

**Scope and Mechanism of the Pt-Catalyzed Enantioselective  
Diboration of Monosubstituted Alkenes.**

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**Supporting Information**

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## General Information

$^1\text{H}$  NMR spectra were measured using a Varian Unity Inova 500 MHz or a Varian Gemini 400 MHz spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ( $\text{CDCl}_3$ : 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.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on Varian Unity Inova 500 MHz (125 MHz) or a Varian Gemini 400 MHz (100 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ( $\text{CDCl}_3$ : 77.00 ppm).  $^{31}\text{P}\{^1\text{H}\}$  NMR (162 MHz) were recorded on a Varian Unity Inova 500 MHz spectrometer. Chemical shifts are reported for  $^{31}\text{P}$  NMR spectra using phosphoric acid as an external standard ( $\text{H}_3\text{PO}_4$ : 0.0 ppm). Infrared (IR) spectra were recorded on a Bruker  $\alpha$ -P Spectrometer. Frequencies are reported in wavenumbers ( $\text{cm}^{-1}$ ) as follows: strong (s), broad (br), medium (m), and weak (w). High resolution mass spectrometry (HRMS) was performed at Boston College, Chestnut Hill, MA. Elemental analysis on all platinum pre-catalysts was performed by ICP Optical Emission Spectroscopy.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel ( $\text{SiO}_2$ , 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography was performed on 25  $\mu\text{m}$  silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA), and potassium permanganate ( $\text{KMnO}_4$ ). 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 Supelco  $\beta$ -Dex 120 column with helium as the carrier gas. Analytical chiral gas-liquid chromatography (GLC) was also performed on an Agilent Technologies 6850 Series chromatograph with a flame ionization detector, and a Supelco  $\beta$ -Dex 120 column with helium as the carrier gas. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Thar Supercritical Chromatograph equipped with an auto sampler and a Waters photoiodide array detector with isopropanol as the modifier. Analytical chiral high-performance liquid chromatography (HPLC) was performed on an Agilent Technologies 1120 compact LC or an Agilent Technologies 1220 Infinity LC chromatograph equipped with a UV detector and a Daicel Chiracel-OD-H column.

Reaction calorimetry was carried out in a SuperCRC reaction calorimeter in a glass, septum-cap vial equipped with a magnetic stir bar. The calorimeter measures the heat released or consumed in a sample vessel compared with that from a reference compartment over the course of the reaction.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran, dichloromethane, 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. Ethyl acetate was distilled from calcium hydride and sparged with  $\text{N}_2$  before use. Triethylamine was distilled from calcium hydride. Potassium tetrachloroplatinate(II) was purchased from Acros Organics. Dibenzylideneacetone was purchased from Oakwood Chemicals. Sodium acetate was purchased from Fisher Scientific. Bis(pinacolato)diboron was obtained from Allychem Co., Ltd. and recrystallized from pentane prior to use. Dichlorophenylphosphine was purchased from Strem Chemicals, Inc. and used without further purification. Methanol and sulfuric acid were

purchased from Fisher Scientific, Inc. and used without further purification. Diethylamine was purchased from Alfa Aesar and used without further purification. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide was purchased from Advanced ChemTech and used without further purification. 5-Hexenoic acid, 2-methyl-1,5-hexadiene, and 1,2:5,6-Di-*O*-isopropylidene-D-mannitol were purchased from TCI America and used without further purification. *Tert*-butyldiphenylsilyl chloride, tetrabutylammonium chloride, imidazole, bromochloromethane, methyl lithium (1.0 M in tetrahydrofuran), methyltriphenylphosphonium bromide, potassium *tert*-butoxide, *p*-anisaldehyde, *m*-anisaldehyde, *p*-tolualdehyde, *o*-tolualdehyde, *m*-tolualdehyde, cyclopropanecarboxaldehyde, sodium (meta)periodate and N,N-diisopropylethylamine were purchased from Aldrich and used without further purification. Norbornene, cyclohexene, 2-octene, indene, hept-6-en-1-ol, 1-tetradecene, 1-octene, 4,4-dimethyl-1-pentene, 4-phenyl-1-butene, vinyl cyclohexane, 3,3-dimethyl-1-butene, allylbenzene, styrene, 4-(trifluoromethyl)styrene, 3-(trifluoromethyl)styrene were purchased from Aldrich and were sparged with N<sub>2</sub> and distilled prior to use.

## Experimental Procedures

### I. Preparation of Pt(dba)<sub>3</sub>.

Tris(dibenzylideneacetone)platinum(0) was prepared using the literature procedure with slight modification.<sup>1</sup> To a three-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), and the mixture was gently warmed until all solids dissolved. The three-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 and the remaining solids were washed with copious amounts of water and methanol until no yellow dibenzylideneacetone crystals were visible. The resulting solid was placed under high vacuum for 24 h to remove residual methanol and water, to give the product as a dark brown solid (7.09 g, 47% yield). Anal Calc'd for C<sub>51</sub>H<sub>42</sub>O<sub>3</sub>Pt: C, 68.22; H, 4.71. Found: C, 67.09; H, 4.49 (average of two experiments). Platinum analysis was performed by ICP Optical Emission Spectroscopy; calculated for Pt(dba)<sub>3</sub>: 21.73% Pt; found 21.92% (average of two experiments).

### II. Preparation of Pt<sub>2</sub>(dba)<sub>3</sub>.

Tris(dibenzylideneacetone)diplatinum(0) was prepared using the literature procedure.<sup>1</sup> To a two-neck 25 mL round-bottomed flask equipped with a magnetic stir bar and reflux condenser was added dibenzylideneacetone (1.98 g, 8.43 mmol), tetrabutylammonium chloride (1.00 g, 3.61 mmol), and sodium acetate (1.78 g, 21.8 mmol). Methanol (102 mL) was added and the solution was warmed to 70 °C in an oil bath until the solids dissolved (5 minutes). To a separate 50 mL pear-shaped flask was added potassium tetrachloroplatinate (500 mg, 1.20 mmol) and

<sup>1</sup> Lewis, L.N.; Krafft, T.A.; Huffman, J.C. *Inorg. Chem.* **1992**, *31*, 3555.

water (6.3 mL), and the mixture gently warmed until all solids dissolved. The contents of the pear-shaped flask were transferred to the three-neck flask and the reaction was allowed to stir at 70 °C for 3 hours. 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 then filtered on a Büchner funnel and the remaining solids were washed with copious amounts of water and methanol until all yellow dibenzylideneacetone crystals were removed. The resulting solid was dissolved in hot tetrahydrofuran (100 mL) and filtered. The filtrate was concentrated to a volume of 10 mL using rotary evaporation followed by the slow addition of methanol (12 mL). After cooling the solution to - 25 °C in the freezer for 1 h the crystallized product was isolated by filtration, washed with methanol (40 mL) and dried under vacuum to provide the product as a black crystalline solid (348.9 mg, 53%). Anal Calc'd for C<sub>51</sub>H<sub>42</sub>O<sub>3</sub>Pt<sub>2</sub>: C, 56.04; H, 3.87. Found: C, 56.40; H, 3.73 (average of two experiments). Platinum analysis was performed by ICP Optical Emission Spectroscopy; calculated for Pt<sub>2</sub>(dba)<sub>3</sub>: 35.70% Pt; found 33.72% (average of two experiments).

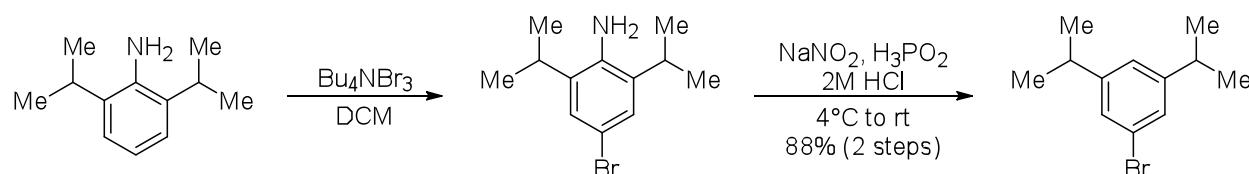
### III. Preparation of Pt(nbe)<sub>3</sub>.

Tris(norbornene)platinum(0) was prepared using the literature procedure.<sup>2</sup> A flame-dried 100 mL three-neck round-bottomed flask equipped with magnetic stir bar and addition funnel was charged with finely powdered PtCl<sub>2</sub>(COD) (3.50 g, 9.35 mmol) and freshly sublimed norbornene (7.00 g, 74.3 mmol) under N<sub>2</sub>. Diethyl ether (10.7 mL, 0.88 M) was added, and the reaction was cooled to -30 °C (dry ice/ethanol/ethylene glycol). The addition funnel was charged with a freshly prepared solution of cyclooctatetraene dilithium (46.3 mL, 0.20 M), which was then added dropwise to the reaction while maintaining an internal temperature of -30 °C. The light brown reaction mixture was allowed to warm to room temperature and the solvent was removed in *vacuo*. The remaining residue was dried for an additional hour before being brought into the glove box where the solid was washed with dry and degassed hexane (3 x 100 mL). The combined hexanes extracts were filtered through a plug of alumina and the filtrate was evaporated in *vacuo* to give the product as an off-white solid which was used without further purification (1.67 g, 52%). Anal Calc'd for C<sub>21</sub>H<sub>30</sub>Pt: C, 52.82; H, 6.33. Found: C, 52.84; H, 6.29.

### IV. Ligand Synthesis.

#### Preparation of 1-bromo-3,5-di-*iso*-propylbenzene

1-bromo-3,5-di-*iso*-propylbenzene was prepared according to the literature procedure from 2,6-di-*iso*-propylaniline as shown below.<sup>3</sup>

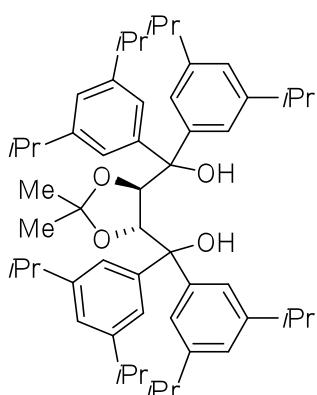


<sup>2</sup> Reagents for Transition Metal Complex and Organometallic Syntheses. *Inorganic Syntheses*; Angelici, R.J., Ed.; Wiley: New York, 1990; Vol. 28, p 127.

<sup>3</sup> Diemer, V.; Chaumeil, H.; Defoain, A.; Fort, A.; Boeglin, A.; Carré, C. *Eur. J. Org. Chem.* **2006**, 12, 2727.

*Preparation of (R,R)-3,5-di-iso-propylphenylTADDOL.*

(R,R)-3,5-Di-iso-propylphenylTADDOL was prepared according to the literature procedure with slight modification.<sup>4</sup> To a flame-dried 500 mL two-neck round-bottomed flask equipped with magnetic stir bar and reflux condenser was added crushed magnesium turnings (4.10 mg, 169 mmol) under N<sub>2</sub>. The apparatus was flame-dried again, followed by addition of a single crystal of I<sub>2</sub> along with tetrahydrofuran (175 mL). To a separate flame dried 250 mL round-bottomed flask was added 1-bromo-3,5-di-iso-propylbenzene (33.7 g, 140 mmol) (which was prepared according to the literature procedure from 2,6-di-iso-propylaniline as shown above) and tetrahydrofuran (175 mL). The resulting solution was slowly added to the magnesium mixture at room temperature *via* cannula transfer. The reaction was heated to reflux at 80 °C in an oil bath for 3 h, at which time the reaction was cooled to 0 °C, and a solution of (4*R*,5*R*)-dimethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (6.13 g, 28.1 mmol) in tetrahydrofuran (10.0 mL) was added slowly *via* syringe. The reaction was allowed to reflux at 80 °C for 12 h, after which it was cooled to 0 °C and quenched with saturated aqueous NH<sub>4</sub>Cl (100 mL). The organic and aqueous layers were separated and the aqueous layer was further extracted with ethyl acetate (3 x 70 mL). The combined organics were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude material was purified by recrystallization from methanol (50 mL). The crystallized solid was isolated by filtration, washed with cold methanol, and dried under vacuum to afford the product as a white solid (20.1 g, 89.2%).

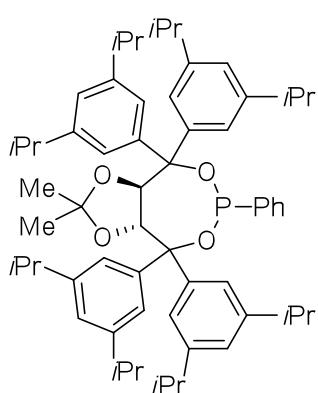


**(R,R)-3,5-di-iso-propylphenylTADDOL.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.84 (6H, s), 1.06 (24H, dd, *J* = 7.5 Hz, 7.0 Hz), 1.16 (24H, dd, *J* = 7.0 Hz, 1.5 Hz), 2.72 (4H, dq, *J* = 7.0 Hz, 7.0 Hz), 2.81 (4H, dq, *J* = 7.0 Hz, 7.0 Hz), 3.63 (2H, s), 4.61 (2H, s), 6.86 (2H, s), 6.92 (2H, s), 6.95 (4H, d, *J* = 1.5 Hz), 7.16 (4H, d, *J* = 1.7 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  23.9, 24.0, 24.0, 24.4, 27.0, 30.3, 34.2, 34.3, 78.5, 81.2, 108.9, 123.2, 123.4, 123.5, 124.5, 142.5, 145.8, 147.3, 148.0; IR (neat): 3235.4 (w), 2967.2 (s), 2868.4 (m), 1599.3 (m), 1463.7 (m), 1073.2 (m), 872.4 (s), 739.8 (s), 709.6 (m) cm<sup>-1</sup>; HRMS-(+MALDI) for C<sub>55</sub>H<sub>78</sub>O<sub>4</sub>Na [M+Na]: calculated 825.5792, found: 825.5770. [α]<sub>D</sub><sup>25</sup> = +19.88 (*c* = 0.97, CHCl<sub>3</sub>, *l* = 50 mm)

*Preparation of (R,R)-di-iso-propylphenylTADDOLPPh.*

To a flame dried 150 mL round bottom flask equipped with magnetic stir bar was added (R,R)-3,5-diisopropylphenylTADDOL (3.50g, 4.36 mmol) and tetrahydrofuran (44.0 mL) under N<sub>2</sub>. Triethylamine (2.06 mL, 14.8 mmol) was added *via* syringe and the reaction mixture was cooled to 0 °C in an ice bath. Dichlorophenylphosphine (0.650 mL, 4.79 mmol) was added dropwise *via* syringe at 0 °C. The reaction was warmed to room temperature and was allowed to stir for 2 h. The reaction was diluted with Et<sub>2</sub>O, filtered quickly through celite and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (2% ethyl acetate in hexanes, with 1% Et<sub>3</sub>N to prevent hydrolysis) to afford the product as a white solid (3.65g, 92.0 %).

<sup>4</sup> Seiber, J.D.; Morken, J.P. *J. Am. Chem. Soc.* **2008**, 130, 4978.



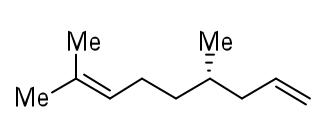
**(R,R)-3,5-di-iso-propylphenylTADDOLPPh.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.11 (3H, s), 1.10-1.25 (48H, m), 1.51 (3H, s), 2.78-2.84 (8H, m), 4.91 (1H, d,  $J$  = 8.5 Hz), 5.58 (1H, dd,  $J$  = 8.5 Hz, 4.0 Hz), 6.83 (1H, s), 6.91 (2H, s), 6.94 (1H, s), 6.98 (2H, d,  $J$  = 2.0 Hz), 7.18 (2H, br s), 7.34 (2H, s), 7.44-7.47 (3H, m), 7.51 (2H, s), 7.86-7.90 (2H, m);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  23.9, 23.9, 24.0, 24.1, 24.2, 28.0, 34.0, 34.1, 34.2, 34.4, 82.8, 82.8, 83.2, 83.4, 83.8, 83.9, 84.3, 84.3, 110.4, 123.1, 123.3, 123.4, 123.5, 123.6, 124.7, 124.8, 125.1, 128.1, 128.2, 129.9, 130.1, 130.4, 141.4, 141.7, 142.1, 142.2, 146.2, 146.3, 146.8, 147.1, 147.3, 147.8, 147.9;  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.4; IR (neat): 2957.6 (s), 2868.3 (w), 1598.6 (w), 1464.9 (m), 1162.7 (w), 1027.6 (m), 877.8 (s), 799.7 (m), 735.3 (s), 693.3 (m)  $\text{cm}^{-1}$ .  $[\alpha]_D^{25} = -50.40$  ( $c$  = 0.34,  $\text{CHCl}_3$ ,  $l$  = 50 mm).

#### V. Preparation of Terminal Alkenes.

A. The following 1-alkenes were prepared by Wittig olefination of the commercially available aldehydes with methyltriphenylphosphonium bromide and potassium tert-butoxide in tetrahydrofuran: *p*-methoxystyrene,<sup>5</sup> *m*-methoxystyrene,<sup>6</sup> *p*-methylstyrene,<sup>7</sup> *o*-methylstyrene,<sup>7</sup> *m*-methylstyrene.<sup>7</sup> Spectral data are in accordance with the literature references.

The following 1-alkenes were prepared by the literature procedure: allyloxy(*tert*-butyl)diphenylsilane,<sup>8</sup> (but-3-enyloxy)(*tert*-butyl)diphenylsilane.<sup>8</sup> Spectral data are in accordance with the literature references.

B. Preparation of (*S*)-4,8-dimethylnona-1,7-diene. The title compound was synthesized by wittig olefination of commercially available (*S*)-3,7-dimethyloct-6-enal.



**(S)-4,8-dimethylnona-1,7-diene (Table 4.11, entry 9).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86-0.88 (3H, d,  $J$  = 7.0 Hz); 1.09-1.61 (1H, m), 1.29-1.36 (1H, m), 1.45-1.52 (1H, m), 1.58 (3H, s), 1.66 (3H, s), 1.83-1.90 (1H, m), 1.92-2.01 (2H, m), 2.03-2.08 (1H, m), 4.94-4.99 (2H, m), 5.06-5.09 (1H, m), 5.76 (1H, dddd,  $J$  = 17.5 Hz, 10.5 Hz, 7.5 Hz, 7.5 Hz);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  17.7, 19.3, 25.6, 25.7, 32.4, 36.6, 41.3, 115.4, 124.8, 131.1, 137.7; IR (neat): 2955.0 (m), 2923.3 (s), 2853.8 (m), 1724.5 (w), 1458.7 (w), 1376.7 (w), 1272.0 (w)  $\text{cm}^{-1}$ ; HRMS-(ESI $^+$ ) for  $\text{C}_{11}\text{H}_{21}$  [M+H] $^+$ : calculated: 153.1643, found: 153.1639.

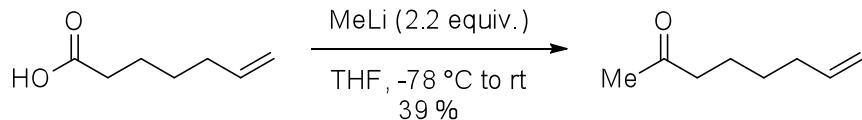
<sup>5</sup> Alacid, E.; Nájera, C.; *J. Org. Chem.* **2009**, 74, 2321.

<sup>6</sup> Deguest, G.; Bischoff, L.; Fruit, C.; Marsais, F.; *Org. Lett.* **2007**, 9, 1165.

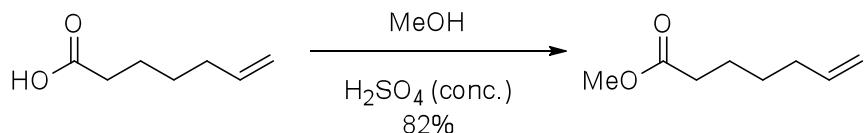
<sup>7</sup> Smith, C. R.; RajanBabu, T. V.; *Tetrahedron*, **2010**, 66, 1102.

<sup>8</sup> Kliman, L. T.; Mlynarski, S. N.; Morken, J. P.; *J. Am. Chem. Soc.* **2009**, 131, 13210.

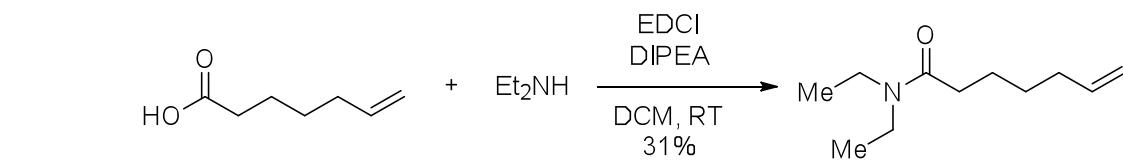
*C. Preparation of oct-7-en-2-one.* The title compound was synthesized as shown below.<sup>9</sup> The spectral data was in accordance with the literature reference.<sup>9</sup>



*D. Preparation of methyl hept-6-enoate.* The title compound was prepared by esterification of hept-1-enoic acid with MeOH and catalytic concentrated H<sub>2</sub>SO<sub>4</sub>, as shown below.<sup>9</sup> The spectral data was in accordance with the literature reference.<sup>9</sup>



*E. Preparation of N,N-diethylhept-6-enamide.* The title compound was synthesized as shown below to afford a clear, pale yellow liquid.<sup>10</sup>

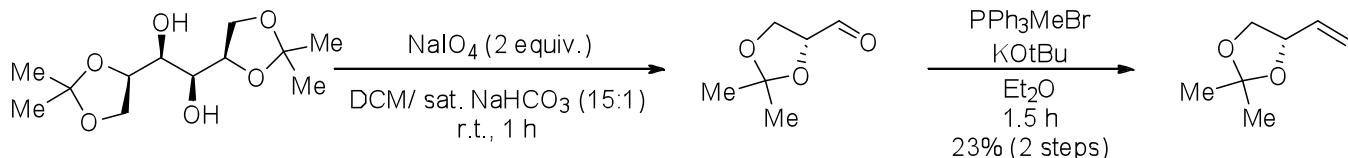


**N,N-diethylhept-6-enamide.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.07 (3H, t, *J* = 7.0 Hz), 1.14 (3H, t, *J* = 7.0 Hz), 1.41 (2H, tt, *J* = 8.0, 8.0 Hz), 1.64 (2H, tt, *J* = 7.5, 7.5 Hz), 2.05 (2H, dt, *J* = 7.0, 7.0 Hz), 3.27 (2H, q, *J* = 7.0 Hz), 3.34 (2H, q, *J* = 7.0 Hz), 4.91 (1H, dd, *J* = 10.0, 1.0 Hz), 4.98 (1H, dd, *J* = 17.5, 1.5 Hz), 5.78 (1H, dddd, *J* = 17.0, 10.0, 6.5, 6.5 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  13.1, 14.4, 24.9, 28.7, 32.9, 33.6, 40.0, 41.9, 114.4, 138.6, 172.0; IR (neat): 2972.5 (w), 2931.2 (w), 1636.8 (s), 1458.6 (m), 1426.3 (m), 1378.9 (w), 1362.5 (w), 1260.3 (w), 1222.3 (w), 1140.7 (w), 1096.7 (w), 1071.6 (w), 907.4 (m), 792.6 (w) cm<sup>-1</sup>; HRMS-(ESI+) for C<sub>11</sub>H<sub>22</sub>NO [M+H]: calculated: 184.1701, found: 184.1710.

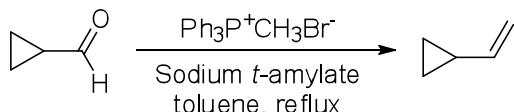
<sup>9</sup> Rosillo, M.; Arnaiz, E.; Abdi, D.; Blanco-Urgoiti, J.; Dominguez, G.; Perez-Castells, J.; *Eur. J. Org. Chem.* **2008**, 23, 3917.

<sup>10</sup> Buswell, M.; Fleming, I.; Ghosh, U.; Mack, S.; Russell, M.; Clark, B. P.; *Org. Biomol. Chem.* **2004**, 2, 3006.

*F. Preparation of (S)-2,2-dimethyl-4-vinyl-1,3-dioxolane.* The title compound was synthesized as shown below.<sup>11</sup> The spectral data was in accordance with the literature reference.<sup>11</sup>



*G. Preparation of vinylcyclopropane.* The title compound was synthesized from cyclopropanecarboxaldehyde by the Conia-Dauben modification of the Wittig reaction, as shown below.<sup>12</sup> The spectral data was in accordance with the literature.<sup>13</sup>



#### VI. Representative Procedure for Alkene Diboration/Oxidation.

To an oven-dried vial equipped with a magnetic stir bar in air was added Pt(dba)<sub>3</sub> (6.9 mg, 7.6  $\mu$ mol), (*R,R*)-3,5-diisopropylphenyl-TADDOLPPh (8.3 mg, 9.2  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (203.7 mg, 802.0  $\mu$ mol). The vial was sealed with a septum cap and purged with N<sub>2</sub>. Tetrahydrofuran (0.76 mL, 1.0 M) was added via syringe, and the vial was heated to 80 °C in an oil bath for 30 minutes. The vial was then cooled to room temperature and charged with freshly distilled and deoxygenated 1-tetradecene (150.0 mg, 763.8  $\mu$ mol). After purging once more with N<sub>2</sub>, the vial was stirred at 60 °C for 3 hours. The reaction mixture was cooled to 0 °C (ice/water) and charged with 3 M sodium hydroxide (2 mL), followed by dropwise addition of 30% hydrogen peroxide (1 mL). The reaction was gradually warmed to room temperature and stirred 4 hours at which time the vial was cooled to 0 °C (ice/water) and saturated aqueous sodium thiosulfate (4 mL) was added dropwise over 5 minutes. The reaction mixture was diluted with ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was further extracted with ethyl acetate (3 x 15 mL), and the combined organics were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes) to afford the product as a white solid (148.0 mg, 84% yield).

<sup>11</sup> Racha, S.; Mallela, S. S. P.; Elie, A. *Syn. Commun.* **1989**, *19*, 3077.

<sup>12</sup> Tsunoda, T.; Hudlicky, T. *Synlett.* **1990**, *6*, 322.

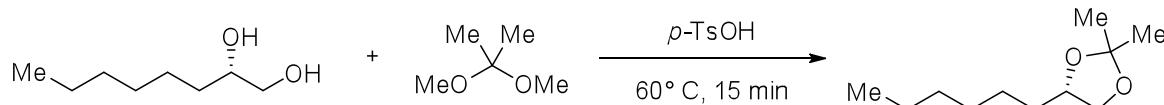
<sup>13</sup> Schrumpf, G. *Tetrahedron Lett.* **1970**, 2571.

## VII. Full Characterization and Proof of Stereochemistry

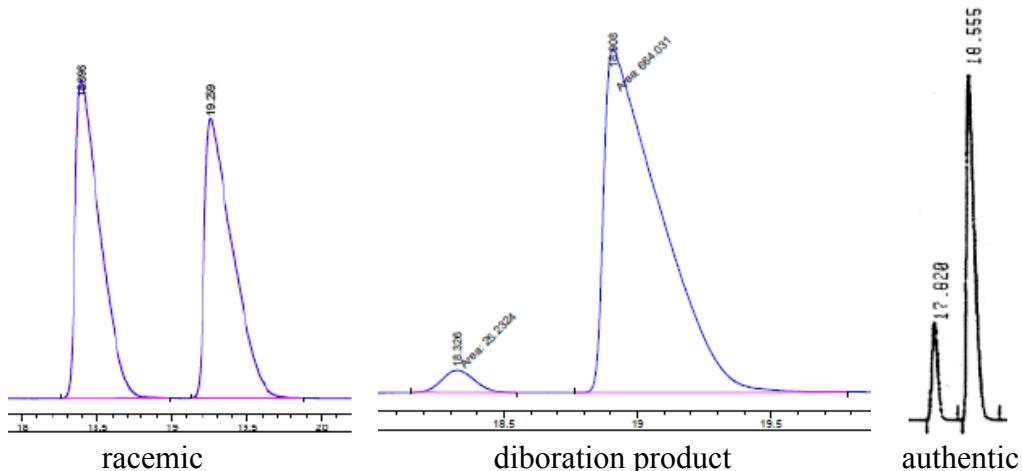
**(S)-octane-1,2-diol (3).** The diboration was performed according to the general procedure with 1-octene (84.6 mg, 763  $\mu$ mol), Pt(dba)<sub>3</sub> (6.9 mg, 7.6  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (8.3 mg, 9.2  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (203.7 mg, 802.0  $\mu$ mol) in tetrahydrofuran (0.76 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford the product as a white solid (91.5 mg, 82% yield). Spectral data and optical rotation are in accordance with the literature.<sup>14,15</sup> HRMS-(ESI<sup>+</sup>) for C<sub>8</sub>H<sub>19</sub>O<sub>2</sub> [M+H]<sup>+</sup>: calculated: 147.1385, found: 147.1380.

### Proof of Stereochemistry:

The 1,2-diol was treated with 2,2-dimethoxypropane and catalytic toluenesulfonic acid (below). The resulting ketal was compared to the racemic ketal of octane-1,2-diol prepared from dihydroxylation of 1-octene with osmium tetroxide and 4-methylmorpholine N-oxide. The authentic (S)-isomer was prepared from the Sharpless asymmetric dihydroxylation of 1-octene utilizing AD-mix- $\alpha$ .<sup>16</sup>



*Chiral GLC ( $\beta$ -dex, Supelco, 100 °C, 20 psi, s/r = 35:1)- analysis of the acetonide of octane-1,2-diol.*

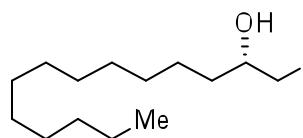


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.326	MM	0.1430	25.23242	2.94025	3.66078
2	18.908	MM	0.2444	664.03119	45.27691	96.33922

<sup>14</sup> Emmanuvel, L.; Shaikh, T. M. A.; Sudalai, A. *Org. Lett.*, **2005**, 7, 5071.

<sup>15</sup> Kliman, L. T.; Mlynarski, S. N.; Morken, J. P. *J. Am. Chem. Soc.* **2009**, 131, 13210.

<sup>16</sup> Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schroeder, G.; Sharpless, K. B. *J. Am. Chem. Soc.*, **1988**, 110, 1968.

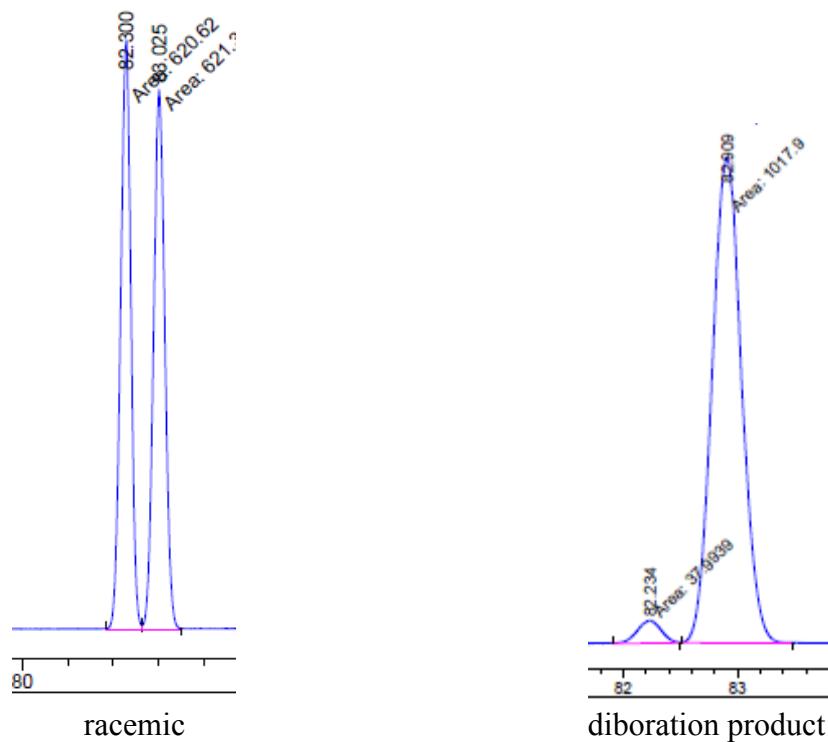


**(S)-tetradecane-1,2-diol (4).** The diboration was performed according to the general procedure with 1-tetradecene (150.0 mg, 763.8  $\mu$ mol), Pt(dba)<sub>3</sub> (6.9 mg, 7.6  $\mu$ mol), (R,R)-3,5-diisopropylphenyl-TADDOLPPh (8.3 mg, 9.2  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (203.7 mg, 802.0  $\mu$ mol) in tetrahydrofuran (0.76 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford the product as a white solid (148.0 mg, 84% yield). Spectral data are in accordance with the literature.<sup>17</sup> HRMS-(ESI<sup>+</sup>) for C<sub>14</sub>H<sub>34</sub>NO<sub>2</sub> [M+NH<sub>4</sub>]: calculated: 248.2590, found: 248.2580.  $[\alpha]_D^{20} = -1.261$  ( $c = 1.015$ , CHCl<sub>3</sub>,  $l = 50$  mm).

#### Analysis of Stereochemistry:

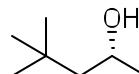
The 1,2-diol was treated with 2,2-dimethoxypropane and catalytic toluenesulfonic acid (below). The resulting ketal was compared to the racemic ketal of octane-1,2-diol prepared from dihydroxylation of 1-tetradecene with osmium tetroxide and 4-methylmorpholine N-oxide. The absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -dex, Supelco, 100 °C, 20 psi)- analysis of the acetonide of tetradecane-1,2-diol.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	82.234	MM	0.2410	37.99389	2.62780	3.59826
2	82.909	MM	0.2981	1017.90234	56.91163	96.40174

<sup>17</sup> Stallforth, P.; Adibekian, A.; Seeburger, P.H. *Org. Lett.* **2008**, *10*, 1573.

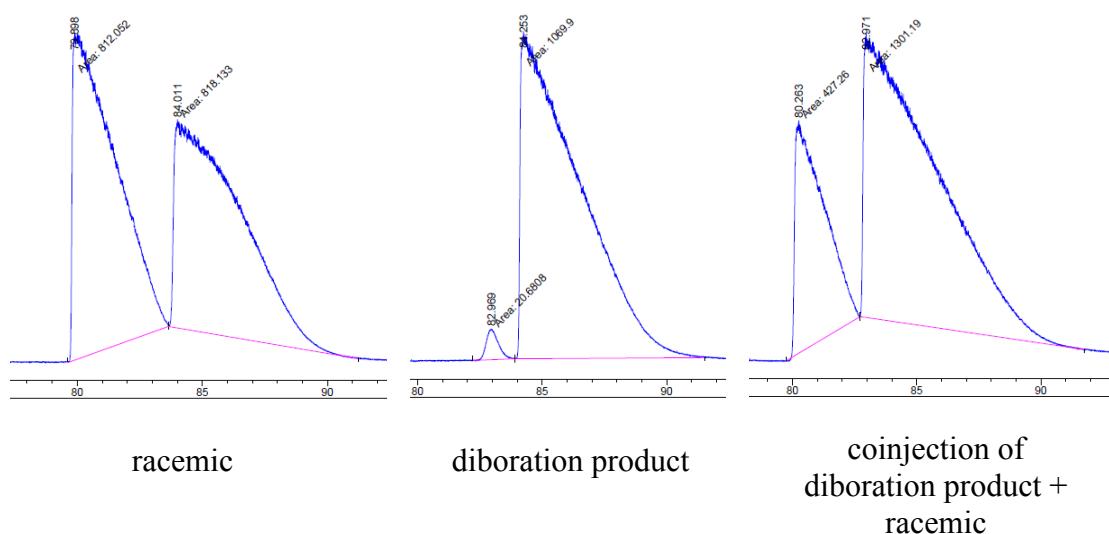


**(S)-4,4-dimethylpentane-1,2-diol (5).** The diboration was performed according to the general procedure with 4,4-dimethyl-1-pentene (63.2 mg, 644  $\mu$ mol), Pt(dba)<sub>3</sub> (5.8 mg, 6.4  $\mu$ mol), (R,R)-3,5-di-*iso*-propylphenylTADDOLPPh (7.0 mg, 7.7  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (171.7 mg, 676.3  $\mu$ mol) in tetrahydrofuran (0.64 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford the product as a clear, colorless oil that could not be separated from pinacol (145.9 mg, 1:1.3 product:pinacol = 78% yield). Spectral data are in accordance with the literature.<sup>18</sup>

## *Analysis of Stereochemistry:*

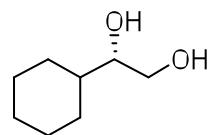
The title compound was compared to racemic 4,4-dimethylpentane-1,2-diol prepared from treatment of 4,4-dimethylpentane-1,2-diol with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -dex, Supelco, 90 °C, 20 psi, s/r = 35:1)- analysis of 4,4-dimethylpentane-1,2-diol.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	82.969	MM	0.5540	20.68082	6.22113e-1	1.89631
2	84.253	MM	2.6906	1069.90186	6.62750	98.10369

<sup>18</sup> Trudeau, S.; Morgan, J. M.; Shrestha, M.; Morken, J. P. *J. Org. Chem.* **2005**, *70*, 9538.

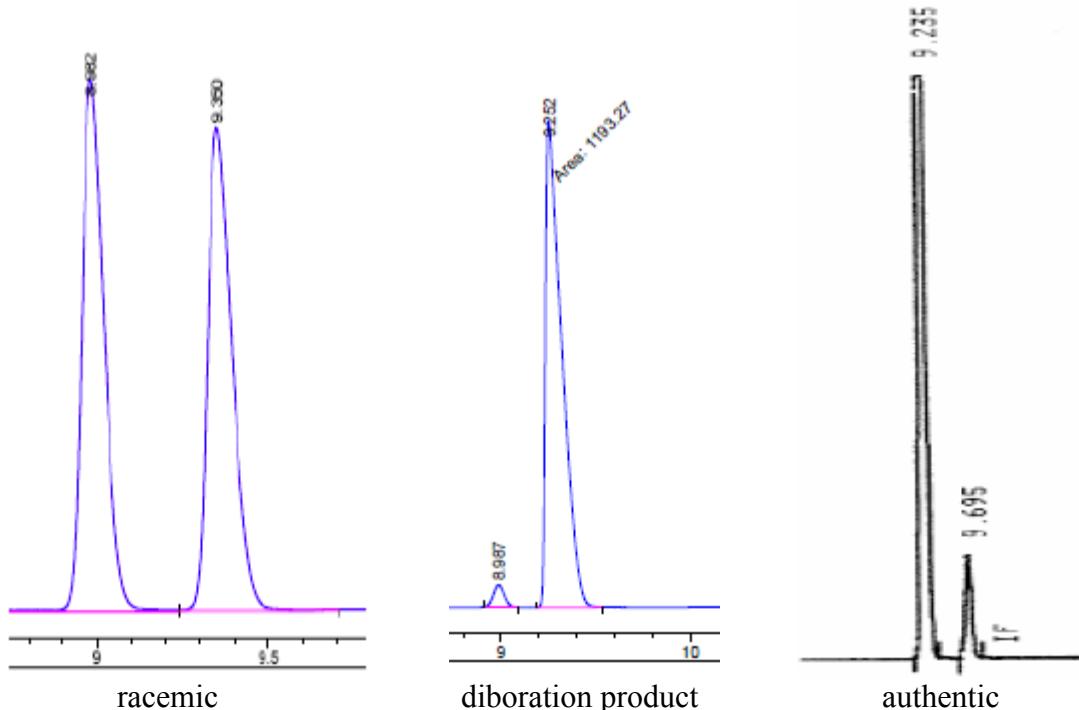


**(S)-1-cyclohexylethane-1,2-diol (6).** The diboration was performed according to the general procedure with vinyl cyclohexane (100.0 mg, 907.4  $\mu$ mol), Pt(dba)<sub>3</sub> (8.1 mg, 9.1  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (9.9 mg, 11  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (258.8 mg, 1.019  $\mu$ mol) in tetrahydrofuran (0.91 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford the product as a clear, colorless oil (107.6 mg, 82% yield). Spectral data and optical rotation are in accordance with the literature.<sup>19,15</sup> [M+H]: calculated: 145.1229, found: 145.1222.

**Proof of Stereochemistry:**

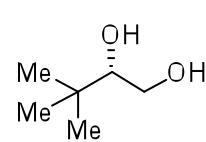
The 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of 1-cyclohexylethane-1,2-diol prepared from treatment of vinyl cyclohexane with osmium tetroxide and 4-methylmorpholine *N*-oxide. The authentic (*R*)-isomer was prepared from the Sharpless asymmetric dihydroxylation of vinyl cyclohexane utilizing AD-mix- $\beta$ .

*Chiral GLC (Supelco  $\beta$ -dex, 130 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 1-cyclohexylethane-1,2-diol.*



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.987	BB	0.0627	36.78653	9.18231	2.99064
2	9.252	MM	0.0999	1193.26807	199.09114	97.00936

<sup>19</sup> Miller, S. P.; Morgan, J. B.; Nepveux, F. J.; Morken, J. P. *Org. Lett.* **2004**, 6, 131.

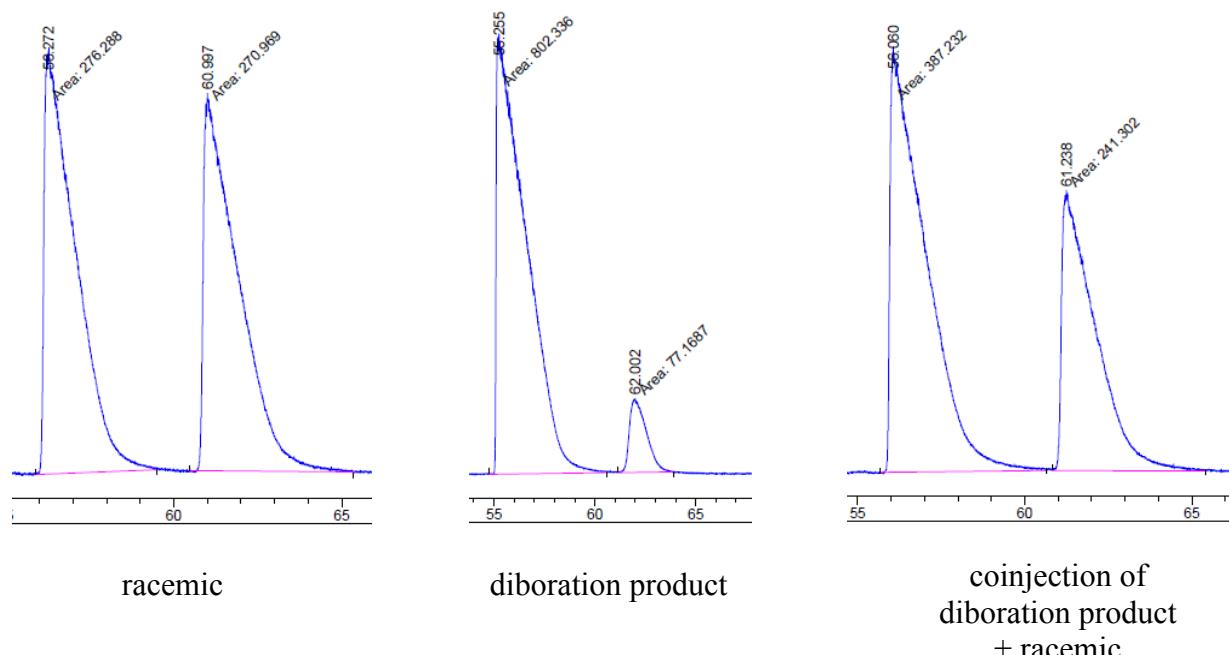


**(S)-3,3-dimethylbutane-1,2-diol (7).** The diboration was performed according to the general procedure with 3,3-dimethylbut-1-ene (50.0 mg, 594.1  $\mu$ mol),  $\text{Pt}(\text{dba})_3$  (16.0 mg, 17.8  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (19.4 mg, 21.4  $\mu$ mol), and  $\text{B}_2(\text{pin})_2$  (158.4 mg, 623.8  $\mu$ mol) in tetrahydrofuran (0.59 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in  $\text{KMnO}_4$ ) to afford a clear, colorless oil that was inseparable from pinacol (69.6 mg, 1:1 product:pinacol, 50% yield). Spectral data and optical rotation are in accordance with the literature.<sup>15, 19</sup>  $[\text{M}+\text{H}]$ : calculated: 119.1072, found: 119.1074.

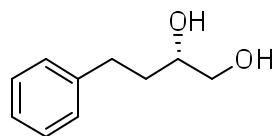
### Analysis of Stereochemistry:

The title compound was compared to racemic 3,3-dimethylbutane-1,2-diol prepared from treatment of 3,3-dimethyl-1-butene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -dex, Supelco, 90 °C, 20 psi, *s/r* = 35:1) – analysis of 3,3-dimethylbutane-1,2-diol.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	55.255	MM	1.6795	802.33582	7.96203	91.22589
2	62.002	MM	0.9635	77.16866	1.33488	8.77411

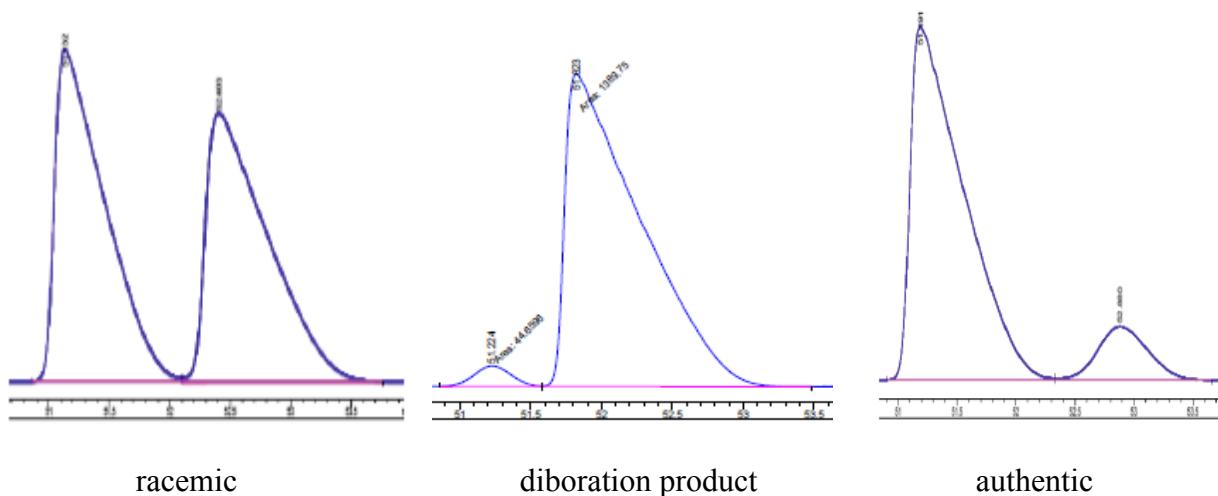


**(S)-4-phenylbutane-1,2-diol (8).** The diboration was performed according to the general procedure with 4-phenyl-1-butene (88.3 mg, 668  $\mu$ mol), Pt(dba)<sub>3</sub> (6.0 mg, 6.68  $\mu$ mol), (*R,R*)-3,5-diisopropylphenyl-TADDOLPPh (7.3 mg, 8.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (178.2 mg, 701.6  $\mu$ mol) in tetrahydrofuran (0.67 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford the product as a clear, colorless oil (86.6 mg, 78% yield). Spectral data are in accordance with the literature.<sup>20</sup> HRMS-(ESI<sup>+</sup>) for C<sub>10</sub>H<sub>15</sub>O<sub>2</sub> [M+H]: calculated: 167.1072, found: 167.1080.  $[\alpha]_D^{20} = -13.294$  ( $c = 1.050$ , CHCl<sub>3</sub>,  $l = 50$  mm).

### Proof of stereochemistry:

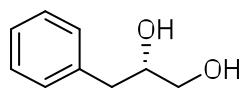
The 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of 4-phenylbutane-1,2-diol prepared from treatment of 4-phenyl-1-butene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The authentic (*R*)-isomer was prepared from the Sharpless asymmetric dihydroxylation of 4-phenyl-1-butene utilizing AD-mix- $\beta$ .

Chiral GLC ( $\beta$ -dex, Supelco, 90 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 4-phenylbutane-1,2-diol.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	51.224	MM	0.3009	44.65959	2.47390	3.11345
2	51.823	MM	0.6127	1389.74744	37.80545	96.88655

<sup>20</sup> Stead, D.; O'Brien, P.; Sanderson, A.; *Org. Lett.*, **2008**, *10*, 1409.

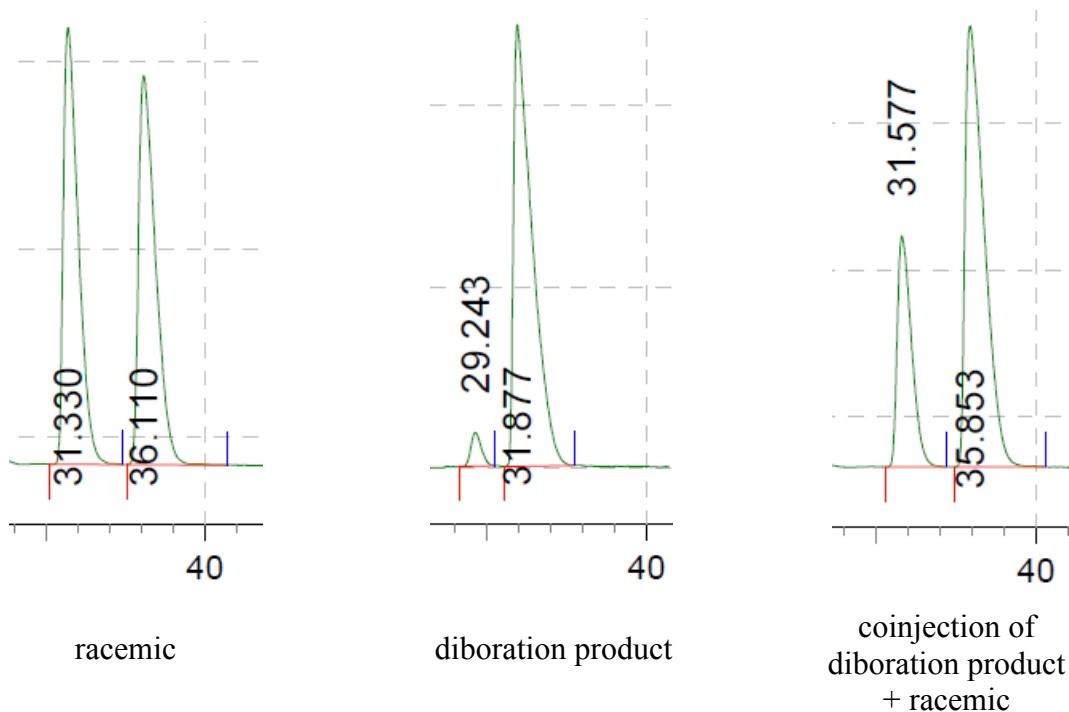


**(S)-3-phenylpropane-1,2-diol (9).** The diboration was performed according to the general procedure with allylbenzene (79.0 mg, 668  $\mu$ mol), Pt(dba)<sub>3</sub> (6.0 mg, 6.7  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (7.3 mg, 8.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (178.2 mg, 701.6  $\mu$ mol) in tetrahydrofuran (0.67 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford the product as a clear, colorless oil (81.4 mg, 80% yield). Spectral data and optical rotation are in accordance with the literature.<sup>15</sup> HRMS-(ESI+) for C<sub>9</sub>H<sub>16</sub>NO<sub>2</sub> [M+NH<sub>4</sub>]: calculated: 170.1180, found: 170.1181.

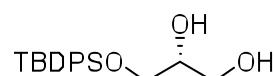
#### Analysis of Stereochemistry:

The title compound was compared to racemic 3-phenylpropane-1,2-diol prepared from treatment of allylbenzene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

*Chiral HPLC (Chiracel OD-H, 2.0% IPA, 1.5 mL/min, 220 nm)-analysis of 3-phenylpropane-1,2-diol.*



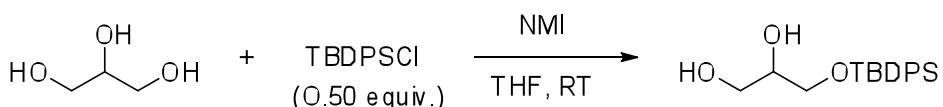
Retention Time	Area	Area %	Height	Height %
29.243	3531421	4.11	77445	7.06
31.877	82491494	95.89	1019684	92.94



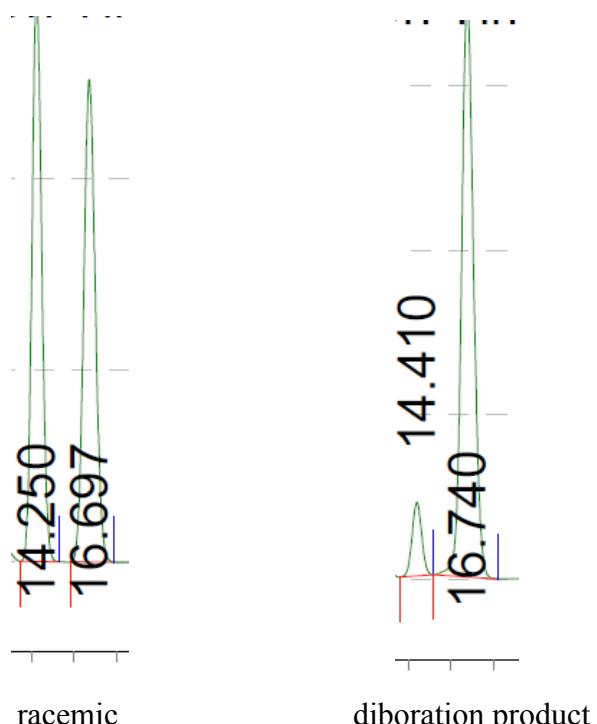
**(R)-3-(*tert*-butyldiphenylsilyloxy)propane-1,2-diol (10).** The diboration was performed according to the general procedure with allyloxy(*tert*-butyl) diphenylsilane (66.7 mg, 224  $\mu$ mol), Pt(dba)<sub>3</sub> (6.1 mg, 6.7  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (7.4 mg, 8.1  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (60.0 mg, 236  $\mu$ mol) in tetrahydrofuran (0.22 mL, 1.0 M). The crude reaction mixture was purified on silica gel (20-30% ethyl acetate in hexanes) to afford the product as a white solid (59.5 mg, 80% yield).  $R_f$  = 0.39 (50% ethyl acetate/hexane, stain in KMnO<sub>4</sub>). Spectral data and optical rotation are in accordance with the literature.<sup>15</sup>

#### Analysis of Stereochemistry:

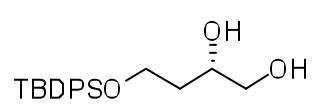
The title compound was compared to racemic 3-(*tert*-butyldiphenylsilyloxy)propane-1,2-diol prepared by silyl protection of glycerol, as shown below. Absolute stereochemistry was assigned by analogy.



Chiral HPLC (Chiracel-OD, 2.0 % IPA, 1.5 mL/min, 220 nm) – analysis of 3-(*tert*-butyldiphenylsilyloxy)propane-1,2-diol.



Retention Time	Area	Area %	Height	Height %
14.410	58717514	9.26	1876785	11.27
16.740	575118998	90.74	14775893	88.73

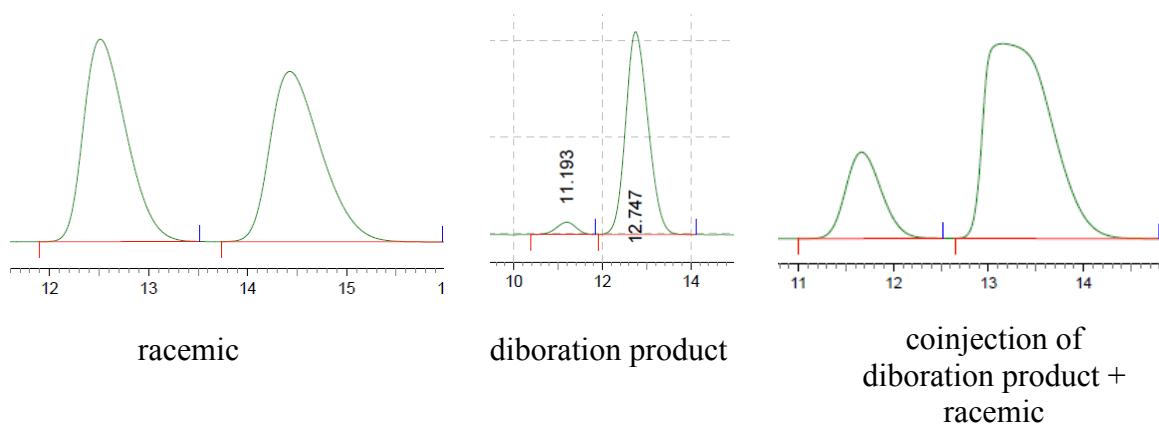


**(S)-4-(*tert*-butyldiphenylsilyloxy)butane-1,2-diol (11).** The diboration was performed according to the general procedure with (but-3-enyloxy)(*tert*-butyl)diphenylsilane (200.0 mg, 644.1  $\mu$ mol), Pt(dba)<sub>3</sub> (5.8 mg, 6.4  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (7.0 mg, 7.7  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (171.1 mg, 676.3  $\mu$ mol) in tetrahydrofuran (0.64 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-60% ethyl acetate in hexanes) to afford the product as a clear, colorless oil that could not be separated from pinacol (350.9 mg, 1:1 product:pinacol, 91% yield).  $R_f$  = 0.26 (50% ethyl acetate/hexane, stain in KMnO<sub>4</sub>). Spectral data and optical rotation are in accordance with the literature.<sup>15</sup> HRMS-(ESI<sup>+</sup>) for C<sub>20</sub>H<sub>29</sub>O<sub>3</sub>Si [M+H]<sup>+</sup>: calculated: 345.1886, found: 345.1878.

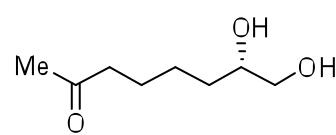
#### Analysis of Stereochemistry:

The title compound was compared to racemic 4-(*tert*-butyldiphenylsilyloxy)butane-1,2-diol prepared from treatment of allylbenzene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

Chiral HPLC (Chiracel OD-H, 2.0% IPA, 1.5 mL/min, 220 nm)-analysis of 4-(*tert*-butyldiphenylsilyloxy)butane-1,2-diol.



Retention Time	Area	Area %	Height	Height %
11.193	1339227	5.12	42971	5.76
12.747	24803241	94.88	703609	94.24

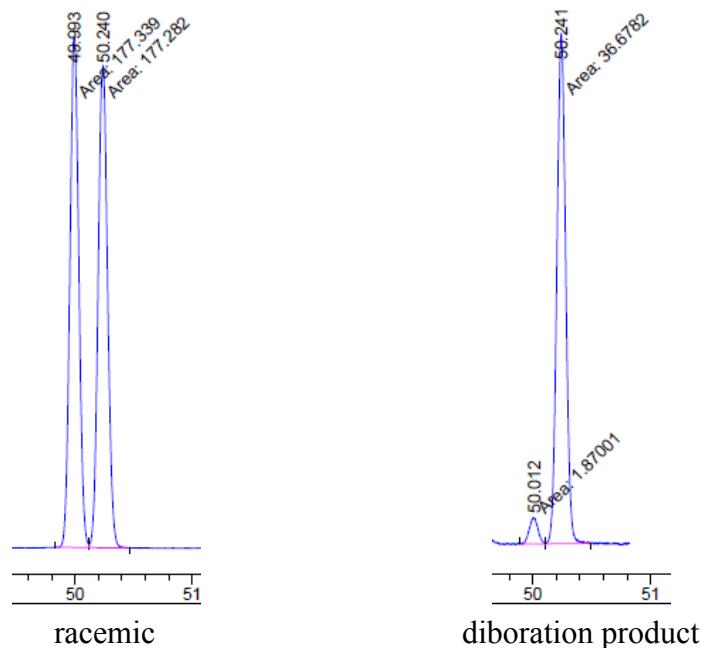


**(S)-7,8-dihydroxyoctan-2-one (12).** The diboration was performed according to the general procedure with oct-7-en-2-one (100.0 mg, 792.4  $\mu$ mol), Pt(dba)<sub>3</sub> (7.1 mg, 7.9  $\mu$ mol), (R,R)-3,5-diisopropylphenylTADDOLPPh (8.6 mg, 9.5  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (211.3 mg, 832.0  $\mu$ mol) in tetrahydrofuran (0.79 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-85% ethyl acetate in hexanes) to afford a clear, colorless oil (73.2 mg, 58% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.30-1.36 (1H, m), 1.38-1.46 (3H, m), 1.53-1.62 (2H, m), 2.11 (3H, s), 2.43 (2H, t,  $J$  = 7.5 Hz), 3.41 (1H, dd,  $J$  = 11.0, 7.5 Hz), 3.62 (1H, dd,  $J$  = 11.0, 3.0 Hz), 3.68-3.72 (1H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  23.5, 25.0, 29.9, 32.8, 43.5, 66.7, 71.9, 209.2; IR (neat): 3398.9 (br s), 2926.2 (s), 2858.8 (m), 1706.4 (s), 1459.5 (w), 1408.9 (w), 1363.0 (m), 1163.4 (w), 1054.2 (m), 599.8 (w) cm<sup>-1</sup>; HRMS-(ESI<sup>+</sup>) for C<sub>8</sub>H<sub>17</sub>O<sub>3</sub> [M+H]<sup>+</sup>: calculated: 161.1178, found: 161.1180.  $[\alpha]_D^{20}$  = +2.769 ( $c$  = 0.650, CHCl<sub>3</sub>,  $l$  = 50 mm).

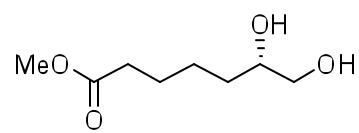
### Analysis of stereochemistry:

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 7,8-dihydroxyoctan-2-one prepared from treatment of oct-7-en-2-one with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -dex, Supelco, 70 °C for 5 min, ramp 2 °C/min to 180 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 7,8-dihydroxyoctan-2-one.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	50.012	MM	0.0850	1.87001	3.66484e-1	4.85110
2	50.241	MM	0.0864	36.67818	7.07375	95.14890

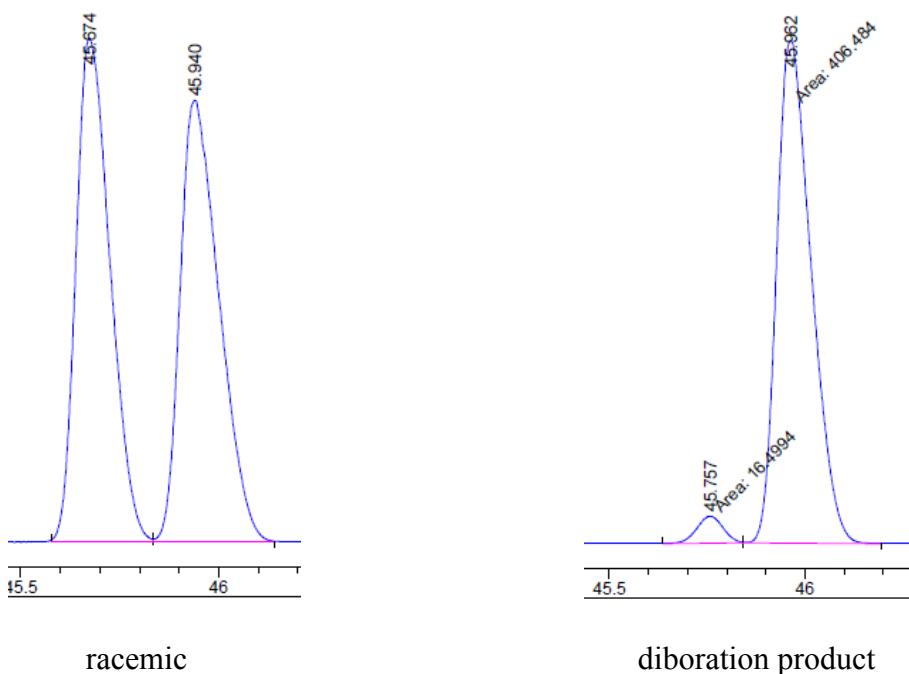


**(S)-methyl 6,7-dihydroxyheptanoate (13).** The diboration was performed according to the general procedure with methyl hept-6-enoate (150.0 mg, 1.058 mmol), Pt(dba)<sub>3</sub> (9.5 mg, 11  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (11.5 mg, 127  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (281.9 mg, 1.108 mmol) in tetrahydrofuran (1.05 mL, 1.0 M). The crude reaction mixture was purified on silica gel (0-10% methanol in dichloromethane, stain in KMnO<sub>4</sub>) to afford a clear, colorless oil (124.9 mg, 67% yield). Spectral data are in accordance with the literature.<sup>21</sup> HRMS-(ESI<sup>+</sup>) for C<sub>8</sub>H<sub>17</sub>O<sub>4</sub> [M+H]: calculated: 177.1127, found: 177.1130.  $[\alpha]_D^{20} = -2.644$  (*c* = 1.195, CHCl<sub>3</sub>, *l* = 50 mm).

#### Analysis of stereochemistry:

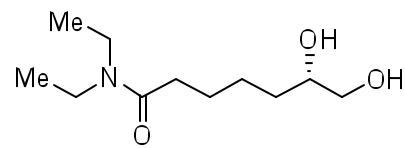
The resulting 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of methyl 6,7-dihydroxyheptanoate prepared from treatment of hept-6-enoate with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -dex, Supelco, 70 °C for 5 min, ramp 2 °C/min to 180 °C, 20 psi, *s/r* = 35:1) – analysis of the acetonide of methyl 6,7-dihydroxyheptanoate.



Peak	RetTime	Type	Width	Area	Height	Area
#	[min]		[min]	[pA*s]	[pA]	%
1	45.757	MM	0.0775	16.49937	3.54979	3.90071
2	45.962	MM	0.1024	406.48438	66.18299	96.09929

<sup>21</sup> Chen, A.; Xu, J.; Chiang, W.; Chai, C. L. L.; *Tetrahedron*, **2010**, *66*, 1489.

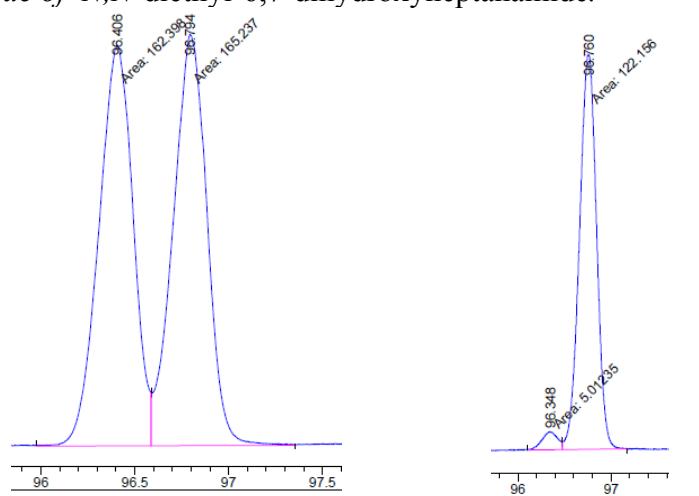


**(S)-N,N-diethyl-6,7-dihydroxyheptanamide (14).** The diboration was performed according to the general procedure with *N,N*-diethylhept-6-enamide (150.0 mg, 818.4  $\mu$ mol), Pt(dba)<sub>3</sub> (7.3 mg, 8.2  $\mu$ mol), (R,R)-3,5-diisopropylphenylTADDOLPPh (8.9 mg, 9.8  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (218.2 mg, 859.3  $\mu$ mol) in tetrahydrofuran (0.82 mL, 1.0 M). The crude reaction mixture was purified on silica gel (0-10% methanol in dichloromethane, stain in KMnO<sub>4</sub>) to afford the product as a clear, colorless oil (135.4 mg, 76% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.06 (3H, t, 7.5 Hz), 1.13 (3H, t, *J* = 7.5 Hz), 1.34-1.47 (4H, m), 1.55-1.69 (2H, m), 2.28 (2H, t, *J* = 7.0 Hz), 3.26 (2H, q, *J* = 7.0 Hz), 3.31 (2H, q, *J* = 7.0 Hz), 3.40 (1H, dd, *J* = 11.0, 6.5 Hz), 3.58 (1H, dd, *J* = 11.5, 3.0 Hz), 3.68-3.70 (1H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  13.0, 14.5, 24.9, 25.2, 32.6, 32.8, 40.2, 42.0, 66.8, 71.8, 172.4; IR (neat): 3393.3 (br m), 2971.3 (w), 2933.4 (m), 2870.7 (w), 1617.1 (s), 1459.9 (m), 1433.1 (m), 1310.3 (m), 1265.0 (w), 1142.1 (w), 1096.9 (m), 1072.4 (m), 1052.3 (m), 606.3 (w) cm<sup>-1</sup>; HRMS-(ESI+) for C<sub>11</sub>H<sub>24</sub>NO<sub>3</sub> [M+H]: calculated: 218.1756, found: 218.1760.  $[\alpha]_D^{20}$  = -4.374 (*c* = 1.015, CHCl<sub>3</sub>, *l* = 50 mm).

#### Analysis of stereochemistry:

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 methyl *N,N*-diethyl-6,7-dihydroxyheptanamide prepared from treatment of *N,N*-diethylhept-6-enamide with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -dex, Supelco, 140 °C for 60 min, ramp 1 °C/min to 180 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of *N,N*-diethyl-6,7-dihydroxyheptanamide.



racemic

diboration product

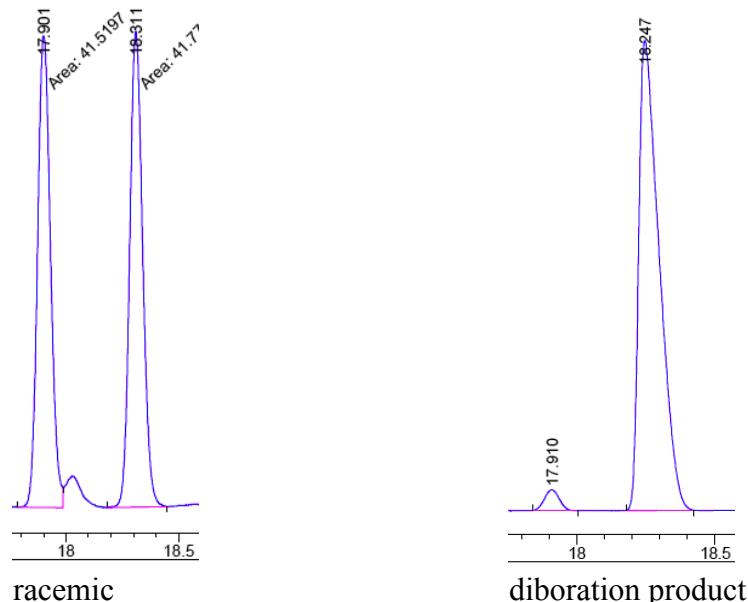
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	96.348	MF	0.1891	4.80400	4.23356e-1	3.79610
2	96.760	FM	0.2124	121.74680	9.55517	96.20390

**(S)-5-methylhex-5-ene-1,2-diol (16).** The diboration was performed according to the general procedure with 2-methylhexa-1,5-diene (75.0 mg, 779.9  $\mu$ mol), Pt(dba)<sub>3</sub> (7.0 mg, 7.8  $\mu$ mol), (R,R)-3,5-diisopropylphenylTADDOLPPh (8.5 mg, 9.4  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (207.9 mg, 818.9  $\mu$ mol) in tetrahydrofuran (0.8 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-50% ethyl acetate in hexanes) to afford the product as a clear, colorless oil (84.3 mg, 83% yield).  $R_f$  = 0.13 (50% ethyl acetate in hexane, stain in KMnO<sub>4</sub>) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.56-1.60 (2H, m), 1.72 (3H, s), 2.01 (2H, br s), 2.07 (1H, dddd,  $J$  = 7.5, 7.5, 7.5, 7.5 Hz), 2.17 (1H, dddd,  $J$  = 7.5, 7.5, 7.5, 7.5 Hz), 3.45 (1H, dd,  $J$  = 11.0, 8.0 Hz), 3.65 (1H, d,  $J$  = 11.0 Hz), 3.69-3.73 (1H, m), 4.70 (1H, s), 4.72 (1H, s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  22.3, 31.0, 33.8, 66.7, 72.0, 110.4, 145.4; IR (neat): 3363.6 (s), 3074.1 (w), 2929.6 (s), 1649.6 (w), 1447.6 (s), 1375.0 (m), 1333.5 (w), 1100.2 (m), 1053.3 (s), 886.0 (s) cm<sup>-1</sup>; HRMS-(ESI<sup>+</sup>) for C<sub>7</sub>H<sub>15</sub>O<sub>2</sub> [M+H]: calculated: 131.1072, found: 131.1075.  $[\alpha]_D^{20}$  = -2.714 ( $c$  = 1.665, CHCl<sub>3</sub>,  $l$  = 50 mm).

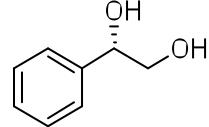
#### Analysis of Stereochemistry:

The enantiopurity was determined by treating the resulting 1,2-diol with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The racemic material of 5-methylhex-5-ene-1,2-diol was prepared using PCy<sub>3</sub> as the achiral ligand in the diboration reaction. Absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -Dex, Supelco, 70 °C for 5 min, ramp 3 °C/min to 120 °C, 20 psi, s/r = 35:1) – analysis of the acetonide.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	17.910	BB	0.0577	10.21409	2.72514	3.12745
2	18.247	BB	0.0759	316.38113	61.59937	96.87255

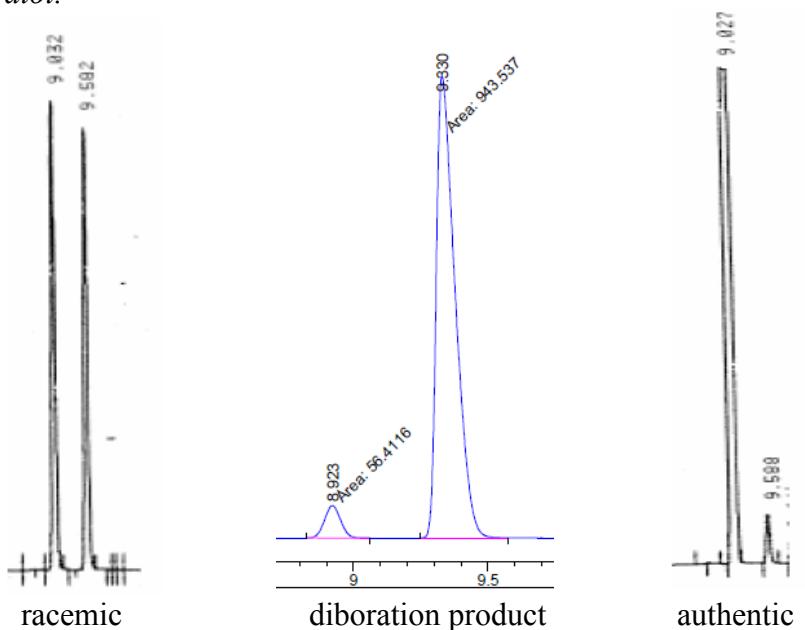


**(S)-1-phenylethane-1,2-diol (17).** The diboration was performed according to the general procedure with styrene (80.0 mg, 768  $\mu$ mol), Pt(dba)<sub>3</sub> (6.9 mg, 7.7  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (8.4 mg, 9.2  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (204.8 mg, 806.5  $\mu$ mol) in tetrahydrofuran (0.77 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate/hexanes, stain in KMnO<sub>4</sub>) to afford the product as a white solid (90.6 mg, 85% yield). Spectral data and optical rotation are in accordance with the literature.<sup>8,19</sup> HRMS-(ESI<sup>+</sup>) for C<sub>8</sub>H<sub>9</sub>O<sub>1</sub> [M-H<sub>2</sub>O+H]: calculated: 121.0653, found: 121.0657.

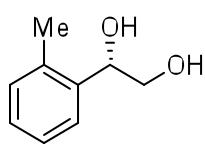
**Proof of stereochemistry:**

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-phenylethane-1,2-diol prepared from treatment of styrene with osmium tetroxide and 4-methylmorpholine N oxide. The authentic (*R*)-isomer was prepared from the Sharpless asymmetric dihydroxylation of vinyl cyclohexane utilizing AD-mix- $\beta$ .

*Chiral GLC ( $\beta$ -dex, Supelco, 140 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of *I*-phenylethane-1,2-diol.*



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.923	MM	0.0691	56.41163	13.60868	5.64146
2	9.330	MM	0.0810	943.53656	194.25536	94.35854

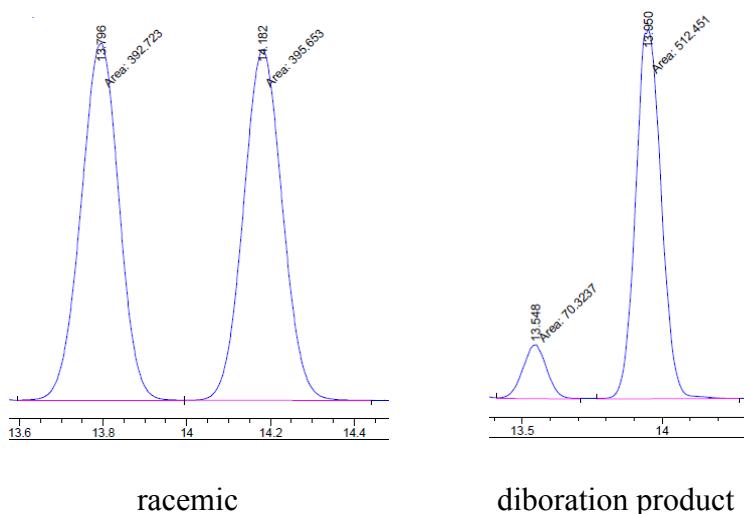


**(S)-1-(2-methylphenyl)ethane-1,2-diol (18).** The diboration was performed according to the general procedure with 2-methylstyrene (79.0 mg, 668  $\mu$ mol), Pt(dba)<sub>3</sub> (6.0 mg, 6.7  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (7.3 mg, 8.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (178.2 mg, 701.6  $\mu$ mol) in tetrahydrofuran (0.67 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes) to afford the product as a white solid (84.4 mg, 83% yield). Spectral data and optical rotation are in accordance with the literature.<sup>22</sup> HRMS-(ESI<sup>+</sup>) for C<sub>9</sub>H<sub>16</sub>NO<sub>2</sub> [M+NH<sub>4</sub>]<sup>+</sup>: calculated: 170.1181, found: 170.1187.  $[\alpha]_D^{20} = +58.769$  ( $c = 1.555$ , CHCl<sub>3</sub>,  $l = 50$  mm).

#### Analysis of stereochemistry:

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-(2-methylphenyl)ethane-1,2-diol prepared from treatment of *o*-methylstyrene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

*Chiral GLC (β-dex, Supelco, 140 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 1-(2-methyl-phenyl)ethane-1,2-diol.*



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.548	MM	0.0996	70.32373	11.76942	12.06705
2	13.950	MM	0.1062	512.45099	80.44946	87.93295

<sup>22</sup> Kadyrov, R.; Koenigs, R. M.; Brinkmann, C.; Voigtlaender, D.; Rueping, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 7556.

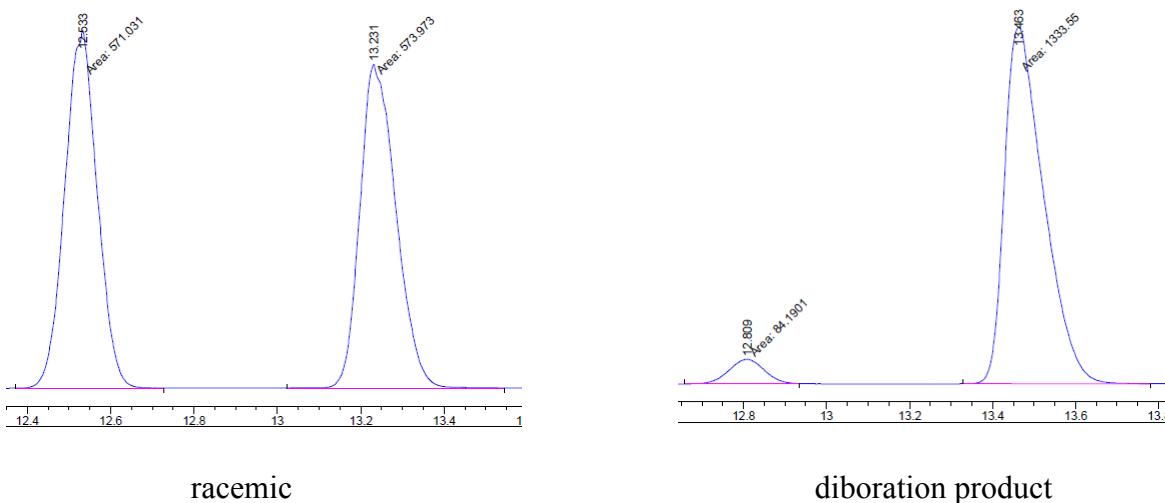


**(S)-1-(3-methylphenyl)ethane-1,2-diol (19).** The diboration was performed according to the general procedure with 3-methylstyrene (79.0 mg, 668  $\mu$ mol), Pt(dba)<sub>3</sub> (6.0 mg, 6.7  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (7.3 mg, 8.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (178.2 mg, 701.6  $\mu$ mol) in tetrahydrofuran (0.67 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes) to afford the product as a clear, colorless oil (85.2 mg, 84% yield).  $R_f$  = .20 (40% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  2.16 (1H, br s), 2.34 (3H, s), 2.57 (1H, br s), 3.65 (1H, dd, *J* = 11.0 Hz, 8.0 Hz), 3.74 (1H, dd, *J* = 11.5, 3.5 Hz), 4.77 (1H, dd, *J* = 8.5 Hz, 3.5 Hz), 7.09-7.16 (3H, m) 7.23 (1H, dd, *J* = 7.5, 7.5 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  21.4, 68.1, 74.7, 123.1, 126.7, 128.5, 128.8, 138.3, 140.4; IR (neat): 3346.7 (br s), 2921.3 (w), 1454.6 (w), 1075.5 (s), 1029.0 (s), 786.5 (m), 702.6 (s), 444.4 (w) cm<sup>-1</sup>; HRMS-(ESI+) for C<sub>9</sub>H<sub>16</sub>NO<sub>2</sub> [M+NH<sub>4</sub>]: calculated: 170.1181, found: 170.1184.  $[\alpha]_D^{20}$  = +58.750 (*c* = 0.290, CHCl<sub>3</sub>, *l* = 50 mm).

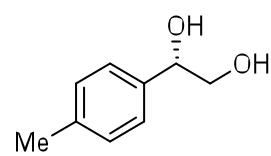
**Proof of stereochemistry:**

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-(3-methylphenyl)ethane-1,2-diol prepared from treatment of 3-methylstyrene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

*Chiral GLC (β-dex, Supelco, 140 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 1-(3-methyl-phenyl)ethane-1,2-diol.*



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	12.809	MM	0.0995	84.19008	14.09868	5.93831
2	13.463	MM	0.1091	1333.55408	203.72780	94.06169

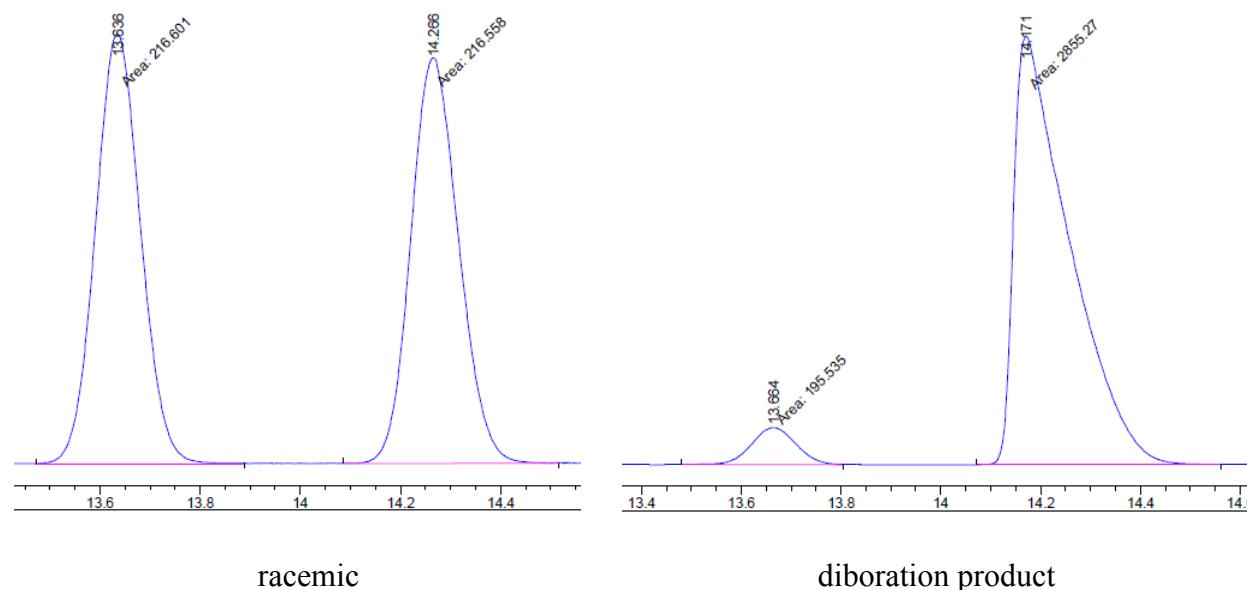


**(S)-1-(4-methylphenyl)ethane-1,2-diol (20).** The diboration was performed according to the general procedure with 4-methylstyrene (79.0 mg, 668  $\mu$ mol), Pt(dba)<sub>3</sub> (6.0 mg, 6.7  $\mu$ mol), (R,R)-3,5-diisopropylphenylTADDOLPPh (7.3 mg, 8.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (178.2 mg, 701.6  $\mu$ mol) in tetrahydrofuran (0.67 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford a clear, colorless oil (78.1 mg, 77% yield). Spectral data and optical rotation are in accordance with the literature.<sup>23</sup> HRMS-(ESI<sup>+</sup>) for C<sub>9</sub>H<sub>16</sub>NO<sub>2</sub> [M+NH<sub>4</sub>]: calculated: 170.1181, found: 170.1187.  $[\alpha]_D^{20} = +50.480$  ( $c = 2.060$ , CHCl<sub>3</sub>,  $l = 50$  mm).

### Proof of stereochemistry:

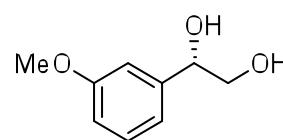
The title compound was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of 1-(4-methylphenyl)ethane-1,2-diol prepared from treatment of *p*-methylstyrene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -dex, Supelco, 140 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 1-(4-methylphenyl)ethane-1,2-diol.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	13.664	MM	0.1032	195.53534	31.57282	6.40929
2	14.171	MM	0.1292	2855.27393	368.32419	93.59071

<sup>23</sup> Wang, L.; Nakamura, S.; Ito, Y.; Toru, T. *Tetrahedron: Asymm.* **2004**, *15*, 3059.

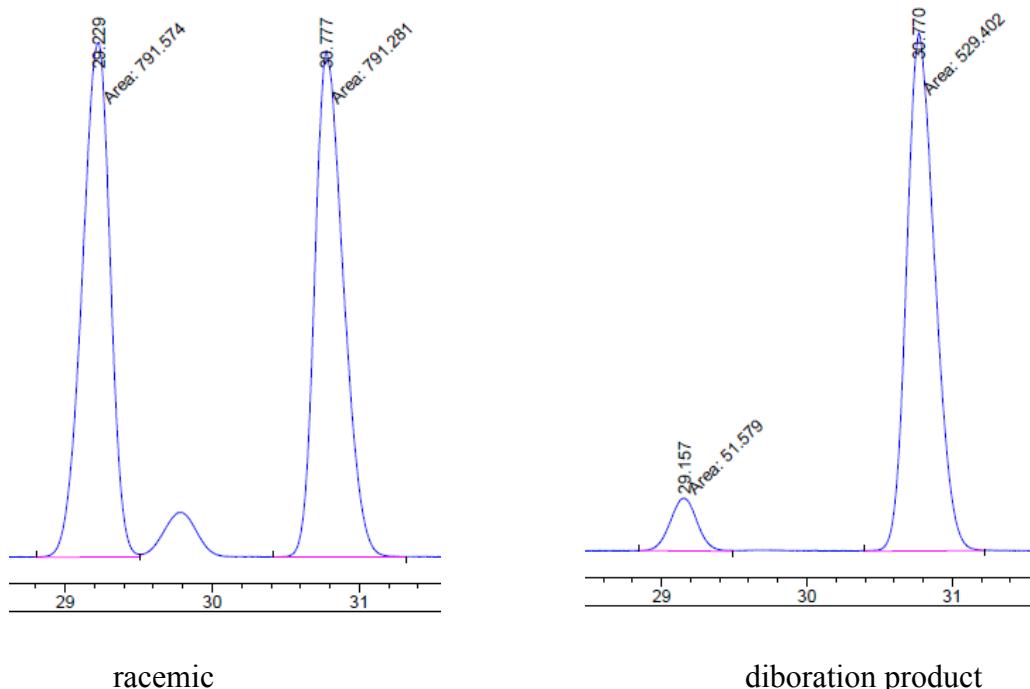


**(S)-1-(3-methoxyphenyl)ethane-1,2-diol (21).** The diboration was performed according to the general procedure with 3-methoxystyrene (30.0 mg, 223  $\mu$ mol), Pt(dba)<sub>3</sub> (6.0 mg, 6.7  $\mu$ mol), (R,R)-3,5-diisopropylphenylTADDOLPPh (7.3 mg, 8.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (59.4 mg, 234  $\mu$ mol) in tetrahydrofuran (0.22 mL, 1.0 M). The crude reaction mixture was purified on silica gel (20-75% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford a clear, colorless oil (27.9 mg, 75% yield). Spectral data and optical rotation are in accordance with the literature.<sup>22</sup> HRMS-(ESI<sup>+</sup>) for C<sub>9</sub>H<sub>16</sub>NO<sub>3</sub> [M+NH<sub>4</sub>]: calculated: 186.1130, found: 186.1122.  $[\alpha]_D^{20} = +39.358$  ( $c = 2.070$ , CHCl<sub>3</sub>,  $l = 50$  mm).

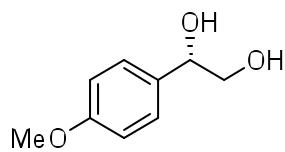
**Proof of stereochemistry:**

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-(3-methoxyphenyl)ethane-1,2-diol prepared from treatment of 3-methoxystyrene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

*Chiral GLC (β-dex, Supelco, 140 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 1-(3-methoxyphenyl)-ethane-1,2-diol.*



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	29.157	MM	0.2147	51.57898	4.00369	8.87792
2	30.770	MM	0.2250	529.40173	39.21622	91.12208

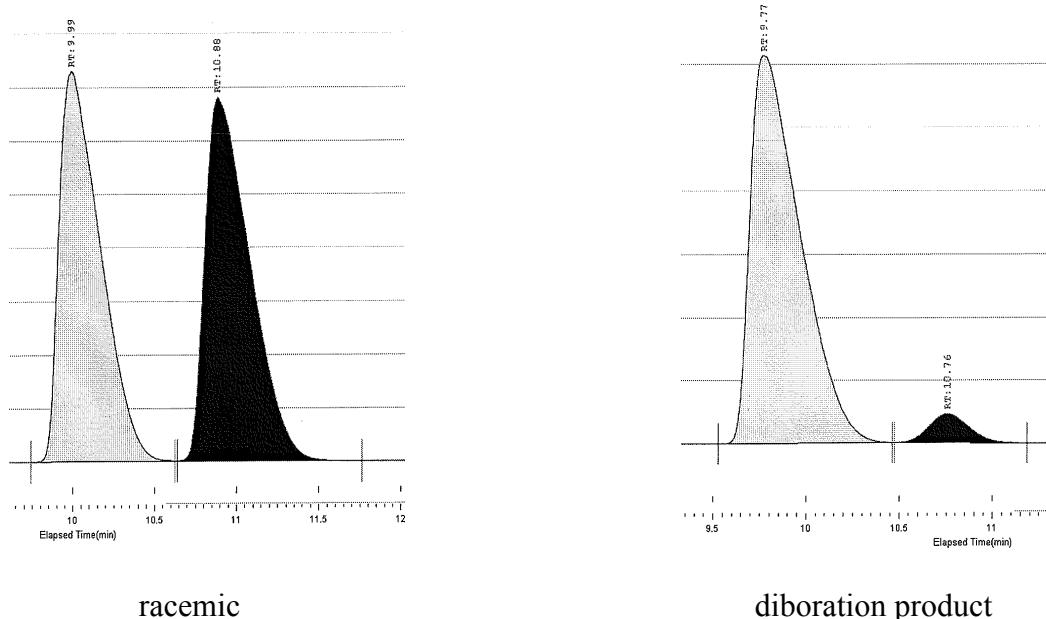


**(S)-1-(4-methoxyphenyl)ethane-1,2-diol (22).** The diboration was performed according to the general procedure with 4-methoxystyrene (99.6 mg, 742.3  $\mu$ mol), Pt(dba)<sub>3</sub> (6.7 mg, 7.45  $\mu$ mol), (*R,R*)-3,5-di-*iso*-propylphenylTADDOLPPh (**L8**) (8.1 mg, 8.94  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (198.7 mg, 782.5  $\mu$ mol) in tetrahydrofuran (0.75 mL, 1.0 M). The crude reaction mixture was purified on silica gel (20-80% ethyl acetate/hexanes, stain in KMnO<sub>4</sub>) to afford a white solid (90.2 mg, 72% yield). Spectral data and optical rotation are in accordance with the literature.<sup>24</sup> HRMS-(ESI<sup>+</sup>) for C<sub>9</sub>H<sub>11</sub>O<sub>2</sub> [M+H-H<sub>2</sub>O]: calculated: 151.0759, found: 151.0762.  $[\alpha]_D^{20} = +48.369$  ( $c = 1.075$ , CHCl<sub>3</sub>,  $l = 50$  mm).

#### Analysis of stereochemistry:

The resulting 1,2-diol was compared to the racemic sample of 1-(4-methoxyphenyl)ethane-1,2-diol prepared from treatment of 4-methoxystyrene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

*Chiral SFC (Chiracel AD-H, 5% MeOH, 5 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of 1-(4-methoxyphenyl)-ethane-1,2-diol.*



Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	94.4322	22871.8001	9.77	1225.916	0.0145
2	5.5678	1348.5343	10.76	91.1619	0.0159
Total:	100	24220.3344			

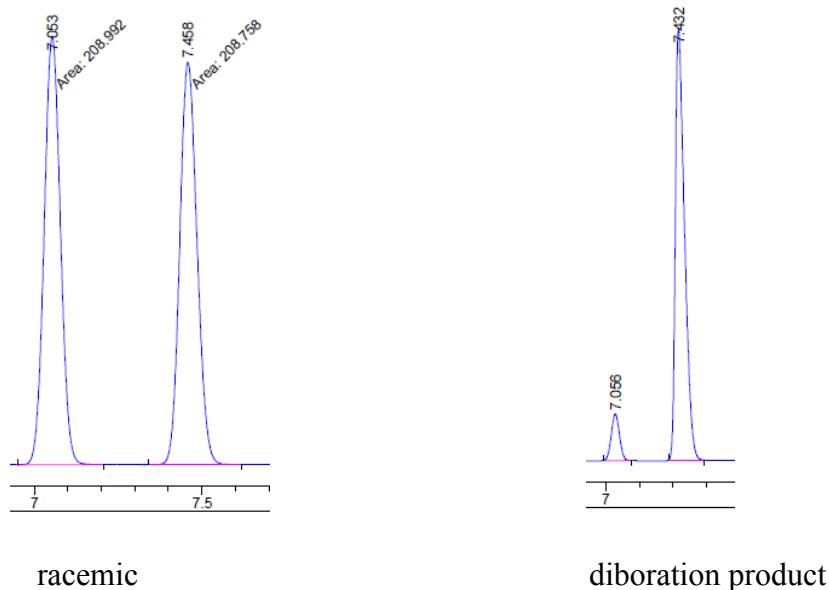
<sup>24</sup> Peach, P.; Cross, D. J.; Kenny, J. A.; Mann, I.; Houson, I.; Campbell, L.; Walsgrove, T.; Wills, M. *Tetrahedron* **2006**, *62*, 1864.

**(S)-1-(3-(trifluoromethyl)phenyl)ethane-1,2-diol (23).** The diboration was performed according to the general procedure with 3-(trifluoromethyl)styrene (100.0 mg, 574.3  $\mu$ mol), Pt(dba)<sub>3</sub> (5.2 mg, 5.7  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (6.3 mg, 6.9  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (153.1 mg, 603.0  $\mu$ mol) in tetrahydrofuran (0.57 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford the product as a white solid (70.7 mg, 60% yield). Spectral data and optical rotation are in accordance with the literature.<sup>25</sup> IR (neat): 3370.7 (br s), 2926.2 (w), 1451.3 (w), 1329.0 (s), 1164.5 (m), 1123.6 (s), 1173.2 (m), 804.1 (w), 703.2 (w)  $\text{cm}^{-1}$ . HRMS-(ESI<sup>+</sup>) for C<sub>9</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>2</sub> [M+NH<sub>4</sub>]: calculated: 224.0898, found: 224.0899.  $[\alpha]_D^{20} = +37.917$  ( $c = 0.250$ , CHCl<sub>3</sub>,  $l = 50$  mm).

#### Analysis of stereochemistry:

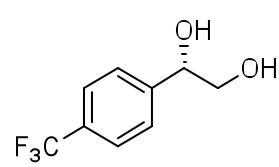
The resulting 1,2-diol was treated with 2,2-dimethoxypropane and catalytic *p*-toluenesulfonic acid. The resulting ketal was compared to the racemic ketal of 1-(3-(trifluoromethyl)phenyl)ethane-1,2-diol prepared from treatment of 3-(trifluoromethyl)styrene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

Chiral GLC ( $\beta$ -dex, Supelco, 140 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 1-(3-(trifluoromethyl)phenyl)ethane-1,2-diol.



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	7.056	BB	0.0536	112.27570	33.10232	8.78842
2	7.432	BB	0.0583	1165.26562	306.69888	91.21158

<sup>25</sup> Ohkuma, T.; Utsumi, N.; Watanabe, M.; Tsutsumi, K.; Arai, N.; Murata, K. *Org. Lett.* **2007**, 9, 2565.

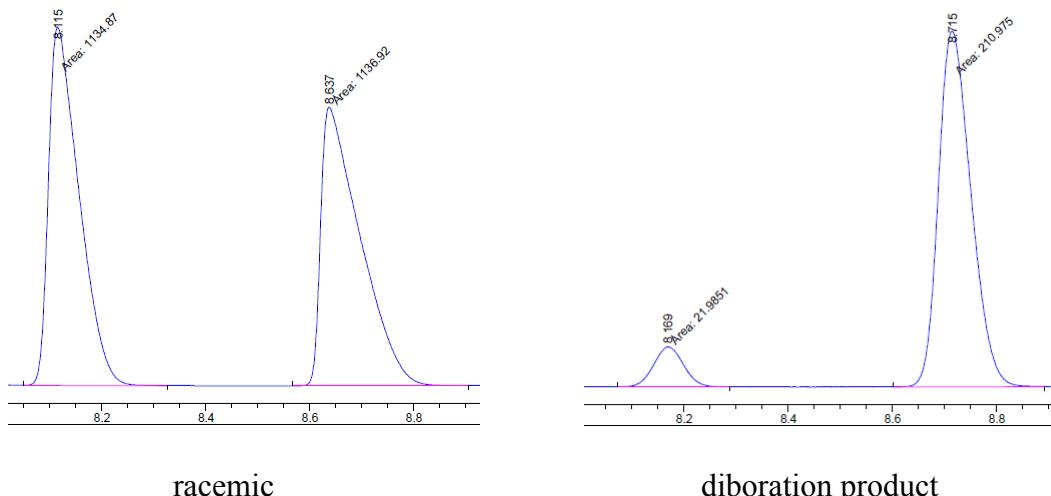


**(S)-1-(4-(trifluoromethyl)phenyl)ethane-1,2-diol (24).** The diboration was performed according to the general procedure with 4-(trifluoromethyl)styrene (34.8 mg, 200.0  $\mu$ mol), Pt(dba)<sub>3</sub> (5.4 mg, 6.0  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (6.5 mg, 7.2  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (53.3 mg, 210.  $\mu$ mol) in tetrahydrofuran (0.20 mL, 1.0 M). The crude reaction mixture was purified on silica gel (0-60% ethyl acetate in hexanes) to afford a clear, colorless oil (30.4 mg, 74% yield).  $R_f$  = 0.18 (40% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>); <sup>1</sup>H NMR (500MHz, CDCl<sub>3</sub>):  $\delta$  1.96 (1H, br s), 2.59 (1H, br s), 3.63 (1H, dd, *J* = 11.5, 8.5 Hz), 3.80 (1H, dd, *J* = 11.5, 3.0 Hz), 4.89 (1H, dd, *J* = 8.5, 3.5 Hz), 7.49 (2H, d, *J* = 8.0 Hz), 7.61 (2H, d, *J* = 8.0 Hz); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  67.9, 74.0, 125.1 (q), 125.4, 125.5, 130.3 (q), 144.4; IR (neat): 3396.7 (br m), 3317.0 (br m), 2926.6 (w), 1406.8 (w), 1322.5 (s), 1231.0 (w), 1173.8 (s), 125.8 (s), 1093.6 (m), 1064.9 (s), 1033.4 (m), 1017.0 (m), 895.3 (m), 837.7 (s), 762.2 (w), 681.8 (w), 636.0 (w), 607.3 (m), 523.1 (m), 429.3 (w) cm<sup>-1</sup>. HRMS-(ESI+) for C<sub>9</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>2</sub> [M+NH<sub>4</sub>]: calculated: 224.0898, found: 224.0906.  $[\alpha]_D^{20}$  = +30.564 (*c* = 1.265, CHCl<sub>3</sub>, *l* = 50 mm).

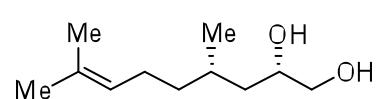
#### Analysis of stereochemistry:

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-(3-(trifluoromethyl)phenyl)ethane-1,2-diol prepared from treatment of 4-(trifluoromethyl)styrene with osmium tetroxide and 4-methylmorpholine *N*-oxide. The absolute stereochemistry was assigned by analogy.

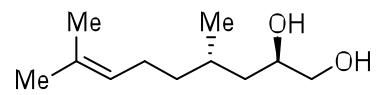
Chiral GLC ( $\beta$ -dex, Supelco, 140 °C, 20 psi, s/r = 35:1) – analysis of the acetonide of 1-(4-(trifluoro-methyl)phenyl)ethane-1,2-diol.



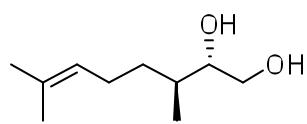
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	8.169	MM	0.0667	21.98512	5.49291	9.43729
2	8.715	MM	0.0723	210.97491	48.62221	90.56271



**(2S,4S)-4,8-dimethylnon-7-ene-1,2-diol (25).** The diboration was performed according to the general procedure with (*S*)-4,8-dimethylnona-1,7-diene (100.0 mg, 656.7  $\mu$ mol), Pt(dba)<sub>3</sub> (5.9 mg, 6.6  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (7.2 mg, 7.9  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (175.1 mg, 689.5  $\mu$ mol) in tetrahydrofuran (1.3 mL, 0.5 M). The crude reaction mixture was purified on silica gel (20-40% ethyl acetate in hexanes) to afford the product as a clear, colorless oil (97.7 mg, 80% yield).  $R_f$  = 0.32 (50% ethyl acetate in hexane, stain in KMnO<sub>4</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.92 (3H, d, *J* = 6.5 Hz), 1.09-1.16 (1H, m), 1.28-1.42 (3H, m), 1.58 (3H, s), 1.66 (3H, s), 1.53-1.61 (1H, m), 1.88-2.02 (2H, m), 3.38 (1H, dd, *J* = 11.0, 8.0 Hz), 3.62 (1H, dd, *J* = 11.0, 3.0 Hz), 3.77-3.82 (1H, m), 5.05-5.08 (1H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  20.1, 25.3, 25.7, 29.2, 29.4, 36.7, 40.5, 66.9, 70.5, 124.6, 135.3; IR (neat): 3363.4 (m), 2954.5 (m), 2924.6 (s), 2872.2 (m), 1457.4 (m), 1376.9 (s), 1145.0 (m), 1110.0 (m), 1063.3 (s), 1031.9 (m), 949.9 (w), 884.8 (w) cm<sup>-1</sup>; HRMS-(ESI<sup>+</sup>) for C<sub>11</sub>H<sub>23</sub>O<sub>2</sub> [M+H]<sup>+</sup>: calculated: 187.1698, found: 187.1693.  $[\alpha]_D^{20}$  = -4.866 (*c* = 3.435, CHCl<sub>3</sub>, *l* = 50 mm). The diasteriomic ratio was determined by <sup>1</sup>H NMR spectroscopy. The relative stereochemistry was assigned by analogy.



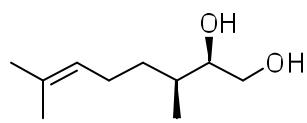
**(2R,4S)-4,8-dimethylnon-7-ene-1,2-diol (26).** The diboration was performed according to the representative procedure with (*S*)-4,8-dimethylnona-1,7-diene (100.0 mg, 656.7  $\mu$ mol), Pt(dba)<sub>3</sub> (5.9 mg, 6.6  $\mu$ mol), (*S,S*)-3,5-diisopropylphenylTADDOLPPh (7.2 mg, 7.9  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (175.1 mg, 689.5  $\mu$ mol) in tetrahydrofuran (1.3 mL, 0.5 M). The crude reaction mixture was purified on silica gel (20-40% ethyl acetate in hexanes) to afford a clear, colorless oil that could not be separated from pinacol (88.8 mg, 73% yield).  $R_f$  = 0.36 (50% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.89 (3H, d, *J* = 7.0 Hz), 1.02-1.12 (1H, m), 1.14-1.23 (1H, m), 1.27-1.34 (1H, m), 1.42-1.48 (1H, m), 1.57 (3H, s), 1.59-1.68 (1H, m), 1.65 (3H, s), 1.90-2.02 (2H, m), 2.32 (2H, br s), 3.38 (1H, ddd, *J* = 11.0, 7.5, 1.0 Hz), 3.59 (1H, d, *J* = 11.0 Hz), 3.76-3.81 (1H, m), 5.05-5.08 (1H, m); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  17.6, 19.1, 25.4, 25.7, 28.7, 37.8, 40.2, 67.4, 70.1, 124.6, 131.3; IR (neat): 3363.1 (s), 2926.6 (s), 2872.6 (m), 1457.0 (m), 1377.0 (s), 1145.1 (m), 1065.3 (s), 1027.0 (m), 973.0 (m), 949.8 (m), 736.4 (m) cm<sup>-1</sup>; HRMS-(ESI<sup>+</sup>) for C<sub>11</sub>H<sub>23</sub>O<sub>2</sub> [M+H]<sup>+</sup>: calculated: 187.1698, found: 187.1703.  $[\alpha]_D^{20}$  = +2.930 (*c* = 5.740, CHCl<sub>3</sub>, *l* = 50 mm). The diasteriomic ratio was determined by <sup>1</sup>H NMR spectroscopy. The relative stereochemistry was assigned by analogy.



**(2S,3S)-3,7-dimethyloct-6-ene-1,2-diol (27).** The diboration was performed according to the general procedure with (*S*)-3,8-dimethylnona-1,7-diene (50.0 mg, 361.7  $\mu$ mol), Pt(dba)<sub>3</sub> (9.7 mg, 10.8  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (11.8 mg, 13.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (96.0 mg, 378  $\mu$ mol) in tetrahydrofuran (0.35 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-65% ethyl acetate in hexanes) to afford a clear, colorless oil that could not be separated from pinacol (41.7 mg, 67% yield).  $R_f$  = 0.37 (50% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>). The diasteriomic ratio was determined by <sup>1</sup>H NMR spectroscopy. Spectral data are in accordance with the literature.<sup>26</sup> HRMS-(ESI+) for C<sub>10</sub>H<sub>21</sub>O<sub>2</sub> [M+H]: calculated: 173.1542, found: 173.1539.  $[\alpha]_D^{20}$  = -9.284 ( $c$  = 1.025, CHCl<sub>3</sub>,  $l$  = 50 mm).

**Proof of stereochemistry:**

The relative configuration was assigned by comparison of the <sup>13</sup>C NMR and <sup>1</sup>H NMR spectrum with that reported in the literature.<sup>26</sup>

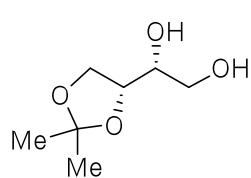


**(2R,3S)-3,7-dimethyloct-6-ene-1,2-diol (28).** The diboration was performed according to the general procedure with (*S*)-3,8-dimethylnona-1,7-diene (50.0 mg, 362  $\mu$ mol), Pt(dba)<sub>3</sub> (9.7 mg, 11  $\mu$ mol), (*S,S*)-3,5-diisopropylphenylTADDOLPPh (11.8 mg, 13.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (96.0 mg, 378.0  $\mu$ mol) in tetrahydrofuran (0.35 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-65% ethyl acetate in hexanes) to afford a clear, colorless oil that could not be separated from pinacol (43.0 mg, 69% yield).  $R_f$  = 0.35 (50% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>). The diasteriomic ratio was determined by <sup>1</sup>H NMR spectroscopy. Spectral data are in accordance with the literature.<sup>26</sup> HRMS-(ESI+) for C<sub>10</sub>H<sub>21</sub>O<sub>2</sub> [M+H]: calculated: 173.1542, found: 173.1541.  $[\alpha]_D^{20}$  = -14.893 ( $c$  = 1.045, CHCl<sub>3</sub>,  $l$  = 50 mm).

**Proof of stereochemistry:**

The relative configuration was assigned by comparison of the <sup>13</sup>C NMR and <sup>1</sup>H NMR spectrum with that reported in the literature.<sup>26</sup>

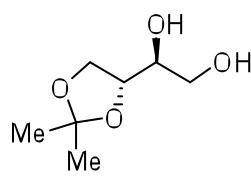
<sup>26</sup> Miyazawa, M.; Marumoto, S.; Masuda, A.; Kano, H.; Takechi, H. *J. Agric. Food Chem.* **2009**, *57*, 7800.



**(R)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)ethane-1,2-diol (29).** The dibor-ation was performed according to the general procedure with (*S*)-2,2-dimethyl-4-vinyl-1,3-dioxolane (60.0 mg, 468.1  $\mu$ mol), Pt(dba)<sub>3</sub> (12.6 mg, 14.0  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (15.3 mg, 16.9  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (124.8 mg, 491.5  $\mu$ mol) in tetrahydrofuran (0.46 mL, 1.0 M). The crude reaction mixture was purified on silica gel (50-80% ethyl acetate in hexanes, stain in KMnO<sub>4</sub>) to afford the product as a clear, colorless oil (41.8 mg, 55% yield). The diasteriomic ratio was determined by <sup>1</sup>H NMR spectroscopy. Spectral data are in accordance with the literature.<sup>27</sup> HRMS-(ESI+) for C<sub>10</sub>H<sub>21</sub>O<sub>2</sub> [M+H]: calculated: 173.1542, found: 173.1541.  $[\alpha]_D^{20} = +1.791$  ( $c = 0.335$ , CHCl<sub>3</sub>,  $l = 50$  mm).

**Proof of stereochemistry:**

The relative configuration was assigned by comparison of the <sup>13</sup>C NMR and <sup>1</sup>H NMR spectrum with that reported in the literature.<sup>27</sup>



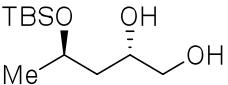
**(S)-1-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)ethane-1,2-diol (31).** The dibor-ation was performed according to the general procedure with (*S*)-2,2-dimethyl-4-vinyl-1,3-dioxolane (60.0 mg, 468  $\mu$ mol), Pt(dba)<sub>3</sub> (12.6 mg, 14.0  $\mu$ mol), (*S,S*)-3,5-diisopropylphenylTADDOLPPh (15.3 mg, 16.9  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (124.8 mg, 491.5  $\mu$ mol) in tetrahydrofuran (0.46 mL, 1.0 M). The crude reaction mixture was purified on silica gel (50-80% ethyl acetate/hexanes, stain in KMnO<sub>4</sub>) to afford the product as a clear, colorless oil (38.7 mg, 51% yield). The diasteriomic ratio was determined by <sup>1</sup>H NMR spectroscopy. Spectral data are in accordance with the literature.<sup>28</sup> HRMS-(ESI+) for C<sub>7</sub>H<sub>15</sub>O<sub>4</sub> [M+H]: calculated: 163.0970, found: 163.0972.  $[\alpha]_D^{20} = +12.6082$  ( $c = 0.720$ , CHCl<sub>3</sub>,  $l = 50$  mm).

**Proof of stereochemistry:**

The relative configuration was assigned by comparison of the <sup>13</sup>C NMR and <sup>1</sup>H NMR spectrum with that reported in the literature.<sup>28</sup>

<sup>27</sup> Cren, S.; Wilson, C.; Thomas, N.R.; *Org. Lett.*, **2005**, 7, 3521.

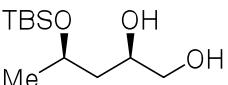
<sup>28</sup> Wroblewski, A.E.; Karolczak, W.; *Tetrahedron*, **2003**, 59, 6075.



**(2S,4R)-4-((tert-butyldimethylsilyl)oxy)pentane-1,2-diol (30).** The diboration was performed according to the general procedure with (*R*)-tert-butyldimethyl(pent-4-en-2-yloxy)silane (120.2 mg, 600.0  $\mu$ mol), Pt(dba)<sub>3</sub> (5.4 mg, 6.0  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (6.5 mg, 7.2  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (160.0 mg, 630.0  $\mu$ mol) in tetrahydrofuran (0.60 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate/hexanes, stain in PMA) to afford the product as a clear, colorless oil that could not be separated from pinacol (174.9 mg, 1:0.885 product:pinacol = 86% yield). The diasteriomic ratio was determined by <sup>1</sup>H NMR spectroscopy. Spectral data are in accordance with the literature.<sup>29</sup> <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  68.9, 67.3, 67.1, 40.1, 25.7, 22.8, 17.9, -4.6, -5.1; IR (neat): 3382.0 (br m), 2929.9 (m), 2857.4 (m), 1462.9 (w), 1375.2 (m), 1254.2 (m), 1106.1 (s), 1032.2 (s), 834.1 (s), 773.7 (s), 664.8 (w) cm<sup>-1</sup>; HRMS-(ESI<sup>+</sup>) for C<sub>11</sub>H<sub>27</sub>O<sub>3</sub>Si [M+H]: calculated: 235.1730, found: 235.1723.  $[\alpha]_D^{20} = -24.307$  (*c* = 3.233, CHCl<sub>3</sub>, *l* = 50 mm).

**Proof of stereochemistry:**

The relative configuration was assigned by comparison of the <sup>13</sup>C NMR and <sup>1</sup>H NMR spectrum with that reported in the literature.<sup>29</sup>



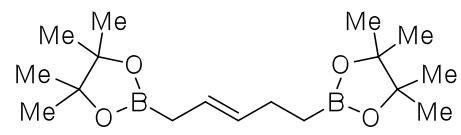
**(2R,4R)-4-((tert-butyldimethylsilyl)oxy)pentane-1,2-diol (32).** The diboration was performed according to the general procedure with (*R*)-tert-butyldimethyl(pent-4-en-2-yloxy)silane (120.2 mg, 600.0  $\mu$ mol), Pt(dba)<sub>3</sub> (5.4 mg, 6.0  $\mu$ mol), (*S,S*)-3,5-diisopropylphenylTADDOLPPh (6.5 mg, 7.2  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (160.0 mg, 630.0  $\mu$ mol) in tetrahydrofuran (0.60 mL, 1.0 M). The crude reaction mixture was purified on silica gel (30-70% ethyl acetate/hexanes, stain in PMA) to afford the product as a clear, colorless oil that could not be separated from pinacol (167.8 mg, 1:0.676 product:pinacol = 89% yield). The diasteriomic ratio was determined by <sup>1</sup>H NMR spectroscopy. Spectral data are in accordance with the literature.<sup>30</sup> <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  71.5, 69.5, 66.8, 41.9, 25.8, 24.4, 17.9, -3.9, -4.9; IR (neat): 3380.2 (br m), 2929.5 (m), 2857.0 (m), 1462.6 (w), 1373.5 (m), 1253.9 (m), 1150.0 (m), 1037.9 (m), 833.6 (s), 773.9 (s), 664.8 (w) cm<sup>-1</sup>; HRMS-(ESI<sup>+</sup>) for C<sub>11</sub>H<sub>27</sub>O<sub>3</sub>Si [M+H]: calculated: 235.1730, found: 235.1727.  $[\alpha]_D^{20} = -25.027$  (*c* = 3.210, CHCl<sub>3</sub>, *l* = 50 mm).

**Proof of stereochemistry:**

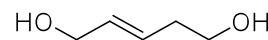
The relative configuration was assigned by comparison of the <sup>13</sup>C NMR and <sup>1</sup>H NMR spectrum with that reported in the literature.<sup>29</sup>

<sup>29</sup> Kumar, P.; Gupta, P.; Vasudeva Naida, S.; *Chem. Eur. J.* **2006**, *12*, 1397.

<sup>30</sup> Kumar, P.; Gupta, P.; Vasudeva Naida, S.; *Chem. Eur. J.* **2006**, *12*, 1397.



**2,2'-(pent-2-ene-1,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-di-oxaborolane) (44).** The diboration was performed according to the general procedure with vinylcyclopropane (52.0 mg, 764  $\mu$ mol), Pt(dba)<sub>3</sub> (6.9 mg, 7.6  $\mu$ mol), (*R,R*)-3,5-diisopropylphenylTADDOLPPh (8.2 mg, 9.2  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (203.7 mg, 802.0  $\mu$ mol) in tetrahydrofuran (0.76 mL, 1.0 M). The crude reaction mixture was concentrated *in vacuo* to afford the crude product as a pale yellow oil (crude mass=258.9 mg). The crude material was characterized prior to oxidation. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): **mixture of isomers**  $\delta$  5.45-5.34 (2H, m), 2.18-2.02 (2H, m), 2.68-2.58 (2H, m), 1.30-1.11 (24H, m), 0.82-0.78 (2H, m) <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): **mixture of isomers**  $\delta$  132.6, 131.9, 123.7 123.1, 83.4, 83.1, 83.0, 82.8, 26.9, 24.98, 24.90, 24.86, 24.79, 24.72, 24.51, 21.4; HRMS-(ESI<sup>+</sup>) for C<sub>17</sub>H<sub>33</sub>B<sub>2</sub>O<sub>4</sub> [M+H]: calculated: 323.2565, found: 323.2562.



**pent-2-ene-1,5-diol.** The oxidation was performed on (44) according to the general procedure for oxidation of 1,2-diols. The crude reaction mixture was purified on silica gel (0-10% methanol in ethyl acetate, stain in PMA) to afford a clear, colorless oil (78.0 mg, 64% yield, *trans:cis* isomer = 3.8:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): **Z-isomer:**  $\delta$  5.85 (1H, dt, *J* = 11.0 Hz, 7.0 Hz), 5.59 (1H, dt, *J* = 11.0 Hz, 8.0 Hz), 4.14 (2H, d, *J* = 7.0 Hz), 3.68-3.64 (2H, t, overlaps with *E*-isomer), 2.36 (2H, dt, *J* = 7.0 Hz, 7.0 Hz), 1.22 (1H, br s); **E-isomer:**  $\delta$  5.72 (1H, dt, *J* = 5.5 Hz, 15 Hz), 5.67 (1H, dt, *J* = 6.5 Hz, 15.0 Hz), 4.10 (2H, d, *J* = 5.5 Hz), 3.66 (2H, t, *J* = 6.5 Hz), 2.31 (2H, dt, *J* = 6.5 Hz, 6.5 Hz), 1.84 (1H, br s); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): **mixture of isomers**  $\delta$  132.1, 131.5, 129.6, 128.7, 63.5, 61.8, 61.2, 57.8, 35.5, 30.5; IR (neat): 3314.1 (br s), 2923.6 (s), 2858.4 (s), 1457.9 (m), 1421.0 (m), 1085.8 (s), 999.3 (s), 970.4 (s), 697.8 (w), 670.8 (w), 631.5 (w), 413.5 (w) cm<sup>-1</sup>; HRMS-(ESI<sup>+</sup>) for C<sub>5</sub>H<sub>14</sub>NO<sub>2</sub> [M+NH<sub>4</sub>]: calculated: 120.1025, found: 120.1021.

### VIII. Catalyst activation experiments

To an oven-dried J. Young tube in the dry box was added Pt(dba)<sub>3</sub> (20.0 mg, 22.3  $\mu$ mol) and d<sup>8</sup>-THF (1.0 mL). The tube was capped and removed from the dry box. The solution was analyzed by <sup>1</sup>H NMR, and the tube was returned to the dry box. (R,R)-3,5-diethylphenyl-TADDOLPPh (21.3 mg, 26.7  $\mu$ mol) was added, and the tube was sealed and removed from the dry box. After again analyzing the solution by <sup>1</sup>H NMR, the tube was returned to the dry box, and B<sub>2</sub>(pin)<sub>2</sub> (28.3 mg, 111  $\mu$ mol) was added. The tube was once again removed from the glovebox and analyzed by <sup>1</sup>H NMR. The reaction mixture was then heated in the J. Young tube to 80 °C in an oil bath for 30 minutes. The tube was cooled to room temperature, and analyzed by <sup>1</sup>H NMR, indicating full consumption of dibenzylideneacetone and formation of 2-((1,5-diphenyl-1-(pinacolborolanyl)penta-1,4-dien-3-yl)oxy)-pinacolborolane.

### IX. Calorimeter Experiments

#### *Representative procedure for diboration reactions in calorimeter studies.*

To an oven-dried reaction calorimeter vial equipped with a magnetic stir bar was added Pt(dba)<sub>3</sub> (6.9 mg, 7.6  $\mu$ mol), (R,R)-3,5-diethylphenyl-TADDOLPPh (8.3 mg, 8.0  $\mu$ mol), and B<sub>2</sub>(pin)<sub>2</sub> (203.7 mg, 802.1  $\mu$ mol) on the benchtop. The vial was sealed with a septum cap and purged with N<sub>2</sub>. Tetrahydrofuran (0.8 mL, 1.0 M) was then added *via* syringe under N<sub>2</sub>. The N<sub>2</sub> line was removed and the reaction mixture was heated to 80 °C in an oil bath for 20 minutes. The reaction mixture was cooled to room temperature and placed in the Omnical SuperCRC calorimeter. To the reference vial was added tetrahydrofuran (0.8 mL) and B<sub>2</sub>(pin)<sub>2</sub> (203.7 mg, 802.1  $\mu$ mol). The reference vial was then placed in the calorimeter. 1-Tetradecene (194  $\mu$ L, 764  $\mu$ mol) was taken up in a 250  $\mu$ L gas-tight glass syringe, and the syringe was placed into the sample syringe inlet. Another sample of 1-tetradecene (194  $\mu$ L, 764  $\mu$ mol) was taken up in a separate 250  $\mu$ L gas-tight glass syringe, and the syringe was placed into the reference syringe inlet. The system was then thermostated to 60 °C and was allowed to stand for 1 hour to reach thermal equilibrium. The reaction was initiated by addition of 1-tetradecene to both the reaction vial and the reference vial simultaneously and all at once *via* microsyringe, with minimal disturbance of the calorimeter. The microsyringe was not removed from the vial. The top of the calorimeter was then fully insulated, and the reaction was allowed to run without disturbance until the heat evolved from the reaction returned to baseline. After the reaction was complete and the instrument was re-equilibrated, a correction factor to account for heat flow lag of the instrument was performed. Data from the calorimeter was then analyzed using Microsoft Excel.

### X. Determination of $^{12}\text{C}/^{13}\text{C}$ Kinetic Isotope Effect<sup>31,32</sup>

#### Sample Collection for Determination of $^{12}\text{C}/^{13}\text{C}$ Kinetic Isotope Effect

To an oven-dried 50 mL round-bottomed flask equipped with a magnetic stir bar in the dry box was added Pt(dbu)<sub>3</sub> (137 mg, 152  $\mu\text{mol}$ ), (R,R)-3,5-di-*iso*-propylphenyl-TADDOLPPh (115 mg, 127  $\mu\text{mol}$ ), B<sub>2</sub>(pin)<sub>2</sub> (3.87 g, 15.2 mmol), and tetrahydrofuran (12.7 mL, 1.0 M). The vial was sealed with a septum, taped, and brought out of the dry box. The reaction mixture was heated to 80 °C in an oil bath for 25 minutes. The flask was cooled to room temperature and brought back into the dry box. To the reaction flask was added distilled and degassed allylbenzene (1.50 g, 12.7 mmol). The flask was sealed once more, taped, brought out of the dry box, and then allowed to stir at 60 °C for 55 minutes. The progress of the reaction was previously monitored by <sup>1</sup>H NMR spectroscopy. The reaction mixture was cooled to 0 °C (ice/water) and charged with 3 M sodium hydroxide (45 mL), and 30% hydrogen peroxide (20 mL). The reaction was gradually warmed to room temperature and allowed to stir for 3 hours at which time the vial was cooled to 0 °C (ice/water) and saturated aqueous sodium thiosulfate was added dropwise over 5 minutes. The reaction mixture was diluted with ethyl acetate and the aqueous and organic layers were separated. The aqueous layer was washed with ethyl acetate (3 x 15 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated by rotary evaporation. The conversion was determined by <sup>1</sup>H NMR to be 83 ± 3%. The resulting residue was purified on silica gel (0-65% ethyl acetate in hexanes) to yield 247 mg of recovered starting material. Labeled as **Trial 1**.

This process was repeated with a second sample from the same source of starting material. This reaction proceeded to 81% ± 3% completion, and 274 mg of starting material was recovered. Labeled as **Trial 2**.

#### $^{13}\text{C}$ NMR measurements.

Purified samples of the recovered starting material (**42**) and standard (**42**) were analyzed individually by <sup>13</sup>C NMR spectroscopy, following Singleton's protocol. The spectra were acquired using a Varian Unity Inova 500 MHz spectrometer (125 MHz, CDCl<sub>3</sub>) at 25 °C with inverse-gated decoupling and acquisition time of 4.920 s collecting 300000 points. T1 values were determined prior to the acquisitions, and delays of 125 s (125s > 8 x T1, with the exception of C4, which had a T1 of 23.8 s) were utilized between pulses. Three independent acquisitions were obtained for each sample (~10 hour acquisition time). Each spectrum was manually integrated three times to ensure integration accuracy, utilizing minimal baseline and phase correction.

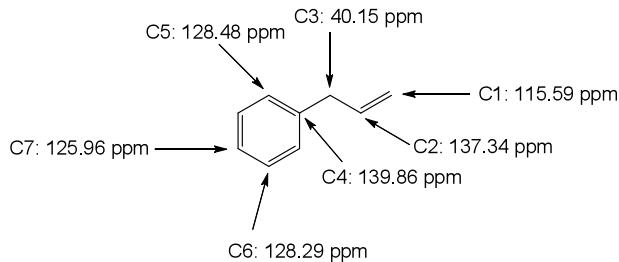
The integration of the recovered starting material (**42**) in comparison to the standard (**42**) for **Trial 1** and **Trial 2** are provided in Table S1. Table S2 contains the relative integration of the "enriched" sample (recovered starting material) to the "unreacted" or standard sample. This value is determined by  $R/R_0$ , where  $R$  = "enriched" integration and  $R_0$  = "unreacted" integration. The calculated  $^{12}\text{C}/^{13}\text{C}$  isotope effects, as obtained using equation (1), are provided in Table S3. Standard deviations were determined following reported procedures.<sup>31</sup>

<sup>31</sup> Singleton, D. A.; Thomas, A. A. *J Am. Chem. Soc.* **1995**, *117*, 9357.

<sup>32</sup> For Similar analyses, see: a) Frantz, D. E.; Singleton, D. A.; Snyder, J.P. *J. Am. Chem. Soc.* **1997**, *119*, 3383. b) Denmark, S. E.; Bui, T. *J. Org. Chem.* **2005**, *70*, 10393. c) Edwards, D. R.; Montoya-Perez, P.; Crudden, C. M. *Org. Lett.* **2007**, *9*, 5481. d) Gao, R.; Yi, C. S. *J. Org. Chem.* **2010**, *75*, 3144.

$$KIE = \frac{\ln(1-F)}{\ln[(1-F)R/R_0]} \quad (1)$$

$F$  = percent conversion of the substrate during diboration reaction (determined by  $^1\text{H}$  NMR spectroscopy)



**Table S1.** Average integrations for **Trial 1** and **Trial 2** for the diboration/oxidation of allylbenzene. The starting material was recovered after the reaction was run to  $83.6\pm3\%$  and  $81.4\%\pm3\%$  completion, respectively.

	C1	C2	C3	C4	C5	C6	C7
$^{13}\text{C}$ NMR $\delta$ (125 MHz, $\text{CDCl}_3$ )	115.59	137.34	40.15	139.86	128.48	128.29	125.96
<b>Control<sup>a</sup>- Spec. #1</b>	1047.18	920.98	1104.33	520.28	1988.43	1970.72	1000 (std)
Spec. #2	1049.67	921.61	1109.63	520.75	1998.67	1966.12	-
Spec. #3	1046.87	914.97	1106.77	521.03	1986.10	1968.78	-
<b>Control Avg.</b>	1047.91	919.19	1106.92	520.69	1991.07	1968.54	1000 (std)
Std. Dev. <sup>b</sup>	1.878	3.240	2.611	1.954	6.918	2.496	-
<b>Enriched Trial 1<sup>a</sup></b>							
Spec. #1	1069.92	943.65	1108.20	517.27	1991.45	1971.82	1000 (std)
Spec. #2	1069.73	944.42	1109.69	516.43	1986.42	1966.35	-
Spec. #3	1068.08	939.36	1107.94	521.09	1982.43	1966.00	-
<b>Enriched Avg.</b>	1069.24	942.48	1108.61	518.26	1986.77	1968.06	1000 (std)
Std. Dev. <sup>b</sup>	1.878	3.563	1.834	2.894	6.704	3.573	-
<b>Enriched Trial 2<sup>a</sup></b>							
Spec. #1	1070.48	940.89	1108.65	519.79	1987.91	1968.93	1000 (std)
Spec. #2	1070.45	939.23	1005.69	523.00	1991.41	1969.40	-
Spec. #3	1067.76	937.67	1113.31	523.28	1988.09	1972.99	-
<b>Enriched Avg.</b>	1069.76	939.26	1109.22	522.02	1989.14	1970.44	1000 (std)
Std. Dev. <sup>b</sup>	2.196	1.501	3.660	2.018	2.833	3.284	-

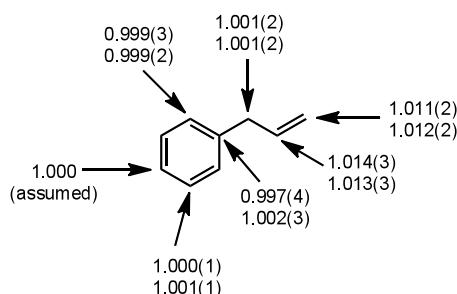
a) Each spectrum was integrated three times. The average value is provided. b) The standard deviation is from all integrated spectra (three for each run).

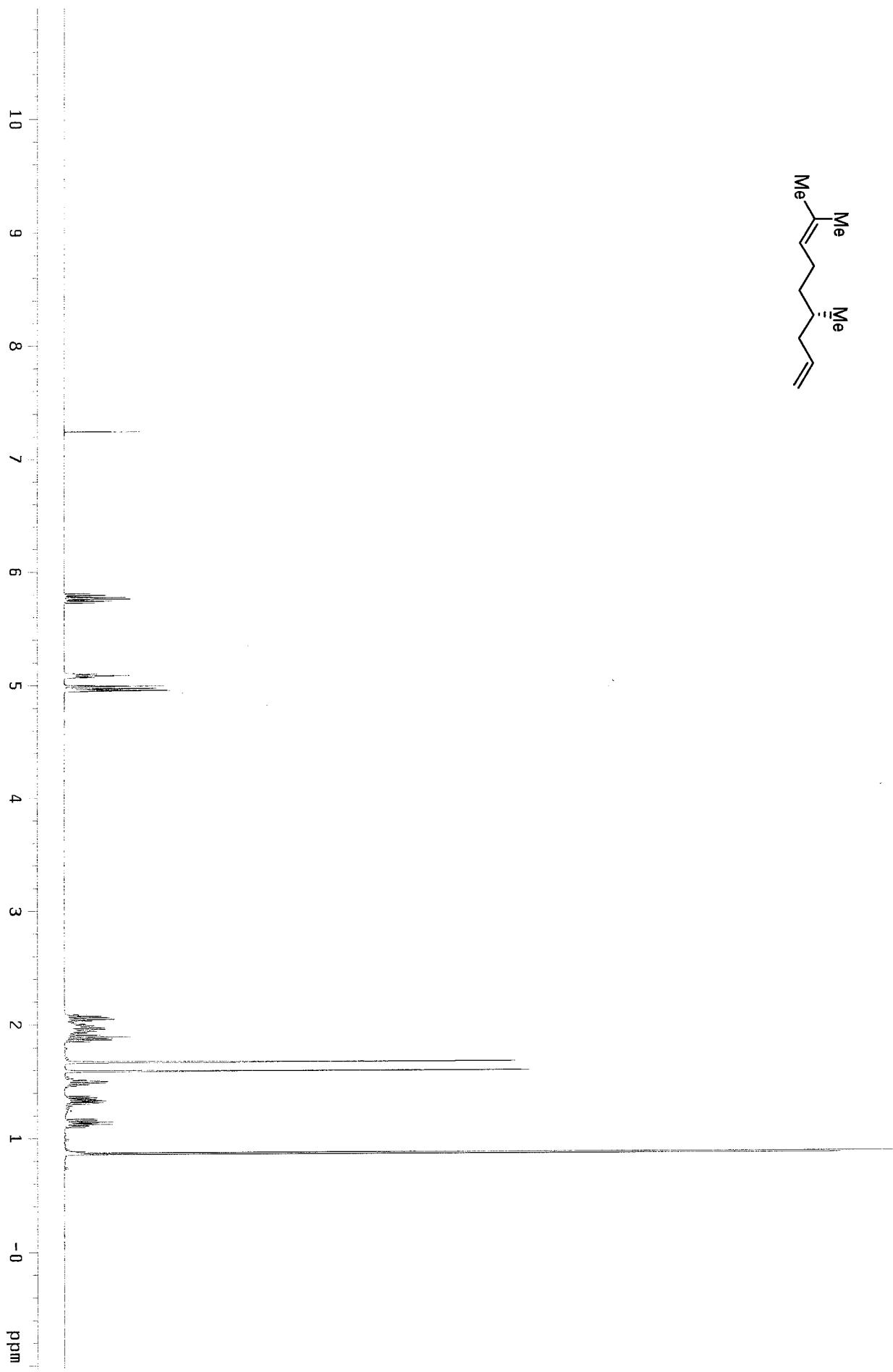
**Table S2.** Relative integrations of **Trial 1** and **Trial 2** for the diboration/oxidation of allylbenzene.

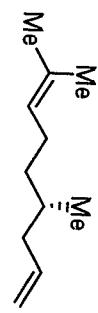
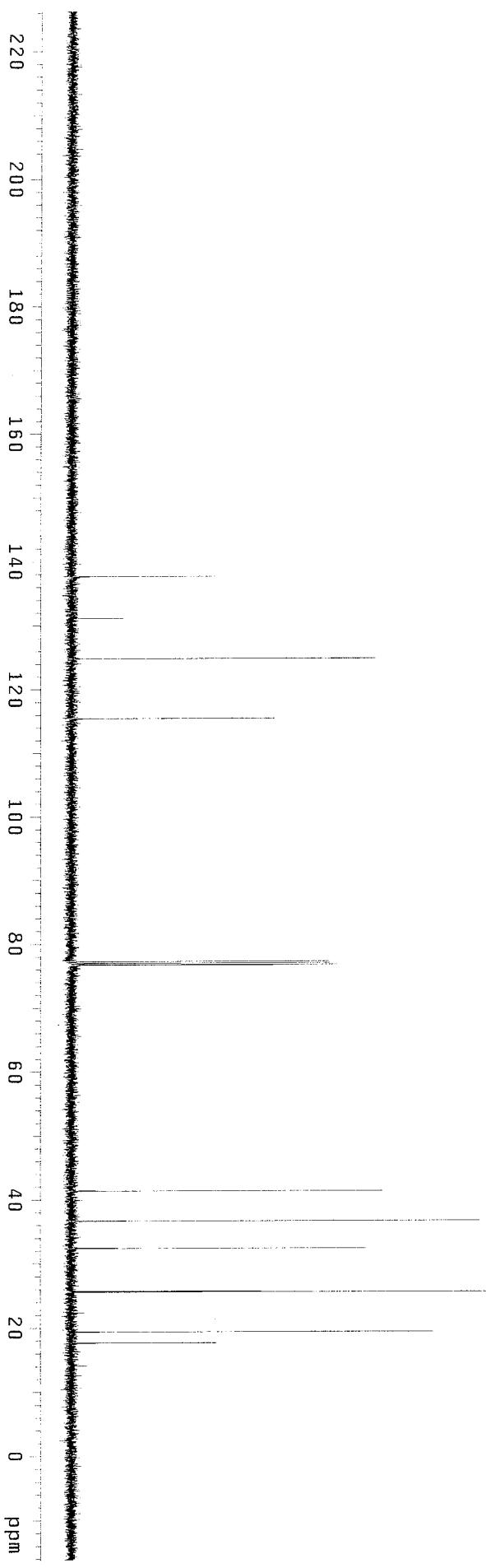
	C1	C2	C3	C4	C5	C6	C7
<sup>13</sup> C NMR δ (125 MHz, CDCl <sub>3</sub> )	115.59	137.34	40.15	139.86	128.48	128.29	125.96
<b>Control/Enriched</b> <b>(R/R<sub>0</sub>) - Trial 1</b>	1.0204	1.0253	1.0015	0.9951	0.9978	0.9998	1.0000
Std. Dev.	±0.0025	±0.0052	±0.0029	±0.0067	±0.0048	±0.0022	-
<b>Control/Enriched</b> <b>(R/R<sub>0</sub>) - Trial 2</b>	1.0207	1.0218	1.0022	1.0026	0.9990	1.0010	1.0000
Std. Dev.	±0.0028	±0.0040	±0.0041	±0.0054	±0.0038	±0.0021	-

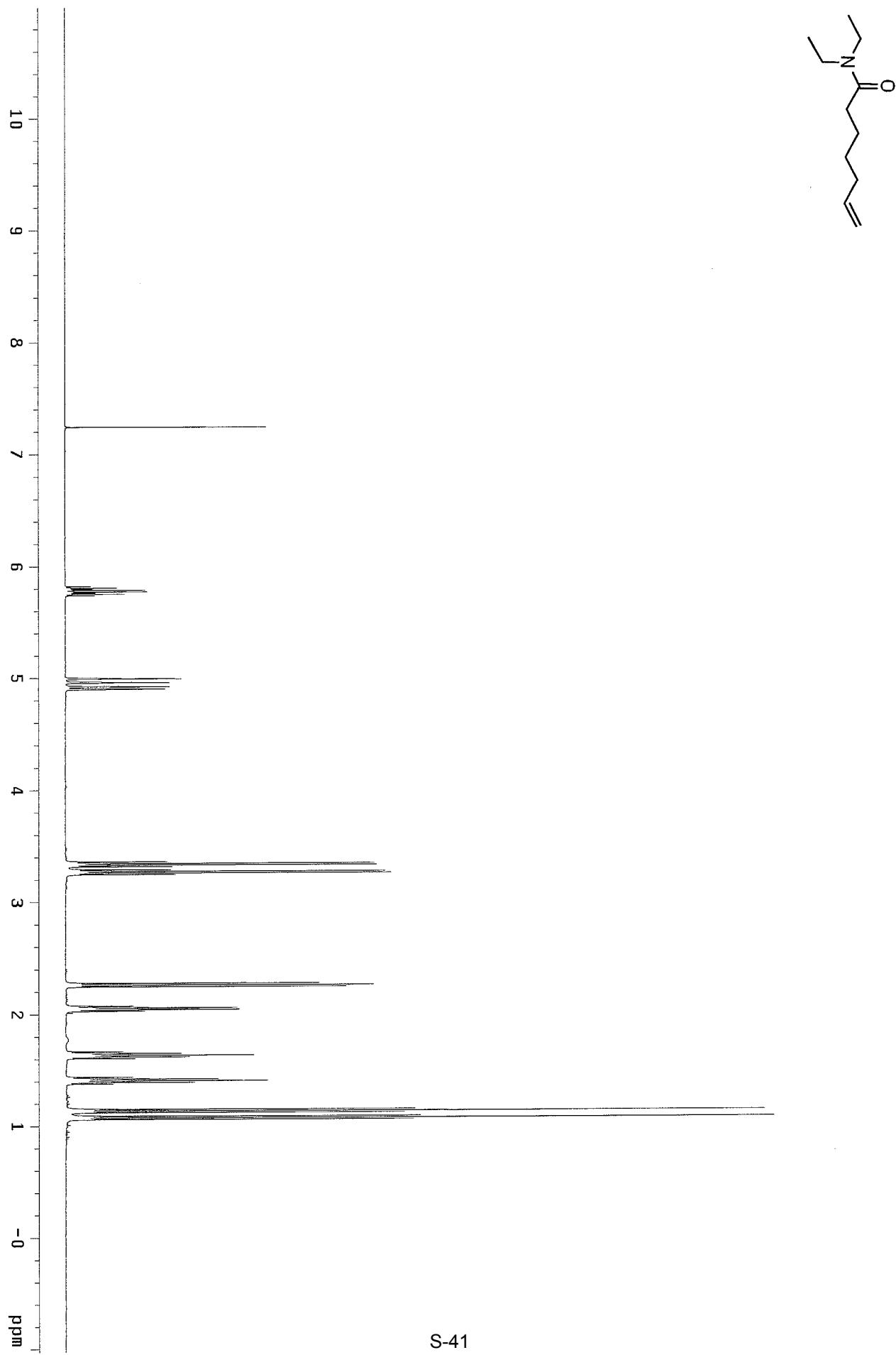
**Table S3.** Calculated <sup>12</sup>C/<sup>13</sup>C kinetic isotope effects for the diboration/oxidation of allylbenzene.

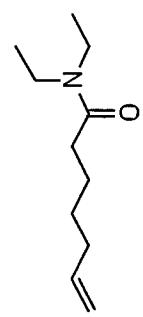
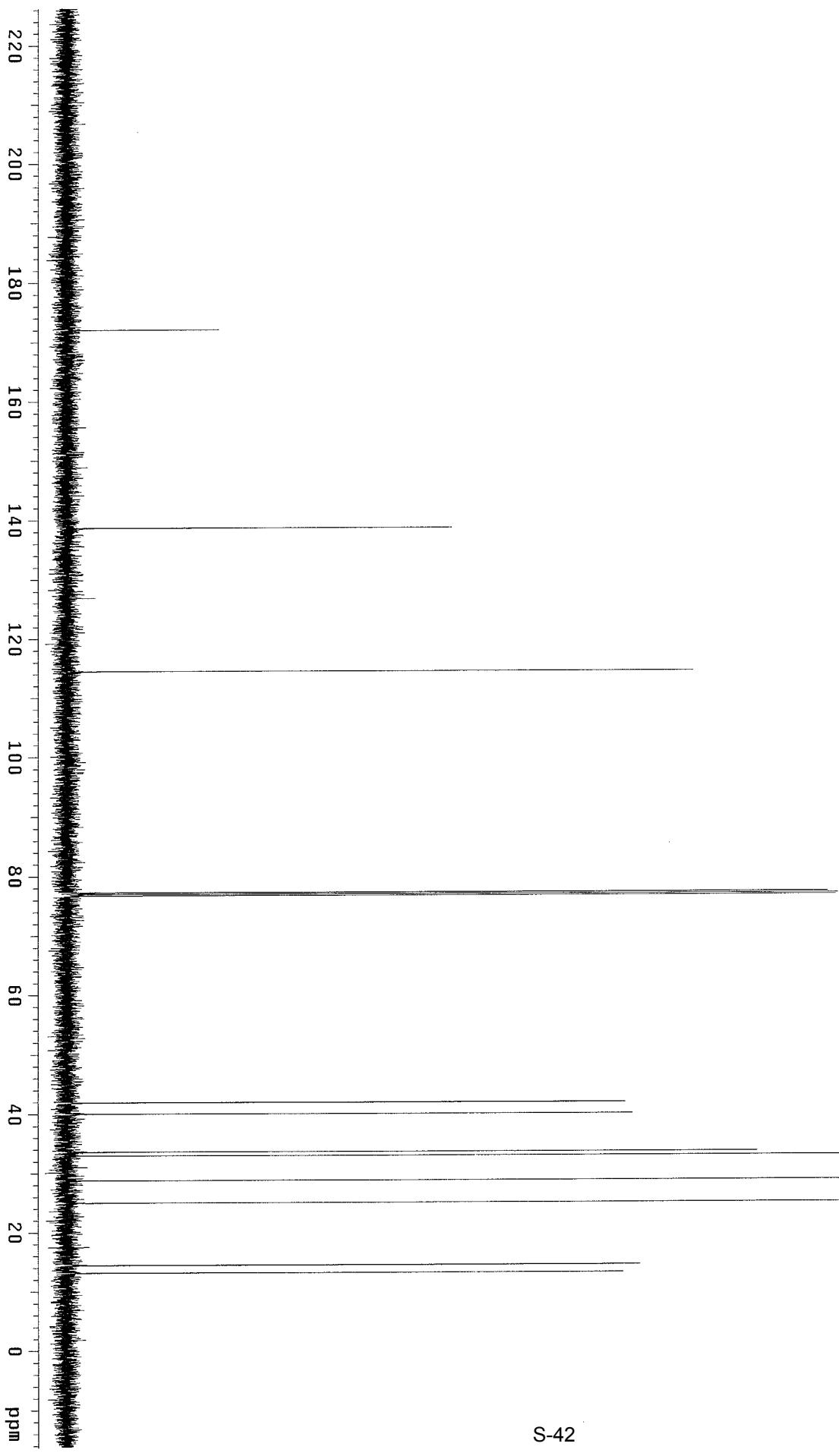
	C1	C2	C3	C4	C5	C6	C7
<sup>13</sup> C NMR δ (125 MHz, CDCl <sub>3</sub> )	115.59	137.34	40.15	139.86	128.48	128.29	125.96
<b>KIE (83.6 ± 3%)</b> <b>conv) - Trial 1</b>	1.0113	1.0140	1.0008	0.9973	0.9988	0.9999	1.0000
Std. Dev.	±0.0018	±0.0032	±0.0016	±0.0037	±0.0027	±0.0012	-
<b>KIE (81.4 ± 3%)</b> <b>conv) - Trial 2</b>	1.0123	1.0130	1.0013	1.0015	0.9994	1.0006	1.0000
Std. Dev.	±0.0020	±0.0027	±0.0024	±0.0032	±0.0022	±0.0012	-

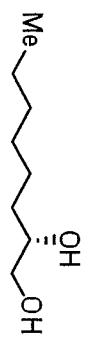
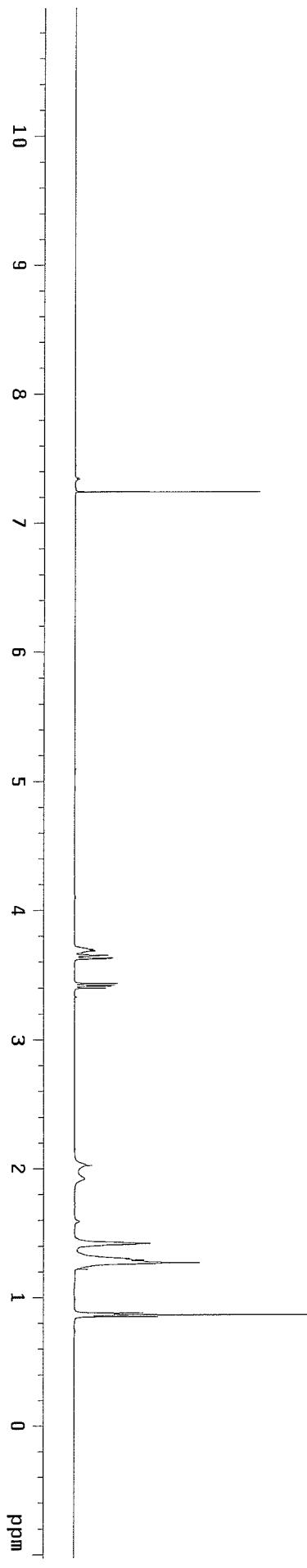
**Figure S1.** <sup>12</sup>C/<sup>13</sup>C kinetic isotope effects for each trial of the diboration/oxidation of allylbenzene.

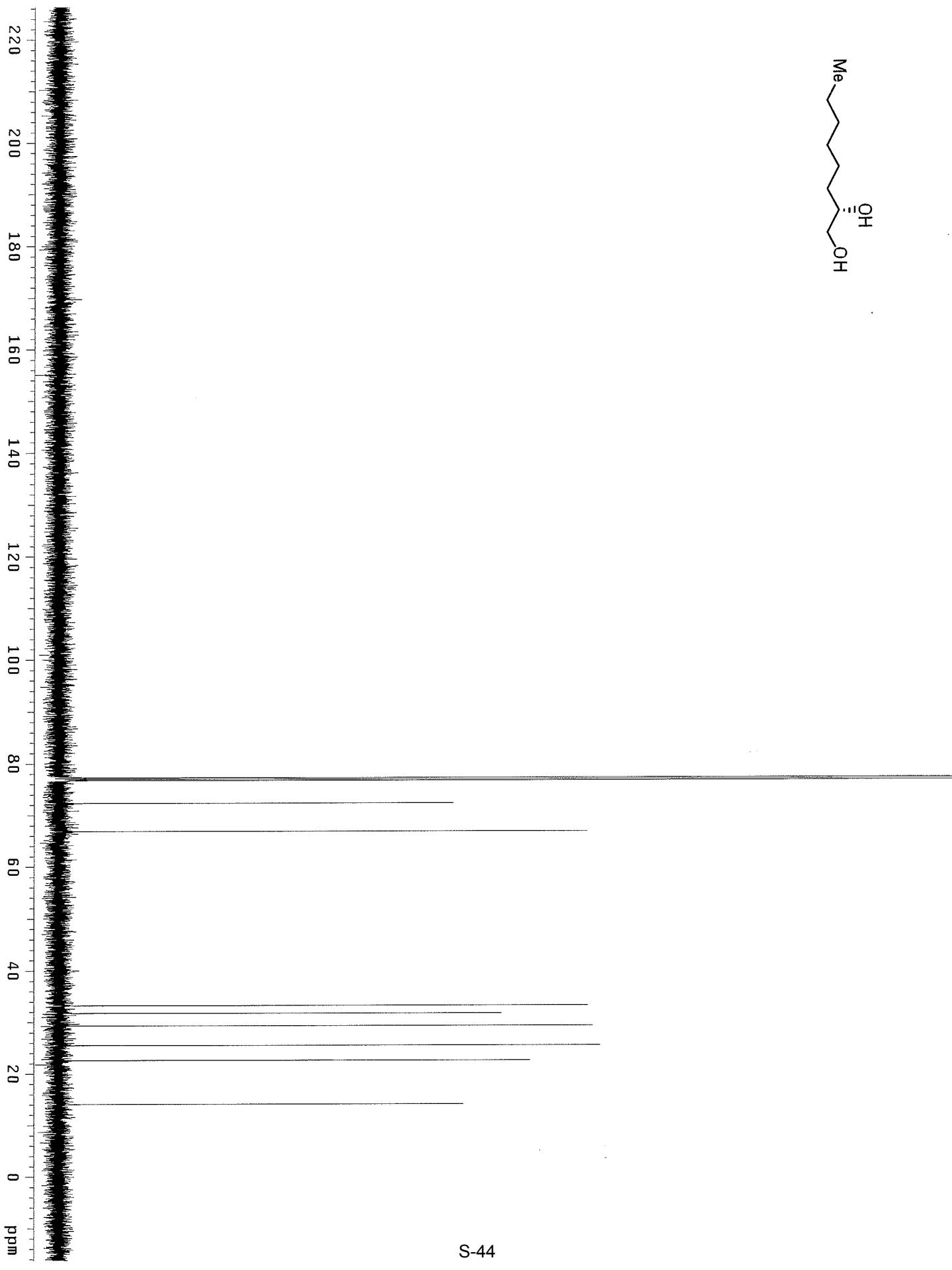


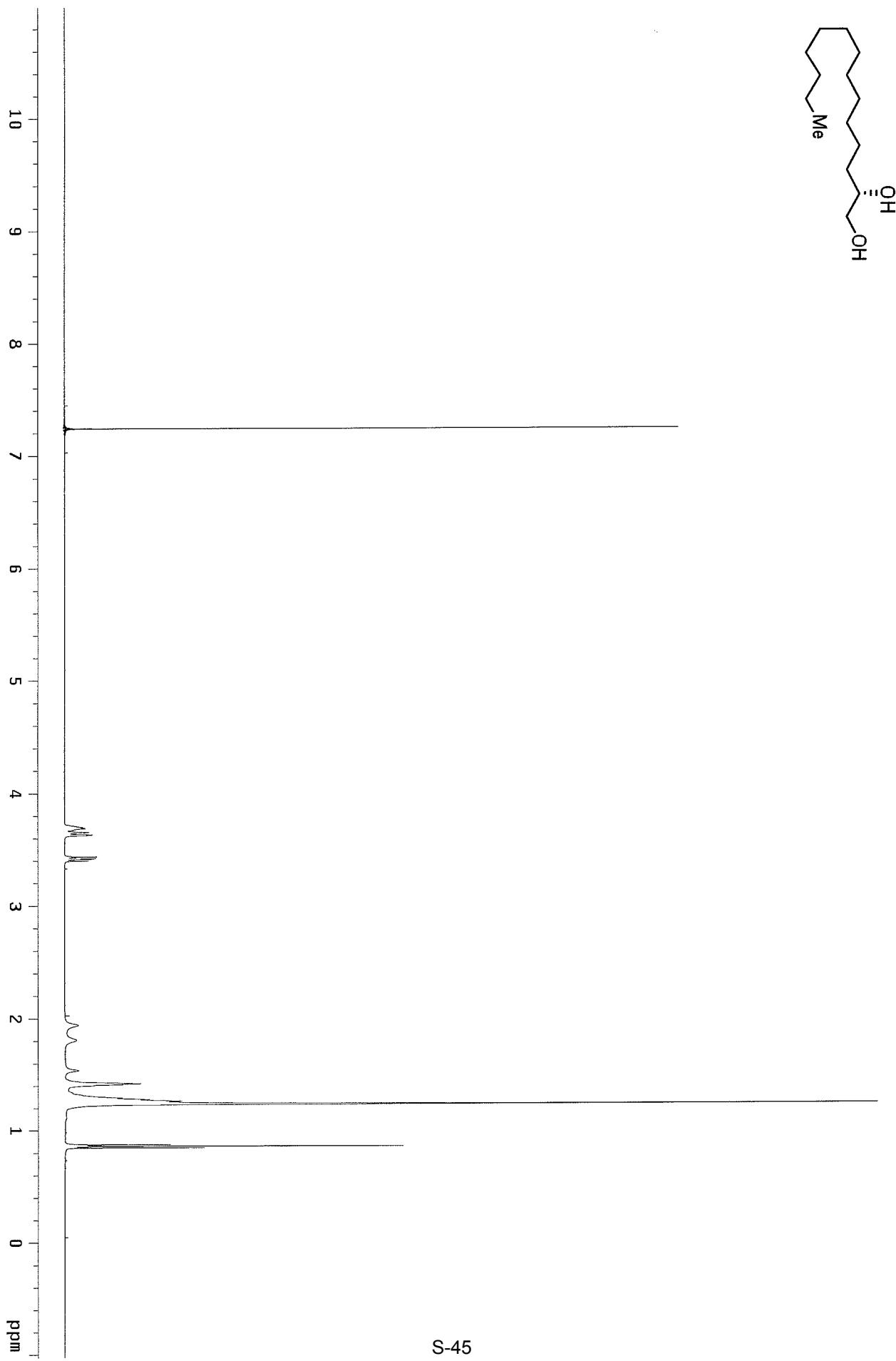


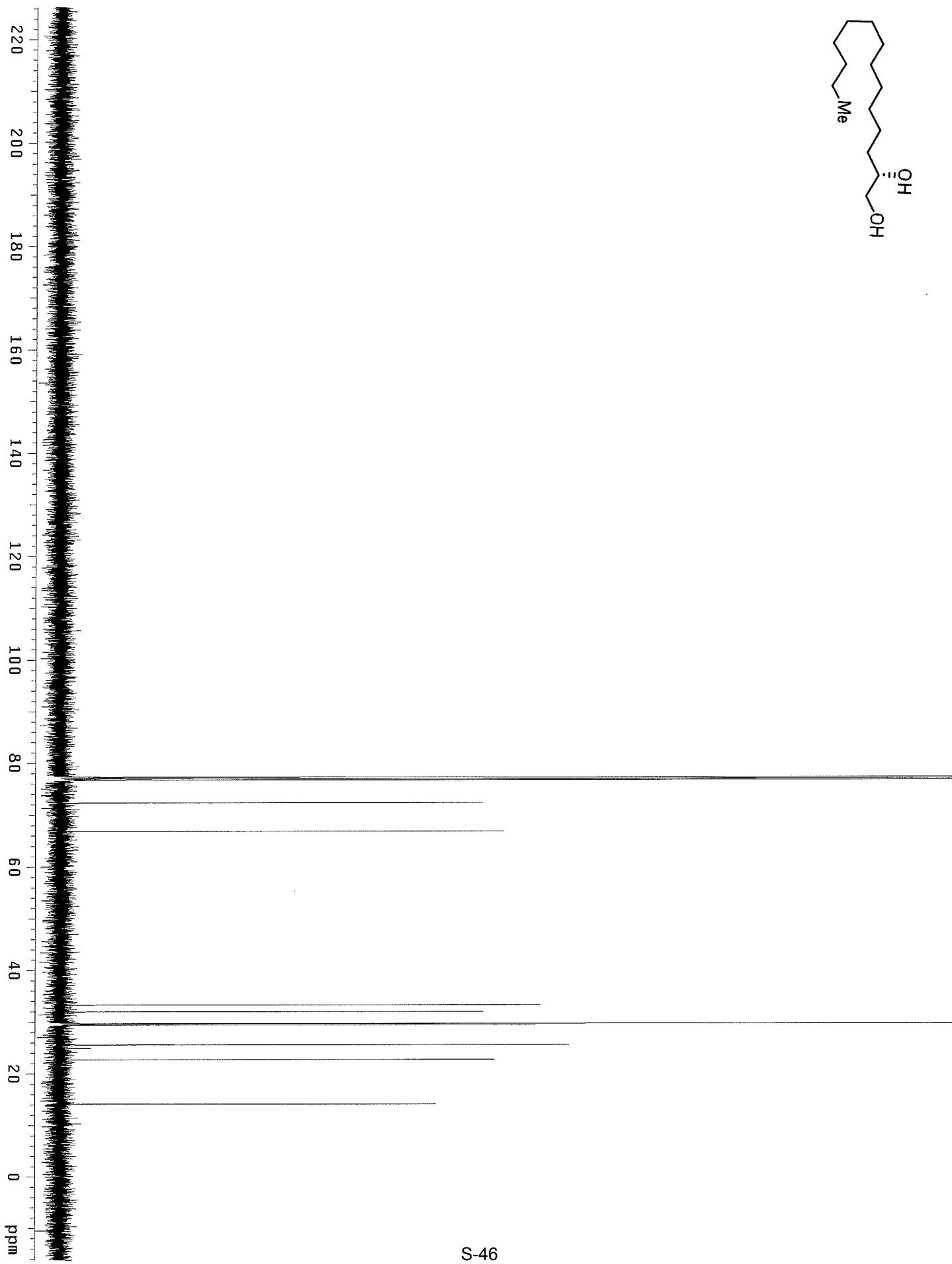


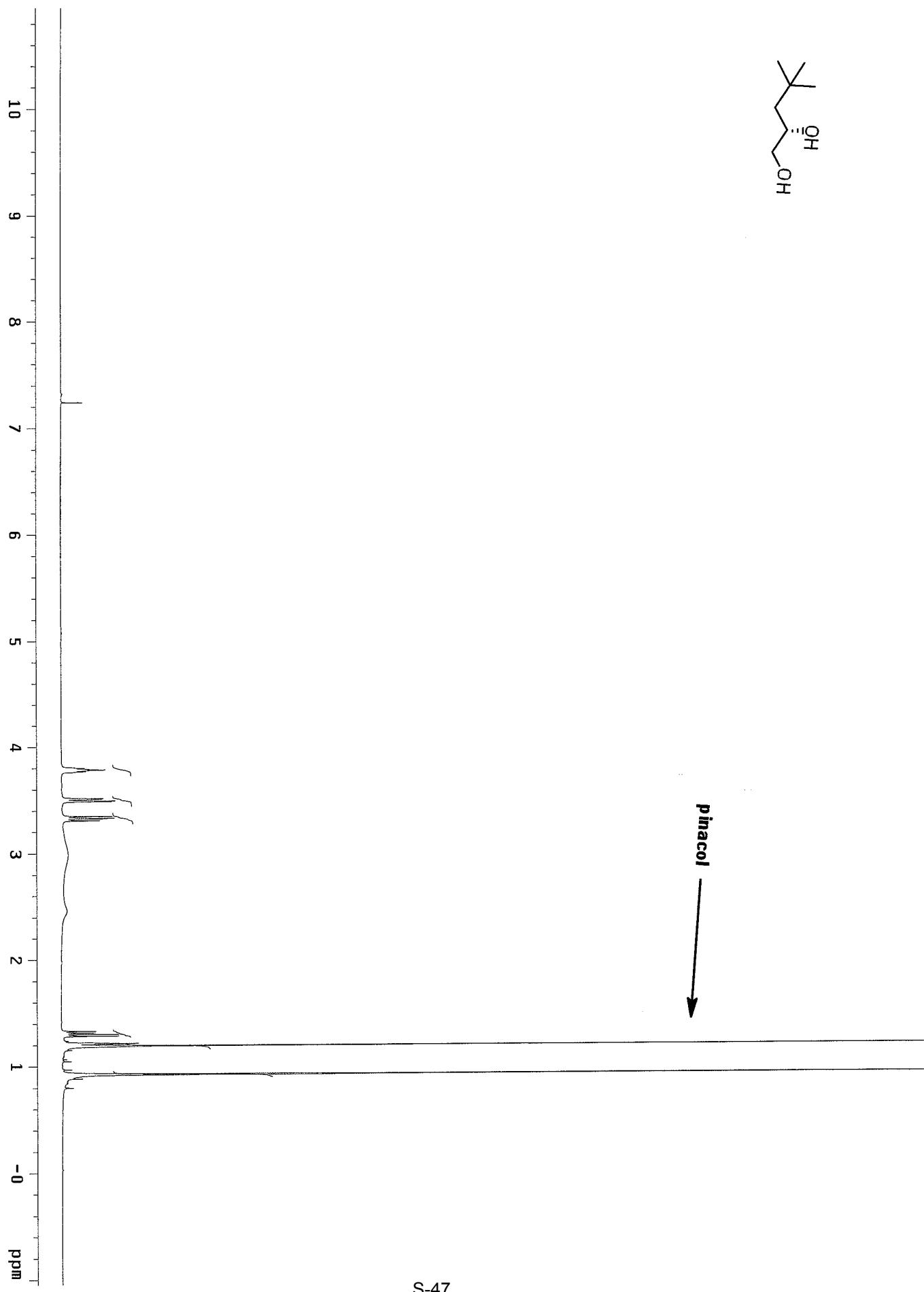


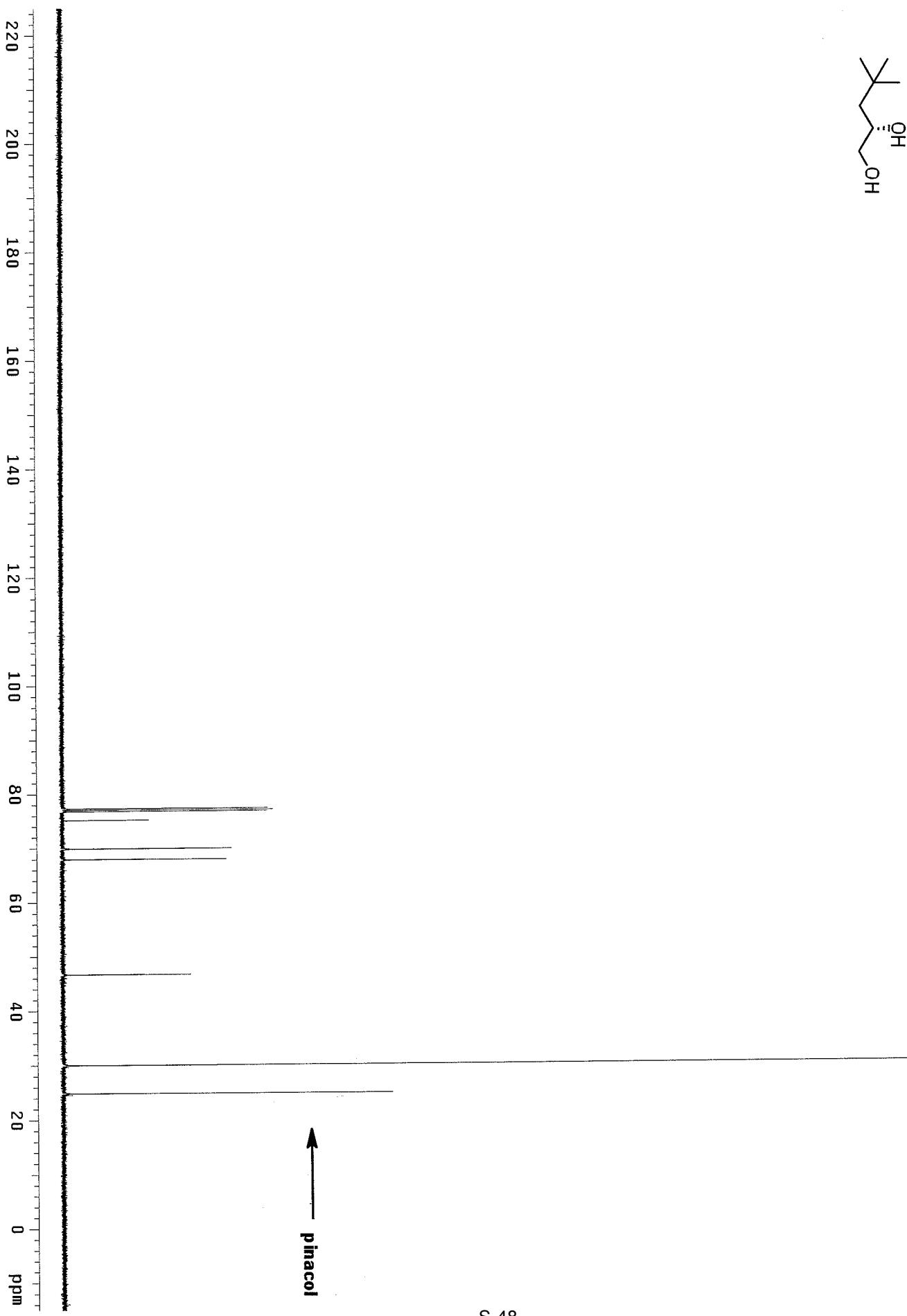


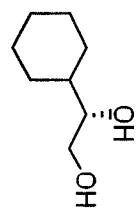
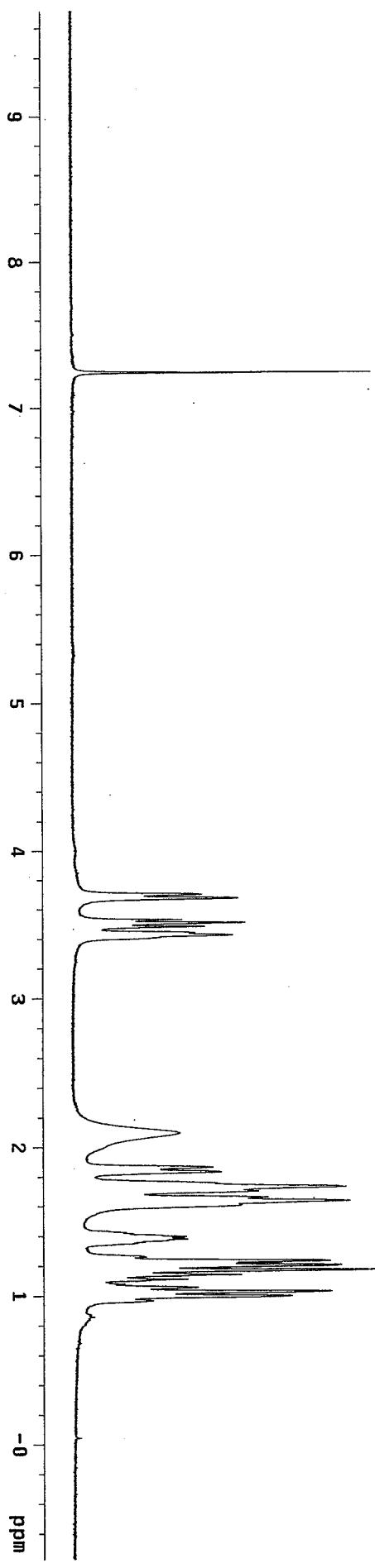


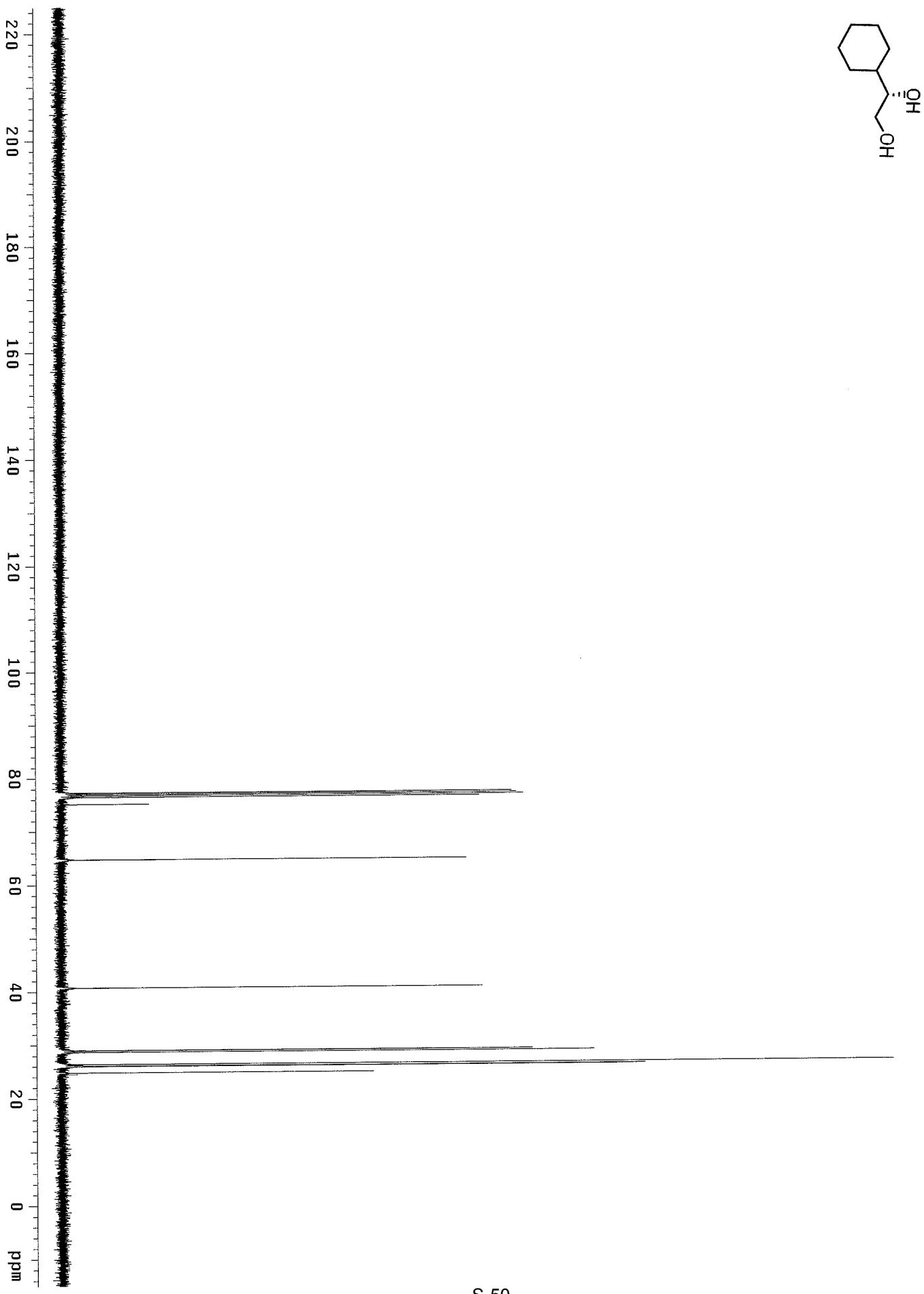




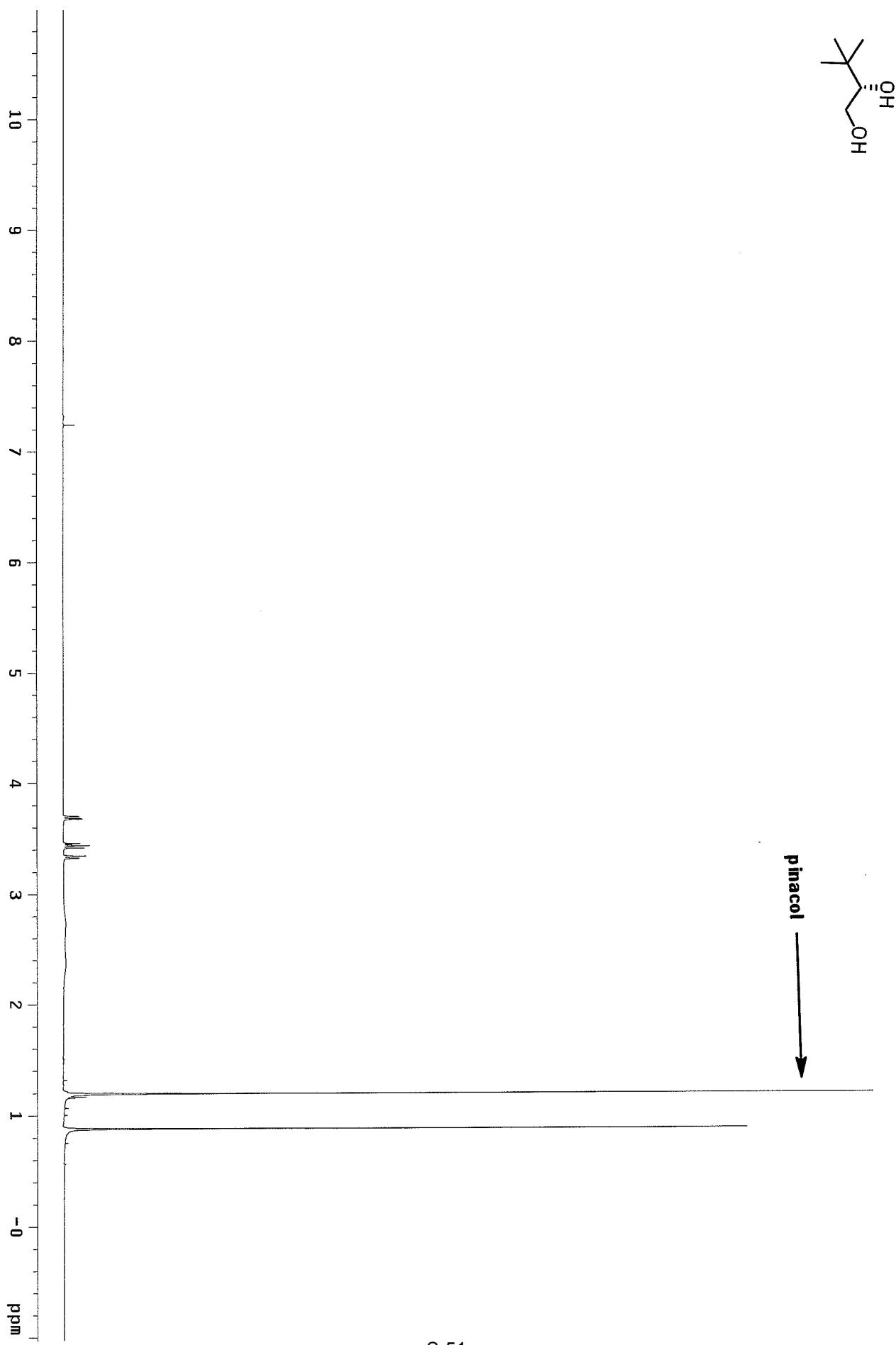


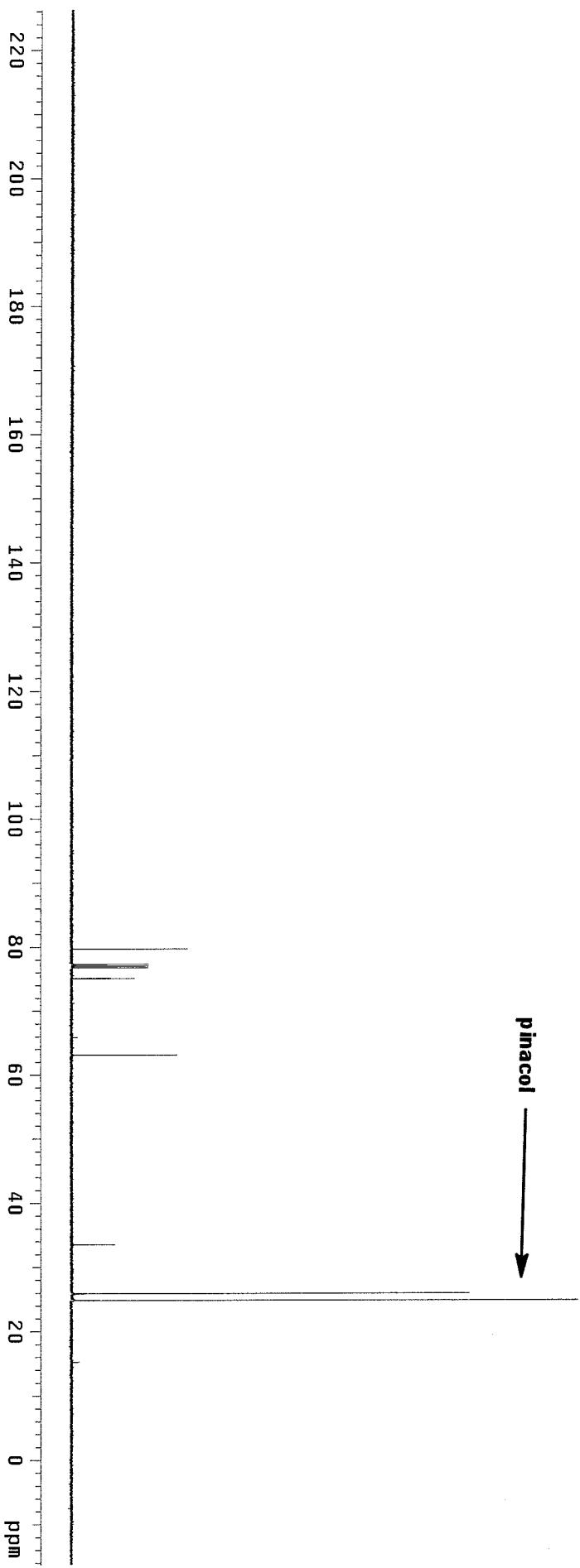
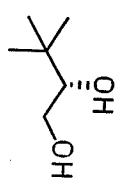




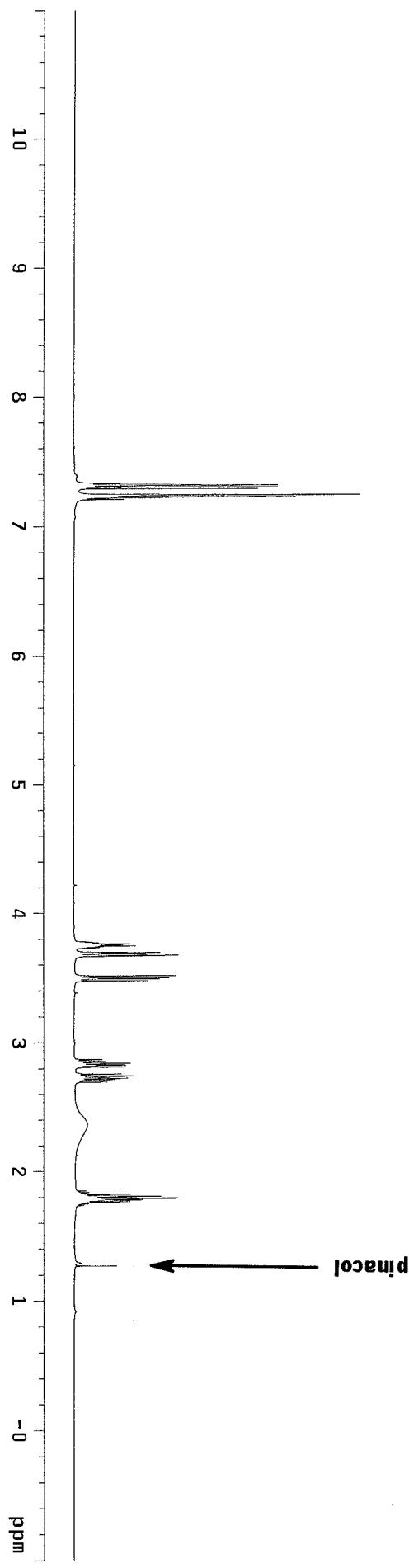


S-50

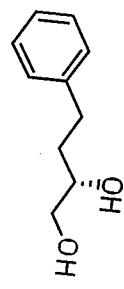


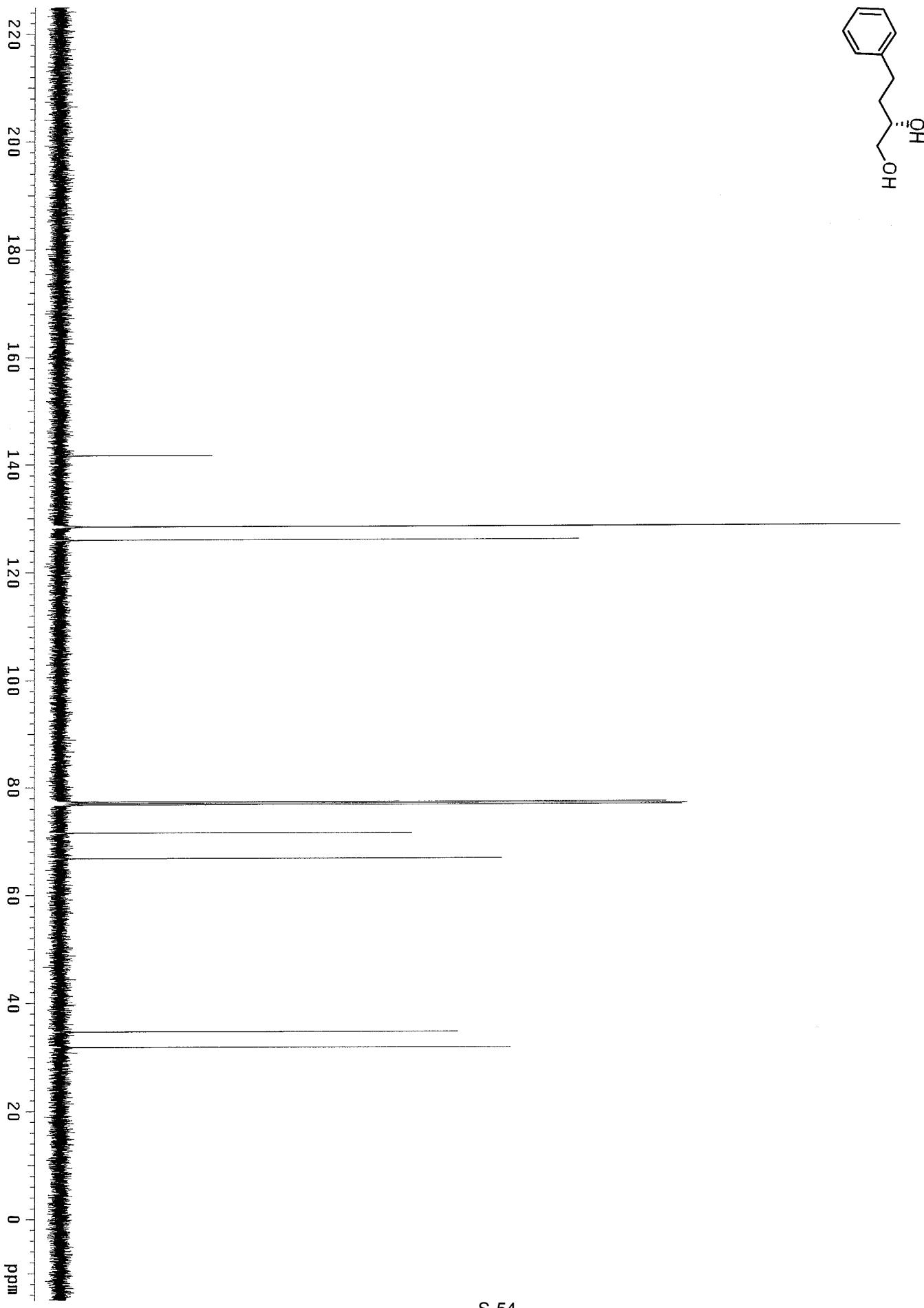


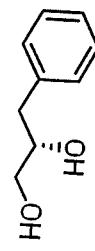
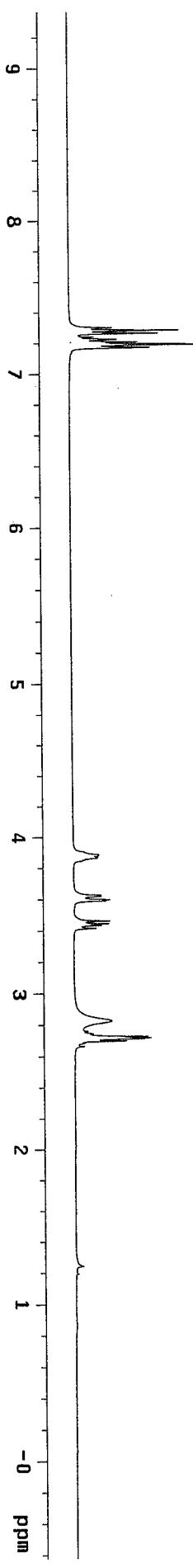
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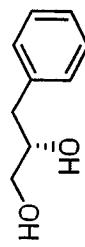
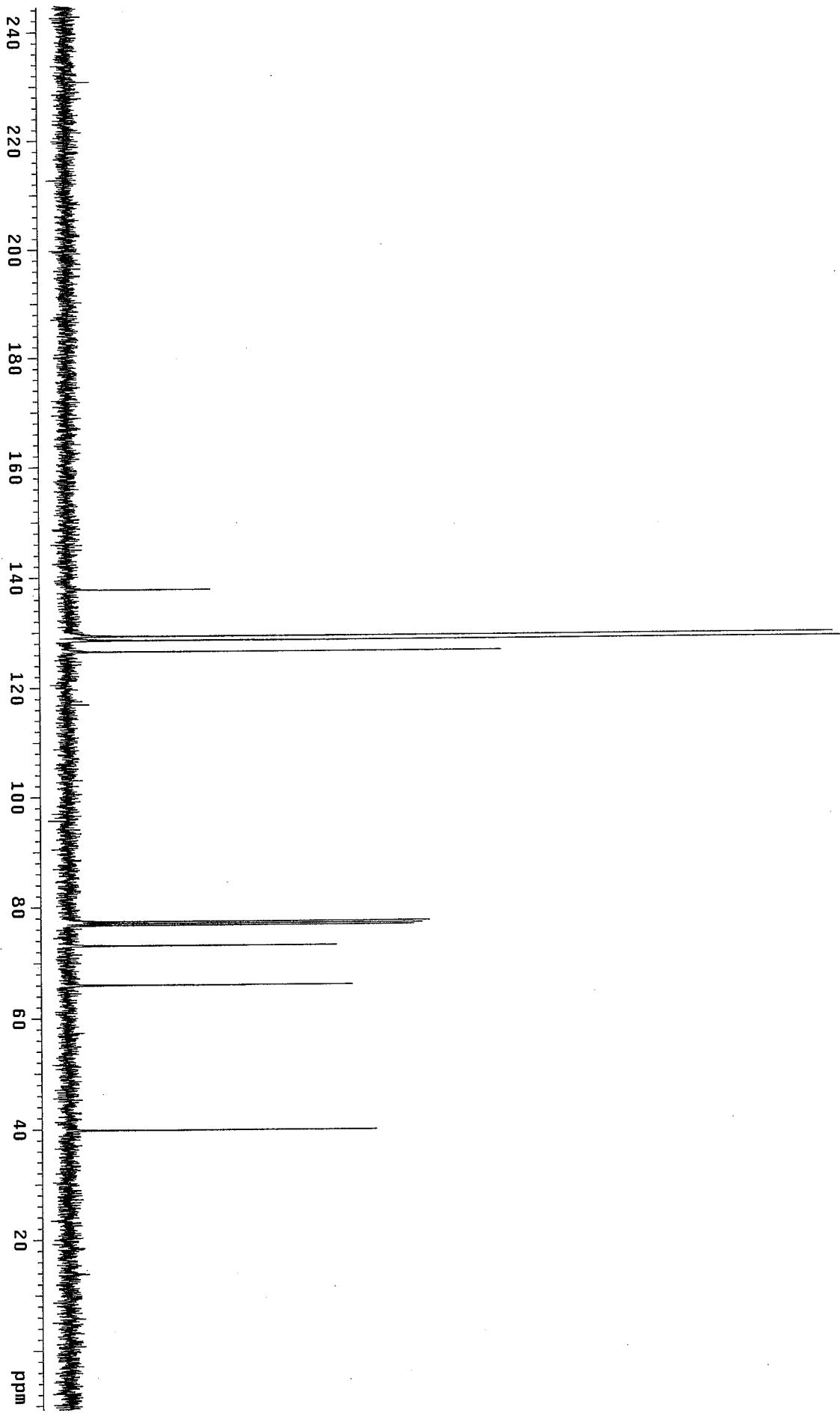


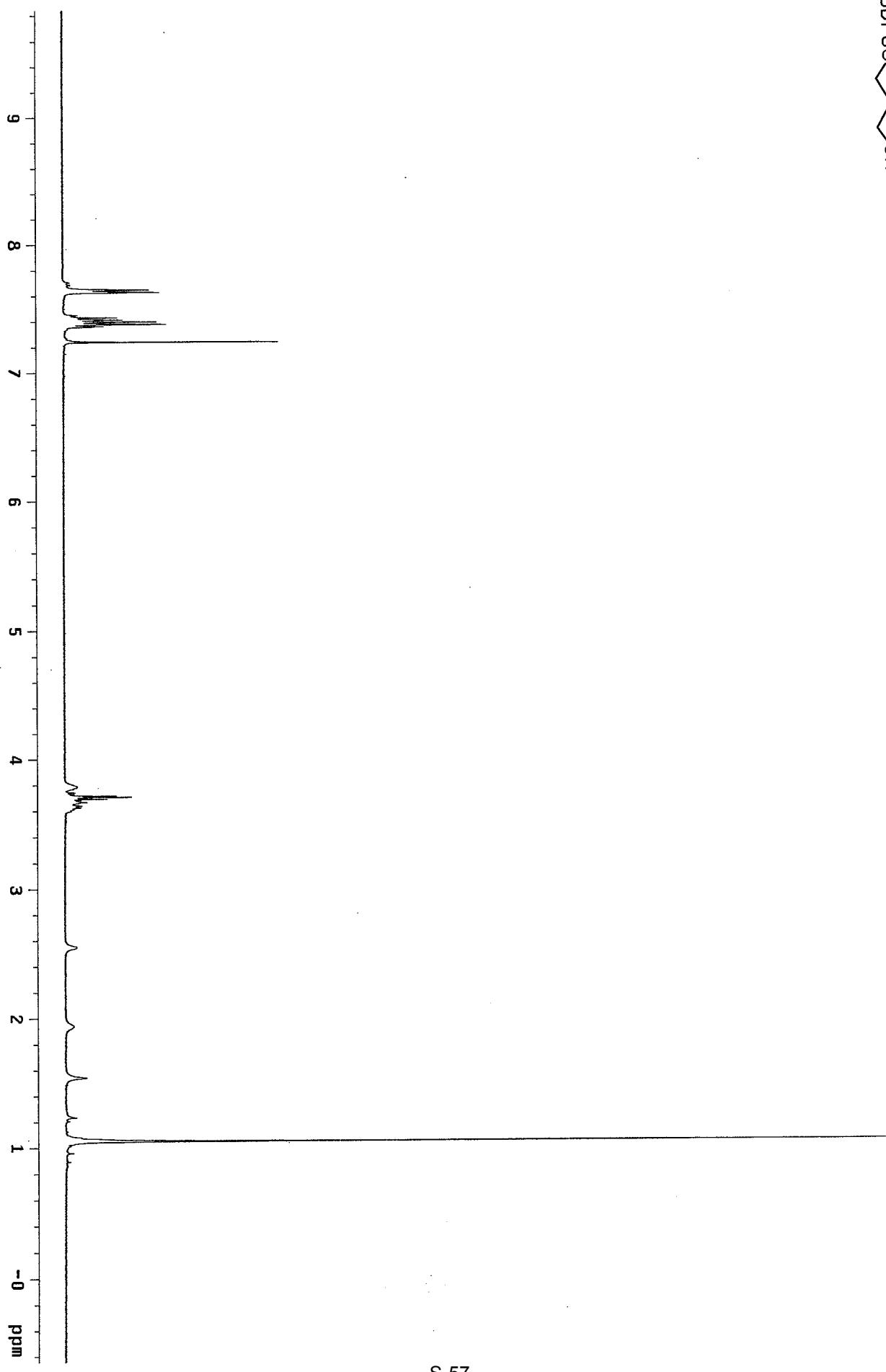
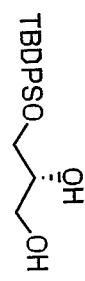
S-53

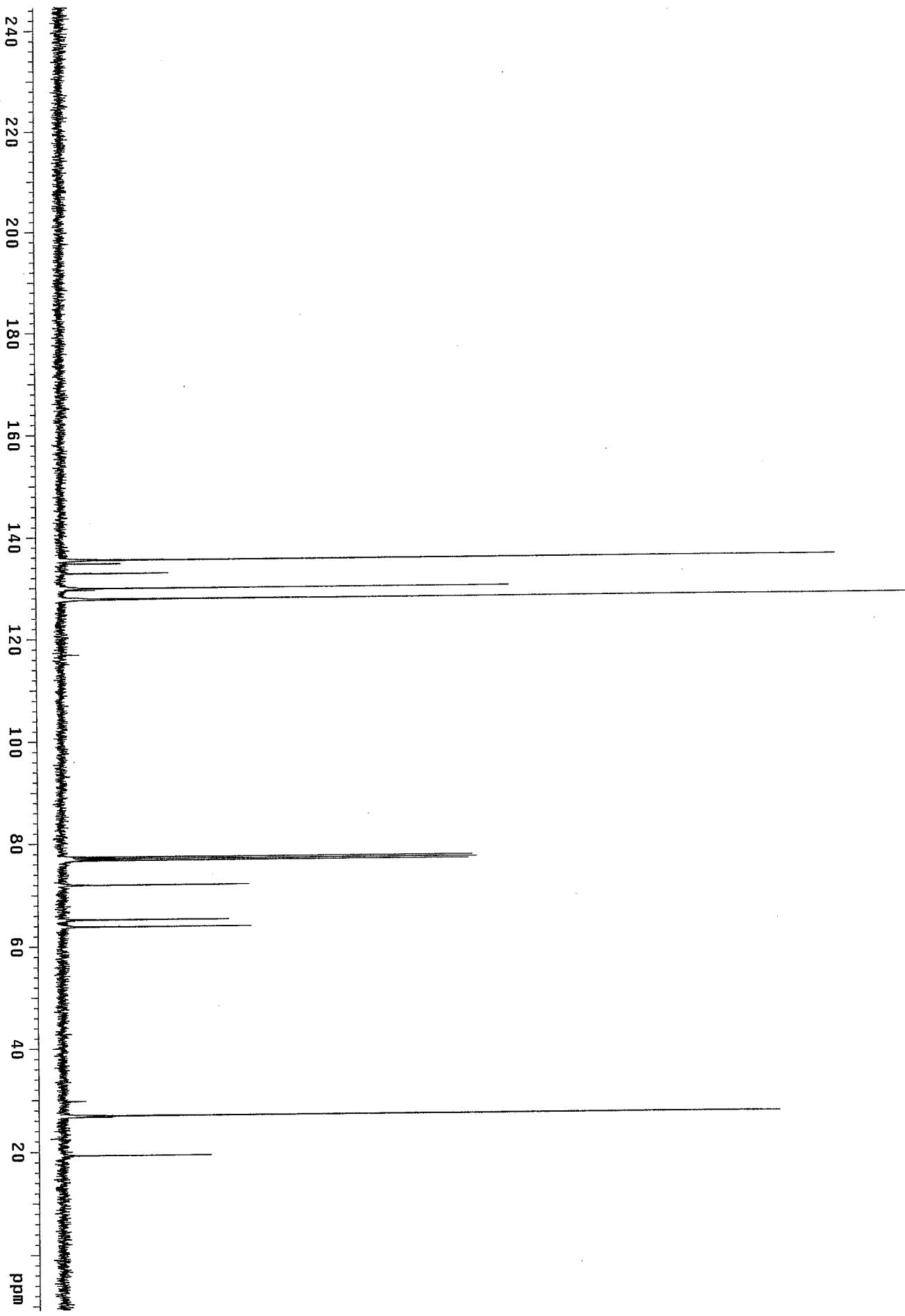
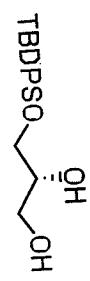


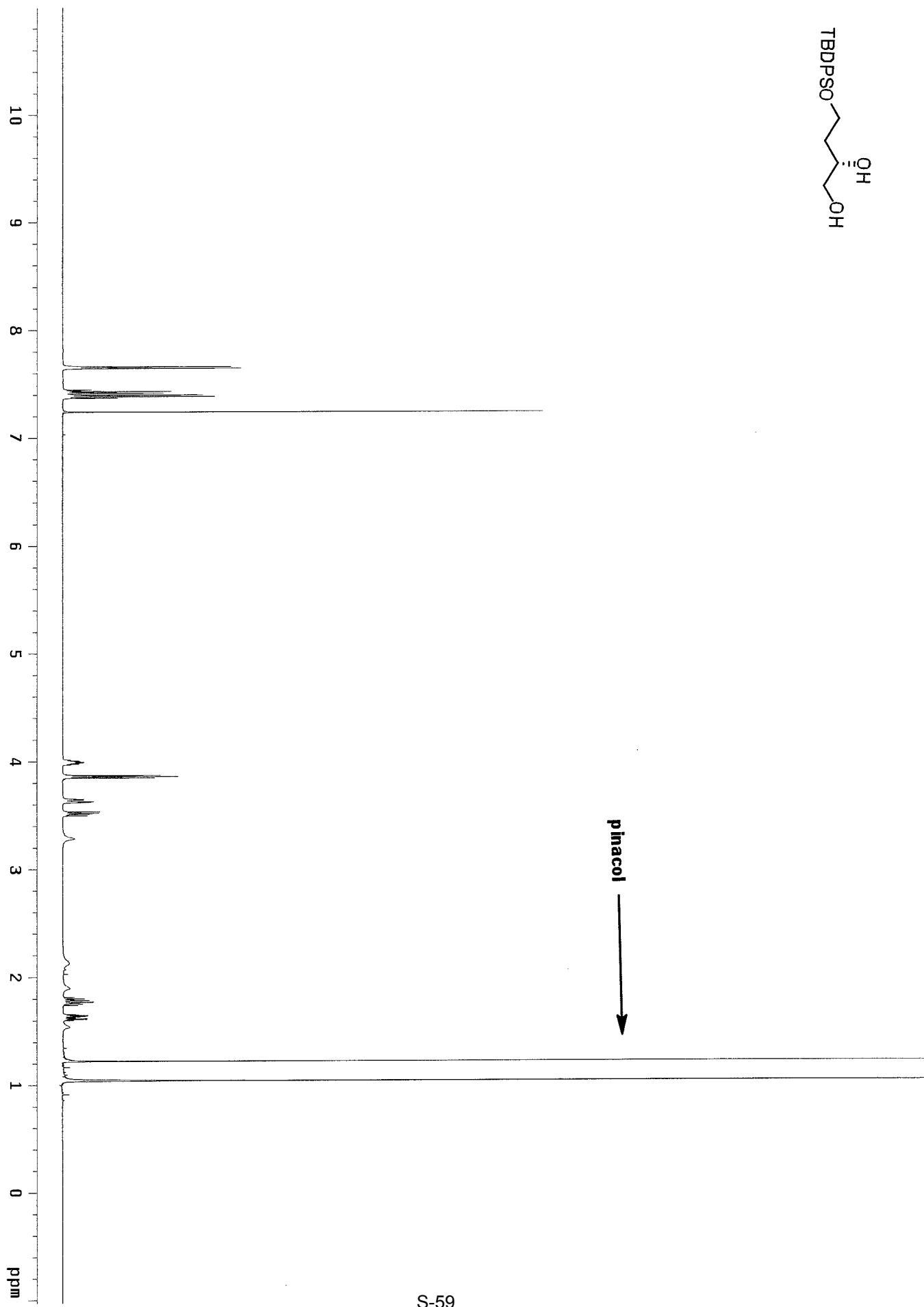
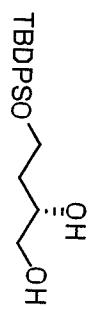


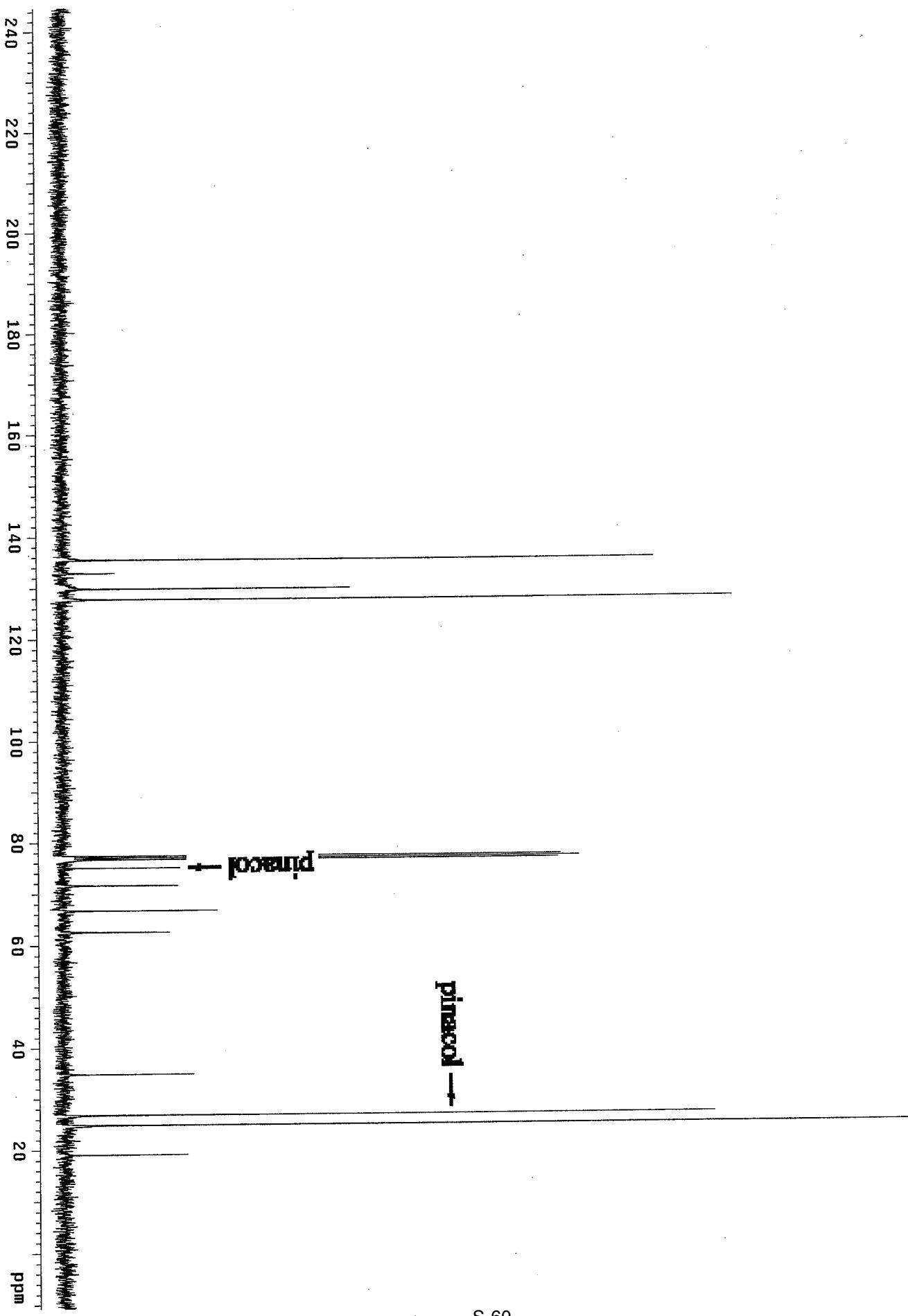
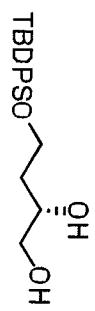


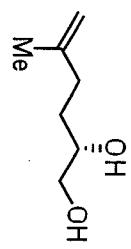
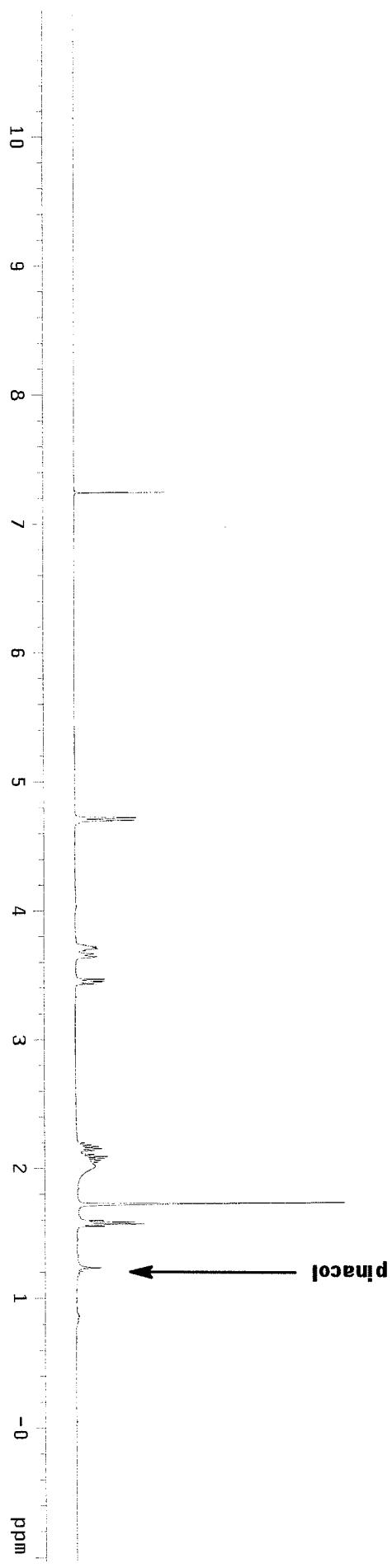


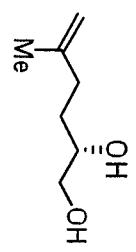
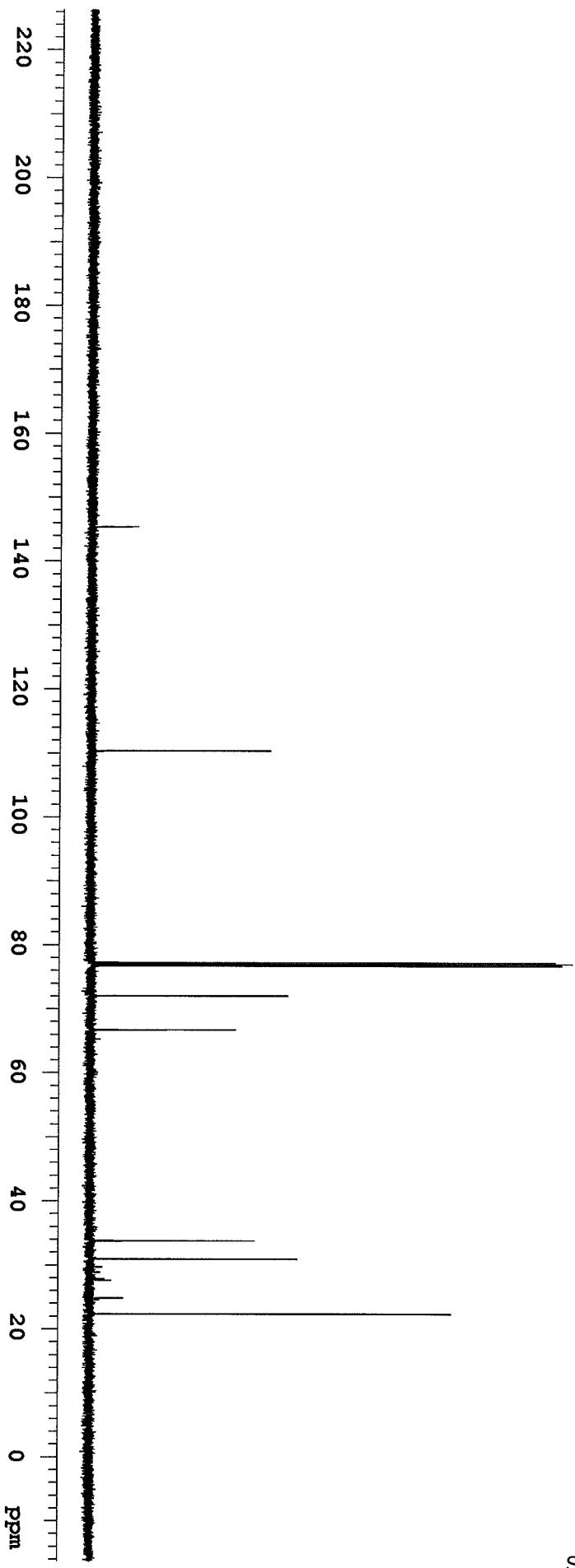


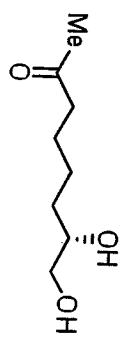
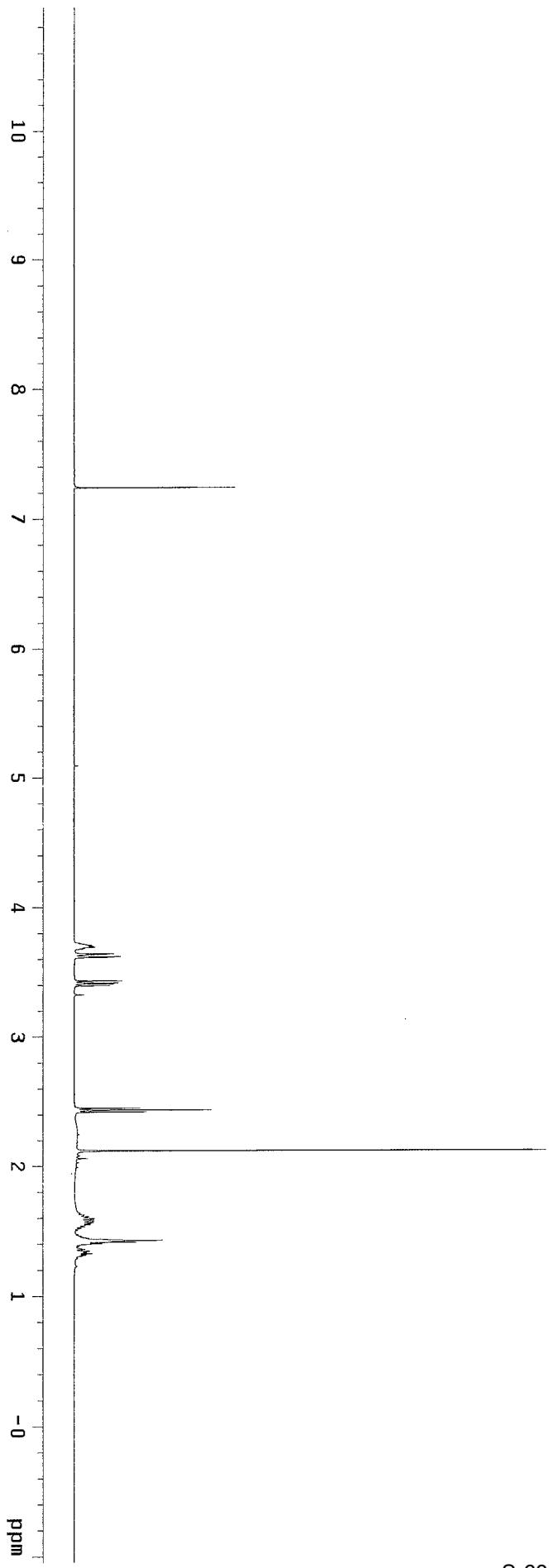


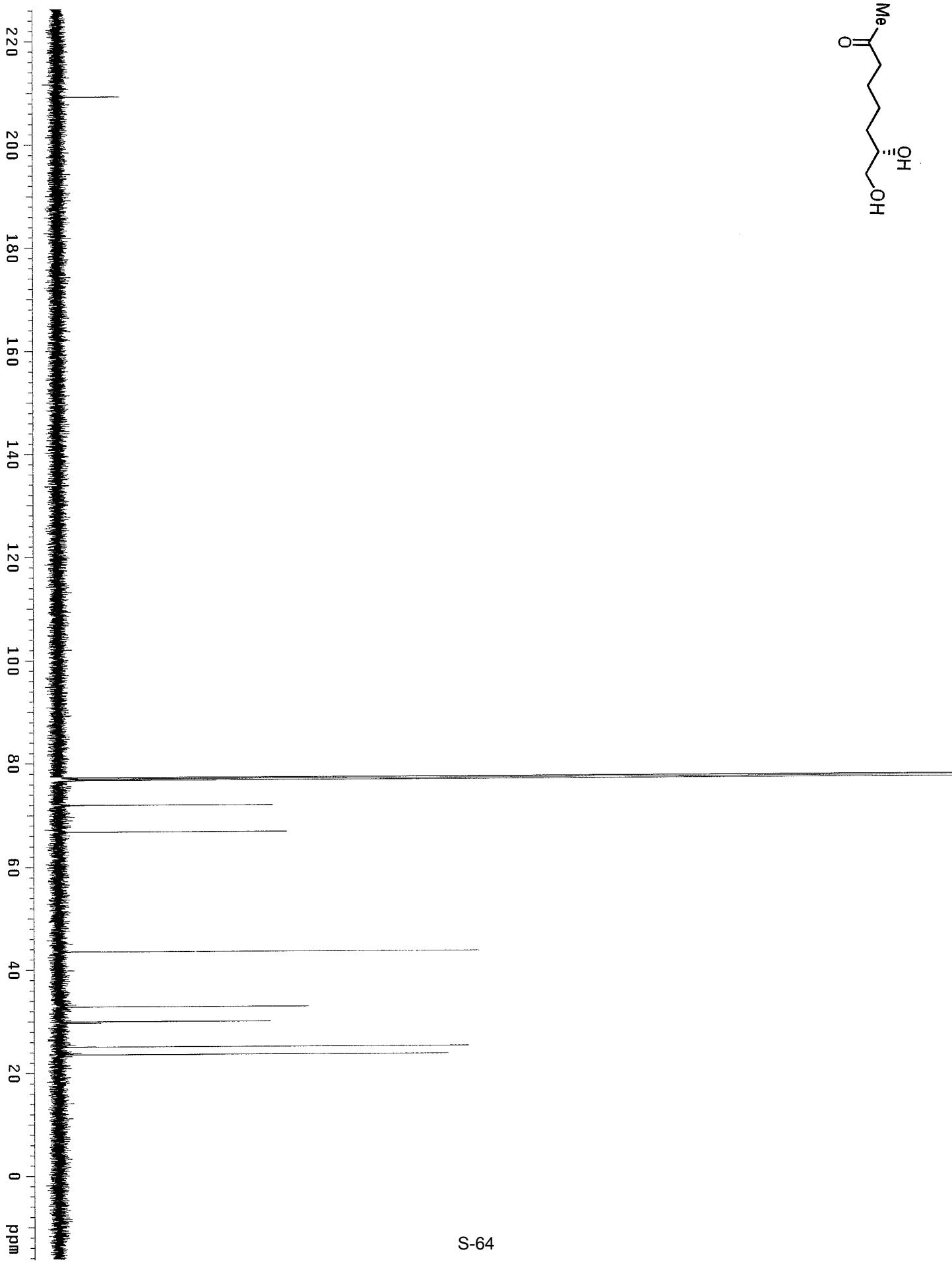


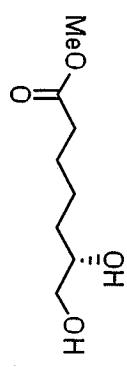
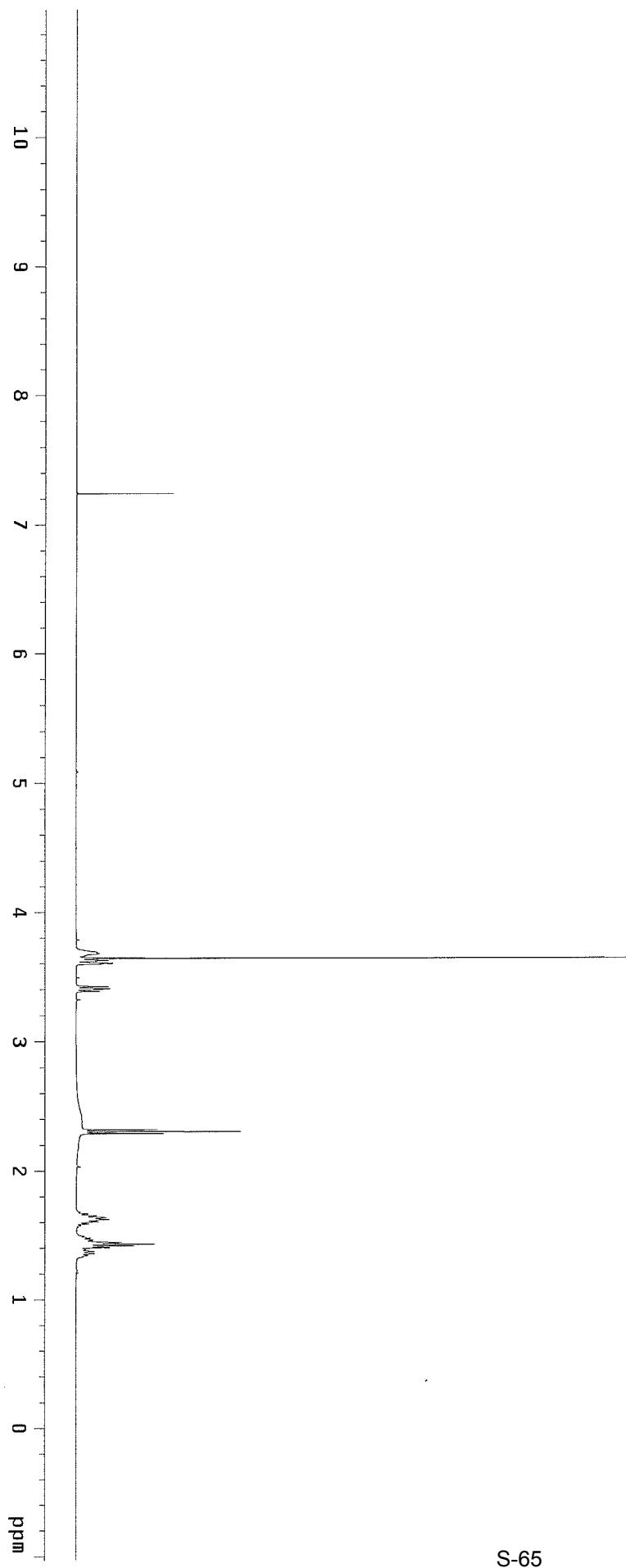


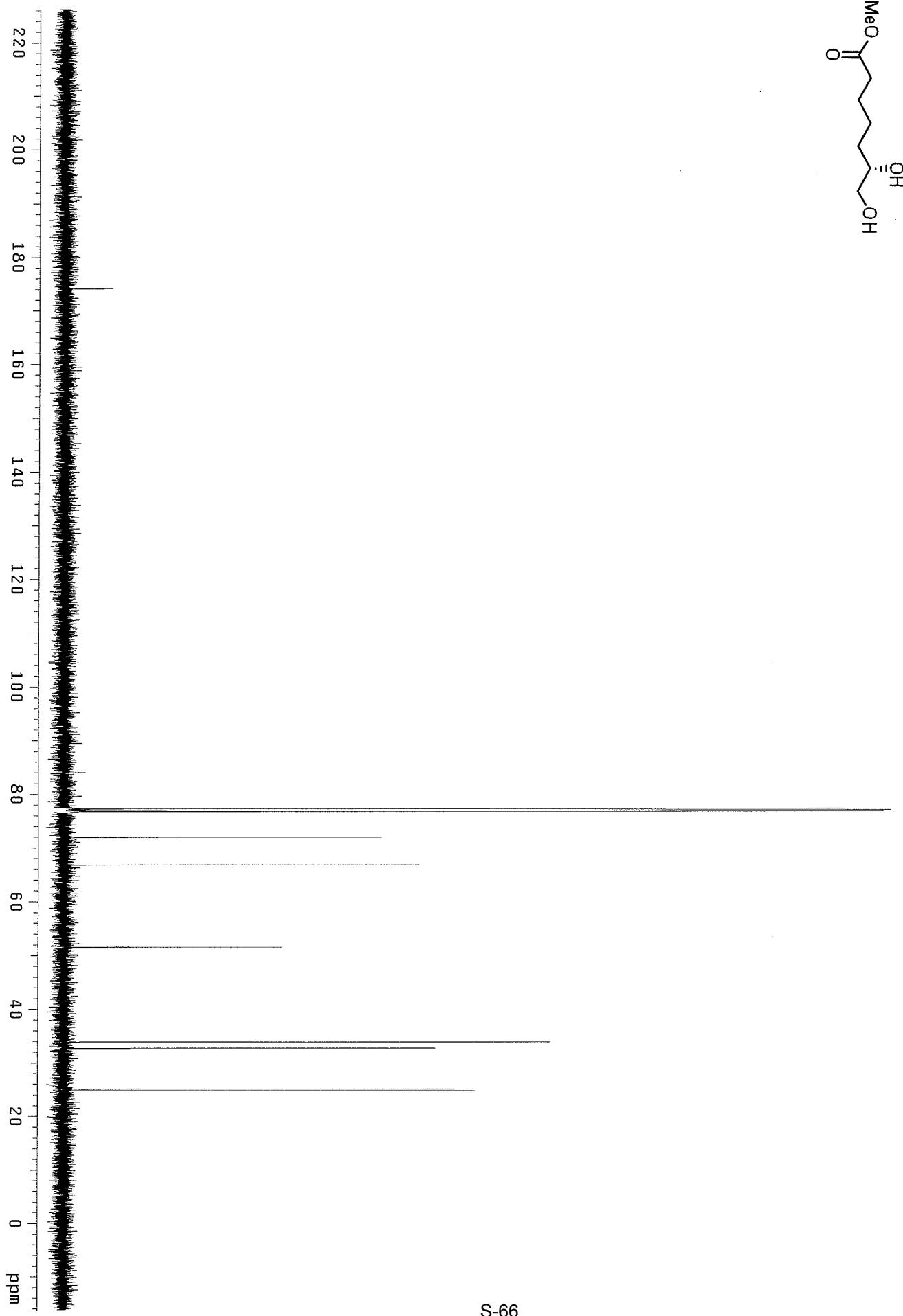


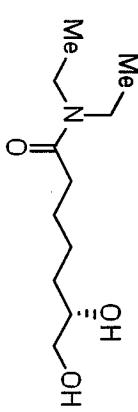
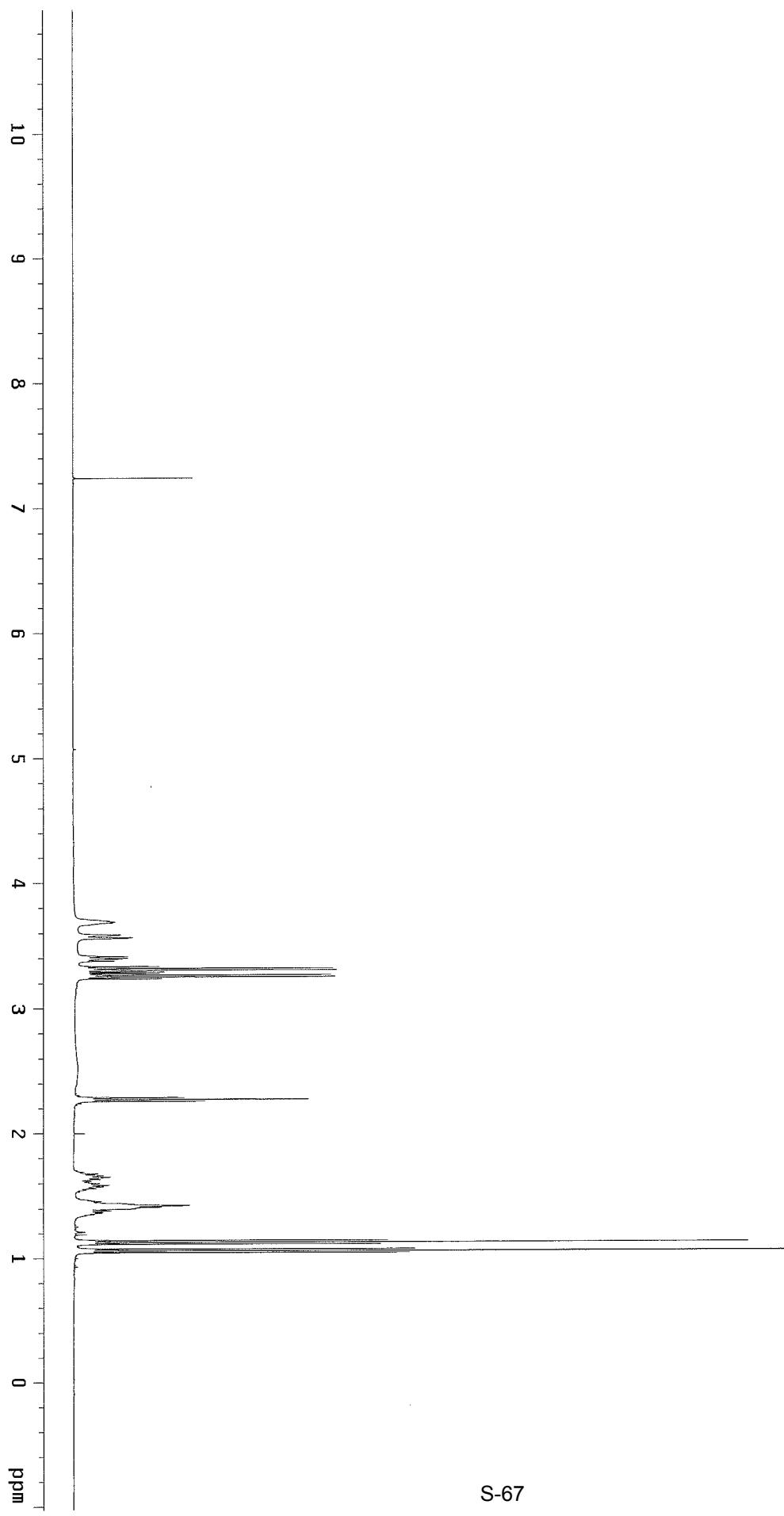


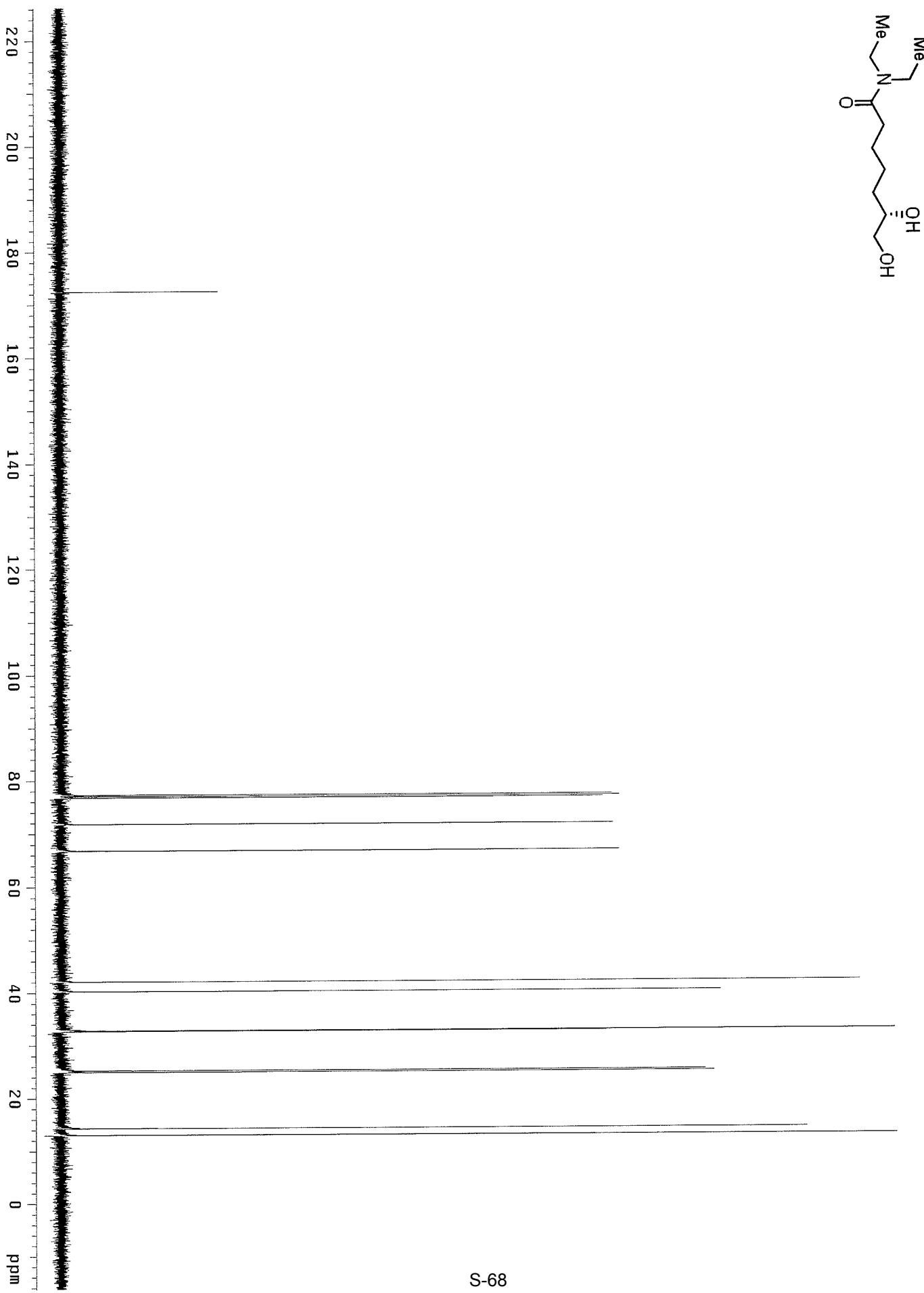


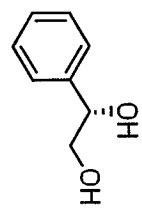
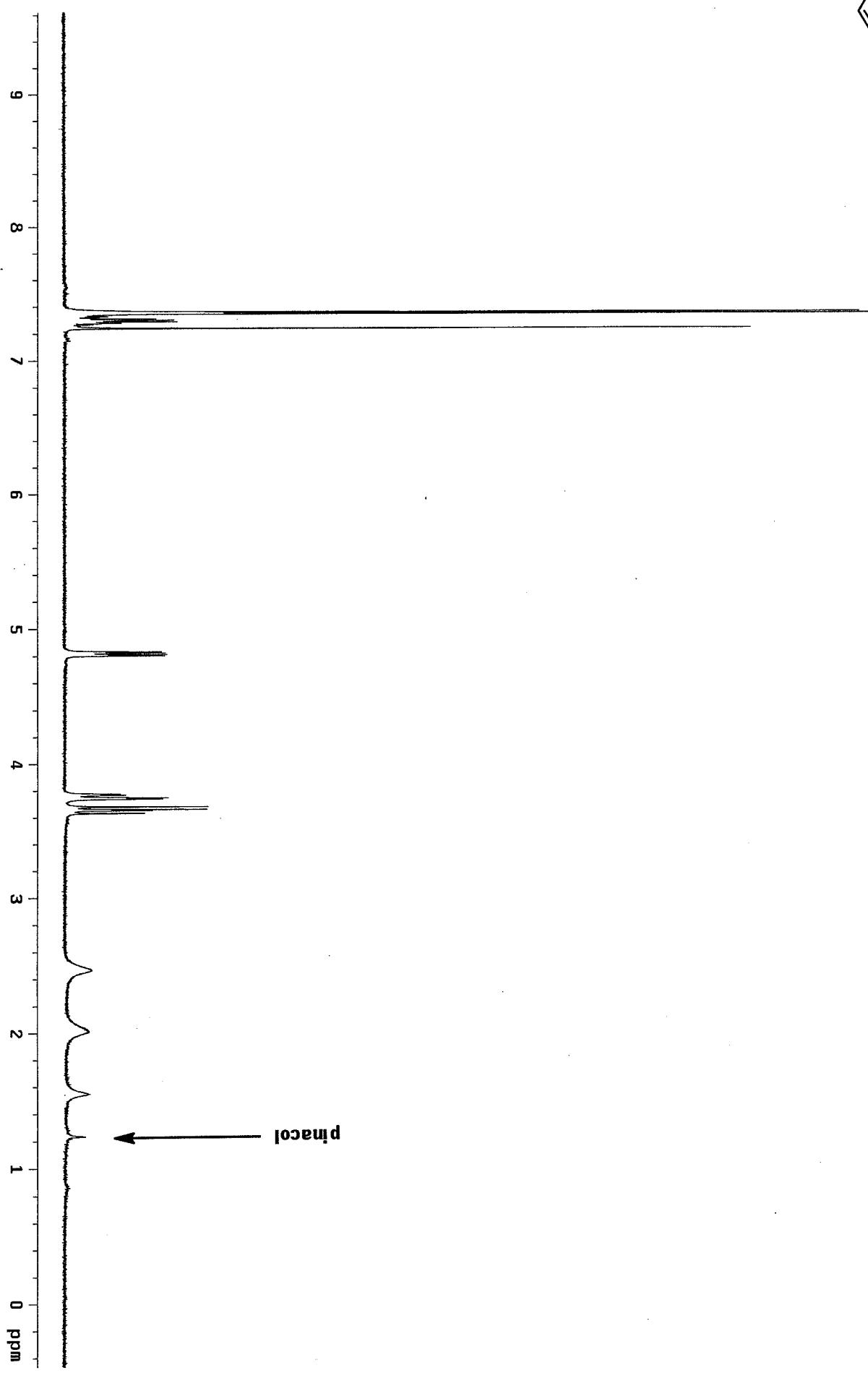


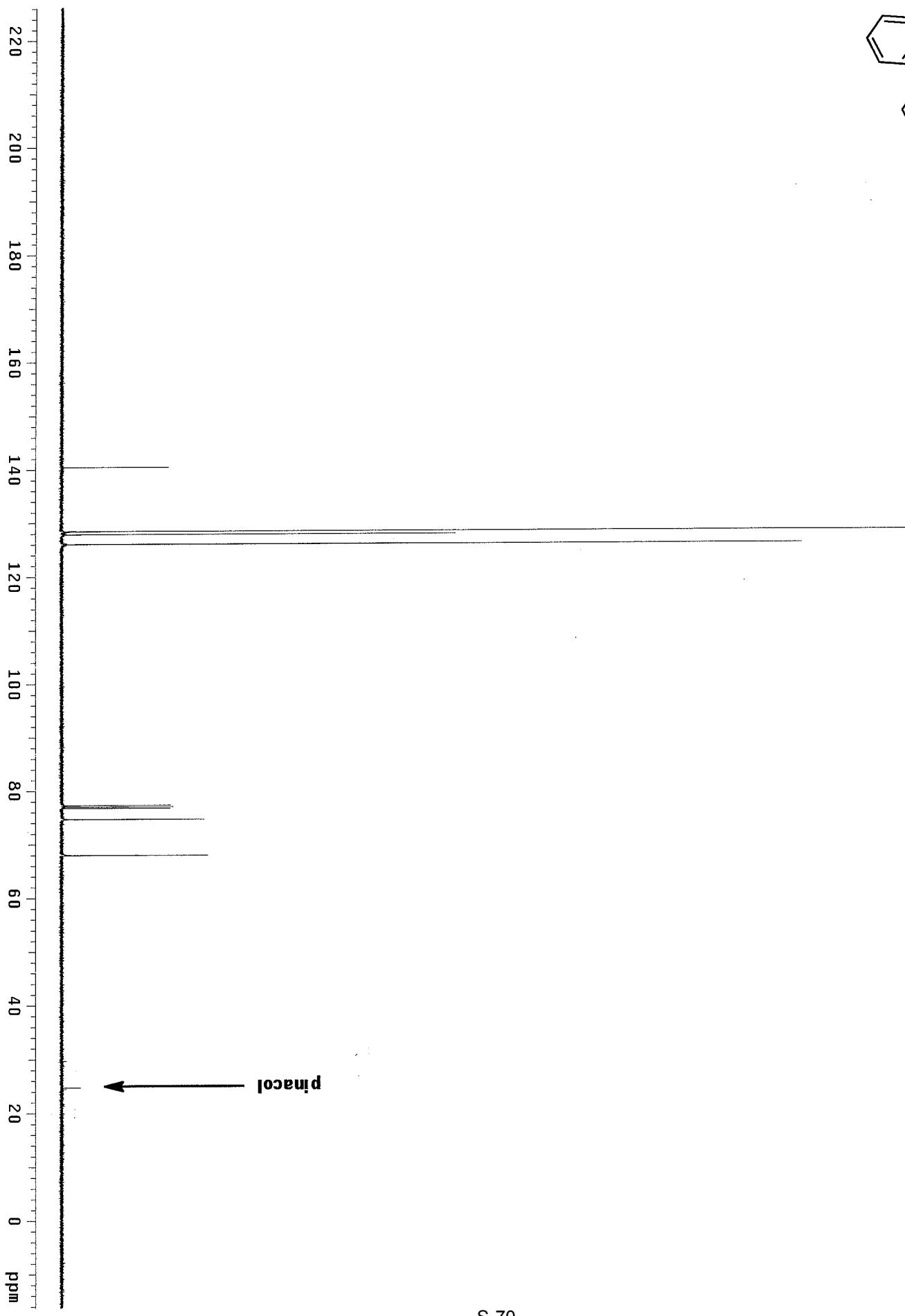
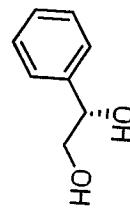


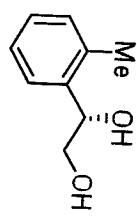
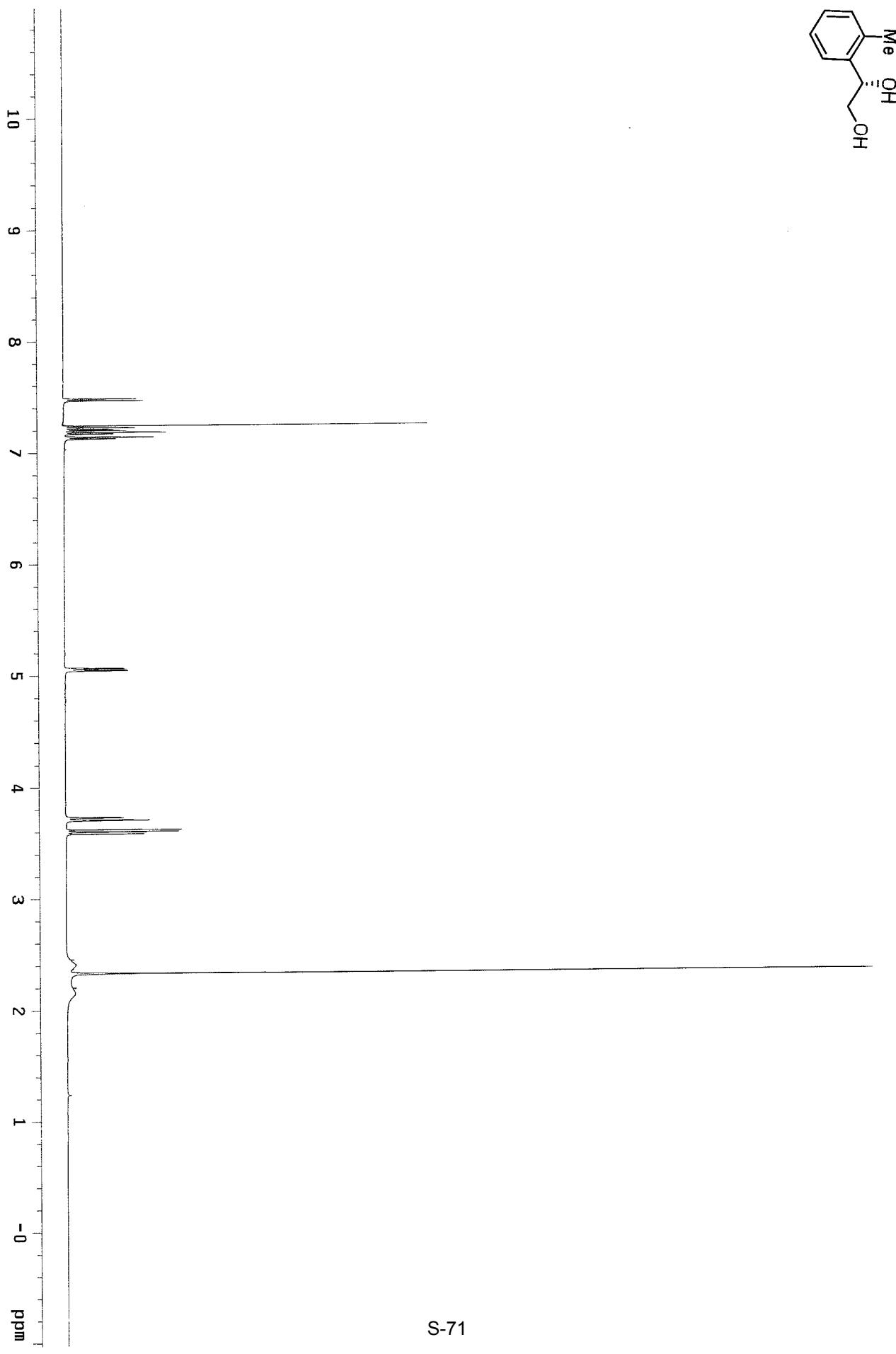


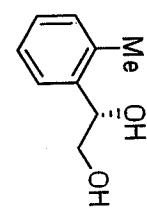
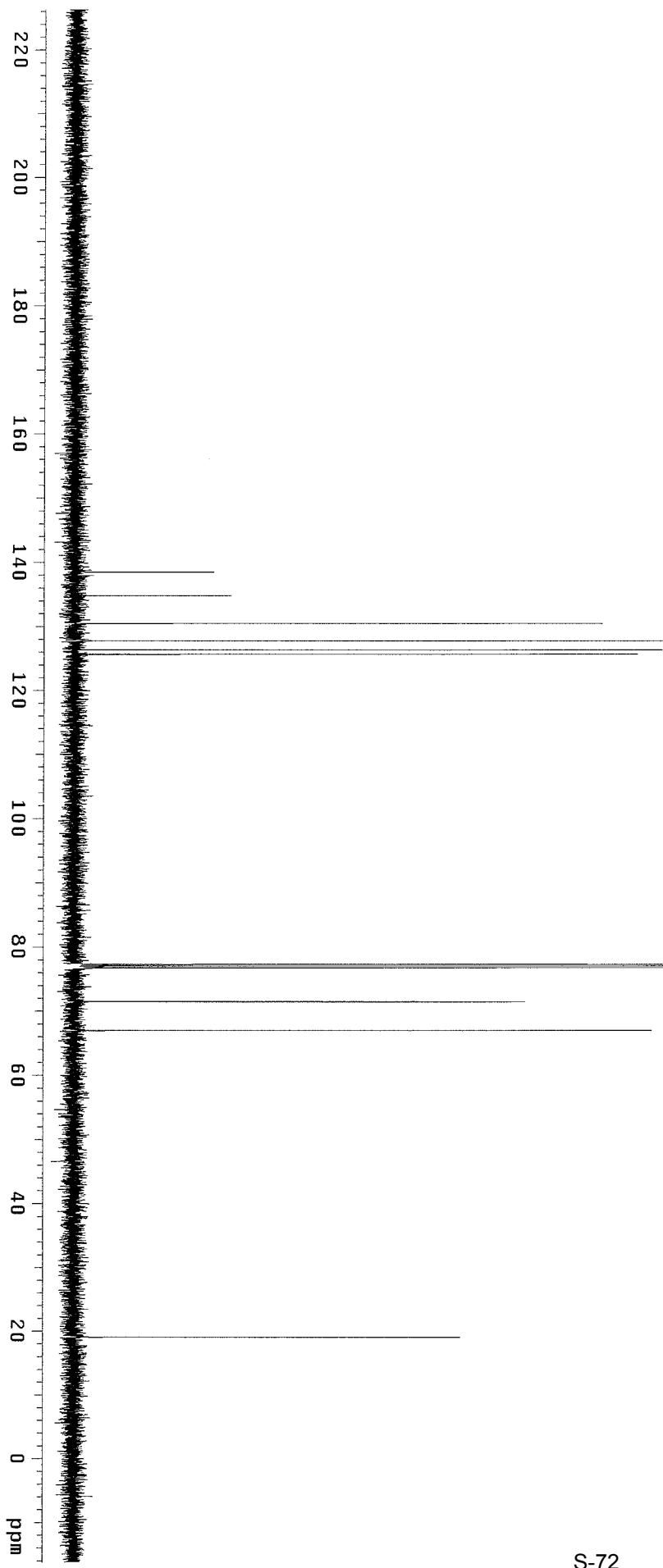


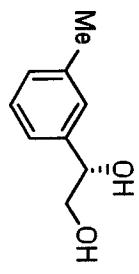
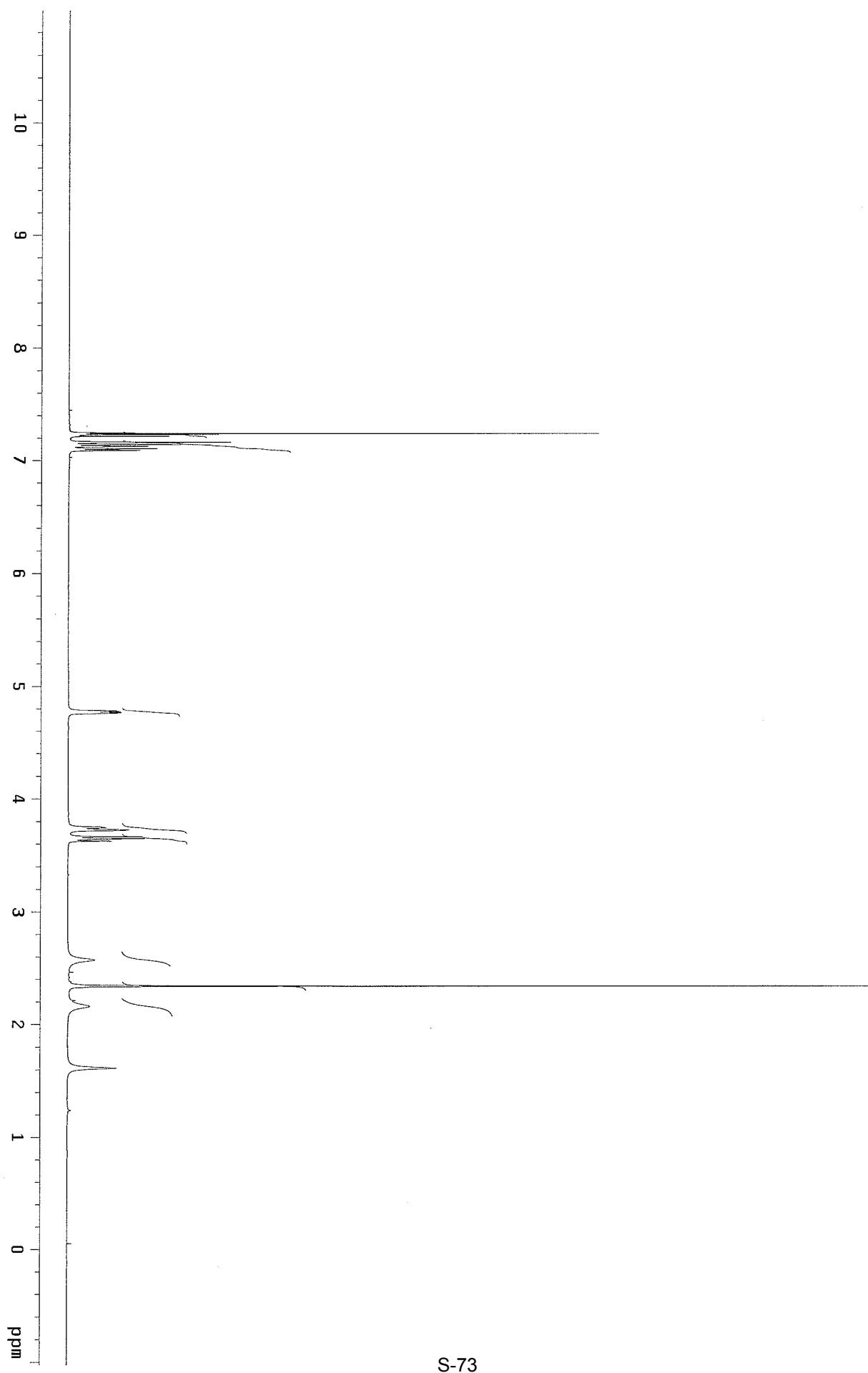


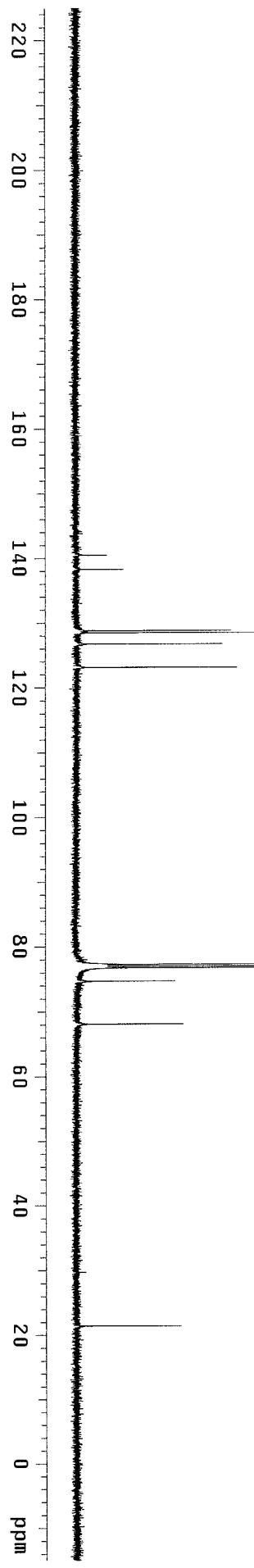




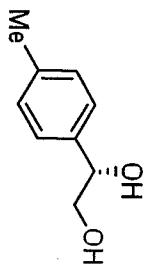
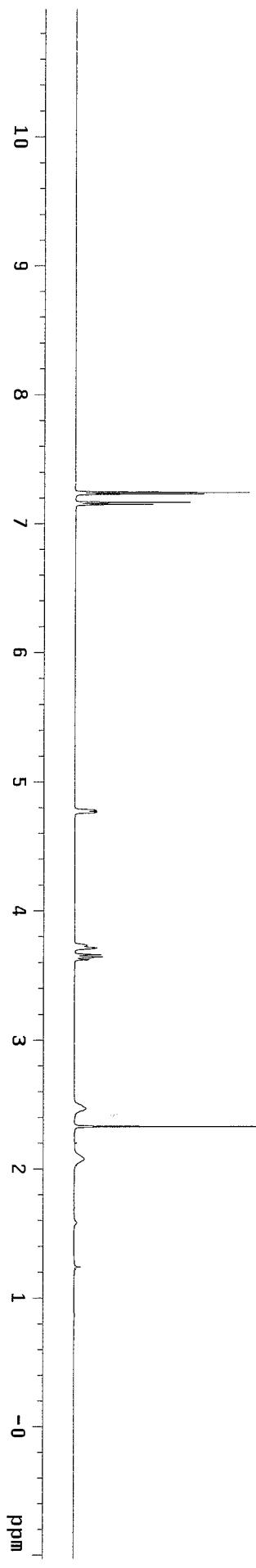


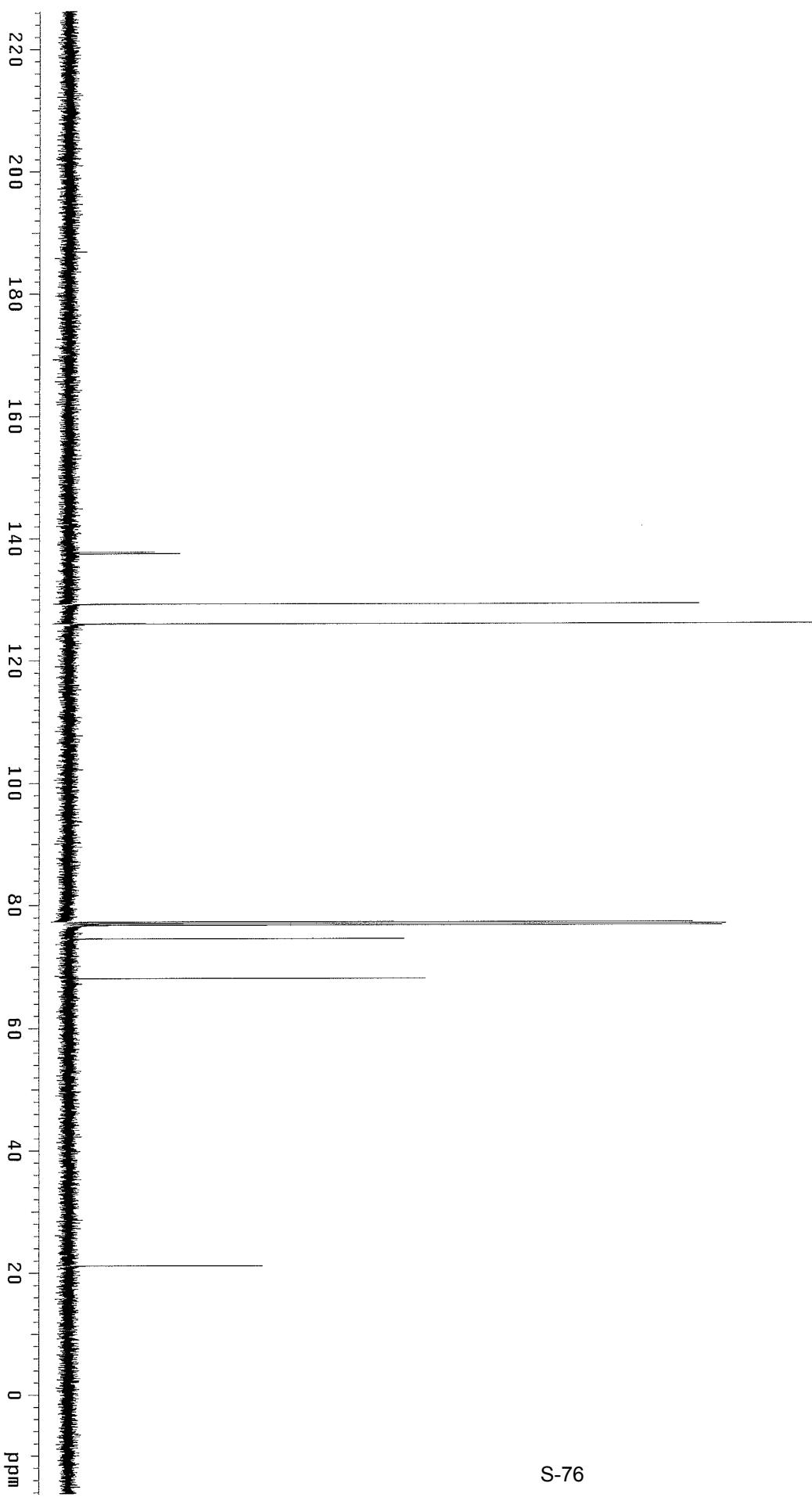


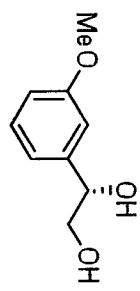
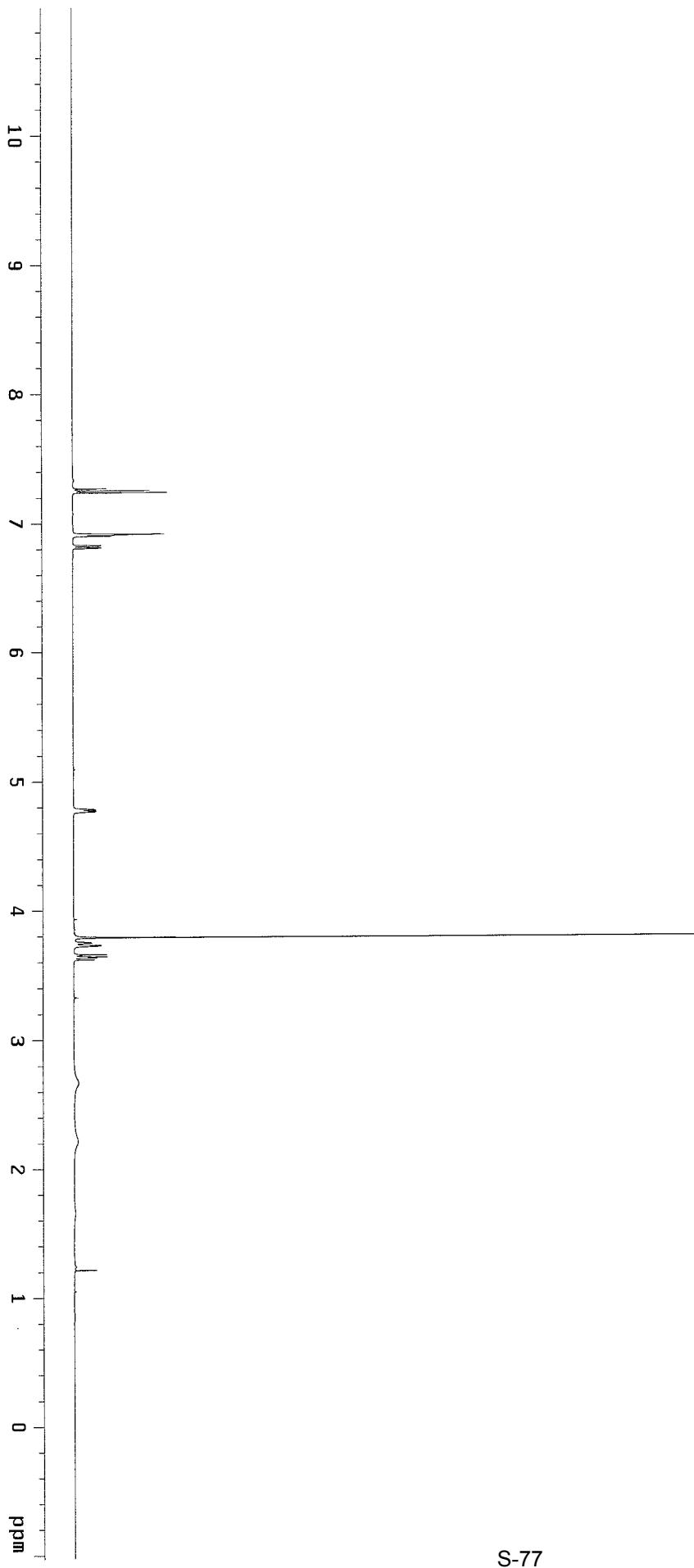


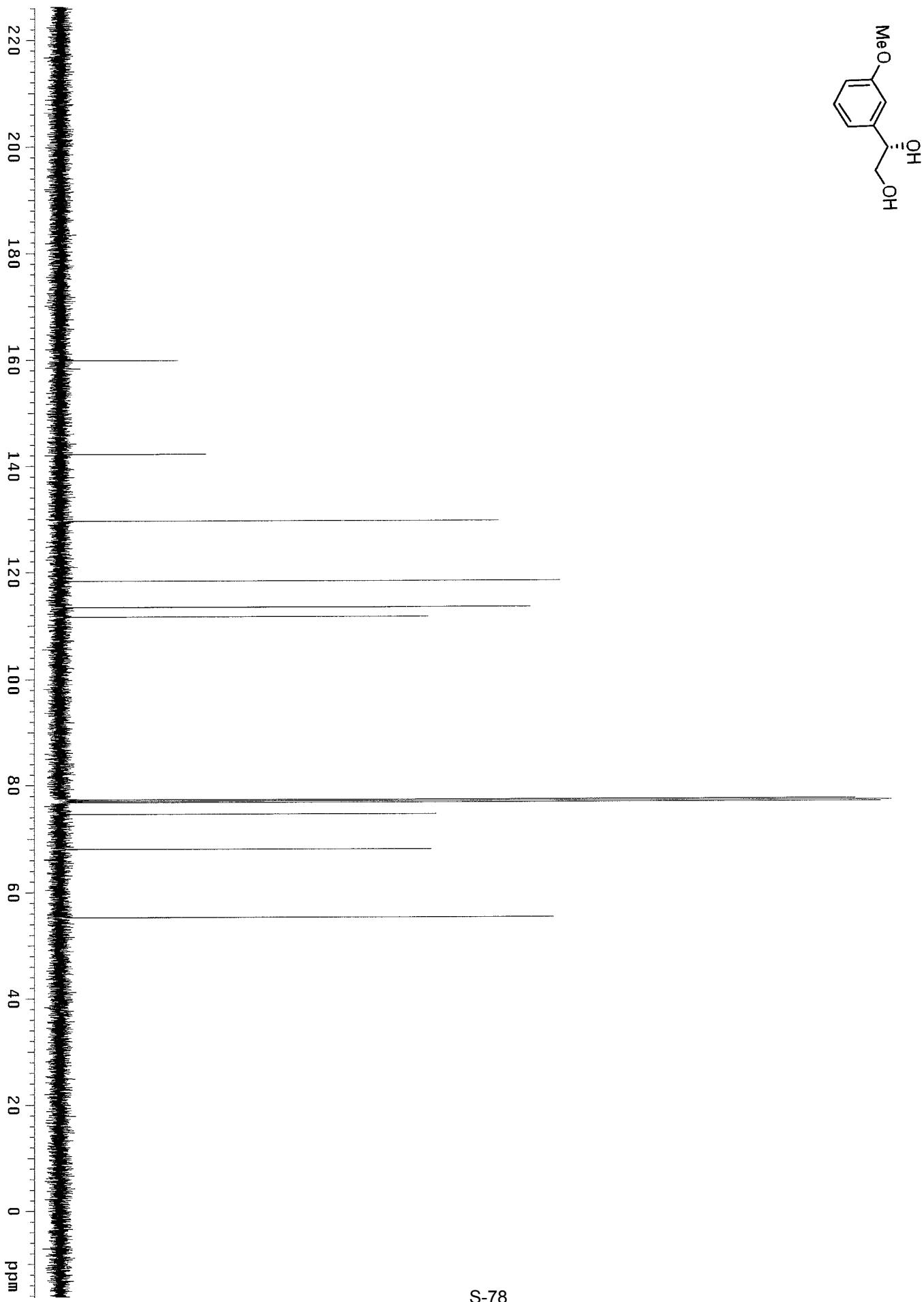


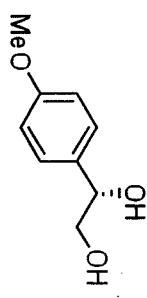
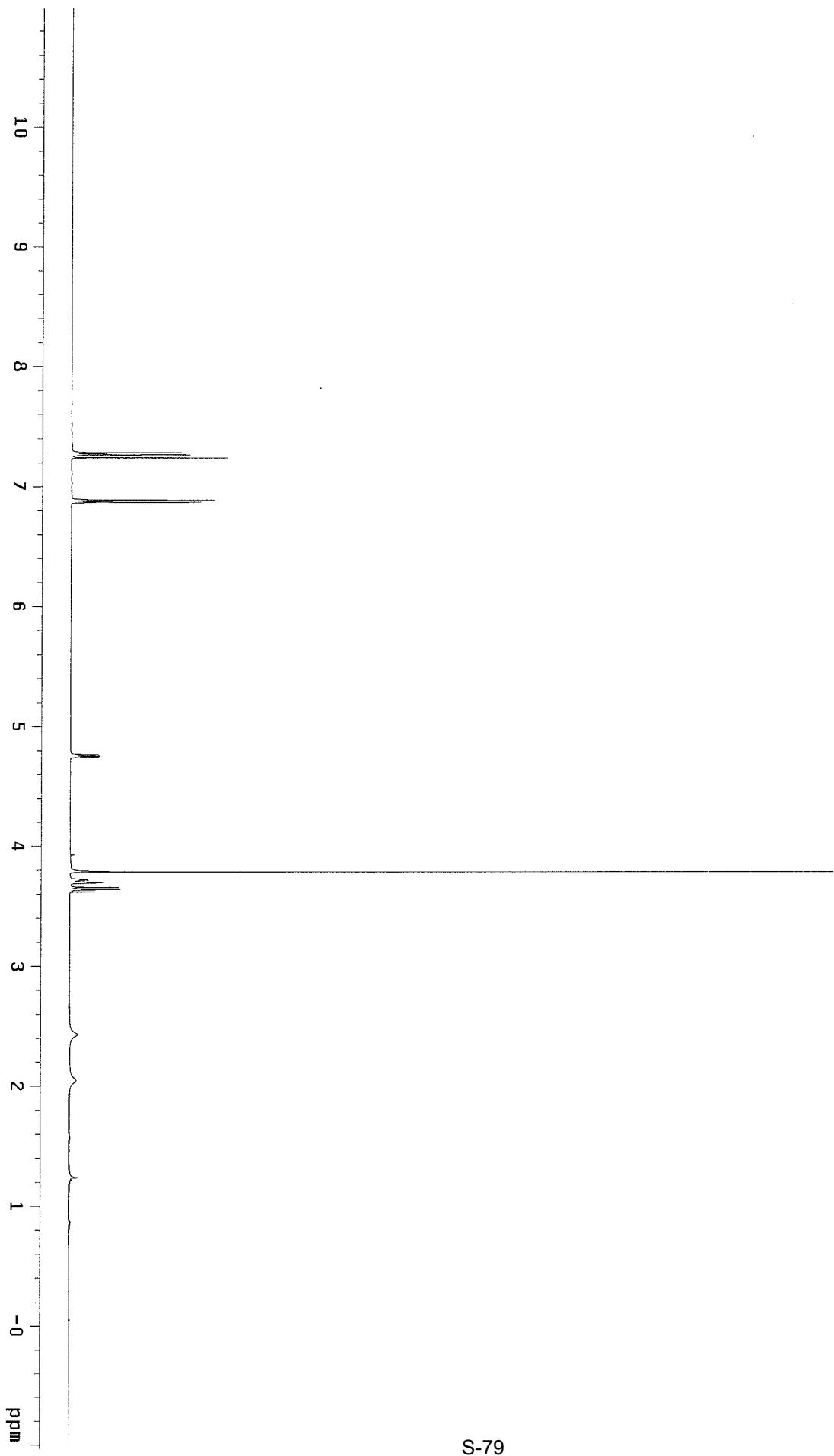
S-74

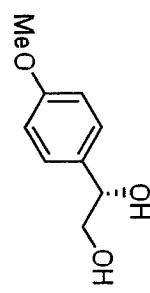
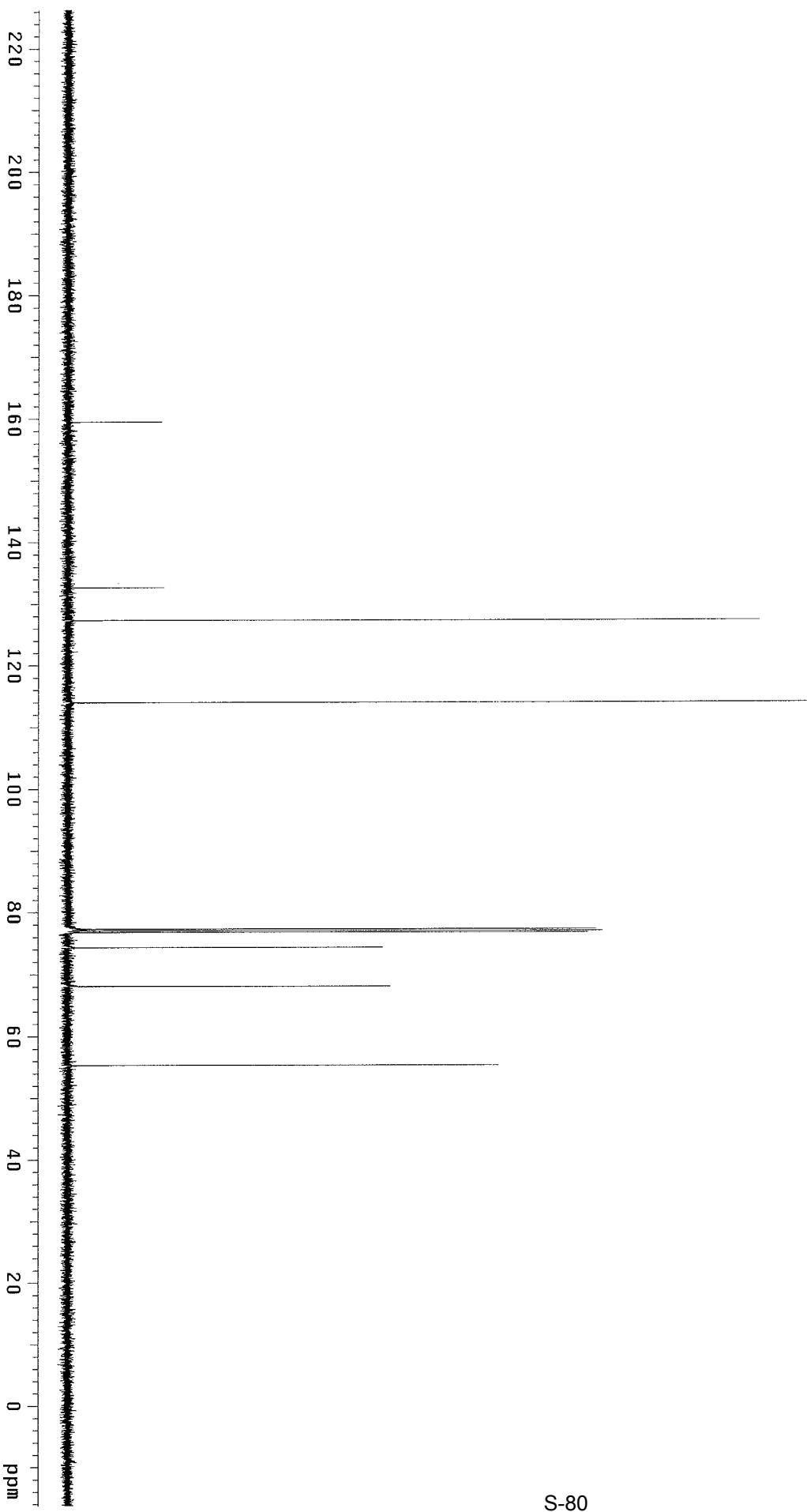


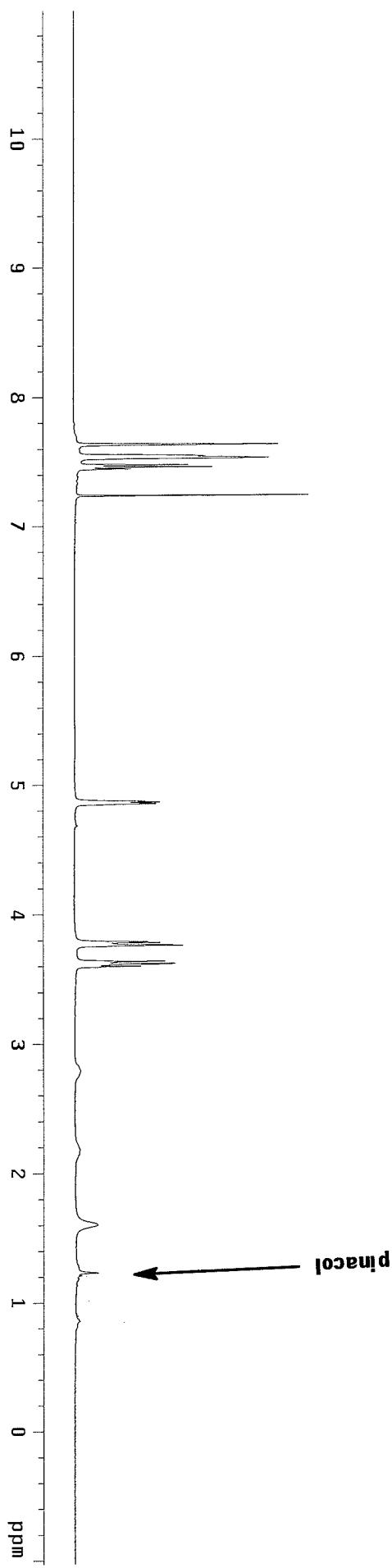
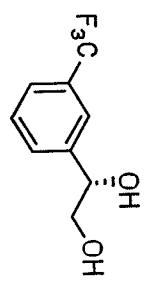


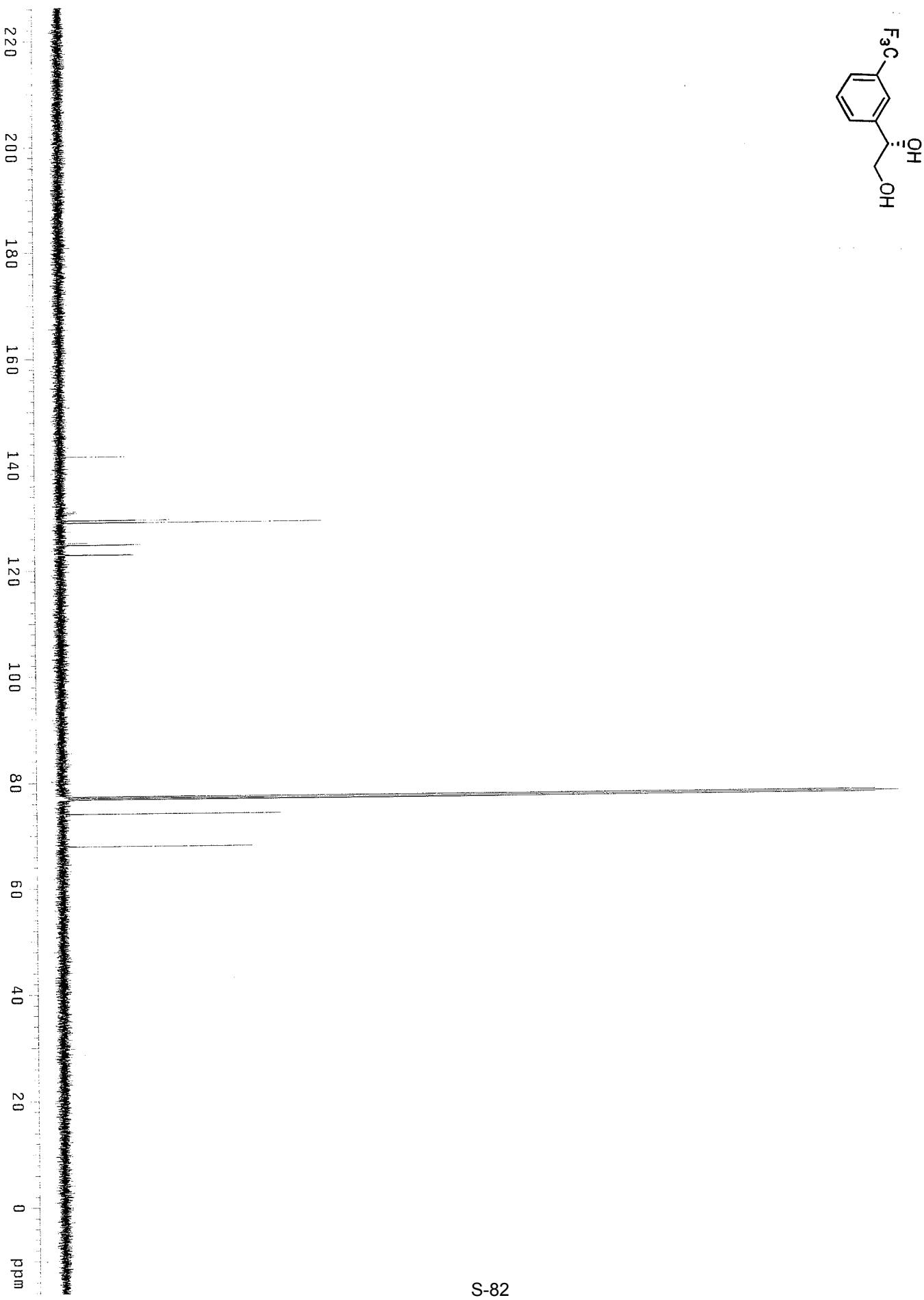


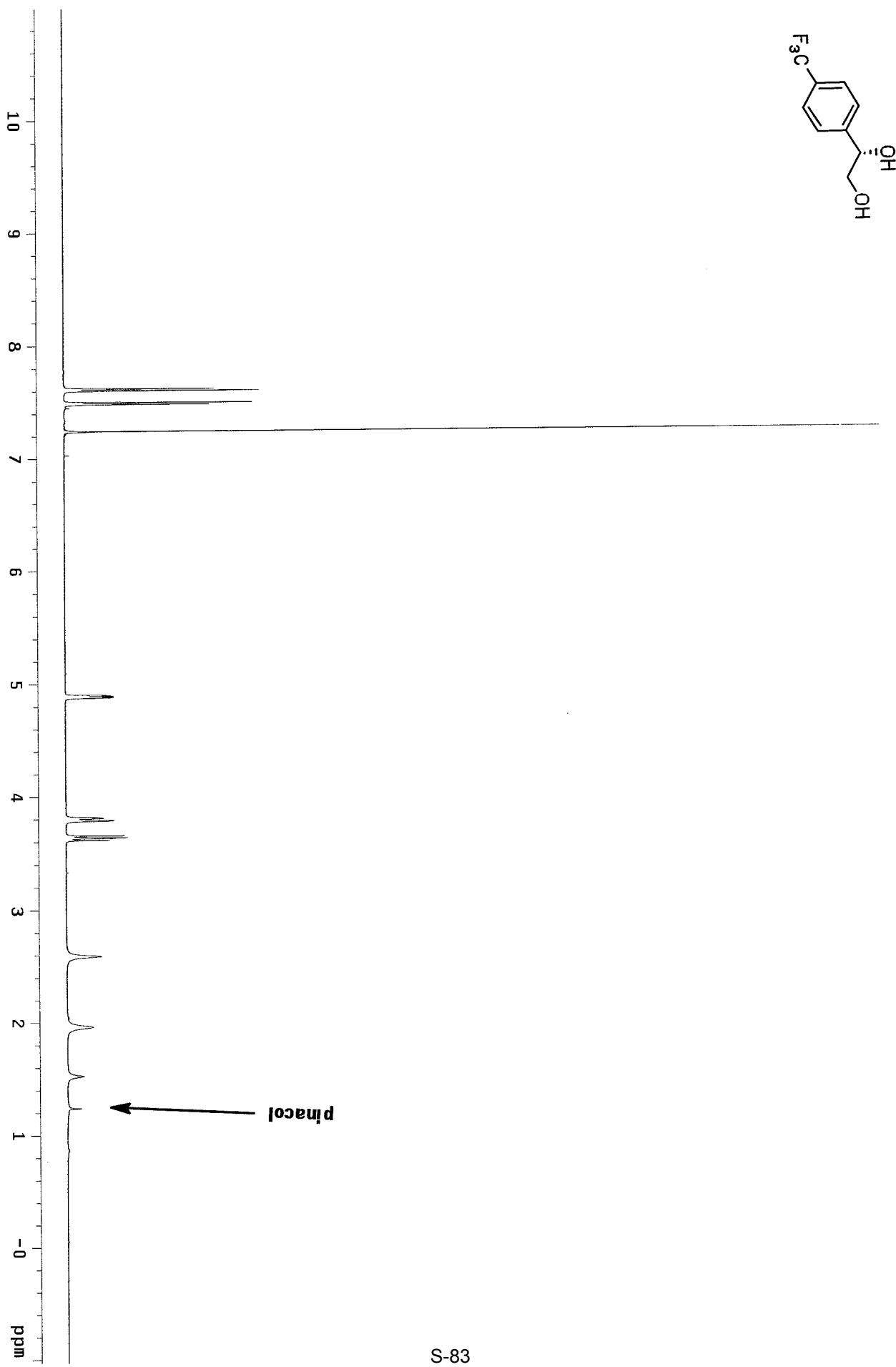


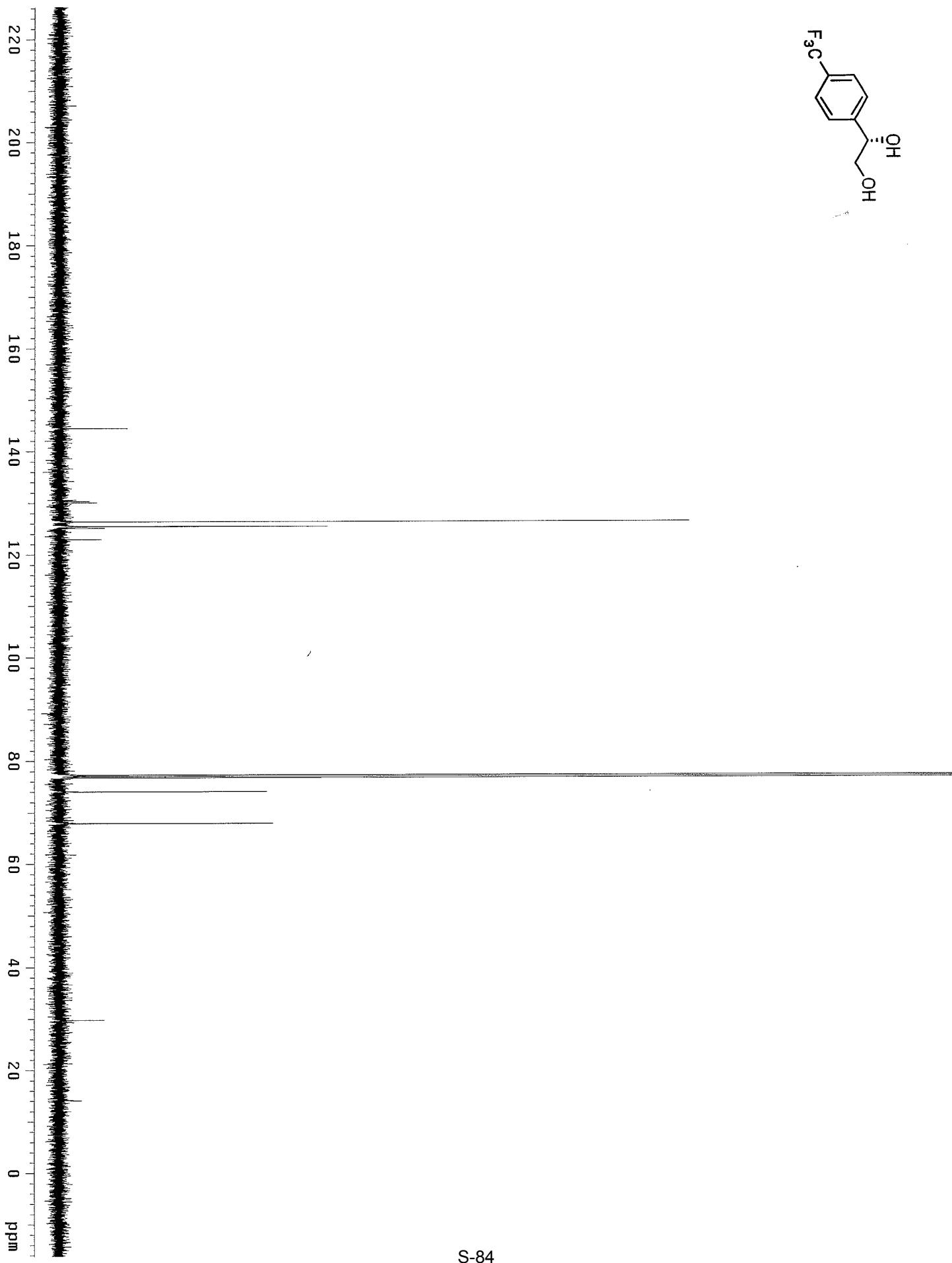


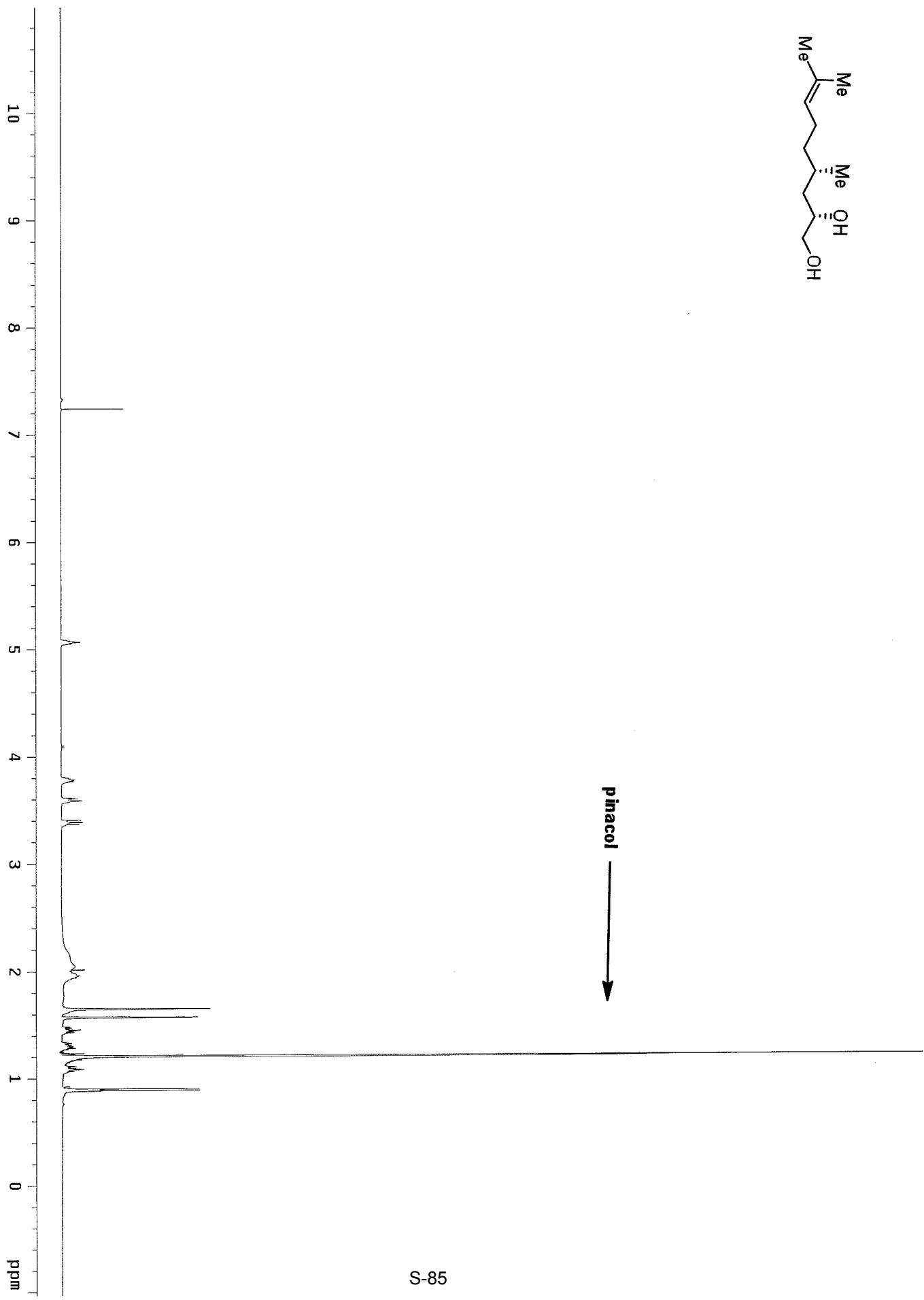


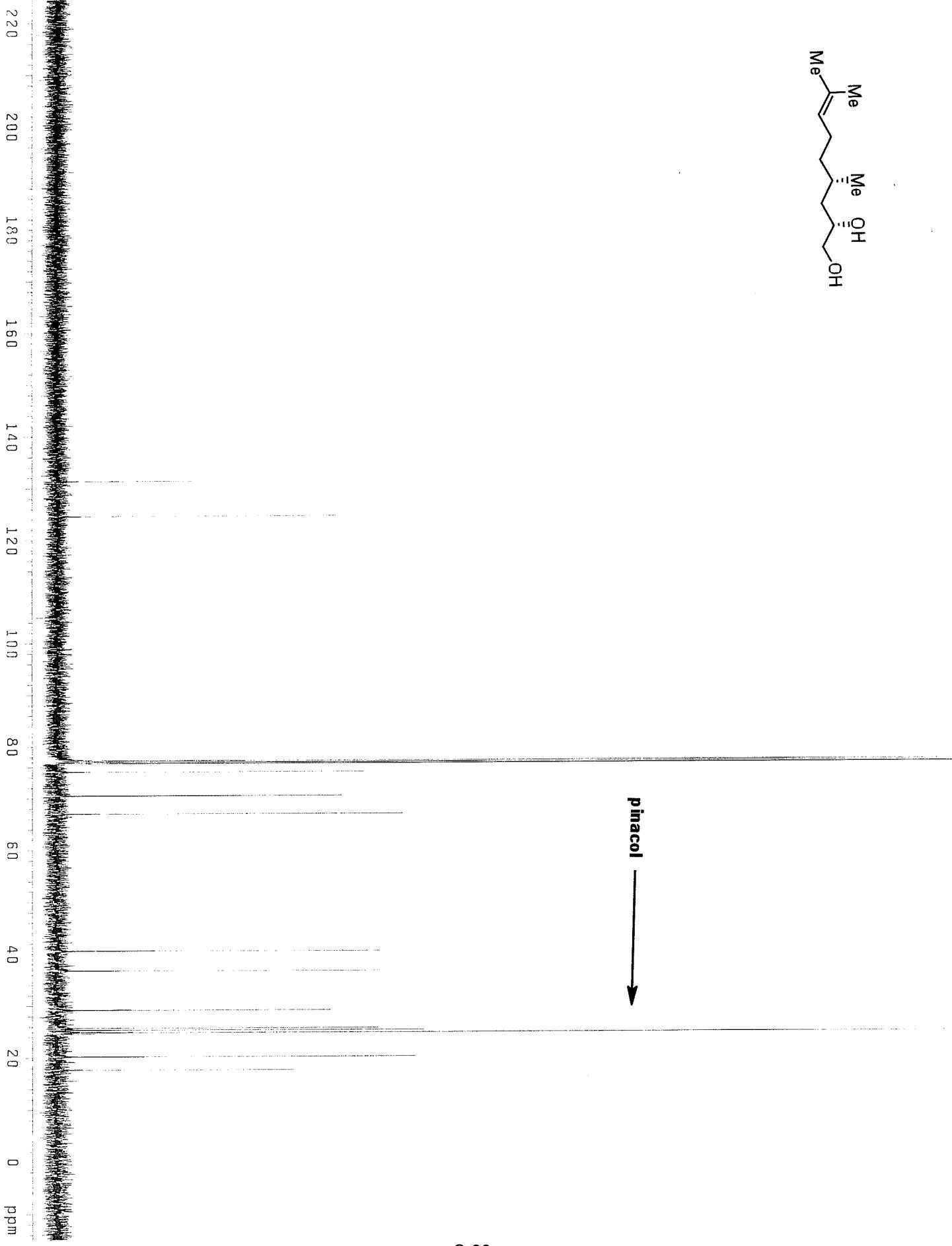


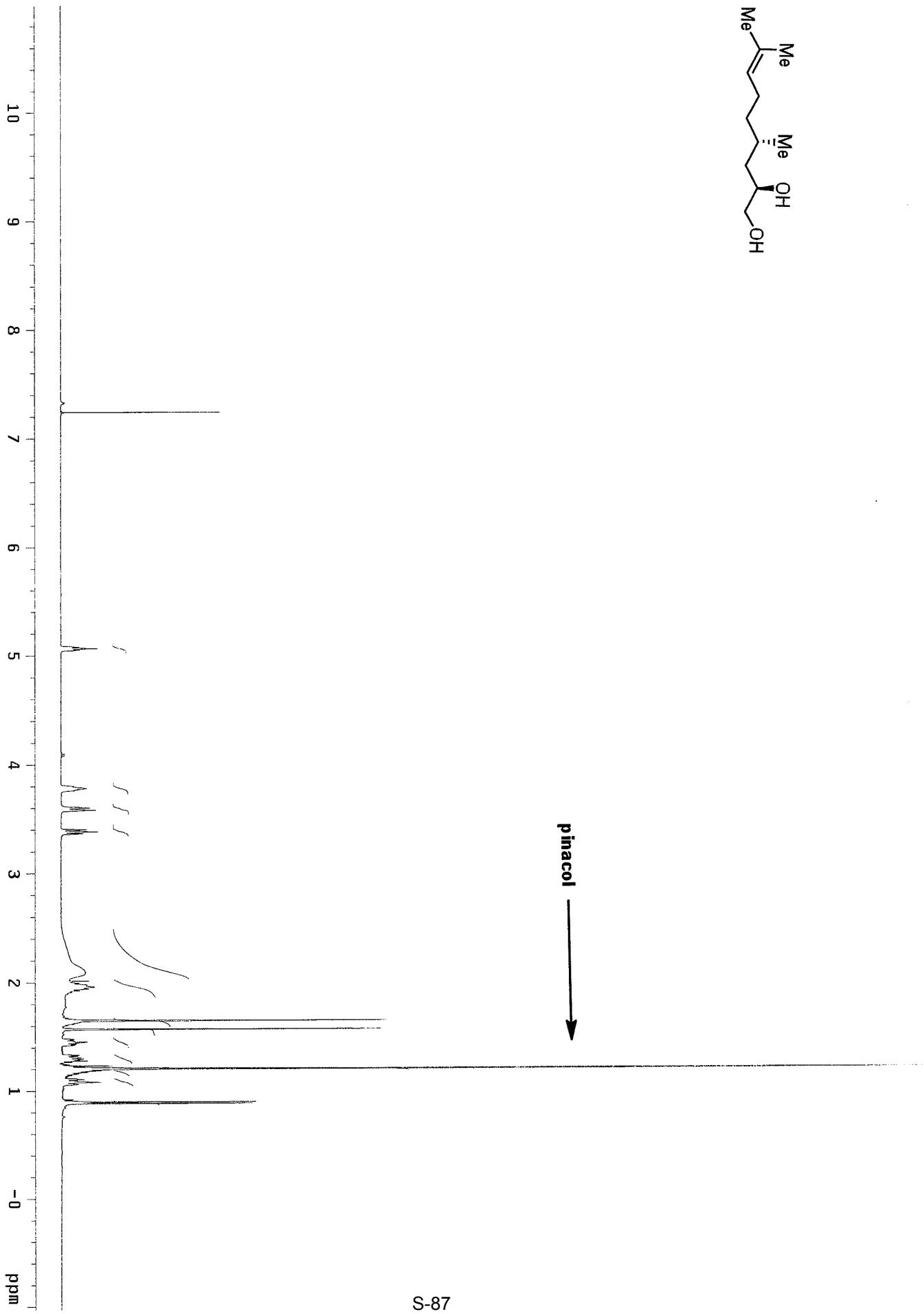


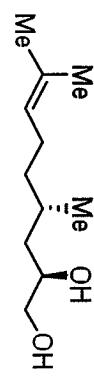




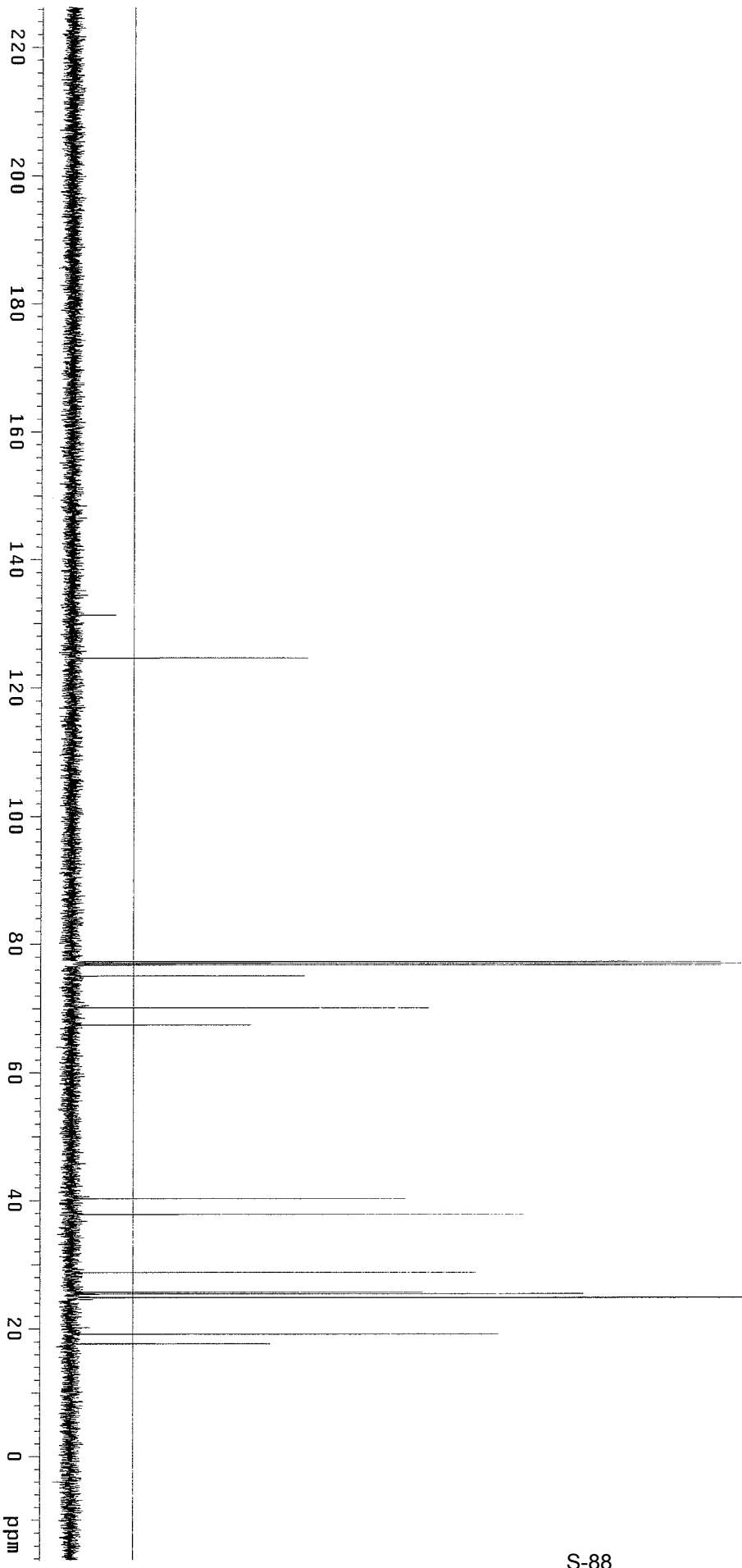


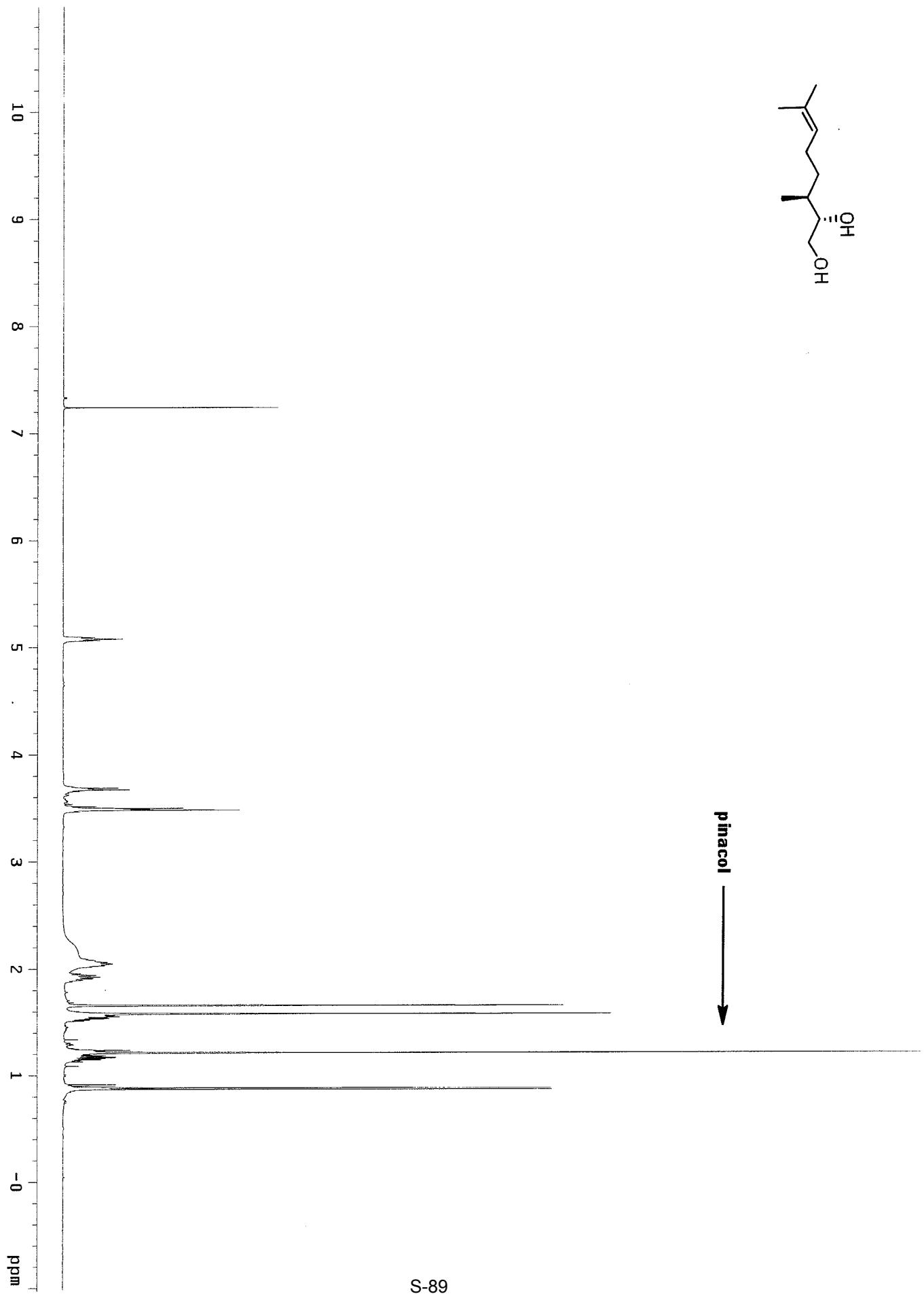


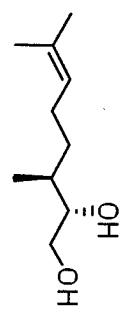
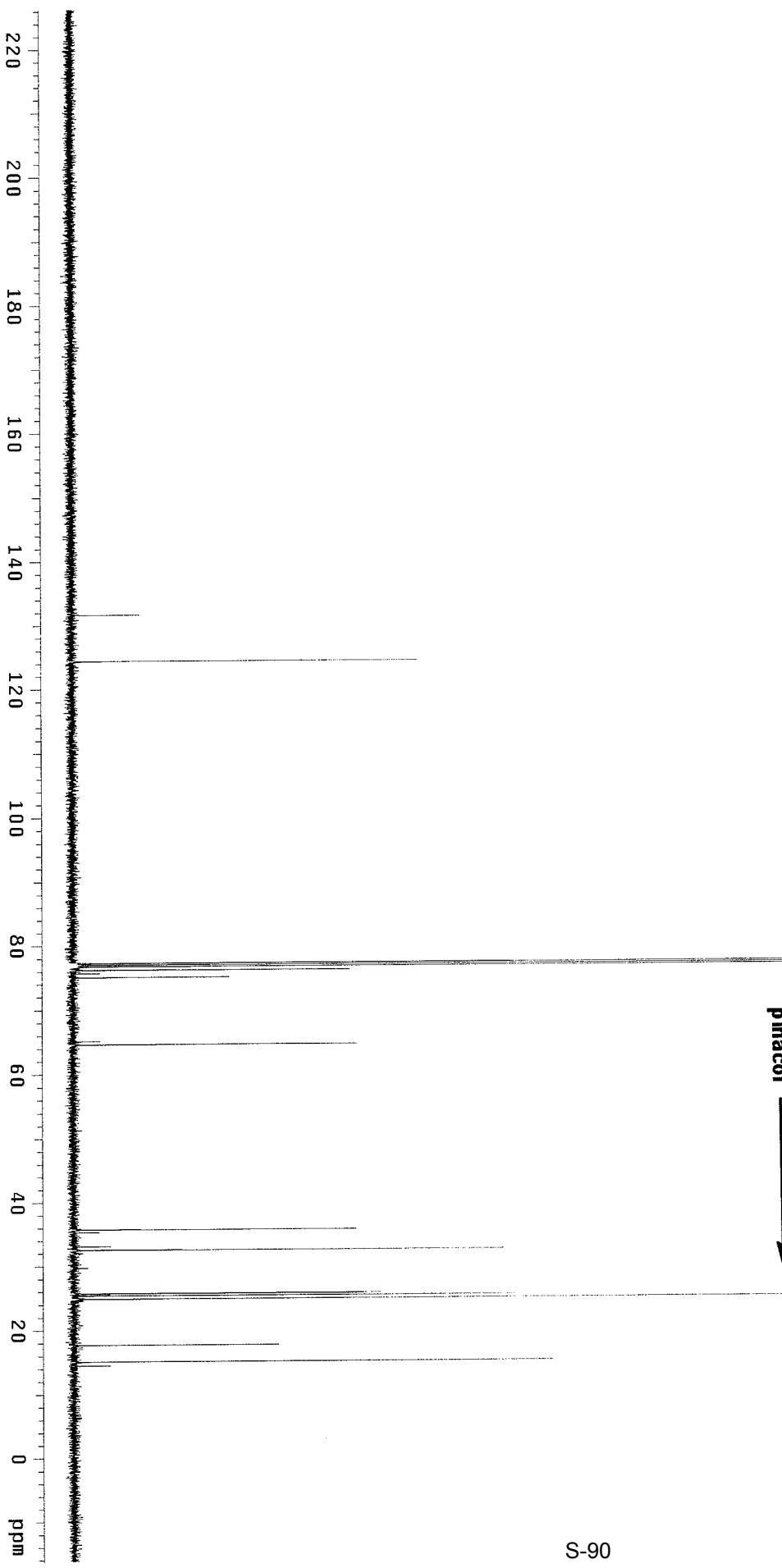


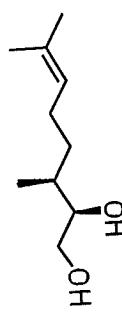
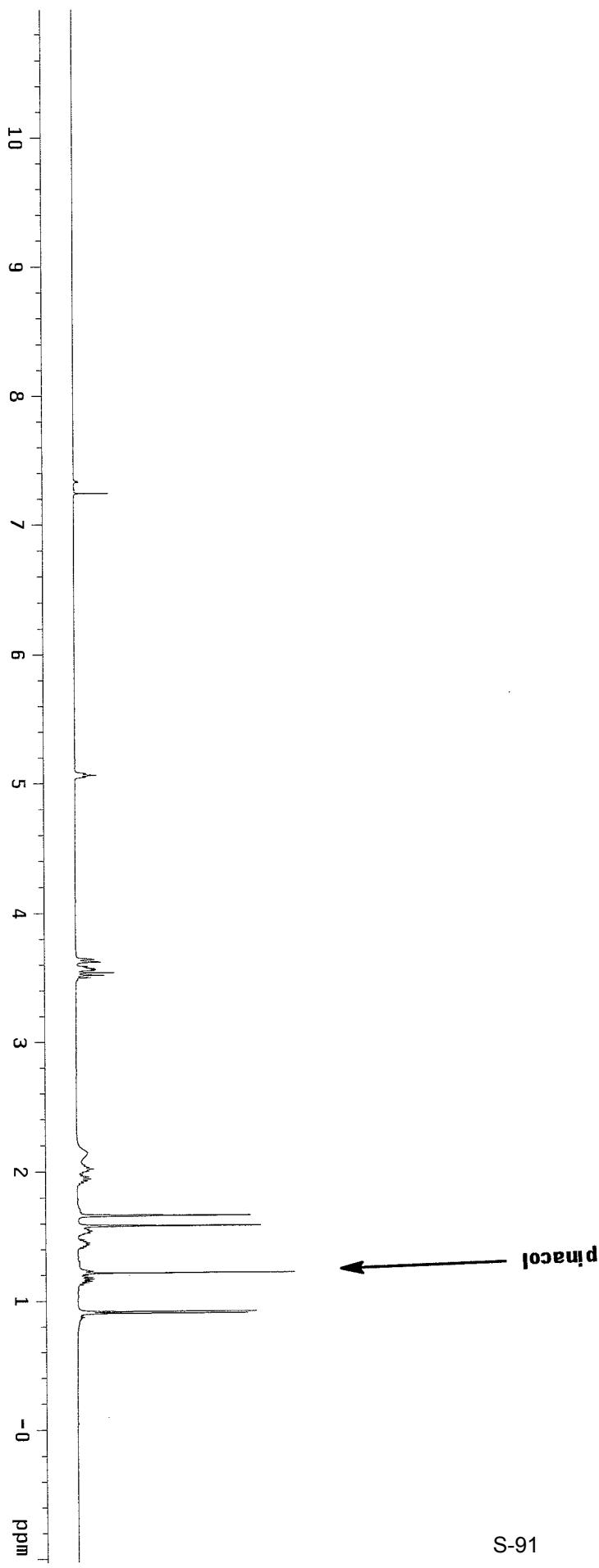


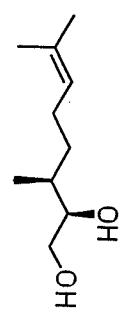
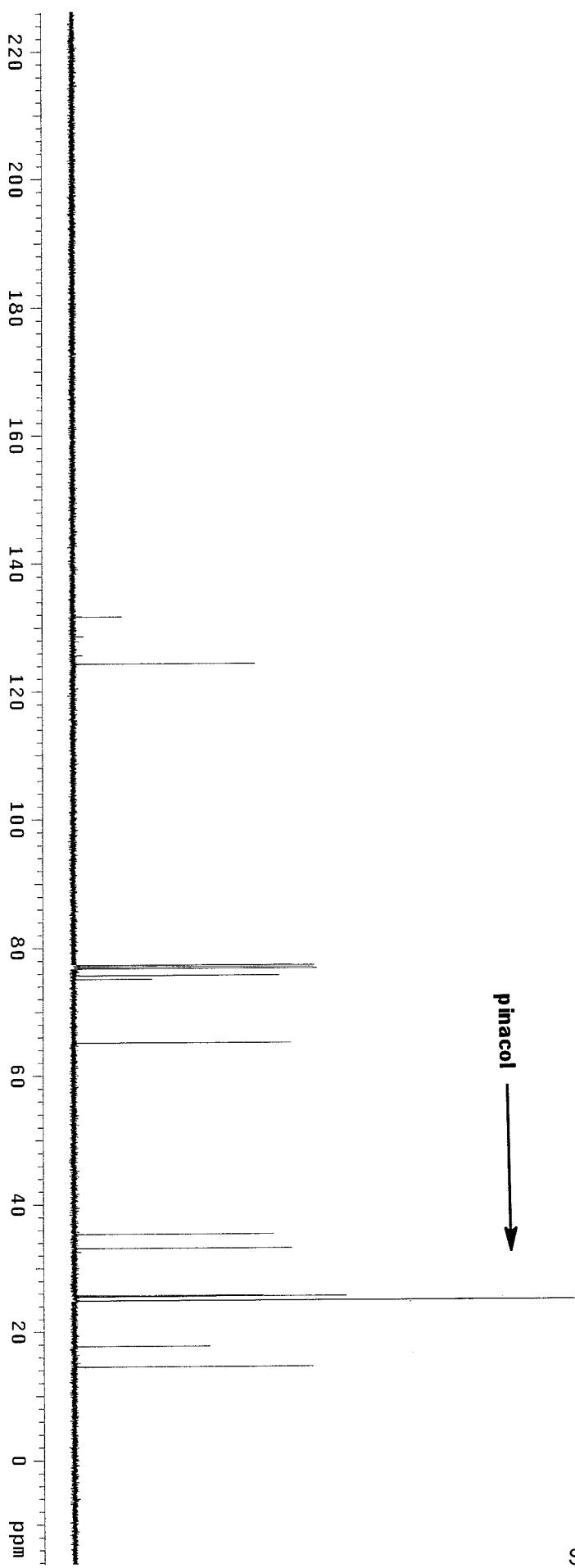
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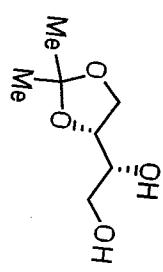
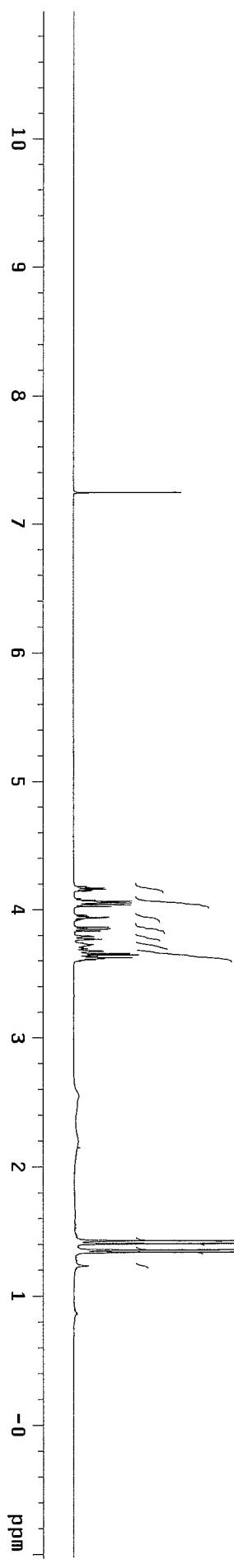


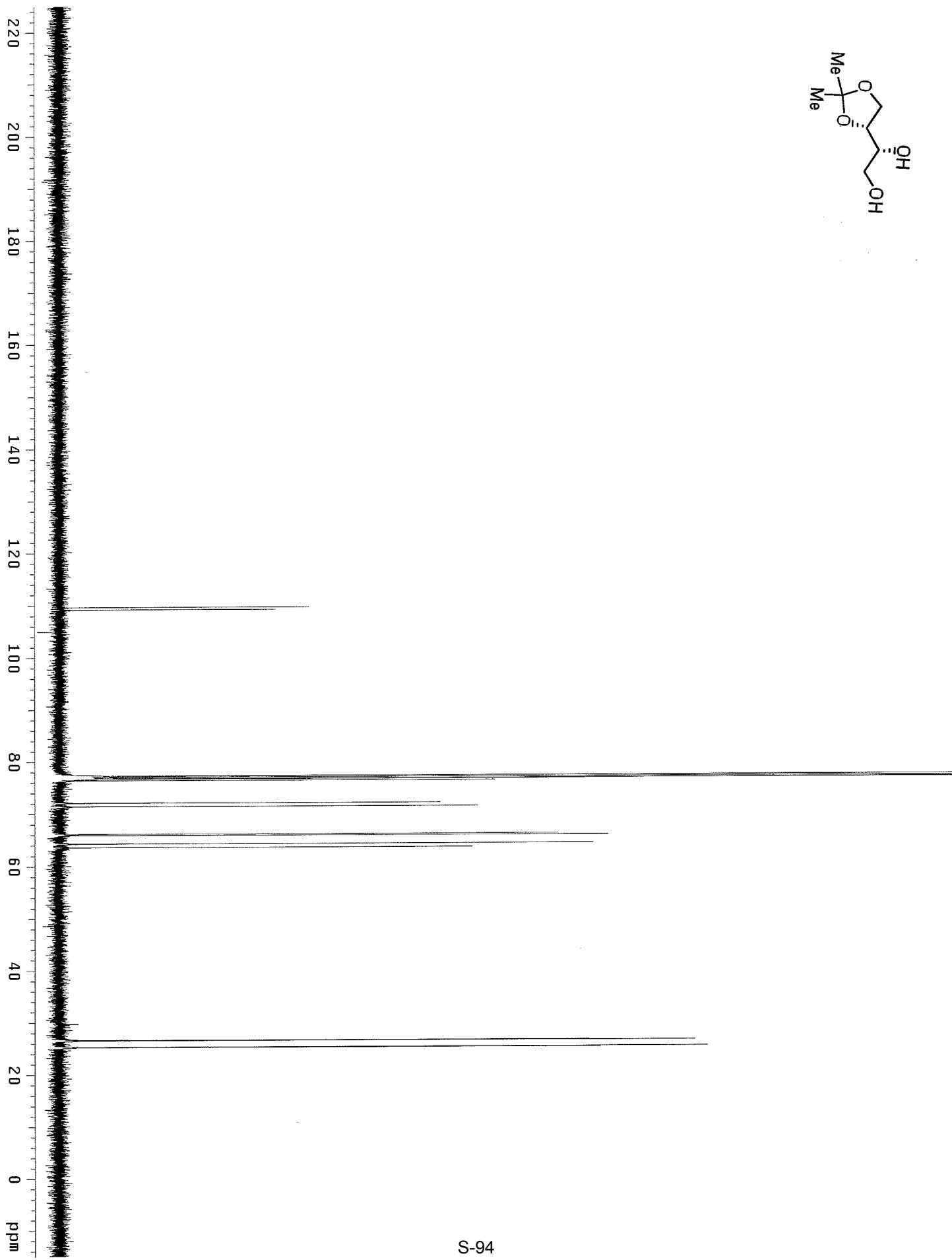


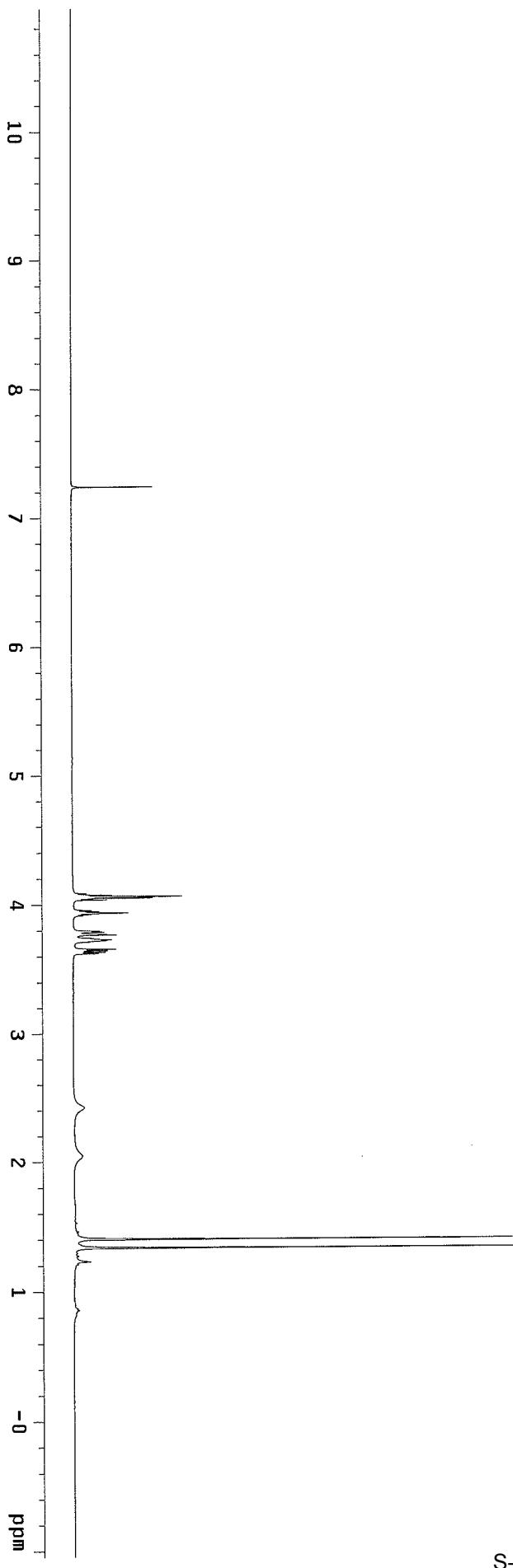




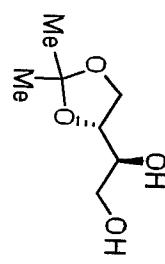


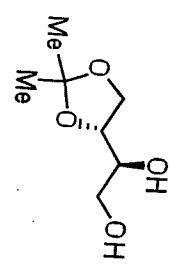
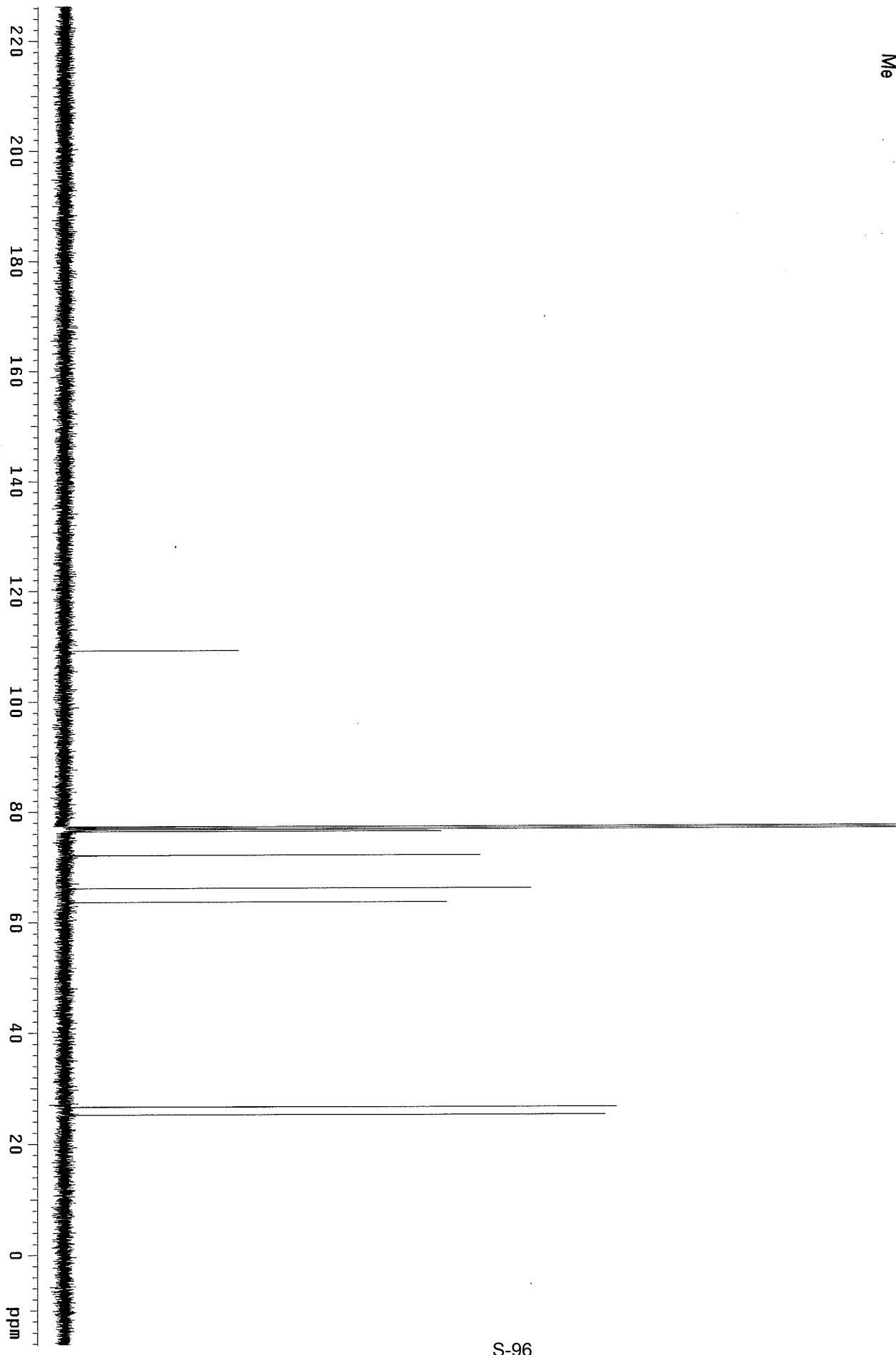


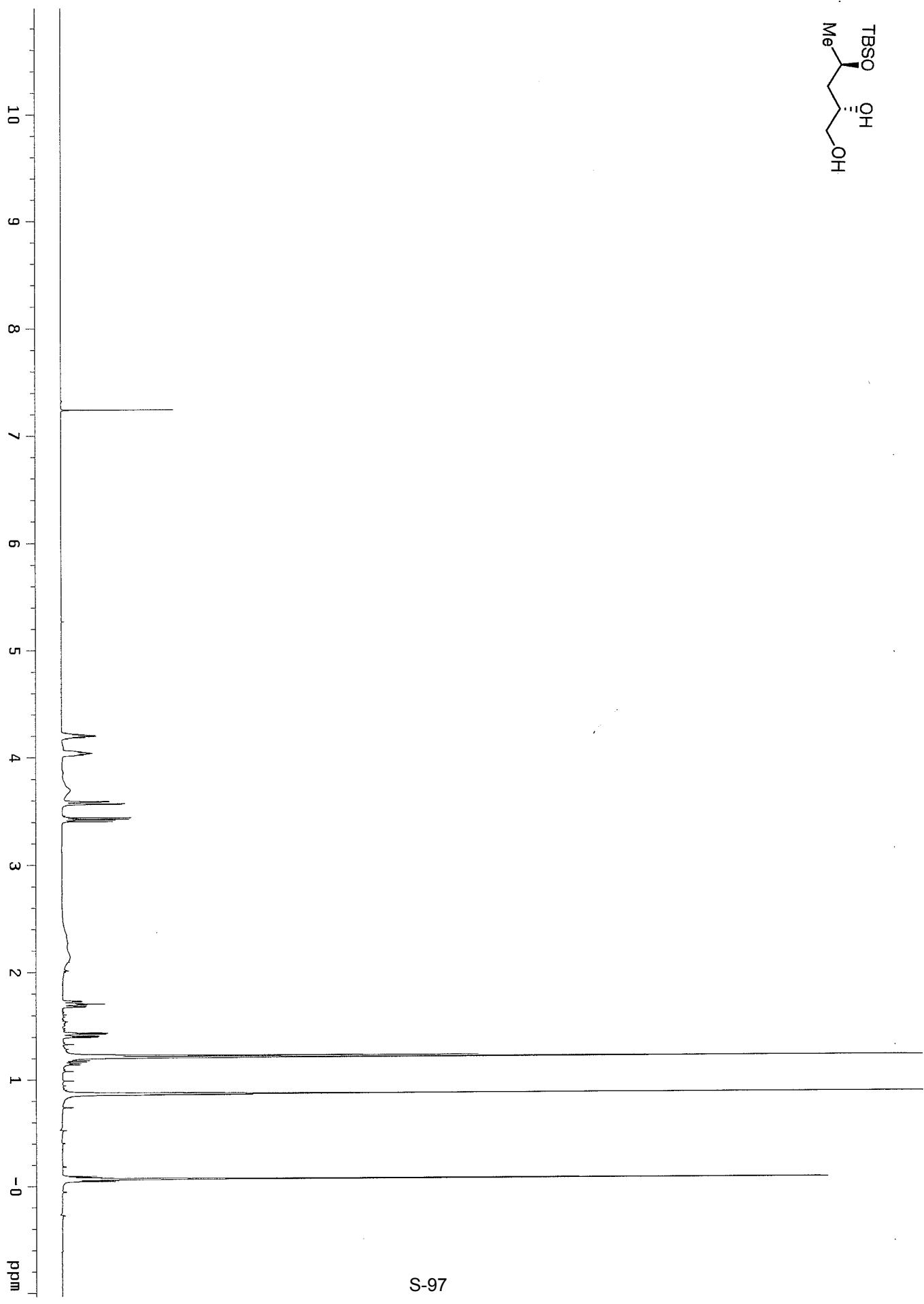


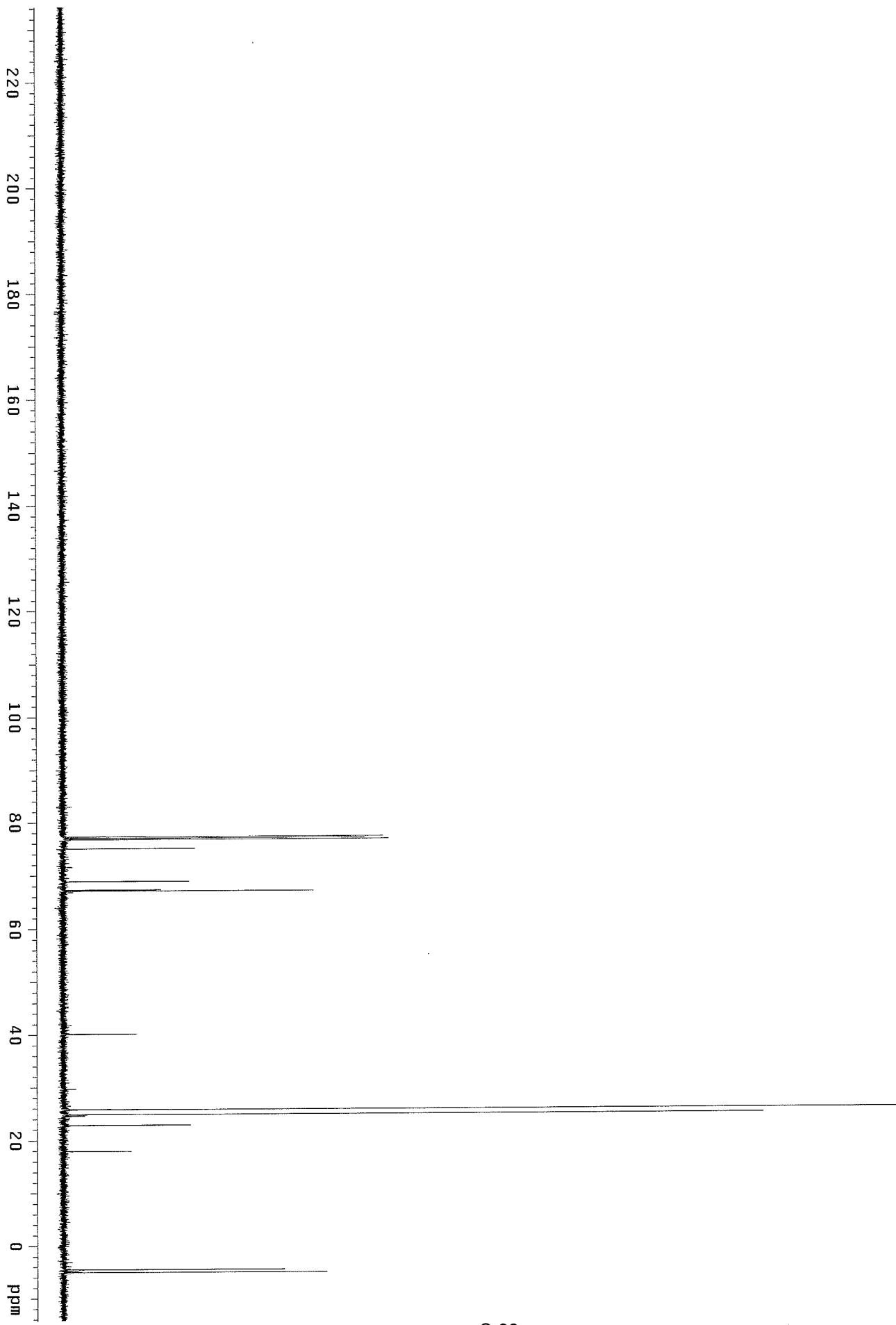


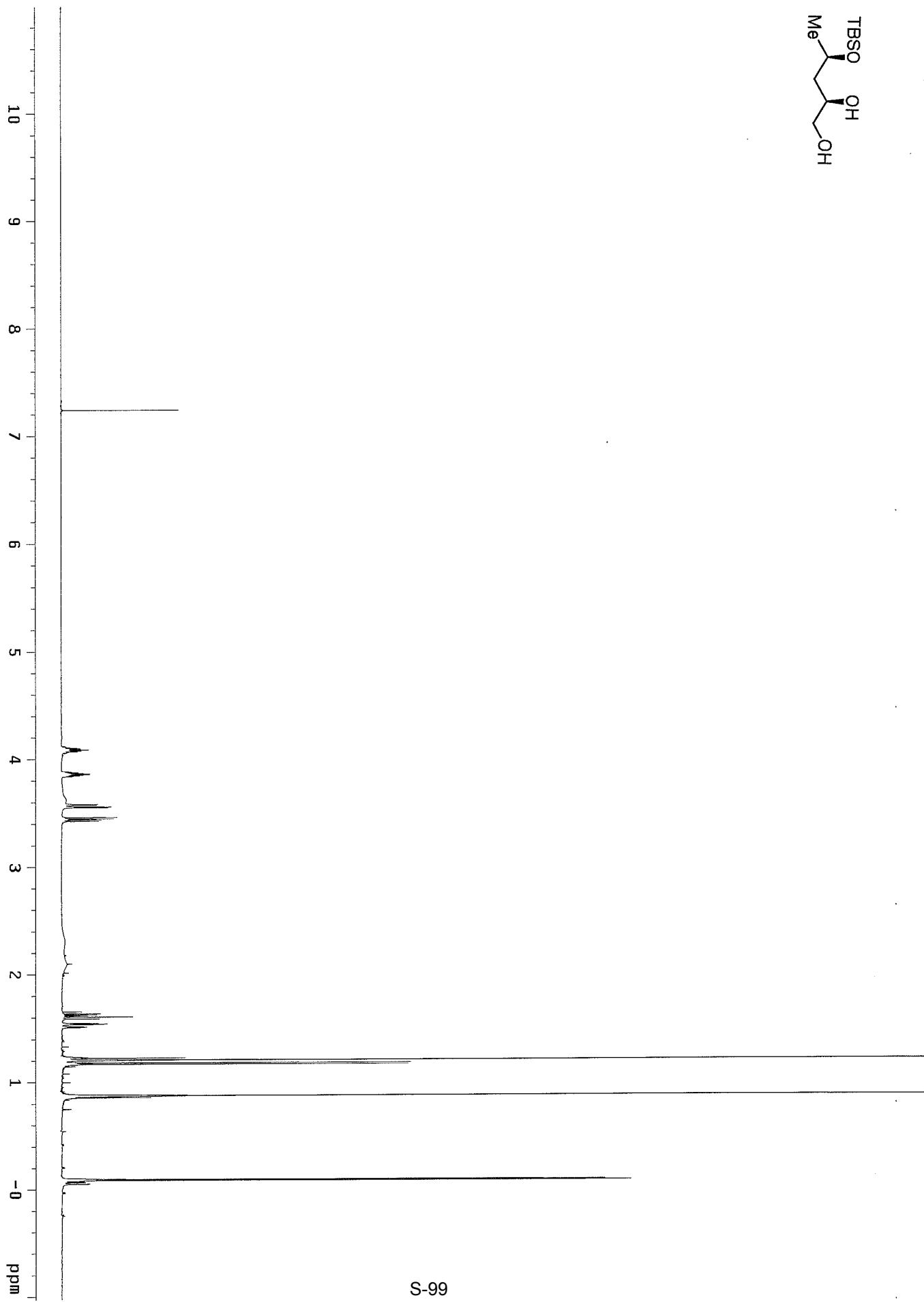
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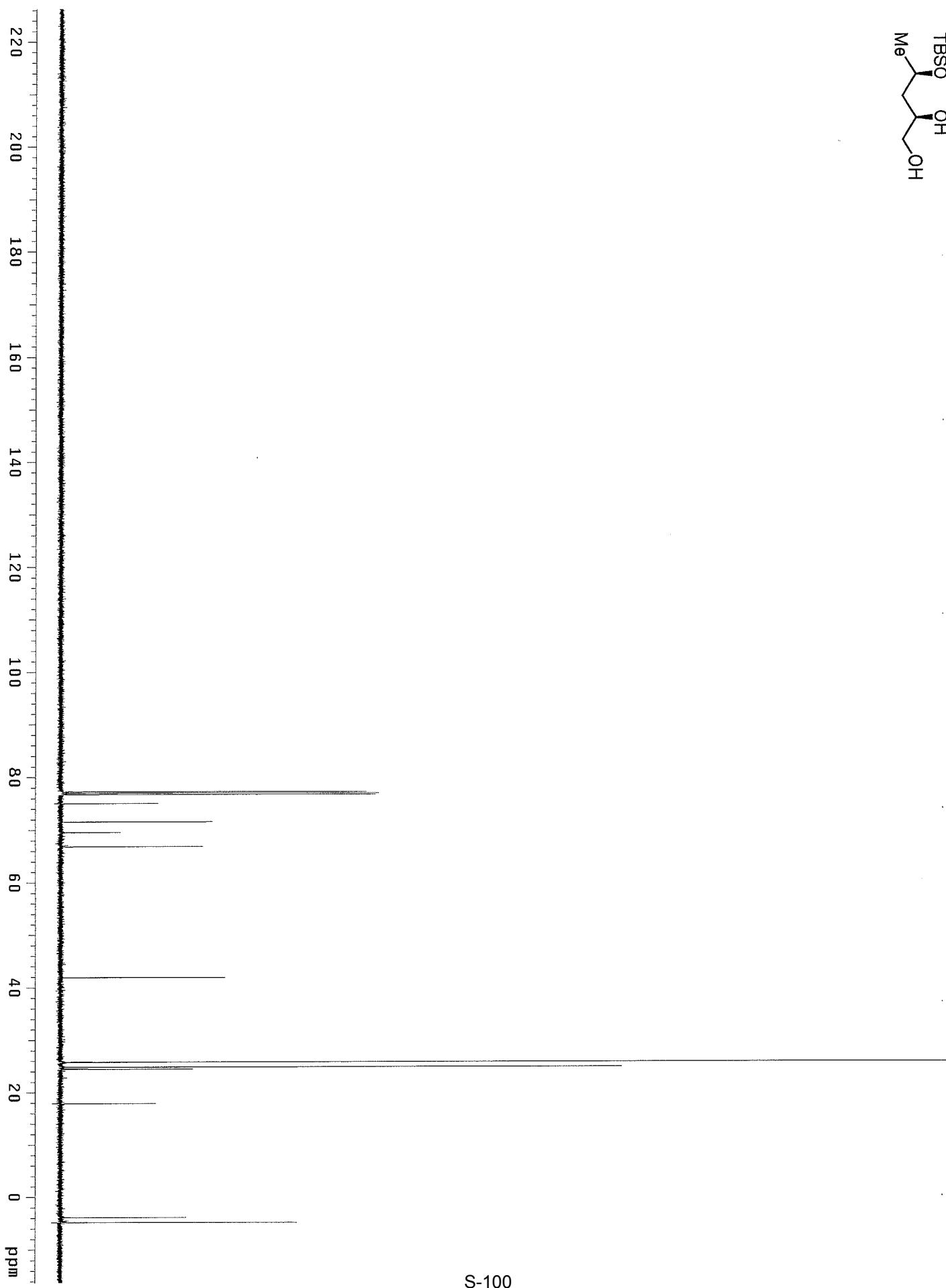
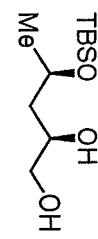




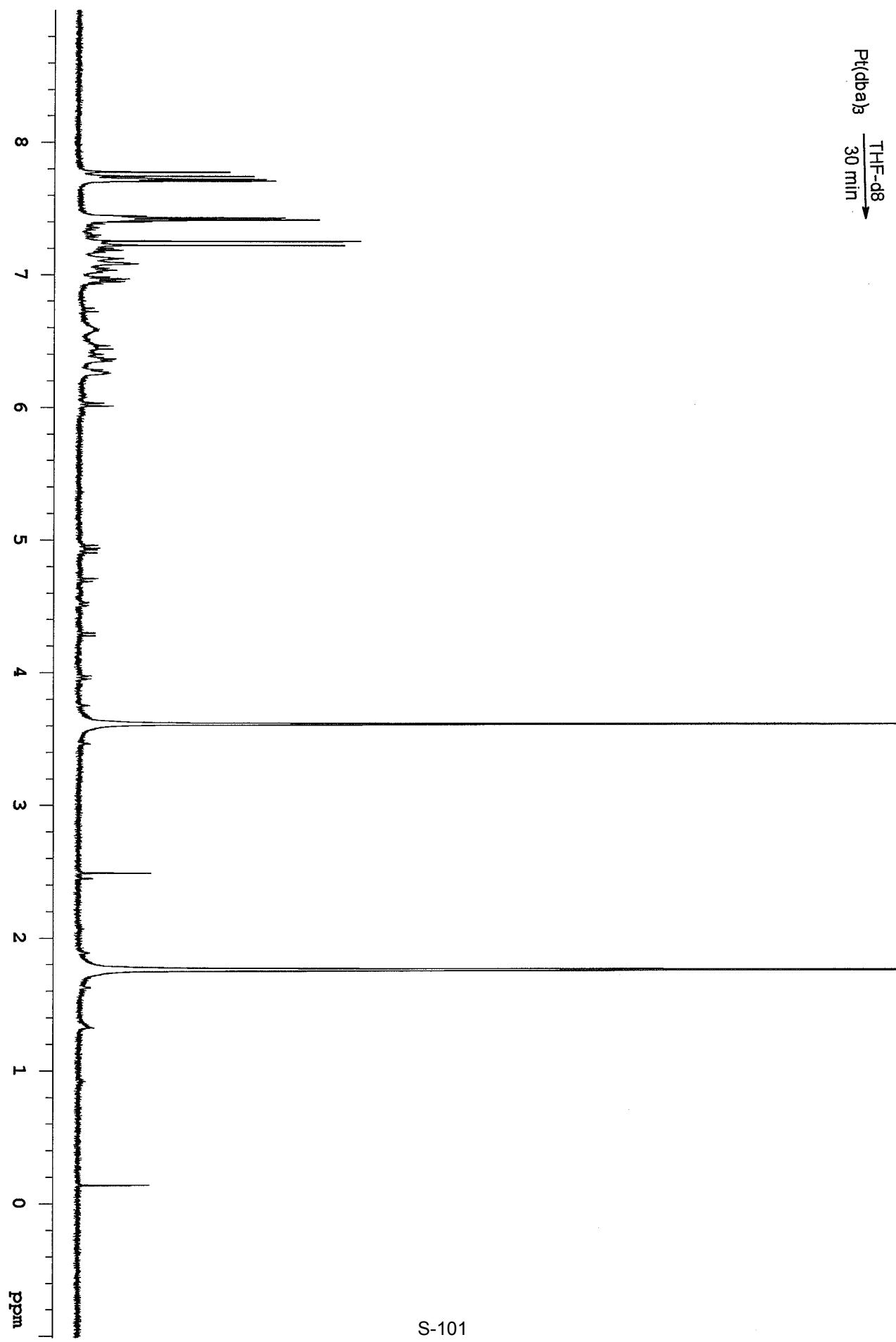


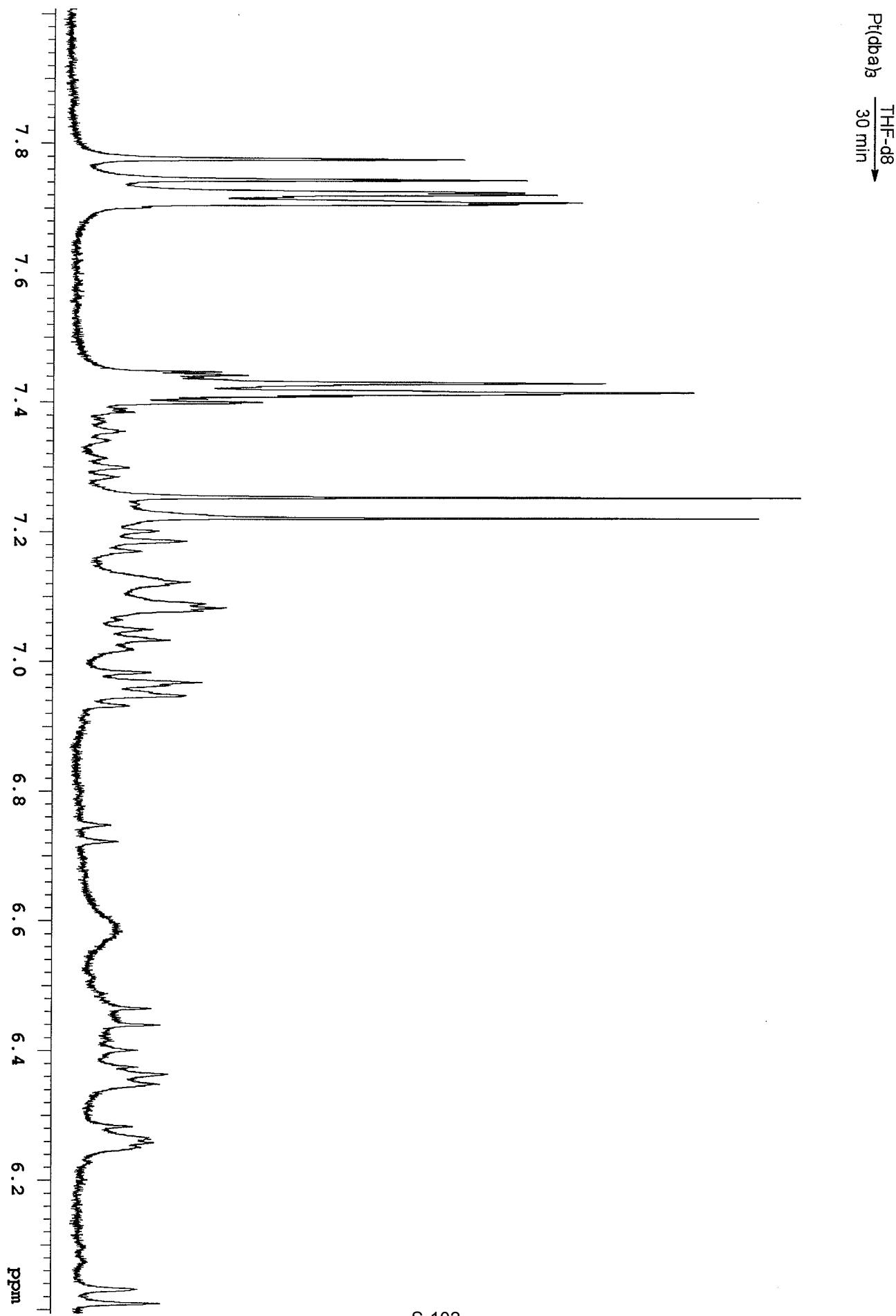


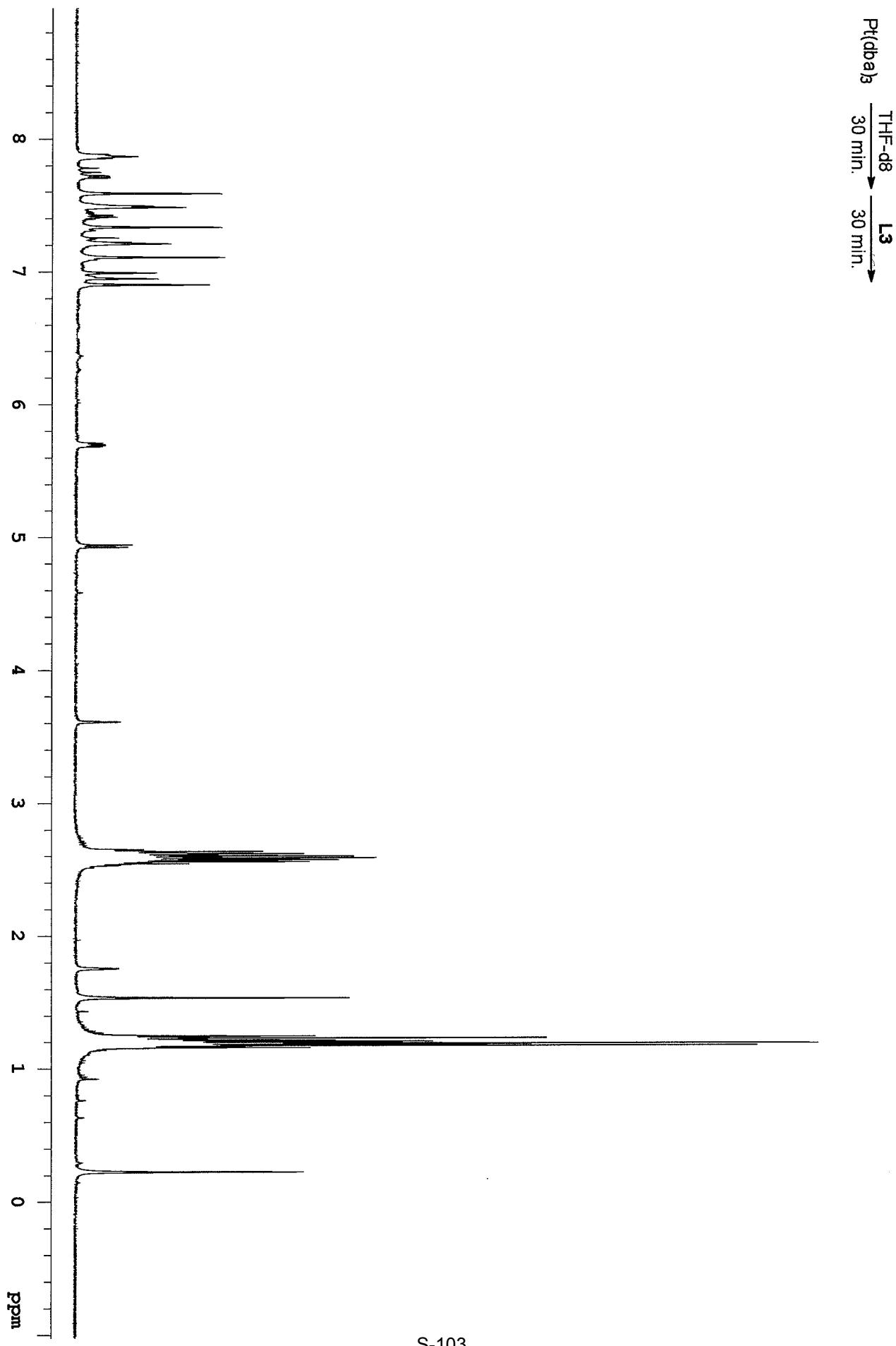


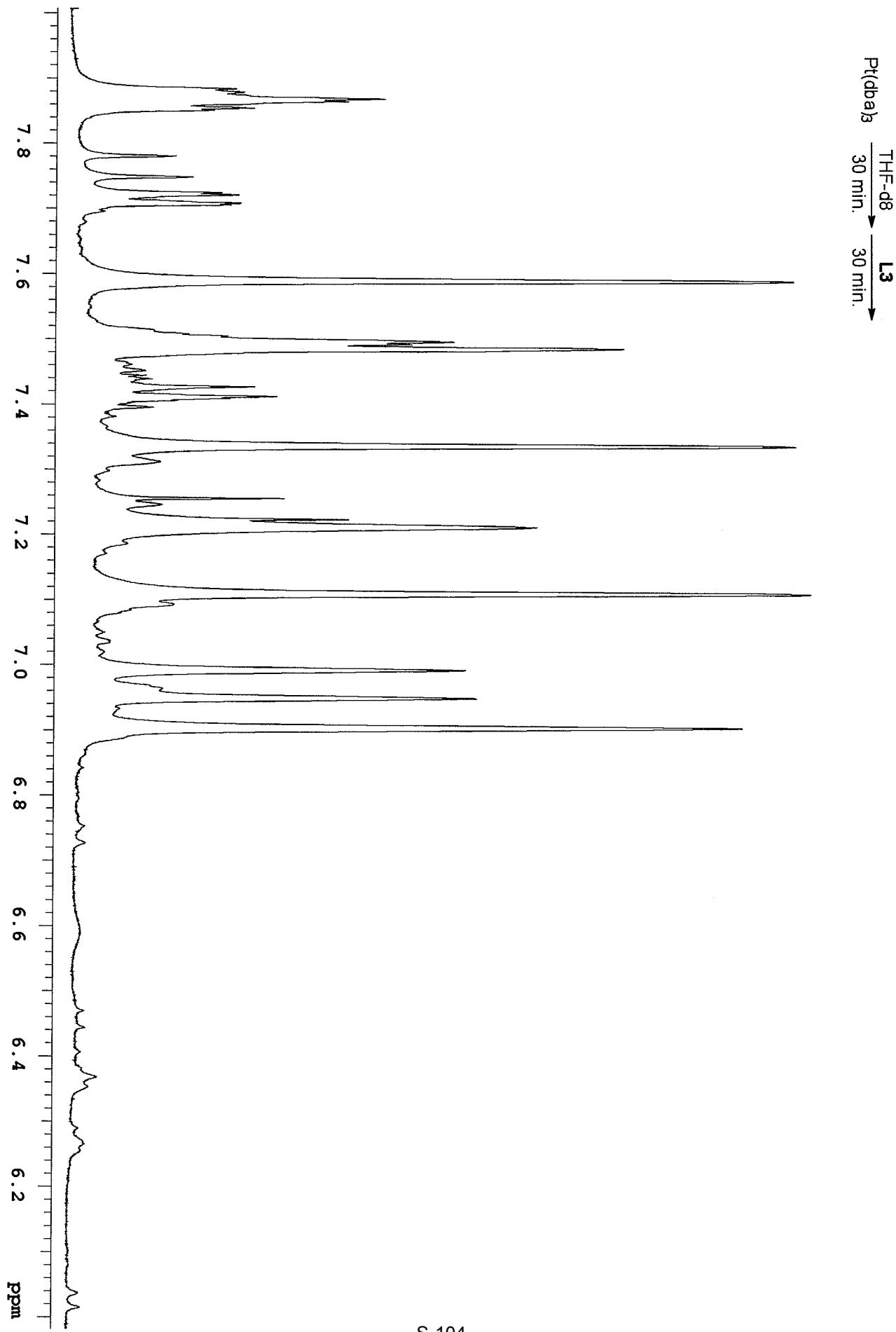


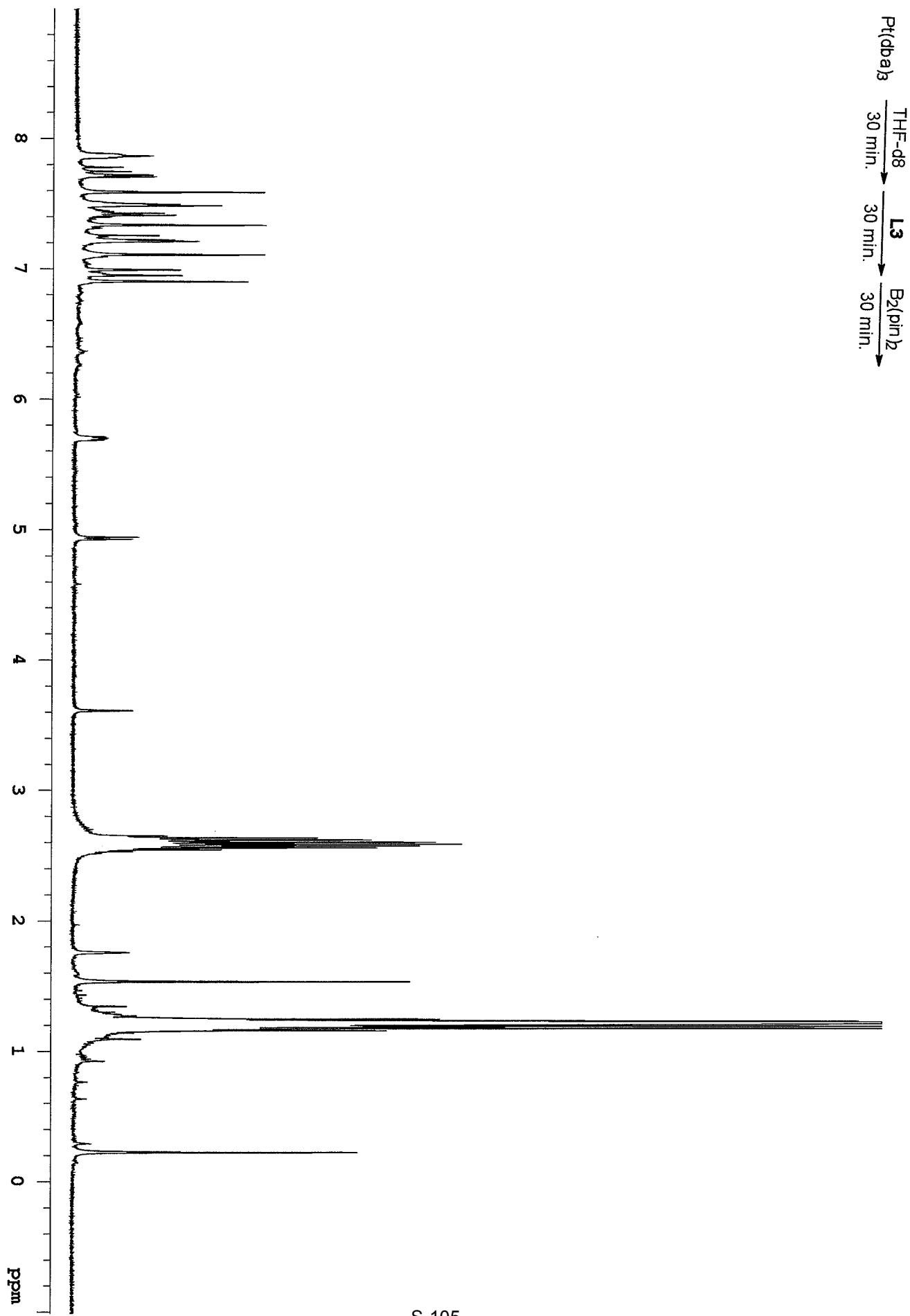
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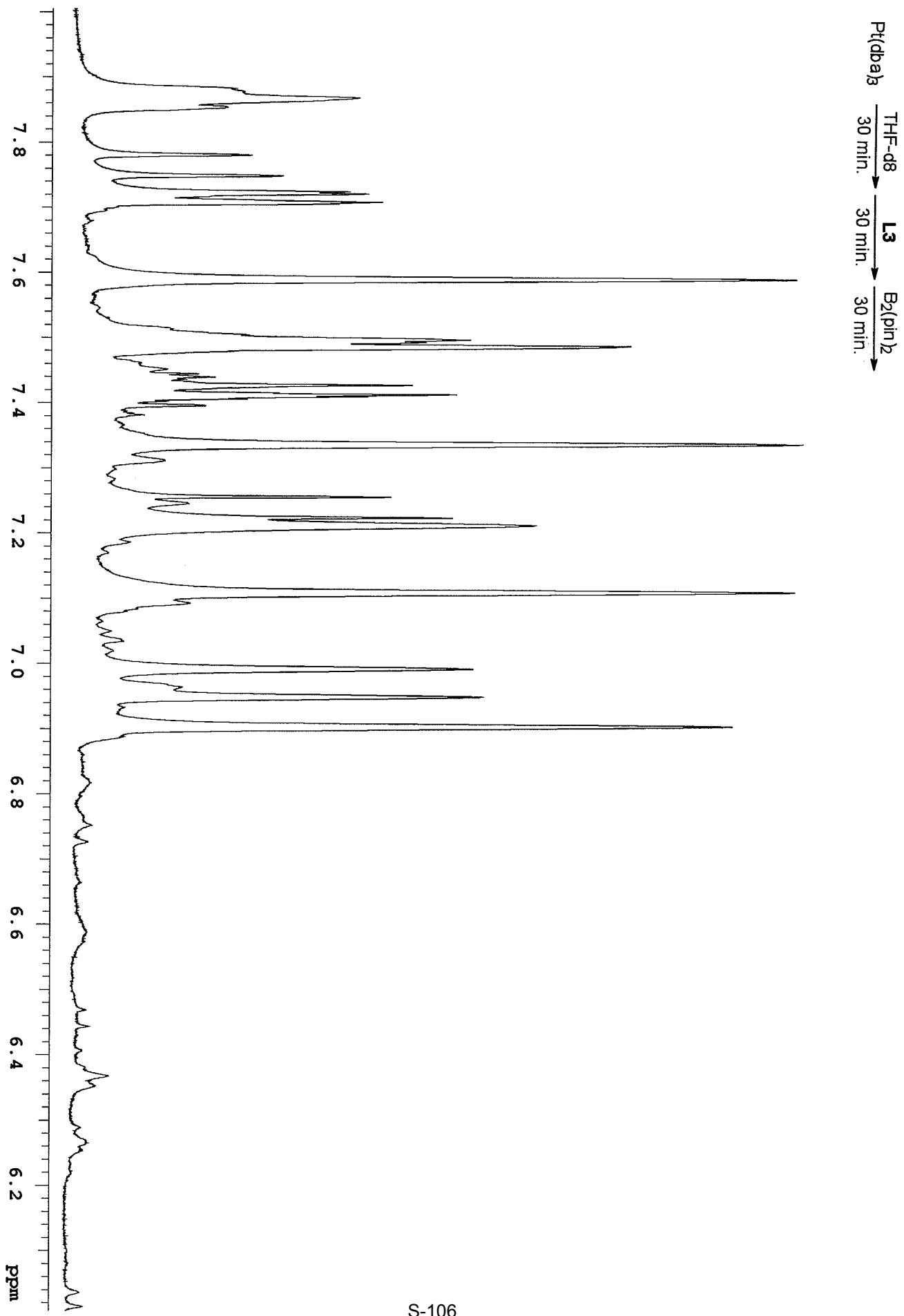


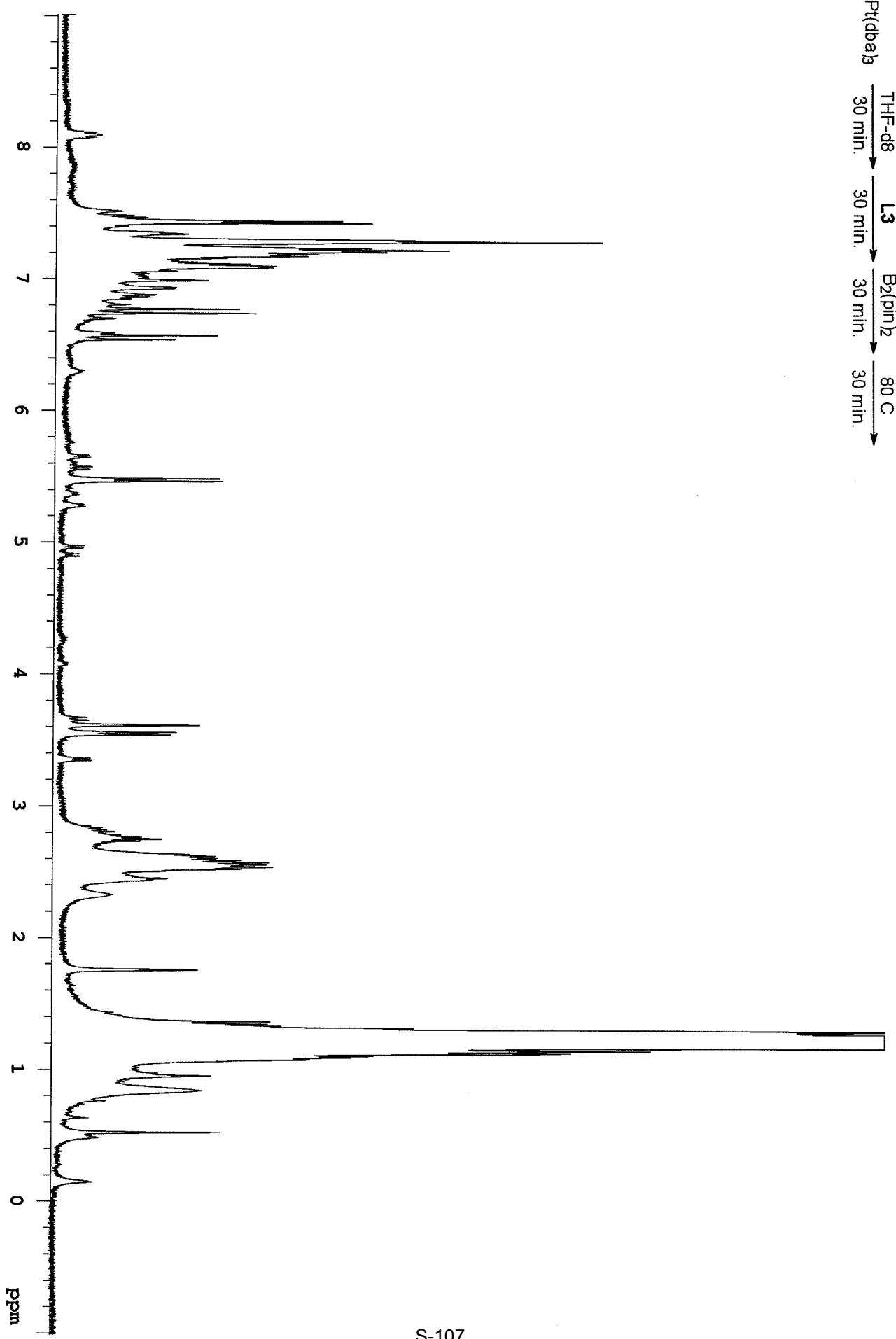




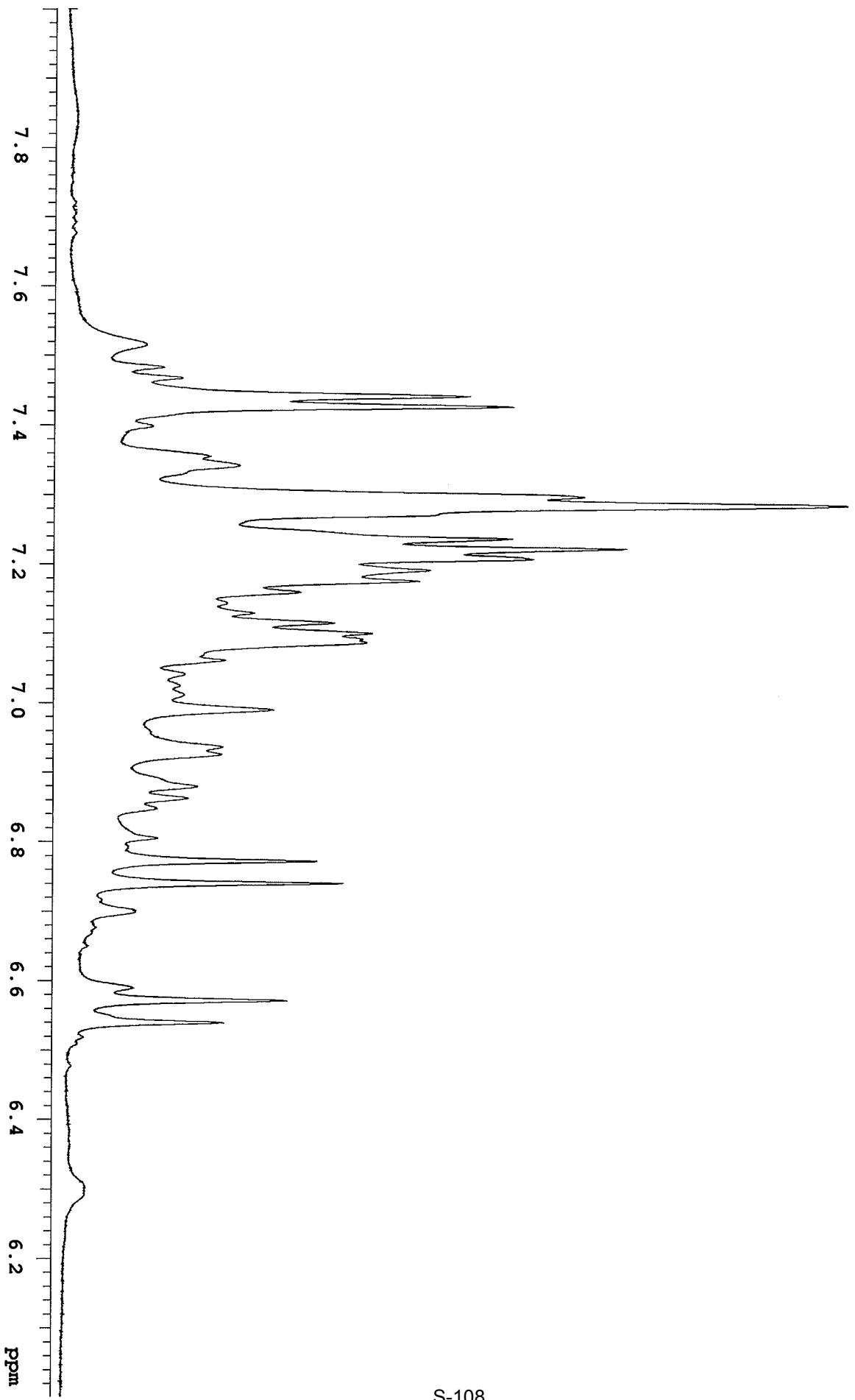




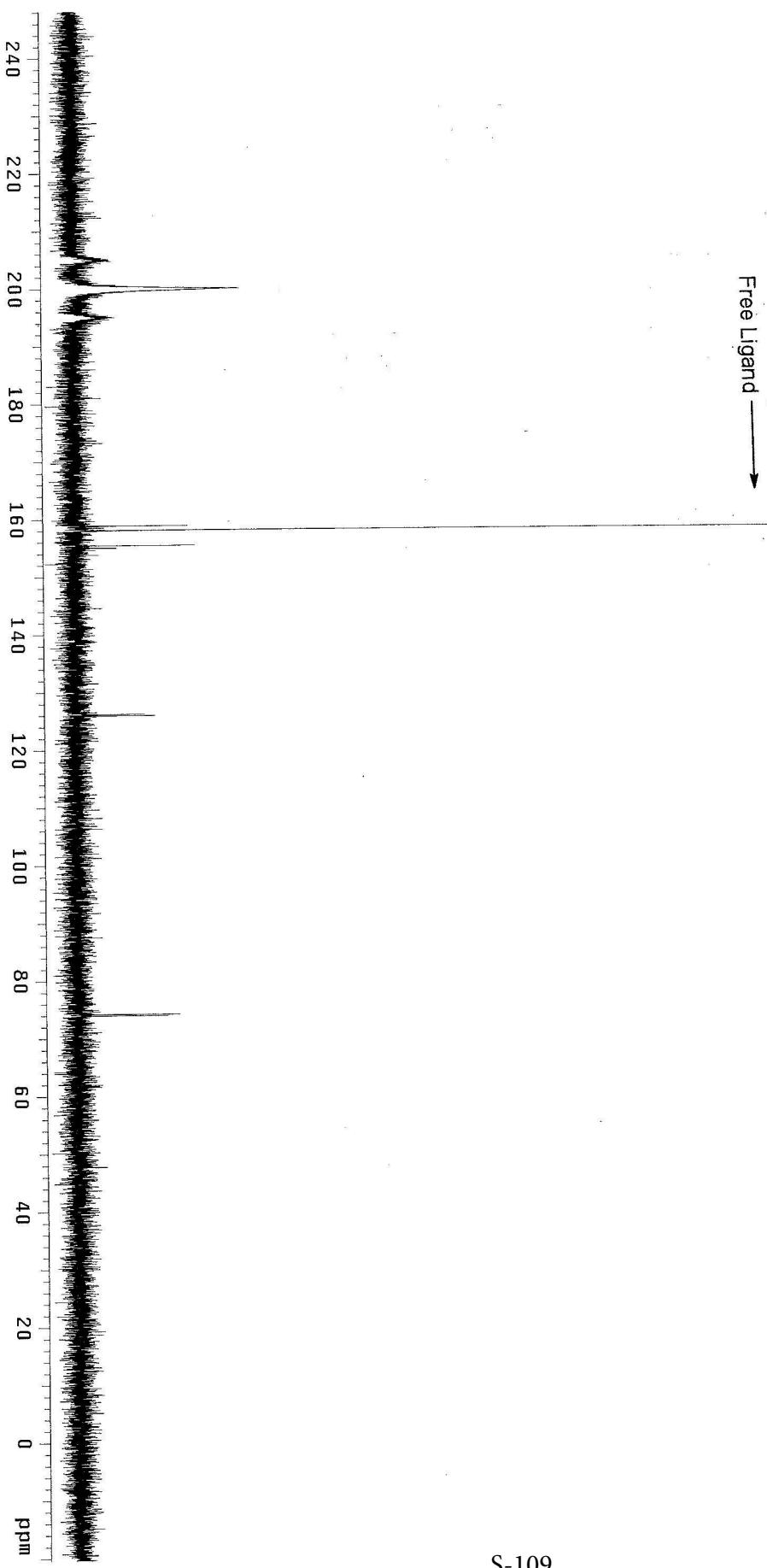




Pt(dba)<sub>3</sub>    THF-d<sub>8</sub>    30 min.    L<sub>3</sub>    30 min.    B<sub>2</sub>(pin)<sub>2</sub>    30 min.    80 C    30 min.

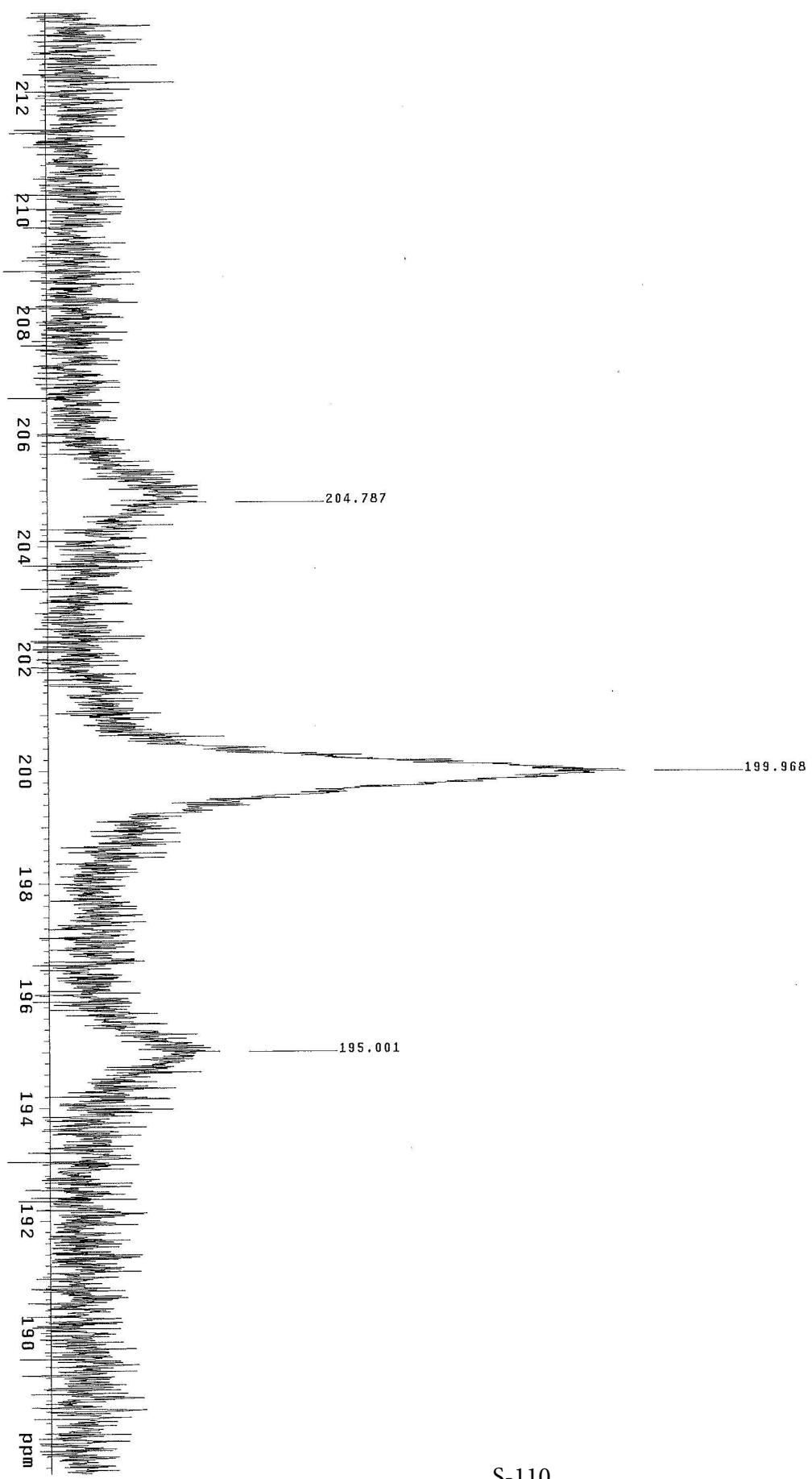


31P NMR  
202 MHz  $^{31}\text{P}$   
 $\text{B}_2(\text{pin})_2$   $\xrightarrow[\text{THF-d}_8]{\quad}$   
3% Pt(dba)<sub>3</sub>  
3.6% **L4**  
80 °C, 30 min.



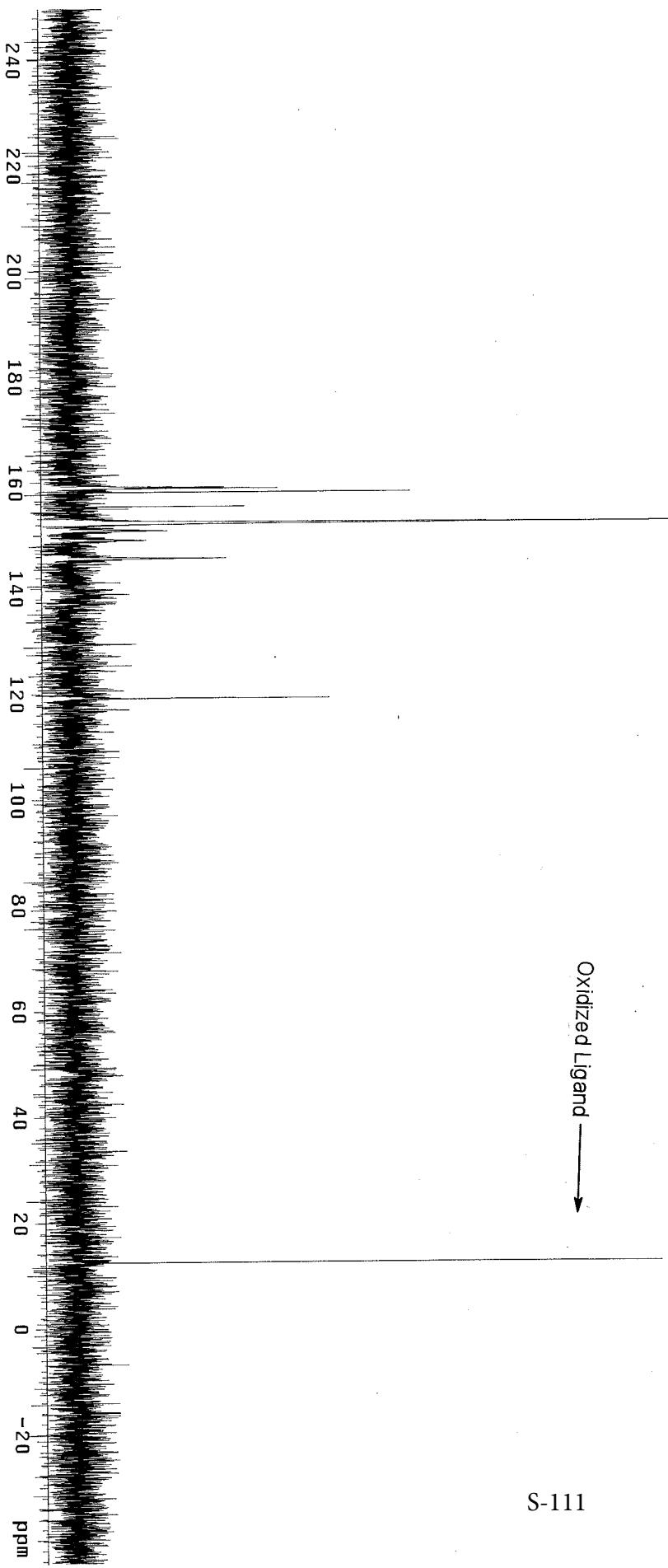
202 MHz  $^{31}\text{P}$

$\text{B}_2(\text{pin})\text{b}$   $\xrightarrow[\text{THF-}d_8]{\substack{3\% \text{ Pt}(\text{dba})\beta \\ 3.6\% \text{ L4}}}$   
80 °C, 30 min.

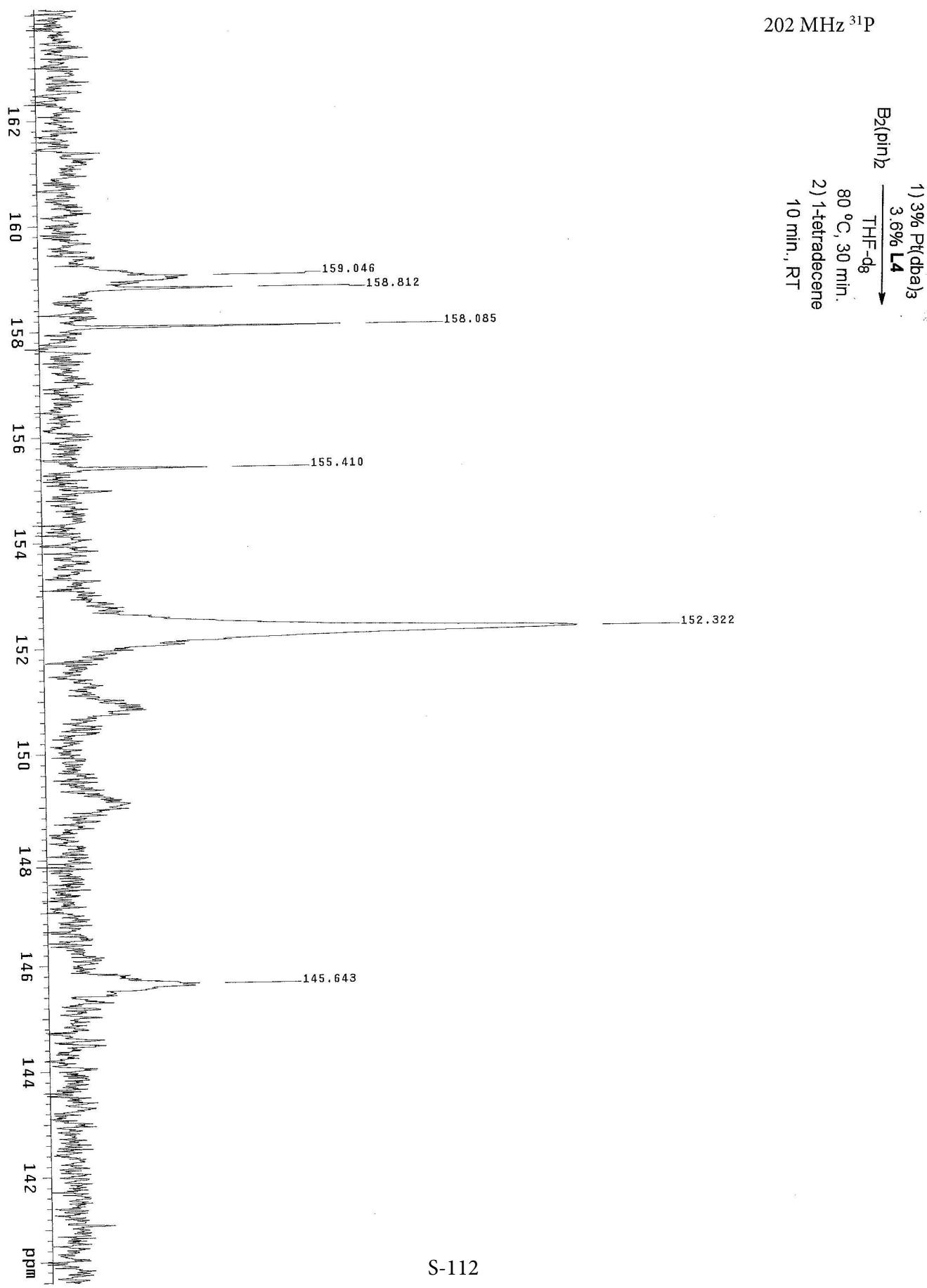


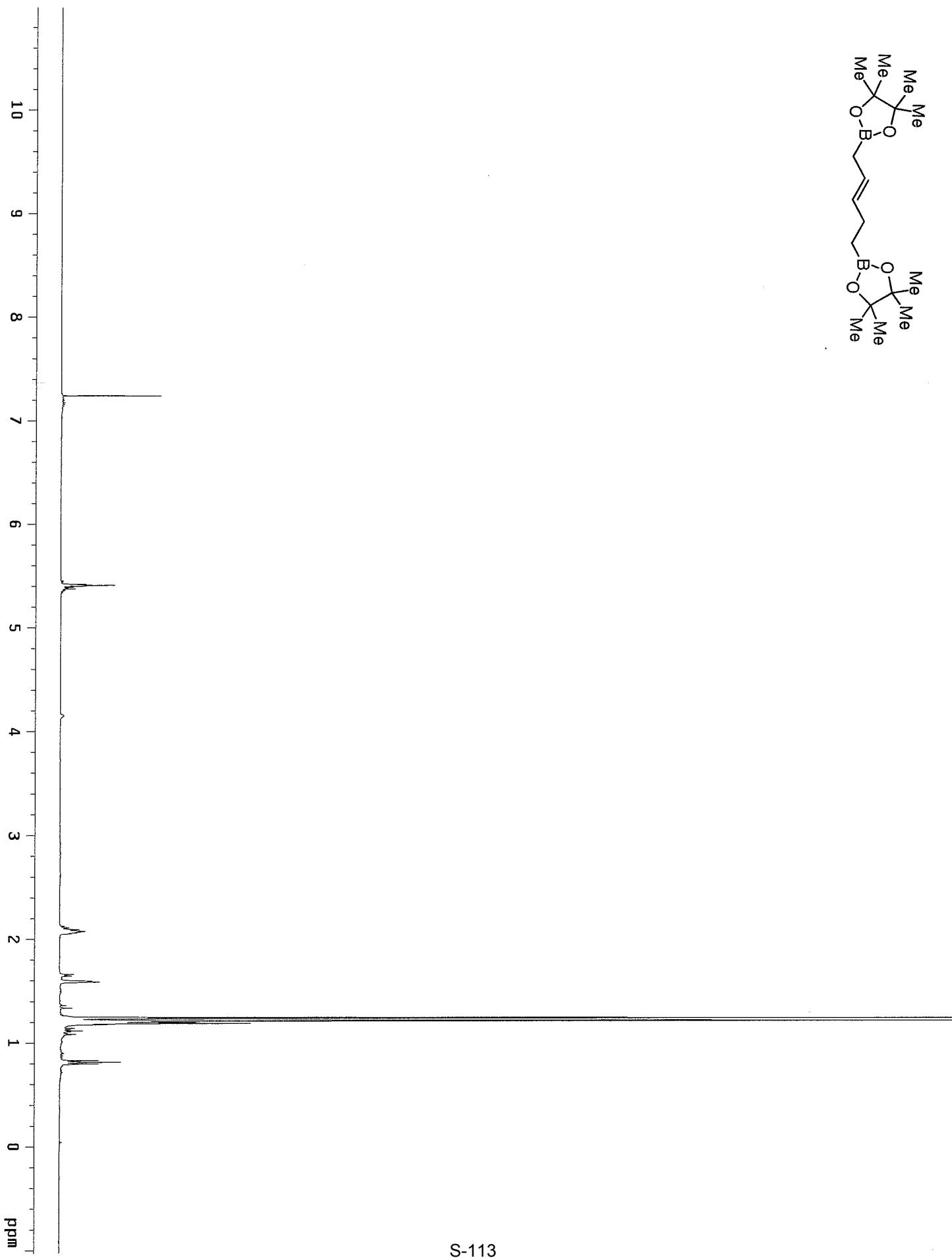
202 MHz 31P

1) 3% Pt(dba)<sub>3</sub>  
3.6% **L4** →  
B<sub>2</sub>(pin)<sub>2</sub>      THF-d<sub>8</sub>  
80 °C, 30 min.  
2) 1-tetradecene  
10 min., RT

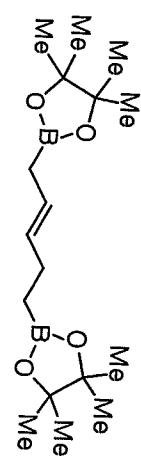
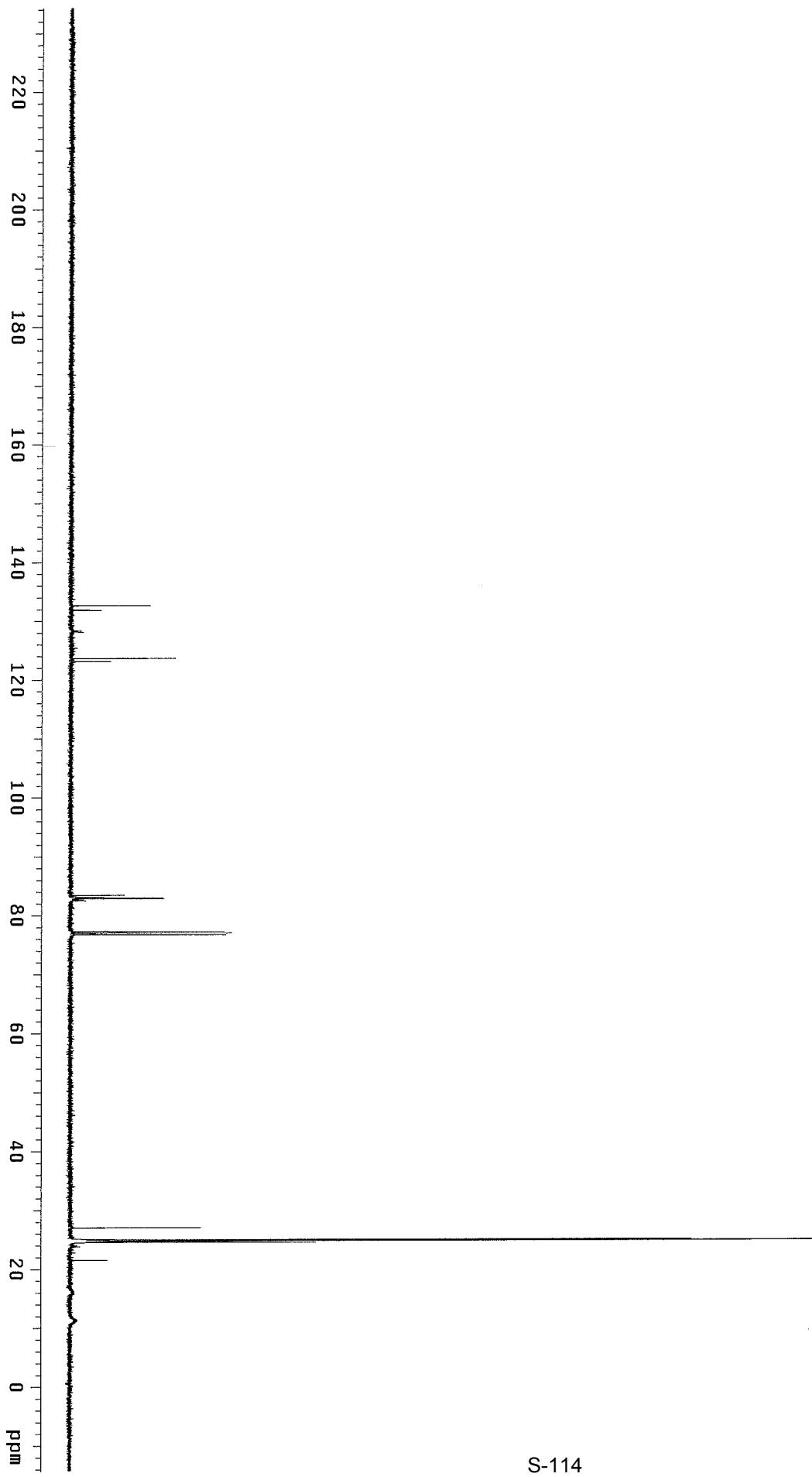


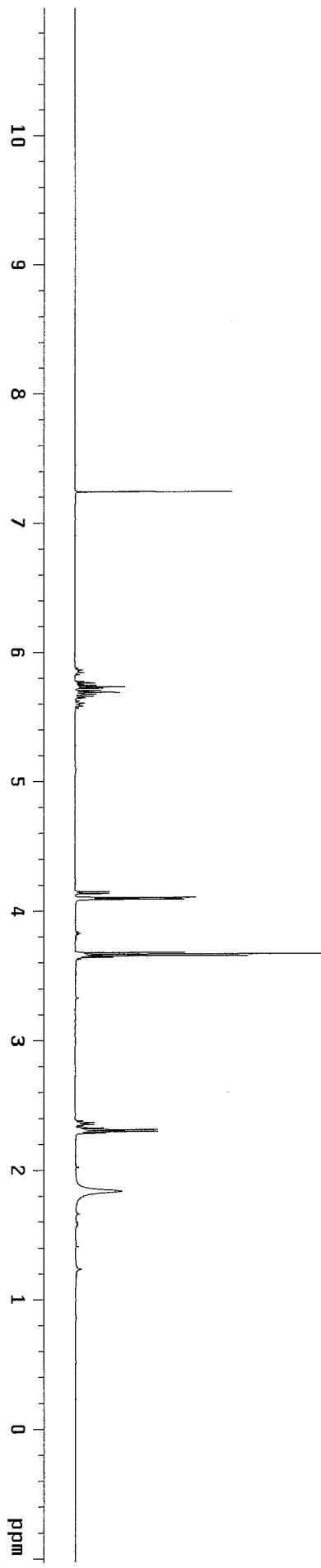
202 MHz  $^{31}\text{P}$

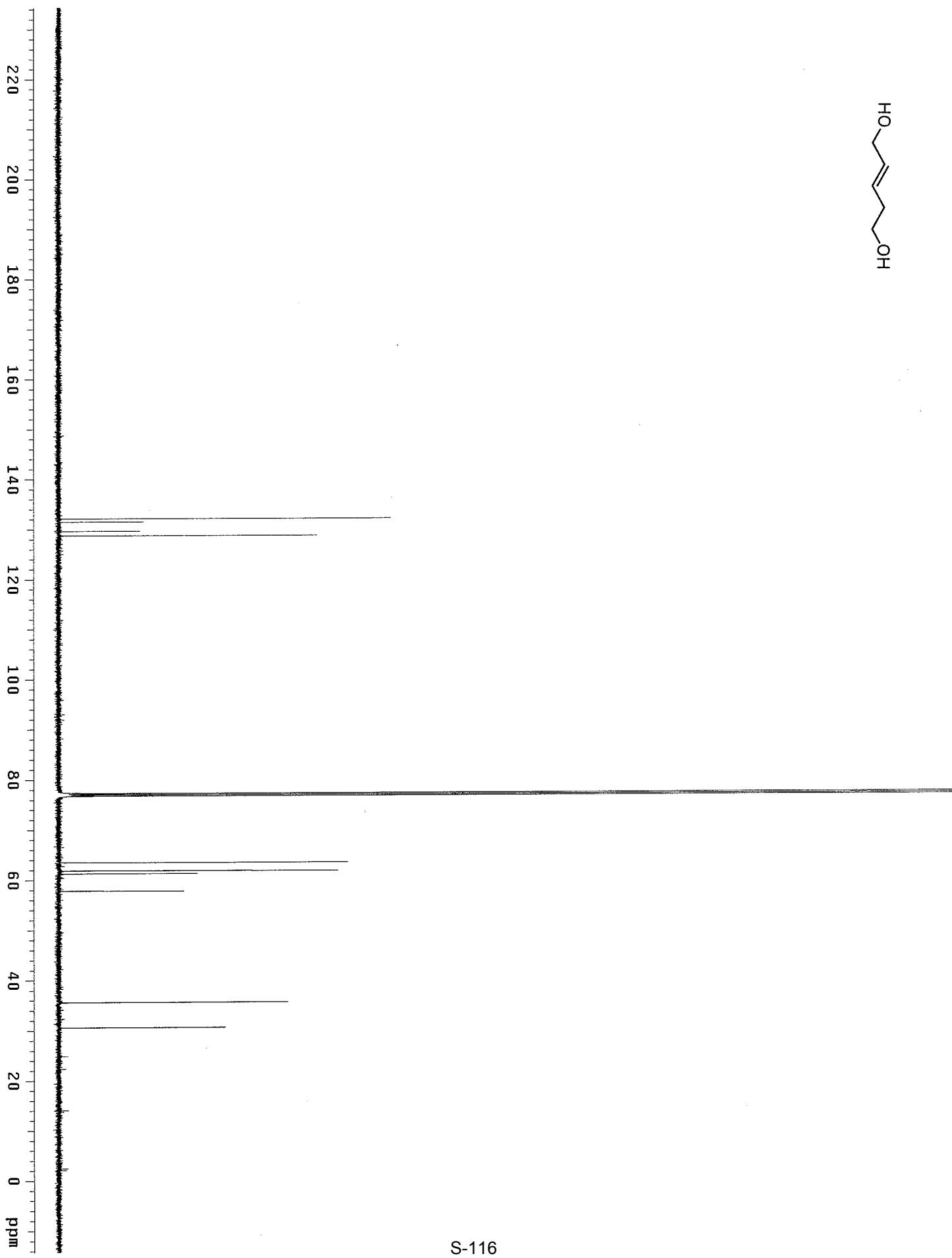




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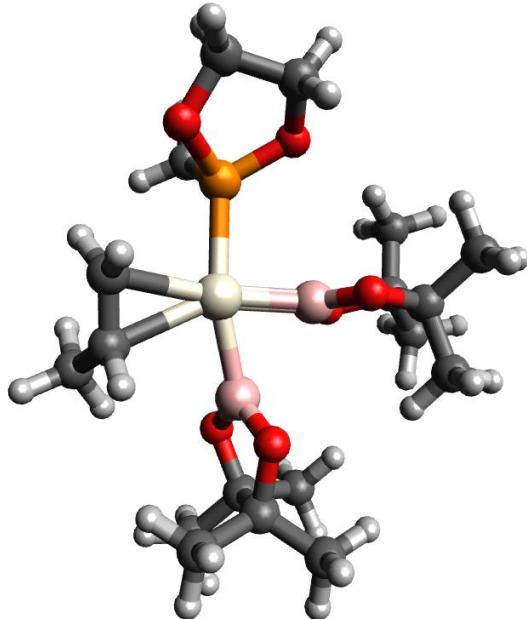




## Quantum Chemical Calculations

All geometries were optimized using the BP86 functional<sup>1</sup>. The electrons on the Pt atom were described with the LANL2DZ basis set, which utilizes the Los Alamos effective core pseudo-potential (ECP) for the core electrons and the double-zeta quality basis for valence electrons. The description of the valence electrons on the metal were augmented with one polarization basis function of d-type, described by one Gaussian function with an exponent value of  $\alpha=0.451$ . All other atoms were described by the split-valence 6-31++G\*\* basis set. The optimized geometries were checked by means of frequency calculations to ensure that all ground state geometries contain only real frequencies and that the transition state geometries contain one imaginary frequency. Intrinsic Reaction Coordinate<sup>2</sup> (IRC) calculations were carried out to ensure that the transition state geometries connect with the correct minima. The LQA integration scheme was used with a step size of 0.30 bohr. The thermal corrections to the free energies were calculated at 1.0 atm. and 333.15 K using the computed unscaled harmonic frequencies. All geometry optimizations and frequency calculations were carried out in THF solvent simulated by the polarizing continuum model<sup>3</sup> (PCM). All calculations were carried out with the Gaussian 09 computer program<sup>4</sup>.

gs\_minor\_methyls\_same\_side.xyz



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Cartesian coordinates (Angstroms):  
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H -4.204 1.766 -1.374  
H -4.995 1.587 1.005

H	-4.479	0.635	-2.726
H	-5.656	0.720	-1.387
H	-3.244	1.864	0.738
C	-4.581	0.766	-1.635
C	-3.984	1.189	1.198
H	-3.813	1.191	2.287
C	-3.812	-0.342	-0.909
O	-2.378	-0.195	-1.216
C	-3.835	-0.248	0.669
H	-5.882	-0.896	1.057
H	-4.017	-1.766	-2.528
B	-1.645	-0.556	-0.079
H	-5.326	-1.883	-1.317
C	-4.243	-1.718	-1.449
C	-4.854	-1.163	1.357
O	-2.481	-0.701	1.034
H	-4.779	-1.045	2.451
Pt	0.413	-0.965	-0.054
H	-3.702	-2.539	-0.950
H	-4.683	-2.223	1.114
O	3.564	0.598	-0.038
H	-0.519	4.056	2.703
H	-1.687	3.926	1.360
C	-0.644	4.172	1.613
H	-0.462	5.232	1.361
H	1.792	3.301	2.495
O	0.019	1.863	1.185
C	0.351	3.266	0.880
C	1.775	3.509	1.412
H	-1.926	3.024	-0.764
H	2.088	4.556	1.259
H	-1.404	4.718	-1.029
C	-1.152	3.661	-1.223
H	2.504	2.843	0.922
C	0.251	3.308	-0.699
H	1.183	5.244	-1.080
H	-1.180	3.494	-2.312
O	0.505	1.907	-1.072
C	1.300	4.189	-1.386
H	2.324	3.865	-1.146
H	1.169	4.137	-2.480
B	0.260	1.097	0.040
C	-0.474	-3.158	-0.240
C	0.902	-3.200	-0.488
H	1.576	-3.612	0.272
H	1.294	-3.155	-1.509
H	2.791	-0.296	2.658
H	2.786	-2.064	2.391

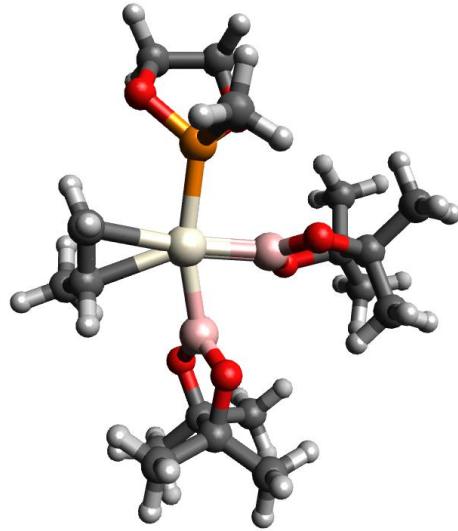
H 4.311 -1.122 2.158  
 C 3.214 -1.109 2.047  
 P 2.721 -0.831 0.294  
 H 5.686 -1.253 0.001  
 O 3.749 -1.817 -0.610  
 H 5.429 1.049 -0.826  
 C 4.600 0.353 -1.030  
 C 5.001 -1.115 -0.856  
 H 4.189 0.543 -2.039  
 H 5.450 -1.549 -1.763  
 H -1.142 -3.076 -1.106  
 C -1.090 -3.689 1.036  
 H -1.942 -3.075 1.365  
 H -0.350 -3.728 1.853  
 H -1.459 -4.718 0.861

	1	2	3
	A	A	A
Frequencies --	18.0453	23.7317	28.9417
Red. masses --	4.0325	3.9727	3.9929

Sum of electronic and thermal Free Energies= -1669.744615 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000011	0.000450	YES
RMS Force	0.000002	0.000300	YES

gs\_minor\_methyls\_opposite\_side.xyz



-----  
Cartesian coordinates (Angstroms):  
-----

H -4.312 1.696 -1.164  
H -4.997 1.427 1.232  
H -4.603 0.608 -2.548  
H -5.738 0.616 -1.171  
H -3.259 1.737 0.911  
C -4.673 0.697 -1.451  
C -3.974 1.037 1.373  
H -3.763 1.002 2.455  
C -3.856 -0.418 -0.790  
O -2.436 -0.228 -1.137  
C -3.826 -0.379 0.790  
H -5.850 -1.077 1.213  
H -4.083 -1.792 -2.449  
B -1.657 -0.612 -0.038  
H -5.351 -1.976 -1.203  
C -4.276 -1.784 -1.363  
C -4.809 -1.333 1.478  
O -2.455 -0.824 1.091  
H -4.707 -1.245 2.573  
Pt 0.410 -0.944 -0.147  
H -3.705 -2.610 -0.907  
H -4.624 -2.382 1.200  
O 3.827 -1.916 0.008  
H -0.808 3.990 2.660  
H -1.849 3.886 1.215  
C -0.837 4.135 1.567  
H -0.645 5.202 1.360  
H 1.523 3.248 2.638  
O -0.114 1.843 1.135  
C 0.230 3.258 0.903  
C 1.599 3.496 1.566  
H -1.874 2.970 -0.937  
H 1.910 4.551 1.478  
H -1.408 4.694 -1.105  
C -1.095 3.656 -1.309  
H 2.376 2.853 1.121  
C 0.271 3.342 -0.675  
H 1.153 5.321 -0.933  
H -1.023 3.524 -2.402  
O 0.610 1.960 -1.054  
C 1.343 4.279 -1.243  
H 2.353 3.993 -0.911  
H 1.319 4.244 -2.346  
B 0.254 1.112 0.003  
C -0.385 -3.167 0.054

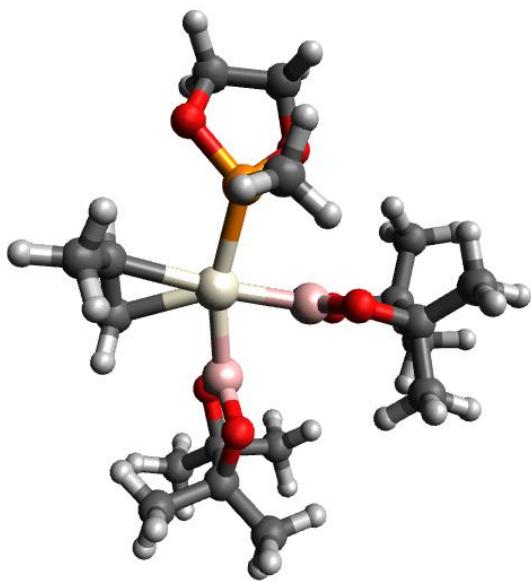
C 0.860 -3.201 -0.576  
 H 1.754 -3.487 -0.012  
 H 0.930 -3.249 -1.668  
 H 3.067 -1.128 -2.764  
 H 2.706 0.600 -2.452  
 H 4.365 -0.052 -2.137  
 C 3.286 -0.271 -2.105  
 P 2.726 -0.690 -0.403  
 H 5.477 0.387 0.069  
 O 3.435 0.471 0.587  
 H 5.725 -1.928 0.852  
 C 4.749 -1.450 1.033  
 C 4.803 0.075 0.889  
 H 4.365 -1.747 2.025  
 H 5.094 0.584 1.820  
 H -1.278 -3.203 -0.582  
 C -0.587 -3.530 1.508  
 H -1.335 -2.876 1.983  
 H 0.357 -3.464 2.074  
 H -0.957 -4.572 1.579

	1	2	3
	A	A	A
Frequencies --	10.5705	30.0888	30.9433
Red. masses --	4.0833	4.1078	3.5996

Sum of electronic and thermal Free Energies= -1669.746618 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000029	0.000450	YES
RMS Force	0.000004	0.000300	YES

gs\_major\_methyls\_same\_side.xyz



-----  
Cartesian coordinates (Angstroms):  
-----

H	4.479	1.174	1.202
H	5.145	1.071	-1.220
H	4.694	-0.068	2.465
H	5.808	-0.016	1.071
H	3.442	1.508	-0.861
C	4.758	0.125	1.381
C	4.091	0.792	-1.390
H	3.881	0.879	-2.469
C	3.839	-0.843	0.628
O	2.444	-0.554	1.008
C	3.810	-0.652	-0.942
H	5.757	-1.492	-1.458
H	3.934	-2.383	2.147
B	1.633	-0.753	-0.115
H	5.181	-2.565	0.881
C	4.129	-2.290	1.066
C	4.695	-1.628	-1.726
O	2.402	-0.936	-1.268
H	4.591	-1.436	-2.807
Pt	-0.459	-0.913	-0.043
H	3.483	-3.011	0.537
H	4.418	-2.676	-1.536
O	-3.971	-1.510	-0.208
H	1.328	4.134	-2.282
H	2.318	3.792	-0.837
C	1.342	4.168	-1.180
H	1.246	5.224	-0.872
H	-1.065	3.634	-2.368

O 0.390 1.926 -0.995  
 C 0.180 3.338 -0.623  
 C -1.142 3.776 -1.277  
 H 2.203 2.648 1.199  
 H -1.353 4.842 -1.083  
 H 1.905 4.380 1.558  
 C 1.486 3.362 1.636  
 H -1.989 3.171 -0.914  
 C 0.110 3.264 0.953  
 H -0.574 5.287 1.394  
 H 1.373 3.117 2.705  
 O -0.380 1.893 1.181  
 C -0.872 4.245 1.602  
 H -1.899 4.094 1.238  
 H -0.869 4.104 2.697  
 B -0.085 1.124 0.047  
 C 0.192 -3.093 -0.365  
 C -1.148 -3.194 0.022  
 H -1.912 -3.250 -0.763  
 C -1.565 -3.668 1.399  
 H -3.099 -0.799 2.562  
 H -2.535 0.866 2.220  
 H -4.270 0.415 1.936  
 C -3.224 0.070 1.895  
 P -2.729 -0.424 0.195  
 H -5.332 0.972 -0.278  
 O -3.296 0.809 -0.800  
 H -5.859 -1.298 -1.048  
 C -4.833 -0.943 -1.234  
 C -4.703 0.578 -1.098  
 H -4.491 -1.289 -2.225  
 H -4.933 1.115 -2.031  
 H 0.981 -3.352 0.350  
 H -1.681 -4.770 1.388  
 H -2.534 -3.248 1.713  
 H -0.808 -3.417 2.161  
 H 0.474 -3.112 -1.422

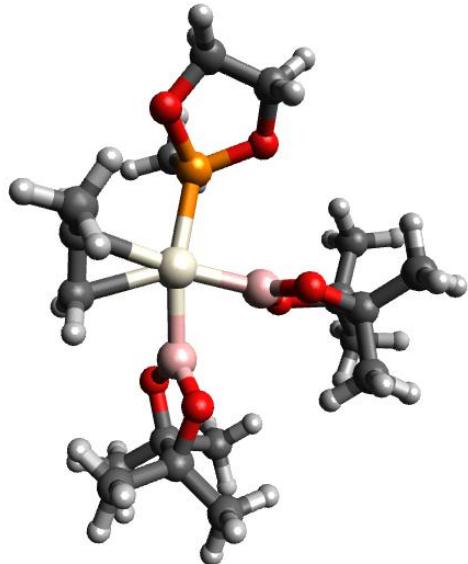
	1	2	3
	A	A	A
Frequencies --	19.5557	22.3286	30.6321
Red. masses --	4.4984	3.5593	4.3527

Sum of electronic and thermal Free Energies= -1669.746228 Hartree

Item	Value	Threshold	Converged?
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Maximum Force	0.000017	0.000450	YES
RMS Force	0.000003	0.000300	YES

gs\_major\_methyls\_opposite\_side.xyz



-----  
Cartesian coordinates (Angstroms):

H	-4.485	1.279	-1.098
H	-5.089	1.046	1.312
H	-4.725	0.122	-2.435
H	-5.819	0.088	-1.025
H	-3.381	1.469	0.959
C	-4.772	0.245	-1.340
C	-4.040	0.735	1.453
H	-3.815	0.752	2.532
C	-3.850	-0.775	-0.665
O	-2.458	-0.473	-1.048
C	-3.794	-0.684	0.912
H	-5.749	-1.518	1.403
H	-3.987	-2.215	-2.277
B	-1.633	-0.755	0.045
H	-5.212	-2.467	-1.000
C	-4.160	-2.189	-1.188
C	-4.686	-1.689	1.648
O	-2.386	-1.012	1.196
H	-4.565	-1.564	2.738
Pt	0.459	-0.928	0.021
H	-3.512	-2.948	-0.719
H	-4.430	-2.729	1.392
O	3.398	0.978	0.210

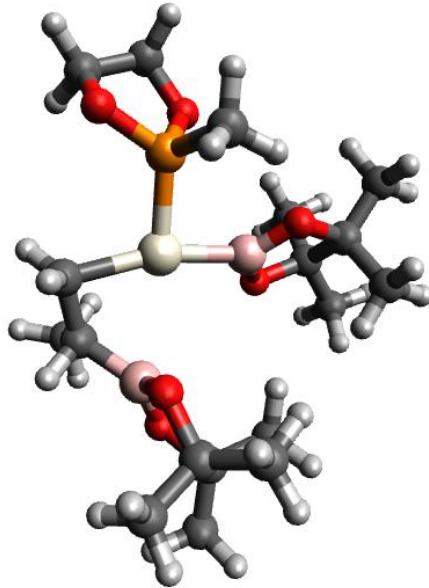
H -1.144 4.178 2.300  
 H -2.245 3.784 0.952  
 C -1.248 4.177 1.201  
 H -1.188 5.224 0.854  
 H 1.248 3.693 2.209  
 O -0.295 1.937 1.005  
 C -0.128 3.338 0.577  
 C 1.239 3.804 1.111  
 H -2.293 2.623 -1.065  
 H 1.423 4.866 0.874  
 H -2.011 4.344 -1.487  
 C -1.608 3.320 -1.574  
 H 2.060 3.196 0.698  
 C -0.184 3.222 -0.999  
 H 0.485 5.226 -1.543  
 H -1.581 3.049 -2.642  
 O 0.272 1.841 -1.232  
 C 0.752 4.175 -1.749  
 H 1.804 4.019 -1.466  
 H 0.659 4.007 -2.836  
 B 0.083 1.108 -0.057  
 C -0.233 -3.121 -0.072  
 C 1.141 -3.179 -0.333  
 H 1.809 -3.432 0.499  
 C 1.705 -3.355 -1.726  
 H 2.435 0.116 2.859  
 H 2.661 -1.652 2.694  
 H 4.084 -0.545 2.567  
 C 3.013 -0.668 2.342  
 P 2.695 -0.528 0.532  
 H 5.697 -0.609 0.655  
 O 3.941 -1.417 -0.183  
 H 5.304 1.615 -0.307  
 C 4.598 0.822 -0.598  
 C 5.129 -0.582 -0.293  
 H 4.332 0.929 -1.665  
 H 5.748 -0.993 -1.105  
 H -0.944 -3.221 -0.900  
 H 1.921 -4.426 -1.906  
 H 2.648 -2.801 -1.854  
 H 0.987 -3.020 -2.494  
 H -0.622 -3.331 0.929

	1	2	3
	A	A	A
Frequencies --	21.2574	27.5149	28.5717
Red. masses --	4.4011	3.6231	3.8927

Sum of electronic and thermal Free Energies= -1669.745315 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000006	0.000450	YES
RMS Force	0.000001	0.000300	YES

ts\_minor\_methyls\_opposite\_side.xyz



-----  
Cartesian coordinates (Angstroms):  
-----

H	2.981	0.880	2.466
H	4.076	2.288	0.700
H	3.627	-0.569	3.284
H	4.750	0.656	2.632
H	2.426	1.679	0.342
C	3.793	0.137	2.453
C	3.470	1.695	-0.006
H	3.492	2.197	-0.988
C	3.839	-0.630	1.129
O	2.515	-1.246	0.899
C	4.030	0.273	-0.162
H	6.139	0.780	0.039
H	4.537	-2.468	2.034
B	2.271	-1.192	-0.468
H	5.860	-1.426	1.441
C	4.844	-1.792	1.219
C	5.462	0.323	-0.704
O	3.182	-0.411	-1.160

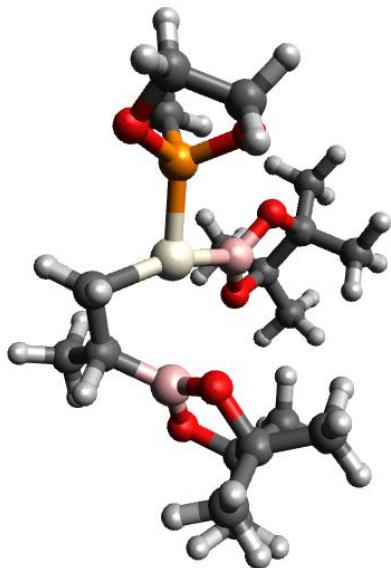
H	5.490	0.943	-1.615
Pt	-0.467	-0.900	-0.150
H	4.881	-2.375	0.284
H	5.842	-0.679	-0.956
O	-3.205	-2.648	0.717
H	0.429	4.335	-2.524
H	1.245	4.319	-0.938
C	0.272	4.444	-1.438
H	-0.092	5.469	-1.247
H	-1.760	3.294	-2.872
O	-0.189	2.062	-1.165
C	-0.751	3.408	-0.959
C	-2.025	3.492	-1.820
H	1.080	3.417	1.176
H	-2.487	4.493	-1.764
H	0.295	5.021	1.308
C	0.143	3.935	1.438
H	-2.770	2.742	-1.508
C	-1.039	3.425	0.595
H	-2.268	5.225	0.732
H	-0.067	3.743	2.504
O	-1.201	1.994	0.901
C	-2.323	4.157	1.005
H	-3.213	3.718	0.529
H	-2.452	4.094	2.099
B	-0.602	1.224	-0.114
C	1.359	-2.309	-1.243
C	0.133	-2.907	-0.551
H	-0.514	-3.479	-1.233
H	0.368	-3.496	0.350
H	-1.896	-1.329	3.060
H	-2.166	0.373	2.542
H	-3.582	-0.732	2.813
C	-2.539	-0.660	2.465
P	-2.423	-1.154	0.709
H	-5.485	-1.037	0.622
O	-3.641	-0.352	-0.116
H	-5.022	-3.385	0.045
C	-4.276	-2.637	-0.267
C	-4.818	-1.205	-0.242
H	-3.870	-2.903	-1.260
H	-5.331	-0.920	-1.173
H	2.195	-3.041	-1.090
C	1.188	-2.079	-2.760
H	2.086	-1.624	-3.208
H	0.332	-1.413	-2.965
H	0.993	-3.040	-3.269

	1	2	3
	A	A	A
Frequencies --	-73.0005	16.5828	20.6227
Red. masses --	5.9084	5.3009	4.4073

Sum of electronic and thermal Free Energies= -1669.704661 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000011	0.000450	YES
RMS Force	0.000002	0.000300	YES

ts\_minor\_methyls\_same\_side.xyz



-----  
Cartesian coordinates (Angstroms):  
-----

H	2.515	0.204	2.833
H	3.938	1.890	1.611
H	3.001	-1.420	3.395
H	4.234	-0.144	3.198
H	2.332	1.507	0.898
C	3.304	-0.561	2.773
C	3.418	1.515	0.713
H	3.608	2.218	-0.114
C	3.534	-1.025	1.332
O	2.249	-1.507	0.787
C	3.937	0.125	0.315
H	6.018	0.423	0.895
H	4.054	-3.049	1.903

B	2.203	-1.135	-0.551
H	5.471	-1.974	1.739
C	4.490	-2.231	1.306
C	5.433	0.195	-0.013
O	3.218	-0.267	-0.915
H	5.612	1.002	-0.744
Pt	-0.550	-0.753	-0.529
H	4.649	-2.602	0.279
H	5.806	-0.747	-0.443
O	-2.907	-0.916	1.721
H	1.487	4.642	-1.296
H	1.527	4.322	0.459
C	0.874	4.609	-0.379
H	0.488	5.627	-0.192
H	-0.354	3.846	-2.718
O	0.275	2.264	-0.722
C	-0.282	3.620	-0.565
C	-1.045	3.940	-1.864
H	0.433	3.075	2.083
H	-1.445	4.969	-1.856
H	-0.252	4.727	2.196
C	-0.498	3.664	2.031
H	-1.881	3.238	-2.020
C	-1.222	3.451	0.689
H	-2.276	5.362	0.629
H	-1.158	3.332	2.850
O	-1.582	2.026	0.618
C	-2.509	4.283	0.650
H	-3.125	4.041	-0.230
H	-3.108	4.083	1.555
B	-0.604	1.338	-0.128
C	1.388	-2.002	-1.674
C	0.057	-2.651	-1.290
H	-0.510	-3.033	-2.153
H	0.145	-3.426	-0.511
H	-3.738	0.863	-0.472
H	-3.751	-0.312	-1.833
H	-4.865	-0.551	-0.429
C	-3.871	-0.195	-0.745
P	-2.564	-1.163	0.098
H	-4.943	-2.753	1.085
O	-3.102	-2.755	0.067
H	-3.949	-1.949	3.183
C	-3.252	-2.177	2.362
C	-3.888	-3.033	1.262
H	-2.336	-2.643	2.765
H	-3.819	-4.114	1.461
H	2.164	-2.806	-1.585

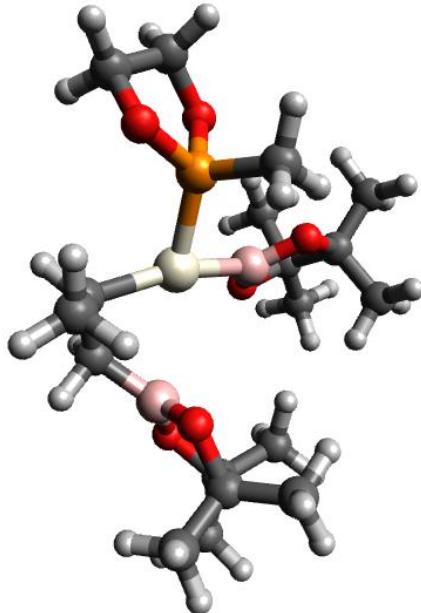
C 1.440 -1.442 -3.112  
 H 2.415 -0.976 -3.331  
 H 0.660 -0.680 -3.276  
 H 1.271 -2.255 -3.841

	1	2	3
	A	A	A
Frequencies --	-45.0870	16.8662	21.9879
Red. masses --	5.9781	3.9240	4.9370

Sum of electronic and thermal Free Energies= -1669.70248 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000009	0.000450	YES
RMS Force	0.000001	0.000300	YES

ts\_major\_methyls\_same\_side.xyz



-----  
 Cartesian coordinates (Angstroms):  
 -----

H 3.185 0.455 2.555  
 H 4.108 2.190 0.975  
 H 3.920 -1.096 3.047  
 H 4.965 0.258 2.537  
 H 2.447 1.585 0.665  
 C 4.004 -0.250 2.344  
 C 3.453 1.703 0.232

H	3.371	2.364	-0.646
C	3.950	-0.769	0.905
O	2.617	-1.362	0.671
C	4.029	0.351	-0.214
H	6.140	0.875	-0.072
H	4.733	-2.725	1.406
B	2.277	-1.089	-0.648
H	5.996	-1.562	0.912
C	4.968	-1.906	0.707
C	5.416	0.542	-0.836
O	3.125	-0.177	-1.256
H	5.366	1.318	-1.618
Pt	-0.475	-0.796	-0.358
H	4.933	-2.308	-0.320
H	5.791	-0.386	-1.294
O	-3.120	-2.680	0.569
H	0.427	4.611	-2.314
H	1.259	4.480	-0.741
C	0.281	4.638	-1.220
H	-0.085	5.644	-0.951
H	-1.757	3.582	-2.718
O	-0.171	2.240	-1.121
C	-0.734	3.565	-0.810
C	-2.016	3.707	-1.653
H	1.116	3.427	1.302
H	-2.480	4.700	-1.526
H	0.322	5.009	1.568
C	0.179	3.915	1.612
H	-2.757	2.935	-1.389
C	-1.009	3.465	0.742
H	-2.244	5.247	1.014
H	-0.021	3.637	2.661
O	-1.166	2.015	0.943
C	-2.291	4.162	1.215
H	-3.185	3.752	0.720
H	-2.408	4.024	2.304
B	-0.578	1.323	-0.134
C	1.316	-2.047	-1.546
C	0.091	-2.770	-0.978
H	-0.567	-3.141	-1.781
C	0.362	-3.844	0.071
H	-1.693	-1.471	2.903
H	-2.031	0.252	2.508
H	-3.402	-0.906	2.793
C	-2.385	-0.784	2.389
P	-2.368	-1.168	0.601
H	-5.405	-1.085	0.813
O	-3.656	-0.345	-0.088

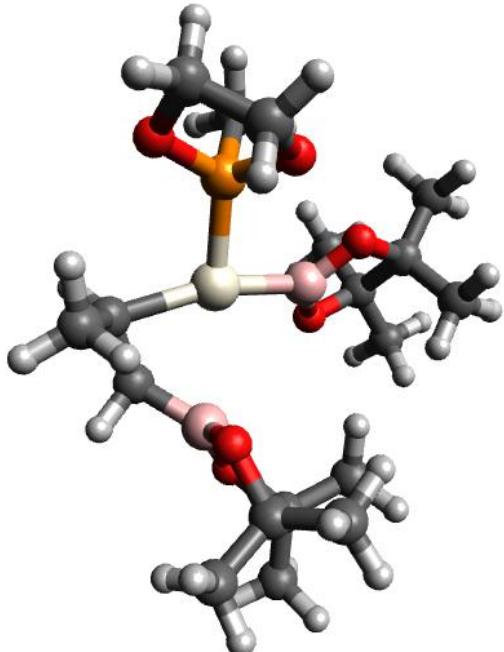
H -4.999 -3.394 0.063  
 C -4.294 -2.624 -0.288  
 C -4.836 -1.201 -0.127  
 H -4.001 -2.833 -1.333  
 H -5.451 -0.873 -0.979  
 H 2.130 -2.798 -1.707  
 H 0.920 -4.707 -0.354  
 H -0.587 -4.235 0.476  
 H 0.956 -3.452 0.914  
 H 1.129 -1.605 -2.539

	1	2	3
	A	A	A
Frequencies --	-38.9242	6.9868	24.2578
Red. masses --	6.0431	4.8942	3.9228

Sum of electronic and thermal Free Energies= -1669.707595 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000001	0.000300	YES

ts\_major\_methyls\_opposite\_side.xyz



-----  
 Cartesian coordinates (Angstroms):

-----  
H 2.801 -0.047 2.831  
H 3.902 1.917 1.690  
H 3.481 -1.677 3.098  
H 4.574 -0.275 2.938  
H 2.270 1.432 1.122  
C 3.633 -0.720 2.571  
C 3.314 1.597 0.813  
H 3.326 2.410 0.070  
C 3.710 -0.968 1.063  
O 2.399 -1.468 0.602  
C 3.912 0.332 0.179  
H 6.006 0.747 0.614  
H 4.412 -3.007 1.261  
B 2.192 -0.954 -0.673  
H 5.735 -1.814 1.123  
C 4.729 -2.080 0.755  
C 5.355 0.590 -0.264  
O 3.109 0.027 -1.023  
H 5.395 1.501 -0.883  
Pt -0.512 -0.677 -0.643  
H 4.796 -2.284 -0.326  
H 5.760 -0.246 -0.855  
O -2.692 -0.986 1.772  
H 1.019 4.830 -1.660  
H 1.428 4.489 0.043  
C 0.606 4.751 -0.640  
H 0.216 5.744 -0.354  
H -1.028 3.977 -2.701  
O 0.071 2.386 -0.927  
C -0.512 3.702 -0.615  
C -1.538 4.007 -1.723  
H 0.753 3.209 1.842  
H -1.985 5.008 -1.599  
H -0.013 4.807 2.102  
C -0.210 3.728 1.977  
H -2.348 3.259 -1.738  
C -1.166 3.458 0.800  
H -2.354 5.281 1.001  
H -0.673 3.353 2.906  
O -1.424 2.010 0.782  
C -2.495 4.186 1.034  
H -3.251 3.909 0.284  
H -2.889 3.925 2.031  
B -0.593 1.397 -0.176  
C 1.357 -1.748 -1.834  
C 0.087 -2.544 -1.536  
H -0.497 -2.742 -2.449

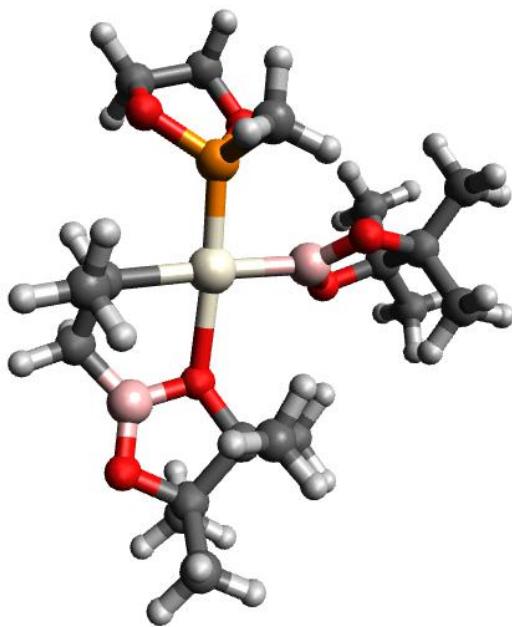
C 0.245 -3.793 -0.678  
 H -3.724 0.894 -0.238  
 H -3.833 -0.198 -1.662  
 H -4.825 -0.539 -0.190  
 C -3.863 -0.149 -0.562  
 P -2.480 -1.145 0.112  
 H -4.771 -2.798 1.210  
 O -3.022 -2.737 0.043  
 H -3.602 -2.105 3.258  
 C -2.979 -2.283 2.369  
 C -3.705 -3.082 1.282  
 H -2.030 -2.765 2.665  
 H -3.620 -4.171 1.418  
 H 2.200 -2.463 -1.996  
 H 0.796 -4.594 -1.216  
 H -0.744 -4.198 -0.404  
 H 0.798 -3.583 0.253  
 H 1.289 -1.153 -2.760

	1	2	3
	A	A	A
Frequencies --	-50.7747	16.3030	26.6715
Red. masses --	6.6319	4.1058	4.1945

Sum of electronic and thermal Free Energies= -1669.70525 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000014	0.000450	YES
RMS Force	0.000002	0.000300	YES

prod\_major\_methyls\_same\_side.xyz



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Cartesian coordinates (Angstroms):  
-----

H	2.453	2.440	-1.491
H	4.923	2.389	-1.575
H	1.328	2.583	-0.125
H	2.968	3.291	-0.001
H	4.047	1.037	-2.359
C	2.385	2.440	-0.393
C	4.792	1.294	-1.587
H	5.753	0.835	-1.870
C	2.899	1.138	0.213
O	2.138	-0.007	-0.381
C	4.382	0.763	-0.203
H	5.456	2.219	1.010
H	1.555	1.146	1.898
B	3.036	-1.089	-0.539
H	3.123	1.942	2.234
C	2.643	1.090	1.724
C	5.439	1.129	0.843
O	4.339	-0.711	-0.322
H	6.435	0.825	0.481
Pt	0.015	-0.792	-0.011
H	3.015	0.155	2.174
H	5.255	0.628	1.805
O	-2.137	-3.332	0.098
H	-1.301	4.376	-2.387
H	-0.505	4.667	-0.816
C	-1.462	4.409	-1.296

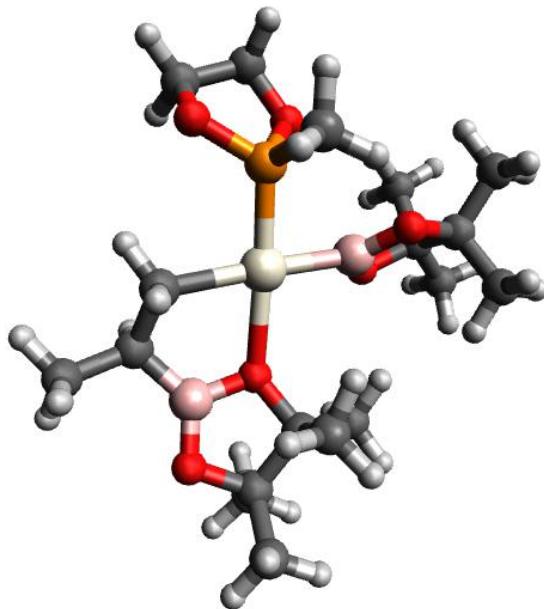
H -2.187 5.214 -1.083  
 H -2.929 2.574 -2.704  
 O -0.967 2.029 -1.051  
 C -1.997 3.056 -0.812  
 C -3.226 2.648 -1.644  
 H -0.253 3.757 1.286  
 H -4.036 3.393 -1.565  
 H -1.592 4.933 1.462  
 C -1.311 3.872 1.575  
 H -3.613 1.665 -1.329  
 C -2.228 2.953 0.748  
 H -4.051 4.141 0.937  
 H -1.403 3.605 2.641  
 O -1.819 1.568 1.037  
 C -3.683 3.132 1.197  
 H -4.348 2.387 0.733  
 H -3.751 3.020 2.292  
 B -0.995 1.094 -0.003  
 C 1.139 -2.697 -0.048  
 C 2.429 -2.483 -0.889  
 H -1.923 -2.047 2.736  
 H -2.534 -0.414 2.292  
 H -3.599 -1.872 2.098  
 C -2.569 -1.485 2.042  
 P -1.910 -1.680 0.347  
 H -4.750 -2.512 -0.422  
 O -3.127 -1.206 -0.709  
 H -3.435 -4.513 -1.003  
 C -2.933 -3.538 -1.100  
 C -3.912 -2.360 -1.127  
 H -2.275 -3.539 -1.988  
 H -4.304 -2.146 -2.133  
 H 0.523 -3.481 -0.524  
 C 1.497 -3.167 1.374  
 H 2.128 -4.085 1.360  
 H 0.597 -3.396 1.972  
 H 2.070 -2.403 1.937  
 H 3.165 -3.307 -0.759  
 H 2.175 -2.469 -1.970

	1	2	3
	A	A	A
Frequencies --	18.9487	26.6811	32.7751
Red. masses --	3.5496	4.3423	3.6403

Sum of electronic and thermal Free Energies= -1669.723141 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000012	0.000450	YES
RMS Force	0.000002	0.000300	YES

prod\_minor\_methyls\_same\_side.xyz



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 Cartesian coordinates (Angstroms):  
 -----

H	1.995	2.753	-1.243
H	4.439	3.009	-1.451
H	0.956	2.744	0.201
H	2.516	3.616	0.238
H	3.737	1.556	-2.225
C	2.001	2.718	-0.144
C	4.469	1.908	-1.479
H	5.475	1.599	-1.809
C	2.694	1.465	0.381
O	2.078	0.254	-0.249
C	4.196	1.307	-0.091
H	5.104	2.885	1.102
H	1.419	1.191	2.099
B	3.104	-0.705	-0.426
H	2.855	2.208	2.432
C	2.496	1.314	1.895
C	5.230	1.803	0.923
O	4.349	-0.158	-0.230

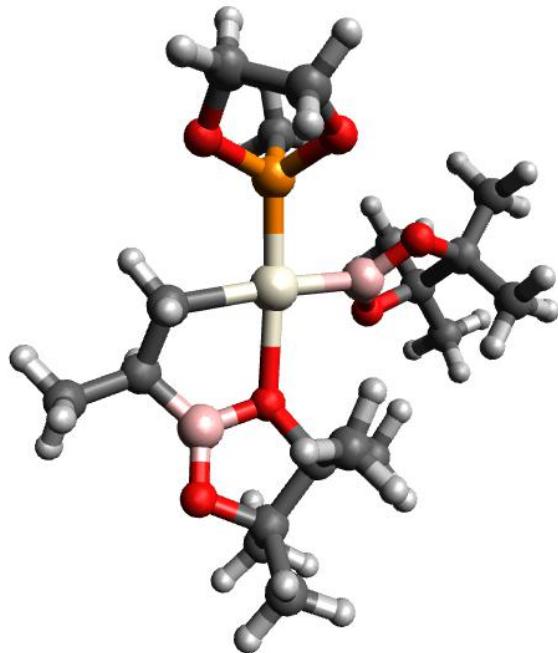
H	6.245	1.640	0.525
Pt	0.073	-0.764	0.092
H	3.024	0.430	2.290
H	5.146	1.276	1.885
O	-1.785	-3.519	0.288
H	-1.876	3.967	-2.677
H	-1.165	4.498	-1.129
C	-2.064	4.066	-1.594
H	-2.902	4.773	-1.459
H	-3.219	1.941	-2.867
O	-1.241	1.812	-1.140
C	-2.413	2.695	-1.004
C	-3.548	2.048	-1.819
H	-0.864	3.842	1.049
H	-4.460	2.669	-1.808
H	-2.375	4.797	1.103
C	-1.934	3.808	1.312
H	-3.794	1.045	-1.435
C	-2.672	2.688	0.555
H	-4.661	3.588	0.610
H	-2.012	3.619	2.396
O	-2.064	1.413	0.973
C	-4.150	2.675	0.963
H	-4.676	1.799	0.556
H	-4.231	2.646	2.063
B	-1.165	0.973	-0.017
C	1.423	-2.491	0.083
C	2.692	-2.178	-0.761
C	3.821	-3.226	-0.624
H	2.379	-2.155	-1.830
H	4.692	-2.989	-1.264
H	3.457	-4.232	-0.903
H	4.180	-3.284	0.420
H	-1.673	-2.149	2.889
H	-2.463	-0.602	2.419
H	-3.369	-2.168	2.283
C	-2.387	-1.677	2.195
P	-1.741	-1.846	0.493
H	-4.494	-2.990	-0.160
O	-3.022	-1.539	-0.550
H	-2.999	-4.867	-0.713
C	-2.603	-3.852	-0.866
C	-3.698	-2.781	-0.898
H	-1.982	-3.825	-1.780
H	-4.141	-2.646	-1.897
H	0.933	-3.413	-0.281
H	1.727	-2.689	1.134

	1 A	2 A	3 A
Frequencies --	23.2196	27.3543	30.4387
Red. masses --	3.8903	3.6679	4.3639

Sum of electronic and thermal Free Energies= -1669.723407 Hartree

	Item	Value	Threshold	Converged?
Maximum Force	0.000008	0.000450	YES	
RMS Force	0.000002	0.000300	YES	

prod\_minor\_methyls\_opposite\_side.xyz



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Cartesian coordinates (Angstroms):  
-----

H	2.021	3.054	-0.495
H	4.483	3.291	-0.473
H	0.875	2.678	0.812
H	2.427	3.476	1.199
H	3.819	2.102	-1.635
C	1.943	2.725	0.551
C	4.502	2.232	-0.779
H	5.524	1.988	-1.112
C	2.593	1.364	0.774
O	2.025	0.371	-0.195
C	4.126	1.305	0.388

H	4.939	2.509	2.010
H	1.197	0.685	2.273
B	3.063	-0.533	-0.528
H	2.614	1.544	2.951
C	2.287	0.828	2.179
C	5.082	1.509	1.566
O	4.290	-0.078	-0.109
H	6.123	1.440	1.212
Pt	0.008	-0.740	-0.197
H	2.778	-0.141	2.366
H	4.933	0.751	2.350
O	-2.658	-1.915	1.324
H	-1.254	4.599	-2.005
H	-0.931	4.670	-0.252
C	-1.696	4.436	-1.008
H	-2.534	5.146	-0.889
H	-2.519	2.767	-3.020
O	-1.030	2.088	-0.971
C	-2.191	2.990	-0.891
C	-3.099	2.653	-2.089
H	-1.161	3.446	1.685
H	-3.970	3.328	-2.141
H	-2.620	4.482	1.648
C	-2.263	3.438	1.680
H	-3.464	1.614	-2.041
C	-2.821	2.613	0.506
H	-4.739	3.641	0.343
H	-2.604	2.987	2.627
O	-2.358	1.229	0.700
C	-4.354	2.627	0.550
H	-4.792	1.931	-0.182
H	-4.700	2.331	1.554
B	-1.226	0.998	-0.102
C	1.404	-2.398	-0.513
C	2.684	-1.880	-1.229
C	3.824	-2.922	-1.317
H	2.393	-1.606	-2.268
H	4.705	-2.532	-1.859
H	3.480	-3.834	-1.838
H	4.160	-3.225	-0.308
H	-3.507	-0.721	-1.241
H	-2.568	-1.748	-2.377
H	-3.818	-2.494	-1.307
C	-3.046	-1.710	-1.385
P	-1.764	-1.952	-0.098
H	-3.404	-4.442	0.332
O	-1.512	-3.614	-0.075
H	-3.571	-3.339	2.523

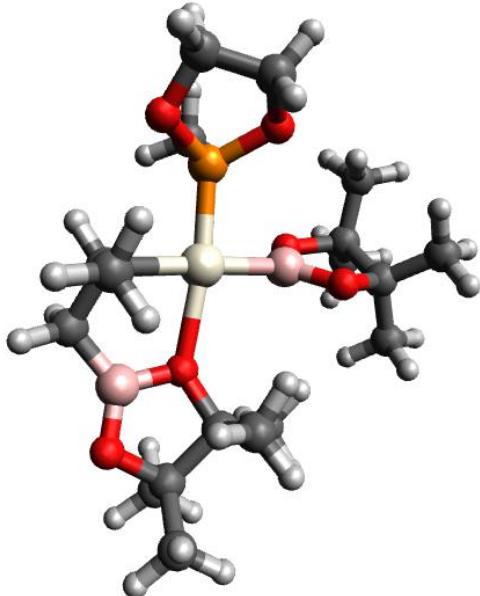
C -2.623 -3.216 1.977  
 C -2.447 -4.236 0.848  
 H -1.775 -3.243 2.685  
 H -1.999 -5.183 1.187  
 H 0.962 -3.239 -1.077  
 H 1.674 -2.800 0.487

	1	2	3
	A	A	A
Frequencies --	15.7485	23.3991	26.3340
Red. masses --	4.1546	3.7550	4.2138

Sum of electronic and thermal Free Energies= -1669.722372 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000011	0.000450	YES
RMS Force	0.000002	0.000300	YES

prod\_major\_methyls\_opposite\_side.xyz



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 Cartesian coordinates (Angstroms):  
 -----

H 2.269 2.592 -0.980  
 H 4.752 2.681 -1.252  
 H 1.310 2.528 0.528  
 H 2.932 3.276 0.536  
 H 3.893 1.383 -2.138

C	2.326	2.457	0.111
C	4.680	1.590	-1.393
H	5.640	1.230	-1.797
C	2.935	1.112	0.487
O	2.195	0.023	-0.224
C	4.401	0.874	-0.061
H	5.489	2.236	1.243
H	1.697	0.799	2.224
B	3.122	-0.991	-0.549
H	3.236	1.637	2.586
C	2.774	0.835	1.986
C	5.508	1.171	0.953
O	4.418	-0.578	-0.355
H	6.490	0.959	0.499
Pt	0.056	-0.759	-0.194
H	3.227	-0.127	2.276
H	5.406	0.558	1.861
O	-3.092	-1.232	0.731
H	-3.197	3.402	-2.636
H	-1.708	4.168	-2.022
C	-2.706	3.803	-1.734
H	-3.303	4.660	-1.376
H	-4.390	1.686	-1.399
O	-1.767	1.624	-1.162
C	-2.629	2.709	-0.662
C	-4.025	2.096	-0.442
H	-0.215	4.108	-0.337
H	-4.750	2.854	-0.098
H	-1.432	5.247	0.314
C	-0.908	4.293	0.500
H	-3.991	1.273	0.290
C	-1.907	3.136	0.680
H	-3.493	4.313	1.613
H	-0.315	4.404	1.423
O	-1.130	1.930	1.028
C	-2.848	3.448	1.850
H	-3.489	2.589	2.100
H	-2.253	3.704	2.744
B	-1.007	1.099	-0.098
C	1.218	-2.644	-0.273
C	2.546	-2.360	-1.030
H	-2.872	-0.560	-2.179
H	-2.003	-2.037	-2.712
H	-3.631	-2.184	-1.942
C	-2.683	-1.621	-1.952
P	-1.864	-1.713	-0.317
H	-3.971	-3.840	0.127
O	-1.930	-3.334	0.118

H -4.518 -2.207 1.878  
 C -3.452 -2.321 1.625  
 C -3.161 -3.605 0.842  
 H -2.839 -2.256 2.543  
 H -2.980 -4.475 1.493  
 H 0.666 -3.438 -0.806  
 C 1.499 -3.136 1.158  
 H 2.149 -4.042 1.165  
 H 0.566 -3.395 1.689  
 H 2.020 -2.371 1.767  
 H 3.286 -3.184 -0.916  
 H 2.351 -2.280 -2.120

	1 A	2 A	3 A
Frequencies --	20.2390	27.9794	32.6844
Red. masses --	3.8138	4.1880	3.6912

Sum of electronic and thermal Free Energies= -1669.720129 Hartree

Item	Value	Threshold	Converged?
Maximum Force	0.000013	0.000450	YES
RMS Force	0.000002	0.000300	YES

### References

<sup>1</sup>J. P. Perdew, *Phys. Rev. B.* **1986**, 33, 8822-8824.  
<sup>2</sup>Hratchian H. P. and Schlegel H. B., *J. Chem. Phys.* **2004**, 120, 9918-9924.  
<sup>3</sup>Miertuš S., Scrocco E., and Tomasi J., *Chem. Phys.* **1981**, 55, 117-129.  
<sup>4</sup>Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.