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

Supporting Infomation

BINOL-Al Catalysed Asymmetic Cyclization and Amplification: Preparation of Optically Active Menthol Analogs

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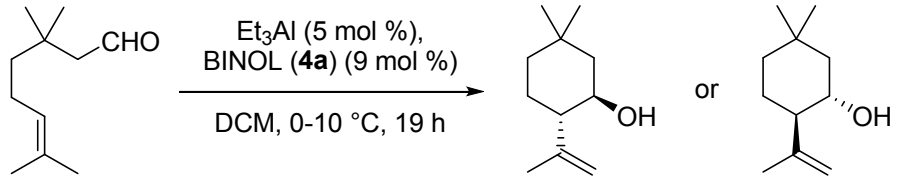
Table S1. Asymmetric Amplification on Asymmetric cyclization of 3-methylcitronellal (1) by BINOL-Al catalyst



1 (-)-*trans*-**2** (+)-*trans*-**2**

Entry	BINOL (**4a**)	*ee* of **4a** (%)	Conv. (%)[a]	*ee* of *trans*-**2** (%) [a,b]
1	(*R*)-**4a**	10	83	17(-)
2	(*R*)-**4a**	30	90	49(-)
3	(*R*)-**4a**	40	97	52(-)
4	(*S*)-**4a**	40	86	53(+)
5	(*R*)-**4a**	50	92	65(-)
6	(*R*)-**4a**	60	93	66(-)
7	(*R*)-**4a**	80	99	83(-)
8	(*S*)-**4a**	80	94	81(+)
9	(*R*)-**4a**	100	98	89(-)
10	(*S*)-**4a**	100	94	90(+)

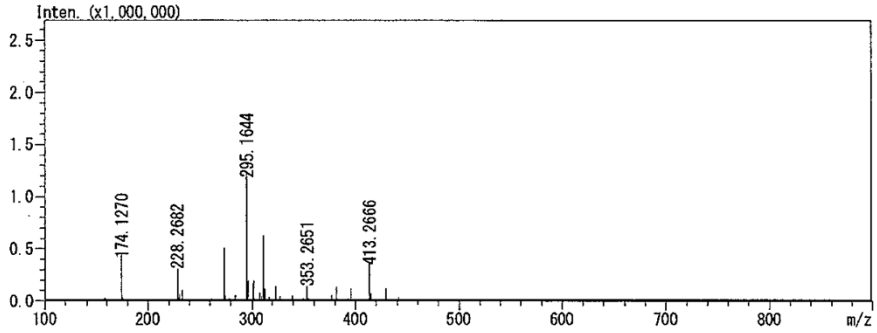
[a]Determined by GC analysis.

[b]Optical rotation of *trans*-**2** are shown in parentheses.

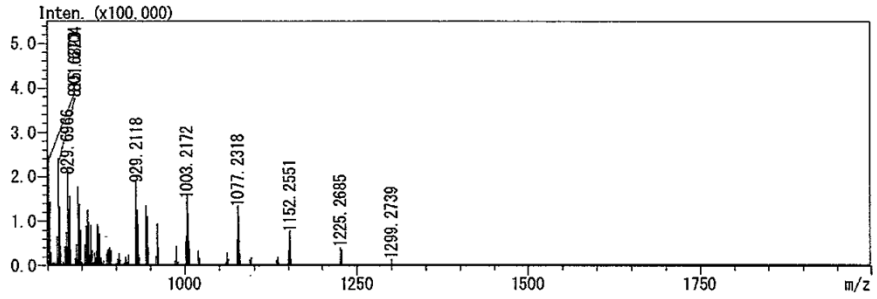
ESI-MS analysis of (*R*)-BINOL ((*R*)-4a)-Al

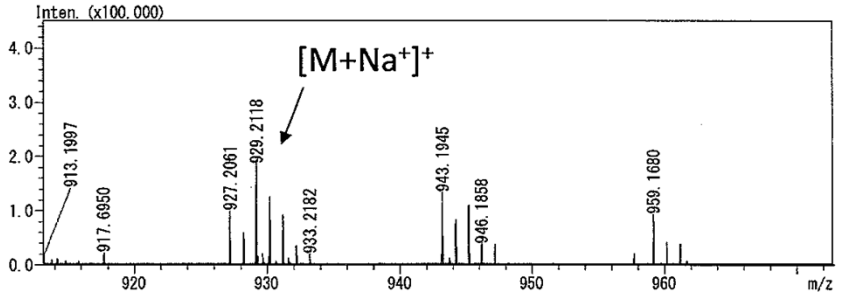
MS range : 100-1000

Positive



MS range : 800-2000





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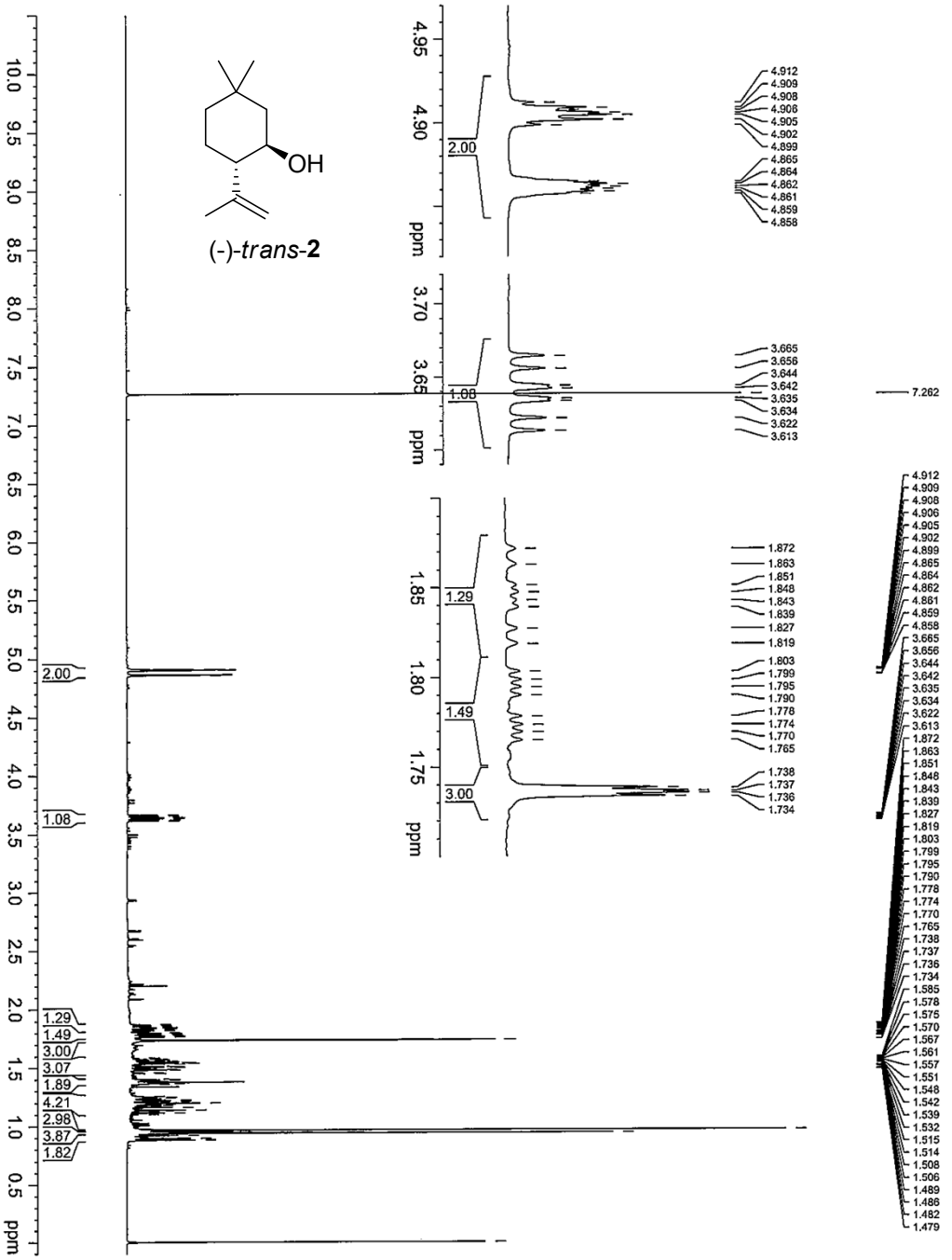
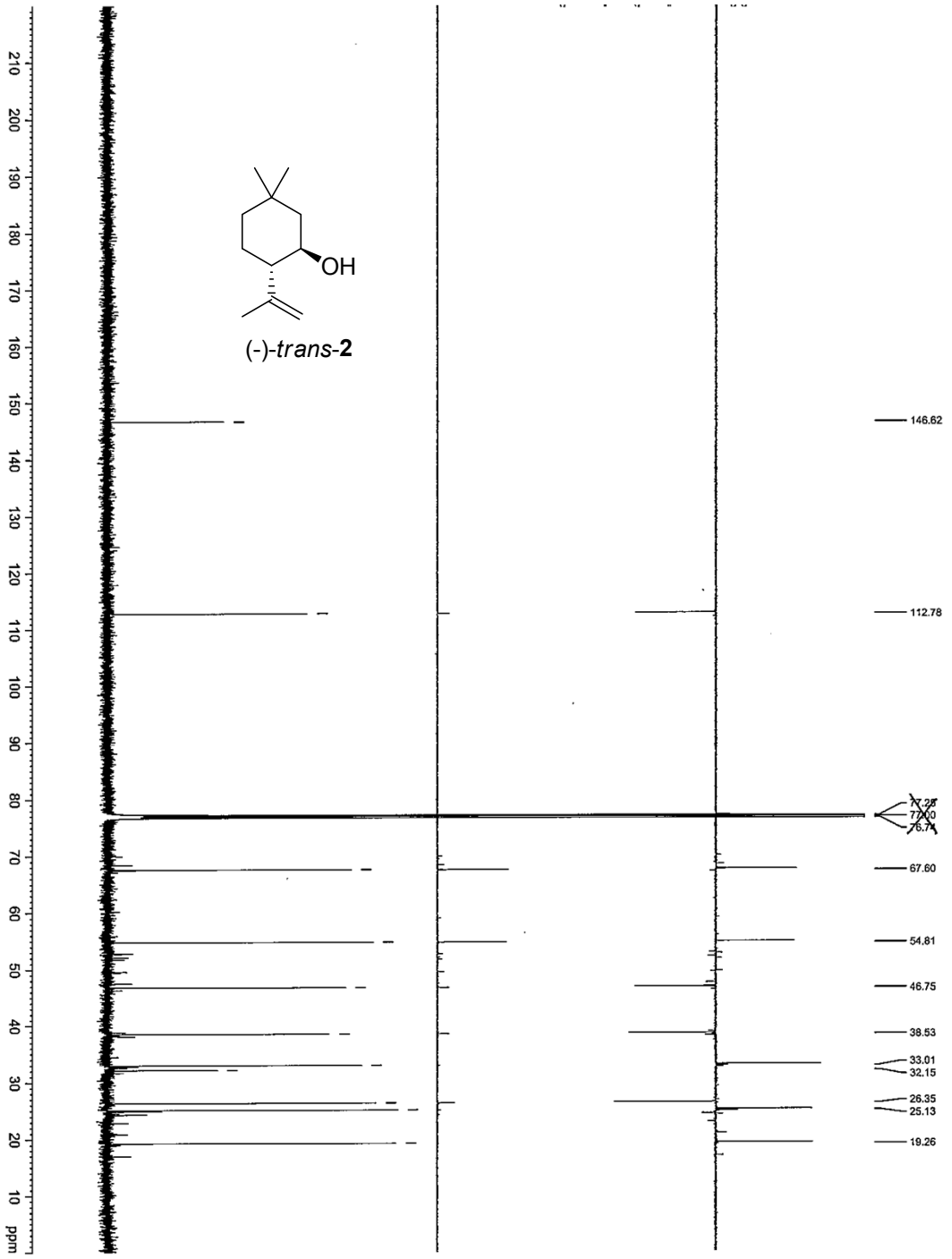
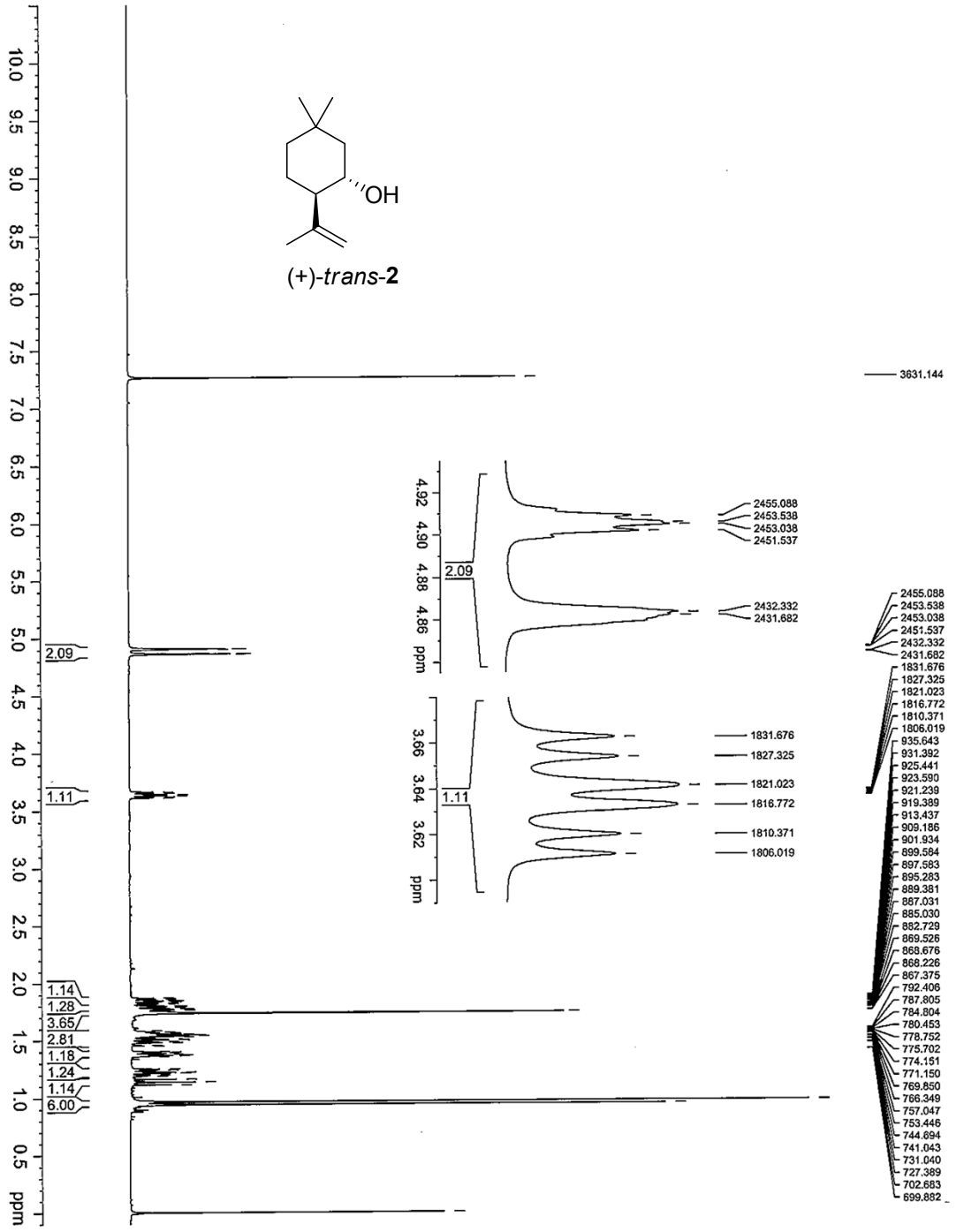
NMR data of products

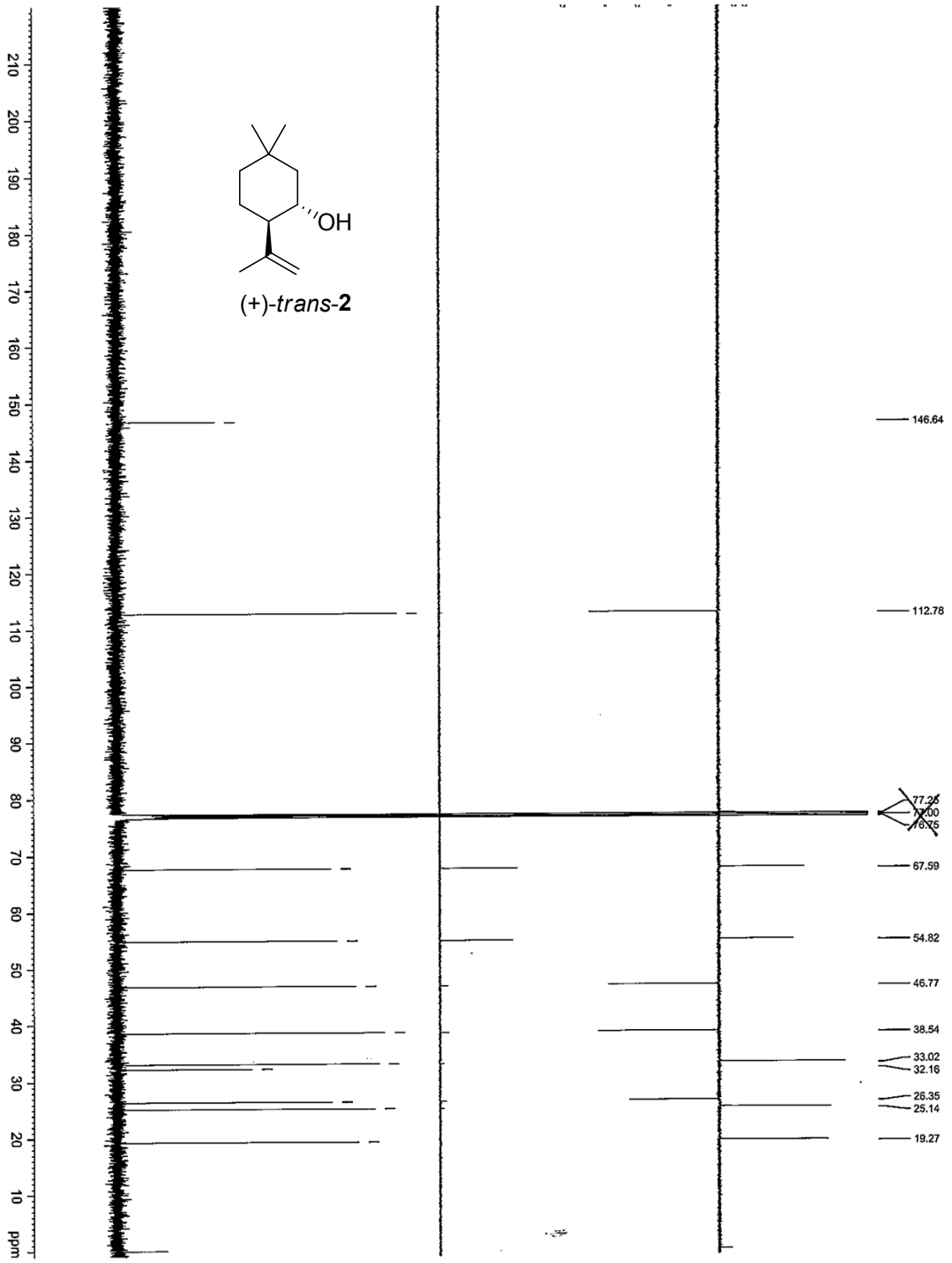
(-)-(*1R,2S*)-5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexanol ((-)-*trans*-5-methylisopulegol) ((-)-*trans*-2) (Table 2, entry 3)



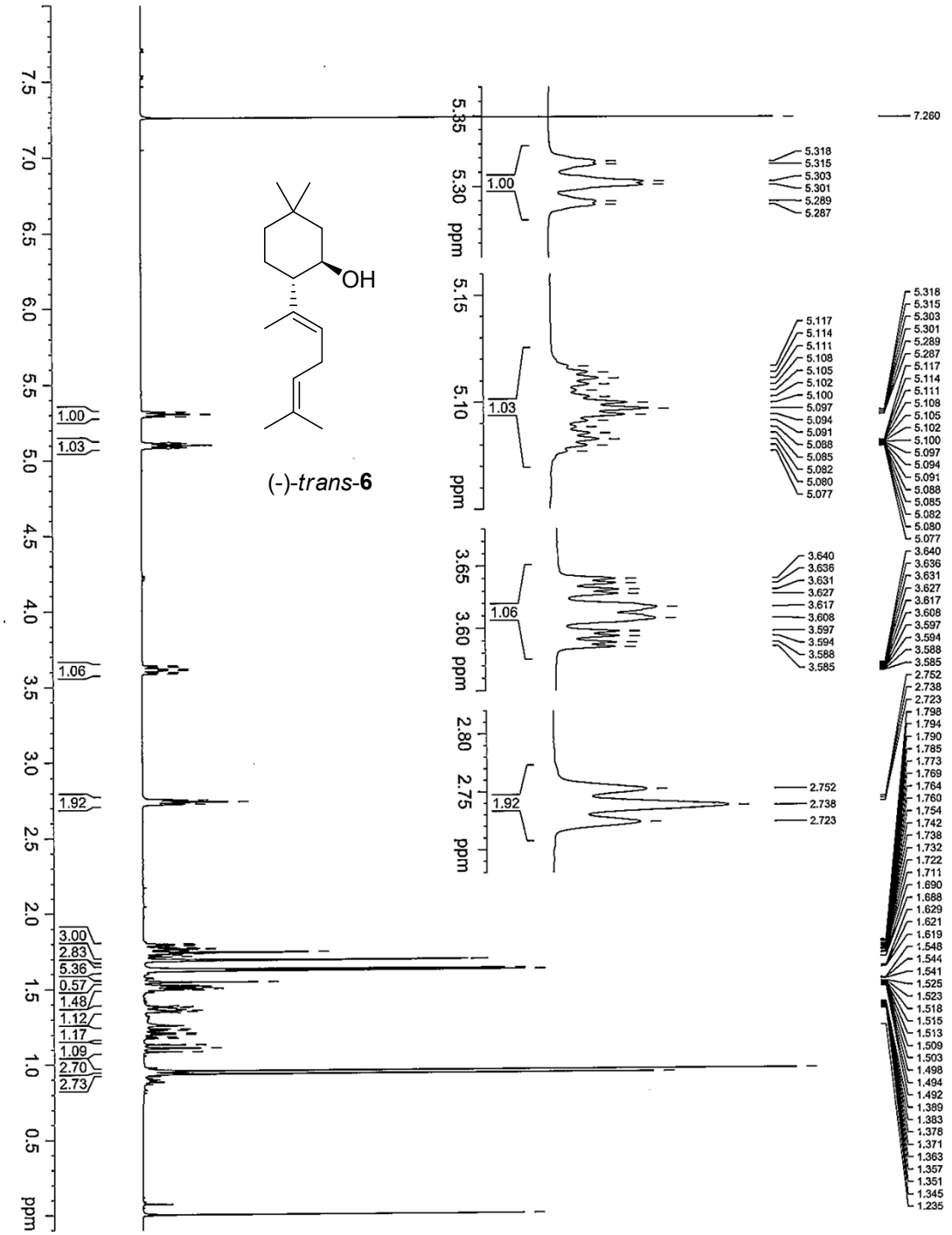

OH
(-)-trans-2
146.62
112.78
77.25
77.00
76.74
67.60
54.81
46.75
38.53
33.01
32.15
26.35
25.13
19.26
ppm

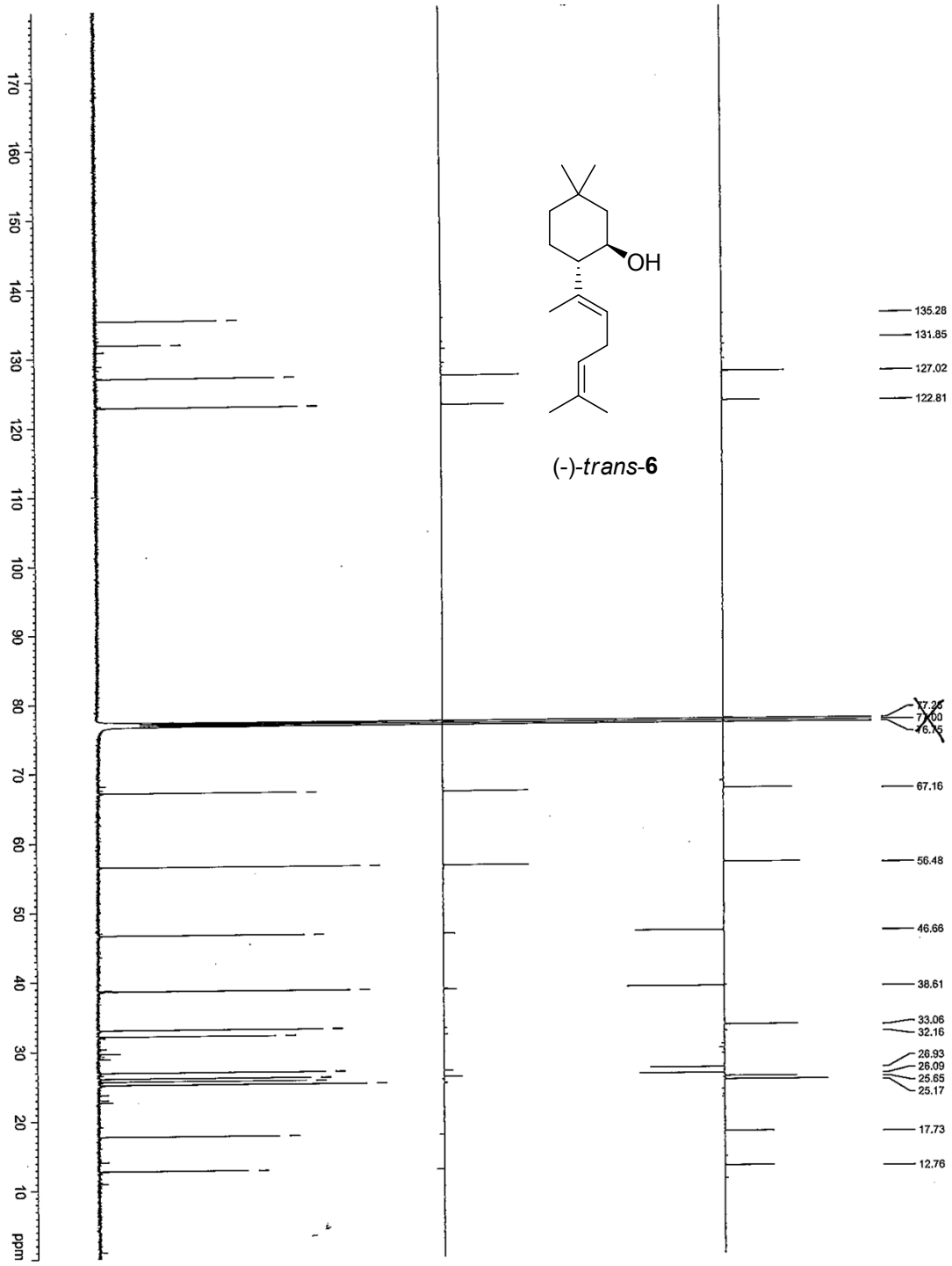
(+)-(*1R*,*2S*)-5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexanol ((+)-*trans*-5-methylisopulegol) ((+)-*trans*-2) (Table 2, entry 4)




OH
(+)-trans-2
146.64
112.78
77.25
77.00
76.75
67.59
54.82
46.77
38.54
33.02
32.16
26.35
25.14
19.27
ppm

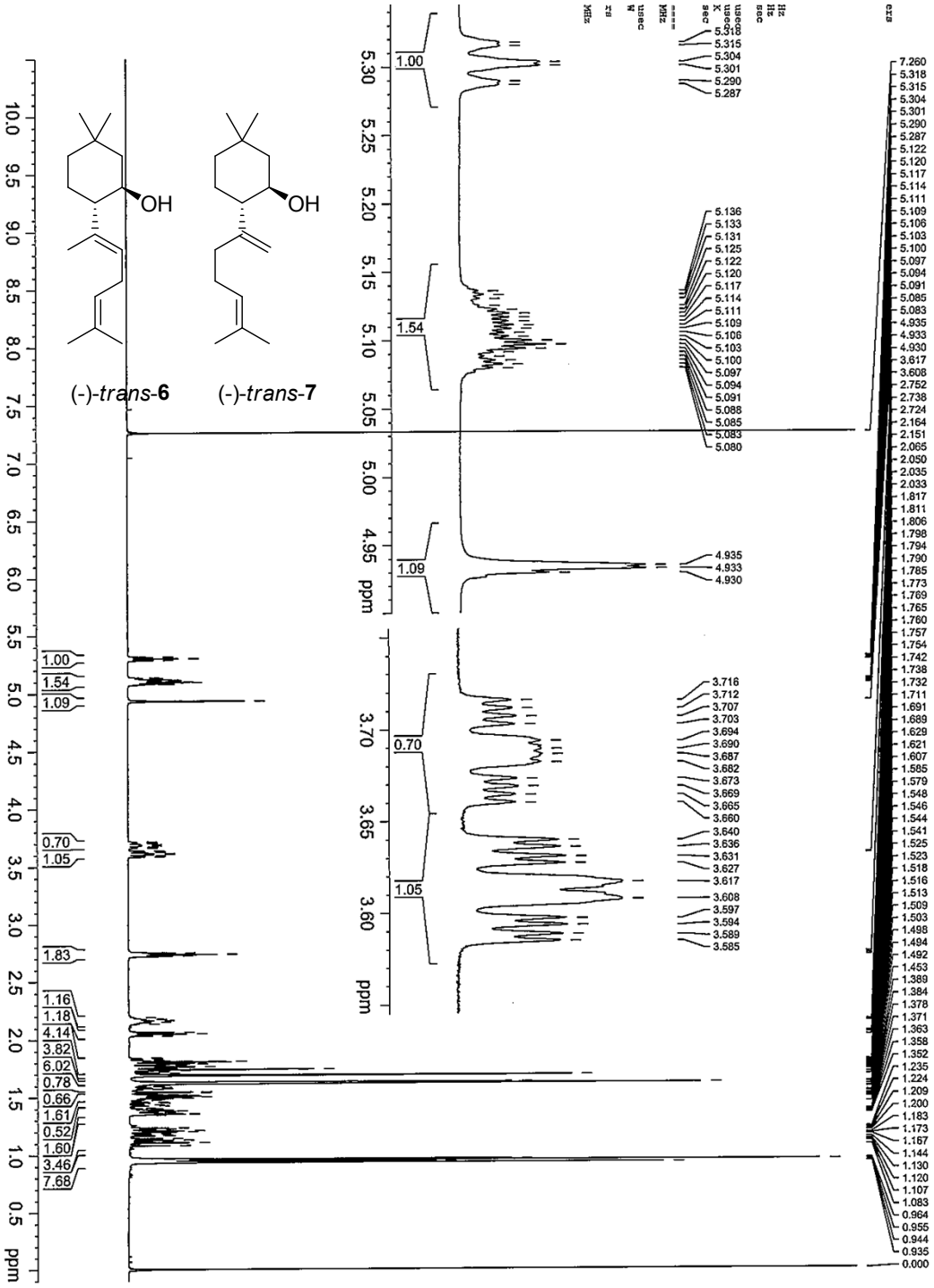
(-)-(*1R,2S*)-5,5-Dimethyl-2-(*E*-6-methylhepta-2,5-dien-2-yl)cyclohexanol ((-)-*trans*-6) (Table 2, entry 5)

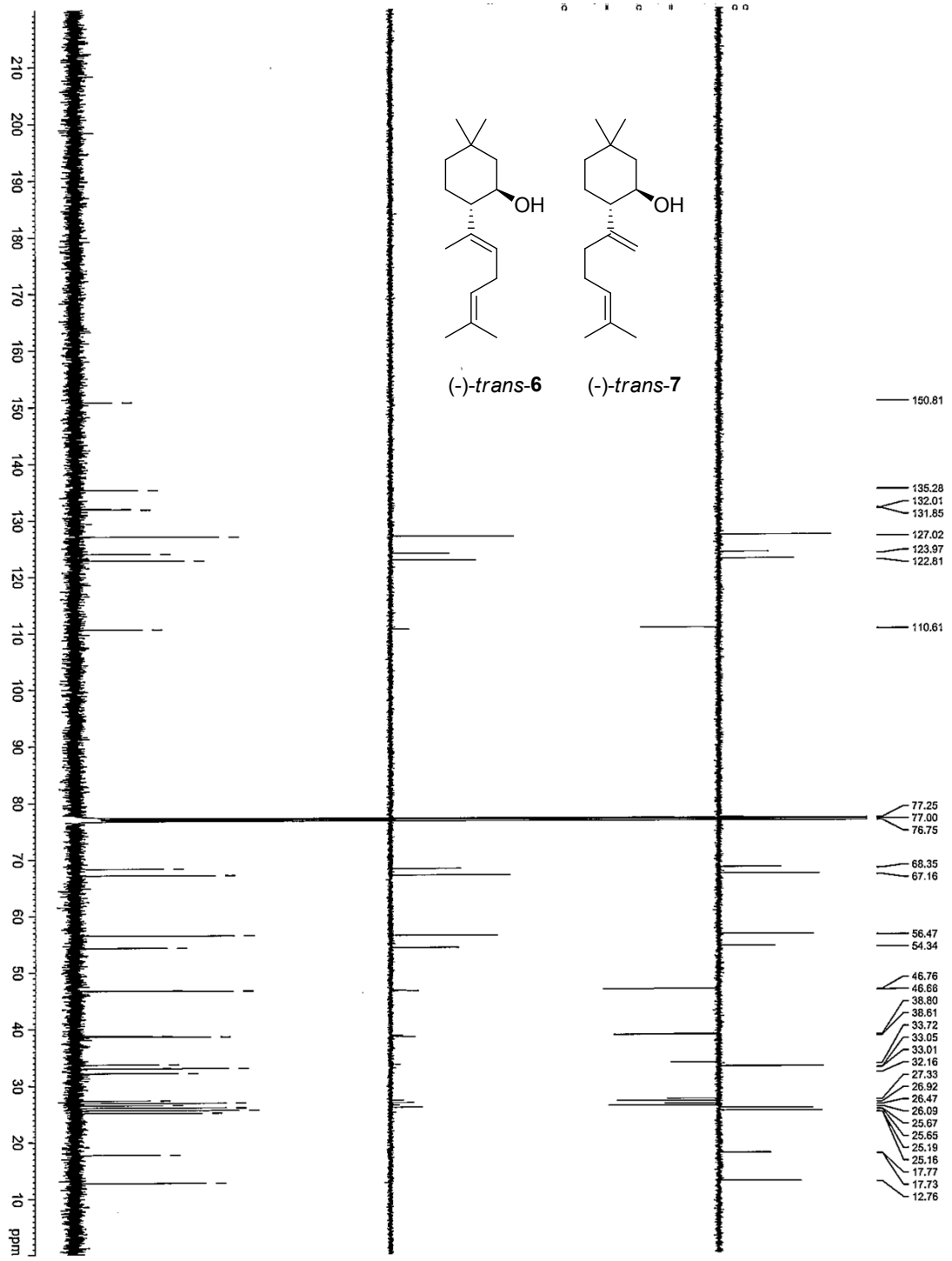



OH
135.28
131.85
127.02
122.81
77.25
77.00
76.75
67.16
56.48
46.66
38.61
33.06
32.16
26.93
26.09
25.65
25.17
17.73
12.76
ppm

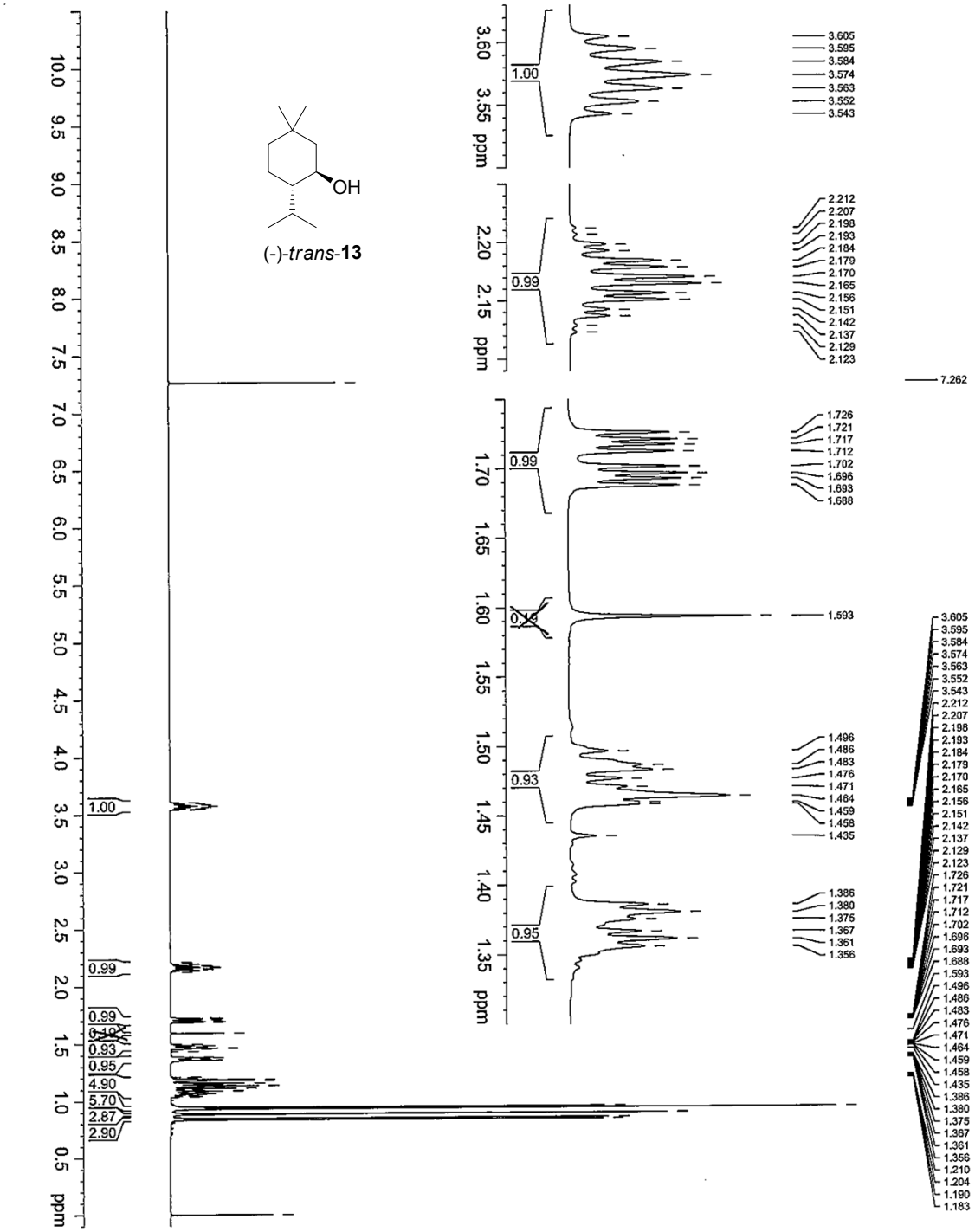
(-)-*trans*-**6**

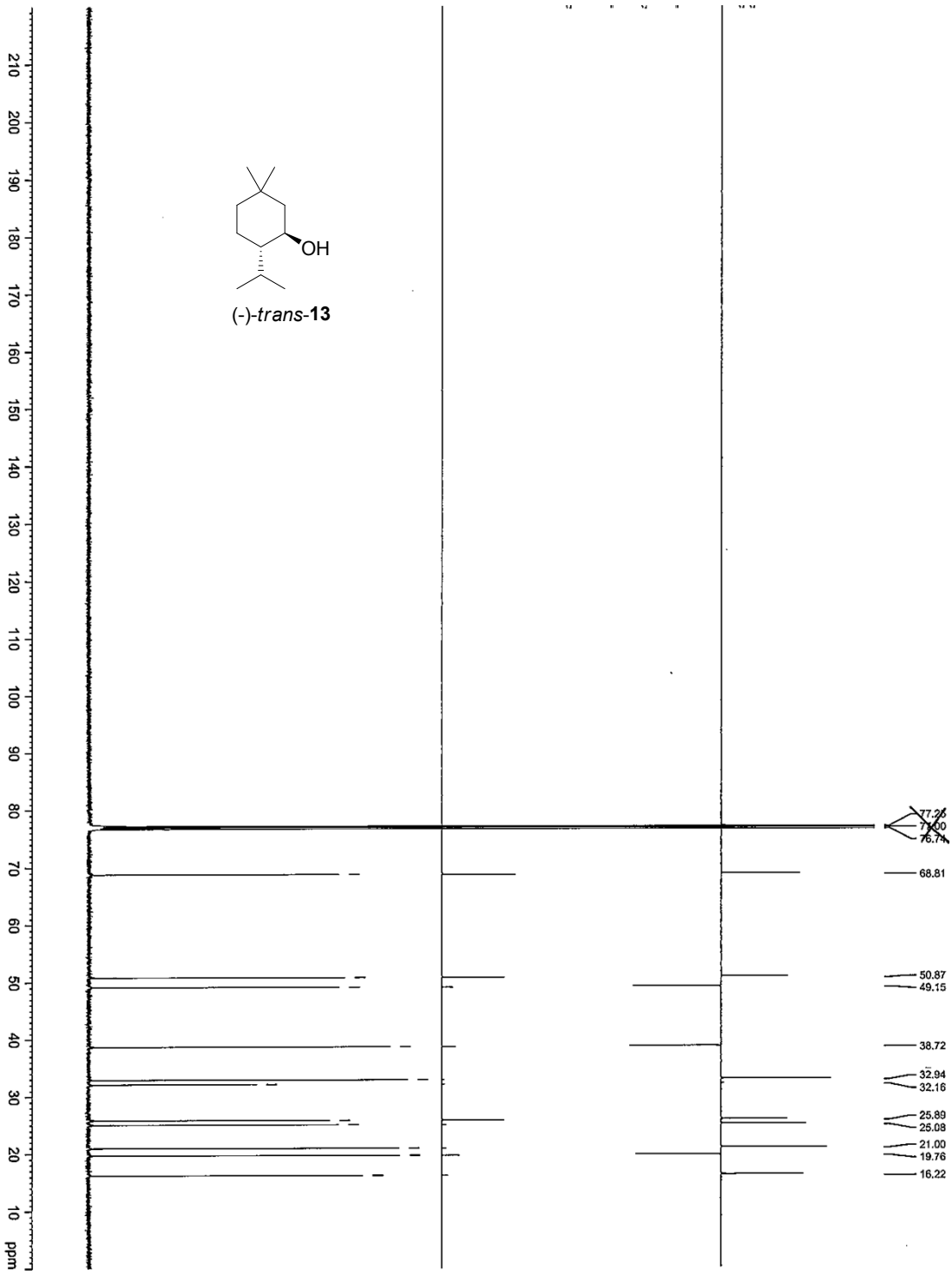
(-)-(*1R,2S*)-5,5-Dimethyl-2-(*E*-6-methylhepta-2,5-dien-2-yl)cyclohexanol ((-)-*trans*-6), (-)- (*1R,2S*)-5,5-dimethyl-2-(6-methylhepta-1,5-dien-2-yl)cyclohexanol ((-)-*trans*-7) (*E*/*Z* = 64/36) (Table 2, entry 6)




OH
OH
(-)-trans-6
(-)-trans-7
150.81
135.28
132.01
131.85
127.02
123.97
122.81
110.61
77.25
77.00
76.75
68.35
67.16
56.47
54.34
46.76
46.68
38.80
38.61
33.72
33.05
33.01
32.16
27.33
26.92
26.47
26.09
25.67
25.65
25.19
25.16
17.77
17.73
12.76
ppm

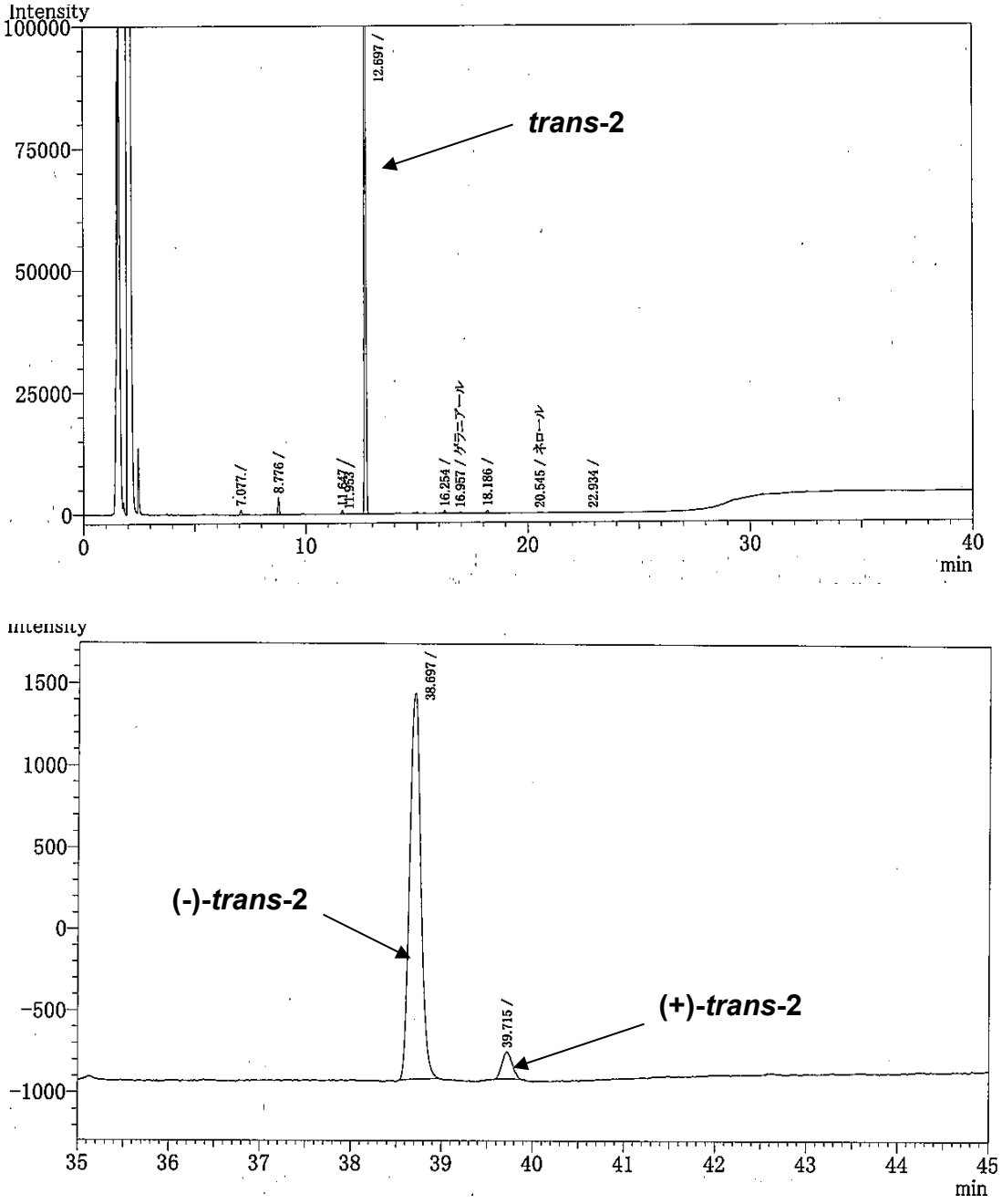
(-)-(*1R,2S*)-2-Isopropyl-5,5-dimethylcyclohexanol ((-)-*trans*-5-methylmenthol) ((-)-*trans*-13) (Scheme 1)



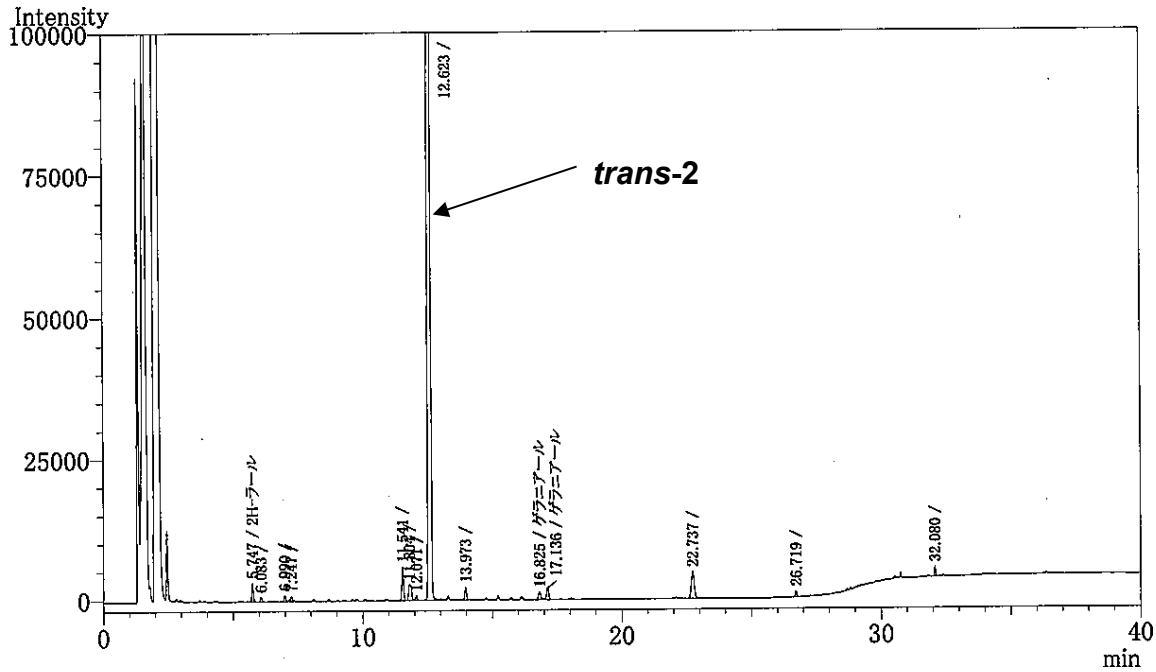

OH
(-)-trans-13
77.26
77.00
76.74
68.81
50.87
49.15
38.72
32.94
32.16
25.89
25.08
21.00
19.76
16.22
ppm

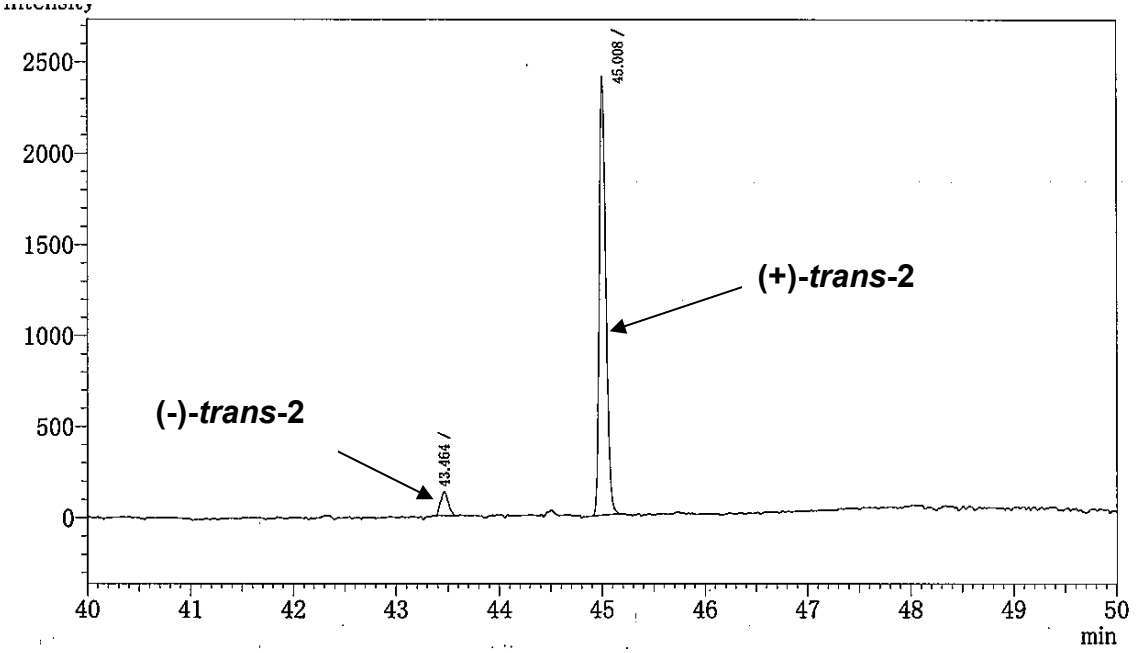
GC data of products

(-)-(*1R,2S*)-5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexanol ((-)-*trans*-5-methylisopulegol) ((-)-*trans*-2) (Table 2, entry 3)

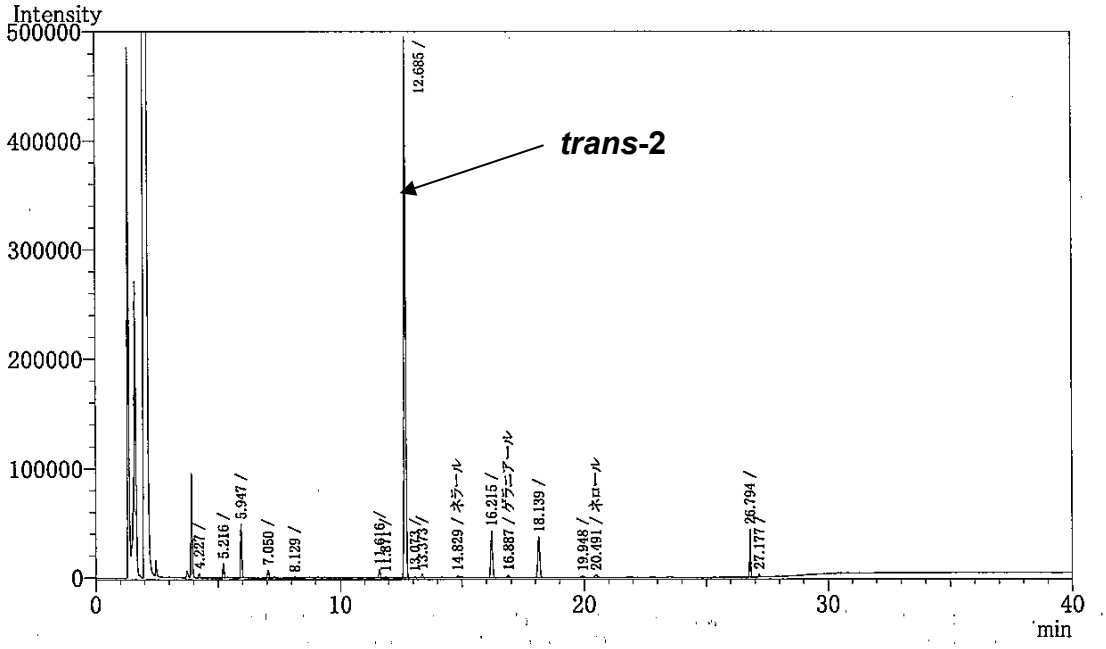


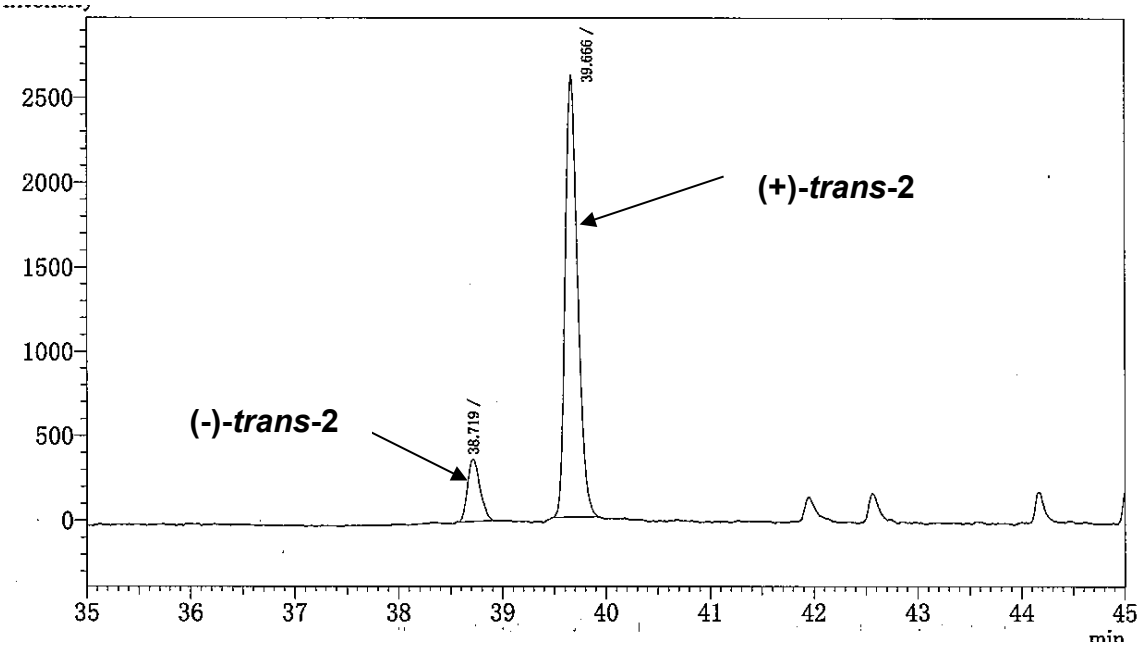
(+)-(*1R*,*2S*)-5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexanol ((+)-*trans*-5-methylisopulegol) ((+)-*trans*-2) (Table 2, entry 4)



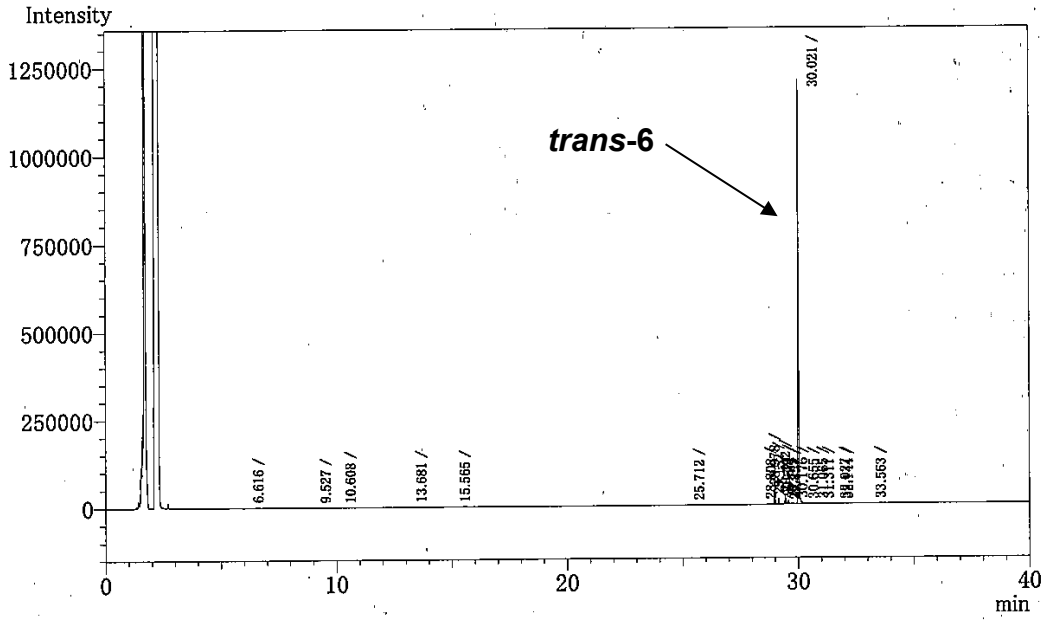


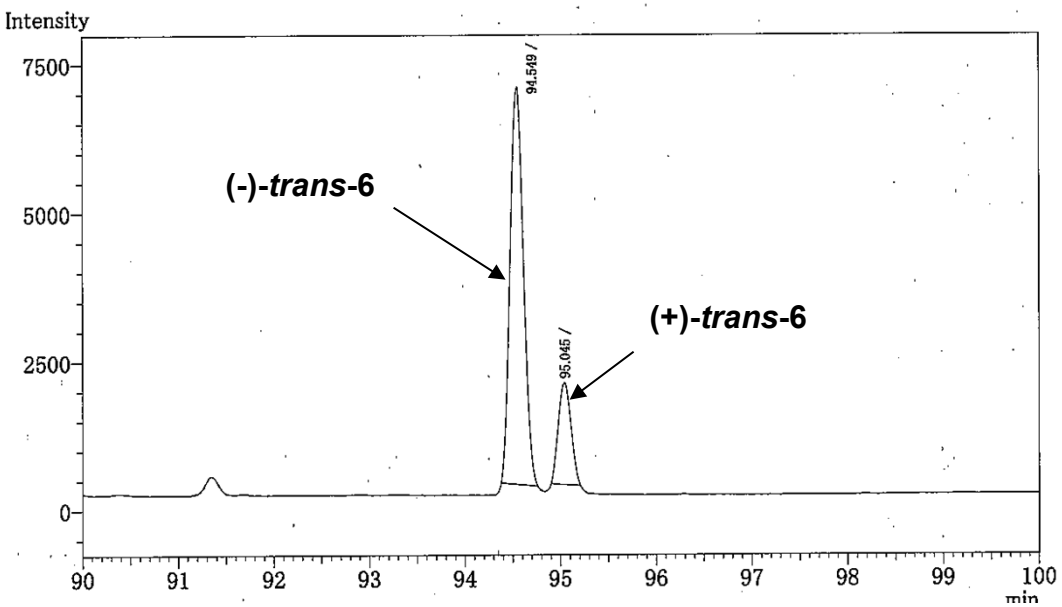
(+)-(*1R*,*2S*)-5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexanol by (*R*)-BINOL-Zn ((+)-*trans*-5-methylisopulegol) ((+)-*trans*-2) (Table 1, entry 10)



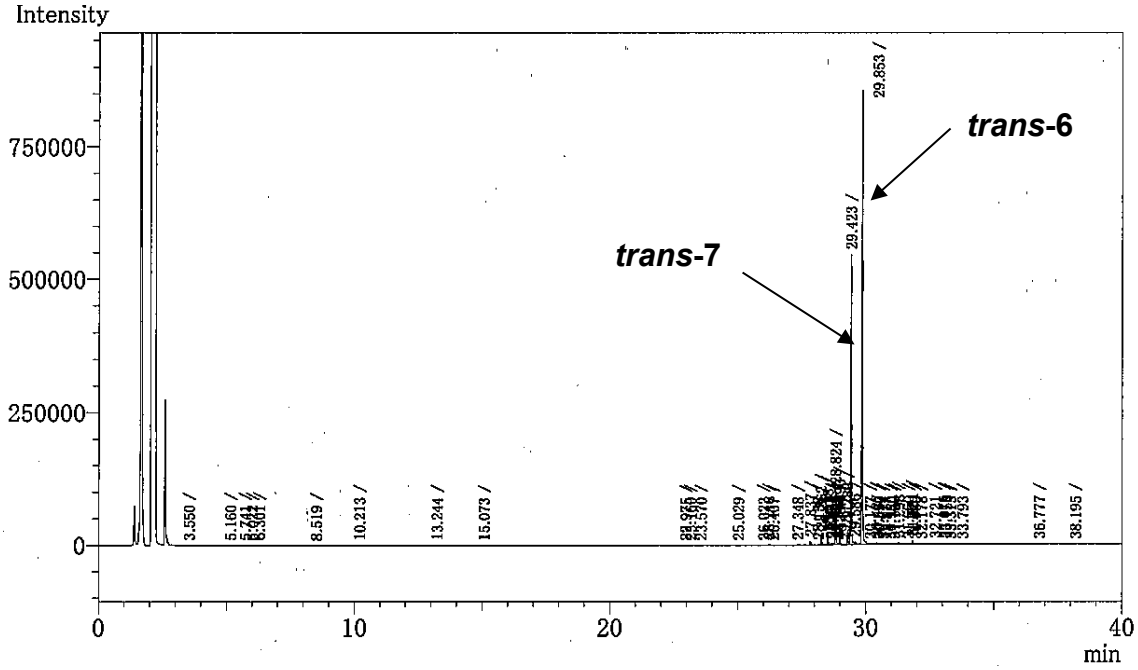


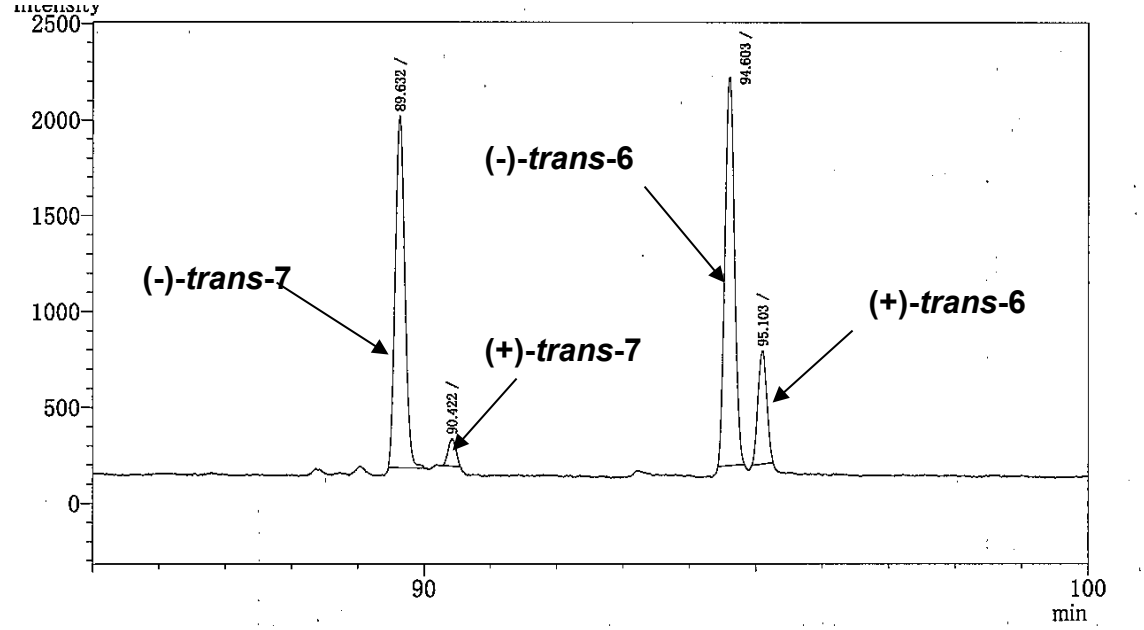
(-)-(*1R,2S*)-5,5-Dimethyl-2-(*E*-6-methylhepta-2,5-dien-2-yl)cyclohexanol) ((-)-*trans*-6) (Table 2, entry 5)



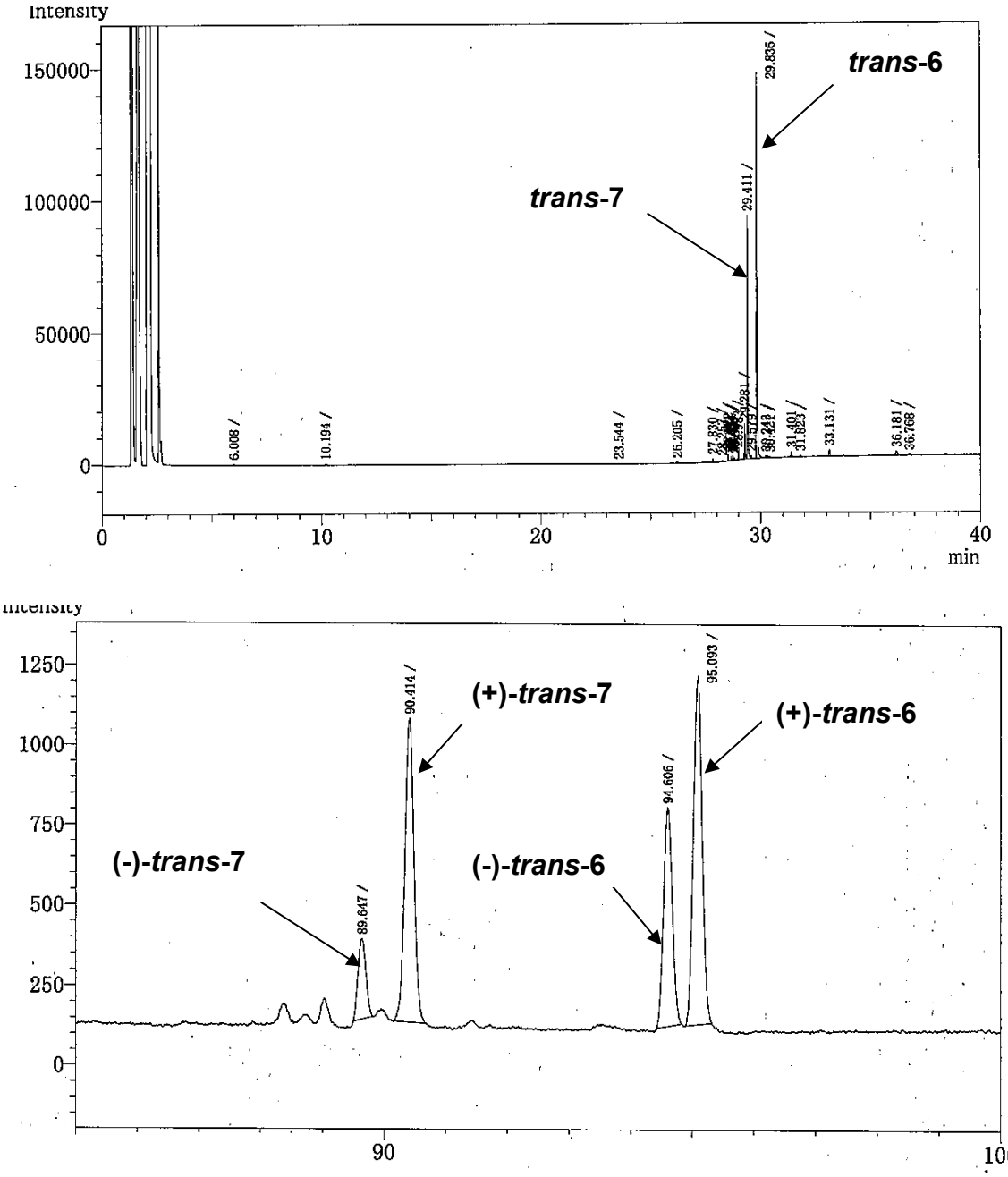


(-)-(*1R,2S*)-5,5-Dimethyl-2-(*E*-6-methylhepta-2,5-dien-2-yl)cyclohexanol ((-)-*trans*-6), (-)- (*1R,2S*)-5,5-dimethyl-2-(6-methylhepta-1,5-dien-2-yl)cyclohexanol ((-)-*trans*-7) (*E*/*Z* = 64/36) (Table 2, entry 6)

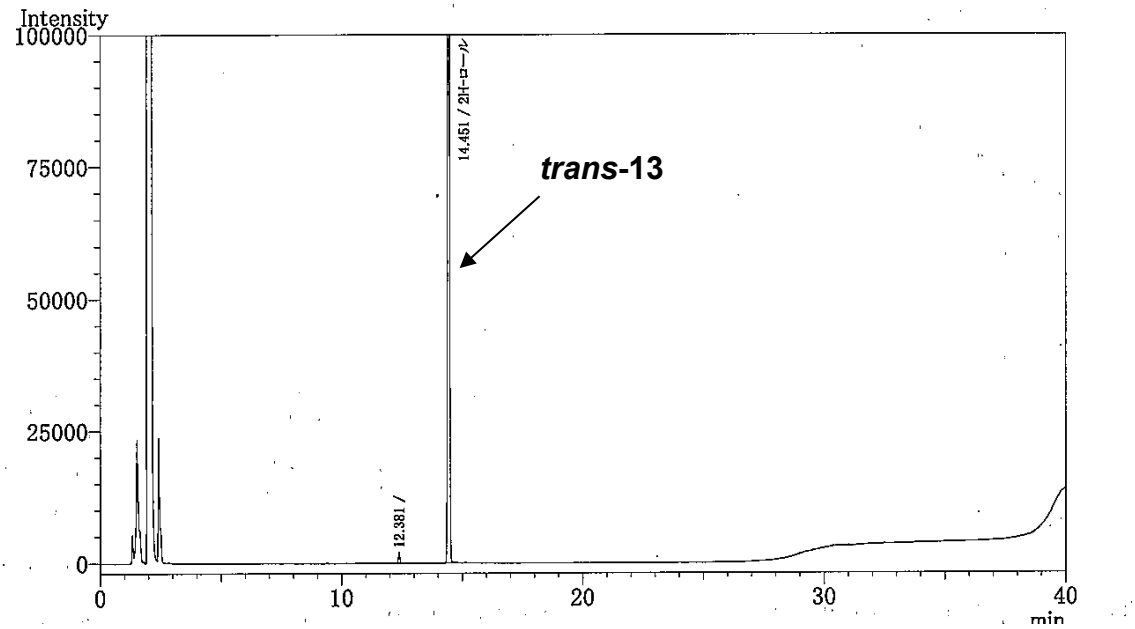


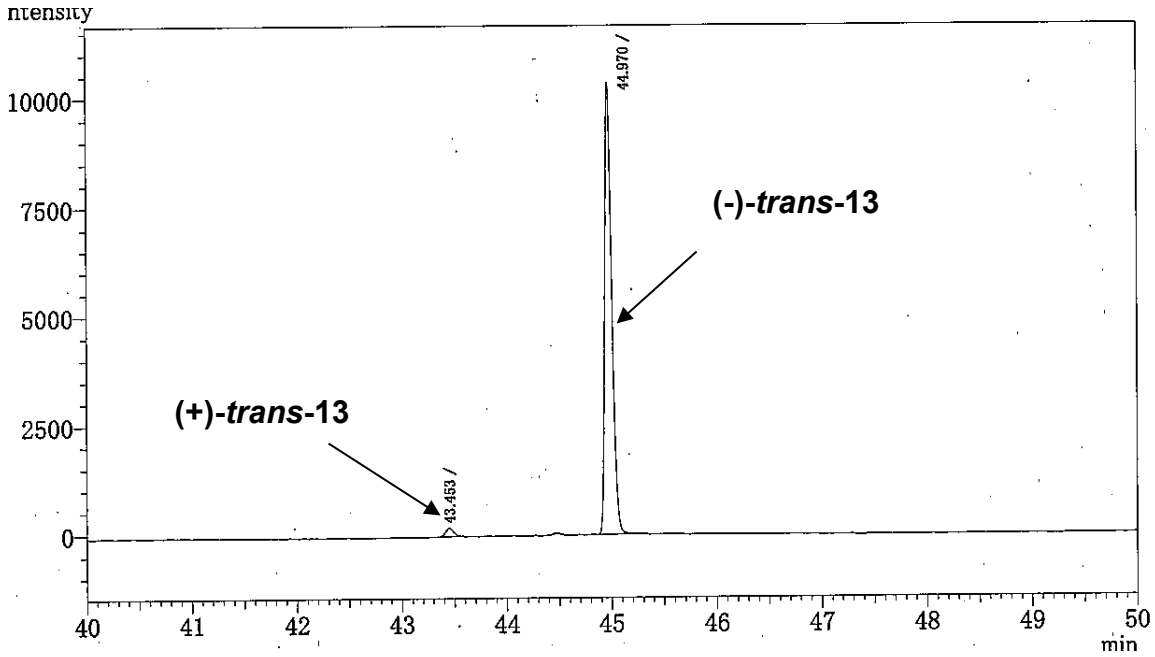


(+)-(*1R,2S*)-5,5-Dimethyl-2-(*E*-6-methylhepta-2,5-dien-2-yl)cyclohexanol ((+)-*trans*-6), (+)- (*1R,2S*)-5,5-dimethyl-2-(6-methylhepta-1,5-dien-2-yl)cyclohexanol ((+)-*trans*-7) by (*R*)-BINOL-Zn (*E*/*Z* = 62 / 38) [S1]



(-)-(*1R,2S*)-2-Isopropyl-5,5-dimethylcyclohexanol ((-)-*trans*-5-methylmenthol) ((-)-*trans*-13) (Scheme 1)





S1 (a) S. Sakane, K. Maruoka and H. Yamamoto, *Tetrahedron Lett.*, **1985**, 5535; (b) S. Sakane, K. Maruoka and H. Yamamoto, *Tetrahedron*, **1986**, 2203.