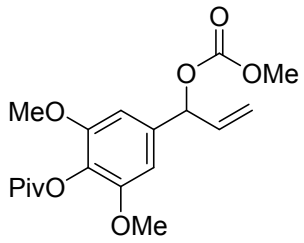
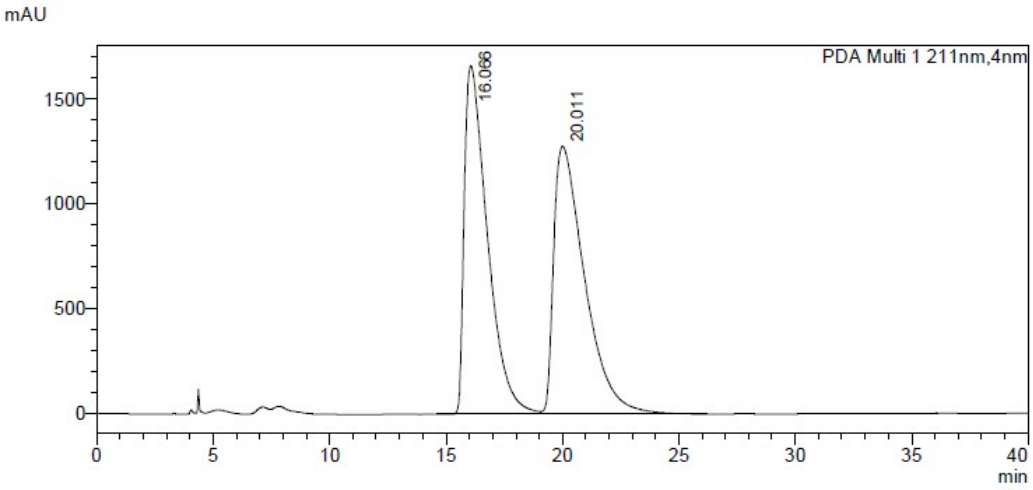
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

HPLC traces for the synthesis of Descurainolide A (3)

(±)-2,6-dimethoxy-4-(1-((methoxycarbonyl)oxy)allyl)phenyl pivalate

Chiralcel OJ-H (99.5:0.5) Hexane: IPA, flow rate 1.0 mL min^{-1}, 30 °C) t_R (*R*-enantiomer) = 16.1 min, t_R (*S*-enantiomer) = 20.0 min

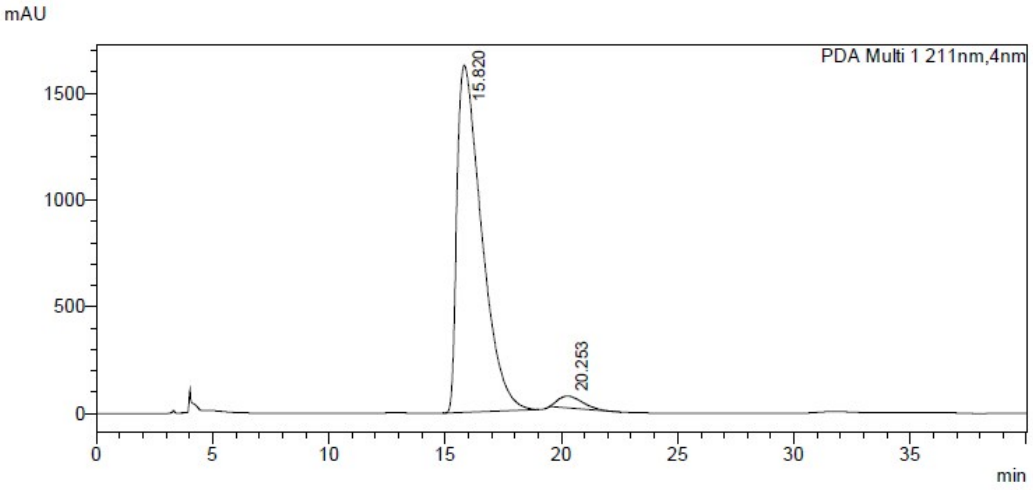




PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	16.066	49.240
2	20.011	50.760
Total		100.000

(*R*)- 2,6-dimethoxy-4-(1-((methoxycarbonyl)oxy)allyl)phenyl pivalate

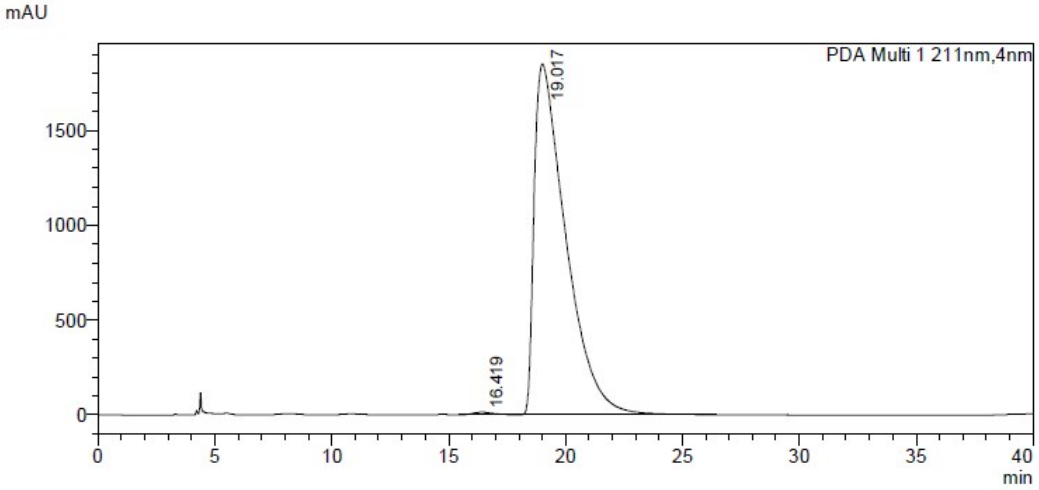


PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	15.820	96.707
2	20.253	3.293
Total		100.000

Therefore *ee* = 93%

(*S*)-2,6-dimethoxy-4-(1-((methoxycarbonyl)oxy)allyl)phenyl pivalate



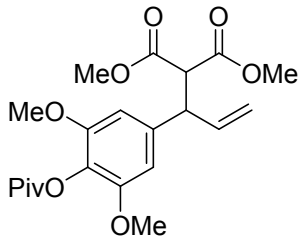
PDA Ch1 211nm

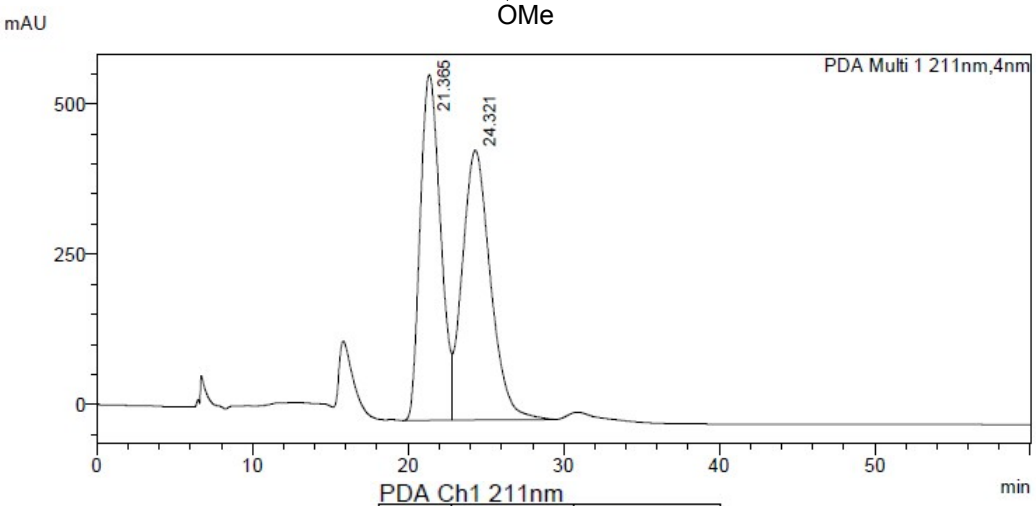
Peak#	Ret. Time	Area%
1	16.419	0.453
2	19.017	99.547
Total		100.000

Therefore *ee* = 99%

(±)-Dimethyl 2-(1-(3,5-dimethoxy-4-(pivaloyloxy)phenyl)allyl)malonate

Chiralcel OJ-H (97:3 Hexane:IPA, flow rate 0.5 mL min^{-1}, 40 °C) t_R (*R*-enantiomer) = 21.4 min, t_R (*S*-enantiomer) = 24.3 min

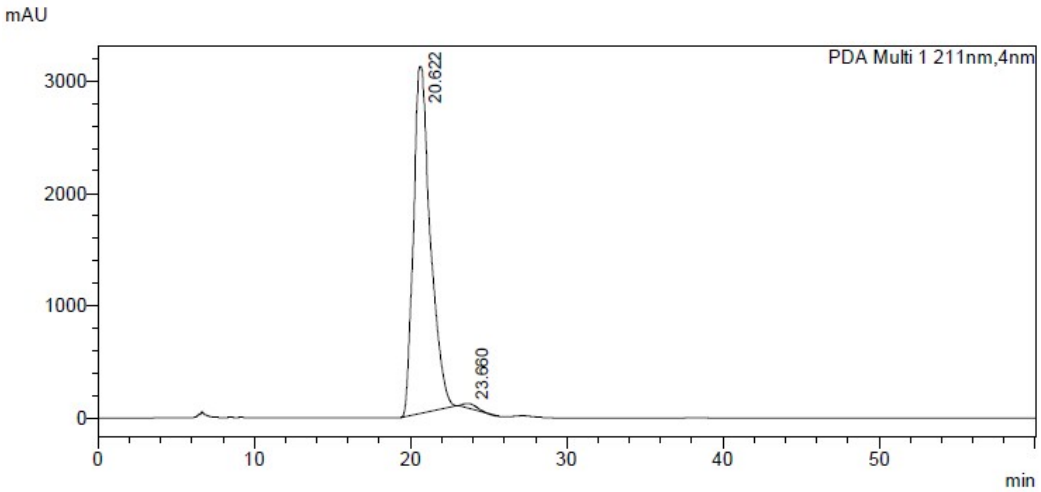




PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	21.365	47.997
2	24.321	52.003
Total		100.000

(*R*)-Dimethyl 2-(1-(3,5-dimethoxy-4-(pivaloyloxy)phenyl)allyl)malonate

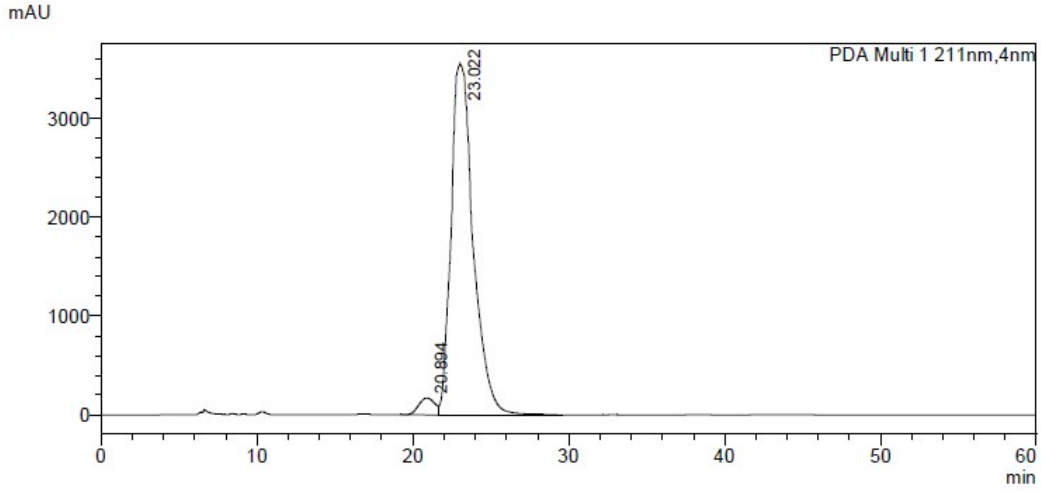


PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	20.622	99.048
2	23.660	0.952
Total		100.000

Therefore *ee* = 98%

(*S*)-Dimethyl 2-(1-(3,5-dimethoxy-4-(pivaloyloxy)phenyl)allyl)malonate



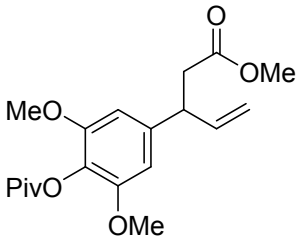
PDA Ch1 211nm

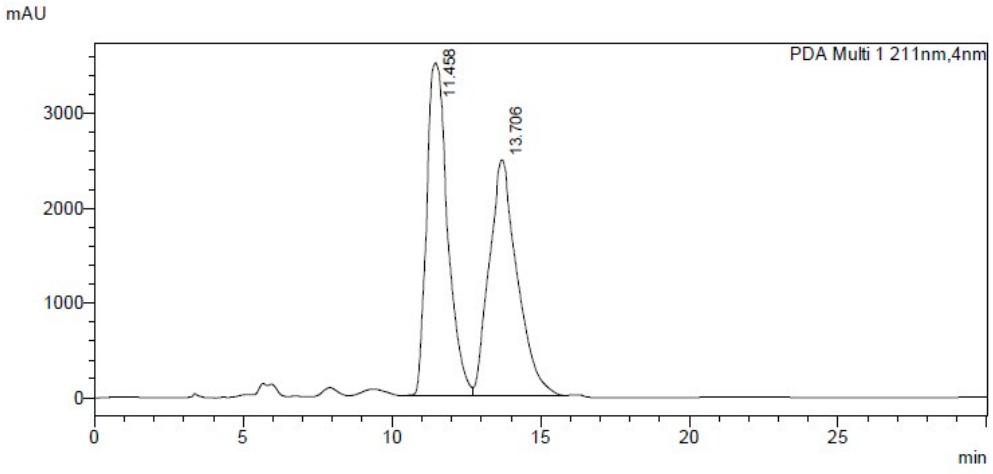
Peak#	Ret. Time	Area%
1	20.894	3.296
2	23.022	96.704
Total		100.000

Therefore ee = 93%

(±)-Methyl 3-(3,5-dimethoxy-4-(pivaloyloxy)phenyl)pent-4-enoate

Chiralcel OJ-H (97:3 Hexane:IPA, flow rate 1 mL min^{-1}, 30 ^{o}C) t_R (*S*) = 11.5 min, t_R (*R*) = 13.7 min.

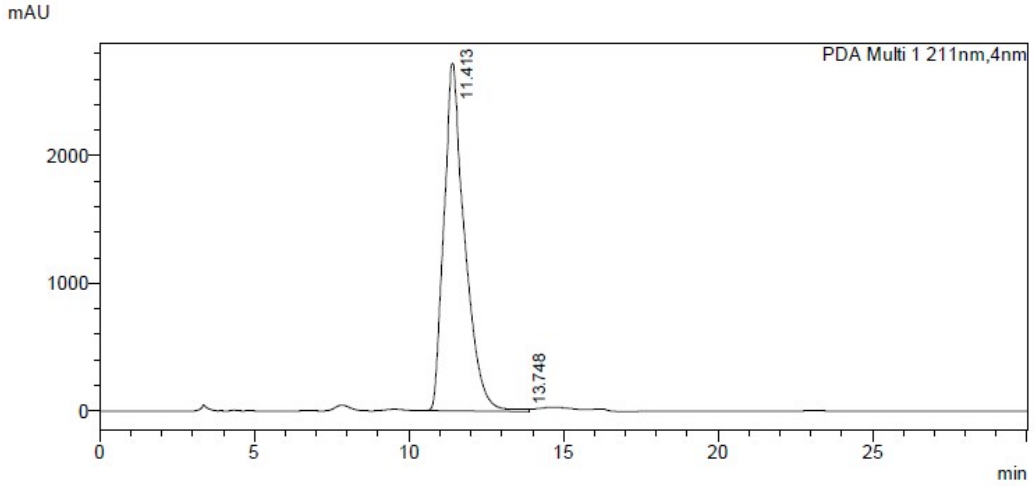




PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	11.458	51.406
2	13.706	48.594
Total		100.000

(*S*)- Methyl 3-(3,5-dimethoxy-4-(pivaloyloxy)phenyl)pent-4-enoate

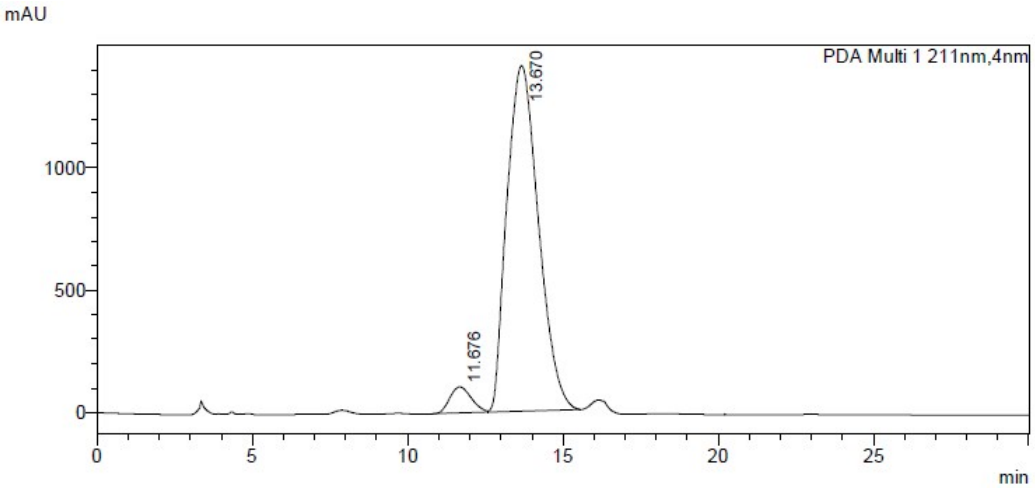


PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	11.413	99.994
2	13.748	0.006
Total		100.000

Therefore *ee* = >99%

(*R*)- Methyl 3-(3,5-dimethoxy-4-(pivaloyloxy)phenyl)pent-4-enoate



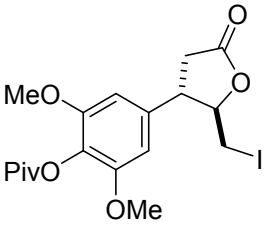
PDA Ch1 211nm

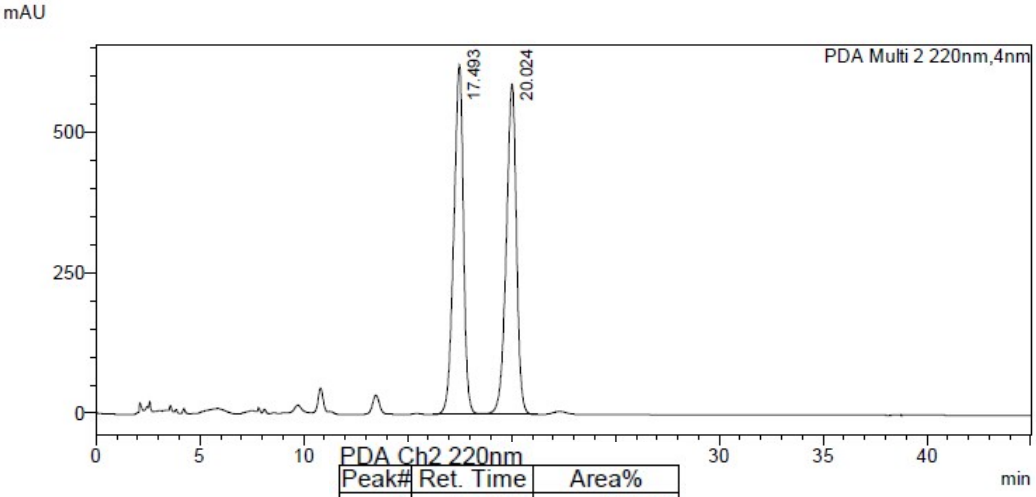
Peak#	Ret. Time	Area%
1	11.676	4.918
2	13.670	95.082
Total		100.000

Therefore *ee* = 90%

(±)-2-(iodomethyl)-5-oxotetrahydrofuran-3-yl)-2,6-dimethoxyphenyl pivalate

Chiralpak AD-H, 95:5 IPA Hexane: IPA, flow rate 1.5 mL min^{-1}, 30 °C) t_R (2*S*,3*R*) = 17.5 min, t_R (2*R*,3*S*) = 20.0 min.

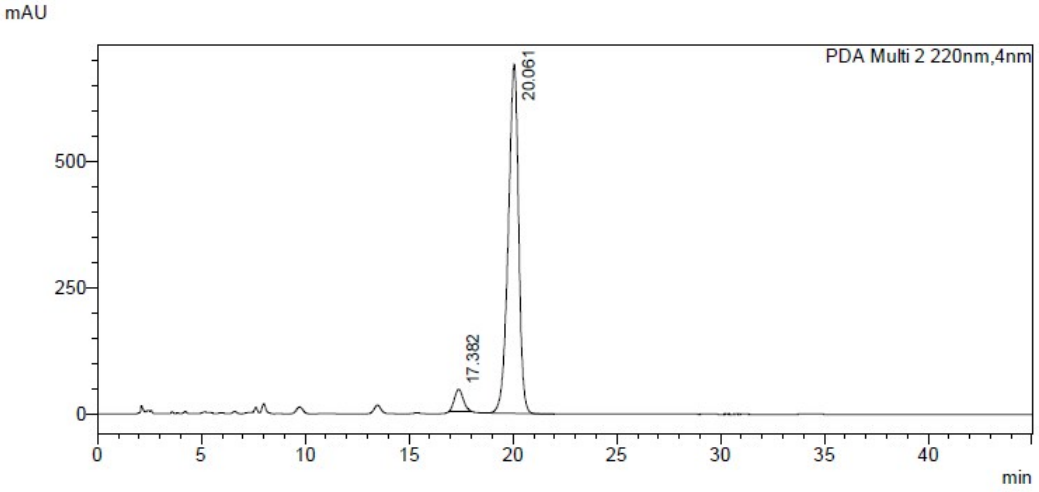




PDA Ch2 220nm

Peak#	Ret. Time	Area%
1	17.493	49.909
2	20.024	50.091
Total		100.000

(2*R*,3*S*)-2-(iodomethyl)-5-oxotetrahydrofuran-3-yl)-2,6-dimethoxyphenyl pivalate

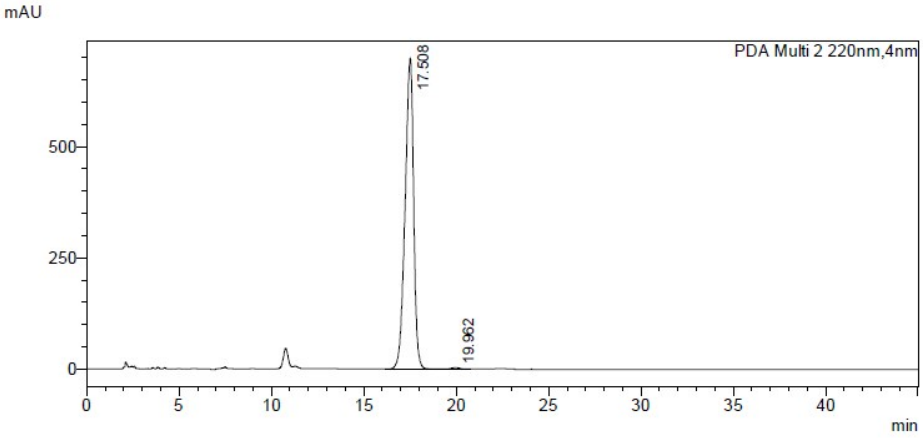


PDA Ch2 220nm

Peak#	Ret. Time	Area%
1	17.382	4.983
2	20.061	95.017
Total		100.000

Therefore *ee* = 90%

(2*S*,3*R*)-2-(iodomethyl)-5-oxotetrahydrofuran-3-yl)-2,6-dimethoxyphenyl pivalate



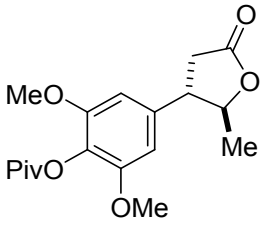
PDA Ch2 220nm

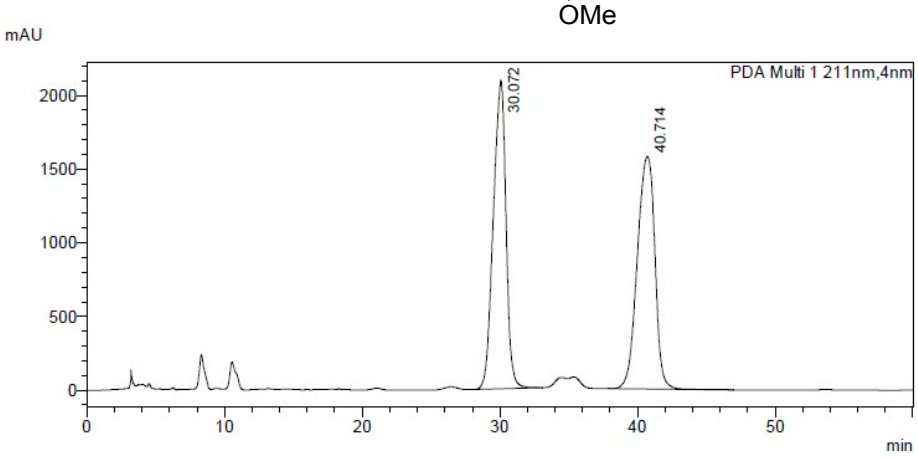
Peak#	Ret. Time	Area%
1	17.508	99.493
2	19.962	0.507
Total		100.000

Therefore *ee* = 99%

(±)-2,6-dimethoxy-4-((2,3-*anti*)-2-methyl-5-oxotetrahydrofuran-3-yl)phenyl pivalate

Chiralpak AD-H 97:3 Hexane: IPA, flow rate 1.0 mL min^{-1}, 30 ^{o}C) t_R (2*R*,3*R*) = 30.1 min, t_R (2*S*,3*S*) = 40.7 min

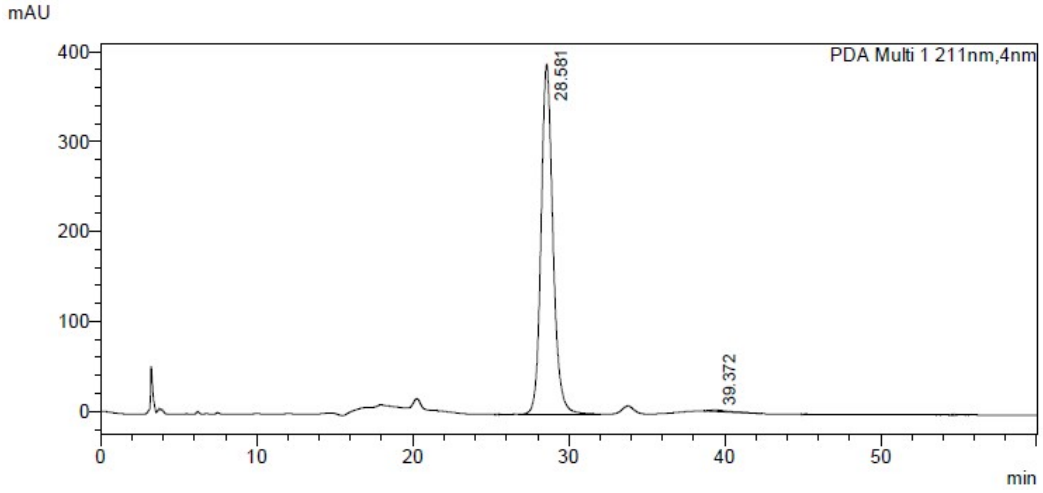




PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	30.072	48.781
2	40.714	51.219
Total		100.000

(2*R*,3*R*)-2,6-dimethoxy-4-((2,3-*anti*)-2-methyl-5-oxotetrahydrofuran-3-yl)phenyl pivalate

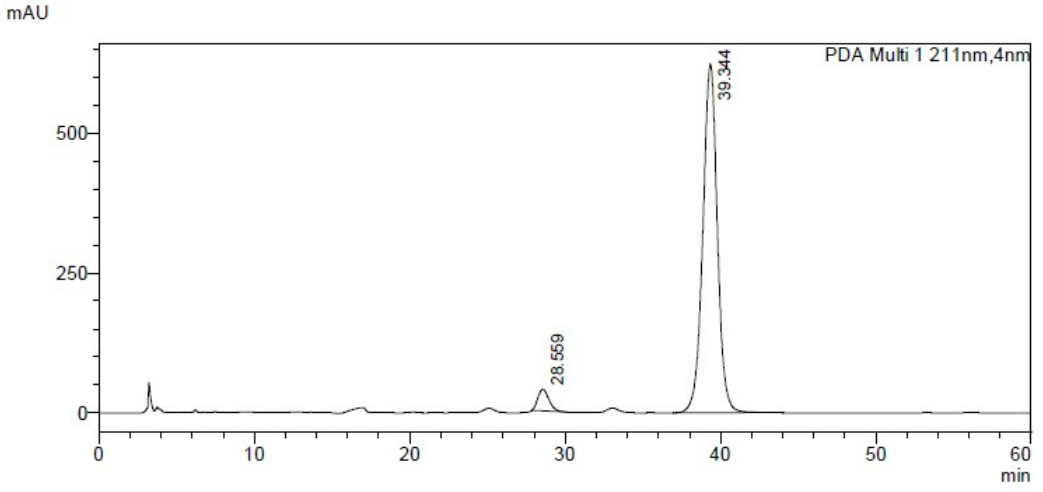


PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	28.581	99.308
2	39.372	0.692
Total		100.000

Therefore *ee* = 99%

(2*S*,3*S*)-2,6-dimethoxy-4-((2,3-*anti*)-2-methyl-5-oxotetrahydrofuran-3-yl)phenyl pivalate



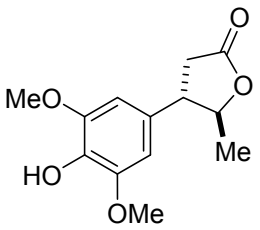
PDA Ch1 211nm

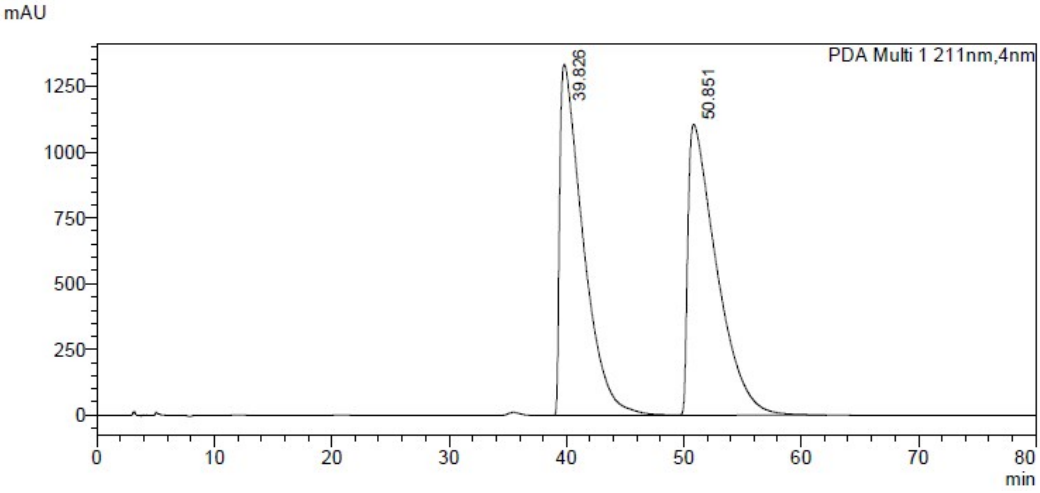
Peak#	Ret. Time	Area%
1	28.559	4.586
2	39.344	95.414
Total		100.000

Therefore *ee* = 91%

(±)-4-(4-hydroxy-3,5-dimethoxyphenyl)-5-methyldihydrofuran-2(3*H*)-one (Descurainolide A)

Chiralcel OD-H (85:15 Hexane: IPA, flow rate 1.0 mL min^{-1}, 30 °C) t_R (2*R*,3*R*) = 39.8 min, t_R (2*S*,3*S*) = 50.9 min.

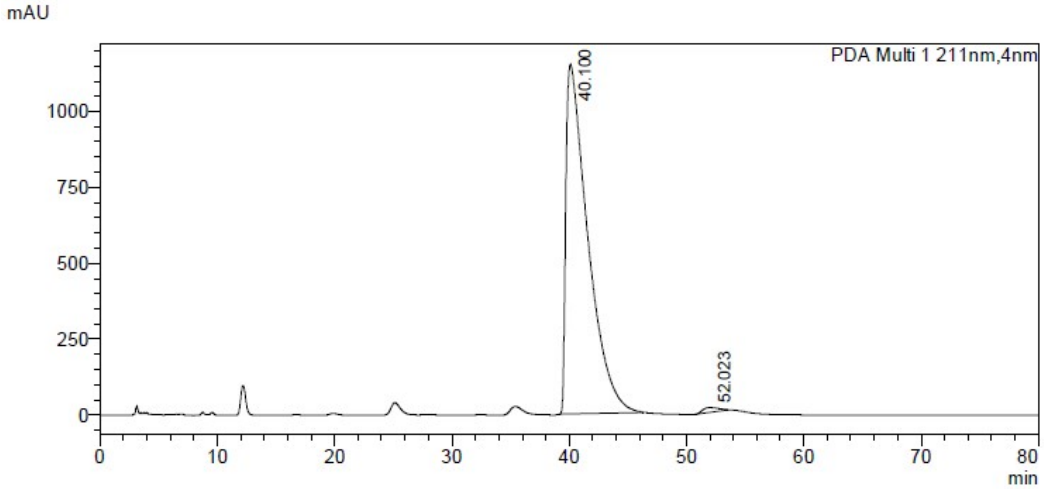




PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	39.826	49.564
2	50.851	50.436
Total		100.000

(2*R*,3*R*)-4-(4-hydroxy-3,5-dimethoxyphenyl)-5-methyldihydrofuran-2(3*H*)-one (Descurainolide A)

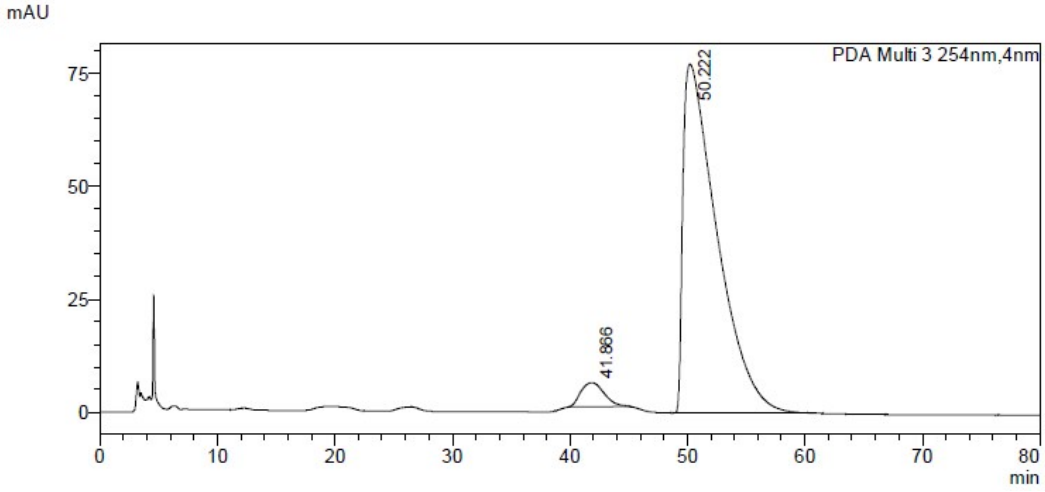


PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	40.100	99.096
2	52.023	0.904
Total		100.000

Therefore *ee* = 98%

(2*S*,3*S*)-4-(4-hydroxy-3,5-dimethoxyphenyl)-5-methyldihydrofuran-2(3*H*)-one (Descurainolide A)



PDA Ch3 254nm

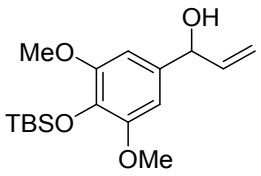
Peak#	Ret. Time	Area%
1	41.866	4.508
2	50.222	95.492
Total		100.000

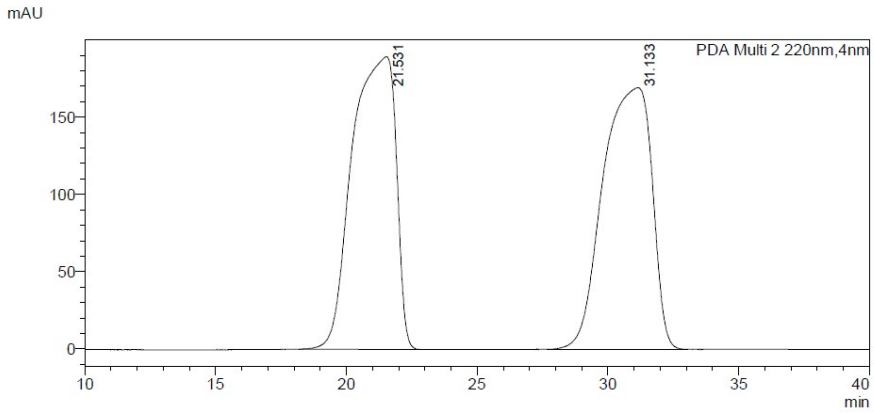
Therefore *ee* = 91%

HPLC traces KR lignin-based monomers

(±)-1-(4-((*tert*-butyldimethylsilyl)oxy)-3,5-dimethoxyphenyl)prop-2-en-1-ol

Chiralpak AD-H (99:1 hexane: IPA, flow rate 1 mL min^{-1}, 30 °C) t_R (*S*) = 21.5 min, t_R (*R*) = 31.1 min



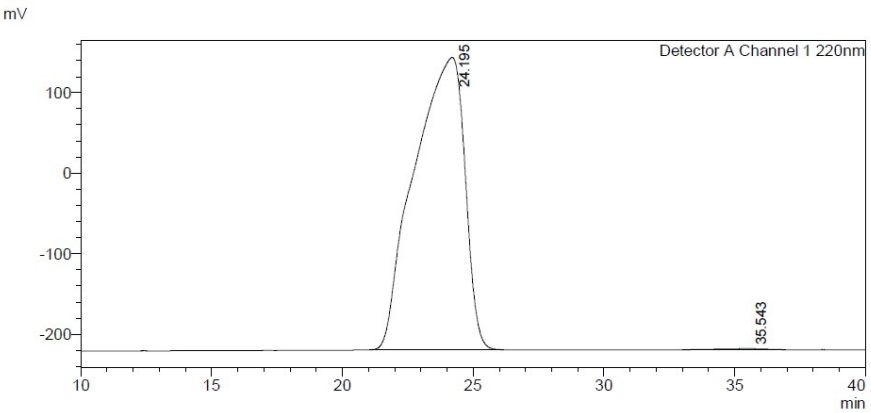


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area%
1	21.531	49.946
2	31.133	50.054
Total		100.000

(*S*)



<Peak Table>

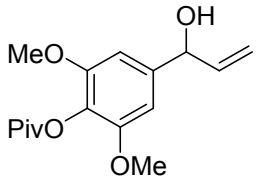
Detector A Channel 1 220nm

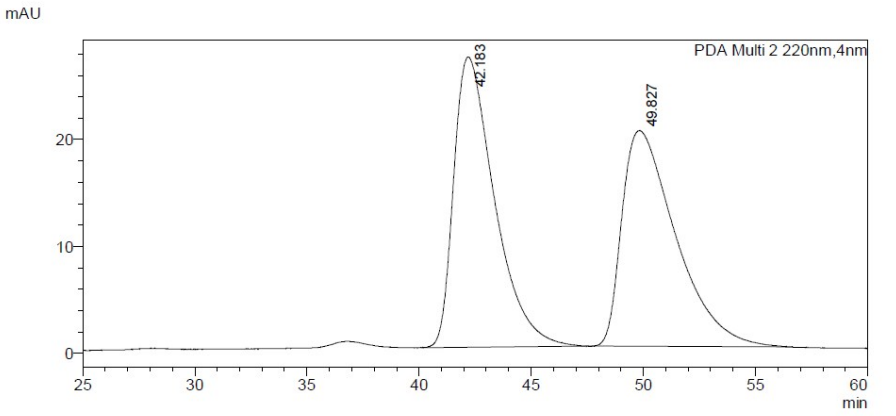
Peak#	Ret. Time	Area%
1	24.195	99.659
2	35.543	0.341
Total		100.000

Therefore *ee* = 99%

(±)-4-(1-hydroxyallyl)-2,6-dimethoxyphenyl pivalate

Chiralcel OJ-H (99:1 hexane: IPA, flow rate 1 mL min^{-1}, 30 °C) t_R (*S*) = 42.2 min, t_R (*R*) = 49.8 min



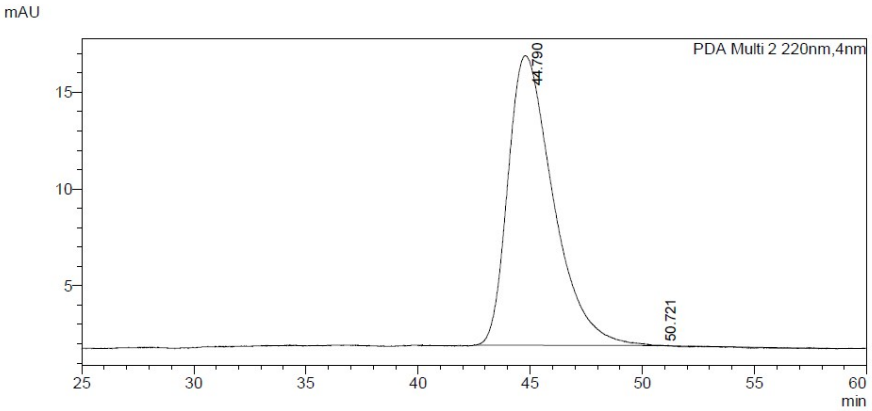


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area%
1	42.183	50.499
2	49.827	49.501
Total		100.000

(*S*)



<Peak Table>

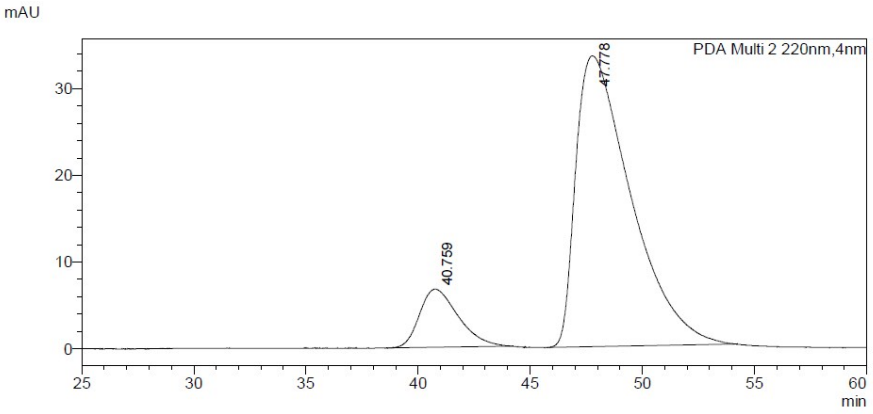
PDA Ch2 220nm

Peak#	Ret. Time	Area%
1	44.790	100.357
2	50.721	-0.357
Total		100.000

Therefore *ee* = >99%

(*R*)

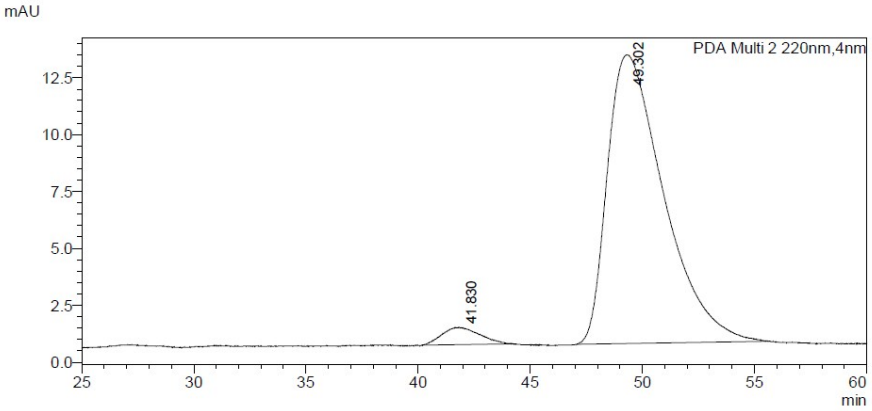
HPLC before second KR with ent-HyperBTM



<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area%
1	40.759	12.341
2	47.778	87.659
Total		100.000



<Peak Table>

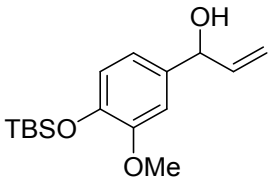
PDA Ch2 220nm

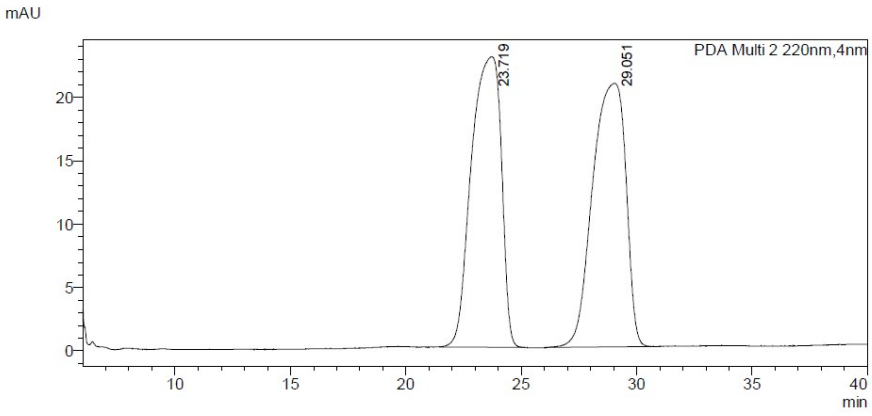
Peak#	Ret. Time	Area%
1	41.830	3.863
2	49.302	96.137
Total		100.000

Therefore *ee* = 92%

(±)-1-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)prop-2-en-1-ol

Chiralpak AD-H (99.5:0.5 hexane: IPA, flow rate 1 mLmin^{-1}, 30 °C) t_R (*S*) = 23.7 min, t_R (*R*) = 29.1 min.



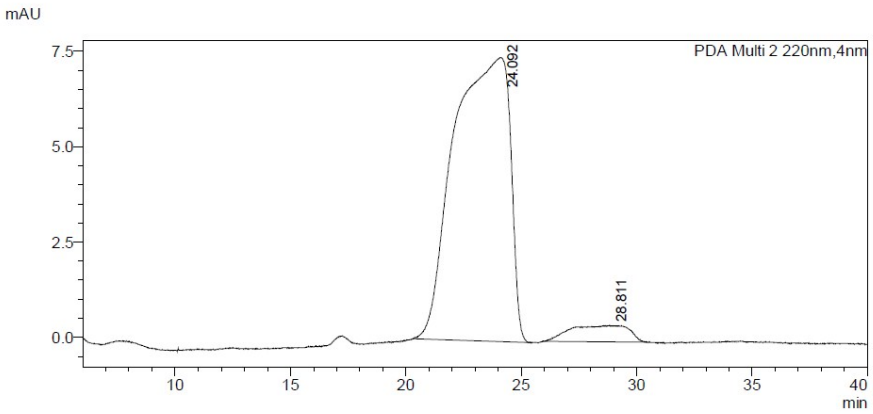


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area%
1	23.719	49.816
2	29.051	50.184
Total		100.000

(*S*)



<Peak Table>

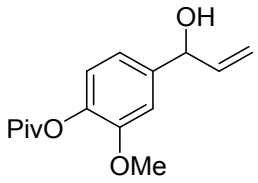
PDA Ch2 220nm

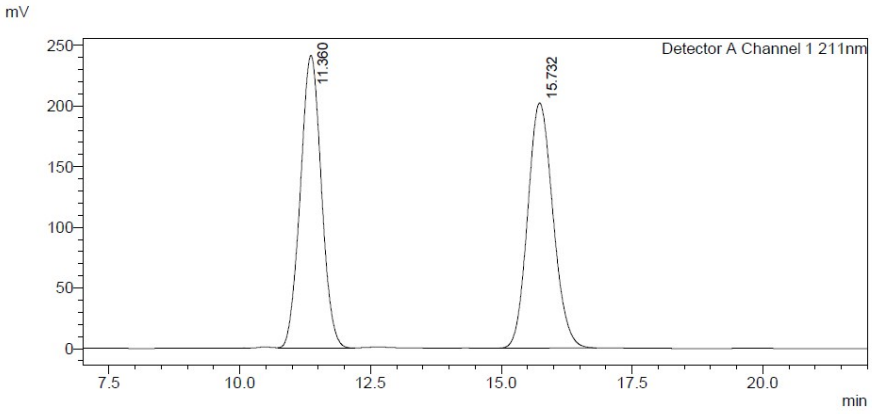
Peak#	Ret. Time	Area%
1	24.092	94.301
2	28.811	5.699
Total		100.000

Therefore *ee* = 89%

(±)-4-(1-hydroxyallyl)-2-methoxyphenyl pivalate

Chiralpak AD-H (95:5 hexane: IPA, flow rate 1 mL min^{-1}, 30 °C) t_R (*S*) = 11.4 min, t_R (*R*) = 15.7 min.



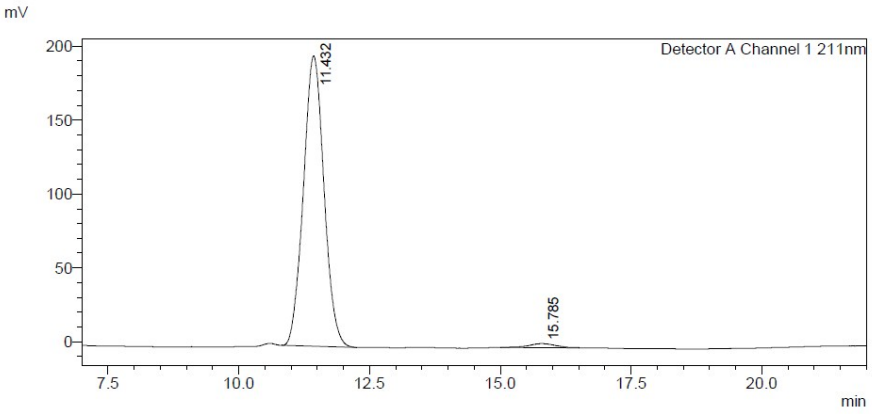


<Peak Table>

Detector A Channel 1 211nm

Peak#	Ret. Time	Area%
1	11.360	49.751
2	15.732	50.249
Total		100.000

(*S*)



<Peak Table>

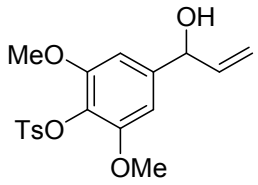
Detector A Channel 1 211nm

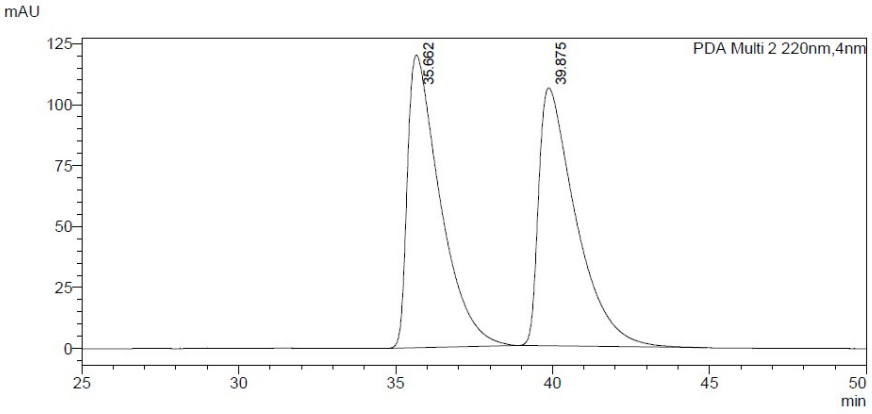
Peak#	Ret. Time	Area%
1	11.432	98.357
2	15.785	1.643
Total		100.000

Therefore *ee* = 97%

(±)-4-(1-hydroxyallyl)-2,6-dimethoxyphenyl 4-methylbenzenesulfonate

Chiralpak IB (92:8 hexane: IPA, flow rate 1 mL min^{-1}, 30 °C) t_R (*S*) = 35.7 min, t_R (*R*) = 39.9 min.



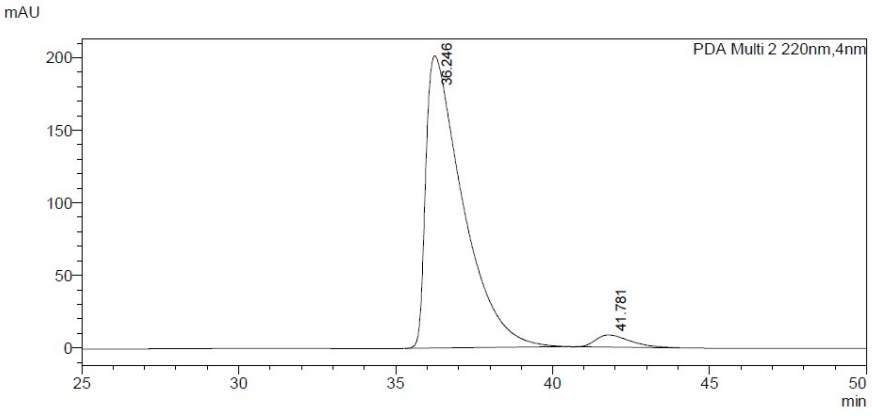


<Peak Table>

PDA Ch2 220nm

Peak#	Ret. Time	Area%
1	35.662	50.010
2	39.875	49.990
Total		100.000

(*S*)



<Peak Table>

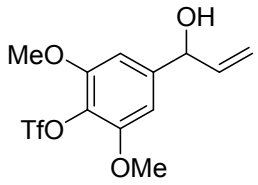
PDA Ch2 220nm

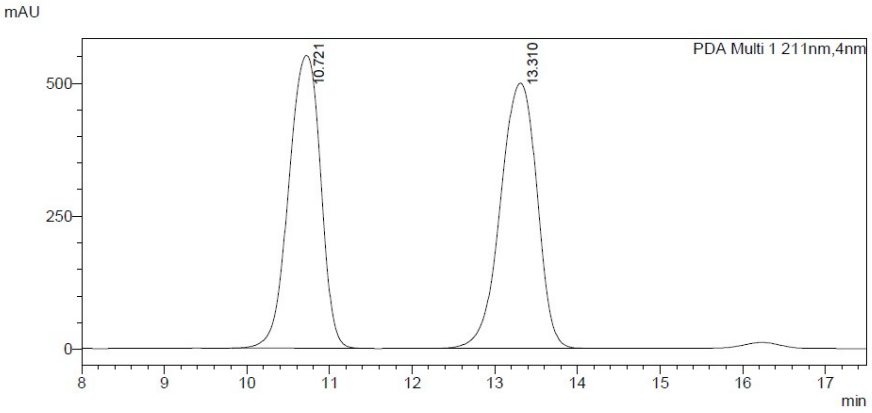
Peak#	Ret. Time	Area%
1	36.246	96.352
2	41.781	3.648
Total		100.000

Therefore *ee* = 93%

(±)-4-(1-hydroxyallyl)-2,6-dimethoxyphenyl trifluoromethanesulfonate

Chiralpak AD-H (95:5 hexane : IPA, flow rate 1 mL min^{-1}, 30 °C) t_R (*S*) = 10.7 min, t_R (*R*) = 13.3 min.



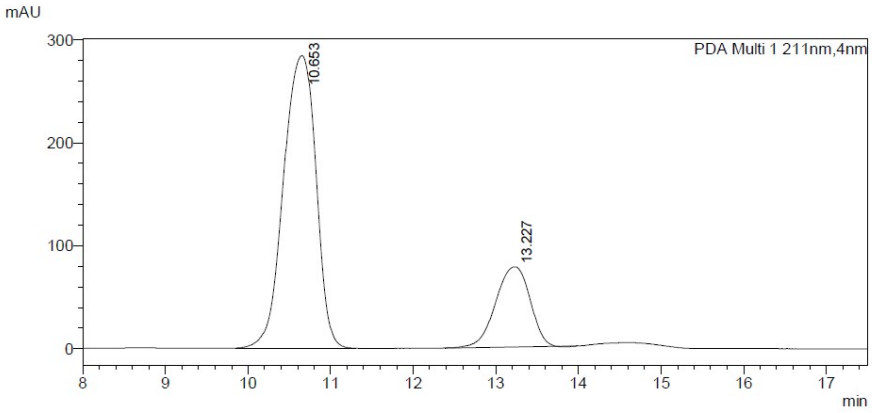


<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	10.721	49.015
2	13.310	50.985
Total		100.000

(*S*)



<Peak Table>

PDA Ch1 211nm

Peak#	Ret. Time	Area%
1	10.653	77.564
2	13.227	22.436
Total		100.000

Therefore *ee* = 55%