

Supporting Information

Enzymatic cascades for the stereo-complementary epimerisation of *in situ* generated epoxy alcohols

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Table S1. Construction of plasmids in this work

Constructed plasmid	Vector	Target enzyme	Primer set	
			Forward	Reverse
pET(AB)	pET15b	SMO	<i>Nde</i> I_AB	<i>Xho</i> I_AB
pET(RE)	pET15b	READH	<i>Nde</i> I_RE	<i>Xho</i> I_RE
pET(LK)	pET15b	LKADH	<i>Nde</i> I_LK	<i>Xho</i> I_LK
pRSFD(LKAB)	pRSFDuet-1	LKADH	<i>EcoR</i> I_LK	<i>Hind</i> III_LK
		SMO	<i>Nde</i> I_AB	<i>Xho</i> I_AB
pRSFD(REAB)	pRSFDuet-1	READH	<i>EcoR</i> I_RE	<i>Hind</i> III_RE
		SMO	<i>Nde</i> I_AB	<i>Xho</i> I_AB
pRSFD(RELK)	pRSFDuet-1	READH	<i>EcoR</i> I_RE	<i>Hind</i> III_RE
		LKADH	<i>Nde</i> I_LK	<i>Xho</i> I_LK
pRSFD(LKRE)	pRSFDuet-1	LKADH	<i>EcoR</i> I_LK	<i>Hind</i> III_LK
		READH	<i>Nde</i> I_RE	<i>Xho</i> I_RE
pRSFD(PFC05)	pRSFDuet-1	PFADH	<i>EcoR</i> I_PF	<i>Hind</i> III_PF
		<i>ChKRED05</i>	<i>Nde</i> I_C05	<i>Xho</i> I_C05

Table S2. Sequences of oligonucleotides used in this work

Primer	Sequence
<i>EcoR</i> I_RE	CCGGAATTTCGATGAAGGCAATCCAGTACACGAG
<i>Hind</i> III_RE	CCCAAGCTTCTACAGACCAGGGACCACAAC
<i>Nde</i> I_AB	CGCCATATGATGAAAAAGCGTATCGGTATTGTTGGT
<i>Xho</i> I_AB	CCGCTCGAGTTAATTCAGGGGCAGCGGATTG
<i>Nde</i> I_LK	CGCCATATGATGACTGATCGTTTTAAAAGGCAAAGTAGCAATTG
<i>Xho</i> I_LK	CCGCTCGAGTTATTGAGCAGTGTATCCACCATCGACAACGAACTCTG
<i>EcoR</i> I_LK	CCGGAATTTCGATGACTGATCGTTTTAAAAGGCAAAGTAGCAATTG
<i>Hind</i> III_LK	CCCAAGCTTTTTATTGAGCAGTGTATCCACCATCGACAACGAACTCTG
<i>Nde</i> I_RE	CGCCATATGATGAAGGCAATCCAGTACACGAG
<i>Xho</i> I_RE	CCGCTCGAGCTACAGACCAGGGACCACAAC
<i>EcoR</i> I_PF	CCGGAATTTCGATGAGCTATAACTTCCATAAT
<i>Hind</i> III_PF	CCCAAGCTTACTGCGCGGTATAGCCGCCATCCACCGGCAAG
<i>Nde</i> I_C05	CGCCATATGATGAATATCAACGGAAAAAATGC
<i>Xho</i> I_C05	CCGCTCGAGTTAAGGATTTGTAGAGAAAATTG

Table S3. Separation conditions for chiral HPLC analysis^a

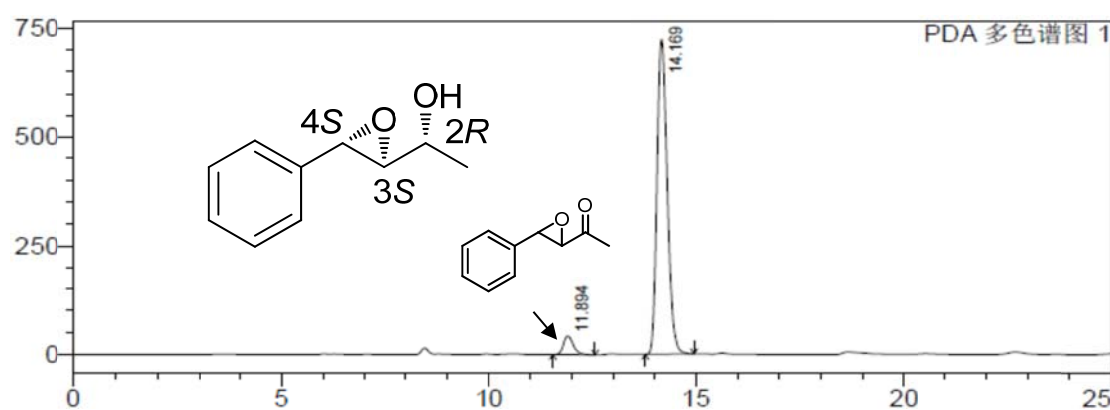
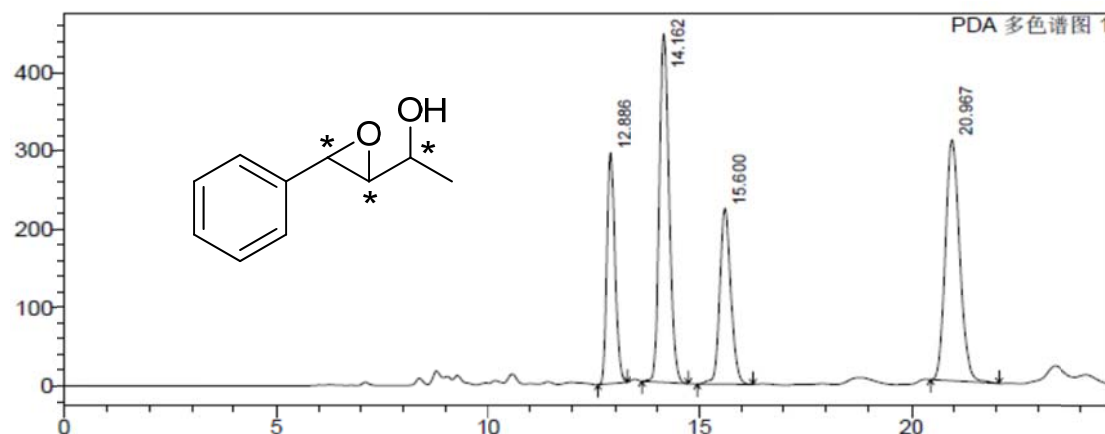
Entry	Substrate	Column	Column temperature (°C)	Hexane/2-propanol	Flow rate (mL/min)
1	1a	AD-H	35	90/10	0.5
2	2a	AD-H	35	95/5	0.5
3	3a	AS-H	35	90/10	0.5
4	4a	AS-H	25	98/2	0.5
5	5a	AS-H	35	95/5	0.5
6	6a	AD-H	35	90/10	0.5
7	7a	AD-H	35	90/10	0.5
8	8a	AS-H	35	95/5	0.5
9	9a	AS-H	35	95/5	0.5
10	10a	AS-H	35	95/5	0.5
11	11a	AD-H	35	95/5	0.5
12	12a	AD-H	35	90/10	0.5

^a All the products and by-products derived from the same substrate were analyzed under the same conditions. The analysis was conducted with a Shimadzu Prominence LC-20AD system connected to a PDA-detector.

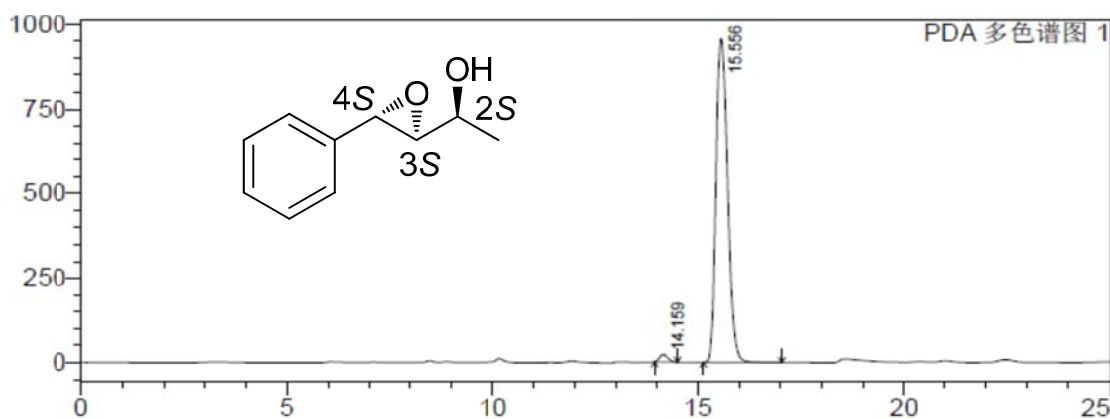
Chiral HPLC chromatograms

Shown are chromatograms detected at 220 nm using a photo diode array (PDA) detector.

Chiral HPLC analysis for **1b** production (top to bottom):
 Standard sample of (*rac*)-**1b**; products of the (*2R*)- and (*2S*)-system

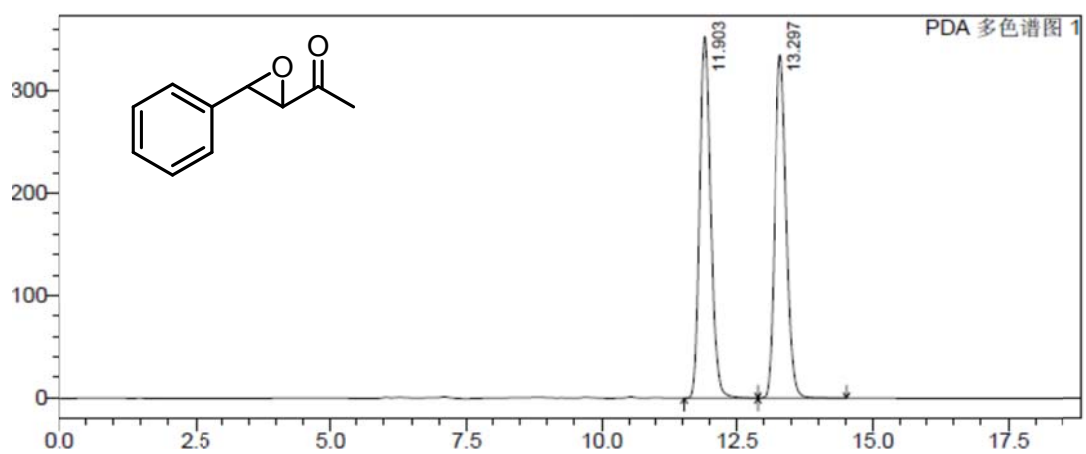


Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.894	690974	41839	5.307	5.465
2	14.169	12329584	723804	94.693	94.535
总计		13020557	765643	100.000	100.000

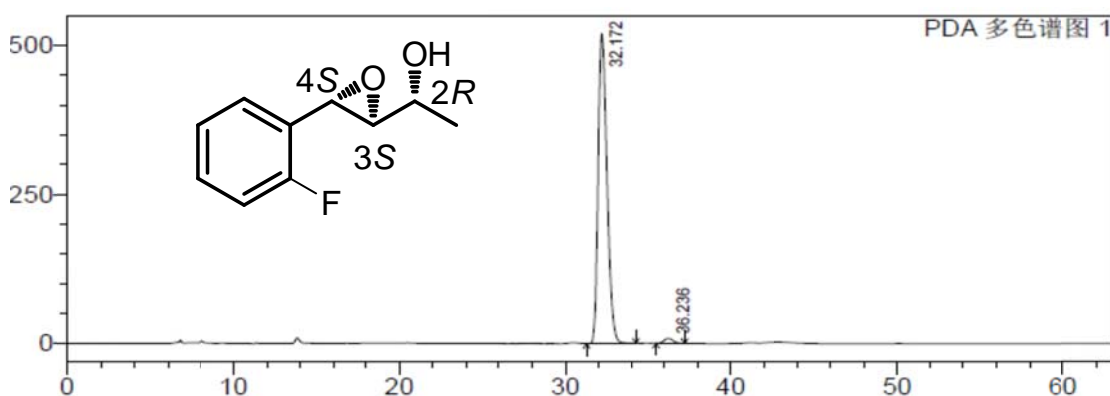
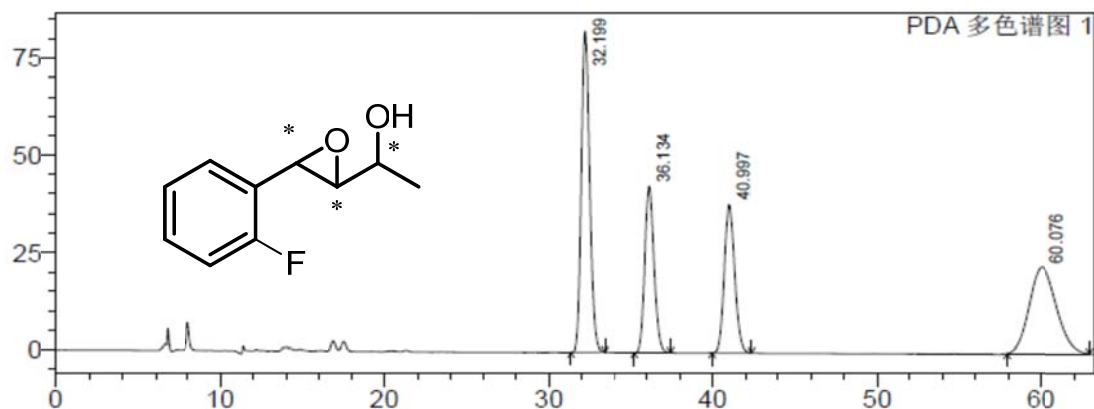


Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.159	305087	21024	1.605	2.151
2	15.556	18708984	956613	98.395	97.849
总计		19014071	977637	100.000	100.000

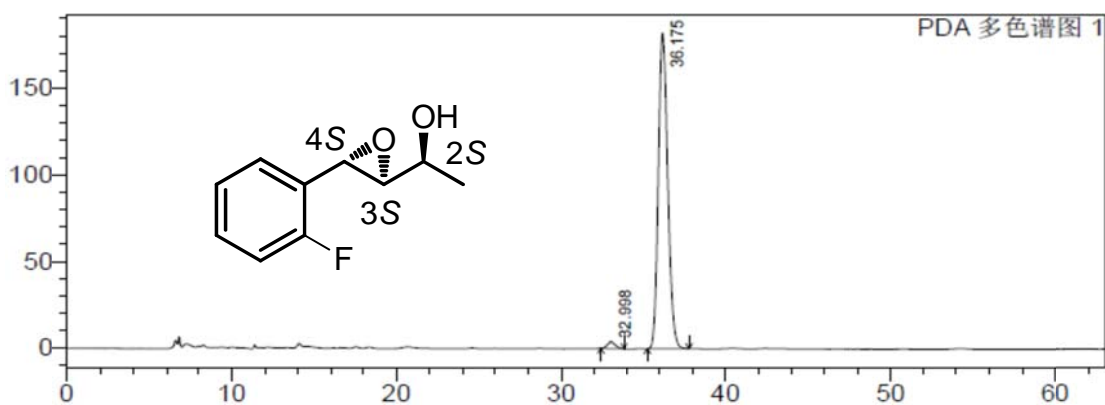
Standard sample of (*rac*)-1c



Chiral HPLC analysis for **2b** production (2nd of two attempts) (top to bottom):
 Standard samples of (*rac*)-**2b**; products of the (*2R*)- and (*2S*)-system



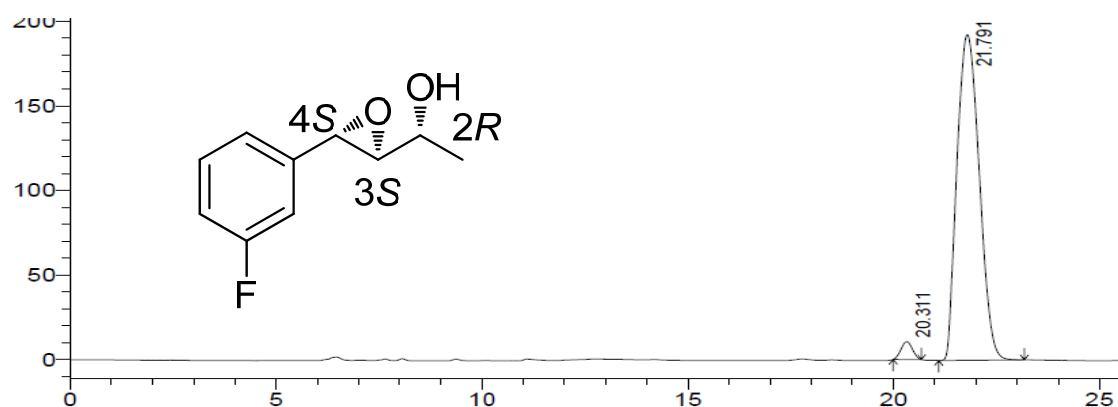
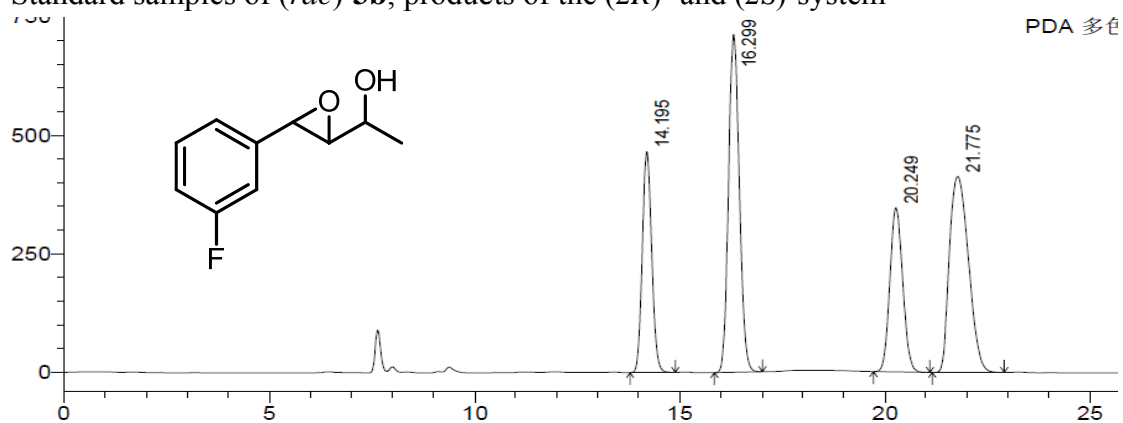
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.172	19195815	520253	98.333	98.416
2	36.236	325448	8373	1.667	1.584
总计		19521263	528625	100.000	100.000



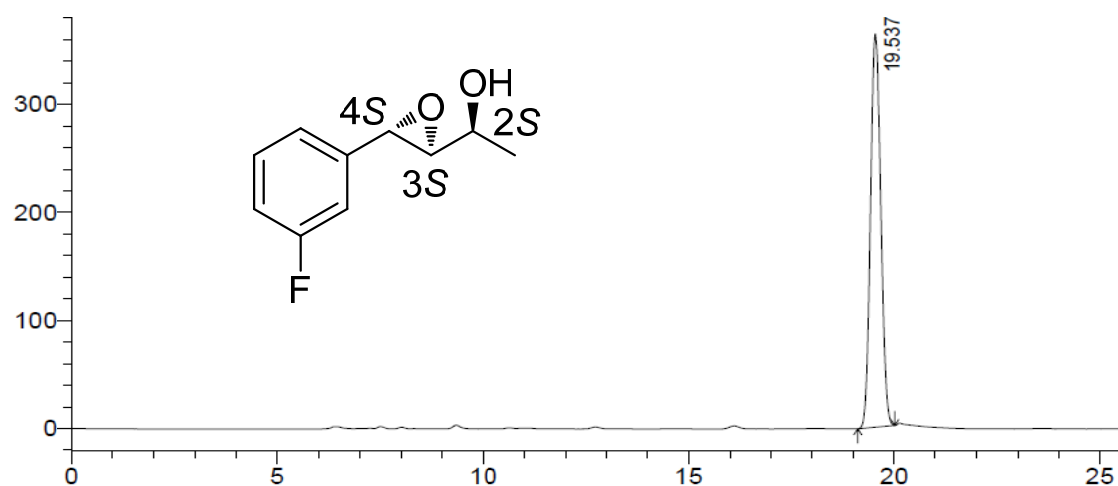
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.998	126714	3554	1.731	1.917
2	36.175	7193268	181879	98.269	98.083
总计		7319982	185433	100.000	100.000

Chiral HPLC analysis for **3b** production (top to bottom):

Standard samples of (*rac*)-**3b**; products of the (*2R*)- and (*2S*)-system



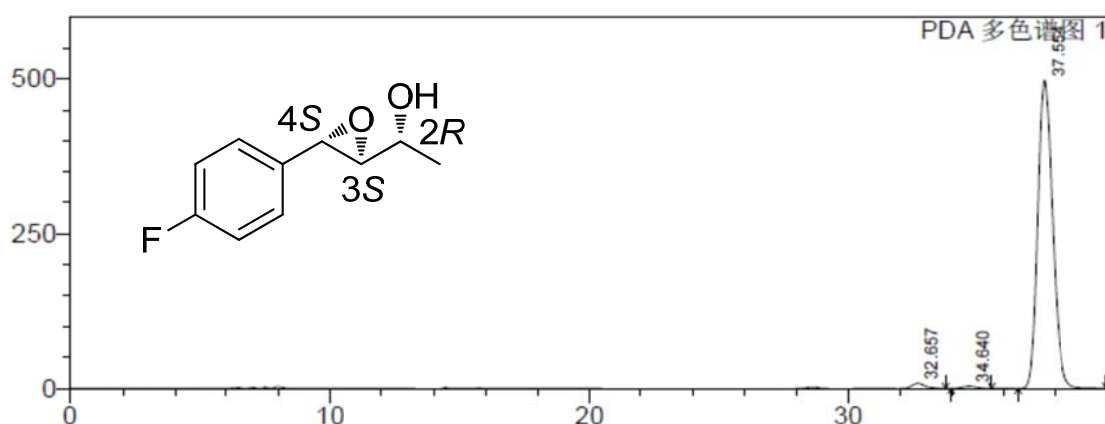
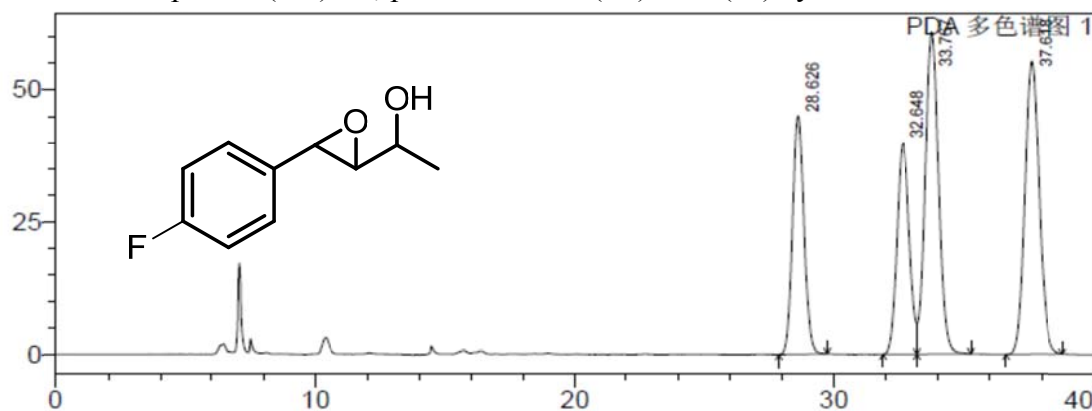
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.311	203371	10536	2.757	5.193
2	21.791	7173724	192350	97.243	94.807
总计		7377095	202886	100.000	100.000



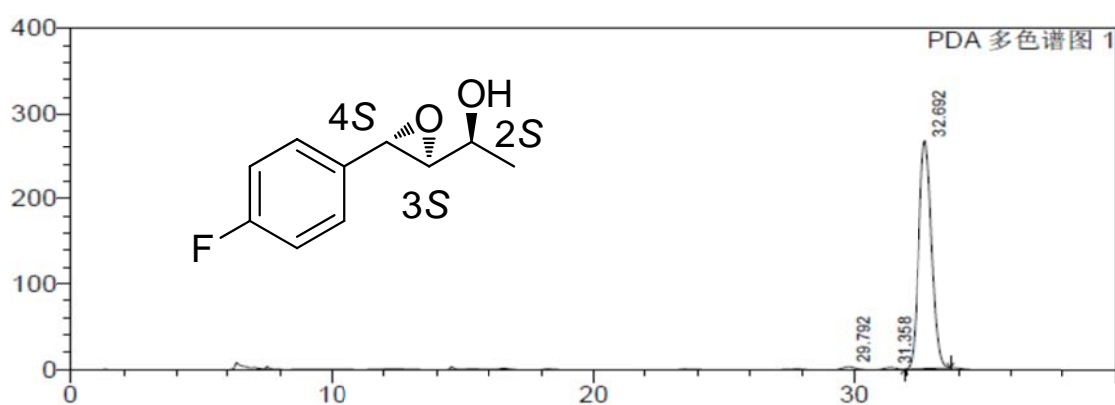
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.537	6326853	364211	100.000	100.000
总计		6326853	364211	100.000	100.000

Chiral HPLC analysis for **4b** production (top to bottom):

Standard samples of (*rac*)-**4b**; products of the (*2R*)- and (*2S*)-system

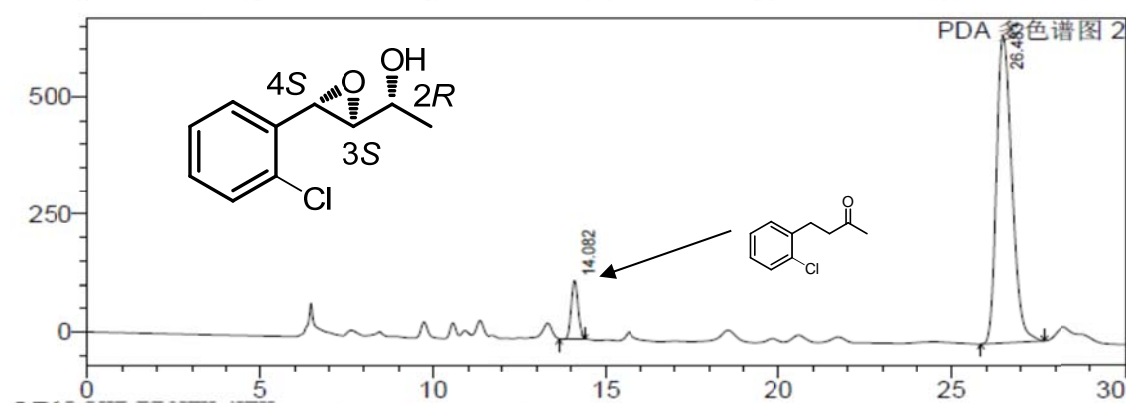
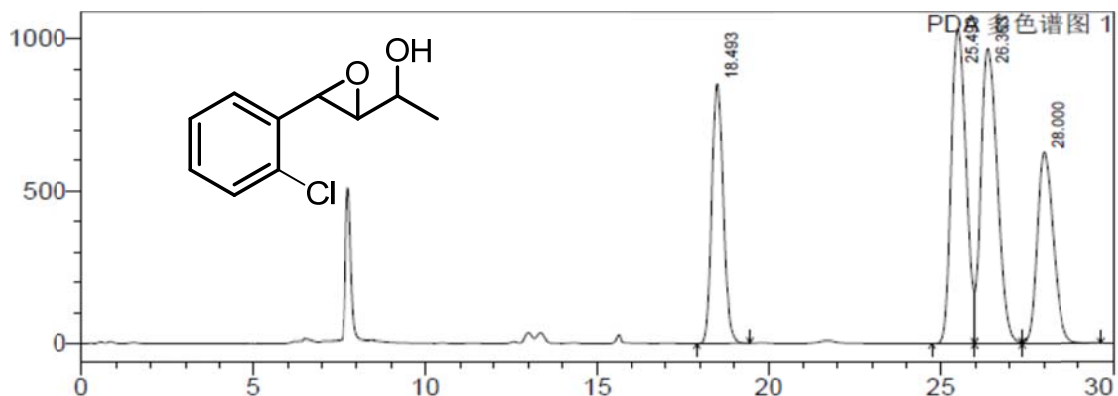


Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.657	319985	8547	1.557	1.674
2	34.640	143160	3801	0.697	0.745
3	37.554	20086240	498165	97.746	97.581
总计		20549385	510513	100.000	100.000

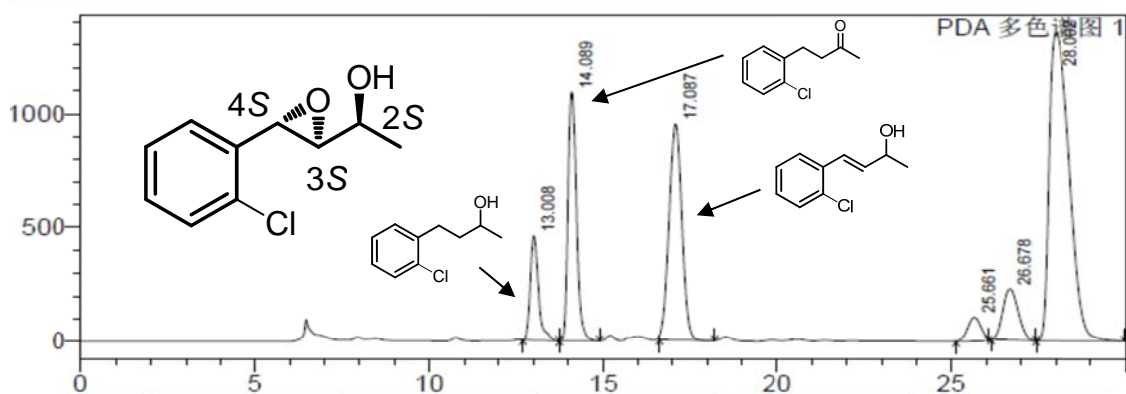


Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.792	109244	3407	1.157	1.244
2	31.358	71284	2386	0.755	0.871
3	32.692	9262151	268074	98.088	97.885
总计		9442680	273866	100.000	100.000

Chiral HPLC analysis for **5b** production (top to bottom):
 Standard samples of (*rac*)-**5b**; products of the (*2R*)- and (*2S*)-system

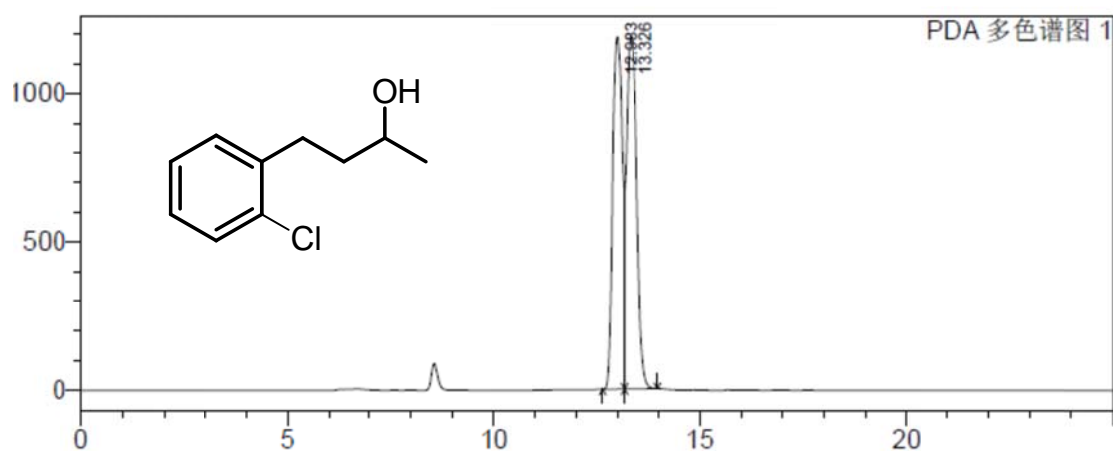
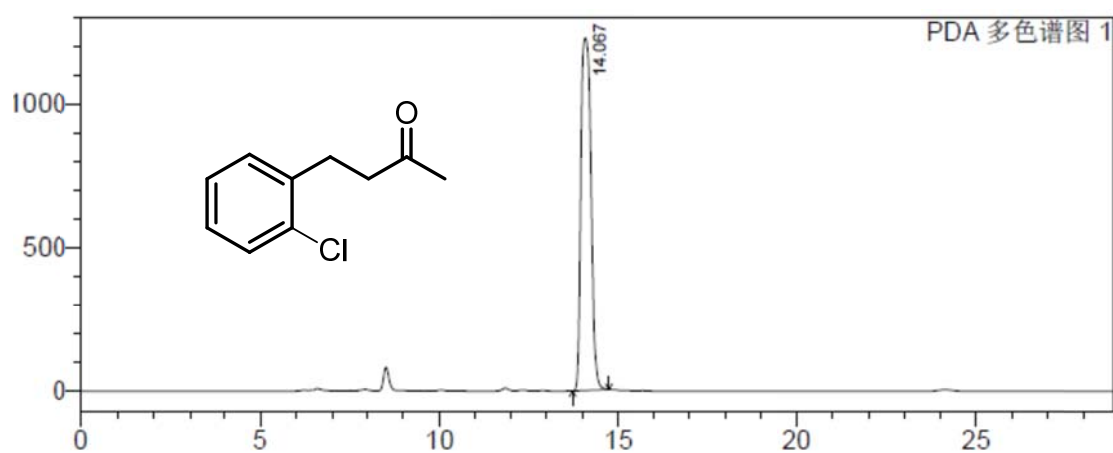
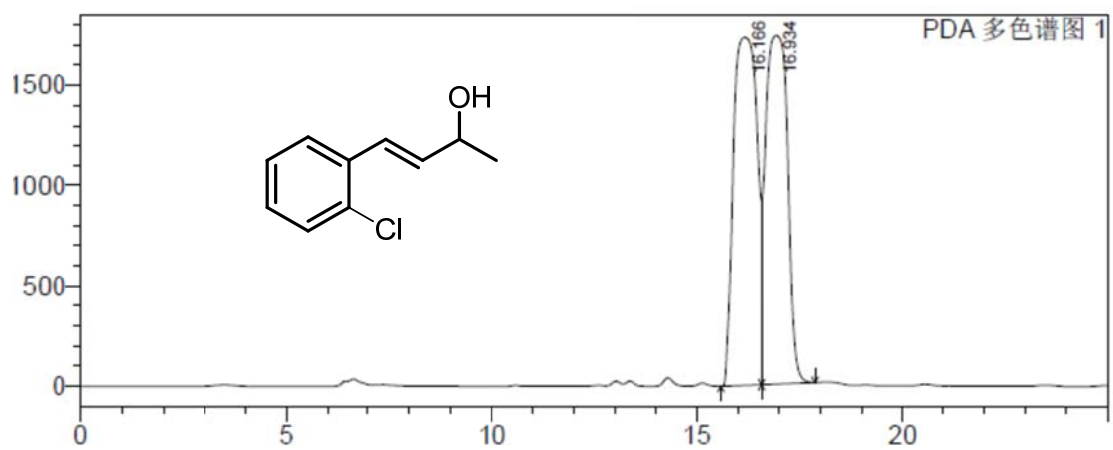


Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.082	1746002	123910	7.961	15.947
2	26.483	20186550	653111	92.039	84.053
总计		21932552	777021	100.000	100.000



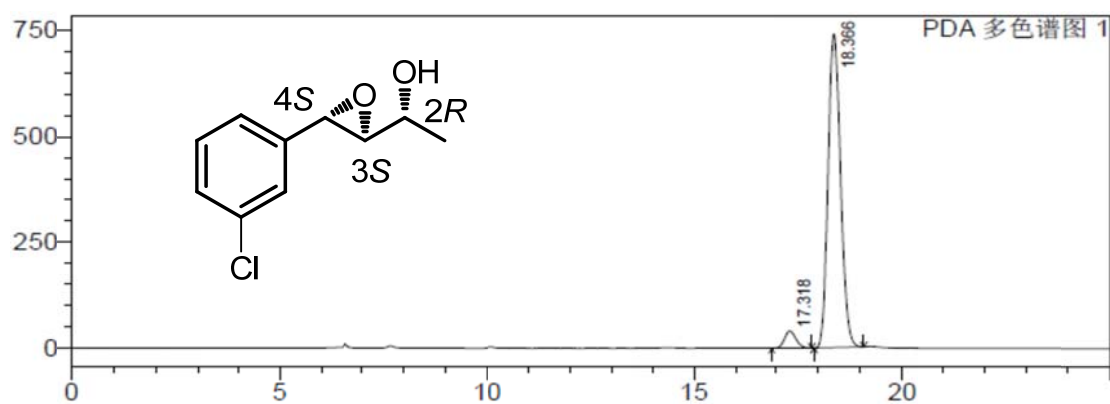
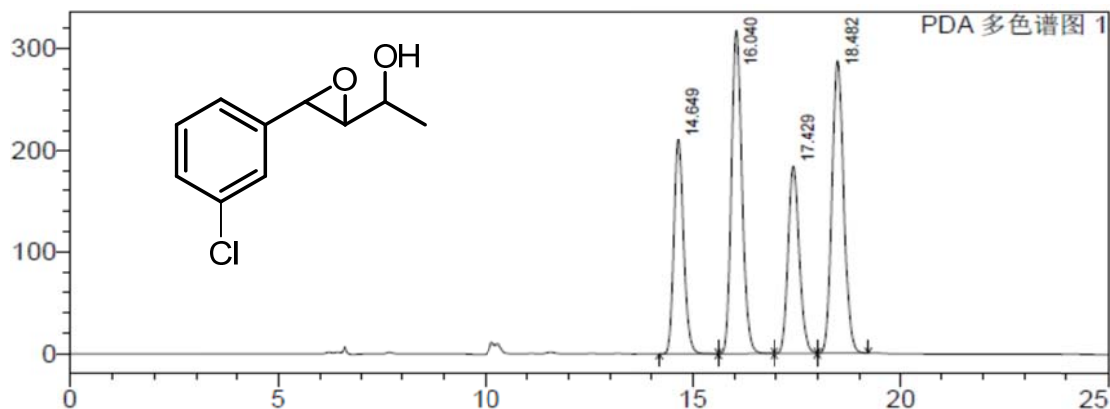
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.008	7487143	456852	6.544	10.932
2	14.089	18434091	1091307	16.113	26.114
3	17.087	24149949	949039	21.109	22.709
4	25.661	2833479	105382	2.477	2.522
5	26.678	6887867	225473	6.021	5.395
6	28.002	54611284	1351017	47.736	32.328
总计		114403814	4179071	100.000	100.000

Standard samples of (*rac*)-**5a**, **5e** and (*rac*)-**5f**;

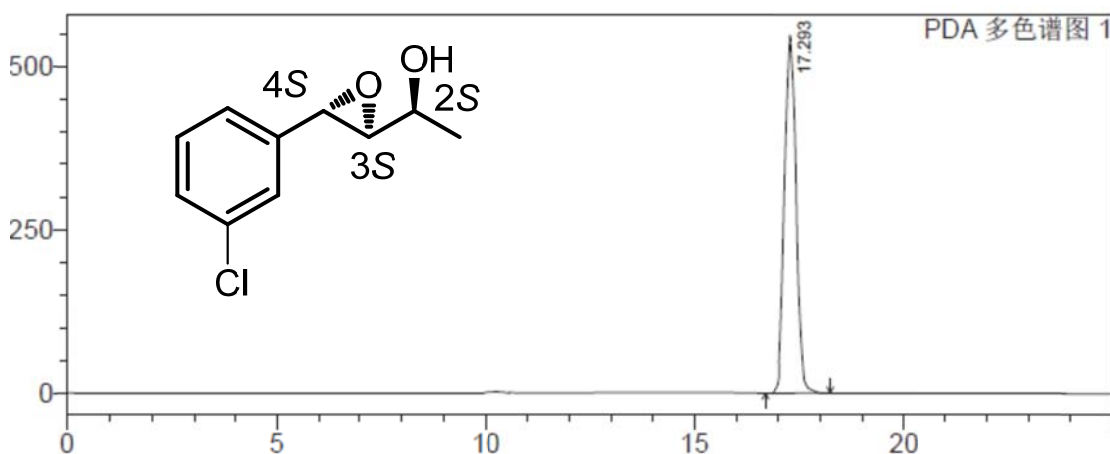


Chiral HPLC analysis for **6b** production (top to bottom):

Standard samples of (*rac*)-**6b**; products of the (*2R*)- and (*2S*)-system



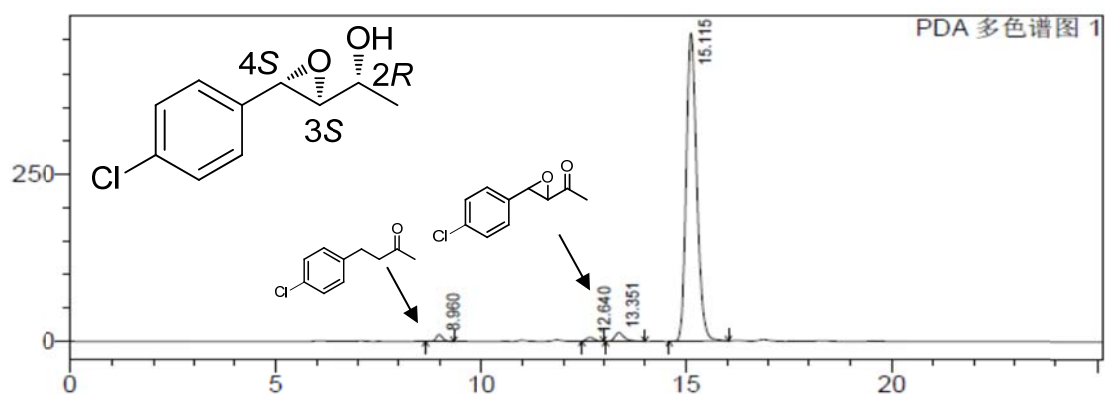
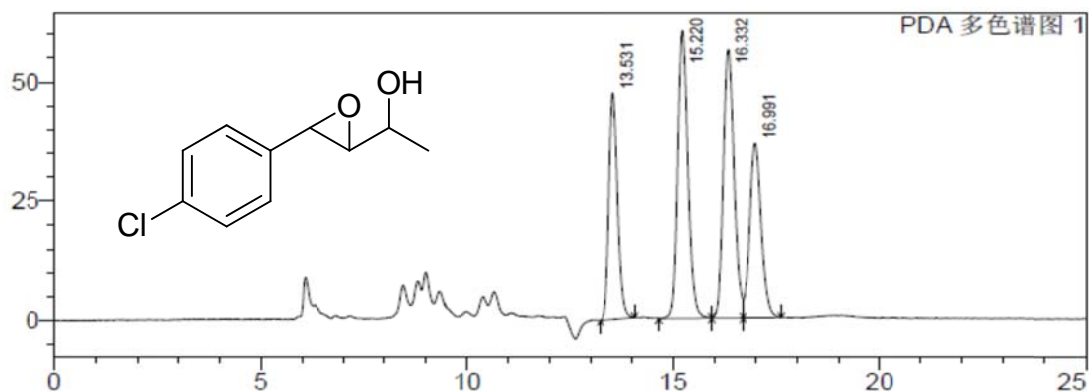
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.318	755309	40263	4.682	5.160
2	18.366	15376914	740017	95.318	94.840
总计		16132222	780280	100.000	100.000



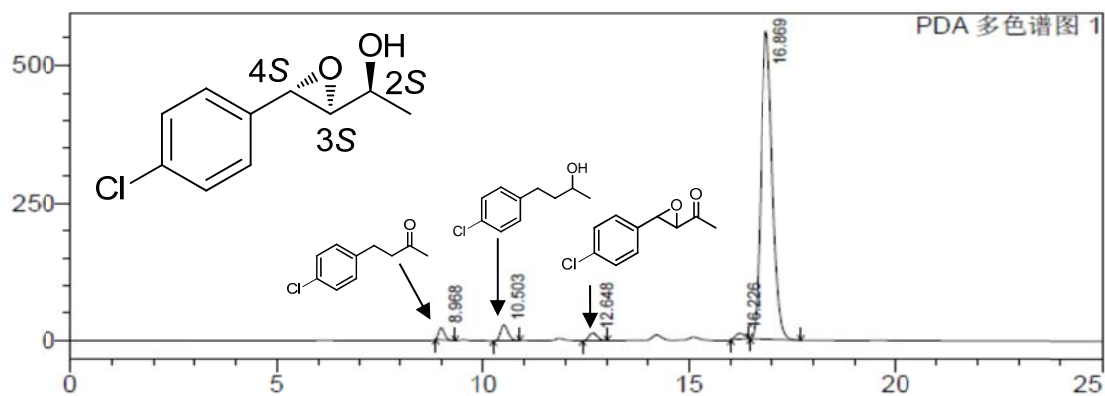
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.293	10522178	547646	100.000	100.000
总计		10522178	547646	100.000	100.000

Chiral HPLC analysis for **7b** production (top to bottom):

Standard samples of (*rac*)-**7b**; products of the (*2R*)- and (*2S*)-system

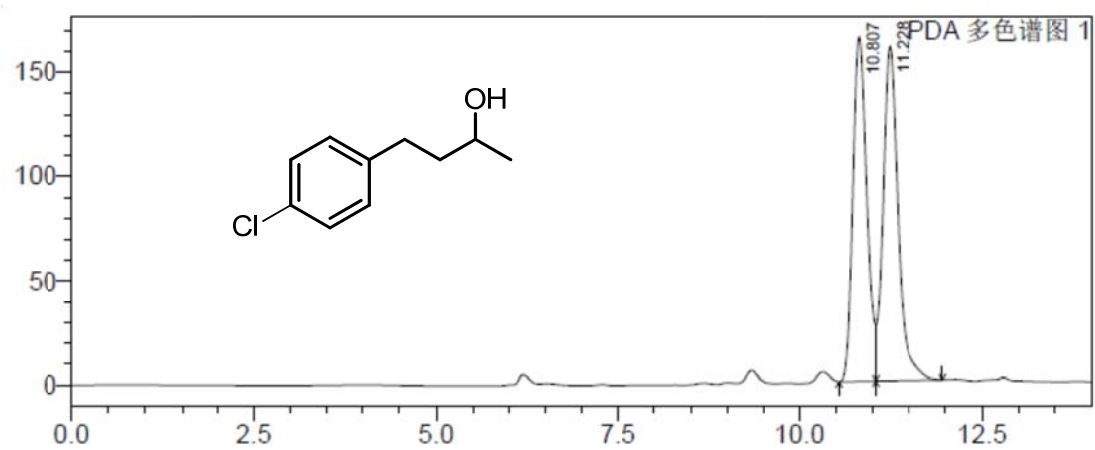
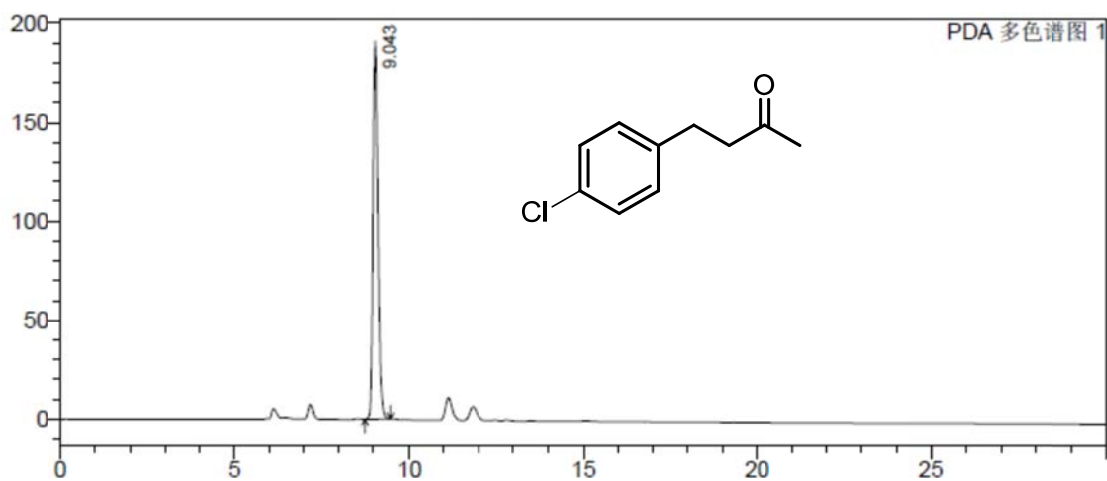
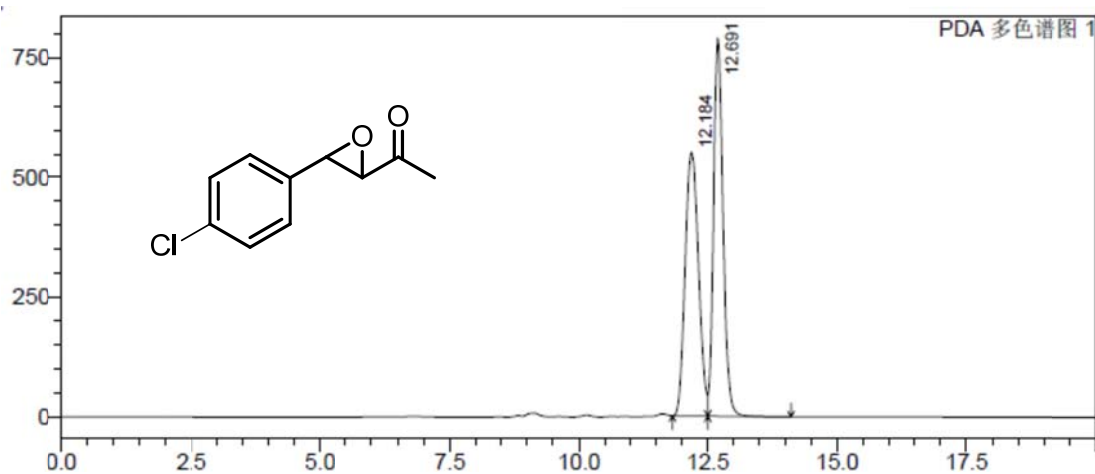


Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.960	107692	10046	1.254	2.053
2	12.640	76225	5751	0.887	1.175
3	13.351	227044	13566	2.643	2.773
4	15.115	8178675	459868	95.216	93.998
总计		8589636	489230	100.000	100.000



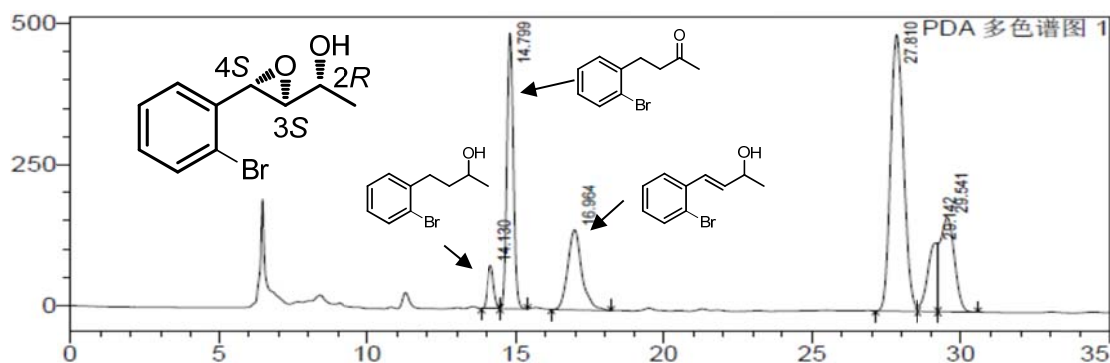
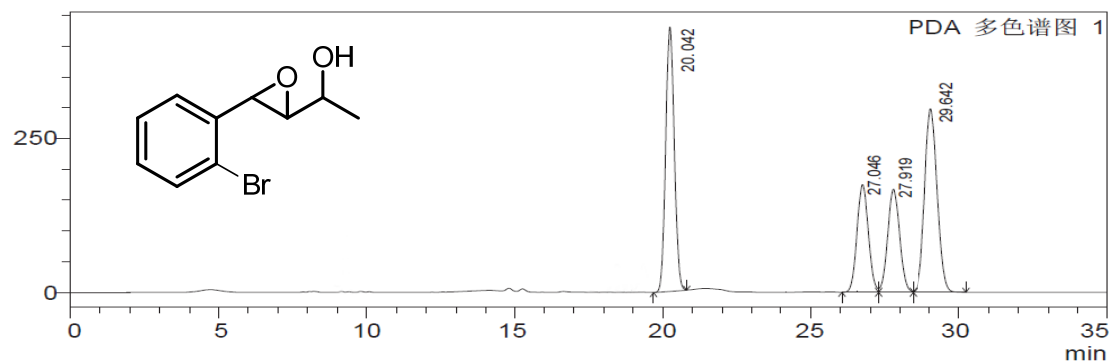
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.968	209454	21503	1.773	3.391
2	10.503	357525	28155	3.027	4.440
3	12.648	193739	14126	1.640	2.228
4	16.226	154922	10810	1.312	1.705
5	16.869	10894958	559534	92.247	88.237
总计		11810598	634128	100.000	100.000

Standard samples of (*rac*)-**7c**, **7e** and (*rac*)-**7f**;

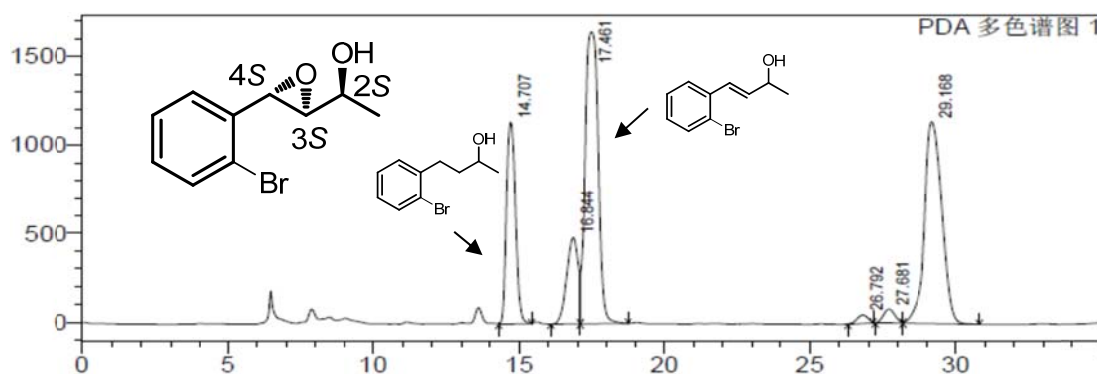


Chiral HPLC analysis for **8b** production (top to bottom):

Standard samples of (*rac*)-**8b**; products of the (*2R*)- and (*2S*)-system

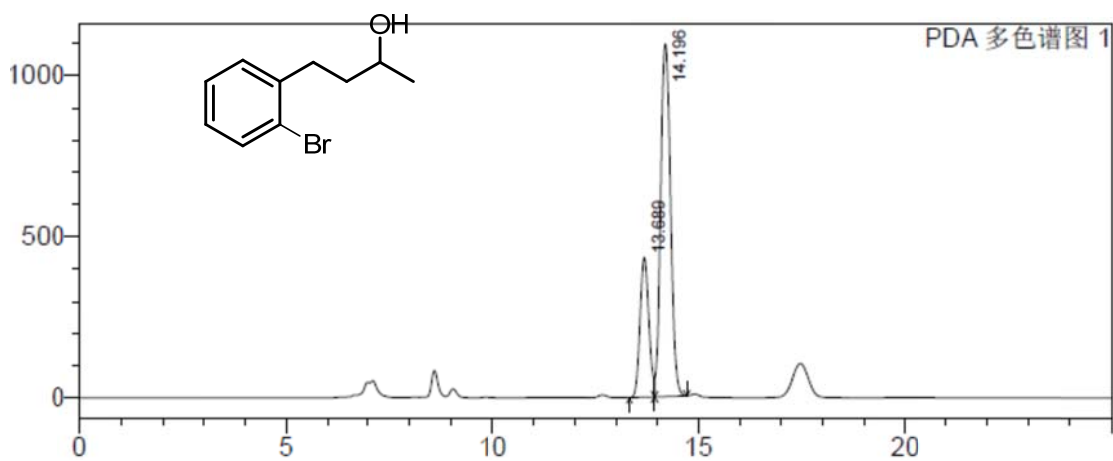
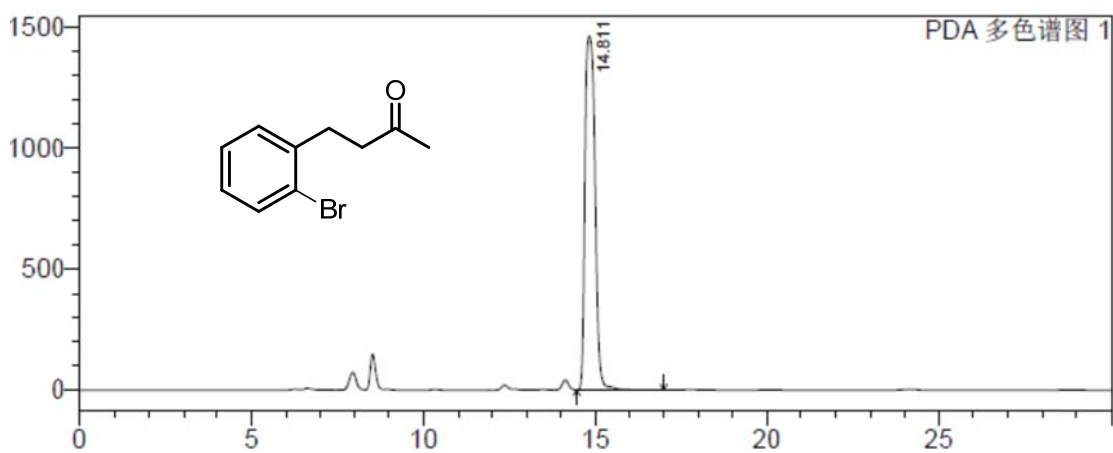
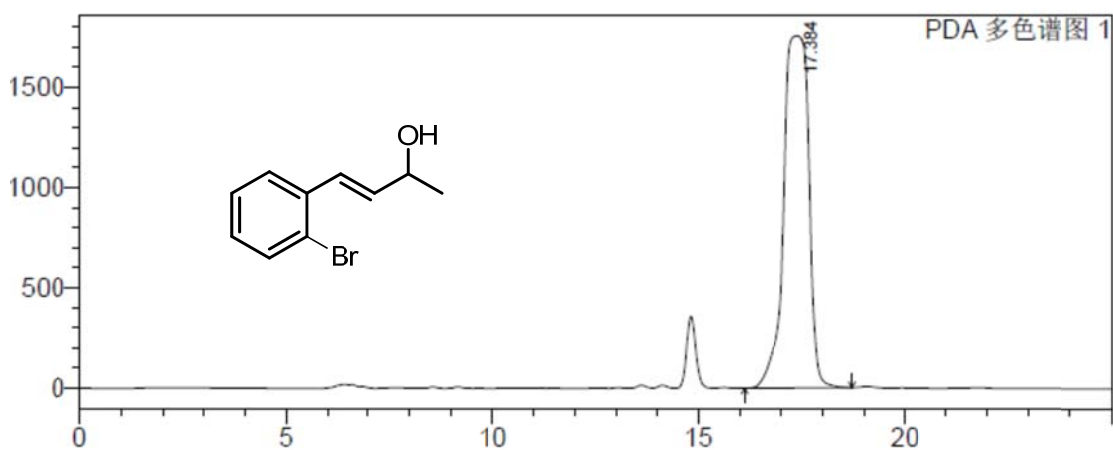


Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.130	1146070	76485	3.163	5.162
2	14.799	7340260	488024	20.260	32.938
3	16.964	4652307	141279	12.841	9.535
4	27.810	14794767	489021	40.835	33.006
5	29.142	2795985	120800	7.717	8.153
6	29.541	5501184	166016	15.184	11.205
总计		36230574	1481625	100.000	100.000



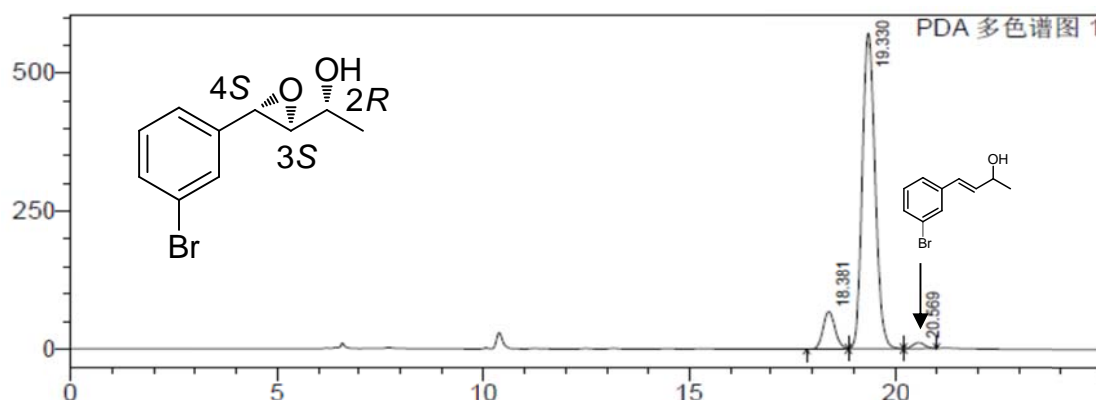
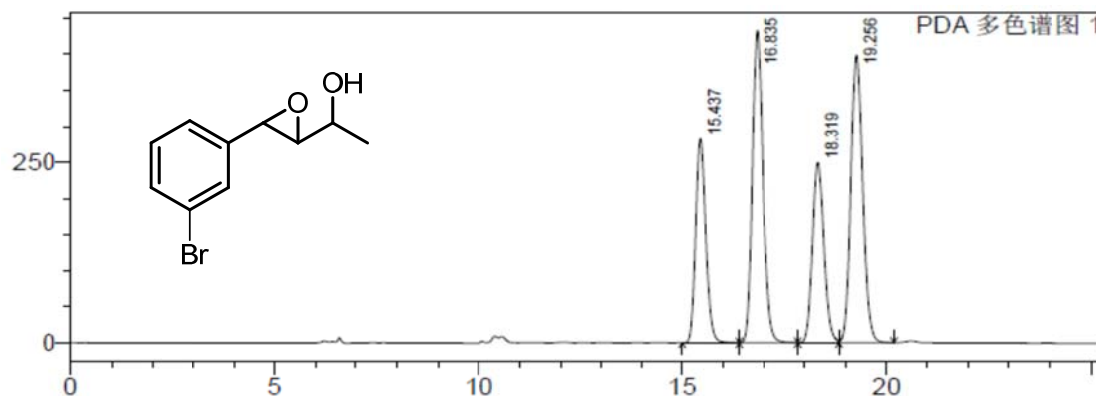
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.707	24573445	1141415	17.593	25.152
2	16.844	13137455	483994	9.405	10.665
3	17.461	51103947	1644680	36.586	36.242
4	26.792	1258890	48506	0.901	1.069
5	27.681	2108345	78579	1.509	1.732
6	29.168	47498743	1140874	34.005	25.140
总计		139680825	4538049	100.000	100.000

Standard samples of (*rac*)-**8c**, **8e** and (*rac*)-**8f**;

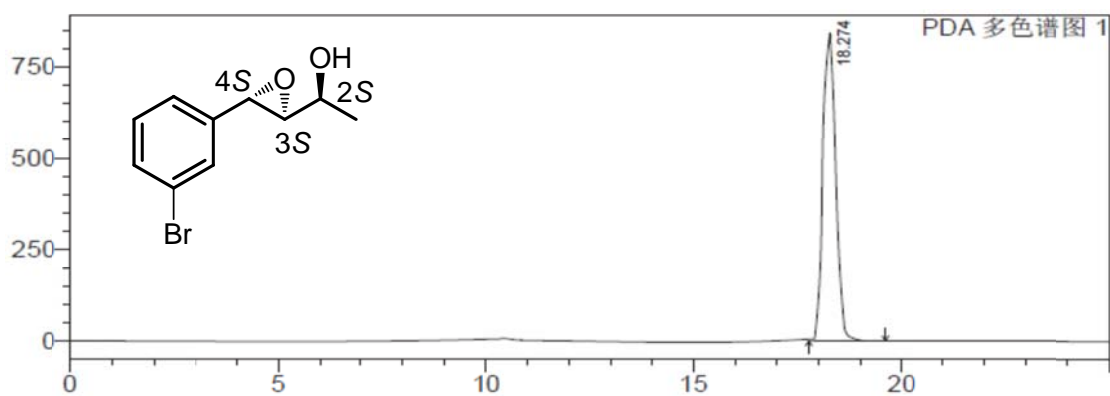


Chiral HPLC analysis for **9b** production (top to bottom):

Standard samples of (*rac*)-**9b**; products of the (*2R*)- and (*2S*)-system

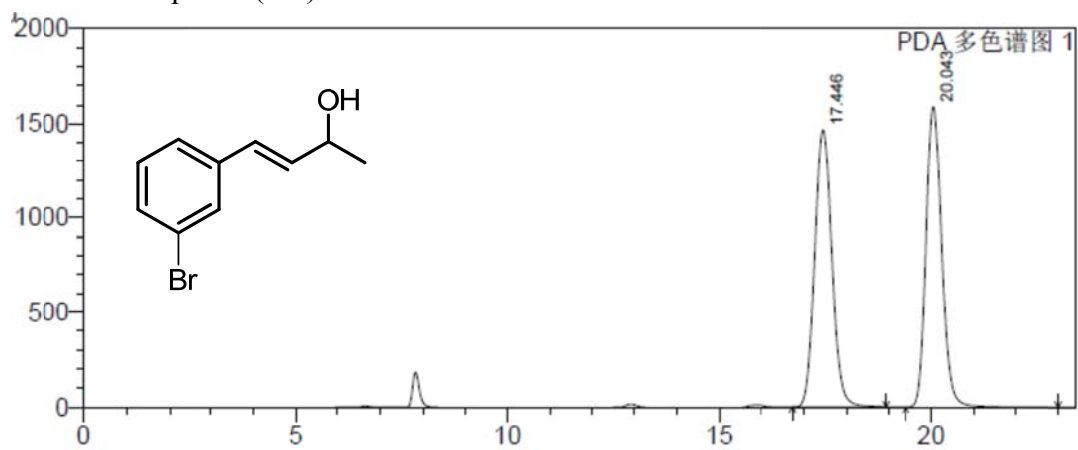


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.381	1362641	68254	9.800	10.491
2	19.330	12322112	571550	88.624	87.851
3	20.569	219087	10785	1.576	1.658
总计		13903839	650590	100.000	100.000



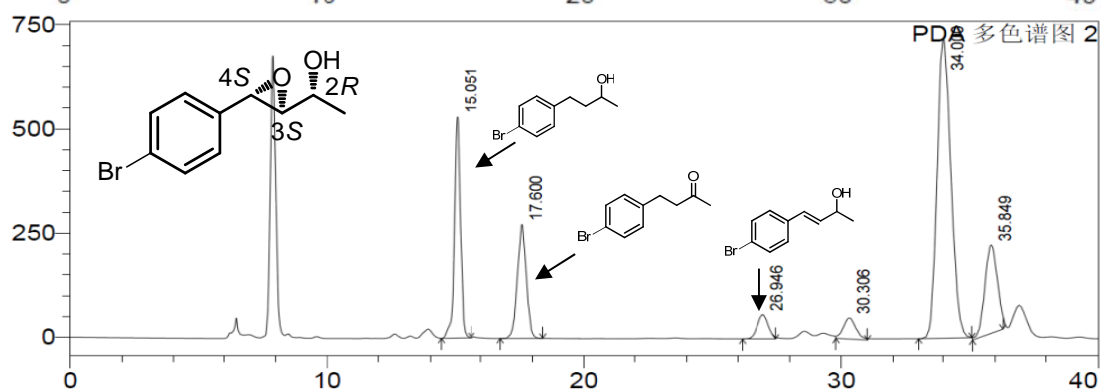
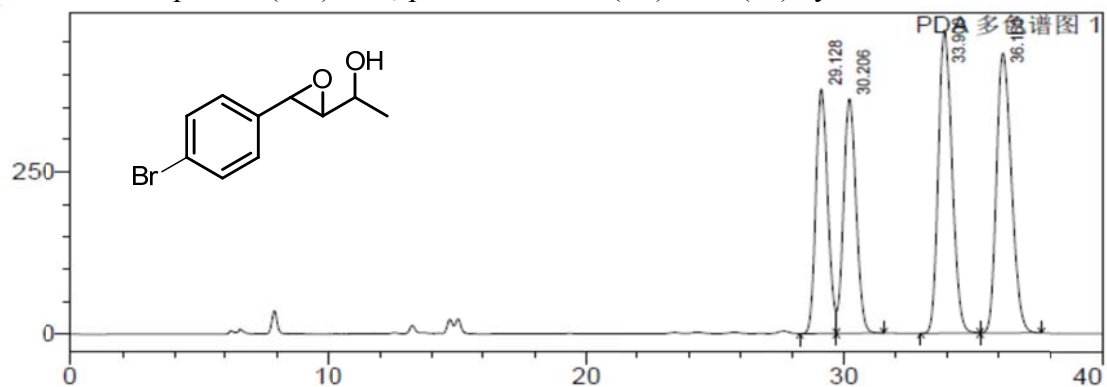
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.274	17294922	842290	100.000	100.000
总计		17294922	842290	100.000	100.000

Standard sample of (*rac*)-**9a**

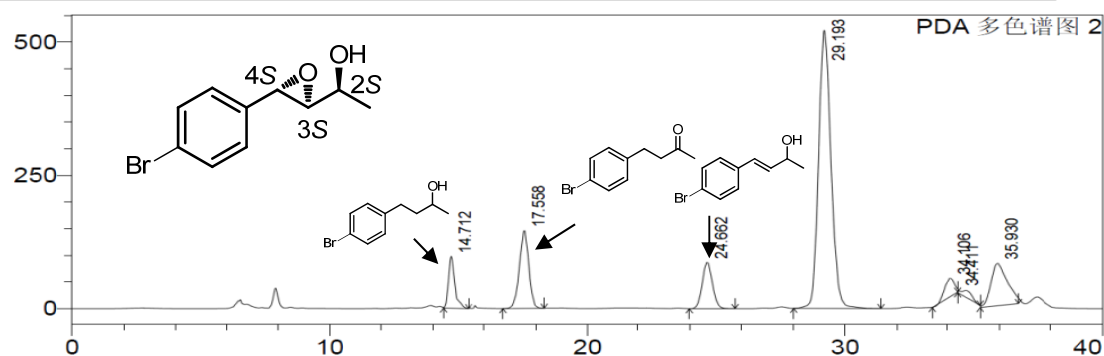


Chiral HPLC analysis for **10b** production (top to bottom):

Standard samples of (*rac*)-**10b**; products of the (*2R*)- and (*2S*)-system

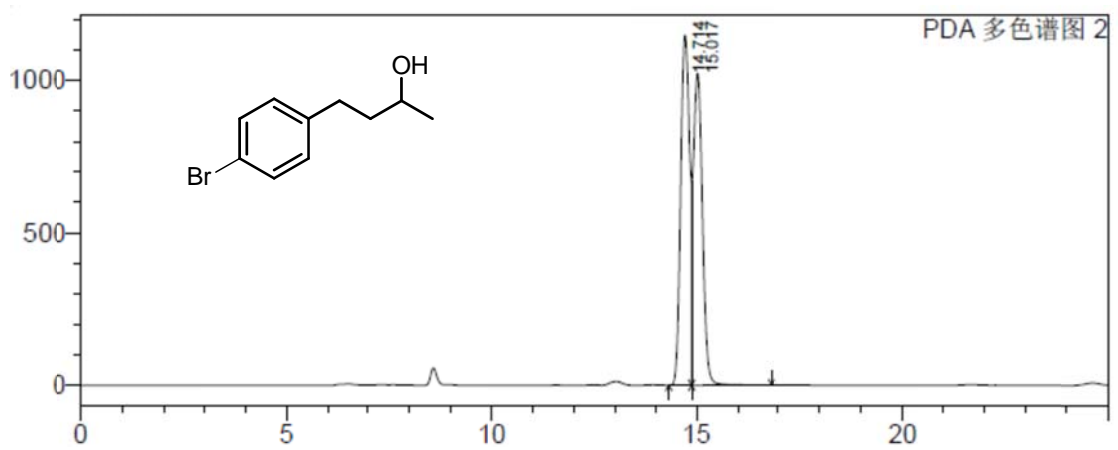
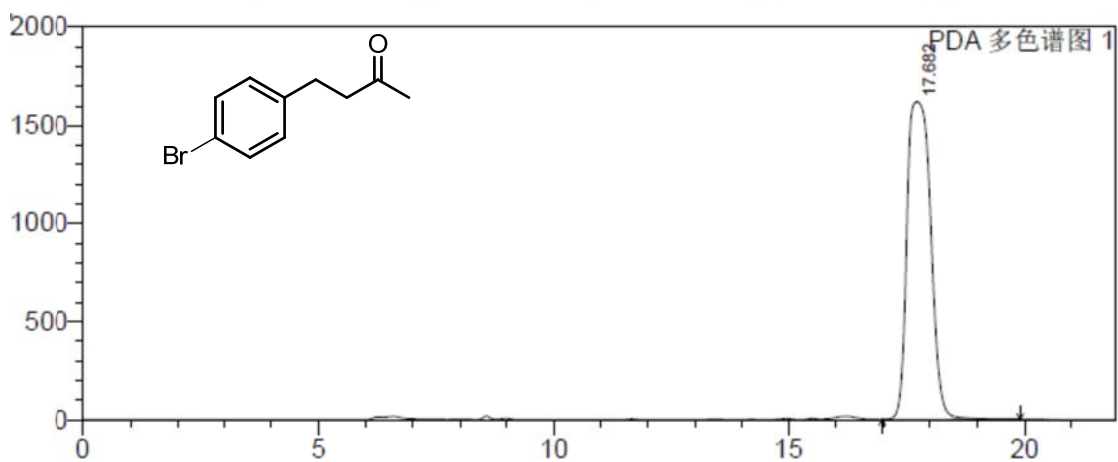
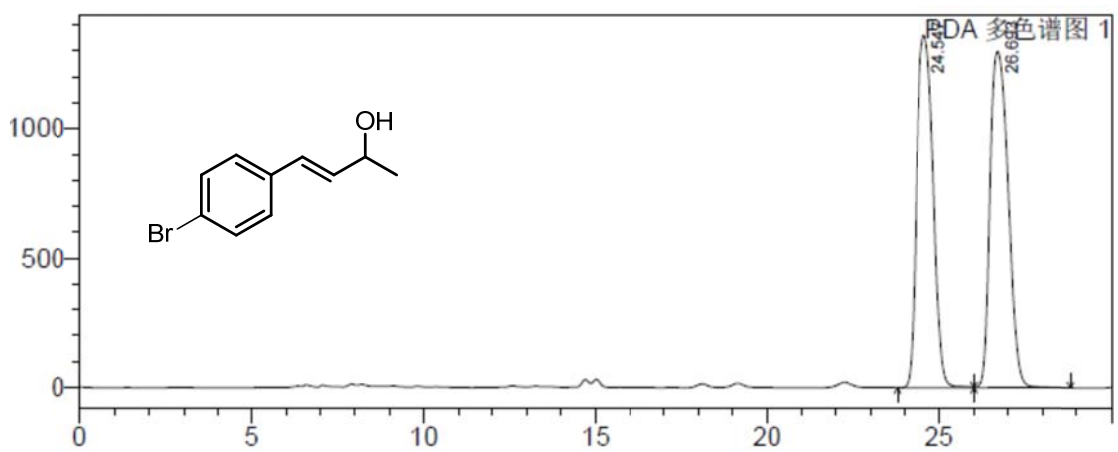


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.051	8479524	530642	16.218	28.757
2	17.600	6609417	272966	12.641	14.793
3	26.946	1783980	58960	3.412	3.195
4	30.306	1703110	50524	3.257	2.738
5	34.000	26603480	720149	50.881	39.028
6	35.849	7105941	211993	13.591	11.489
总计		52285452	1845234	100.000	100.000



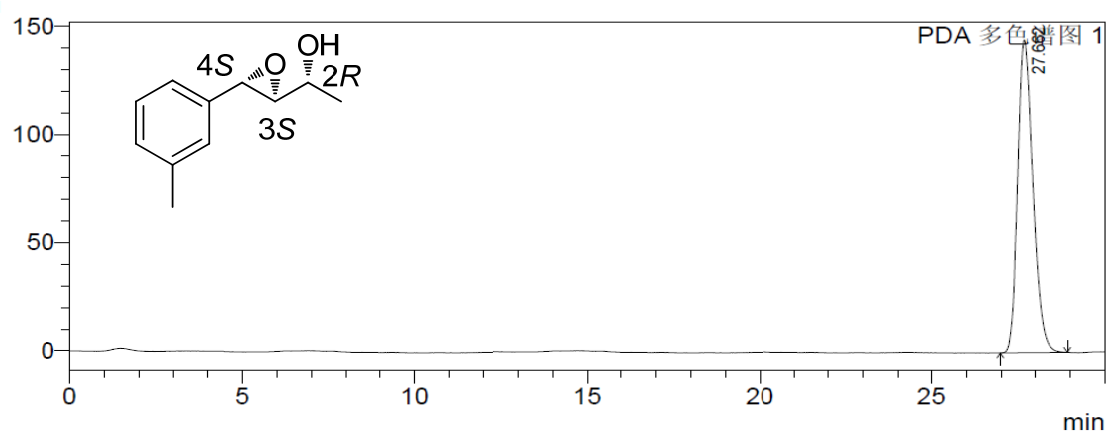
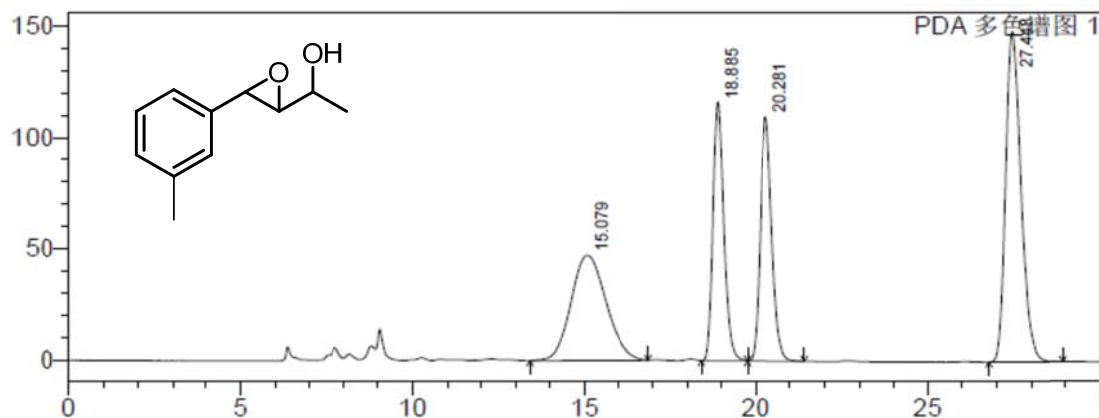
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.712	1626527	97080	5.486	10.004
2	17.558	3660263	145458	12.345	14.989
3	24.662	2363311	86762	7.971	8.941
4	29.193	17268645	521199	58.244	53.710
5	34.106	894935	34490	3.018	3.554
6	34.411	354265	5913	1.195	0.609
7	35.930	3480662	79497	11.740	8.192
总计		29648608	970397	100.000	100.000

Standard samples of (*rac*)-**10a**, **10e** and (*rac*)-**10f**

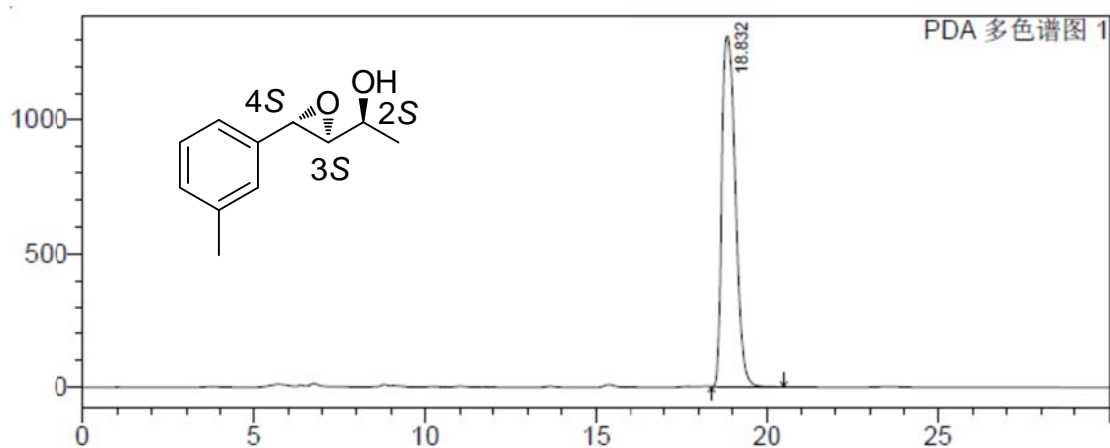


Chiral HPLC analysis for **11b** production (top to bottom):

Standard samples of (*rac*)-**11b**; products of the (*2R*)- and (*2S*)-system



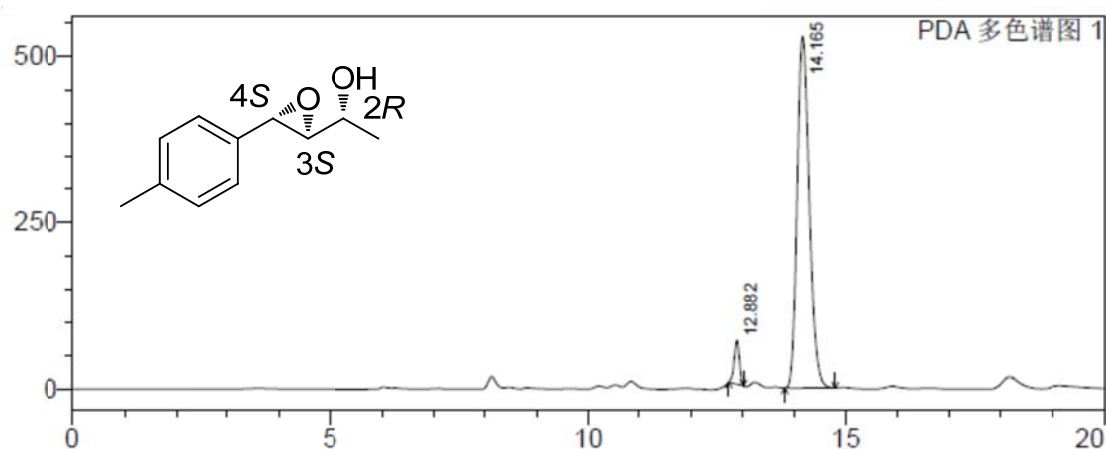
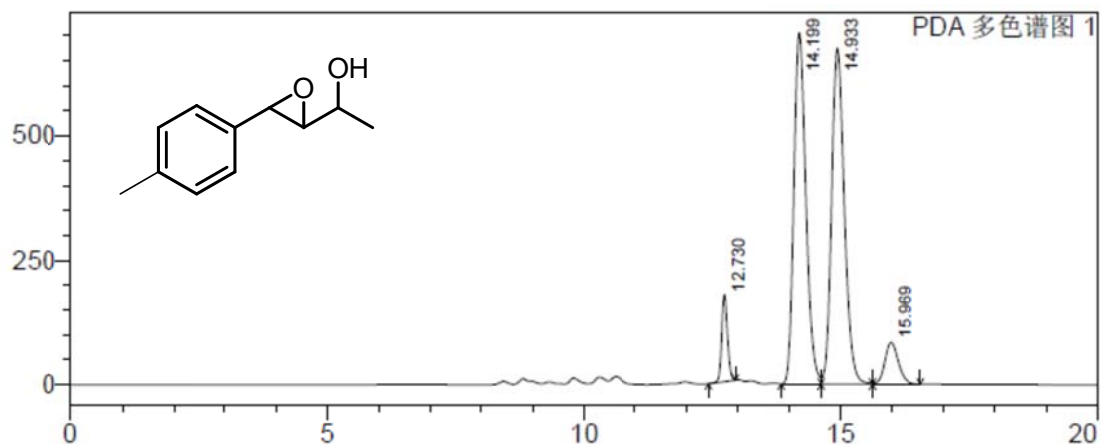
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.662	4451576	144602	100.000	100.000
总计		4451576	144602	100.000	100.000



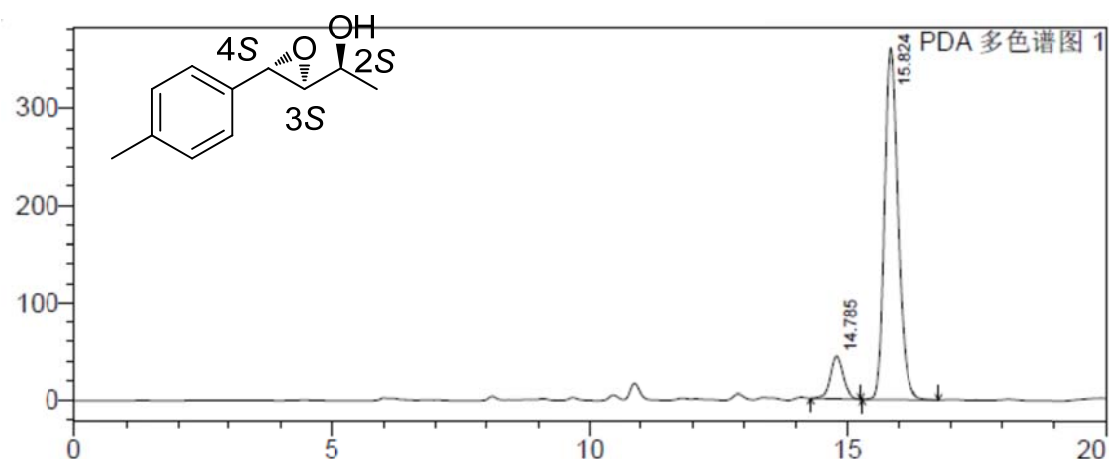
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.832	35968125	1311268	100.000	100.000
总计		35968125	1311268	100.000	100.000

Chiral HPLC analysis for **12b** production (top to bottom):

Standard samples of (*rac*)-**12b**; products of the (*2R*)- and (*2S*)-system



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.882	453542	65582	5.044	11.057
2	14.165	8538400	527534	94.956	88.943
总计		8991942	593116	100.000	100.000

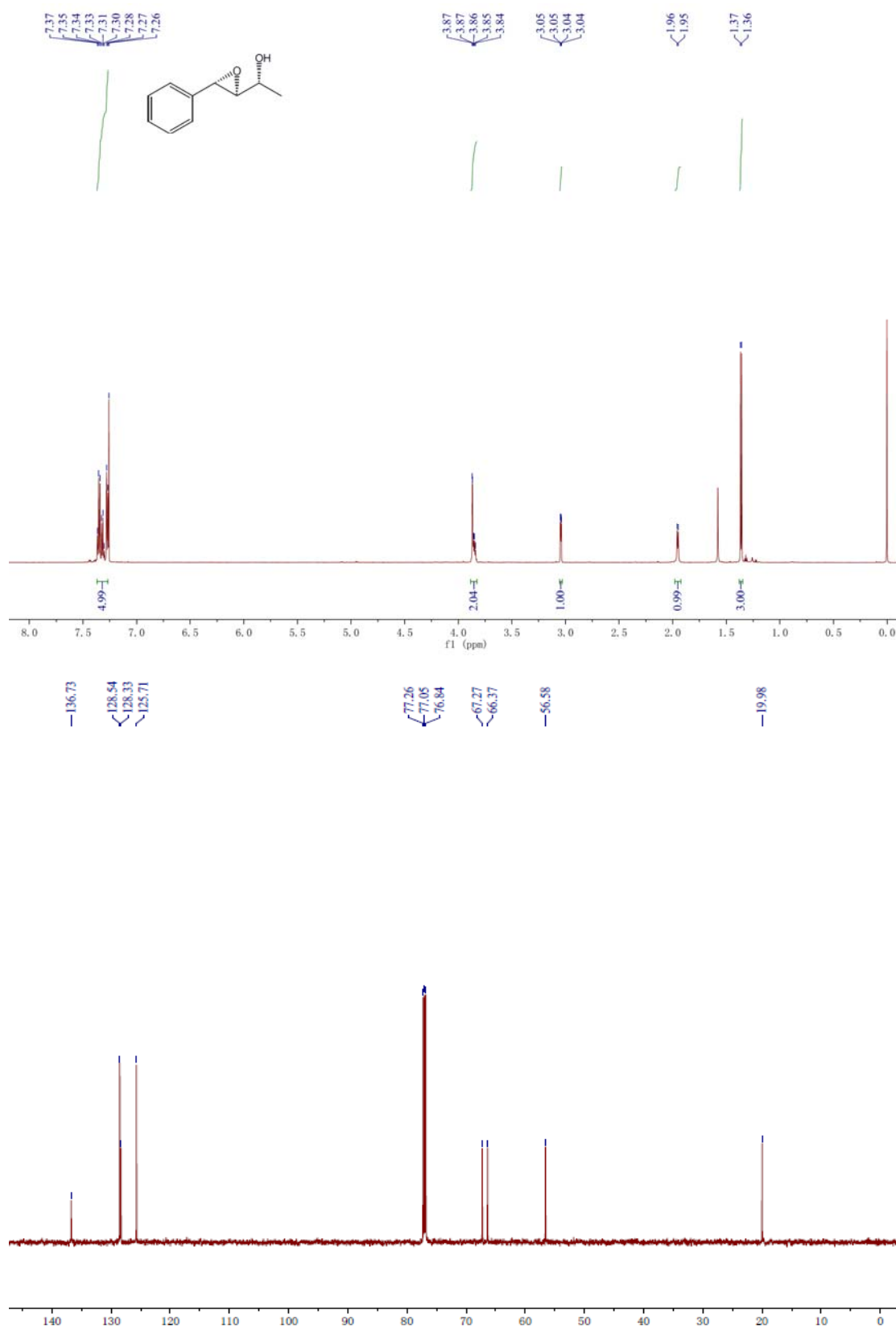


Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.785	744772	43215	10.141	10.702
2	15.824	6599243	360592	89.859	89.298
总计		7344015	403808	100.000	100.000

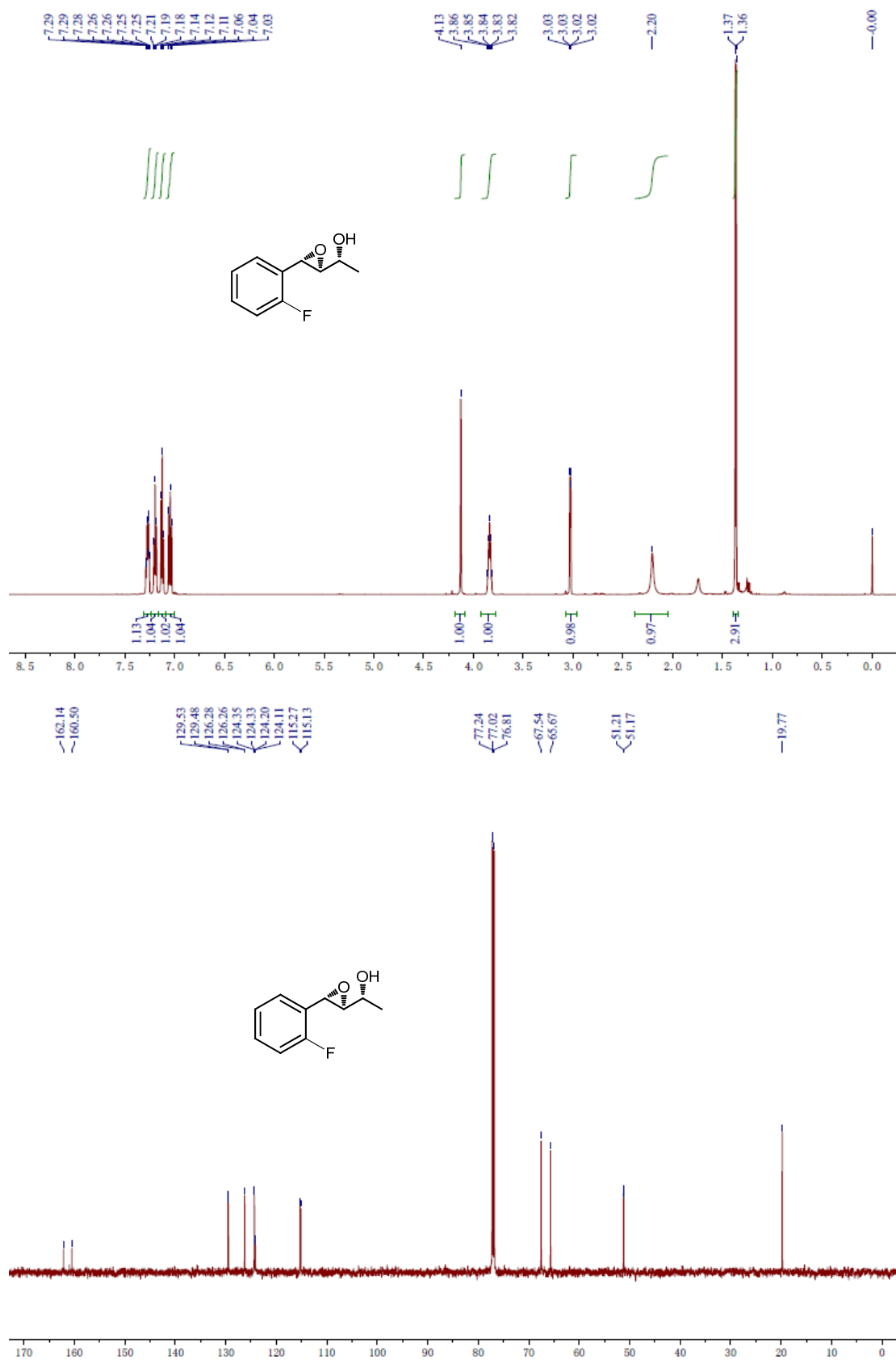
NMR spectra of products

^1H -NMR and ^{13}C NMR spectra of (2*R*)-b

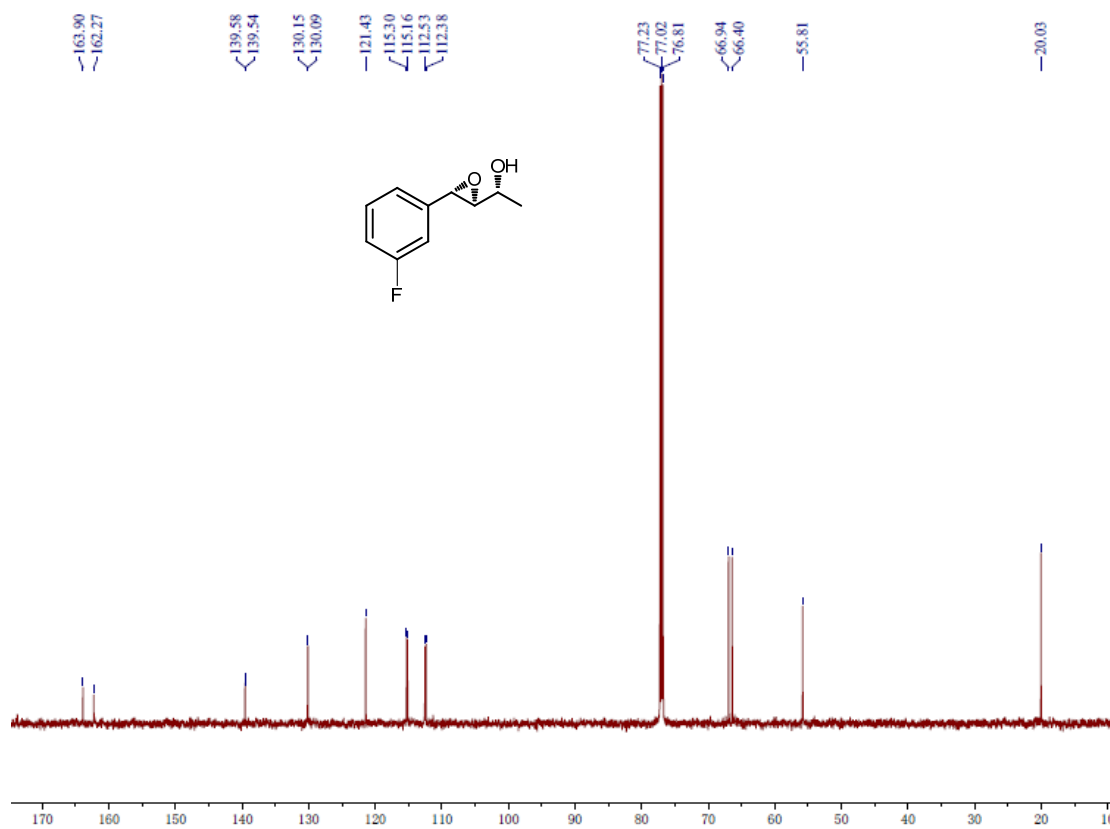
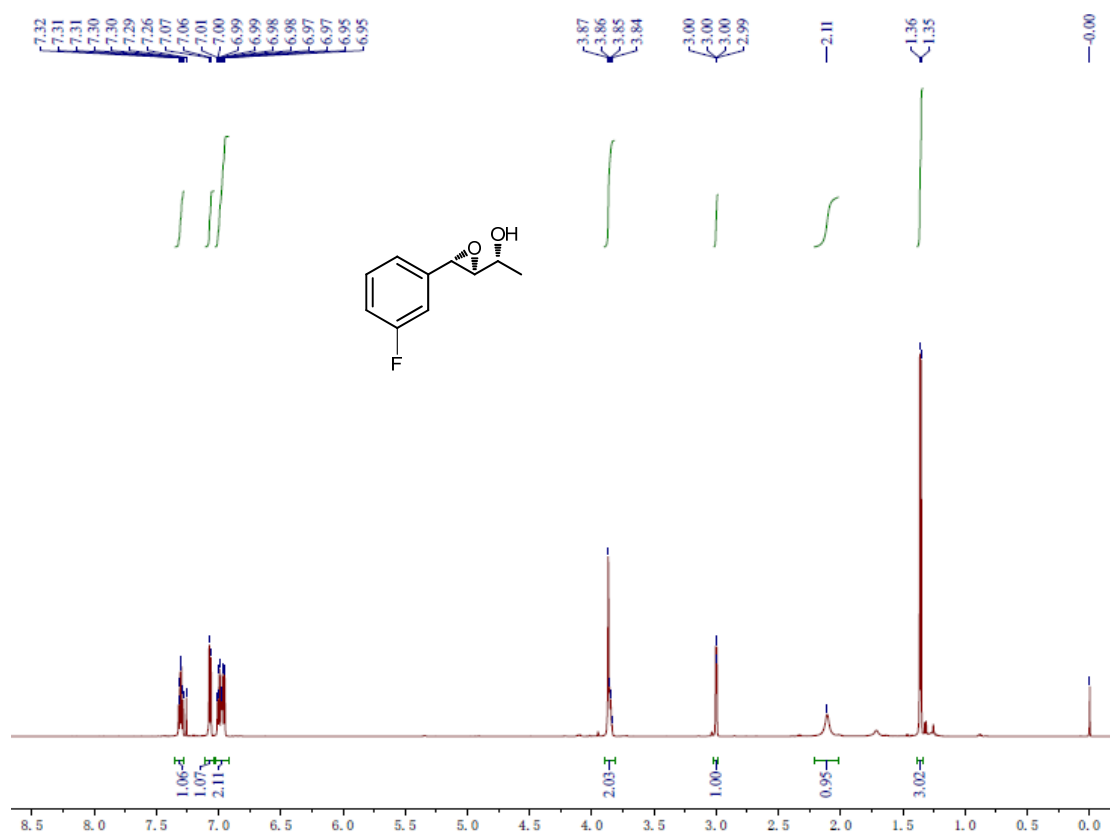
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**1b**



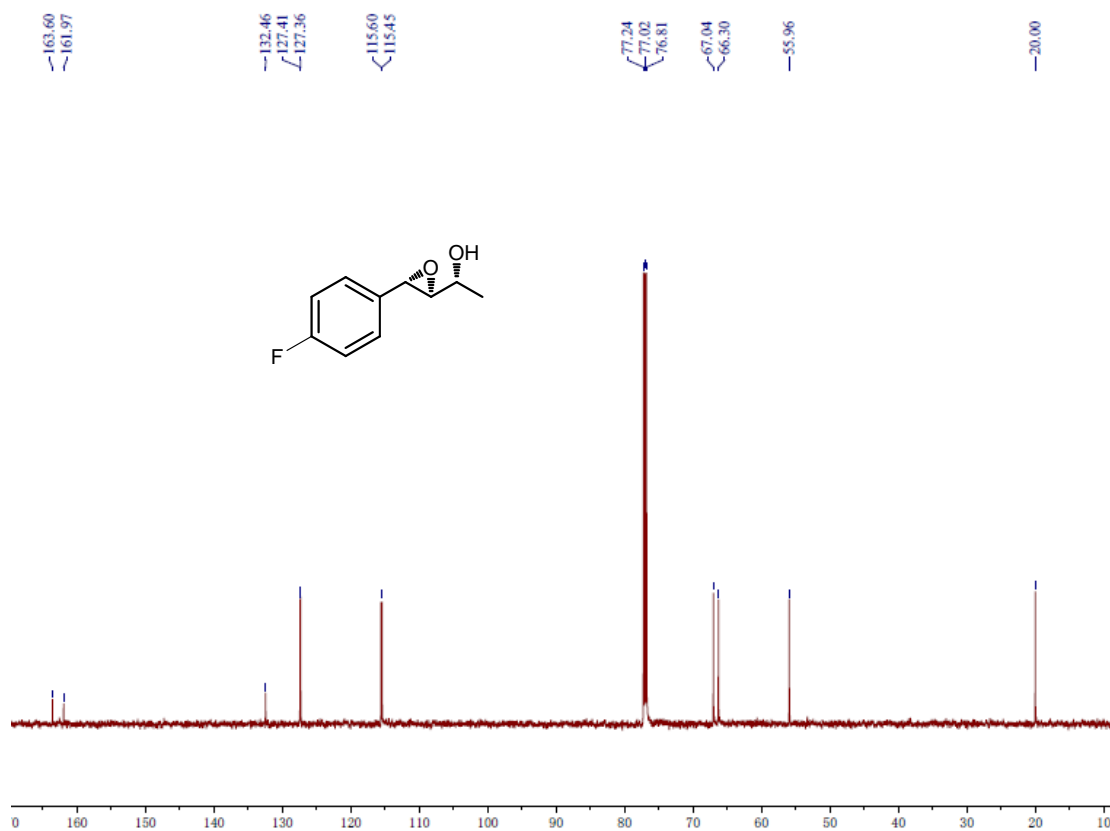
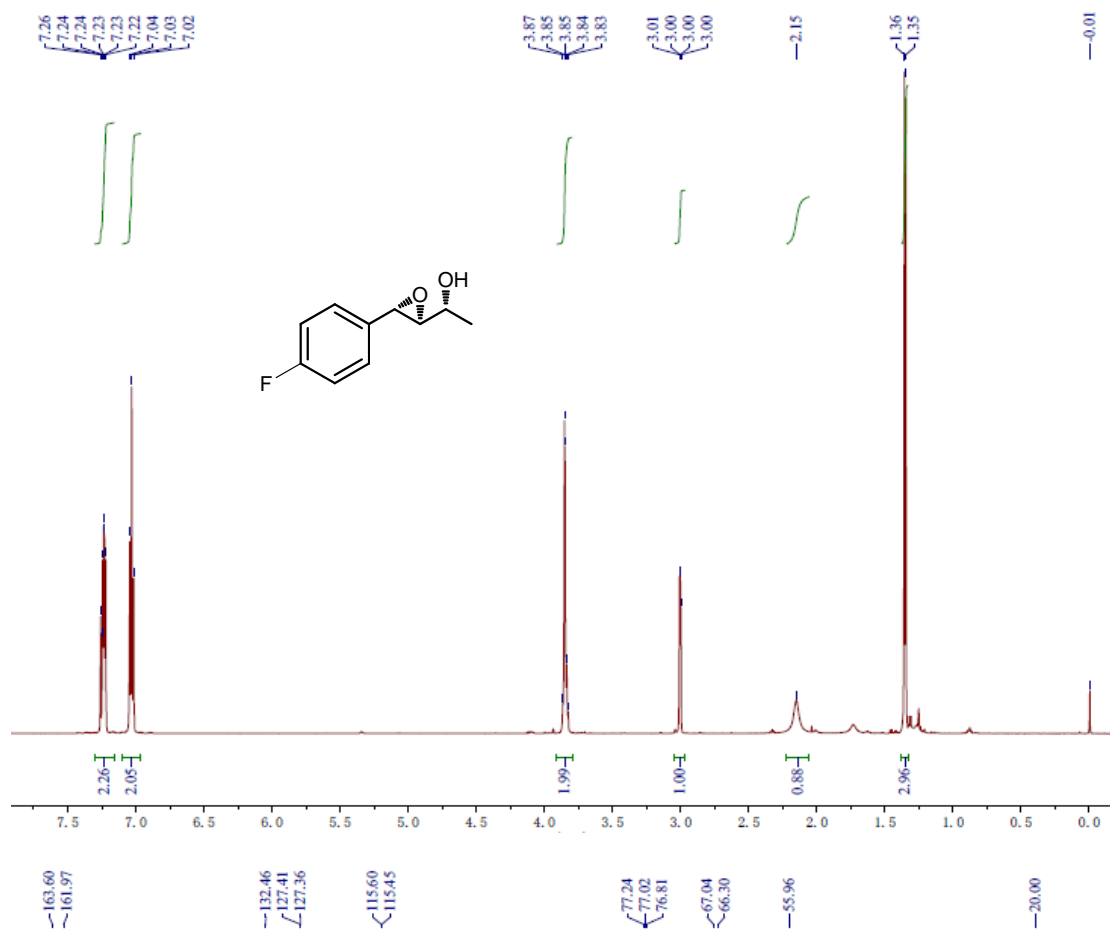
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**2b**



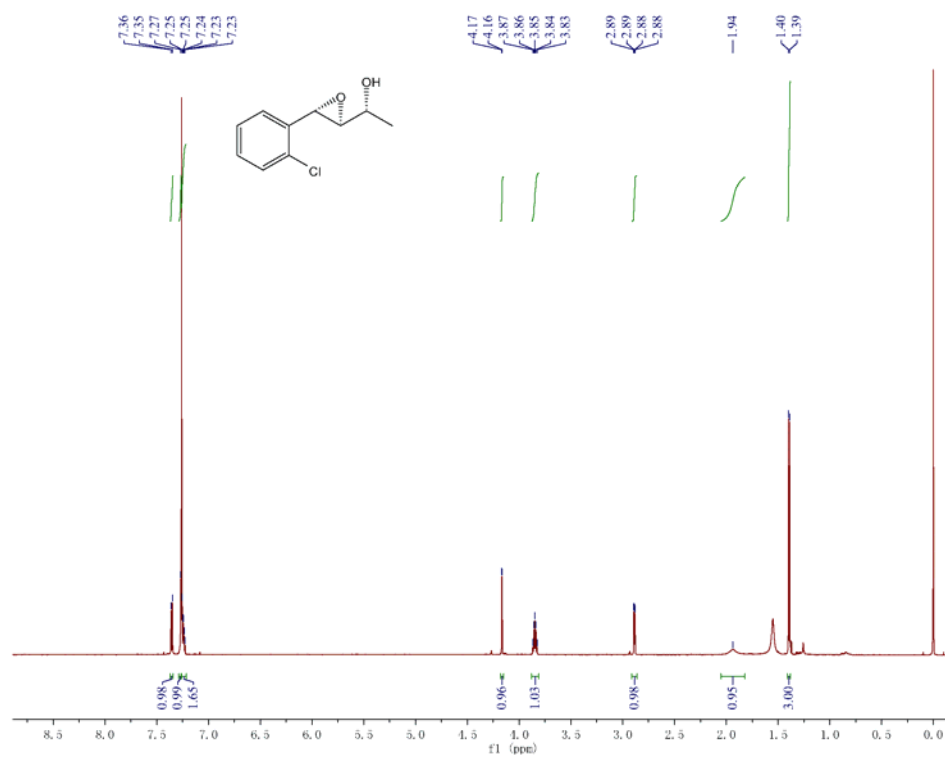
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**3b**



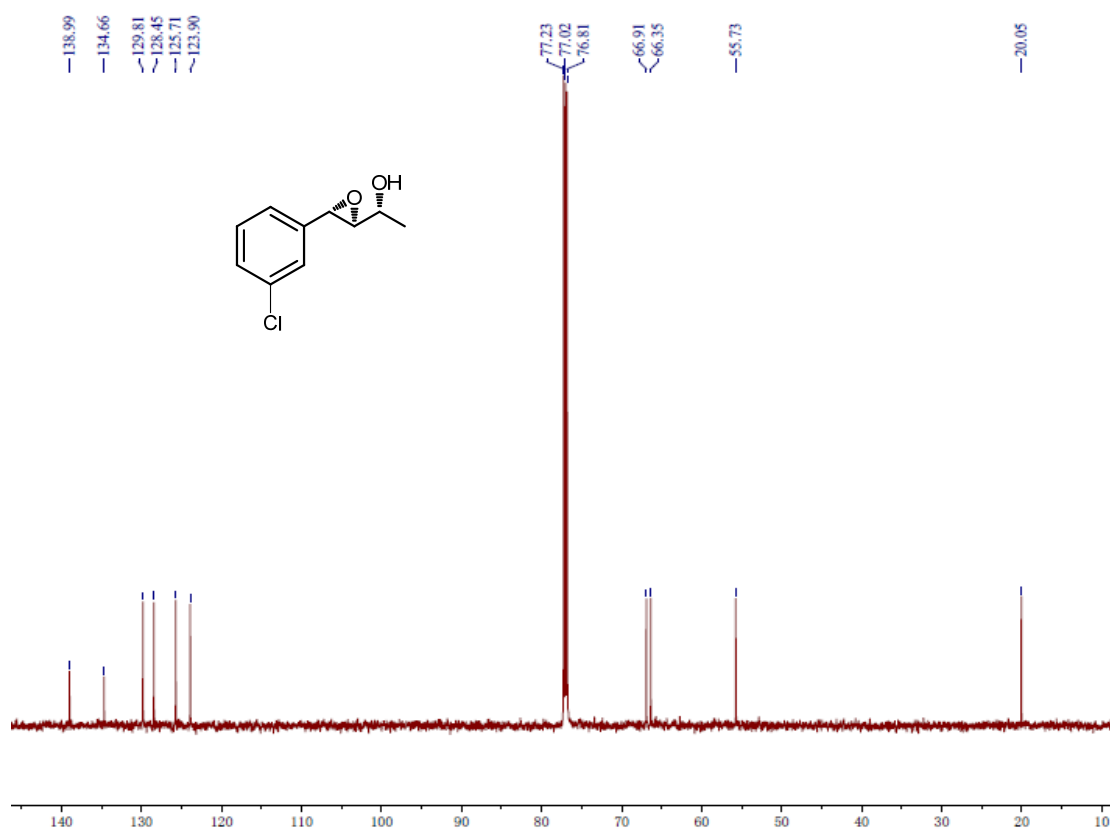
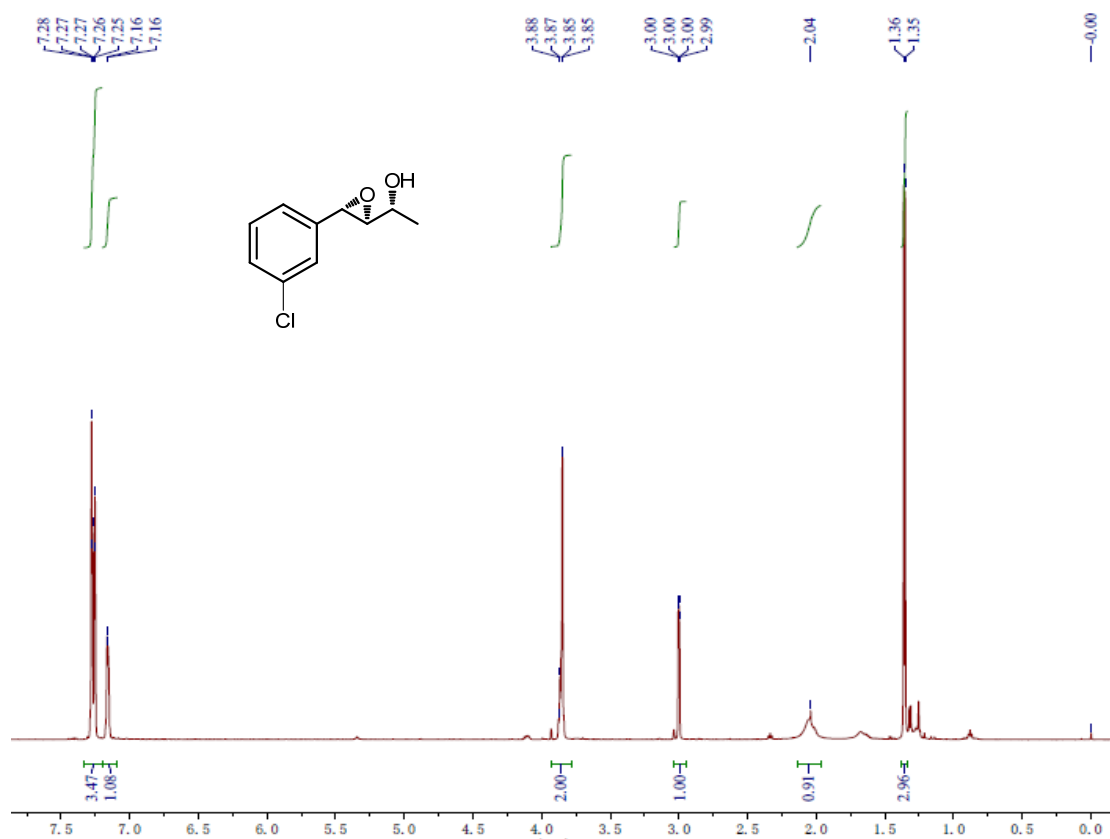
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**4b**



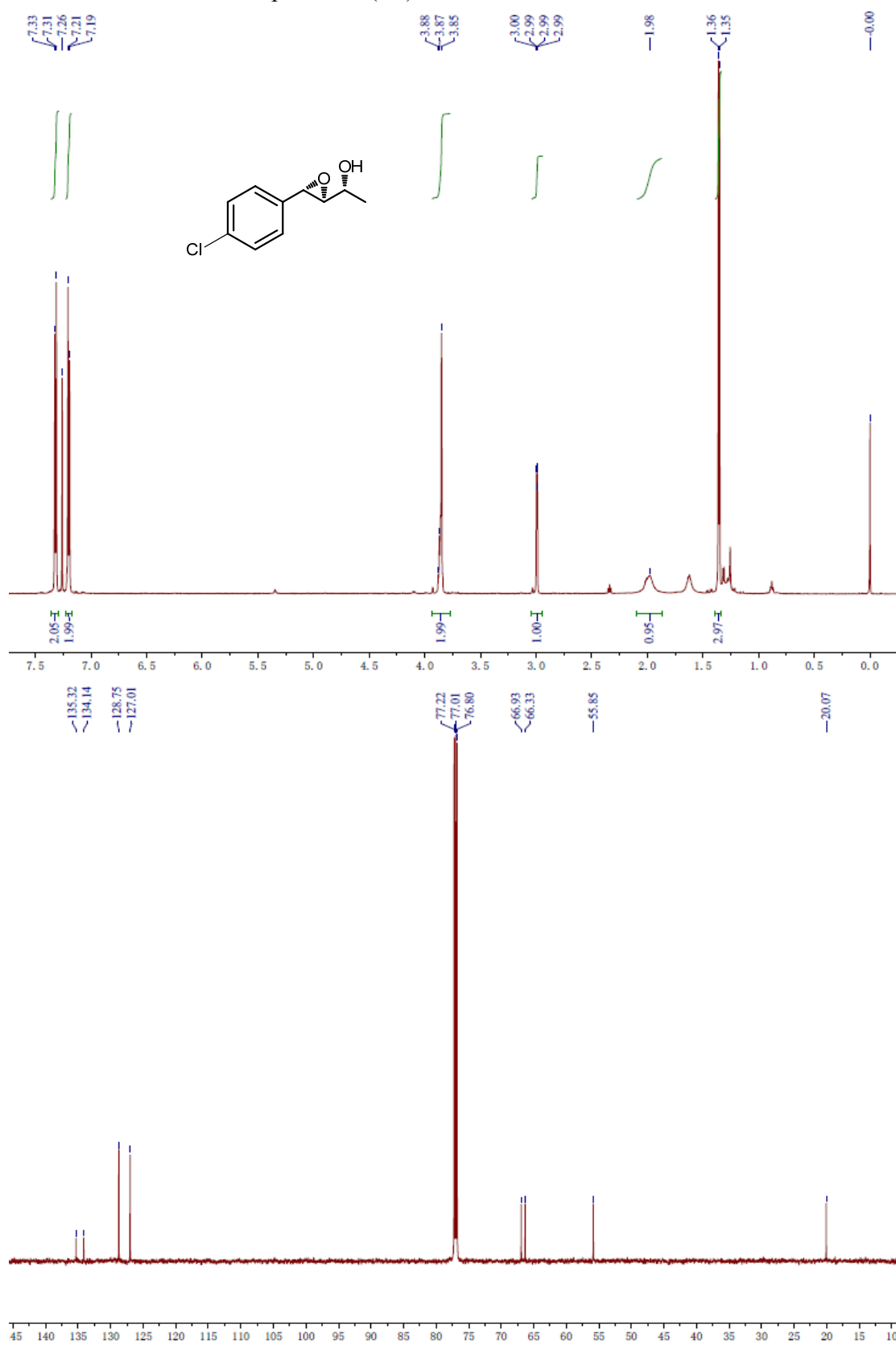
¹H-NMR spectra of (2*R*)-**5b**



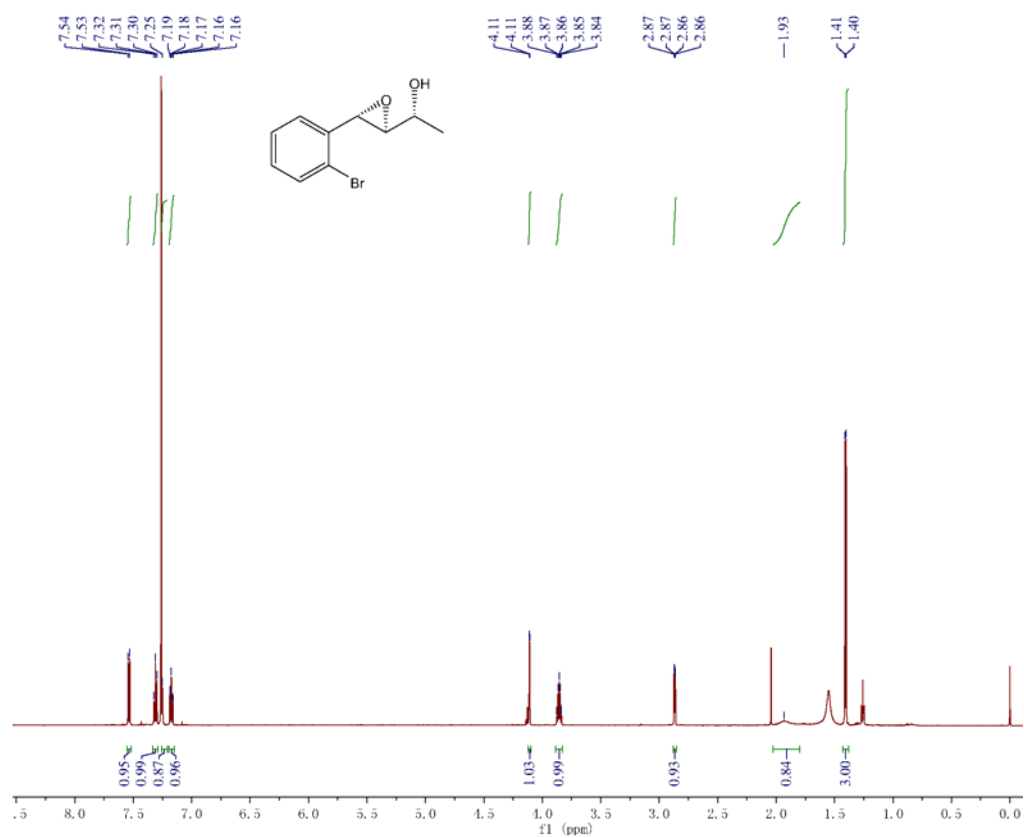
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**6b**



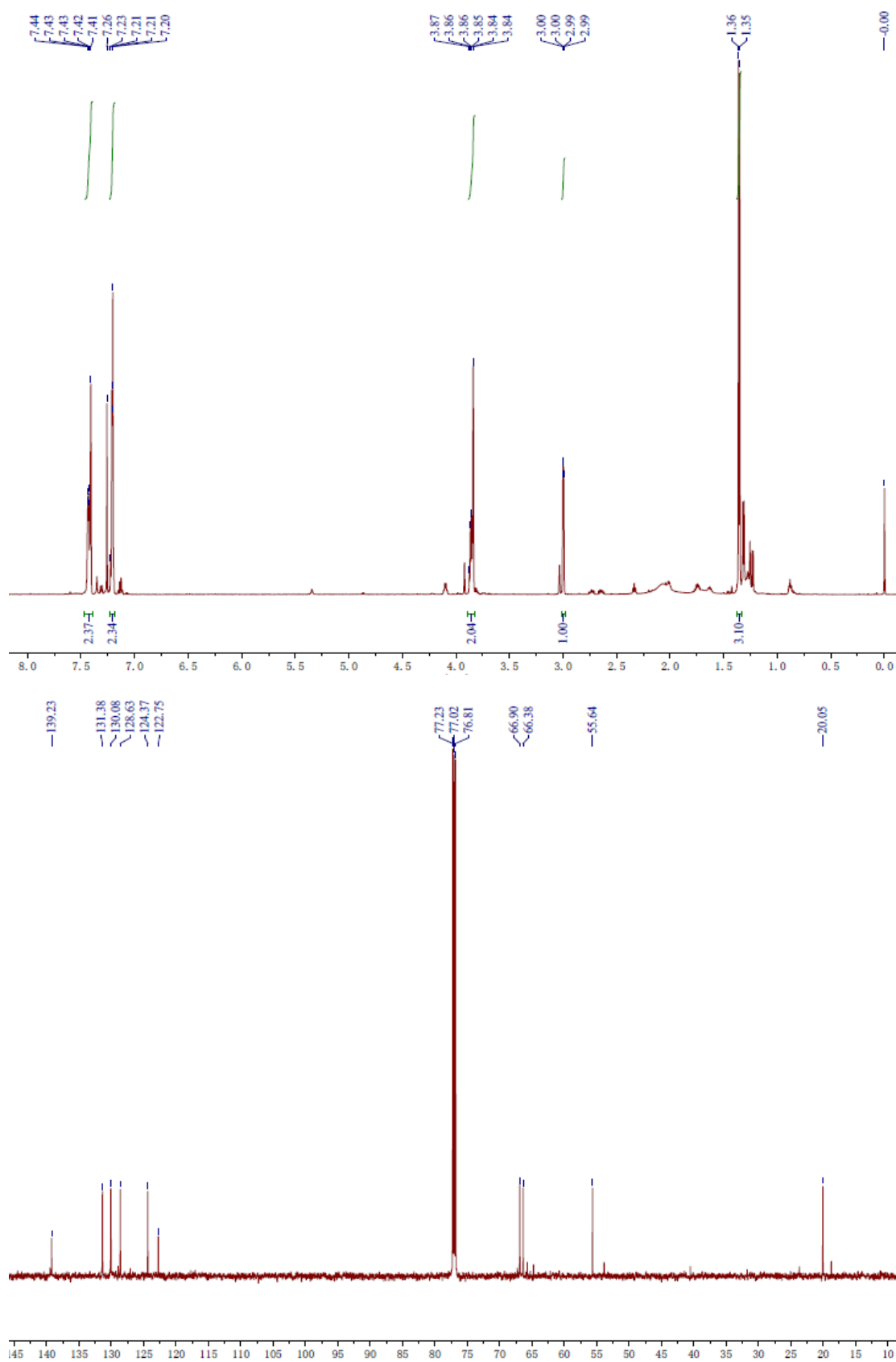
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**7b**



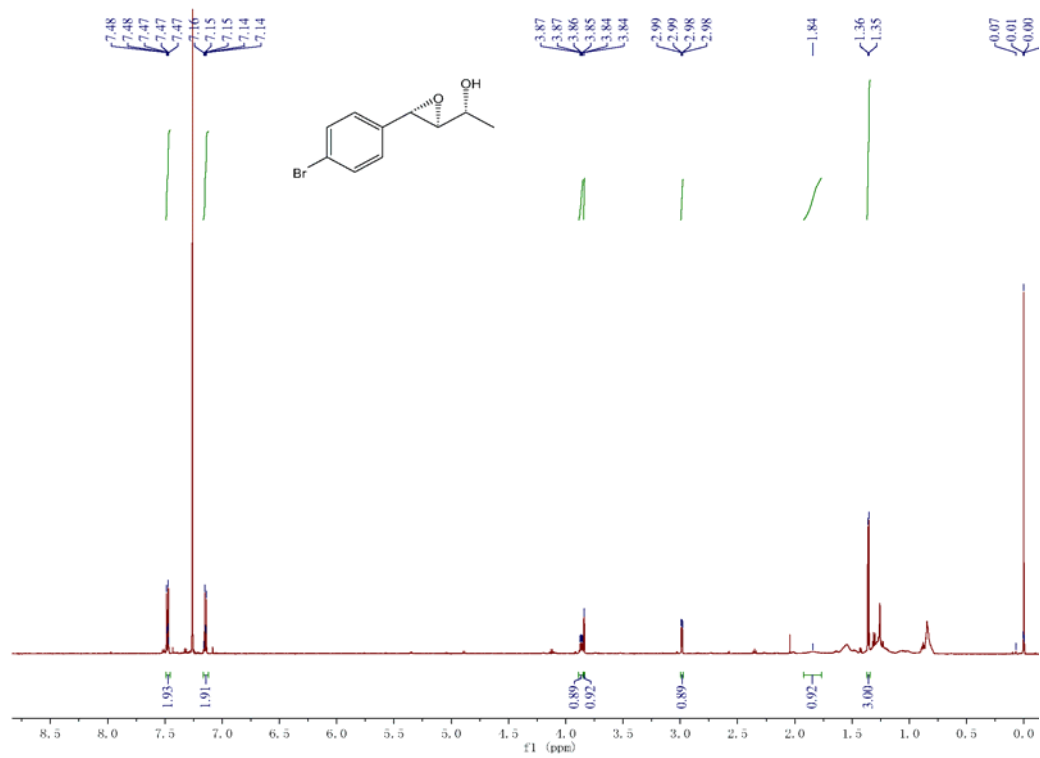
¹H-NMR spectra of (2*R*)-**8b**



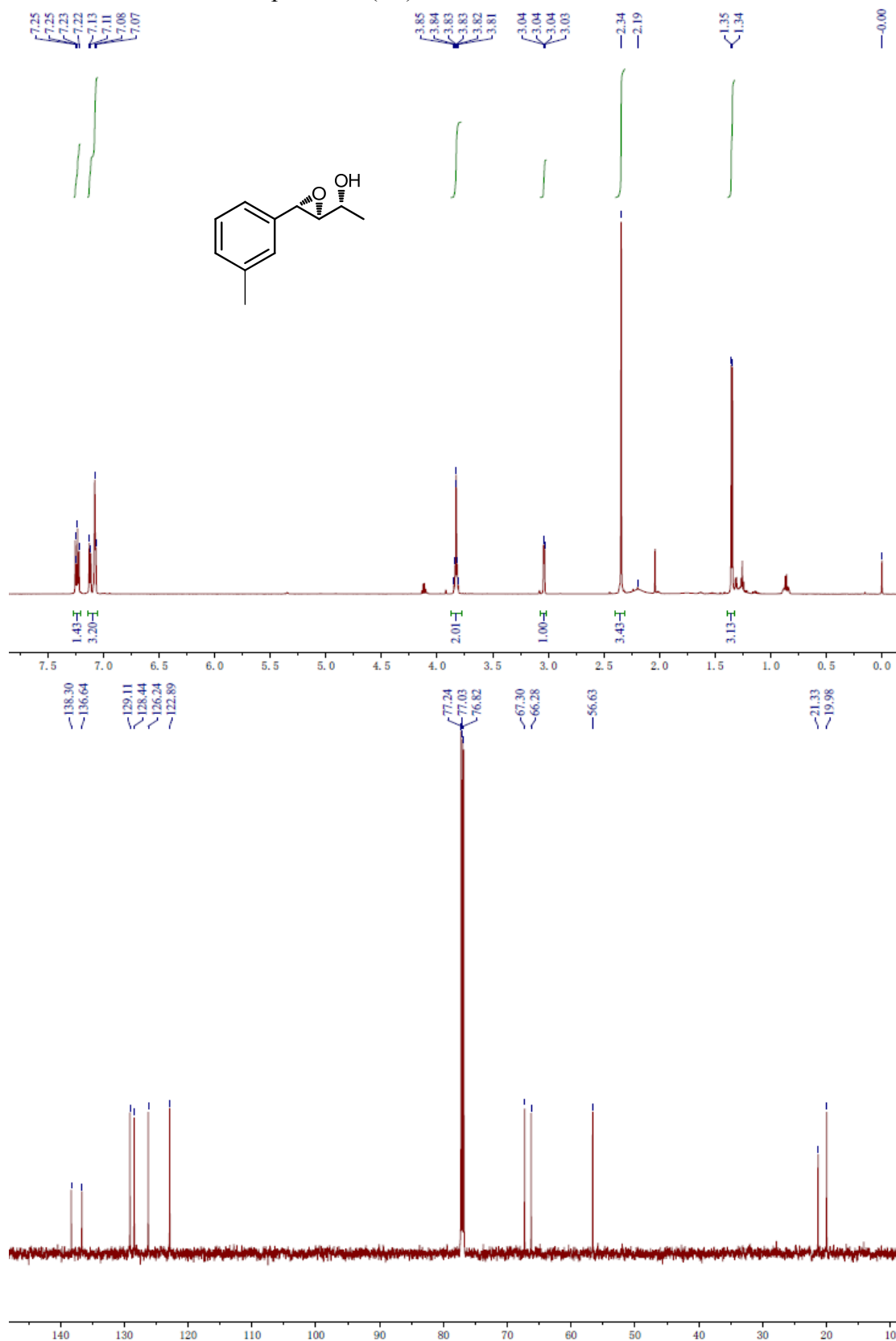
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**9b**



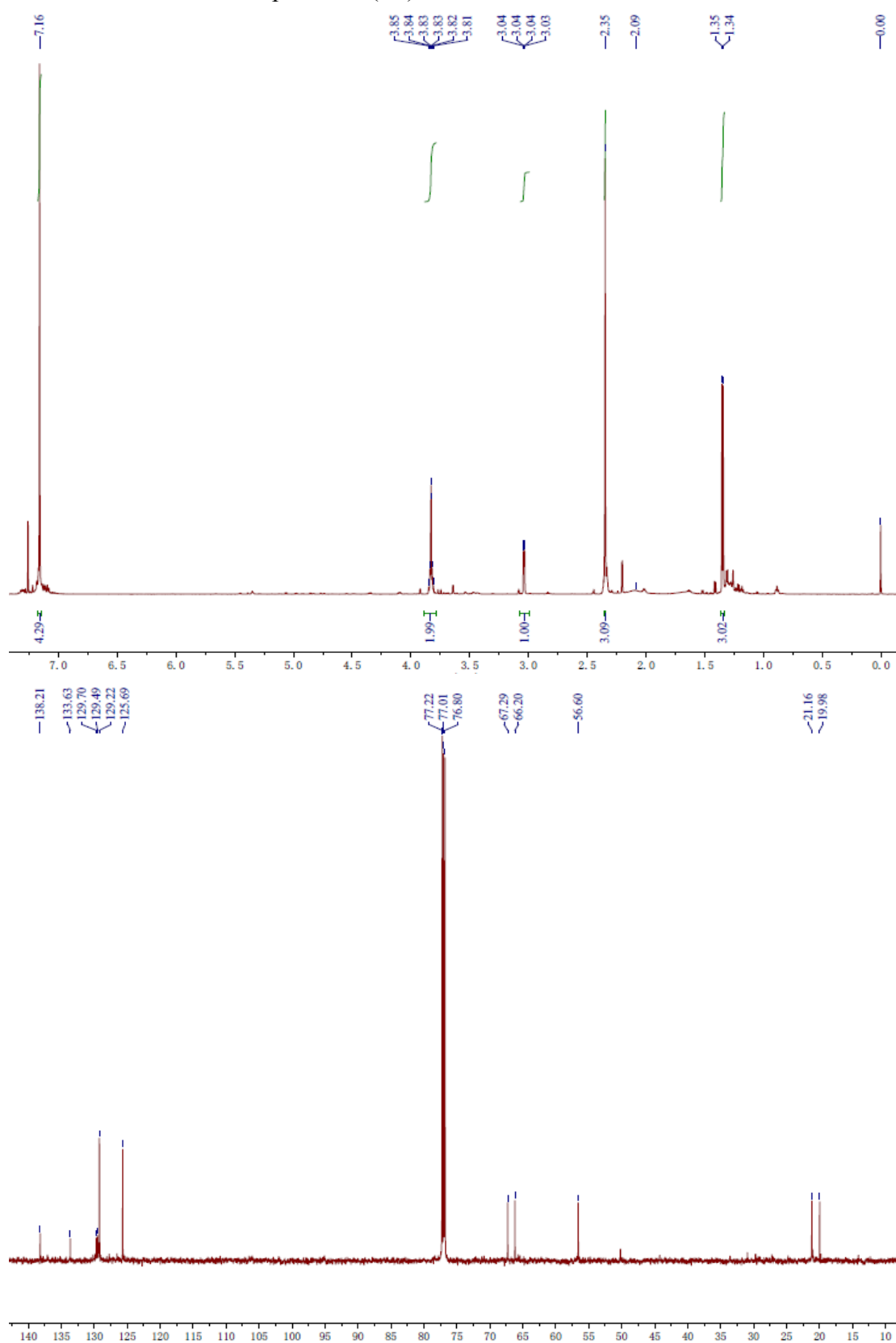
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**10b**



$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**11b**

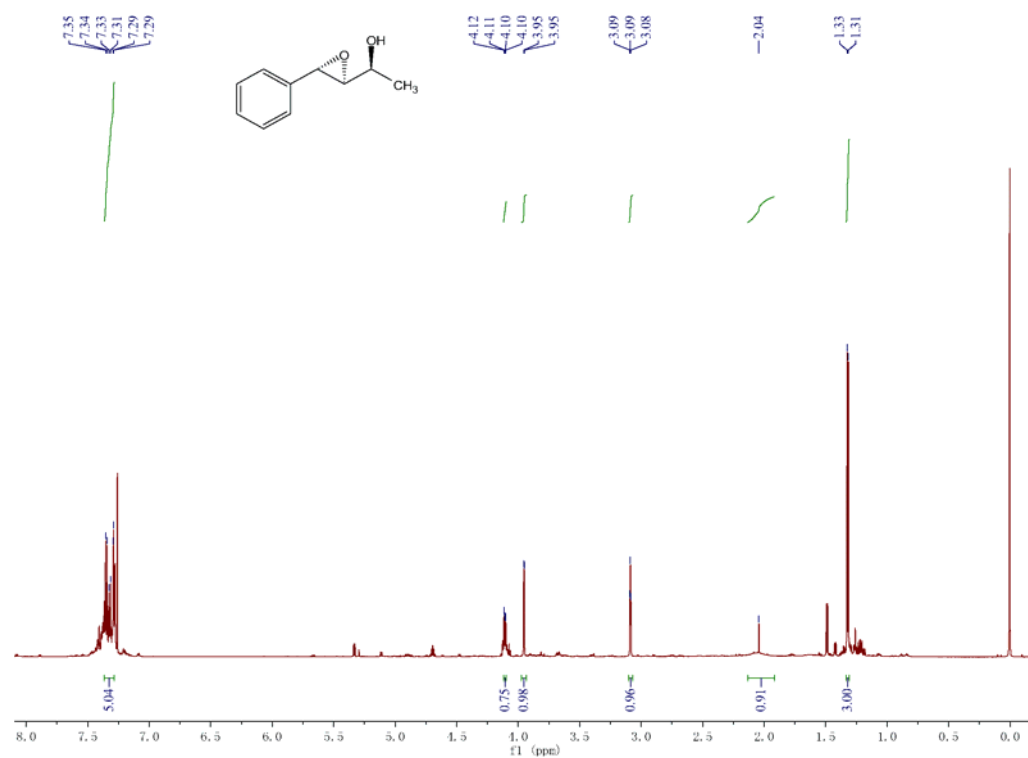


$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of (2*R*)-**12b**

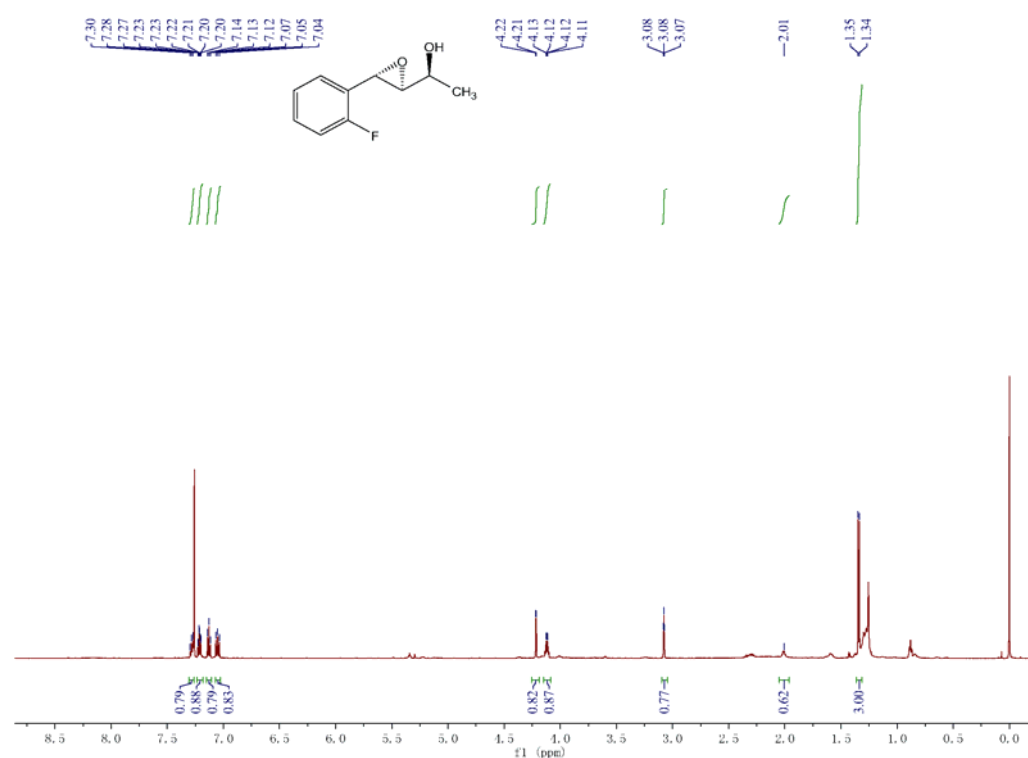


¹H-NMR spectra of (2*S*)-b

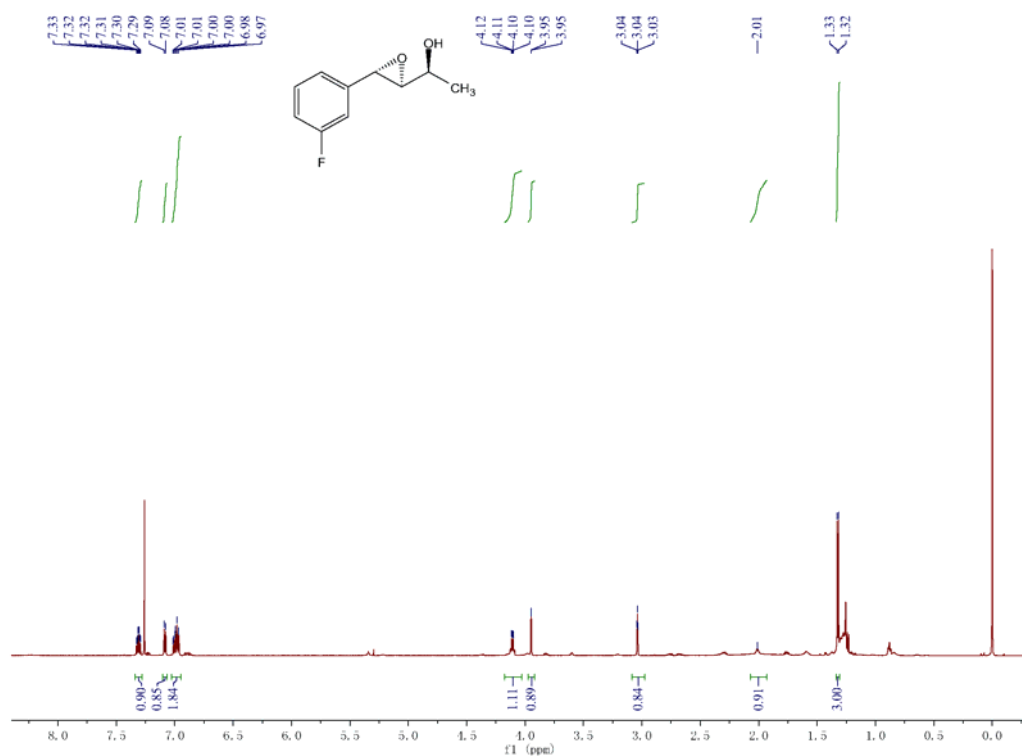
$^1\text{H-NMR}$ spectrum of (2*S*)-**1b**



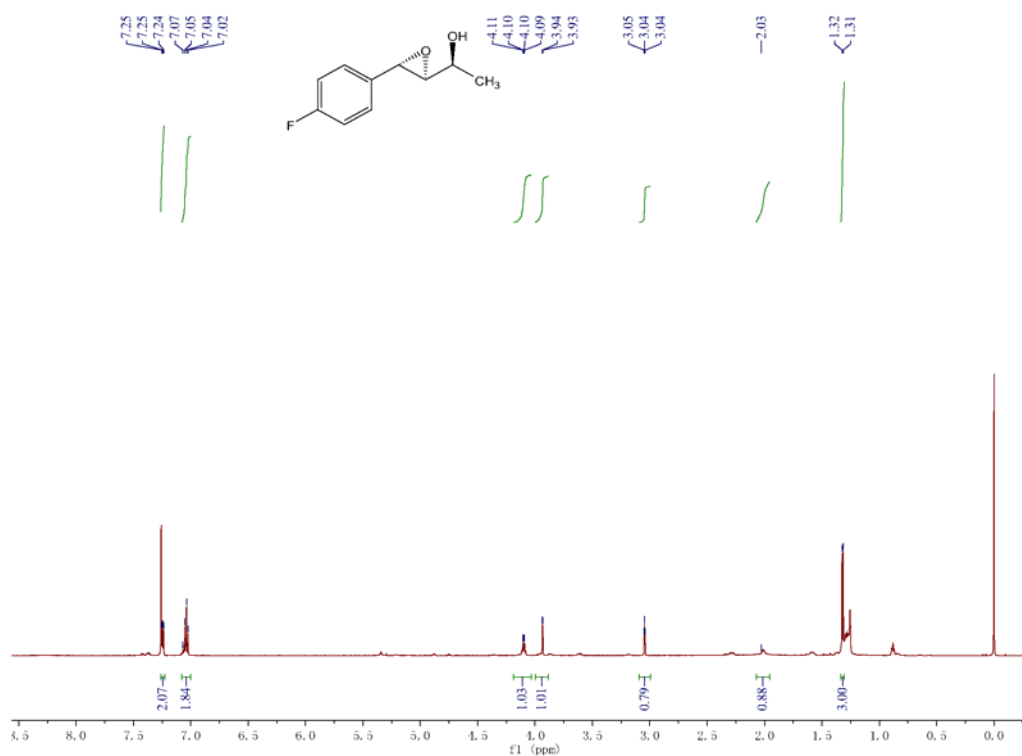
$^1\text{H-NMR}$ spectrum of (2*S*)-**2b**



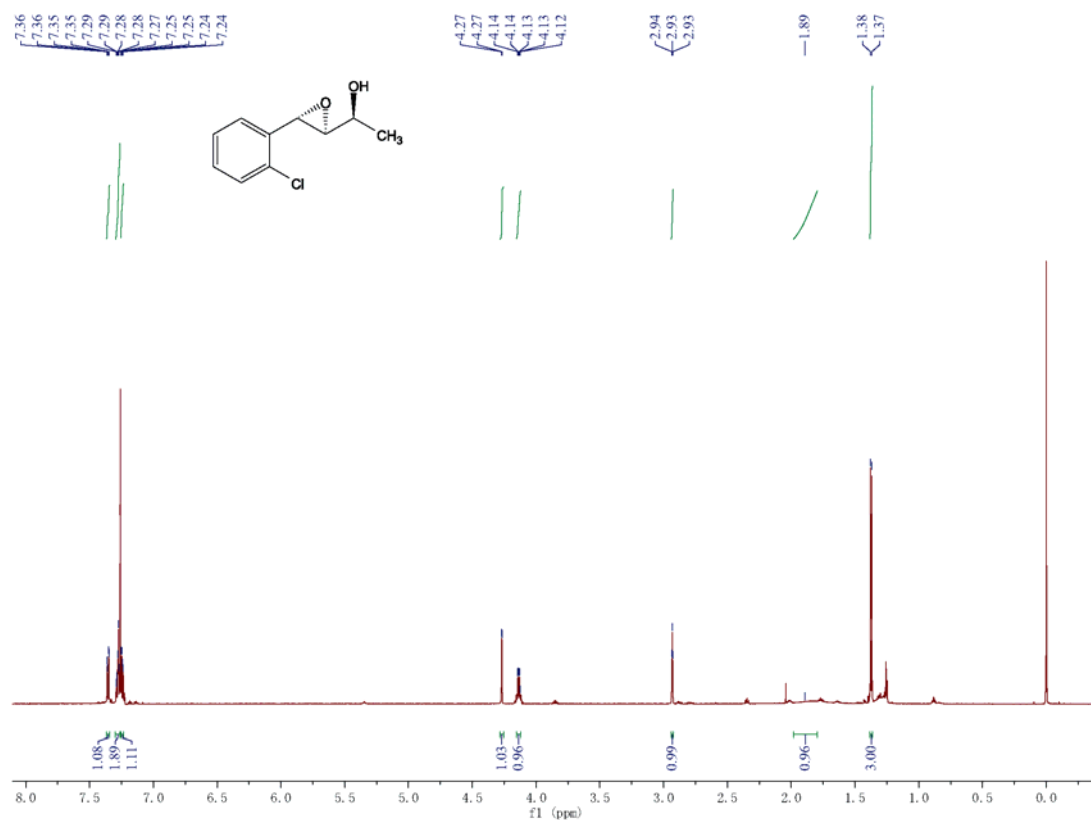
$^1\text{H-NMR}$ spectrum of (2*S*)-**3b**



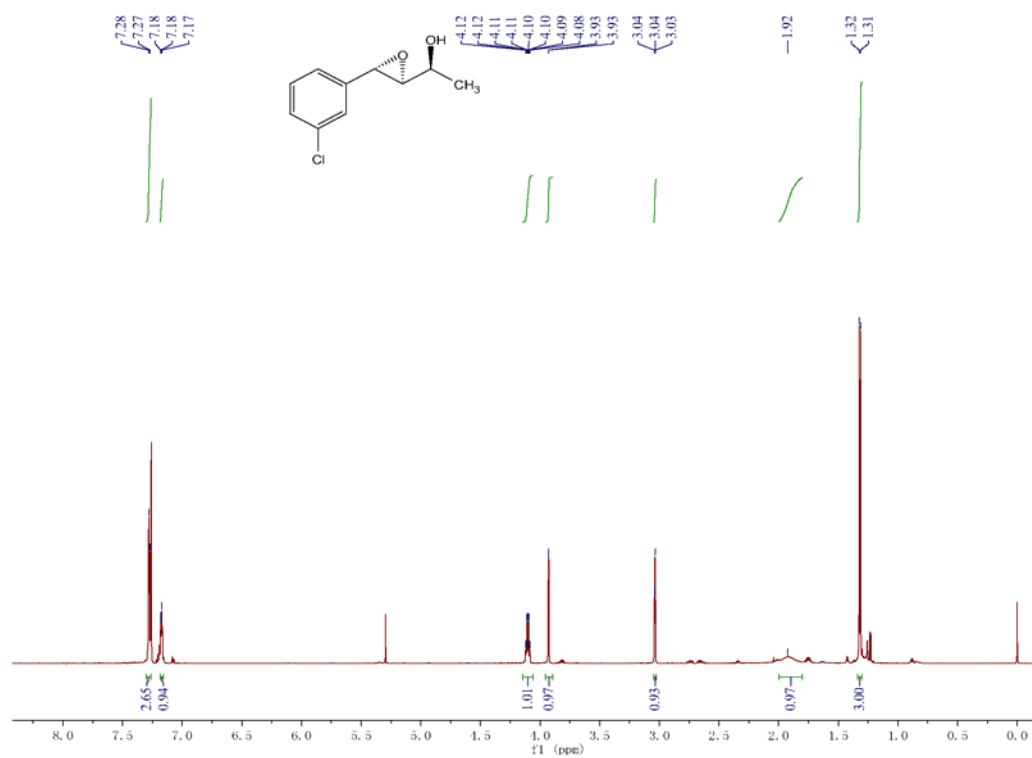
$^1\text{H-NMR}$ spectrum of (2*S*)-**4b**



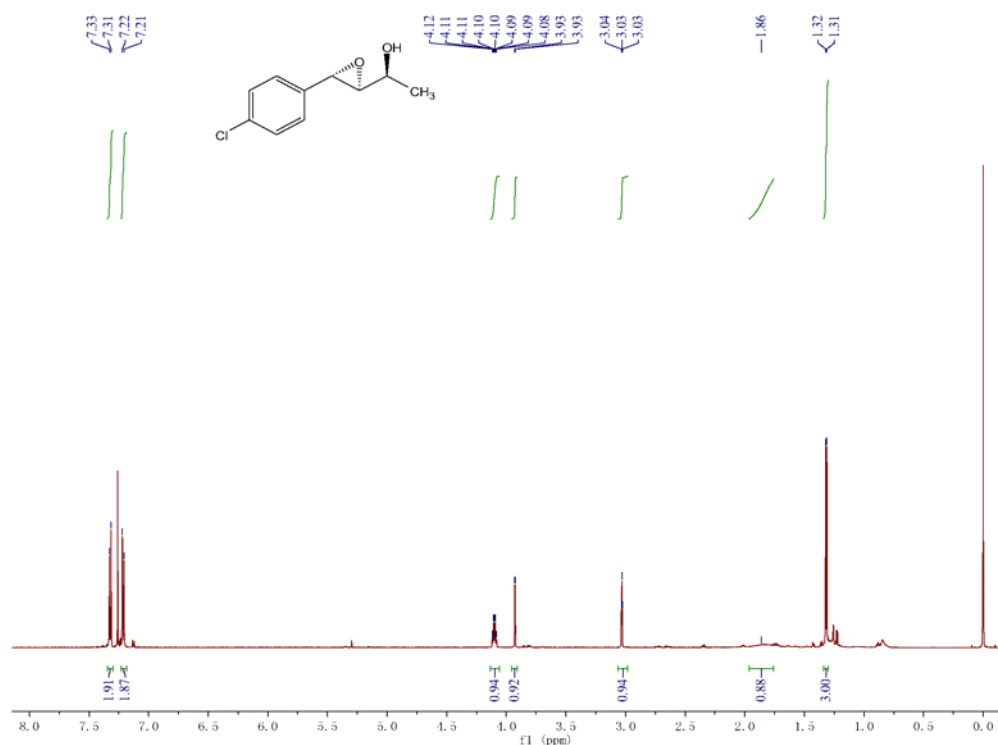
$^1\text{H-NMR}$ spectrum of (2*S*)-**5b**



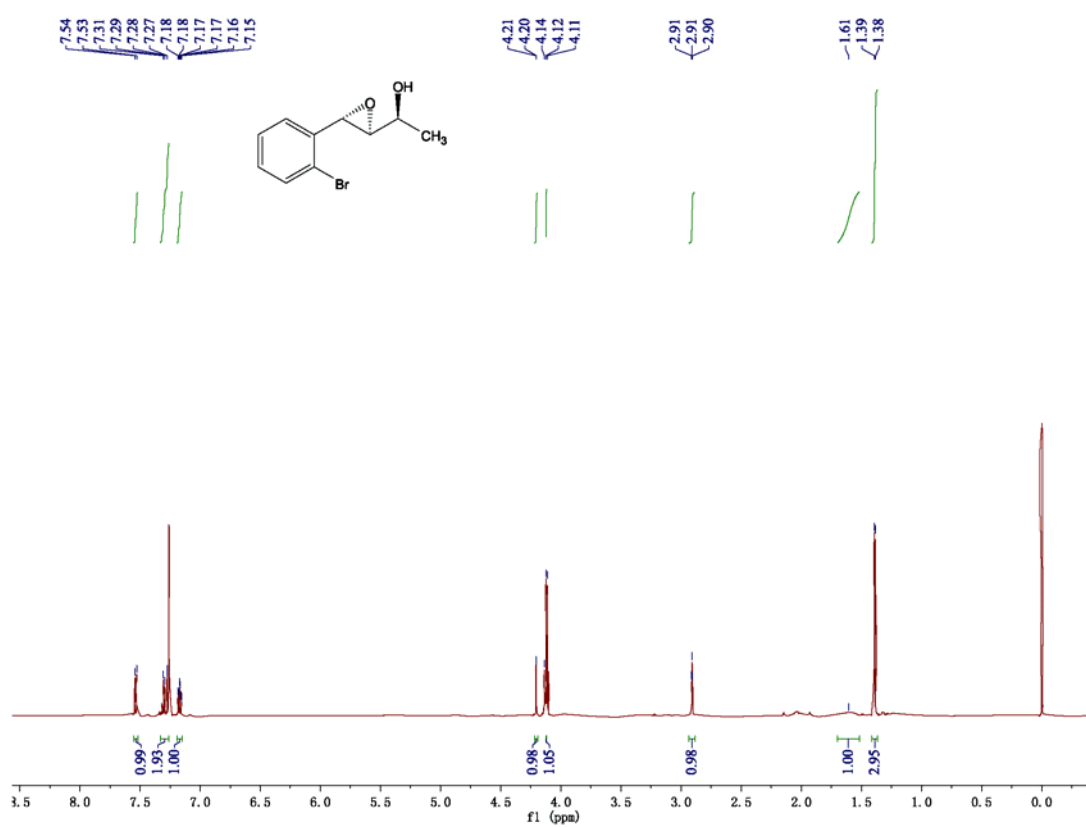
$^1\text{H-NMR}$ spectrum of (2*S*)-**6b**



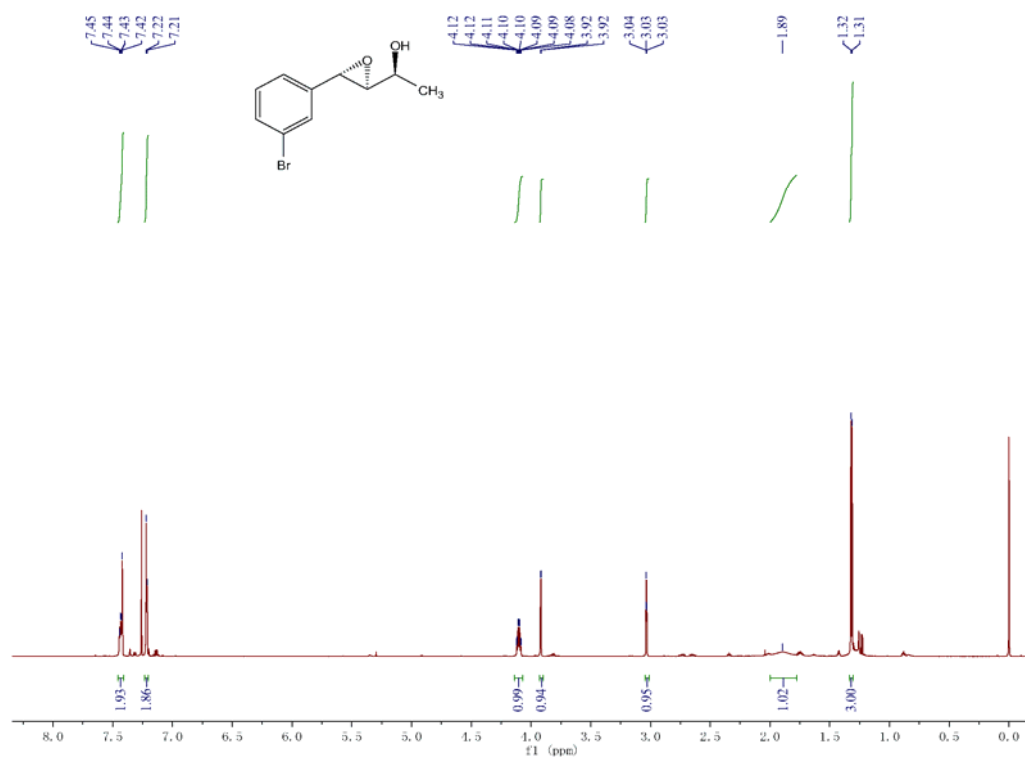
$^1\text{H-NMR}$ spectrum of (2*S*)-**7b**



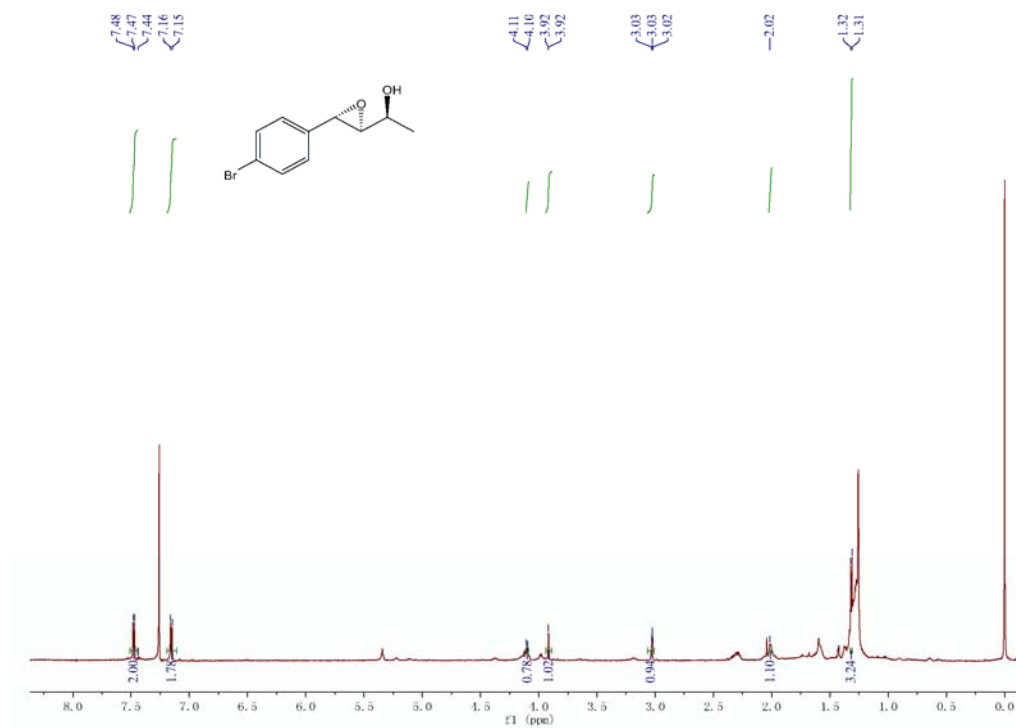
$^1\text{H-NMR}$ spectrum of (2*S*)-**8b**



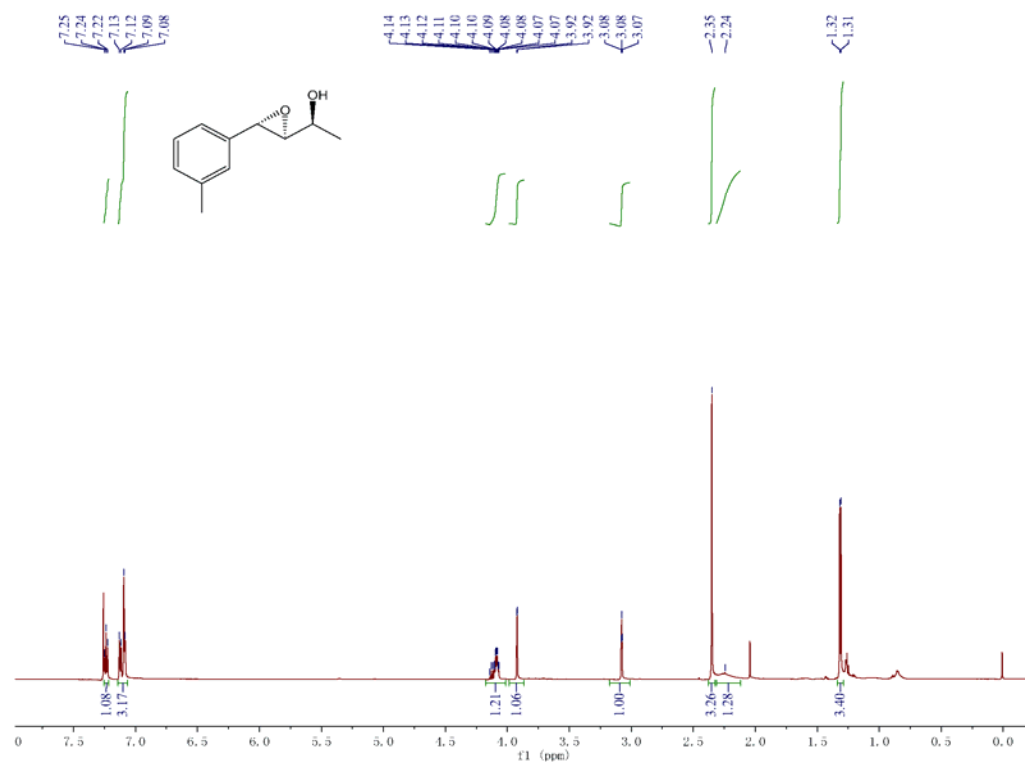
$^1\text{H-NMR}$ spectrum of (2*S*)-**9b**



$^1\text{H-NMR}$ spectrum of (2*S*)-**10b**



$^1\text{H-NMR}$ spectrum of (2*S*)-**11b**



$^1\text{H-NMR}$ spectrum of (2*S*)-**12b**

