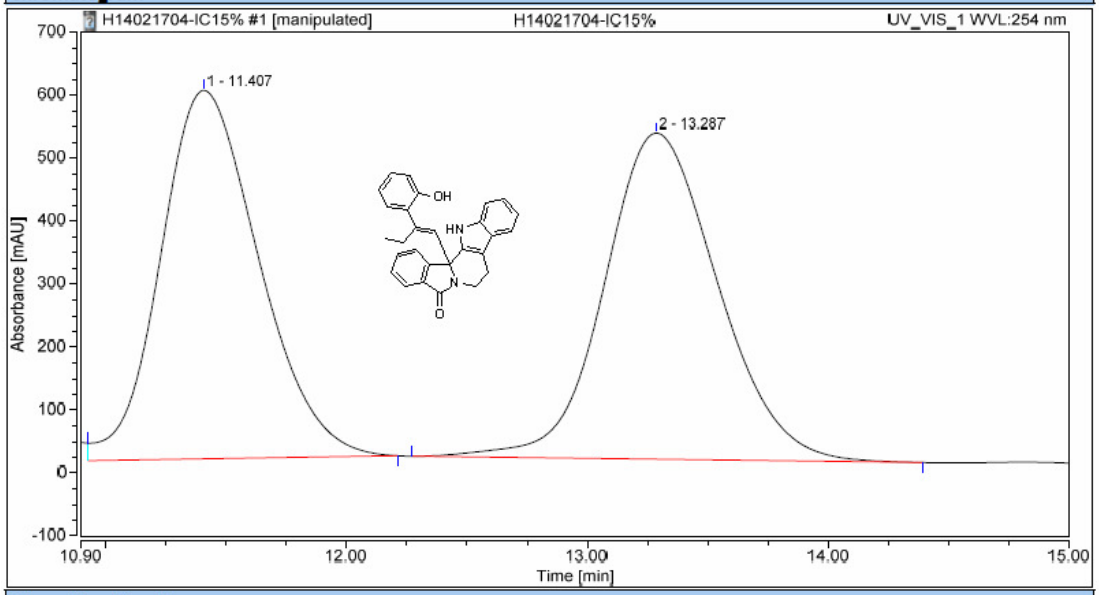


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.487	61.805	212.319	12.41	14.00	n.a.
2		9.437	436.339	1304.390	87.59	86.00	n.a.
Total:			**498.144**	**1516.709**	**100.00**	**100.00**	

3ae:

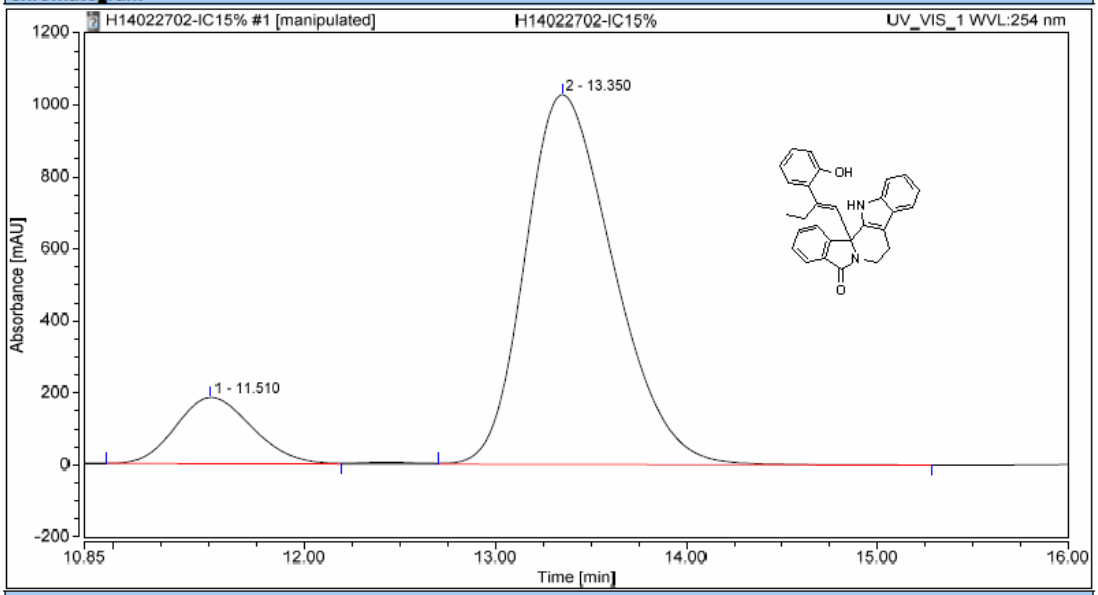
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.407	276.480	585.335	49.43	53.04	n.a.
2		13.287	282.842	518.167	50.57	46.96	n.a.
Total:			**559.322**	**1103.502**	**100.00**	**100.00**	

Chromatogram

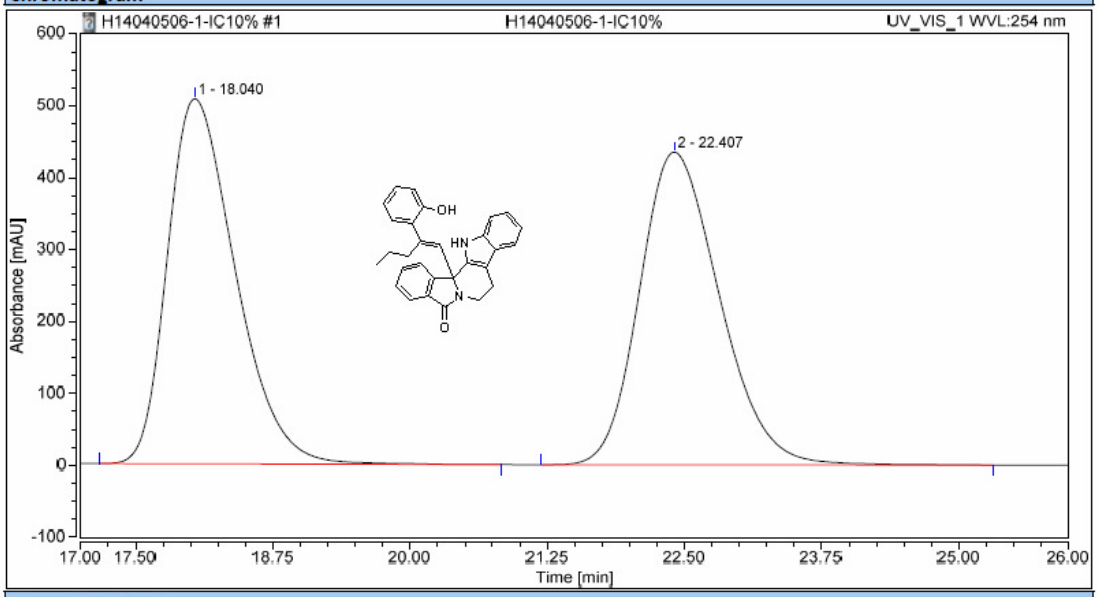


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.510	85.211	183.928	13.41	15.19	n.a.
2		13.350	550.375	1026.603	86.59	84.81	n.a.
Total:			**635.585**	**1210.530**	**100.00**	**100.00**	

3af:

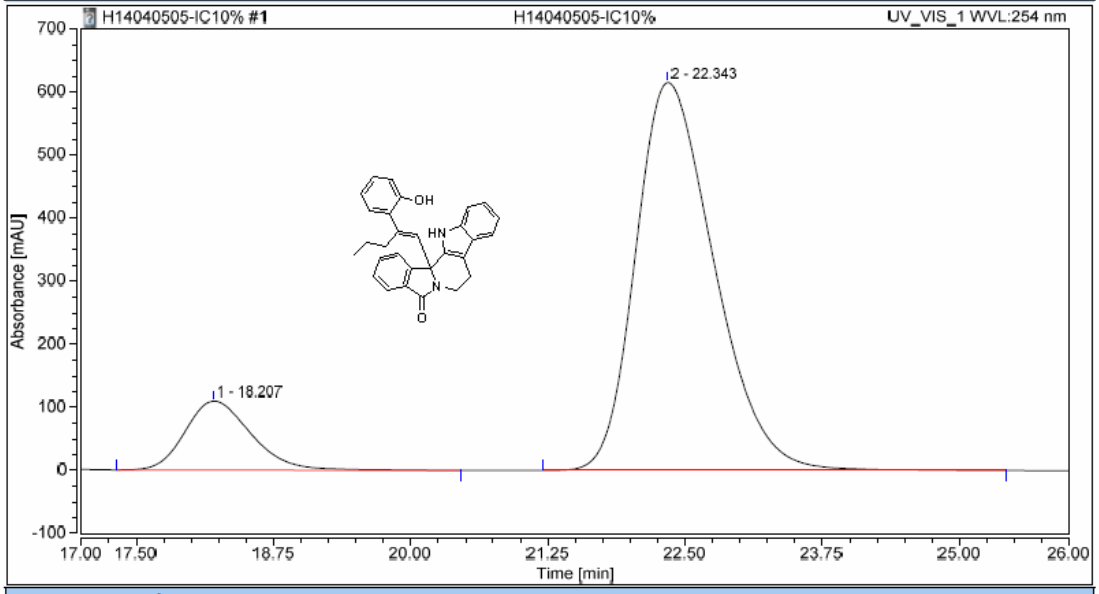
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.040	364.180	507.450	49.77	53.86	n.a.
2		22.407	367.494	434.668	50.23	46.14	n.a.
Total:			**731.674**	**942.119**	**100.00**	**100.00**	

Chromatogram

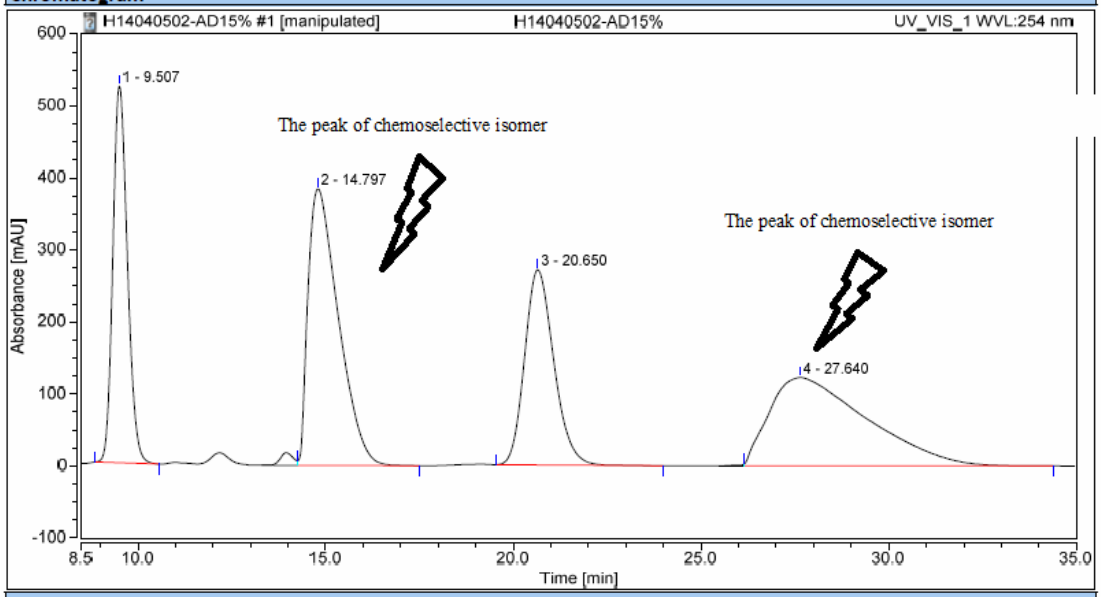


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.207	76.454	109.434	13.04	15.09	n.a.
2		22.343	510.014	615.619	86.96	84.91	n.a.
Total:			**586.467**	**725.053**	**100.00**	**100.00**	

3cb:

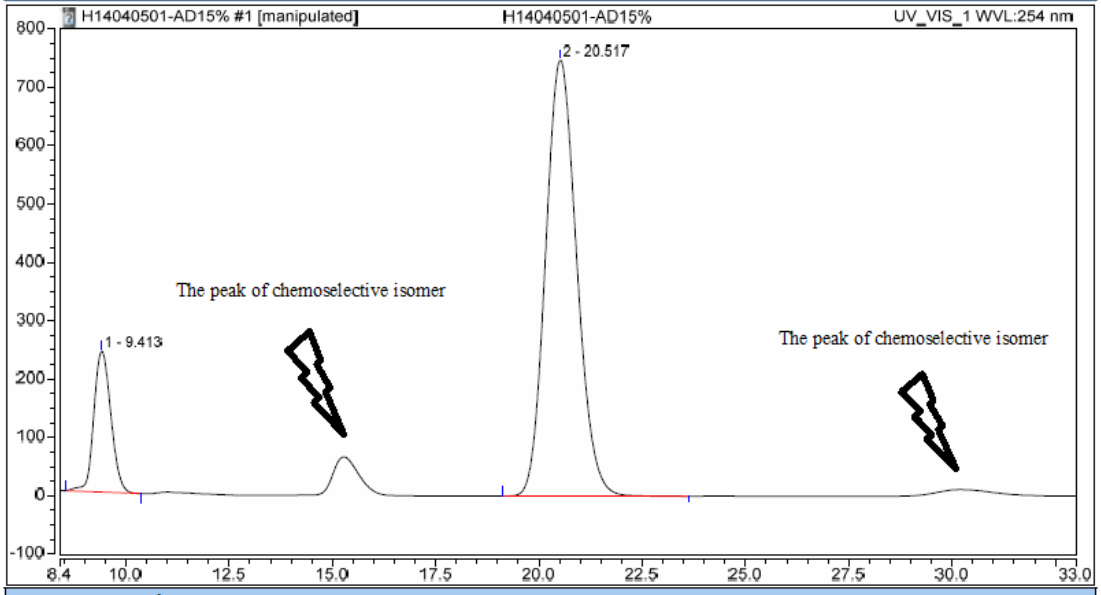
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.507	234.175	523.205	19.44	40.22	n.a.
2		14.797	359.203	384.133	29.82	29.53	n.a.
3		20.650	244.216	270.998	20.28	20.83	n.a.
4		27.640	366.902	122.556	30.46	9.42	n.a.
Total:			1204.497	1300.891	100.00	100.00	

Chromatogram

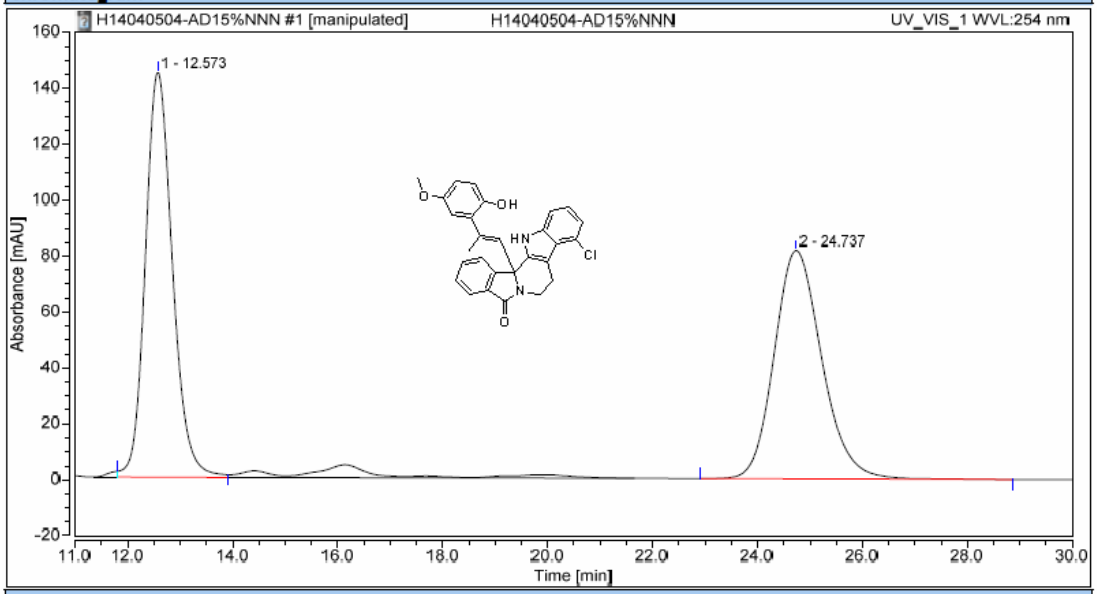


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.413	115.780	241.556	15.07	24.43	n.a.
2		20.517	652.429	747.398	84.93	75.57	n.a.
Total:			768.209	988.955	100.00	100.00	

3cc:

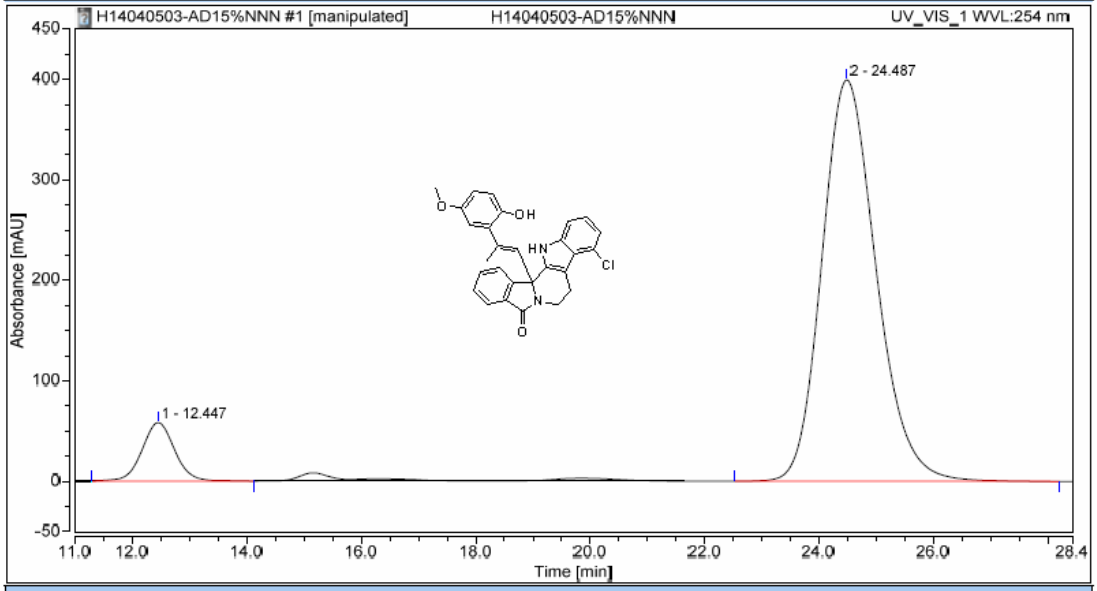
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.573	86.535	144.802	50.26	63.95	n.a.
2		24.737	85.629	81.627	49.74	36.05	n.a.
Total:			**172.164**	**226.429**	**100.00**	**100.00**	

Chromatogram

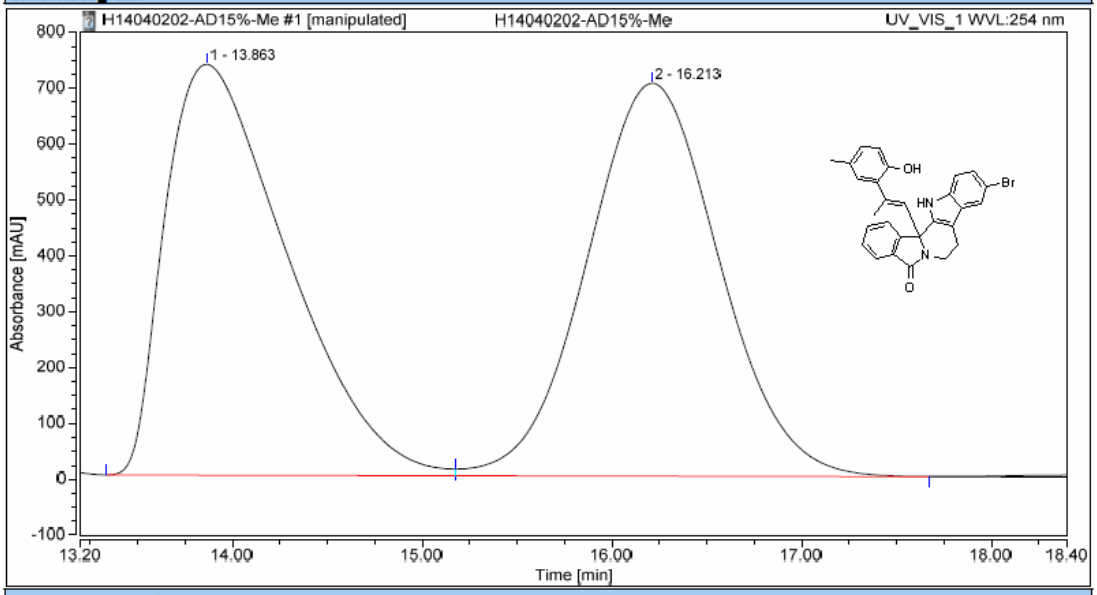


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.447	39.021	58.300	8.17	12.74	n.a.
2		24.487	438.830	399.185	91.83	87.26	n.a.
Total:			**477.852**	**457.486**	**100.00**	**100.00**	

3gb:

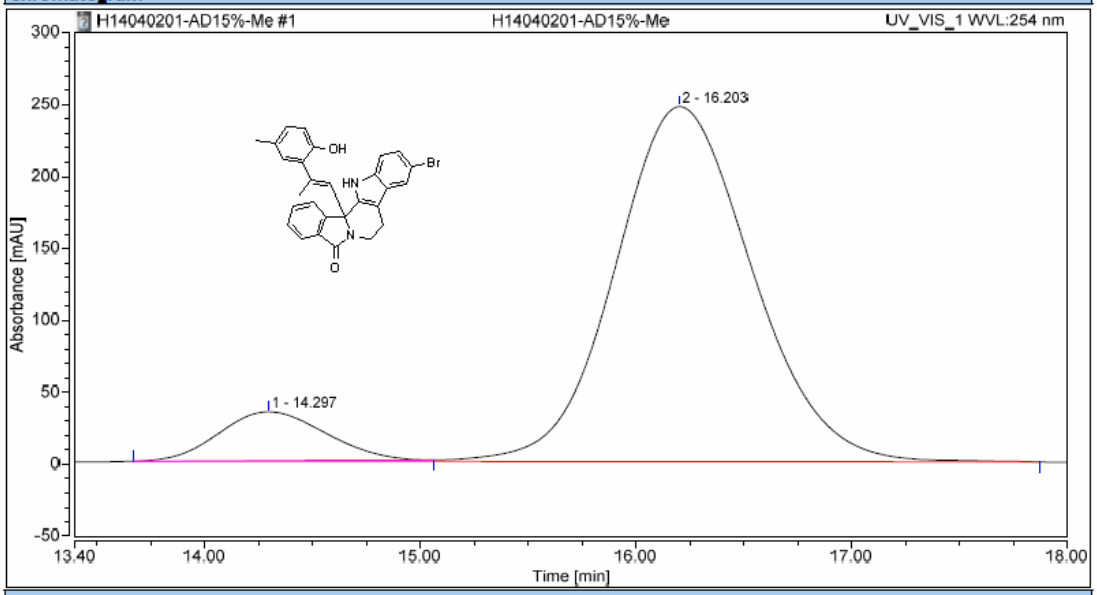
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.863	547.177	735.466	49.03	51.12	n.a.
2		16.213	568.755	703.241	50.97	48.88	n.a.
Total:			**1115.932**	**1438.707**	**100.00**	**100.00**	

Chromatogram

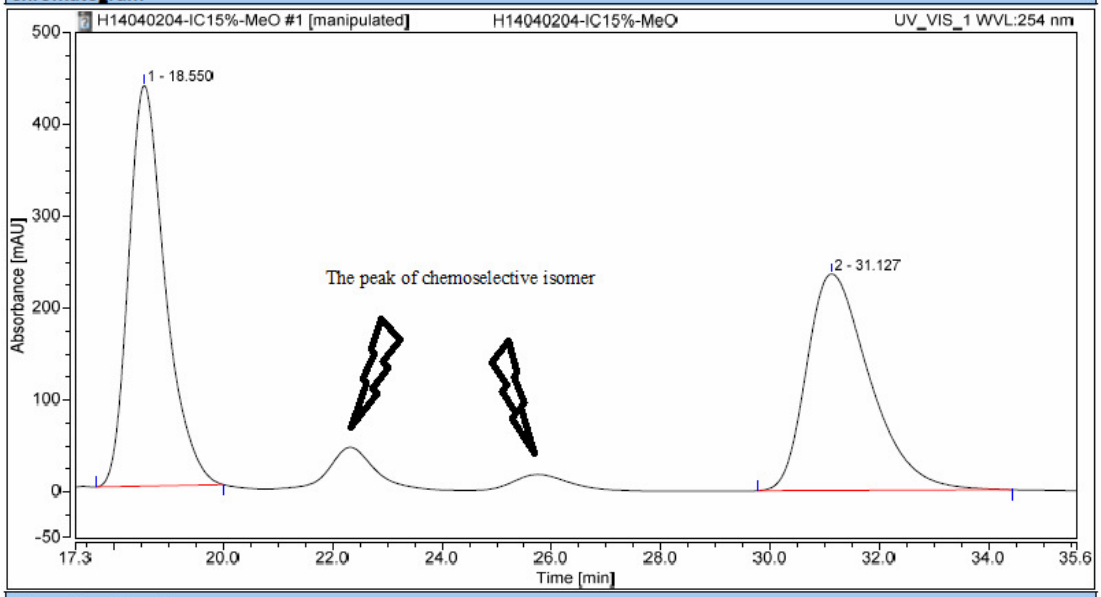


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.297	19.330	33.986	9.57	12.10	n.a.
2		16.203	182.660	246.903	90.43	87.90	n.a.
Total:			**201.990**	**280.889**	**100.00**	**100.00**	

3gc:

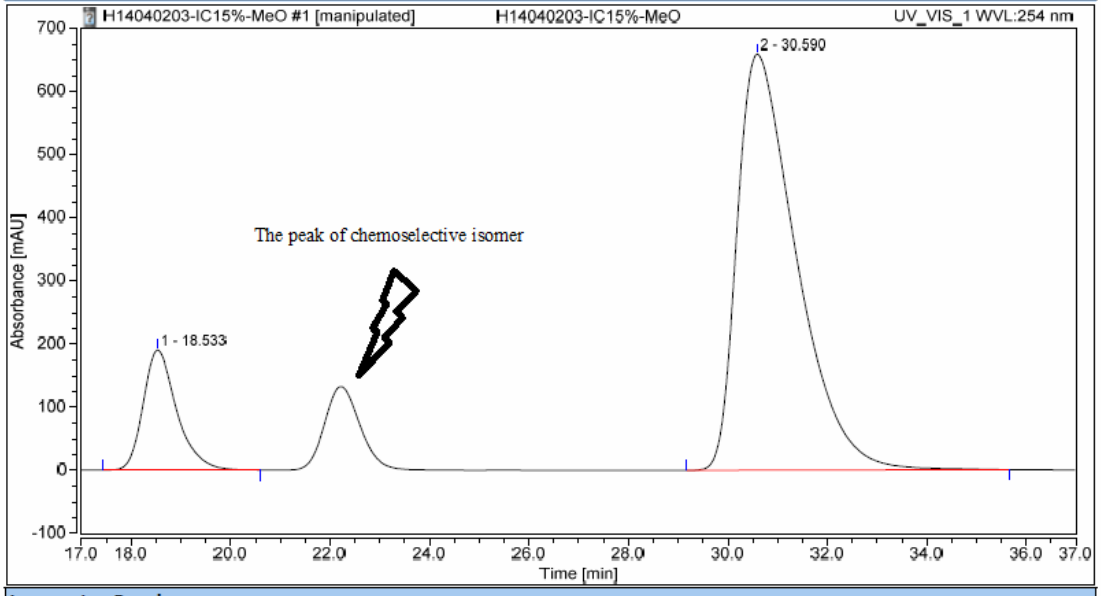
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.550	338.762	436.422	51.76	64.91	n.a.
2		31.127	315.716	235.903	48.24	35.09	n.a.
Total:			654.477	672.326	100.00	100.00	

Chromatogram

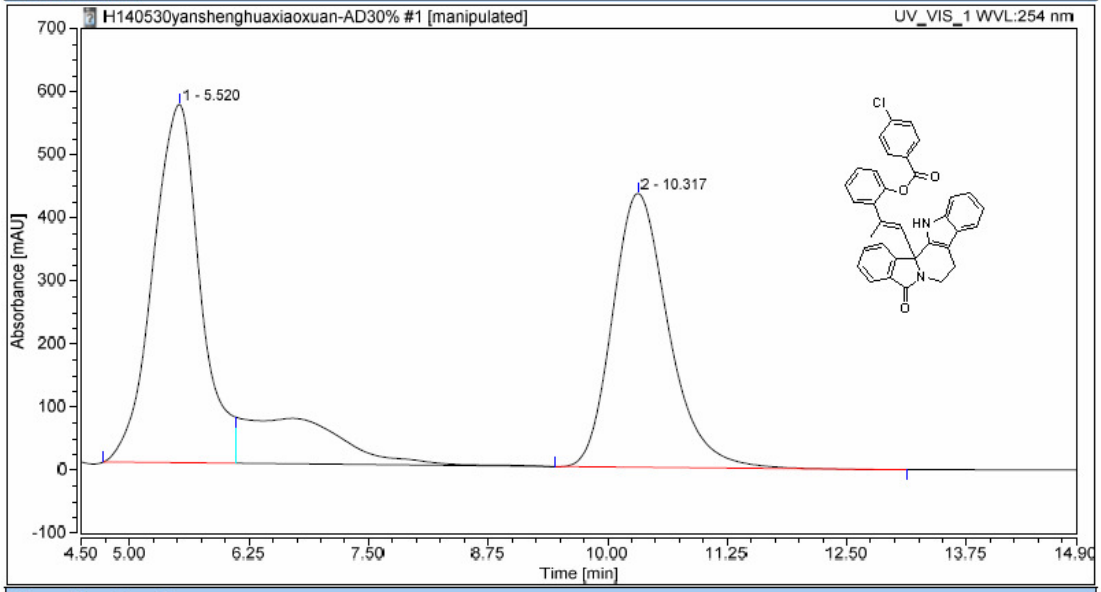


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.533	148.289	190.224	14.03	22.39	n.a.
2		30.590	908.934	659.246	85.97	77.61	n.a.
Total:			1057.223	849.469	100.00	100.00	

Compound 8:

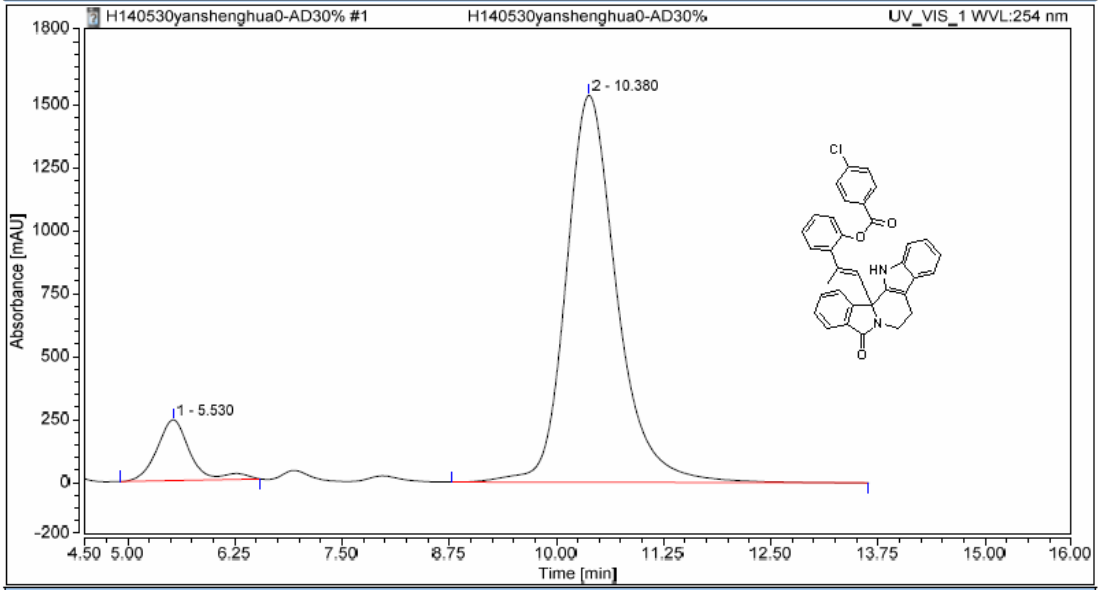
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.520	325.335	568.303	52.53	56.69	n.a.
2		10.317	293.951	434.097	47.47	43.31	n.a.
Total:			**619.286**	**1002.400**	**100.00**	**100.00**	

Chromatogram

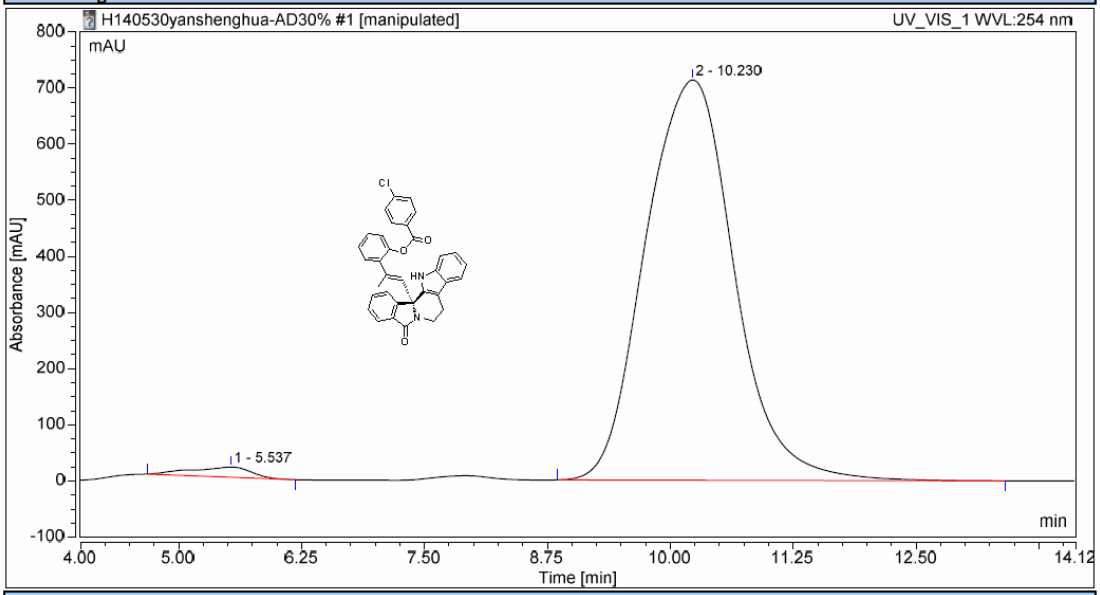


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.530	109.405	241.056	9.42	13.58	n.a.
2		10.380	1051.888	1534.396	90.58	86.42	n.a.
Total:			**1161.293**	**1775.452**	**100.00**	**100.00**	

After recrystallization:

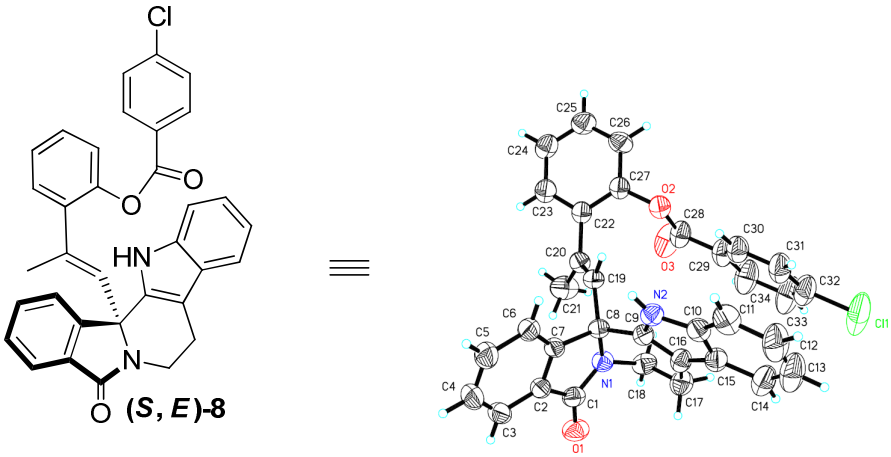
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.537	12.534	18.201	1.65	2.49	n.a.
2		10.230	747.288	713.274	98.35	97.51	n.a.
Total:			**759.822**	**731.475**	**100.00**	**100.00**	

X-ray single crystal data for compound 8



_chemical_formula_sum	'C34 H25 Cl N2 O3'
_chemical_formula_weight	545.01
_space_group_crystal_system	monoclinic
_space_group_IT_number	4
_space_group_name_H-M_alt	'P 21'
_space_group_name_Hall	'P 2yb'
_cell_length_a	13.720(3)
_cell_length_b	7.2534(18)
_cell_length_c	14.954(4)
_cell_angle_alpha	90
_cell_angle_beta	90.634(14)
_cell_angle_gamma	90
_cell_volume	1488.1(6)
_cell_formula_units_Z	2
_cell_measurement_temperature	296(2)
_cell_measurement_reflns_used	6660
_cell_measurement_theta_min	2.72
_cell_measurement_theta_max	20.46
_exptl_crystal_density_diffrn	1.216
_exptl_crystal_F_000	568
_exptl_crystal_size_max	0.200
_exptl_crystal_size_mid	0.050
_exptl_crystal_size_min	0.030
_exptl_absorpt_coefficient_mu	0.164
_shelx_estimated_absorpt_T_min	0.968
_shelx_estimated_absorpt_T_max	0.995
_diffrn_ambient_temperature	296(2)
_diffrn_radiation_wavelength	0.71073
_diffrn_radiation_type	MoK\a

_diffrn_reflns_number 22859
_diffrn_reflns_av_unetI/netI 0.1079
_diffrn_reflns_av_R_equivalents 0.0670
_diffrn_reflns_limit_h_min -17
_diffrn_reflns_limit_h_max 17
_diffrn_reflns_limit_k_min -8
_diffrn_reflns_limit_k_max 9
_diffrn_reflns_limit_l_min -19
_diffrn_reflns_limit_l_max 19
_diffrn_reflns_theta_min 1.362
_diffrn_reflns_theta_max 28.011
_diffrn_reflns_theta_full 25.242
_diffrn_measured_fraction_theta_max 0.961
_diffrn_measured_fraction_theta_full 0.989
_diffrn_reflns_Laue_measured_fraction_max 0.961
_diffrn_reflns_Laue_measured_fraction_full 0.989
_diffrn_reflns_point_group_measured_fraction_max 0.859
_diffrn_reflns_point_group_measured_fraction_full 0.920
_reflns_number_total 6197
_reflns_number_gt 2697
_reflns_threshold_expression 'I > 2\s(I)'
_reflns_Friedel_coverage 0.659
_reflns_Friedel_fraction_max 0.740
_reflns_Friedel_fraction_full 0.838
_refine_ls_abs_structure_Flack -0.04(6)
_chemical_absolute_configuration AD
_refine_ls_number_reflns 6197
_refine_ls_number_parameters 363
_refine_ls_number_restraints 1
_refine_ls_R_factor_all 0.1803
_refine_ls_R_factor_gt 0.0655
_refine_ls_wR_factor_ref 0.2103
_refine_ls_wR_factor_gt 0.1470
_refine_ls_goodness_of_fit_ref 0.939
_refine_ls_restrained_S_all 0.939
_refine_ls_shift/su_max 0.011
_refine_ls_shift/su_mean 0.001