

Supporting Information-III

HPLC Data

Trienamine catalysed unprecedented remote olefin E/Z isomerisation/[4+2]-cycloaddition reaction to access spirooxindole hexahydroindoles

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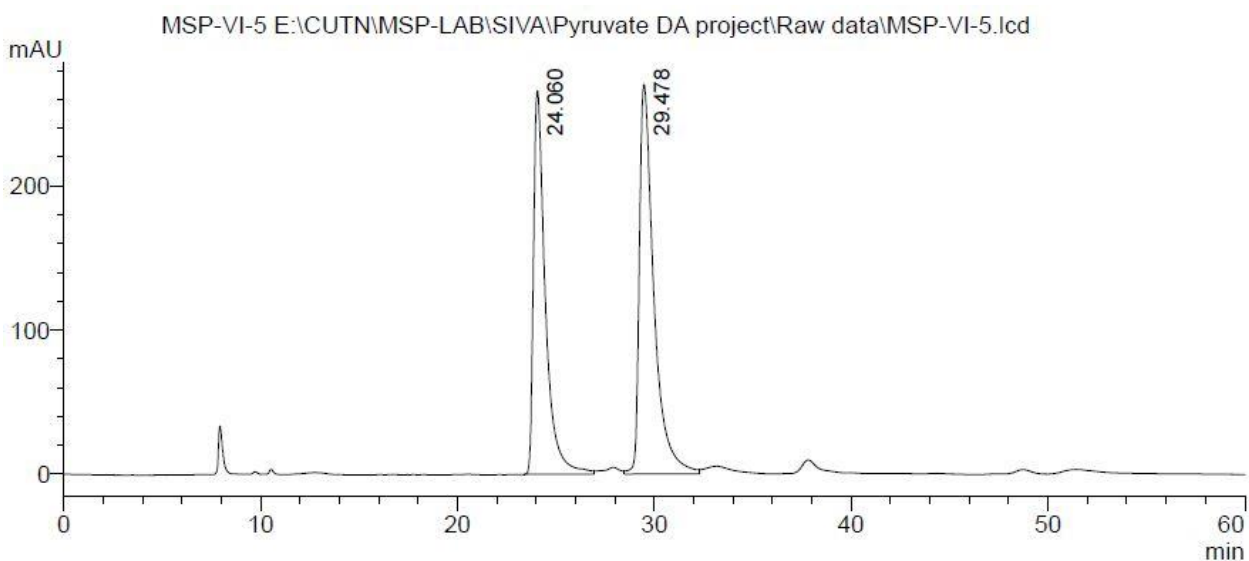
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General Information:

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

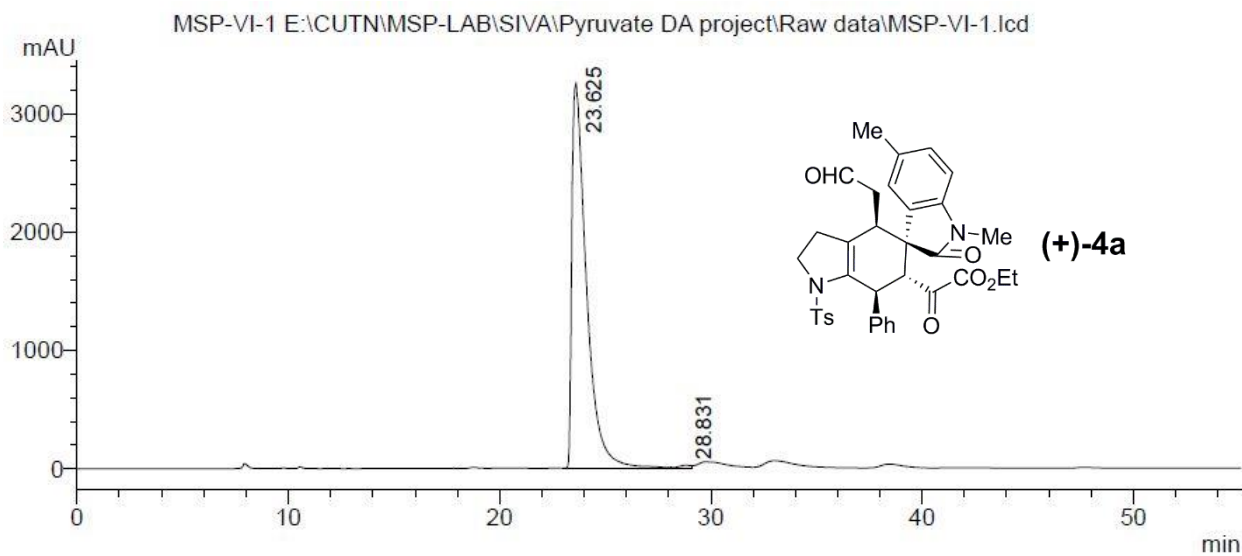
HPLC Data of racemic **4a**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	24.060	11214875	266278	44.717
2	29.478	13864575	270339	55.283
Total		25079450	536618	100.000

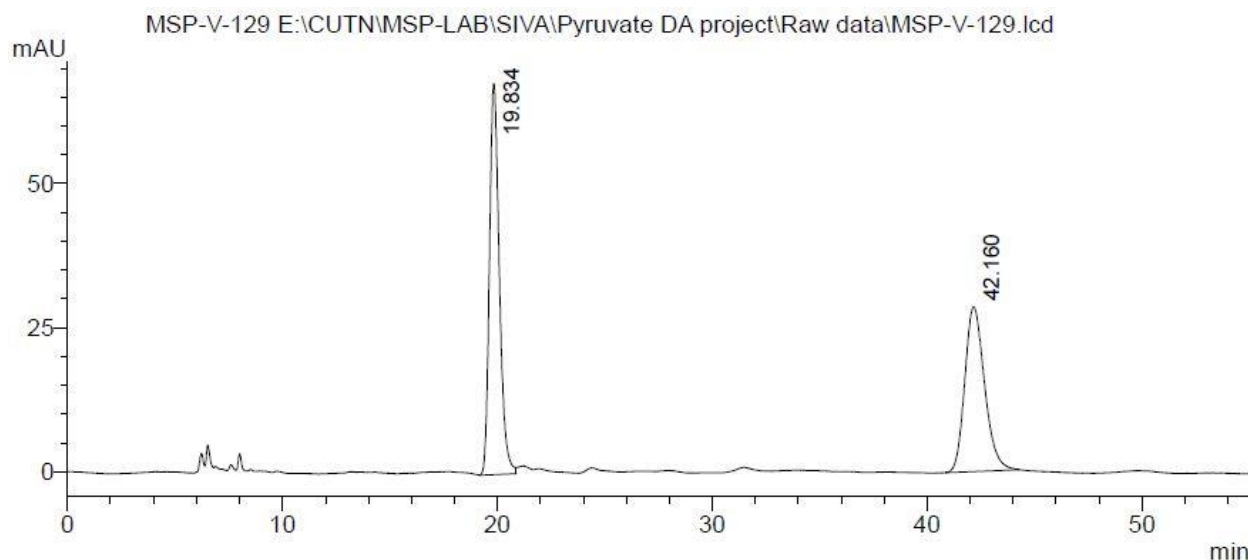
HPLC Data of chiral **4a**: 99% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	23.625	155520372	3256707	99.424
2	28.831	901691	22037	0.576
Total		156422063	3278743	100.000

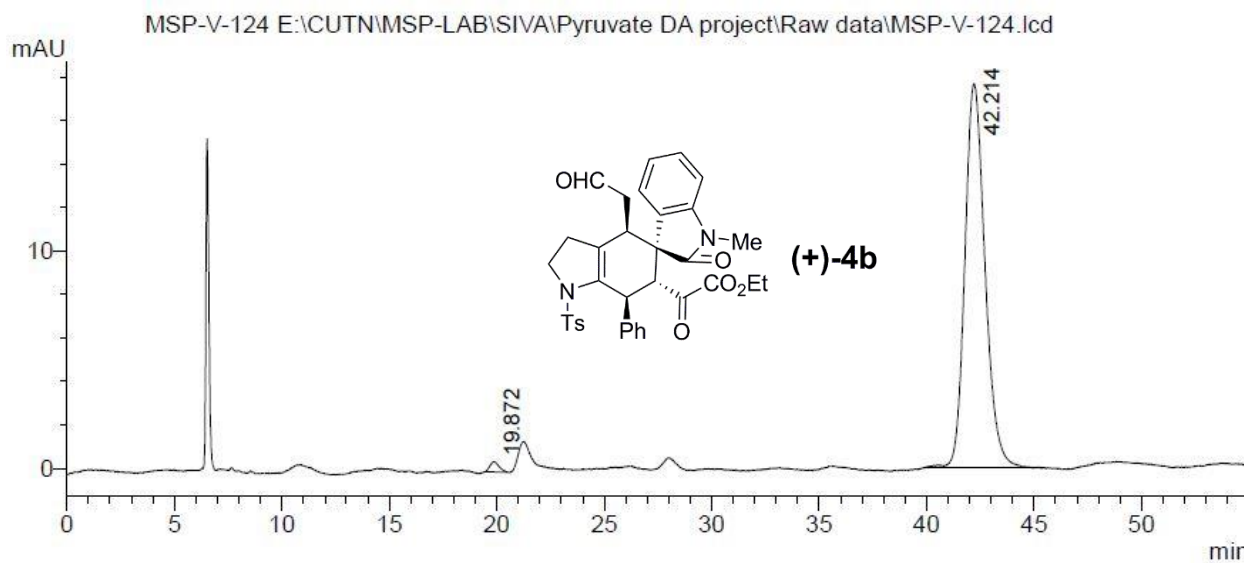
HPLC Data of racemic **4b**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.834	2166984	67818	54.234
2	42.160	1828668	28567	45.766
Total		3995651	96385	100.000

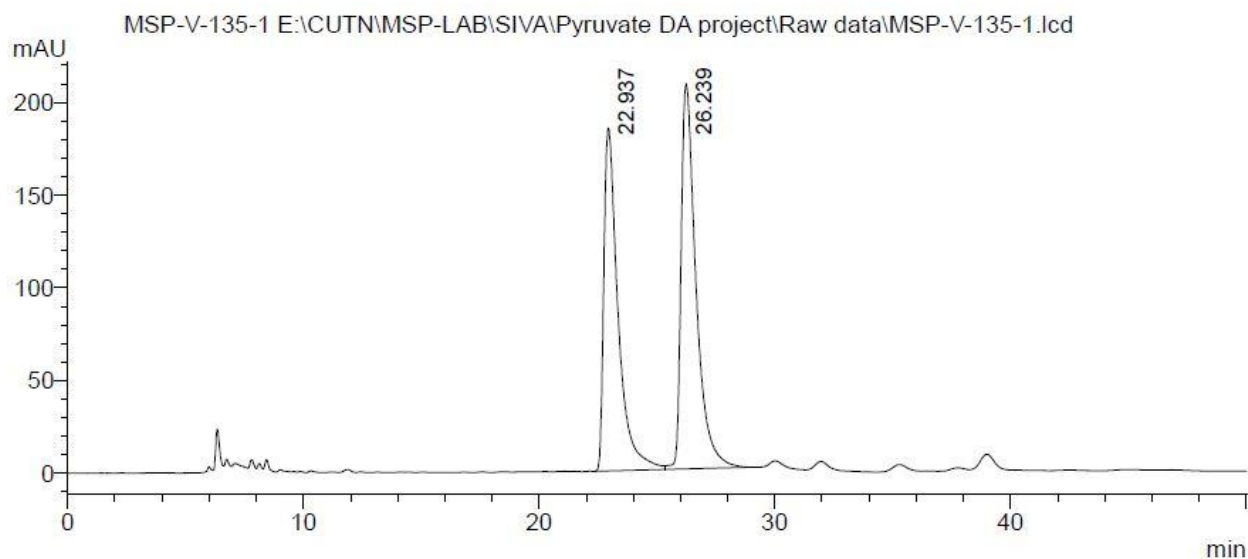
HPLC Data of chiral **4b**: 97.6% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.872	14023	489	1.199
2	42.214	1155520	17687	98.801
Total		1169543	18177	100.000

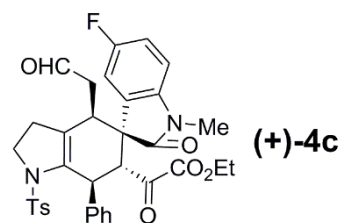
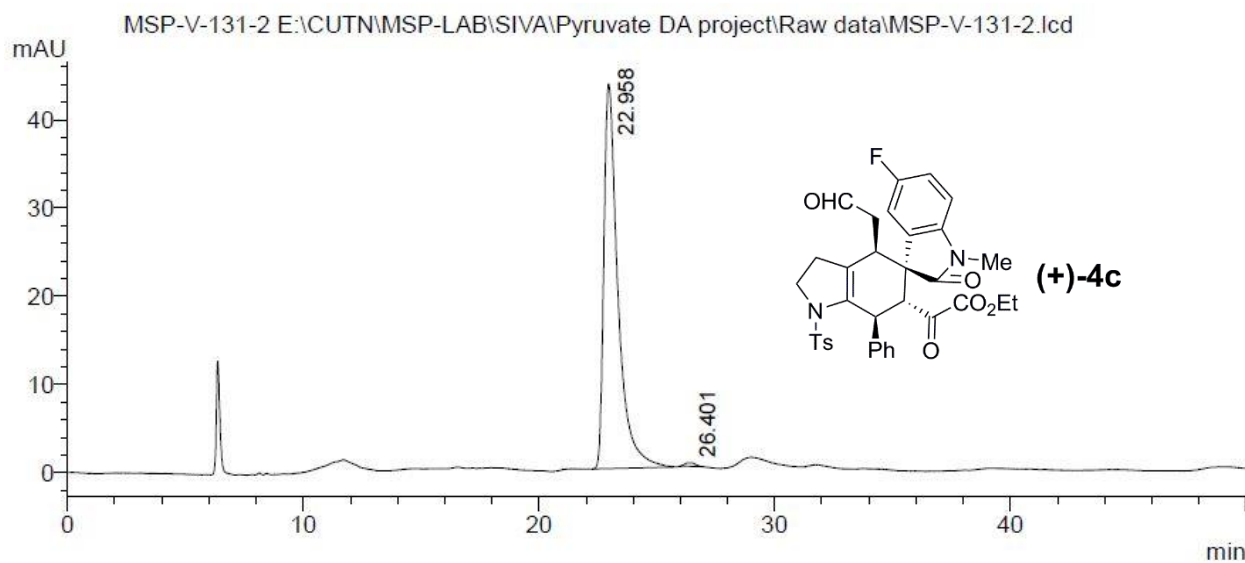
HPLC Data of racemic **4c**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.937	7779934	185065	46.023
2	26.239	9124596	207887	53.977
Total		16904530	392952	100.000

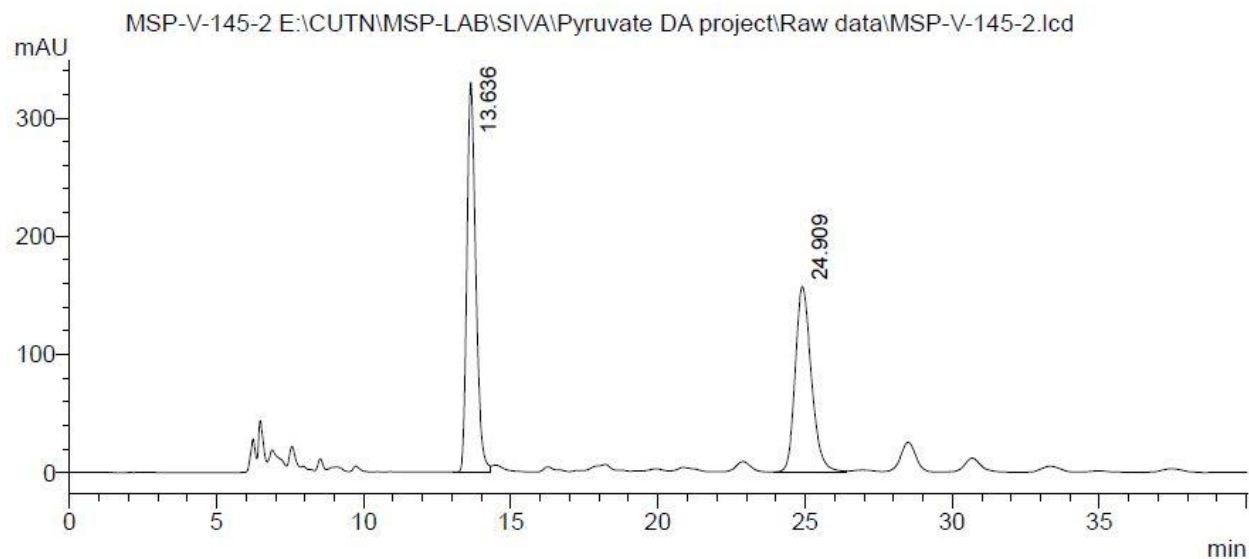
HPLC Data of chiral **4c**: 98.6% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.958	1808929	43584	99.304
2	26.401	12675	414	0.696
Total		1821604	43998	100.000

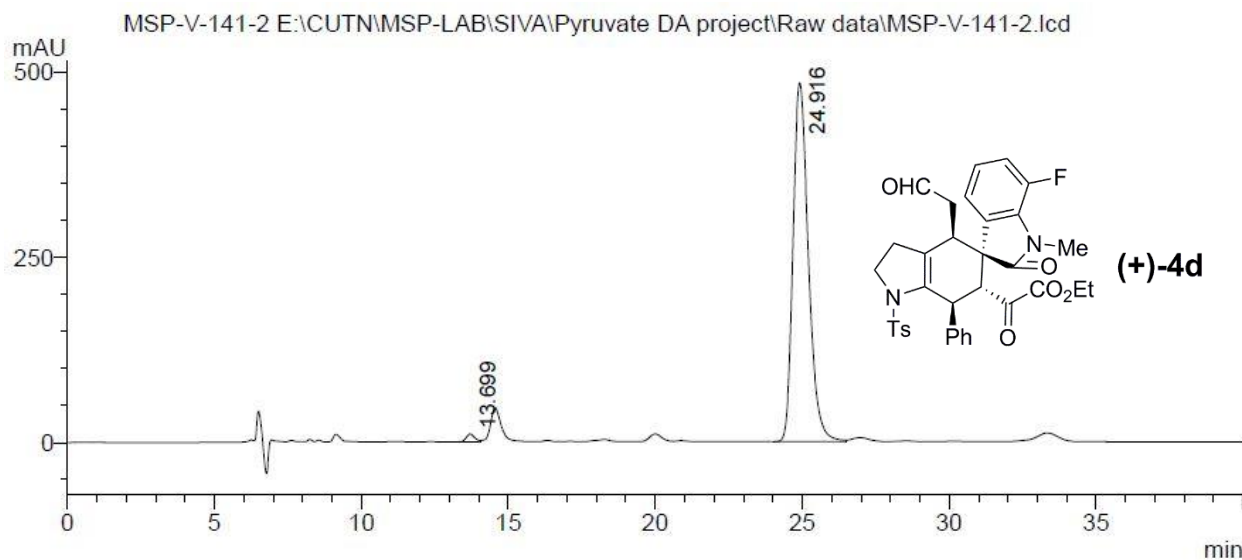
HPLC Data of racemic **4d**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.636	6939960	330133	53.734
2	24.909	5975369	156706	46.266
Total		12915329	486838	100.000

HPLC Data of chiral **4d**: 98% *ee*

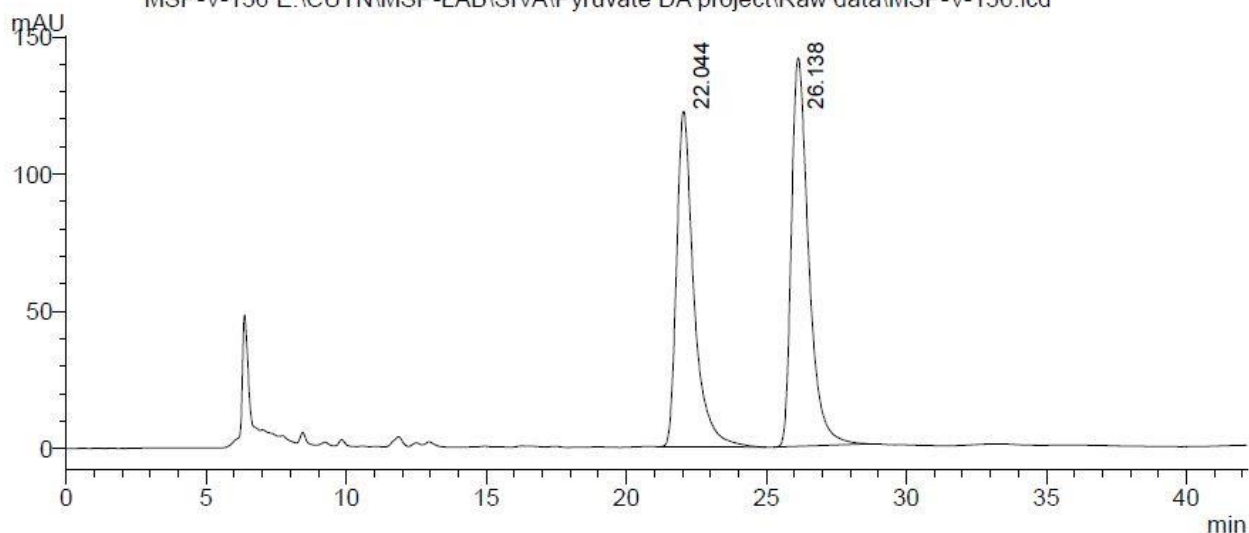


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.699	216507	10627	1.217
2	24.916	17568054	484123	98.783
Total		17784562	494750	100.000

HPLC Data of racemic **4e**

MSP-V-136 E:\CUTN\MSP-LAB\SIVA\Pyruvate DA project\Raw data\MSP-V-136.lcd

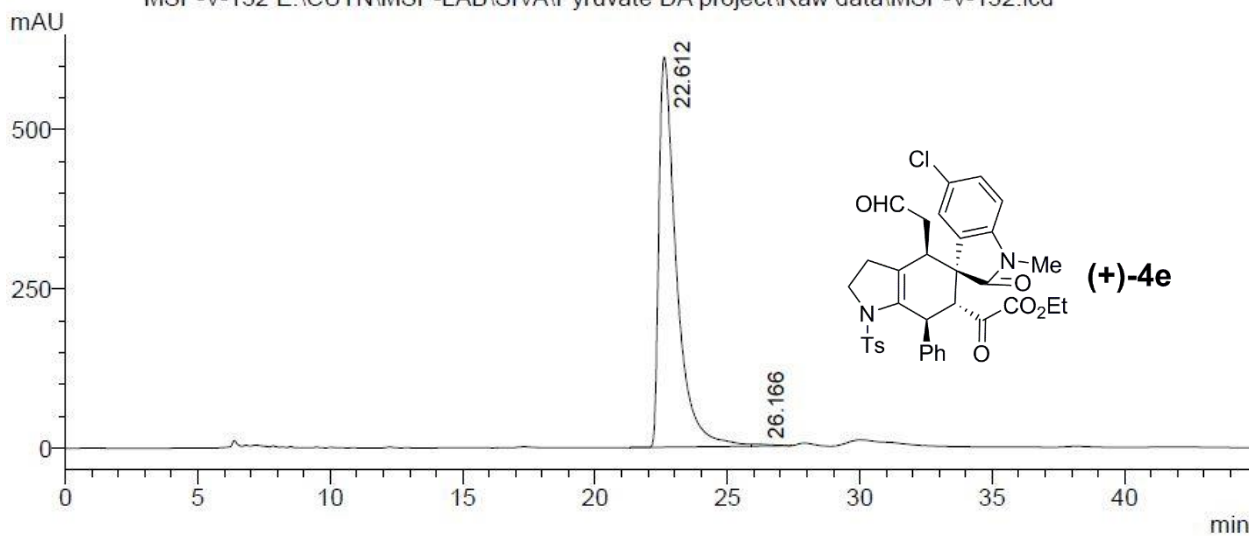


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.044	5255620	122195	46.442
2	26.138	6060822	141491	53.558
Total		11316442	263686	100.000

HPLC Data of chiral **4e**: 99% *ee*

MSP-V-132 E:\CUTN\MSP-LAB\SIVA\Pyruvate DA project\Raw data\MSP-V-132.lcd

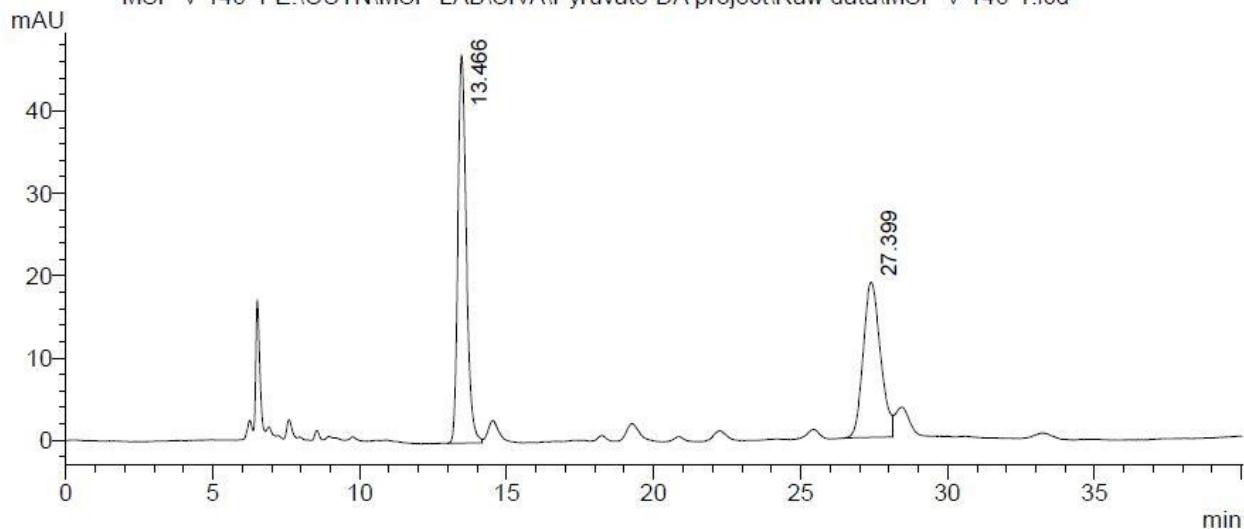


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.612	28179350	611871	99.517
2	26.166	136899	2728	0.483
Total		28316249	614599	100.000

HPLC Data of racemic **4f**

MSP-V-146-1 E:\CUTN\MSP-LAB\SIVA\Pyruvate DA project\Raw data\MSP-V-146-1.lcd

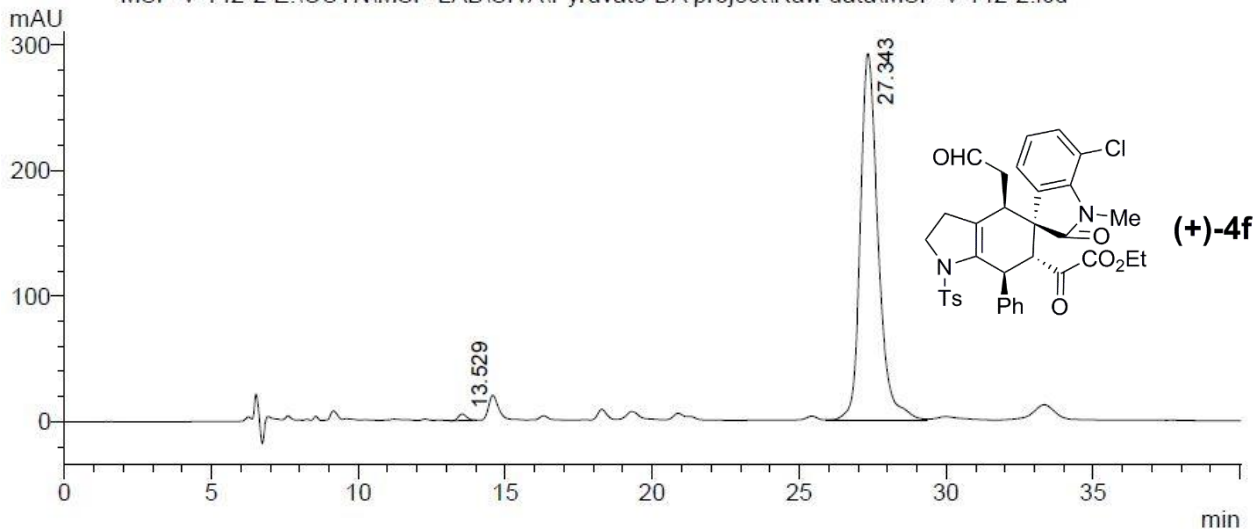


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.466	937480	47131	54.898
2	27.399	770194	18851	45.102
Total		1707674	65982	100.000

HPLC Data of chiral **4f**: 98% *ee*

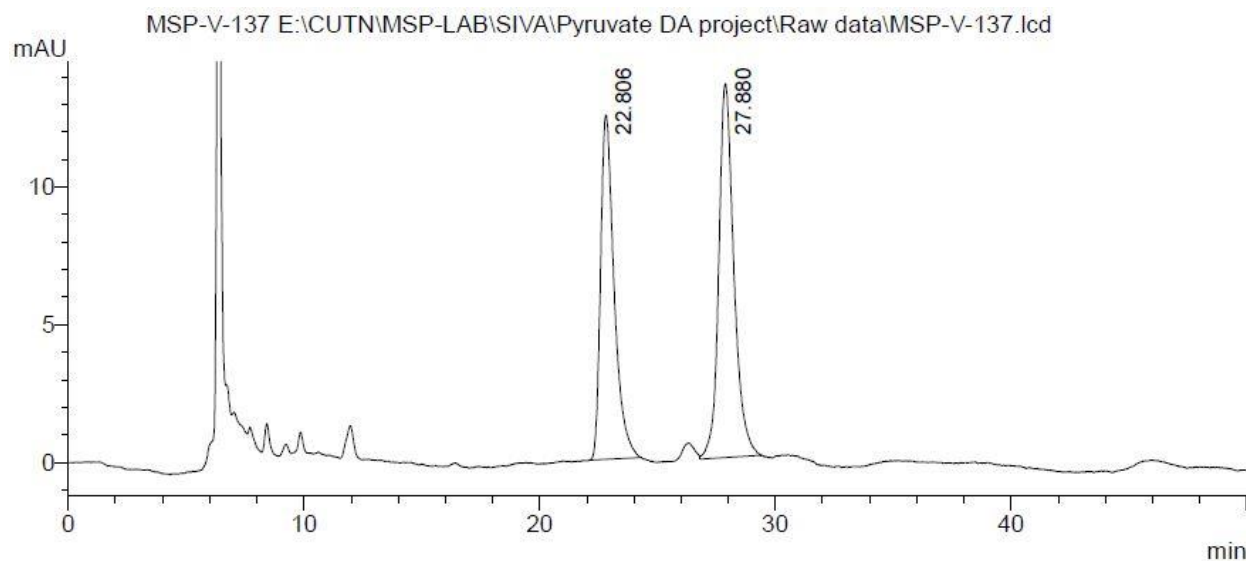
MSP-V-142-2 E:\CUTN\MSP-LAB\SIVA\Pyruvate DA project\Raw data\MSP-V-142-2.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.529	96790	5046	0.781
2	27.343	12291756	291664	99.219
Total		12388546	296710	100.000

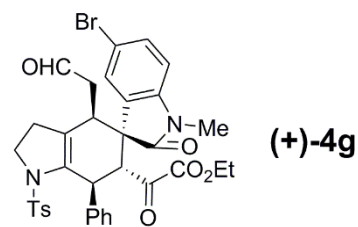
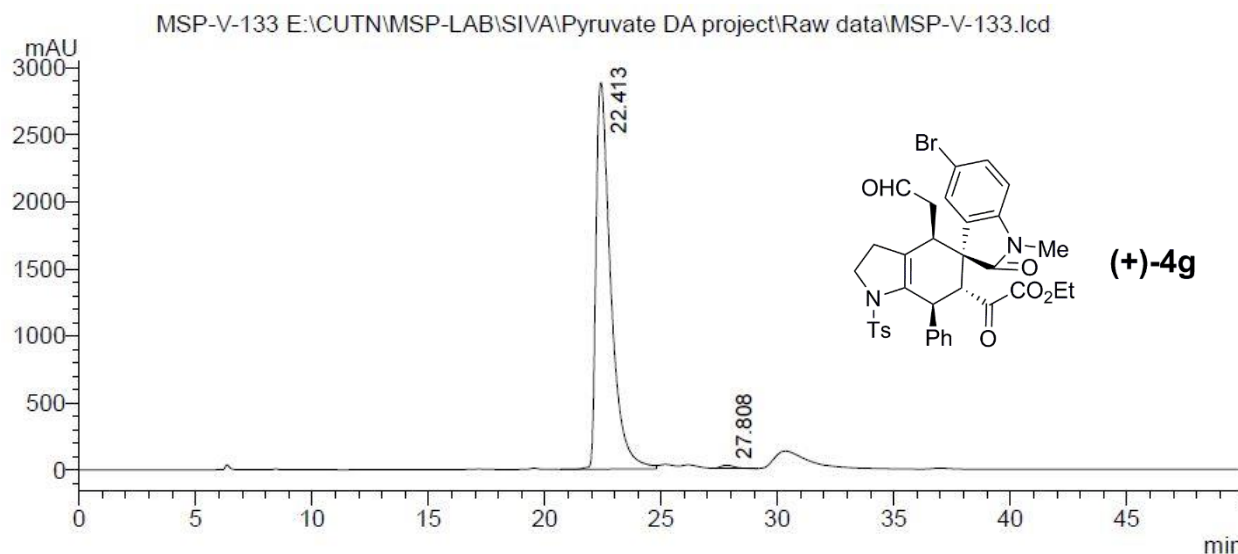
HPLC Data of racemic **4g**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.806	498969	12493	45.172
2	27.880	605635	13566	54.828
Total		1104603	26060	100.000

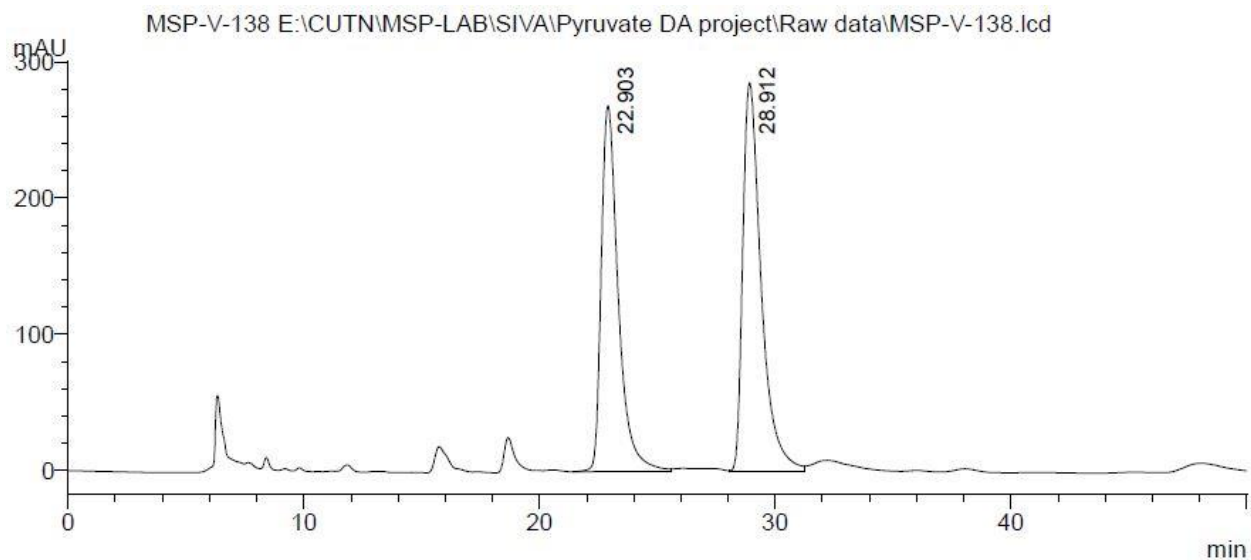
HPLC Data of chiral **4g**: 98.6% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.413	126878217	2880319	99.306
2	27.808	886593	22681	0.694
Total		127764810	2903000	100.000

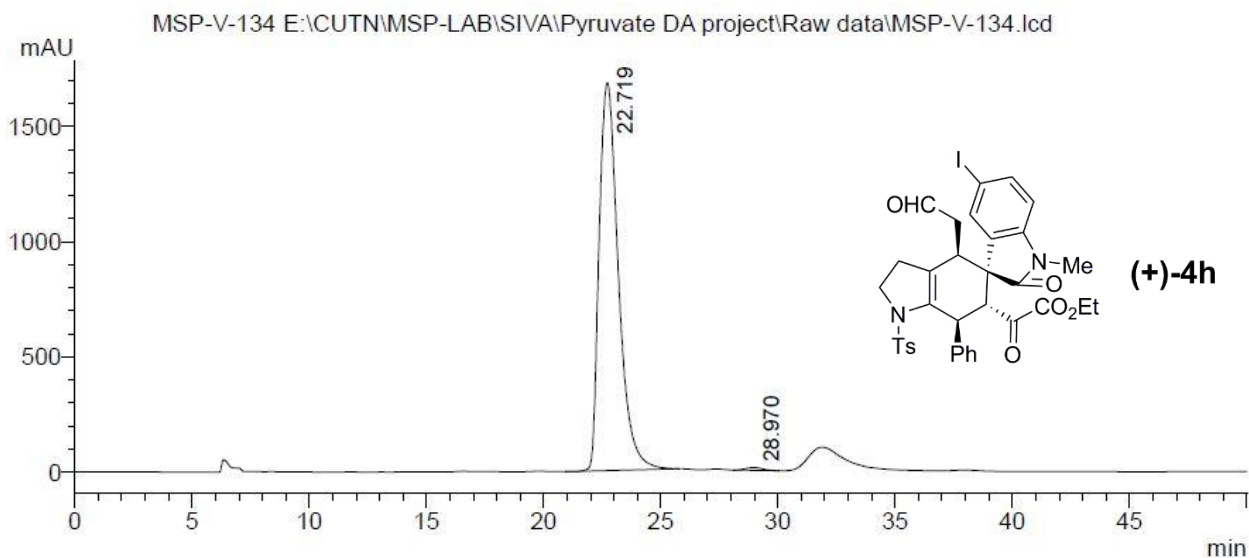
HPLC Data of racemic **4h**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.903	13494207	268550	46.522
2	28.912	15511765	285186	53.478
Total		29005972	553736	100.000

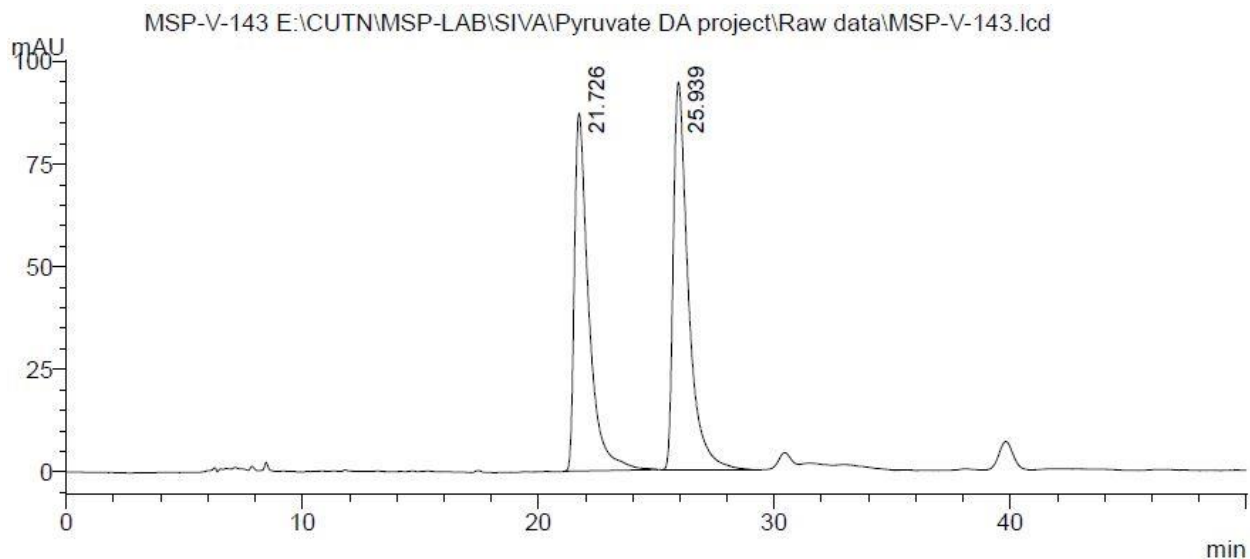
HPLC Data of chiral **4h**: 99% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.719	96045149	1683468	99.401
2	28.970	579009	11442	0.599
Total		96624158	1694911	100.000

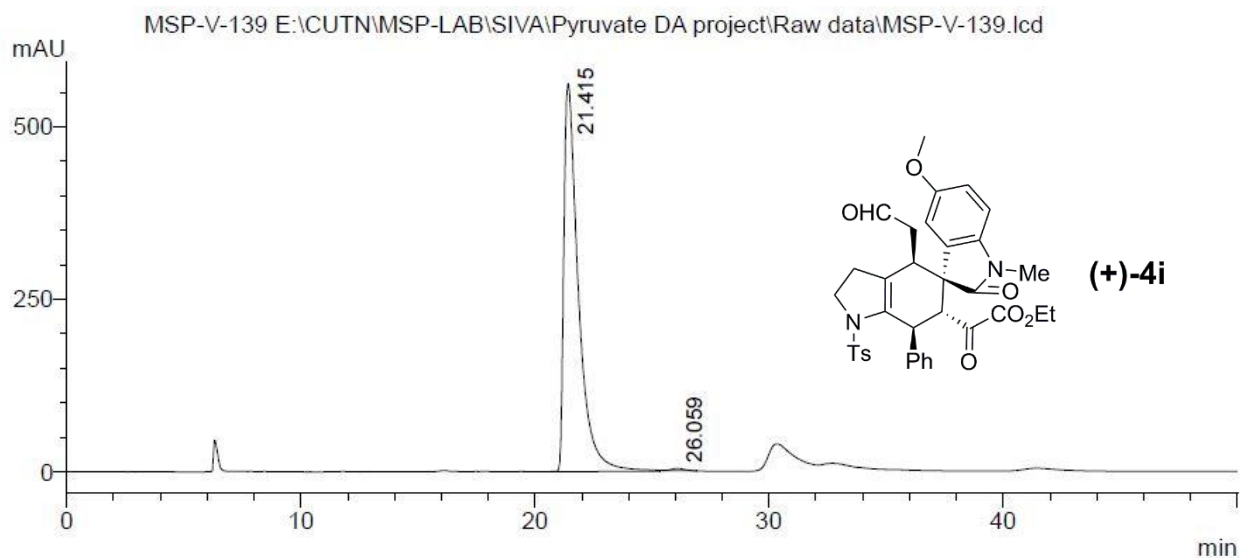
HPLC Data of racemic **4i**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	21.726	3695143	87247	46.857
2	25.939	4190790	94486	53.143
Total		7885933	181733	100.000

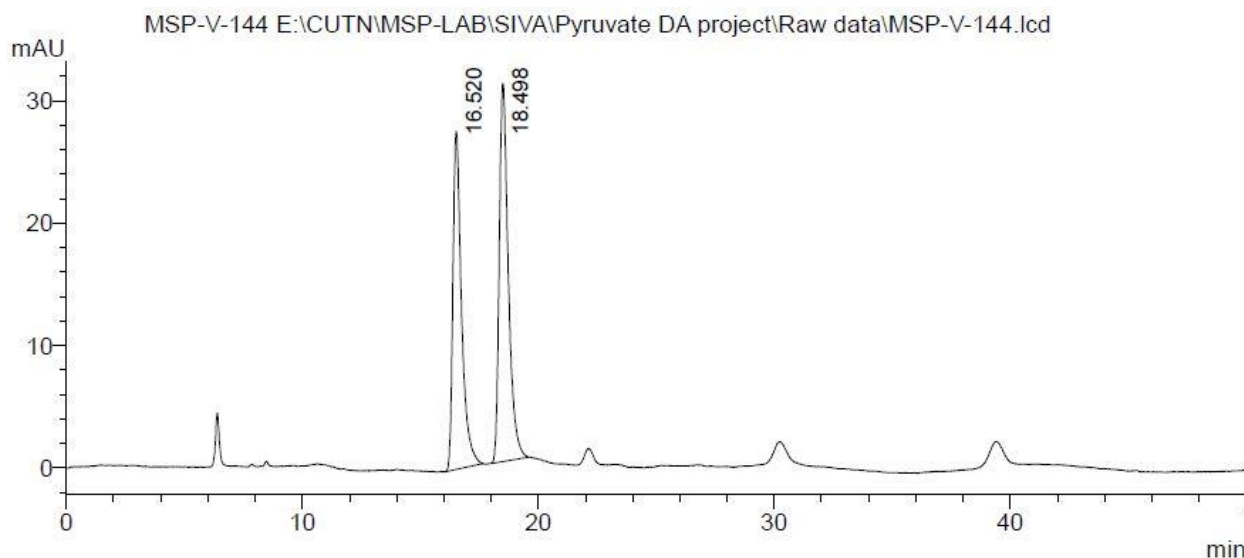
HPLC Data of chiral **4i**: 99% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	21.415	24286970	562109	99.526
2	26.059	115736	3024	0.474
Total		24402705	565132	100.000

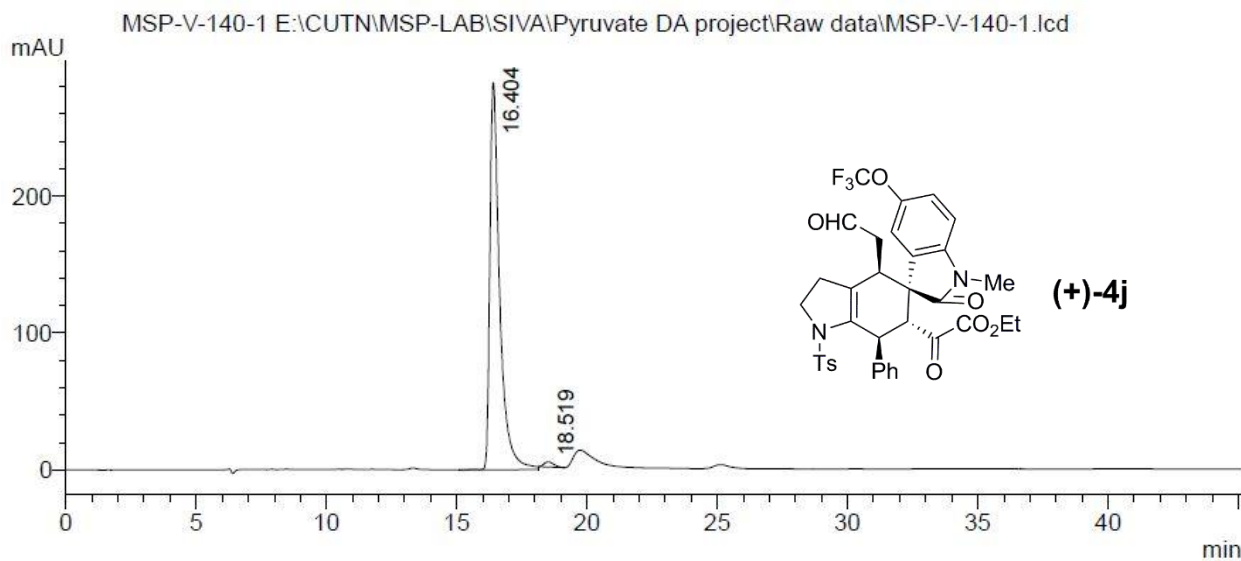
HPLC Data of racemic **4j**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.520	702254	27621	46.072
2	18.498	821989	30881	53.928
Total		1524243	58501	100.000

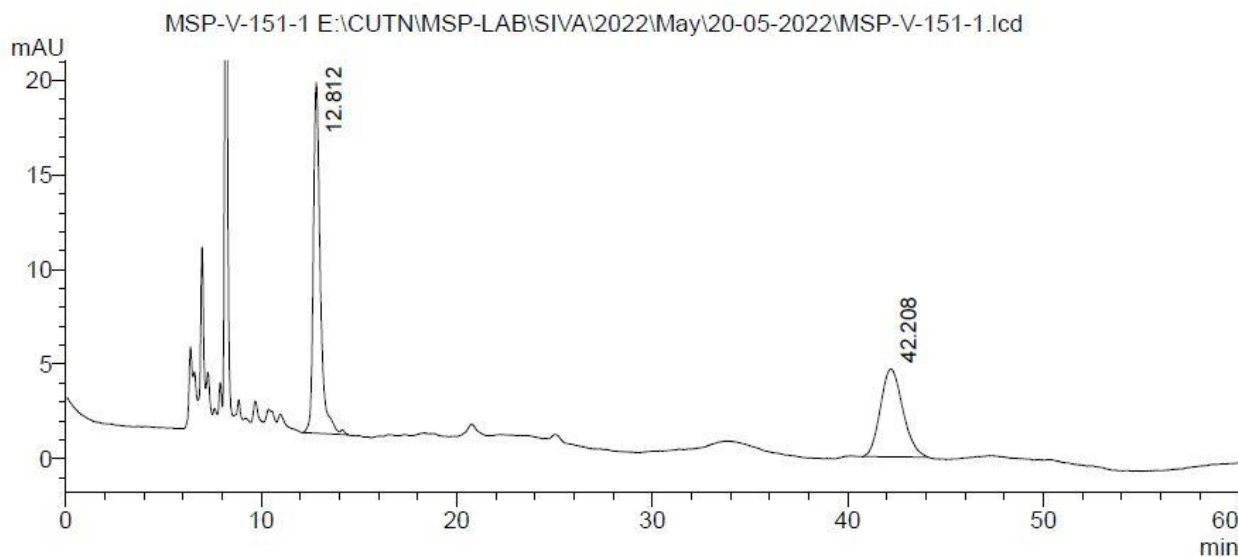
HPLC Data of chiral **4j**: 98% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	16.404	7416960	282704	98.757
2	18.519	93361	3598	1.243
Total		7510321	286302	100.000

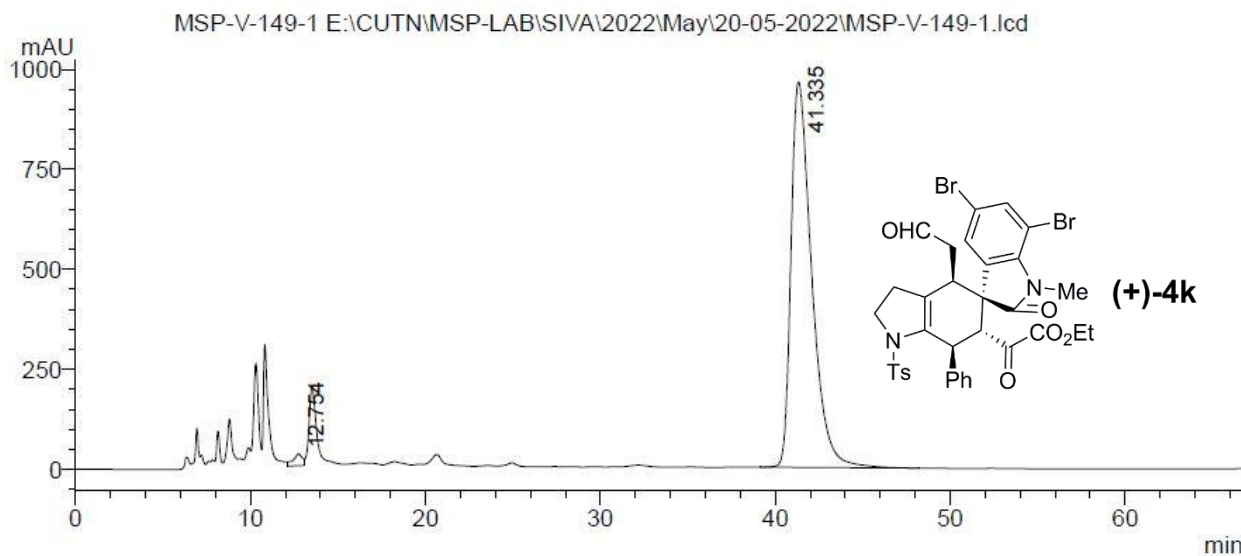
HPLC Data of racemic **4k**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	12.812	459767	18558	55.410
2	42.208	369988	4643	44.590
Total		829755	23201	100.000

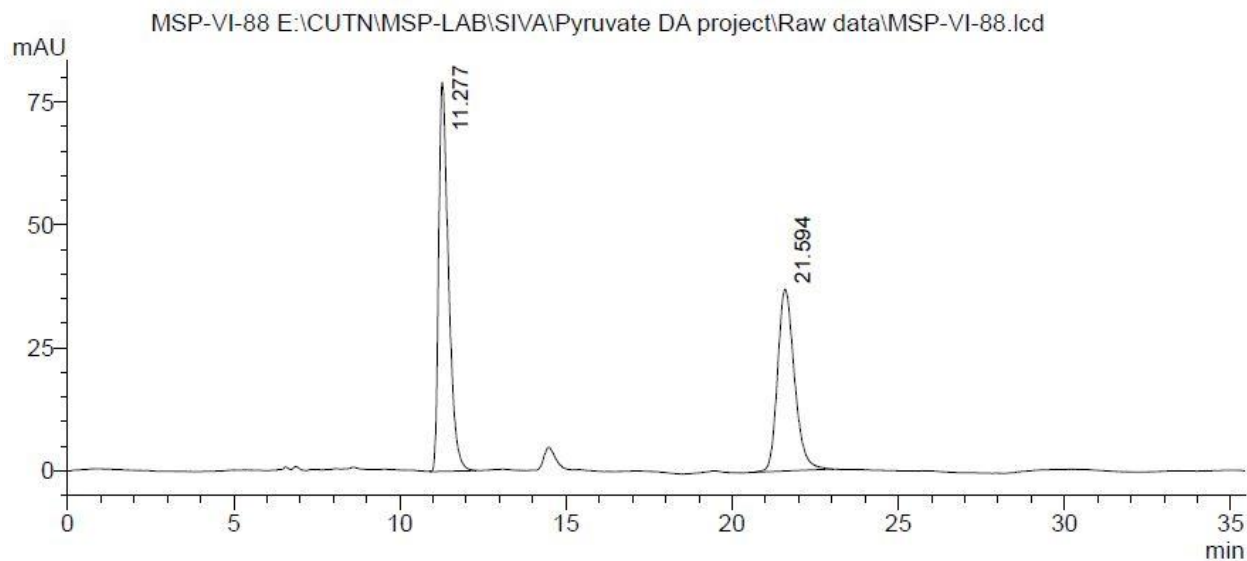
HPLC Data of chiral **4k:97% ee**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	12.754	1096904	29477	1.366
2	41.335	79210155	963943	98.634
Total		80307058	993420	100.000

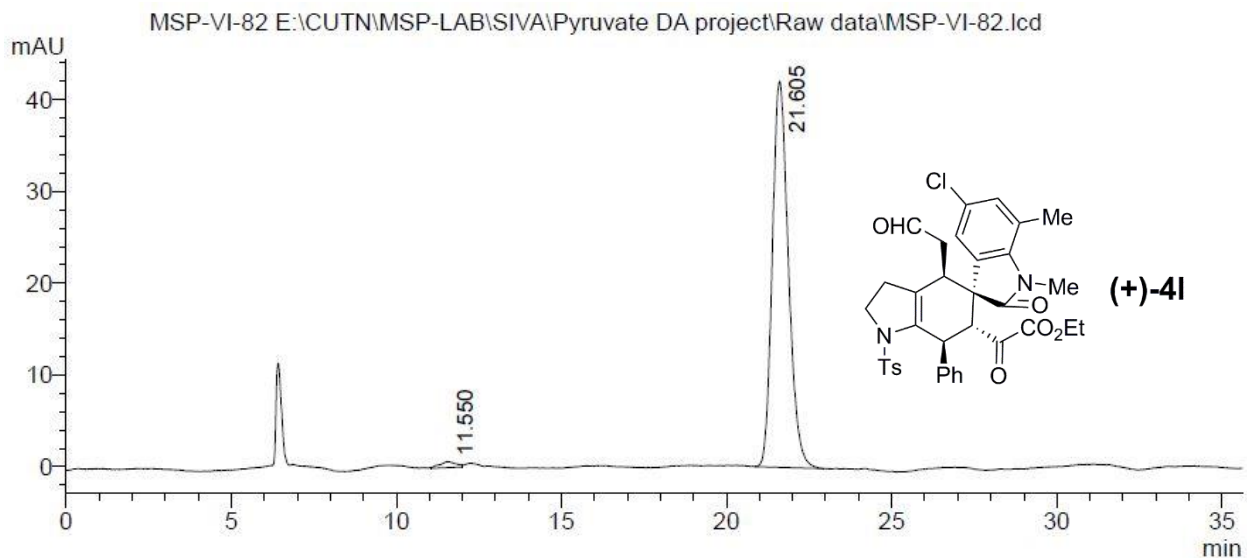
HPLC Data of racemic **4I**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.277	1625855	79096	55.441
2	21.594	1306742	36997	44.559
Total		2932598	116093	100.000

HPLC Data of chiral **4I**: 97% *ee*

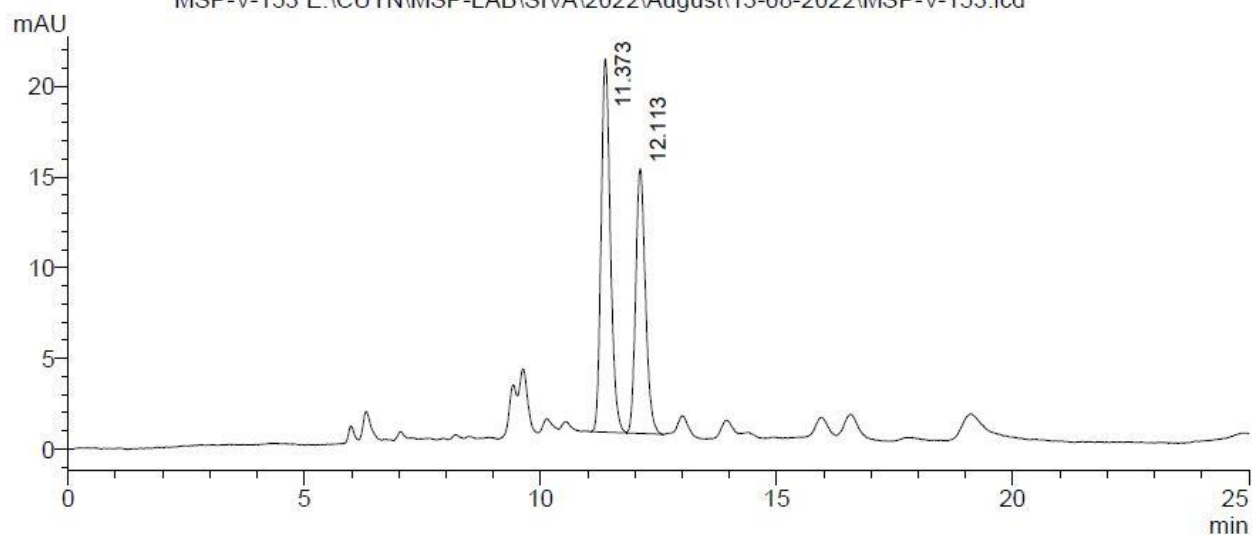


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.550	22037	664	1.523
2	21.605	1425341	42068	98.477
Total		1447377	42732	100.000

HPLC Data of racemic **4m**

MSP-V-153 E:\CUTN\MSP-LAB\SIVA\2022\August\13-08-2022\MSP-V-153.lcd

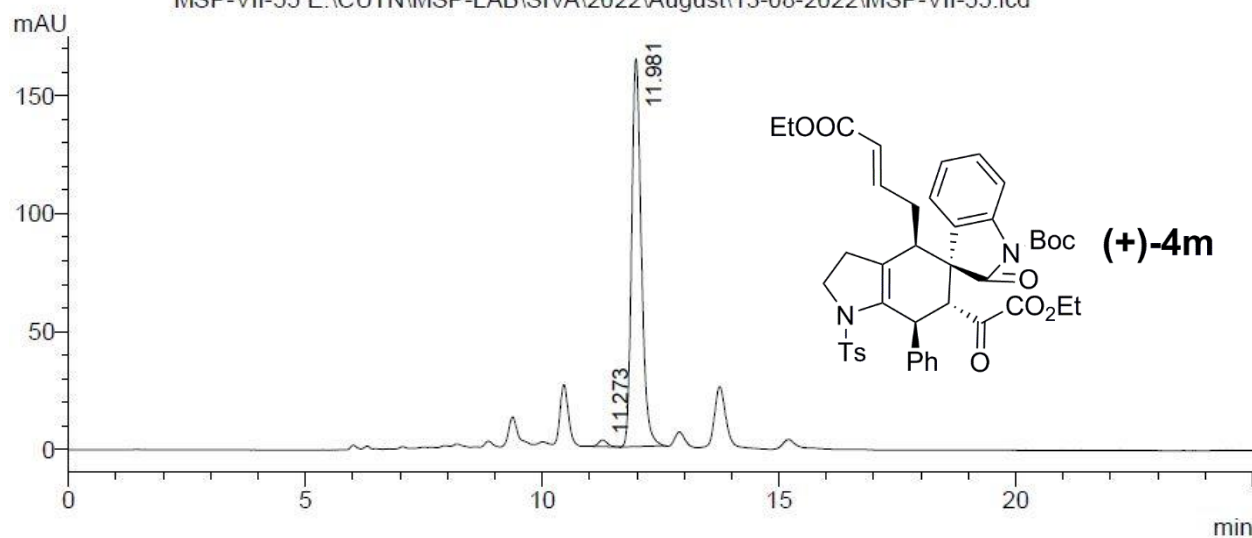


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.373	279890	20579	57.254
2	12.113	208965	14580	42.746
Total		488856	35159	100.000

HPLC Data of chiral **4m**: 97% ee

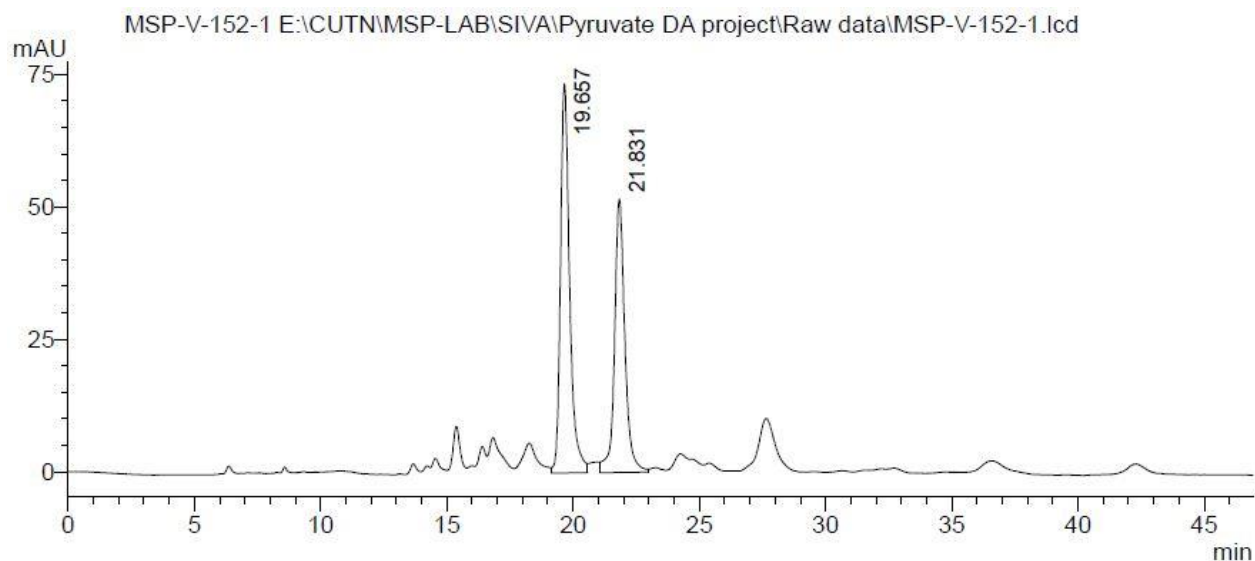
MSP-VII-55 E:\CUTN\MSP-LAB\SIVA\2022\August\13-08-2022\MSP-VII-55.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.273	36177	2804	1.519
2	11.981	2345960	164432	98.481
Total		2382137	167236	100.000

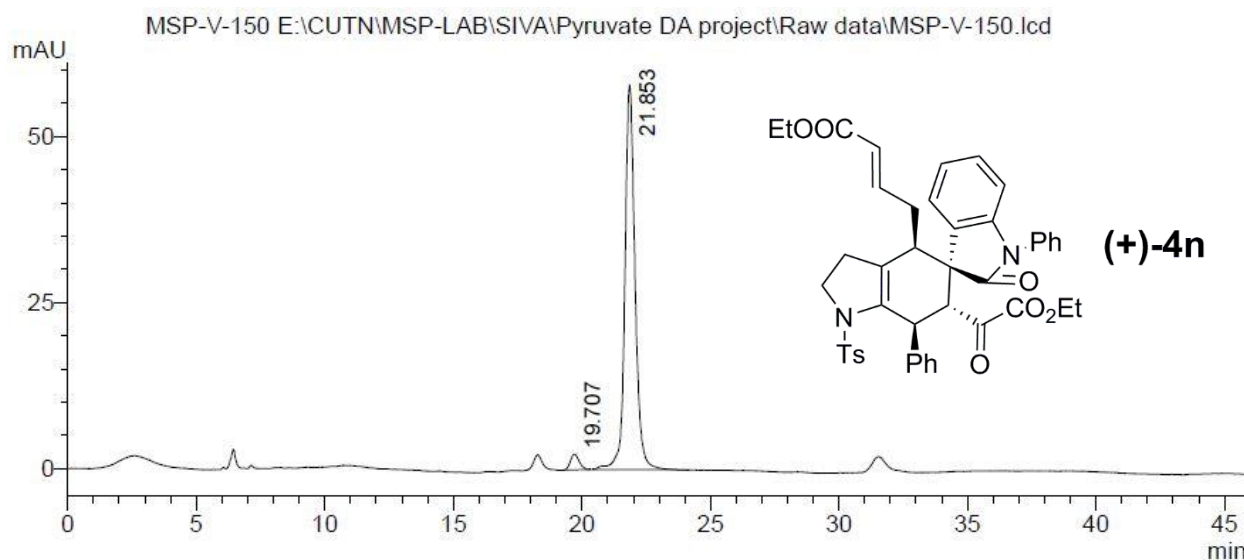
HPLC Data of racemic **4n**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.657	1858408	73486	55.929
2	21.831	1464390	51614	44.071
Total		3322798	125101	100.000

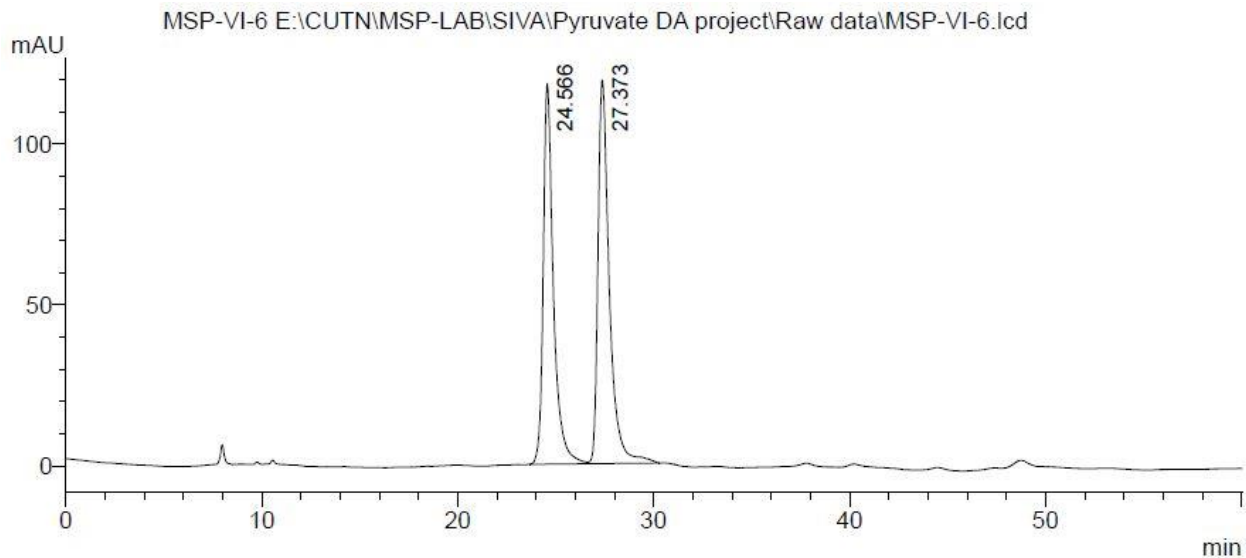
HPLC Data of chiral **4n**: 93% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.707	56855	2401	3.452
2	21.853	1590404	57954	96.548
Total		1647260	60355	100.000

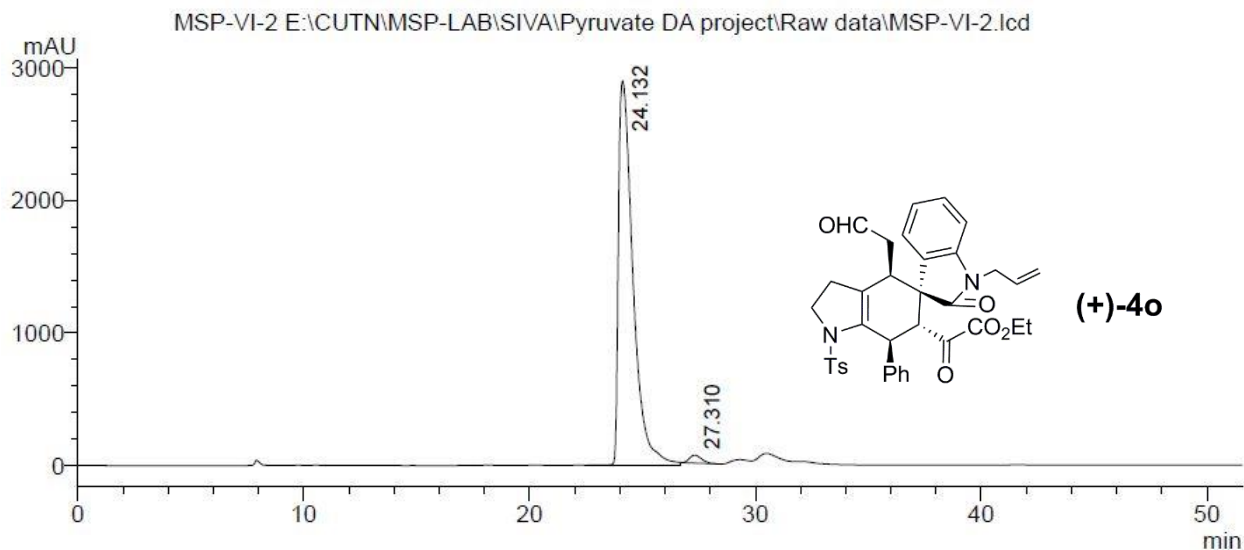
HPLC Data of racemic **4o**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	24.566	4266227	118310	47.057
2	27.373	4799946	119185	52.943
Total		9066174	237495	100.000

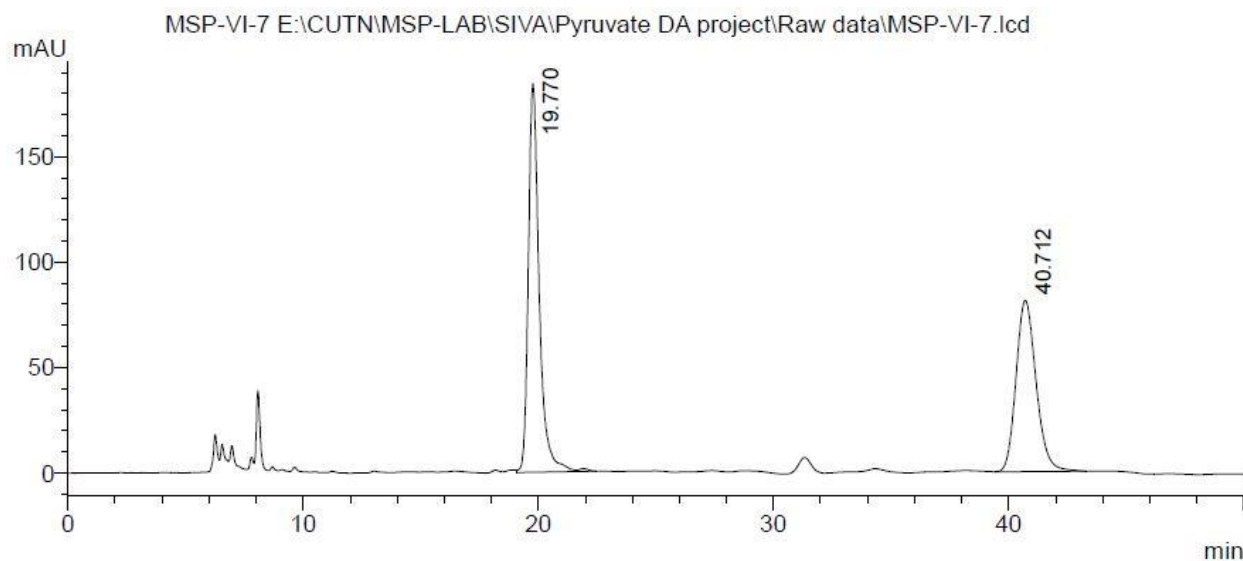
HPLC Data of chiral **4o**: 97% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	24.132	130015058	2901289	98.329
2	27.310	2209922	59913	1.671
Total		132224980	2961202	100.000

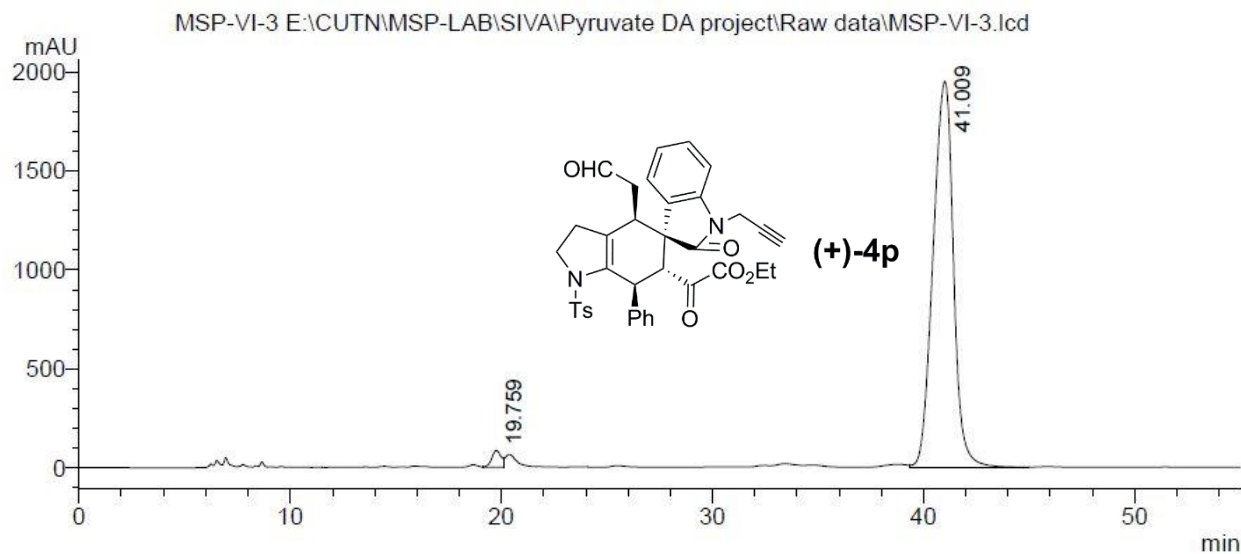
HPLC Data of racemic **4p**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.770	5923617	184255	55.194
2	40.712	4808792	81157	44.806
Total		10732409	265412	100.000

HPLC Data of chiral **4p**: 96% *ee*

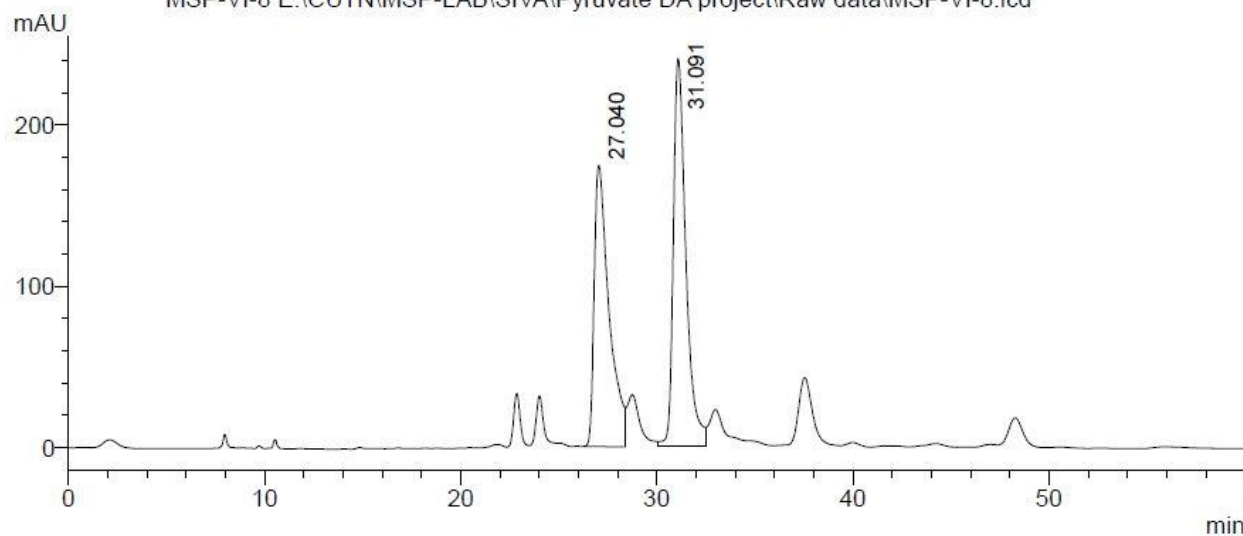


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.759	2607291	84909	1.957
2	41.009	130627432	1949677	98.043
Total		133234723	2034586	100.000

HPLC Data of racemic **4q**

MSP-VI-8 E:\CUTN\MSP-LAB\SIVA\Pyruvate DA project\Raw data\MSP-VI-8.lcd

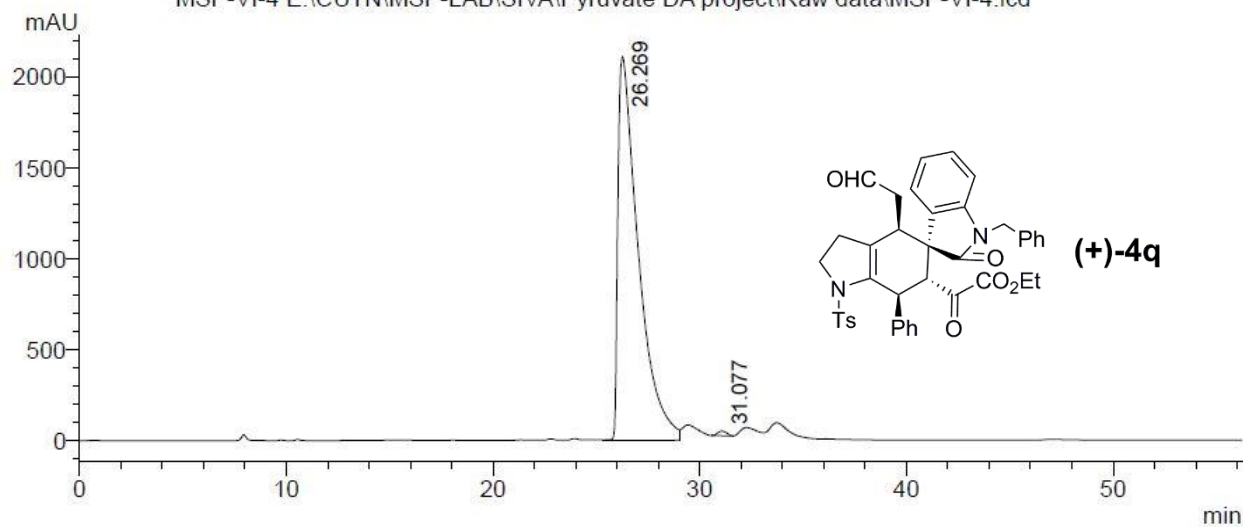


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	27.040	9182686	174350	46.127
2	31.091	10724617	240668	53.873
Total		19907304	415018	100.000

HPLC Data of chiral **4q**: 99% *ee*

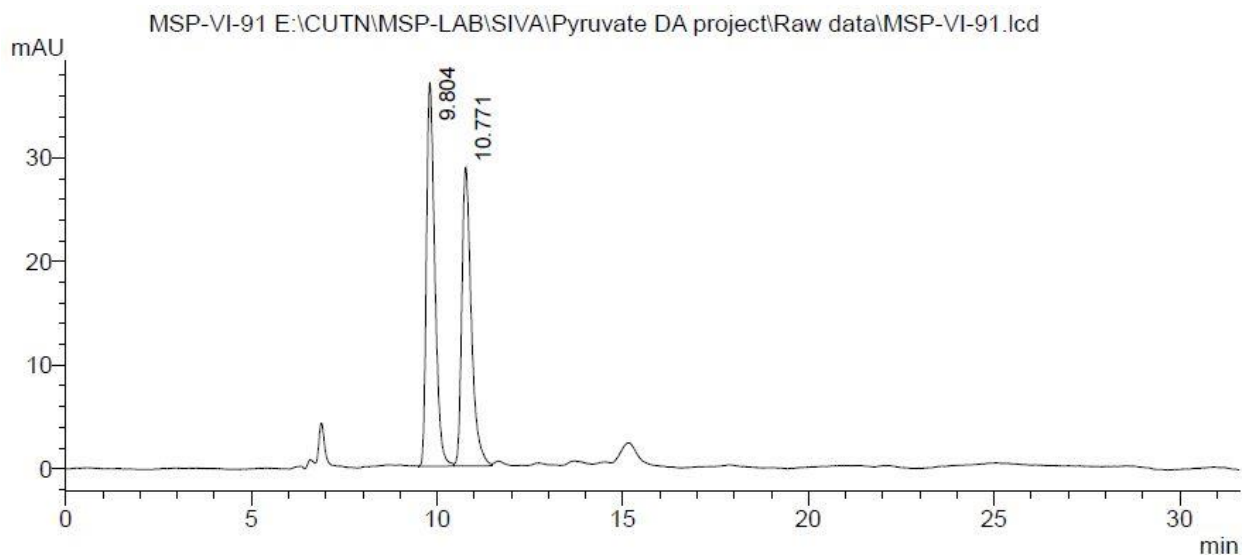
MSP-VI-4 E:\CUTN\MSP-LAB\SIVA\Pyruvate DA project\Raw data\MSP-VI-4.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	26.269	144786813	2111060	99.441
2	31.077	814239	26301	0.559
Total		145601052	2137361	100.000

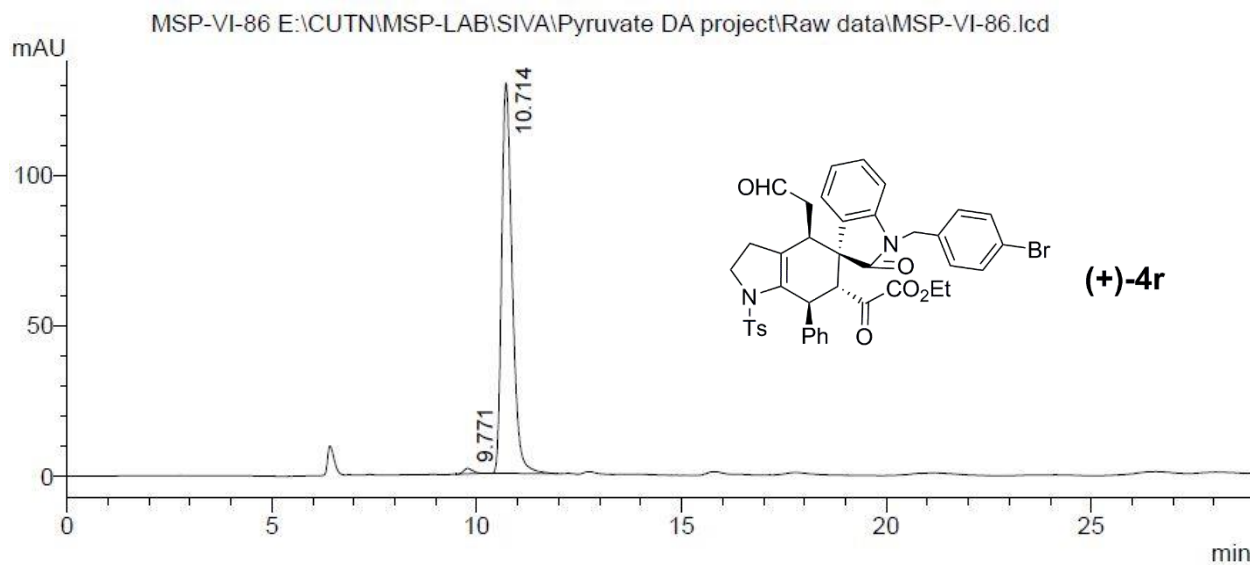
HPLC Data of racemic **4r**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	9.804	579972	37101	53.032
2	10.771	513645	28886	46.968
Total		1093617	65987	100.000

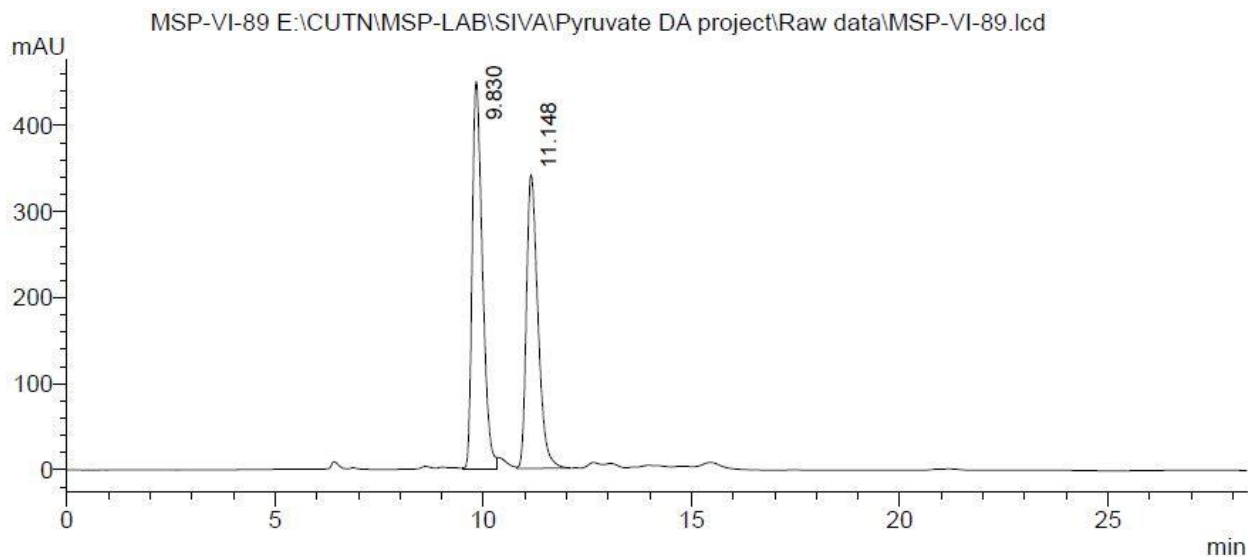
HPLC Data of chiral **4r**: 98% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	9.771	28132	1785	1.195
2	10.714	2326803	129683	98.805
Total		2354935	131468	100.000

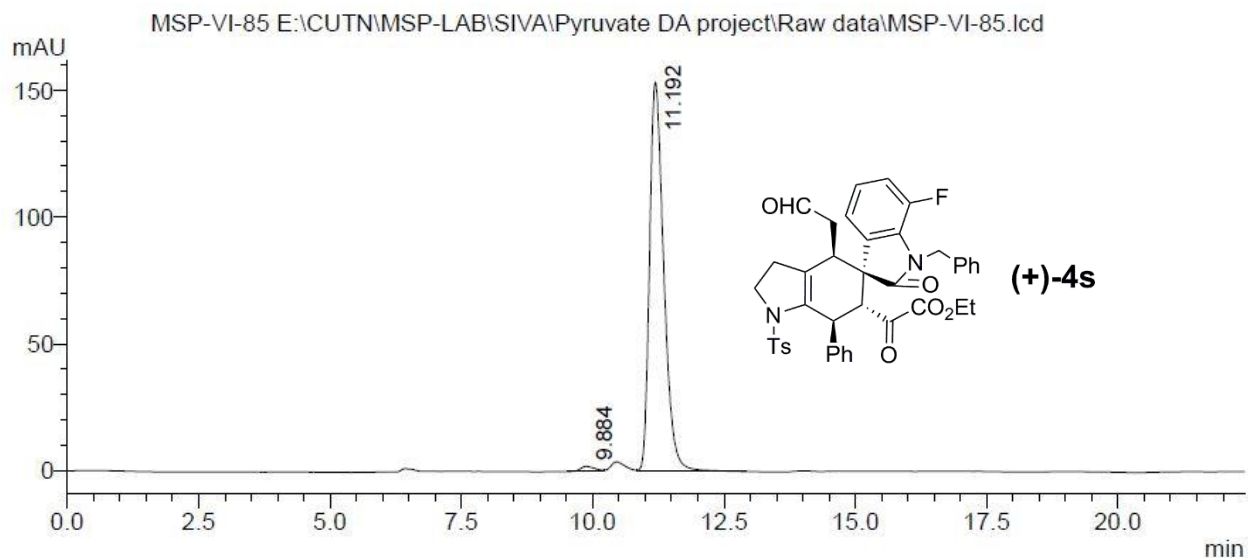
HPLC Data of racemic **4s**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	9.830	7676650	450117	53.894
2	11.148	6567374	341391	46.106
Total		14244024	791508	100.000

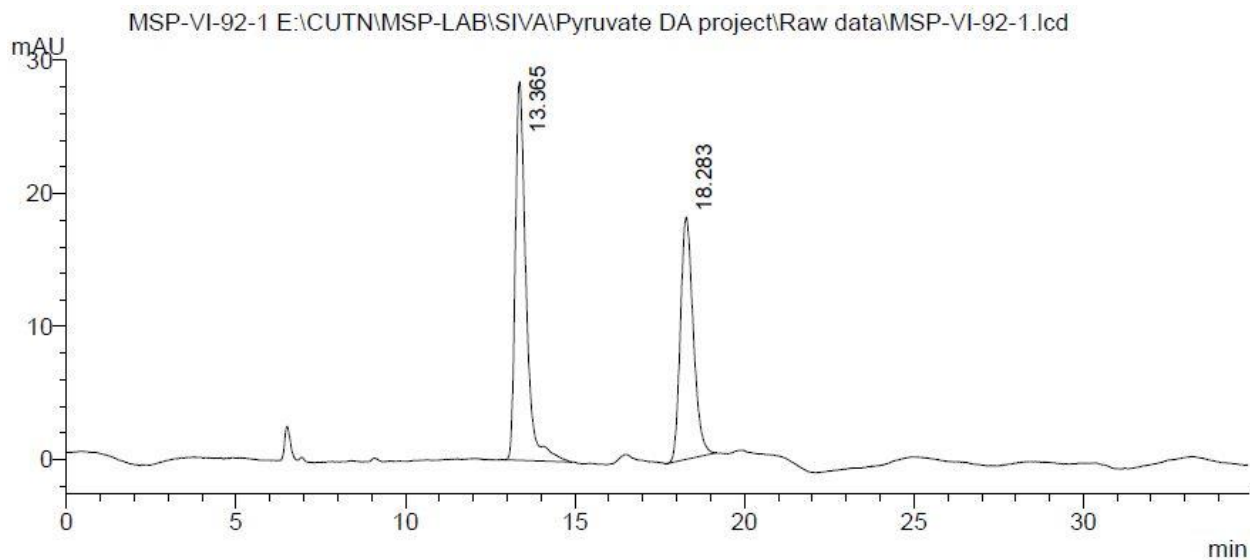
HPLC Data of chiral **4s**: 97% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	9.884	39175	2005	1.331
2	11.192	2903074	153403	98.669
Total		2942249	155409	100.000

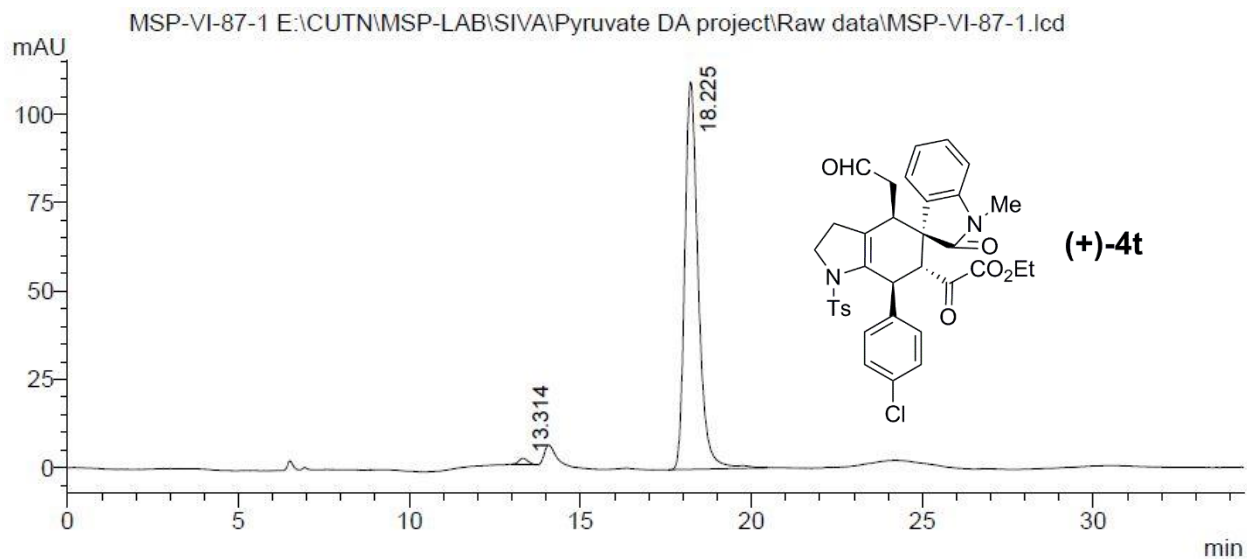
HPLC Data of racemic **4t**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.365	627572	28467	56.600
2	18.283	481211	18216	43.400
Total		1108782	46683	100.000

HPLC Data of chiral **4t**: 98% *ee*

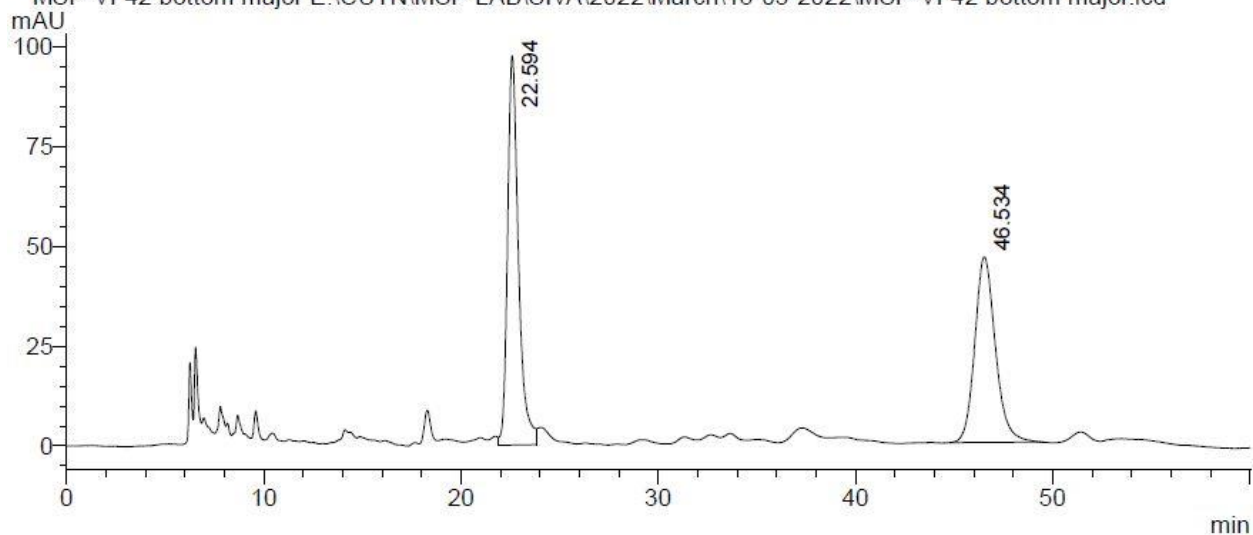


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	13.314	36686	1873	1.209
2	18.225	2998541	109630	98.791
Total		3035227	111504	100.000

HPLC Data of racemic **4u**

MSP-VI-42 bottom major E:\CUTN\MSP-LAB\SIVA\2022\March\18-03-2022\MSP-VI-42 bottom major.lcd

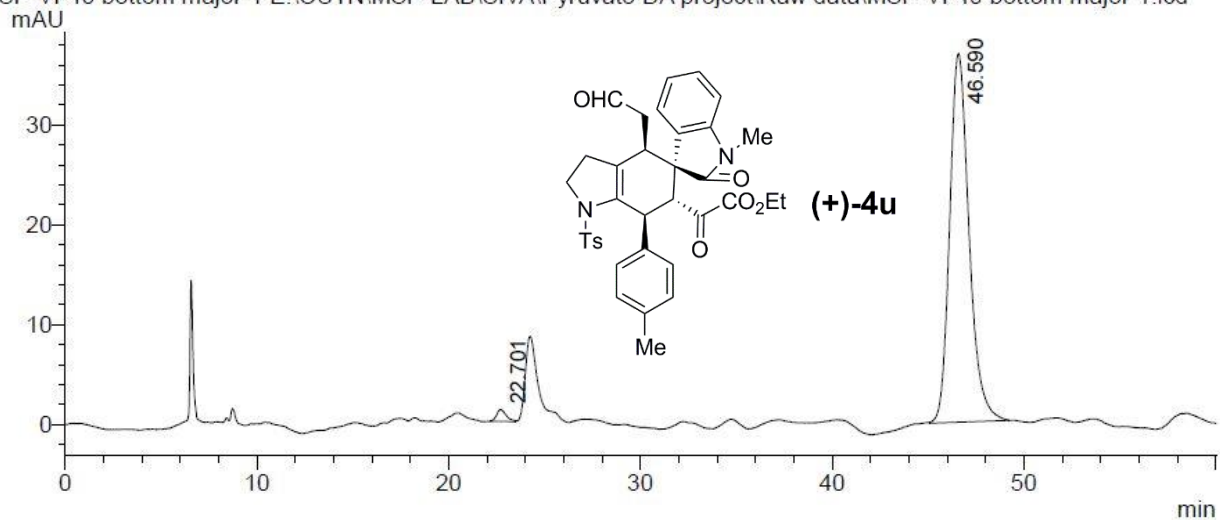


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.594	3734728	97383	52.484
2	46.534	3381157	46445	47.516
Total		7115885	143828	100.000

HPLC Data of chiral **4u**: 97% ee

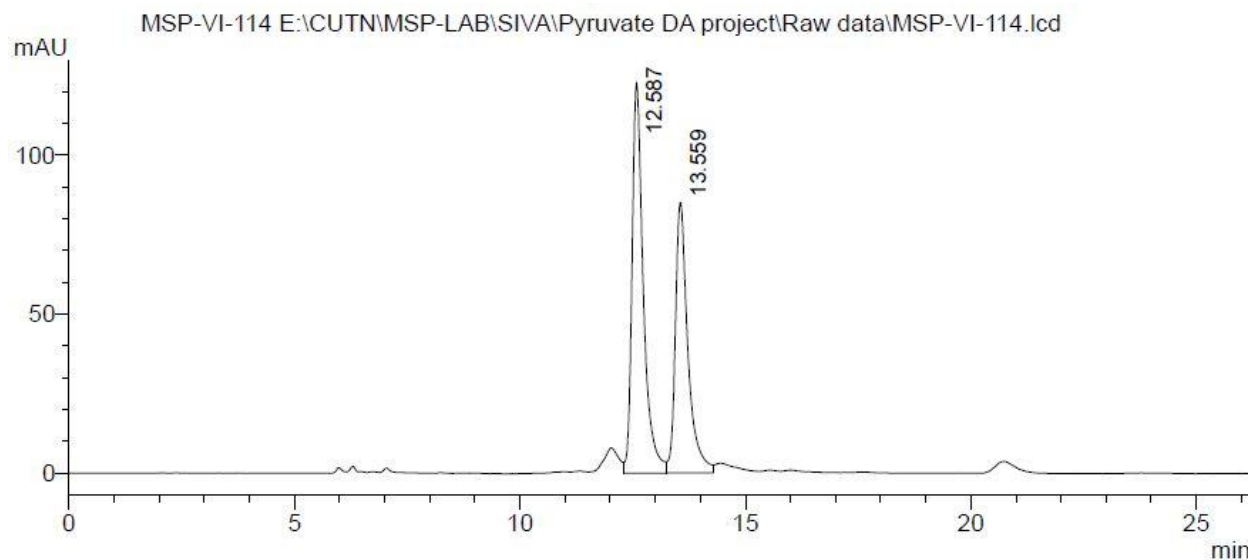
MSP-VI-40 bottom major-1 E:\CUTN\MSP-LAB\SIVA\Pyruvate DA project\Raw data\MSP-VI-40 bottom major-1.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	22.701	41256	1196	1.566
2	46.590	2593960	36912	98.434
Total		2635216	38108	100.000

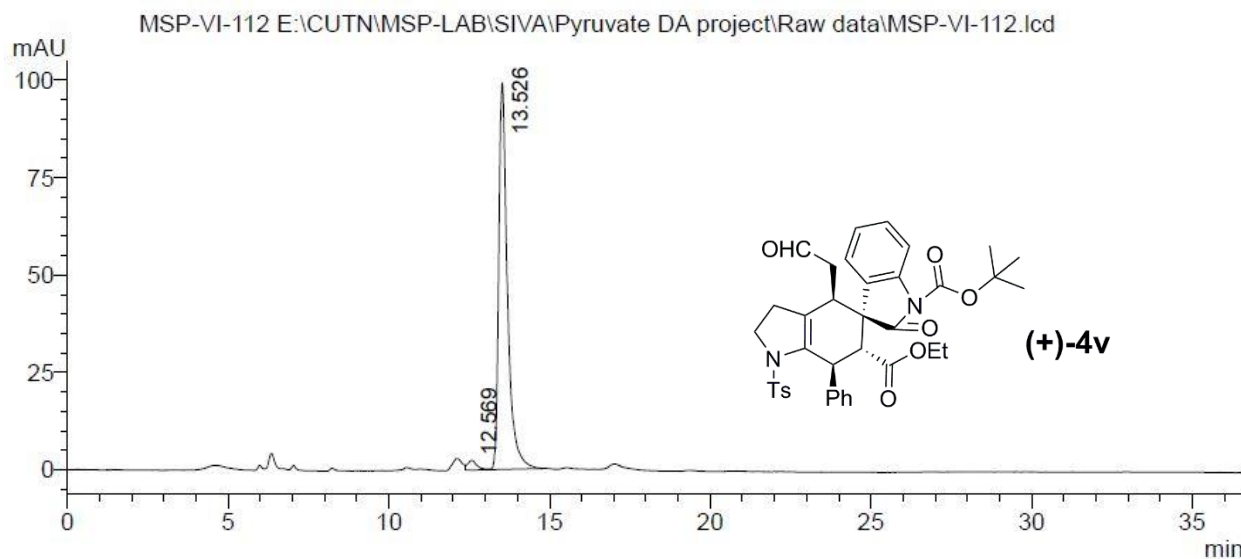
HPLC Data of racemic **4v**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	12.587	2131261	122679	56.533
2	13.559	1638652	85049	43.467
Total		3769913	207728	100.000

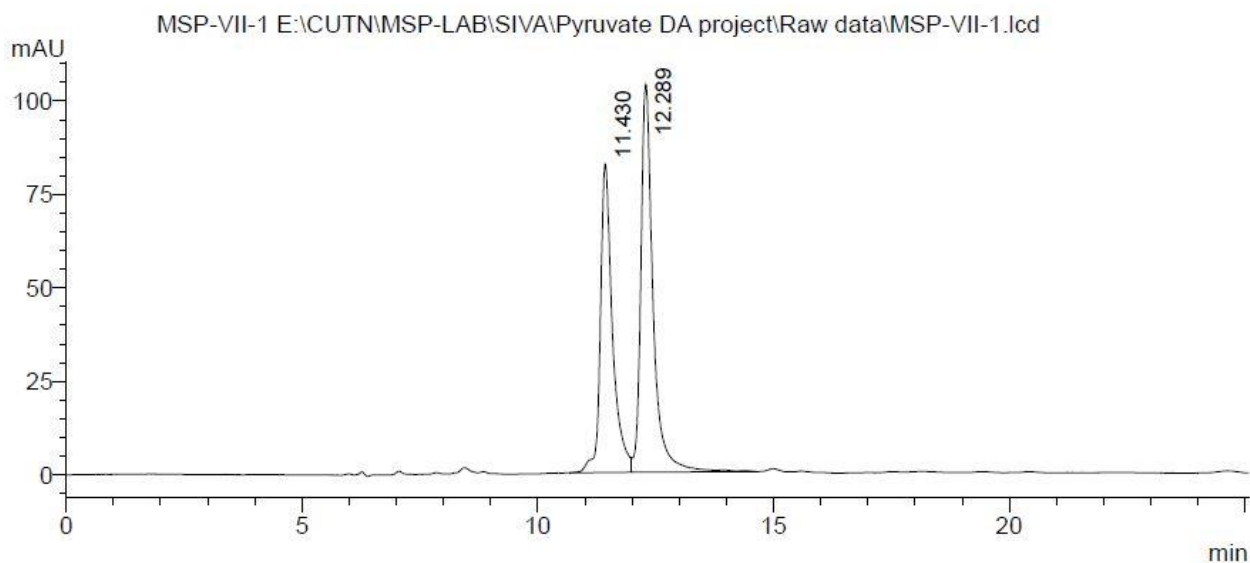
HPLC Data of chiral **4v**: 95% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	12.569	48943	2540	2.554
2	13.526	1867210	99287	97.446
Total		1916153	101826	100.000

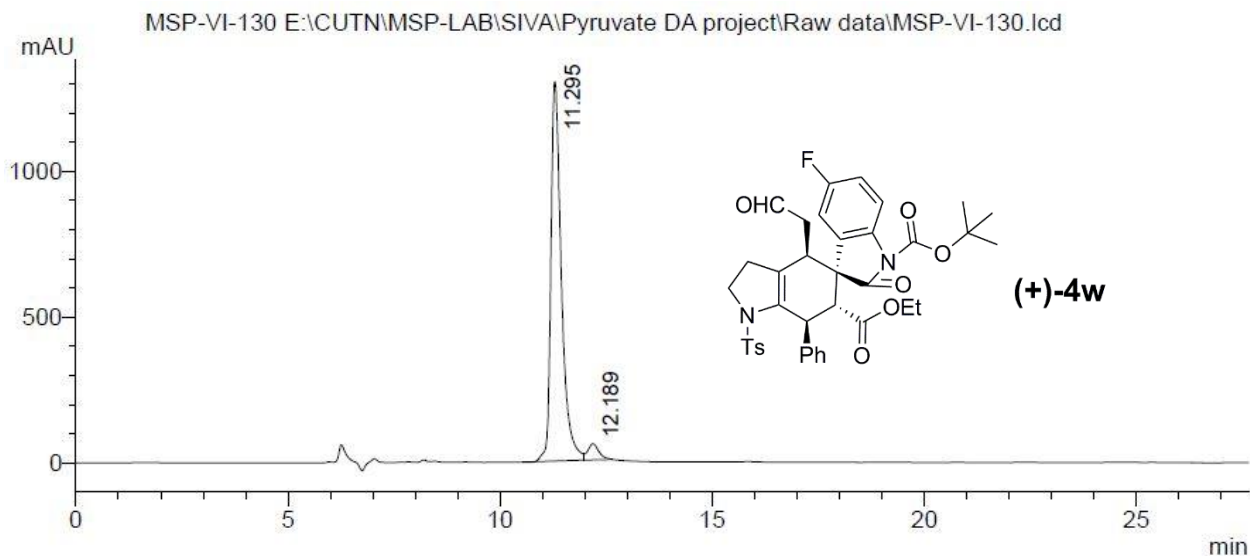
HPLC Data of racemic **4w**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.430	1474643	82497	44.089
2	12.289	1870070	103866	55.911
Total		3344713	186363	100.000

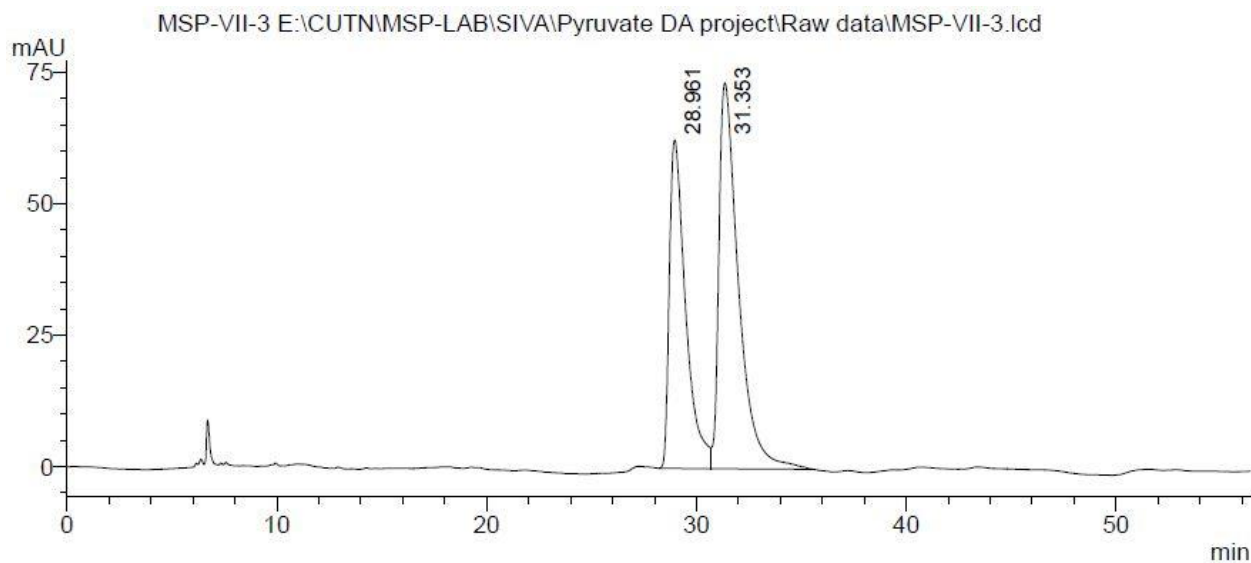
HPLC Data of chiral **4w**: 91% ee



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	11.295	22429980	1301467	95.654
2	12.189	1019043	55688	4.346
Total		23449023	1357156	100.000

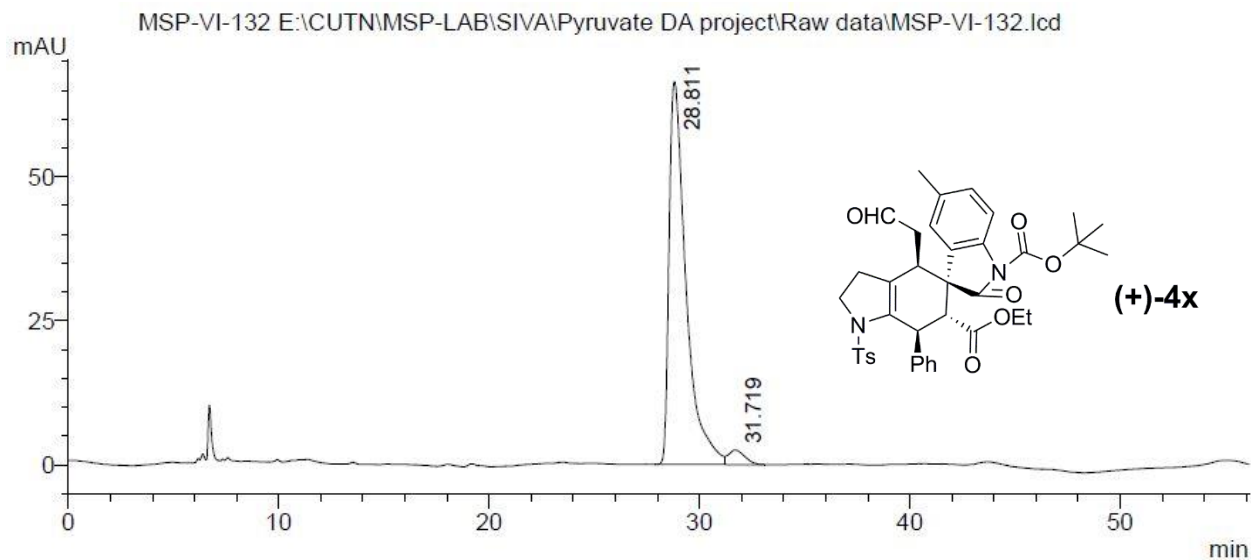
HPLC Data of racemic **4x**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	28.961	3381029	62456	41.546
2	31.353	4756943	73376	58.454
Total		8137972	135832	100.000

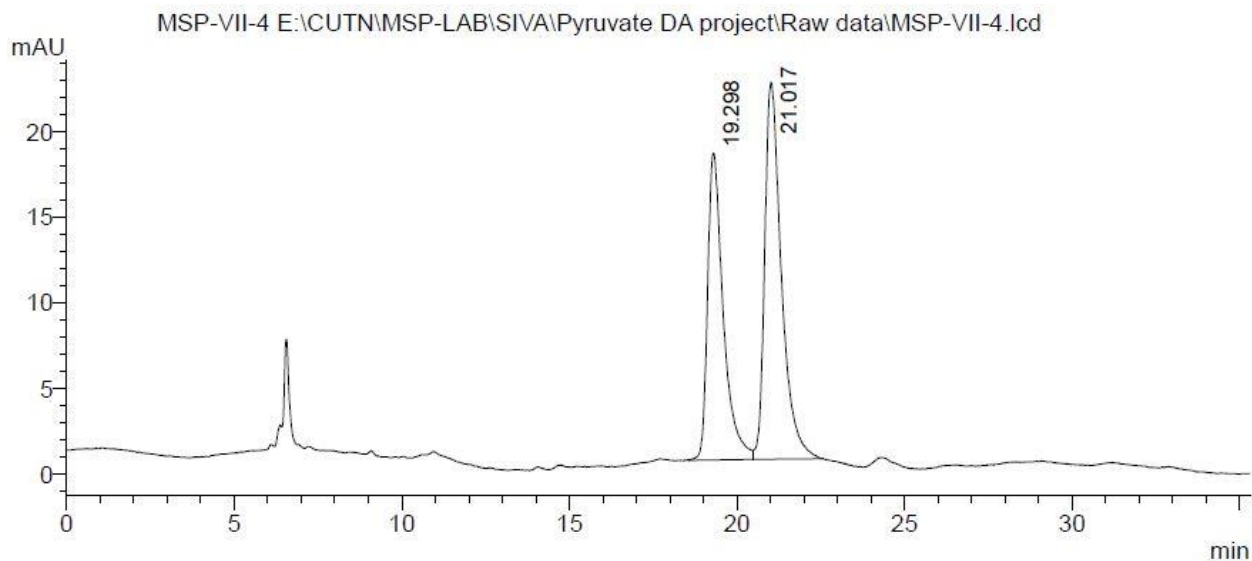
HPLC Data of chiral **4x**: 93% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	28.811	3701980	66382	96.316
2	31.719	141610	2526	3.684
Total		3843590	68908	100.000

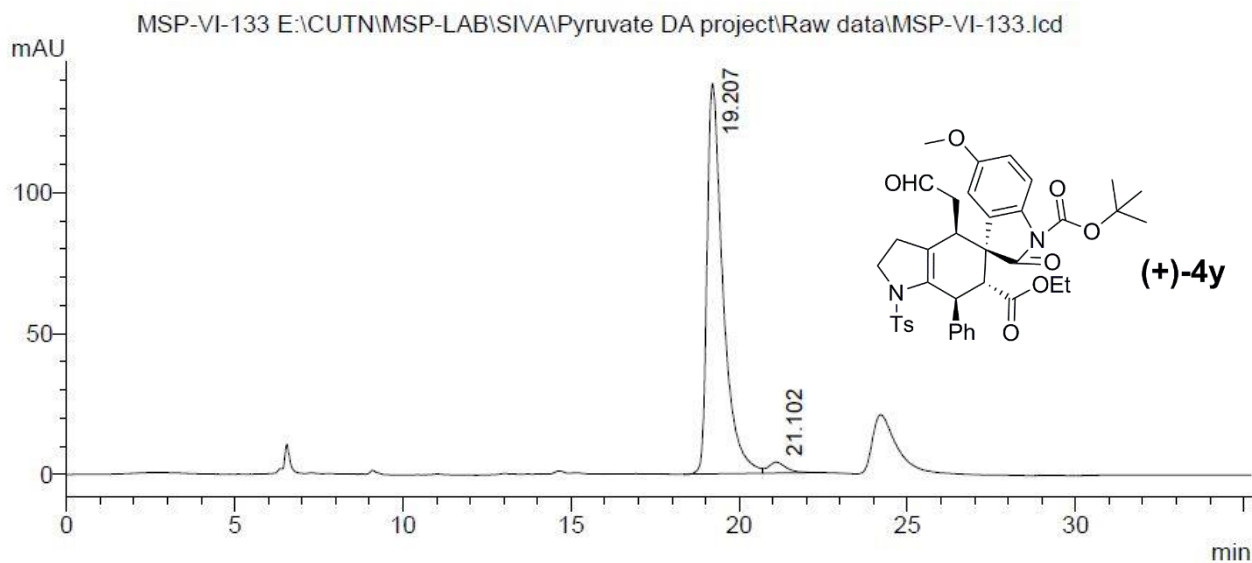
HPLC Data of racemic **4y**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.298	584297	17946	43.348
2	21.017	763615	22038	56.652
Total		1347912	39984	100.000

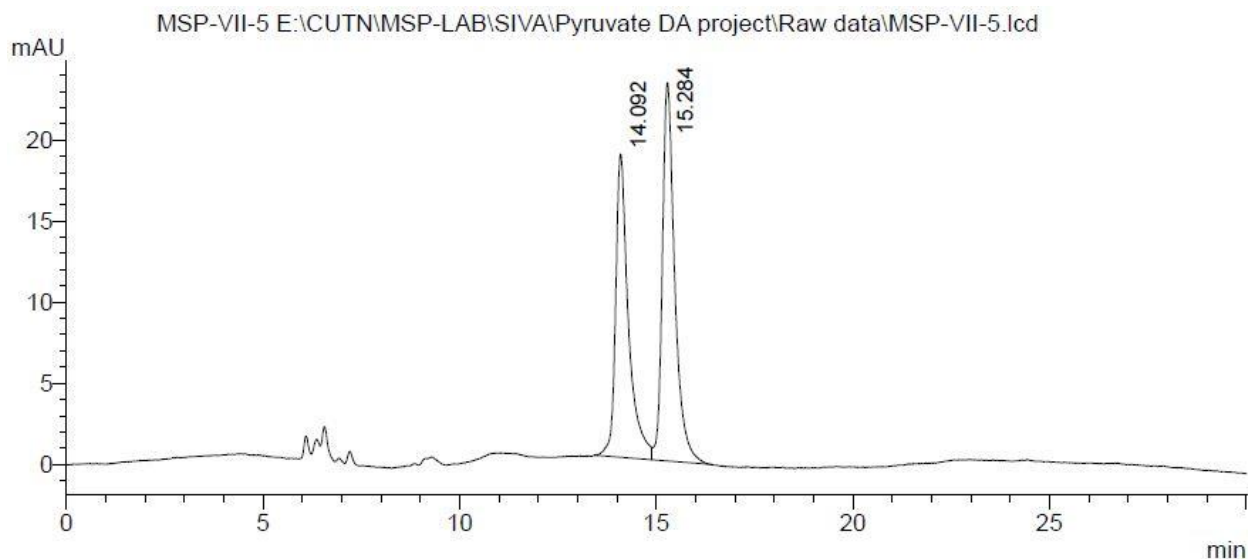
HPLC Data of chiral **4y**: 94% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.207	4566071	138487	96.969
2	21.102	142716	3872	3.031
Total		4708787	142359	100.000

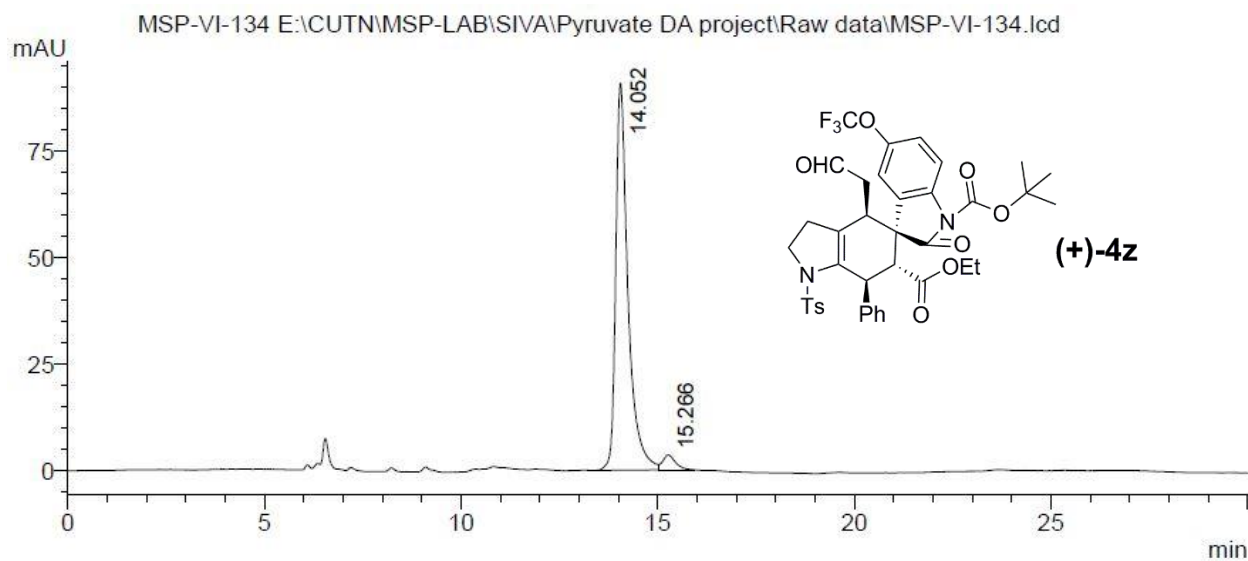
HPLC Data of racemic **4z**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.092	424537	18694	45.390
2	15.284	510764	23318	54.610
Total		935301	42012	100.000

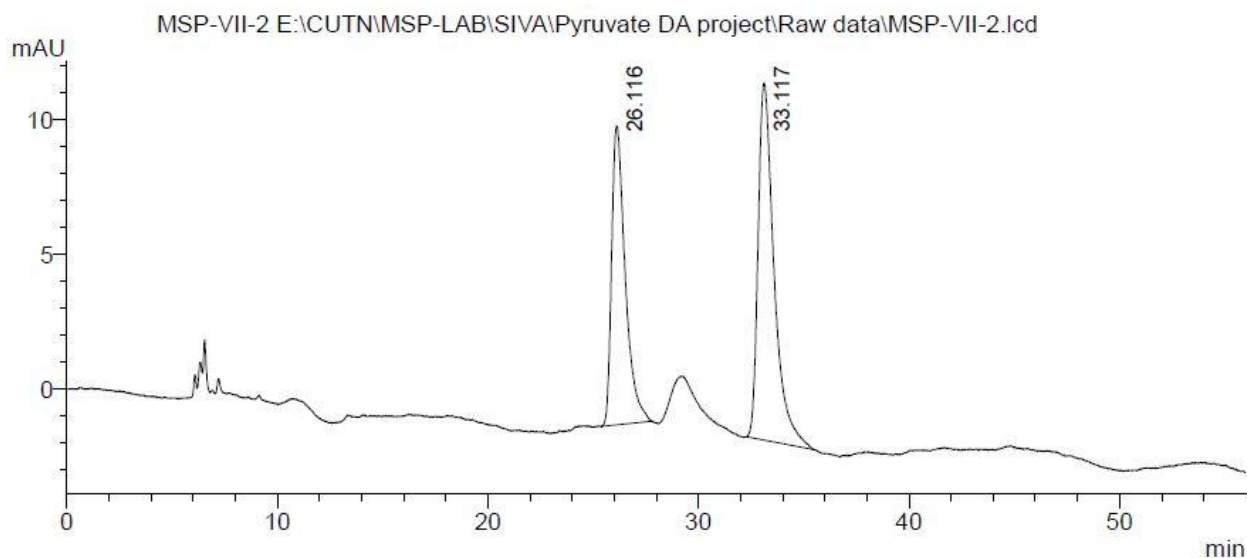
HPLC Data of chiral **4z**: 92% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	14.052	1963680	90748	96.075
2	15.266	80218	3502	3.925
Total		2043898	94250	100.000

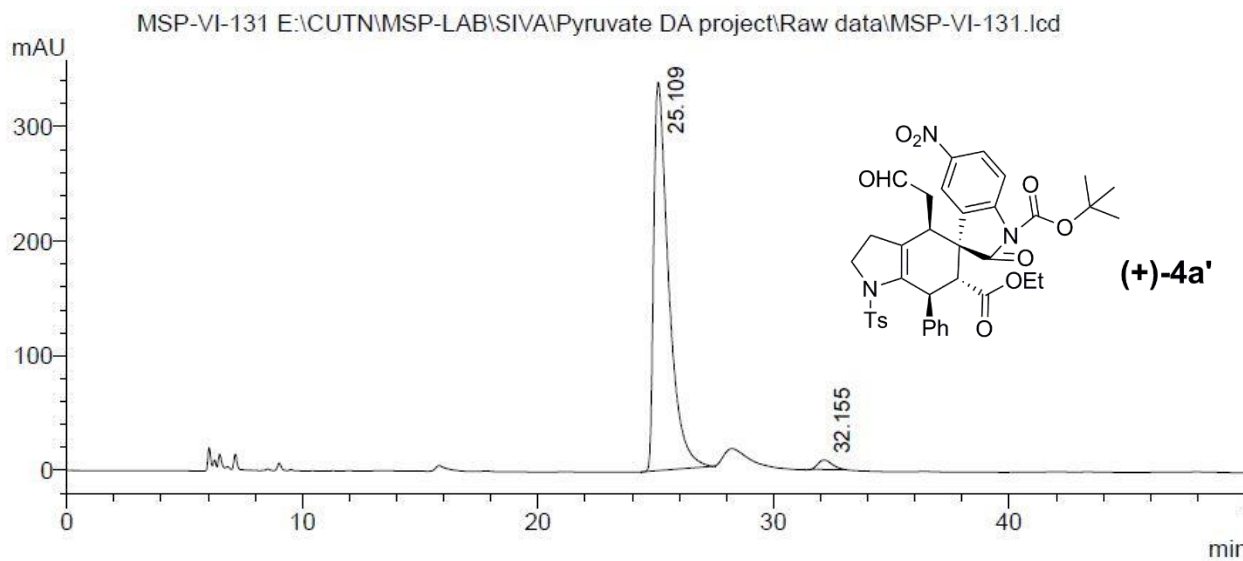
HPLC Data of racemic **4a'**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	26.116	499643	11112	41.737
2	33.117	697480	13265	58.263
Total		1197123	24377	100.000

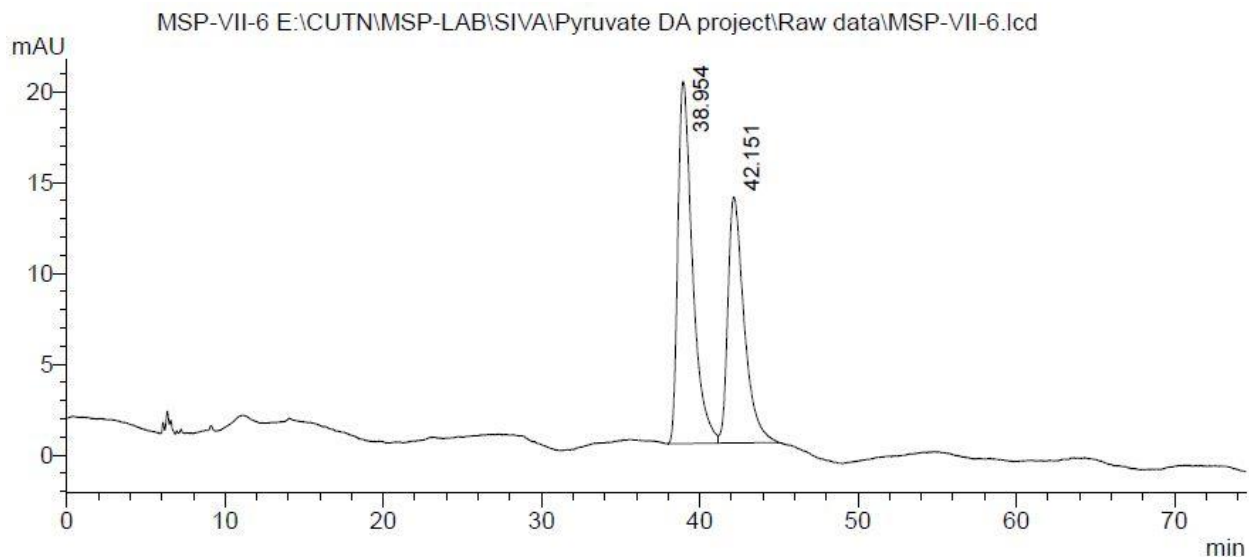
HPLC Data of chiral **4a'**: 95% *ee*



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	25.109	14912420	338477	97.688
2	32.155	352887	8345	2.312
Total		15265308	346823	100.000

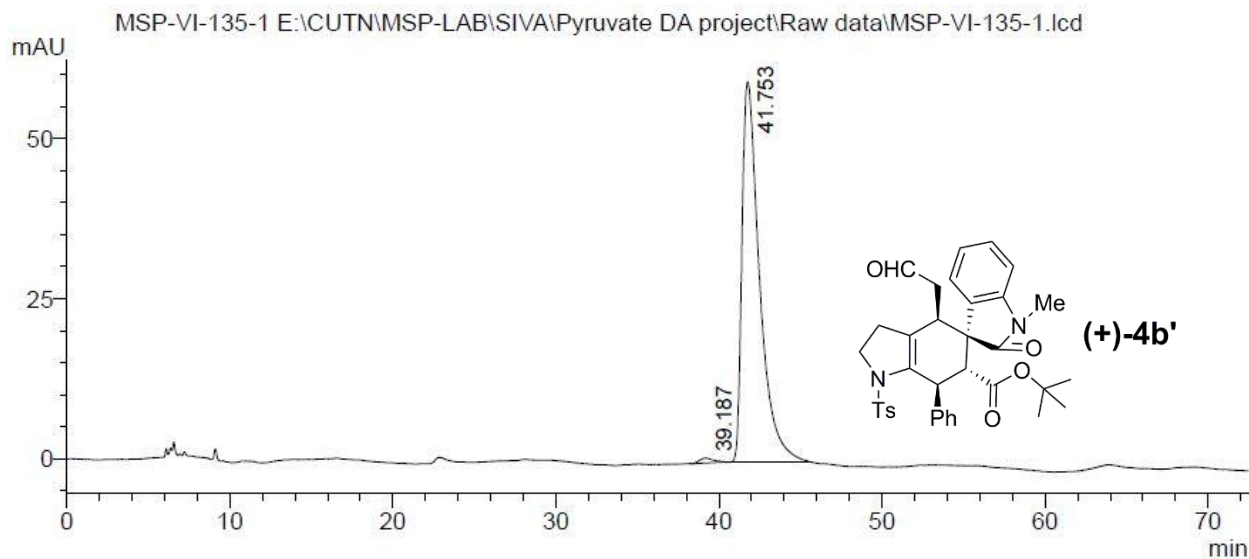
HPLC Data of racemic **4b'**



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	38.954	1279731	19928	56.897
2	42.151	969492	13534	43.103
Total		2249223	33462	100.000

HPLC Data of chiral **4b'**: 98% ee

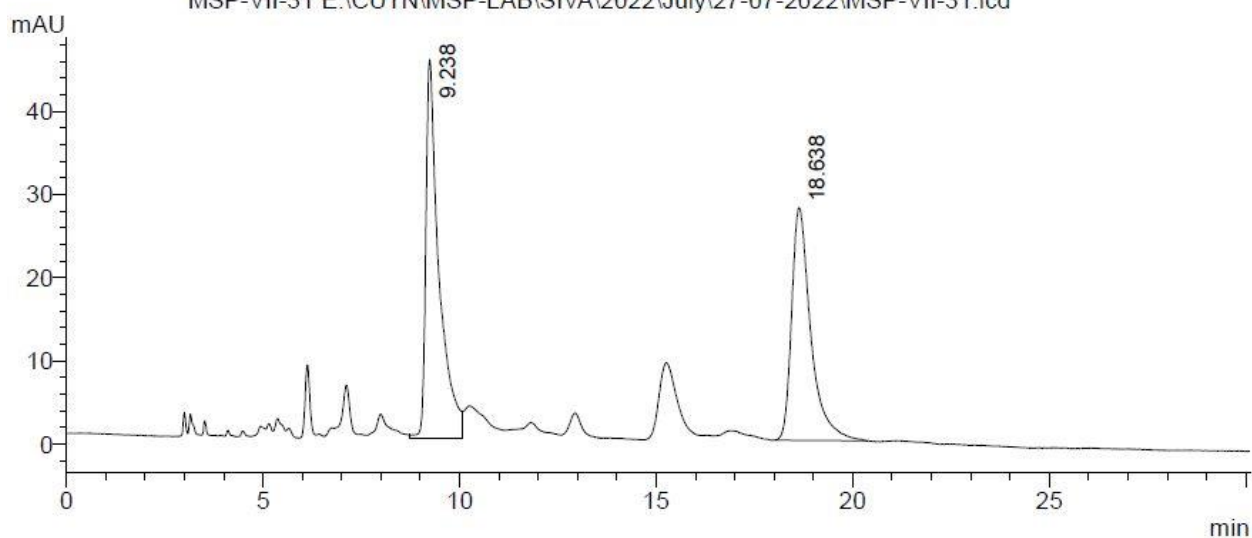


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	39.187	44668	771	0.993
2	41.753	4455235	59354	99.007
Total		4499903	60124	100.000

HPLC Data of racemic 4'a

MSP-VII-31 E:\CUTN\MSP-LAB\SIVA\2022\July\27-07-2022\MSP-VII-31.lcd

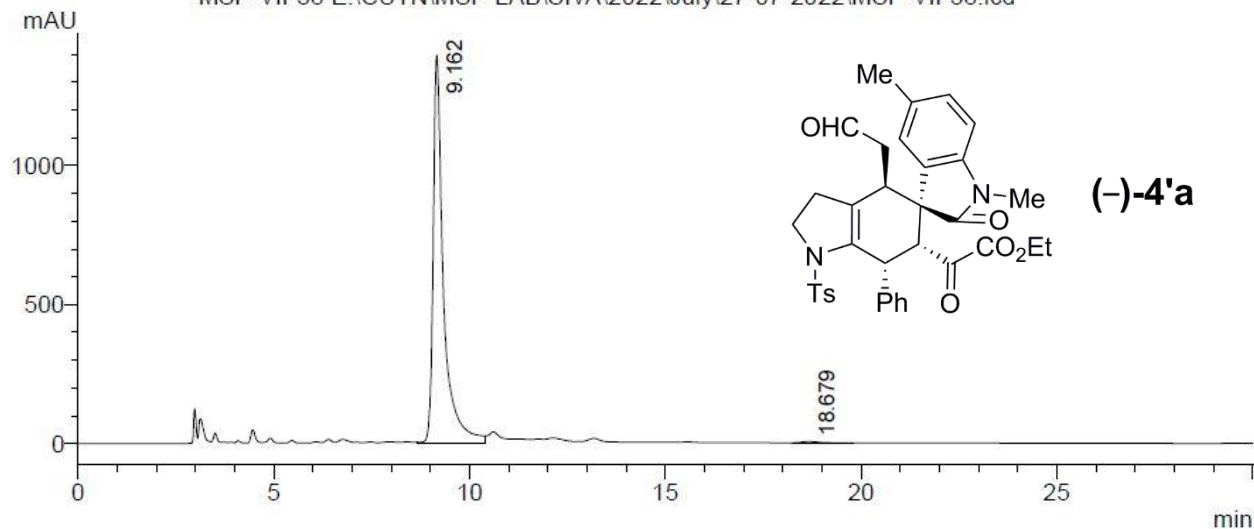


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	9.238	1054400	45507	52.718
2	18.638	945692	27976	47.282
Total		2000092	73483	100.000

HPLC Data of chiral 4'a: 99% ee

MSP-VII-38 E:\CUTN\MSP-LAB\SIVA\2022\July\27-07-2022\MSP-VII-38.lcd

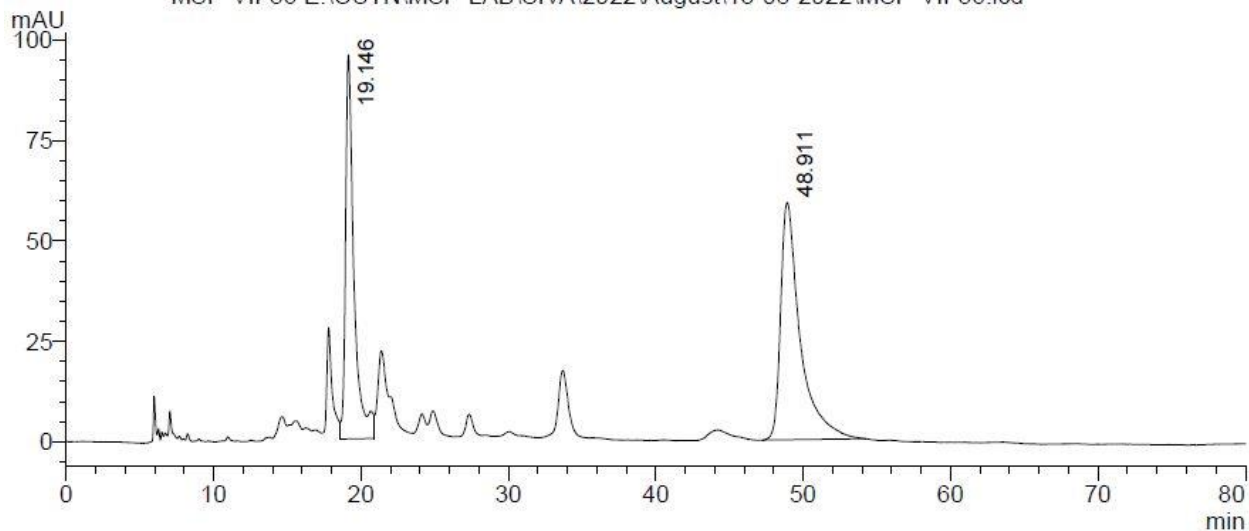


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	9.162	25754639	1396090	99.434
2	18.679	146603	4472	0.566
Total		25901242	1400562	100.000

HPLC Data of racemic 4'I

MSP-VII-56 E:\CUTN\MSP-LAB\SIVA\2022\August\13-08-2022\MSP-VII-56.lcd

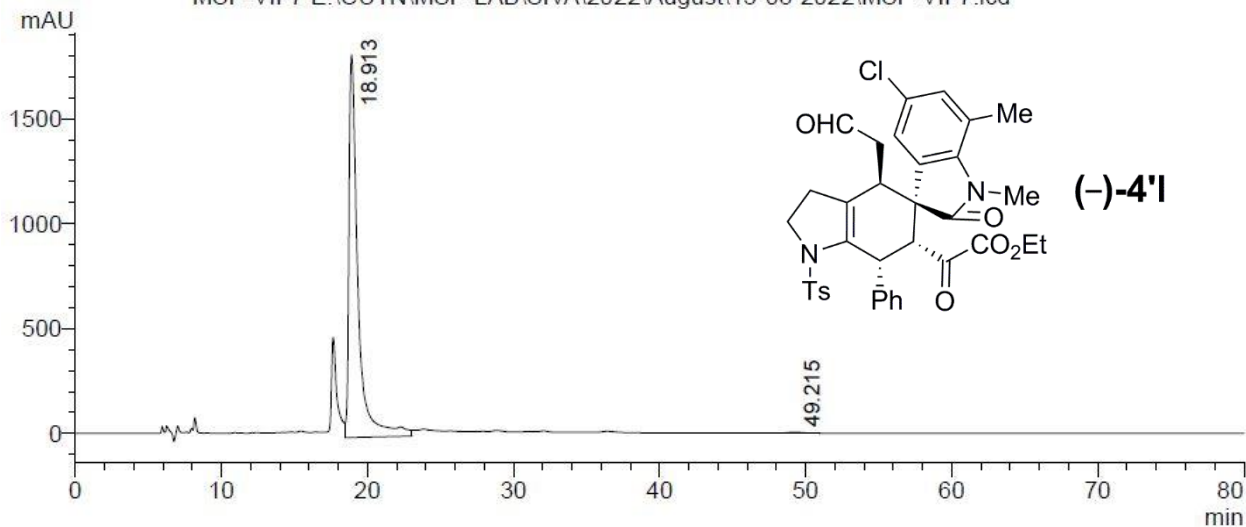


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	19.146	3801121	95610	41.144
2	48.911	5437458	59088	58.856
Total		9238579	154698	100.000

HPLC Data of chiral 4'I: 99% ee

MSP-VII-7 E:\CUTN\MSP-LAB\SIVA\2022\August\13-08-2022\MSP-VII-7.lcd

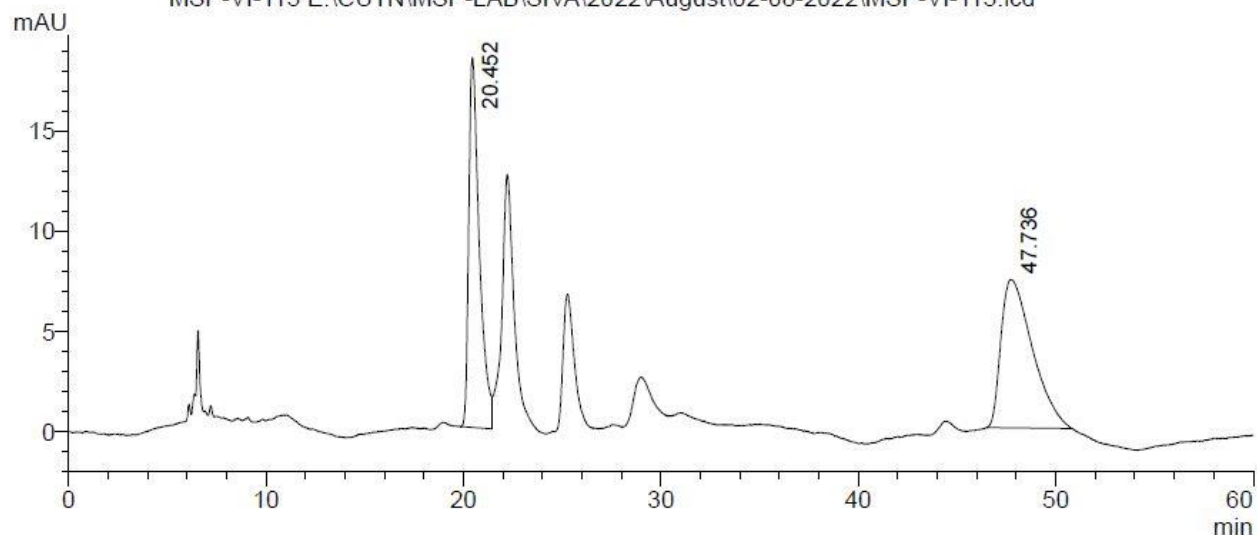


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	18.913	78367783	1822987	99.630
2	49.215	291270	4267	0.370
Total		78659053	1827254	100.000

HPLC Data of racemic 4'v

MSP-VI-115 E:\CUTN\MSP-LAB\SIVA\2022\August\02-08-2022\MSP-VI-115.lcd

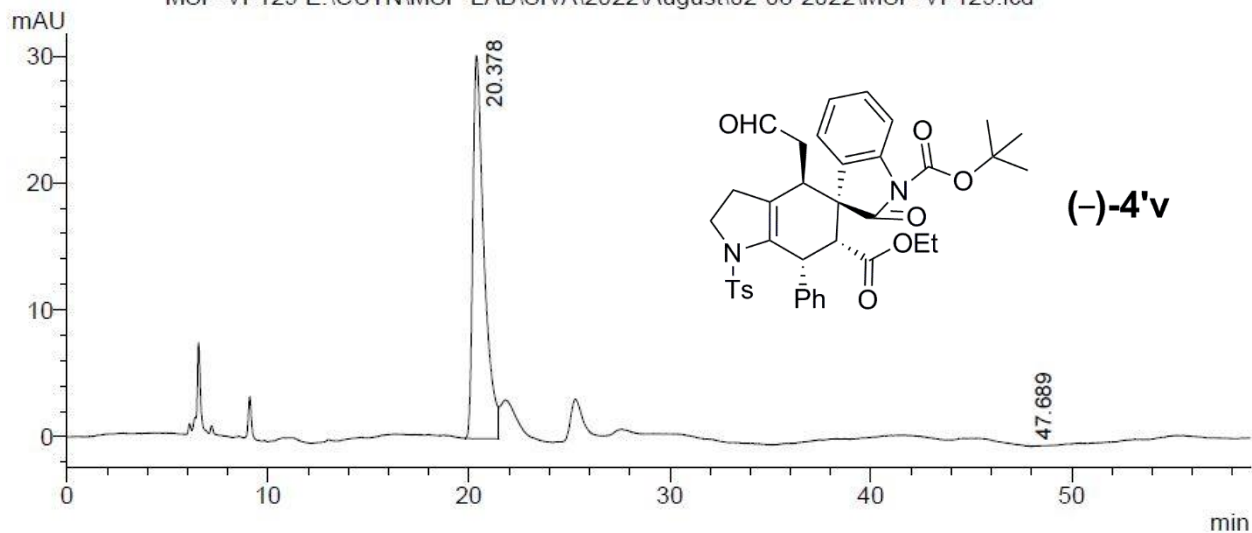


PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	20.452	688785	18464	45.675
2	47.736	819221	7397	54.325
Total		1508006	25862	100.000

HPLC Data of chiral 4'v: 99% ee

MSP-VI-129 E:\CUTN\MSP-LAB\SIVA\2022\August\02-08-2022\MSP-VI-129.lcd



PDA Ch1 254nm

Peak #	Ret. Time (min)	Area	Height	Area%
1	20.378	1171578	30146	99.971
2	47.689	337	22	0.029
Total		1171915	30169	100.000