

Supporting Information-III

Conformation-controlled Catalytic Asymmetric Synthesis of Swaminathan Ketones

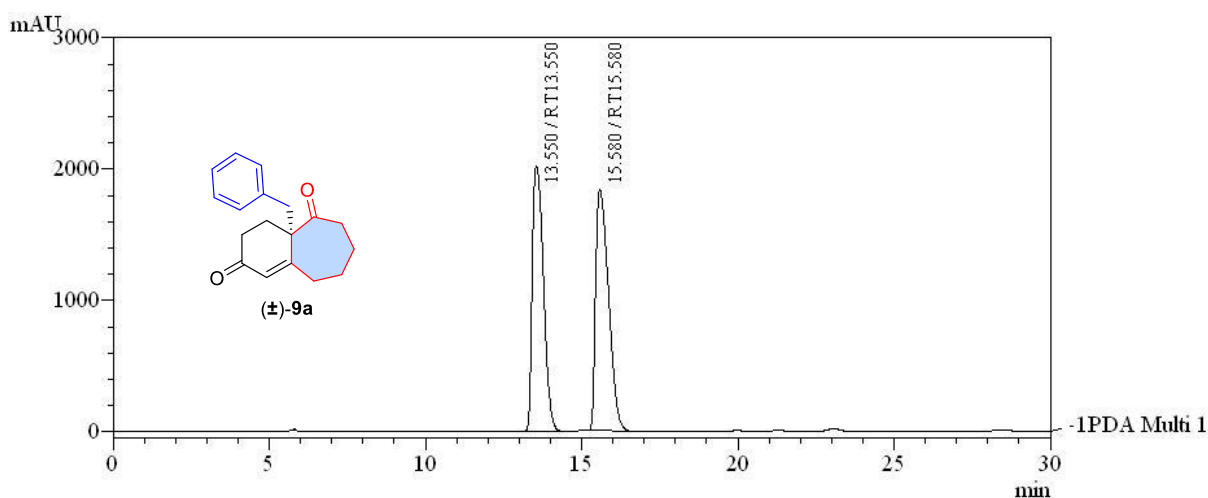
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and Dhevalapally B. Ramachary**

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[‡]These authors contributed equally.

The enantiomeric excess (*ee*) of the products **9** were determined by chiral stationary phase HPLC using a Daicel Chiralpak IG or Daicel Chiralpak IC-3 or Daicel Chiralpak AD-H column or Daicel Chiralpak ID column and hexane/2-propanol as the eluent. Retention times and solvent ratios are indicated in the respective entries.

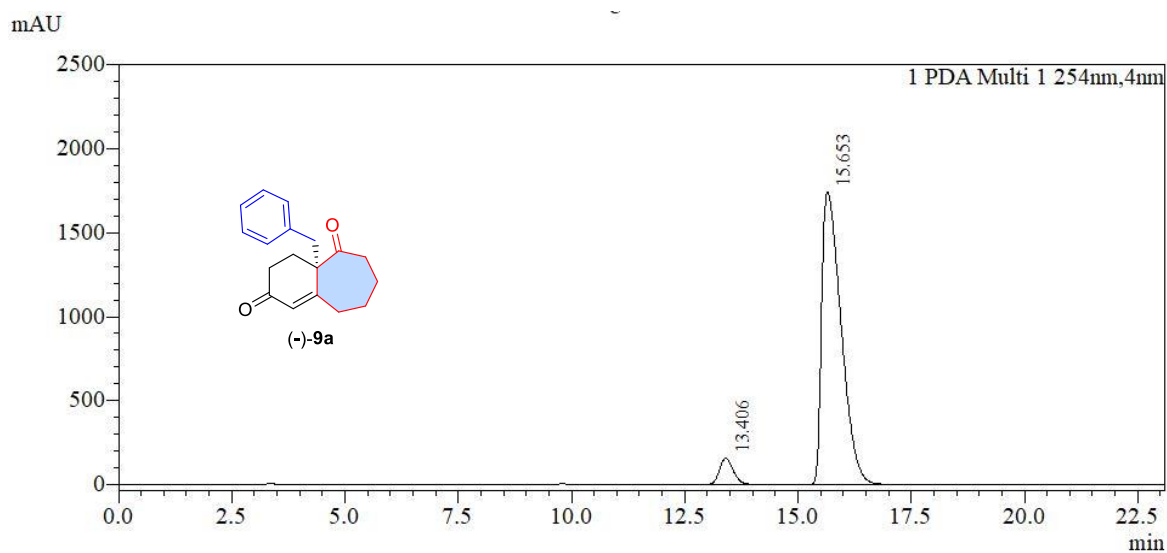
Racemic (\pm)-**9a**:



Chiralpak IG, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

PeakTable						
PDA Ch1 254nm 4nm						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT13.550	13.550	50568890	2022666	48.892	52.378
2	RT15.580	15.580	52861884	1838985	51.108	47.622
Total			103430774	3861651	100.000	100.000

Chiral (-)-**9a** (88% *ee*)

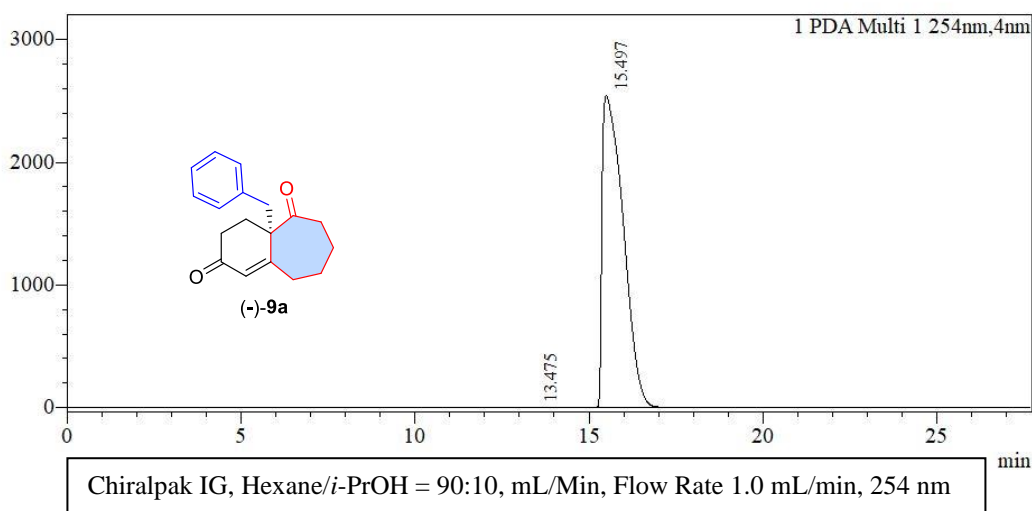


Chiralpak IG, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254

Peak Table							
PDA Ch1 254nm							
Peak#	Name	Ret. Time	Area	Height	Area%	Height%	
1	RT:13.406	13.406	3322008	157074	5.952	8.255	
2	RT:15.653	15.653	52488616	1745667	94.048	91.745	
Total			55810623	1902741	100.000	100.000	

Chiral (-)-**9a** [$>99\%$ *ee*; Crystals after slow crystallization as mentioned in the manuscript]

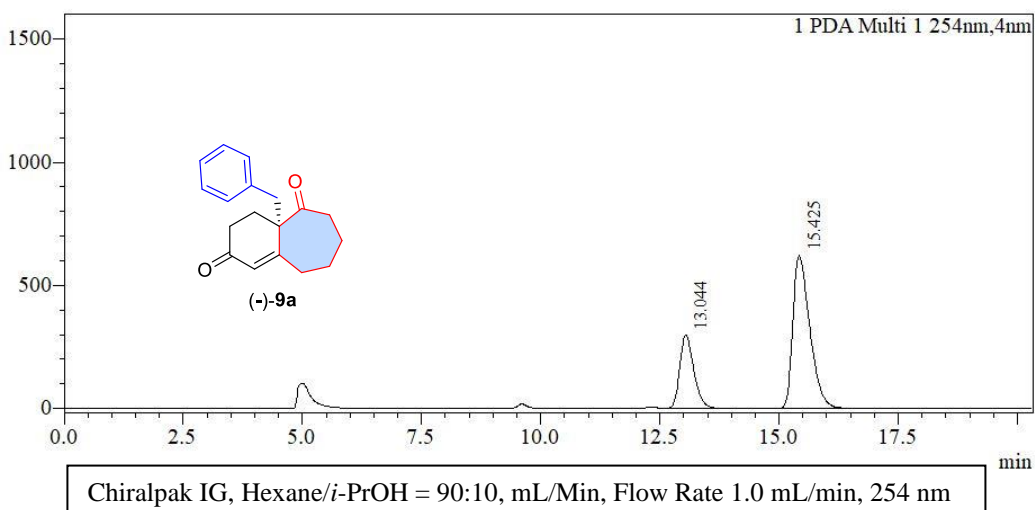
mAU



Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:13.475	13.475	31967	1619	0.030	0.064
2	RT:15.497	15.497	106550113	2547063	99.970	99.936
Total			106582080	2548682	100.000	100.000

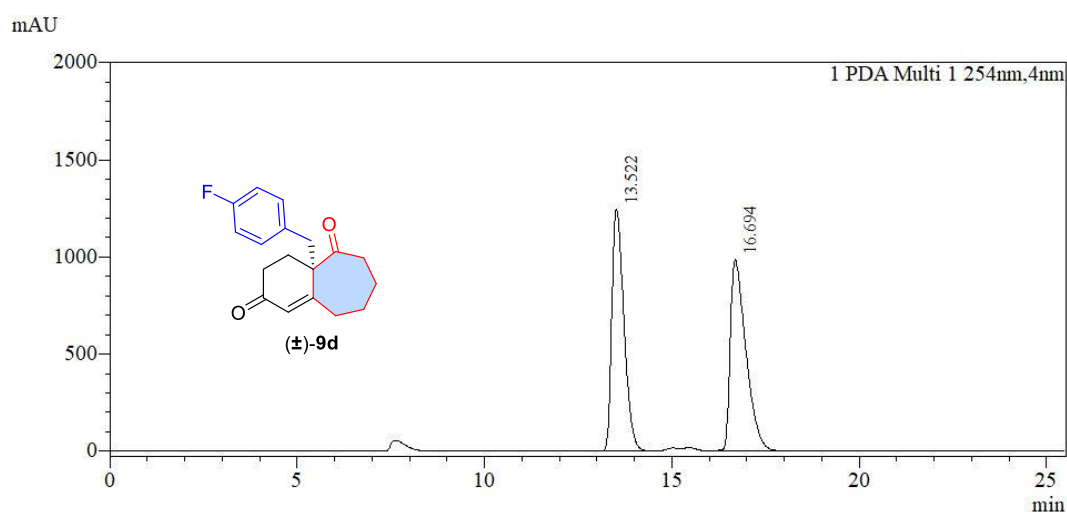
Chiral (-)-**9a** [43% *ee*; Filtrate after slow crystallization as mentioned in the manuscript]

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Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:13.044	13.044	6088621	296454	28.337	32.330
2	RT:15.425	15.425	15397729	620515	71.663	67.670
Total			21486351	916969	100.000	100.000

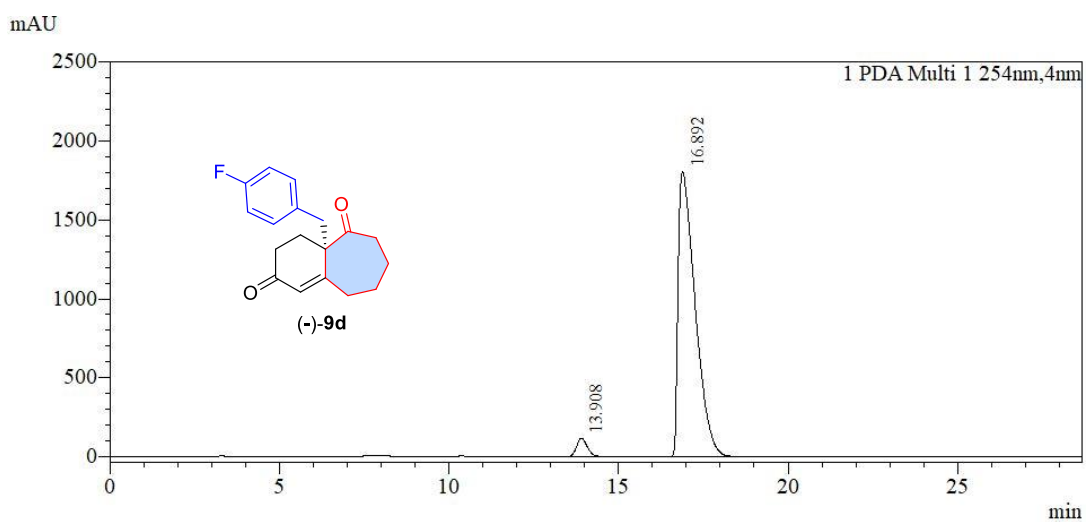
Racemic (\pm)-**9d**:



Chiralpak AD-H, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

Peak Table							
PDA Ch1 254nm							
Peak#	Name	Ret. Time	Area	Height	Area%	Height%	
1	RT:13.522	13.522	28109069	1247011	49.480	55.853	
2	RT:16.694	16.694	28700073	985660	50.520	44.147	
Total			56809142	2232671	100.000	100.000	

Chiral (-)-**9d** (92% *ee*)

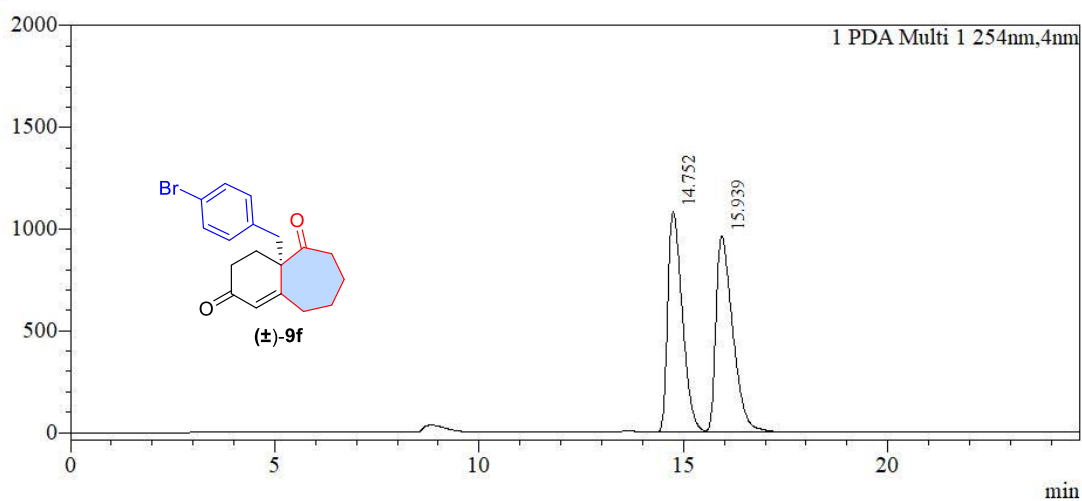


Chiralpak AD-H, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

Peak Table							
PDA Ch1 254nm							
Peak#	Name	Ret. Time	Area	Height	Area%	Height%	
1	RT:13.908	13.908	2548123	117535	3.887	6.111	
2	RT:16.892	16.892	63014469	1805875	96.113	93.889	
Total			65562593	1923410	100.000	100.000	

Racemic (\pm)-**9f**:

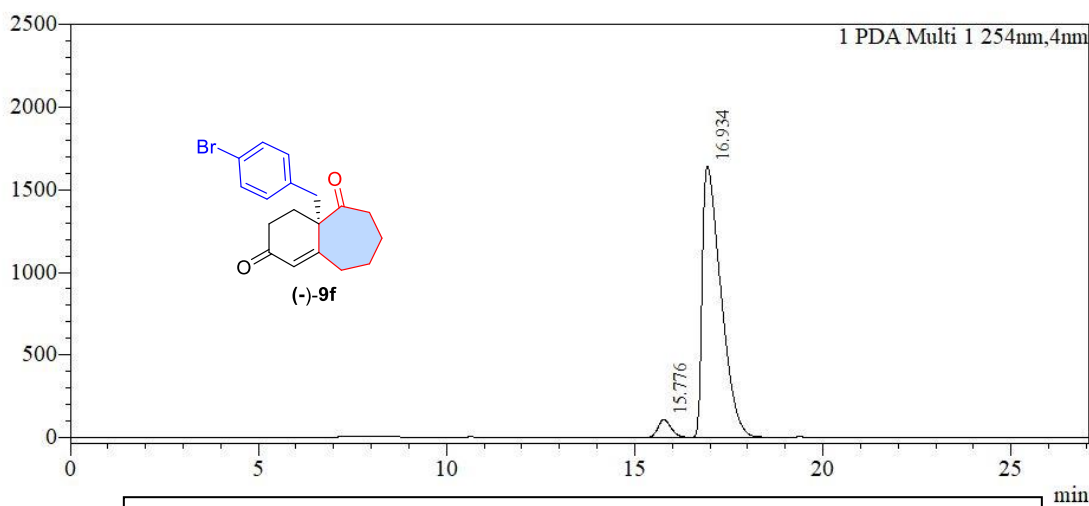
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Peak Table							
PDA Ch1 254nm							
Peak#	Name	Ret. Time	Area	Height	Area%	Height%	
1	RT:14.752	14.752	26994485	1083301	49.274	52.957	
2	RT:15.939	15.939	27790219	962334	50.726	47.043	
Total			54784704	2045635	100.000	100.000	

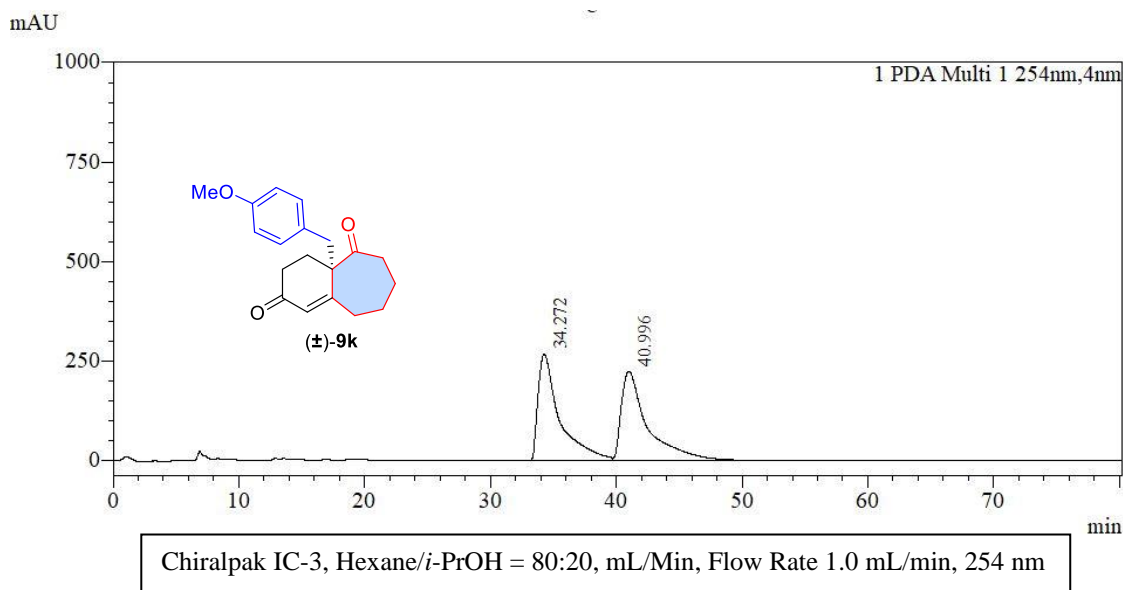
Chiral (-)-**9f** (91% *ee*)

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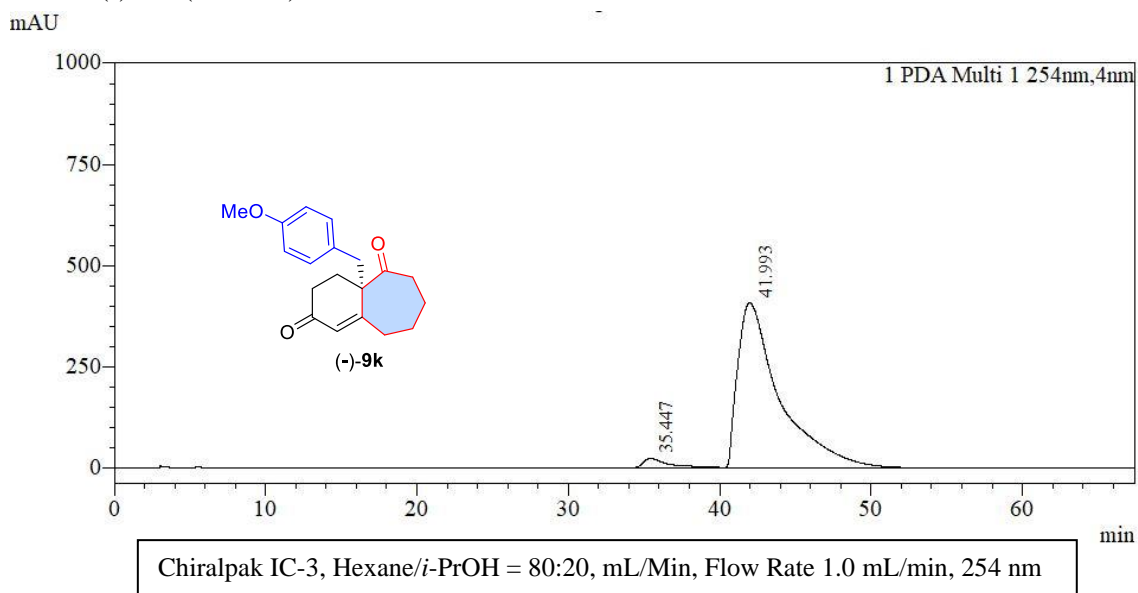
Peak Table							
PDA Ch1 254nm							
Peak#	Name	Ret. Time	Area	Height	Area%	Height%	
1	RT:15.776	15.776	2722972	108855	4.550	6.222	
2	RT:16.934	16.934	57119358	1640624	95.450	93.778	
Total			59842330	1749480	100.000	100.000	

Racemic (\pm)-**9k**:



Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:34.272	34.272	31568414	267321	49.568	54.411
2	RT:40.996	40.996	32118257	223983	50.432	45.589
Total			63686671	491304	100.000	100.000

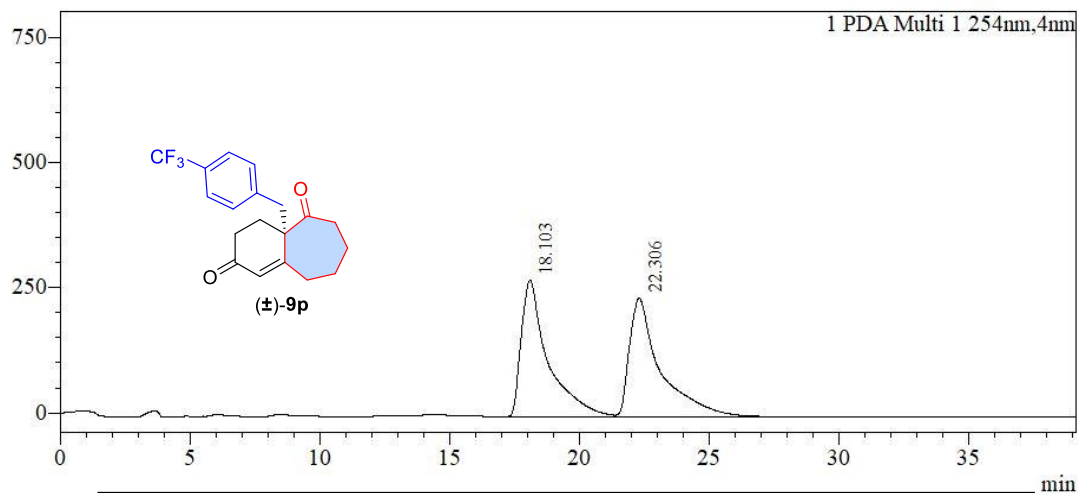
Chiral (-)-**9k** (93% *ee*)



Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:35.447	35.447	2782627	23278	3.414	5.404
2	RT:41.993	41.993	78716444	407479	96.586	94.596
Total			81499070	430757	100.000	100.000

Racemic (\pm)-**9p**:

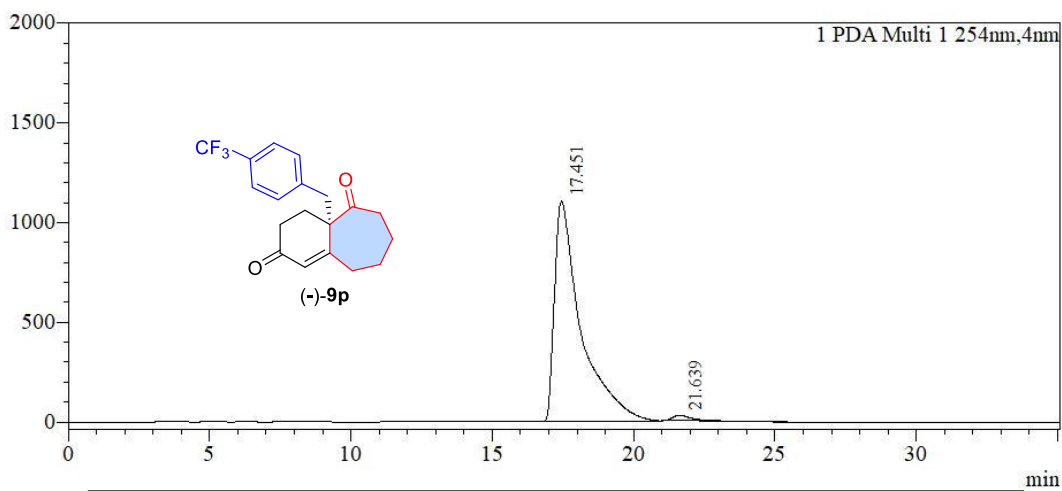
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Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:18.103	18.103	19372333	272329	49.887	53.538
2	RT:22.306	22.306	19459930	236338	50.113	46.462
Total			38832263	508667	100.000	100.000

Chiral (-)-**9p** (96% *ee*)

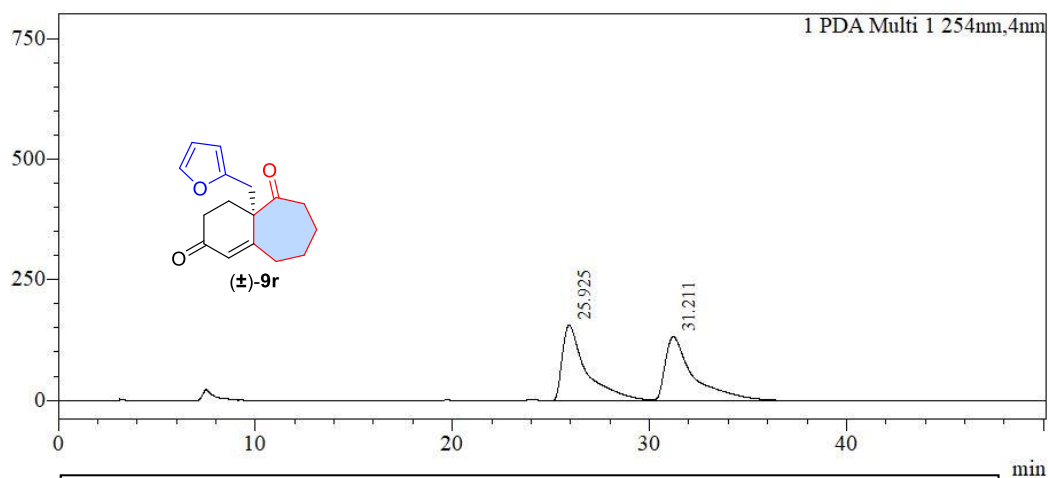
mAU



Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:17.451	17.451	72112855	1105872	97.845	97.515
2	RT:21.639	21.639	1588420	28187	2.155	2.485
Total			73701275	1134059	100.000	100.000

Racemic (\pm)-**9r**:

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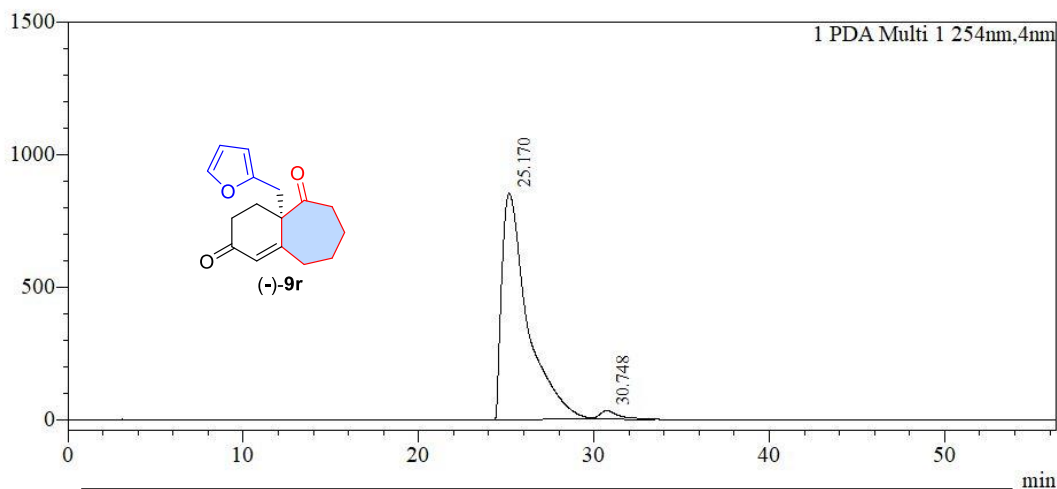


Chiralpak IC-3, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:25.925	25.925	13233611	156198	50.018	54.108
2	RT:31.211	31.211	13224114	132481	49.982	45.892
Total			26457725	288679	100.000	100.000

Chiral (-)-**9r** (95% *ee*)

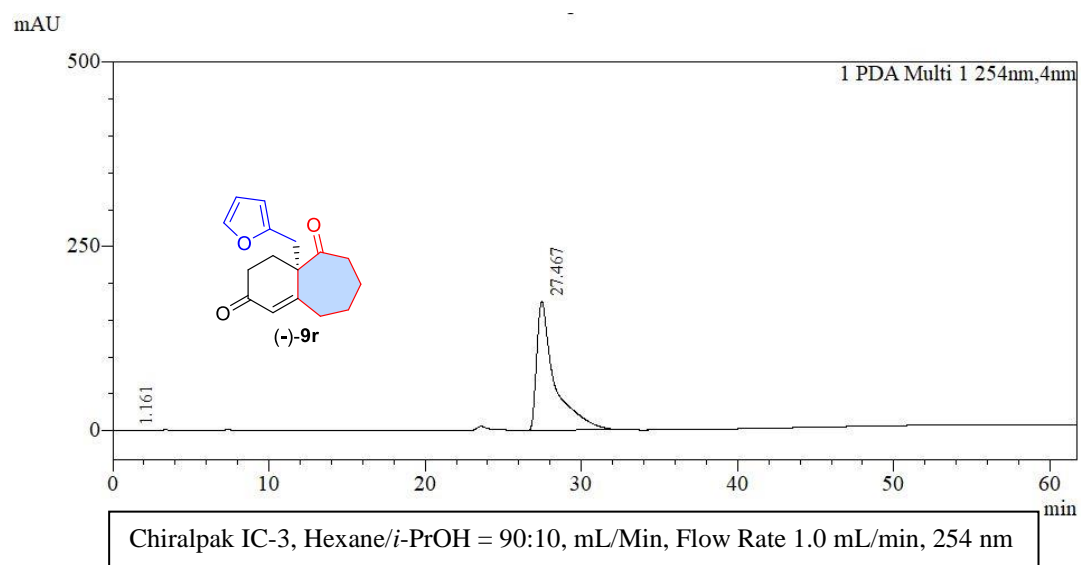
mAU



Chiralpak IC-3, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

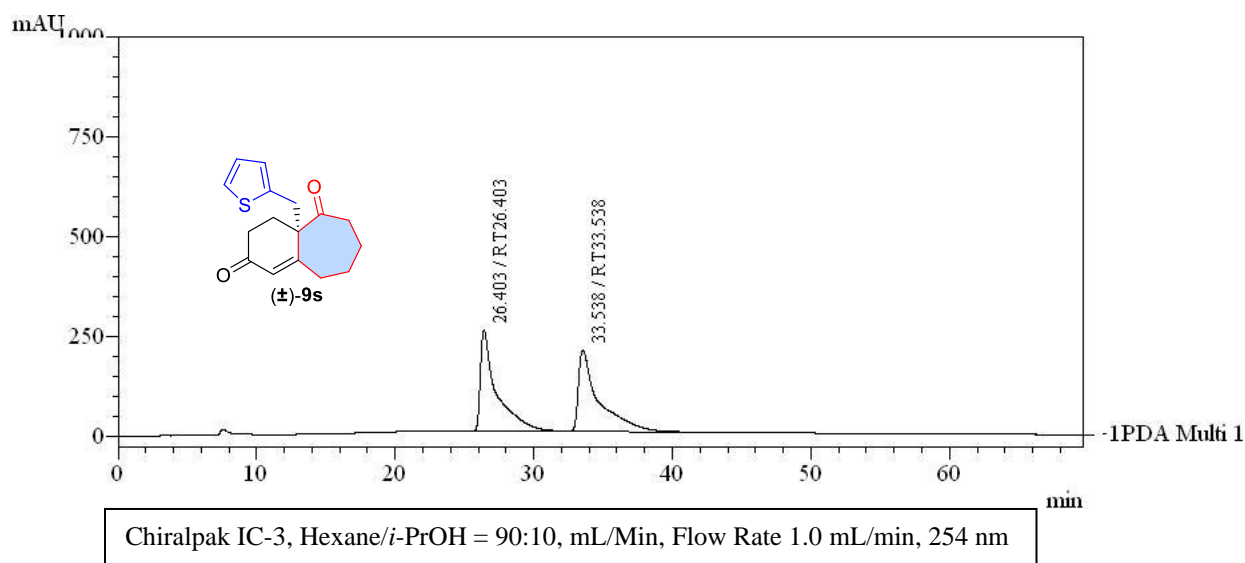
Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:25.170	25.170	87273352	854342	97.325	96.471
2	RT:30.748	30.748	2398404	31255	2.675	3.529
Total			89671756	885597	100.000	100.000

Chiral (-)-**9r** (>99% *ee*, single crystal used for X-ray structure analysis)



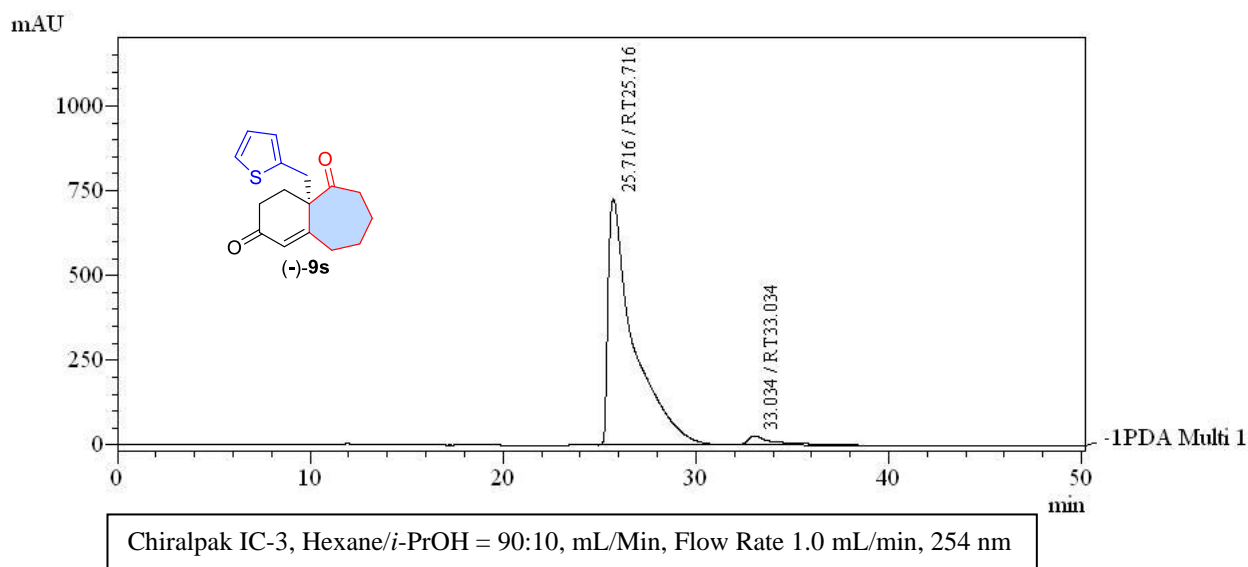
Peak Table						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1		1.161	-37	4	-0.000	0.003
2	RT:27.467	27.467	14073218	174961	100.000	99.997
Total			14073181	174966	100.000	100.000

Racemic (\pm)-**9s**:



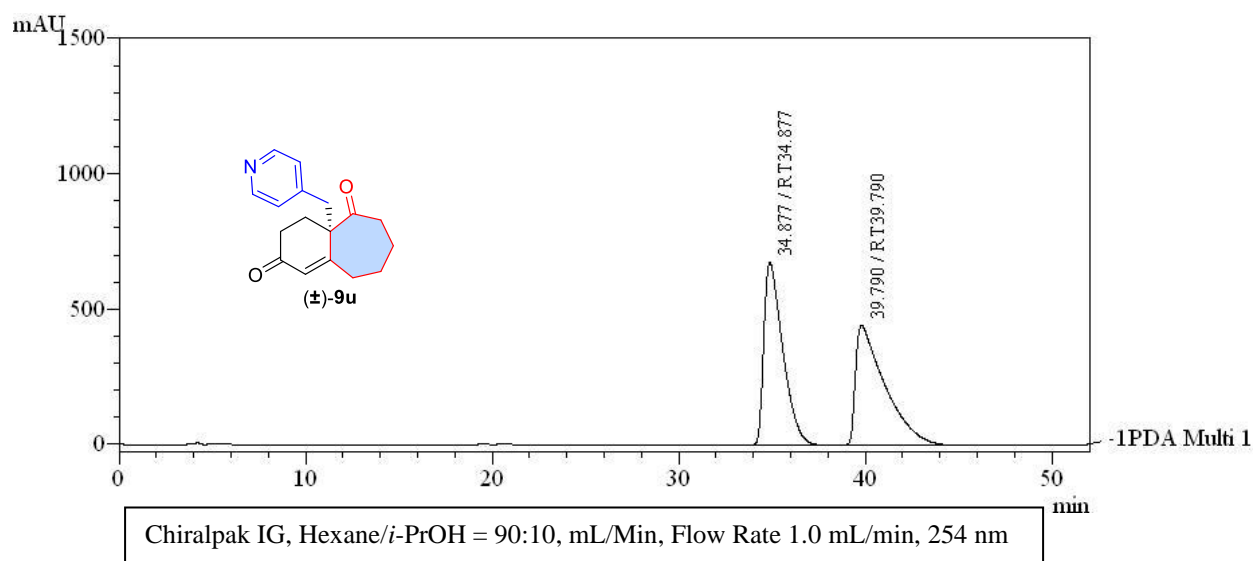
PeakTable						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT26.403	26.403	20403064	252935	49.927	55.474
2	RT33.538	33.538	20462787	203014	50.073	44.526
Total			40865850	455949	100.000	100.000

Chiral (-)-**9s** (92% *ee*)



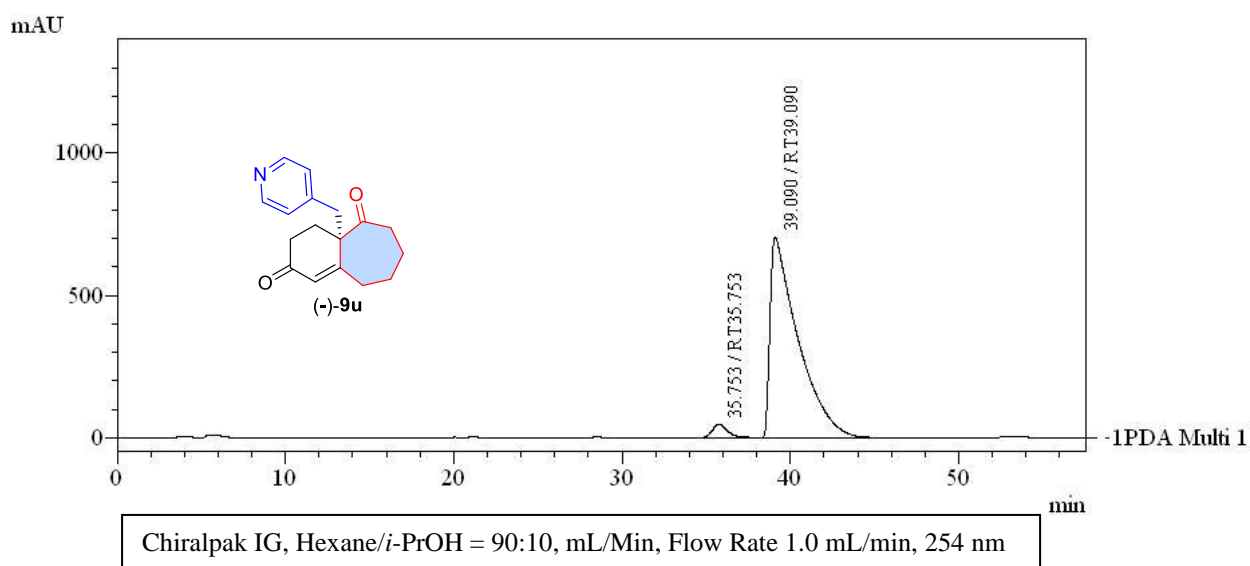
PeakTable						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT25.716	25.716	66462936	724879	96.138	96.404
2	RT33.034	33.034	2669579	27039	3.862	3.596
Total			69132515	751919	100.000	100.000

Racemic (\pm)-**9u**:



PeakTable						
PDA Ch1 254nm 4nm						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT34.877	34.877	47678484	675287	49.692	60.430
2	RT39.790	39.790	48269863	442181	50.308	39.570
Total			95948346	1117467	100.000	100.000

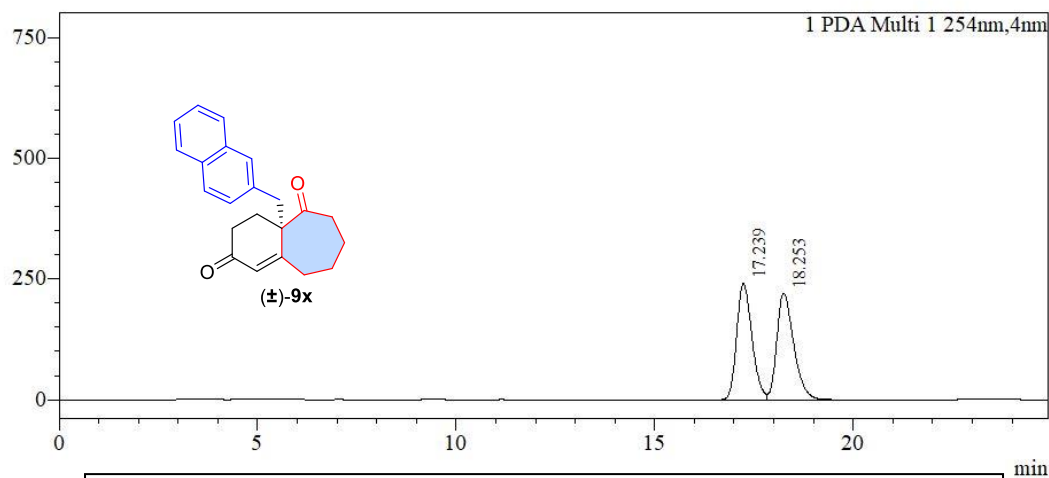
Chiral (-)-**9u** (93% *ee*)



PeakTable						
PDA Ch1 254nm 4nm						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT35.753	35.753	2976790	47076	3.532	6.269
2	RT39.090	39.090	81293073	703832	96.468	93.731
Total			84269863	750909	100.000	100.000

Racemic (\pm)-**9x**:

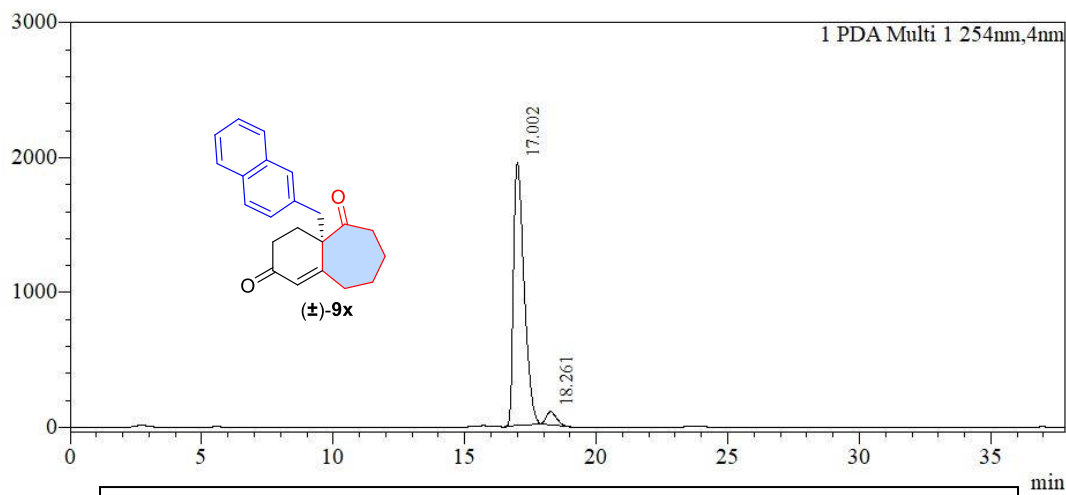
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Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:17.239	17.239	6457933	240880	49.639	52.218
2	RT:18.253	18.253	6551766	220415	50.361	47.782
Total			13009699	461295	100.000	100.000

Chiral (-)-**9x** (91% *ee*)

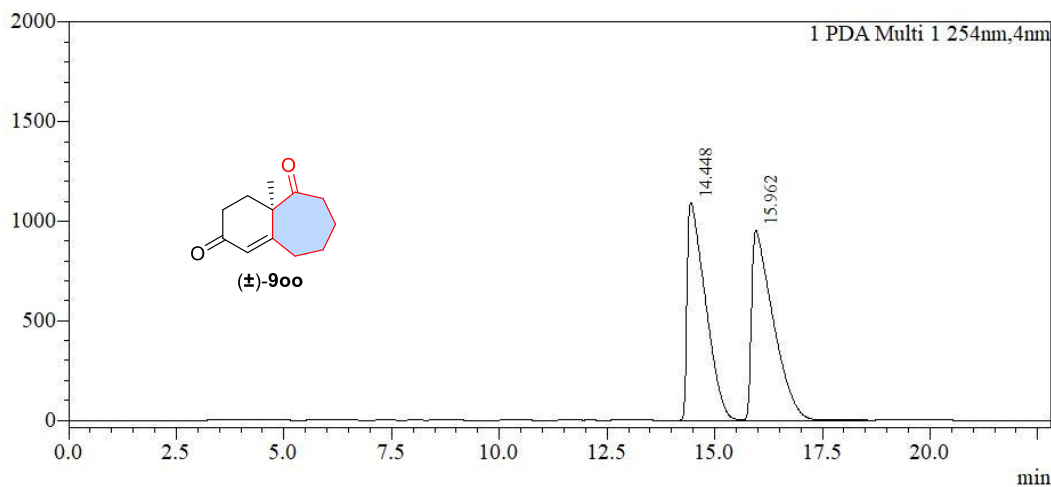
mAU



Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:17.002	17.002	54684325	1950804	95.542	95.218
2	RT:18.261	18.261	2551521	97967	4.458	4.782
Total			57235847	2048771	100.000	100.000

Racemic (\pm)-**9oo**:

mAU



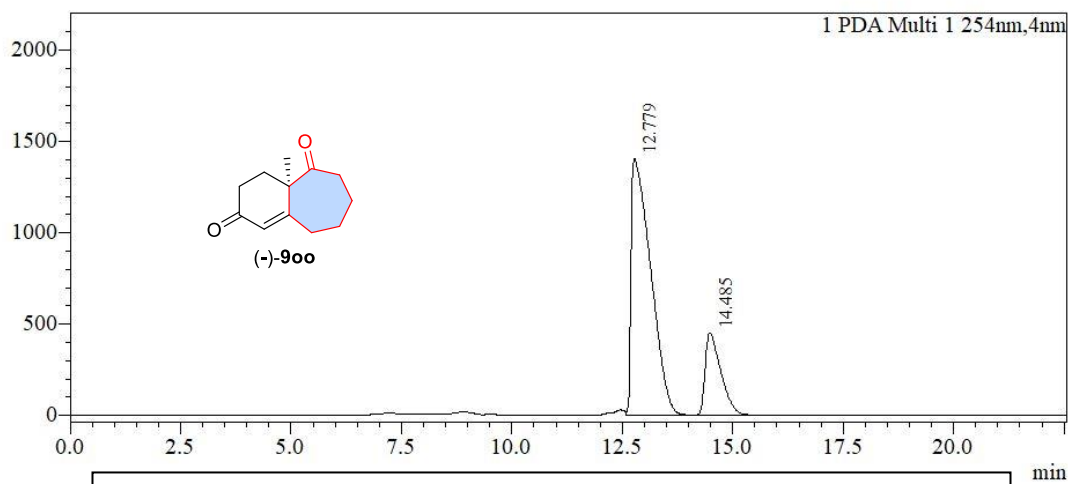
PDA Ch1 254nm

Peak Table

Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:14.448	14.448	32431820	1094791	49.304	53.502
2	RT:15.962	15.962	33347605	951467	50.696	46.498
Total			65779425	2046258	100.000	100.000

Chiral (-)-**9oo** (59% *ee*)

mAU

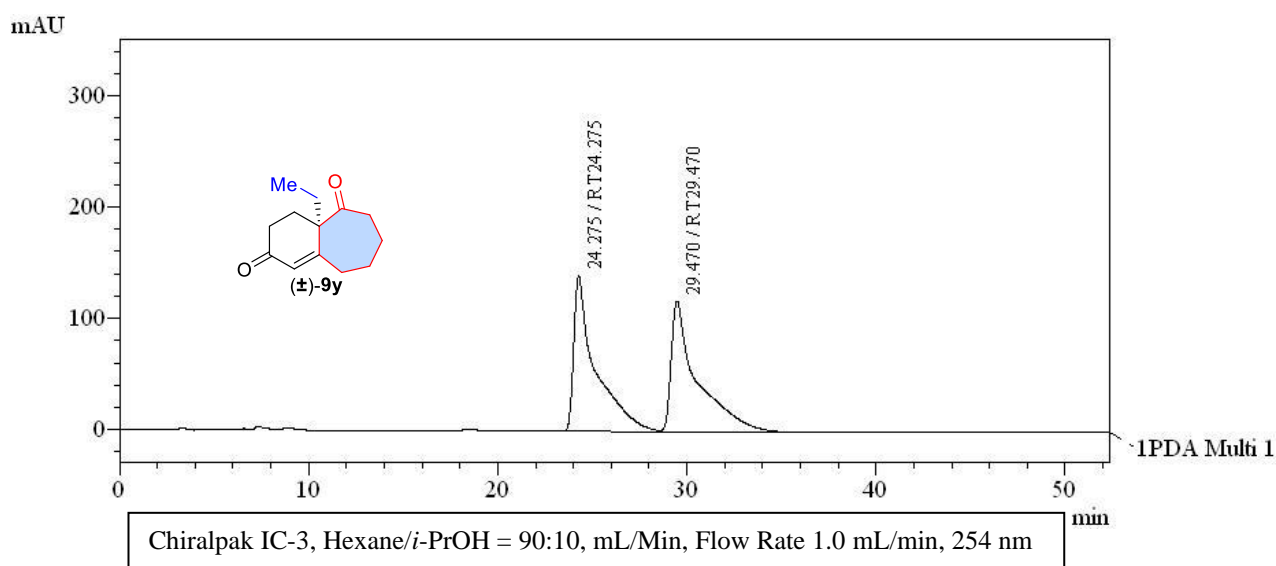


PDA Ch1 254nm

Peak Table

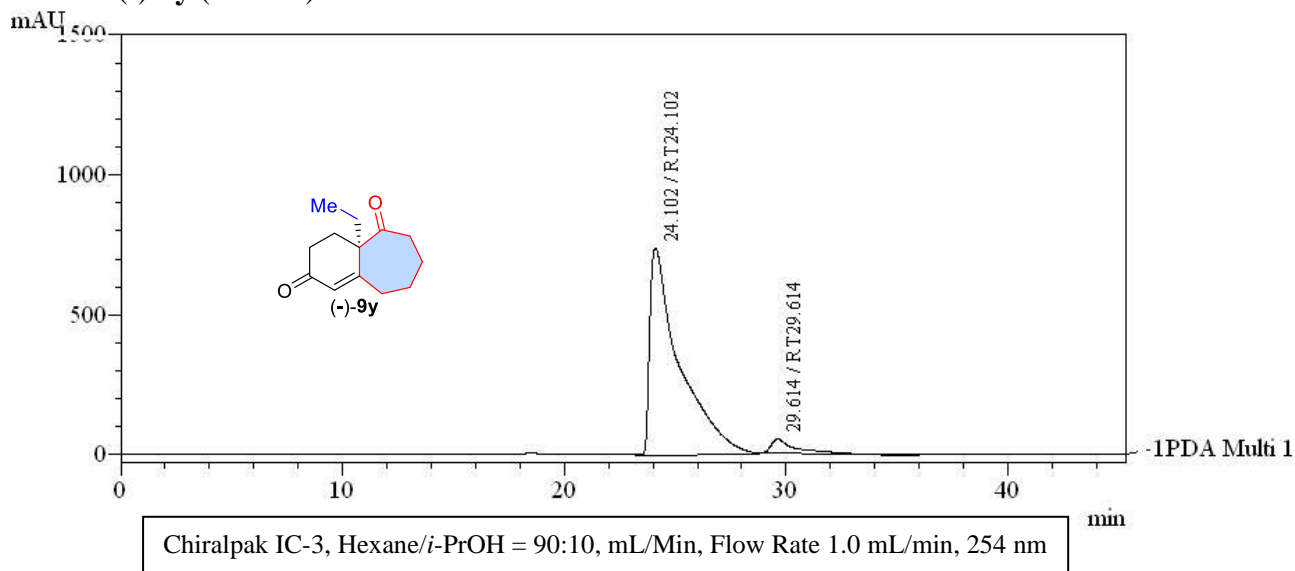
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:12.779	12.779	43585722	1406369	79.434	75.679
2	RT:14.485	14.485	11284423	451975	20.566	24.321
Total			54870145	1858344	100.000	100.000

Racemic (\pm)-**9y**:



PeakTable						
PDA Ch1 254nm 4nm						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT24.275	24.275	11131445	139400	50.023	54.299
2	RT29.470	29.470	11121054	117327	49.977	45.701
Total			22252499	256728	100.000	100.000

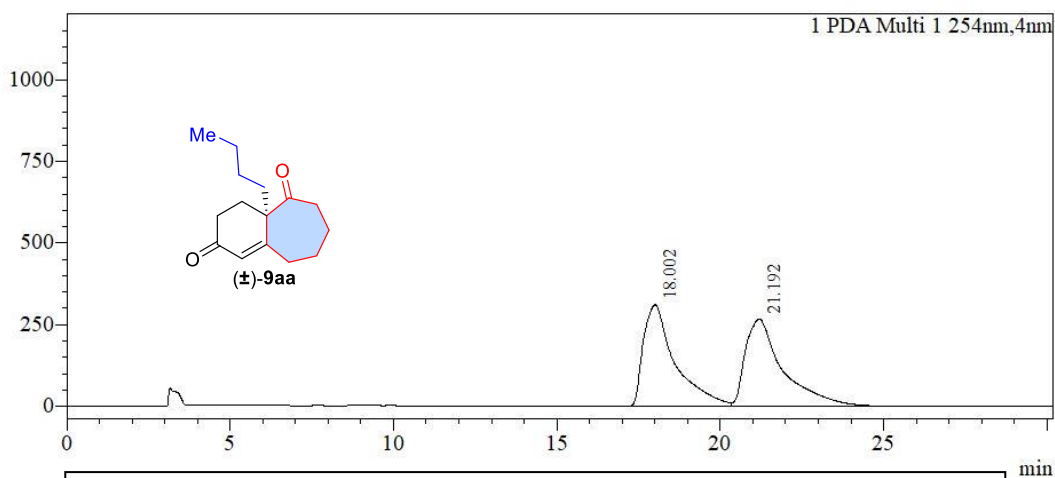
Chiral (-)-**9y** (88% *ee*)



PeakTable						
PDA Ch1 254nm 4nm						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT24.102	24.102	68812069	737997	94.186	93.498
2	RT29.614	29.614	4247577	51322	5.814	6.502
Total			73059646	789319	100.000	100.000

Racemic (\pm)-**9aa**:

mAU

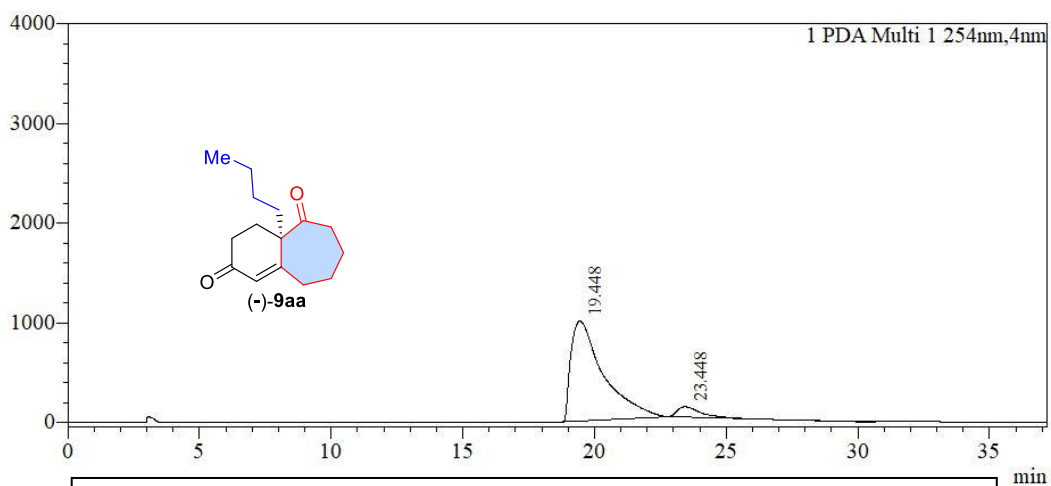


Chiralpak IC-3, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

Peak Table						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:18.002	18.002	20921320	310113	49.473	53.767
2	RT:21.192	21.192	21367423	266663	50.527	46.233
Total			42288744	576776	100.000	100.000

Chiral (-)-**9aa** (86% *ee*)

mAU

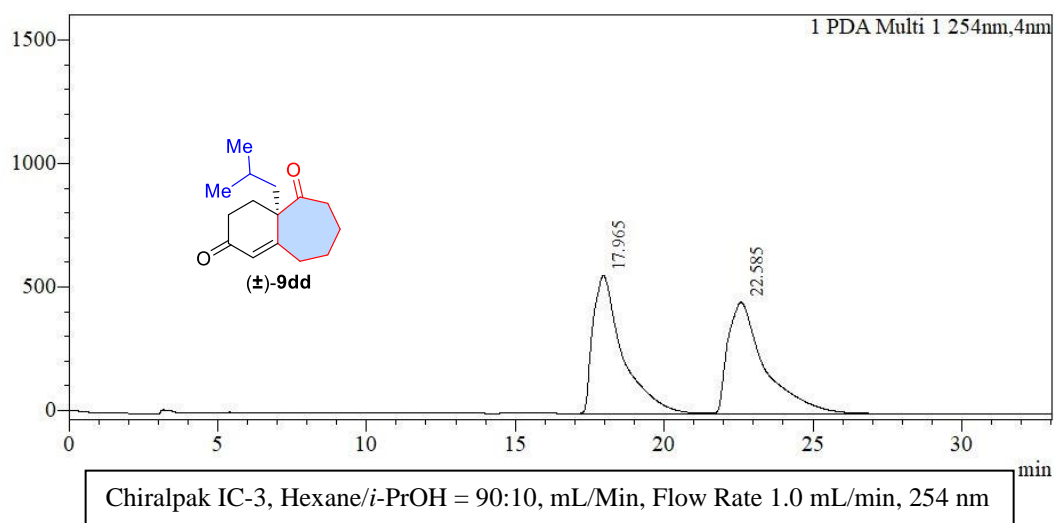


Chiralpak IC-3, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

Peak Table						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:19.448	19.448	85862984	1002047	92.972	90.702
2	RT:23.448	23.448	6490944	102727	7.028	9.298
Total			92353927	1104775	100.000	100.000

Racemic (\pm)-9dd:

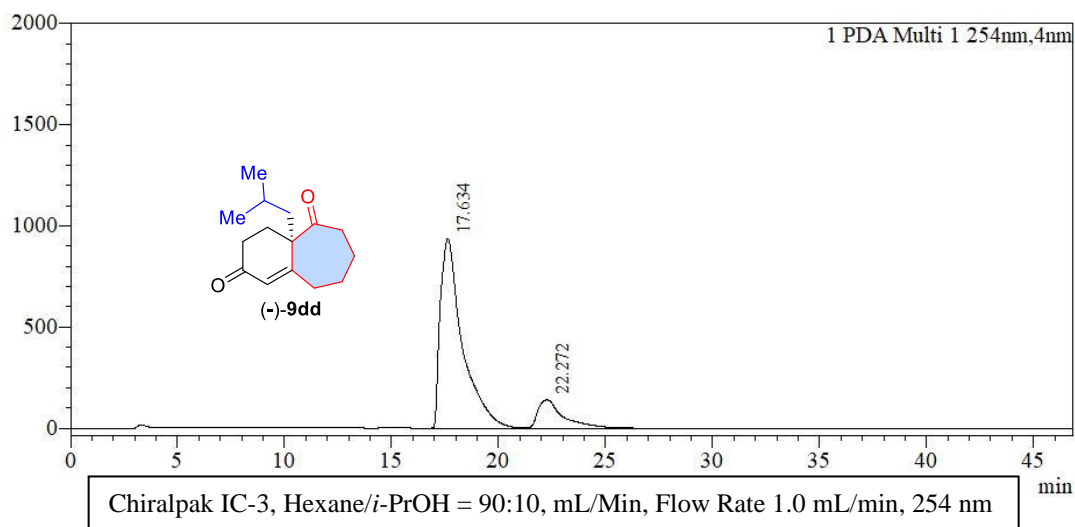
mAU



Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:17.965	17.965	38627409	558297	49.945	55.364
2	RT:22.585	22.585	38712861	450108	50.055	44.636
Total			77340269	1008404	100.000	100.000

Chiral (-)-9dd (71% ee)

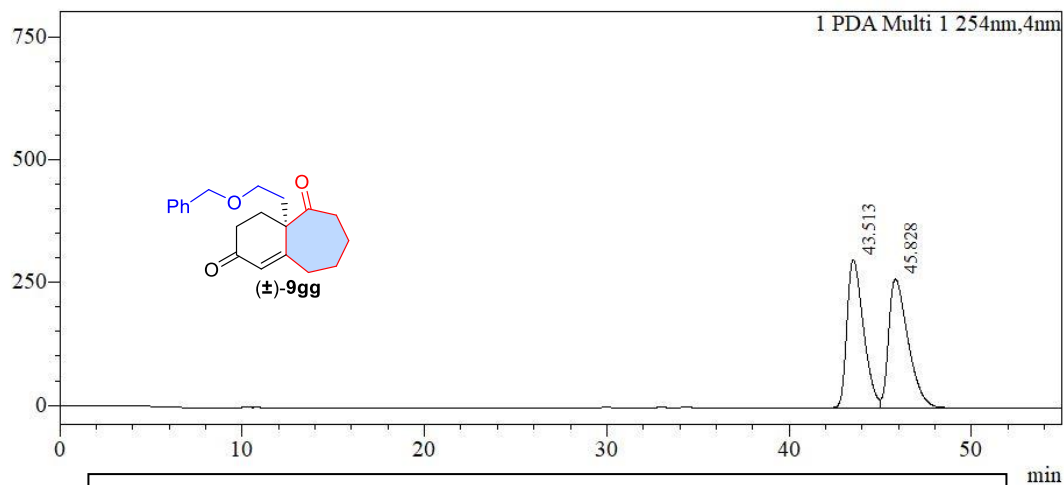
mAU



Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:17.634	17.634	67256576	938511	85.464	87.053
2	RT:22.272	22.272	11438822	139584	14.536	12.947
Total			78695398	1078095	100.000	100.000

Racemic (\pm)-**9gg**:

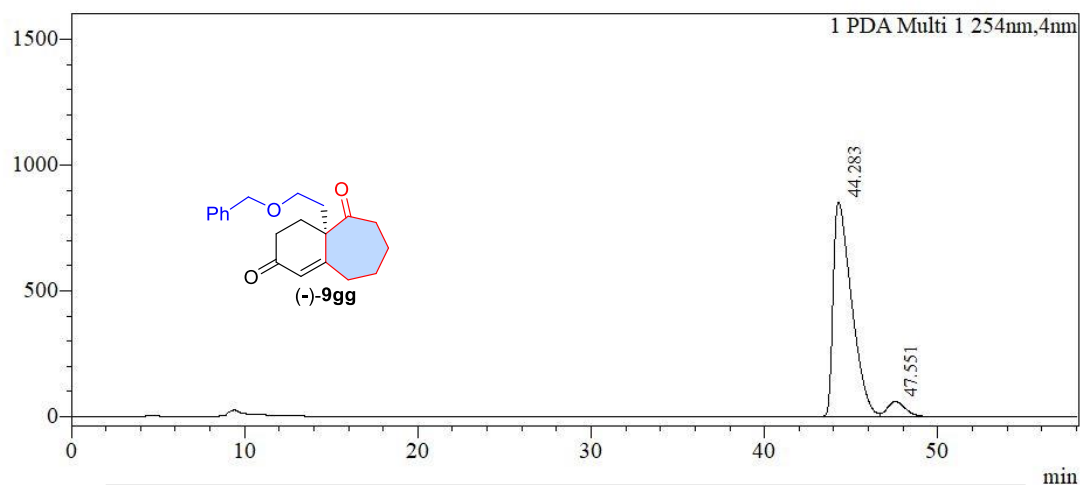
mAU



Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:43.513	43.513	19009236	301361	49.689	53.512
2	RT:45.828	45.828	19246972	261805	50.311	46.488
Total			38256208	563166	100.000	100.000

Chiral (-)-**9gg** (87% *ee*)

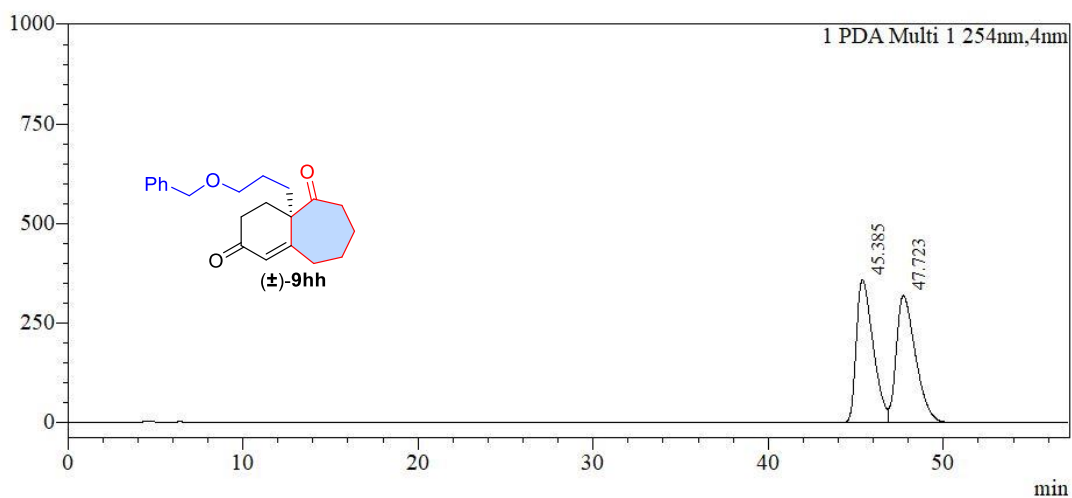
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Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:44.283	44.283	63190445	853864	93.557	93.417
2	RT:47.551	47.551	4351469	60170	6.443	6.583
Total			67541913	914034	100.000	100.000

Racemic (\pm)-9hh:

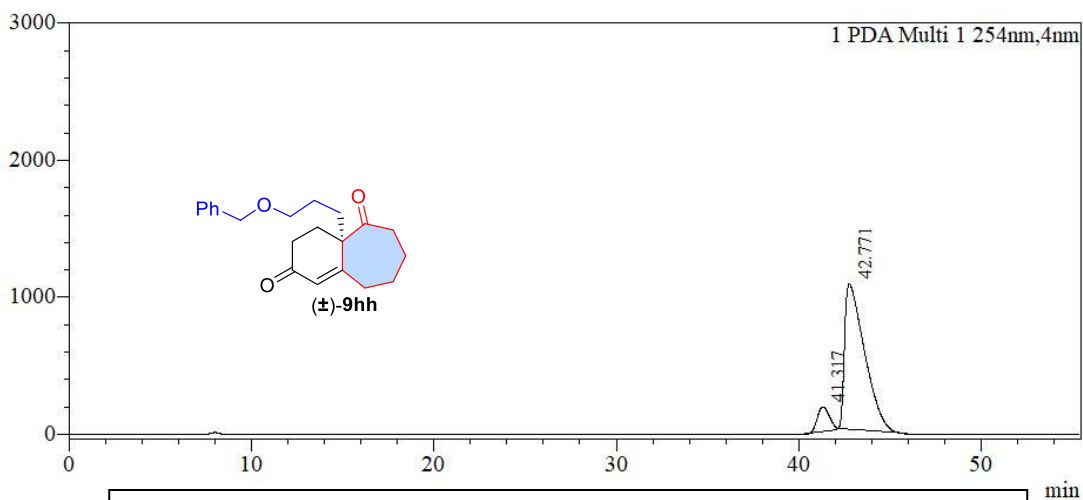
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Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:45.385	45.385	23914563	359072	49.392	52.900
2	RT:47.723	47.723	24503212	319698	50.608	47.100
Total			48417775	678770	100.000	100.000

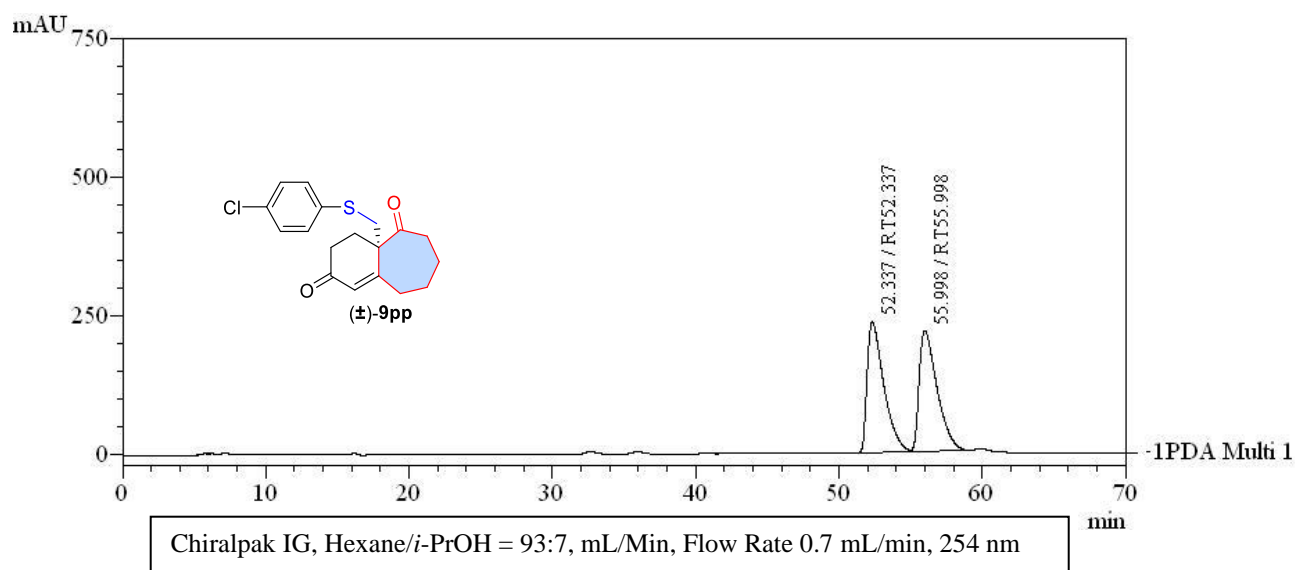
Chiral (-)-9hh (82% ee)

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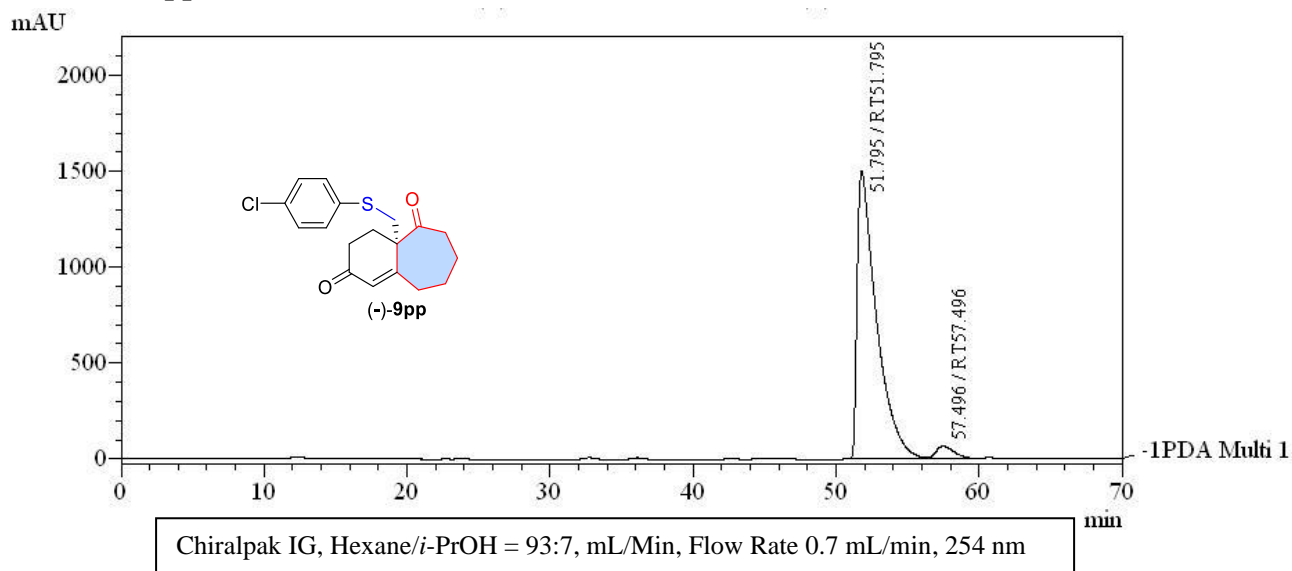
Peak Table						
PDA Ch1 254nm						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:41.317	41.317	7974392	177293	9.001	14.345
2	RT:42.771	42.771	80618744	1058667	90.999	85.655
Total			88593136	1235961	100.000	100.000

Racemic (\pm)-**9pp**:



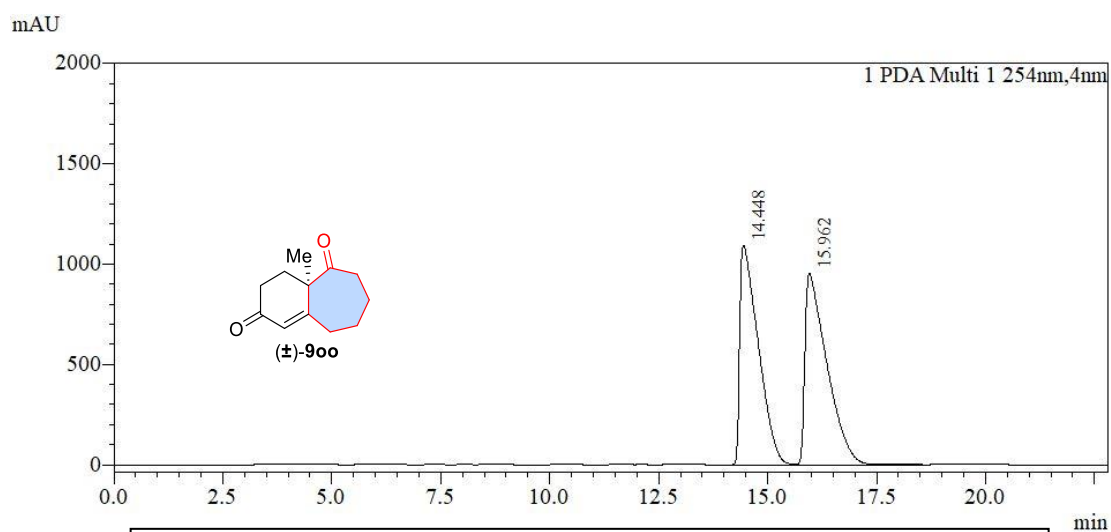
PeakTable						
PDA Ch1 254nm 4nm						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT52.337	52.337	19256715	236522	50.320	51.981
2	RT55.998	55.998	19011717	218490	49.680	48.019
Total			38268432	455013	100.000	100.000

Chiral (-)-**9pp** (92.7% *ee*)



PeakTable						
PDA Ch1 254nm 4nm						
Peak#	Name	Ret. Time	Area	Height	Area %	Height %
1	RT51.795	51.795	140768619	1498966	96.351	95.991
2	RT57.496	57.496	5331269	62599	3.649	4.009
Total			146099888	1561565	100.000	100.000

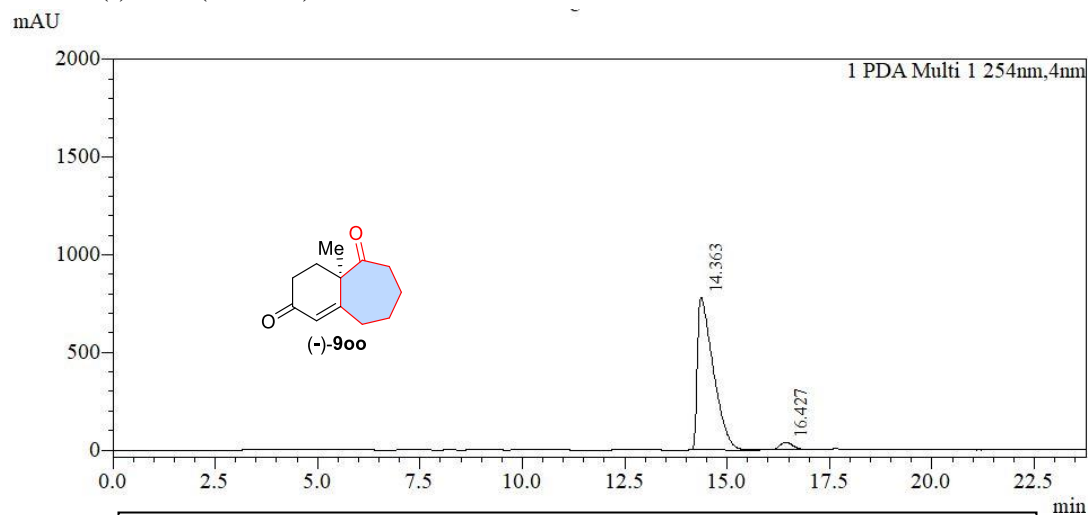
Racemic (\pm)-**9oo**:



Chiralpak ID, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

Peak Table						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:14.448	14.448	32431820	1094791	49.304	53.502
2	RT:15.962	15.962	33347605	951467	50.696	46.498
Total			65779425	2046258	100.000	100.000

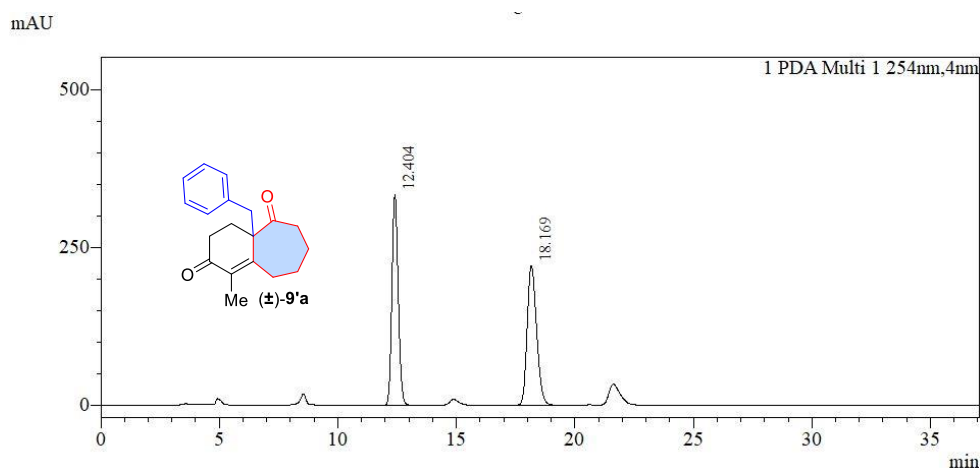
Chiral (-)-**9oo** (92% *ee*)



Chiralpak ID, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

Peak Table						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:14.363	14.363	21232006	782667	96.111	95.427
2	RT:16.427	16.427	859196	37507	3.889	4.573
Total			22091202	820174	100.000	100.000

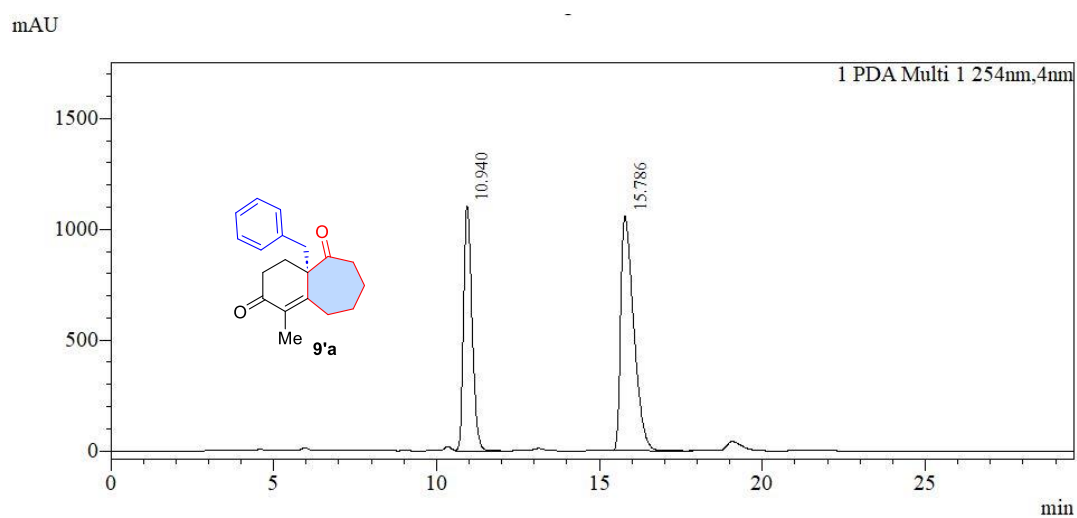
Racemic (\pm)-**9'a**:



Chiralpak IG, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min,

Peak Table						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:12.404	12.404	6108026	333233	50.027	60.160
2	RT:18.169	18.169	6101543	220681	49.973	39.840
Total			12209569	553914	100.000	100.000

Chiral **9'a** (19% *ee*):



Chiralpak IG, Hexane/*i*-PrOH = 90:10, mL/Min, Flow Rate 1.0 mL/min, 254 nm

Peak Table						
Peak#	Name	Ret. Time	Area	Height	Area%	Height%
1	RT:10.940	10.940	20064698	1107029	40.551	51.060
2	RT:15.786	15.786	29415907	1061073	59.449	48.940
Total			49480605	2168102	100.000	100.000