

Supporting Information

Chiral bicyclo[2.2.2]octa-2,5-diene ligand substituted with ferrocenyl group and its use for rhodium-catalyzed asymmetric 1,4-addition reactions

Bo Zhou,^a Chau Ming So,^b Yixin Lu*^a and Tamio Hayashi*^{a,b}

^a Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

^b Institute of Materials Research and Engineering, A*STAR, 3 Research Link, Singapore 117602, Singapore

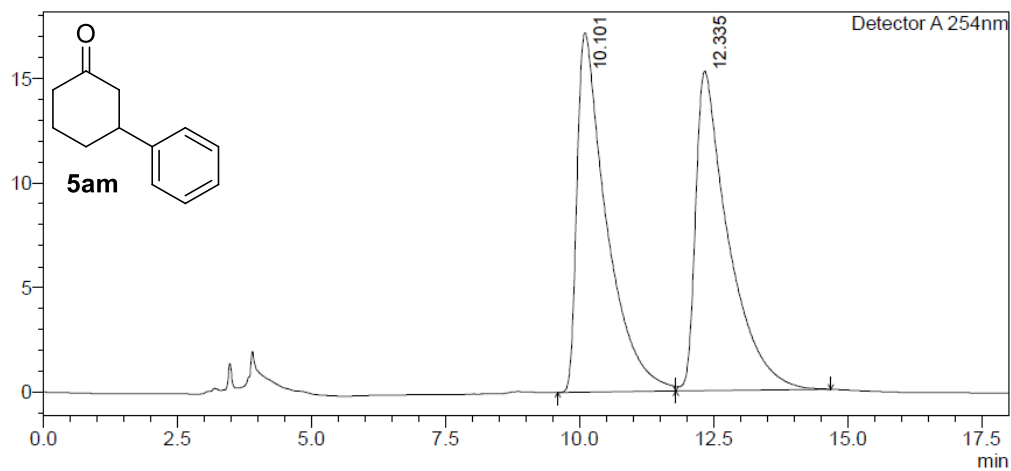
Contents of Supporting Information:

I.	HPLC charts for determination of % ee	S2-S19
II.	NMR spectra for new compounds	S20-S23

I. HPLC charts for determination of % ee

<Chromatogram>

mV



<Peak Table>

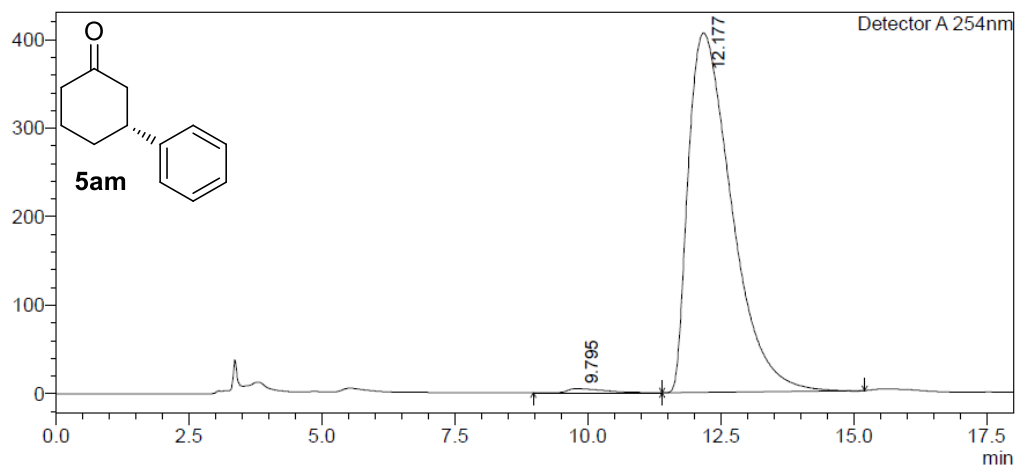
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.101	657237	17185	50.252		M	
2	12.335	650651	15280	49.748		V M	
Total		1307887	32465				

Racemic **5am**

<Chromatogram>

mV



<Peak Table>

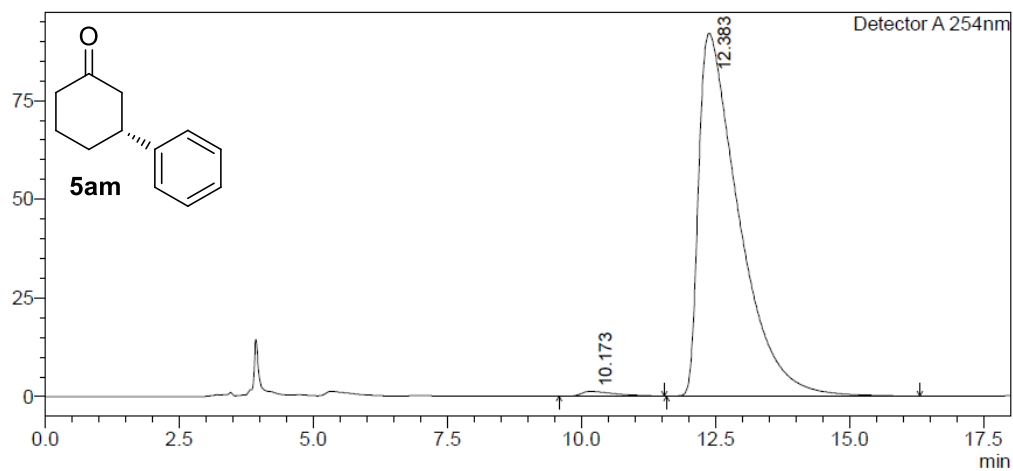
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.795	241743	4905	1.038		M	
2	12.177	23038960	405952	98.962		M	
Total		23280704	410857				

Enantiomerically enriched **5am** with $[\text{RhCl}((R,R)\text{-Fc,Ph-bod})_2]$

<Chromatogram>

mV



<Peak Table>

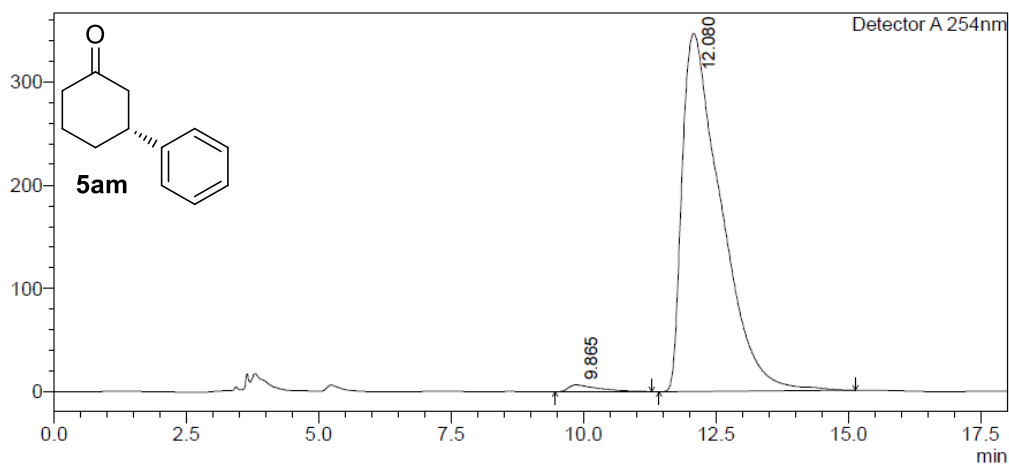
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.173	51357	1215	1.059		M	
2	12.383	4798438	91847	98.941		M	
Total		4849795	93062				

Enantiomerically enriched **5am** with (*R,R*)-Fc,Ph-bod

<Chromatogram>

mV



<Peak Table>

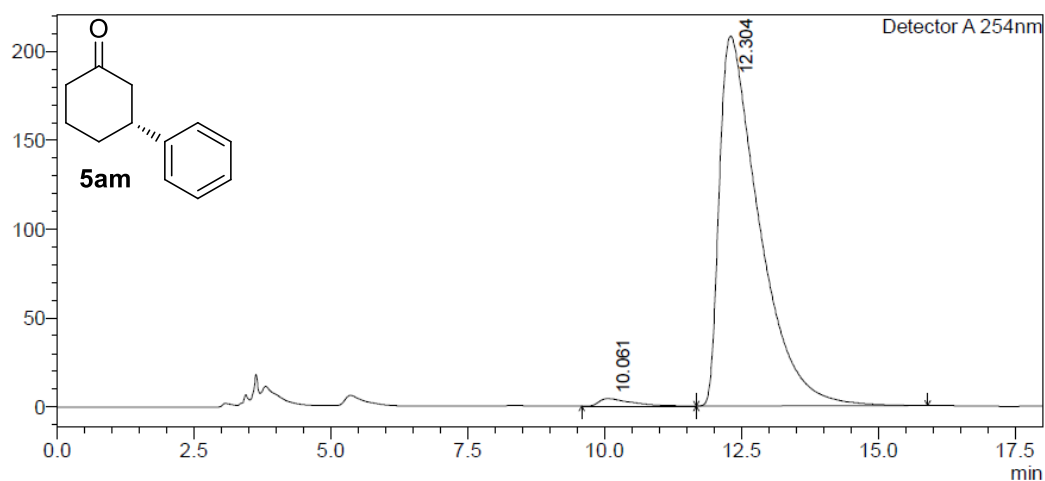
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.865	264326	6529	1.470		M	
2	12.080	17716078	346901	98.530		M	
Total		17980405	353430				

Enantiomerically enriched **5am** with [RhCl(*(R,R)*-Ph-bod)]₂

<Chromatogram>

mV



<Peak Table>

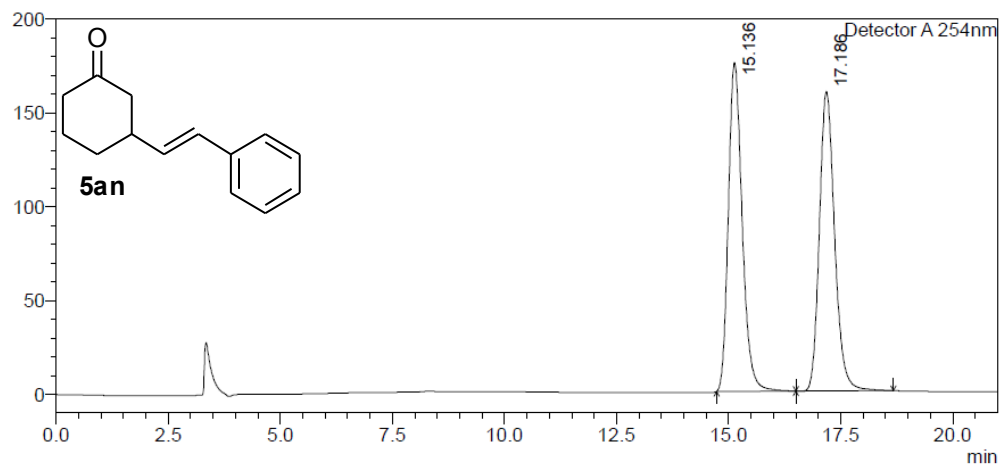
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.061	176078	4255	1.641		M	
2	12.304	10554414	208118	98.359		M	
Total		10730492	212373				

Enantiomerically enriched **5am** with (*R,R*)-Ph-bod

<Chromatogram>

mV



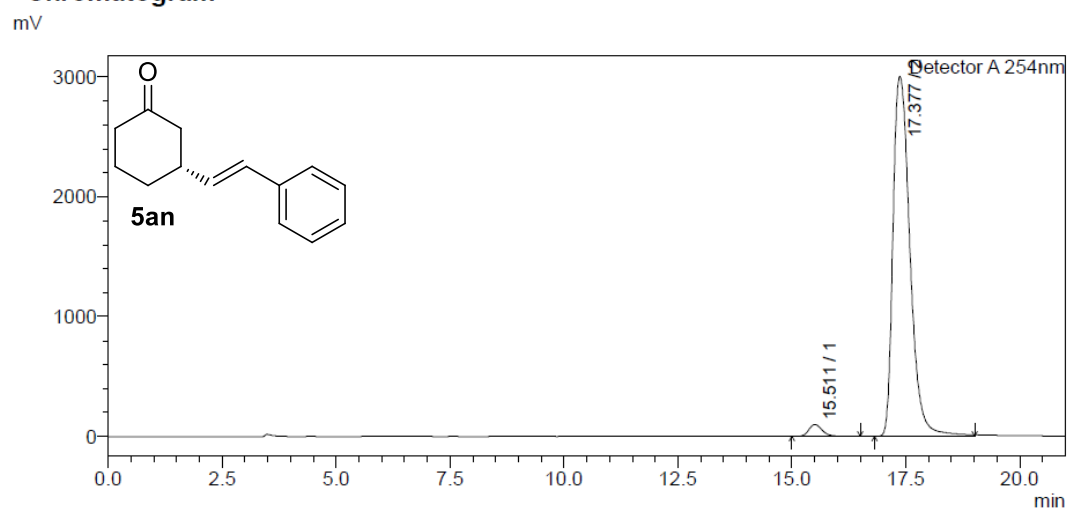
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.136	3771479	175340	49.926		M	
2	17.186	3782591	159772	50.074		M	
Total		7554069	335112				

Racemic **5an**

<Chromatogram>

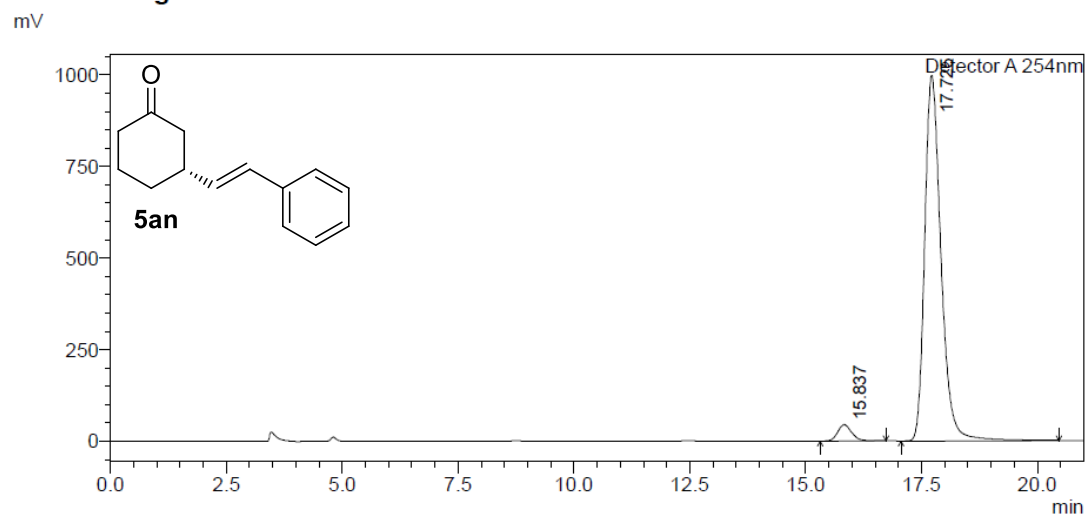


<Peak Table>

Detector A 254nm							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.511	2026461	99637	2.541		M	
2	17.377	77717749	3002335	97.459		M	
Total		79744209	3101972				

Enantiomerically enriched **5an** with (*R,R*)-Fc,Ph-bod

<Chromatogram>



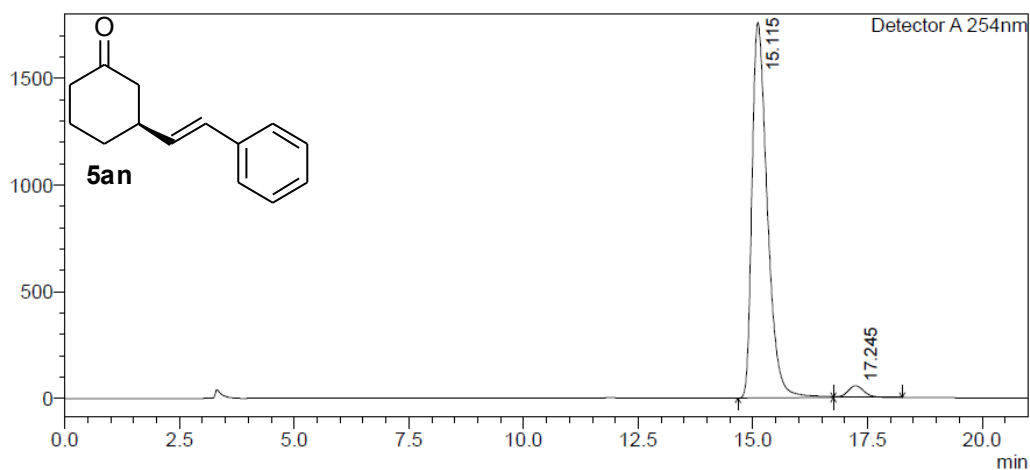
<Peak Table>

Detector A 254nm							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.837	943051	44393	3.725		M	
2	17.725	24377024	995938	96.275		M	
Total		25320075	1040332				

Enantiomerically enriched **5an** with (*R,R*)-Ph-bod

<Chromatogram>

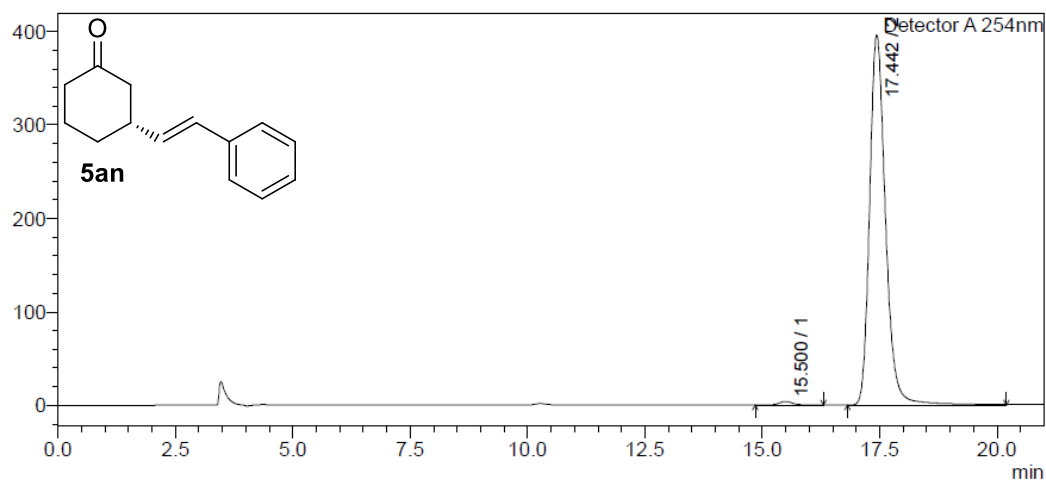
mV



Enantiomerically enriched **5an** with $[\text{RhCl}((S,S)\text{-Ph-tfb})]_2$

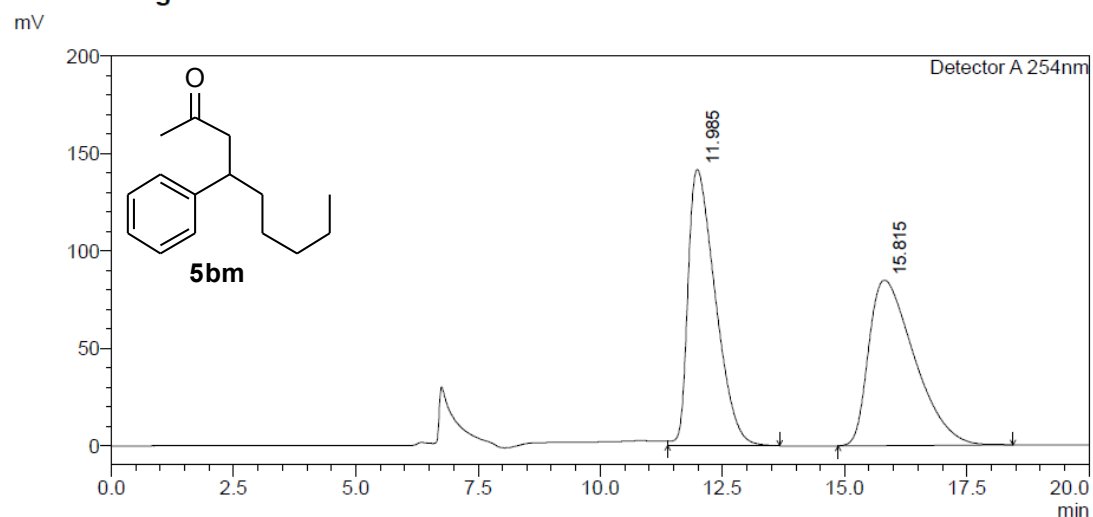
<Chromatogram>

mV



Enantiomerically enriched **5an** with $[\text{RhCl}((S,S)\text{-Fc-tfb})]_2$

<Chromatogram>

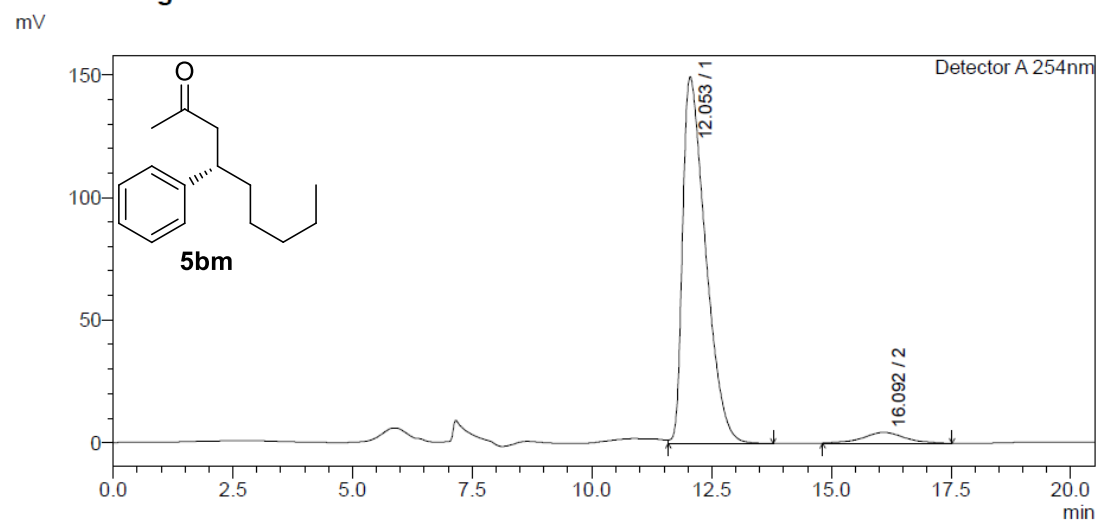


<Peak Table>

Detector A 254nm							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.985	5528080	141839	50.022		M	
2	15.815	5523270	84968	49.978		M	
Total		11051350	226807				

Racemic **5bm**

<Chromatogram>



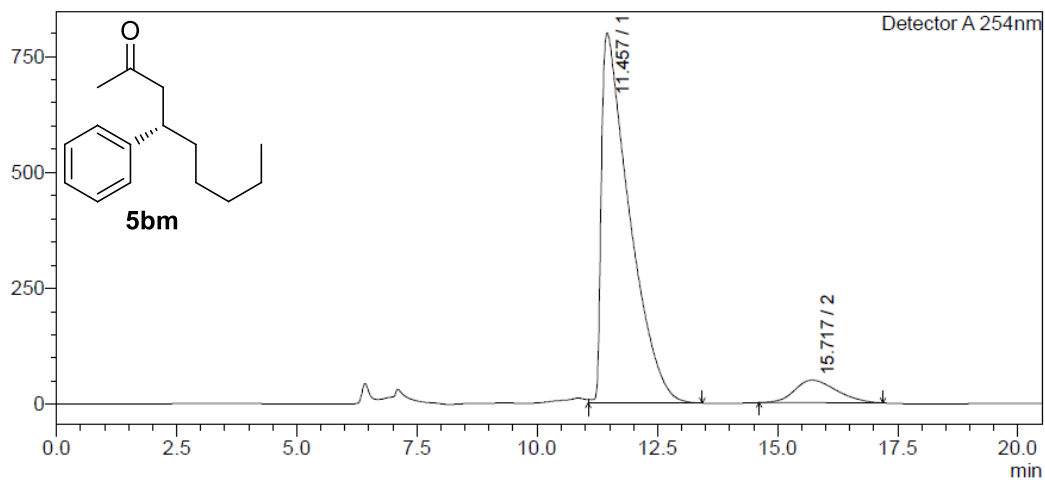
<Peak Table>

Detector A 254nm							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.053	4983541	149491	94.957		M	
2	16.092	264683	4402	5.043		M	
Total		5248224	153894				

Enantiomerically enriched **5bm** with (*R,R*)-Fc,Ph-bod

<Chromatogram>

mV



<Peak Table>

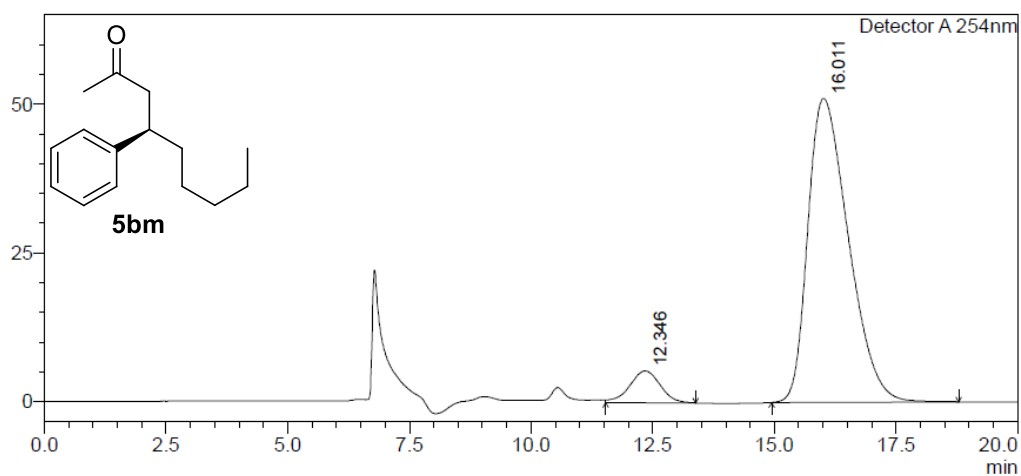
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.457	32340525	798414	91.566		M	
2	15.717	2978711	48772	8.434		M	
Total		35319235	847186				

Enantiomerically enriched **5bm** with (*R,R*)-Ph-bod

<Chromatogram>

mV



<Peak Table>

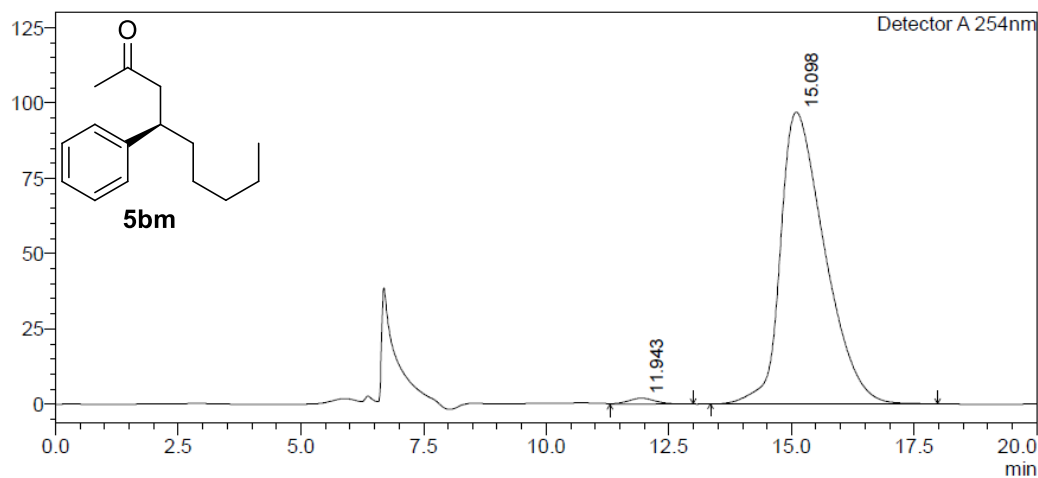
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.346	233318	5335	7.301		M	
2	16.011	2962170	51136	92.699		M	
Total		3195488	56471				

Enantiomerically enriched **5bm** with [RhCl((*S,S*)-Ph-tfb)]₂

<Chromatogram>

mV



<Peak Table>

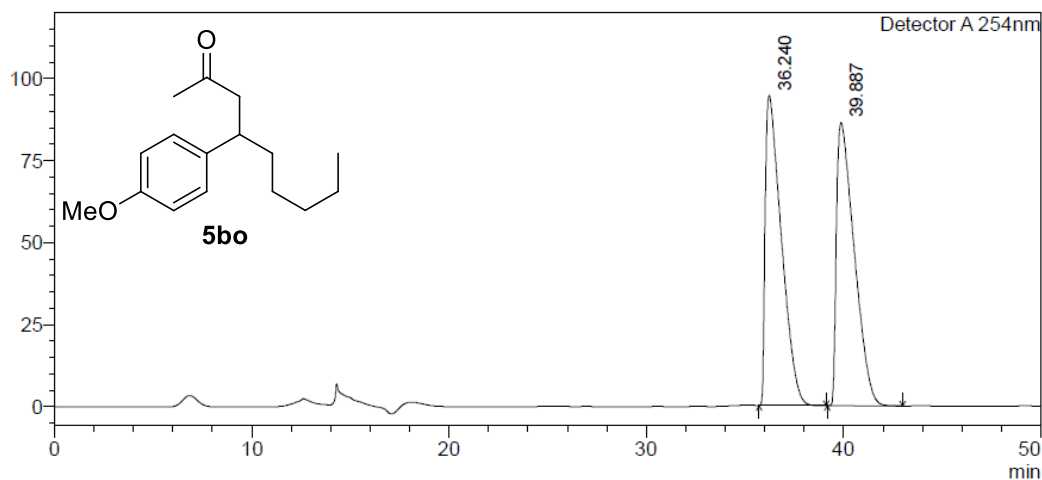
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.943	72987	1899	1.183		M	
2	15.098	6094959	96991	98.817		M	
Total		6167946	98890				

Enantiomerically enriched **5bm** with $[\text{RhCl}((R,R)\text{-Fc-tfb})_2]$

<Chromatogram>

mV



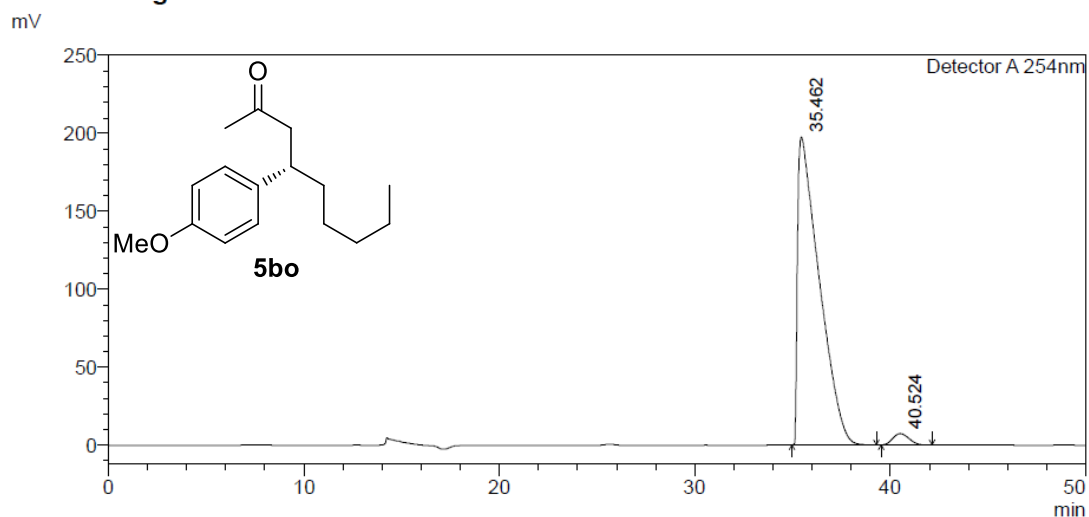
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	36.240	5405584	94661	49.870		M	
2	39.887	5433667	86425	50.130		M	
Total		10839251	181086				

Racemic **5bo**

<Chromatogram>



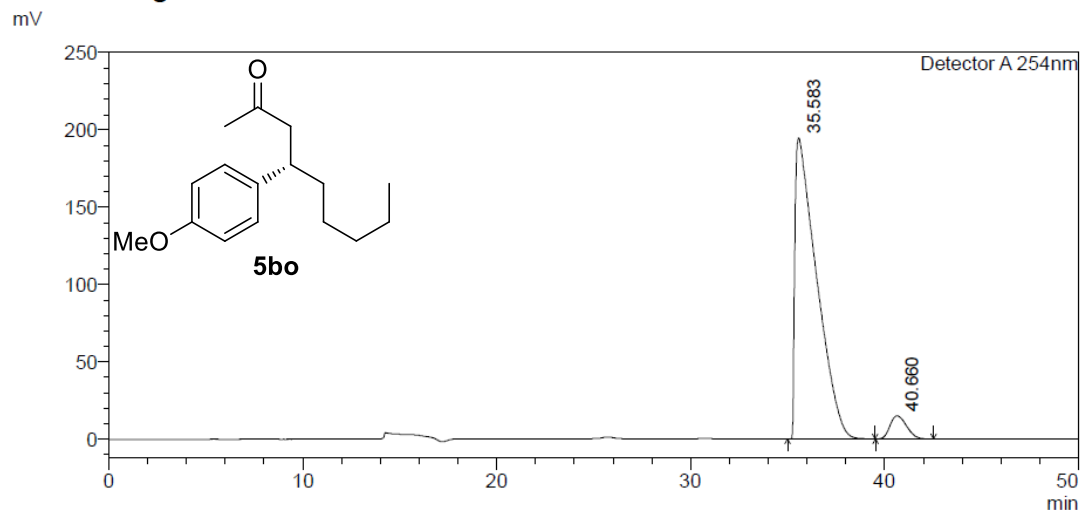
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.462	15188649	197404	97.336		M	
2	40.524	415628	7227	2.664		M	
Total		15604277	204632				

Enantiomerically enriched **5bo** with (*R,R*)-Fc,Ph-bod

<Chromatogram>



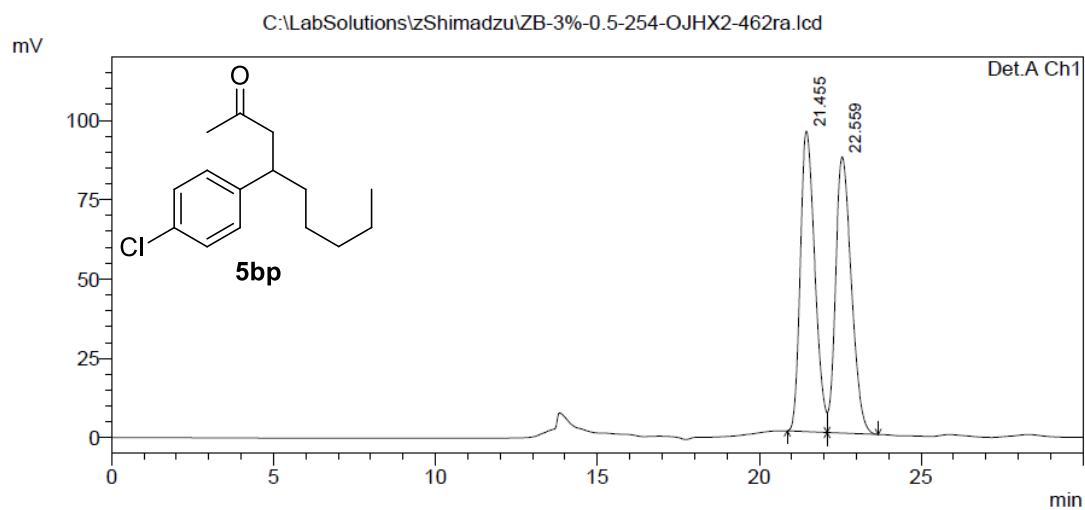
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.583	15118157	194733	94.505		M	
2	40.660	878968	14907	5.495		M	
Total		15997125	209640				

Enantiomerically enriched **5bo** with (*R,R*)-Ph-bod

<Chromatogram>

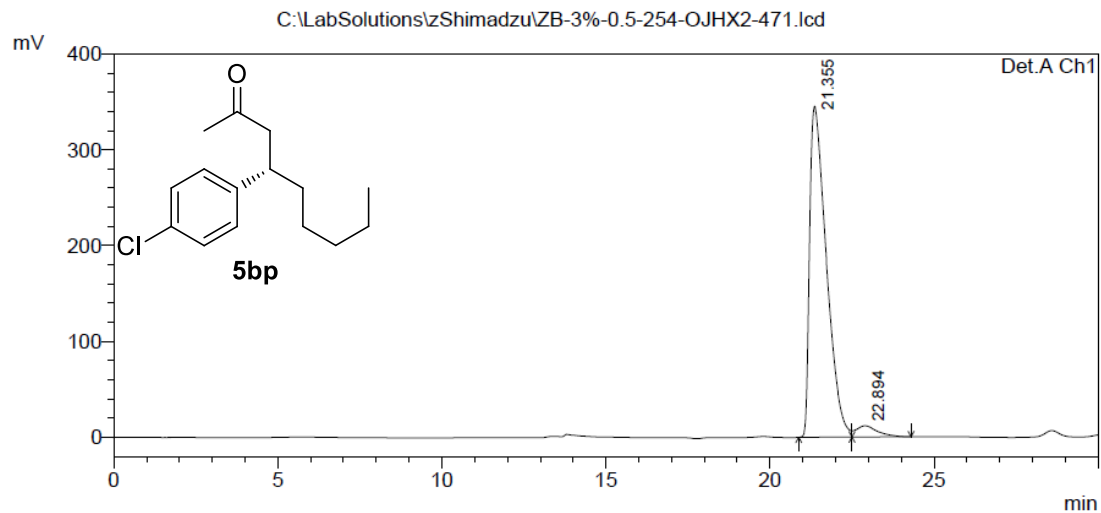


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.455	2950729	94661	50.011	52.112
2	22.559	2949437	86986	49.989	47.888
Total		5900165	181647	100.000	100.000

Racemic **5bp**

<Chromatogram>

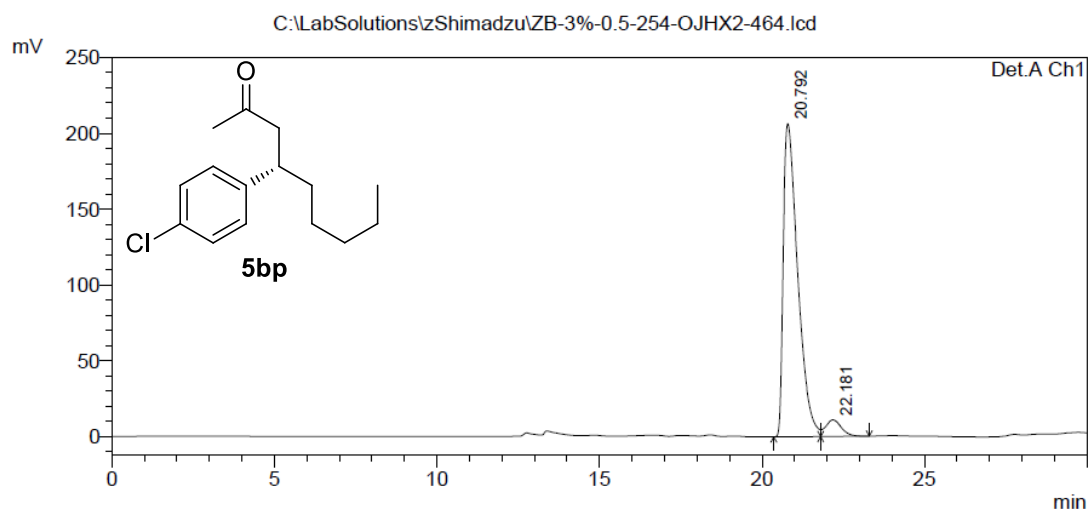


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.355	12238628	345554	95.804	96.736
2	22.894	536049	11660	4.196	3.264
Total		12774677	357215	100.000	100.000

Enantiomerically enriched **5bp** with (*R,R*)-Fc,Ph-bod

<Chromatogram>



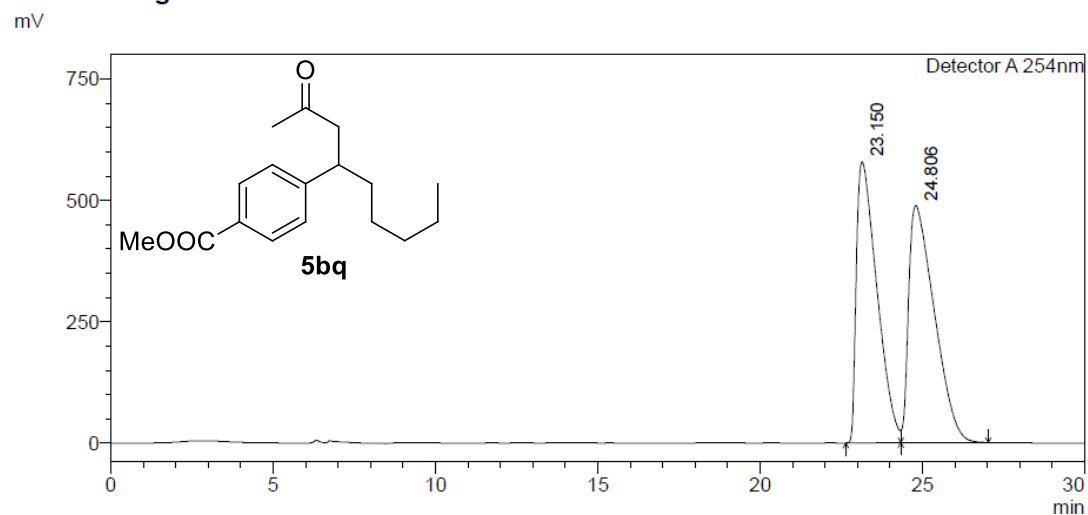
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.792	6383571	206482	94.559	95.014
2	22.181	367309	10835	5.441	4.986
Total		6750880	217317	100.000	100.000

Enantiomerically enriched **5bp** with (*R,R*)-Ph-bod

<Chromatogram>



<Peak Table>

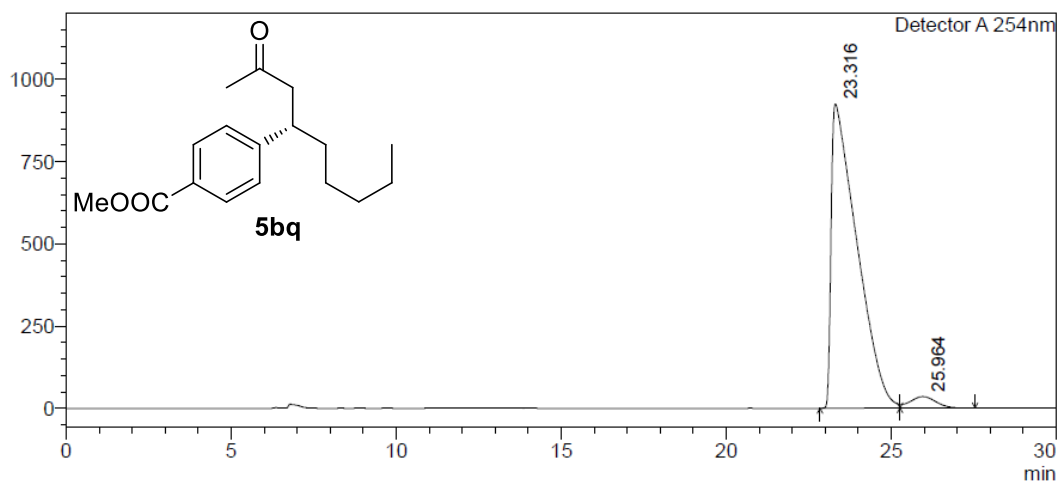
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.150	25648894	579811	48.866		M	
2	24.806	26839627	489263	51.134		V M	
Total		52488521	1069073				

Racemic **5bq**

<Chromatogram>

mV



<Peak Table>

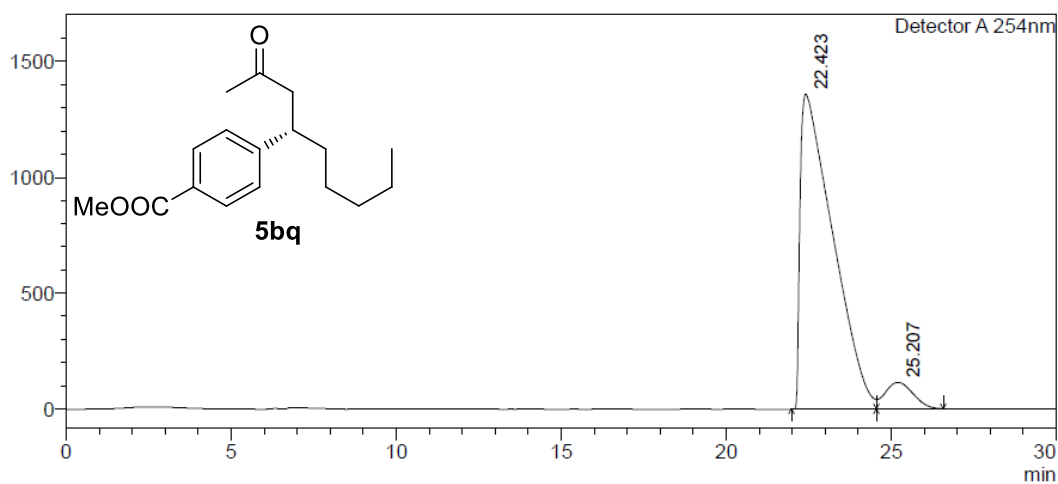
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.316	50321672	925477	96.344		M	
2	25.964	1909313	34895	3.656		V M	
Total		52230985	960372				

Enantiomerically enriched **5bq** with (*R,R*)-Fc,Ph-bod

<Chromatogram>

mV

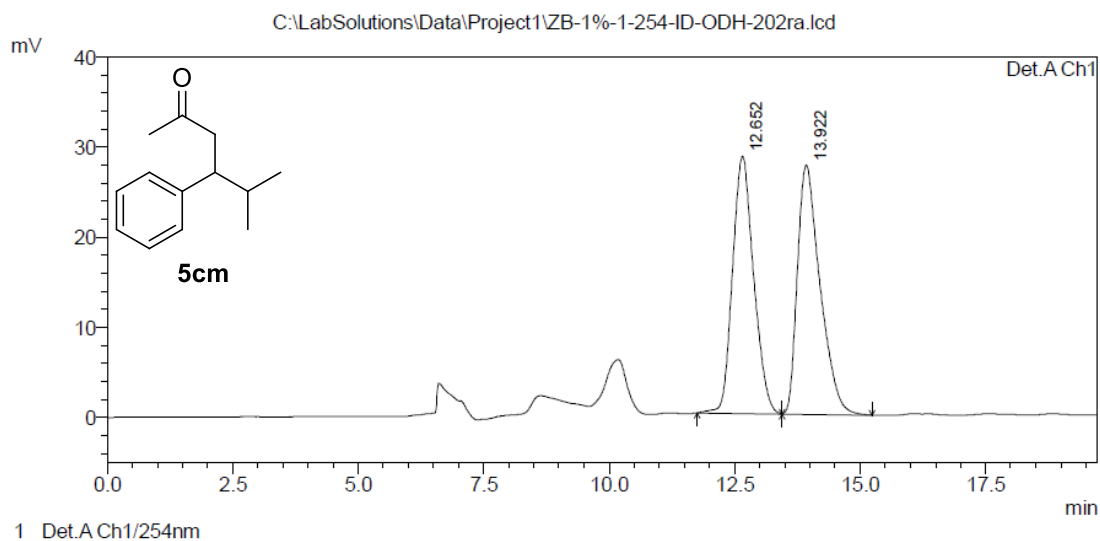


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.423	93085345	1358427	93.256		M	
2	25.207	6731801	114033	6.744		V M	
Total		99817147	1472461				

Enantiomerically enriched **5bq** with (*R,R*)-Ph-bod

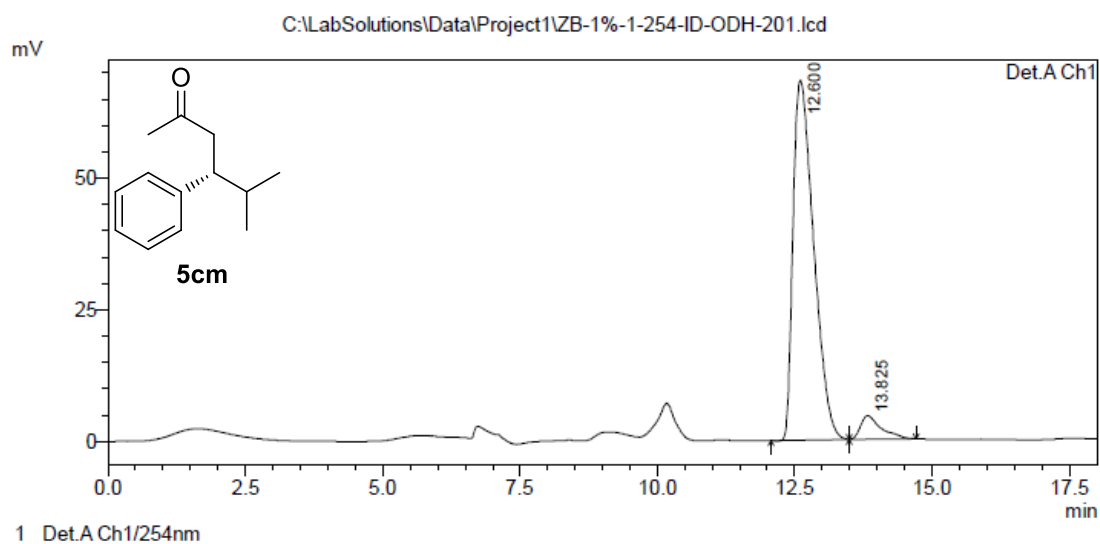


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.652	837117	28576	49.063	50.787
2	13.922	869075	27690	50.937	49.213
Total		1706192	56266	100.000	100.000

Racemic **5cm**

<Chromatogram>

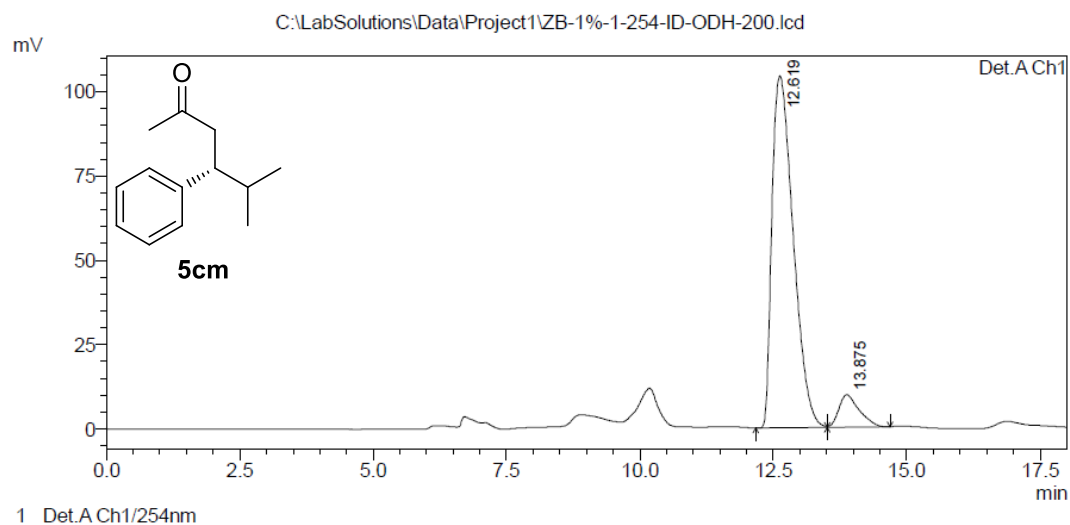


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.600	1788188	68302	93.838	93.848
2	13.825	117423	4477	6.162	6.152
Total		1905611	72779	100.000	100.000

Enantiomerically enriched **5cm** with (*R,R*)-Fc,Ph-bod

<Chromatogram>

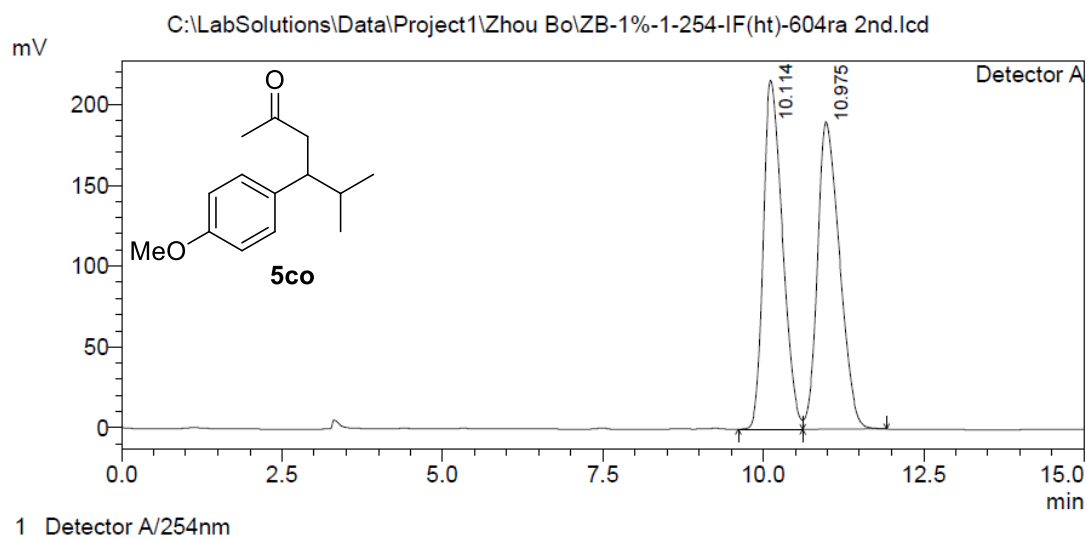


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.619	2889628	104377	91.873	91.562
2	13.875	255610	9619	8.127	8.438
Total		3145239	113996	100.000	100.000

Enantiomerically enriched **5cm** with (*R,R*)-Ph-bod

<Chromatogram>

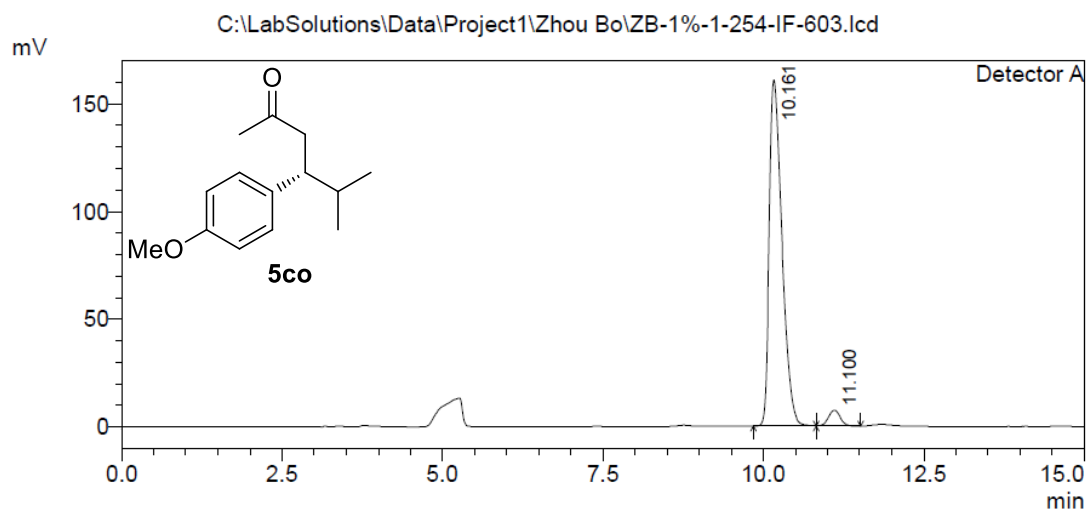


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.114	4482666	215460	49.605	53.141
2	10.975	4554131	189986	50.395	46.859
Total		9036798	405446	100.000	100.000

Racemic **5co**

<Chromatogram>

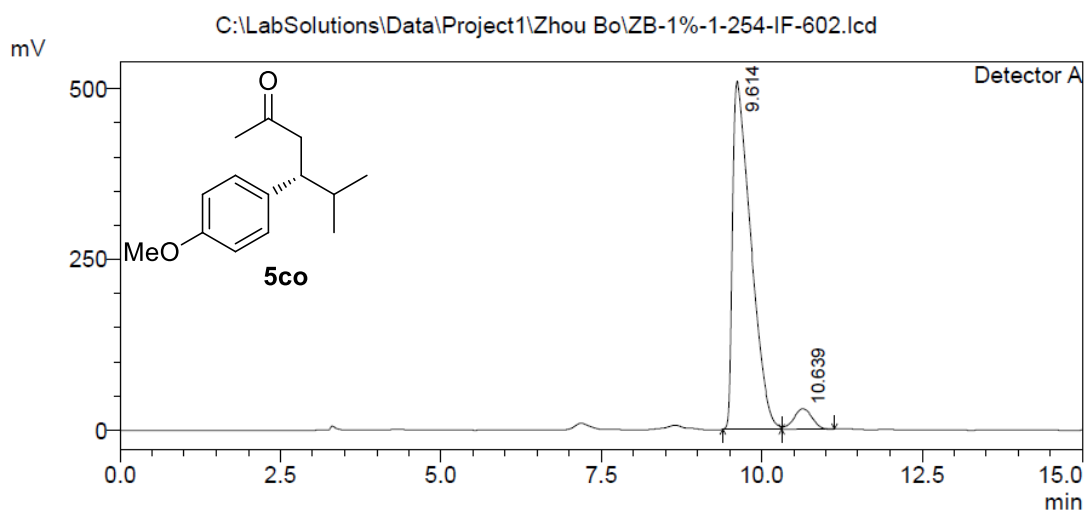


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.161	2213946	160815	95.920	95.641
2	11.100	94183	7330	4.080	4.359
Total		2308129	168145	100.000	100.000

Enantiomerically enriched **5co** with (*R,R*)-Fc,Ph-bod

<Chromatogram>



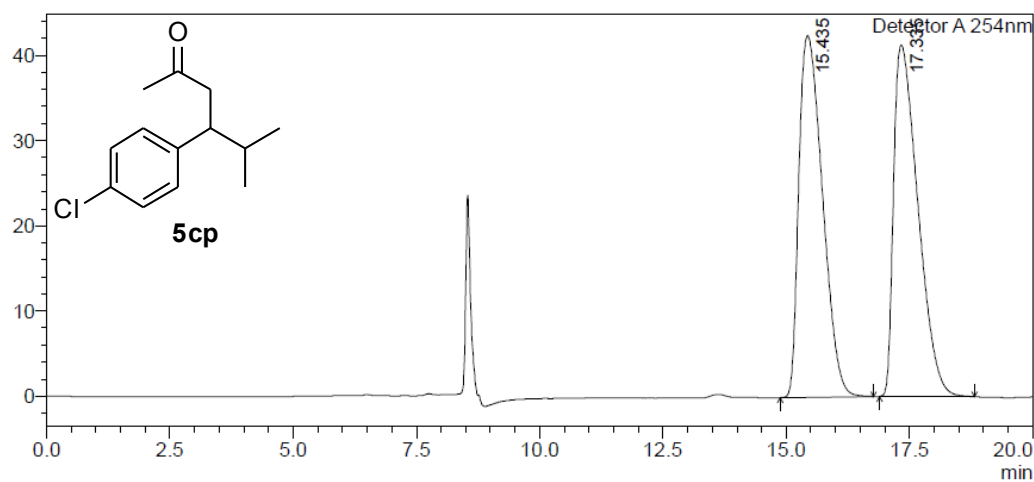
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.614	10152311	509771	94.549	94.484
2	10.639	585321	29758	5.451	5.516
Total		10737631	539530	100.000	100.000

Enantiomerically enriched **5co** with (*R,R*)-Ph-bod

<Chromatogram>

mV



<Peak Table>

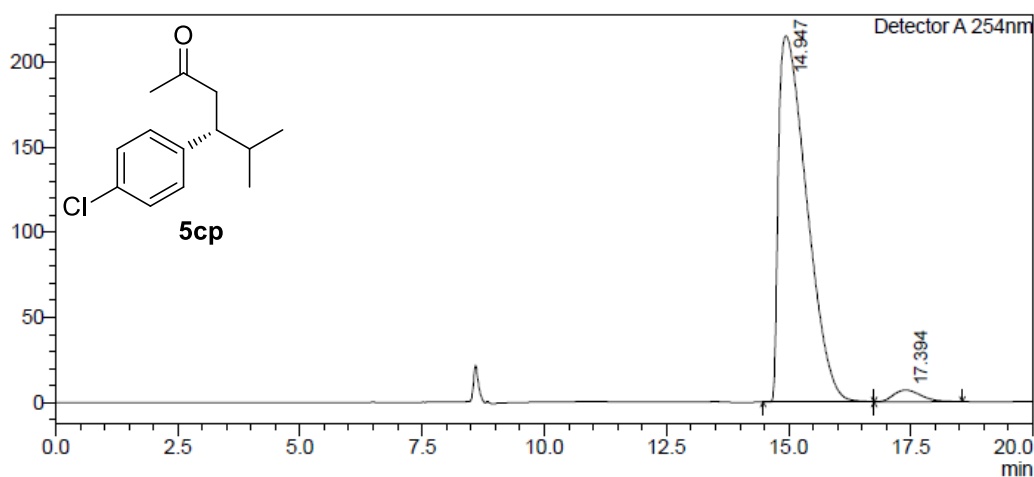
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.435	1417516	42424	50.100		M	
2	17.335	1411878	41240	49.900		M	
Total		2829394	83664				

Racemic **5cp**

<Chromatogram>

mV



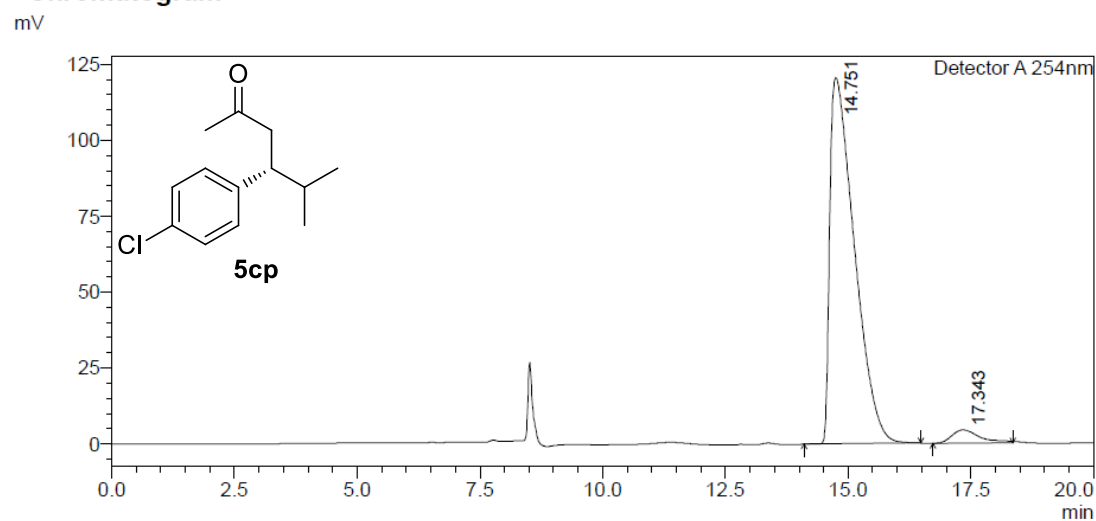
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.947	8623042	215084	96.928		M	
2	17.394	273265	6888	3.072		V M	
Total		8896306	221971				

Enantiomerically enriched **5cp** with (*R,R*)-Fc,Ph-bod

<Chromatogram>



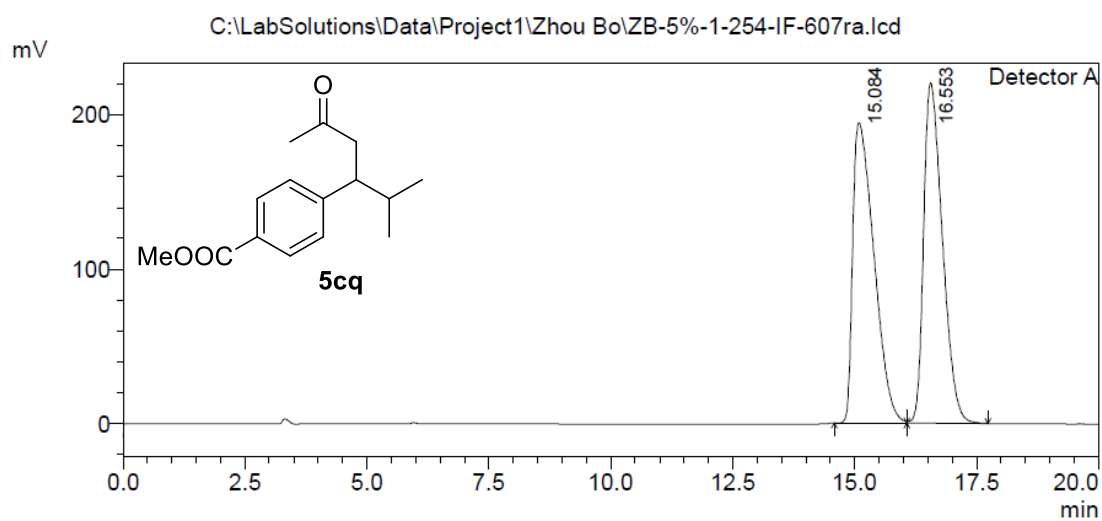
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.751	4202194	120721	95.978		M	
2	17.343	176101	4368	4.022		M	
Total		4378295	125089				

Enantiomerically enriched **5cp** with (*R,R*)-Ph-bod

<Chromatogram>



1 Detector A/254nm

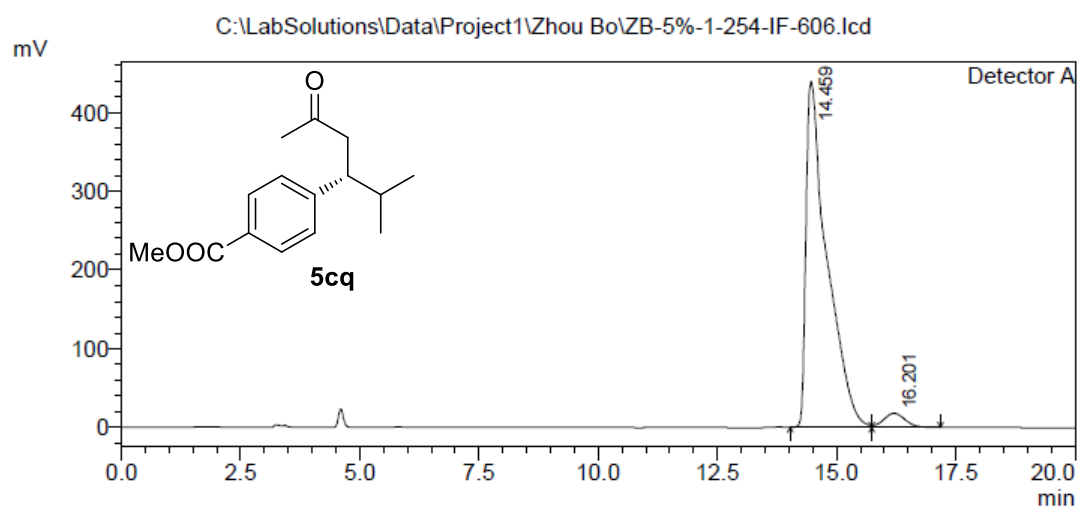
PeakTable

Detector A 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.084	5906104	194486	49.966	46.890
2	16.553	5914248	220281	50.034	53.110
Total		11820352	414767	100.000	100.000

Racemic **5cq**

<Chromatogram>



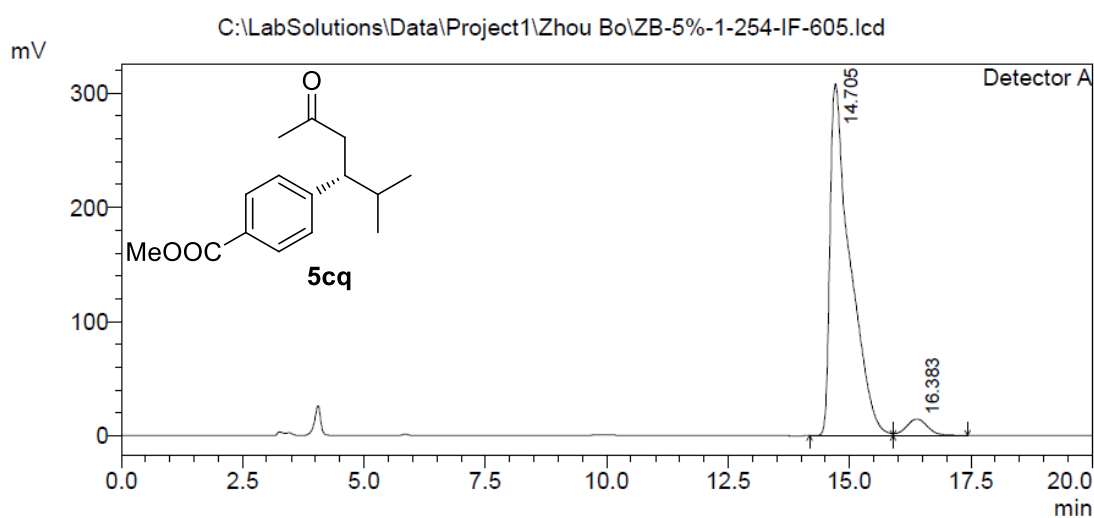
1 Detector A/254nm

PeakTable

Detector A 254nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.459	13417447	438744	96.000	96.125
2	16.201	559101	17686	4.000	3.875
Total		13976548	456430	100.000	100.000

Enantiomerically enriched **5cq** with (*R,R*)-Fc,Ph-bod

<Chromatogram>



1 Detector A/254nm

PeakTable

Detector A 254nm					
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.705	8877990	308269	95.239	95.510
2	16.383	443799	14493	4.761	4.490
Total		9321788	322762	100.000	100.000

Enantiomerically enriched **5cq** with (*R,R*)-Ph-bod

II. NMR spectra for new compounds

