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Supporting Infomation

Highly Selective Aluminum-Catalyzed Intramolecular Prins Reaction for *l*-Menthol Synthesis

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Note added after first publication: This Supplementary Information file replaces the one originally published on 19th November 2014, due to errors in the analysis of the NMR data for cyclization products **14**, **16** and **18**.

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A. Experimental section

GC was performed on a GC-2010AF system (Shimadzu) or using DB-WAX (30 m × 0.32 mm × 0.5 μm) and IC-1 (30 m × 0.25 mm × 0.25 μm). GC-MS was performed on a GC-QP2010 system (Shimadzu) using Rtx-1 (30 m × 0.25 mm × 0.25 μm) columns. ^{1}H-NMR spectra were recorded on a Bruker 500 MHz spectrometer. Chloroform was used as the NMR solvent, and chemical shifts reported as δ values in parts per million relative to trimethylsilane (δ=0). Optical rotations were determined using a JASCO P-1020 digital polarimeter (JASCO).
All other reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd., Nacalai Tesque, Inc., Takasago International Corporation, or Strem Chemicals Inc. They were used as received. All compounds used were of commercial grade.

Cyclization of (*R*)-1 with aluminum complexes bearing a phenol-type ligand 6 (Table 1)
A mixture of a phenol-type ligand **5** (9.3 mol%), triethylaluminum 1.0 mol/L toluene solution (0.20 mL, 0.20 mmol, 3 mol%), and toluene (1 mL) were added to a 50-mL schlenk tube under a N_2 atmosphere. After being stirred at room temperature for 1 h, the solution was cooled to -10 °C. (*R*)-**1** (1.00 g, 6.48 mmol) was added dropwise, and the solution stirred for 1 h. The reaction products were analyzed by GC.

Cyclization of carbonyl compounds with ACPP (4b) (Table 2)
A mixture of **5b** (15.5 mol%), triethylaluminum 1.0 mol/L toluene solution (5 mol%), and toluene (1 mL) were added to a 50-mL schlenk tube under a N_2 atmosphere. After being stirred at room temperature for over 1 h, the solution was cooled to a temperature lower than 5 °C. A substrate (1.00 g) was added dropwise, and the solution stirred for a specific amount of time (4–19 h). The reaction products were analyzed with GC, and isolated by silica-gel chromatography or preparative TLC.

Synthesis of 3: cyclization of (*R*)-1 with ACPP (4b) (Scheme 2)

A mixture of **5b** (10.4 g, 40.2 mmol, 6.2 mol%), triethylaluminum 1.0 mol/L toluene solution (13.0 mL, 13.0 mmol, 2 mol%), and toluene (87 mL) was added to a 500-mL reactor under a N_2 atmosphere. After being stirred at room temperature for 1 h, the solution was cooled to a temperature lower than 5 °C. (*R*)-**1** (100 g, 648 mmol) and ethyl glyoxylate 47wt% toluene solution (polymer form, 1.00 mL, 54.6 mmol, 8.43 mol%) were added dropwise, and the solution stirred for 4 h. The reaction mixture was poured into toluene/*dil.*HCl after quenching. The oil layer was washed with brine and dried on $MgSO_4$. After filtration and evaporation, a residue was obtained as a colorless oil. After purification with distillation (bath 85 °C, top 70 °C, press. 0.5 mmHg), 94.5 g of **2a** (95% yield, 99.5% ratio of **2a** in **2**) was obtained.

(5*R*)-*n*-isopulegol (**2a**) (500 mg, 3.24 mmol) was then hydrogenated with Raney-Ni (10 mg, 2 wt%) in the presence of H_2 (1 MPa) and MeOH (3 mL) at 60 °C for 10 h. After filtration and evaporation, 462 mg of **3** (91% yield, 99.5% of **3** in diastereoisomers) was obtained.

Preparation of 2-cycloalkyl-6-phenylphenols

The preparation of 2-cyclohexyl-6-phenylphenol (5b)
The preparation of 2-cycloalkyl-6-phenylphenol (**5b**) was based on that described by Nakagawa.[S1] o-Phenylphenol (170.1 g, 1.00 mol) were added into 500mL reactor and stirred at 257 °C. Aluminium sheet (1.35 g, 5 mol%, 0.05 mol) was added slowly into the reactor at 257 °C in 1 h. After stirring the mixture for 1.5 h, cyclohexene (101.4 mL, 1.0 eq., 1.00 mol) was dropwised into the stirred mixture at 192 °C in 1 h under N_2 atmosphere. The reaction mixture was stirred for 1.5 h at 192 °C. On completion, the mixture was directly purified by claisen distillation (bath 170 °C, top 110-126 °C, press. 0.2 mmHg). A color less heavy oil was obtained as the target product (201 g, 80% y., 97% GCP). This heavy oil gradually crystallised in a week (mp 54 – 56 °C).
2-Cyclohexyl-6-phenylphenol (5b)
^{1}H-NMR (500 Hz, $CDCl_3$): δ 1.25-1.94 (m, 10H), 2.90-3.04 (m, 1H), 5.24 (s, 1H, -O*H*), 6.95 (t, 1H, *J* = 7.8 Hz), 7.05 (dd, 1H, *J* = 7.5, 1.8 Hz), 7.20 (dd, 1H, *J* = 7.5, 1.5 Hz), 7.36-7.41 (m, 1H), 7.43-7.50 (m, 4H).
^{13}C-NMR (125 Hz, $CDCl_3$): 26.4 (CH_2), 27.1 (2C, CH_2), 33.2 (2C, CH_2), 37.4 (CH), 120.4 (CH), 126.4 (CH), 127.4 (CH), 127.8 (C), 127.9 (CH), 129.3 (2C, CH), 129.4 (2C, CH), 134.2 (C), 137.5 (C), 149.5 (C).

The preparation of 2-cyclooctyl-6-phenylphenol (5c)
2-Cyclooctyl-6-phenylphenol (**5c**) was obtained using the same method as the preparation of **5b**. o-Phenylphenol (32.9 g, 193 mmol) were added into 500mL reactor and stirred at 265 °C. Aluminium sheet (0.54 g, 10 mol%, 19.3 mmol) was added slowly into the reactor at 263 °C in 30 min. After stirring the mixture for 2 h, cyclooctene (21.3 mL, 1.0 eq., 193 mmol) was dropwised into the stirred mixture at 165 °C in 1 h under N_2 atmosphere. The reaction mixture was stirred for 2 h at 165 °C. On completion, the mixture was cooled to r.t. and poured into toluene. The solution was washed with HClaq. (1M) and tap water. The collected oil layer was dried on $MgSO_4$. After a filtration and evaporation, the residue was purified by claisen distillation (bath 146 °C, top 86 °C, press. 0.5 mmHg) and cut the remained o-phenylphenol. The residue of the distillation was purified by silica-gel column chromatography

(heptane / AcOEt = 7 / 1) and a color less heavy oil was obtained as the target product (37.8 g, 69% y., >99% GCP).

2-Cyclooctyl-6-phenylphenol (5c)

^{1}H-NMR (500 Hz, $CDCl_3$): δ 1.55-2.35 (m, 14H), 3.21-3.27 (m, 1H), 5.24 (s, 1H), 6.93 (t, 1H, *J* = 7.6 Hz), 7.04 (dd, 1H, *J* = 7.5, 1.7 Hz), 7.19 (dd, 1H, *J* = 7.6, 1.7 Hz), 7.36-7.40 (m, 1H), 7.44-7.50 (m, 4H).
^{13}C-NMR (125 Hz, $CDCl_3$): 26.2 (2C,CH_2), 26.6 (CH_2), 26.9 (2C, CH_2), 33.4 (2C, CH_2), 37.0 (CH), 120.3 (CH), 127.0 (CH), 127.1 (CH), 127.8 (CH), 127.9 (C), 129.3 (2C, CH), 129.3 (2C, CH), 136.6 (C), 137.6 (C), 149.0 (C).
HRMS calcd for $C_{20}H_{24}O$ (M+) 280.1816, found 280.1827.
IR (neat): 3552s, 2919s, 2850s, 1453s, 1432m, 1324m, 1220m, 1193m, 1071m, 758s, 745m, 704s.

The preparation of 2-cyclododecyl-6-phenylphenol (5d)

2-Cyclodecyl-6-phenylphenol (**5d**) was obtained using the same method as the preparation of **5b**. o-Phenylphenol (25.5 g, 150 mmol) were added into 500mL reactor and stirred at 260 °C. Aluminium sheet (0.40 g, 10 mol%, 15.0 mmol) was added slowly into the reactor at 260 °C. After stirring the mixture for 2 h, cyclododecene (25.0 g, 1.0 eq., 150 mmol) was dropwised into the stirred mixture at 130 °C in 30 min under N_2 atmosphere. The reaction mixture was stirred for 3 h at 160 °C. On completion, the mixture was cooled to r.t. and poured into toluene. The solution was washed with HClaq. (1M) and tap water. The collected oil layer was dried on $MgSO_4$. After a filtration and evaporation, the residue was purified by silica-gel column chromatography (heptane / AcOEt = 7 / 1). A color less heavy oil was obtained as the target product (15.5 g, 31% y., >99% GCP).

2-Cyclododecyl-6-phenylphenol (5d)

^{1}H-NMR (500 Hz, $CDCl_3$): δ 1.33-1.58 (m, 20H), 1.81-1.85 (m, 2H), 3.33 (qui, 1H, *J* = 6.5 Hz), 5.24 (s, 1H, -O*H*), 6.93 (t, 1H, *J* = 7.6 Hz), 7.04 (dd, 1H, *J* = 7.5, 1.7 Hz), 7.16-7.20 (m, 1H), 7.36-7.40 (m, 1H), 7.44-7.49 (m, 4H).
^{13}C-NMR (125 Hz, $CDCl_3$): 22.9 (2C, CH_2), 23.3 (CH_2), 23.6 (2C, CH_2), 23.8 (2C, CH_2), 24.0 (2C, CH_2), 30.5 (2C, CH_2), 32.0 (CH), 120.2 (CH), 127.2 (CH), 127.4 (CH), 127.7 (C), 127.8 (CH), 129.3 (2C, CH), 129.3 (2C, CH), 133.9 (C), 137.6 (C), 150.0 (C).
HRMS calcd for $C_{24}H_{32}O$ (M+) 336.2455, found 336.2453.
IR (neat): 3554m, 2931s, 2861s, 2848s, 1469m, 1454m, 1433m, 1221m, 759m, 749m, 704m.

The preparation of *endo*-2-norbornyl-6-phenylphenol (5e)

endo-2-Norbornyl-6-phenylphenol (**5e**) was obtained using the same method as the preparation of **5b**. o-Phenylphenol (45.2 g, 266 mmol) were added into 500mL reactor and stirred at 260 °C. Aluminium sheet (0.72 g, 10 mol%, 26.6 mmol) was added slowly into the reactor at 260 °C. After stirring the mixture for 2 h, norbornene (25.0 g, 1.0 eq., 266 mmol) was dropwised into the stirred mixture at 135 °C in 1 h under N_2 atmosphere. The reaction mixture was stirred for 6 h at 135 °C. On completion, the mixture was cooled to r.t. and poured into toluene. The solution was washed with HClaq. (1M) and tap water. The collected oil layer was dried on $MgSO_4$. After a filtration and evaporation, the residue was purified by the residue was purified by claisen distillation (bath 160-170 °C, top 140-142 °C, press. 0.2 mmHg). A color less heavy oil was obtained as the target product (55.4 g, 79% y., >99% GCP).

***endo*-2-Norbornyl-6-phenylphenol (5e)**

^{1}H-NMR (500 Hz, $CDCl_3$): δ 1.22-1.41 (m, 3H), 1.55-1.70 (m, 4H), 1.77-1.86 (m, 1H), 2.35 (d, 1H, *J* = 3.7 Hz), 2.44 (d, 1H, *J* = 3.7 Hz), 2.98-3.01 (m, 1H), 5.25 (s, 1H), 6.93 (dt, 1H, *J* = 7.7, 0.4 Hz), 7.06 (dd, 1H, *J* = 7.6, 1.7 Hz), 7.21-7.23 (m, 1H) 7.36-7.4 (m, 1H) 7.43-7.50 (m, 4H).
^{13}C-NMR (125 Hz, $CDCl_3$): 29.1(CH_2), 30.4 (CH_2), 36.3 (CH_2), 36.9 (CH), 38.4 (CH_2), 40.8 (CH), 41.2 (CH), 119.9 (CH), 125.6 (CH), 127.2 (CH), 127.77 (C), 127.78 (CH), 129.2 (2C, CH), 129.3 (2C, CH), 133.8 (C), 137.5 (C), 150.1 (C).
HRMS calcd for $C_{19}H_{20}O$ (M+) 264.1512, found 264.1514.
IR (neat): 3552s, 3060m, 2996s, 2868s, 1458s, 1430s, 1325s, 1265s, 1222s, 1201s, 1138m, 1078s, 827m, 792m, 758s, 704s, 631s.

Preparation of authentic sample

Preparation of isopulegol (2) diastereo isomers mixture by silica-gel[S1]
A mixture of (*R*)-citronellal ((*R*)-**1**) (500 mg), silica-gel (5 mg, 1 wt.%), and toluene (3 mL) were added to a 50-mL schlenk tube under a N_2 atmosphere. After stirred at 135 ˚C for over 4 h, the solution was cooled to r.t.. The reaction mixture was analyzed by GC.

B. Characterization of products

2-(Prop-1-en-2-yl)cyclohexanol (8) (Table 2, entry 1)[S2]
^{1}H-NMR (500 Hz, $CDCl_3$): δ 1.22-1.40 (m, 5H), 1.65-1,71 (m, 3H), 1.72 (br, 3H, C*H*$_3$-C), 1.92-1.95 (m, 1H), 2.02-2.08 (m, 1H), 3.42 (dt, 1H, *J* = 10.0, 4.2 Hz, C*H*-OH), 4.85 (br, 1H, C=C*H*$_2$), 4.90 (br, 1H, C=C*H*$_2$) (major).
^{1}H-NMR (500 Hz, $CDCl_3$): δ 1.22-1.40 (m, 2H), 1.44-1.48 (m, 3H), 1.61-1.66 (m, 2H), 1.74-1.77 (m, 1H), 1.78 (br, 3H), 2.00-2.03 (m, 2H), 3.97 (br, 1H), 4.77 (s, 1H, C=C*H*$_2$), 4.95 (br, 1H, C=C*H*$_2$) (minor).
^{13}C-NMR (125 Hz, $CDCl_3$): 19.2 (CH_3), 24.9 (CH_2), 25.6 (CH_2), 30.2 (CH_2), 34.1 (CH_2), 54.6 (CH), 70.7 (CH), 111.5 (CH_2), 146.6 (C) (major).
^{13}C-NMR (125 Hz, $CDCl_3$): 19.7 (CH_3), 22.6 (CH_3), 23.9 (CH_2), 26.0 (CH_2), 32.2 (CH_2), 48.7 (CH), 65.8 (CH), 111.2 (CH_2), 147.0 (C) (minor).

5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexanol (*trans*-5-methylisopulegol) (10) (Table 2, entry 3)
^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.94 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.14 (t, *J* = 11.5 Hz, 1H), 1.17-1.31 (m, 2H), 1.35-1.42 (m, 1H), 1.45-1.58 (m, 2H), 1.74 (dd, *J* = 1.5, 1.0 Hz, 3H, C*H*$_3$-C=C), 1.78 (dq, 1H, *J* = 12.5, 2.0 Hz), 1.81-1.87 (m, 1H), 3.61-3.67 (m, 1H, >C*H*-O), 4.86-4.87 (m, 1H, C=C*H*$_2$), 4.89-4.91(m, 1H, C=C*H*$_2$).
^{13}C-NMR (125 MHz, $CDCl_3$): 19.3 (CH_3), 25.1 (CH_3), 26.4 (CH_2), 32.1 (C), 33.0 (CH_3), 38.5 (CH_2), 46.8 (CH_2), 54.8 (CH), 67.6 (CH), 112.8 (CH_2), 146.6 (C).
HRMS calcd for $C_{11}H_{20}O$ (M+) 168.1514, found 168.1516.
IR (neat): 3419m, 2952s, 2928s, 2866s, 1722m, 1645m, 1455m, 1386m, 1365m, 1051m, 1027m, 1013m, 885m.

5,5-Dimethyl-2-((*E*)-6-methylhepta-2,5-dien-2-yl)cyclohexanol (12) (Table 2, entry 4)
^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.94 (d, 6H, *J* = 10.0 Hz, C*H*$_3$-C-C*H*$_3$), 1.10 (t, 1H, *J* = 12.0 Hz), 1.19-1.26 (m, 1H), 1.34-1.40 (m, 1H), 1.49-1.56 (m, 1H), 1.60 (s, 3H), 1.62 (d, 3H, *J* = 4.2 Hz), 1.69 (br, 3H), 1.72-2.10 (m, 4H), 2.74 (t, 2H, *J* = 7.0 Hz, =CH-C*H*$_2$-CH=), 3.61 (td, 1H, *J* = 10.5, 4.5 Hz, C*H*-OH), 5.08-5.12 (m, 1H, C=C*H*), 5.30 (td, 1H, *J* = 7.0, 1.0 Hz, C=C*H*).
^{13}C-NMR (125 MHz, $CDCl_3$): 12.8 (CH_3), 17.8 (CH_3), 25.2 (CH_3), 25.7 (CH_3), 26.1 (CH_2), 26.9 (CH_2), 32.1 (C), 33.0 (CH_3), 38.6 (CH_2), 46.7 (CH_2), 56.5 (CH), 67.2 (CH), 122.8 (CH), 127.0 (CH), 131.9 (C), 135.3 (C).
HRMS calcd for $C_{16}H_{28}O$ (M+) 236.2140, found 236.2213.
IR (neat):3368m, 2926s 1453m, 1384m, 1364m, 1256w, 1140w, 1045m, 985m, 921w.

5-Ethyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol (5-ethylisopulegol) (14) (1α,2β,5β / 1α,2β,5α = 78 / 22) (Table 2, entry 5)
^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.82-0.87 (m, 3H), 0.90 (s, 3H, C-C*H*$_3$), 1.02-1.63 (m, 7H), 1.76 (s, 3H, C=C-C*H*$_3$), 1.80-1.96 (m, 3H), 3.66 (ddd, 1H, *J* = 10.5, 10.5, 4.5 Hz), 4.88 (d, 2H, *J* = 21.0 Hz, C=C*H*$_2$) (major).
^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.82-0.85 (m, 3H), 0.88 (s, 3H, C-C*H*$_3$), 1.02-1.63 (m, 7H), 1.73 (s, 3H, C=C-C*H*$_3$), 1.80-1.96 (m, 3H), 3.60 (ddd, 1H, *J* = 10.7, 10.7, 4.5 Hz), 4.88 (d, 2H, *J* = 21.0 Hz, C=C*H*$_2$) (minor).
^{13}C-NMR (125 MHz, $CDCl_3$): 7.6 (CH_3), 19.3 (CH_3), 22.1 (CH_3), 26.1 (CH_2), 34.7 (C), 36.4 (CH_2), 38.2 (CH_2), 44.6 (CH_2), 55.1 (CH), 67.6 (CH), 112.7 (CH_2), 146.7 (C) (major).
^{13}C-NMR (125 MHz, $CDCl_3$): 7.9 (CH_3), 19.3 (CH_3), 22.1 (CH_3), 25.8 (CH_2), 34.6 (C), 36.6 (CH_2), 38.2 (CH_2), 44.6 (CH_2), 54.8 (CH), 67.1 (CH), 112.7 (CH_2), 146.7 (C) (minor).
HRMS calcd for $C_{12}H_{22}O$ (M+) 182.1662, found 182.1671.
IR (neat): 3405m, 3073m, 2965s, 2928s, 1645m, 1461m, 1378m, 1140w, 1061m, 1033m, 885m.

5-Butyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol (5-buthylisopulegol) (16) (1α,2β,5β / 1α,2β,5α = 87 / 13) (Table 2, entry 6)
^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.90-0.93 (m, 6H), 1.10 (t, 1H, *J* = 11.5 Hz), 1.15-1.41 (m, 7H), 1.45-1.62 (m, 3H), 1.74 (br, 3H, C=C-C*H*$_3$), 1.77-1.90 (m, 3H), 3.65 (ddd, 1H, *J* = 10.7, 10.7, 4.4 Hz), 4.84-4.87 (br, 1H, C=CH_2), 4.89-4.92 (br, 1H, C=CH_2) (major).
^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.88-0.91 (m, 6H), 1.02-1.40 (m, 8H), 1.45-1.62 (m, 3H), 1.75 (d, 3H, *J* = 2.0 Hz, C=C-CH_3), 1.77-1.90 (m, 3H), 3.61 (ddd, 1H, *J* = 10.8, 10.5, 4.2 Hz), 4.84-4.87 (br, 1H, C=CH_2), 4.89-4.92 (br, 1H, C=CH_2) (minor).
^{13}C-NMR (125 MHz, $CDCl_3$): 14.1 (CH_3), 19.3 (CH_3), 22.7 (CH_3), 23.6 (CH_2), 25.4 (CH_2), 26.1 (CH_2), 34.7 (C), 36.9 (CH_2), 45.1 (CH_2), 45.9 (CH_2), 55.1 (CH), 67.6 (CH), 112.7 (CH_2), 146.7 (C) (major).
^{13}C-NMR (125 MHz, $CDCl_3$): 14.1 (CH_3), 19.3 (CH_3), 23.6 (CH_2), 25.4 (CH_2), 25.9 (CH_2), 29.4 (CH_3), 34.7 (C), 37.1 (CH_2), 44.9 (CH_2), 45.9 (CH_2), 54.8 (CH), 67.1 (CH), 112.7 (CH_2), 146.7 (C) (minor).
HRMS calcd for $C_{14}H_{26}O$ (M+) 210.1984, found 210.1984.
IR (neat): 3405m, 2958s, 2929s, 1643m, 1461m, 1378m, 1036m, 885m.

5-Methyl-5-phenyl-2-(prop-1-en-2-yl)cyclohexanol (5-phenylisopulegol) (18) (1α,2β,5β / 1α,2β,5α = 62 / 38) (Table 2, entry 7)
^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.32 (s, 3H, C-C*H*$_3$), 1.32-1.50 (m, 2H), 1.52 (s, 3H, C=C-C*H*$_3$), 1.53-1.75 (m, 2H), 1.88-2.04 (m, 2H), 2.38 (dq, 1H, *J* = 13.8, 3.0 Hz), 2.71 (dt, 1H, *J* = 13.3, 2.9 Hz, C=CH-C*H*), 3.85 (ddd, 1H, *J* = 10.5, 10.5, 4.5 Hz), 4.77-4.85 (m, 2H, C=C*H*$_2$), 7.10-7.45 (m, 5H, -C_6H_5) (major).
^{1}H-NMR (500 MHz, $CDCl_3$): δ 1.20 (s, 3H, C-C*H*$_3$), 1.35-1.73 (m, 5H), 1.79 (s, 3H, C=C-C*H*$_3$), 1.86-2.04 (m, 2H), 2.30 (dq, 1H, *J* = 12.5, 2.0 Hz), 3.45 (ddd, 1H, *J* = 10.6, 10.6, 4.7 Hz), 4.90-4.96 (m, 2H, C=C*H*$_2$), 7.10-7.45 (m, 5H, -C_6H_5) (minor).
^{13}C-NMR (125 MHz, $CDCl_3$): 19.3 (CH_3), 25.5 (CH_3), 26.3 (CH_2), 37.1 (CH_2), 38.8 (C), 44.8 (CH_2), 54.6 (CH), 67.8 (CH), 112.9 (CH_2), 124.9 (CH), 125.8 (CH), 125.9 (CH), 128.2 (CH), 128.5 (CH), 146.4 (C), 151.3 (C) (major).

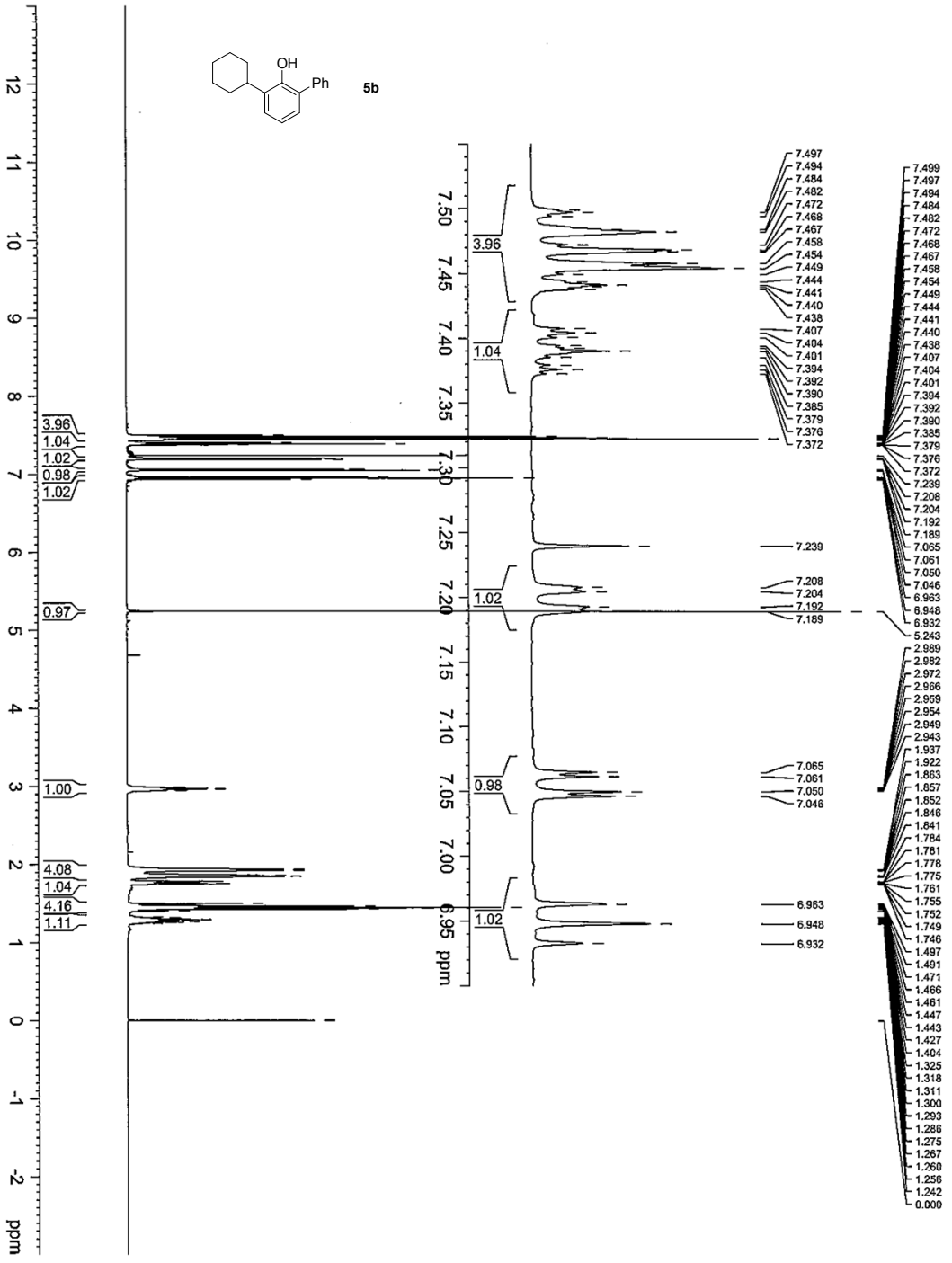
^{13}C-NMR (125 MHz, $CDCl_3$): 19.1 (CH_3), 26.5 (CH_2), 35.3 (CH_3), 37.0 (CH_2), 40.0 (C), 44.9 (CH_2), 54.9 (CH), 67.3 (CH), 112.7 (CH_2), 124.9 (CH), 125.6 (CH), 125.9 (CH), 128.2 (CH), 128.5 (CH), 146.3 (C), 146.6 (C) (minor).
HRMS calcd for $C_{14}H_{26}O$ (M+) 230.1670, found 230.1644.
IR (neat): 3404m, 2933s, 2963s, 1644m, 1496m, 1445s, 1376m, 1064m, 1034s, 889m, 764s, 700s.

(5*R*)-*n*-Isopulegol (2a) (Scheme 2)
$[\alpha]^{20}_{D}$ = -10.0 (c = 0.27, $CHCl_3$, 98% *ee*).
^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.86-0.94 (m, 1H), 0.95 (d, 3H, *J* = 7.0 Hz, C*H*$_3$-CH), 0.95-1.01 (m, 1H), 1.24-1.37 (m, 1H), 1.45-1.55 (m, 1H), 1.64-1.70 (m, 2H), 1.71 (s, 3H, C*H*$_3$-C=CH$_2$), 1.84 (s, 1H), 1.85-1.92 (m, 1H), 2.02-2.08 (m, 1H), 3.47 (td, 1H, *J* = 10.5, 3.5 Hz, C*H*-OH), 4.85 (br, 1H, C=C*H*$_2$), 4.90 (br, 1H, C=C*H*$_2$).
^{13}C-NMR (125 MHz, $CDCl_3$): 19.2 (CH_3), 22.2 (CH_3), 29.7 (CH_2), 31.5 (CH), 34.3 (CH_2), 42.7 (CH_2), 54.2 (CH), 70.4 (CH), 112.8 (CH_2), 146.6 (C).

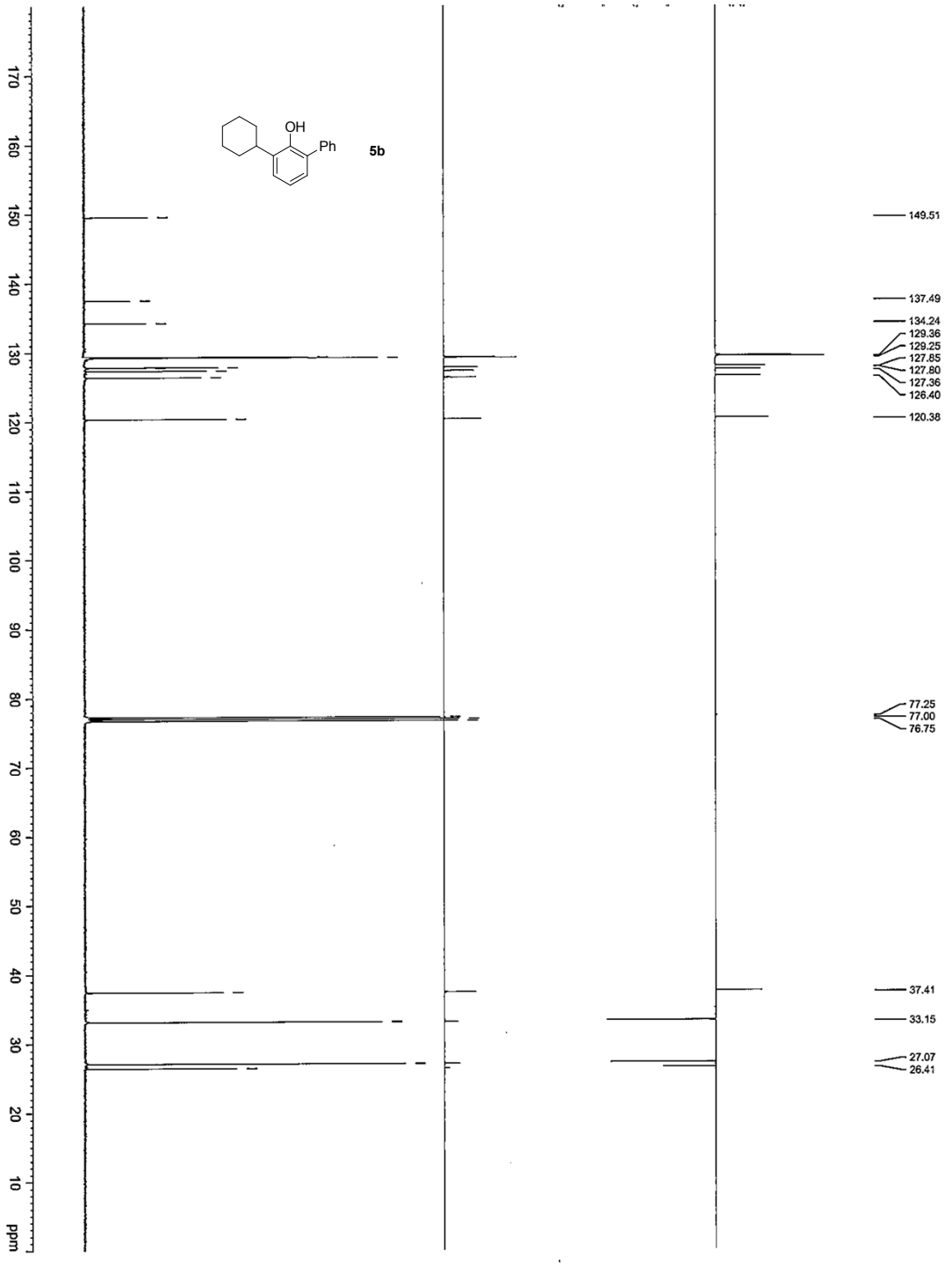
***l*-Menthol (3) (Scheme 2)**
$[\alpha]^{20}_{D}$ = -41.8 (c = 0.28, $CHCl_3$, 99% *ee*).
^{1}H-NMR (500 MHz, $CDCl_3$): δ 0.81 (d, 3H, *J* = 7.0 Hz), 0.83-0.89 (m, 2H), 0.91 (d, 3H, *J* = 6.8 Hz), 0.93 (d, 3H, *J* = 7.0 Hz), 0.94-1.02 (m, 2H), 1.07-1.15 (m, 1H), 1.38-1.46 (m, 1H), 1.58-1.69 (m, 2H), 1.94-2.00 (m, 1H), 2.14-2.22 (m, 1H), 3.41 (td, 1H, *J* = 10.5, 4.0 Hz).
^{13}C-NMR (125 MHz, $CDCl_3$): 16.1 (CH_3), 21.0 (CH_3), 22.2 (CH_3), 23.2 (CH_2), 25.8 (CH), 31.6 (CH), 34.5 (CH_2), 45.1 (CH_2), 50.2 (CH), 71.5 (CH).

C. NMR DATA of 2-cycloalkyl-6-phenylphenols

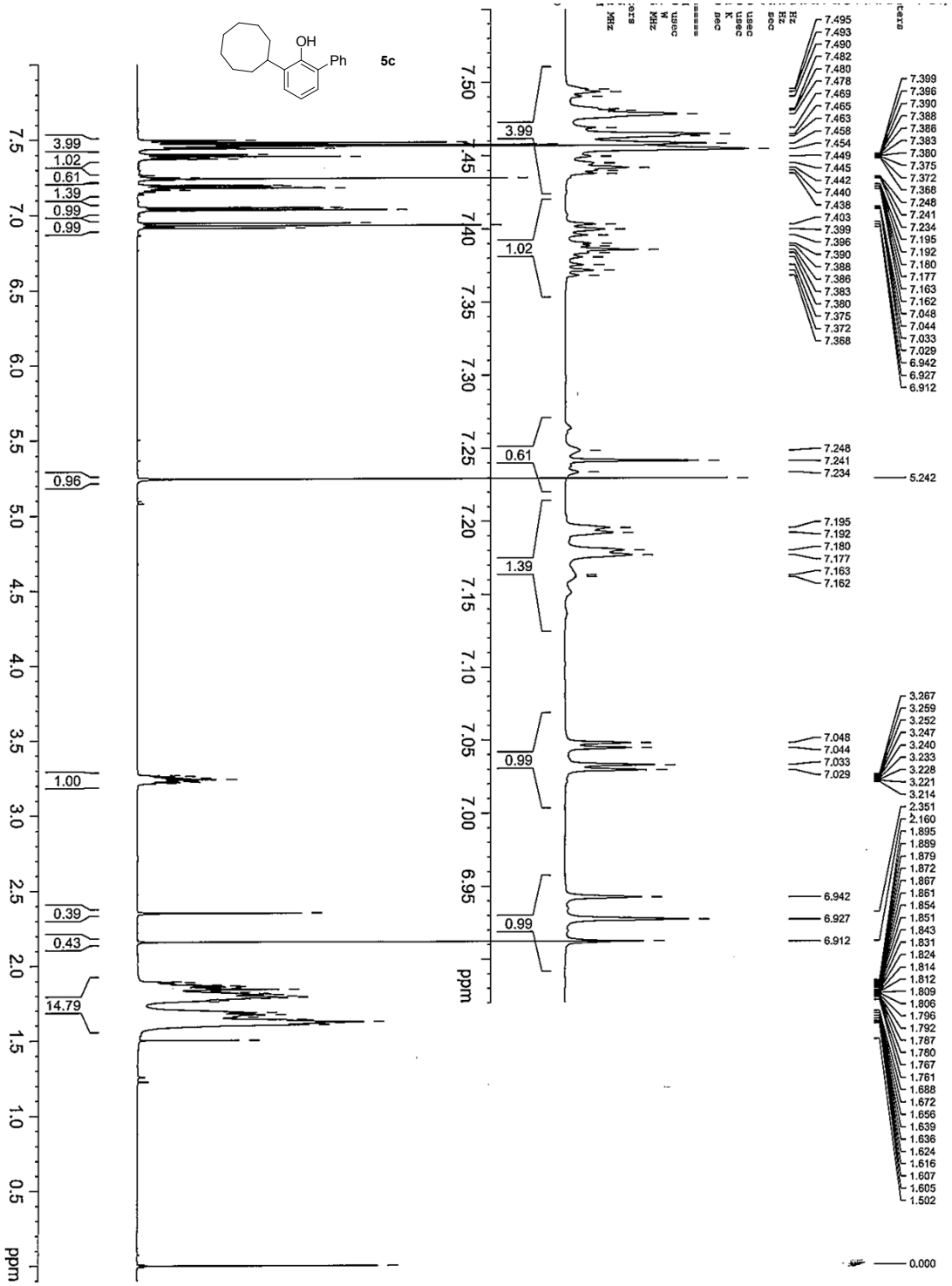
2-Cyclohexyl-6-phenylphenol (5b)



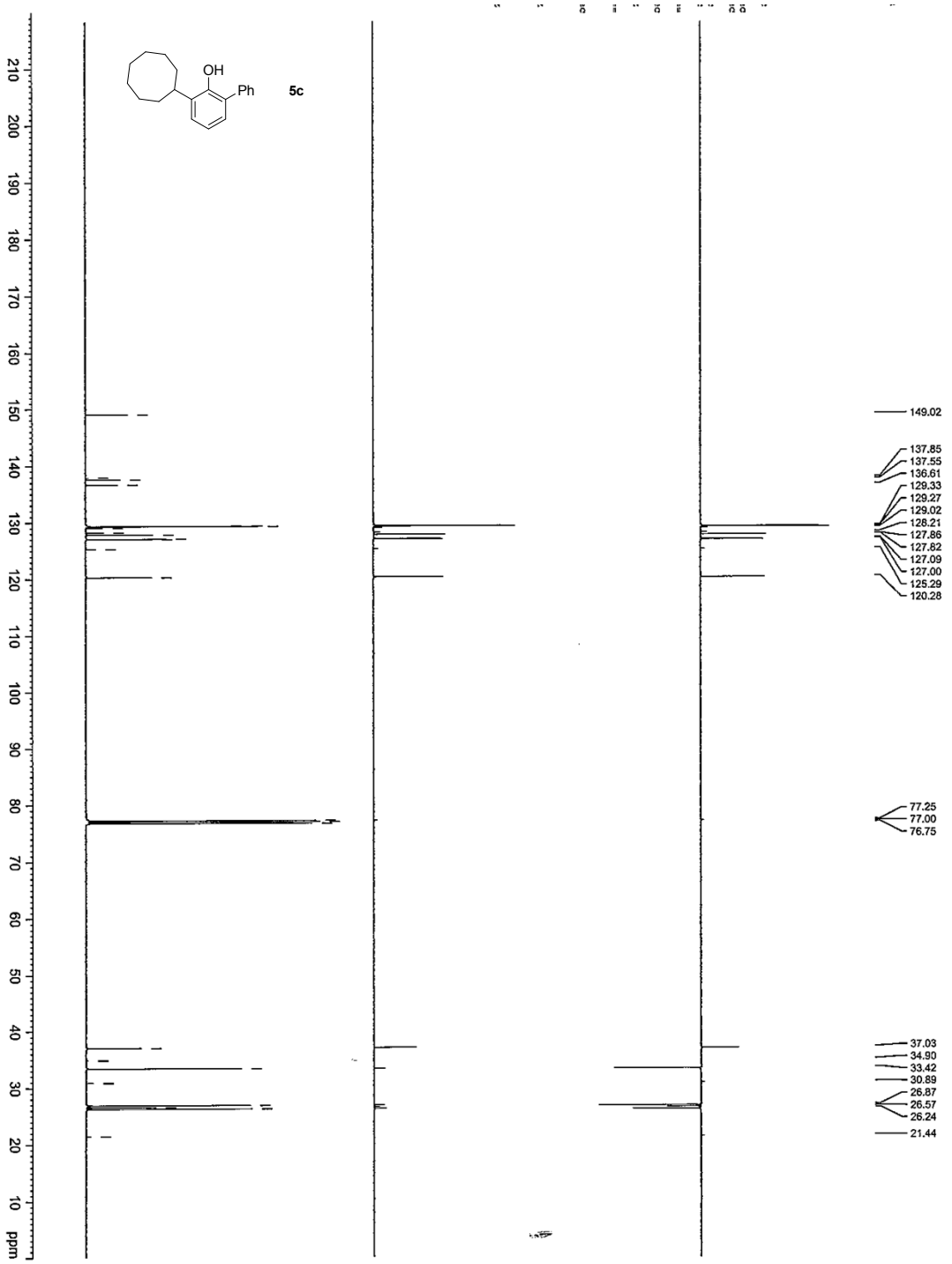
2-Cyclohexyl-6-phenylphenol (5b)



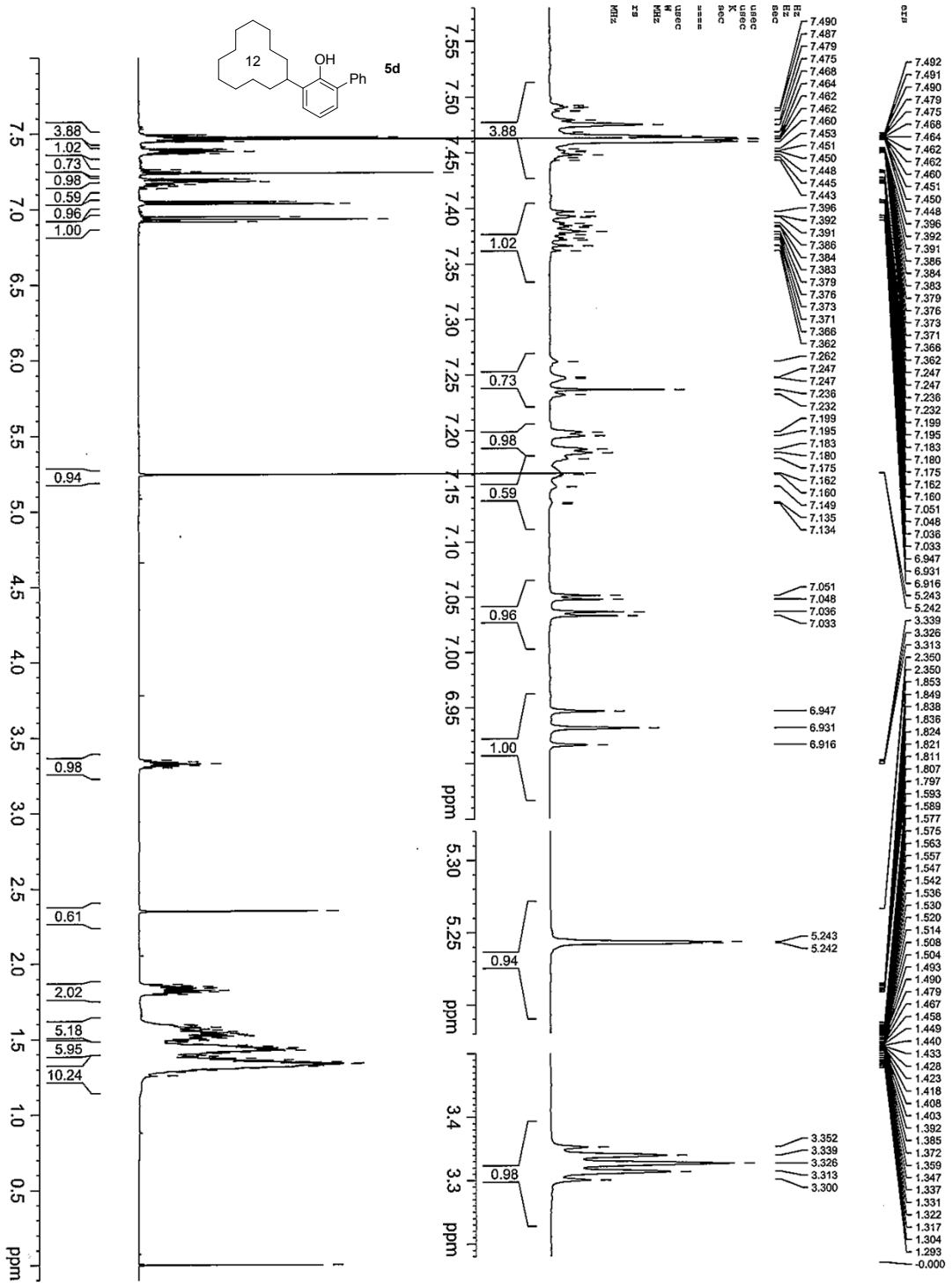
2-Cyclooctyl-6-phenylphenol (5c)



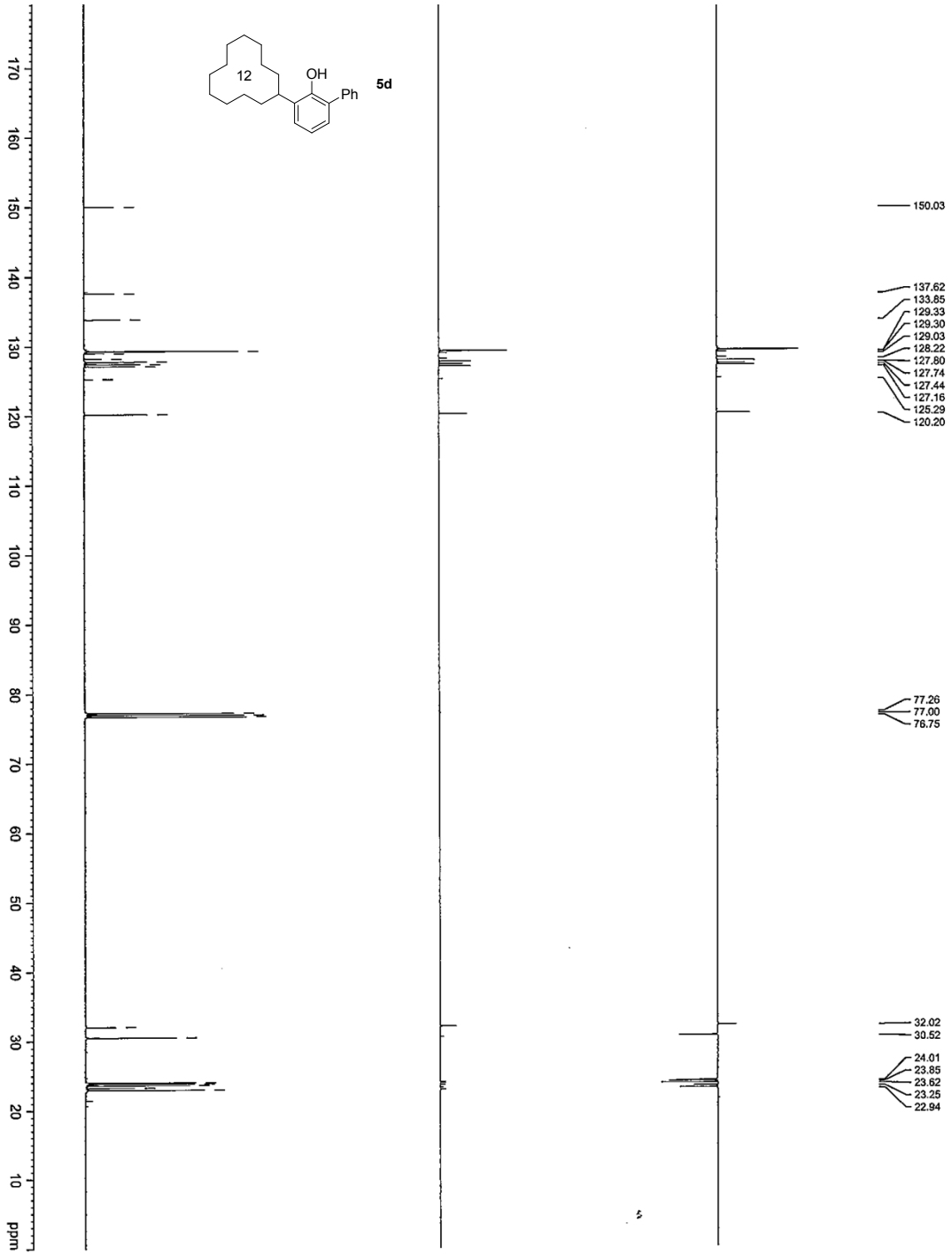
2-Cyclooctyl-6-phenylphenol (5c)



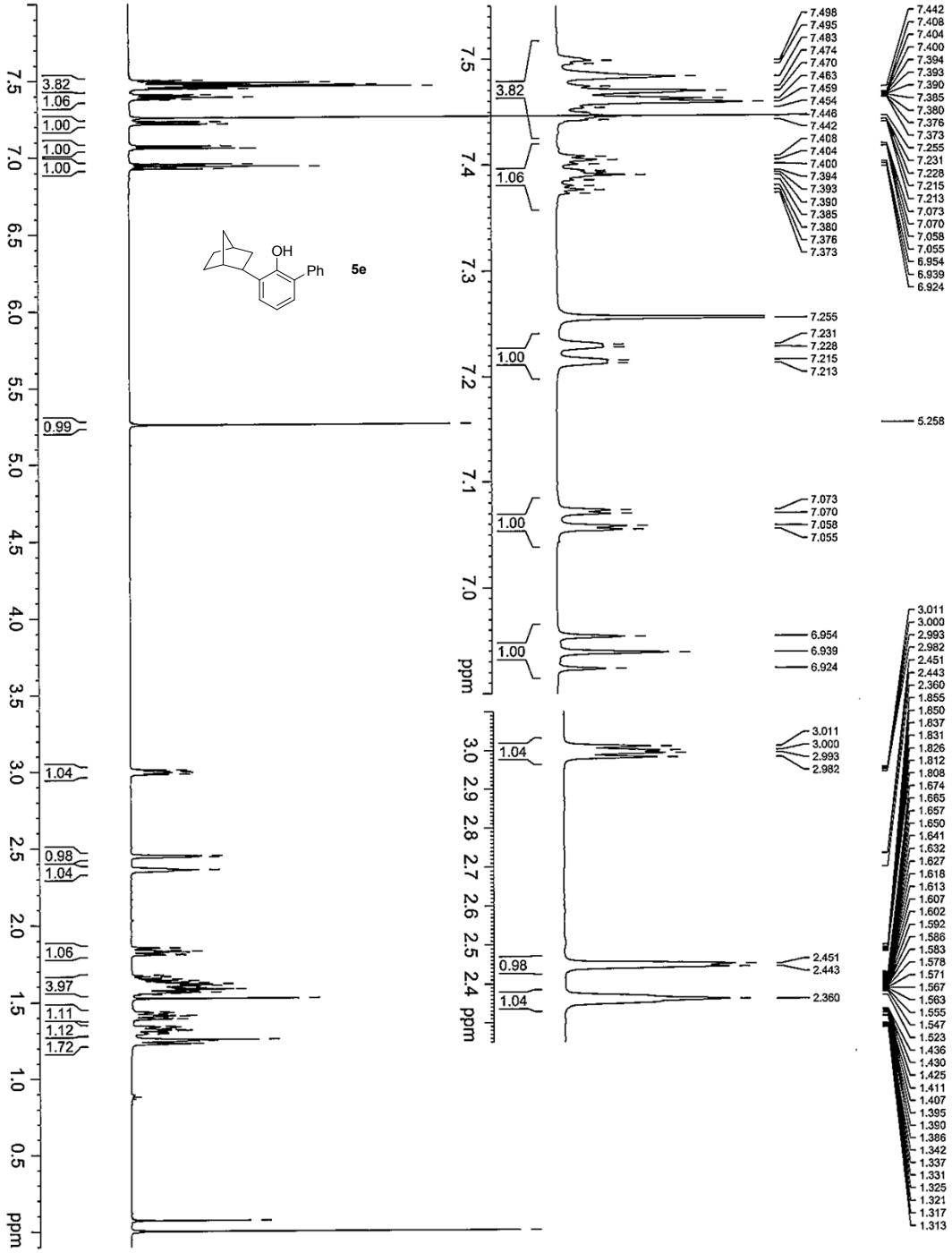
2-Cyclodecyl-6-phenylphenol (5d)



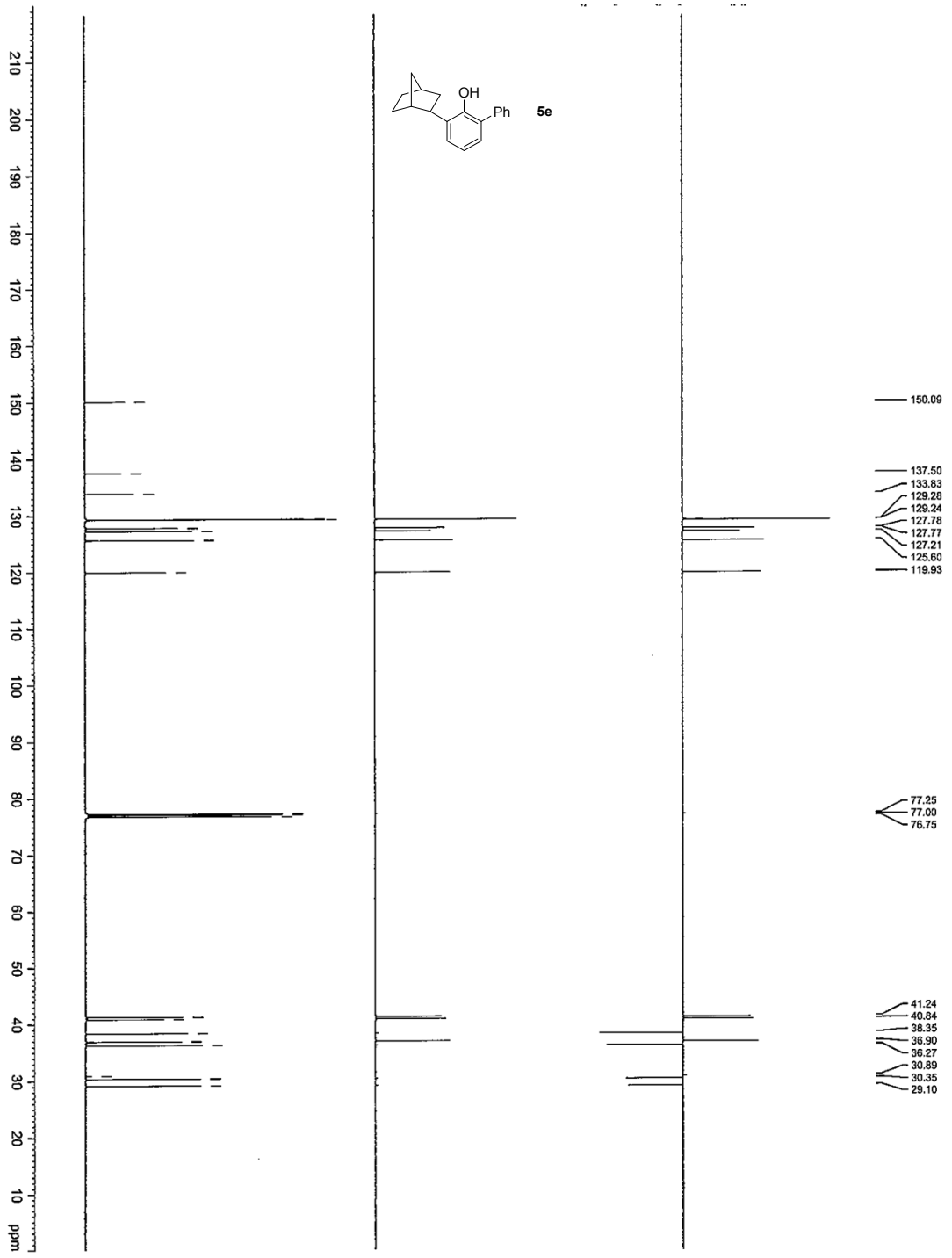
2-Cyclodecyl-6-phenylphenol (5d)



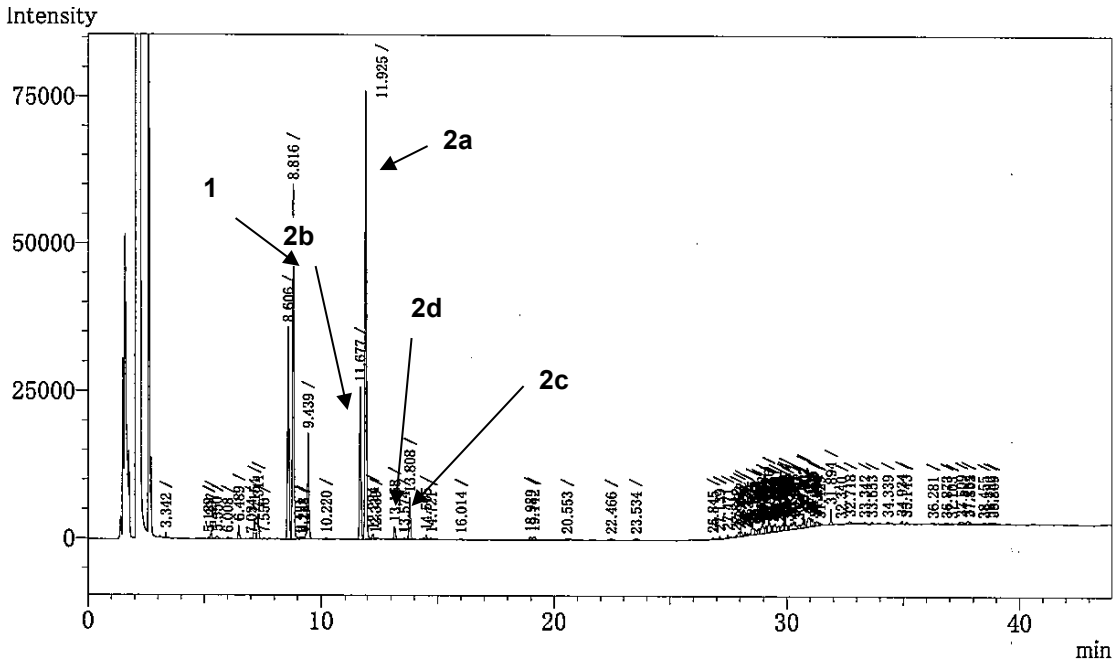
***endo*-2-Norbornyl-6-phenylphenol (5e)**



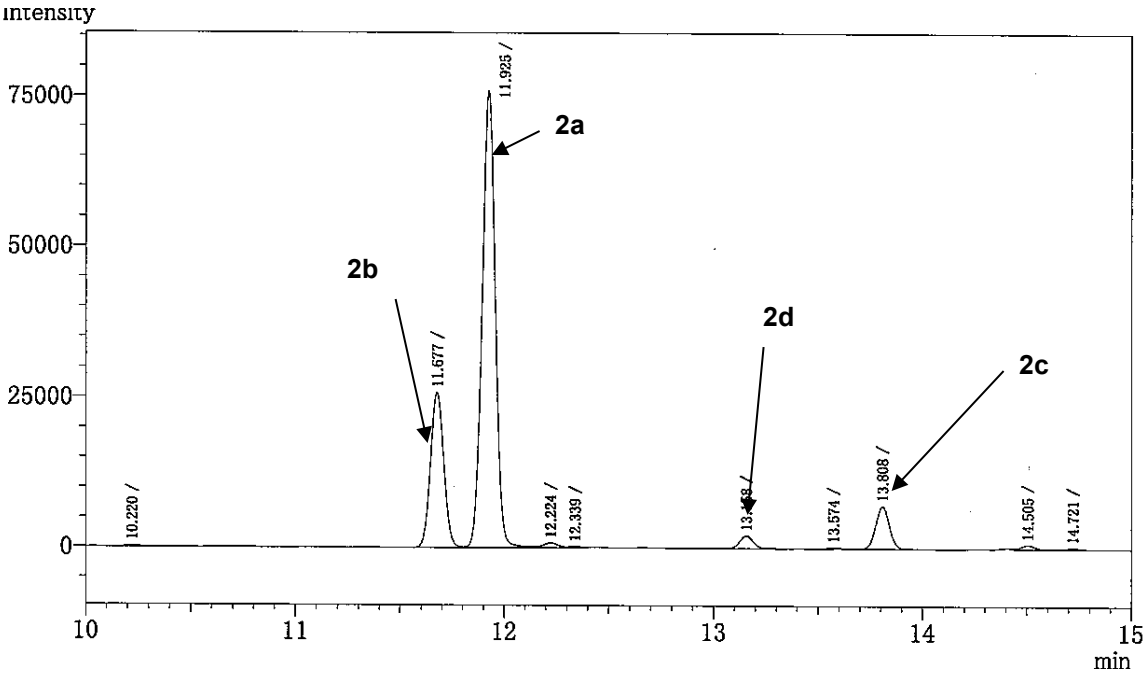
***endo*-2-Norbornyl-6-phenylphenol (5e)**



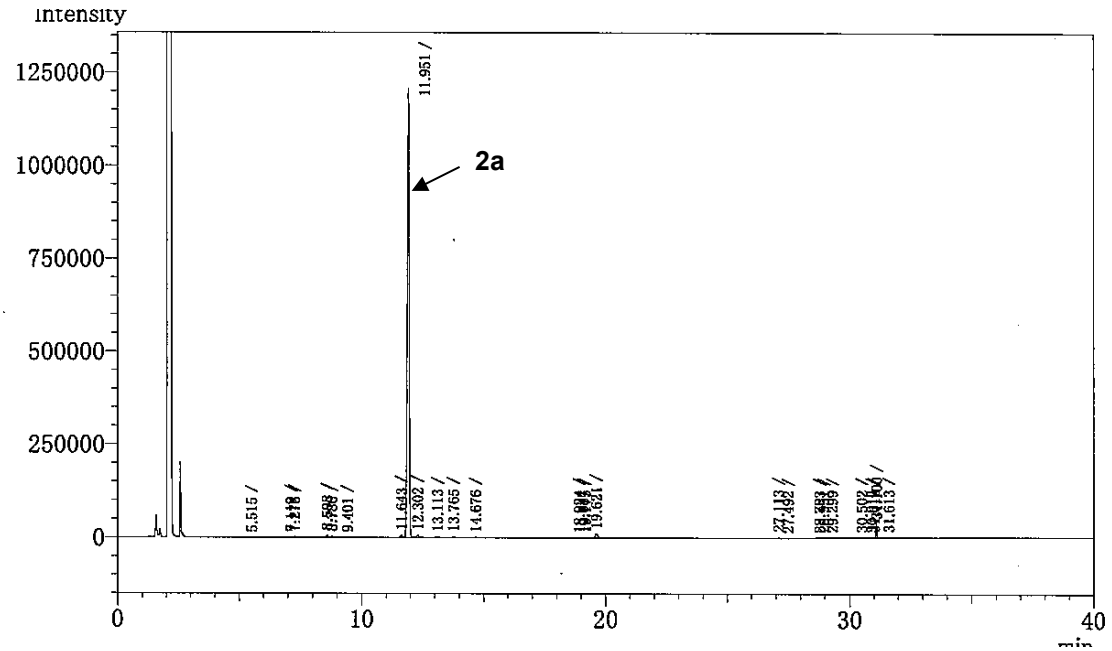
(5*R*)-Isopulegols (**2**) by silica-gel



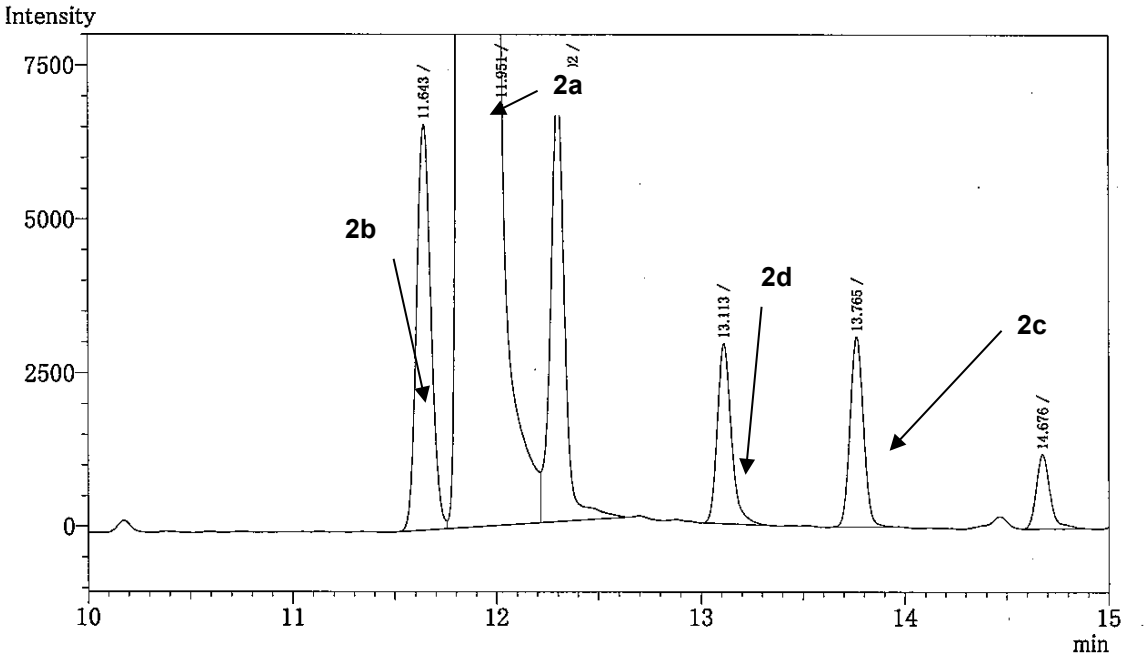
(5*R*)-Isopulegols (**2**) by silica-gel (magnified)



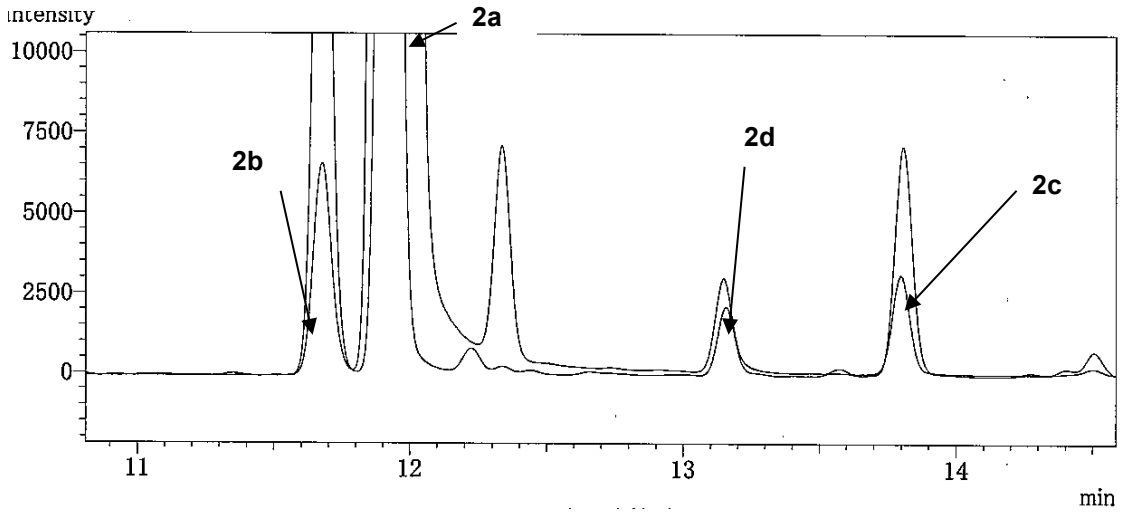
(5*R*)-Isopulegols (**2**) by the ACPP catalyst (Table 1, entry 1)



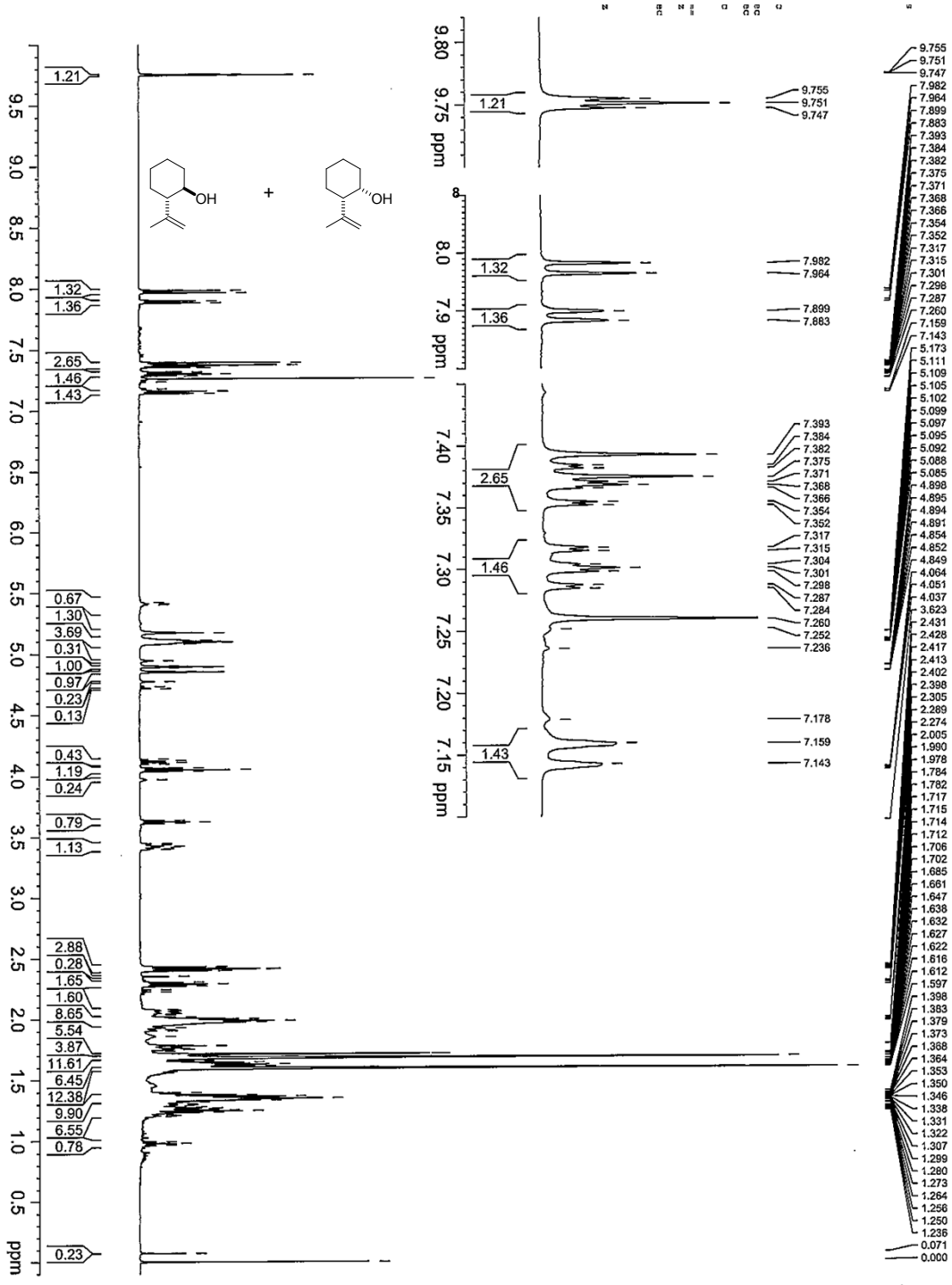
(5*R*)-Isopulegols (**2**) by the ACPP catalyst (Table 1, entry 1) (magnified)



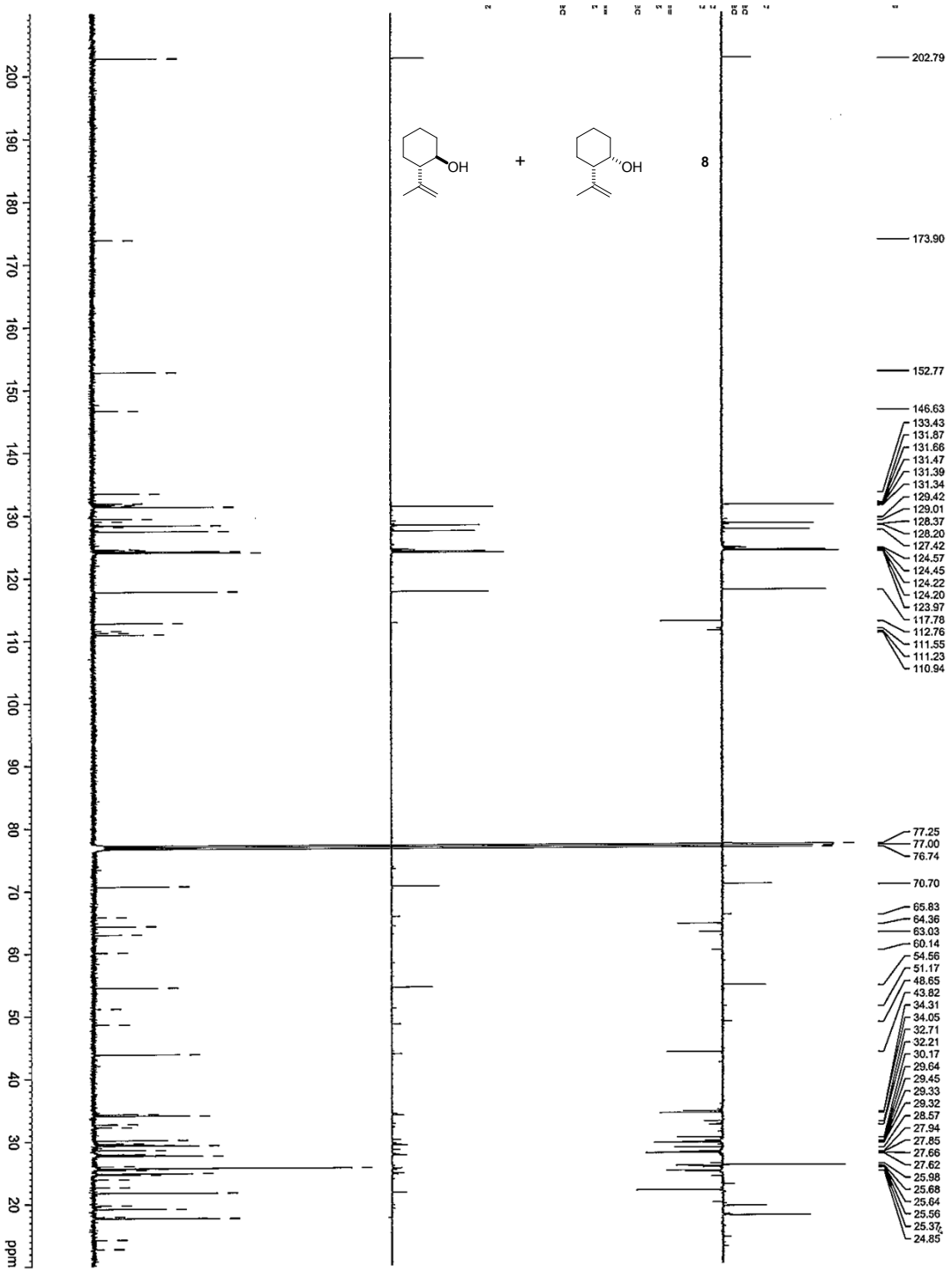
Superimposed chart of (5*R*)-Isopulegols (**2**) by silica-gel and by the ACPP catalyst (Table 1, entry 1)



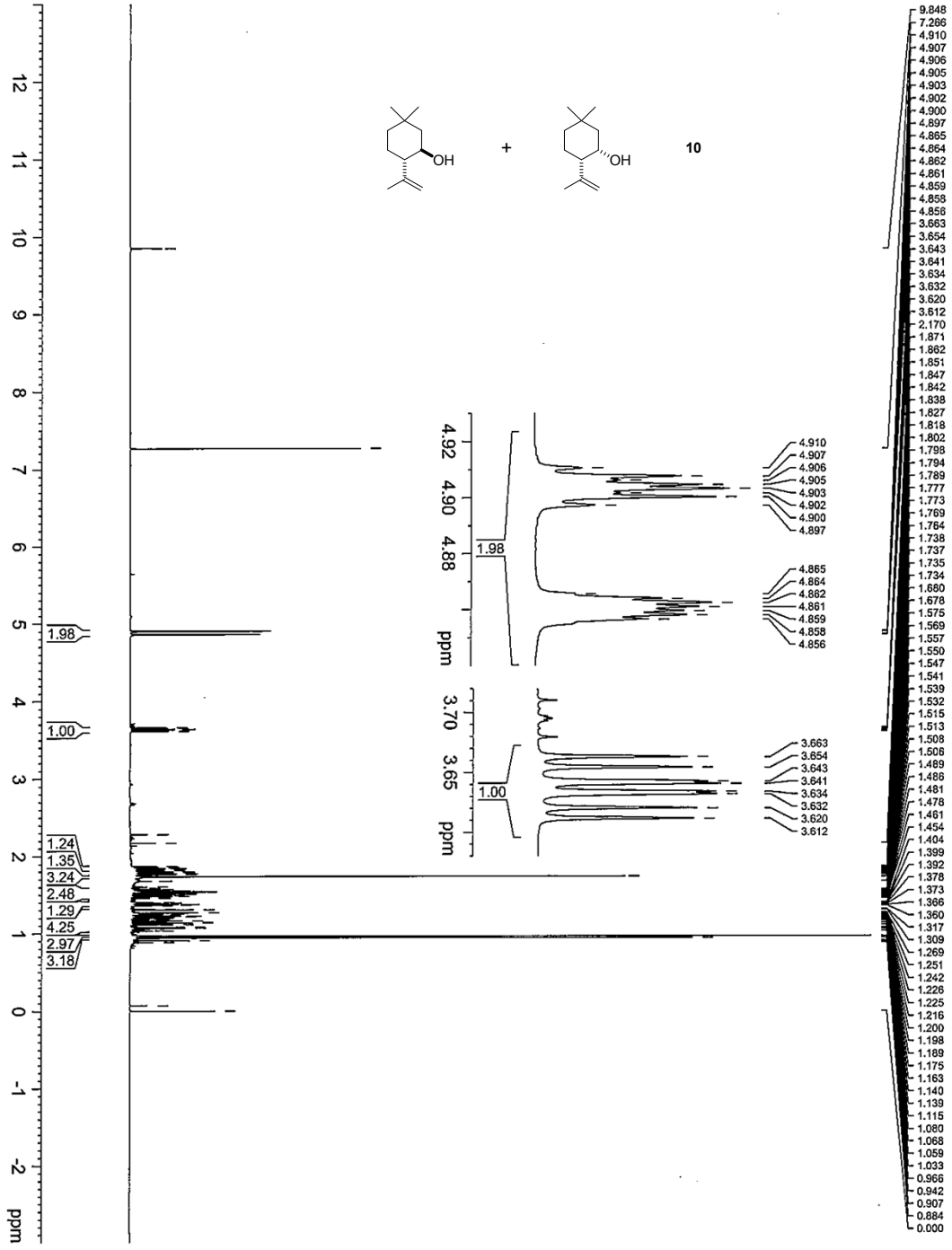
2-(Prop-1-en-2-yl)cyclohexanol (8) (Table 2, entry 1)



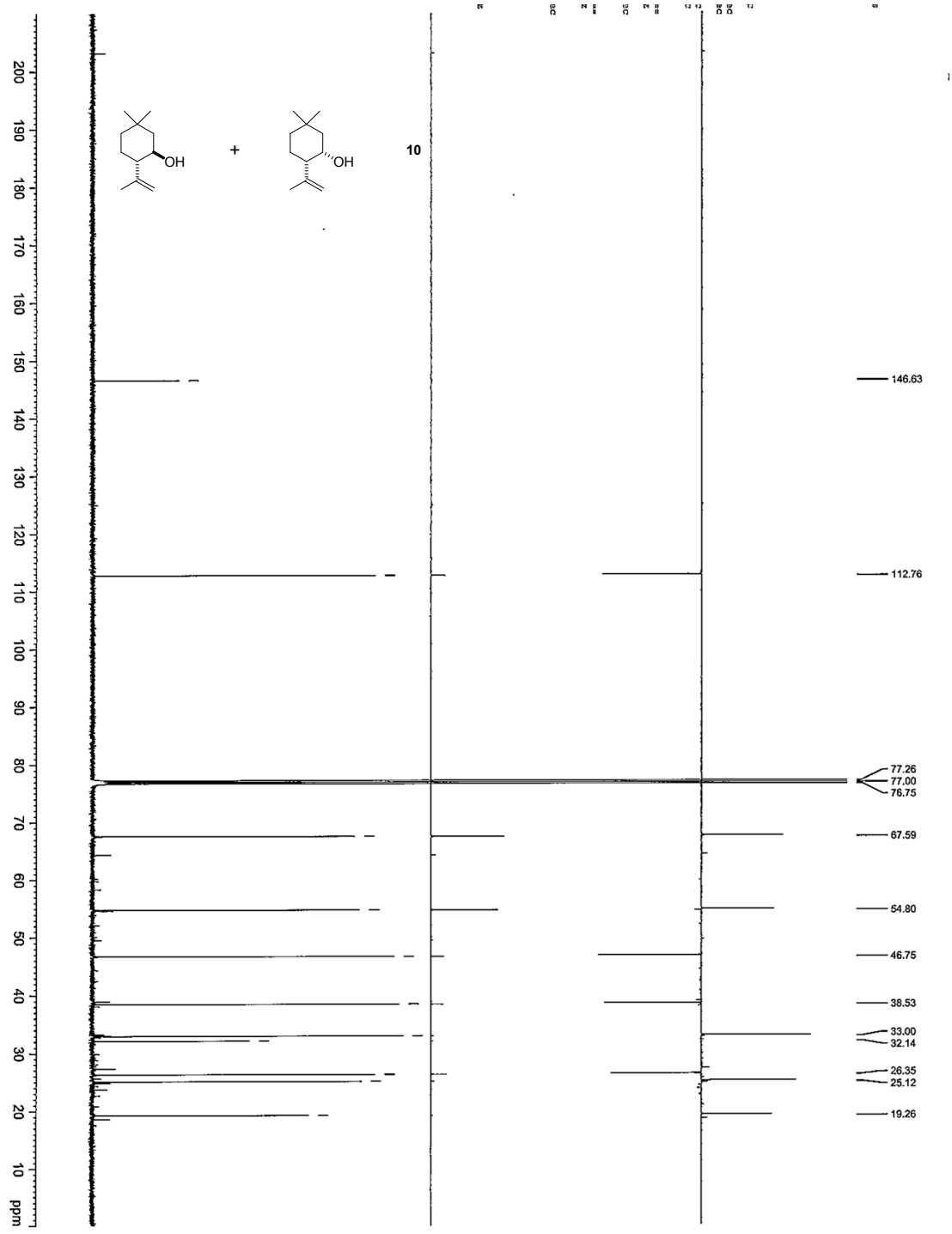
2-(Prop-1-en-2-yl)cyclohexanol (8) (Table 2, entry 1)



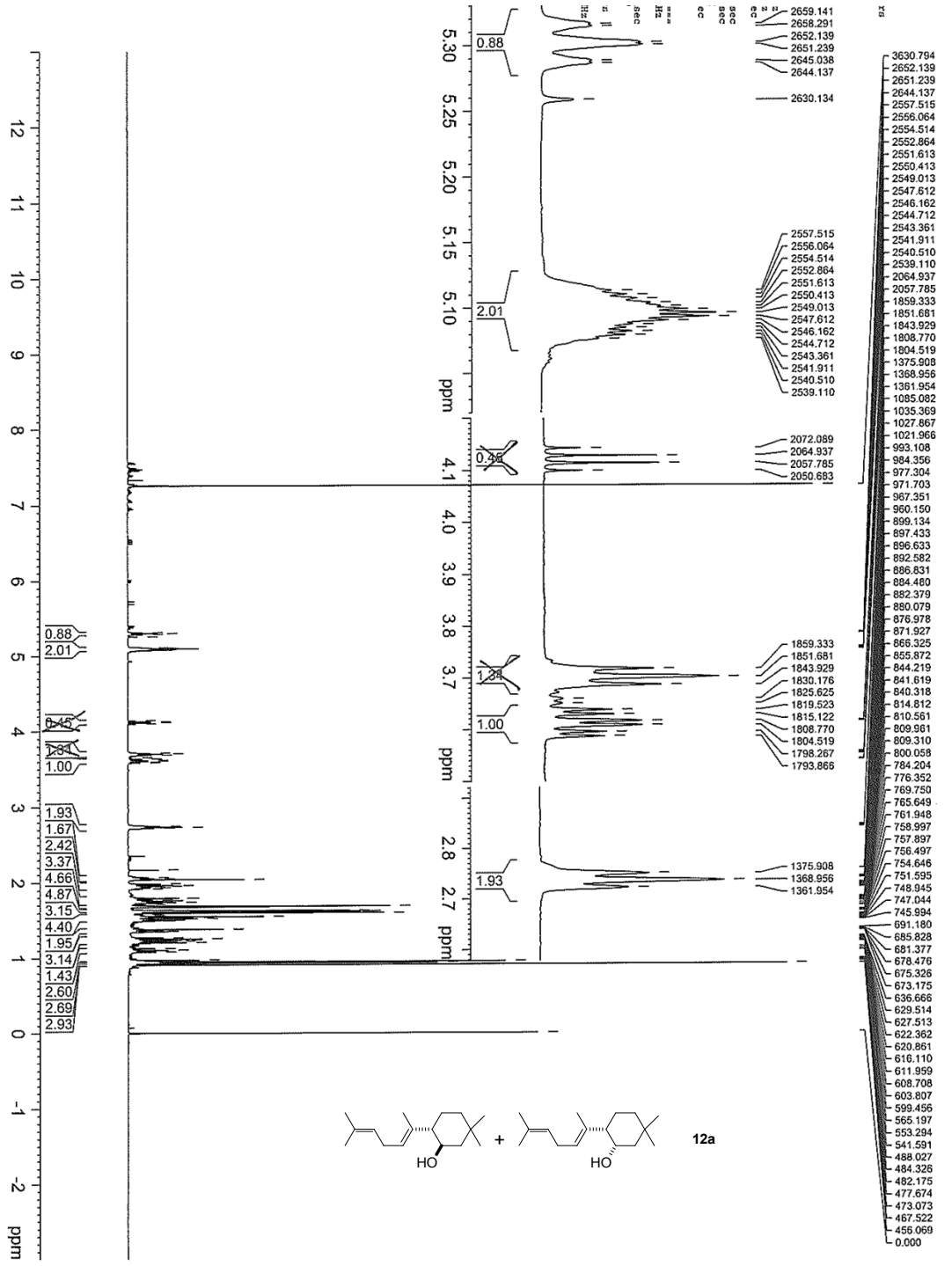
5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexanol (*trans*-5-methylisopulegol) (10) (Table 2, entry 3)



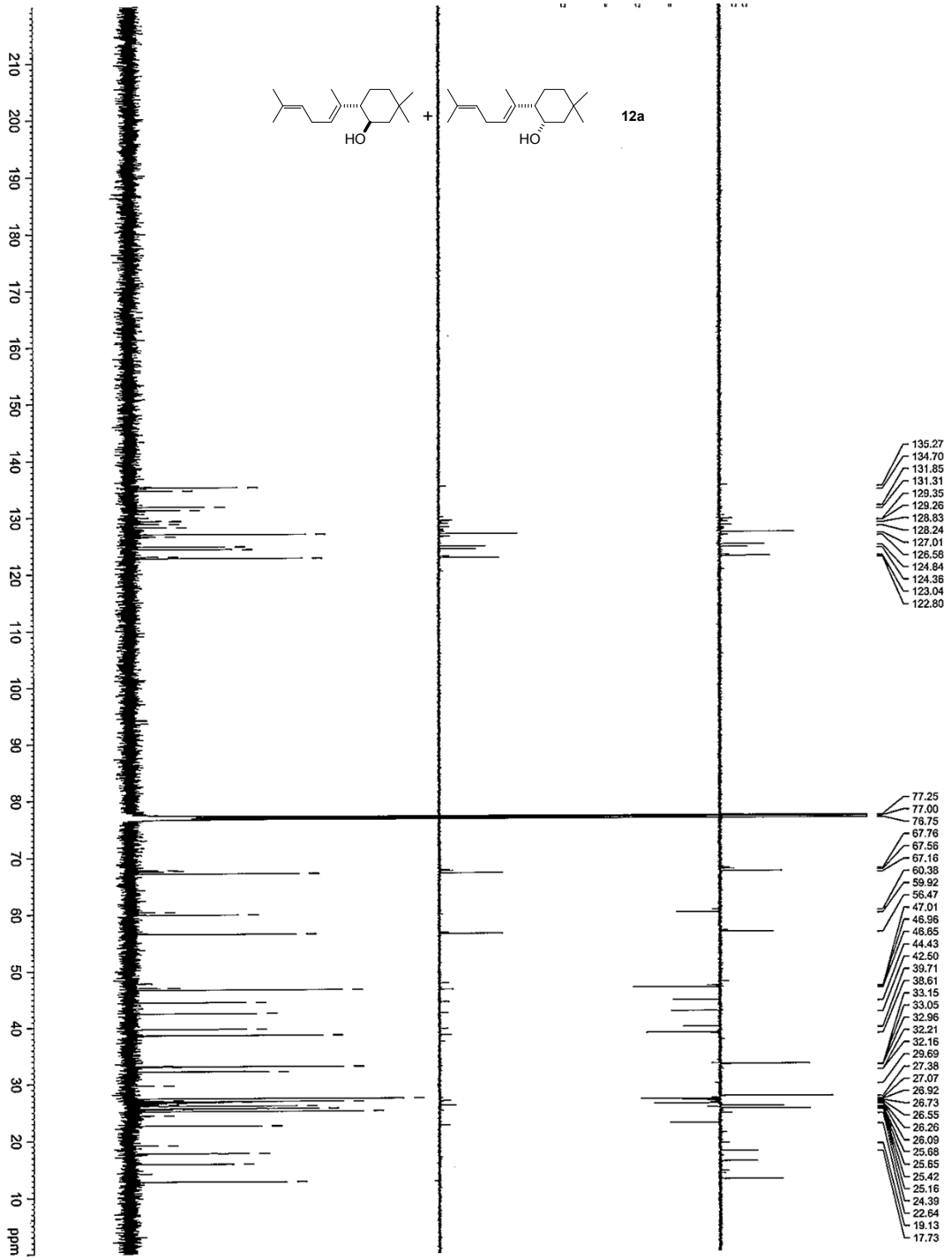
5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexanol (*trans*-5-methylisopulegol) (10) (Table 2, entry 3)



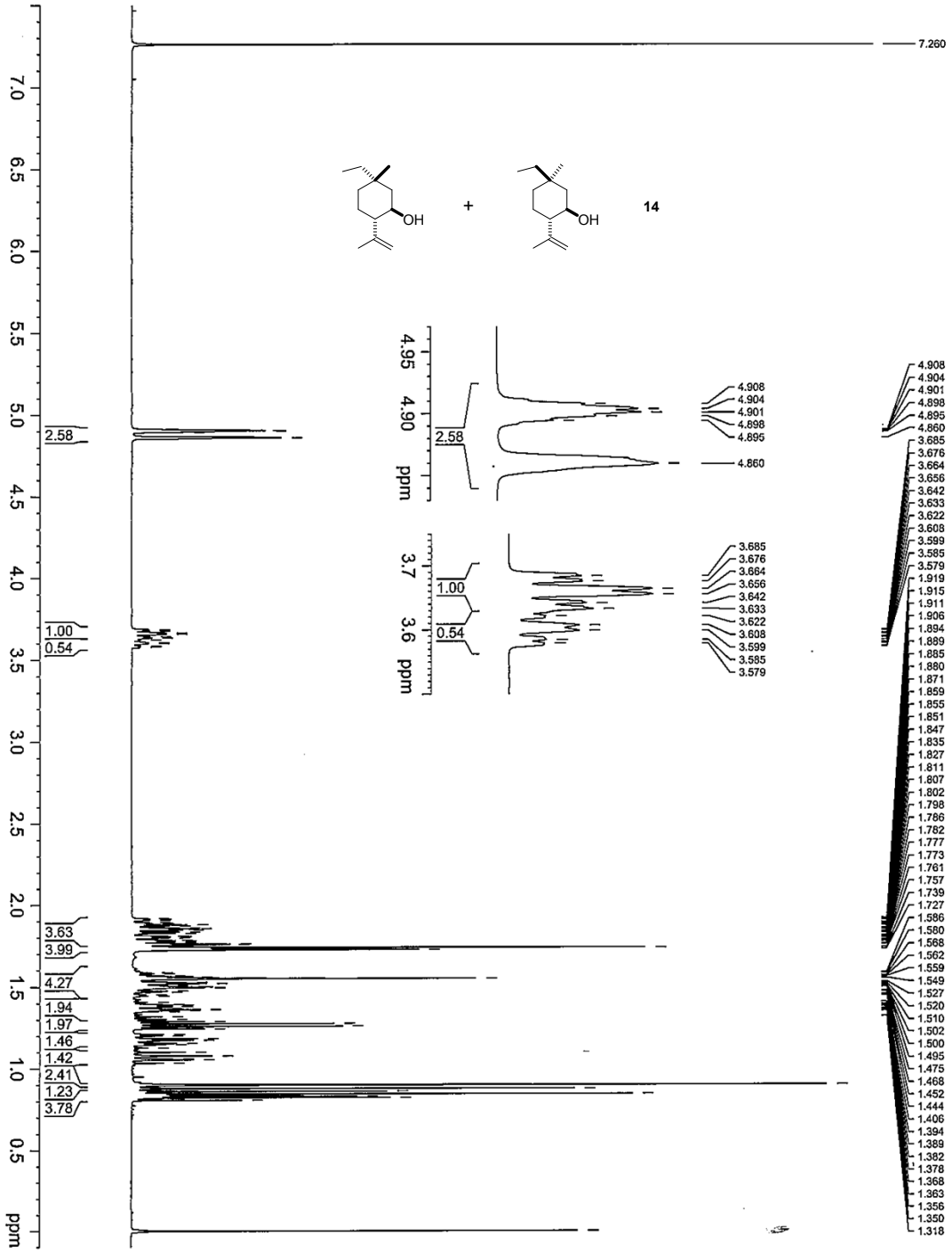
5,5-Dimethyl-2-((*E*)-6-methylhepta-2,5-dien-2-yl)cyclohexanol (12) (Table 2, entry 4)



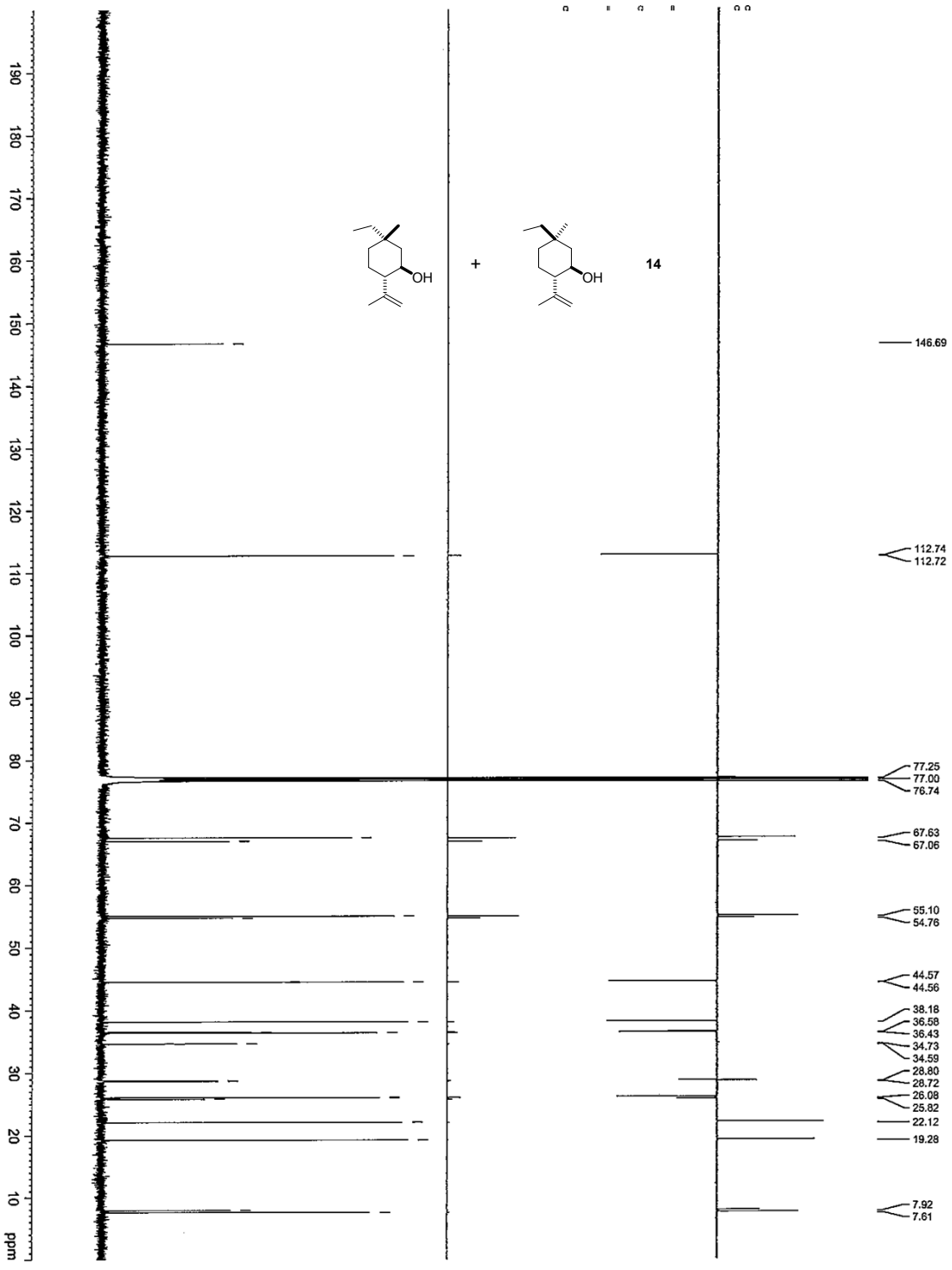
5,5-Dimethyl-2-((*E*)-6-methylhepta-2,5-dien-2-yl)cyclohexanol (12) (Table 2, entry 4)



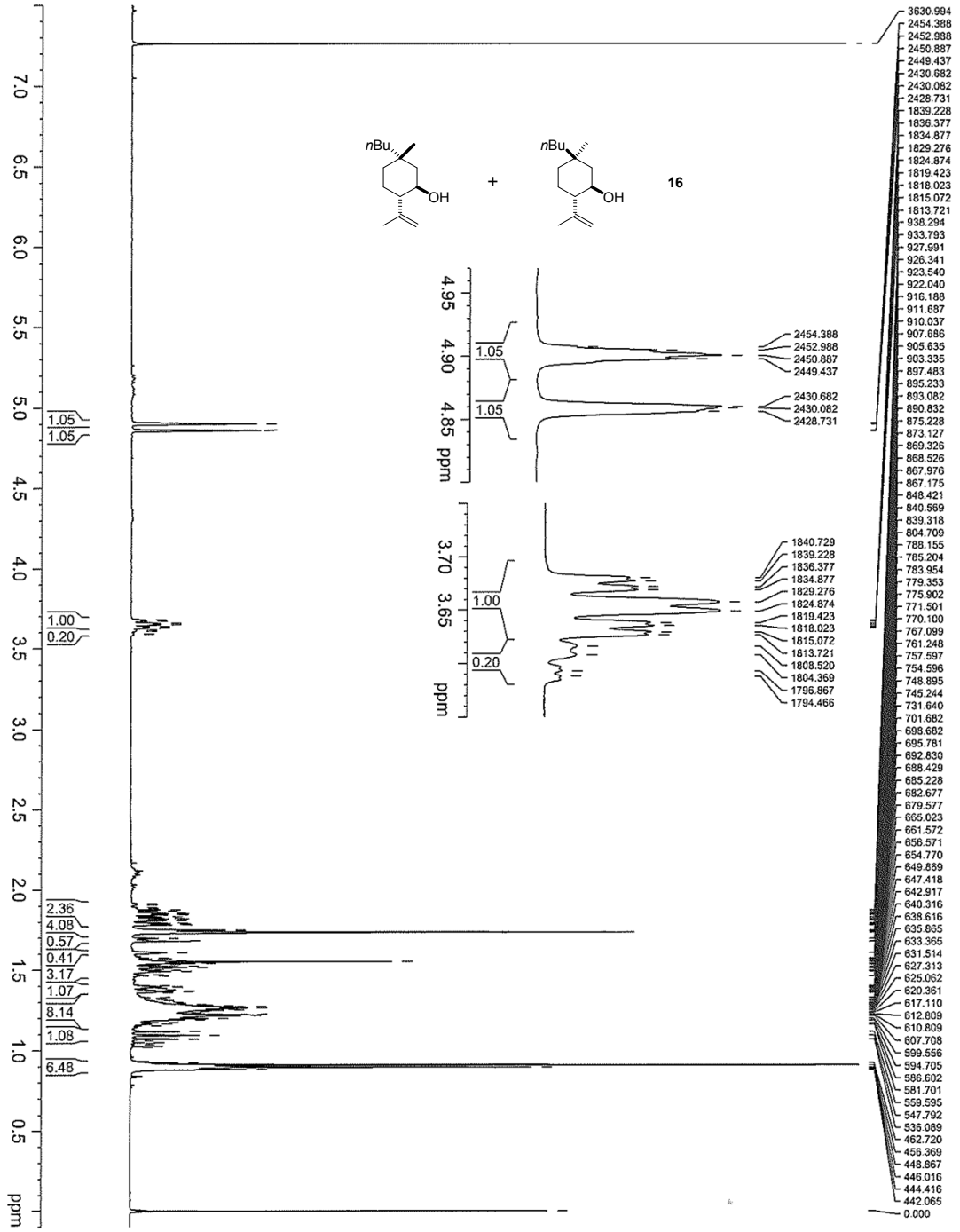
5-Ethyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol (5-ethylisopulegol) (14) (1α,2β,5β / 1α,2β,5α = 78 / 22) (Table 2, entry 5)



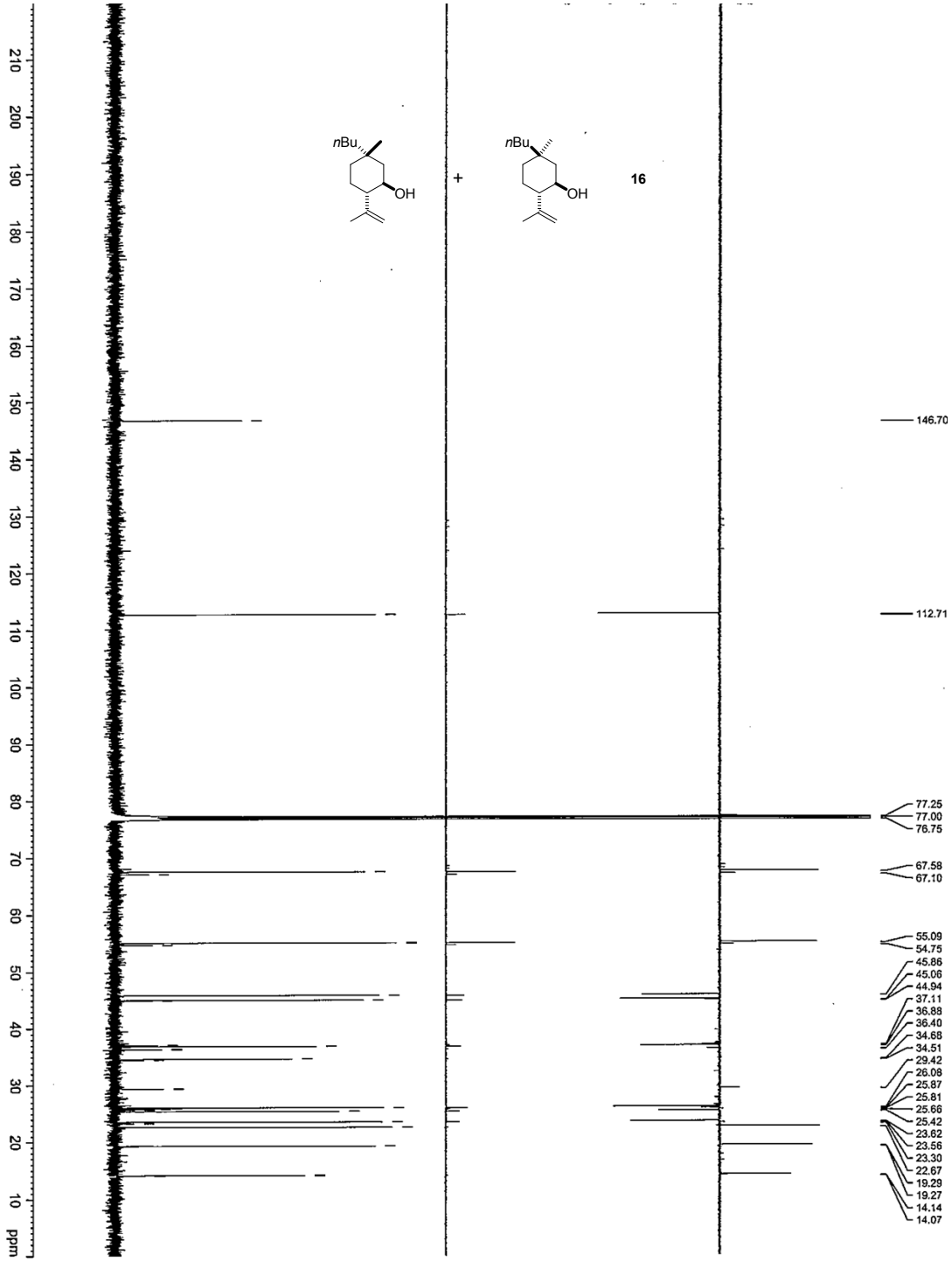
5-Ethyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol (5-ethylisopulegol) (14) (1α,2β,5β / 1α,2β,5α = 78 / 22) (Table 2, entry 5)



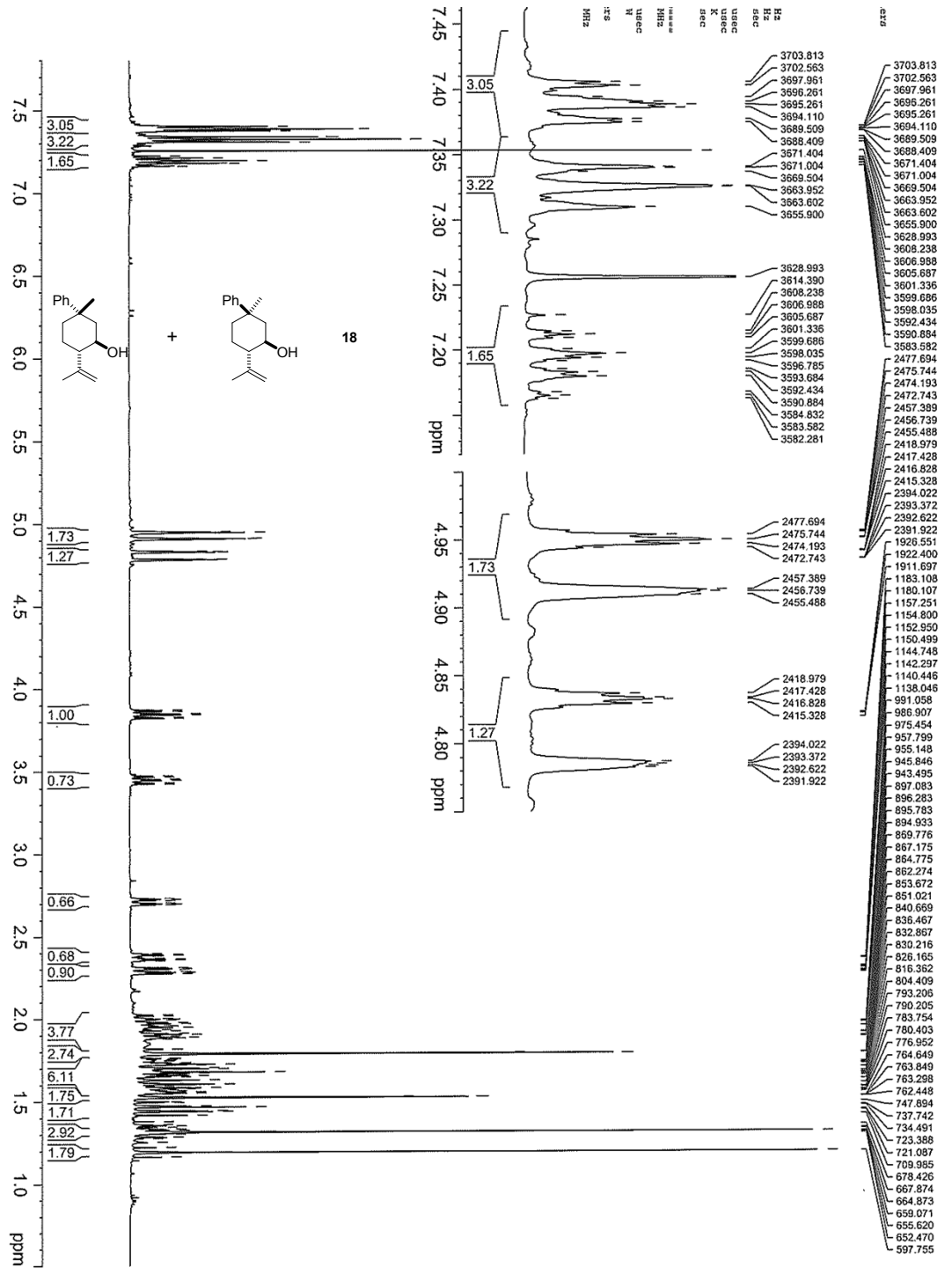
5-Butyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol (5-butylisopulegol) (16) (1α,2β,5β / 1α,2β,5α = 85 / 15) (Table 2, entry 6)



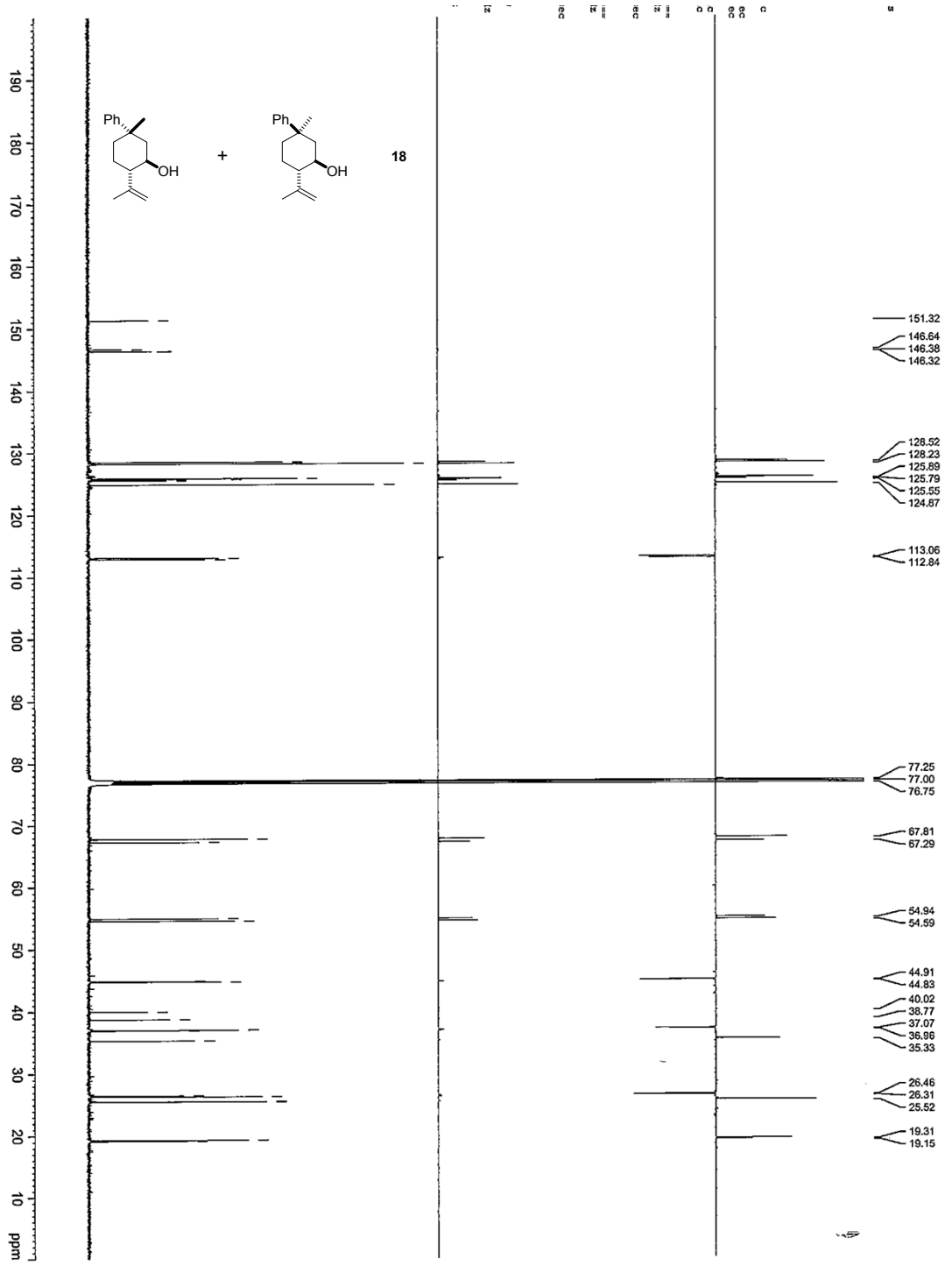
5-Butyl-5-methyl-2-(prop-1-en-2-yl)cyclohexanol (5-butylisopulegol) (16) (1α,2β,5β / 1α,2β,5α = 85 / 15) (Table 2, entry 6)



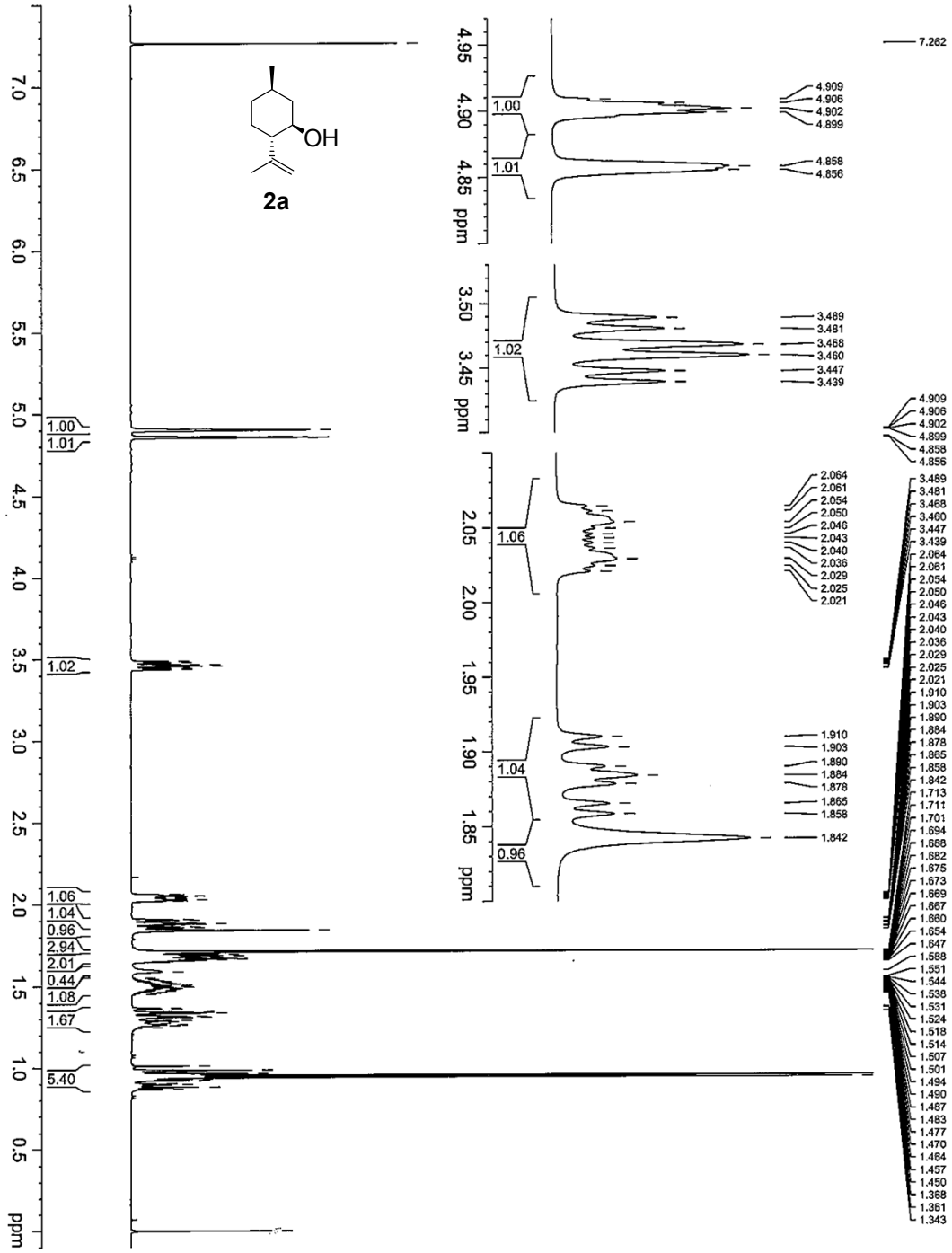
5-Methyl-5-phenyl-2-(prop-1-en-2-yl)cyclohexanol (5-phenylisopulegol) (18) (1α,2β,5β / 1α,2β,5α = 62 / 38) (Table 2, entry 7).



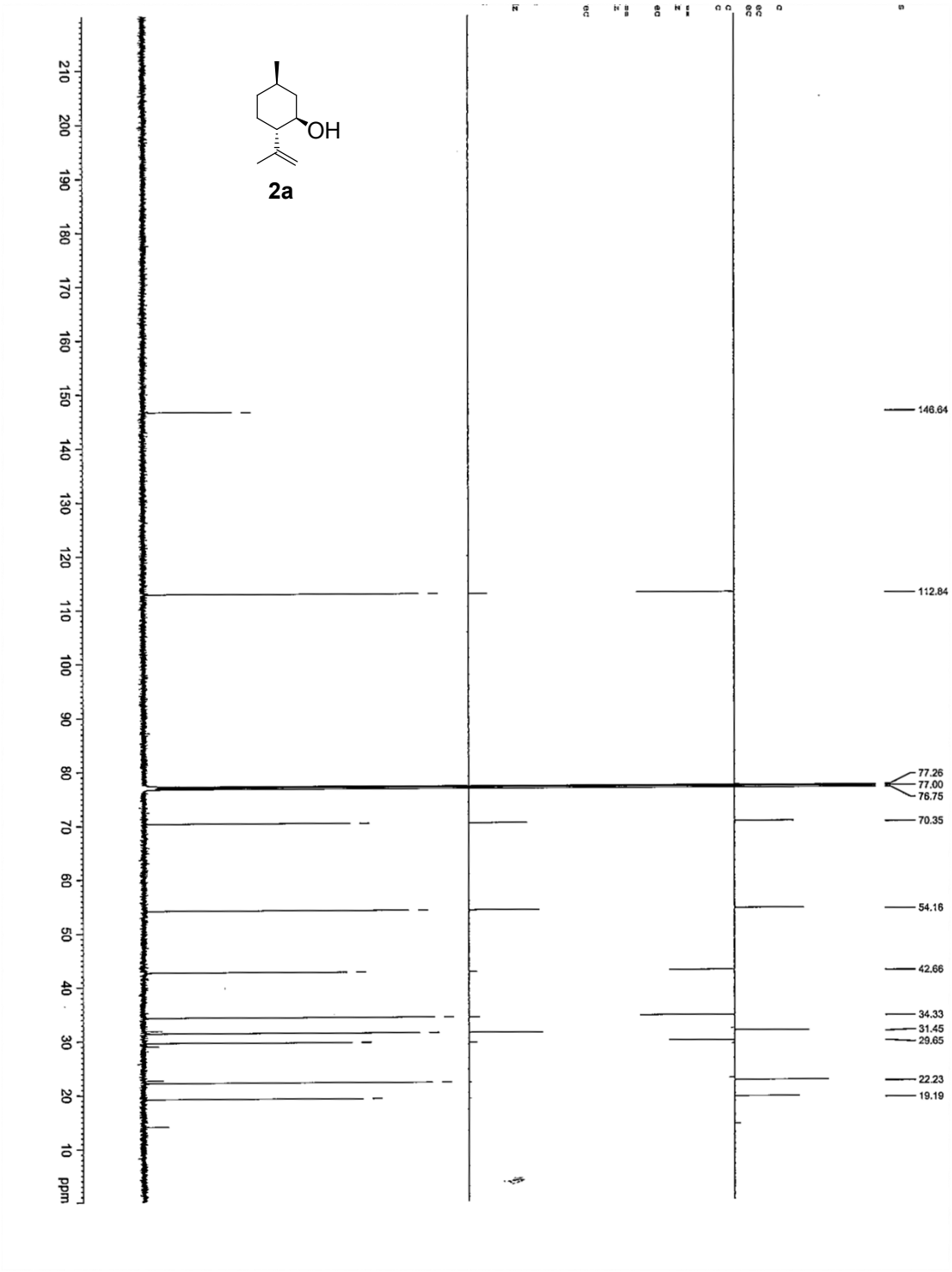
5-Methyl-5-phenyl-2-(prop-1-en-2-yl)cyclohexanol (5-phenylisopulegol) (18) (1α,2β,5β / 1α,2β,5α = 62 / 38) (Table 2, entry 7).



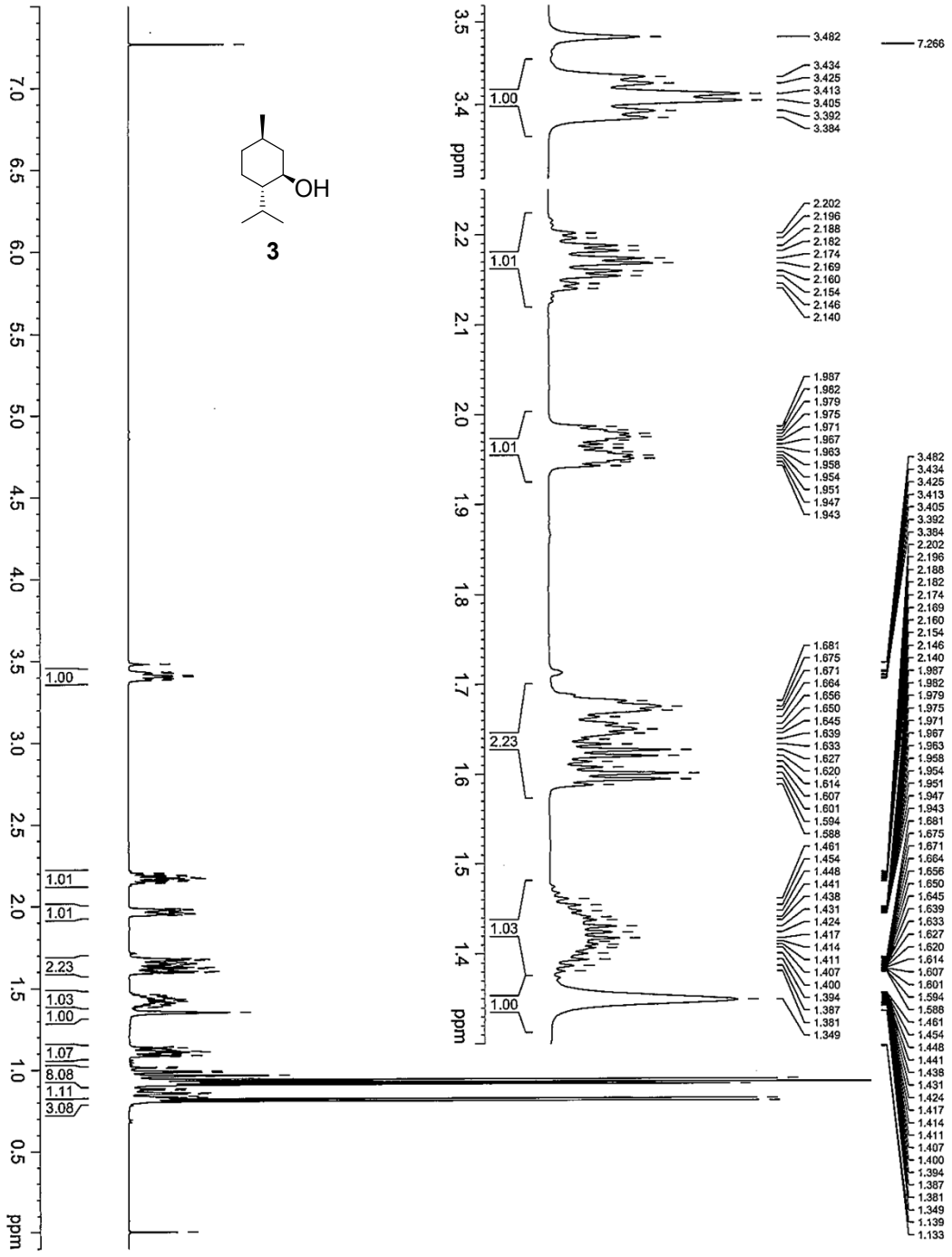
(5*R*)-*n*-Isopuelgol (2a) (Scheme 2)



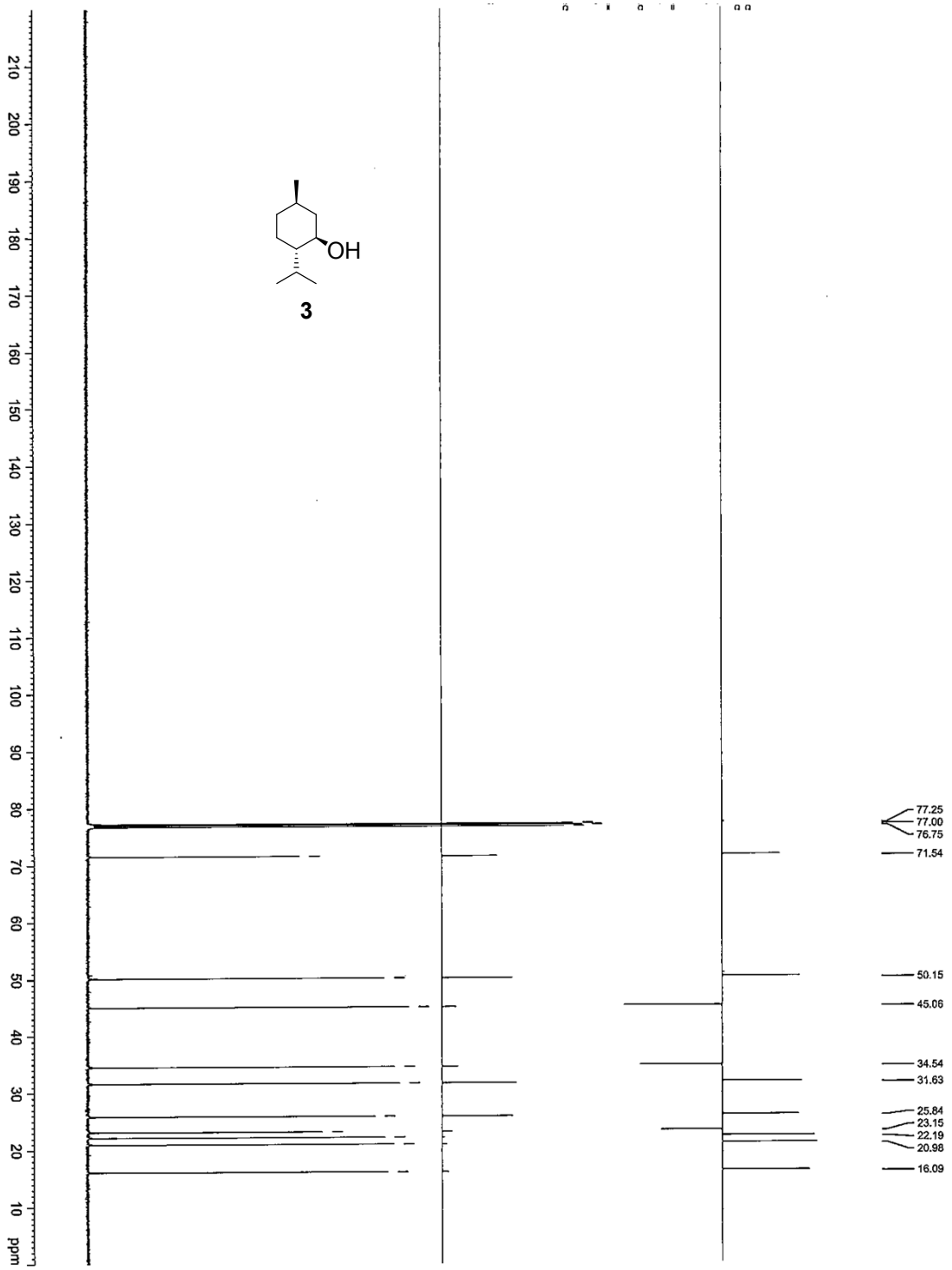
(5*R*)-*n*-Isopuelgol (2a) (Scheme 2)



***l*-Menthol (3) (Scheme 2)**



***l*-Menthol (3) (Scheme 2)**



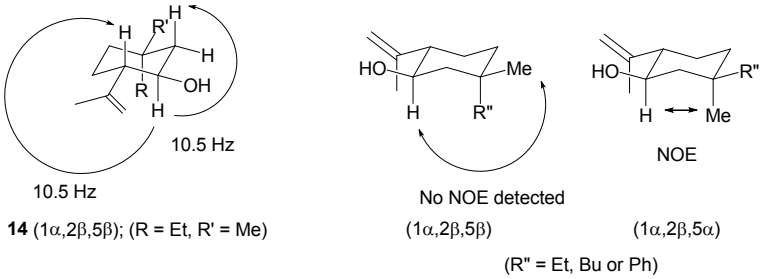


Figure S1. ^{1}H-NMR Analysis of **14**, **16**, and **18** [S3]

[S1] H. B. Glass, US2117414, **1936**.
[S2] a) S. Sakane, K. Maruoka, H. Yamamoto, *Tetrahedron Lett.*, **1985**, *46*, 5535-5538; b) S. Sakane, K. Maruoka, H. Yamamoto, *Tetrahedron*, **1986**, *42*, 2203-2209; c) K. Mikami, E. Sawa, M. Terada, *Tetrahedron Asymm.*,**1991**, *2*, 1403-1412.
[S3] S. Saito, K. Shimada, H. Yamamoto, *Synlett*, **1996**, 720.