Asymmetric 1,4-Dihydroxylation of 1,3-Dienes by Catalytic Enantioselective Diboration

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Supporting Information

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General Information

^{1}H NMR spectra were recorded on Varian Unity Inova 500 MHz and Varian Gemini 400 MHz spectrometers. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.24 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and assignment. $^{13}C\{^{1}H\}$NMR spectra were recorded on Varian Unity Inova 500 MHz (125 MHz) and Varian Gemini 400 MHz (100 MHz) spectrometers. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.00 ppm). $^{31}P\{^{1}H\}$NMR (121 MHz) were recorded on a Varian Unity Inova 300 spectrometer. Chemical shifts are reported for ^{31}P NMR spectra using phosphoric acid as an external standard. Infrared (IR) spectra were recorded on a Bruker α-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (ESI) was performed at Boston College, Chestnut Hill, MA.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA), and potassium permanganate ($KMnO_4$).

Analytical chiral gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series chromatograph equipped with a split mode capillary injection system, a flame ionization detector, and a Supleco β-Dex 120 column with helium as the carrier gas. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Berger Instruments Supercritical Chromatograph equipped with an Alcott auto sampler and a Knauer UV detector with methanol as the modifier. Analytical chiral high-performance liquid chromatography (HPLC) was performed on a Shimadzu SCL-10A liquid chromatograph equipped with a UV detector and a Daicel Chiracel-OD column.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Toluene, tetrahydrofuran, methylene chloride, and diethyl ether were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after being purged with argon. Triethylamine was distilled from calcium hydride. Potassium tetrachloroplatinate(II) was purchased from Strem Chemicals, Inc. Bis(pinacolato)diboron was obtained from Allychem Co., Ltd. and recrystallized from pentanes prior to use. Dibenzylideneacetone was purchased from Oakwood Chemicals. 1-methyl-1,3-cyclohexadiene were purchased from ChemSampCo. *trans*-1,3-hexadiene and *cis*-1,3-pentadiene were purchased from TCI America. Tetrapropylammonium perruthenate was purchased from Strem Chemicals, Inc. All other reagents were purchased from Aldrich and used without further purification. (*R*,*R*)-xylylTADDOLPPh (**L1**) was prepared according to literature procedure.[1]

[1] Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2008**, *130*, 4978.

Experimental Procedures

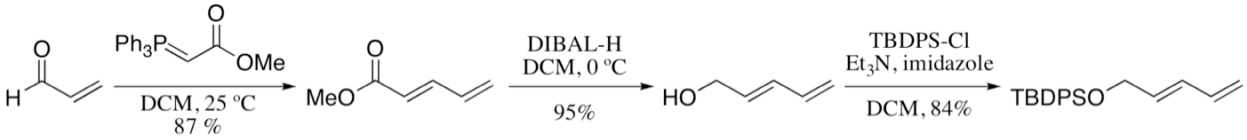
I. Preparation of $Pt_2(dba)_3$.

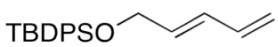
Tris(dibenzylideneacetone)diplatinum was prepared using the literature procedure[2] with slight modification. To a 3-neck 500-mL round-bottomed flask equipped with a magnetic stir bar and reflux condenser was added dibenzylideneacetone (3.95 g, 16.8 mmol), tetrabutylammonium chloride (2.0 g, 7.2 mmol), and sodium acetate (3.55 g, 43.3 mmol). Salts were dissolved in methanol and the solution was warmed to 70 °C and allowed to stir for 5 min. To a 50-mL pear-shaped flask was added potassium tetrachloroplatinate (1.00 g, 2.41 mmol). The potassium salt was dissolved in water (8 mL) with mild heating. The 3-neck round-bottomed flask was charged with the potassium tetrachloroplatinate solution and the reaction was allowed to stir at 70 °C for 3 h. After 3 h, the reaction was cooled to ambient temperature, transferred to a 500-mL round-bottomed flask and concentrated by rotary evaporation to half the volume. The reaction mixture was filtered on a Büchner funnel; solids were washed with copious amounts of water and methanol until all yellow dibenzylideneacetone crystals were no longer visible. The platinum catalyst was placed under the high vacuum for 24h to remove residual methanol and water, and tris(dibenzylideneacetone)diplatinum was obtained as a brown solid (1.84 g, 70% yield). Spectroscopic characterization of the platinum catalyst was in accord with spectra reported in the literature.[2]

II. Preparation of 1,3-Dienes.

A. The following dienes were prepared by Wittig olefination of the commercially available α,β-unsaturated aldehydes with methyltriphenylphosphonium bromide and potassium *tert*-butoxide in tetrahydrofuran: *trans*-1-Phenyl-1,3-butadiene (Table 1, entry 6),[3] *trans*-1-cyclohexyl-1,3-butadiene (Table 1, entry 3),[4] *trans*-1,3-decadiene (Table 1, entry 1),[5] *trans*-6-phenyl-1,3-hexadiene (Table 1, entry 2).[5] Spectral data are in accordance with the literature references.

B. Preparation of (E)-tert-butyl(penta-2,4-dienyloxy)diphenylsilane.



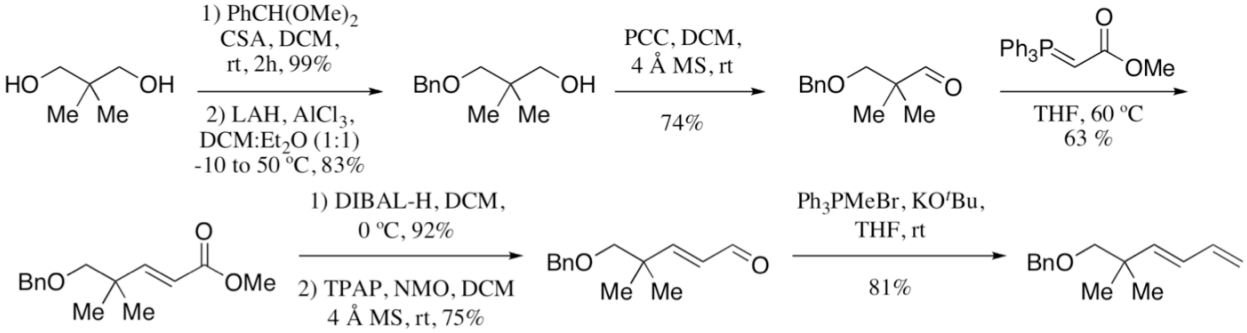


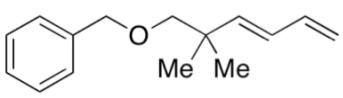
(*E*)-tert-butyl(penta-2,4-dienyloxy)diphenylsilane (Table 1, entry 8). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (9H, s, C(C**H$_3$)$_3$**, 4.23 (2H, d, *J* = 5.2 Hz, SiOC**H$_2$**CH), 5.05 (1H, d, *J* = 10.4 Hz, CH–CH=C**H$_{cis}$**H$_{trans}$), 5.17 (1H, d, *J* = 16.8 Hz, CH–CH=CH$_{cis}$**H$_{trans}$**), 5.77 (1H, dt, *J* = 14.4 Hz, 4.8 Hz, SiOCH$_2$C**H**), 6.25-6.36 (2H, m, CH$_2$CH=C**H**C**H**), 7.34-7.43 (6H, m, Si**Ar**), 7.65-7.68 (4H, m, Si**Ar**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.6, 135.5, 133.6, 132.8, 130.3, 129.6, 127.6, 116.5, 64.0, 26.9, 19.3; IR (neat):

[2] Lewis, L. N.; Krafft, T. A.; Huffman, J. C. *Inorg. Chem.* **1992,** *31*, 3555.
[3] Yeh, K. L.; Liu, B.; Lo, C. Y.; Huang, H. L.; Liu, R. S. *J. Am. Chem. Soc.* **2002**, *124*, 6510.
[4] Habrant, D.; Stengel, B.; Meunier, S.; Mioskowski, C. *Chem. –Eur. J.* **2007**, *13*, 5433.
[5] Meyers, A. I.; Ford, M. E. *J. Org. Chem.* **1976**, *41*, 1735.

2930.6 (w), 2856.9 (w), 1427.6 (m), 1111.1 (s), 1003.8 (m), 822.8 (w), 739.3 (w), 701.0 (s), 504.3 (m); HRMS-(ESI+) for $C_{21}H_{27}O_1Si_1$ [M+H]: calculated: 323.1831, found: 323.1835.

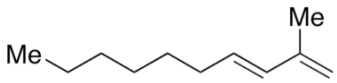
C. Preparation of (E)-((2,2-dimethylhexa-3,5-dienyloxy)methyl)benzene.





(*E*)-((2,2-dimethylhexa-3,5-dienyloxy)methyl)benzene (Table 1, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (6H, s C(C**H$_3$**)$_2$), 3.12 (2H, s, BnOC**H$_2$**), 4.44 (2H, s, PhC**H$_2$**), 4.91 (1H, dd, *J* = 10.2 Hz, 1.8 Hz, CH=C**H$_{cis}$**H$_{trans}$), 5.04 (1H, dd, *J* = 17.0 Hz, 1.8 Hz, CH=CH$_{cis}$**H$_{trans}$**), 5.68 (1H, d, *J* = 16.0 Hz, (CH$_3$)$_2$CC**H**=CH), 5.97 (1H, dd, *J* = 15.6 Hz, 10.4 Hz, CH=C**H**CH=CH$_2$), 6.24 (1H, dt, *J* = 16.8 Hz, 8.6 Hz, CH$_2$=C**H**CH), 7.14-7.27 (5H, m, **Ph**CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 138.7, 137.6, 128.2, 127.9, 127.3, 115.2, 79.2, 73.3, 37.6, 24.6; IR (neat): 2959.9 (w), 2859.1 (w), 1496.3 (w), 1377.4 (w), 1096.0 (s), 1004.1 (s), 951.6 (w), 898.1 (m), 734.3 (s), 696.6 (s); HRMS-(ESI+) for $C_{15}H_{21}O_1$ [M+H]: calculated: 217.1592, found: 217.1604.

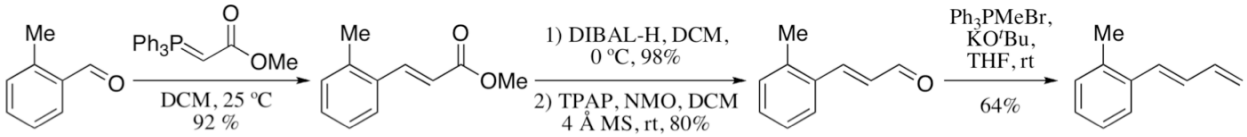
D. Preparation of (E)-2-methyldeca-1,3-diene. To a flame-dried two-neck flask with a magnetic stir bar equipped with a reflux condenser was added CsF (2.14 g, 14.11 mmol, 2.4 equiv). The apparatus was flame-dried again, brought into the dry box, and *trans*-1-octen-1-yl boronic acid (1.00 g, 6.41 mmol, 1.1 equiv) was added, followed by $Pd(PPh_3)_4$ (203.8 mg, 0.18 mmol, 0.03 equiv) and 2-bromopropene (520 μL, 5.88 mmol, 1.0 equiv). The reaction mixture was removed from the dry box, benzene (32 mL) was added under nitrogen, and the reaction was heated to 70 °C for 17 h. After being cooled to room temperature, the reaction was quenched with the addition of deionized water (15 mL) and the layers were separated. The organic layer was extracted with ethyl acetate (3 x 20 mL), and the combined organics were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by silica gel chromatography (100% hexanes) to afford the title compound as a clear, colorless liquid (741 mg, 83%).

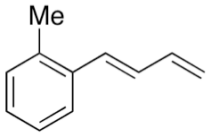


(*E*)-2-methyldeca-1,3-diene (Table 1, entry 5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 7.0 Hz, CH$_2$C**H$_3$**), 1.23-1.40 (8H, m, aliphatic), 1.81 (3H, s, CH$_2$CC**H$_3$**), 2.08 (2H, q, *J* = 6.8 Hz, CHC**H$_2$**), 4.84 (2H, s, C=C**H$_2$**), 5.64 (1H, dt, *J* = 15.6 Hz, 6.8 Hz, CH$_2$C**H**=CH), 6.12 (1H, d, *J* = 15.6 Hz, CH$_2$CH=C**H**C); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 132.7, 131.0, 114.0, 32.8, 31.8, 29.5, 29.0, 22.7, 18.7, 14.1; IR (neat): 2923.9 (s), 2855.2 (m), 1609.2 (w), 1455.9 (m), 1377.3 (w),

963.2 (s), 880.2 (s), 724.2 (w) cm^{-1}; HRMS-(ESI+) for $C_{11}H_{21}$ [M+H]: calculated: 153.1643, found: 153.1644.

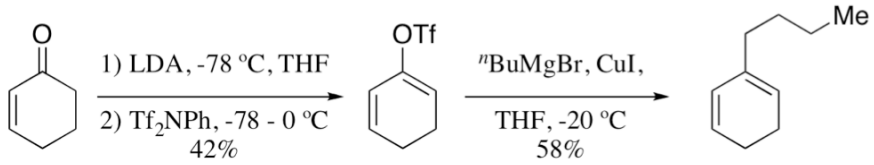
E. Preparation of (E)-1-(buta-1,3-dienyl)-2-methylbenzene





(*E*)-1-(buta-1,3-dienyl)-2-methylbenzene (Table 1, entry 7). The reaction was performed according to the general procedure with potassium *tert*-butoxide (1.99 g, 17.77 mmol), methyltriphenylphosphonium bromide (6.56 g, 18.37 mmol), 2-methyl-*trans*-cinnamaldehyde (866.1 mg, 5.92 mmol), and THF (24 mL) to give the title compound as a clear, colorless liquid (549 mg, 64%). R_f = 0.56 (100% hexanes, stain in $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (3H, s, Ar**CH_3**), 5.16 (1H, dd, *J* = 10 Hz, 1.6 Hz, CH=C**H_{cis}**H_{trans}), 5.32 (1H, dd, *J* = 16.8 Hz, 1.2 Hz, CH=CH_{cis}**H_{trans}**), 6.53 (1H, dt, *J* = 16.8 Hz, 9.6 Hz, CH_2=C**H**CH), 6.68 (1H, dd, *J* = 15.2 Hz, 10.0 Hz, , CH_2=CHC**H**CH), 6.77 (1H, d, *J* = 15.6 Hz, ArC**H**=CH), 7.12-7.17 (3H, m, aromatic), 7.48 (1H, d, *J* = 6.4 Hz, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 135.9, 135.5, 130.7, 130.4, 130.3, 127.4, 126.0, 125.1, 117.4, 19.8; IR(neat): 2968.8 (w), 1598.9 (w), 1482.9 (w), 1459.7 (w), 1000.7 (s), 947.2 (m), 897.6 (m), 750.3 (s), 718.3 (m); HRMS-(ESI+) for $C_{11}H_{13}$ [M+H]: calculated: 145.1017, found: 145.1019.

F. Preparation of 2-butylcyclohexa-1,3-diene (Table 1, entry 9). The title compound was synthesized from the requisite triflate as shown below. The spectral data was in accordance with the literature.[6]

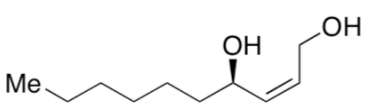


[6] Karlström, A.S.E; Rönn, M; Thorarensen, A; Bäckvall, J.E, *J. Org. Chem.* **1998**, *63*, 2517.

III. Representative Procedure for Diene Diboration/Oxidation.

In the dry box, an oven-dried 6-dram vial with magnetic stir bar was charged with $Pt_2(dba)_3$ (6 mg, 5.5 μmol), (*R,R*)-xylylTADDOLPPh (**L1**) (9 mg, 13.2 μmol), and toluene (2.20 mL, 0.1 M). After stirring in the dry box for 1 h, $B_2(pin)_2$ (58.6 mg, 32.1 μmol) was added to the mixture followed by (*E*)-1-cyclohexyl-1,3-butadiene (30.0 mg, 22.0 μmol). The vial was sealed with a polypropylene cap, removed from the dry box, and stirred at 60 °C for 12 h. The reaction mixture was cooled to 0 °C (ice/water) and charged with tetrahydrofuran (3 mL), 3 M sodium hydroxide (2 mL), and 30% hydrogen peroxide (1 mL). The reaction was gradually warmed to room temperature and allowed to stir for 4 h at which time the vial was cooled to 0 °C (ice/water) and saturated aqueous sodium thiosulfate was added dropwise over 5 min. The reaction mixture was diluted ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was washed with ethyl acetate (3 x 15 mL) and the combined organics were washed with brine. The organic layer was dried over Na_2SO_4, filtered, and the volatiles were removed by rotary evaporation. The crude reaction mixture was purified on silica gel (30-50% ethyl acetate/hexanes) to afford a clear, colorless oil (31.0 mg, 80% yield).

IV. Full Characterization and Proof of Stereochemistry

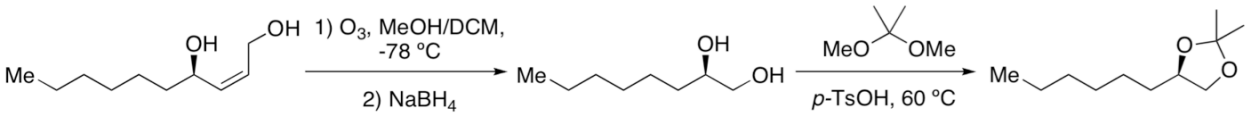


(*R,Z*)-dec-2-ene-1,4-diol (Table 1, entry 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 6.8 Hz, C**H$_3$**CH$_2$), 1.22-1.28 (8H, br s, (C**H$_2$**)$_4$), 1.30-1.46 (1H, m, CH$_2$C**H$_A$**H$_B$CHOH), 1.56-1.60 (1H, m, CH$_2$CH$_A$**H$_B$**CHOH), 4.09 (1H, dd, *J* = 12.9 Hz, 5.6 Hz, HOC**H$_A$**H$_B$C), 4.30 (1H, dd, *J* = 13.2 Hz, 7.6 Hz, HOCH$_A$**H$_B$**C), 4.42 (1H, q, *J* = 7.0 Hz, CH$_2$C**H**OH), 5.54 (1H, dd, *J* = 11.2 Hz, 8.4 Hz, CC**H**CHOH), 5.70 (1H, ddd, *J* = 11.2 Hz, 7.6 Hz, 5.6 Hz, CC**H**CH$_2$OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.7, 25.4, 29.3, 31.9, 37.5, 58.7, 67.9, 130.3, 135.5; IR (neat): 3314 (br s), 2955 (s), 2855 (s), 1459 (m), 1378 (m), 1018 (s) cm^{-1}. HRMS-(ESI+) for $C_{10}H_{20}O_2Na$ [M+Na]: calculated: 195.1361, found: 195.1372. $[\alpha]_D$ = +11.02 (c = 0.42, $CHCl_3$, *l* = 50 mm). The crude reaction mixture was purified on silica gel (50% ethyl acetate/hexanes) to afford a clear, colorless oil (31.0 mg, 83% yield). R_f = 0.16 (50% ethyl acetate/hexanes, stain in PMA).

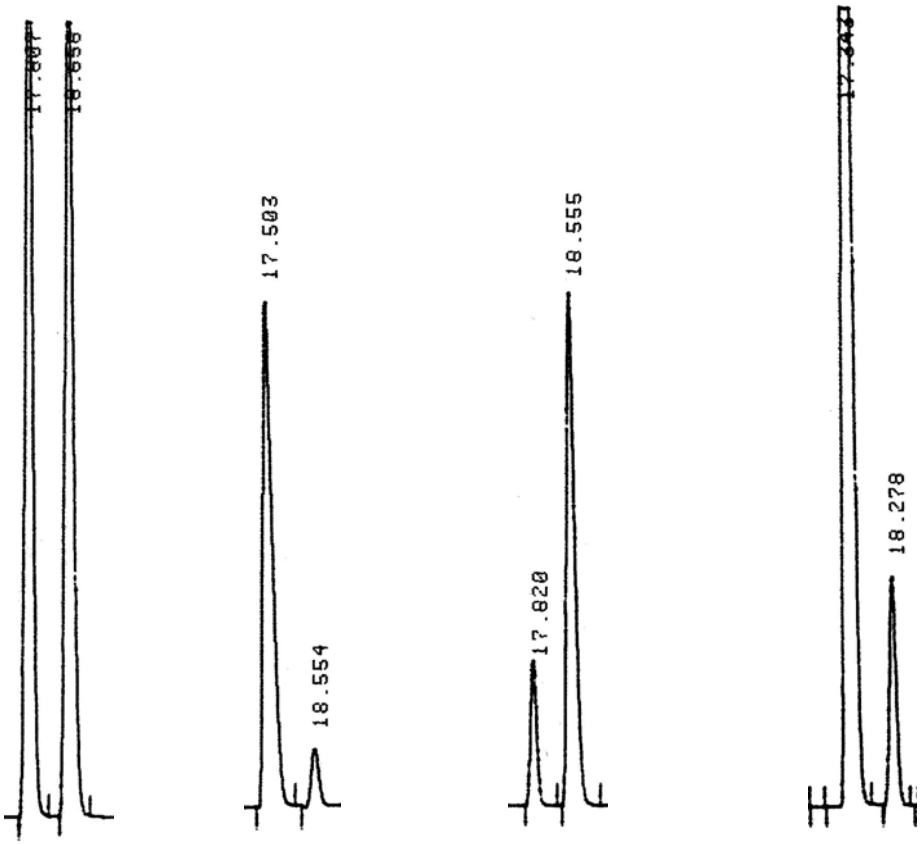
Proof of Stereochemistry:

The title compound was subjected to ozonolysis and reduction as described below. To a 25-mL round-bottomed flask with magnetic stir bar was added (*R,Z*)-dec-2-1,4-diol (11 mg, 64.6 μmol) and dichloromethane (1.6 mL). The flask was cooled to -78 °C (dry ice/isopropanol) and treated with ozone until a pale blue color was observed. To the cooled solution was added methanol (1.6 mL) and sodium borohydride (24 mg, 37.8 mmol). The reaction mixture was gradually warmed to room temperature and allowed to stir for 2 h, at which time volatiles were removed by rotary evaporation. The solid residue was dissolved in ethyl acetate and water and the aqueous and organic layers were separated. The aqueous layer was washed with ethyl acetate (3 x 10 mL) and the combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resultant oil was purified by column chromatography on silica gel with (50% ethyl acetate/hexanes) to afford a clear oil in 79% yield (9.3 mg). The resulting 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid (below). The resulting ketal was compared to the racemic ketal of octane-1,2-diol prepared from

dihydroxylation of octene with osmium tetraoxide and 4-methylmorpholine *N*-oxide. The authentic sample was prepared from the Sharpless asymmetric dihydroxylation of octene utilizing AD-mix α.[7]

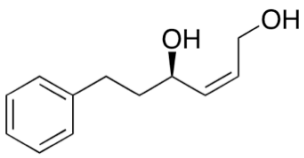


Chiral GLC (β-dex, Supelco, 100 °C) – analysis of the acetonide of octane-1,2-diol.



racemic | reaction product | authentic | coinjection of reaction product + racemic

[7] Jacobsen, E.N.; Markd, I; Mungall, W.S.; Schrcider, G.; Sharpless, K.B.; *J. Am. Chem. Soc.*, **1988**, *110*, 1968.

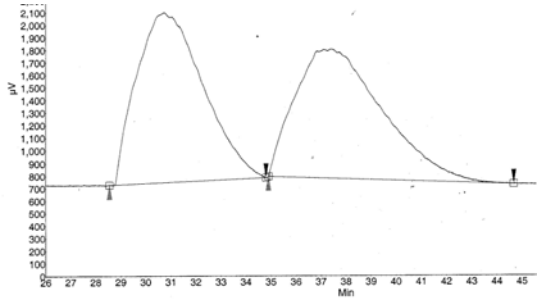


(*R,Z*)-6-Phenylhex-2-ene-1,4-diol (Table 1, entry 2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (1H, br s, O**H**), 1.75-2.01 (1H, br s, O**H**), 1.79 (1H, m, C$\mathbf{H_A}H_B$CHOH), 1.95 (1H, m, $CH_A\mathbf{H_B}$CHOH), 2.69 (2H, m, PhC$\mathbf{H_2}$), 4.13 (1H, dd, *J* = 13.2 Hz, 6 Hz, C$\mathbf{H_A}H_B$OH), 4.25 (1H, ddd, *J* = 13.2 Hz, 7.2 Hz, 1.6 Hz, $CH_A\mathbf{H_B}$OH), 4.45 (1H, q, *J* = 7.0 Hz, C**H**OH), 5.62 (1H, ddt, *J* = 11.2 Hz, 8.0 Hz, 1.6 Hz, CHOHC**H**C), 5.75 (1H, ddd, *J* = 11.2 Hz, 7.2 Hz, 6 Hz, C**H**CH_2OH), 7.17-7.21 (2H, m, Ar**H**), 7.26-7.30 (3H, m, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.8, 39.0, 58.9, 67.4, 126.0, 128.4, 128.5, 130.6, 135.1, 141.6; IR (neat): 3312 (br s), 3024 (m), 2925 (m), 2859 (m), 1453 (m), 1012 (s), 696 (s) cm^{-1}; HRMS-(ESI+) for $C_{12}H_{16}O_2Na$ [M+Na]: calculated: 215.1048, found: 215.1039; $[\alpha]_D$ = +35.56 (c = 1.03, $CHCl_3$, *l* = 50 mm). The crude reaction mixture was purified on silica gel (50% ethyl acetate/hexanes) to afford a clear, colorless oil (95 mg, 78% yield). R_f = 0.25 (50% ethyl acetate, stain in PMA).

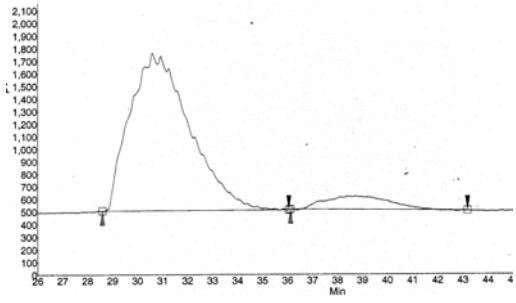
Proof of Stereochemistry:

The title compound was treated with ozone in the procedure described for (*R,Z*)-dec-2-ene-1,4-diol. The resulting 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of 4-phenyl-butane-1,2-diol prepared from dihydroxylation of 4-phenyl-1-butene with osomium tetraoxide and 4-methylmorpholine *N*-oxide.

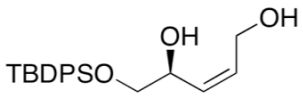
Chiral SFC (OD-H, 1.5% MeOH, 4 mL/min, 50 °C, 150 psi) – analysis of the diol of 4-phenyl-butane-1,2-diol.



racemic



reaction product

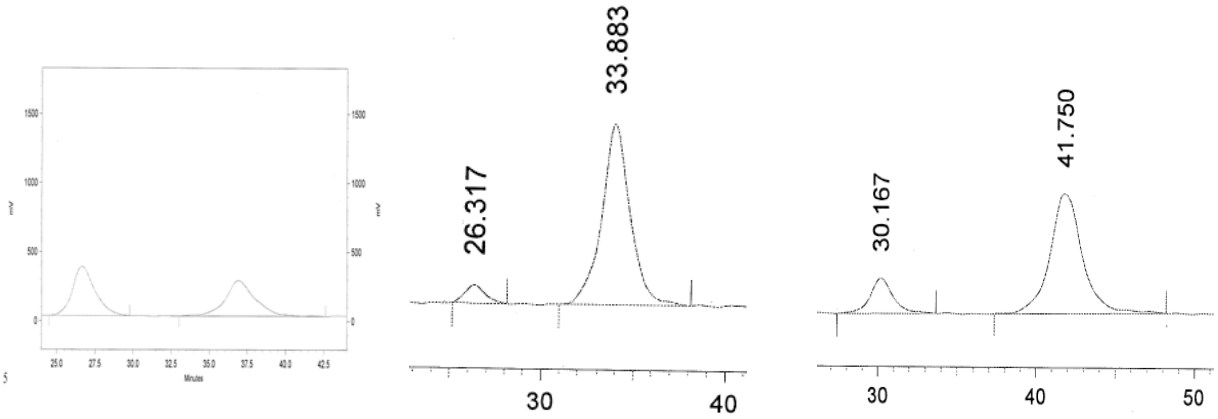


(*S*,*Z*)-5-(*tert*-butyldiphenylsilyloxy)pent-2-ene-1,4-diol (Table 1, entry 8). The reaction was performed according to the general procedure with $Pt_2(dba)_3$ (6.4 mg, 5.8 μmol), (*R*,*R*)-xylylTADDOLPPh (**L1**) (9.6 mg, 13.9 μmol), (*E*)-((2,2-dimethylhexa-3,5-dienyloxy)methyl)benzene (75 mg, 0.23 mmol), $B_2(pin)_2$ (177.1 mg, 0.70 mmol) in toluene (2.3 mL) for 12h at 60 °C, followed by oxidation, to afford an inseparable 1:4 mixture of the 1,2- and 1,4-dihydroxylation prodcuts. To facilitate purification, the crude reaction mixture was dissolved in THF:Et_2O:H_2O (1:1:1) and $NaIO_4$ (4 equiv) was added at room temperature (oxidative cleavage of both the 1,2-diboration product and pinacol). The reaction mixture was stirred for 2h, after which time it was diluted with ethyl acetate, and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by column chromatography on SiO_2 to afford the title compound as a clear, colorless oil (58.0 mg, 70% yield) R_f = 0.38 (30-50% ethyl acetate/hexane, stain in PMA). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (9H, s, SiC(C**H**$_3$)$_3$), 2.29 (1H, br s, O**H**), 2.92 (1H, br s, O**H**), 3.53-3.62 (2H, m, SiOC**H**$_2$), 4.02 (1H, ddd, *J* = 13.4 Hz, 6.0 Hz, 1.2 Hz, C**H**$_A$H$_B$OH), 4.16 (1H, ddd, *J* = 13.6 Hz, 7.2 Hz, 1.2 Hz, CH$_A$**H**$_B$OH), 4.49-4.53 (1H, m, C**H**OH), 5.43-5.53 (1H, m, HC=C**H**CH$_2$OH), 5.76 (1H, dddd, *J* = 8.4 Hz, 7.2 Hz, 6.0 Hz, 1.6 Hz, HC=C**H**CHOH), 7.36-7.45 (6H, m, Si**Ar**), 7.63-7.68 (4H, m, Si**Ar**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 26.8, 26.9 (1,2-diol), 58.0 (1,2-diol), 58.8, 66.2 (1,2-diol), 67.4, 68.7, 70.1 (1,2-diol), 127.5 (1,2-diol), 127.65 (1,2-diol), 127.73 (1,2-diol), 127.8, 129.7 (1,2-diol), 129.8 (1,2-diol), 129.90, 129.92, 130.1, 130.8 (1,2-diol), 132.3 (1,2-diol), 132.6, 132.8 (1,2-diol), 132.9 (1,2-diol), 133.5 (1,2-diol), 135.5, 135.8, 135.9; IR (neat): 3353.5 (br s), 2892.6 (w), 2857.5 (w), 1471.8 (m), 1111.0 (s), 1047.2 (m), 739.8 (m), 701.4 (s), 504.9 (m) cm^{-1}; HRMS-(ESI+) for $C_{21}H_{29}O_3Si$ [M+H]: calculated: 357.1886, found: 357.1891; $[\alpha]_D$ = -4.5 (c = 1.33, $CHCl_3$, *l* =10 mm).

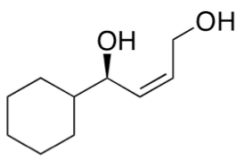
Proof of Stereochemistry:

The absolute stereochemistry was assigned by analogy.

Chiral HPLC (Chiracel-OD, 1.5 mL/min, 2% IPA, 220 nm) – analysis of the title compound



racemic reaction product coinjection of reaction product + racemic

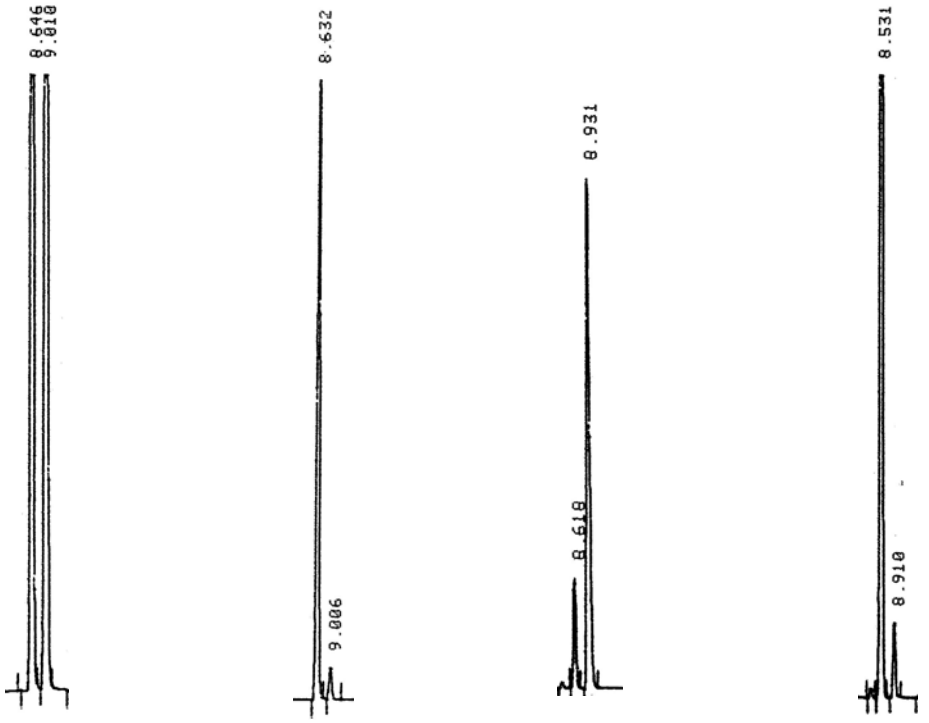


(*R,Z*)-1-Cyclohexylbut-2-ene-1,4-diol (Table 1, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89-1.01 (2H, m, Cy**H**), 1.10-1.25 (3H, m, Cy**H**), 1.34-1.41 (1H, m, Cy**H**), 1.65-1.90 (5H, m, Cy**H**), 2.38 (2H, br s, O**H** x 2), 4.06-4.15 (1H, m, C**H**$_A$H$_B$OH), 4.06-4.15 (1H, m, C**H**OH), 4.29 (1H, ddd, *J* = 12.8 Hz, 7.6 Hz, 1.6 Hz, CH$_A$**H**$_B$OH), 5.55 (1H, ddt, *J* = 11.2 Hz, 8.4 Hz, 1.6 Hz, C2-**H**), 5.77 (1H, m, C3-**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.1, 26.2, 26.6, 28.7, 28.8, 43.9, 58.8, 72.2, 130.9, 133.9; IR (neat): 3325 (br s), 2923 (s), 2851 (s), 2300 (w), 1449 (m), 1015 (s) cm^{-1}; HRMS-(ESI+) for $C_{10}H_{18}O_2Na$ [M+Na]: calculated: 193.1204, found: 193.1199; $[\alpha]_D$ = +18.01 (c = 0.98, $CHCl_3$, *l* = 50 mm). The crude reaction mixture was purified on silica gel (50% ethyl acetate/hexanes) to afford a clear, colorless oil (31.0 mg, 80% yield). R_f = 0.17 (50% ethyl acetate, stain in PMA).

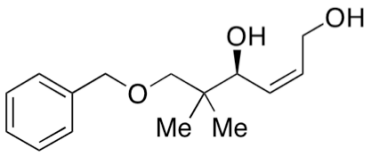
Proof of stereochemistry:

The title compound was treated with ozone in the procedure described for (*R,Z*)-dec-2-ene-1,4-diol. The resulting 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of 1-cyclohexylethane-1,2-diol prepared from treatment of vinyl cyclohexane with osmium tetraoxide and 4-methylmorpholine *N*-oxide. The authentic sample was prepared from the Sharpless asymmetric dihydroxylation of vinyl cyclohexane utilizing AD-mix α.

Chiral GLC (β-dex, Supelco, 130 °C) – analysis of the acetonide of 1-cyclohexylethane-1,2-diol.



racemic reaction product authentic coinjection of reaction product + racemic

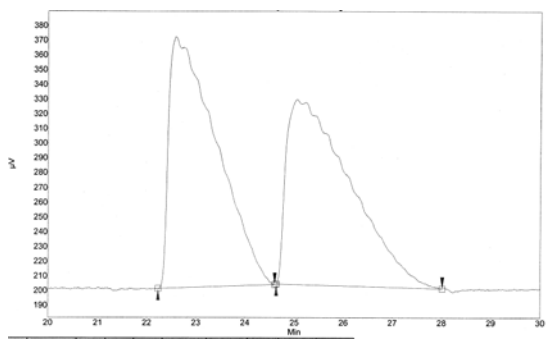


(*S,Z*)-6-(benzyloxy)-5,5-dimethylhex-2-ene-1,4-diol (Table 1, entry 4). The reaction was performed according to the general procedure with $Pt_2(dba)_3$ (5.1 mg, 4.6 μmol), (*R,R*)-xylylTADDOLPPh (**L1**) (7.6 mg, 11.1 μmol), (*E*)-((2,2-dimethylhexa-3,5-dienyloxy)methyl)benzene (40 mg, 0.18 mmol), $B_2(pin)_2$ (49.3 mg, 0.19 mmol) in toluene (1.8 mL) for 12h at 60 °C, followed by oxidation, to afford an inseparable 1:1 mixture of the 1,2- and 1,4-dihydroxylation prodcuts. To facilitate purification, the crude reaction mixture was dissolved in THF:Et_2O:H_2O (1:1:1) and $NaIO_4$ (4 equiv) was added at room temperature (oxidative cleavage of both the 1,2-diboration product and pinacol). The reaction mixture was stirred for 2h, after which time it was diluted with ethyl acetate, and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude material was purified by column chromatography on SiO_2 to afford the title compound as a clear, colorless oil (22.2 mg, 48% yield) R_f = 0.31 (30-50% ethyl acetate/hexane, stain in PMA); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (3H, s, C**H$_3$**), 0.93 (3H, s, C**H$_3$**), 3.32 (1H, d, *J* = 9.0 Hz, OC**H$_A$**H$_B$C(CH$_3$)$_2$), 3.39 (1H, d, *J* = 9.0 Hz, OCH$_A$**H$_B$**C(CH$_3$)$_2$), 3.57 (1H, br s, OH), 4.11 (1H, dd, *J* = 13.0 Hz, 6.0 Hz, HOC**H$_A$**H$_B$), 4.29 (1H, ddd, *J* = 13.0 Hz, 7.5 Hz, 1.5 Hz, HOCH$_A$**H$_B$**), 4.32 (1H, d, *J* = 8.5 Hz, C**H**OH), 4.51 (2H, m, PhC**H$_2$**), 5.56-5.60 (1H, m, C**H**CHCH$_2$OH), 5.79-5.84 (1H, m, CHC**H**CH$_2$OH), 7.29-7.37 (5H, m, Ar**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.9, 22.3, 38.6, 58.9, 73.8, 74.6, 79.5, 127.7, 128.0, 128.6, 131.3, 137.7; IR (neat): 3376 (s), 2960 (s), 2924 (s), 2854 (s), 1453 (s), 1361 (s), 1281 (s), 1091 (s), 1074 (s), 1001 (m) cm^{-1}; HRMS-(ESI+) for $C_{15}H_{23}O_3$ [M+H]: calculated: 251.1647, found: 251.1658. $[\alpha]_D$ = -22.8 (c = 0.75, $CHCl_3$, *l* = 10 mm).

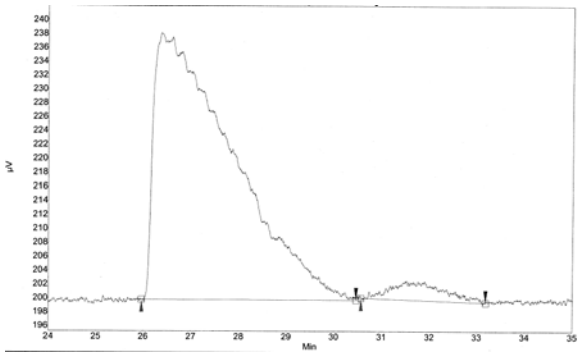
Proof of Stereochemistry:

The absolute stereochemistry was assigned by analogy.

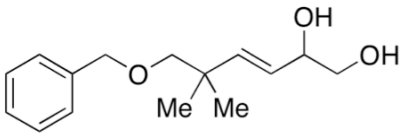
Chiral SFC (AD-H, 2% MeOH, 4 mL/min, 50 °C, 150 psi, 254 nm) – analysis of the title compound



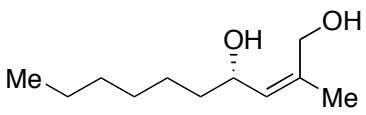
racemic



reaction product



(*E*)-6-(benzyloxy)-5,5-dimethylhex-3-ene-1,2-diol. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.03 (3H, s, C**H$_3$**), 1.04 (3H, s, C**H$_3$**), 3.19 (2H, s, $(CH_3)_2CC$**H$_2$**O), 3.48 (1H, m, C**H$_A$**H$_B$OH), 4.21 (1H, m, C**H**OH), 4.51 (1H, s, PhC**H$_2$**), 4.52 (1H, dd, *J* = 16.0 Hz, 6.5 Hz, CHC**H**CHOH), 5.80 (1H, dd, *J* = 16.0 Hz, 1.5 Hz,, C**H**CHOH), 7.27-7.35 (5H, m, Ar**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.5, 24.6, 37.5, 66.6, 73.3, 73.4, 77.4, 79.2, 125.8, 127.5, 127.6, 128.4, 138.7, 141.3; IR (neat): 3379 (s), 2959 (s), 2930 (s), 2868 (s), 1454 (s), 1378 (s), 1361 (s), 10941 (s), 1075 (s), 1027 cm^{-1}. HRMS-(ESI+) for $C_{15}H_{23}O_3$ [M+H]: calculated: 251.1647, found: 251.1657. The crude reaction mixture was purified on silica gel (50% ethyl acetate/hexane) to afford a clear oil (22.2 mg, 48% yield). R_f = 0.31 (50% ethyl acetate, stain in PMA).

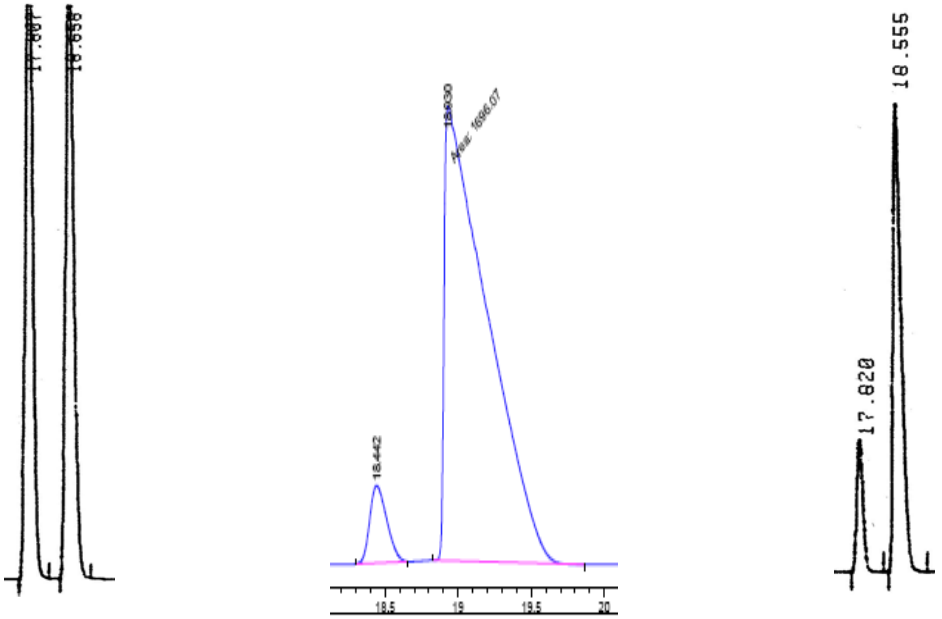


(*S,Z*)-2-methyldec-2-ene-1,4-diol (Table 1, entry 5). The reaction was performed according to the general procedure with $Pt_2(dba)_3$ (8.0 mg, 7.3 μmol), (*R,R*)-3,5-^{t}Bu$_2$PhTADDOLPPh (**L2**) (12.1 mg, 17.6 μmol), (*E*)-2-methyldeca-1,3-diene (44.7 mg, 0.29 mmol), $B_2(pin)_2$ (78.3 mg, 0.31 mmol) in toluene (3.0 mL) for 12h at 60 °C, followed by oxidation, to afford the title compound as a clear, colorless oil (52.2 mg, 95% yield). R_f = 0.22 (50% ethyl acetate/hexane, stain in PMA); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (3H, t, *J* = 6.6 Hz, C**H$_3$**CH=CH), 1.18-1.32 (8H, m, aliphatic), 1.36-1.42 (1H, m, HOCHC**H$_A$**H$_B$CH$_2$), 1.52-1.58 (1H, m, HOCHCH$_A$**H$_B$**CH$_2$), 1.79 (3H, s, CH=CHC**H$_3$**), 2.88 (2H, br s, O**H**), 3.88 (1H, d, *J* = 12.0 Hz, CH$_3$CC**H$_A$**H$_B$OH), 4.28 (1H, d, *J* = 12.4 Hz, CH$_3$CCH$_A$**H$_B$**OH), 4.36 (1H, q, *J* = 6.8 Hz, CHC**H**OH), 5.29 (1H, d, *J* = 8.4 Hz, CH$_3$C=C**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1, 131.1, 67.7, 61.7, 37.6, 31.8, 29.2, 25.4, 22.6, 21.8, 14.0; IR(neat): 3333.1 (br), 2955.6 (m), 2927.0 (s), 2856.9 (m), 1455.2 (w), 1377.3 (w), 1005.1 (s), 950.5 (w) cm^{-1}; HRMS-(ESI+) for $C_{11}H_{21}O_1$ [M-H_2O+H]: calculated: 169.1592, found: 169.1560; $[\alpha]_D$ = -4.36 (c = 1.34, $CHCl_3$, *l* = 50 mm).

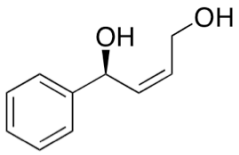
Proof of Stereochemistry:

The title compound was treated with ozone in the procedure described for (*R,Z*)-dec-2-ene-1,4-diol. The resulting 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of octane-1,2-diol prepared from dihydroxylation of octene with osmium tetraoxide and 4-methylmorpholine *N*-oxide. The authentic sample was prepared from the Sharpless asymmetric dihydroxylation of octene utilizing AD-mix α.

Chiral GLC (β-dex, Supelco, 100 °C, 20 psi) – analysis of the acetonide of octane-1,2-diol.



racemic reaction product authentic

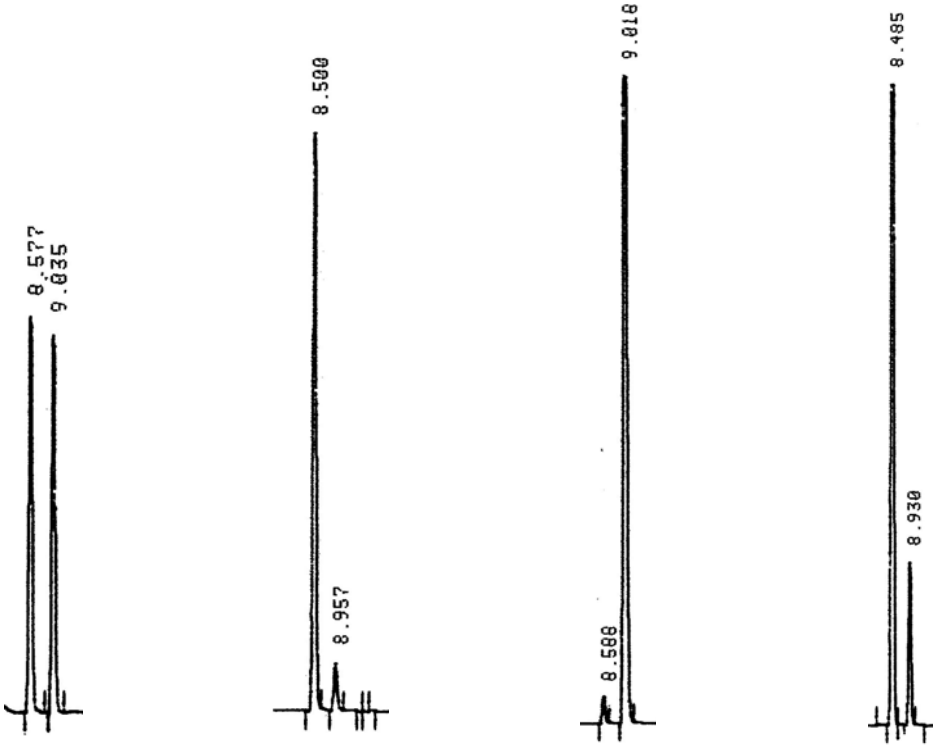


(*S,Z*)-1-Phenylbut-2-ene-1,4-diol (Table 1, entry 6). The reaction was performed according to the general procedure; however, the diboration was run at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.8-2.0 (1H, br s, O**H**), 2.3-3.5 (1H, br s, O**H**), 4.23 (1H, dd, *J* = 13.2 Hz, 4.3 Hz, HOC$\mathbf{H_A}$H$_B$), 4.43 (1H, dd, *J* = 13 Hz, 5.5 Hz, HOCH$_A$$\mathbf{H_B}$), 5.57 (1H, d, *J* = 7.0 Hz, CC**H**CHOH), 5.79-5.81 (1H, m, PhC**H**OH), 5.79-5.81 (1H, m, CC**H**CH$_2$OH), 7.29 (1H, tt, *J* = 6.8 Hz, 2.0 Hz, *p*-Ar**H**), 7.34-7.40 (4H, m, Ar**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ 59.0, 70.3, 126.1, 127.9, 128.8, 130.2, 134.6, 143.2; IR (neat): 3319 (br s), 3026 (m), 2923 (m), 2854 (m), 1450 (m), 1016 (s), 968 (s), 845 (s), 696 (s) cm^{-1}; HRMS-(ESI+) for $C_{10}H_{12}O_2Na$ [M+Na]: calculated: 187.0735, found: 187.0741; $[\alpha]_D$ = +123.29 (c = 0.99, $CHCl_3$, *l* = 50 mm). The crude reaction mixture was purified on silica gel (50% ethyl acetate/hexanes) to afford a white solid (83 mg, 83% yield). R_f = 0.16 (50% ethyl acetate, stain in PMA).

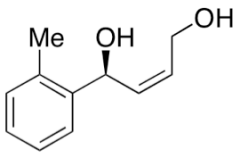
Proof of Stereochemistry:

The 1,4-dihydroxylation product (*S,Z*)-1-phenylbut-2-ene-1,4-diol was treated with ozone in the procedure described for (*R,Z*)-dec-2-ene-1,4-diol. The resulting 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of 1-phenyl-ethane-1,2-diol prepared from the dihydroxylation of styrene with osmium tetraoxide and 4-methylmorpholine *N*-oxide. The authentic sample was prepared from the Sharpless asymmetric dihydroxylation of styrene utilizing AD-mix α.

Chiral GLC (β-dex, Supelco, 140 °C, 20 psi) – analysis of the acetonide of 1-phenylethane-1,2-diol.



racemic reaction product authentic coinjection of reaction product + racemic

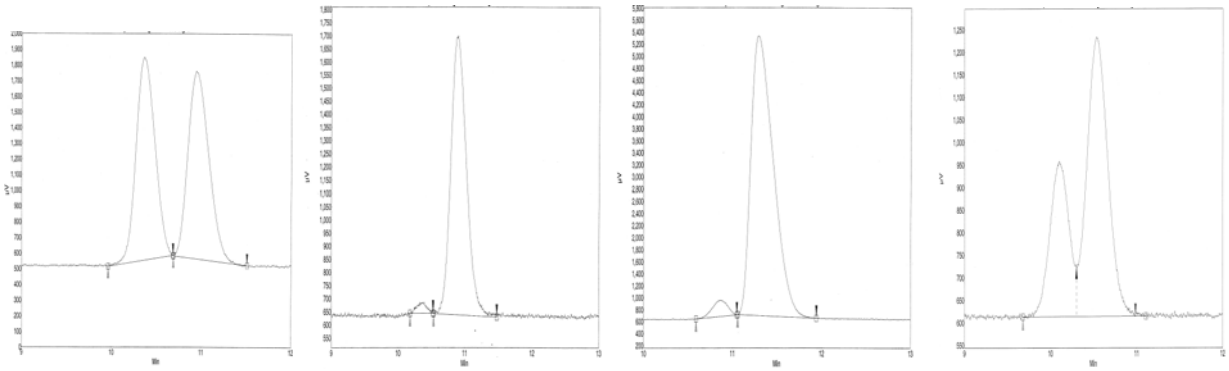


(*S,Z*)-1-*o*-tolylbut-2-ene-1,4-diol (Table 1, entry 7). The reaction was performed according to the general procedure with $Pt_2(dba)_3$ (14.2 mg, 13.0 μmol), (*R,R*)-xylylTADDOLPPh (**L1**) (21.4 mg, 31.2 μmol), (*E*)-1-(buta-1,3-dienyl)-2-methylbenzene (75 mg, 0.52 mmol), $B_2(pin)_2$ (138.7 mg, 0.55 mmol) in toluene (5.2 mL) for 12h at room temperature, followed by oxidation, to afford the title compound as a clear, colorless oil (82.4 mg, 89% yield). R_f = 0.17 (50% ethyl acetate/hexane, stain in PMA); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24 (2H, br s, O**H**), 2.34 (3H, s, ArC**H$_3$**), 4.25 (1H, dd, *J* = 12.8 Hz, 5.2 Hz, CH=CHC**H$_A$**H$_B$OH), 4.41 (1H, dd, *J* = 12.8 Hz, 6.0 Hz, CH=CHCH$_A$**H$_B$**OH), 5.74-5.82 (2H, m, ArCHC**H**C**H**CH$_2$), 7.12-7.22 (3H, m, Ar**H**), 7.49 (1H, d, *J* = 7.2 Hz, Ar**H$_3$**); ^{13}C NMR (100 MHz, $CDCl_3$): δ140.9, 134.9, 133.8, 130.5, 130.3, 127.6, 126.3, 125.6, 67.3, 58.7, 19.2; IR (neat): 3317.5 (br), 3021.4 (w), 2924.1 (w), 1460.6 (m), 1211.6 (w), 1016.3 (s), 940.7 (w), 753.7 (m) cm^{-1}; HRMS-(ESI+) for $C_{11}H_{13}O_1$ [M-H_2O+H]: calculated: 161.0966, found: 161.0962; $[\alpha]_D$ = +16.30 (c = 0.43, $CHCl_3$, *l* = 10 mm).

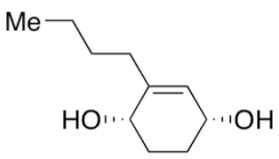
Proof of Stereochemistry:

The title compound was treated with ozone in the procedure described for (*R,Z*)-dec-2-ene-1,4-diol. The resulting 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of 1-*ortho*-tolylethane-1,2-diol prepared from treatment of 2-methylstyrene with osmium tetraoxide and 4-methylmorpholine *N*-oxide. The authentic sample was prepared from the Sharpless asymmetric dihydroxylation of 2-methylstyrene utilizing AD-mix β.

Chiral SFC (AD-H, 4% MeOH, 3 mL/min, 50 °C, 150 psi, 220 nm)-analysis of 1-ortho-tolylethane-1,2-diol



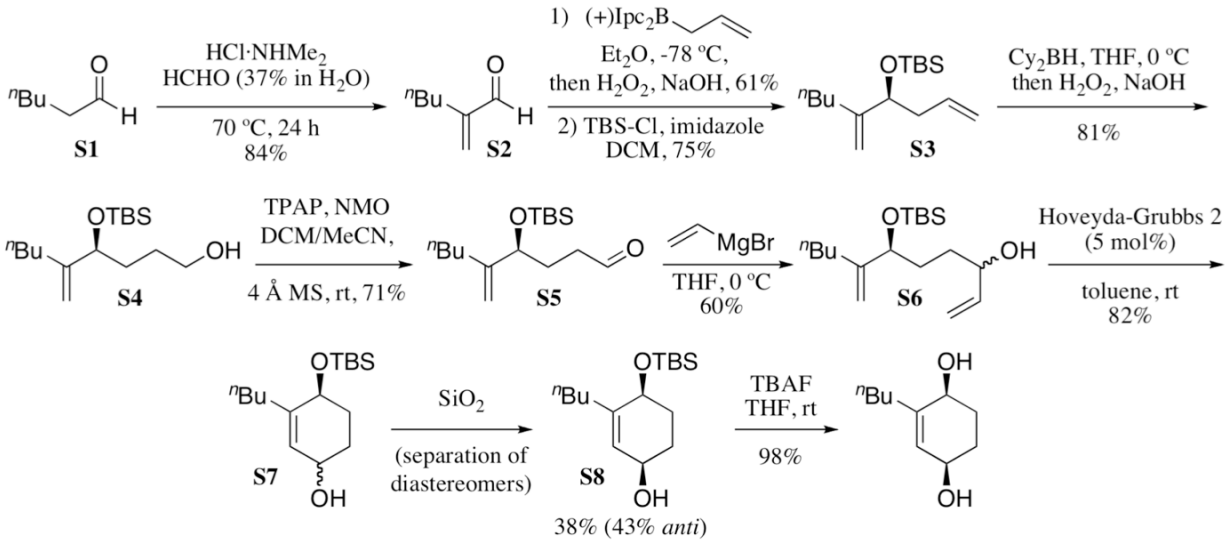
racemic | reaction product | authentic | coinjection of reaction product + racemic



(1*S*,4*R*)-2-butylcyclohex-2-ene-1,4-diol (Table 1, entry 9). The reaction was performed according to the general procedure with $Pt_2(dba)_3$ (4.0 mg, 3.7 μmol), (*R*,*R*)-xylylTADDOLPPh (**L1**) (6.0 mg, 8.8 μmol), 2-butylcyclohexa-1,3-diene (20 mg, 0.147 mmol), $B_2(pin)_2$ (39.1 mg, 0.154 mmol) in toluene (1.5 mL) for 12h at 60 °C, followed by oxidation, to afford the title compound as a clear, colorless oil (20.8 mg, 83% yield). R_f = 0.20 (50% ethyl acetate/hexane, stain in PMA); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 7.0 Hz, CHC**H$_3$**), 1.21-1.47 (3H, m, aliphatic), 1.61-1.85 (5H, m, aliphatic), 2.01-2.20 (2H, m, aliphatic), 3.99 (1H, s, C**H**OH), 4.13 (1H, s, C**H**OH), 5.53 (1H, s, C**H**=CHOH); ^{13}C NMR (100 MHz, $CDCl_3$): δ141.7, 127.4, 66.66, 66.62, 33.3, 29.9, 29.2, 27.9, 22.6, 14.0; IR (neat): 3301.0 (br), 2928.4 (s), 2858.7 (m), 1457.1 (w), 1276.5 (w), 1049.2 (m), 1027.7 (w), 979.8 (m), 957.4 (w) cm^{-1}; HRMS-(ESI+) for $C_{10}H_{17}O_1$ [M-H_2O+H]: calculated: 153.1279, found: 153.1279; $[\alpha]_D$ = +29.02 (c = 0.90, $CHCl_3$, *l* = 50 mm).

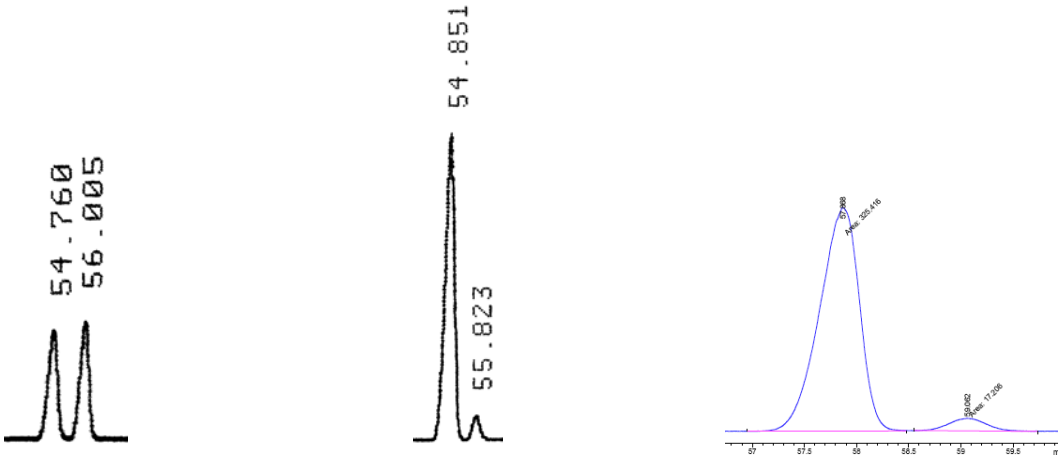
Proof of Stereochemistry:

The authentic compound was synthesized as shown below. Treatment of hexanal with aqueous formaldehyde and dimethylamine hydrochloride provided aldehyde **S2**[8]. Brown allylation[9] followed by TBS-protection furnished the protected allylic alcohol **S3**. Hydroboration with dicyclohexylborane[10] gave primary alcohol **S4**, which was then oxidized with TPAP/NMO[11] followed by addition of vinylmagnesium bromide to afford diene **S6**. Ring-closing metathesis, using Hoveyda-Grubbs 2nd generation catalyst[12], followed by TBAF deprotection provided the desired 1,4-diol in 4% overall yield.

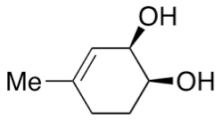


[8] *J. Agric. Food Chem.* **2007**, 55, 5050.
[9] Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1989**, *54*, 1570.
[10] Atsushi Abiko; *Organic Syntheses*; Wiley & Sons: New York, 2002; Collect. Vol. X, p 103.
[11] Griffith, W.P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *J. Chem. Soc. Chem. Commun.* **1987**, 1625.
[12] Garber, S. B.; Kingsbury, J. S.; Gray, B. L; Hoveyda, A. H. *J. Amer. Chem. Soc.* **2000**, *122*, 8168.

Chiral GLC (β-dex, Supelco, 140 ℃, 20 psi) – analysis of the bis(acylated) 1,4-diol.



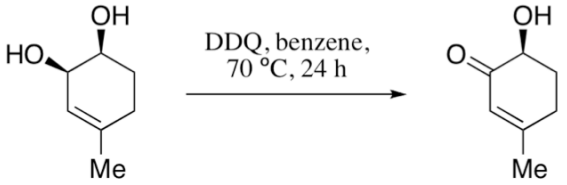
racemic reaction product authentic



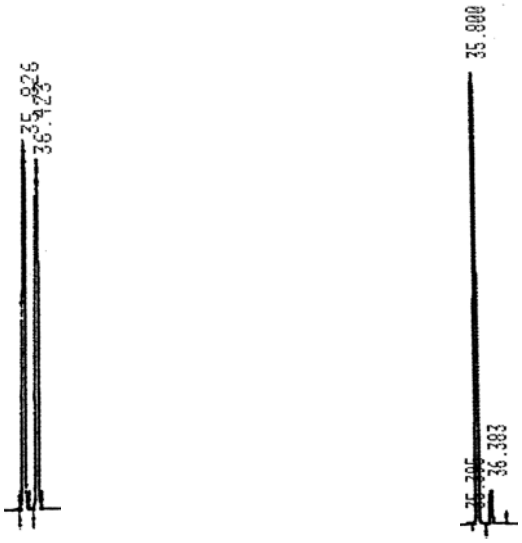
(1S,2R) -4-methylcyclohex-3-ene-1,2-diol (Table 1, entry 10). The reaction was performed according to the general procedure with $Pt_2(dba)_3$ (20.3 mg, 18.6 μmol), (*S,S*)-xylylTADDOLPPh (*ent*-**L1**) (30.6 mg, 44.6 μmol), 1-methylcyclohexa-1,3-diene (70 mg, 0.74 mmol), $B_2(pin)_2$ (198.3 mg, 0.78 mmol) in toluene (7.4 mL) for 12h at room temperature, followed by oxidation, to afford the title compound as a white solid (79.1 mg, 83% yield of inseparable mixture of 1,2- and 1,4-product). R_f = 0.12 (50% ethyl acetate/hexane, stain in PMA); mp 76-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61-1.82 (7H, m, C**H**$_3$CH=CH and alphatic), 2.81 (2H, br s, O**H**), 3.88 (1H, br s, CH_2C**H**OH), 4.09 (1H, br s, CHC**H**OH), 5.52 (1H, br s, CH_2C=C**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.6, 128.1, 68.0, 66.3, 29.0, 27.8, 20.3; IR (neat): 3312.5 (br), 2940.3 (m), 2865.1 (w), 1443.2 (m), 1280.1 (w), 1039.7 (s), 980.4 (m), 950.2 (s) cm^{-1}; HRMS-(ESI+) for $C_7H_{11}O_1$ [M-H_2O+H]: calculated: 111.0810, found: 111.0815; $[\alpha]_D$ = -15.62 (c = 0.32, $CHCl_3$, *l* = 10 mm).

Proof of Stereochemistry:

The title compound was subjected to allylic oxidation with DDQ[13] as shown below. The specific rotation of the enone was compared to the known value in the literature.[14] $[\alpha]_D$ = +142.5 (c = 1.08, $CHCl_3$).



Chiral GLC (β-dex, Supelco, 90 °C for 5 min, ramp 2 °C/min to 160 °C, 20 psi) – analysis of the bis(acylated) 1,2-diol.

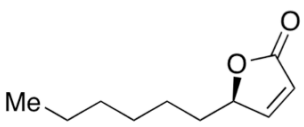


racemic reaction product

[13] Iyer, R. S.; Kuo, G. H.; Helquist, P. *J. Org. Chem.* **1985**, *50*, 5898.
[14] Sakakura, A.; Takayanagi, Y.; Shimogawa, H.; Kigoshi, H. *Tetrahedron*, **2004**, *60*, 7067

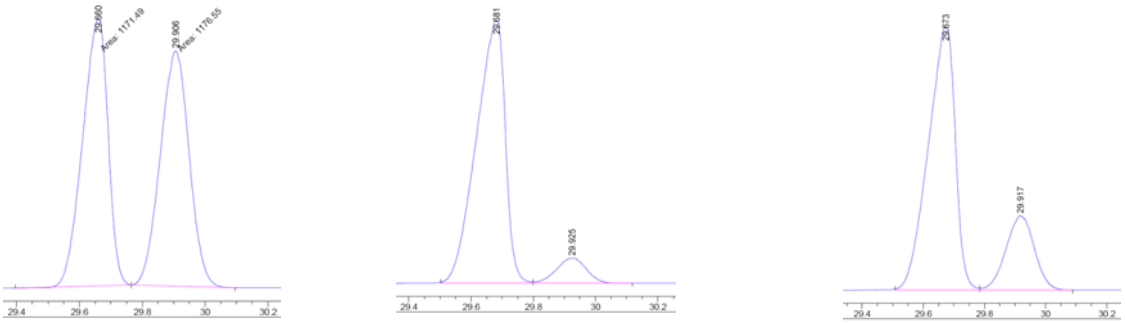
V. Procedure for Butenolide Formation (Scheme 3).

Oxidation of the 1,4-hydroxylated product was performed according to the literature procedure.[15] To a flame-dried flask was added a solution of (*R,Z*)-dec-2-ene-1,4-diol (50 mg, 0.29 mmol) in DCM:MeCN (3.0 mL, 9:1), followed by 4-methylmorpholine *N*-oxide (102.0 mg, 0.87 mmol) under N_2 atmosphere. The reaction mixture was stirred at room temperature for 10 min, after which time tetrapropylammonium perruthenate (5.1 mg, 14.5 μmol) was added. The reaction was allowed to stir for 5 h, and was then diluted with CH_2Cl_2 (5 mL), filtered over a pad of silica, and was washed with CH_2Cl_2. The volatiles were removed by rotary evaporation and the crude product was purified by column chromatography on SiO_2 (10-20% ethyl acetate/hexanes) to afford the desired product as a clear, colorless oil (33.2 mg, 68% yield).



(*R*)-5-hexylfuran-2(5*H*)-one. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (3H, t, *J* = 7.0 Hz, $CH_2C\mathbf{H_3}$), 1.22-1.45 (8H, m, aliphatic), 1.58-1.78 (2H, m, $CH_2C\mathbf{H_2}CHOC{=}O$), 4.98-5.02 (1H, m, $CH_2C\mathbf{H}OC{=}O$), 6.07 (1H, dd, *J* = 5.6 Hz, 2.0 Hz, $CHC\mathbf{H}C{=}O$), 7.42 (1H, dd, *J* = 6.0 Hz, 1.6 Hz, $C\mathbf{H}CHC{=}O$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 156.4, 126.8, 83.6, 33.4, 31.7, 29.1, 25.1, 22.7, 14.2; IR (neat): 2924.6 (m), 2856.88 (w), 1746.4 (s), 1464.8 (w), 1160.3 (m), 1099.4 (m), 815.8 (s); HRMS-(ESI+) for $C_{10}H_{17}O_2$ [M+H]: calculated: 169.1229, found: 169.1231.

Chiral GLC (β-dex, Supelco, 100 °C for 5 min, ramp 3 °C/min to 160 °C, 20 psi)



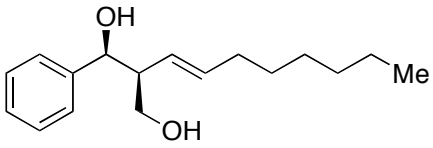
racemic reaction product coinjection of reaction product + racemic

VI. Procedure for Diene Diboration/Allylation/Oxidation (Scheme 4).

In the dry box, an oven-dried 6-dram vial with magnetic stir bar was charged with $Pt_2(dba)_3$ (15.8 mg, 14.4 μmol), (*R,R*)-xylylTADDOLPPh (**L1**) (23.7 mg, 34 μmol), and toluene (5.8 mL, 0.1 M). After stirring for 1 h, $B_2(pin)_2$ (154.1 mg, 0.606 mmol) was added to the mixture followed by *(E)*-1,3-decadiene (80 mg, 0.578 mmol). The vial was sealed with a polypropylene cap, removed from the dry box, and stirred at 60 °C for 12 h. The reaction mixture was cooled to ambient temperature and charged with freshly washed (10% sodium carbonate followed by sodium sulfite) and distilled benzaldehyde (65 μL, 0.606 mmol). The reaction was allowed to stir at room temperature for 24 h at which time the reaction mixture was cooled to 0 °C (ice/water) and charged with tetrahydrofuran (3.0 mL), 3 M sodium hydroxide

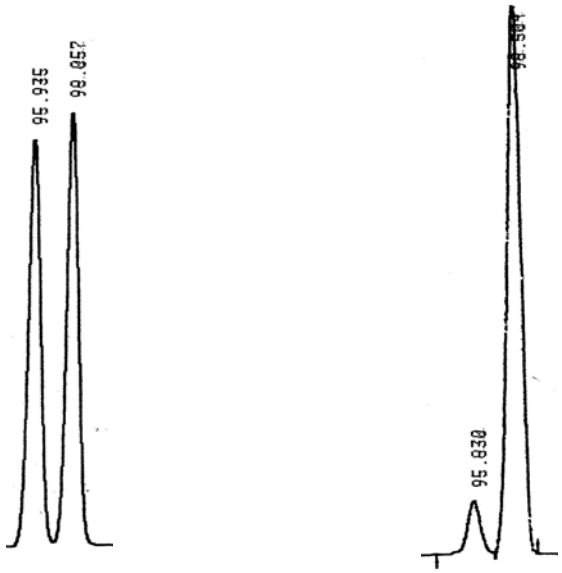
[15] Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis*, **1994**, 639.

(2.0 mL), and 30% hydrogen peroxide (1.0 mL). The reaction was gradually warmed to room temperature and allowed to stir for 12 h at which time the vial was cooled to 0 °C (ice/water). Saturated aqueous sodium thiosulfate was added dropwise over 5 min, the reaction mixture was diluted with ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was rinsed with ethyl acetate (3 x 15 mL), and the combined organic were washed with brine. The organic layer was dried over Na_2SO_4, filtered, and volatiles were removed by rotary evaporation. The crude reaction mixture was purified on silica gel (50% ethyl acetate/hexanes) to afford a clear, colorless oil (99.6 mg, 66% yield).



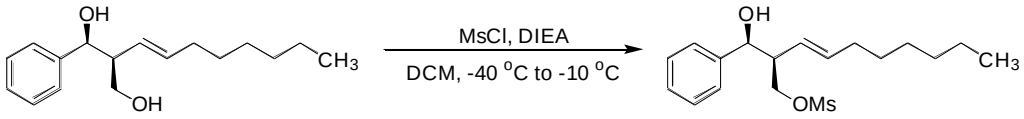
(1*S*,2*S*)-2-((*E*)-oct-1-enyl)-1-phenylpropane-1,3-diol. ^{1}H (500 MHz, $CDCl_3$): δ 0.86 (3H, t, *J* = 7.5 Hz, C**H**$_3$CH$_2$), 1.09-1.26 (8H, m, (C**H**$_2$)$_4$), 1.86-1.91 (2H, m, CCC**H**$_2$), 2.46 (1H, br s, OH), 2.59-2.63 (1H, m, C**H**CH$_2$OH), 3.73 (1H, dd, *J* = 10.5 Hz, 4.5 Hz, HOC**H**$_A$H$_B$), 3.82 (1H, dd, *J* = 11.0 Hz, 7.3 Hz, HOCH$_A$**H**$_B$), 4.73 (1H, d, *J* = 8 Hz, PhC**H**OH), 5.15 (1H, ddt, *J* = 15.5 Hz, 8.5 Hz, 1.5 Hz, C**H**CHAlkyl), 5.38 (1H, dt, *J* = 15.5 Hz, 7.0 Hz, CHC**H**Alkyl), 7.24-7.36 (5H, m, Ar**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 22.7, 28.7, 29.2, 31.8, 32.7, 51.6, 65.5, 78.2, 126.5, 126.8, 127.8, 128.4, 135.1, 142.9; IR (neat): 3334 (br s), 2954 (s), 2923 (s), 2853 (s), 1453 (s), 1377 (w), 1015 (s), 967 (s), 758 (s), 698 (s) cm^{-1}; HRMS-(ESI+) for $C_{17}H_{26}O_2Na$ [M+Na]: calculated 285.1831, observed: 285.1841. The crude reaction mixture was purified on silica gel (50% ethyl acetate/hexanes) to afford a clear, colorless oil (99.6 mg, 66% yield). R_f = 0.62 (50% ethyl acetate, stain in PMA).

Chiral GLC (β-dex, Supelco, 160 °C) – analysis of the acetonide of (1S,2S)-2-((E)-oct-1-enyl)-1-phenylpropane-1,3-diol.

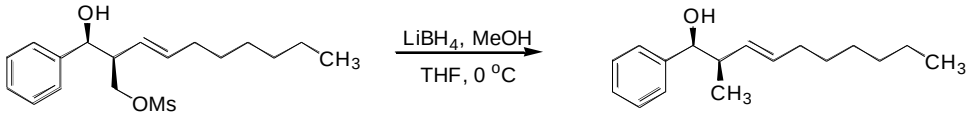


racemic diboration/allylation/oxidation reaction product

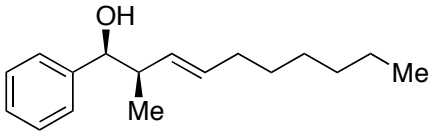
Proof of Stereochemistry:



To a flame-dried 10 mL round-bottomed flask with magnetic stir bar was added 1,3-diol (52.8 mg, 0.201 mmol) and dichloromethane (2.51 mL, 0.08 M) under nitrogen. The reaction mixture was cooled to -40 °C (dry ice with ethylene glycol) and charged with freshly distilled diisopropylethylamine (77 μL, 0.4426 mmol), followed by methanesulfonyl chloride (16 μL, 0.201 mmol). The reaction mixture was allowed to warm to -10 °C over 3 h and was then quenced with 1 M K_2CO_3 (20 mL) and allowed to stir at rt for 20 min. The reaction mixture was transferred to a separatory funnel and the aqueous and organic layers separated. The aqueous layer was washed three times with dichloromethane. The organic extracts were combined, dried (Na_2SO_4), and filtered over cotton. Volatiles were removed by rotary evaporation. The unpurified material was carried onto the next step. Procedure was adapted from the literature.[16]



To a 10 mL flame-dried round-bottomed flask with magnetic stir bar was added the unpurified mesylate and tetrahydrofuran (338 μL). The flask was cooled to 0 °C and charged with anhydrous methanol (26 μL, 7.1 M, distilled over calcium hydride) and 2.0 M lithium borohydride in THF (331 mL, 0.663 mmol) over a 10 min period. The reaction was allowed to stir for 4 h at 0 °C, at which time 1 M NaOH (10 mL) was added over 15 min. Ethyl acetate was then added to the reaction mixture. The aqueous and organic layers were separated, and the aqueous layer was washed three times with ethyl acetate. The organic layers were combined, washed with brine, dried (Na_2SO_4), filtered, and concentrated by rotary evaporation. The unpurified material was purified by silica gel chromatography with 5% ethyl acetate/hexanes as the eluant to afford 18.9 mg of a clear oil (40% yield). Procedure was adapted from the literature.[3]



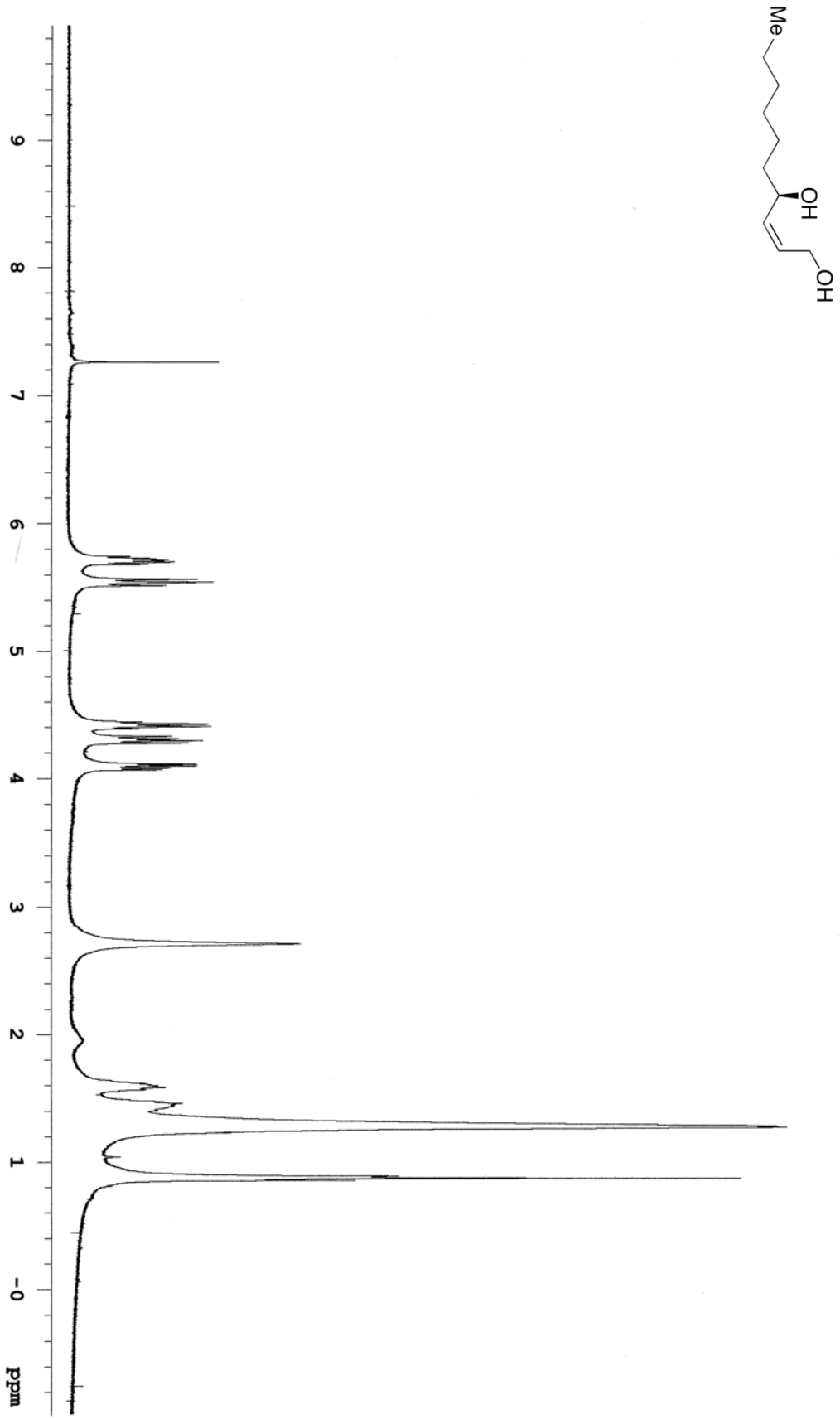
(1S,2*R*,*E*)-2-methyl-1-phenyldec-3-en-1-ol. ^{1}H (500 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 7 Hz, C**H**$_3$CH$_2$), 0.97 (3H, d, *J* = 6.5 Hz, C**H**$_3$CH), 1.22-1.30 (8H, m, (C**H**$_2$)$_4$), 1.94-1.98 (2H, m, CHC**H**$_2$), 2.51-2.54 (1H, m, C**H**CH$_3$), 4.58 (1H, t, *J* = 4.8 Hz, PhC**H**OH), 5.30 (1H, ddt, *J* = 15.5 Hz, 7.5 Hz, 1.5 Hz, C**H**CH$_2$), 5.44 (1H, m, C**H**CHCH$_2$), 7.23-7.34 (5H, m, Ar**H**); ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.2, 14.9, 22.7, 28.9, 29.5, 31.8, 32.7, 43.8, 77.6, 126.6, 127.3, 128.0, 131.5, 132.3, 142.7; IR (neat): 3387 (m), 3028 (s), 2957 (s), 2871 (s), 1453 (s), 1018 (m), 967 (s), 700 (s) cm^{-1}; HRMS-(ESI+) for $C_{17}H_{25}$ [M-H_2O+H]: calculated: 229.1956, found: 229.1960. The crude reaction

[16] Pattenden, G.; Ashweek, N. J.; Baker-Glenn, C. A. G.; Walker, G. M.; Yee, J. G. K. *Angew. Chem. Int. Ed.* **2007**, *46*, 4359

mixture was purified on silica gel (50% ethyl acetate/hexanes) to afford a clear oil (18.9 mg, 40% yield). R_f = 0.57 (50% ethyl acetate, stain in PMA). $[\alpha]_D$ = -7.24 (c = 1.1, $CHCl_3$).

Optical rotation is in accordance with the literature.[17]

[17] Han, J. W.; Hayashi, T. *Tetrahedron: Asymmetry*, **2002**, *13*, 325.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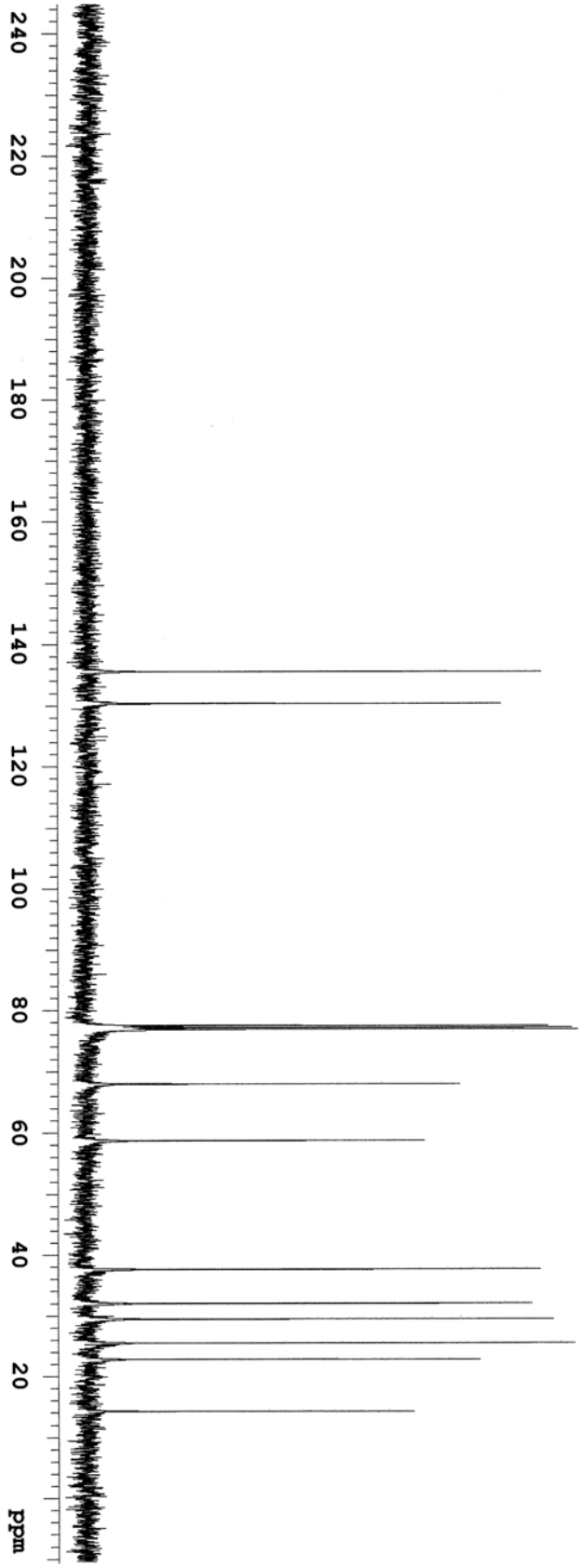
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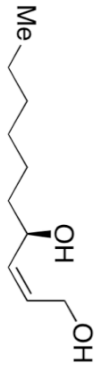
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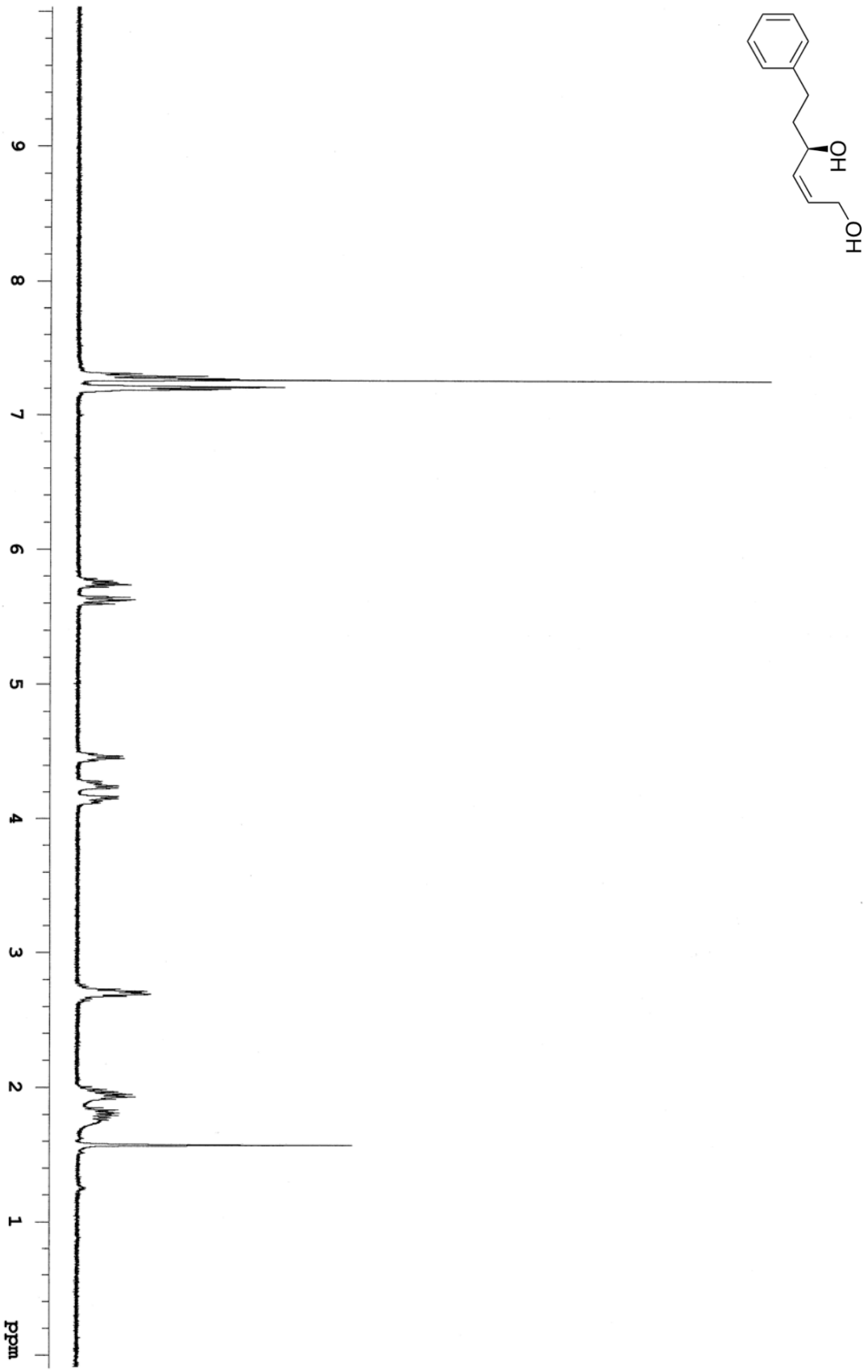
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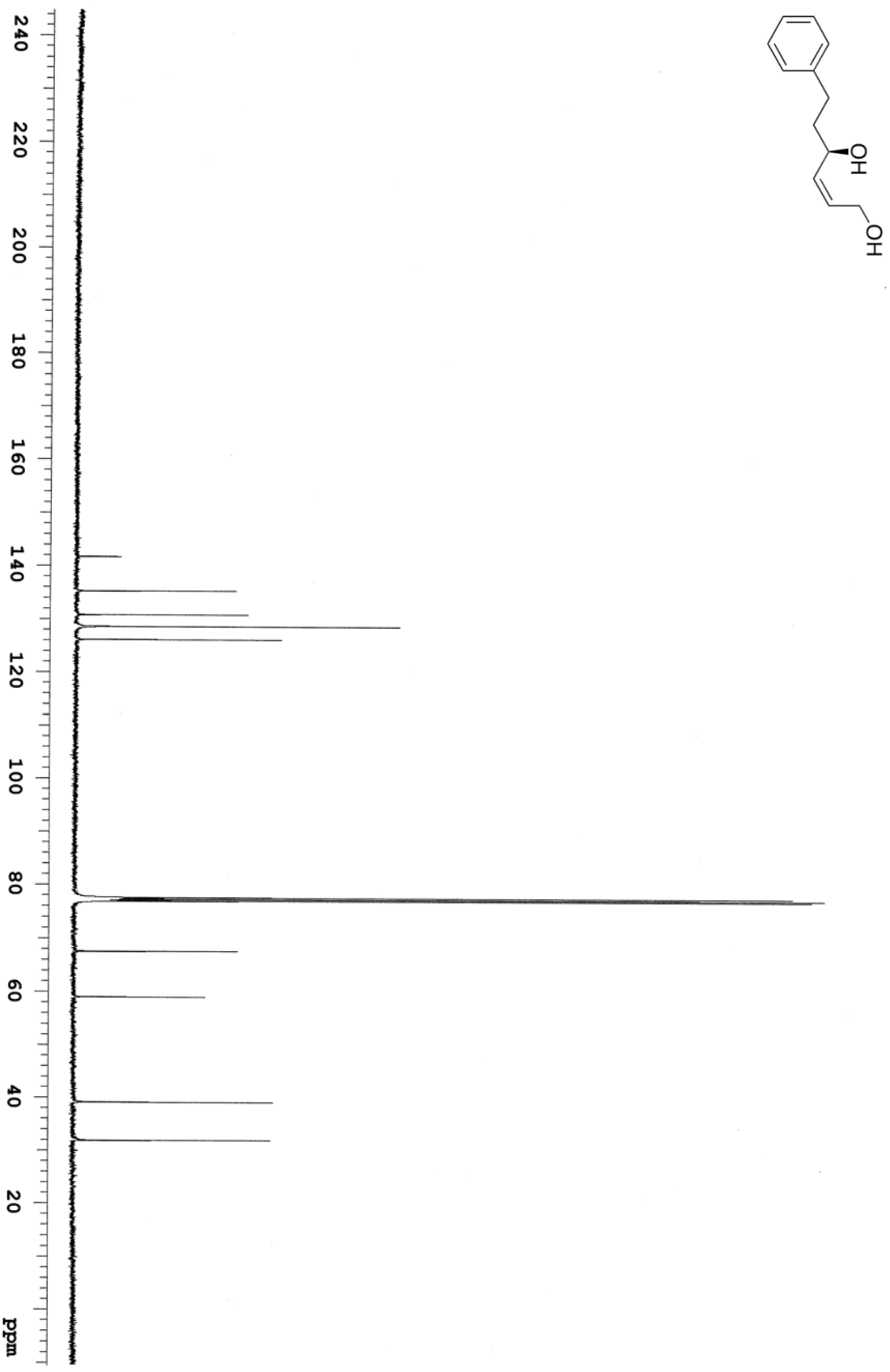
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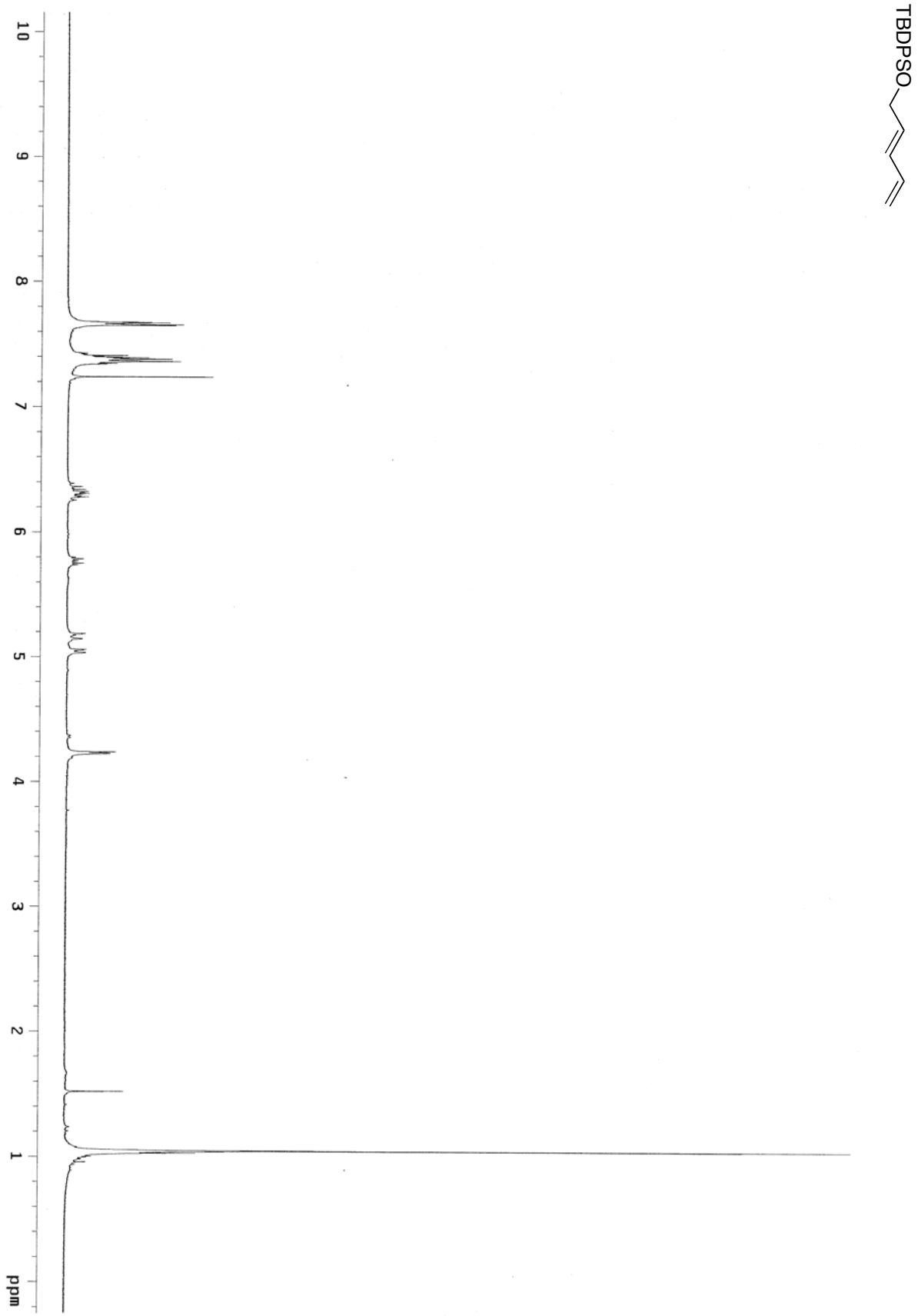
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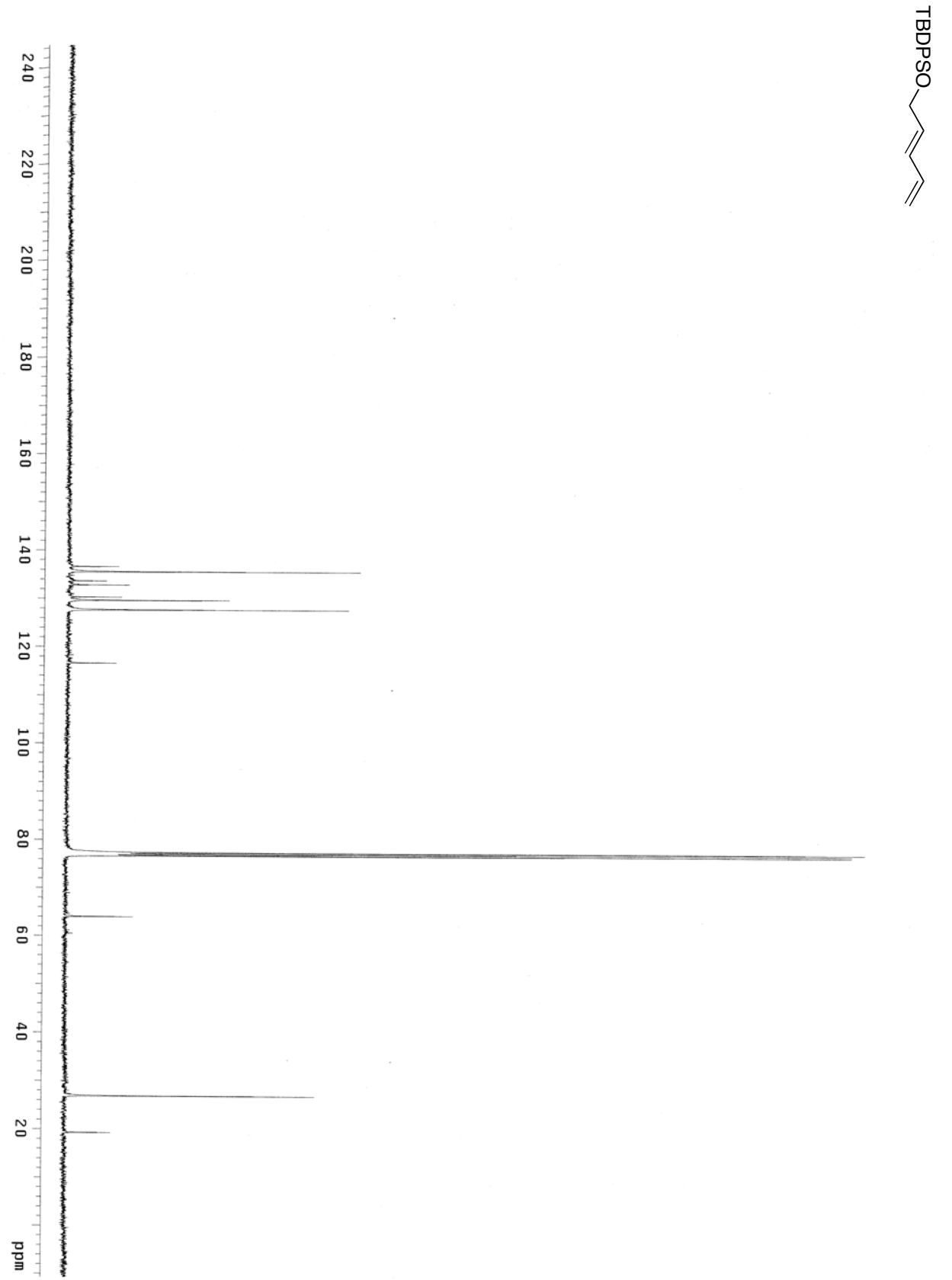
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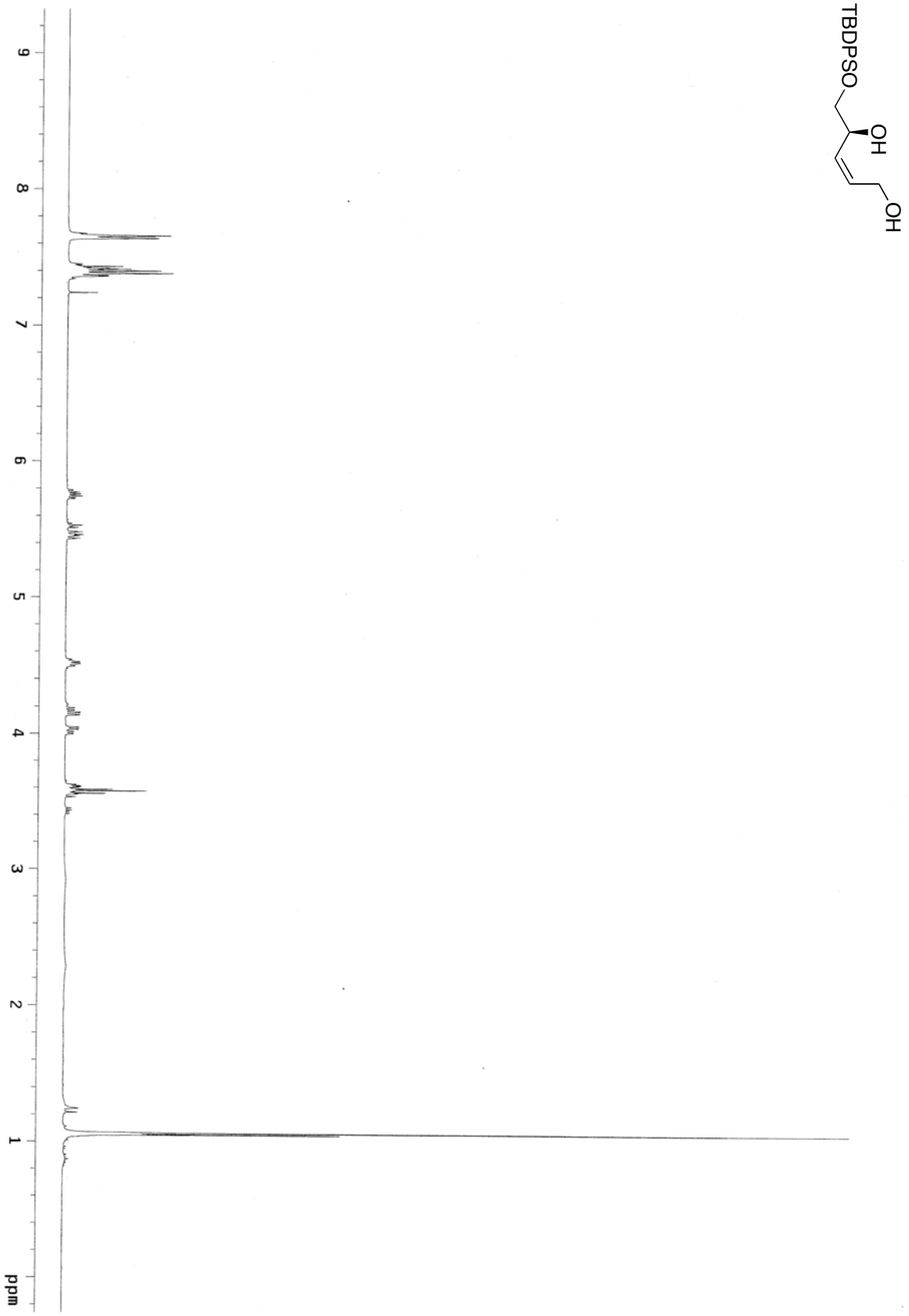
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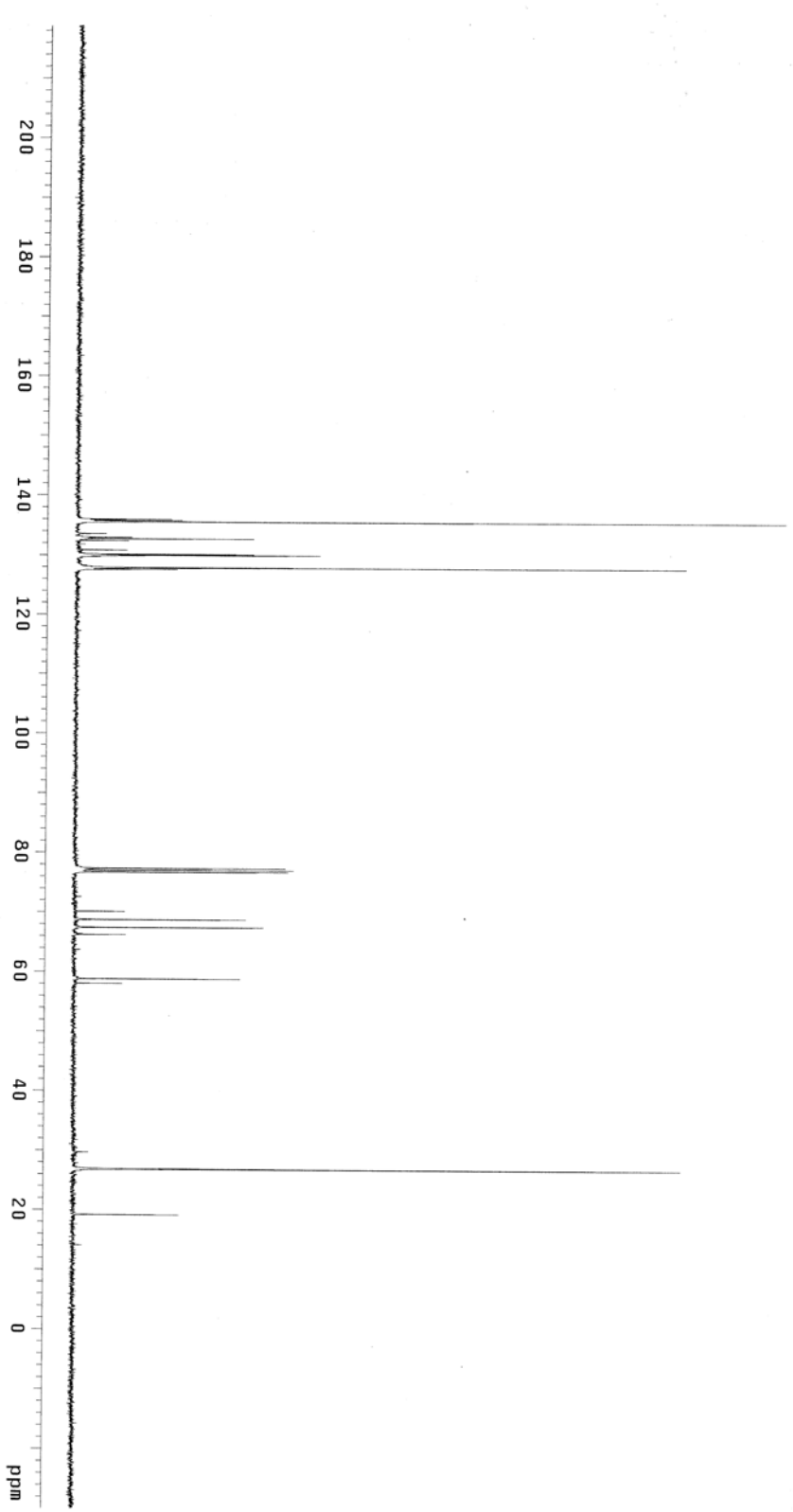
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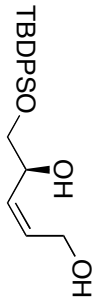
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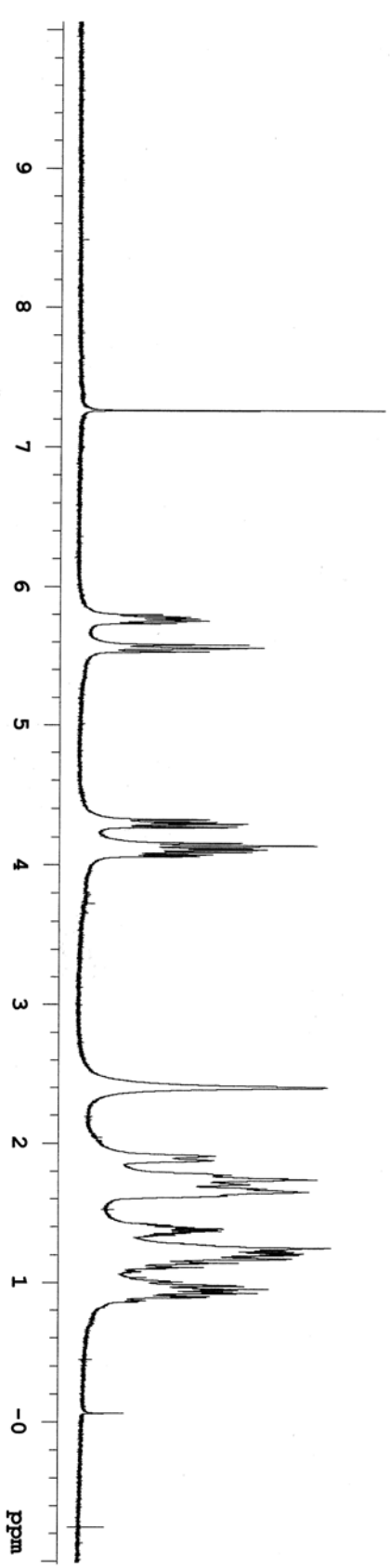
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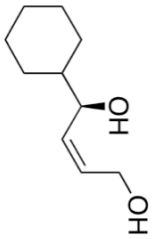
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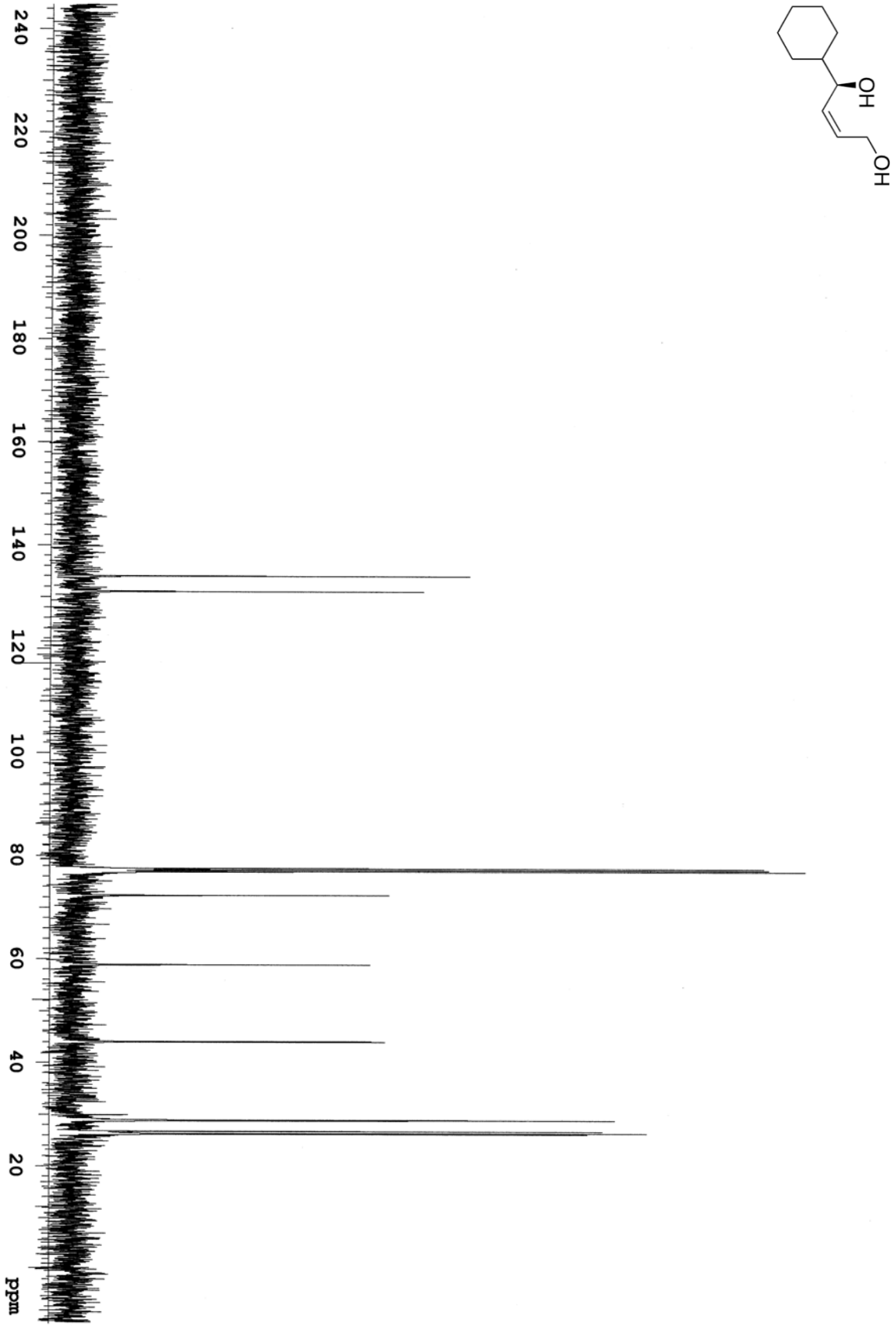
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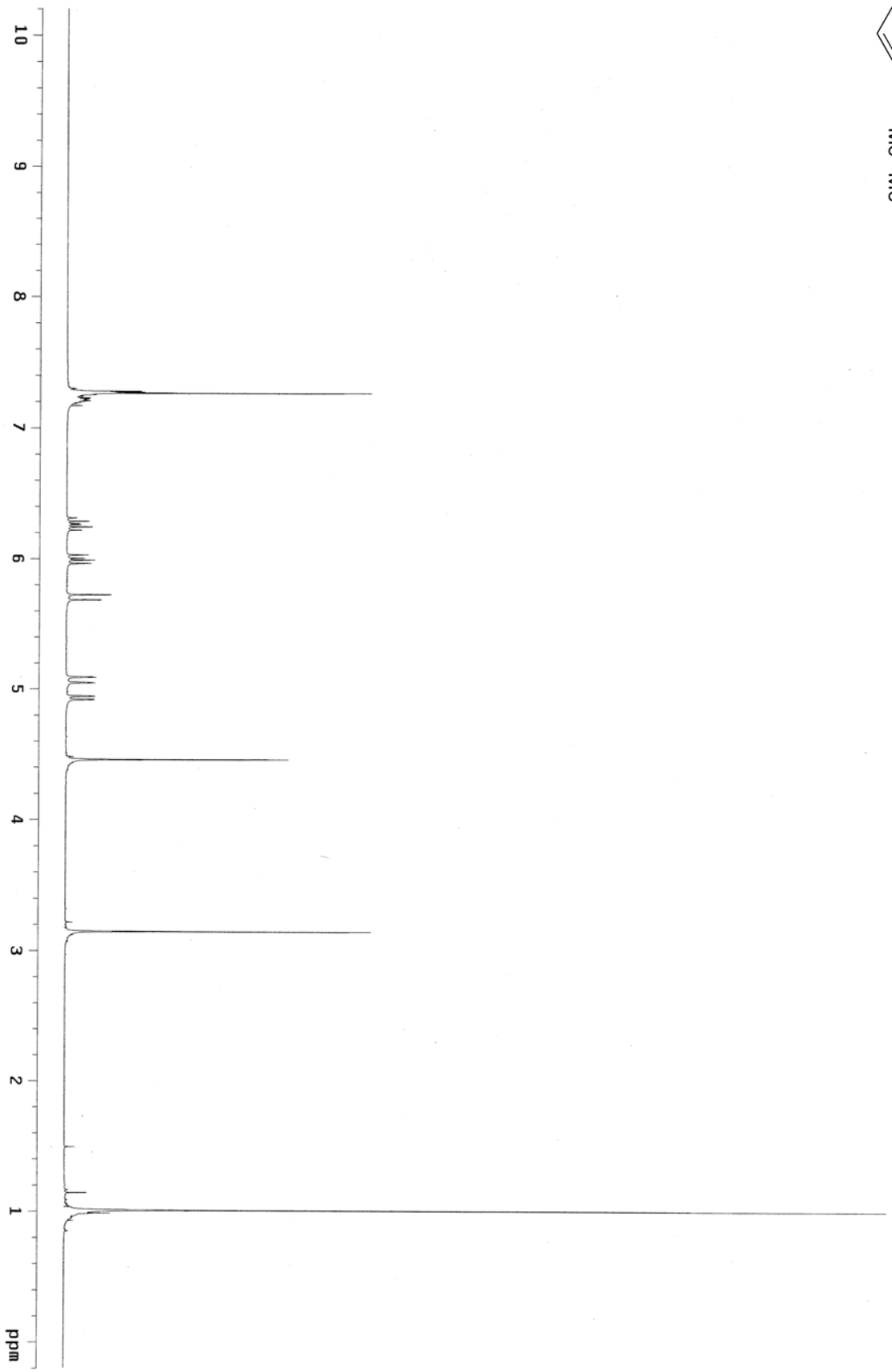
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Me Me
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3
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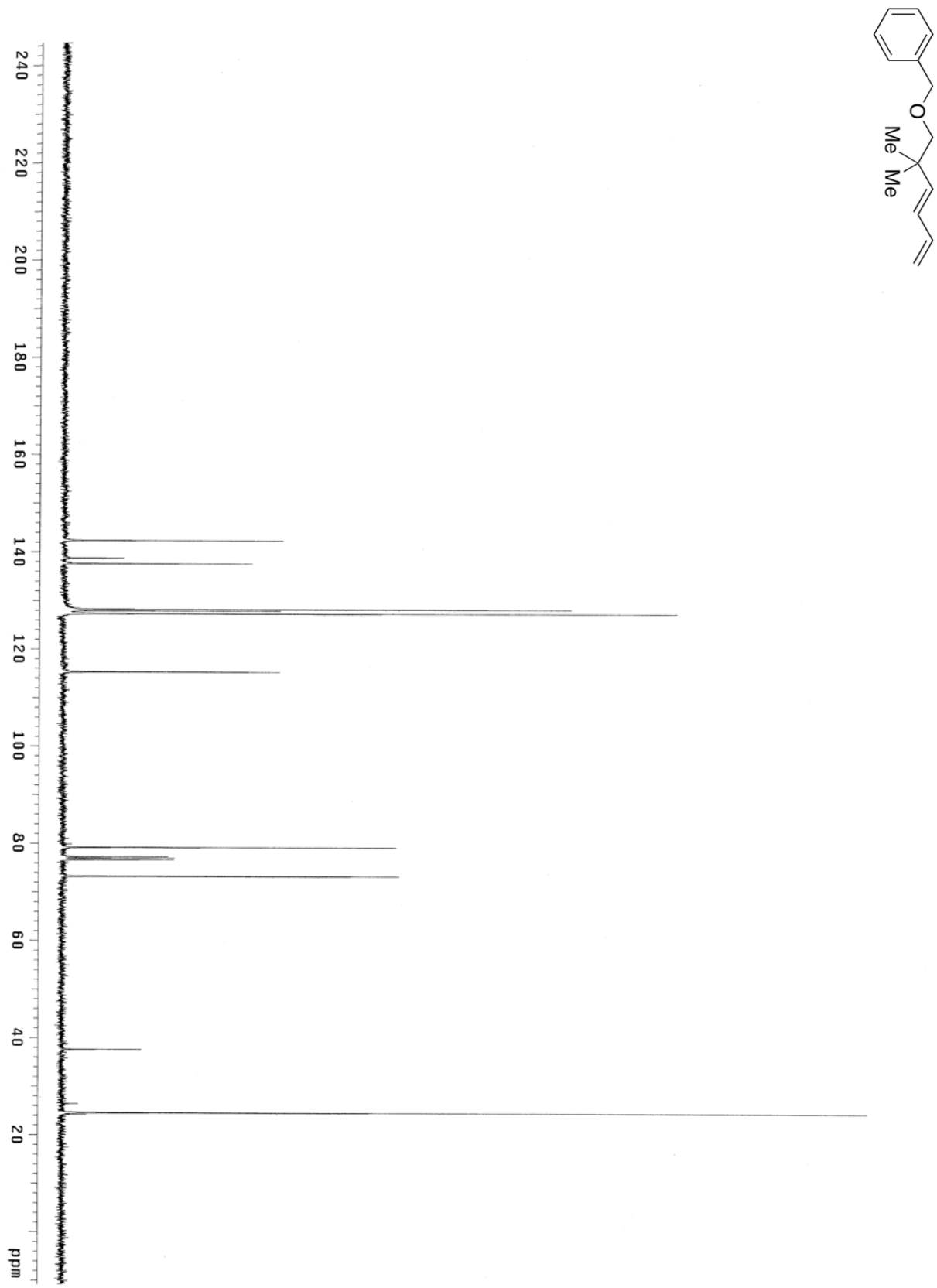
ppm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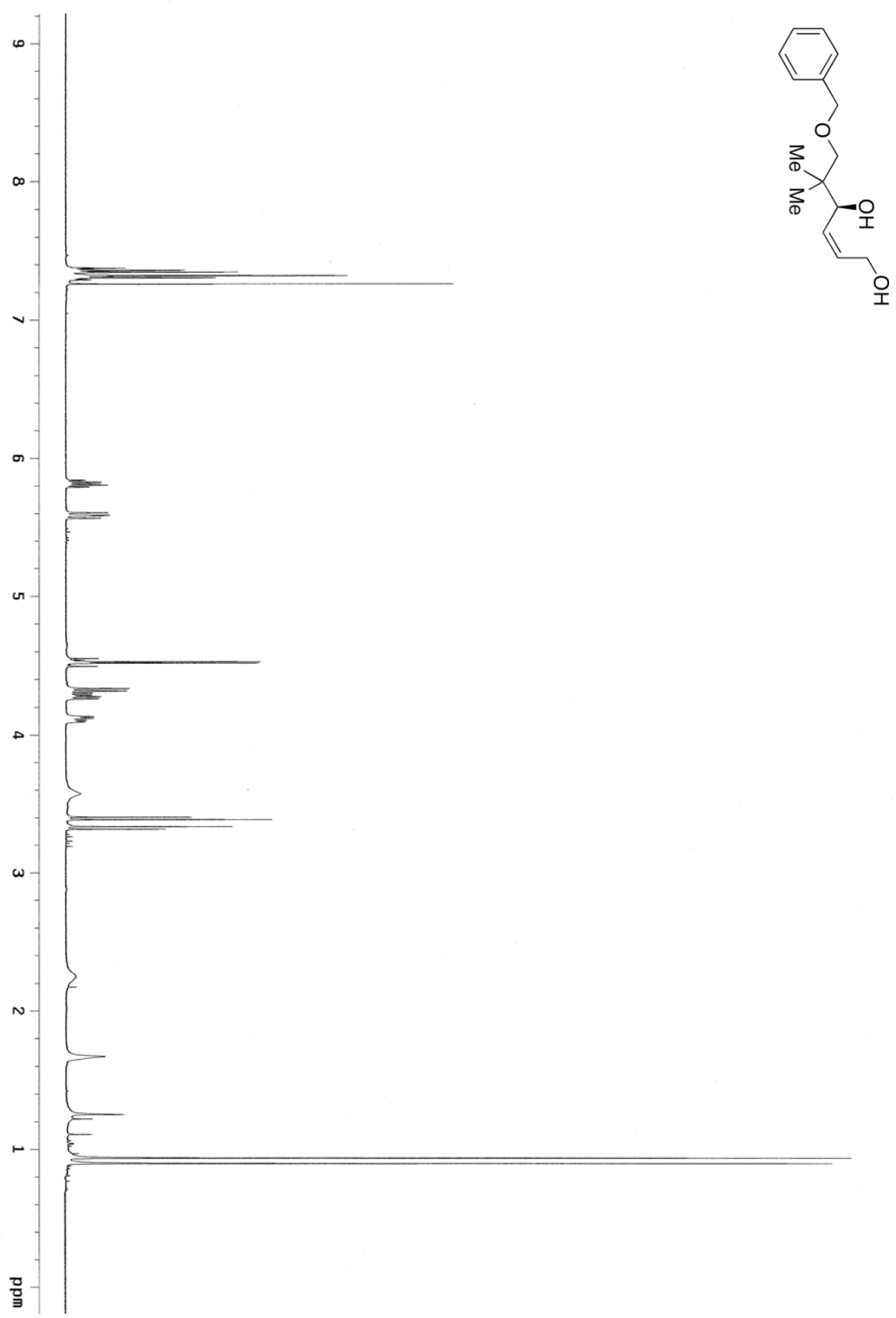
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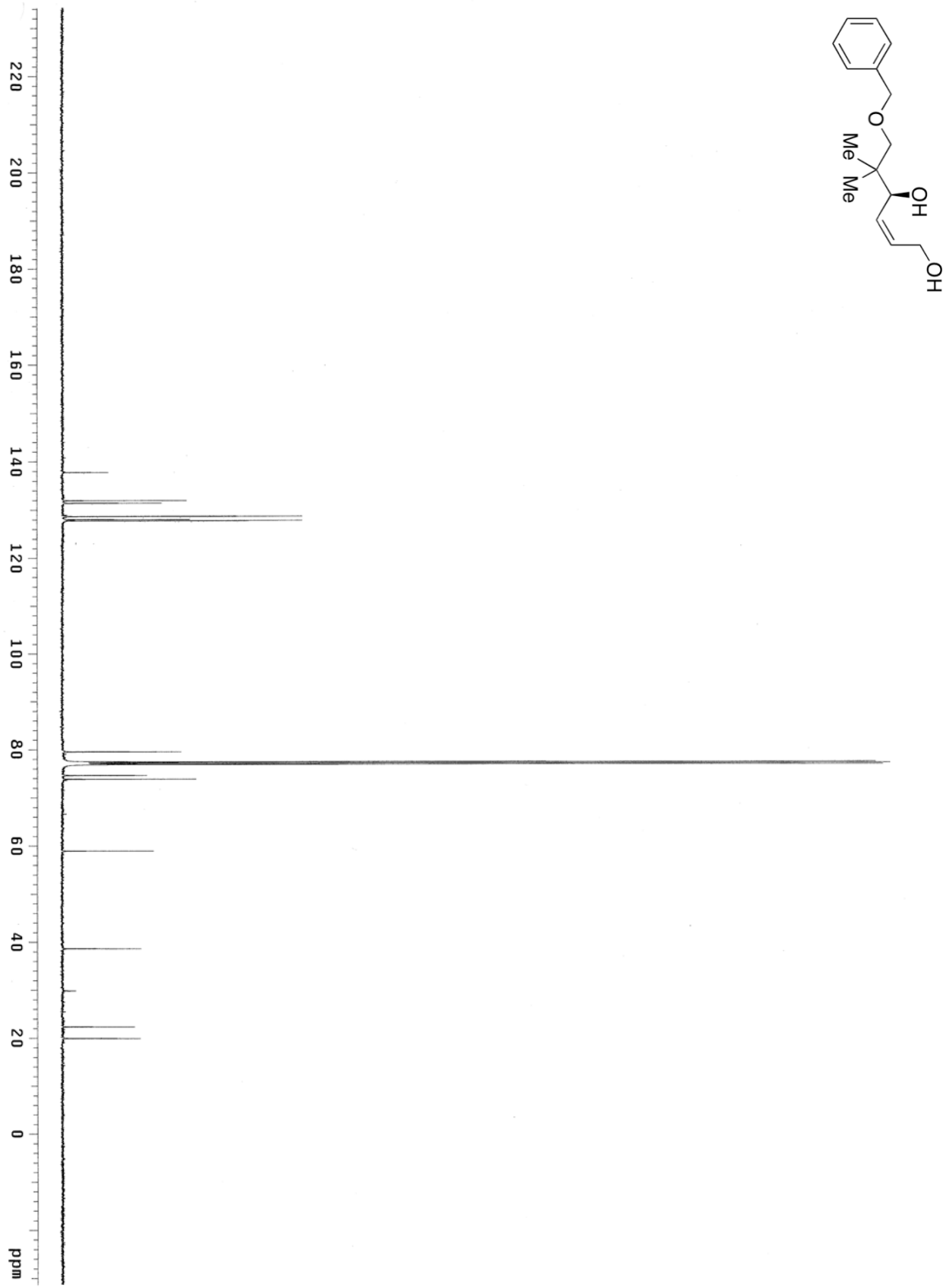
Me
Me
OH
OH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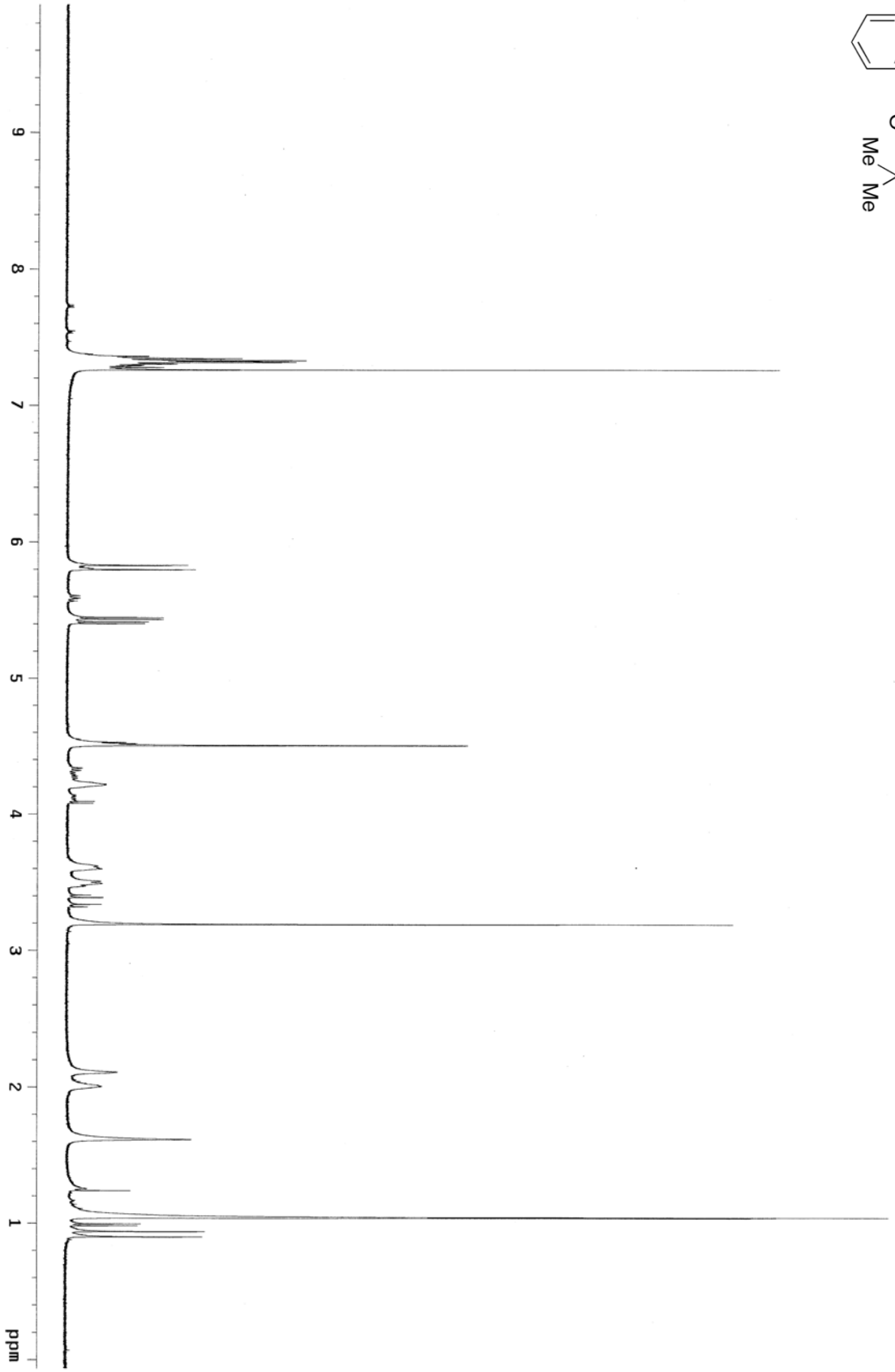
Me
OH
OH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Me
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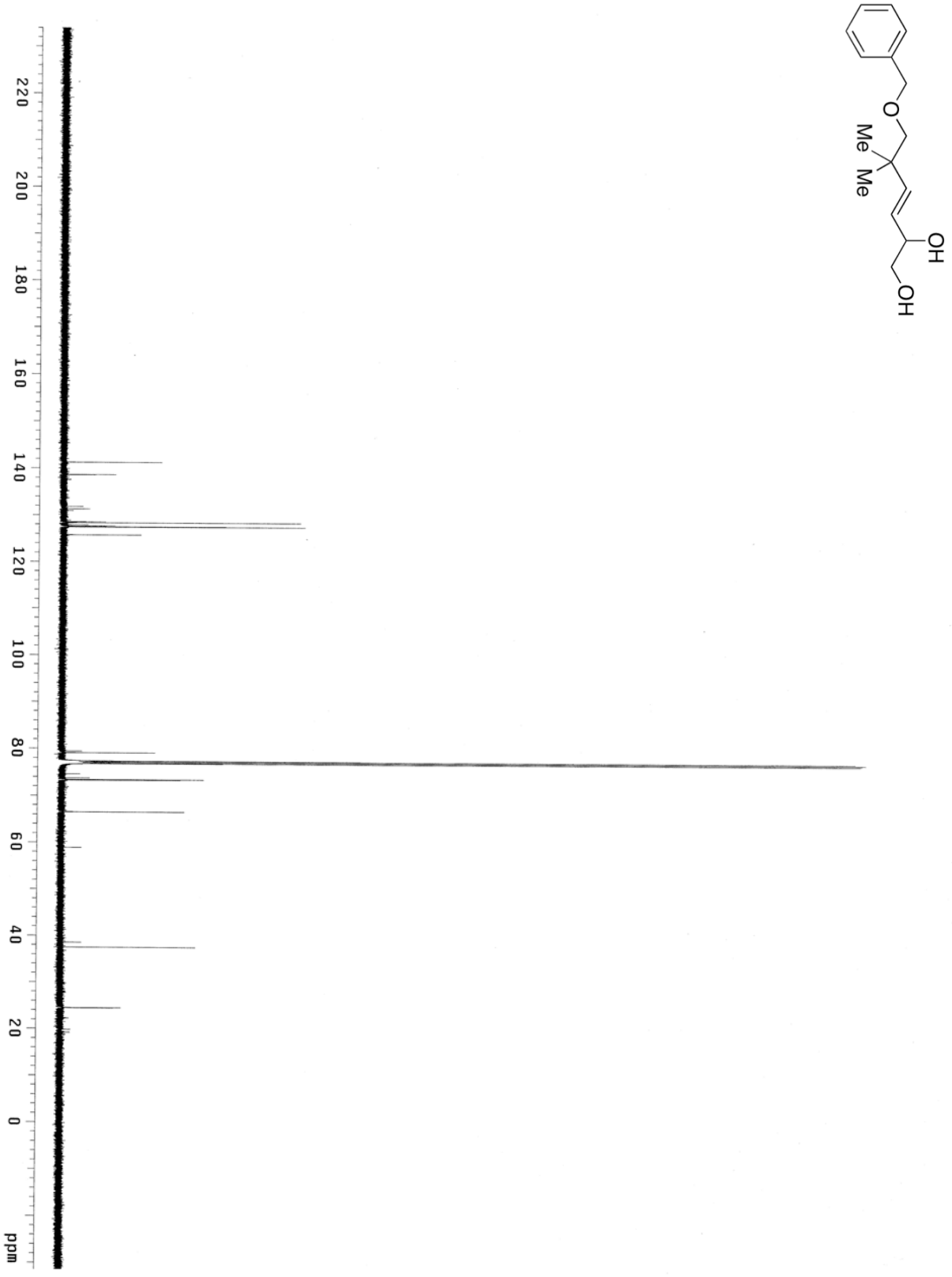
ppm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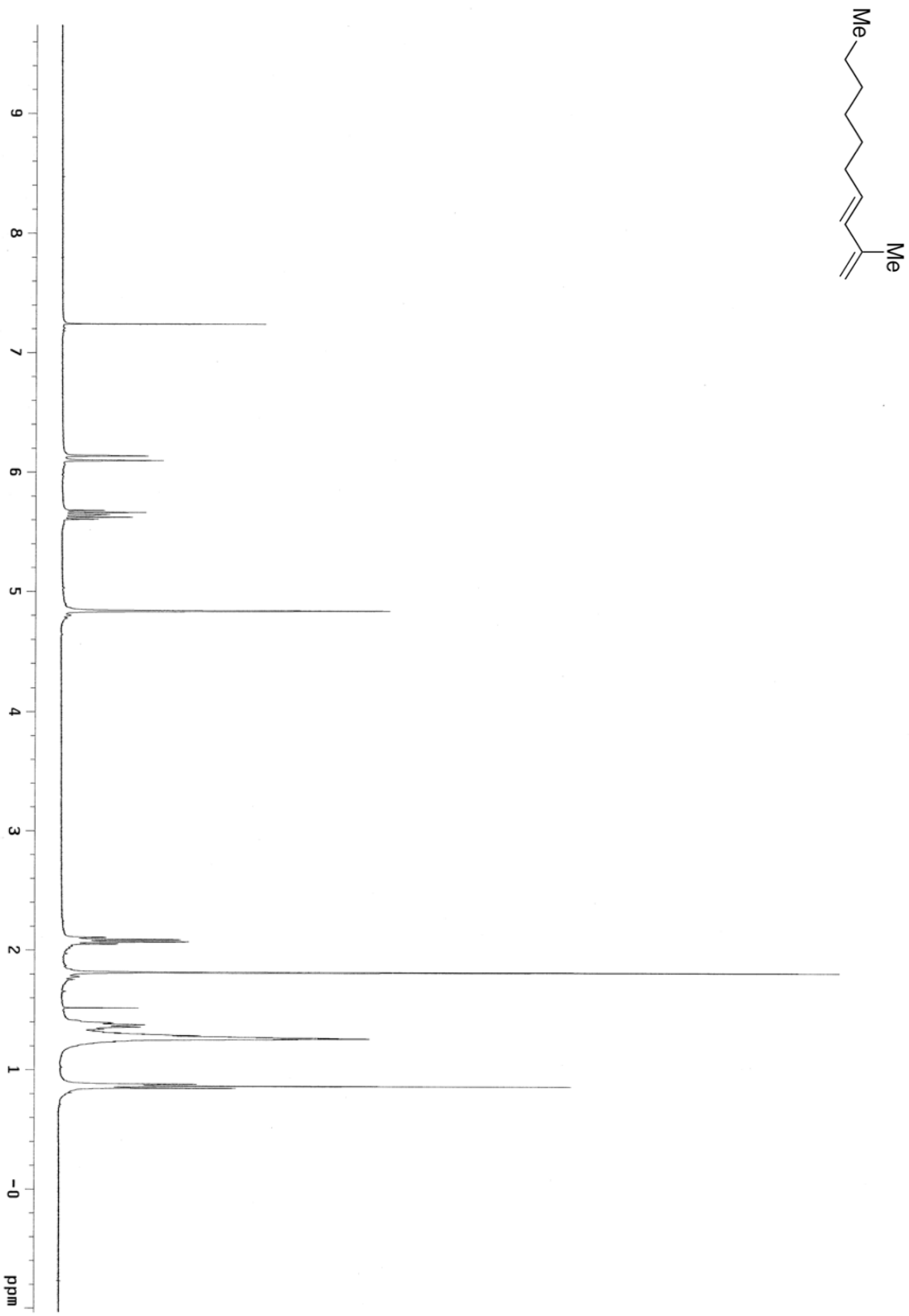
Me
OH
OH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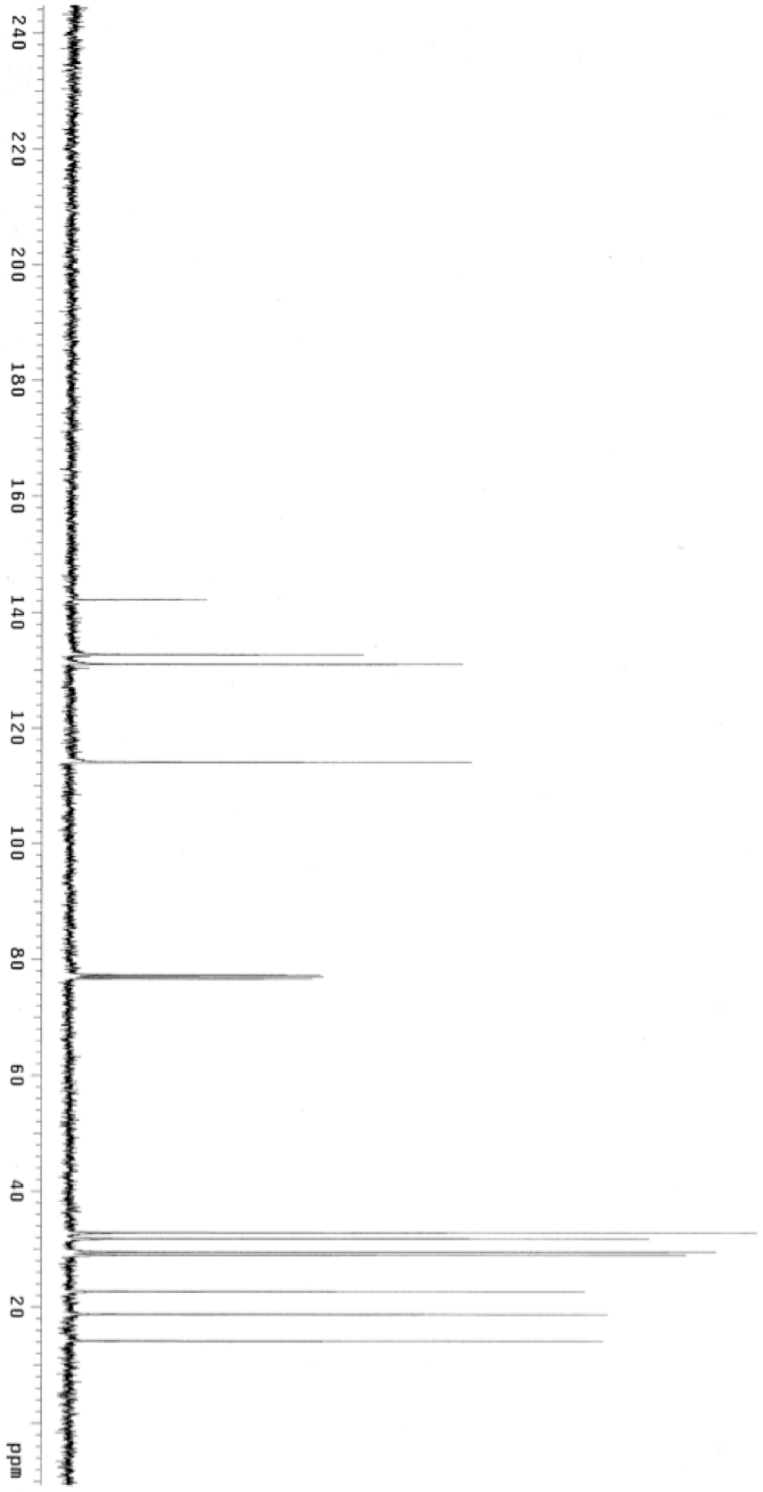
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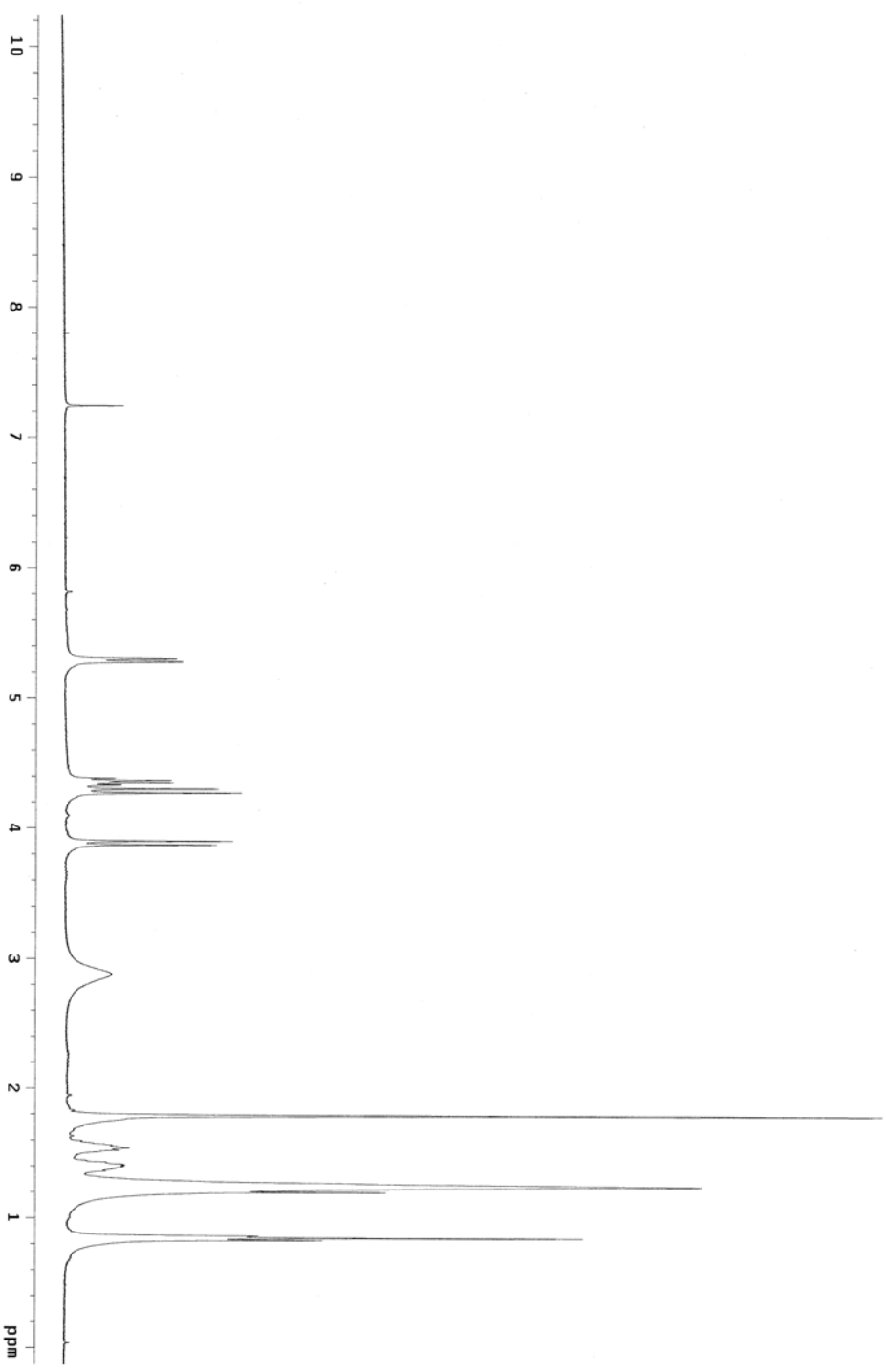
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Me
OH
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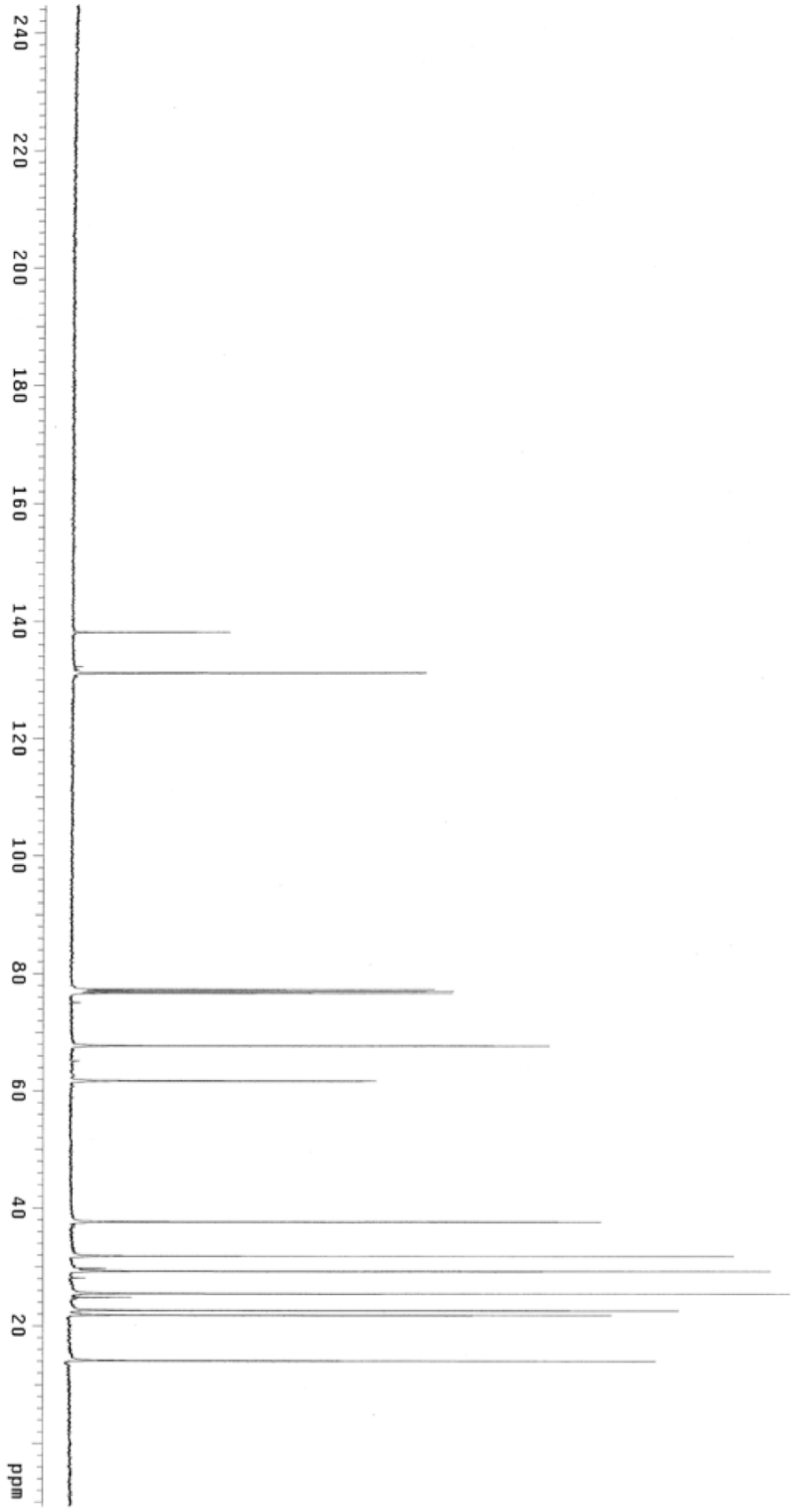
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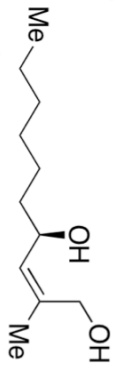
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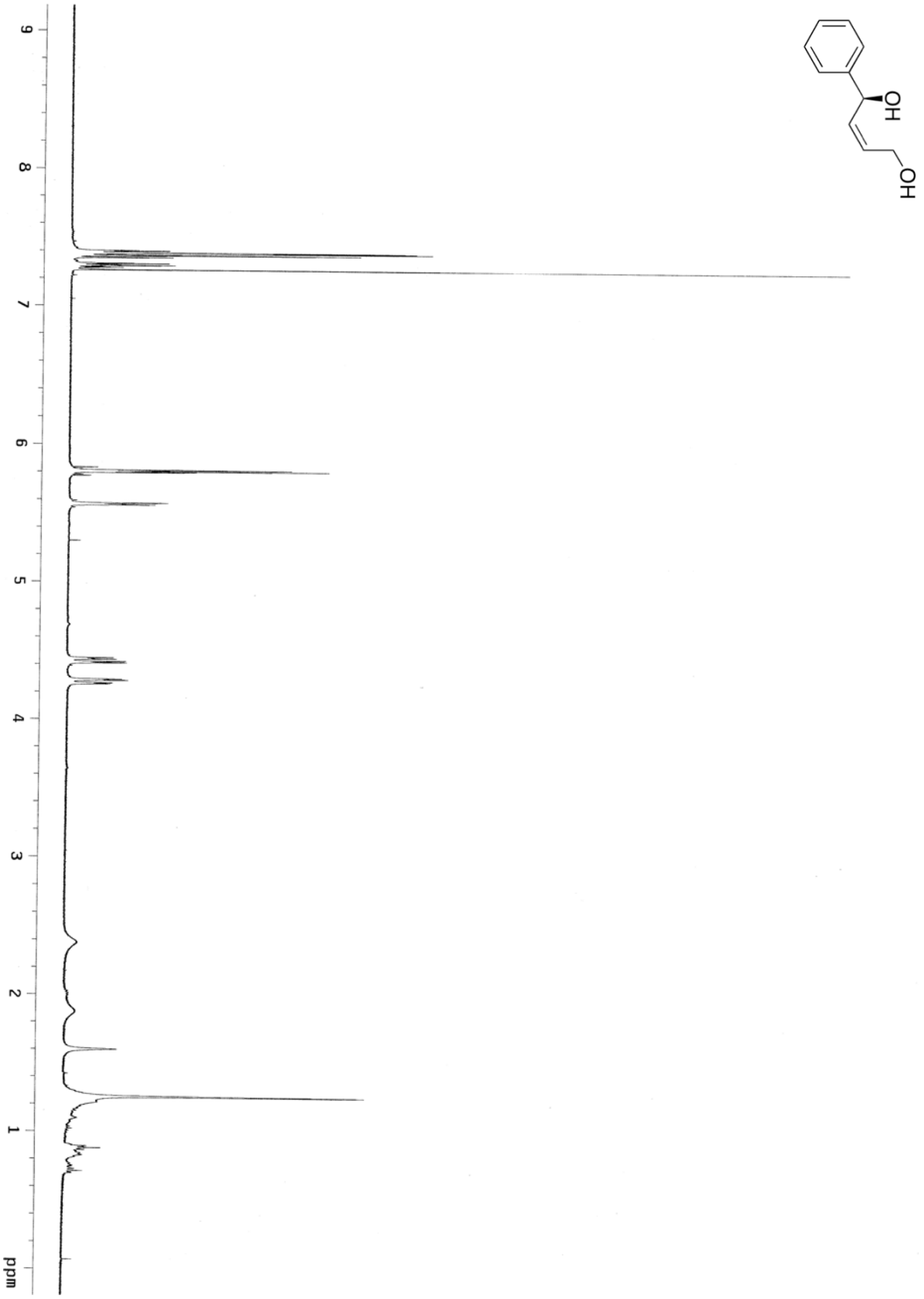
OH
Me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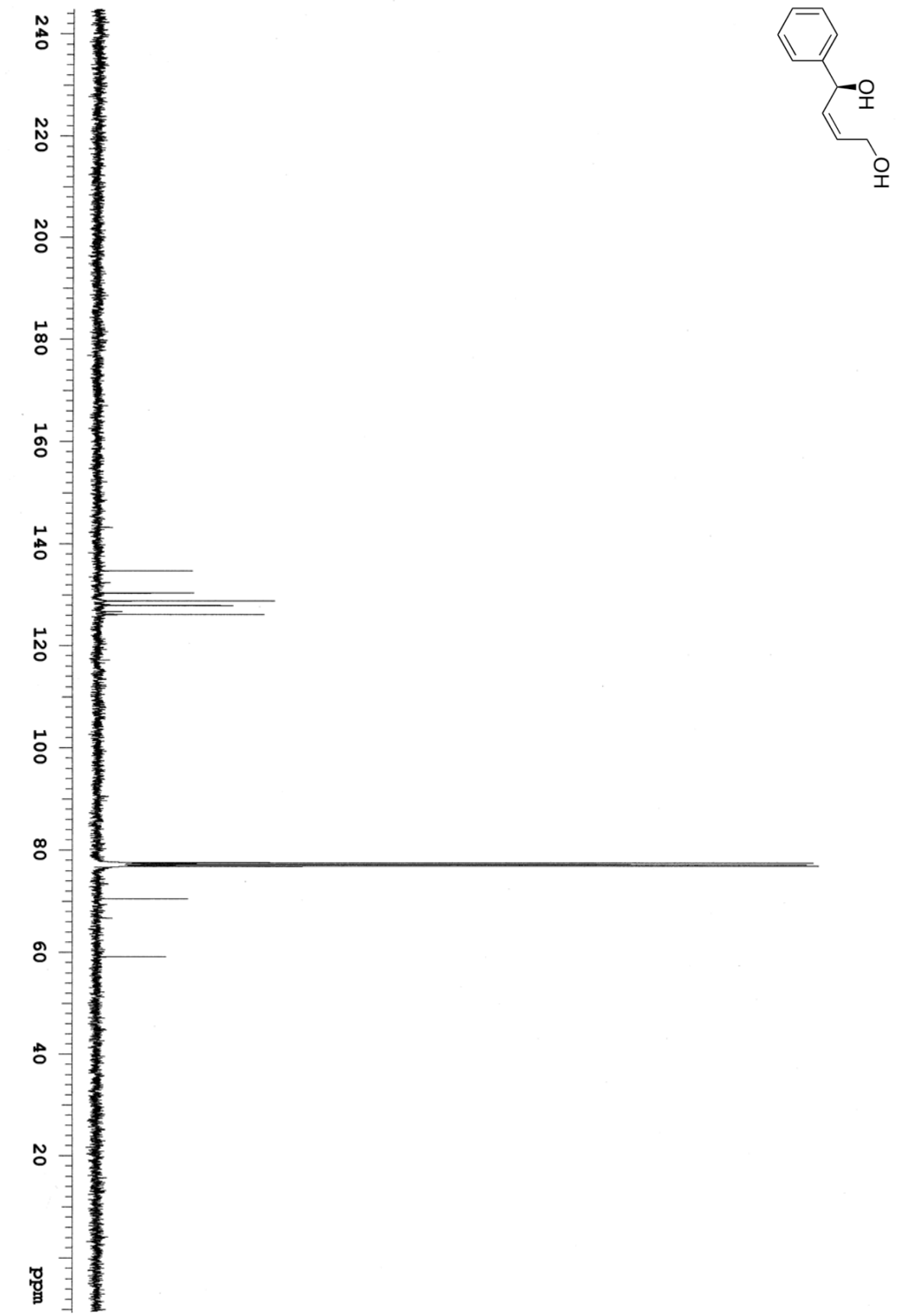
1
ppm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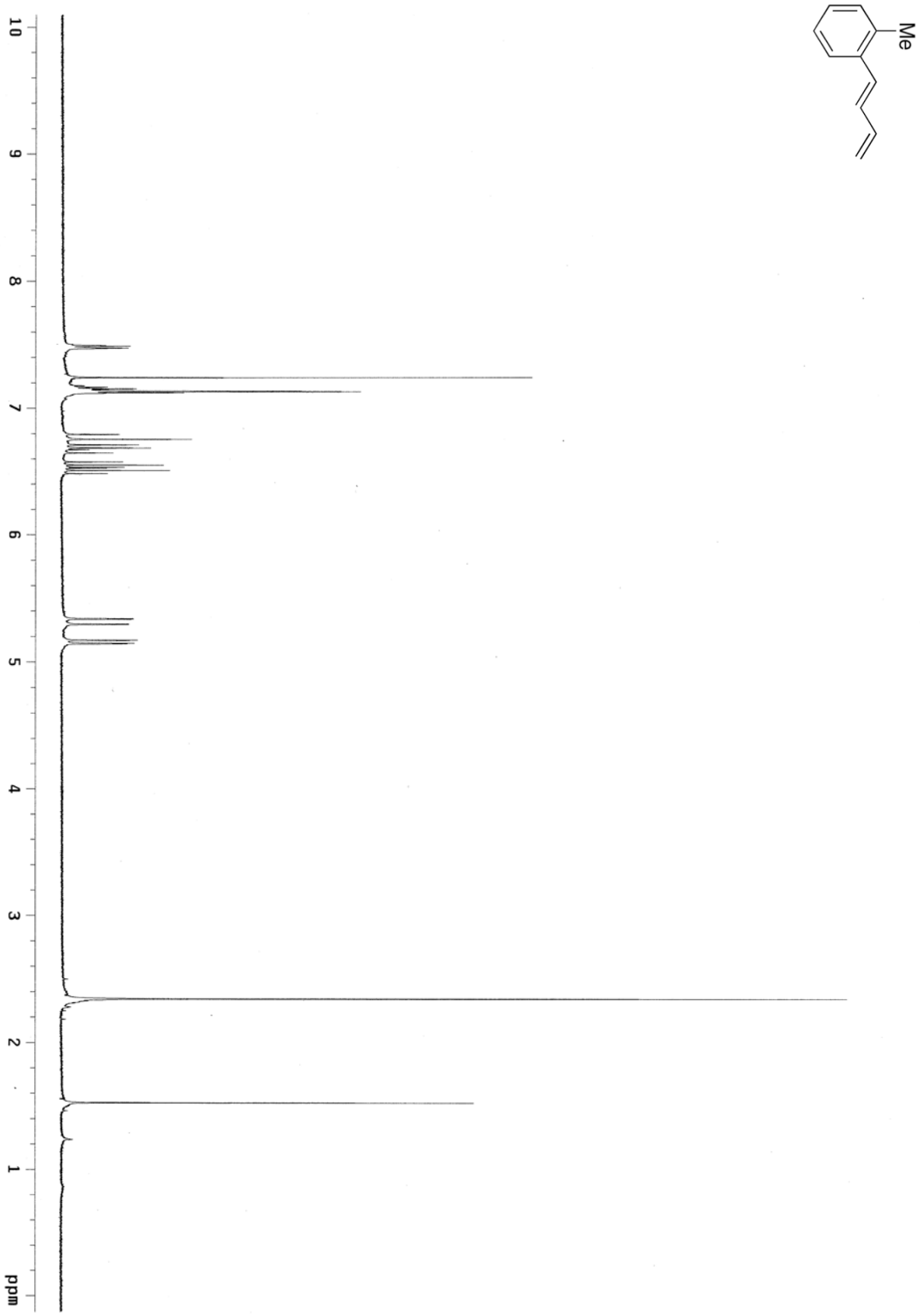
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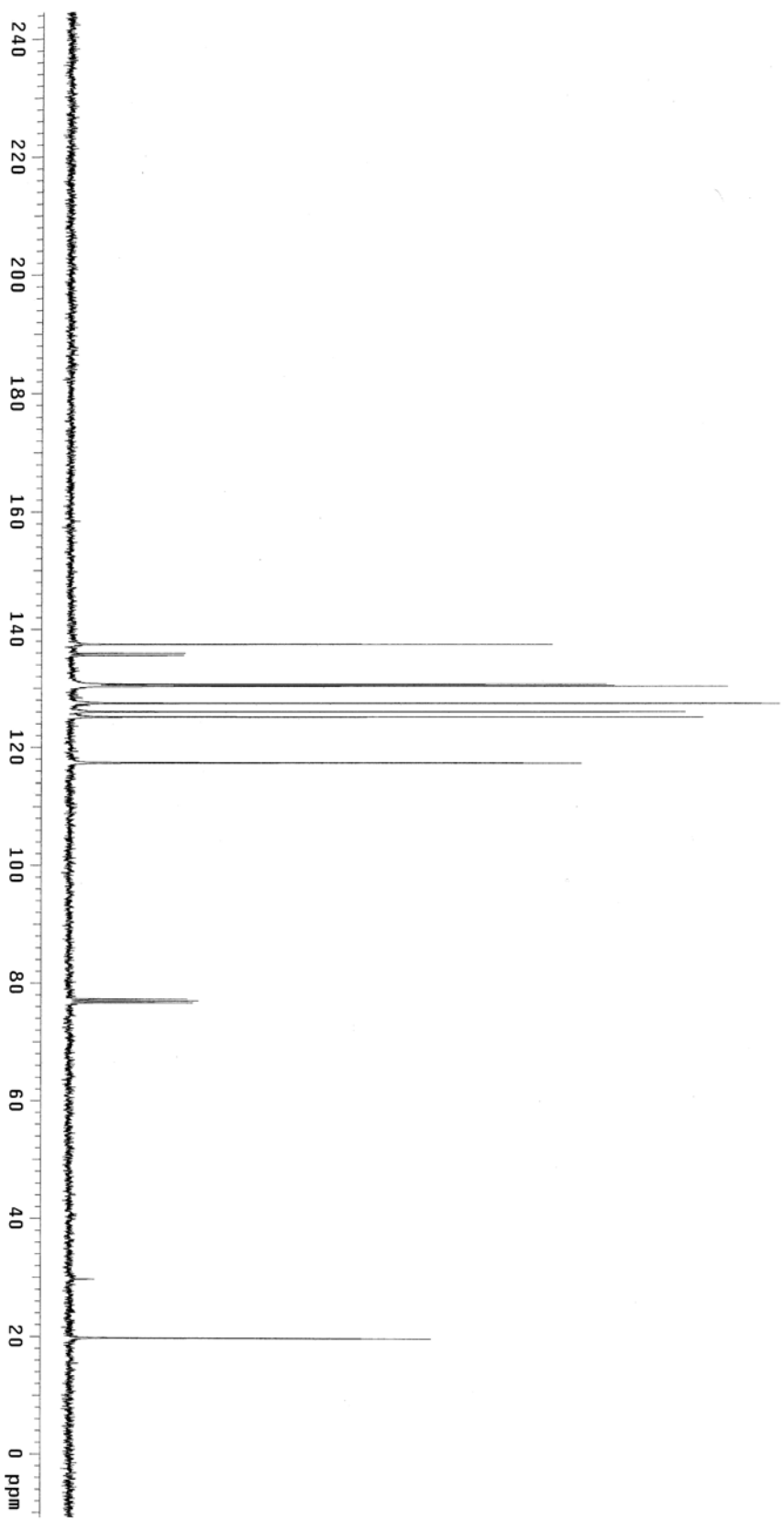
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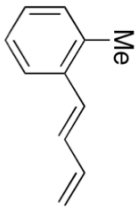
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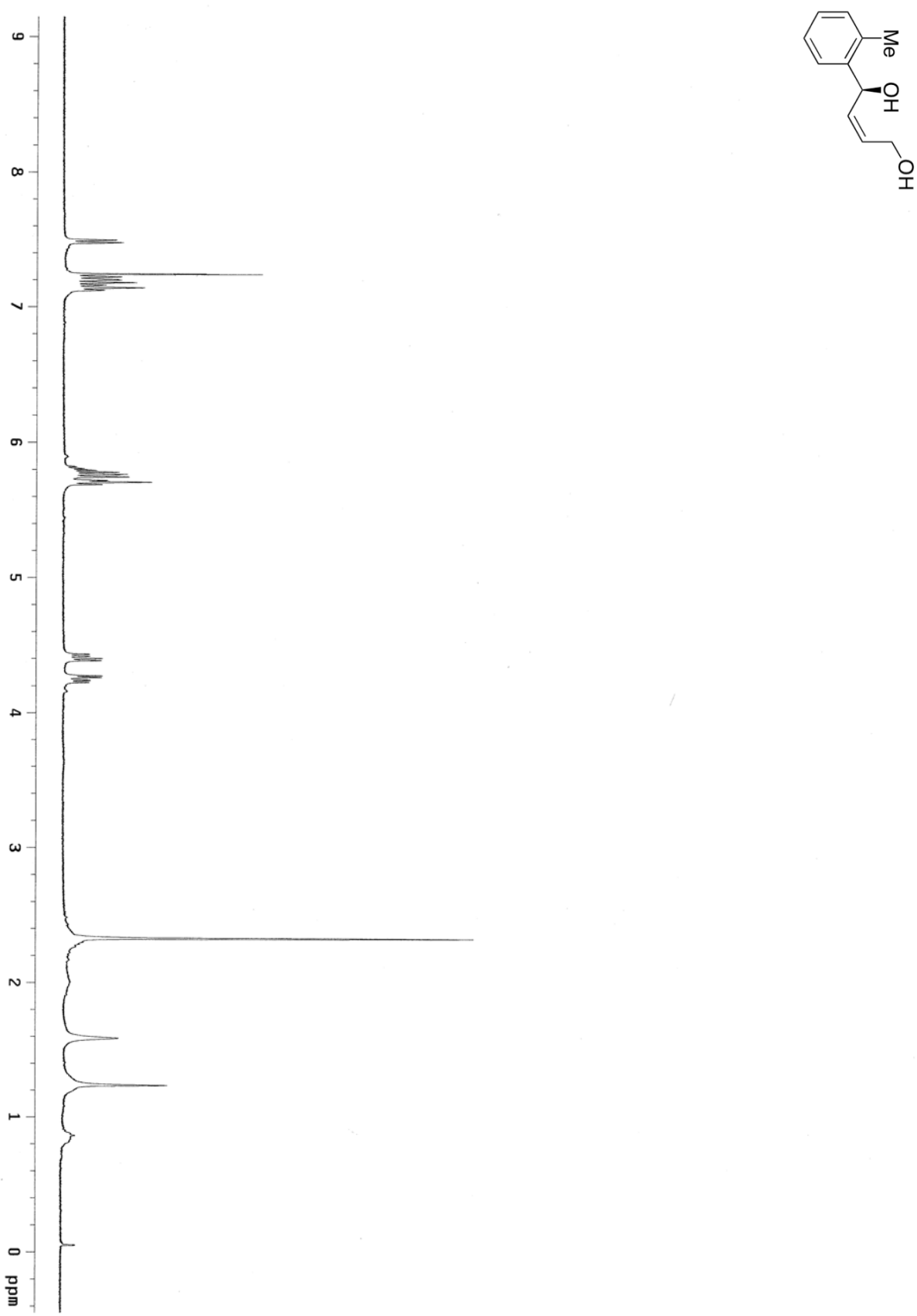
Me
OH
OH
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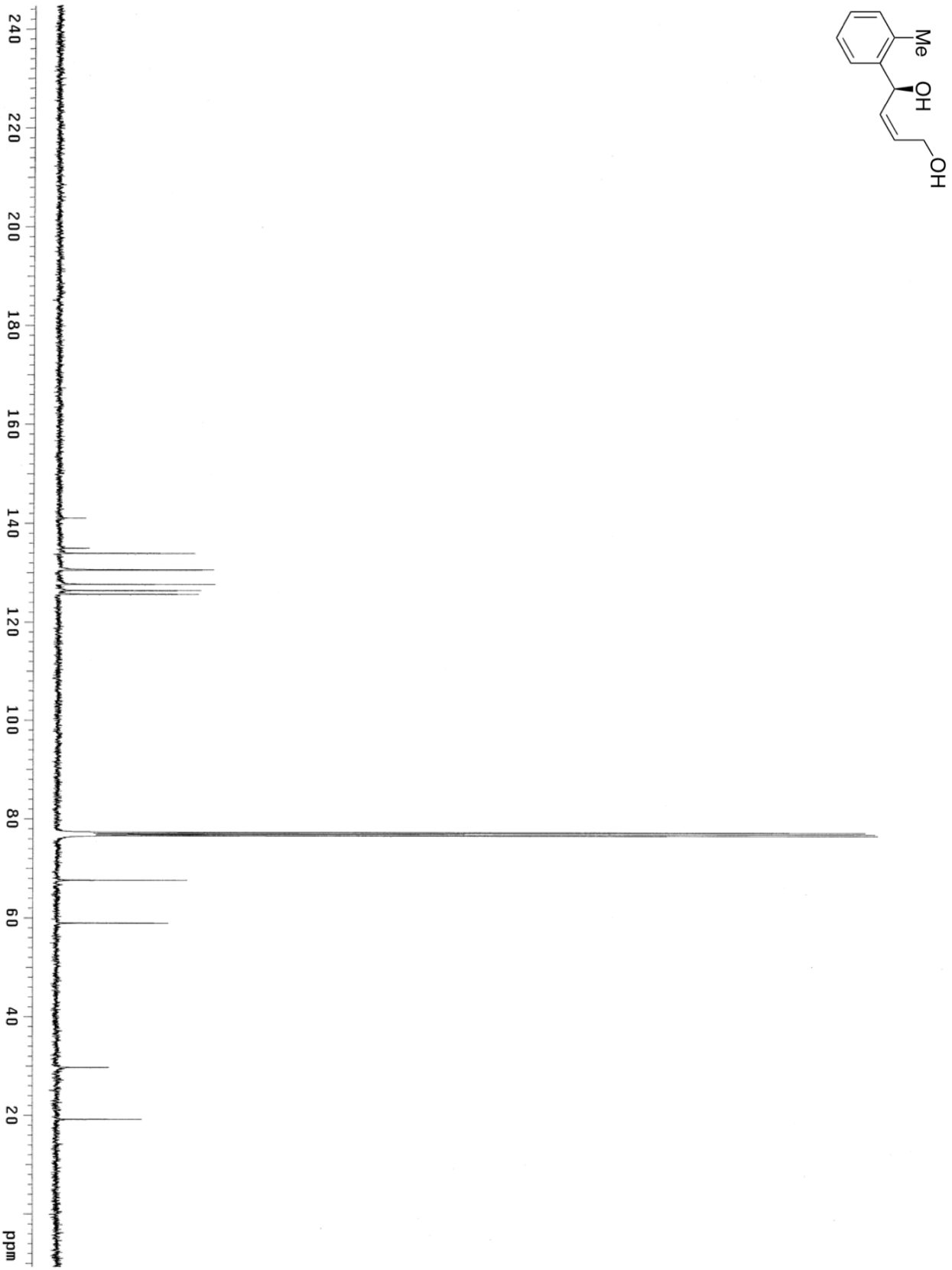
0
ppm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OH
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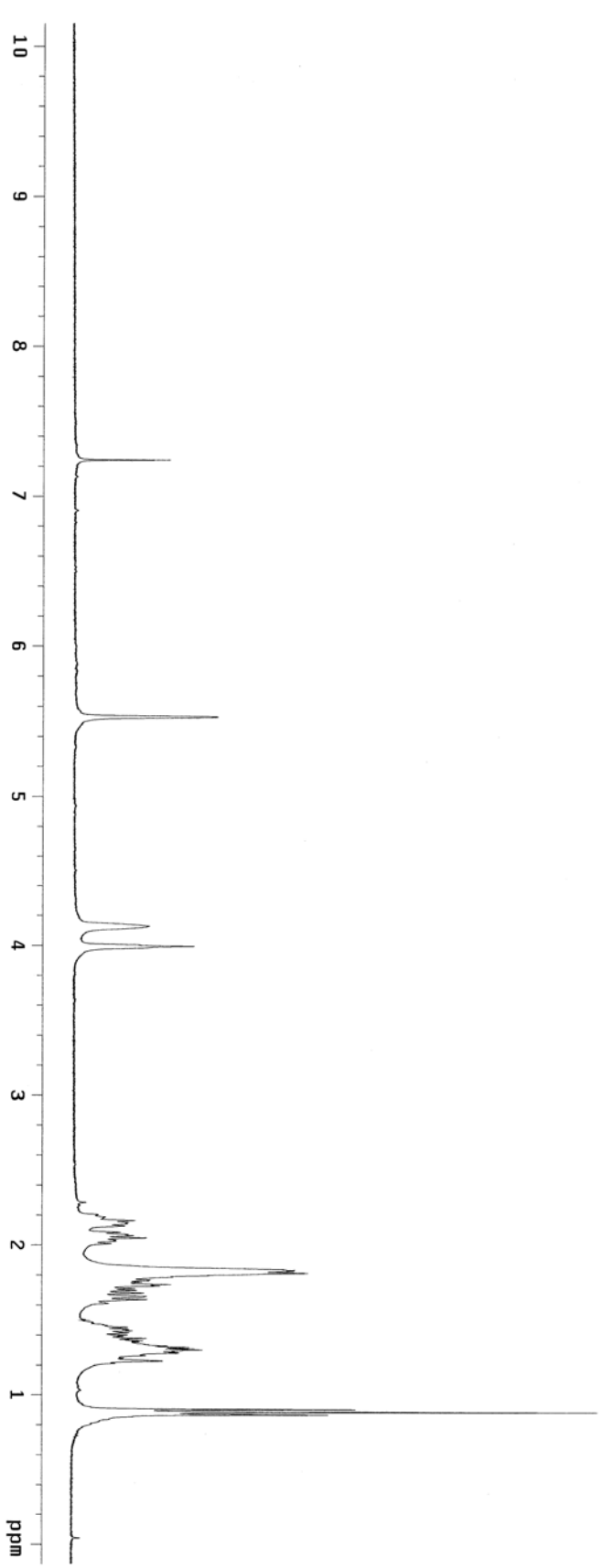
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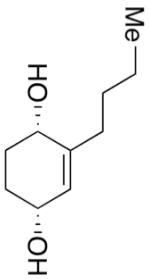
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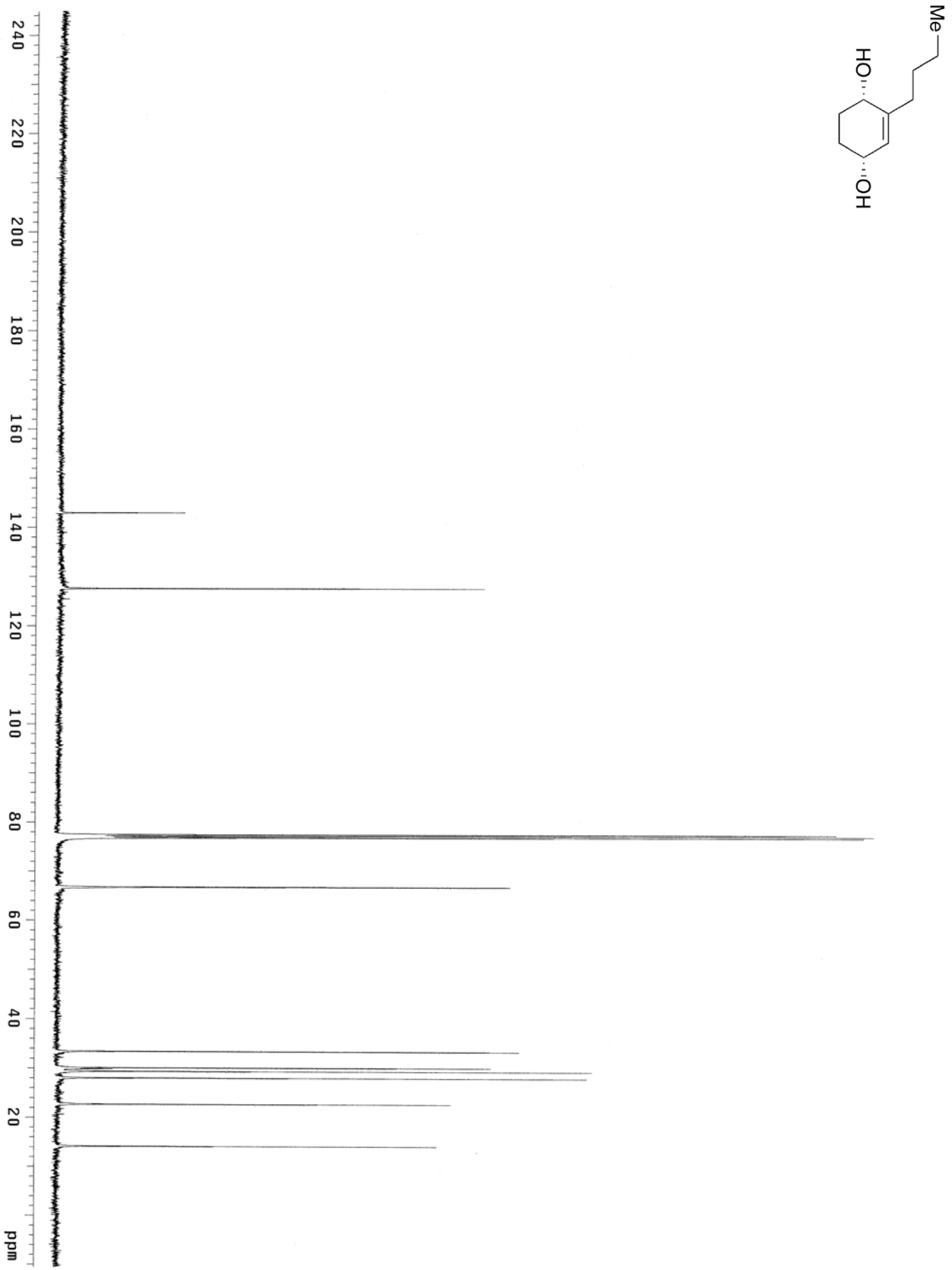
HO
OH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OH
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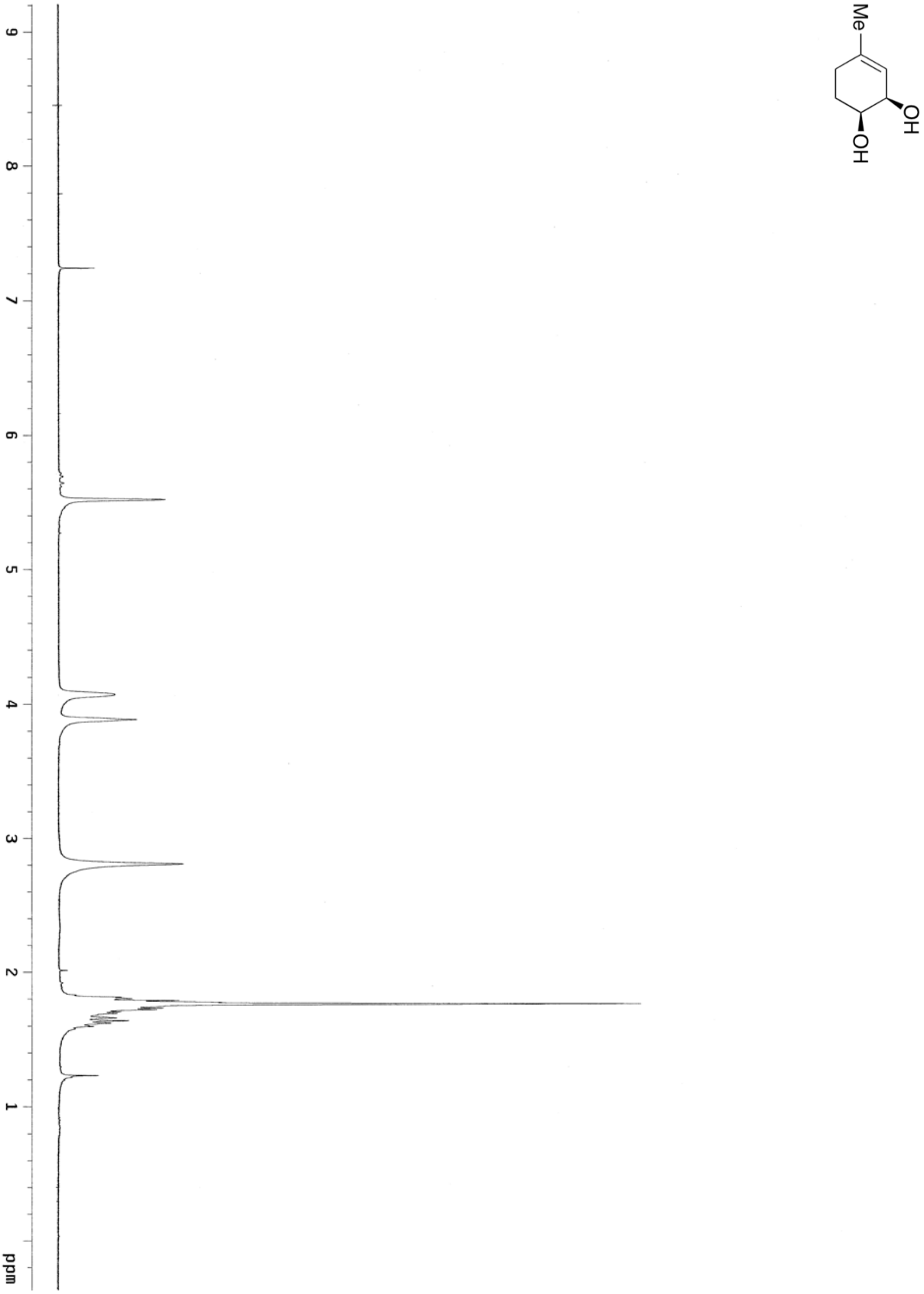
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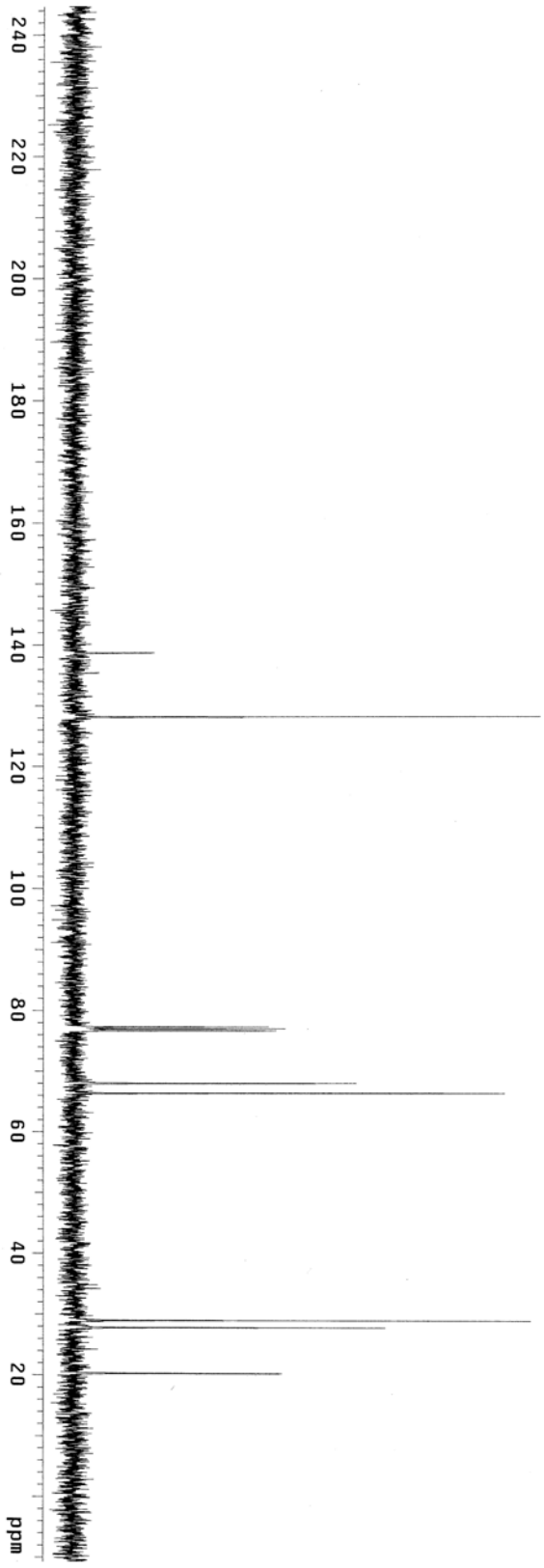
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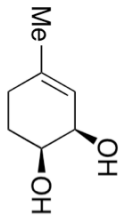
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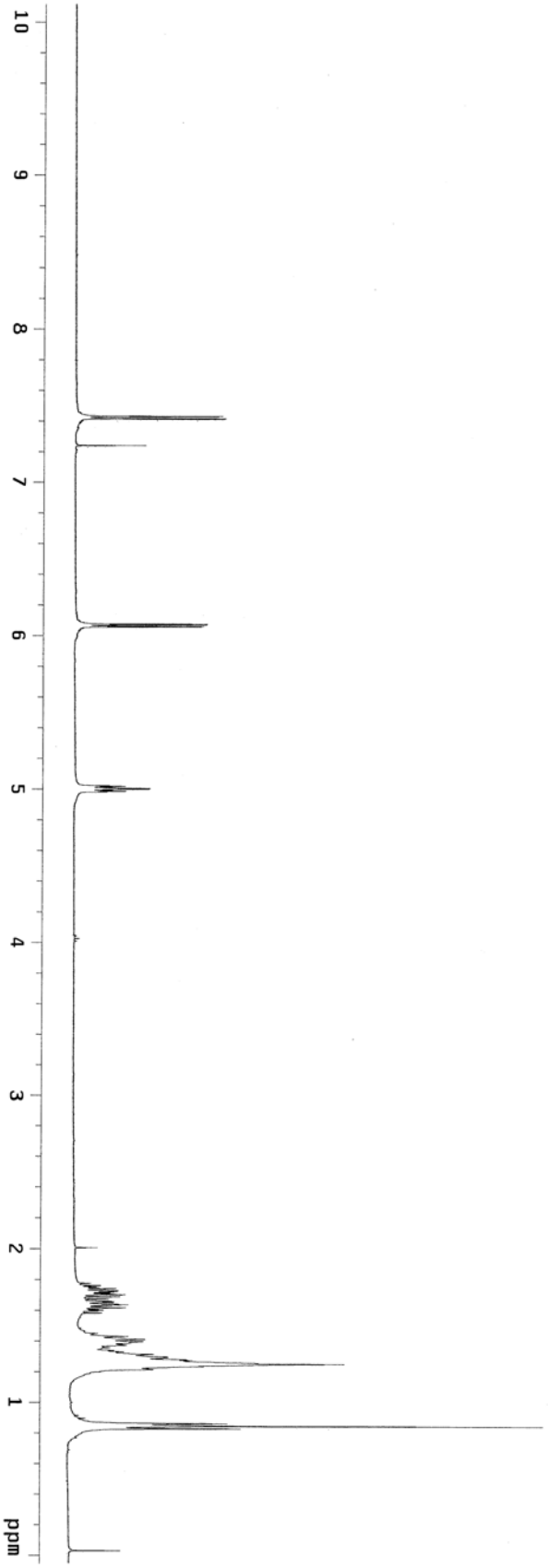
OH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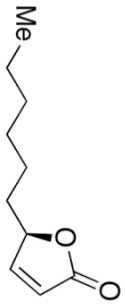
1
ppm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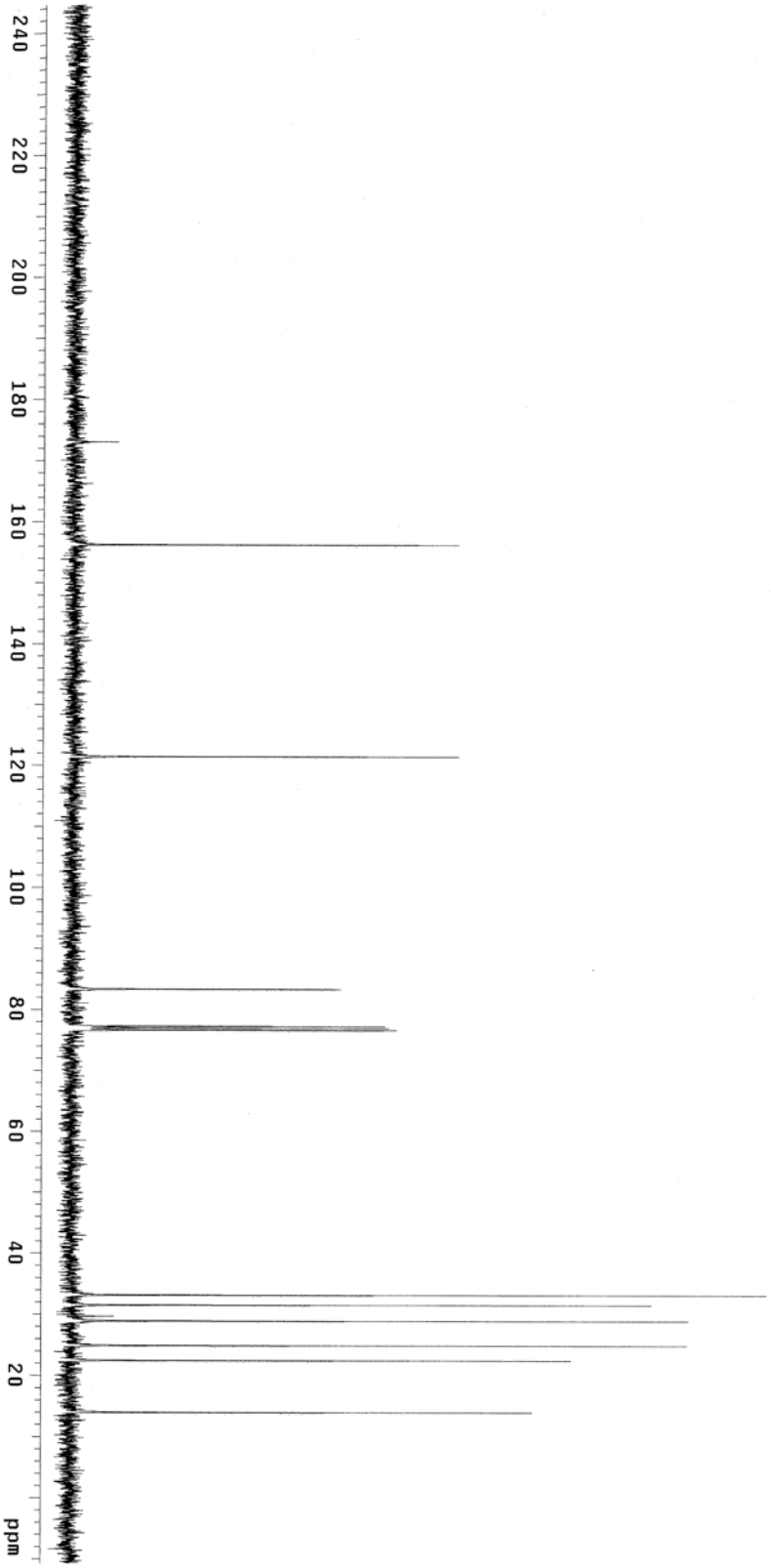
O
O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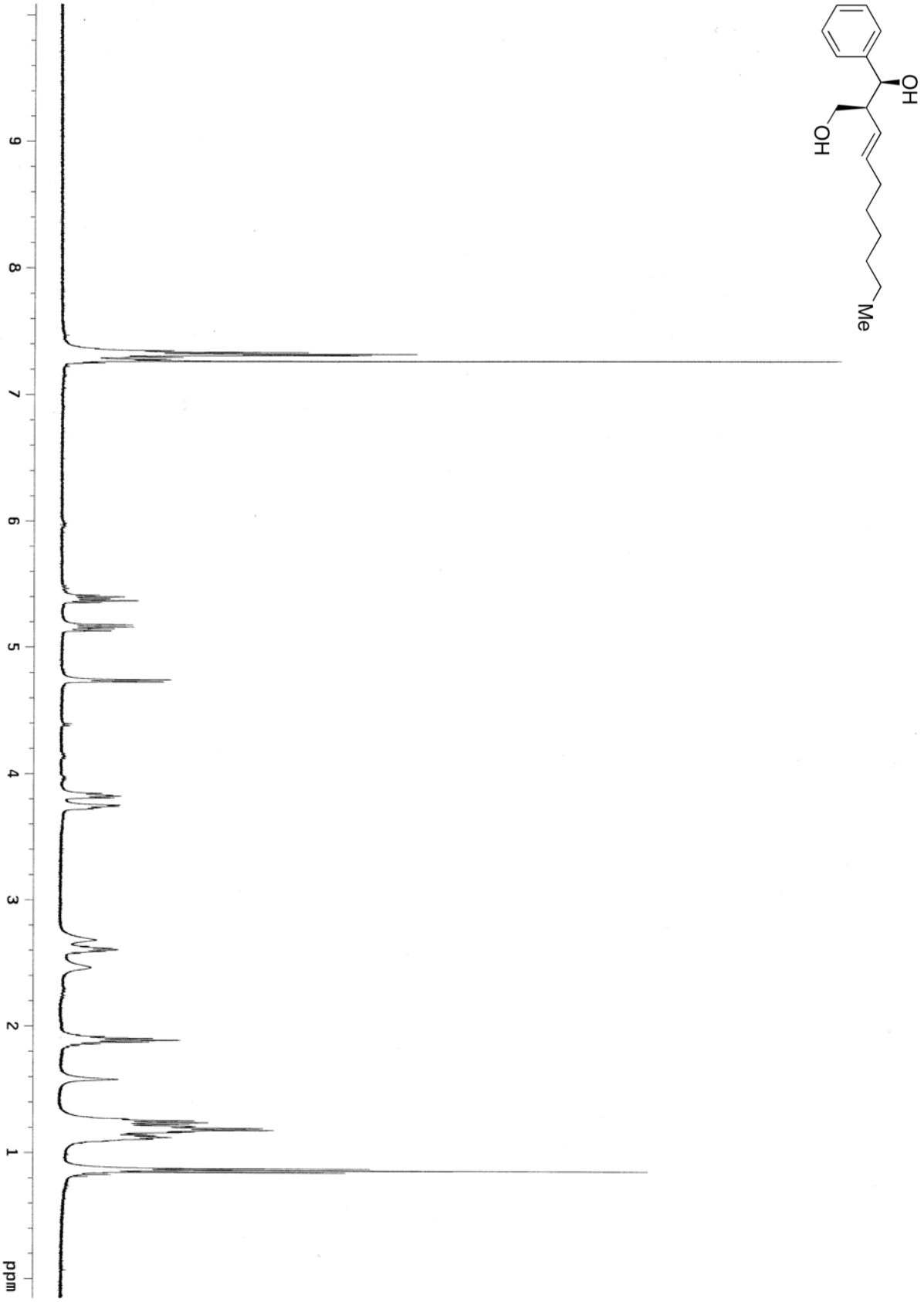
60
40
20
ppm


Me
O
O


OH
OH
Me
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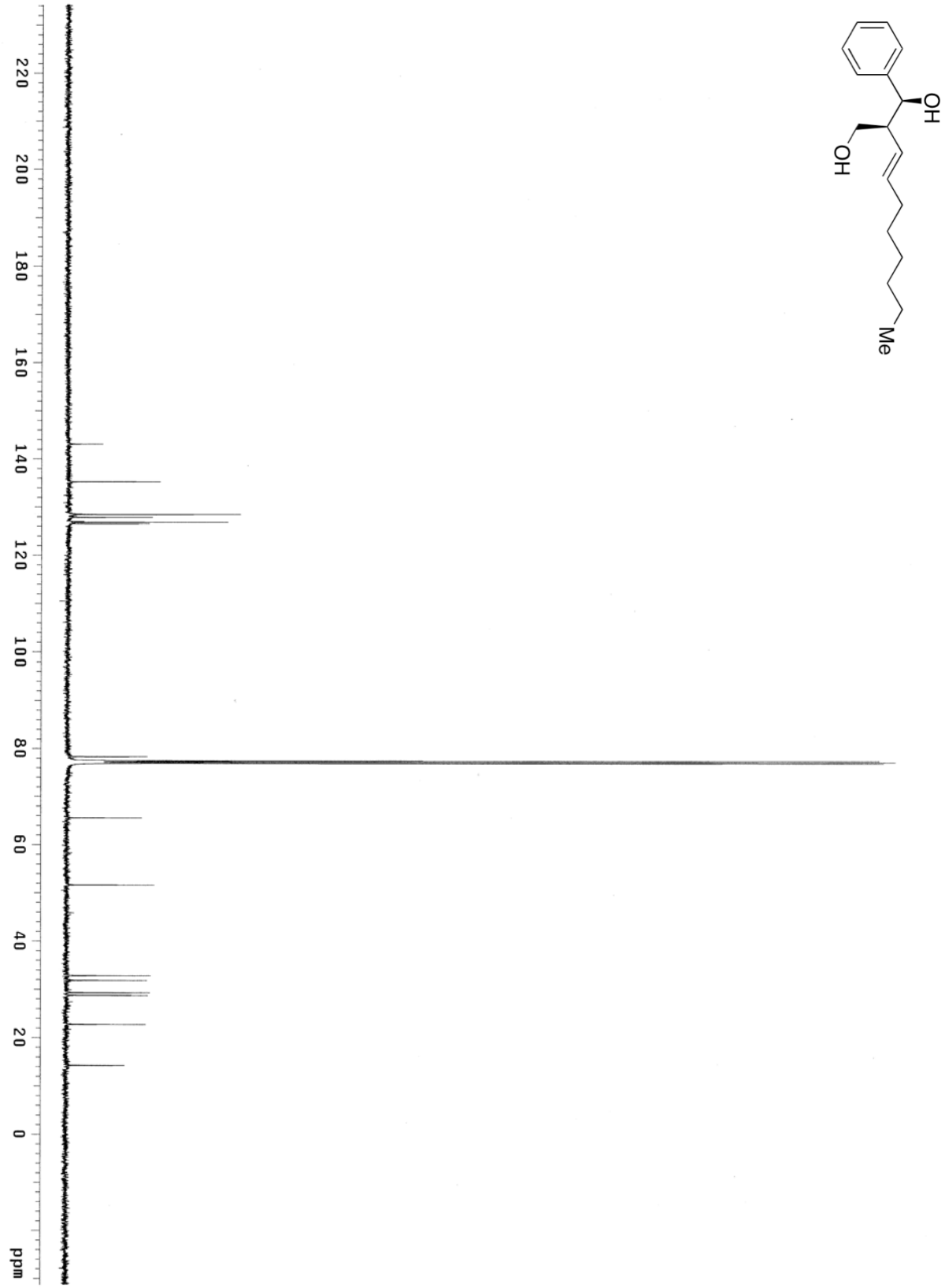
1
ppm


OH
OH
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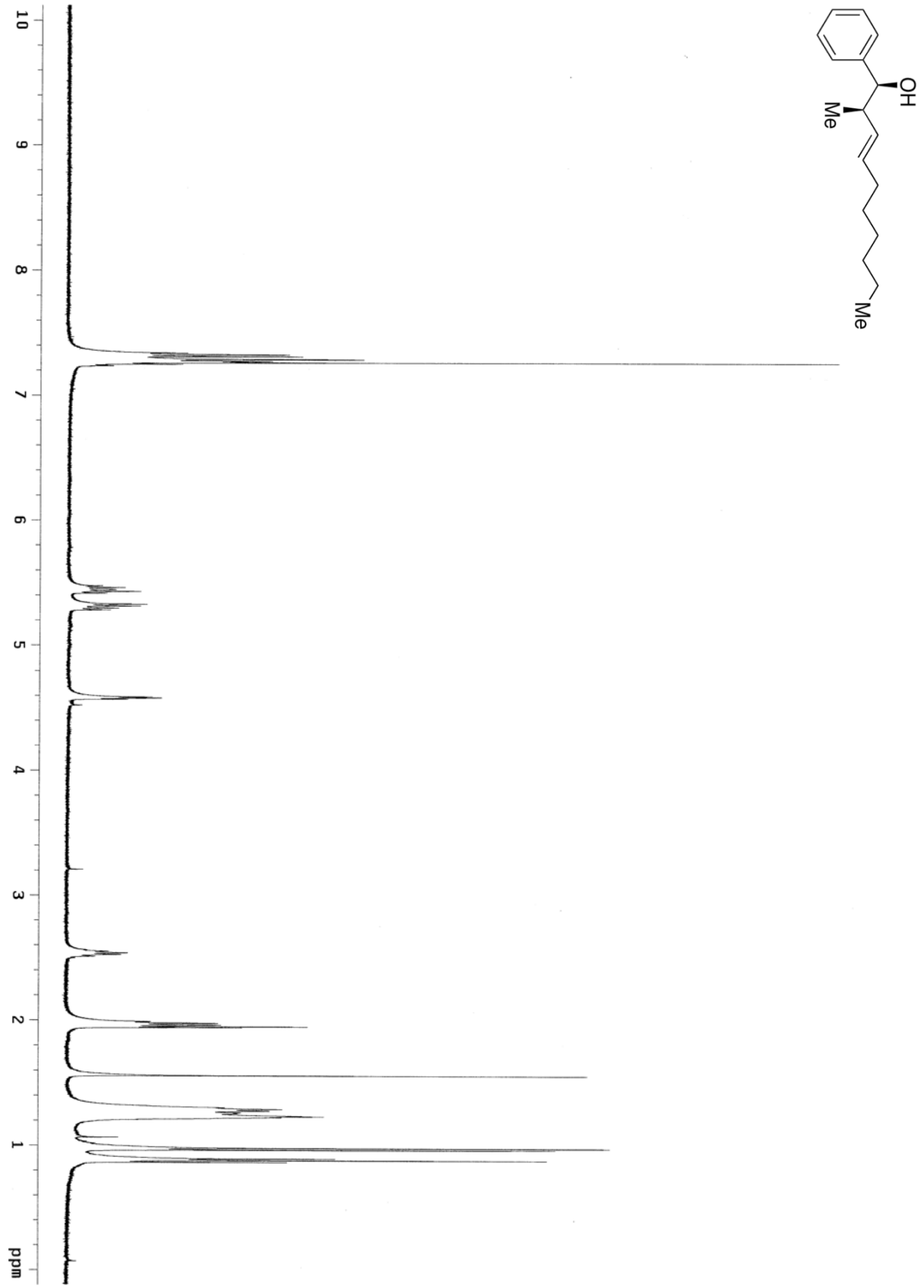
0
ppm


OH
Me
Me
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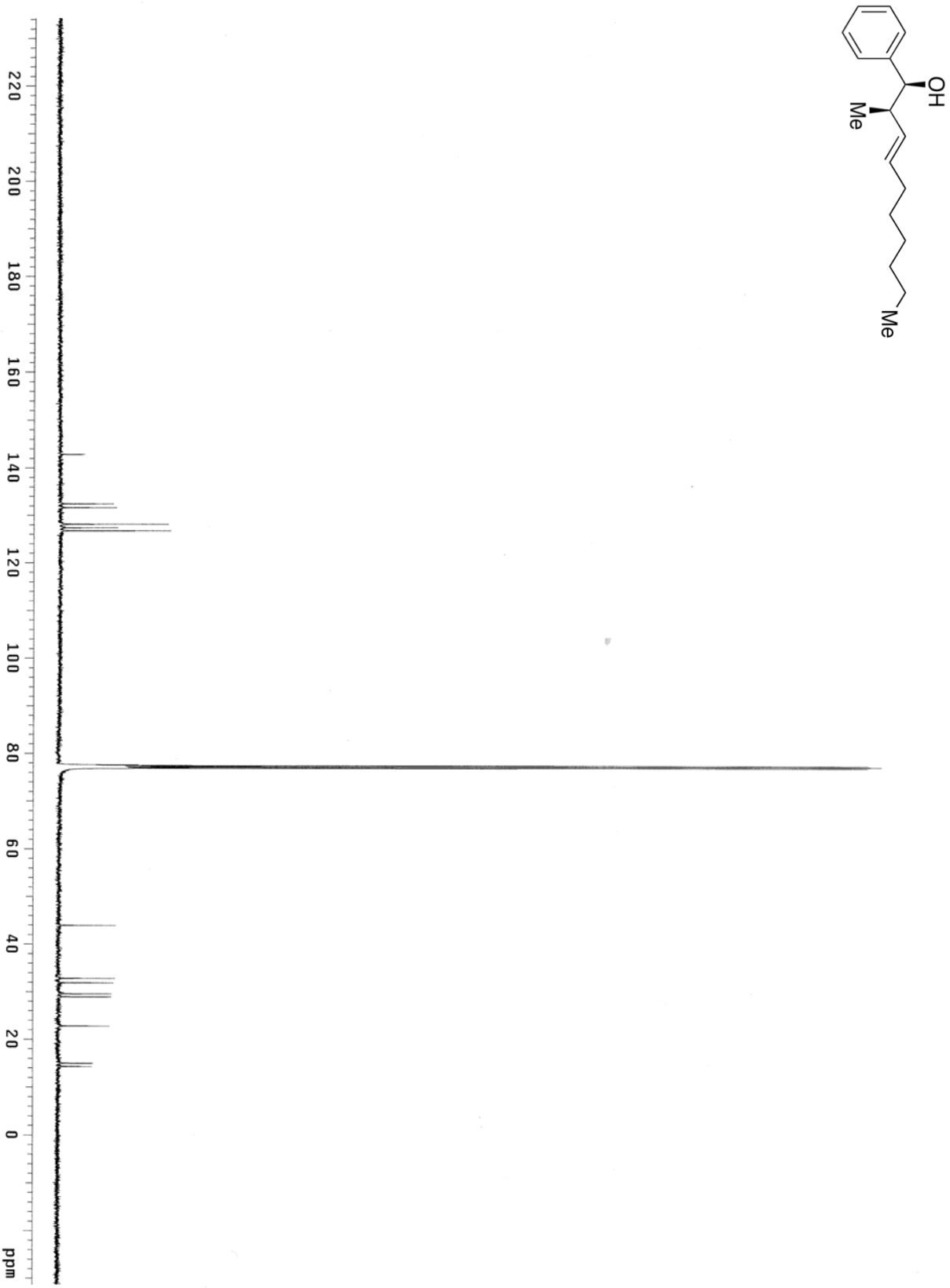
ppm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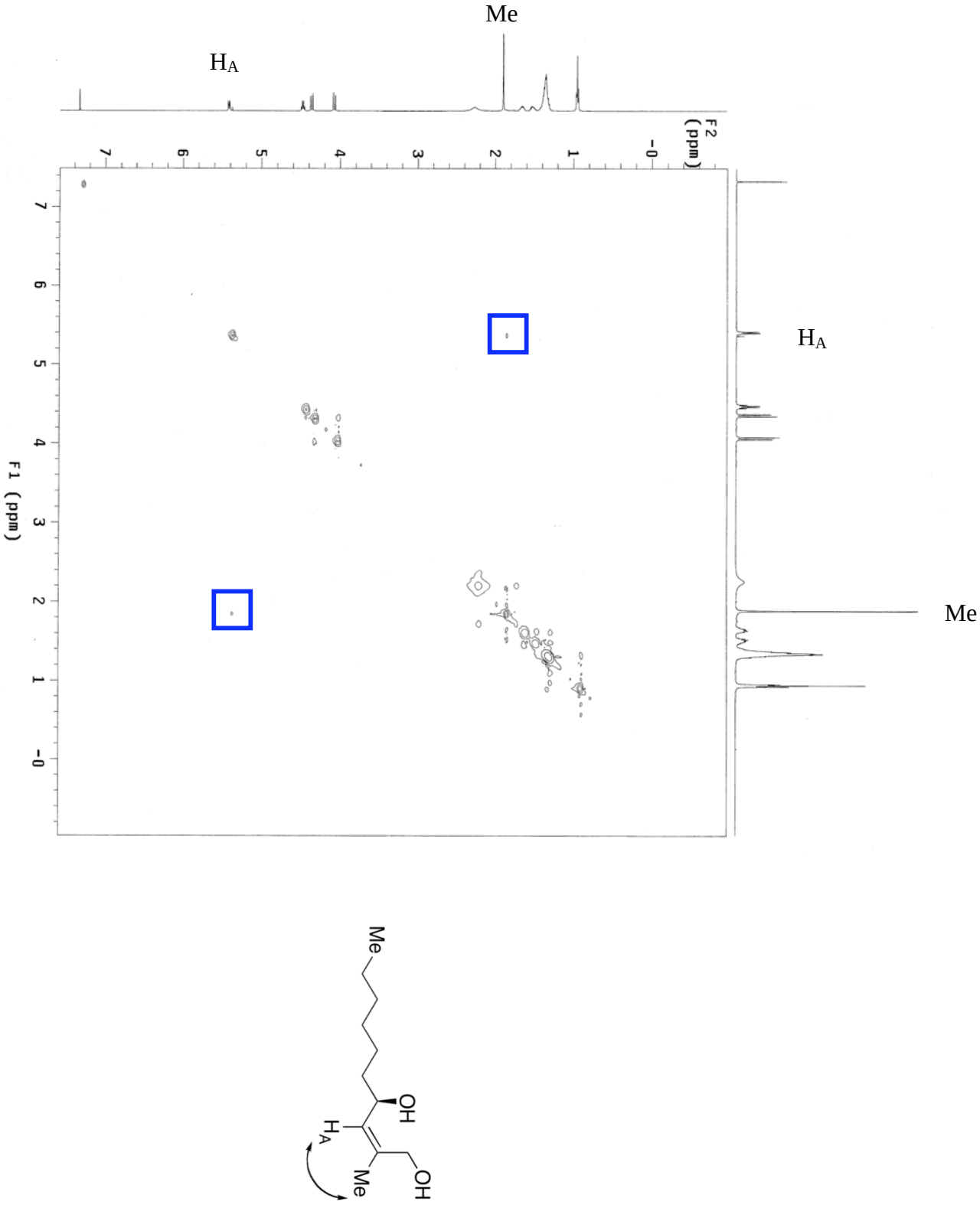
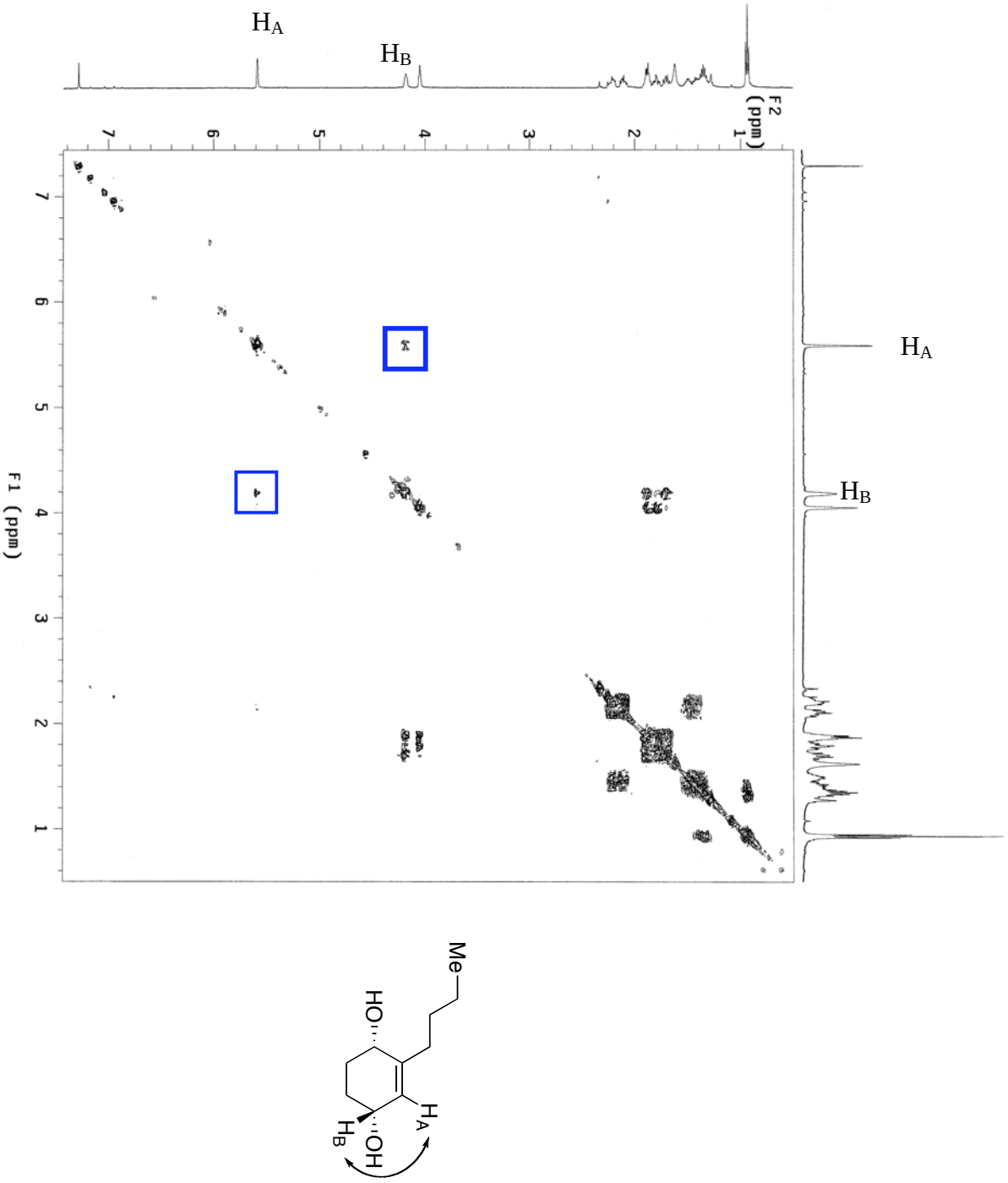
ppm


Me
HA
F2 (ppm)
F1 (ppm)
HA
Me
Me
OH
HA
Me
OH


HA
HB
F2 (ppm)
F1 (ppm)
HA
HB
Me
HO
HA
HB
OH