Supporting information for

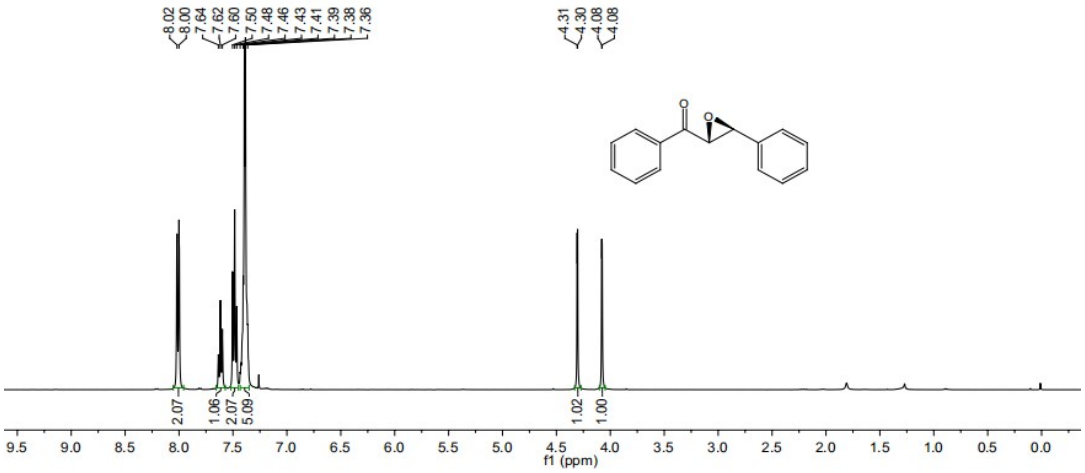
Lanthanide complexes combined with chiral Salen ligands: the application in the enantioselective epoxidation reaction of α,β-unsaturated ketones

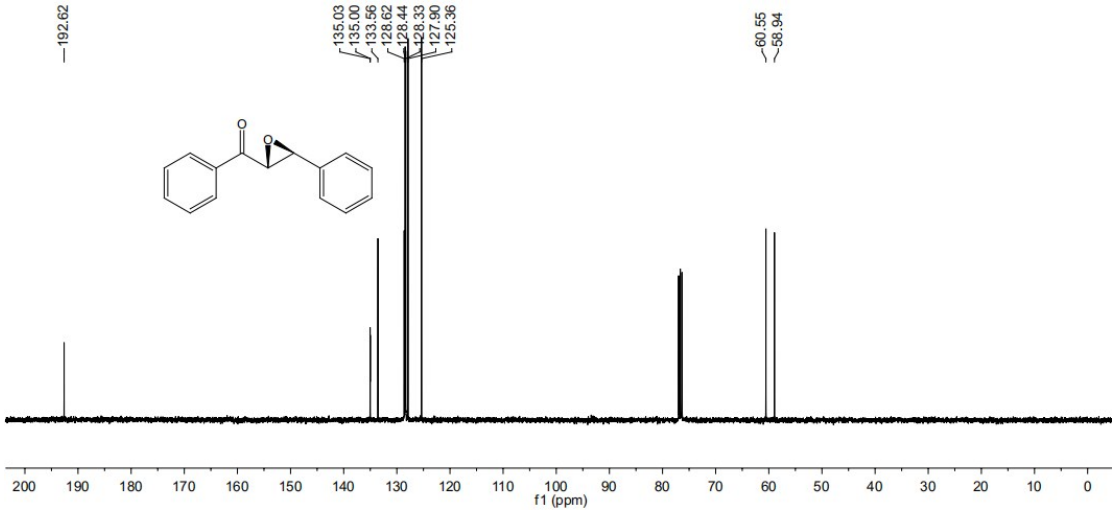
Xuexiu Xia[a], Chengrong Lu, *[a] Bei Zhao, *[a,b] Yingming Yao [a,b]

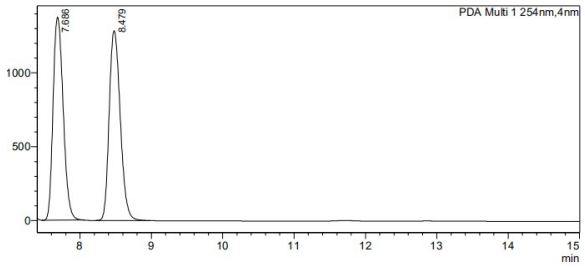
Key Laboratory of Organic Synthesis of Jiangsu Province,[a] College of Chemistry, Chemical Engineering and Materials Science,[b] Dushu Lake Campus, Soochow University, Suzhou 215123 (P. R. China)
Fax: +86-512-65880305; Tel: +86-512-65880305; E-mail: zhaobei@suda.edu.cn; yaoym@suda.edu.cn

Table of contents **page**

The NMR spectra and HPLC spectrum of compound **7a**



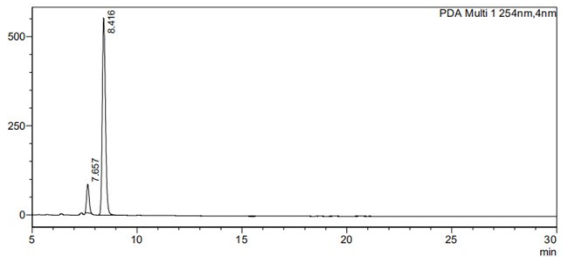




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.686	13541838	1373213	49.397
2	8.479	13872190	1284366	50.603
Total		27414028	2657578	100.000

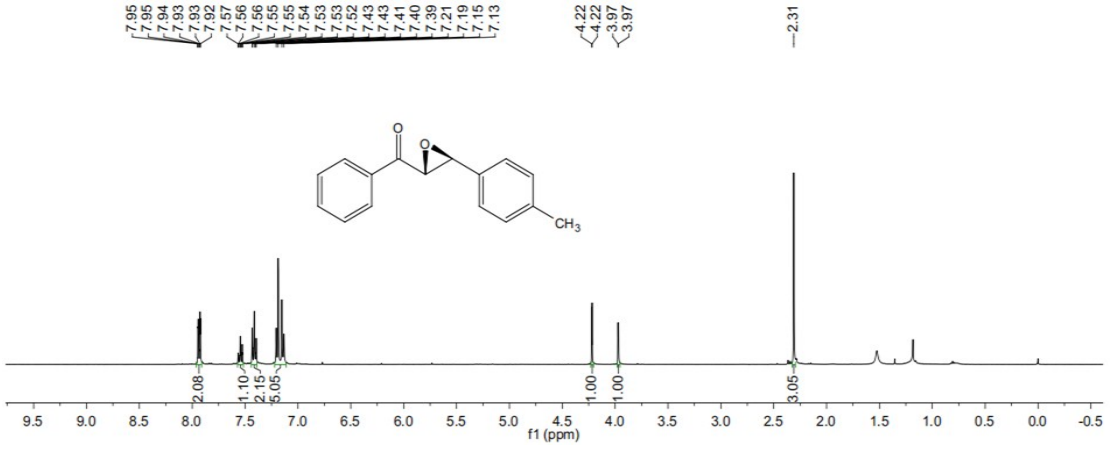


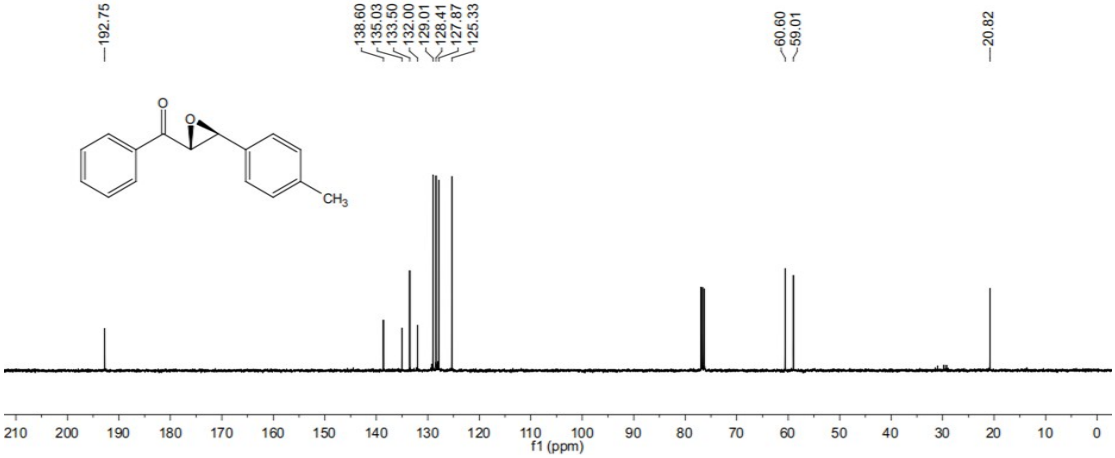
<Peak Table>

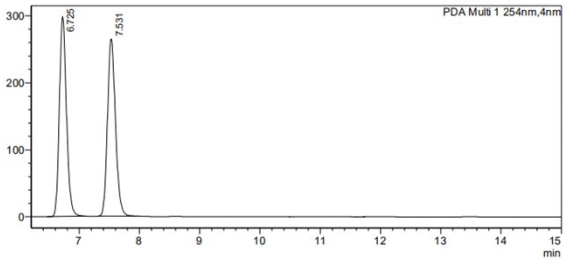
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.657	672005	80383	10.432
2	8.416	5769625	552399	89.568
Total		6441630	632782	100.000

The NMR spectra and HPLC spectrum of compound **7b**



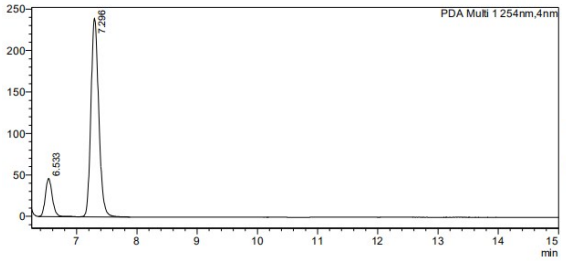




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.725	2442398	297764	49.941
2	7.531	2448166	264714	50.059
Total		4890564	562478	100.000

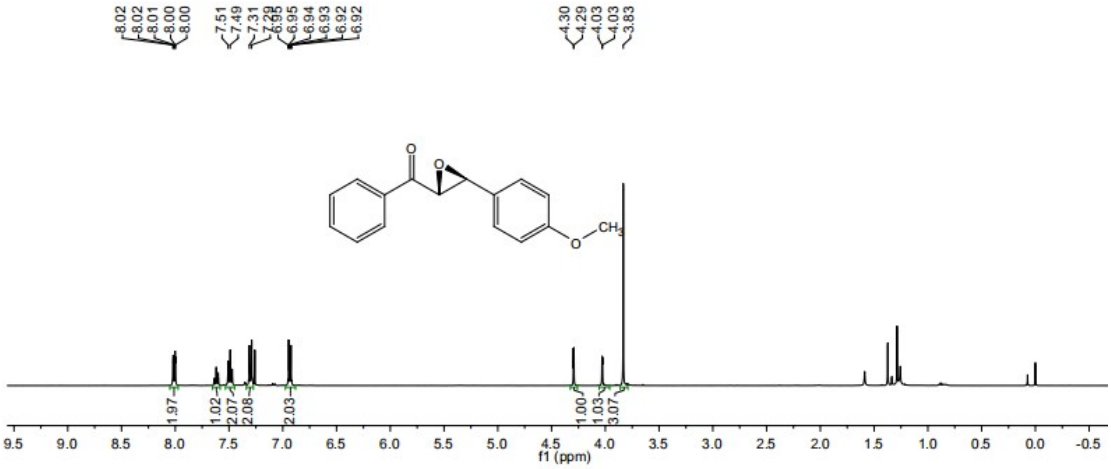


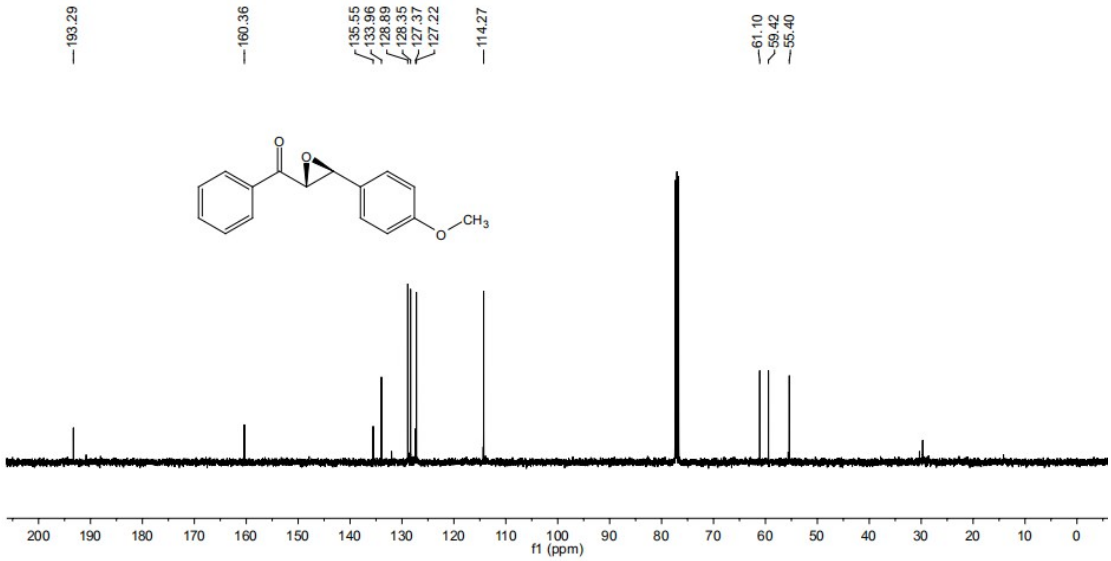
<Peak Table>

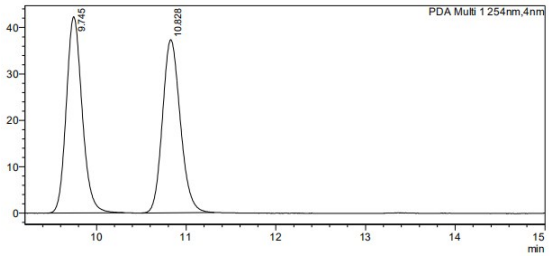
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.533	351231	45465	13.999
2	7.296	2157762	239063	86.001
Total		2508993	284528	100.000

The NMR spectra and HPLC spectrum of compound **7c**



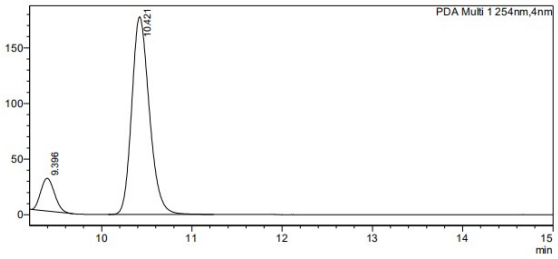




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.745	520418	42281	50.267
2	10.828	514885	37304	49.733
Total		1035303	79585	100.000

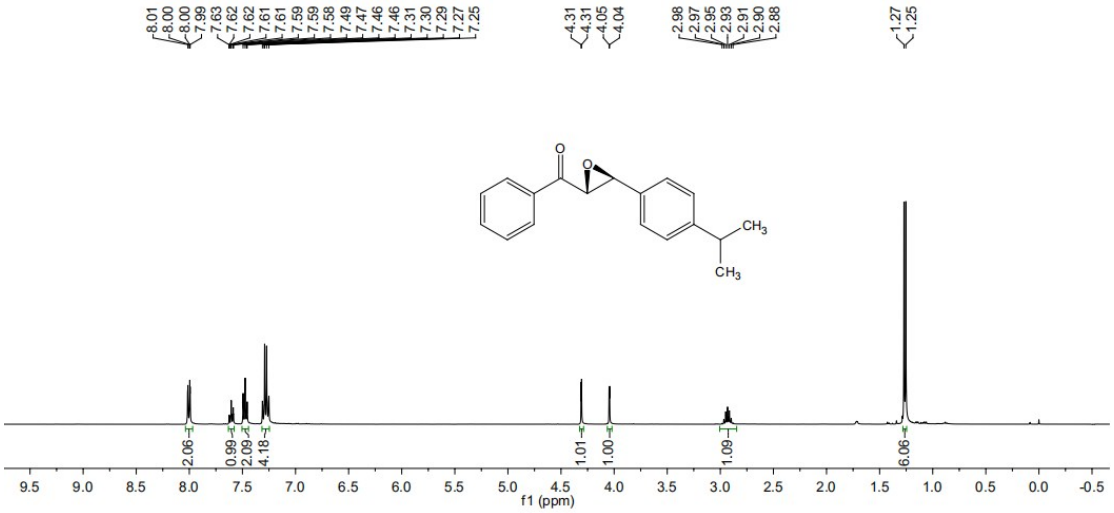


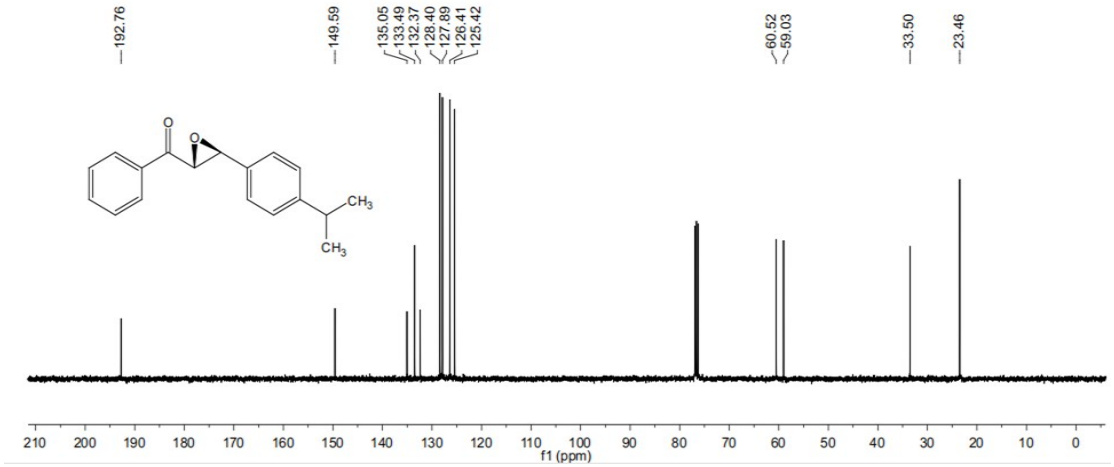
<Peak Table>

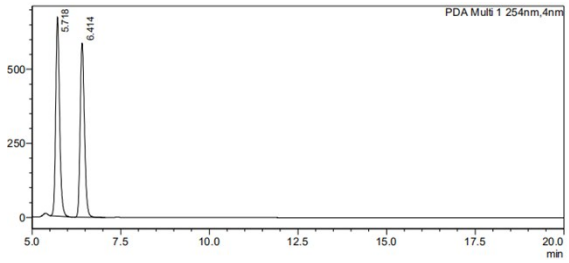
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	9.396	290491	29078	10.738
2	10.421	2414669	177574	89.262
Total		2705160	206652	100.000

The NMR spectra and HPLC spectrum of compound **7d**



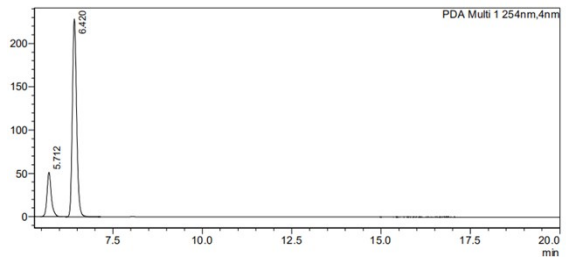




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.718	5192051	671292	51.089
2	6.414	4970691	586978	48.911
Total		10162742	1258270	100.000

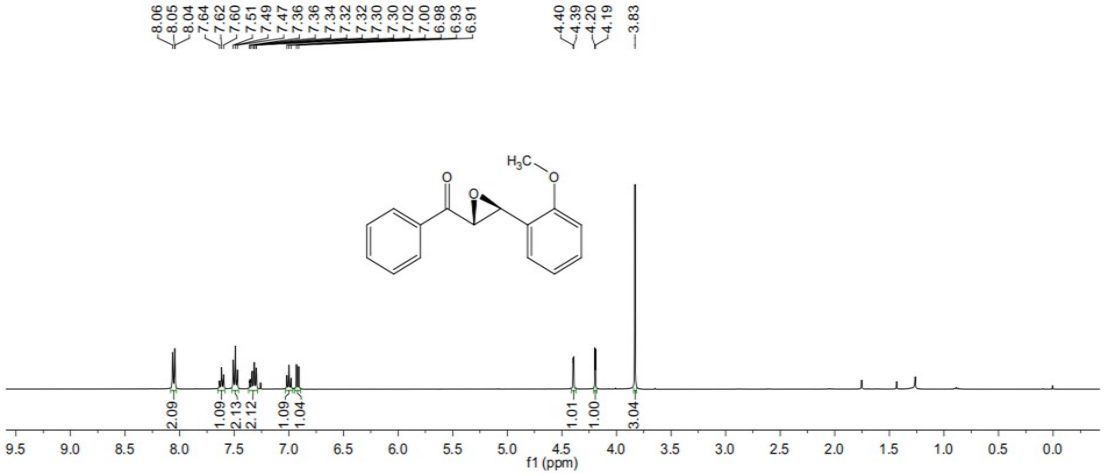


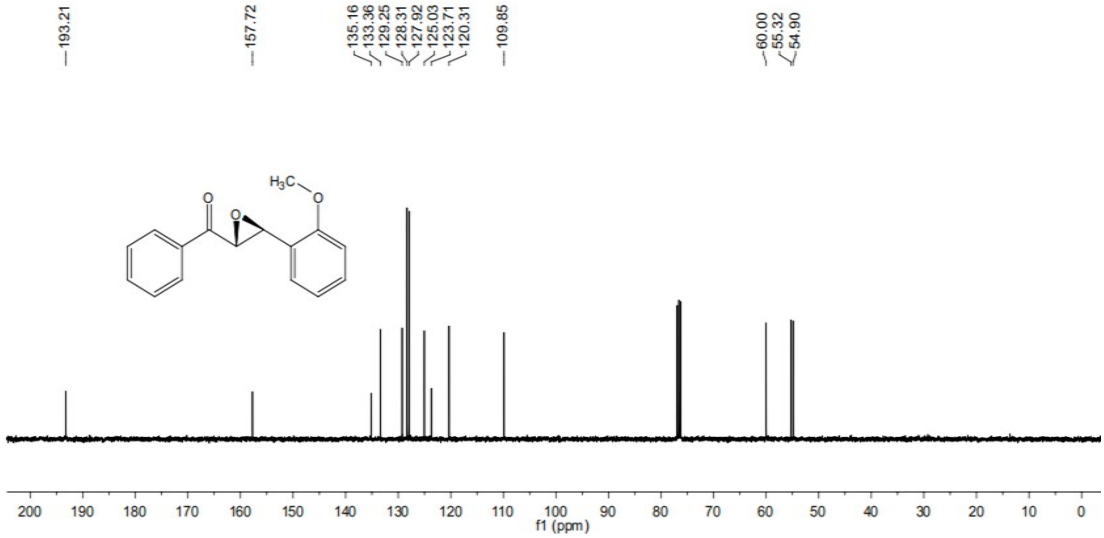
<Peak Table>

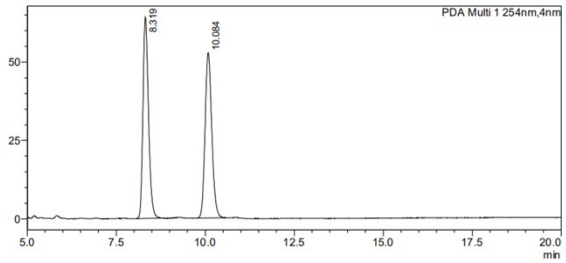
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.712	425862	51160	18.322
2	6.420	1898435	228309	81.678
Total		2324297	279469	100.000

The NMR spectra and HPLC spectrum of compound **7e**



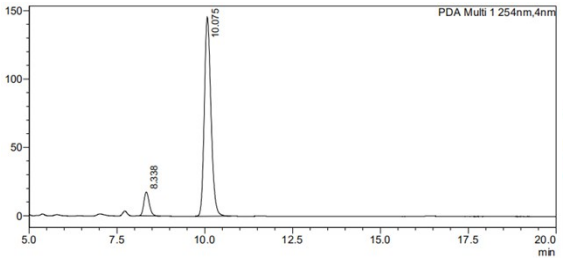




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.319	690782	64110	49.970
2	10.084	691617	52642	50.030
Total		1382399	116753	100.000

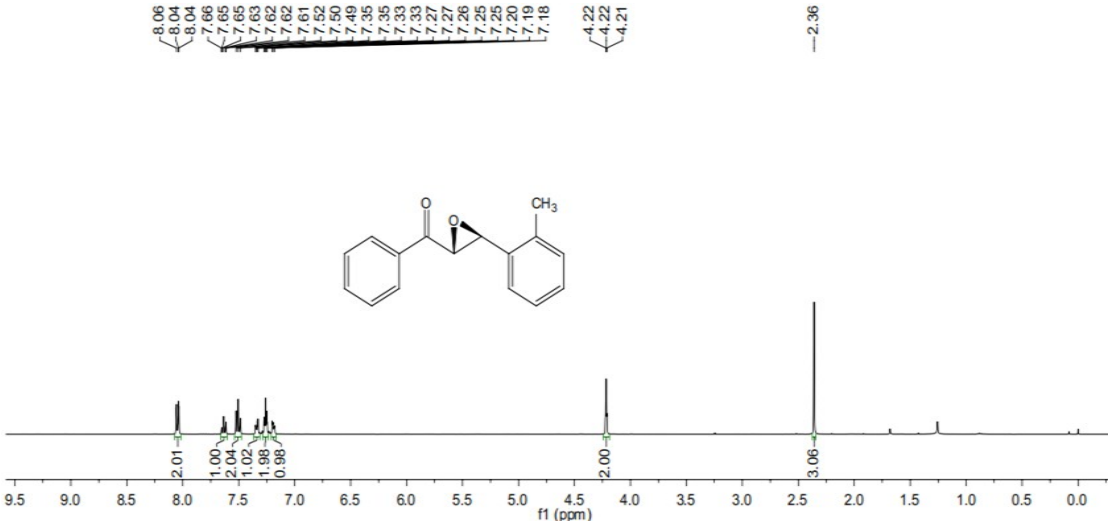


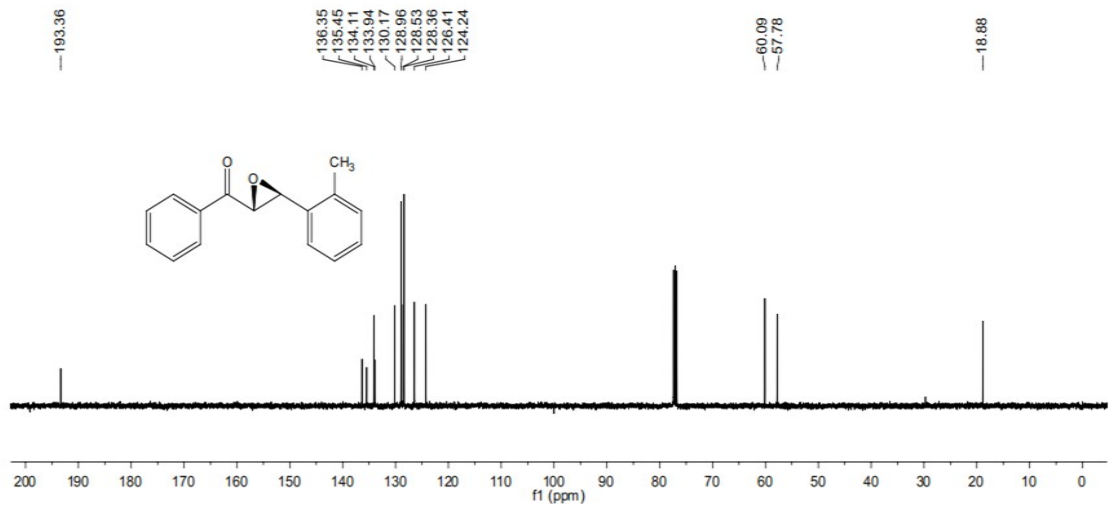
<Peak Table>

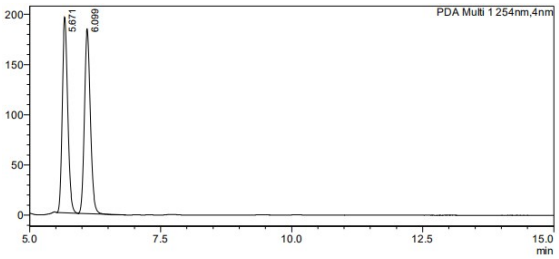
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.338	188222	17572	8.921
2	10.075	1921579	145540	91.079
Total		2109801	163111	100.000

The NMR spectra and HPLC spectrum of compound **7f**



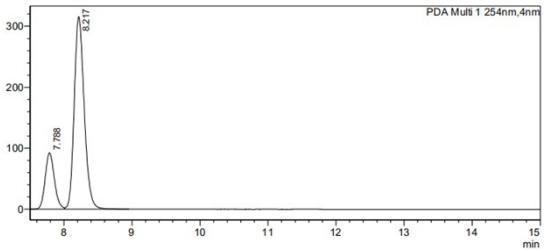




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.804	2531227	303397	48.952
2	7.655	2639593	274843	51.048
Total		5170820	578240	100.000

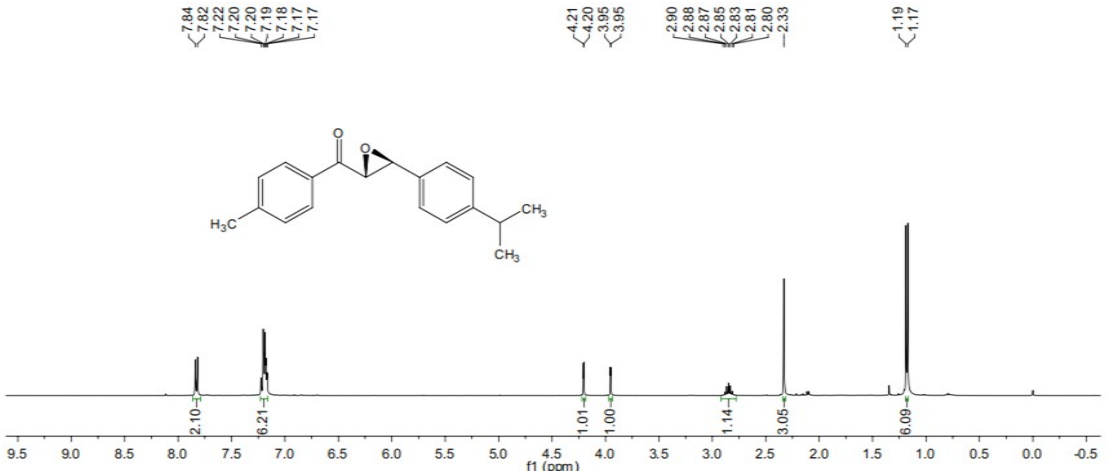


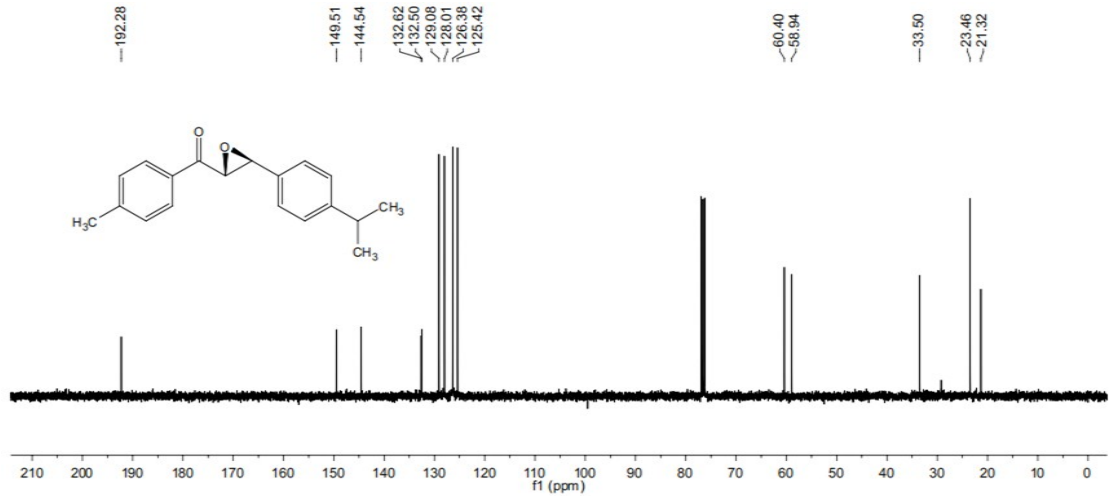
<Peak Table>

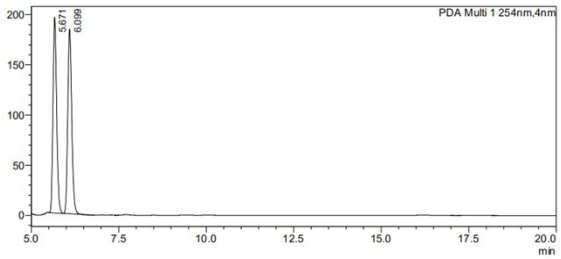
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.836	278618	30527	13.336
2	7.685	1810635	192879	86.664
Total		2089254	223406	100.000

The NMR spectra and HPLC spectrum of compound **7g**



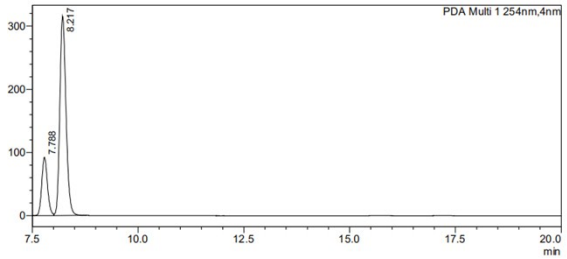




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	5.671	1413096	194828	49.255
2	6.099	1455859	184151	50.745
Total		2868955	378980	100.000

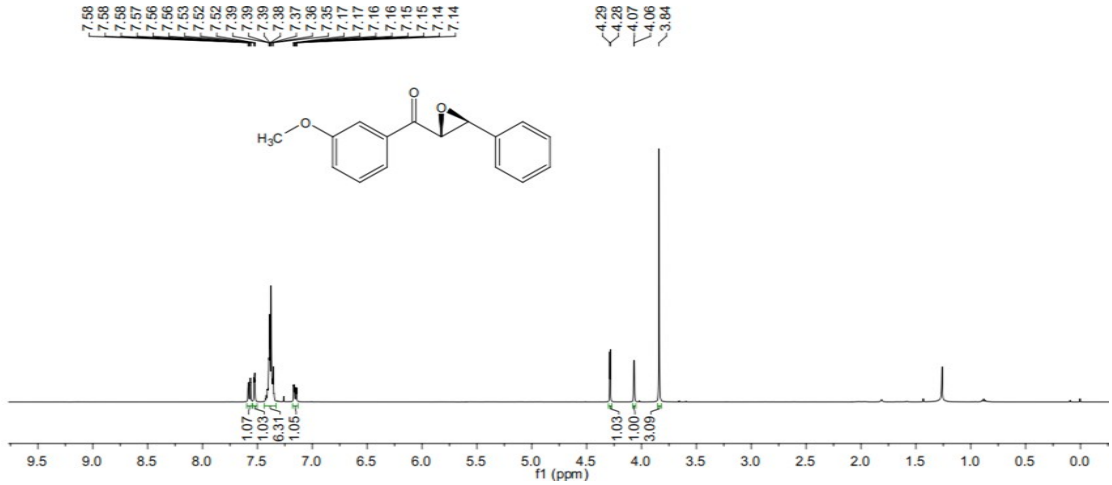


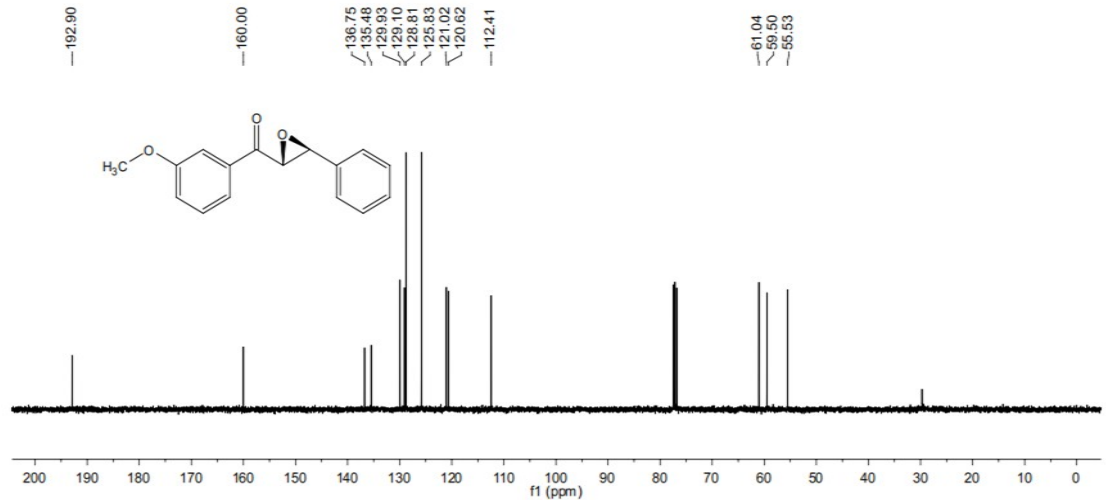
<Peak Table>

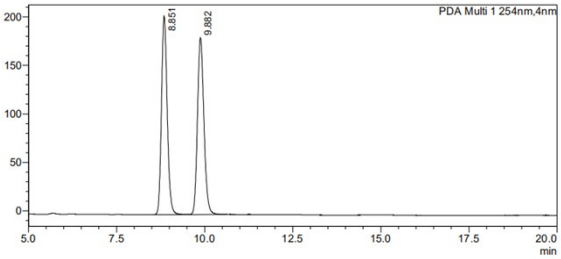
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.788	867509	92242	21.272
2	8.217	3210661	315122	78.728
Total		4078170	407364	100.000

The NMR spectra and HPLC spectrum of compound **7h**



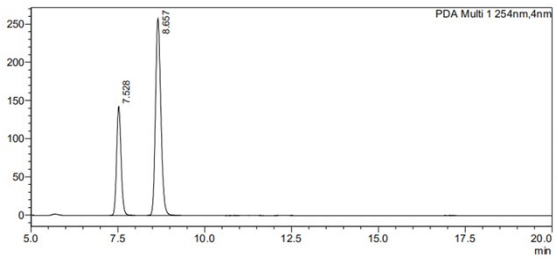




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.851	2321009	204891	49.931
2	9.882	2327390	182544	50.069
Total		4648399	387435	100.000

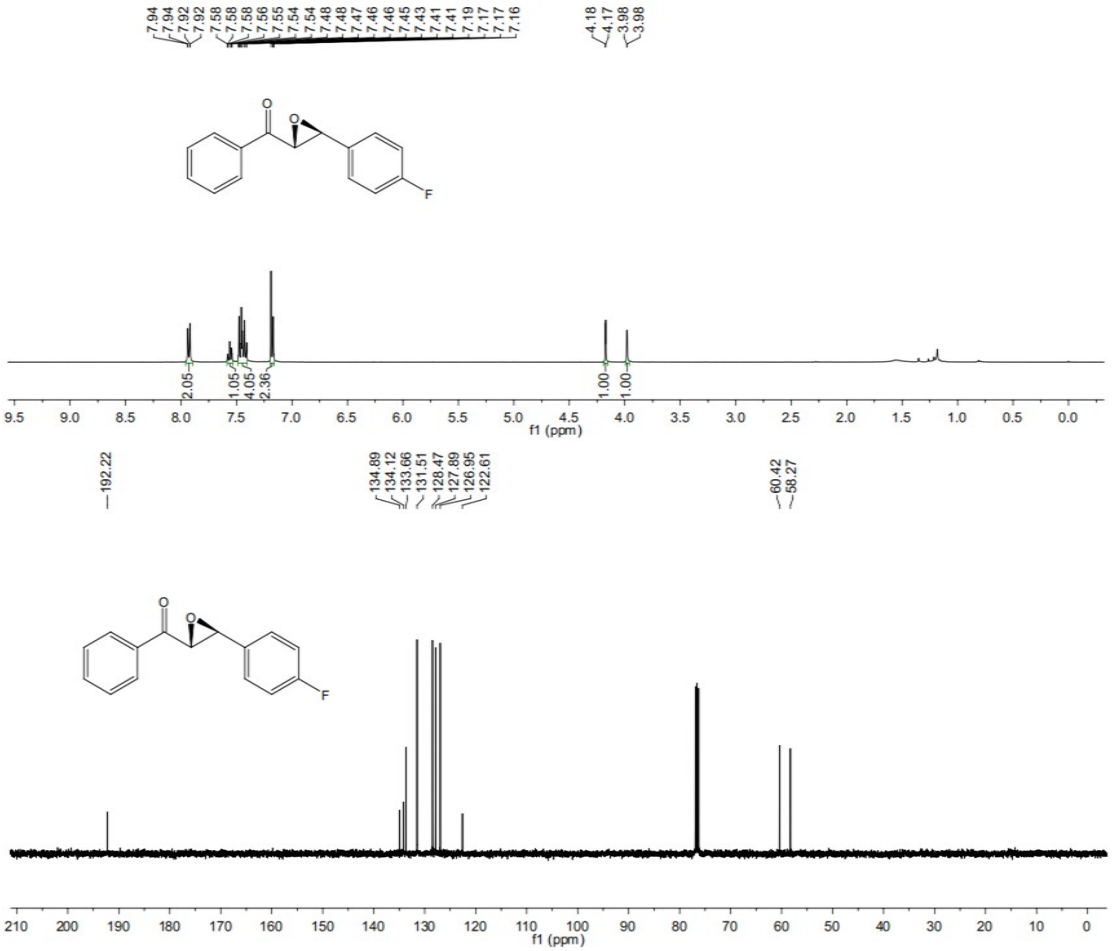


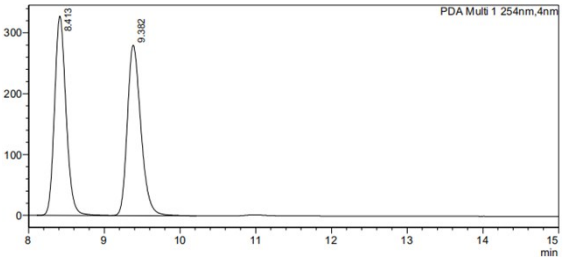
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.528	1273597	142767	31.368
2	8.657	2786519	257407	68.632
Total		4060116	400174	100.000

The NMR spectra and HPLC spectrum of compound **7i**

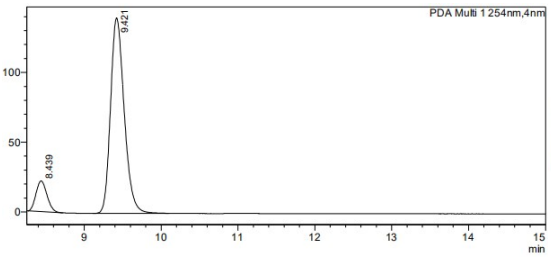




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.413	3463621	327131	49.852
2	9.382	3484177	280296	50.148
Total		6947799	607427	100.000

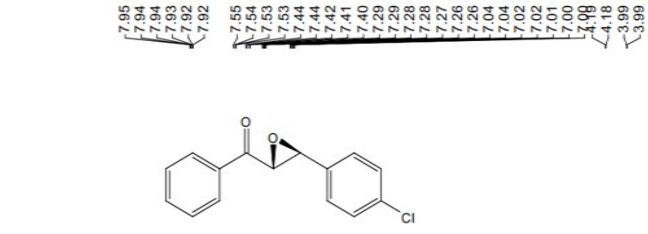


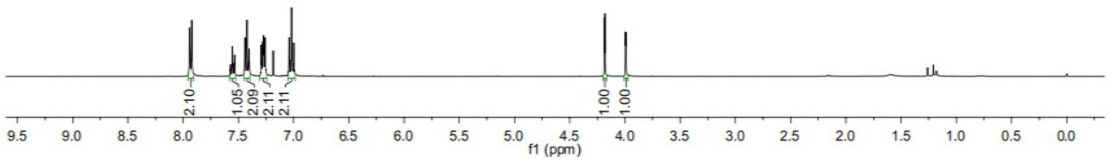
<Peak Table>

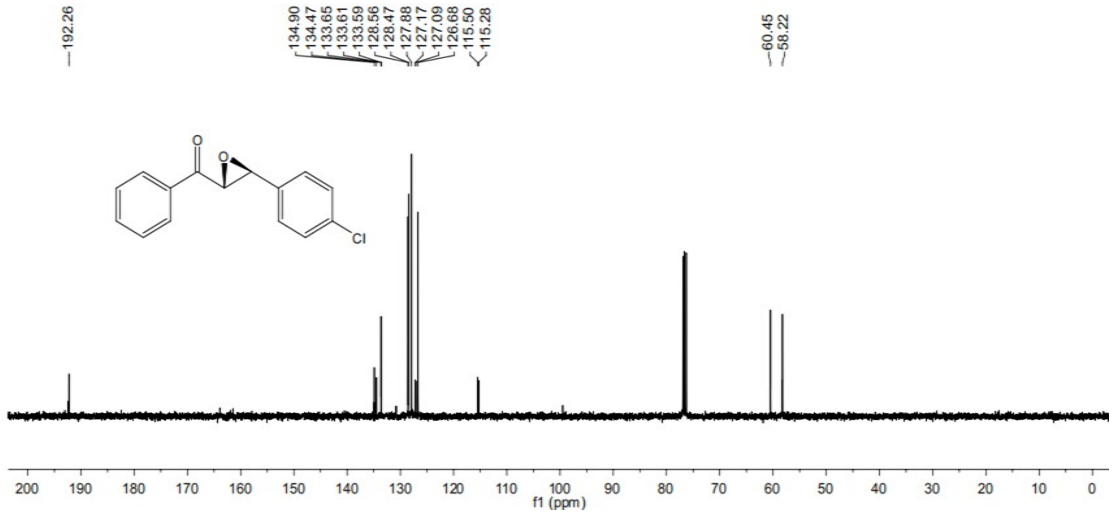
PDA Ch1 254nm

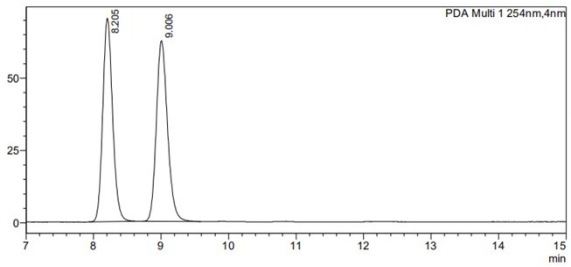
Peak#	Ret. Time	Area	Height	Area%
1	8.439	219240	21997	11.231
2	9.421	1732826	140074	88.769
Total		1952066	162071	100.000

The NMR spectra and HPLC spectrum of compound **7j**





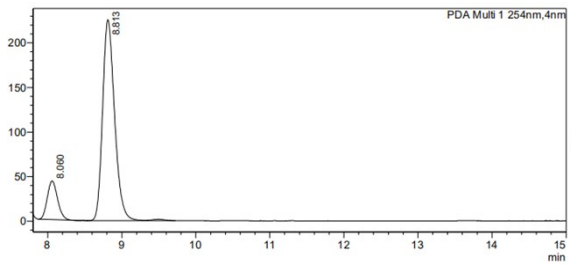




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.205	714522	70315	49.769
2	9.006	721149	62441	50.231
Total		1435671	132756	100.000

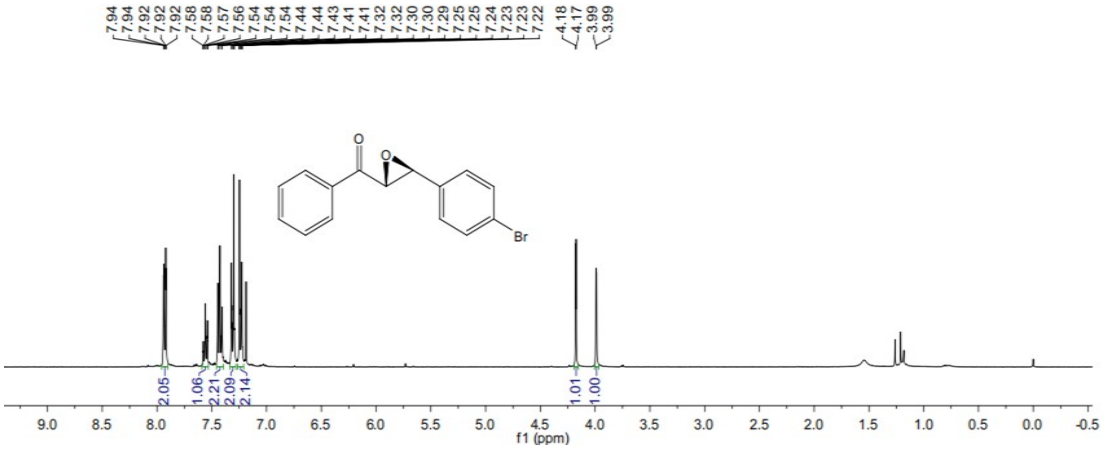


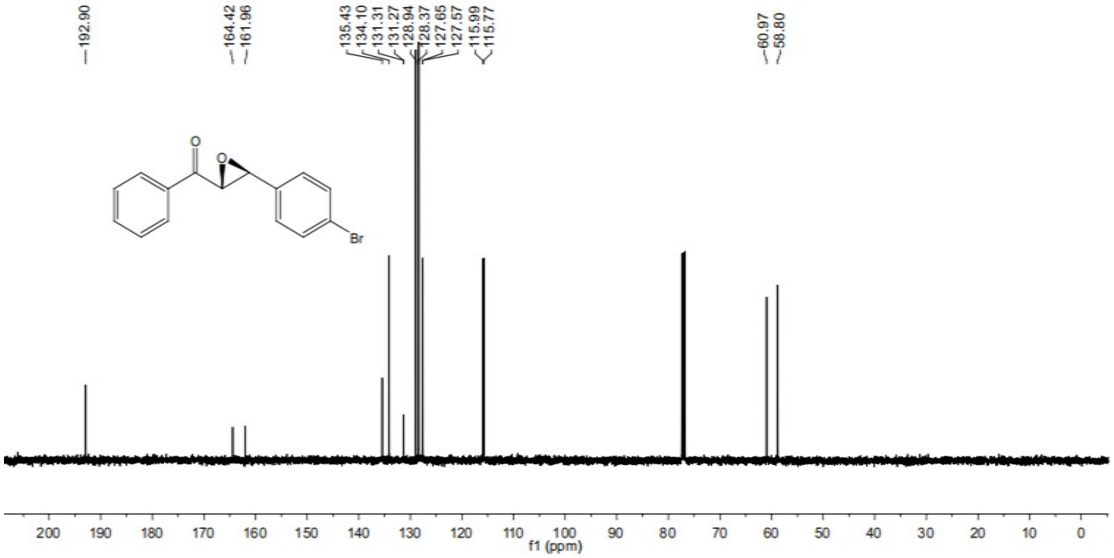
<Peak Table>

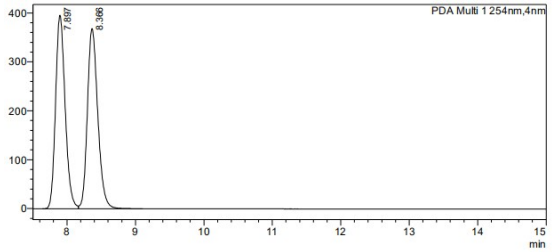
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.060	416446	43457	14.104
2	8.813	2536147	224937	85.896
Total		2952593	268394	100.000

The NMR spectra and HPLC spectrum of compound **7k**



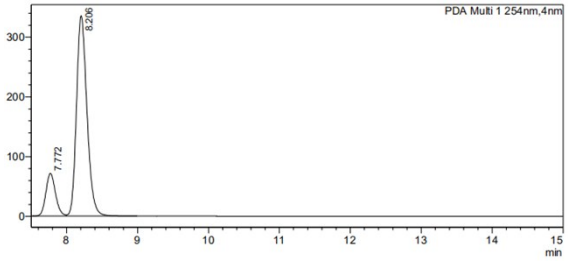




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.897	3858441	395409	49.699
2	8.366	3905118	368093	50.301
Total		7763559	763502	100.000

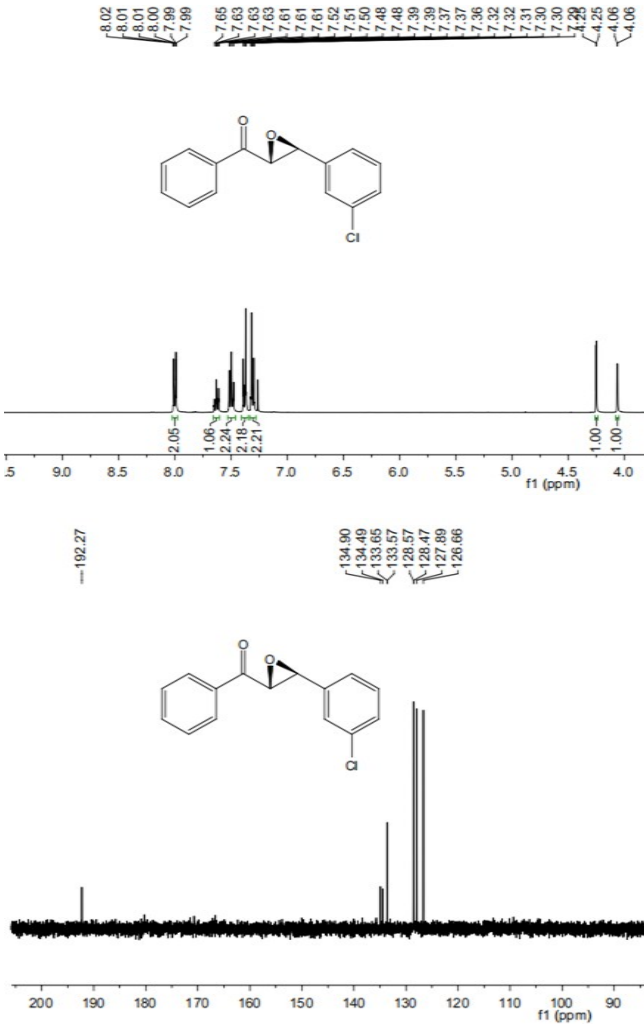


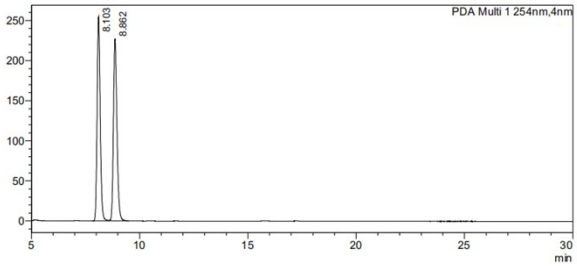
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.772	670865	71326	16.302
2	8.206	3444473	335010	83.698
Total		4115339	406336	100.000

The NMR spectra and HPLC spectrum of compound **7l**

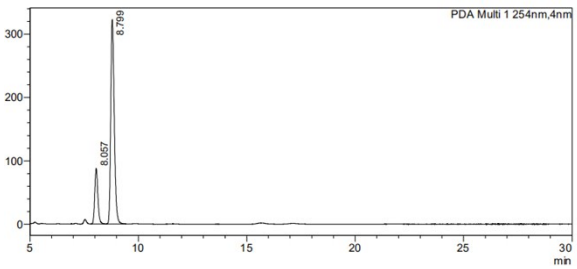




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.103	2562296	254556	49.877
2	8.862	2574891	226582	50.123
Total		5137187	481138	100.000

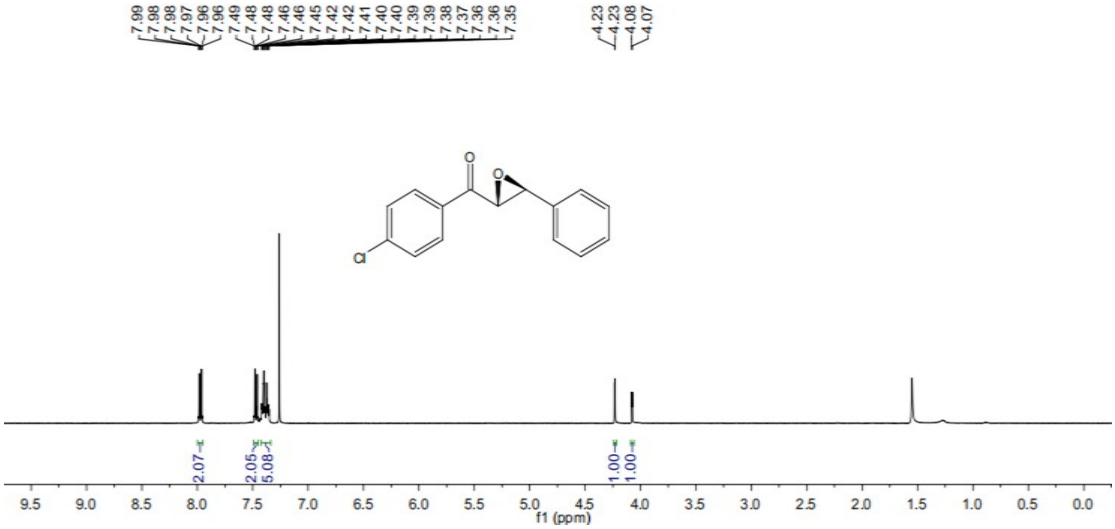


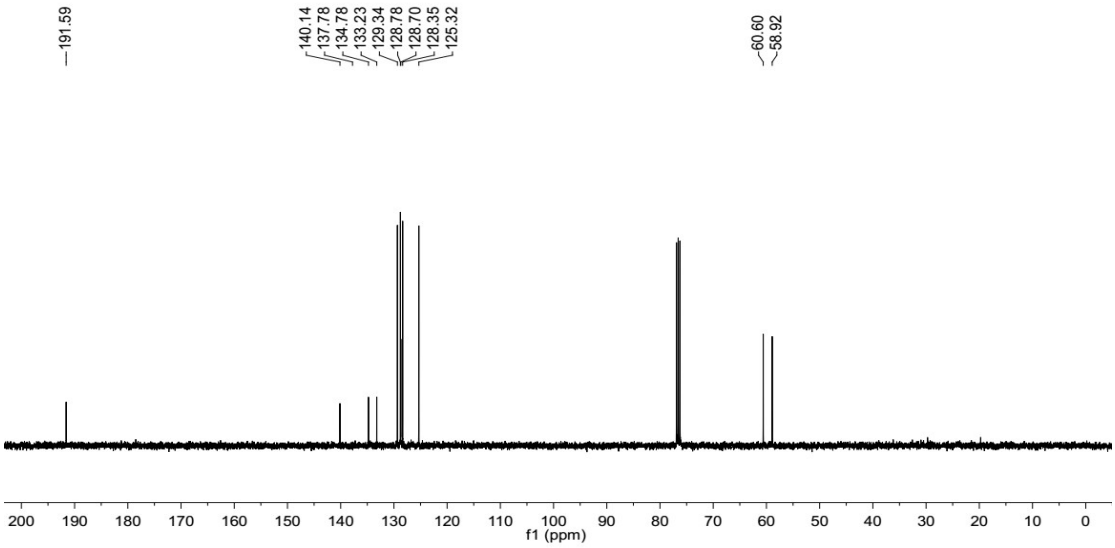
<Peak Table>

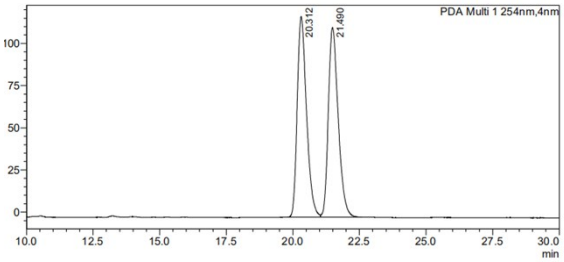
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.057	869199	87235	19.310
2	8.799	3632010	322447	80.690
Total		4501209	409682	100.000

The NMR spectra and HPLC spectrum of compound **7m**



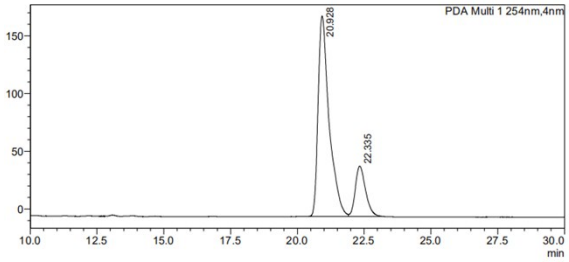




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.312	2888124	118916	49.933
2	21.490	2895923	112434	50.067
Total		5784046	231350	100.000

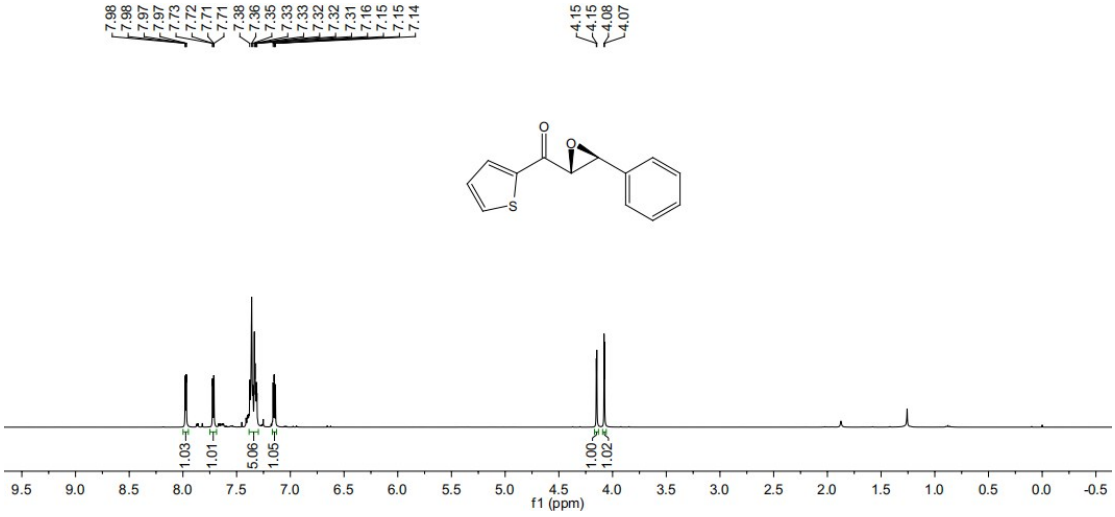


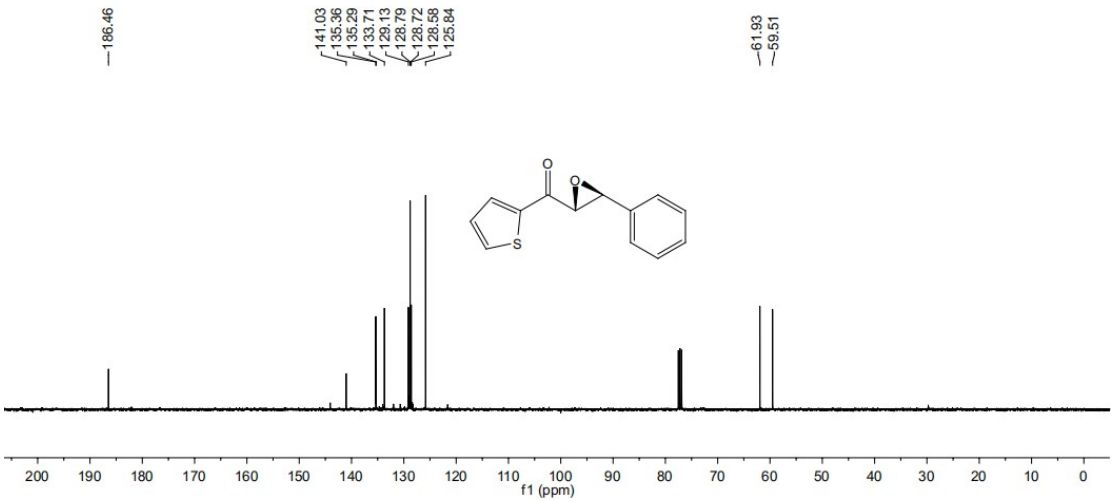
<Peak Table>

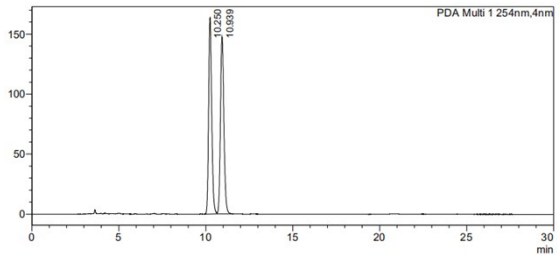
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.928	4982604	173582	80.954
2	22.335	1172267	43696	19.046
Total		6154872	217278	100.000

The NMR spectra and HPLC spectrum of compound **7n**



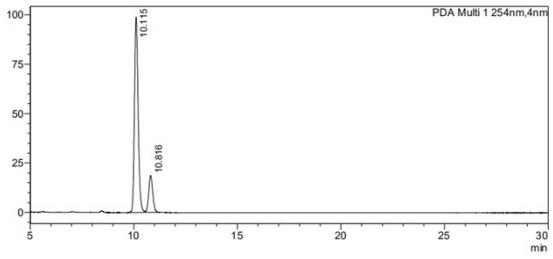




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.250	2015756	163580	49.944
2	10.939	2020278	147742	50.056
Total		4036034	311321	100.000

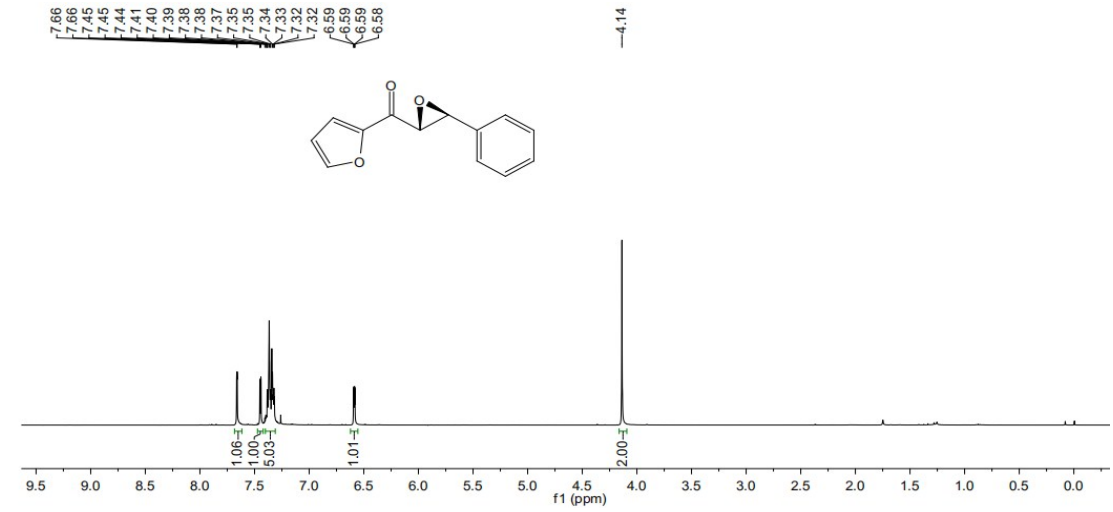


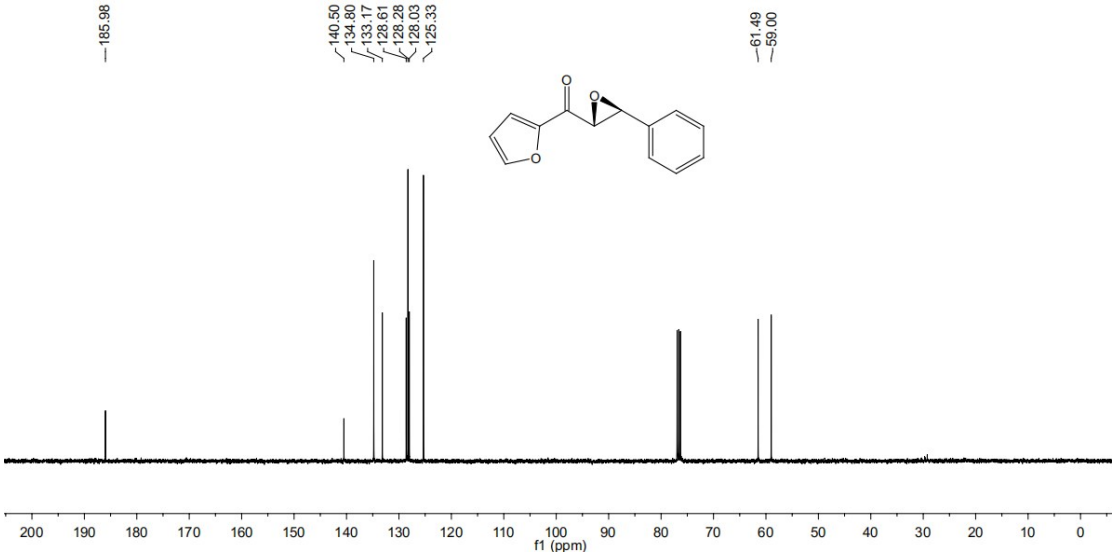
<Peak Table>

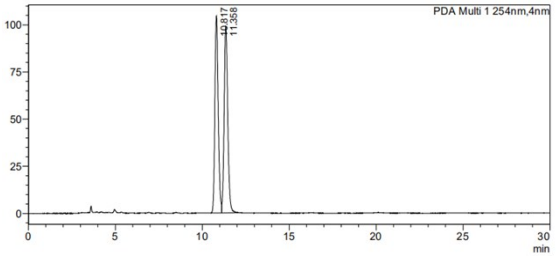
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.115	1223095	98718	82.871
2	10.816	252815	18617	17.129
Total		1475910	117336	100.000

The NMR spectra and HPLC spectrum of compound **7o**



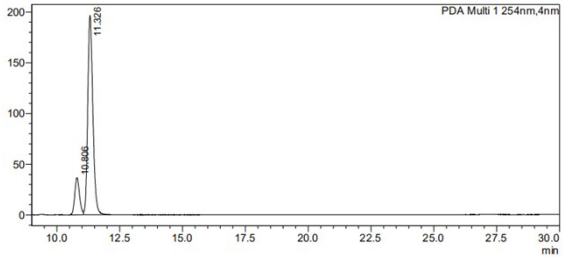




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.817	1393282	104431	49.538
2	11.358	1419256	98837	50.462
Total		2812538	203267	100.000

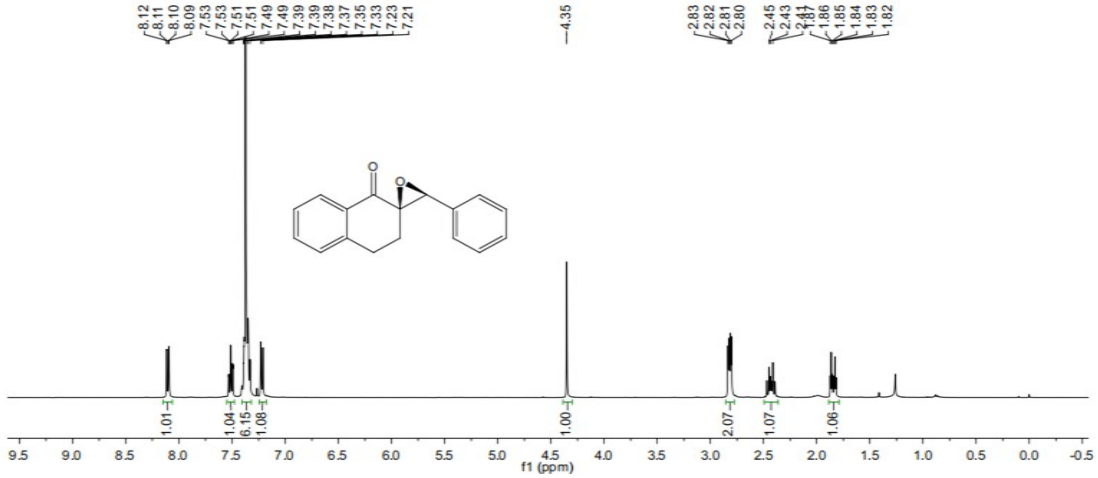


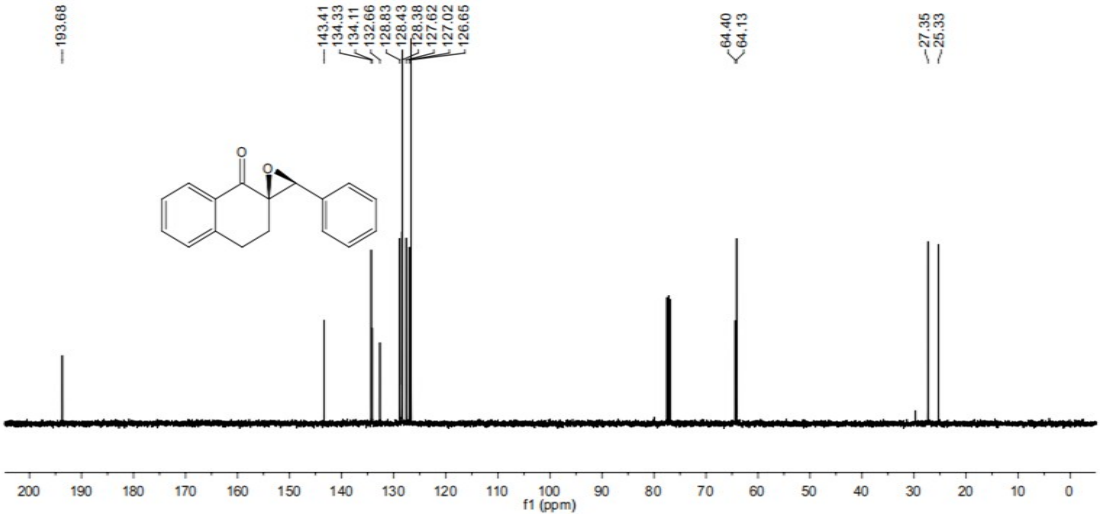
<Peak Table>

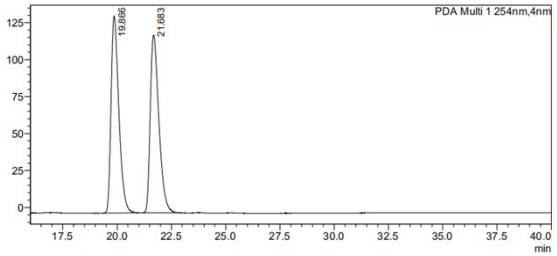
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	10.806	479573	36618	14.711
2	11.326	2780359	196059	85.289
Total		3259932	232677	100.000

The NMR spectra and HPLC spectrum of compound **7p**



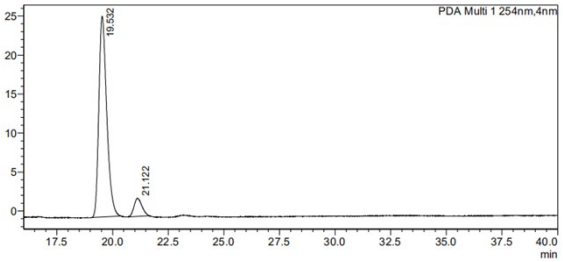




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.866	3324273	133137	50.052
2	21.683	3317390	120393	49.948
Total		6641663	253530	100.000

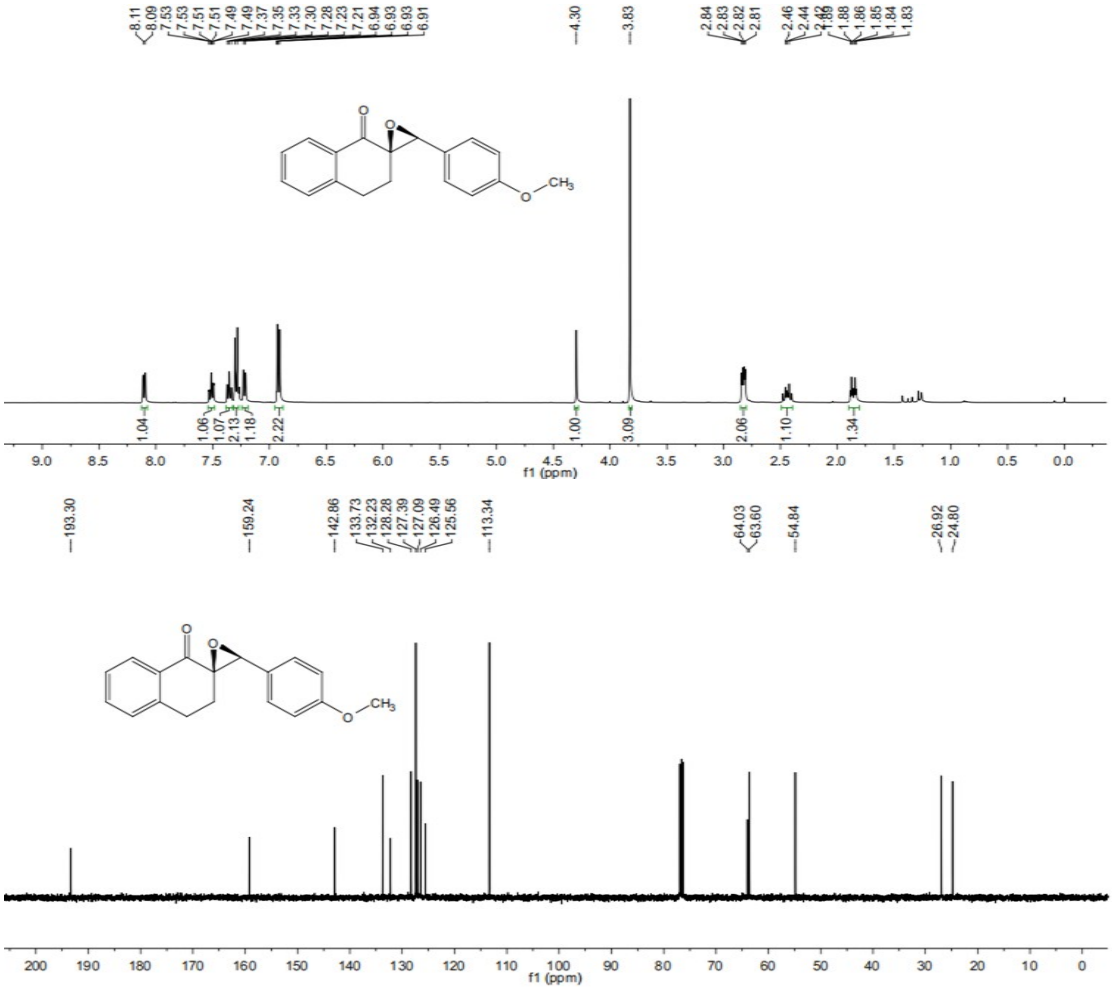


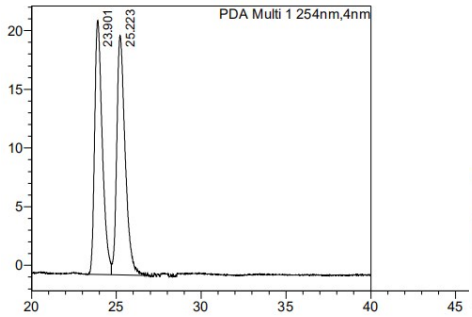
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.532	636246	25737	91.615
2	21.122	58236	2319	8.385
Total		694482	28056	100.000

The NMR spectra and HPLC spectrum of compound **7q**

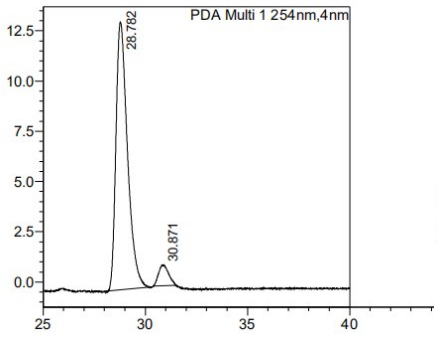




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	23.901	682396	21653	49.353
2	25.223	700285	20401	50.647
Total		1382680	42054	100.000

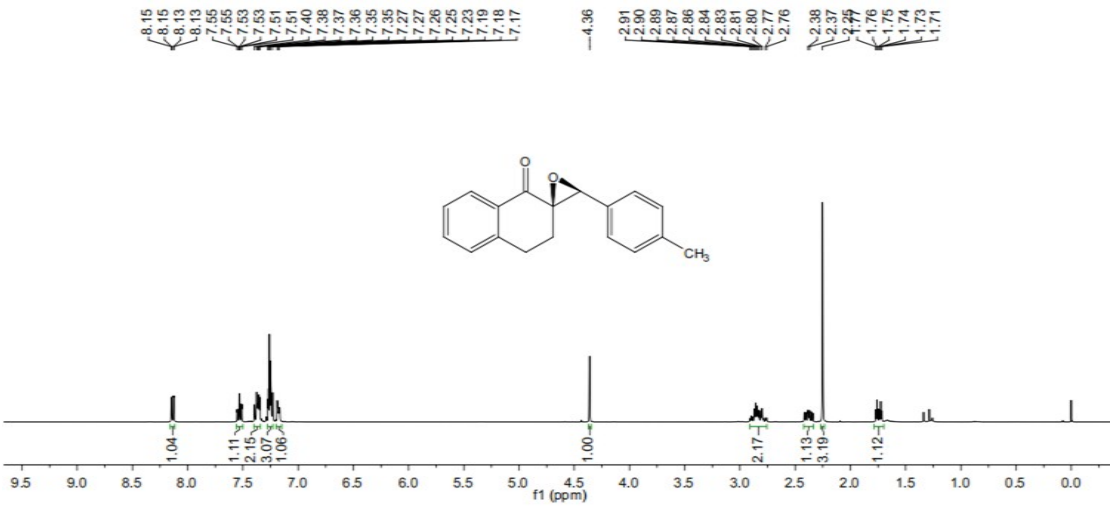


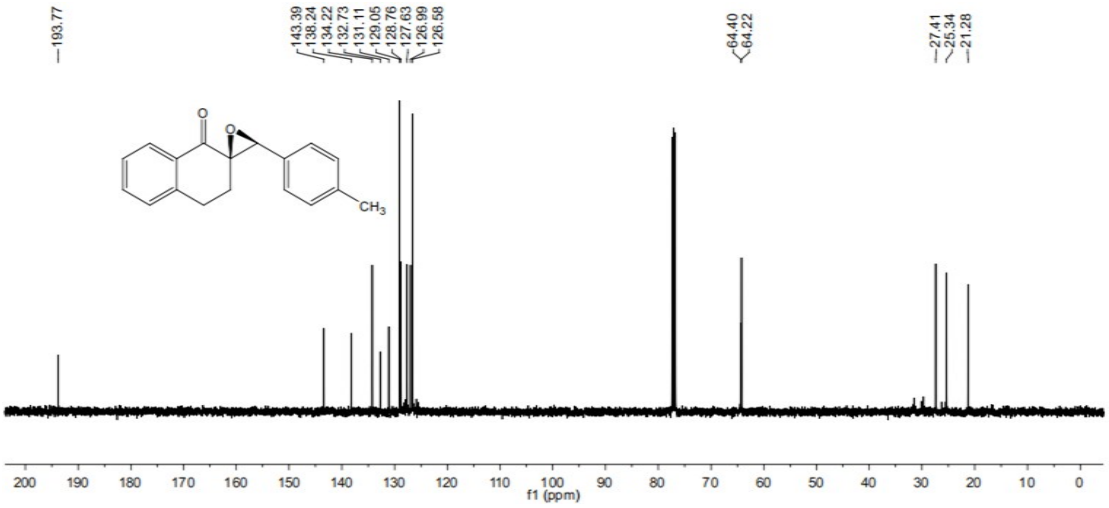
<Peak Table>

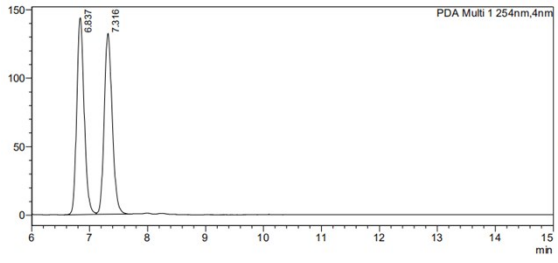
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	28.782	522436	13332	93.653
2	30.871	35405	1035	6.347
Total		557841	14367	100.000

The NMR spectra and HPLC spectrum of compound **7r**



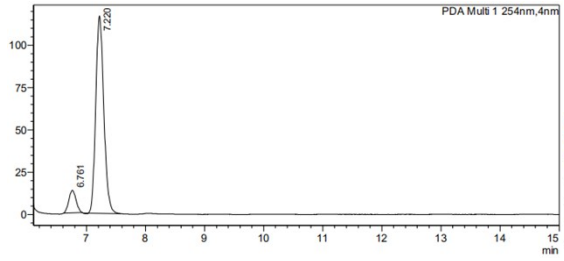




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.837	1275785	143419	50.146
2	7.316	1268341	131877	49.854
Total		2544126	275296	100.000

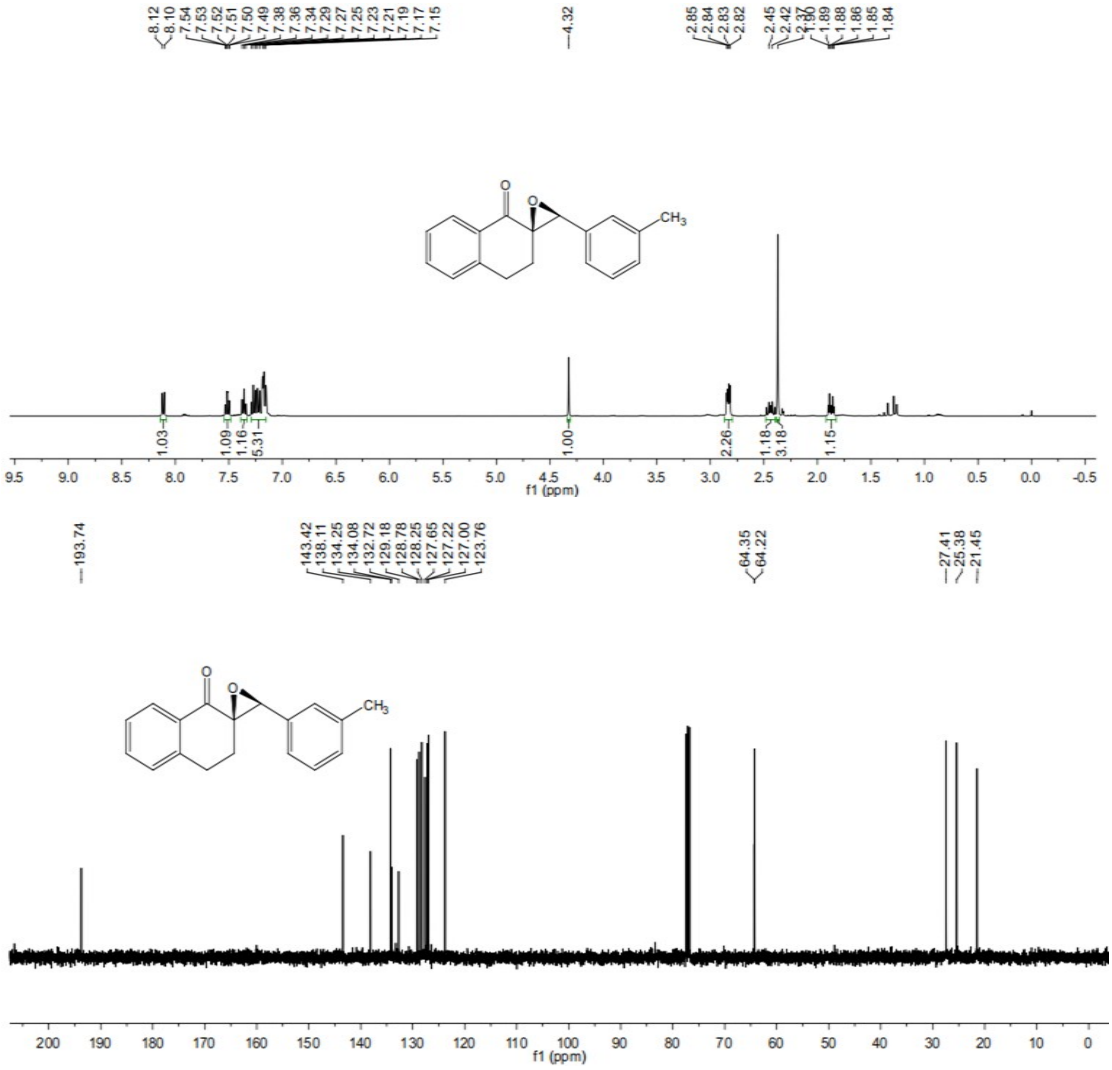


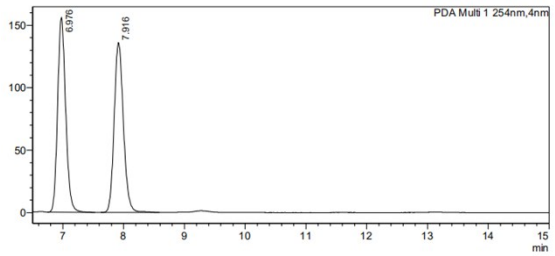
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.761	112226	13254	9.248
2	7.220	1101225	116437	90.752
Total		1213450	129691	100.000

The NMR spectra and HPLC spectra of compound **7s**

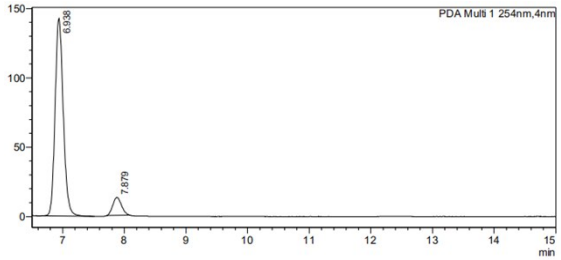




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.976	1436457	155752	49.991
2	7.916	1436978	136030	50.009
Total		2873435	291782	100.000

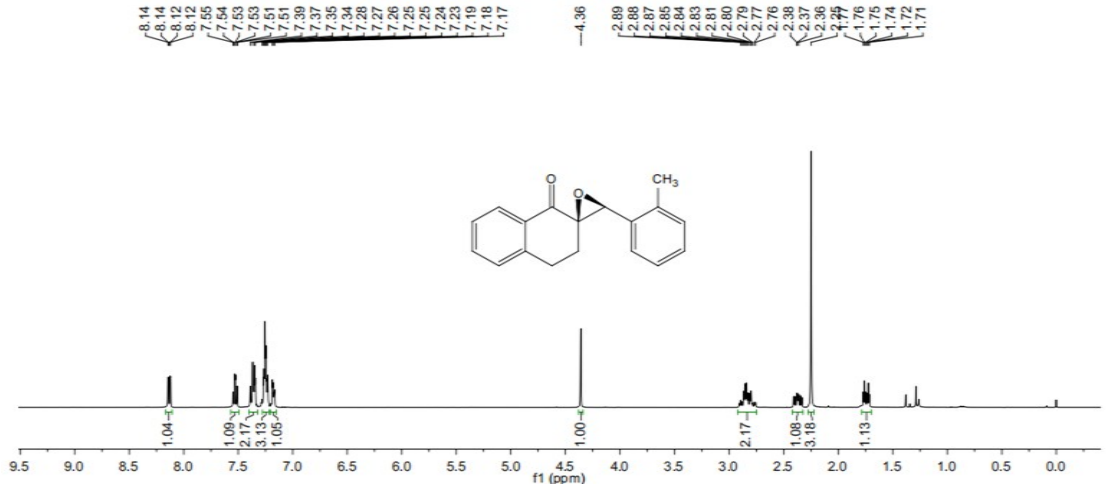


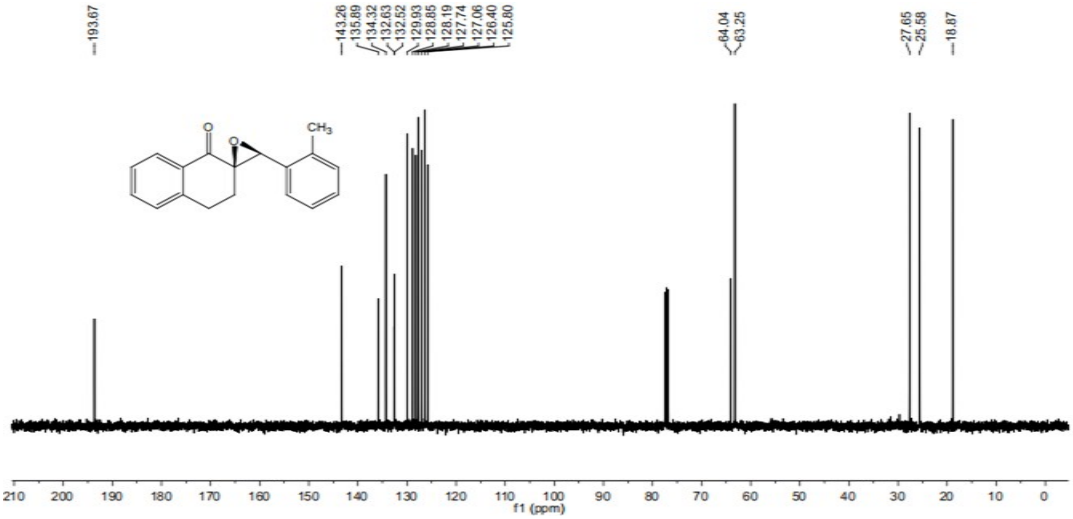
<Peak Table>

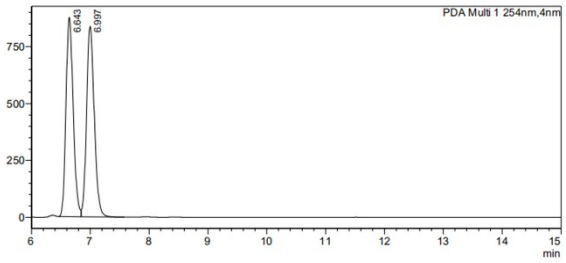
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.938	1311453	142381	91.135
2	7.879	127562	12909	8.865
Total		1439016	155289	100.000

The NMR spectra and HPLC spectrum of compound **7t**



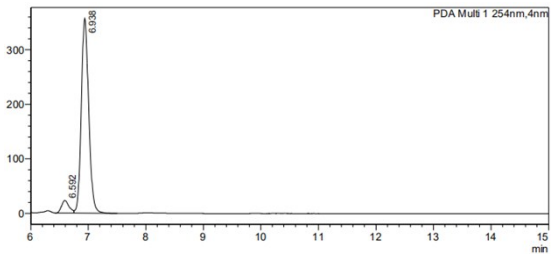




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.643	7496354	875764	49.483
2	6.997	7653146	836726	50.517
Total		15149500	1712490	100.000

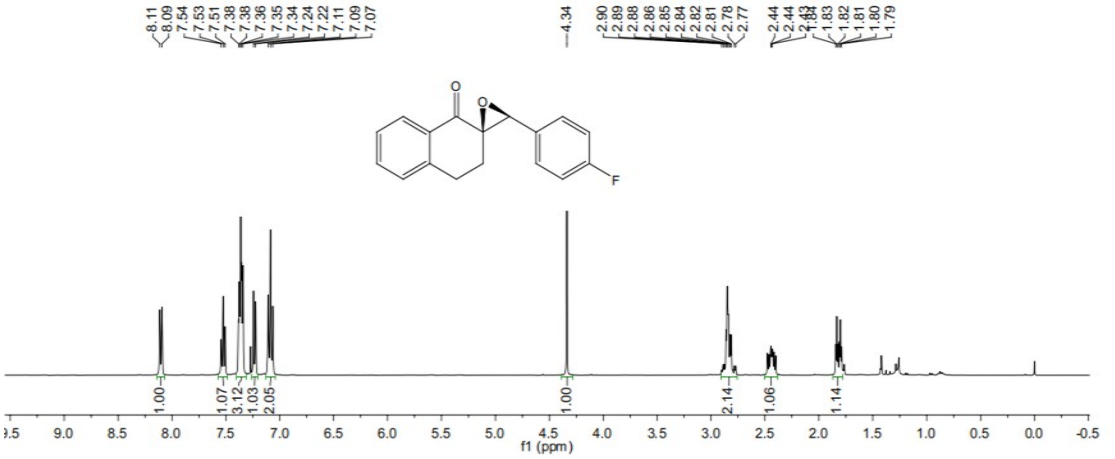


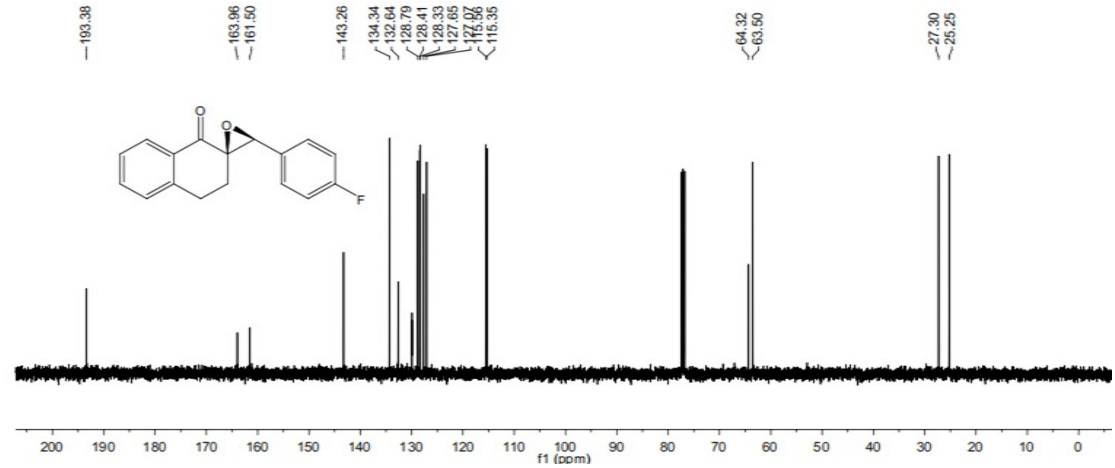
<Peak Table>

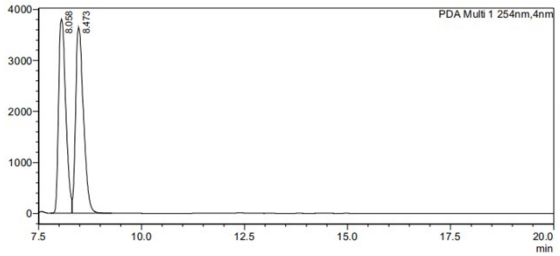
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	6.592	210928	23002	6.143
2	6.938	3222542	356917	93.857
Total		3433470	379919	100.000

The NMR spectra and HPLC spectrum of compound **7u**



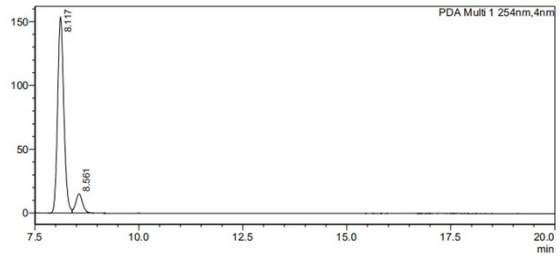




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.058	46390095	3809010	48.991
2	8.473	48301670	3640175	51.009
Total		94691765	7449186	100.000

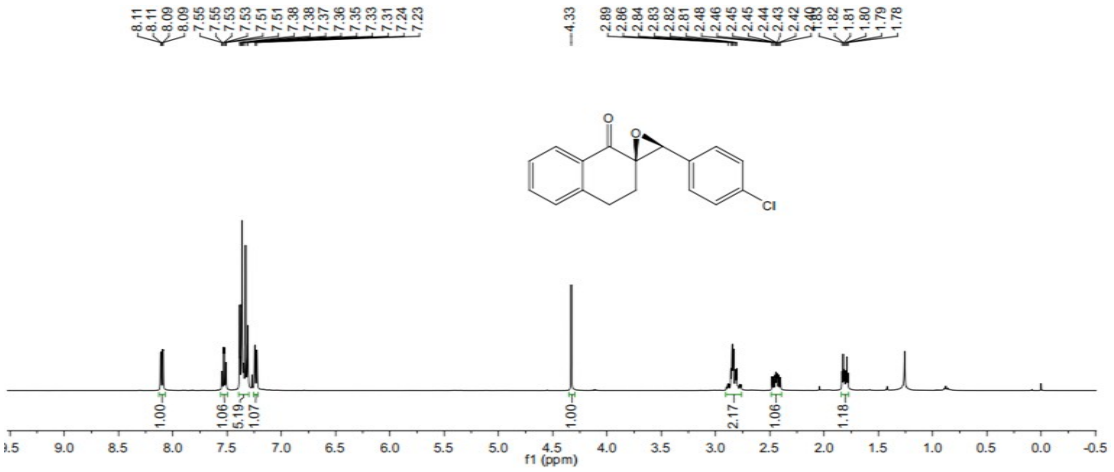


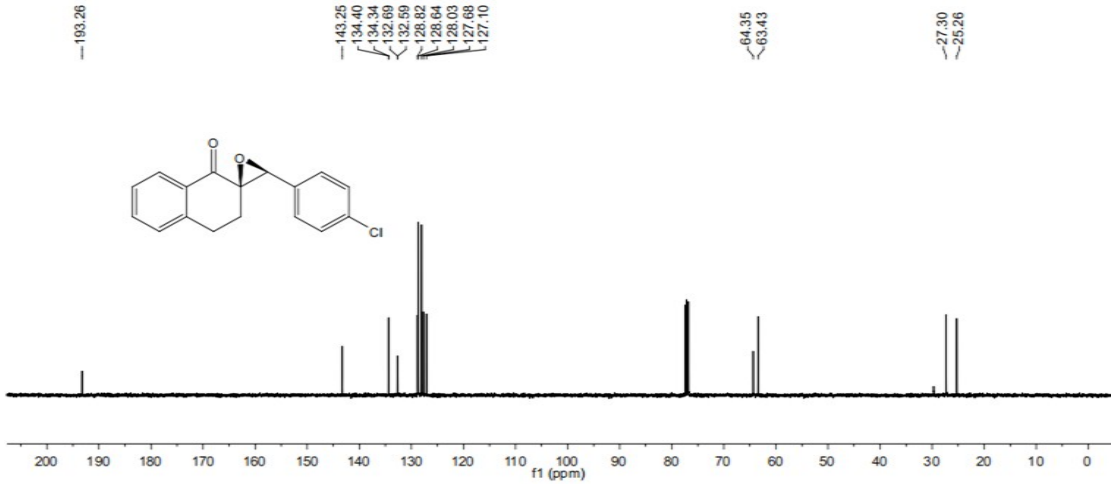
<Peak Table>

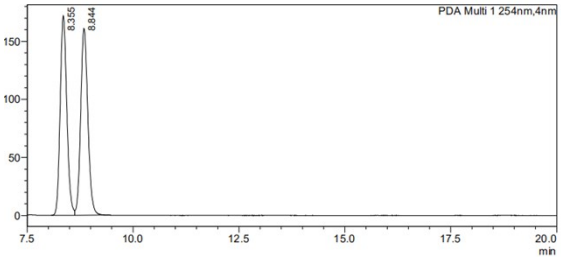
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.117	1605693	153229	90.366
2	8.561	171193	14940	9.634
Total		1776886	168169	100.000

The NMR spectra and HPLC spectrum of compound **7v**



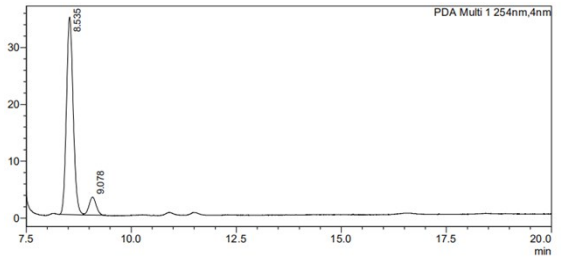




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.355	1877878	171609	49.717
2	8.844	1899229	160752	50.283
Total		3777107	332362	100.000

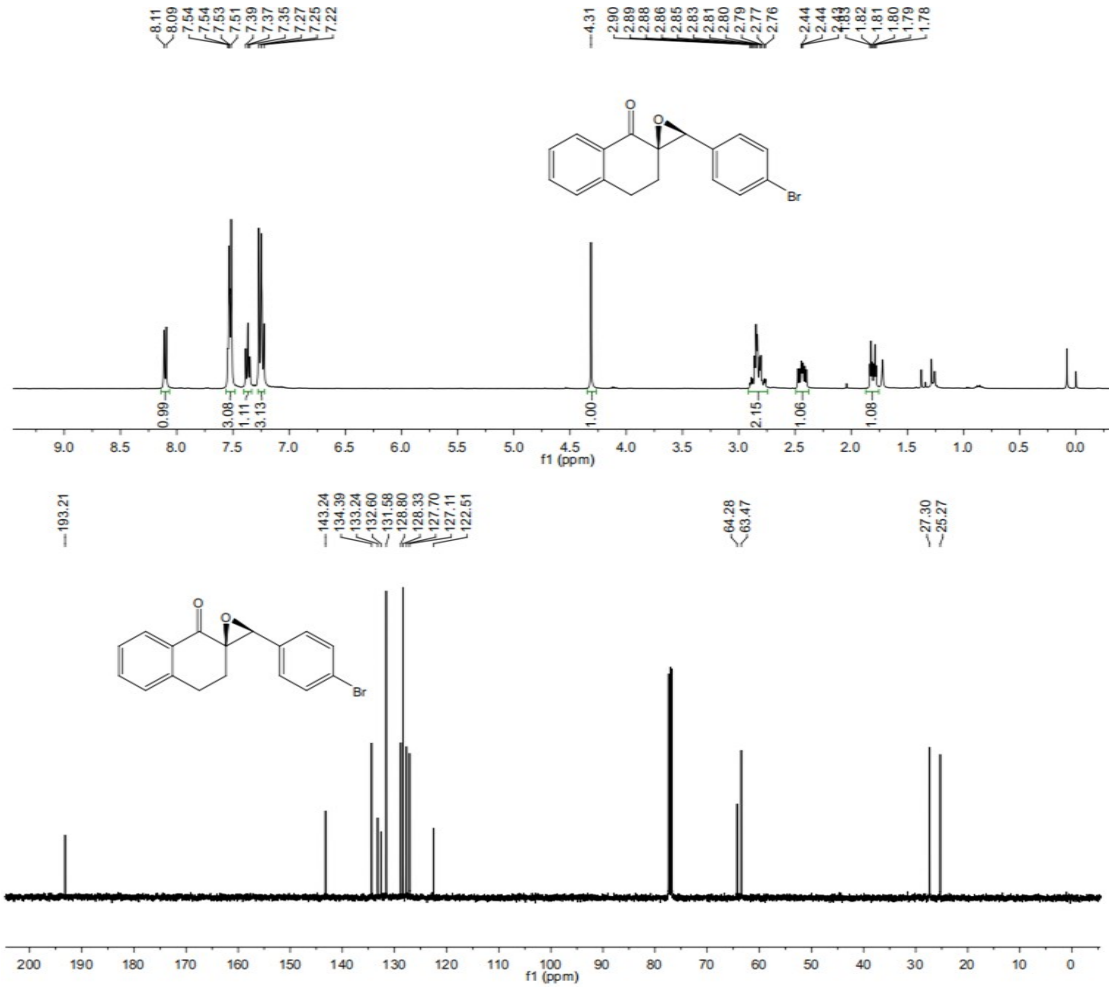


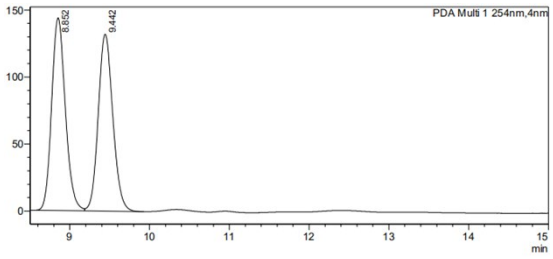
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.535	387023	34735	91.100
2	9.078	37808	3178	8.900
Total		424831	37912	100.000

The NMR spectra and HPLC spectrum of compound **7w**

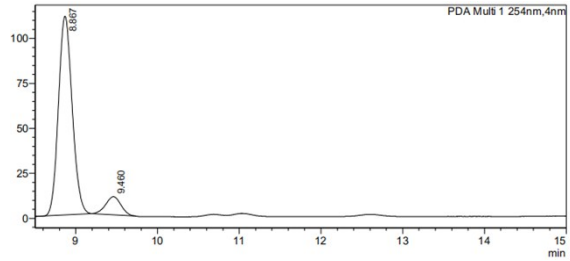




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.852	1714102	143630	50.530
2	9.442	1678159	132053	49.470
Total		3392260	275684	100.000

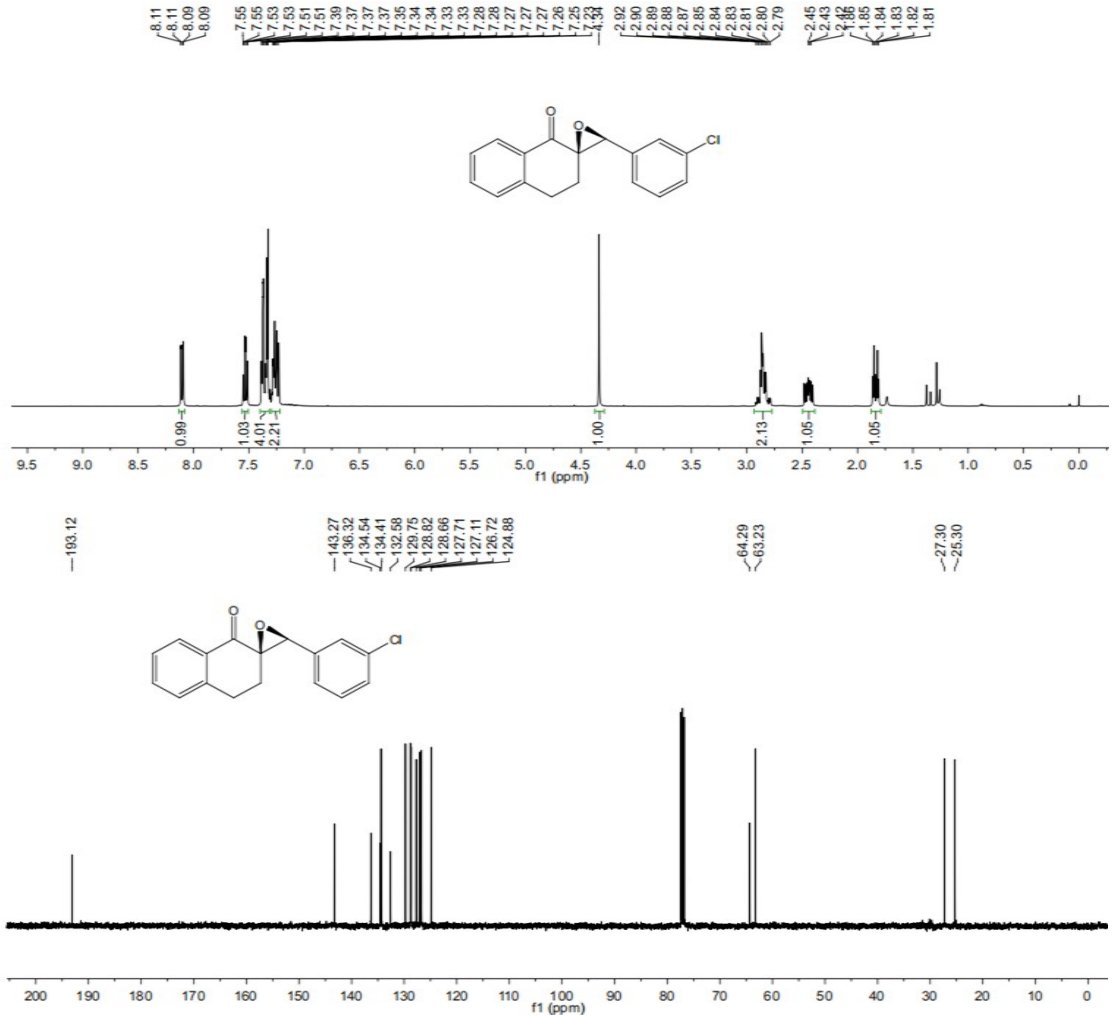


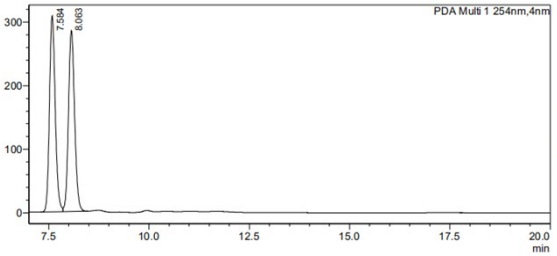
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.867	1292614	110415	90.765
2	9.460	131524	10115	9.235
Total		1424137	120529	100.000

The NMR spectra and HPLC spectrum of compound **7x**

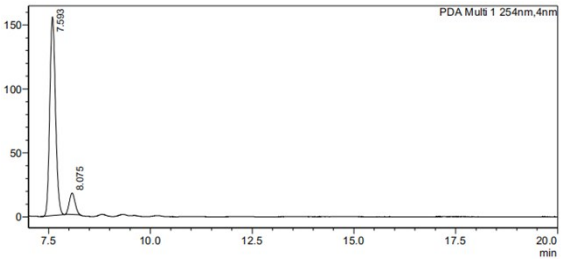




<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	7.584	3081420	308014	50.414
2	8.063	3030859	284441	49.586
Total		6112279	592455	100.000

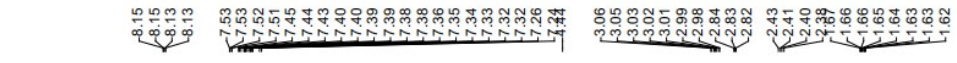


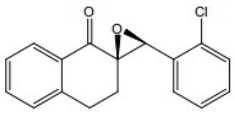
<Peak Table>

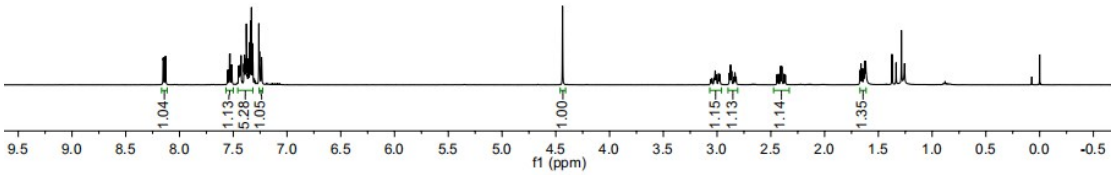
PDA Ch1 254nm

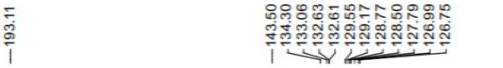
Peak#	Ret. Time	Area	Height	Area%
1	7.593	1520526	155169	90.184
2	8.075	165496	16643	9.816
Total		1686022	171813	100.000

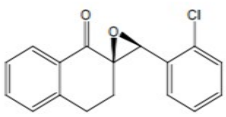
The NMR spectra and HPLC spectrum of compound **7y**

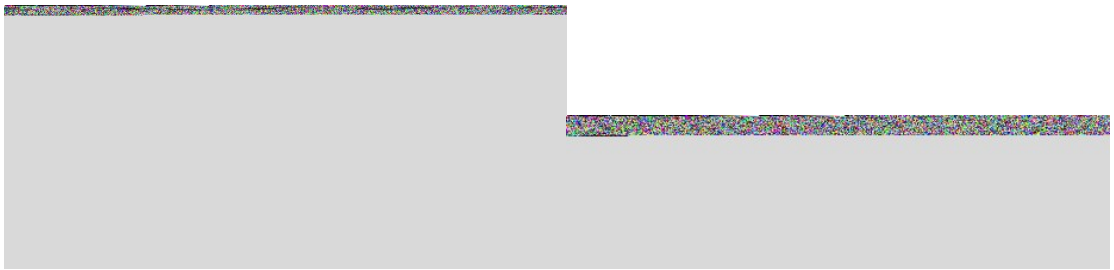




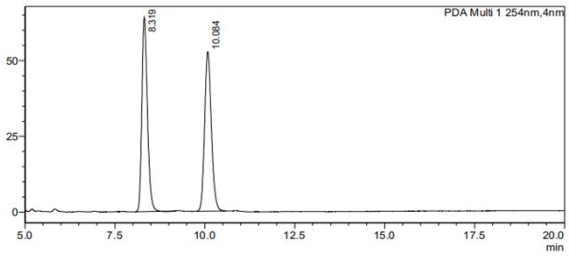








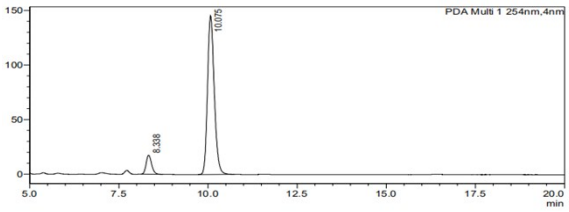
The HPLC spectrum of compound 7e after recrystallization



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.319	690782	64110	49.970
2	10.084	691617	52642	50.030
Total		1382399	116753	100.000

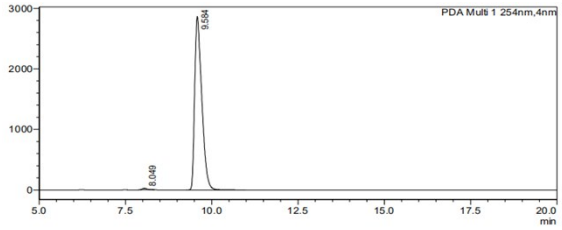


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.338	188222	17572	8.921
2	10.075	1921579	145540	91.079
Total		2109801	163111	100.000

The HPLC spectrum of single crystal of **7e**

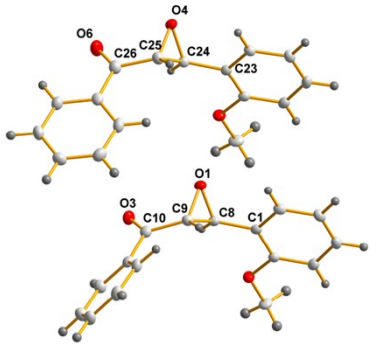


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	8.049	241640	23027	0.585
2	9.584	41038623	2862578	99.415
Total		41280263	2885606	100.000

The crystallographic parameter of 7e



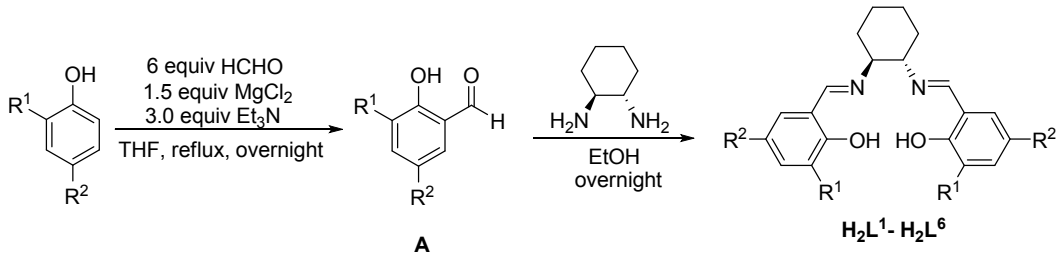
7e

Compound	**7e**
Formula	$C_{16}H_{14}O_3$
fw	29.02
Temperature/K	120.03
Crystal system	monoclinic
Space group	C2
a/Å	31.6601(8)
b/Å	5.7080(2)
c/Å	15.2031(4)
α/°	90
β/°	112.639(2)

γ/°	90
Volume/Å^3	2535.75(13)
Z	8
ρcalcg/cm^3	1.406
μ/mm^{-1}	1.151
F(000)	1110
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54178 Å)

General procedure for the synthesis of chiral salen ligands H_2L^1-H_2L^9

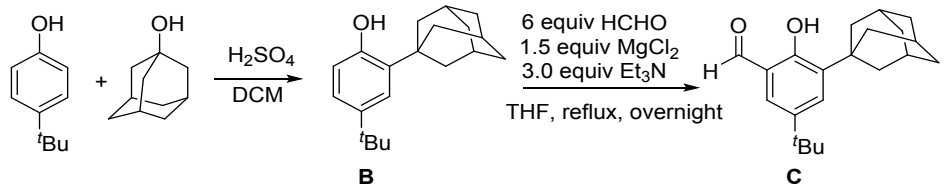
General procedure for the synthesis of ligands H_2L^1-H_2L^6



To a THF solution of 30 mmol substituted phenol and 45 mmol $MgCl_2$, 90 mmol Et_3N was added, and the mixture was continued to stir for 30 min at the room temperature. Then, the mixture was shifted to an oil bath and added 180 mmol Paraformaldehyde, the mixture was refluxed at 75 °C overnight. Finally, Cooled to room temperature, The reaction is quenched by hydrochloric acid. The crude product was extracted with ethyl acetate (3×50 mL). The combined organic layers were washed with $NaHCO_3$ (3×20 mL) and brine (3×20 mL) in turn and dried over Na_2SO_4. After removing solvent in vacuo, the crude product disubstituted salicylaldehyde **A** was purified by column chromatography using eluent of ethyl acetate to petroleum ether 1:10.

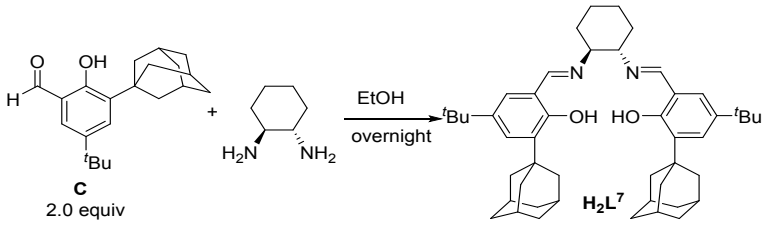
The (1*S*, 2*S*)-1,2-diaminocyclohexane (10 mmol) was added to the ethanol solution of disubstituted salicylaldehyde **A**. The mixture was stirred for 5 h and the yellow solid product was separated and collected by vacuum filtration without recrystallization.

The synthesis of ligand H_2L^7

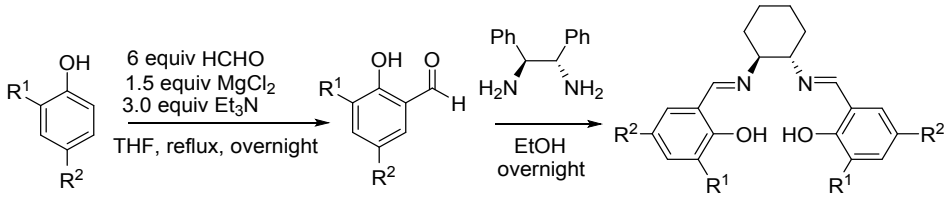


4-*tert*-Butylphenol (20 mmol) and 1-adamantanol (20 mmol) were dissolved in dichloromethane (DCM) at the room temperature. The sulfuric acid H_2SO_4 (1.5 mL) was added dropwise to the mixture and stir for 30 min. The reaction is quenched by NaOH solution (2M). The organic layer was dried over Na_2SO_4. The crude product was concentrated and purified by column chromatography using eluent of ethyl acetate to petroleum ether 1:20.

The procedure for the synthesis of disubstituted salicylaldehyde **C** is similar to that of **A**. The following procedure for the synthesis of H_2L^7 is similar to the above method.

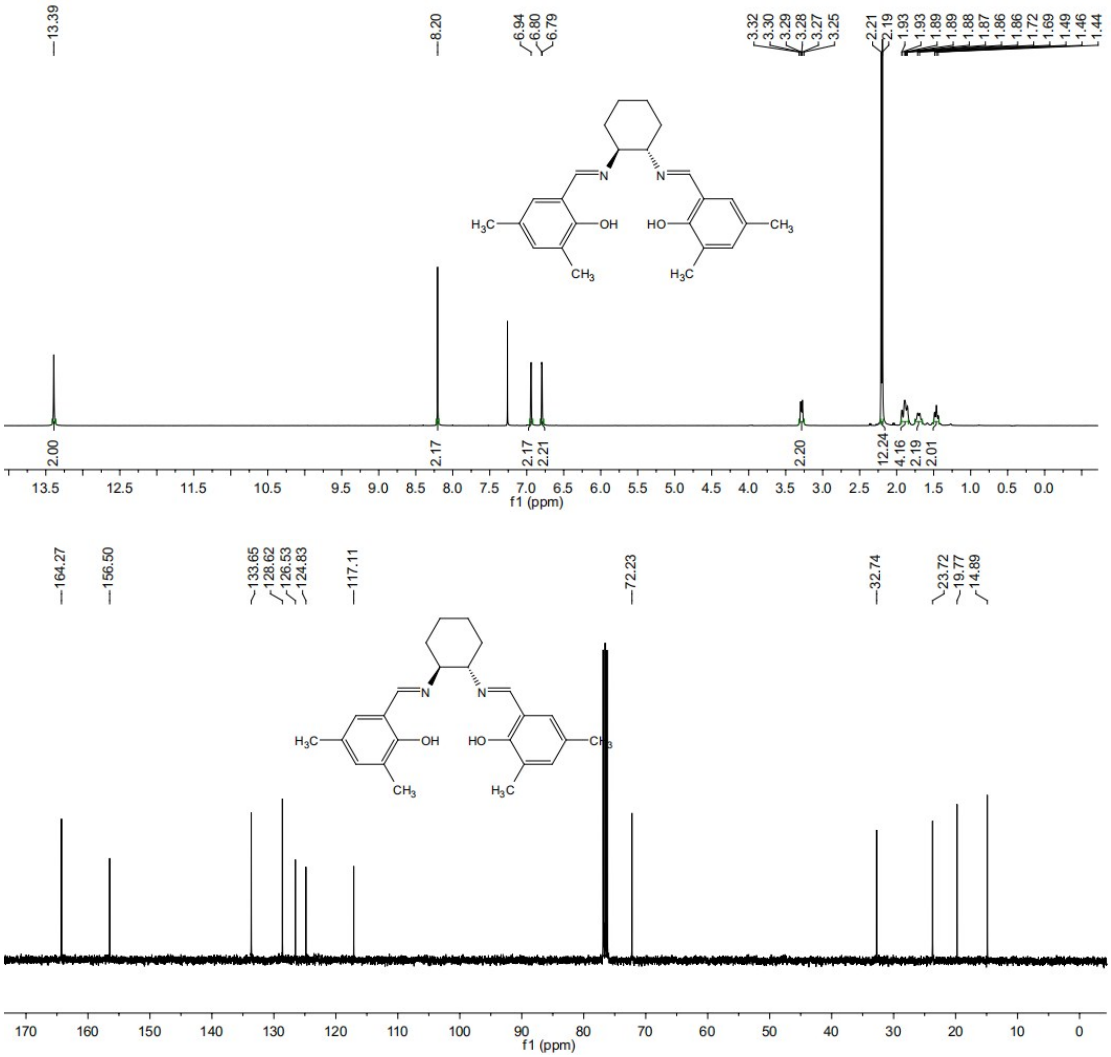


General procedure for the synthesis of ligands H_2L^8 - H_2L^9

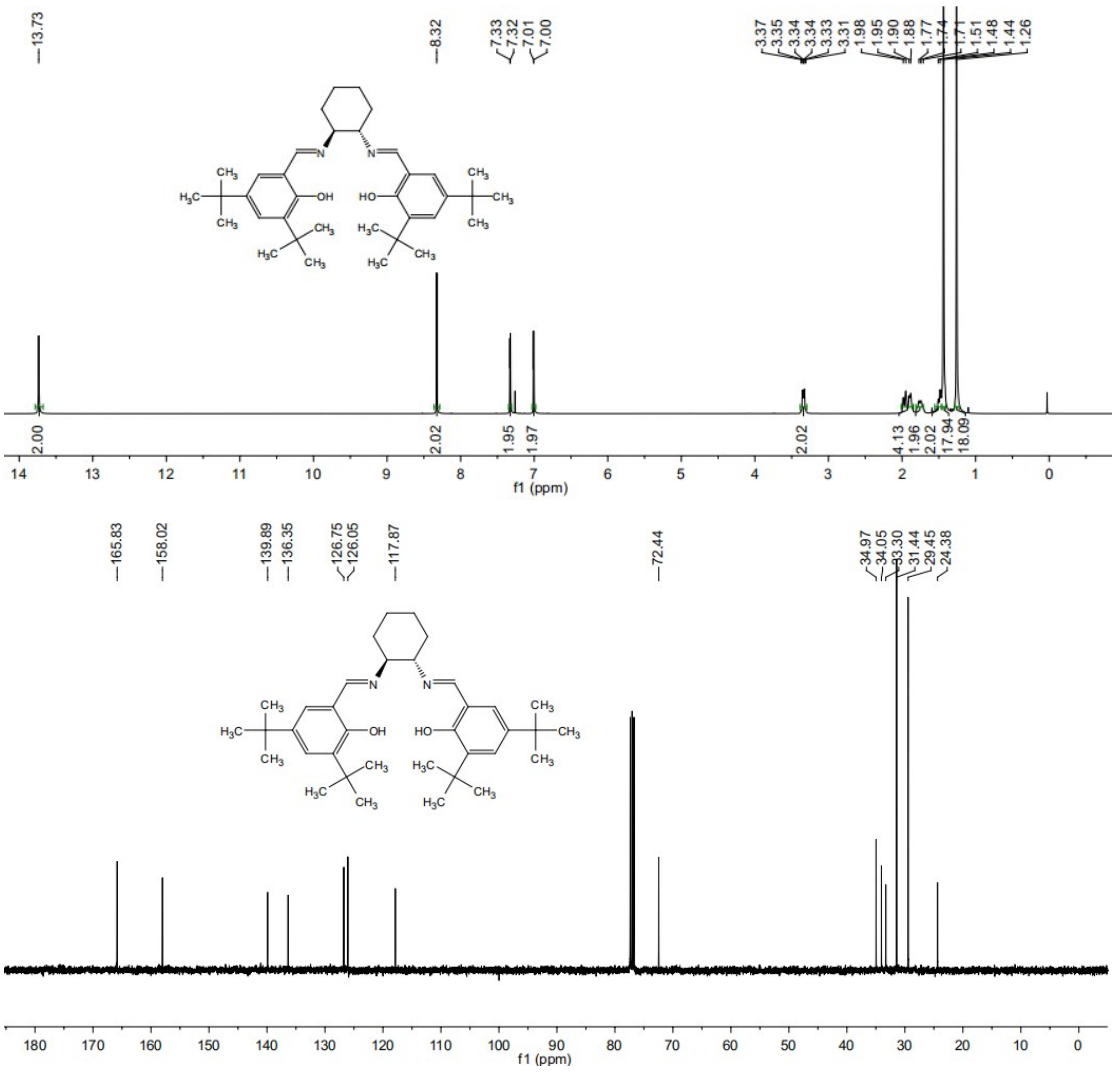


The (1*S*, 2*S*)-diphenyl-1,2-ethanediamine (10 mmol) was added to the ethanol solution of disubstituted salicylaldehyde **A**. The mixture was stirred for 5 h and the yellow solid product was separated and collected by vacuum filtration without recrystallization.

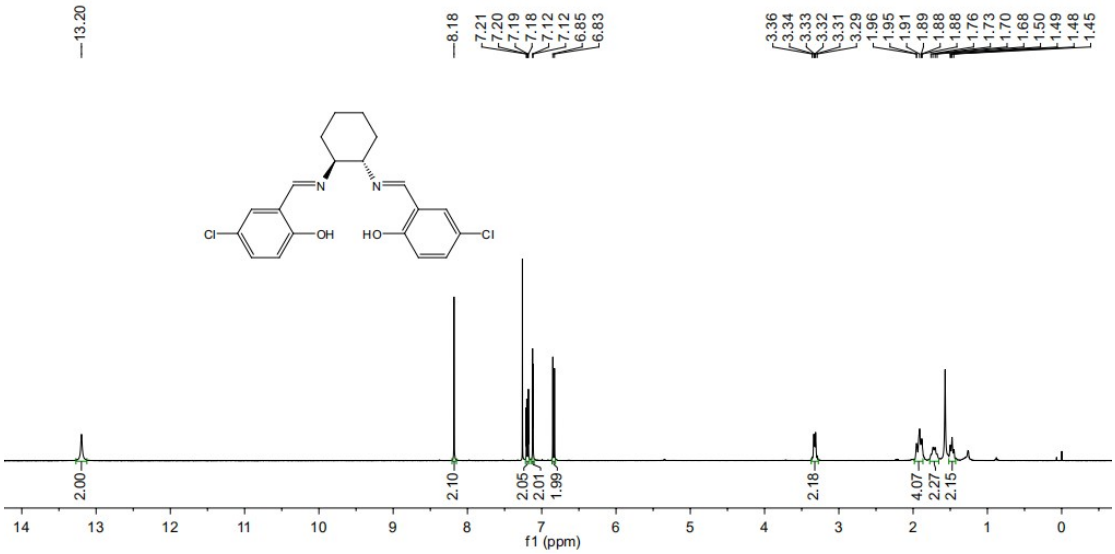
The ^{1}H NMR and ^{13}C NMR spectra of ligand H_2L^1

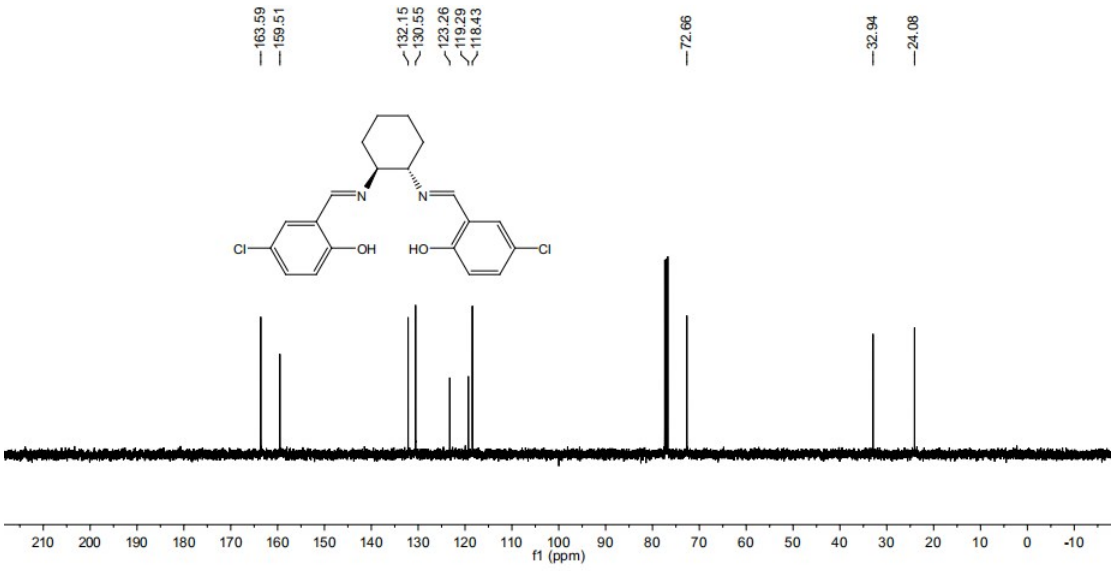


The ^{1}H NMR and ^{13}C NMR spectrum of ligand H_2L^2

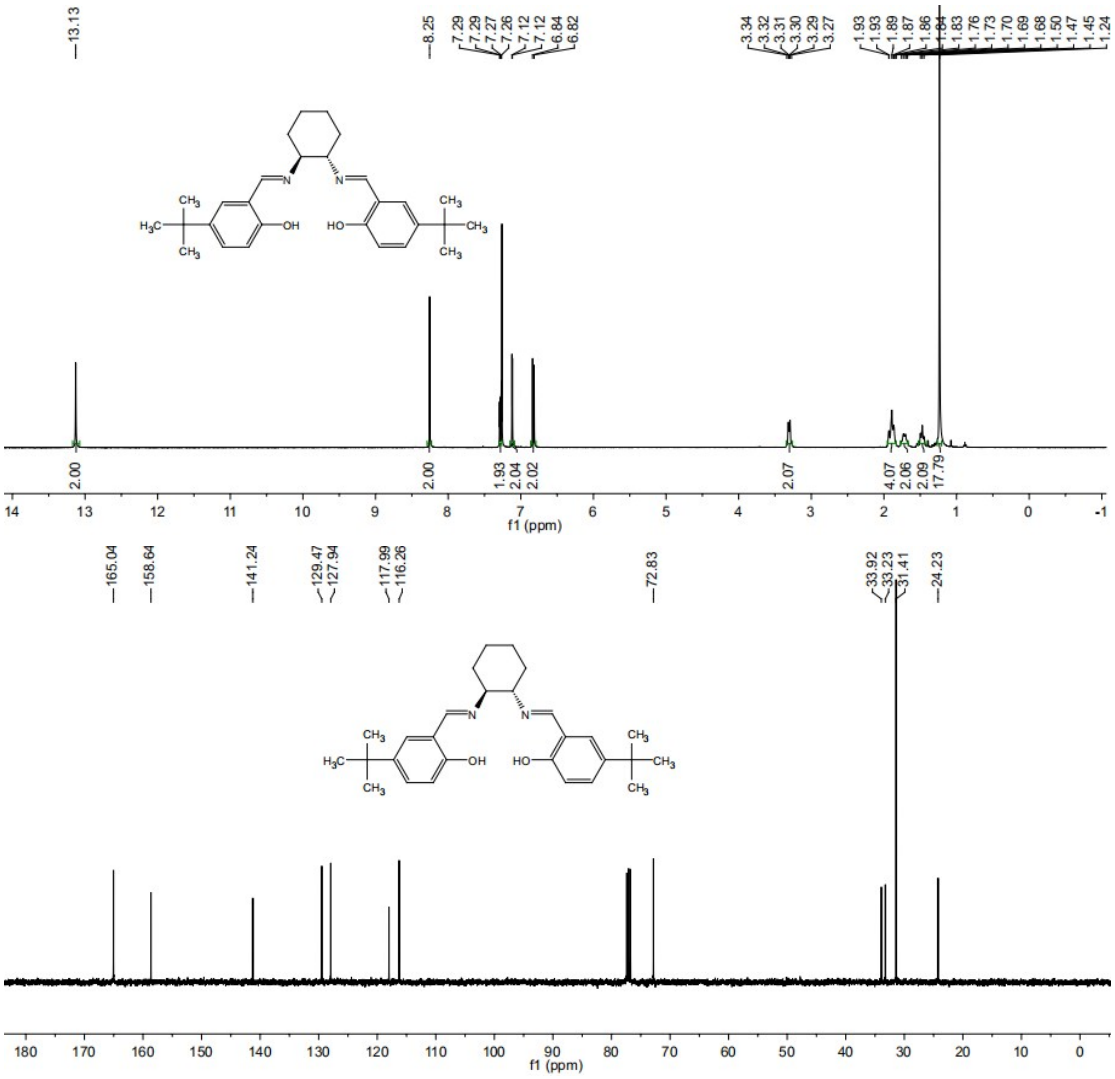


The ^{1}H NMR and ^{13}C NMR spectrum of ligand H_2L^3

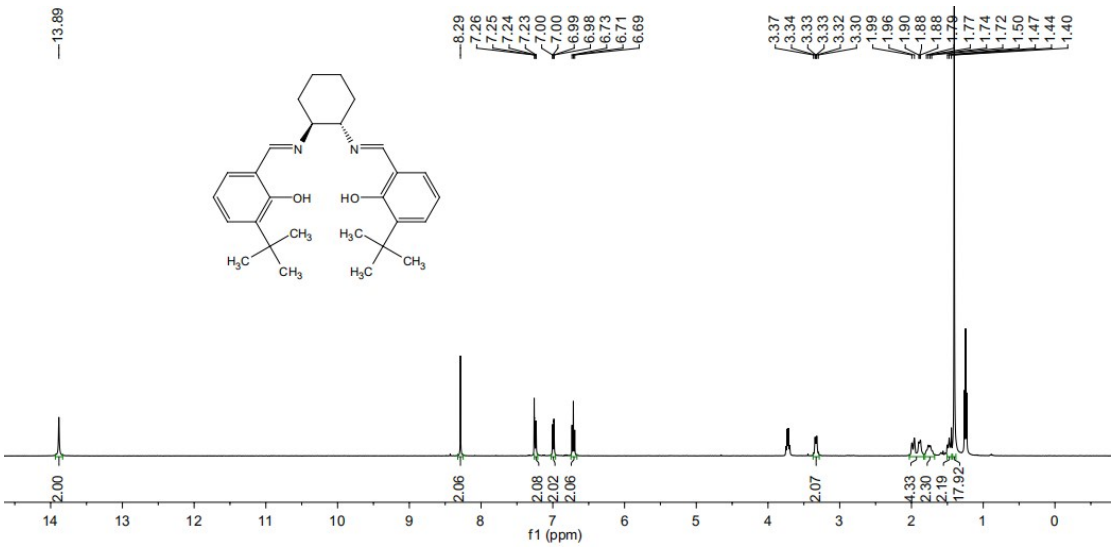


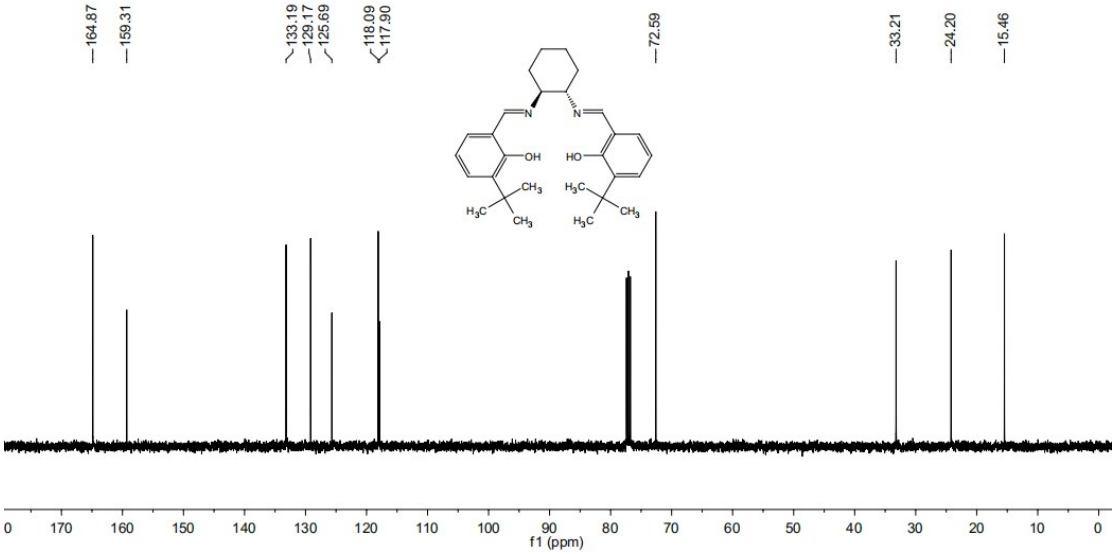


The ^{1}H NMR and ^{13}C NMR spectrum of ligand H_2L^4

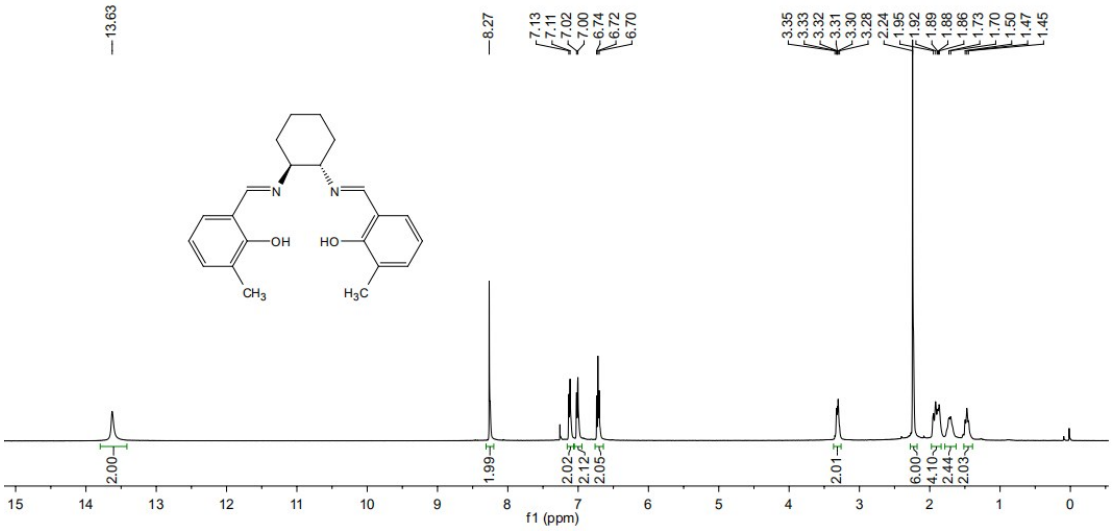


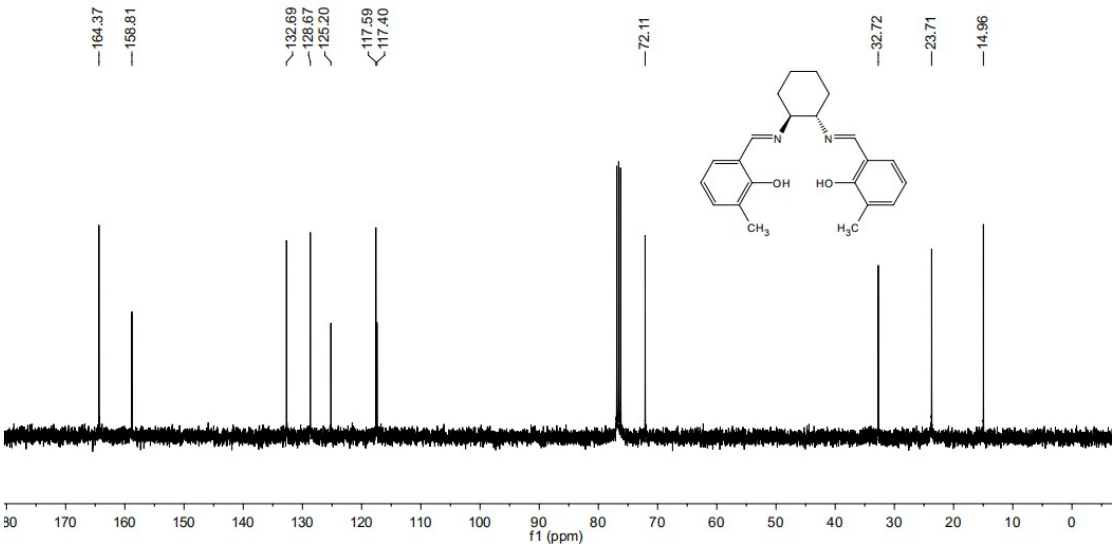
The ^{1}H NMR and ^{13}C NMR spectrum of ligand H_2L^5



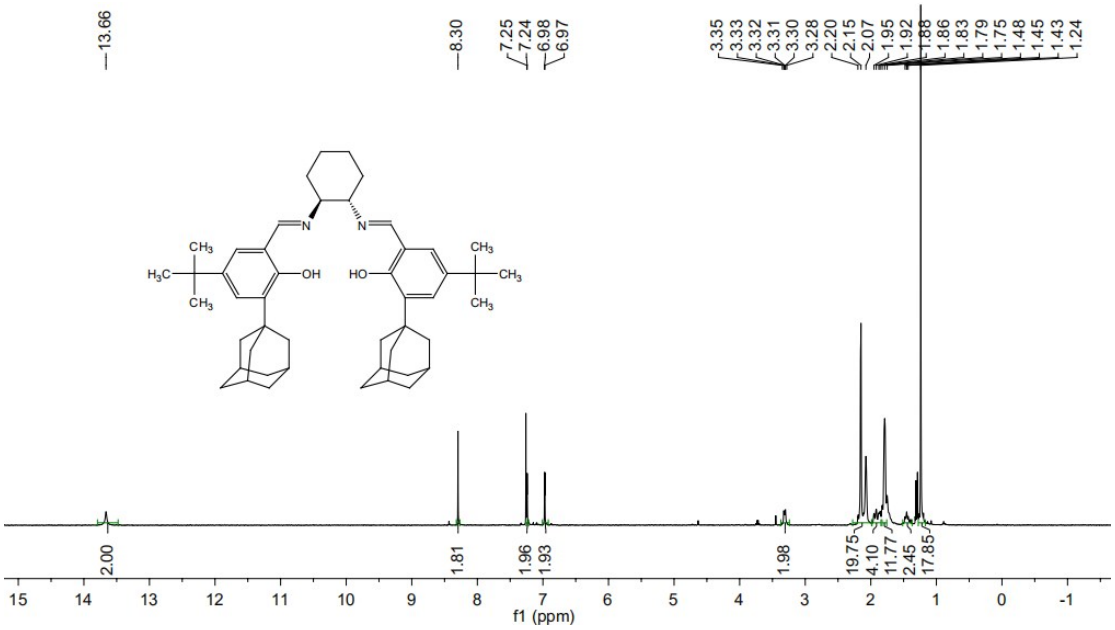


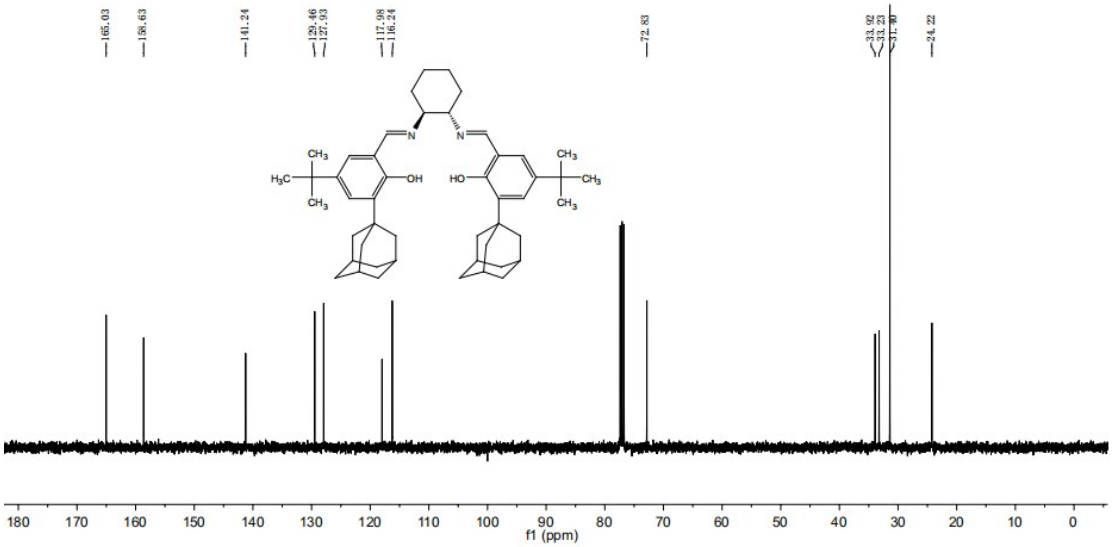
The ^{1}H NMR and ^{13}C NMR spectrum of ligand H_2L^6



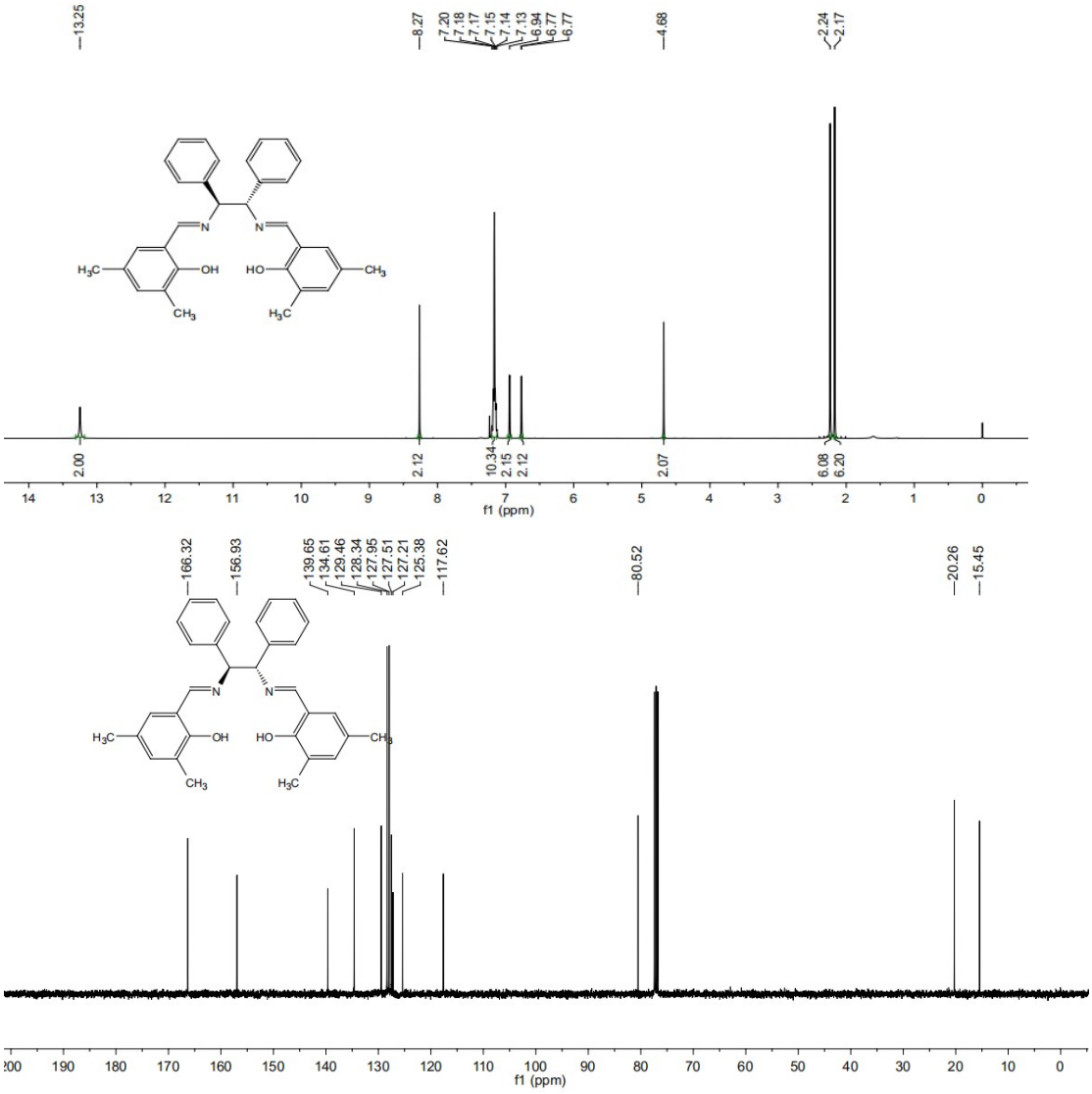


The ^{1}H NMR and ^{13}C NMR spectrum of ligand H_2L^7

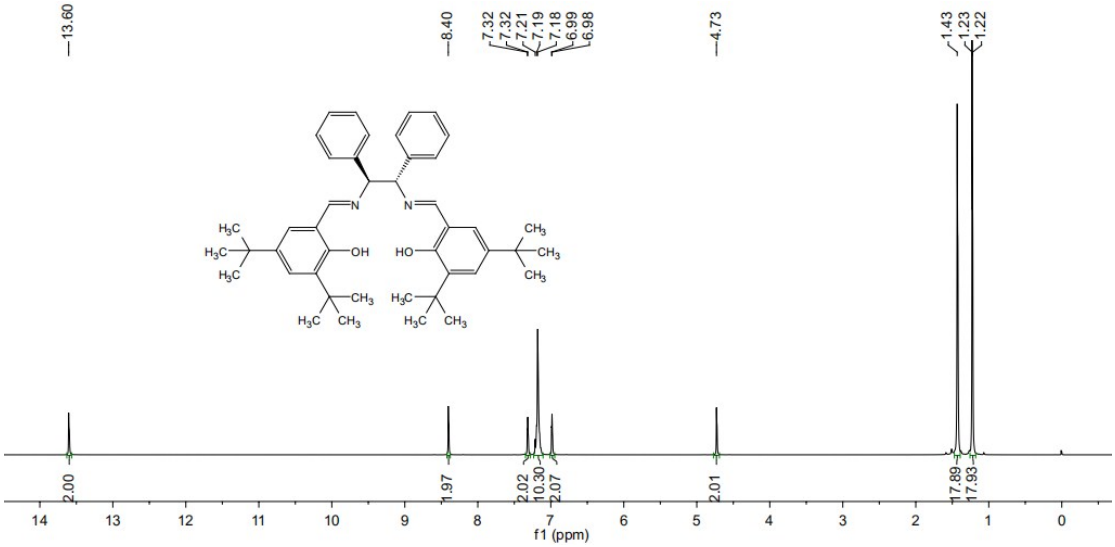


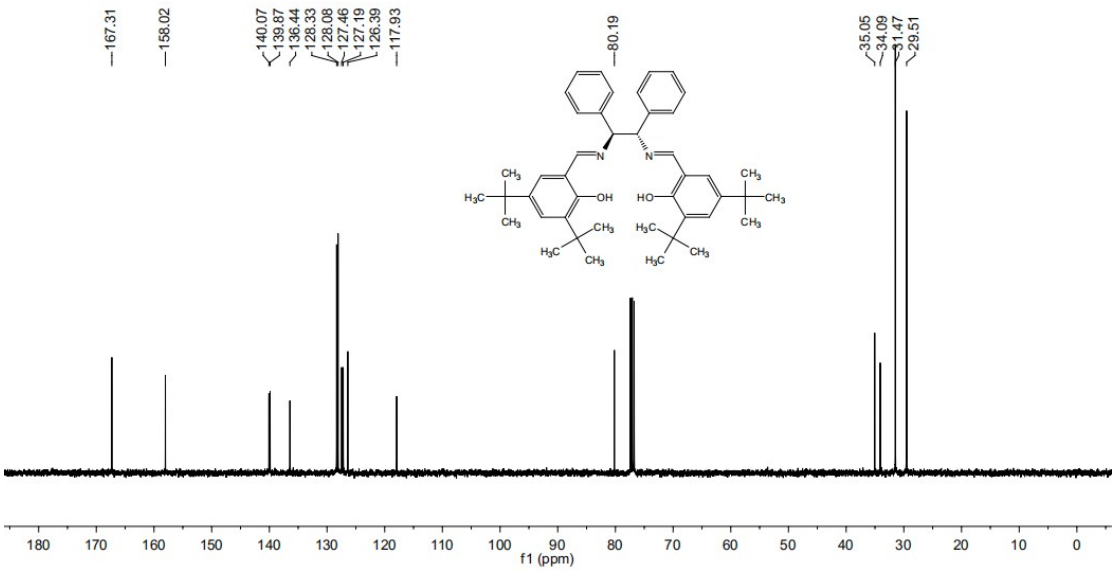


The ^{1}H NMR and ^{13}C NMR spectrum of ligand H_2L^8

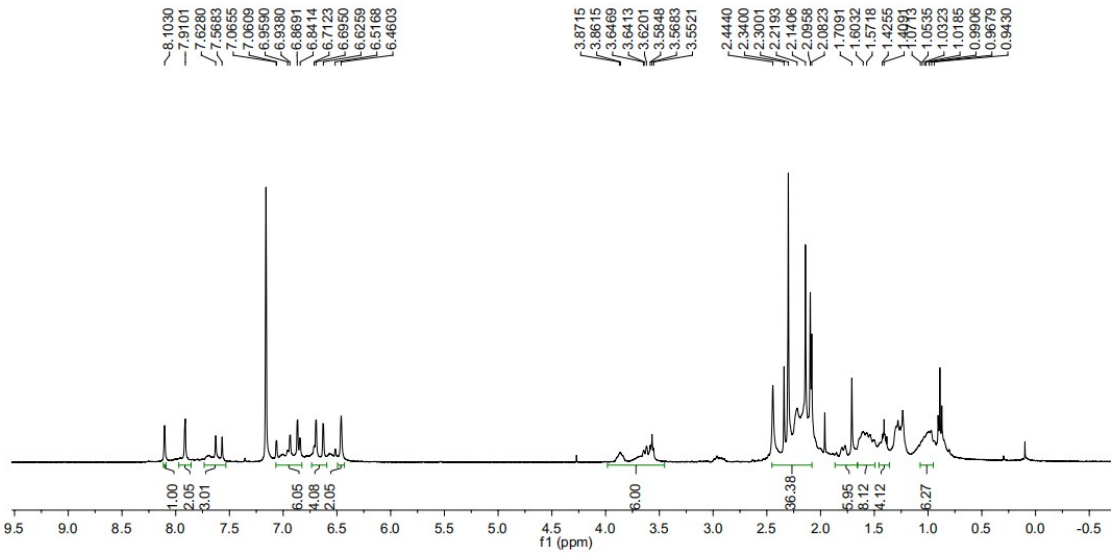


The ^{1}H NMR and ^{13}C NMR spectrum of ligand H_2L^9





The ^{1}H NMR spectrum of complex 8



The characterization data of complex 8

^{1}H NMR (400 MHz, C_6D_6) δ 8.10 (s, 1H, CH), 7.91 (s, 2H, CH), 7.60 (m, 3H, CH), 6.95 (m, 6H, Ar-H), 6.68 (m, 4H, Ar-H), 6.46 (s, 2H, Ar-H), 3.67 (m, 6H, CH), 2.27 (m, 36H, CH_3), 1.77 (m, 6H, CH), 1.57 (m, 8H, CH), 1.41 (m, 4H, CH), 1.01 (m, 6H, CH).

The elemental analysis of complex 8

Complex **8**	color		RE (%)	C (%)	H (%)	N (%)
$L_3{}^1La_2$	yellow	Found	19.786	61.240	6.265	5.621
		calcd	19.530	61.582	6.234	5.906

References

(1) Qian, Q.; Tan, Y.; Zhao, B.; Feng, T.; Shen, Q.; Yao, Y. *Org. Lett.* **2014**, *16*, 4516-4519.

(2) Zeng, C.; Yuan, D.; Zhao, B.; Yao, Y. *Org. Lett.* **2015**, *17*, 2242-2245.

(3) Bin, W.; Shoufang, W.; Chungu, X.; Wei, S. *Chem. Eur. J.* **2012**, *18*, 7332-7335.