

Enantiomerically-Enriched Tris(boronates): Readily Accessible Conjunctive Reagents for Asymmetric Synthesis

John R. Coombs, Liang Zhang and James P. Morken

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

Supporting Information

Table of Contents

General Information	S-2
Experimental Procedures	S-3
I. <i>Preparation of Pt(dba)₃ and phosphonite ligands</i>	S-3
II. <i>Preparation of vinyl boronate starting materials</i>	S-4
III. <i>Representative procedure for Pt-catalyzed vinyl(boronate) diboration</i>	S-8
IV. <i>Representative procedure for deborylative alkylation of 1,1,2-tris(boronate)-esters</i>	S-9
V. <i>Characterization and proof of stereochemistry of 1,1,2-tris(boronate)esters</i>	S-11
VI. <i>Characterization and proof of stereochemistry of deborylative alkylation products</i>	S-32
VII. <i>Additional transformations of 1,1,2-tris(boronate)esters</i>	S-38
VIII. <i>Procedures for the formal synthesis of exo-Brevicomine</i>	S-39
Spectral Data and Analysis of Diastereoselectivity for Deborylative Alkylation	S-42

General Information

^1H NMR spectra were measured using a Varian Gemini-500 (500 MHz) spectrometer or a Varian Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl_3 : 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, pent = pentet, sept = septet, br = broad, m = multiplet), and coupling constants (Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured using a Varian Inova 500 (126 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl_3 : 77.0 ppm). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were measured using a Varian Inova 500 (202 MHz) spectrometer. Chemical shifts are reported in ppm using phosphoric acid as the external standard (H_3PO_4 : 0.0 ppm). Infrared (IR) spectra were measured using a Bruker α -P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). High-resolution mass spectrometry (HRMS) was performed at the chemistry department at Boston College, Chestnut Hill, MA.

Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2 , 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm), phosphomolybdic acid (PMA), potassium permanganate (KMnO_4), and Seebach's "magic" stain¹ (phosphomolybdic acid, $\text{Ce}(\text{SO}_4)_2$, sulfuric acid). Analytical chiral gas-liquid chromatography (GLC) was also performed on an Agilent Technologies 6850 Series chromatograph with a flame ionization detector, and a Supelco β -Dex 120 column with helium as the carrier gas. Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. Analytical chiral supercritical fluid chromatography (SFC) was performed on a Thar Supercritical Fluid Chromatograph equipped with auto sampler and a Waters photodiode array detector with methanol as the modifier.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran, dichloromethane, toluene, 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. Dimethylformamide was dispensed from a Glass Contour Solvent Purification System (SG Water, USA LLC). Triethylamine was purchased from Aldrich and refluxed over calcium hydride prior to use. Schwartz's reagent, phenyldichlorophosphine, and sodium *tert*-butoxide were purchased from Strem Chemicals and used as received. 3-Phenyl-1-propyne, imidazole, ethynylcyclohexane, and 1-bromo-2-methylpropane purchased from Alfa Aesar and used as received. $\text{B}_2(\text{pin})_2$ was obtained from AllyChem and recrystallized from pentane prior to use. Dibenzylideneacetone and 1-bromo-6-chlorohexane were purchased from Oakwood and used as received. *tert*-Butylchlorodiphenylsilane was purchased from Gelest and used as received.

¹ Seebach, D.; Imwinkelried, R.; Stucky, G. *Helv. Chim. Acta.* **1987**, *70*, 448.

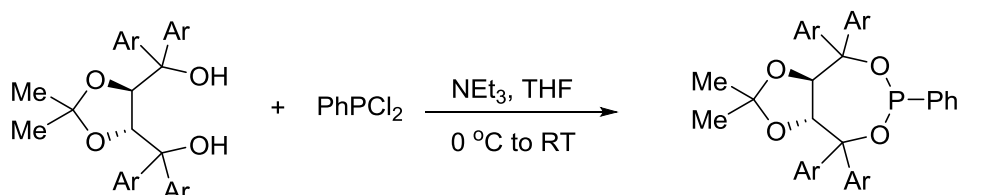
Pinacol borane was purchased from BASF and distilled prior to use. 5-Chloro-1-pentyne was purchased from Chemsampco and used as received. Iodomethane was purchased from Acros and used as received. All other reagents were obtained from Aldrich or Fisher and used as received.

Experimental Procedures

(I) Preparation of $Pt(dba)_3$ and phosphonite ligands

Tris(dibenzylideneacetone)platinum(0) was prepared according to the literature procedure.² All spectral data and elemental analysis were in accordance with the literature.

Ligands **L1**³, **L2**⁴, **L3**², and **L4**⁵ were prepared according to the general reaction scheme shown below. All spectral data were in accordance with the literature.

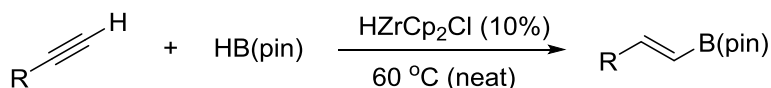


(R,R)-L1: Ar = 3,5-diisobutylphenyl
 (R,R)-L2: Ar = 3,5-diethylphenyl
 (R,R)-L3: Ar = 3,5-diisopropylphenyl
 (R,R)-L4: Ar = 3,5-di-*t*-butylphenyl

(II) Preparation of vinyl boronate starting materials

Unless otherwise noted, vinyl boronate starting materials were prepared according to the general method shown below.

General procedure for vinyl boronate synthesis



To an oven-dried 2-dram vial equipped with magnetic stir bar in the glovebox was added alkyne (1.10 equiv.) and pinacol borane (1.00 equiv.), followed immediately by Schwartz's reagent

² Coombs, J.R.; Haeffner, F.; Kliman, L.T.; Morken, J.P. *J. Am. Chem. Soc.* **2013**, *135*, 11222.

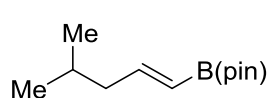
³ Kliman, L.T.; Mlynarski, S.N.; Ferris, G.E.; Morken, J.P. *Angew. Chem. Int. Ed.* **2012**, *51*, 521.

⁴ Kliman, L.T.; Mlynarski, S.N.; Morken, J.P. *J. Am. Chem. Soc.* **2009**, *131*, 13210.

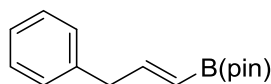
⁵ Burks, H.E.; Kliman, L.T.; Morken, J.P. *J. Am. Chem. Soc.* **2009**, *131*, 9134.

(0.10 equiv.). The vial was sealed with a polypropylene cap, taped, and removed from the glovebox. The mixture was heated in an oil bath to 60 °C for 14 hours, at which point it was cooled to room temperature. The pure vinyl(boronate) products were isolated after SiO₂ gel chromatography, unless otherwise noted.

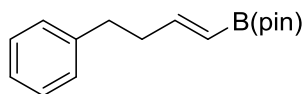
The following starting materials were purchased from Aldrich and used without further purification: (*E*)-1-octen-1-ylboronic acid pinacol ester, (*E*)-4-(*tert*-butyldimethylsiloxy)-1-buten-1-ylboronic acid pinacol ester, (*E*)-6-chloro-1-hexen-1-ylboronic acid pinacol ester, (*E*)-2-cyclopropylvinylboronic acid pinacol ester, and (*E*)-2-phenylvinylboronic acid pinacol ester.



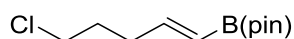
(*E*)-4,4,5,5-tetramethyl-2-(4-methylpent-1-en-1-yl)-1,3,2-dioxaborolane (1). Prepared according to the general procedure utilizing pinacolborane (1.28 g, 10.0 mmol), Schwartz' reagent (258 mg, 1.00 mmol), and 4-methylpent-1-yne (904 mg, 11.0 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.74 g, 83%). All spectral data are in accordance with the literature.⁶



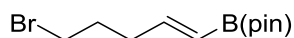
(*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (S1). Prepared according to the general procedure utilizing pinacolborane (1.28 g, 10.0 mmol), Schwartz' reagent (258 mg, 1.00 mmol), and 3-phenyl-1-propyne (1.28 g, 11.0 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.94 g, 79%). All spectral data are in accordance with the literature.⁷



(*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (S2). Prepared according to the general procedure utilizing pinacolborane (1.28 g, 10.0 mmol), Schwartz' reagent (258 mg, 1.00 mmol), and 4-phenyl-1-butyne (1.56 g, 12.0 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (2.07 g, 80%). All spectral data are in accordance with the literature.⁶



(*E*)-2-(5-chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S3). Prepared according to the general procedure utilizing pinacolborane (1.28 g, 10.0 mmol), Schwartz' reagent (258 mg, 1.00 mmol), and 5-chloropent-1-yne (1.13 g, 11.0 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a white solid (1.87 g, 81%). All spectral data are in accordance with the literature.⁶

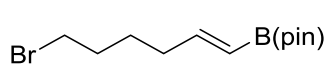


(*E*)-2-(5-bromopent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S4). To a solution of pent-4-yn-1-ol (1.26 g, 15.0 mmol) in dry

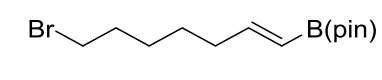
⁶ Yoshida, H.; Kageyuki, I.; Takaki, K. *Org. Lett.* **2014**, *16*, 3512.

⁷ Shimizu, H.; Igasrashi, T.; Miura, T.; Murakami, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 11465.

dichloromethane (20 mL) were added the tetrabromomethane (7.46 g, 22.5 mmol) and the triphenylphosphine (5.90 g, 22.5 mmol). The mixture was stirred at room temperature for 1 hour. The reaction mixture was directly distilled under vacuum to afford the 5-bromopent-1-yne as clear, colorless oil (2.05 g, 93%), which was used in the subsequent step without further purification. Next, (*E*)-2-(5-bromopent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure utilizing pinacolborane (1.28 g, 10.0 mmol), Schwartz' reagent (258 mg, 1.00 mmol), and 5-bromopent-1-yne (1.62 g, 11.0 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a white solid (1.32 g, 48%). ¹H NMR (500 MHz, CDCl₃): δ 6.55 (1H, dt, *J*=18.0, 6.5 Hz), 5.47 (1H, d, *J*=17.5 Hz), 3.38 (2H, t, *J*=7.0 Hz), 2.29 (2H, q, *J*=7.0 Hz), 1.96 (2H, pent, *J*= 7.0 Hz), 1.24 (12H, s); ¹³C NMR (100 MHz, CDCl₃): δ 152.1, 83.3, 34.2, 33.3, 31.3, 24.9; IR (neat): 2911.4 (m), 1638.1 (m), 1397.6 (m), 1361.5 (s), 1320.1 (s), 1217.1 (s), 1002.0 (m), 969.4 (m), 849.1 (m); HRMS-(DART+) for C₁₀H₂₁B₁Br₁O₂ [M+H]⁺: calculated: 275.0818, found: 275.0819.

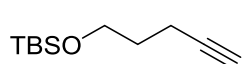
 **(*E*)-2-(6-bromohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S5).** To a solution of hex-5-yn-1-ol (1.47 g, 15.0 mmol) in dry dichloromethane (20 mL) were added the tetrabromomethane (7.46 g, 22.5 mmol) and the triphenylphosphine (5.90 g, 22.5 mmol). The mixture was stirred at room temperature for 1 hour.

The reaction mixture was directly distilled under vacuum to afford the 6-bromohex-1-yne as clear, colorless oil (2.39 g, 99%), which was used in the subsequent step without further purification. Next, (*E*)-2-(6-bromohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure utilizing pinacolborane (1.92 g, 15.0 mmol), Schwartz' reagent (387 mg, 1.50 mmol), and 6-bromohex-1-yne (2.66 g, 16.5 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a white solid (2.17 g, 50%). ¹H NMR (500 MHz, CDCl₃): δ 6.58 (1H, dt, *J*= 17.5, 7.0 Hz), 5.43 (1H, d, *J*= 17.5 Hz), 3.38 (2H, t, *J*= 7.0 Hz), 2.16 (2H, q, *J*= 7.5 Hz), 1.85(2H, pent, *J*= 7.0 Hz), 1.56 (2H, pent, *J*= 7.0 Hz), 1.24 (12H, s); ¹³C NMR (100 MHz, CDCl₃): δ 153.6, 83.3, 34.7, 33.6, 32.1, 26.7, 24.7; IR (neat):2977.5 (m), 2933.9 (m), 1638.1 (s), 1359.5 (s), 1318.5 (s), 1164.4 (s), 994.8 (m), 969.5 (m), 848.8 (m); HRMS-(DART+) for C₁₂H₂₃B₁Br₁O₂ [M+H]⁺: calculated: 289.09745, found: 289.0980.

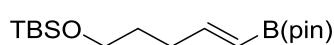
 **(*E*)-2-(7-bromohept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S6).** To a solution of hept-6-yn-1-ol (1.68 g, 15.0 mmol) in dry dichloromethane (20 mL) were added the tetrabromomethane (7.46 g, 22.5 mmol) and the triphenylphosphine (5.90 g, 22.5 mmol). The mixture was stirred at room temperature for 1 hour.

The solvent was removed under reduced pressure. A solution of hexane/ethyl acetate (9:1) was added and the resulting precipitate was filtered and washed abundantly. The filtrate was evaporated and the crude material was purified by silica gel chromatography (SiO₂, 100% hexane) to give 7-bromohept-1-yne as a clear, colorless oil (2.18 g, 83%), which was used in the subsequent step without further purification. Next, (*E*)-2-(7-bromohept-1-en-1-yl)-4,4,5,5-

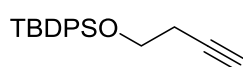
tetramethyl-1,3,2-dioxaborolane was prepared according to the general procedure utilizing pinacolborane (1.08 g, 8.47 mmol), Schwartz's reagent (218 mg, 0.847 mmol), and 7-bromohept-1-yne (1.63 g, 9.32 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.85 g, 72%). ¹H NMR (500 MHz, CDCl₃): δ 6.59 (1H, dt, *J*= 17.5, 6.5 Hz), 5.41 (1H, d, *J*= 17.5 Hz), 3.37 (2H, t, *J*= 6.5 Hz), 2.14 (2H, q, *J*= 7.0 Hz), 1.83 (2H, pent, *J*= 7.0 Hz), 1.44-1.41 (4H, m), 1.24 (12H, s); ¹³C NMR (100 MHz, CDCl₃): δ 154.2, 83.2, 35.7, 33.9, 32.8, 27.9, 27.5, 25.0; IR (neat): 2977.9 (m), 2931.6 (m), 1638.3 (s), 1361.3 (s), 1318.9 (s), 1144.6 (s), 997.2 (m), 970.5 (m), 849.4 (m); HRMS-(DART+) for C₁₃H₂₅B₁Br₁O₂ [M+H]⁺: calculated: 303.1131, found: 303.1134.



***tert*-butyldimethyl(pent-4-yn-1-yloxy)silane (S7).** To an oven-dried 100 mL round-bottomed flask was added imidazole (4.41 g, 64.2 mmol) followed by CH₂Cl₂ (9.0 mL). To the flask was added pent-4-yn-1-ol (2.21 mL, 23.8 mmol) and the reaction mixture was allowed to stir at room temperature for 5 minutes. To the flask was added *tert*-butyldimethylsilyl chloride (4.96 g, 35.7 mmol) in one portion. The flask wash flushed with nitrogen and the reaction mixture was allowed to stir at room temperature for 18 hours, at which point the mixture was diluted with deionized H₂O (20 mL) and CH₂Cl₂ (20 mL). The crude mixture was extracted with CH₂Cl₂ (3x20 mL), and the organics were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (3.54 g, 75%). All spectral data are in accordance with the literature.⁸



***(E)*-*tert*-butyldimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)silane (S8).** Prepared according to the general procedure utilizing pinacolborane (640 mg, 5.00 mmol), Schwartz' reagent (129 mg, 0.500 mmol), and *tert*-butyldimethyl(pent-4-yn-1-yloxy)silane (1.09 g, 5.50 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.32 g, 81%). All spectral data are in accordance with the literature.⁹

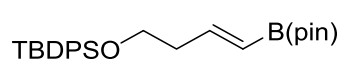


(but-3-yn-1-yloxy)(*tert*-butyl)diphenylsilane (S9). To an oven-dried 100 mL round-bottomed flask was added imidazole (1.09 g, 16.0 mmol) followed by CH₂Cl₂ (20.0 mL). To the flask was added but-3-yn-1-ol (0.610 mL, 8.06 mmol) and the reaction mixture was allowed to stir at room temperature for 5 minutes. To the flask was added *tert*-butyl(chloro)diphenylsilane (2.31 mL, 8.88 mmol) in one portion. The flask wash flushed with nitrogen and the reaction mixture was allowed to stir at room temperature for 18 hours, at which point the mixture was diluted with deionized H₂O (20 mL) and CH₂Cl₂ (20 mL). The crude mixture was extracted with CH₂Cl₂ (3x20 mL), and the organics were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified

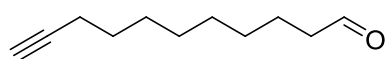
⁸ Kleinbeck, F.; Toste, F.D. *J. Am. Chem. Soc.* **2009**, *131*, 9178.

⁹ Varseev, G.N.; Maier, M.E. *Angew. Chem. Int. Ed.* **2006**, *45*, 4767.

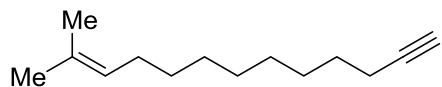
(SiO₂, 3% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (2.28 g, 92%). All spectral data are in accordance with the literature.¹⁰



(E)-tert-butylidiphenyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)oxy)silane (S10). Prepared according to the general procedure utilizing pinacolborane (640 mg, 5.00 mmol), Schwartz' reagent (129 mg, 0.500 mmol), and (but-3-yn-1-yloxy)(tert-butyl)diphenylsilane (1.70 g, 5.50 mmol). The crude material was purified (SiO₂, 2.5% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.98 g, 91%). ¹H NMR (500 MHz, CDCl₃): δ 7.67 (4H, d, *J* = 6.5 Hz), 7.44-7.36 (6H, m), 6.60 (1H, dt, *J* = 18.0, 7.0 Hz), 5.49 (1H, d, *J* = 18.0 Hz), 3.74 (2H, t, *J* = 7.0 Hz), 2.44 (2H, q, *J* = 7.0 Hz), 1.26 (12H, s), 1.05 (9H, s); ¹³C NMR (126 MHz, CDCl₃): δ 150.6, 135.6, 133.9, 129.5, 127.6, 83.0, 62.9, 39.2, 26.8, 24.7, 19.2; IR (neat): 2976.6 (w), 2930.8 (w), 2857.8 (w), 1639.1 (m), 1472.0 (w), 1388.7 (s), 1359.1 (s), 1144.1 (s), 1107.6 (s), 996.3 (m), 849.3 (m), 822.6 (m), 737.6 (s), 612.8 (m), 504.3 (s) cm⁻¹; HRMS-(DART) for: C₂₆H₃₈BO₃Si [M+H]⁺: calculated: 437.2683, found: 437.2696.



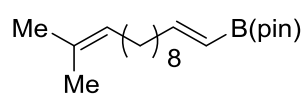
undec-10-ynal (S11). A 50-mL flame-dried round-bottomed flask was charged with a solution of Dess-Martin periodinane (6.36 g) in 20 mL of dichloromethane and then cooled in an ice bath. To the reaction vessel was added undec-10-yn-1-ol (2.87 mL, 15.0 mmol), dropwise over 1 min. The reaction was allowed to stir for 5 min at 0 °C, at which point the reaction vessel was allowed to stir for an additionally 3 hours at room temperature. The reaction mixture was washed with saturated NaHCO₃, and concentrated under vacuum. The crude was purified by silica gel chromatography (3% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.98 g, 80%). All spectral data are in accordance with the literature.

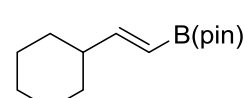


12-methyltridec-11-en-1-yne (S12). A solution of *n*-butyllithium in hexanes (2.48 M, 5.40 mL, 13.4 mmol, 2.0 equiv) was added dropwise via syringe to a stirred suspension of 2-propyltriphenylphosphonium bromide (5.16 g, 13.4 mmol) in tetrahydrofuran (40 mL) at -78 °C. After completion of the addition, the cooling bath was removed and the reaction vessel was placed in an ice bath. The mixture was allowed to stir for 1 hour at 0 °C. The dark red solution that formed was cooled to -78 °C and undec-10-ynal (1.12 g, 6.70 mmol) was added dropwise via syringe over 5 minutes. The reaction mixture was stirred for 1 hour at -78 °C, at which point the vessel was placed in an ice bath. The mixture was allowed to stir for an additional 2 hours at 0 °C. The product mixture was diluted sequentially with saturated ammonium chloride solution (10 mL) and water (30 mL). The diluted product mixture was transferred to a separatory funnel and extracted with ether (3x40 mL). The organic layers were combined and the combined layers were dried over sodium sulfate. The dried solution was filtered and the filtrate was concentrated. The residue obtained was purified by silica gel

¹⁰ Greshock, T.J.; Johns, D.M.; Noguchi, Y.; Williams, R.M. *Org. Lett.* **2008**, *10*, 613.

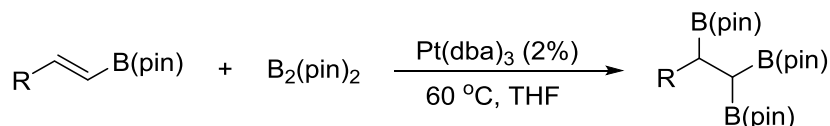
chromatography (100% hexanes) to afford the desired product as a clear, colorless oil (847.5 mg, 66%). All spectral data are in accordance with the literature.¹¹


(E)-4,4,5,5-tetramethyl-2-(12-methyltrideca-1,11-dien-1-yl)-1,3,2-dioxaborolane (S13). Prepared according to the general procedure utilizing pinacolborane (640 mg, 5.00 mmol), Schwartz' reagent (129 mg, 0.500 mmol), and 12-methyltridec-11-en-1-yne (1.70 g, 5.50 mmol). The crude material was purified (SiO₂, 2.5% ethyl acetate in hexane) to give the desired product as a clear, colorless oil (1.37 g, 86%). All spectral data are in accordance with the literature. ¹H NMR (500 MHz, CDCl₃): δ 6.61 (1H, dt, *J*= 18.0, 6.5 Hz), 5.40 (1H, d, *J*= 17.5 Hz), 5.10 (1H, tt, *J*= 6.0, 1.5 Hz), 2.11 (2H, q, *J*= 7.0 Hz), 1.93 (2H, q, *J*=6.5 Hz), 1.66 (3H, s), 1.57 (3H, s), 1.40-1.36 (2H, m), 1.24-1.22 (22H, m); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 131.1, 124.9, 82.9, 35.8, 29.8, 29.5, 29.3, 29.2, 28.2, 28.0, 25.7, 24.8, 24.7, 17.6; IR (neat): 2977.3 (m), 2923.8 (m), 2853.7 (m), 1637.9 (m), 1360.3.5 (s), 1317.2 (s), 1144.6 (s), 970.6 (m), 849.4 (m); HRMS-(DART+) for C₂₀H₃₈B₁O₂ [M+H]⁺: calculated: 321.2965, found: 321.2961.


(E)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S14). Prepared according to the general procedure utilizing pinacolborane (1.28 g, 10.0 mmol), Schwartz' reagent (258 mg, 1.00 mmol), and ethynylcyclohexane (1.19 g, 11.0 mmol). The crude material was purified (SiO₂, 3% ethyl acetate in hexane) to give the desired product as a white solid (2.00 g, 85%). All spectral data are in accordance with the literature.⁶

(III) Representative procedure for Pt-catalyzed vinyl(boronate) diboration

General procedure for racemic Pt-catalyzed vinyl(boronate) diboration

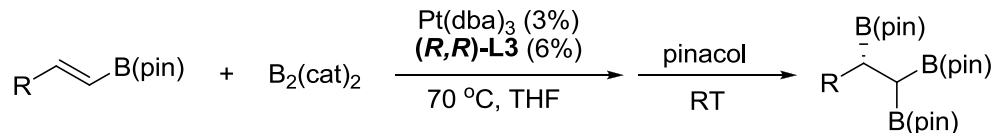


To an oven-dried 6-dram scintillation vial equipped with a magnetic stirbar in the glovebox was added Pt(dba)₃ (0.02 equiv.) and B₂(pin)₂ (1.05 equiv.), followed by THF (1.0 M in vinyl(boronate)). The mixture was allowed to stir at room temperature for 2 minutes, at which point the vinyl(boronate) (1.00 equiv.) was added all at once. The vial was sealed with a polypropylene cap, taped, brought outside of the glovebox, and heated in an oil bath at 60 °C for 13 hours. The resulting mixture was cooled to room temperature and concentrated under

¹¹ Li, L.; Herzon, S.B. *J. Am. Chem. Soc.* **2012**, *134*, 17376.

reduced pressure to give the crude material, which was subsequently purified using SiO₂ gel column chromatography.

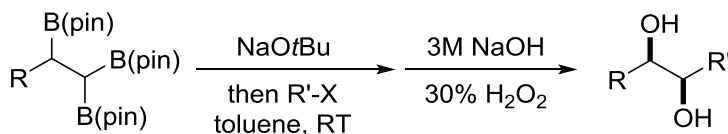
General procedure for asymmetric Pt-catalyzed vinyl(boronate) diboration



To an oven-dried 2-dram vial equipped with a magnetic stirbar in the glovebox was added Pt(dba)₃ (0.03 equiv.), (**R,R**)-**L3** (0.06 equiv.), and B₂(cat)₂ (1.20 or 2.00 equiv.), followed by THF (1.0 M in vinyl(boronate)). The vial was sealed with a polypropylene cap, taped, brought outside of the glovebox, and heated to 80 °C for 25 minutes (**Caution:** While we have not experienced any explosions, this reaction involves heating of a closed system, and therefore appropriate safety measures should be followed). Over this period, the mixture turned from a deep purple solution to a pale yellow solution. The mixture was cooled to room temperature and brought into the glovebox, at which point the vinyl(boronate) (1.00 equiv.) was added all at once. The vial was sealed with a polypropylene, taped, brought outside of the glovebox, and heated to 60 °C for 24 hours. The resulting mixture was cooled to room temperature and brought back into the glovebox, at which point pinacol (7.2 equiv.) was added all at once. The vial was sealed, taped, brought out of the glovebox, and allowed to stir at room temperature for 14 hours. The resulting mixture was cooled to room temperature, concentrated under reduced pressure, and subsequently purified via SiO₂ gel column chromatography to provide the pure diboration products (**Note:** All tris(boronates) tested are adequately stable to SiO₂ gel column chromatography with minimal degradation observed).

(IV) Representative procedure for deborylative alkylation of 1,1,2-tris(boronate)esters

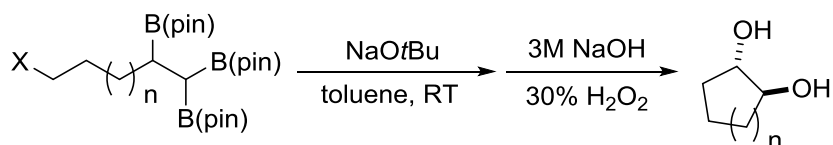
General procedure for deborylative alkylation/oxidation of 1,1,2-tris(boronate)esters



To an oven-dried 2-dram vial equipped with a magnetic stirbar in the glovebox was added 1,1,2-tris(boronate) (1.50 equiv.) and NaOtBu (5.0 equiv.), followed by toluene (0.22 M in tris(boronate)). The mixture was allowed to stir at room temperature for 3-5 minutes, at which point alkyl halide (1.00 equiv.) was added dropwise. The reaction vessel was sealed with a polypropylene cap, taped, and brought out of the glovebox where it was allowed to stir at room temperature for 14-18 hours. The reaction mixture was then transferred to a 6-dram vial and diluted with THF (2 mL). The crude mixture was cooled to 0 °C and 3M NaOH (1.5 mL) was

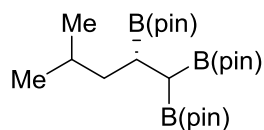
added, followed by 30% H₂O₂ (1.0 mL), dropwise. The reaction mixture was allowed to warm to room temperature, and was allowed to stir at room temperature for 4 hours. The reaction mixture was cooled to 0 °C and saturated aq. Na₂S₂O₃ (1.5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The pure diol products were isolated after SiO₂ chromatography, unless otherwise noted.

General procedure for deborylative cyclization/oxidation of 1,1,2-tris(boronate)esters



To an oven-dried 2-dram vial equipped with a magnetic stirbar in the glovebox was added 1,1,2-tris(boronate) (1.00 equiv.) and NaOtBu (5.0 equiv.), followed by toluene (0.22 M in tris(boronate)). The reaction vessel was sealed with a polypropylene cap, taped, and brought out of the glovebox where it was allowed to stir at room temperature for 14-18 hours. The reaction mixture was then transferred to a 6-dram vial and diluted with THF (2 mL). The crude mixture was cooled to 0 °C and 3M NaOH (1.5 mL) was added, followed by 30% H₂O₂ (1.0 mL), dropwise. The reaction mixture was allowed to warm to room temperature, and was allowed to stir at room temperature for 4 hours. The reaction mixture was cooled to 0 °C and saturated aq. Na₂S₂O₃ (1.5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The pure diol products were isolated after SiO₂ chromatography, unless otherwise noted.

(V) Characterization and proof of stereochemistry of 1,1,2-tris(boronate)esters



(R)-2,2,2'-(4-methylpentane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), **(R,R)-L3** (16.4 mg, 0.0180 mmol), methylpent-1-en-1-yl)-1,3,2-dioxaborolane (63.1 mg, 0.300 mmol), and

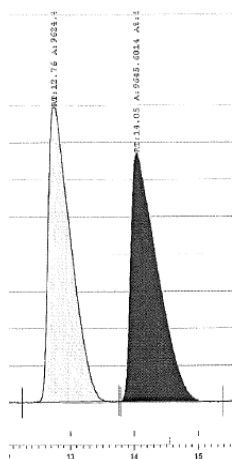
THF (0.30 mL), followed by pinacol (425.3 mg, 3.600 mmol). The crude material was purified (SiO_2 , 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (96.1 mg, 70%). ^1H NMR (500 MHz, CDCl_3): δ 1.57-1.53 (1H, m), 1.42-1.31 (2H, m), 1.20-1.12 (37 H, m), 0.84 (3H, d, J = 6.0 Hz), 0.81 (3H, d, J = 6.5 Hz), 0.78 (1H, d, J = 9.5 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 82.9, 82.8, 82.8, 43.2, 27.2, 25.2, 25.2, 25.0, 24.9, 24.8, 24.8, 23.7, 22.6; IR (neat): 2976.3 (m), 2952.2 (m), 1378.8 (m), 1369.8 (m), 1344.7 (s), 1307.1 (s), 1165.4 (s), 968.6 (m), 848.4 (m) cm^{-1} ; HRMS-(DART) for: $\text{C}_{24}\text{H}_{48}\text{B}_3\text{O}_6$ $[\text{M}+\text{H}]^+$: calculated: 465.3730, found: 465.3726. $[\alpha]_{\text{D}}^{20} = -12.351$ ($c = 0.340$, CHCl_3 , $l = 50$ mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-4,4,5,5-tetramethyl-2-(4-methylpent-1-en-1-yl)-1,3,2-dioxaborolane and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to the general procedure for deborylative alkylation with (3-bromopropyl)benzene followed by oxidation to give (4*S*,5*S*)-7-methyl-1-phenyloctane-4,5-diol. Further analysis of stereochemistry was performed on (4*S*,5*S*)-7-methyl-1-phenyloctane-4,5-diol. Absolute stereochemistry was assigned by analogy (see product **6** and **7**).

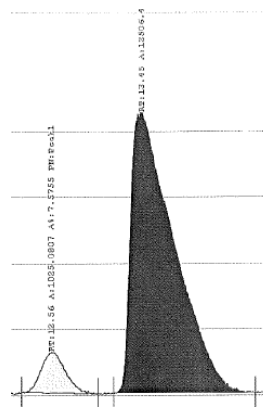
Chiral SFC (Chiralcel OD-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (4*S*,5*S*)-7-methyl-1-phenyloctane-4,5-diol

Racemic Material

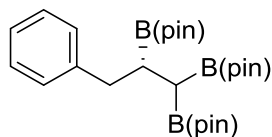


Peak No	% Area	Area	RT (min)
1	49.9449	9624.4423	12.76
2	50.0551	9645.6814	14.05
Total:	100	19270.1237	

Standard Conditions



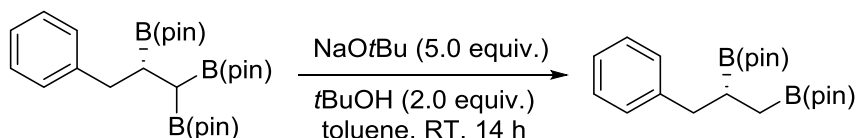
Peak No	% Area	Area	RT (min)
1	7.5755	1025.0807	12.56
2	92.4245	12506.4458	13.45
Total:	100	13531.5265	



(*R*)-2,2',2''-(3-phenylpropane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (3). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), (*R,R*)-**L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (85.6 mg, 0.360 mmol), (*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane (73.2 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (255.2 mg, 2.160 mmol). The crude material was purified (SiO_2 , 5-7% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (121.5 mg, 81%). ^1H NMR (500 MHz, CDCl_3): δ 7.23-7.17 (4H, m), 7.10 (1H, tt, $J = 6.5, 2.0$ Hz), 2.80 (1H, dd, $J = 13.5, 7.0$ Hz), 2.71 (1H, dd, $J = 13.5, 8.5$ Hz), 1.68 (1H, dt, $J = 7.0, 9.0$ Hz), 1.23 (24 H, s), 1.13 (6H, s), 1.10 (6H, s), 0.85 (1H, d, $J = 9.0$ Hz); ^{13}C NMR (126 MHz, CDCl_3): δ 142.7, 129.3, 127.8, 125.3, 82.8, 82.8, 82.8, 39.2, 25.0, 24.9, 24.8, 24.8, 24.6, 24.6; IR (neat): 2976.6 (m), 2929.1 (w), 1454.9 (w), 1369.8 (s), 1350.4 (s), 1309.6 (s), 1264.6 (m), 1213.7 (w), 1140.0 (s), 969.6 (m), 850.4 (m), 744.7 (w), 699.7 (w), 669.9 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{27}\text{H}_{46}\text{B}_3\text{O}_6$ $[\text{M}+\text{H}]^+$: calculated: 499.3574, found: 499.3592. $[\alpha]_{\text{D}}^{20} = -15.837$ ($c = 0.500$, CHCl_3 , $l = 50$ mm).

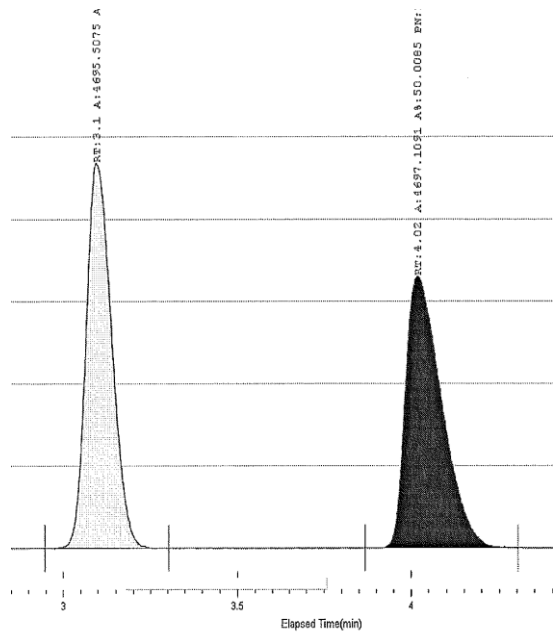
Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-4,4,5,5-tetramethyl-2-(3-phenylprop-1-en-1-yl)-1,3,2-dioxaborolane and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to protodeboronation as shown below to give (*R*)-2,2'-(3-phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). Further analysis of stereochemistry was performed on (*R*)-2,2'-(3-phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). Absolute stereochemistry was assigned by analogy (see product **6** and **7**).



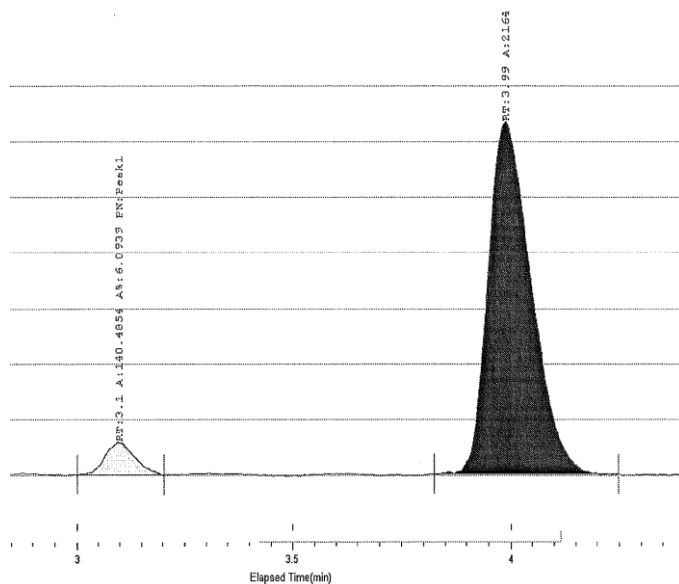
Chiral SFC (Chiracel OD-H, 5% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (R)-2,2'-(3-phenylpropane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

Racemic Material

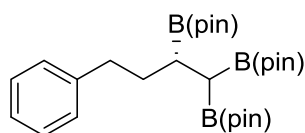


Peak No	% Area	Area	RT (min)
1	49.9915	4695.5075	3.1
2	50.0085	4697.1091	4.02
Total:	100	9392.6166	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	6.0939	140.4854	3.1
2	93.9061	2164.8638	3.99
Total:	100	2305.3492	



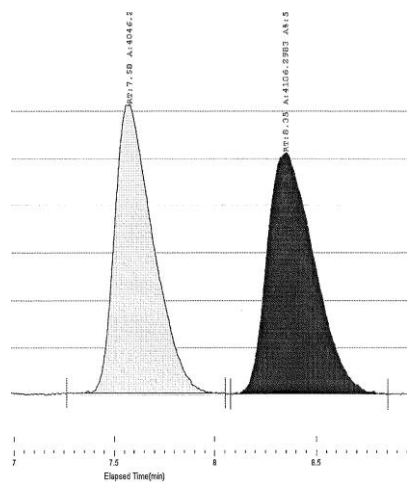
(*R*)-2,2',2''-(4-phenylbutane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (4). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), (*R,R*)-**L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (85.6 mg, 0.360 mmol), (*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane (77.5 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (255.2 mg, 2.160 mmol). The crude material was purified (SiO_2 , 5-7% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (121.5 mg, 81%). ^1H NMR (500 MHz, CDCl_3): δ 7.26-7.22 (2H, m), 7.17 (2H, d, $J = 7.0$ Hz), 7.13 (1H, t, $J = 7.5$ Hz), 2.66 (1H, ddd, $J = 13.5, 10.5, 6.5$ Hz), 2.52 (1H, ddd, $J = 13.5, 11.0, 6.5$ Hz), 1.80-1.70 (2H, m), 1.47-1.43 (1H, m), 1.24-1.21 (36H, m), 0.94 (1H, d, $J = 10.0$ Hz); ^{13}C NMR (126 MHz, CDCl_3): δ 143.7, 128.4, 128.1, 125.2, 82.8, 82.8, 82.8, 35.7, 35.3, 25.1, 25.0, 24.8, 24.7, 24.7, 24.6; IR (neat): 2977.2 (m), 2929.6 (w), 1496.1 (w), 1455.9 (w), 1378.0 (s), 1370.1 (s), 1348.3 (s), 1312.2 (s), 1267.6 (m), 1214.4 (w), 1141.0 (s), 969.4 (m), 849.0 (m), 699.4 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{28}\text{H}_{48}\text{B}_3\text{O}_6$ $[\text{M}+\text{H}]^+$: calculated: 513.3730, found: 513.3751. $[\alpha]_D^{20} = -20.472$ ($c = 0.969$, CHCl_3 , $l = 50$ mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-4,4,5,5-tetramethyl-2-(4-phenylbut-1-en-1-yl)-1,3,2-dioxaborolane and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to protodeboronation to give (*R*)-2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). Further analysis of stereochemistry was performed on this product. Absolute stereochemistry assigned by analogy (see product **6** and **7**).

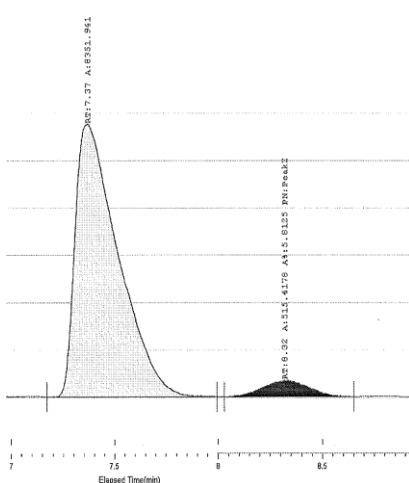
Chiral SFC (Chiracel OD-H, 1% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (*R*)-2,2'-(4-phenylbutane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

Racemic Material

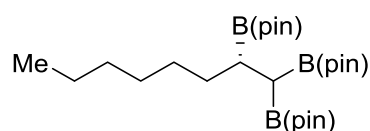


Peak No	% Area	Area	RT (min)
1	49.6317	4046.2516	7.58
2	50.3683	4106.2983	8.35
Total:	100	8152.5499	

Standard Conditions



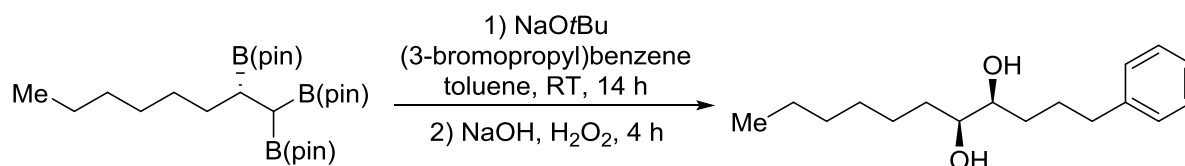
Peak No	% Area	Area	RT (min)
1	94.1875	8351.9413	7.37
2	5.8125	515.4178	8.32
Total:	100	8867.3591	



(*R*)-2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), (*R,R*)-**L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (85.6 mg, 0.360 mmol), (*E*)-1-octen-1-ylboronic acid pinacol ester (71.8 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (255.2 mg, 2.160 mmol). The crude material was purified (SiO_2 , 5-7% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (115.6 mg, 78%). ^1H NMR (500 MHz, CDCl_3): δ 1.44-1.36 (2H, m), 1.35-1.28 (2H, m), 1.27-1.16 (43H, m), 0.86-0.82 (4H, m); ^{13}C NMR (126 MHz, CDCl_3): δ 82.7, 82.6, 82.6, 33.4, 31.8, 29.6, 28.6, 25.0, 24.9, 24.8, 24.7, 24.6, 22.6, 14.1; IR (neat): 2976.0 (m), 2924.6 (m), 2855.2 (w), 1466.8 (w), 1370.1 (s), 1346.7 (s), 1306.2 (s), 1262.4 (s), 1213.3 (w), 1136.1 (m), 876.3 (m), 712.9 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{26}\text{H}_{52}\text{B}_3\text{O}_6$ $[\text{M}+\text{H}]^+$: calculated: 493.4043, found: 493.4062. $[\alpha]_{\text{D}}^{20} = -23.179$ ($c = 1.025$, CHCl_3 , $l = 50$ mm).

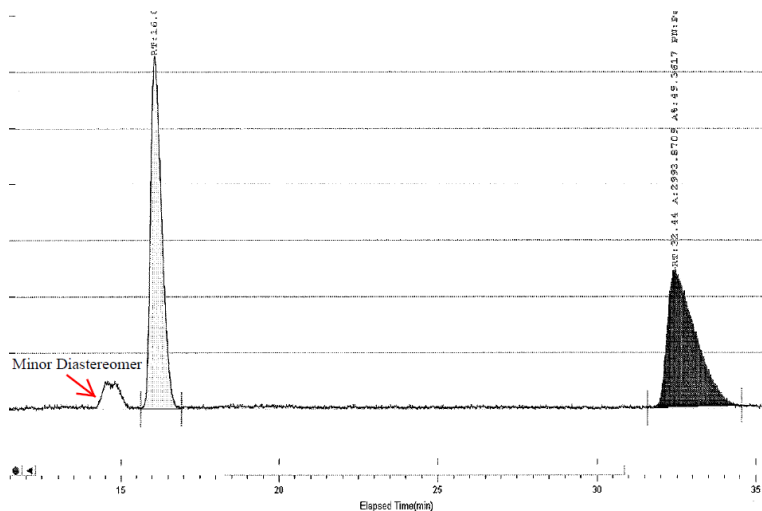
Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-1-octen-1-ylboronic acid pinacol ester and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to the general procedure for deborylative alkylation with (3-bromopropyl)benzene followed by oxidation as shown below to give (4*S*,5*S*)-1-phenylundecane-4,5-diol. Further analysis of stereochemistry was performed on (4*S*,5*S*)-1-phenylundecane-4,5-diol. Absolute stereochemistry was assigned by analogy (see product **6** and **7**).



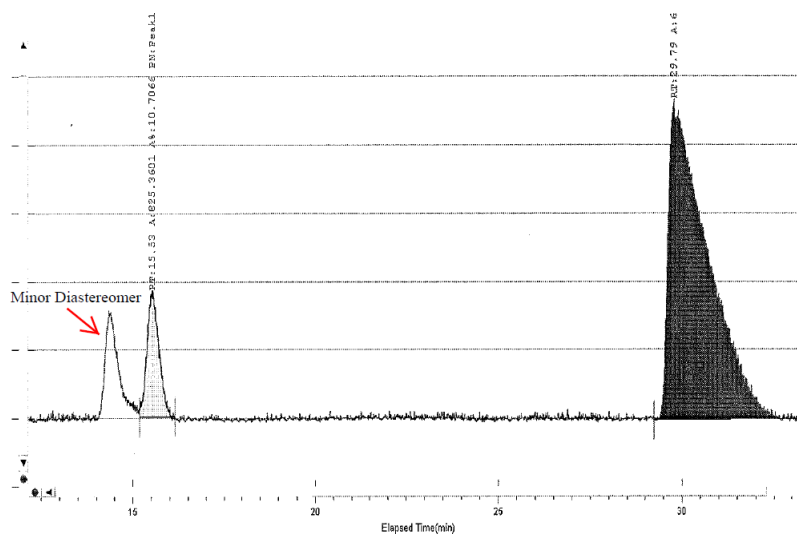
Chiral SFC (Chiracel OD-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (4*S*,5*S*)-1-phenylundecane-4,5-diol

Racemic Material

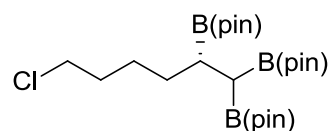


Peak No	% Area	Area	RT (min)
1	50.6383	3071.2958	16.08
2	49.3617	2993.8709	32.44
Total:	100	6065.1667	

Standard Conditions



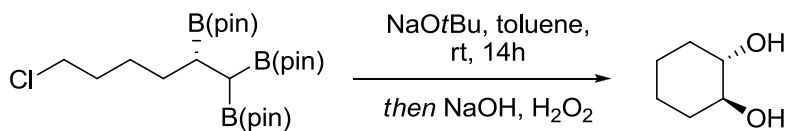
Peak No	% Area	Area	RT (min)
1	10.7066	825.3601	15.53
2	89.2934	6883.5181	29.79
Total:	100	7708.8782	



(R)-2,2',2''-(6-chlorohexane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), **(R,R)-L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (142.7 mg, 0.600 mmol), (*E*)-2-(6-chlorohex-1-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (72.9 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (425.3 mg, 3.600 mmol). The crude material was purified (SiO_2 , 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (114.3 mg, 76%). ^1H NMR (500 MHz, CDCl_3): δ 3.49 (2H, t, $J = 7.0$ Hz), 1.74-1.70 (2H, m), 1.46-1.31 (5H, m), 1.20-1.18 (36H, m), 0.83 (1H, d, $J = 9.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 83.0, 83.0, 82.9, 45.4, 33.1, 32.6, 26.2, 25.2, 25.1, 25.0, 24.9, 24.8, 24.9; IR (neat): 2976.1 (m), 2928.2 (m), 1460.9 (w), 1370.1 (m), 1348.7 (m), 1303.3 (s), 1262.4 (m), 1136.0 (s), 968.6 (m), 846.5 (m) cm^{-1} ; HRMS-(DART) for: $\text{C}_{24}\text{H}_{47}\text{B}_3\text{Cl}_1\text{O}_6$ $[\text{M}+\text{H}]^+$: calculated: 499.3340, found: 499.3344. $[\alpha]_{\text{D}}^{20} = -16.084$ ($c = 0.470$, CHCl_3 , $l = 50$ mm).

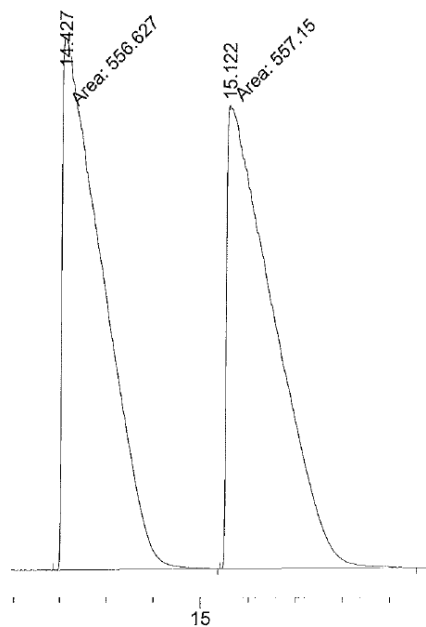
Analysis and Proof of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-2-(6-chlorohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to the general procedure for deborylative cyclization followed by oxidation to give (1*S*,2*S*)-cyclohexane-1,2-diol. Absolute configuration of stereochemistry was assigned by comparing the prepared (1*S*,2*S*)-cyclohexane-1,2-diol with an authentic sample purchased from Fluka.



Chiral GLC (β -dex 225, Supelco, 100 °C for 5 min, ramp 3 °C/min to 160 °C, 20 psi) – analysis of (1S,2S)-cyclohexane-1,2-diol

Racemic Material



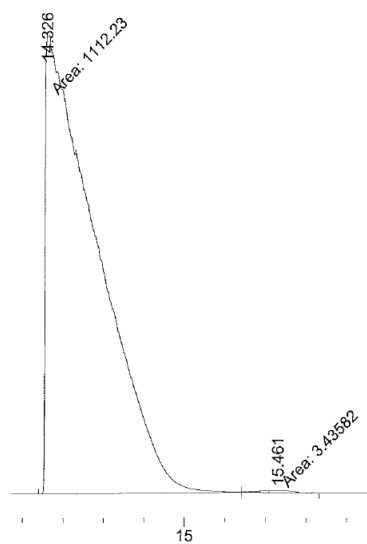
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.427	MM	0.1997	556.62695	46.46300	49.97651
2	15.122	MM	0.2298	557.15027	40.40024	50.02349
Totals :				1113.77722	86.86324	

Standard Conditions

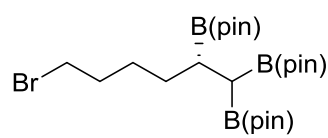


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.327	MM	0.2887	1120.20935	64.67873	94.74193
2	15.404	MM	0.1941	62.17039	5.33910	5.25807

Authentic Material

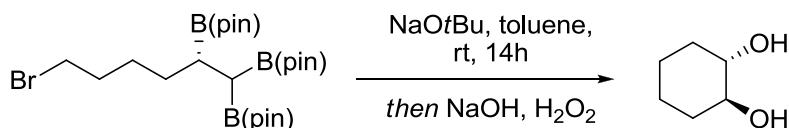


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.326	MM	0.2958	1112.23303	62.67395	99.69204
2	15.461	MM	0.1717	3.43582	3.33552e-1	0.30796
Totals :				1115.66886	63.00751	


(R)-2,2',2''-(6-bromohexane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (7). Prepared according to the general procedure utilizing Pt(dba)₃ (8.1 mg, 0.0090 mmol), (*R,R*)-**L3** (16.4 mg, 0.0180 mmol), B₂(cat)₂ (142.7 mg, 0.6000 mmol), (*E*)-2-(6-bromohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (71.8 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (425.3 mg, 3.600 mmol). The crude material was purified (SiO₂, 5-7% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid, which co-eluted with B₂(pin)₂ (135.1 mg, product: B₂(pin)₂ = 1.00:0.26, 74%). ¹H NMR (500 MHz, CDCl₃): δ 3.38 (2H, t, 6.5 Hz), 1.87-1.76 (2H, m), 1.50-1.30 (5H, m), 1.23-1.18 (36H, m), 0.84 (1H, d, *J*= 10.0 Hz); ¹³C NMR (126 MHz, CDCl₃): δ 82.8, 82.8, 82.7, 34.0, 33.1, 32.3, 27.3, 25.0, 25.0, 24.9, 24.8, 24.7, 24.6; IR (neat): 2976.4 (m), 2930.2 (w), 1461.3 (w), 1369.4 (s), 1347.1 (s), 1304.5 (s), 1267.1 (s), 1213.4 (m), 1137.7 (s), 968.9 (m), 848.8 (m), 644.6 (w), 578.2 (w) cm⁻¹; HRMS-(DART) for: C₂₄H₄₇B₃BrO₆ [M+H]⁺: calculated: 543.2835, found: 543.2855. [α]_D²⁰ = -16.415 (*c* = 2.975, CHCl₃, *l* = 50 mm).

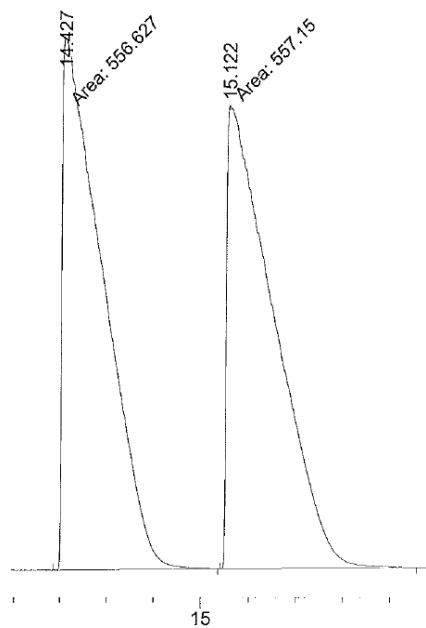
Analysis and Proof of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-2-(6-bromohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane and Pt(dba)₃ as the catalyst. The title compound was subjected to the general procedure for deborylative cyclization followed by oxidation to give (*1S,2S*)-cyclohexane-1,2-diol. Absolute configuration of stereochemistry was assigned by comparing the prepared (*1S,2S*)-cyclohexane-1,2-diol with an authentic sample purchased from Fluka.



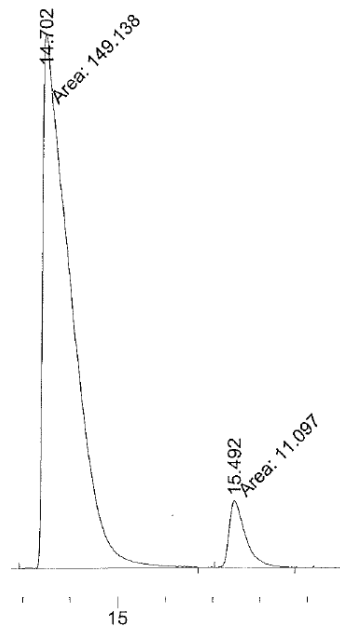
Chiral GLC (β -dex 225, Supelco, 100 °C for 5 min, ramp 3 °C/min to 160 °C, 20 psi) – analysis of (1S,2S)-cyclohexane-1,2-diol

Racemic Material



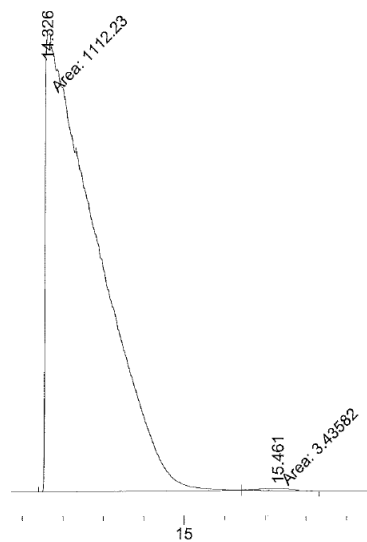
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.427	MM	0.1997	556.62695	46.46300	49.97651
2	15.122	MM	0.2298	557.15027	40.40024	50.02349
Totals :				1113.77722	86.86324	

Standard Conditions

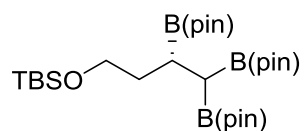


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.702	MM	0.1368	149.13812	18.17207	93.07457
2	15.492	MM	0.0809	11.09697	2.28523	6.92543
Totals :				160.23509	20.45730	

Authentic Material



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.326	MM	0.2958	1112.23303	62.67395	99.69204
2	15.461	MM	0.1717	3.43582	3.33552e-1	0.30796
Totals :				1115.66886	63.00751	



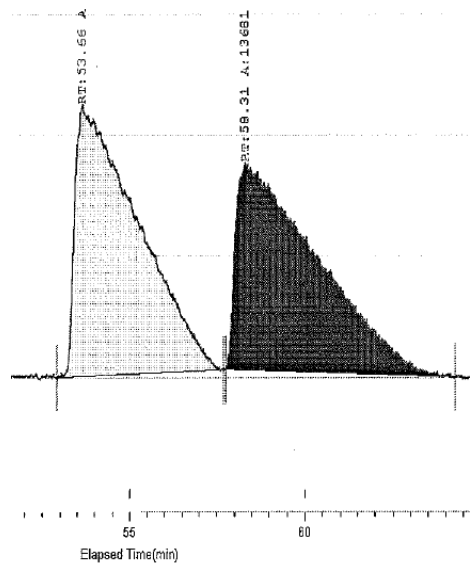
(*R*)-tert-butyltrimethylsilyloxybutylboronic acid pinacol ester (8). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), (*R,R*)-**L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (85.6 mg, 0.360 mmol), (*E*)-4-(*tert*-butyltrimethylsilyloxy)-1-butene-1-ylboronic acid pinacol ester (93.7 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (255.2 mg, 2.160 mmol). The crude material was purified (SiO_2 , 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (135.4 mg, 80%). ^1H NMR (500 MHz, CDCl_3): δ 3.63 (1H, dt, $J=6.0, 10.5$ Hz), 3.53 (1H, dt, $J=6.0, 10.5$ Hz), 1.76-1.69 (1H, m), 1.65-1.59 (1H, m), 1.32-1.18 (37H, m), 0.86 (9H, s), 0.80 (1H, d, $J=8.5$ Hz), 0.02 (6H, s); ^{13}C NMR (126 MHz, CDCl_3): δ 82.7, 82.7, 82.7, 63.2, 36.4, 26.1, 25.1, 25.0, 24.9, 24.7, 24.7, 24.6, 18.4, -5.1; IR (neat): 2976.8 (m), 2929.5 (m), 2857.2 (w), 1470.1 (w), 1369.6 (s), 1347.5 (s), 1305.9 (s), 1256.4 (m), 1214.7 (m), 1138.8 (s), 1091.2 (s), 1005.4 (m), 846.5 (s), 835.0 (s), 775.0 (m), 668.7 (w), 578.1 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{28}\text{H}_{58}\text{B}_3\text{O}_7\text{Si}$ $[\text{M}+\text{H}]^+$: calculated: 567.4231, found: 567.4257. $[\alpha]_{\text{D}}^{20} = -11.340$ ($c = 2.155$, CHCl_3 , $l = 50$ mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-4-(*tert*-butyltrimethylsilyloxy)-1-butene-1-ylboronic acid pinacol ester and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to the general procedure for deborylative alkylation with (3-bromopropyl)benzene followed by oxidation to give (3*S*,4*S*)-1-((*tert*-butyltrimethylsilyloxy)-7-phenylheptane-3,4-diol. Further analysis of stereochemistry was performed on (3*S*,4*S*)-1-((*tert*-butyltrimethylsilyloxy)-7-phenylheptane-3,4-diol. Absolute stereochemistry was assigned by analogy (see product **6** and **7**).

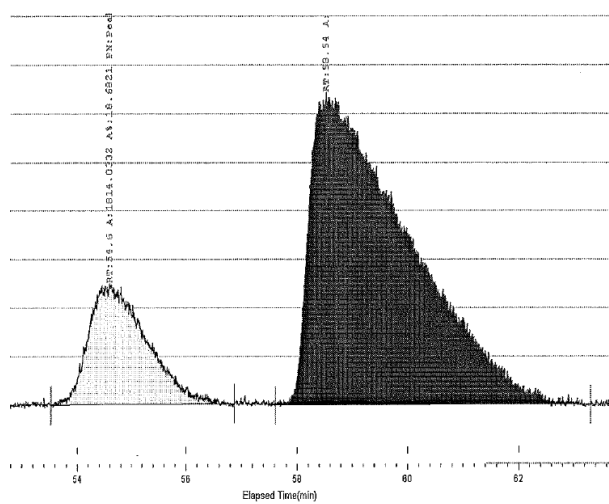
Chiral SFC (Chiracel OD-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (3*S*,4*S*)-1-((*tert*-butyldimethylsilyl)oxy)-7-phenylheptane-3,4-diol

Racemic Material

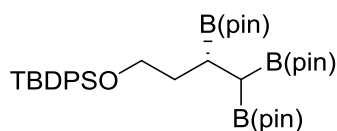


Peak No	% Area	Area	RT (min)
1	50.5769	14000.6213	53.66
2	49.4231	13681.2508	58.31
Total:	100	27681.8721	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	18.6821	1814.0332	54.6
2	81.3179	7895.9517	58.54
Total:	100	9709.9849	



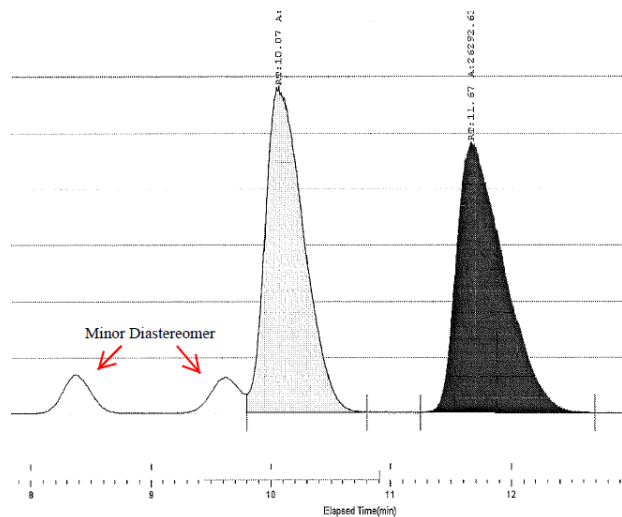
(R)-tert-butylidiphenyl(3,4,4-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butoxy)silane (9). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), **(R,R)-L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (142.7 mg, 0.6000 mmol), (*E*)-tert-butylidiphenyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)oxy)silane (130.9 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (425.3 mg, 3.600 mmol). The crude material was purified (SiO_2 , 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid, which co-eluted with $\text{B}_2(\text{pin})_2$ (203.1 mg, product: $\text{B}_2(\text{pin})_2 = 1.0:0.66$, 79%). ^1H NMR (500 MHz, CDCl_3): δ 7.66 (4H, dd, $J = 7.5, 1.5$ Hz), 7.39-7.32 (6H, m), 3.71 (1H, dt, $J = 5.5, 10.0$ Hz), 3.63 (1H, dt, $J = 6.0, 9.5$ Hz), 1.89-1.76 (2H, m), 1.40-1.33 (1H, m), 1.21 (12H, s), 1.19 (12H, s), 1.13 (6H, s), 1.12 (6H, s), 1.02 (9H, s), 0.81 (1H, d, $J = 8.5$ Hz); ^{13}C NMR (126 MHz, CDCl_3): δ 135.5, 135.5, 129.2, 127.4, 82.7, 82.7, 82.7, 63.8, 36.1, 25.0, 24.9, 24.9, 24.7, 24.7, 24.6, 19.2; IR (neat): 2977.0 (m), 2930.9 (m), 2858.0 (w), 1469.3 (w), 1348.4 (s), 1308.7 (s), 1279.6 (s), 1213.6 (w), 1139.7 (s), 1124.4 (s), 1109.7 (s), 969.2 (m), 849.0 (m), 742.3 (w), 703.1 (m), 578.7 (w), 505.6 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{38}\text{H}_{62}\text{B}_3\text{O}_7\text{Si}$ $[\text{M}+\text{H}]^+$: calculated: 691.4544, found: 691.4555. $[\alpha]_{\text{D}}^{20} = -7.697$ ($c = 1.190$, CHCl_3 , $l = 50$ mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing), (*E*)-tert-butylidiphenyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)oxy)silane and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to the general procedure for deborylative alkylation with (3-bromopropyl)benzene followed by oxidation to give (3*S*,4*S*)-1-((tert-butylidiphenylsilyl)oxy)-7-phenylheptane-3,4-diol. Further analysis of stereochemistry was performed on (3*S*,4*S*)-1-((tert-butylidiphenylsilyl)oxy)-7-phenylheptane-3,4-diol. Absolute stereochemistry was assigned by analogy (see product **6** and **7**).

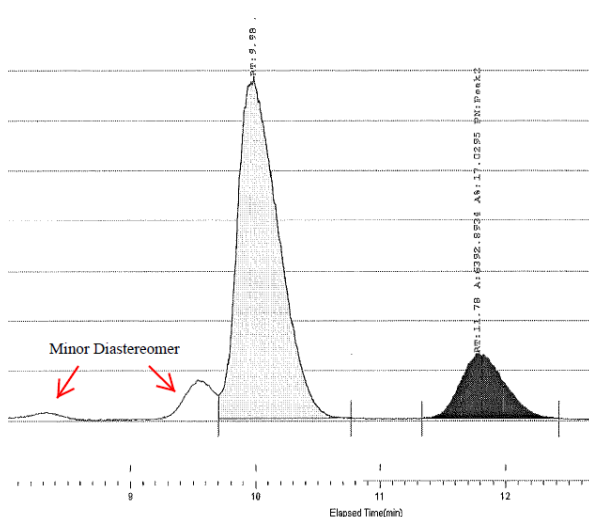
Chiral SFC (Chiracel OD-H, 20% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (3S,4S)-1-((tert-butyl-diphenylsilyl)oxy)-7-phenylheptane-3,4-diol

Racemic Material

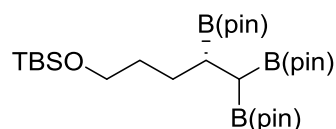


Peak No	% Area	Area	RT (min)
1	49.4598	25730.5679	10.07
2	50.5402	26292.634	11.67
Total:	100	52023.2019	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	82.9705	31147.197	9.98
2	17.0295	6392.8934	11.78
Total:	100	37540.0904	



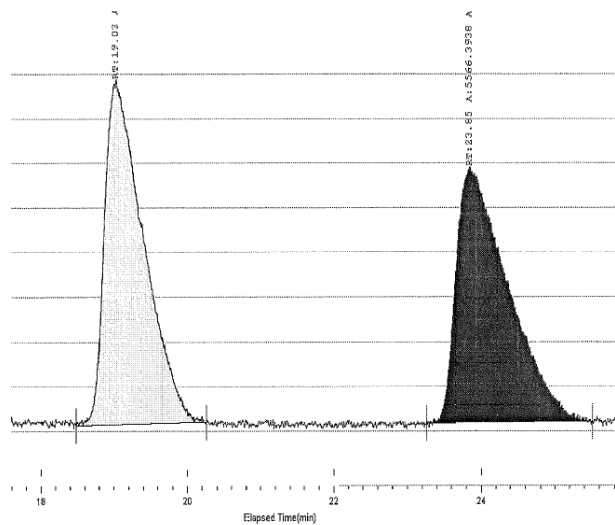
(*R*)-tert-butyl dimethyl((4,5,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)oxy)silane (10). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), (*R,R*)-**L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (85.6 mg, 0.360 mmol), (*E*)-tert-butyl dimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)silane (97.9 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (255.2 mg, 2.160 mmol). The crude material was purified (SiO_2 , 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (123.6 mg, 71%). ^1H NMR (500 MHz, CDCl_3): δ 3.56 (2H, t, $J=7.0$ Hz), 1.62-1.54 (1H, m), 1.49-1.30 (4H, m), 1.21 (18H, s, overlap), 1.21 (18H, s, overlap), 0.87 (9H, s), 0.88-0.86 (1H, overlaps), 0.02 (6H, s); ^{13}C NMR (126 MHz, CDCl_3): δ 82.7, 82.7, 64.1, 32.3, 29.6, 26.0, 25.0, 24.9, 24.8, 24.6, 24.6, 24.6, 18.4, -5.2; IR (neat): 2976.8 (m), 2929.5 (m), 2857.1 (w), 1470.4 (w), 1369.7 (s), 1345.8 (s), 1308.6 (s), 1266.0 (m), 1214.4 (m), 1140.3 (s), 1100.5 (m), 1005.4 (w), 969.8 (m), 836.0 (s), 775.1 (m), 669.3 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{29}\text{H}_{60}\text{B}_3\text{O}_7\text{Si}$ $[\text{M}+\text{H}]^+$: calculated: 581.4388, found: 581.4391. $[\alpha]_{\text{D}}^{20} = -15.094$ ($c = 1.060$, CHCl_3 , $l = 50$ mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing), (*E*)-tert-butyl dimethyl((5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)oxy)silane and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to the general procedure for deborylative alkylation with (3-bromopropyl)benzene followed by oxidation to give (4*S*,5*S*)-1-((tert-butyl dimethylsilyl)oxy)-8-phenyloctane-4,5-diol. Further analysis of stereochemistry was performed on (4*S*,5*S*)-1-((tert-butyl dimethylsilyl)oxy)-8-phenyloctane-4,5-diol. Absolute stereochemistry was assigned by analogy (see product **6** and **7**).

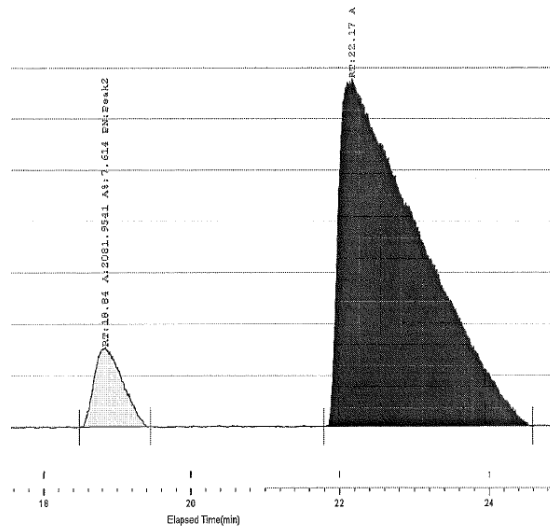
Chiral SFC (Chiracel OD-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (4*S*,5*S*)-1-((*tert*-butyldimethylsilyl)oxy)-8-phenyloctane-4,5-diol

Racemic Material

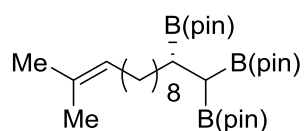


Peak No	% Area	Area	RT (min)
1	50.5133	5681.8675	19.03
2	49.4867	5566.3938	23.85
Total:	100	11248.2613	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	7.614	2081.9541	18.84
2	92.386	25261.846	22.17
Total:	100	27343.8001	



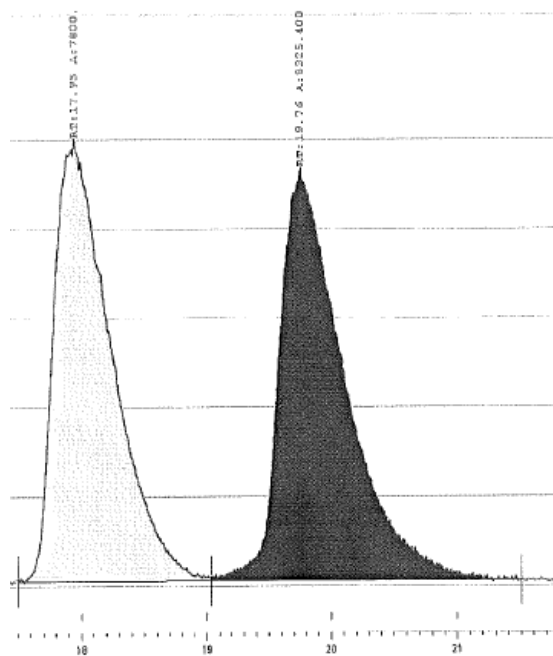
(R)-2,2',2''-(12-methyltridec-11-ene-1,1,2-triyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (11). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), **(R,R)-L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (142.7 mg, 0.600 mmol), (*E*)-4,4,5,5-tetramethyl-2-(12-methyltrideca-1,11-dien-1-yl)-1,3,2-dioxaborolane (96.1 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (425.3 mg, 3.600 mmol). The crude material was purified (SiO_2 , 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear colorless oil (118.3 mg, 69%). ^1H NMR (500 MHz, CDCl_3): δ 5.08 (1H, tt, $J= 7.0, 1.5$ Hz), 1.93-1.89 (2H, m), 1.66 (3H, s), 1.57 (3H, s), 1.40-1.17 (52H, m), 0.84 (1H, d, $J= 8.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 131.2, 125.2, 82.9, 82.9, 82.8, 33.6, 30.2, 30.1, 29.7, 29.6, 28.8, 28.3, 25.9, 25.2, 25.1, 25.0, 24.9, 24.8, 24.7, 17.8; IR (neat): 2976.6 (m), 2924.5 (m), 2854.1 (m), 1462.4 (m), 1369.5 (m), 1345.6 (s), 1306.2 (m), 1139.3 (s), 849.3 (m), 756.2 (m) cm^{-1} ; HRMS-(DART) for: $\text{C}_{32}\text{H}_{63}\text{B}_3\text{O}_6$ $[\text{M}+\text{H}]^+$: calculated: 575.4826, found: 575.4853. $[\alpha]_{\text{D}}^{20} = -16.084$ ($c = 0.470$, CHCl_3 , $l = 50$ mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-4,4,5,5-tetramethyl-2-(12-methyltrideca-1,11-dien-1-yl)-1,3,2-dioxaborolane and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to the general procedure for deborylative alkylation with (3-bromopropyl)benzene followed by oxidation to give (4*S*,5*S*)-15-methyl-1-phenylhexadec-14-ene-4,5-diol. Further analysis of stereochemistry was performed on (4*S*,5*S*)-15-methyl-1-phenylhexadec-14-ene-4,5-diol. Absolute stereochemistry was assigned by analogy (see product **6** and **7**).

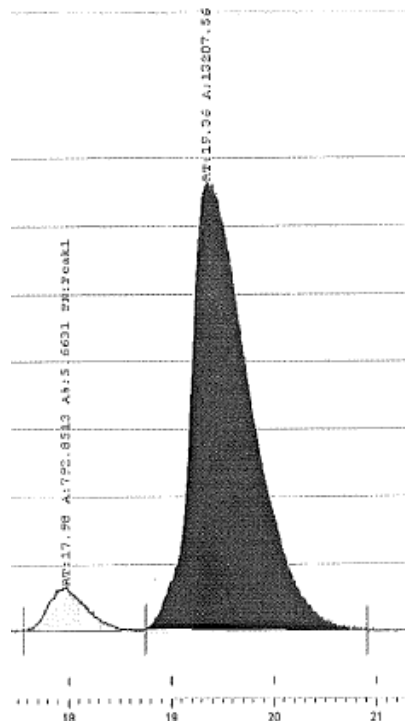
Chiral SFC (Chiracel AD-H, 10% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (4*S*,5*S*)-15-methyl-1-phenylhexadec-14-ene-4,5-diol.

Racemic Material

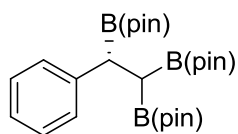


Peak No	% Area	Area	RT (min)
1	48.3725	7800.5002	17.95
2	51.6275	8325.4009	19.76
Total:	100	16125.9011	

Standard Conditions



Peak No	% Area	Area	RT (min)
1	5.6631	792.8513	17.98
2	94.3369	13207.5682	19.36
Total:	100	14000.4195	



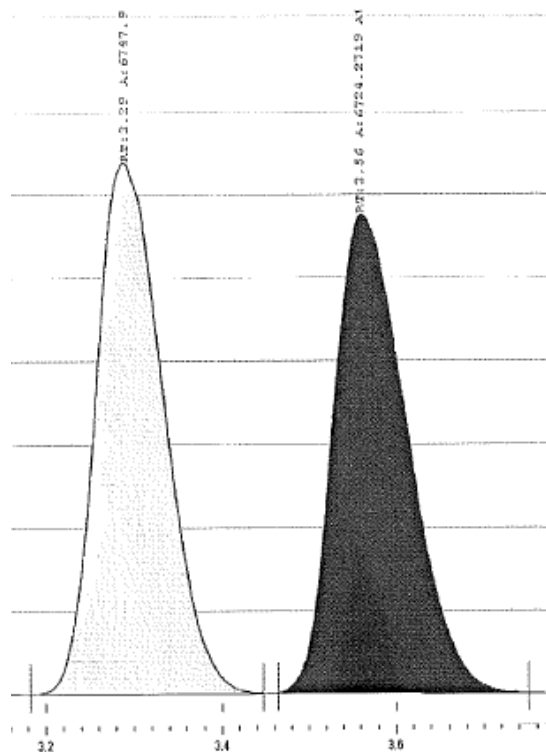
(R)-2,2',2''-(2-phenylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (12). Prepared according to the general procedure utilizing $\text{Pt}(\text{dba})_3$ (8.1 mg, 0.0090 mmol), **(R,R)-L3** (16.4 mg, 0.0180 mmol), $\text{B}_2(\text{cat})_2$ (142.7 mg, 0.600 mmol), (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (69.1 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (425.3 mg, 3.600 mmol). The crude material was purified (SiO_2 , 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (68.7 mg, 47%). ^1H NMR (500 MHz, CDCl_3): δ 7.19-7.12 (4H, m), 7.02-6.99 (1H, m), 2.64 (1H, d, $J=12.5$ Hz), 1.42 (1H, d, $J=12.5$ Hz), 1.21 (6H, s), 1.20 (6H, s), 1.13 (6H, s), 1.11 (6H, s), 0.92 (6H, s), 0.90 (6H, s); ^{13}C NMR (100 MHz, CDCl_3): δ 145.5, 128.7, 128.0, 124.8, 83.2, 83.2, 82.8, 25.0, 24.8, 24.6, 24.5, 24.4; IR (neat): 2978.3 (m), 1370.2 (m), 1309.1 (s), 1263.8 (m), 1214.3 (w), 1137.7 (s), 968.0 (m), 908.3 (m), 846.5 (m), 739.4 (s), 668.9 (m) cm^{-1} ; HRMS-(DART) for: $\text{C}_{26}\text{H}_{44}\text{B}_3\text{O}_6$ $[\text{M}+\text{H}]^+$: calculated: 485.3417, found: 485.3431. $[\alpha]_{\text{D}}^{20} = -9.267$ ($c = 0.650$, CHCl_3 , $l = 50$ mm).

Analysis of stereochemistry:

Racemic compound was prepared according to the general procedure for racemic vinyl boronate diboration utilizing (*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane and $\text{Pt}(\text{dba})_3$ as the catalyst. The title compound was subjected to protodeboronation to give (*R*)-2,2'-(1-phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). Further analysis of stereochemistry was performed on (*R*)-2,2'-(1-phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). Absolute stereochemistry was assigned by analogy (see product **6** and **7**).

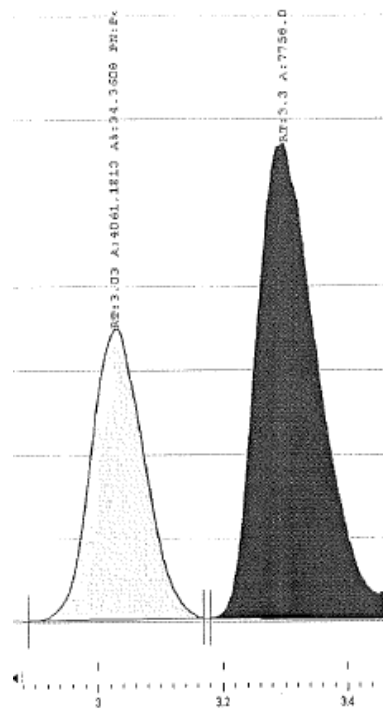
Chiral SFC (Chiracel OD-H, 3% IPA, 3 mL/min, 100 bar, 35 °C, 210-270 nm) – analysis of (R)-2,2'-(1-phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

Racemic Material

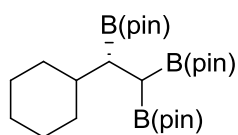


Peak No	% Area	Area	RT (min)
1	50.088	6747.9698	3.29
2	49.912	6724.2719	3.56
Total:	100	13472.2417	

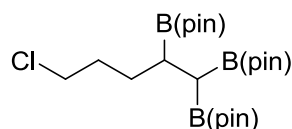
Standard Conditions



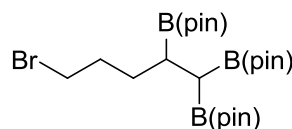
Peak No	% Area	Area	RT (min)
1	34.3608	4061.1813	3.03
2	65.6392	7758.0581	3.3
Total:	100	11819.2394	



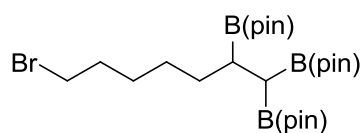
(R)-2,2',2''-(2-cyclohexylethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (13). Prepared according to the general procedure utilizing Pt(dba)₃ (8.1 mg, 0.0090 mmol), **(R,R)-L3** (16.4 mg, 0.0180 mmol), B₂(cat)₂ (142.7 mg, 0.600 mmol), (*E*)-2-(2-cyclohexylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70.8 mg, 0.300 mmol), and THF (0.30 mL), followed by pinacol (425.3 mg, 3.600 mmol). The crude material was purified (SiO₂, 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (24.3 mg, 17%). ¹H NMR (500 MHz, CDCl₃): δ 1.78-1.57 (5H, m), 1.35-1.30 (2H, m), 1.27-1.02 (42H, m), 0.85-0.79 (1H, m); ¹³C NMR (100 MHz, CDCl₃): δ 82.9, 82.8, 82.8, 42.6, 33.9, 30.6, 27.4, 27.3, 27.1, 25.5, 25.3, 25.0, 24.9, 24.8, 24.6; IR (neat): 3026.4 (w), 2925.1 (m), 2858.3 (m), 1495.6 (m), 1453.9 (m), 1099.6 (m), 1063.4 (m), 1030.9 (m), 747.3 (m), 699.2 (s) cm⁻¹; HRMS-(DART) for: C₂₆H₅₀B₃O₆ [M+H]⁺: calculated: 491.3887, found: 491.3905.



racemic-2,2',2''-(5-chloropentane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S15). Prepared according to the general procedure for racemic vinyl boronate diboration utilizing Pt(dba)₃ (26.9 mg, 0.030 mmol), B₂(pin)₂ (799.9 mg, 3.150 mmol), (*E*)-2-(5-chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (691.6 mg, 3.000 mmol), and THF (3.00 mL). The crude material was purified (SiO₂, 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (767.1mg, 58%). ¹H NMR (500 MHz, CDCl₃): δ 3.50 (2H, t, *J*= 7.0Hz), 1.87-1.80 (1H, m), 1.74-1.67 (1H, m), 1.59-1.51 (2H, m), 1.37-1.32 (1H, m), 1.26-1.21 (36H, m), 0.84 (1H, d, *J*= 10.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 83.0, 83.0, 45.9, 32.3, 30.9, 25.2, 25.1, 25.1, 25.0, 24.9, 24.8; IR (neat): 2976.9 (m), 1370.1 (m), 1347.4 (m), 1307.4 (s), 1264.8 (m), 1164.5 (m), 1137.1 (s), 1108.0 (m), 847.4 (m), 699.1 (m) cm⁻¹; HRMS-(DART) for: C₂₃H₄₅B₃Cl₁O₆ [M+H]⁺: calculated: 485.3184, found: 485.3181.



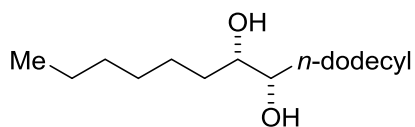
racemic-2,2',2''-(5-bromopentane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S16). Prepared according to the general procedure for racemic vinyl boronate diboration utilizing Pt(dba)₃ (26.9 mg, 0.030 mmol), B₂(pin)₂ (799.9 mg, 3.150 mmol), (*E*)-2-(5-bromopent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (824.9 mg, 3.000 mmol), and THF (3.00 mL). The crude material was purified (SiO₂, 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (528.9 mg, 36%). ¹H NMR (500 MHz, CDCl₃): δ 3.35 (2H, t, *J*= 7.5 Hz), 1.94-1.87 (1H, m), 1.81-1.74 (1H, m), 1.54-1.49 (2H, m), 1.35-1.30 (1H, m), 1.23-1.18 (36H, m), 0.81 (1H, d, *J*= 10.0 Hz); ¹³C NMR (100 MHz, CDCl₃): δ 83.0, 83.0, 45.8, 32.5, 32.2, 25.2, 25.2, 25.1, 25.0, 24.9, 24.8; IR (neat): 2976.6 (m), 1369.5 (m), 1346.5 (m), 1306.5 (s), 1263.8 (m), 1213.5 (m), 1137.3 (s), 968.6 (m), 847.8 (m) cm⁻¹; HRMS-(DART) for: C₂₃H₄₅B₃Br₁O₆ [M+H]⁺: calculated: 529.2679, found: 529.2669.



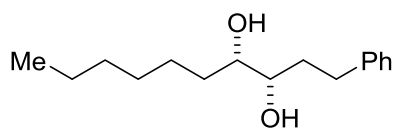
racemic-2,2',2''-(7-bromoheptane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (S17). Prepared according to the general procedure for racemic vinyl boronate diboration utilizing $\text{Pt}(\text{dba})_3$ (26.9 mg, 0.030 mmol), $\text{B}_2(\text{pin})_2$ (799.9 mg, 3.150 mmol), (*E*)-2-(7-bromohept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (909.1 mg, 3.000 mmol), and THF (3.00 mL). The crude material was purified (SiO_2 , 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (1.027g, 60%). ^1H NMR (500 MHz, CDCl_3): δ 3.36 (2H, t, $J = 7.5$ Hz), 1.81 (2H, pent, $J = 7.0$ Hz), 1.42-1.31 (7H, m), 1.19-1.18 (36H, m), 0.82 (1H, d, $J = 10.5$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ 82.9, 82.9, 34.2, 33.1, 32.9, 28.6, 27.9, 25.2, 25.1, 25.0, 24.9, 24.9, 24.8; IR (neat): 2976.5 (m), 2929.4 (m), 1464.7 (w), 1369.5 (m), 1346.0 (m), 1306.2 (s), 1265.9 (m), 1139.2 (s), 1108.1 (m), 969.2 (m), 848.6 (m) cm^{-1} ; HRMS-(DART) for: $\text{C}_{25}\text{H}_{49}\text{B}_3\text{Br}_1\text{O}_6$ $[\text{M}+\text{H}]^+$: calculated: 557.2992, found: 557.3019.

(VI) Characterization and proof of stereochemistry of deborylative alkylation products

Note: For analysis of diastereoselective, see ^1H NMR spectra in the Spectral Data section

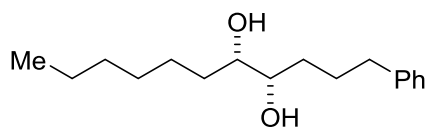


icosane-7,8-diol (15). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), 1-bromododecane (49.8 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO_2 , 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (58.6 mg, 93%). ^1H NMR (500 MHz, CDCl_3): δ (major isomer) 3.44-3.36 (2H, m), 1.98 (2H, br s), 1.52-1.40 (7H, m), 1.38-1.20 (25H, m), 0.90-0.86 (6H, m); ^{13}C NMR (126 MHz, CDCl_3): δ (major isomer) 74.5, 33.6, 31.9, 31.8, 29.7, 29.6, 29.6, 29.6, 29.3, 29.3, 25.7, 25.6, 22.7, 22.6, 14.1, 14.1; IR (neat): 3336.9 (br), 2952.6 (m), 2914.2 (s), 2847.0 (s), 1466.3 (s), 1415.2 (w), 1378.1 (w), 1142.1 (m), 1117.1 (m), 1100.3 (m), 1016.7 (m), 850.4 (w), 720.9 (m), 660.7 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{20}\text{H}_{41}\text{O}$ $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$: calculated: 297.3157, found: 297.3145.

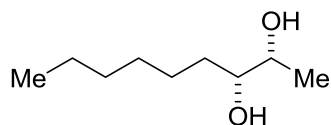


1-phenyldecane-3,4-diol (16). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), (2-bromoethyl)benzene (37.0 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO_2 , 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (60.4 mg, 80%). ^1H NMR (500 MHz, CDCl_3): δ (major isomer) 7.29 (2H, t, $J = 8.0$ Hz), 7.23-7.18 (4H, m), 3.46-3.42 (2H, m), 2.85 (1H, ddd, $J = 14.0, 9.5, 6.0$ Hz), 2.71 (1H, ddd, $J = 14.0, 9.5, 7.0$ Hz), 2.11 (1H, br s), 1.99 (1H, br s), 1.86-1.74 (2H, m), 1.54-1.23 (10H, m), 0.88 (3H, t, $J = 6.5$ Hz); ^{13}C NMR (126 MHz,

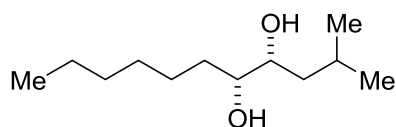
CDCl₃): δ (major isomer) 141.9, 128.4, 125.9, 74.6, 73.8, 35.3, 33.6, 32.0, 31.7, 29.3, 25.5, 22.6, 14.1; IR (neat): 3360.9 (br), 3063.1 (w), 3026.7 (w), 2926.9 (s), 2856.5 (s), 1603.5 (w), 1496.1 (m), 1176.7 (w), 1130.5 (s), 925.5 (w), 747.4 (m), 724.3 (s) cm⁻¹; HRMS-(DART) for: C₁₆H₂₅O [M+H-H₂O]⁺: calculated: 233.1905, found: 233.1904.



1-phenylundecane-4,5-diol (17). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), (3-bromopropyl)benzene (39.8 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO₂, 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (41.8 mg, 79%). ¹H NMR (500 MHz, CDCl₃): δ (major isomer) 7.32-7.29 (2H, m), 7.22 (2H, d, *J* = 7.0 Hz), 3.48-3.40 (2H, m), 2.73-2.63 (2H, m), 2.05 (1H, br s), 1.98 (1H, br s), 1.91-1.82 (1H, m), 1.79-1.70 (1H, m), 1.63-1.42 (6H, m), 1.37-1.27 (6H, m), 0.92 (3H, t, *J* = 5.0 Hz); ¹³C NMR (126 MHz, CDCl₃): δ (major isomer) 142.2, 128.4, 128.3, 125.8, 74.5, 74.3, 35.8, 33.6, 33.2, 31.8, 29.3, 27.4, 25.6, 22.6, 14.1; IR (neat): 3326.9 (br), 3062.1 (w), 3026.9 (w), 2918.3 (s), 2851.8 (s), 1605.3 (w), 1494.5 (m), 1456.4 (m), 1334.5 (m), 1286.4 (m), 1226.0 (w), 1067.1 (m), 1019.7 (m), 938.4 (w), 854.6 (m), 746.3 (s), 719.5 (s), 695.9 (s), 491.6 (m) cm⁻¹; HRMS-(DART) for: C₁₇H₂₉O₂ [M+H]⁺: calculated: 265.2168, found: 265.2168.



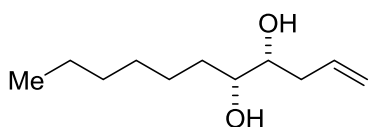
nonane-2,3-diol (18). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), (3-bromopropyl)benzene (39.8 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO₂, 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear, colorless oil (41.8 mg, 79%). All spectral data are in accordance with the literature.¹² HRMS-(DART) for: C₉H₁₉O [M+H-H₂O]⁺: calculated: 143.1436, found: 143.1442.



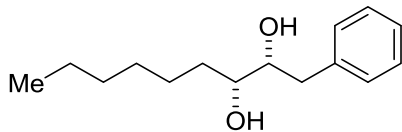
2-methylundecane-4,5-diol (19). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), 1-bromo-2-methylpropane (27.4 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO₂, 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear, colorless oil (34.4 mg, 85%). ¹H NMR (500 MHz, CDCl₃): δ 3.48 (1H, dt, *J* = 9.0, 4.5 Hz), 3.37-3.34 (1H, m), 2.20 (2H, br s), 1.86-1.78 (1H, m), 1.51-1.20 (12H, m), 0.94 (3H, s, *J* = 7.0 Hz), 0.92 (3H, d, *J* = 6.5 Hz), 0.88 (3H, t, *J* = 6.0 Hz); ¹³C NMR (126 MHz, CDCl₃): δ 75.0, 72.5, 42.7, 33.6, 31.8, 29.3, 25.6, 25.0, 23.7, 22.6, 21.7, 14.0; IR

¹² Li, X.; Tanasova, M.; Vasileiou, C.; Borhan, B. *J. Am. Chem. Soc.* **2008**, *130*, 1885.

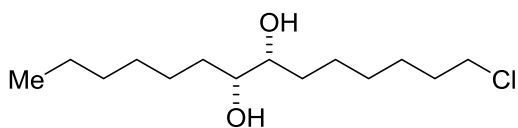
(neat): 3363.2 (br), 2954.8 (s), 2927.4 (s), 2858.6 (s), 1466.9 (m), 1382.9 (w), 1367.2 (w), 1147.6 (w), 1066.5 (m), 843.5 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{12}\text{H}_{25}\text{O}$ $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$: calculated: 185.1905, found: 185.1904.



undec-1-ene-4,5-diol (20). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), allyl chloride (15.3 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO_2 , 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear, colorless oil (34.7 mg, 93%). ^1H NMR (500 MHz, CDCl_3): δ (major isomer) 5.85 (1H, ddt, $J=17.5, 10.5, 7.5$ Hz), 5.17-5.14 (2H, m), 3.51-3.43 (2H, m), 2.38-2.32 (1H, m), 2.26-2.20 (3H, m), 1.53-1.42 (3H, m), 1.37-1.25 (7H, m), 0.87 (3H, t, $J=7.0$ Hz); ^{13}C NMR (126 MHz, CDCl_3): δ (major isomer) 134.5, 118.1, 73.9, 73.3, 38.3, 33.5, 31.8, 29.3, 25.6, 22.6, 14.0; IR (neat): 3376.1 (br), 3077.3 (w), 2954.8 (s), 2926.9 (s), 2857.1 (s), 1641.4 (w), 1458.7 (m), 1433.6 (m), 1285.7 (w), 1128.9 (w), 1062.5 (m), 996.1 (m), 913.1 (m), 870.4 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{11}\text{H}_{23}\text{O}_2$ $[\text{M}+\text{H}]^+$: calculated: 187.1698, found: 187.1692.

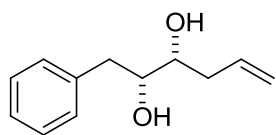


1-phenylnonane-2,3-diol (21). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), benzyl chloride (25.3 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO_2 , 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (42.6 mg, 90%). ^1H NMR (500 MHz, CDCl_3): δ (major isomer) 7.32 (2H, t, $J=8.0$ Hz), 7.26-7.23 (3H, m), 3.68 (1H, dt, $J=8.5, 4.5$ Hz), 3.49 (1H, dt, $J=8.5, 4.5$ Hz), 2.90 (1H, dd, $J=13.5, 4.5$ Hz), 2.75 (1H, dd, $J=13.5, 9.0$ Hz), 2.09 (1H, br s), 1.97 (1H, br s), 1.59-1.23 (10H, m), 0.87 (3H, t, $J=7.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3): δ (major isomer) 138.1, 129.4, 128.6, 126.6, 75.0, 73.6, 40.3, 33.7, 31.8, 29.3, 25.6, 22.6, 14.1; IR (neat): 3379.6 (br), 3062.4 (w), 2953.6 (s), 2925.7 (s), 2856.0 (s), 1603.8 (w), 1495.7 (m), 1454.9 (m), 1179.7 (w), 1128.8 (m), 1060.7 (m), 747.7 (m), 699.3 (s) 514.4 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{15}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$: calculated: 219.1749, found: 219.1751.

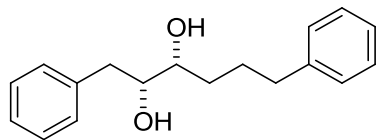


1-chlorotetradecane-7,8-diol (22). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), 1-bromo-6-chlorohexane (39.9 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO_2 , 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (43.0 mg, 81%). ^1H NMR (500 MHz, CDCl_3): δ (major isomer) 3.53 (2H, t, $J=7.0$ Hz), 3.42-3.38 (2H, m), 2.07 (1H, br s), 2.00 (1H, s), 1.78 (2H, dt, $J=14.0, 7.0$ Hz), 1.52-1.25 (18H, m), 0.88 (3H, t,

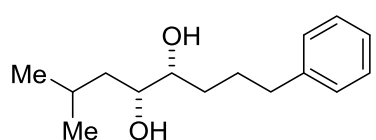
$J=7.0$ Hz); ^{13}C NMR (126 MHz, CDCl_3): δ (major isomer) 74.5, 74.4, 45.1, 33.6, 33.5, 32.5, 31.8, 29.3, 28.9, 26.8, 25.6, 25.5, 22.6, 14.0; IR (neat): 3337.8 (br), 2928.4 (s), 2854.7 (s), 1463.4 (m), 1408.1 (w), 1377.5 (w), 1284.1 (w), 1135.0 (m), 1009.7 (m), 724.8 (m), 652.1 (m) cm^{-1} ; HRMS-(DART) for: $\text{C}_{14}\text{H}_{28}\text{ClO}$ $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$: calculated: 247.1829, found: 247.1820.



1-phenylhex-5-ene-2,3-diol (23). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(3-phenylpropane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (149.4 mg, 0.3000 mmol), allyl chloride (15.3 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO_2 , 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (32.1 mg, 83%). ^1H NMR (500 MHz, CDCl_3): δ (major isomer) 7.33-7.30 (2H, m), 7.25-7.22 (3H, m), 5.85 (1H, ddt, $J=17.5, 10.5, 7.5$ Hz), 5.17-5.13 (2H, m), 3.72 (1H, dt, $J=8.5, 4.0$ Hz), 3.57 (1H, dt, $J=8.5, 4.0$ Hz), 2.90 (1H, dd, $J=14.0, 5.0$ Hz), 2.78 (1H, dd, $J=14.0, 9.0$ Hz), 2.41-2.29 (2H, m), 2.13 (1H, br s), 2.01 (1H, br s); ^{13}C NMR (100 MHz, CDCl_3): δ (major isomer) 138.3, 134.6, 129.6, 128.8, 126.8, 118.4, 74.6, 72.4, 40.4, 38.6; IR (neat): 3377.7 (br), 2919.4 (m), 1495.1 (m), 1454.0 (m), 1434.0 (m), 1077.0 (m), 1041.6 (s), 994.8 (m), 914.0 (s), 868.8 (m), 745.1 (m), 698.2 (s) cm^{-1} ; HRMS-(DART) for: $\text{C}_{12}\text{H}_{15}\text{O}$ $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$: calculated: 175.1123, found: 175.1122. The relative configuration (*syn* diol) was assigned by comparing the ^1H and ^{13}C NMR spectra of the prepared sample of the title compound with the spectra of *syn*-1-phenylhex-5-ene-2,3-diol previously reported in the literature.¹³



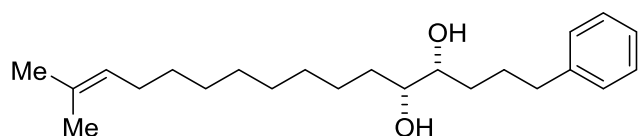
1,6-diphenylhexane-2,3-diol (24). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(3-phenylpropane-1,1,2-triyl) tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (149.4 mg, 0.3000 mmol), (3-bromopropyl)benzene (39.8 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO_2 , 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (46.5 mg, 88%). ^1H NMR (500 MHz, CDCl_3): δ (major isomer) 7.31-7.17 (10H, m), 3.67 (1H, dt, $J=9.0, 4.5$ Hz), 3.50 (1H, dt, $J=8.5, 4.5$ Hz), 2.86 (1H, dd, $J=14.0, 5.0$ Hz), 2.73 (1H, dd, $J=14.0, 9.0$ Hz), 2.70-2.60 (2H, m), 2.04 (2H, br s), 1.89-1.80 (1H, m), 1.76-1.67 (1H, m), 1.64-1.54 (2H, m); ^{13}C NMR (100 MHz, CDCl_3): δ (major isomer) 142.4, 138.2, 129.6, 128.9, 128.6, 128.5, 126.8, 126.0, 75.1, 73.5, 40.4, 36.0, 33.4, 27.6; IR (neat): 3377.7 (br), 2976.8 (m), 2924.6 (m), 1312.7 (m), 1264.9 (s), 1137.9 (s), 969.7 (m), 844.5 (m) cm^{-1} ; HRMS-(DART) for: $\text{C}_{18}\text{H}_{21}\text{O}$ $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$: calculated: 253.1592, found: 253.1587.



7-methyl-1-phenyloctane-4,5-diol (25). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(4-methylpentane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-

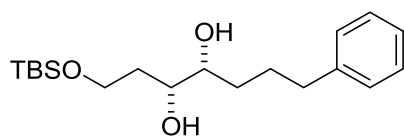
¹³ Jiao, P.; Kaasaki, M.; Yamamoto, H. *Angew. Chem. Int. Ed.* **2009**, *48*, 3333.

1,3,2-dioxaborolane) (139.2 mg, 0.3000 mmol), (3-bromopropyl)benzene (39.8 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO₂, 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (33.6 mg, 71%). ¹H NMR (500 MHz, CDCl₃): δ (major isomer) 7.28-7.25 (2H, m), 7.18-7.15 (3H, m), 3.46 (1H, dt, *J* = 8.5, 4.0 Hz), 3.37 (1H, dt, *J* = 8.5, 4.5 Hz), 2.69-2.58 (2H, m), 2.04 (1H, br s), 1.92(1H, br s), 1.85-1.74 (2H, m), 1.72-1.66 (1H, m), 1.58-1.43 (2H, m), 1.39 (1H, ddd, *J* = 14.5, 10.0, 5.0 Hz), 1.91 (1H, ddd, *J* = 13.0, 9.5, 3.5 Hz), 0.92 (3H, d, *J* = 7.0 Hz), 0.89(3H, d, *J* = 6.5 Hz); ¹³C NMR (100 MHz, CDCl₃): δ (major isomer) 142.4, 128.6, 128.5, 126.0, 75.0, 72.7, 42.9, 36.0, 33.8, 27.6, 24.7, 23.9, 21.9; IR (neat): 3363.5 (br), 2951.6 (m), 2927.7 (m), 2866.8 (m), 1495.9 (m), 1453.4 (m), 1142.1 (m), 1064.1 (m), 1030.3 (m), 746.9 (m), 697.3 (s), 489.6 (m) cm⁻¹; HRMS-(DART) for: C₁₅H₂₃O [M+H-H₂O]⁺: calculated: 219.1749, found: 219.1951.



15-methyl-1-phenylhexadec-14-ene-4,5-diol (26). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(12-methyltridec-11-

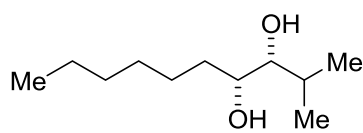
ene-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (172.3 mg, 0.3000 mmol), (3-bromopropyl)benzene (39.8 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO₂, 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid (46.3 mg, 67%). ¹H NMR (500 MHz, CDCl₃): δ (major isomer) 7.27-7.24 (2H, m), 7.17-7.14 (3H, m), 5.10 (1H, tt, *J* = 7.0, 1.5 Hz), 3.43-3.36 (2H, m), 2.68-2.58 (2H, m), 1.94 (2H, q, *J* = 6.5 Hz), 1.85-1.77 (1H, m), 1.72-1.67 (4H, m), 1.65-1.35 (7H, m), 1.30-1.26 (12H, m); ¹³C NMR (100 MHz, CDCl₃): δ (major isomer) 142.4, 131.3, 128.6, 128.5, 126.0, 125.1, 74.7, 74.5, 36.0, 33.8, 33.4, 30.1, 29.8, 29.7, 29.7, 29.5, 28.2, 27.6, 25.9, 25.8, 17.9; IR (neat): 3385.0 (br), 2925.0 (s), 2854.0 (m), 1603.3 (m), 1496.1 (m), 1454.0 (m), 1376.7 (w), 1313.2 (m), 1069.5 (m), 1030.1 (m), 747.9 (m), 698.8 (m), 558.2 (w) cm⁻¹; HRMS-(DART) for: C₂₃H₃₇O [M+H-H₂O]⁺: calculated: 329.2844, found: 329.2846.



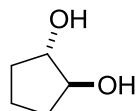
1-((*tert*-butyldimethylsilyloxy)-7-phenylheptane-3,4-diol (27). Prepared according to the general procedure for deborylative alkylation utilizing racemic *tert*-butyldimethyl(3,4,4-tris-(4,4,5,5-tetramethyl-1,3,2-

dioxaborolan-2-yl)butoxy)silane (169.9 mg, 0.3000 mmol), (3-bromopropyl)benzene (39.8 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO₂, 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear, colorless oil (61.2 mg, 94%). Diastereoselectivity was determined by SFC (see spectral data section). ¹H NMR (500 MHz, CDCl₃): δ (major isomer) 7.27 (2H, t, *J* = 7.5 Hz), 7.19-7.16 (3H, m), 3.90-3.82 (2H, m), 3.68 (1H, dt, *J* = 3.0, 7.5 Hz), 3.57 (1H, d, *J* = 7.5 Hz), 3.45 (1H, dt, *J* = 11.0, 5.5 Hz), 2.65 (1H, dt, *J* = 6.5, 8.5 Hz), 2.60 (1H, d, *J* = 5.5 Hz), 1.90-1.63 (4H, m), 1.58-1.51 (2H, m), 0.90 (9H, s), 0.09 (6H, s); ¹³C NMR (126 MHz, CDCl₃): δ (major

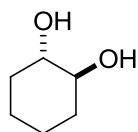
isomer) 142.4, 128.4, 128.3, 125.7, 74.2, 74.1, 62.0, 35.9, 35.1, 33.1, 27.6, 25.8, 18.1, -5.6, -5.6; IR (neat): 3402.9 (br), 3026.6 (w), 2950.8 (s), 2928.2 (s), 2856.8 (s), 1496.3 (w), 1471.0 (m), 1462.1 (m), 1361.2 (w), 1254.3 (s), 1090.6 (br), 1005.9 (m), 938.0 (m), 834.9 (s), 776.8 (s), 747.9 (m), 698.6 (m), 663.6 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{11}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$: calculated: 339.2356, found: 339.2345.



2-methyldecane-3,4-diol (28). Prepared according to the general procedure for deborylative alkylation utilizing racemic 2,2',2''-(octane-1,1,2-triyl)tris-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (147.6 mg, 0.3000 mmol), 2-bromopropane (24.6 mg, 0.200 mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (1.30 mL). The crude material was purified (SiO_2 , 20% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear, colorless oil (28.5 mg, 76%). ^1H NMR (500 MHz, CDCl_3): δ (major isomer) 3.59 (1H, dt, $J= 8.0, 4.5$ Hz), 3.13 (1H, t, $J= 5.0$ Hz), 2.14 (1H, br s), 1.79 (1H, sept, $J= 7.0$ Hz), 1.50-1.25 (10H, m), 0.96 (3H, d, $J= 7.0$ Hz), 0.93 (3H, d, $J= 6.5$ Hz), 0.88 (3H, t, $J= 7.0$ Hz); ^{13}C NMR (126 MHz, CDCl_3): δ (major isomer) 79.0, 71.9, 33.9, 31.8, 30.1, 29.3, 25.6, 22.6, 19.7, 17.0, 14.0; IR (neat): 3378.4 (br), 2956.6 (s), 1926.6 (s), 2871.7 (s), 2857.2 (s), 1466.4 (m), 1383.5 (w), 1366.6 (w), 1176.9 (w), 1063.2 (m), 998.9 (m), 725.5 (w) cm^{-1} ; HRMS-(DART) for: $\text{C}_{11}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$: calculated: 171.1749, found: 171.1751.



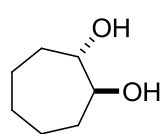
anti-cyclopentane-1,2-diol (29). Prepared according to the general procedure for deborylative cyclization/oxidation utilizing racemic 2,2',2''-(5-chloropentane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (96.9 mg, 0.2000 mmol), or 2,2',2''-(5-bromopentane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (105.8 mg, 0.2000mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (0.87 mL). The crude material was purified (SiO_2 , 50% ethyl acetate in hexane, magic stain) to give the desired product as a white solid (9.0 mg, 44% from chloro-1,1,2-tris(boronate)esters, 7.4 mg, 36% from bromo-1,1,2-tris(boronate)esters). All spectral data are in accordance with the literature.¹⁴ The relative configuration (*anti* diol) was assigned by comparing the ^1H and ^{13}C NMR spectra of the prepared sample of the title compound with the spectra of *anti*-cyclopentane-1,2-diol previously reported in the literature.¹⁴



anti-cyclohexane-1,2-diol (30). Prepared according to the general procedure for deborylative cyclization/oxidation utilizing racemic 2,2',2''-(6-chlorohexane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (99.7 mg, 0.2000 mmol), or 2,2',2''-(6-bromohexane-1,1,2-triyl)tris (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (111.4 mg, 0.2000mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (0.87 mL). The crude material was purified (SiO_2 , 50% ethyl acetate in hexane, magic stain) to give the desired product as a white solid (15.6 mg, 67% from chloro-1,1,2-tris(boronate)esters, 14.4 mg, 62% from bromo-1,1,2-tris(boronate)esters). All spectral data are in accordance with the

¹⁴ Muller, C.E.; Wanka, L.; Jewell, K.; Schreiner, P.R. *Angew. Chem. Int. Ed.* **2008**, *47*, 6180.

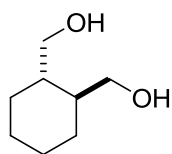
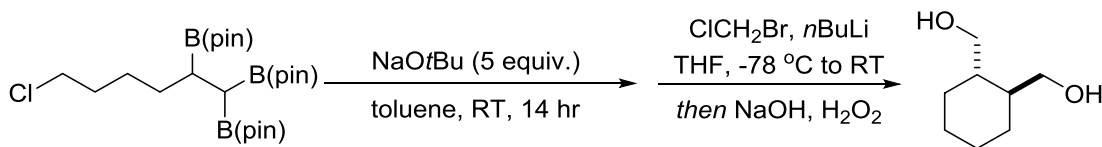
literature.¹⁴ The relative configuration (*anti* diol) was assigned by comparing the ¹H and ¹³C NMR spectra of the prepared sample of the title compound with the spectra of *anti*-cyclohexane-1,2-diol previously reported in the literature.¹⁴



***anti*-cycloheptane-1,2-diol (31).** Prepared according to the general procedure for deborylative cyclization/oxidation utilizing racemic 2,2',2''-(7-bromoheptane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (113.4 mg, 0.2000mmol), sodium *tert*-butoxide (96.1 mg, 1.00 mmol) and toluene (0.87 mL). The crude material was purified (SiO₂, 50% ethyl acetate in hexane, magic stain) to give the desired product as a white solid (15.1 mg, 58%). All spectral data are in accordance with the literature.¹⁴ The relative configuration (*anti* diol) was assigned by comparing the ¹H and ¹³C NMR spectra of the prepared sample of the title compound with the spectra of *anti*-cyclohexane-1,2-diol previously reported in the literature.¹⁴

(VII) Additional transformations of 1,1,2-tris(boronate)esters

Procedure for deborylative cyclization/homologation/oxidation of 2,2',2''-(6-chlorohexane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

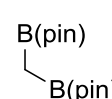


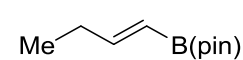
***anti*-cyclohexane-1,2-diyl dimethanol (33).** To an oven-dried 2-dram vial equipped with a magnetic stirbar in the glovebox was added 2,2',2''-(6-chlorohexane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (99.7 mg, 0.2000 mmol) and sodium *tert*-butoxide (96.1 mg, 1.00 mmol), followed by toluene (0.87 mL). The reaction vessel was sealed with a polypropylene cap, taped, and brought out of the glovebox where it was allowed to stir at room temperature for 14 hours. The reaction mixture was pushed through a silica gel plug with diethyl ether, and the obtained crude was used in next step without future purification.

To an oven-dried 2-dram vial equipped with a septum cap was added the crude material followed by THF (2.0 mL), and the flask cooled to 78°C. To the reaction vial was added bromochloromethane (28μL, 0.44 mmol) and *n*-BuLi (0.18 mL, 0.44 mmol), sequentially. After 10 min, the cooling bath was removed and the contents stirred for 12 h. The reaction mixture was then transferred to a 6-dram vial and diluted with THF (2 mL). The crude mixture was cooled to 0 °C and 3M NaOH (1.5 mL) was added, followed by 30% H₂O₂ (1.0 mL), dropwise. The reaction mixture was allowed to warm to room temperature, and was allowed to stir at room temperature for 4 hours. The reaction mixture was cooled to 0 °C and saturated aq. Na₂S₂O₃ (1.5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and the aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers

were dried over Na₂SO₄, filtered, and concentrated under reduced pressure and purified by silica gel chromatography (50% ethyl acetate in hexane) give the desired product as a colorless oil (10.4 mg, 36% yield). All spectral data are in accordance with the literature.¹⁵ The relative configuration (*anti*) was assigned by comparing the ¹H and ¹³C NMR spectra of the prepared sample of the title compound with the spectra of *anti*-cyclohexane-1,2-diylidimethanol previously reported in the literature.¹⁵

(VIII) Procedures for the formal synthesis of *exo*-Brevicomine

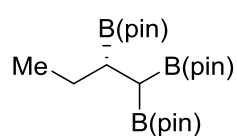
 **4,4,5,5-tetramethyl-2-((4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)methyl)-1,3,2-dioxaborolane (S18).** To an oven-dried 150 mL round-bottomed flask equipped with a stirbar was added copper(I) iodide (571 mg, 3.00 mmol) and lithium methoxide (3.42 g, 90.0 mmol) in the glovebox. The flask was sealed with a septum, brought out of the glovebox, and DMF (40 mL) was added. To the stirring mixture under nitrogen was added a solution of bis(pinacolato)diboron (15.2 g, 60.0 mmol) in DMF (20 mL total, with washings), resulting in a dark black solution. Next, to the stirring solution was added dibromomethane (4.17 mL, 60.0 mmol), dropwise. The reaction mixture was allowed to stir at room temperature for 24 hours, at which point the mixture was diluted with diethyl ether (40 mL) and run through a layer of celite. The resulting solution was concentrated under reduced pressure, and the resulting residue was diluted with hexane (50 mL) and washed with deionized H₂O (3 x 50 mL). The organic layers were combined, dried over sodium sulfate, filtered and concentrated under reduced pressure to provide the title compound as a clear, colorless oil (5.99 g, 75%). No further purification was necessary. All spectral data are in accordance with the literature.¹⁶

 **(*E*)-2-(but-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (34).** To an oven-dried 250 mL round-bottomed flask equipped with a stirbar was added lithium tetramethylpiperidide (LTMP, 2.33 g, 15.8 mmol), and the flask was sealed and brought out of the glovebox. To the reaction flask was added THF (40 mL), and the solution was cooled in an ice bath to 0 °C. Once the solution was cooled, a solution of 4,4,5,5-tetramethyl-2-((4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)methyl)-1,3,2-dioxaborolane (3.85 g, 14.4 mmol) in THF (17 mL) was added dropwise, and the reaction mixture was allowed to stir at 0 °C for 5 minutes. Next, propionaldehyde (1.13 mL, 15.8 mmol) was added dropwise at 0 °C, and the mixture was allowed to stir at this temperature for an additional 3 hours. After completion, the reaction mixture was warmed to room temperature, diluted with diethyl ether (50 mL) and run through a pad of silica gel (100% diethyl ether). The resulting mixture was concentrated under reduced pressure and purified using silica gel column chromatography (2.5% ethyl acetate in hexane) to provide the title compound as a clear, colorless oil as a 97:3 mixture of *E*:*Z* isomers

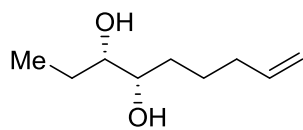
¹⁵ Zhang, X.; Huang, K.; Hou, G.; Cao, B.; Zhang, X. *Angew. Chem.* **2010**, *122*, 6565.

¹⁶ Hong, K.; Liu, X.; Morken, J.P. *J. Am. Chem. Soc.* **2014**, *136*, 10581.

(1.99 g, 76%). All spectral data are in accordance with the literature.¹⁷ Note: The addition of propionaldehyde can also be performed at -78 °C to provide higher *E:Z* ratios (99:1).



(R)-2,2',2''-(butane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (35). Prepared according to the general procedure in a 15 mL pressure vessel utilizing Pt(dba)₃ (80.8 mg, 0.0900 mmol), **(R,R)-L3** (165 mg, 0.1800 mmol), B₂(cat)₂ (1.43 g mg, 6.00 mmol), (*E*)-2-(but-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (546 mg, 3.00 mmol), and THF (3.0 mL), followed by pinacol (4.25 g, 36.0 mmol). The crude material was purified (SiO₂, 5% ethyl acetate in hexane, UV/magic stain) to give the desired product as a white solid, which co-eluted with B₂(pin)₂ (1.46 g, product: B₂(pin)₂ = 1.00:0.75, 77%). ¹H NMR (500 MHz, CDCl₃): δ 3.63 (1H, dt, *J* = 6.0, 10.5 Hz), 3.53 (1H, dt, *J* = 6.0, 10.5 Hz), 1.76-1.69 (1H, m), 1.49-1.38 (2H, m), 1.33-1.16 (37H, m), 0.89-0.85 (4H, m); ¹³C NMR (126 MHz, CDCl₃): δ 82.7, 82.6, 26.0, 25.0, 24.8, 24.8, 24.6, 24.6, 13.2; IR (neat): 2977.2 (m), 2930.6 (w), 1464.5 (w), 1370.3 (s), 1348.3 (s), 1306.6 (s), 1278.7 (s), 1212.6 (w), 1139.2 (s), 1123.7 (s), 969.1 (m), 848.8 (s), 835.0 (s), 668.4 (w), 555.3 (w) cm⁻¹; HRMS-(DART) for: C₂₂H₄₄B₃O₆ [M+H]⁺: calculated: 437.3417, found: 437.3420. [α]_D²⁰ = -14.107 (*c* = 1.015, CHCl₃, *l* = 50 mm).



(3*S*,4*S*)-non-8-ene-3,4-diol (36). Prepared according to the general procedure for deborylative alkylation utilizing (*R*)-2,2',2''-(butane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (218.0 mg, 0.5000 mmol), 5-bromopent-1-ene (62.1 mg, 0.417 mmol), sodium *tert*-butoxide (200 mg, 2.08 mmol) and toluene (2.20 mL). The crude material was purified (SiO₂, 30% ethyl acetate in hexane, UV/magic stain) to give the desired product as a clear, colorless oil, which co-eluted with pinacol (166.6 mg, product:pinacol = 1.00:3.31, 73%). All spectral data are in accordance with the literature.¹⁸ HRMS-(DART) for: C₉H₁₉O₂ [M+H]⁺: calculated: 159.1385, found: 159.1385. [α]_D²⁰ = -16.200 (*c* = 1.695, CHCl₃, *l* = 50 mm).

Analysis of stereochemistry:

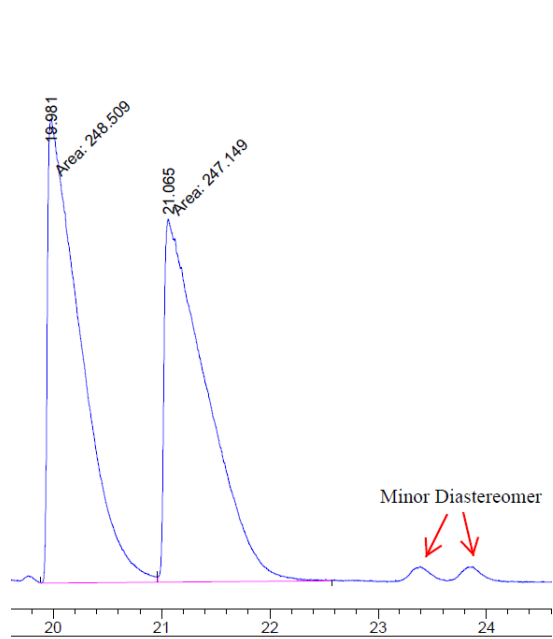
Racemic compound was prepared according to the same procedure utilizing racemic 2,2',2''-(butane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 5-bromopent-1-ene. Further analysis of stereochemistry was performed on non-8-ene-3,4-diol. Absolute stereochemistry was assigned by comparing the specific rotation of the title compound to that of (3*R*,4*R*)-non-8-ene-3,4-diol.¹⁸ Diastereoselectivity was determined by both GLC (14:1 *syn:anti*) and ¹H NMR (16:1 *syn:anti*) analysis (See spectral data section for NMR analysis).

¹⁷ Bruckner, R.; Burghart-Stoll, H. *Org. Lett.* **2011**, *13*, 2730.

¹⁸ Page, P.C.B.; Rayner, C.M.; Sutherland, I.O. *J. Chem.Soc. Perkin Trans. I.* **1990**, *5*, 1375.

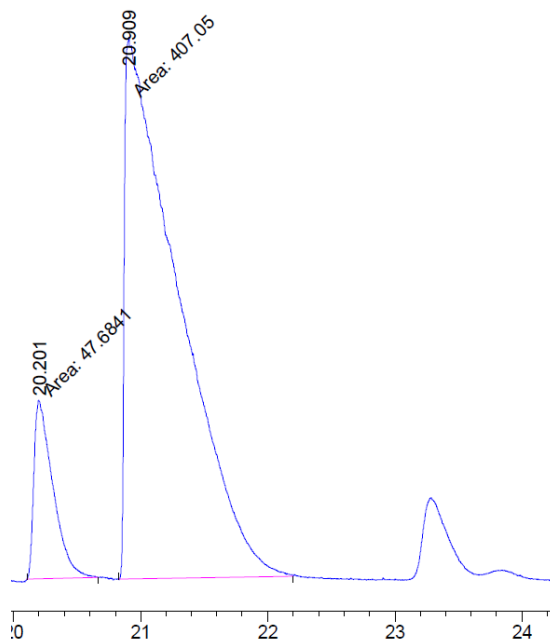
Chiral GLC (β -dex 225, Supelco, 100 °C for 5 min, ramp 3 °C/min to 160 °C, 20 psi) – analysis of (3*S*,4*S*)-non-8-ene-3,4-diol

Racemic Material



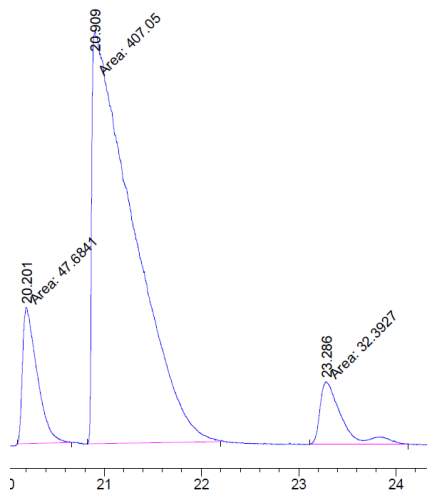
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.981	MF	0.3543	248.50932	11.69048	50.13722
2	21.065	FM	0.4503	247.14902	9.14740	49.86278
Totals :				495.65834	20.83788	

Standard Conditions



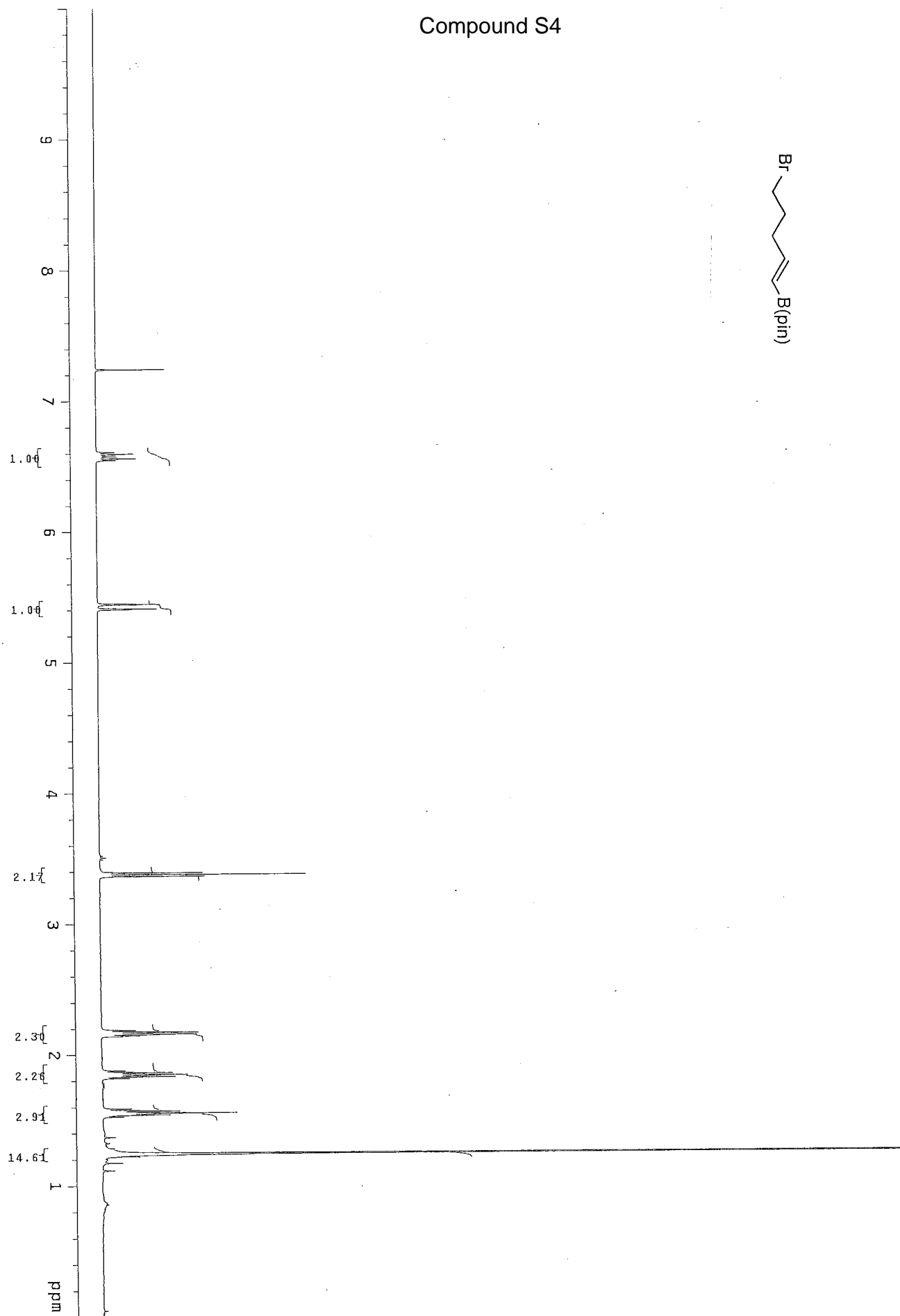
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.201	MM	0.1734	47.68409	4.58331	10.48614
2	20.909	MM	0.4881	407.05023	13.89834	89.51386
Totals :				454.73433	18.48165	

Standard Conditions- Analysis of Diastereoselectivity

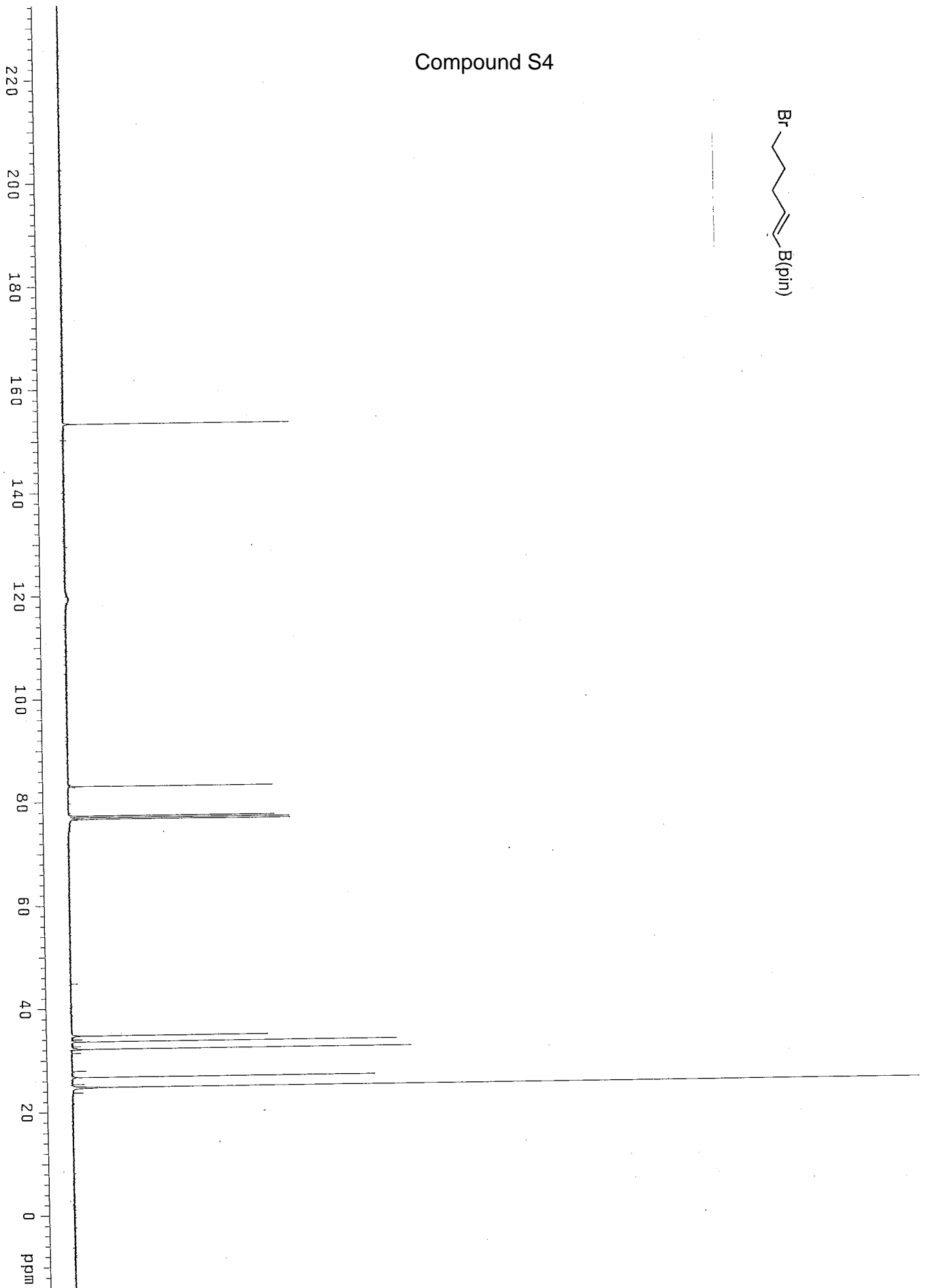


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	20.201	MM	0.1734	47.68409	4.58331	9.78884
2	20.909	MM	0.4881	407.05023	13.89834	83.56141
3	23.286	MM	0.2578	32.39273	2.09410	6.64975
Totals :				487.12706	20.57575	

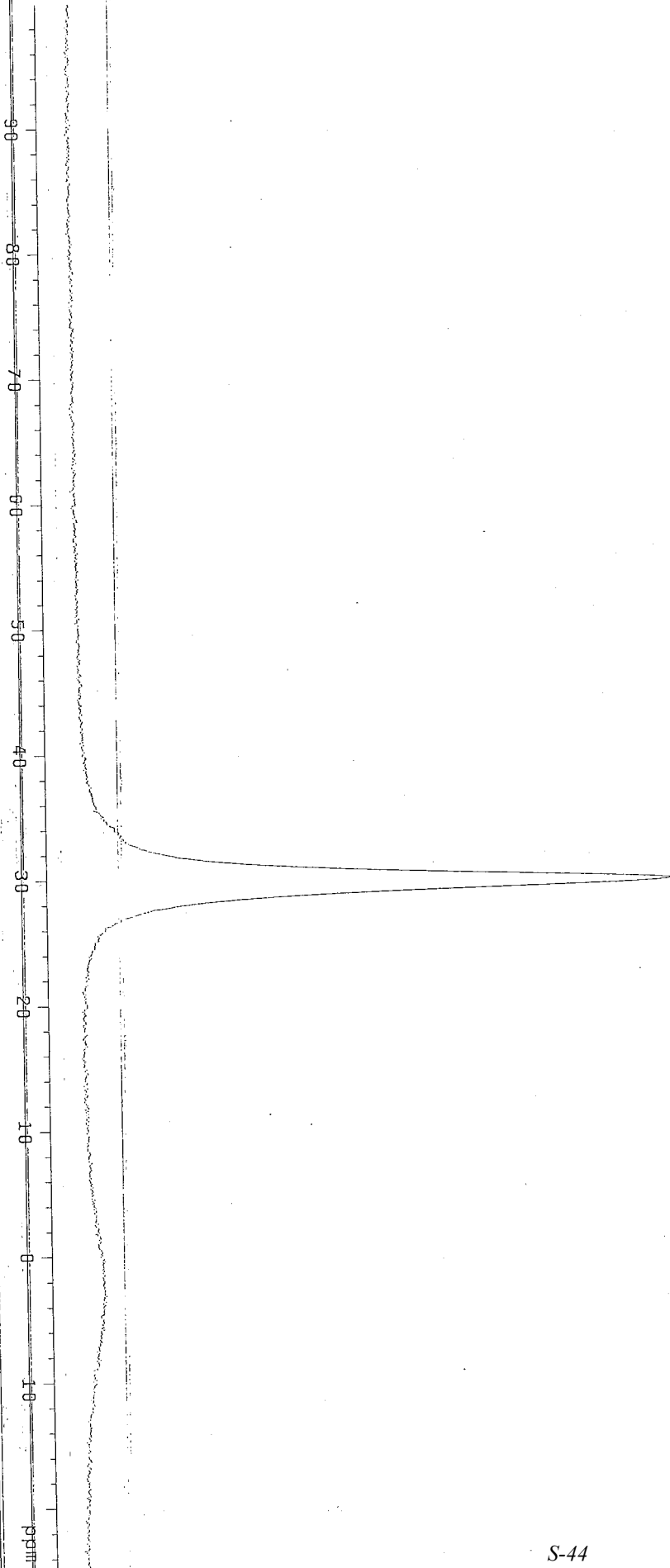
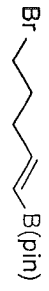
Compound S4



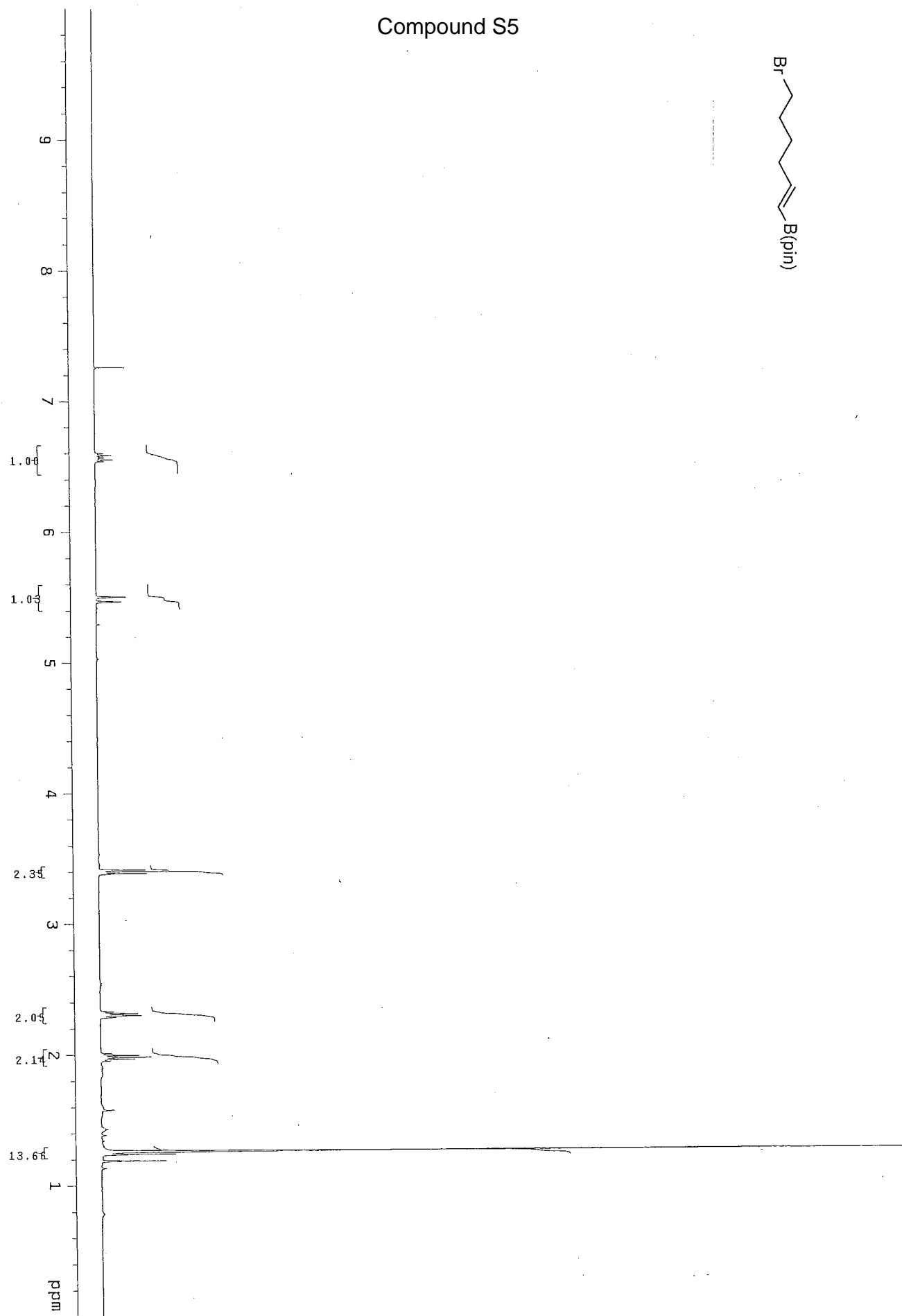
Compound S4



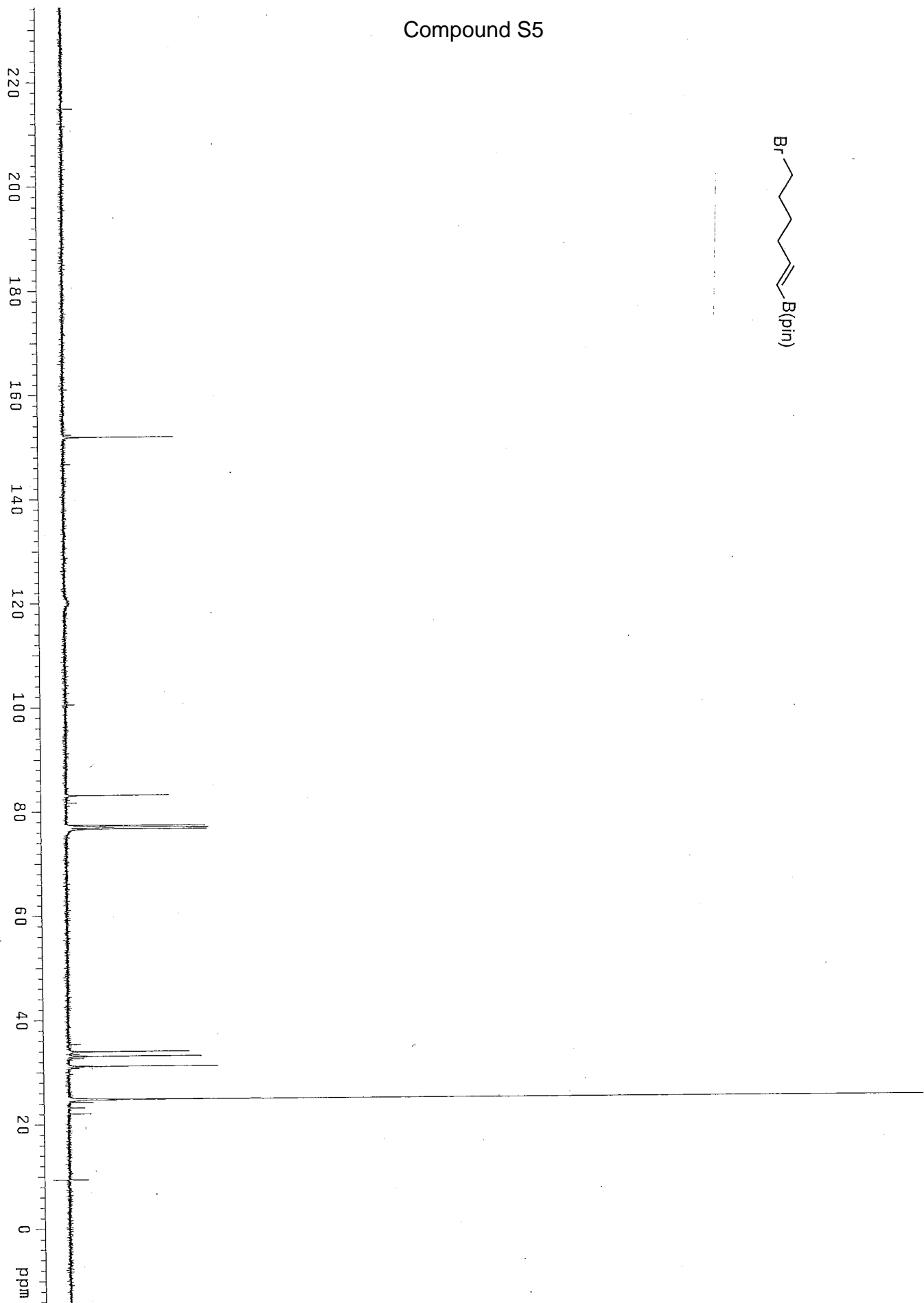
Compound S4



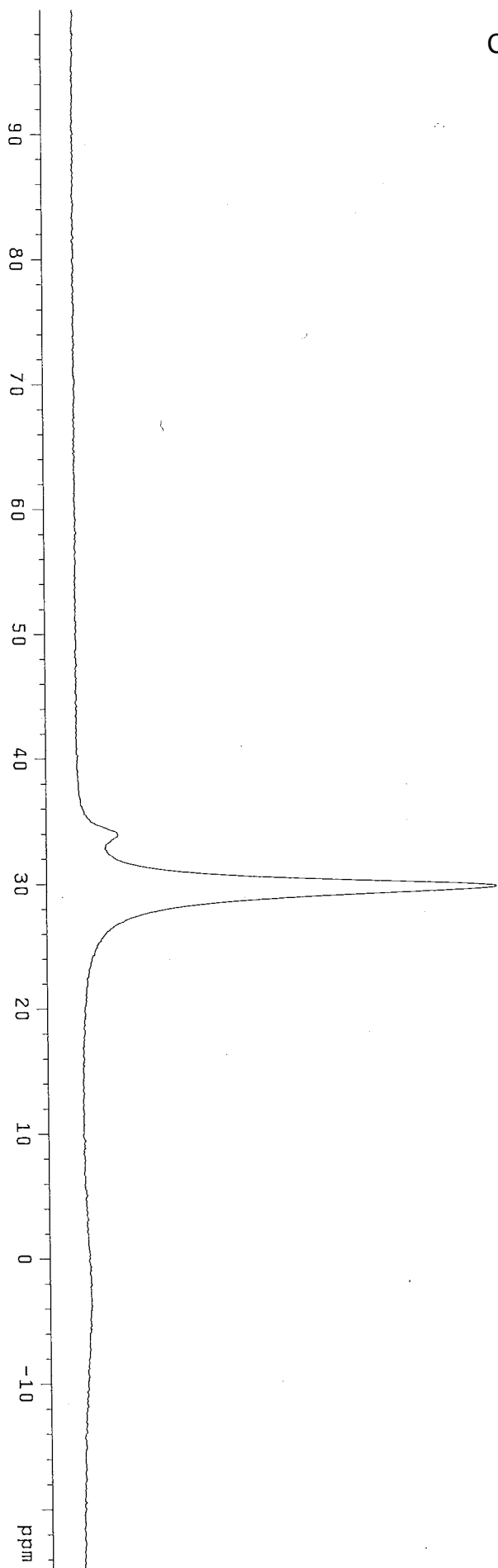
Compound S5



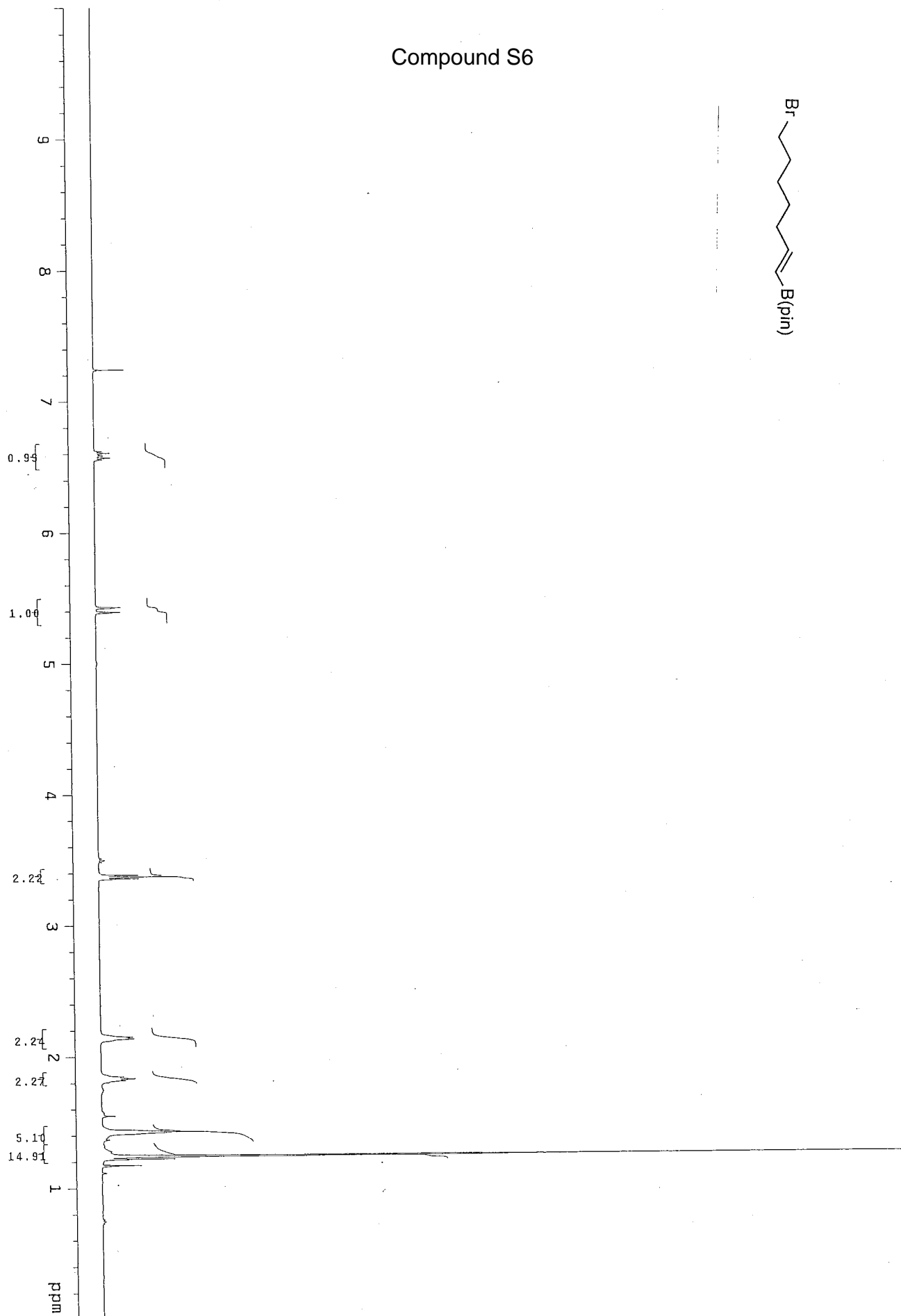
Compound S5



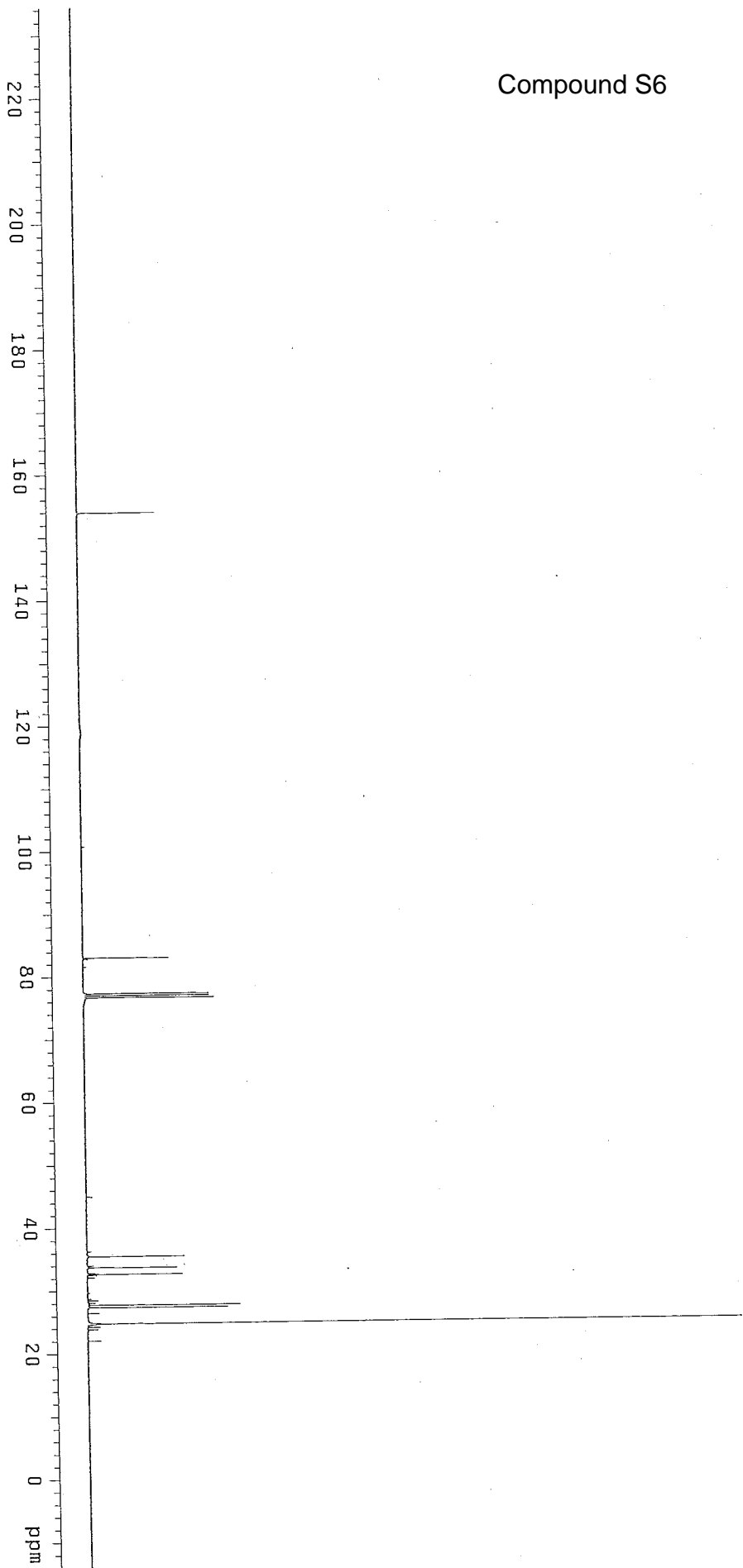
Compound S5



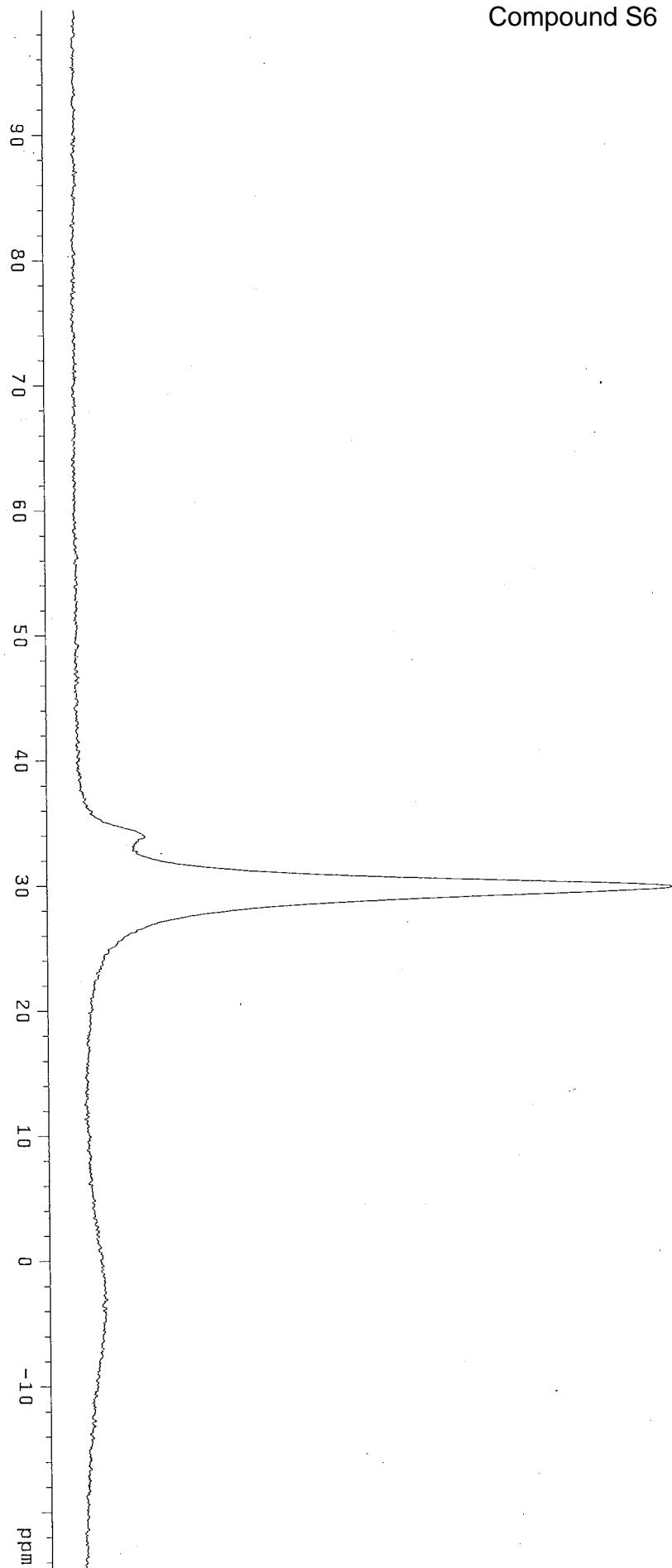
Compound S6



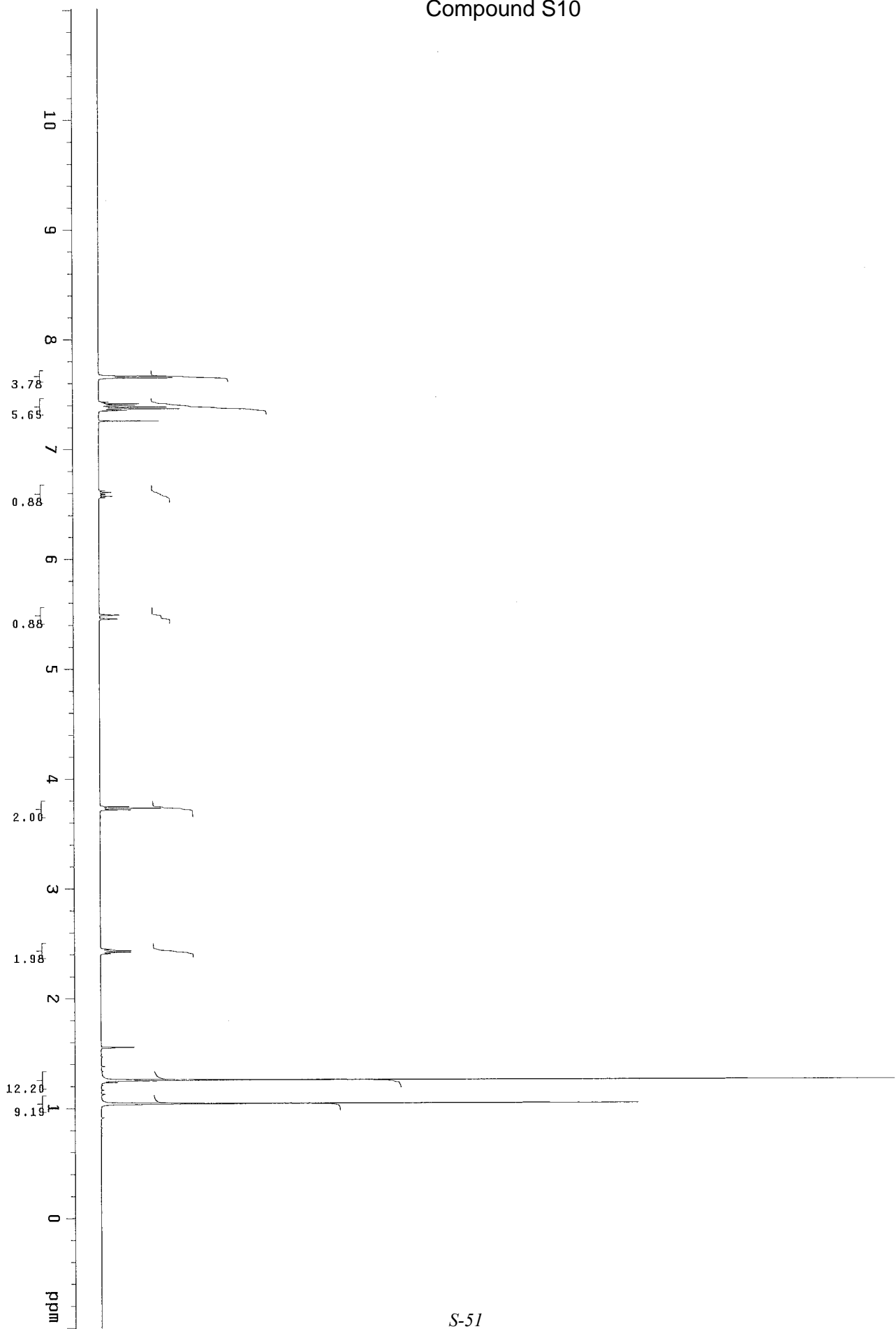
Compound S6



Compound S6

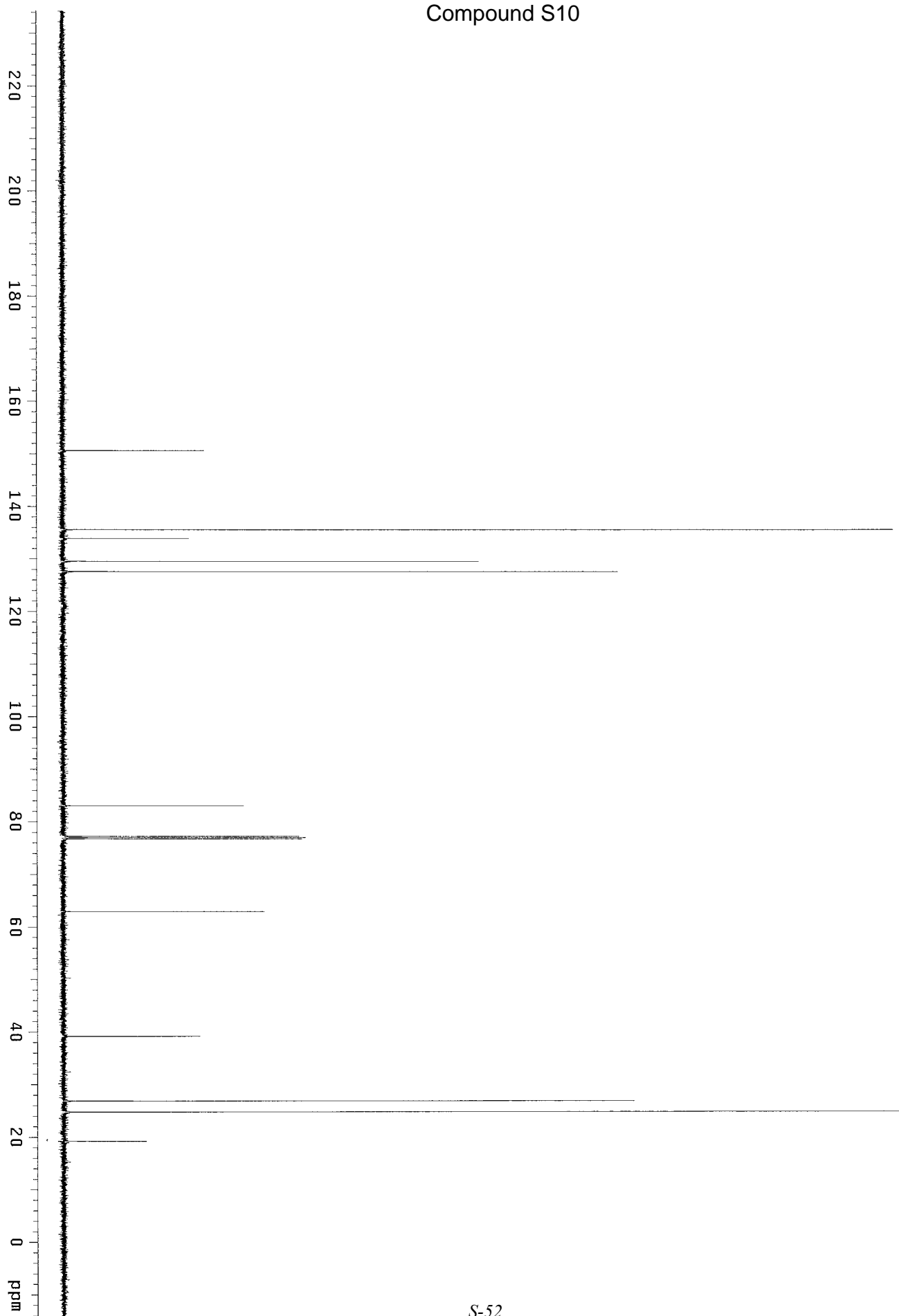


Compound S10



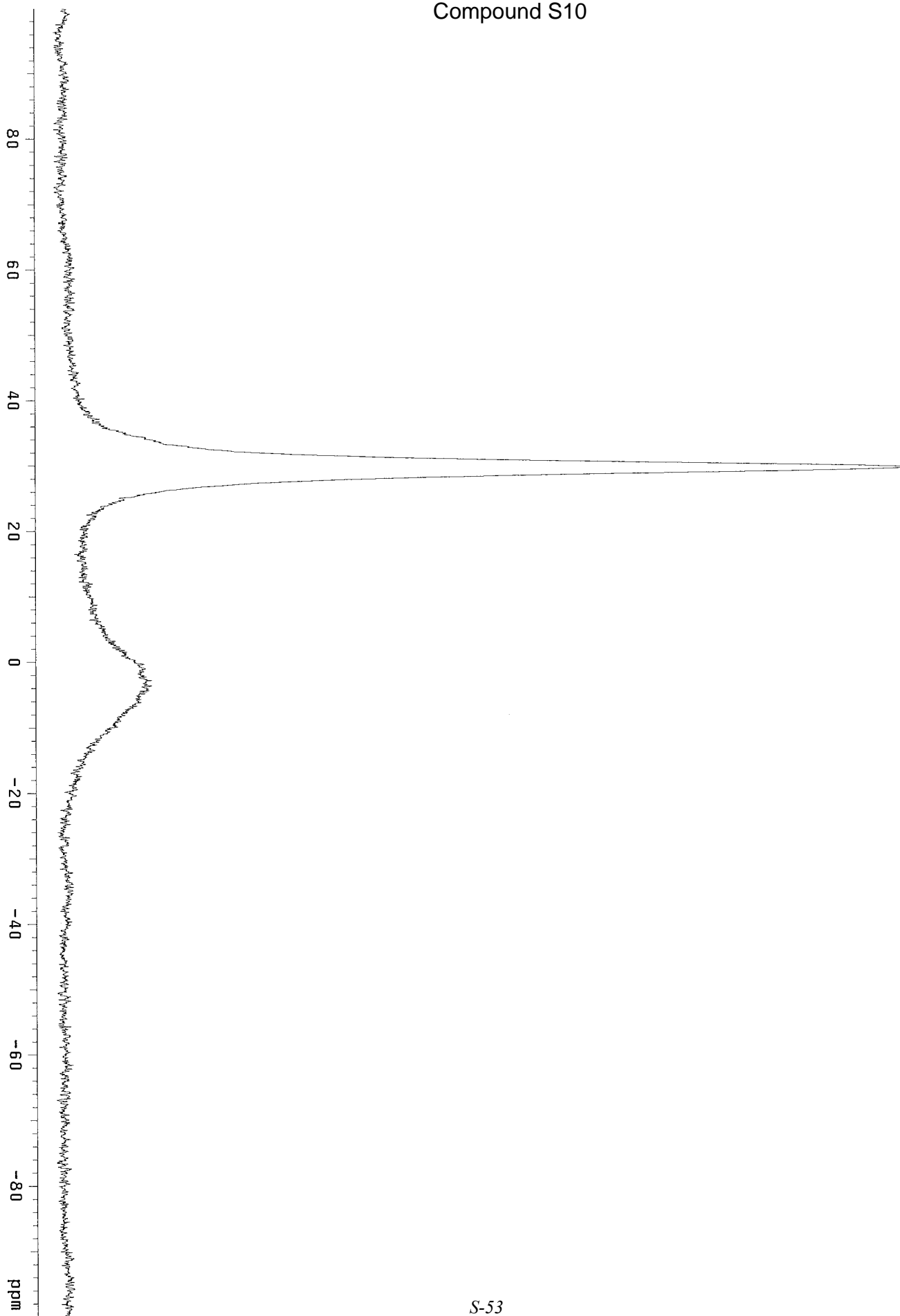


Compound S10

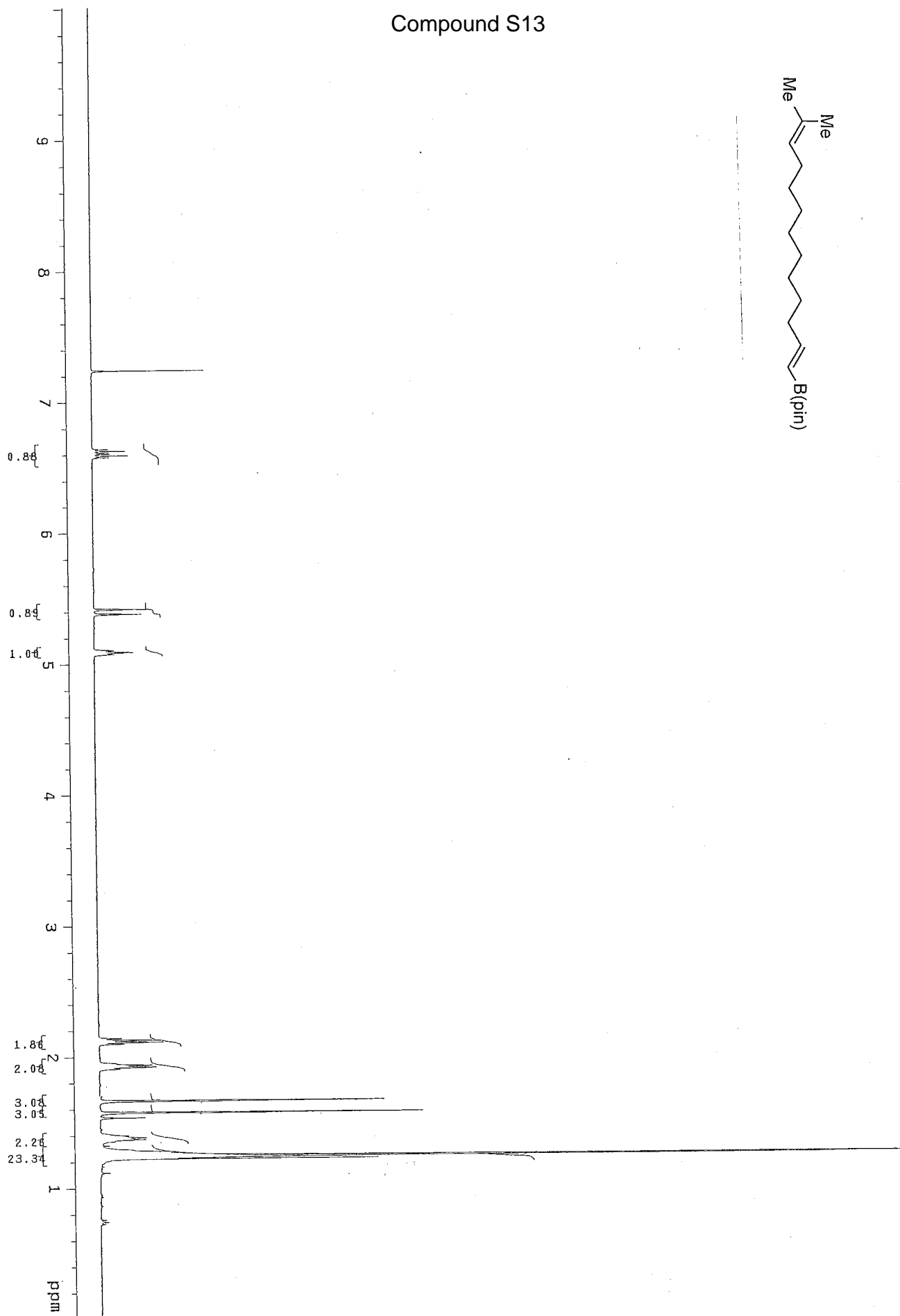




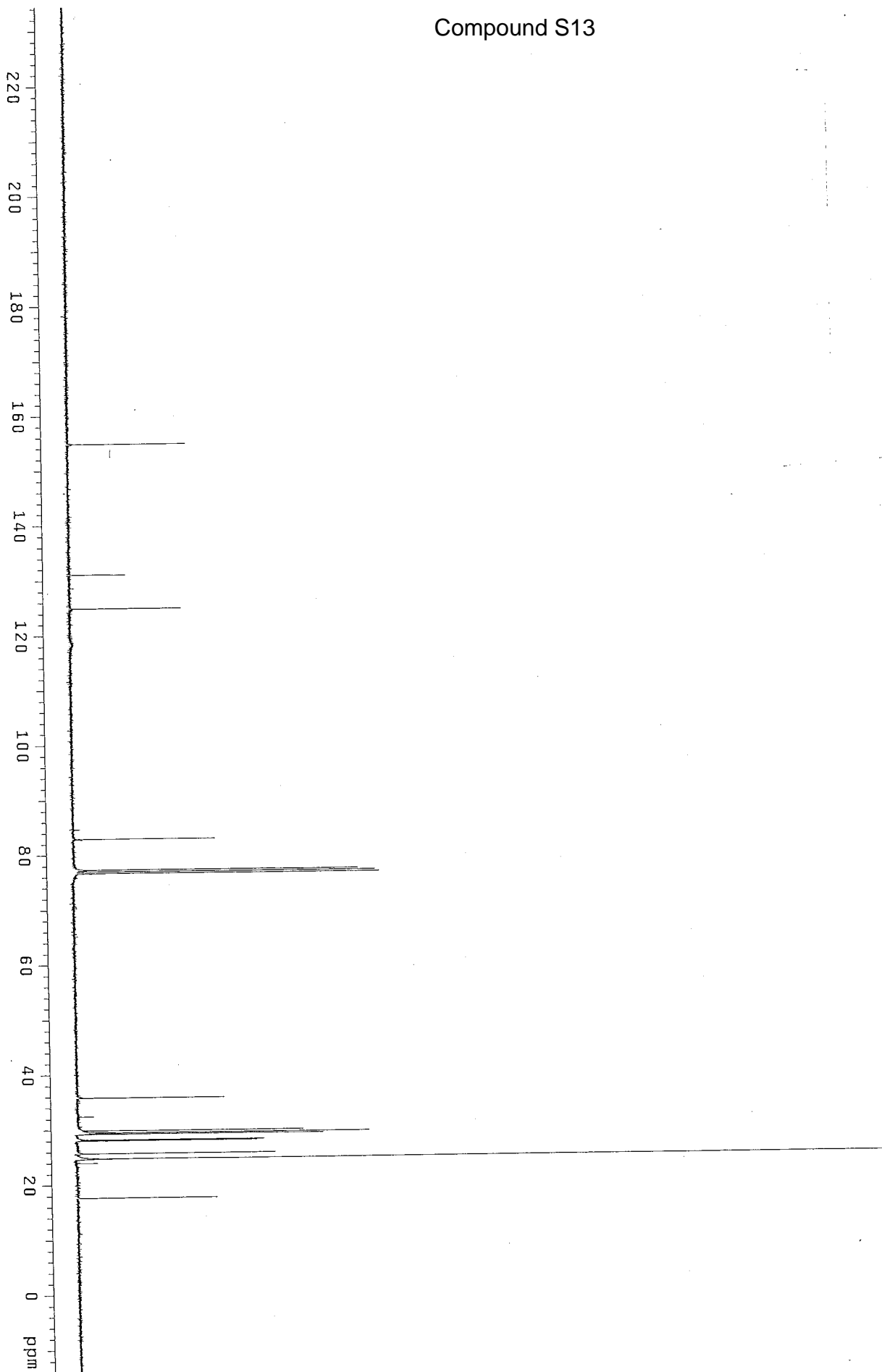
Compound S10



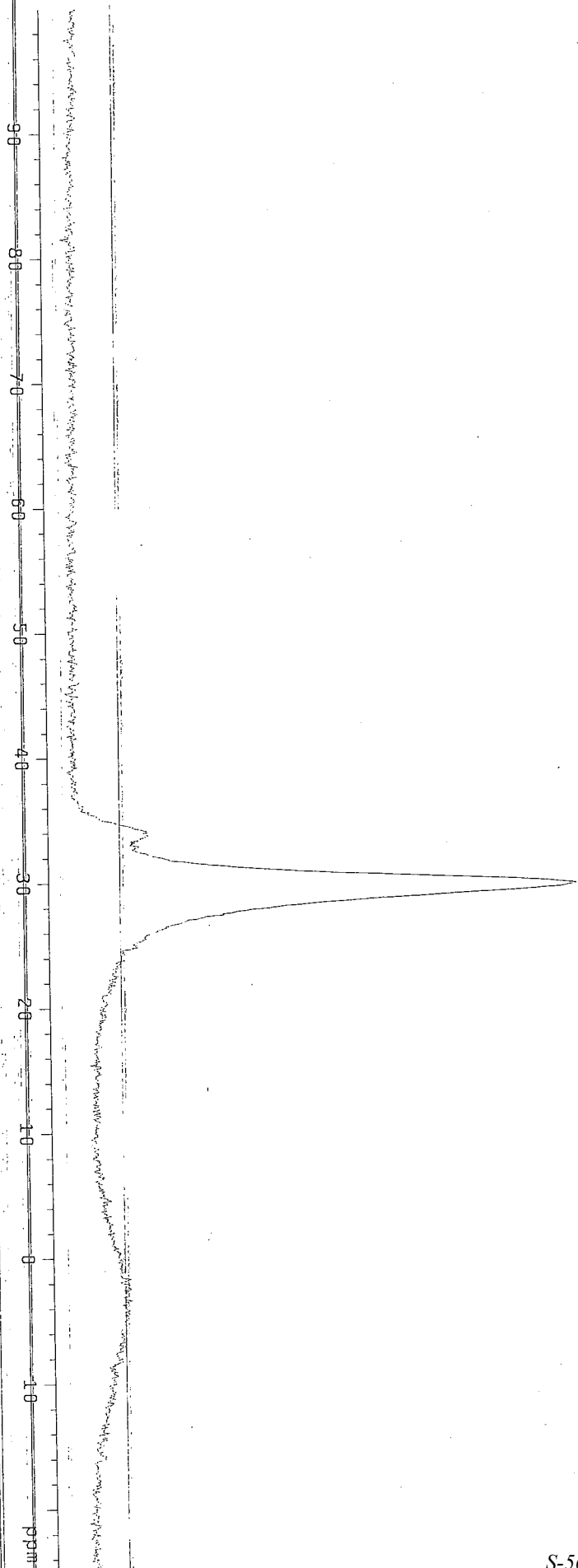
Compound S13



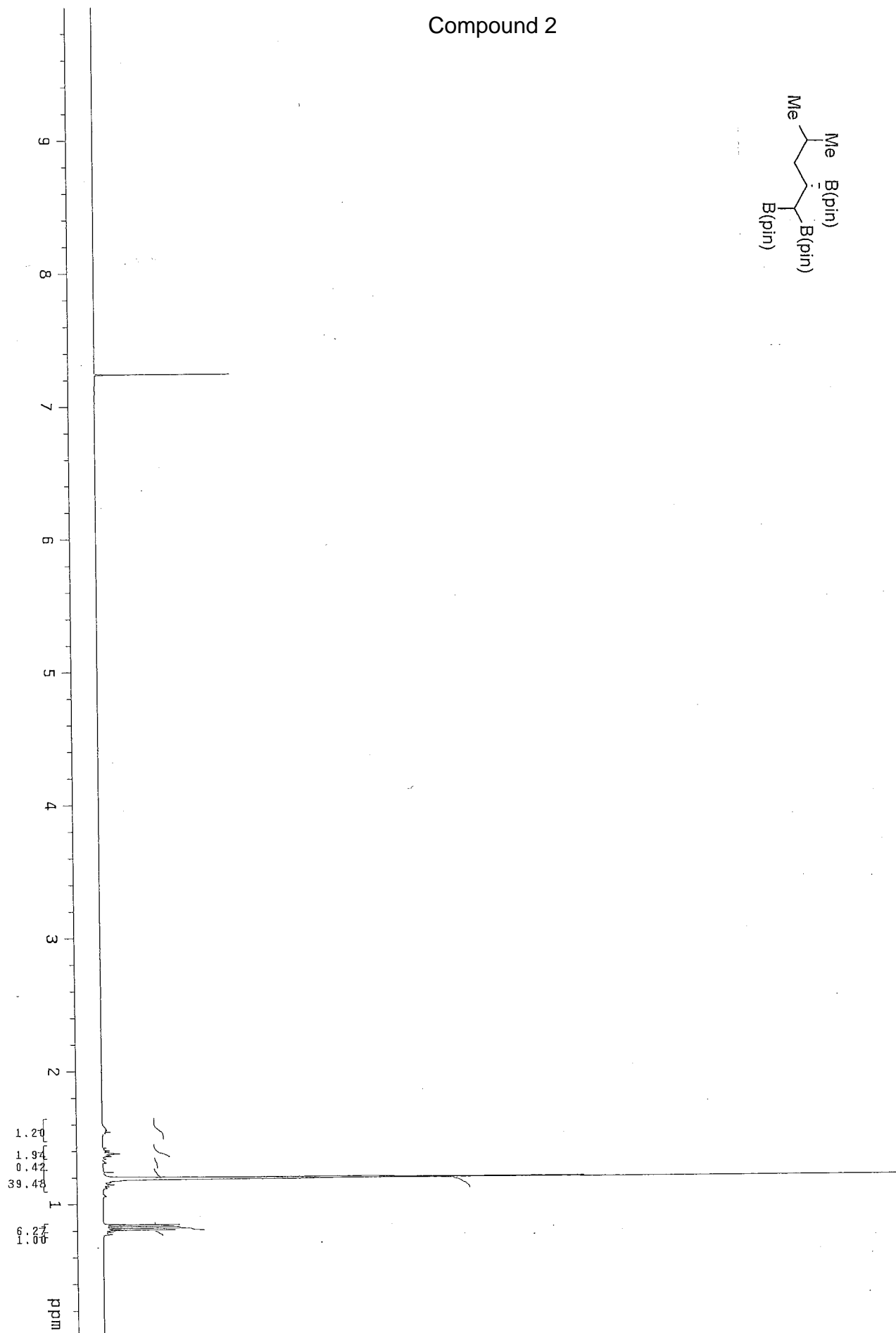
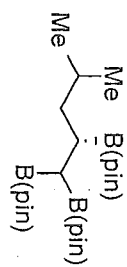
Compound S13



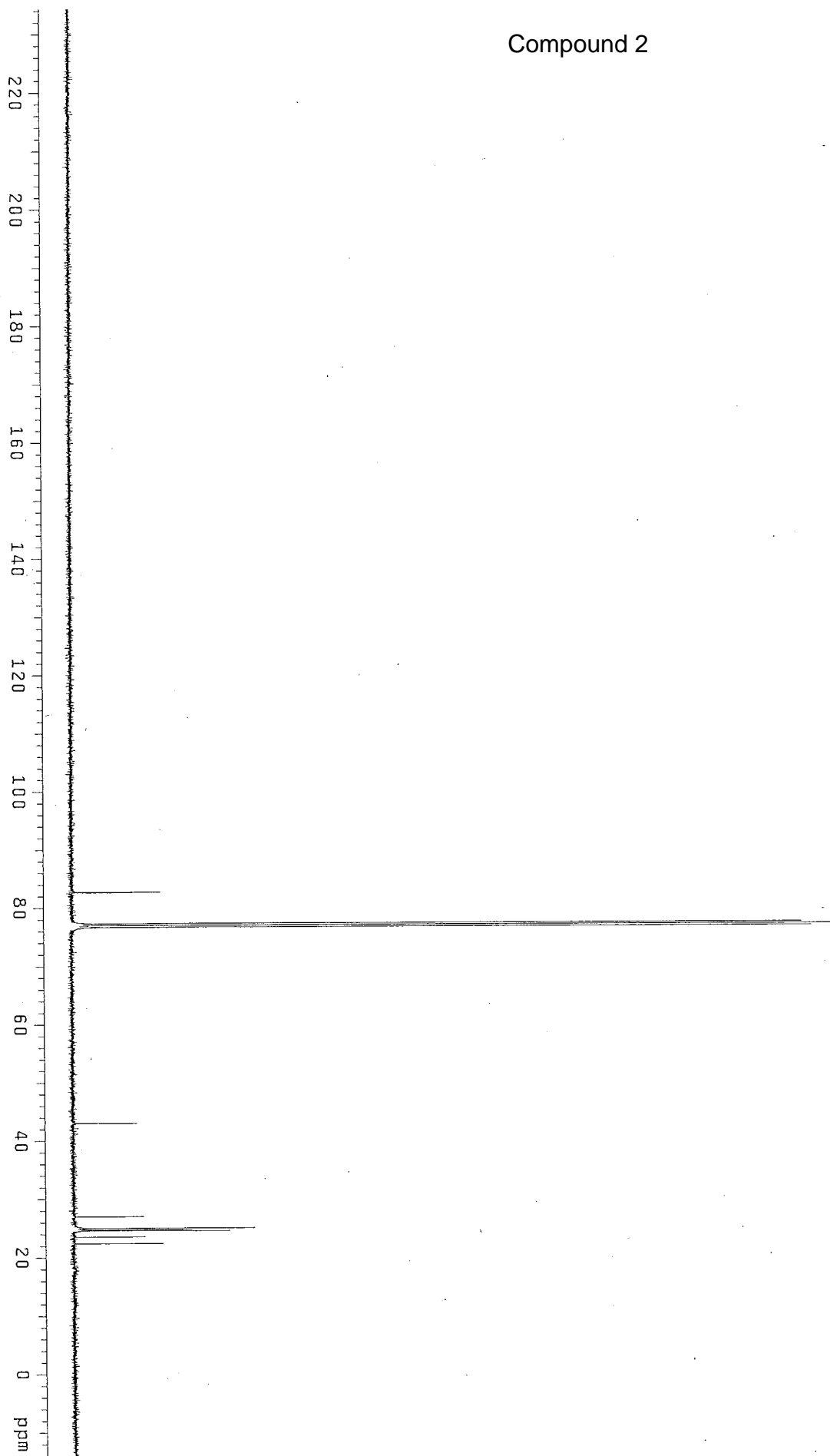
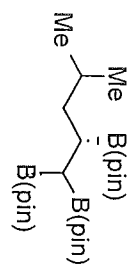
Compound S13



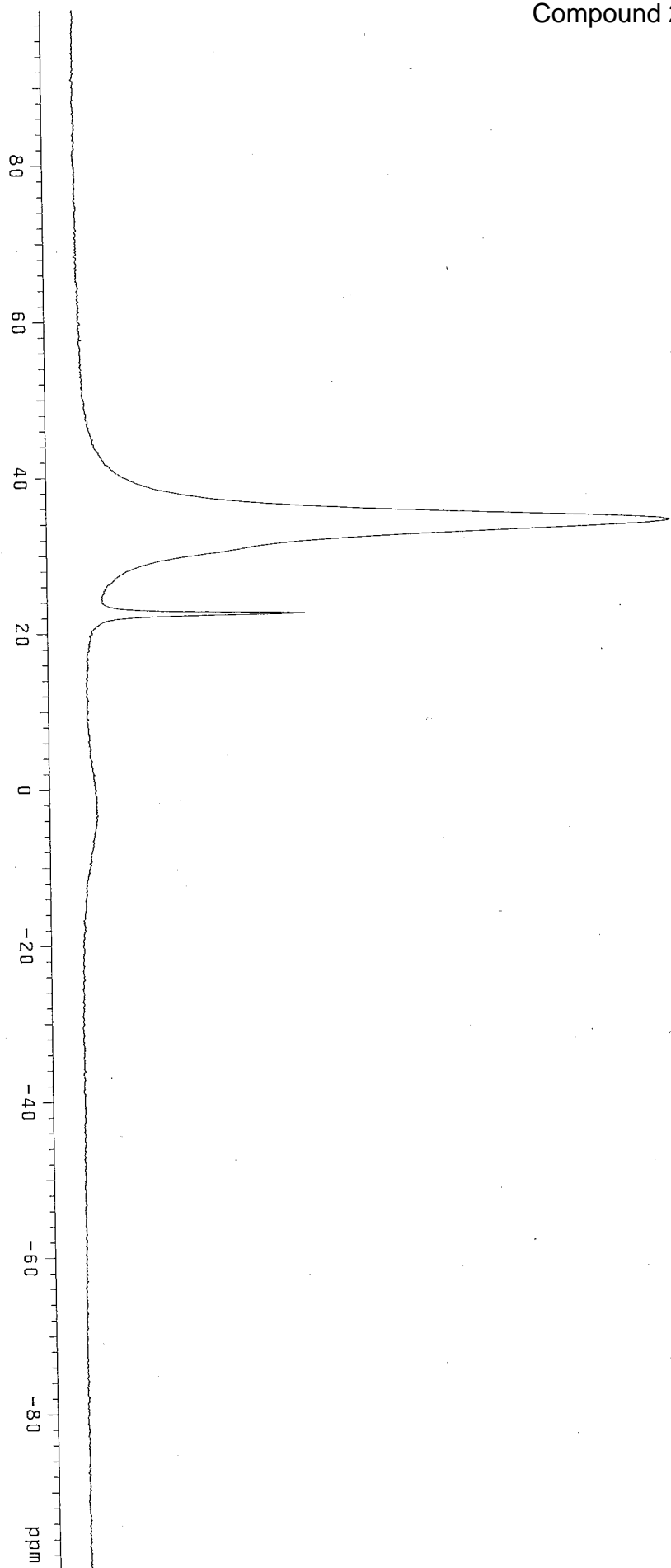
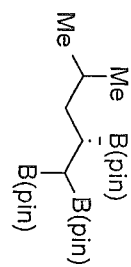
Compound 2



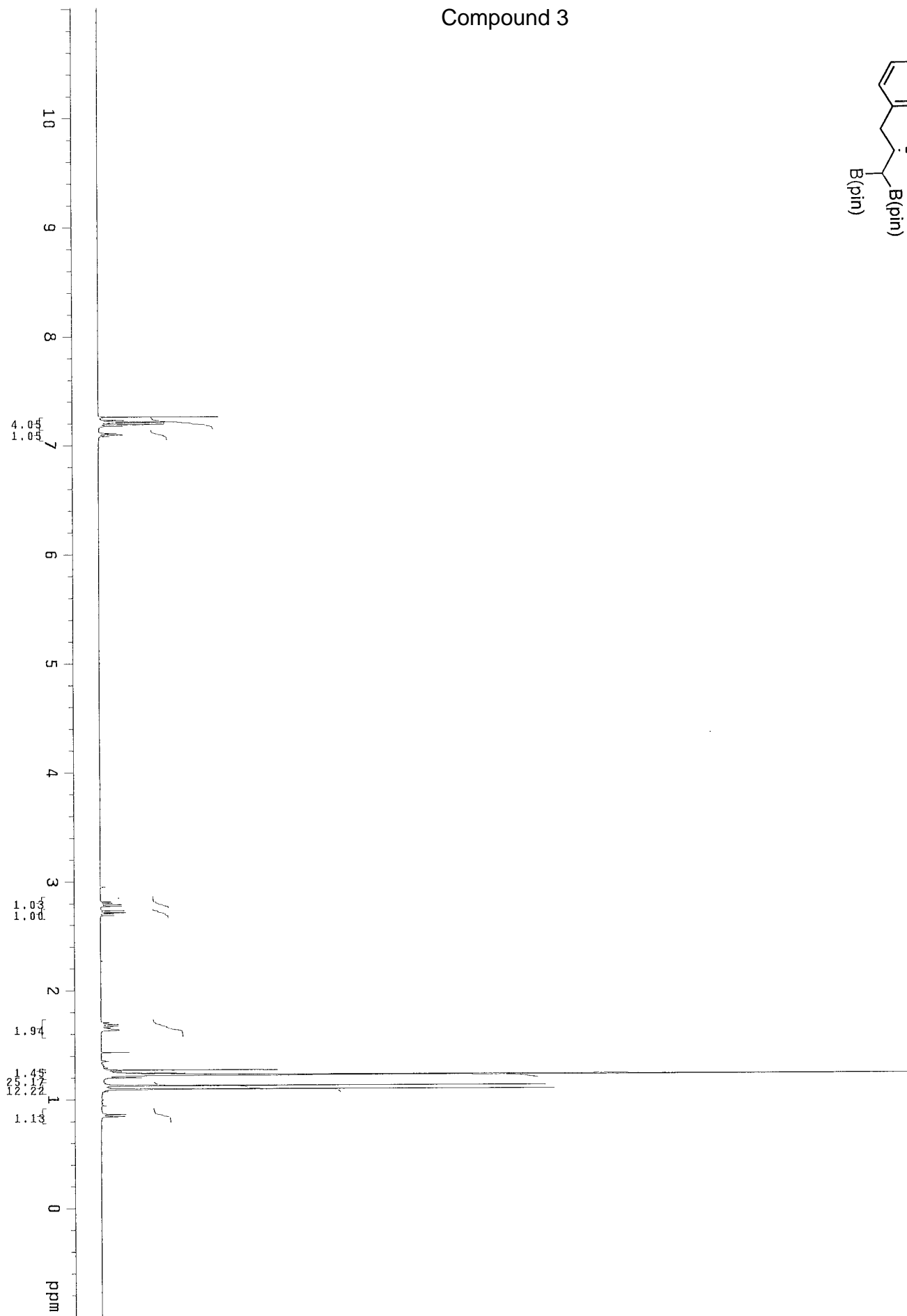
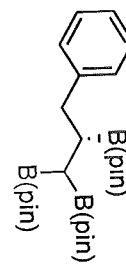
Compound 2



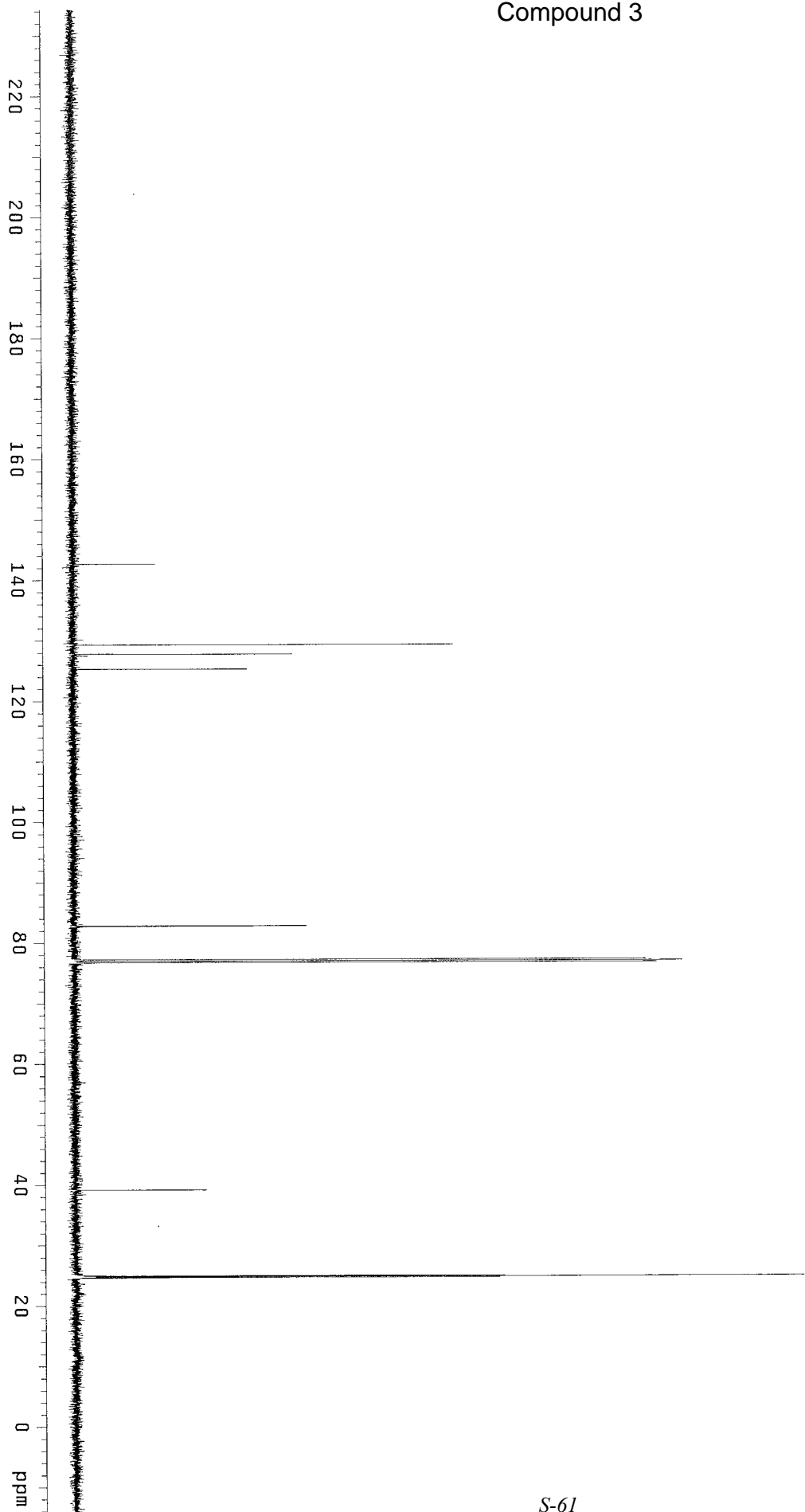
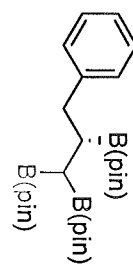
Compound 2



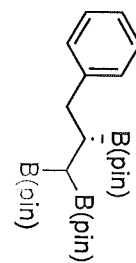
Compound 3



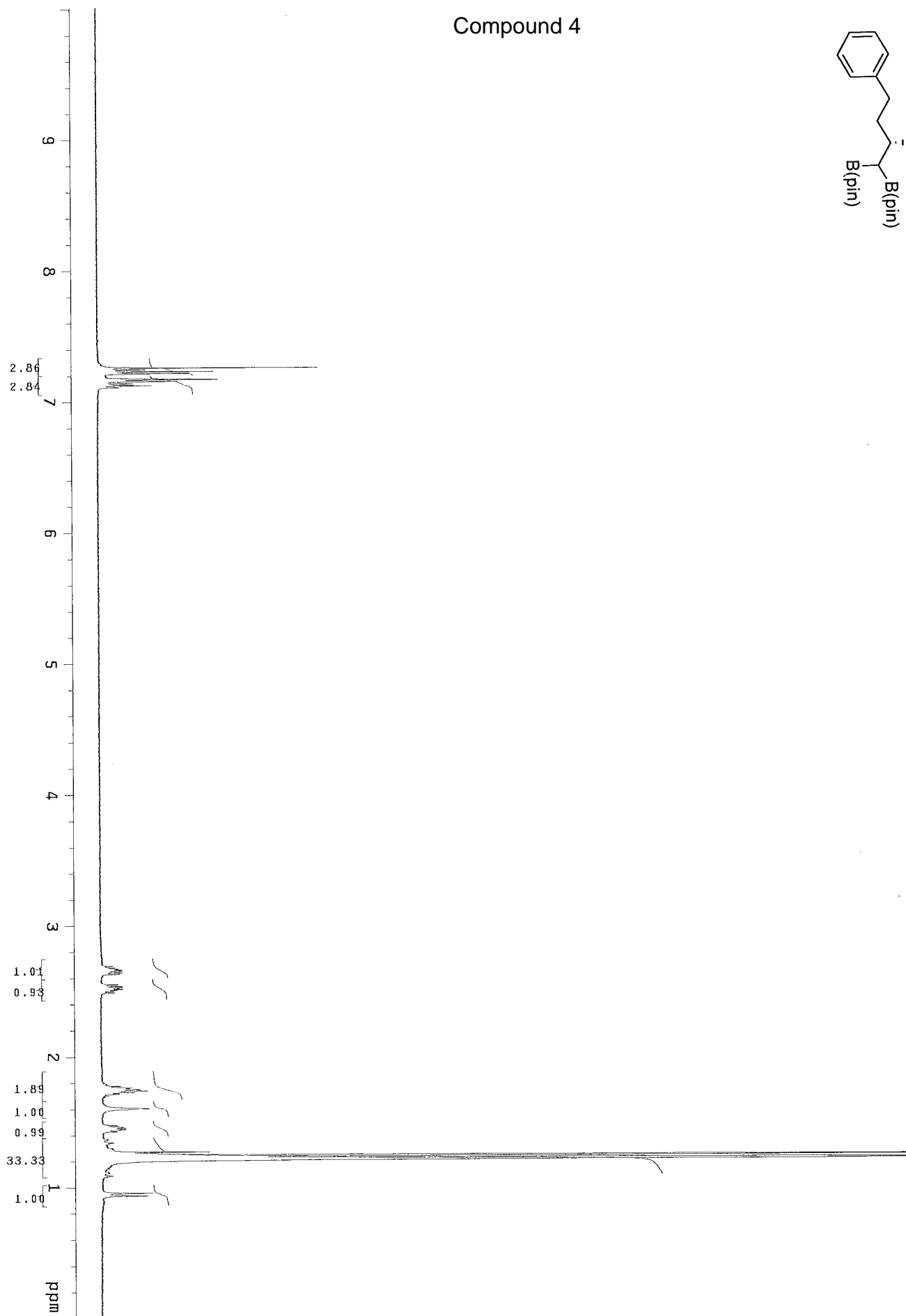
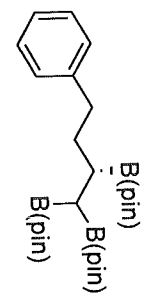
Compound 3

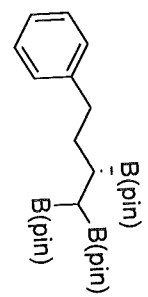


Compound 3

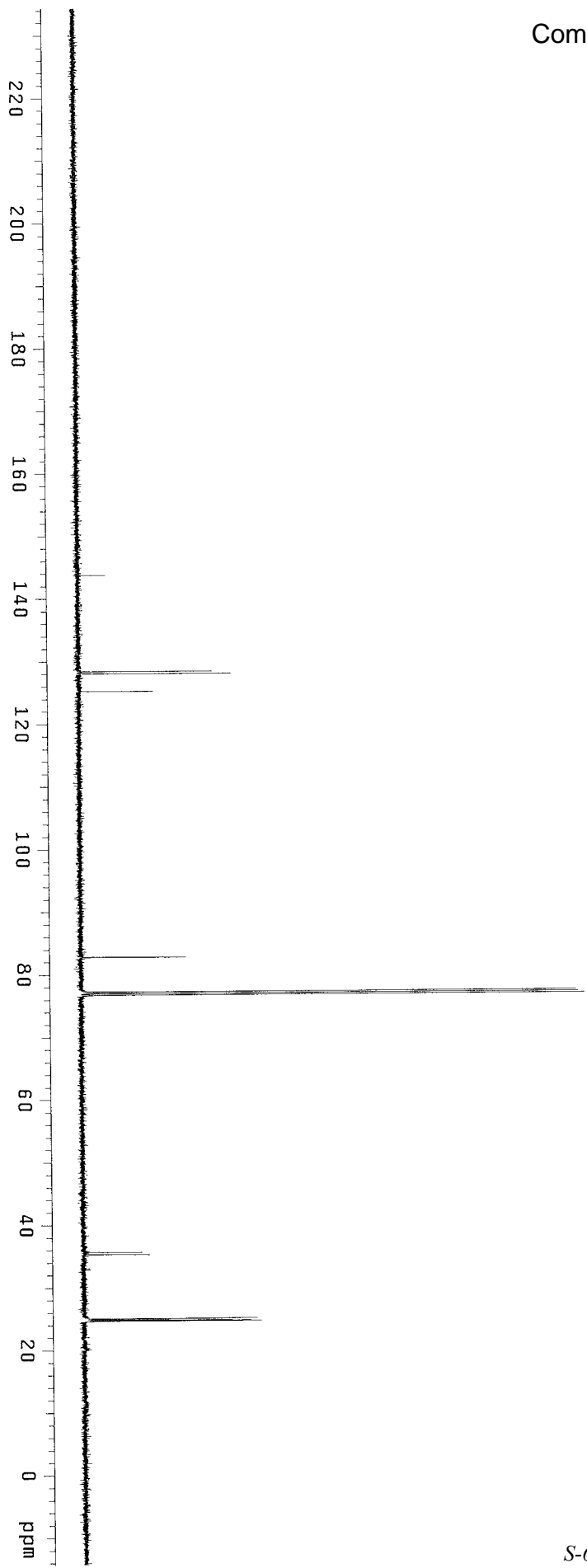


Compound 4

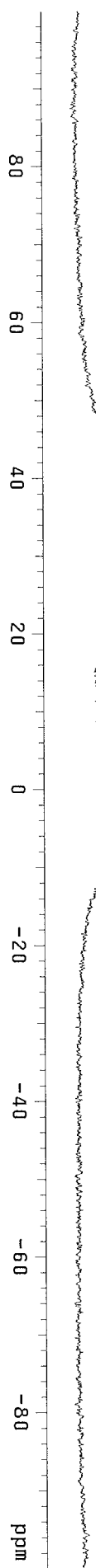
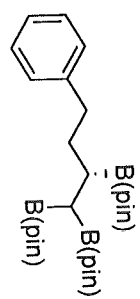




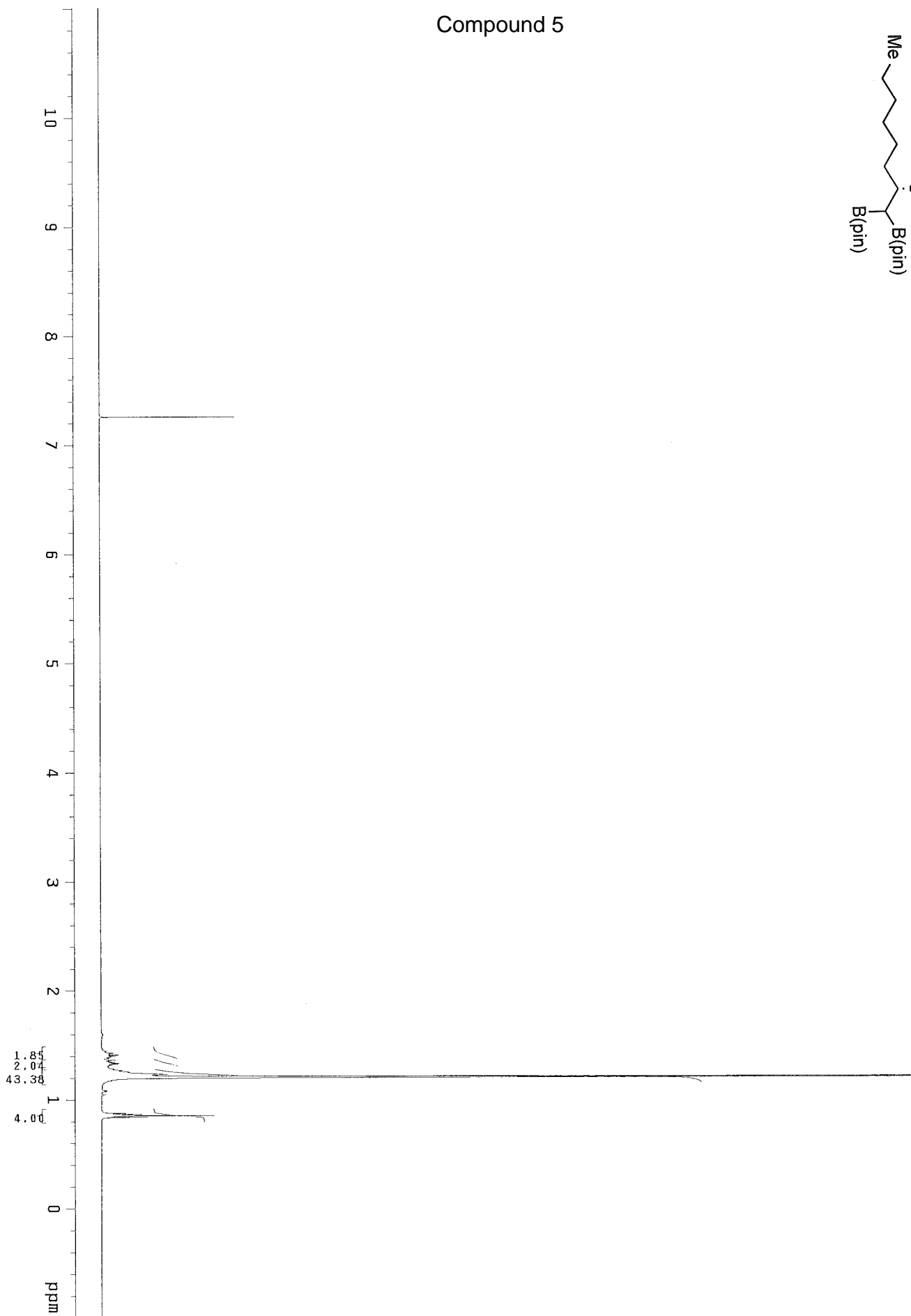
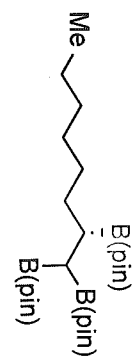
Compound 4



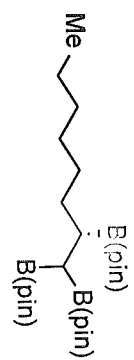
Compound 4



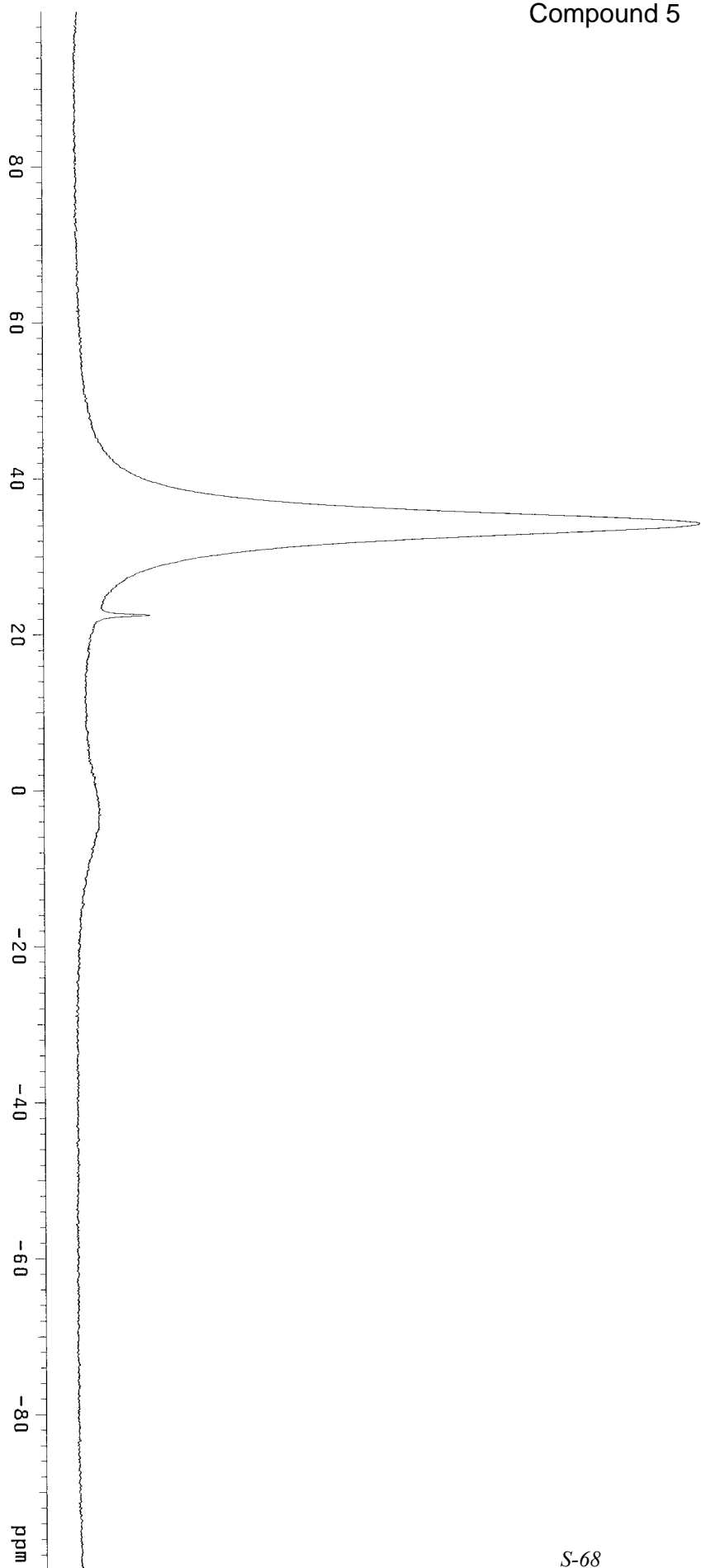
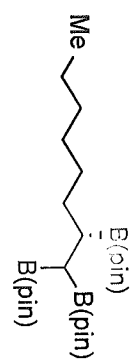
Compound 5



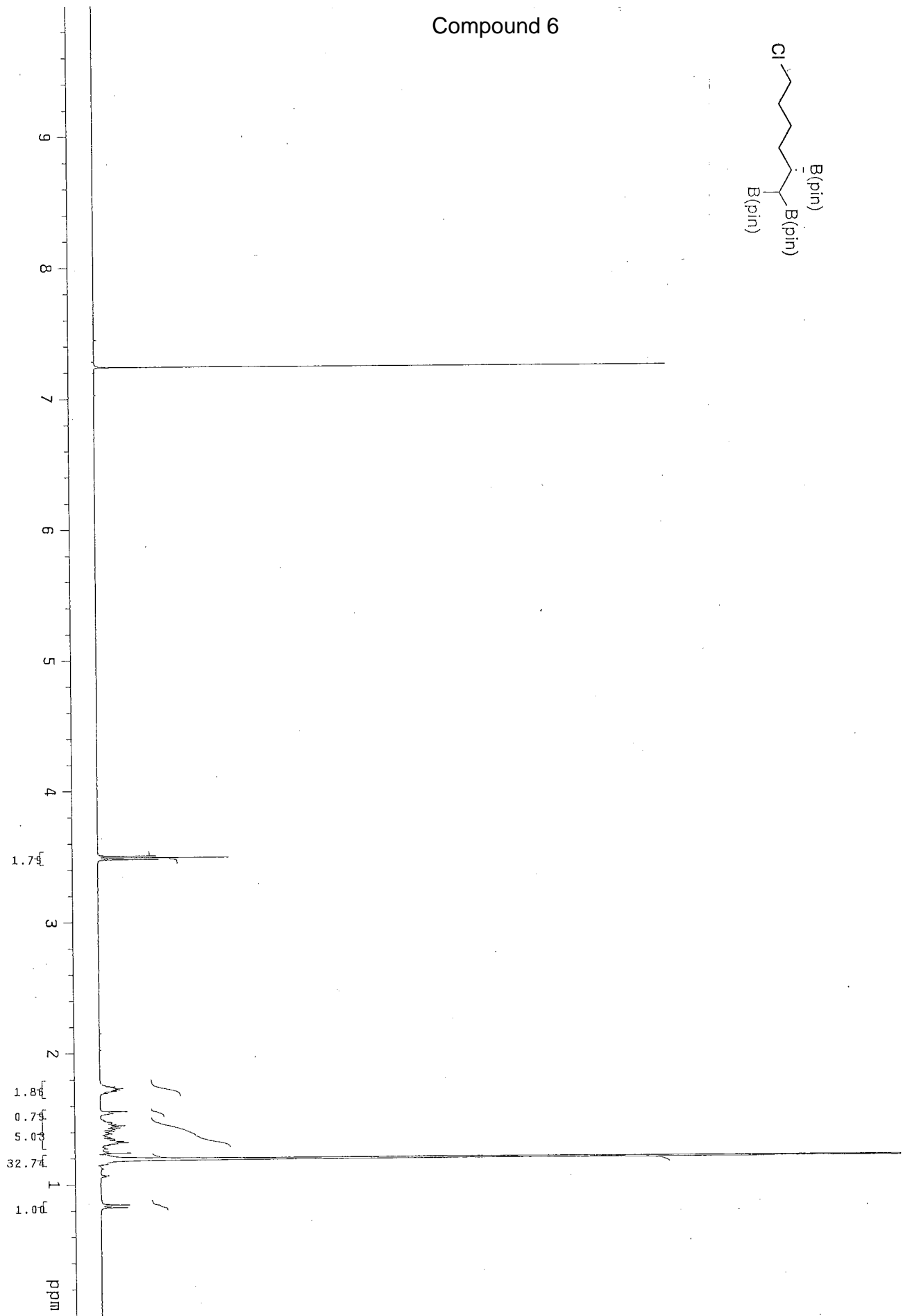
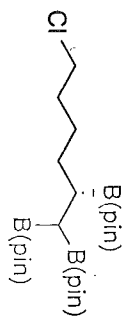
Compound 5



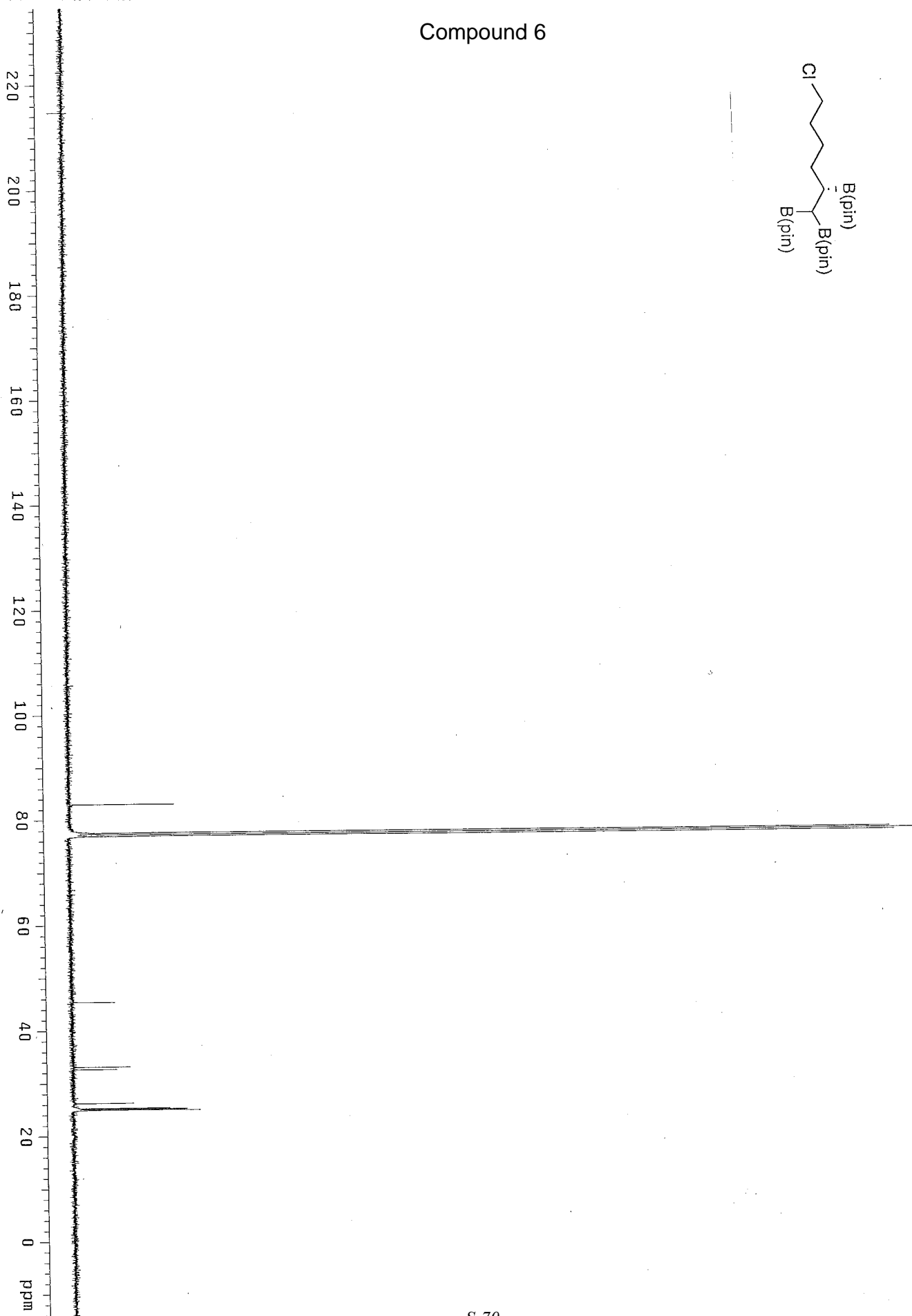
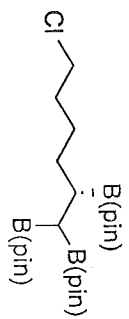
Compound 5



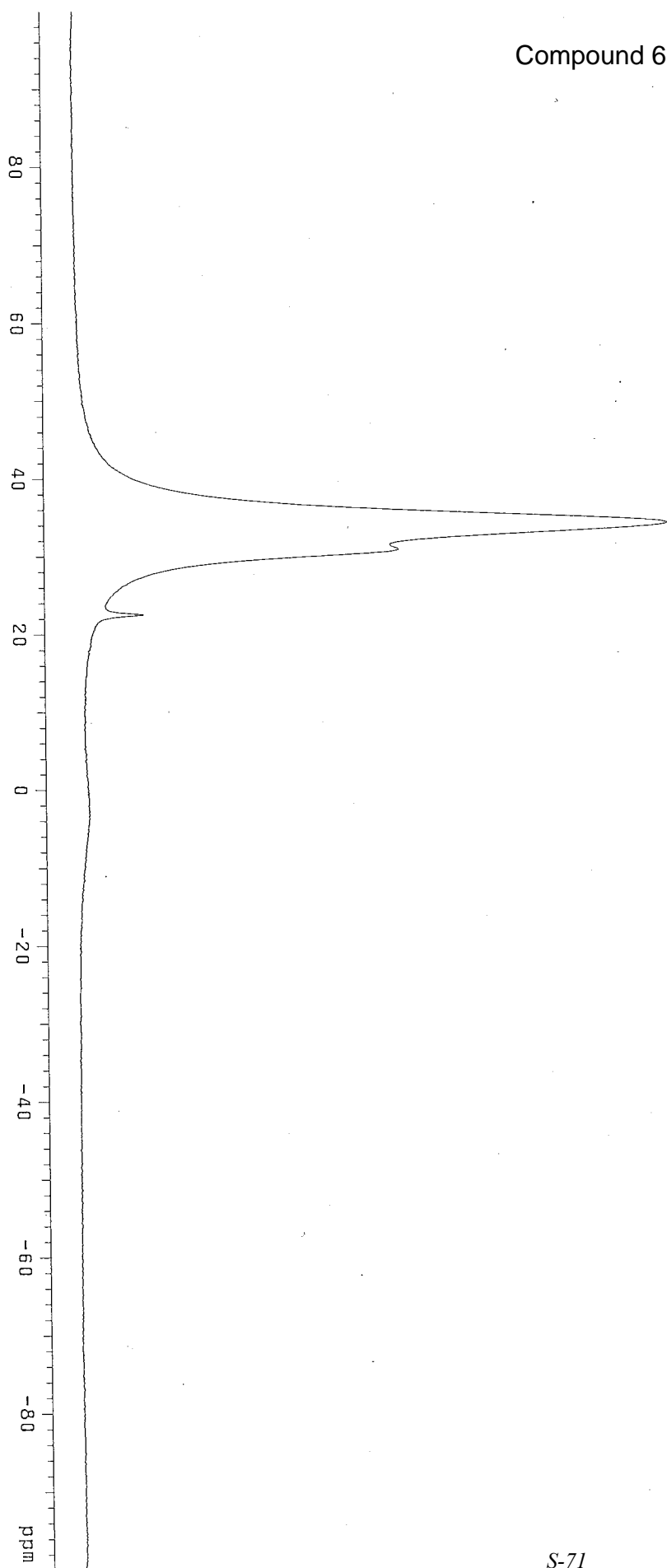
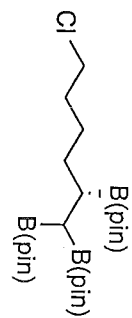
Compound 6



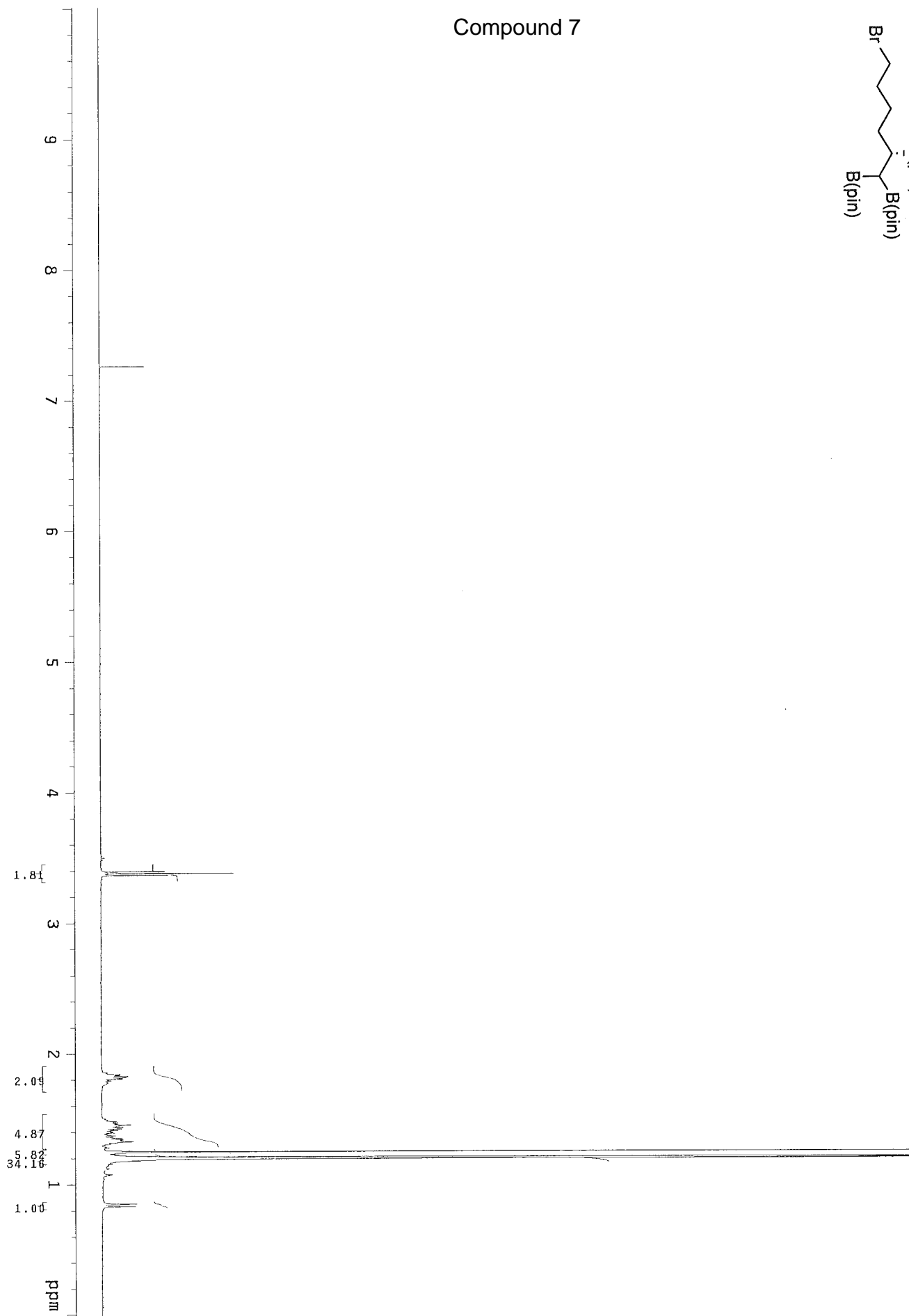
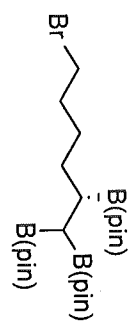
Compound 6

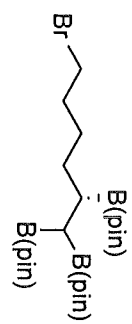


Compound 6

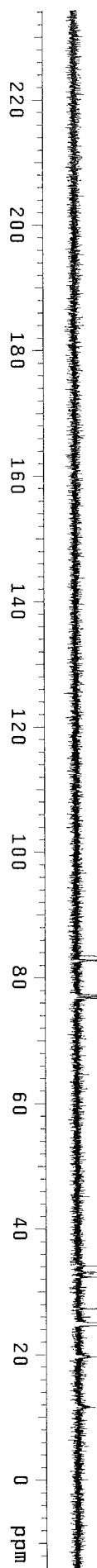


Compound 7

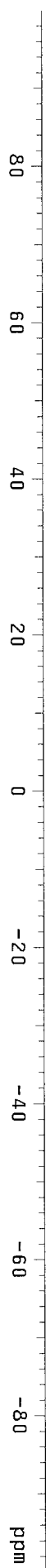
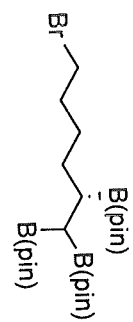




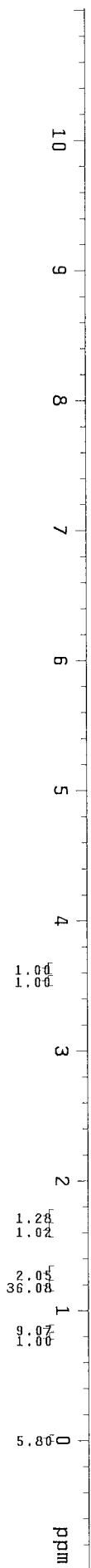
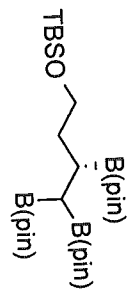
Compound 7



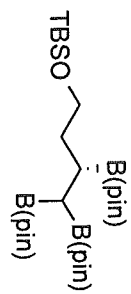
Compound 7



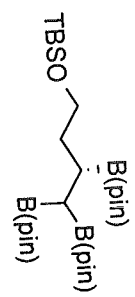
Compound 8



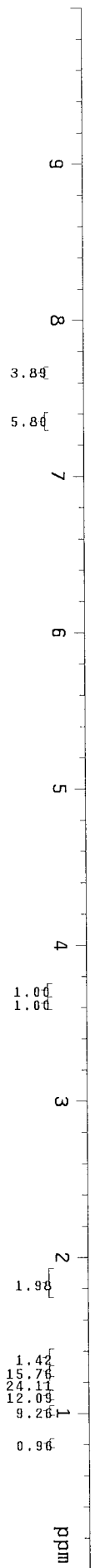
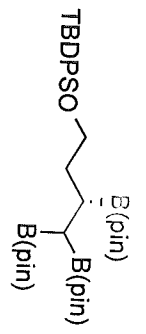
Compound 8

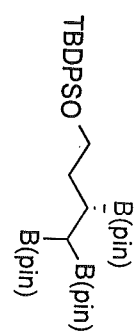


Compound 8

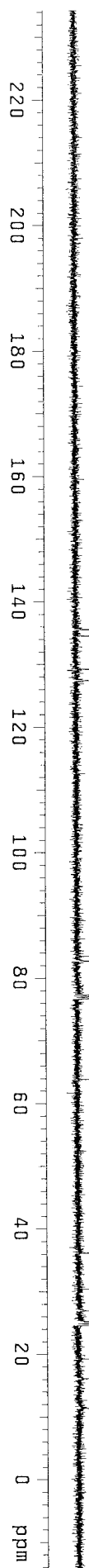


Compound 9

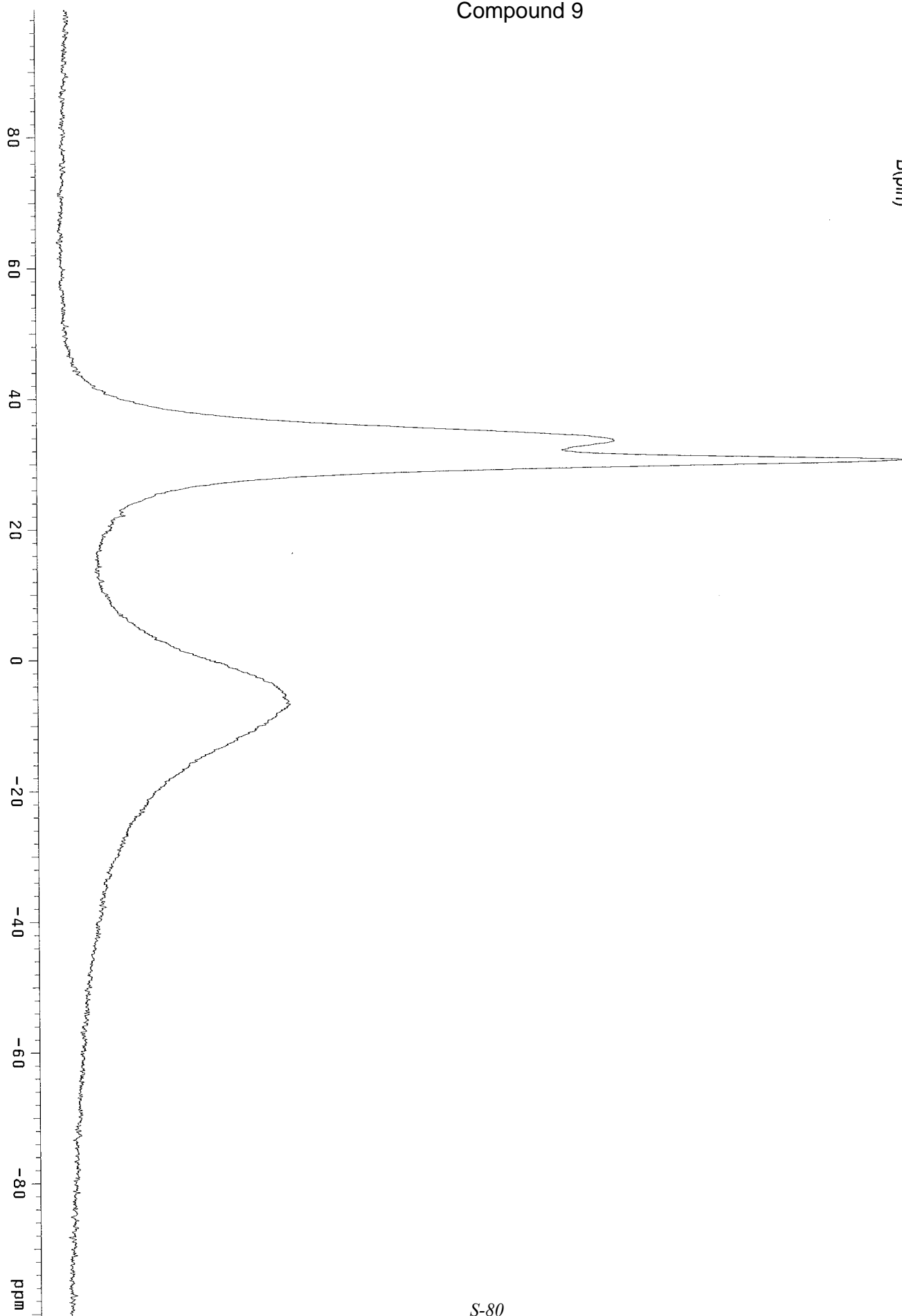
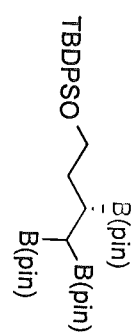




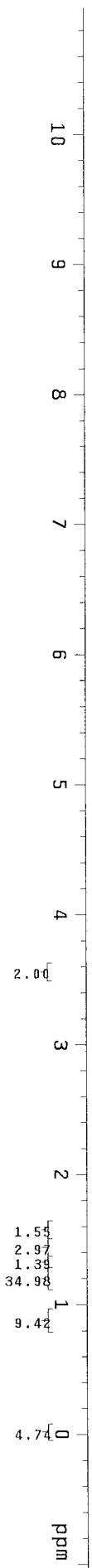
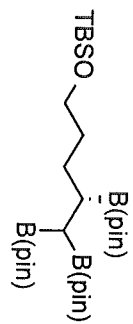
Compound 9



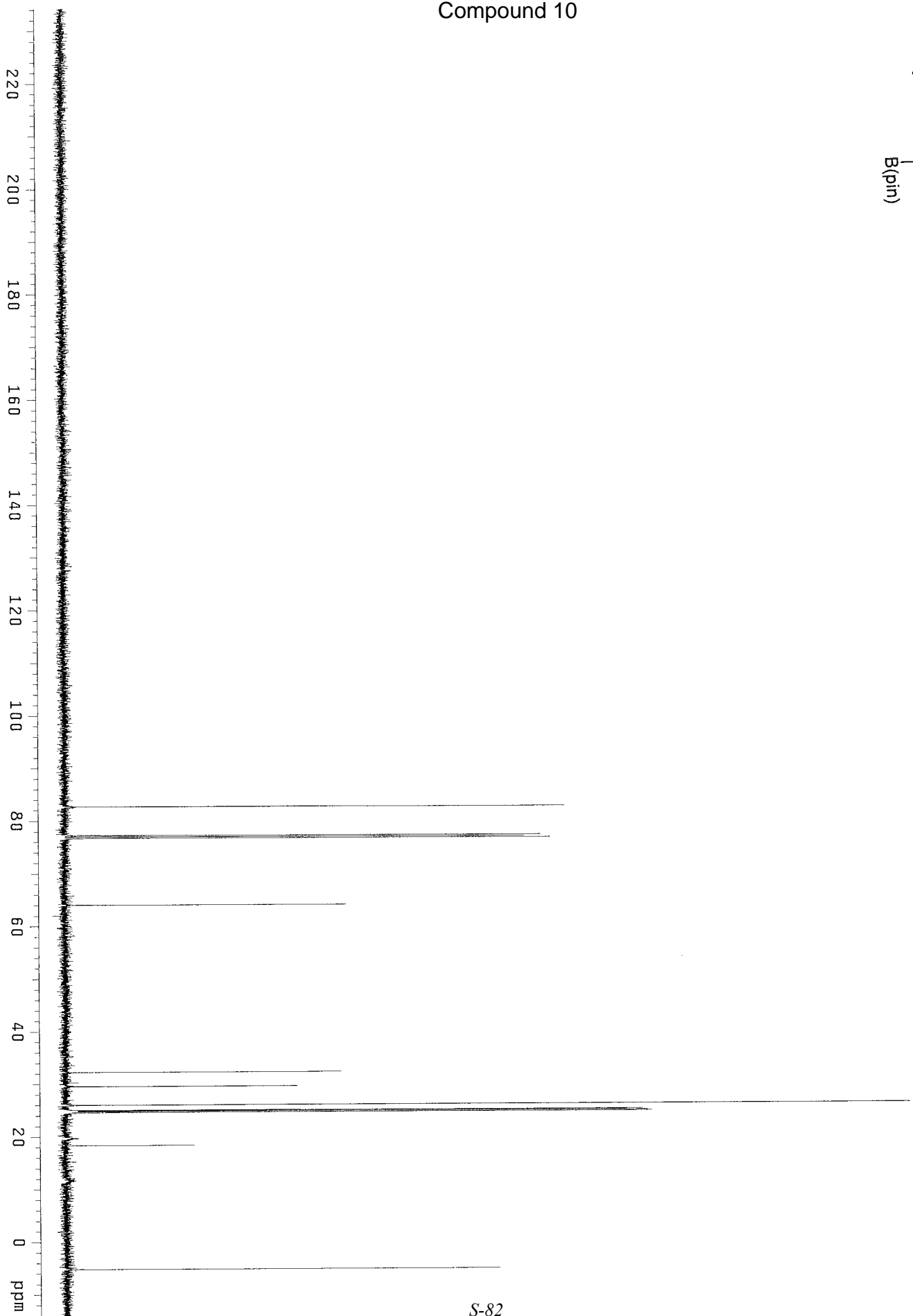
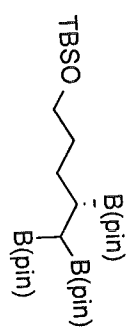
Compound 9



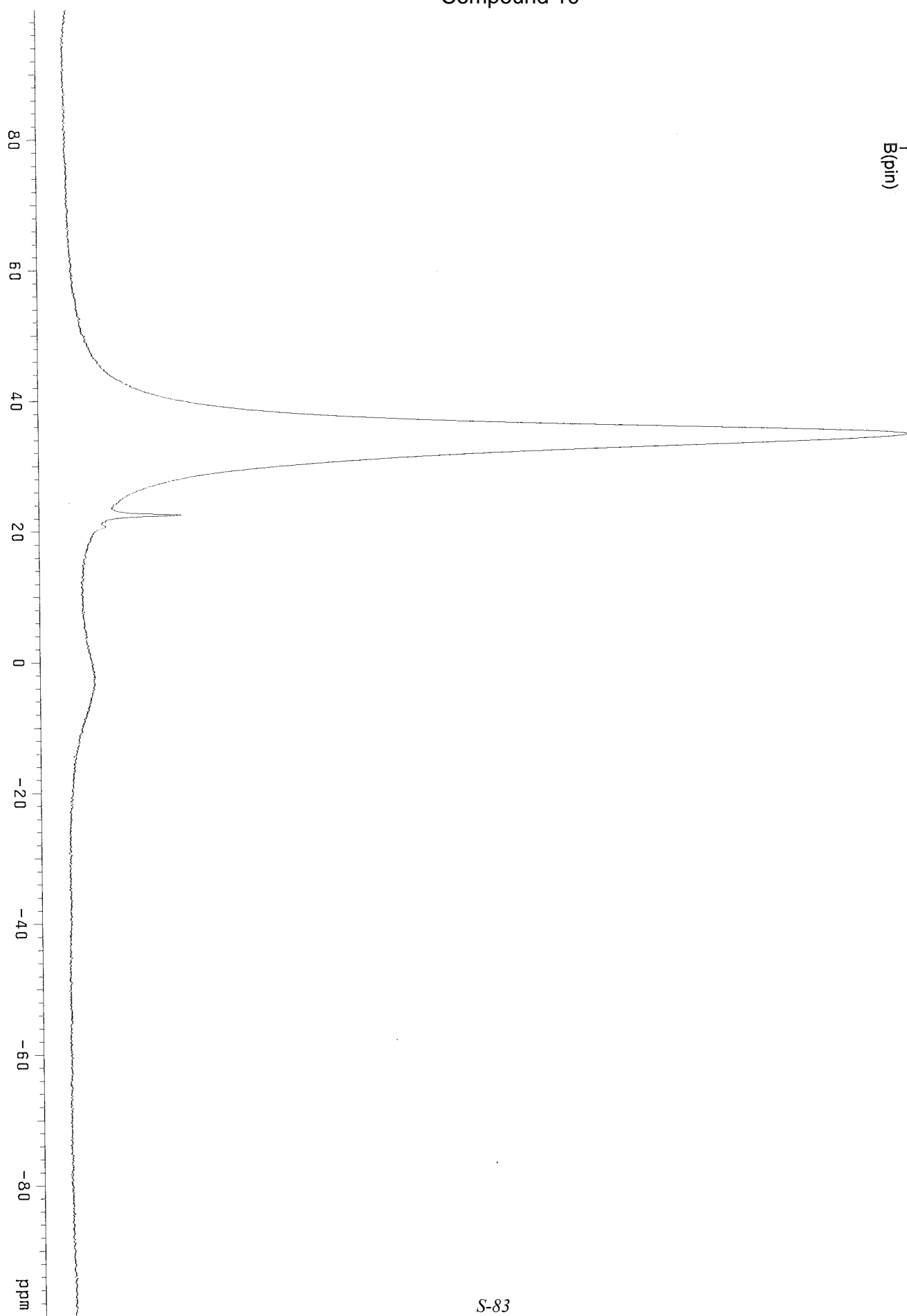
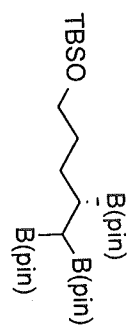
Compound 10



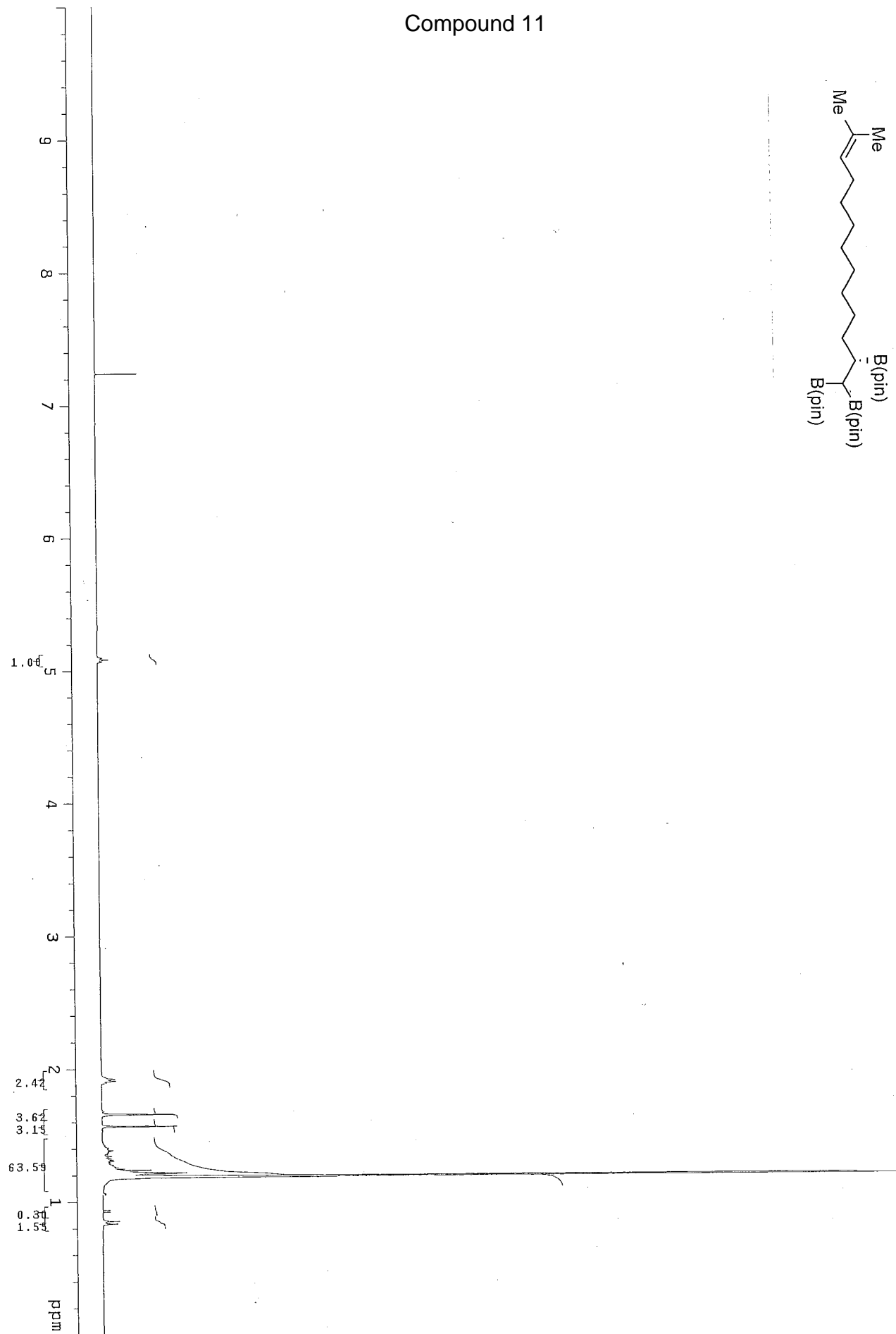
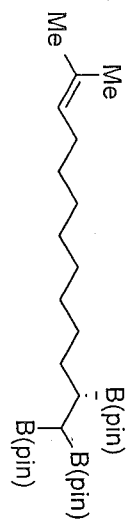
Compound 10



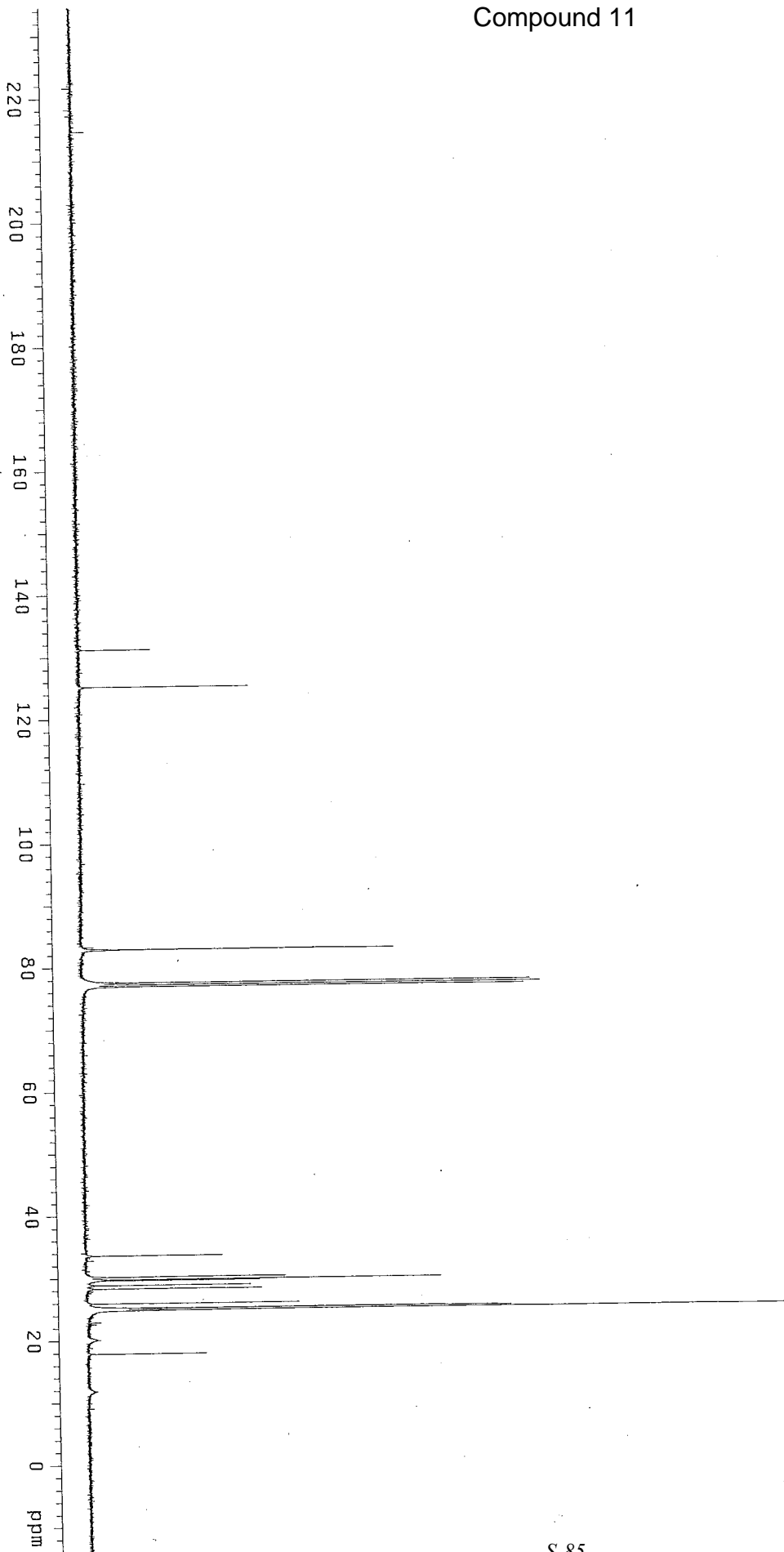
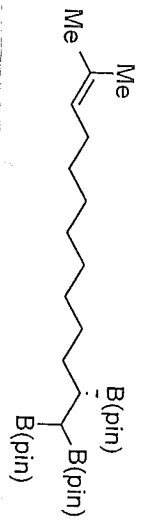
Compound 10



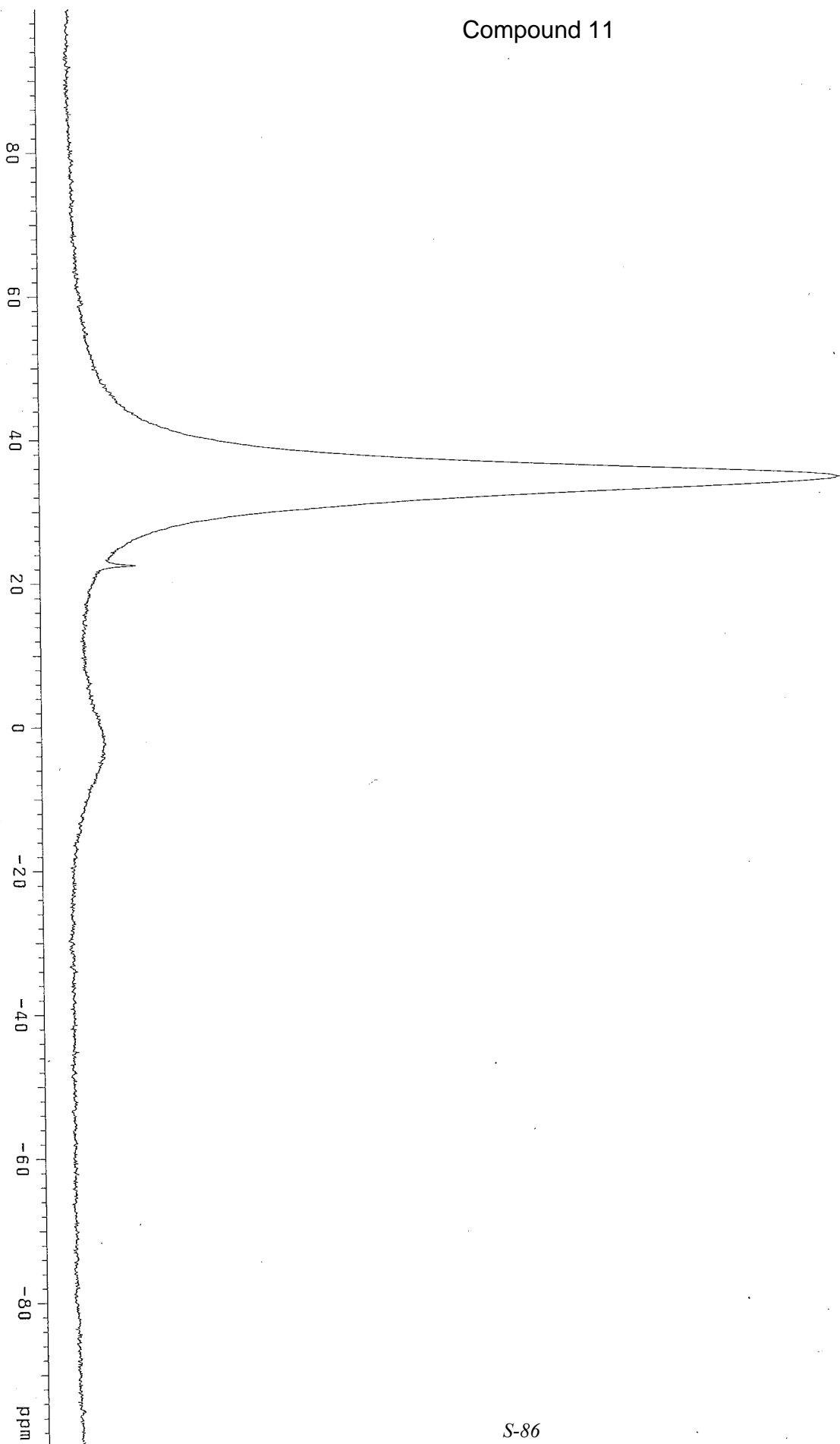
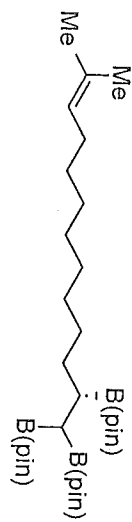
Compound 11



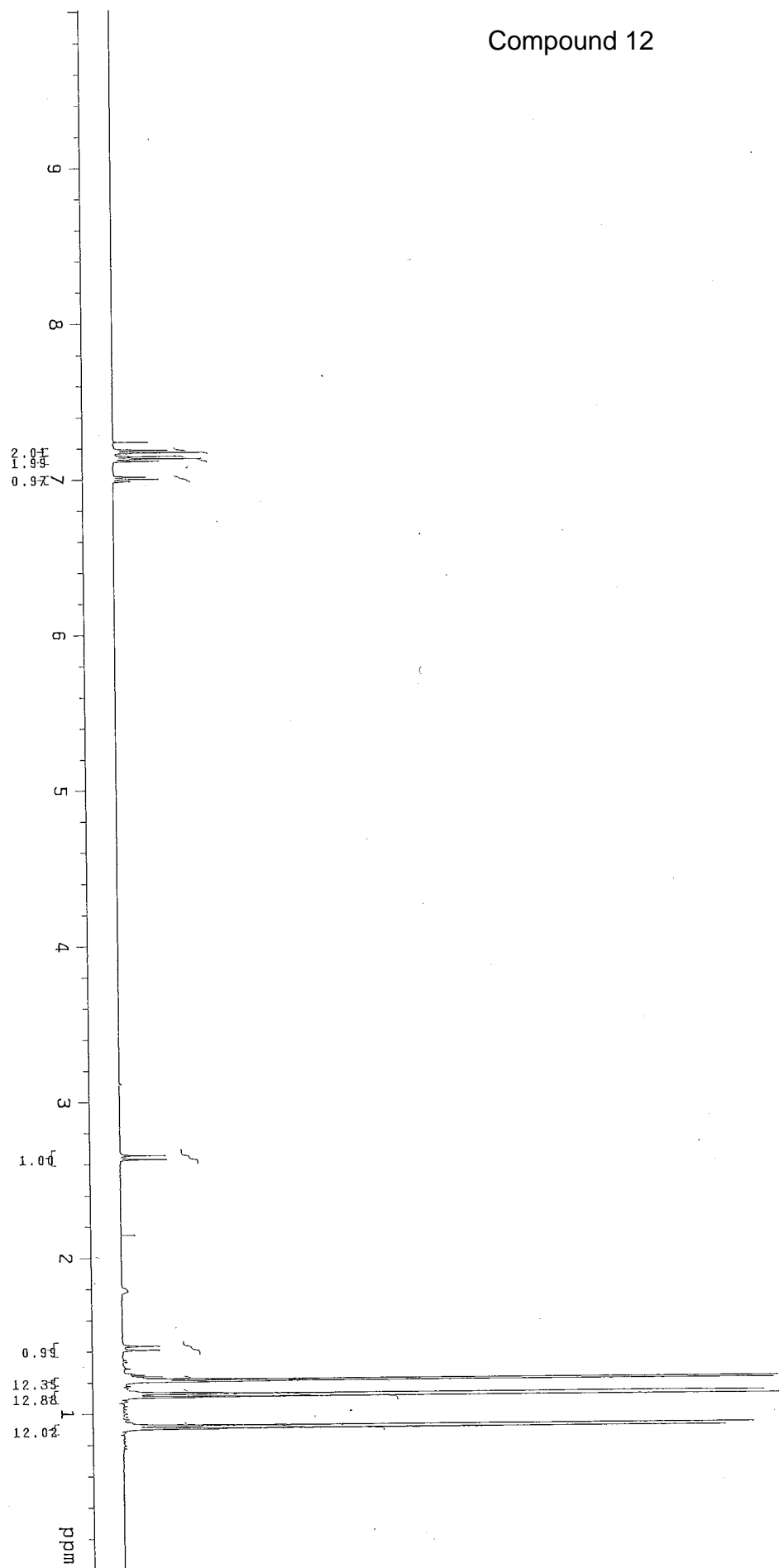
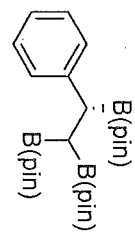
Compound 11



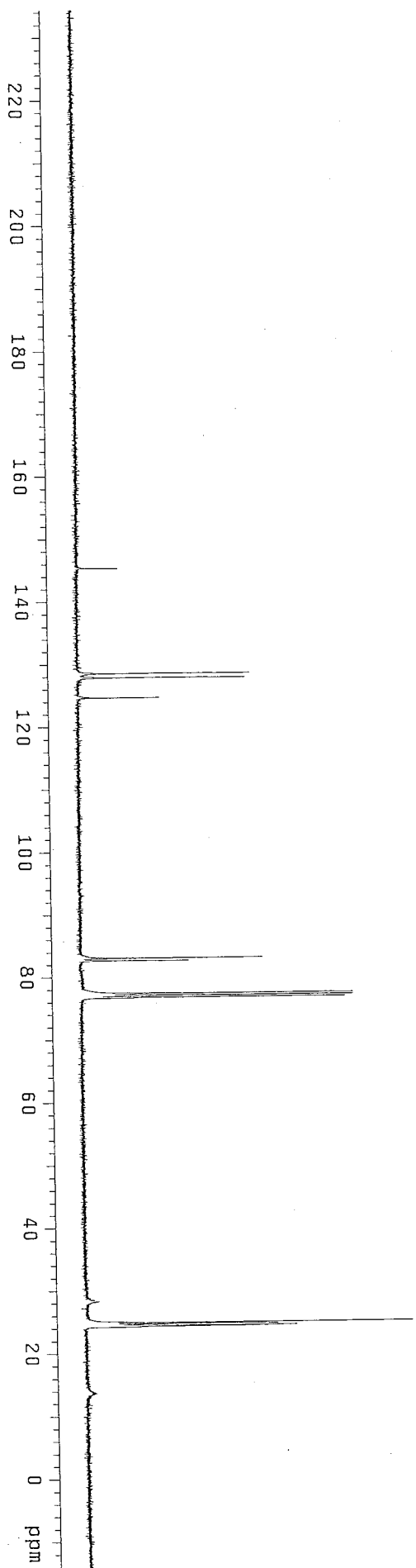
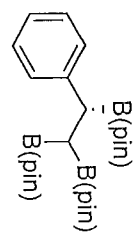
Compound 11



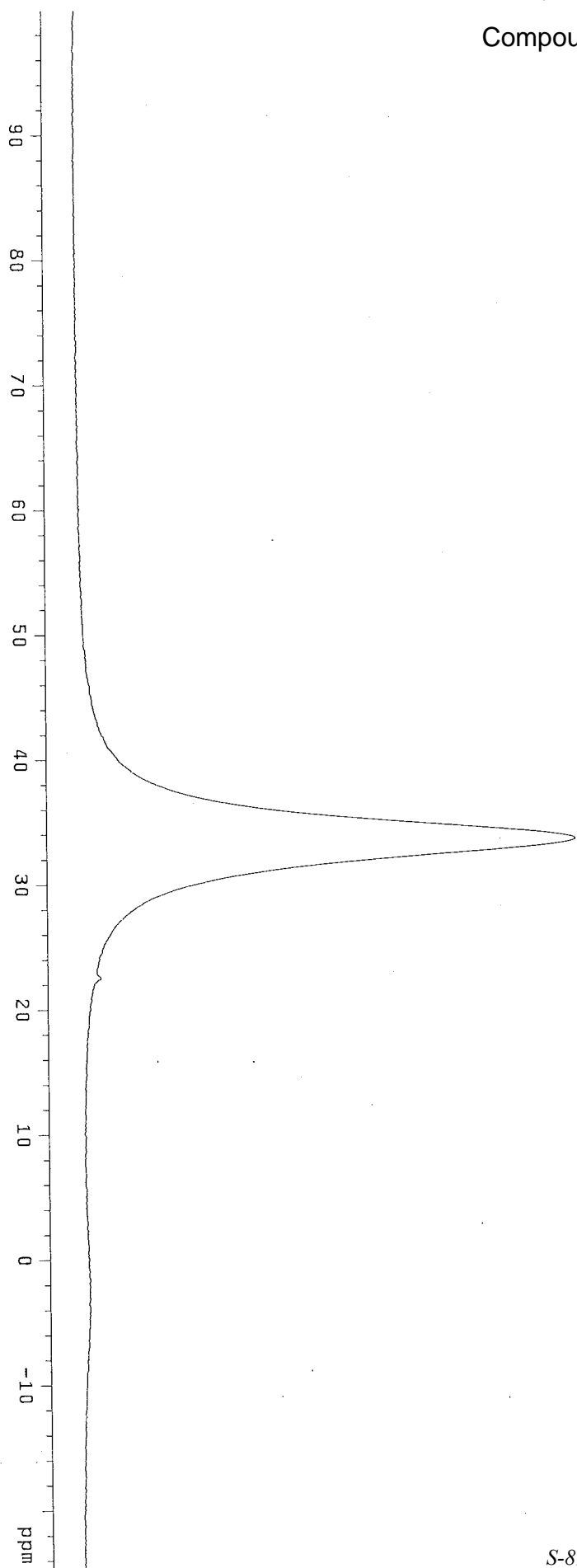
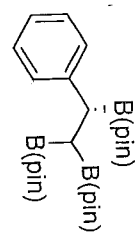
Compound 12



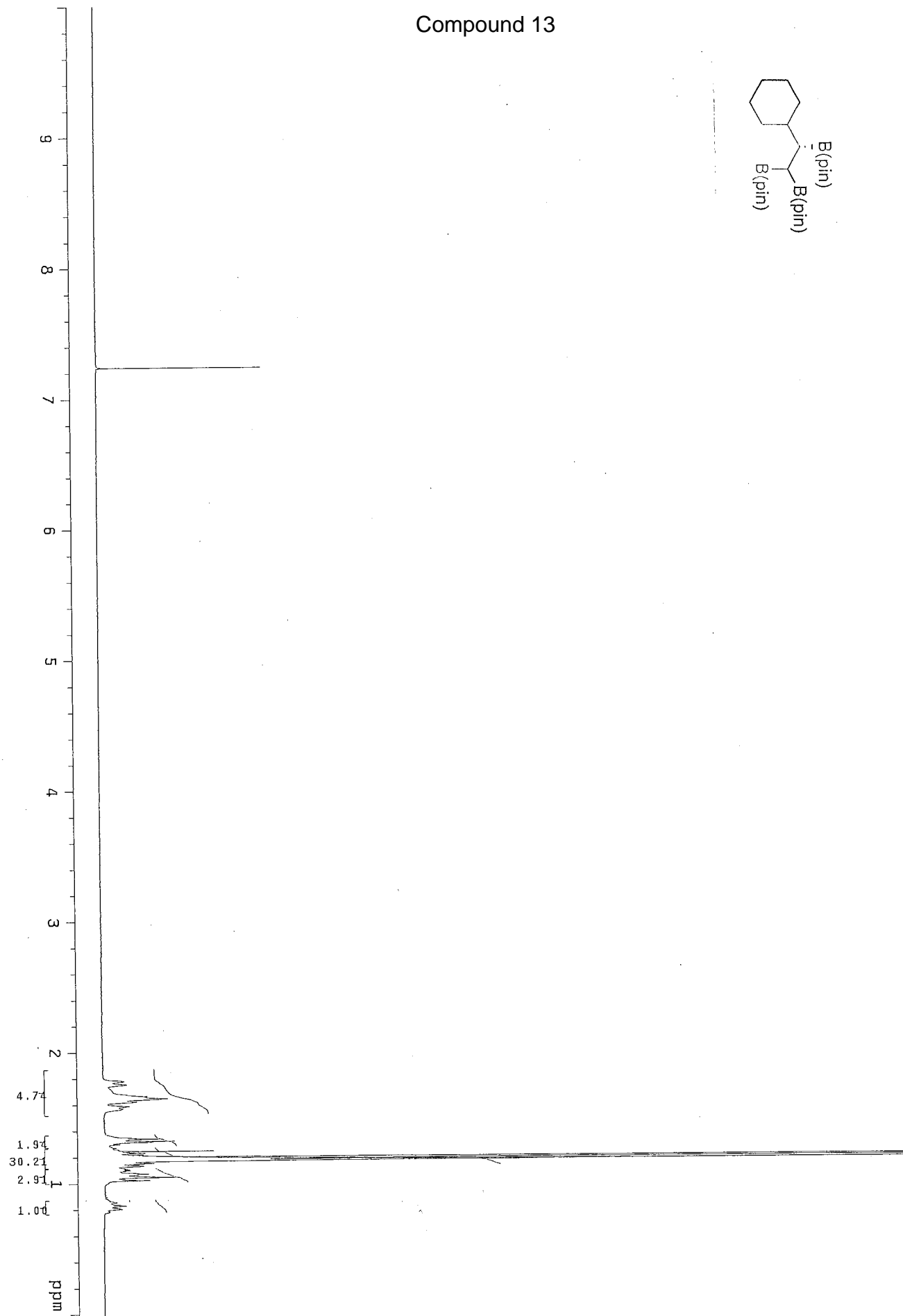
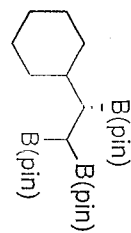
Compound 12



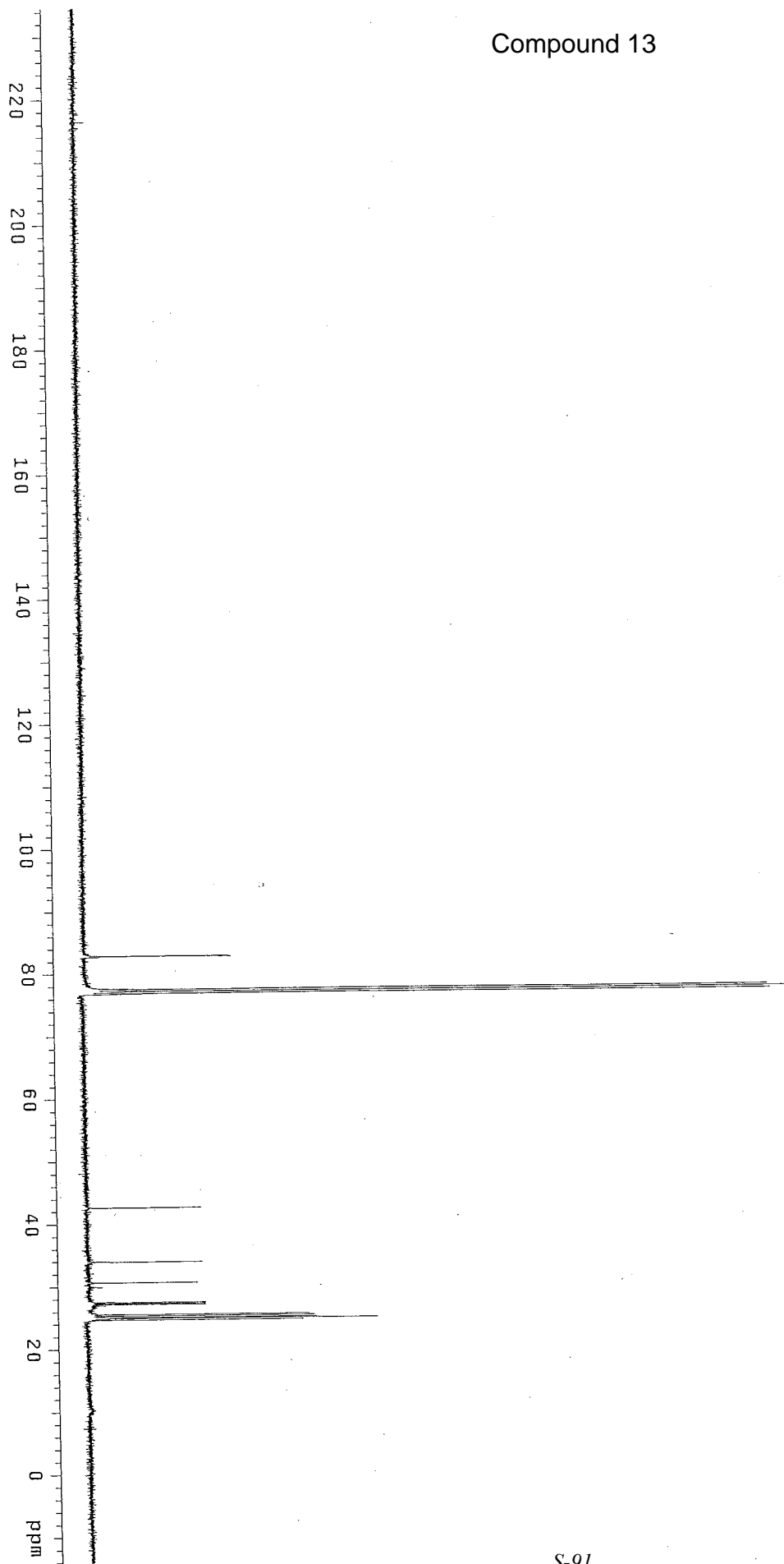
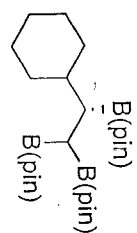
Compound 12



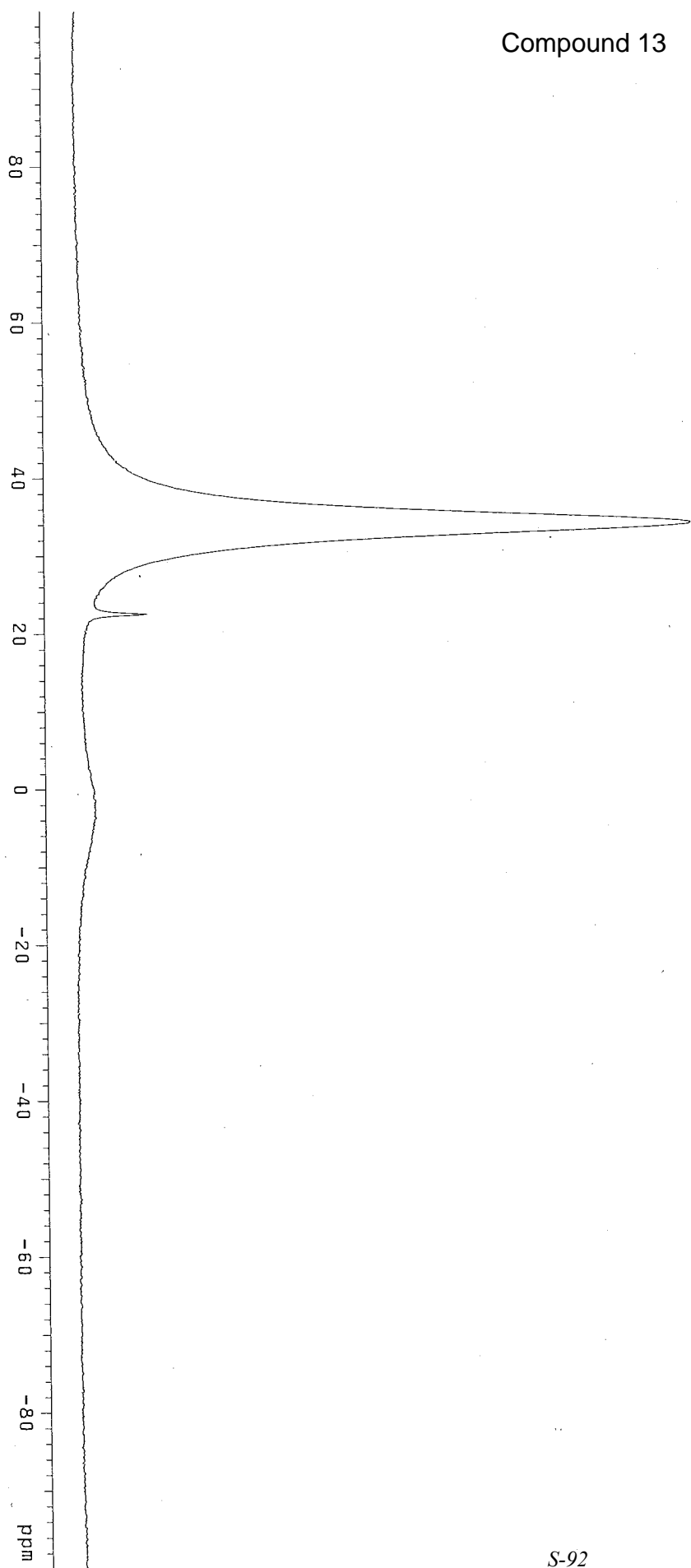
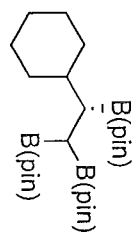
Compound 13



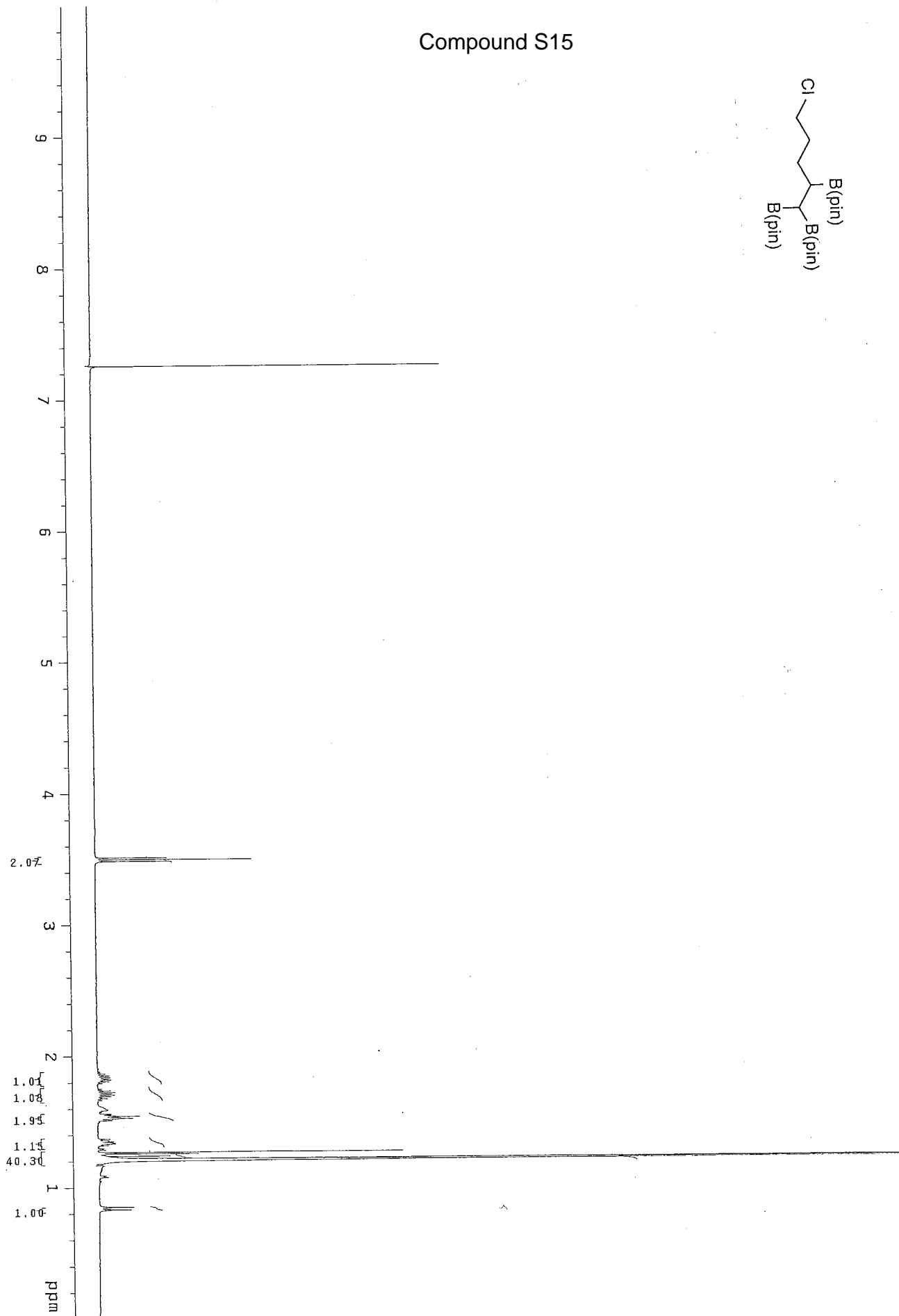
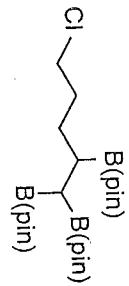
Compound 13



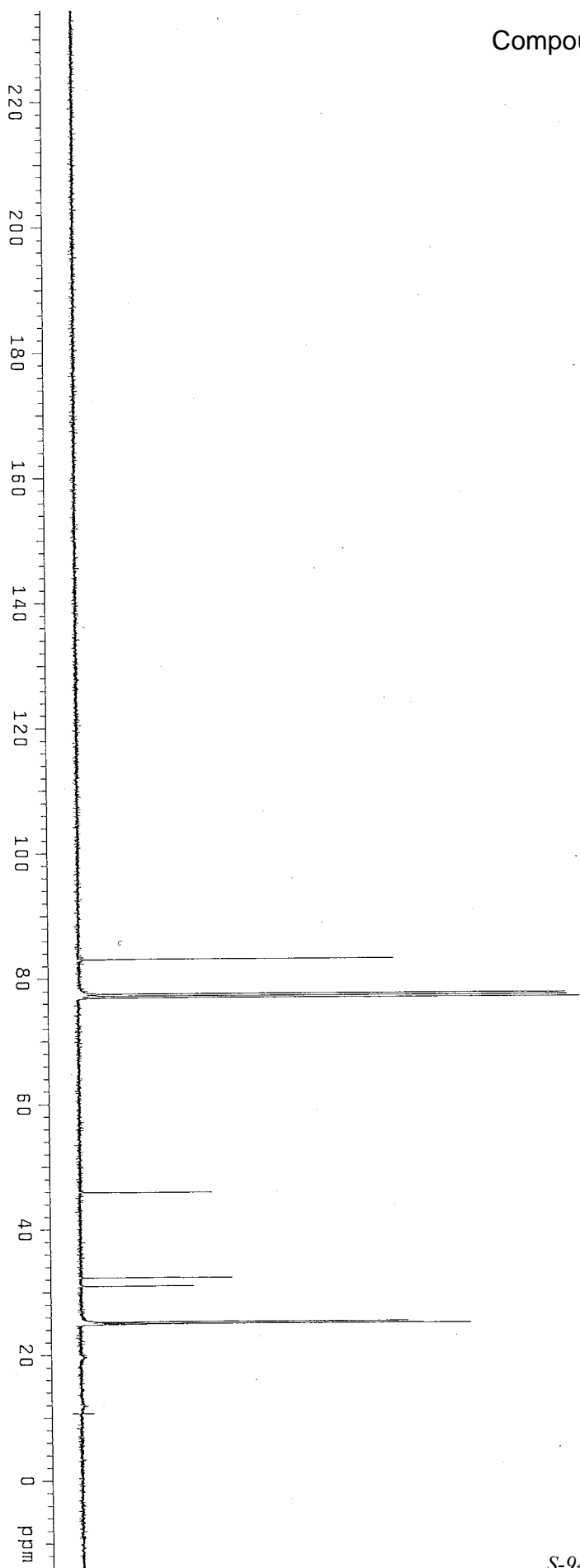
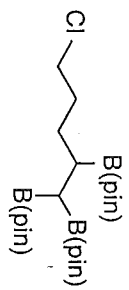
Compound 13



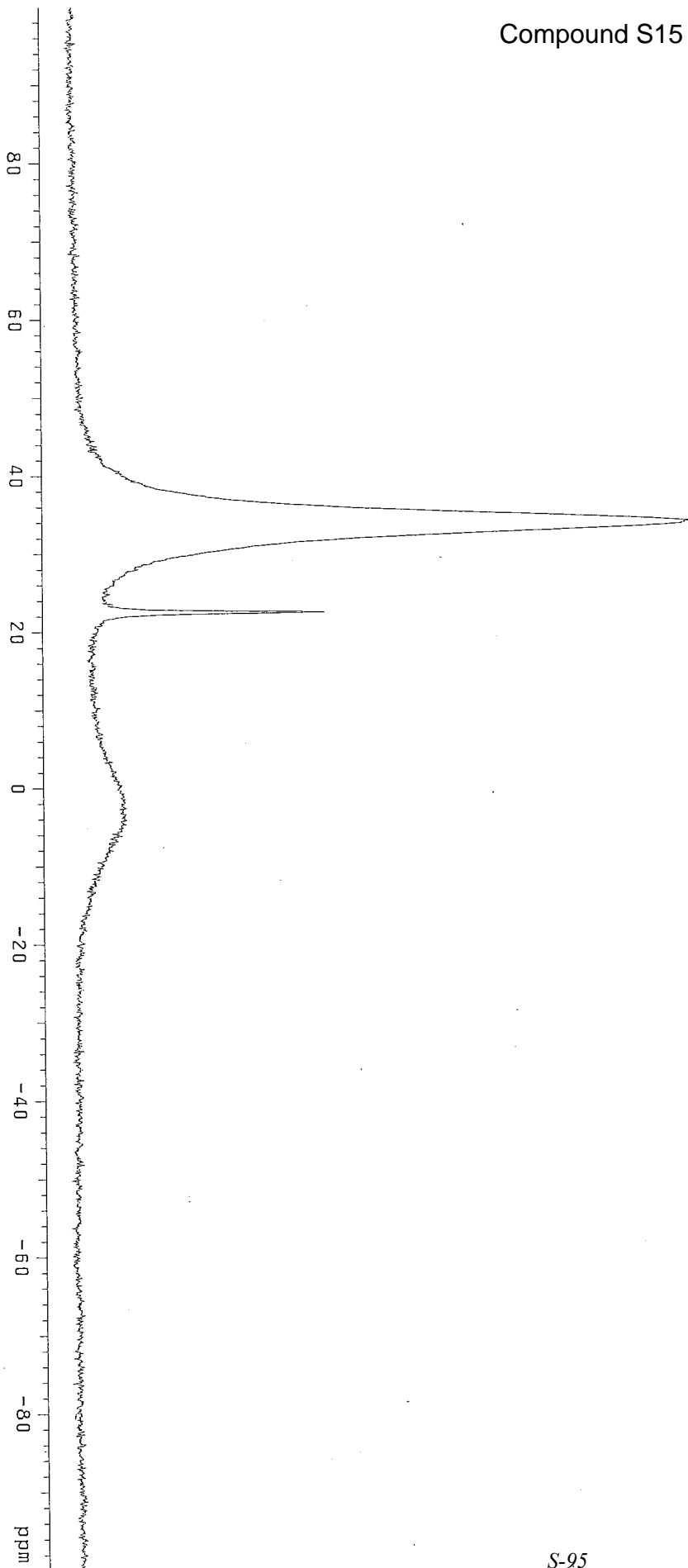
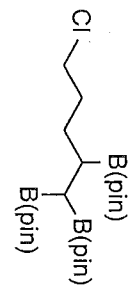
Compound S15



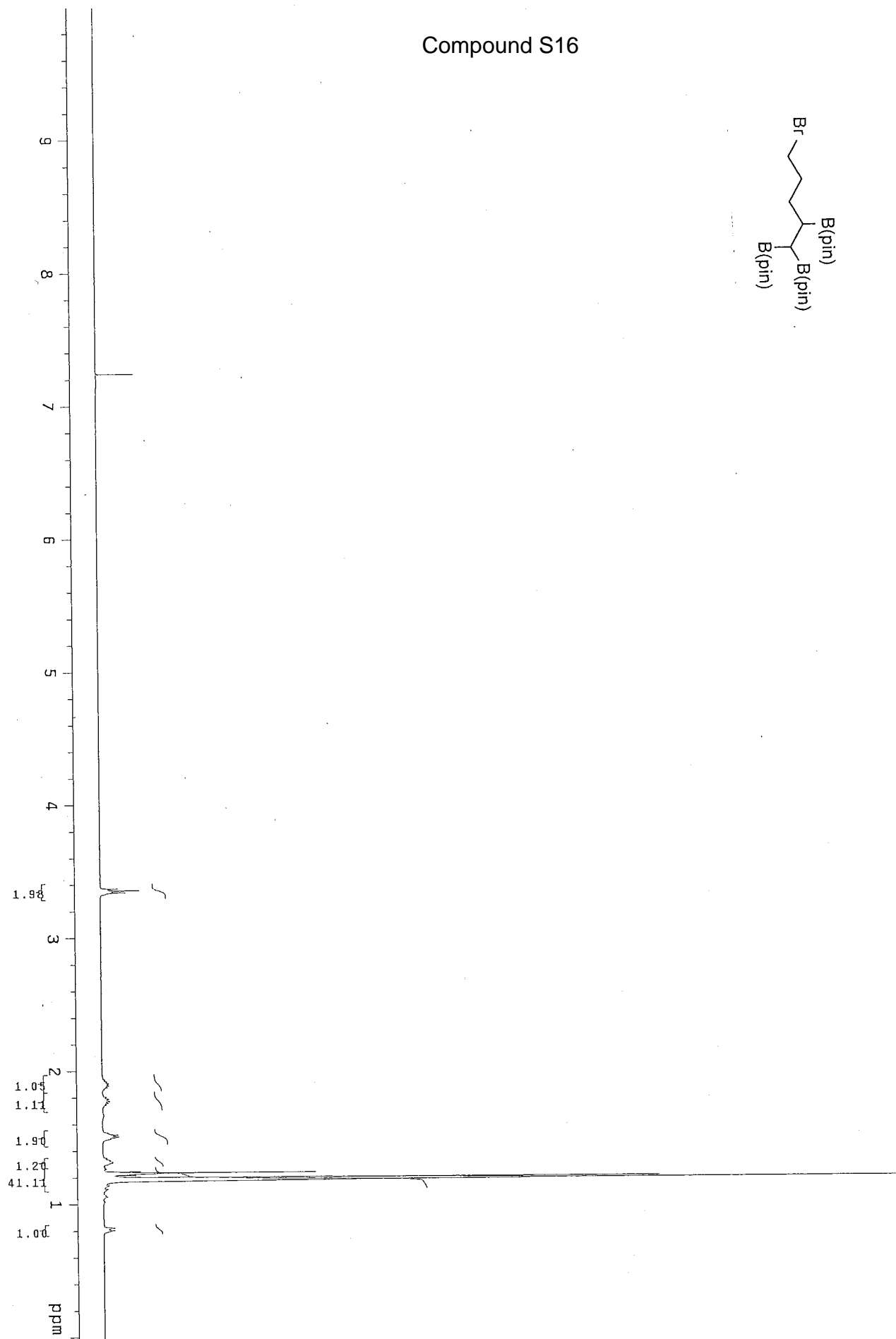
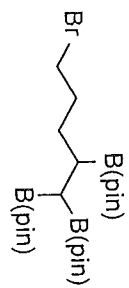
Compound S15



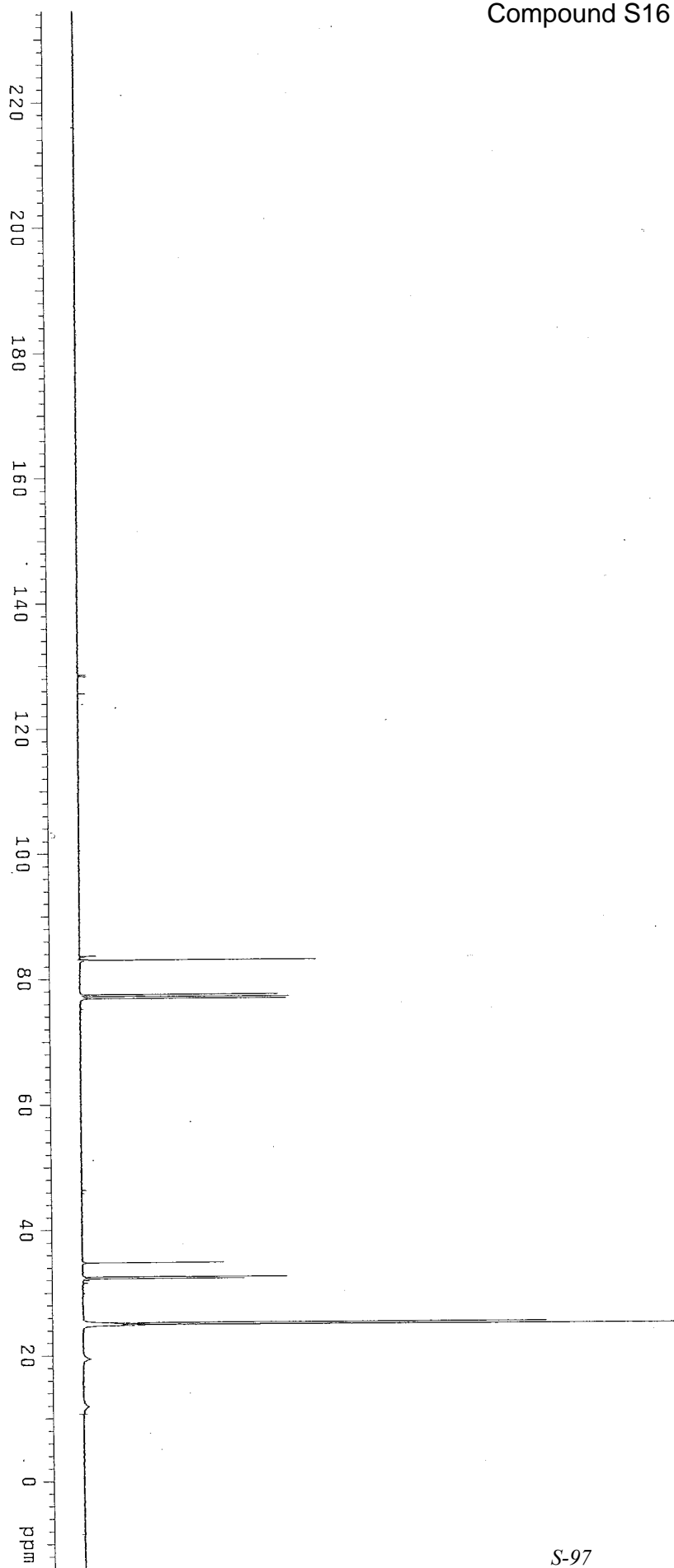
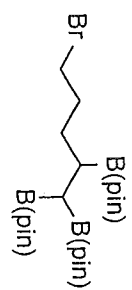
Compound S15



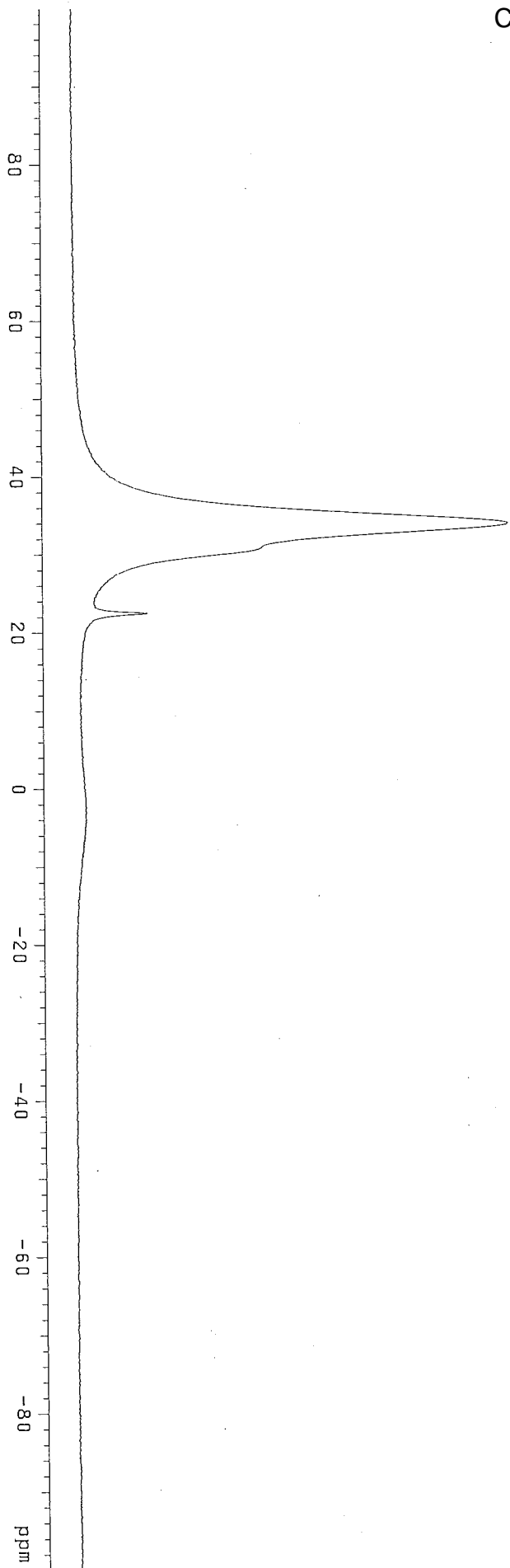
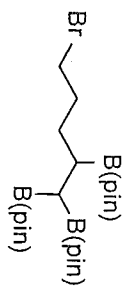
Compound S16



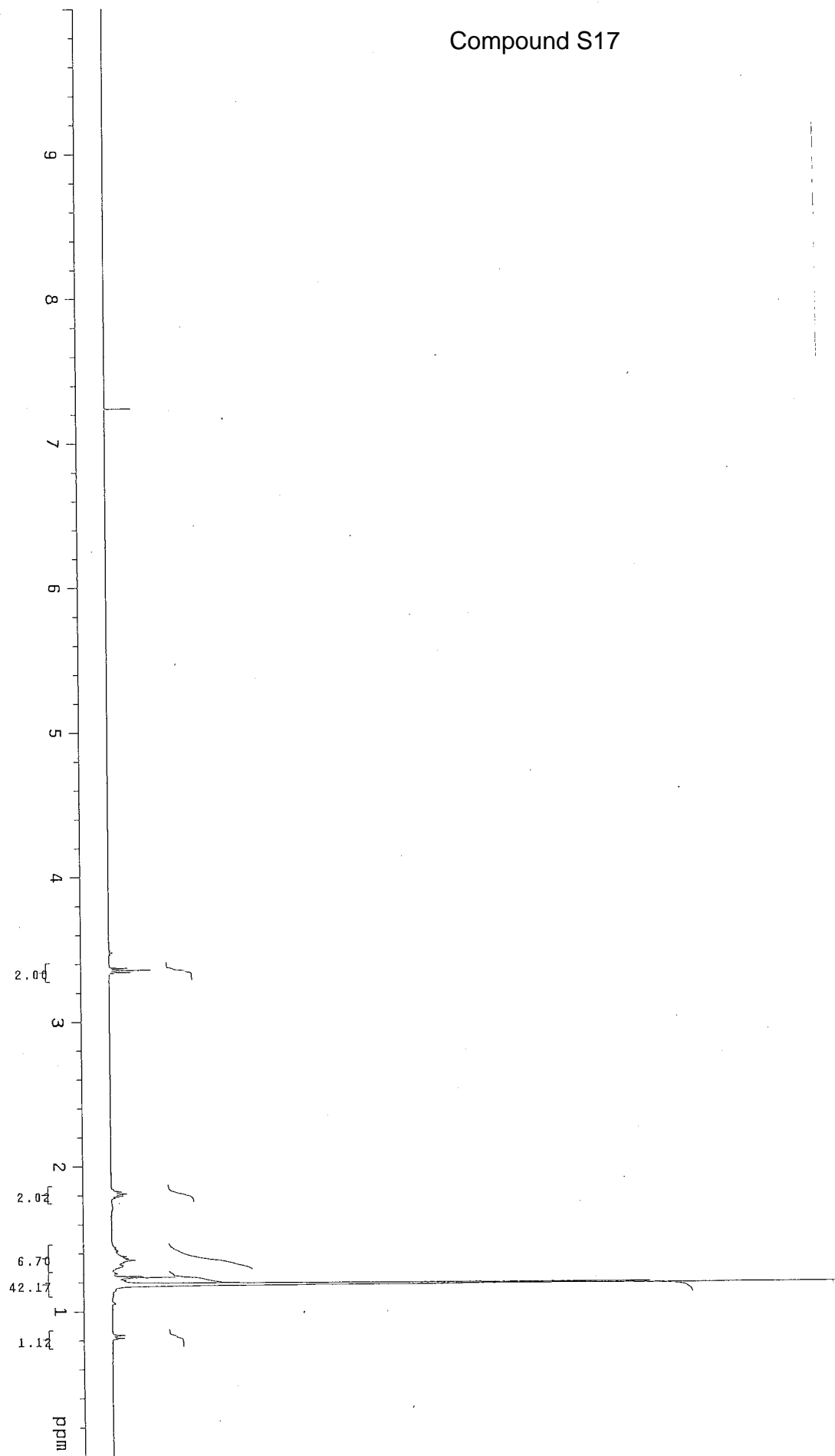
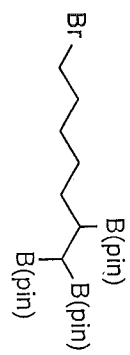
Compound S16



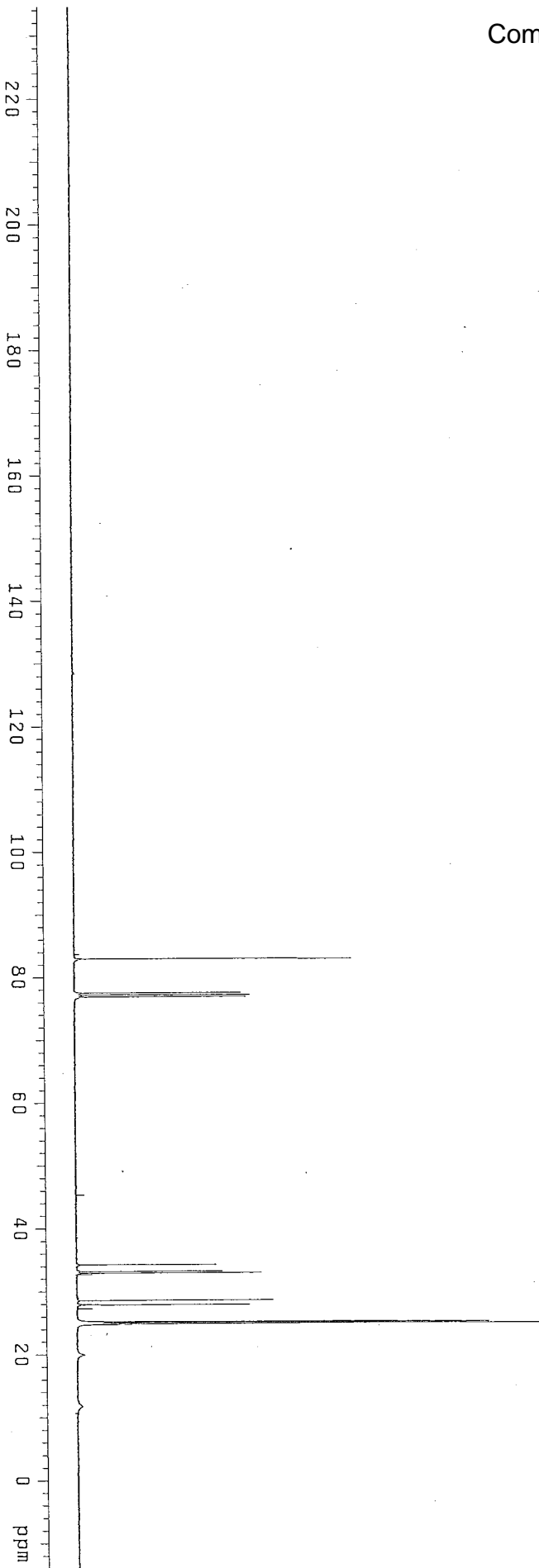
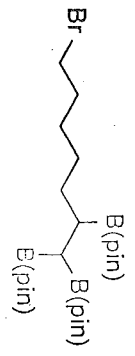
Compound S16



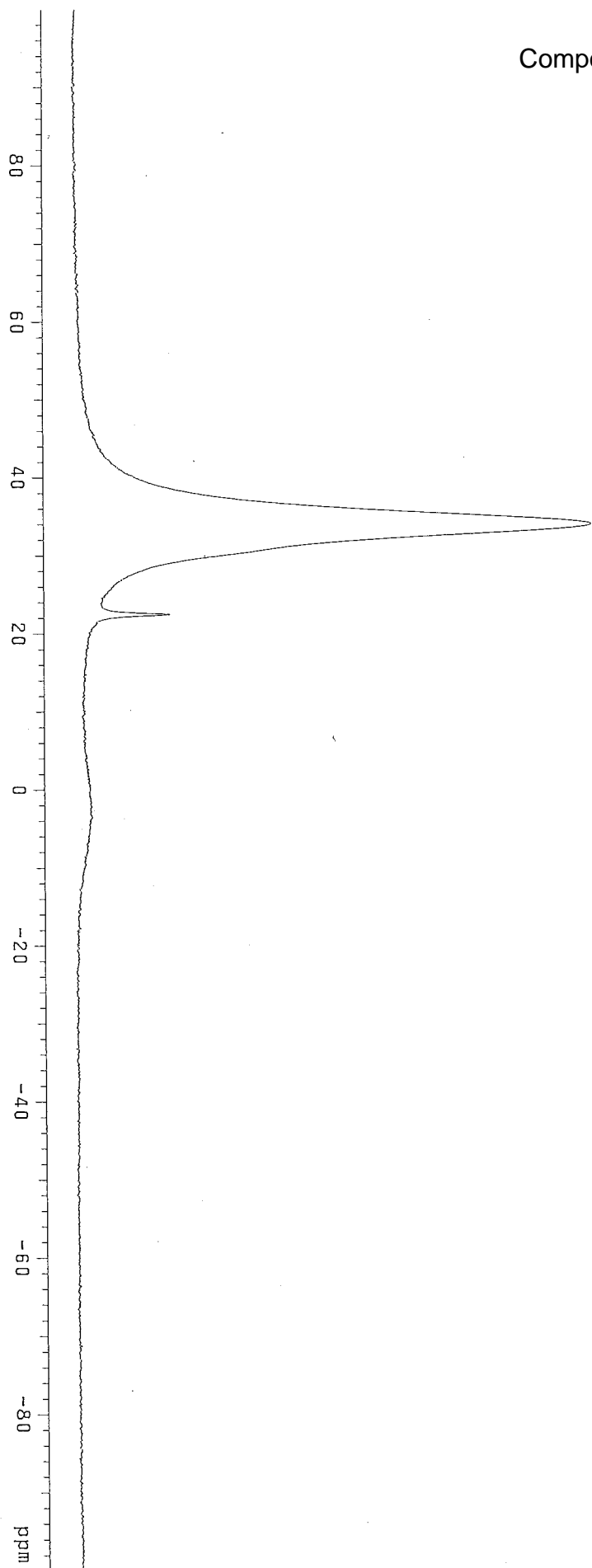
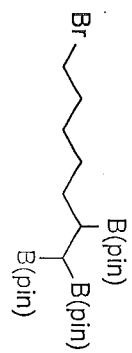
Compound S17



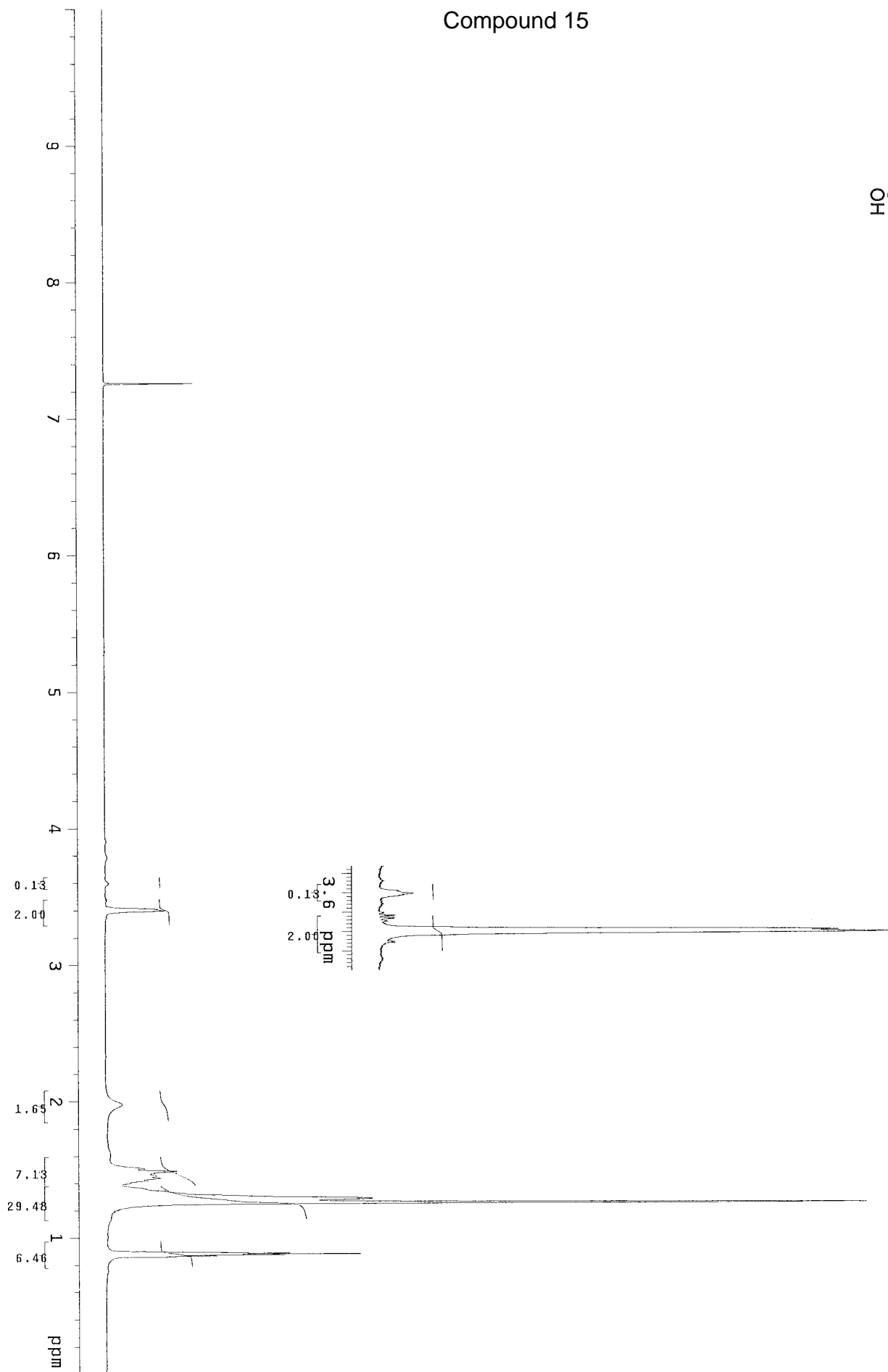
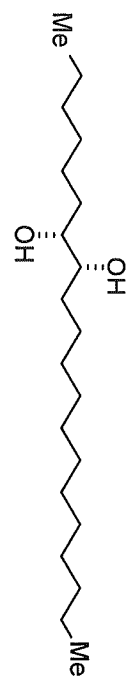
Compound S17



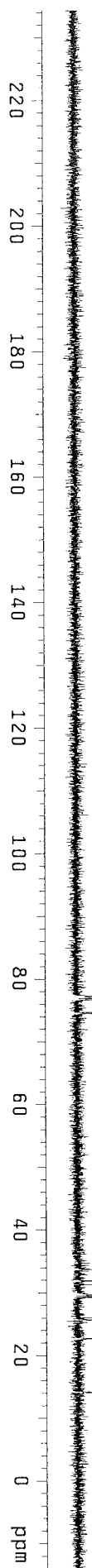
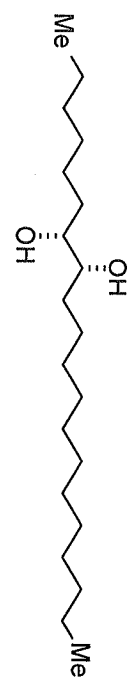
Compound S17



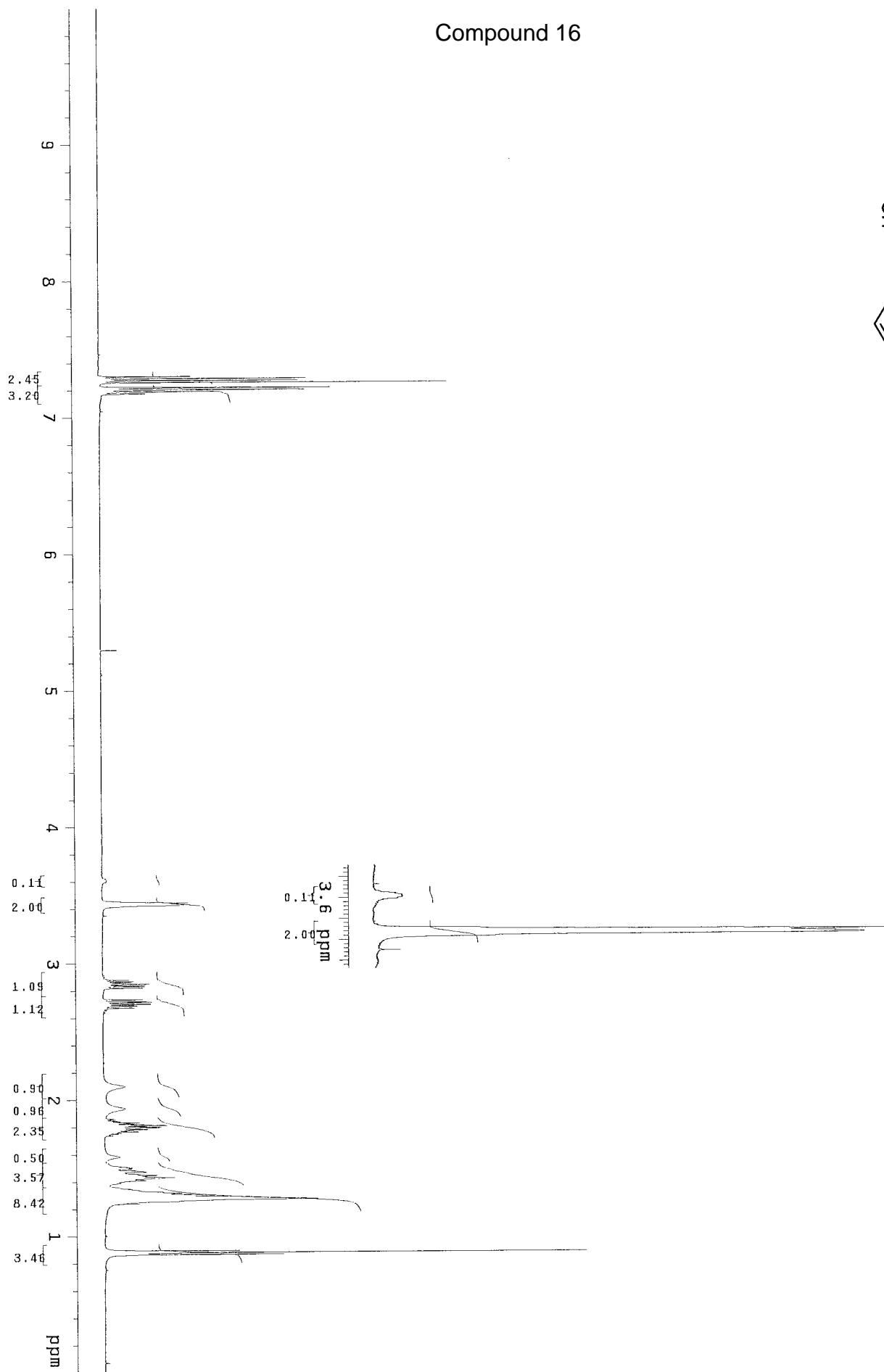
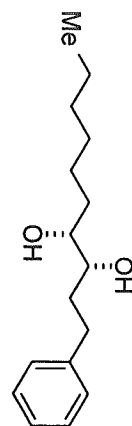
Compound 15



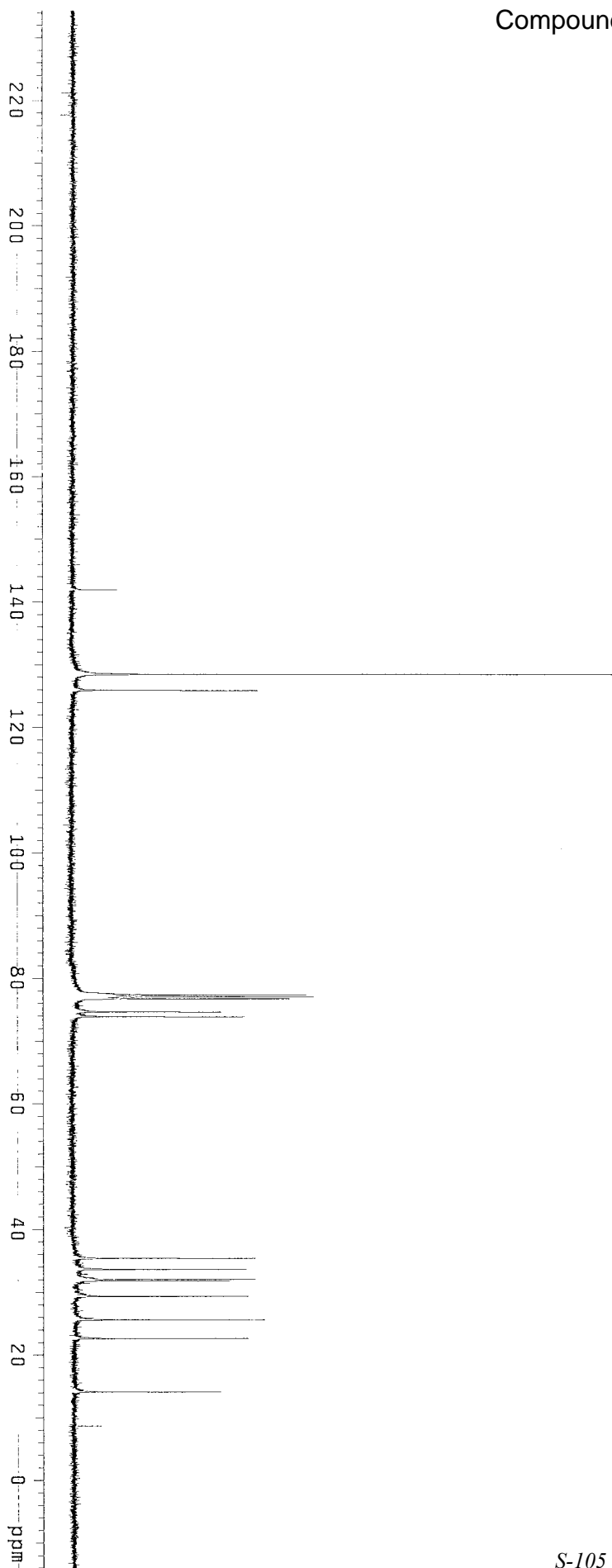
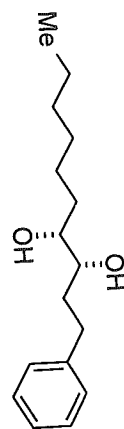
Compound 15



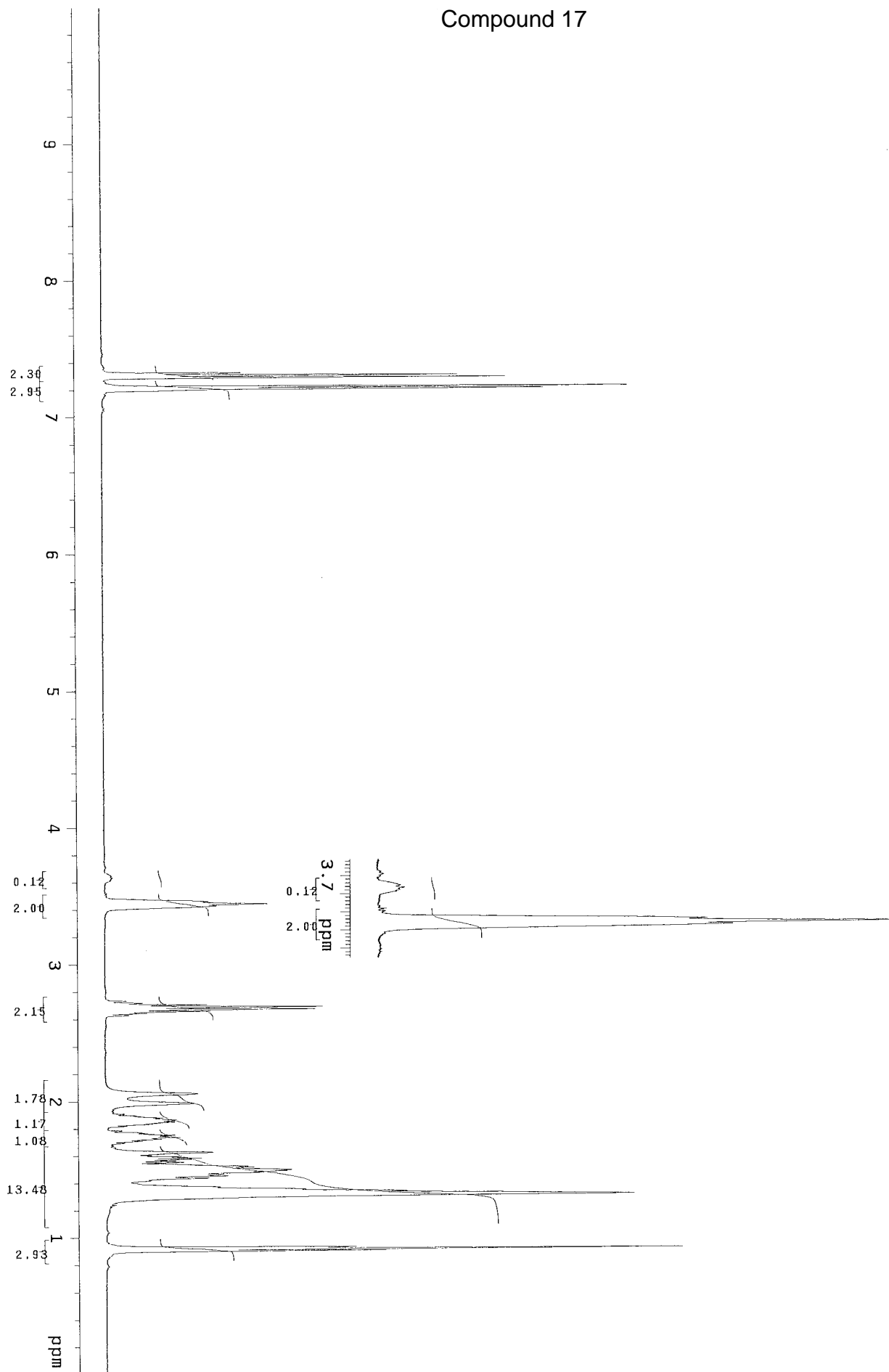
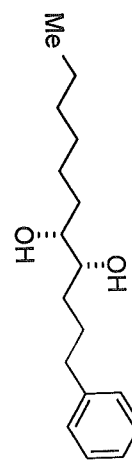
Compound 16



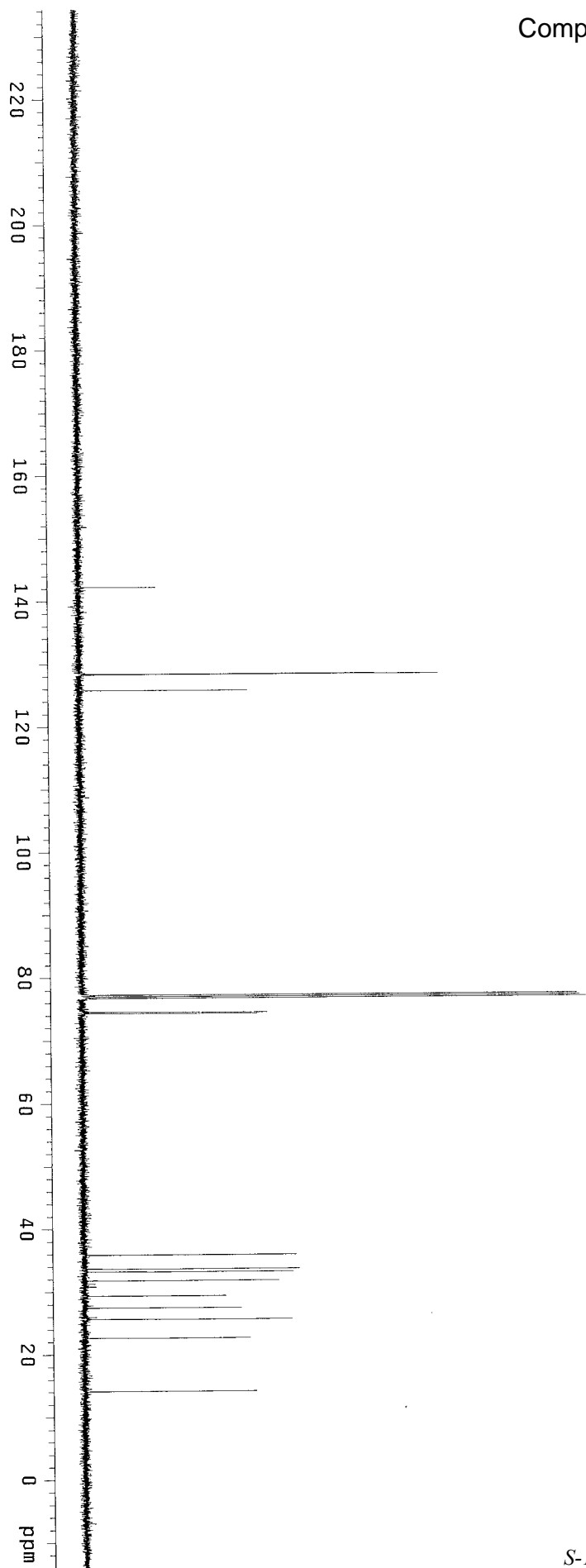
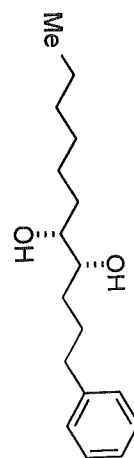
Compound 16



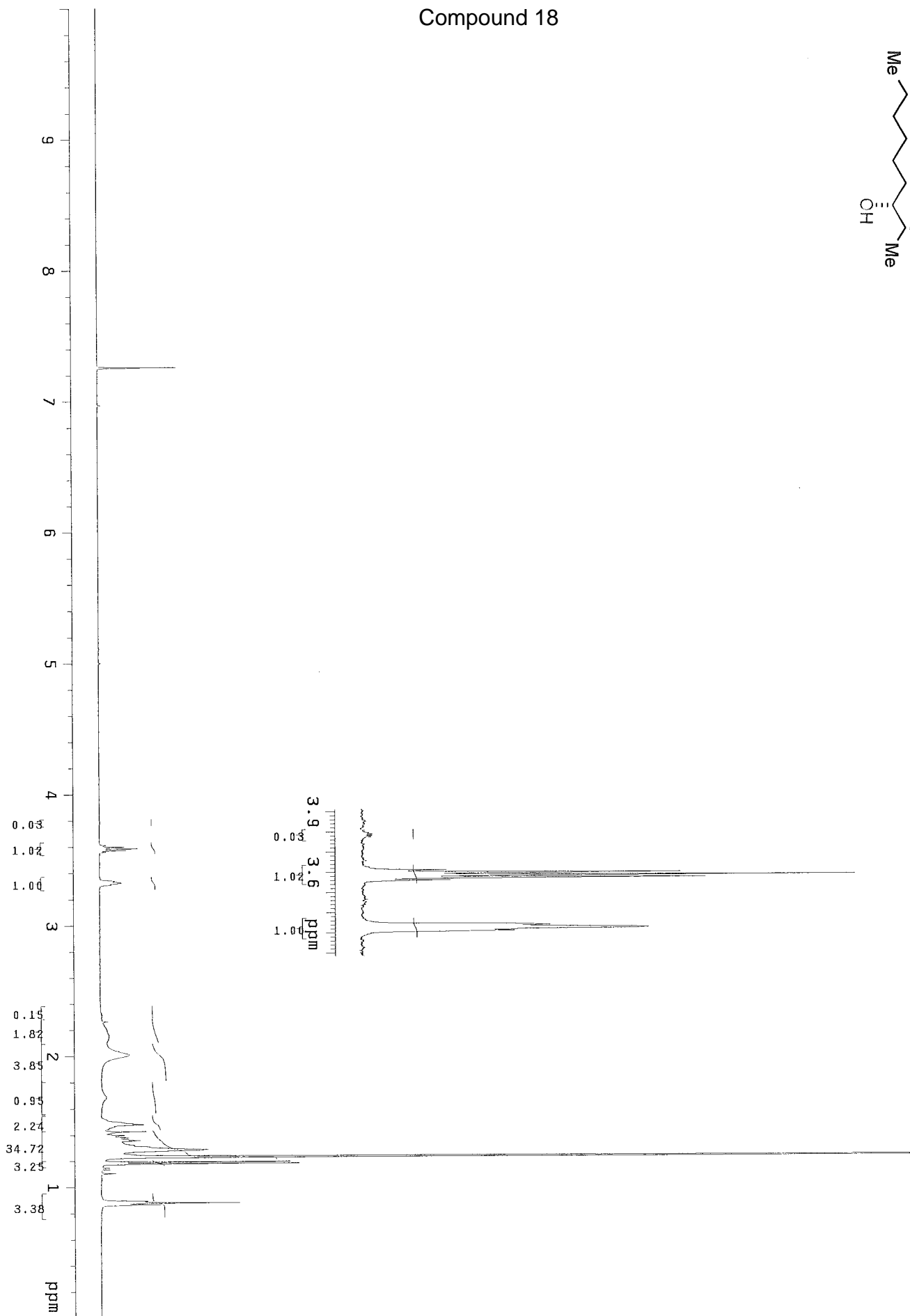
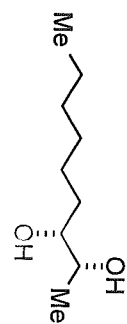
Compound 17



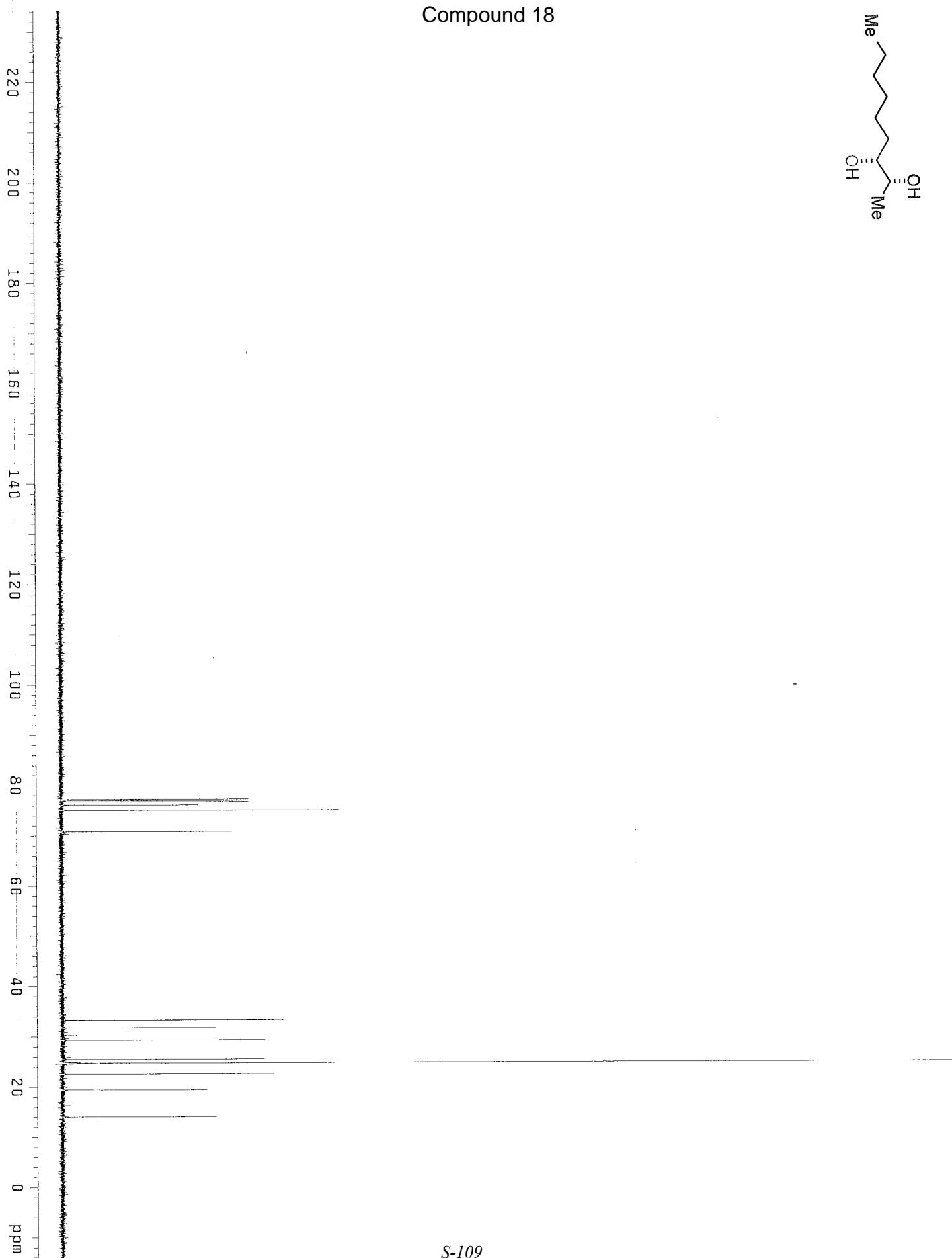
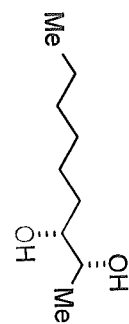
Compound 17



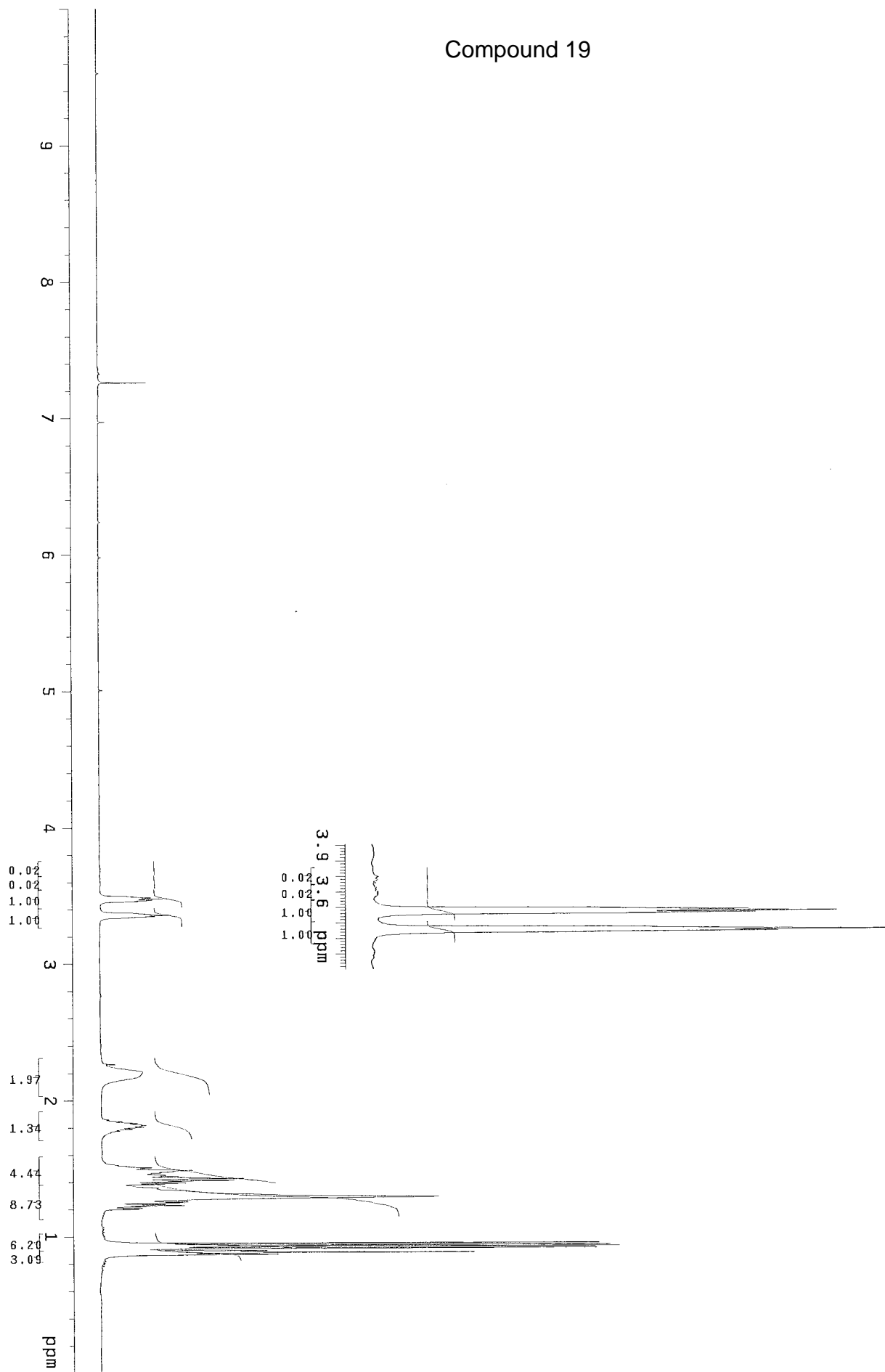
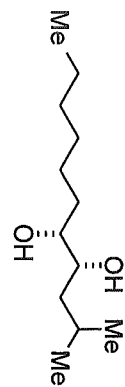
Compound 18

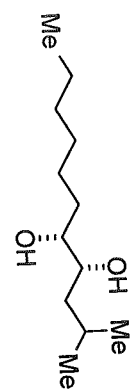


Compound 18

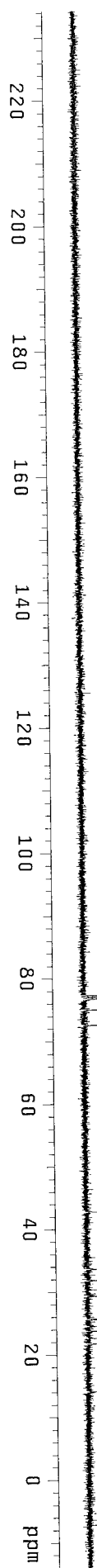


Compound 19

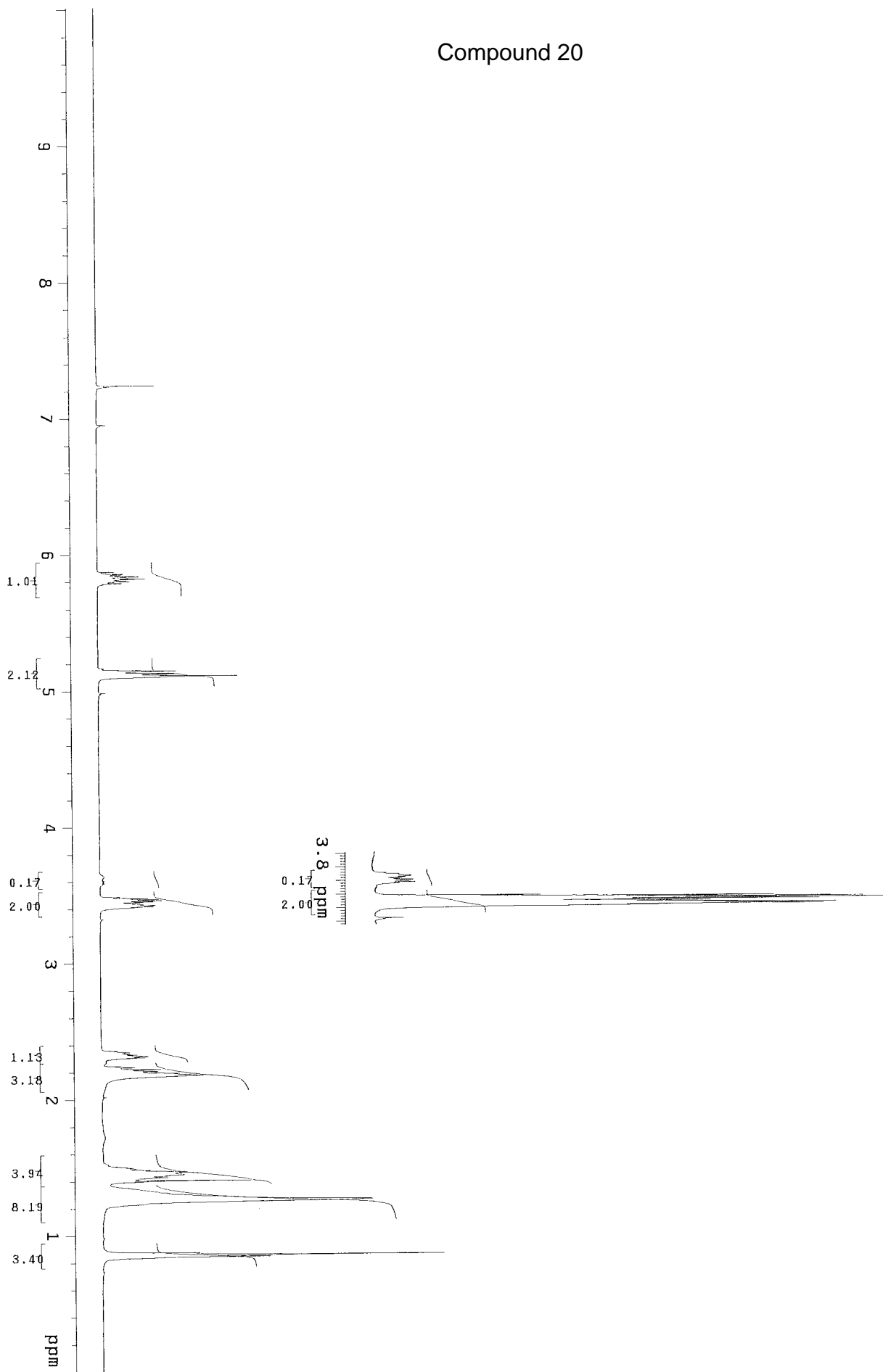
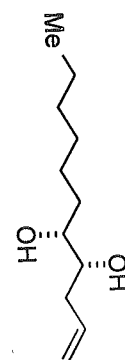


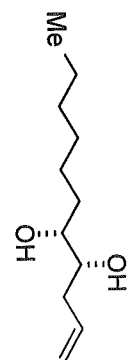


Compound 19



Compound 20

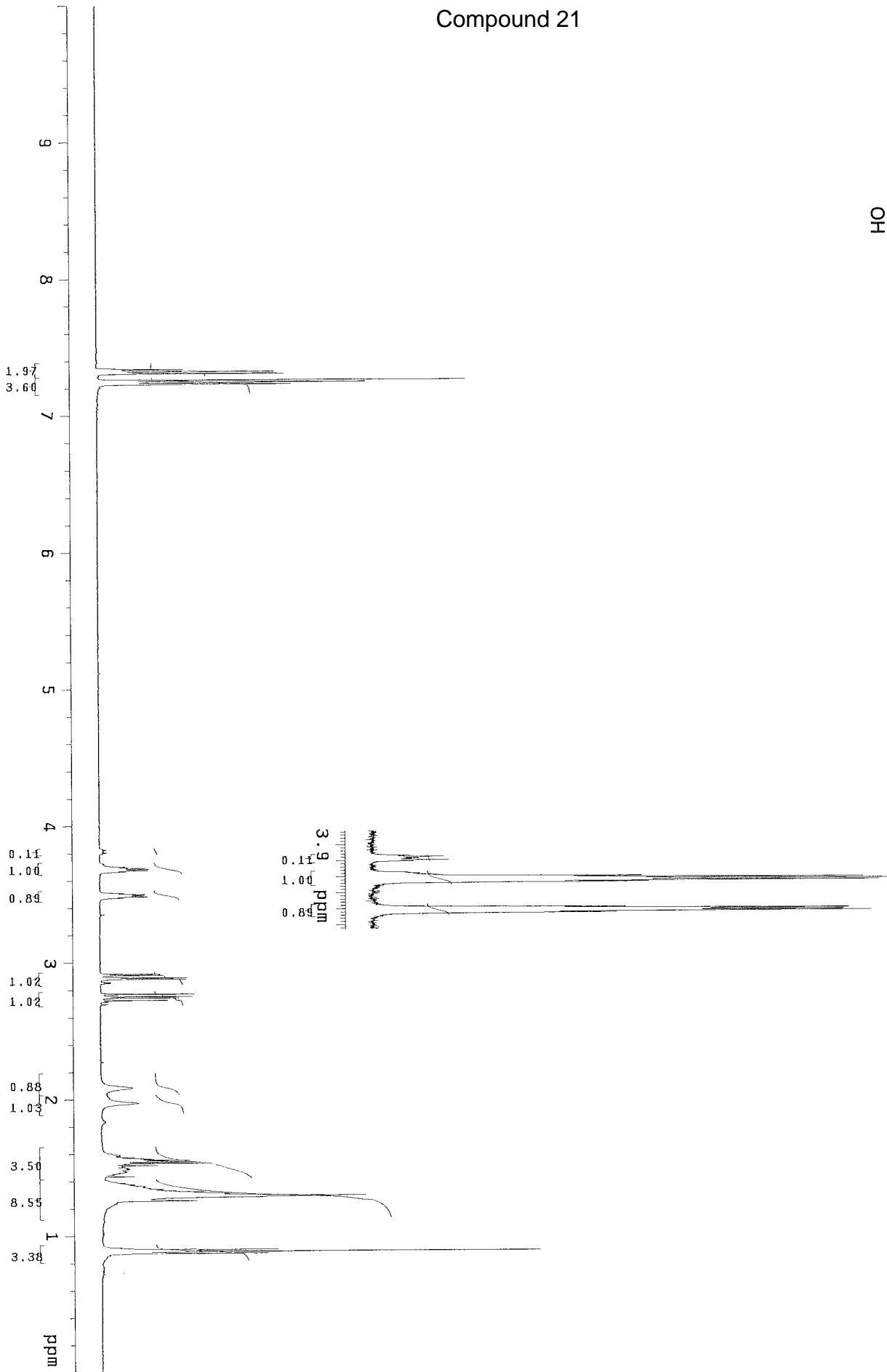
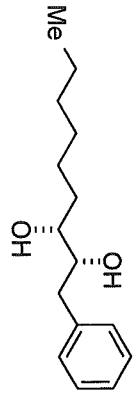




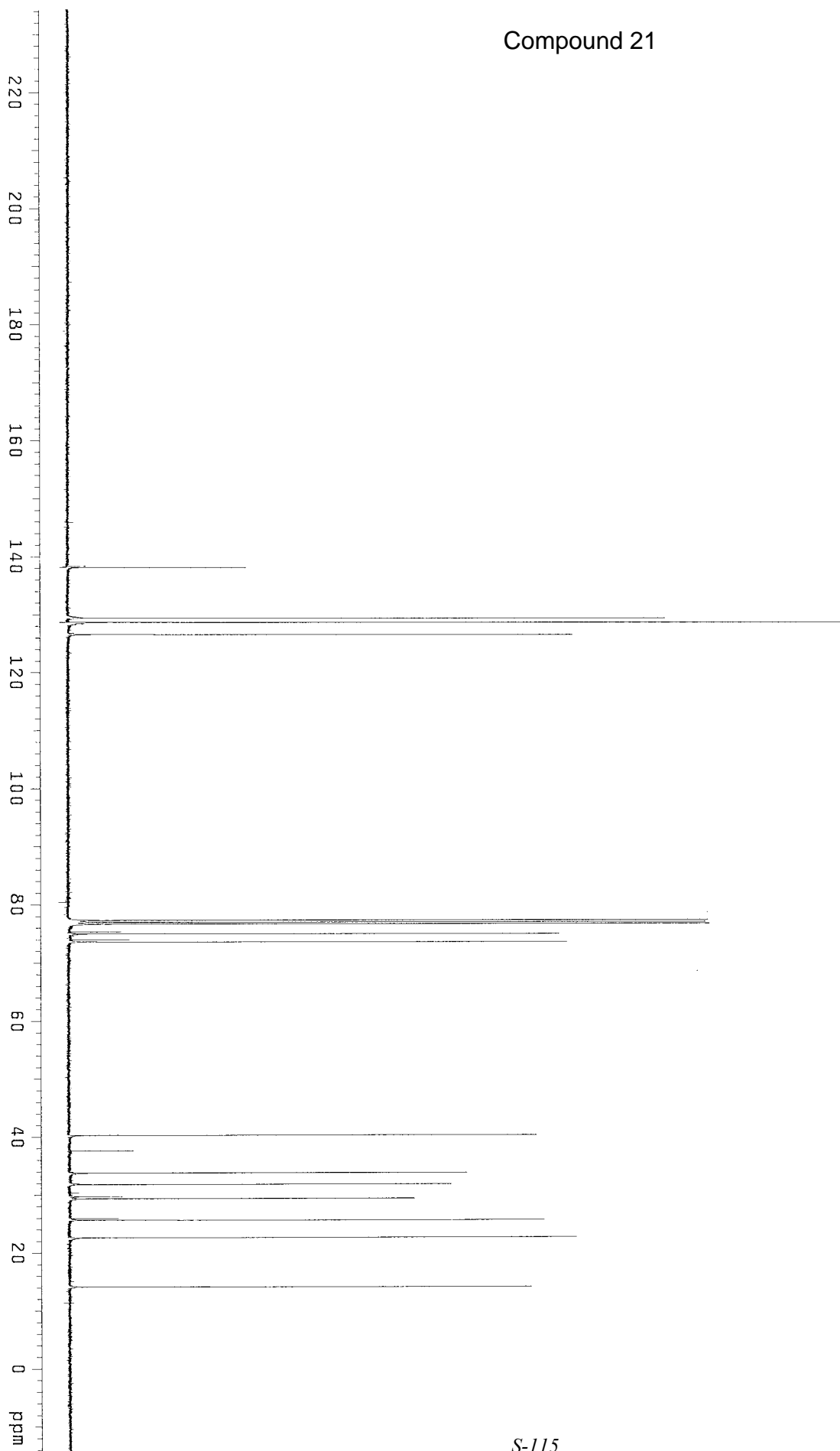
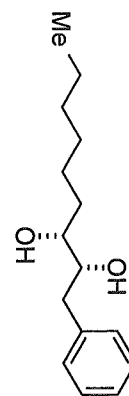
Compound 20



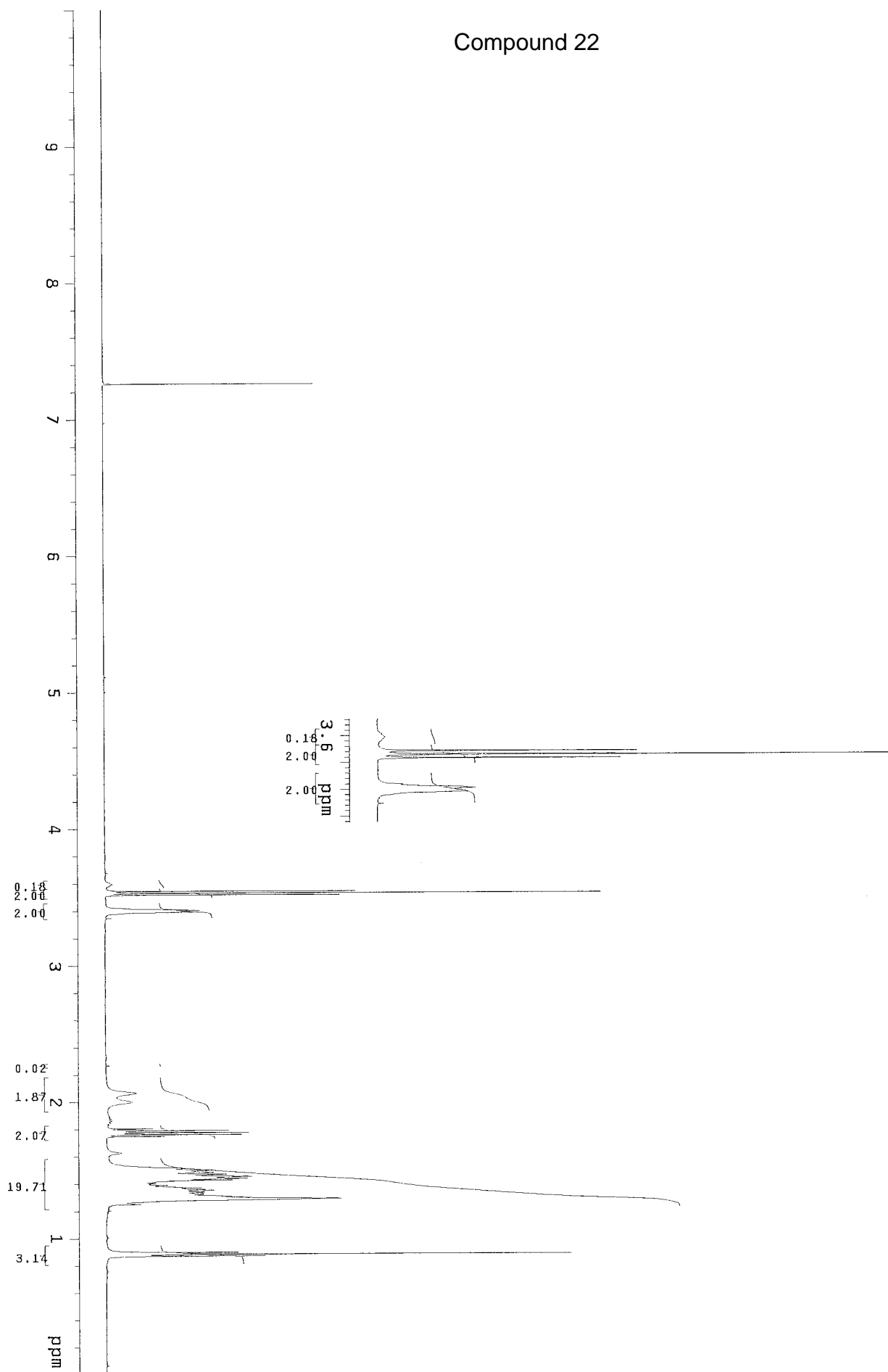
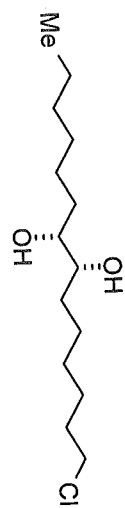
Compound 21



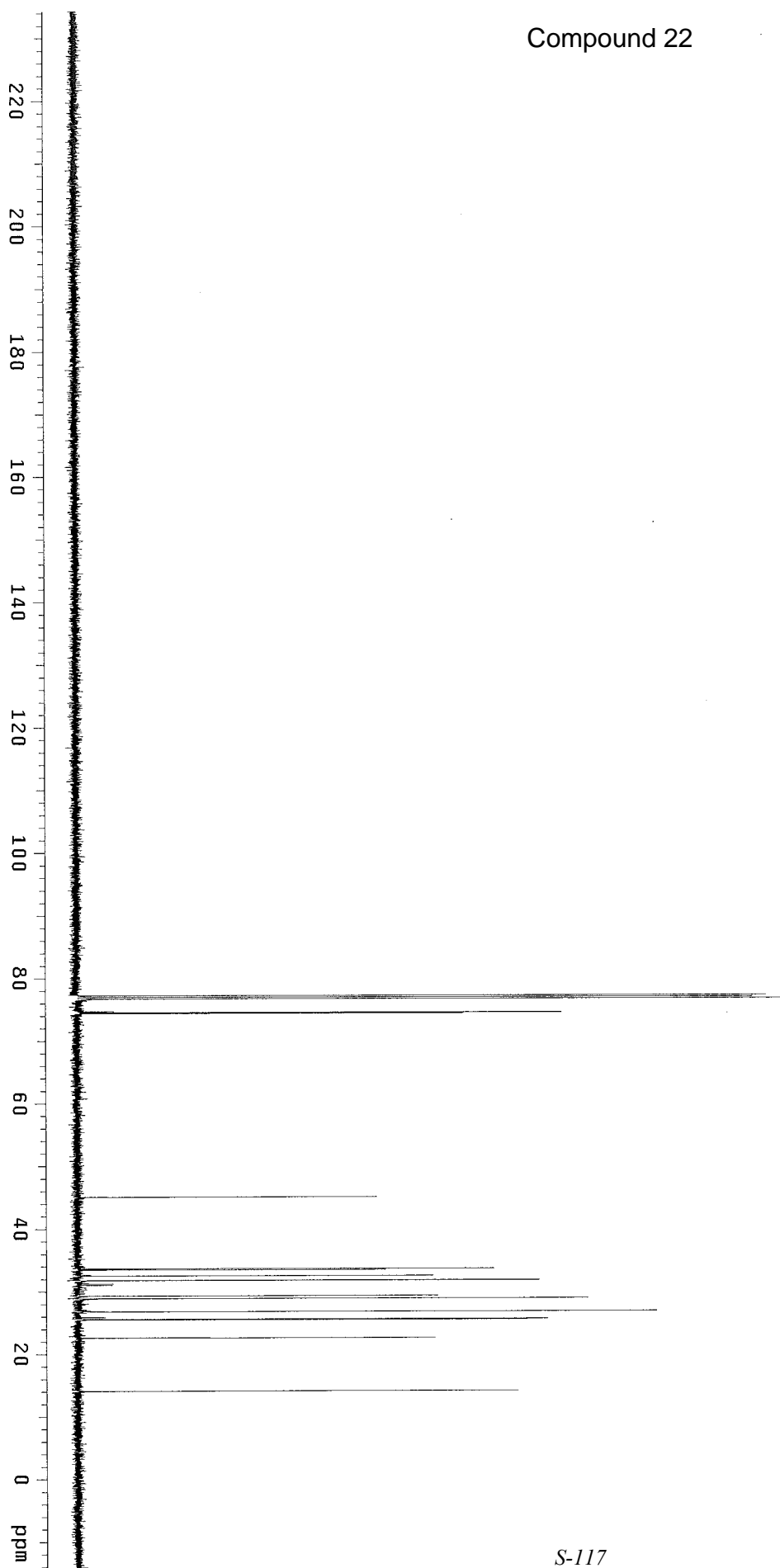
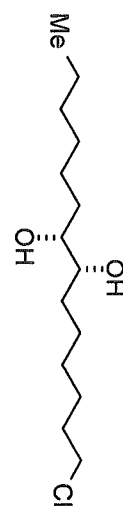
Compound 21



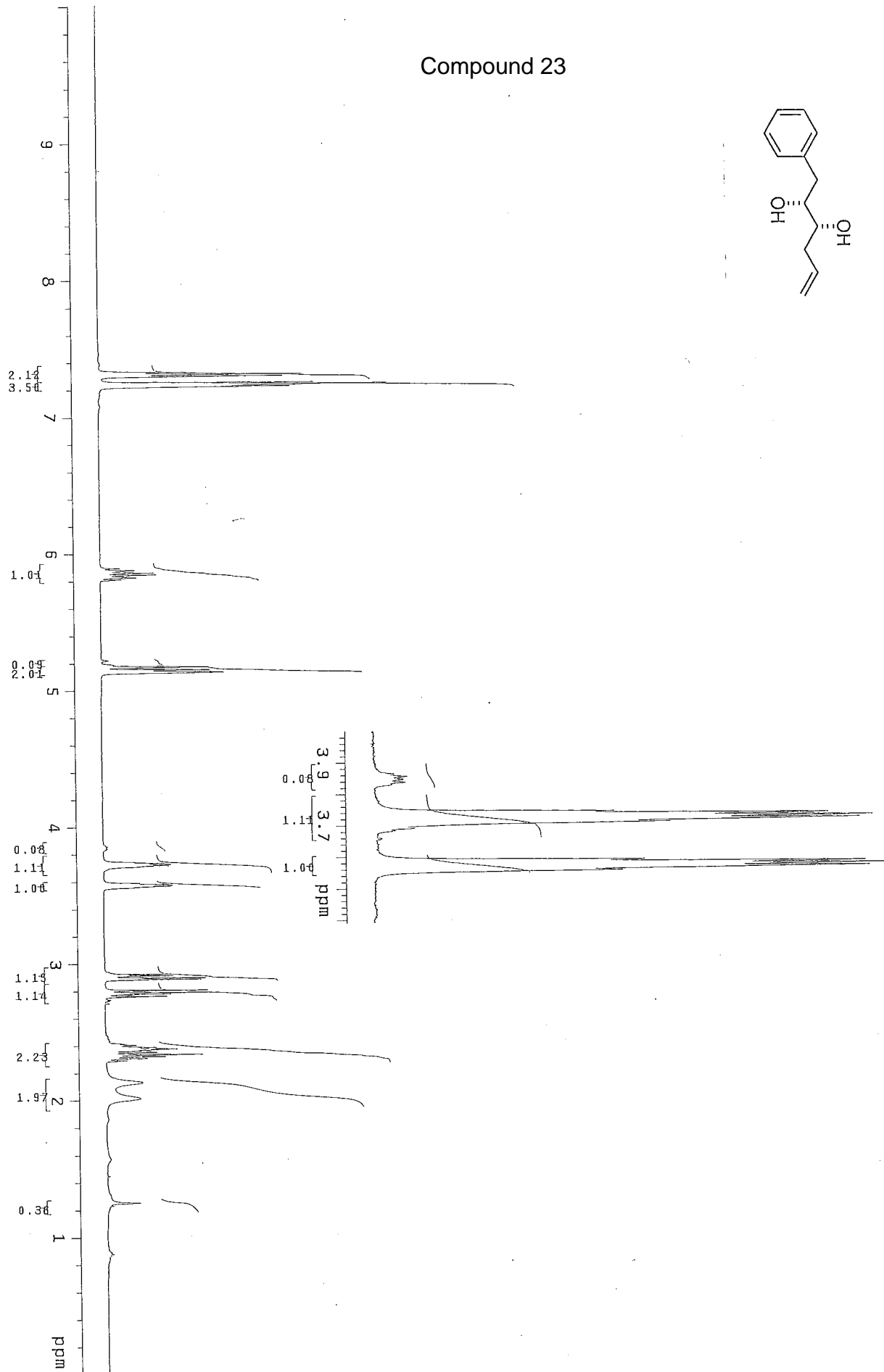
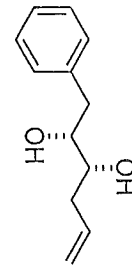
Compound 22



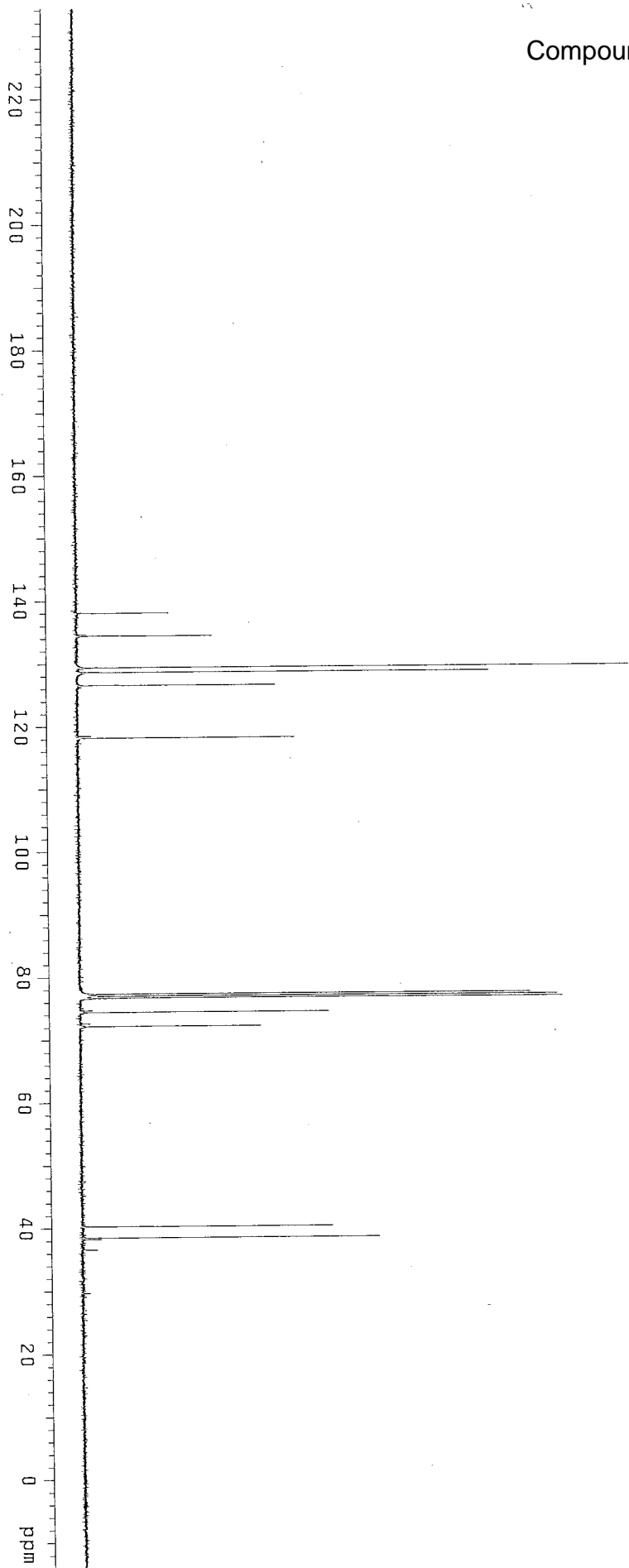
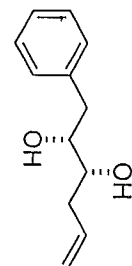
Compound 22



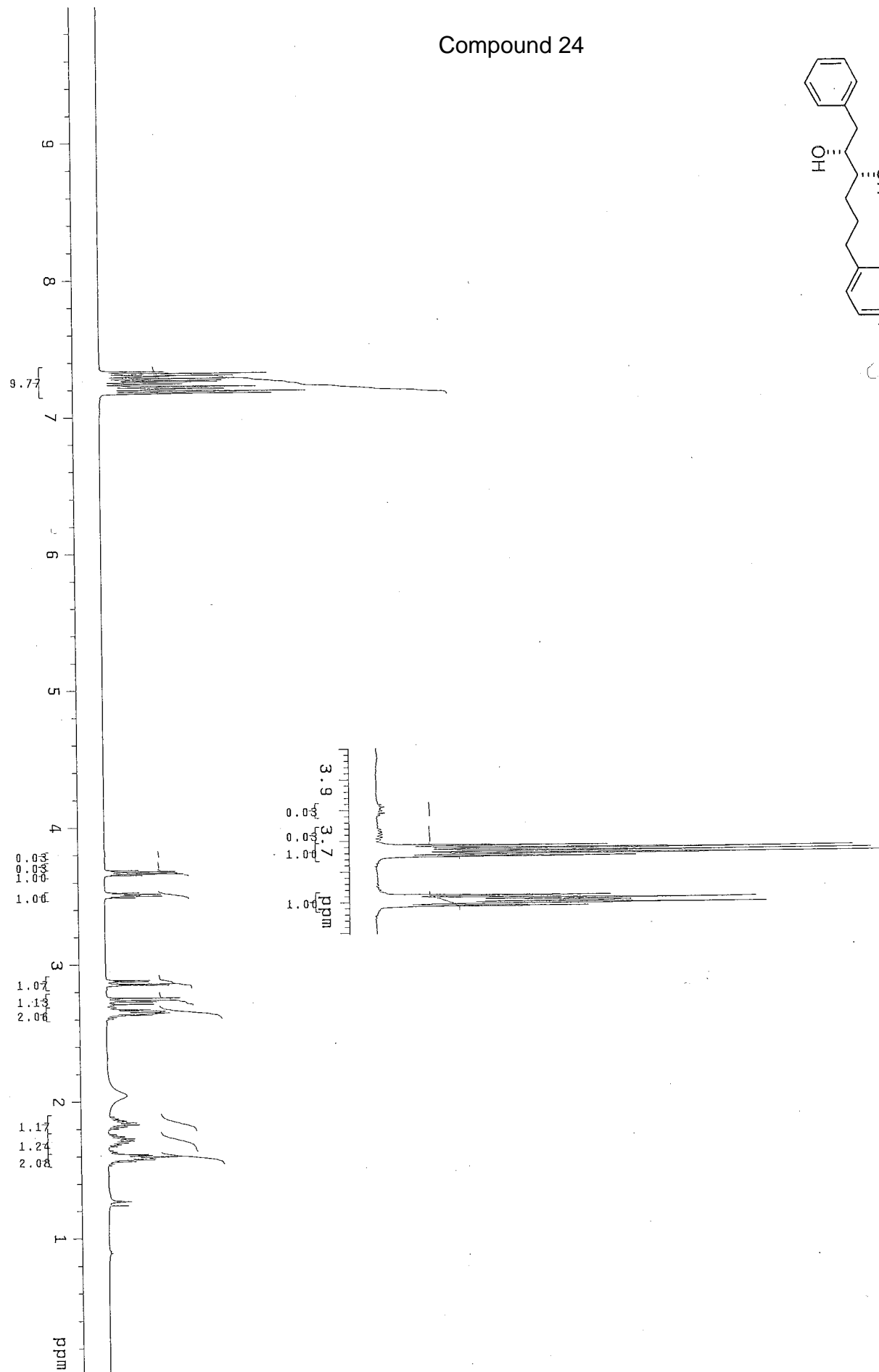
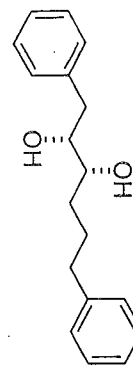
Compound 23



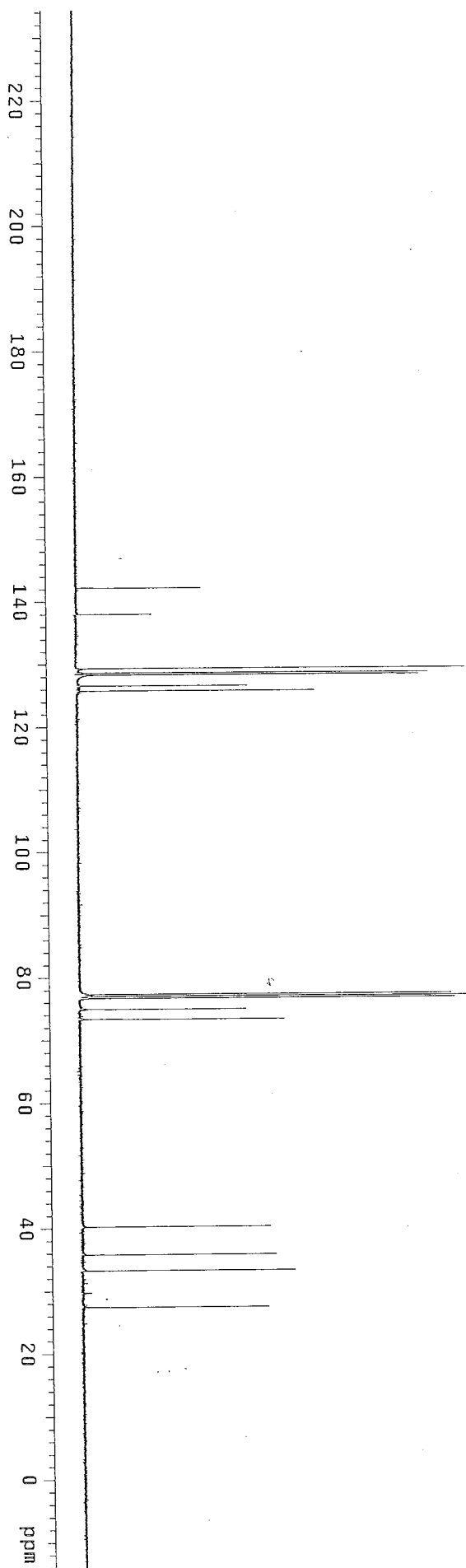
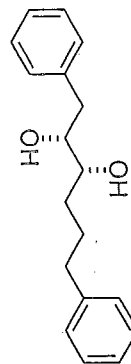
Compound 23



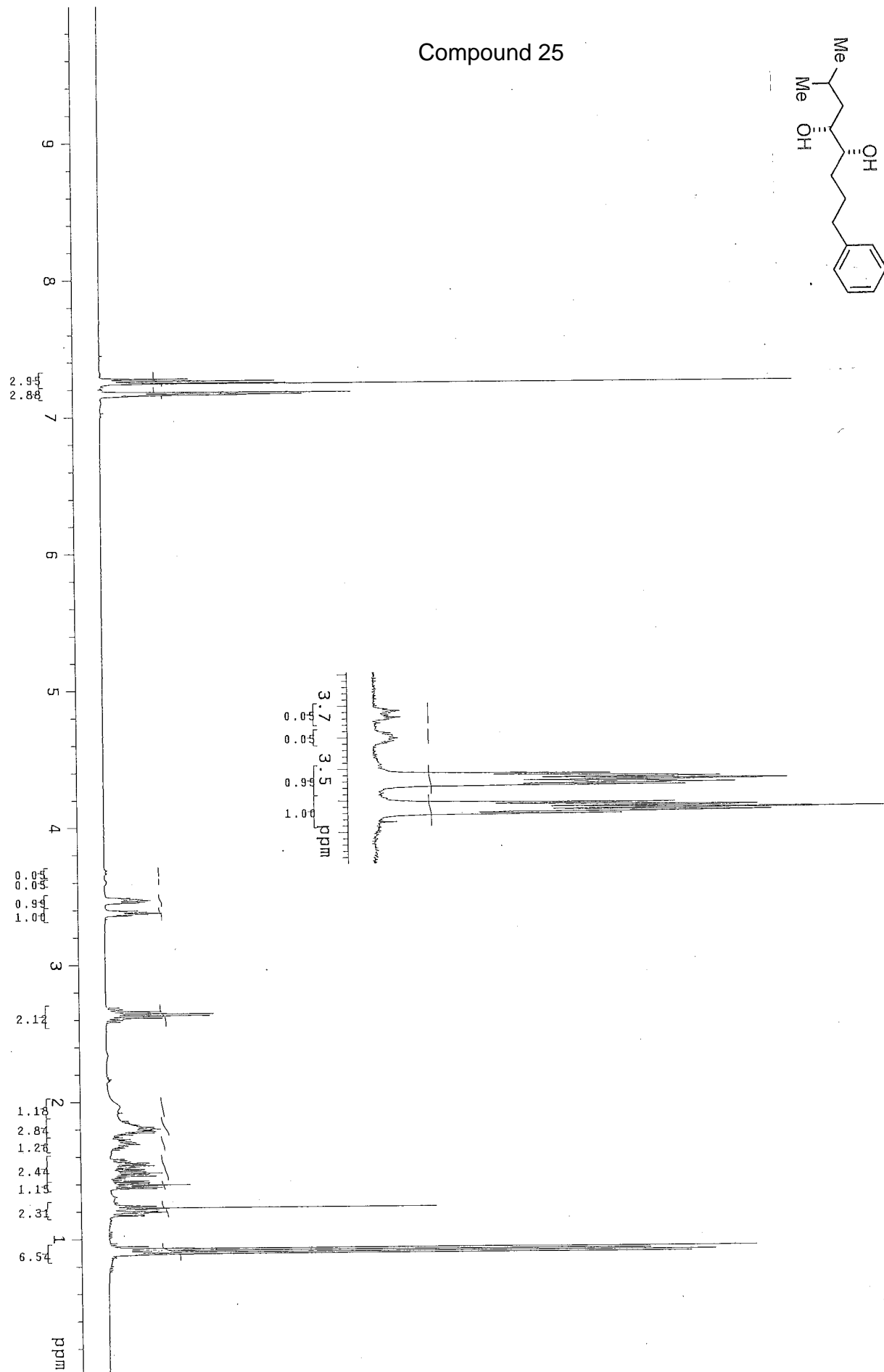
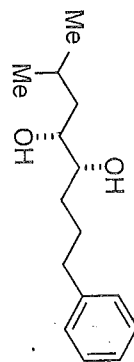
Compound 24



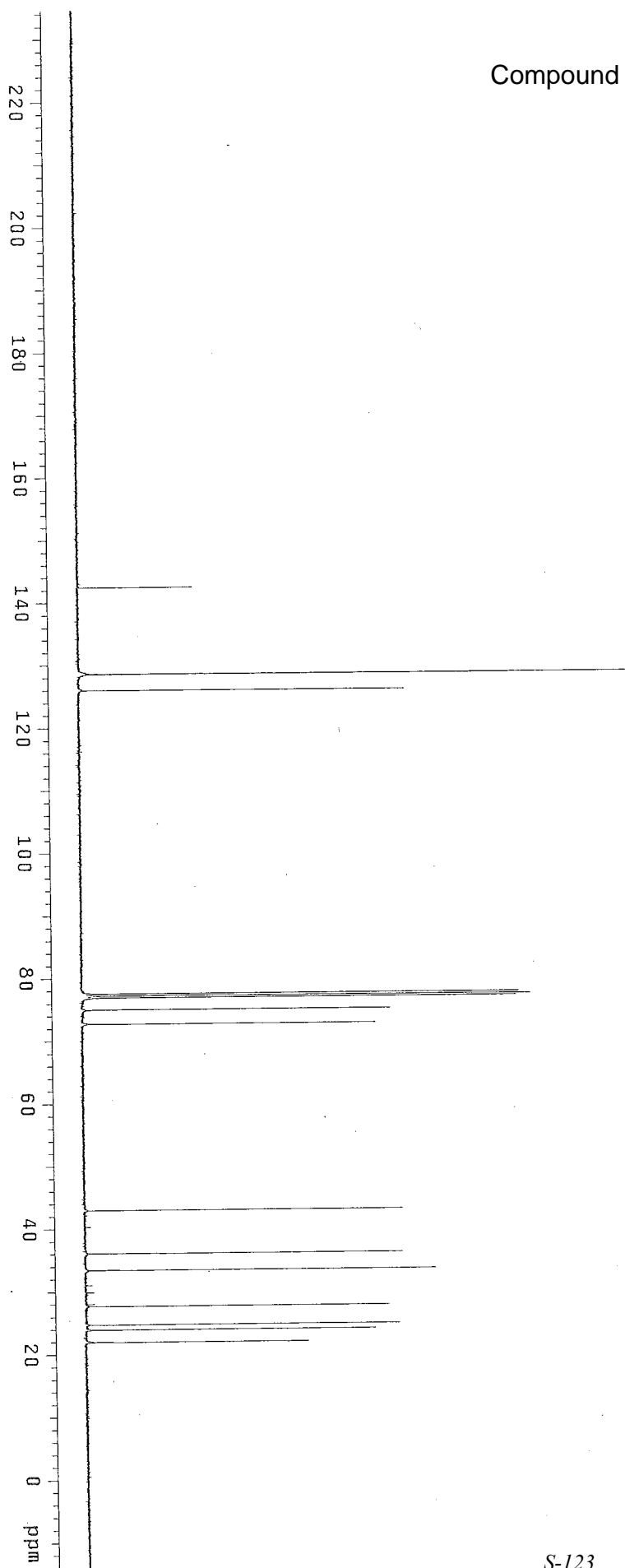
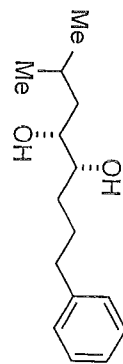
Compound 24



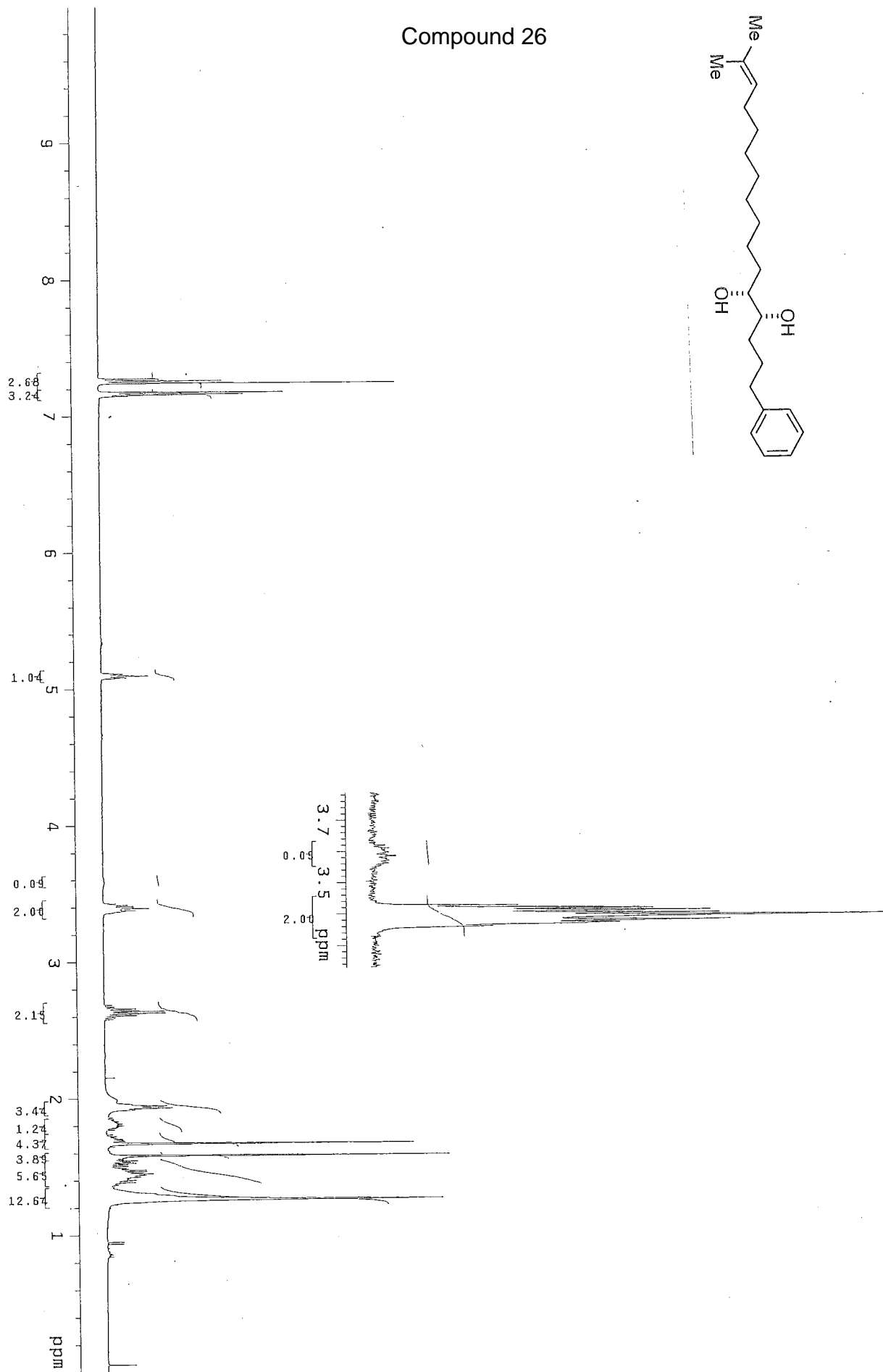
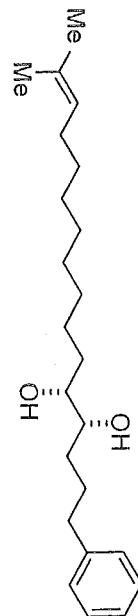
Compound 25



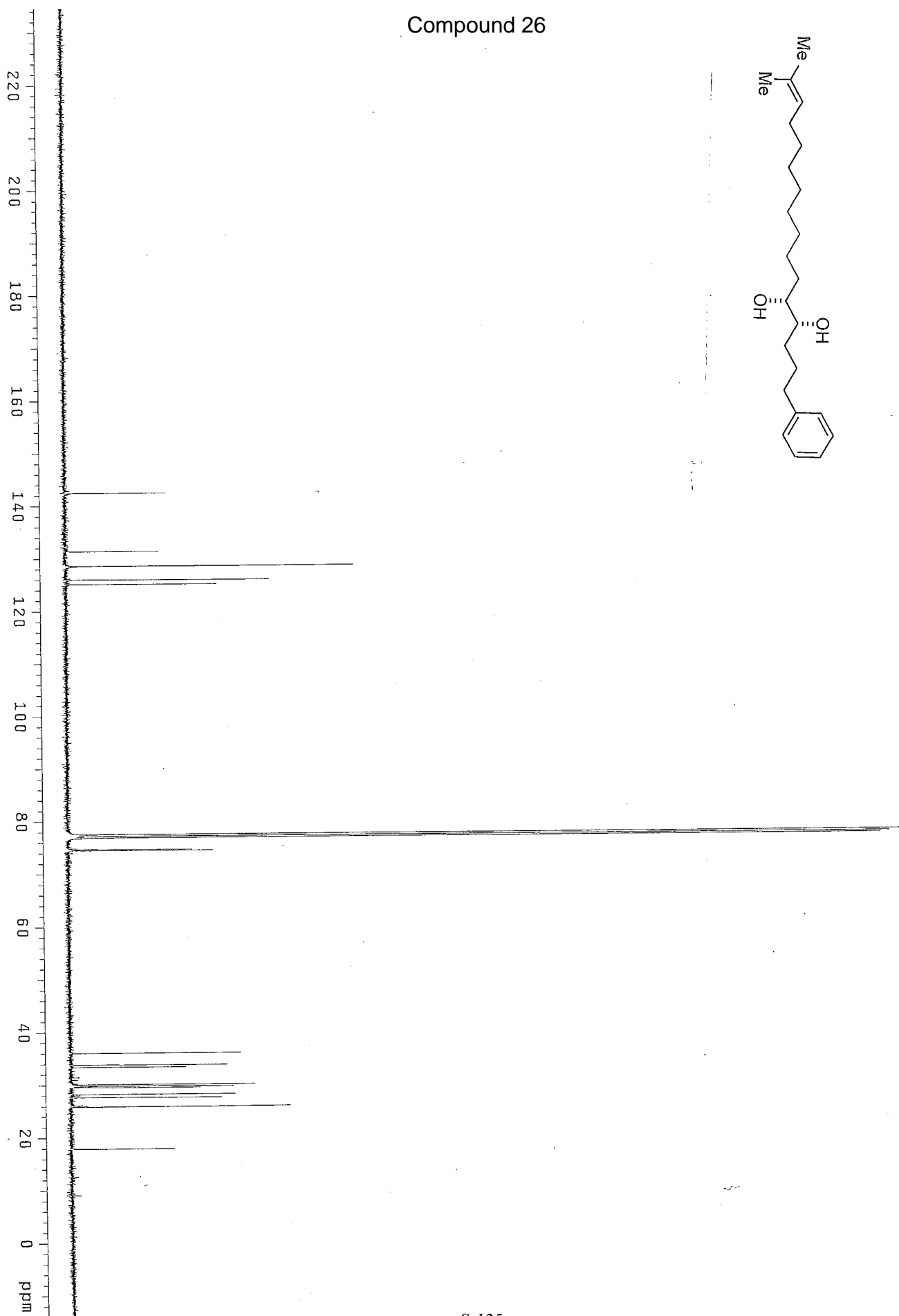
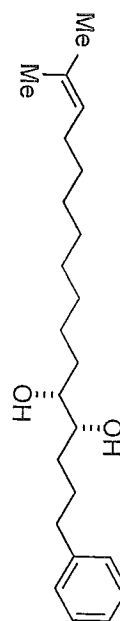
Compound 25



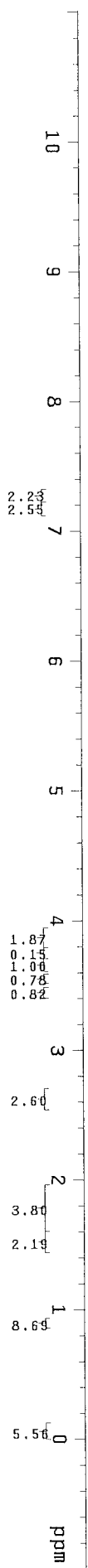
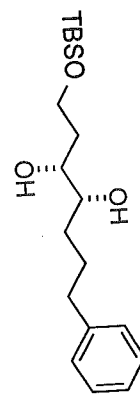
Compound 26



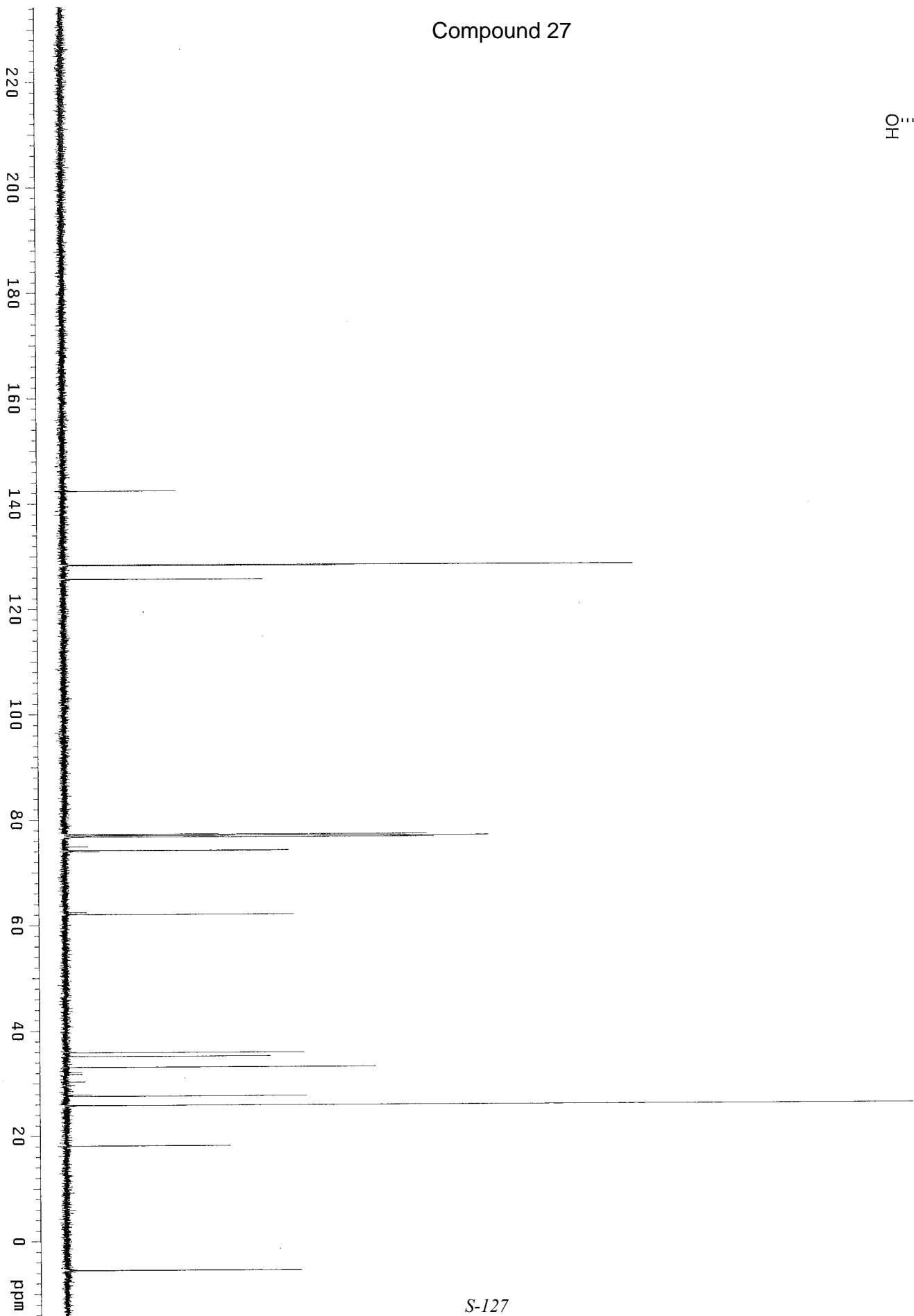
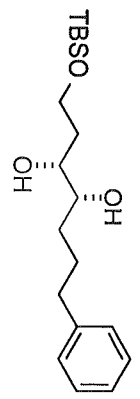
Compound 26

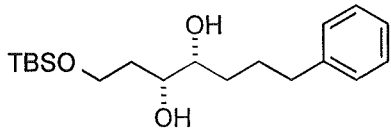


Compound 27

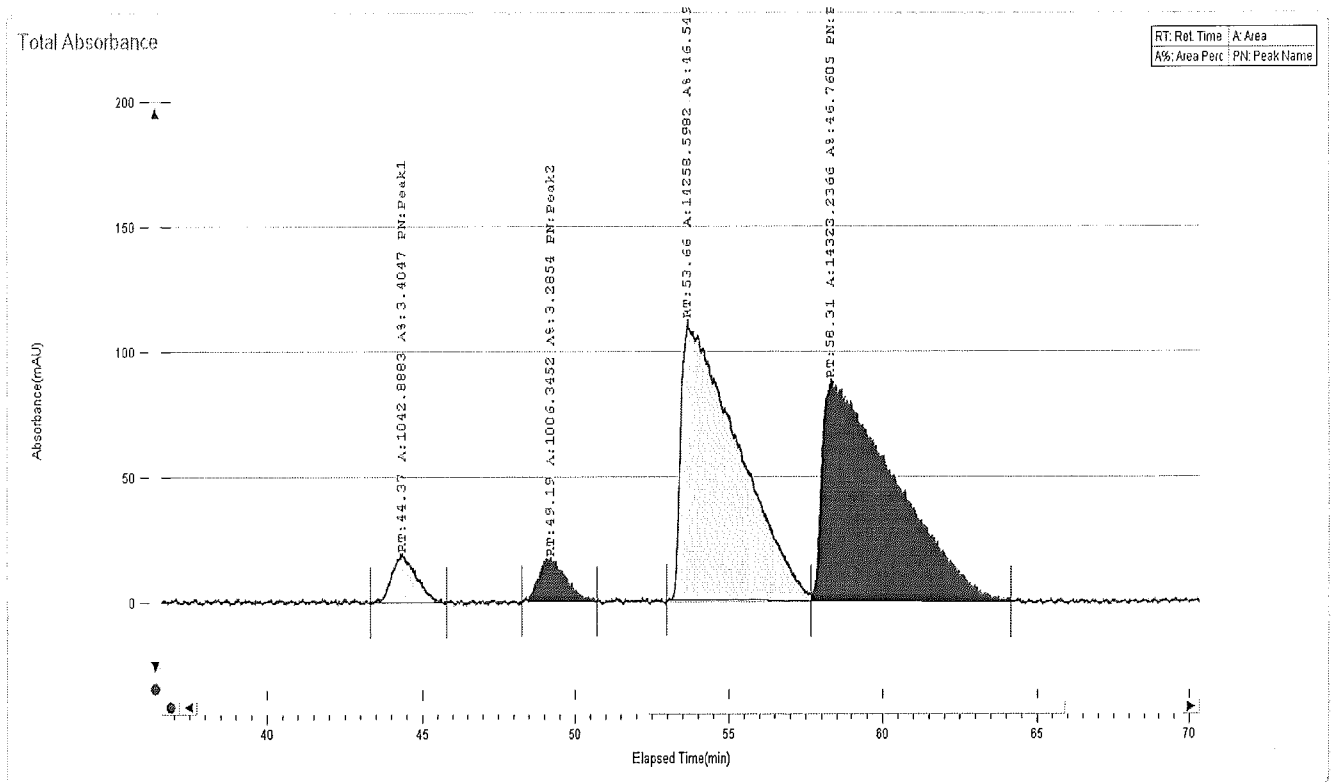


Compound 27





Compound 27



General Info

Log Author
 Log Date 3/19/2014 1:59:01 PM
 Report By current_User
 Report Date 9/3/2014
 Method Name JRC-AD-H.met
 Notes OD-H, 100 bar, 3 mL/min, 3% IPA, 35 deg C

Injection Info

Inj Vol	5	Temp	35.1
Solvent	Isopropanol	Flow	3
Column	OD-H	% Modifier	3
Sample	JRC-4-225	Pressure	100
Well location	P1: 1D		

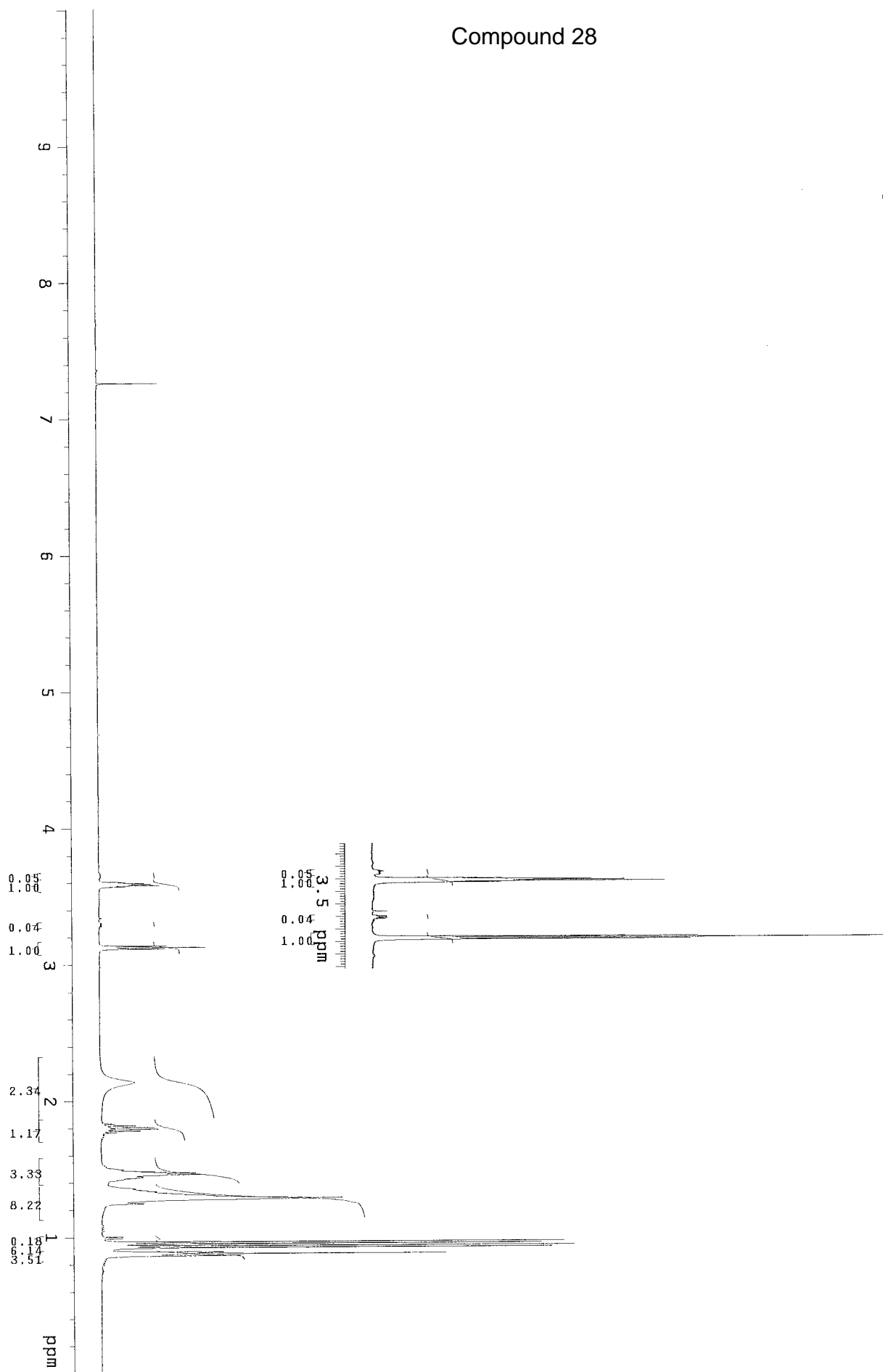
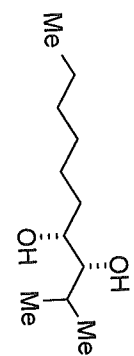
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	3.4047	1042.8883	44.37	19.4386	0.0529
2	3.2854	1006.3452	49.19	17.089	0.0586
3	46.5495	14258.5982	53.66	112.08	0.064
4	46.7605	14323.2366	58.31	88.5212	0.0695
Total:	100.0001	30631.0683			

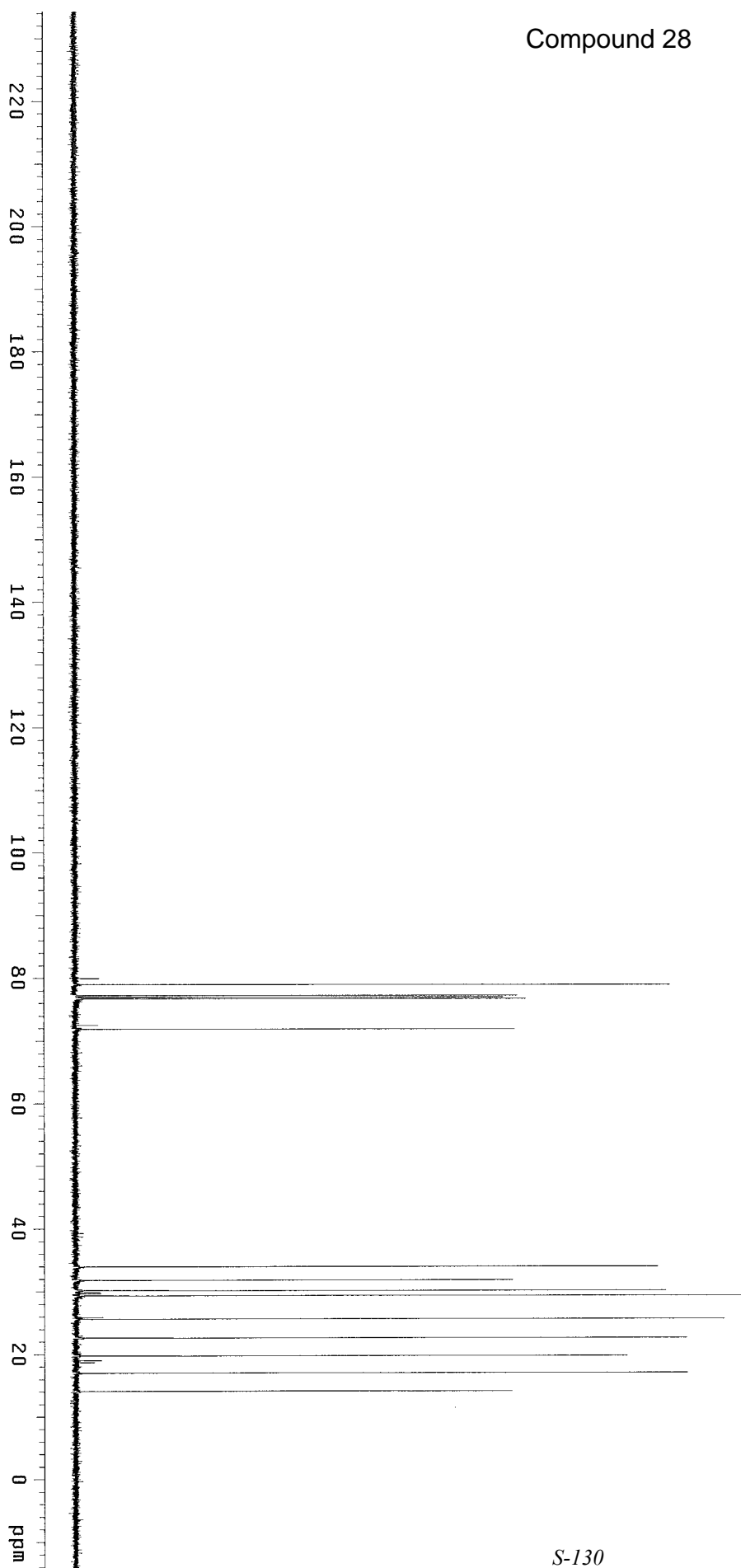
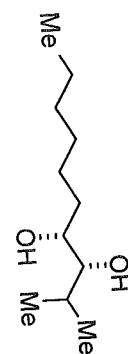
TharSFC

C:\Program Files\SuperChrom\logs\Data\JRC\JRC-4-225-3_3-19-2014_1.tta

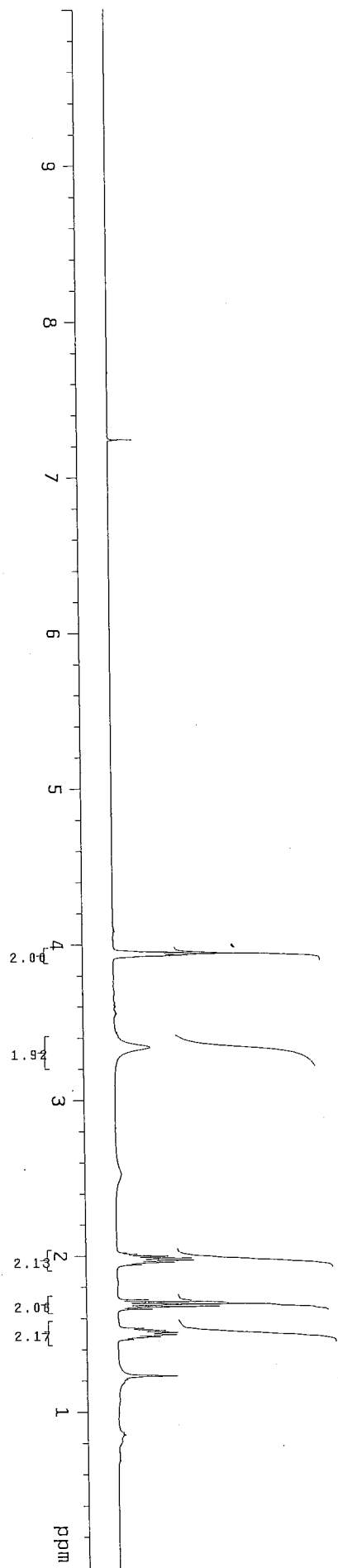
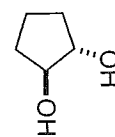
Compound 28



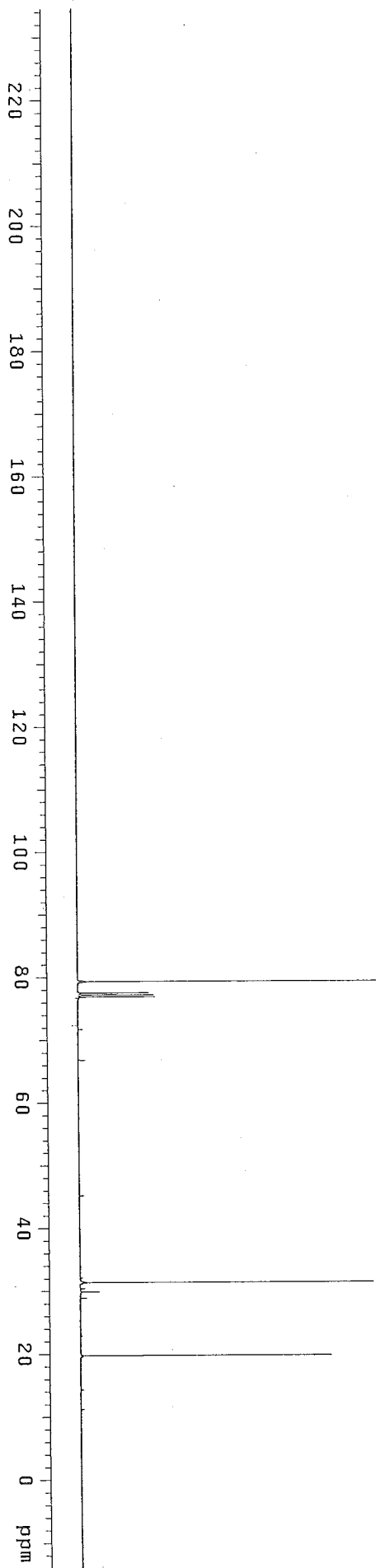
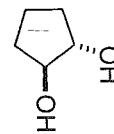
Compound 28



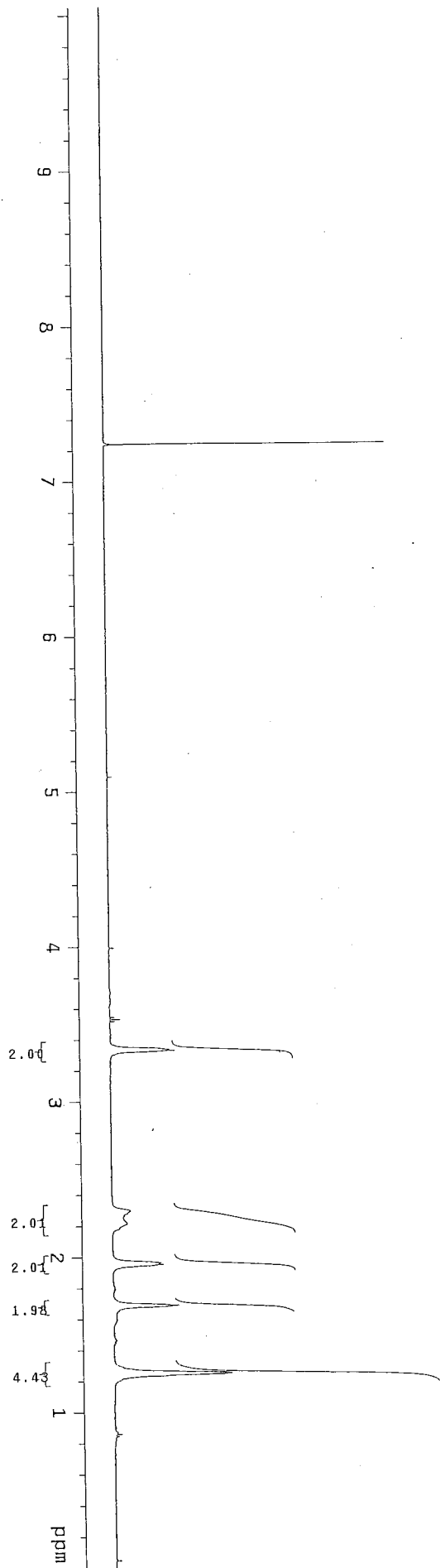
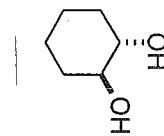
Compound 29



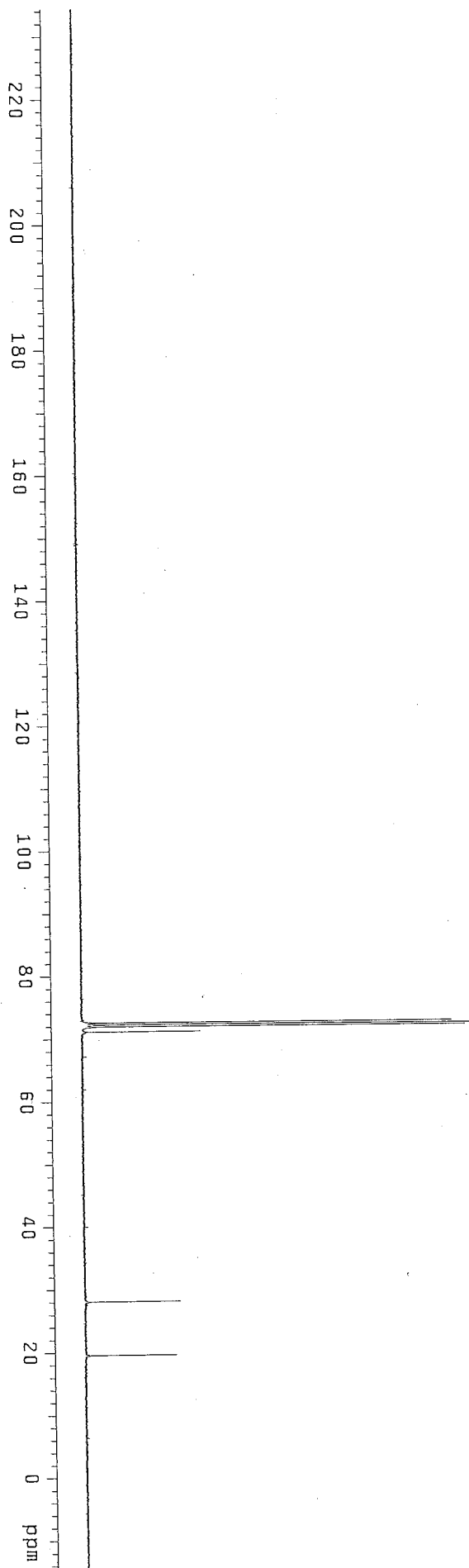
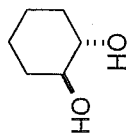
Compound 29



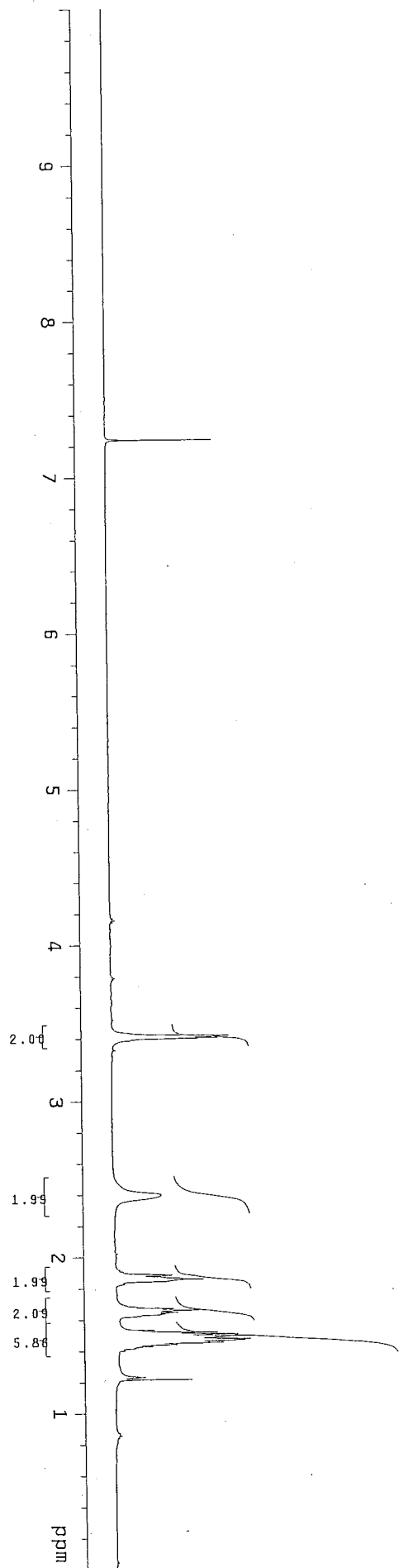
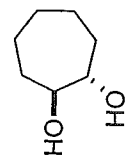
Compound 30



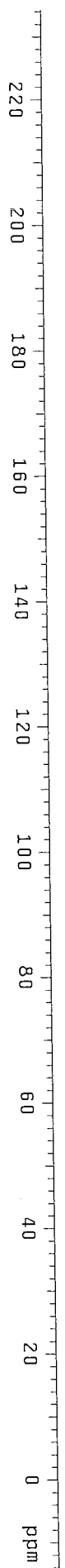
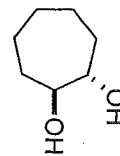
Compound 30



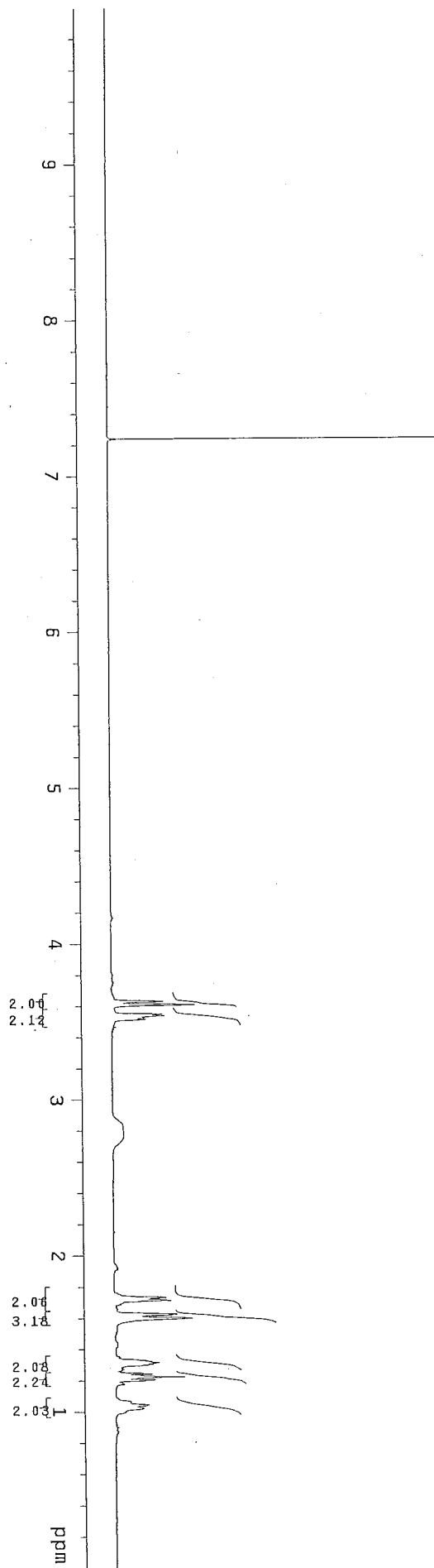
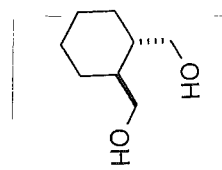
Compound 31



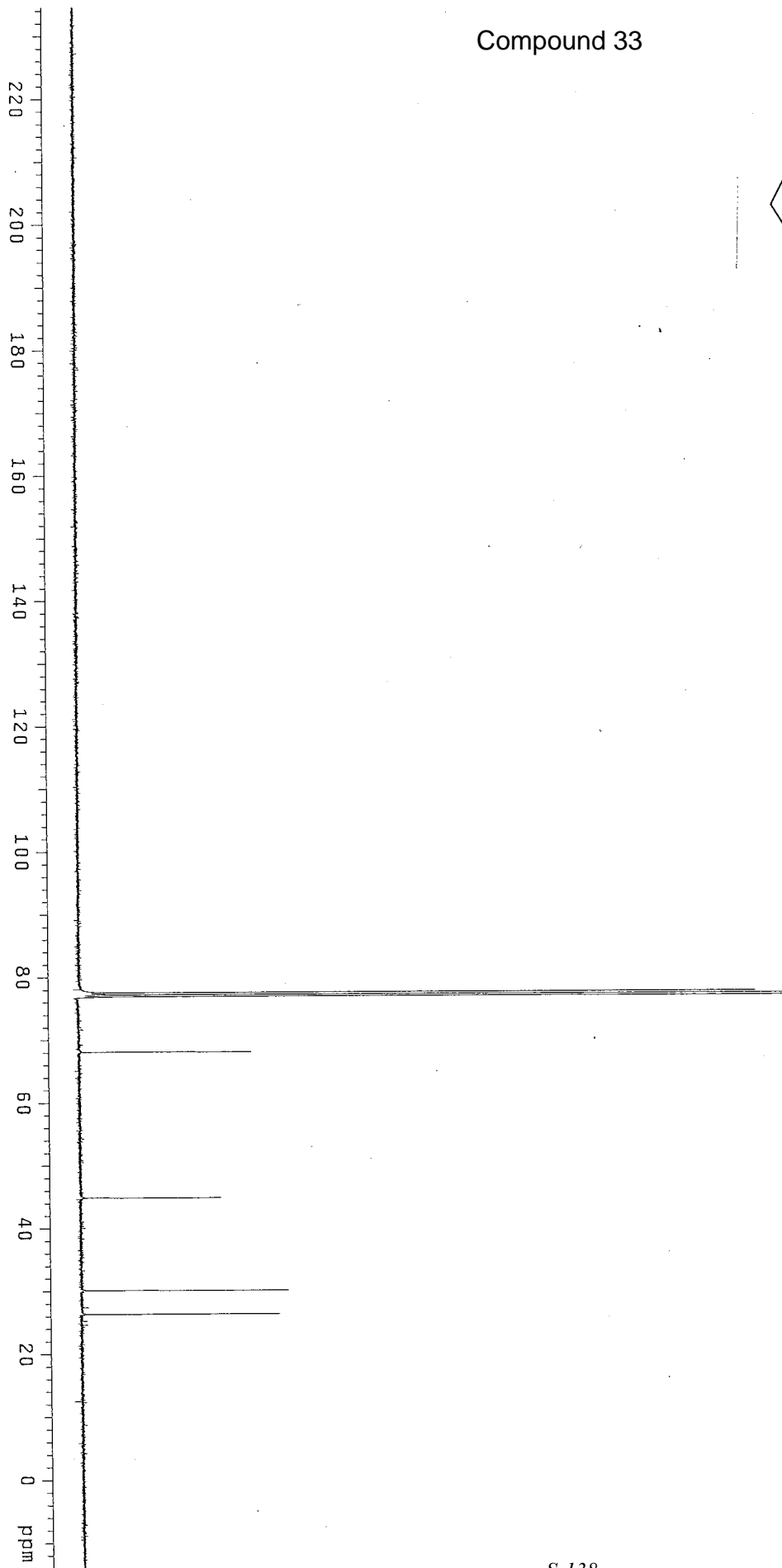
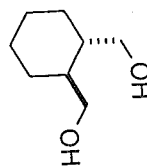
Compound 31



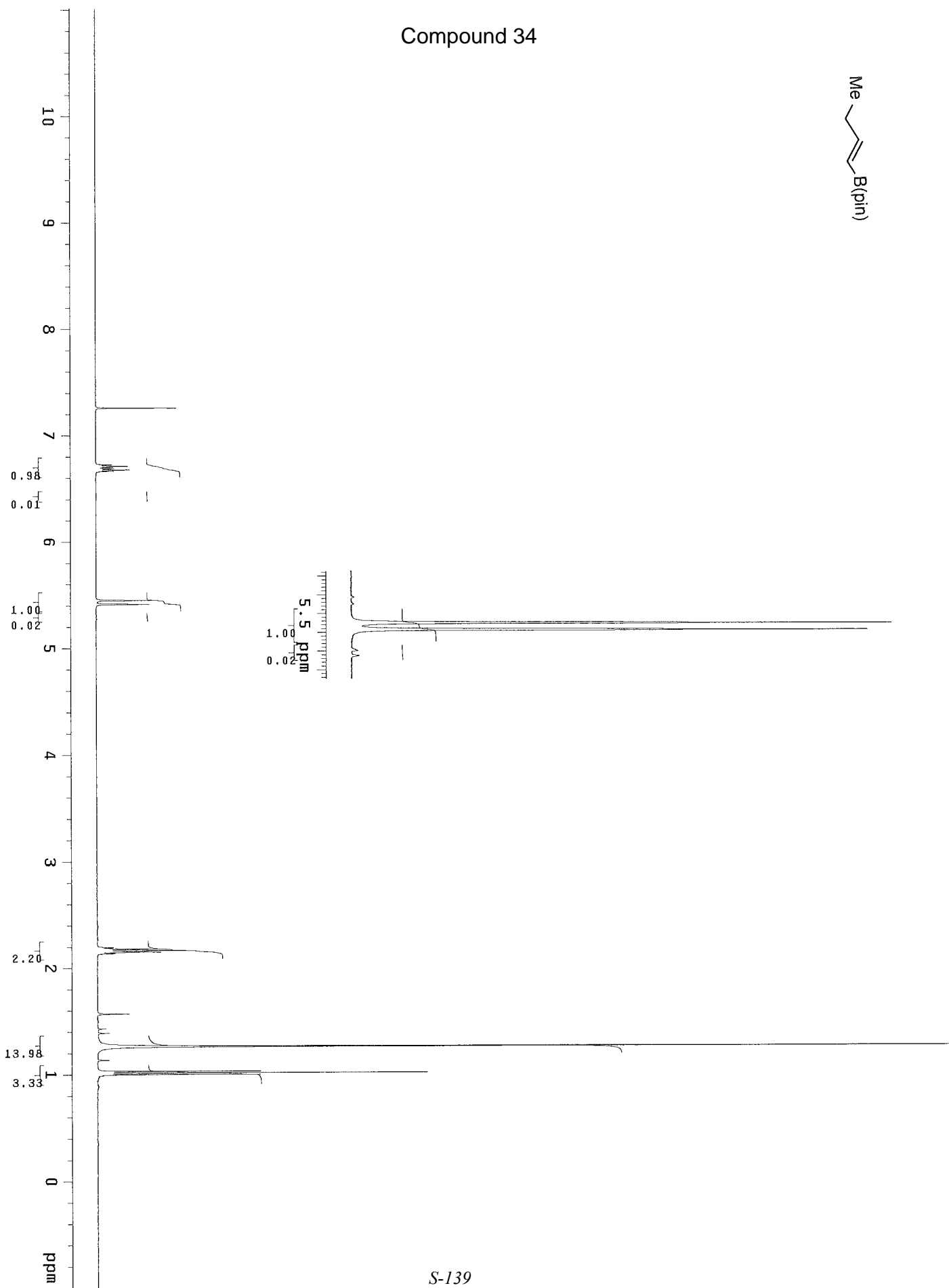
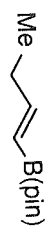
Compound 33



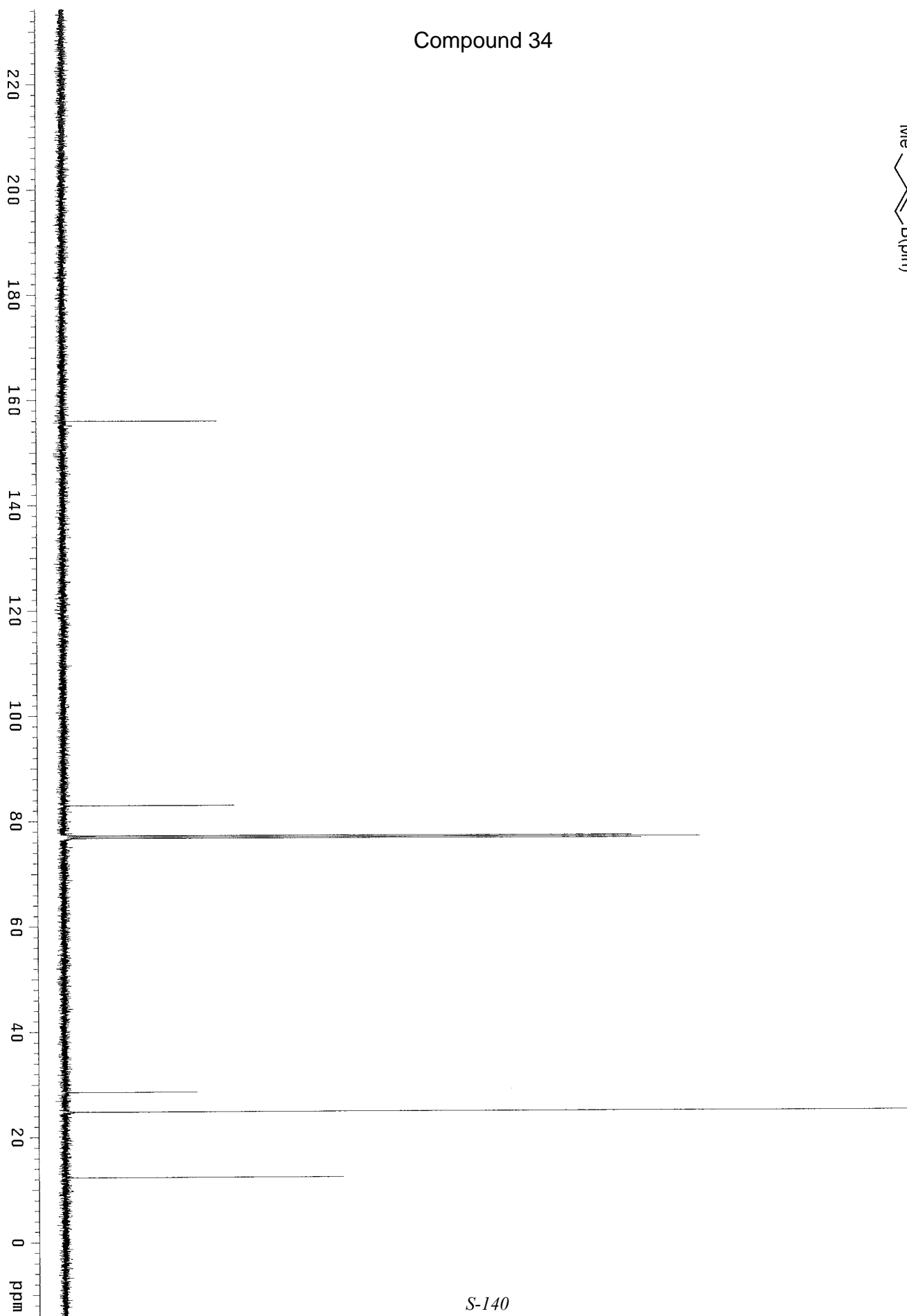
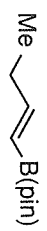
Compound 33



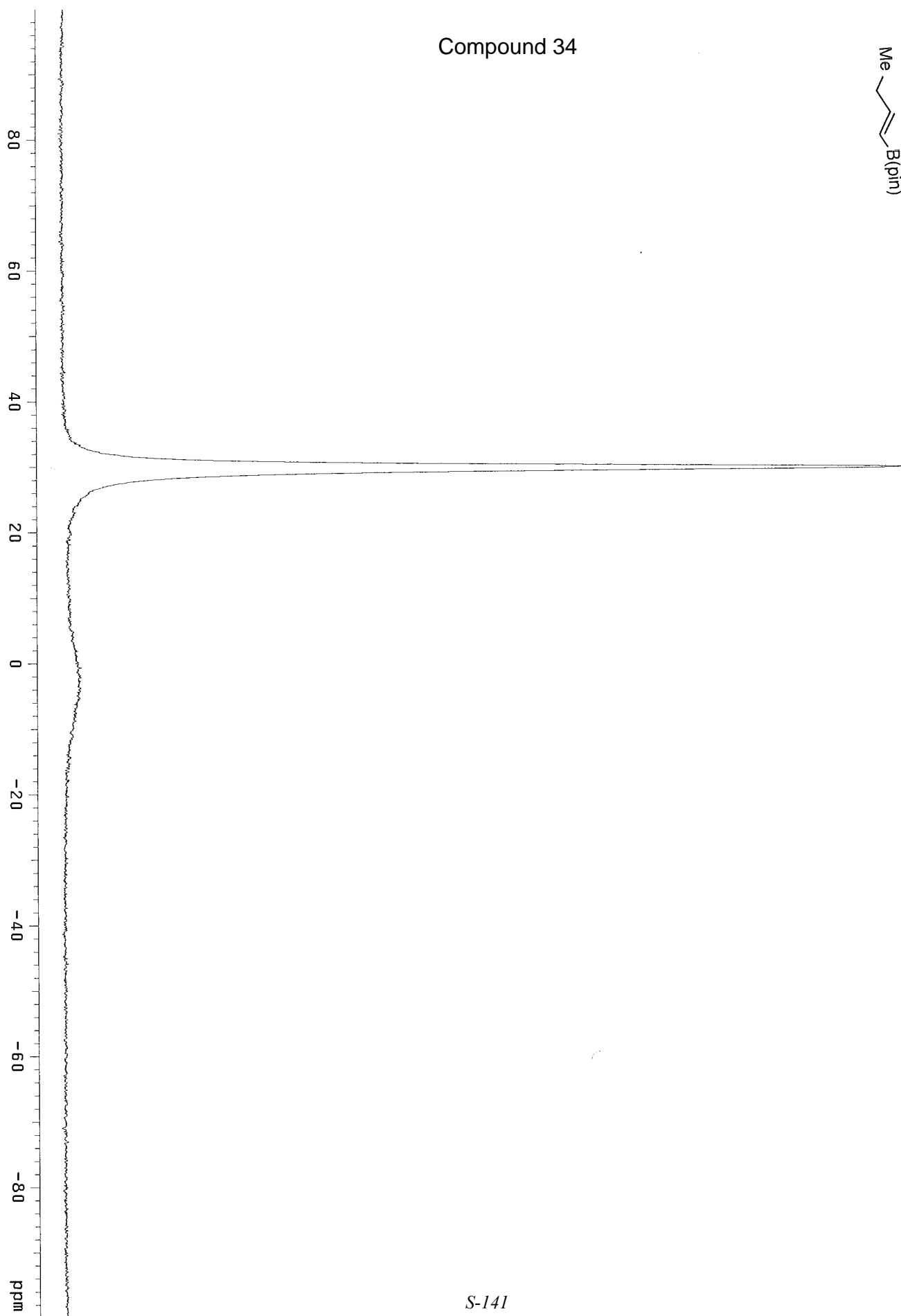
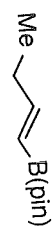
Compound 34



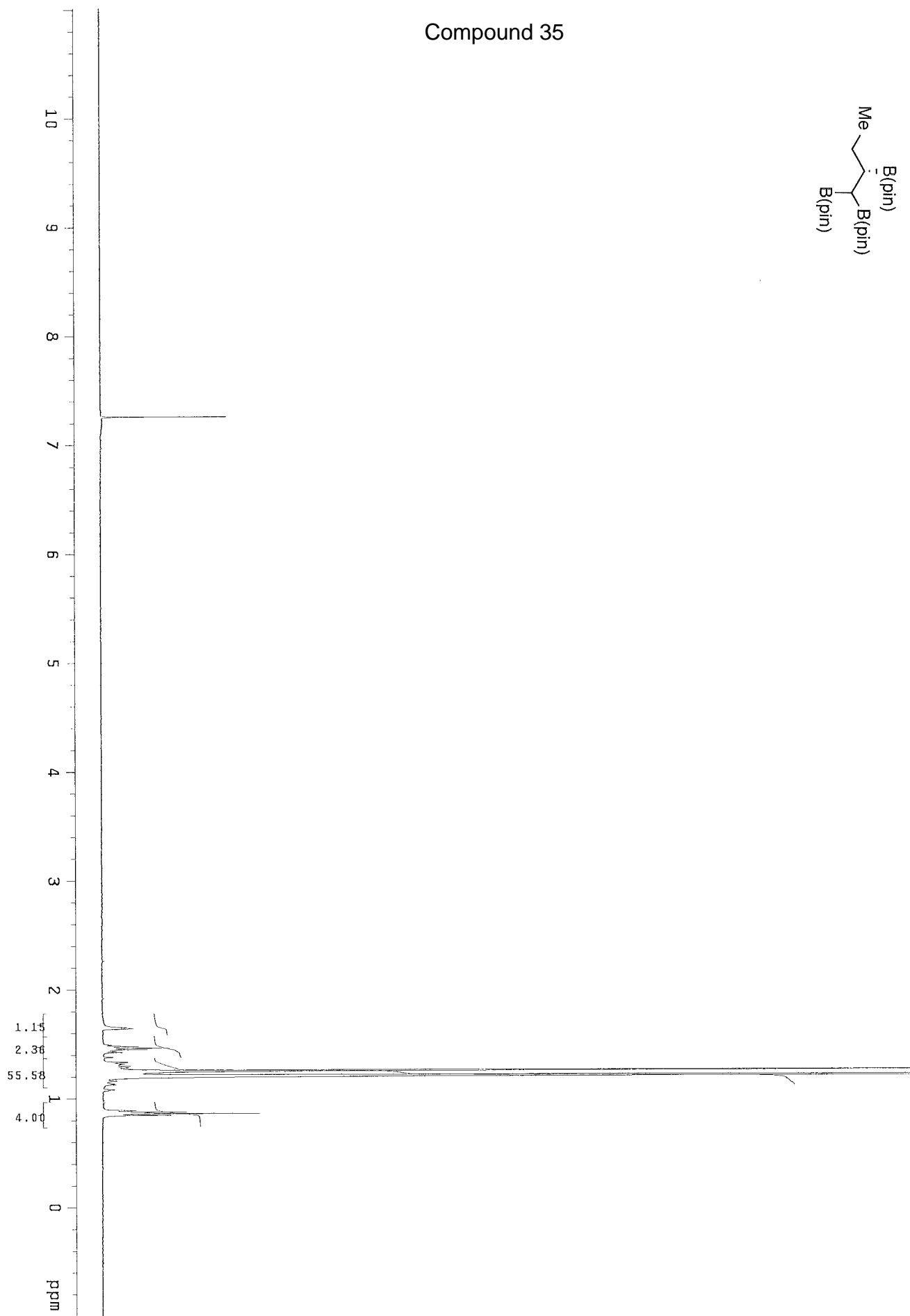
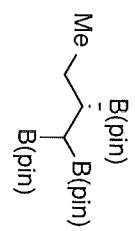
Compound 34



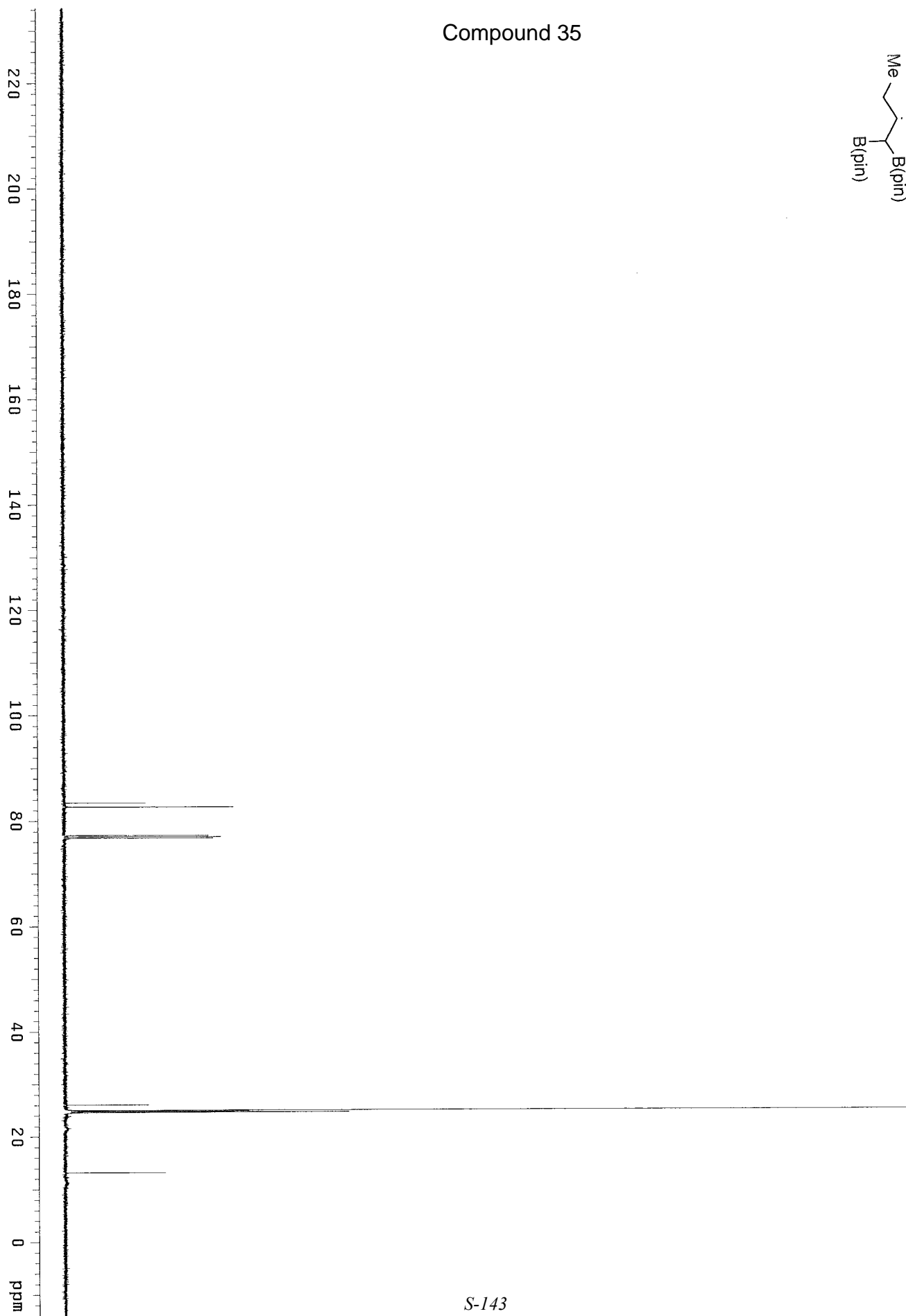
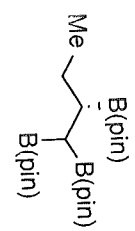
Compound 34



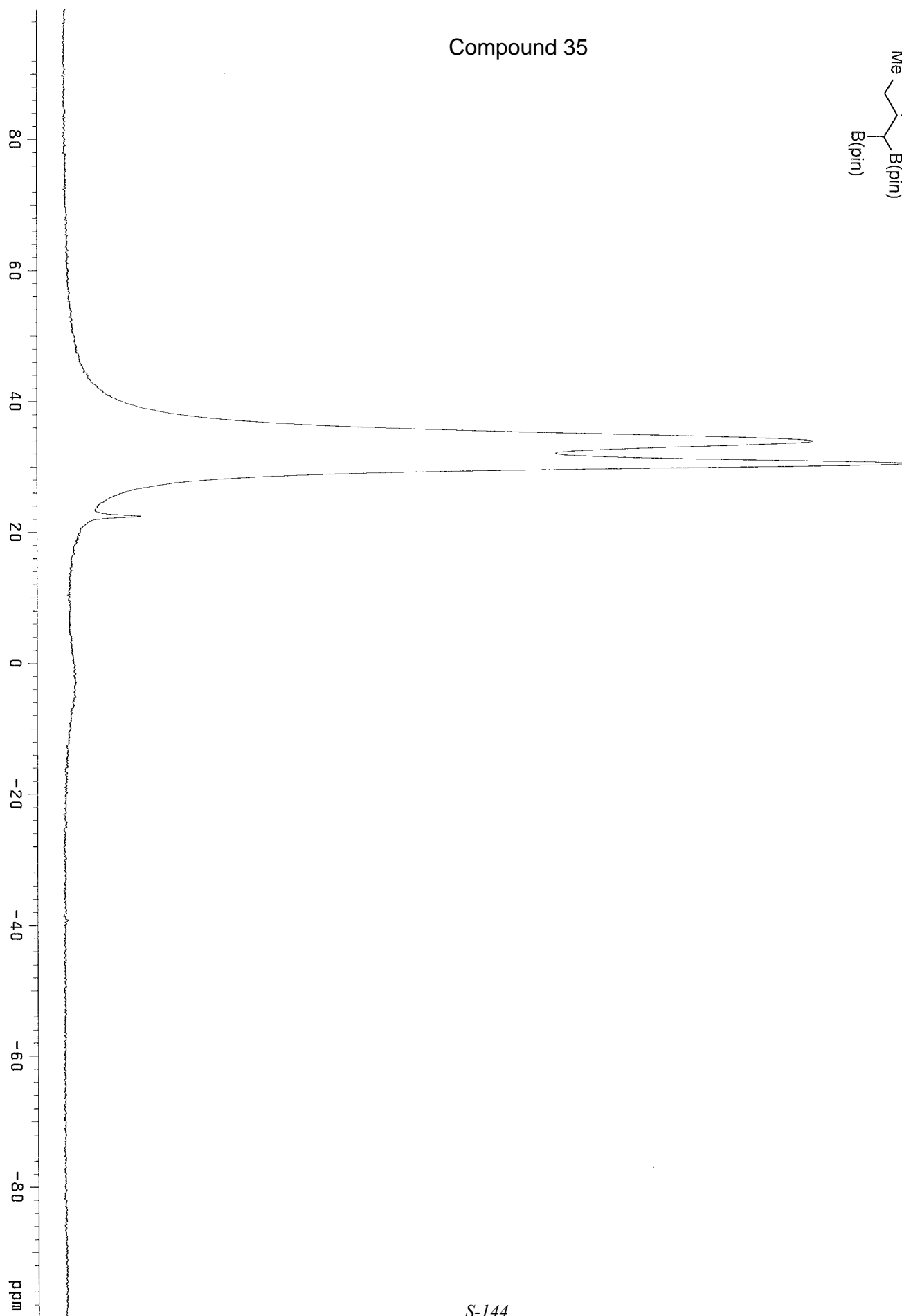
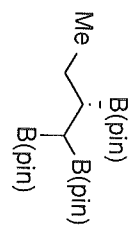
Compound 35



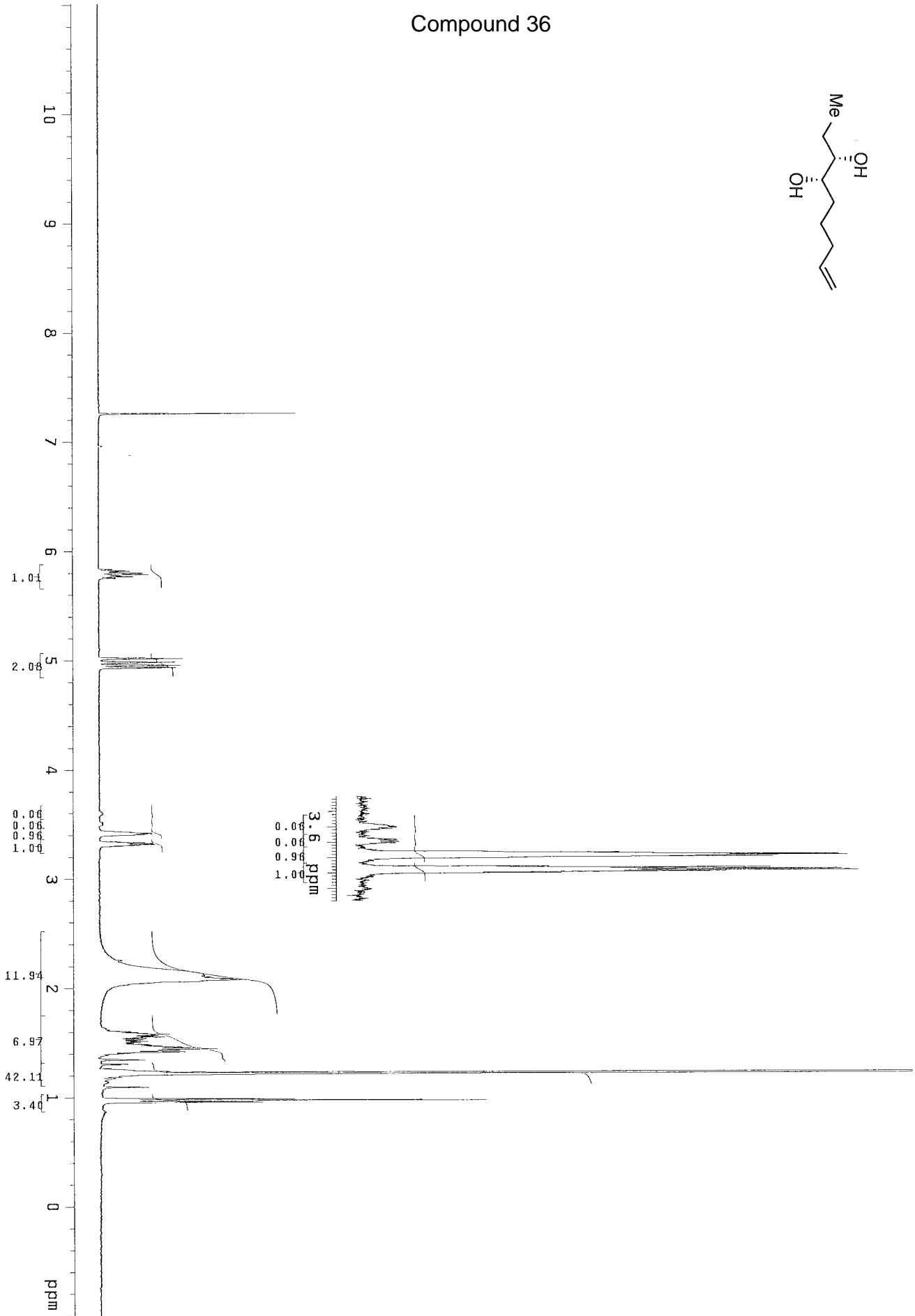
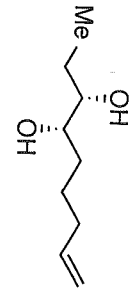
Compound 35



Compound 35



Compound 36



Compound 35

