Supporting Information

Palladium-Catalyzed 1,3-Diol Fragmentation: Synthesis of ω-Dienyl Aldehydes

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Experimental Section

Reactions employed oven-dried glassware unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator (Merck, Silica gel $60F_{254}$). Flash chromatography columns were packed with silica gel (Wakogel-C300) as a slurry in hexane. Gradient flash chromatography was conducted eluting with a continuous gradient from hexane to the indicated solvent. Proton and carbon NMR data were obtained with a JEOL-GX400 with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard. Infrared spectra were recorded with a JASCO A-100 FT-IR spectrophotometer. High resolution mass spectra (HRMS) were measured with a JEOL JMS-DX303. Combustion analyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within ± 0.4%.

Solvents and Reagents. Tetrahydrofuran and ether were distilled from a blue solution of sodium benzophenone ketyl under N_2 immediately prior to use. Toluene was distilled under

nitrogen from calcium hydride. $Pd(PPh_3)_4$ (Nakalai tesque, Inc.), *B*-methoxy-9-BBN (1.0 M solution in hexane, Aldrich), PhLi (1.0 M solution in cyclohexane-diethyl ether solution, Kanto Chemical, Co., Inc.) were purchased and used without further purification. 4-Penten-1,3-diols **1a** – **1o** were prepared according to the method reported previously from our laboratories.[1~4] One typical example is shown below.

Preparation of 4-Penten-1,3-diol (**1k**): A solution of β-pinene (2.4 mL, 15 mmol) in a mixture of methanol (8 mL) and dichloromethane (8 mL) was cooled to – 78 ºC in a nitrogen purged Schlenk flask. While the mixture was stirred at the same temperature, ozone was bubbled through the solution by means of a sinter-glass-ended tube for 3 h, until the blue color persisted. The reaction progress was monitored by TLC (hexane/AcOEt = 95:5, v/v). Nitrogen was then bubbled through the reaction mixture for 1 h, which was then allowed to warm to room temperature. Zinc powder (2.9 g, 45 mmol, 3 equiv.) and acetic acid (4.2 mL, 75 mmol, 5 equiv.) were then added carefully over 1 h period. The resulting suspension was filtered and the solid was washed with dichloromethane repeatedly. The organic layer was carefully washed with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was purified by distillation (100 ºC/20 mmHg) to give nopinone in 91% yield.[5]

A 200 mL of three-necked round-bottomed flask, equipped with a dropping funnel, a rubber septum, and an air condenser at the top of which is attached a three-way stopcock fitted a nitrogen balloon, is charged with freshly distilled THF (10 mL) and diisopropylamine (0.8 mL, 5.5 mmol) via syringe under nitrogen. Into the flask was added *n*-butyllithium (3.4 mL, 5.5 mmol; 1.6 M hexane solution) at - 78 ˚C, and the mixture was stirred for 1 h. To the reaction mixture was added nopinone (0.69 g, 5 mmol) dissolved in THF (10 mL) via a dropping funnel at - 78 ˚C, and the mixture was stirred at 0 ˚C for 1 h.

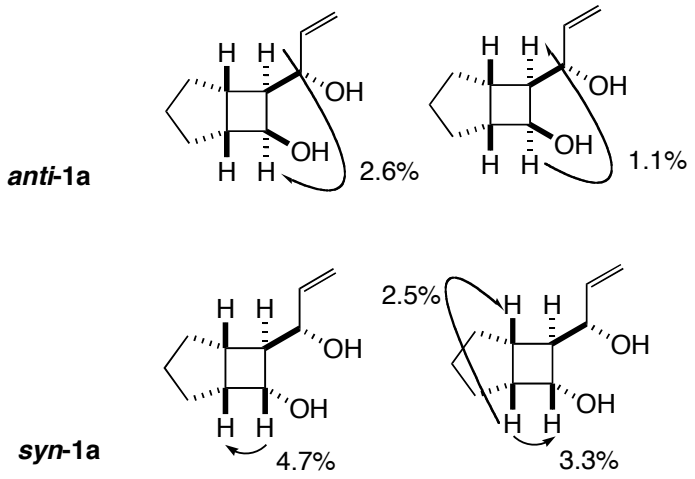
A solution of freshly distilled acrolein (0.4 mL, 6 mmol) in dry THF (10 mL) was quickly added at - 78 ˚C and stirred for 1 minute. The reaction mixture was quenched with 2M HCl at - 78 ˚C and extracted with ethyl acetate (2 x 30 mL). The organic extracts were washed with sat. $NaHCO_3$ and sat. NaCl, and dried ($MgSO_4$). The solvent was removed *in vacuo*, and the residue was subjected to column chromatography on silica gel (hexane/ethyl acetate = 8:1, v/v) to give the aldol product in 98% yield.

Into a suspension of lithium aluminum hydride (0.28 g, 7.4 mmol) in ether (20 mL) was added the aldol (0.95 g, 4.9 mmol) dissolved in dry ether (10 mL) at 0 ˚C. After stirring for 30 min at the same temperature, the excess lithium aluminum hydride was decomposed by adding aqueous THF (THF/water = 1:1, v/v) dropwise until gray slurry turned into white granules. After filtration with suction through a celite pad on a glass filter, the filtrate was washed with 15% aqueous NaOH and sat. NaCl. The organic phase was dried ($MgSO_4$) and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ethyl acetate = 8:1, v/v) to give diol **1k** (0.82 g) in 85% yield.

3-(1-Hydroxyallyl)-6,6-dimethylbicyclo[3.1.1]heptan-2-ol (**1k**): X-ray crystallography[6], mp 88.5 ºC (dichloromethane – hexane); IR (neat) 3287 (s), 3086 (s), 2924 (s), 1466 (s), 1335 (s), 1157 (s), 1126 (s), 1080 (s), 1018 (s), 934 (s), 795 (m), 687 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.70 (d, *J* = 10.0 Hz, 1 H), 1.11 (s, 3 H), 1.25 (s, 3 H), 1.37 (ddd, *J* = 2.2, 6.8, 13.4 Hz, 1 H), 1.95 (dd, *J* = 3.4, 5.9 Hz, 1 H), 2.01 (ddd, *J* = 2.4, 3.4, 13.4 Hz, 1 H), 2.05 (d, *J* = 3.4 Hz, 1 H), 2.11 (ddt, *J* = 2.2, 10.0, 3.4 Hz, 1 H), 2.23 (d, *J* = 2.7 Hz, 1 H), 2.30 (dddd, *J* = 2.4, 5.9, 6.8, 13.4 Hz, 1 H), 3.92 (dt, *J* = 2.9, 6.8 Hz, 1 H), 4.11 (dt, *J* = 6.8, 2.7 Hz, 1 H), 5.18 (dm, *J* = 10.3 Hz, 1 H), 5.30 (dm, *J* = 17.1 Hz, 1 H), 5.90 (ddd, *J* = 6.8, 10.3, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 27.7, 29.5, 30.3, 37.8, 41.5, 45.0, 48.0, 77.2, 80.2, 116.2, 139.7; HRMS calcd for $C_{12}H_{29}O_2$: 196.1463. Found *m*/*z* (relative

intensity) 196.1449 (M^+, 2), 195 (1), 179 (16), 178 (100), 139 (49).

7-(1-Hydroxyallyl)bicyclo[3.2.0]heptan-6-ol (**1a**): (a mixture of 3 isomers in a 1 : 6 : 7 ratio): Yields: Aldol, 100%; LAH reduction, 78%; IR (neat) 3400 (s), 2930 (w), 1650 (m), 1065 (w), 985 (w), 915 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ***anti*-1a**) δ 1.36-1.49 (m, 3 H), 1.53 (dt, *J* = 5.9, 12.0 Hz, 1 H), 1.66 (dd, *J* = 5.9, 12.0 Hz, 1 H), 1.77 (dt, *J* = 12.0, 5.9 Hz, 1 H), 1.86 (dt, *J* = 4.6, 7.6 Hz, 1 H), 2.42 (m, 1 H, coalescing to t, *J* = 7.6 Hz by irradiation at 1.86), 2.53 (dt, *J* = 2.9, 7.6 Hz, 1 H), 3.35 (br s, 1 H), 3.42 (br s, 1 H), 3.98 (dd, *J* = 2.9, 7.6 Hz, 1 H), 4.42 (dd, *J* = 6.8, 7.6 Hz, 1 H), 5.13 (dm, *J* = 10.5 Hz, 1 H), 5.25 (dm, *J* = 17.2 Hz, 1 H), 5.81 (ddd, *J* = 6.8, 10.5, 17.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***anti*-1a**) δ 25.7, 30.9, 31.4, 36.2, 46.1, 47.7, 72.2, 74.1, 115.5, 138.6; ^1H NMR (400 MHz, $CDCl_3$, ***syn*-1a**) δ 1.41-1.55 (m, 3 H), 1.65 (ddd, *J* = 5.6, 6.3, 8.5 Hz, 1 H), 1.72 (dt, *J* = 12.6, 6.6 Hz, 1 H), 1.82 (m, 1 H), 1.97 (dd, *J* = 7.1, 13.4 Hz, 1 H), 2.14 (dt, *J* = 7.3, 5.6 Hz, 1 H), 2.39 (m, 2 H), 2.79 (dt, *J* = 7.3, 8.3 Hz, 1 H), 4.05 (dd, *J* = 6.3, 8.5 Hz, 1 H), 4.17 (dd, *J* = 6.3, 8.3 Hz, 1 H), 5.12 (dm, *J* = 10.5 Hz, 1 H), 5.25 (dm, *J* = 17.1 Hz, 1 H), 5.81 (ddd, *J* = 6.3, 10.5, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***syn*-1a**) δ 24.4, 26.2, 32.2, 35.2, 41.4, 54.2, 67.4, 76.1, 115.1, 138.7. HRMS calcd for $C_{10}H_{16}O_2$: 168.1150. Found *m/z* (relative intensity) 168.1135 (M^+, 1), 167 (2), 151 (18), 150 (100).



NOE Increments (%) Observed for *anti*-**1a** and *syn*-**1a.**

7-(1-Hydroxy-2-methylallyl)bicyclo[3.2.0]heptan-6-ol (**1b**): (a mixture of 2 isomers in a

1 : 1 ratio): Yields: Aldol, 30%; LAH reduction, 63%; IR (neat) 3356 (s), 3078 (m), 2939 (s), 2855 (s), 1651 (m), 1443 (m), 1327 (m), 1072 (m), 964 (w), 903 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ***anti*-1b**) δ 1.38-1.48 (m, 3 H), 1.57 (m, 1 H), 1.68 (dd, *J* = 5.4, 12.2 Hz, 1 H), 1.73 (s, 3 H), 1.79 (m, 1 H), 2.01 (dddd, *J* = 1.2, 4.6, 7.3, 9.7 Hz, 1 H), 2.35 (br dq, *J* = 7.8, 4.6 Hz, 1 H), 2.43 (d, *J* = 3.5 Hz, 1 H), 2.53 (dt, *J* = 3.2, 7.8 Hz, 1 H), 2.55 (d, *J* = 3.2 Hz, 1 H), 4.02 (dt, *J* = 7.3, 3.2 Hz, 1 H), 4.43 (dd, *J* = 3.5, 9.7 Hz, 1 H), 4.90 (s, 1 H), 4.97 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***anti*-1b**) δ 17.7, 25.7, 30.8, 31.5, 36.4, 45.4, 45.9, 72.3, 76.8, 112.9, 144.9; ^1H NMR (400 MHz, $CDCl_3$, ***syn*-1b**) δ 1.38-1.52 (m, 3 H), 1.68-1.84 (m, 2 H), 1.72 (s, 3 H), 1.76 (ddd, *J* = 5.9, 6.6, 9.3 Hz, 1 H), 1.95 (br s, 1 H), 1.97 (dd, *J* = 7.1, 13.7 Hz, 1 H), 2.06 (m, 1 H), 2.11 (br q, *J* = 6.6 Hz, 1 H), 2.79 (dt, *J* = 6.6, 7.8 Hz, 1 H), 4.01 (d, *J* = 9.3 Hz, 1 H), 4.19 (dt, *J* = 7.8, 5.9 Hz, 1 H), 4.84 (s, 1 H), 4.95 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***syn*-1b**) δ 17.7, 24.4, 26.2, 32.1, 35.6, 41.4, 52.3, 67.8, 79.3, 111.8, 145.7; HRMS calcd for $C_{11}H_{18}O_2$: 182.1307. Found *m/z* (relative intensity) 182.1331 (M^+, 1), 165 (16), 164 (100).

7-[(2*E*)-1-Hydroxy-2-butenyl]bicyclo[3.2.0]heptan-6-ol (**1c**): (a mixture of 4 isomers in a 1 : 5 : 6 : 6 ratio): Yields: Aldol, 63%; LAH reduction, 93%; IR (neat) 3418 (s), 3024 (w), 2947 (s), 2862 (m), 1651 (s), 1443 (m), 1319 (m), 1250 (m), 1072 (s), 972 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, ***anti*-1c**) δ 1.33-1.49 (m, 3 H), 1.54 (dq, *J* = 17.6, 6.0 Hz, 1 H), 1.66 (dd, *J* = 6.0, 12.2 Hz, 1 H), 1.71 (dd, *J* = 1.0, 6.6 Hz, 3 H), 1.77 (dt, *J* = 12.2, 6.0 Hz, 1 H), 1.85 (dddd, *J* = 1.0, 4.6, 7.6, 8.5 Hz, 1 H), 2.38 (dt, *J* = 4.6, 7.3 Hz, 1 H), 2.48 (dt, *J* = 3.2, 7.3 Hz, 1 H), 2.68 (m, 1 H), 3.98 (dd, *J* = 3.2, 7.3 Hz, 1 H), 4.38 (dd, *J* = 7.3, 8.5 Hz, 1 H), 5.46 (dd, *J* = 7.3, 15.4 Hz, 1 H), 5.72 (ddq, *J* = 1.0, 15.4, 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***anti*-1c**) δ 17.8, 25.7, 30.9, 31.4, 36.2, 46.2, 47.8, 72.4, 74.1, 127.9, 131.7; ^1H NMR (400 MHz, $CDCl_3$, ***syn*-1c**) δ 1.38-1.58 (m, 3 H), 1.63 (dt, *J* = 8.5, 6.6 Hz, 1 H), 1.70 (dd, *J* = 1.6, 6.6 Hz, 1 H), 1.71 (m, 1 H), 1.81 (m, 1 H), 1.95 (m, 2 H), 1.96 (dd, *J* = 7.3, 13.4 Hz, 1H), 2.10 (q, *J* = 6.6 Hz, 1 H), 2.77 (dt, *J* = 6.6, 7.8 Hz, 1 H), 3.99 (dd, *J* = 7.6, 8.5 Hz, 1 H), 4.15 (dd, *J*

= 6.6, 7.8 Hz, 1 H), 5.43 (ddq, *J* = 7.6, 15.4, 1.6 Hz, 1 H), 5.69 (dq, *J* = 15.4, 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ***syn*-1c**) δ 17.7, 24.4, 26.2, 32.2, 35.2, 41.3, 54.4, 67.5, 75.9, 127.4, 131.7; ^{1}H NMR (400 MHz, $CDCl_3$, other stereoisomer **1c**) δ 1.36-1.63 (m, 4 H), 1.67 (dd, *J* = 5.1, 12.2 Hz, 1 H), 1.71 (d, *J* = 6.6 Hz, 3 H), 1.77 (dq, *J* = 12.2, 6.1 Hz, 1 H), 1.95 (ddd, *J* = 3.3, 5.2, 7.8 Hz, 1 H), 2.44 (br s, 1 H), 2.48 (dt, *J* = 3.7, 7.8 Hz, 1 H), 2.81 (*J* = 7.8, 5.1 Hz, 1 H), 3.19 (br d, *J* = 7.8 Hz, 1 H), 3.91 (m, 1 H), 4.50 (m, 1 H), 5.53 (dd, *J* = 6.6, 15.4 Hz, 1 H), 5.70 (dq, *J* = 15.4, 6.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, other stereoisomer **1c**) δ 17.8, 25.7, 31.2, 31.8, 33.5, 47.9, 49.2, 71.5, 73.5, 126.8, 131.2; HRMS calcd for $C_{11}H_{18}O_2$: 182.1307. Found *m/z* (relative intensity) 182.1330 (M^+, 1), 165 (13), 164 (100).

3-(1-Hydroxyallyl)bicyclo[2.2.1]heptan-2-ol (**1d**): (a mixture of 3 isomers in a 1 : 6 : 19 ratio): Yields: Aldol, 86%; LAH reduction, 88%; IR (neat) 3371 (s), 2955 (s), 2878 (s), 1427 (m), 1304 (m), 1126 (m), 1042 (s), 995 (s), 926 (s), 764 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.09 (br dt, *J* = 9.8, 2.0 Hz, 1 H), 1.19 (dq, *J* = 10.3, 2.0 Hz, 1 H), 1.32 (m, 1 H), 1.40 (ddt, *J* = 1.5, 11.5, 4.0 Hz, 1 H), 1.47 (br d, *J* = 10.3 Hz, 1 H), 1.59 (dt, *J* = 11.5, 4.6 Hz, 1 H), 1.73 (br s, 1 H), 1.87 (m, 1 H), 1.98 (br s, 2 H), 2.31 (br s, 1 H), 3.80 (br t, *J* = 7.3 Hz, 1 H), 4.10 (br s, 1 H), 5.14 (ddd, *J* = 1.0, 1.5, 10.3 Hz, 1 H), 5.21 (dt, *J* = 17.3, 1.5 Hz, 1 H), 5.86 (ddd, *J* = 7.3, 10.3, 17.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 19.6, 30.6, 35.1, 39.5, 42.5, 57.0, 76.6, 77.0, 115.7, 140.3; HRMS calcd for $C_{10}H_{16}O_2$: 168.1150. Found *m/z* (relative intensity) 168.1145 (M^+, 5), 167 (1), 151 (12), 150 (100).

3-(1-Hydroxyallyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**1e**):[6] a mixture of 2 isomers in a 1 : 3 ratio: Yields: Aldol, 96%; LAH reduction, 83%; major isomer: mp 91.0 – 92.0 ºC (dichloromethane – hexane); IR (KBr) 3352 (s), 3084 (w), 3040 (w), 2937 (s), 1435 (s), 1367 (s), 1288 (s), 1271 (s), 1119 (s), 1051 (s), 926 (s), 793 (w), 712 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.80 (s, 3 H), 0.95 (s, 3 H), 0.99 (ddd, *J* = 4.0, 9.1, 11.7 Hz, 1 H), 1.06 (ddd, *J* = 4.0, 9.1, 11.7 Hz, 1 H), 1.19 (s, 3 H), 1.48 (dt, *J* = 11.7, 4.0 Hz, 1 H), 1.57 (d, *J* = 4.0 Hz, 1 H), 1.70 (tt, *J* = 4.0, 11.7 Hz, 1 H), 1.79 (dd, *J* = 7.8, 11.0 Hz, 1 H), 2.58

(d, *J* = 2.0 Hz, 1 H), 2.83 (br s, 1 H), 3.90 (dd, *J* = 2.0, 7.8 Hz, 1 H), 4.54 (dd, *J* = 7.1, 11.0 Hz, 1 H), 5.17 (dm, *J* = 10.3 Hz, 1 H), 5.24 (dm, *J* = 17.3 Hz, 1 H), 5.86 (ddd, *J* = 7.1, 10.3, 17.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 11.4, 21.6, 22.0, 29.7, 33.4, 47.0, 47.5, 49.6, 56.2, 74.3, 82.1, 116.1, 140.2; HRMS calcd for $C_{13}H_{22}O_2$: 210.1620. Found *m*/*z* (relative intensity) 210.1595 (M^+, 27), 209 (3), 208 (10), 193 (19), 192 (100).

3-(1-Hydroxy-2-methylallyl)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**1f**): a mixture of 2 isomers in a 1 : 4 ratio: Yields: Aldol, 100%; LAH reduction, 93%; IR (neat) 3326 (s), 2951 (s), 2885 (s), 1452 (m), 1371 (m), 1288 (m), 1103 (s), 1053 (s), 1016 (s), 959 (s), 905 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.78 (s, 3 H), 0.96 (s, 3 H), 1.00 (ddd, *J* = 3.3, 9.3, 12.7 Hz, 1 H), 1.08 (ddd, *J* = 4.6, 9.3, 12.7 Hz, 1 H), 1.18 (s, 3 H), 1.45 (d, *J* = 4.6 Hz, 1 H), 1.48 (dt, *J* = 3.3, 12.7 Hz, 1 H), 1.69 (dtt, *J* = 1.0, 12.7, 4.6 Hz, 1 H), 1.75 (dd, *J* = 1.0, 1.5 Hz, 1 H), 1.93 (dd, *J* = 7.8, 11.2 Hz, 1 H), 2.50 (d, *J* = 2.2 Hz, 1 H), 2.49 (d, *J* = 2.2 Hz, 1 H), 3.90 (dd, *J* = 2.2, 7.8 Hz, 1 H), 4.59 (dd, *J* = 2.2, 11.2 Hz, 1 H), 4.91 (q, *J* = 1.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 11.4, 16.8, 21.6, 22.0, 29.9, 33.6, 47.0, 47.6, 49.6, 53.5, 81.9, 113.9, 146.0; HRMS calcd for $C_{14}H_{24}O_2$: 224.1776. Found *m*/*z* (relative intensity) 225 (M^++1, 1), 224.1787 (M^+, 6), 207 (16), 206 (100).

3-[(2*E*)-1-hydroxy-3-phenylallyl]-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (**1g**): a mixture of 3 isomers in a 1 : 5 : 8 ratio: Yields: Aldol, 100%; LAH reduction, 95%; IR (neat) 3402 (s), 2955 (s), 1651 (w), 1450 (m), 1103 (m), 1042 (m), 964 (m), 748 (s), 694 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.80 (s, 3 H), 0.96 (s, 3 H), 1.01 (ddd, *J* = 3.4, 9.0, 11.7 Hz, 1 H), 1.08 (ddd, *J* = 4.2, 9.0, 11.7 Hz, 1 H), 1.25 (s, 3 H), 1.52 (dt, *J* = 3.4, 11.7 Hz, 1 H), 1.60 (d, *J* = 4.2 Hz, 1 H), 1.69 (tt, *J* = 4.2, 11.7 Hz, 1 H), 1.90 (dd, *J* = 7.8, 11.7 Hz, 1 H), 2.59 (d, *J* = 2.2 Hz, 1 H), 2.90 (s, 1 H), 3.93 (dd, *J* = 2.2, 7.8 Hz, 1H), 4.73 (ddd, *J* = 1.7, 7.8, 11.7 Hz, 1 H), 6.21 (dd, *J* = 7.8, 15.6 Hz, 1 H), 6.58 (d, *J* = 15.6 Hz, 1 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 7.38 (d, *J* = 7.4 Hz, 1 H), 7.41 (d, *J* = 7.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 11.4, 21.7, 22.0, 29.8, 33.4, 47.0, 47.6, 49.6, 56.6,

74.0, 82.1, 126.4, 127.6, 128.4, 131.4, 131.5, 136.6; HRMS calcd for $C_{19}H_{26}O_2$: 286.1933. Found *m/z* (relative intensity) 287 (M^++1, 26), 286.1921 (M^+, 100), 285 (7), 269 (71).

3-(1-Hydroxyallyl)-1,2,7,7-tetramethylbicyclo[2.2.1]heptan-2-ol (**1h**): a mixture of 2 isomers in a 1 : 7 ratio: Yields: Aldol, 96%; MeLi, 22%; IR (neat) 3333 (s), 2955 (s), 1736 (s), 1450 (s), 1381 (s), 1119 (s), 1042 (s), 995 (s), 918 (s), 826 (w), 694 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.82 (s, 3 H), 0.88 (s, 3 H), 1.01 (ddd, *J* = 4.5, 9.0, 12.2 Hz, 1 H), 1.26 (s, 3 H), 1.35 (s, 3 H), 1.37 (dd, *J* = 4.5, 13.4 Hz, 1 H), 1.47 (ddd, *J* = 4.5, 9.0, 13.4 Hz, 1 H), 1.47 (d, *J* = 10.7 Hz, 1 H), 1.55 (d, *J* = 4.5 Hz, 1 H), 1.74 (tt, *J* = 4.5, 12.2 Hz, 1 H), 2.23 (s, 1 H), 2.55 (br s, 1 H), 4.54 (dd, *J* = 7.1, 10.7 Hz, 1 H), 5.15 (dm, *J* = 10.3 Hz, 1 H), 5.22 (dm, *J* = 17.3 Hz, 1 H), 5.85 (ddd, *J* = 7.1, 10.3, 17.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 9.7, 22.7, 22.8, 29.2, 29.7, 31.2, 47.5, 49.4, 52.7, 62.7, 75.2, 82.6, 115.9, 140.3; HRMS calcd for $C_{14}H_{24}O_2$: 224.1776. Found *m/z* (relative intensity) 225 (M^++1, 15), 224.1763 (M^+, 100), 209 (11), 206 (87).

2,3-Dihydro-2-[(2*E*)-1-hydroxy-2-butenyl]-1*H*-inden-1-ol (**1i**): a mixture of 3 isomers in a 1.8 : 1.5 : 1 ratio: Yields: Aldol, 93%; LAH reduction, 90%; IR (neat) 3379 (s), 3032 (m), 2916 (s), 2855 (m), 1443 (s), 1312 (m), 1211 (m), 1173 (w), 1057 (s), 972 (s), 748 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.73 (dd, *J* = 1.5, 6.3 Hz, 1 H), 2.45 (m, 1 H), 2.48 (dd, *J* = 9.5, 15.6 Hz, 1 H), 2.88 (dd, *J* = 8.3, 15.6 Hz, 1 H), 4.21 (t, *J* = 7.6 Hz, 1 H), 5.18 (d, *J* = 7.8 Hz, 1 H), 5.56 (ddq, *J* = 7.6, 15.1, 1.5 Hz, 1 H), 5.75 (dq, *J* = 15.1, 6.3 Hz, 1 H), 7.14-7.27 (m, 3 H), 7.36 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 3 isomers) δ 17.7, 32.8, 56.0, 77.4, 79.9, 123.6, 124.4, 126.6, 127.8, 128.7, 132.7, 140.5, 144.1; HRMS calcd for $C_{13}H_{16}O_2$: 204.1150. Found *m/z* (relative intensity) 205 (M^++1, 1), 204.1154 (M^+, 7), 187 (14), 186 (100).

2-(1-Hydroxyallyl)-4-phenylcyclohexanol (**1j**): a mixture of 4-isomers, the ratio was not determined: Yields: Aldol, 70%; LAH reduction, 100%; IR (KBr) 3275 (s), 2930 (s), 1498 (m), 1450 (s), 1349 (m), 1150 (m), 1085 (s), 1020 (s), 925 (s), 765 (s), 700 (s) cm^{-1}; ^1H NMR

(400 MHz, $CDCl_3$, major isomer) δ 1.11 (dt, *J* = 13.4, 12.2 Hz, 1 H), 1.53 (m, 2 H), 1.64 (ddt, *J* = 3.4, 5.9, 9.3 Hz, 1 H), 1.82 (dq, *J* = 13.4, 3.4 Hz, 1 H), 1.90 (m, 1 H), 2.11 (m, 1 H), 2.56 (tt, *J* = 3.4, 12.2 Hz, 1 H), 3.04 (m, 1 H), 3.72 (dt, *J* = 4.6, 9.3 Hz, 1 H), 3.76 (m, 1 H), 4.12 (dd, *J* = 5.9, 6.3 Hz, 1 H), 5.14 (dm, *J* = 10.3 Hz, 1 H), 5.21 (dm, *J* = 17.1 Hz, 1 H), 5.84 (ddd, *J* = 6.3, 10.3, 17.1 Hz, 1 H), 7.17 (d, *J* = 6.8 Hz, 2 H), 7.27 (d, *J* = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ 31.9, 35.2, 35.4, 43.2, 48.5, 75.2, 79.7, 117.1, 126.1, 126.6, 128.3, 139.0, 146.1; HRMS calcd for $C_{15}H_{20}O_2$: 232.1463. Found *m/z* (relative intensity) 233 (M^++1, 2), 232.1454 (M^+, 12), 215 (18), 214 (100).

2-(1-Hydroxyallyl)cycloheptanol (**1l**): a mixture of 4 isomers, the ratio being not determined: Yields: Aldol, 80%; LAH reduction, 92%; IR (neat) 3356 (s), 2924 (s), 2862 (s), 1450 (s), 1296 (m), 1134 (m), 1057 (m), 995 (s), 926 (s), 725 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.08-1.88 (m, 11 H), 2.60 (m, 1 H), 2.92 (m, 1 H), 4.25 (m, 1 H), 4.43 (m, 1 H), 5.17 (dt, *J* = 10.7, 1.5 Hz, 1 H), 5.27 (dt, *J* = 17.1, 1.7 Hz, 1 H), 5.89 (ddd, *J* = 4.6, 10.7, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 19.2, 21.6, 21.9, 22.7, 25.4, 26.0, 26.4, 27.2, 27.3, 27.7, 28.0, 28.3, 28.4, 28.8, 29.7, 35.7, 36.3, 36.8, 37.1, 48.0, 48.1, 50.8, 51,6, 70.4, 73.3, 74.8, 75.8, 78.9, 114.1, 115.2, 115.7, 117.2, 137.8, 139.7, 140.0, 140.3; HRMS calcd for $C_{10}H_{18}O_2$: 170.1307. Found *m/z* (relative intensity) 171 (M^++1, 56), 170.1335 (M^+, 22), 169 (100).

2-(1-Hydroxyallyl)cyclooctanol (**1m**): a mixture of 4 isomers, the ratio being not determined: Yields: Aldol, 100%; LAH reduction, 93%; IR (neat) 3248 (s), 2932 (s), 1643 (s), 1450 (m), 1304 (m), 1126 (m), 988 (m), 926 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.14-2.00 (m, 13 H), 2.70 (m, 1 H), 3.07 (m, 1 H), 4.16 (m, 1 H), 4.45 (m, 1 H), 5.19 (dt, *J* = 10.6, 1.7 Hz, 1H), 5.34 (dt, *J* = 17.1, 1.7 Hz, 1 H), 5.87 (ddd, *J* = 4.6, 10.6, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 18.5, 21.1, 21.7, 22.0, 23.8, 24.4, 24.7, 25.0, 25.1, 25.4, 25.8, 26.2, 26.6, 27.1, 27.3, 27.4, 27.5, 27.6, 28.4, 28.6, 32.6, 32.8, 33.0, 33.4, 44.3, 44.4, 46.6, 47.8, 70.6, 73.2, 75.9, 77.7, 77.8, 79.3, 114.4, 115.2, 115.6, 117.0,

137.8, 139.6, 139.8, 140.2; HRMS calcd for $C_{11}H_{20}O_2$: 184.1463. Found *m/z* (relative intensity) 185 (M^++1, 1), 184.1463 (M^+, 1), 183 (2), 167 (13), 166 (100).

2-(1-Hydroxyallyl)cyclodecanol (**1n**): a mixture of 4 isomers, the ratio being not determined: Yields: Aldol, 94%; LAH reduction, 96%; IR (neat) 3379 (s), 2932 (s), 1643 (m), 1443 (m), 1242 (w), 1111 (w), 1042 (w), 995 (m), 918 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.23-2.18 (m, 17 H), 2.92 (m, 1 H), 3.28 (m, 1 H), 4.26 (m, 1 H), 4.46 (m, 1 H), 5.11 (dt, *J* = 10.6, 1.7 Hz, 1 H), 5.33 (dt, *J* = 17.1, 1.6 Hz, 1 H), 5.91 (ddd, *J* = 5.3, 10.6, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 17.3, 20.8, 21.5, 21.9, 22.1, 22.4, 24.0, 24.2, 24.3, 24.7, 25.0, 25.1, 25.3, 25.4, 25.5, 25.6, 25.7, 26.0, 26.1, 26.8, 31.7, 32.3, 33.1, 42.6, 43.0, 45.1, 46.3, 71.9, 73.1, 75.1, 75.4, 75.7, 78.0, 79.4, 113.8, 114.9, 115.7, 116.2, 138.1, 139.9, 140.0, 140.5; HRMS calcd for $C_{13}H_{24}O_2$: 212.1776. Found *m/z* (relative intensity) 213 (M^++1, 1), 212.1754 (M^+, 3), 211 (2), 195 (15), 194 (100).

Preparation of *B*-Ph-9-BBN.[7] Into a nitrogen purged Schlenk flask, were introduced dry pentane (5 mL) and *B*-methoxy-9-BBN (5 mL, 1.0 M hexanes solution, 5 mmol) via syringe. The mixture was cooled at – 78 ºC. PhLi (5 mL, 1.0 M cyclohexane-diethyl ether solution, 5 mmol) was added slowly via syringe. A white precipitate formed immediately. The mixture was stirred at – 78 ºC for 15 minutes and then allowed to warm to room temperature and was stirred for 12 h. The supernatant solution was used as 0.3 M *B*-Ph-9-BBN.

General Procedure for the Palladium Catalyzed C-C Bond Cleavage Reaction of 1,3-Diol 1 (Table 2, Run 11). Into a flask containing $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) purged with N_2 were successively added dry toluene (2.5 mL), **1k** (98.1 mg, 0.5 mmol), and *B*-Ph-9-BBN (0.8 mL, 0.3 M solution , 0.25 mmol) via syringe at room temperature. The homogeneous solution was stirred at 50 ºC for 24 h under N_2. After dilution with ethyl acetate, the mixture was washed with brine, dried ($MgSO_4$), and concentrated *in vacuo*. The

residue was purification by column chromatography over silica gel (hexane/ethyl acetate = 64:1, v/v) to give **2k** in 92% yield (80.2 mg). R_f(**2k**) = 0.83 (hexane/ethyl acetate = 2:1, v/v). The structures of **2e**, **2f**, **2i**, **2j**, **2m**, and **2n** were determined by comparison of the spectral data with those of authentic samples reported.[1]

2,2-Dimethyl-3-(2,4-pentadienyl)cyclobutanecarbaldehyde (**2k**): a mixture of *E*- and *Z*-isomers in a ratio of 1 : 1: IR (neat) 3086 (w), 3007 (m), 2955 (s), 2712 (m), 1715 (s), 1651 (m), 1603 (w), 1464 (s), 1369 (s), 1157 (m), 1005 (s), 901 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*)-2k**) δ 1.03 (s, 3 H), 1.28 (s, 3 H), 1.97 (dt, *J* = 2.0, 8.3 Hz, 2 H), 2.01-2.10 (m, 2 H), 2.14 (m, 1 H), 2.75 (dt, *J* = 2.0, 8.8 Hz, 1 H), 4.96 (dm, *J* = 10.5 Hz, 1 H), 5.09 (dm, *J* = 16.8 Hz, 1 H), 5.57 (dt, *J* = 15.1, 7.8 Hz, 1 H), 6.05 (ddm, *J* = 10.5, 15.1 Hz, 1 H), 6.28 (dt, *J* = 16.8, 10.5 Hz, 1 H), 9.71 (dd, *J* = 1.2, 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-2k**) δ 18.0, 22.4, 31.1, 33.3, 42.3, 53.2, 114.9, 131.7, 132.4, 136.9, 203.4; ^1H NMR (400 MHz, $CDCl_3$, **(*Z*)-2k**) δ 1.04 (s, 3 H), 1.29 (s, 3 H), 2.23 (m, 1 H), 5.11 (dm, *J* = 10.0 Hz, 1 H), 5.19 (dm, *J* = 16.8 Hz, 1 H), 5.33 (br dt, *J* = 11.0 Hz, 7.8 Hz, 1 H), 5.99 (tm, *J* = 11.0 Hz, 1 H), 6.63 (dddd, *J* = 1.0, 10.0, 11.0, 16.8 Hz, 1 H), 9.85 (d, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-2k**) δ 22.0, 22.6, 31.6, 33.8, 42.6, 53.1, 117.2, 129.8, 131.9, 136.9, 203.9; HRMS calcd for $C_{12}H_{18}O$: 178.1358. Found *m/z* (relative intensity) 179 (M^++1, 14), 178.1339 (M^+, 100), 163 (5).

2-(1,3-Butadienyl)cyclopentanecarbaldehyde (**2a**): mixture of *E*- and *Z*- isomers in a ratio of 11 : 1; IR (neat) 2955 (s), 2870 (m), 1720 (s), 1003 (m), 903 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*)-2a**) δ 1.41-2.09 (m, 6 H), 2.54 (dq, *J* = 2.7, 8.9 Hz, 1 H), 2.78 (dq, *J* = 7.8, 8.9 Hz, 1 H), 5.00 (dm, *J* = 10.3 Hz, 1 H), 5.13 (dm, *J* = 17.1 Hz, 1 H), 5.67 (dd, *J* = 7.8, 15.6 Hz, 1 H), 6.08 (dd, *J* = 10.3, 15.6 Hz, 1 H), 6.28 (dt, *J* = 17.1, 10.3 Hz, 1 H), 9.61 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-2a**) δ 24.7, 26.2, 33.4, 57.8, 115.9, 130.8, 136.2, 136.5, 202.6; ^1H NMR (400 MHz, $CDCl_3$, epimer of **(*E*)-2a**) δ 2.88 (ddt, *J* = 2.7, 6.3,

8.5 Hz, 1 H), 2.98 (dq, *J* = 6.3, 8.3 Hz, 1 H), 5.01 (dm, *J* = 10.3 Hz, 1 H), 5.21 (dm, *J* = 16.8 Hz, 1 H), 5.71 (dd, *J* = 8.3, 15.9 Hz, 1 H), 6.13 (dd, *J* = 10.3, 15.9 Hz, 1 H), 6.23 (dt, *J* = 16.8, 10.3 Hz, 1 H), 9.66 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, epimer of **(*E*)-2a**) δ 24.1, 25.0, 32.3, 45.8, 55.7, 116.2, 131.9, 133.5, 136.5, 204.2; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*)-2a**) δ 2.52 (dq, *J* = 2.7 , 8.9 Hz, 1 H), 3.21 (dq, *J* = 11.0, 8.9 Hz, 1 H), 5.16 (dm, *J* = 11.0 Hz, 1 H), 5.21 (dm, *J* = 16.8 Hz, 1 H), 5.38 (br t, *J* = 11.0 Hz, 1 H), 6.00 (t, *J* = 11.0 Hz, 1 H), 6.63 (dtm, *J* = 16.8, 11.0 Hz, 1 H), 9.62 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(Z)-2a**) δ 24.2, 26.2, 34.1, 39.8, 58.9, 118.0, 131.8, 134.3, 136.4 202.6; HRMS calcd for $C_{10}H_{14}O$: 150.1045. Found *m*/*z* (relative intensity) 151 (M^++1, 11), 150.1039 (M^+, 100), 149 (9).

2-[(1*E*)-3-Methyl-1,3-butadienyl]cyclopentanecarbaldehyde (**2b**): IR (neat) 2955 (s), 2870 (m), 1720 (s), 1612 (w), 1450 (w), 964 (w), 887 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, **(*E*)-2b**, major isomer) δ 1.42-2.10 (m, 6 H), 1.83 (s, 3 H), 2.56 (dq, *J* = 2.7, 8.8 Hz, 1 H), 2.80 (dq, *J* = 7.8, 8.8 Hz, 1 H), 4.90 (s, 2 H), 5.60 (dd, *J* = 7.8 Hz, 15.6 Hz, 1 H), 6.17 (d, *J* = 15.6 Hz, 1 H), 9.61 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-2b**, major isomer) δ 18.6, 24.8, 26.2, 33.7, 44.7, 58.0, 115.4, 131.8, 132.9, 141.4, 203.0; ^{1}H NMR (400 MHz, $CDCl_3$, **(*E*)-2b**, minor isomer) δ 1.80 (s, 3 H), 2.89 (ddt, *J* = 2.7, 6.1, 8.1 Hz, 1 H), 3.00 (dq, *J* = 6.1, 8.5 Hz, 1 H), 5.64 (dd, *J* = 8.5, 15.6 Hz, 1 H), 6.22 (d, *J* = 15.6 Hz, 1 H), 9.67 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-2b**, minor isomer) δ 24.2, 25.0, 32.5, 46.1, 55.8, 115.6, 129.2, 133.8, 204.3; HRMS calcd for $C_{11}H_{16}O$-CH_3: 149.0966. Found *m*/*z* (relative intensity) 149.0961 (M^+-CH_3, 63), 135 (100).

2-[(1*E*)-1,3-Pentadienyl]cyclopentanecarbaldehyde (**2c**): a mixture of *E*,*E*- and *Z*,*E*-isomers in a ratio of 2 : 1; IR (neat) 3425 (m), 3017 (s), 2955 (s), 2870 (s), 2816 (m), 2716 (m), 1720 (s), 1450 (m), 988 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, **(*E*,*E*)-2c**) δ 1.46 (m, 1 H), 1.54-1.70 (m, 2 H), 1.73 (d, *J* = 6.8 Hz, 3 H), 1.75 (m, 1 H), 1.82-1.98 (m, 2 H), 2.52 (dq, *J* = 2.7, 8.5 Hz, 1 H), 2.73 (dq, *J* = 7.8, 8.5 Hz, 1 H), 5.11 (dd, *J* = 7.8, 14.4 Hz, 1 H),

5.61 (dq, *J* = 14.4, 6.8 Hz, 1 H), 5.95 (dd, *J* = 10.3, 14.4 Hz, 1 H), 6.01 (dd, *J* = 10.3, 14.4 Hz, 1 H), 9.60 (d, *J* = 2.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*,*E*)-2c**) δ 18.0, 24.7, 33.6, 40.0, 44.3, 58.0, 128.2, 130.3, 131.0, 132.8, 203.1; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*,*E*)-2c**, major isomer) δ 1.77 (d, *J* = 6.8 Hz, 1 H), 2.50 (dq, *J* = 2.4, 8.3 Hz, 1 H), 3.16 (dq, *J* = 10.0, 8.3 Hz, 1 H), 5.20 (t, *J* = 10.0 Hz, 1 H), 5.70 (dq, *J* = 14.9, 6.8 Hz, 1 H), 6.22 (ddm, *J* = 10.0, 11.0 Hz, 1 H), 9.62 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*,*E*)-2c**, major isomer) δ 18.3, 24.9, 34.2, 40.7, 45.9, 59.0, 126.5, 129.1, 130.4, 131.1, 203.0; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*,*E*)-2c**, minor isomer) δ 2.87 (m, 1 H), 2.95 (dq, *J* = 10.3, 8.3 Hz, 1 H), 5.21 (t, *J* = 10.3 Hz, 1 H), 6.09 (dd, *J* = 10.3, 16.6 Hz, 1 H), 6.35 (tm, *J* = 10.3 Hz, 1 H), 9.66 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*,*E*)-2c**, minor) δ 24.1, 32.5, 55.7, 128.4, 130.1, 130.8, 131.3, 204.5; HRMS calcd for $C_{11}H_{16}O$-CH_3: 149.0966. Found *m*/*z* (relative intensity) 149.0932 (M^+-CH_3, 83), 135 (100).

3-(1,3-Butadienyl)cyclopentanecarbaldehyde (**2d**): a mixture of *E*- and *Z*- isomers in a ratio of 4 : 1; IR (neat) 2955 (s), 2870 (m), 2176 (w), 1720 (s), 1450 (w), 1003 (s), 903 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, **(*E*)-2d**) δ 1.41 (m, 1 H), 1.60 (m, 1 H), 1.78-1.96 (m, 3 H), 2.04 (dt, *J* = 12.9, 7.1 Hz, 2 H), 2.61 (dquint, *J* = 6.8, 9.8 Hz, 1 H), 2.84 (m, 1 H), 4.98 (d, *J* = 10.3 Hz, 1 H), 5.11 (d, *J* = 17.2 Hz, 1 H), 5.65 (dd, *J* = 7.6, 15.2 Hz, 1 H), 6.07 (dd, *J* = 10.3, 15.2 Hz, 1 H), 6.29 (dt, *J* = 17.2, 10.3 Hz, 1 H), 9.62 (d, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-2d**) δ 25.8, 32.5, 33.2, 43.5, 51.3, 115.4, 130.1, 136.8, 137.4, 202.9; ^{1}H NMR (400 MHz, $CDCl_3$, **(*Z*)-2d**) δ 2.13 (ddd, *J* = 4.6, 7.1, 12.2 Hz, 2 H), 3.02 (m, 1 H), 5.10 (dm, *J* = 10.5 Hz, 1 H), 5.19 (dm, *J* = 16.8 Hz, 1 H), 5.33 (dt *J* = 10.5, 6.3 Hz, 1 H), 5.96 (dt, *J* = 10.5, 4.6 Hz, 1 H), 6.61 (dt, *J* = 16.8, 10.5 Hz, 1 H), 9.64 (d, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-2d**) δ 25.9, 33.2, 33.9, 38.9, 51.5, 117.4, 128.9, 135.6, 202.9; HRMS calcd for $C_{10}H_{14}O$: 150.1045. Found *m*/*z* (relative intensity) 151 (M^++1, 12), 150.1057 (M^+, 100), 149 (1), 121 (10).

1,2,2-Trimethyl-3-(4-phenyl-1,3-butadienyl)cyclopentanecarbaldehyde (**2g**): mixture

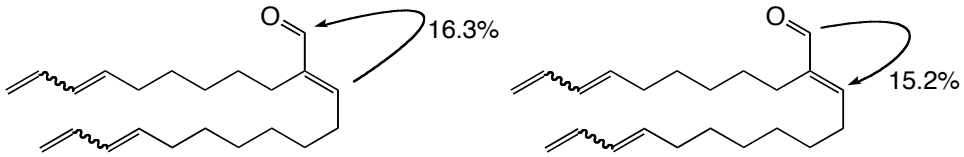
of *E,E*- and *Z,E*- isomers in a ratio of 8 : 1; IR (KBr disk) 3010 (w), 2950 (m), 2850 (w), 1740 (s), 1460 (w), 1440 (m), 1380 (m), 1360 (m), 1300 (w), 1060 (w), 980 (s), 900 (m), 820 (w), 740 (s), 680 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*,*E*)-2g**) δ 0.82 (s, 3 H), 1.00 (s, 3 H), 1.10 (s, 3 H), 1.39 (ddd, *J* = 5.1, 9.2, 13.9 Hz, 1 H), 1.67 (dddd, *J* = 5.1, 9.2, 11.7, 13.9 Hz, 1 H), 1.96 (ddt, *J* = 5.1, 13.9, 9.2 Hz, 1 H), 2.45 (ddd, *J* = 5.1, 11.7, 13.9 Hz, 1 H), 2.56 (q, *J* = 9.2 Hz, 1 H), 5.69 (dd, *J* = 9.2, 15.0 Hz, 1 H), 6.21 (dd, *J* = 10.6, 15.0 Hz, 1 H), 6.48 (d, *J* = 15.0 Hz, 1 H), 6.77 (dd, *J* = 10.6, 15.0 Hz, 1 H), 7.21 (tt, *J* = 1.7, 7.0 Hz, 1 H), 7.30 (dt, *J* = 1.7, 7.0 Hz, 2 H), 7.37 (dd, *J* = 1.7, 7.0 Hz, 2 H), 9.65 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*,*E*)-2g**) δ ; 18.8, 19.4, 22.6, 27.5, 30.5, 47.7, 52.0, 58.3, 126.1, 127.1, 128.4, 128.9, 130.7, 132.0, 134.3, 137.3, 205.9; ^1H NMR (400 MHz, $CDCl_3$, **(*Z*,*E*)-2g**) δ .086 (s, 3 H), 1.00 (s, 3 H), 1.17 (s, 3 H), 3.11 (q, *J* = 9.8 Hz, 1 H), 5.36 (t, *J* = 11.0 Hz, 1 H), 6.28 (t, *J* = 11.0 Hz, 1 H), 6.56 (d, *J* = 15.5 Hz, 1 H), 7.00 (dd, *J* = 11.0, 15.5 Hz, 1 H), 9.66 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*,*E*)-2g**) δ 18.9, 19.3, 22.8, 28.6, 30.8, 46.6, 60.3, 124.2, 126.2, 127.4, 128.5, 130.6, 132.3, 133; HRMS calcd for $C_{19}H_{24}O$: 268.1897. Found *m/z* (relative intensity) 269 (M^++1, 17), 268.1832 (100); Anal calcd for $C_{19}H_{24}O$: C, 84.94; H, 9.09. Found: C, 84.61, H, 9.05.

***cis*-1-Acetyl-3-[*(E)*-1,3-butadienyl]-1,2,2-trimethylcyclopentane (2h):** IR (neat) 2950 (s), 2860 (m), 1700 (s), 1650 (w), 1600 (w), 1460 (m), 1350 (m), 1230 (m), 1080 (m), 1000 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.67 (s, 3 H), 1.06 (s, 3 H), 1.17 (d, *J* = 0.7 Hz, 3 H), 1.39 (ddd, *J* = 5.1, 9.2, 13.6 Hz, 1 H), 1.57 (dddd *J* = 5.1, 9.2, 11.7, 13.6 Hz, 1 H), 1.83 (ddt, *J* = 5.5, 13.6, 9.2 Hz, 1 H), 2.10 (s, 3 H), 2.48 (q, *J* = 9.2 Hz, 1 H), 2.55 (ddd, *J* = 5.5, 11.7, 13.7 Hz, 1 H), 5.00 (dd, *J* = 1.8, 10.3 Hz, 1 H), 5.10 (dd, *J* = 1.8, 17.2 Hz, 1 H), 5.59 (dd, *J* = 9.2, 15.4 Hz, 1 H), 6.03 (ddd, *J* = 1.8, 10.3, 15.4 Hz, 1 H), 6.33 (dt, *J* = 17.2, 10.3 Hz, 1 H); HRMS calcd for $C_{14}H_{22}O$: 206.1671. Found *m/z* (relative intensity) 206.1676 (M^+, 100), 191 (14), 122 (18), 83 (70); Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.51; H, 10.83.

2-(5,7-Octadienyl)-(2*E*,9,11)-decatrienal (**2l'**): a mixture of *E*- and *Z*- isomers in a ratio of 7 : 1: IR (neat) 3086 (w), 3009 (m), 2932 (s), 2855 (s), 1690 (s), 1643 (m), 1458 (w), 1003 (s), 895 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*)-isomer**) δ 1.30-1.46 (m, 4 H), 1.50 (quint, *J* = 7.3 Hz, 2 H), 2.09 (quint, *J* = 6.6 Hz, 4 H), 2.23 (t, *J* = 7.3 Hz, 2 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 4.94 (d, *J* = 10.3 Hz, 1 H), 4.96 (d, *J* = 10.3 Hz, 1 H), 5.07 (d, *J* = 16.8 Hz, 1 H), 5.08 (d, *J* = 16.8 Hz, 1 H), 5.67 (dt, *J* = 15.1, 7.3 Hz, 1 H), 5.69 (dt, *J* = 15.1, 7.3 Hz, 1 H), 6.03 (dd, *J* = 5.6, 15.1 Hz, 1 H), 6.05 (dd, *J* = 5.6, 15.1 Hz, 1 H), 6.28 (ddd, *J* = 5.6, 10.3 Hz, 16.8 Hz, 1 H), 6.31 (ddd, *J* = 5.6, 10.3, 16.8 Hz, 1 H), 6.42 (t, *J* = 7.3 Hz, 1 H), 9.35 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-isomer**) δ 28.2, 28.5, 28.9, 29.1, 32.2, 32.3, 114.6, 114.7, 131.0, 131.1, 134.8, 137.0, 137.1, 143.5, 154.9, 194.9; ^1H NMR (400 MHz, $CDCl_3$, **(*Z*)-isomer**) δ 2.37 (q, *J* = 7.6 Hz, 2 H), 5.16 (d, *J* = 17.1 Hz, 1 H), 5.18 (d, *J* = 17.1 Hz, 1 H), 5.43 (dt, *J* = 9.6, 7.6 Hz, 2 H), 6.62 (dt, *J* = 16.8, 10.3 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-isomer**) δ 27.5, 28.2, 29.5, 29.6, 116.7, 116.8, 129.2, 129.3, 132.0, 132.1, 132.3; HRMS calcd for $C_{20}H_{30}O$: 286.2297. Found *m/z* (relative intensity) 287 (M^++1, 25), 286.2284 (M^+, 100), 285 (1).

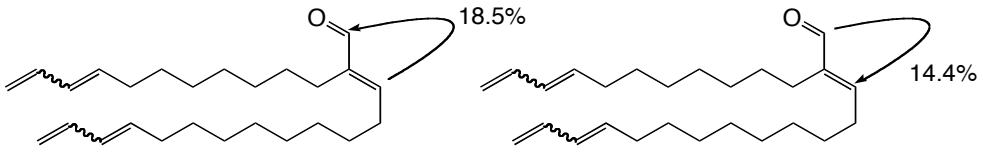
2-(6,8-Nonadecadienyl)-(2*E*,10,12)-tridecatrienal (**2m'**): a mixture of *E*- and *Z*- isomers in a ratio of 3 : 1: IR (neat) 3307 (w), 2928 (s), 2855 (s), 1688 (s), 1308 (s), 1003 (s), 897 (m), 701 (w); cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*)-isomer**) δ 1.22-1.68 (m, 14 H), 2.07 (br dt, *J* = 14.3, 7.1 Hz, 4 H), 2.22 (t, *J* = 7.3 Hz, 2 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 4.95 (d, *J* = 10.3 Hz, 2 H), 5.08 (d, *J* = 16.8 Hz, 2 H), 5.68 (ddt, *J* = 3.7, 15.1, 7.1 Hz, 2 H), 6.04 (ddd, *J* = 4.9, 10.3, 15.1 Hz, 2 H), 6.30 (ddt, *J* = 1.5, 16.8, 10.3 Hz, 2 H), 6.42 (t, *J* = 7.3 Hz, 1 H), 9.75 (t, *J* = 1.7 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-isomer**) δ 28.6, 28.6, 28.8, 28.9 , 29.0, 29.2, 32.4, 114.5, 114.6, 130.9, 135.0, 135.1, 137.1, 143.6, 154.9, 195.0; ^1H NMR (400 MHz, $CDCl_3$, **(*Z*)-isomer**) δ 5.17 (dm, *J* = 16.8 Hz, 2 H), 5.44 (dd, *J* = 7.3, 11.0 Hz, 2 H), 6.62 (dt, *J* = 16.8 Hz, 10.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-isomer**) δ 29.3, 29.4, 30.9, 32.7, 117.5, 127.3, 130.3, 132.1, 132.6, 133.7, 137.8, 148.5; HRMS calcd for

$C_{22}H_{34}O_2$: 314.2610. Found *m/z* (relative intensity) 315 (M^++1, 28), 314.2594 (M^+, 100), 313 (3), 285 (8).



NOE Increments (%) Observed for **2m'**

2-(8,10-Undecadienyl)-(2*E*,12,14)-pentadecatrienal (**2n'**): a mixture of *E*- and *Z*- isomers in a ratio of 3 : 1: IR (neat) 2926 (s), 2855 (s), 1726 (s), 1688 (s), 1641 (m), 1441 (s), 1308 (s), 1003 (s), 899 (s), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, **(*E*)-isomer**) δ 1.22- 1.68 (m, 22 H), 2.03 (m, 4 H), 2.22 (t, *J* = 7.3 Hz, 2 H), 2.34 (q, *J* = 7.3 Hz, 2 H), 4.94 (d, *J* = 10.3 Hz, 2 H), 5.08 (d, *J* = 17.1 Hz, 2 H), 5.69 (dt, *J* = 15.1, 7.3 Hz, 2 H), 6.03 (ddm, *J* = 10.3, 15.1 Hz, 2 H), 6.42 (t, J = 7.3 Hz, 1 H), 6.30 (dt, *J* = 17.1, 10.3 Hz, 2 H), 9.75 (t, *J* = 2.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*E*)-isomer**) δ 27.7, 28.7, 28.9, 29.1, 29.3, 29.6, 32.5, 114.4, 114.5, 130.7, 130.8, 135.3, 137.2, 143.7, 155.0, 195.0; ^1H NMR (400 MHz, $CDCl_3$, **(*Z*)-isomer**) δ 5.17 (d, *J* = 16.7 Hz, 2 H), 5.54 (dt, J = 11.0, 7.3 Hz, 2 H), 5.99 (br t, *J* = 11.0 Hz, 2 H), 6.62 (dt, *J* = 16.7, 11.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, **(*Z*)-isomer**) δ 116.5, 116.6, 129.0, 129.1, 132.2, 132.8 ; HRMS calcd for $C_{26}H_{42}O_2$: 370.3236. Found *m/z* (relative intensity) 371 (M^++1, 29), 370.3238 (M^+, 100), 369 (2), 353 (11).



NOE Increments (%) Observed for **2n'**

2-Ethyl-decahydro-4-vinyl-4*H*-cyclodeca[*d*][1,3,2]dioxaborinine (**4a**): IR (neat) 3100 (w), 2930 (s), 1405 (s), 1338 (s), 1290 (s), 1220 (s), 990 (m), 930 (m), 764 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, major isomer) δ 0.70 (q, *J* = 7.6 Hz, 2 H), 0.92 (t, *J* = 7.6 Hz, 3 H), 1.30-1.80 (m, 15 H), 1.81 (dt, *J* = 13.4, 4.6 Hz, 1 H), 1.89 (ddd, *J* = 3.7, 7.1, 10.7 Hz, 1 H),

4.08 (ddd, *J* = 3.7, 4.6, 9.3 Hz, 1 H), 4.29 (m, 1 H), 5.23 (d, *J* = 10.5 Hz, 1 H), 5.25 (dt, *J* = 17.1, 1.5 Hz, 1 H), 5.86 (ddd, *J* = 4.6, 10.5, 17.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 7.9, 20.7, 21.3, 22.0, 22.4, 22.6, 23.3, 23.8, 24.3, 24.4, 24.6, 24.7, 24.8, 24.9, 25.0, 25.3, 25.4, 25.9, 26.0, 26.1, 27.5, 30.0, 30.9, 31.1, 38.7, 39.8, 41.3, 43.5, 70.0, 72.3, 74.0, 74.7, 75.1, 75.8, 76.3, 77.1, 78.2, 114.5, 115.3, 116.7, 135.6, 137.3, 138.1, 139.0; HRMS calcd for $C_{15}H_{27}BO_2$: 250.2104. Found *m/z* (relative intensity) 251 (M^++1, 11), 250.2087 (M^+, 51), 249 (13), 235 (8), 221 (100).

Decahydro-2-phenyl-4-vinyl-4*H*-cyclodeca[*d*][1,3,2]dioxaborinine (**4b**): IR (neat) 3076 (w), 2930 (m), 1601 (w), 1441 (m), 1306 (m), 1130 (w), 1028 (w), 989 (w), 924 (w), 700 (m), 646 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ 1.32- 1.90 (m, 15 H), 1.95 (m, 1 H), 2.00 (ddd, *J* = 4.2, 6.8, 11.2 Hz, 1 H), 4.27 (ddd, *J* = 3.2, 4.9, 9.3 Hz, 1 H), 4.49 (m, 1 H), 5.26 (dt, *J* = 10.5, 1.5 Hz, 1 H), 5.32 (dt, *J* = 17.1, 1.5 Hz, 1 H), 5.95 (ddd, *J* = 4.6, 10.5, 17.1 Hz, 1 H), 7.33 (tm, *J* = 7.6 Hz, 2 H), 7.41 (tm, *J* = 7.6 Hz, 1 H), 7.82 (dm, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of 4 isomers) δ 17.8, 20.8, 21.5, 22.1, 22.5, 22.7, 23.3, 23.8, 24.0, 24.3, 24.4, 24.6, 24.7, 24.8, 24.9, 25.0, 25.2, 25.4, 25.6, 25.8, 25.9, 26.0, 26.1, 26.2, 26.4, 26.6, 26.7, 27.1, 27.5, 28.1, 28.3, 29.9, 30.0, 30.1, 30.5, 30.9, 31.1, 38.1, 39.0, 40.1, 41.4, 42.1, 42.5, 43.6, 44.1, 69.7, 70.5, 70.7, 72.7, 72.9, 73.8, 74.2, 74.4, 75.1, 75.5, 76.1, 76.8, 77.1, 78.5, 114.6, 114.7, 115.0, 115.4, 115.5, 116.7, 116.9, 117.7, 127.3, 127.4, 130.3, 130.4, 133.7, 135.4, 136.3, 137.2, 137.4, 137.5, 138.0, 138.6, 138.8; HRMS calcd for $C_{19}H_{27}BO_2$: 298.2104. Found *m/z* (relative intensity) 299 (M^++1, 20), 298.2088 (M^+, 100), 297 (26), 283 (4).

Reference

[1] Mori, M.; Kimura, M.; Takahashi, Y.; Tamaru, Y. *Chem. Commun.* **2006**, 4303-4305.

[2] Harayama, H.; Kuroki, T.; Kimura, M.; Tanaka, S.; Tamaru, Y. *Angew. Chem. Int. Ed.* **1997**, *36*, 2352-2354; See also: Harayama, H.; Kimura, M.; Tanaka, S.; Tamaru, Y. *Tetrahedron Lett.* **1998**, *39*, 8475-8478.

[3] Tamaru, Y.; Hojo, M.; Kawamura, S.; Sawada, S.; Yoshida, Z. *J. Org. Chem.*, **1987**, *52*, 4062-4072.

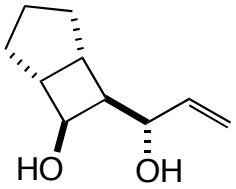
[4] Bando, T.; Tanaka, S.; Fugami, K.; Yoshida, Z.; Tamaru, Y. *Bull. Chem. Soc. Jpn.*, **1992**, *65*, 97-110.

[5] Malkov, A. V.; Pernazza, D.; Bell, M.; Bella, M.; Massa, A.; Teply, F.; Meghani, P.; Kocovsky, P. *J. Org. Chem.* **2003**, *68*, 4727-4742.

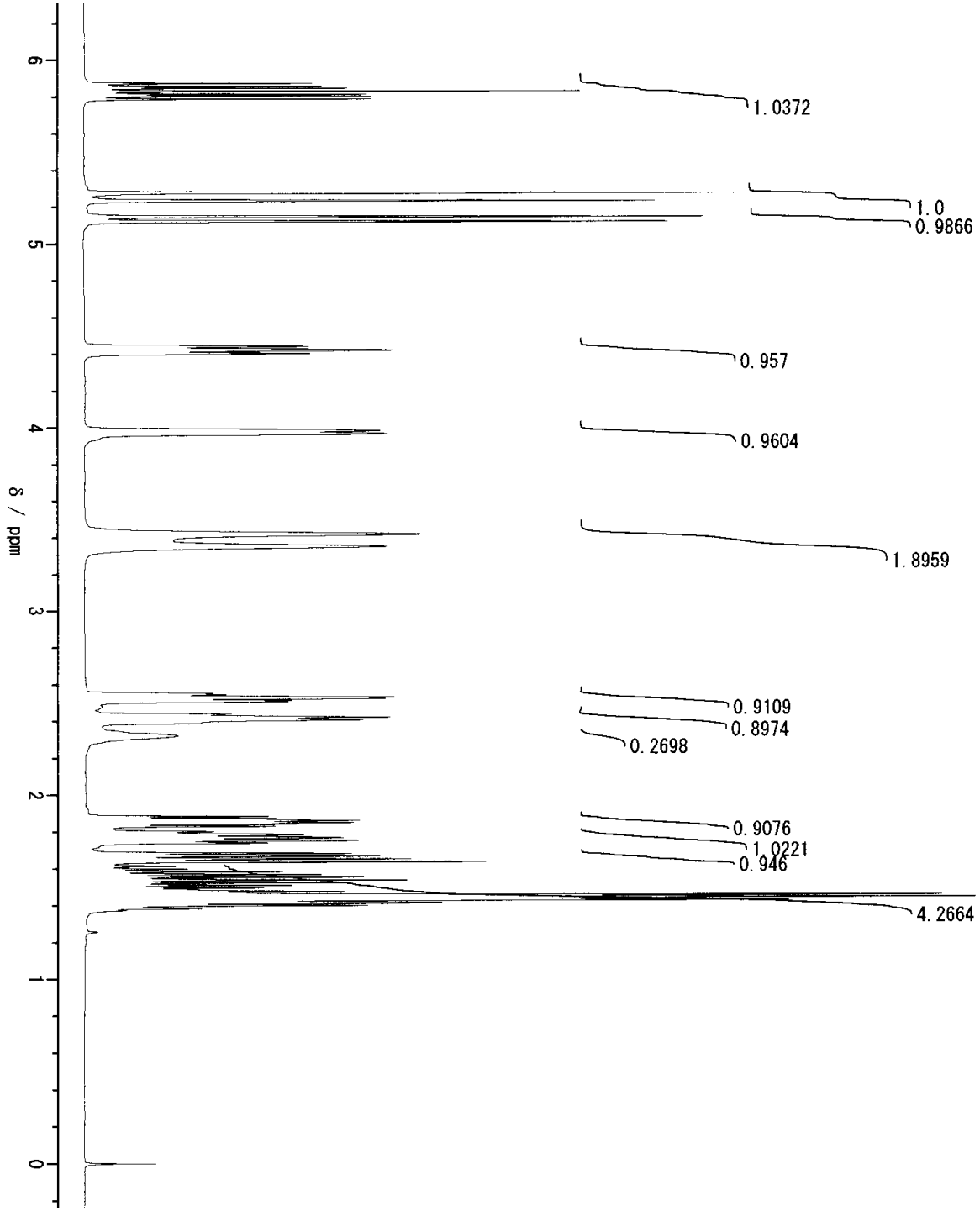
[6] Crystallographic data of *anti*-**1e** and *syn*-**1k** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-639709 and CCDC-631058, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax: (+41)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

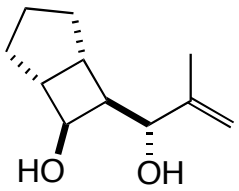
[7] Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1-15.

^{1}H NMR spectra

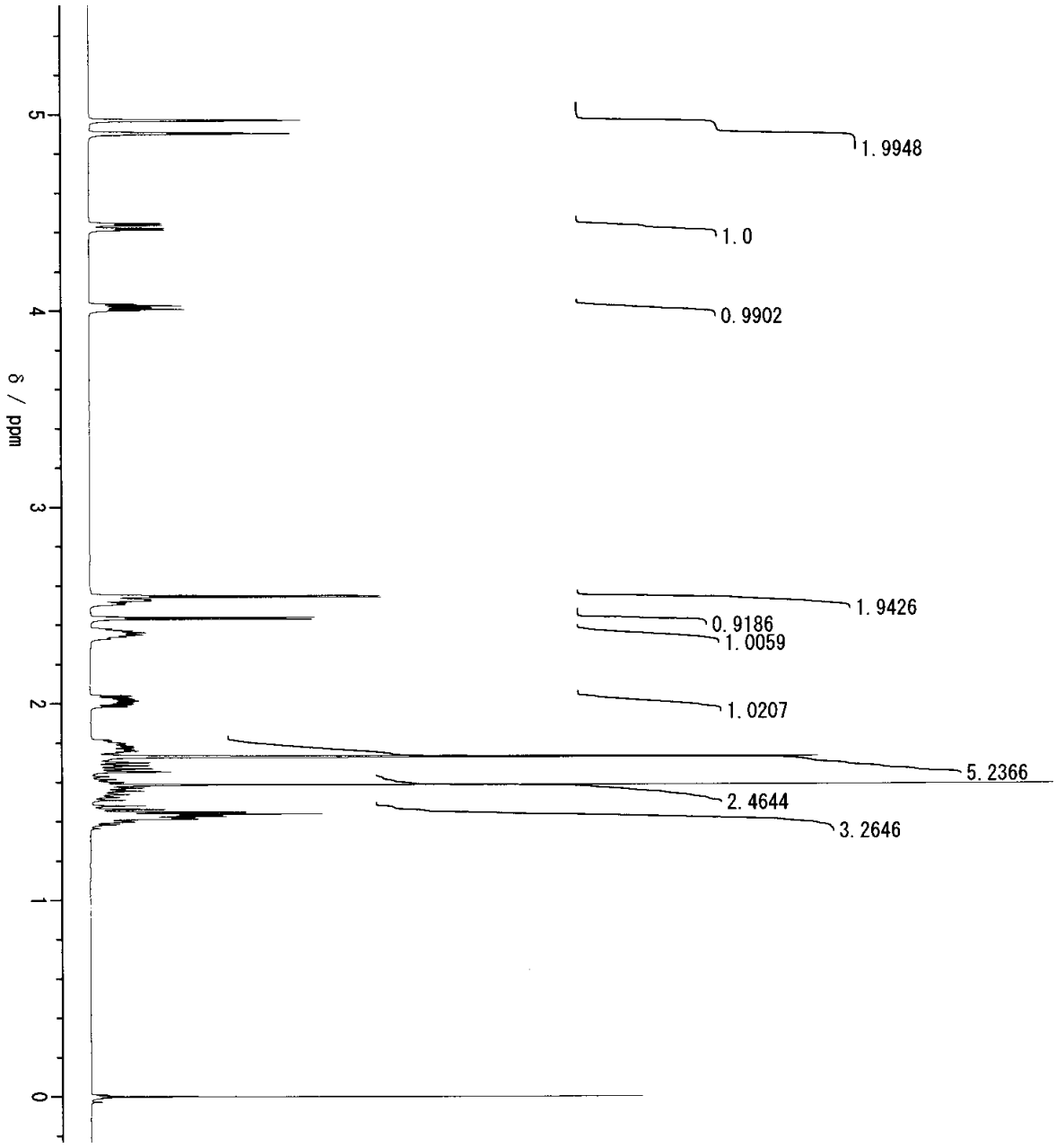


anti-**1a**




HO
OH

anti-**1b**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3
2
1
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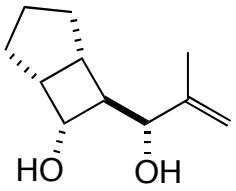
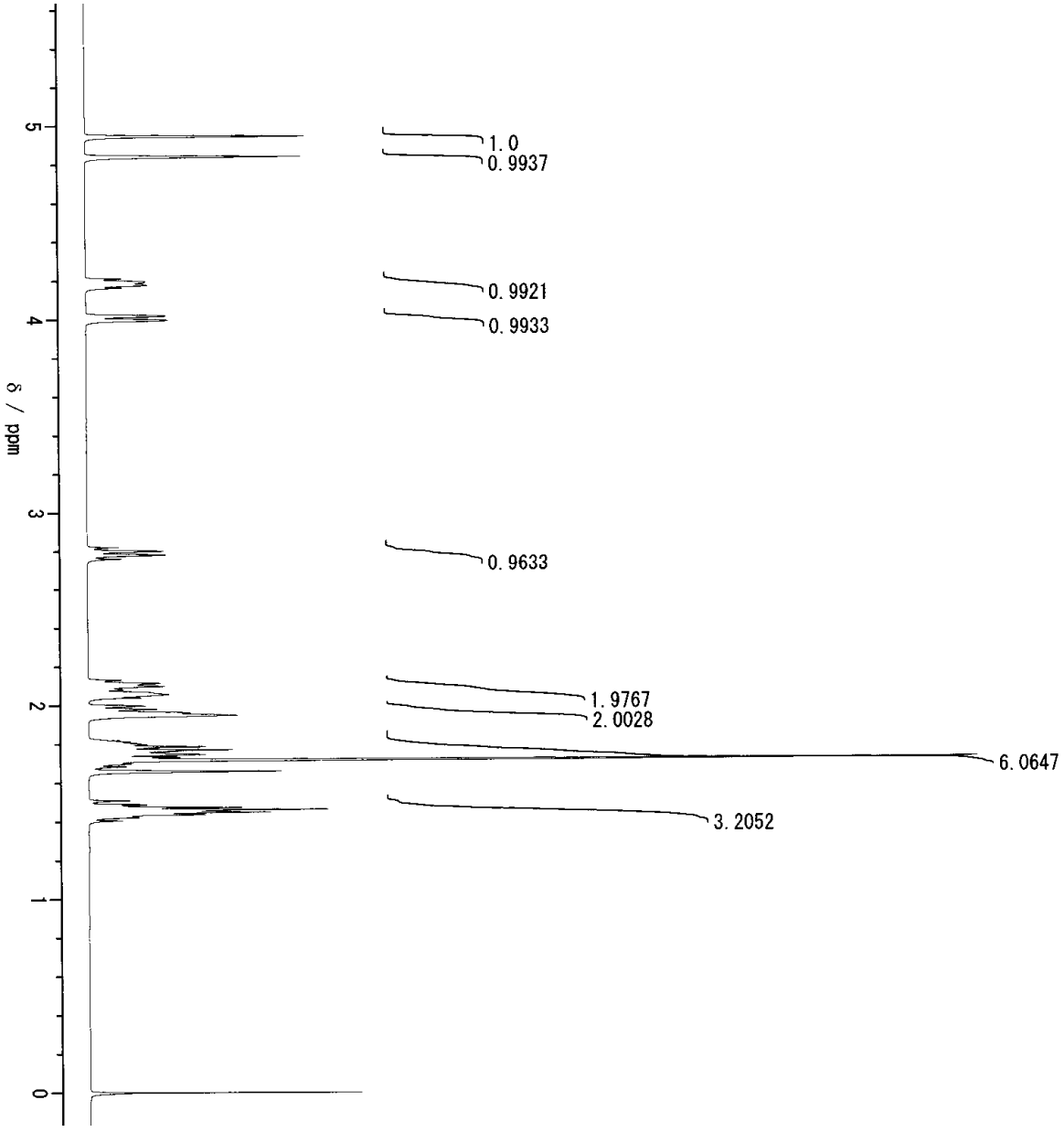

HO
OH

syn-**1b**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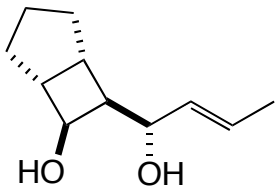
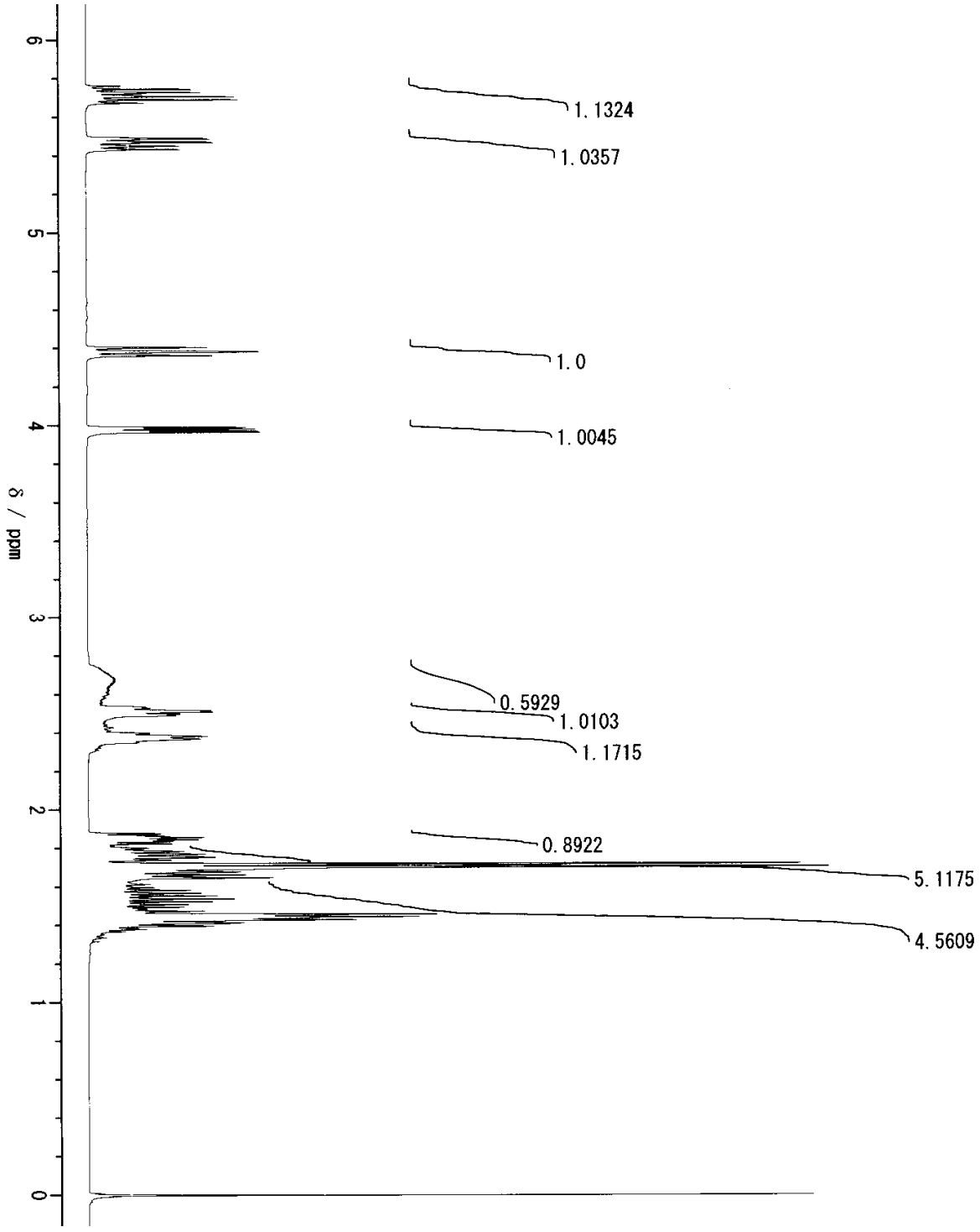
6.0647
3.2052


HO
OH

anti-**1c**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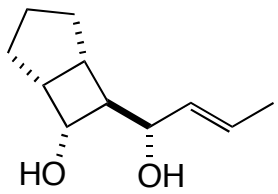
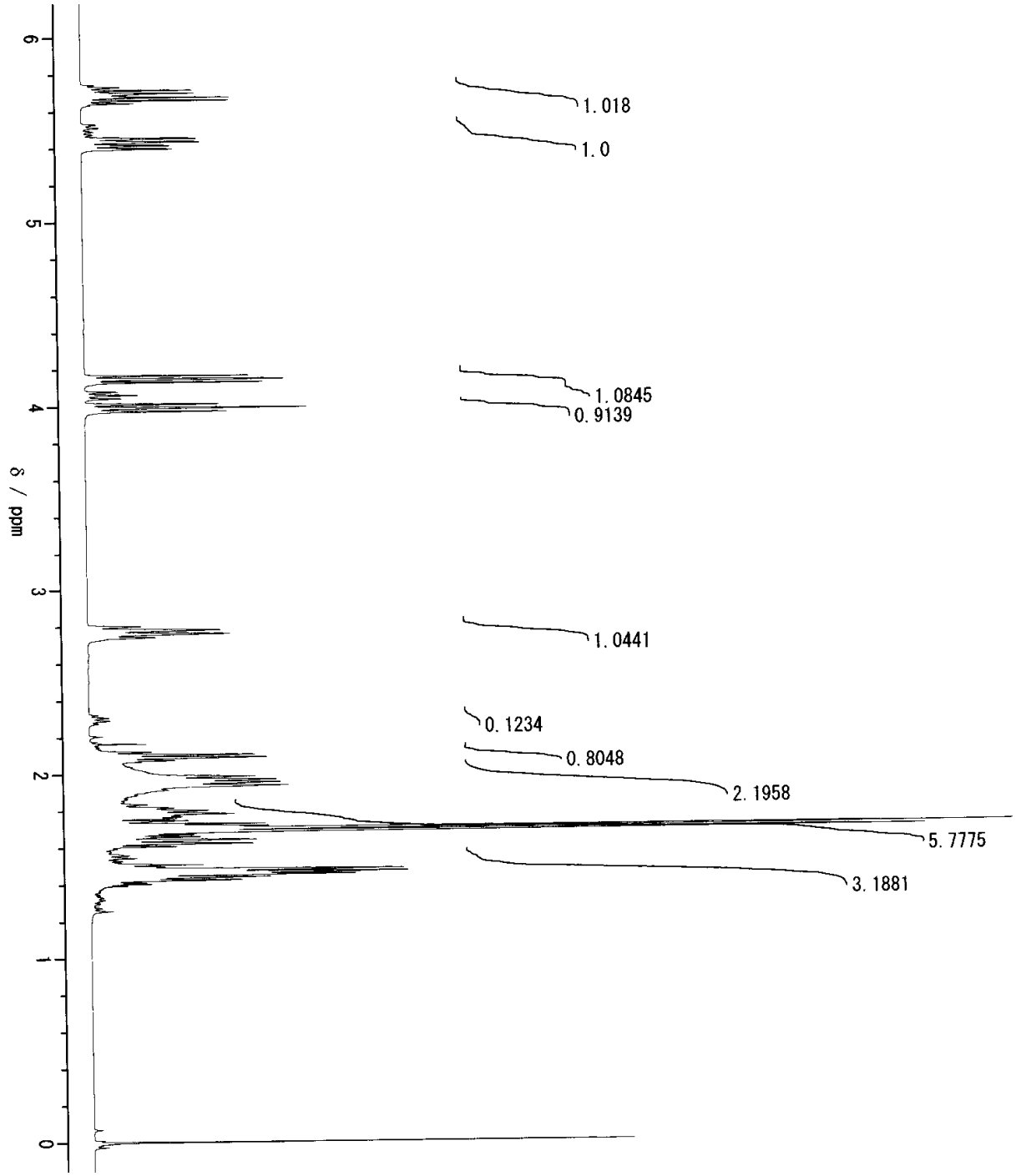
4.5609

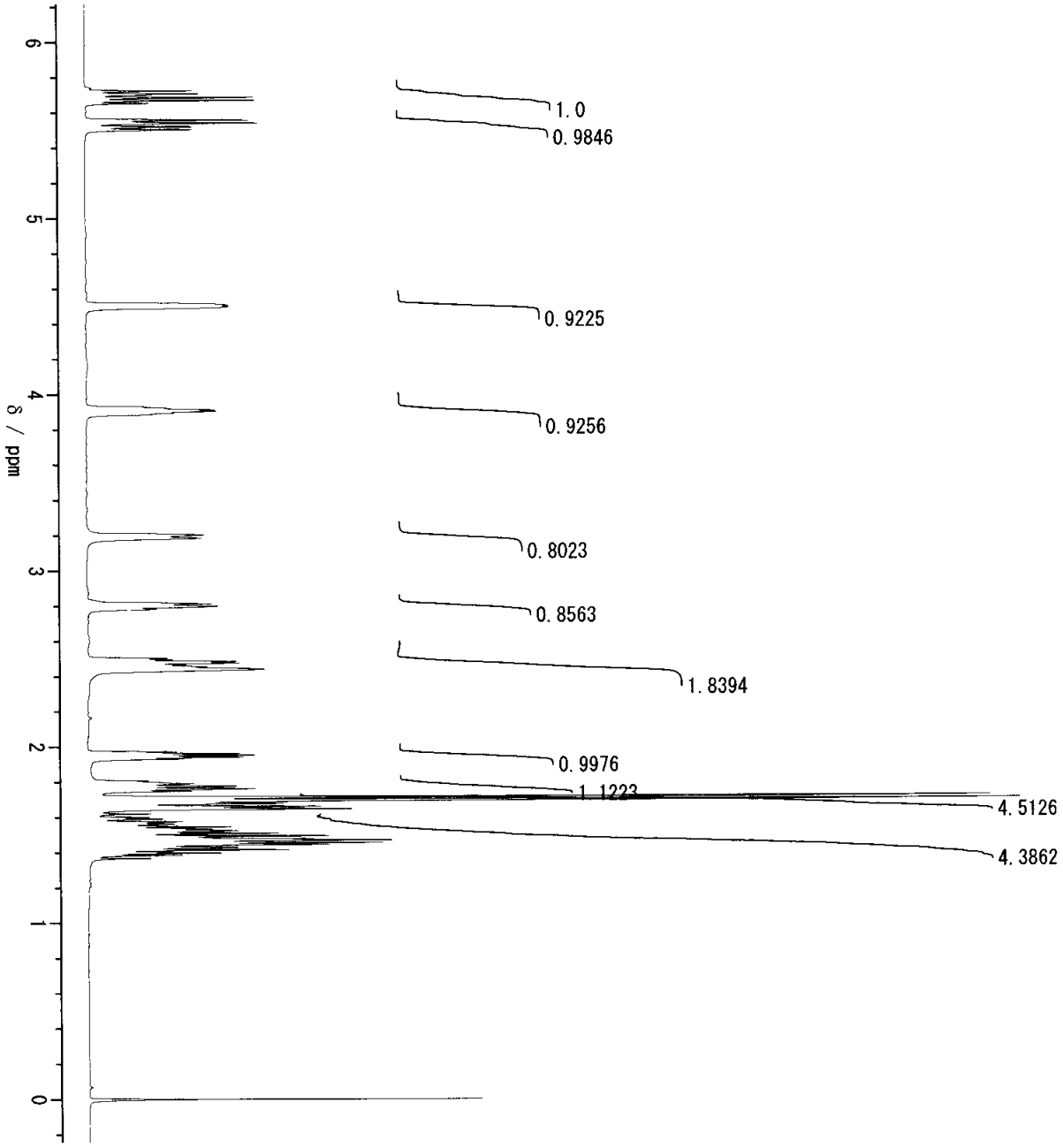


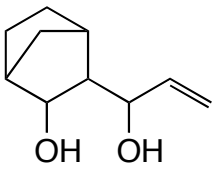
syn-**1c**

and another small amount of stereoisomer

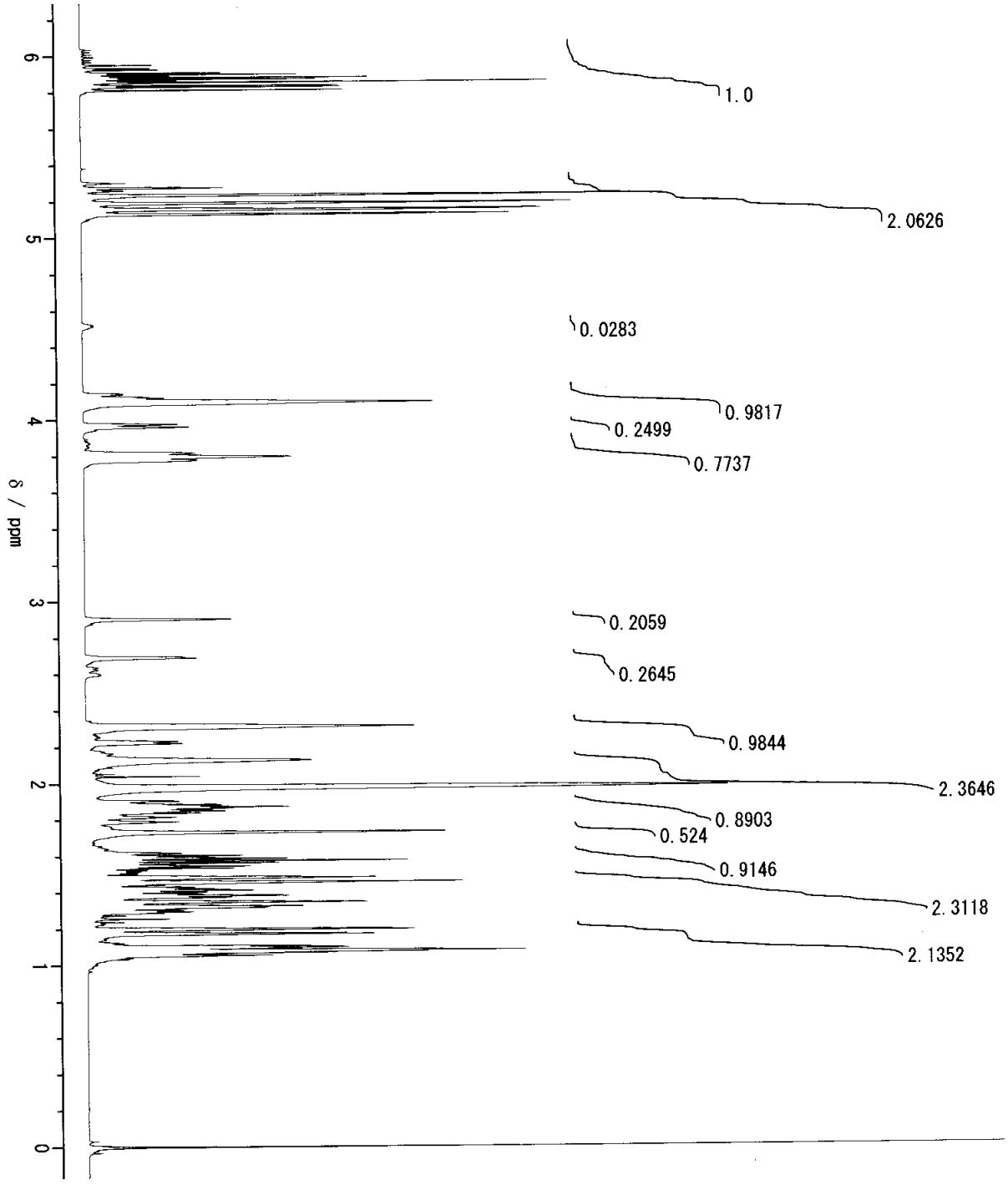


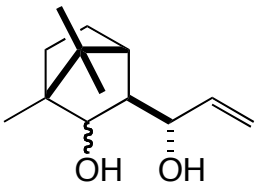
The fourth diastereomer of **1c**, whose stereochemistry is unknown.



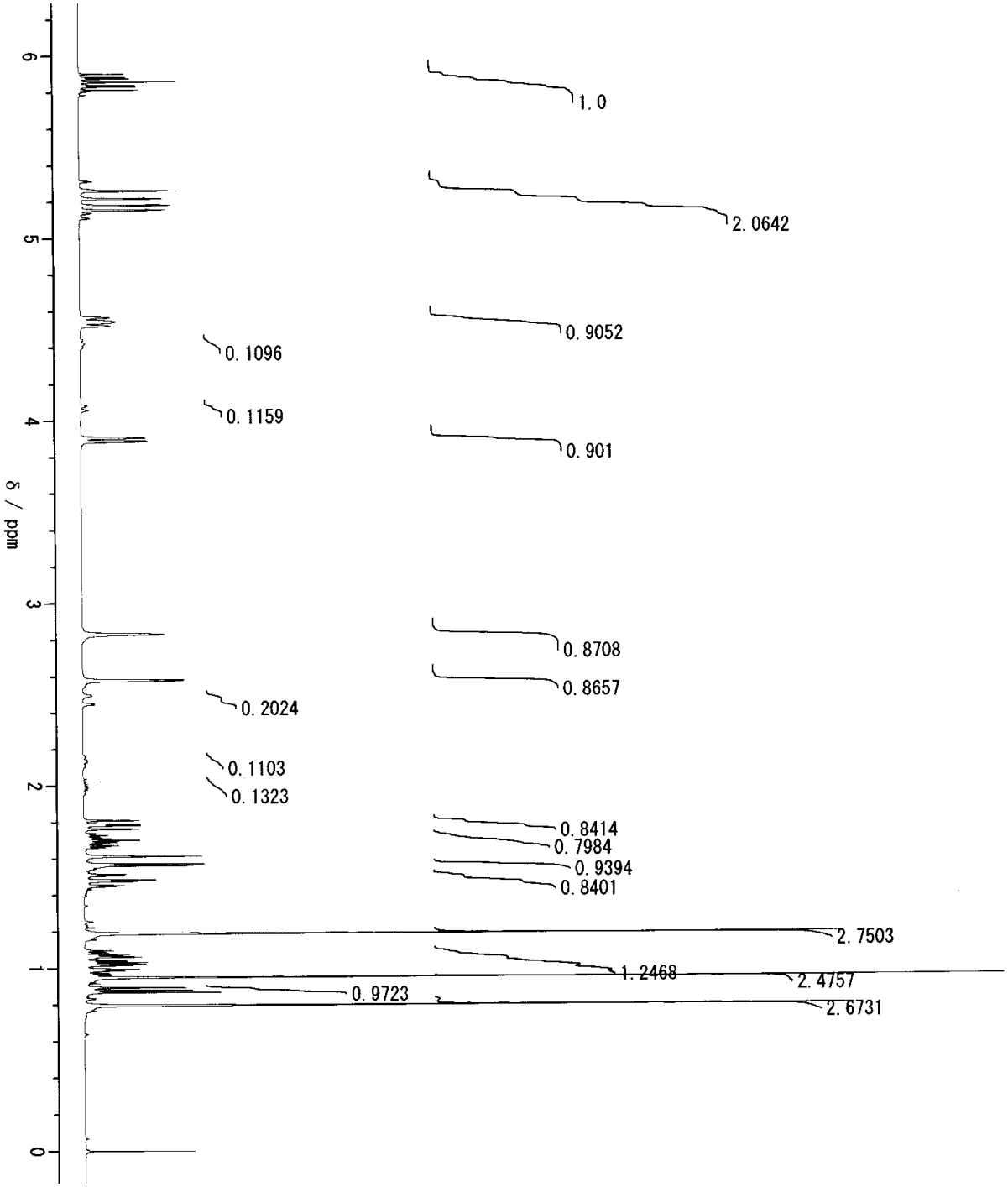


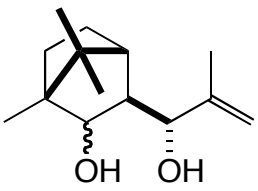
1d mixture of isomers



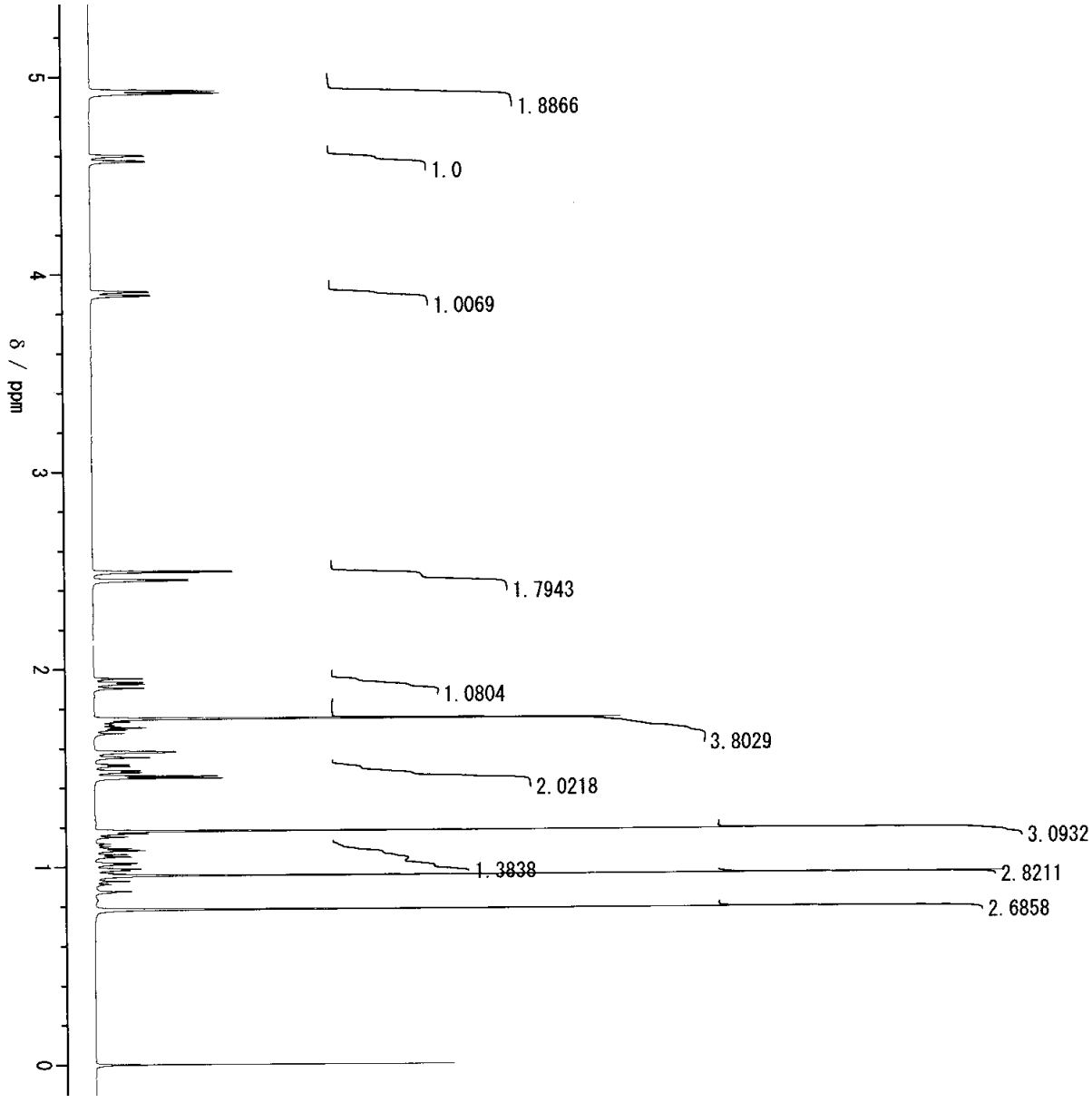

OH
OH

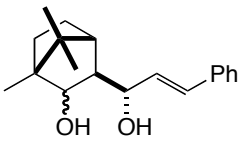
1e


δ / ppm
1.0
2.0642
0.9052
0.1096
0.1159
0.901
0.8708
0.8657
0.2024
0.1103
0.1323
0.8414
0.7984
0.9394
0.8401
2.7503
1.2468
2.4757
0.9723
2.6731

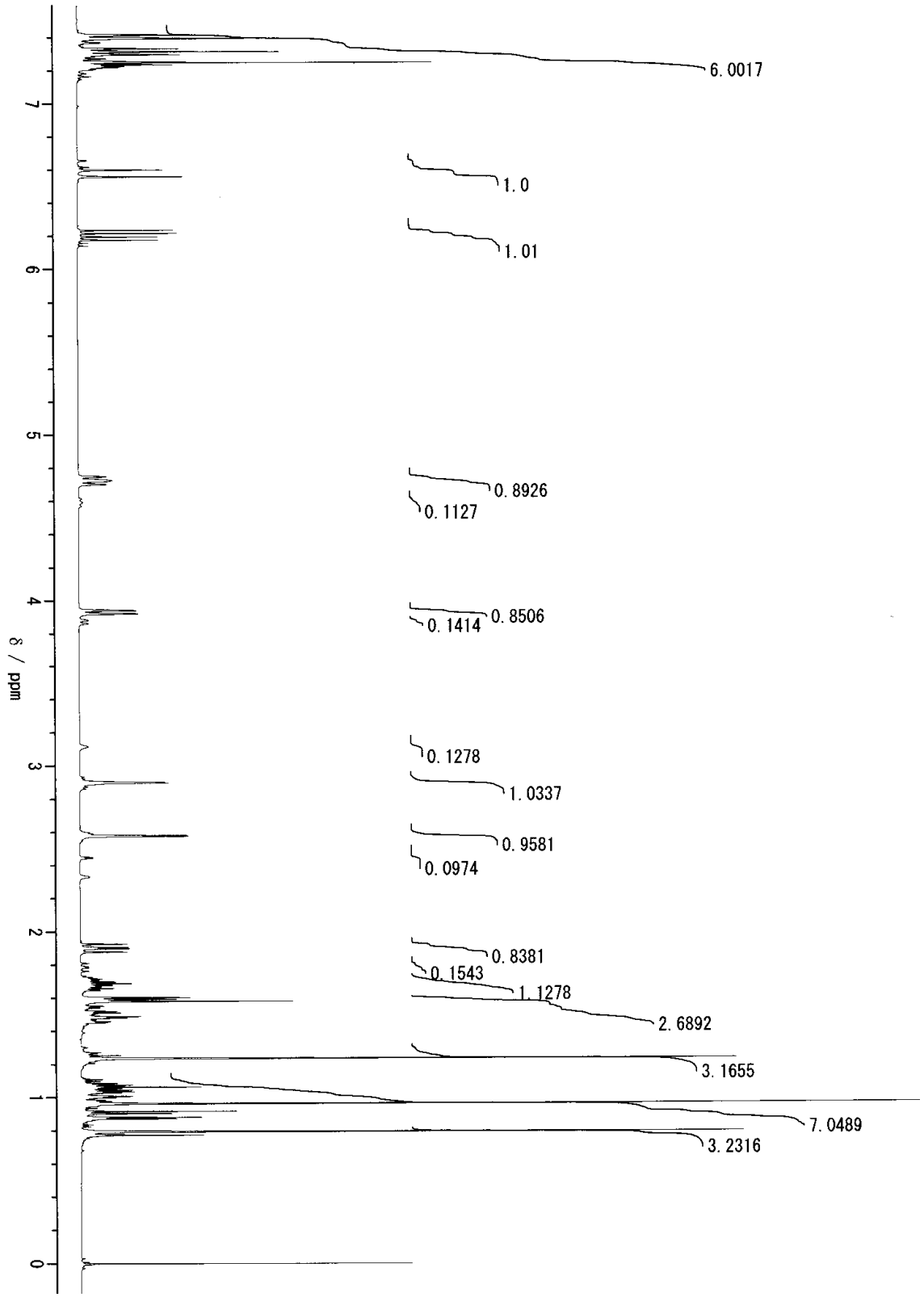

OH
OH

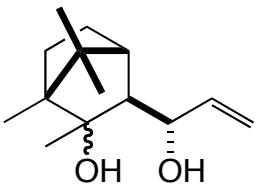
1f


δ / ppm
0
1
2
3
4
5
1.8866
1.0
1.0069
1.7943
1.0804
3.8029
2.0218
3.0932
1.3838
2.8211
2.6858

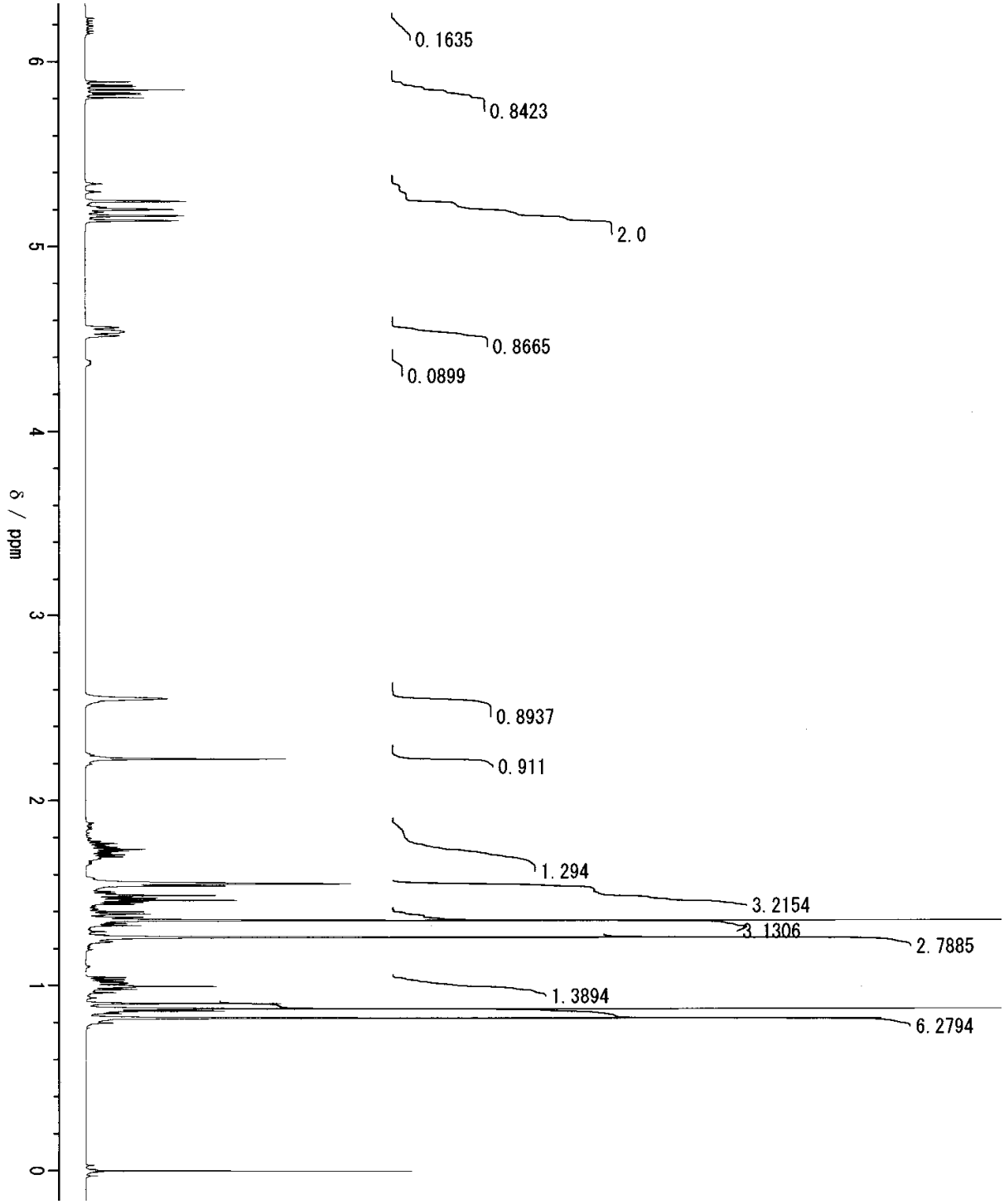

Ph
OH
OH

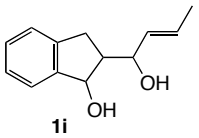
1g


6.0017
1.0
1.01
0.8926
0.1127
0.8506
0.1414
0.1278
1.0337
0.9581
0.0974
0.8381
0.1543
1.1278
2.6892
3.1655
7.0489
3.2316
δ / ppm

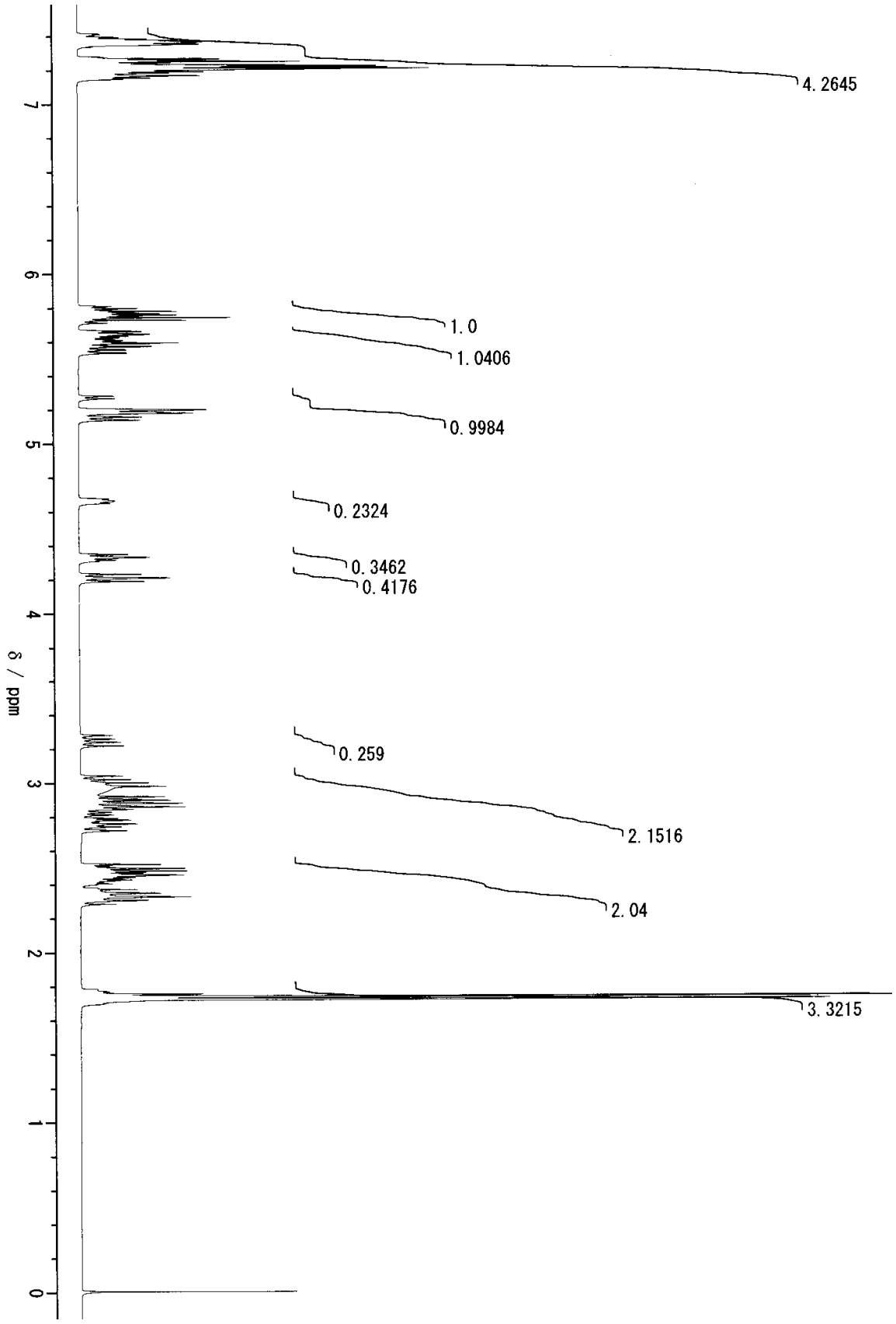

OH
OH

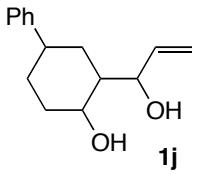
1h


0.1635
0.8423
2.0
0.8665
0.0899
0.8937
0.911
1.294
3.2154
3.1306
2.7885
1.3894
6.2794
δ / ppm
0
1
2
3
4
5
6

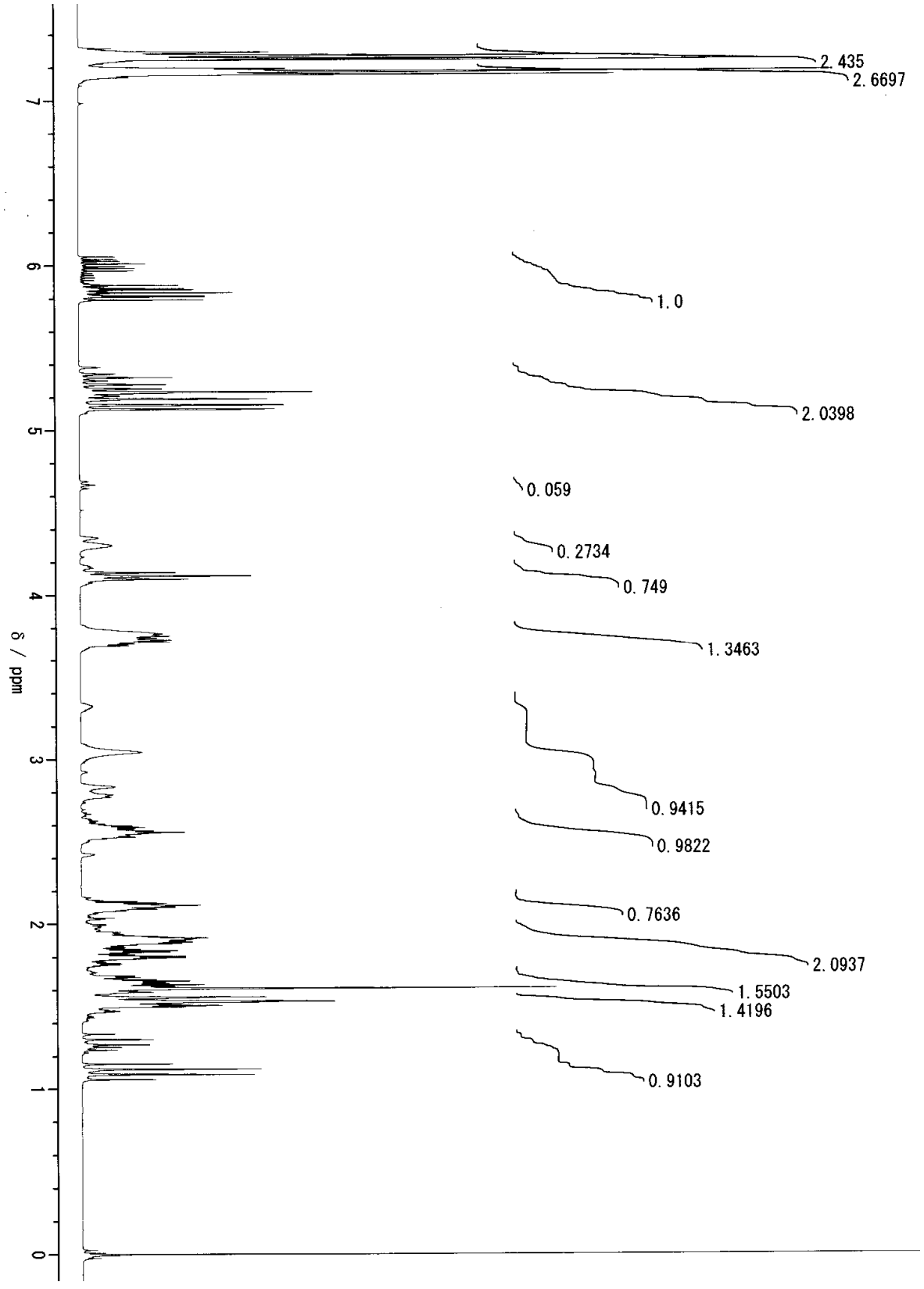

OH
OH

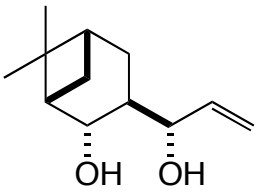
1i


4.2645
1.0
1.0406
0.9984
0.2324
0.3462
0.4176
0.259
2.1516
2.04
3.3215
δ / ppm
0
1
2
3
4
5
6
7

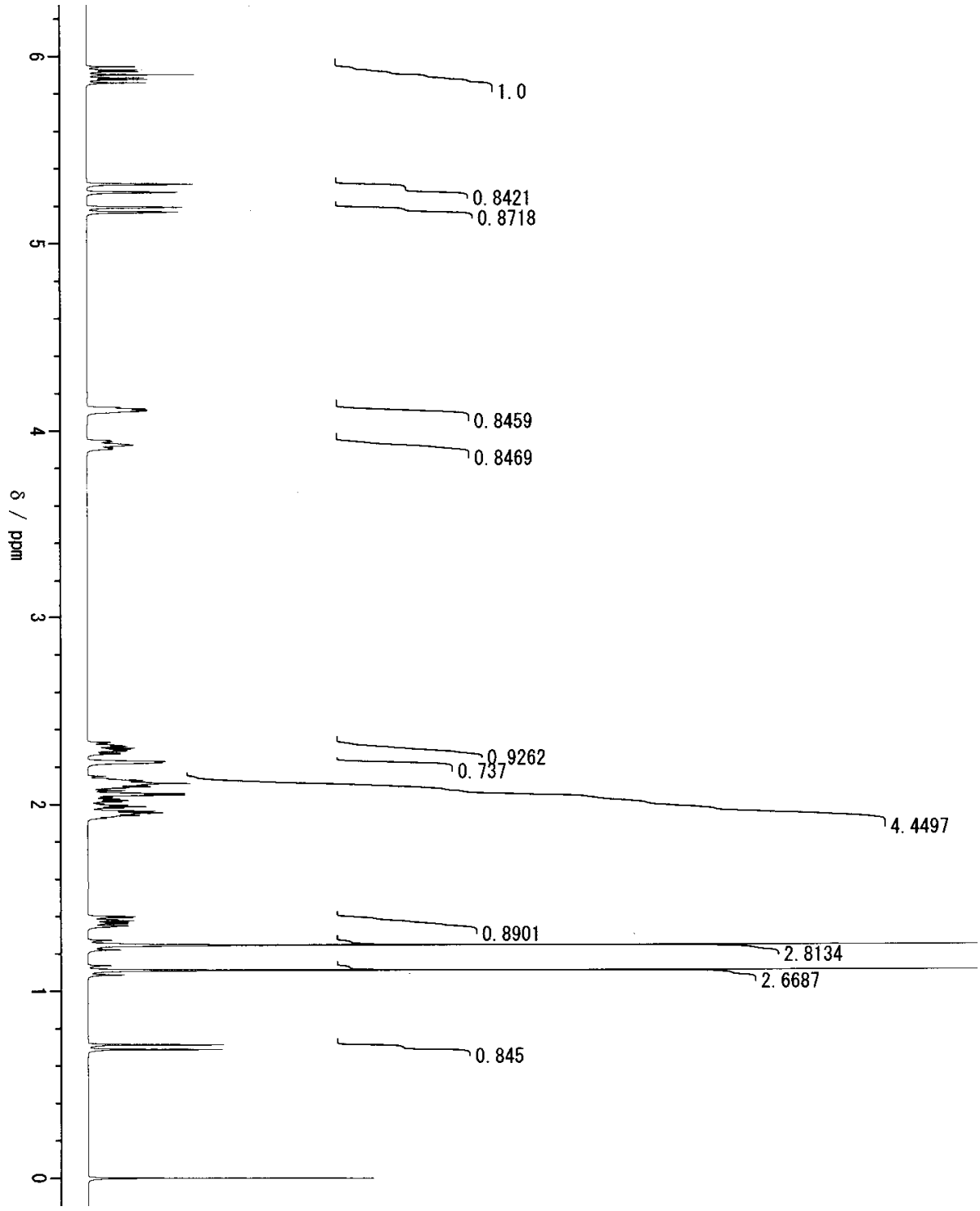

Ph
OH
OH

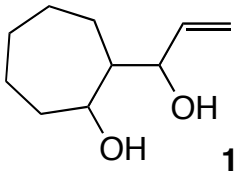
1j


2.435
2.6697
1.0
2.0398
0.059
0.2734
0.749
1.3463
0.9415
0.9822
0.7636
2.0937
1.5503
1.4196
0.9103
δ / ppm
0
1
2
3
4
5
6
7

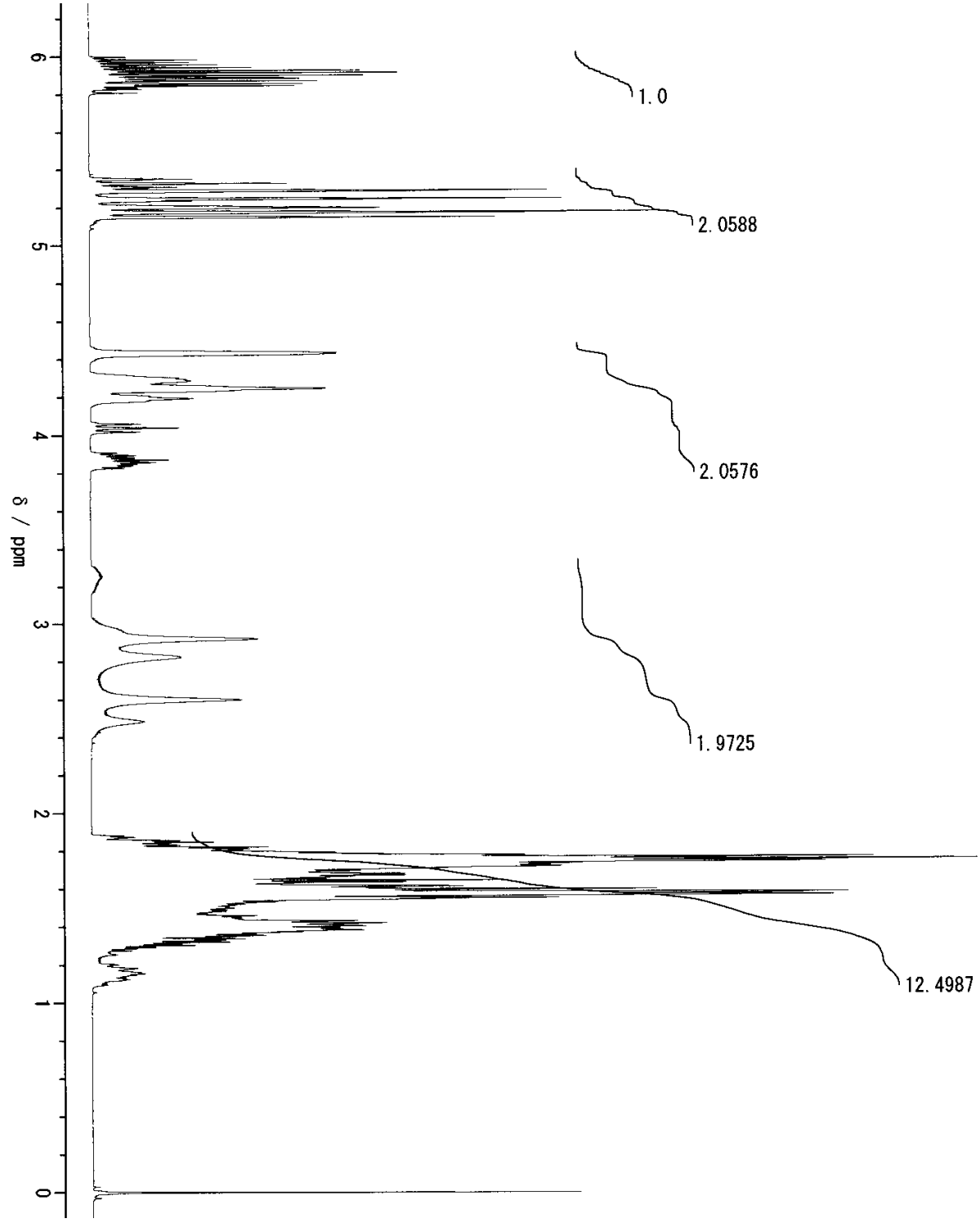

OH
OH

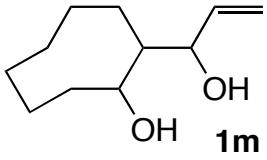
1k


δ / ppm
6
5
4
3
2
1
0
1.0
0.8421
0.8718
0.8459
0.8469
0.9262
0.737
4.4497
0.8901
2.8134
2.6687
0.845

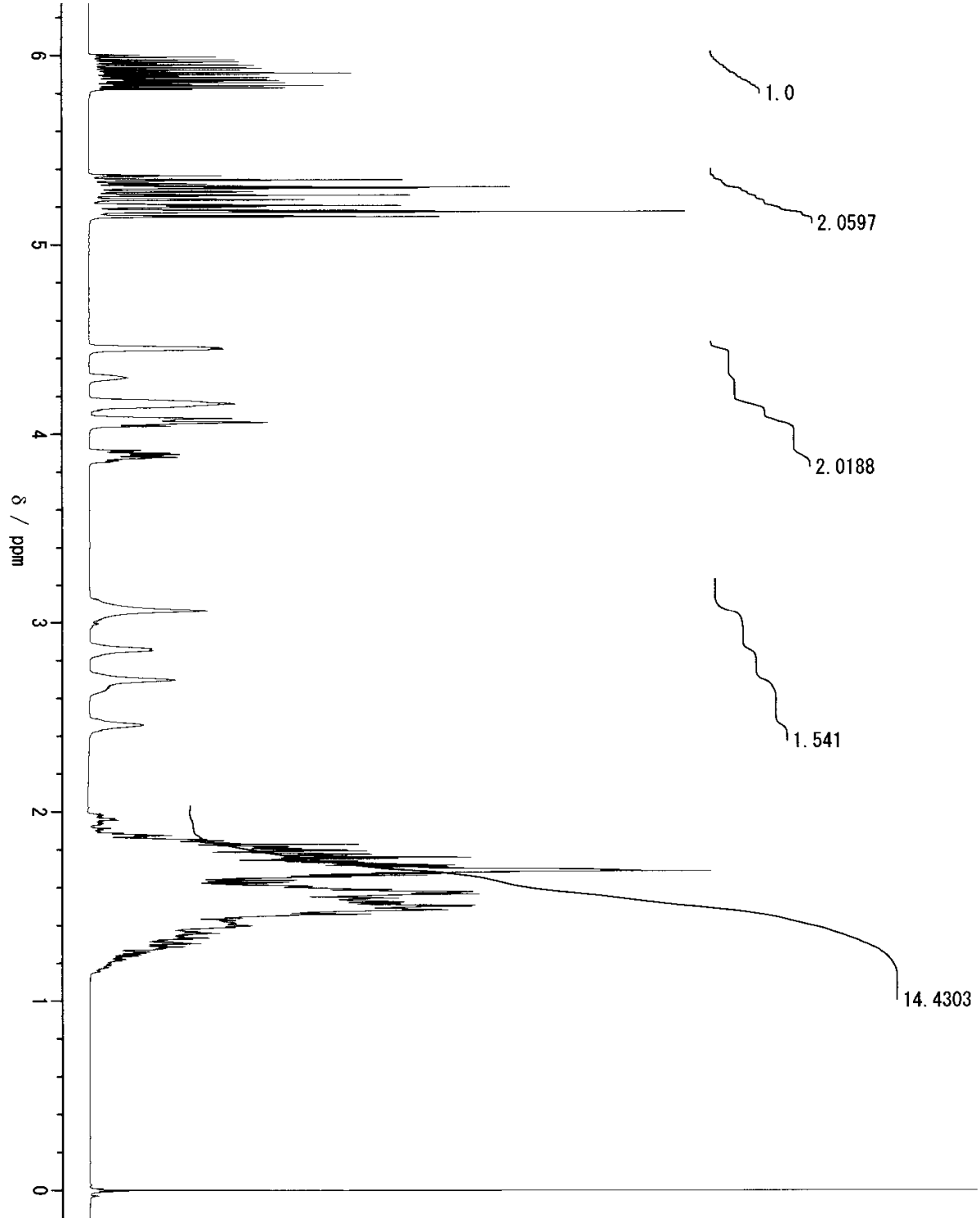


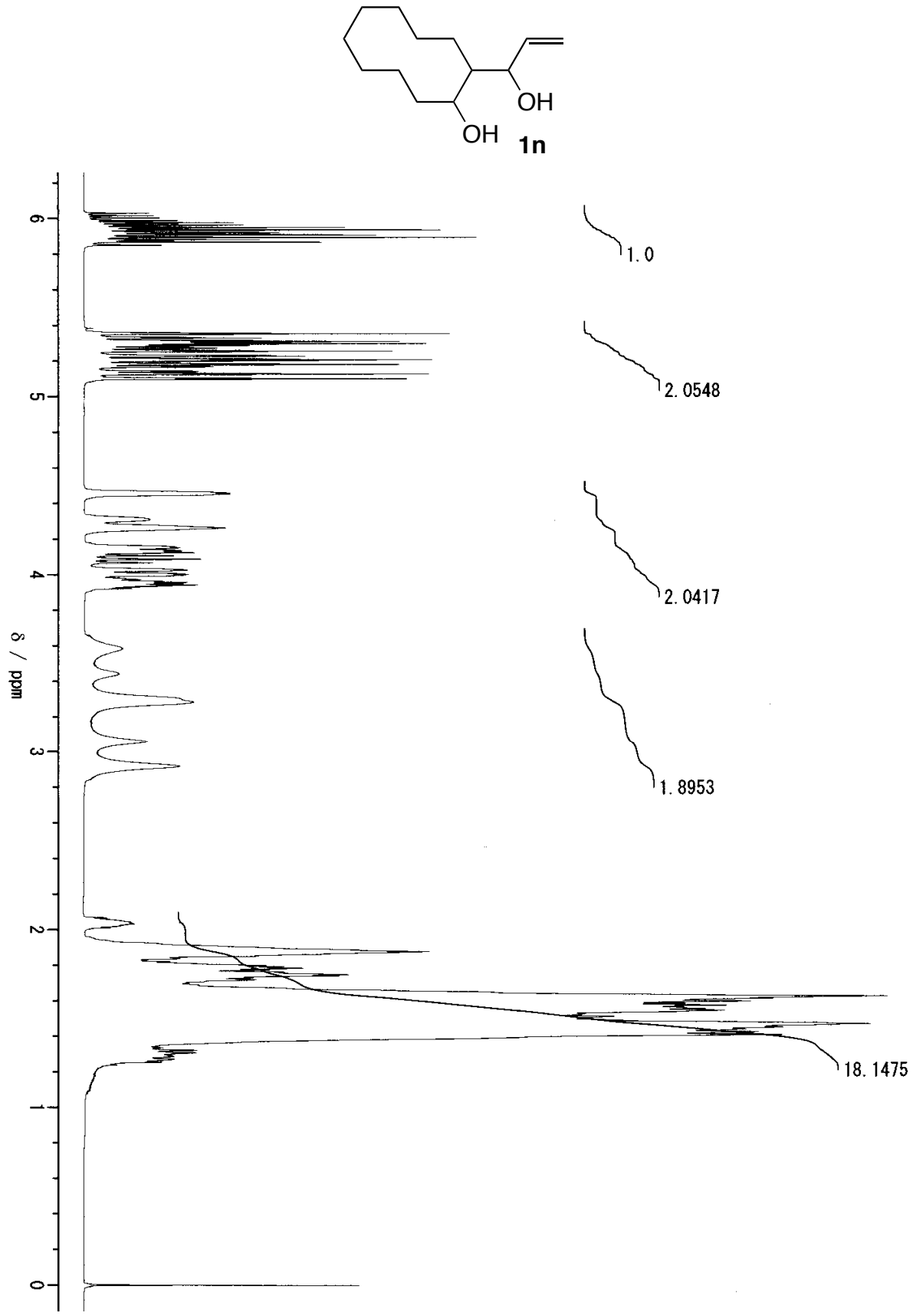
1l

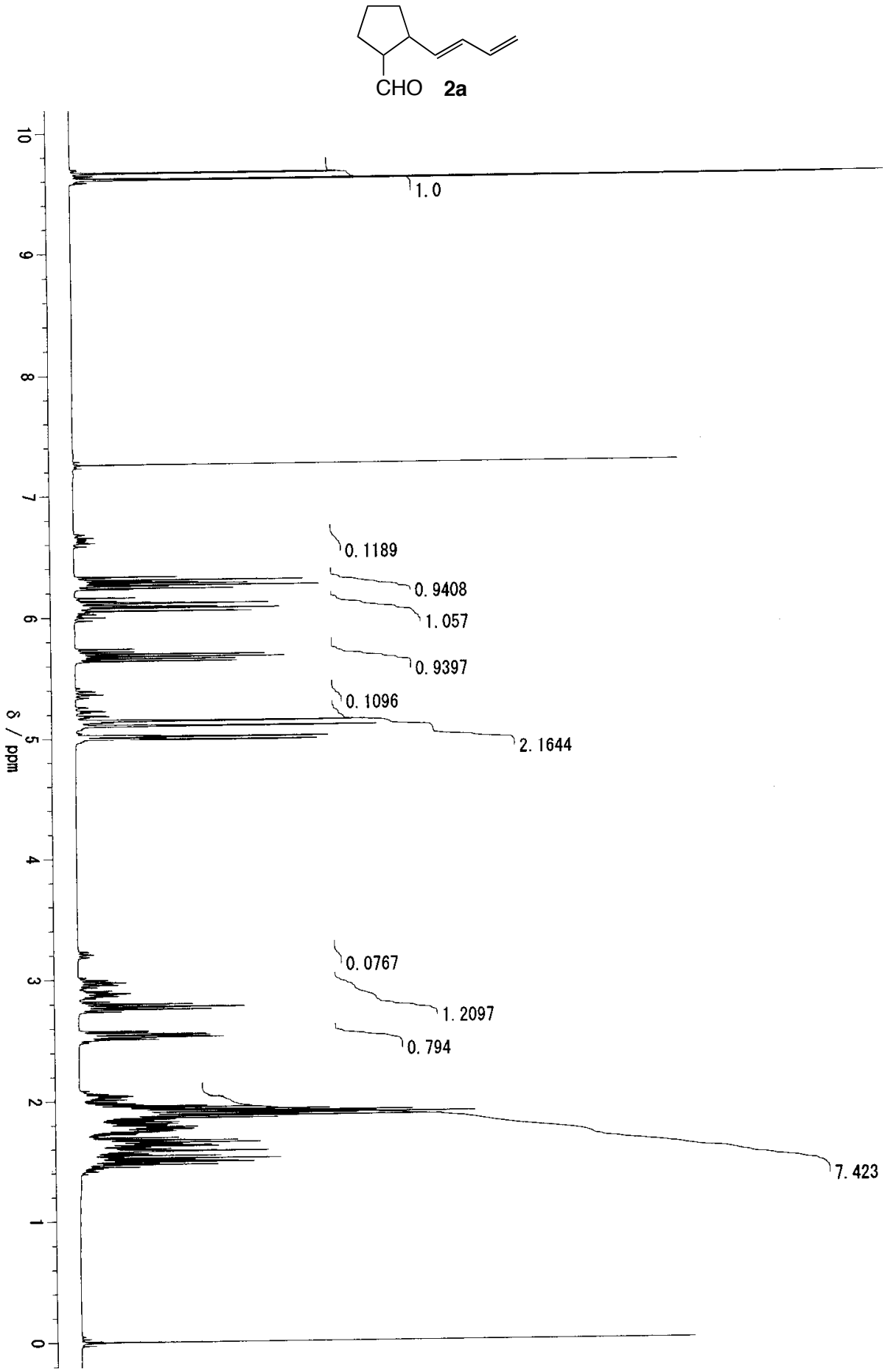


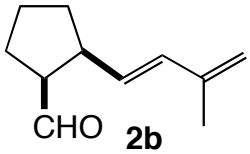


1m



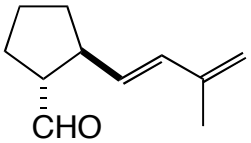

OH
OH
1n
1.0
2.0548
2.0417
1.8953
18.1475
δ / ppm
0
1
2
3
4
5
6

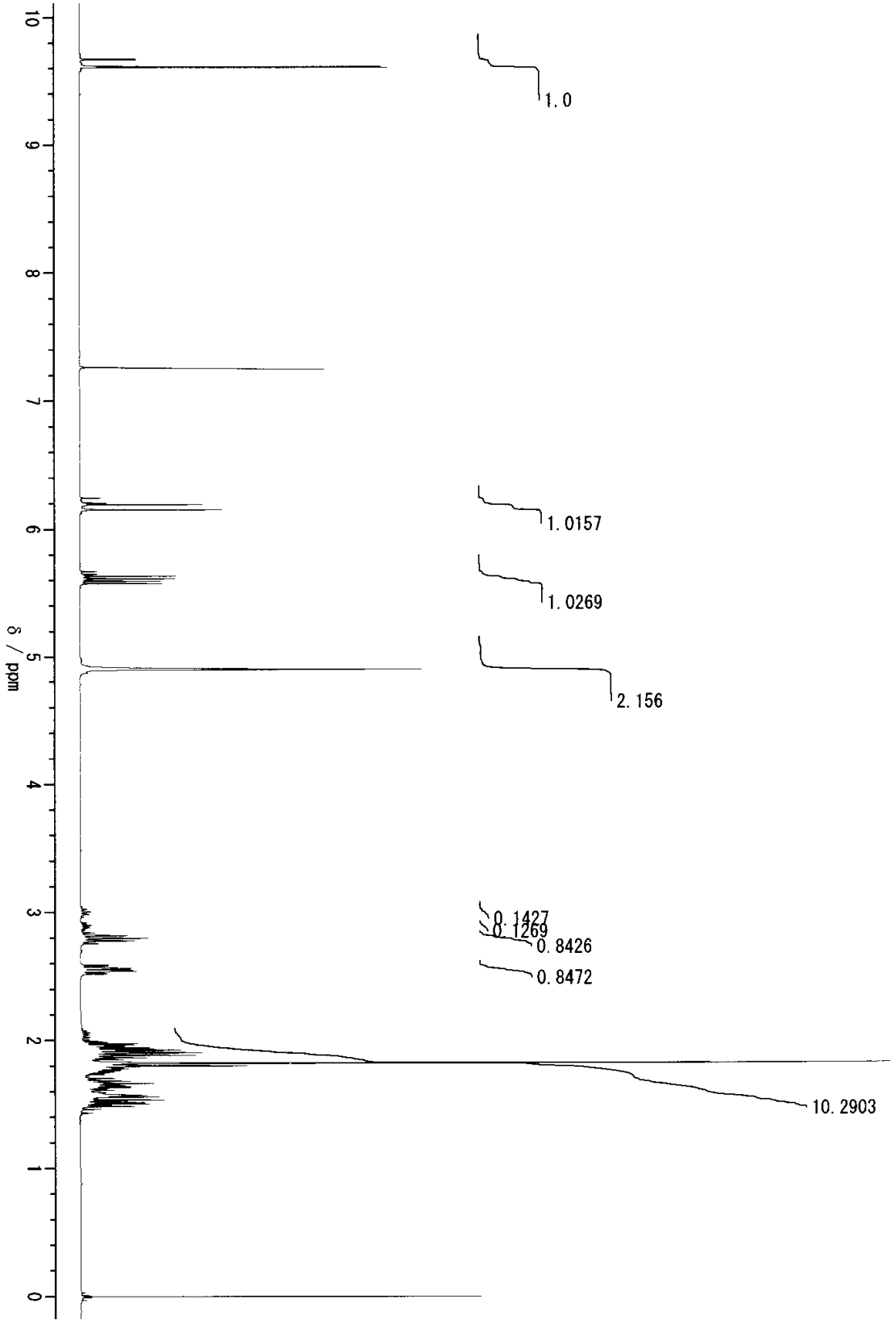

CHO
2a
δ / ppm
1.0
0.1189
0.9408
1.057
0.9397
0.1096
2.1644
0.0767
1.2097
0.794
7.423

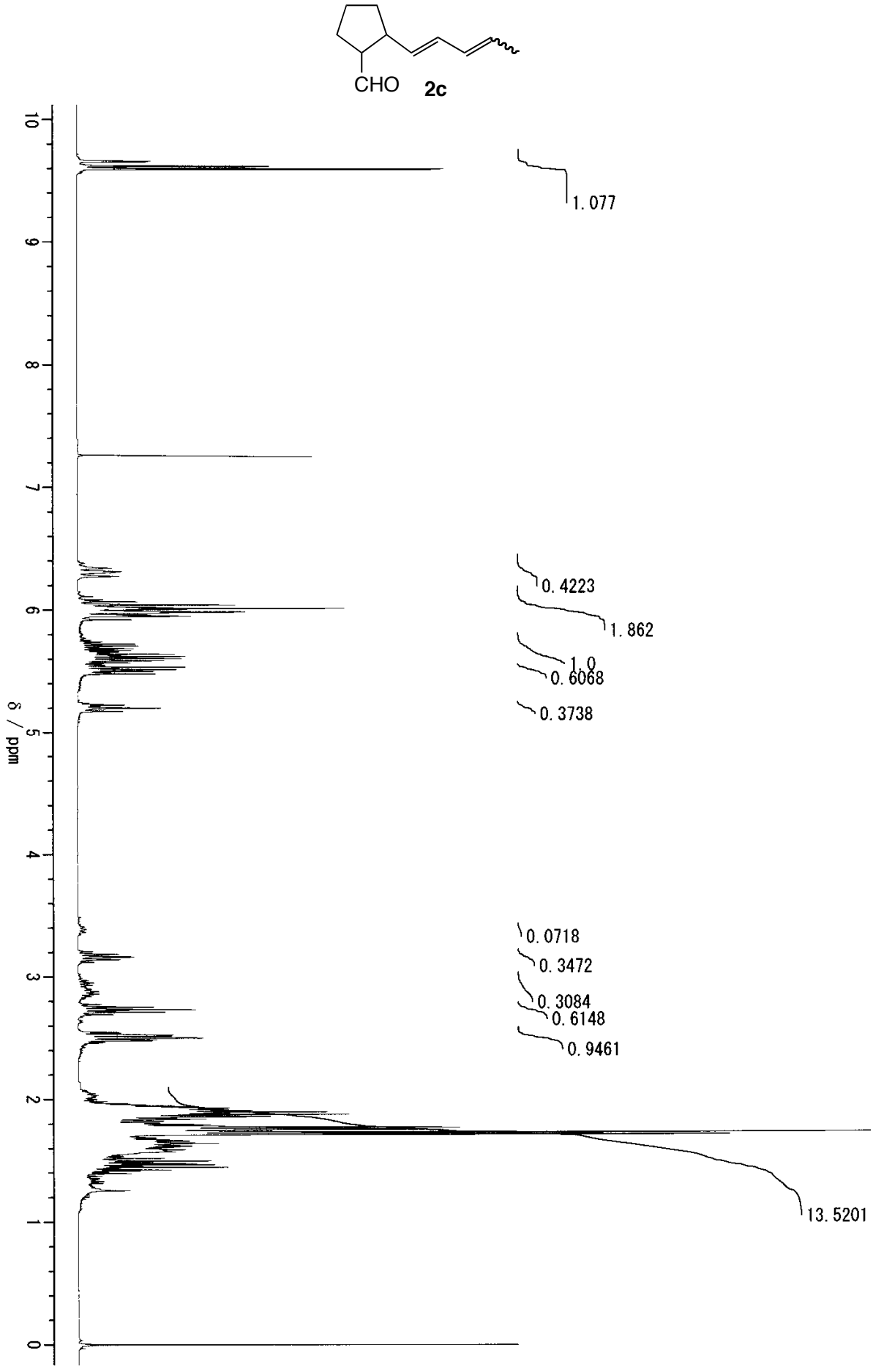


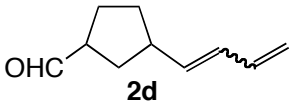
2b

contaminated by a small amount of an epimer of **2b**,

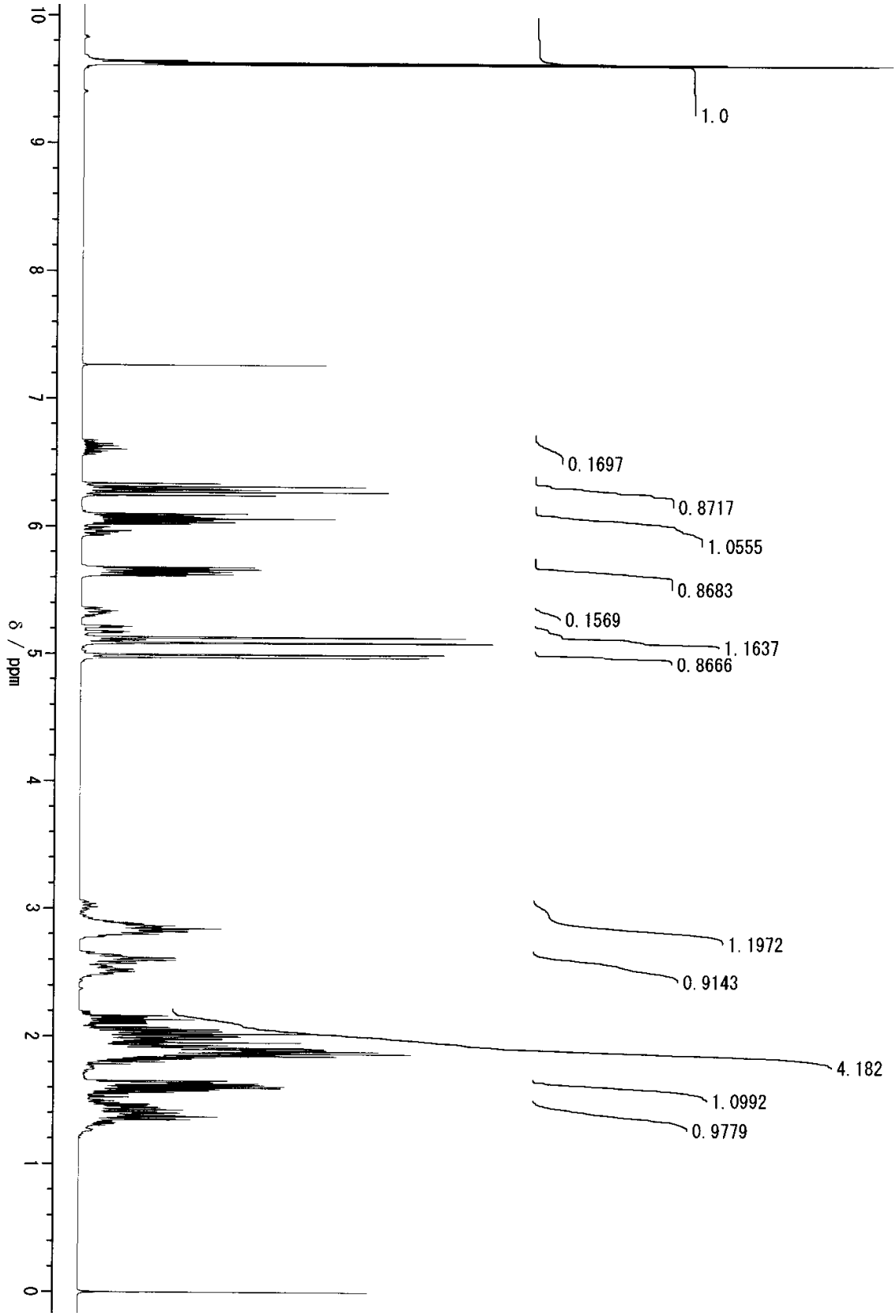


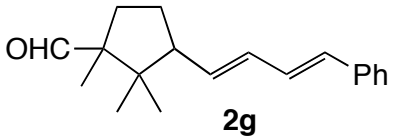



CHO
2c
1.077
0.4223
1.862
1.0
0.6068
0.3738
0.0718
0.3472
0.3084
0.6148
0.9461
13.5201
δ / ppm

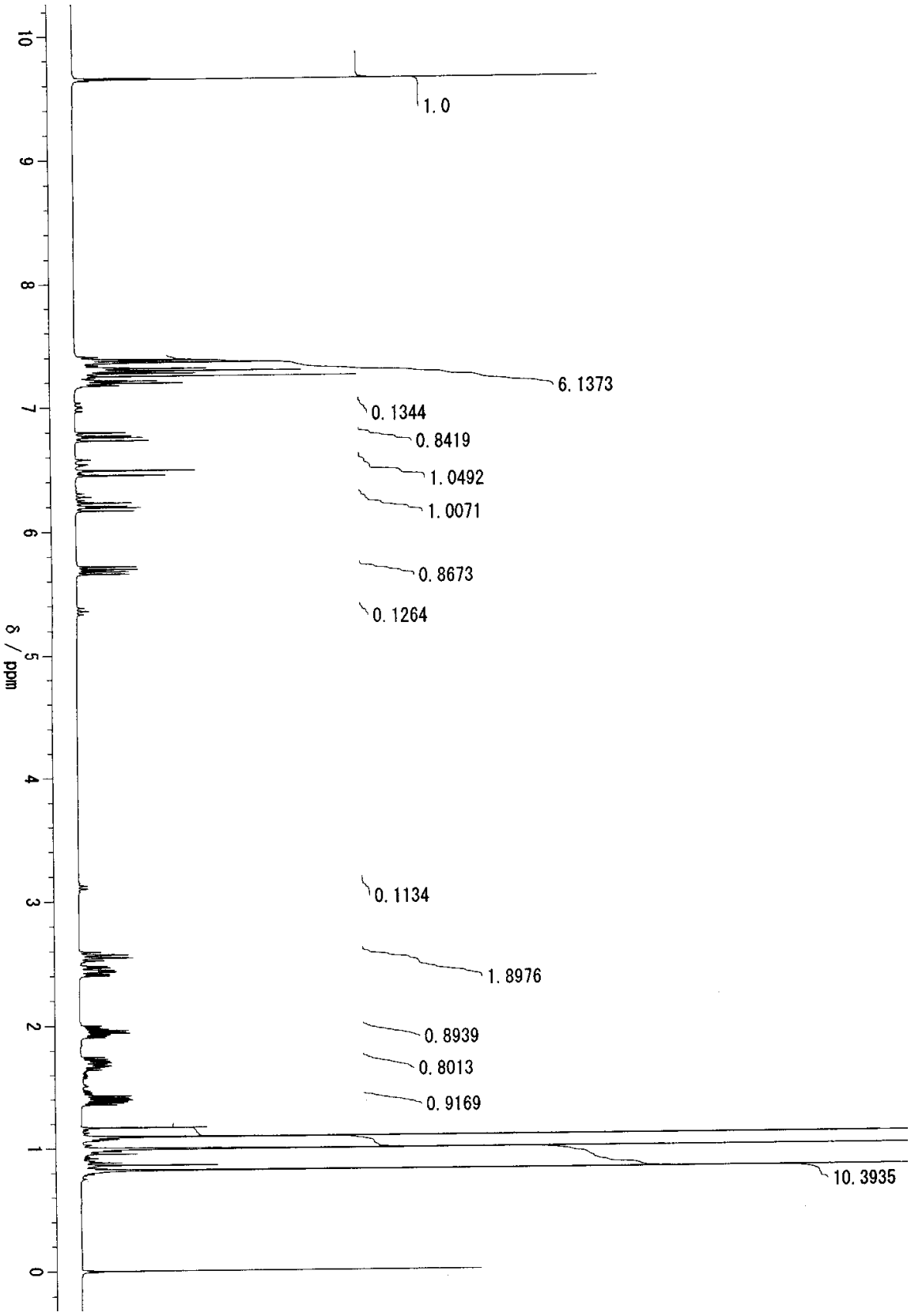

OHC

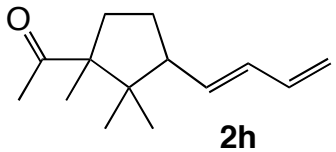
2d


δ / ppm
10
9
8
7
6
5
4
3
2
1
0
1.0
0.1697
0.8717
1.0555
0.8683
0.1569
1.1637
0.8666
1.1972
0.9143
4.182
1.0992
0.9779

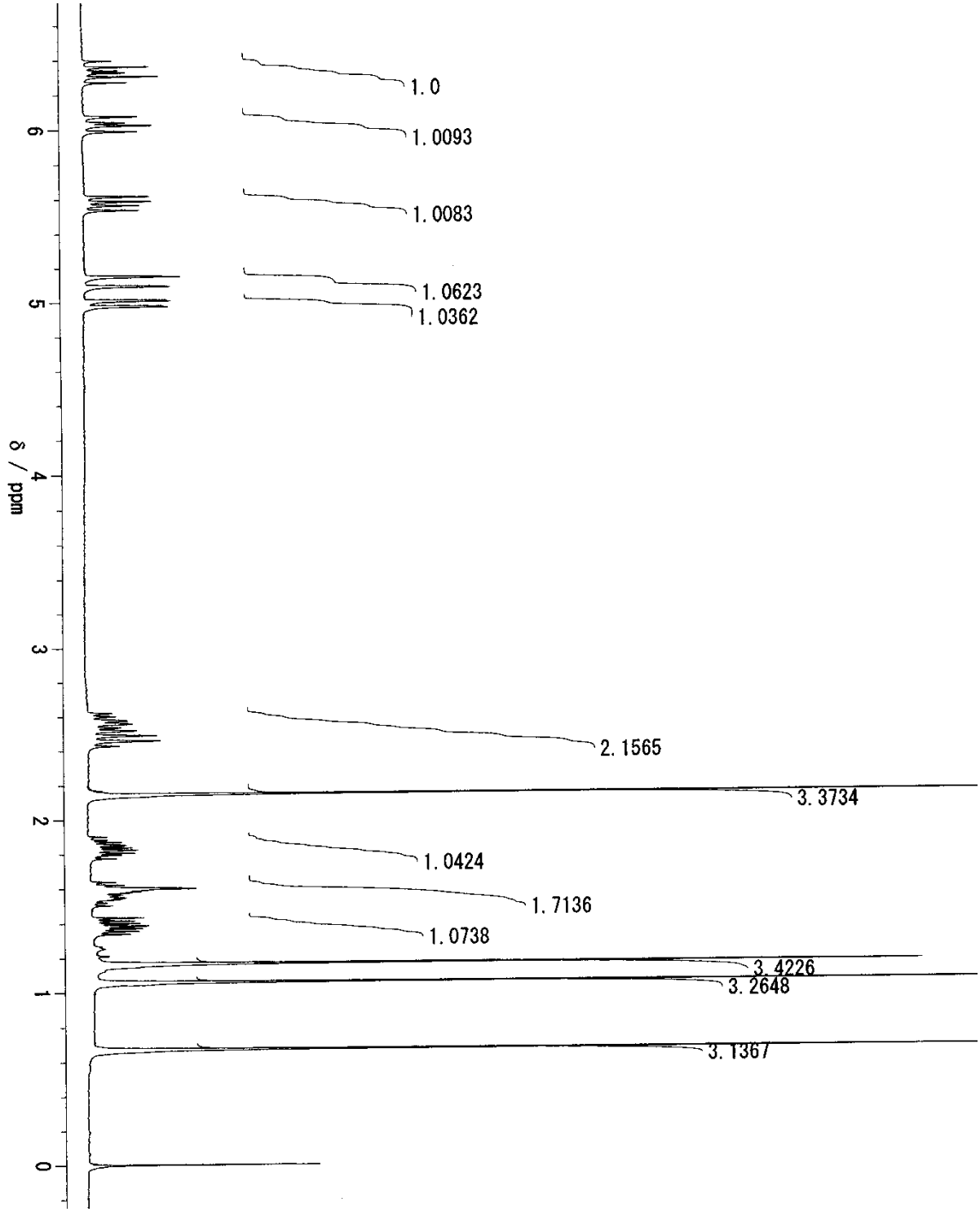

OHC
Ph

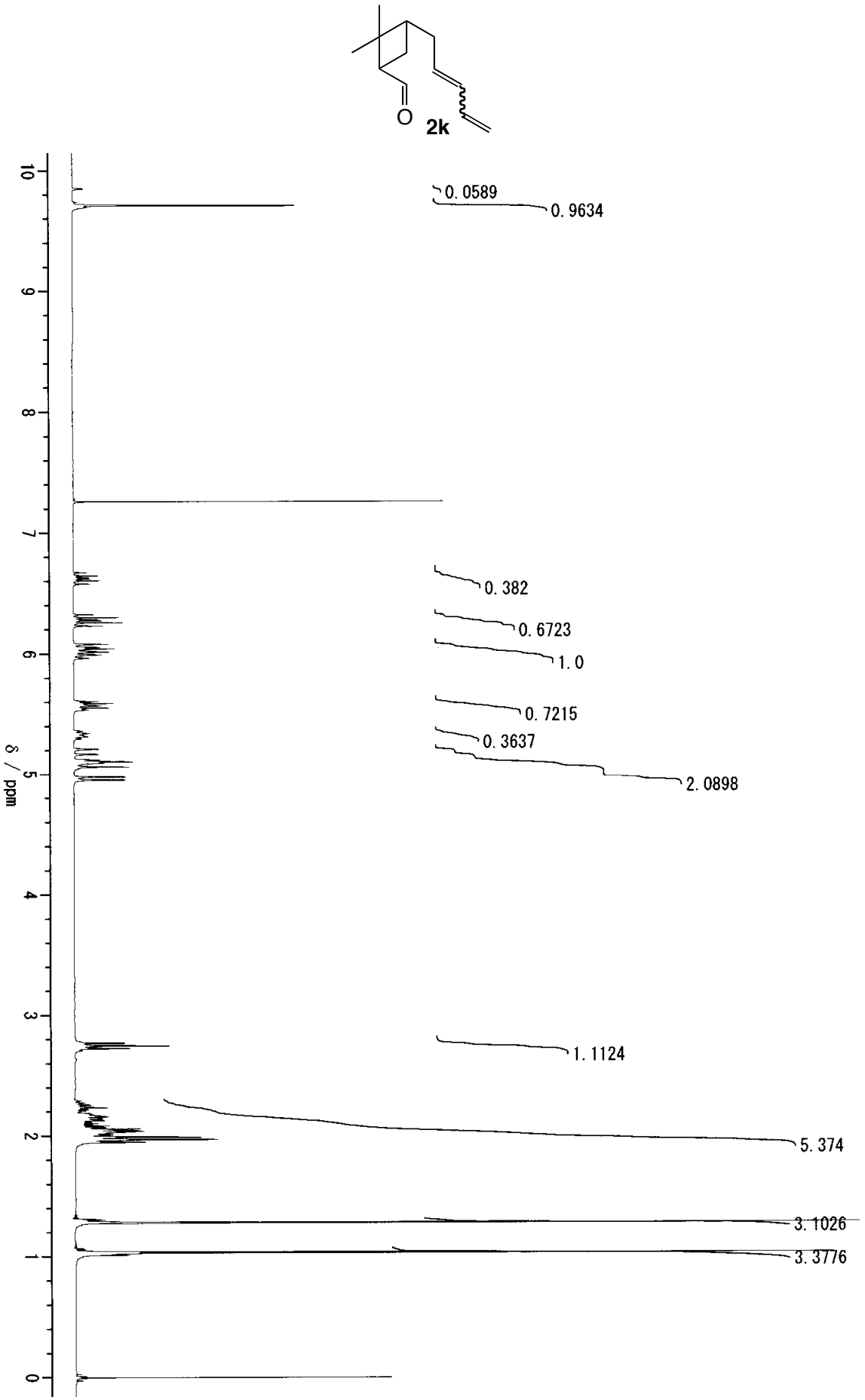
2g

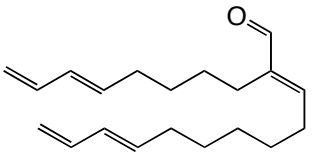

1.0
6.1373
0.1344
0.8419
1.0492
1.0071
0.8673
0.1264
0.1134
1.8976
0.8939
0.8013
0.9169
10.3935
δ / ppm



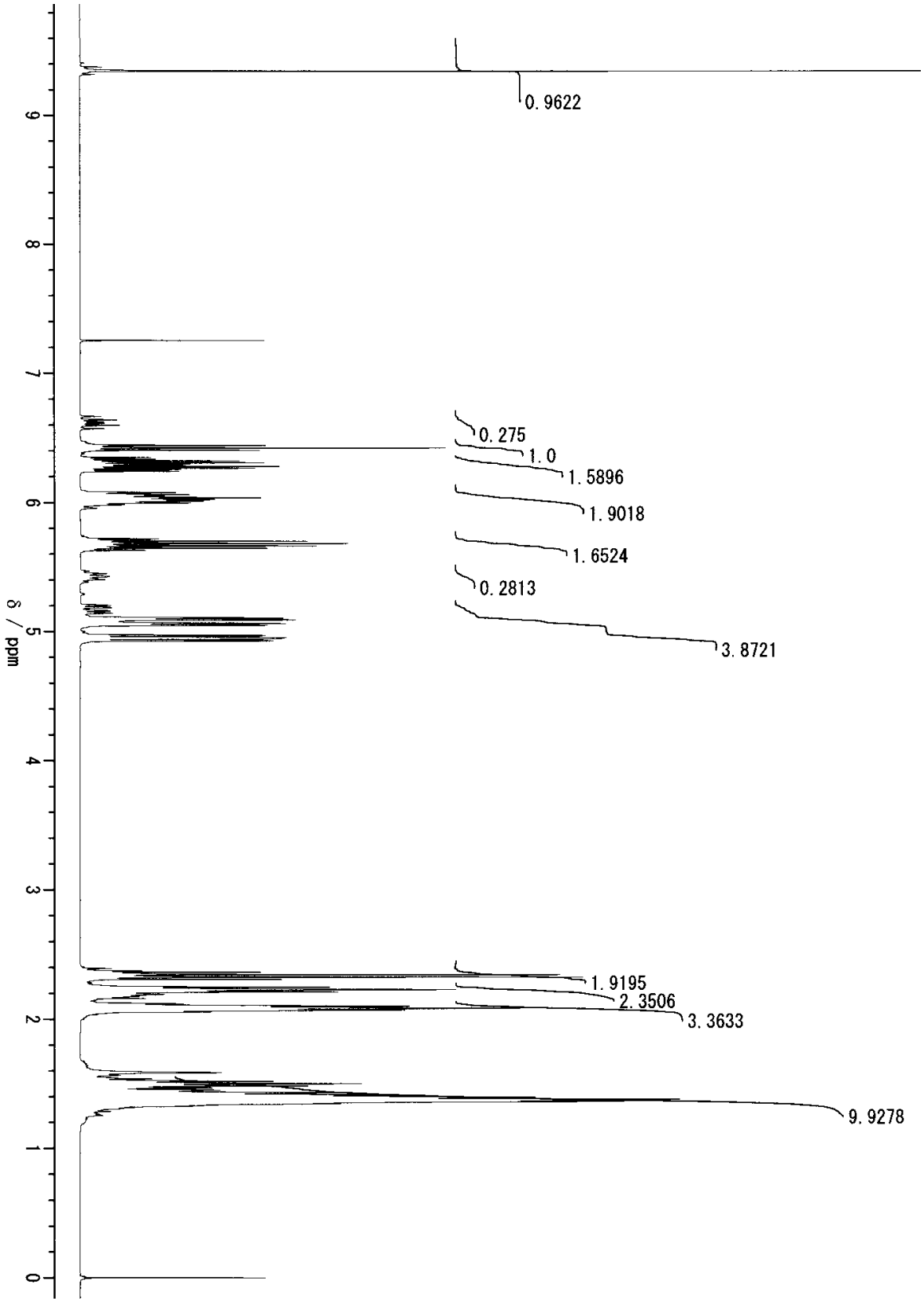
2h

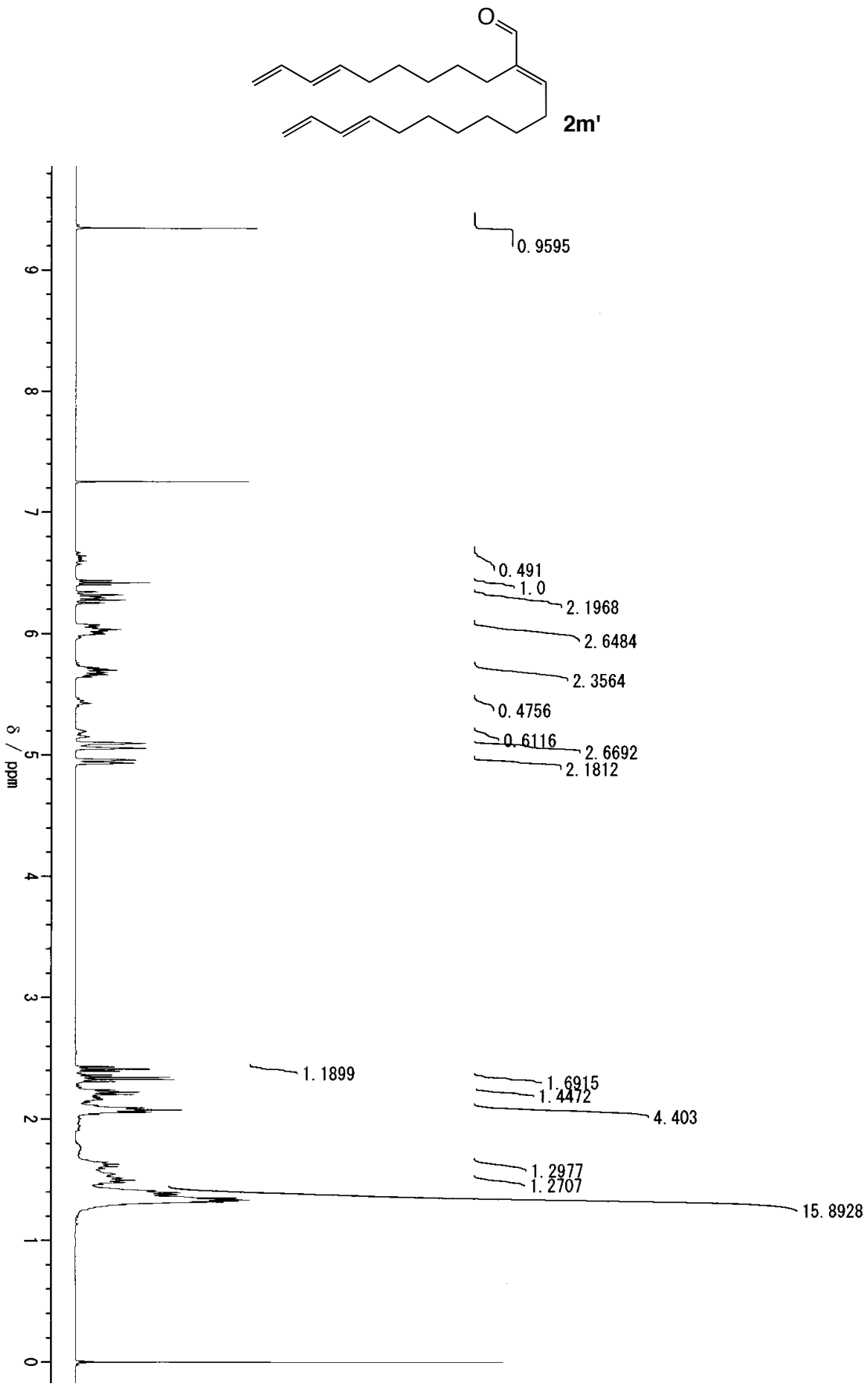

1.0
1.0093
1.0083
1.0623
1.0362
2.1565
3.3734
1.0424
1.7136
1.0738
3.4226
3.2648
3.1367
δ / ppm
0
1
2
3
4
5
6

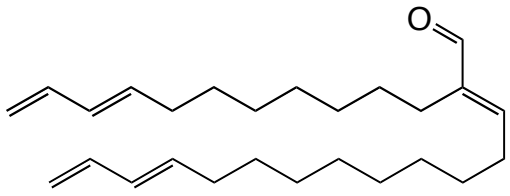

O
2k
0.0589
0.9634
0.382
0.6723
1.0
0.7215
0.3637
2.0898
1.1124
5.374
3.1026
3.3776
δ / ppm


O

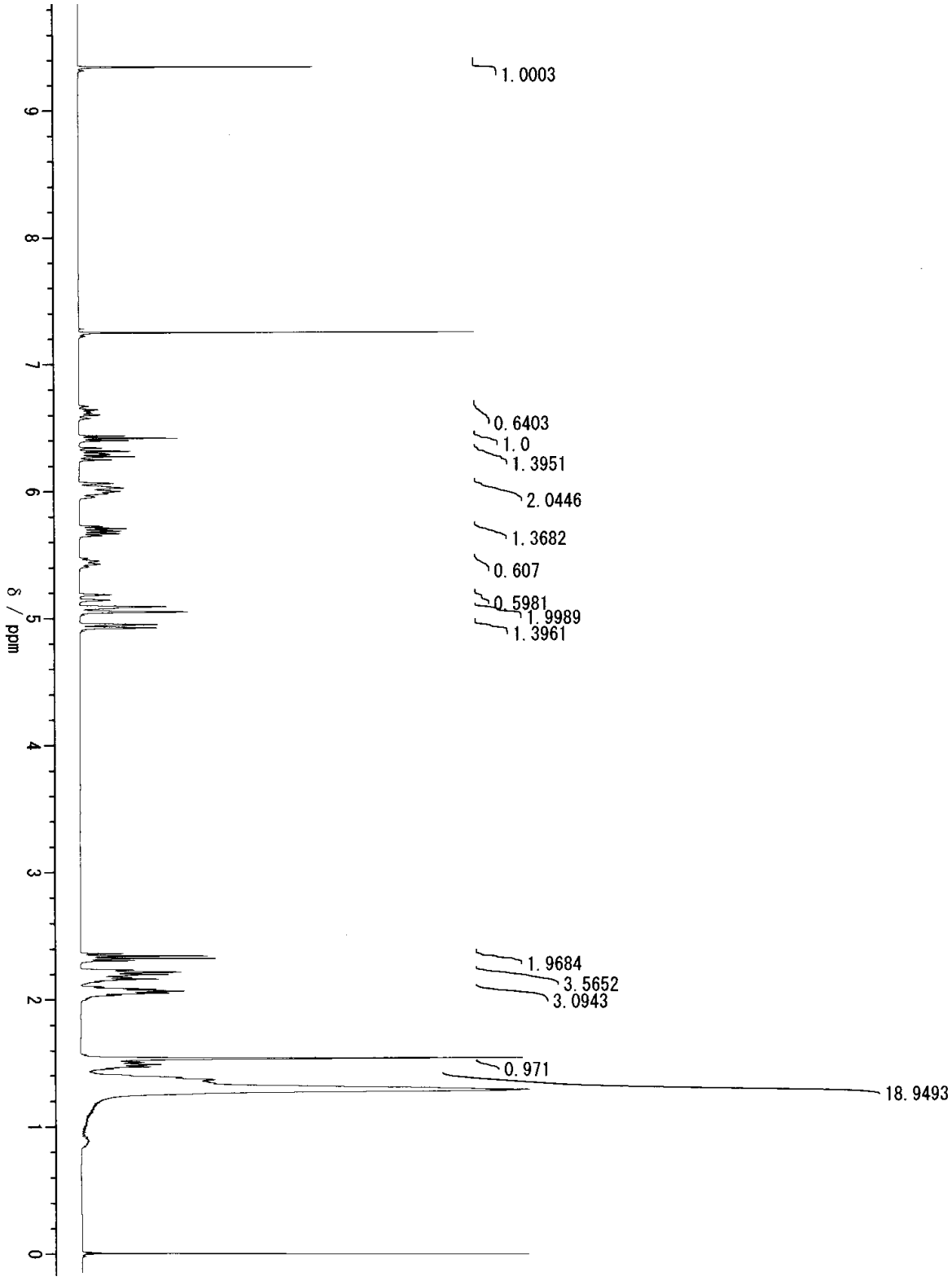
2l'

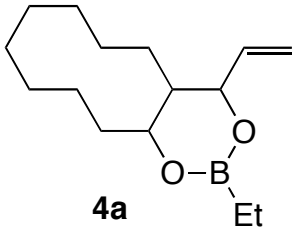

0.9622
0.275
1.0
1.5896
1.9018
1.6524
0.2813
3.8721
1.9195
2.3506
3.3633
9.9278
δ / ppm
9
8
7
6
5
4
3
2
1
0


O
2m'
0.9595
0.491
1.0
2.1968
2.6484
2.3564
0.4756
0.6116
2.6692
2.1812
1.1899
1.6915
1.4472
4.403
1.2977
1.2707
15.8928
δ / ppm
0
1
2
3
4
5
6
7
8
9

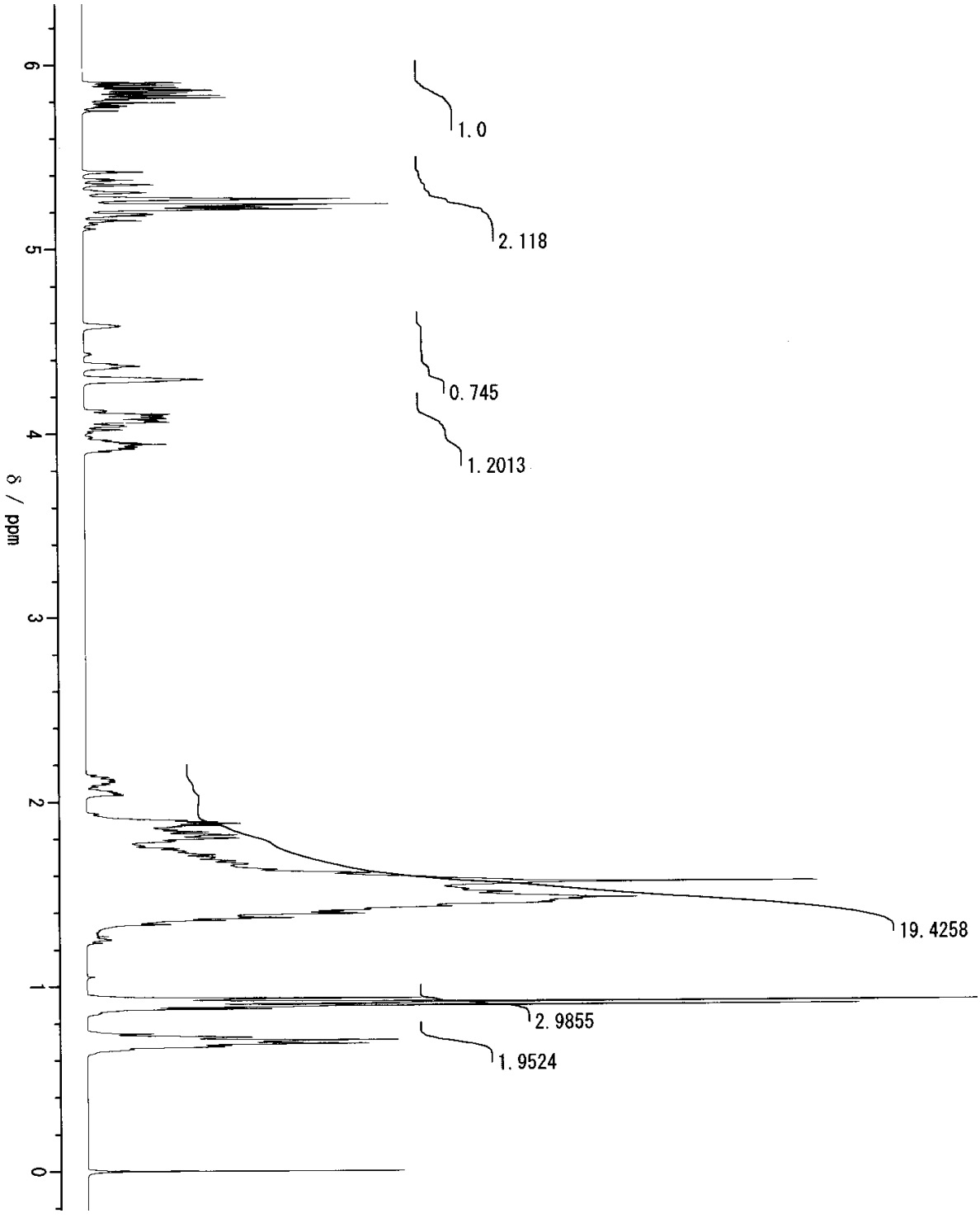

O

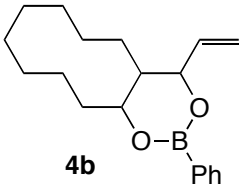
2n'


1.0003
0.6403
1.0
1.3951
2.0446
1.3682
0.607
0.5981
1.9989
1.3961
1.9684
3.5652
3.0943
0.971
18.9493
δ / ppm



4a





4b