Regio- and Stereoselective Ni-Catalyzed 1,4-Hydroboration of 1,3-Dienes: Access to Stereodefined Allylboron Reagents and Derived Allylic Alcohols

Robert J. Ely and James P. Morken*

Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467

Supporting Information

Table of Contents

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 ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 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 ($CDCl_3$: 77.23 ppm). 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 ($KMnO_4$).

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. Benzene and toluene-d_8 were distilled from calcium hydride. Bis(1,5-cyclooctadiene)nickel(0) ($Ni(cod)_2$), tricyclohexylphosphine (PCy_3), tetrapropylammonium perruthenate, and tetrakis(triphenylphosphine) palladium(0) were purchased from Strem Chemicals, Inc. 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (pinacolborane) was purchased from Aldrich and used without further purification. Triphenylphosphine was purchased from Aldrich and recrystallized from hexanes before use. 2,4-dimethyl-1,3-pentadiene was purchased from Acros and distilled before use. 3-methyl-1,3-pentadiene was purchased from ChemSampCo and used without further purification. Styrene and benzaldehyde were purchased from Aldrich and distilled before use. Potassium phthalamide was purchased from Eastman and used without further purification. All other reagents were purchased from Aldrich or Fisher and used without further purification.

Experimental Procedures

I. Representative Procedure for Ligand Screen (Scheme 2).

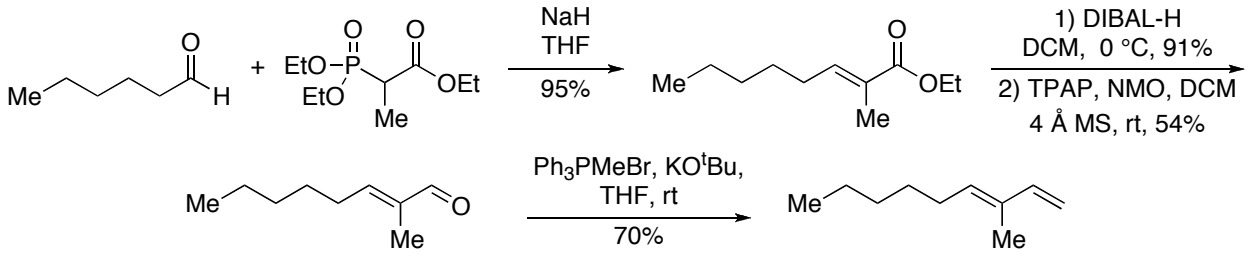
In the dry box, an oven-dried 6-dram vial with magnetic stir bar was charged successively with $Ni(cod)_2$ (0.2 mL of a 18.2 μM solution of $Ni(cod)_2$ in toluene-d_8, 3.60 μmol), PCy_3 (0.2 mL of a 44.0 μM solution of PCy_3 in toluene-d_8, 8.70 μmol), pinacolborane (27.8 mg, 0.22 mmol), and (*Z*)-dec-2-en-1-ol (0.18 mL of a 0.80 mM solution of (*Z*)-dec-2-en-1-ol in toluene-d_8 , 0.14 mmol). The vial was capped and allowed to stir in the dry box for 5 min, at rt, then transferred by syringe into a J-Young tube. The reaction was analyzed by ^{1}H NMR 20 minutes after the addition of the diene. Conversion was determined by integration of the alkene protons of the product relative to the starting material.

II. Preparation of Starting Material.

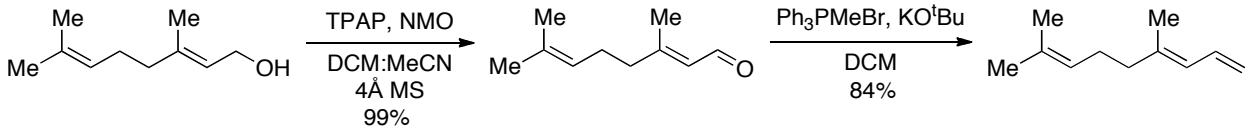
A. The following dienes were prepared by Wittig olefination of the commercially available α,β-unsaturated aldehydes with methyltriphenylphosphonium bromide and potassium *tert*-butoxide in tetrahydrofuran: *trans*-1,3-decadiene (Table 1, entry 1),[1] *trans*-1-phenyl-1,3-butadiene (Table 1, entry 2),[2]

The following dienes were prepared by the literature procedure: (*E*)-2-methyldeca-1,3-diene[3] (Table 1, entry 3), (*E*)-*tert*-butyl(penta-2,4-dienyloxy)diphenylsilane[3] (Table 1, entry 7), (*E*)-((2,2-dimethylhexa-3,5-dienyloxy)methyl)benzene[3] (Table 1, entry 8), (*E*)-ethylhepta-4,6-dienoate[4] (Table 1, entry 9), (*E*)-hepta-4,6-dien-1-ol[5] (Table 1, entry 11), and (2*E*,4*E*)-5-phenylpenta-2,4-dien-1-ol[6] (Table 2, entry 3). Spectral data are in accordance with the literature references.

B. Preparation of (E)-3-methylnona-1,3-diene (Table 1, entry 4). The title compound was synthesized as shown below. The spectral data was in accordance with the literature.[7]



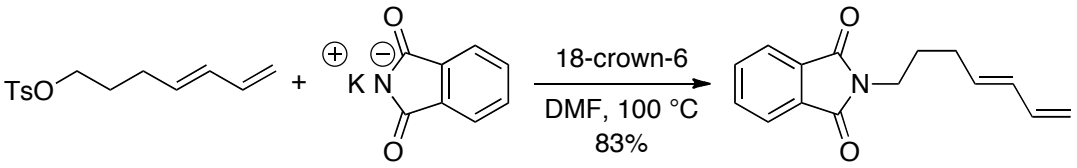
C. Preparation of (E)-4,8-dimethylnona-1,3,7-triene (Table 1, entry 5). The title compound was synthesized as shown below. The spectral data was in accordance with the literature.[8]

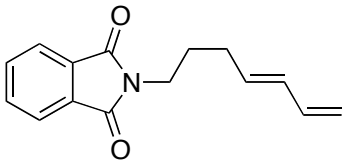


D. Preparation of (E)-2-(hepta-4,6-dienyl)isoindoline-1,3-dione. To a flame-dried round-bottom flask equipped with a reflux condenser and a magnetic stir bar was added (*E*)-hepta-4,6-

[1] Meyers, A. I.; Ford, M. E. *J. Org. Chem.* **1976**, *41*, 1735.
[2] Yeh, K. L.; Liu, B.; Lo, C. Y.; Huang, H. L.; Liu, R. S. *J. Am. Chem. Soc.* **2002**, *124*, 6510.
[3] Burks, H. E.; Kliman, L. T.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 9134.
[4] Crawford, J.; Bishop, J.; Spino, C. *J. Org. Chem.* **1995**, *60*, 844.
[5] Ware Jr., R. W.; Day, C. S.; King, S. B. *J. Org Chem.* **2002**, *67*, 6174.
[6] Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12168.
[7] Pospíšil, J.; Markó, I. E. *Org. Lett.* **2006**, *8*, 5983.
[8] Davies, H. M. L.; Loe, Ø; Stafford, D. G. *Org. Lett.* **2005**, *7*, 5561.

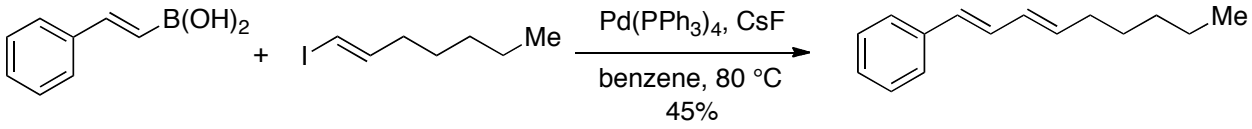
dienyl 4-methylbenzenesulfonate (1.6 g, 5.9 mmol) in DMF (19.8 mL) under nitrogen. Potassium phthlamide (3.31 g, 17.9 mmol) and 18-crown-6 (4.70 g, 17.9 mmol) were added, and the reaction was heated to 100 °C for 10 h. After being cooled to room temperature, the reaction was quenched with the addition of water (20 mL) and methylene chloride (20 mL) and the layers were separated. The organic layer was washed with water (3 x 20 mL), dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by silica gel chromatography (10:1 hexanes:ethyl acetate) to afford the title compound as a clear, yellow liquid (1.20 g, 83%). R_f=0.26 (10:1 hexanes:ethyl acetate, stain with $KMnO_4$).



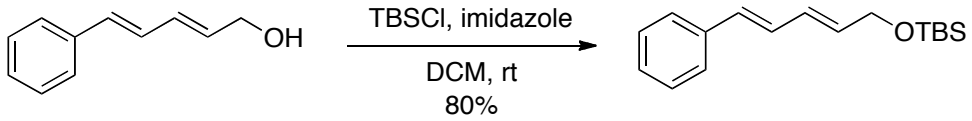


(*E*)-2-(hepta-4,6-dienyl)isoindoline-1,3-dione (Table 1, entry 10). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80 (2H, ddd, *J* = 15 Hz, 8.0 Hz, 8.0 Hz, $CH_2C\mathbf{H_2}CH_2$), 2.16 (2H, ddd, *J* = 7.5 Hz, 7.5 Hz, 7.5 Hz, $NCH_2CH_2C\mathbf{H_2}$), 3.70 (2H, t, *J* = 7.0 Hz, $NC\mathbf{H_2}$), 4.95 (1H, d, *J* = 10.5 Hz, $CH=CH_tC\mathbf{H_c}$), 5.08 (1H, d, *J* = 17.5 Hz, $CH=C\mathbf{H_t}CH_c$), 5.69 (1H, ddd, J=15.0 Hz, 6.5 Hz, 6.5 Hz, $CH_2C\mathbf{H}$=CH), 6.08 (1H, dd, J=15.0 Hz, 10.5 Hz, $CH_2CH=C\mathbf{H}$), 6.26 (1H, ddd, *J* = 17.5 Hz, 10.5 Hz, 10.5 Hz, $C\mathbf{H}=CH_2$), 7.71 (2H, dd, *J* = 5.0 Hz, 2.4 Hz, Ar**H**), 7.84 (2H, dd, *J* = 5.5 Hz, 3.5 Hz, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 137.1, 134.0, 133.5, 132.3, 131.9, 123.3, 115.4, 37.7, 30.0, 28.0; IR (neat): 2928 (w), 2919 (w), 2849 (w), 1711 (s), 1396 (m), 719 (m); HRMS-(ESI+) for $C_{15}H_{19}N_2O_2$ [M+NH_4]: calculated: 259.14465, found: 259.14554.

E. Preparation of (1E,3E)-nona-1,3-dienylbenzene (Table 2, entry 1). The title compound was synthesized as shown below. The spectral data was in accordance with the literature.[9]

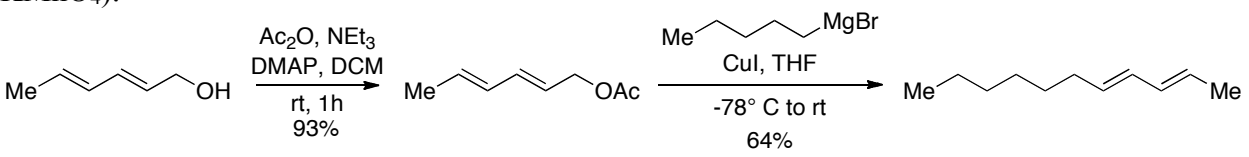


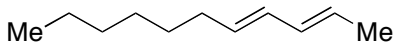
***F. Preparation of tert*-butyldimethyl((2*E*,4*E*)-5-phenylpenta-2,4-dienyloxy)silane (Table 2, entry 2).** The title compound was synthesized as shown below. The spectral data was in accordance with the literature.[10]



[9] Choi, J. Y.; Denmark, S. E. *J. Am. Chem. Soc*. **1999**, 121, 5821.
[10] Chin, L.; Gu, Y.G.; Burnett, F. N.; Wang, K. K. *J. Org. Chem*. **1991**, 56, 1914.

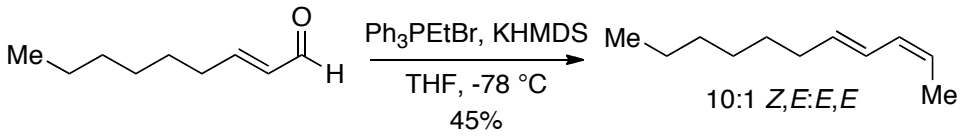
G. Prepartion of (2E,4E)-undeca-2,4-diene. To a 100 mL flame-dried round-bottom flask was added CuI (4.7 g, 25 mmol), THF (25 mL), and (2*E*,4*E*)-hexa-2,4-dien-1-yl acetate (3.5 g, 25 mmol). The flask was flushed with nitrogen then cooled to -78 °C. Pentyl magnesiumbromide (35 mL of a 0.72 M solution in THF, 25 mmol) was then added dropwise. The reaction was allowed to stir at -78 °C for 1 h, then allowed to warm to rt overnight. The reaction was quenched with the addition of aqueous ammonium chloride, diluted with pentane (20 mL) and water (30 mL) and the layers were separated. The aqueous layer was extracted with pentane (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude material was purified by silica gel chromatography (pentane) to afford the title compound as a clear, colorless liquid (1.90 g, 50%). R_f=0.8 (pentane, stain with $KMnO_4$).

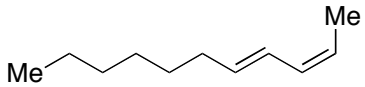




(2*E*,4*E*)-undeca-2,4-diene (Table 2 entry 4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.8 Hz, $CH_2C\mathbf{H_3}$), 1.24-1.40 (8H, m, $(C\mathbf{H_2})_\mathbf{4}$), 1.74 (3H, d, *J* = 6.8 Hz, CH=CHC$\mathbf{H_3}$), 2.06 (2H, ddd, *J* = 6.8 Hz, 6.8 Hz, 6.8 Hz, C$\mathbf{H_2}$CH=CH), 5.50-5.64 (2H, m, C**H**=C**H**), 5.96-6.08 (2H, m, C**H**=C**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.4, 132.0, 130.4, 126.8, 32.8, 32.0, 29.7, 29.1, 22.9, 18.2, 14.3; IR (neat): 3016 (w), 2958 (m), 2925 (s), 2855(m), 985(m); HRMS-(ESI+) for $C_{11}H_{21}$ [M+H]: calculated: 153.16433, found: 153.16404.

H. Preparation of (2Z,4E)-undeca-2,4-diene. In the dry box, to a flame-dried 250 mL round-bottom flask was added potassium bis(trimethylsilyl)amide (2.65 g, 7.13 mmol) and ethyltriphenylphosphonium bromide (1.46 g, 14.3 mmol). The reaction flask was removed from the dry box and a nitrogen line was attached. The flask was cooled to -78 °C and THF (143 mL) was added. The reaction was allowed to stir for 1 h at -78 °C, then (*E*)-2-nonenal (0.59 mL, 3.57 mmol in 10 mL THF) was added dropwise. The reaction was allowed to stir at -78 °C for 1 h, then warmed to room temperature and stirred for 5 h. The solvent was removed by rotary evaporation, and the residue was then taken up in diethyl ether, filtered through silica gel, and washed with diethyl ether. The filtrate was concentrated by rotary evaporation. The crude material was purified by silica gel chromatography (pentane) to afford the title compound with a 10:1 *Z*,*E*:*E*,*E* ratio (490 mg, 45%). R_f=0.8 (pentane, stain with $KMnO_4$).

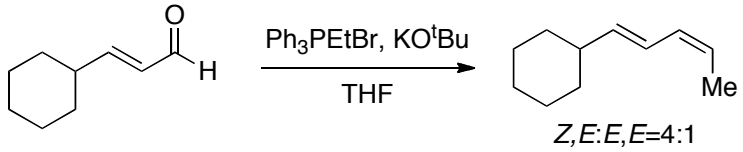




(2*Z*,4*E*)-undeca-2,4-diene (Table 2, entry 5.) ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (3H, t, *J* = 7.0 Hz, $CH_2C\mathbf{H_3}$), 1.27-1.42 (8H, m, $(C\mathbf{H_2})_\mathbf{4}$), 1.75 (3H, dd, *J* = 6.8 Hz, 1.6 Hz, CH=CHC$\mathbf{H_3}$), 2.11 (2H, ddd, *J* = 7.0 Hz, 7.0 Hz, 7.0 Hz, C$\mathbf{H_2}$CH=CH), 5.38 (1H, dddd, *J* = 10.8 Hz, 6.8 Hz, 6.8 Hz, 6.8 Hz, CH=C**H**CH_3), 5.67 (1H, ddd, *J* = 14.6 Hz, 7.0 Hz, 7.0 Hz, $CH_2C\mathbf{H}$=CH), 5.98 (1H, ddd, *J* = 10.8 Hz, 10.8 Hz, 1.6 Hz, C**H**=CHCH_3), 6.33 (1H, ddd, *J* = 14.6 Hz, 10.8 Hz, 1.2 Hz,

$CH_2CH=C\mathbf{H}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.8, 129.8, 125.5, 124.0, 33.1, 32.0, 29.6, 29.2, 22.9, 14.3, 13.5; IR (neat): 3019 (w), 2957 (m), 2924 (s), 2855 (m), 943 (m), 709 (m); HRMS-(ESI+) for $C_{11}H_{21}$ [M+H]: calculated: 153.16433, found: 153.16404. R_f=0.8 (pentanes, stain in $KMnO_4$).

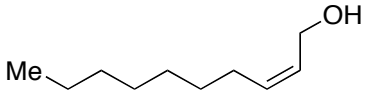
I. Prepartion of (1E,3Z)-penta-1,3-dien-1-ylcyclohexane (Table 2, entry 6). The title compound was synthesized as shown below. The spectral data was in accordance with the literature.[11]



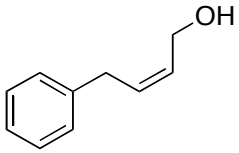
III. Representative Procedure for Diene Hydroboration/Oxidation.

In the dry box, an oven-dried 6-dram vial with magnetic stir bar was charged successively with $Ni(cod)_2$ (0.2 mL of a 54.5 μM solution of $Ni(cod)_2$ in toluene, 10.9 μmol), PCy_3 (0.2 mL of a 54.5 μM solution of PCy_3 in toluene, 10.9 μmol), toluene (1.33 mL, 0.25M), pinacolborane (58.4 mg, 0.456 mmol), and *trans*-1,3-decadiene (60 mg, 0.434 mmol). The vial was sealed with a polypropylene cap, removed from the dry box, and allowed to stir at room temperature for 3 h. The reaction mixture was cooled to 0 °C (ice/water) and charged with tetrahydrofuran (1.5 mL), 3 M sodium hydroxide (1 mL), and 30% hydrogen peroxide (0.75 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) and saturated aqueous sodium thiosulfate (1 mL) added dropwise. The reaction mixture was diluted with ethyl acetate and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified on silica gel (7:1 hexanes:ethyl acetate) to afford a clear, colorless oil (57.6 mg, 85%).

IV. Full Characterization and Proof of Stereochemistry.



(*Z*)-dec-2-en-1-ol (Table 1, entry 1).[12] Spectral data is in accordance with the literature.

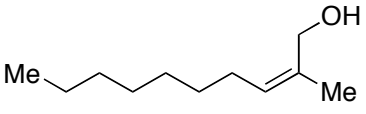


(*Z*)-4-phenylbut-2-en-1-ol (Table 1, entry 2). The reaction was performed with the general procedure, but with 1 mol % $Ni(cod)_2$ and 1 mol % PCy_3. ^1H NMR (400 MHz, $CDCl_3$): δ 3.45 (2H, d, J = 5.6 Hz, PhC$\mathbf{H_2}$), 4.32 (2H, d, J = 4.4 Hz, C$\mathbf{H_2}$OH), 5.75 (2H, m, C**H**=C**H**), 7.20-7.30 (5H, m, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ140.3, 131.2, 129.5, 128.7, 128.4, 126.3, 58.8, 33.9; IR (neat): 3322 (br w), 3024 (w), 2919 (w), 1494 (m), 1453 (m), 1018 (s), 697 (s); HRMS-(ESI+) for $C_{10}H_{11}$ [M-H_2O+H]: calculated: 131.08608, found:131.08591. The crude reaction mixture was purified on

[11] Morgan, I. T.; Sarkar, A. K.; Fleming, I. *J. Chem. Soc., Perkin Trans. 1*, **1998**, 2749.
[12] Mayer, S. F.; Steinreiber, A.; Orru, R. V. A.; Faber, K. *J. Org. Chem.* **2002**, *67*, 9115.

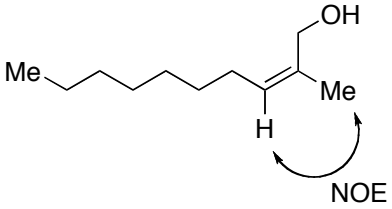
silica gel (8:1 hexanes:ethyl acetate) to afford a clear, colorless oil (62.8 mg, 91%). R_f=0.24 (8:1 hexanes:ethyl acetate, stain in PMA).

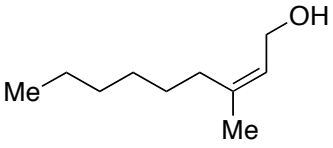
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by analogy to entry 1.



(*Z*)-2-methyldec-2-en-1-ol (Table 1, entry 3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (3H, t, *J* = 6.0 Hz, C**H$_3$**CH$_2$), 1.15-1.40 (10 H, m, CH$_3$(C**H$_2$**)$_5$), 1.8 (3H, d, *J* = 1.6 Hz, CH=CC**H$_3$**), 2.03 (2H, ddd, J = 8.0 Hz, 8.0 Hz, 8.0 Hz, CH$_2$C**H$_2$**CH=CH), 4.13 (2H, d, *J* = 2.0 Hz, C**H$_2$**OH), 5.30 (1H, t, *J* = 8.0 Hz, C**H**=C); ^{13}C NMR (100 MHz, $CDCl_3$): δ134.2, 129.1, 61.8, 32.1, 30.3, 29.5, 29.4, 27.8, 22.9, 21.5, 14.3; IR (neat): 3311 (br w), 2956 (m), 2922 (s), 2854 (m), 1456 (w), 1005 (s); HRMS-(ESI+) for $C_{11}H_{21}$ [M-H_2O+H]: calculated: 153.16433, found: 153.16462. The crude reaction mixture was purified on silica gel (13:1 hexane:ethyl acetate) to afford a clear, colorless oil (62.4 mg, 93%). R_f=0.13 (13:1 hexanes:ethyl acetate, stain in PMA).

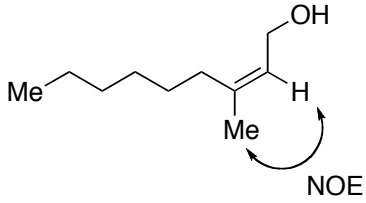
Proof of Stereochemistry: (*Z*)-alkene stereochemistry proven by NOE correlation as shown below.

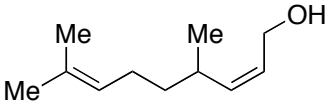




(*Z*)-3-methylnon-2-en-1-ol (Table 1, entry 4). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (3H, t, J = 7.4 Hz, CH$_2$C**H$_3$**), 1.24-1.38 (8H, m, CH$_2$(C**H$_2$**)$_4$CH$_3$), 1.72 (3H, d, *J* = 1.6 Hz, CH=CHC**H$_3$**), 2.05 (2H, t, *J* = 7.6 Hz, C**H$_2$**C=CH), 4.11 (2H, d, *J* = 7.2 Hz, C**H$_2$**OH), 5.4 (1H, t, *J* = 6.8 Hz, C=C**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 124.2, 59.3, 32.2, 32.0, 29.4, 28.5, 23.7, 22.8, 14.3; IR (neat): 3326 (br w), 2925 (s), 2856 (m), 1448 (w), 1067 (m); HRMS-(ESI+) for $C_{10}H_{19}$ [M-H_2O+H]: calculated: 139.14868, found: 139.1482. The crude reaction mixture was purified on silica gel (7:1 hexanes:ethyl acetate) to afford a clear, colorless oil (54.9 mg, 81%). R_f=0.18 (7:1 hexanes:ethyl acetate, stain in PMA).

Proof of Stereochemistry: : (*Z*)-alkene stereochemistry proven by NOE correlation as shown below.

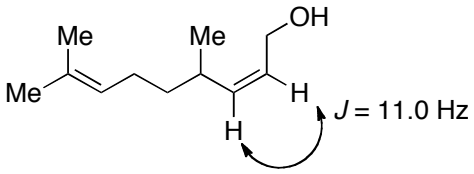


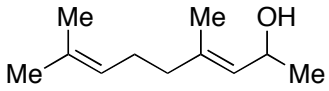


(*Z*)-4,8-dimethylnona-2,7-dien-1-ol (Table 1, entry 5). The reaction was performed with the general procedure, but allowed to stir for 12 h at 60 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (3H, d, *J* = 6.5 Hz, CHC**H$_3$**), 1.60 (3H, s, C**H$_3$**), 1.69 (3H, s, C**H$_3$**), 1.88-1.97 (2H, m, C**H$_2$**), 2.08-2.14 (2H,

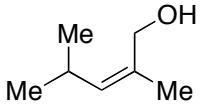
m, C**H₂**), 2.42-2.52 (1H, m, C**H**CH$_3$), 4.18 (2H, ddd, *J* = 7.0 Hz, 3.5 Hz, 1.5 Hz, C**H₂**OH), 5.07-5.13 (1H, m, C=C**H**CH$_2$CH$_2$), 5.31 (1H, dddd, *J* = 11.0 Hz, 10.0 Hz, 1.5 Hz, 1.5 Hz, C**H**=CHCH$_2$OH), 5.57 (1H, dddd, *J* = 11.0 Hz, 7.0 Hz, 7.0 Hz, 1.0Hz, CH=C**H**CH$_2$OH)); ^{13}C NMR (125 MHz, CDCl$_3$): δ 139.4, 131.8, 127.4, 124.6, 59.0, 37.5, 31.9, 25.9, 25.8, 21.6, 17.9; IR (neat): 3328 (br w), 2962 (s), 2925 (s), 1454 (w), 1006 (w); HRMS-(ESI+) for $C_{11}H_{19}$ [M-H$_2$O+H]: calculated: 151.14868, found: 151.14873. The crude reaction mixture contained a 1:1 inseparable mixture of (*Z*)-4,8-dimethylnona-2,7-dien-1-ol and (*E*)-4,8-dimethylnona-3,7-dien-2-ol. The two products were purified on silica gel (15:1 hexanes:ethyl acetate) to afford a clear, colorless oil (39.6 mg, 58%). R$_f$=0.23 (15:1 hexanes:ethyl acetate, stain in PMA). Product was separated from (*E*)-4,8-dimethylnona-3,7-dien-2-ol by selective protection of the primary alcohol with TBDPSiCl, followed by deprotection with TBAF.

Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.



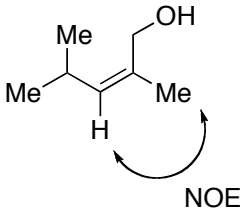


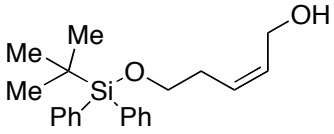
(*E*)-4,8-dimethylnona-3,7-dien-2-ol (Table 1, entry 5 byproduct). The reaction was performed with the general procedure, but allowed to stir for 12 h at 60 ºC. ^{1}H NMR (500 MHz, CDCl$_3$): δ 1.24 (3H, d, *J* = 6.0 Hz, CHOHC**H₃**), 1.33 (1H, br, O**H**), 1.61 (3H, s, C**H₃**), 1.69 (6H, d, *J* = 1.5 Hz, C**H₃**+C**H₃**), 1.99-2.02 (2H, m, C**H₂**), 2.08-2.40 (2H, m, C**H₂**), 4.59 (1H, dddd, *J* = 8.5 Hz, 6.0 Hz, 6.0 Hz, 6.0 Hz, C**H**OH), 5.08-5.11 (1H, m, C=C**H**CH$_2$), 5.23 (1H, ddd, *J* = 8.5 Hz, 1.5 Hz, 1.0 Hz, C=C**H**CHOH); ^{13}C NMR (125 MHz, CDCl$_3$): δ 137.8, 131.9, 129.3, 124.1, 65.0, 39.7, 32.8, 26.6, 25.9, 17.9, 16.6; IR (neat): 3328 (br w), 2962 (s), 2925 (s), 1454 (w), 1006 (w); HRMS-(ESI+) for $C_{11}H_{19}$ [M-H$_2$O+H]: calculated: 151.14868, found: 151.14873. The crude reaction mixture contained a 1:1 inseparable mixture of (*Z*)-4,8-dimethylnona-2,7-dien-1-ol and (*E*)-4,8-dimethylnona-3,7-dien-2-ol. The two products were purified on silica gel (15:1 hexanes:ethyl acetate) to afford a clear, colorless oil (39.6 mg, 58%). R$_f$=0.23 (15:1 hexanes:ethyl acetate, stain in PMA). Product was separated from (*Z*)-4,8-dimethylnona-2,7-dien-1-ol by selective protection of the primary alcohol with TBDPSiCl.



(*Z*)-2,4-dimethylpent-2-en-1-ol (Table 1, entry 6). The reaction was performed with the general procedure, but allowed to stir for 12 h. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.93 (6H, d, *J* = 6.8 Hz, CH(C**H₃**)**₂**), 1.76 (3H, d, *J* = 1.6 Hz, CH=CC**H₃**), 2.58 (1H, dddd, *J* = 13.2 Hz, 9.6 Hz, 6.8 Hz, 6.8 Hz, C**H**(CH$_3$)$_2$), 4.12 (2H, s, C**H₂**OH), 5.11 (1H, d, *J* = 9.2 Hz, C**H**=C); ^{13}C NMR (100 MHz, CDCl$_3$): δ 136.6, 132.0, 62.0, 27.1, 23.8, 21.4; IR (neat): 3319 (br w), 2957 (s), 2868 (m), 1466 (w), 1007 (s); HRMS-(ESI+) for C_7H_{13} [M-H$_2$O+H]: calculated: 97.10173, found: 97.10101. The crude reaction mixture was purified on silica gel (7:1 hexanes:ethyl acetate) to afford a clear, colorless oil (44.9 mg, 63%). R$_f$=0.24 (7:1 hexanes:ethyl acetate, stain in PMA).

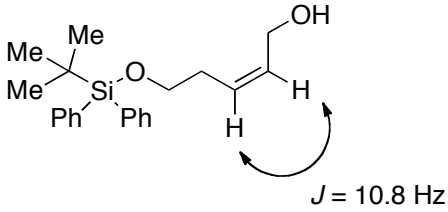
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by NOE correlation as shown below.

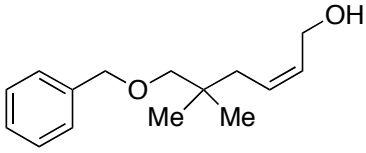




(*Z*)-5-(*tert*-butyldiphenylsilyloxy)pent-2-en-1-ol (Table 1, entry 7). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06 (9H, s, OSiC(C**H$_3$**)$_3$), 1.6 (1H, s br, O**H**), 2.37 (2H, ddd, *J* = 6.4 Hz, 6.4 Hz, 6.4 Hz, SiOCH$_2$C**H$_2$**), 3.67 (2H, t, *J* = 6.4 Hz, SiOC**H$_2$**CH$_2$), 4.15 (2H, d, *J* = 6.4, C**H$_2$**OH), 5.59 (1H, ddd, *J* = 10.8 Hz, 8.0 Hz, 8.0 Hz, C**H**=CHCH$_2$OH), 5.77 (1H, ddd, *J* = 10.8 Hz, 6.8 Hz, 6.8 Hz, CH=C**H**CH$_2$OH), 7.37-7.46 (6H, m, Ar**H**), 7.67-7.69 (4H, m, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 133.8, 130.8, 129.8, 129.6, 127.8, 63.4, 58.7, 31.1, 27.1, 19.4; IR (neat): 3363 (br w), 3070 (w), 3017 (m), 2858 (m), 1389 (m), 1110 (s), 701 (s), 505 (m); HRMS-(ESI+) for $C_{21}H_{29}O_2Si$ [M+H]: calculated: 341.19368, found: 341.19268. The crude reaction mixture was purified on silica gel (7:1 hexanes:ethyl acetate) to afford a clear, colorless oil (38.0 mg, 56%). R_f=0.20 (7:1 hexanes:ethyl acetate, stain in PMA).

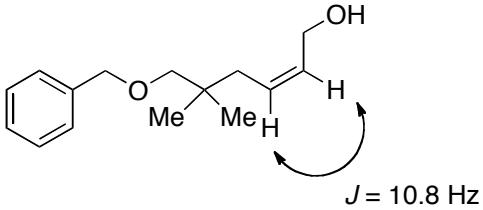
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.

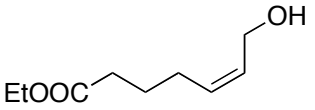




(*Z*)-6-(benzyloxy)-5,5-dimethylhex-2-en-1-ol (Table 1, entry 8). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (6H, s, (C**H$_3$**)$_2$), 2.11 (2H, d, *J* = 8.0 Hz, CH=CHC**H$_2$**C(CH$_3$)$_2$), 3.14 (2H, s, OC**H$_2$**C), 4.15 (2H, d, *J* = 6.8 Hz, C**H$_2$**OH), 4.51 (2H, s, PhC**H$_2$**O), 5.59 (1H, ddd, *J* = 10.8 Hz, 7.8 Hz, 7.8 Hz, C**H**=CHCH$_2$OH), 5.74 (1H, ddd, *J* = 10.8 Hz, 6.6 Hz, 6.6 Hz, CH=C**H**CH$_2$OH), 7.27-7.34 (5H, m, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 130.6, 129.5, 128.5, 127.7, 127.6, 78.5, 73.5, 58.5, 36.5, 35.5, 24.9; IR (neat): 3372 (br w), 2956 (m), 2868 (m), 1454 (w), 1099 (s), 1029 (s), 697 (s); HRMS-(ESI+) for $C_{15}H_{23}O_2$ [M+H]: calculated: 235.16980, found: 235.17019. The crude reaction mixture was purified on silica gel (10:1 hexanes:ethyl acetate) to afford a clear, colorless oil (58.4 mg, 89%). R_f=0.14 (10:1 hexanes:ethyl acetate, stain in PMA).

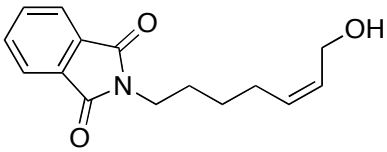
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.





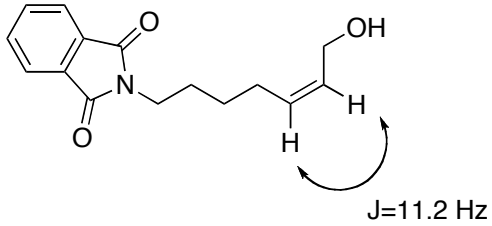
(*Z*)-ethyl-7-hydroxyhept-5-enoate (Table 1, entry 9). The reaction was performed with the general procedure, but allowed to stir for 12 h. Upon oxidation, pH=7 phosphate buffer (1 mL) was used instead of a 3.0 M solution of sodium hydroxide. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H_3}$), 1.66-1.73 (2H, m, $CH_2C\mathbf{H_2}CH_2COOEt$), 2.11 (2H, ddd, *J* = 7.2 Hz, 7.2 Hz, 7.2 Hz, $CH{=}CHC\mathbf{H_2}$), 2.28 (2H, t, *J* = 7.6 Hz, $C\mathbf{H_2}COOEt$), 4.11 (2H, q, *J* = 7.3 Hz, $COOC\mathbf{H_2}CH_3$), 4.14 (2H, d, *J* = 7.2 Hz, $HOC\mathbf{H_2}$), 5.47 (1H, m, $HOCH_2C\mathbf{H}{=}CH$), 5.64 (1H, m, $HOCH_2CH{=}C\mathbf{H}$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 131.6, 129.9, 60.5, 58.4, 33.7, 26.7, 24.8, 14.4; IR (neat): 3421 (br w), 2926 (m), 1734 (s), 1031 (m); HRMS-(ESI+) for $C_9H_{17}O_3$ [M+H]: calculated: 173.11777, found: 341.11815. The crude reaction mixture was purified on silica gel (3:1 hexanes:ethyl acetate) to afford a clear, colorless oil (53.9 mg, 81%). R_f=0.23 (3:1 hexanes:ethyl acetate, stain in PMA).

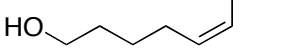
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by analogy.



(*Z*)-2-(7-hydroxyhept-5-enyl)isoindoline-1,3-dione (Table 1, entry 10). The reaction was performed with the general procedure, but upon oxidation, pH=7 phosphate buffer (1 mL) was used instead of a 3.0 M solution of sodium hydroxide. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (2H, dddd, *J* = 7.2 Hz, 7.2 Hz, 7.2 Hz, 7.2 Hz, $CH{=}CHCH_2C\mathbf{H_2}$), 1.67 (2H, dddd, *J* = 7.2 Hz, 7.2 Hz, 7.2 Hz, 7.2 Hz, $NCH_2C\mathbf{H_2}$), 2.14 (2H, ddd, *J* = 7.6 Hz, 7.6 Hz, 1.6 Hz, $CH{=}CHC\mathbf{H_2}$), 3.67 (2H, t, *J* = 9.5 Hz, $NC\mathbf{H_2}$), 4.20 (2H, dd, *J* = 6.8 Hz, 1.2 Hz, $HOC\mathbf{H_2}$), 5.48 (1H, dddd, *J* = 11.2 Hz, 7.6 Hz, 7.6 Hz, 0.8 Hz, $C\mathbf{H}{=}CHCH_2OH$), 5.63 (1H, dddd, *J* = 11.2 Hz, 6.8 Hz, 6.8 Hz, 1.6 Hz, $CH{=}C\mathbf{H}CH_2OH$), 7.67 (2H, dd, *J* = 5.2 Hz, 3.2 Hz, Ar**H**), 7.79 (2H, dd, *J* = 5.2 Hz, 3.2 Hz, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 133.9, 132.1, 132.0, 129.2, 123.2, 58.4, 37.6, 27.7, 26.5, 26.4; IR (neat): 3466 (w br), 3013 (w), 2929 (m), 1706 (s), 1438 (m), 719 (m); HRMS-(ESI+) for $C_{15}H_{21}N_2O_3$ [M+NH_4]: calculated: 277.15522, found: 277.15531. The crude reaction mixture was purified on silica gel (3:1 hexanes:ethyl acetate) to afford a clear, colorless oil (39.4 mg, 61% (after subtraction of inseparable pinacol and unknown impurity)). R_f=0.16 (3:1 hexanes:ethyl acetate, stain in PMA).

Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.

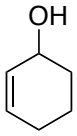




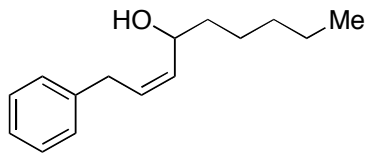
(*Z*)-hept-2-ene-1,7-diol (Table 1, entry 11). The reaction was performed with the general procedure, but 2.1 equiv. of pinacolborane was used.^{1}H NMR (400 MHz, $CDCl_3$): δ 1.42 (2H, dddd, *J* = 14.4 Hz, 7.2 Hz, 7.2 Hz, 7.2 Hz, $C\mathbf{H_2}CH_2CH_2OH$), 1.55 (2H, dddd, *J* = 13.2 Hz, 7.2 Hz, 7.2 Hz, 7.2 Hz, $CH_2C\mathbf{H_2}CH_2OH$), 2.09 (2H, ddd, *J* = 7.6 Hz, 7.6 Hz, 7.6 Hz, $CH{=}CHC\mathbf{H_2}CH_2$), 2.53 (1H, s br,

O**H**), 3.60 (2H, t, *J* = 6.4 Hz, $CH_2C\mathbf{H_2}OH$), 4.15 (2H, d, *J* = 6.4 Hz, $C\mathbf{H_2}OH$), 5.47-5.53 (1H, m, C**H**=$CHCH_2OH$), 5.56-5.62 (1H, m, CH=C**H**H_2OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.7, 129.0, 62.6, 58.4, 32.1, 27.2, 25.9; IR (neat): 3287 (br m), 2928 (s), 2859 (m), 1431 (w), 1006 (s); HRMS-(ESI+) for $C_7H_{18}NO_2$ [M+NH_4]: calculated: 148.13375, found: 148.13360. The crude reaction mixture was purified on silica gel (1:2 hexanes:ethyl acetate) to afford a clear, colorless oil (50.1 mg, 72%). R_f=0.12 (1:2 hexanes:ethyl acetate, stain in PMA).

Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by analogy.

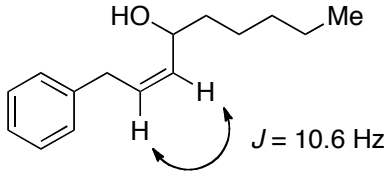


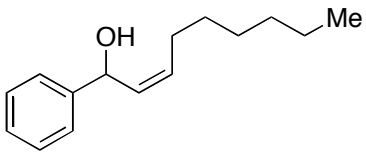
cyclohex-2-enol (Table 1, entry 12). Spectral data is in accordance with an authentic sample from Sigma-Aldrich. The crude reaction mixture was purified on silica gel (2:1 pentane:diethyl ether) to afford a clear, colorless oil (44.1 mg, 60%). R_f=0.22 (2:1 pentane:diethyl ether, stain in PMA).



(*Z*)-1-phenylnon-2-en-4-ol (Table 2, entry 1). The reaction was performed with the general procedure, but allowed to stir for 12 h.^{1}H NMR (400 MHz, $CDCl_3$): δ 0.9 (3H, t, *J* = 6.8 Hz, $C\mathbf{H_3}CH_2$), 1.26-1.58 (6H, m, $(C\mathbf{H_2})_3CH_3$), 1.6-1.68 (2H, m, $C\mathbf{H_2}$CHOH), 3.40-3.54 (2H, m, Ph$C\mathbf{H_2}$), 4.56 (1H, dddd, *J* = 7.5 Hz, 7.5 Hz, 7.5 Hz, 1.0 Hz, C**H**OH), 5.52 (1H, dddd, *J* = 10.6 Hz, 3.2 Hz, 1.6 Hz, 1.6 Hz, HC=C**H**CHOH), 5.69 (1H, dddd, *J* = 10.6 Hz, 7.6 Hz, 7.6 Hz, 1Hz, $PhCH_2C\mathbf{H}$=CH), 7.19-7.23 (3H, m, Ar**H**), 7.28-7.32 (2H, m, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 133.8, 130.4, 128.5, 127.7, 126.3, 67.9, 37.8, 34.1, 32.0, 25.3, 22.9, 14.3; IR (neat): 3342 (br w), 3063 (w), 3026 (m), 2857 (m), 1602 (w), 1453 (m), 1052 (m), 739 (s), 696 (s); HRMS-(ESI+) for $C_{15}H_{26}NO$ [M+NH_4]: calculated: 236.20144, found: 236.20211. The crude reaction mixture was purified on silica gel (20:1 hexanes:ethyl acetate) to afford a clear, colorless oil (29.9 mg, 85%). R_f=0.11 (20:1 hexanes:ethyl acetate, stain in PMA). Regioselectivity was determined by the mass of the collected products.

Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.

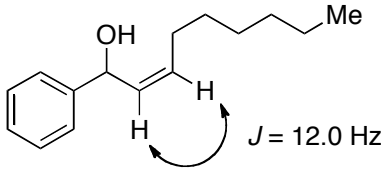


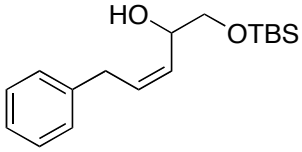


(*Z*)-1-phenylnon-2-en-1-ol (Table 2, entry 1 minor regioisomer). The reaction was performed with the general procedure, but allowed to stir for 12 h. ^{1}H NMR (400 MHz, C_6D_6): δ 0.89 (3H, t, *J* = 8.0 Hz, $C\mathbf{H_3}$), 1.20-1.36 (8 H, m, $CH_3(C\mathbf{H_2})_4$), 2.02 (2H, dddd, *J* = 16 Hz, 16 Hz, 8 Hz, 8 Hz, CH=CHC$\mathbf{H_2}$), 5.35-5.41 (1H+1H, m, PhC**H**OH+CHC**H**=CH), 5.61 (1H, dddd, *J* = 12 Hz, 4 Hz, 3.8 Hz, 3.8 Hz CH=C**H**CH_2), 7.09-7.2 (3H, m, Ar**H**), 7.41 (2H, d, 8 Hz, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 132.7, 132.0, 128.7, 127.6, 126.1, 69.7, 31.9, 29.9, 29.2, 28.0, 22.8, 14.3; IR (neat): 3354 (br w), 3062 (w), 2955 (s), 2854 (m), 1453 (w), 1023 (w), 698 (m); HRMS-(ESI+) for $C_{15}H_{21}$ [M-H_2O+H]: calculated: 201.16433, found: 201.16497. The crude reaction mixture was purified

on silica gel (20:1 hexanes:ethyl acetate) to afford a clear, colorless oil (3.0 mg, 9%). R_f=0.12 (20:1 hexanes:ethyl acetate, stain in PMA).

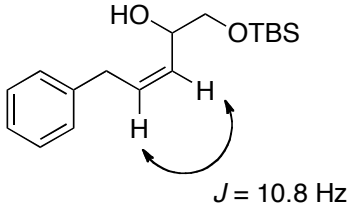
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.

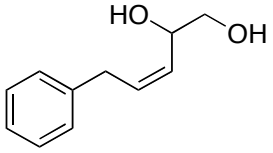




(*Z*)-1-(*tert*-butyldimethylsilyloxy)-5-phenylpent-3-en-2-ol (Table 2, entry 2). The reaction was performed with the general procedure, but with 1 mol % $Ni(cod)_2$ and 1 mol % PCy_3. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.095 (6H, s, $OSi(C\mathbf{H_3})_2CH(CH_3)_3$), 0.92 (9H, s, $OSi(CH_3)_2CH(C\mathbf{H_3})_3$), 2.63 (1H, br s, CHO**H**), 3.41-3.65 (2H + 1H, m, $PhCH_AC\mathbf{H_B}$ + $C\mathbf{H_2}OSi$), 3.63 (1H, dd, *J* = 10.2 Hz, 3.8 Hz, $PhC\mathbf{H_A}CH_B$), 4.61 (1H, ddd, *J* = 8.4 Hz, 8.4 Hz, 3.6 Hz, C**H**OH), 5.49 (1H, dd, *J* = 10.8 Hz, 8.4 Hz, CH=C**H**COH), 5.77 (1H, ddd, *J* = 10.8 Hz, 8.0 Hz, 8.0 Hz, $CH_ACH_BC\mathbf{H}$=CH), 7.19-7.32 (5H, m, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 132.4, 129.0, 128.7, 128.5, 126.3, 68.6, 67.1, 34.4, 26.1, 18.6, -5.1; IR (neat): 3412 (br w), 3026 (w), 2953 (w), 2856 (w), 1253 (w), 1104 (m), 884 (s); HRMS-(ESI+) for $C_{17}H_{32}NO_2Si$ [M+NH_4]: calculated: 310.22023, found: 196.22011. The crude reaction mixture was purified on silica gel (15:1 hexanes:ethyl acetate) to afford a clear, colorless oil (58.0 mg, 91%). R_f=0.22 (15:1 hexanes:ethyl acetate, stain in PMA).

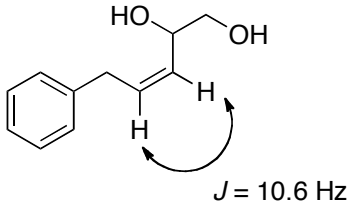
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.

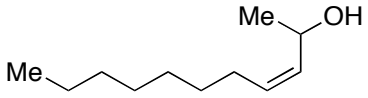




(*Z*)-5-phenylpent-3-ene-1,2-diol (Table 2, entry 3). The reaction was performed with the general procedure, but with 1 mol % $Ni(cod)_2$, 1 mol % PCy_3, and 2.1 equiv. pinacolborane. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30 (1H, br s, O**H**), 3.44-3.48 (2H+1H, m, $PhCH_AC\mathbf{H_B}$ + $C\mathbf{H_2}OH$), 3.56 (1H, dd, *J* = 11.2 Hz, 3.6 Hz, $PhC\mathbf{H_A}CH_B$), 4.60 (1 H, ddd, *J* = 8.0 Hz, 8.0 Hz, 3.6 Hz, C**H**OH), 5.43 (1H, dd, *J* = 10.6 Hz, 8.4 Hz, CH_2CH=C**H**COH), 5.71 (1H, ddd, *J* = 10.6 Hz, 7.6 Hz, 7.6 Hz, $CH_2C\mathbf{H}$=CH), 7.16 (5H, m, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 132.8, 129.0, 128.8, 128.4, 126.4, 68.8, 66.6, 34.3; IR (neat): 3344 (br, w), 3025 (w), 2921 (w), 1452 (w), 1072 (s), 1026 (s), 738 (s), 697 (s); HRMS-(ESI+) for $C_{11}H_{18}N_1O_2$ [M+NH_4]: calculated: 196.13375, found: 196.13433. The crude reaction mixture was purified on silica gel (1:1 hexanes:ethyl acetate) to afford a clear, colorless oil (36.1 mg, 54%). R_f=0.18 (1:1 hexanes:ethyl acetate, stain in PMA).

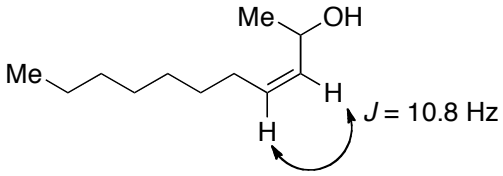
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.



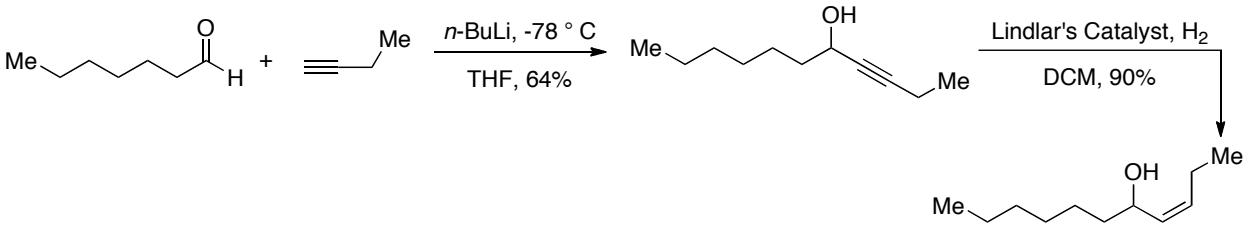


(*Z*)-undec-3-en-2-ol (Table 2, entry 4 and 5). The reaction was performed with the general procedure, but allowed to stir for 12 h. ^{1}H NMR (400 MHz, C_6D_6): δ 0.90 (3H, t, *J* = 6.8 Hz, C**H$_3$**), 1.20-1.34 (10H, m, (C**H$_2$**)$_5$), 1.76 (3H, d, *J* = 6.4 Hz, CHOHC**H$_3$**), 1.91-2.01 (2H, m, C**H$_2$**CH=CH), 4.52 (1H, br dddd, *J* = 6.4 Hz, 6.4 Hz, 6.4 Hz, 6.4 Hz, C**H**OH), 5.31 (1H, dddd, *J* = 10.8 Hz, 7.2 Hz, 7.2Hz, 1.2 Hz, CH_2C**H**=CH), 5.44 (1H, ddd, *J* = 10.8 Hz, 8.4 Hz, 1.2 Hz, CH=C**H**CHOH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.9, 131.6, 64.1, 32.0, 29.9, 29.4, 29.3, 27.7, 23.8, 22.9, 14.3; IR (neat): 3331 (br w), 3008 (m), 2924 (s), 2855 (m), 1459 (w), 1058 (m); HRMS-(ESI+) for $C_{11}H_{21}$ [M-H_2O+H]: calculated: 153.16433, found: 153.16455. The crude reaction mixture was purified on silica gel (15:1 hexanes:ethyl acetate) to afford a clear, colorless oil (40.9 mg, 61% for entry 4; 50.0 mg, 82% for entry 5). R_f=0.23 (15:1 hexanes:ethyl acetate, stain in PMA). Product from Table 2, entry 5 contained a small amount of (*Z*)-undec-2-en-1-ol (isomerization / hydroboration product) could not be separated.

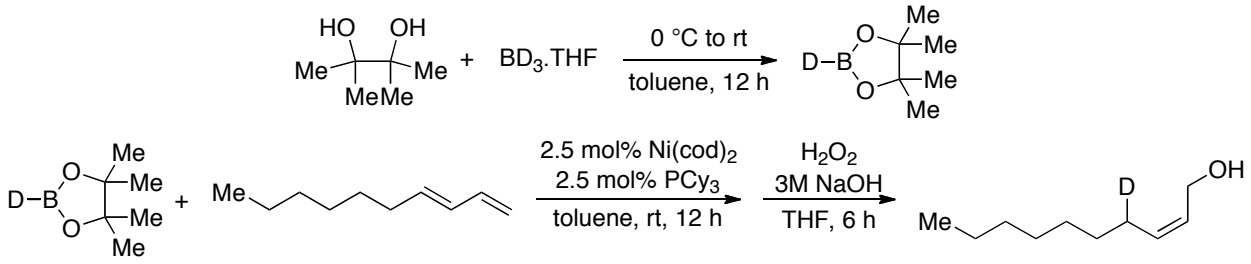
Proof of Stereochemistry: (*Z*)-alkene stereochemistry determined by coupling constants as shown below.



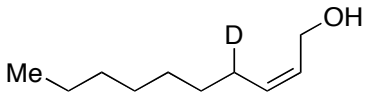
Proof of Regioselectivity: The regioisomeric 1,4-hydroboration product was synthesized as shown below, and compared to the crude reaction product. It was detected in a 5:1 ratio as determined by crude ^{1}H NMR for Table 2 entry 4, but not detected for Table 2 entry 5.



V. Deuterium Labeling Experiment (Scheme 3).



Deuterated pinacolborane was made in accordance with the literature[13] with a slight modification. To a solution of freshly recrystallized pinacol (59 mg, 0.5 mmol) in toluene (0.1 mL) in a 5 mL round-bottom flask with a magnetic stir bar was added borane-d_3-THF 1.0 M complex (0.5 mL, 0.5 mmol) under nitrogen at 0 °C. The reaction was allowed to warm to room temperature overnight. The solution was taken into the dry box and added to a oven-dried 6-dram vial with a magnetic stir bar charged with $Ni(cod)_2$ (2.6 mg, 9.52 μmol), PCy_3 (2.6 mg, 9.52 μmol), (*E*)-deca-1,3-diene (69 mg, 0.5 mmol), and toluene (1.0 mL). The vial was sealed with a polypropylene cap, removed from the dry box, and allowed to stir at room temperature for 12 h. The reaction was oxidized and worked-up in accordance with the representative procedure. The crude reaction mixture was purified on silica gel (7:1 hexanes:ethyl acetate) to afford a clear, colorless oil (10 mg, 13%). R_f=0.17 (7:1 hexanes:ethyl acetate, stain in PMA). The deuterium incorporation was determined to be 81% at C-4 by integration of the proton resonance at 1.91 ppm in C_6D_6 as assigned by HSQC of (*Z*)-dec-2-en-1-ol.



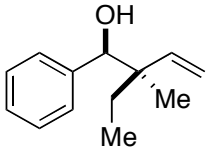
(*Z*)- dec-2-en-1-ol-4-d_1. ^{1}H NMR (500 MHz, C_6D_6): δ 0.90 (3H, t, *J* = 6.8 Hz, $CH_2C\mathbf{H_3}$), 1.21-1.36 (10 H, m, $(C\mathbf{H_2})_5$), 1.89-1.93 (1H, m, C**H**DCH=CH), 3.99 (2H, d, *J* = 6.4 Hz, $C\mathbf{H_2}OH$), 5.37-5.42 (1H, m, CHDC**H**=CH), 5.56 (1H, dddd, *J* = 10.8 Hz, 6.6 Hz, 6.6 Hz, 1.6 Hz, CH=C**H**CH_2OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.5, 128.5, 58.9, 32.0, (29.8-non-deuterated), 29.7, (29.4-non-deuterated), 29.4, 29.4, (27.6-non-deuterated), 27.3 (t, J=15.3 Hz), 22.9, 14.3; IR (neat): 3314 (br w), 2956 (w), 2923 (m), 2855 (m), 1264 (s), 908 (m), 729 (s); HRMS-(ESI+) for $C_{10}H_{18}D$ [M-H_2O+H]: calculated: 140.15495, found: 140.15491.

VI. Procedure for Hydroboration/Allylation (Scheme 4).

In the dry box, an oven-dried 6-dram vial with magnetic stir bar was charged successively with $Ni(cod)_2$ (0.5 mL of a 36.3 μM solution of $Ni(cod)_2$ in toluene, 18.3 μmol), PCy_3 (0.5 mL of a 56.3 μM solution of PCy_3 in toluene, 18.3 μmol), toluene (1.9 mL, 0.25M), pinacolborane (98.2 mg, 0.77 mmol), and (*E*)-3-methylpenta-1,3-diene (60 mg, 0.73 mmol). The vial was sealed with a polypropylene cap, removed from the dry box, and allowed to stir at room temperature for 3 h. The solvent was then removed by rotary evaporation, and DCM (0.73 mL) and benzaldehyde (0.08 mL, 0.77 mmol) were added. The reaction mixture was allowed to stir at room temperature for 16 h. The solvent was removed by rotary evaporation and the crude reaction mixture was

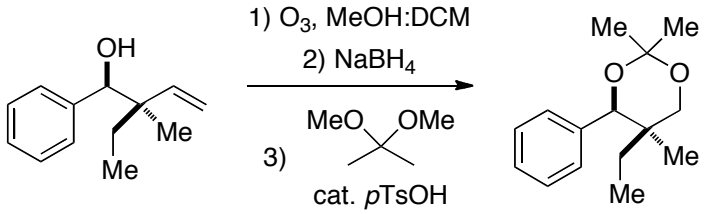
[13] Lessard, S.; Peng, F.; Hall, D. G. *J. Am. Chem. Soc.*, **2009**, *131*, 9612.

purified on silica gel (100:1 hexanes:ethyl acetate) to afford a clear, colorless oil (90.3 mg, 65%). R_f=0.32 (100:1 hexanes:ethyl acetate, stain in $KMnO_4$).

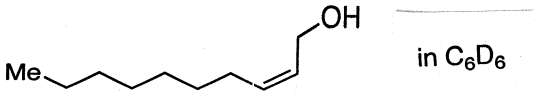


2-ethyl-2-methyl-1-phenylbut-3-en-1-ol (9). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.8 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H_3}$), 1.06 (3H, s, $C\mathbf{H_3}$), 1.36-1.43 (2H, m, $C\mathbf{H_2}CH_3$), 2.13 (1H, d, *J* = 4.8 Hz, O**H**), 4.45 (1H, d, *J* = 4.4 Hz, C**H**OH), 5.02 (1H, dd, *J* = 17.6 Hz, 1.2 Hz, CH=C$\mathbf{H_t}H_c$), 5.22 (1H, dd, *J* = 10.8, J=1.6 Hz, CH=C$H_t\mathbf{H_c}$), 5.76 (1H, dd, *J* = 17.6 Hz, 11.2 Hz, C**H**=CH_2), 7.25-7.34 (5H, m, Ar**H**); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 141.5, 128.0, 127.6, 115.6, 80.9, 45.7, 29.0, 18.6, 8.5; IR (neat): 3473 (br w), 3063 (w), 2968 (s), 1453 (m), 1022 (m), 725 (s); HRMS-(ESI+) for $C_{13}H_{18}ONa$ [M+Na]: calculated: 213.1255, found: 213.1266.

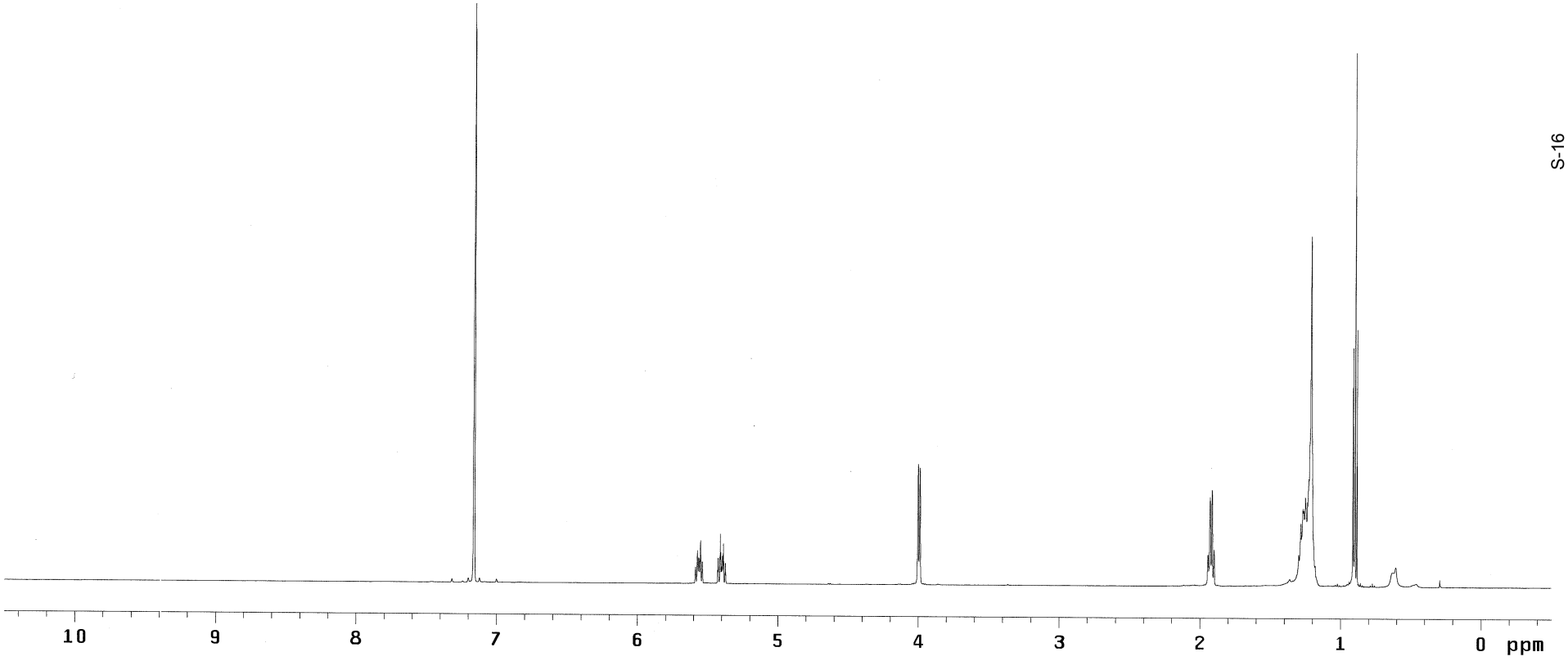
Proof of stereochemistry. The relative configuration was assigned by comparison of the ^{1}H NMR spectrum with that reported in the literature,[14] after conversion of the title compound into the protected-1,3-diol by ozonolysis/reduction/acetonide formation as shown below.

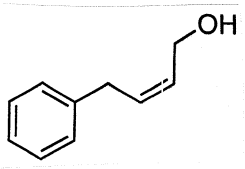


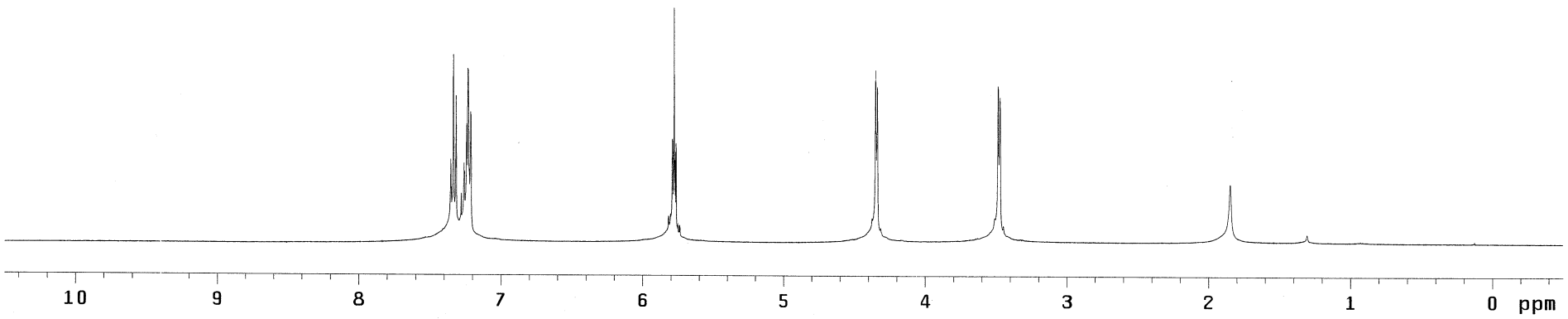
[14] Burke, E. D.; Gleason, G. L. *Org. Lett*. **2004**, *6*, 405.

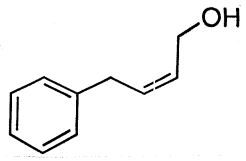


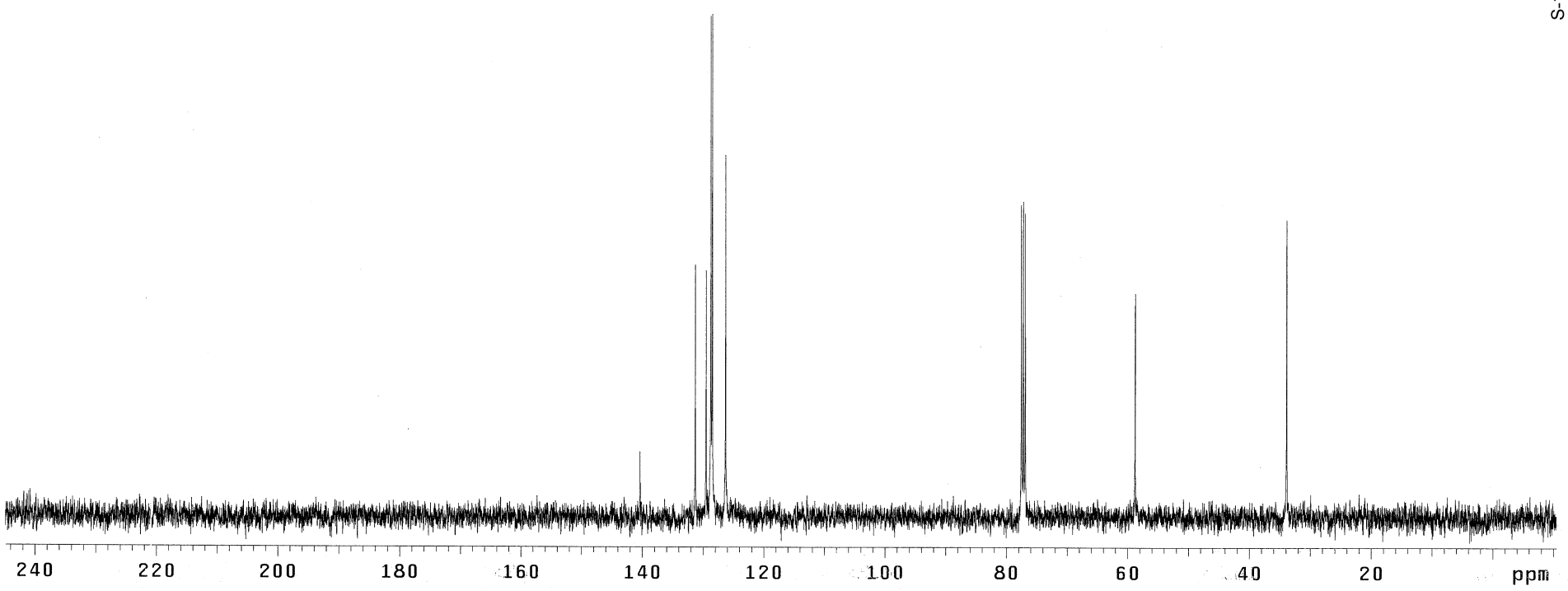
in C_6D_6

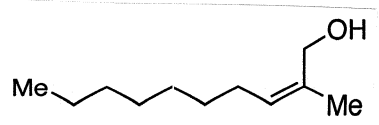


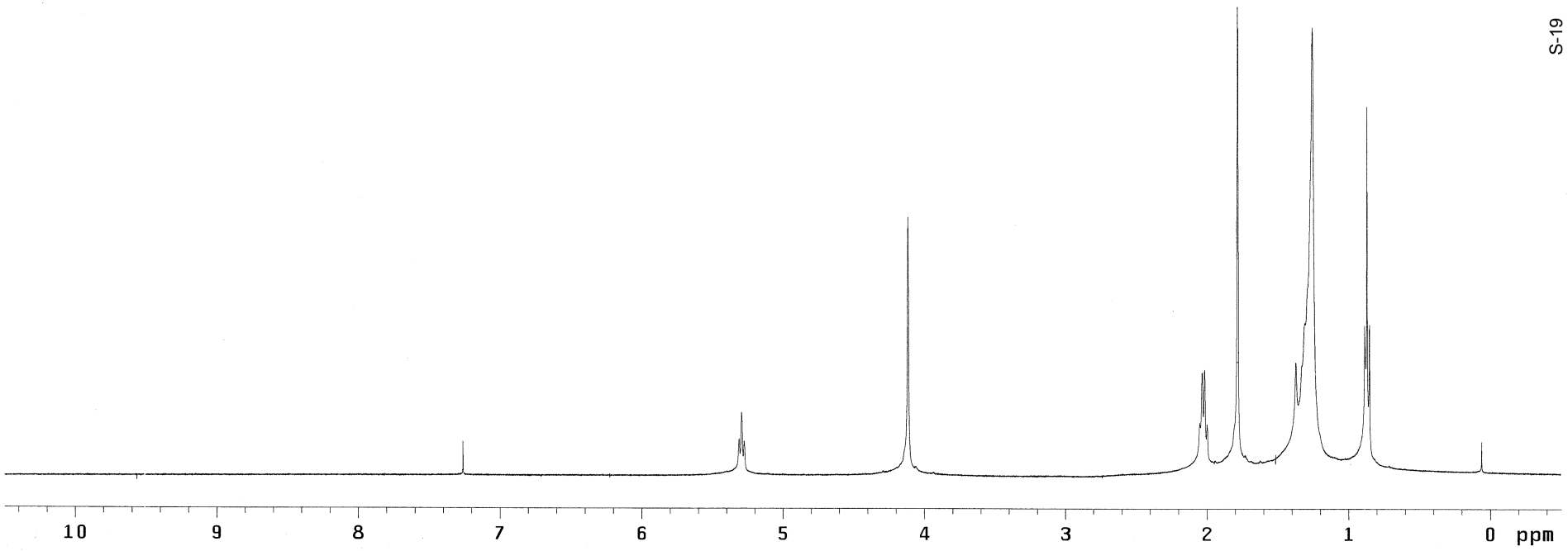

OH

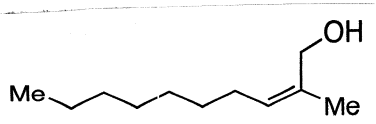

10
9
8
7
6
5
4
3
2
1
0
ppm

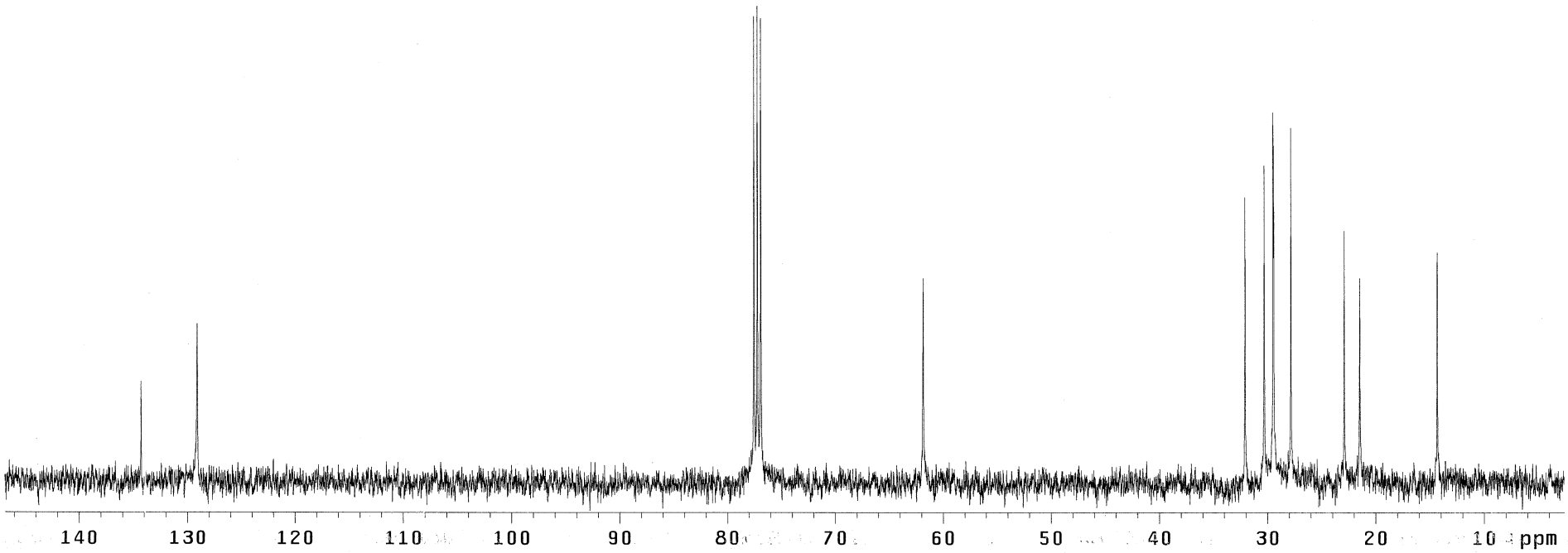

OH

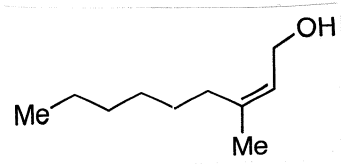

240
220
200
180
160
140
120
100
80
60
40
20
ppm

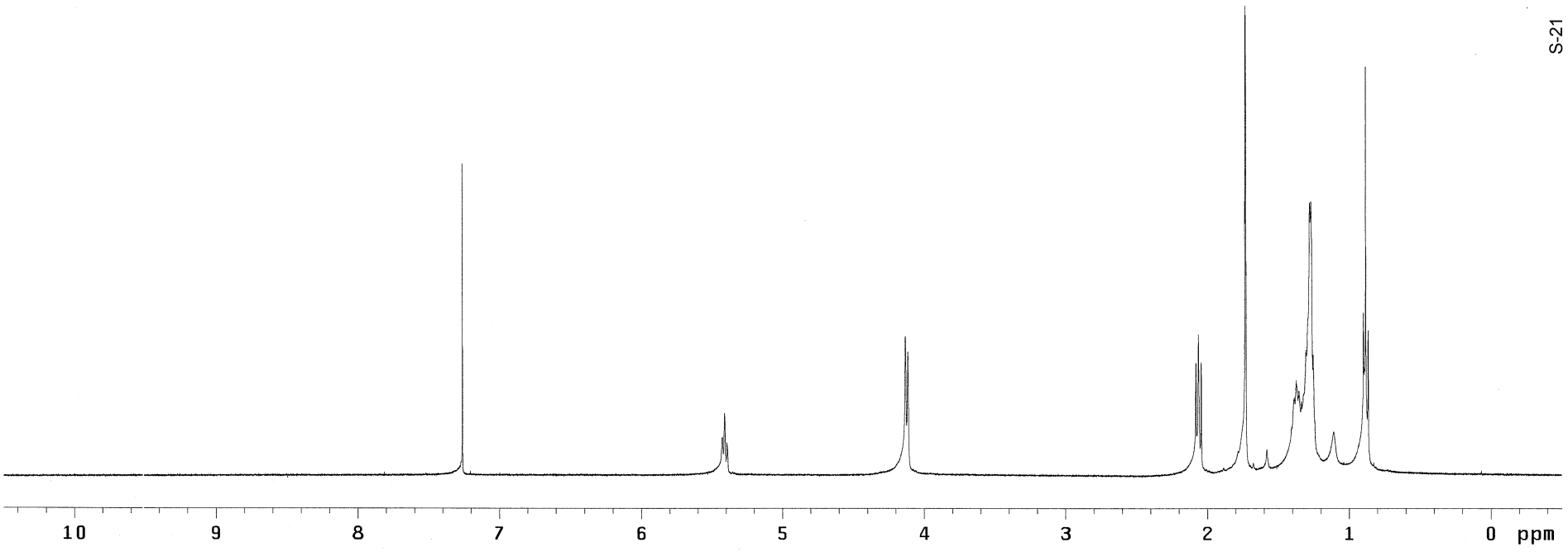

OH
Me
Me

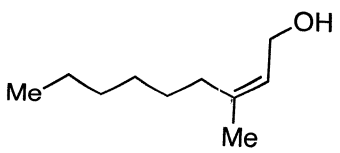

10
9
8
7
6
5
4
3
2
1
0
ppm

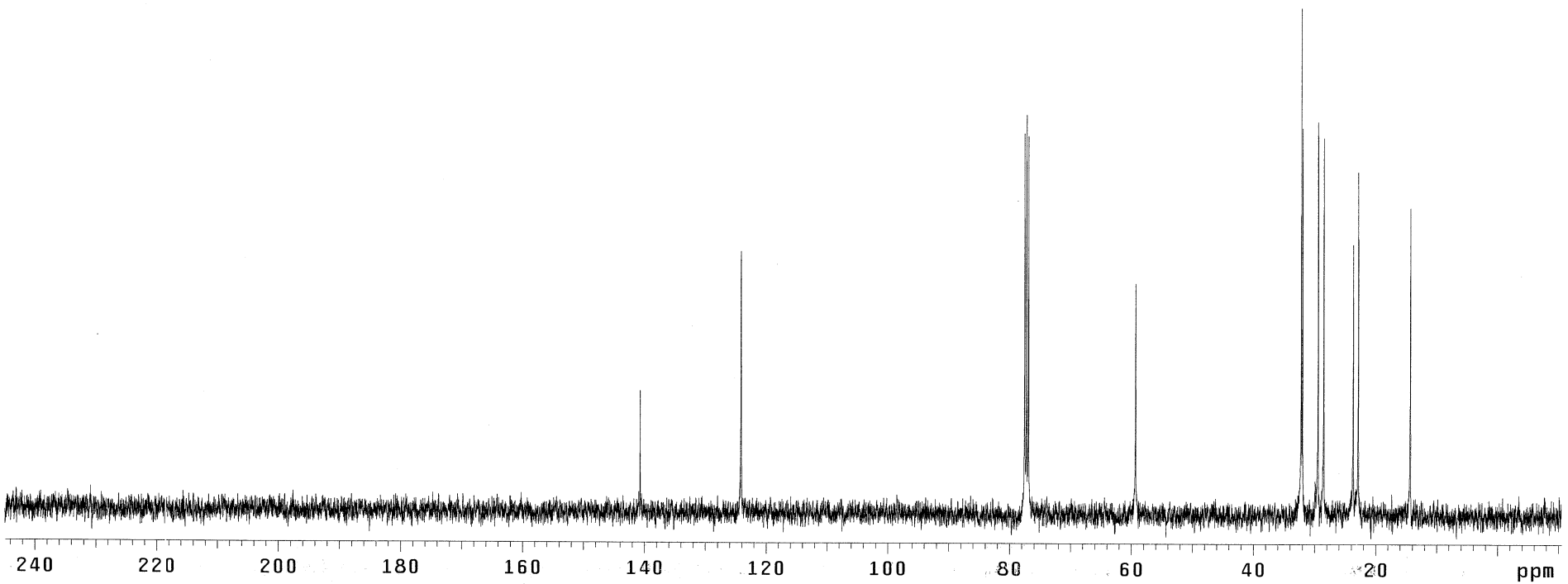

OH
Me
Me

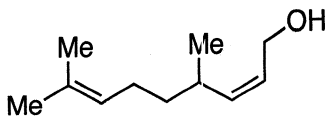

140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

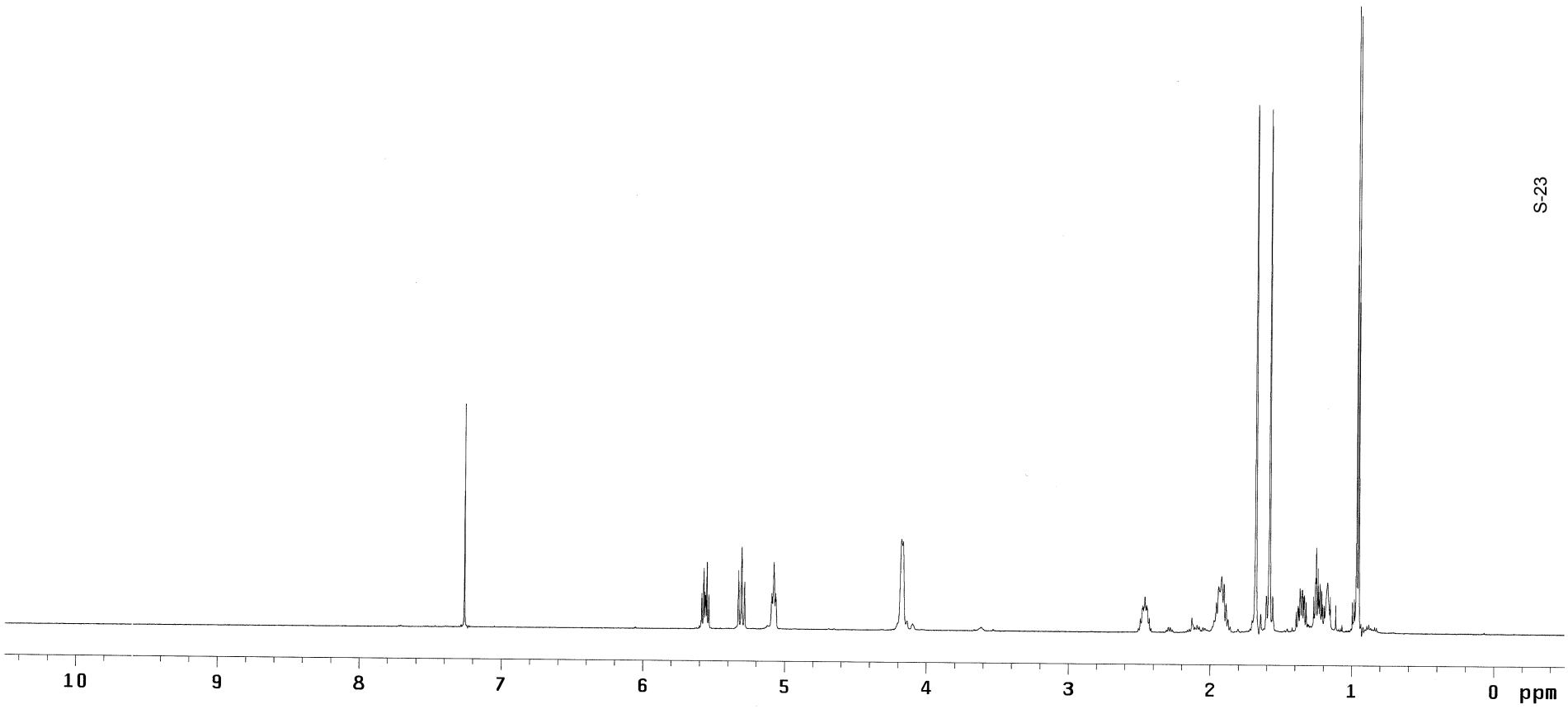

OH
Me
Me

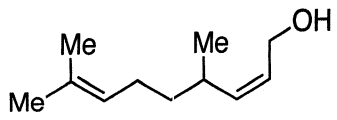

10
9
8
7
6
5
4
3
2
1
0
ppm

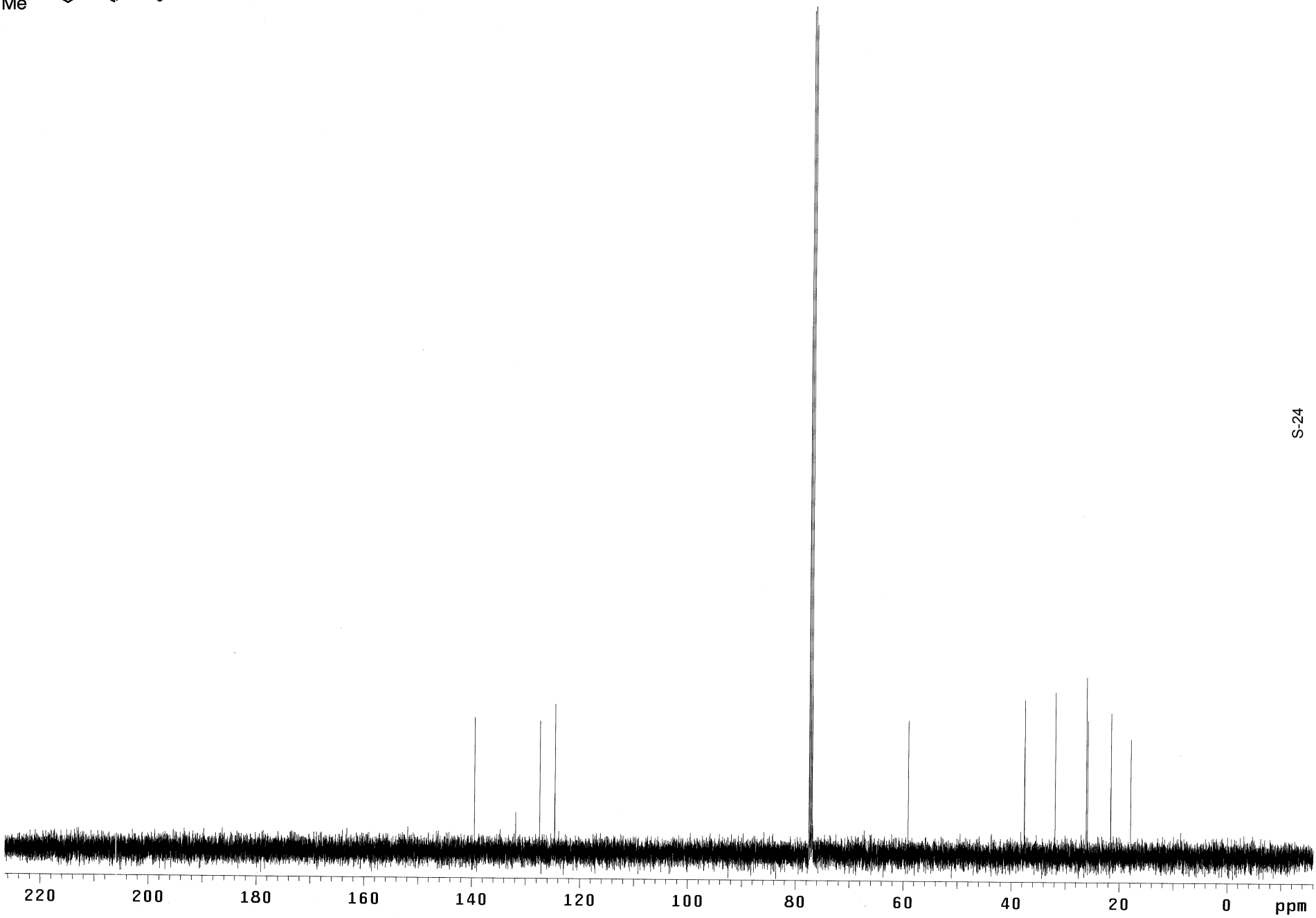

OH
Me
Me

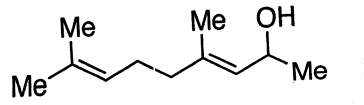

240
220
200
180
160
140
120
100
80
60
40
20
ppm

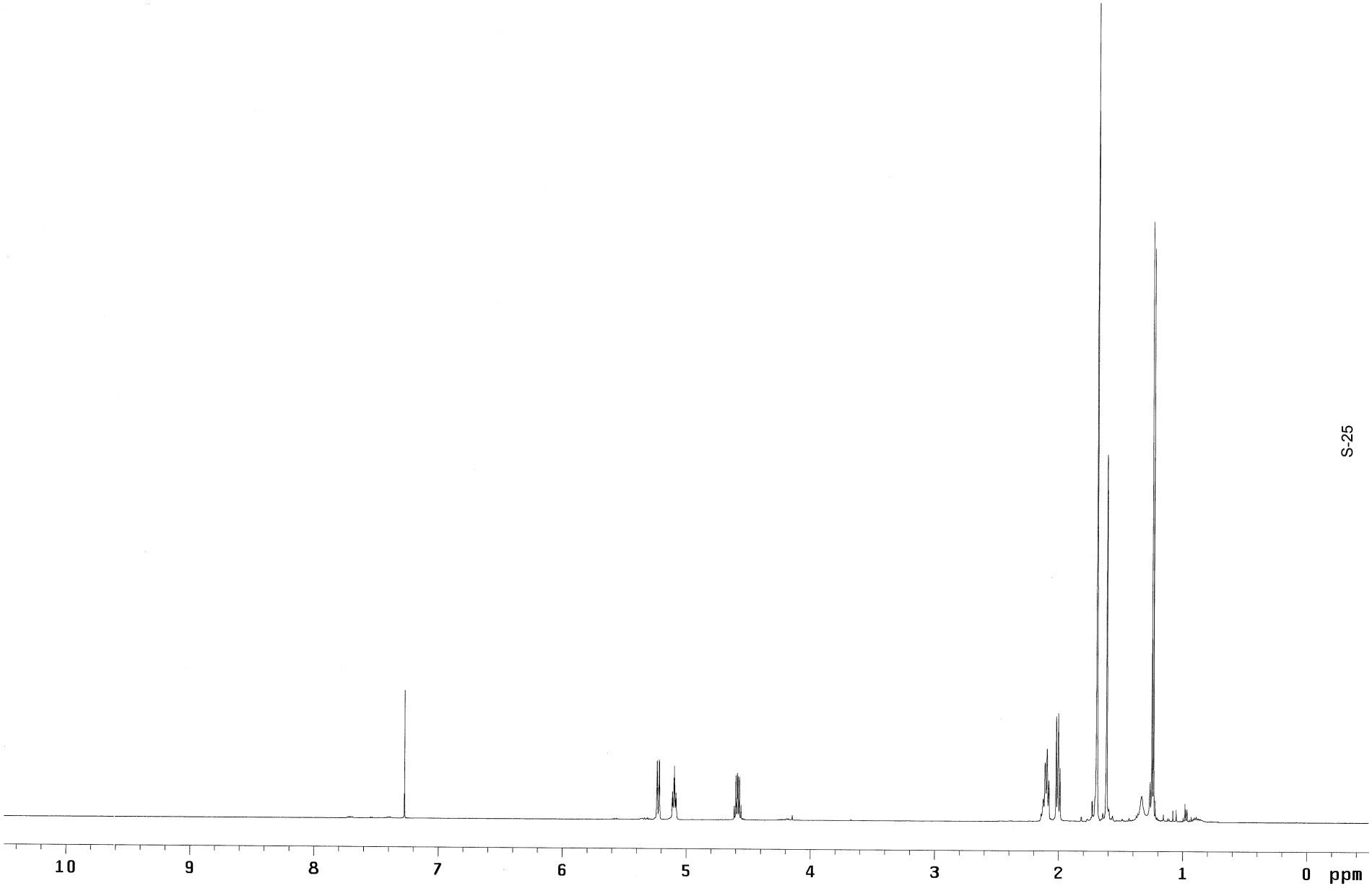

Me
Me
Me
OH

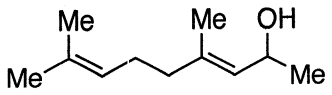

10
9
8
7
6
5
4
3
2
1
0 ppm

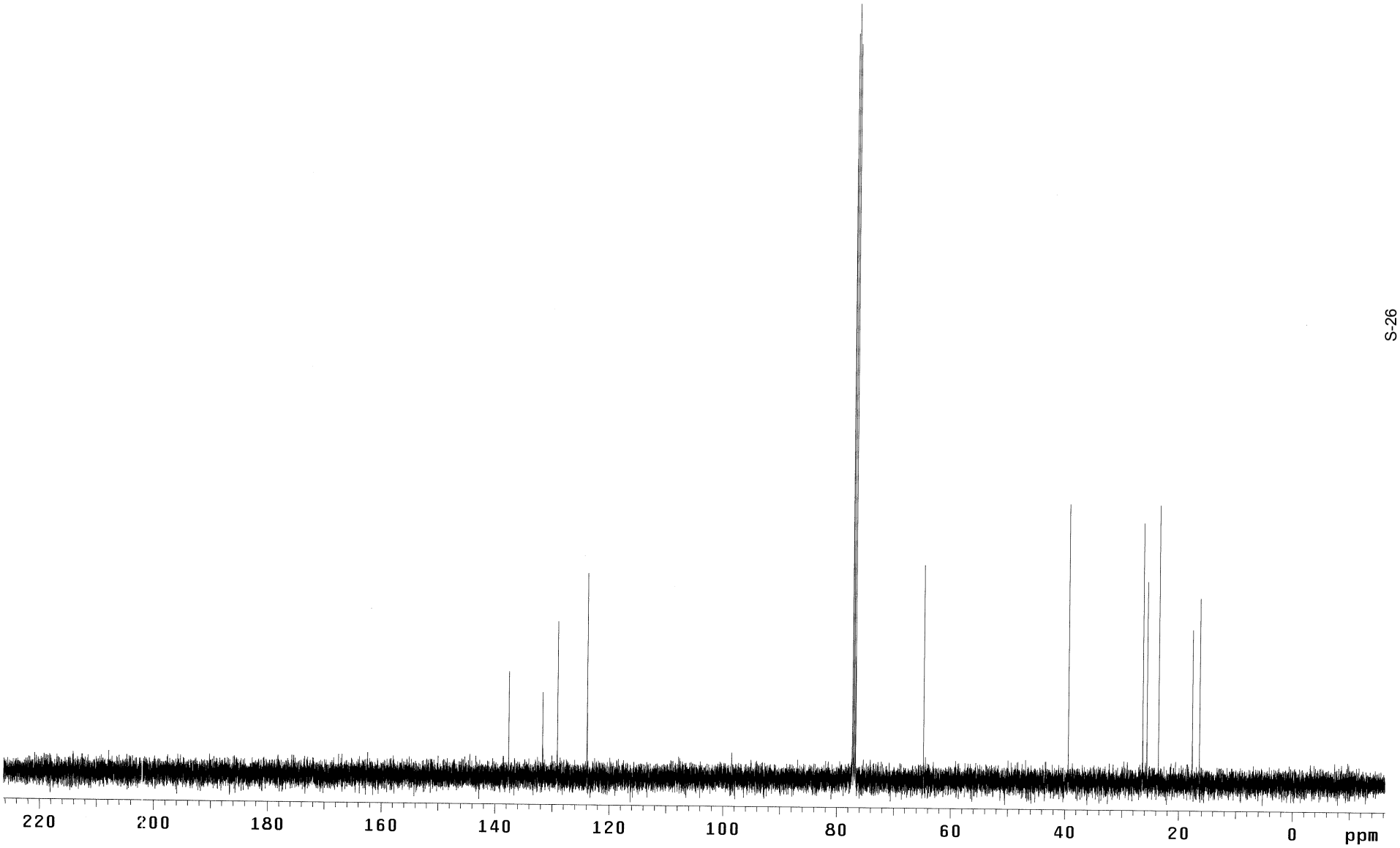

Me
Me
Me
OH

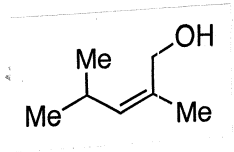

220
200
180
160
140
120
100
80
60
40
20
0
ppm

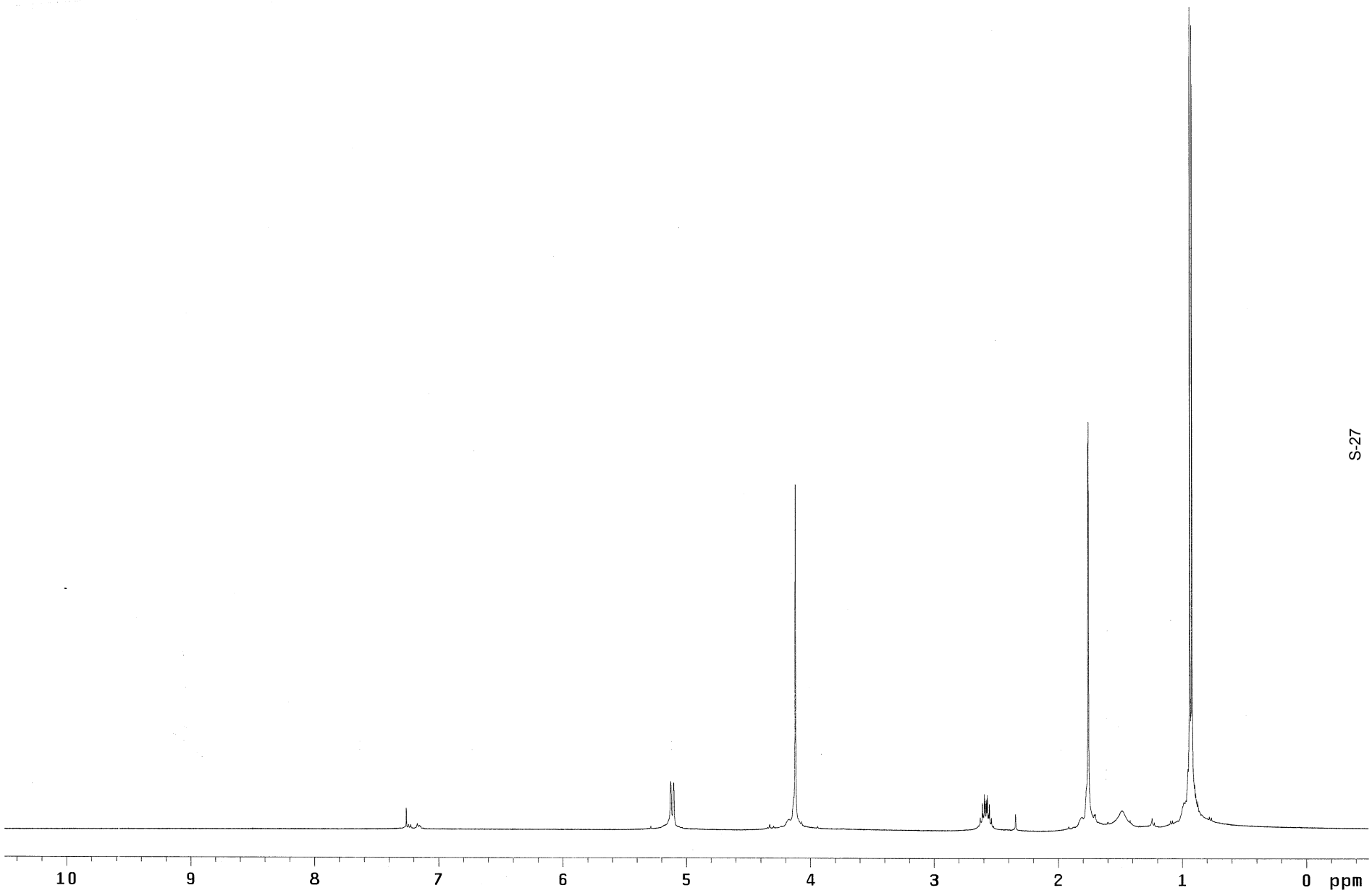

Me
Me
Me
OH
Me

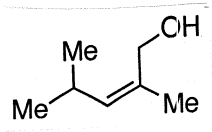

10
9
8
7
6
5
4
3
2
1
0
ppm

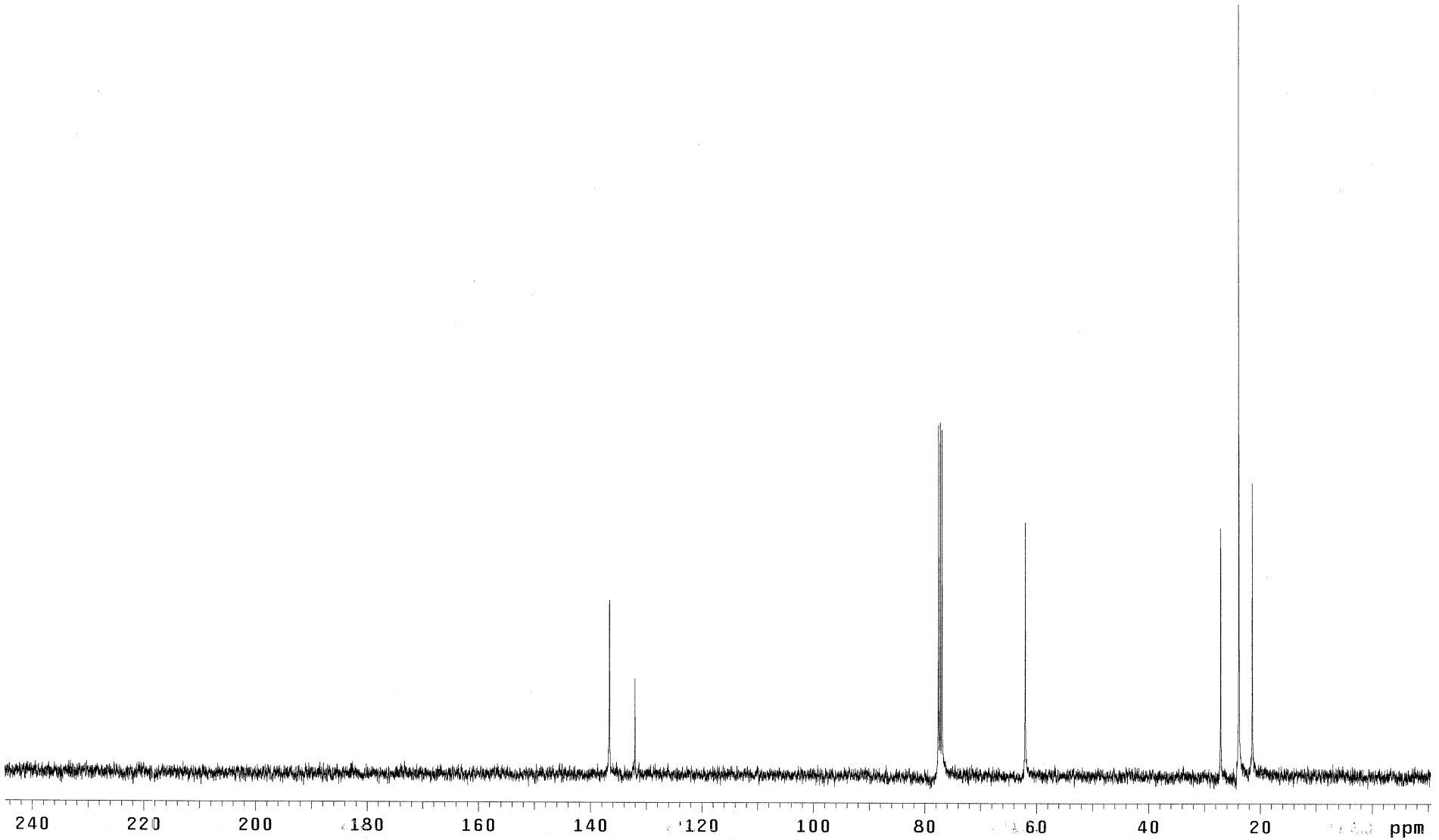

Me
Me
Me
OH
Me

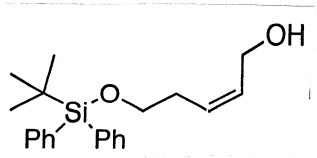

220
200
180
160
140
120
100
80
60
40
20
0
ppm


Me
OH
Me
Me

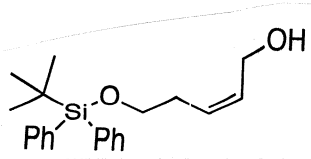

10
9
8
7
6
5
4
3
2
1
0 ppm

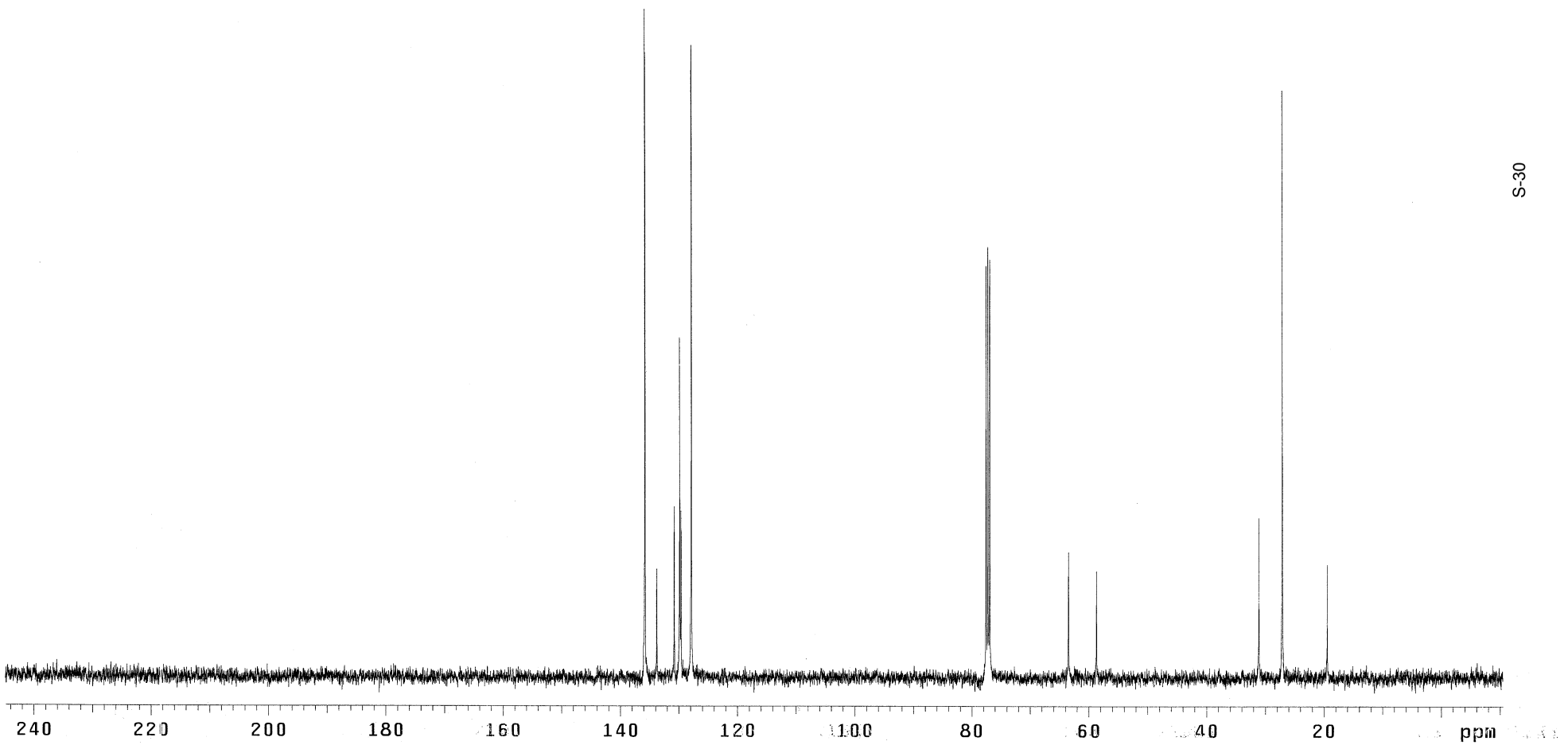

OH
Me
Me
Me

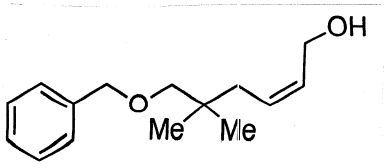

240
220
200
180
160
140
120
100
80
60
40
20
ppm

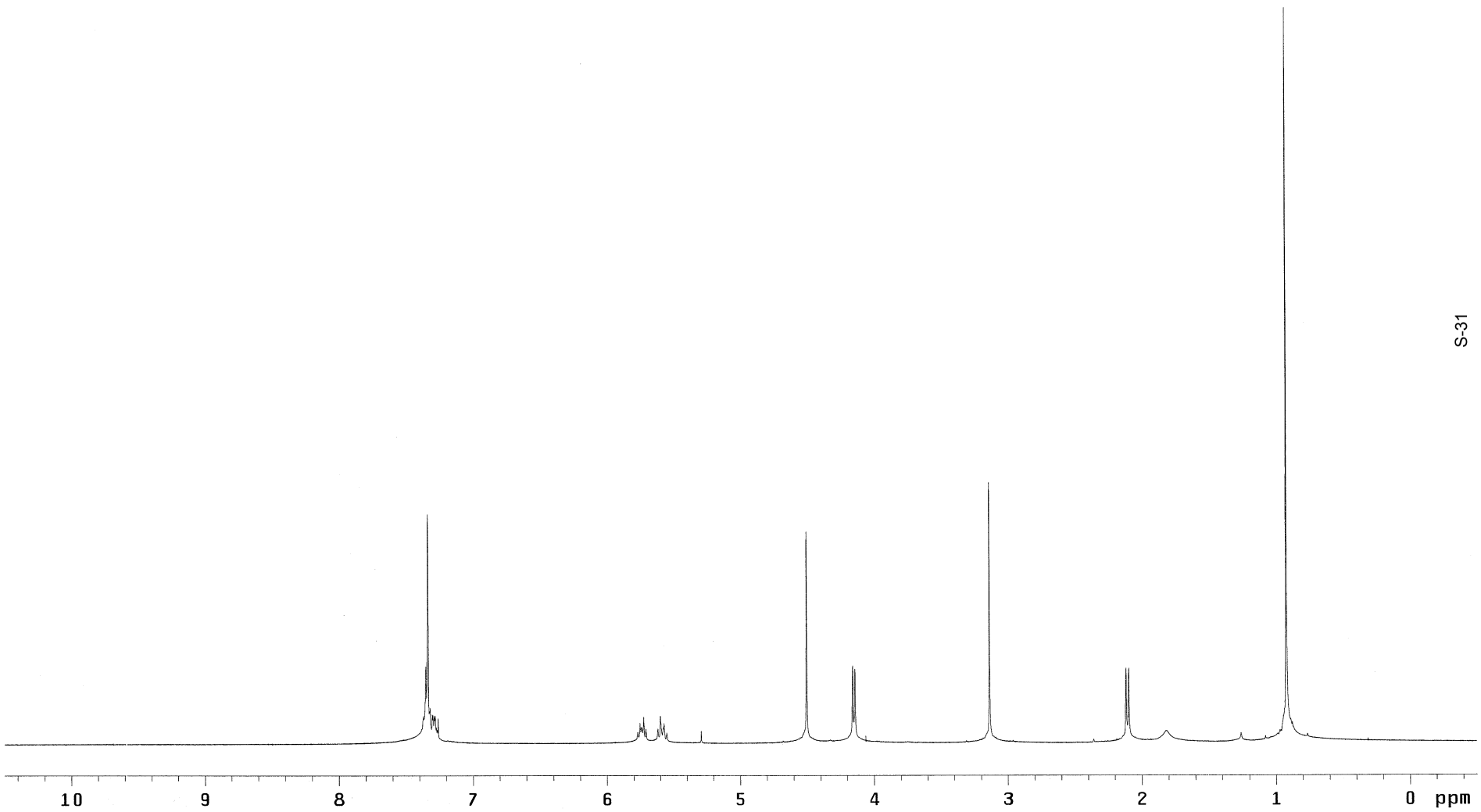

OH
O
Si
Ph
Ph

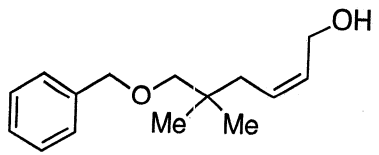
10
9
8
7
6
5
4
3
2
1
0
ppm

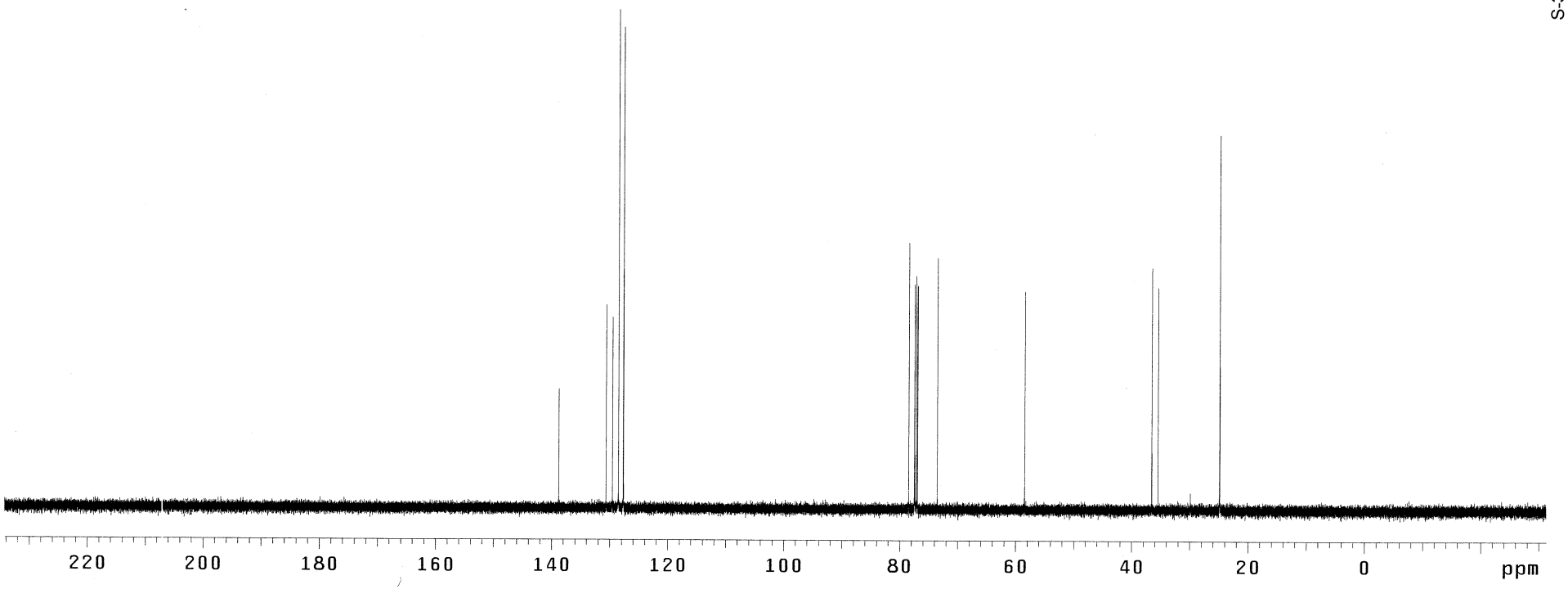

OH
O
Si
Ph
Ph

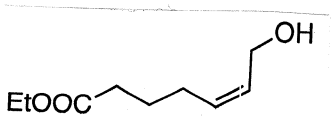

240
220
200
180
160
140
120
100
80
60
40
20
ppm

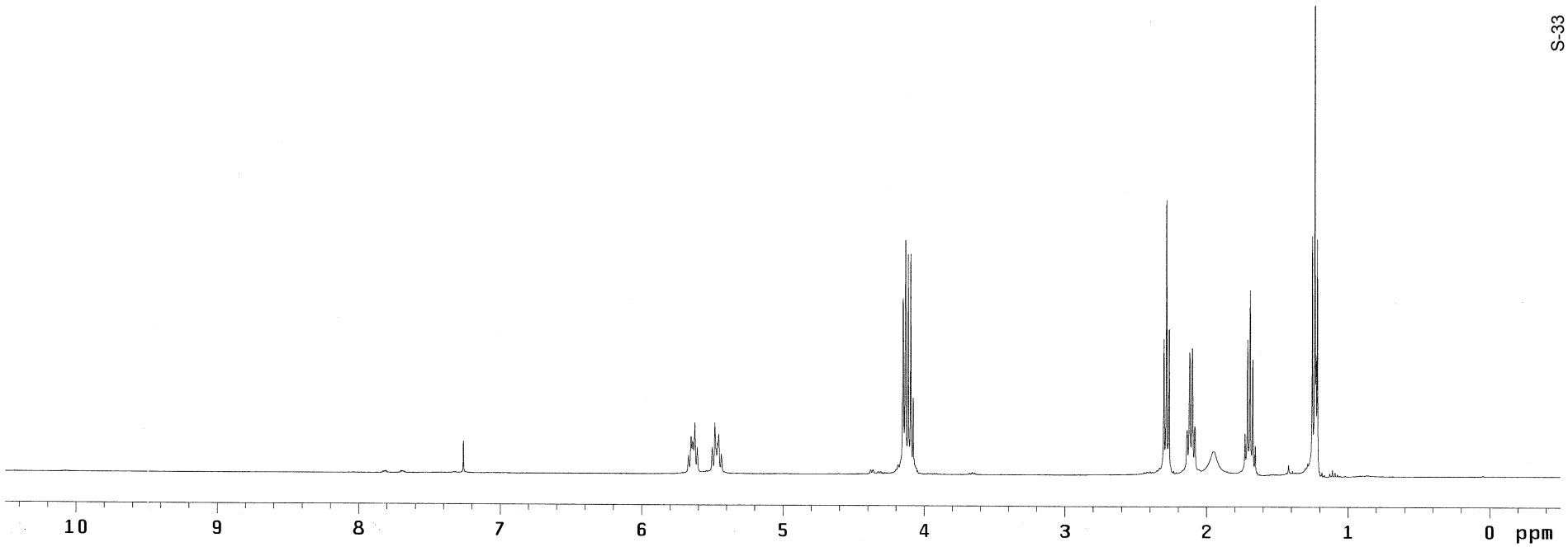

OH
O
Me
Me

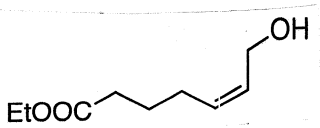

10
9
8
7
6
5
4
3
2
1
0
ppm

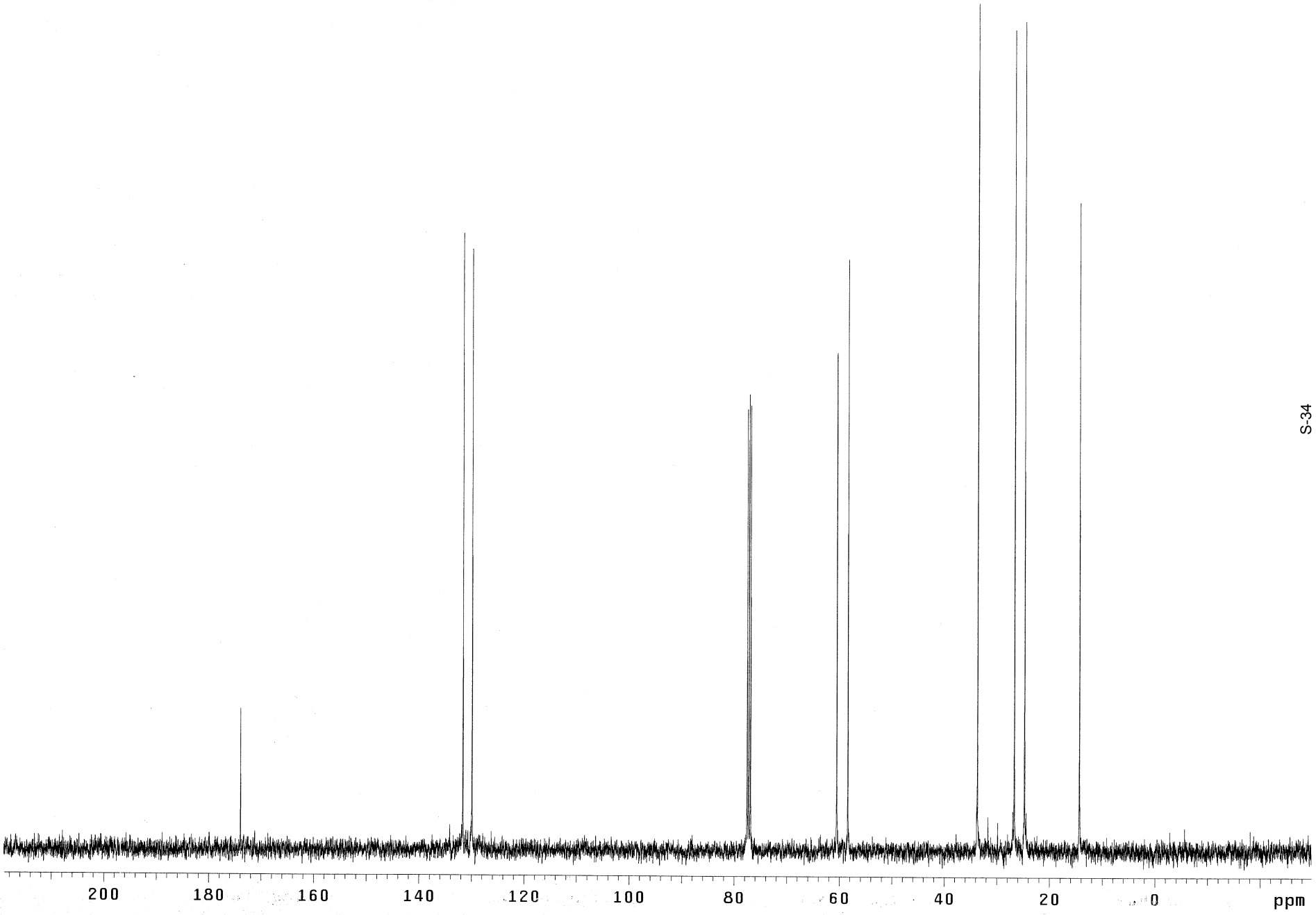

OH
O
Me
Me

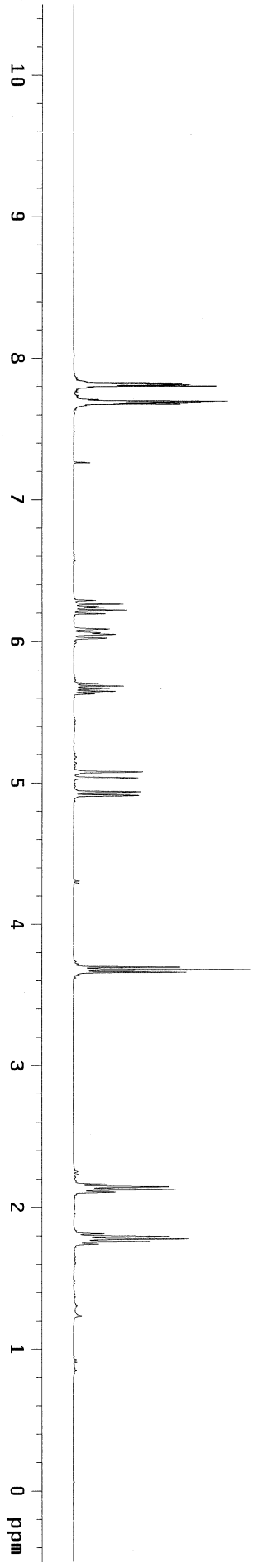

220
200
180
160
140
120
100
80
60
40
20
0
ppm

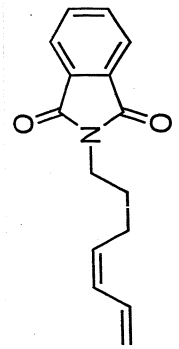

OH
EtOOC

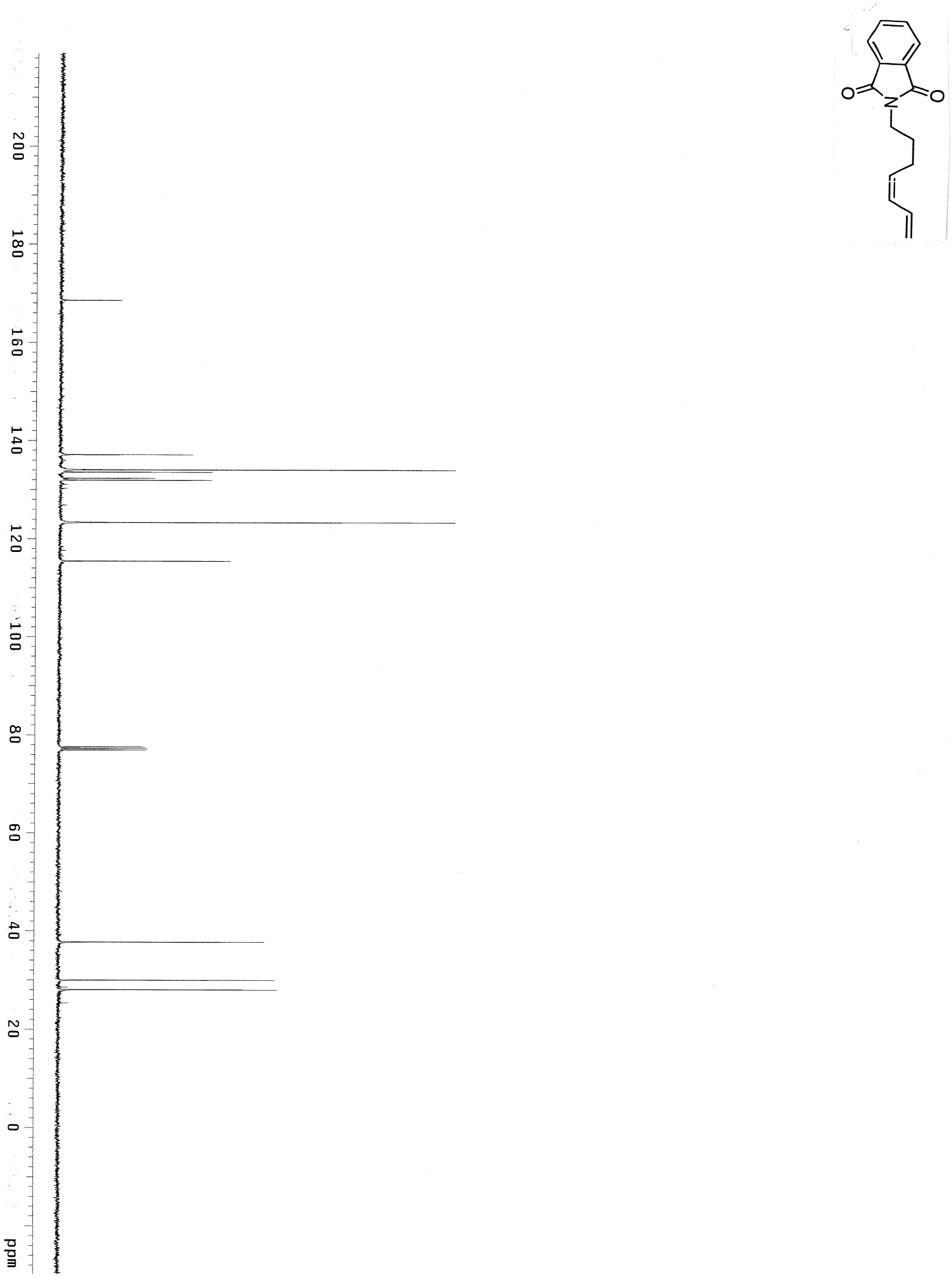

10
9
8
7
6
5
4
3
2
1
0 ppm

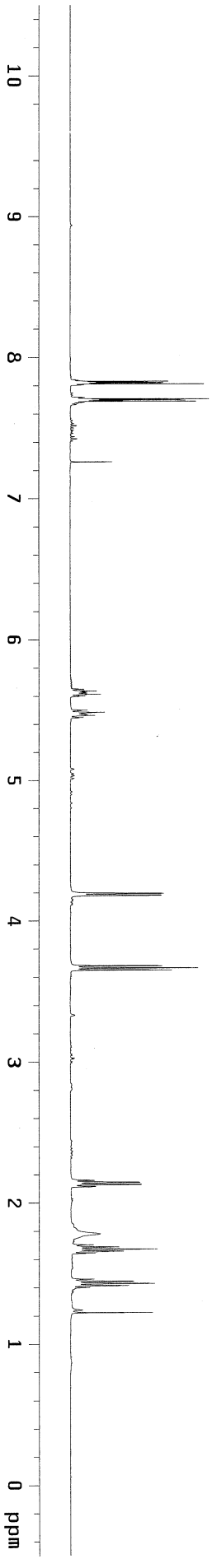

OH
EtOOC

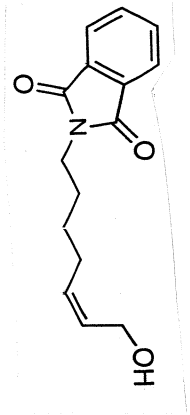

200
180
160
140
120
100
80
60
40
20
0
ppm

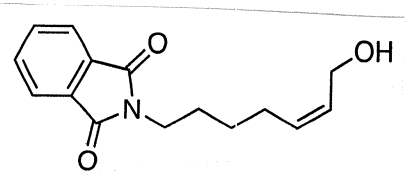

10
9
8
7
6
5
4
3
2
1
0
ppm

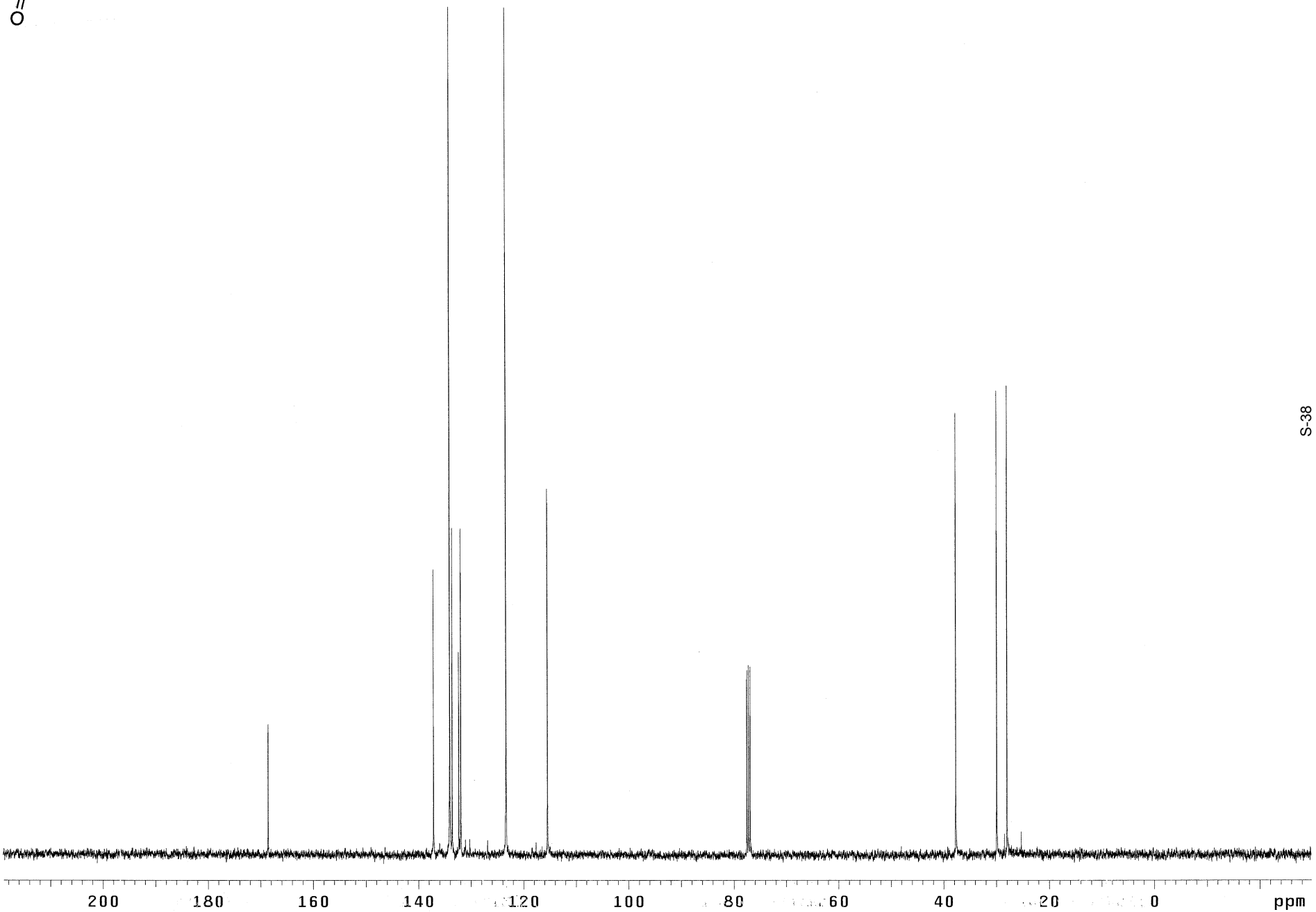


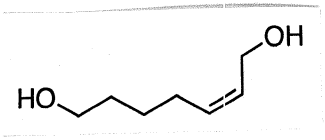

200
180
160
140
120
100
80
60
40
20
0
ppm

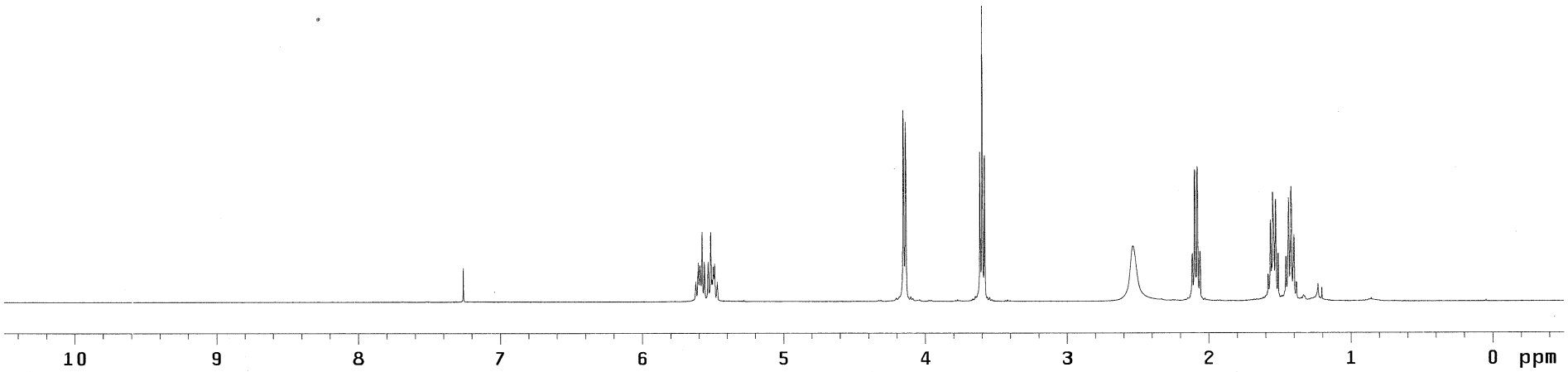

10
9
8
7
6
5
4
3
2
1
0
ppm

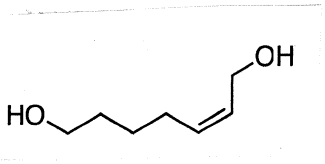

O
N
O
OH

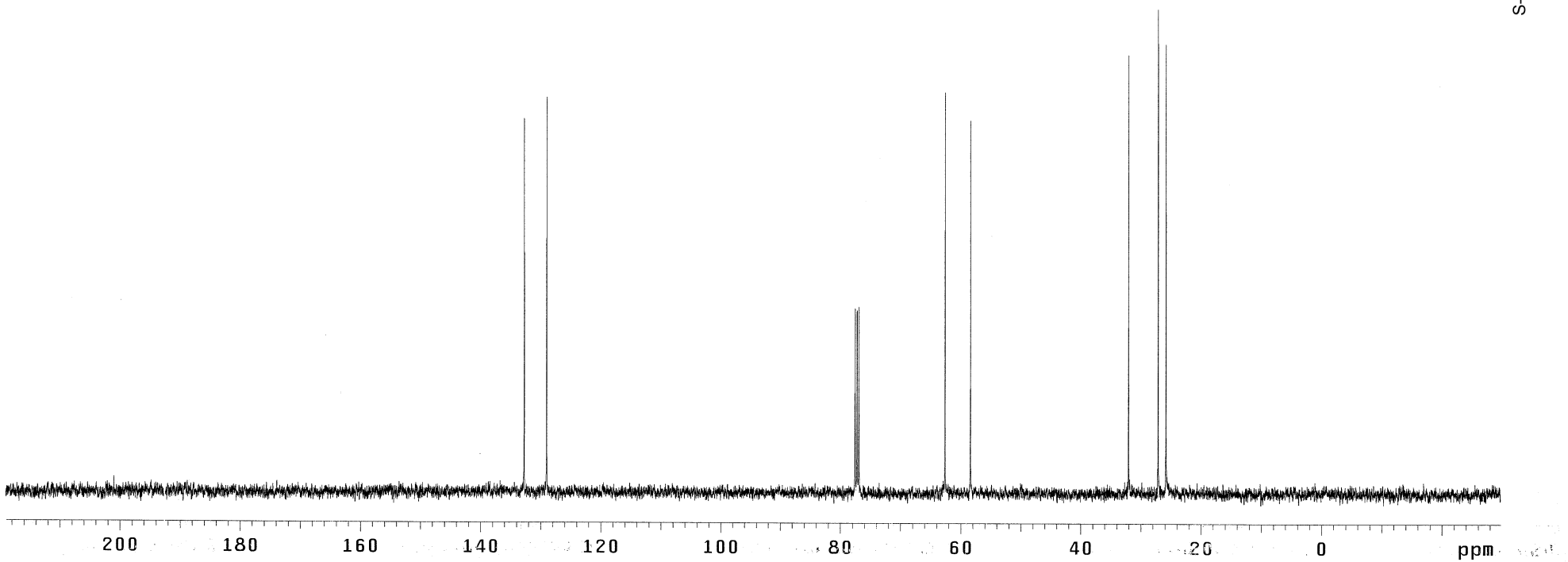

O
N
O
OH

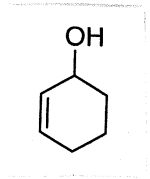

200
180
160
140
120
100
80
60
40
20
0
ppm

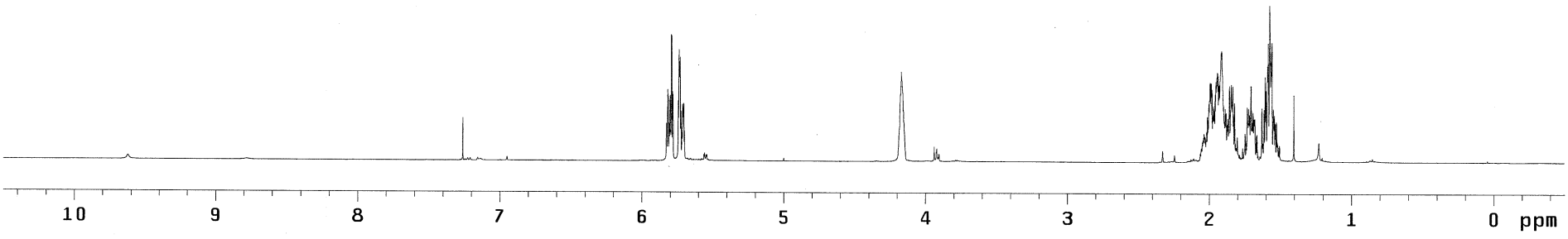

OH
HO

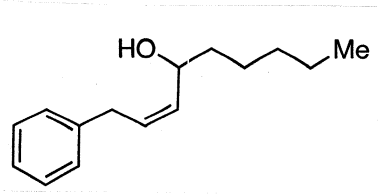

10
9
8
7
6
5
4
3
2
1
0
ppm

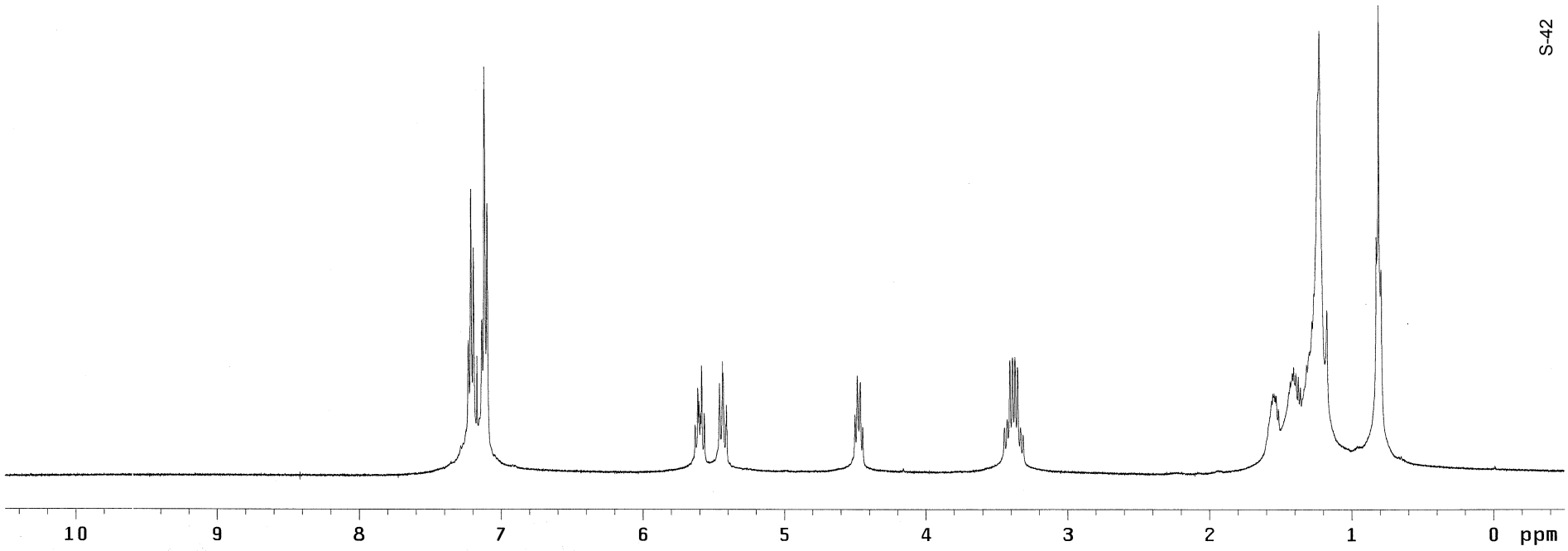

OH
HO

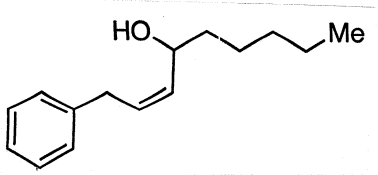

200
180
160
140
120
100
80
60
40
20
0
ppm

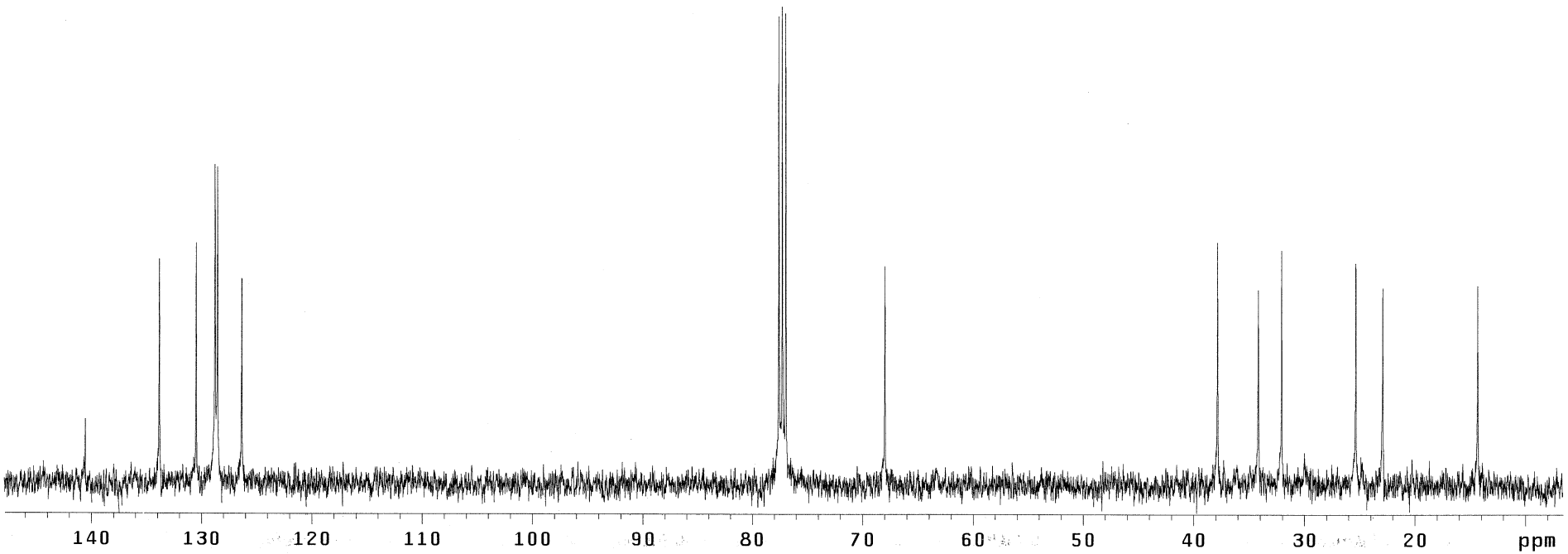

OH

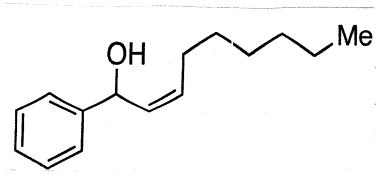

10
9
8
7
6
5
4
3
2
1
0 ppm


HO
Me

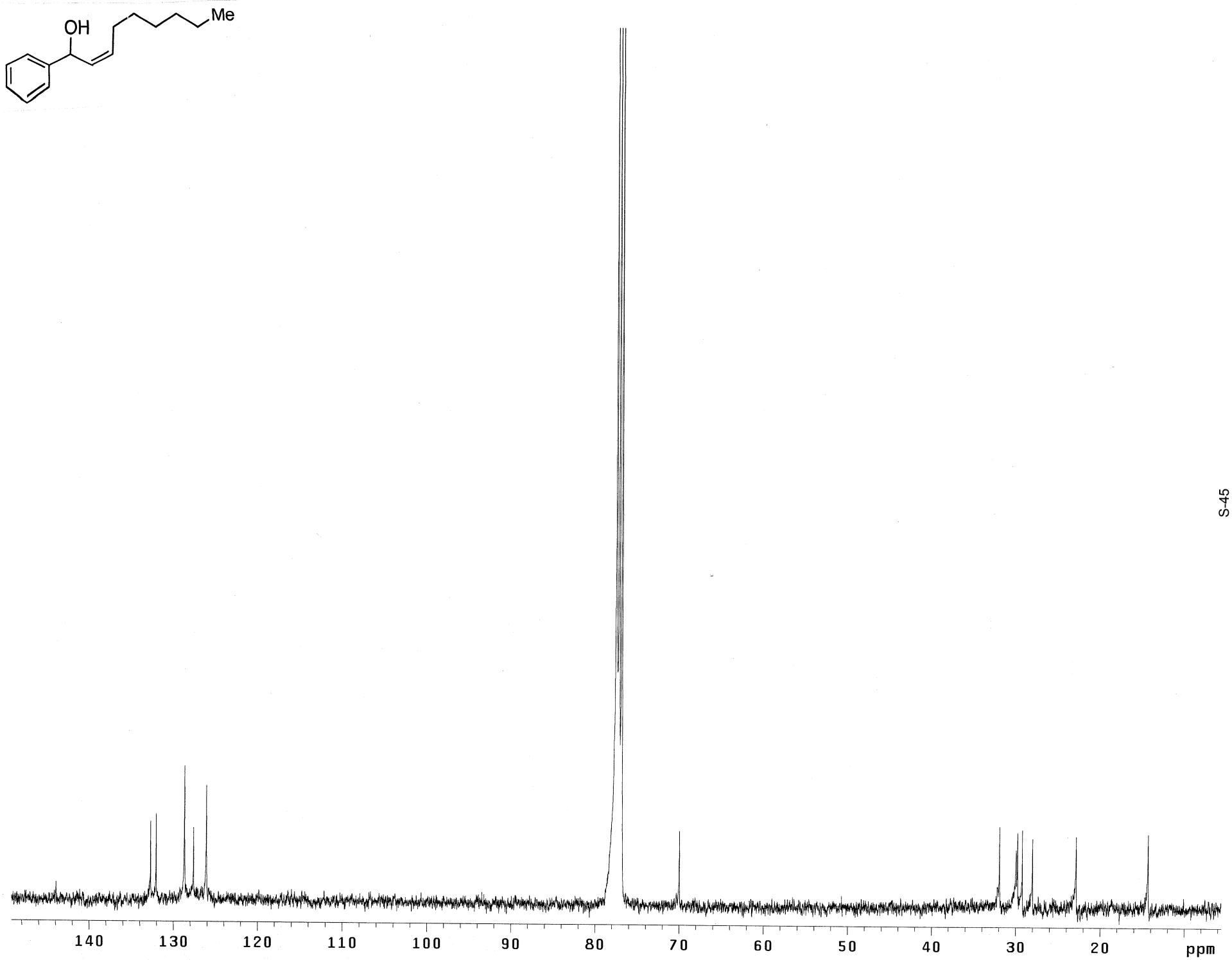

10
9
8
7
6
5
4
3
2
1
0
ppm

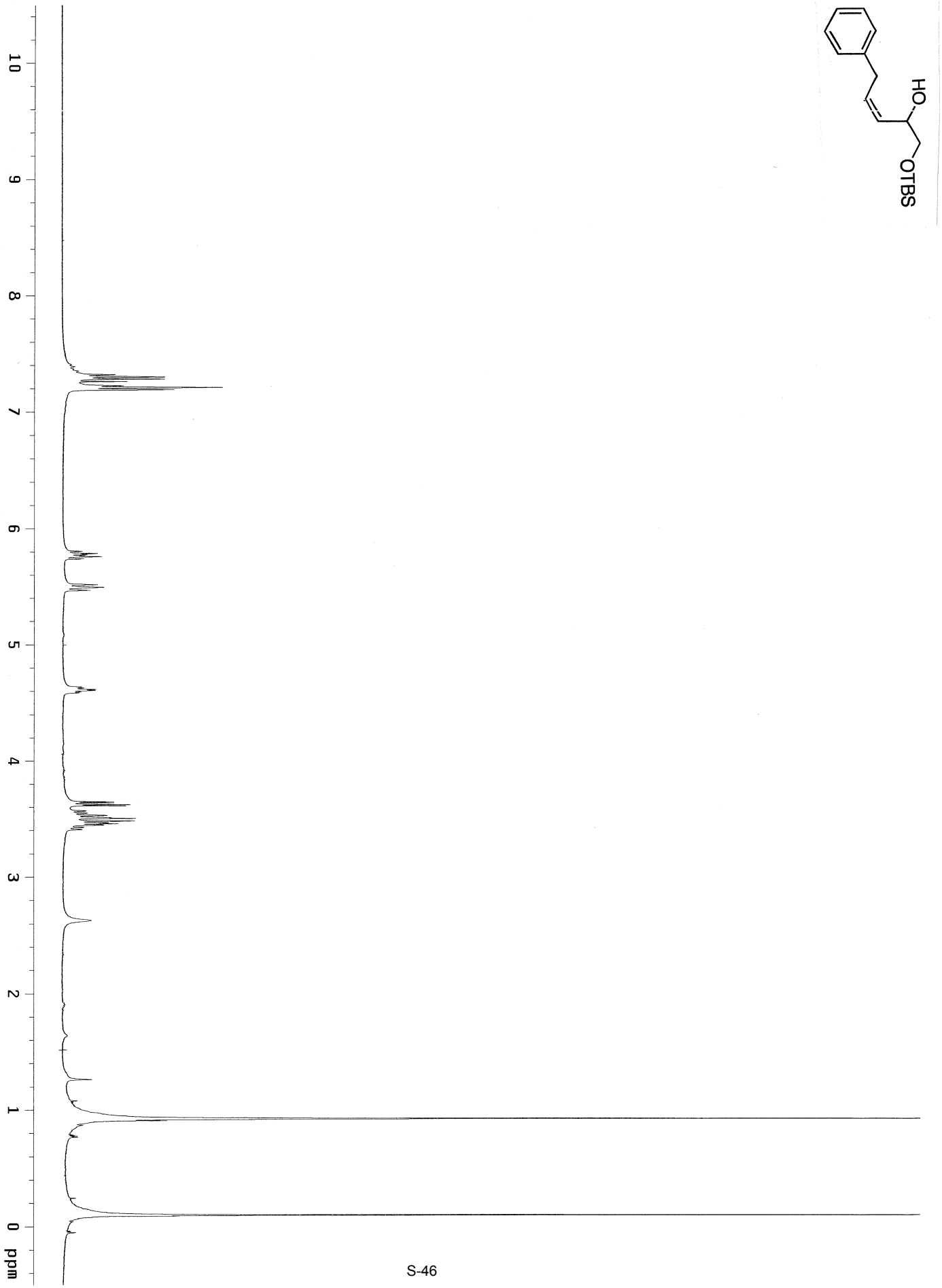

HO
Me

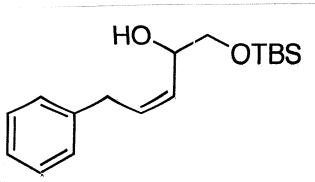

140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

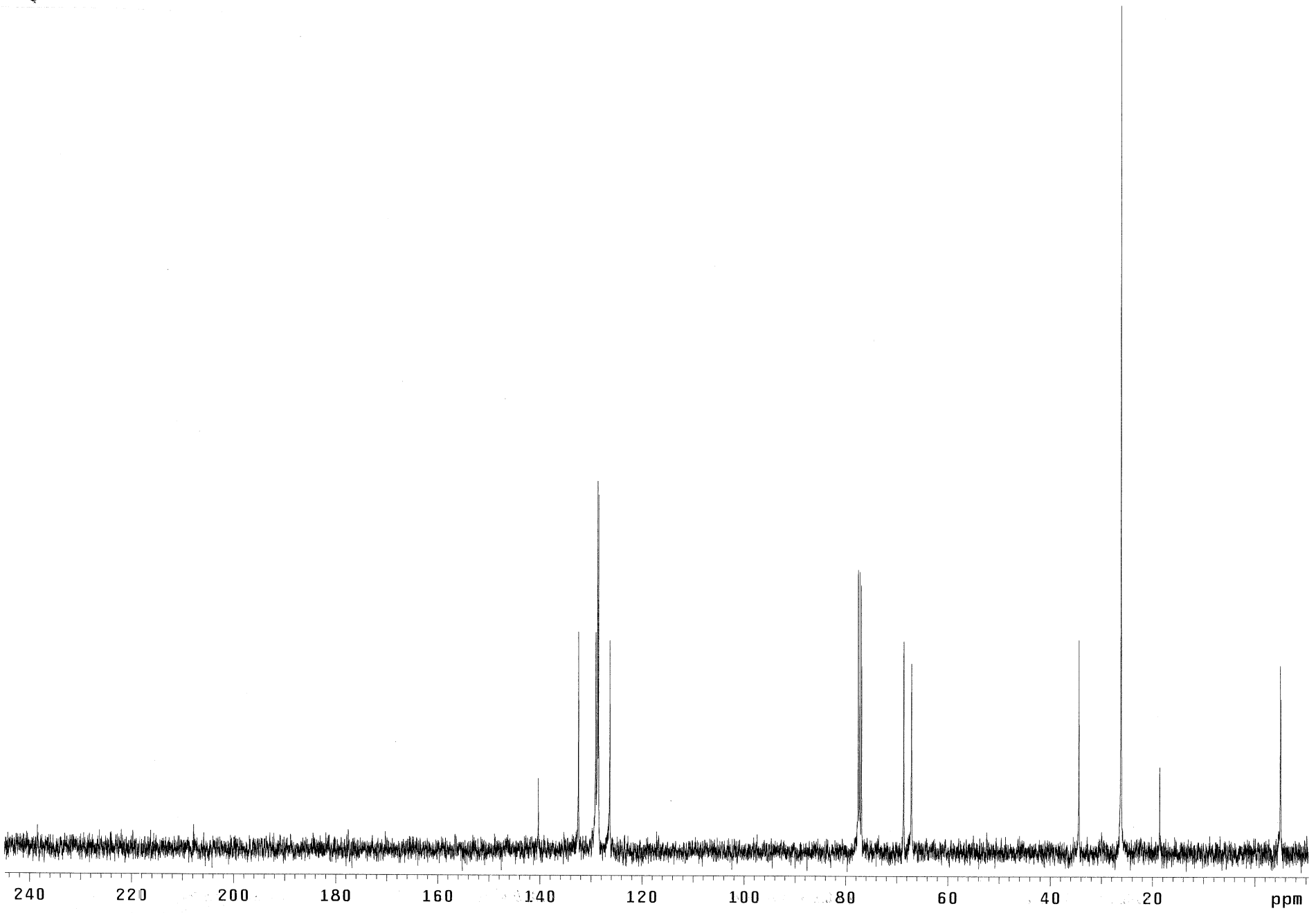

OH
Me

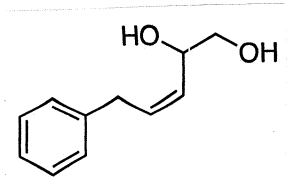
10
9
8
7
6
5
4
3
2
1
0 ppm

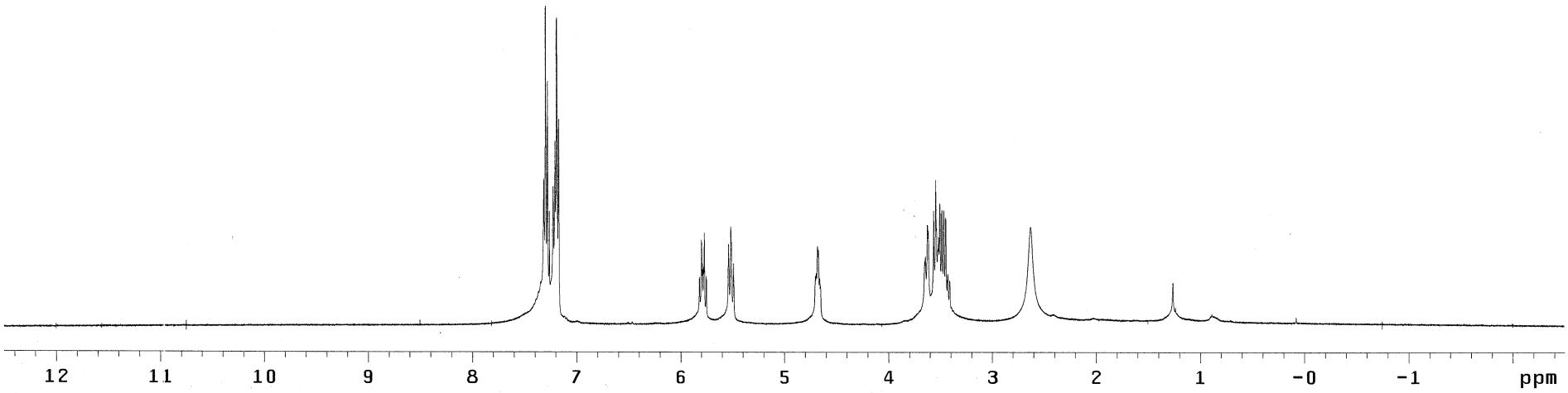

OH
Me
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

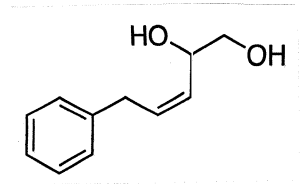

HO
OTBS
10
9
8
7
6
5
4
3
2
1
0
ppm

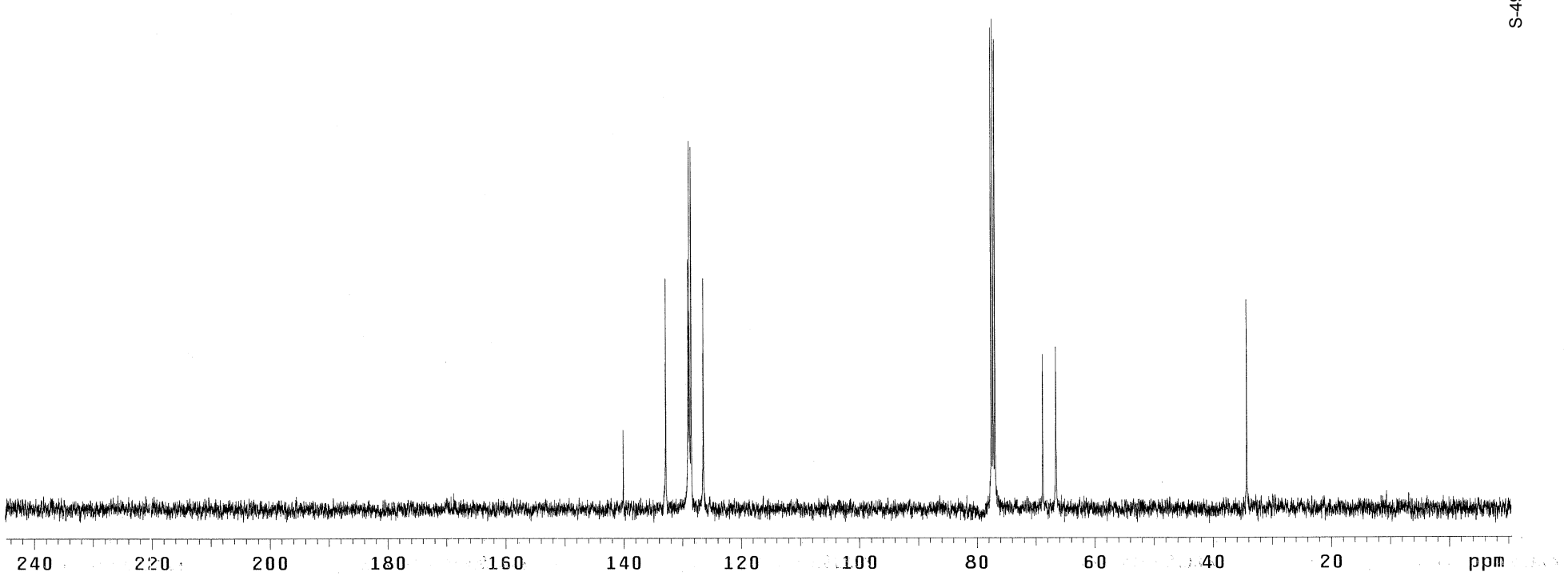

HO
OTBS

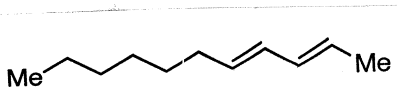

240
220
200
180
160
140
120
100
80
60
40
20
ppm

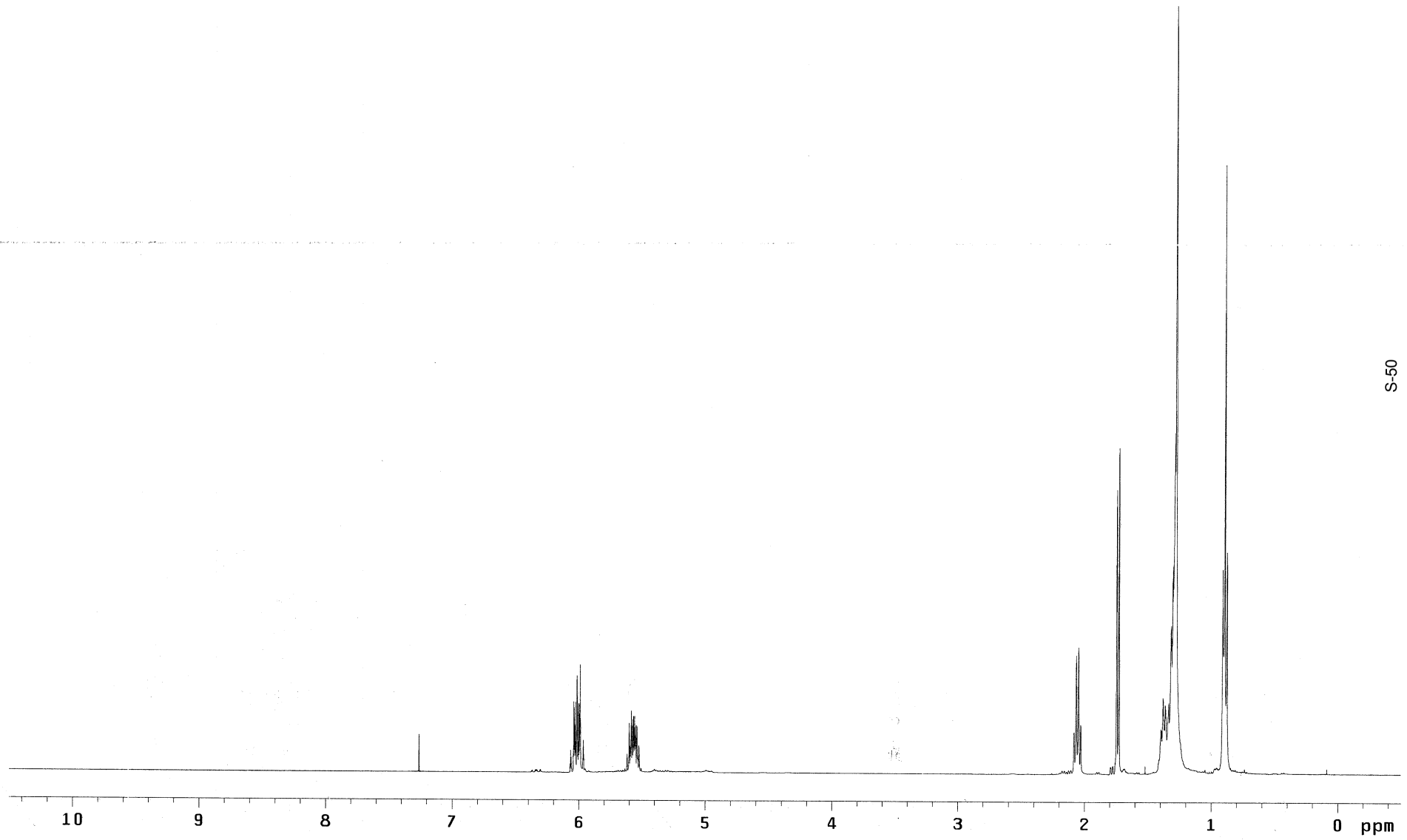

HO
OH

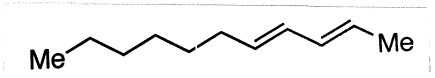

12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

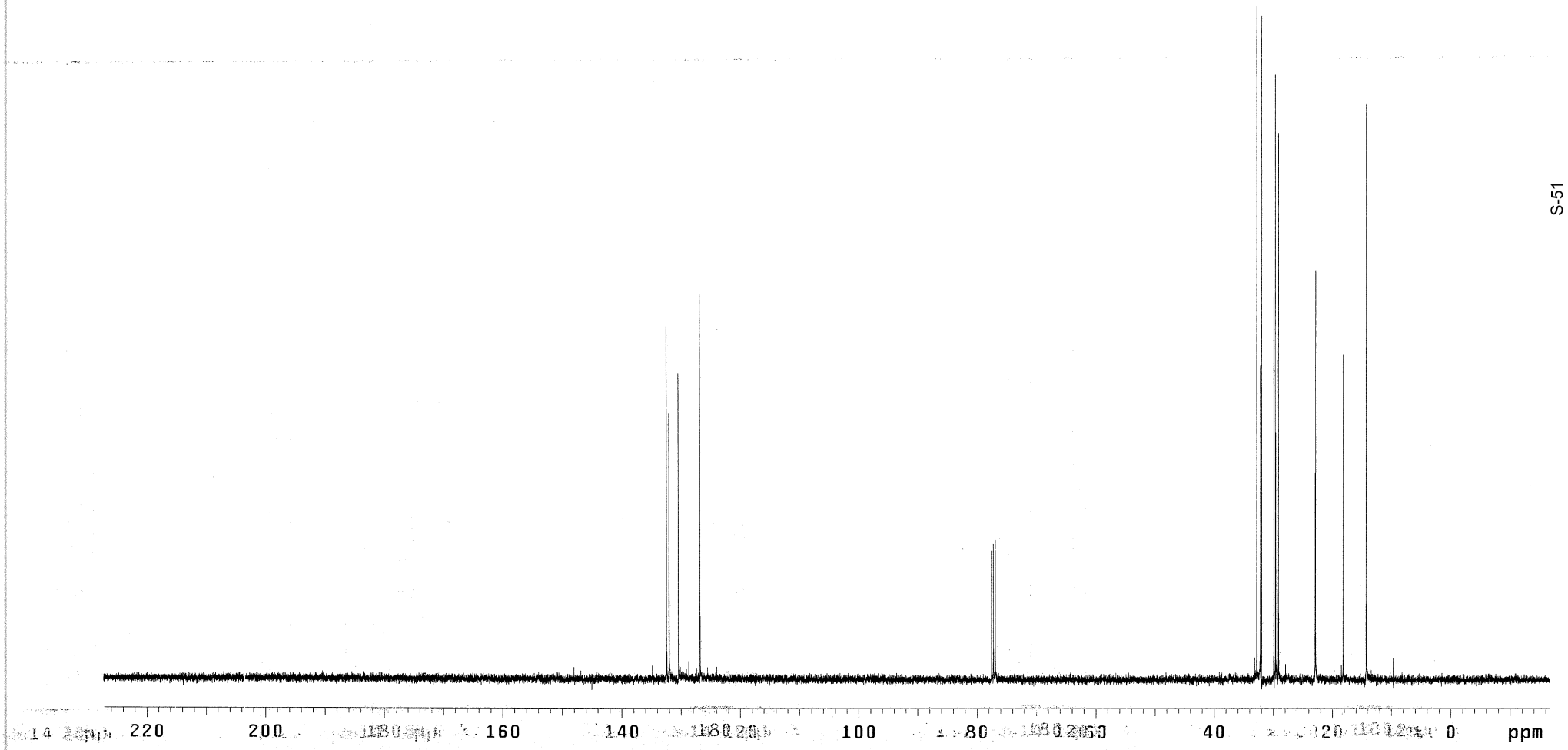

HO
OH

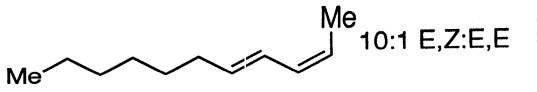

240
220
200
180
160
140
120
100
80
60
40
20
ppm


Me
Me

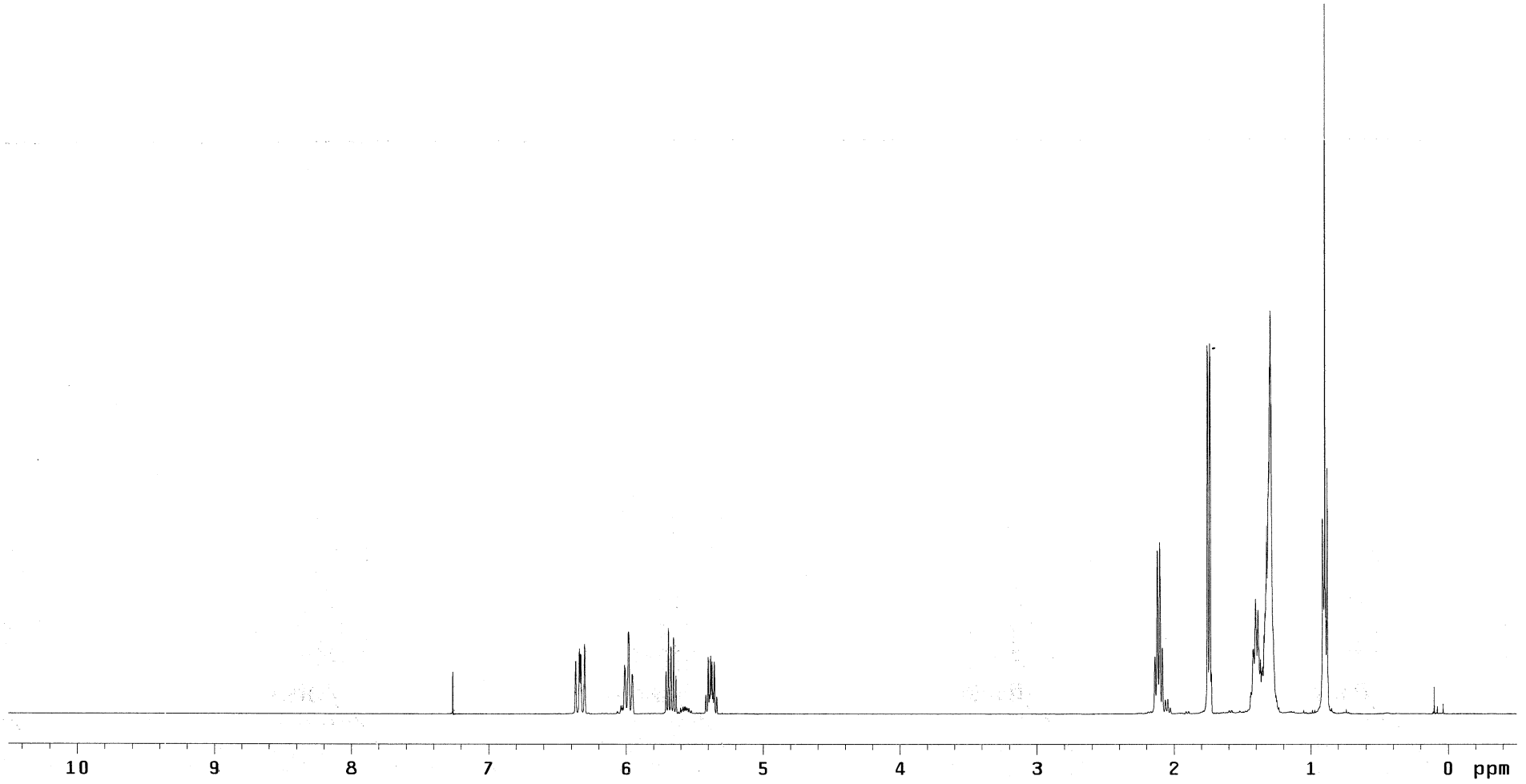

10
9
8
7
6
5
4
3
2
1
0
ppm

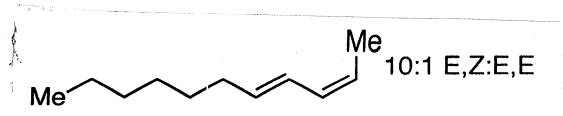

Me
Me


220
200
160
140
100
80
40
0
ppm

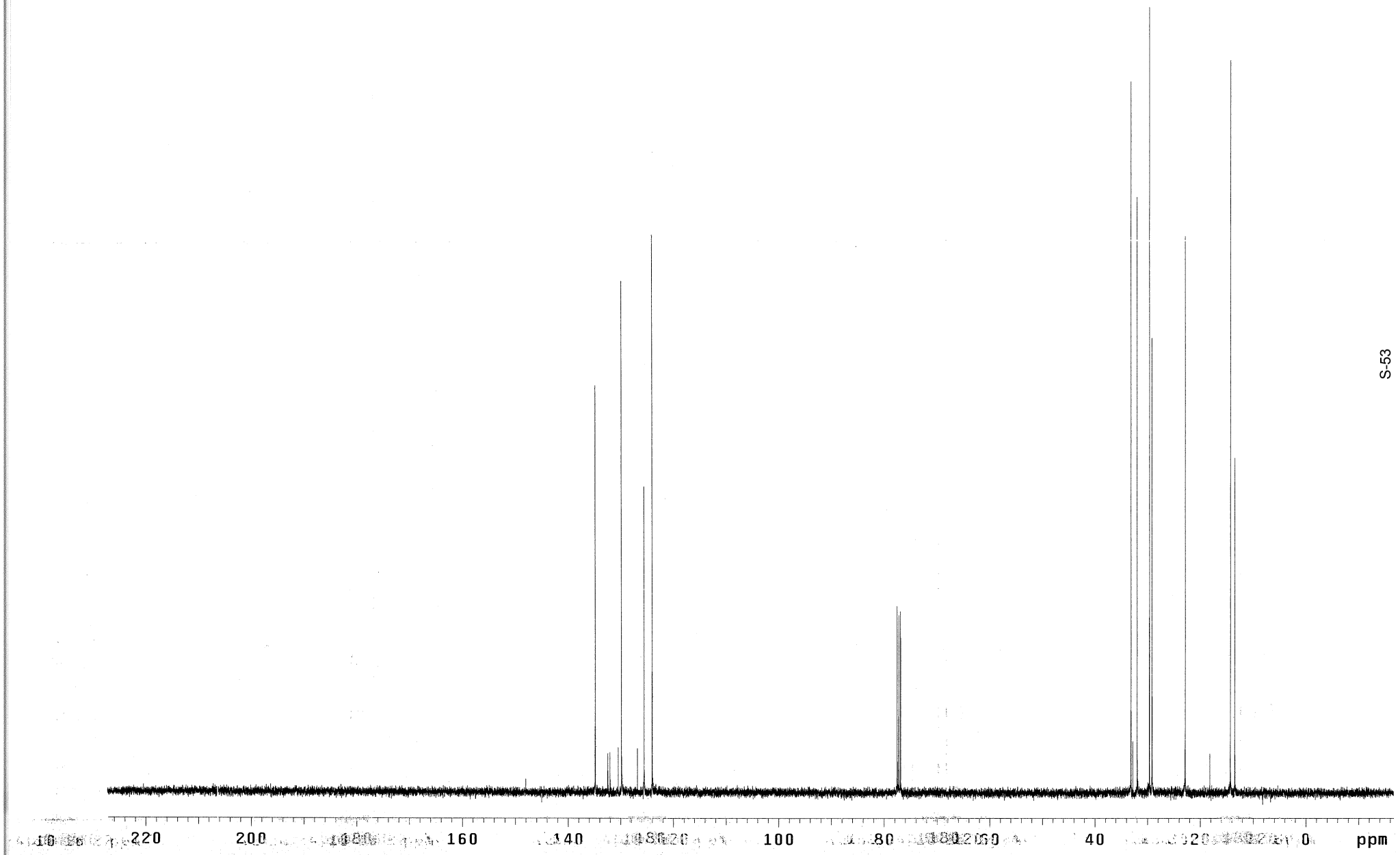


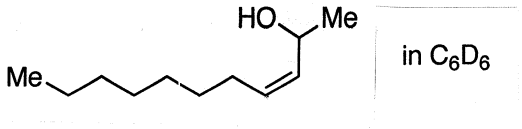
10:1 E,Z:E,E



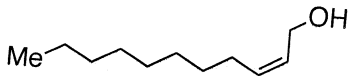


10:1 E,Z:E,E

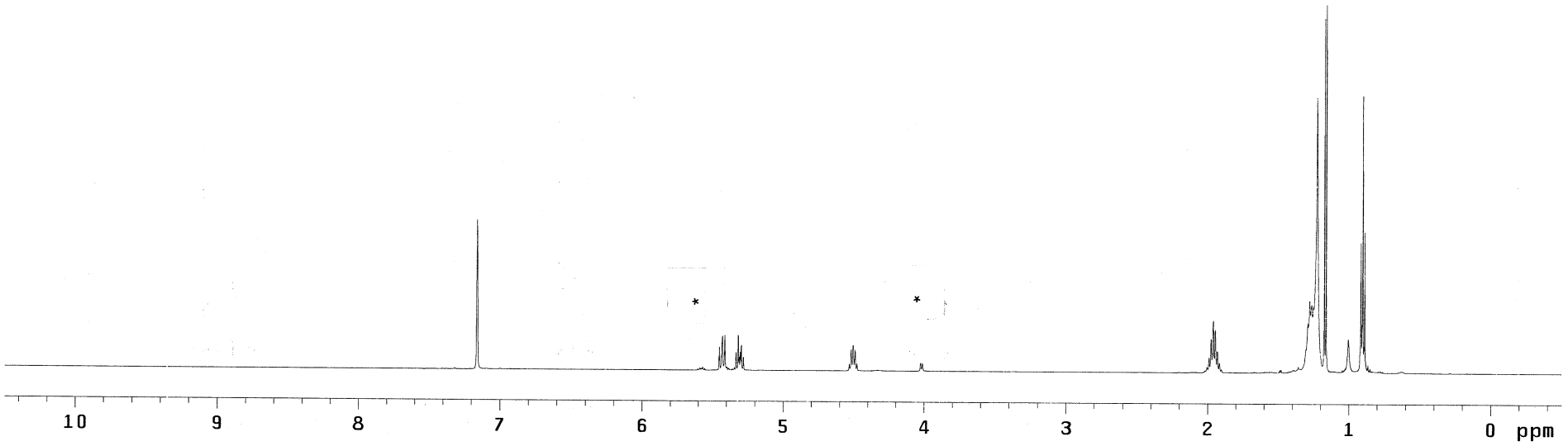


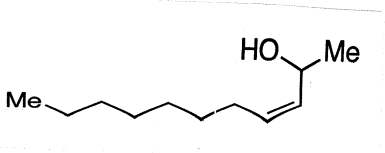


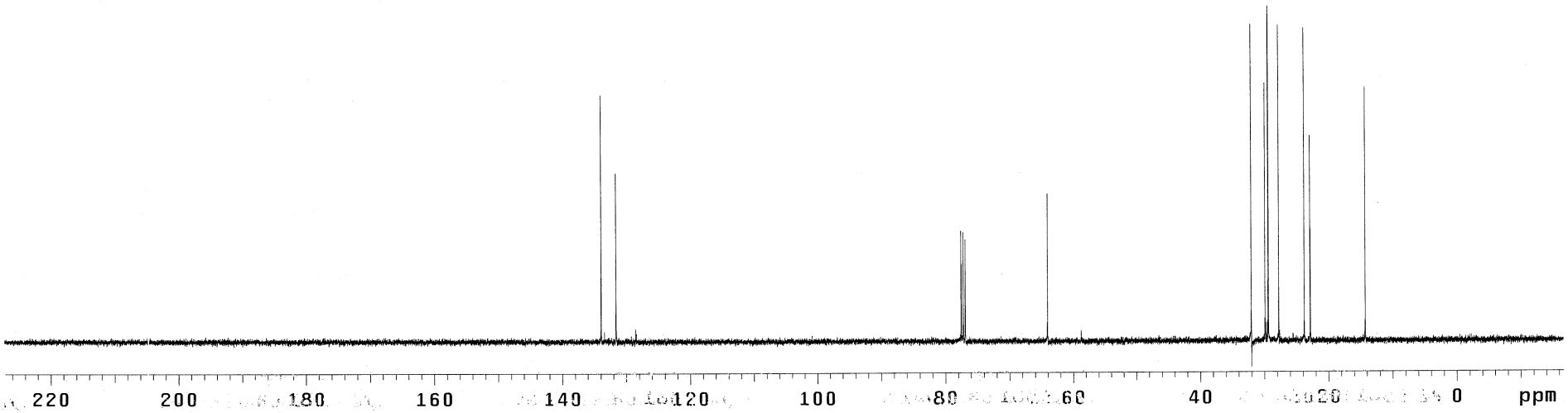
in C_6D_6

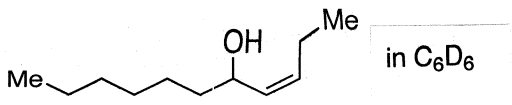


*

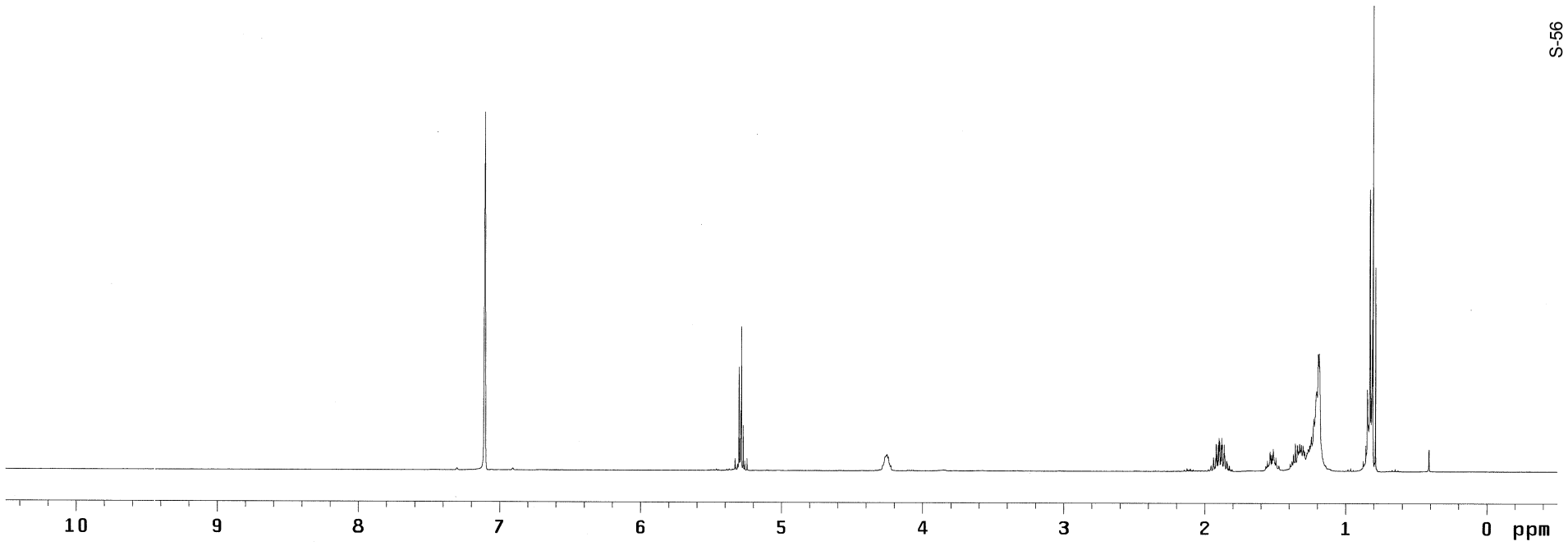


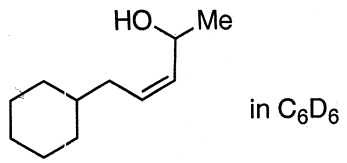

HO
Me
Me


220
200
180
160
140
120
100
80
60
40
20
0
ppm

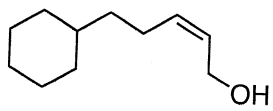


in C_6D_6

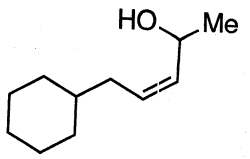


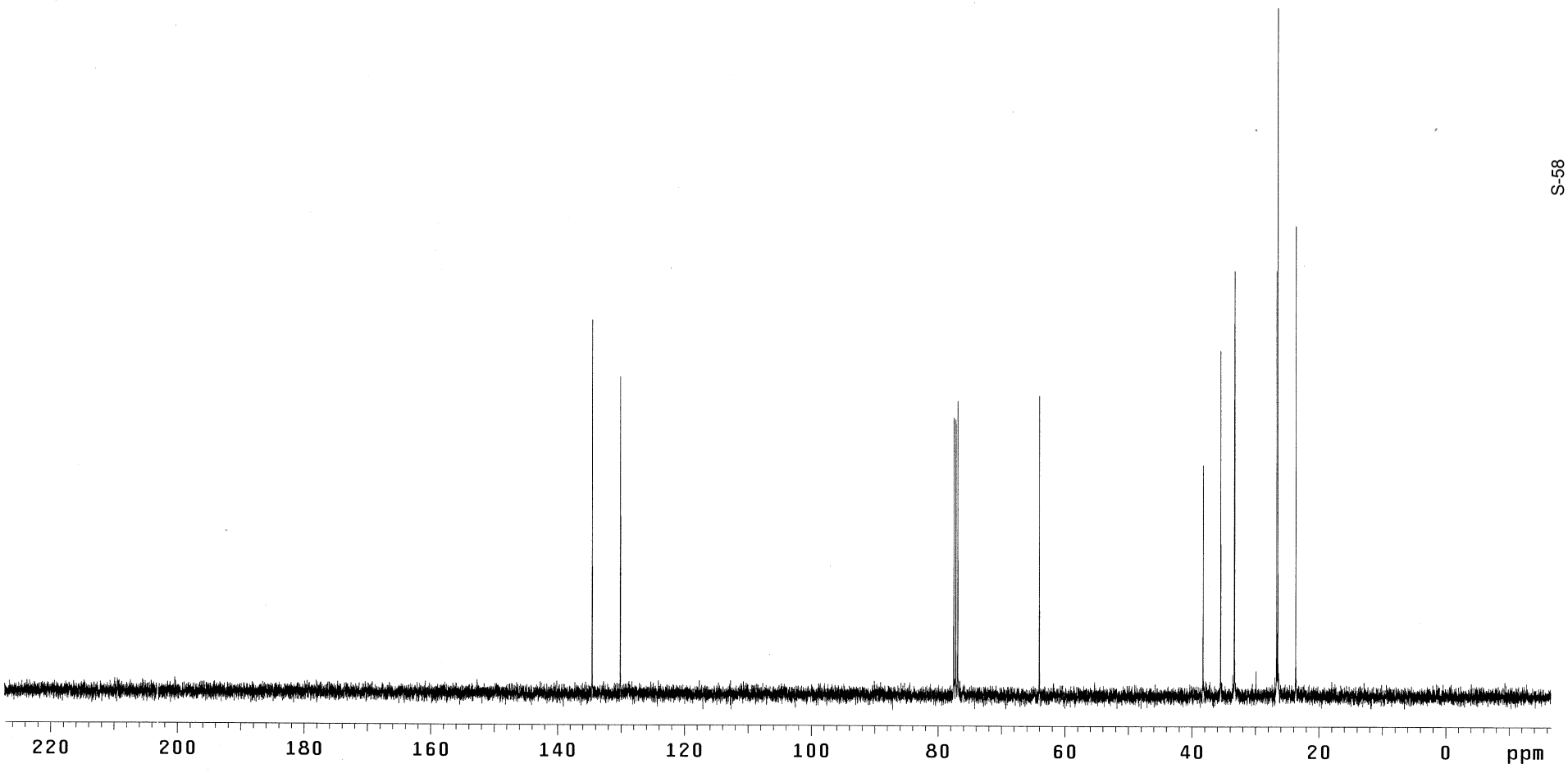


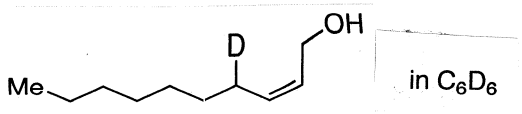
in C_6D_6



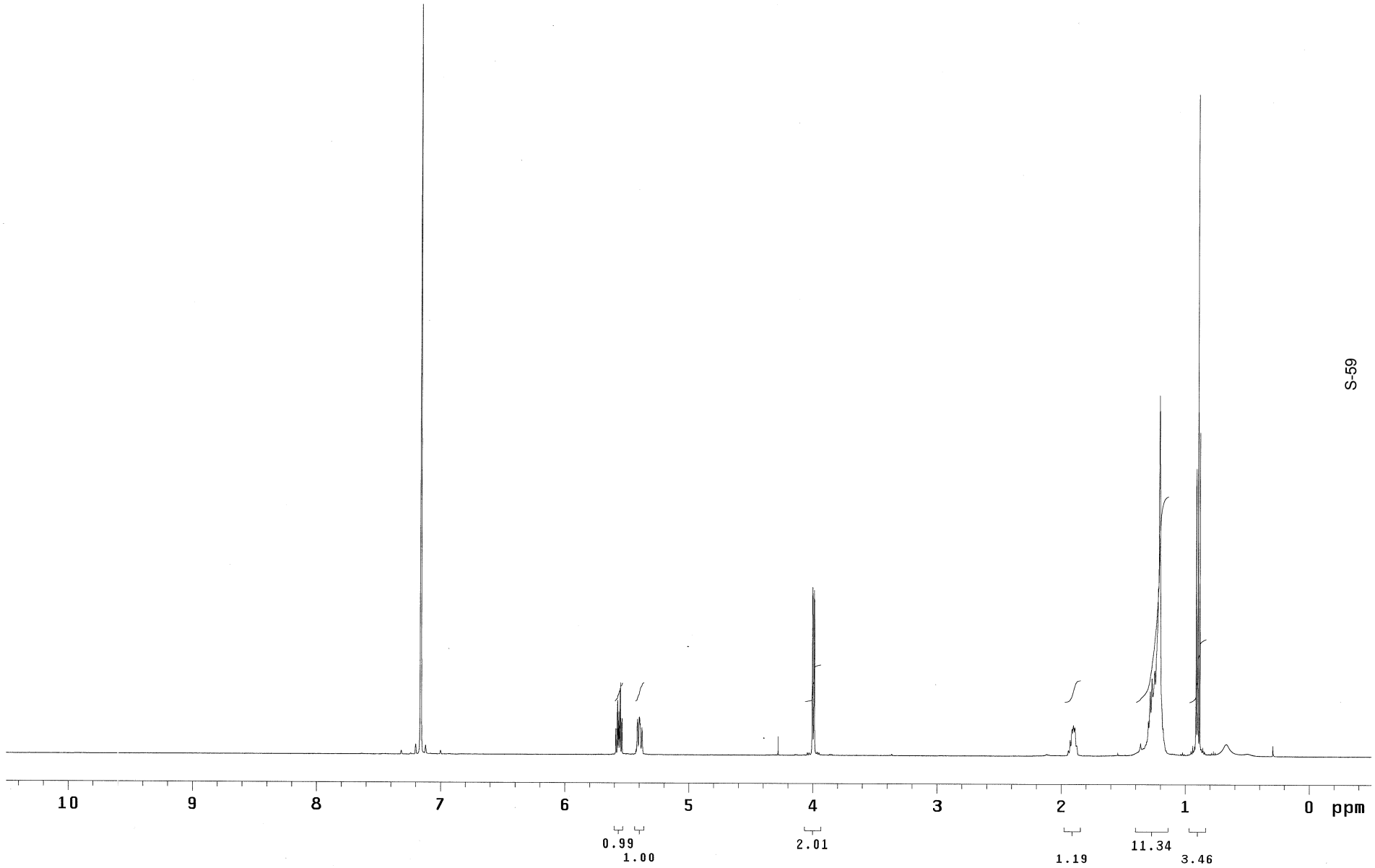
*

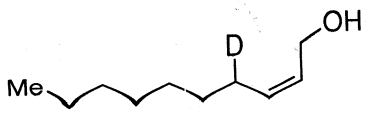

HO
Me

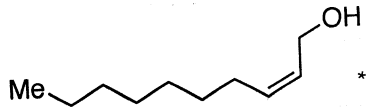

220
200
180
160
140
120
100
80
60
40
20
0
ppm



in C_6D_6

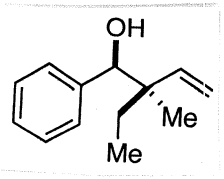


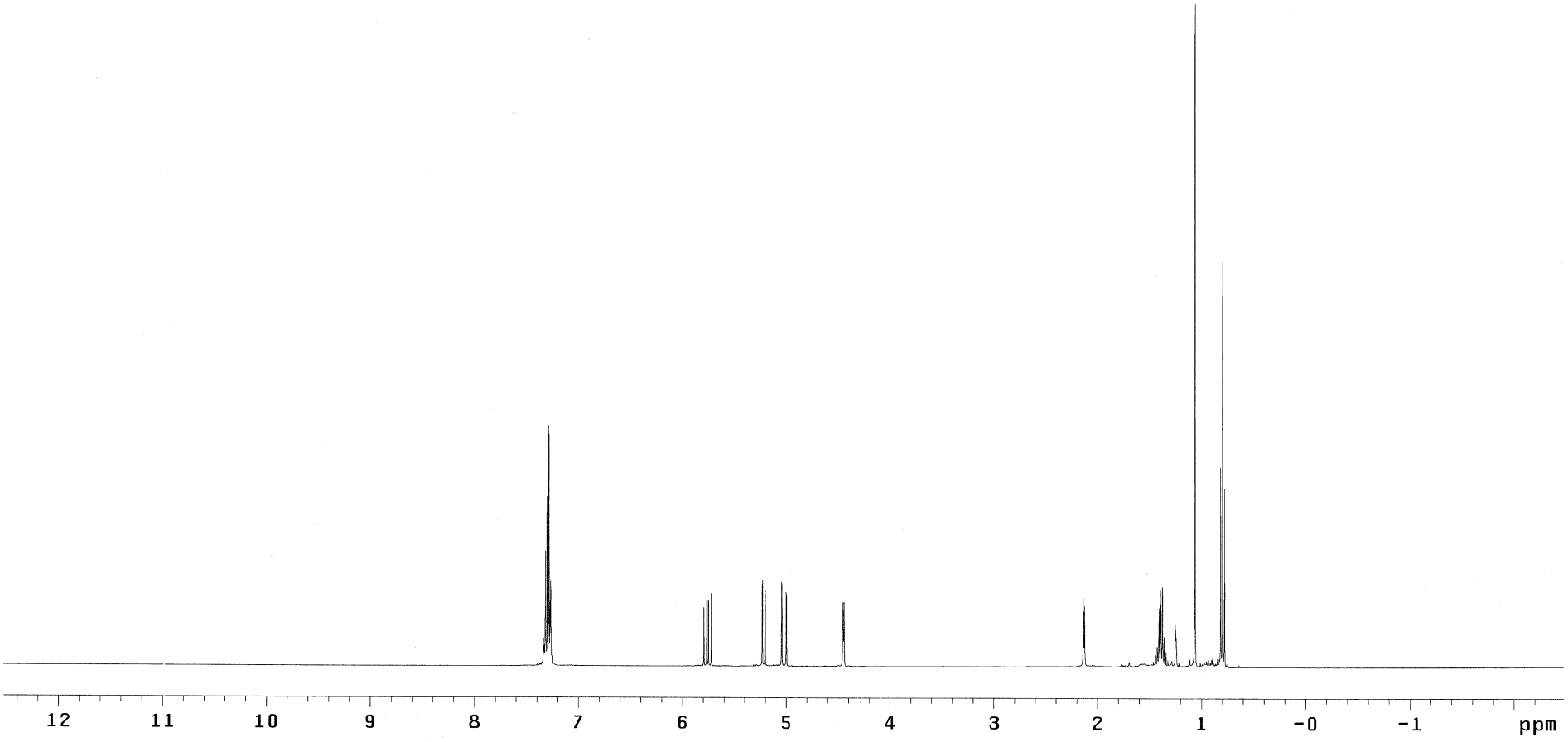


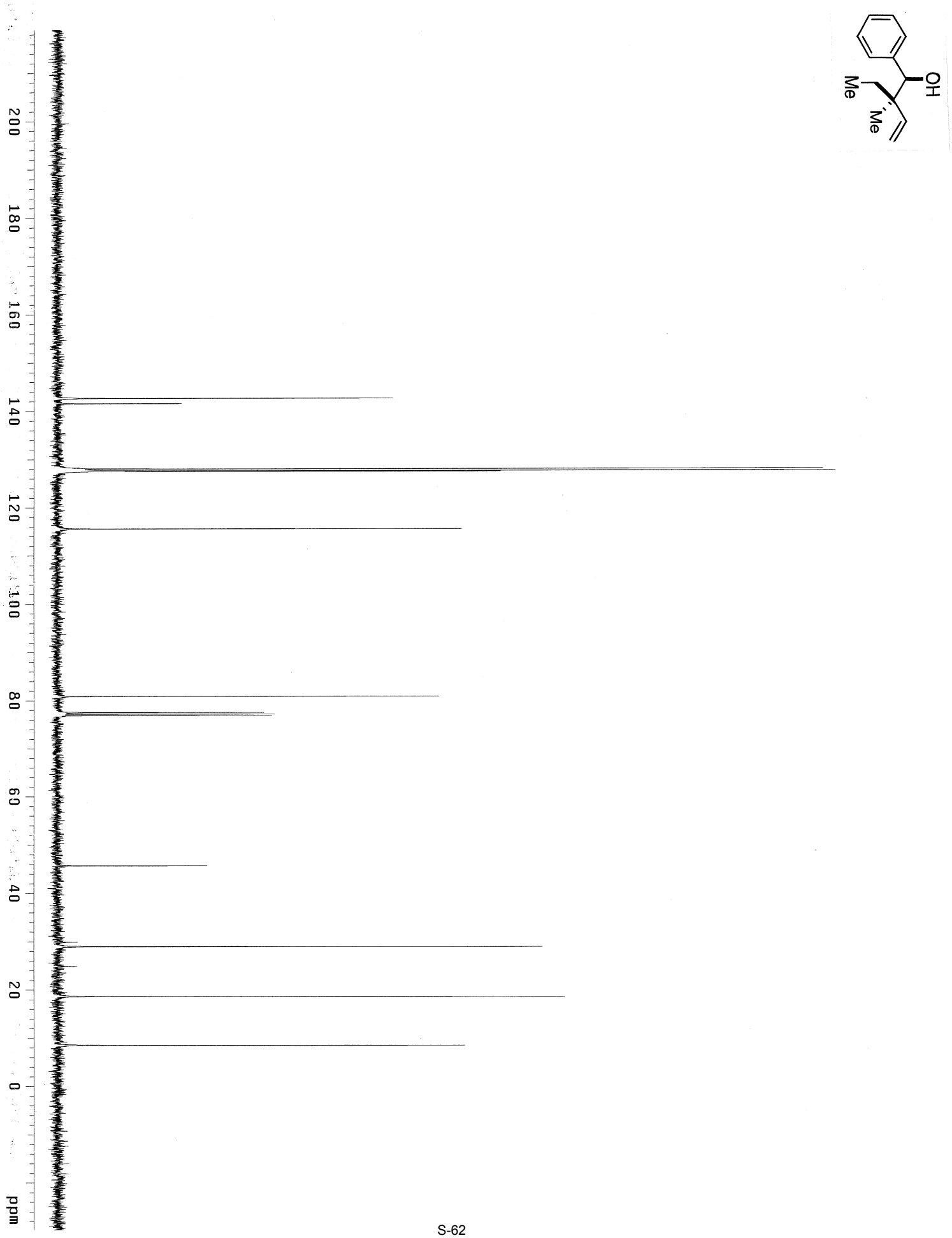


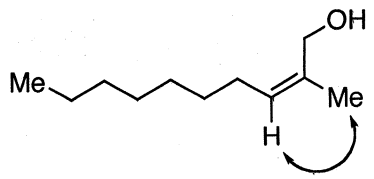
S-60

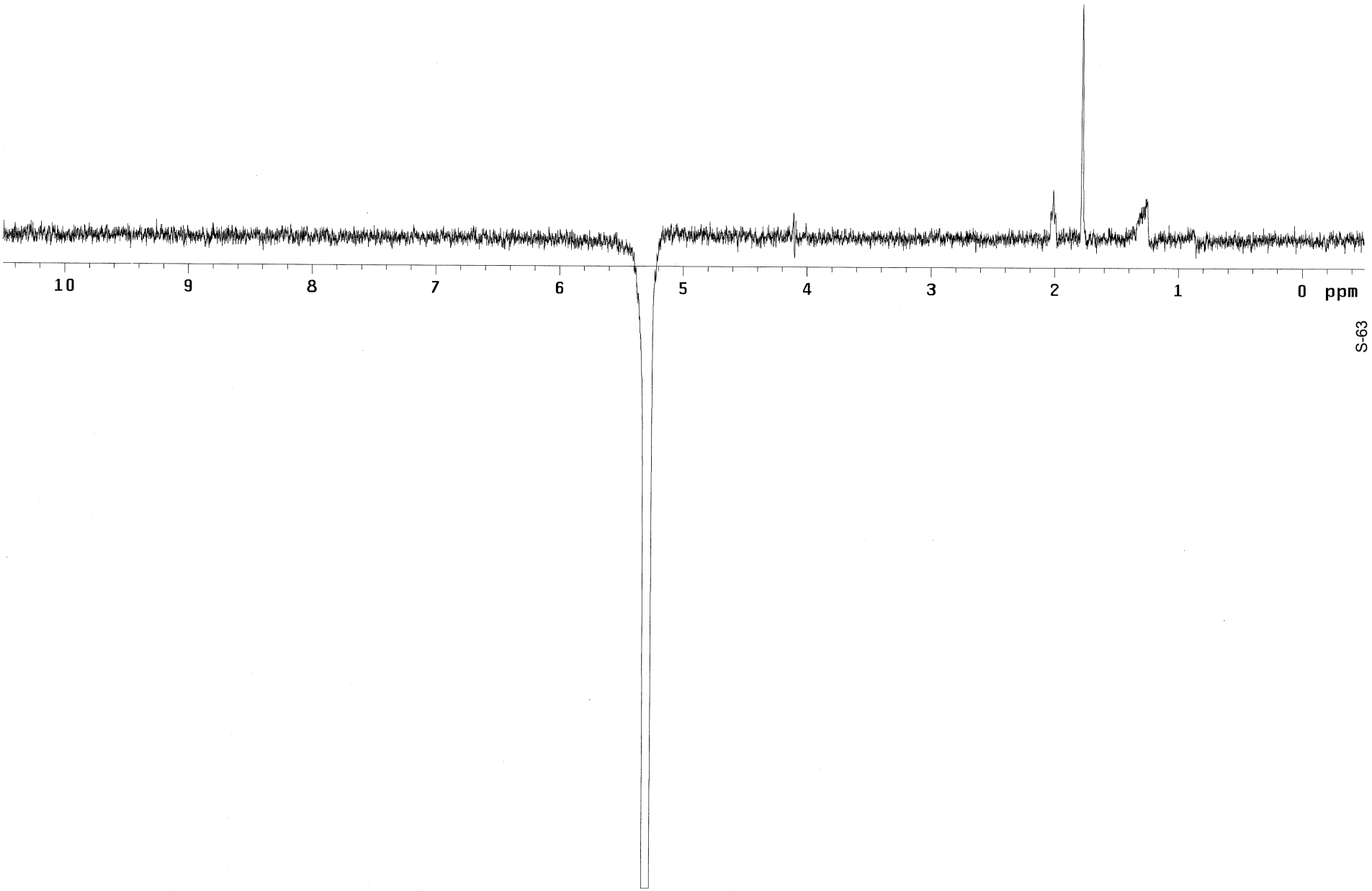
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

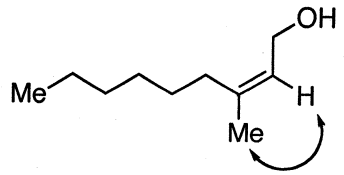

OH
Me
Me

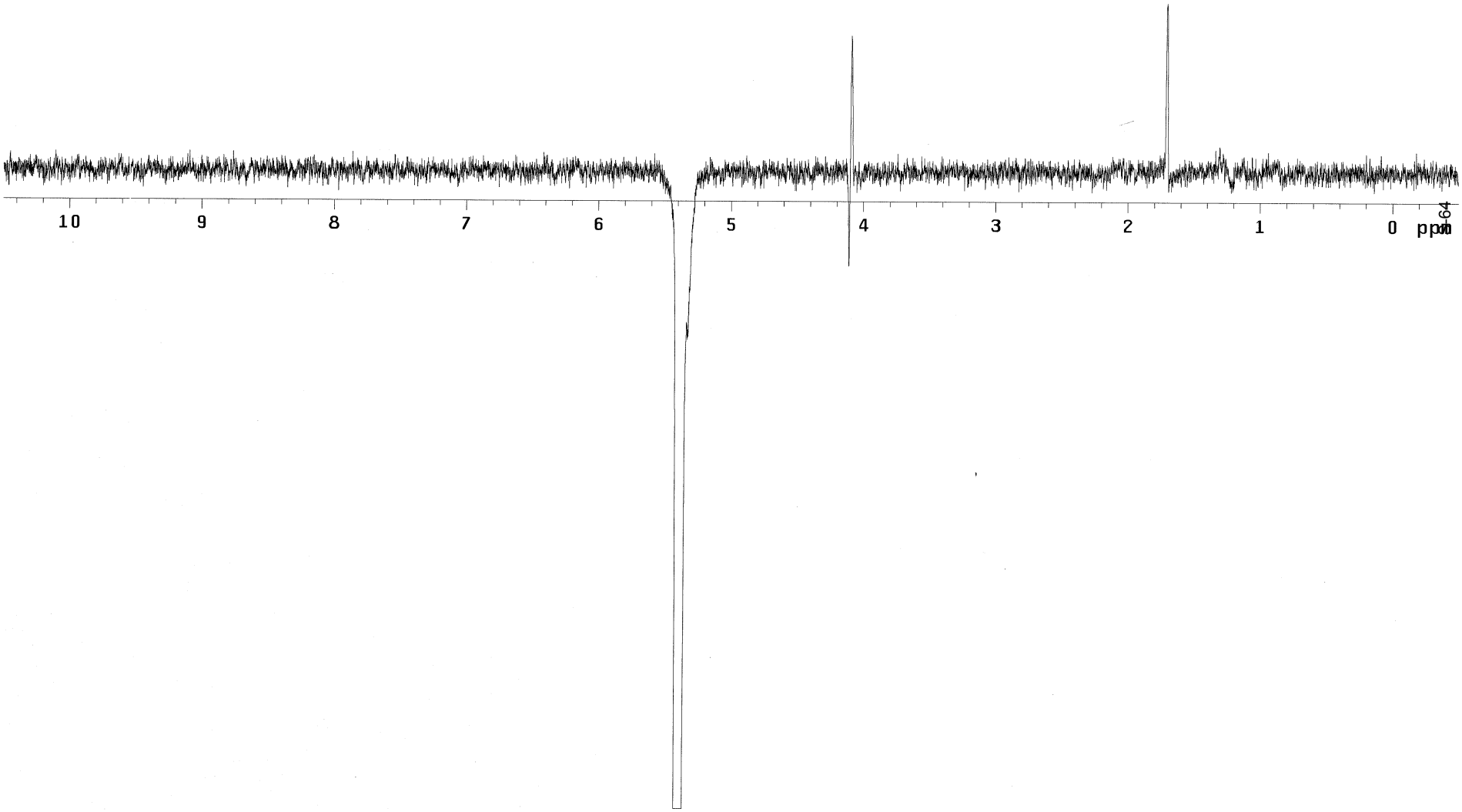

12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm

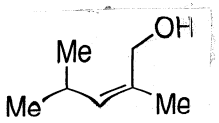

OH
Me
Me
200
180
160
140
120
100
80
60
40
20
0
ppm

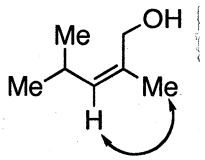

OH
Me
Me
H

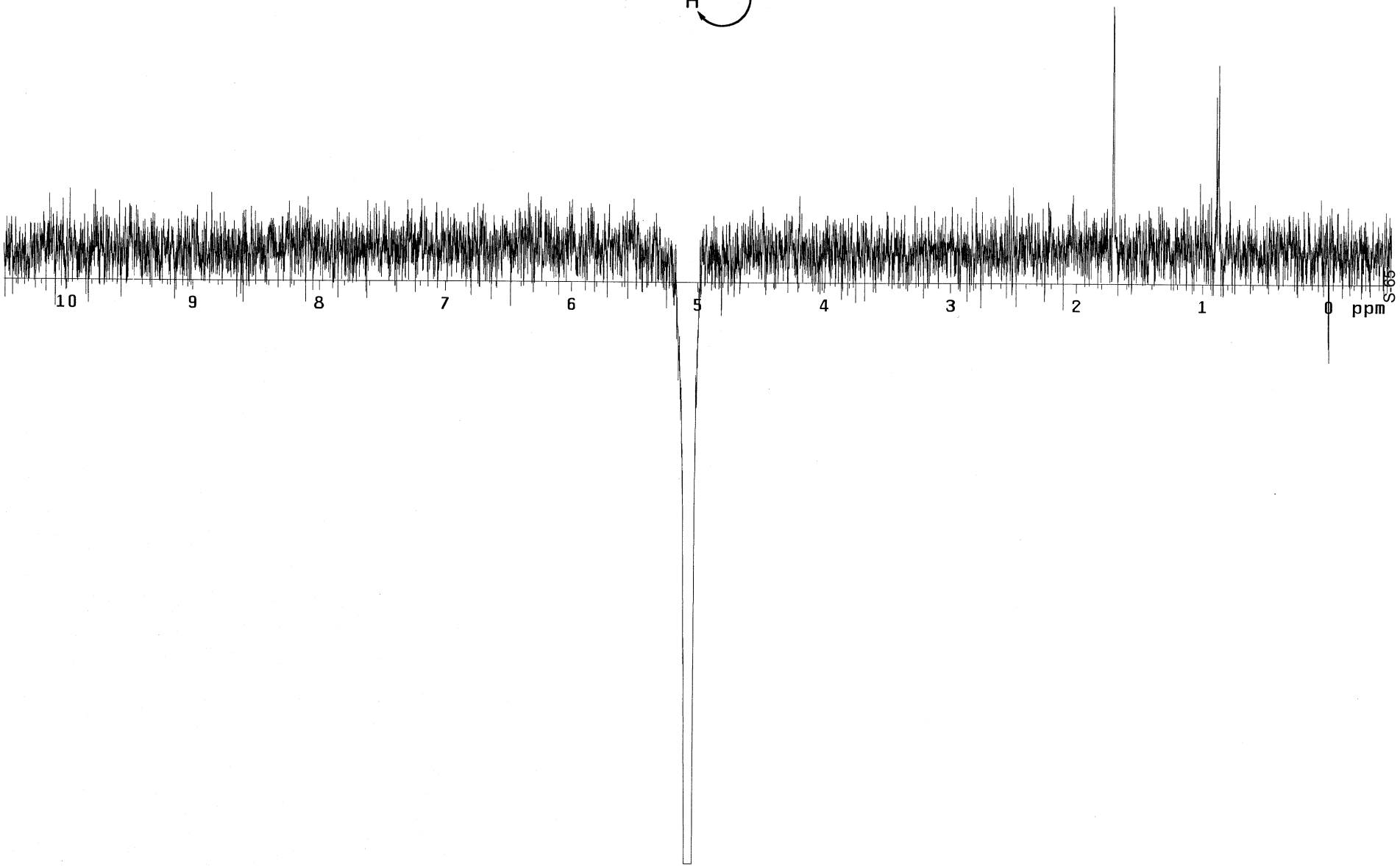

10
9
8
7
6
5
4
3
2
1
0 ppm


OH
Me
H
Me


10
9
8
7
6
5
4
3
2
1
0
ppm
64


OH
Me
Me
Me


OH
Me
Me
Me
H


10
9
8
7
6
5
4
3
2
1
0
ppm
S-65

Sample: RJE-III-016-Ghsqcad
Sample ID: s_20091216_01
File: home/All/jpm/RJE/RJE-II-016-Ghsqcad.fid

Pulse Sequence: gHSQCAD

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: morken
File: RJE-II-016-Ghsqcad
VNMRS-500 "nmr16"

Relax. delay 1.000 sec
Mixing 0.500 sec
Acq. time 0.230 sec
Width 4629.6 Hz
2D Width 21367.5 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 499.8853989 MHz
DECOUPLE C13, 125.7057015 MHz
Power 37 dB
on during acquisition
off during delay
W40_oneNMR_MR0905W008 modulated
DATA PROCESSING
Gauss apodization 0.106 sec
F1 DATA PROCESSING
Gauss apodization 0.006 sec
FT size 4096 x 2048
Total time 22 min, 5 sec