Supplementary Information

Iron-catalyzed asymmetric intramolecular cyclopropanation reactions using chiral tetramethyl-1, 1'-spirobiindane-based bisoxazoline (TMSI-BOX) ligands

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Zhejiang University, Hangzhou 310027, China.
*Email:lxfok@zju.edu.cn.

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1. X-Ray Structures and Crystal Data of (R_a,*S*,*S*)-1d

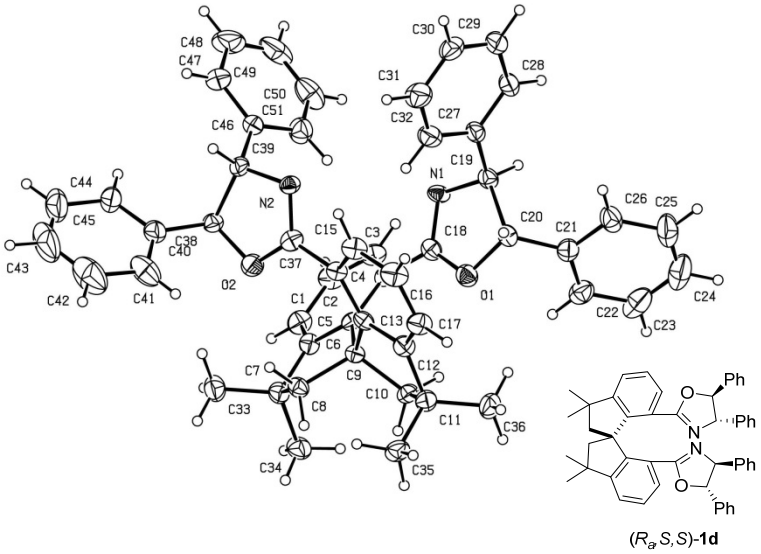


Table S1. Crystal data and structure refinement for (R_a,*S*,*S*)-1d

Bond precision: C-C = 0.0105 A Wavelength = 1.54178

Cell: a = 19.3333 (8) b = 13.2563 (5) c = 24.6689 (10)

alpha = 90 beta = 108.952 gamma = 90

Temperature: 170 K

	Calculated	Reported
Volume	5979.6 (4)	5979.6 (4)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C51 H46 N2 O2	C51 H46 N2 O2
Sum formula	C51 H46 N2 O2	C51 H46 N2 O2
Mr	718.90	718.90
Dx, g cm^{-3}	1.198	1.198
Z	6	6
Mu (mm^{-1})	0.559	0.559
F000	2292.0	2292.0

F000’	2298.17	
h,k,lmax	23,15,29	23,15,29
Nref	22018[11526]	21886
Tmin, Tmax	0.865,0.904	0.547,0.753
Tmin’	0.865	

Correction method = # Reported T Limits: Tmin = 0.547Tmax = 0.753

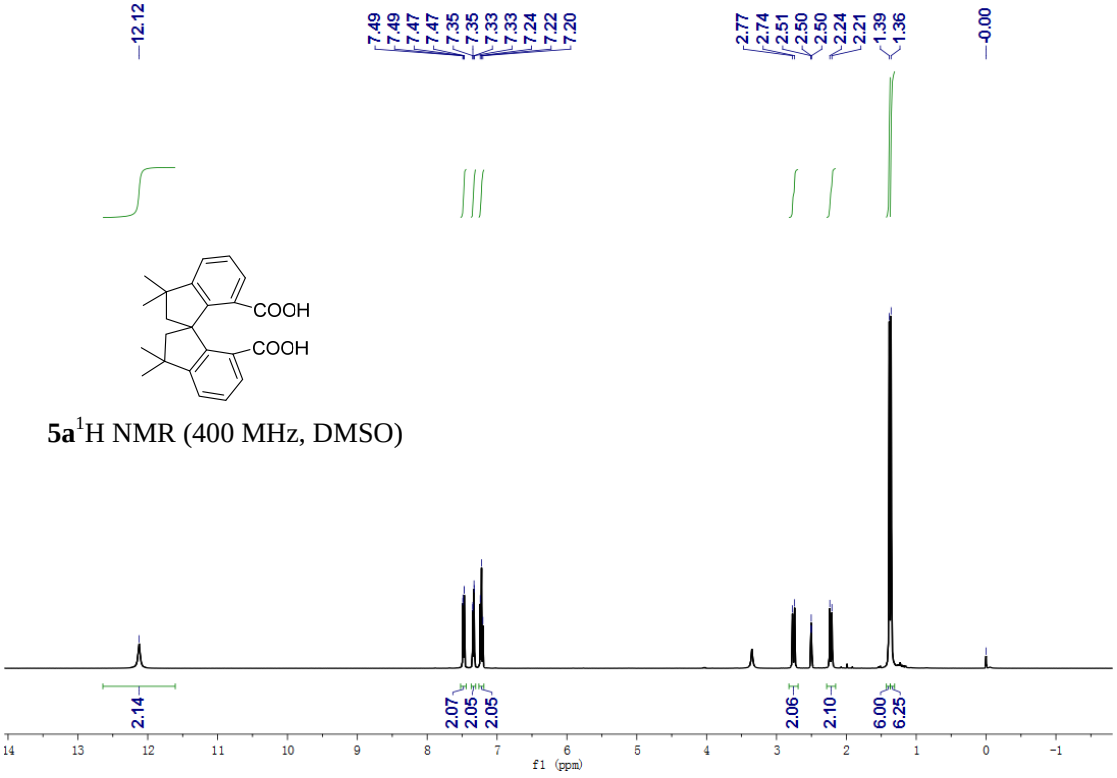
AbsCorr = MULTI-SCAN

Data completeness = 1.90/0.99 Theta (max) = 68.488

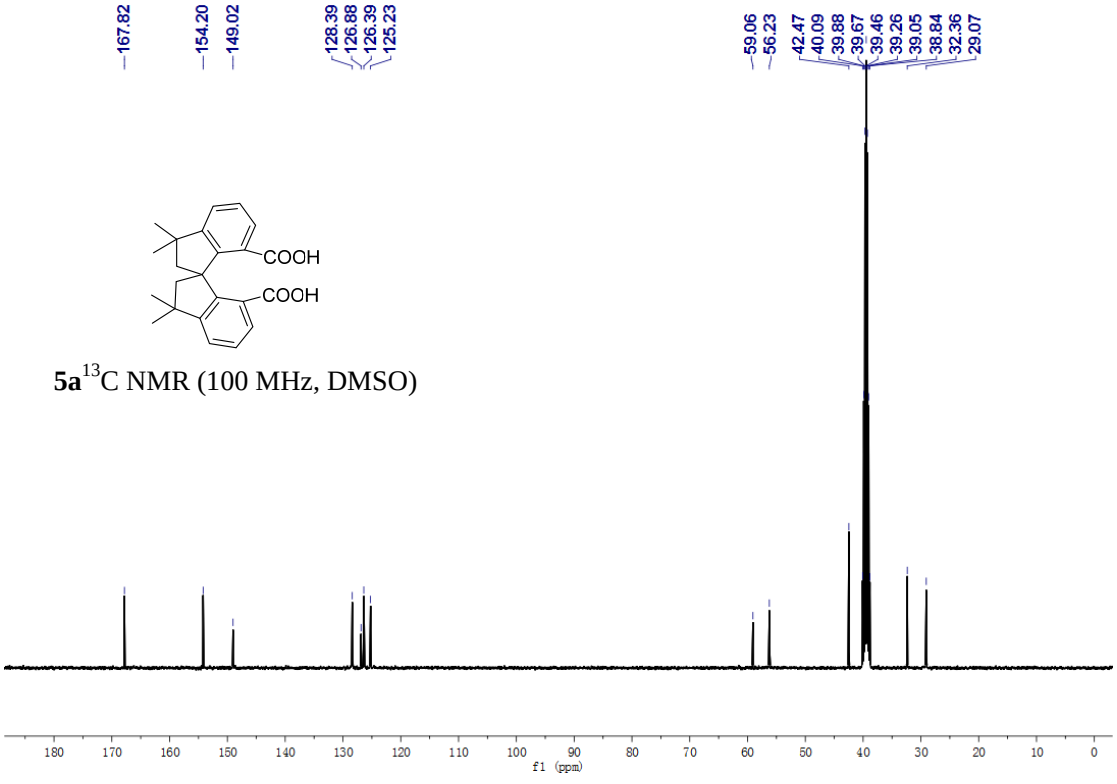
R (reflections) = 0.0802(19537) wR2 (reflections) = 0.2237(21886)

S = 1.028Npar = 1498

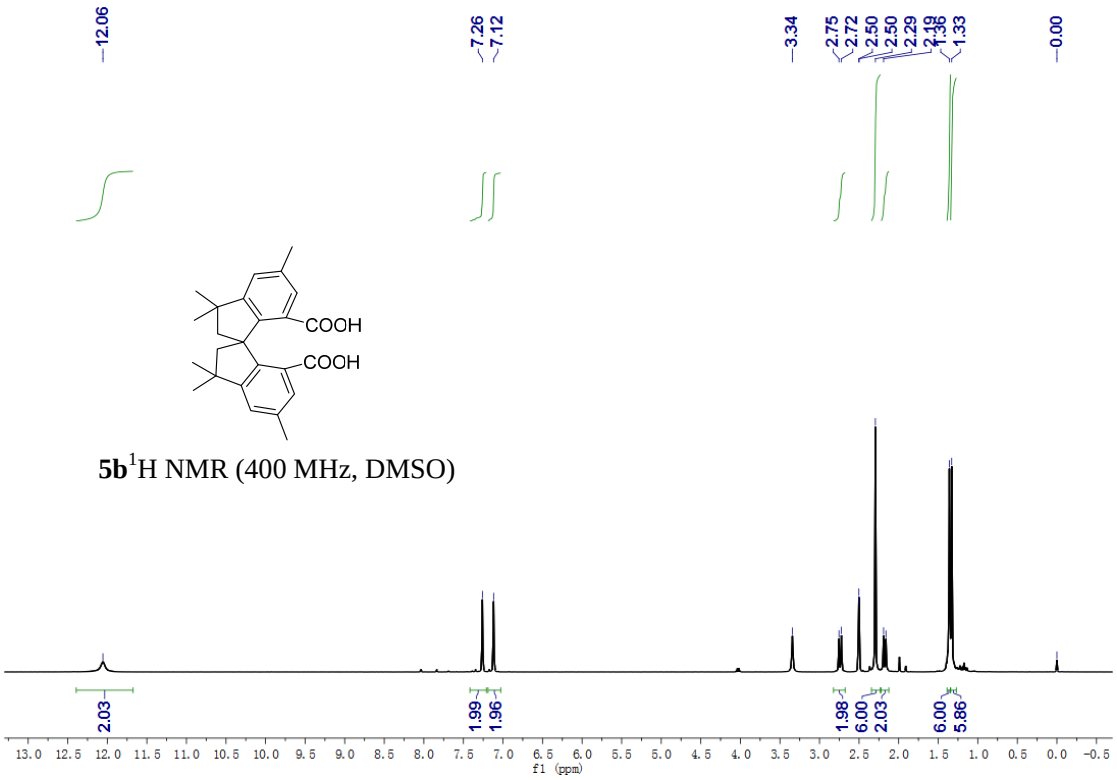
2. Copies ofNMR and HPLC spectra



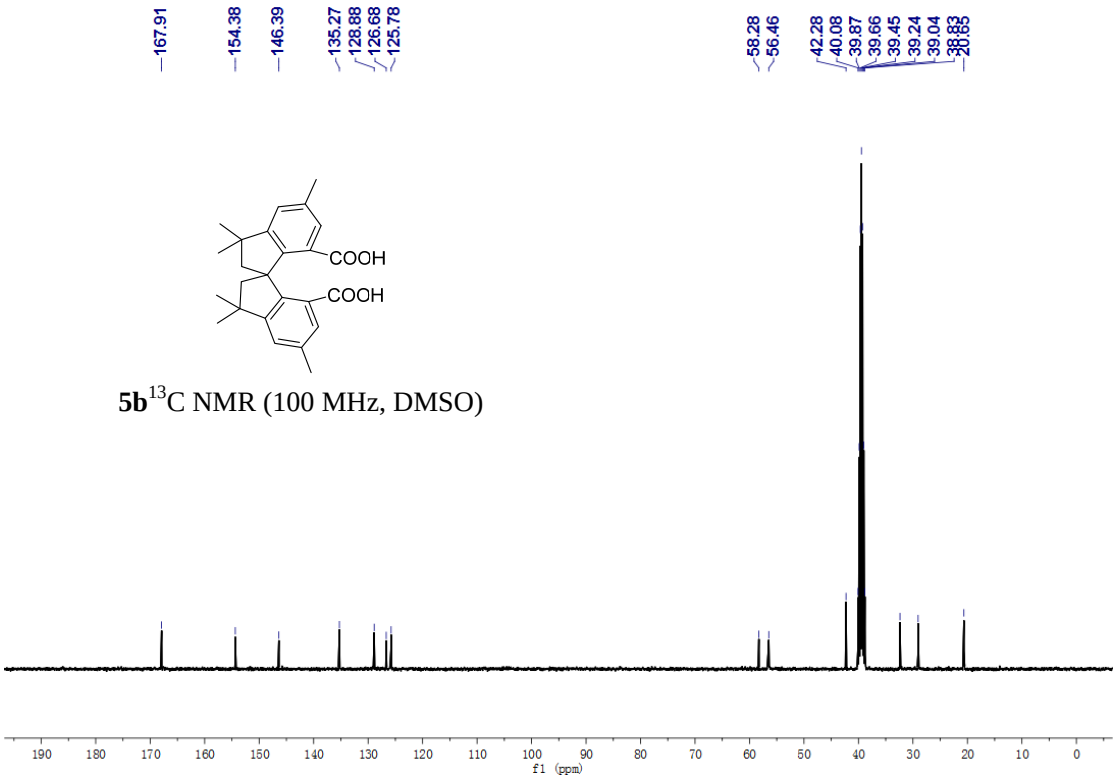
5a ^{1}H NMR (400 MHz, DMSO)



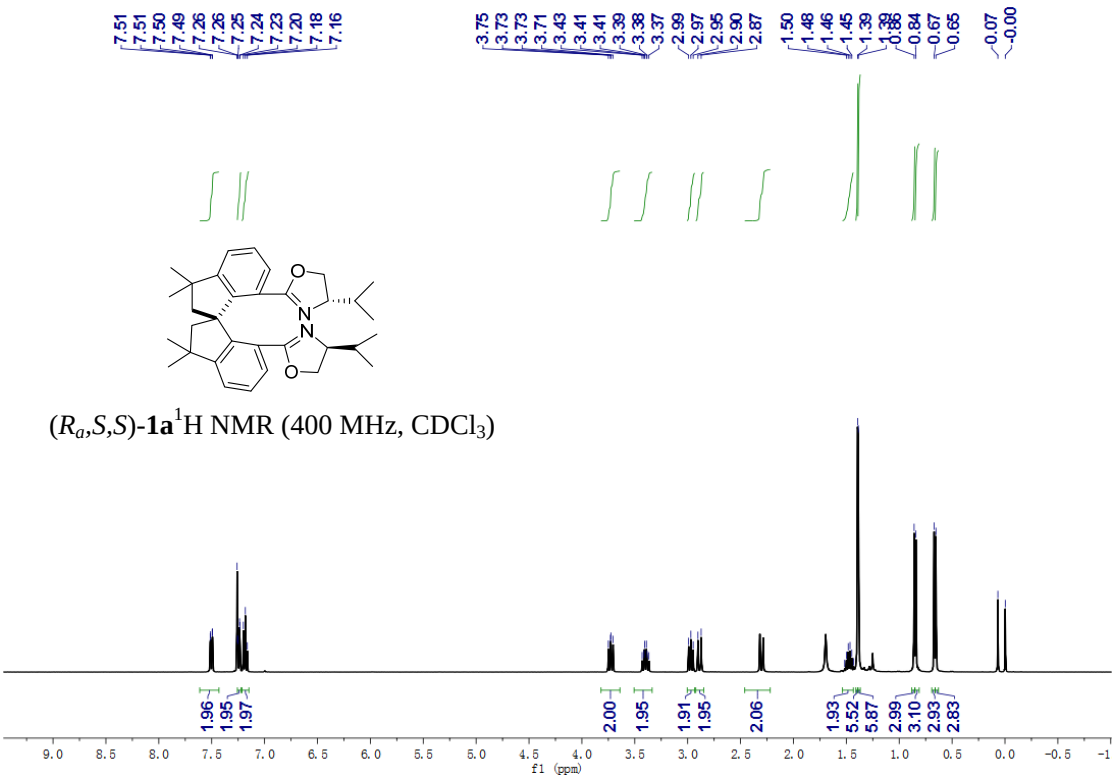
5a ^{13}C NMR (100 MHz, DMSO)



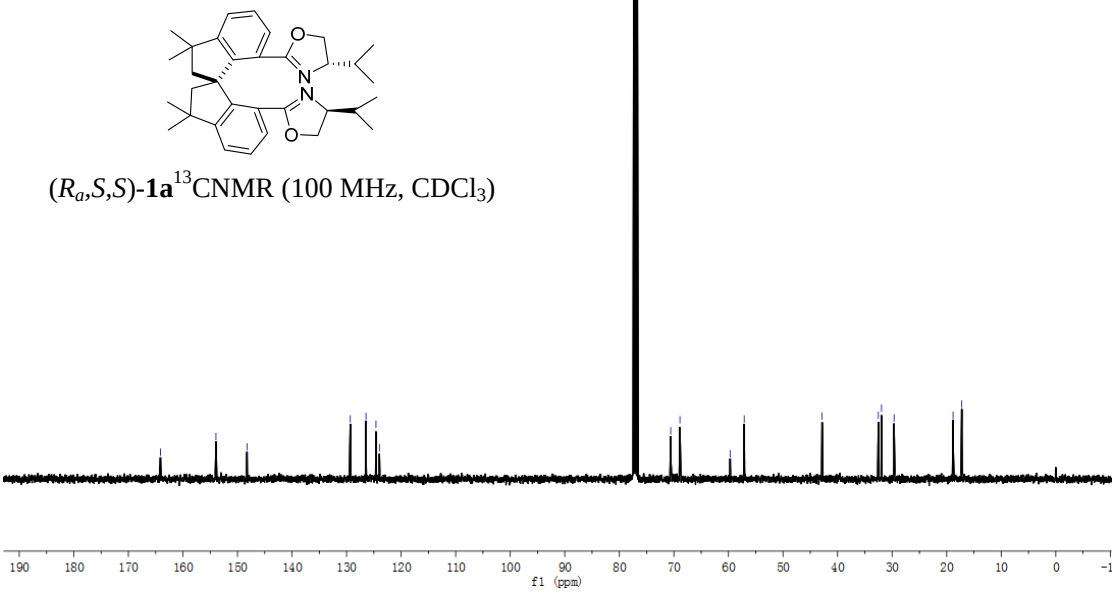
5b ^{1}H NMR (400 MHz, DMSO)



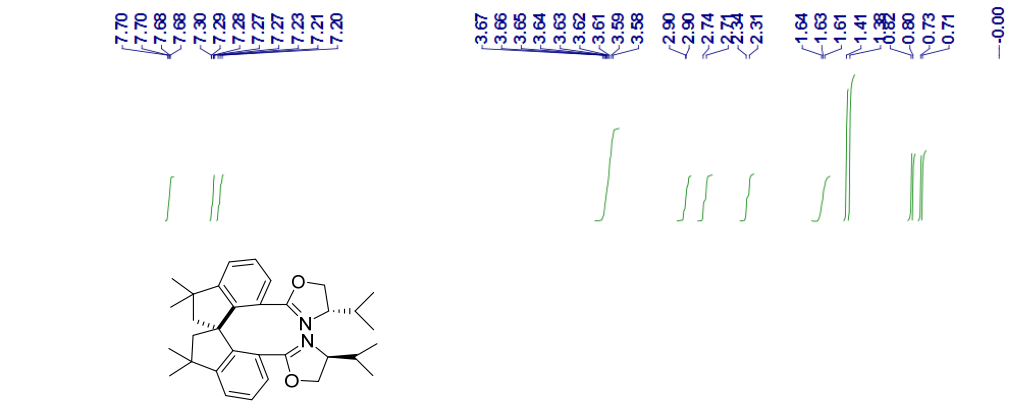
5b ^{13}C NMR (100 MHz, DMSO)



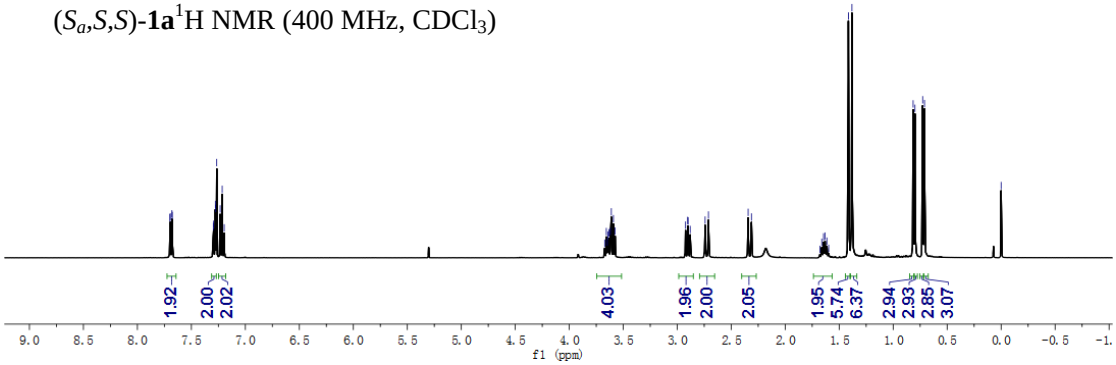
(R_a,*S*,*S*)-**1a** ^{1}H NMR (400 MHz, $CDCl_3$)

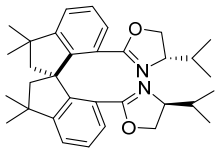


(R_a,*S*,*S*)-**1a** ^{13}CNMR (100 MHz, $CDCl_3$)

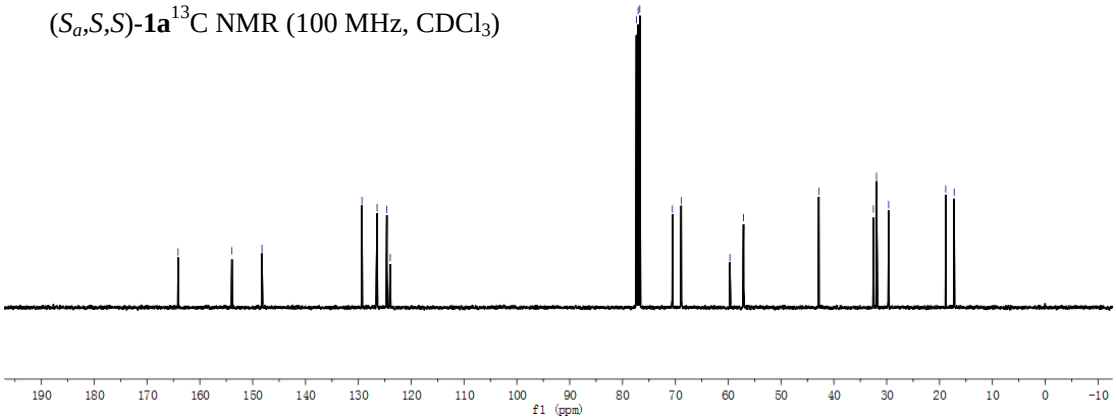


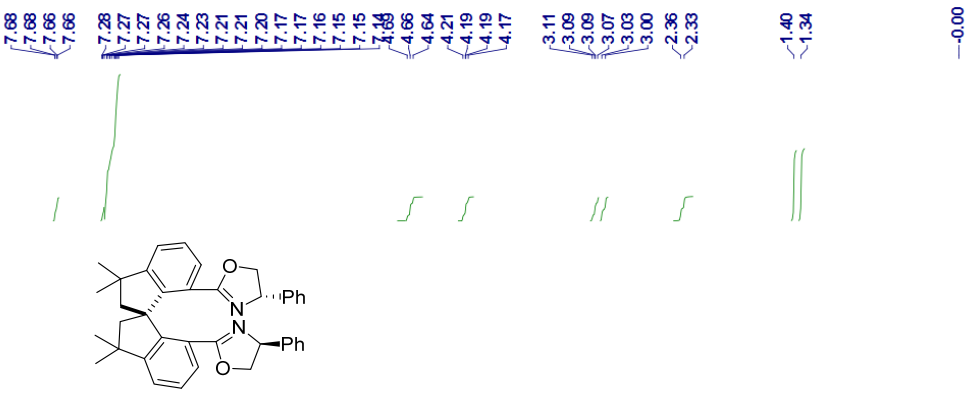
(S_a,*S*,*S*)-**1a** ^{1}H NMR (400 MHz, $CDCl_3$)



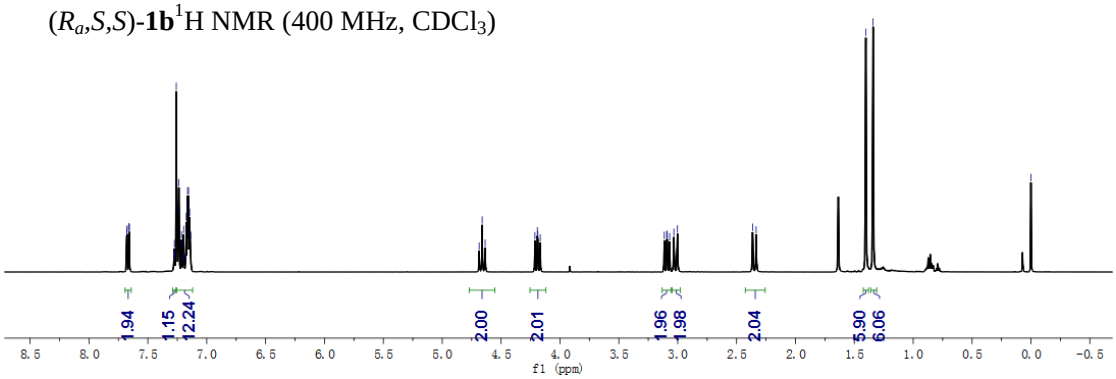


(S_a,*S*,*S*)-**1a** ^{13}C NMR (100 MHz, $CDCl_3$)

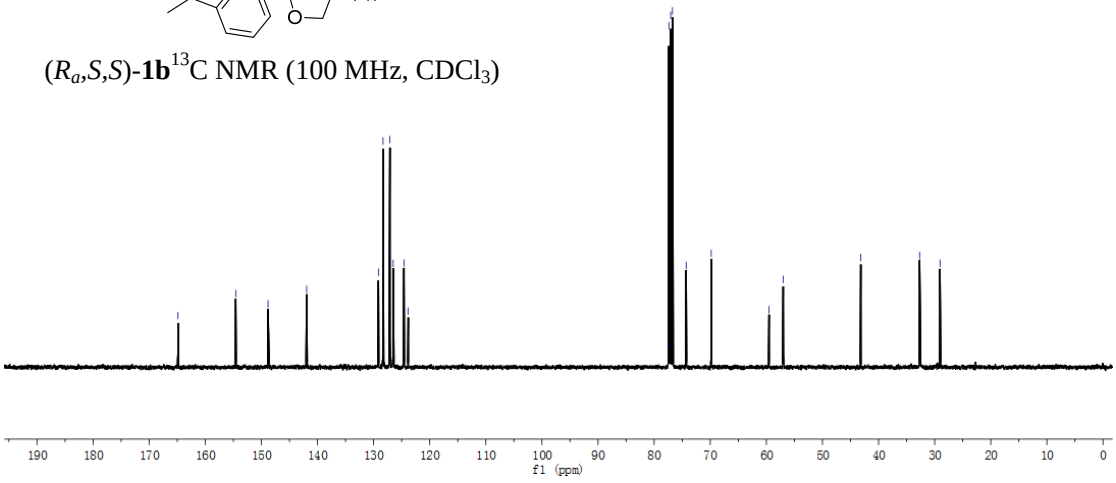


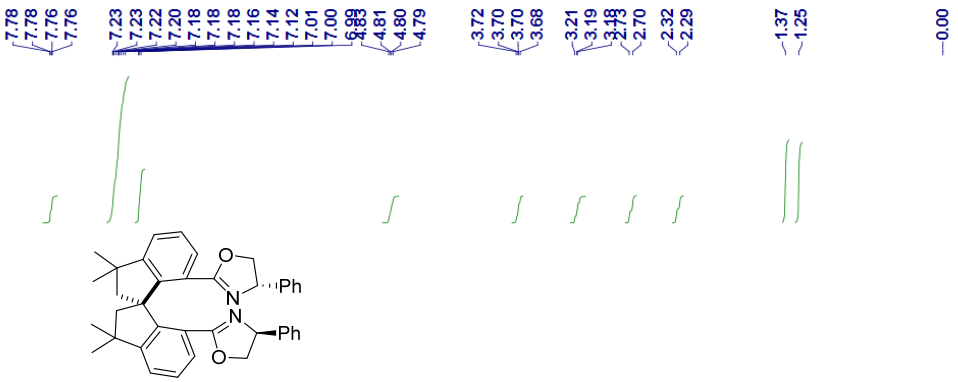


(R_a,*S*,*S*)-**1b** ^{1}H NMR (400 MHz, $CDCl_3$)

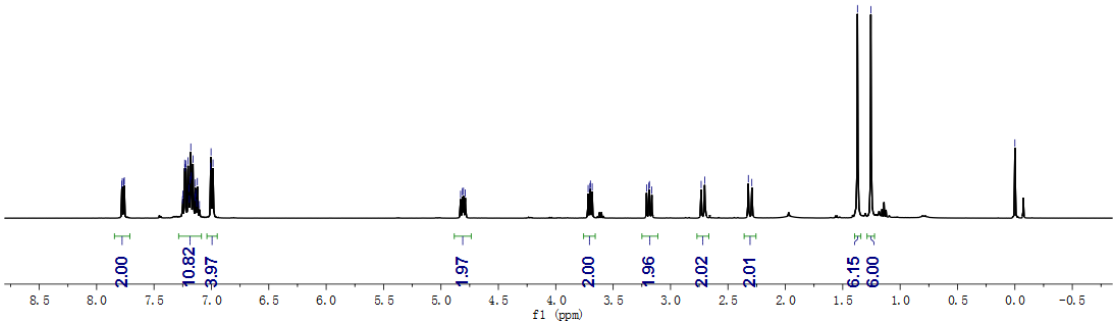


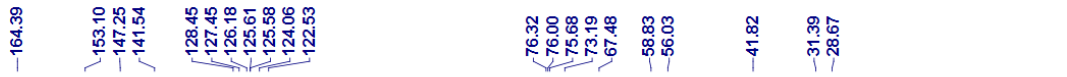
(R_a,*S*,*S*)-**1b** ^{13}C NMR (100 MHz, $CDCl_3$)

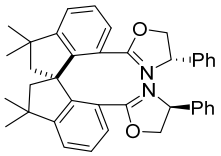




(S_a,*S*,*S*)-**1b** ^{1}H NMR (400 MHz, $CDCl_3$)







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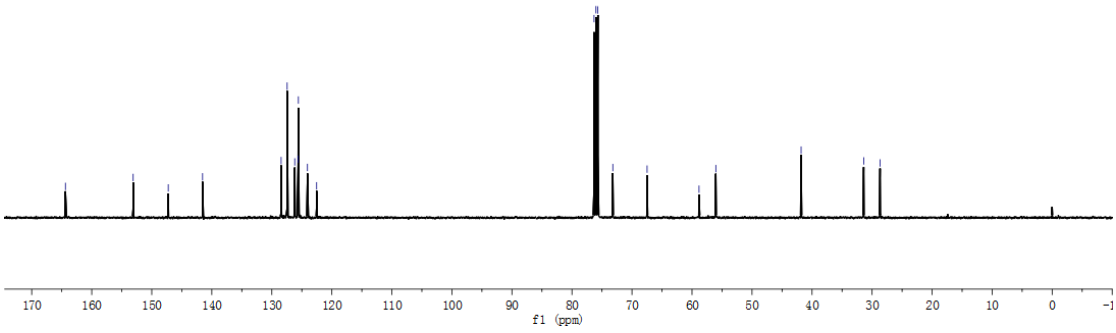
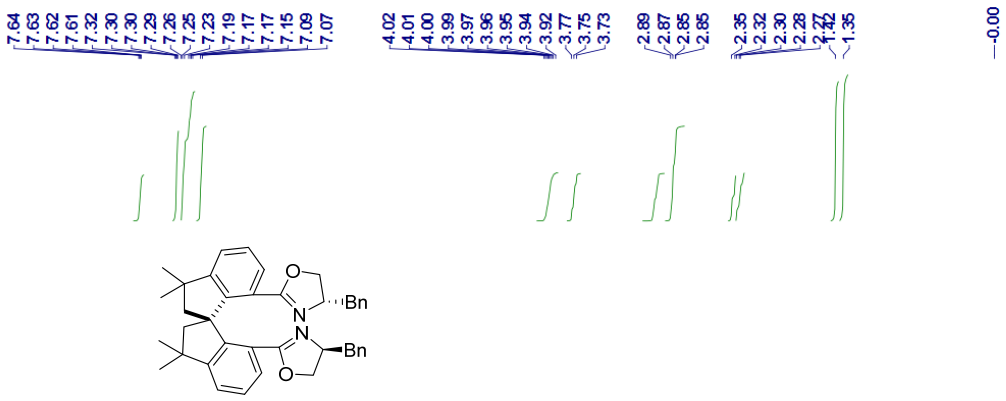
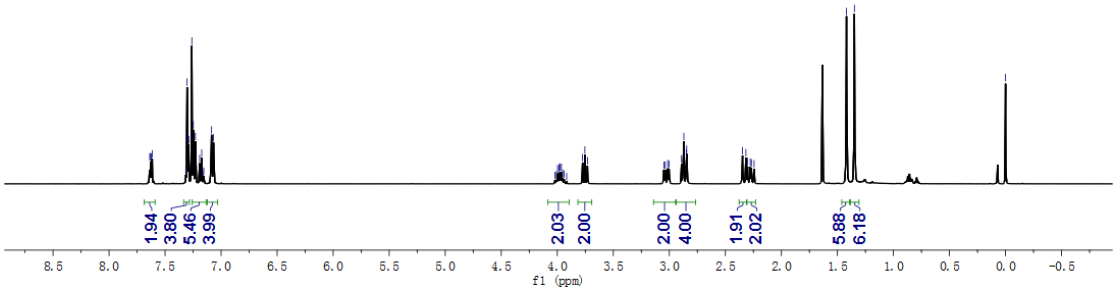
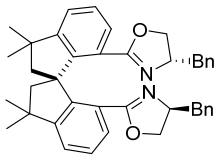


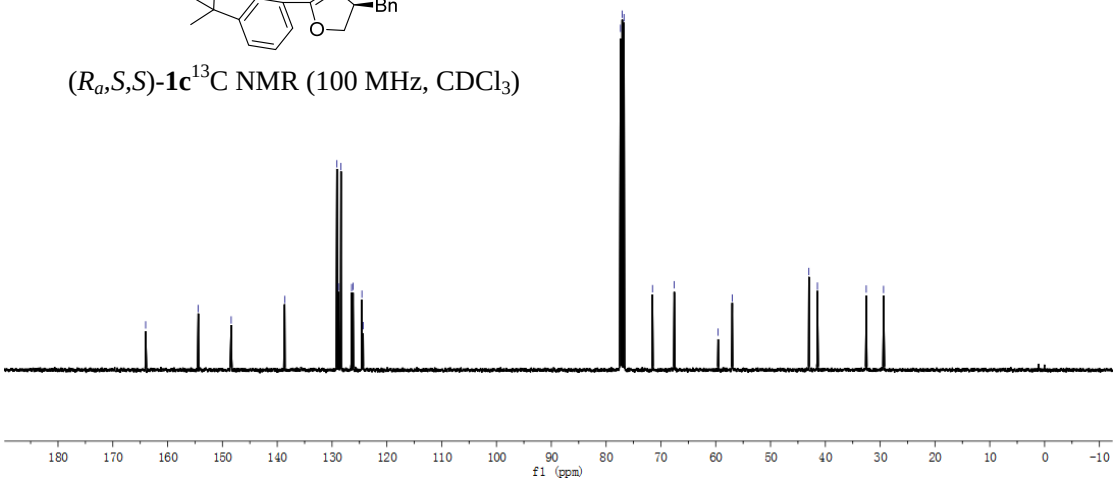


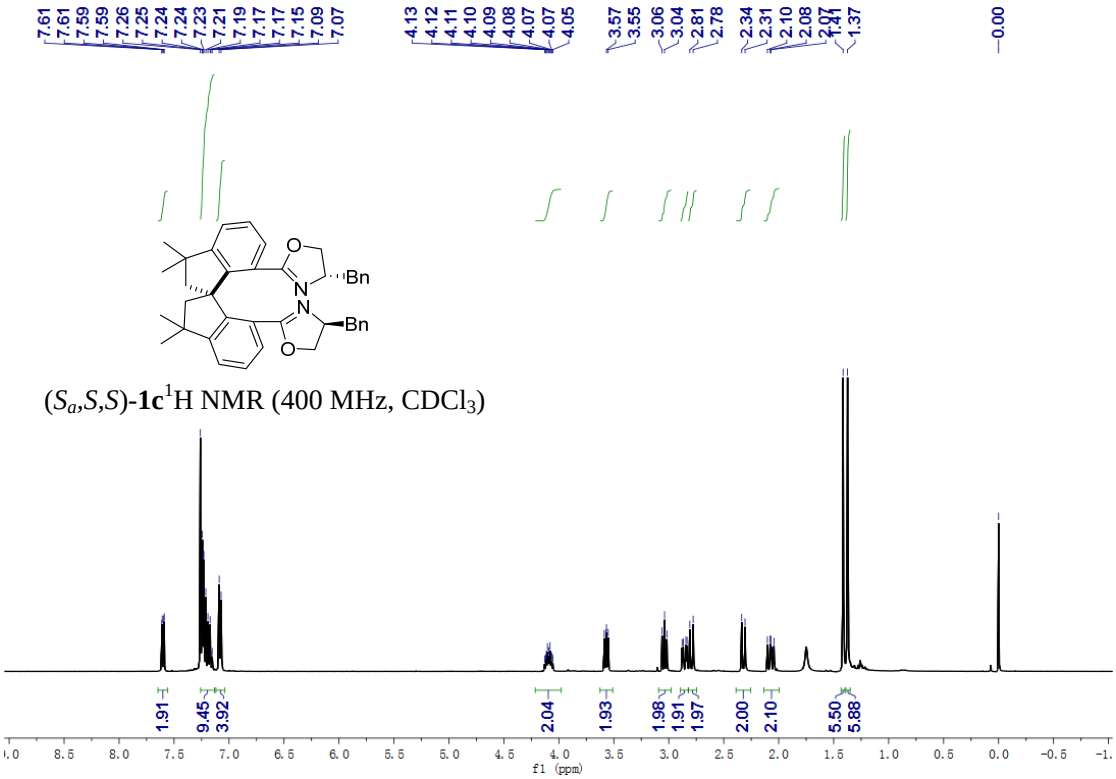
(R_a,*S*,*S*)-**1c** ^{1}H NMR (400 MHz, $CDCl_3$)





(R_a,*S*,*S*)-**1c** ^{13}C NMR (100 MHz, $CDCl_3$)





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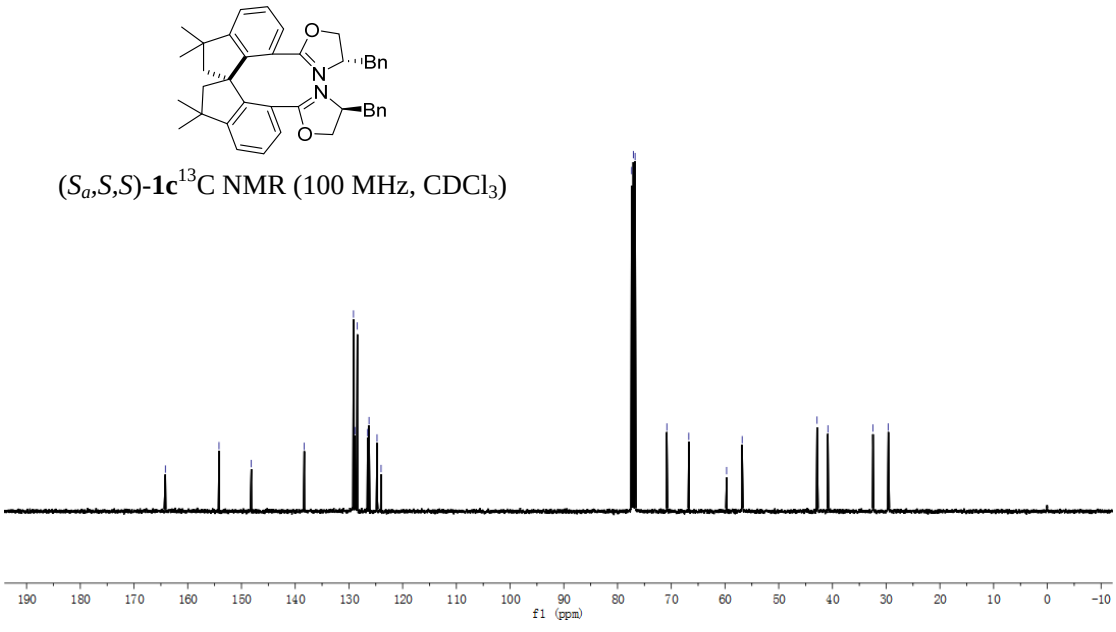

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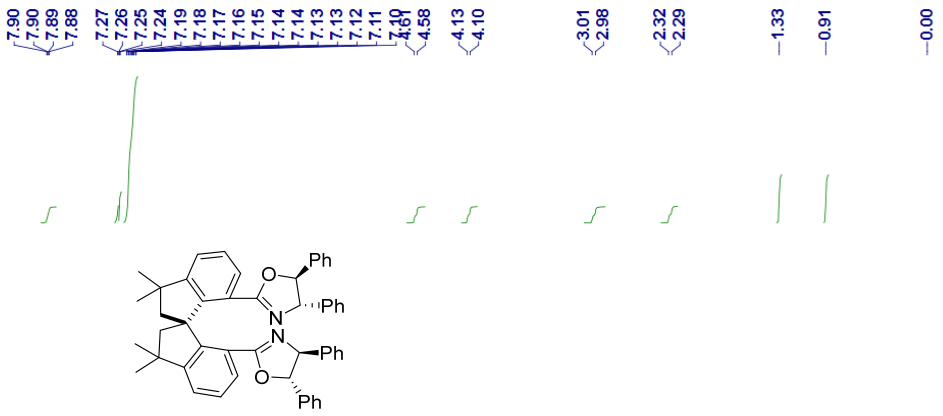
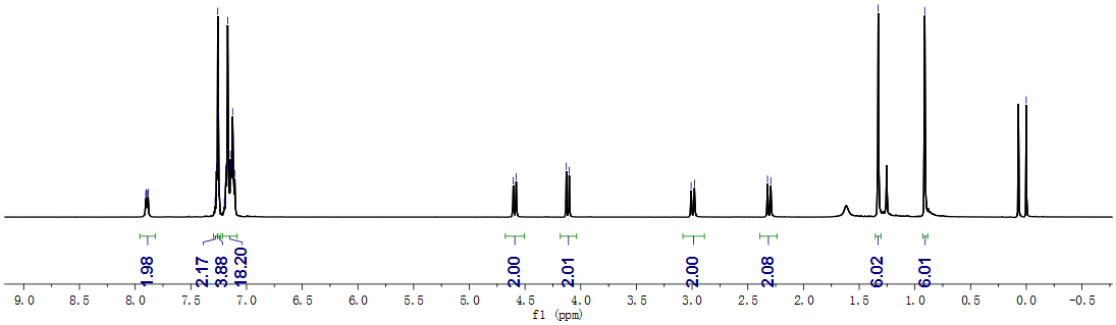
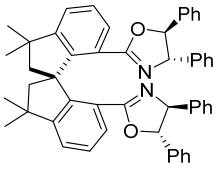
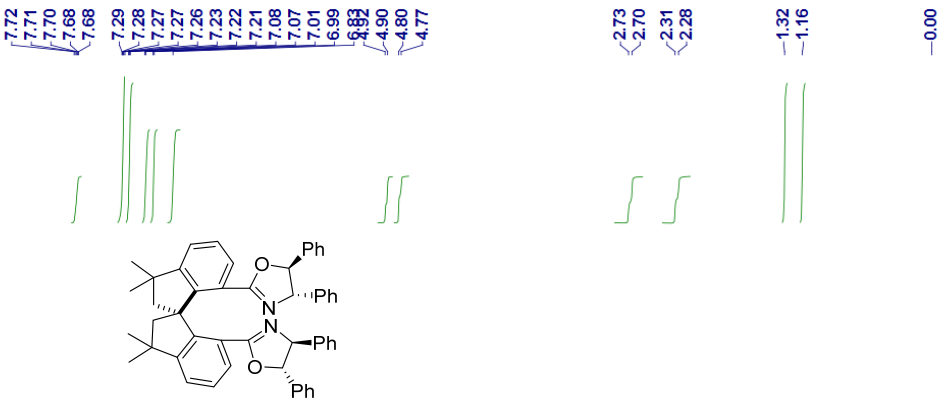


(R_a,4*S*,4'*S*,5*S*,5'*S*)-**1d**^{1}H NMR (400 MHz, $CDCl_3$)





(R_a,4*S*,4'*S*,5*S*,5'*S*)-**1d**^{13}C NMR (100 MHz, $CDCl_3$)



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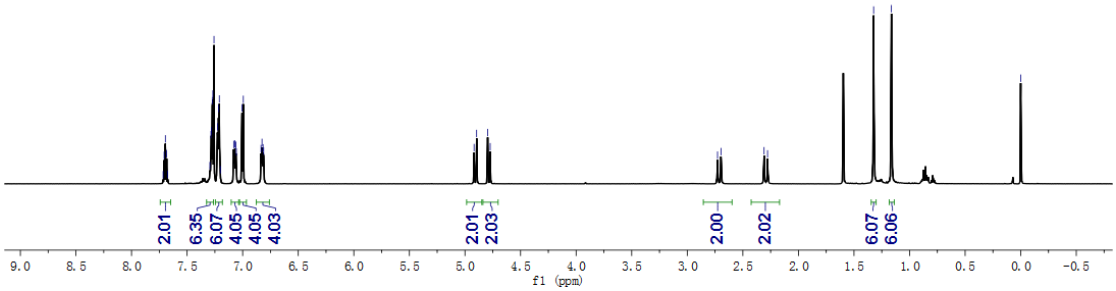
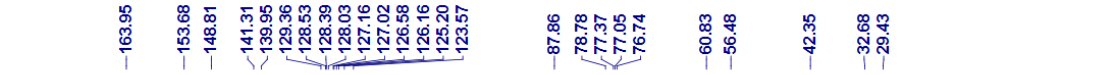
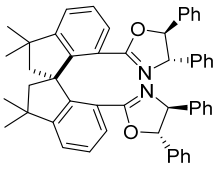
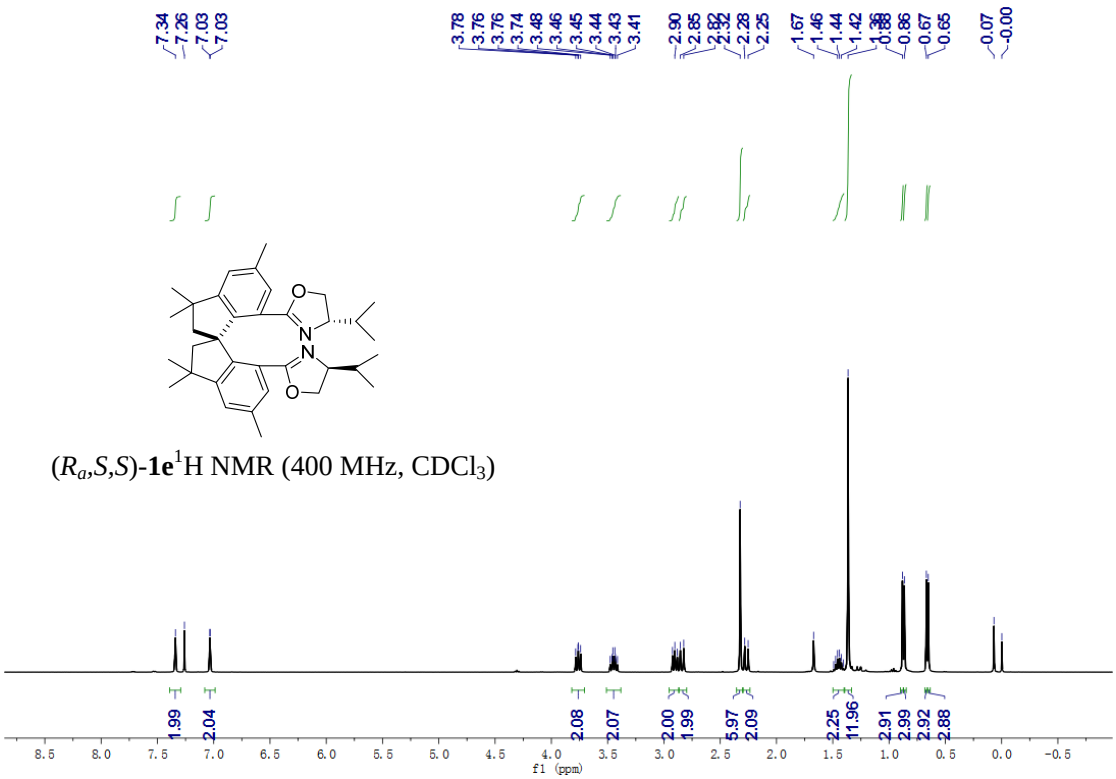


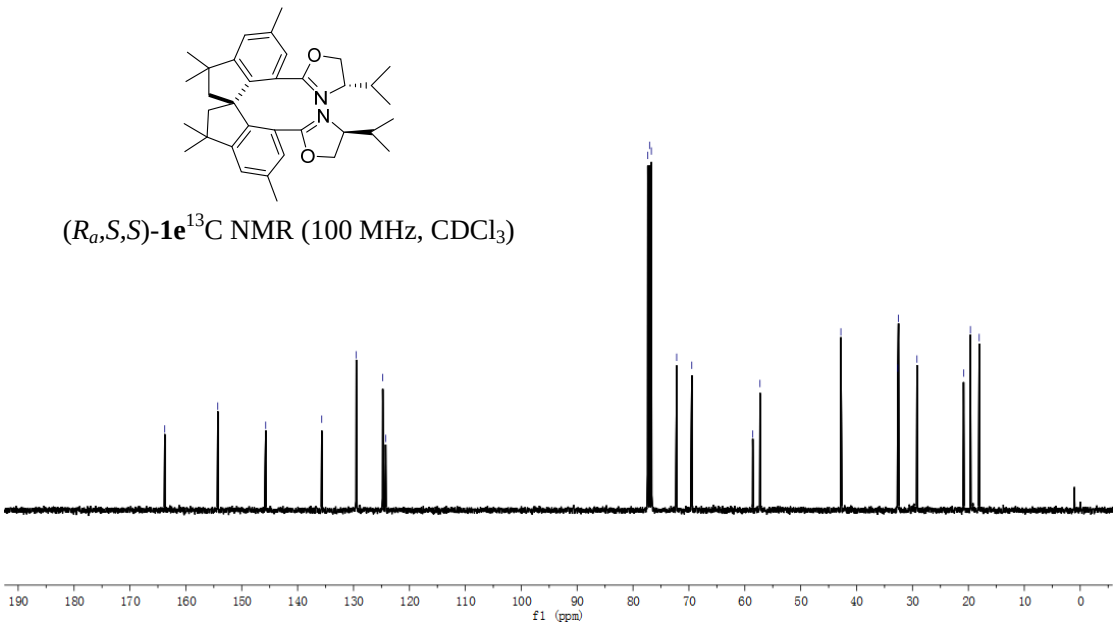




(S_a,4*S*,4'*S*,5*S*,5'*S*)-**1d**^{13}C NMR (100 MHz, $CDCl_3$)



(R_a,*S*,*S*)-**1e** ^{1}H NMR (400 MHz, $CDCl_3$)



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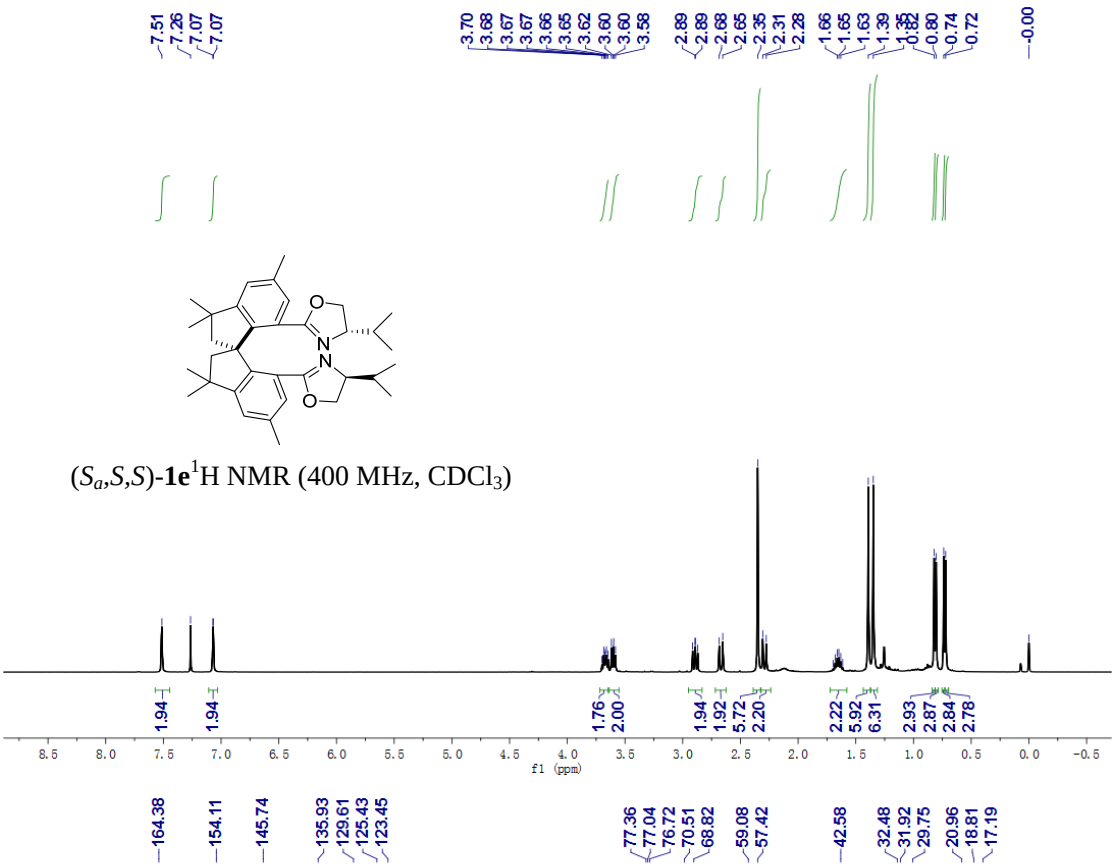
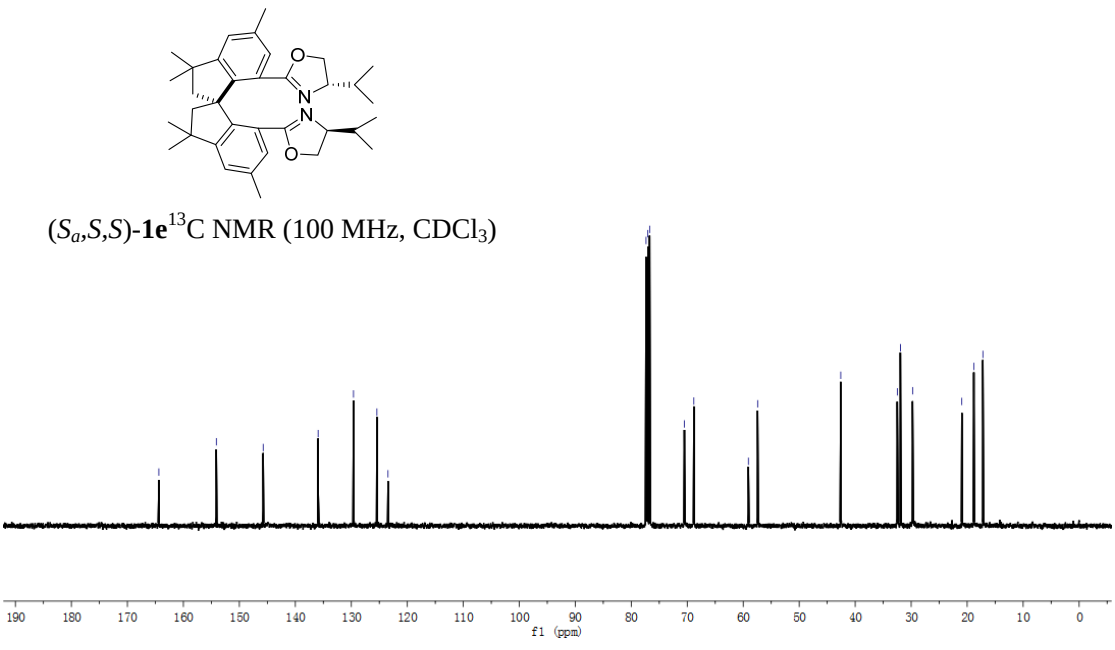
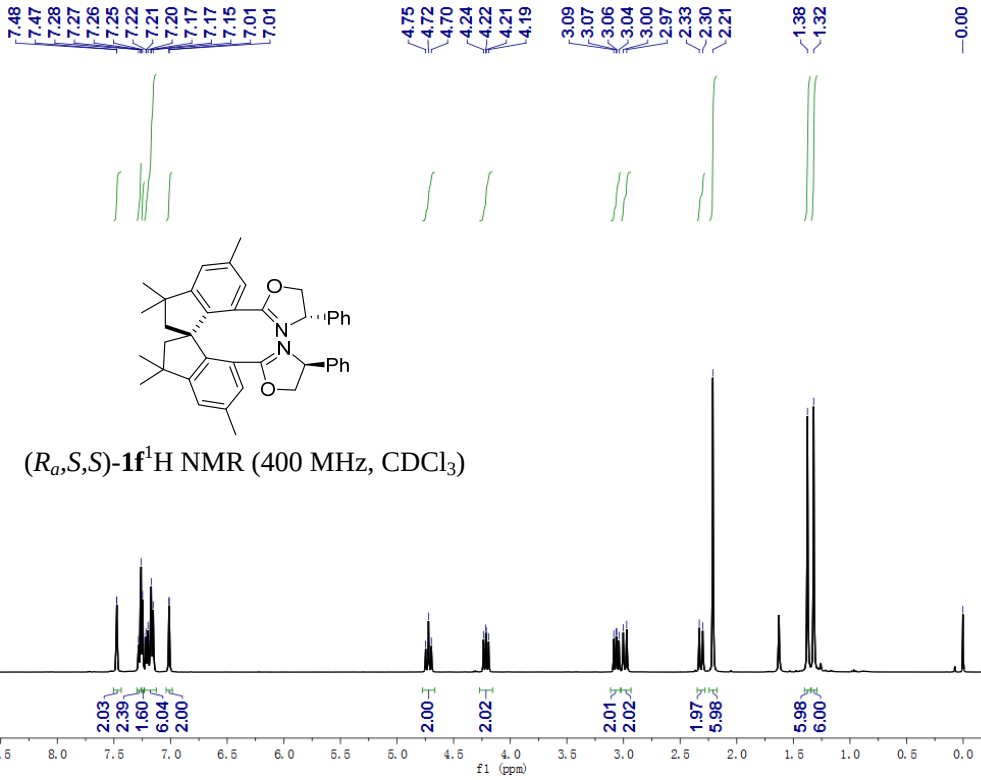


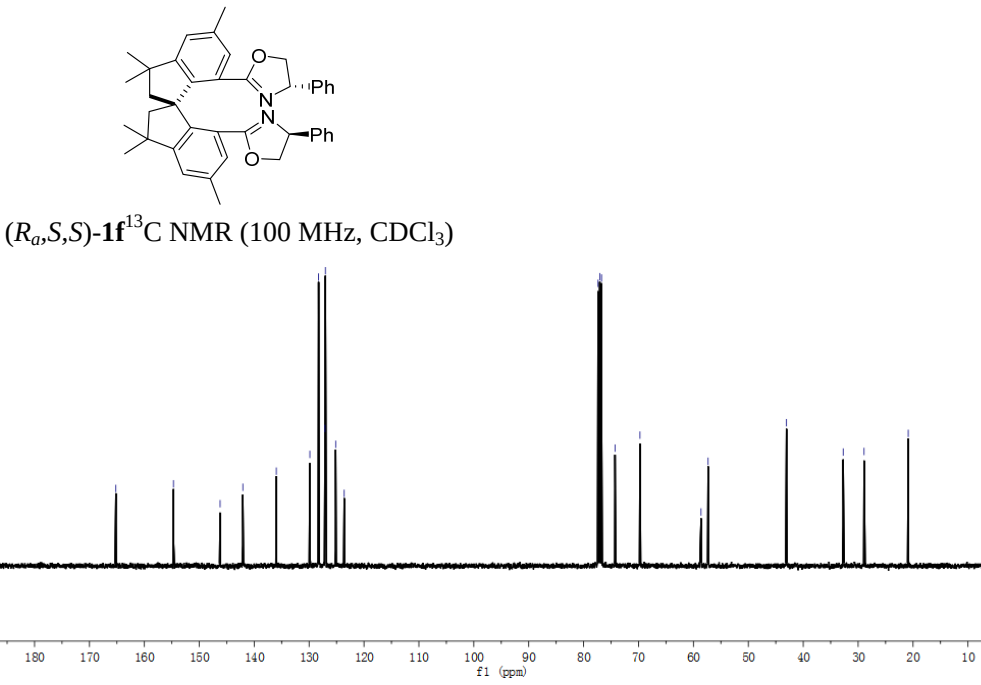
(S_a,*S*,*S*)-**1e** ^{1}H NMR (400 MHz, $CDCl_3$)



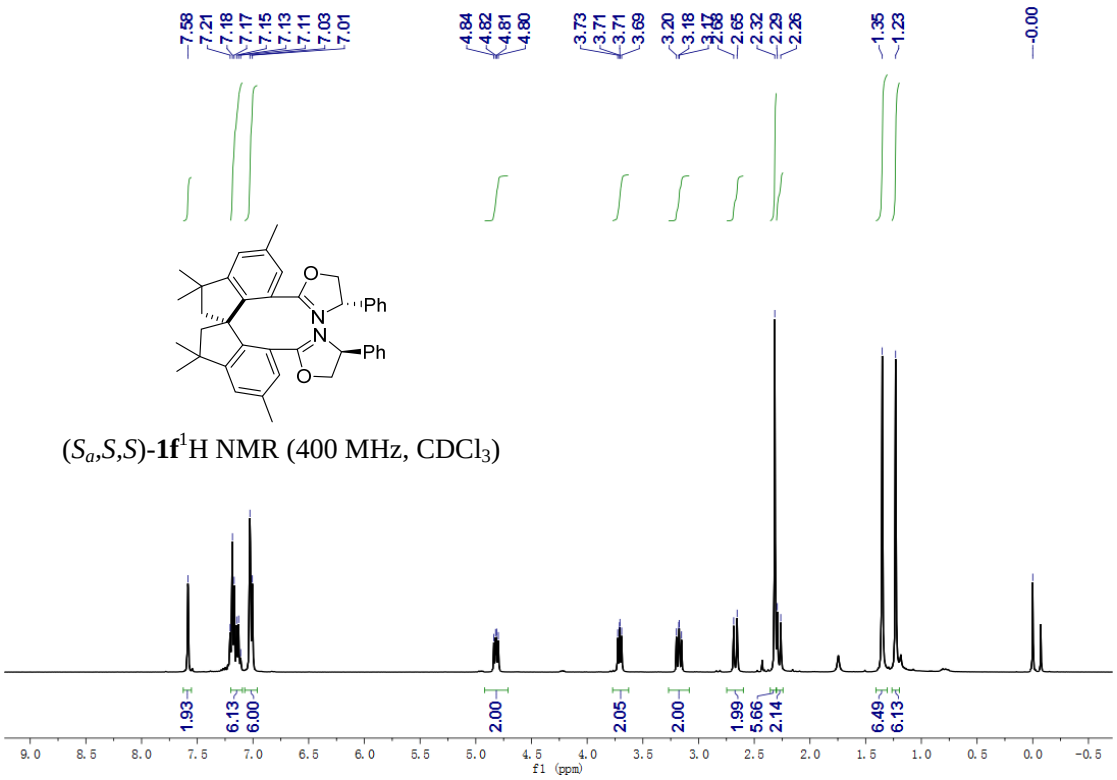
(S_a,*S*,*S*)-**1e** ^{13}C NMR (100 MHz, $CDCl_3$)



(R_a,*S*,*S*)-**1f** ^{1}H NMR (400 MHz, $CDCl_3$)



(R_a,*S*,*S*)-**1f** ^{13}C NMR (100 MHz, $CDCl_3$)



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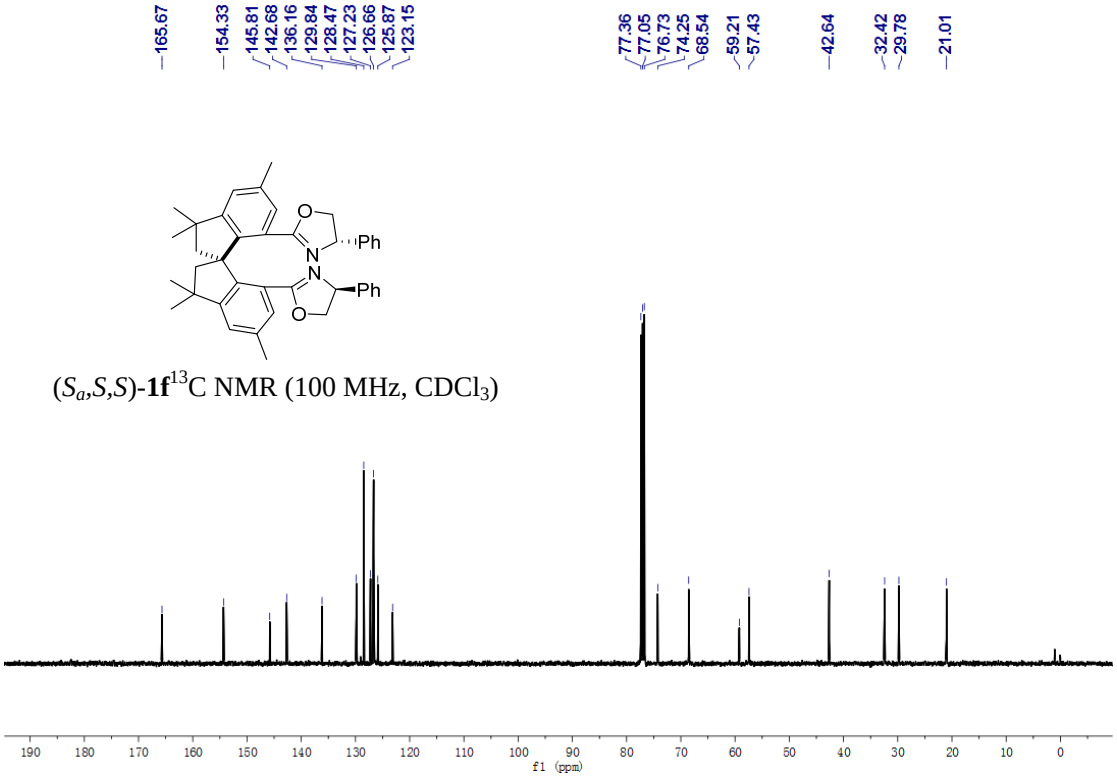
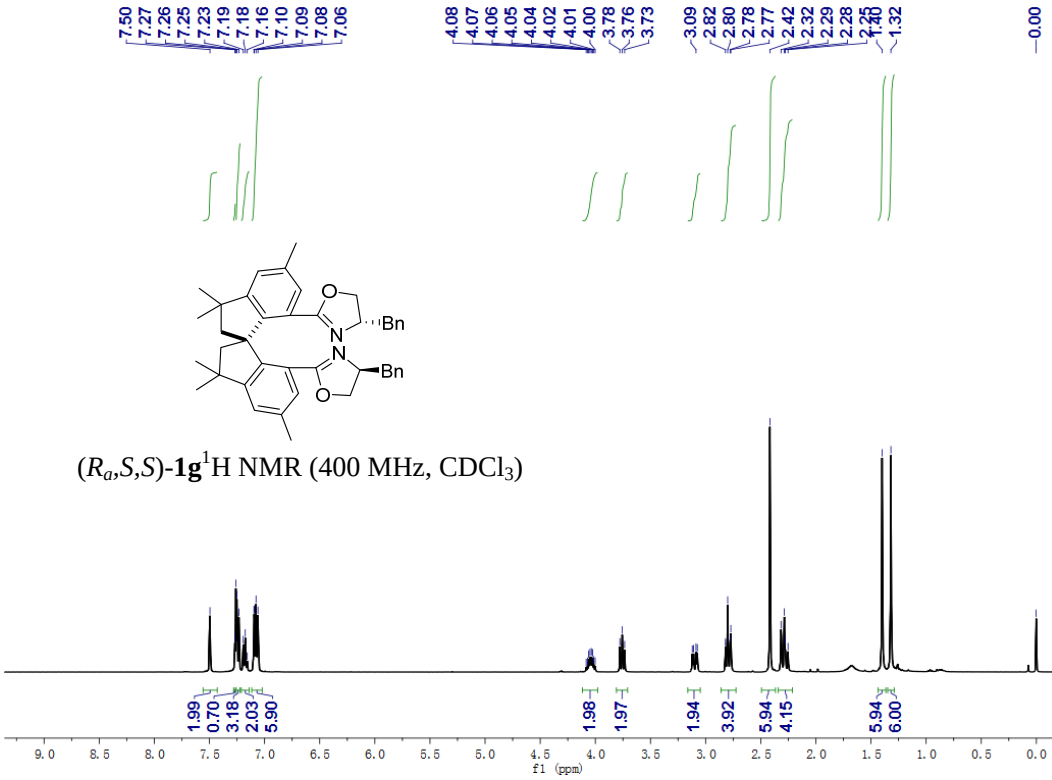
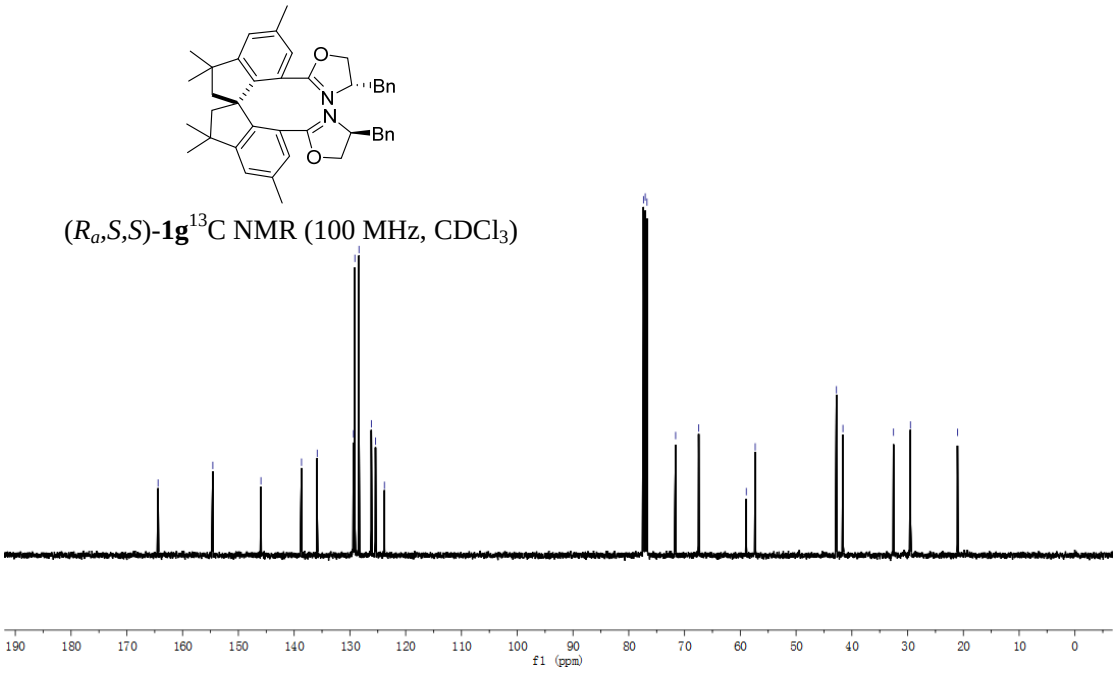


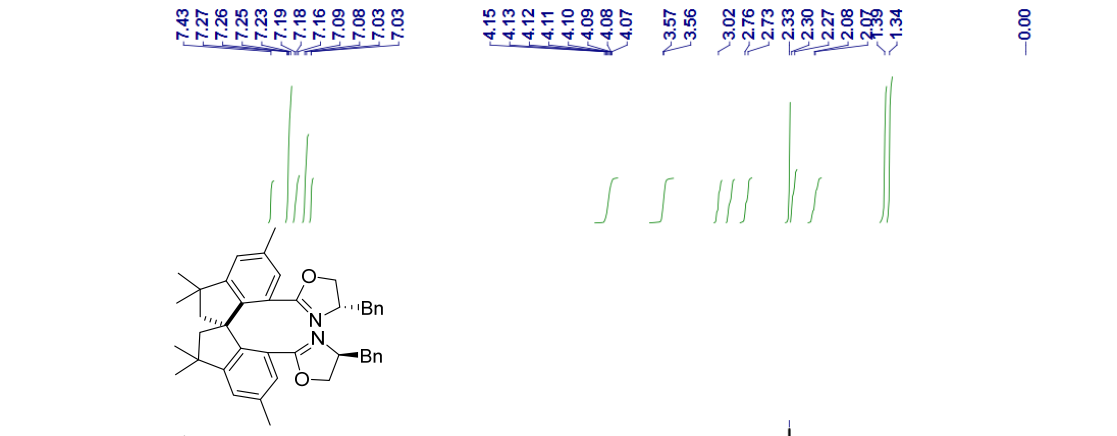
(S_a,*S*,*S*)-**1f** ^{13}C NMR (100 MHz, $CDCl_3$)



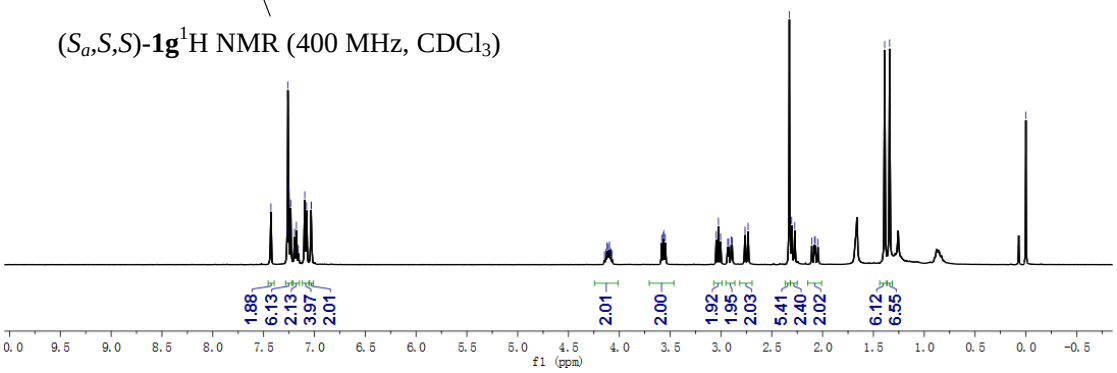
(R_a,*S*,*S*)-**1g** ^{1}H NMR (400 MHz, $CDCl_3$)

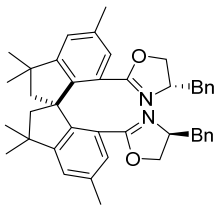


(R_a,*S*,*S*)-**1g** ^{13}C NMR (100 MHz, $CDCl_3$)

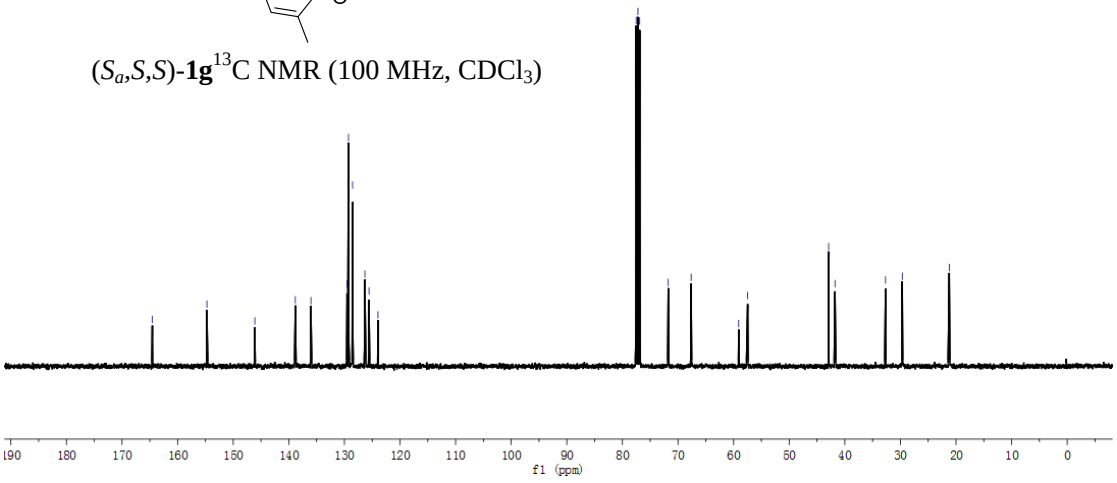


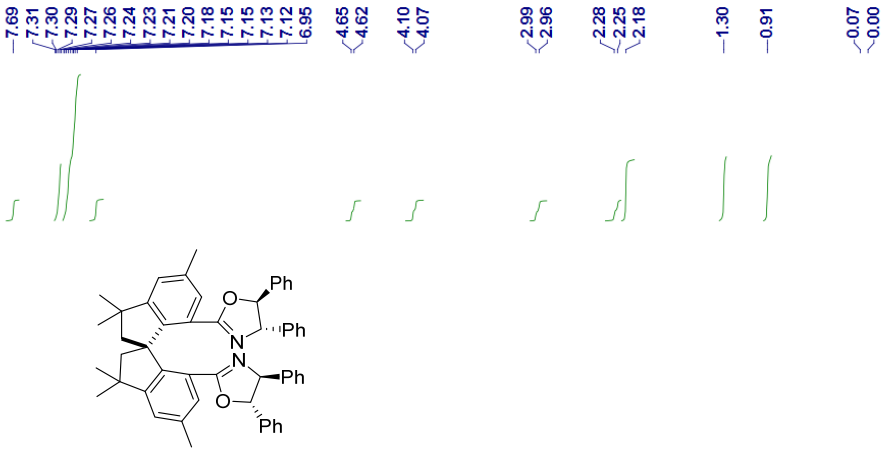
(S_a,*S*,*S*)-**1g** ^{1}H NMR (400 MHz, $CDCl_3$)



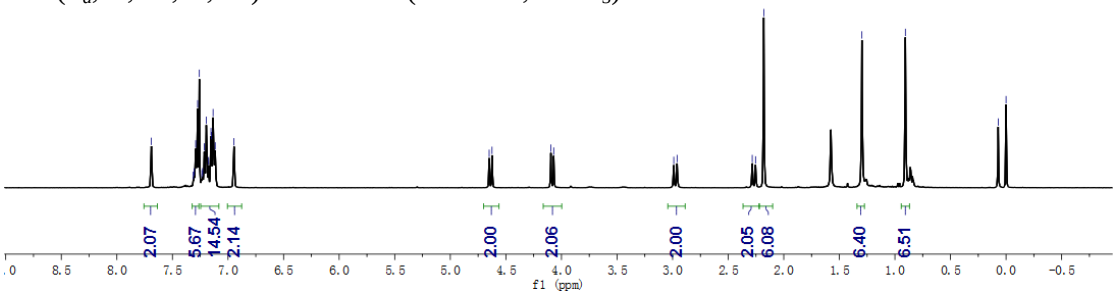


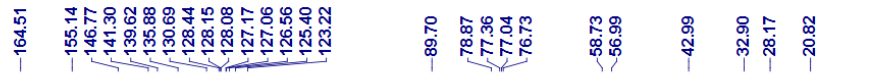
(S_a,*S*,*S*)-**1g** ^{13}C NMR (100 MHz, $CDCl_3$)

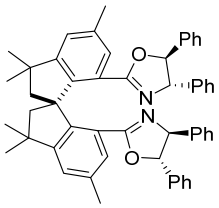




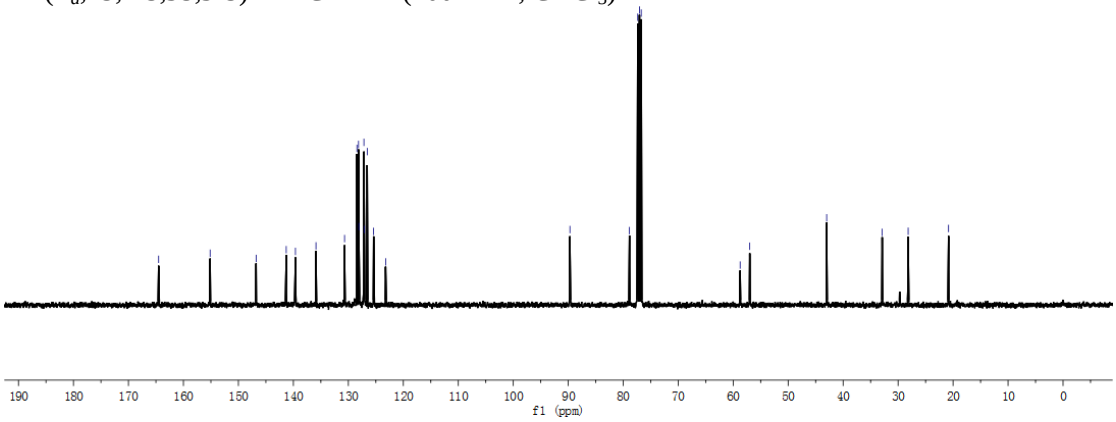
(R_a,4*S*,4'*S*,5*S*,5'*S*)-**1h** ^{1}H NMR (400 MHz, $CDCl_3$)

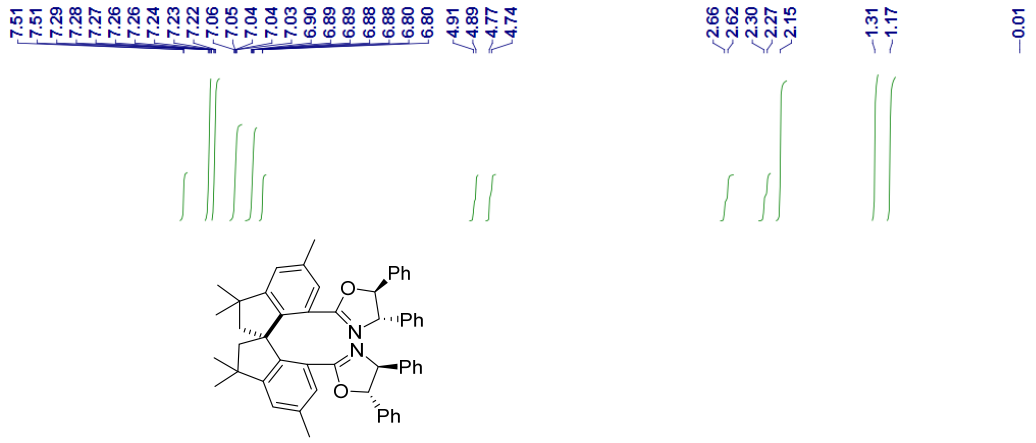




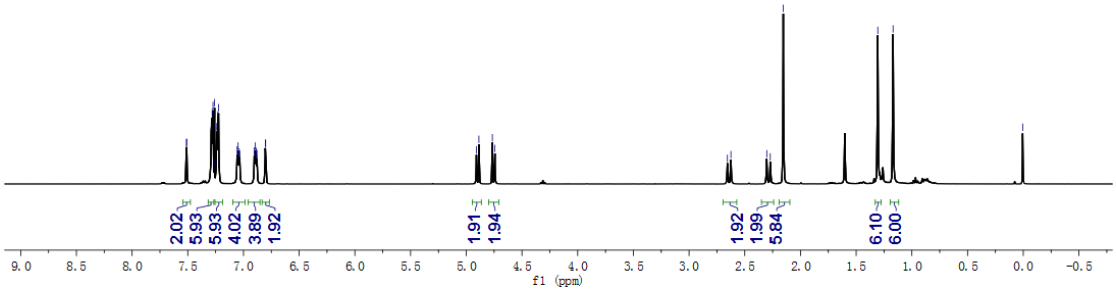


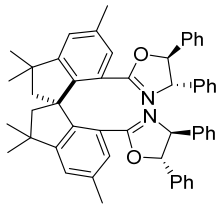
(R_a,4*S*,4'*S*,5*S*,5'*S*)-**1h** ^{13}C NMR (100 MHz, $CDCl_3$)



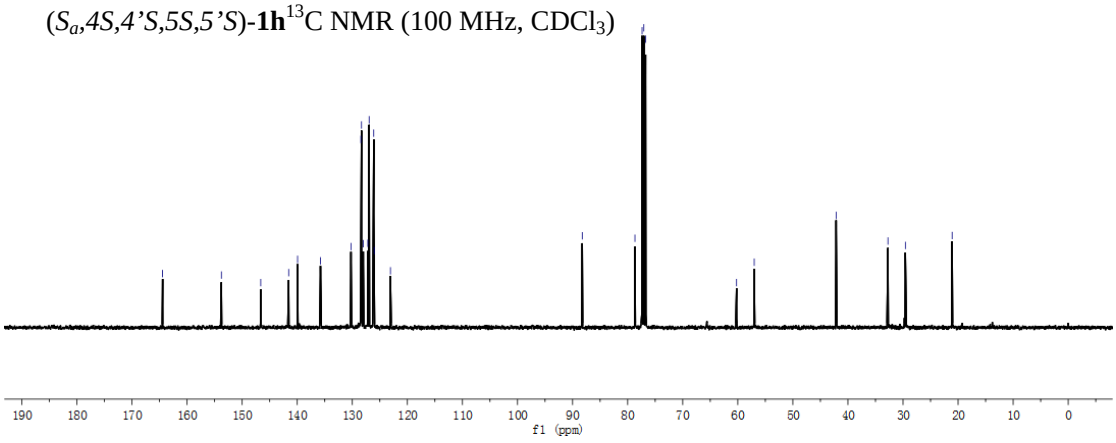


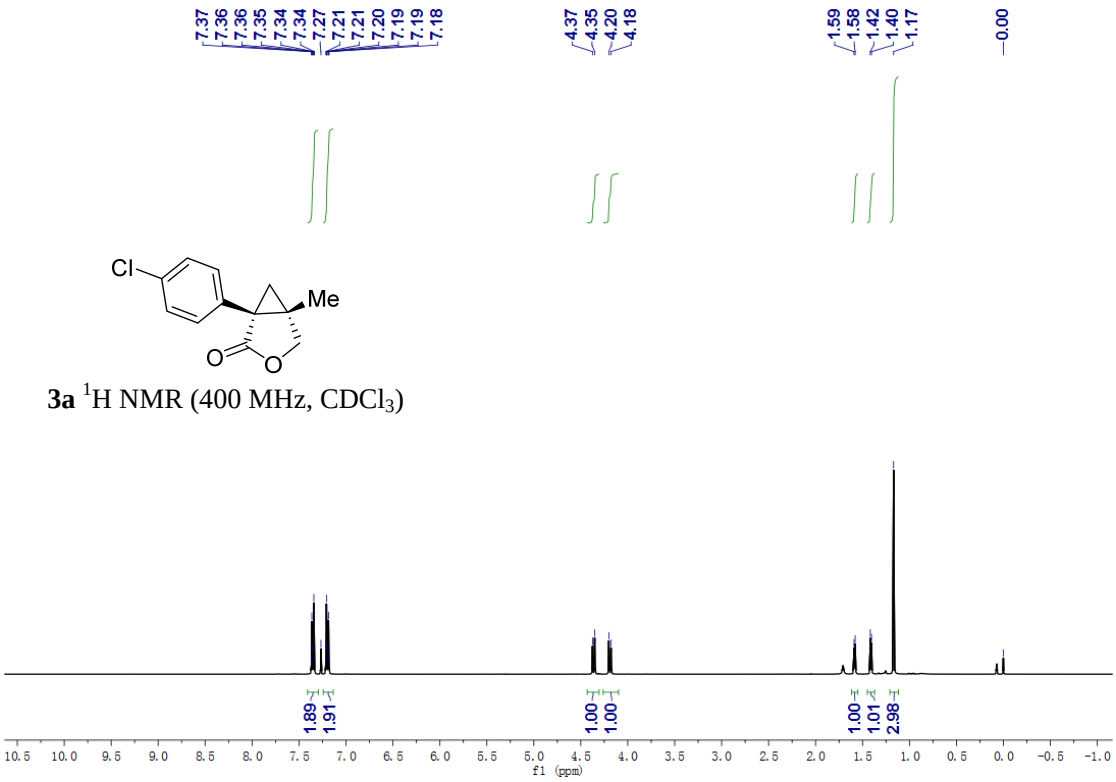
(*S*$_a$,4*S*,4'*S*,5*S*,5'*S*)-**1h**^{1}H NMR (400 MHz, $CDCl_3$)



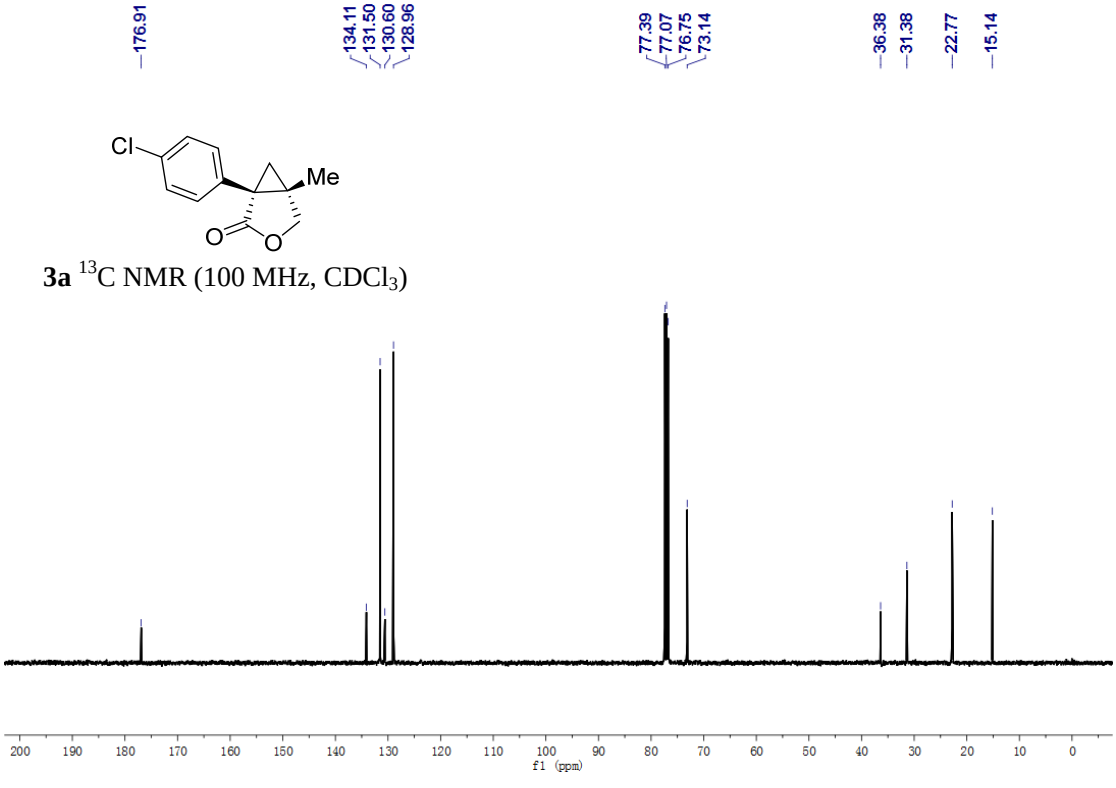


(*S*$_a$,4*S*,4'*S*,5*S*,5'*S*)-**1h**^{13}C NMR (100 MHz, $CDCl_3$)

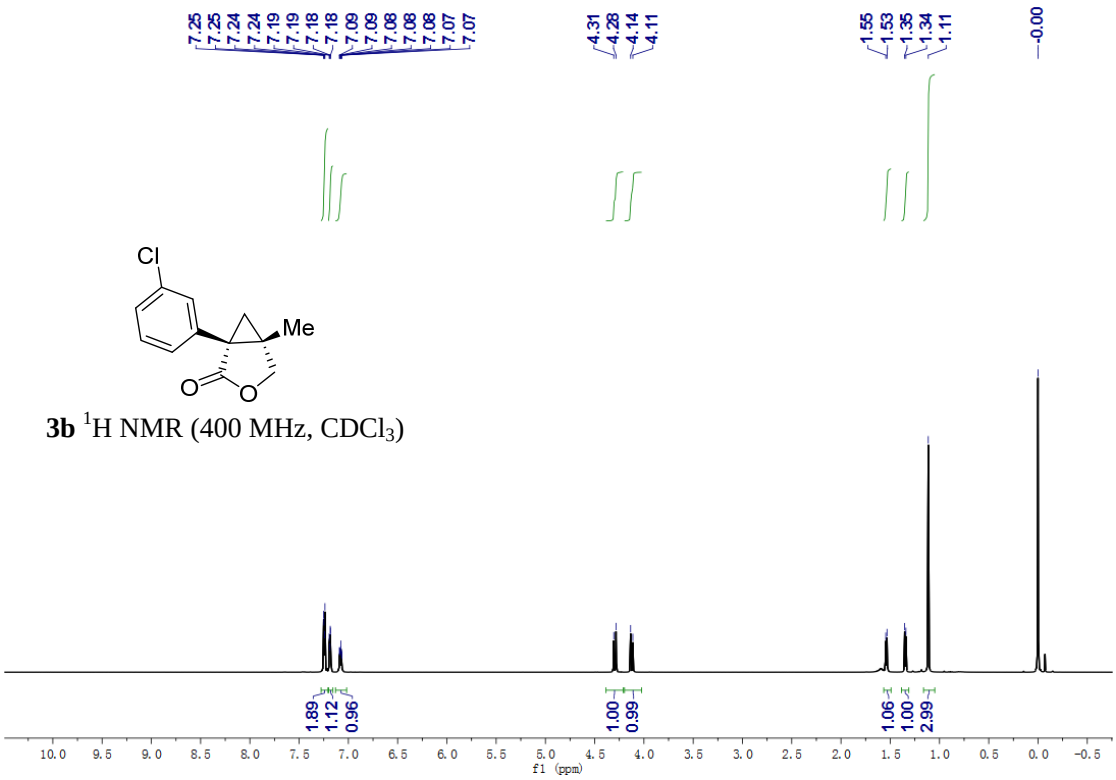




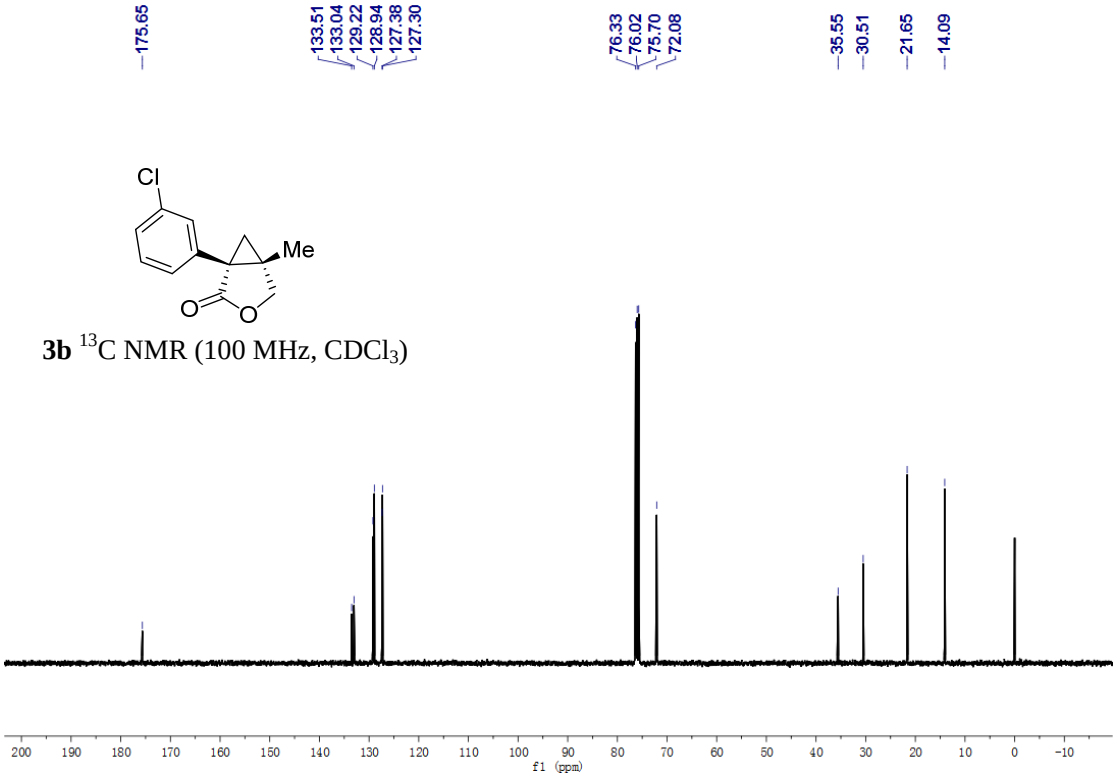
3a ^{1}H NMR (400 MHz, $CDCl_3$)



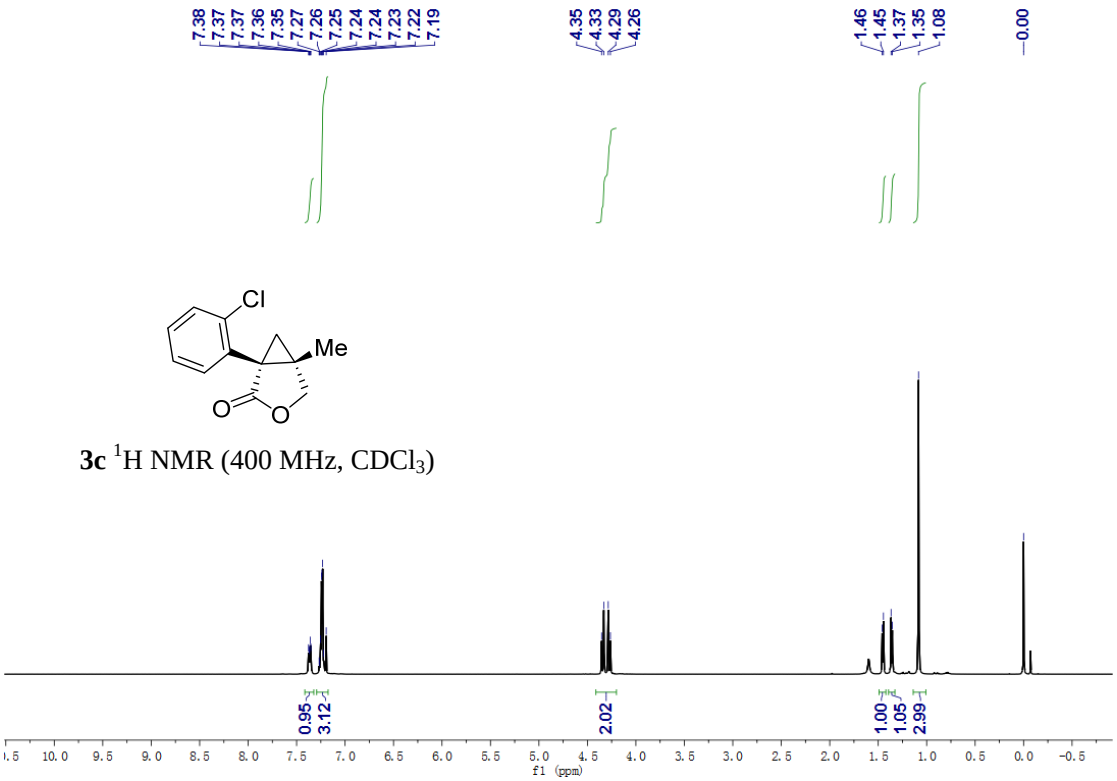
3a ^{13}C NMR (100 MHz, $CDCl_3$)



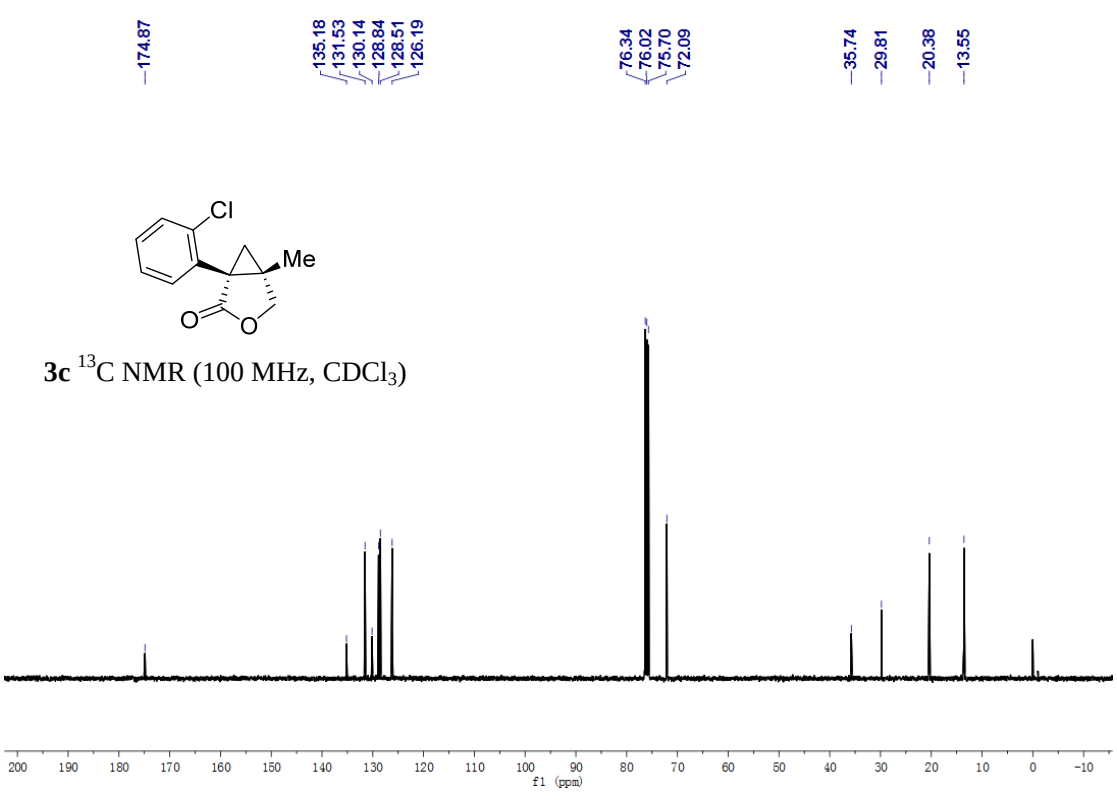
3b ^{1}H NMR (400 MHz, $CDCl_3$)



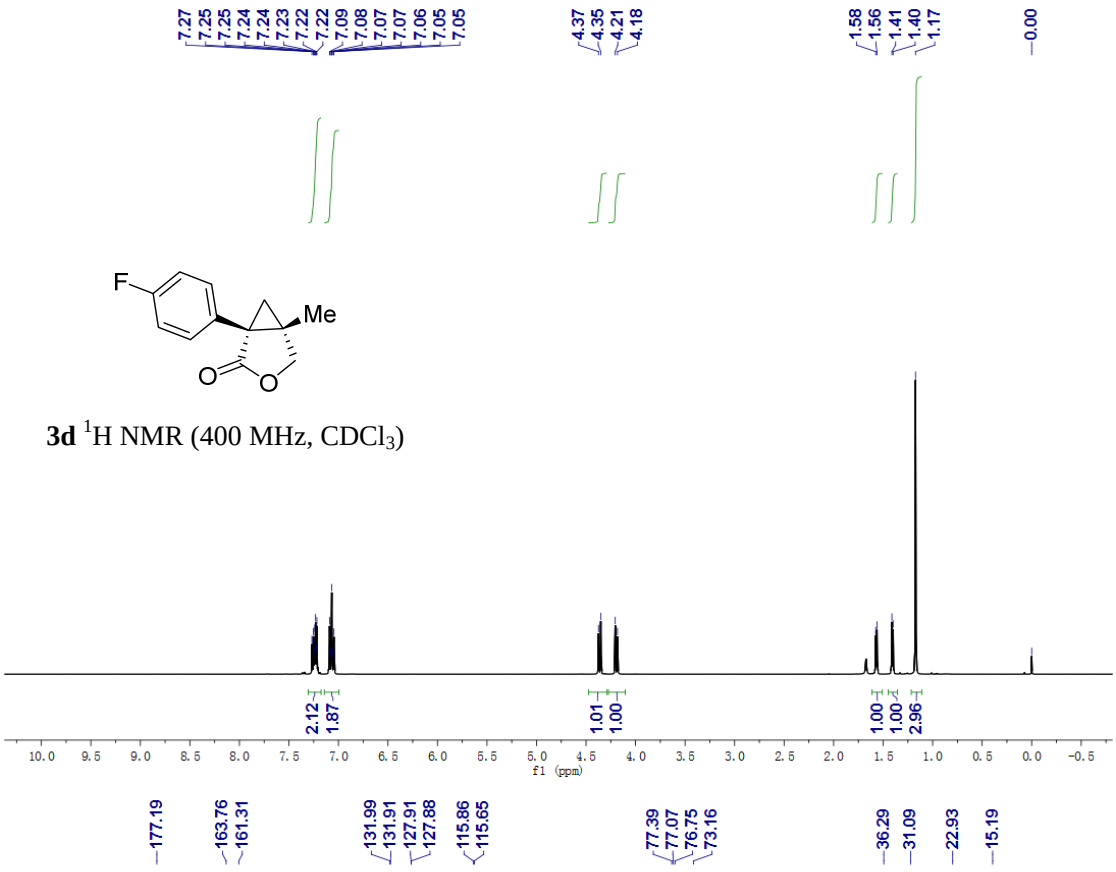
3b ^{13}C NMR (100 MHz, $CDCl_3$)



3c ^{1}H NMR (400 MHz, $CDCl_3$)

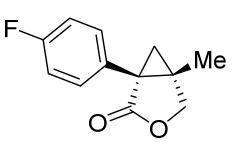


3c ^{13}C NMR (100 MHz, $CDCl_3$)

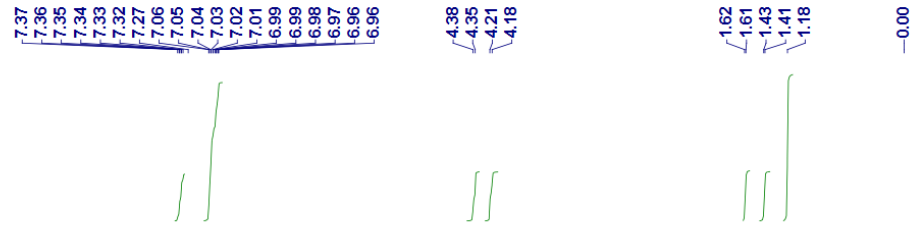


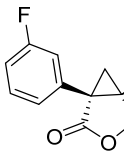
3d ^{1}H NMR (400 MHz, $CDCl_3$)

3d ^{13}C NMR (100 MHz, $CDCl_3$)

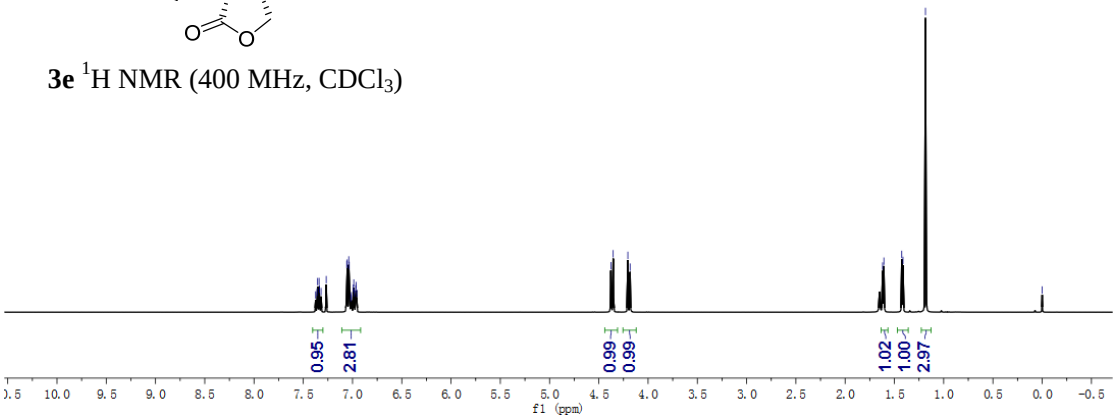


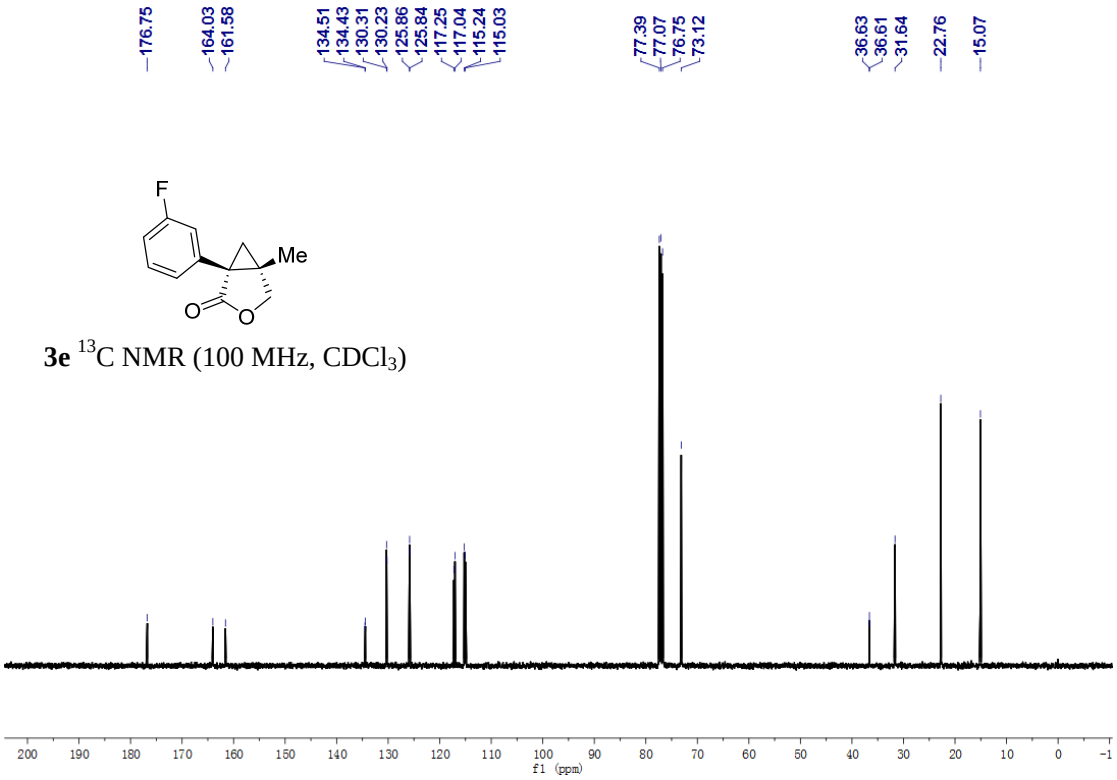
3d ^{19}F NMR (376 MHz, $CDCl_3$)



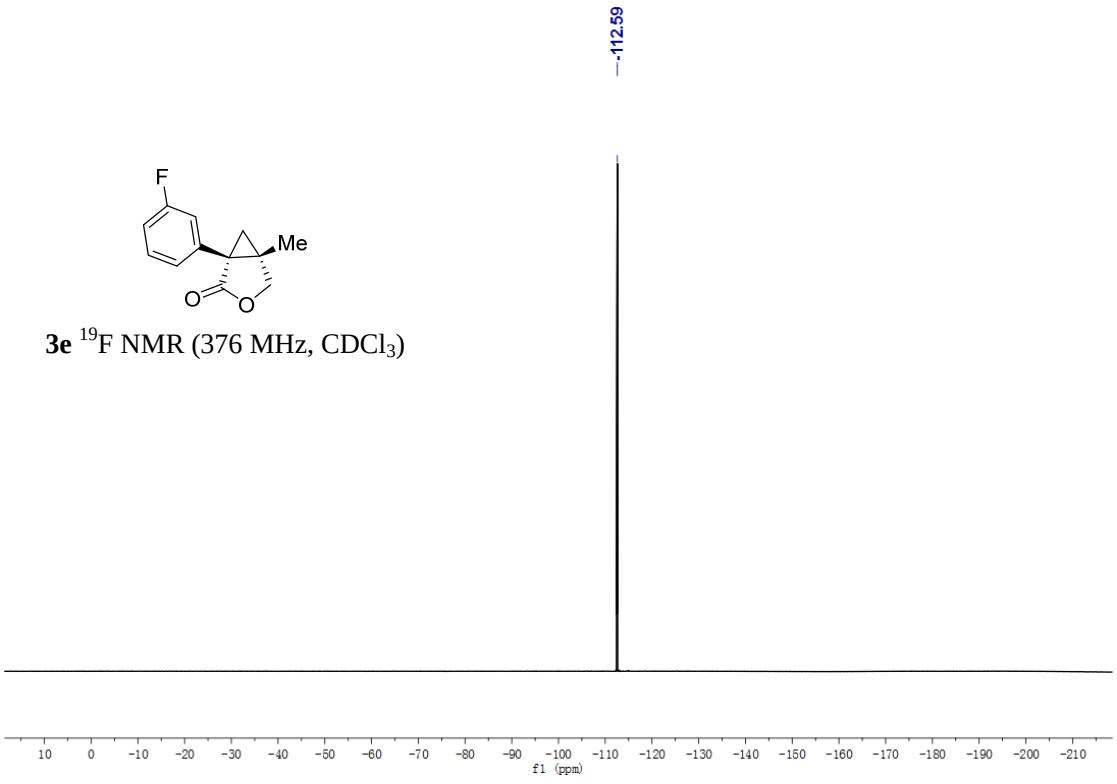


3e ^{1}H NMR (400 MHz, $CDCl_3$)

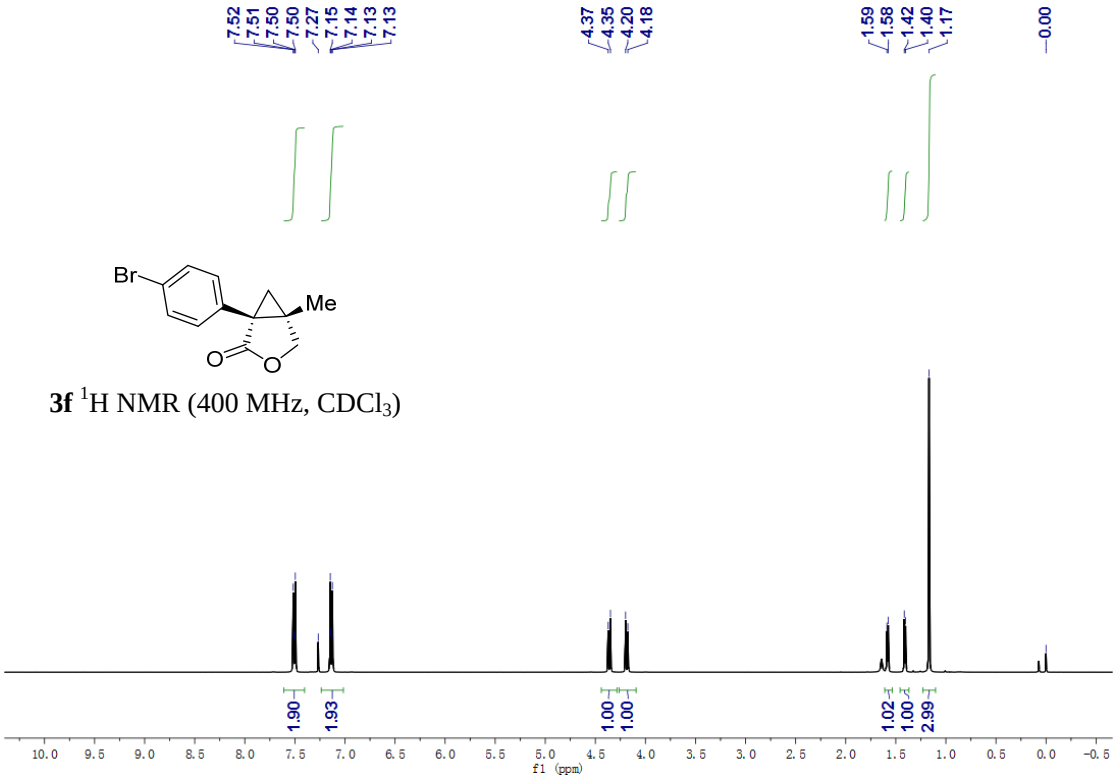




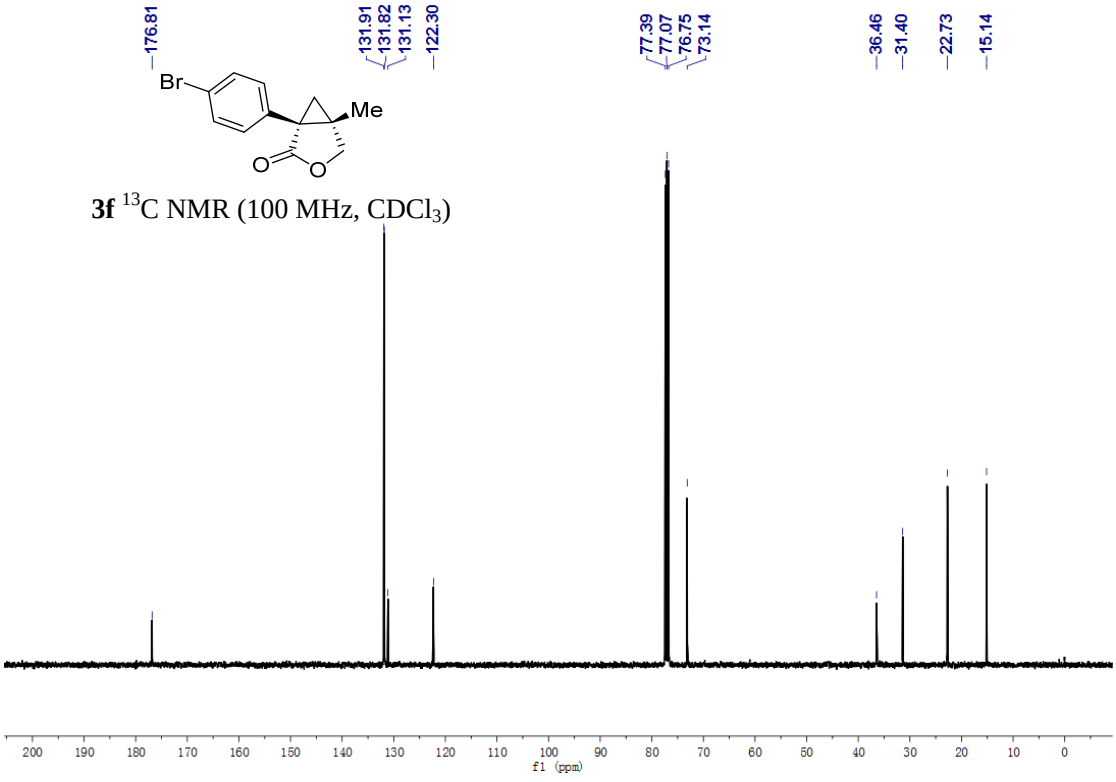
3e ^{13}C NMR (100 MHz, $CDCl_3$)



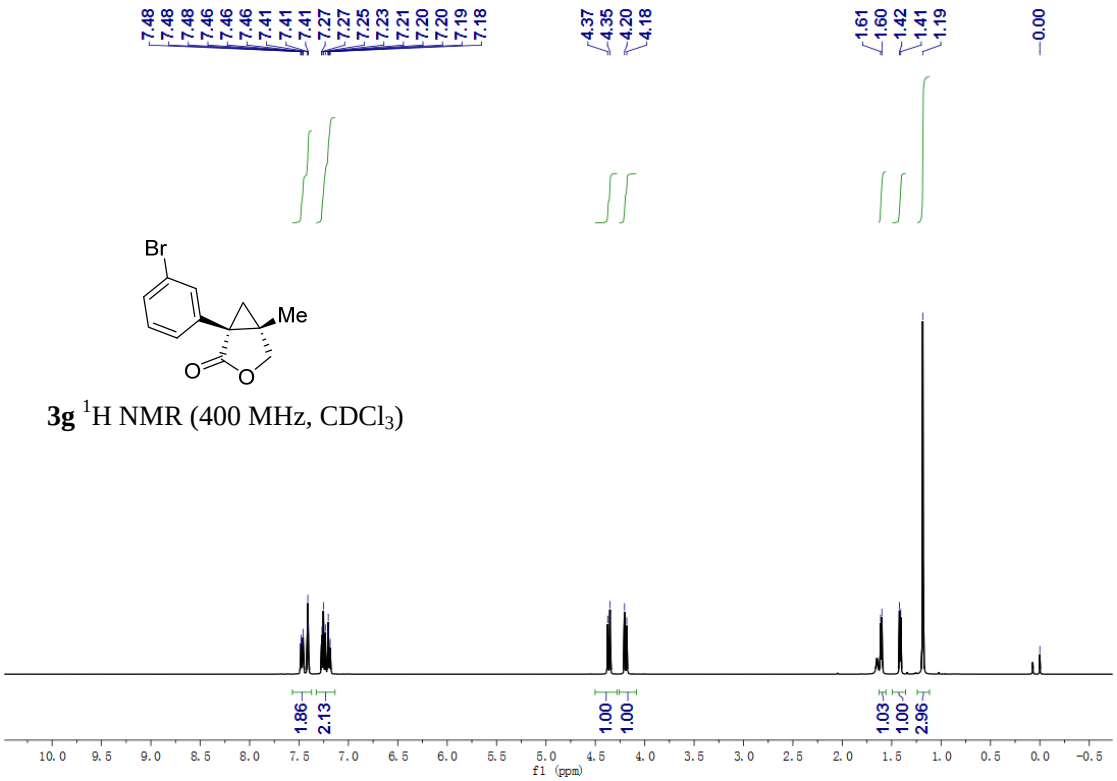
3e ^{19}F NMR (376 MHz, $CDCl_3$)



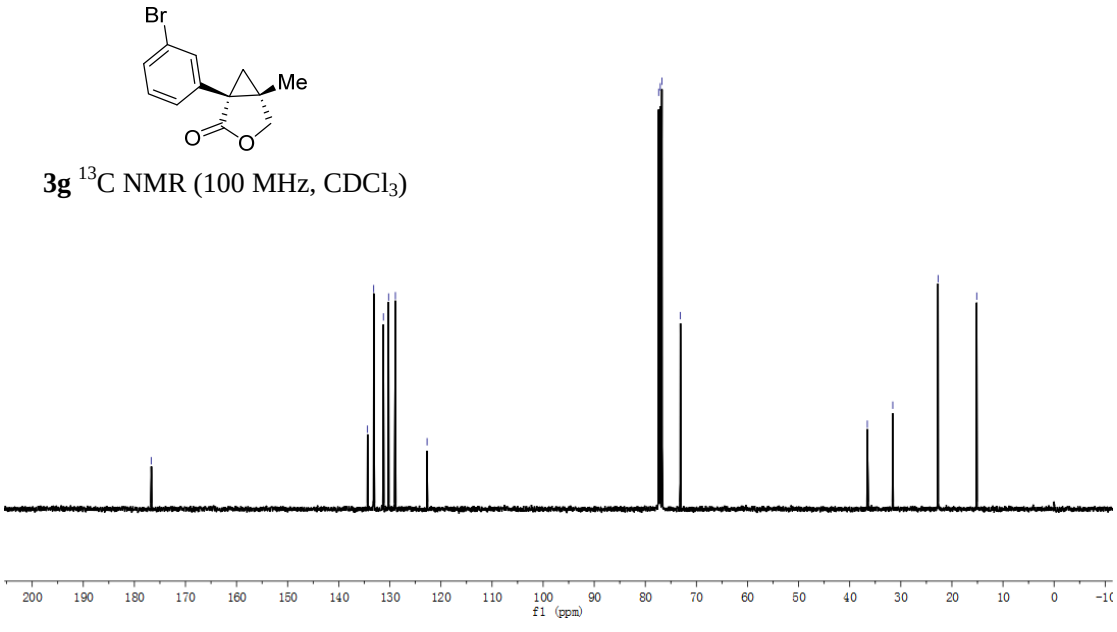
3f ^{1}H NMR (400 MHz, $CDCl_3$)



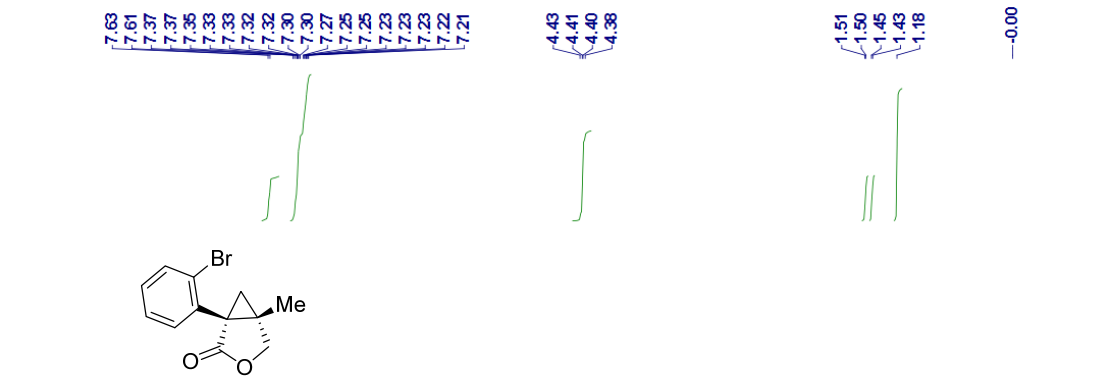
3f ^{13}C NMR (100 MHz, $CDCl_3$)



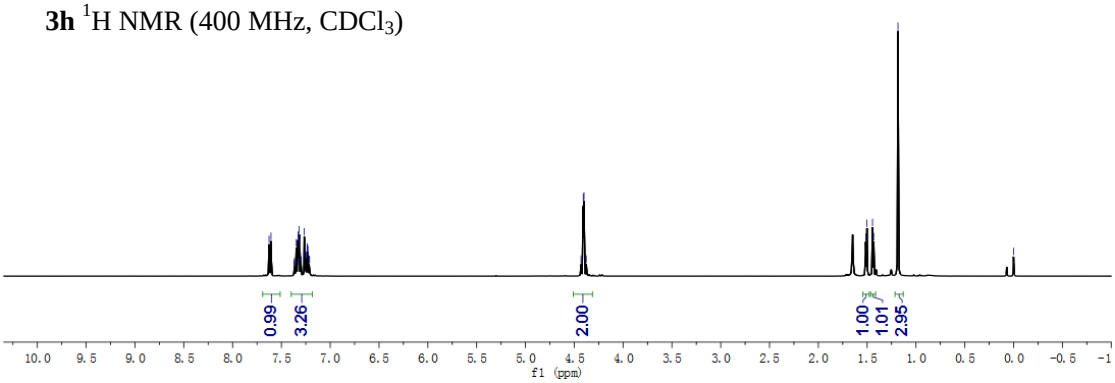
3g ^{1}H NMR (400 MHz, $CDCl_3$)

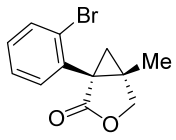


3g ^{13}C NMR (100 MHz, $CDCl_3$)

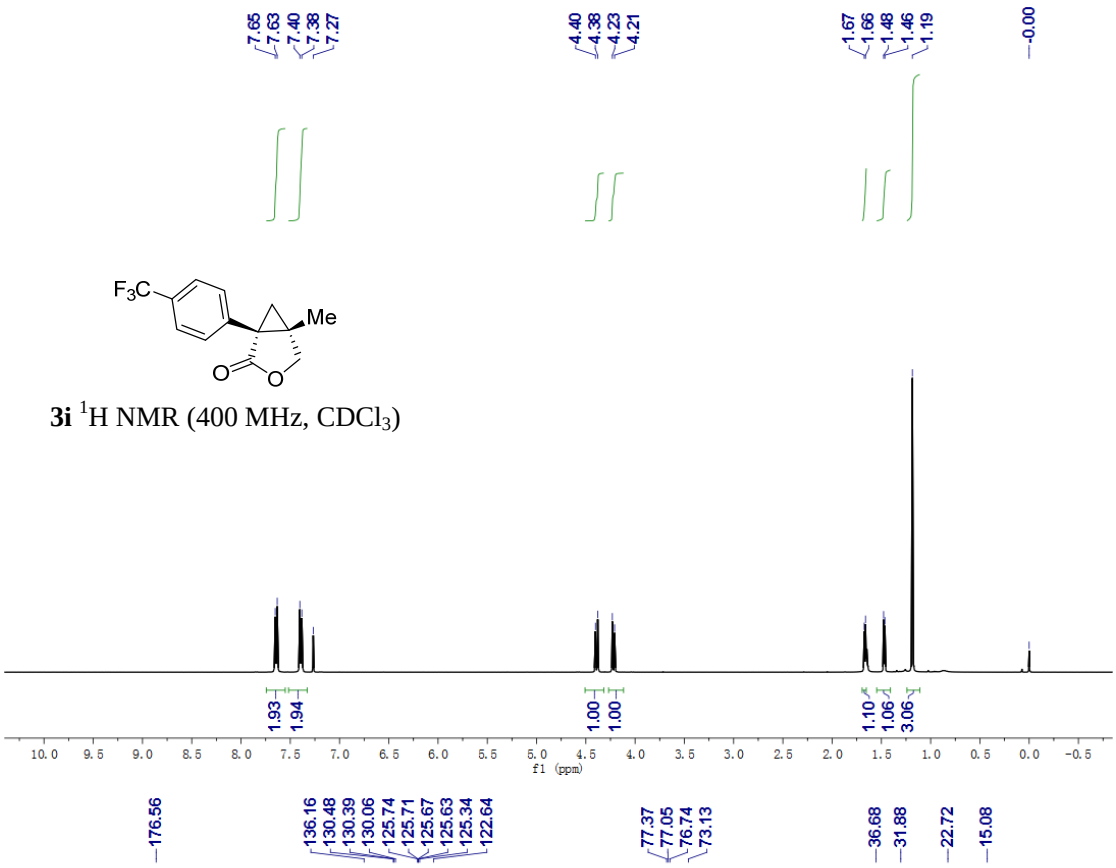


3h ^{1}H NMR (400 MHz, $CDCl_3$)



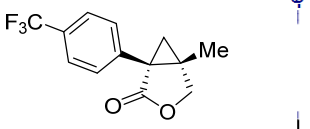


3h ^{13}C NMR (100 MHz, $CDCl_3$)

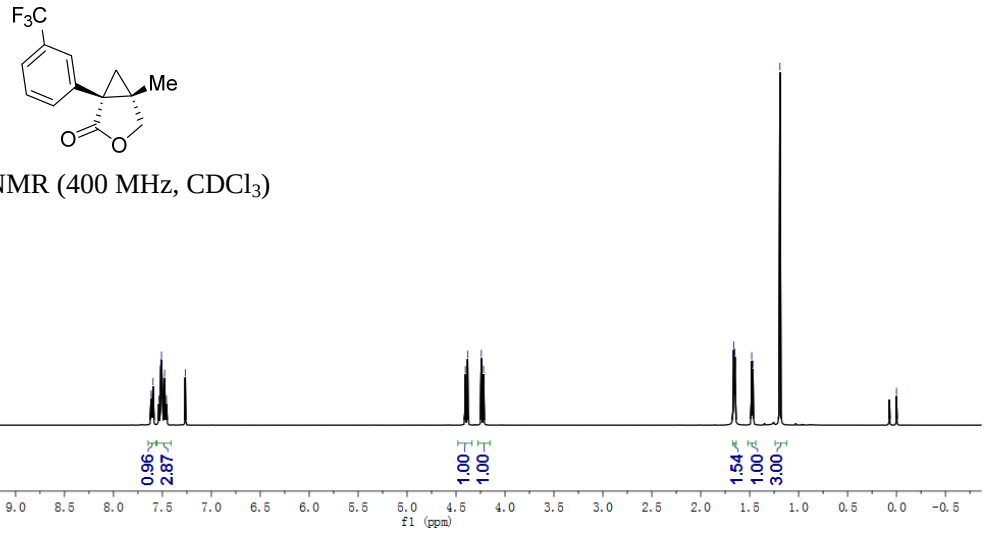


3i ^{1}H NMR (400 MHz, $CDCl_3$)

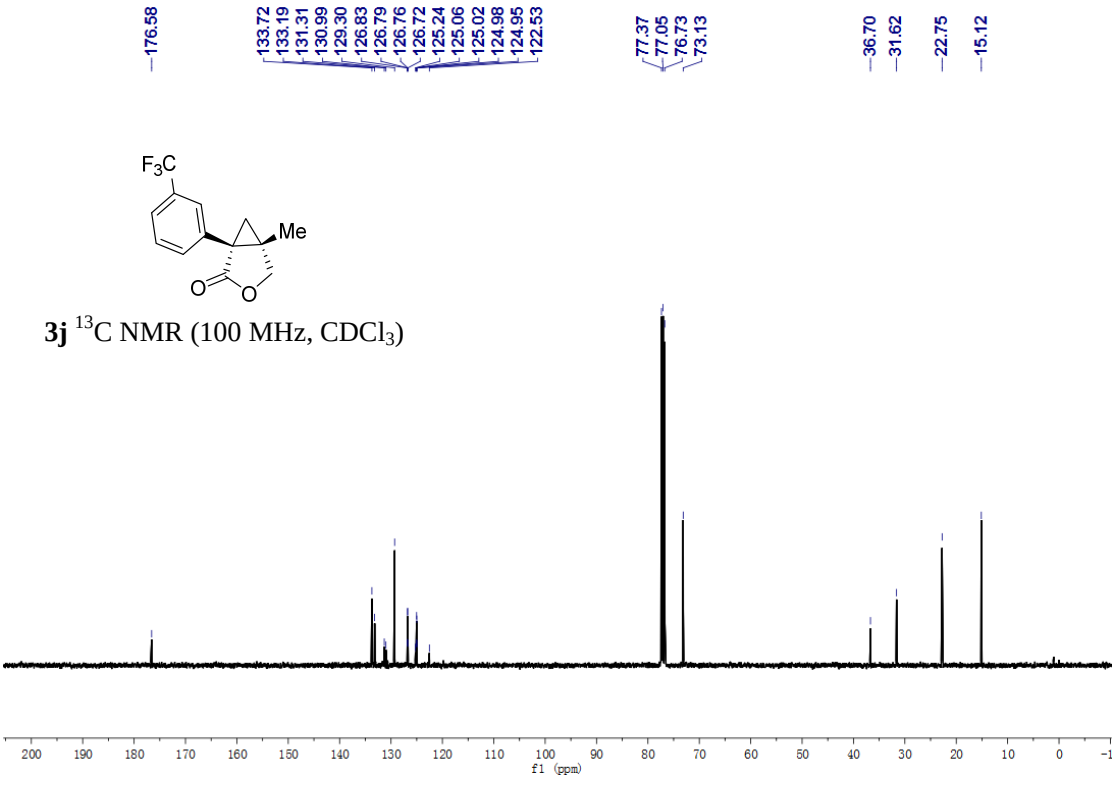
3i ^{13}C NMR (100 MHz, $CDCl_3$)



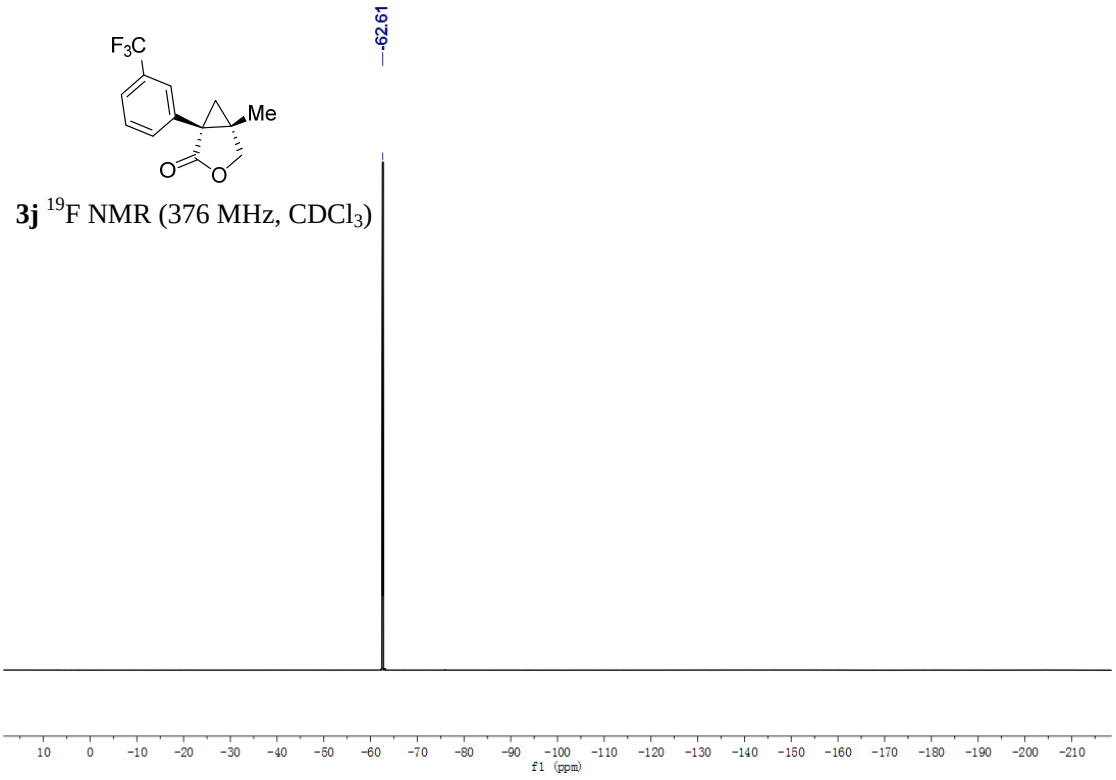
3i ^{19}F NMR (376 MHz, $CDCl_3$)



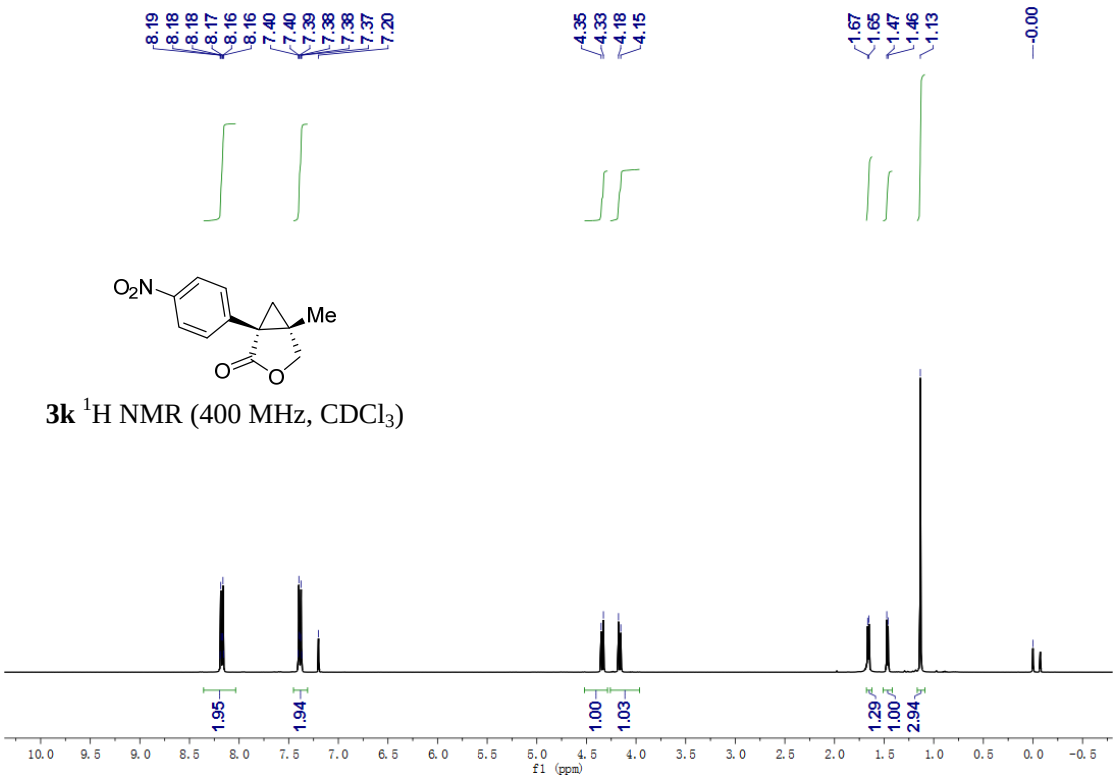
3j ^{1}H NMR (400 MHz, $CDCl_3$)



3j ^{13}C NMR (100 MHz, $CDCl_3$)

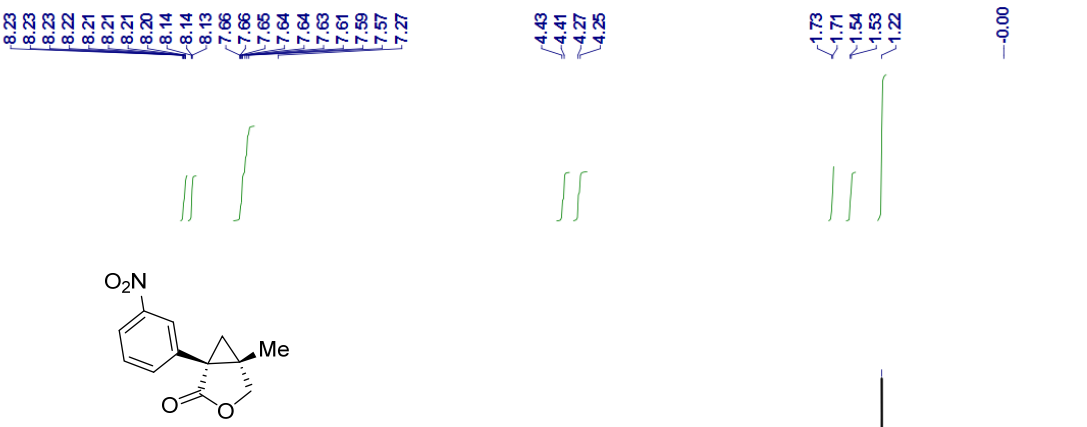


3j ^{19}F NMR (376 MHz, $CDCl_3$)

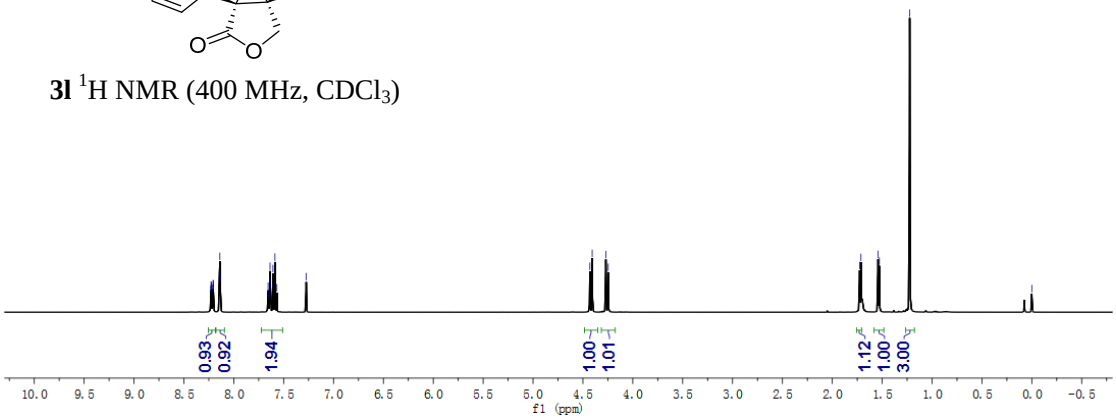


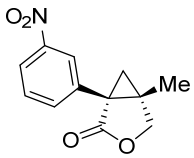
3k ^{1}H NMR (400 MHz, $CDCl_3$)

3k ^{13}C NMR (100 MHz, $CDCl_3$)

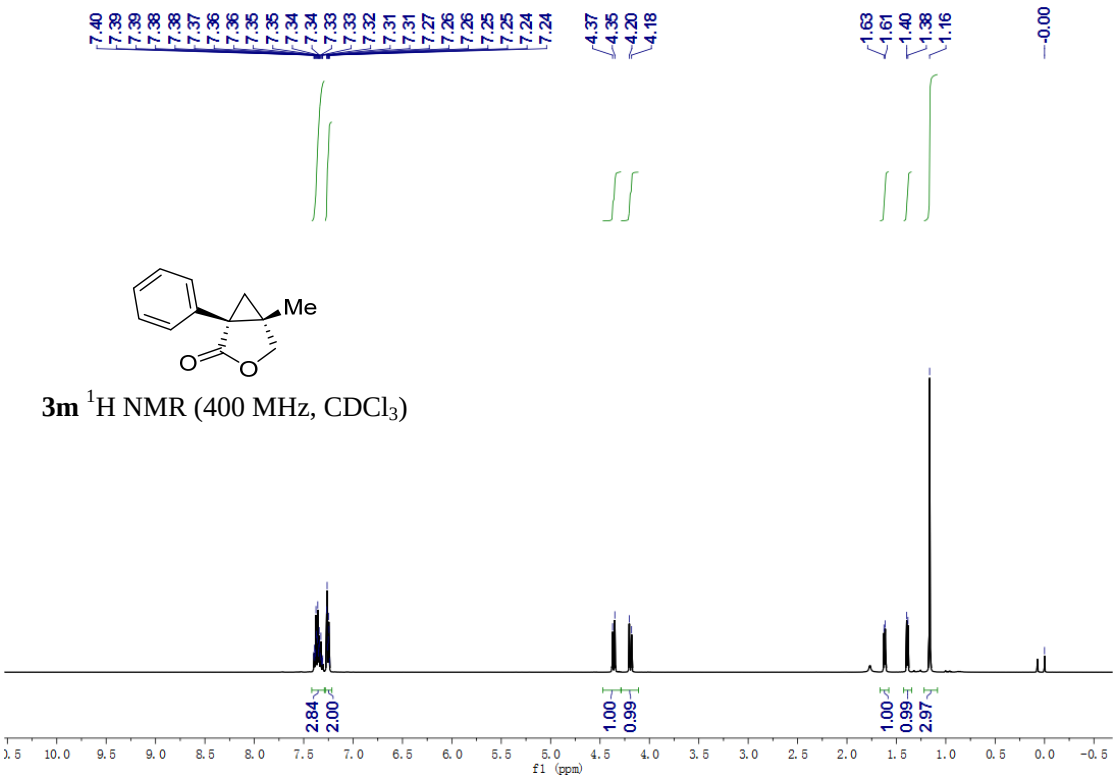


3l ^{1}H NMR (400 MHz, $CDCl_3$)

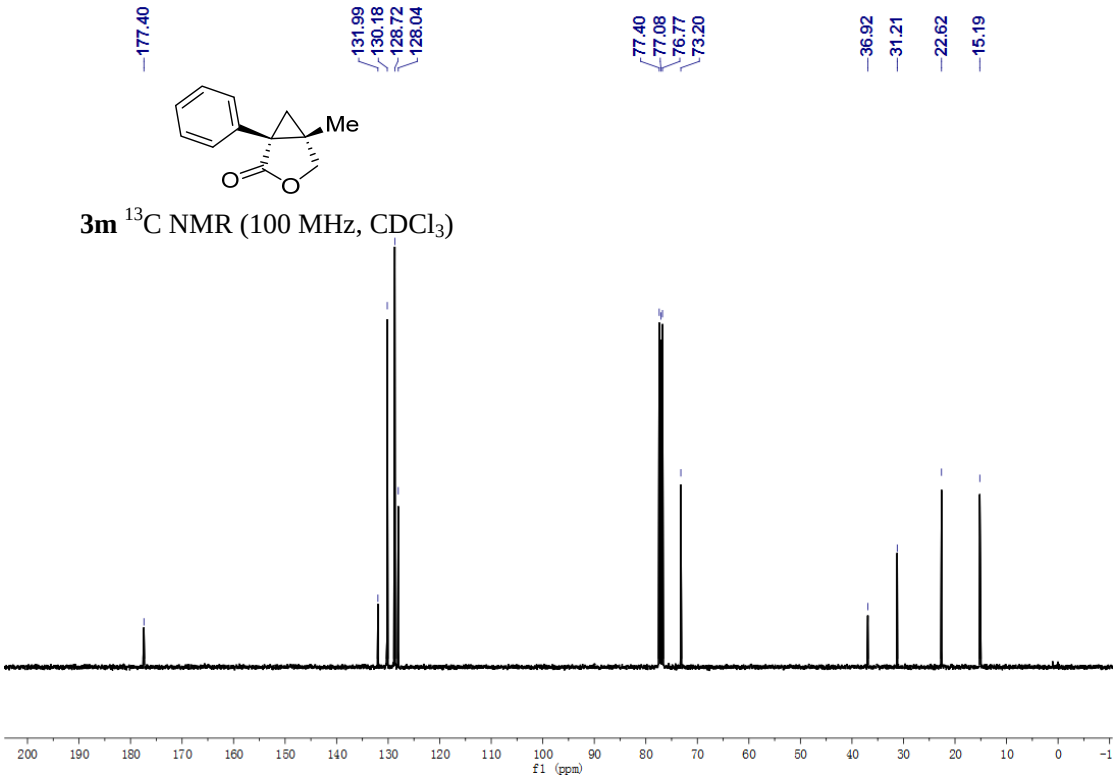




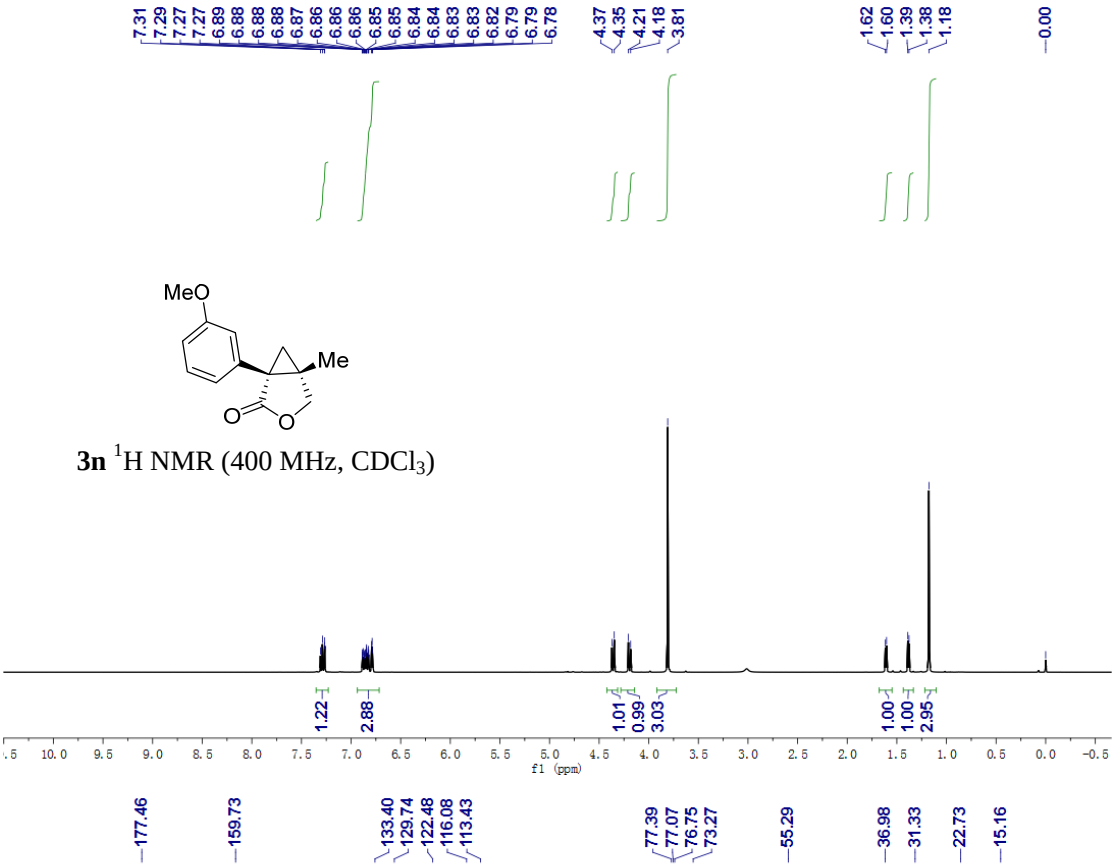
3l ^{13}C NMR (100 MHz, $CDCl_3$)



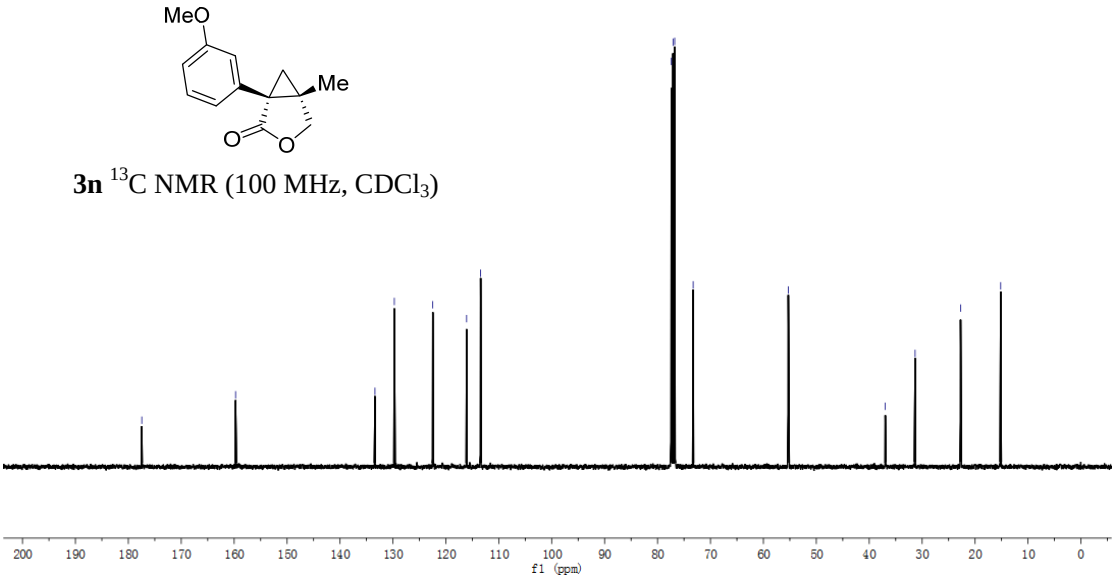
3m ^{1}H NMR (400 MHz, $CDCl_3$)



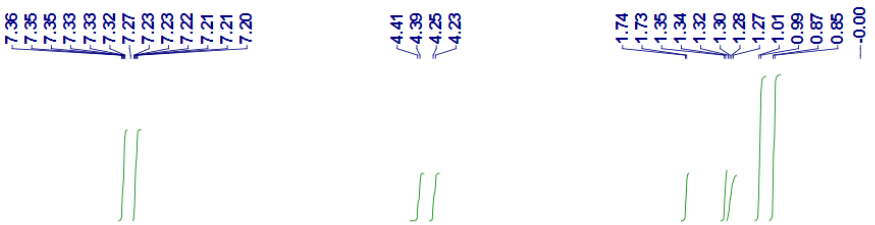
3m ^{13}C NMR (100 MHz, $CDCl_3$)

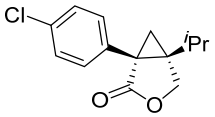


3n ^{1}H NMR (400 MHz, $CDCl_3$)

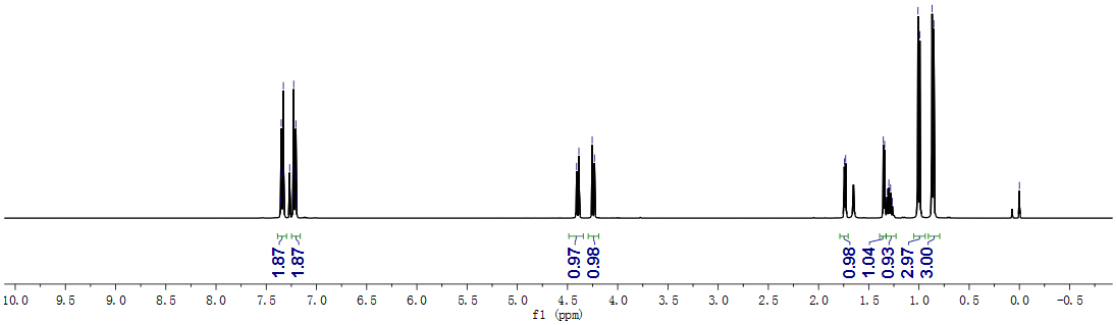


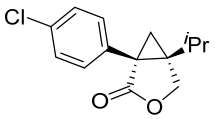
3n ^{13}C NMR (100 MHz, $CDCl_3$)



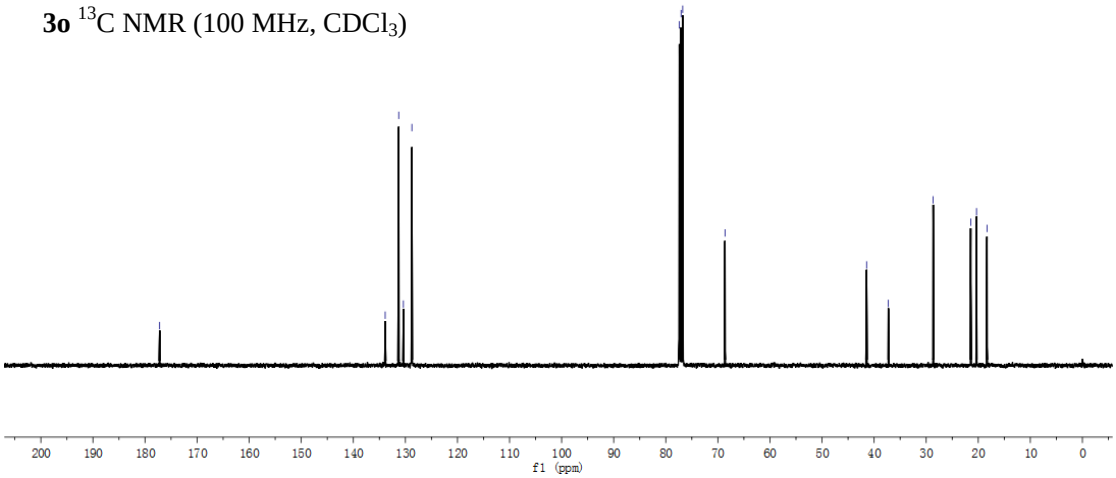


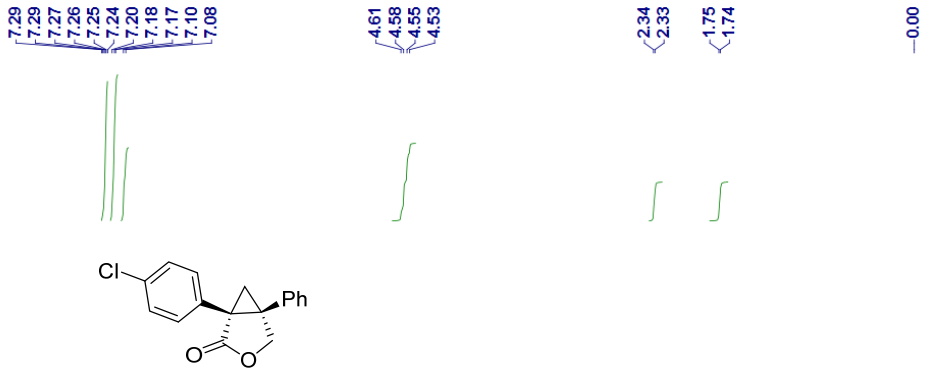
3o ^{1}H NMR (400 MHz, $CDCl_3$)



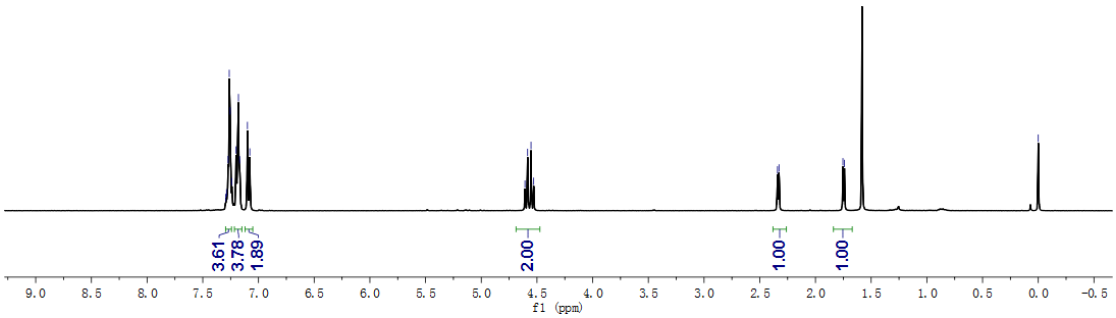


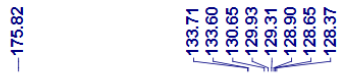
3o ^{13}C NMR (100 MHz, $CDCl_3$)

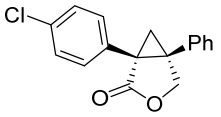




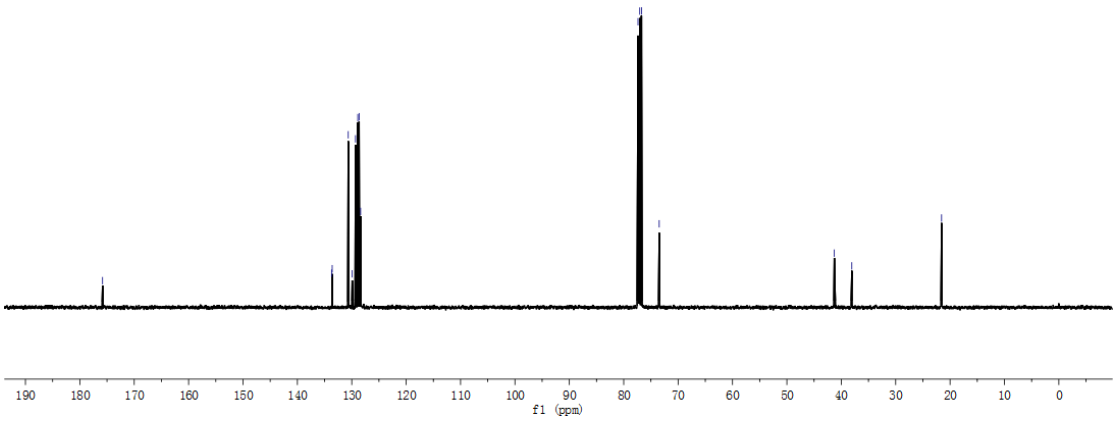
3p ^{1}H NMR (400 MHz, $CDCl_3$)

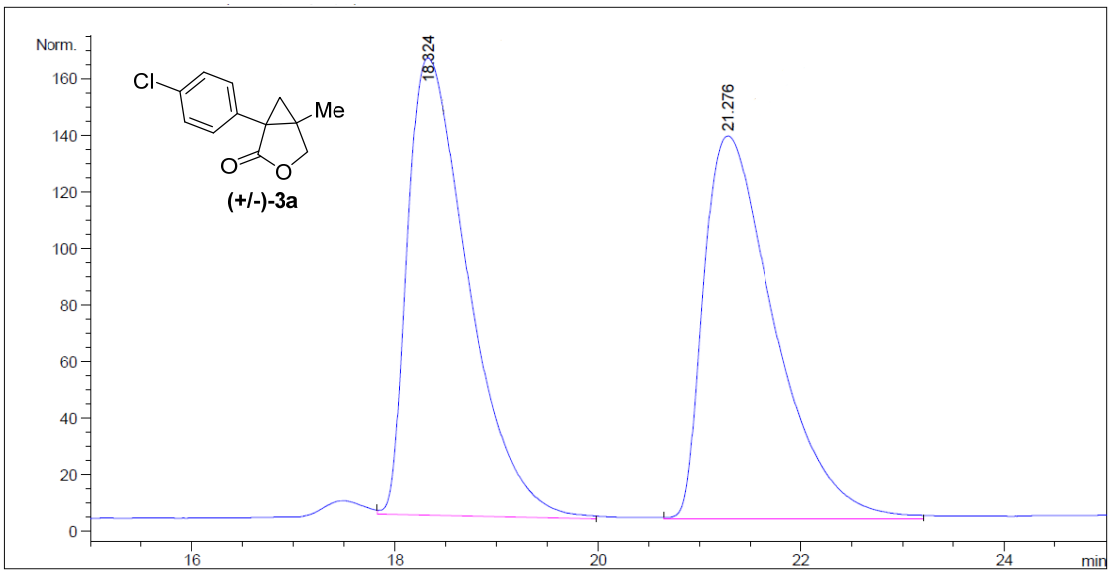






3p ^{13}C NMR (100 MHz, $CDCl_3$)





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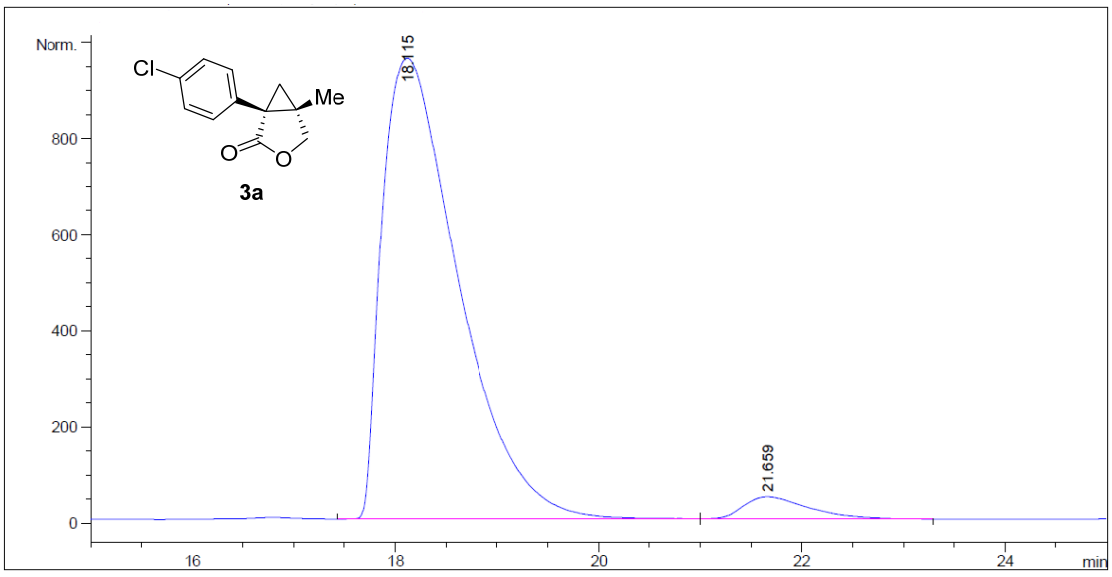
1	18.324	MM	0.6940	6733.79736		161.72314		50.3852
2	21.276	MM	0.8163	6630.82324		135.38246		49.6148



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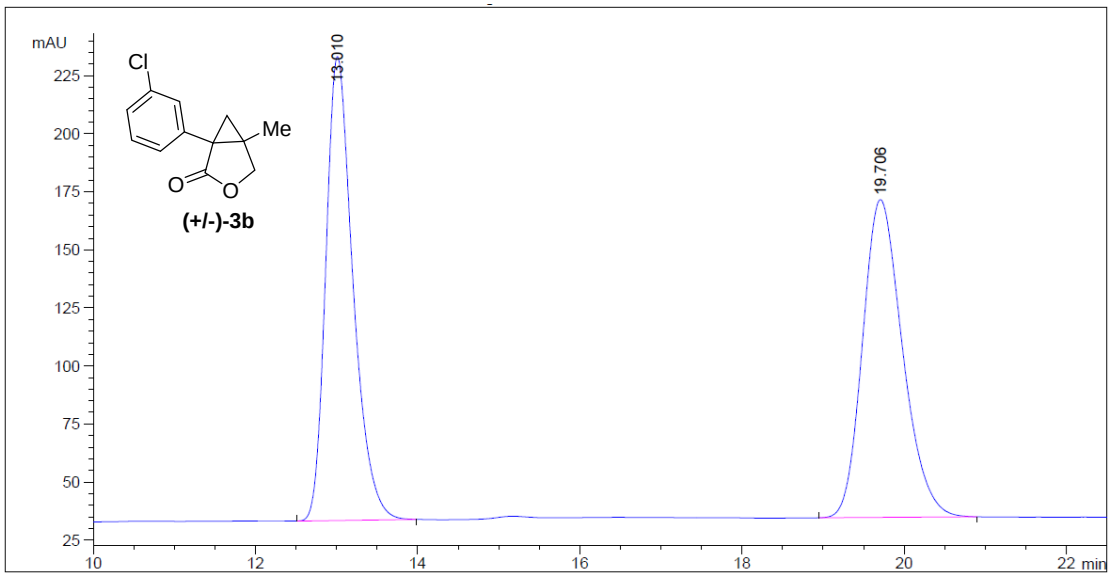
1	18.115	VV	0.8132	5.01645e4		960.50421		95.8221
2	21.659	VV	0.7072	2187.22632		47.14868		4.1779



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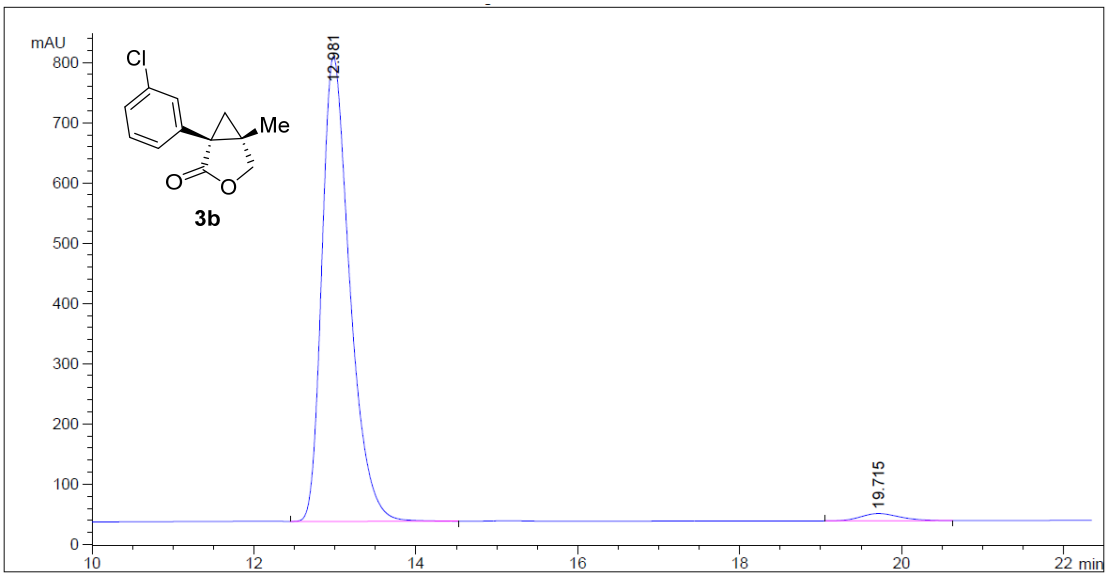
1	13.010	PB	0.3536	4659.19971		199.79237		49.8641
2	19.706	BB	0.5259	4684.59375		136.88747		50.1359



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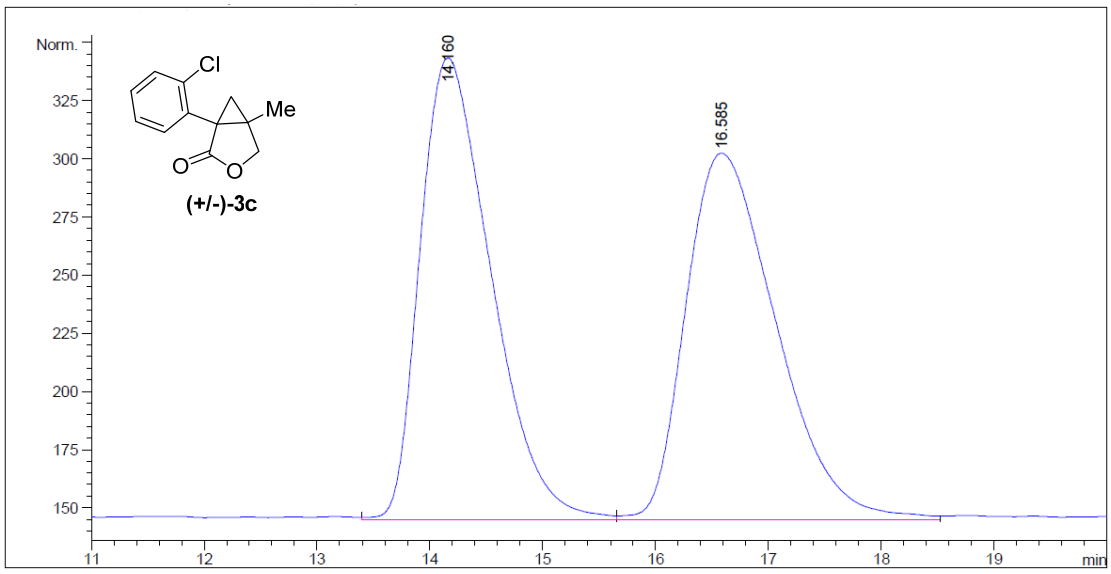
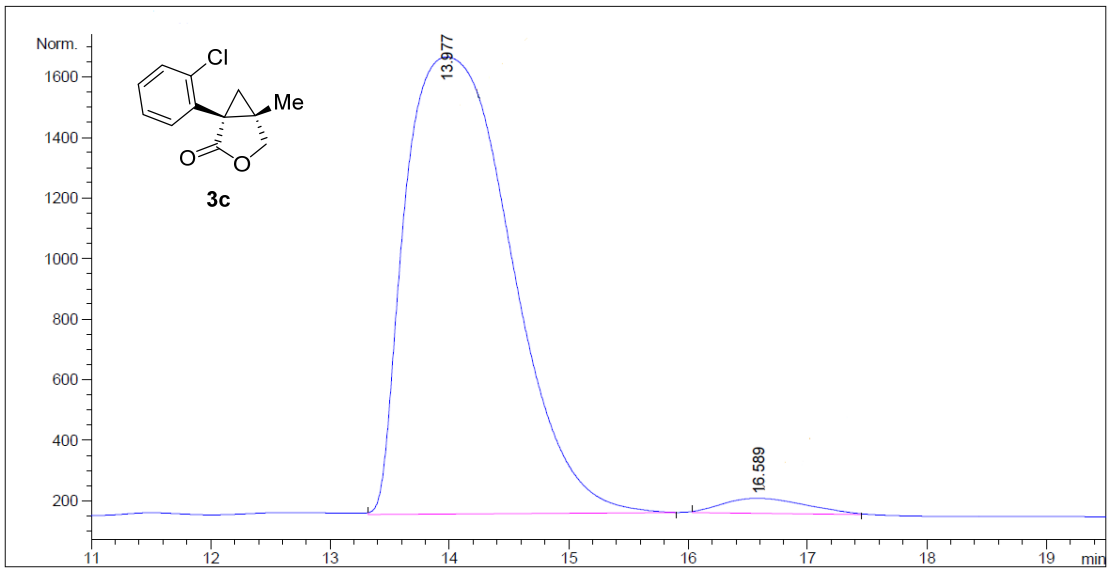
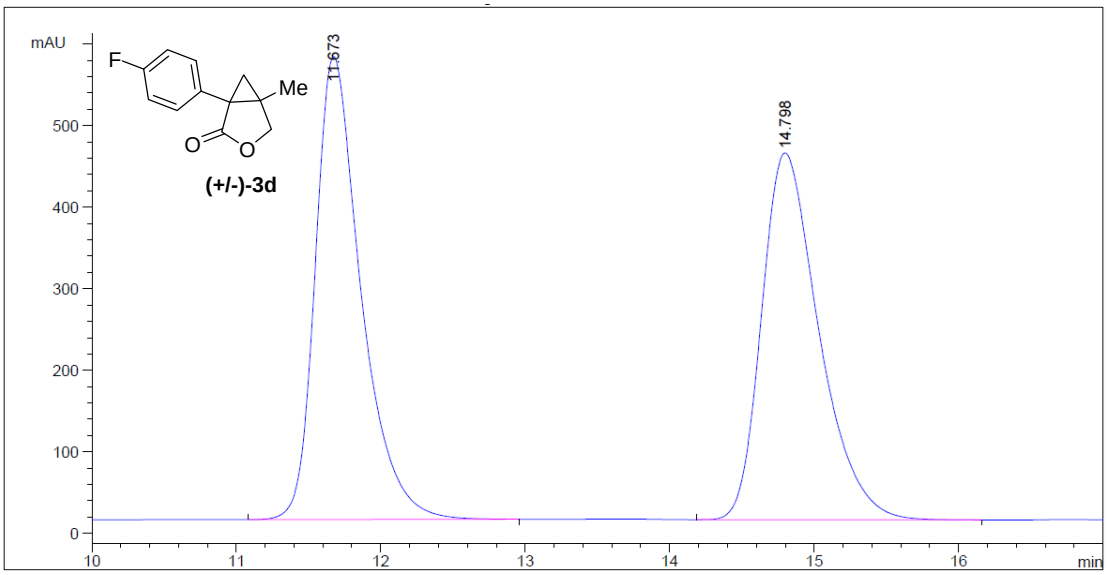
1	12.981	VB	0.3643	1.85043e4		771.45123		97.8397
2	19.715	PB	0.5104	408.58325		12.19163		2.1603



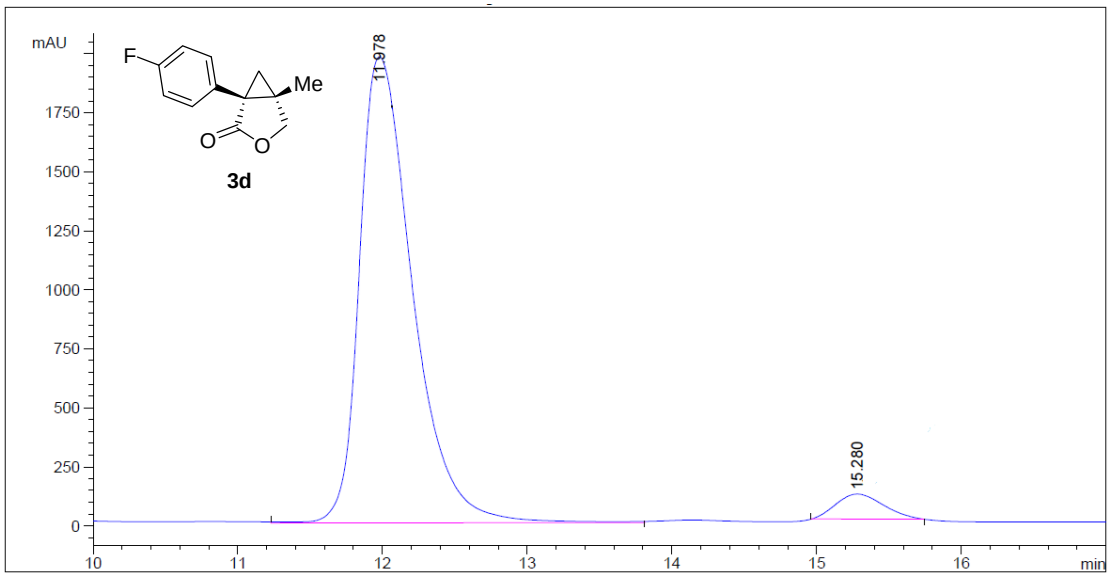
#	[min]		[min]	mAU	*s	[mAU	]	%
1	14.160	VV	0.6790	8673.33984		198.36174		49.8029
2	16.585	VV	0.8520	8742.00488		157.35201		50.1971



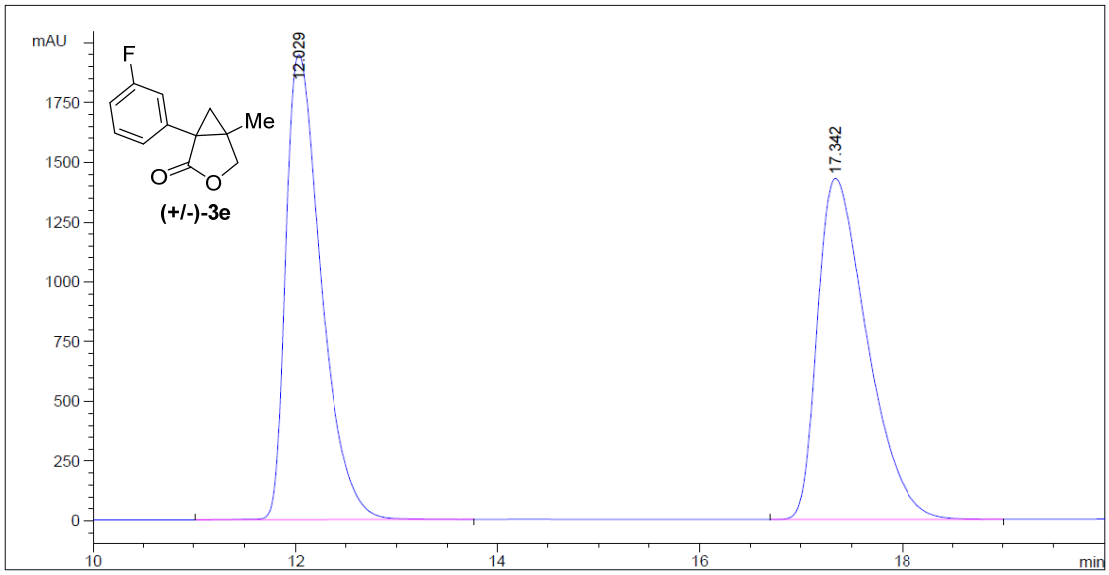
#	[min]		[min]	mAU	*s	[mAU	]	%
1	13.977	MM	1.0235	9.26605e4		1508.95459		97.4640
2	16.589	MM	0.8060	2411.00928		49.85814		2.5360



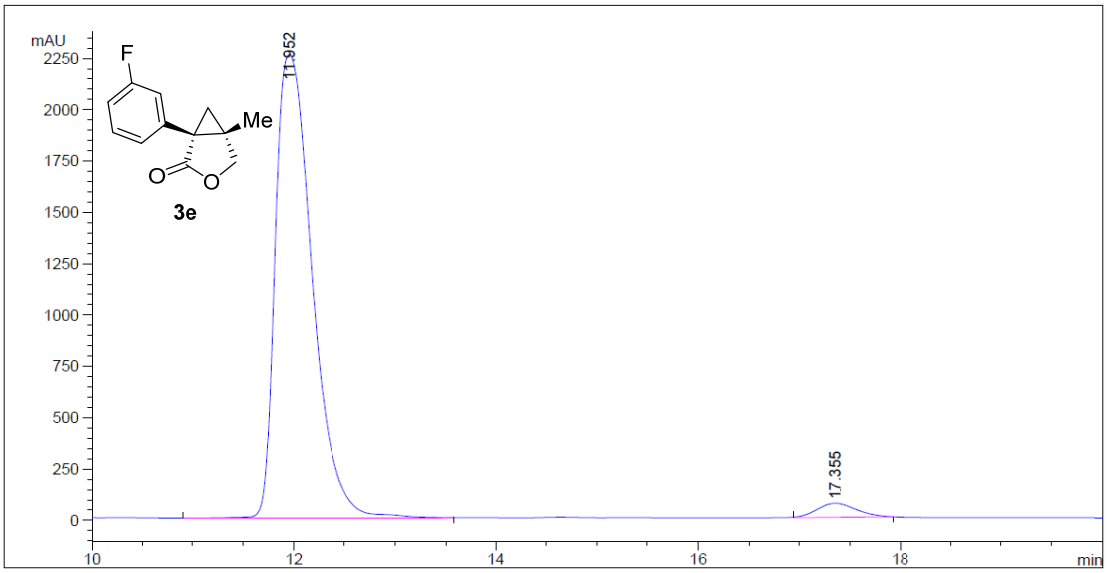
#	[min]		[min]	mAU	*s	[mAU]	%
1	11.673	BB	0.3295	1.24915e4		567.76746	50.1892
2	14.798	VB	0.4191	1.23973e4		449.82877	49.8108



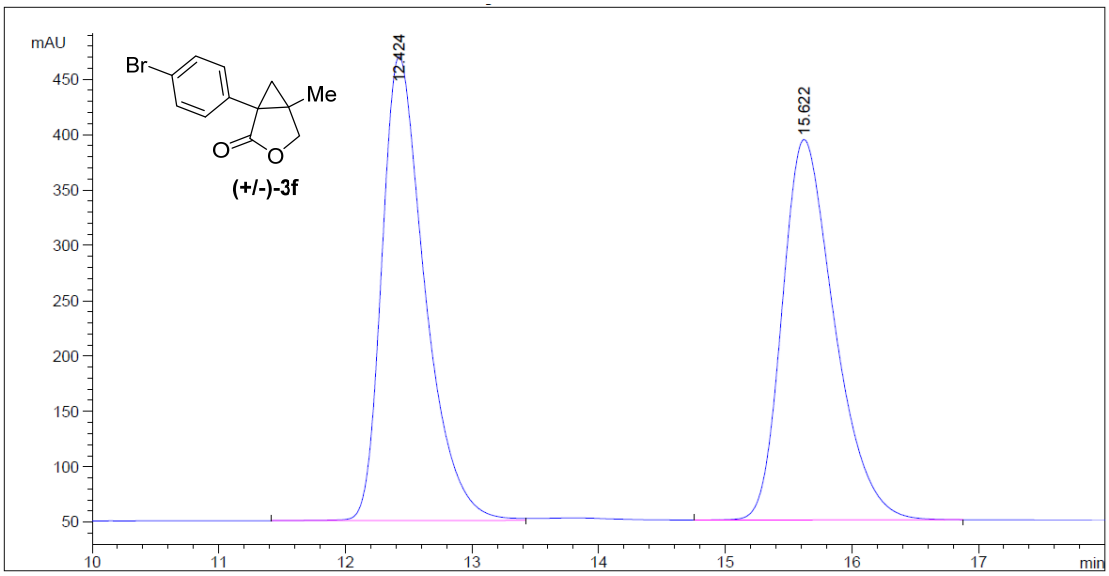
#	[min]		[min]	mAU	*s	[mAU]	%
1	11.978	MM	0.4257	5.04592e4		1975.42395	95.3922
2	15.280	MM	0.3821	2437.34692		106.31580	4.6078



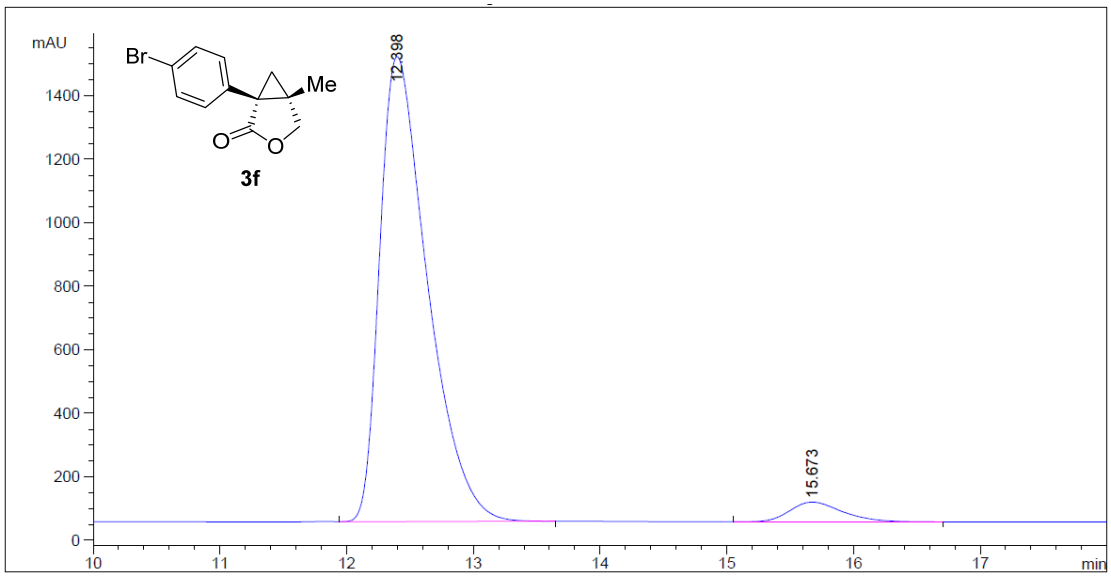
#	[min]		[min]	mAU	*s	[mAU	]	%
1	12.029	PB	0.3710	4.72977e4		1945.64758		49.4851
2	17.342	PB	0.5185	4.82821e4		1426.88513		50.5149



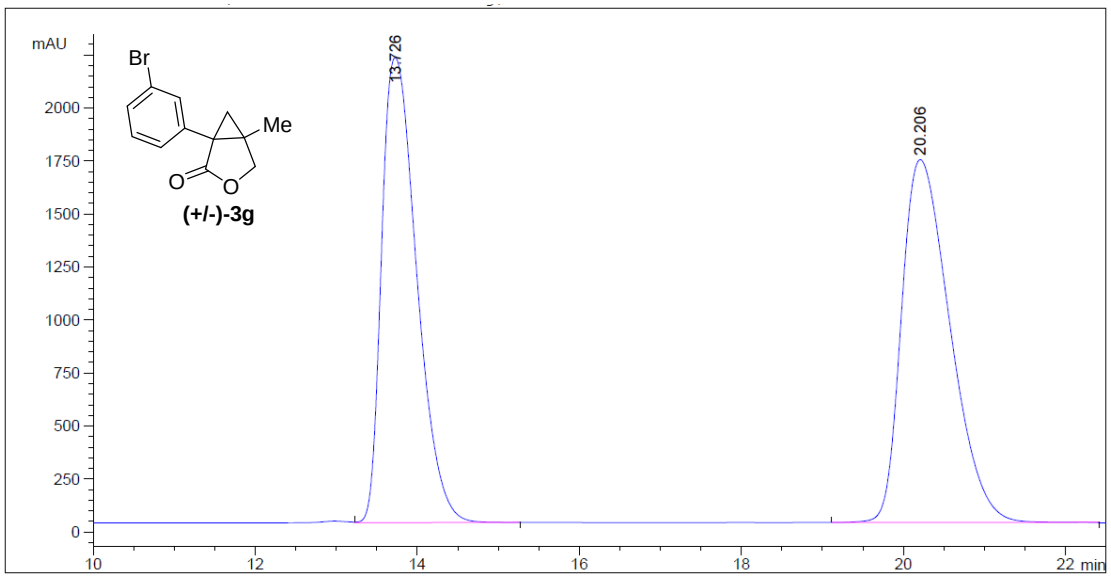
#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.952	VB	0.3959	5.71781e4		2257.61450		96.8551
2	17.355	MM	0.4482	1856.57812		69.04144		3.1449



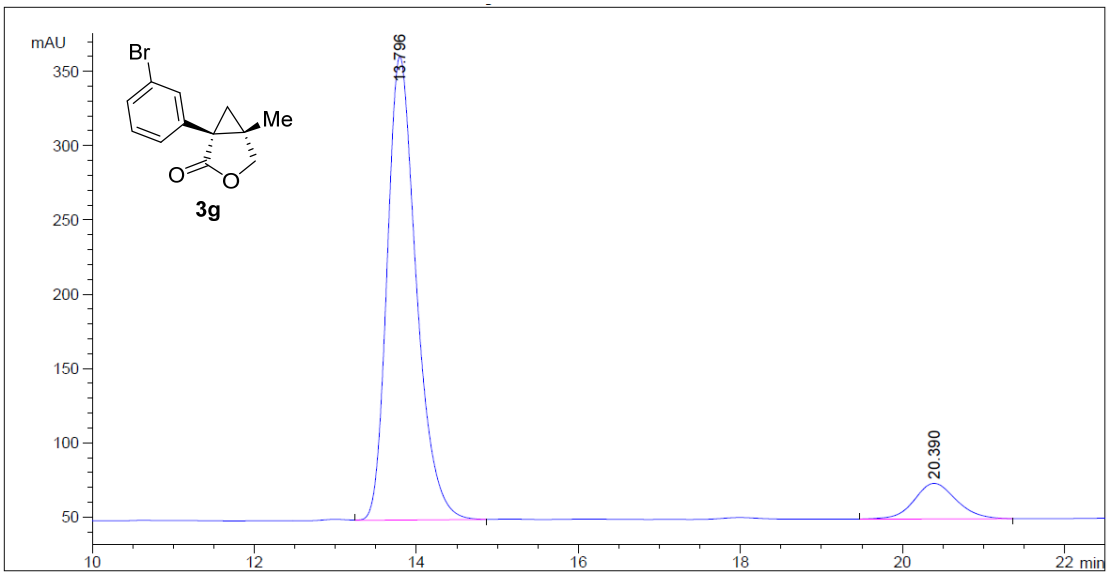
#	[min]		[min]	mAU	*s	[mAU]	%
1	12.424	BB	0.3576	9917.21484		419.04379	50.1142
2	15.622	VB	0.4371	9872.01562		343.64252	49.8858



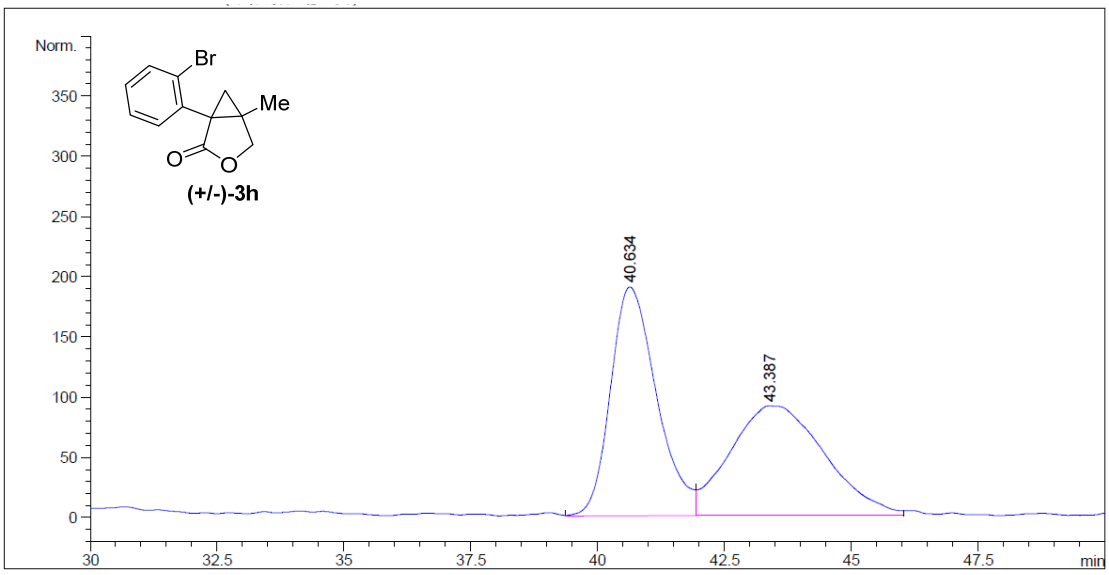
#	[min]		[min]	mAU	*s	[mAU]	%
1	12.398	VB	0.3943	3.83518e4		1464.48743	95.4900
2	15.673	BB	0.4431	1811.36353		62.46429	4.5100



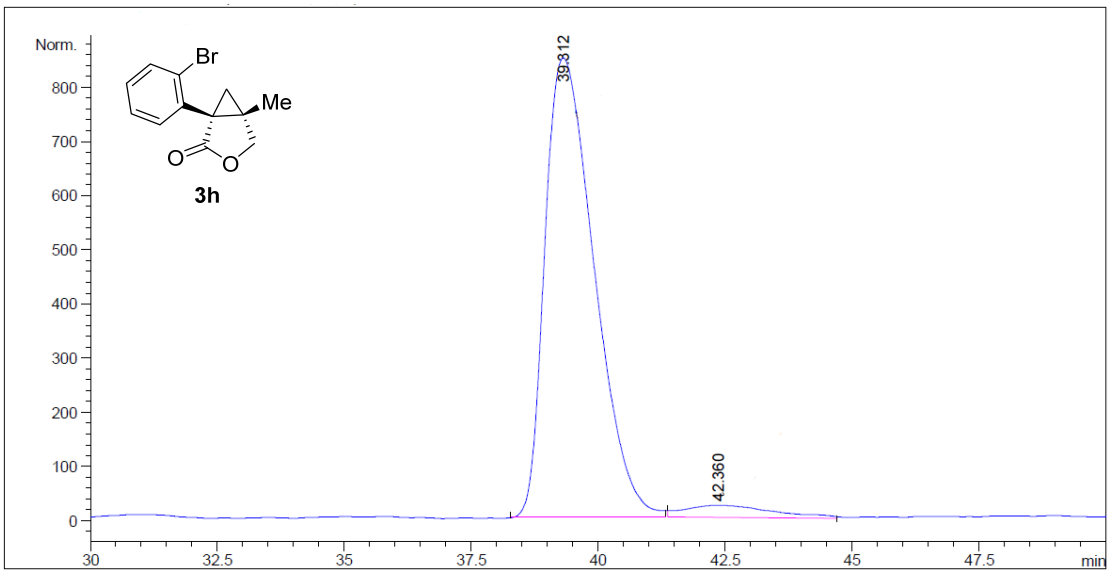
#	[min]		[min]	mAU *s	[mAU]	%
1	13.726	VB	0.4672	6.59437e4	2193.51855	48.1274
2	20.206	VB	0.6489	7.10755e4	1711.90332	51.8726



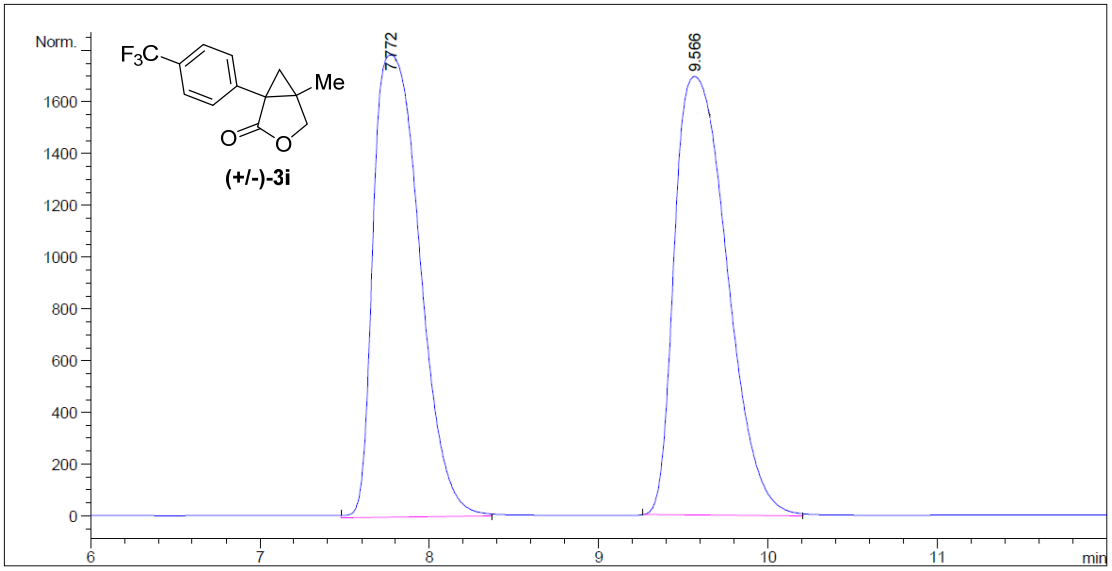
#	[min]		[min]	mAU *s	[mAU]	%
1	13.796	VB	0.3806	7804.82910	312.07544	89.9928
2	20.390	BB	0.5482	867.90100	24.01960	10.0072



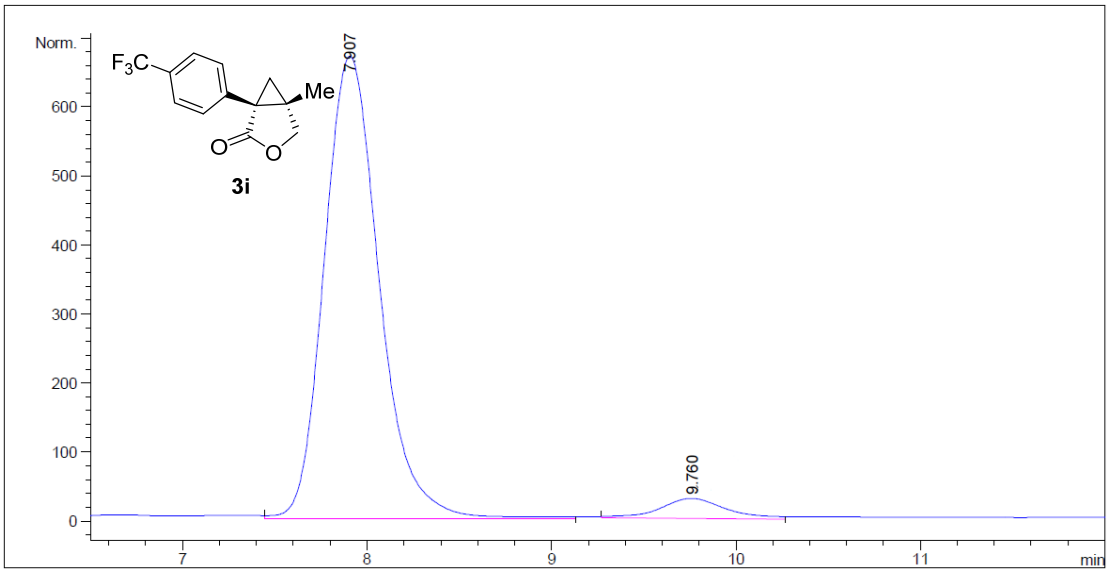
#	[min]		[min]	mAU	*s	[mAU]	%
1	40.634	VV	0.9824	1.20133e4		189.97034	50.3007
2	43.387	VV	1.5997	1.18696e4		91.21732	49.6993



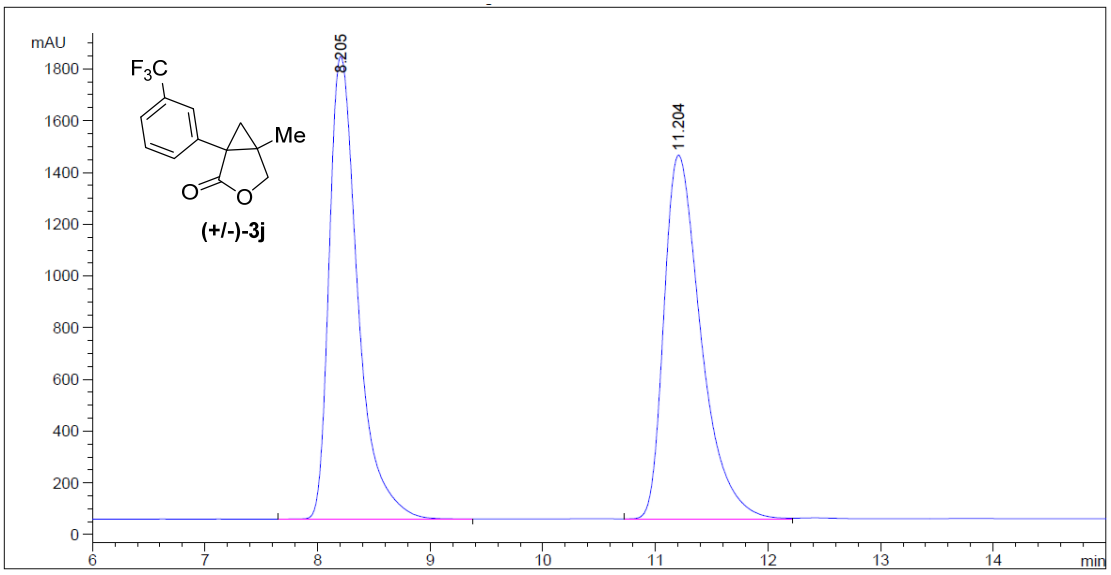
#	[min]		[min]	mAU	*s	[mAU]	%
1	39.312	MM	1.1233	5.71346e4		847.70135	95.3752
2	42.360	MM	2.0381	2770.49878		22.65578	4.6248



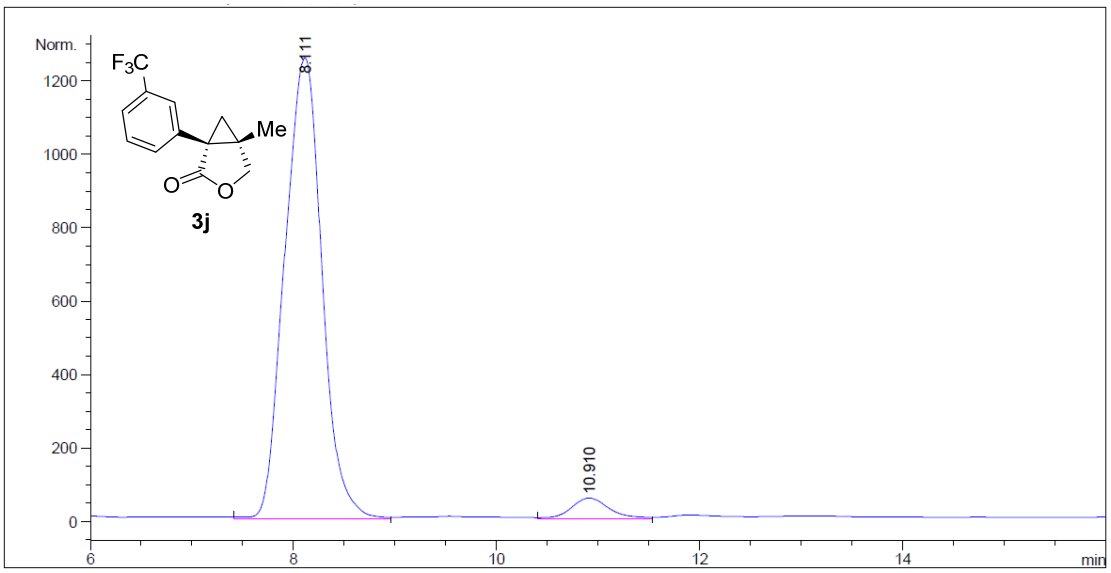
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.772	MM	0.3178	3.40646e4		1786.22937	48.1793
2	9.566	MM	0.3602	3.66392e4		1695.09131	51.8207



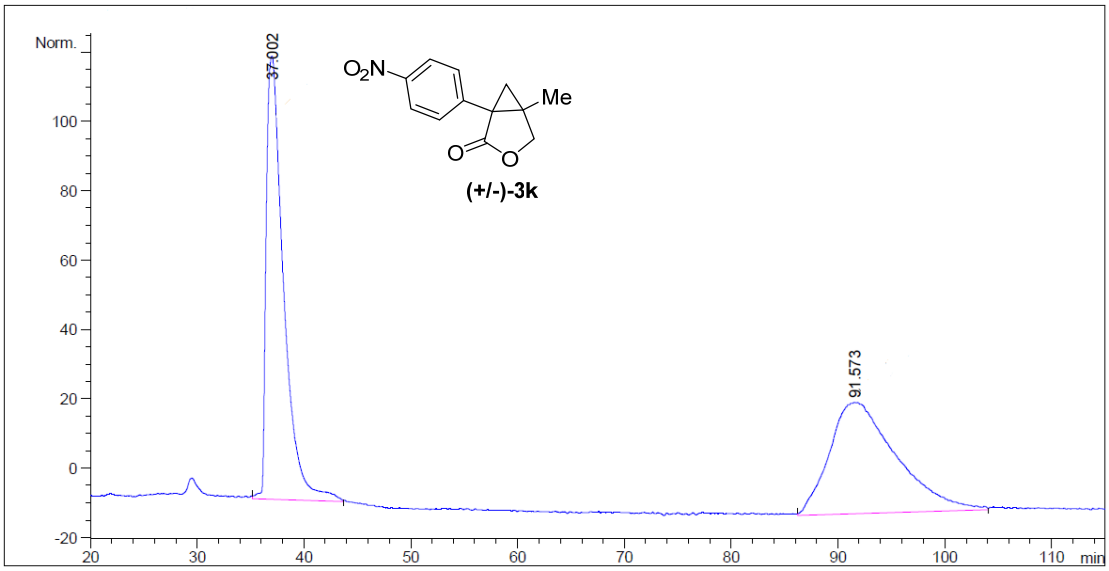
#	[min]		[min]	mAU	*s	[mAU]	%
1	7.907	VV	0.3241	1.39431e4		670.54883	95.0094
2	9.760	MM	0.4184	732.39484		29.17498	4.9906



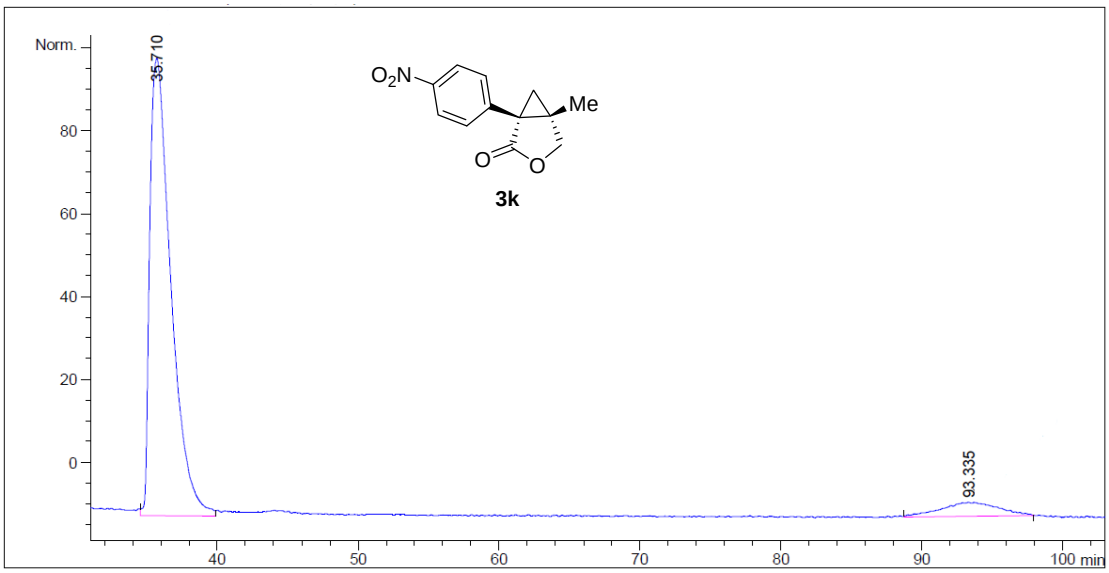
#	[min]		[min]	mAU	*s	[mAU]	%
1	8.205	BB	0.2710	3.17401e4		1789.37634	49.5458
2	11.204	VV	0.3524	3.23220e4		1407.53723	50.4542



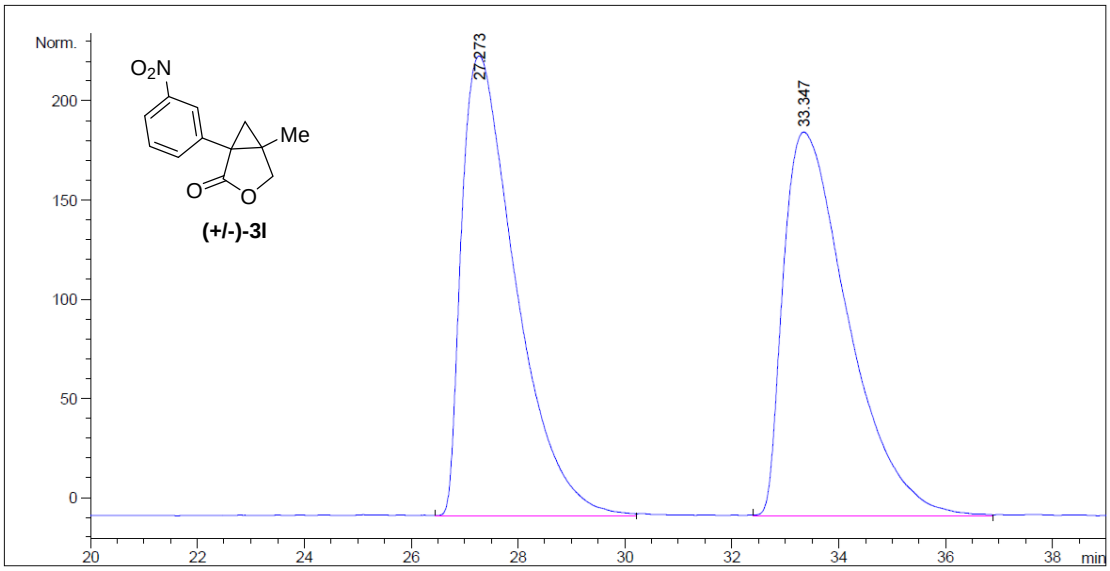
#	[min]		[min]	mAU	*s	[mAU]	%
1	8.111	VV	0.4189	3.18977e4		1254.66296	95.6667
2	10.910	VV	0.3951	1444.84485		55.82951	4.3333



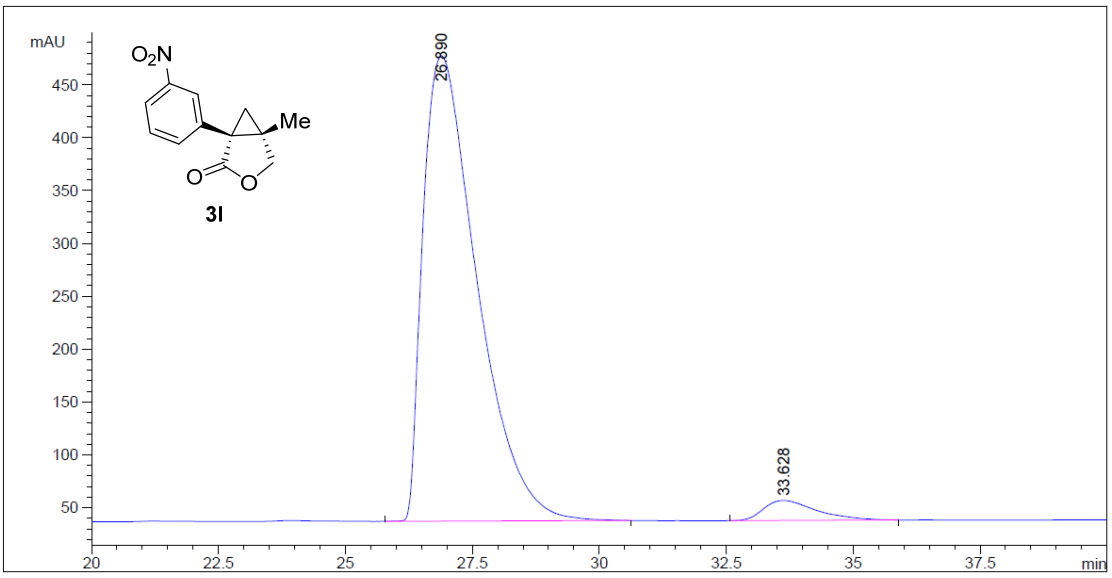
#	[min]		[min]	mAU	*s	[mAU]	%
1	37.002	MM	1.8799	1.44311e4		127.94479	50.8064
2	91.573	MM	7.2280	1.39730e4		32.21963	49.1936



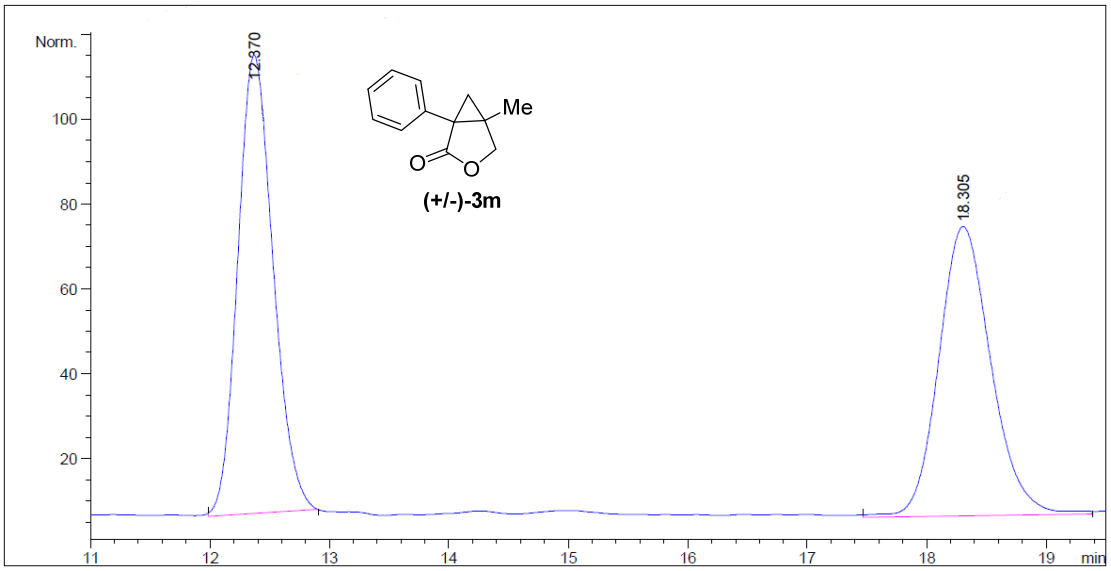
#	[min]		[min]	mAU	*s	[mAU]	%
1	35.710	VV	1.5200	1.14691e4		110.46165	92.2756
2	93.335	MM	4.6947	960.07935		3.40836	7.7244



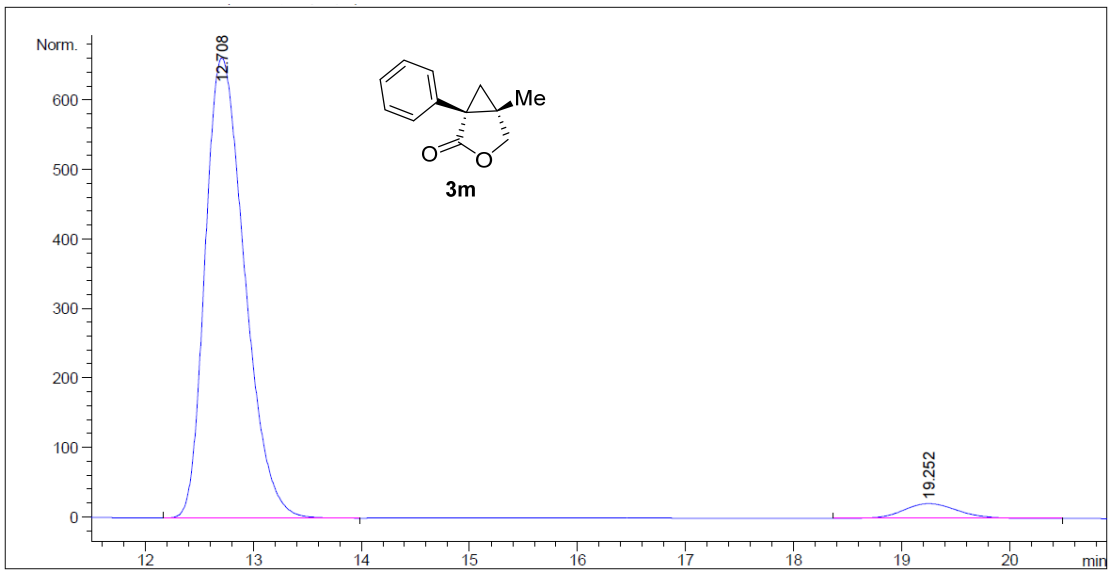
#	[min]		[min]	mAU	*s	[mAU]	%
1	27.273	VV	1.0298	1.63147e4		232.07182	49.9849
2	33.347	VV	1.2980	1.63246e4		193.65681	50.0151



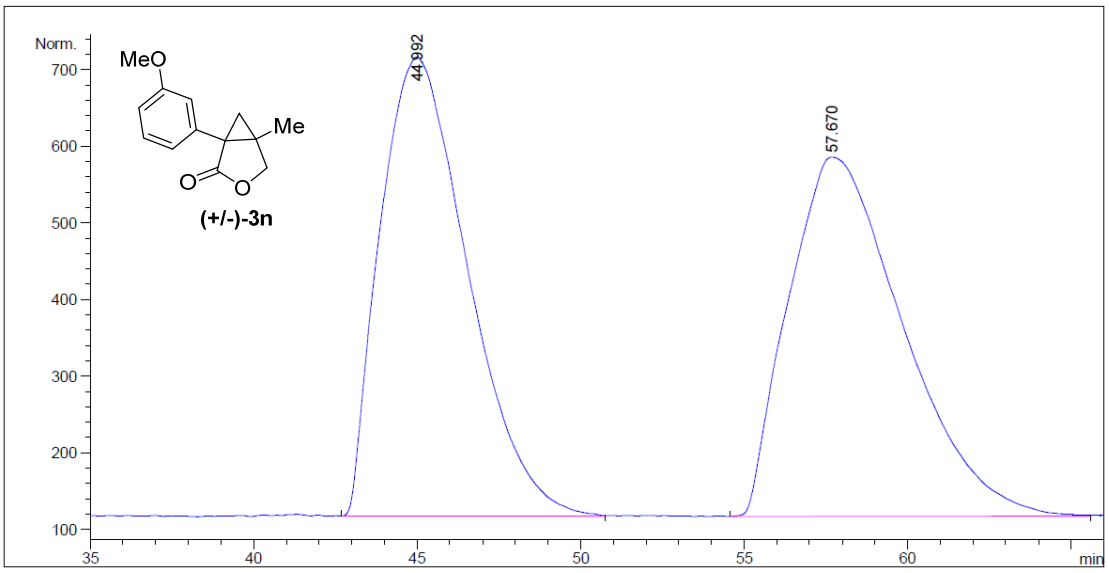
#	[min]		[min]	mAU	*s	[mAU]	%
1	26.890	BP	1.1283	3.25728e4		440.18179	95.9111
2	33.628	BP	1.0558	1388.65613		19.04949	4.0889



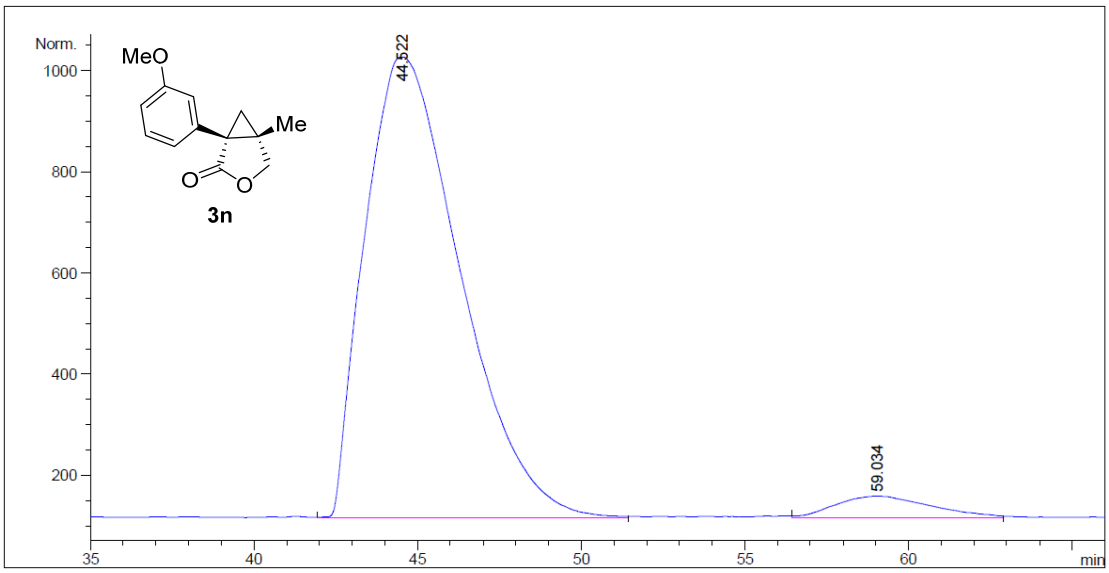
#	[min]		[min]	mAU	*s	[mAU]	%
1	12.370	MM	0.3428	2222.19116	108.04562	51.7409
2	18.305	MM	0.5064	2072.65503	68.22098	48.2591



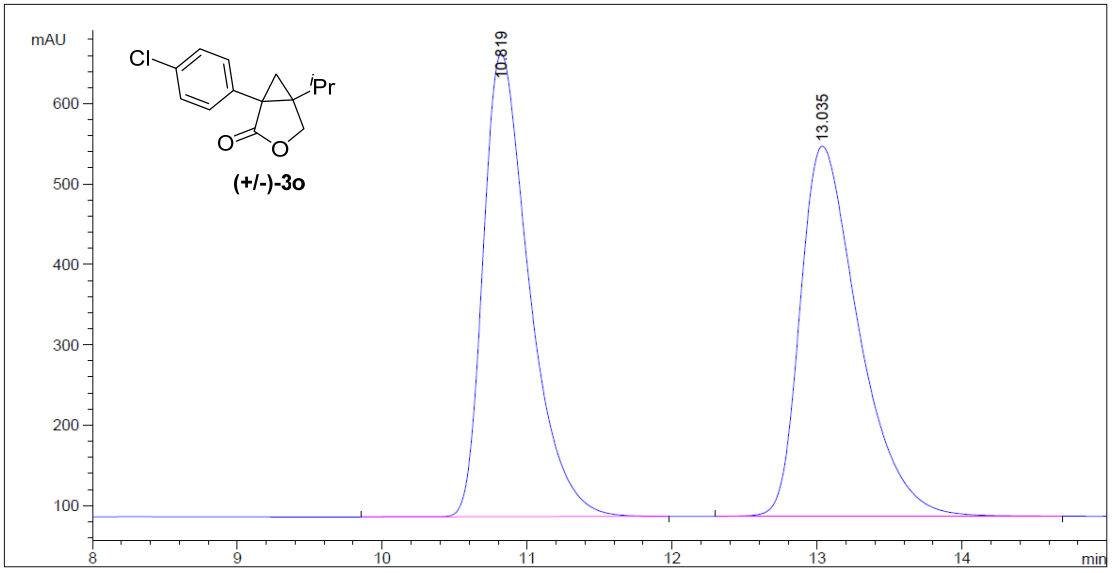
#	[min]		[min]	mAU	*s	[mAU]	%
1	12.708	VV	0.3948	1.67788e4	661.75269	95.6675
2	19.252	VV	0.5477	759.86914	21.42406	4.3325



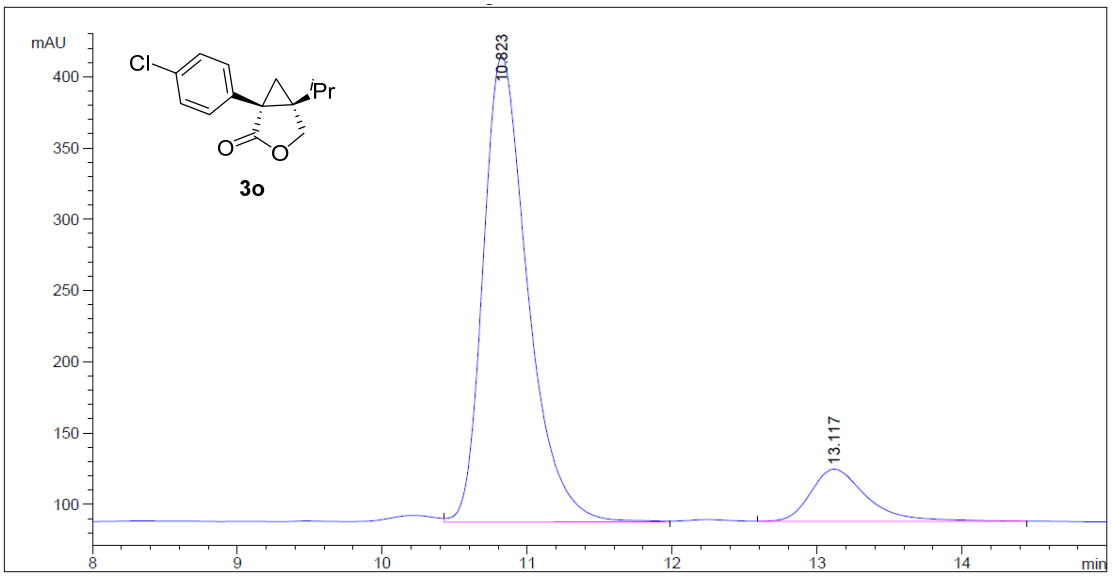
#	[min]		[min]	mAU	*s	[mAU]	%
1	44.992	VV	2.6096	1.11870e5		599.85797	49.5876
2	57.670	VV	3.1928	1.13730e5		468.56491	50.4124



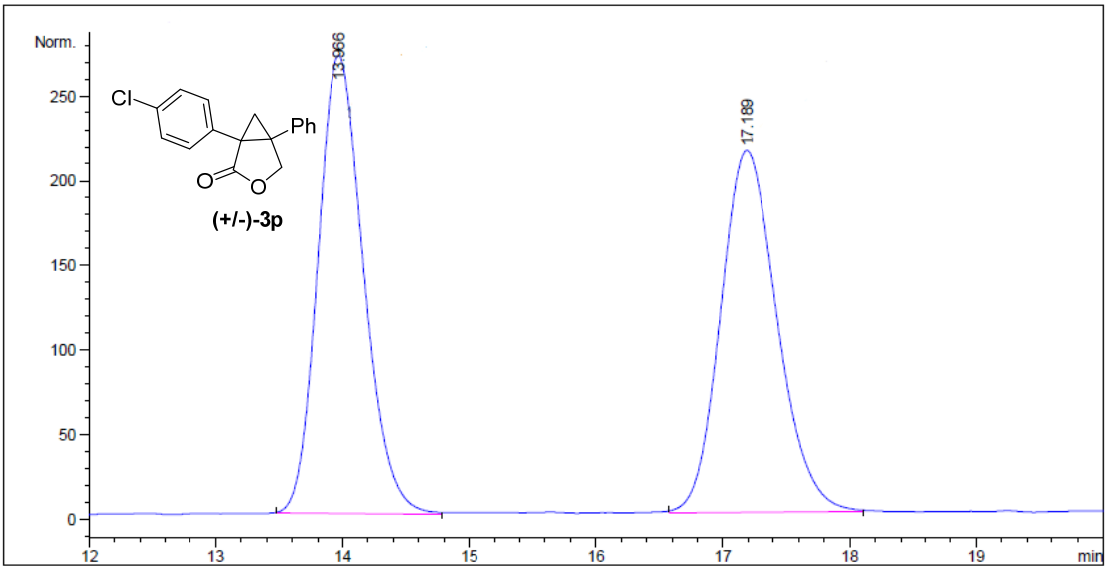
#	[min]		[min]	mAU	*s	[mAU]	%
1	44.522	VV	2.5133	1.84608e5		910.77350	95.4666
2	59.034	VV	2.4203	8766.45508		42.82449	4.5334



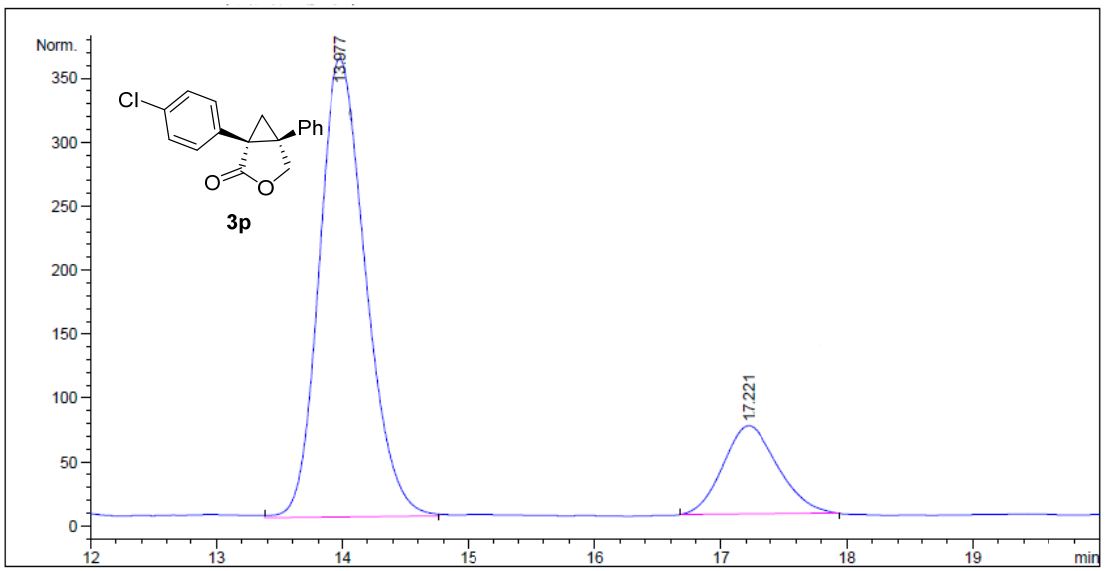
#	[min]		[min]	mAU	*s	[mAU]	%
1	10.819	BB	0.3344	1.27144e4		576.55688	49.5670
2	13.035	PB	0.4251	1.29365e4		460.77203	50.4330



#	[min]		[min]	mAU	*s	[mAU]	%
1	10.823	VB	0.3249	6975.48145		326.60455	87.4967
2	13.117	VB	0.4066	996.80225		36.76594	12.5033



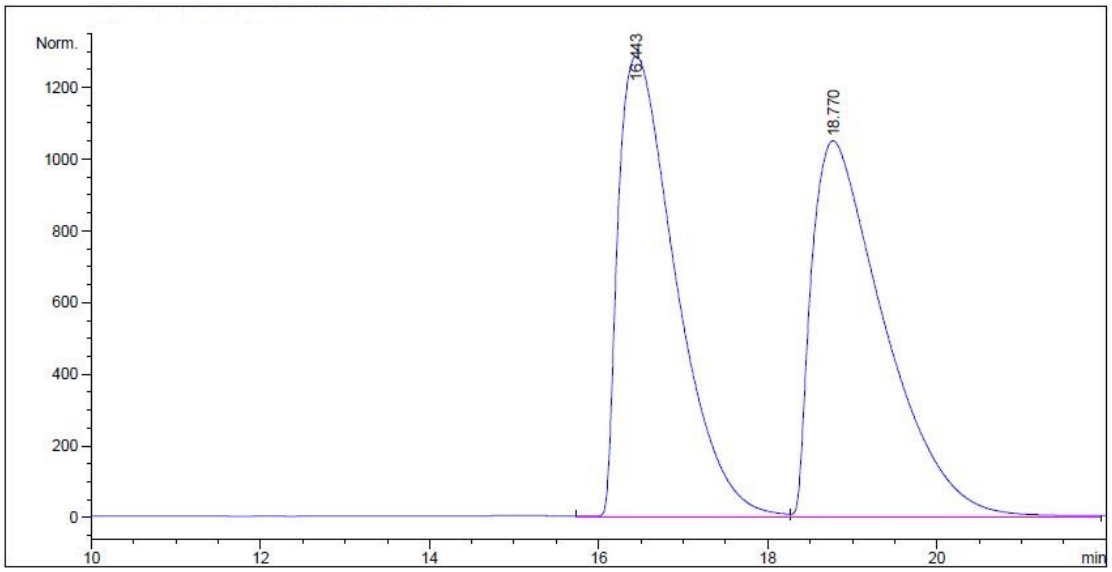
#	[min]		[min]	mAU	*s	[mAU	]	%
1	13.966	MM	0.4189	6811.21191		271.00687		50.5387
2	17.189	MM	0.5190	6666.00635		214.06985		49.4613



#	[min]		[min]	mAU	*s	[mAU	]	%
1	13.977	MM	0.4317	9285.46777		358.48062		81.5956
2	17.221	MM	0.5065	2094.39233		68.91335		18.4044

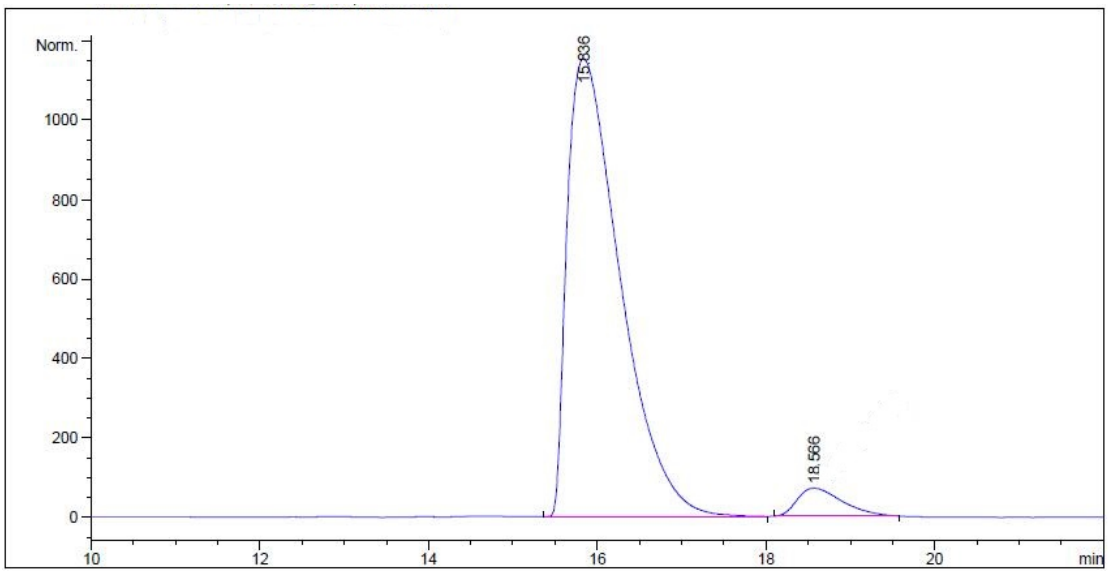
For a 2.0 mmol scale:

±3a：



#	[min]		[min]	mAU	*s	[mAU]	%
1	16.443	VV	0.7278	6.09834e4		1286.43530	49.1331
2	18.770	VV	0.9194	6.31355e4		1050.81445	50.8669

3a：



#	[min]		[min]	mAU	*s	[mAU]	%
1	15.836	VV	0.6704	5.08370e4		1155.85217	95.0566
2	18.566	MM	0.6210	2643.74878		70.95589	4.9434