

## Supporting Information-III

### HPLC Data

#### Asymmetric synthesis of perhydroepoxyethanoindole cores *via* sequential [4+2]-addition/reduction/fluoroannulation reactions

Madavi S. Prasad,<sup>\*a</sup> and Murugesan Sivaprakash<sup>a</sup>

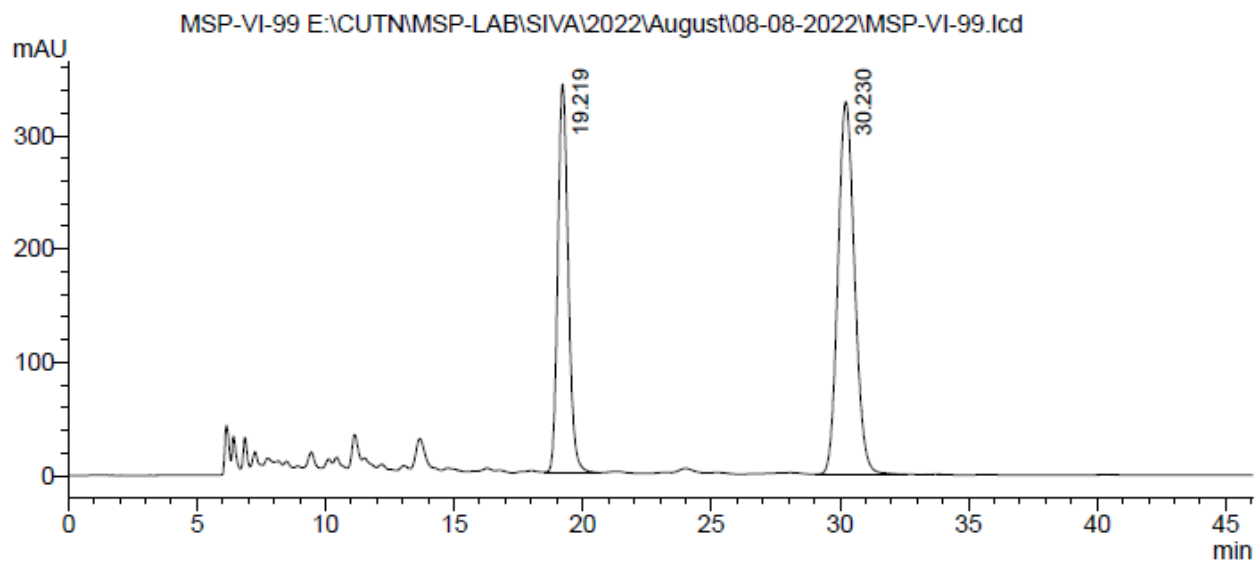
*Asymmetric Synthesis and Catalysis Laboratory, Department of Chemistry, Central University of Tamil Nadu, Thiruvavur, 610 005, India*

[shivaprasad@cutn.ac.in](mailto:shivaprasad@cutn.ac.in) and [shivacutn@gmail.com](mailto:shivacutn@gmail.com)

#### General Information:

The enantiomeric excess (ee) of the bridged bicyclic compounds **6a-6y** were determined by chiral stationary phase HPLC using a *Daicel Chiralpak IA & IC* in hexane/ethyl acetate as the eluent.

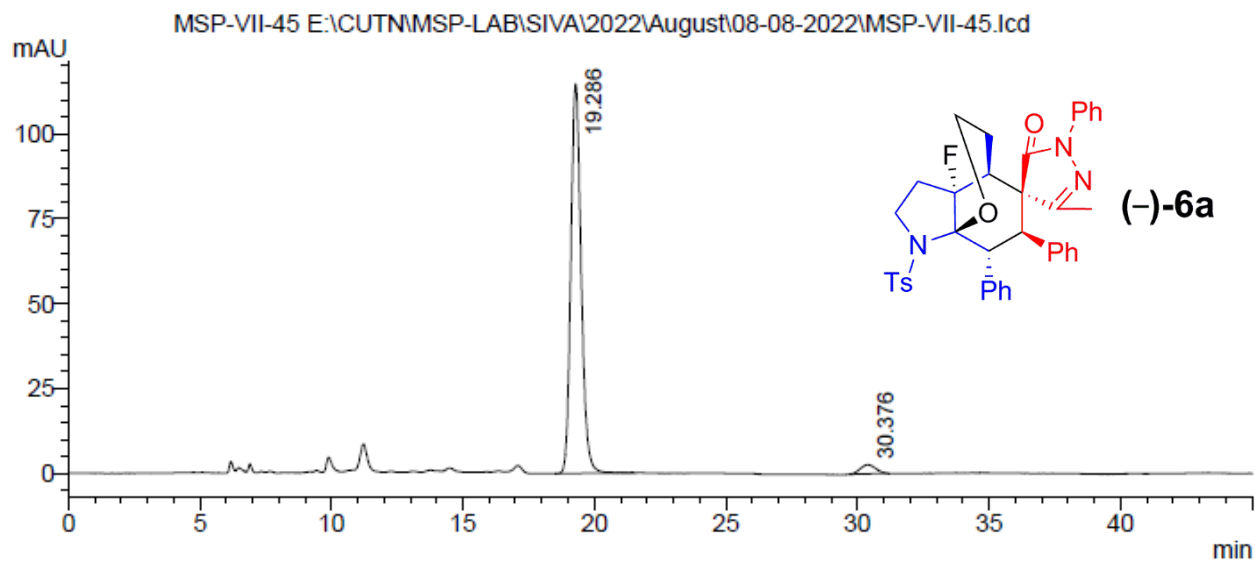
### HPLC Data of racemic **6a**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.219	9807326	343725	39.816
2	30.230	14824047	328827	60.184
Total		24631373	672552	100.000

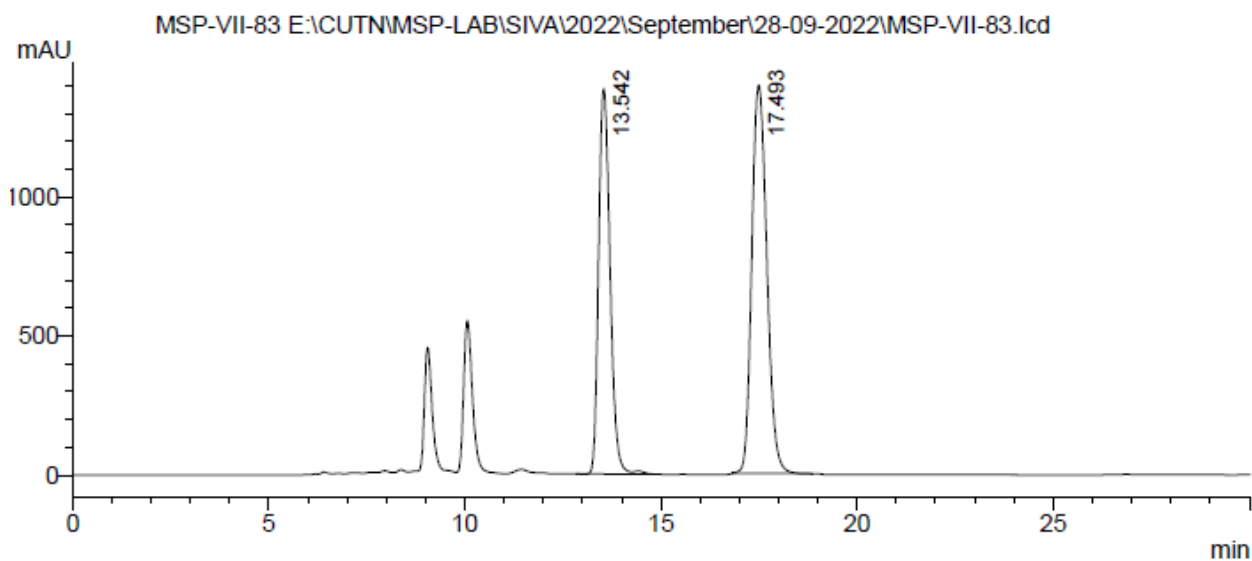
### HPLC Data of chiral **6a**: 93% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.286	3130230	114612	96.634
2	30.376	109048	2650	3.366
Total		3239278	117261	100.000

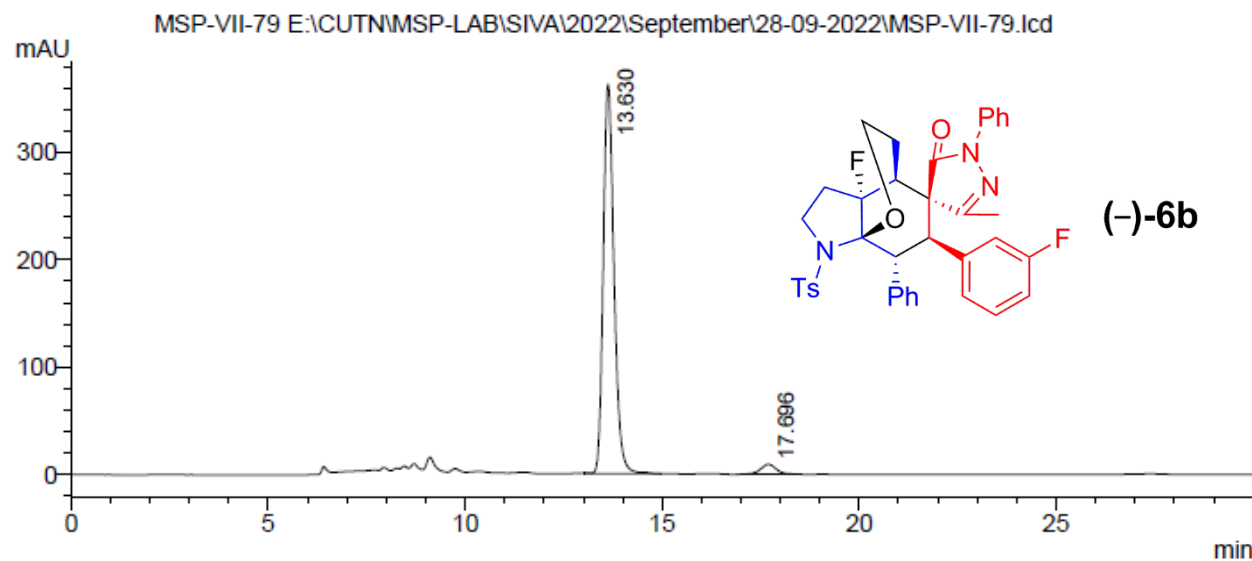
### HPLC Data of racemic **6b**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.542	28235547	1385839	43.062
2	17.493	37333655	1396647	56.938
Total		65569201	2782485	100.000

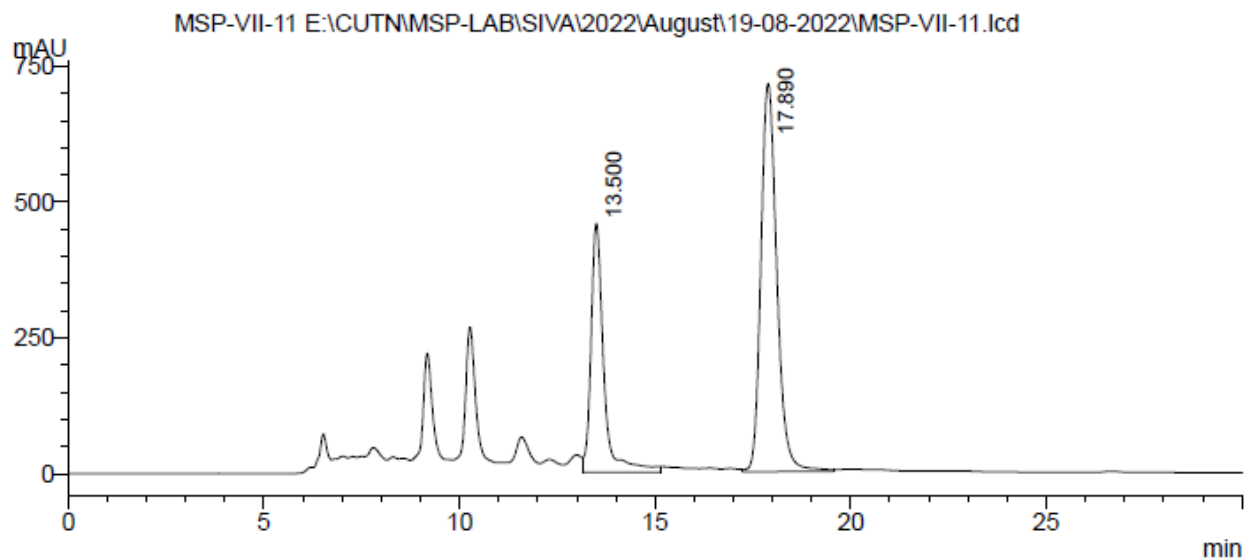
### HPLC Data of chiral **6b**: 93% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.630	6874435	362577	96.571
2	17.696	244104	9162	3.429
Total		7118539	371739	100.000

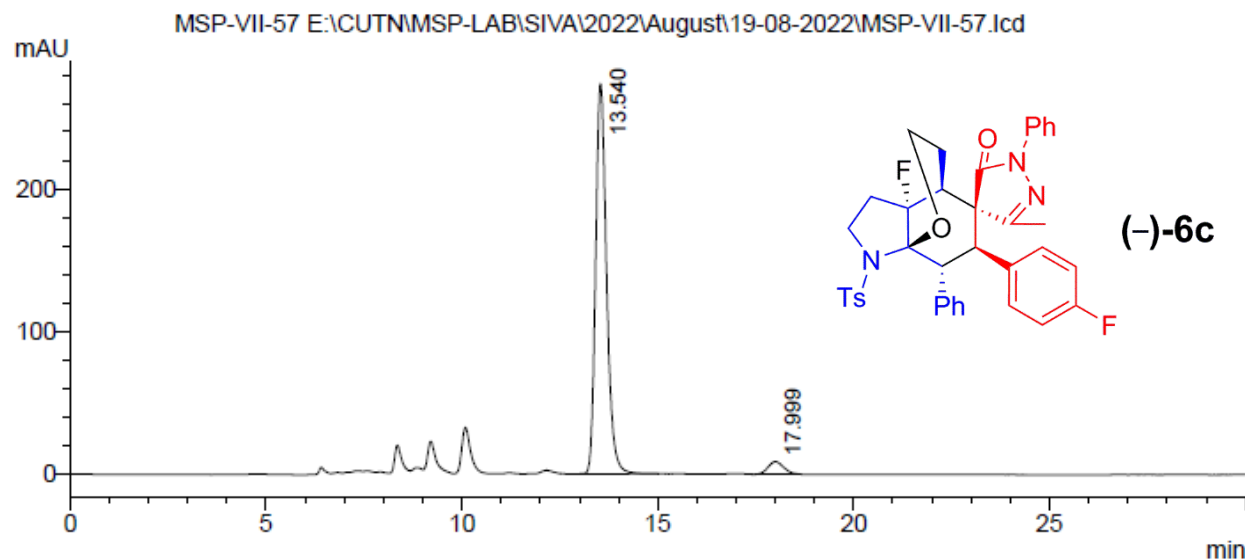
HPLC Data of racemic **6c**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.500	10441246	457892	34.024
2	17.890	20246963	714970	65.976
Total		30688210	1172863	100.000

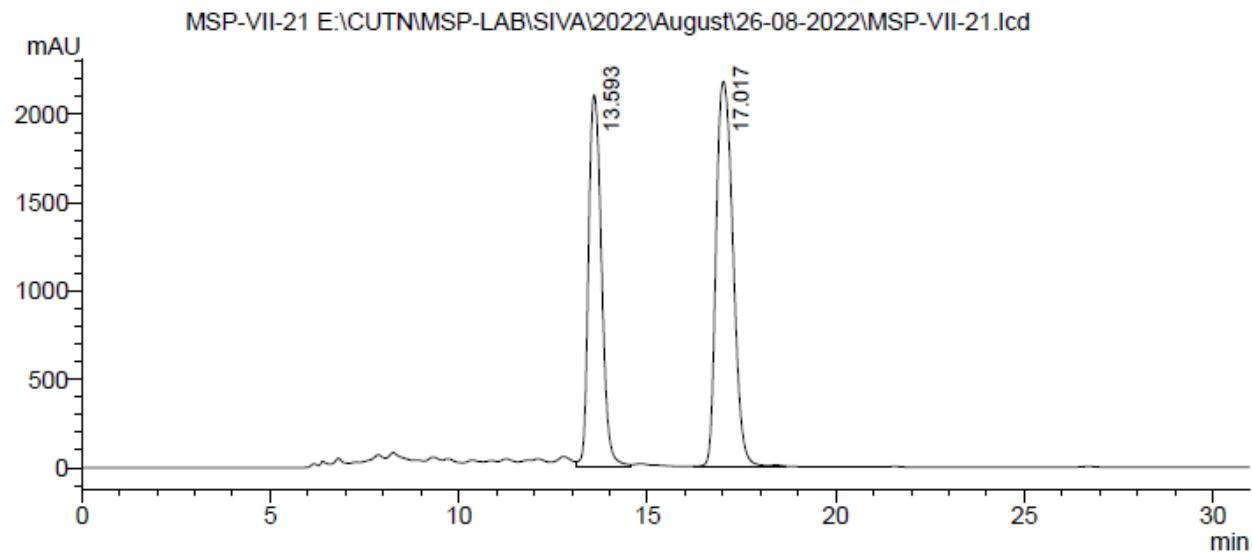
HPLC Data of chiral **6c**: 91% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.540	5319858	273692	95.708
2	17.999	238562	8762	4.292
Total		5558420	282453	100.000

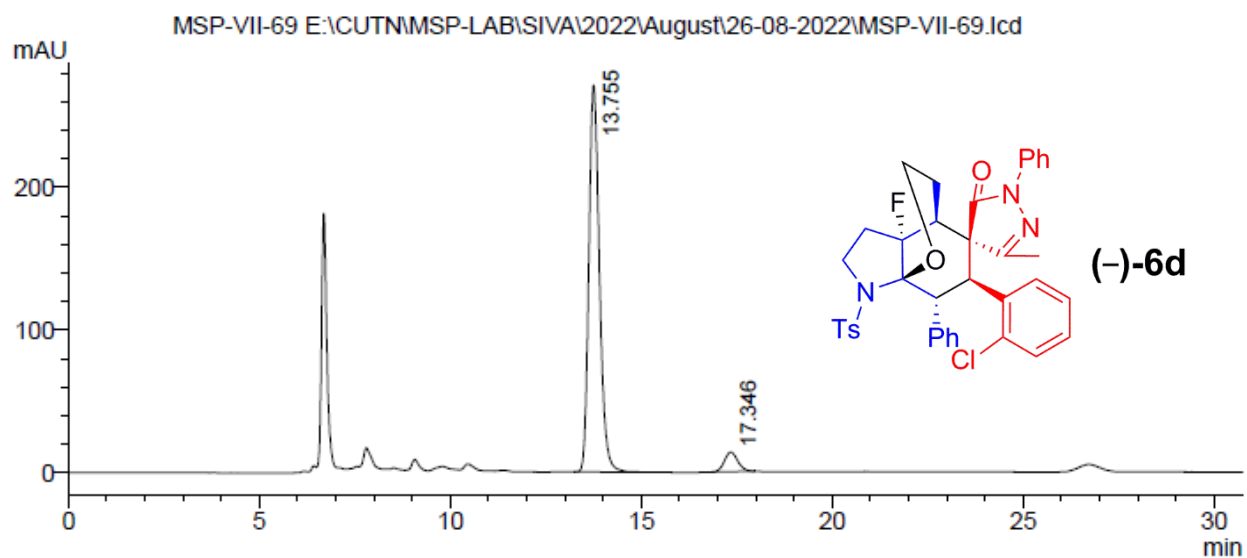
### HPLC Data of racemic **6d**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.593	50881617	2108084	42.641
2	17.017	68444668	2184086	57.359
Total		119326284	4292170	100.000

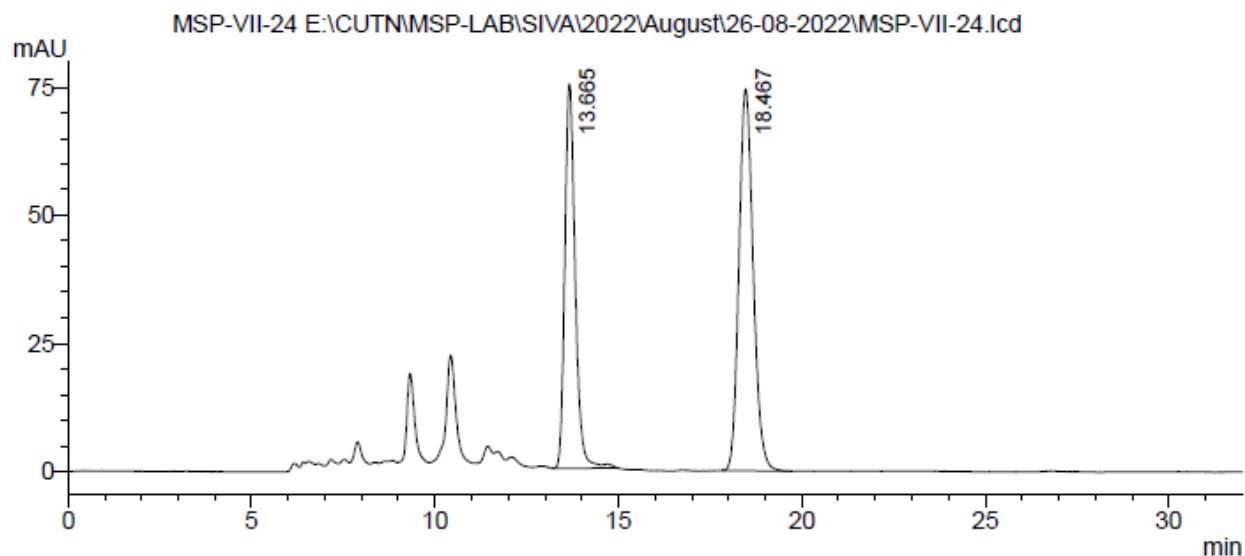
### HPLC Data of chiral **6d**: 88% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.755	5212153	271104	93.949
2	17.346	335729	13718	6.051
Total		5547882	284822	100.000

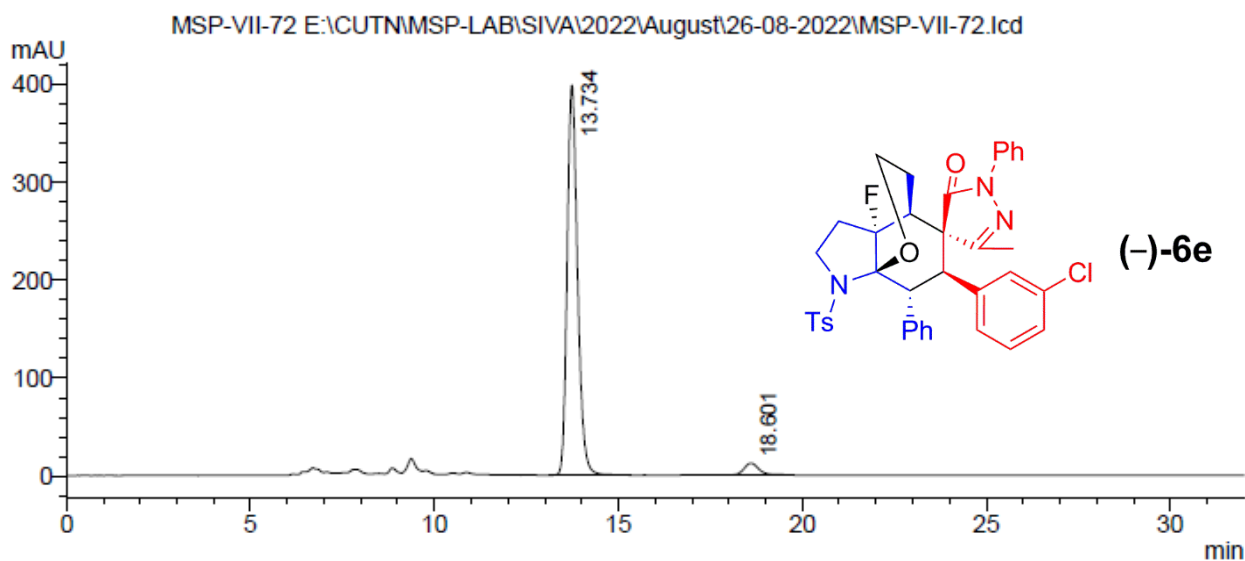
### HPLC Data of racemic **6e**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.665	1479505	75068	42.425
2	18.467	2007818	74508	57.575
Total		3487323	149576	100.000

### HPLC Data of chiral **6e**: 92% ee

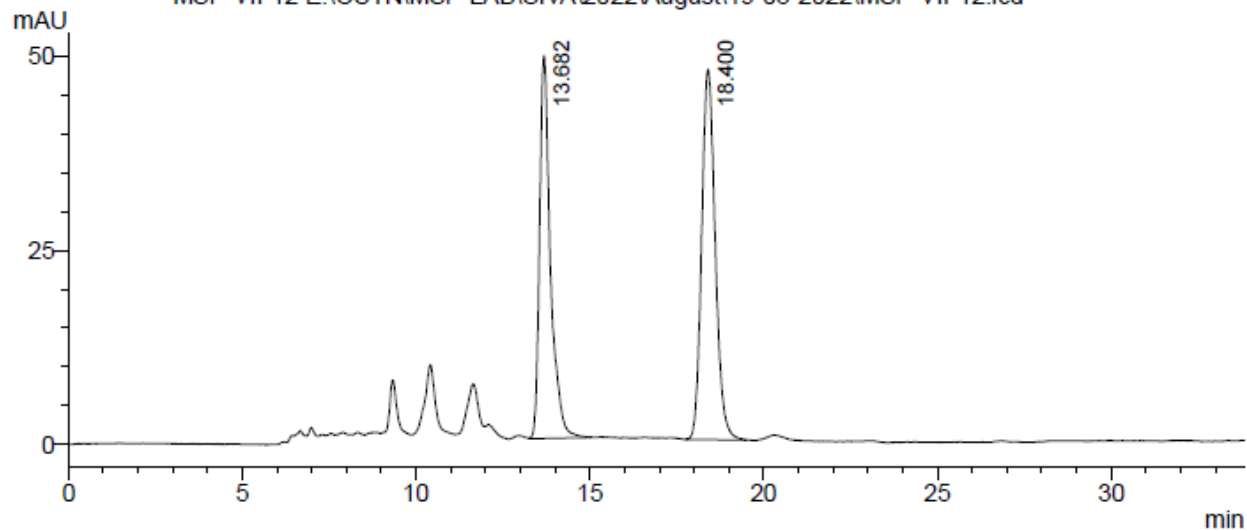


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.734	7837961	398662	95.972
2	18.601	328997	11943	4.028
Total		8166958	410606	100.000

HPLC Data of racemic **6f**

MSP-VII-12 E:\CUTNMSP-LAB\SIVA\2022\August\19-08-2022\MSP-VII-12.lcd

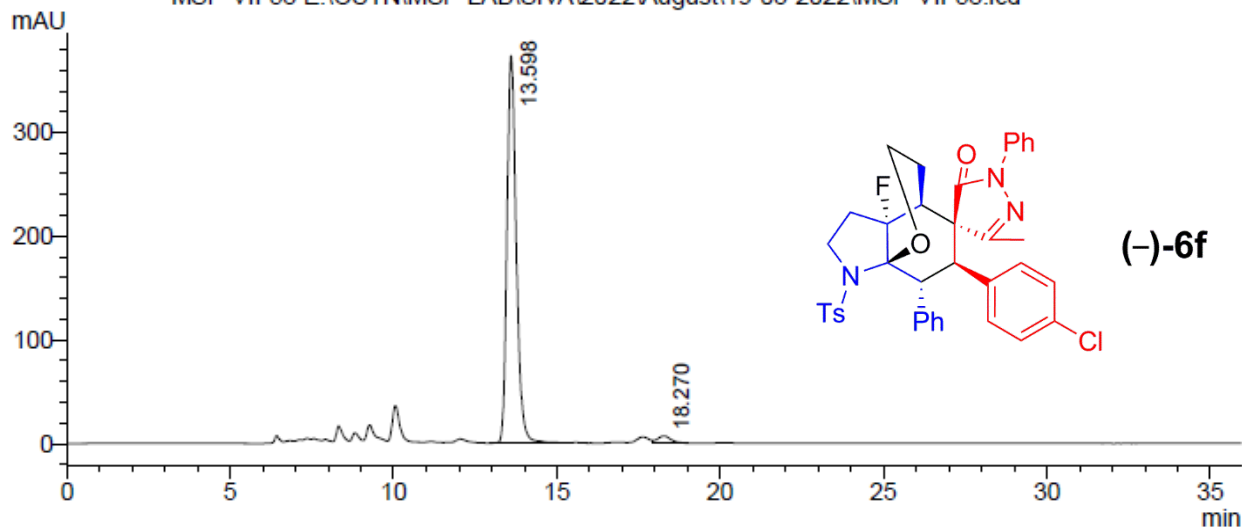


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.682	1067619	49254	45.235
2	18.400	1292540	47649	54.765
Total		2360159	96903	100.000

HPLC Data of chiral **6f**: 95% ee

MSP-VII-58 E:\CUTNMSP-LAB\SIVA\2022\August\19-08-2022\MSP-VII-58.lcd

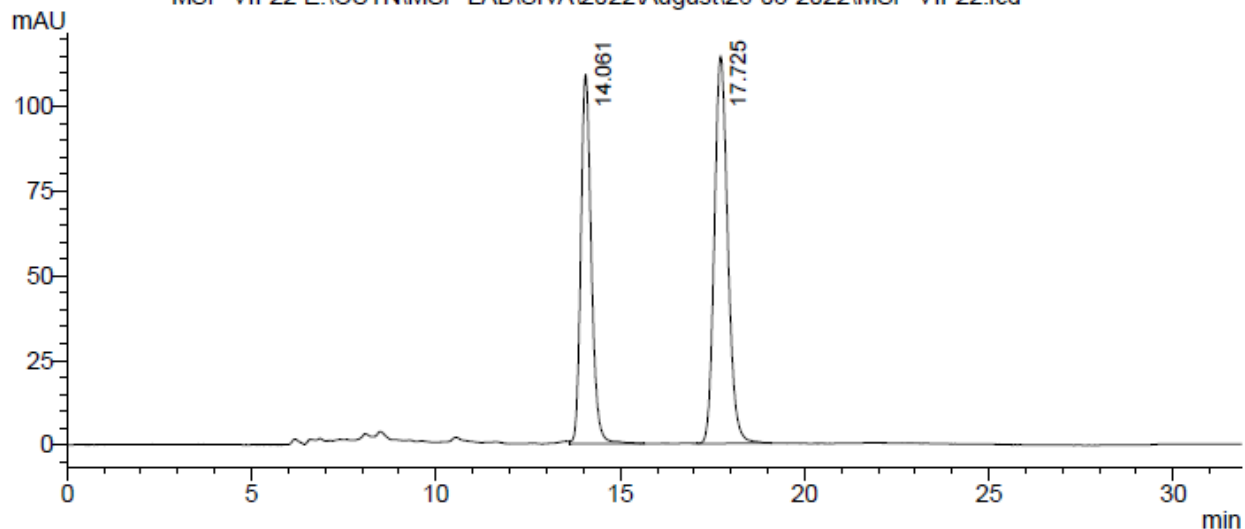


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.598	7409582	373258	97.500
2	18.270	189955	6822	2.500
Total		7599537	380080	100.000

HPLC Data of racemic **6g**

MSP-VII-22 E:\CUTNMSP-LAB\SIVA\2022\August26-08-2022\MSP-VII-22.lcd

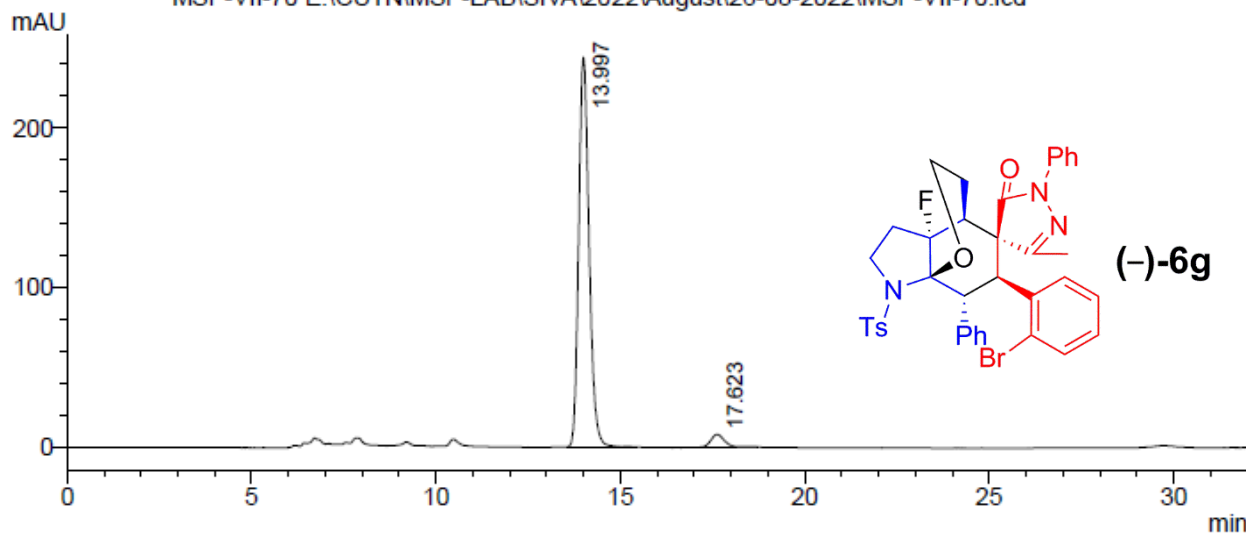


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.061	2152319	109125	42.676
2	17.725	2891099	114455	57.324
Total		5043417	223580	100.000

HPLC Data of chiral **6g**: 92% ee

MSP-VII-70 E:\CUTNMSP-LAB\SIVA\2022\August26-08-2022\MSP-VII-70.lcd



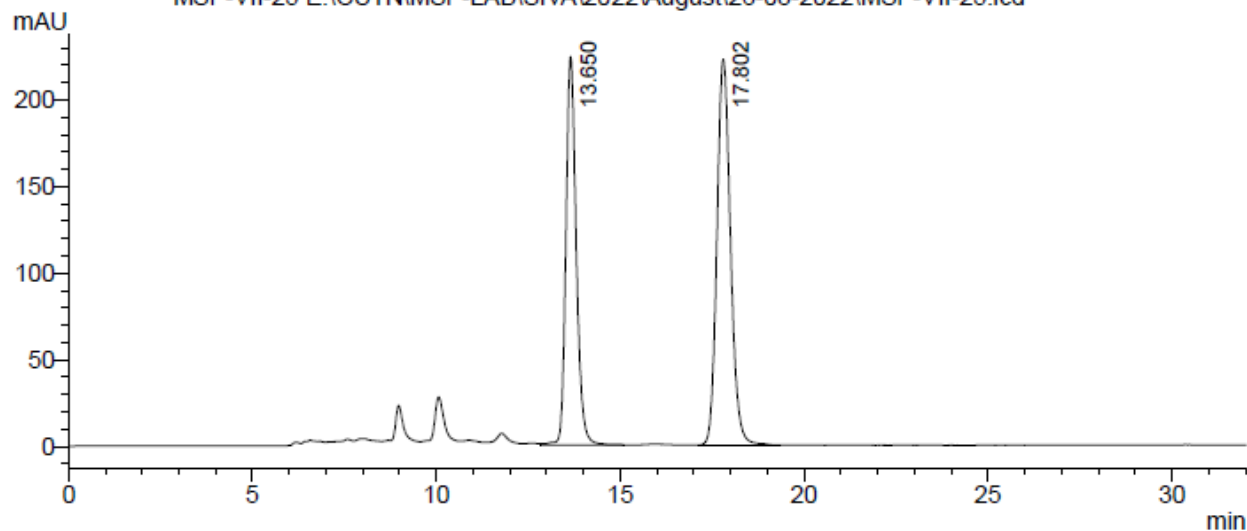
PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.997	4786450	243927	95.914
2	17.623	203918	7956	4.086
Total		4990367	251883	100.000



### HPLC Data of racemic **6h**

MSP-VII-25 E:\CUTNMSP-LAB\SIVA\2022\August\26-08-2022\MSP-VII-25.lcd

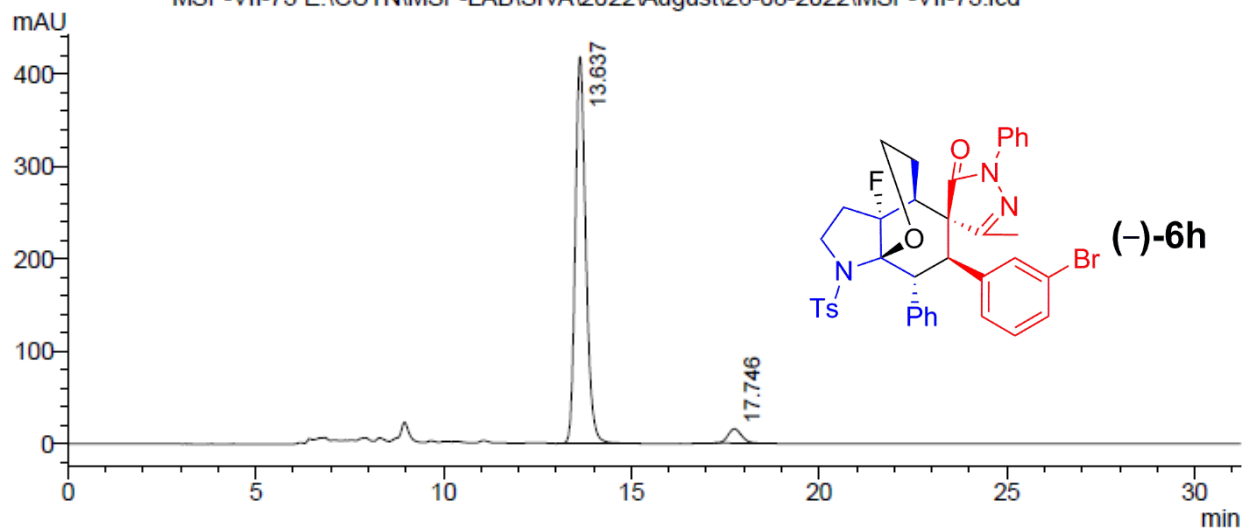


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.650	4365193	224149	43.269
2	17.802	5723398	222802	56.731
Total		10088591	446951	100.000

### HPLC Data of chiral **6h**: 91% ee

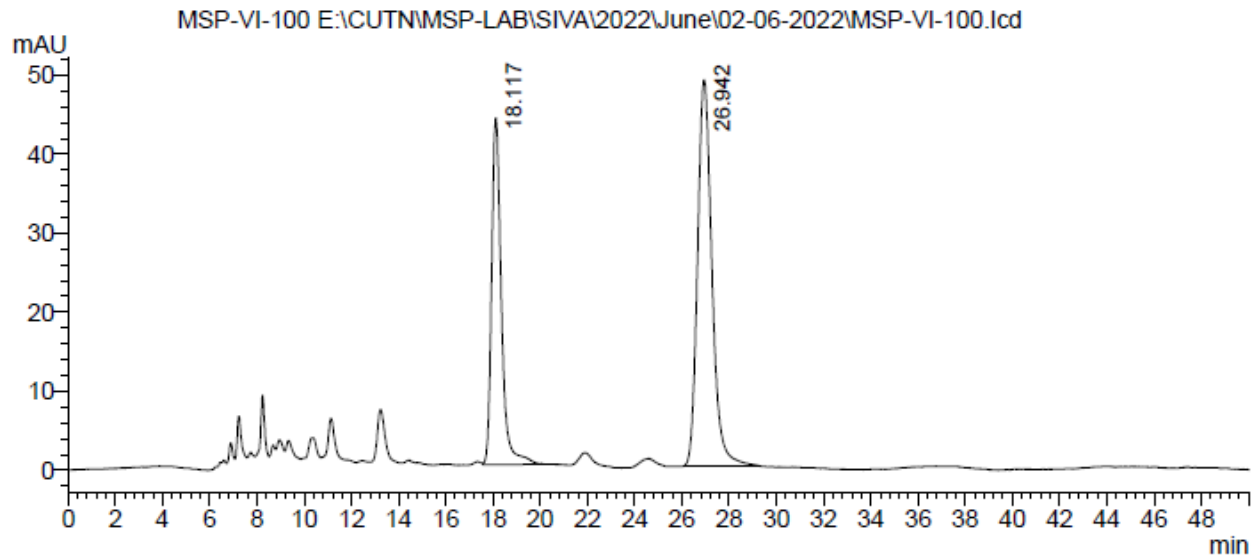
MSP-VII-73 E:\CUTNMSP-LAB\SIVA\2022\August\26-08-2022\MSP-VII-73.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.637	8094498	417965	95.475
2	17.746	383628	15376	4.525
Total		8478126	433341	100.000

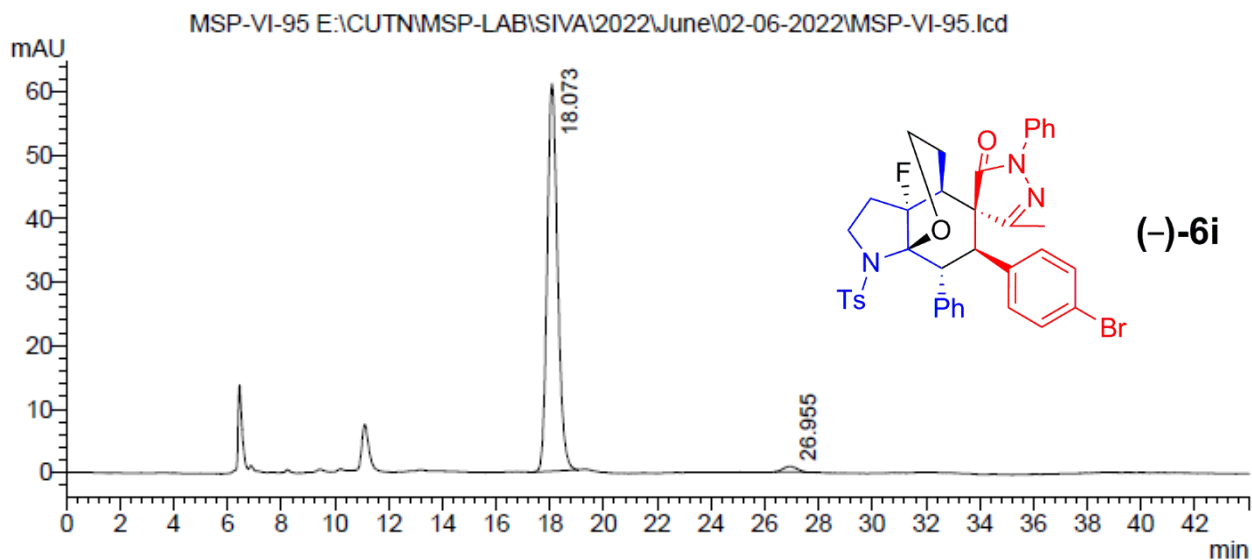
HPLC Data of racemic **6i**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.117	1260988	43872	37.802
2	26.942	2074770	48905	62.198
Total		3335758	92777	100.000

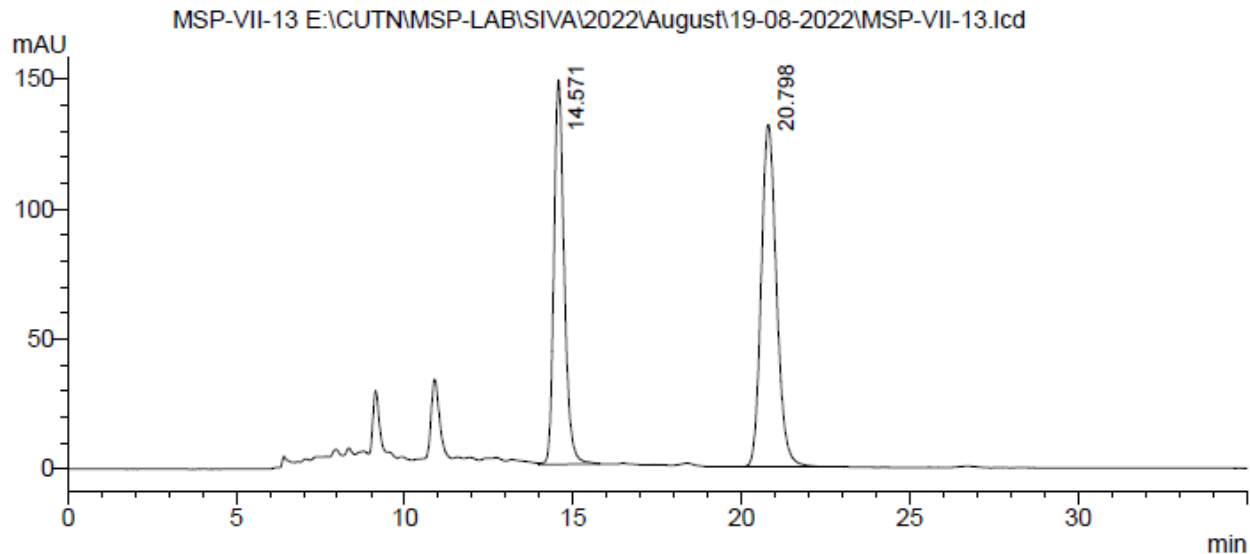
HPLC Data of chiral **6i**: 96% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.073	1649844	61036	98.140
2	26.955	31274	898	1.860
Total		1681118	61934	100.000

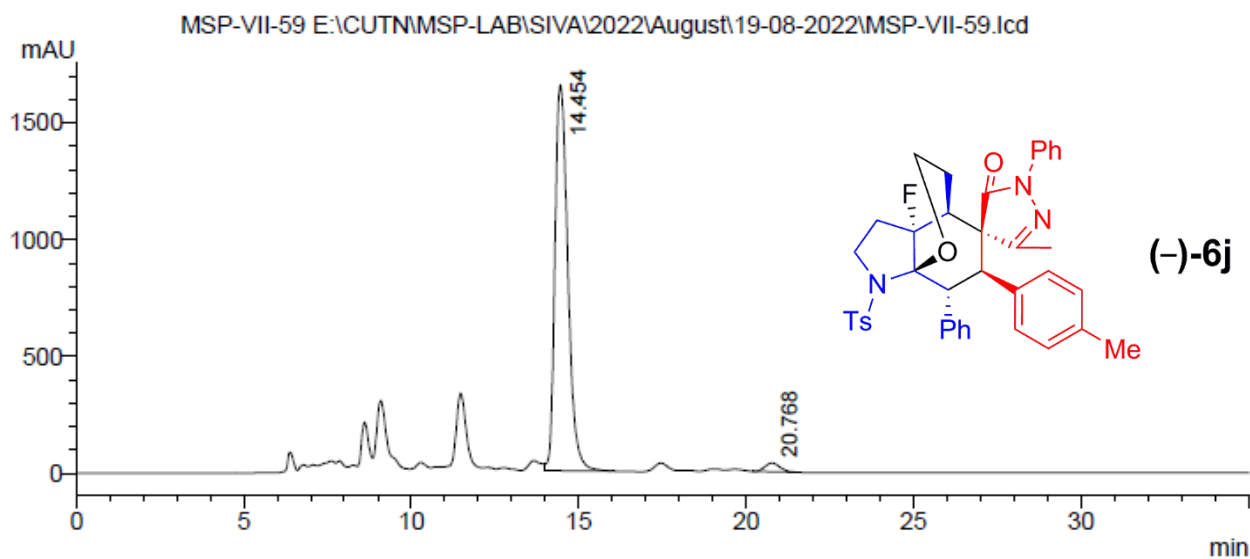
HPLC Data of racemic **6j**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.571	3147768	147992	43.115
2	20.798	4153152	131687	56.885
Total		7300920	279679	100.000

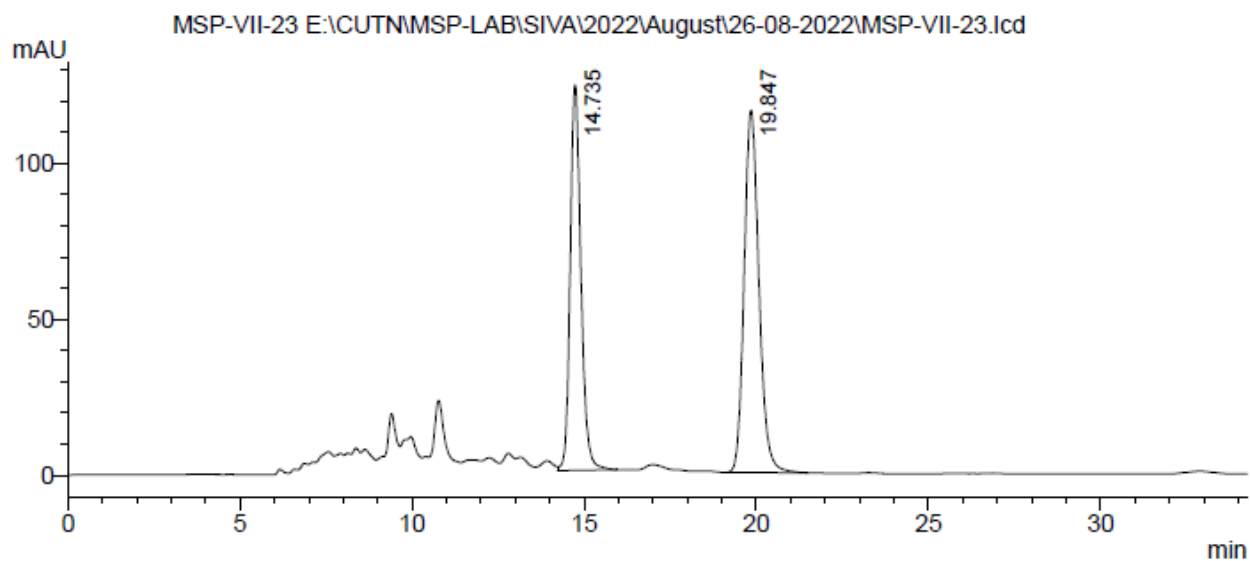
HPLC Data of chiral **6j**: 95% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.454	44422887	1653102	97.466
2	20.768	1154973	37238	2.534
Total		45577860	1690340	100.000

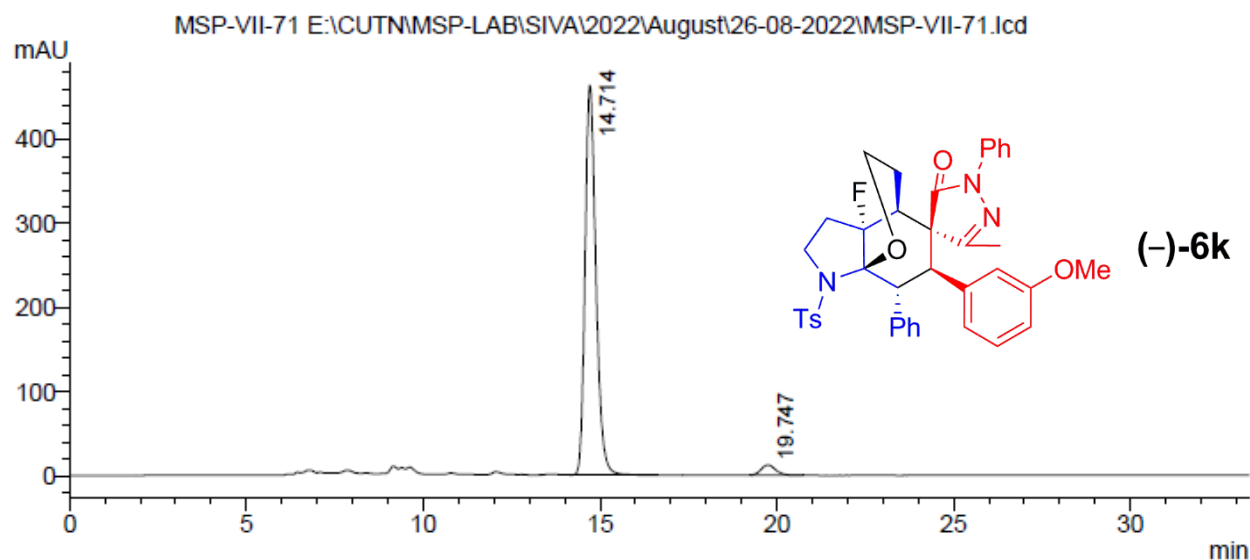
HPLC Data of racemic **6k**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.735	2675826	123594	43.535
2	19.847	3470545	116126	56.465
Total		6146371	239720	100.000

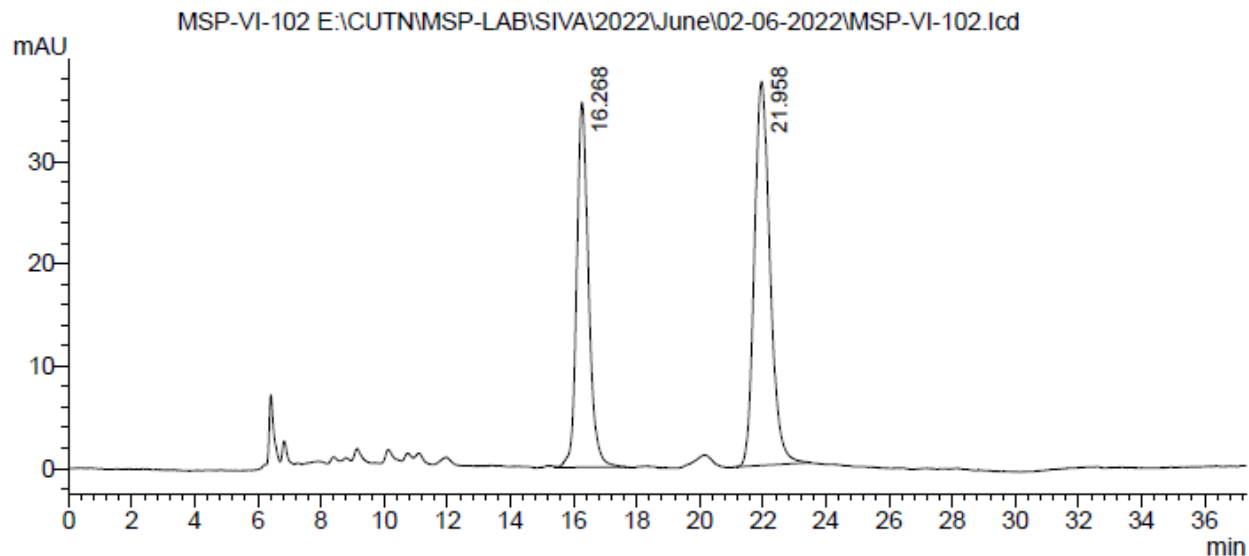
HPLC Data of chiral **6k**: 93% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.714	9900343	463575	96.567
2	19.747	351963	12173	3.433
Total		10252306	475748	100.000

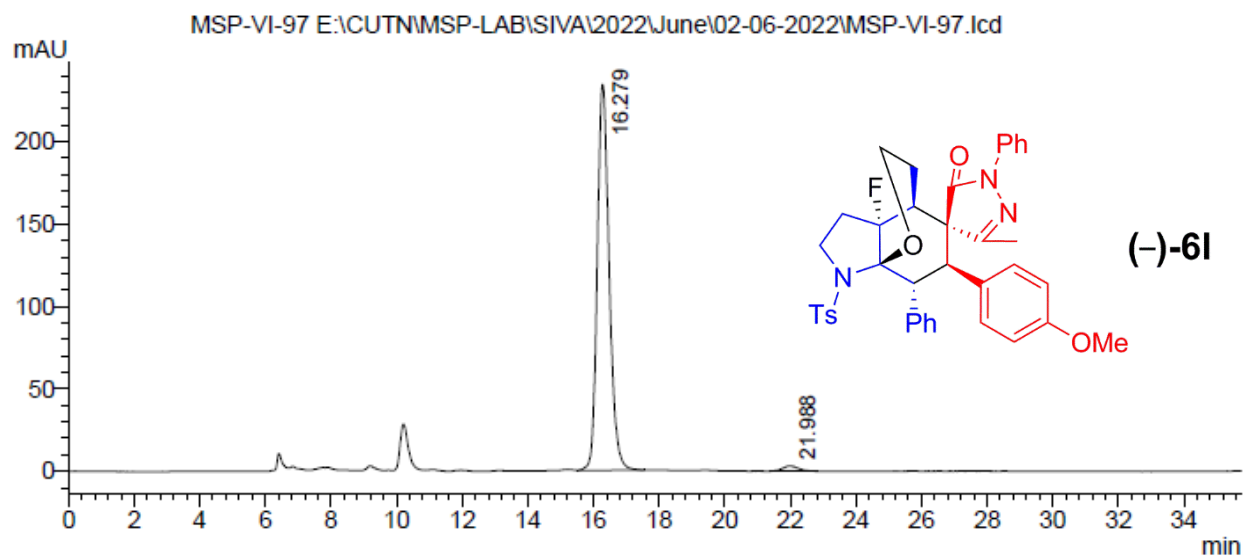
HPLC Data of racemic **6I**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.268	931220	35705	41.769
2	21.958	1298232	37521	58.231
Total		2229453	73226	100.000

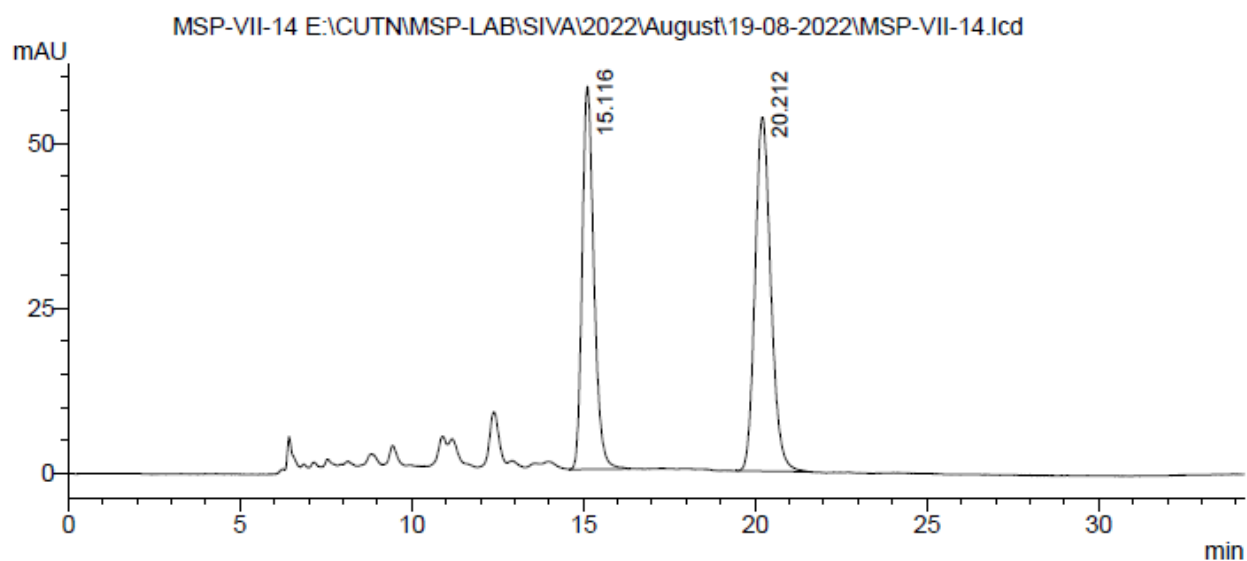
HPLC Data of chiral **6I**: 97% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.279	5902959	234154	98.290
2	21.988	102719	3095	1.710
Total		6005678	237249	100.000

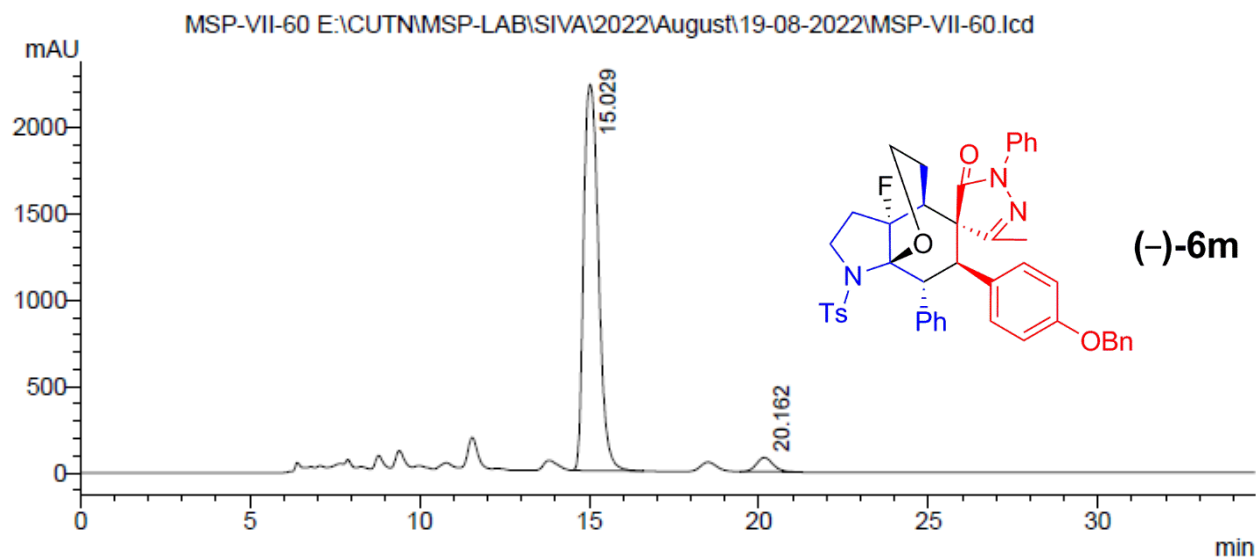
### HPLC Data of racemic **6m**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.116	1374983	57966	44.497
2	20.212	1715075	53660	55.503
Total		3090059	111625	100.000

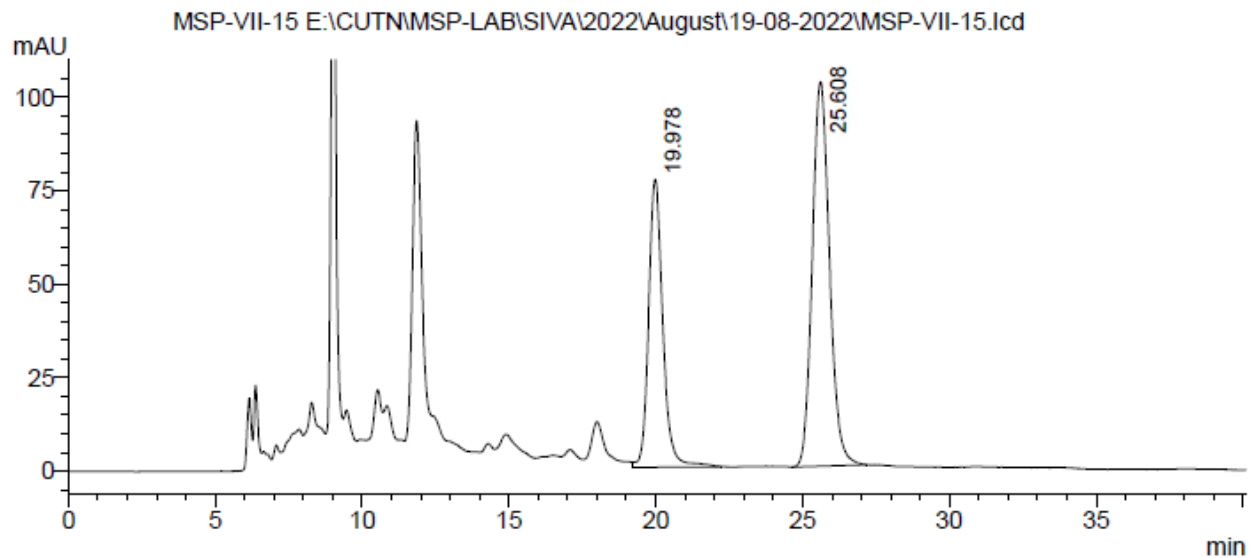
### HPLC Data of chiral **6m**: 92% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.029	67909354	2237007	96.059
2	20.162	2786085	82106	3.941
Total		70695438	2319113	100.000

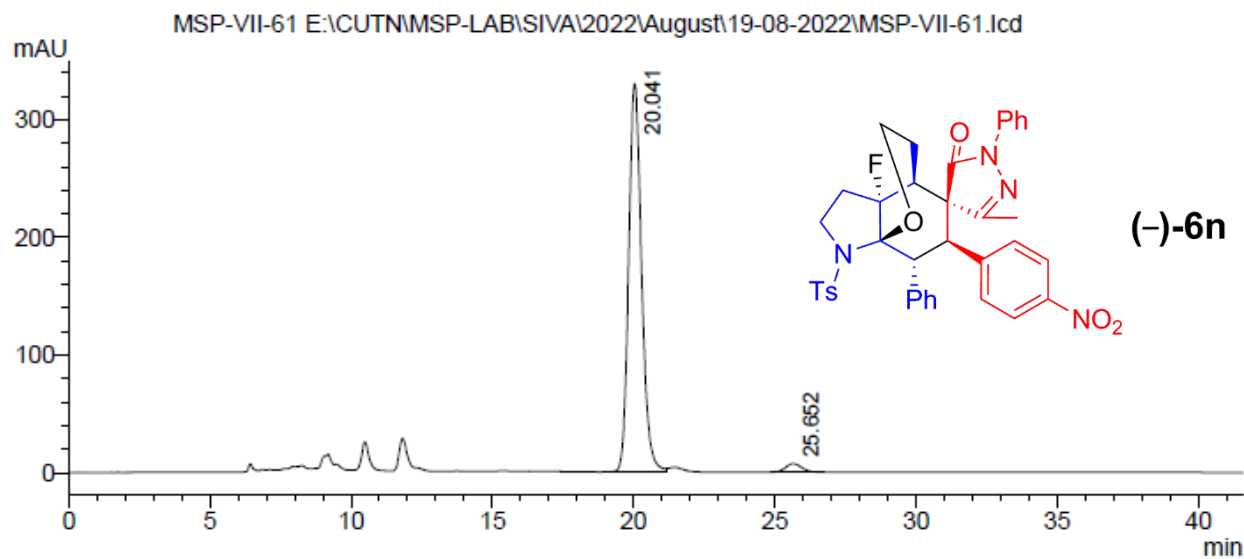
### HPLC Data of racemic **6n**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.978	2595851	77005	38.221
2	25.608	4195749	102830	61.779
Total		6791600	179835	100.000

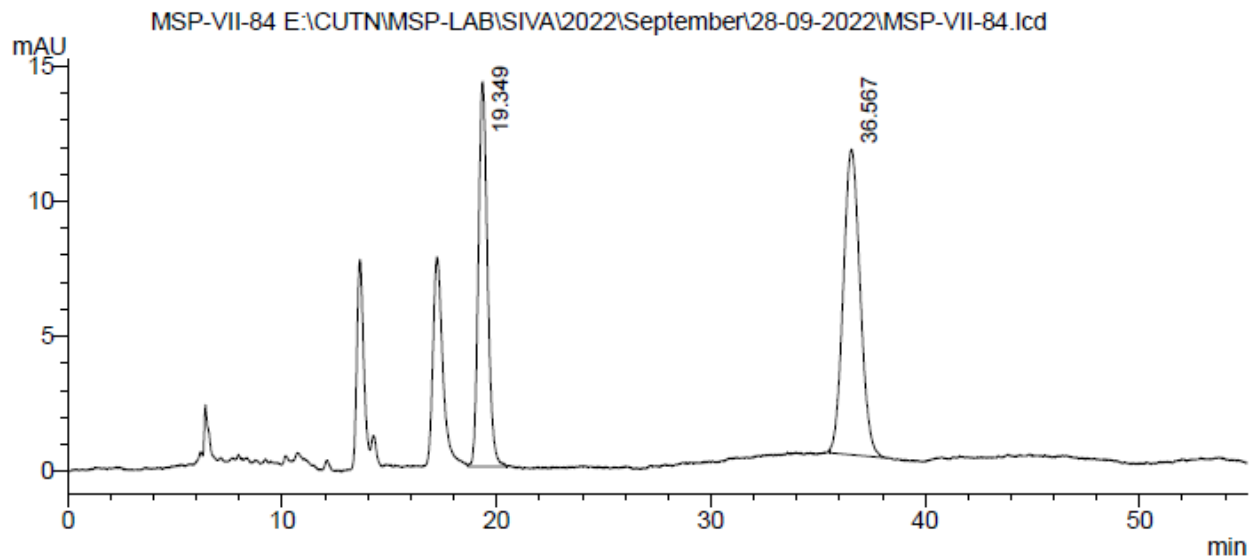
### HPLC Data of chiral **6n**: 95% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	20.041	10467600	330021	97.253
2	25.652	295672	7300	2.747
Total		10763272	337320	100.000

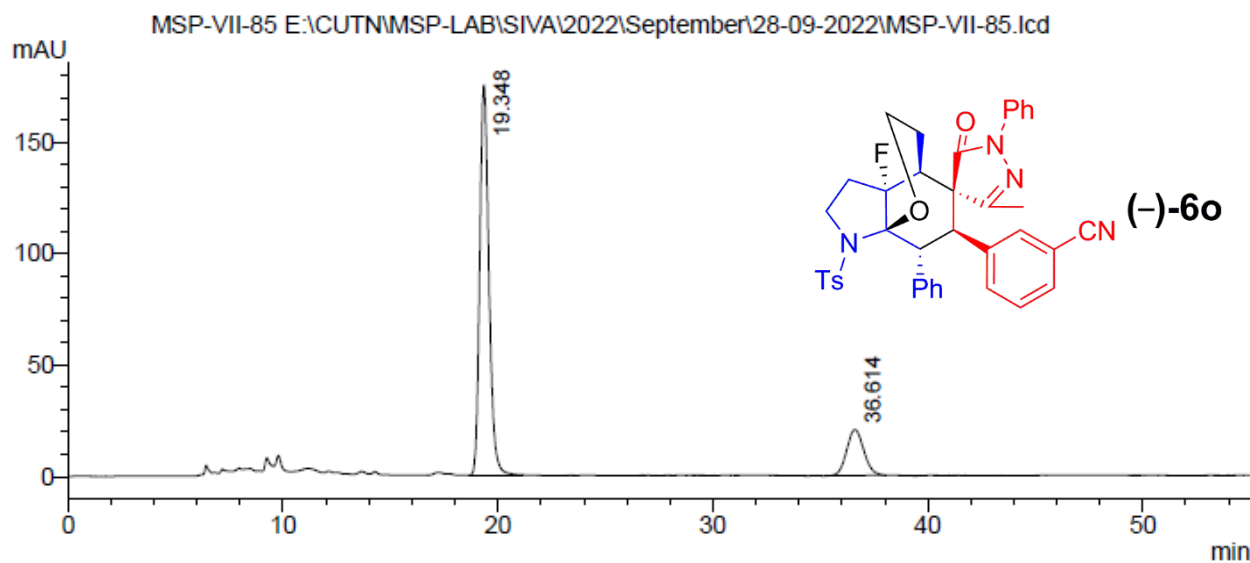
HPLC Data of racemic **6o**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.349	421656	14261	40.576
2	36.567	617511	11321	59.424
Total		1039167	25583	100.000

HPLC Data of chiral **6o**: 64% ee

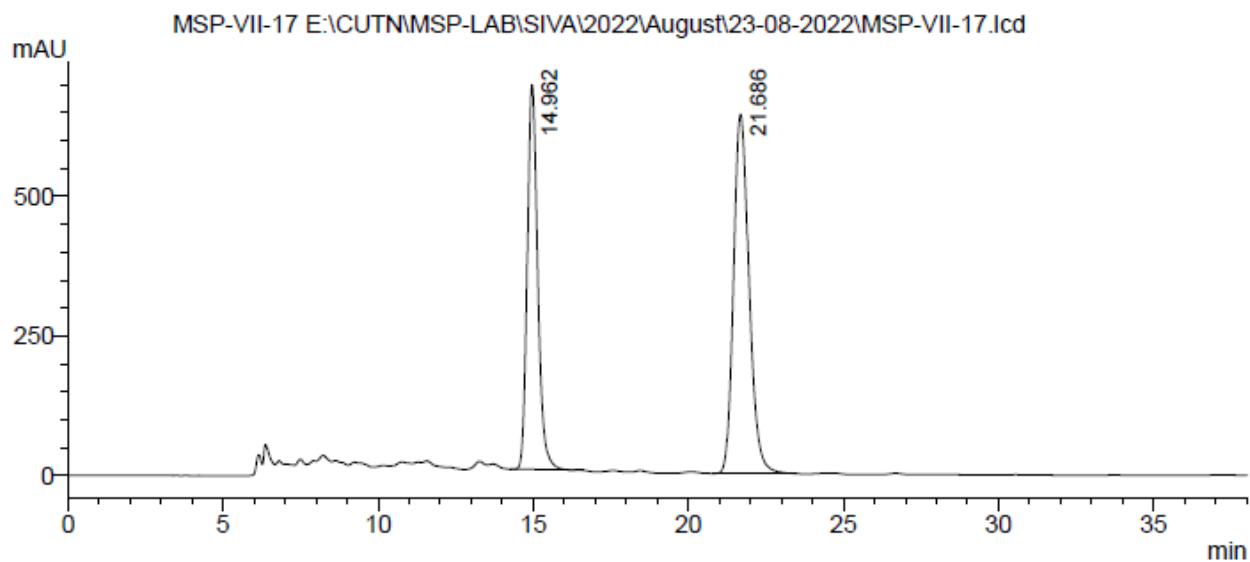


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.348	5183599	174825	82.047
2	36.614	1134247	20548	17.953
Total		6317846	195374	100.000



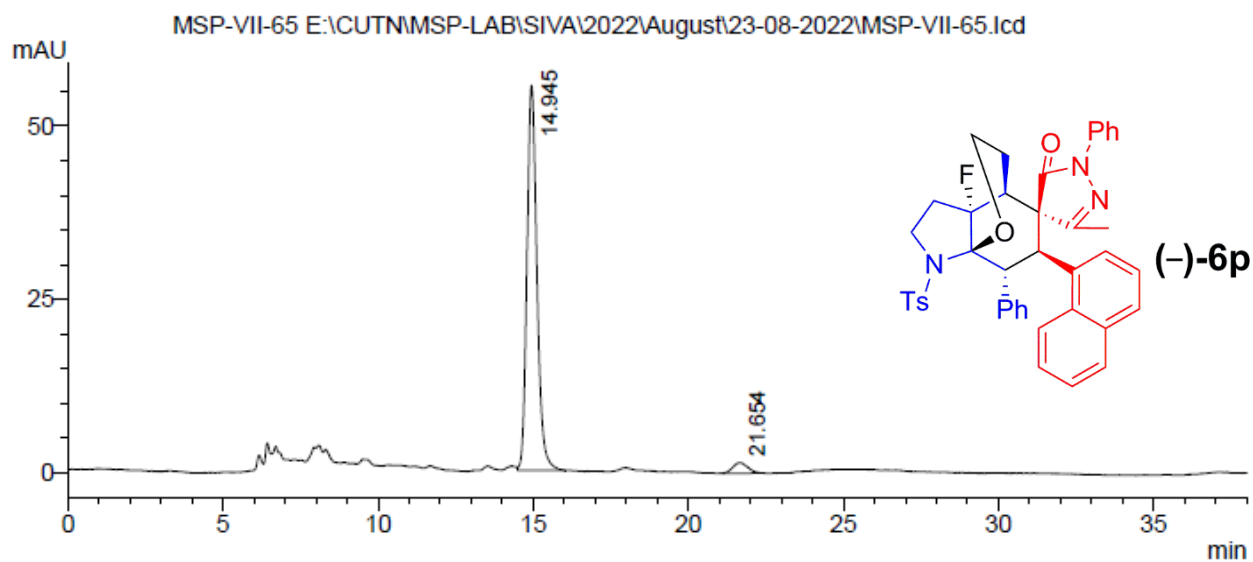
HPLC Data of racemic **6p**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.962	16148090	688914	41.799
2	21.686	22485067	643178	58.201
Total		38633157	1332093	100.000

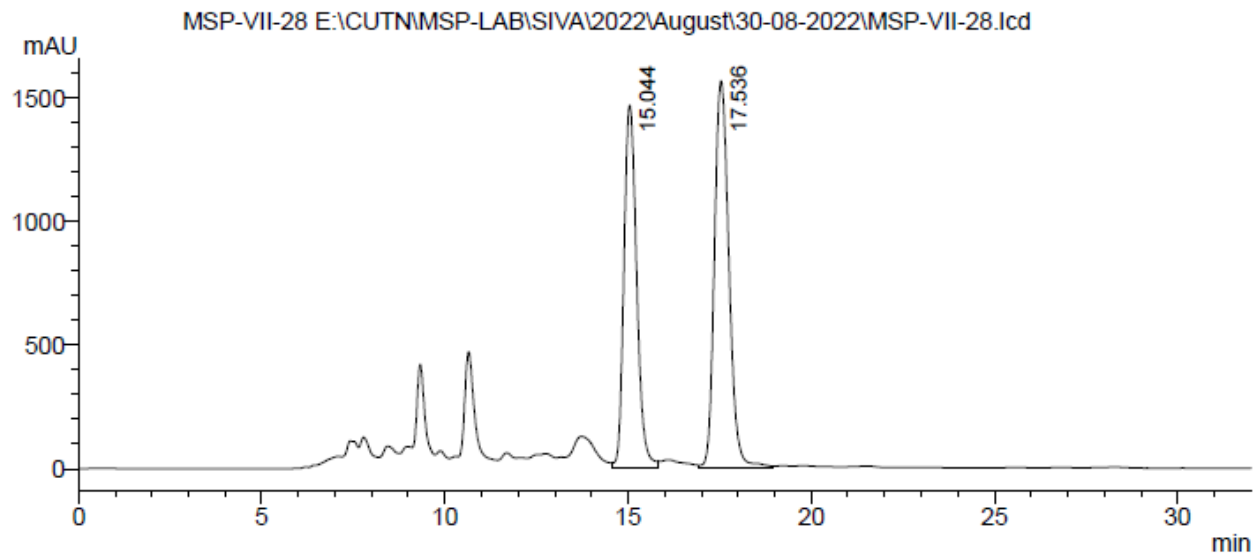
HPLC Data of chiral **6p**: 92% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.945	1234565	55380	96.083
2	21.654	50324	1518	3.917
Total		1284889	56898	100.000

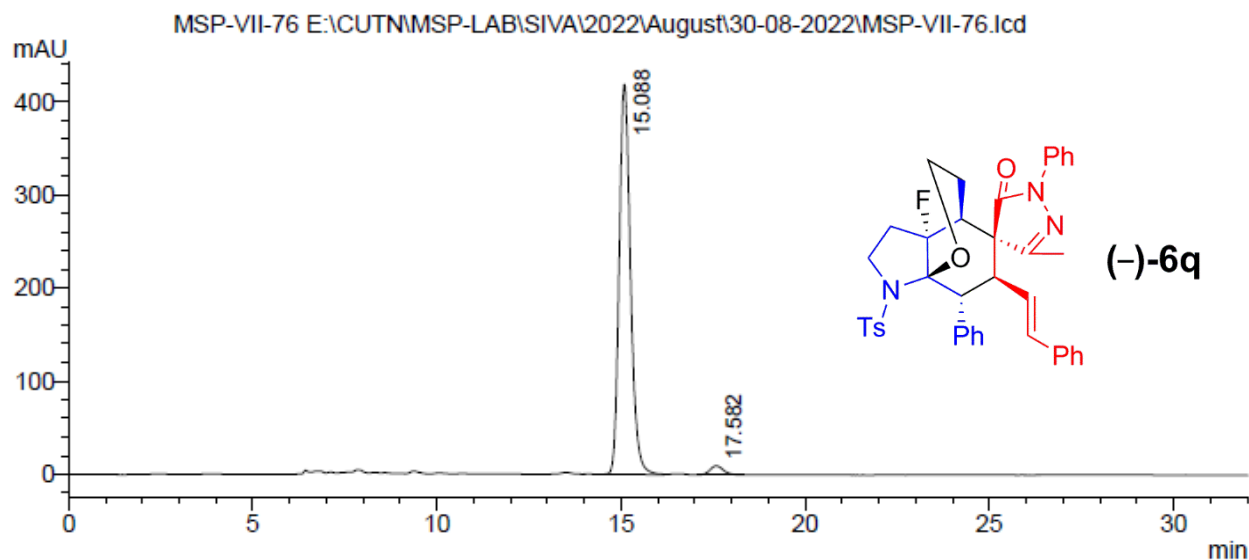
### HPLC Data of racemic **6q**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.044	35640103	1469383	45.175
2	17.536	43252962	1566401	54.825
Total		78893065	3035783	100.000

### HPLC Data of chiral **6q**: 95% *ee*

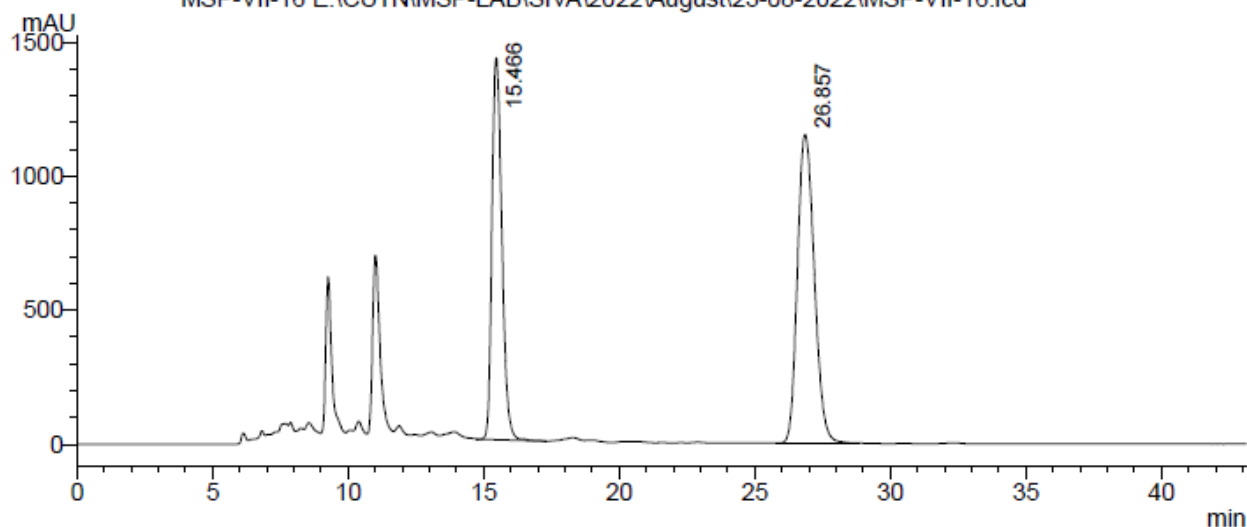


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.088	8948794	418573	97.432
2	17.582	235851	9601	2.568
Total		9184644	428174	100.000

### HPLC Data of racemic **6r**

MSP-VII-16 E:\CUTNMSP-LAB\SIVA\2022\August\23-08-2022\MSP-VII-16.lcd

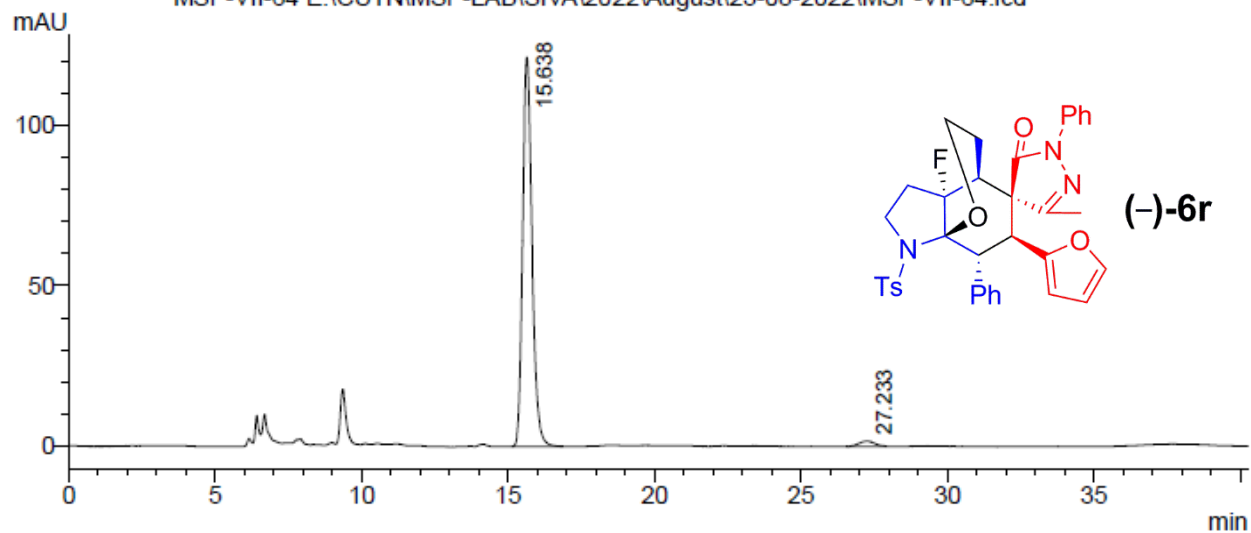


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.466	36237747	1423766	42.145
2	26.857	49746312	1150331	57.855
Total		85984059	2574096	100.000

### HPLC Data of chiral **6r**: 95% ee

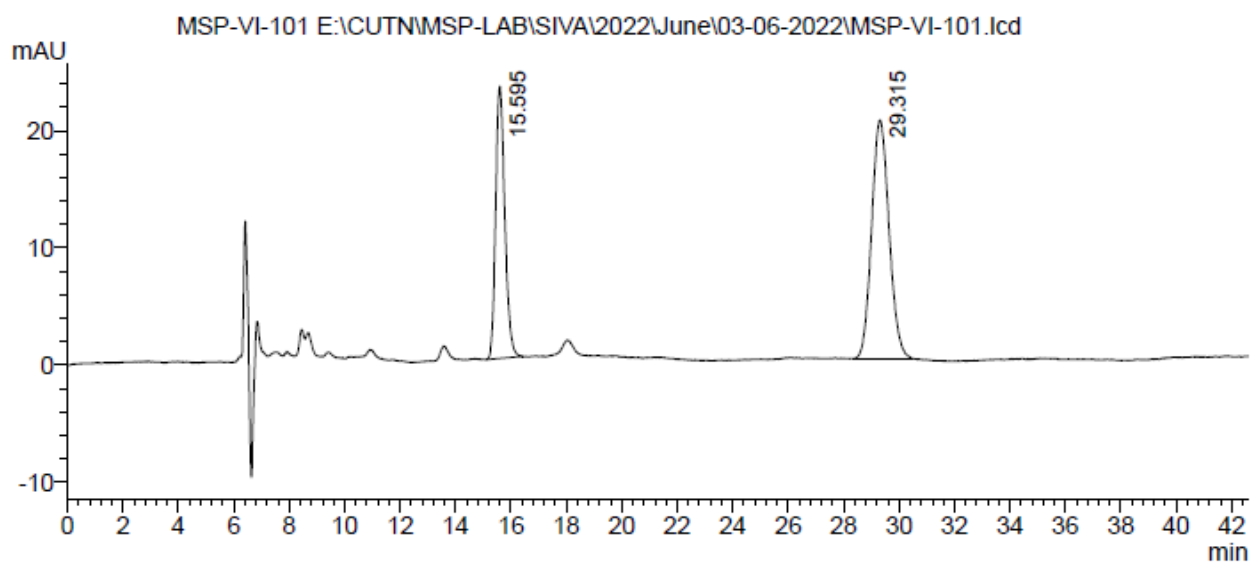
MSP-VII-64 E:\CUTNMSP-LAB\SIVA\2022\August\23-08-2022\MSP-VII-64.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.638	2718185	121490	97.722
2	27.233	63367	1662	2.278
Total		2781553	123151	100.000

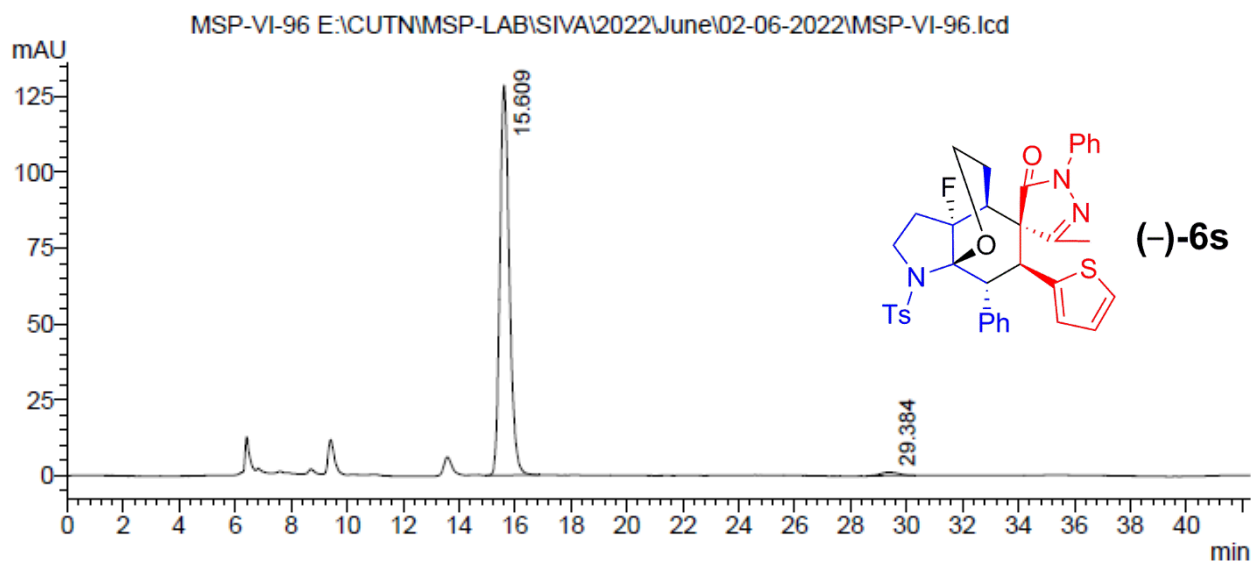
### HPLC Data of racemic **6s**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.595	533437	23249	37.461
2	29.315	890558	20365	62.539
Total		1423995	43613	100.000

### HPLC Data of chiral **6s**: 97% ee

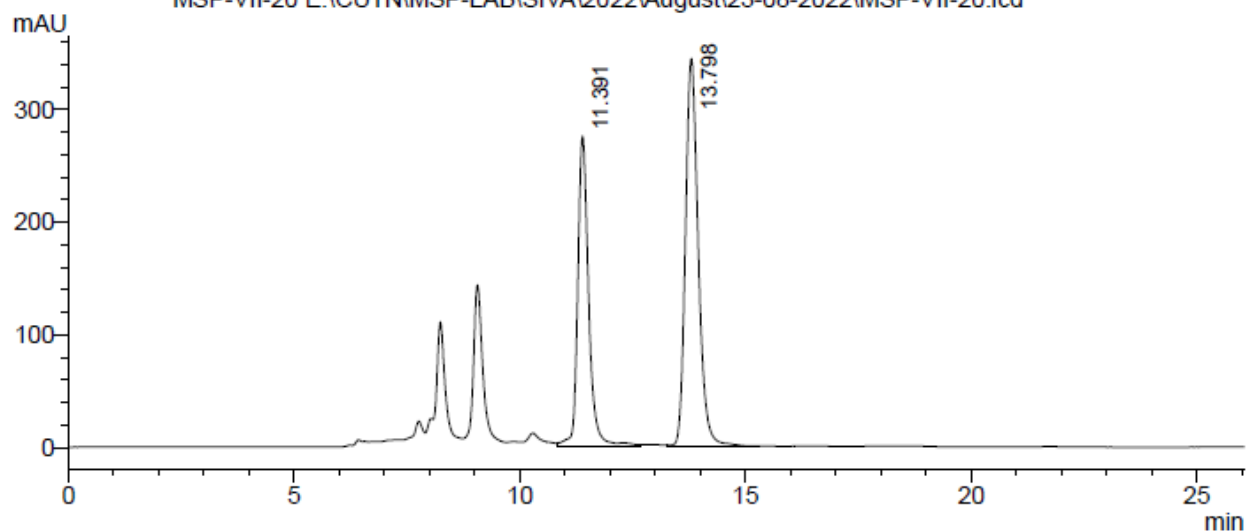


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	15.609	3027892	128549	98.345
2	29.384	50941	1183	1.655
Total		3078833	129732	100.000

HPLC Data of racemic **6t**

MSP-VII-20 E:\CUTNMSP-LAB\SIVA\2022\August\23-08-2022\MSP-VII-20.lcd

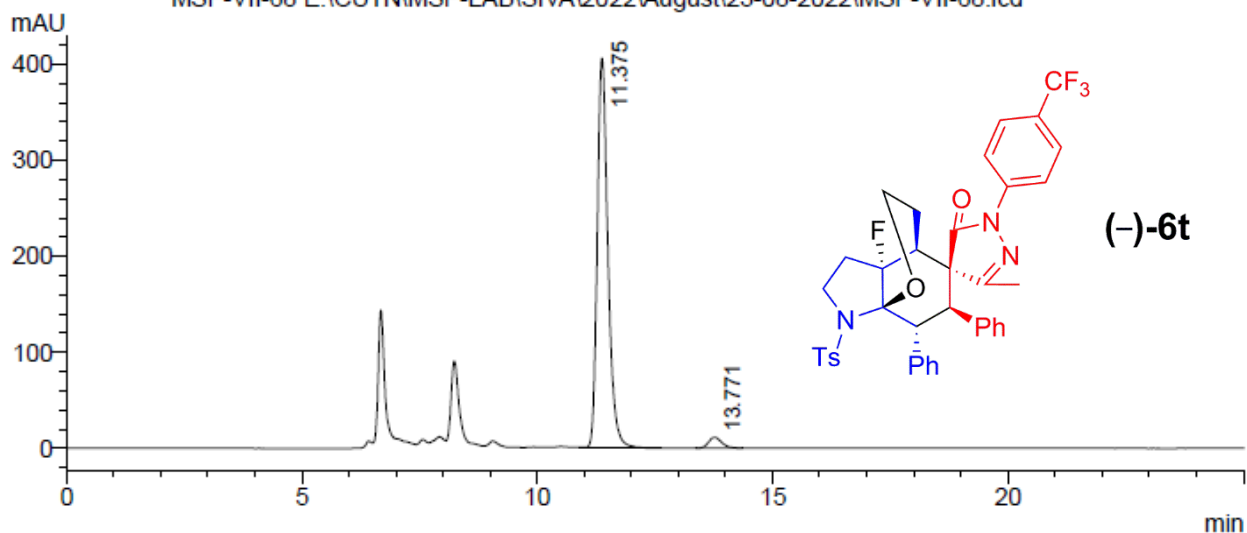


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.391	4647506	275644	40.568
2	13.798	6808547	344330	59.432
Total		11456053	619974	100.000

HPLC Data of chiral **6t**: 93% ee

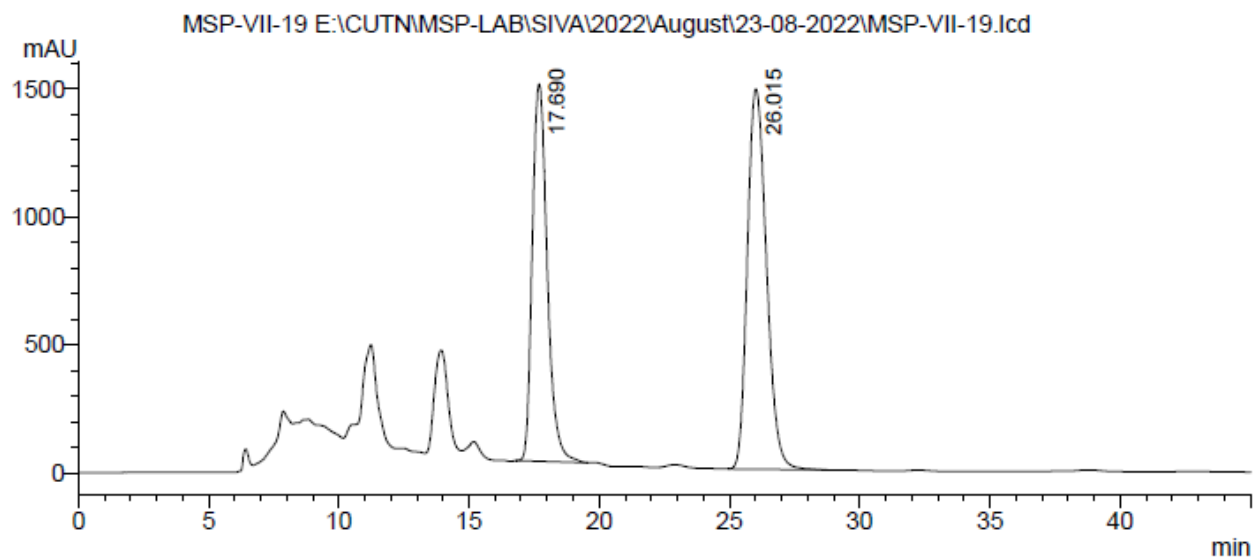
MSP-VII-68 E:\CUTNMSP-LAB\SIVA\2022\August\23-08-2022\MSP-VII-68.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.375	6434845	406294	96.650
2	13.771	223023	11431	3.350
Total		6657868	417725	100.000

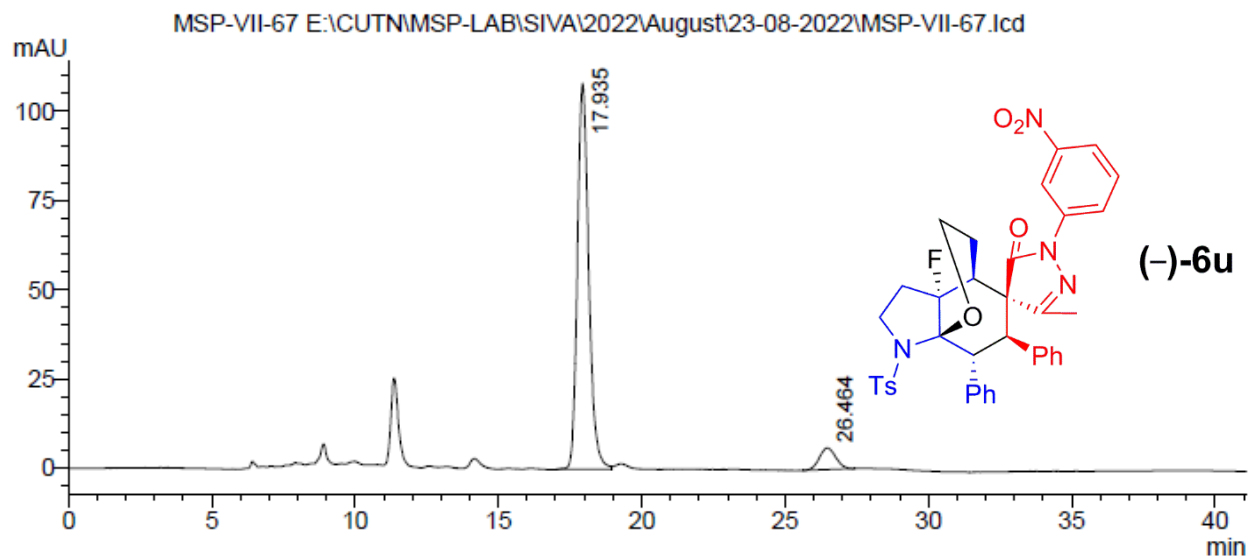
### HPLC Data of racemic **6u**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.690	58792922	1474131	43.723
2	26.015	75675059	1485905	56.277
Total		134467981	2960036	100.000

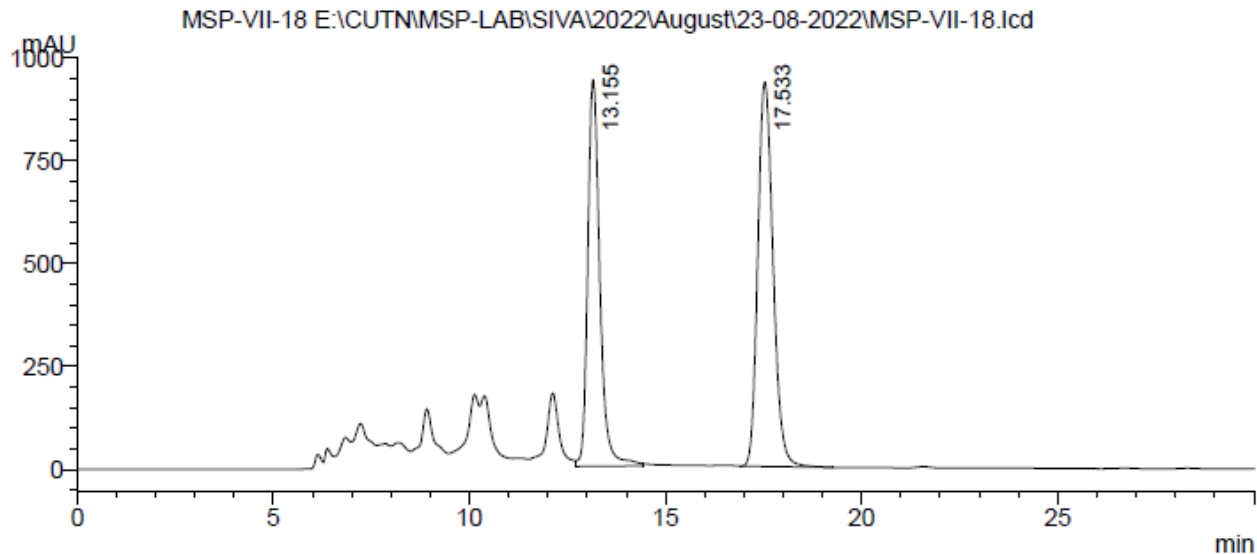
### HPLC Data of chiral **6u**: 85% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	17.935	2980068	108141	92.525
2	26.464	240743	6065	7.475
Total		3220811	114206	100.000

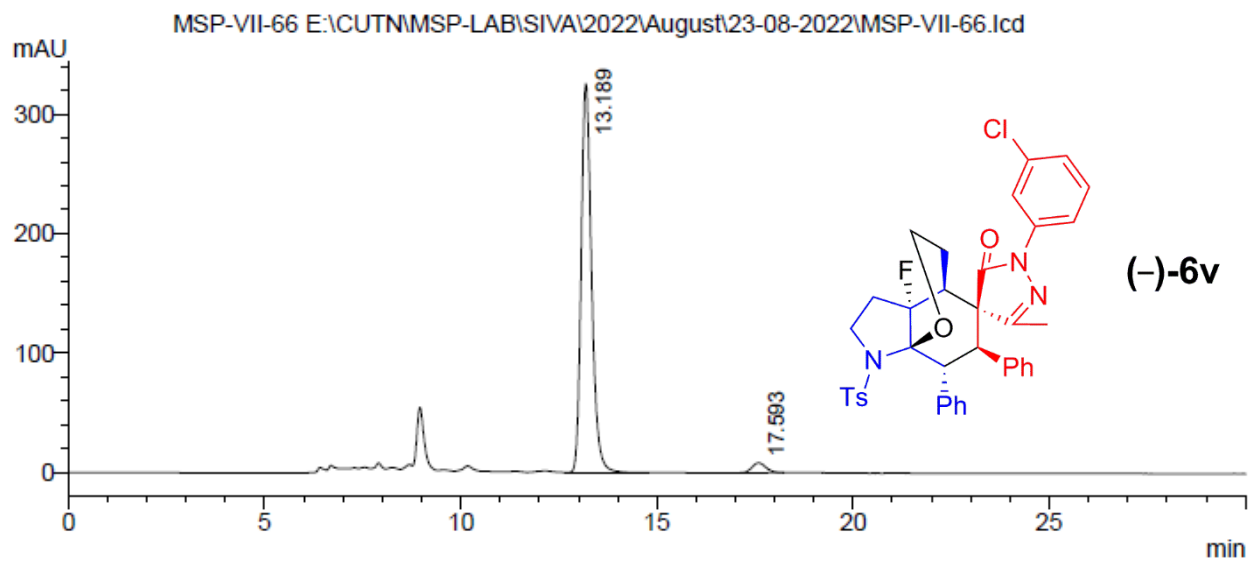
HPLC Data of racemic **6v**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.155	20109745	939778	44.240
2	17.533	25345929	934811	55.760
Total		45455675	1874589	100.000

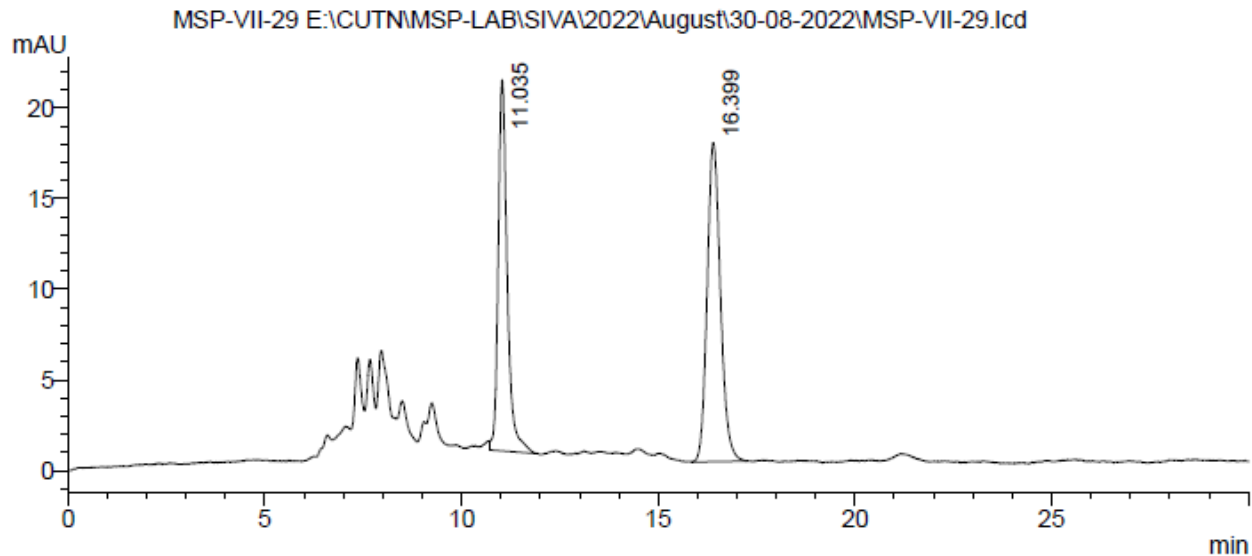
HPLC Data of chiral **6v**: 93% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.189	6048164	325440	96.728
2	17.593	204567	8281	3.272
Total		6252731	333721	100.000

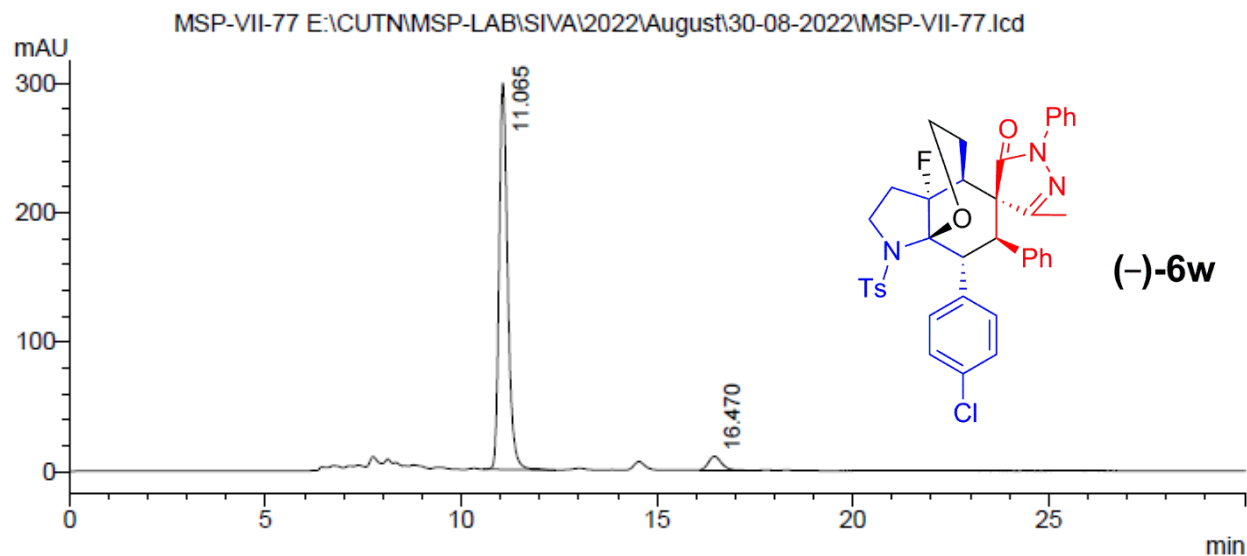
HPLC Data of racemic **6w**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.035	325635	20466	44.040
2	16.399	413779	17606	55.960
Total		739414	38072	100.000

HPLC Data of chiral **6w**: 90% *ee*

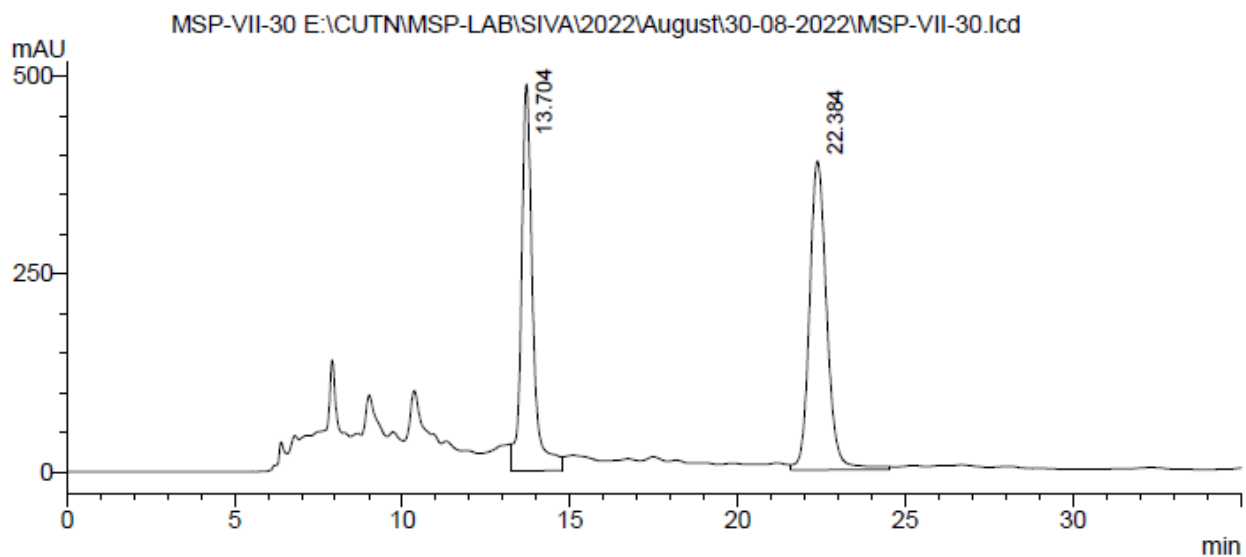


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.065	4570720	298676	94.932
2	16.470	244027	10656	5.068
Total		4814747	309333	100.000



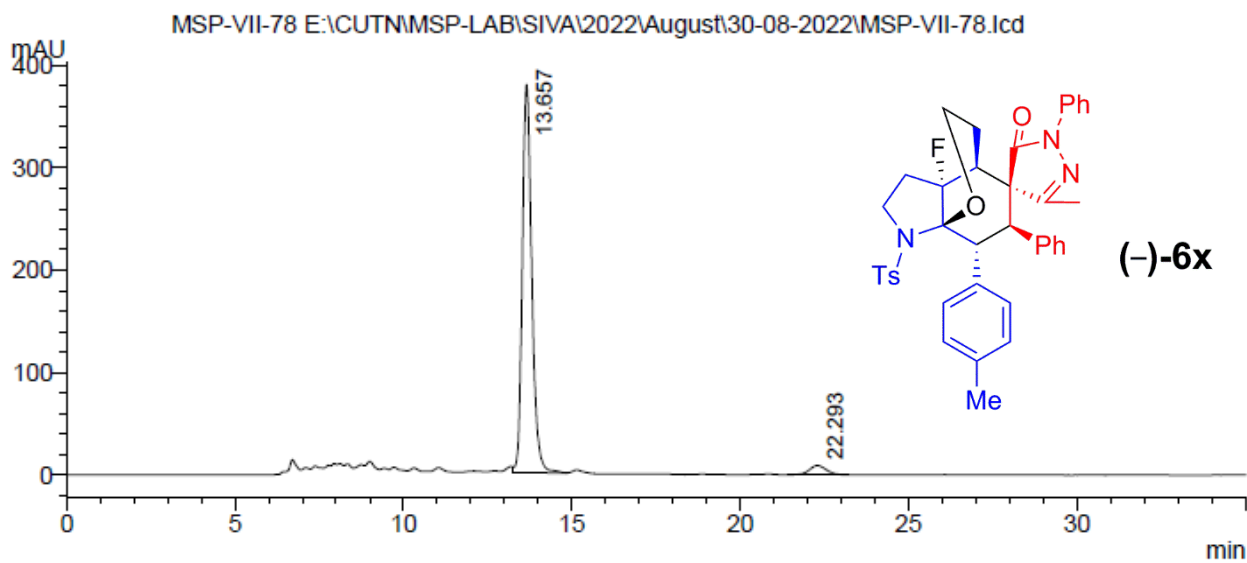
### HPLC Data of racemic **6x**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.704	11400979	488672	44.948
2	22.384	13963906	390449	55.052
Total		25364885	879121	100.000

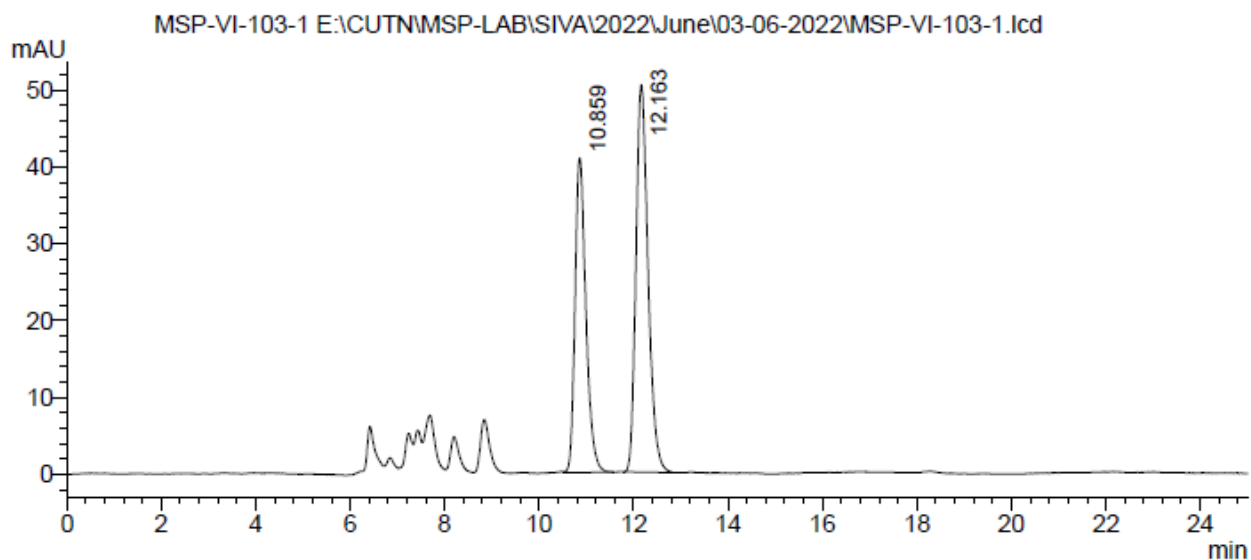
### HPLC Data of chiral **6x**: 92% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.657	7422174	379191	95.912
2	22.293	316322	9018	4.088
Total		7738496	388209	100.000

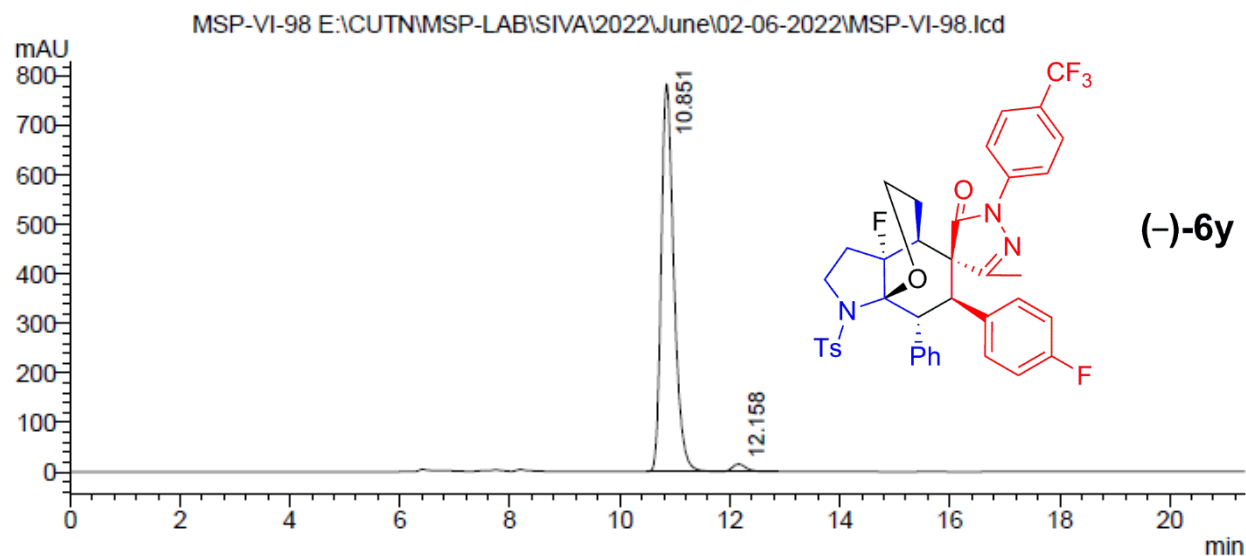
### HPLC Data of racemic **6y**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	10.859	654902	40928	42.099
2	12.163	900709	50429	57.901
Total		1555611	91357	100.000

### HPLC Data of chiral **6y**: 96% ee

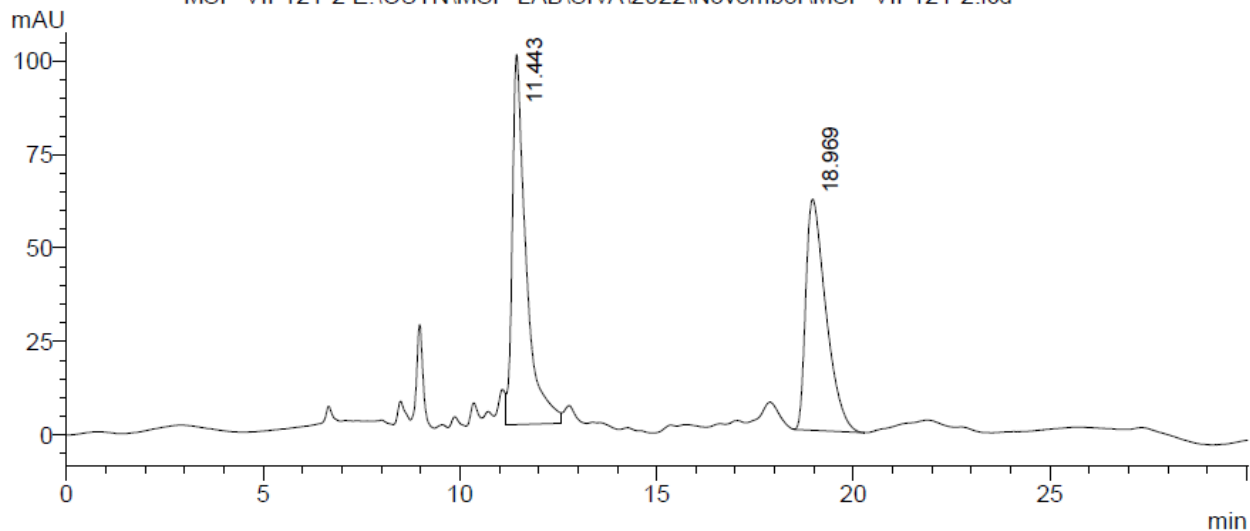


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	10.851	12541658	783907	97.843
2	12.158	276504	15380	2.157
Total		12818162	799288	100.000

### HPLC Data of racemic 6'a

MSP-VII-121-2 E:\CUTN\MSP-LAB\SIVA\2022\November\MSP-VII-121-2.lcd

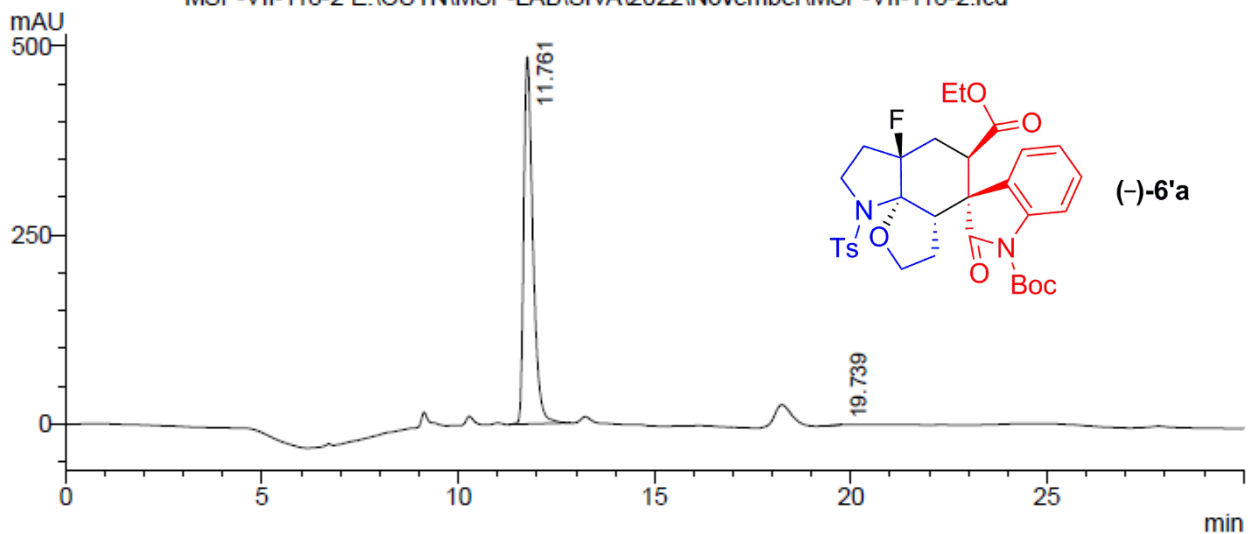


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.443	2404135	98897	52.176
2	18.969	2203639	61791	47.824
Total		4607774	160688	100.000

### HPLC Data of chiral 6'a: 99% ee

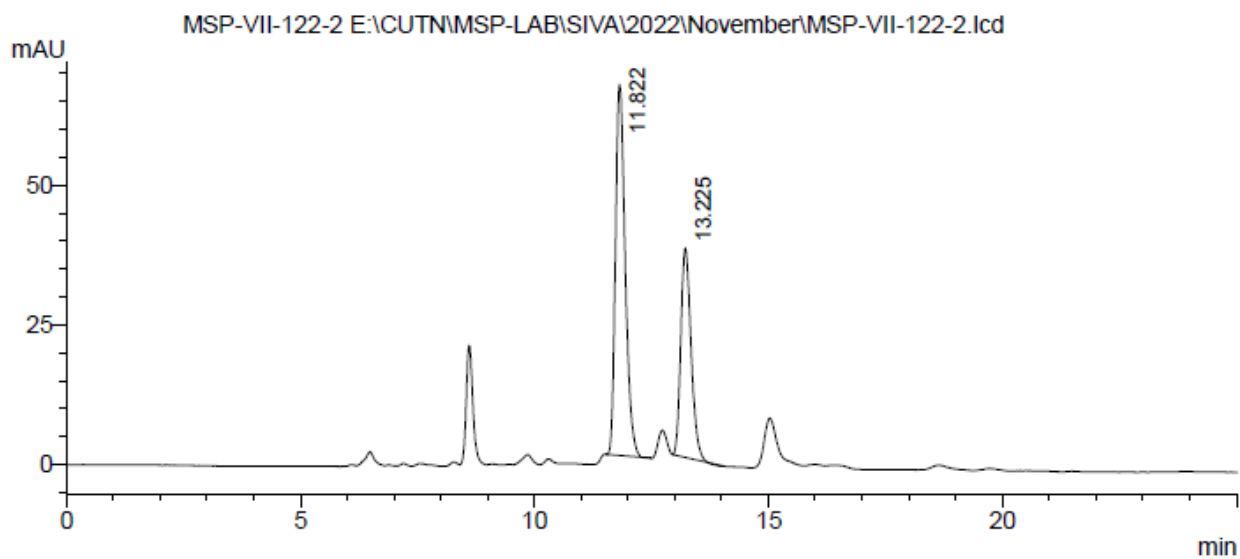
MSP-VII-118-2 E:\CUTN\MSP-LAB\SIVA\2022\November\MSP-VII-118-2.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.761	7863501	484636	99.998
2	19.739	138	-31	0.002
Total		7863639	484605	100.000

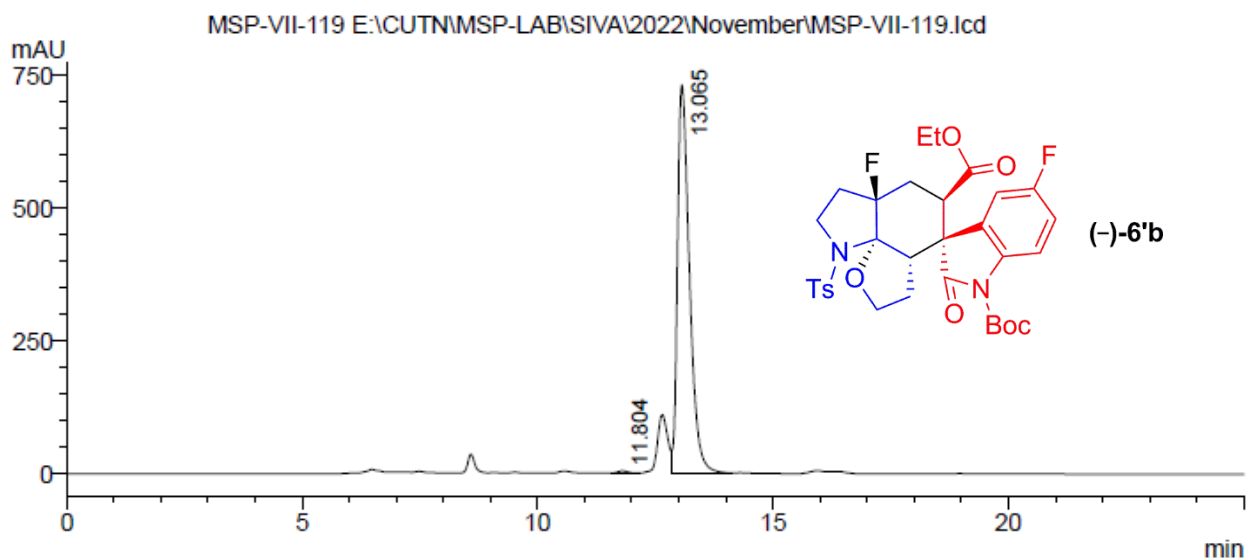
HPLC Data of racemic **6'b**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.822	961146	66422	62.733
2	13.225	570987	37466	37.267
Total		1532134	103888	100.000

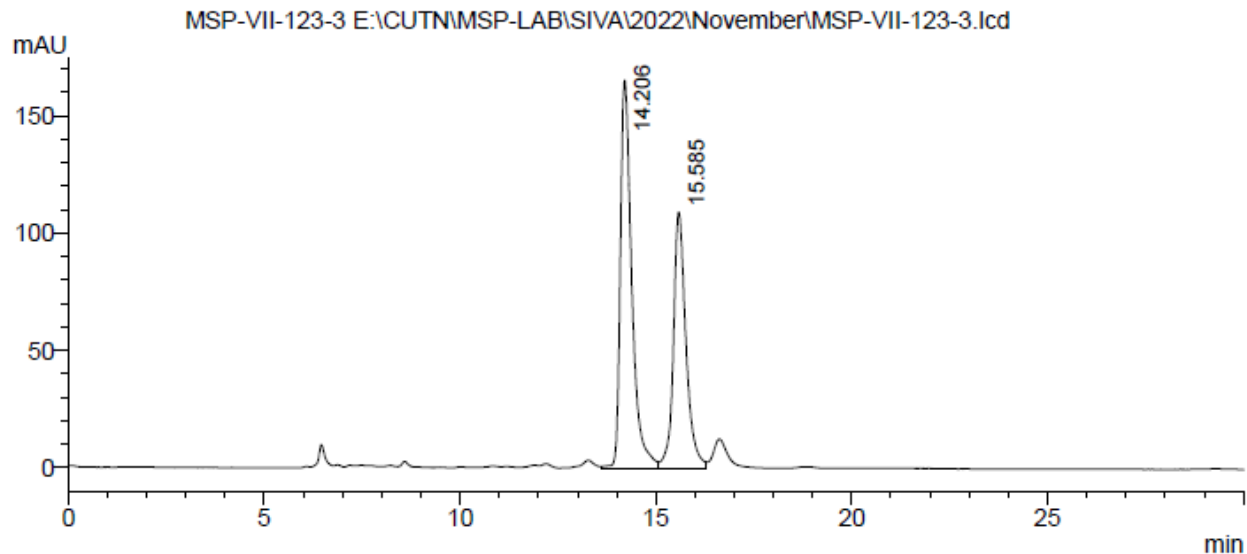
HPLC Data of chiral **6'b**: 98% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.804	117114	5651	0.889
2	13.065	13057738	732531	99.111
Total		13174852	738183	100.000

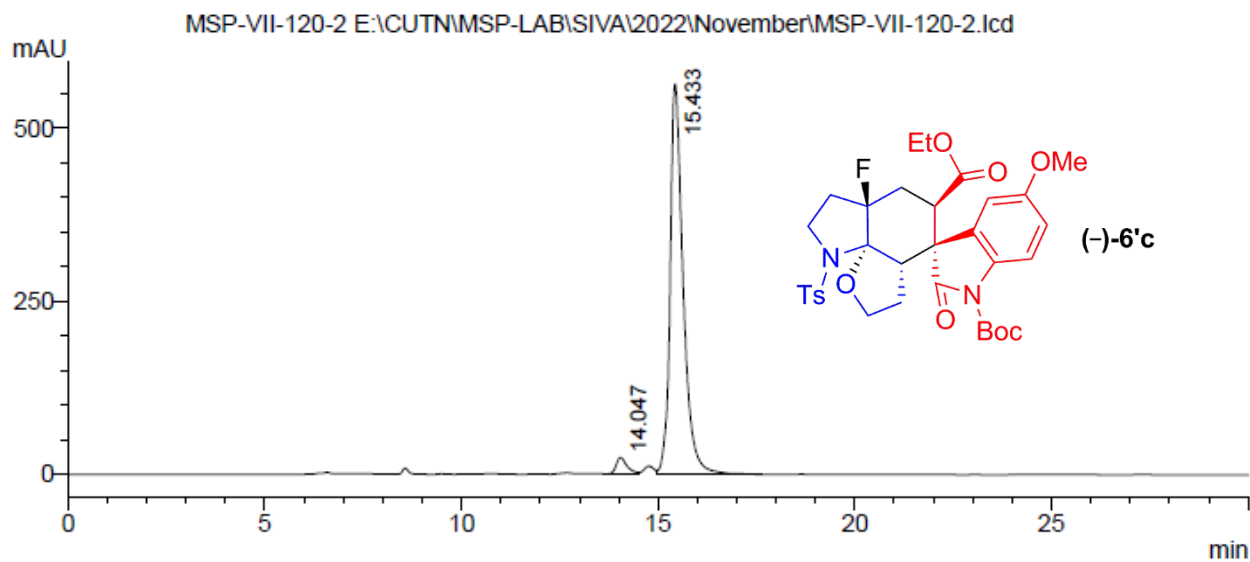
HPLC Data of racemic **6'**c



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.206	3357996	165302	58.059
2	15.585	2425801	109113	41.941
Total		5783798	274414	100.000

HPLC Data of chiral **6'**c: 93% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.047	480451	24413	3.578
2	15.433	12947364	563205	96.422
Total		13427815	587618	100.000