

Supporting Information-III

HPLC Data

Aminocatalytic asymmetric [4+2]-annulation to access functionally rich hexahydrospiroindole pyrazolones

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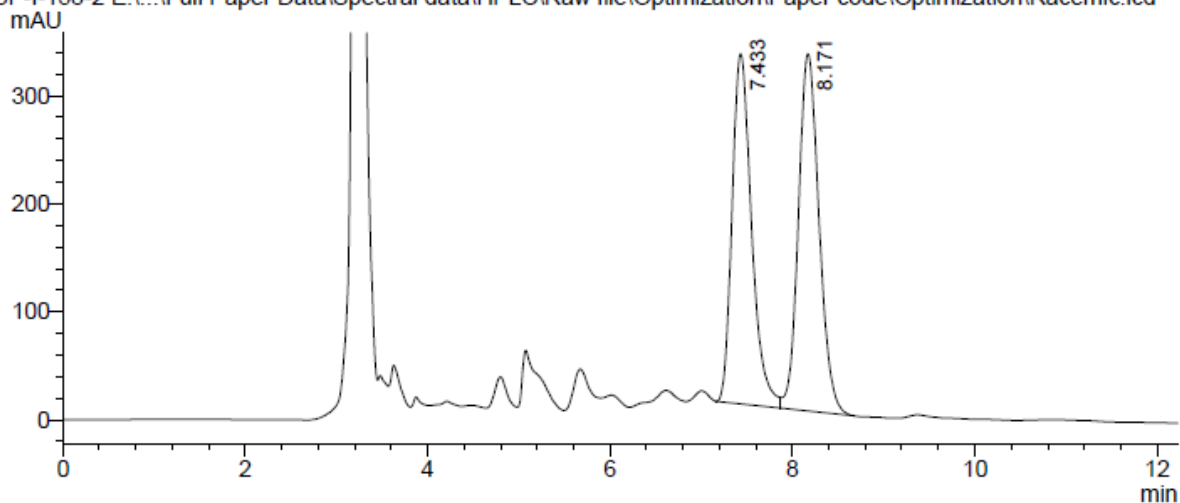
shivaprasad@cutn.ac.in and shivacutn@gmail.com

General Information:

The enantiomeric excess (*ee*) of the [4+2]-annulation adducts **4**, **5** and **7** were determined by chiral stationary phase HPLC using a Daicel Chiralpak IA, Chiralpak IC, and hexane/ethyl acetate as the eluent. Retention times and solvent ratios are indicated in the respective entries.

HPLC data of racemic **4aaa**

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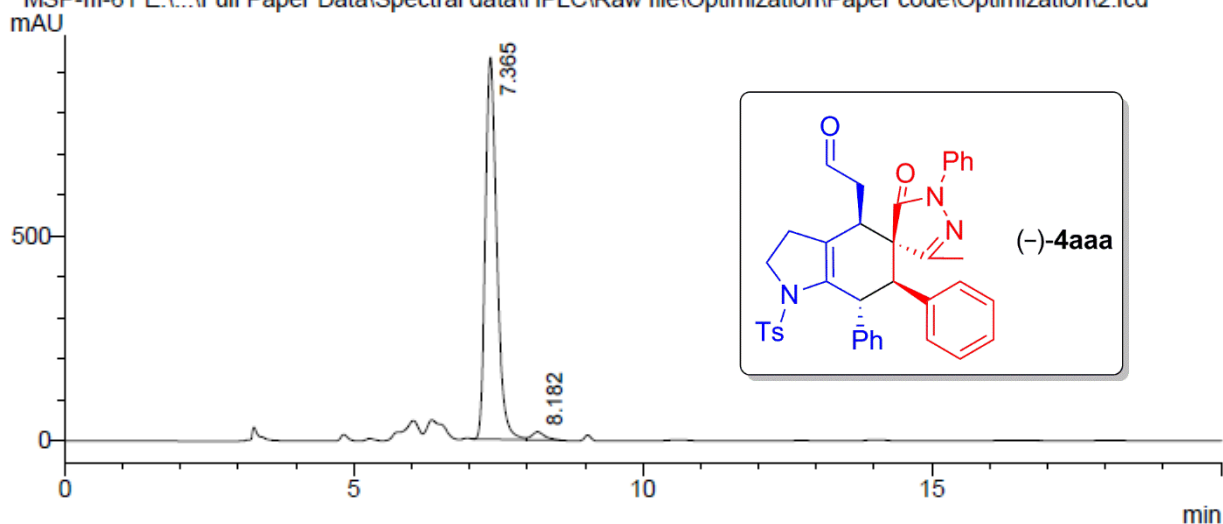


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	7.433	4813827	324273	48.044
2	8.171	5205694	330868	51.956
Total		10019522	655141	100.000

HPLC data of chiral **5aaa**: 96% ee

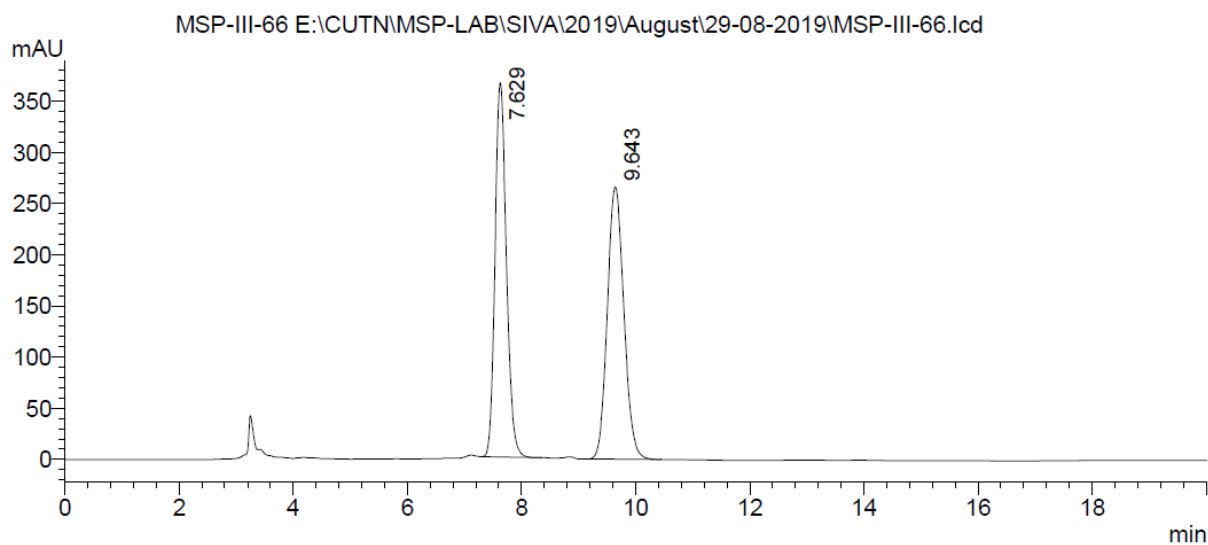
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PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	7.365	12779440	930806	97.732
2	8.182	296549	19314	2.268
Total		13075989	950120	100.000

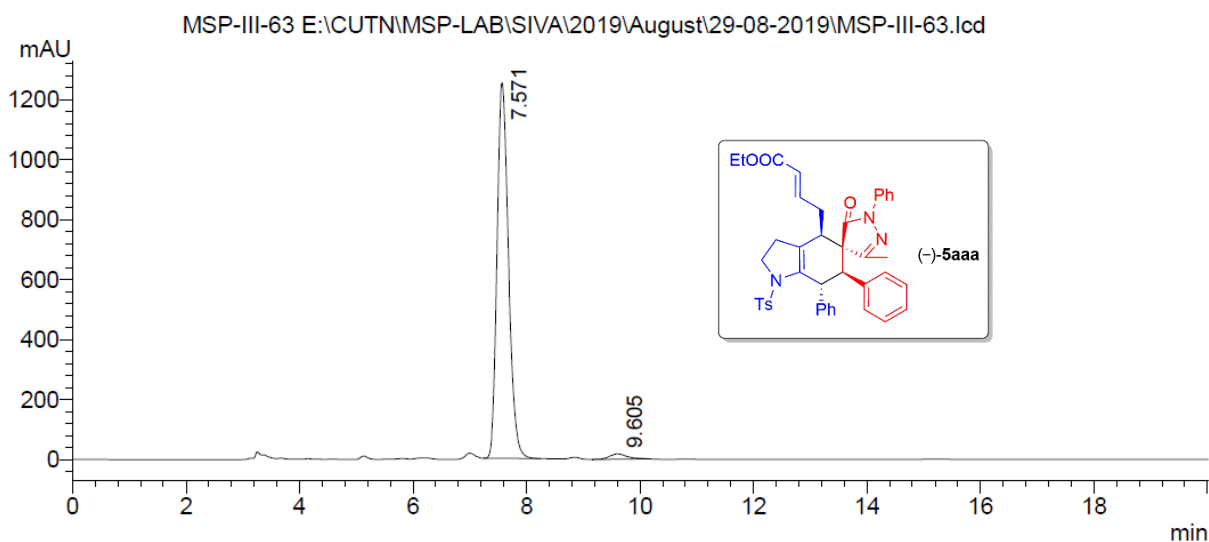
HPLC data of racemic **5aaa**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	7.629	5053933	365789	48.554
2	9.643	5354880	266145	51.446
Total		10408813	631934	100.000

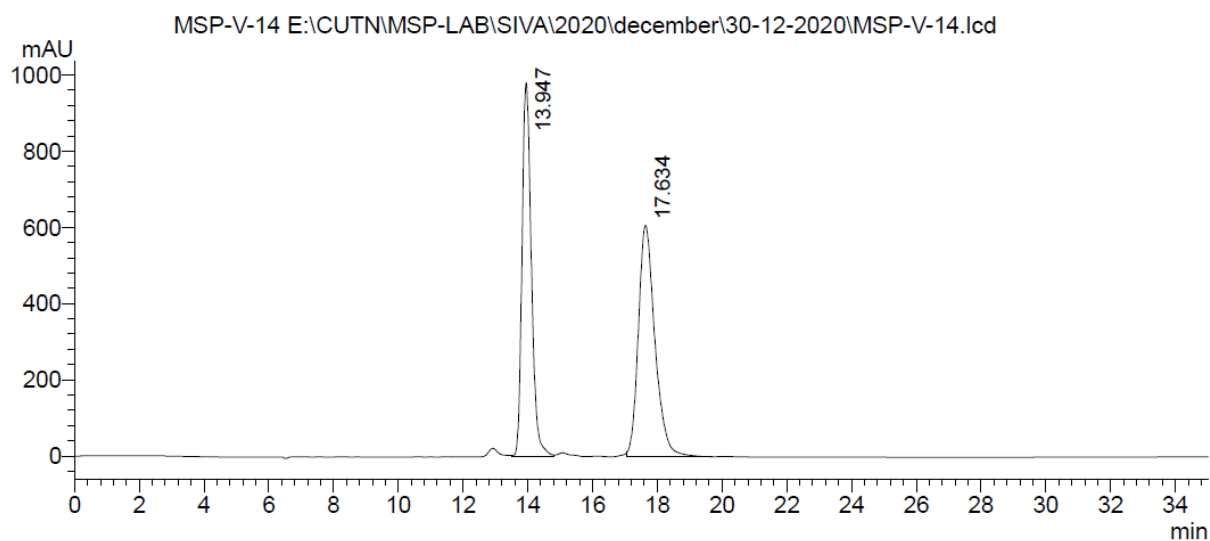
HPLC data of chiral **5aaa**: 96% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	7.571	17556609	1252706	97.922
2	9.605	372635	17366	2.078
Total		17929244	1270072	100.000

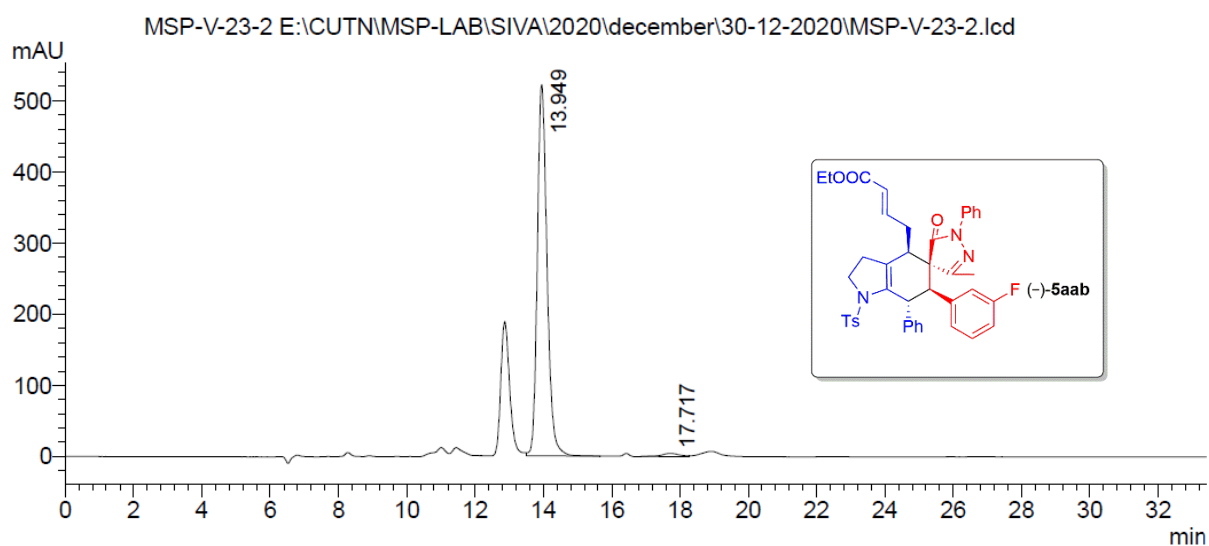
HPLC data of racemic **5aab**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.947	19729374	981892	47.616
2	17.634	21704817	607931	52.384
Total		41434191	1589823	100.000

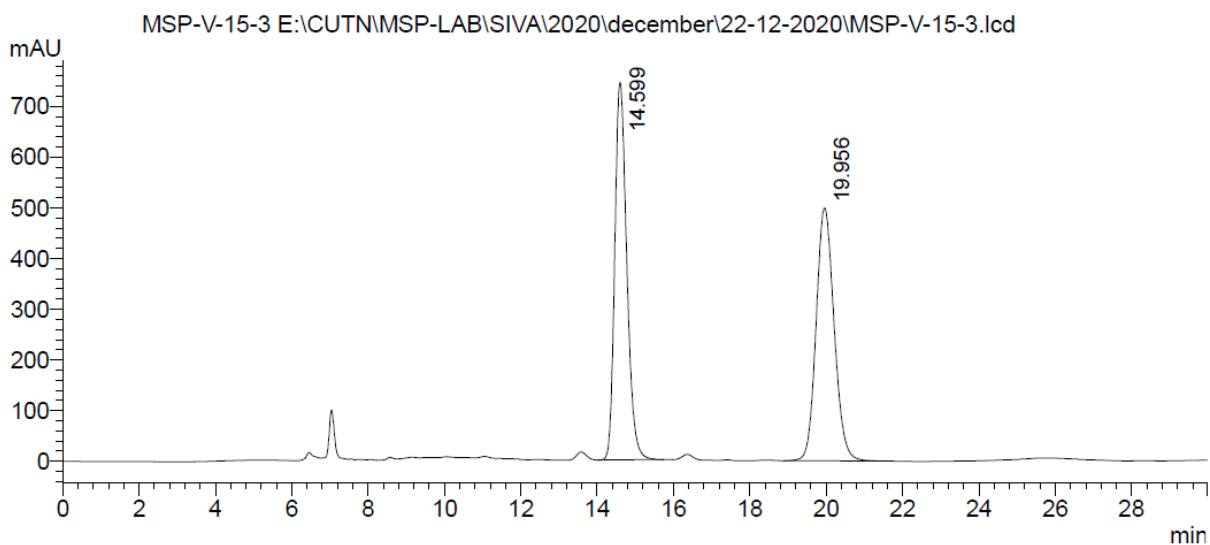
HPLC data of chiral **5aab**: 97% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.949	10329690	521906	98.486
2	17.717	158805	4336	1.514
Total		10488495	526242	100.000

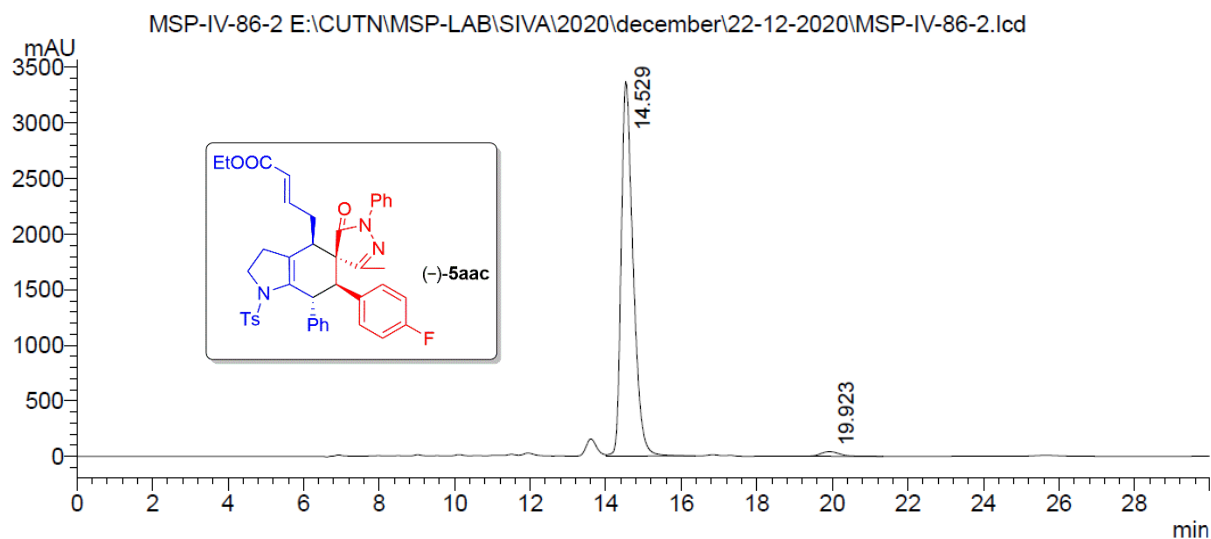
HPLC data of racemic **5aac**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.599	16239011	744237	49.856
2	19.956	16332666	498719	50.144
Total		32571677	1242956	100.000

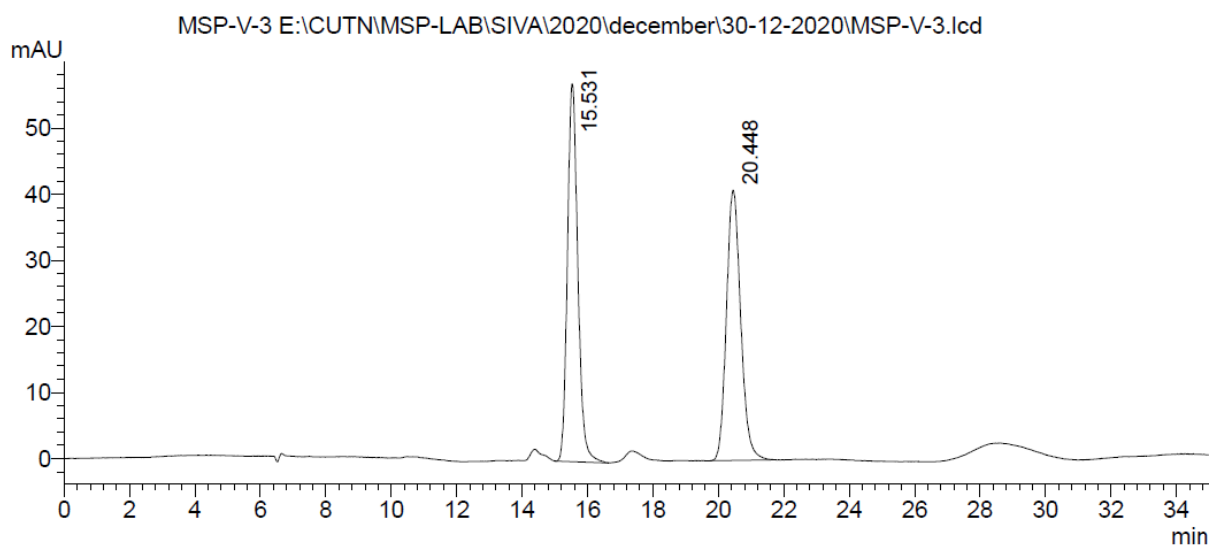
HPLC data of chiral **5aac**: 96% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.529	73835656	3369805	98.021
2	19.923	1490459	43280	1.979
Total		75326114	3413085	100.000

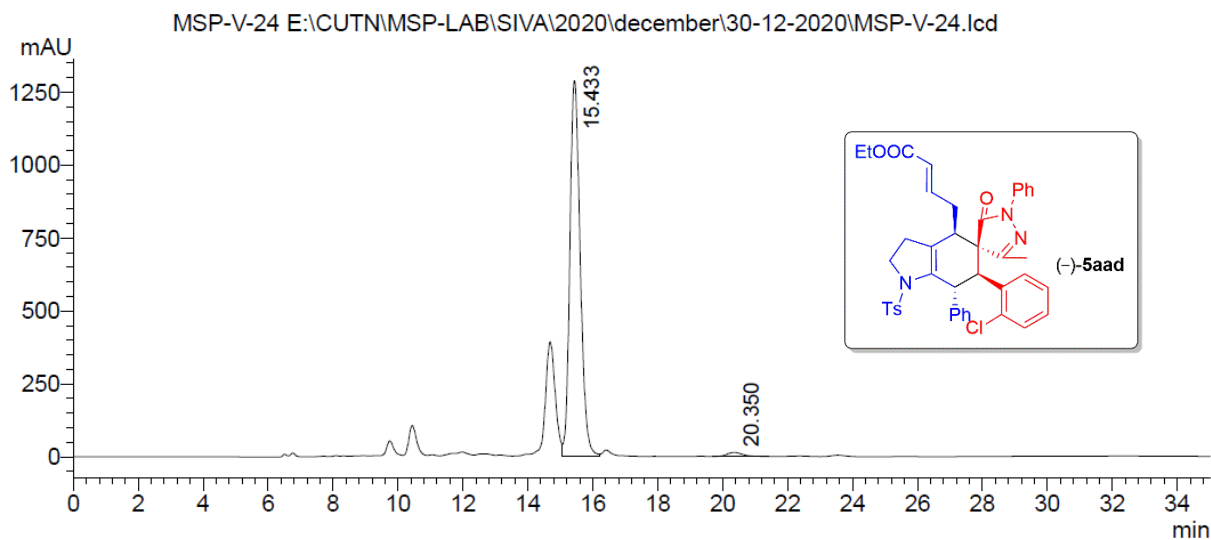
HPLC data of racemic **5aad**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.531	1261348	57210	50.409
2	20.448	1240894	40930	49.591
Total		2502242	98139	100.000

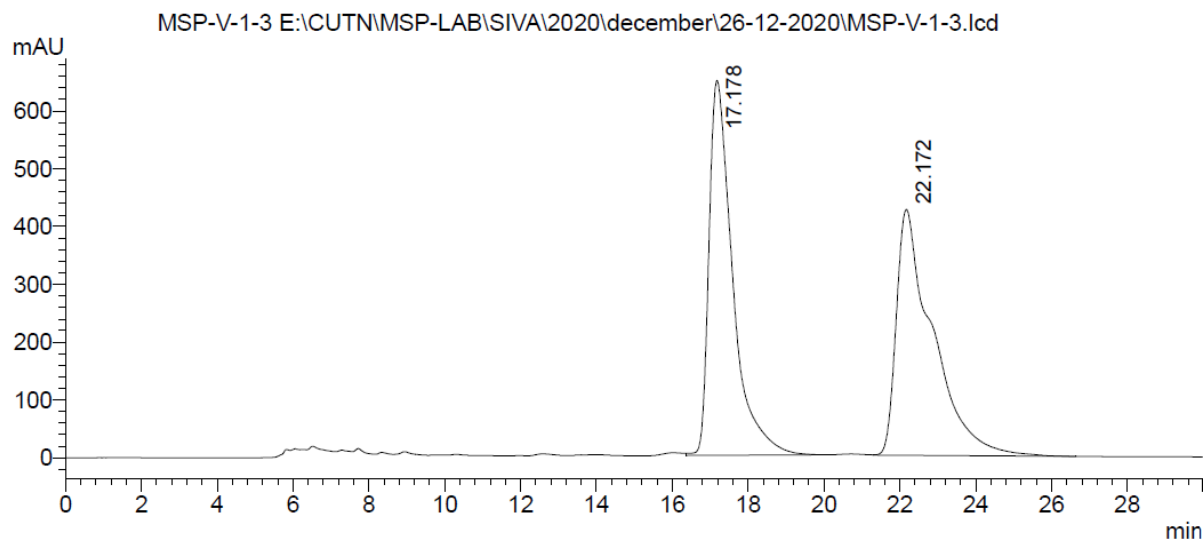
HPLC data of chiral **5aad**: 97% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.433	28433563	1286973	98.348
2	20.350	477490	14187	1.652
Total		28911052	1301160	100.000

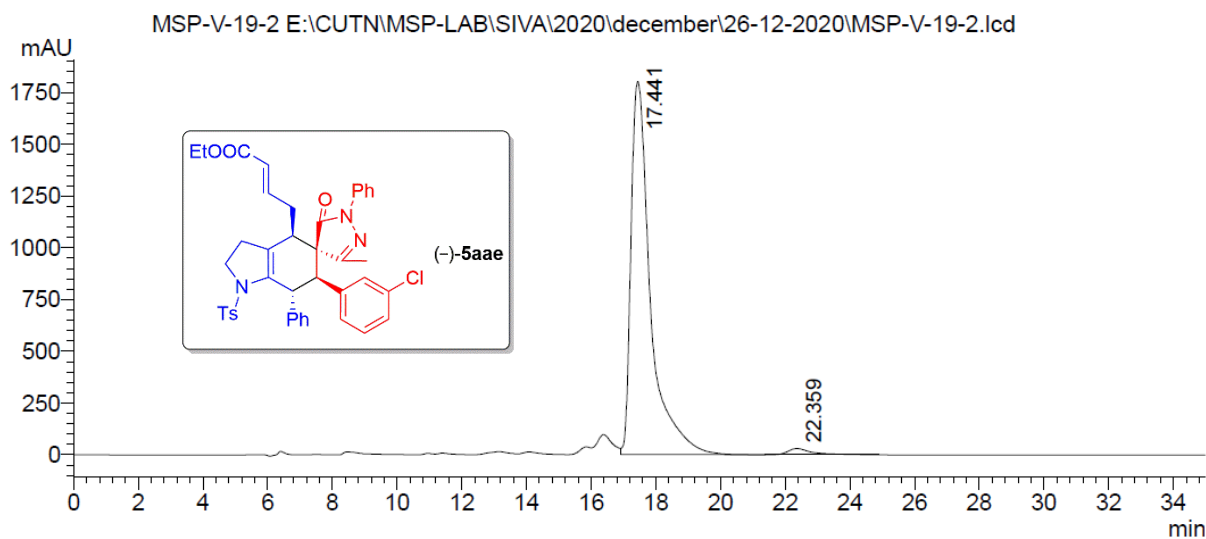
HPLC data of racemic **5a***ae*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.178	28131441	648324	49.850
2	22.172	28301035	424796	50.150
Total		56432476	1073120	100.000

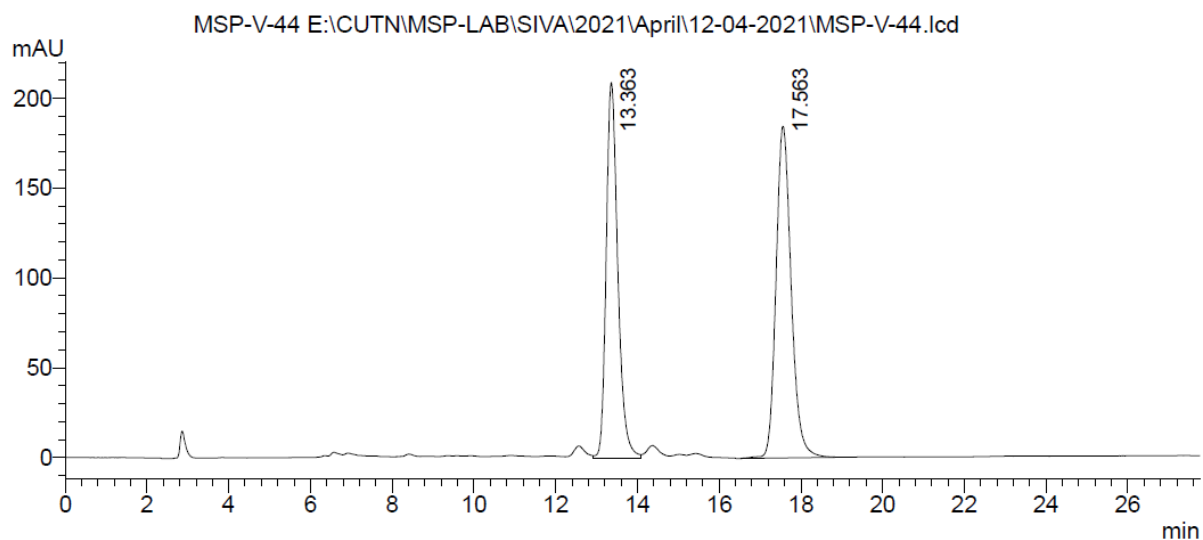
HPLC data of chiral **5a***ae*: 96% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.441	75213606	1802250	97.944
2	22.359	1579237	30068	2.056
Total		76792843	1832317	100.000

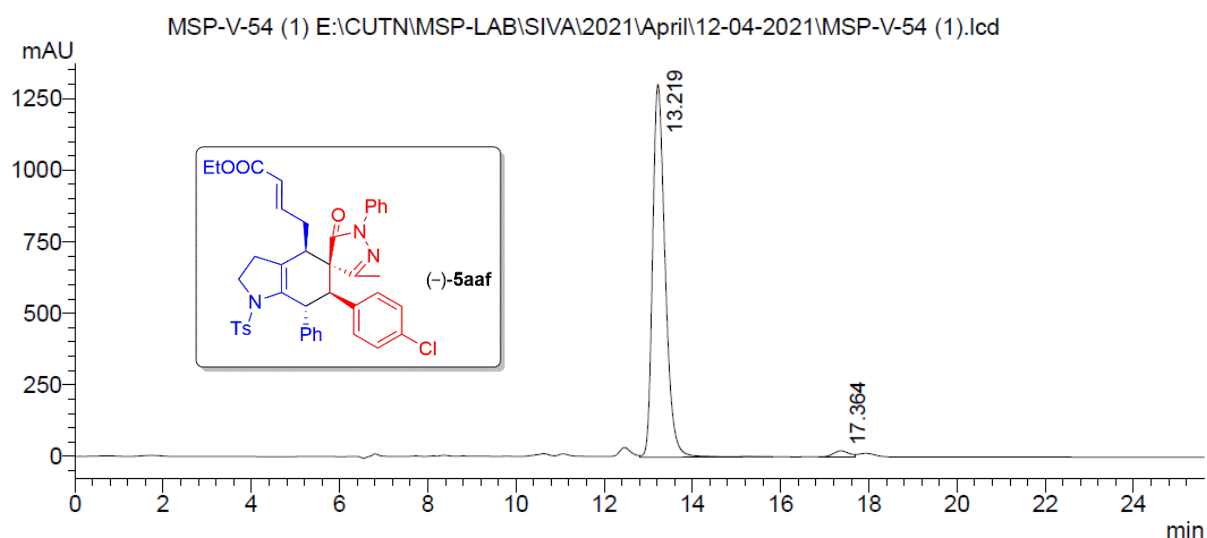
HPLC data of racemic **5aaf**



PDA Ch1 254nm

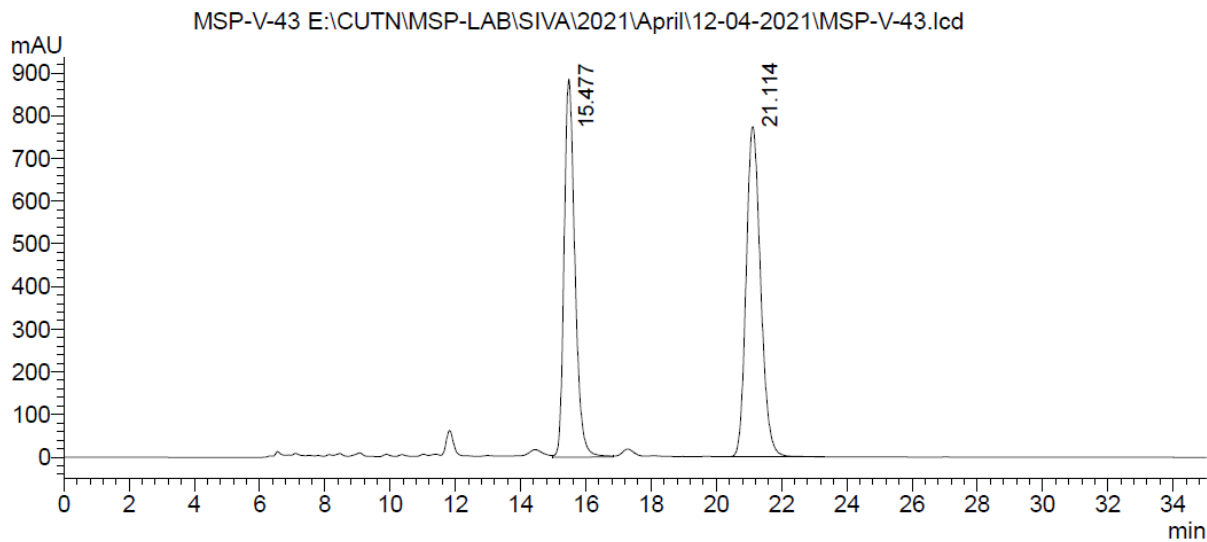
Peak #	Ret. Time (min)	Area	Height	Area%
1	13.363	4120296	209046	46.405
2	17.563	4758707	184625	53.595
Total		8879003	393671	100.000

HPLC data of chiral **5aaf**: 96% *ee*

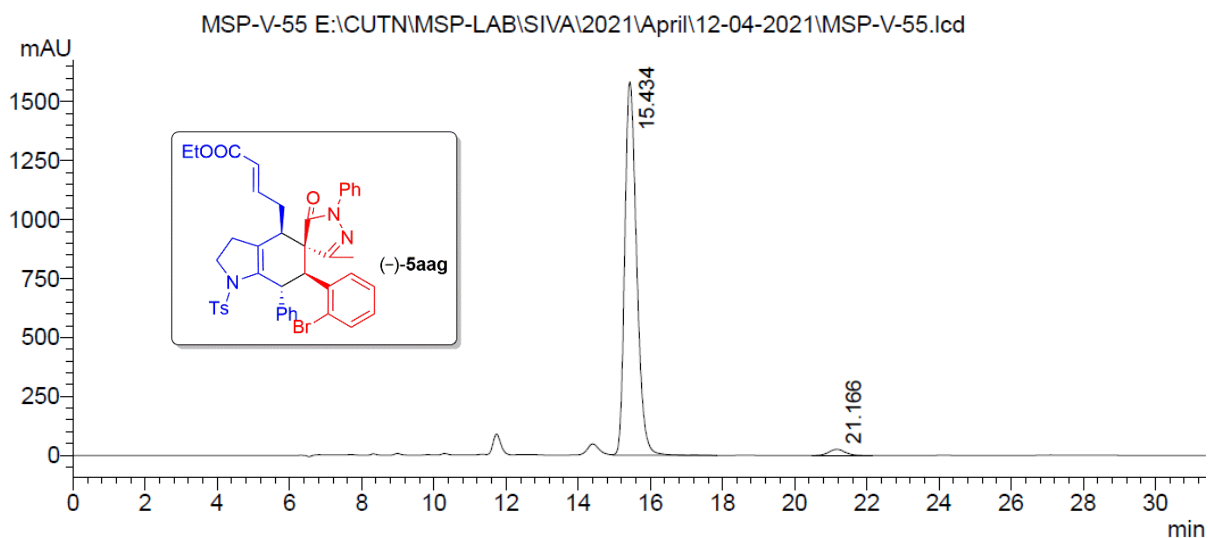


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.219	25779768	1303206	97.945
2	17.364	540979	21318	2.055
Total		26320747	1324525	100.000

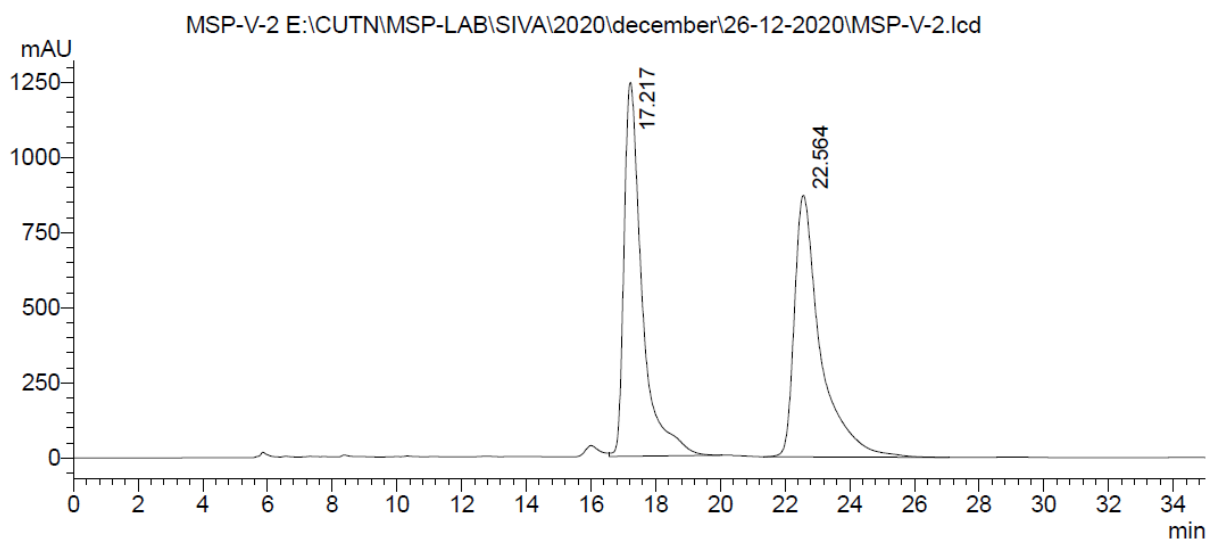
HPLC data of racemic **5aag**

PDA Ch1 254nm				
Peak #	Ret. Time (min)	Area	Height	Area%
1	15.477	20393242	885817	46.034
2	21.114	23907439	774063	53.966
Total		44300681	1659880	100.000

HPLC data of chiral **5aag**: 96% *ee*

PDA Ch1 254nm				
Peak #	Ret. Time (min)	Area	Height	Area%
1	15.434	36230061	1584271	97.807
2	21.166	812315	25858	2.193
Total		37042377	1610130	100.000

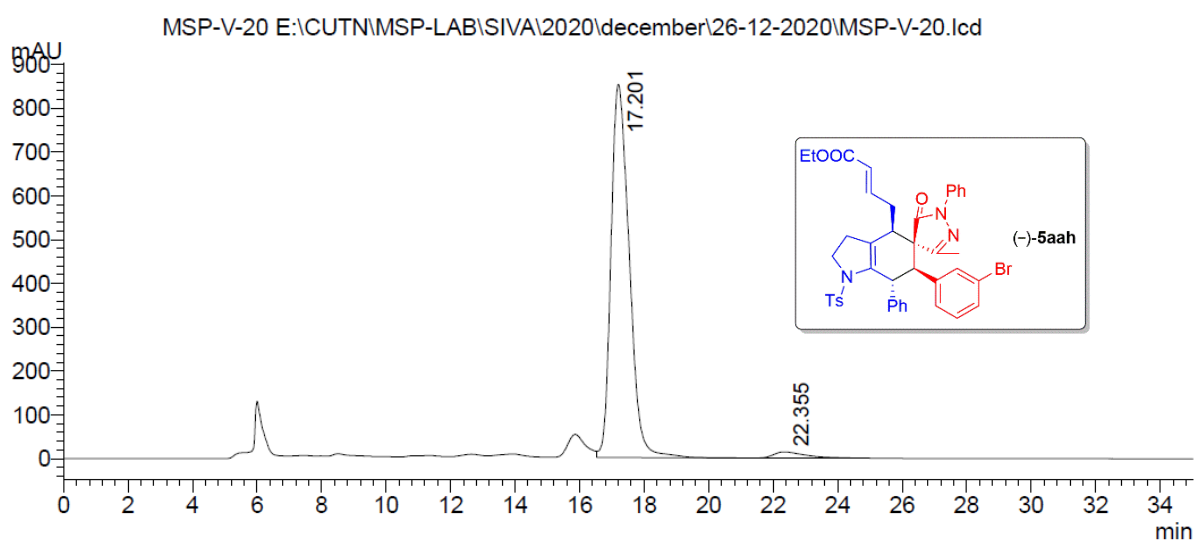
HPLC data of racemic **5aah**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.217	48286332	1244231	49.873
2	22.564	48532223	870643	50.127
Total		96818555	2114874	100.000

HPLC data of chiral **5aah**: 95% *ee*

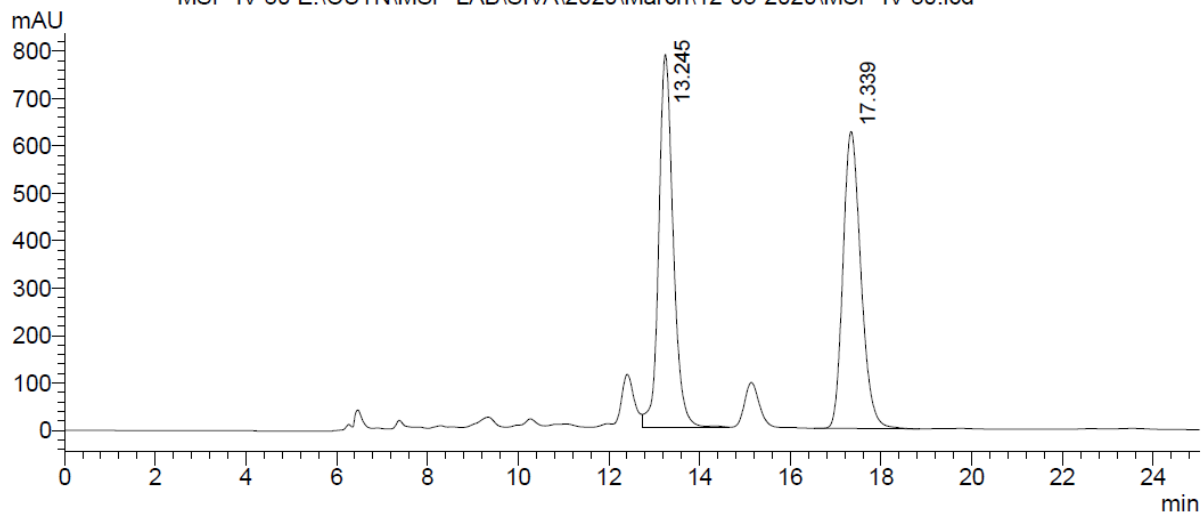


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.201	33460277	851274	97.359
2	22.355	907539	13647	2.641
Total		34367816	864921	100.000

HPLC data of racemic **5aai**

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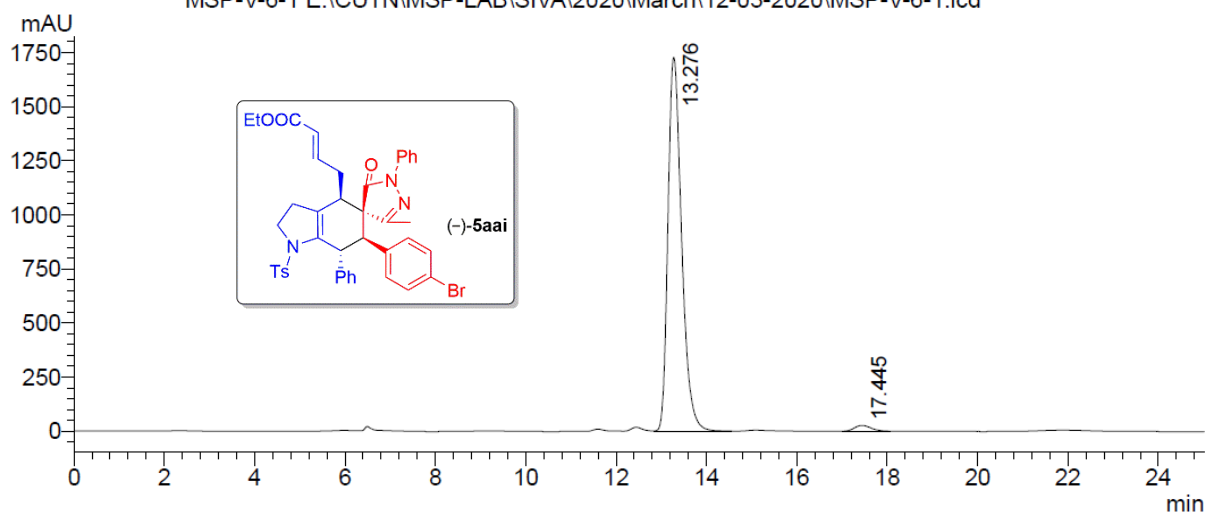


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.245	17385063	786455	50.226
2	17.339	17228734	625888	49.774
Total		34613797	1412343	100.000

HPLC data of chiral **5aai**: 96% *ee*

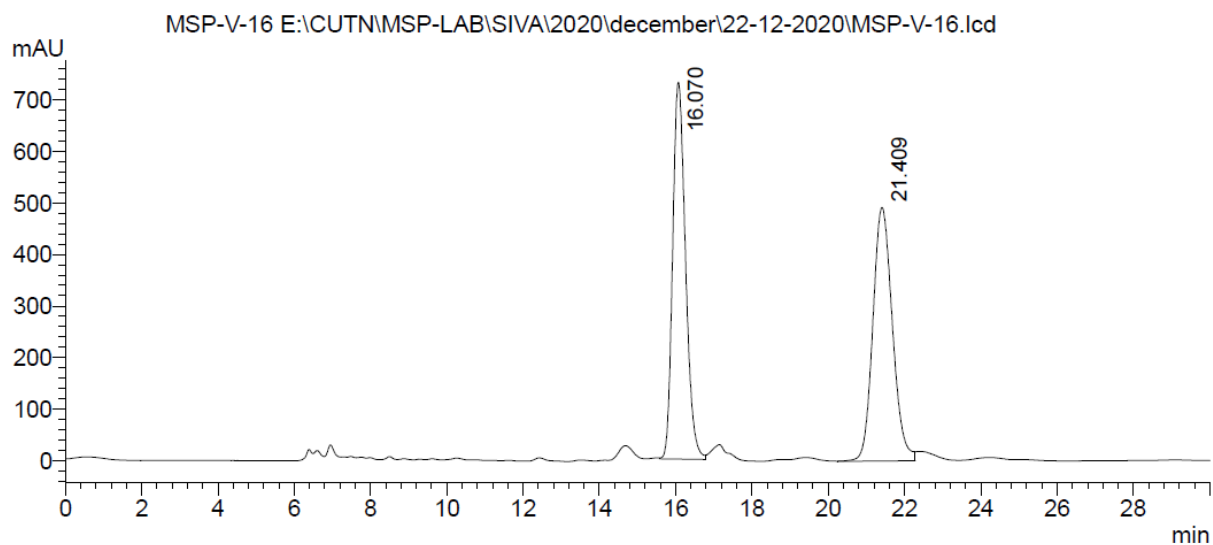
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PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.276	36280100	1727875	98.083
2	17.445	708964	27757	1.917
Total		36989064	1755632	100.000

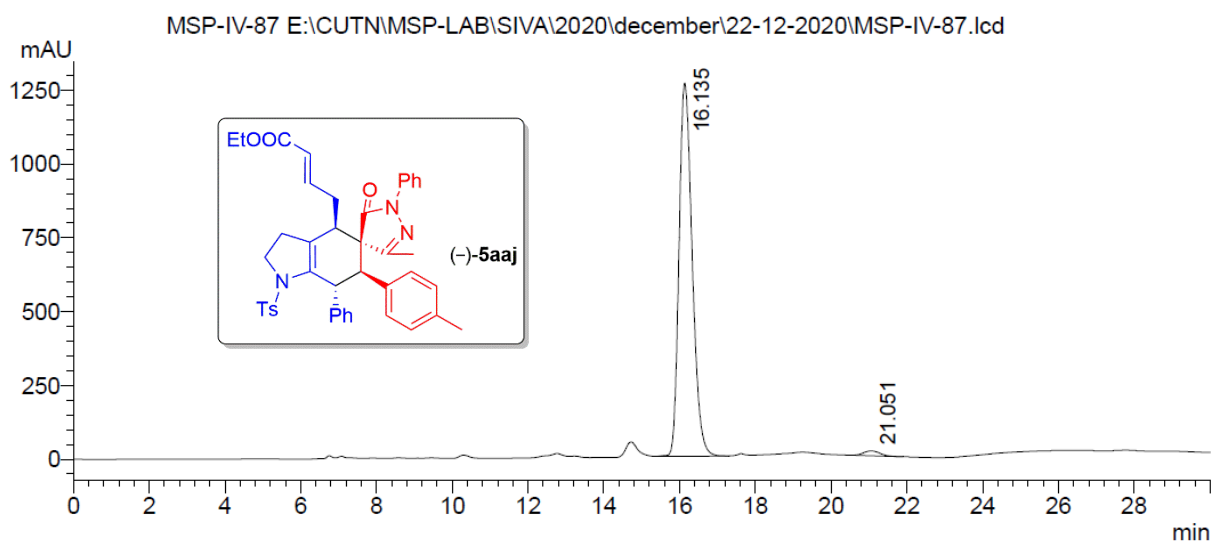
HPLC data of racemic **5aaj**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.070	17121287	731300	49.453
2	21.409	17499916	491755	50.547
Total		34621203	1223054	100.000

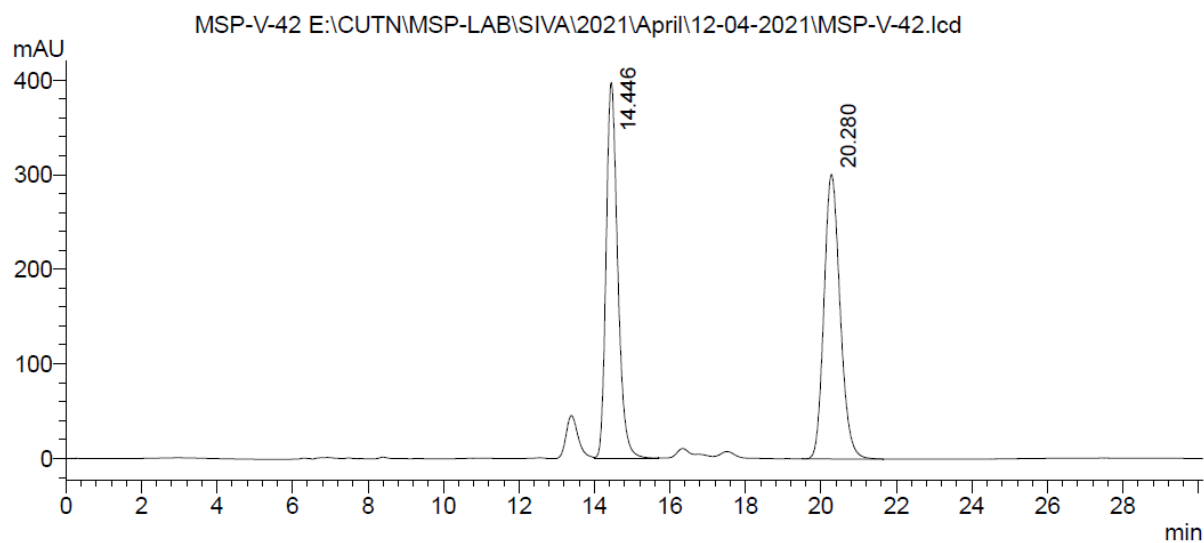
HPLC data of chiral **5aaj**: 97% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.135	30492903	1263535	98.385
2	21.051	500602	17061	1.615
Total		30993505	1280595	100.000

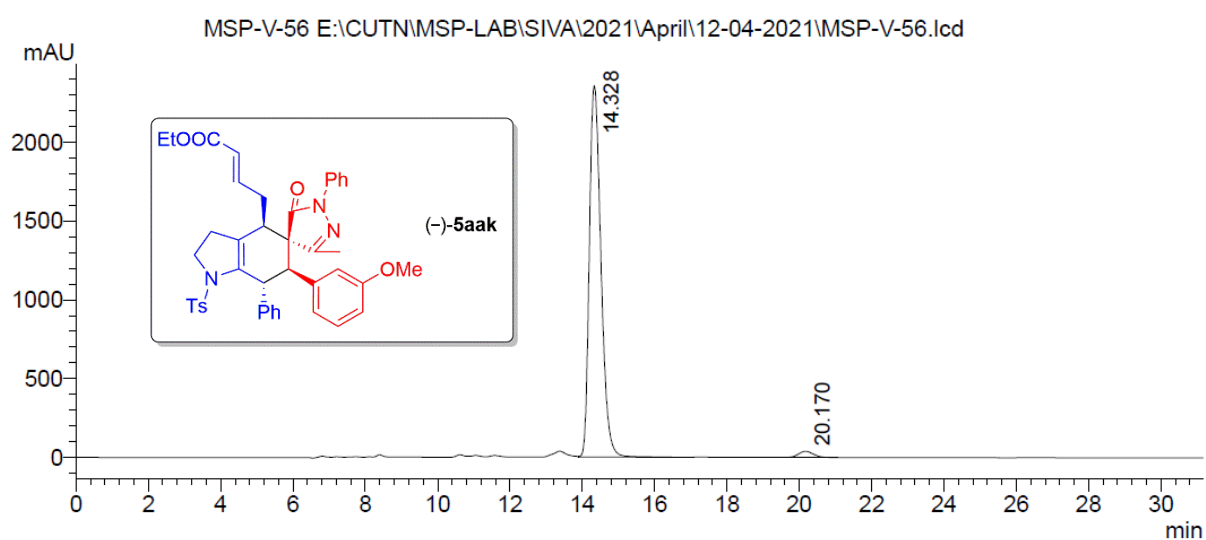
HPLC data of racemic **5aak**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.446	8507529	397717	48.768
2	20.280	8937363	300962	51.232
Total		17444892	698679	100.000

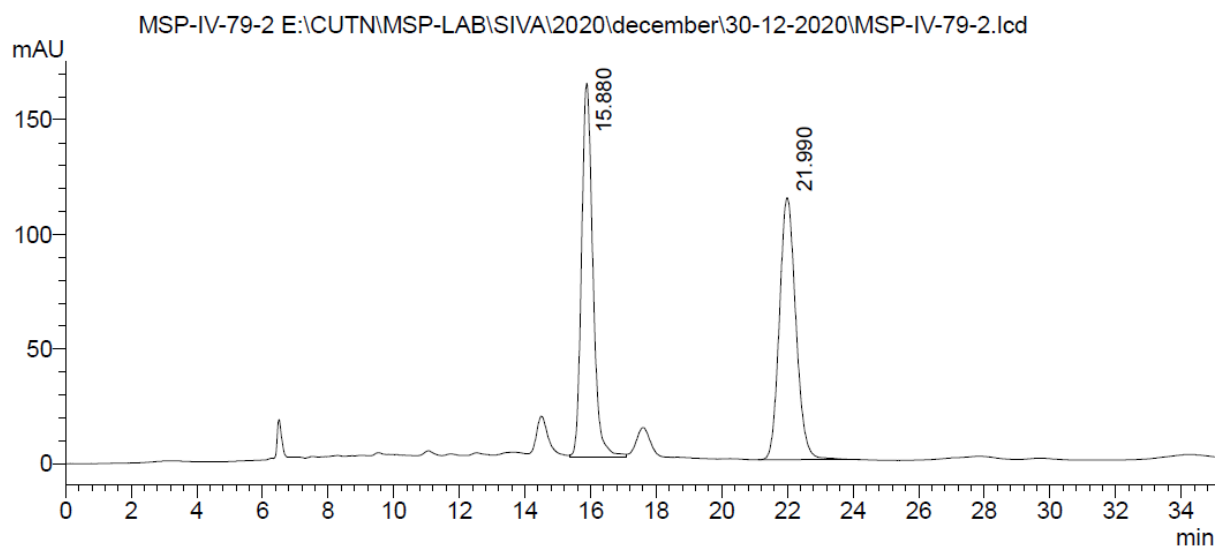
HPLC data of chiral **5aak**: 96% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.328	52620756	2356410	97.836
2	20.170	1164083	39678	2.164
Total		53784839	2396088	100.000

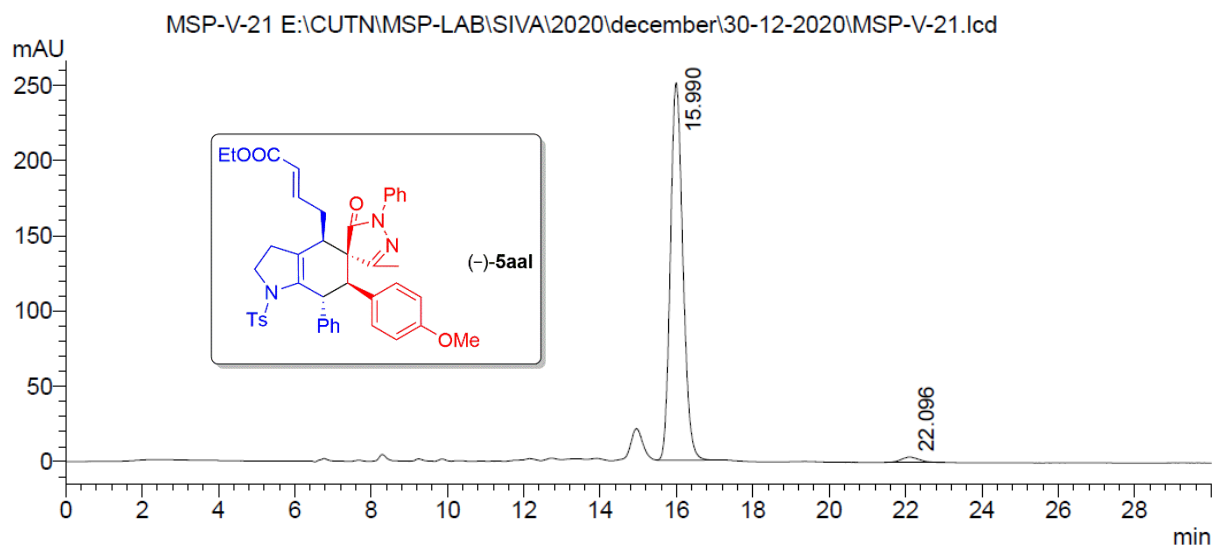
HPLC data of racemic **5aal**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.880	3925873	163195	49.675
2	21.990	3977271	114247	50.325
Total		7903145	277442	100.000

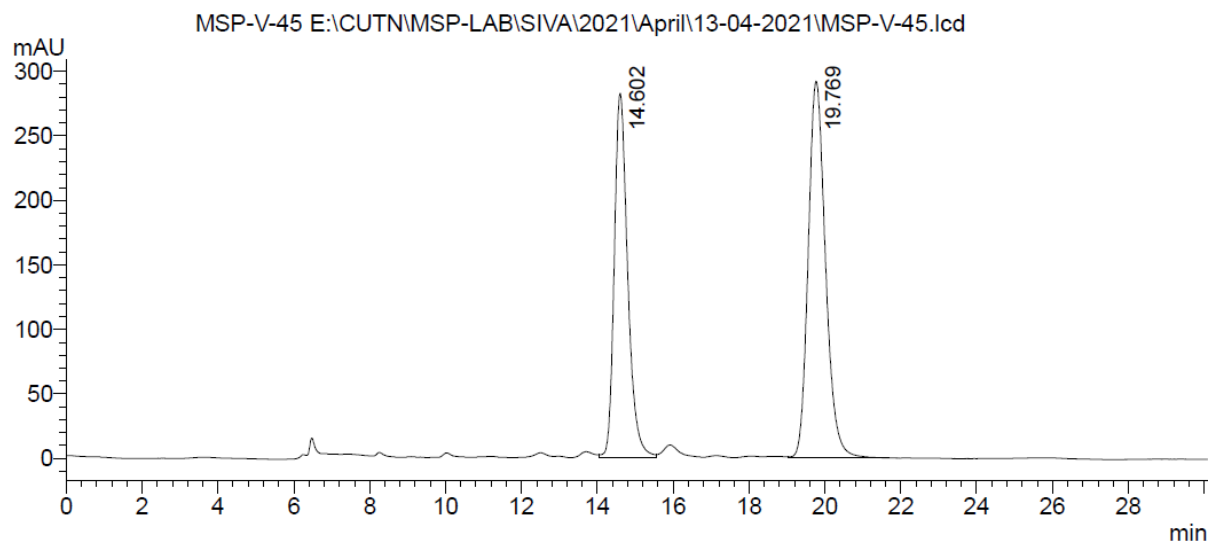
HPLC data of chiral **5aal**: 96% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.990	5701876	250692	97.929
2	22.096	120570	3572	2.071
Total		5822446	254265	100.000

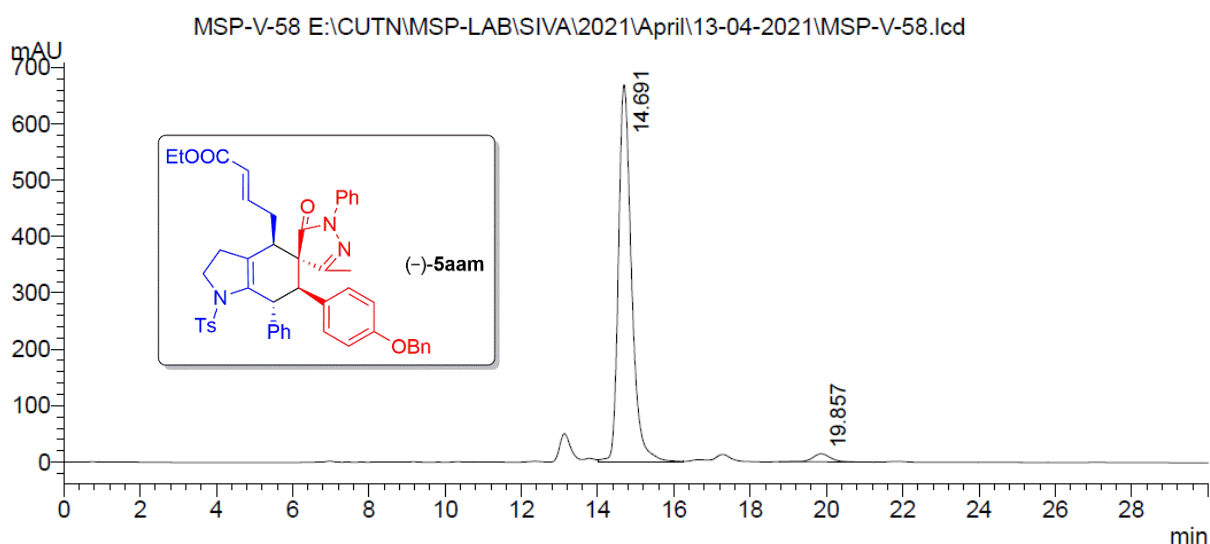
HPLC data of racemic **5aam**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.602	6951747	282447	42.913
2	19.769	9248037	291671	57.087
Total		16199784	574118	100.000

HPLC data of chiral **5aam**: 94% *ee*

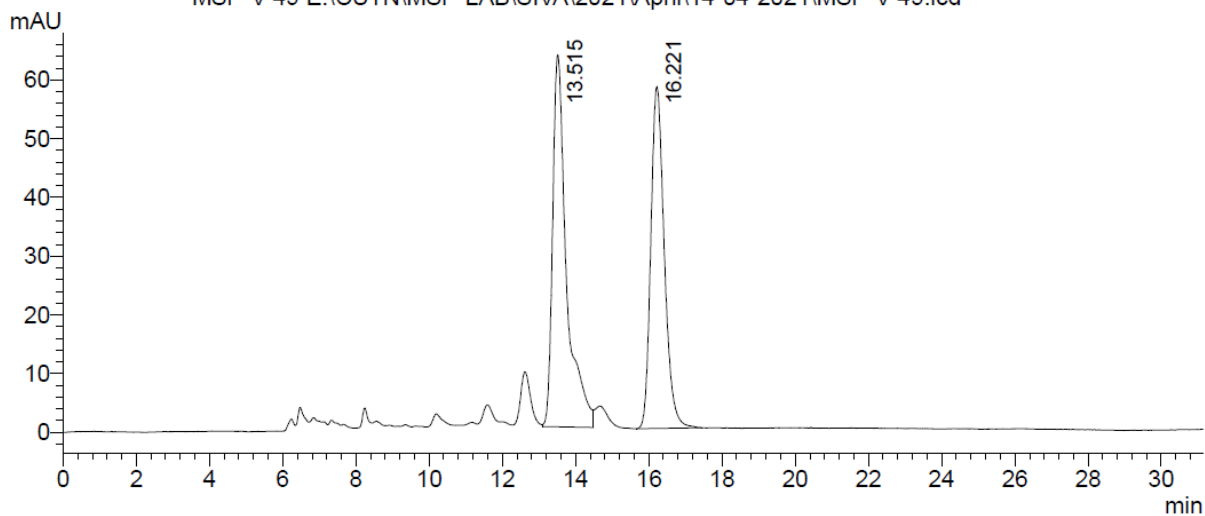


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.691	15954817	669486	96.986
2	19.857	495861	14536	3.014
Total		16450678	684022	100.000

HPLC data of racemic **5aan**

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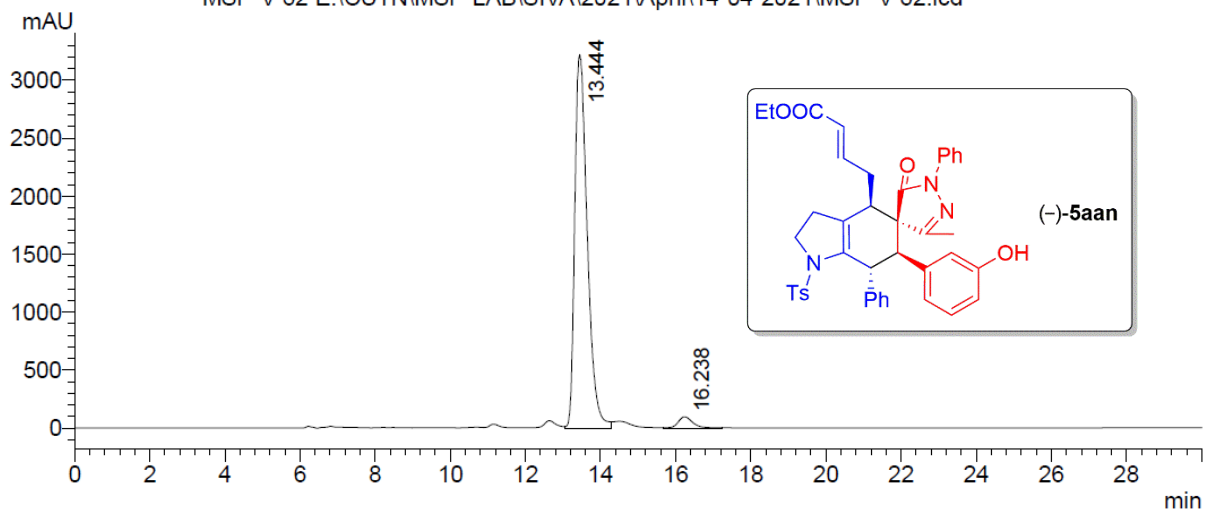


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.515	1668854	63345	52.835
2	16.221	1489751	58209	47.165
Total		3158606	121554	100.000

HPLC data of chiral **5aan**: 93% *ee*

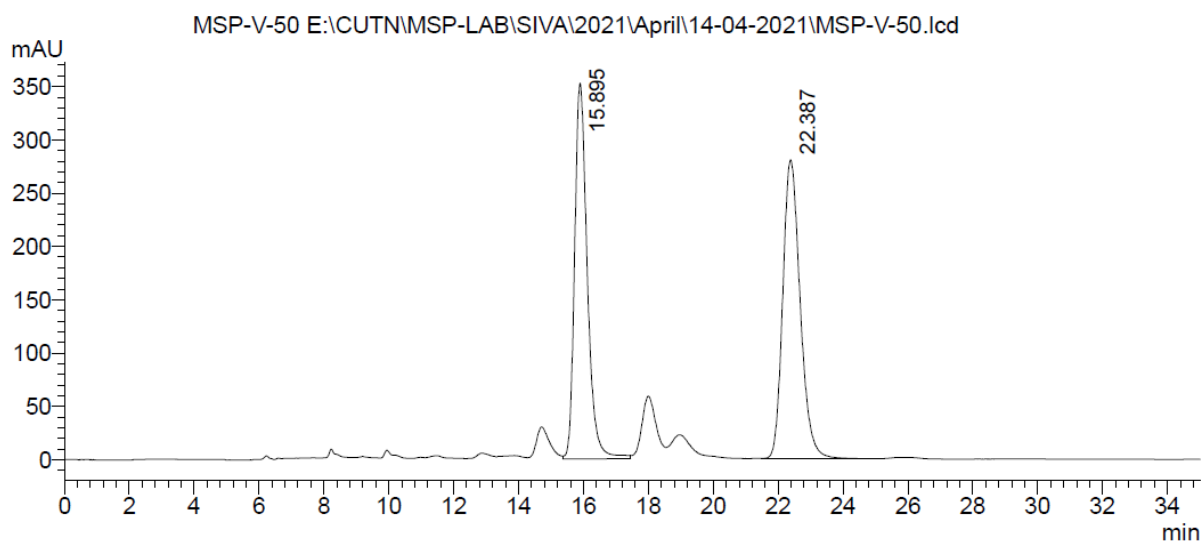
MSP-V-62 E:\CUTN\MSP-LAB\SIVA\2021\April\14-04-2021\MSP-V-62.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.444	74621142	3220041	96.618
2	16.238	2612143	97497	3.382
Total		77233285	3317538	100.000

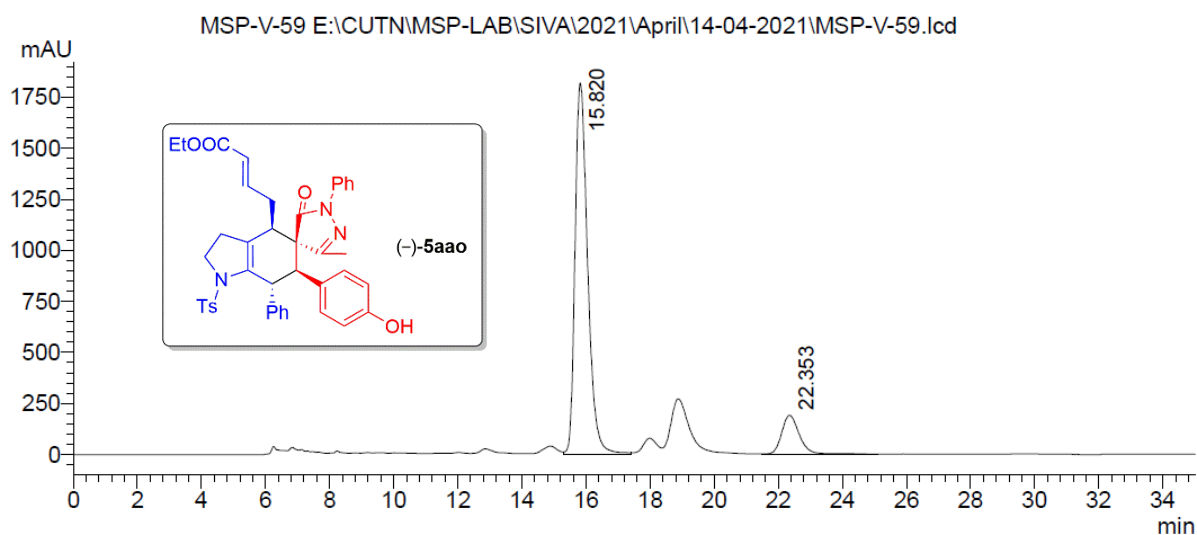
HPLC data of racemic **5aao**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.895	9547163	352487	47.804
2	22.387	10424184	280291	52.196
Total		19971347	632777	100.000

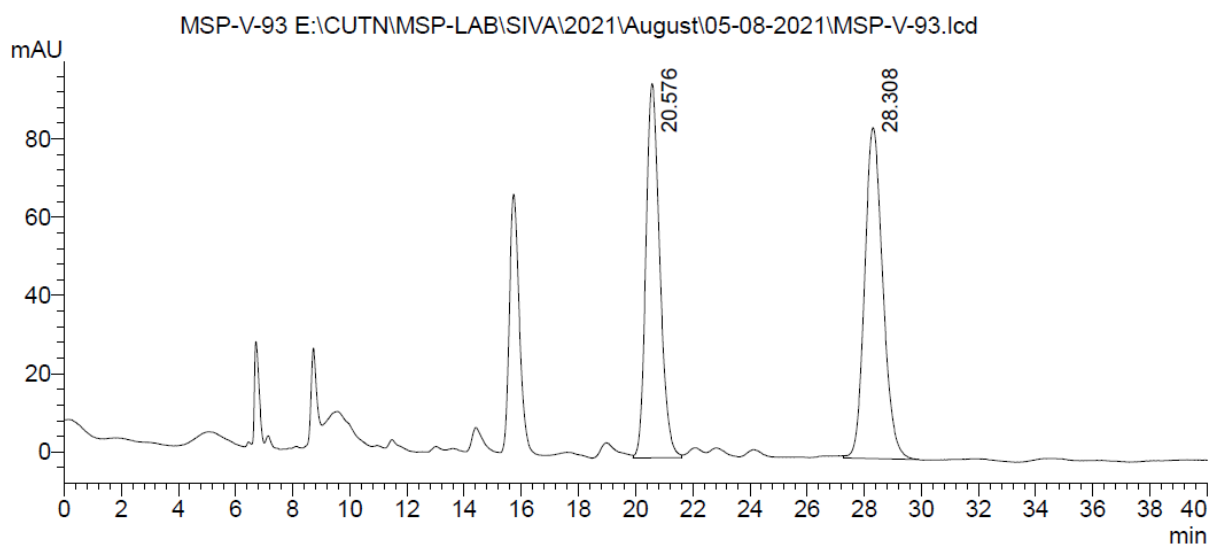
HPLC data of chiral **5aao**: 74% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.820	49779266	1818787	87.081
2	22.353	7385340	190883	12.919
Total		57164606	2009670	100.000

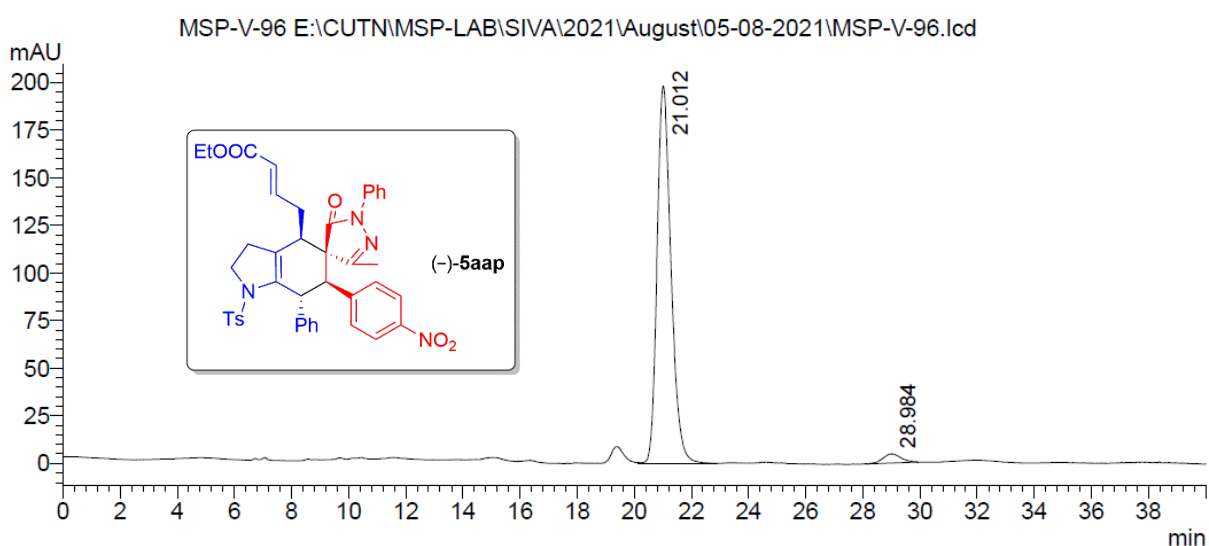
HPLC data of racemic **5aap**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	20.576	3223935	95685	46.310
2	28.308	3737777	84613	53.690
Total		6961713	180298	100.000

HPLC data of chiral **5aap**: 94% *ee*

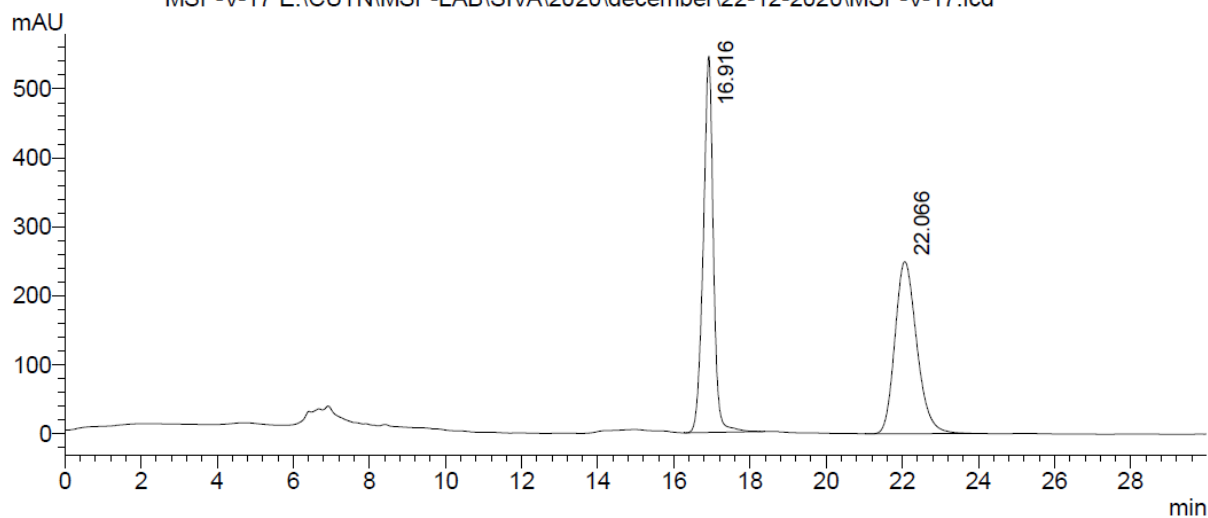


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	21.012	6713556	198183	96.982
2	28.984	208912	4887	3.018
Total		6922468	203069	100.000

HPLC data of racemic **5aaq**

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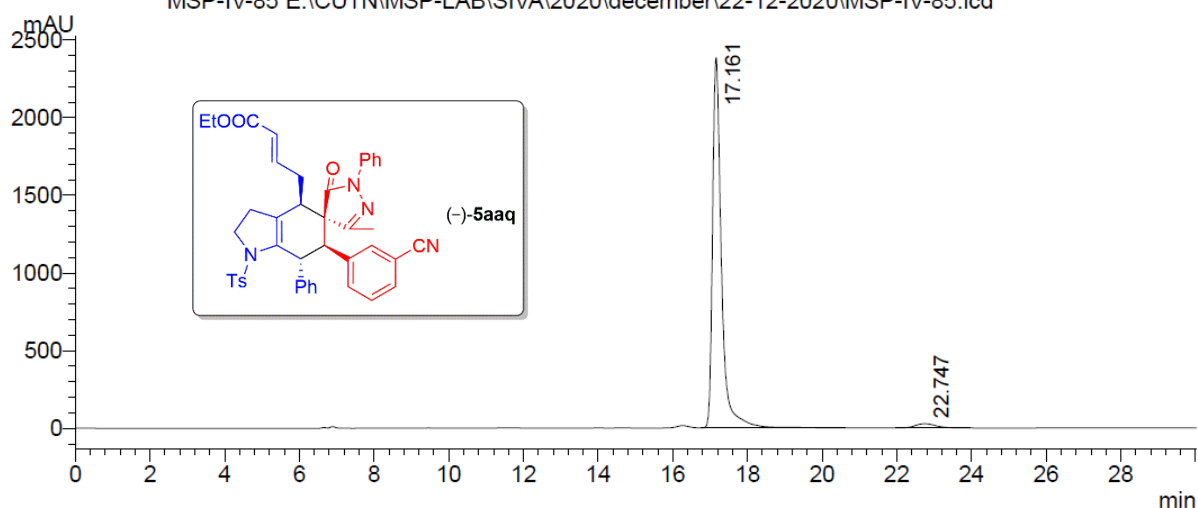


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.916	10034637	545402	50.075
2	22.066	10004435	249565	49.925
Total		20039071	794967	100.000

HPLC data of chiral **5aaq**: 95% *ee*

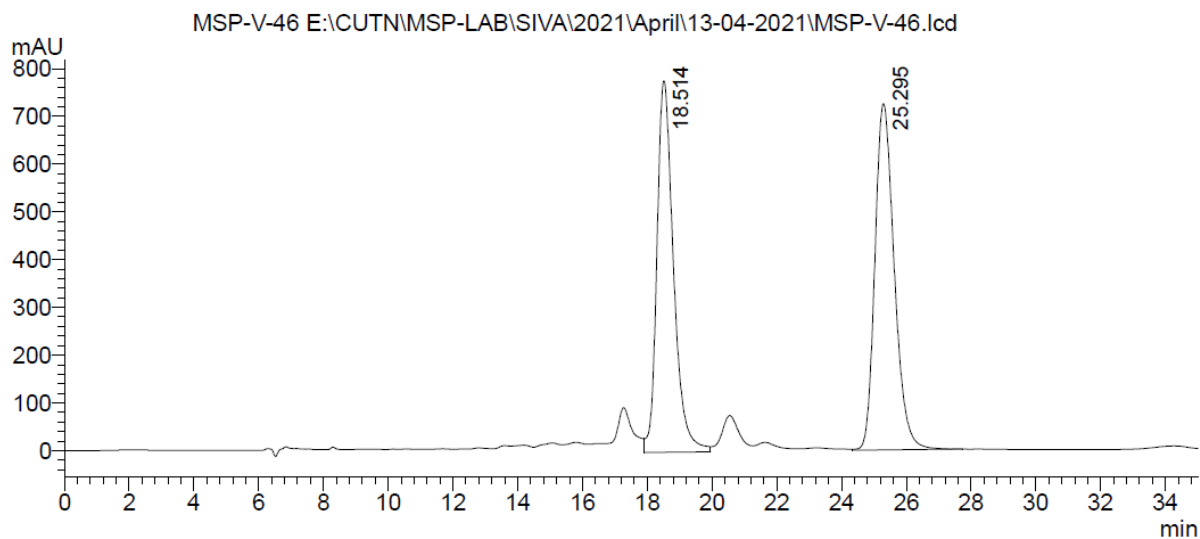
MSP-IV-85 E:\CUTN\MSP-LAB\SIVA\2020\december\22-12-2020\MSP-IV-85.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.161	39465697	2386015	97.344
2	22.747	1076935	27890	2.656
Total		40542632	2413905	100.000

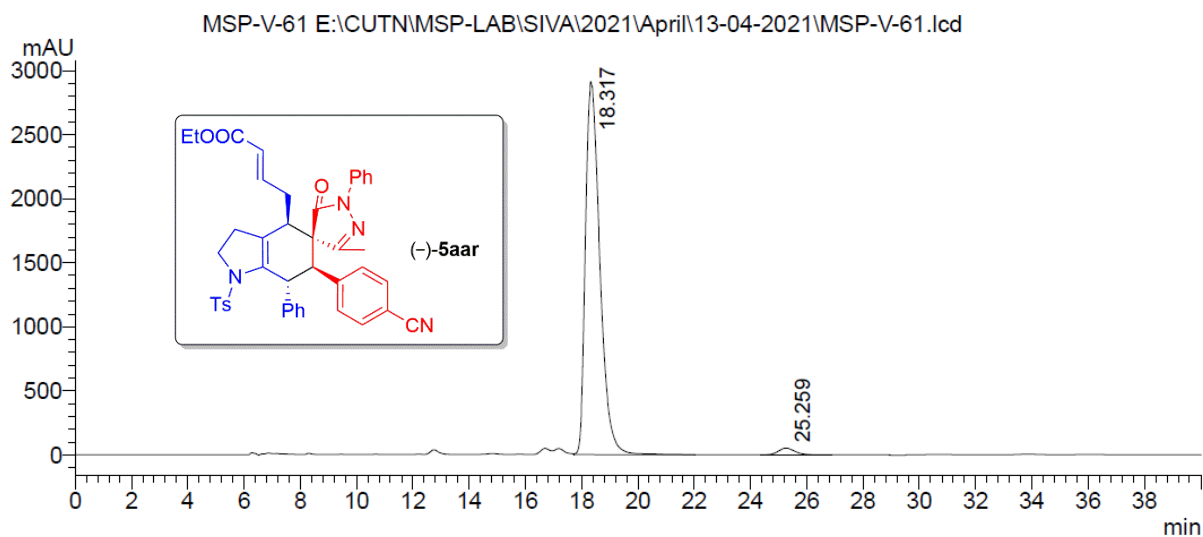
C data of racemic **5aar**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.514	27691558	778248	47.876
2	25.295	30148384	725581	52.124
Total		57839942	1503830	100.000

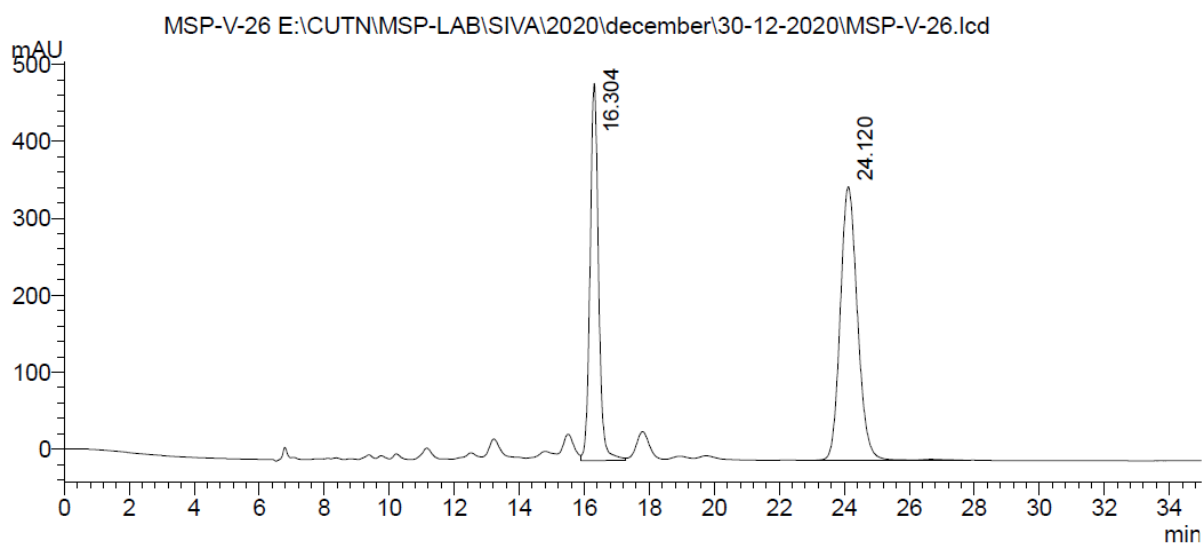
HPLC data of chiral **5aar**: 96% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.317	103855457	2912602	97.968
2	25.259	2153920	52022	2.032
Total		106009378	2964624	100.000

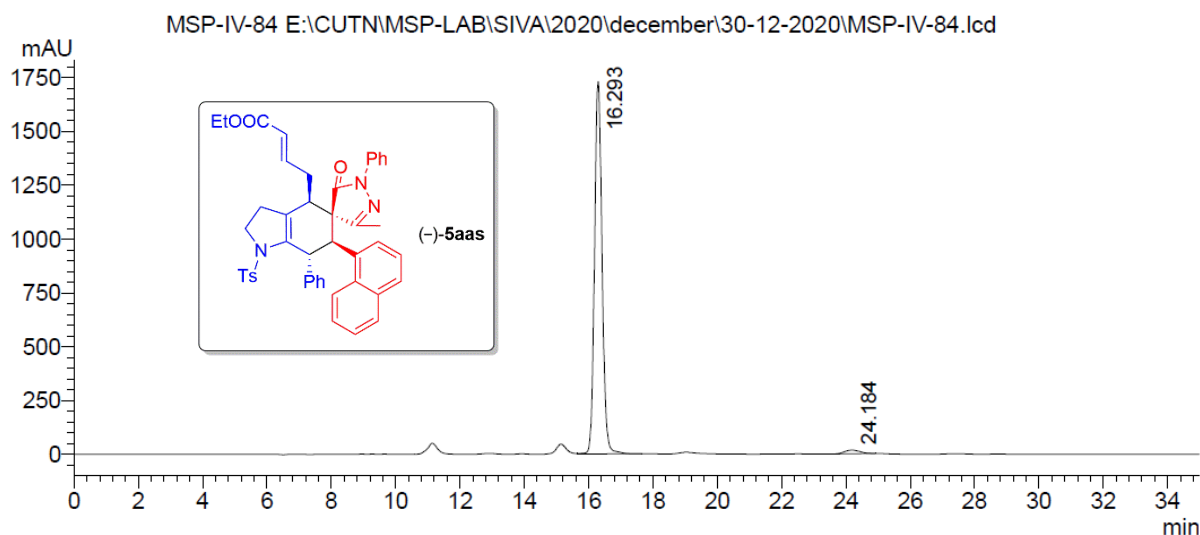
HPLC data of racemic **5aas**



PDA Ch1 254nm

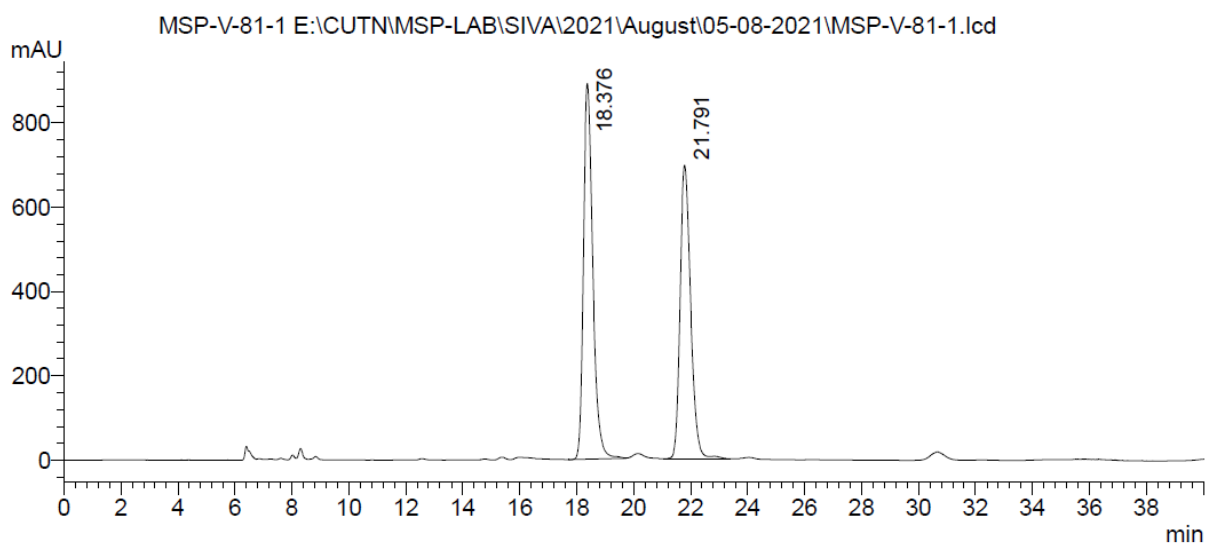
Peak #	Ret. Time (min)	Area	Height	Area%
1	16.304	8888194	490263	40.384
2	24.120	13121173	355885	59.616
Total		22009367	846148	100.000

HPLC data of chiral **5aas**: 96% *ee*



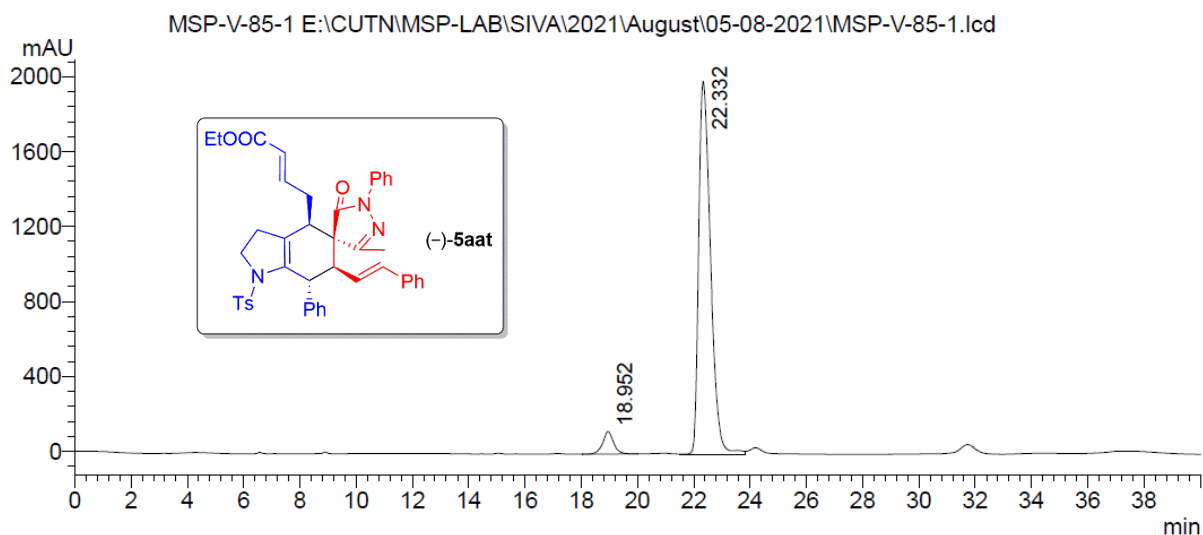
PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.293	28193095	1729156	98.008
2	24.184	572940	17335	1.992
Total		28766035	1746492	100.000

HPLC data of racemic **5aat**

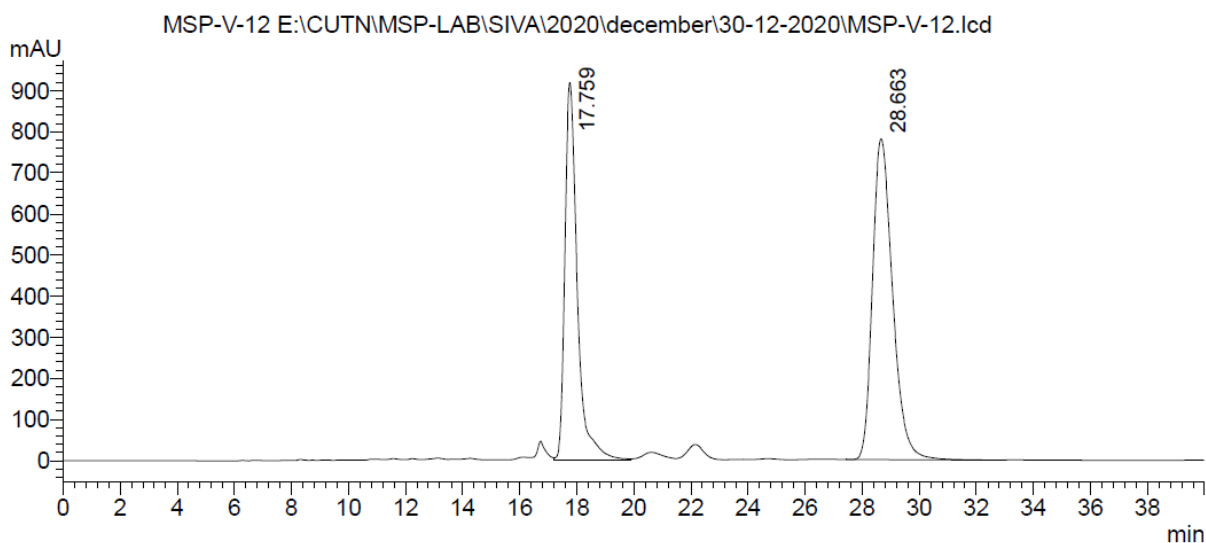
Peak #	Ret. Time (min)	Area	Height	Area%
1	18.376	20307992	891832	53.179
2	21.791	17880107	696148	46.821
Total		38188098	1587980	100.000

HPLC data of chiral **5aat**: 90% *ee*



PDA Ch1 254nm				
Peak #	Ret. Time (min)	Area	Height	Area%
1	18.952	3224977	120895	5.255
2	22.332	58146192	1989517	94.745
Total		61371169	2110412	100.000

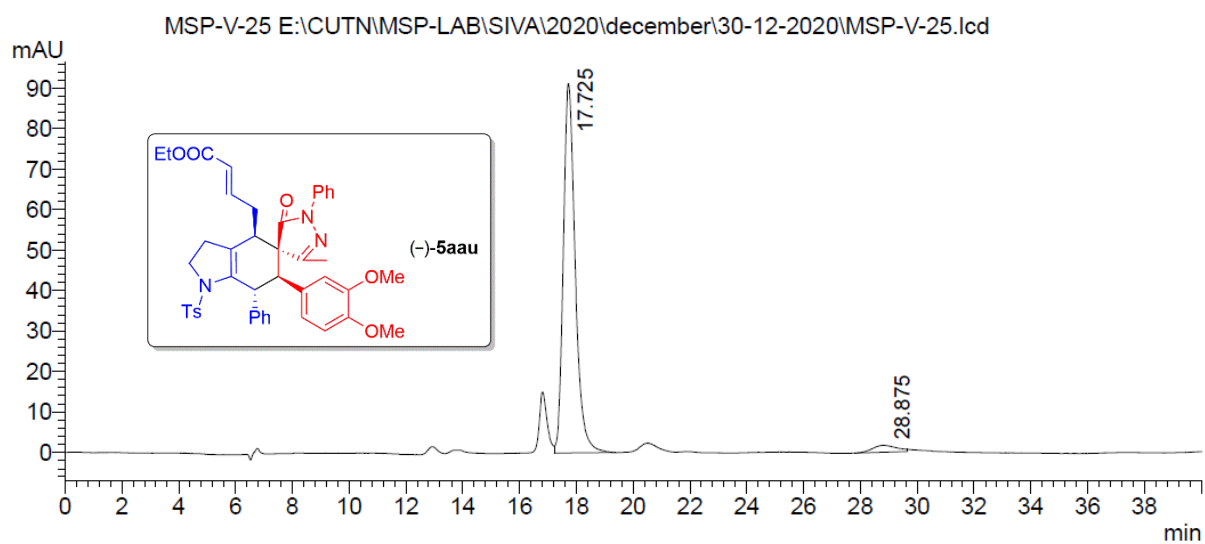
HPLC data of racemic **5aau**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.759	27488791	917145	41.887
2	28.663	38137757	780157	58.113
Total		65626549	1697302	100.000

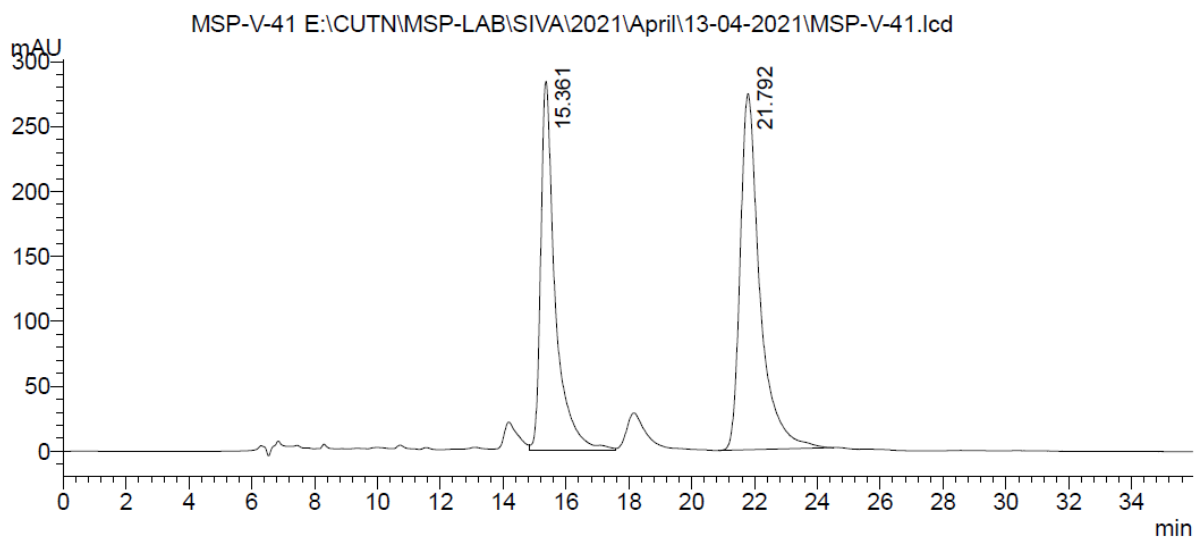
HPLC data of chiral **5aau**: 93% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.725	2657396	91252	96.269
2	28.875	102996	1712	3.731
Total		2760392	92964	100.000

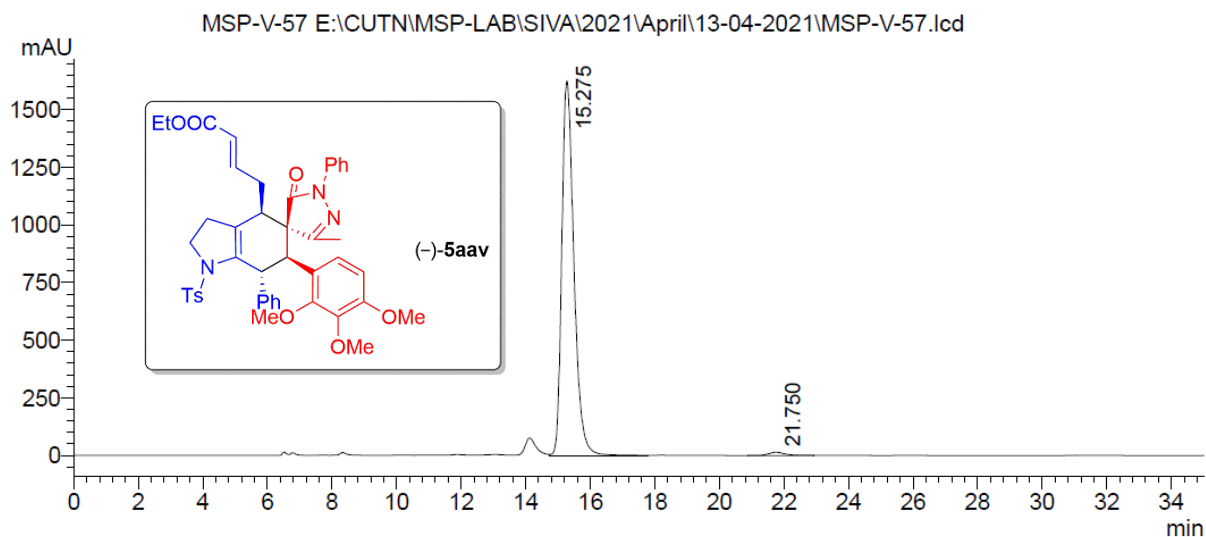
HPLC data of racemic **5aav**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.361	9085326	283860	43.252
2	21.792	11920080	273955	56.748
Total		21005407	557815	100.000

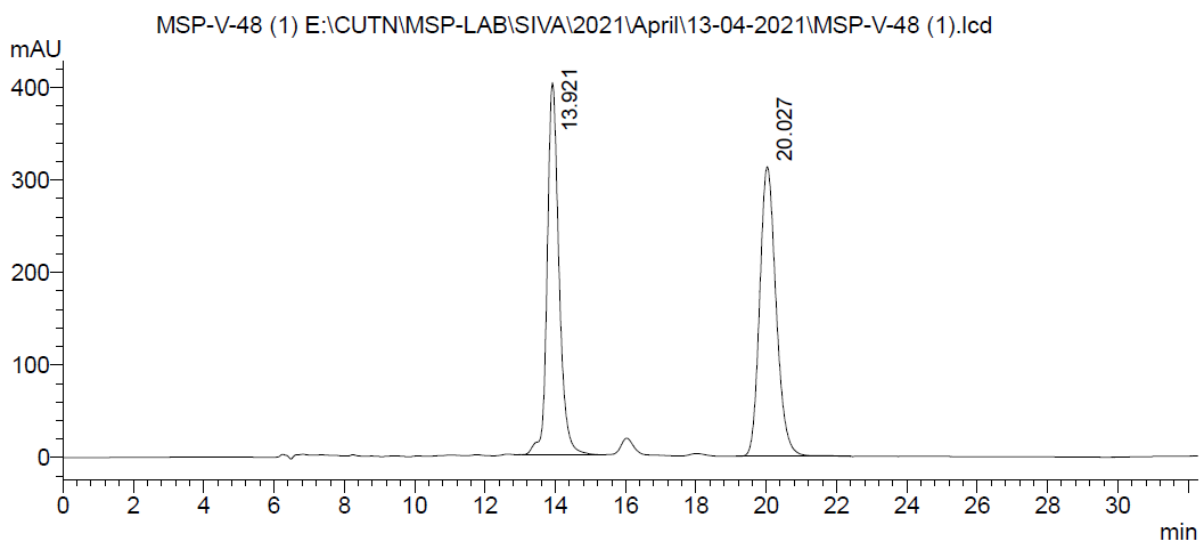
HPLC data of chiral **5aav**: 98% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.275	42297000	1623985	98.824
2	21.750	503265	13970	1.176
Total		42800265	1637956	100.000

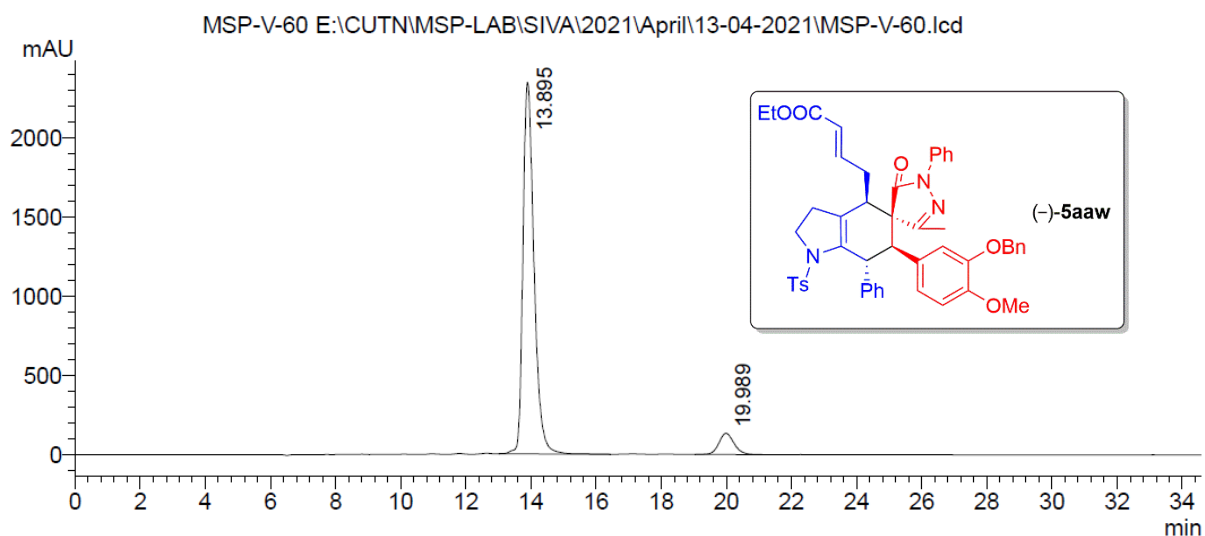
HPLC data of racemic **5aaw**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.921	9335888	401762	47.791
2	20.027	10199082	312910	52.209
Total		19534970	714672	100.000

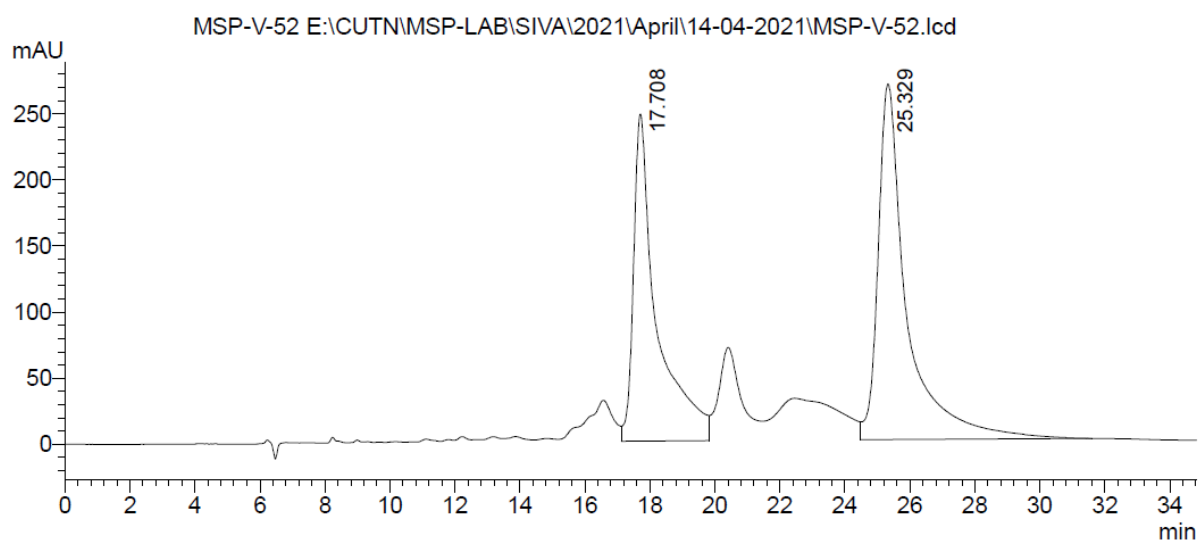
HPLC data of chiral **5aaw**: 85% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.895	55300584	2347009	92.655
2	19.989	4384048	134169	7.345
Total		59684631	2481177	100.000

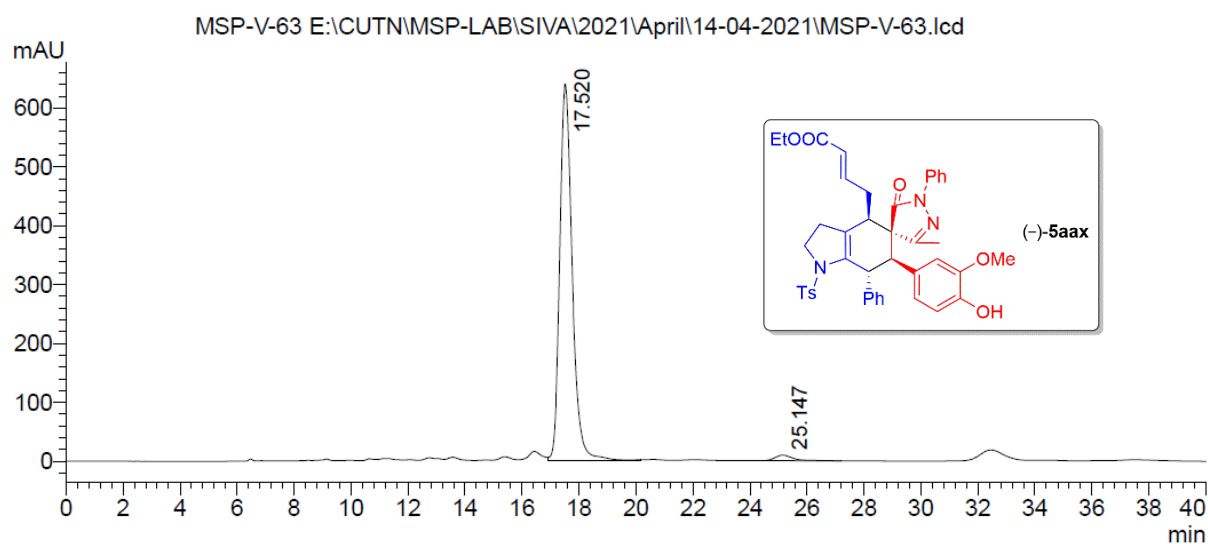
HPLC data of racemic **5aax**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.708	12262258	247515	42.549
2	25.329	16556966	269218	57.451
Total		28819224	516733	100.000

HPLC data of chiral **5aax**: 96% *ee*

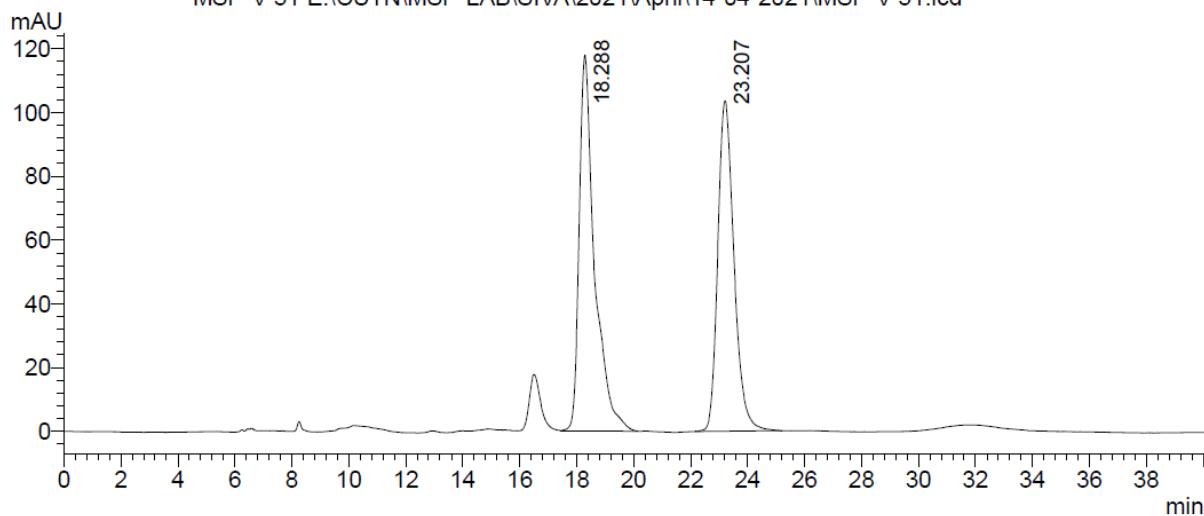


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.520	19615251	640221	97.826
2	25.147	435950	9432	2.174
Total		20051201	649653	100.000

HPLC data of racemic **5aay**

MSP-V-51 E:\CUTN\MSP-LAB\SIVA\2021\April\14-04-2021\MSP-V-51.lcd

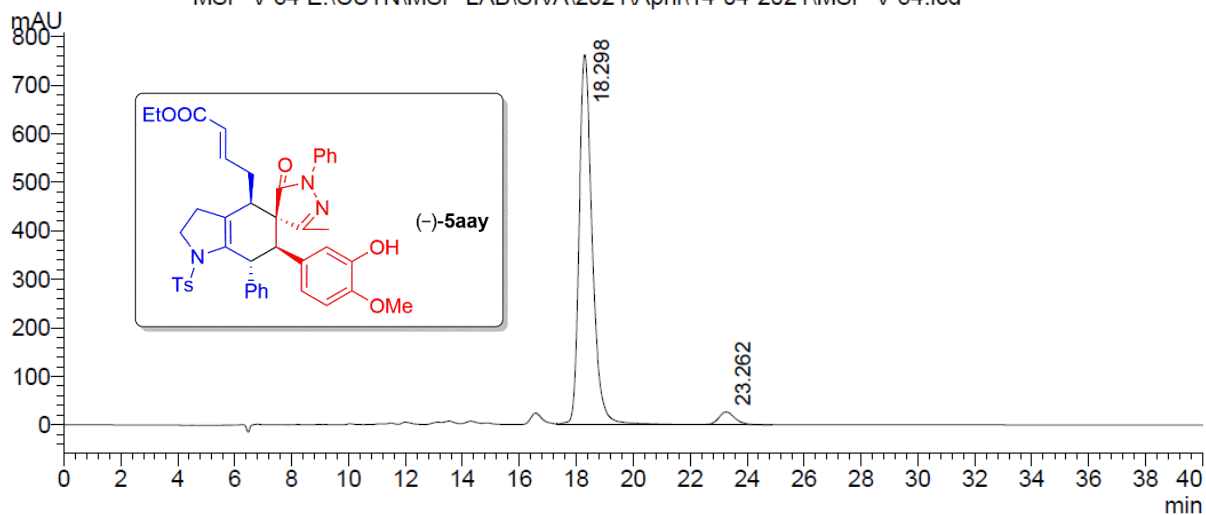


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.288	4416069	117848	51.892
2	23.207	4094091	103580	48.108
Total		8510160	221428	100.000

HPLC data of chiral **5aay**: 92% *ee*

MSP-V-64 E:\CUTN\MSP-LAB\SIVA\2021\April\14-04-2021\MSP-V-64.lcd

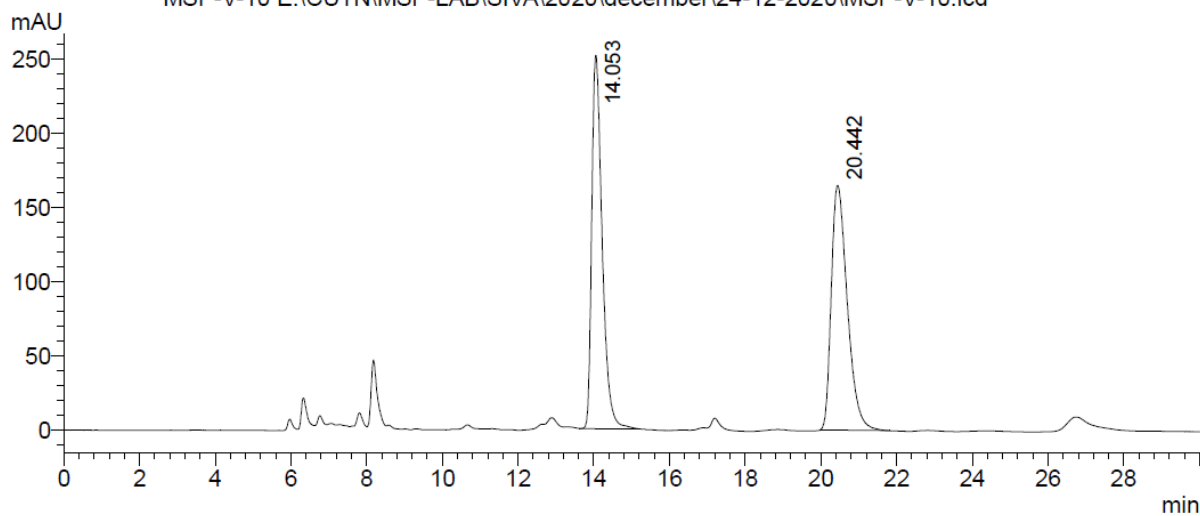


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.298	24342213	762769	96.024
2	23.262	1007823	25845	3.976
Total		25350037	788613	100.000

HPLC data of racemic **5aaz**

MSP-V-10 E:\CUTN\MSP-LAB\SIVA\2020\december\24-12-2020\MSP-V-10.lcd

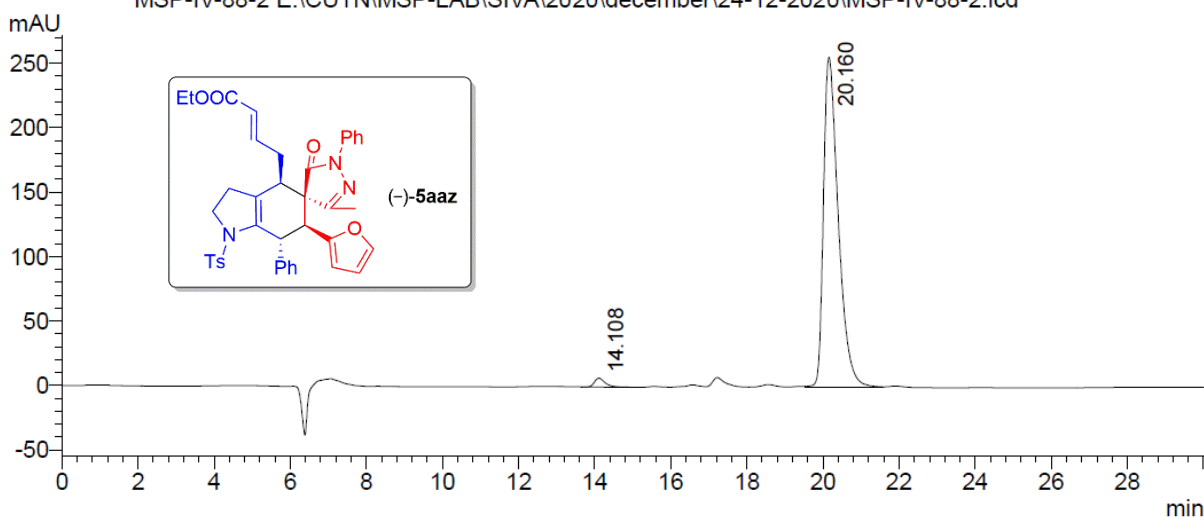


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.053	4817456	251655	49.831
2	20.442	4850222	165087	50.169
Total		9667677	416742	100.000

HPLC data of chiral **5aaz**: 96% *ee*

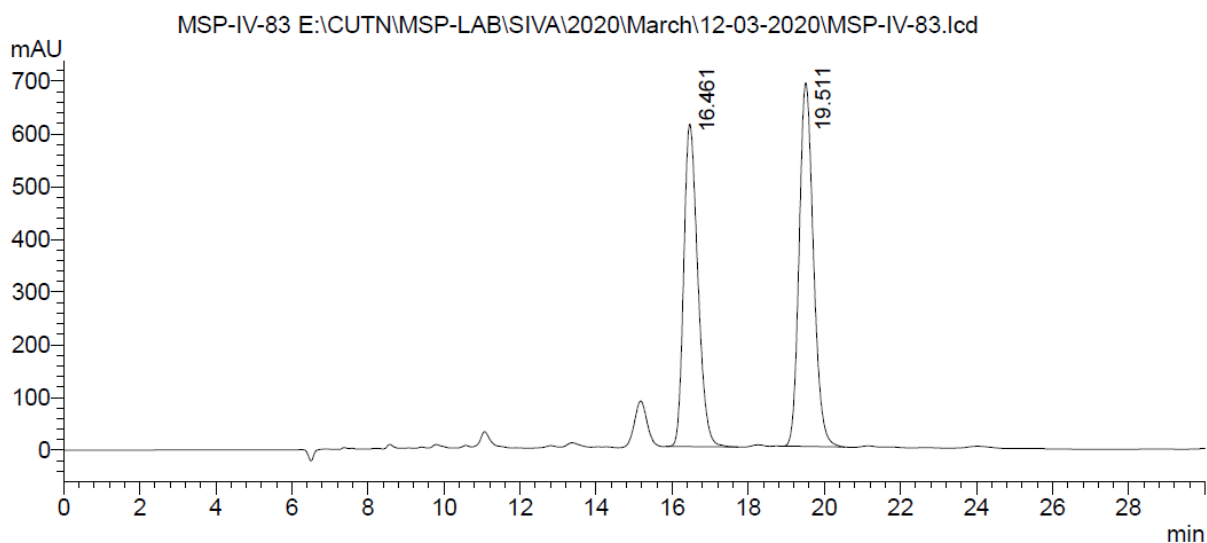
MSP-IV-88-2 E:\CUTN\MSP-LAB\SIVA\2020\december\24-12-2020\MSP-IV-88-2.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.108	135079	6875	1.920
2	20.160	6901364	255801	98.080
Total		7036443	262676	100.000

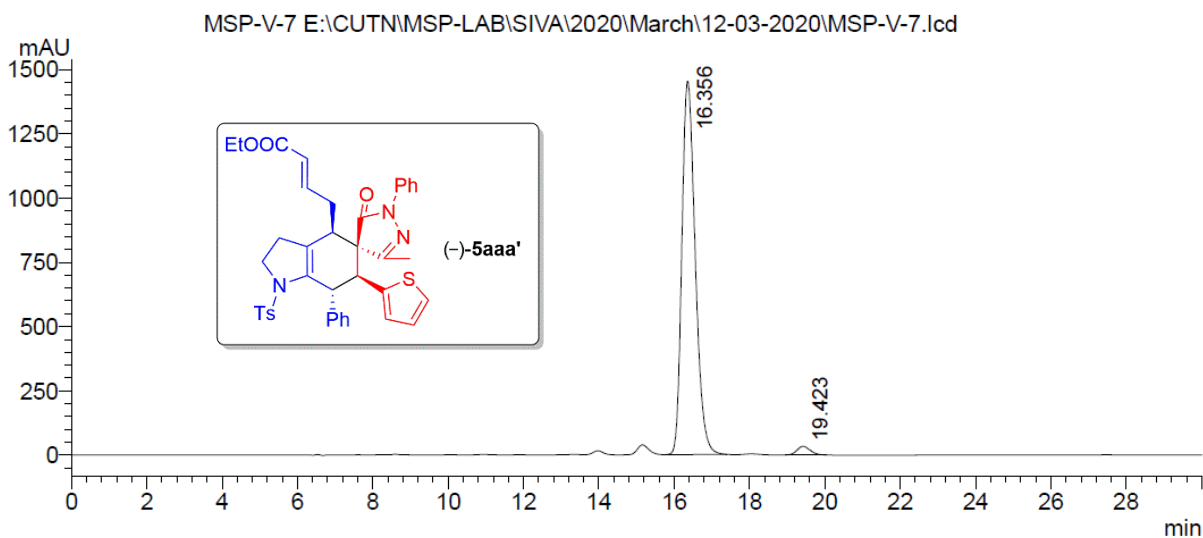
HPLC data of racemic **5aaa'**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.461	15742370	612167	46.707
2	19.511	17962139	689844	53.293
Total		33704510	1302010	100.000

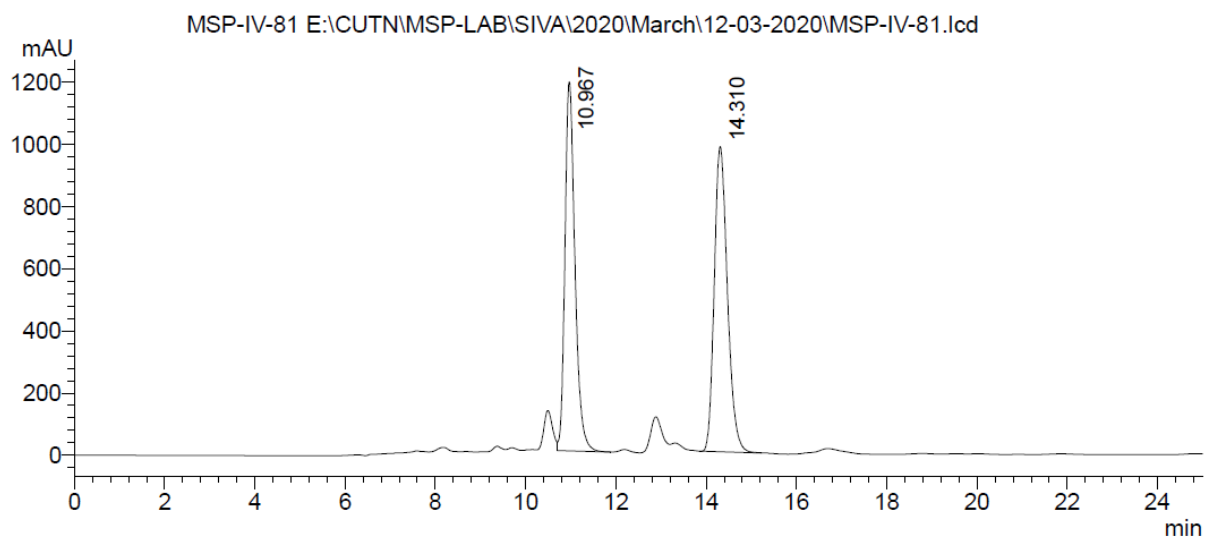
HPLC data of chiral **5aaa'**: 96% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.356	35826499	1452802	97.758
2	19.423	821500	33496	2.242
Total		36647999	1486298	100.000

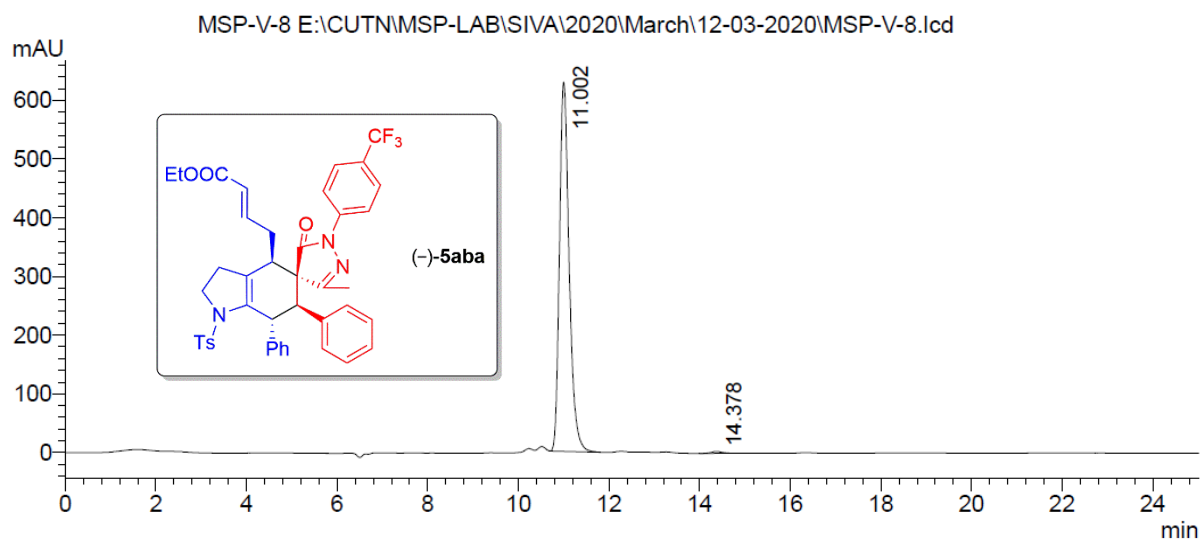
HPLC data of racemic **5aba**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	10.967	18317972	1187688	47.924
2	14.310	19905345	982619	52.076
Total		38223317	2170307	100.000

HPLC data of chiral **5aba**: 99% *ee*

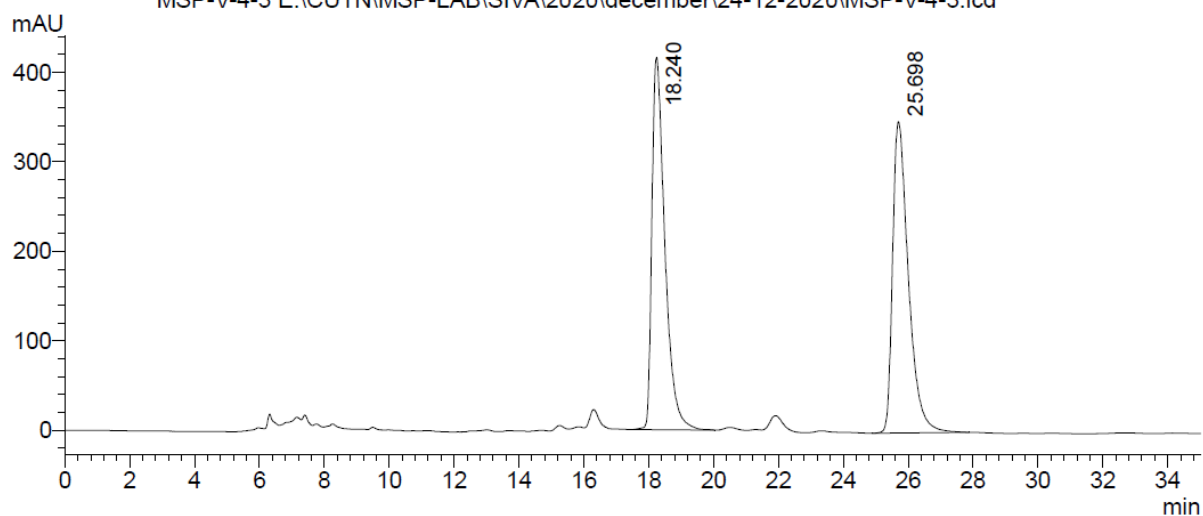


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.002	9347022	628667	99.464
2	14.378	50326	2864	0.536
Total		9397348	631531	100.000

HPLC data of racemic **5abb**

MSP-V-4-3 E:\CUTN\MSP-LAB\SIVA\2020\december\24-12-2020\MSP-V-4-3.lcd

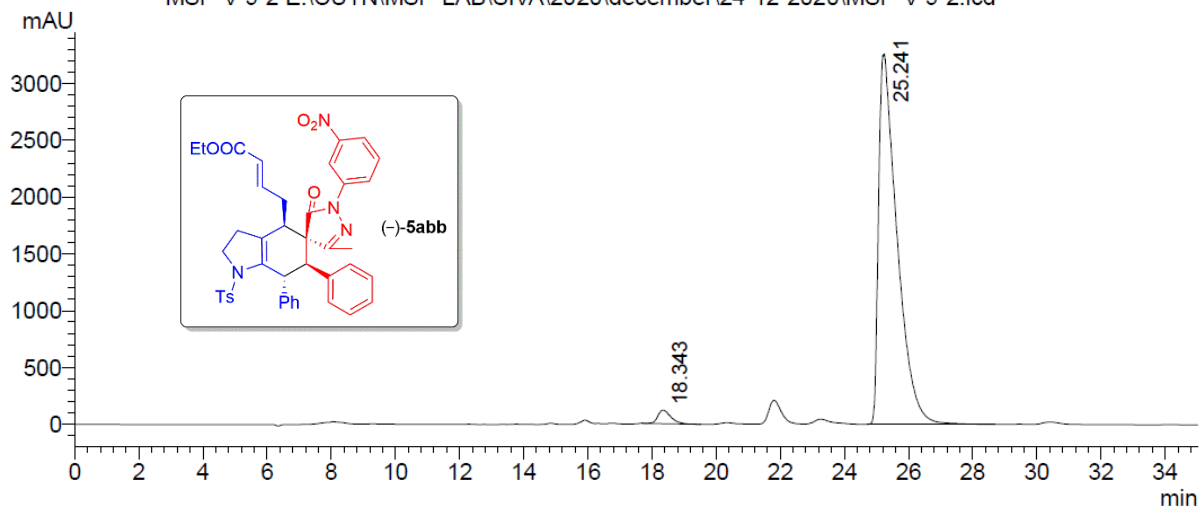


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.240	11551133	415805	49.522
2	25.698	11774240	347832	50.478
Total		23325373	763636	100.000

HPLC data of chiral **5abb**: 95% *ee*

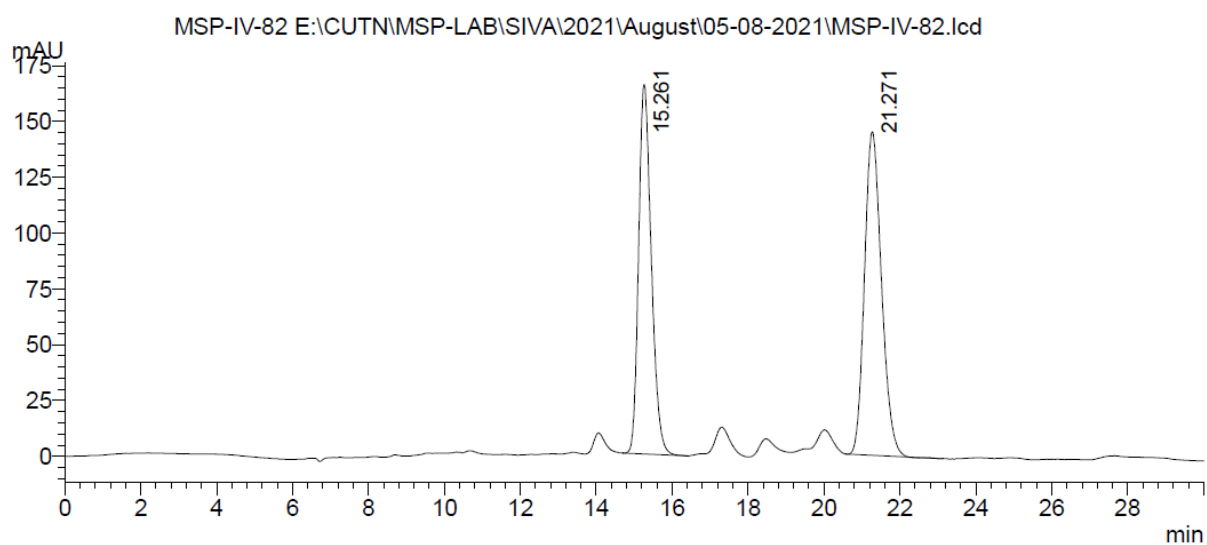
MSP-V-9-2 E:\CUTN\MSP-LAB\SIVA\2020\december\24-12-2020\MSP-V-9-2.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.343	3379093	119057	2.528
2	25.241	130283510	3258782	97.472
Total		133662602	3377839	100.000

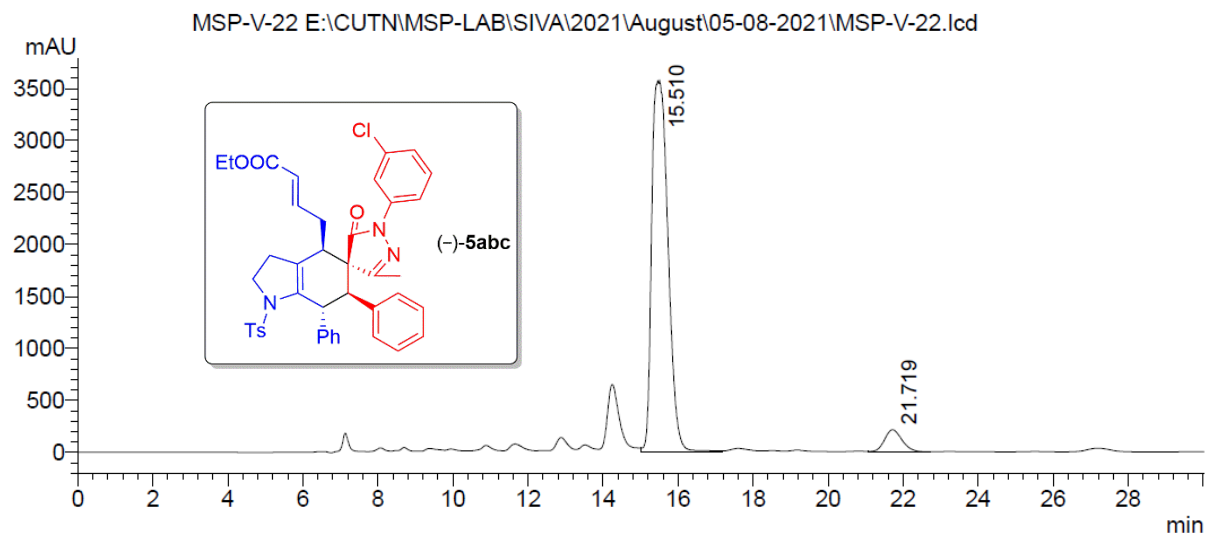
HPLC data of racemic **5abc**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.261	3844521	165617	45.973
2	21.271	4518125	144962	54.027
Total		8362646	310579	100.000

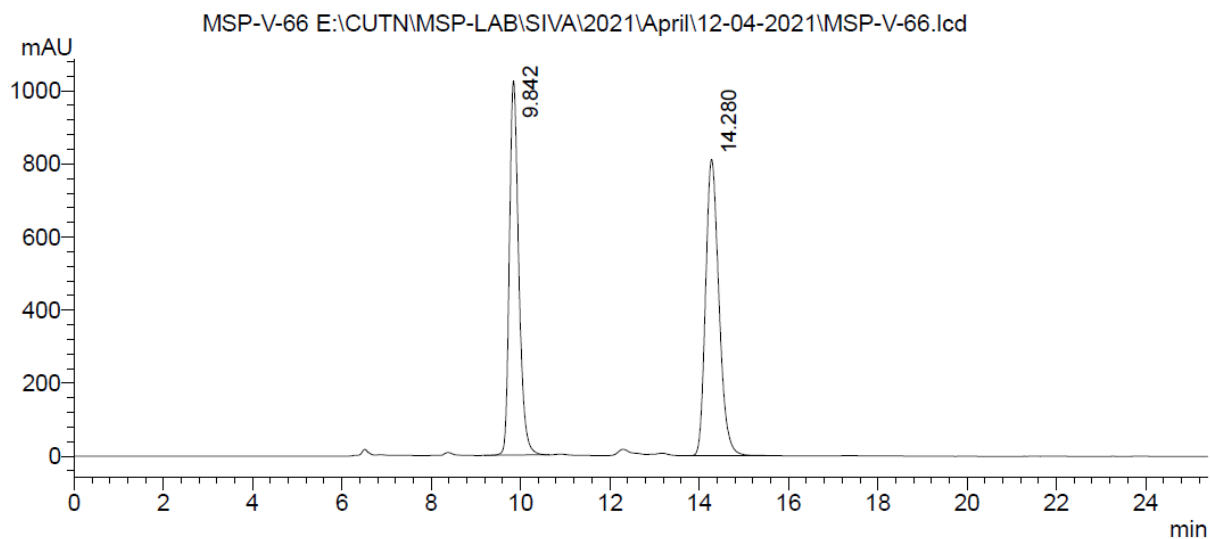
HPLC data of chiral **5abc**: 88% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.510	108796156	3581205	94.116
2	21.719	6801833	211466	5.884
Total		115597989	3792671	100.000

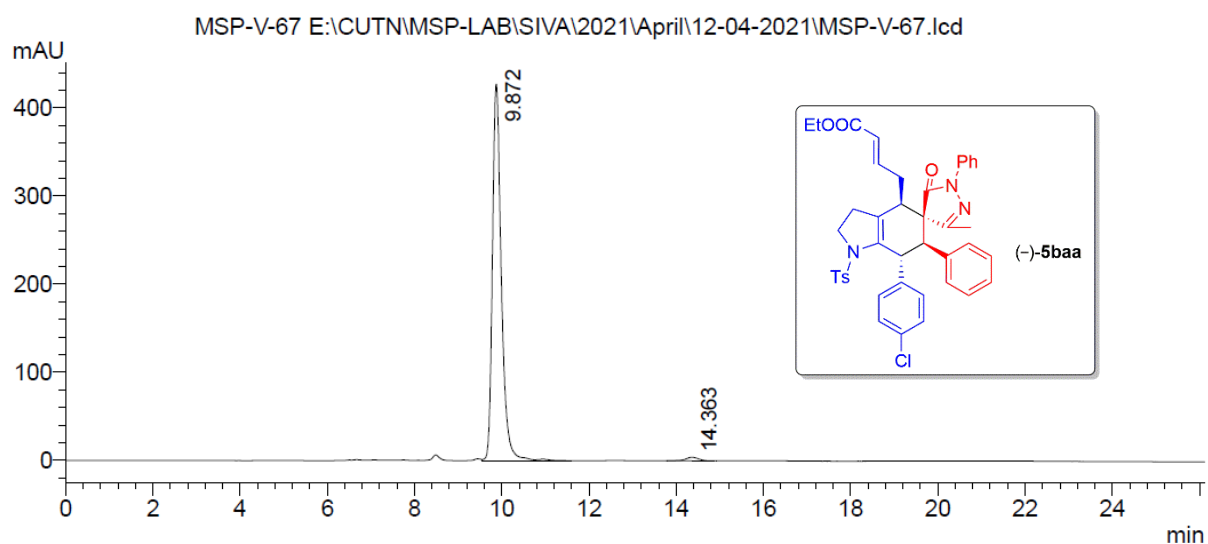
HPLC data of racemic **5baa**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	9.842	14953528	1023619	47.011
2	14.280	16855011	810242	52.989
Total		31808538	1833860	100.000

HPLC data of chiral **5baa**: 97% *ee*

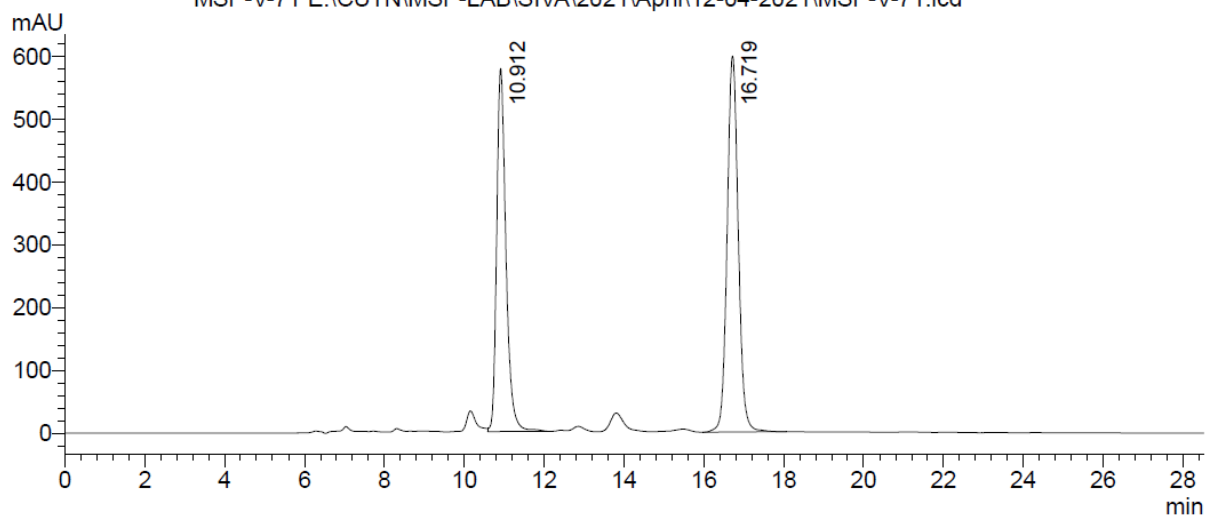


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	9.872	6074819	427207	98.582
2	14.363	87353	4186	1.418
Total		6162172	431393	100.000

HPLC data of racemic **5caa**

MSP-V-71 E:\CUTN\MSP-LAB\SIVA\2021\April\12-04-2021\MSP-V-71.lcd

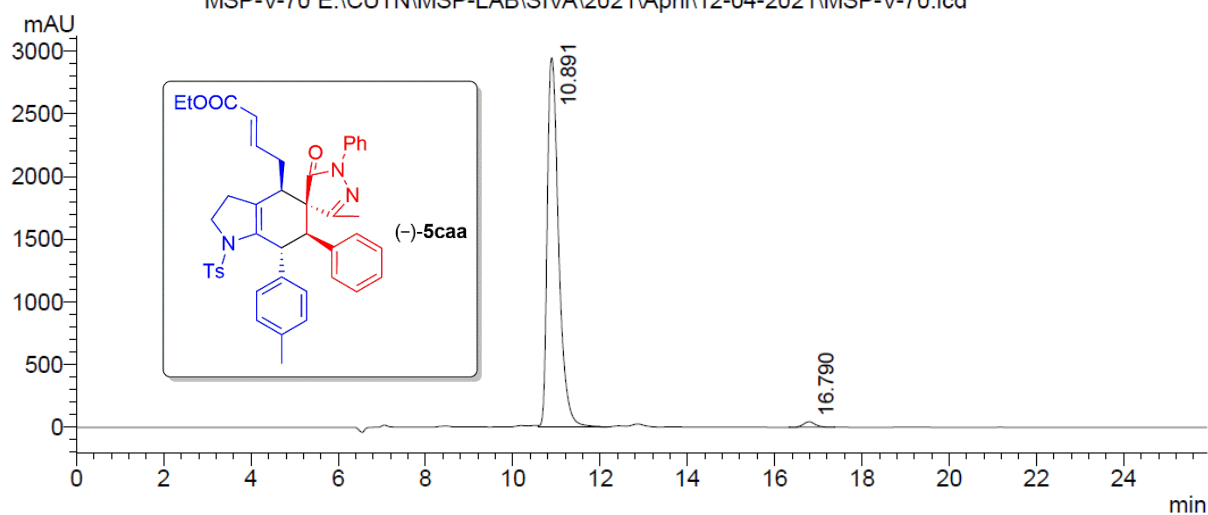


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	10.912	9345275	578690	44.598
2	16.719	11609317	598689	55.402
Total		20954593	1177379	100.000

HPLC data of chiral **5caa**: 97% *ee*

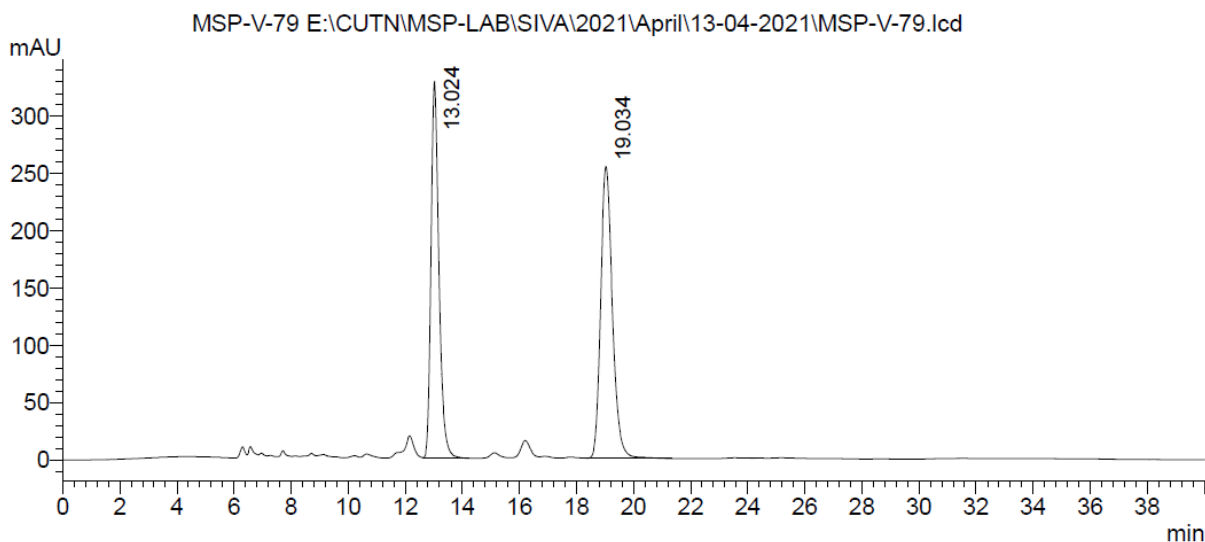
MSP-V-70 E:\CUTN\MSP-LAB\SIVA\2021\April\12-04-2021\MSP-V-70.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	10.891	53342401	2942638	98.456
2	16.790	836396	42967	1.544
Total		54178797	2985605	100.000

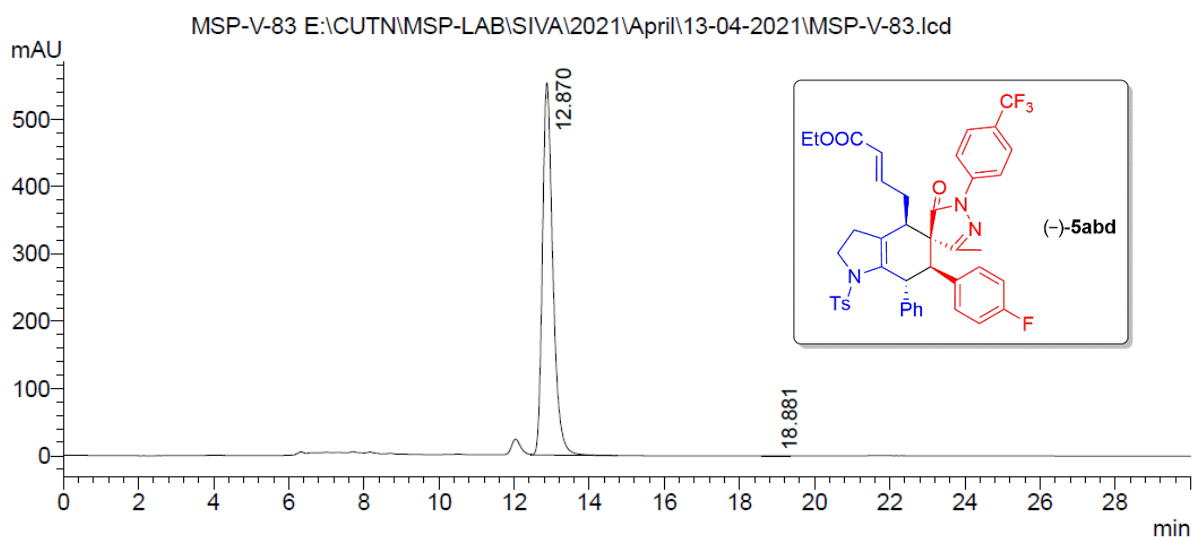
HPLC data of racemic **5abd**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.024	6381584	328980	46.629
2	19.034	7304241	254842	53.371
Total		13685825	583822	100.000

HPLC data of chiral **5abd**: 99.9% *ee*

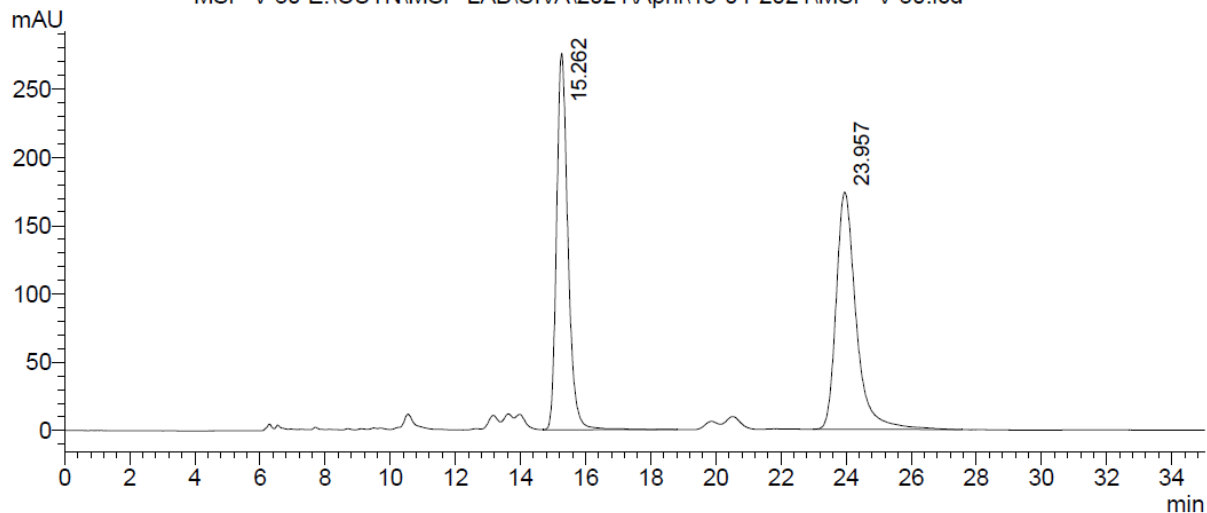


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	12.870	10665156	552744	99.971
2	18.881	3061	142	0.029
Total		10668218	552886	100.000

HPLC data of racemic **5abe**

MSP-V-80 E:\CUTN\MSP-LAB\SIVA\2021\April\13-04-2021\MSP-V-80.lcd

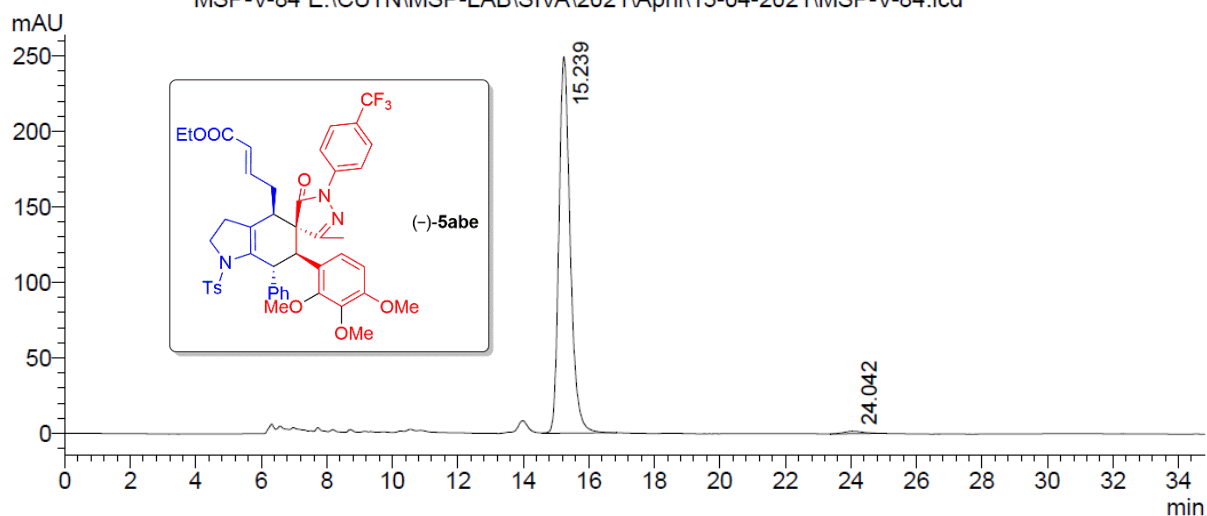


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.262	6702558	275624	47.457
2	23.957	7420971	173599	52.543
Total		14123529	449223	100.000

HPLC data of chiral **5abe**: 98% *ee*

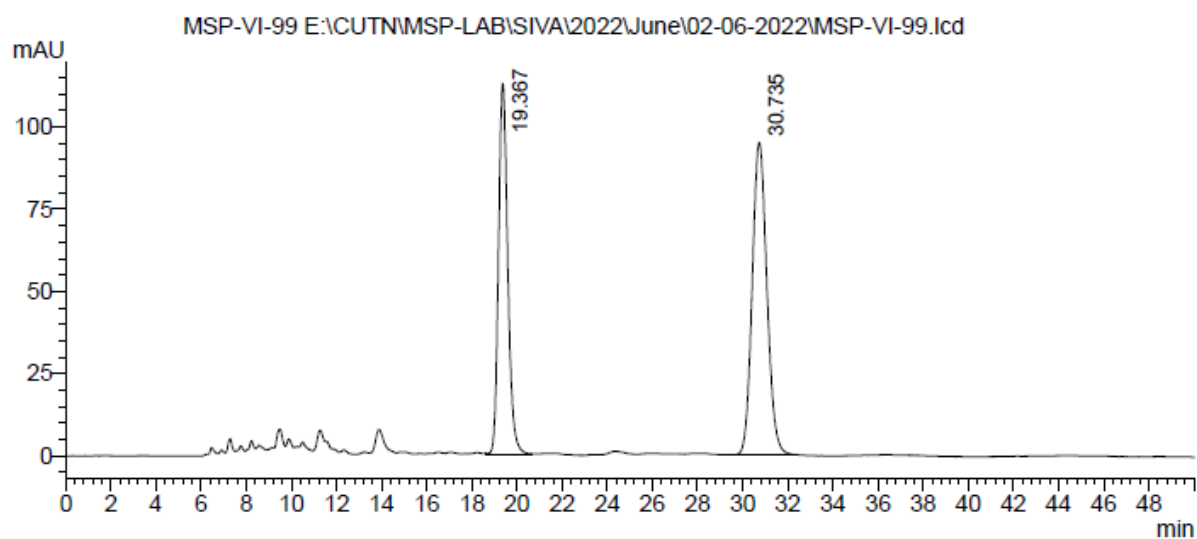
MSP-V-84 E:\CUTN\MSP-LAB\SIVA\2021\April\13-04-2021\MSP-V-84.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.239	5992942	249307	98.870
2	24.042	68513	1604	1.130
Total		6061454	250911	100.000

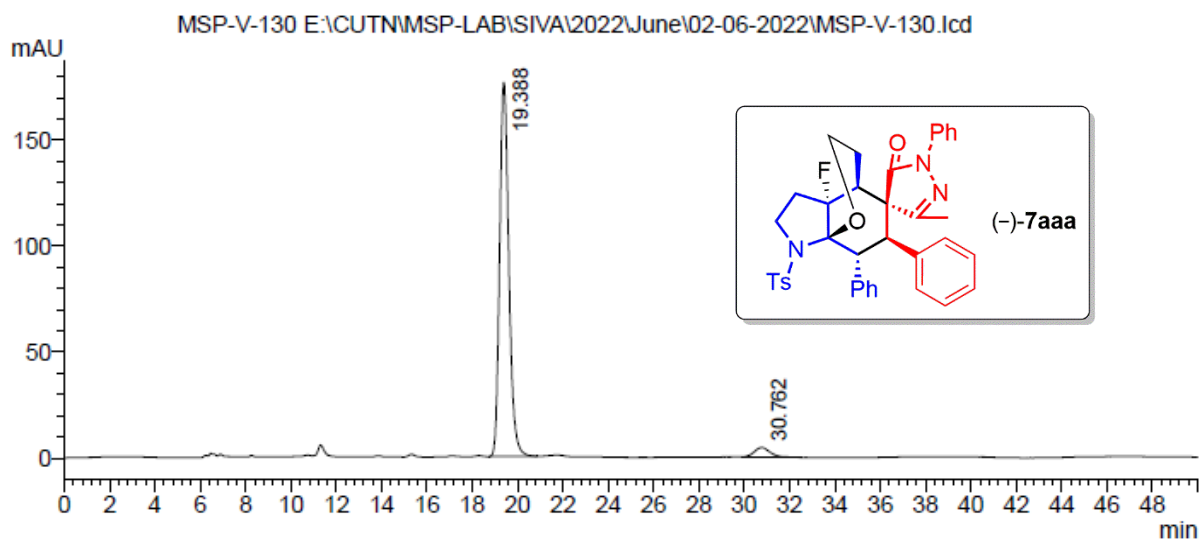
HPLC data of racemic **7aaa**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.367	3193490	112501	42.702
2	30.735	4285013	94865	57.298
Total		7478503	207366	100.000

HPLC data of chiral **7aaa**: 92% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.388	4993491	176620	95.850
2	30.762	216203	4504	4.150
Total		5209695	181124	100.000