Nonracemic Allylic Boronates through Enantiotopic-Group-Selective Cross-Coupling of Geminal Bis(boronates) and Vinyl Halides

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Table of Contents

I. General Information

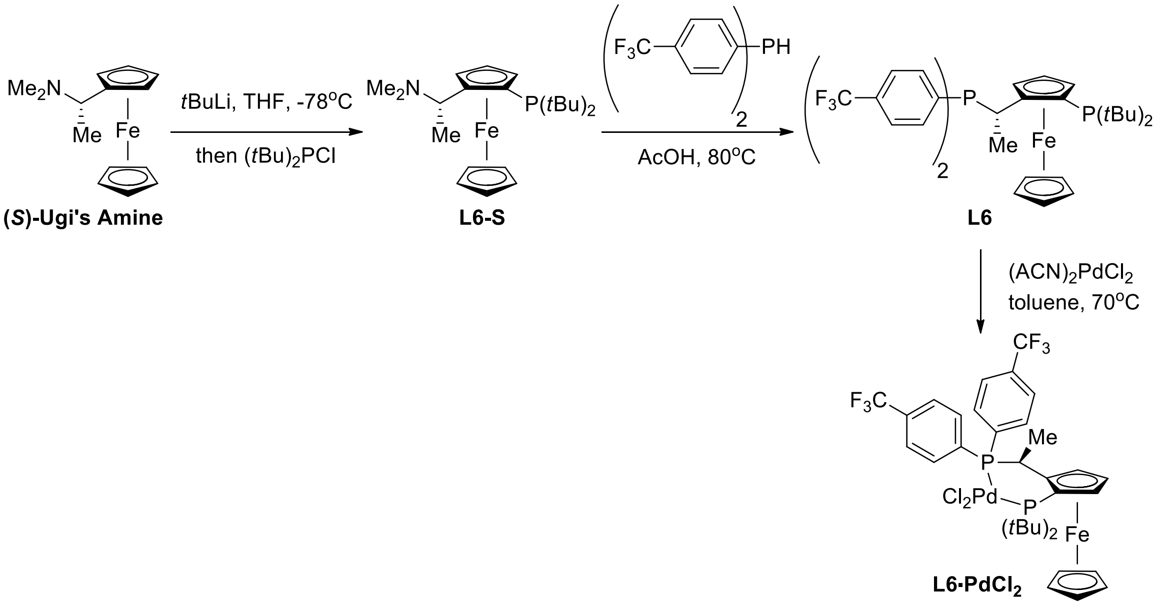
^{1}H NMR spectra were recorded on either a Varian Gemini-500 (500 MHz), Varian Inova-500 (500 MHz), or Varian Gemini-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on either a Varian Gemini-500 (125 MHz), or Varian Gemini-600 (150 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). ^{31}P NMR spectra were recorded on a Varian Gemini-500 (202 MHz), or Varian Gemini-600 (240 MHz) spectrometer. Chemical shifts are reported in ppm using phosphoric acid as the external standard (H_3PO_4: 0.0 ppm). ^{11}B NMR spectra were recorded on a Varian Gemini-500 (128 MHz) spectrometer. ^{19}F NMR spectra were recorded on a Varian Gemini-500 (470 MHz) spectrometer. Infrared (IR) spectra were recorded on a Bruker alpha-P Spectrometer. Frequencies are reported in wavenumbers (cm^{-1}) as follows: strong (s), broad (br), medium (m), and weak (w). Optical rotations were measured on a Rudolph Analytical Research Autopol IV Polarimeter. High-resolution mass spectrometry (ESI+) was performed at the Mass Spectrometry Facility, Boston College, Chestnut Hill, MA.

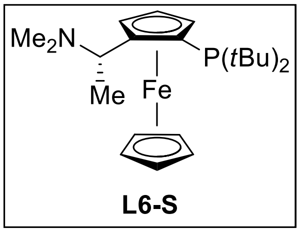
Liquid chromatography was performed using forced flow (flash chromatography) on silica gel (SiO_2, 230 x 450 Mesh) purchased from Silicycle. Thin layer chromatography (TLC) was performed on 25 μm silica gel glass backed plates from Silicycle. Visualization was performed using ultraviolet light (254 nm) and ceric ammonium molybdate (CAM) in ethanol.

Analytical chiral supercritical fluid chromatography (SFC) was performed on a TharSFC Method Station II equipped with Waters 2998 Photodiode Array Detector with isopropanol or methanol as the modifier. Analytical chiral gas chromatography (GC) was performed on an Agilent Technologies 6850 Network GC System equipped with a Flame Ionization Detector.

All reactions were conducted in oven- or flame-dried glassware under an inert atmosphere of nitrogen or argon. Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (CH_2Cl_2), and toluene were purified using Pure Solv MD-4 solvent purification system, from Innovative Technology, Inc., by passing the solvent through two activated alumina columns after purging with argon. Hexane was purified using a Glass Contour solvent purification system custom manufactured by SG Waters, LLC (Nashua, NH). Bis(pinacolato)diboron was generously donated by Allychem Co., Ltd. and used without further purification. Palladium (II) acetate, bis(acetonitrile)dichloropalladium (II), di-*tert*-butylchlorophosphine, **L2**, and **L3** were purchased from Strem Chemicals, Inc. and used without further purification. Lithium 2,2,6,6-tetramethylpiperidide (LTMP), bis(4-trifluoromethlphenyl)phosphine, **L4**, and **L5** were purchased from Aldrich and used without purification. 1-Bromo-2-methylprop-1-ene was purchased from Combi-Blocks and used without further purification. All other reagents were purchased from either Aldrich, Alfa Aesar or Acros and used without further purification. **L1** was prepared according to a literature procedure.[1]

II. Ligand Synthesis and Characterization





L6-S

Dimethyl{(*S*)-1-[(*R*)-2-(di*tert*butylphosphanyl)ferrocenyl]ethyl}amine (L6-S). Prepared according to a literature precedent with slight modification.[2] To a 100-mL round-bottom flask equipped with a magnetic stir bar and reflux condenser was added (*S*)-Ugi's amine[3] (1.32 g, 5.12 mmol). The amine was azeotroped with benzene (3 x 100 μL) and placed under N_2. Et_2O (33 mL) was added and the reaction was cooled to -78°C. *t*BuLi (3.60 mL, 6.14 mmol, 1.7M in pentanes) was cautiously

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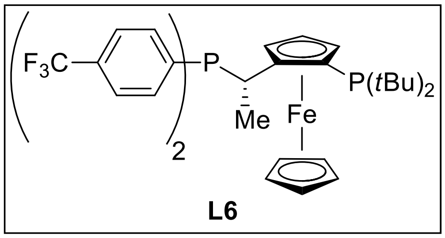
[1] Sun, C.; Potter, B.; Morken, J. P. *J. Am. Chem. Soc*. **2014**, *136*, 6534.

[2] Mejía, E.; Aardoom, R.; Togni, A. *Eur. J. Inorg. Chem*. **2012**, 5021.

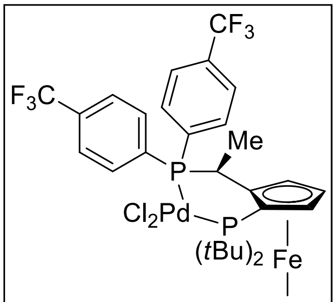
[3] Gokel, G. W.; Ugi, I. K. *J. Chem. Ed*. **1972**, *49*, 294.

added dropwise. The reaction was stirred at -78°C for 30 minutes and then warmed to room temperature for 1 hour. The reaction was re-cooled to -78°C and di-*tert*-butylchlorophosphine (1.07 mL, 5.60 mmol) was added as a solution in Et_2O (1 mL) *via* syringe. The reaction stirred at -78°C for 5 minutes before warming to room temperature. After stirring for 18 hours, the reaction was quenched with a saturated solution of Na_2CO_3 (10 mL). The reaction was poured into a separatory funnel with Et_2O (30 mL). The layers were separated and the organic layer was successively washed with H_2O (20 mL) and brine (20 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (5% ethyl acetate/hexanes to 30% ethyl acetate/hexanes) to afford the title compound as a red solid (1.36 g, 66% yield), which was stored in an Ar-filled drybox. $R_f = 0.05$ in 50% ethyl acetate/hexanes on TLC. ^1H NMR (500 MHz, $CDCl_3$) δ 4.54 (s, 1H), 4.38 (t, *J* = 2.0 Hz, 1H), 4.26 (s, 1H), 4.16 (s, 5H), 3.60 (dq, *J* = 10.0, 6.0 Hz, 1H), 2.19 (s, 6H), 1.50 (d, *J* = 12.0 Hz, 9H), 1.46 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 11.5 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 101.60 (d, *J* = 25.5 Hz), 77.21, 72.25 (d, *J* = 5.7 Hz), 70.09, 68.39 (d, *J* = 4.5 Hz), 68.20, 56.75 (d, *J* = 12.7 Hz), 41.91, 33.26 (d, *J* = 20.8 Hz), 31.84 (d, *J* = 18.5 Hz), 30.87 (d, *J* = 15.1 Hz), 30.39 (d, *J* = 13.9 Hz), 16.85. ^{31}P NMR (202 MHz, $CDCl_3$) δ 14.21. IR (neat) ν_{max} 3097 (w), 2970 (m), 2940 (m), 2888 (m), 2857 (s), 2813 (m), 2769 (m), 1473 (m), 1455 (s), 1384 (w), 1359 (s), 1262 (w), 1240 (w), 1194 (w), 1176 (w), 1154 (s), 1109 (s), 1089 (s), 1061 (m), 1041 (s), 1002 (s), 929 (s), 817 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{22}H_{37}FeNP$ $[M+H]^+$ 402.2013, found 402.2008. $[\alpha]^{20}_D$: +260.2 (c = 0.722, $CHCl_3$, *l* = 50 mm). Melting point: 47-51 °C.



L6

(*S*)-1-[(*R*)-2-(Di*tert*butylphosphanyl)ferrocenyl]ethyldi[4-(trifluoromethyl)phenyl]phosphine (L6). Prepared according to a literature precedent with slight modification.[2] In an Ar-filled drybox, an oven-dried 2-dram vial with magnetic stir bar was charged with **L6-S** (330 mg, 0.82 mmol). The vial was sealed with a rubber septum and removed from the glove box. Freshly degassed (*via* constant bubbling with N_2 for one hour prior to use) glacial AcOH (500 μL) was added under an atmosphere of N_2. The reaction was stirred and bis(4-trifluoromethlphenyl)phosphine (278 mg, 0.86 mmol) was added in a solution of glacial AcOH (500 μL) *via* syringe. The reaction was heated to 80°C for 18 hours. The reaction was cooled to room temperature and the solvent removed *in vacuo*. The mixture was diluted with CH_2Cl_2 (30 mL) and poured into a separatory funnel containing a saturated solution of Na_2CO_3 (15 mL). The layers were separated and the organic layer was successively washed with H_2O (20 mL) and brine (20 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (hexanes to 3% ethyl acetate/hexanes) to afford the title compound as a red solid (306.2 mg, 55% yield, 95% purity), which was stored in an Ar-filled drybox. R_f = 0.5 in 10% ethyl acetate/hexanes on TLC. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58-7.46 (m, 8H), 4.34 (m, 2H), 4.18 (s, 5H), 4.10 (s, minor conformer), 4.00 (s, 1H), 3.91 (s, minor conformer), 3.62 (m, 1H), 1.53 (d, *J* = 12.0 Hz, 9H), 1.44 (t, *J* = 7.8 Hz, 3H), 1.04 (d, *J* = 10.8 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.50 (d, *J* = 22.0 Hz), 141.06 (d, *J* = 23.2 Hz), 136.07 (d, *J* = 20.8 Hz), 132.25 (d, *J* = 15.1 Hz), 131.52 (q, *J* = 32.4 Hz), 129.85 (q, *J* = 32.4 Hz), 125.03 (m), 124.85 (m), 98.87 (dd, *J* = 27.7, 18.4 Hz), 77.87 (dd, *J* = 36.9, 3.5 Hz), 72.67 (d, *J* = 5.9 Hz), 70.31, 68.85 (dd, *J* = 11.6, 4.7 Hz), 68.49, 33.46 (d, *J* = 20.8 Hz), 32.15 (d, *J* = 19.6 Hz), 31.03 (dd, *J* = 13.9, 2.4 Hz), 30.70 (d, *J* = 13.9 Hz), 29.38 (dd, *J* = 17.3, 12.7 Hz), 20.34 (dd, *J* = 4.7 Hz). ^{31}P NMR (242 MHz, $CDCl_3$) δ 13.13 (d, *J* = 17.5 Hz), -0.32 (d, *J* = 16.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.76, -62.82. IR (neat) ν_{max} 3092 (w), 2971 (w), 2942 (w), 2891 (w), 2861 (w), 1606 (m), 1395 (m), 1321 (s), 1164 (m), 1125 (s), 1107 (m), 1059 (s), 1015 (m), 908 (w), 826 (s), 733 (m), 699 (m) cm^{-1}. HRMS (ESI+) calc. for $C_{34}H_{39}F_6FeP_2$ $[M+H]^+$ 679.1781, found 679.1779. $[\alpha]^{20}_D$: +75.4 (c = 0.740, $CHCl_3$, *l* = 50 mm). Melting point: 156-163 °C (decomposition).



L6•PdCl2

L6·PdCl₂. In an Ar-filled glove box, an oven-dried 100-mL round bottom flask with magnetic stir bar was charged with $(ACN)_2PdCl_2$ (290 mg, 1.12 mmol) and **L6** (758 mg, 1.12 mmol). The flask was removed from the drybox. Toluene (60 mL) was added and the reaction was heated to 70°C for 3 hours under N_2. The reaction was cooled to room temperature and the solvent removed *in vacuo*. CH_2Cl_2 (10 mL) was added and the solution was filtered through a plug of Celite. The solvent was removed *in vacuo* and the solid washed with Et_2O (3 x 4 mL). The red solid was dried under vacuum for 12 hours to afford the title compound as a red solid (921 mg, 96% yield), which was stored under air in a dessicator. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (t, *J* = 9.0 Hz, 2H), 7.79 (dd, *J* = 11.4, 7.8 Hz, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 6.6

Hz, 2H), 4.99 (s, 1H), 4.73 (m, 2H), 4.23 (s, 5H), 3.61 (dq, *J* = 14.4, 7.2 Hz, 1H), 2.10 (d, *J* = 15.6 Hz, 9H), 1.39 (dd, *J* = 13.8, 7.2 Hz, 3H), 1.10 (d, *J* = 14.4 Hz, 9H). ^{31}P NMR (242 MHz, $CDCl_3$) δ 53.75 (d, *J* = 4.6 Hz), 43.91 (d, *J* = 4.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -63.04, -63.37. IR (neat) ν_{max} 3080 (w), 2960 (w), 2898 (w), 2870 (w) 1608 (w), 1458 (w), 1396 (m), 1321 (s), 1281 (w), 1168 (m), 1128 (s), 1061 (s), 1015 (m), 909 (m), 830 (m), 729 (m) cm^{-1}. HRMS (ESI+) calc. for $C_{34}H_{38}ClF_6FeP_2Pd$ $[M-Cl]^+$ 819.0426, found 819.0432. $[\alpha]^{20}_D$: -401.3 (c = 1.03, $CHCl_3$, *l* = 50 mm). Melting point: 204-219 °C (decomposition).

III. Ligand Optimization

JosiPhos ligands were either purchased according to the general information or prepared according to the procedures above (**Section II**).

Method A. An oven-dried 2-dram vial with magnetic stir bar was charged with (*S,R*)-JosiPhos (0.0055 mmol) and geminal bis(boronate) **1** (74.0 mg, 0.20 mmol) in an Ar-filled drybox. The vial was sealed with rubber septum and removed from the drybox. $Pd(OAc)_2$ in dioxane (500 μL, 0.005 mmol, 0.01M) was added *via* syringe and the reaction stirred at room temperature under N_2 for 1 hour. Then 1-bromo-2-methylprop-1-ene (10.2 μL, 0.10 mmol) and 8M $KOH_{(aq)}$[4] (56 μL, 0.45 mmol) were added sequentially *via* syringe. The reaction was stirred under an atmosphere of N_2 at room temperature for 18 hours. The reaction was diluted with Et_2O (2 mL) and filtered through a plug of Celite with additional Et_2O (5 mL). The filtrate was concentrated *in vacuo*. 1,1,2,2-Tetrachloroethane was added as an internal standard (~10 mg) and yield was determined by ^{1}H-NMR analysis. THF (3 mL) was added to a scintillation vial containing the crude filtrate and equipped with a stir bar. The vial was sealed with a septum and an exit needle inserted. The reaction was cooled to 0°C, and H_2O_2 (500 μL, 30 wt% in H_2O) and 3M NaOH (500 μL) were added sequentially *via* syringe. The reaction was warmed to room temperature and stirred for no less than 3 hours. The reaction was re-cooled to 0°C and quenched with a saturated solution of $Na_2S_2O_3$ (200 μL). The reaction was warmed to room temperature, diluted with Et_2O (3 mL), and then filtered through a plug of silica gel with additional Et_2O (5 mL). The solvent was removed *in vacuo* and the crude mixture was purified by silica gel

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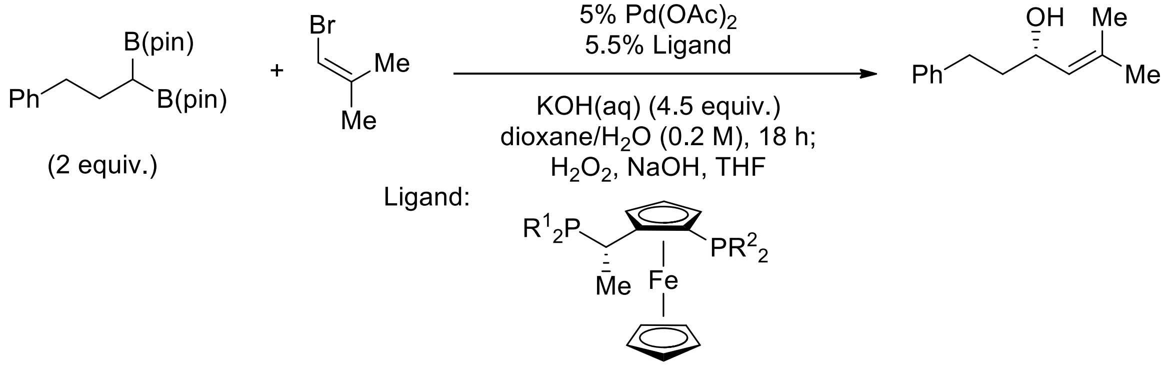
[4] $KOH_{(aq.)}$ was sparged with N_2 for 30 min at room temperature before use.

chromatography (10% ethyl acetate/hexanes) to afford secondary allylic alcohol **3-OH.** The enantiomeric excess was determined by chiral SFC analysis (for full characterization see below).

Table S1: Ligand Optimization



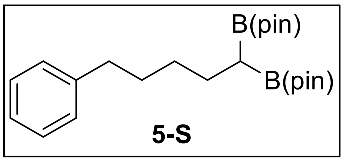
entry	R$_1$	R$_2$	mono (%)[a]	bis (%)[a]	ee[b]
1	3,5-Xylyl	Ph	22	27	13
2	Cy	Ph	21	13	7
3	Cy	3,5-dimethyl-4-methoxyPh	14	20	27
4	Cy	Cy	40	5	35
5	*t*Bu	Cy	50	<2	37
6	Ph	Cy	50	15	30
7	Ph	*i*Pr	40	<2	56
8	Ph	1-Adamantyl	24	<2	23
9	Ph	*t*Bu	60	<2	81
10	2-MethylPh	*t*Bu	14	<2	26
11	4-FluoroPh	*t*Bu	44	<5	80
12	4-MethoxyPh	*t*Bu	16	10	70
13	3,5-DimethoxyPh	*t*Bu	45	<2	57
14	4-MethylPh	*t*Bu	22	<5	64
15	3-MethylPh	*t*Bu	48	10	66
16	3,5-Xylyl	*t*Bu	29	22	<5
17	2-Furyl	*t*Bu	85	<5	52
18	2-Naphthyl	*t*Bu	27	10	40
19	Benzo[b]phosphinodle	*t*Bu	20	23	9
20	*t*Bu	*t*Bu	25	<2	14
21	Cy	*t*Bu	<10	<2	n.d.[d]
22	4-CF$_3$Ph	*t*Bu	95	<2	82
23	2-CF$_3$Ph	*t*Bu	89	<2	50
24	3,4,5-TrifluoroPh	*t*Bu	97	<2	70

[a]Yield was determined by ^{1}H-NMR in comparison to 1,1,2,2-tetrachloroethane as an internal standard. [c]Enantiomeric excess (*ee*) determined by chiral SFC analysis of corresponding alcohol. [d]Not Determined.

IV. Synthesis and Characterization of Geminal bis(Boronates)

Geminal bis(boronates) were prepared according to literature procedures.[1,5]

Method B. Prepared according to a literature precedent with slight modification.[6] In an Ar-filled drybox, an oven-dried 50-mL round bottom flask with magnetic stir bar was charged with lithium 2,2,6,6-tetramethylpiperidide (440 mg, 3.0 mmol). The flask was sealed with a rubber septum, removed from the drybox. THF (10 mL) was added and the reaction was cooled to 0 °C. A solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane[1,5] (804 mg, 3.0 mmol) in THF (5 mL) was added *via* syringe and the mixture was allowed to stir at 0 °C for 5 minutes. Then a solution of the corresponding alkyl bromide (3.3 mmol) in THF (5 mL) was added. The reaction mixture was allowed to warm to room temperature and stir for 2 hours. The reaction was diluted with Et_2O (10 mL) and filtered through Celite with Et_2O (10 mL). The solvent was removed *in vacuo* and the crude mixture was purified by silica gel chromatography.



5-S

2,2'-(4-Phenylpentane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5-S). Prepared according to *Method B* with (4-bromobutyl)benzene[7] as the electrophile. The crude mixture was purified by silica gel chromatography (5% ethyl acetate/hexanes, stain in CAM) to afford the title compound as a white solid (43%). R_f = 0.5 in 10% ethyl acetate/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.21 (m, 2H), 7.18-7.12 (m, 3H), 2.59 (t, *J* = 7.0 Hz, 2H), 1.59 (m, 4H), 1.32 (m, 2H), 1.22 (s, 12H), 1.20 (s, 12H), 0.72 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 1.43.13, 128.59, 128.27, 125.56, 83.03, 35.94, 32.26, 31.50, 25.70, 24.96, 24.66. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.85. IR (neat) ν_{max} 3085 (w), 3061 (w), 3026 (w), 2976 (s), 2928 (m), 2856 (m), 1584 (w), 1454 (m), 1354 (s), 1308 (s), 1265 (s), 1214 (m), 1137 (s), 969 (s), 849 (s), 745 (m), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{23}H_{39}B_2O_4$ $[M+H]^+$ 401.3034, found 401.3014. Melting point: 41-42 °C.

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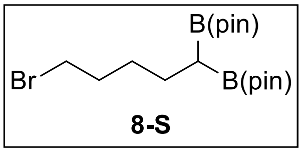
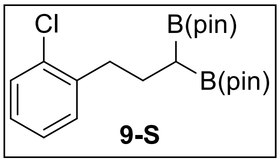
[5] Hong, K.; Liu, X.; Morken, J.P. *J. Am. Chem. Soc.* **2014**, *136*, 10581.
[6] Matteson, D. S.; Moody, R. J. *Organometallics*, **1982**, *1*, 20.
[7] Hardouin, C.; Kelso, M. J.; Romero, F. A.; Rayl, T. J.; Leung, D.; Hwang, I.; Cravatt, B. F.; Boger, D. L. *J. of Med. Chem.*, **2007**, *50*, 3359.



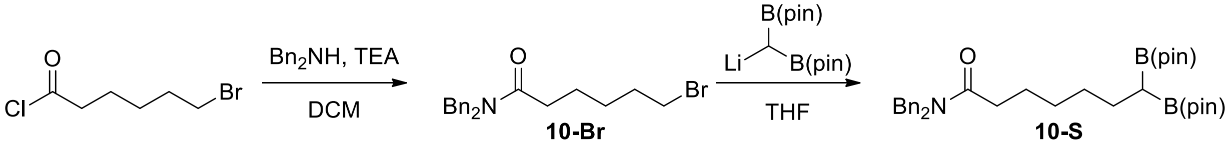
8-S

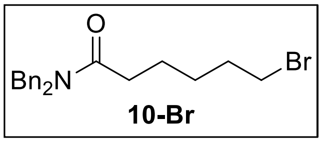
2,2'-(5-Bromopentane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8-S). Prepared according to *Method B* with 1,4-dibromobutane as the electrophile. The crude mixture was purified by silica gel chromatography (5% ethyl acetate/hexanes, stain in CAM) to afford the title compound as a white solid (52%). R_f = 0.5 in 10% ethyl acetate/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.39 (t, *J* = 7.0 Hz, 2H), 1.84 (p, *J* = 7.0 Hz, 2H), 1.57 (q, *J* = 8.0 Hz, 2H), 1.42 (m, 2H), 1.23 (s, 12H), 1.22 (s, 12H), 0.72 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.13, 34.21, 33.03, 31.08, 25.01, 24.99, 24.66. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.81. IR (neat) ν_{max} 2976 (s), 2930 (m), 2861 (w), 1459 (w), 1354 (s), 1306 (s), 1245 (s), 1213 (m), 1164 (s), 1004 (w), 968 (s), 905 (w), 849 (s), 734 (w) cm^{-1}. HRMS (ESI+) calc. for $C_{17}H_{37}B_2BrNO_4$ $[M+NH_4]^+$ 420.2092, found 402.2100. Melting point: 48-50 °C.



9-S

2,2'-(3-(2-Chlorophenyl)propane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (9-S). Prepared according to *Method A* with 2-chlorophenethylbromide as the electrophile. The crude mixture was purified by silica gel chromatography (10% ethyl acetate/hexanes, stain in CAM) to afford the title compound as a white solid (75%). R_f = 0.3 in 10% ethyl acetate/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.22 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.14 (dt, *J* = 7.0, 1.5 Hz, 1H), 7.08 (dt, *J* = 8.0, 2.0 Hz, 1H), 2.73-2.79 (m, 2H), 1.87 – 1.82 (m, 2H), 1.24 (s, 12H), 1.23 (s, 12H), 0.83 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.54, 134.01, 130.71, 129.35, 127.07, 126.64, 83.15, 36.18, 26.25, 25.05, 24.65. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.82. IR (neat) ν_{max} 2977 (w), 2929 (w), 2865 (w), 1474 (w), 1356 (m), 1310 (s), 1258 (m), 1215 (s), 1137 (s), 1105 (w), 970 (m), 846 (m), 755 (m), 679 (w) cm^{-1}. HRMS (ESI+) calc. for $C_{21}H_{34}B_2ClO_4$ $[M+H]^+$ 407.2332, found 407.2340. Melting point: 87-90 °C.

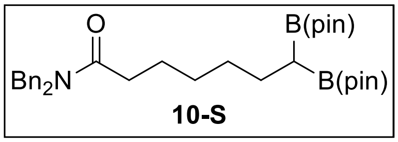




10-Br

***N,N*-Dibenzyl-6-bromohexanamide (10-Br).** To an oven-dried, 100-

mL round-bottom flask equipped with a magnetic stir bar under an atmosphere of N_2, was added CH_2Cl_2 (18 mL), triethylamine (1.2 mL, 8.4 mmol) and dibenzylamine (1.6 mL, 8.4 mmol) *via* syringe. The reaction was stirred and cooled to 0^{o}C. 6-Bromohexanoyl chloride (1.1 mL, 7.0 mmol) was added dropwise *via* syringe over a period of 10 minutes. The reaction was warmed to room temperature and stirred for 4 hours under N_2. The reaction was quenched by addition of H_2O (4 mL) and poured into a separatory funnel containing 3M NaOH (15 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 15 mL). The organic layers were combined, dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography (25% ethyl acetate/hexanes, stain in CAM) to afford the title compound as a yellow oil (2.3g, 88%). R_f = 0.2 in 20% ethyl acetate/hexanes on TLC.

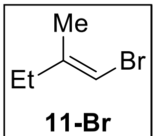


10-S

***N,N*-Dibenzyl-7,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanamide (10-S).** Prepared according to *Method B* with *N,N*-dibenzyl-6-bromohexanamide as the electrophile. The crude mixture was purified by silica gel chromatography (25% ethyl acetate/hexanes, stain in CAM) to afford the title compound as a yellow oil (55%). R_f = 0.2 in 20% ethyl acetate/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.24 (m, 8H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.0 Hz, 2H), 4.59 (s, 2H), 4.43 (s, 2H), 2.39 (t, *J* = 8.0 Hz, 2H), 1.70 (p, *J* = 7.5 Hz, 2H), 1.53 (q, *J* = 7.0 Hz, 2H), 1.35-1.22 (m, 4H), 1.21 (s, 6H), 1.20 (s, 6H), 0.69 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.87, 137.68, 136.77, 129.00, 128.64, 128.35, 127.63, 127.37, 126.49, 82.95, 49.99, 48.06, 33.47, 32.40, 29.63, 25.66, 25.57, 24.94, 24.60. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.71. IR (neat) ν_{max} 3029 (w), 2978 (m), 2929 (w), 2858 (w), 1641 (m), 1452 (m), 1358 (m), 1311 (s), 1267 (m), 1213 (m), 1137 (s), 969 (m), 908 (s), 849 (m), 726 (s), 698 (m) cm^{-1}. HRMS (ESI+) calc. for $C_{33}H_{50}B_2NO_5$ $[M+H]^+$ 562.3875, found 562.3861.

V. Synthesis and Characterization of Vinyl Bromides

Method C. Prepared according to a literature precedent with slight modification.[8] In an Ar-filled drybox, an oven-dried 100-mL round bottom flask was charged with Cp_2ZrCl_2 (640 mg, 2.2 mmol). The flask was removed from the drybox and CH_2Cl_2 (15 mL) was added followed cautiously by trimethylaluminium (2.9 mL, 30 mmol) *via* syringe. The reaction was cooled to -23°C and water (270 µL, 15 mmol) was added dropwise with vigorous stirring. After stirring for 10 minutes, the corresponding alkyne (10 mmol) was added in a solution of CH_2Cl_2 (5 mL). The reaction was stirred for an additional 10 minutes at -23°C before adding NBS (5.3 g, 30 mmol) as a solid. The reaction was allowed to warm to room temperature and stirred under N_2 for 12 hours. The reaction was cooled to 0°C and carefully quenched with a saturated solution of K_2CO_3 (3 mL). After stirring for 10 minutes, excess $Na_2SO_{4(s)}$ was added. The mixture was filtered through a short pad of silica and concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography.



11-Br

(*E*)-1-Bromo-2-methylbut-1-ene (11-Br). Prepared according to a literature precedent with slight modification.[7] In an Ar-filled drybox, to an oven-dried 2-neck 100-mL round bottom flask equipped with a magnetic stirbar was charged with Cp_2ZrCl_2 (643 mg, 2.2 mmol). The flask was sealed with rubber septa and removed from the drybox. Under a constant pressure of N_2, one septum was replaced a Dewar condenser. CH_2Cl_2 (15 mL) was added to the reaction vessel followed cautiously by trimethylaluminium (2.88 mL, 30 mmol) *via* syringe. The reaction was cooled to -23°C and water (270 µL, 15 mmol) was added dropwise with vigorous stirring. After stirring for 10 minutes, the Dewar condenser was cooled to -78 °C and butyne (0.9 mL, 10 mmol) was added dropwise *via* the condenser. The reaction was stirred for an additional 10 minutes at -23°C before adding NBS (5.3 g, 30 mmol) as a solid. The reaction was allowed to warm to room temperature and stirred under N_2 for 12 hours. The reaction was cooled to 0°C and carefully quenched with a saturated solution of K_2CO_3 (3 mL). After stirring for 10 minutes, excess $Na_2SO_{4(s)}$ was added. The mixture was filtered through a short pad of silica and concentrated *in vacuo*. The crude mixture was purified on silica gel

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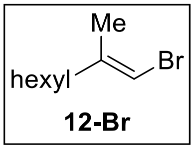
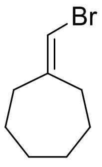
[8] Lim, S.; Wipf, P. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1068.

(pentane, stain in CAM) to afford a clear, colorless oil (44% yield). $R_f = 0.9$ in pentanes on TLC. The spectral data matched those reported in the literature.[9]



12-Br

(*E*)-1-Bromo-2-methyloct-1-ene (12-Br). Prepared according to *Method C*. The crude reaction mixture was purified by silica gel chromatography (pentanes, stain in CAM) to afford a clear, colorless oil (64% yield). $R_f = 0.9$ in pentanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (s, 1H), 2.09 (t, *J* = 7.5 Hz, 2H), 1.78 (s, 3H), 1.42 (p, *J* = 7.0 Hz, 2H), 1.36-1.21 (m, 6H), 0.89 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.18, 100.98, 38.48, 31.77, 28.89, 27.62, 22.72, 19.16, 14.20. IR (neat) ν_{max} 3070 (w), 2955 (m), 2926 (s), 2856 (m), 1632 (w), 1458 (m), 1377 (m), 1283 (m), 1160 (m), 771 (m), 712 (s) cm^{-1}. HRMS (ESI+) calc. for $C_9H_{18}Br$ $[M+H]^+$ 205.0592, found 205.0595.



13-Br

(Bromomethylene)cycloheptane (13-Br). Prepared according to a literature precedent with slight modification.[10] A 50-mL round-bottom flask equipped with a magnetic stir bar was charged with (bromomethyl)triphenylphosphonium bromide[11] (1.13 g, 2.60 mmol). The flask was purged with N_2 for 5 minutes and THF (7 mL) was added. The reaction was cooled to -78°C and a solution of KO*t*Bu (292 mg, 2.60 mmol) in THF (3 mL) was added dropwise. The reaction was stirred at -78°C for 5 minutes before warming to room temperature over 30 minutes. Cycloheptanone (236 μL, 2.00 mmol) was added neat and the reaction was stirred under N_2 at room temperature for 16 hours. The reaction was diluted with Et_2O (10 mL) and quenched with H_2O (10 mL). The mixture was added to a separatory funnel and the layers separated. The aqueous layer was then extracted with Et_2O (3 x 10 mL). The organic layers were combined, dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude mixture was purified by silica gel chromatography (pentanes, stain in CAM) to afford a clear, colorless oil (64% yield). $R_f = 0.9$ in pentanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (s, 1H), 2.37 (t, *J* = 6.0 Hz, 2H), 2.31 (t, *J* = 6.0 Hz, 2H), 1.69-1.47 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.47, 101.14, 36.50, 33.40, 30.11, 29.31, 28.85, 26.18. IR (neat) ν_{max} 3070 (w), 2921

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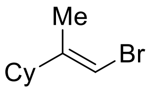
[9] Normant, J. F.; Chuit, C.; Cahiez, G.; Villiera, J. *Synthesis*, **1974**, 803.

[10] Harrowven, D.C.; Pascoe, D.D.; Guy,. I.L. *Angew. Chem. Int. Ed.* **2007**, *46*, 425.

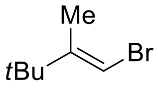
[11] Vassilikogiannakis, G.; Hatzimarinaki, M.; Orfanopoulos, M. *J. Org. Chem*. **2000**, *65*, 8180.

(s), 2850 (m), 1614 (w), 1441 (m), 1291 (m), 1159 (w), 763 (s), 729 (m), 682 (m) cm^{-1}. HRMS (ESI+) calc. for $C_8H_{14}Br$ $[M+H]^+$ 189.0279, found 189.0273.



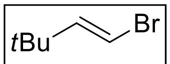
14-Br

(*E*)-(1-Bromoprop-1-en-2-yl)cyclohexane (14-Br). Prepared according to *Method C*. The crude reaction mixture was purified by silica gel chromatography (pentanes, stain in CAM) to afford a clear, colorless oil (47% yield). $R_f = 0.9$ in pentanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.92 (s, 1H), 2.02 (m, 1H), 1.8-1.65 (m, 7H), 1.33-1.09 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.92, 101.12, 47.07, 31.71, 26.60, 26.27, 17.75. IR (neat) ν_{max} 3069 (w), 2924 (s), 2852 (s), 1624 (m), 1447 (s), 1377 (m), 1306 (m), 1280 (m), 1165 (m), 1033 (m), 898 (m), 773 (s), 712 (s) cm^{-1}. HRMS (ESI+) calc. for $C_9H_{16}Br$ $[M+H]^+$ 203.0435, found 203.0435.



15-Br

(*E*)-1-Bromo-2,3,3-trimethylbut-1-ene (15-Br). Prepared according to *Method C*. The crude reaction mixture was purified by silica gel chromatography (pentanes, stain in CAM) to afford a clear, colorless oil (25% yield). $R_f = 0.9$ in pentanes on TLC. The spectral data matched those reported in the literature.[12]



16-Br

(*E*)-1-Bromo-3,3-dimethylbut-1-ene (16-Br). Prepared according to a literature precedent with slight modification.[13] To an oven-dried 25 mL round-bottom flask equipped with a magnetic stir bar under N_2 was added 3,3-dimethylbut-1-yne (370 µL, 3.0 mmol). DIBAL-H (3.3 mL, 3.3 mmol, 1.0 M in hexanes) was added *via* syringe and the reaction was stirred for 15 minutes at room temperature before heating to 50°C for 5 hours. The reaction was cooled to room temperature and Et_2O (2 mL) was added. The reaction was further cooled to -78°C and NBS (640 mg, 3.6 mmol) was added as a solid. Upon warming to room temperature, the reaction was stirred for 16 hours. To quench, the reaction was poured into a mixture of 6M HCl (10 mL), pentanes (20 mL), and ice. The layers were separated in a separatory funnel, and the aqueous layer was extracted with pentanes (3 x 20 mL). The organic layers were combined and washed successively with 1M NaOH (10 mL) and a saturated solution of $Na_2S_2O_3$ (10 mL). The organic layer was dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude

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[12] Lipshutz, B.H.; Butler, T.; Lower, A. *J. Am. Chem. Soc*. **2006**, *128*, 15396.
[13] Hanessian, S.; Tehim, A.; Chen, P. *J. Org. Chem*. **1993**, *58*, 7768

mixture was purified by silica gel chromatography (pentanes, stain in $KMnO_4$) to afford a clear, colorless oil (160 mg, 33% yield). $R_f = 0.9$ in pentanes on TLC. ^1H NMR (500 MHz, $CDCl_3$) δ 6.22 (d, $J = 14.0$ Hz, 1H), 5.98 (d, $J = 13.5$ Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.64, 102.02, 35.83, 29.133. IR (neat) ν_{max} 3085 (w), 2961 (m), 2932 (w), 2905 (w), 2868 (w), 1614 (w), 1463 (w), 1364 (m), 1263 (m), 945 (m), 906 (s), 774 (m) cm^{-1}. HRMS (ESI+) calc. for $C_6H_{12}Br$ $[M+H]^+$ 163.0122, found 163.0125.

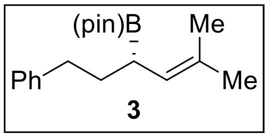
VI. Procedures for Enantiotopic-Group-Selective Suzuki Coupling

Method D. A 2-dram vial with magnetic stir bar was charged with **L6·PdCl₂** (0.9 mg, 0.0010 mmol) and 1,1-diborylalkane (0.15 mmol). The vial was sealed with rubber septum, and purged with N_2 for 10 minutes. Dioxane (250 μL) was added and the reaction stirred for 5 minutes. Then a solution of vinyl bromide in dioxane (250 μL, 0.10 mmol, 0.4M) and 8M $KOH_{(aq)}$[4] (56 μL, 0.45 mmol) were added sequentially *via* syringe. The reaction was stirred under an atmosphere of N_2 at room temperature for 18 hours. The reaction was diluted with Et_2O (2 mL) and filtered through a plug of Celite with additional Et_2O (5 mL). The filtrate was concentrated *in vacuo* and purified by silica gel chromatography to afford the desired compound. The enantiomeric ratio was determined for the alcohol obtained from subjecting the purified allyl boronate product to either hydrogen peroxide oxidation (*Method E*) or benzaldehyde allylation (*Method F*).

Method E, *oxidation to secondary allylic alcohol*. THF (3 mL) was added to the purified allylic boronate in a scintillation vial equipped with a stir bar. The vial was sealed with a septum and an exit needle inserted. The reaction was cooled to 0°C, and H_2O_2 (500 μL, 30 wt% in H_2O) and 3M NaOH (500 μL) were added sequentially *via* syringe. The reaction was warmed to room temperature and stirred for no less than 3 hours. The reaction was re-cooled to 0°C and quenched with a saturated solution of $Na_2S_2O_3$ (200 μL). The reaction was warmed to room temperature, diluted with Et_2O (3 mL), and then filtered through a plug of silica gel with additional Et_2O (5 mL). The solvent was removed *in vacuo* and the crude mixture was purified by silica gel chromatography to afford the corresponding secondary allylic alcohol.

Method F, *allylboration with benzaldehyde*. Toluene (500 μL) was added to the purified allylic boronate in a 2-dram vial equipped with a stir bar under N_2. The reaction was stirred and benzaldehyde (50 μL, 0.5 mmol) was added. The reaction was heated to 60°C for 24 hours under N_2. Upon cooling to room temperature, the reaction was diluted with Et_2O (3 mL) and filtered through a short pad of Celite with additional Et_2O (5 mL). The solvent was removed *in vacuo* and the crude mixture was purified by silica gel chromatography to afford the corresponding secondary homoallylic alcohol.

VII. Characterization of Reaction Products and Analysis of Stereochemistry



3

(*S*)-4,4,5,5-Tetramethyl-2-(5-methyl-1-phenylhex-4-en-3-yl)-1,3,2-dioxaborolane (3). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (27.9mg, 93% yield). R_f = 0.6 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.24 (m, 2H), 7.17-7.13 (m, 3H), 5.09 (d, *J* = 9.5 Hz, 1H), 2.64 (ddd, *J* = 13.5, 10.5, 5.5 Hz, 1H), 2.53 (ddd, *J* = 13.0, 10.5, 6.0 Hz, 1H), 1.99 (q, *J* = 8.5 Hz, 1H), 1.83 (ddt, *J* = 13.0, 10.0, 6.0 Hz, 1H), 1.72 (s, 3H), 1.67 (m, 1H), 1.59 (s, 3H), 1.23 (s, 6H), 1.22 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.06, 131.31, 128.63, 128.32, 125.65, 125.06, 83.09, 35.64, 33.71, 24.92, 24.69, 18.4. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.06. IR (neat) ν_{max} 3084 (w), 3062 (w), 3026 (m), 2976 (s), 2924 (s), 2856 (m), 1603 (s), 1495 (m), 1453 (m), 1369 (s), 1315 (s), 1269 (m), 1214 (m), 1141 (s), 1105 (m), 967 (s), 838 (m), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{19}H_{30}BO_2$ $[M+H]^+$ 301.2339, found 301.2335. $[\alpha]^{20}_D$: +1.73 (c = 0.925, $CHCl_3$, *l* =50 mm).

Gram Scale Procedure

A 50-mL round bottom flask with magnetic stir bar was charged with **L6**·$PdCl_2$ (42.8 mg, 0.050 mmol) and geminal bis(boronate) **1** (2.79 g, 7.5 mmol). The flask was sealed with rubber septum, and purged with N_2 for 20 minutes. Dioxane (25 mL) was added and the reaction stirred for 5 minutes. 1-Bromo-2-methylprop-1-ene (512 μL, 5.0 mmol)[14] and 8M $KOH_{(aq)}$[4] (2.80 mL, 22.5 mmol) were added sequentially *via* syringe. The reaction was stirred under an atmosphere of N_2 at room temperature for 18 hours. The reaction was diluted with Et_2O (15 mL) and poured into a separatory funnel with Et_2O (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 20 mL). The organic layers were combined, dried over $Na_2SO_{4(s)}$, filtered, and concentrated *in vacuo*. The crude material was purified by silica gel

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[14] 1-Bromo-2-methylprop-1-ene was sparged with N_2 for 30 min at room temperature before use.

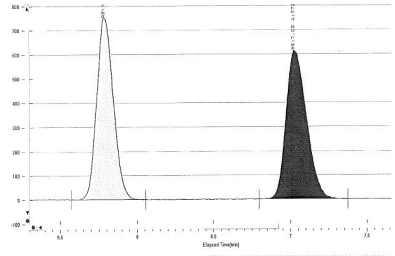
chromatography (20% CH_2Cl_2/hexanes, stain in CAM) to afford the title compound as a yellow oil (1.06 g, 71% yield) which co-eluted with protodeboration of the starting material (380 mg). The spectral data matched those above.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the corresponding geminal bis(boronate) according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

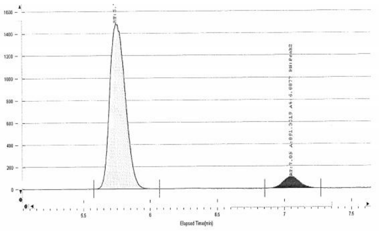
Racemic



Peak Info

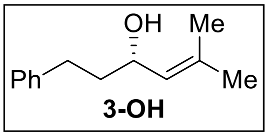
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.442	5595.4807	5.78	748.4358	0.0068
2	50.558	5721.7898	7.02	613.2783	0.0082
Total:	100	11317.2705			

Reaction product



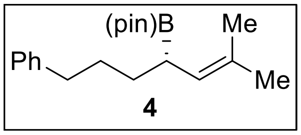
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	93.1123	12049.1209	5.74	1495.2346	0.0057
2	6.8877	891.3019	7.05	104.2689	0.007
Total:	100	12940.4228			



3-OH

(*S*)-5-Methyl-1-phenylhex-4-en-3-ol (3-OH). The reaction was performed according to the *Representative Procedure (Method E).* The crude mixture was purified by silica gel chromatography (8% ethyl acetate/pentanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.4 in 7/2/1 hexanes/CH_2Cl_2/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 7.20-7.17 (m, 3H), 5.22 (d, *J* = 9.0 Hz, 1H), 4.37 (q, *J* = 9.0 Hz), 1H), 2.67 (m, 2H), 1.92 (ddt, *J* = 13.5, 9.5, 6.5 Hz, 1H), 1.76 (ddt, *J* = 13.0, 10.0, 6.0 Hz, 1H), 1.74 (s, 3H), 1.66 (s, 3H), 1.34 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.21, 135.75, 128.53, 128.47, 128.06, 125.89, 68.31, 39.30, 31.95, 25.94, 18.41. IR (neat) ν_{max} 3359 (br), 3061 (w), 3026 (w), 2968 (w), 2926 (s), 2856 (m), 1495 (m), 1453 (s), 1376 (m), 1042 (s), 1006 (m), 746 (m), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{13}H_{17}$ $[M+H-H_2O]^+$ 173.1330, found 173.1338. $[\alpha]^{20}_{D}$: -36.1 (c = 0.400, $CHCl_3$, *l* =50 mm). The absolute stereochemistry was assigned by comparing the optical rotation with a reported value in the literature for (*S*)-**3-OH**, $[\alpha]^{20}_{D}$: -28.3 (c = 0.05, $CDCl_3$, 90:10 er).[15]



4

(*S*)-4,4,5,5-Tetramethyl-2-(2-methyl-7-phenylhept-2-en-4-yl)-1,3,2-dioxaborolane (4). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (26.4 mg, 84% yield). R_f = 0.7 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.24-7.27 (m, 2H), 7.14-7.17 (m, 3H), 5.03 (d, *J* = 9.5 Hz, 1H), 2.54-2.63 (m, 2H), 1.97 (q, *J* = 8.0 Hz, 1H), 1.69 (s, 3H), 1.52-1.66 (m, 6H), 1.39-1.45 (m, 1H), 1.22 (s, 6H), 1.21 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.06, 130.87, 128.53, 128.33, 125.64, 125.33, 83.04, 36.21, 31.48, 31.20, 26.01, 24.89, 24.69, 18.32. ^{11}B-NMR (160 MHz, $CDCl_3$) δ 33.03. IR (neat) ν_{max} 3026 (m), 2977 (s), 2926 (s), 2855 (s), 1603 (w) 1496 (m), 1453 (m) 1370 (s), 1317 (s), 1272 (m), 1214 (m), 1143 (s), 1106 (m), 968 (m), 886 (m), 835 (m), 747 (m), 698 (s). HRMS (ESI) calc. for $C_{20}H_{32}B_1O_2$ $[M+H]^+$ 315.2495, found 315.2490. $[\alpha]^{20}_{D}$: +8.67 (c = 0.870, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the corresponding geminal bis(boronate) according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

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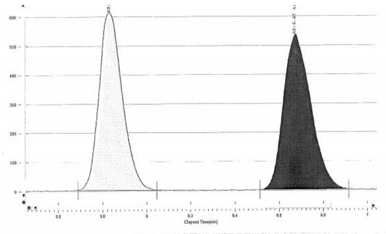
[15] Lurain, A. E.; Maestri, A.; Kelly, A. R.; Carroll, P. J.; Walsh, P. J. *J. Am. Chem. Soc.* **2004**, *126*, 13609.

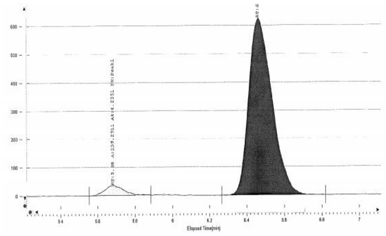
Racemic



Peak Info

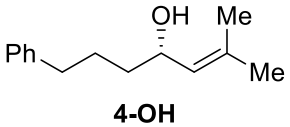
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.5817	4510.7816	5.83	611.7988	0.0069
2	50.4183	4586.8921	6.67	534.2568	0.0079
Total:	100	9097.6737			

Reaction product



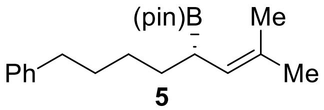
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	4.2351	239.2911	5.68	35.3769	0.0066
2	95.7649	5410.8592	6.46	624.9614	0.0076
Total:	100	5650.1503			



4-OH

(*S*)-2-Methyl-7-phenylhept-2-en-4-ol (4-OH). The reaction was performed according to the *Representative Procedure (Method E).* The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. $R_f = 0.5$ in 20% ethyl acetate/hexanes on TLC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.26-7.29 (m, 2H), 7.16-7.19 (m, 3H), 5.16 (d, $J = 8.5$ Hz, 1H), 4.36 (m, 1H), 2.63 (t, $J = 7.0$ Hz, 2H), 1.72 (s, 3H), 1.59-1.69 (m, 6H), 1.44-1.51 (m, 1H), 1.26 (d, $J = 3.0$ Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 142.58, 135.41, 128.56, 128.42, 128.24, 125.85, 68.72, 37.43, 36.03, 27.43, 25.92, 18.39. IR (neat) ν_{max} 3358 (br), 3063 (w), 3026 (m), 2923 (s), 2855 (s), 1673 (m), 1584 (m), 1553 (m), 1496 (s), 1452 (s), 1375 (s), 1056 (s), 985 (s), 747 (s), 698 (s). HRMS (ESI) calc. for $C_{14}H_{19}$ $[M+H-H_2O]^+$ 187.1486, found 187.1480. $[\alpha]^{20}_D$: -6.53 (c = 0.575, $CHCl_3$, l = 50 mm).



5

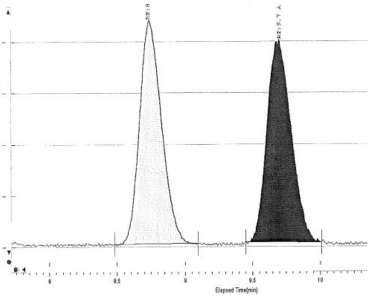
(*S*)-4,4,5,5-Tetramethyl-2-(2-methyl-8-phenyloct-2-en-4-yl)-1,3,2-dioxaborolane (5). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (26.3mg, 80%). $R_f = 0.8$ in 50% CH_2Cl_2/hexanes on TLC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.24-7.27 (m, 2H), 7.14-7.17 (m, 3H), 5.03 (d, $J = 9.0$ Hz, 1H), 2.54-2.63 (m, 2H), 1.91-1.95 (q, *J* = 8.0 Hz, 1H), 1.69 (s, 3H), 1.51-1.63 (m, 5H), 1.25-1.44 (m, 4H), 1.21 (s, 6H), 1.19 (s, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.06, 130.76, 128.56, 128.31, 125.63, 125.50, 83.00, 36.05, 31.68, 31.64, 29.01, 25.99, 24.85, 24.67, 18.29. ^{11}B-NMR (160 MHz, $CDCl_3$) δ 33.01. IR (neat) ν_{max} 3026 (w), 2976 (s), 2925 (s), 2855 (s), 1604 (w), 1453 (m), 1370 (s), 1316 (s), 1266 (m), 1214 (m), 1143 (s), 1107 (m), 967 (m), 838 (m) 746 (m), 698 (s). HRMS (ESI) calc. for $C_{21}H_{34}B_1O_2$ $[M+H]^+$ 329.2651, found 329.2664. $[\alpha]^{20}_D$: +10.7 (c = 0.680, $CHCl_3$, *l* = 50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the corresponding geminal bis(boronate) according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 5% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

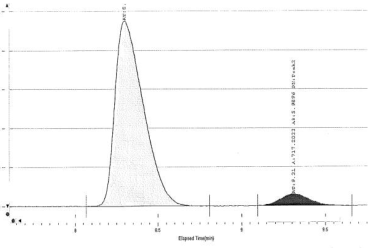
Racemic



Peak Info

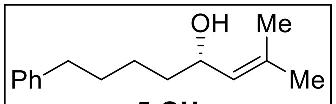
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.7522	2430.8773	8.73	217.4886	0.0126
2	50.2478	2455.0913	9.7	196.8144	0.014
Total:	100	4885.9686			

Reaction product



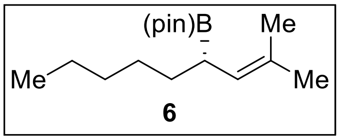
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	94.0104	11257.0005	8.3	949.3018	0.0093
2	5.9896	717.2033	9.31	60.5243	0.0104
Total:	100	11974.2038			



5-OH

(*S*)-2-Methyl-8-phenyloct-2-en-4-ol (5-OH). The reaction was performed according to the *Representative Procedure (Method E)*. The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.5 in 20% ethyl acetate/hexanes on TLC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.26-7.29 (m, 2H), 7.17-7.19 (m, 3H), 5.16 (d, *J* = 8.5 Hz, 1H), 4.31-4.36 (m, 1H), 2.60-2.63 (t, *J* = 8.5 Hz, 2H), 1.72 (s, 3H), 1.59-1.68 (m, 6H), 1.31-1.50 (m, 3H), 1.28 (d, *J* = 3.5 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 142.81, 135.31, 128.54, 128.40, 128.35, 125.78, 68.80, 37.68, 36.10, 31.65, 25.92, 25.33, 18.37. IR (neat) ν_{max} 3344 (br), 3063 (w), 3026 (m), 2927 (s), 2855 (s), 1673 (m), 1603 (m), 1495 (m), 1452 (s), 1375 (m), 1051 (s), 999 (s), 840 (m), 745 (s), 697 (s), 510 (m). HRMS (ESI) calc. for $C_{12}H_{21}$ $[M+H-H_2O]^+$ 201.1643, found 201.1653. $[\alpha]^{20}_D$: -10.1 (c = 0.440, $CHCl_3$, *l* = 50 mm).



6

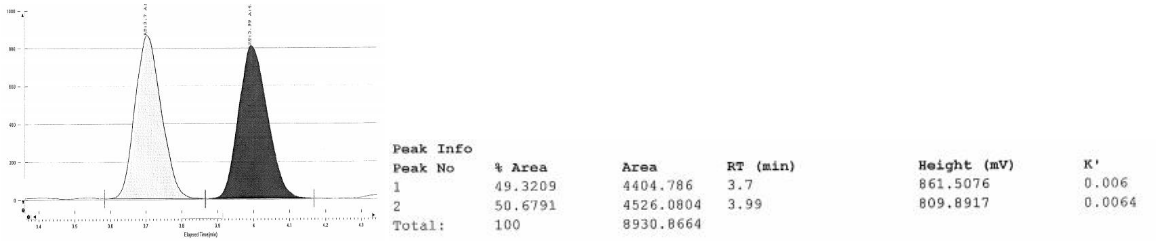
(*S*)-4,4,5,5-Tetramethyl-2-(2-methylnon-2-en-4-yl)-1,3,2-dioxaborolane (6). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (10% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (17.6 mg, 66% yield). R_f = 0.7 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.03 (d, *J* = 9.5 Hz, 1H), 1.92 (q, *J* = 7.5 Hz, 1H), 1.69 (s, 3H), 1.59 (s, 3H), 1.49 (m, 1H), 1.36-1.28 (m, 19H), 0.86 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.60, 125.68, 82.97, 32.11, 31.77, 29.06, 25.99, 24.88, 24.69, 22.76, 18.29, 14.21. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.01. IR (neat) ν_{max} 2976 (w), 2960 (w), 2923 (m), 2855 (w), 1458 (w), 1369 (m), 1314 (s), 1269 (w), 1215 (w), 1142 (s), 967 (m), 881 (w), 836 (m), 672 (w) cm^{-1}. HRMS (ESI+) calc. for $C_{16}H_{32}BO_2$ $[M+H]^+$ 267.2495, found 267.2492. $[\alpha]^{20}_D$: +14.7 (c = 0.875, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary homoallylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the corresponding geminal bis(boronate) according to *Methods A* and *F*.

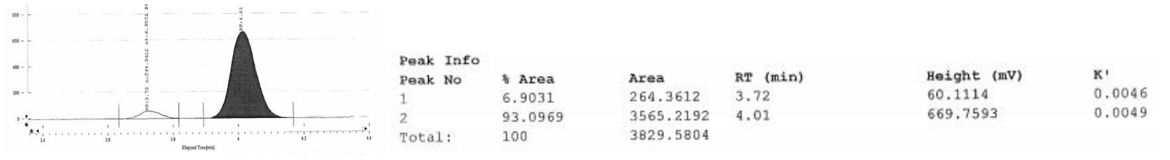
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 °C)-analysis of the reaction product.

Racemic

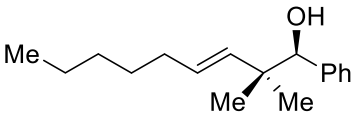


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.3209	4404.786	3.7	861.5076	0.006
2	50.6791	4526.0804	3.99	809.8917	0.0064
Total:	100	8930.8664			

Reaction product

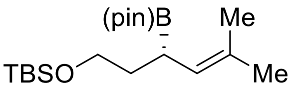


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	6.9031	264.3612	3.72	60.1114	0.0046
2	93.0969	3565.2192	4.01	669.7593	0.0049
Total:	100	3829.5804			



6-OH

(*R*,*E*)-2,2-Dimethyl-1-phenylnon-3-en-1-ol (6-OH). The reaction was performed according to the *Representative Procedure (Method F).* The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/pentanes, stain in CAM) to afford a colorless oil. R_f = 0.1 in 20% CH_2Cl_2/pentanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.23 (m, 5H), 5.49-5.46 (m, 2H), 4.38 (d, *J* = 2.5 Hz, 1H), 2.08-2.02 (m, 3H), 1.41-1.24 (m, 6H), 0.99 (s, 3H), 0.93 (s, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.01, 136.61, 130.56, 127.99, 127.54, 127.41, 80.95, 41.63, 33.00, 31.58, 29.41, 25.29, 22.68, 21.74, 14.21. IR (neat) ν_{max} 3460 (br), 3063 (w), 3028 (w), 2957 (s), 2925 (s), 2855 (m), 1453 (m), 1380 (w), 1186 (w), 1041 (m), 979 (m), 740 (m), 701 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{17}H_{25}$ $[M+H-H_2O]^+$ 229.1956, found 229.1958. $[\alpha]^{20}_D$: +39.7 (c = 0.375, $CHCl_3$, *l* =50 mm).



7

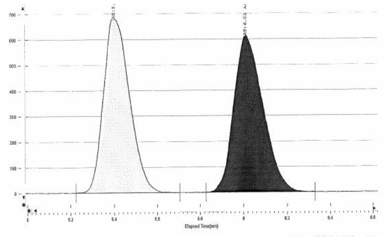
(*S*)-*tert*-Butyldimethyl((5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-1-yl)oxy)silane (7). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (40% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (22.0 mg, 62% yield). R_f = 0.5 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.01 (d, *J* = 9.5 Hz, 1H), 3.56 (m, 2H), 2.03 (q, *J* = 8.5 Hz, 1H), 1.75 (tt, *J* = 13.5, 7.0 Hz, 1H), 1.68 (s, 3H), 1.62-1.50 (m, 4H), 1.22 (s, 6H), 1.21 (s, 6H), 0.88 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 131.29, 124.79, 83.05, 62.75, 34.63, 26.15, 25.96, 24.87, 24.68, 18.53, 18.31, -5.11, -5.13. ^{11}B NMR (160 MHz, CDCl$_3$) δ 32.95. IR (neat) ν_{max} 2976 (w), 2956 (m), 2928 (s), 2857 (s), 1471 (m), 1360 (s), 1315 (s), 1252 (s), 1143 (s), 1093 (s), 1005 (m), 935 (m), 833 (s), 773 (s), 664 (m) cm^{-1}. HRMS (ESI+) calc. for $C_{19}H_{40}BO_3Si$ [M+H]$^+$ 355.2839, found 355.2843. $[\alpha]^{20}_{D}$: +21.6 (c = 1.05, CHCl$_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary homoallylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the corresponding geminal bis(boronate) according to *Methods A* and *F*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 5% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

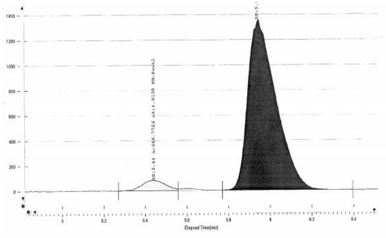
Racemic



Peak Info

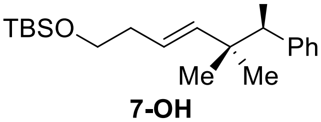
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.8617	5691.7632	5.4	678.3895	0.006
2	50.1383	5723.3385	6.01	611.5664	0.0067
Total:	100	11415.1017			

Reaction product



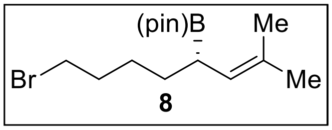
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	4.8138	646.7726	5.44	82.5489	0.0058
2	95.1862	12788.9862	5.94	1352.7745	0.0063
Total:	100	13435.7588			



7-OH

(*R,E*)-6-((*tert*-Butyldimethylsilyl)oxy)-2,2-dimethyl-1-phenylhex-3-en-1-ol (7-OH). The reaction was performed according to the *Representative Procedure (Method F).* The crude mixture was purified by silica gel chromatography (3% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.3 in 5% ethyl acetate/hexanes on TLC. ^{1}H NMR (500 MHz, CDCl$_3$) 7.33-7.23 (m, 5H), 5.54 (d, *J* = 16.5 Hz, 1H), 5.48 (dt, *J* = 16.0, 7.0 Hz, 1H), 4.37 (d, *J* = 3.0 Hz, 1H), 3.65 (t, *J* = 7.0 Hz, 2H), 2.29 (q, *J* = 6.5 Hz, 2H), 2.12 (d, *J* = 3.0 Hz, 1H), 1.00 (s, 3H), 0.93 (s, 3H), 0.90 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 140.96, 138.90, 128.00, 127.55, 127.43, 126.85, 80.81, 63.15, 41.80, 36.64, 26.14, 25.17, 21.55, 18.55, -5.09. IR (neat) ν_{max} 3446 (br), 3086 (w), 3028 (m), 2955 (s), 2928 (s), 2857 (s), 1493 (m), 1384 (m), 1360 (m), 1254 (s), 1187 (m), 1097 (s), 1044 (m), 834 (s), 775 (s), 702 (m) cm^{-1}. HRMS (ESI+) calc. for $C_{20}H_{33}OSi$ [M+H-H$_2$O]$^+$ 317.2301, found 317.2317. $[\alpha]^{20}_D$: +40.0 (c = 0.470, CHCl$_3$, *l* =50 mm).



8

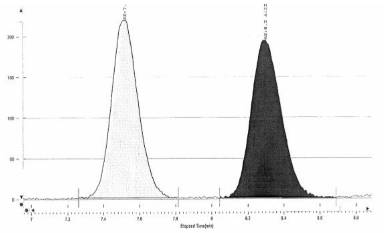
(*S*)-2-(8-Bromo-2-methyloct-2-en-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (20% CH$_2$Cl$_2$/hexanes, stain in CAM) to afford a clear, colorless oil (17.2 mg, 52% yield). R_f = 0.7 in 50% CH$_2$Cl$_2$/hexanes on TLC. ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.01 (d, *J* = 9.5 Hz, 1H), 3.39 (t, *J* = 6.5 Hz, 2H), 1.93 (q, *J* = 7.5 Hz, 1H), 1.84 (p, *J* = 6.5 Hz, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.58-1.33 (m, 4H), 1.23 (s, 6H), 1.22 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 131.00, 124.89, 82.95, 33.94, 32.92, 30.66, 27.73, 25.83, 24.73, 24.53, 18.16. ^{11}B NMR (160 MHz, CDCl$_3$) δ 32.93. IR (neat) ν_{max} 2977 (s), 2927 (s), 2856 (m), 1447 (w), 1370 (s), 1318 (s), 1272 (m), 1213 (w), 1144 (s), 1106 (w), 968 (m), 837 (m), 684 (w) cm^{-1}. HRMS (ESI+) calc. for $C_{15}H_{29}BBrO_2$ [M+H]$^+$ 331.1444, found 331.1437. $[\alpha]^{20}_D$: +15.5 (c = 0.580, CHCl$_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary homoallylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the corresponding geminal bis(boronate) according to *Methods A* and *F.*

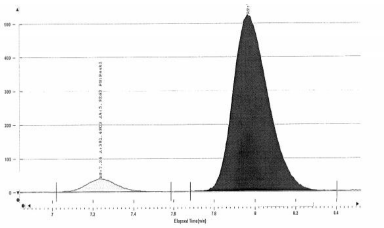
Chiral SFC (OD-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

Racemic

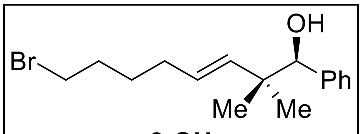


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.8344	2250.631	7.52	218.3679	0.0068
2	50.1656	2265.5901	8.3	194.2613	0.0075
Total:	100	4516.2211			

Reaction product

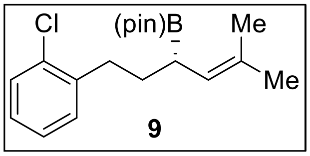


Peak Info					
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	5.9263	391.4903	7.24	38.8167	0.0068
2	94.0737	6214.4968	7.97	523.5658	0.0075
Total:	100	6605.9871			



8-OH

(*R,E*)-8-Bromo-2,2-dimethyl-1-phenyloct-3-en-1-ol (8-OH). The reaction was performed according to the *Representative Procedure (Method F).* The crude mixture was purified by silica gel chromatography (3% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. $R_f = 0.2$ in 5% ethyl acetate/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.24 (m, 5H), 5.52 (d, $J = 15.5$ Hz, 1H), 5.42 (dt, $J = 16.0, 7.0$ Hz, 1H), 4.40 (d, $J = 2.0$ Hz, 1H), 3.41 (t, $J = 7.0$ Hz, 2H), 2.09 (q, $J = 6.5$ Hz, 2H), 1.98 (d, $J = 3.0$ Hz, 1H), 1.86 (p, $J = 7.0$ Hz, 2H), 1.56-1.48 (m, 2H), 1.00 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.08, 137.47, 129.16, 127.95, 127.60, 127.50, 81.10, 41.62, 33.87, 32.38, 32.08, 28.17, 25.12, 22.04. IR (neat) ν_{max} 3455 (br), 3085 (w), 3062 (w), 3028 (w), 2960 (s), 2928 (s), 2856 (m), 1729 (w), 1585 (w), 1492 (w), 1452 (s), 1362 (m), 1249 (m), 1186 (m), 1082 (w), 1040 (s), 1003 (m), 978 (s), 740 (s), 702 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{16}H_{22}Br$ $[M+H-H_2O]^+$ 293.0905, found 293.0905. $[\alpha]^{20}_D$: +32.4 (c = 0.200, $CHCl_3$, l =50 mm).



9

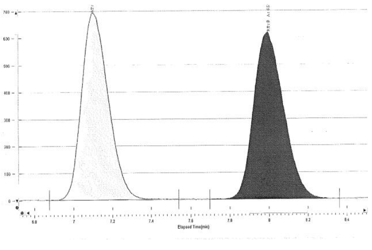
(*S*)-2-(1-(2-Chlorophenyl)-5-methylhex-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9). The reaction was performed according to the *Representative Procedure (Method C).* The crude mixture was purified by silica gel chromatography (30% DCM/hexanes, stain in CAM) to afford a clear, colorless oil (28.3 mg, 85% yield). R$_f$ = 0.3 in 50% DCM/hexanes on TLC. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 (d, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.15 (t, *J* = 7.5, 1H), 7.09 (dt, *J* = 7.0, 2.0 Hz, 1H), 5.11 (dd, *J* = 9.5, 1.5 Hz, 1H), 2.77 (ddd, *J* = 14.0, 11.0, 5.5 Hz, 1H), 2.64 (ddd, *J* = 13.5, 11.0, 5.5 Hz, 1H), 2.02 (q, *J* = 8.5 Hz, 1H), 1.83 (ddt, *J* = 12.0, 10.0, 5.5 Hz, 1H), 1.73 (s, 3H), 1.71–1.60 (m, 4H), 1.24 (s, 6H), 1.23 (s, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 140.57, 134.06, 131.49, 130.57, 129.47, 127.14, 126.73, 124.92, 83.15, 33.30, 31.74, 26.02, 24.93, 24.71, 18.38. ^{11}B NMR (160 MHz, CDCl$_3$) δ 32.97. IR (neat) ν_{max} 3066 (w), 2976 (m), 2925 (m), 2858 (m), 1572 (w), 1474 (m), 1443 (m), 1370 (s), 1341 (s), 1317 (s), 1268 (m), 1244 (m), 1215 (m), 1165 (m), 1141 (s), 1102 (m), 1053 (m), 986 (w), 876 (w), 855 (w), 838 (w), 750 (s), 679 (m) cm^{-1}. HRMS (ESI+) calc. for $C_{19}H_{29}BClO_2$ [M+H]$^+$ 335.1949, found 335.1945. $[\alpha]^{20}_D$: +2.70 c = 1.130, CHCl$_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the corresponding geminal bis(boronate) according to *Method A.*

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

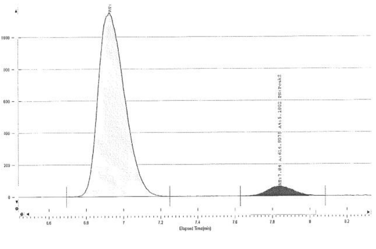
Racemic



Peak Info

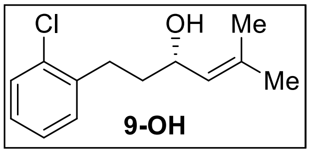
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.9825	6589.0133	7.1	690.7413	0.0075
2	50.0175	6593.6248	8	617.5016	0.0084
Total:	100	13182.6381			

Reaction product



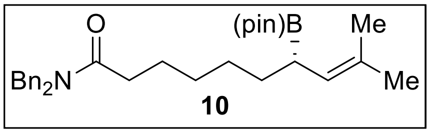
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	94.8198	11255.4809	6.93	1152.1104	0.0071
2	5.1802	614.9075	7.84	61.8495	0.008
Total:	100	11870.3884			



9-OH

(*S*)-1-(2-Chlorophenyl)-5-methylhex-4-en-3-ol (9-OH). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.3 in 7/2/1 hexanes/CH_2Cl_2/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.23 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.18 (dt, *J* = 7.0, 1.0 Hz, 1H), 7.13 (dt, *J* = 8.0, 2.0 Hz, 1H), 5.24 (dt, *J* = 9.0, 1.5 Hz, 1H) 4.39 (q, *J* = 7.0 Hz, 1H), 2.86-2.70 (m, 2H), 1.89 (dddd, *J* = 16.0, 13.5, 7.0, 6.0 Hz, 1H) 1.80-1.71 (m, 4H), 1.68 (d, 1.0 Hz, 3H), 1.59 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.81, 135.86, 134.09, 130.45, 129.60, 127.93, 127.40, 126.88, 68.41, 37.55, 29.83, 25.92, 18.41 IR (neat) ν_{max} 3347 (br), 3066 (w), 3014 (w), 2967 (m), 2928 (m), 2863 (w), 1675 (w), 1571 (w), 1474 (m), 1443 (m), 1376 (w), 1051 (s), 1035 (m), 1003 (w), 9112 (w), 844 (w), 823 (w), 750 (s), 681 (w) cm^{-1}. HRMS (ESI+) calc. for $C_{13}H_{16}Cl$ $[M+H-H_2O]^+$ 207.0941, found 207.0938. $[\alpha]^{20}_D$: -34.8 (c = 0.680, $CHCl_3$, *l* =50 mm).



10

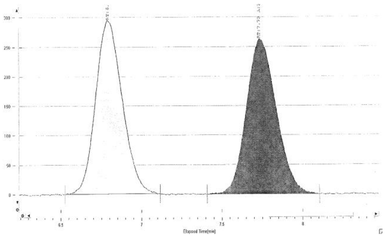
(*S*)-*N*,*N*-Dibenzyl-9-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-8-enamide (10). The reaction was performed according to the *Representative Procedure (Method D).* The crude reaction mixture was purified by column chromatography on SiO_2 (10% ethyl acetate in hexanes, stain in CAM) to afford an inseparable mixture of the title compound and protodeboration of the geminal bis(boronate) **10-S**. The mixture was oxidized according to the *Representative Procedure (Method E)* to **10-OH** as follows.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the corresponding geminal bis(boronate) according to *Method A.*

Chiral SFC (AD-H, Chiraldex, 3 mL/min, 20% MeOH, 100 bar, 35 °C)-analysis of the reaction product.

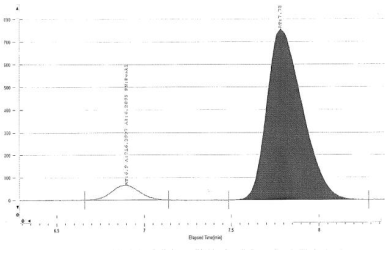
Racemic



Peak Info

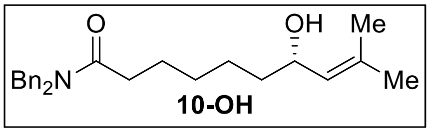
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.8147	3381.5262	6.79	294.5873	0.0112
2	50.1853	3406.6783	7.73	262.9152	0.0127
Total:	100	6788.2045			

Reaction product



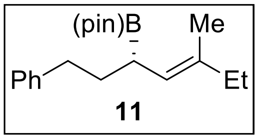
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	6.2895	716.3997	6.9	65.375	0.0085
2	93.7105	10673.9495	7.78	756.9625	0.0096
Total:	100	11390.3492			



10-OH

(*S*)-*N,N*-Dibenzyl-7-hydroxy-9-methyldec-8-enamide (10-OH). The reaction was performed according to the *Representative Procedure (Method E).* The crude reaction mixture was purified by column chromatography on SiO_2 (25% ethyl acetate in hexanes, stain in CAM) to afford a clear, colorless oil. $R_f = 0.29$ in 40% ethyl acetate/hexanes on TLC. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.35-7.38 (t, $J = 6.5$ Hz, 2H), 7.28-7.32 (m, 4H), 7.21 (d, $J = 7.0$ Hz, 2H), 7.15 (d, $J = 7.0$ Hz, 2H), 5.14 (d, $J = 9.0$ Hz, 1H), 4.60 (s, 2H), 4.44 (s, 2H), 4.31 (q, $J = 6.5$ Hz, 1H), 2.41 (t, $J = 7.5$ Hz, 2H), 1.70-1.75 (m, 1H) 1.72 (s, 3H), 1.67 (s, (3H), 1.60-1.54 (m, 1H), 1.26-1.43 (m, 7H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.76, 137.70, 136.80, 135.26, 129.08, 128.73, 128.44, 128.33, 127.72, 127.50, 126.51, 68.78, 50.04, 48.24, 37.71, 33.31, 29.53, 25.92, 25.53, 25.41, 18.39. IR (neat) ν_{max} 3422 (br), 3062 (w), 3029 (w), 2926 (s), 2855 (m), 2363 (w), 2341 (w), 1637 (s), 1494 (m), 1451 (s), 1361 (m), 1301 (w), 1215 (m), 1077 (m), 1011 (m), 954 (w), 732 (m), 699 (s). HRMS (ESI) calc. for $C_{25}H_{33}NO$ $[M+H-H_2O]^+$ 362.2484, found 362.2472. $[\alpha]^{20}_D$: -11.4 (c = 0.280, $CHCl_3$, l = 50 mm).



11

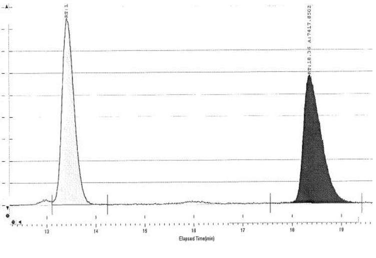
(*S*)-4,4,5,5-Tetramethyl-2-(5-methyl-1-phenylhex-4-en-3-yl)-1,3,2-dioxaborolane (11). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (30% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (25.2 mg, 80% yield). R_f = 0.6 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 7.20-7.13 (m, 3H), 5.08 (d, J = 10.0 Hz, 1H), 2.65 (ddd, J = 13.5, 10.0, 5.0 Hz, 1H), 2.54 (ddd, J = 14.0, 10.5, 6.0 Hz, 1H), 2.06-1.96 (m, 3H), 1.85 (ddt, J = 13.5, 10.5, 6.5 Hz, 1H), 1.69 (ddt, J = 13.5, 8.5, 5.0 Hz, 1H), 1.60 (s, 3H), 1.23 (s, 6H), 1.22 (s, 6H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.06, 137.01, 128.64, 128.32, 125.64, 123.72, 83.04, 35.64, 33.65, 32.79, 24.88, 24.65, 16.48, 13.34. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.92. IR (neat) ν_{max} 3084 (w), 3063 (w), 3026 (w), 2975 (s), 2926 (s), 2855 (m), 1739 (w), 1604 (w), 1496 (w), 1455 (m), 1370 (s), 1317 (s), 1270 (m), 1192 (m), 1143 (s), 1108 (m), 1072 (w), 967 (m), 876 (w), 847 (m), 748 (m), 699 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{20}H_{32}BO_2$ $[M+H]^+$ 315.2495, found 315.2499. $[\alpha]^{20}_D$: +3.21 (c = 0.650, $CHCl_3$, l =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the vinyl bromide **11-Br** according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 3% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

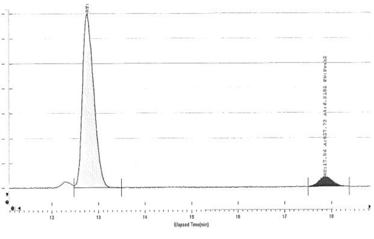
Racemic



Peak Info

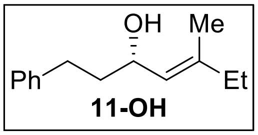
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.5242	7277.9925	13.42	423.4229	0.0183
2	50.4758	7417.8502	18.36	291.7892	0.0251
Total:	100	14695.8427			

Reaction product



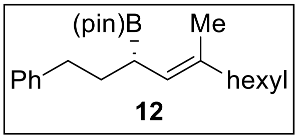
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	93.4818	11871.0159	12.76	702.5557	0.0172
2	6.5182	827.73	17.86	40.9241	0.024
Total:	100	12698.7459			



11-OH

(*S,E*)-5-Methyl-1-phenylhept-4-en-3-ol (11-OH). The reaction was performed according to the *Representative Procedure (Method E).* The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.3 in 7/2/1 hexanes/CH_2Cl_2/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.30-7.25 (m, 2H), 7.22-7.16 (m, 3H), 5.21 (dd, *J* = 8.5, 1.0 Hz, 1H), 4.40 (dq, *J* = 9.5, 3.0 Hz, 1H), 2.74-2.61 (m, 2H), 2.03 (q, *J* = 7.5 Hz, 2H), 1.93 (ddt, *J* = 13.0, 9.5, 6.5 Hz, 1H), 1.77 (ddt, *J* = 12.5, 10.0, 6.0 Hz, 1H), 1.66 (s, 3H), 1.33 (d, *J* = 3.0 Hz, 1H), 1.02 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.23, 141.05, 128.53, 128.47, 126.40, 125.89, 68.25, 39.36, 32.39, 31.98, 16.72, 12.62. IR (neat) ν_{max} 3258 (br), 3024 (w), 3000 (w), 2948 (m), 2926 (m), 2880 (w), 2834 (w), 1608 (m), 1510 (s), 1445 (m), 1341 (w), 1301 (m), 1243 (s), 1176 (m), 1023 (m), 1002 (m), 833 (m), 820 (m), 701 (m) cm^{-1}. HRMS (ESI+) calc. for $C_{14}H_{19}$ $[M+H-H_2O]^+$ 187.1487, found 187.1487. $[\alpha]^{20}_D$: -23.8 (c = 0.375, $CHCl_3$, *l* =50 mm).



12

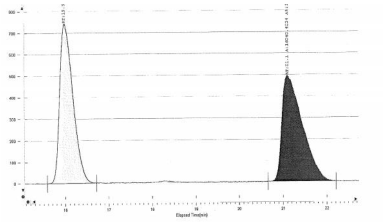
(*S,E*)-4,4,5,5-Tetramethyl-2-(5-methyl-1-phenylundec-4-en-3-yl)-1,3,2-dioxaborolane (12). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (20% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (32.2 mg, 87% yield). R_f = 0.6 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2H), 7.18-7.13 (m, 3H), 5.07 (d, *J* = 9.5 Hz, 1H), 2.65 (ddd, *J* = 13.0, 10.0, 5.0 Hz, 1H), 2.52 (ddd, *J* = 13.5, 10.5, 6.0 Hz, 1H), 2.00 (m, 3H), 1.84 (ddt, *J* = 13.0, 10.0, 6.5 Hz, 1H), 1.68 (ddt, *J* = 14.5, 10.5, 5.5 Hz, 1H), 1.57 (s, 3H), 1.41-1.19 (m, 20H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.09, 135.29, 128.65, 128.32, 125.64, 125.00, 83.05, 40.00, 35.67, 33.68, 31.99, 28.96, 28.22, 24.90, 24.69, 22.85, 16.48, 14.29. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.08. IR (neat) ν_{max} 3085 (w), 3062 (w), 3026 (w), 2976 (m), 2957 (m), 2925 (s), 2856 (s), 1604 (w), 1496 (w), 1479 (m), 1370 (s), 1317 (s), 1269 (m), 1214 (m), 1143 (s), 1108 (m), 968 (m), 847 (m), 747 (m), 699 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{24}H_{40}BO_2$ $[M+H]^+$ 371.3121, found 371.3124. $[\alpha]^{20}_D$: +6.60 (c = 1.39, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the vinyl bromide **12-Br** according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 4% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

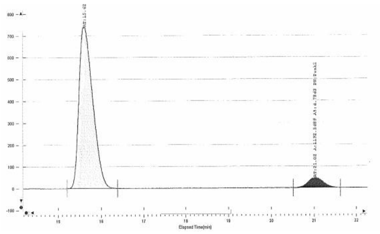
Racemic



Peak Info

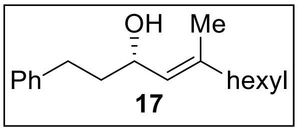
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.6515	15818.3629	15.97	743.0835	0.0211
2	50.3485	16040.4234	21.1	492.201	0.0279
Total:	100	31858.7863			

Reaction Product



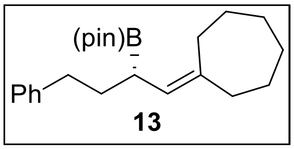
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	93.2137	16380.625	15.62	739.3971	0.0203
2	6.7863	1192.5689	21.02	46.7032	0.0273
Total:	100	17573.1939			



17

(*S,E*)-5-Methyl-1-phenylundec-4-en-3-ol (17). The reaction was performed according to the *Representative Procedure (Method E)* without the need to first purify the allylic boronate by silica gel chromatography. The crude oxidation mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil (21.3 mg, 82% yield). R_f = 0.4 in 7/2/1 hexanes/CH_2Cl_2/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.24-7.15 (m, 3H), 5.22 (d, *J* = 8.5 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 1H), 2.67 (m, 2H), 2.00 (t, *J* = 7.5 Hz, 2H), 1.93 (ddt, *J* = 13.5, 9.5, 6.5 Hz, 1H), 1.76 (ddt, *J* = 13.5, 10.0, 6.5 Hz, 1H), 1.64 (s, 3H), 1.45-1.24 (m, 9H), 0.89 (t, *J* = 5.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.24, 139.62, 128.53, 128.47, 127.59, 125.89, 68.26, 39.73, 39.37, 31.98, 31.88, 29.09, 27.84, 22.78, 16.71, 14.24. IR (neat) ν_{max} 3432 (br), 3084 (w), 3062 (w), 3026 (w), 2954 (m), 2925 (s), 2856 (s), 1667 (w), 1603 (w), 1495 (m), 1454 (s), 1379 (m), 1300 (w), 1272 (w), 1052 (m), 1030 (m), 1006 (m), 914 (w), 746 (m), 724 (m), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{18}H_{27}$ $[M+H-H_2O]^+$ 243.2113, found 243.2122. $[\alpha]^{20}_D$: -18.4 (c = 0.540, $CHCl_3$, *l* =50 mm).



13

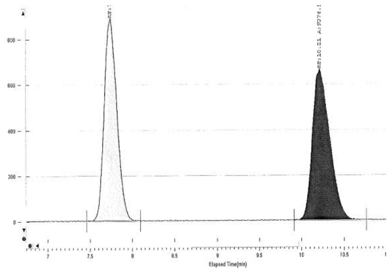
(*S*)-2-(1-Cycloheptylidene-4-phenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (30% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil (31.2 mg, 88% yield). R_f = 0.7 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 7.19-7.13 (m, 3H), 5.10 (d, *J* = 10 Hz), 1H), 2.67 (ddd, *J* = 13.5, 10.5, 5.5 Hz, 1H), 2.54 (ddd, *J* = 14.0, 11.0, 6.5 Hz, 1H), 2.22 (m, 4H), 1.99 (q, *J* = 9.0 Hz, 1H), 1.84 (ddt, *J* = 12.5, 10.0, 6.0 Hz, 1H), 1.69 (ddt, *J* = 14.0, 10.0, 5.5 Hz, 1H), 1.62-1.47 (m, 8H), 1.24 (s, 6H), 1.23 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.05, 140.95, 128.64, 128.31, 125.64, 125.52, 83.04, 38.06, 35.73, 33.63, 30.65, 30.04, 30.03, 29.32, 27.13, 24.91, 24.69. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.85. IR (neat) ν_{max} 3084 (w), 3062 (w), 3026 (w), 2976 (m), 2921 (s), 2852 (m), 1603 (w), 1496 (w), 1454 (m), 1355 (s), 1316 (s), 1270 (m), 1214 (w), 1142 (s), 1106 (m), 967 (m), 852 (m), 837 (m), 748 (m), 699 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{23}H_{36}BO_2$ $[M+H]^+$ 355.2808, found 355. 2805. $[\alpha]^{20}_D$: +15.3 (c = 1.28, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the vinyl bromide **13-Br** according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 10% ^{i}PrOH, 100 bar, 35 °C)-analysis of the reaction product.

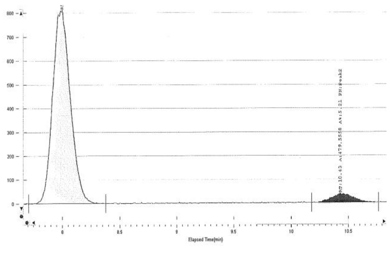
Racemic



Peak Info

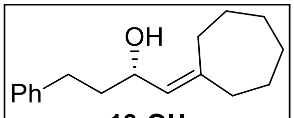
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	49.7253	9272.1324	7.74	887.7173	0.0094
2	50.2747	9374.5651	10.21	662.7859	0.0123
Total:	100	18646.6975			

Reaction product



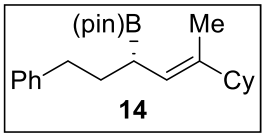
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	94.79	8725.0498	8	811.7093	0.0098
2	5.21	479.5558	10.43	37.6452	0.0128
Total:	100	9204.6056			



13-OH

(*S*)-1-Cycloheptylidene-4-phenylbutan-2-ol (13-OH). The reaction was performed according to the *Representative Procedure (Method E).* The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.4 in 7/2/1 hexanes/CH_2Cl_2/ethyl acetate on TLC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30- 7.15 (m, 5H), 5.23 (d, *J* = 8.5 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 1H), 2.69 (m, 4H), 2.32-2.2 (m, 4H), 1.92 (ddt, *J* = 13.0, 10.0, 6.5 Hz, 1H), 1.76 (ddt, *J* = 13.5, 10.0, 6.0 Hz), 1.66-1.48 (m, 8H), 1.37 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.28, 142.26, 128.52, 128.46, 128.20, 125.88, 67.90, 39.37, 37.97, 32.04, 30.32, 29.73, 29.13, 29.09, 27.48. IR (neat) ν_{max} 3420 (br), 3085 (w), 3061 (w), 3026 (w), 2920 (s), 2851 (s), 2676 (w), 1726 (w), 1655 (w), 1495 (m), 1453 (s), 1276 (w), 1179 (w), 1043 (s), 1030 (m), 996 (m), 914 (w), 746 (s), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{17}H_{23}$ $[M+H-H_2O]^+$ 227.1800, found 227.1801. $[\alpha]^{20}_D$: -34.6 (c = 0.635, $CHCl_3$, *l* =50 mm).



14

(*S,E*)-2-(5-Cyclohexyl-1-phenylhex-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (30% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, colorless oil

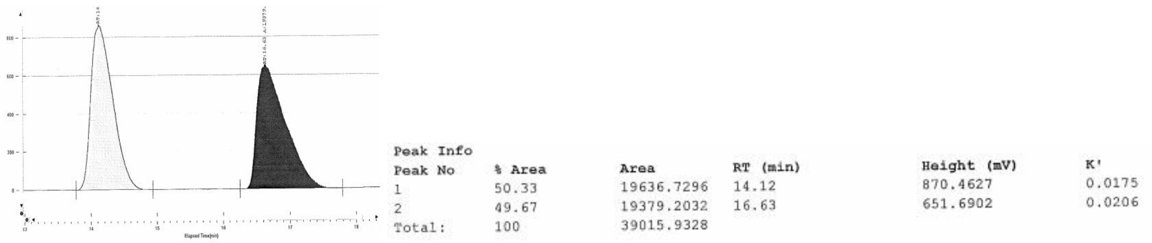
(30.2 mg, 82% yield). $R_f = 0.6$ in 50% CH_2Cl_2/hexanes on TLC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2H), 7.18-7.12 (m, 3H), 5.06 (d, *J* = 9.0 Hz, 1H), 2.64 (ddd, *J* = 14.5, 10.5, 5.5 Hz, 1H), 2.52 (ddd, *J* = 13.5, 10.5, 6.5 Hz, 1H), 1.99 (q, *J* = 9.0 Hz, 1H), 1.90-1.78 (m, 2H), 1.77-1.60 (m, 6H), 1.56 (s, 3H), 1.35-1.06 (m, 17H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.07, 140.57, 128.67, 128.31, 125.64, 123.11, 82.99, 47.79, 35.64, 33.58, 32.34, 32.30, 26.96, 26.58, 24.86, 24.61, 14.94. ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.78. IR (neat) ν_{max} 3084 (w), 3062 (w), 3026 (w), 2977 (m), 2924 (s), 2852 (s), 1603 (w), 1496 (w), 1480 (m), 1370 (s), 1317 (s), 1270 (m), 1215 (w), 1143 (s), 987 (m), 844 (m), 748 (m), 699 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{24}H_{38}BO_2$ $[M+H]^+$ 369.2965, found 369.2965. $[\alpha]^{20}_D$: +10.1 (c = 0.955, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the vinyl bromide **14-Br** according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 6% ^{i}PrOH, 100 bar, 35 ^oC)-analysis of the reaction product.

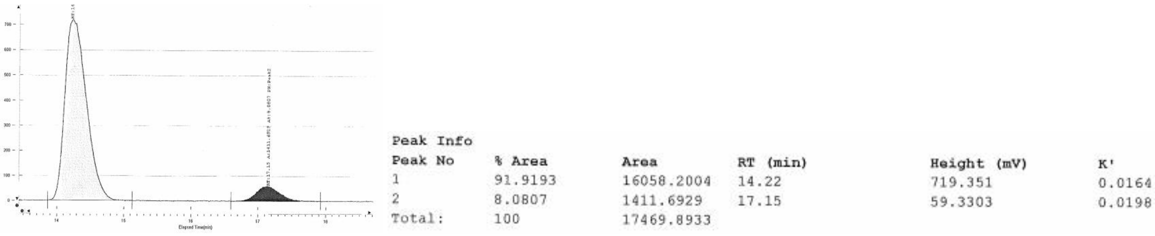
Racemic



Peak Info

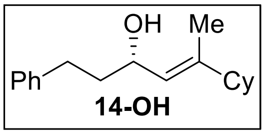
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.33	19636.7296	14.12	870.4627	0.0175
2	49.67	19379.2032	16.63	651.6902	0.0206
Total:	100	39015.9328			

Reaction product



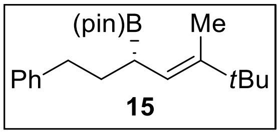
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.9193	16058.2004	14.22	719.351	0.0164
2	8.0807	1411.6929	17.15	59.3303	0.0198
Total:	100	17469.8933			



14-OH

(*S,E*)-5-Cyclohexyl-1-phenylhex-4-en-3-ol (14-OH). The reaction was performed according to the *Representative Procedure (Method E).* The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.6 in 20% ethyl acetate/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 5.21 (d, *J* = 8.0 Hz, 1H), 4.39 (q, *J* = 7.0 Hz, 1H), 2.66 (m, 2H), 1.93 (ddt, *J* = 13.0, 9.5, 6.5 Hz, 1H), 1.85 (m, 1H), 1.81-1.64 (m, 6H), 1.62 (s, 3H), 1.36-1.09 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.53, 142.26, 128.54, 128.47, 125.89, 125.88, 68.18, 47.37, 39.38, 31.99, 31.97, 26.80, 26.47, 15.19. IR (neat) ν_{max} 3329 (br), 3084 (w), 3062 (w), 3026 (w), 2924 (s), 2852 (s), 1662 (w), 1603 (w), 1495 (w), 1382 (m), 1265 (w), 1189 (w), 1052 (m), 1030 (m), 1006 (m), 746 (m), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{18}H_{25}$ $[M+H-H_2O]^+$ 241.1956, found 241.1951. $[\alpha]^{20}_D$: -13.8 (c = 0.600, $CHCl_3$, *l* =50 mm).



15

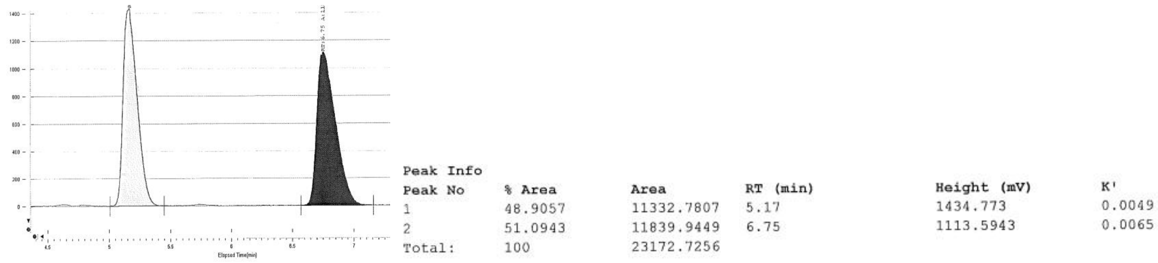
(*S,E*)-4,4,5,5-Tetramethyl-2-(5,6,6-trimethyl-1-phenylhept-4-en-3-yl)-1,3,2-dioxaborolane (15). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (30% CH_2Cl_2/hexanes, stain in CAM) to afford a clear, yellow oil (23.5 mg, 69% yield). R_f = 0.6 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.21 (m, 2H), 7.17-7.12 (m, 3H), 5.11 (d, *J* = 9.0 Hz, 1H), 2.63 (ddd, *J* = 15.0, 10.0, 5.5 Hz, 1H), 2.53 (ddd, *J* = 13.0, 6.5, 3.0 Hz, 1H), 1.99 (q, *J* = 8.5 Hz, 1H), 1.85 (ddt, *J* = 13.5, 10.0, 7.0 Hz 1H) 1.71 (dtd, *J* = 13.5, 9.5, 5.5 Hz, 1H), 1.59 (s, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.03, 128.65, 128.31, 125.64, 121.72, 82.95, 36.33, 35.71, 33.57, 29.38, 24.80, 24.58, 13.50. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.76. IR (neat) ν_{max} 3085 (w), 3062 (w), 3026 (w), 2966 (s), 2930 (s), 2861 (m), 1735 (w), 1604 (w), 1495 (w), 1478 (m), 1455 (m), 1357 (s), 1315 (s), 1263 (m), 1214 (m), 1199 (m), 1143 (s), 1106 (m), 967 (m), 847 (m), 748 (m), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{22}H_{36}BO_2$ $[M+H]^+$ 343.2808, found 343.2806. $[\alpha]^{20}_D$: +14.2 (c = 1.175, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the vinyl bromide **15-Br** according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

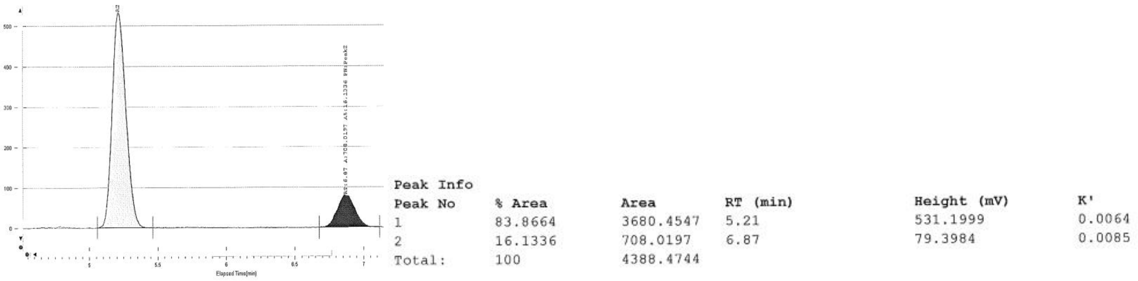
Racemic



Peak Info

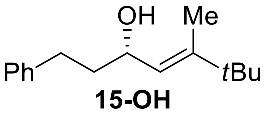
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	48.9057	11332.7807	5.17	1434.773	0.0049
2	51.0943	11839.9449	6.75	1113.5943	0.0065
Total:	100	23172.7256			

Reaction product



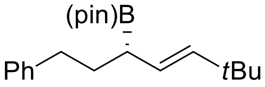
Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	83.8664	3680.4547	5.21	531.1999	0.0064
2	16.1336	708.0197	6.87	79.3984	0.0085
Total:	100	4388.4744			



15-OH

(*S,E*)-5,6,6-Trimethyl-1-phenylhept-4-en-3-ol (15-OH). The reaction was performed according to the *Representative Procedure (Method E).* The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R$_f$ = 0.4 in 7/2/1 hexanes/CH_2Cl_2/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) 7.30-7.24 (m, 2H), 7.22-7.15 (m, 3H), 5.27 (dd, J = 8.5, 1.0 Hz, 1H), 4.40 (q, J = 7.0 Hz, 1H), 2.74-2.60 (m, 2H), 1.94 (ddt, J = 13.0, 9.5, 7.0 Hz, 1H), 1.77 (ddt, J = 13.5, 10.0, 6.0 Hz, 1H), 1.65 (s, 3H), 1.05 (s, 9H) . ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.00, 142.27, 128.54, 128.49, 125.90, 124.74, 68.62, 39.44, 36.28, 32.02, 29.10, 13.30. IR (neat) ν_{max} 3402 (br), 3085 (w), 3062 (w), 3026 (w), 2954 (s), 2867 (m), 1654 (w), 1603 (w), 1495 (m), 1478 (m), 1454 (m), 1377 (m), 1360 (m), 1259 (w), 1052 (m), 1071 (s), 1005 (m), 914 (w), 841 (w), 746 (m), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{16}H_{23}$ $[M+H-H_2O]^+$ 215.1800, found 215.1807. $[\alpha]^{20}_D$: -22.5 (c = 0.485, $CHCl_3$, l =50 mm).



16

(*S,E*)-2-(6,6-Dimethyl-1-phenylhept-4-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16). The reaction was performed according to the *Representative Procedure (Method D).* The crude mixture was purified by silica gel chromatography (30% CH_2Cl_2/hexanes, stain in CAM) to afford a white solid (24.6 mg, 75% yield). R$_f$ = 0.6 in 7:2:1 hexanes/CH_2Cl_2/ethyl acetate on TLC. ^{1}H NMR (500 MHz,

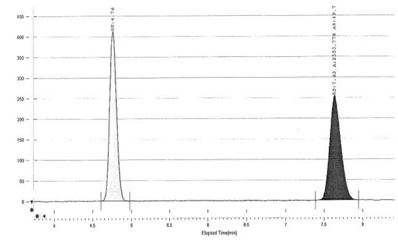
$CDCl_3$) δ 7.28-7.23 (m, 2H) 7.19 – 7.13 (m, 3H), 5.47 (dd, *J* = 15.5, 1.0 Hz, 1H), 5.26 (dd, *J* = 15.5, 8.5 Hz, 1H), 2.63 (ddd, *J* = 14.0, 9.5, 5.5 Hz, 1H) 2.55 (ddd, *J* = 13.5, 10.0, 5.5 Hz, 1H), 1.88-1.75 (m, 2H), 1.70 (ddt, *J* = 12.0, 6.0, 4.5 Hz, 1H) 1.24 (s, 6H), 1.23 (s, 6H), 0.99 (s, 9H) . ^{13}C NMR (126 HMz, $CDCl_3$) δ 143.06, 141.70, 128.66, 128.34, 125.67, 124.94, 83.15, 35.52, 33.15, 33.09, 30.07, 24.88, 24.66. ^{11}B NMR (160 MHz, $CDCl_3$) δ 33.01. IR (neat) ν_{max} 3085 (w), 3063 (w), 3026 (w), 2976 (s), 2957 (s), 2930 (s), 2862 (m), 1604 (w), 1496 (w), 1456 (m), 1360 (s), 1320 (s), 1266 (m), 1214 (m), 1143 (s), 1108 (w), 970 (s), 854 (m), 747 (m), 699 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{21}H_{34}BO_2$ $[M+H]^+$ 329.2652, found 329.2661. $[\alpha]^{20}_D$: +10.6 (c = 0.665, $CHCl_3$, *l* =50 mm). Melting point: 48-51 °C.

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis of the corresponding secondary allylic alcohol. The racemic alcohol was prepared analogously with racemic **L4** and the vinyl bromide **16-Br** according to *Method A*.

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 °C)-analysis of the reaction product.

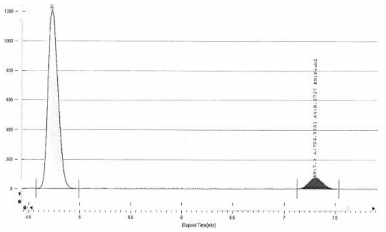
Racemic



Peak Info

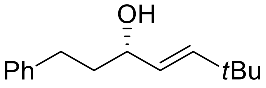
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.2435	2578.7738	4.76	411.9121	0.0064
2	49.7565	2553.778	7.63	254.0157	0.0103
Total:	100	5132.5518			

Reaction product



Peak Info

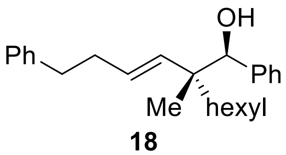
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	91.9263	8272.3213	4.72	1211.6924	0.0044
2	8.0737	726.5453	7.3	76.2806	0.0068
Total:	100	8998.8666			



16-OH

(*S,E*)-6,6-Dimethyl-1-phenylhept-4-en-3-ol (16-OH). The reaction was performed according to the *Representative Procedure (Method E).* The crude mixture was purified by silica gel chromatography (20% ethyl acetate/hexanes, stain in CAM) to afford a clear, colorless oil. R_f = 0.5 in 7/2/1 hexanes/CH_2Cl_2/ethyl acetate on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 7.22-7.16 (m, 3H), 5.67 (d, *J* = 15.5 Hz, 1H), 5.39 (dd, *J* = 15.5, 7.0 Hz, 1H), 4.10-4.04 (m, 1H), 2.75-2.62 (m, 2H), 1.93-1.76 (m, 2H), 1.45 (d, *J* = 3.0 Hz, 1H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.56, 142.19, 128.60, 128.50, 127.64, 125.92, 72.83, 39.07, 32.95, 31.99, 29.67. IR (neat) ν_{max} 3356 (br), 3085 (w), 3062 (w), 3026 (w), 2956 (s), 2863 (s), 1661 (w), 1603 (w), 1496 (m), 1455 (m), 1390 (w), 1362 (m), 1267 (w), 1202 (w), 1100 (w), 1031 (m), 973 (s), 911 (m), 746 (s), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{15}H_{21}$ $[M+H-H_2O]^+$ 201.1643, found 201.1632. $[\alpha]^{20}_D$: -7.94 (c = 0.500, $CHCl_3$, *l* =50 mm). The absolute stereochemistry was assigned by comparing the optical rotation with a reported value in the literature for (*S*)-**16-OH**, $[\alpha]^{20}_D$: -7.5 (c = 0.96, $CHCl_3$, 91:9 er).[16]

VIII. Further Transformations of Allylic Boronate 12



18

(1*R*,2*R*)-2-Methyl-1-phenyl-2-((*E*)-4-phenylbut-1-en-1-yl)octan-1-ol (18). After performing the enantiotopic-group-selective cross-coupling (*Method D*), the crude mixture containing **12** was diluted with Et_2O (3 mL) and filtered through Celite with additional Et_2O (5 mL). The solvent was removed *in vacuo* and the crude residue transferred to a 2-dram vial with Et_2O. The solvent was again removed under vacuum, and the vial equipped with a magnetic stir bar. After purging with N_2, toluene (500 μL) was added. The reaction was stirred and benzaldehyde (50 μL, 0.5 mmol) was added. The reaction was heated to 60°C for 24 hours under N_2. Upon cooling to room temperature, the reaction was diluted with Et_2O (3 mL) and filtered through a short pad of Celite with additional Et_2O (5 mL). To simplify purification, the residue was further oxidized according to *Method E* and the title compound was obtained by silica gel chromatography (30% CH_2Cl_2/hexanes) as a clear, colorless oil (28.0 mg, 80% yield). R_f = 0.4 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30-7.63 (m, 10H), 5.47 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.34 (d, *J* = 16.0 Hz, 1H), 4.29 (s, 1H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.44 (q, *J* = 7.0 Hz, 2H), 1.88 (s, 1H), 1.36-1.04 (m, 10H), 0.87 (t, *J* = 7.0 Hz, 3H), 0.83 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.84, 140.73, 136.74, 130.86, 128.62, 128.51, 128.22, 127.49, 127.36, 126.06, 80.32, 45.24, 38.07, 36.06, 34.89, 32.03, 30.24, 24.15, 22.82, 17.28, 14.22. IR (neat) ν_{max}

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[16] Sprout, C. M.; Richmond, M. L.; Seto, C. T. *J. Org. Chem.* **2005**, *70*, 7408.

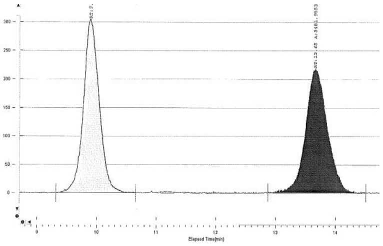
3453 (br), 3085 (w), 3062 (w), 3027 (w), 2954 (m), 2927 (s), 2856 (m), 1495 (w), 1453 (m), 1377 (w), 1037 (m), 981 (m), 745 (s), 699 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{25}H_{33}$ $[M+H-H_2O]^+$ 333.2582, found 333.2576. $[\alpha]^{20}_{D}$: +34.1 (c = 1.19, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis. The racemic alcohol was prepared analogously with racemic **L4.**

Chiral SFC (OJ-H, Chiraldex, 3 mL/min, 7% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

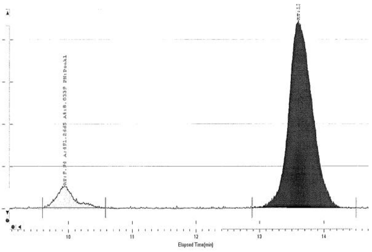
Racemic



Peak Info

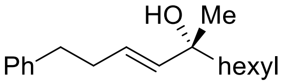
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.3986	5570.0836	9.89	305.0753	0.0125
2	49.6014	5481.9853	13.65	218.2576	0.0173
Total:	100	11052.0689			

Reaction product



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	8.0339	491.2665	9.94	25.9686	0.0123
2	91.9661	5623.661	13.6	221.7518	0.0168
Total:	100	6114.9275			



19

(*R,E*)-5-methyl-1-phenylundec-3-en-5-ol (19).[17] After performing the enantiotopic-group-selective cross-coupling (*Method D*), the crude mixture containing **12** was diluted with Et_2O (3 mL) and filtered through Celite with additional Et_2O (5 mL). The solvent was removed in vacuo and the crude residue transferred to a 2-dram vial with Et_2O. The solvent was again removed under vacuum, and the vial equipped with a magnetic stir bar. After purging with N_2, THF (1 mL) was added and the reaction was cooled to 0^{o}C. Nitrobenzene (32.1 mg, 0.30 mmol) was added as a solution in THF (1 mL) via syringe. The reaction was warmed to room temperature and stirred under N_2 for one hour. The reaction was re-cooled to 0^{o}C and 3M $NH_4OH_{(aq)}$ (500 µL, 1.6 mmol) was

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[17] Kyne, R. E.; Ryan, M. C.; Kliman, L. T.; Morken, J. P. *Org. Lett.* **2010**, *12*, 3796.

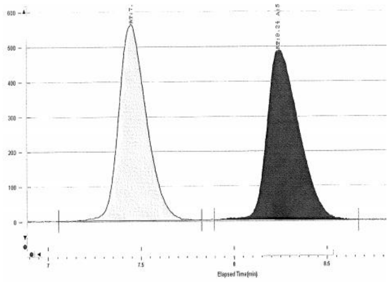
added. The reaction was warmed to room temperature and stirred under N_2 for 16 hours. To quench, the reaction was diluted with Et_2O (3 mL) and filtered through a plug of silica with additional Et_2O (5 mL). The solvent was removed under vacuum. To simplify purification, the crude residue was further oxidized according to *Method E*, and the title compound was obtained by silica gel chromatography (20% CH_2Cl_2/hexanes to 40% CH_2Cl_2/hexanes) as a clear, yellow oil (16.4 mg). R_f = 0.3 in 50% CH_2Cl_2/hexanes on TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.20-7.15 (m, 3H), 5.63 (dtd, *J* = 15.5, 6.5, 2.0 Hz, 1H), 5.51 (dd, *J* = 15.5, 1.5 Hz, 1H), 2.70 (t, *J* = 8.0 Hz, 2H), 2.36 (ddd, *J* = 15.5, 8.0, 1.0 Hz, 2H), 1.46 (m, 2H), 1.32-1.20 (m, 12H), 0.89 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.96, 137.96, 128.62, 128.39, 126.96, 125.92, 72.92, 43.00, 36.00, 34.19, 31.96, 29.88, 28.08, 24.10, 22.78, 14.22. IR (neat) ν_{max} 3470 (br), 3026 (w), 2956 (m), 2928 (s), 2856 (m), 1454 (m), 1375 (w), 971 (m), 746 (m), 698 (s) cm^{-1}. HRMS (ESI+) calc. for $C_{18}H_{27}$ $[M+H-H_2O]^+$ 243.2113, found 243.2102. $[\alpha]^{20}_D$: -0.704 (c = 0.690, $CHCl_3$, *l* =50 mm).

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral SFC analysis. The racemic alcohol was prepared analogously with racemic **L4.**

Chiral SFC (OD-H, Chiraldex, 3 mL/min, 5% ^{i}PrOH, 100 bar, 35 ^{o}C)-analysis of the reaction product.

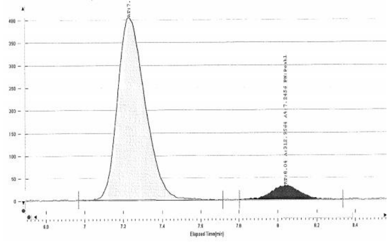
Racemic



Peak Info

Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	50.013	5821.7491	7.45	564.4994	0.0084
2	49.987	5818.7191	8.24	486.3836	0.0093
Total:	100	11640.4682			

Reaction product

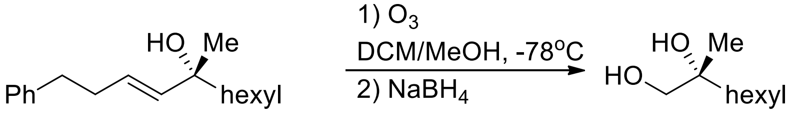


Peak Info

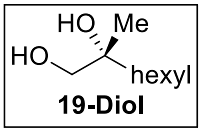
Peak No	% Area	Area	RT (min)	Height (mV)	K'
1	92.7544	4006.2951	7.23	404.4908	0.01
2	7.2456	312.9564	8.04	31.4308	0.0111
Total:	100	4319.2515			

IX. Structure Proof of 19:

The absolute structure of **19** was determined by ozonolysis/reduction to **19-Diol**, and subsequent comparison with the Sharpless Asymmetric Dihydroxylation[18] product of 2-methyloct-1-ene, which is known to afford the (*R*) isomer utilizing AD-mix-β.[19] Racemic **19-Diol** was prepared according to a literature precedent.[20]



19 **19-Diol**



(*R*)-2-Methyloctane-1,2-diol (19-OH). A 4-dram vial was charged with **19** (55 mg, 0.21 mmol), CH_2Cl_2 (2 mL), and MeOH (2 mL). The reaction was stirred and cooled to -78°C. A stream of O_3 was bubbled into the reaction for approximately 3 minutes as the color changed from bright yellow to redish brown. $NaBH_4$ (76 mg, 2.0 mmol) was added as a solid. The reaction stirred at -78°C for 5 minutes before warming to room temperature and further stirring for 12 hours. H_2O (2 mL) was added and the reaction was poured into a separatory funnel with ethyl acetate (10 mL). The layers were separated and the aqueous layer was extracted with ethyl acetate (4 x 10 mL). The organic layers were combined, dried over $Na_2SO_{4(s)}$, filtered and concentrated *in vacuo*. The crude material was purified by silica gel chromatography (20% ethyl acetate/hexanes to 30% ethyl acetate/hexanes) to afford the title compound as a clear, colorless oil (11.7 mg, 38% yield). R_f = 0.3 in 50% ethyl acetate/hexanes on TLC. The spectral data matched those reported in the literature.[21]

Analysis of Stereochemistry:

The enantiomeric ratio was determined by chiral GC analysis of the corresponding acetonide which was prepared as follows: The diol was combined with dimethoxypropane (1 mL) and a single crystal of pTsOH, and heated to 60°C for 20 minutes. The reaction was cooled to room temperature, filtered through a pad of silica gel with ether (5 mL), and concentrated *in vacuo* to afford pure acetonide.

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[18] Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.; Kwong, H.; Morikawa, K.; Wang, Z.; Xu, D.; Zhang, X. *J. Org. Chem.* **1992**, *57*, 2768.

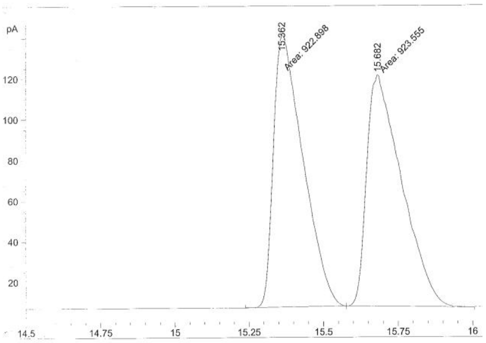
[19] Arasaki, H.; Iwata, M.; Nishimura, D.; Itoh, A.; Masaki, Y. *Synlett* **2004**, *3*, 546.

[20] Albert, B. J.; Sivaramakrihnan, A.;Naka, T.; Czaicki, N.L.; Koide, K. *J. Am. Chem. Soc.* **2007**, *129*, 2648.

[21] Park, J.; Pedersen, S. F. *Tetrahedron*, **1992**, *48*, 2069.

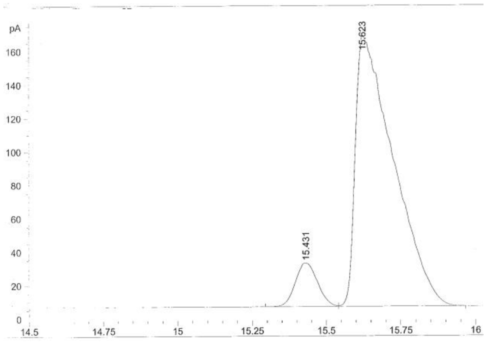
Chiral GC (β-Dex 120, Supelco, 100^{o}C for 5 minutes, then ramp 1.0^{o}C/min, 20 psi)-analysis of the reaction product.

Racemic



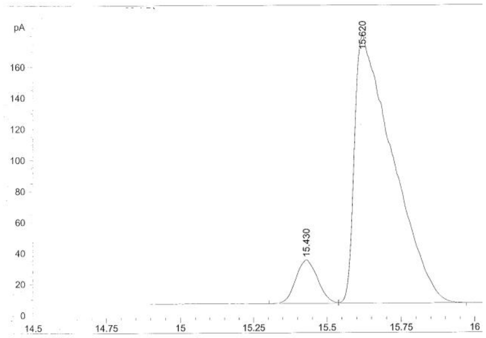
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]     [pA]         %
----|-------|----|-------|----------|----------|--------|
  1  15.362 MM    0.1151  922.89752  133.61723 49.98220
  2  15.682 MM    0.1352  923.55469  113.86636 50.01780
```

(*R*)-Isomer from AD-mix-β



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]     [pA]         %
----|-------|----|-------|----------|----------|--------|
  1  15.431 BV    0.0632  136.16568   25.97442  8.67880
  2  15.623 VB    0.1052 1432.77991  162.38312 91.32120
```

Reaction Product **19-Diol**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]     [pA]         %
----|-------|----|-------|----------|----------|--------|
  1  15.430 BV    0.0635  143.93559   28.23802  8.48570
  2  15.620 VB    0.1056 1552.27844  173.48526 91.51430
```

X. Cross-Coupling of (S)-^{10}B-20

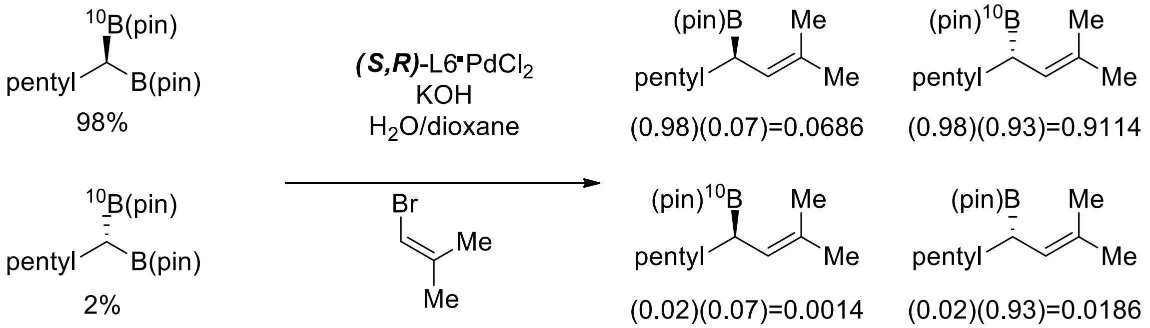
(*S*)-^{10}B-20 was prepared according to a literature procedure.[1]

A. Using (S,R)-Complex and assuming inversion during coupling:

note: bis(boronate) starting material ((**(*S*)-^{10}B-20**) = 98:2 er

cross-coupling reaction selectivity = 93:7 er

natural abundance of boron is ^{10}B:^{11}B = 19.9:80.1



$$^{10}B = (0.199)(0.0686) + 0.9114 + 0.0014 + (0.199)(0.0186) = 0.930$$

$$^{11}B = (0.801)(0.0686) + (0.801)(0.0186) = 0.070$$

Relative [M+H] distributions for ^{10}B:

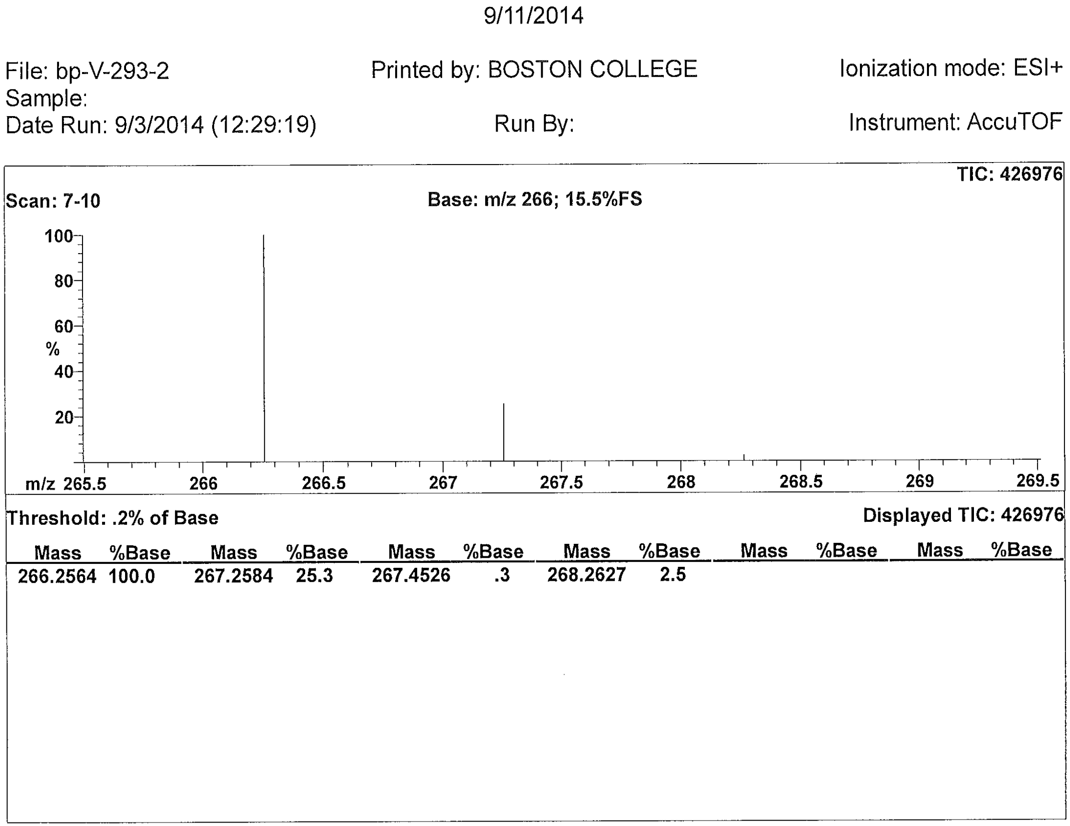
$^{12}C_{16}H_{32}{}^{10}BO_2$ [M+H]:	266.3	0.842
$^{12}C_{15}{}^{13}CH_{32}{}^{10}BO_2$ [M+H]:	267.3	0.146
$^{12}C_{14}{}^{13}C_2H_{32}{}^{10}BO_2$ [M+H]:	268.3	0.012

Relative [M+H] distributions for ^{11}B:

$^{12}C_{16}H_{32}{}^{11}BO_2$ [M+H]:	267.3	0.842
$^{12}C_{15}{}^{13}CH_{32}{}^{11}BO_2$ [M+H]:	268.3	0.146
$^{12}C_{14}{}^{13}C_2H_{32}{}^{11}BO_2$ [M+H]:	269.3	0.012

Calculated Relative Intensities

[M+H] for 266.3 amu = (0.930)(0.842) = 0.783	Found: 0.783
[M+H] for 267.3 amu = (0.930)(0.146) + (0.070)(0.842) = 0.195	Found: 0.195
[M+H] for 268.3 amu = (0.930)(0.012) + (0.070)(0.146) = 0.021	Found: 0.021
[M+H] for 269.3 amu = (0.070)(0.012) = 0.001	Found: <0.01



9/11/2014

File: bp-V-293-2 Printed by: BOSTON COLLEGE Ionization mode: ESI+
Sample:
Date Run: 9/3/2014 (12:29:19) Run By: Instrument: AccuTOF

TIC: 426976
Scan: 7-10 Base: m/z 266; 15.5%FS

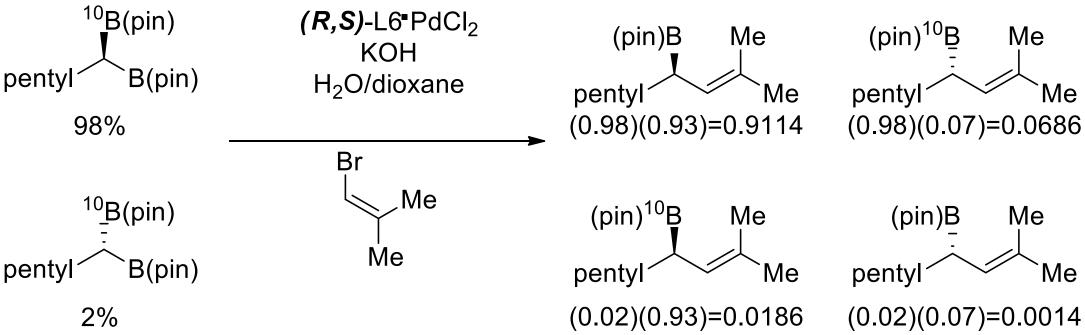
Threshold: .2% of Base Displayed TIC: 426976

Mass	%Base	Mass	%Base	Mass	%Base	Mass	%Base	Mass	%Base	Mass	%Base
266.2564	100.0	267.2584	25.3	267.4526	.3	268.2627	2.5				

Spectrum 1: Mass Spectrum corresponding to the cross-coupling of **(*S*)-^{10}B-20** with **(*S*,*R*)-L6·PdCl$_2$** as described in Part A of Section X.

B. Using (R,S)-Complex assuming inversion during coupling:

note: bis(boronate) starting material ((***S***)-^{10}**B-20**) = 98:2 er
cross-coupling reaction selectivity = 93:7 er
natural abundance of boron is ^{10}B:^{11}B = 19.9:80.1



$$^{10}\mathrm{B} = (0.199)(0.9114) + 0.0686 + 0.0186 + (0.199)(0.0014) = 0.269$$

$$^{11}\mathrm{B} = (0.801)(0.9114) + (0.801)(0.0014) = 0.731$$

Relative [M+H] distributions for ^{10}B:

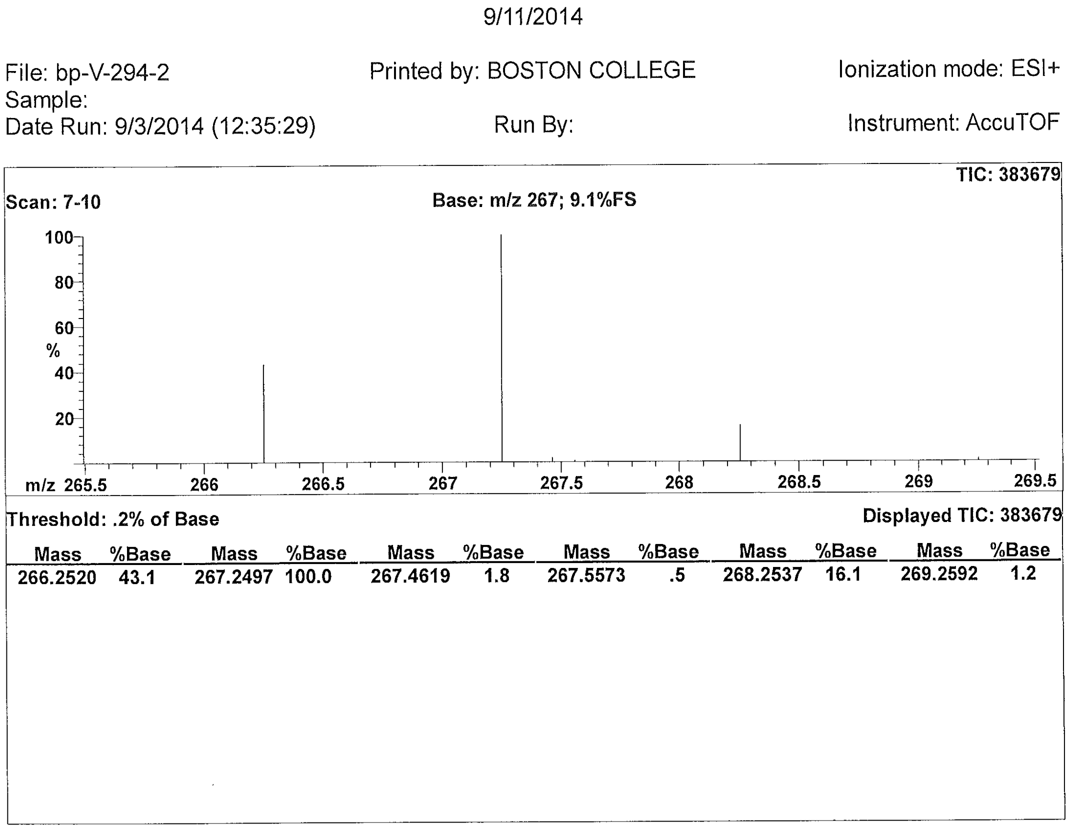
$^{12}C_{16}H_{32}{}^{10}BO_2$ [M+H]:	266.3	0.842
$^{12}C_{15}{}^{13}CH_{32}{}^{10}BO_2$ [M+H]:	267.3	0.146
$^{12}C_{14}{}^{13}C_2H_{32}{}^{10}BO_2$ [M+H]:	268.3	0.012

Relative [M+H] distributions for ^{11}B:

$^{12}C_{16}H_{32}{}^{11}BO_2$ [M+H]:	267.3	0.842
$^{12}C_{15}{}^{13}CH_{32}{}^{11}BO_2$ [M+H]:	268.3	0.146
$^{12}C_{14}{}^{13}C_2H_{32}{}^{11}BO_2$ [M+H]:	269.3	0.012

Calculated Relative Intensities

[M+H] for 266.3 amu = (0.269)(0.842) = 0.226	Found: 0.269
[M+H] for 267.3 amu = (0.269)(0.146) + (0.731)(0.842) = 0.655	Found: 0.623
[M+H] for 268.3 amu = (0.269)(0.012) + (0.731)(0.146) = 0.110	Found: 0.101
[M+H] for 269.3 amu = (0.731)(0.012) = 0.009	Found: 0.007



9/11/2014

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Date Run: 9/3/2014 (12:35:29)

Printed by: BOSTON COLLEGE

Run By:

Ionization mode: ESI+

Instrument: AccuTOF

TIC: 383679

Scan: 7-10

Base: m/z 267; 9.1%FS

Threshold: .2% of Base

Displayed TIC: 383679

Mass	%Base	Mass	%Base	Mass	%Base	Mass	%Base	Mass	%Base	Mass	%Base
266.2520	43.1	267.2497	100.0	267.4619	1.8	267.5573	.5	268.2537	16.1	269.2592	1.2

Spectrum 2: Mass Spectrum corresponding to the cross-coupling of **(*S*)-^{10}B-20** with **(*R*,*S*)- L6$\cdot$PdCl$_2$** as described in Part B of Section X.

XI. X-Ray Crystallographic Data for L6·PdCl$_2$

Table 1. Crystal data and structure refinement for $C_{34}H_{38}Cl_2F_6FeP_2Pd(CH_2Cl_2)$

Identification code	$C_{34}H_{38}Cl_2F_6FeP_2Pd(CH_2Cl_2)$	
Empirical formula	C35 H40 Cl4 F6 Fe P2 Pd	
Formula weight	940.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 20.260(3) Å	a= 90°.
	b = 13.910(2) Å	b= 102.459(4)°.
	c = 29.599(4) Å	g = 90°.
Volume	8145(2) Å^3	
Z	8	
Density (calculated)	1.534 Mg/m^3	
Absorption coefficient	1.190 mm^{-1}	
F(000)	3792	
Crystal size	0.600 x 0.340 x 0.160 mm^3	
Theta range for data collection	1.555 to 28.336°.	
Index ranges	-26<=h<=26, -18<=k<=18, 0<=l<=39	
Reflections collected	39439	
Independent reflections	39439 [R(int) = 0.0659]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4921	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	39439 / 27 / 918	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.0993	
R indices (all data)	R1 = 0.0555, wR2 = 0.1071	
Extinction coefficient	na	
Largest diff. peak and hole	1.309 and -1.052 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $C_{34}H_{38}Cl_2F_6FeP_2Pd(CH_2Cl_2)$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	6960(1)	3474(1)	6438(1)	10(1)
Fe(1)	4596(1)	1943(1)	5722(1)	12(1)
Cl(1)	7967(1)	2968(1)	6229(1)	21(1)
Cl(2)	7684(1)	4167(1)	7091(1)	19(1)
P(1)	6275(1)	3079(1)	5722(1)	10(1)
P(2)	6100(1)	3838(1)	6784(1)	9(1)
F(1)	4653(5)	8160(6)	6138(3)	12(2)
F(2)	5727(3)	8511(5)	6269(3)	18(1)
F(3)	5194(5)	8493(6)	6845(3)	20(2)
F(1X)	4566(8)	8143(13)	6203(6)	24(5)
F(2X)	5626(7)	8417(9)	6120(5)	27(4)
F(3X)	5342(7)	8594(9)	6771(5)	22(3)
F(1Y)	4789(7)	8150(11)	6050(5)	31(5)
F(2Y)	5766(6)	8584(9)	6424(5)	25(3)
F(3Y)	4993(8)	8414(11)	6807(5)	31(4)
F(4)	6736(2)	3840(2)	9136(1)	28(1)
F(5)	7643(1)	3182(2)	9012(1)	33(1)
F(6)	6761(2)	2310(2)	9004(1)	32(1)
C(1)	4887(2)	516(3)	5748(2)	22(1)
C(2)	4377(2)	693(3)	5341(2)	24(1)
C(3)	3792(2)	1042(3)	5488(2)	23(1)
C(4)	3942(2)	1083(3)	5980(2)	20(1)
C(5)	4625(2)	747(3)	6143(2)	21(1)
C(6)	5370(2)	2937(3)	5717(1)	10(1)
C(7)	4830(2)	3009(3)	5306(1)	14(1)
C(8)	4211(2)	3223(3)	5445(1)	13(1)
C(9)	4346(2)	3262(3)	5941(1)	13(1)
C(10)	5057(2)	3069(3)	6113(1)	10(1)
C(11)	6298(2)	4213(3)	5361(1)	13(1)
C(12)	6039(2)	4083(3)	4834(1)	16(1)
C(13)	5859(2)	4973(3)	5534(1)	14(1)

C(14)	7033(2)	4597(3)	5453(2)	18(1)
C(15)	6541(2)	1986(3)	5415(1)	13(1)
C(16)	5959(2)	1645(3)	5021(2)	19(1)
C(17)	6696(2)	1197(3)	5791(2)	20(1)
C(18)	7168(2)	2153(3)	5207(2)	18(1)
C(19)	5386(2)	2990(3)	6622(1)	12(1)
C(20)	4874(2)	3014(3)	6942(1)	15(1)
C(21)	5795(2)	5078(3)	6703(1)	12(1)
C(22)	5123(2)	5312(3)	6504(1)	14(1)
C(23)	4942(2)	6278(3)	6415(1)	16(1)
C(24)	5428(2)	6991(3)	6525(2)	16(1)
C(25)	6099(2)	6759(3)	6738(2)	18(1)
C(26)	6281(2)	5798(3)	6821(1)	16(1)
C(27)	5247(2)	8035(3)	6434(2)	25(1)
C(28)	6349(2)	3675(3)	7412(1)	11(1)
C(29)	6217(2)	4364(3)	7724(1)	16(1)
C(30)	6411(2)	4201(3)	8200(1)	18(1)
C(31)	6726(2)	3346(3)	8366(1)	15(1)
C(32)	6850(2)	2645(3)	8054(1)	17(1)
C(33)	6665(2)	2808(3)	7583(1)	16(1)
C(34)	6960(2)	3176(3)	8876(1)	19(1)
Pd(2)	7665(1)	8483(1)	8316(1)	13(1)
Fe(2)	10193(1)	9582(1)	8714(1)	17(1)
Cl(3)	6828(1)	9468(1)	8531(1)	20(1)
Cl(4)	6780(1)	7663(1)	7814(1)	23(1)
P(3)	8512(1)	8923(1)	8952(1)	14(1)
P(4)	8363(1)	7748(1)	7923(1)	13(1)
F(7)	9760(4)	3357(5)	8522(3)	26(2)
F(8)	9098(4)	3090(5)	7841(3)	21(2)
F(9)	8702(4)	2986(5)	8475(3)	26(2)
F(7X)	9558(7)	3367(9)	8672(5)	46(3)
F(8X)	9281(6)	3111(7)	7977(4)	24(2)
F(9X)	8482(6)	2986(8)	8348(5)	18(2)
F(7Y)	9226(6)	3384(8)	8845(4)	41(3)
F(8Y)	9571(8)	3256(10)	8231(6)	59(3)
F(9Y)	8525(8)	2953(11)	8220(5)	48(5)

F(10)	7616(3)	7347(4)	5584(1)	80(2)
F(11)	6650(2)	7216(3)	5720(1)	70(1)
F(12)	7034(3)	8603(2)	5649(1)	71(2)
C(35)	10029(3)	11019(3)	8537(2)	40(1)
C(36)	10520(4)	10934(5)	8942(2)	54(2)
C(37)	11053(3)	10399(5)	8860(3)	55(2)
C(38)	10899(3)	10134(4)	8385(3)	47(2)
C(39)	10253(3)	10533(3)	8186(2)	36(1)
C(40)	9377(2)	8805(3)	8863(1)	16(1)
C(41)	9976(2)	8718(3)	9230(2)	22(1)
C(42)	10508(2)	8311(3)	9051(2)	23(1)
C(43)	10260(2)	8158(3)	8563(2)	20(1)
C(44)	9565(2)	8474(3)	8442(2)	15(1)
C(45)	8448(2)	7931(3)	9389(2)	21(1)
C(46)	8729(3)	6991(3)	9224(2)	28(1)
C(47)	7688(2)	7778(4)	9393(2)	30(1)
C(48)	8840(2)	8134(4)	9889(2)	27(1)
C(49)	8459(2)	10151(3)	9220(2)	21(1)
C(50)	7887(3)	10240(4)	9496(2)	29(1)
C(51)	9125(2)	10451(4)	9551(2)	28(1)
C(52)	8317(2)	10855(3)	8809(2)	25(1)
C(53)	9138(2)	8484(3)	7953(1)	15(1)
C(54)	9529(2)	8288(3)	7571(2)	21(1)
C(55)	8597(2)	6504(3)	8062(1)	16(1)
C(56)	9270(2)	6183(3)	8149(2)	25(1)
C(57)	9421(3)	5215(3)	8240(2)	32(1)
C(58)	8896(3)	4565(3)	8240(2)	28(1)
C(59)	8232(2)	4868(3)	8158(2)	24(1)
C(60)	8077(2)	5835(3)	8071(2)	20(1)
C(61)	9064(3)	3512(4)	8309(3)	45(2)
C(62)	8008(2)	7724(3)	7297(1)	16(1)
C(63)	8029(2)	6897(3)	7030(2)	19(1)
C(64)	7785(2)	6923(3)	6550(2)	23(1)
C(65)	7514(2)	7764(3)	6338(2)	21(1)
C(66)	7487(2)	8600(3)	6598(2)	21(1)
C(67)	7734(2)	8576(3)	7070(2)	21(1)

C(68)	7224(3)	7757(3)	5823(2)	34(1)
C(1S)	8246(3)	1520(4)	7142(2)	32(1)
C(2S)	6248(3)	118(3)	7398(2)	26(1)
Cl(5S)	8105(1)	1020(1)	7663(1)	29(1)
Cl(6S)	8948(1)	965(1)	6979(1)	60(1)
Cl(7S)	6435(1)	521(1)	6868(1)	22(1)
Cl(8S)	5499(1)	665(1)	7493(1)	33(1)

Table 3. Bond lengths [Å] and angles [°] for $C_{34}H_{38}Cl_2F_6FeP_2Pd(CH_2Cl_2)$.

Pd(1)-P(2)	2.2597(10)
Pd(1)-P(1)	2.3344(10)
Pd(1)-Cl(2)	2.3641(10)
Pd(1)-Cl(1)	2.3642(11)
Fe(1)-C(8)	2.043(4)
Fe(1)-C(7)	2.046(4)
Fe(1)-C(9)	2.046(4)
Fe(1)-C(10)	2.050(4)
Fe(1)-C(4)	2.052(4)
Fe(1)-C(3)	2.054(4)
Fe(1)-C(1)	2.067(4)
Fe(1)-C(2)	2.068(4)
Fe(1)-C(5)	2.072(4)
Fe(1)-C(6)	2.093(4)
P(1)-C(6)	1.840(4)
P(1)-C(15)	1.908(4)
P(1)-C(11)	1.911(4)
P(2)-C(28)	1.831(4)
P(2)-C(21)	1.832(4)
P(2)-C(19)	1.849(4)
F(1)-C(27)	1.337(9)
F(2)-C(27)	1.351(8)
F(3)-C(27)	1.399(9)
F(4)-C(34)	1.343(5)
F(5)-C(34)	1.354(5)
F(6)-C(34)	1.351(5)
C(1)-C(5)	1.422(7)
C(1)-C(2)	1.430(7)
C(1)-H(1)	0.9500
C(2)-C(3)	1.435(7)
C(2)-H(2)	0.9500
C(3)-C(4)	1.422(7)
C(3)-H(3)	0.9500
C(4)-C(5)	1.442(6)

C(4)-H(4)	0.9500
C(5)-H(5)	0.9500
C(6)-C(7)	1.453(5)
C(6)-C(10)	1.461(5)
C(7)-C(8)	1.432(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.434(6)
C(8)-H(8)	0.9500
C(9)-C(10)	1.446(5)
C(9)-H(9)	0.9500
C(10)-C(19)	1.512(5)
C(11)-C(13)	1.538(5)
C(11)-C(12)	1.547(5)
C(11)-C(14)	1.550(5)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(16)	1.543(6)
C(15)-C(18)	1.545(5)
C(15)-C(17)	1.545(6)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(20)	1.548(5)

C(19)-H(19)	1.0000
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(26)	1.395(5)
C(21)-C(22)	1.400(5)
C(22)-C(23)	1.402(5)
C(22)-H(22)	0.9500
C(23)-C(24)	1.387(6)
C(23)-H(23)	0.9500
C(24)-C(25)	1.407(6)
C(24)-C(27)	1.508(6)
C(25)-C(26)	1.394(5)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500
C(28)-C(29)	1.395(5)
C(28)-C(33)	1.408(5)
C(29)-C(30)	1.399(5)
C(29)-H(29)	0.9500
C(30)-C(31)	1.388(6)
C(30)-H(30)	0.9500
C(31)-C(32)	1.403(6)
C(31)-C(34)	1.501(6)
C(32)-C(33)	1.382(6)
C(32)-H(32)	0.9500
C(33)-H(33)	0.9500
Pd(2)-P(4)	2.2609(11)
Pd(2)-P(3)	2.3383(11)
Pd(2)-Cl(4)	2.3615(11)
Pd(2)-Cl(3)	2.3715(11)
Fe(2)-C(43)	2.041(4)
Fe(2)-C(38)	2.046(5)
Fe(2)-C(37)	2.047(5)
Fe(2)-C(44)	2.049(4)
Fe(2)-C(36)	2.059(5)
Fe(2)-C(42)	2.063(4)

Fe(2)-C(41)	2.066(5)
Fe(2)-C(39)	2.071(5)
Fe(2)-C(35)	2.074(5)
Fe(2)-C(40)	2.101(4)
P(3)-C(40)	1.833(4)
P(3)-C(49)	1.895(4)
P(3)-C(45)	1.916(4)
P(4)-C(55)	1.817(4)
P(4)-C(62)	1.837(4)
P(4)-C(53)	1.861(4)
F(7)-C(61)	1.431(10)
F(8)-C(61)	1.520(11)
F(9)-C(61)	1.211(10)
F(10)-C(68)	1.304(7)
F(11)-C(68)	1.363(7)
F(12)-C(68)	1.308(6)
C(35)-C(36)	1.388(9)
C(35)-C(39)	1.395(8)
C(35)-H(35)	0.9500
C(36)-C(37)	1.375(10)
C(36)-H(36)	0.9500
C(37)-C(38)	1.423(10)
C(37)-H(37)	0.9500
C(38)-C(39)	1.427(9)
C(38)-H(38)	0.9500
C(39)-H(39)	0.9500
C(40)-C(41)	1.449(6)
C(40)-C(44)	1.456(6)
C(41)-C(42)	1.420(6)
C(41)-H(41)	0.9500
C(42)-C(43)	1.439(7)
C(42)-H(42)	0.9500
C(43)-C(44)	1.444(6)
C(43)-H(43)	0.9500
C(44)-C(53)	1.516(6)
C(45)-C(48)	1.546(6)

C(45)-C(46)	1.547(7)
C(45)-C(47)	1.558(6)
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-C(52)	1.540(6)
C(49)-C(51)	1.543(6)
C(49)-C(50)	1.562(6)
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-H(52A)	0.9800
C(52)-H(52B)	0.9800
C(52)-H(52C)	0.9800
C(53)-C(54)	1.539(6)
C(53)-H(53)	1.0000
C(54)-H(54A)	0.9800
C(54)-H(54B)	0.9800
C(54)-H(54C)	0.9800
C(55)-C(56)	1.405(6)
C(55)-C(60)	1.410(6)
C(56)-C(57)	1.395(6)
C(56)-H(56)	0.9500
C(57)-C(58)	1.394(7)
C(57)-H(57)	0.9500
C(58)-C(59)	1.381(7)
C(58)-C(61)	1.508(7)

C(59)-C(60)	1.393(6)
C(59)-H(59)	0.9500
C(60)-H(60)	0.9500
C(62)-C(63)	1.402(6)
C(62)-C(67)	1.417(6)
C(63)-C(64)	1.401(6)
C(63)-H(63)	0.9500
C(64)-C(65)	1.384(6)
C(64)-H(64)	0.9500
C(65)-C(66)	1.403(6)
C(65)-C(68)	1.511(6)
C(66)-C(67)	1.377(6)
C(66)-H(66)	0.9500
C(67)-H(67)	0.9500
C(1S)-Cl(5S)	1.772(5)
C(1S)-Cl(6S)	1.773(5)
C(1S)-H(1S1)	0.9900
C(1S)-H(1S2)	0.9900
C(2S)-Cl(8S)	1.774(5)
C(2S)-Cl(7S)	1.782(5)
C(2S)-H(2S1)	0.9900
C(2S)-H(2S2)	0.9900

P(2)-Pd(1)-P(1)	95.68(4)
P(2)-Pd(1)-Cl(2)	86.63(4)
P(1)-Pd(1)-Cl(2)	168.57(4)
P(2)-Pd(1)-Cl(1)	168.14(4)
P(1)-Pd(1)-Cl(1)	93.96(4)
Cl(2)-Pd(1)-Cl(1)	85.28(4)
C(8)-Fe(1)-C(7)	40.99(16)
C(8)-Fe(1)-C(9)	41.06(16)
C(7)-Fe(1)-C(9)	69.23(16)
C(8)-Fe(1)-C(10)	69.42(15)
C(7)-Fe(1)-C(10)	69.48(15)
C(9)-Fe(1)-C(10)	41.34(15)
C(8)-Fe(1)-C(4)	115.79(17)

C(7)-Fe(1)-C(4)	153.87(17)
C(9)-Fe(1)-C(4)	100.40(17)
C(10)-Fe(1)-C(4)	119.18(17)
C(8)-Fe(1)-C(3)	100.91(16)
C(7)-Fe(1)-C(3)	120.60(17)
C(9)-Fe(1)-C(3)	114.86(17)
C(10)-Fe(1)-C(3)	152.62(17)
C(4)-Fe(1)-C(3)	40.53(18)
C(8)-Fe(1)-C(1)	158.88(18)
C(7)-Fe(1)-C(1)	128.14(17)
C(9)-Fe(1)-C(1)	159.64(18)
C(10)-Fe(1)-C(1)	128.44(17)
C(4)-Fe(1)-C(1)	68.18(17)
C(3)-Fe(1)-C(1)	68.05(18)
C(8)-Fe(1)-C(2)	119.68(17)
C(7)-Fe(1)-C(2)	109.37(18)
C(9)-Fe(1)-C(2)	152.62(18)
C(10)-Fe(1)-C(2)	165.69(17)
C(4)-Fe(1)-C(2)	68.47(18)
C(3)-Fe(1)-C(2)	40.74(18)
C(1)-Fe(1)-C(2)	40.45(18)
C(8)-Fe(1)-C(5)	154.06(18)
C(7)-Fe(1)-C(5)	164.49(17)
C(9)-Fe(1)-C(5)	120.40(18)
C(10)-Fe(1)-C(5)	108.89(16)
C(4)-Fe(1)-C(5)	40.92(16)
C(3)-Fe(1)-C(5)	68.28(17)
C(1)-Fe(1)-C(5)	40.19(18)
C(2)-Fe(1)-C(5)	68.17(18)
C(8)-Fe(1)-C(6)	69.12(15)
C(7)-Fe(1)-C(6)	41.09(15)
C(9)-Fe(1)-C(6)	69.33(15)
C(10)-Fe(1)-C(6)	41.28(14)
C(4)-Fe(1)-C(6)	158.94(17)
C(3)-Fe(1)-C(6)	160.37(17)
C(1)-Fe(1)-C(6)	115.27(16)

C(2)-Fe(1)-C(6)	128.65(17)
C(5)-Fe(1)-C(6)	127.68(16)
C(6)-P(1)-C(15)	107.02(17)
C(6)-P(1)-C(11)	103.18(17)
C(15)-P(1)-C(11)	110.39(17)
C(6)-P(1)-Pd(1)	115.40(12)
C(15)-P(1)-Pd(1)	116.51(13)
C(11)-P(1)-Pd(1)	103.45(12)
C(28)-P(2)-C(21)	105.16(17)
C(28)-P(2)-C(19)	102.39(17)
C(21)-P(2)-C(19)	110.07(18)
C(28)-P(2)-Pd(1)	111.21(13)
C(21)-P(2)-Pd(1)	114.99(13)
C(19)-P(2)-Pd(1)	112.08(13)
C(5)-C(1)-C(2)	108.9(4)
C(5)-C(1)-Fe(1)	70.1(2)
C(2)-C(1)-Fe(1)	69.8(2)
C(5)-C(1)-H(1)	125.5
C(2)-C(1)-H(1)	125.5
Fe(1)-C(1)-H(1)	126.1
C(1)-C(2)-C(3)	107.2(4)
C(1)-C(2)-Fe(1)	69.7(2)
C(3)-C(2)-Fe(1)	69.1(2)
C(1)-C(2)-H(2)	126.4
C(3)-C(2)-H(2)	126.4
Fe(1)-C(2)-H(2)	126.3
C(4)-C(3)-C(2)	108.5(4)
C(4)-C(3)-Fe(1)	69.6(2)
C(2)-C(3)-Fe(1)	70.2(2)
C(4)-C(3)-H(3)	125.8
C(2)-C(3)-H(3)	125.8
Fe(1)-C(3)-H(3)	126.0
C(3)-C(4)-C(5)	107.9(4)
C(3)-C(4)-Fe(1)	69.8(2)
C(5)-C(4)-Fe(1)	70.3(2)
C(3)-C(4)-H(4)	126.0

C(5)-C(4)-H(4)	126.0
Fe(1)-C(4)-H(4)	125.4
C(1)-C(5)-C(4)	107.4(4)
C(1)-C(5)-Fe(1)	69.7(2)
C(4)-C(5)-Fe(1)	68.8(2)
C(1)-C(5)-H(5)	126.3
C(4)-C(5)-H(5)	126.3
Fe(1)-C(5)-H(5)	126.8
C(7)-C(6)-C(10)	106.4(3)
C(7)-C(6)-P(1)	124.7(3)
C(10)-C(6)-P(1)	125.7(3)
C(7)-C(6)-Fe(1)	67.7(2)
C(10)-C(6)-Fe(1)	67.8(2)
P(1)-C(6)-Fe(1)	144.8(2)
C(8)-C(7)-C(6)	108.9(3)
C(8)-C(7)-Fe(1)	69.4(2)
C(6)-C(7)-Fe(1)	71.2(2)
C(8)-C(7)-H(7)	125.6
C(6)-C(7)-H(7)	125.6
Fe(1)-C(7)-H(7)	125.4
C(7)-C(8)-C(9)	108.4(3)
C(7)-C(8)-Fe(1)	69.6(2)
C(9)-C(8)-Fe(1)	69.6(2)
C(7)-C(8)-H(8)	125.8
C(9)-C(8)-H(8)	125.8
Fe(1)-C(8)-H(8)	126.6
C(8)-C(9)-C(10)	108.0(3)
C(8)-C(9)-Fe(1)	69.4(2)
C(10)-C(9)-Fe(1)	69.5(2)
C(8)-C(9)-H(9)	126.0
C(10)-C(9)-H(9)	126.0
Fe(1)-C(9)-H(9)	126.7
C(9)-C(10)-C(6)	108.2(3)
C(9)-C(10)-C(19)	123.8(3)
C(6)-C(10)-C(19)	128.0(3)
C(9)-C(10)-Fe(1)	69.2(2)

C(6)-C(10)-Fe(1)	71.0(2)
C(19)-C(10)-Fe(1)	123.7(3)
C(13)-C(11)-C(12)	108.8(3)
C(13)-C(11)-C(14)	107.9(3)
C(12)-C(11)-C(14)	108.7(3)
C(13)-C(11)-P(1)	107.2(3)
C(12)-C(11)-P(1)	115.1(3)
C(14)-C(11)-P(1)	108.9(3)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(16)-C(15)-C(18)	107.7(3)
C(16)-C(15)-C(17)	109.2(3)
C(18)-C(15)-C(17)	109.7(3)
C(16)-C(15)-P(1)	110.9(3)
C(18)-C(15)-P(1)	114.2(3)
C(17)-C(15)-P(1)	105.0(3)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5

H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(10)-C(19)-C(20)	113.4(3)
C(10)-C(19)-P(2)	111.4(3)
C(20)-C(19)-P(2)	114.6(3)
C(10)-C(19)-H(19)	105.5
C(20)-C(19)-H(19)	105.5
P(2)-C(19)-H(19)	105.5
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(26)-C(21)-C(22)	120.6(3)
C(26)-C(21)-P(2)	116.3(3)
C(22)-C(21)-P(2)	123.0(3)
C(21)-C(22)-C(23)	119.5(4)
C(21)-C(22)-H(22)	120.2
C(23)-C(22)-H(22)	120.2
C(24)-C(23)-C(22)	119.8(4)
C(24)-C(23)-H(23)	120.1
C(22)-C(23)-H(23)	120.1
C(23)-C(24)-C(25)	120.6(4)

C(23)-C(24)-C(27)	121.0(4)
C(25)-C(24)-C(27)	118.4(4)
C(26)-C(25)-C(24)	119.4(4)
C(26)-C(25)-H(25)	120.3
C(24)-C(25)-H(25)	120.3
C(25)-C(26)-C(21)	119.9(4)
C(25)-C(26)-H(26)	120.0
C(21)-C(26)-H(26)	120.0
F(1)-C(27)-F(2)	108.5(7)
F(1)-C(27)-F(3)	106.5(7)
F(2)-C(27)-F(3)	106.7(6)
F(1)-C(27)-C(24)	113.1(5)
F(2)-C(27)-C(24)	111.7(5)
F(3)-C(27)-C(24)	110.0(5)
C(29)-C(28)-C(33)	119.2(3)
C(29)-C(28)-P(2)	122.4(3)
C(33)-C(28)-P(2)	118.3(3)
C(28)-C(29)-C(30)	120.2(4)
C(28)-C(29)-H(29)	119.9
C(30)-C(29)-H(29)	119.9
C(31)-C(30)-C(29)	120.2(4)
C(31)-C(30)-H(30)	119.9
C(29)-C(30)-H(30)	119.9
C(30)-C(31)-C(32)	119.8(4)
C(30)-C(31)-C(34)	120.8(4)
C(32)-C(31)-C(34)	119.3(4)
C(33)-C(32)-C(31)	120.1(4)
C(33)-C(32)-H(32)	120.0
C(31)-C(32)-H(32)	120.0
C(32)-C(33)-C(28)	120.5(4)
C(32)-C(33)-H(33)	119.8
C(28)-C(33)-H(33)	119.8
F(4)-C(34)-F(6)	107.1(3)
F(4)-C(34)-F(5)	106.0(3)
F(6)-C(34)-F(5)	105.7(3)
F(4)-C(34)-C(31)	113.2(3)

F(6)-C(34)-C(31)	112.0(4)
F(5)-C(34)-C(31)	112.3(4)
P(4)-Pd(2)-P(3)	95.76(4)
P(4)-Pd(2)-Cl(4)	86.09(4)
P(3)-Pd(2)-Cl(4)	163.52(4)
P(4)-Pd(2)-Cl(3)	164.23(4)
P(3)-Pd(2)-Cl(3)	94.40(4)
Cl(4)-Pd(2)-Cl(3)	87.58(4)
C(43)-Fe(2)-C(38)	100.0(2)
C(43)-Fe(2)-C(37)	119.5(3)
C(38)-Fe(2)-C(37)	40.7(3)
C(43)-Fe(2)-C(44)	41.35(16)
C(38)-Fe(2)-C(44)	122.3(2)
C(37)-Fe(2)-C(44)	158.3(3)
C(43)-Fe(2)-C(36)	157.9(3)
C(38)-Fe(2)-C(36)	66.7(3)
C(37)-Fe(2)-C(36)	39.1(3)
C(44)-Fe(2)-C(36)	160.8(3)
C(43)-Fe(2)-C(42)	41.05(19)
C(38)-Fe(2)-C(42)	112.2(2)
C(37)-Fe(2)-C(42)	102.3(2)
C(44)-Fe(2)-C(42)	69.29(18)
C(36)-Fe(2)-C(42)	125.5(3)
C(43)-Fe(2)-C(41)	68.44(18)
C(38)-Fe(2)-C(41)	148.6(2)
C(37)-Fe(2)-C(41)	118.3(2)
C(44)-Fe(2)-C(41)	68.89(17)
C(36)-Fe(2)-C(41)	113.1(2)
C(42)-Fe(2)-C(41)	40.21(18)
C(43)-Fe(2)-C(39)	115.9(2)
C(38)-Fe(2)-C(39)	40.6(2)
C(37)-Fe(2)-C(39)	67.6(2)
C(44)-Fe(2)-C(39)	108.44(19)
C(36)-Fe(2)-C(39)	66.3(2)
C(42)-Fe(2)-C(39)	148.3(2)
C(41)-Fe(2)-C(39)	170.6(2)

C(43)-Fe(2)-C(35)	153.4(2)
C(38)-Fe(2)-C(35)	67.0(2)
C(37)-Fe(2)-C(35)	66.5(2)
C(44)-Fe(2)-C(35)	125.0(2)
C(36)-Fe(2)-C(35)	39.2(3)
C(42)-Fe(2)-C(35)	164.6(2)
C(41)-Fe(2)-C(35)	134.3(2)
C(39)-Fe(2)-C(35)	39.3(2)
C(43)-Fe(2)-C(40)	68.86(17)
C(38)-Fe(2)-C(40)	163.0(2)
C(37)-Fe(2)-C(40)	156.0(3)
C(44)-Fe(2)-C(40)	41.04(16)
C(36)-Fe(2)-C(40)	127.8(2)
C(42)-Fe(2)-C(40)	68.43(17)
C(41)-Fe(2)-C(40)	40.67(16)
C(39)-Fe(2)-C(40)	131.6(2)
C(35)-Fe(2)-C(40)	117.26(18)
C(40)-P(3)-C(49)	106.4(2)
C(40)-P(3)-C(45)	103.80(19)
C(49)-P(3)-C(45)	110.3(2)
C(40)-P(3)-Pd(2)	114.84(14)
C(49)-P(3)-Pd(2)	118.32(14)
C(45)-P(3)-Pd(2)	102.12(14)
C(55)-P(4)-C(62)	103.74(19)
C(55)-P(4)-C(53)	109.70(19)
C(62)-P(4)-C(53)	101.66(19)
C(55)-P(4)-Pd(2)	118.36(14)
C(62)-P(4)-Pd(2)	112.02(13)
C(53)-P(4)-Pd(2)	109.95(13)
C(36)-C(35)-C(39)	108.4(5)
C(36)-C(35)-Fe(2)	69.8(3)
C(39)-C(35)-Fe(2)	70.2(3)
C(36)-C(35)-H(35)	125.8
C(39)-C(35)-H(35)	125.8
Fe(2)-C(35)-H(35)	125.8
C(37)-C(36)-C(35)	109.7(6)

C(37)-C(36)-Fe(2)	69.9(4)
C(35)-C(36)-Fe(2)	71.0(3)
C(37)-C(36)-H(36)	125.2
C(35)-C(36)-H(36)	125.2
Fe(2)-C(36)-H(36)	125.5
C(36)-C(37)-C(38)	107.6(5)
C(36)-C(37)-Fe(2)	70.9(3)
C(38)-C(37)-Fe(2)	69.6(3)
C(36)-C(37)-H(37)	126.2
C(38)-C(37)-H(37)	126.2
Fe(2)-C(37)-H(37)	124.8
C(37)-C(38)-C(39)	107.0(5)
C(37)-C(38)-Fe(2)	69.7(3)
C(39)-C(38)-Fe(2)	70.7(3)
C(37)-C(38)-H(38)	126.5
C(39)-C(38)-H(38)	126.5
Fe(2)-C(38)-H(38)	124.8
C(35)-C(39)-C(38)	107.3(5)
C(35)-C(39)-Fe(2)	70.5(3)
C(38)-C(39)-Fe(2)	68.8(3)
C(35)-C(39)-H(39)	126.4
C(38)-C(39)-H(39)	126.4
Fe(2)-C(39)-H(39)	126.0
C(41)-C(40)-C(44)	106.6(3)
C(41)-C(40)-P(3)	124.9(3)
C(44)-C(40)-P(3)	125.8(3)
C(41)-C(40)-Fe(2)	68.4(2)
C(44)-C(40)-Fe(2)	67.6(2)
P(3)-C(40)-Fe(2)	143.5(2)
C(42)-C(41)-C(40)	109.5(4)
C(42)-C(41)-Fe(2)	69.8(3)
C(40)-C(41)-Fe(2)	71.0(2)
C(42)-C(41)-H(41)	125.3
C(40)-C(41)-H(41)	125.3
Fe(2)-C(41)-H(41)	125.6
C(41)-C(42)-C(43)	107.8(4)

C(41)-C(42)-Fe(2)	70.0(3)
C(43)-C(42)-Fe(2)	68.7(2)
C(41)-C(42)-H(42)	126.1
C(43)-C(42)-H(42)	126.1
Fe(2)-C(42)-H(42)	126.8
C(42)-C(43)-C(44)	108.3(4)
C(42)-C(43)-Fe(2)	70.3(3)
C(44)-C(43)-Fe(2)	69.6(2)
C(42)-C(43)-H(43)	125.8
C(44)-C(43)-H(43)	125.8
Fe(2)-C(43)-H(43)	125.8
C(43)-C(44)-C(40)	107.8(4)
C(43)-C(44)-C(53)	124.3(4)
C(40)-C(44)-C(53)	127.9(4)
C(43)-C(44)-Fe(2)	69.0(2)
C(40)-C(44)-Fe(2)	71.4(2)
C(53)-C(44)-Fe(2)	123.1(3)
C(48)-C(45)-C(46)	108.0(4)
C(48)-C(45)-C(47)	108.8(4)
C(46)-C(45)-C(47)	108.6(4)
C(48)-C(45)-P(3)	114.8(3)
C(46)-C(45)-P(3)	108.2(3)
C(47)-C(45)-P(3)	108.4(3)
C(45)-C(46)-H(46A)	109.5
C(45)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(45)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(45)-C(47)-H(47A)	109.5
C(45)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(45)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(45)-C(48)-H(48A)	109.5

C(45)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(45)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
C(52)-C(49)-C(51)	108.5(4)
C(52)-C(49)-C(50)	109.2(4)
C(51)-C(49)-C(50)	107.0(4)
C(52)-C(49)-P(3)	105.1(3)
C(51)-C(49)-P(3)	112.9(3)
C(50)-C(49)-P(3)	114.0(3)
C(49)-C(50)-H(50A)	109.5
C(49)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
C(49)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
C(49)-C(51)-H(51A)	109.5
C(49)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(49)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
C(49)-C(52)-H(52A)	109.5
C(49)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(49)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
C(44)-C(53)-C(54)	114.9(3)
C(44)-C(53)-P(4)	110.1(3)
C(54)-C(53)-P(4)	115.4(3)
C(44)-C(53)-H(53)	105.1
C(54)-C(53)-H(53)	105.1
P(4)-C(53)-H(53)	105.1
C(53)-C(54)-H(54A)	109.5

C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
C(53)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5
C(56)-C(55)-C(60)	119.1(4)
C(56)-C(55)-P(4)	122.6(3)
C(60)-C(55)-P(4)	118.3(3)
C(57)-C(56)-C(55)	120.4(4)
C(57)-C(56)-H(56)	119.8
C(55)-C(56)-H(56)	119.8
C(58)-C(57)-C(56)	119.4(5)
C(58)-C(57)-H(57)	120.3
C(56)-C(57)-H(57)	120.3
C(59)-C(58)-C(57)	121.1(4)
C(59)-C(58)-C(61)	120.1(4)
C(57)-C(58)-C(61)	118.7(5)
C(58)-C(59)-C(60)	119.9(4)
C(58)-C(59)-H(59)	120.0
C(60)-C(59)-H(59)	120.0
C(59)-C(60)-C(55)	120.1(4)
C(59)-C(60)-H(60)	119.9
C(55)-C(60)-H(60)	119.9
F(9)-C(61)-F(7)	110.8(7)
F(9)-C(61)-C(58)	120.3(6)
F(7)-C(61)-C(58)	112.2(5)
F(9)-C(61)-F(8)	106.6(6)
F(7)-C(61)-F(8)	96.3(6)
C(58)-C(61)-F(8)	107.8(5)
C(63)-C(62)-C(67)	118.4(4)
C(63)-C(62)-P(4)	122.0(3)
C(67)-C(62)-P(4)	119.5(3)
C(64)-C(63)-C(62)	120.2(4)
C(64)-C(63)-H(63)	119.9
C(62)-C(63)-H(63)	119.9
C(65)-C(64)-C(63)	120.1(4)

C(65)-C(64)-H(64)	120.0
C(63)-C(64)-H(64)	120.0
C(64)-C(65)-C(66)	120.6(4)
C(64)-C(65)-C(68)	118.8(4)
C(66)-C(65)-C(68)	120.5(4)
C(67)-C(66)-C(65)	119.3(4)
C(67)-C(66)-H(66)	120.4
C(65)-C(66)-H(66)	120.4
C(66)-C(67)-C(62)	121.4(4)
C(66)-C(67)-H(67)	119.3
C(62)-C(67)-H(67)	119.3
F(10)-C(68)-F(12)	110.1(5)
F(10)-C(68)-F(11)	103.2(5)
F(12)-C(68)-F(11)	104.2(5)
F(10)-C(68)-C(65)	113.6(5)
F(12)-C(68)-C(65)	114.0(4)
F(11)-C(68)-C(65)	110.8(4)
Cl(5S)-C(1S)-Cl(6S)	110.8(3)
Cl(5S)-C(1S)-H(1S1)	109.5
Cl(6S)-C(1S)-H(1S1)	109.5
Cl(5S)-C(1S)-H(1S2)	109.5
Cl(6S)-C(1S)-H(1S2)	109.5
H(1S1)-C(1S)-H(1S2)	108.1
Cl(8S)-C(2S)-Cl(7S)	110.9(3)
Cl(8S)-C(2S)-H(2S1)	109.5
Cl(7S)-C(2S)-H(2S1)	109.5
Cl(8S)-C(2S)-H(2S2)	109.5
Cl(7S)-C(2S)-H(2S2)	109.5
H(2S1)-C(2S)-H(2S2)	108.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for $C_{34}H_{38}Cl_2F_6FeP_2Pd(CH_2Cl_2)$. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	11(1)	11(1)	8(1)	0(1)	3(1)	0(1)
Fe(1)	15(1)	6(1)	13(1)	0(1)	1(1)	-2(1)
Cl(1)	14(1)	32(1)	18(1)	-3(1)	5(1)	4(1)
Cl(2)	15(1)	25(1)	15(1)	-4(1)	2(1)	-4(1)
P(1)	14(1)	8(1)	8(1)	1(1)	3(1)	1(1)
P(2)	12(1)	7(1)	8(1)	0(1)	3(1)	0(1)
F(4)	41(2)	34(2)	11(1)	-3(1)	7(1)	12(1)
F(5)	23(1)	54(2)	18(1)	1(1)	-3(1)	8(1)
F(6)	55(2)	24(2)	17(1)	8(1)	7(1)	-1(1)
C(1)	27(2)	4(2)	36(3)	1(2)	9(2)	-3(2)
C(2)	35(3)	9(2)	26(2)	-7(2)	6(2)	-7(2)
C(3)	22(2)	13(2)	31(2)	2(2)	-1(2)	-6(2)
C(4)	22(2)	11(2)	28(2)	7(2)	9(2)	-4(2)
C(5)	24(2)	9(2)	27(2)	7(2)	0(2)	-4(2)
C(6)	14(2)	7(2)	9(2)	2(1)	1(1)	0(1)
C(7)	19(2)	10(2)	11(2)	2(1)	3(2)	-1(1)
C(8)	15(2)	8(2)	15(2)	2(1)	-1(2)	-2(1)
C(9)	15(2)	9(2)	16(2)	-1(1)	4(2)	0(1)
C(10)	12(2)	7(2)	12(2)	-2(1)	3(1)	-1(1)
C(11)	20(2)	9(2)	11(2)	1(1)	5(2)	-2(1)
C(12)	23(2)	14(2)	11(2)	4(2)	4(2)	3(2)
C(13)	22(2)	6(2)	16(2)	3(1)	5(2)	1(1)
C(14)	20(2)	16(2)	20(2)	2(2)	6(2)	-6(2)
C(15)	20(2)	13(2)	10(2)	-2(1)	10(2)	0(2)
C(16)	26(2)	13(2)	17(2)	-6(2)	5(2)	-2(2)
C(17)	30(2)	10(2)	21(2)	1(2)	4(2)	5(2)
C(18)	21(2)	17(2)	18(2)	-2(2)	10(2)	1(2)
C(19)	15(2)	7(2)	13(2)	1(1)	4(2)	-2(1)
C(20)	18(2)	18(2)	13(2)	0(2)	8(2)	-2(2)
C(21)	20(2)	7(2)	10(2)	1(1)	4(2)	1(1)
C(22)	16(2)	9(2)	16(2)	-2(1)	4(2)	1(1)

C(23)	18(2)	11(2)	17(2)	0(2)	2(2)	1(1)
C(24)	22(2)	6(2)	20(2)	-1(2)	4(2)	1(2)
C(25)	23(2)	10(2)	19(2)	-3(2)	0(2)	-1(2)
C(26)	17(2)	11(2)	18(2)	-1(2)	-1(2)	1(2)
C(27)	28(2)	13(2)	31(3)	-1(2)	1(2)	1(2)
C(28)	14(2)	11(2)	8(2)	-1(1)	2(1)	-2(1)
C(29)	22(2)	15(2)	11(2)	1(2)	2(2)	10(2)
C(30)	26(2)	14(2)	13(2)	-1(2)	4(2)	6(2)
C(31)	16(2)	19(2)	10(2)	-1(2)	4(2)	2(2)
C(32)	24(2)	12(2)	17(2)	1(2)	5(2)	4(2)
C(33)	26(2)	10(2)	12(2)	-3(1)	6(2)	4(2)
C(34)	25(2)	21(2)	12(2)	2(2)	5(2)	5(2)
Pd(2)	10(1)	17(1)	11(1)	-1(1)	3(1)	0(1)
Fe(2)	14(1)	15(1)	23(1)	-1(1)	2(1)	-2(1)
Cl(3)	15(1)	29(1)	18(1)	0(1)	6(1)	4(1)
Cl(4)	14(1)	31(1)	23(1)	-7(1)	2(1)	-5(1)
P(3)	13(1)	19(1)	11(1)	0(1)	2(1)	0(1)
P(4)	14(1)	11(1)	14(1)	-2(1)	3(1)	-2(1)
F(10)	105(3)	119(4)	17(2)	-7(2)	15(2)	52(3)
F(11)	95(3)	74(3)	30(2)	-4(2)	-14(2)	-32(2)
F(12)	143(4)	29(2)	24(2)	2(1)	-19(2)	16(2)
C(35)	30(3)	12(2)	81(5)	0(2)	20(3)	-3(2)
C(36)	82(5)	39(3)	41(3)	-16(3)	14(3)	-44(4)
C(37)	24(3)	52(4)	79(5)	34(4)	-13(3)	-22(3)
C(38)	48(3)	16(2)	94(5)	6(3)	53(4)	0(2)
C(39)	57(3)	22(2)	28(3)	1(2)	7(3)	-18(2)
C(40)	15(2)	16(2)	16(2)	0(2)	4(2)	1(2)
C(41)	20(2)	24(2)	21(2)	1(2)	4(2)	-2(2)
C(42)	14(2)	22(2)	32(3)	6(2)	2(2)	2(2)
C(43)	17(2)	15(2)	30(2)	0(2)	7(2)	0(2)
C(44)	15(2)	10(2)	20(2)	-2(2)	6(2)	-4(1)
C(45)	23(2)	27(2)	14(2)	3(2)	4(2)	-2(2)
C(46)	37(3)	27(2)	21(2)	8(2)	6(2)	-2(2)
C(47)	25(2)	42(3)	24(2)	11(2)	9(2)	-5(2)
C(48)	28(2)	38(3)	14(2)	5(2)	1(2)	2(2)
C(49)	20(2)	22(2)	19(2)	-7(2)	3(2)	0(2)

C(50)	31(2)	37(3)	22(2)	-7(2)	9(2)	8(2)
C(51)	30(2)	30(3)	22(2)	-11(2)	1(2)	-4(2)
C(52)	28(2)	20(2)	27(2)	1(2)	7(2)	6(2)
C(53)	17(2)	11(2)	17(2)	-2(2)	6(2)	-2(1)
C(54)	20(2)	23(2)	24(2)	-4(2)	12(2)	-4(2)
C(55)	22(2)	9(2)	16(2)	0(2)	3(2)	-2(2)
C(56)	22(2)	12(2)	41(3)	3(2)	7(2)	-1(2)
C(57)	28(2)	16(2)	52(3)	8(2)	8(2)	2(2)
C(58)	35(3)	15(2)	34(3)	3(2)	7(2)	-2(2)
C(59)	29(2)	17(2)	25(2)	0(2)	3(2)	-9(2)
C(60)	21(2)	16(2)	20(2)	2(2)	2(2)	-6(2)
C(61)	41(3)	17(2)	76(5)	10(3)	10(3)	-3(2)
C(62)	16(2)	11(2)	20(2)	-2(2)	7(2)	-1(1)
C(63)	25(2)	12(2)	21(2)	-2(2)	6(2)	1(2)
C(64)	34(2)	15(2)	20(2)	-7(2)	3(2)	1(2)
C(65)	31(2)	18(2)	14(2)	-6(2)	4(2)	0(2)
C(66)	34(2)	12(2)	16(2)	-1(2)	6(2)	6(2)
C(67)	30(2)	14(2)	20(2)	-1(2)	10(2)	-2(2)
C(68)	60(4)	19(2)	19(2)	-1(2)	3(2)	6(2)
C(1S)	34(3)	31(3)	32(3)	9(2)	14(2)	7(2)
C(2S)	33(2)	25(2)	21(2)	6(2)	7(2)	-1(2)
Cl(5S)	38(1)	23(1)	24(1)	-1(1)	5(1)	3(1)
Cl(6S)	58(1)	52(1)	87(1)	26(1)	49(1)	23(1)
Cl(7S)	28(1)	21(1)	20(1)	1(1)	8(1)	3(1)
Cl(8S)	33(1)	38(1)	31(1)	3(1)	16(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for $C_{34}H_{38}Cl_2F_6FeP_2Pd(CH_2Cl_2)$.

	x	y	z	U(eq)
H(1)	5330	282	5754	27
H(2)	4419	596	5030	28
H(3)	3374	1217	5291	27
H(4)	3644	1295	6168	24
H(5)	4857	690	6457	25
H(7)	4879	2927	4997	16
H(8)	3784	3322	5243	16
H(9)	4024	3392	6124	16
H(12A)	5578	3824	4772	24
H(12B)	6336	3635	4716	24
H(12C)	6039	4706	4679	24
H(13A)	5875	5576	5365	21
H(13B)	6031	5082	5866	21
H(13C)	5391	4745	5481	21
H(14A)	7332	4096	5377	28
H(14B)	7179	4774	5779	28
H(14C)	7052	5163	5259	28
H(16A)	6112	1099	4861	28
H(16B)	5821	2172	4802	28
H(16C)	5574	1447	5151	28
H(17A)	6762	581	5647	30
H(17B)	6317	1143	5947	30
H(17C)	7108	1367	6018	30
H(18A)	7536	2418	5445	26
H(18B)	7054	2607	4948	26
H(18C)	7312	1541	5095	26
H(19)	5592	2334	6661	14
H(20A)	4677	3659	6936	23
H(20B)	5107	2856	7259	23
H(20C)	4515	2544	6833	23

H(22)	4792	4820	6429	17
H(23)	4487	6442	6280	19
H(25)	6425	7254	6825	22
H(26)	6735	5634	6957	19
H(29)	5994	4945	7612	20
H(30)	6328	4677	8411	21
H(32)	7062	2057	8167	21
H(33)	6752	2332	7373	19
H(35)	9612	11351	8505	48
H(36)	10492	11205	9232	64
H(37)	11452	10236	9081	66
H(38)	11175	9762	8229	56
H(39)	10018	10478	7872	43
H(41)	10007	8905	9543	26
H(42)	10949	8164	9222	28
H(43)	10510	7895	8356	24
H(46A)	8704	6474	9445	43
H(46B)	9201	7088	9204	43
H(46C)	8460	6815	8919	43
H(47A)	7437	7629	9080	45
H(47B)	7505	8365	9502	45
H(47C)	7643	7244	9601	45
H(48A)	8756	7614	10093	41
H(48B)	8686	8745	9995	41
H(48C)	9324	8172	9895	41
H(50A)	7855	10909	9594	44
H(50B)	7990	9824	9769	44
H(50C)	7455	10045	9299	44
H(51A)	9495	10431	9385	42
H(51B)	9223	10007	9814	42
H(51C)	9079	11105	9663	42
H(52A)	8339	11516	8925	37
H(52B)	7866	10730	8619	37
H(52C)	8656	10766	8621	37
H(53)	8973	9161	7901	18
H(54A)	9923	8715	7613	32

H(54B)	9234	8408	7268	32
H(54C)	9681	7617	7589	32
H(56)	9624	6628	8145	30
H(57)	9876	4999	8301	38
H(59)	7881	4416	8161	29
H(60)	7620	6044	8018	23
H(63)	8211	6316	7175	23
H(64)	7804	6363	6370	28
H(66)	7300	9176	6451	25
H(67)	7720	9144	7246	25
H(1S1)	8332	2219	7184	38
H(1S2)	7838	1432	6893	38
H(2S1)	6192	-589	7389	31
H(2S2)	6630	278	7657	31

Table 6. Torsion angles [°] for $C_{34}H_{38}Cl_2F_6FeP_2Pd(CH_2Cl_2)$.

C(5)-C(1)-C(2)-C(3)	0.2(4)
Fe(1)-C(1)-C(2)-C(3)	-59.2(3)
C(5)-C(1)-C(2)-Fe(1)	59.4(3)
C(1)-C(2)-C(3)-C(4)	0.2(5)
Fe(1)-C(2)-C(3)-C(4)	-59.3(3)
C(1)-C(2)-C(3)-Fe(1)	59.6(3)
C(2)-C(3)-C(4)-C(5)	-0.6(5)
Fe(1)-C(3)-C(4)-C(5)	-60.2(3)
C(2)-C(3)-C(4)-Fe(1)	59.6(3)
C(2)-C(1)-C(5)-C(4)	-0.6(4)
Fe(1)-C(1)-C(5)-C(4)	58.6(3)
C(2)-C(1)-C(5)-Fe(1)	-59.2(3)
C(3)-C(4)-C(5)-C(1)	0.7(4)
Fe(1)-C(4)-C(5)-C(1)	-59.2(3)
C(3)-C(4)-C(5)-Fe(1)	59.9(3)
C(15)-P(1)-C(6)-C(7)	-69.8(3)
C(11)-P(1)-C(6)-C(7)	46.6(3)
Pd(1)-P(1)-C(6)-C(7)	158.7(3)
C(15)-P(1)-C(6)-C(10)	132.9(3)
C(11)-P(1)-C(6)-C(10)	-110.7(3)
Pd(1)-P(1)-C(6)-C(10)	1.4(4)
C(15)-P(1)-C(6)-Fe(1)	30.6(4)
C(11)-P(1)-C(6)-Fe(1)	147.1(3)
Pd(1)-P(1)-C(6)-Fe(1)	-100.8(3)
C(10)-C(6)-C(7)-C(8)	2.6(4)
P(1)-C(6)-C(7)-C(8)	-158.4(3)
Fe(1)-C(6)-C(7)-C(8)	59.4(3)
C(10)-C(6)-C(7)-Fe(1)	-56.8(2)
P(1)-C(6)-C(7)-Fe(1)	142.2(3)
C(6)-C(7)-C(8)-C(9)	-1.6(4)
Fe(1)-C(7)-C(8)-C(9)	58.9(3)
C(6)-C(7)-C(8)-Fe(1)	-60.5(3)
C(7)-C(8)-C(9)-C(10)	0.0(4)
Fe(1)-C(8)-C(9)-C(10)	58.9(3)

C(7)-C(8)-C(9)-Fe(1)	-58.9(3)
C(8)-C(9)-C(10)-C(6)	1.7(4)
Fe(1)-C(9)-C(10)-C(6)	60.5(2)
C(8)-C(9)-C(10)-C(19)	-176.2(3)
Fe(1)-C(9)-C(10)-C(19)	-117.4(3)
C(8)-C(9)-C(10)-Fe(1)	-58.8(3)
C(7)-C(6)-C(10)-C(9)	-2.6(4)
P(1)-C(6)-C(10)-C(9)	158.1(3)
Fe(1)-C(6)-C(10)-C(9)	-59.4(2)
C(7)-C(6)-C(10)-C(19)	175.2(3)
P(1)-C(6)-C(10)-C(19)	-24.1(5)
Fe(1)-C(6)-C(10)-C(19)	118.4(4)
C(7)-C(6)-C(10)-Fe(1)	56.8(2)
P(1)-C(6)-C(10)-Fe(1)	-142.5(3)
C(9)-C(10)-C(19)-C(20)	6.8(5)
C(6)-C(10)-C(19)-C(20)	-170.6(4)
Fe(1)-C(10)-C(19)-C(20)	-79.3(4)
C(9)-C(10)-C(19)-P(2)	-124.3(3)
C(6)-C(10)-C(19)-P(2)	58.3(4)
Fe(1)-C(10)-C(19)-P(2)	149.6(2)
C(28)-P(2)-C(19)-C(10)	175.0(3)
C(21)-P(2)-C(19)-C(10)	63.6(3)
Pd(1)-P(2)-C(19)-C(10)	-65.7(3)
C(28)-P(2)-C(19)-C(20)	44.5(3)
C(21)-P(2)-C(19)-C(20)	-66.9(3)
Pd(1)-P(2)-C(19)-C(20)	163.8(2)
C(28)-P(2)-C(21)-C(26)	69.2(3)
C(19)-P(2)-C(21)-C(26)	178.8(3)
Pd(1)-P(2)-C(21)-C(26)	-53.4(3)
C(28)-P(2)-C(21)-C(22)	-115.1(3)
C(19)-P(2)-C(21)-C(22)	-5.5(4)
Pd(1)-P(2)-C(21)-C(22)	122.3(3)
C(26)-C(21)-C(22)-C(23)	1.2(6)
P(2)-C(21)-C(22)-C(23)	-174.4(3)
C(21)-C(22)-C(23)-C(24)	0.0(6)
C(22)-C(23)-C(24)-C(25)	-1.9(6)

C(22)-C(23)-C(24)-C(27)	179.9(4)
C(23)-C(24)-C(25)-C(26)	2.7(6)
C(27)-C(24)-C(25)-C(26)	-179.1(4)
C(24)-C(25)-C(26)-C(21)	-1.6(6)
C(22)-C(21)-C(26)-C(25)	-0.4(6)
P(2)-C(21)-C(26)-C(25)	175.4(3)
C(23)-C(24)-C(27)-F(1)	-16.7(8)
C(25)-C(24)-C(27)-F(1)	165.1(7)
C(23)-C(24)-C(27)-F(2)	-139.5(6)
C(25)-C(24)-C(27)-F(2)	42.3(7)
C(23)-C(24)-C(27)-F(3)	102.2(6)
C(25)-C(24)-C(27)-F(3)	-76.0(7)
C(21)-P(2)-C(28)-C(29)	7.9(4)
C(19)-P(2)-C(28)-C(29)	-107.2(4)
Pd(1)-P(2)-C(28)-C(29)	132.9(3)
C(21)-P(2)-C(28)-C(33)	-174.3(3)
C(19)-P(2)-C(28)-C(33)	70.6(3)
Pd(1)-P(2)-C(28)-C(33)	-49.2(3)
C(33)-C(28)-C(29)-C(30)	1.5(6)
P(2)-C(28)-C(29)-C(30)	179.3(3)
C(28)-C(29)-C(30)-C(31)	-1.2(7)
C(29)-C(30)-C(31)-C(32)	0.2(7)
C(29)-C(30)-C(31)-C(34)	177.7(4)
C(30)-C(31)-C(32)-C(33)	0.5(6)
C(34)-C(31)-C(32)-C(33)	-177.1(4)
C(31)-C(32)-C(33)-C(28)	-0.2(6)
C(29)-C(28)-C(33)-C(32)	-0.8(6)
P(2)-C(28)-C(33)-C(32)	-178.7(3)
C(30)-C(31)-C(34)-F(4)	10.4(6)
C(32)-C(31)-C(34)-F(4)	-172.1(4)
C(30)-C(31)-C(34)-F(6)	131.7(4)
C(32)-C(31)-C(34)-F(6)	-50.8(5)
C(30)-C(31)-C(34)-F(5)	-109.6(5)
C(32)-C(31)-C(34)-F(5)	67.9(5)
C(39)-C(35)-C(36)-C(37)	-0.4(6)
Fe(2)-C(35)-C(36)-C(37)	59.4(4)

C(39)-C(35)-C(36)-Fe(2)	-59.8(4)
C(35)-C(36)-C(37)-C(38)	0.2(6)
Fe(2)-C(36)-C(37)-C(38)	60.3(4)
C(35)-C(36)-C(37)-Fe(2)	-60.0(4)
C(36)-C(37)-C(38)-C(39)	0.0(6)
Fe(2)-C(37)-C(38)-C(39)	61.1(3)
C(36)-C(37)-C(38)-Fe(2)	-61.1(4)
C(36)-C(35)-C(39)-C(38)	0.4(6)
Fe(2)-C(35)-C(39)-C(38)	-59.1(3)
C(36)-C(35)-C(39)-Fe(2)	59.6(4)
C(37)-C(38)-C(39)-C(35)	-0.3(6)
Fe(2)-C(38)-C(39)-C(35)	60.2(3)
C(37)-C(38)-C(39)-Fe(2)	-60.5(4)
C(49)-P(3)-C(40)-C(41)	68.7(4)
C(45)-P(3)-C(40)-C(41)	-47.8(4)
Pd(2)-P(3)-C(40)-C(41)	-158.4(3)
C(49)-P(3)-C(40)-C(44)	-132.7(4)
C(45)-P(3)-C(40)-C(44)	110.9(4)
Pd(2)-P(3)-C(40)-C(44)	0.3(4)
C(49)-P(3)-C(40)-Fe(2)	-32.0(4)
C(45)-P(3)-C(40)-Fe(2)	-148.5(4)
Pd(2)-P(3)-C(40)-Fe(2)	100.9(4)
C(44)-C(40)-C(41)-C(42)	-2.4(5)
P(3)-C(40)-C(41)-C(42)	159.6(3)
Fe(2)-C(40)-C(41)-C(42)	-59.3(3)
C(44)-C(40)-C(41)-Fe(2)	56.9(3)
P(3)-C(40)-C(41)-Fe(2)	-141.0(3)
C(40)-C(41)-C(42)-C(43)	1.6(5)
Fe(2)-C(41)-C(42)-C(43)	-58.4(3)
C(40)-C(41)-C(42)-Fe(2)	60.1(3)
C(41)-C(42)-C(43)-C(44)	-0.2(5)
Fe(2)-C(42)-C(43)-C(44)	-59.4(3)
C(41)-C(42)-C(43)-Fe(2)	59.3(3)
C(42)-C(43)-C(44)-C(40)	-1.4(5)
Fe(2)-C(43)-C(44)-C(40)	-61.2(3)
C(42)-C(43)-C(44)-C(53)	176.3(4)

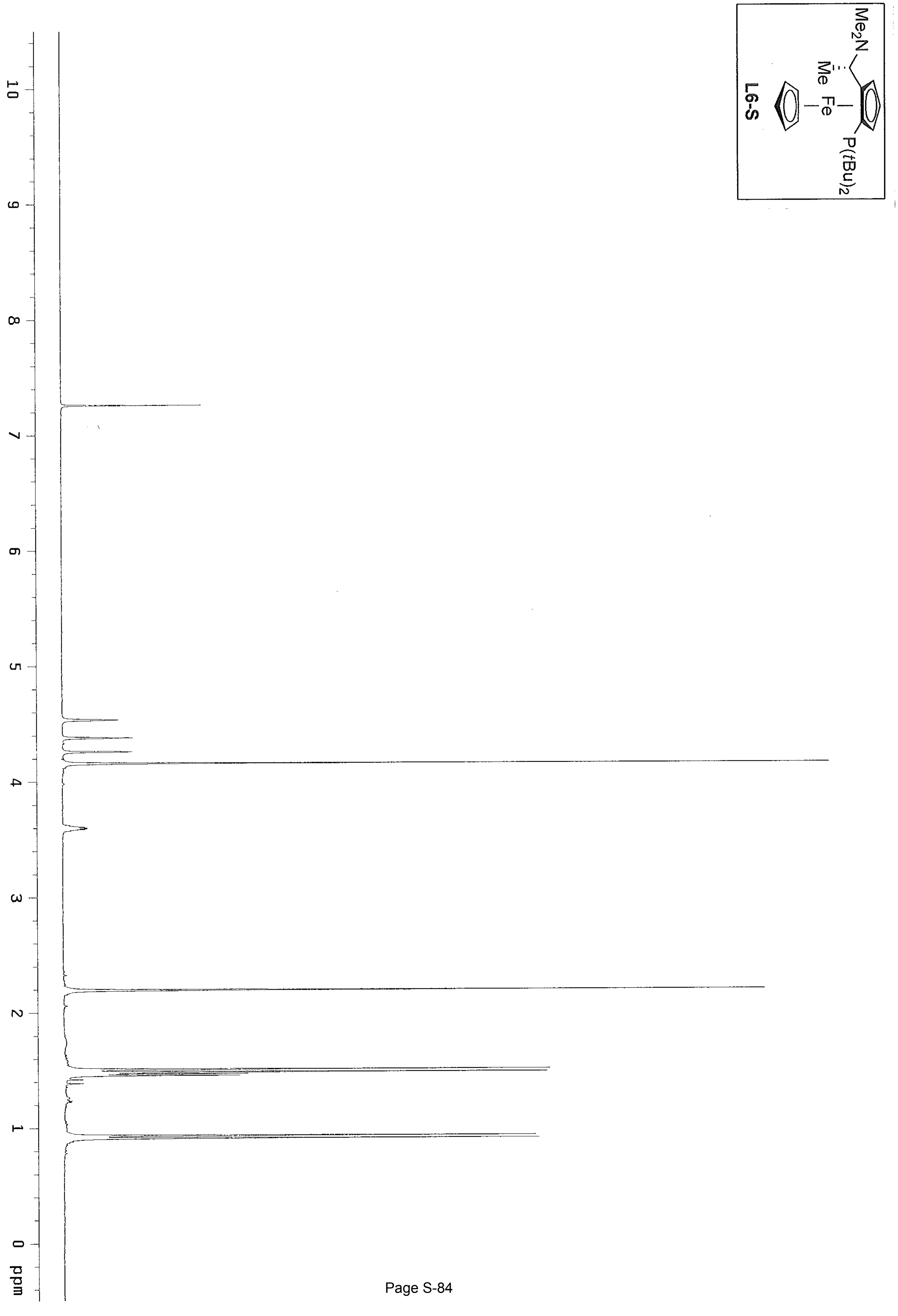
Fe(2)-C(43)-C(44)-C(53)	116.5(4)
C(42)-C(43)-C(44)-Fe(2)	59.9(3)
C(41)-C(40)-C(44)-C(43)	2.3(5)
P(3)-C(40)-C(44)-C(43)	-159.5(3)
Fe(2)-C(40)-C(44)-C(43)	59.7(3)
C(41)-C(40)-C(44)-C(53)	-175.3(4)
P(3)-C(40)-C(44)-C(53)	22.9(6)
Fe(2)-C(40)-C(44)-C(53)	-117.9(4)
C(41)-C(40)-C(44)-Fe(2)	-57.4(3)
P(3)-C(40)-C(44)-Fe(2)	140.8(3)
C(40)-P(3)-C(49)-C(52)	83.3(3)
C(45)-P(3)-C(49)-C(52)	-164.7(3)
Pd(2)-P(3)-C(49)-C(52)	-47.7(3)
C(40)-P(3)-C(49)-C(51)	-34.8(4)
C(45)-P(3)-C(49)-C(51)	77.2(4)
Pd(2)-P(3)-C(49)-C(51)	-165.8(3)
C(40)-P(3)-C(49)-C(50)	-157.1(3)
C(45)-P(3)-C(49)-C(50)	-45.1(4)
Pd(2)-P(3)-C(49)-C(50)	71.9(3)
C(43)-C(44)-C(53)-C(54)	-9.7(5)
C(40)-C(44)-C(53)-C(54)	167.5(4)
Fe(2)-C(44)-C(53)-C(54)	76.1(4)
C(43)-C(44)-C(53)-P(4)	122.6(4)
C(40)-C(44)-C(53)-P(4)	-60.2(5)
Fe(2)-C(44)-C(53)-P(4)	-151.5(2)
C(55)-P(4)-C(53)-C(44)	-62.5(3)
C(62)-P(4)-C(53)-C(44)	-171.9(3)
Pd(2)-P(4)-C(53)-C(44)	69.3(3)
C(55)-P(4)-C(53)-C(54)	69.6(3)
C(62)-P(4)-C(53)-C(54)	-39.8(3)
Pd(2)-P(4)-C(53)-C(54)	-158.6(3)
C(62)-P(4)-C(55)-C(56)	104.4(4)
C(53)-P(4)-C(55)-C(56)	-3.6(4)
Pd(2)-P(4)-C(55)-C(56)	-130.8(4)
C(62)-P(4)-C(55)-C(60)	-73.9(4)
C(53)-P(4)-C(55)-C(60)	178.1(3)

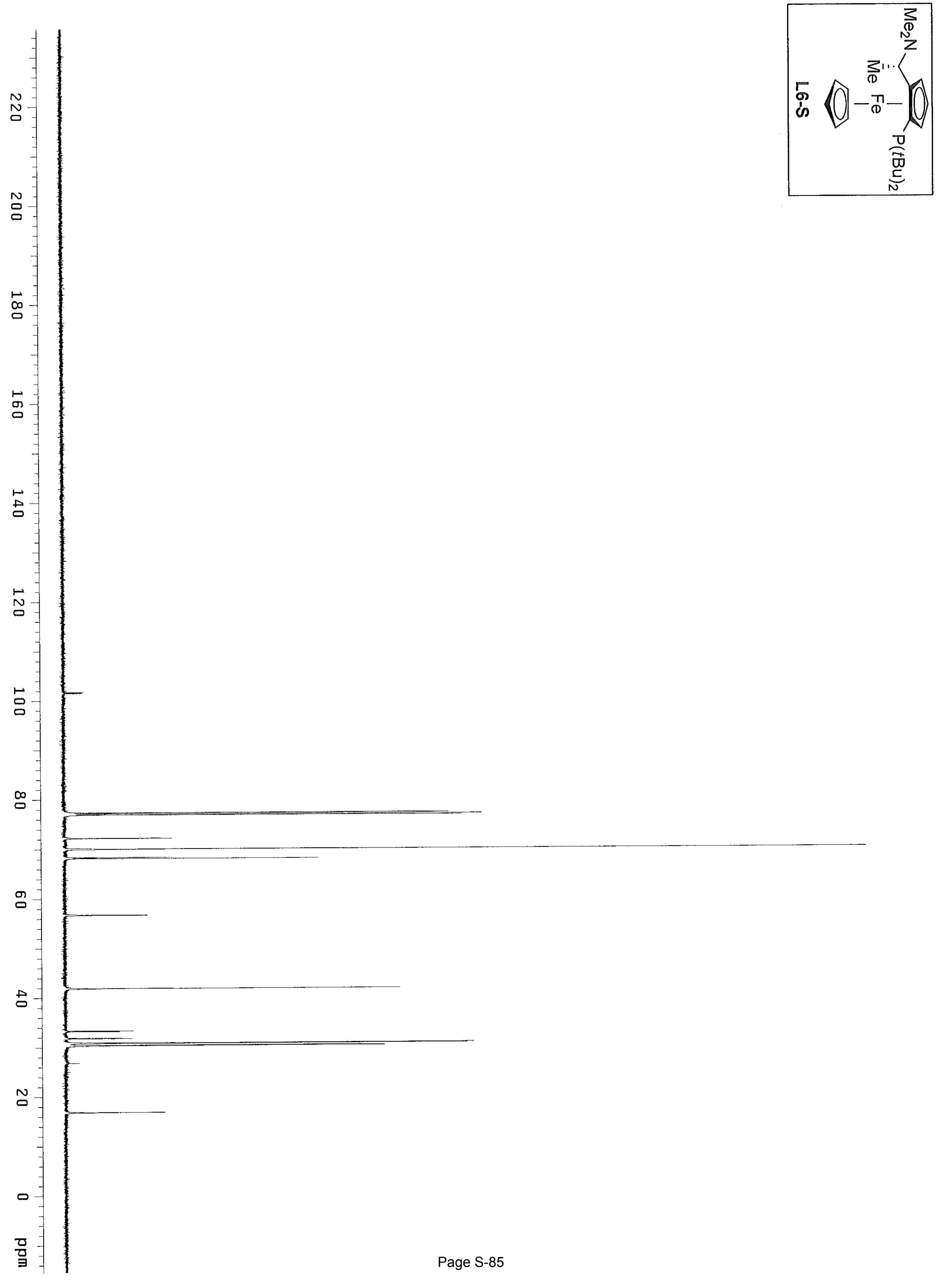
Pd(2)-P(4)-C(55)-C(60)	50.9(4)
C(60)-C(55)-C(56)-C(57)	0.3(7)
P(4)-C(55)-C(56)-C(57)	-178.0(4)
C(55)-C(56)-C(57)-C(58)	0.6(8)
C(56)-C(57)-C(58)-C(59)	-1.0(8)
C(56)-C(57)-C(58)-C(61)	176.1(5)
C(57)-C(58)-C(59)-C(60)	0.3(8)
C(61)-C(58)-C(59)-C(60)	-176.7(5)
C(58)-C(59)-C(60)-C(55)	0.6(7)
C(56)-C(55)-C(60)-C(59)	-0.9(7)
P(4)-C(55)-C(60)-C(59)	177.4(3)
C(59)-C(58)-C(61)-F(9)	-29.6(10)
C(57)-C(58)-C(61)-F(9)	153.3(7)
C(59)-C(58)-C(61)-F(7)	-162.5(6)
C(57)-C(58)-C(61)-F(7)	20.3(9)
C(59)-C(58)-C(61)-F(8)	92.7(6)
C(57)-C(58)-C(61)-F(8)	-84.5(7)
C(55)-P(4)-C(62)-C(63)	-6.9(4)
C(53)-P(4)-C(62)-C(63)	107.0(4)
Pd(2)-P(4)-C(62)-C(63)	-135.6(3)
C(55)-P(4)-C(62)-C(67)	176.5(3)
C(53)-P(4)-C(62)-C(67)	-69.6(4)
Pd(2)-P(4)-C(62)-C(67)	47.7(4)
C(67)-C(62)-C(63)-C(64)	0.0(6)
P(4)-C(62)-C(63)-C(64)	-176.6(3)
C(62)-C(63)-C(64)-C(65)	-0.6(7)
C(63)-C(64)-C(65)-C(66)	0.6(7)
C(63)-C(64)-C(65)-C(68)	-177.1(5)
C(64)-C(65)-C(66)-C(67)	0.1(7)
C(68)-C(65)-C(66)-C(67)	177.7(5)
C(65)-C(66)-C(67)-C(62)	-0.7(7)
C(63)-C(62)-C(67)-C(66)	0.6(6)
P(4)-C(62)-C(67)-C(66)	177.4(4)
C(64)-C(65)-C(68)-F(10)	-47.2(7)
C(66)-C(65)-C(68)-F(10)	135.0(5)
C(64)-C(65)-C(68)-F(12)	-174.4(5)

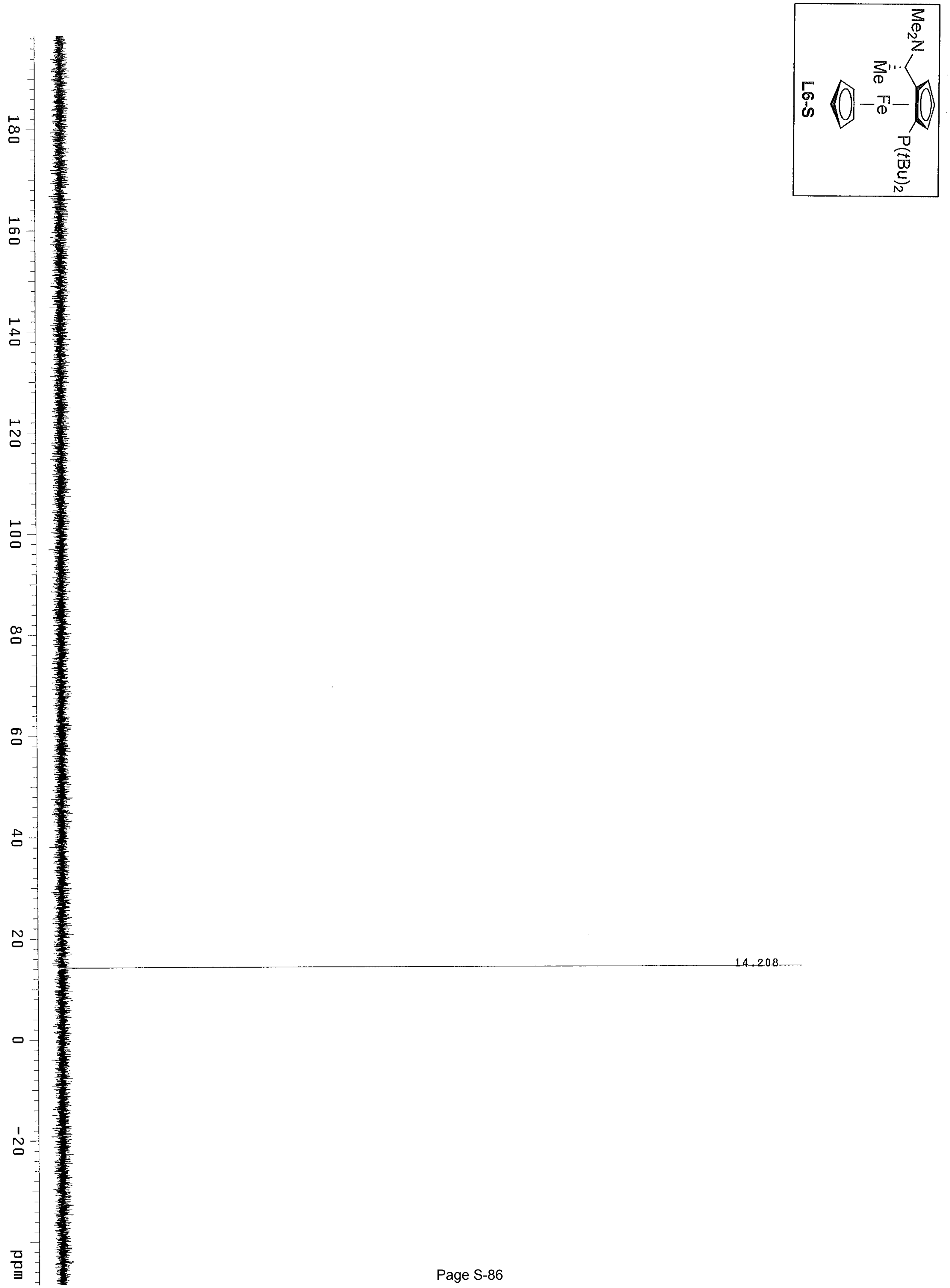
C(66)-C(65)-C(68)-F(12)	7.8(8)
C(64)-C(65)-C(68)-F(11)	68.3(6)
C(66)-C(65)-C(68)-F(11)	-109.4(5)

Symmetry transformations used to generate equivalent atoms:

^{1}H and
^{13}C NMR
Spectral Data


L6-S


Me$_2$N
Me
Fe
P(tBu)$_2$
L6-S
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Me2N
Me
Fe
P(tBu)2
L6-S
14.208
180
160
140
120
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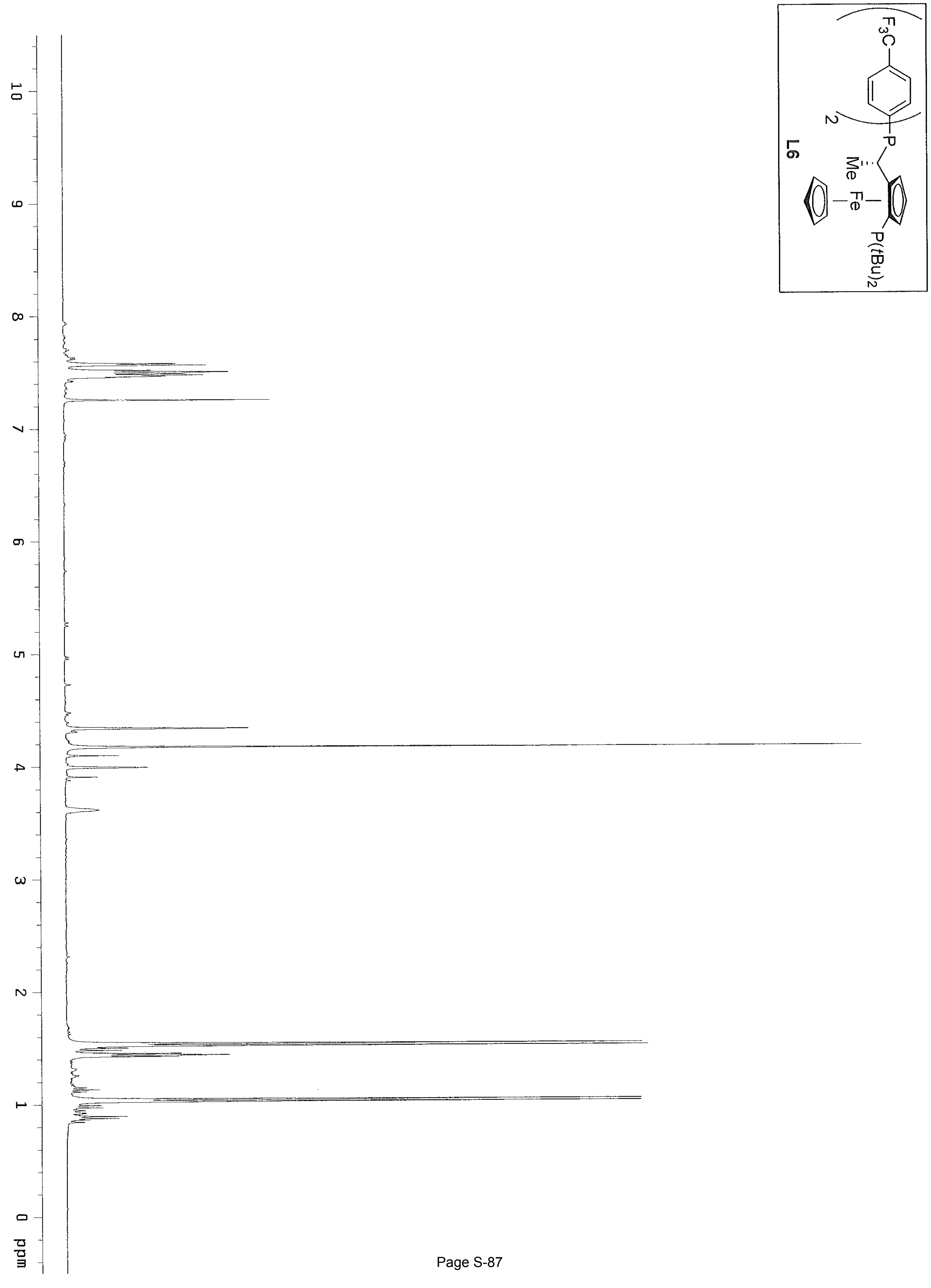
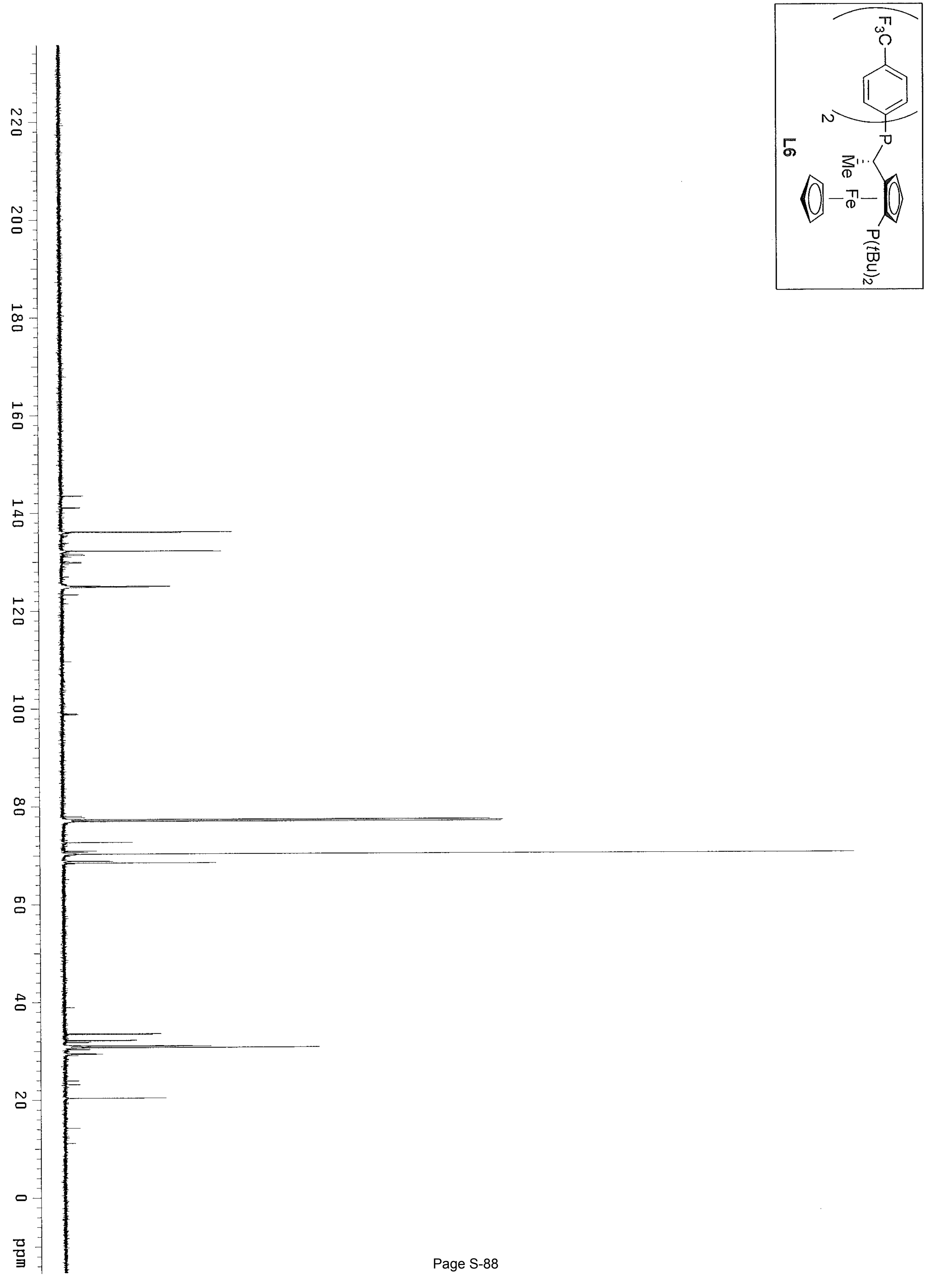
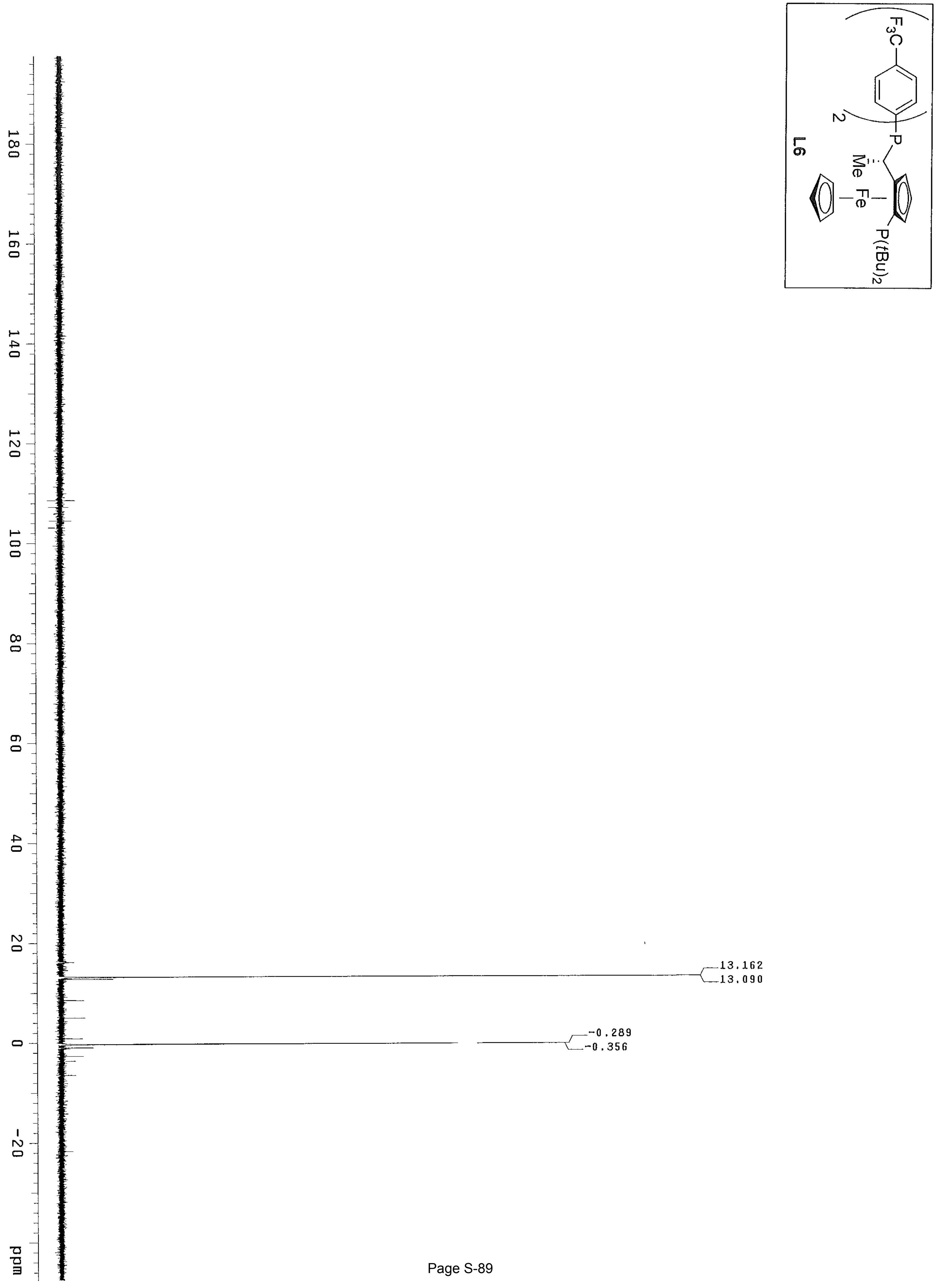
80
60
40
20
0
-20
ppm


F$_3$C
P
2
Me
Fe
P(tBu)$_2$
L6
10
9
8
7
6
5
4
3
2
1
0
ppm


F3C
2
P
Me
Fe
P(tBu)2
L6
220
200
180
160
140
120
100
80
60
40
20
0
ppm


F3C
2
P
Me
Fe
P(tBu)2
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13.090
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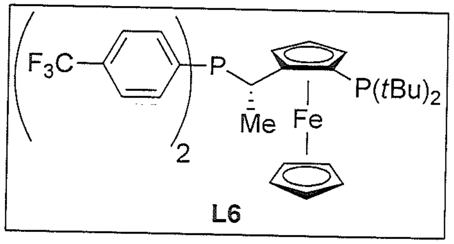
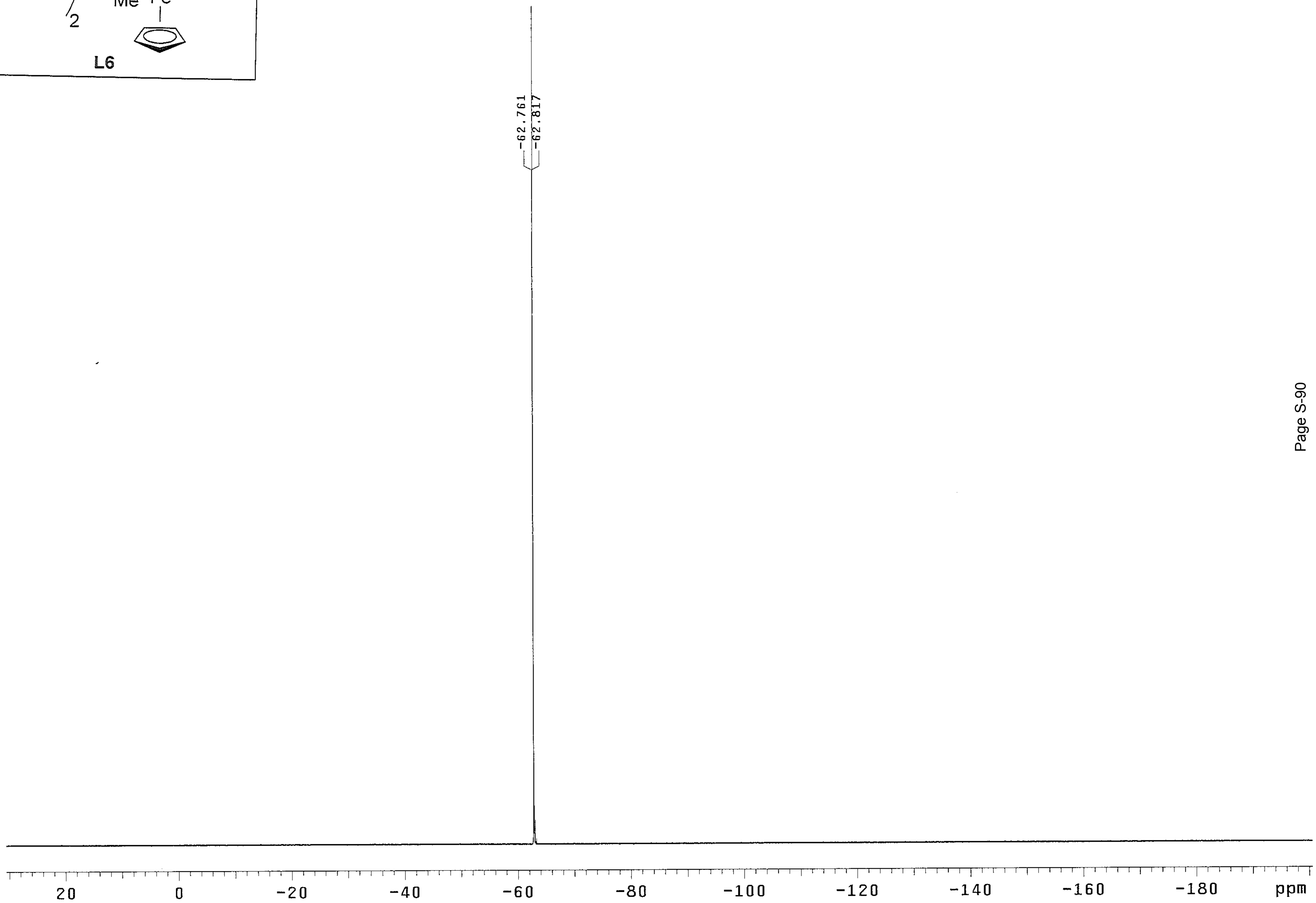
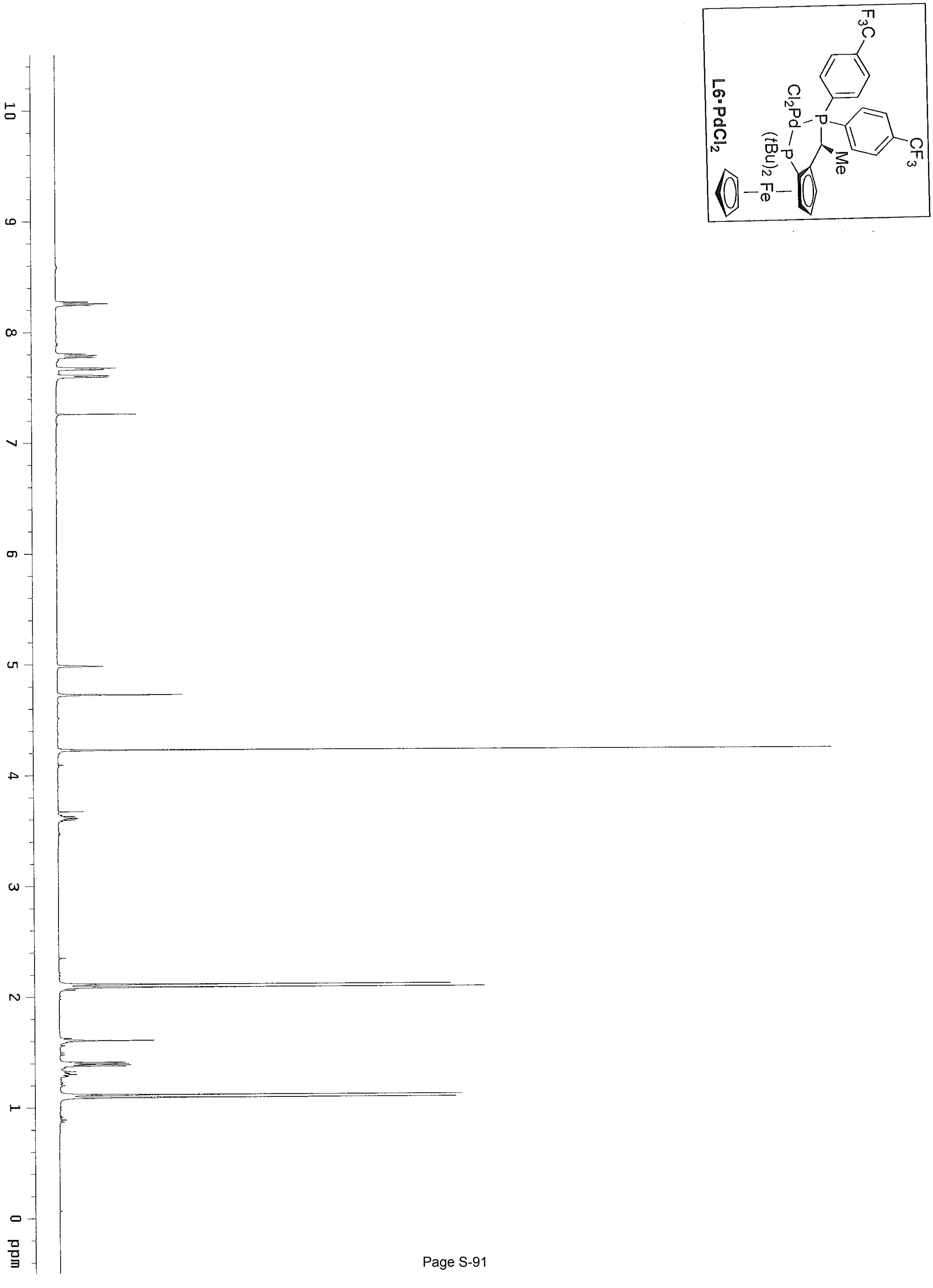
-0.356
180
160
140
120
100
80
60
40
20
0
-20
ppm

L6



L6

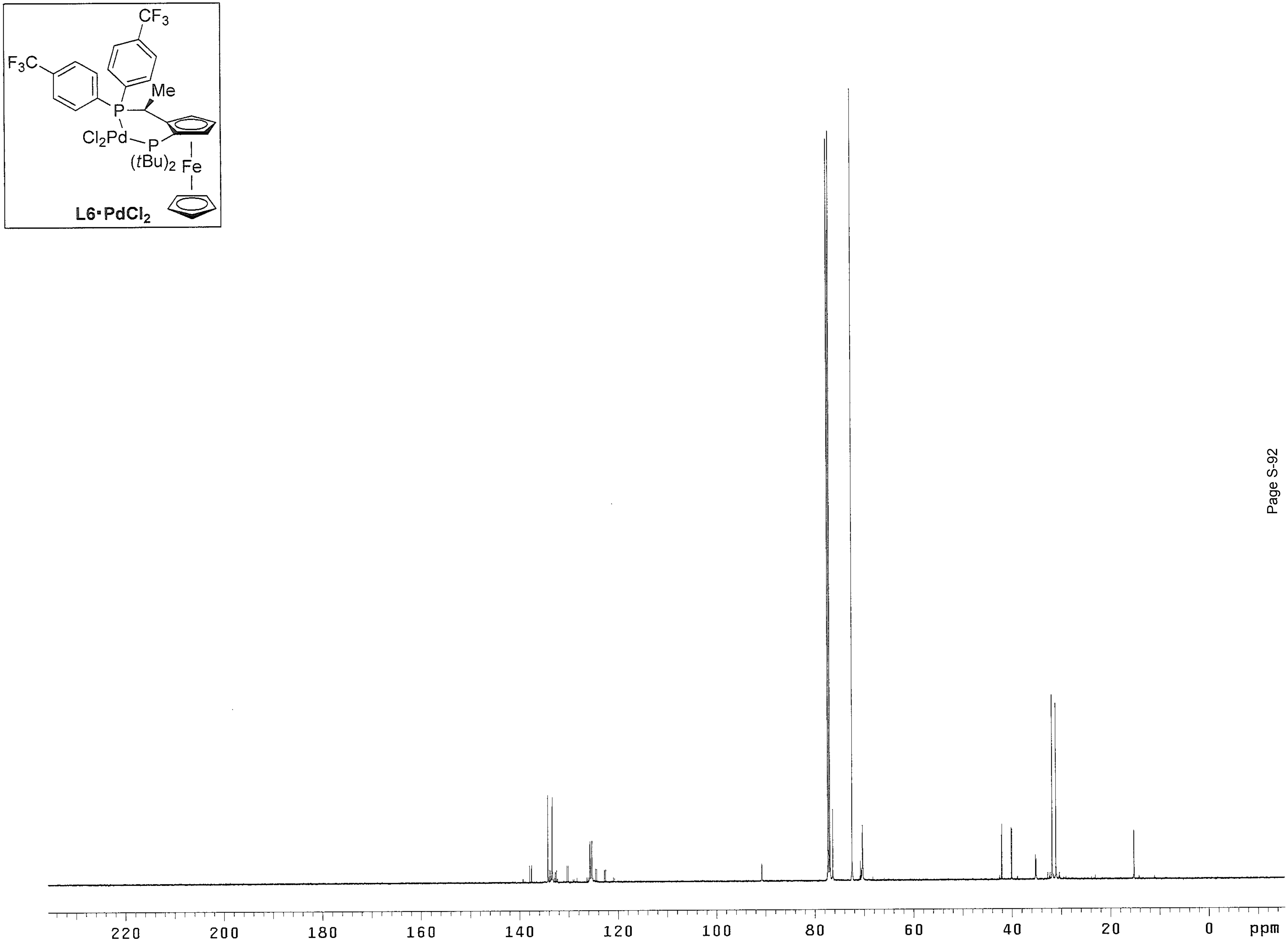


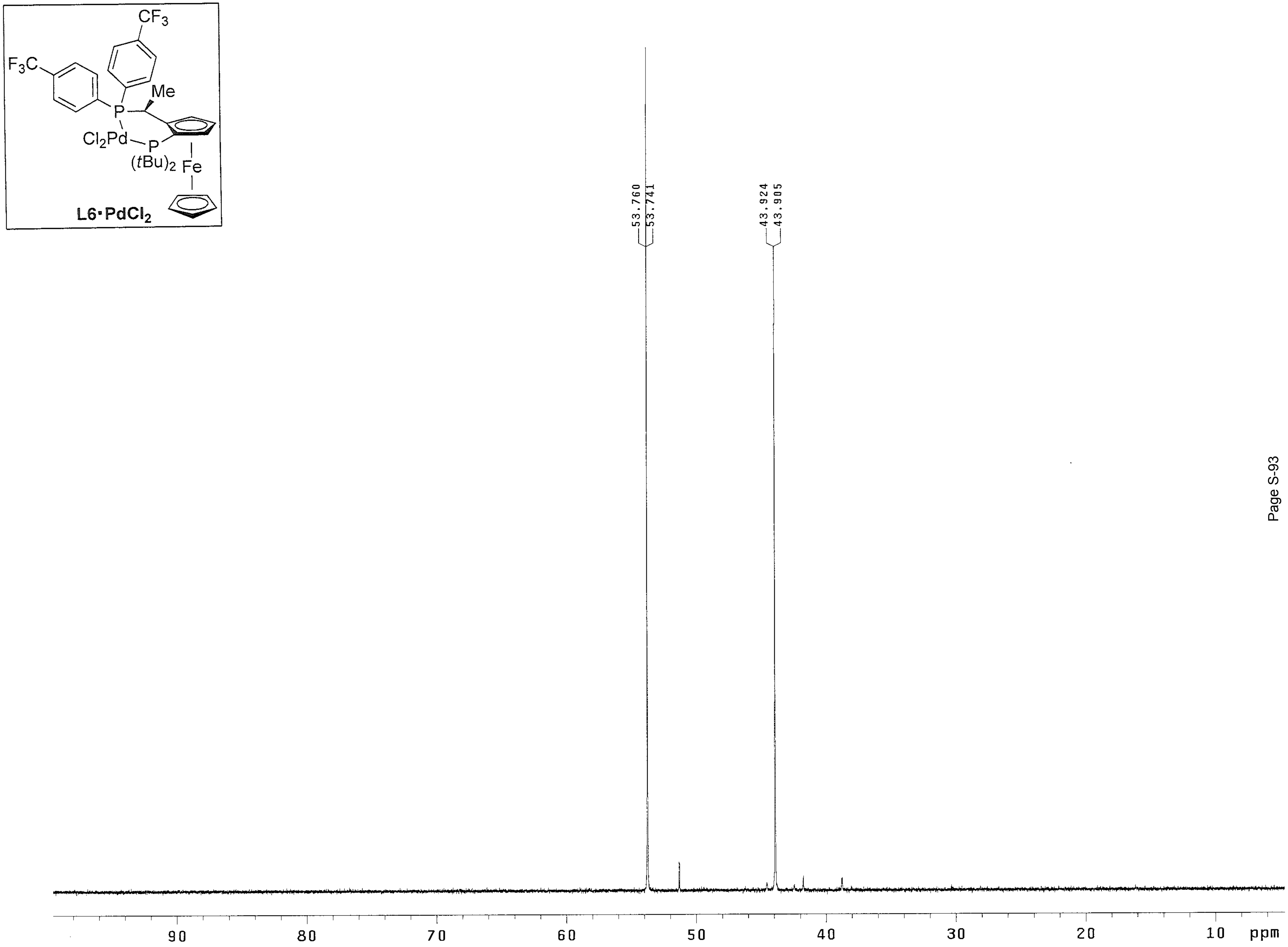


L6•PdCl$_2$

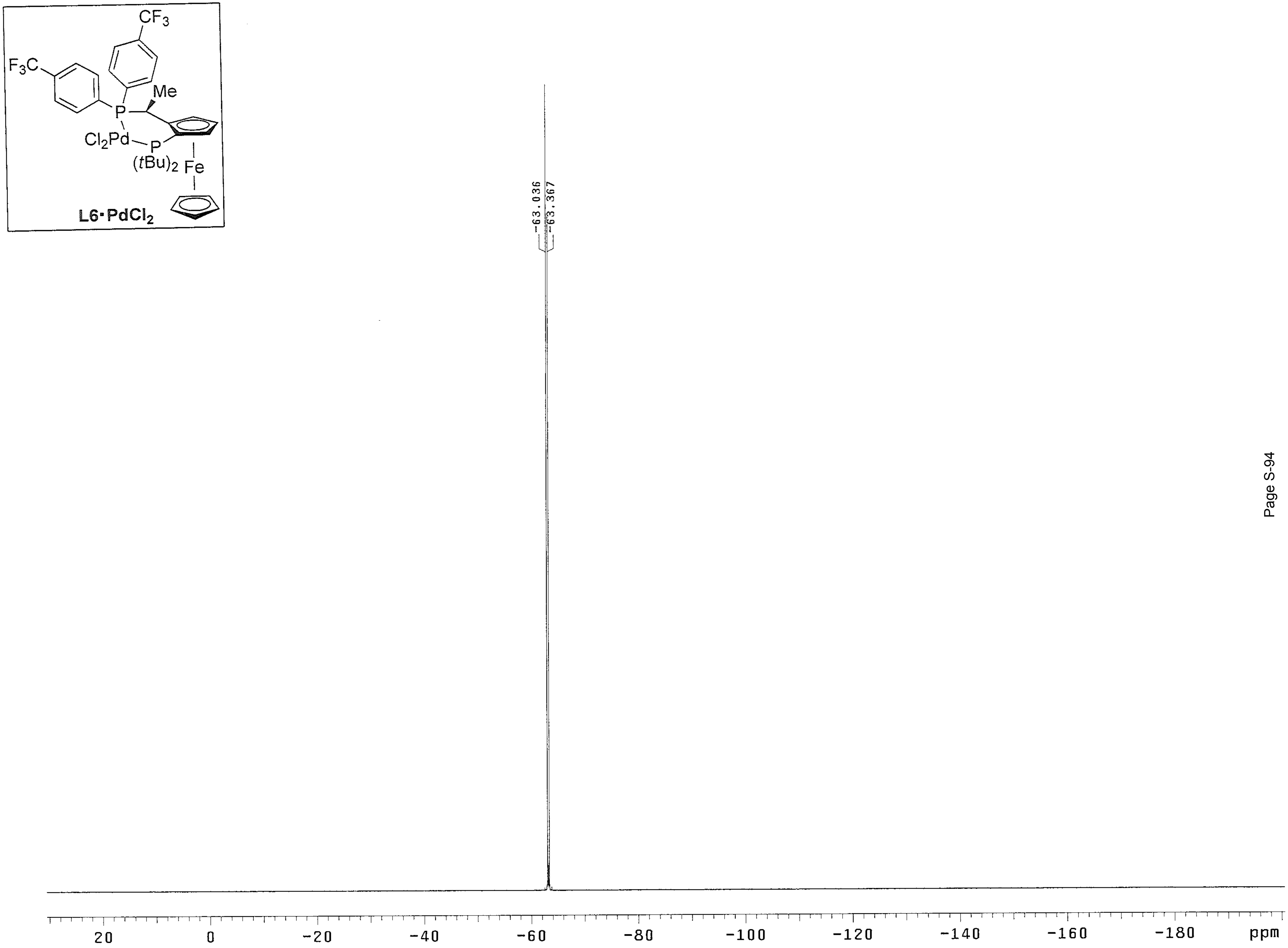
CF3
F3C
Me
P
Cl2Pd
P
(tBu)2
Fe

L6•PdCl2


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



L6•PdCl$_2$


CF3
F3C
Me
P
Cl2Pd
P
(tBu)2
Fe
L6•PdCl2
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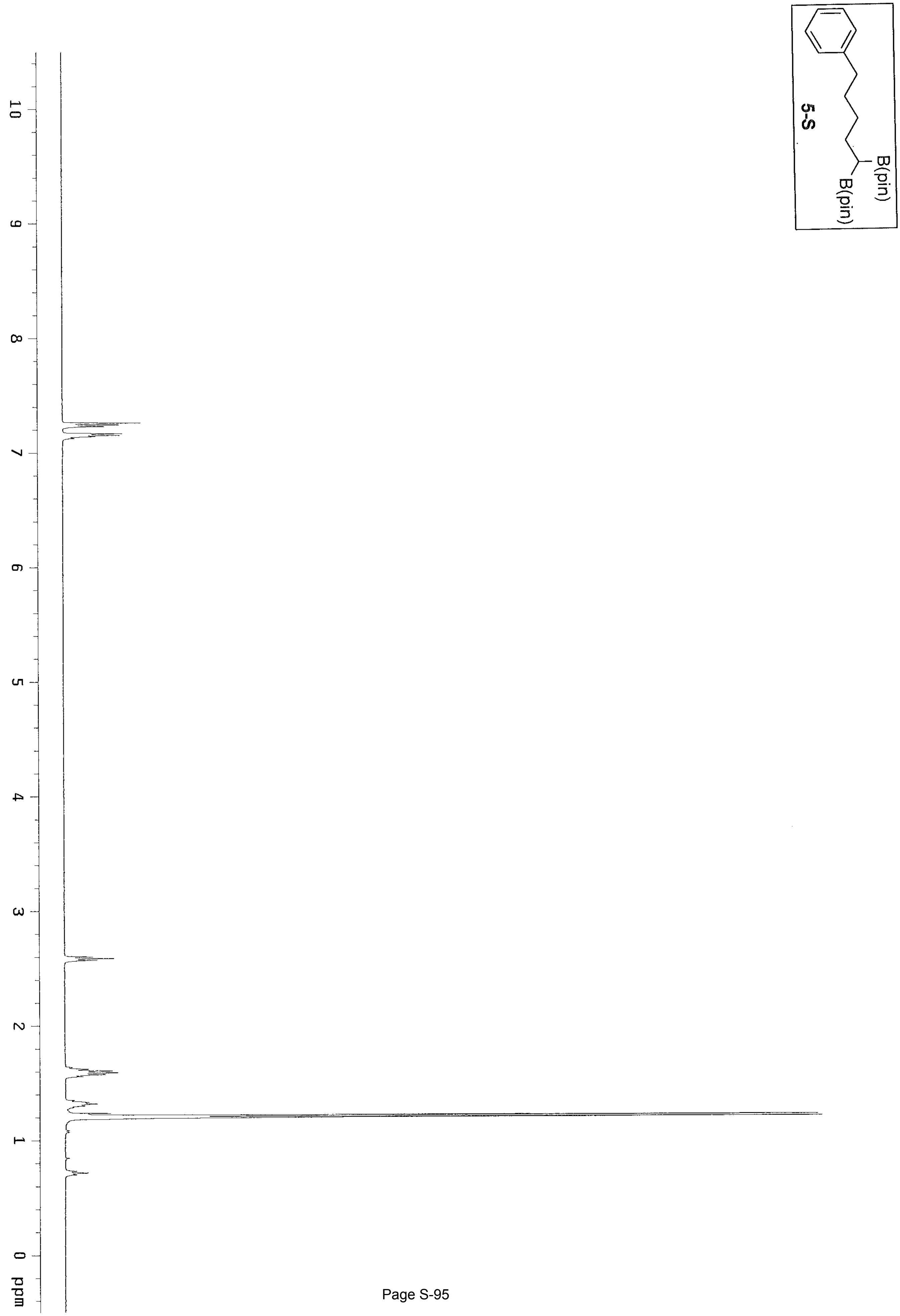
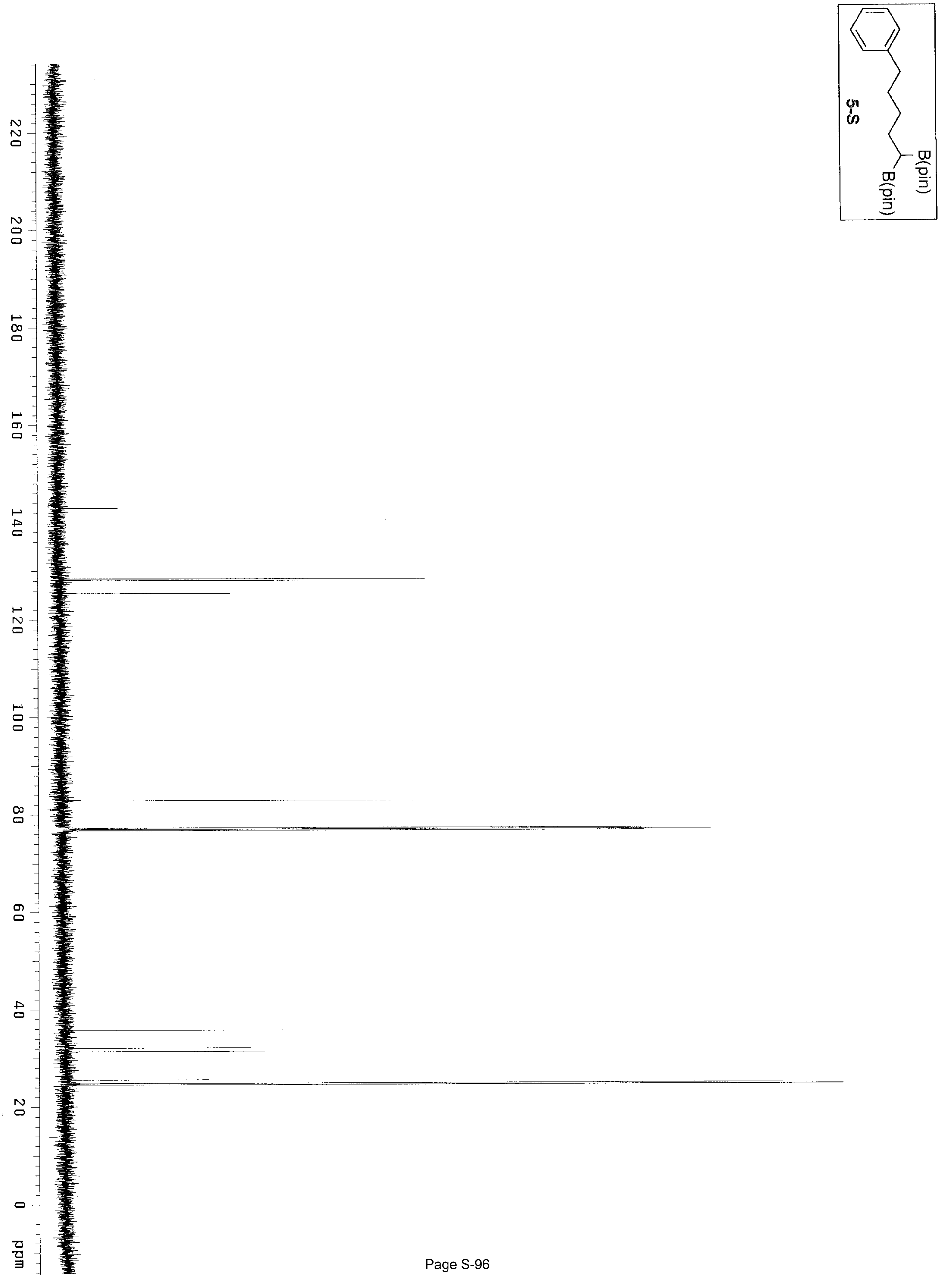
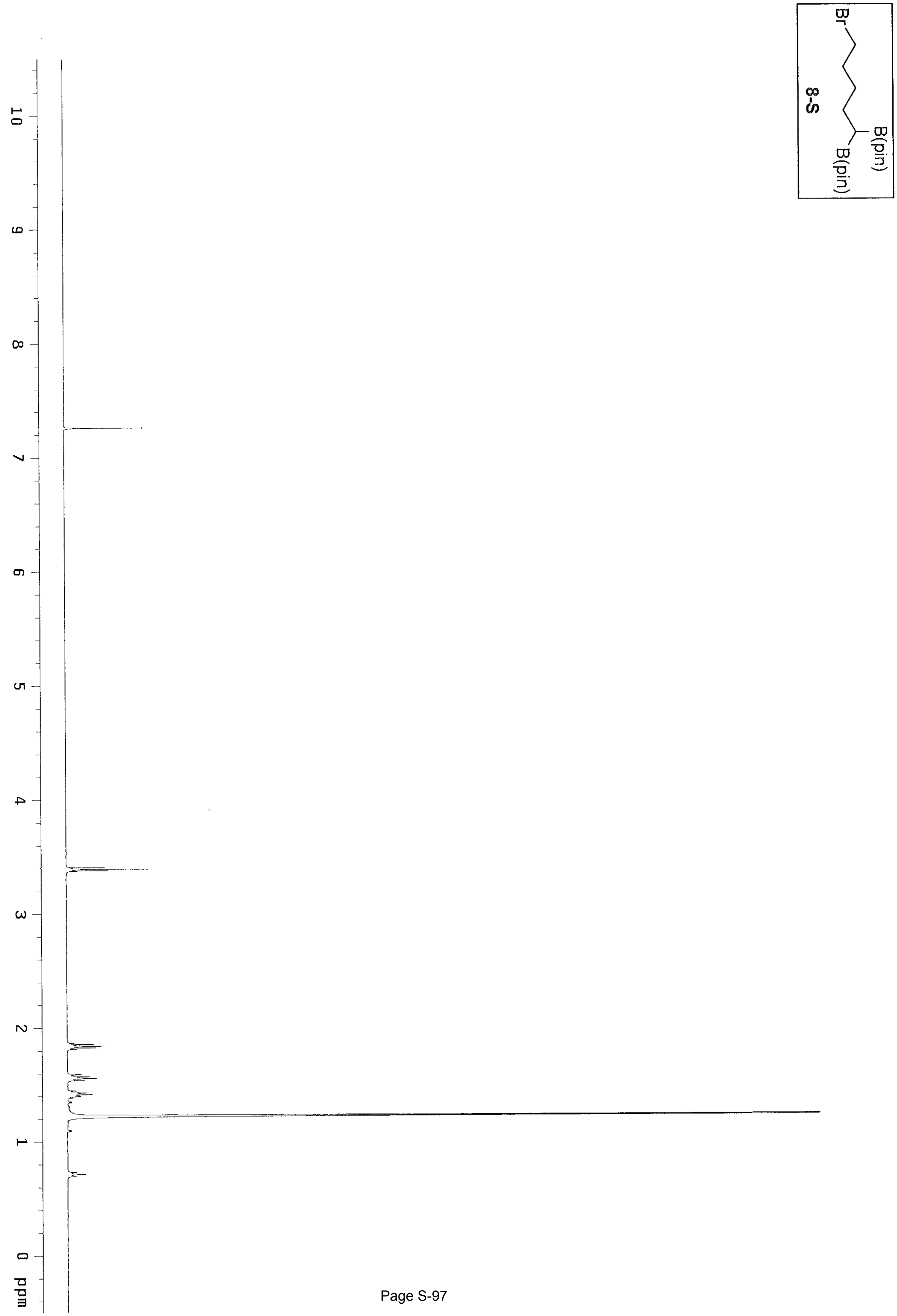
-63.367
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

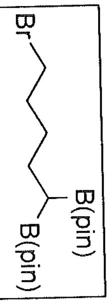

B(pin)
B(pin)
5-S
10
9
8
7
6
5
4
3
2
1
0
ppm



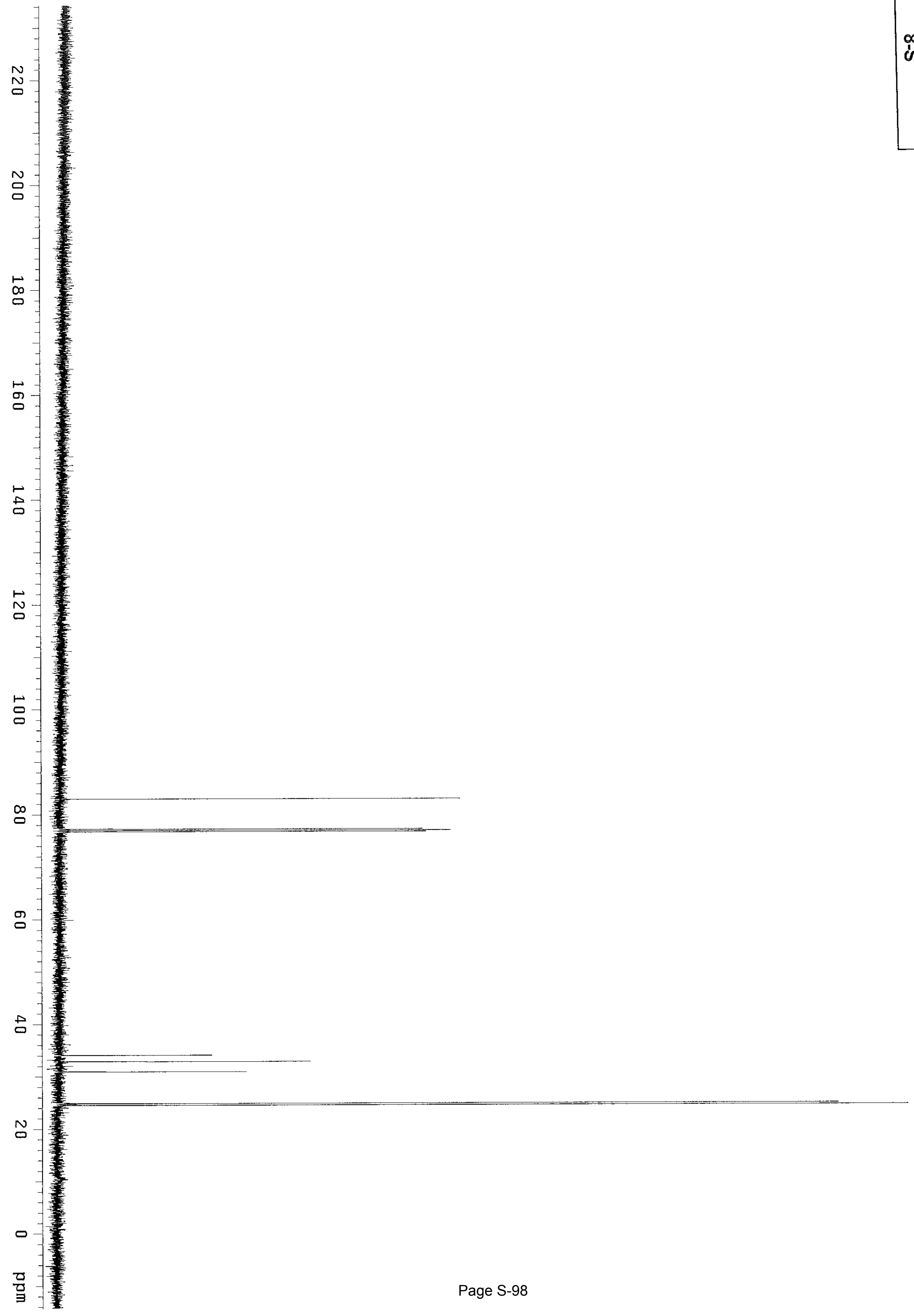
5-S

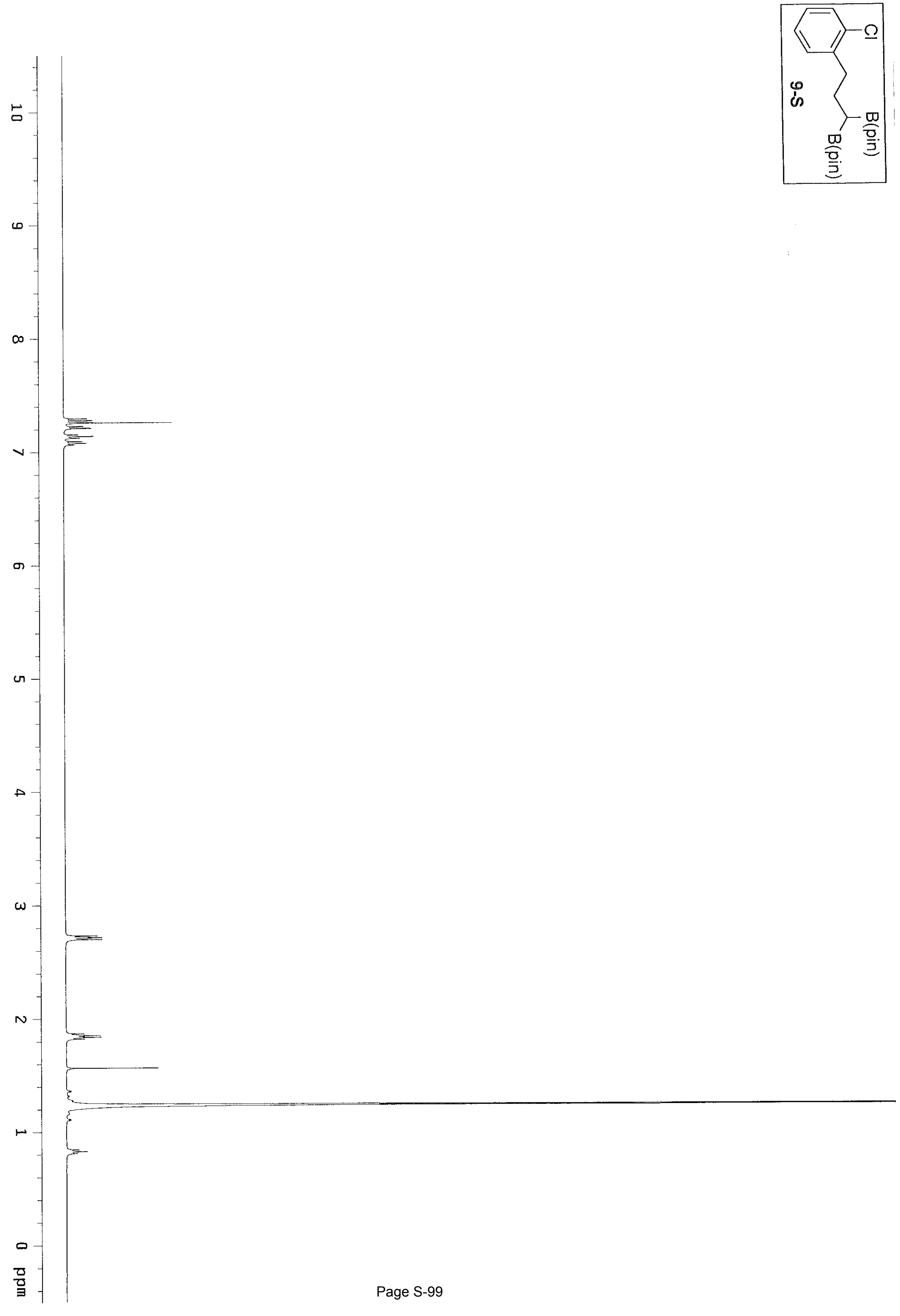


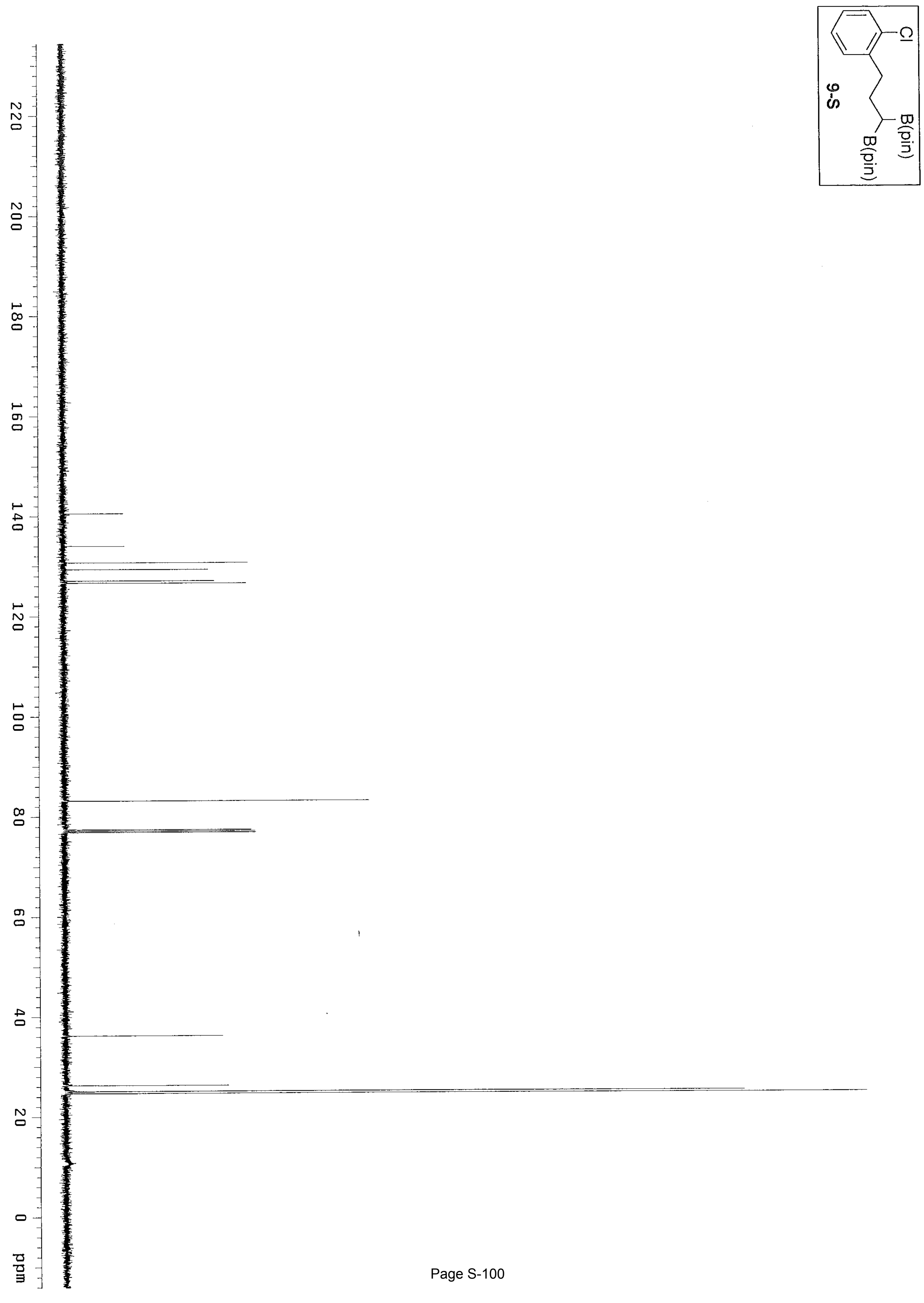
8-S



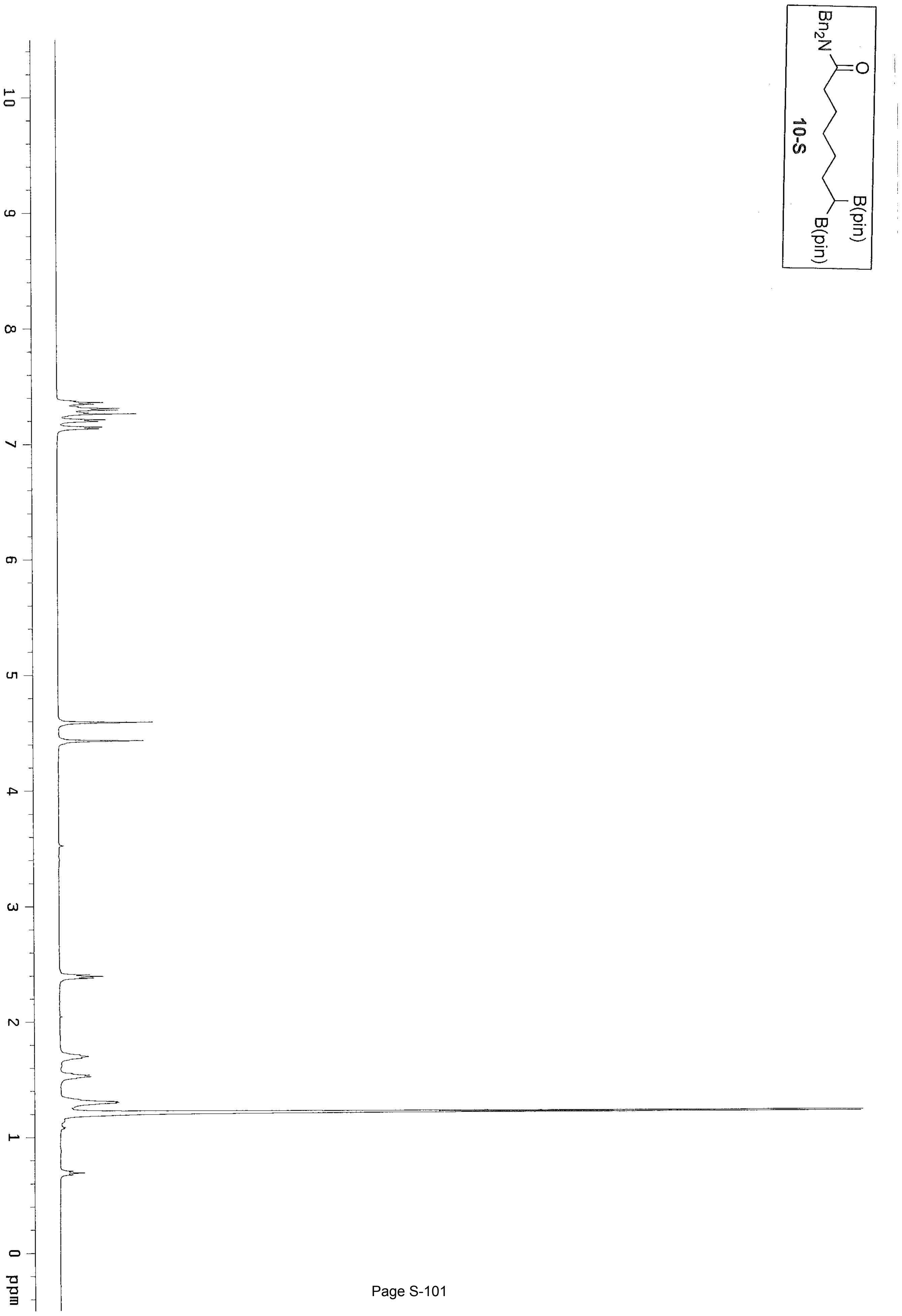
8-S

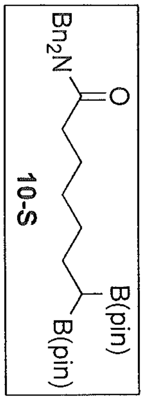



Cl
B(pin)
B(pin)
9-S
10
9
8
7
6
5
4
3
2
1
0
ppm

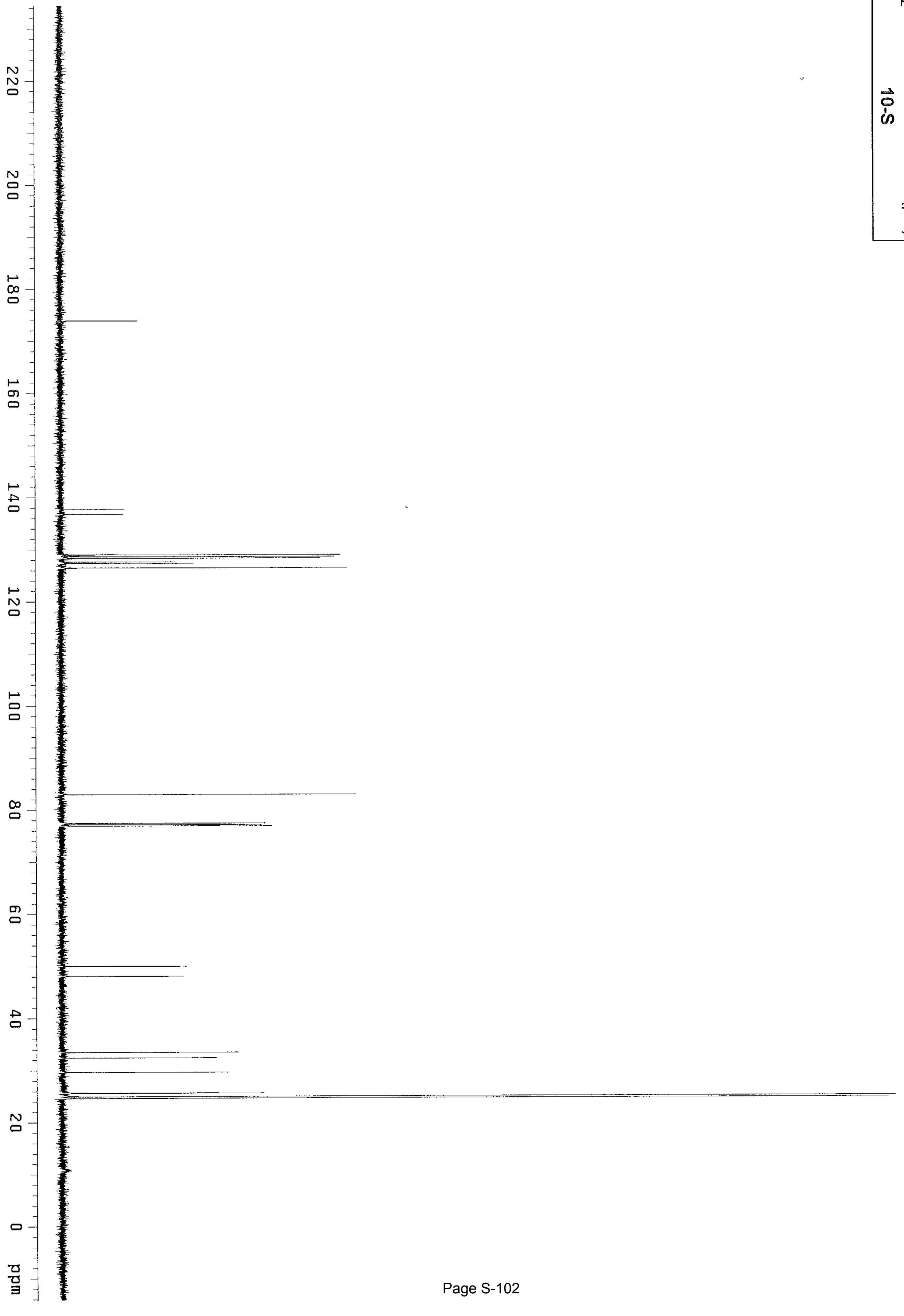


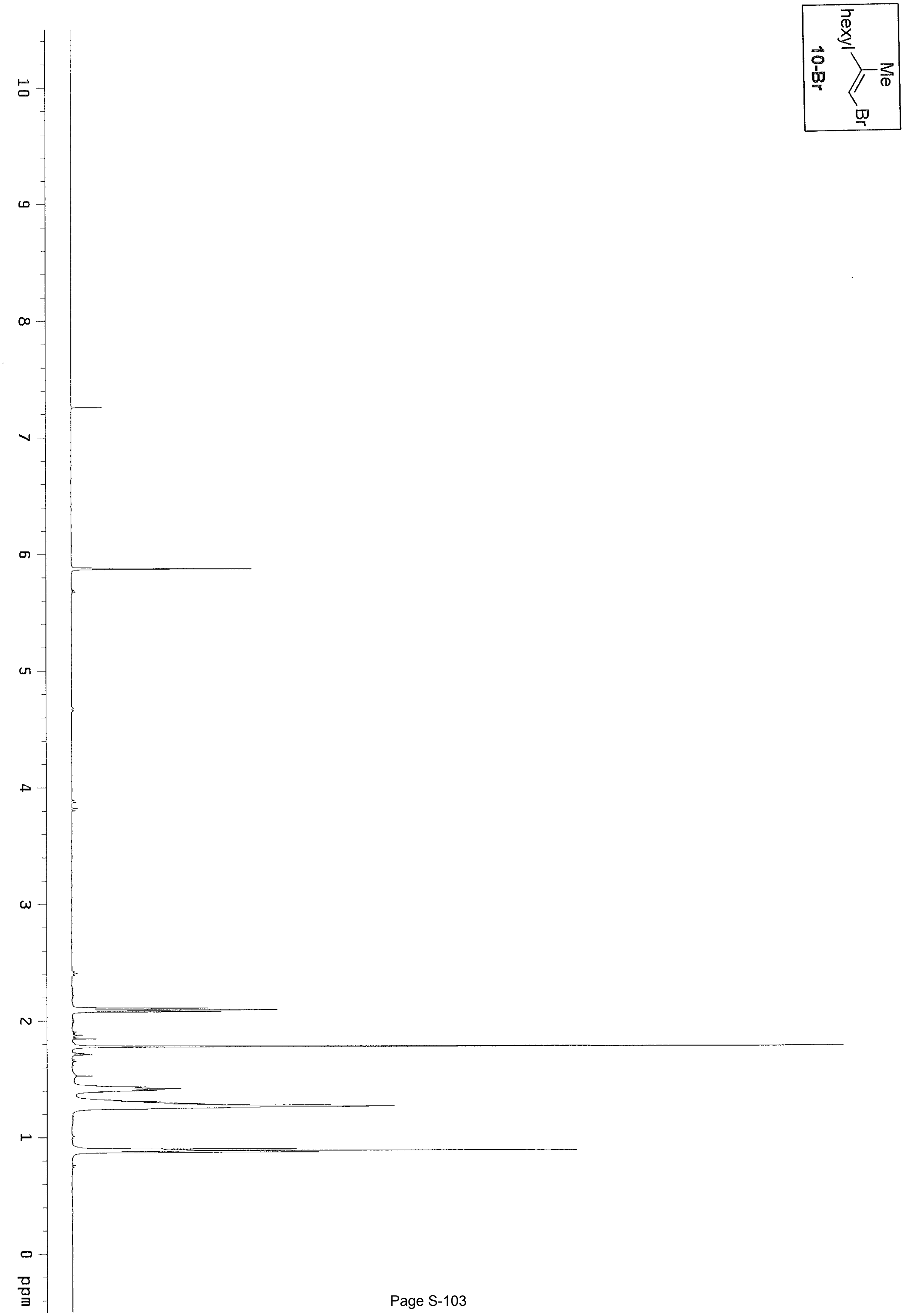
9-S


10-S

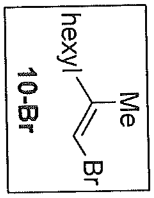


10-S

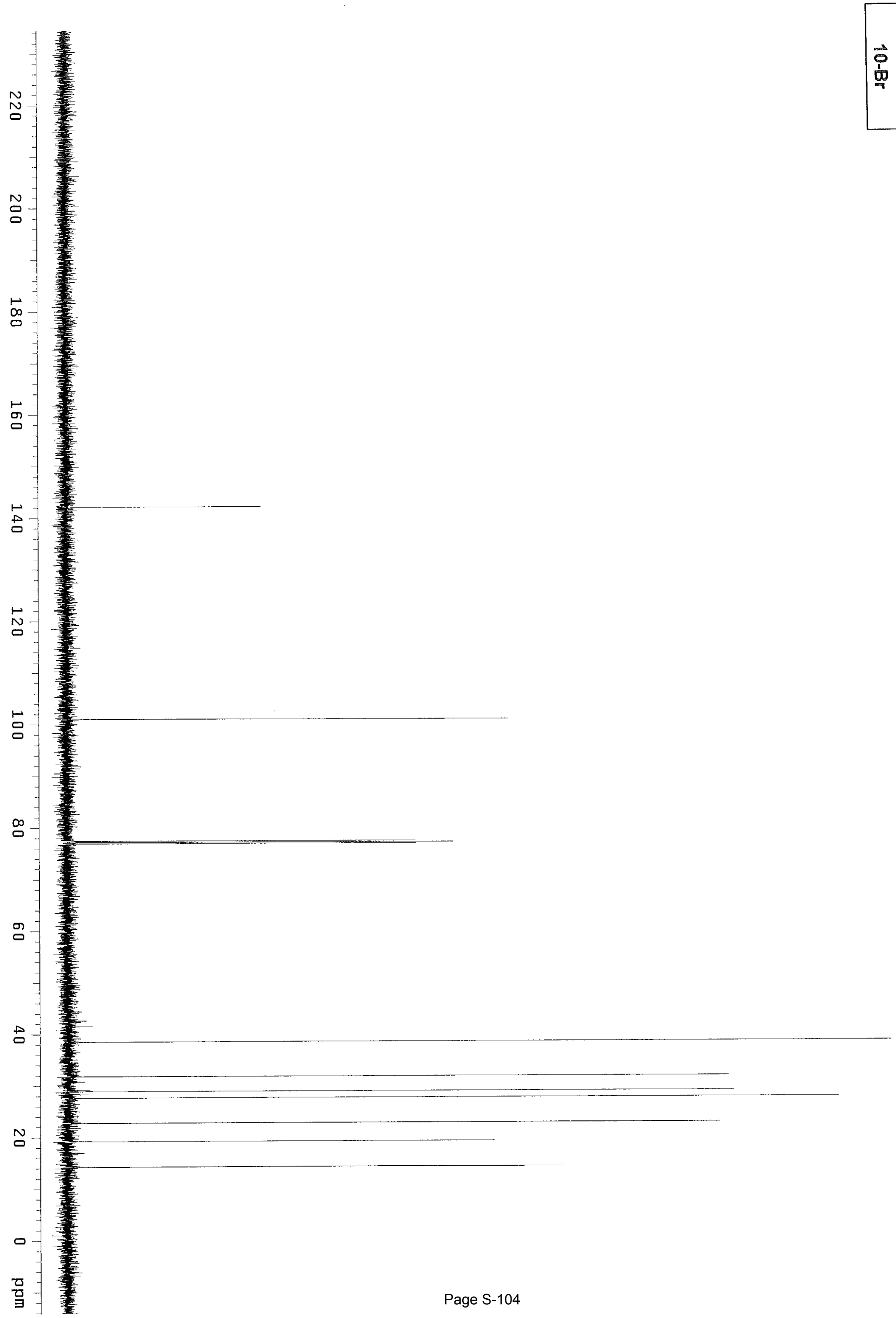


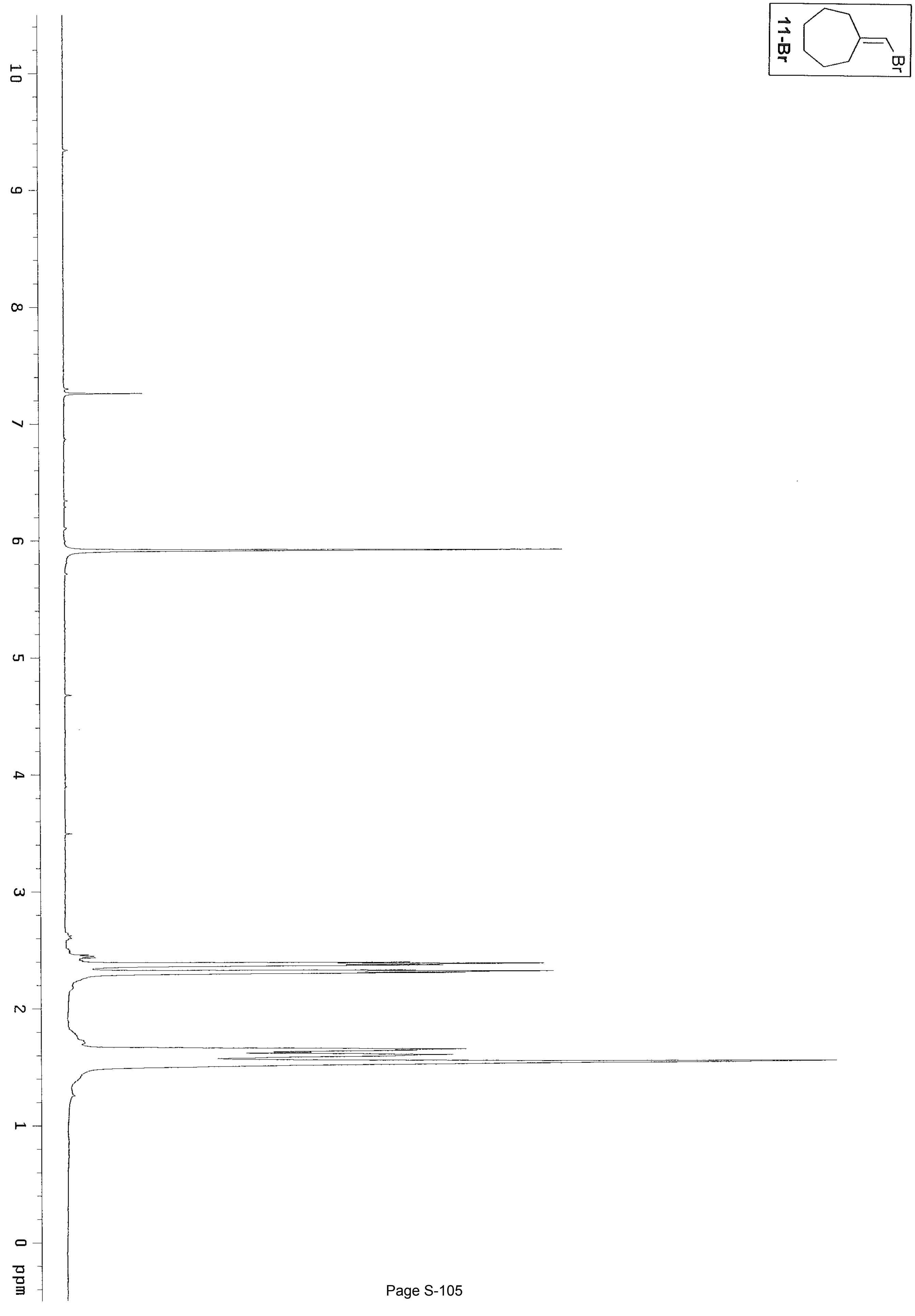


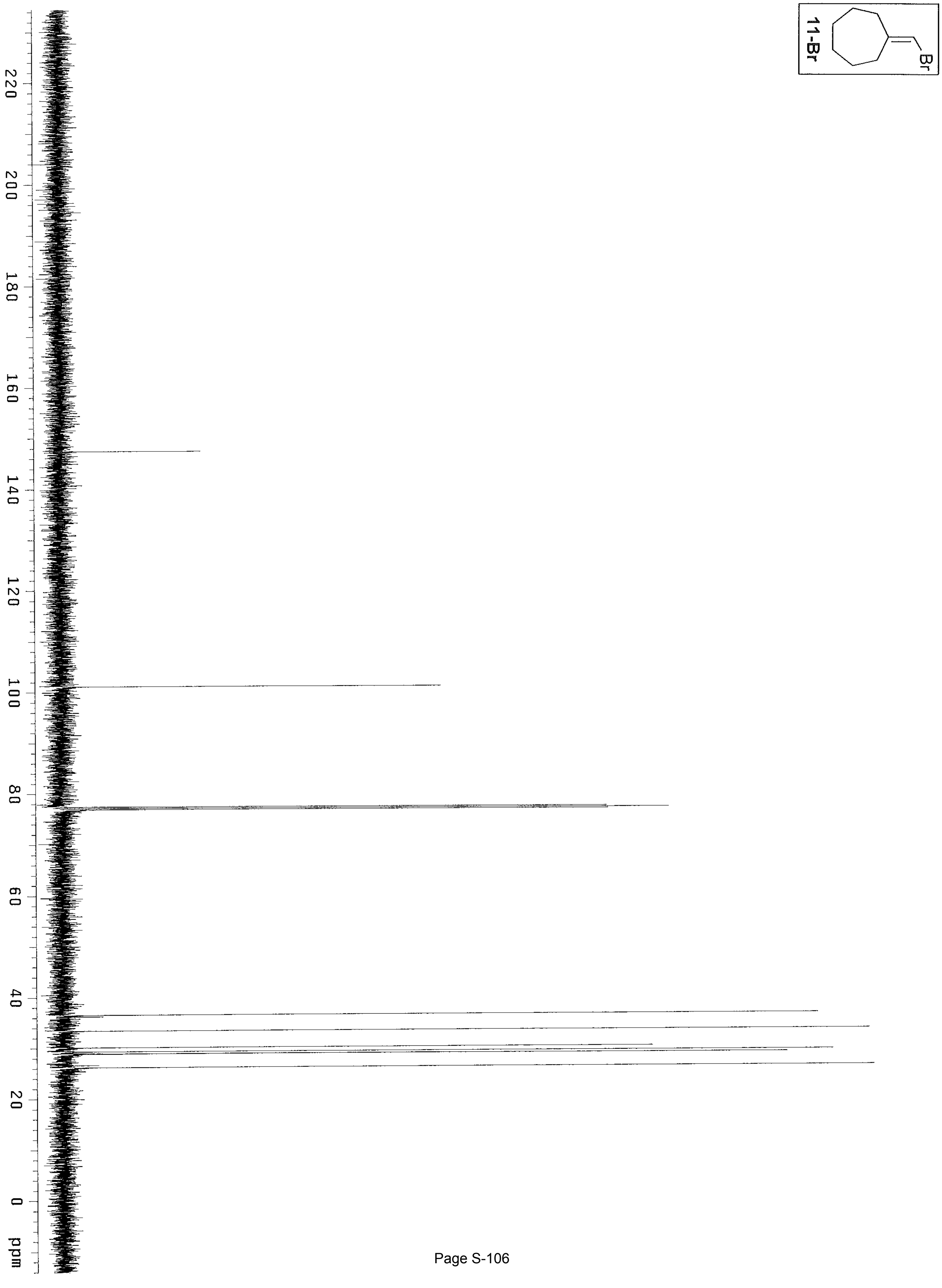
10-Br



10-Br




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


11-Br
Br
220
200
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120
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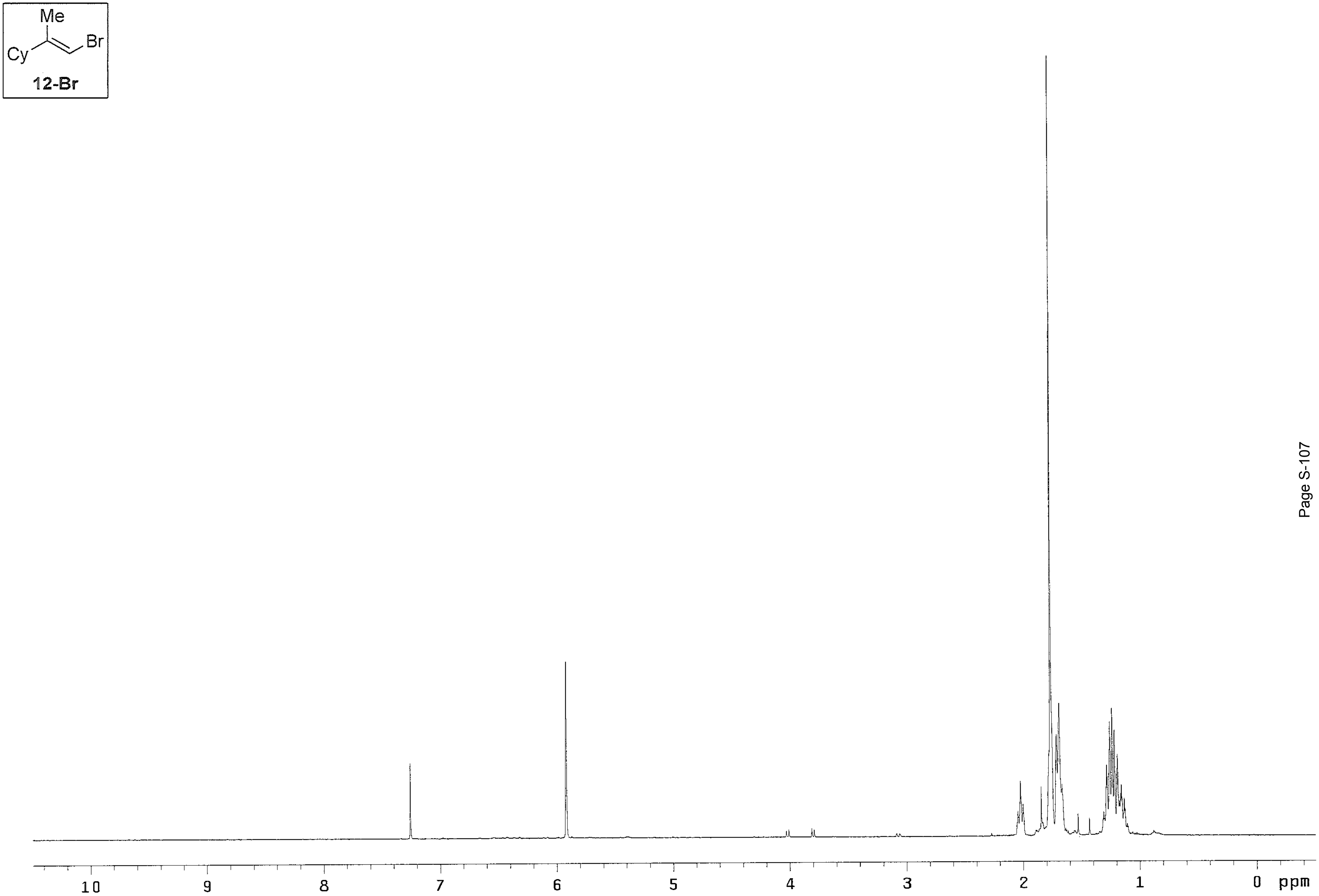
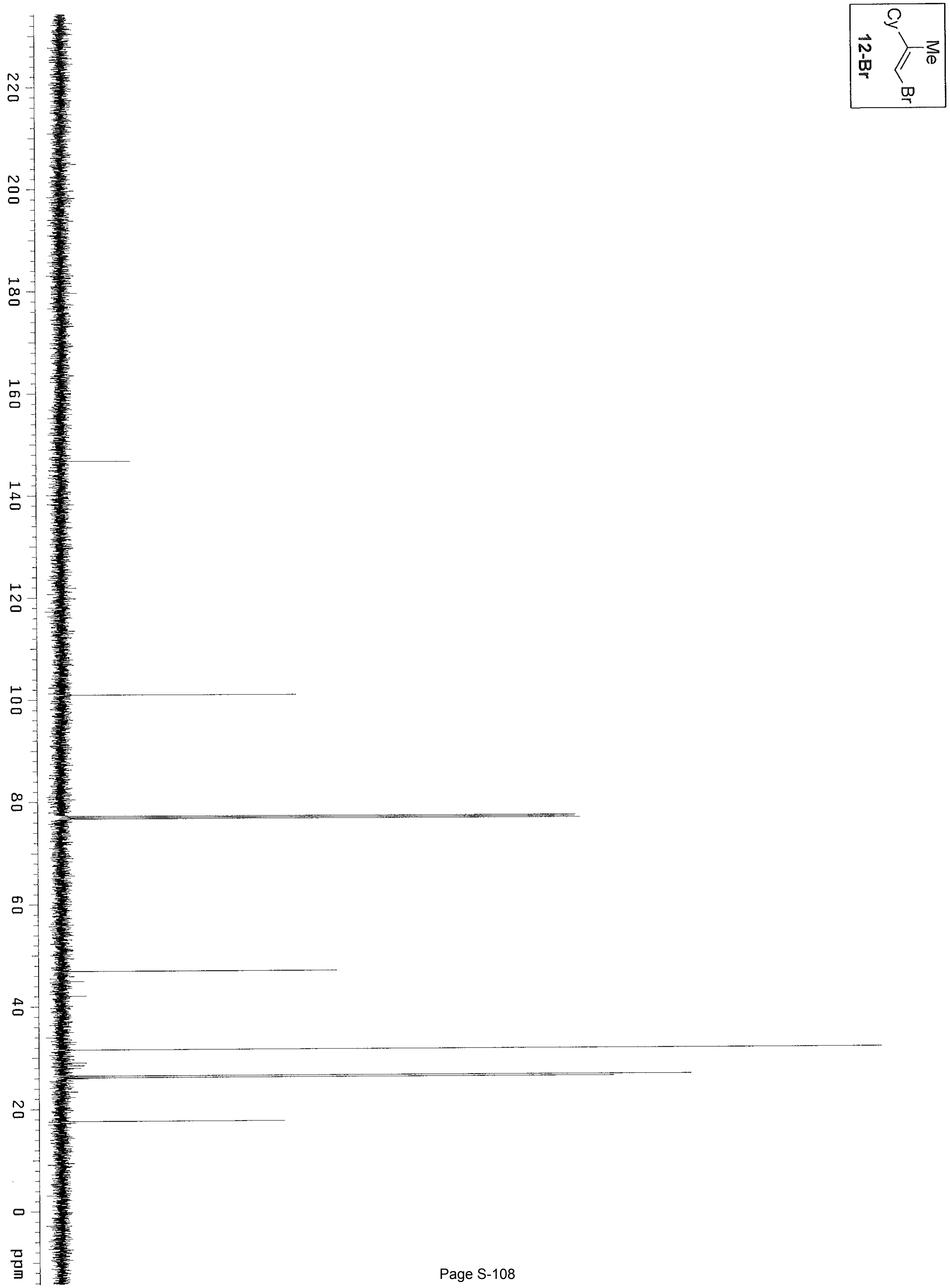
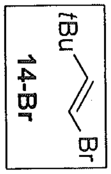
60
40
20
0
ppm



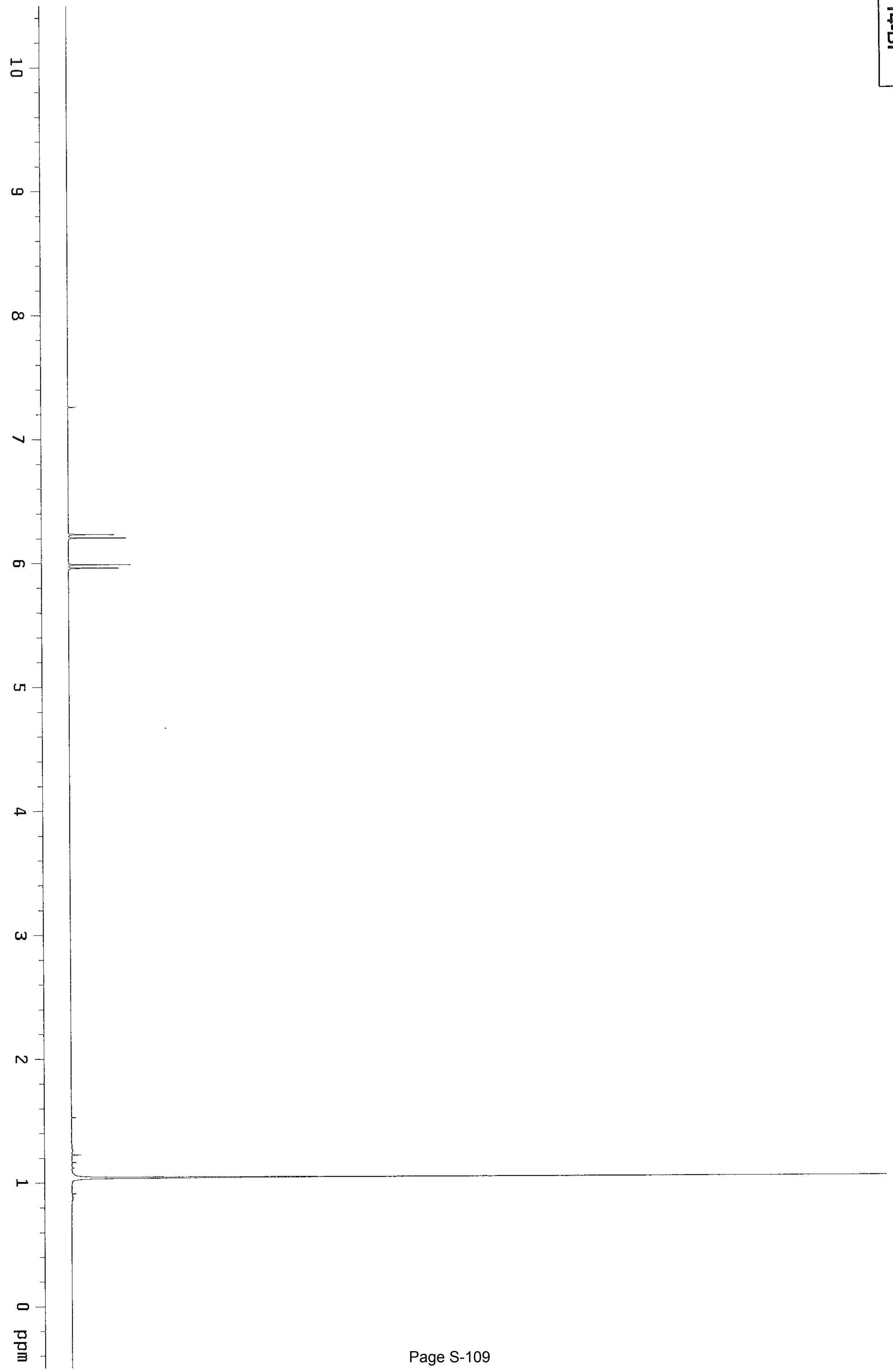
12-Br

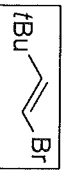


12-Br

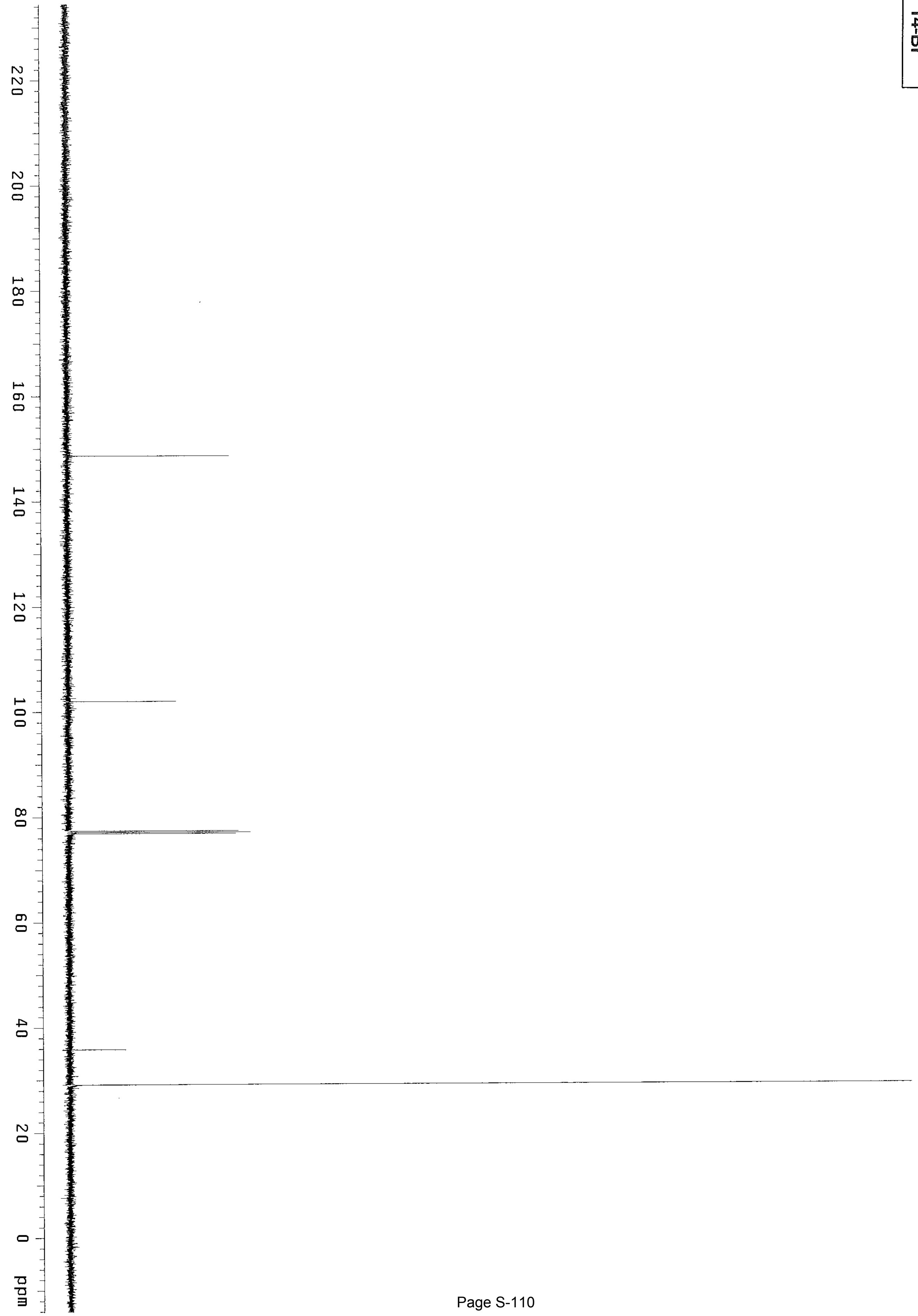


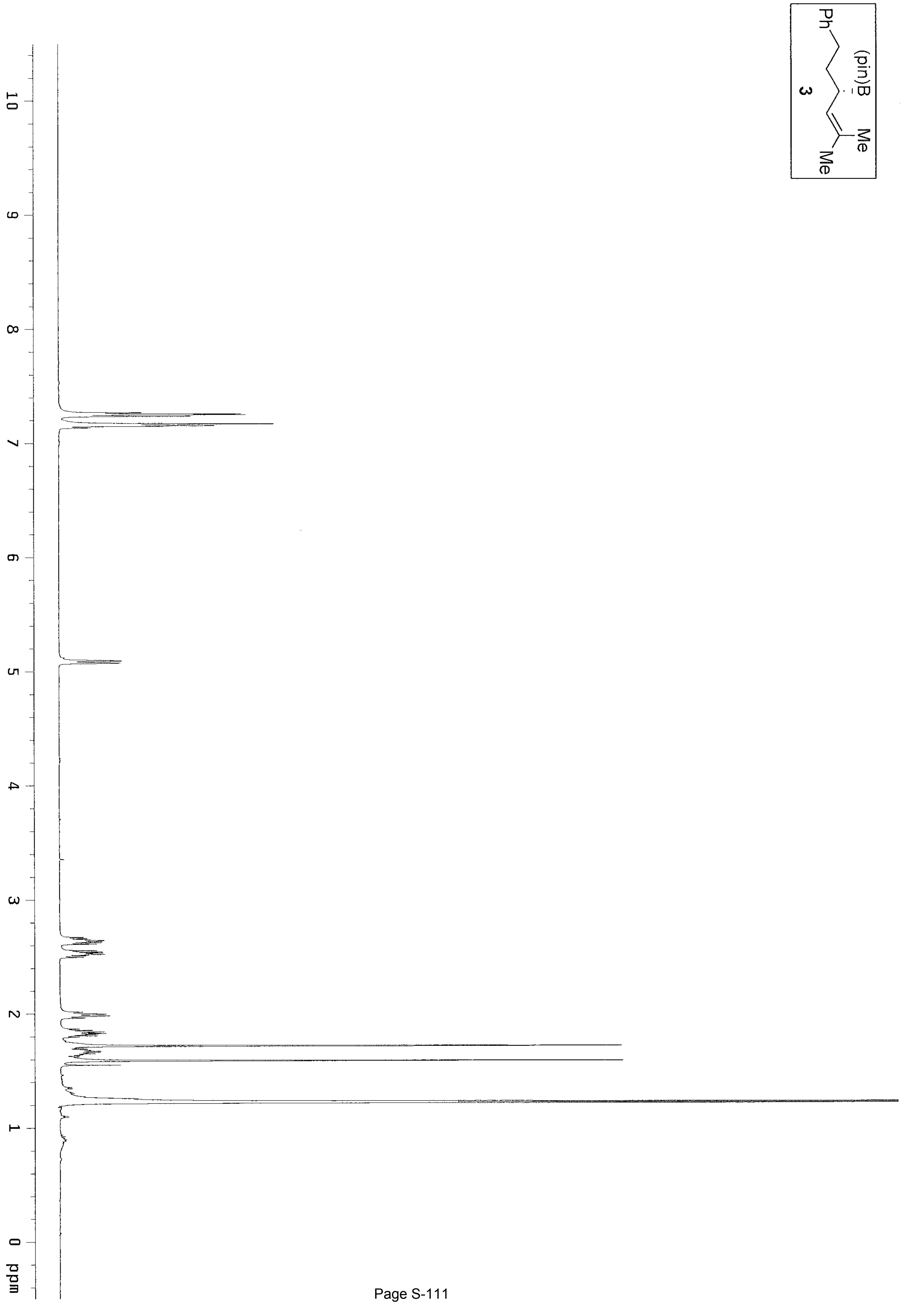
14-Br





14-Br





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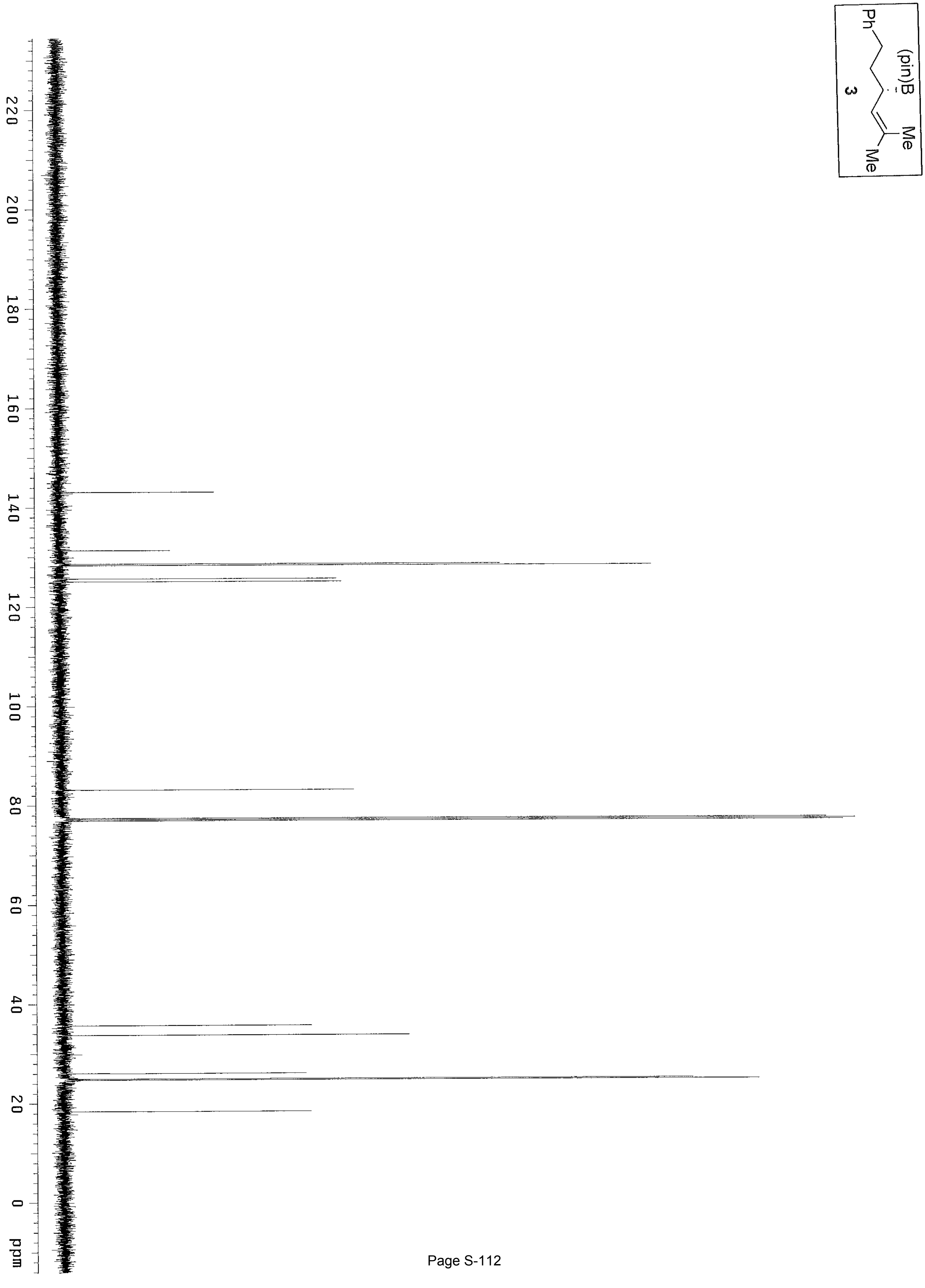
(pin)B
Me
Me
Ph
3
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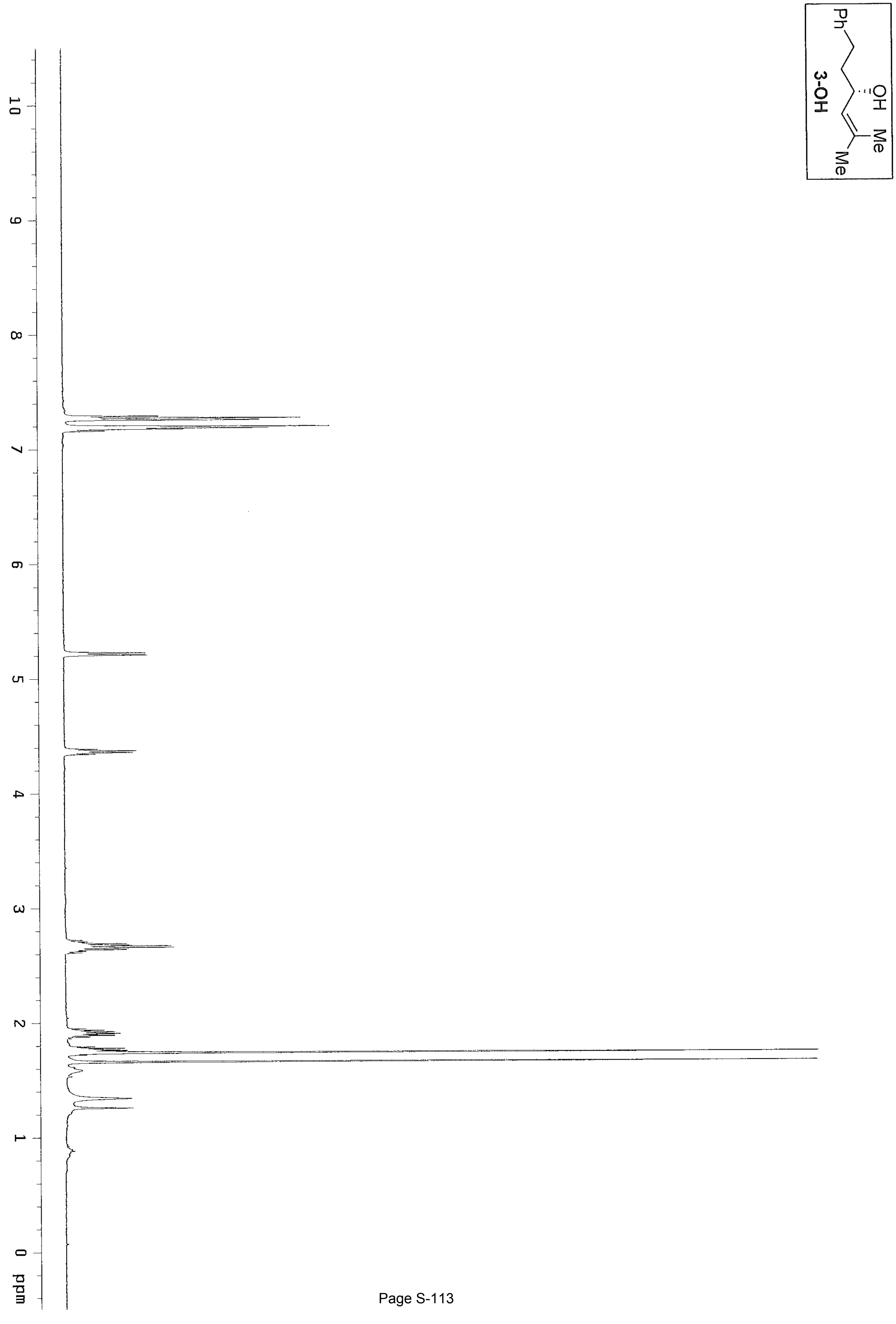
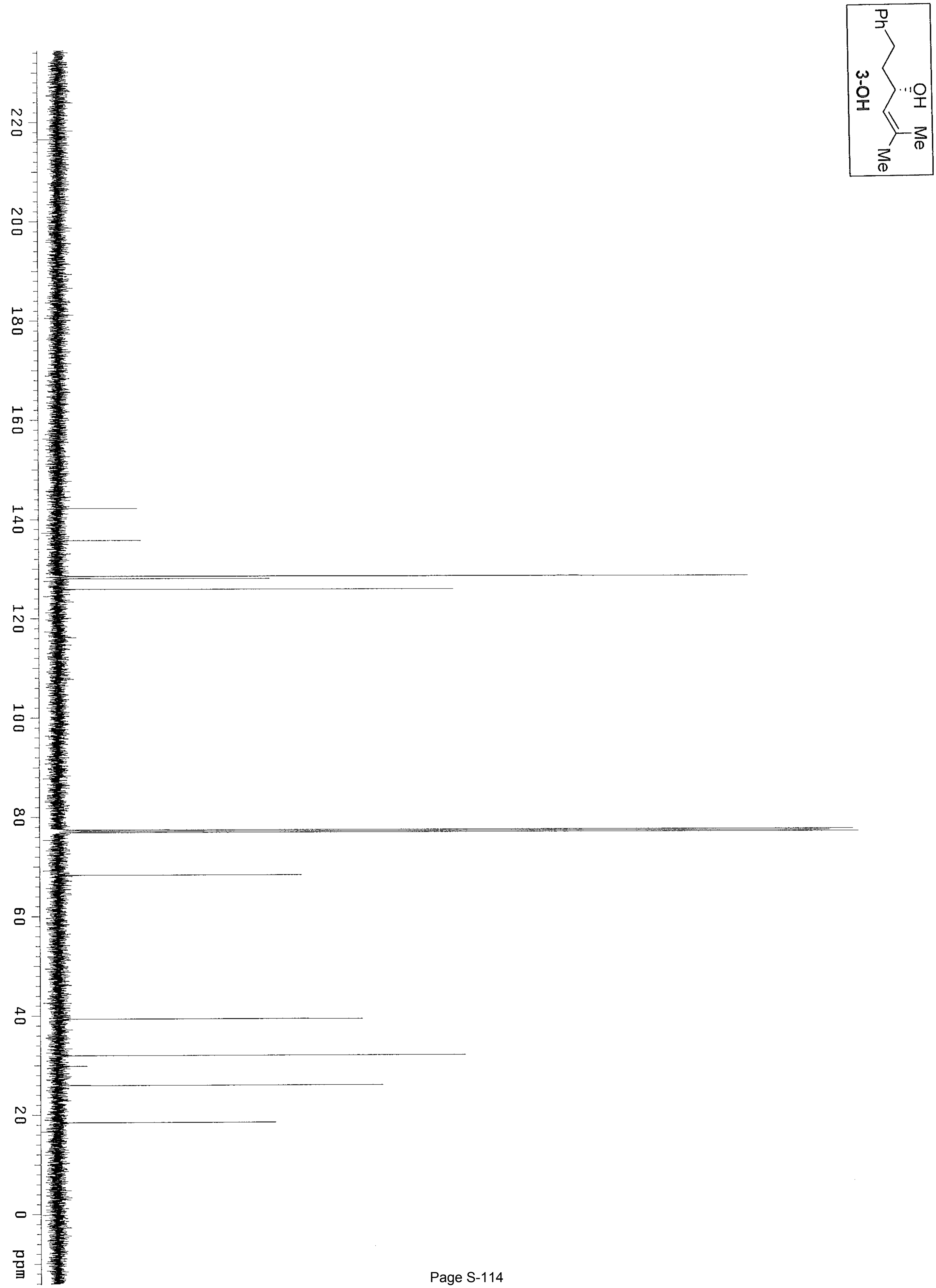
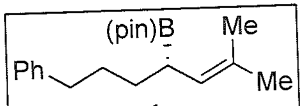
200
180
160
140
120
100
80
60
40
20
0
ppm



3-OH



3-OH



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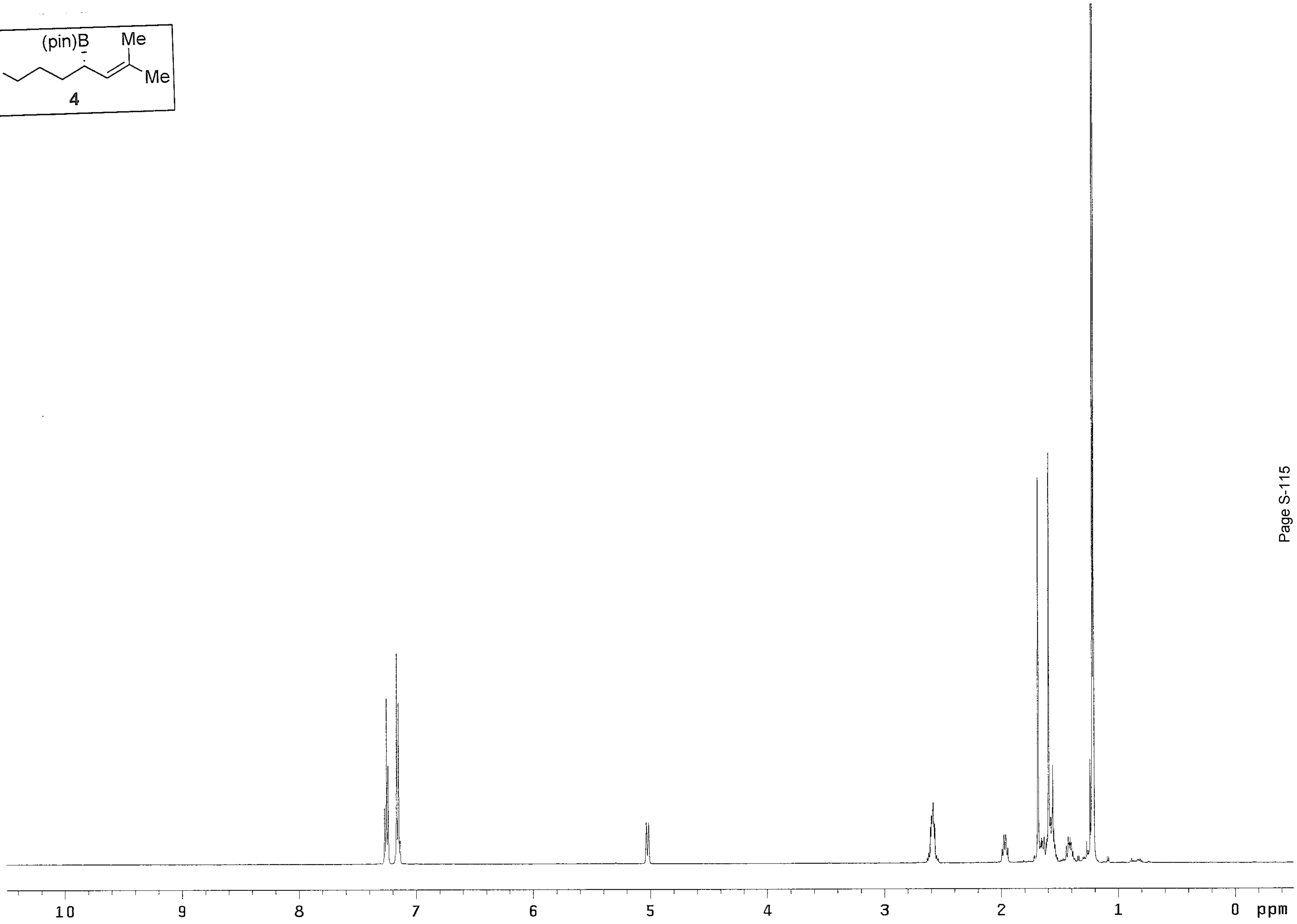

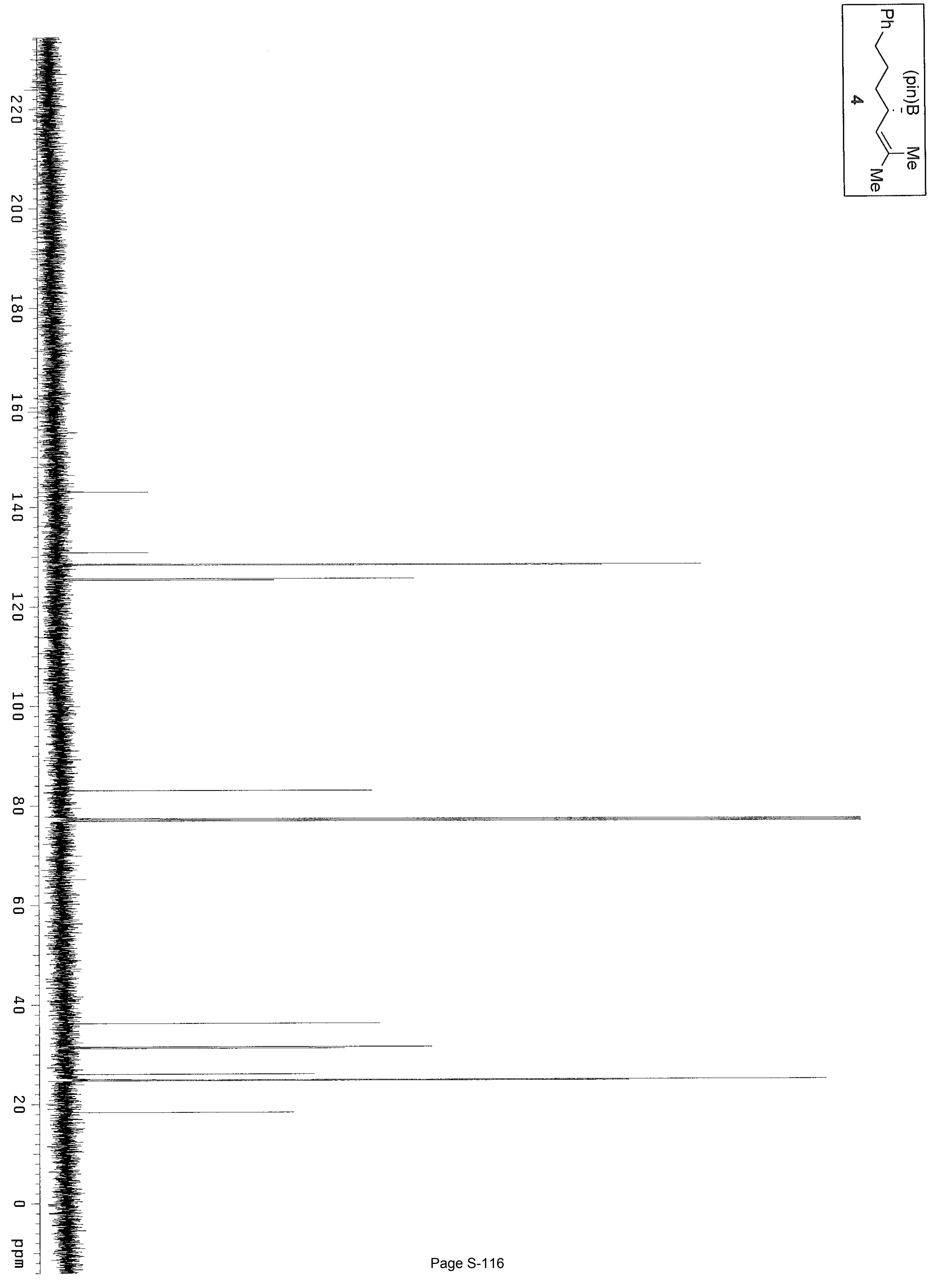
Ph
(pin)B
Me
Me
4
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200
180
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100
80
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40
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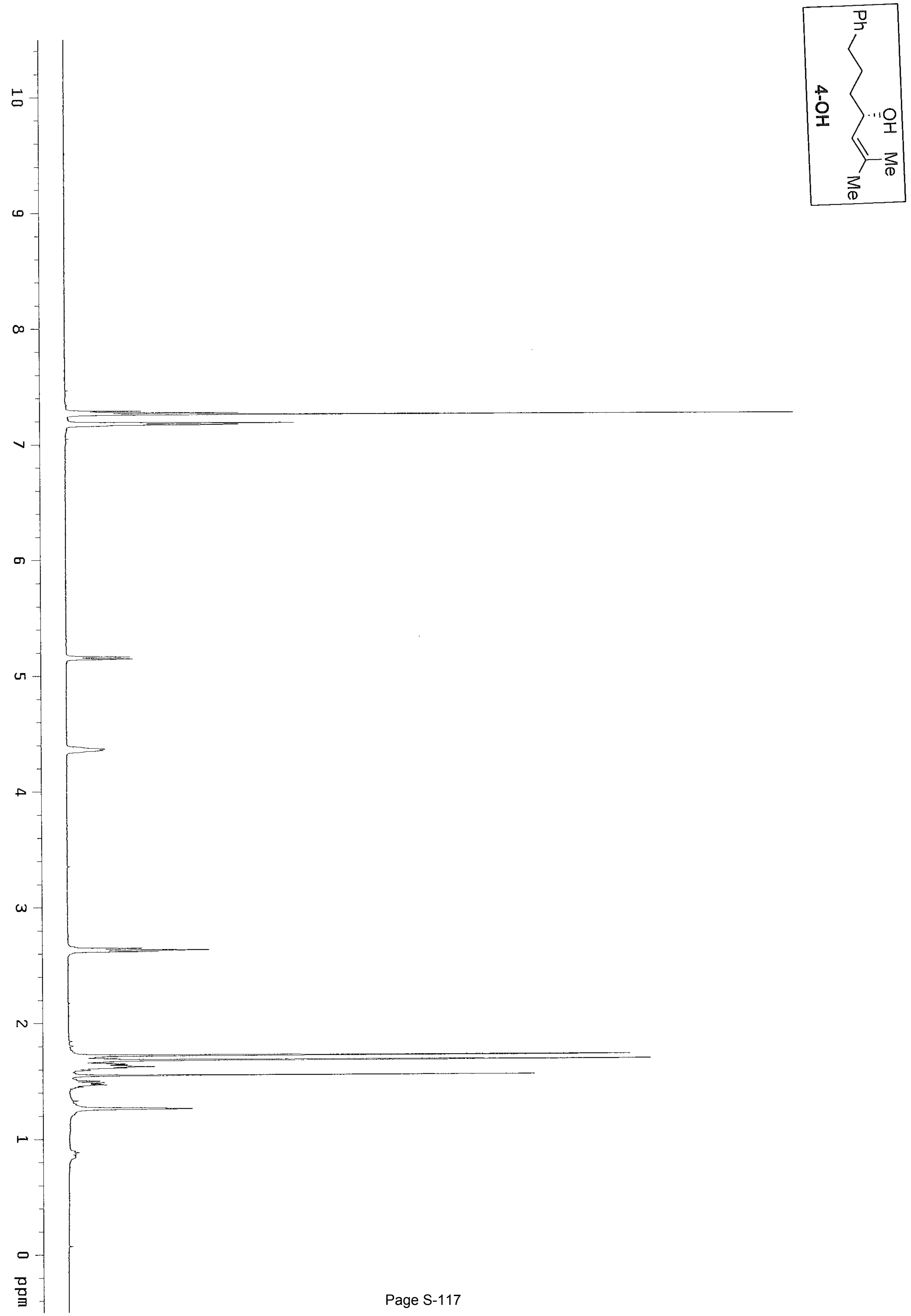
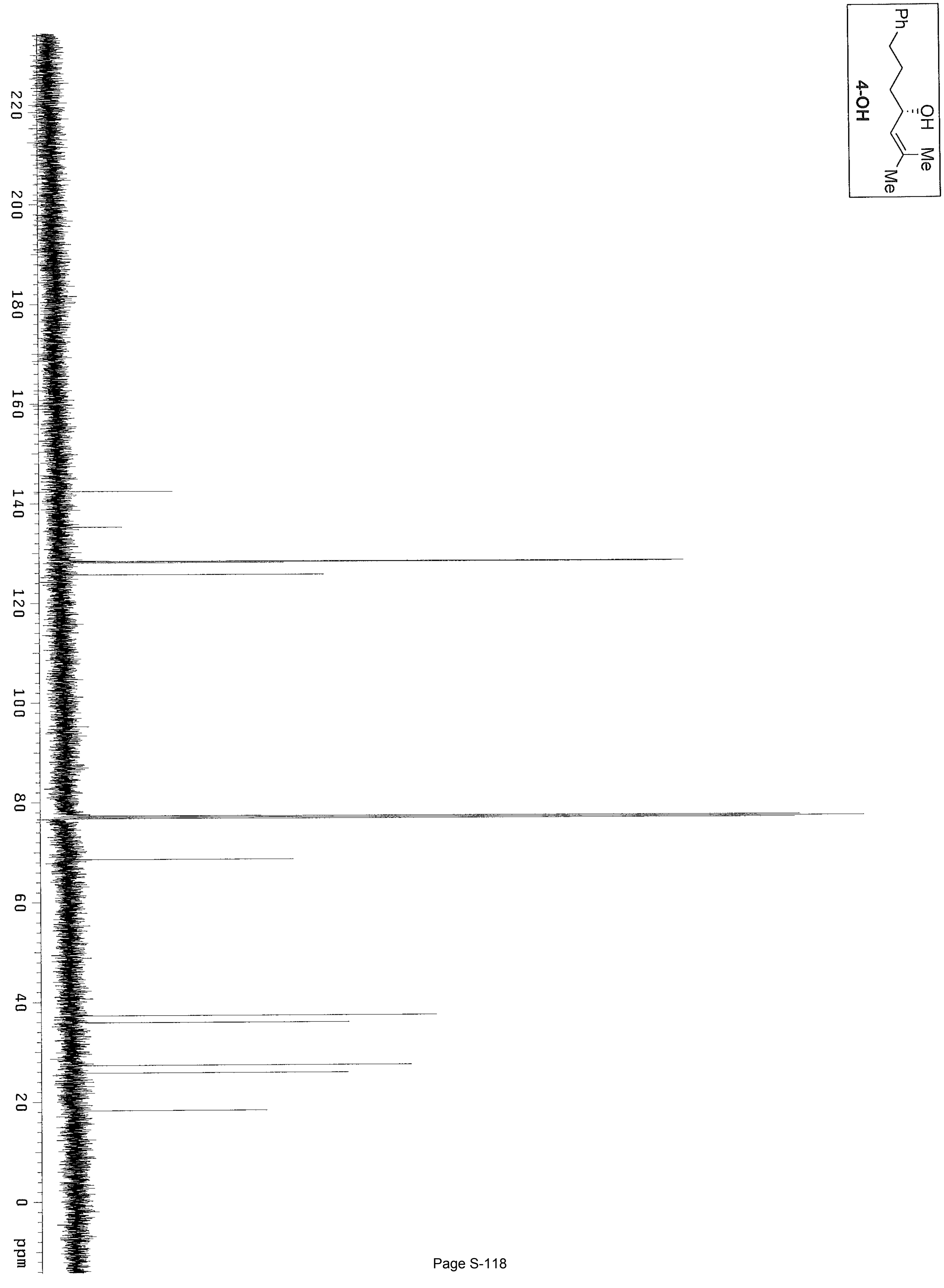
0
ppm



4-OH


Ph
OH
Me
Me
4-OH
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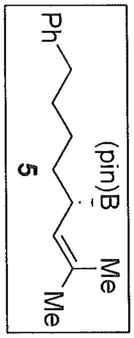
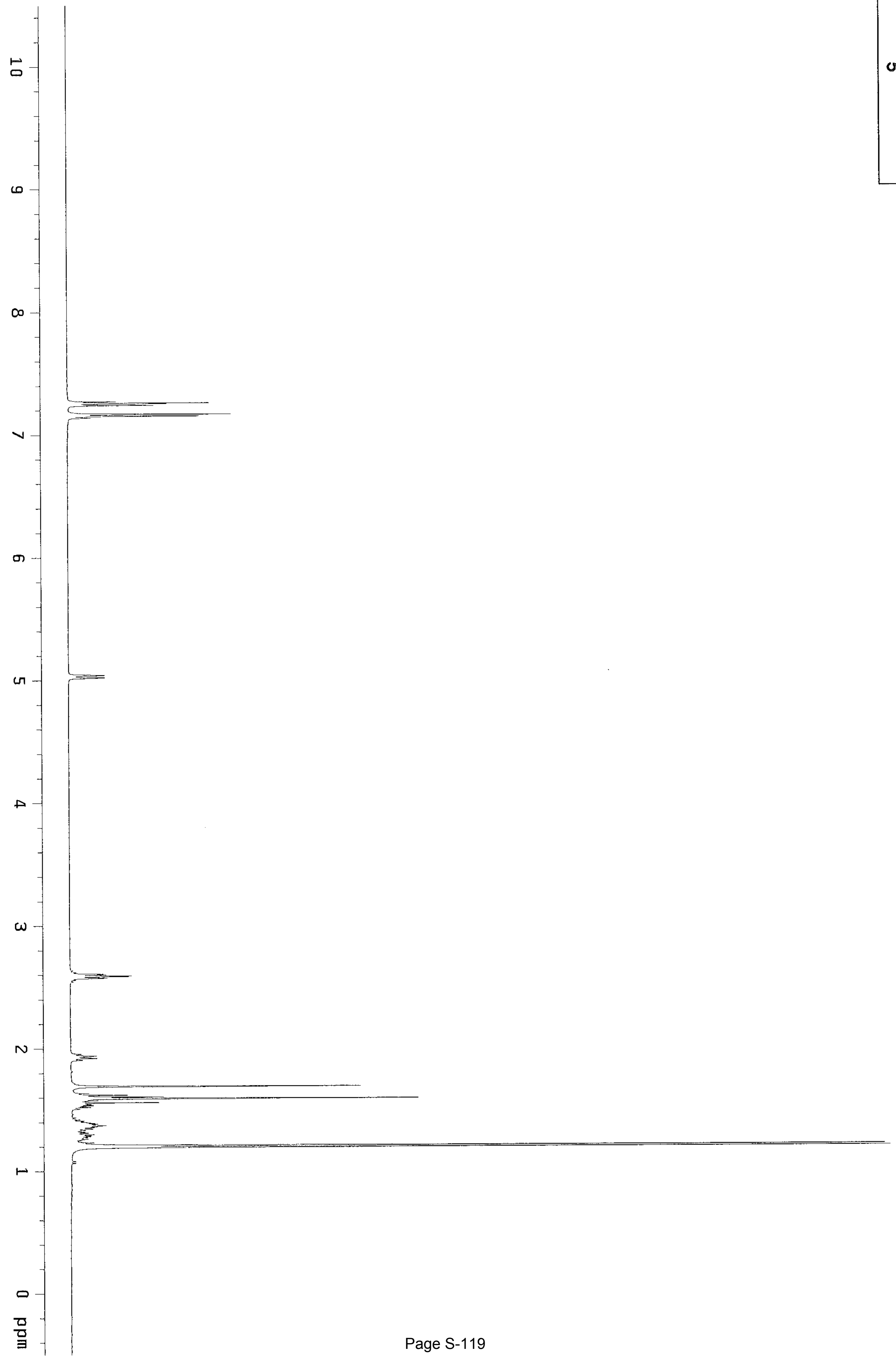
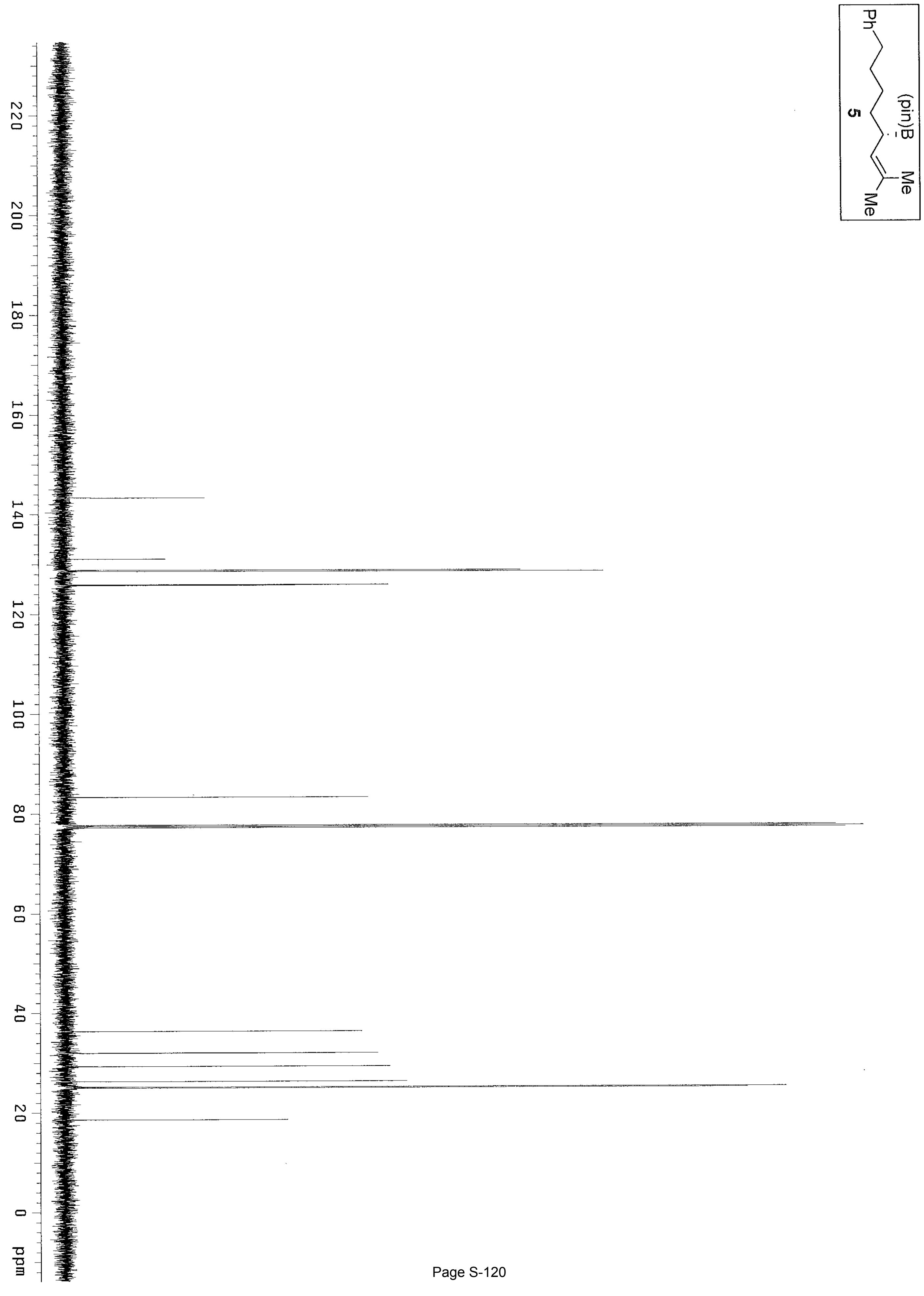
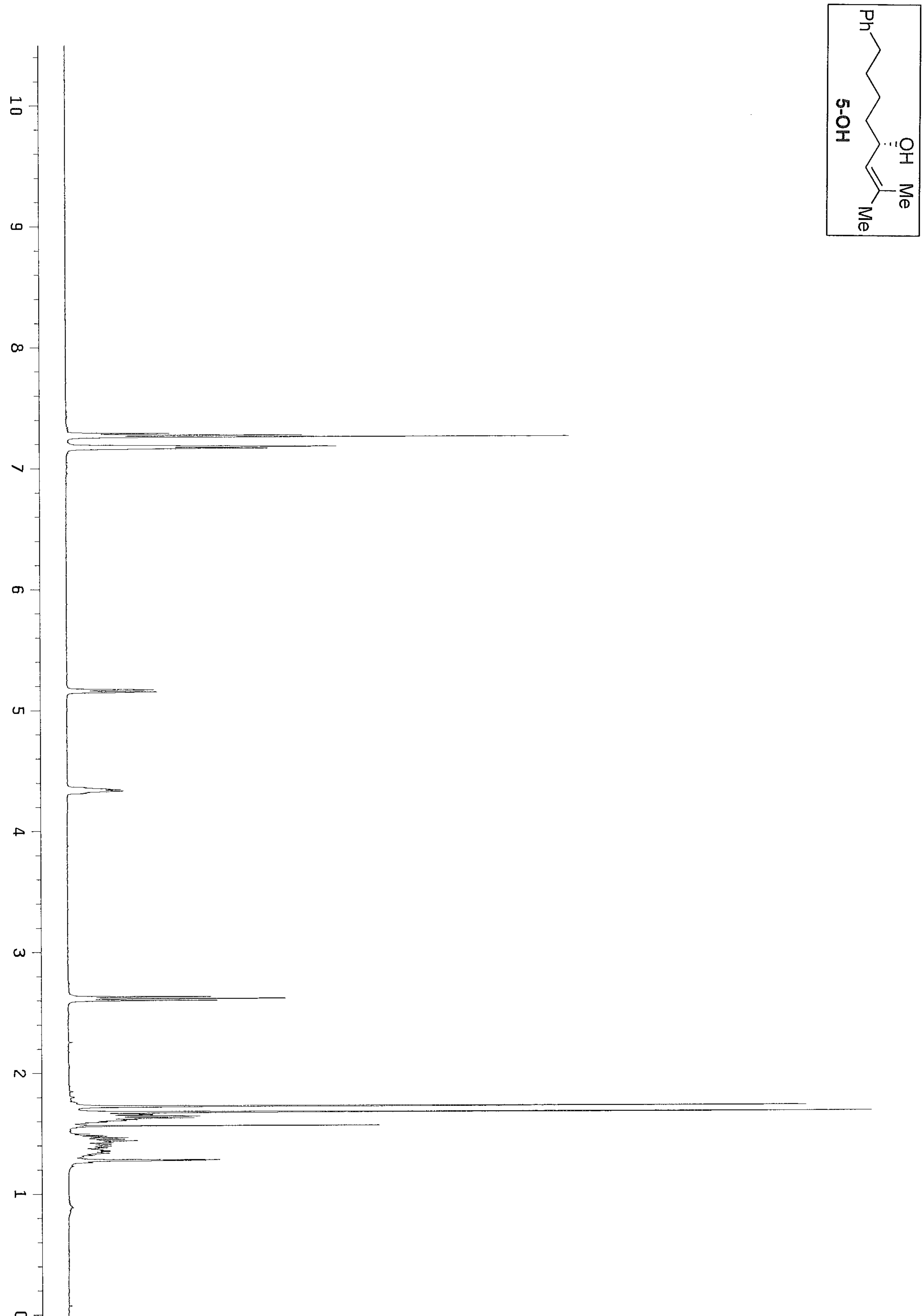
160
140
120
100
80
60
40
20
0
ppm



5




(pin)B
Me
Me
Ph
5
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Ph
OH
Me
Me
5-OH
10
9
8
7
6
5
4
3
2
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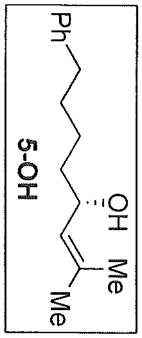
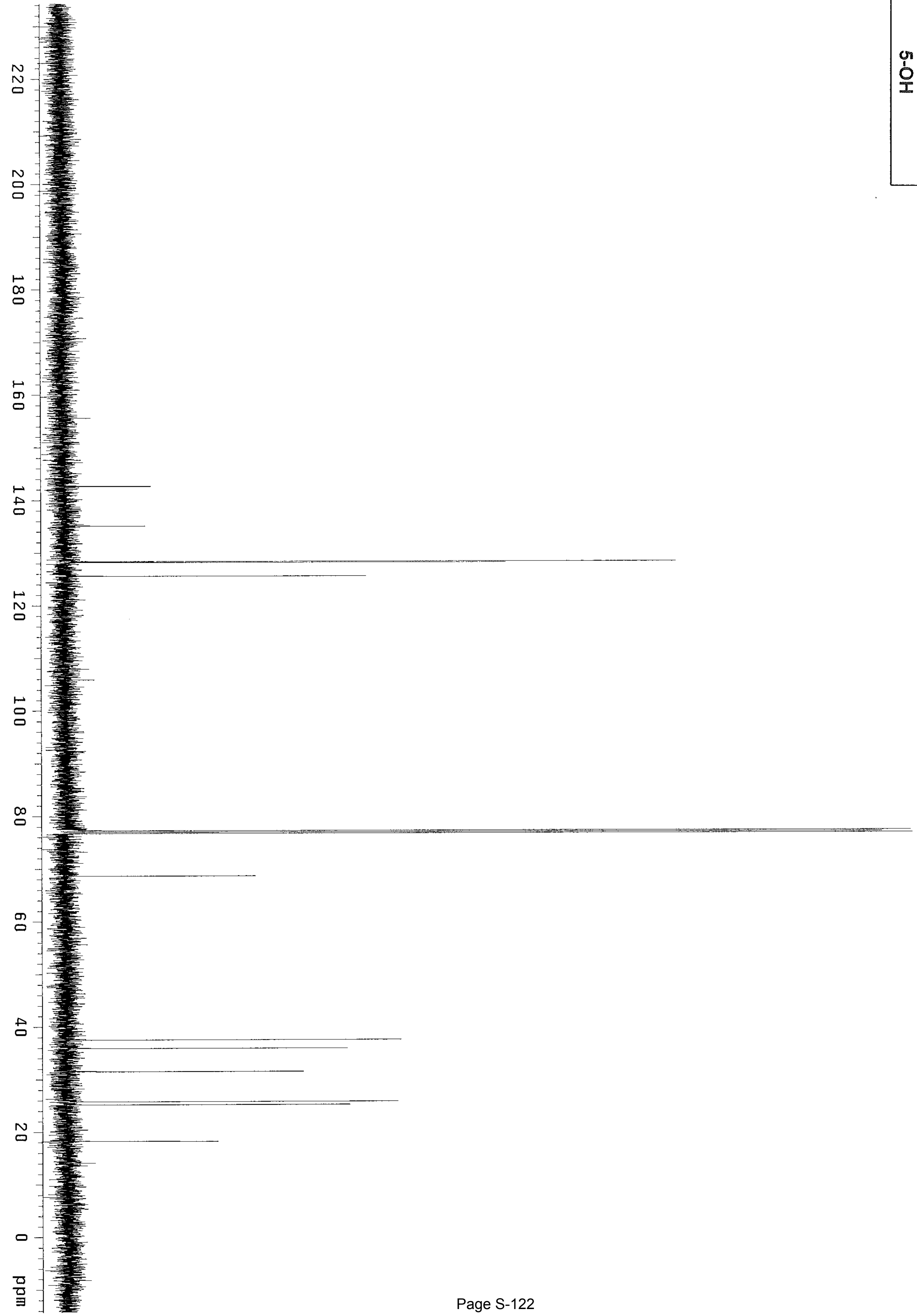
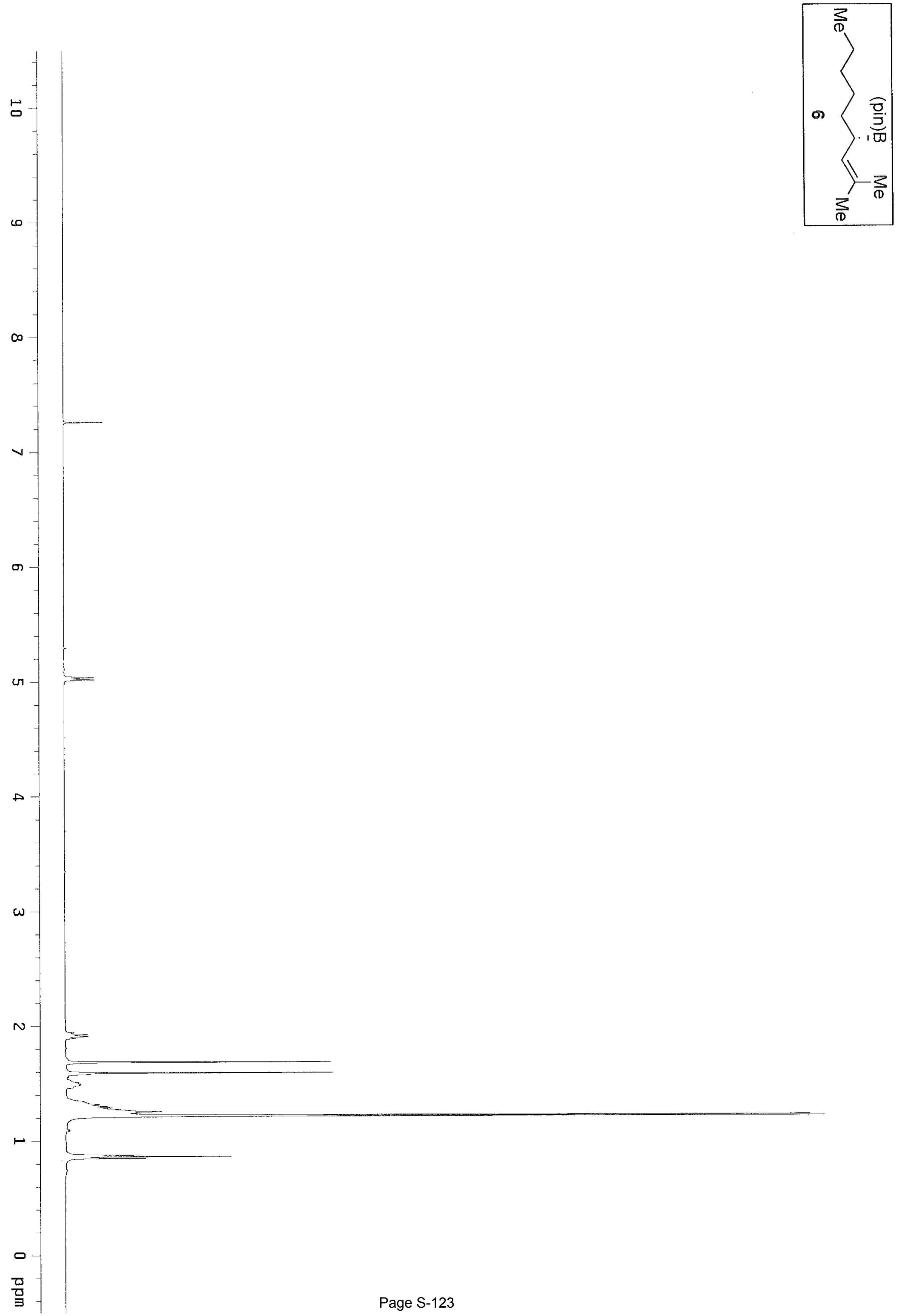
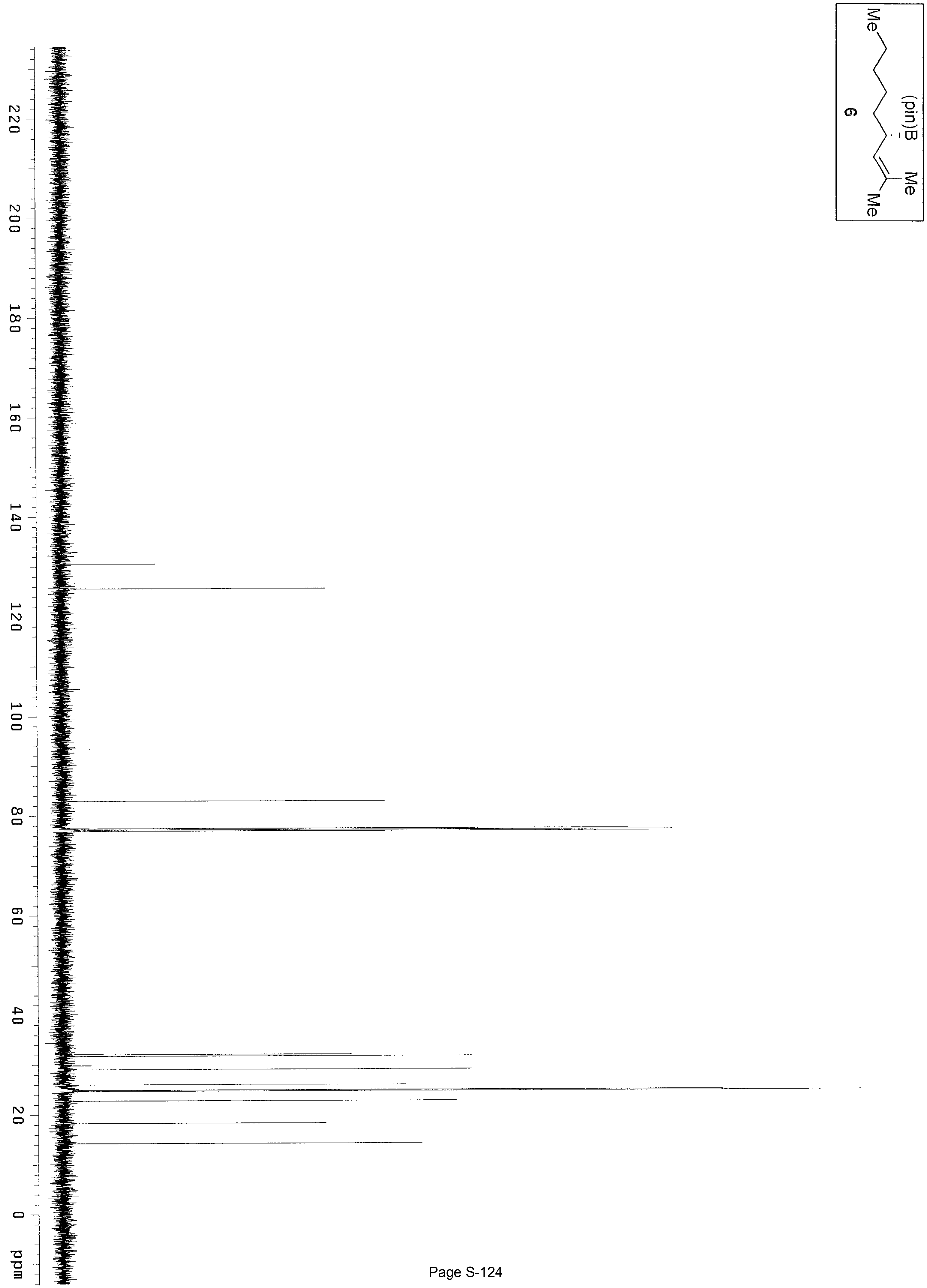
0
ppm

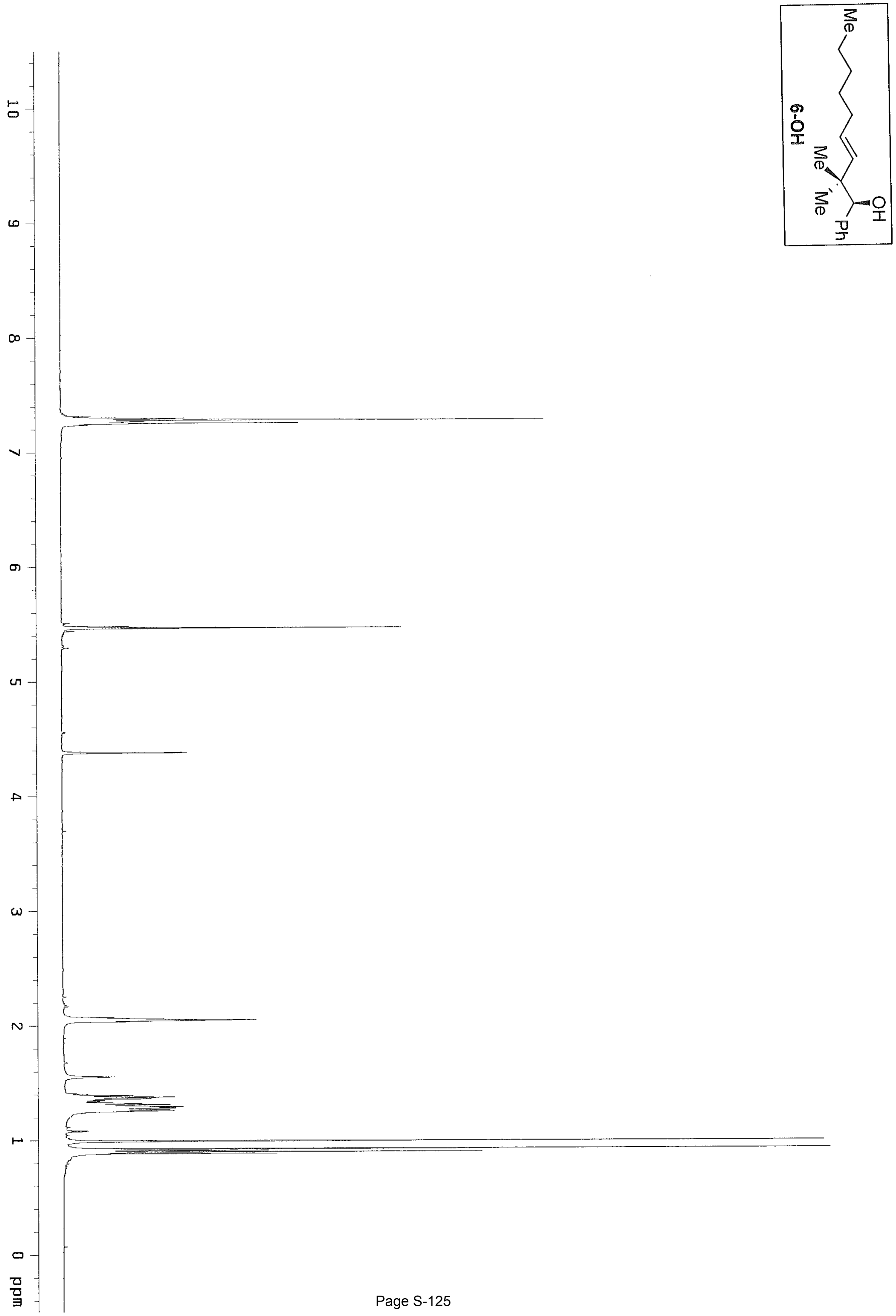

5-OH



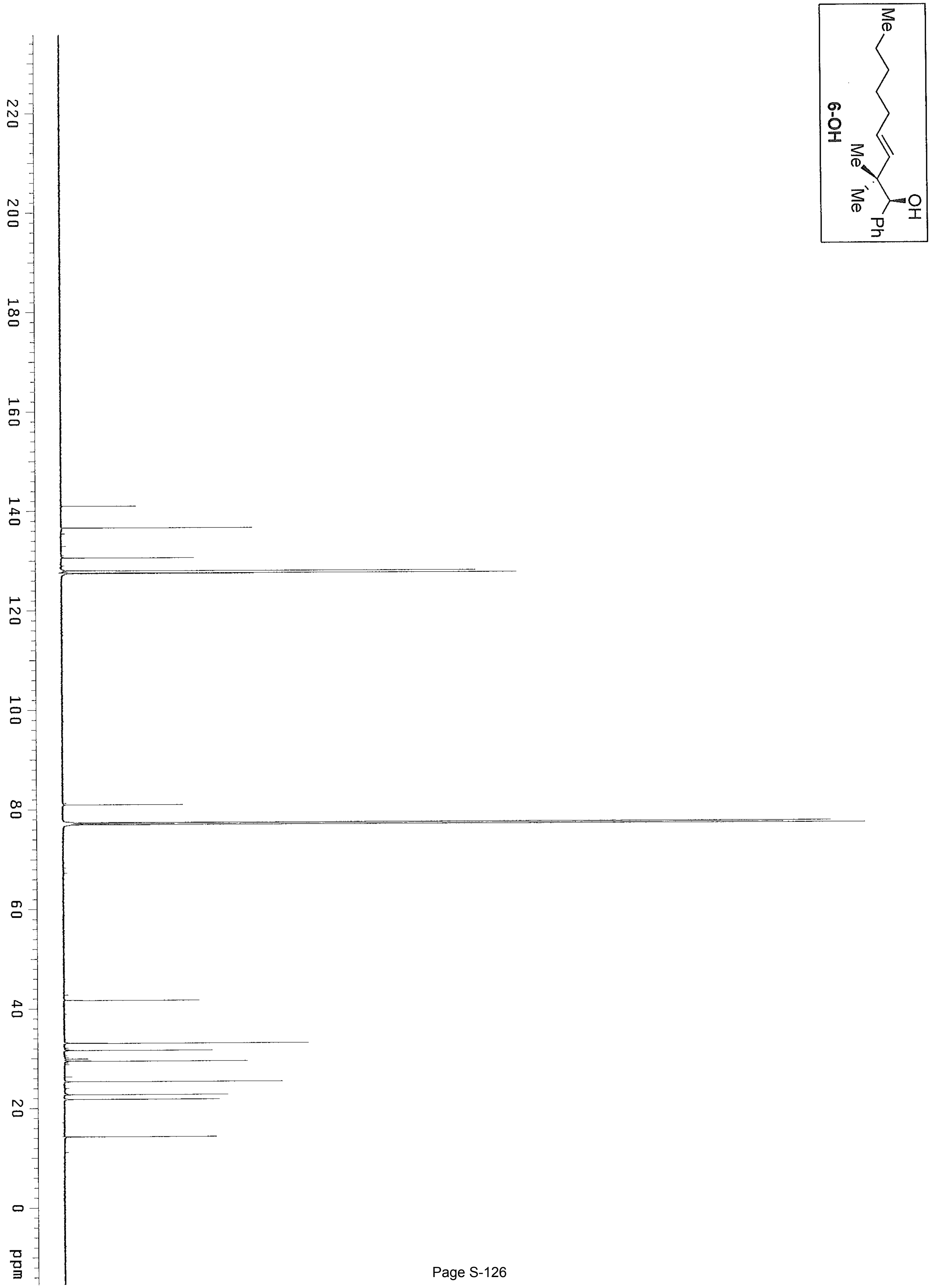

(pin)B
Me
Me
Me
6
10
9
8
7
6
5
4
3
2
1
0
ppm



Me
(pin)B
Me
Me
6
220
200
180
160
140
120
100
80
60
40
20
0
ppm



6-OH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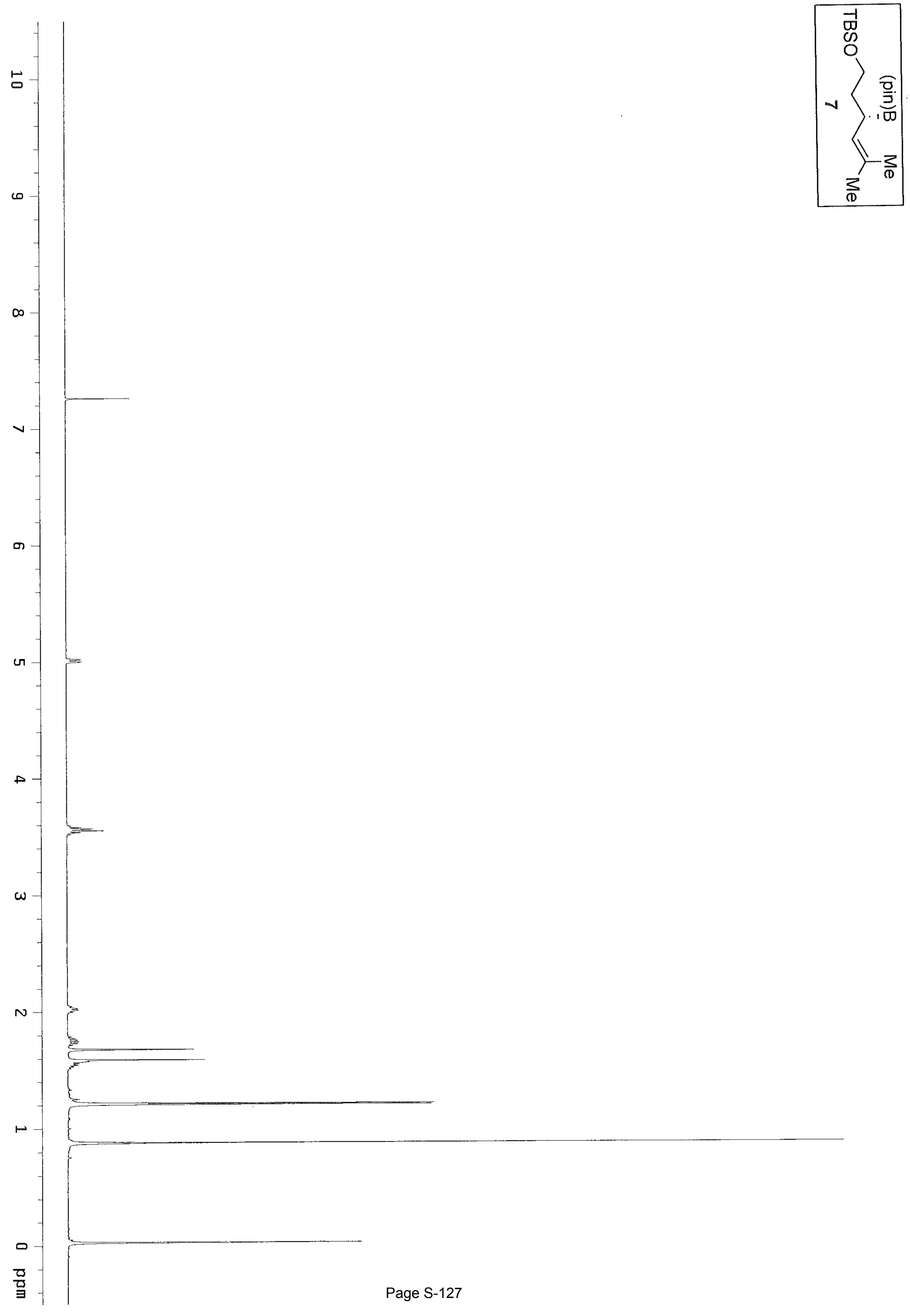
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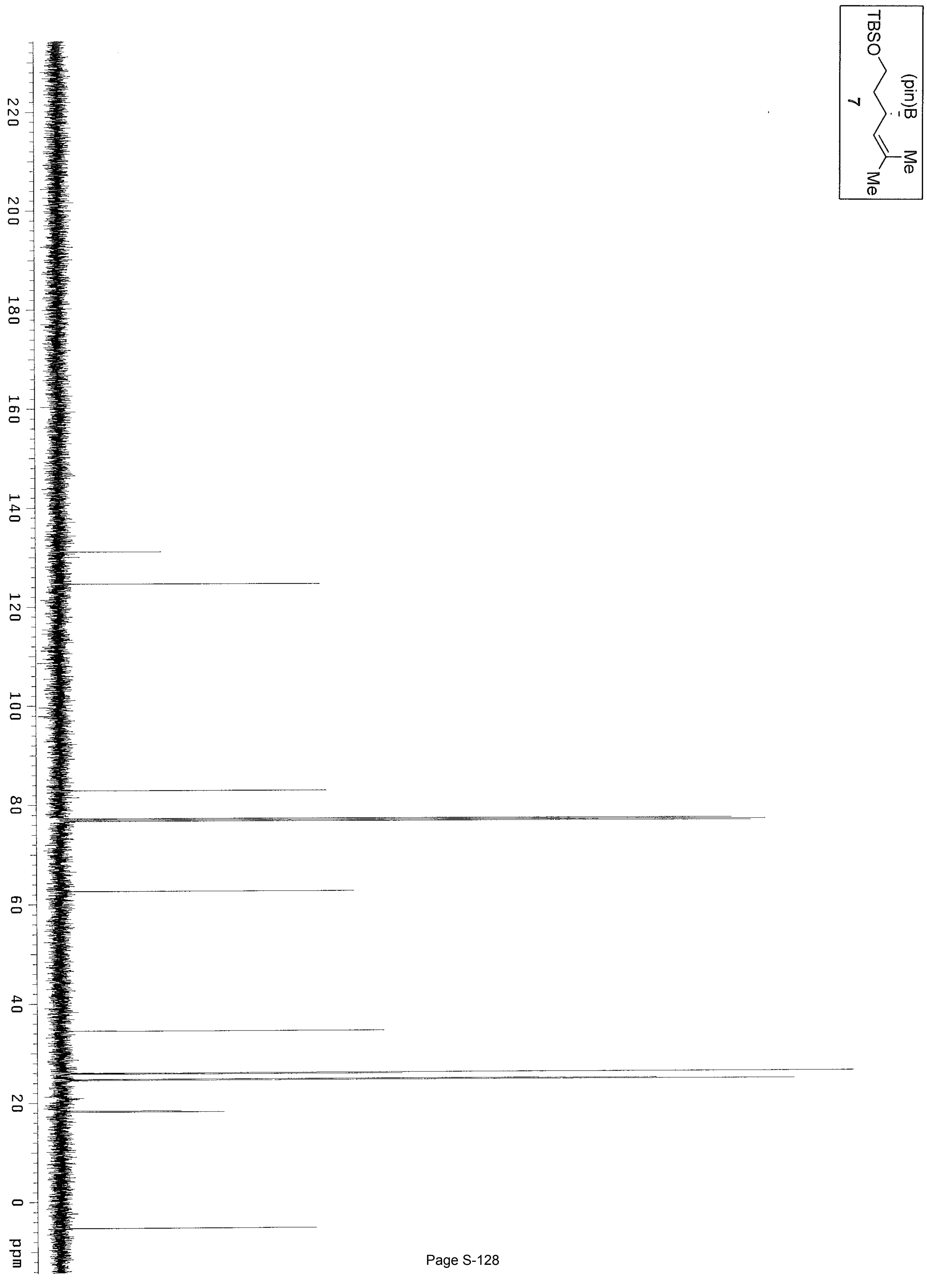
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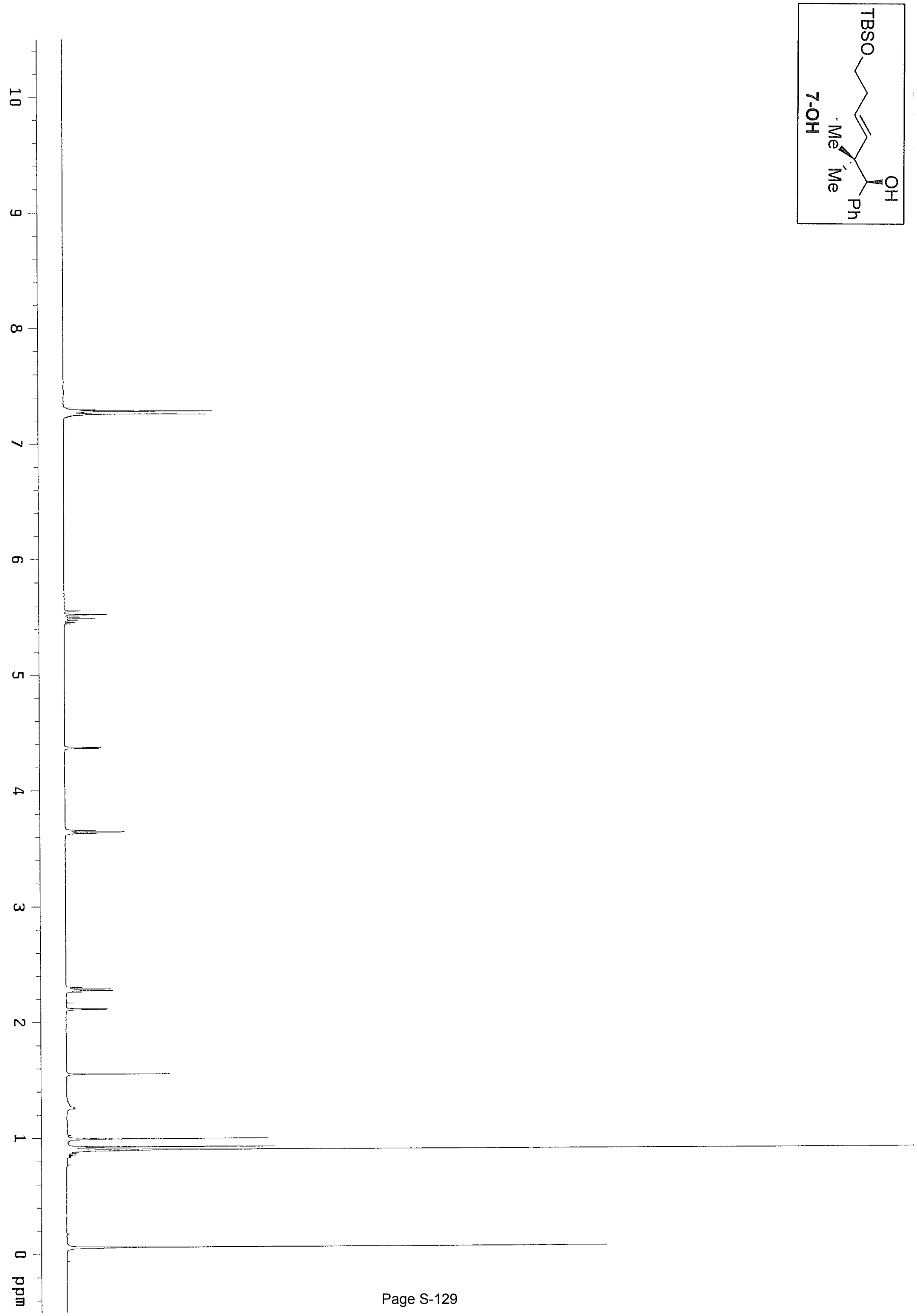
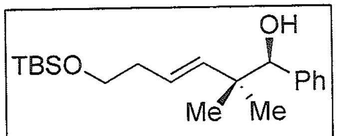


7-OH



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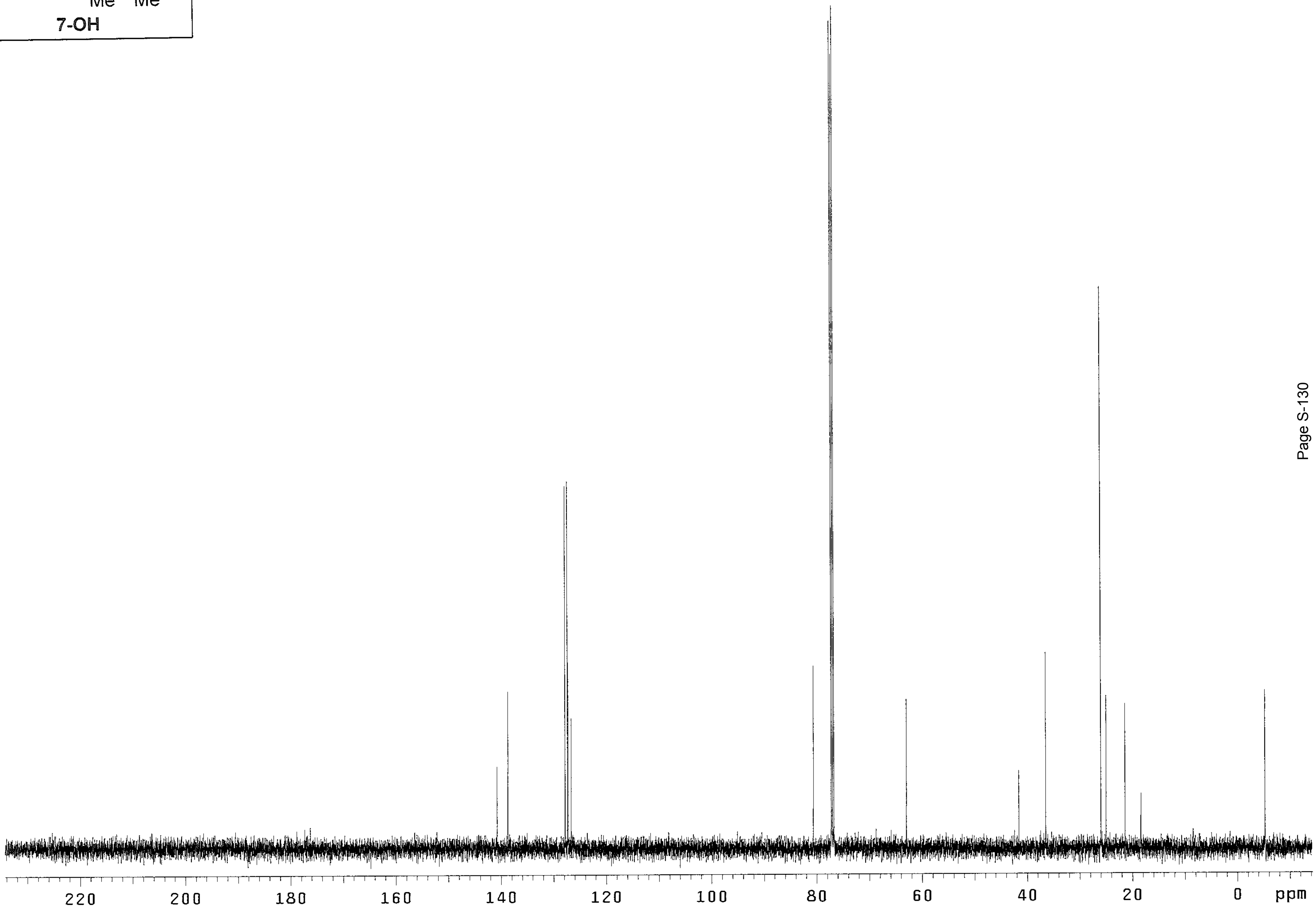

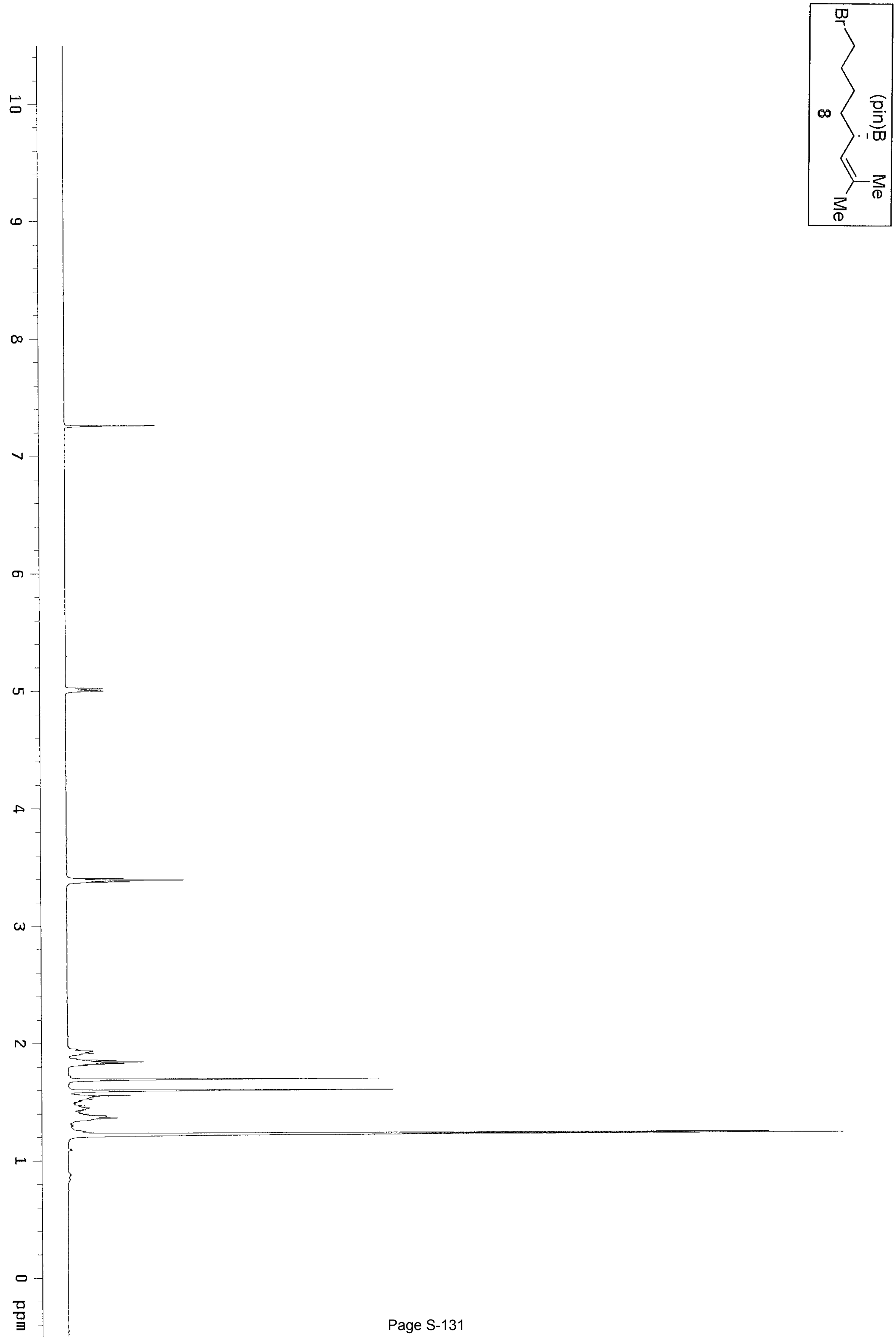
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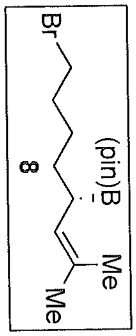

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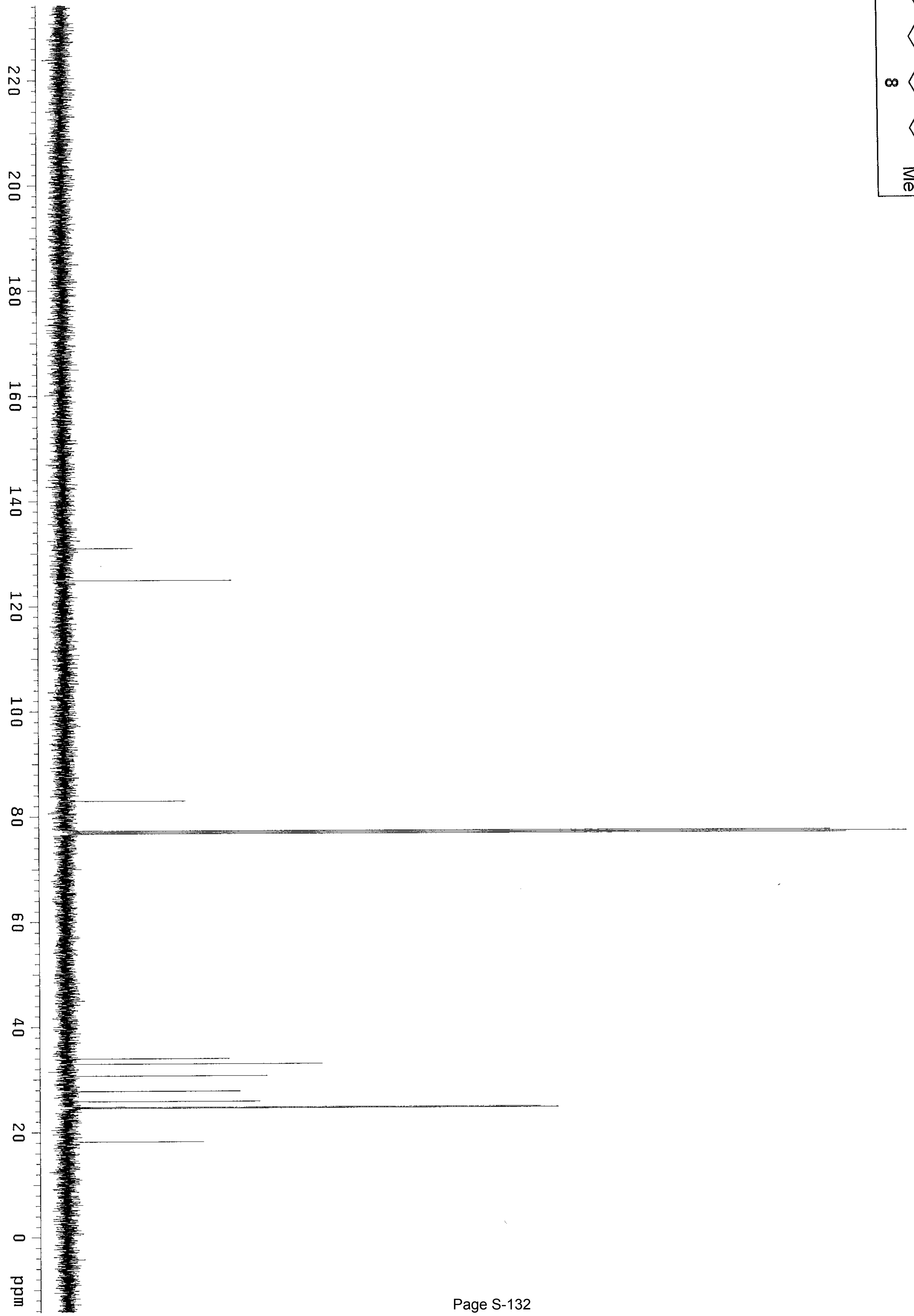
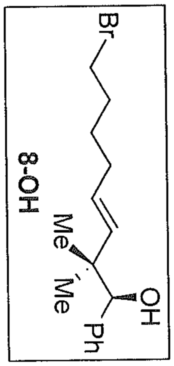
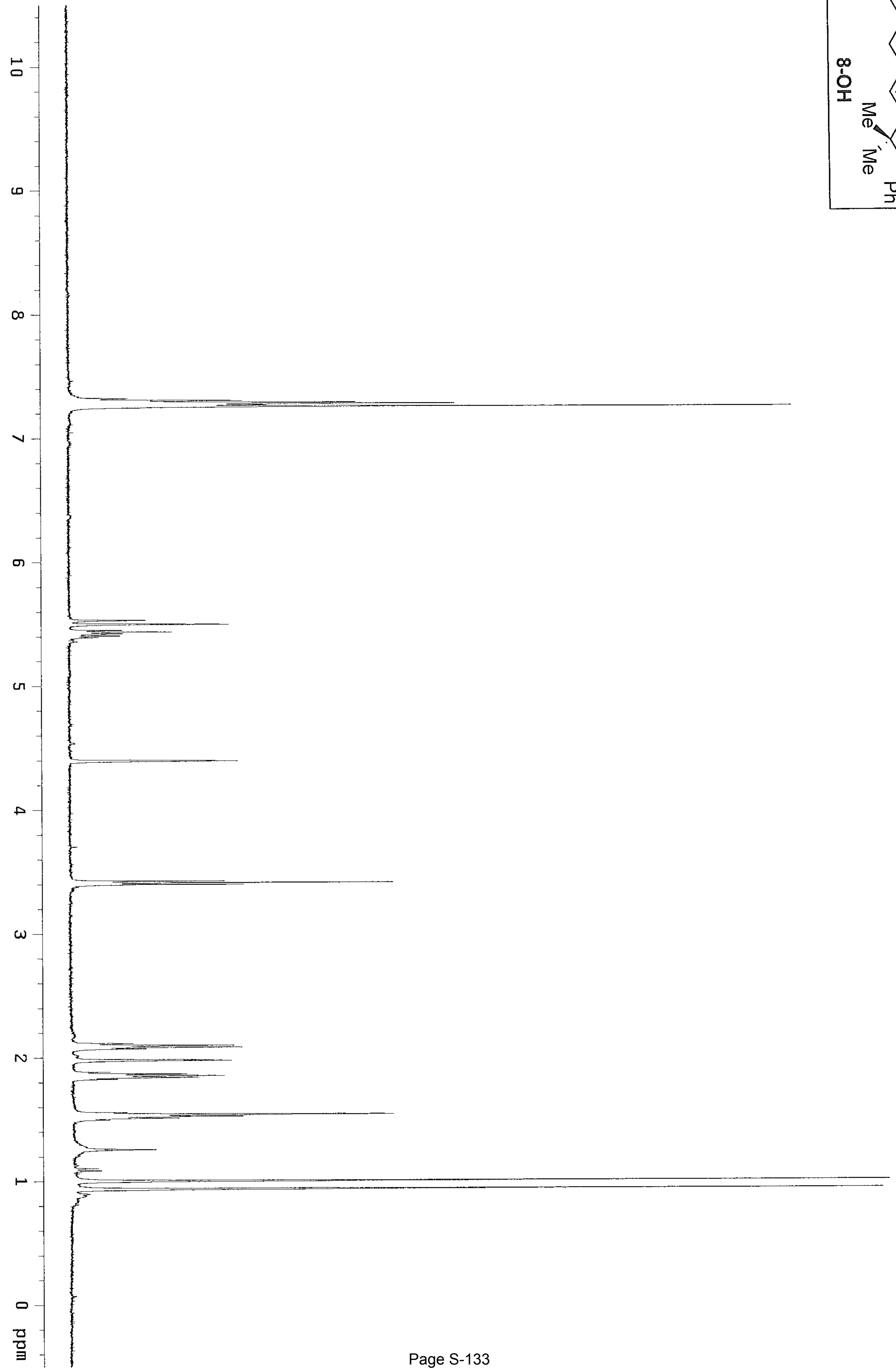
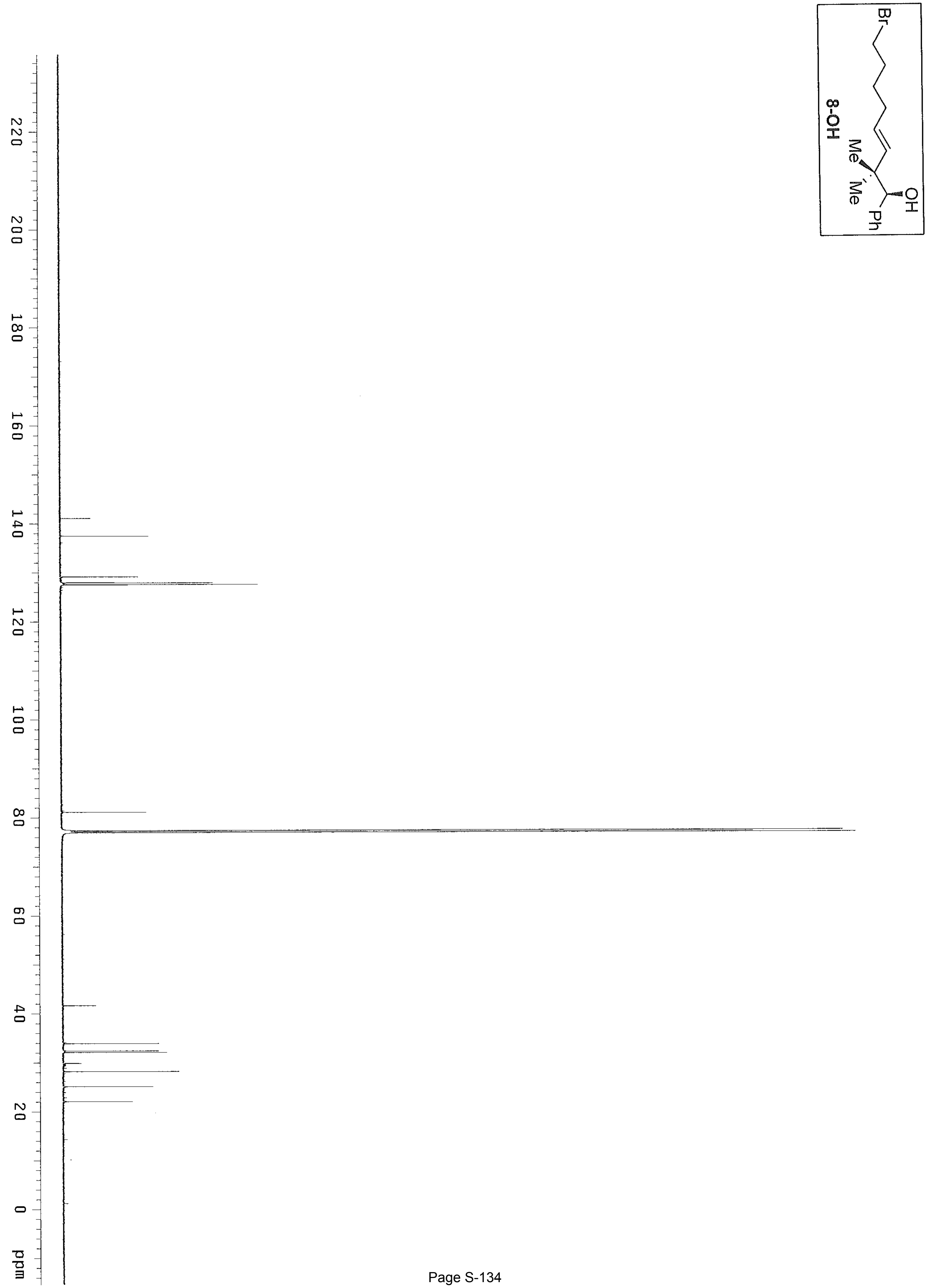




8-OH

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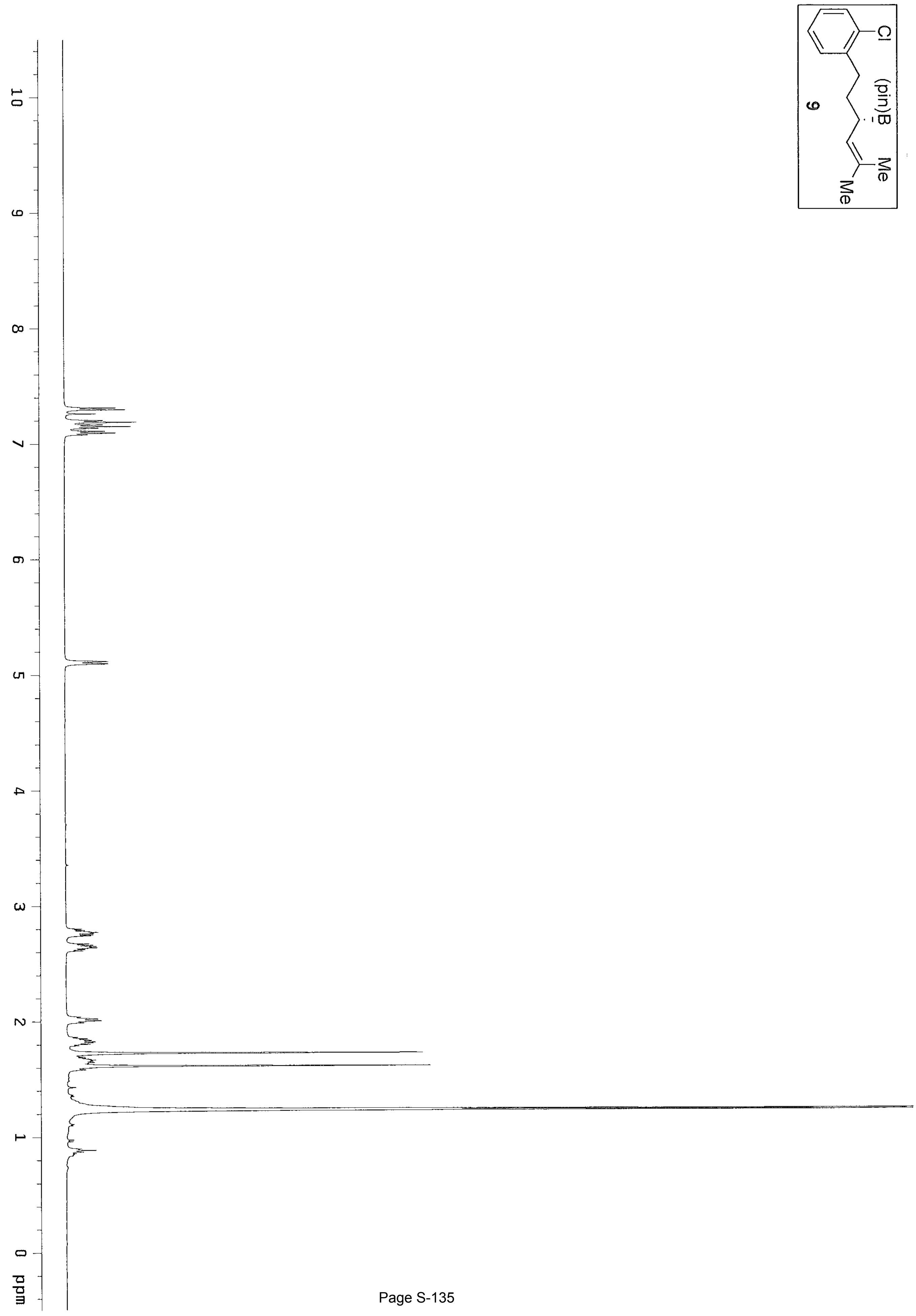
Ph
Me
Me
8-OH



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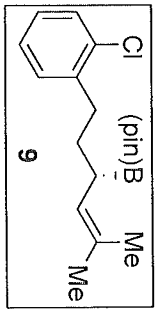
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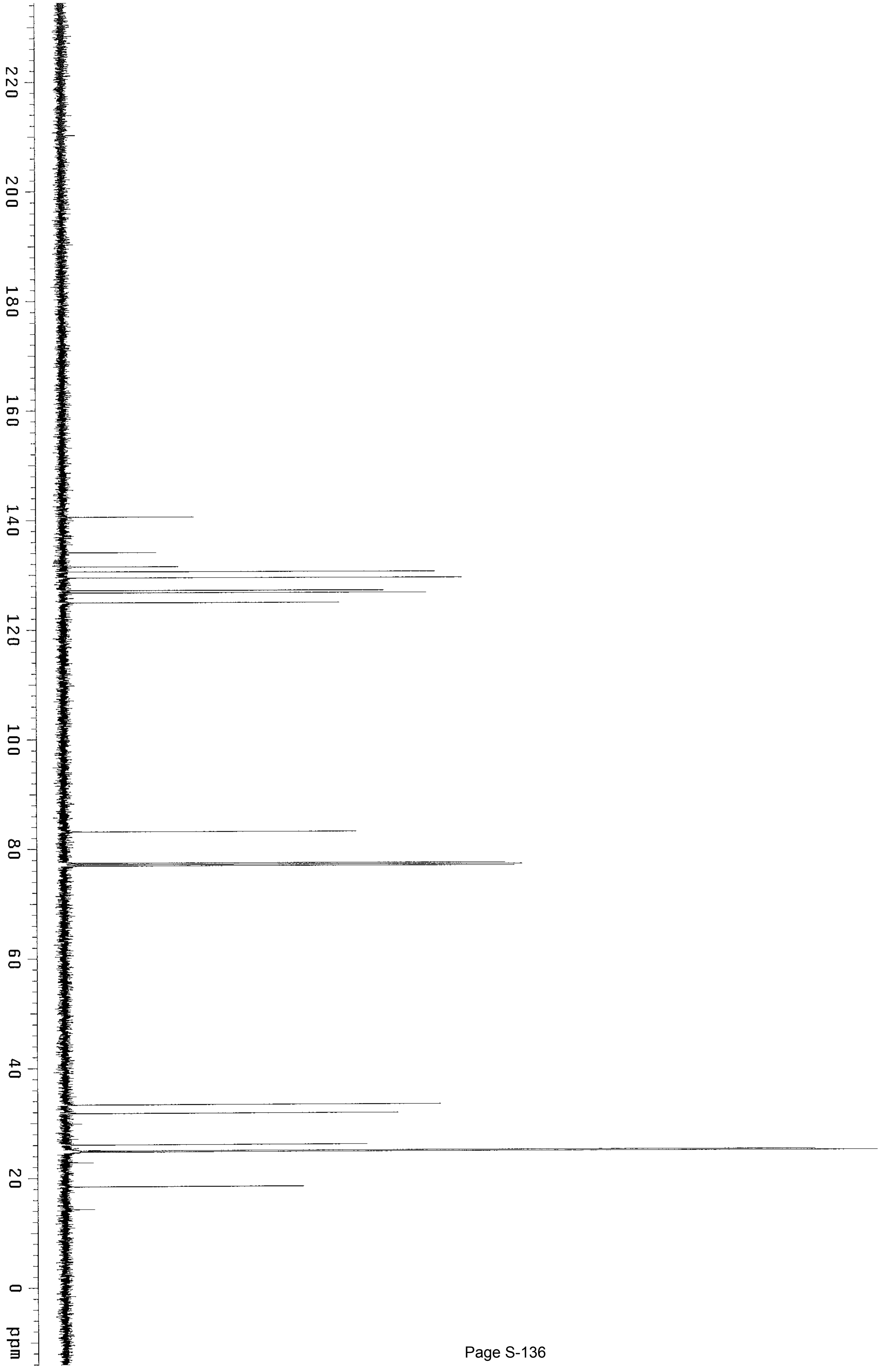
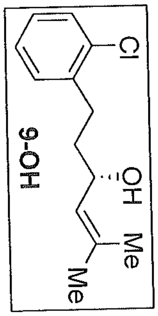
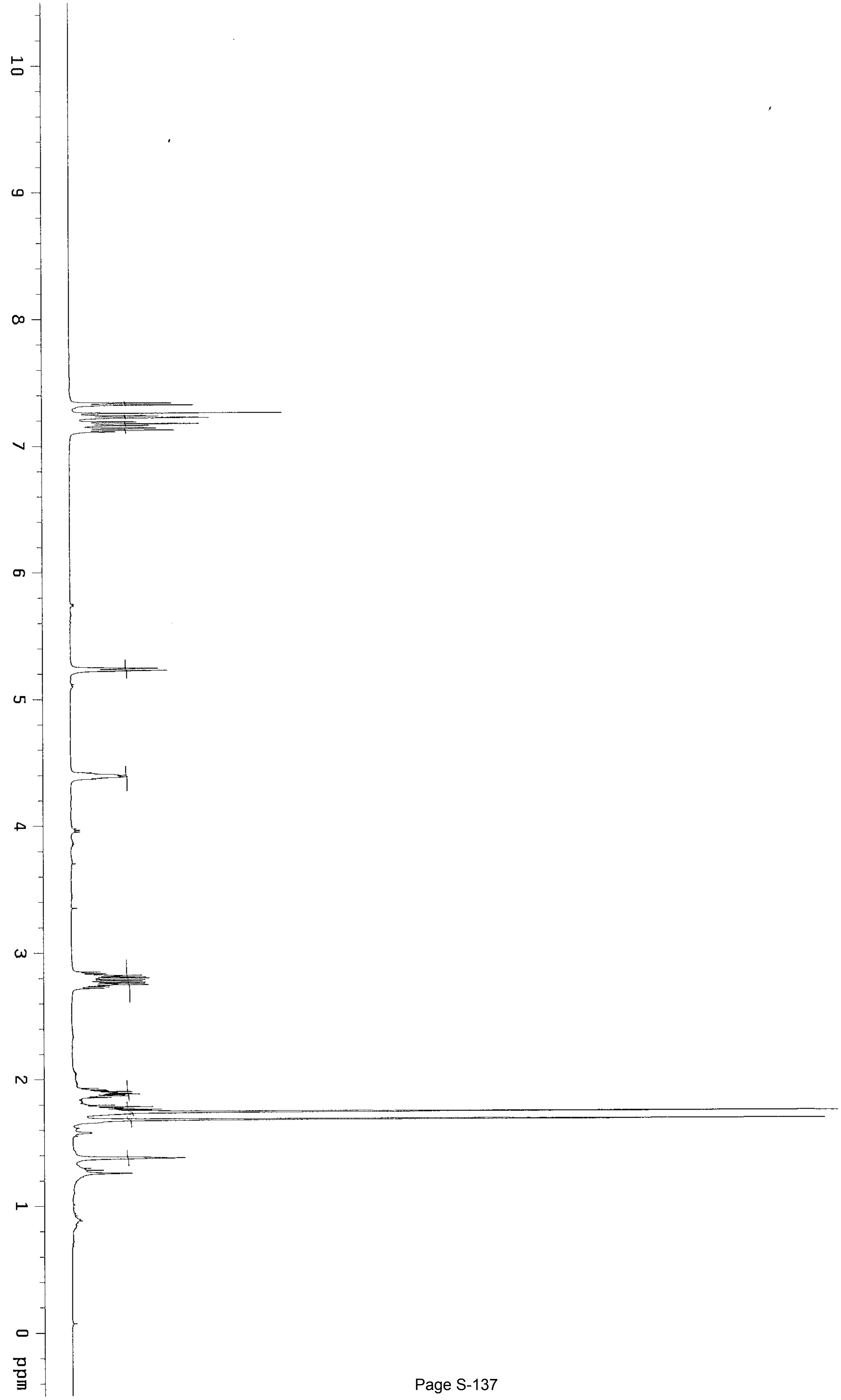
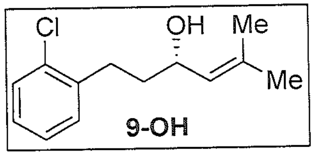




9-OH





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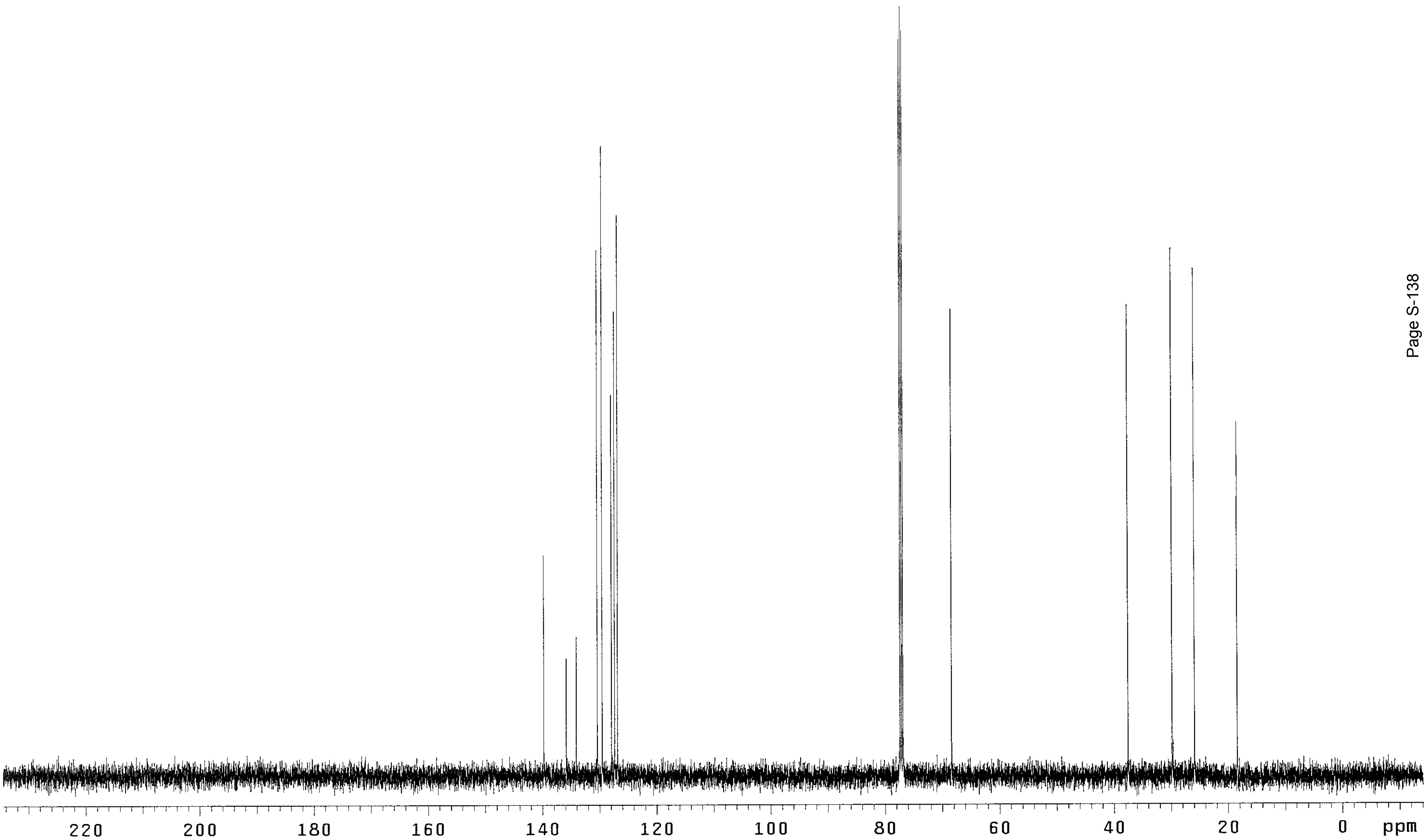

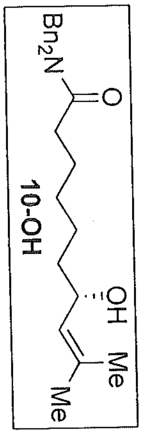

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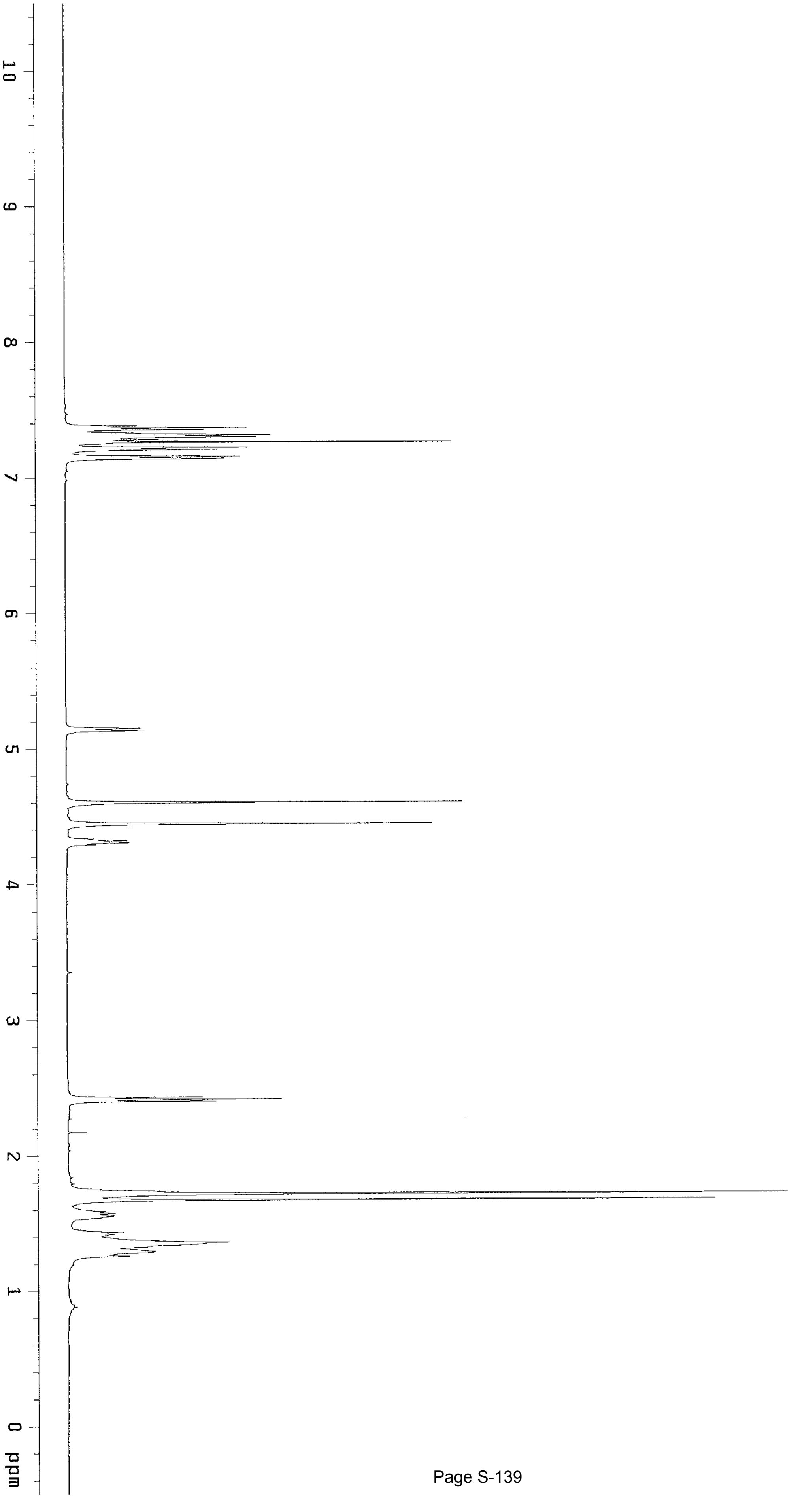

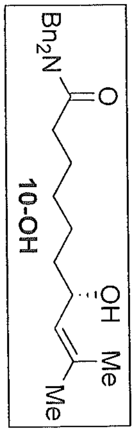

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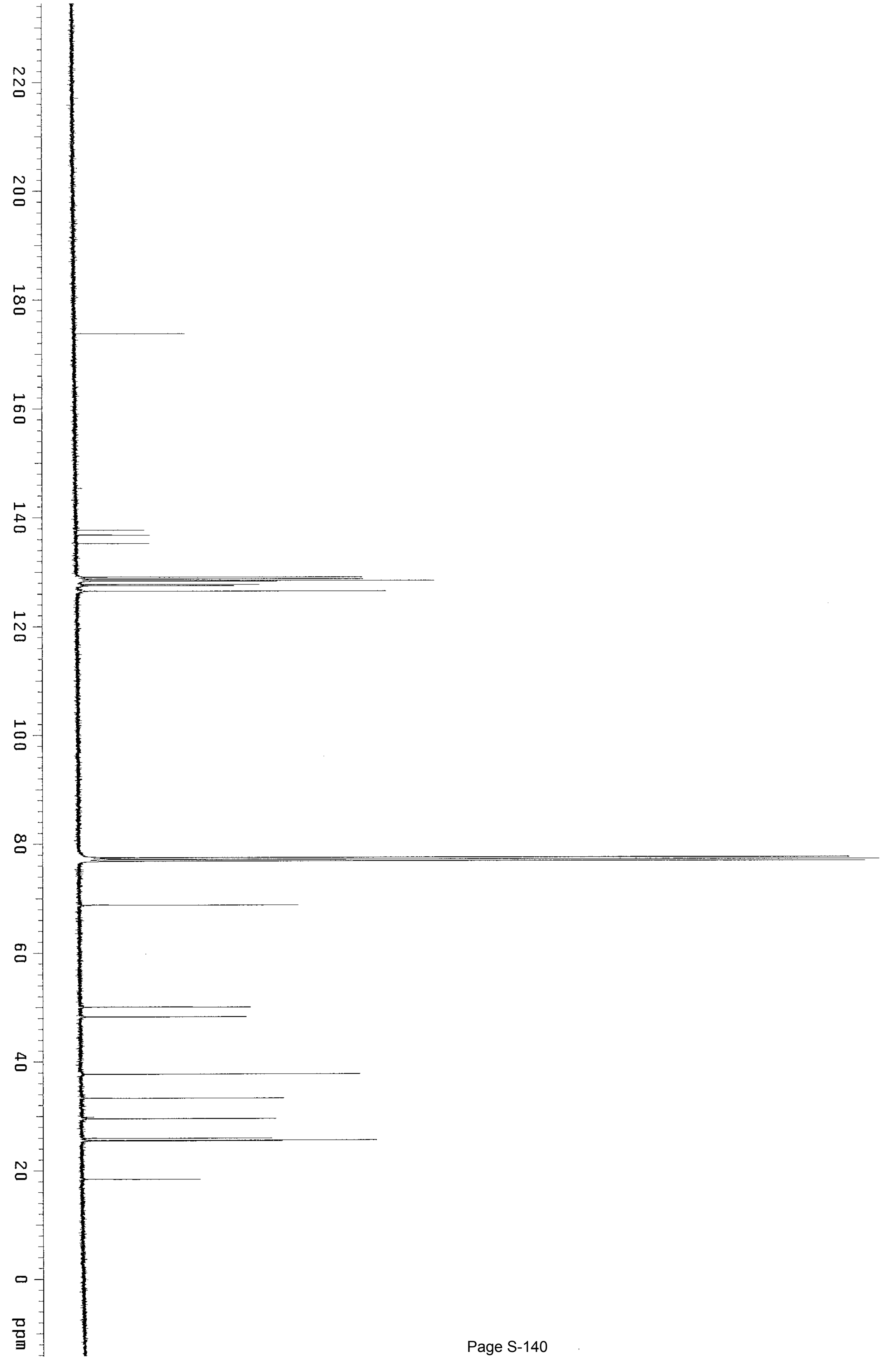

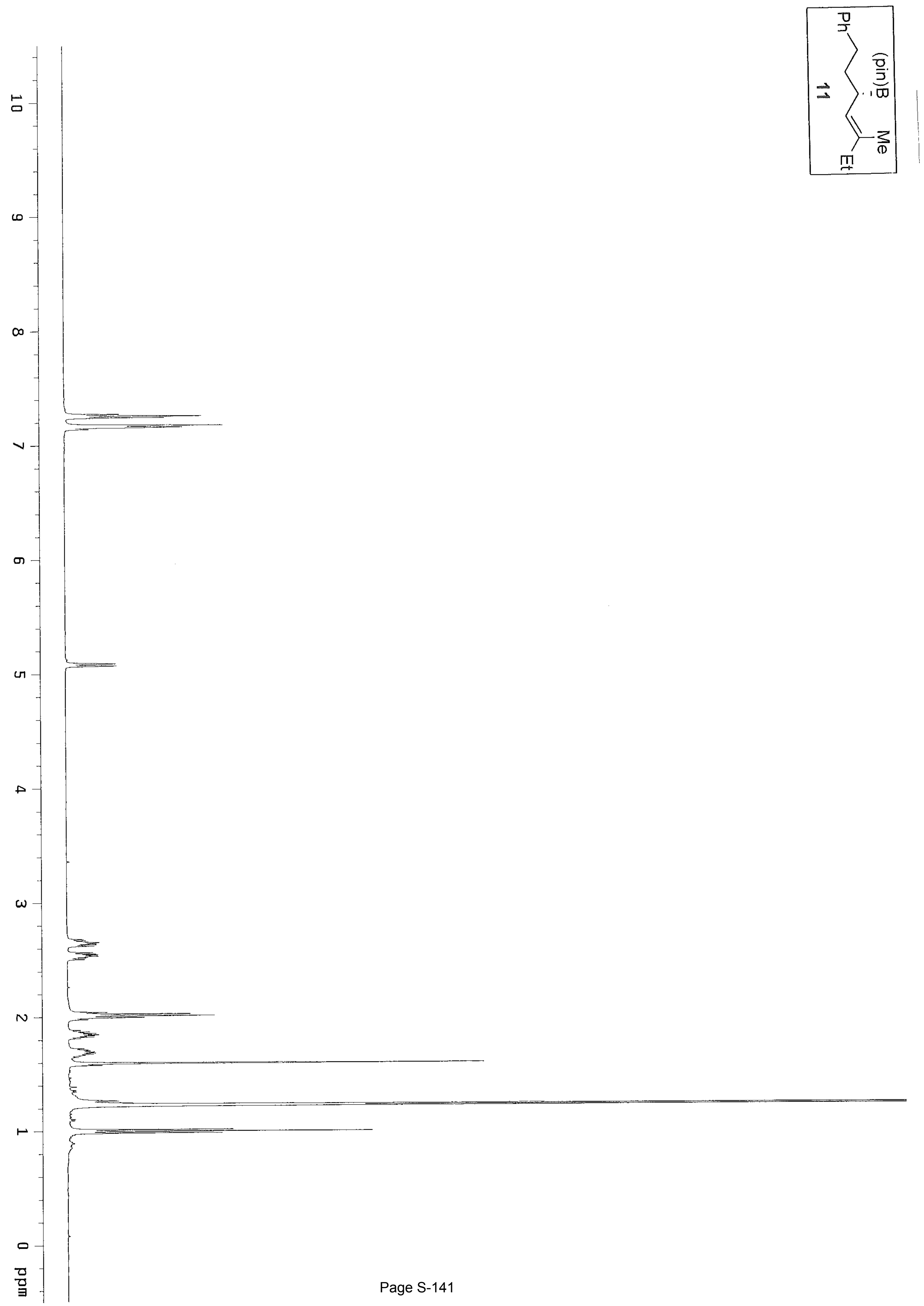
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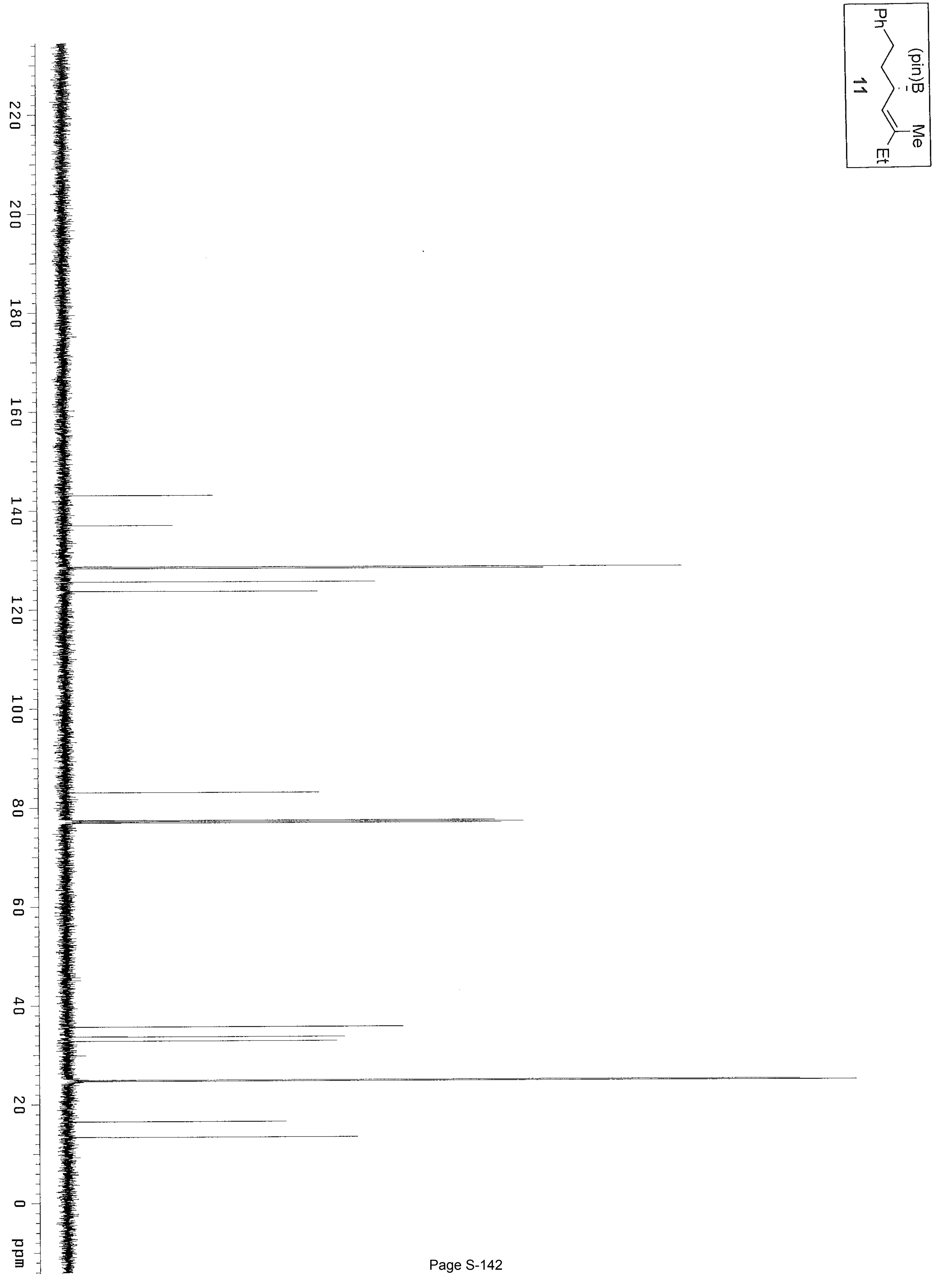
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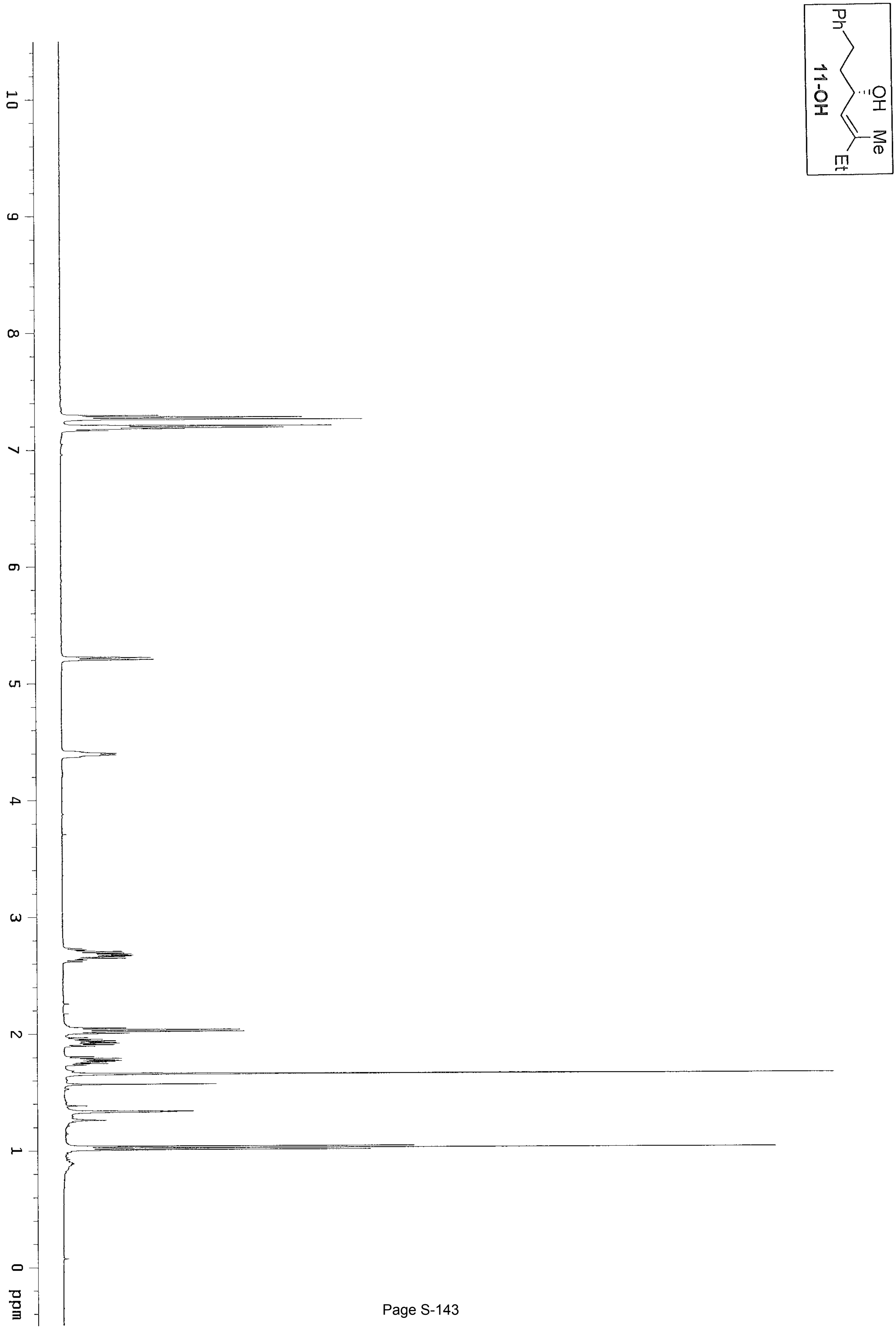
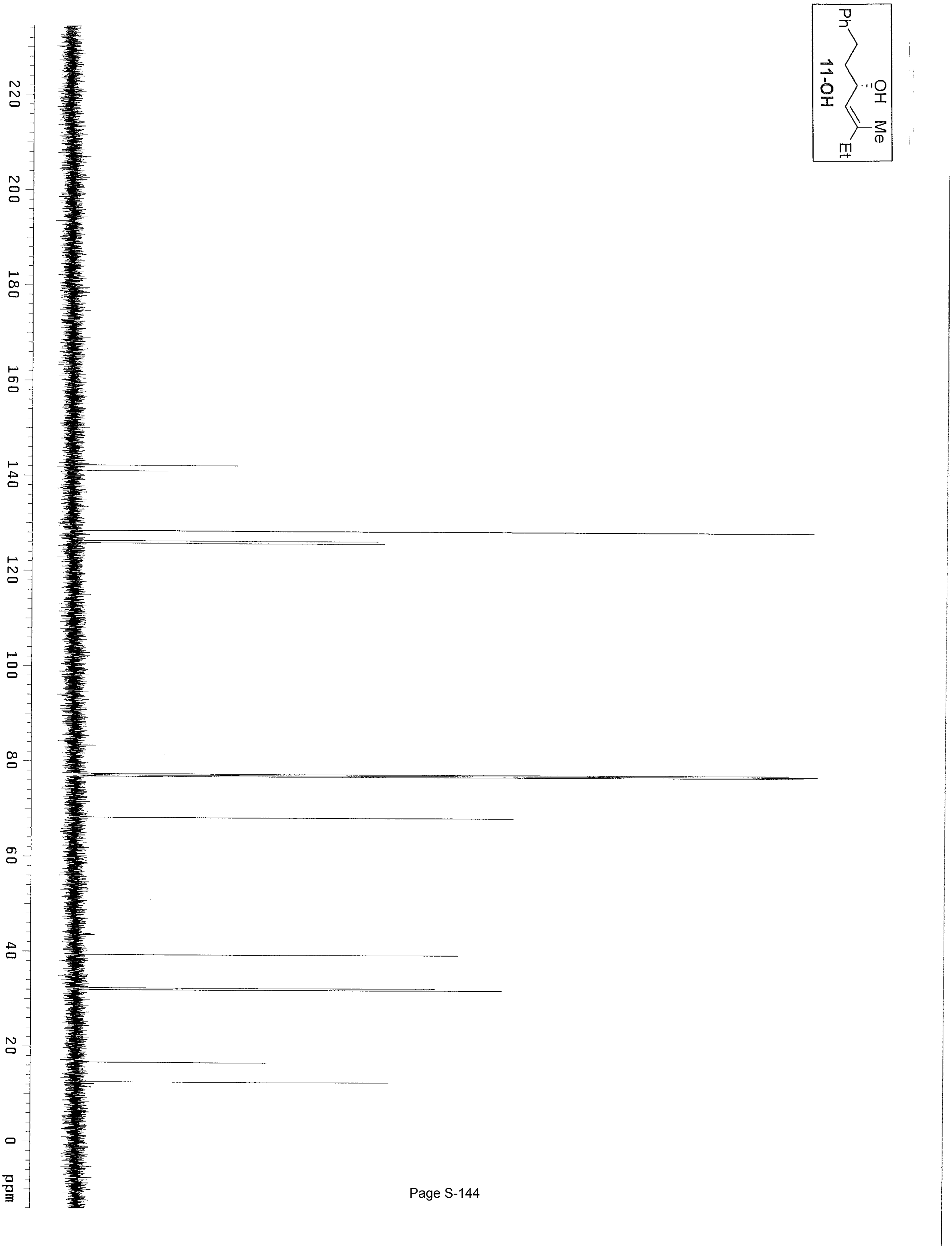
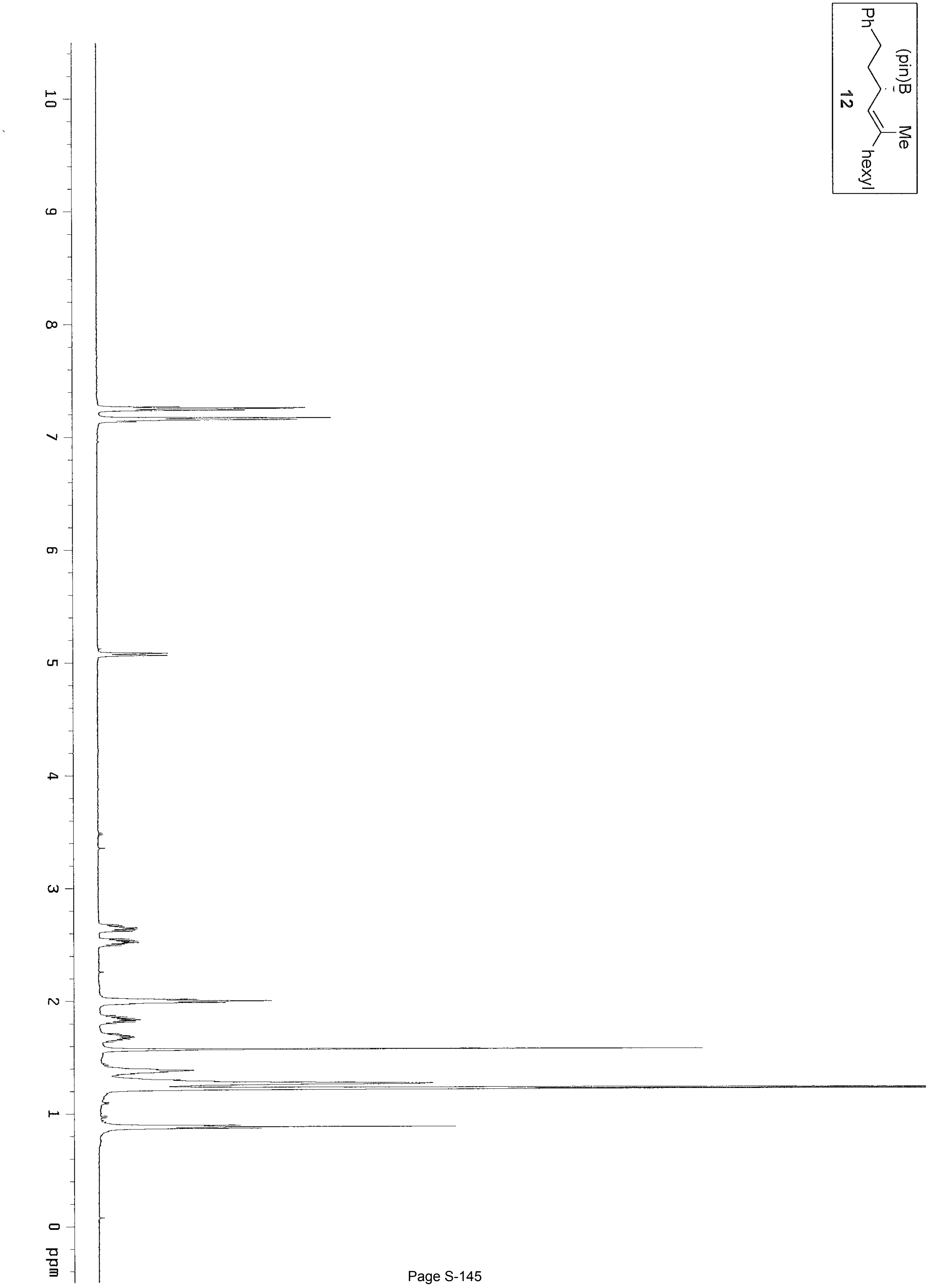


11-OH



11-OH



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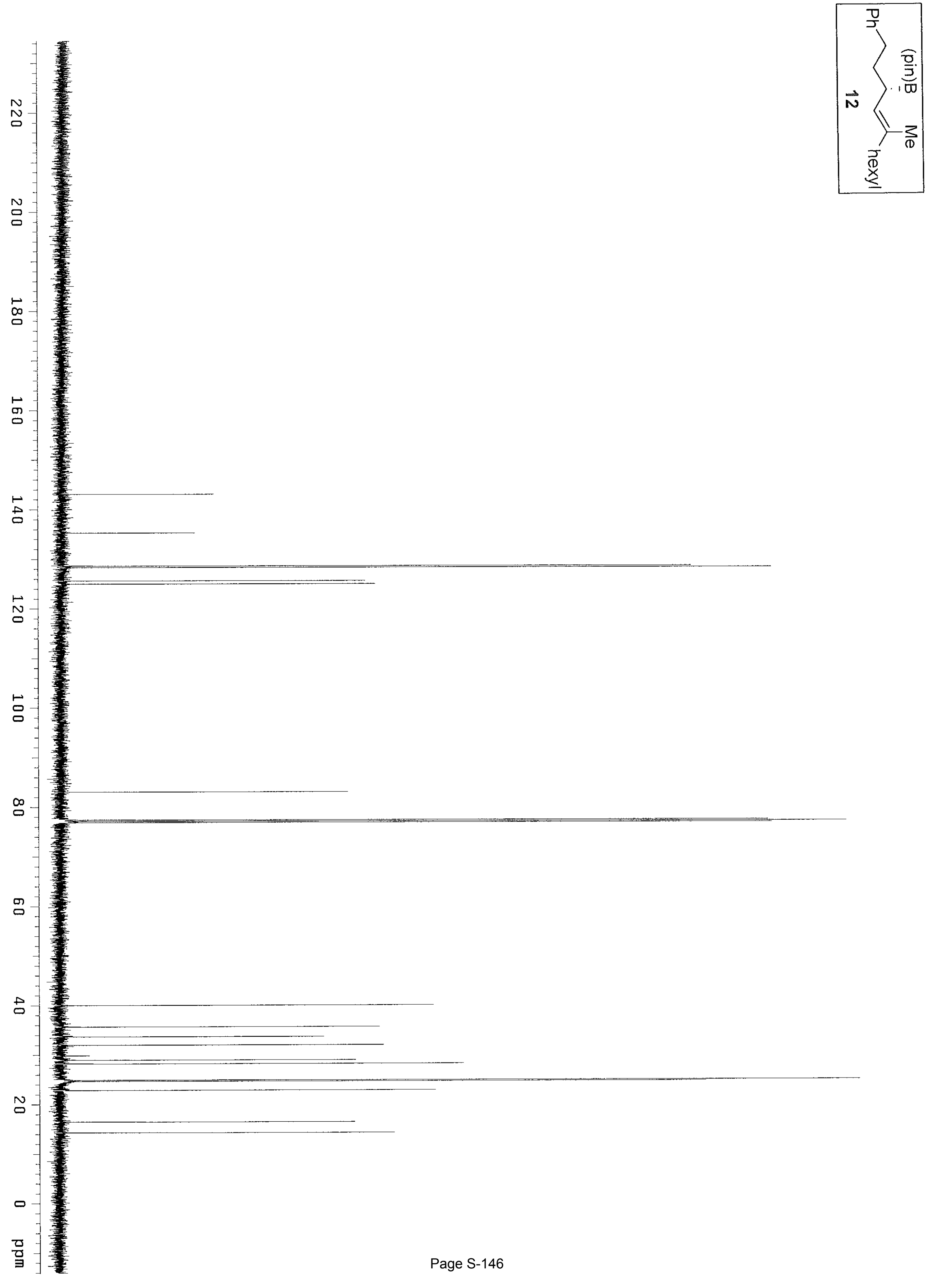
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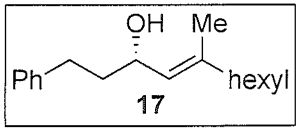
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Ph
hexyl
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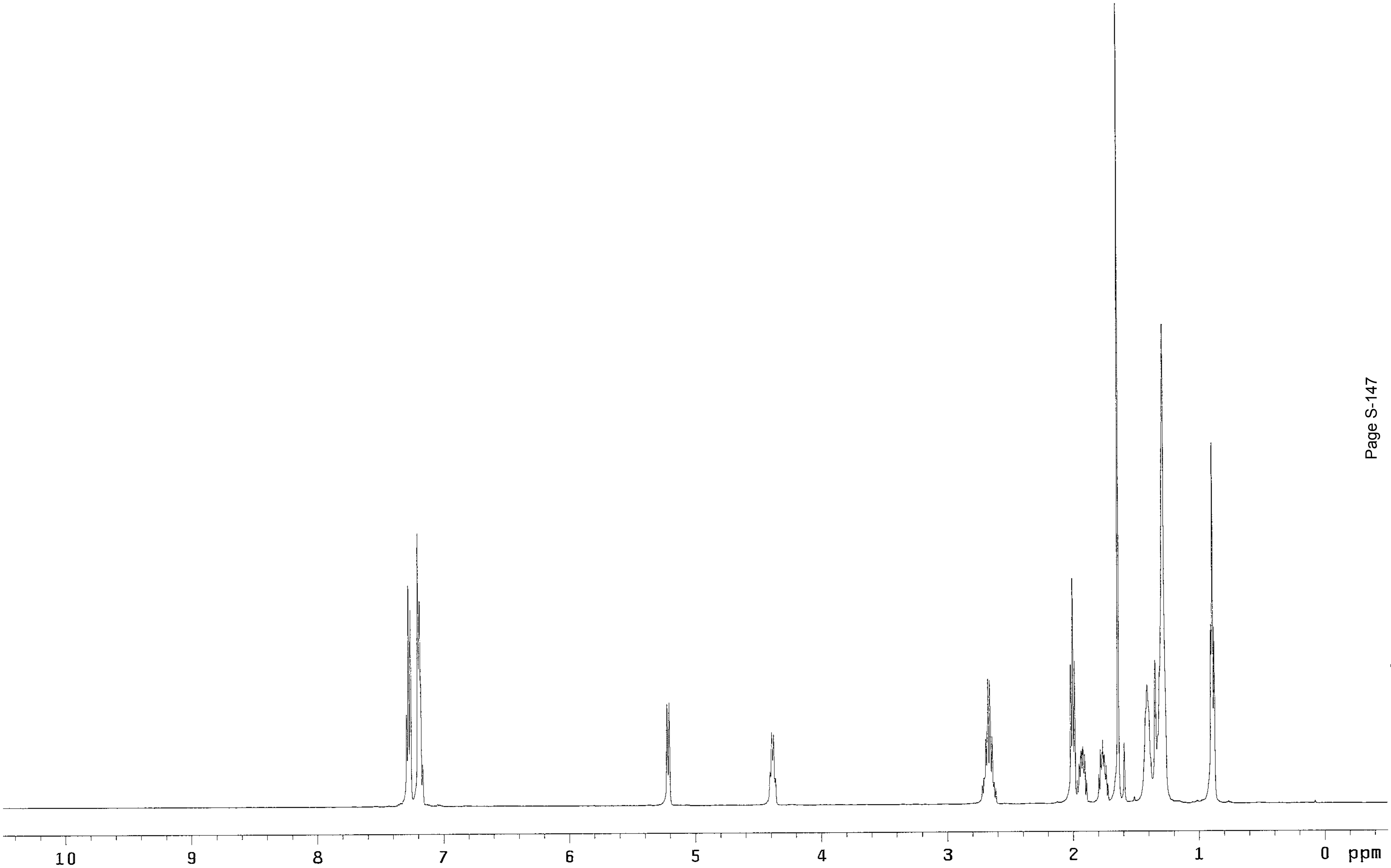
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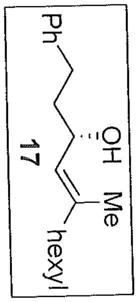

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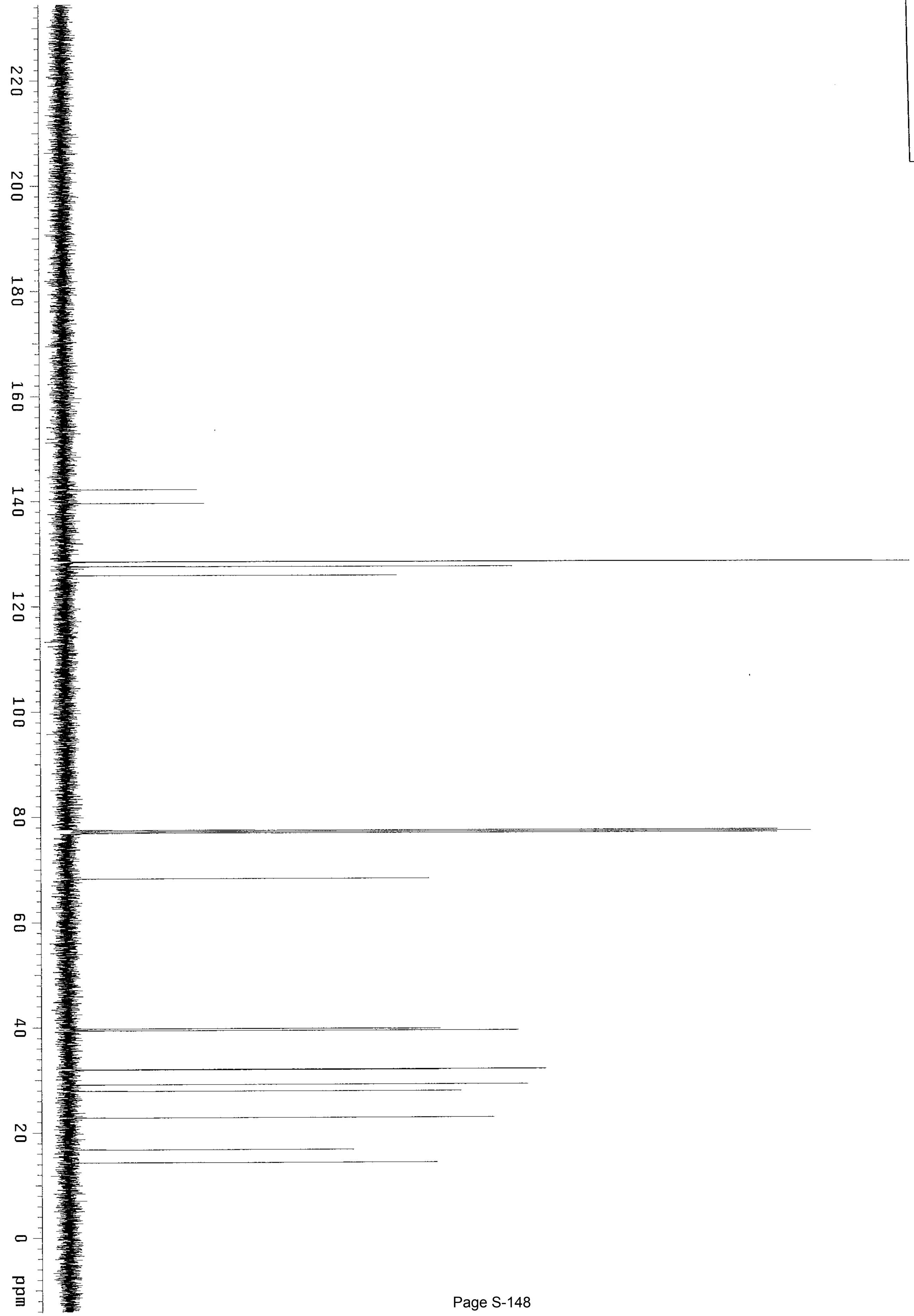

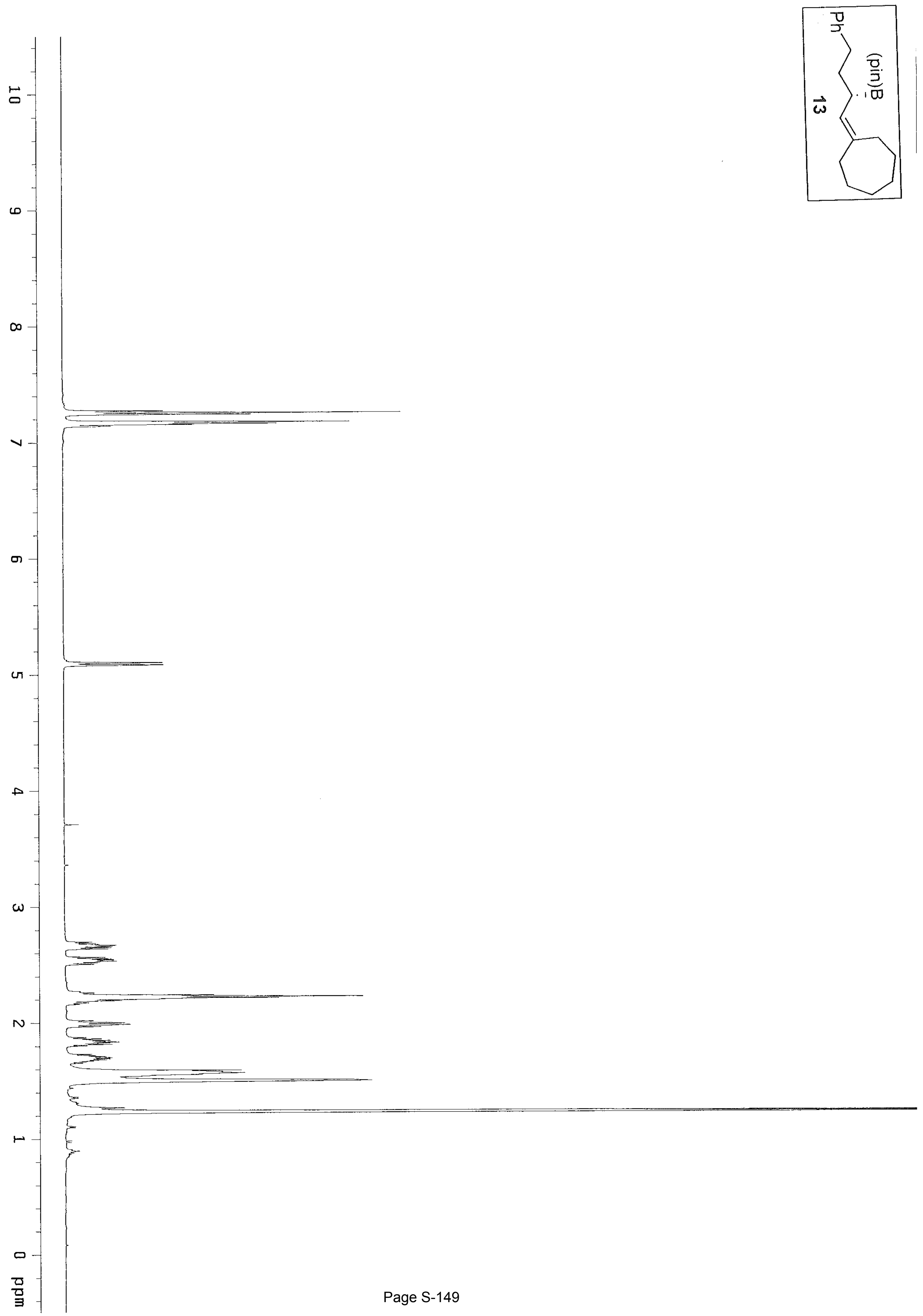
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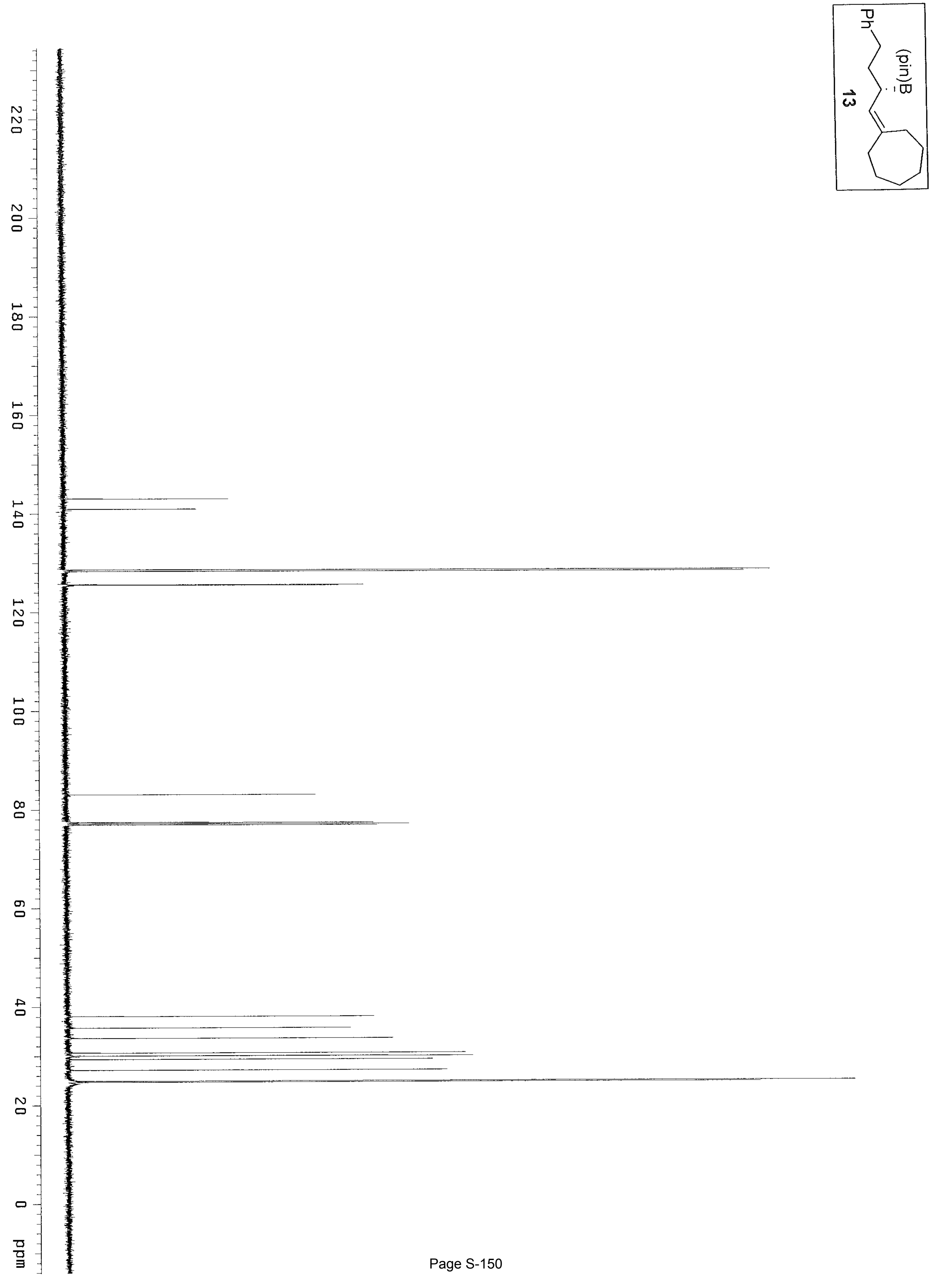

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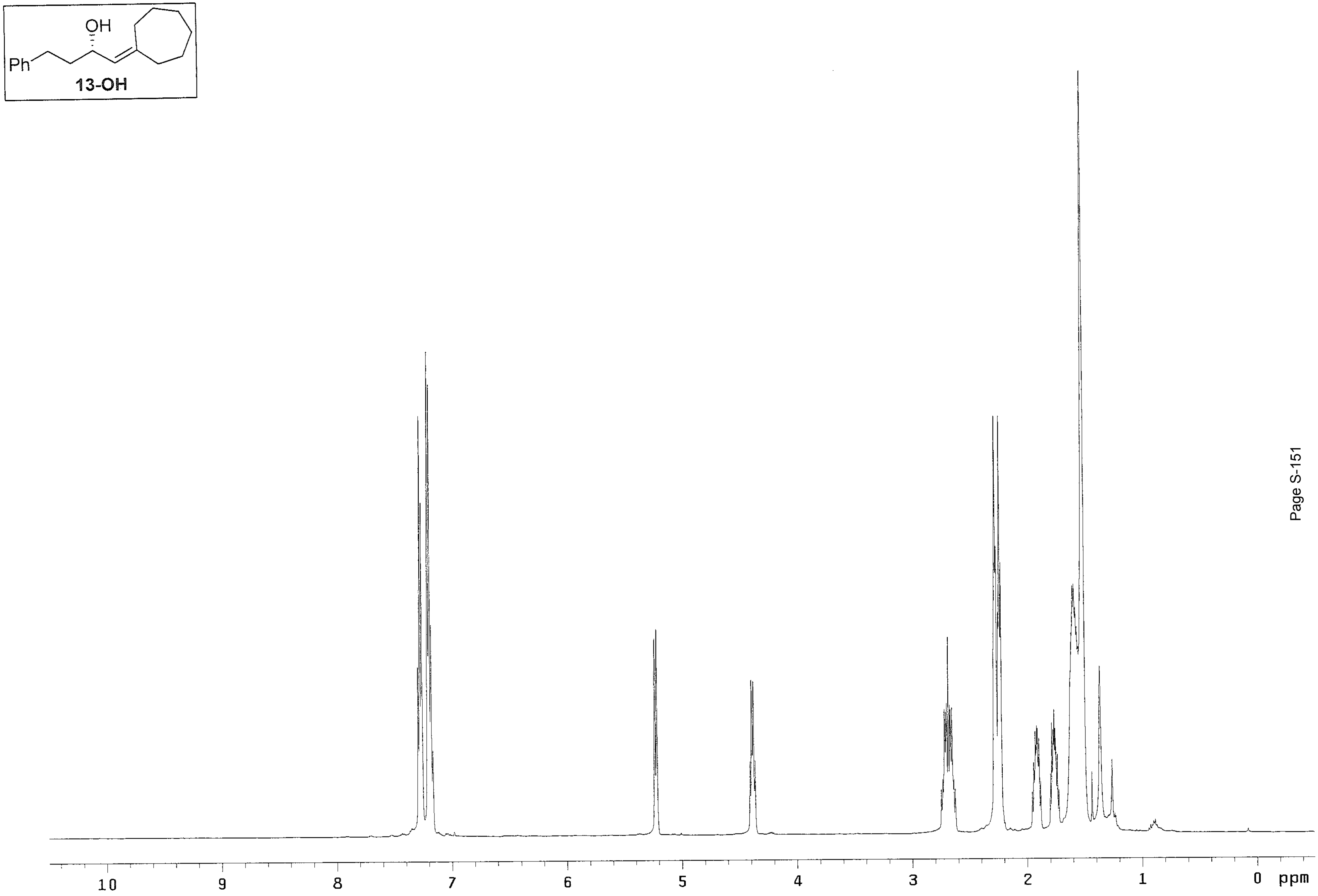
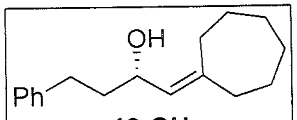


13-OH



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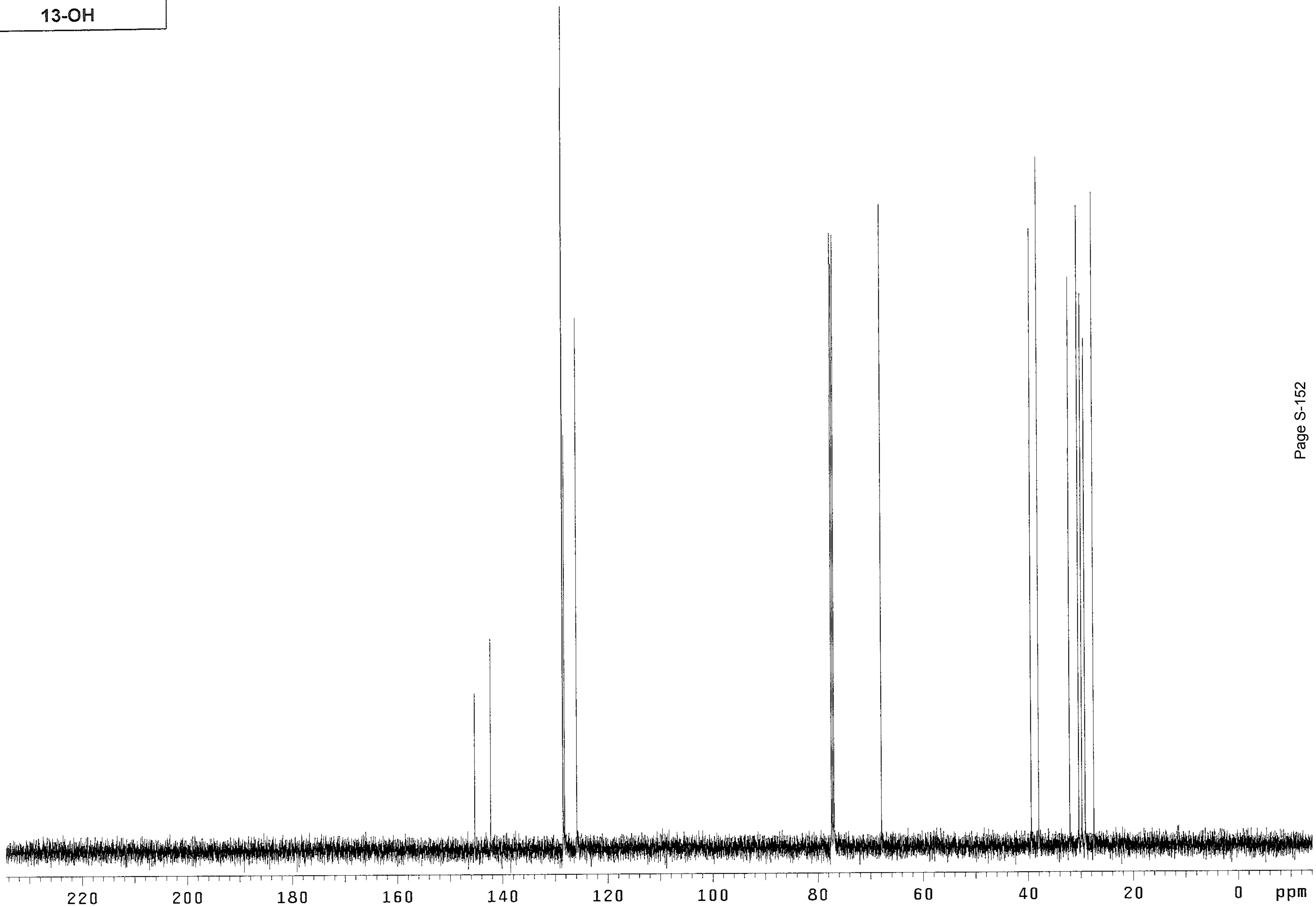

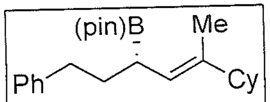

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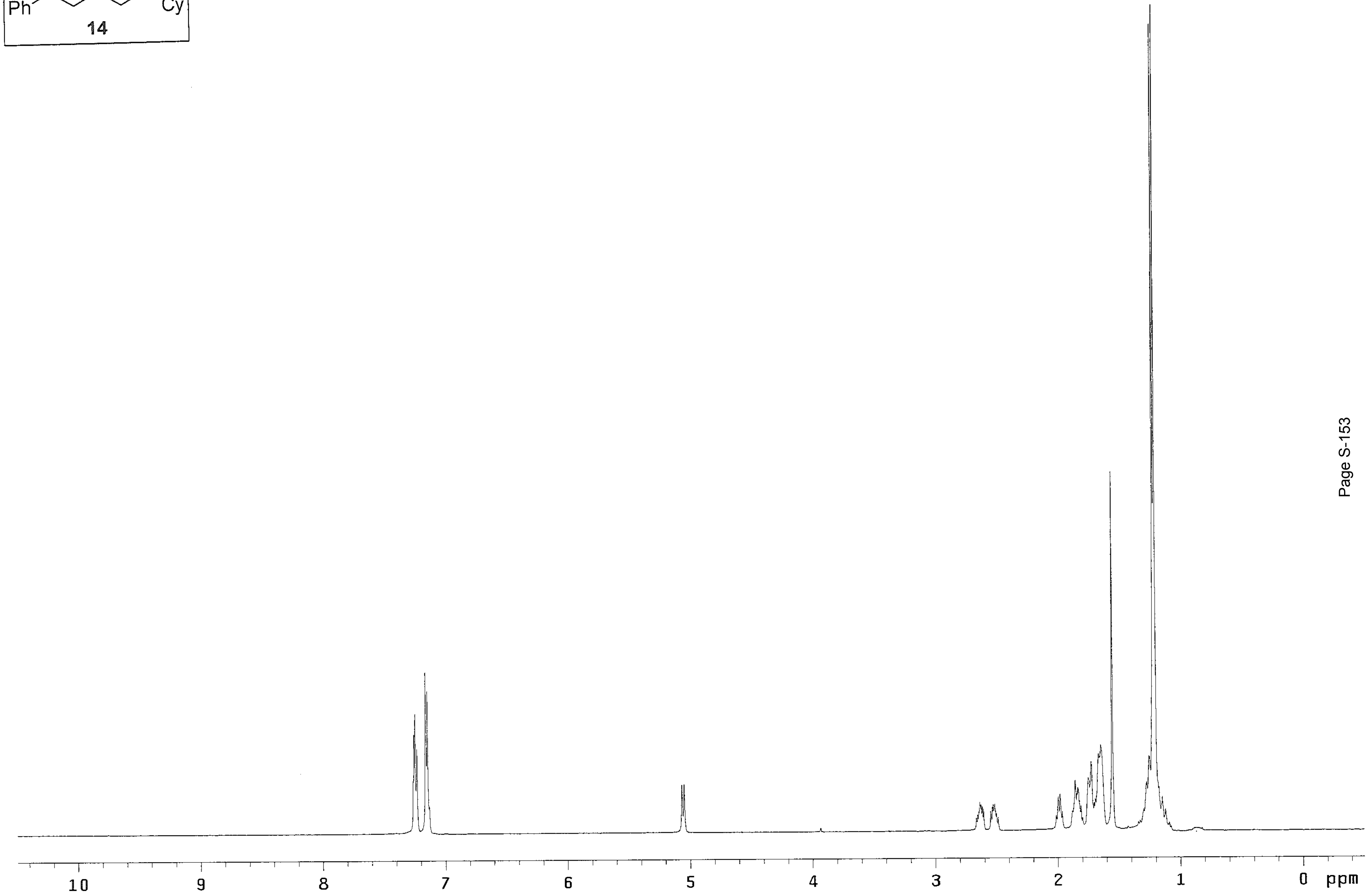

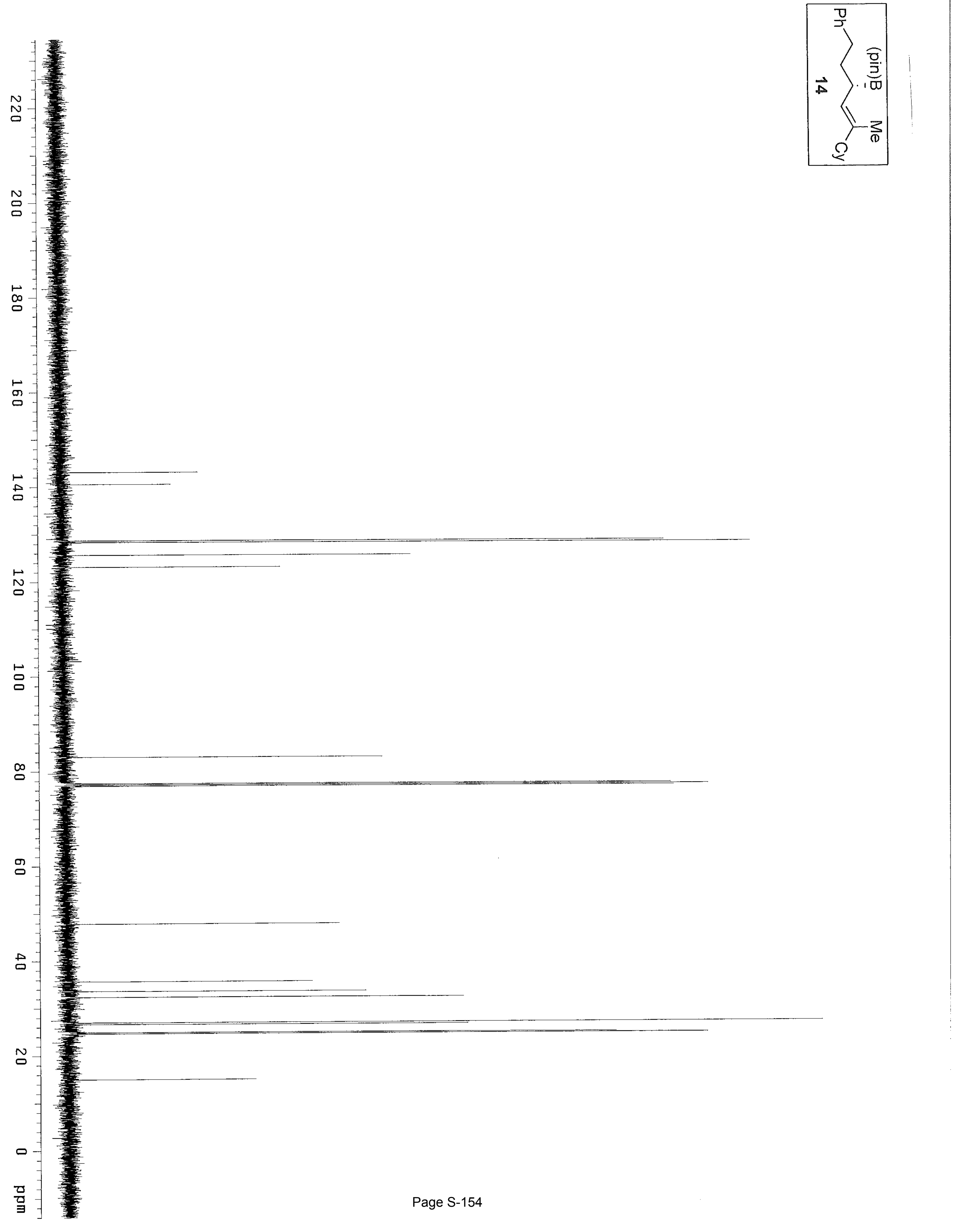
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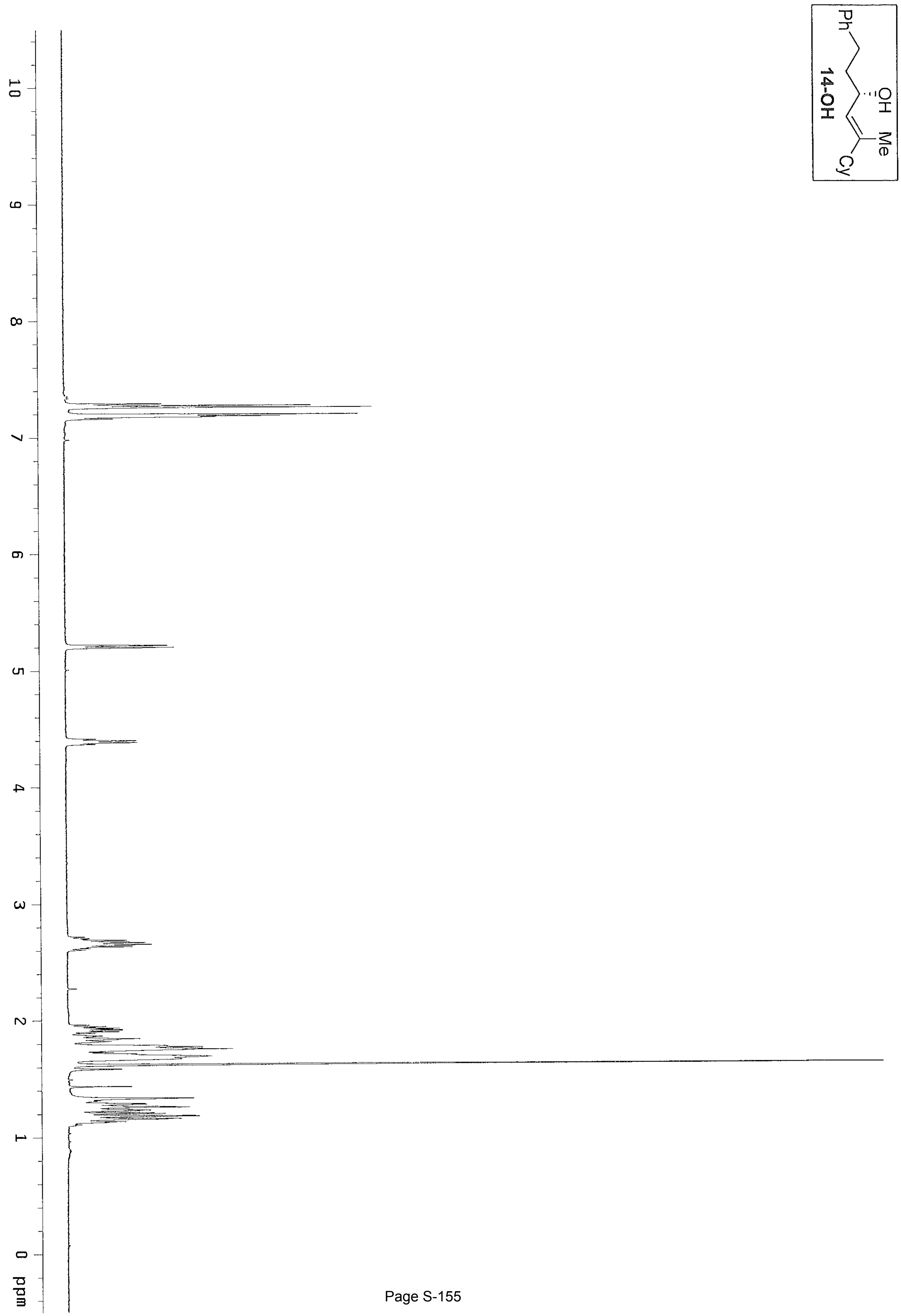
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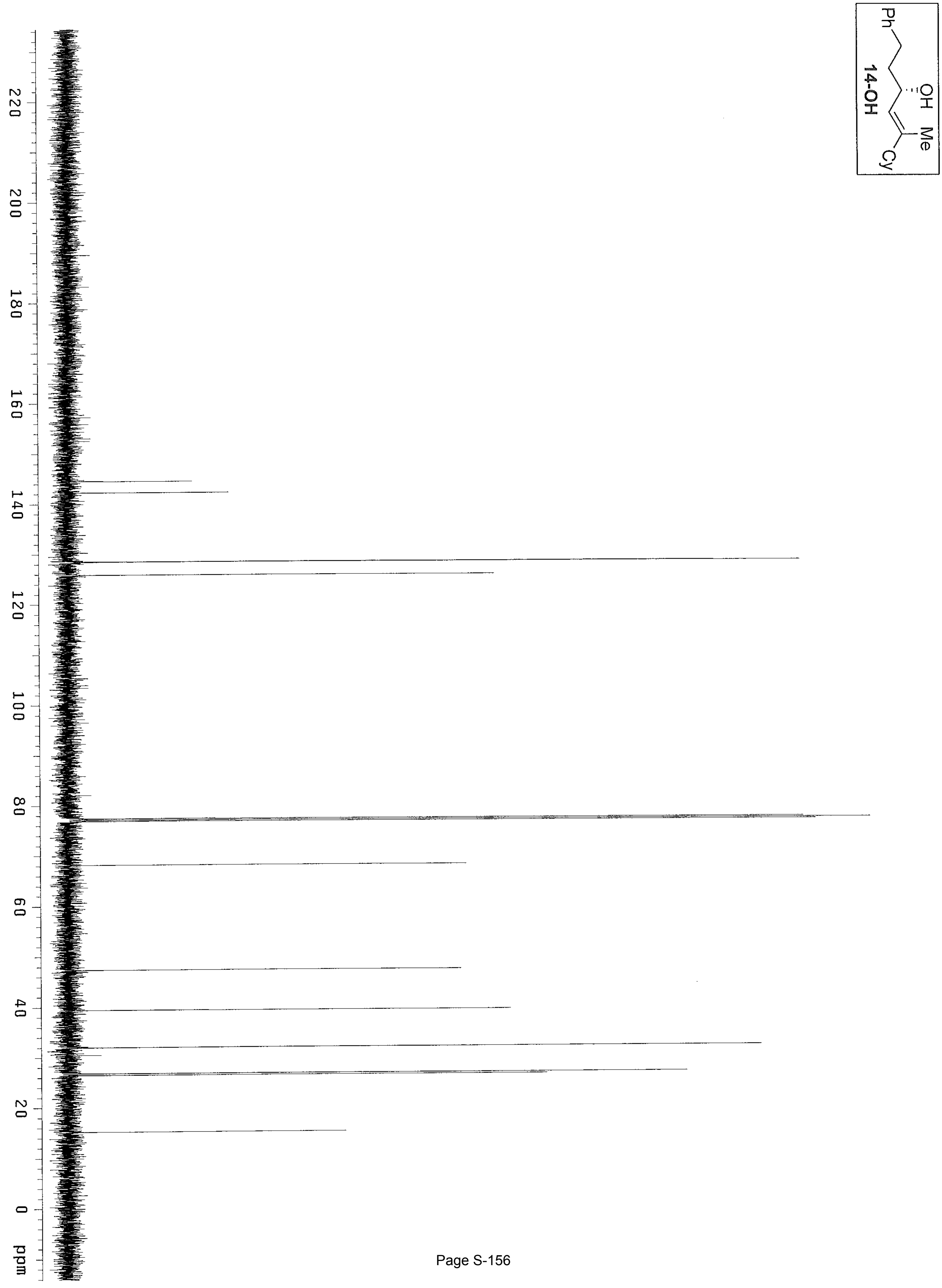
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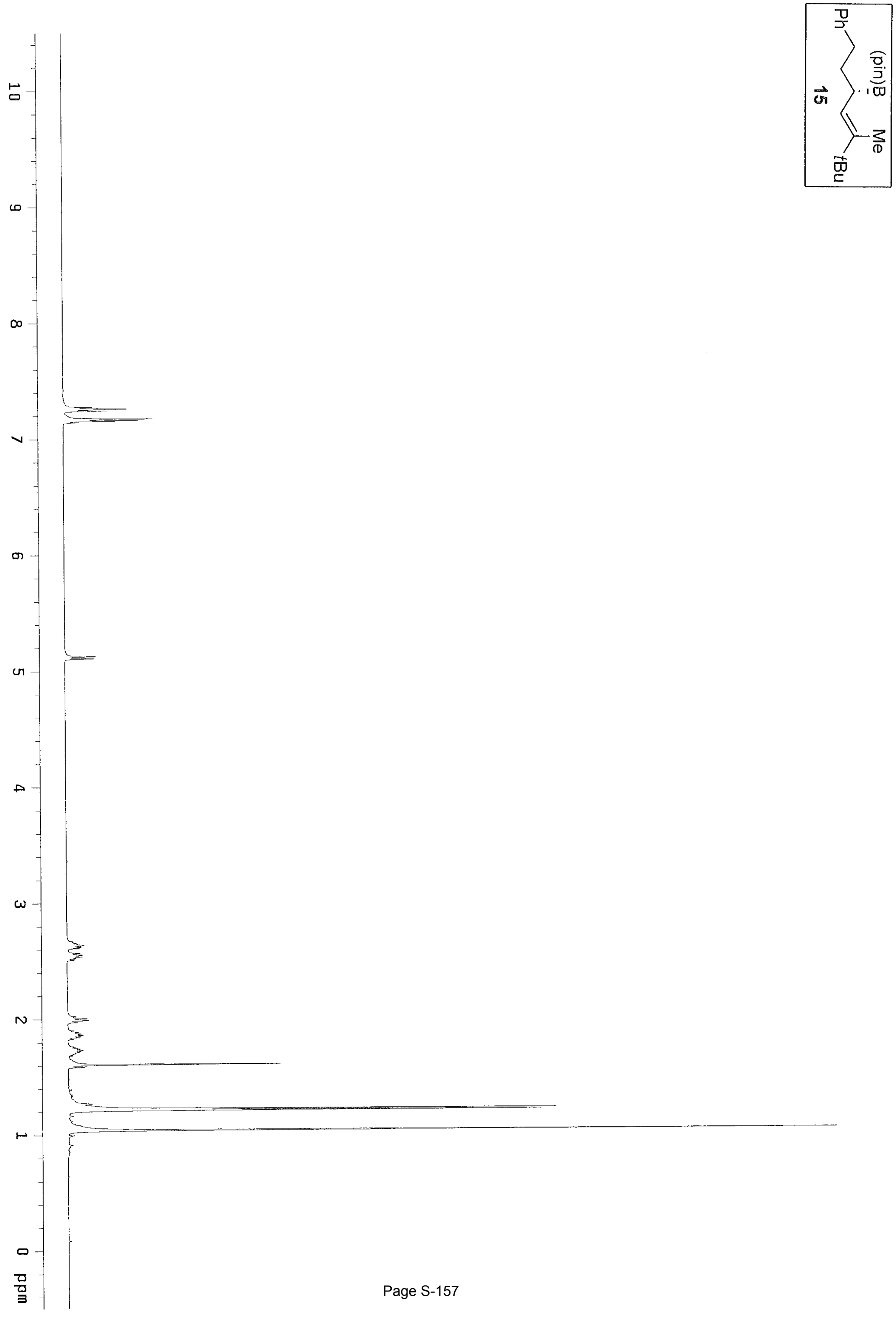

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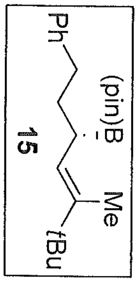

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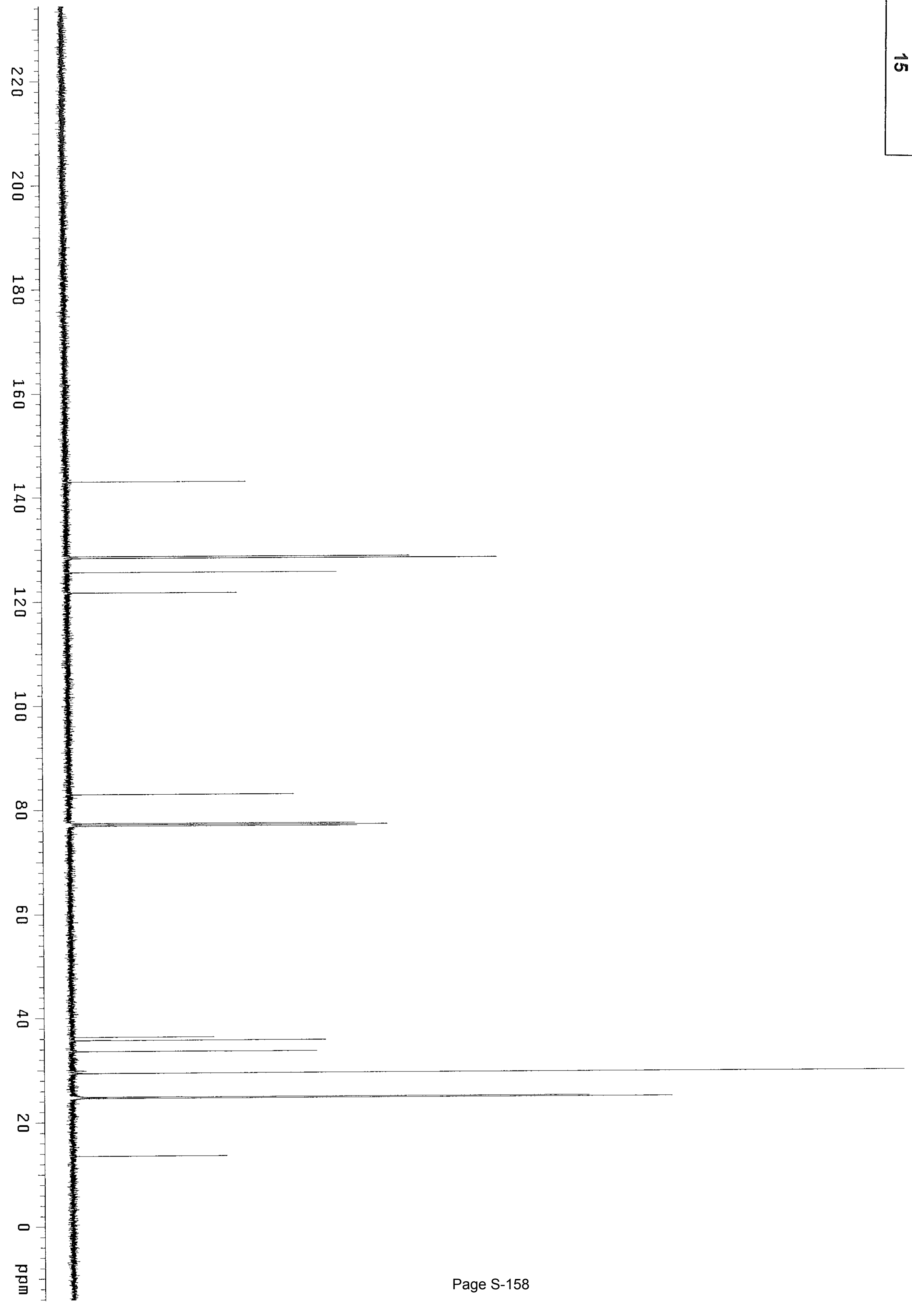
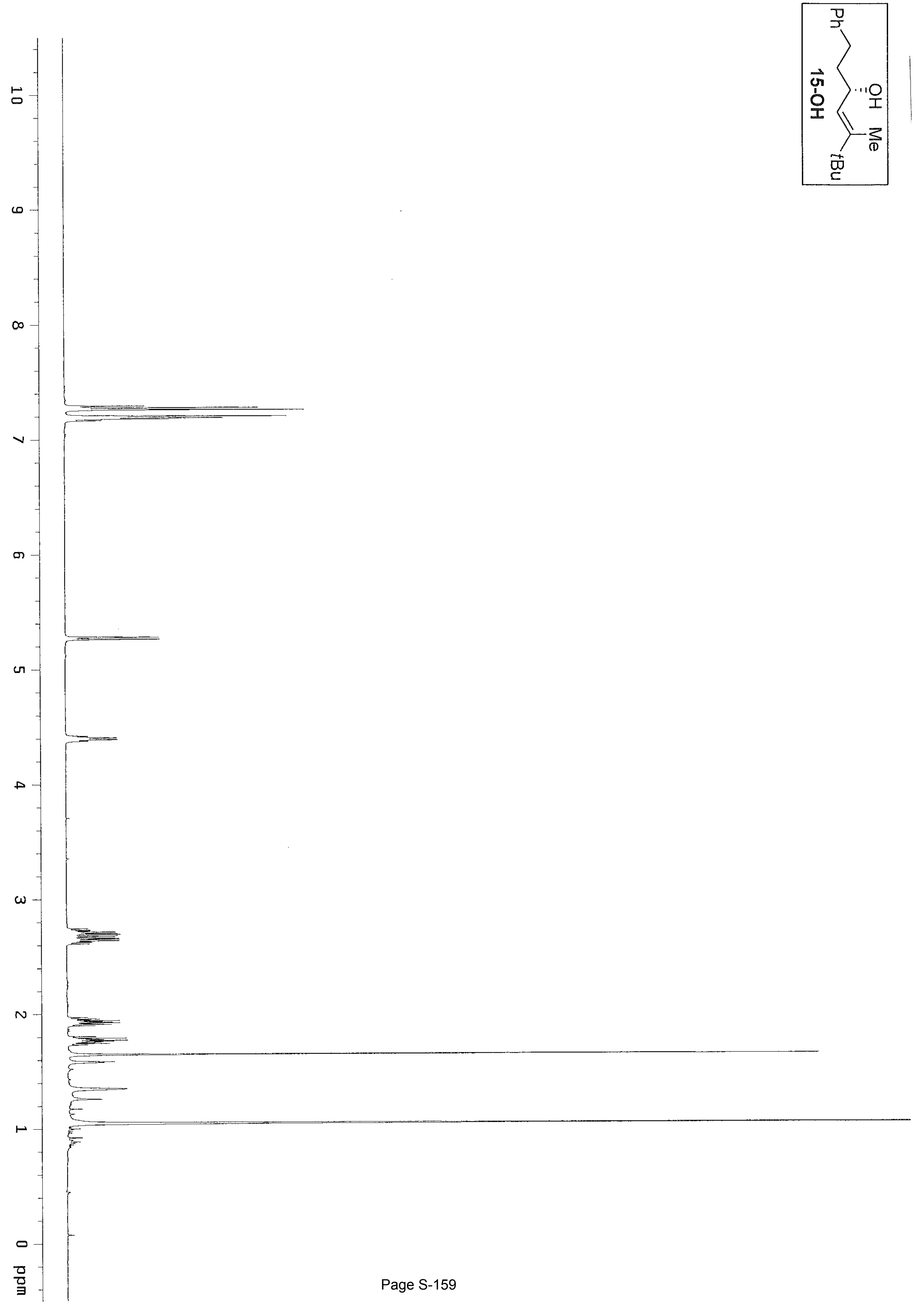
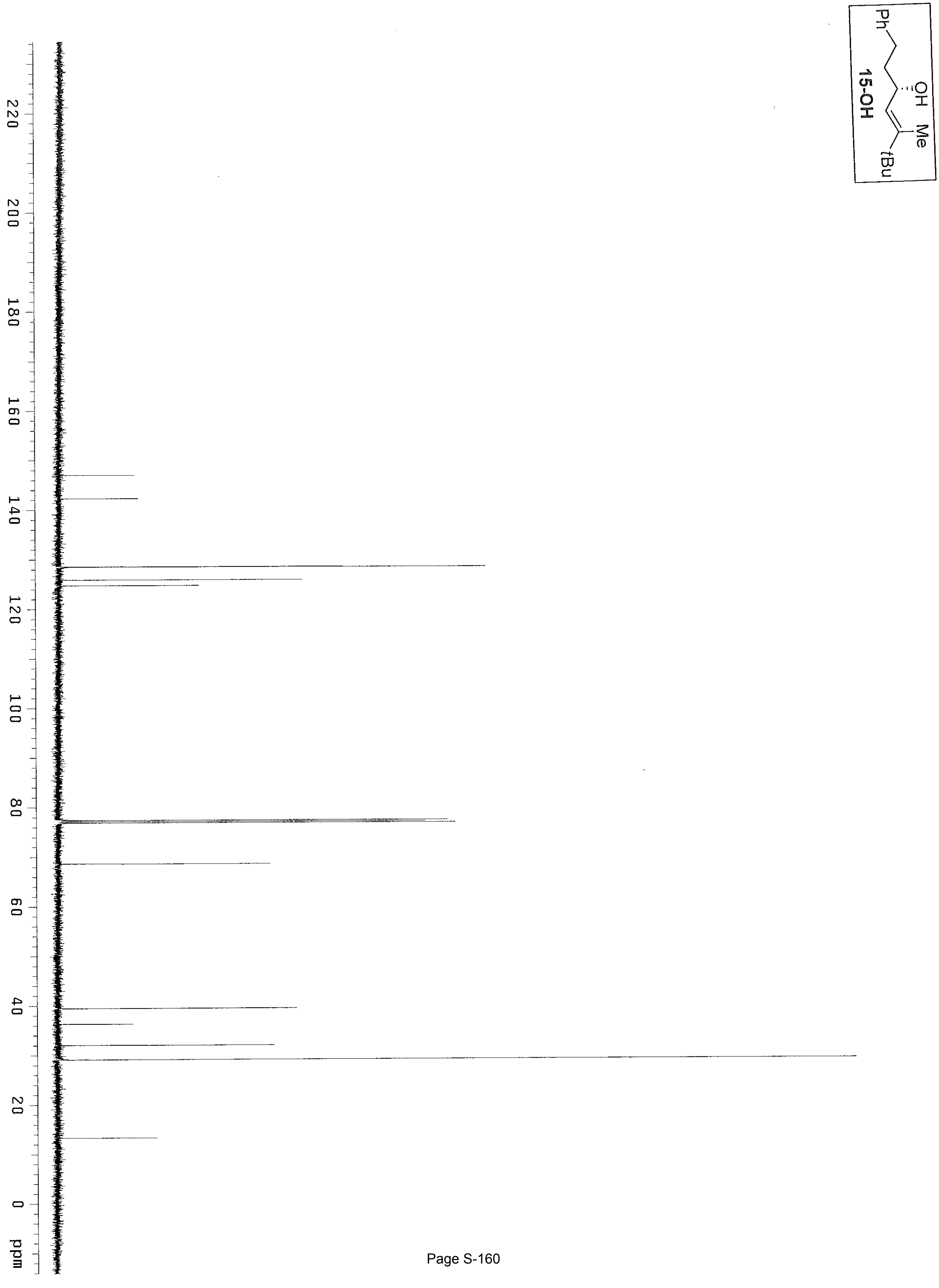




15-OH



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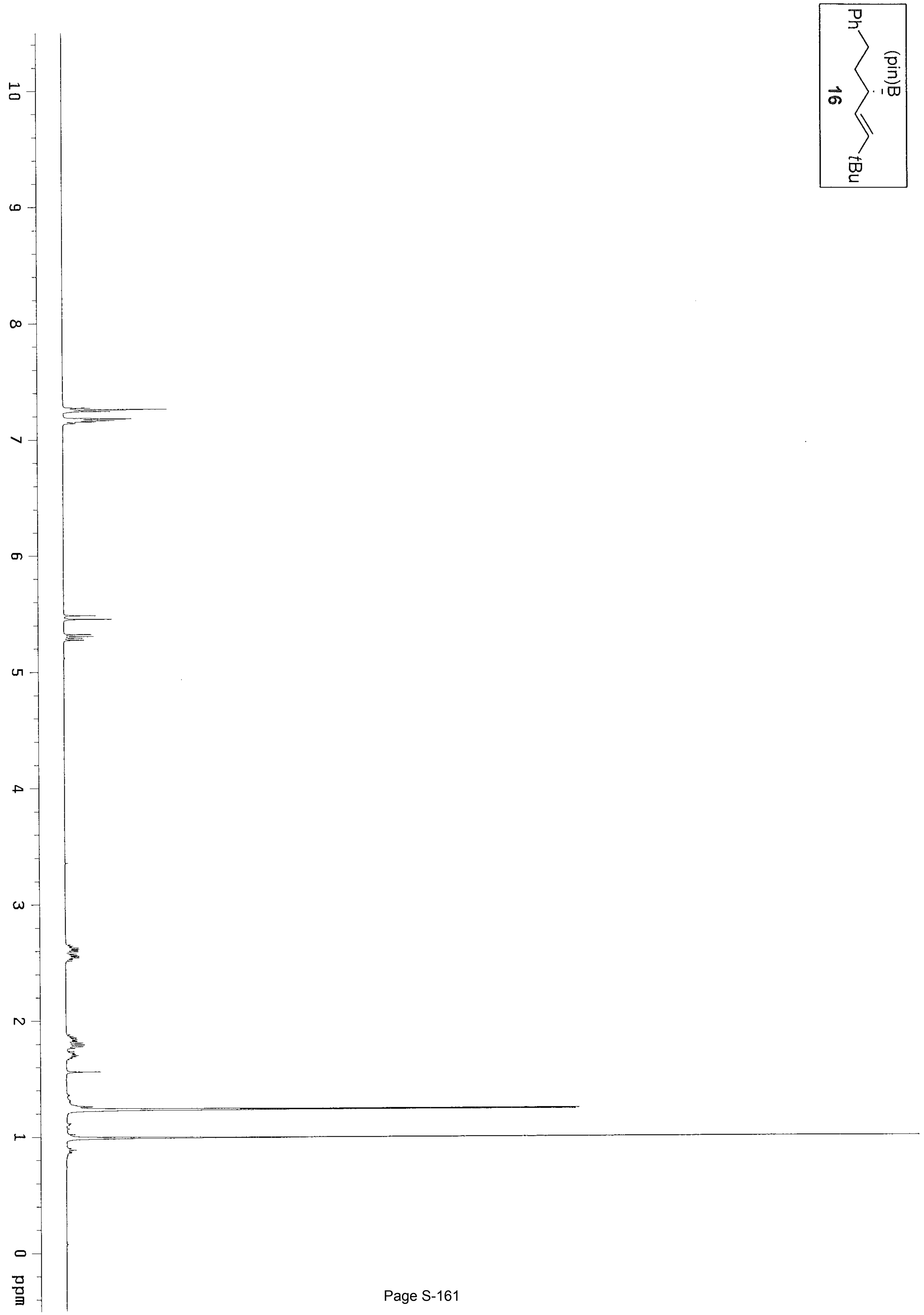

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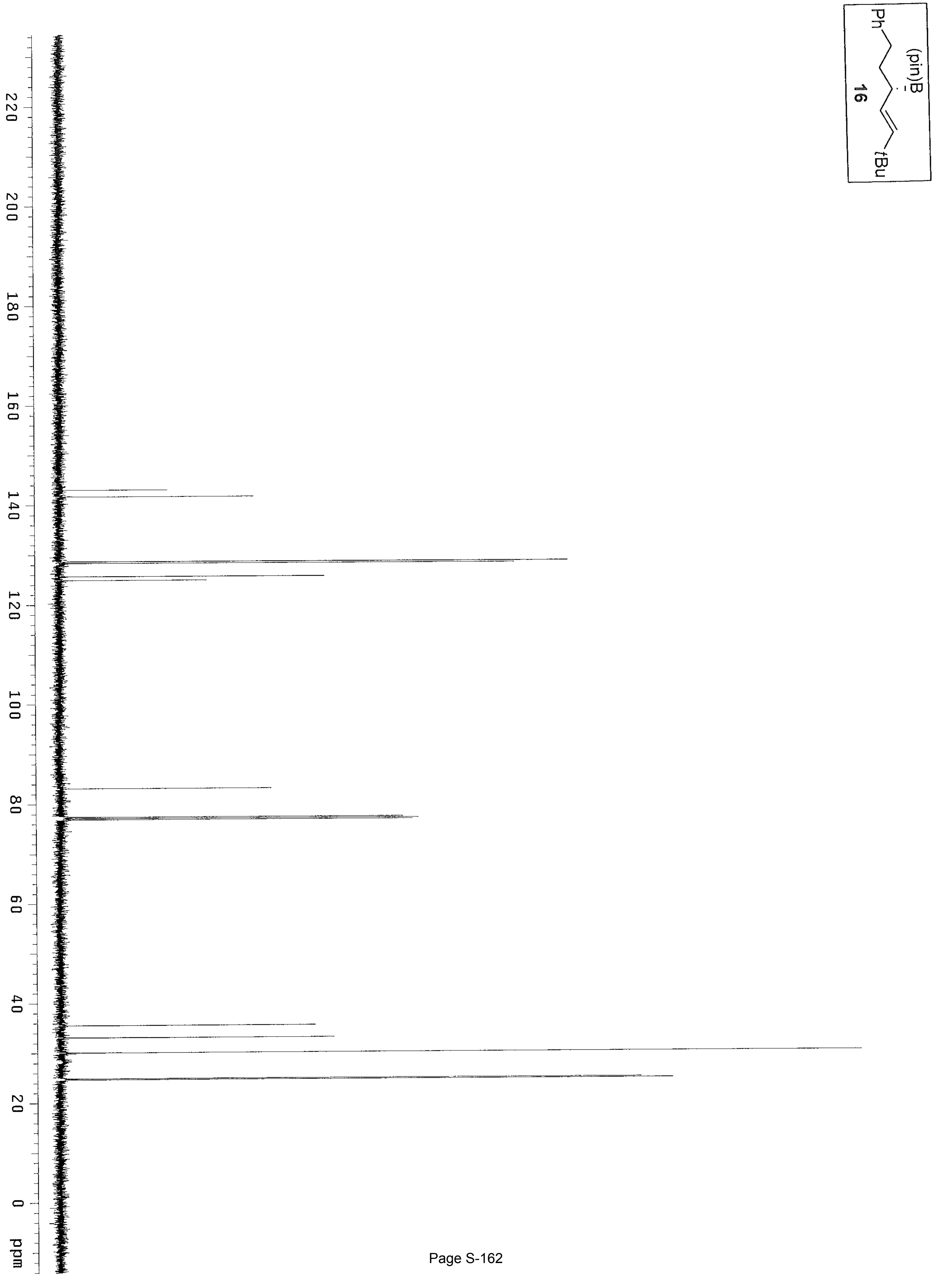
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tBu
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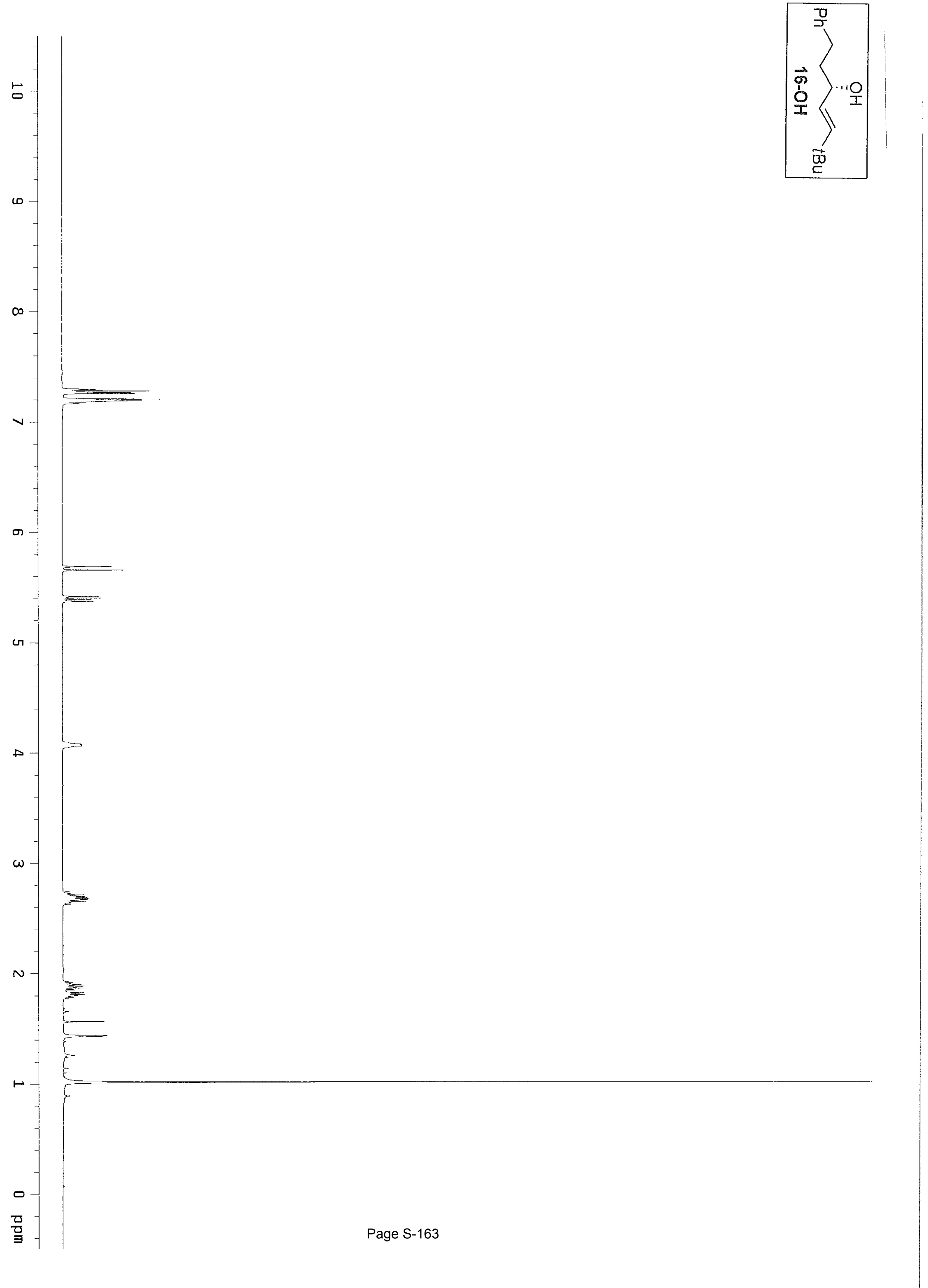
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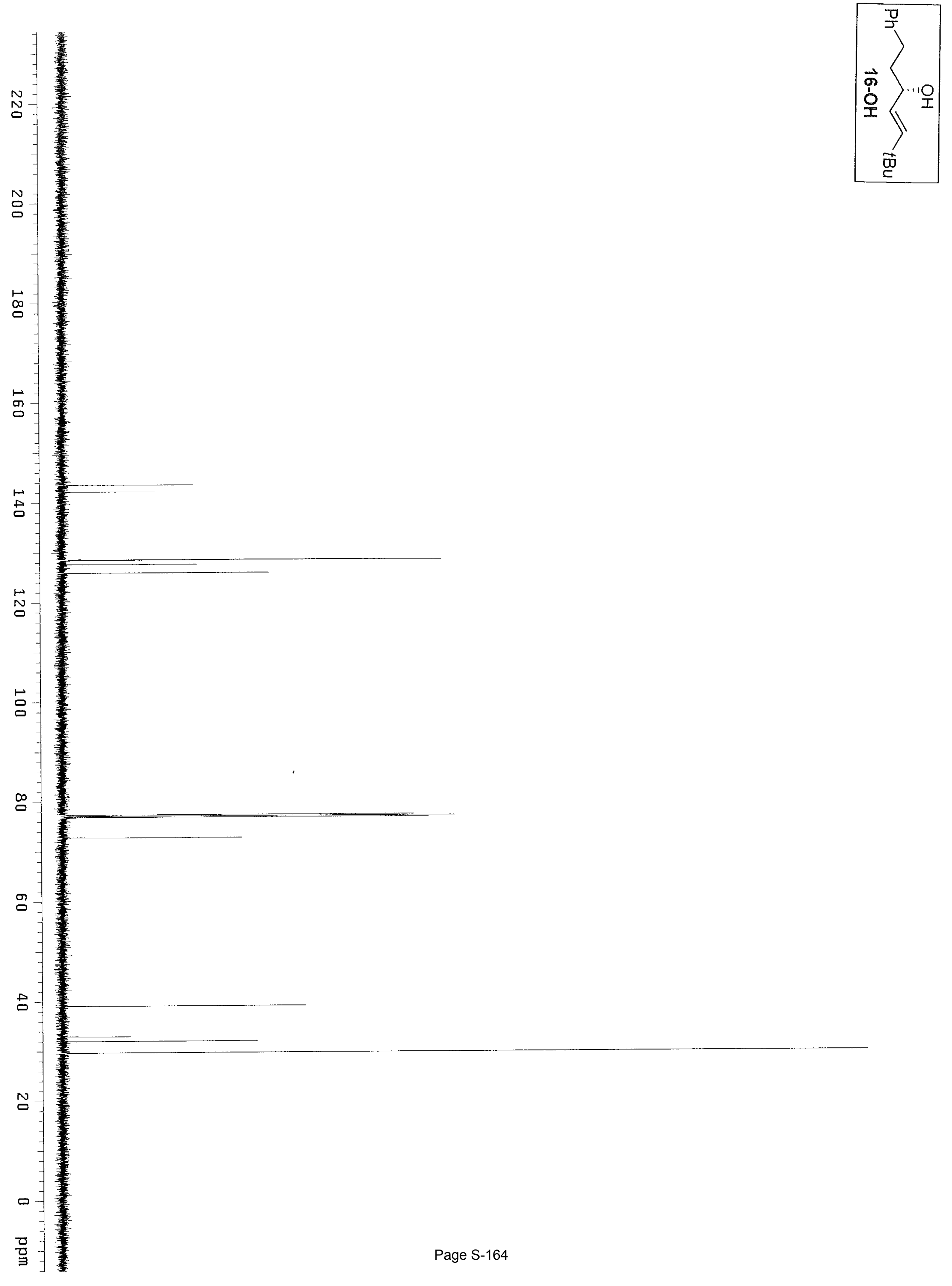
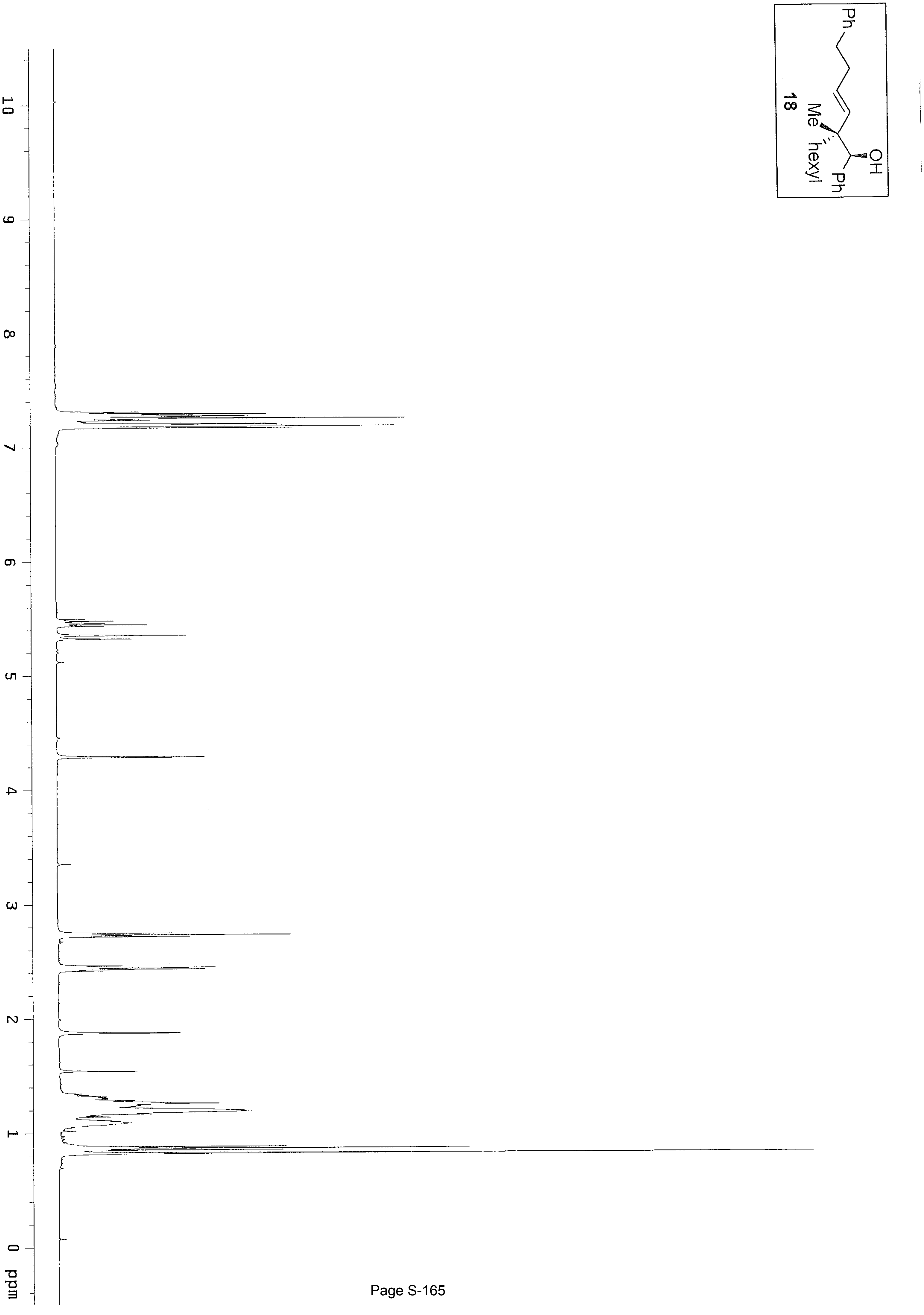


16-OH



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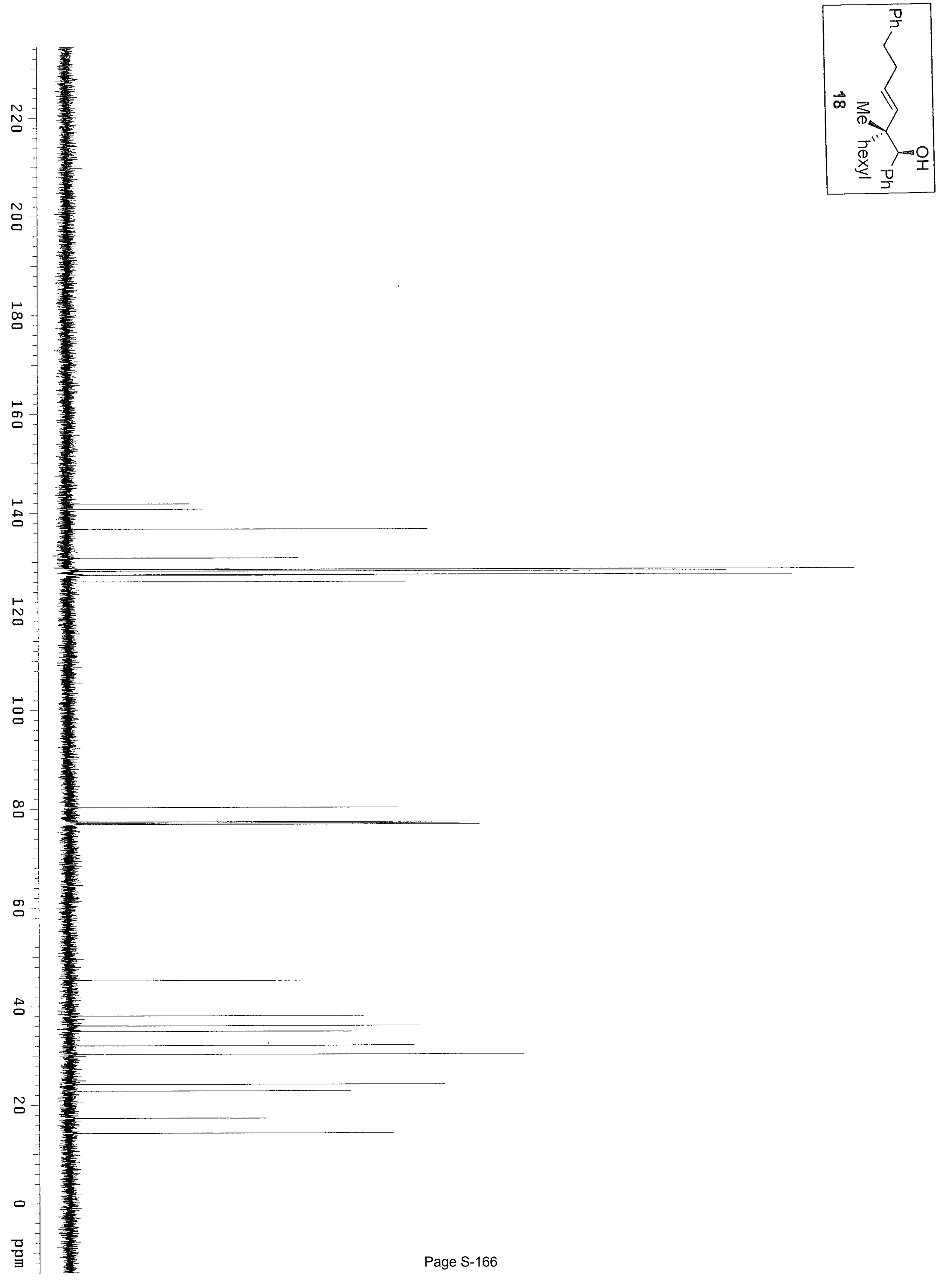
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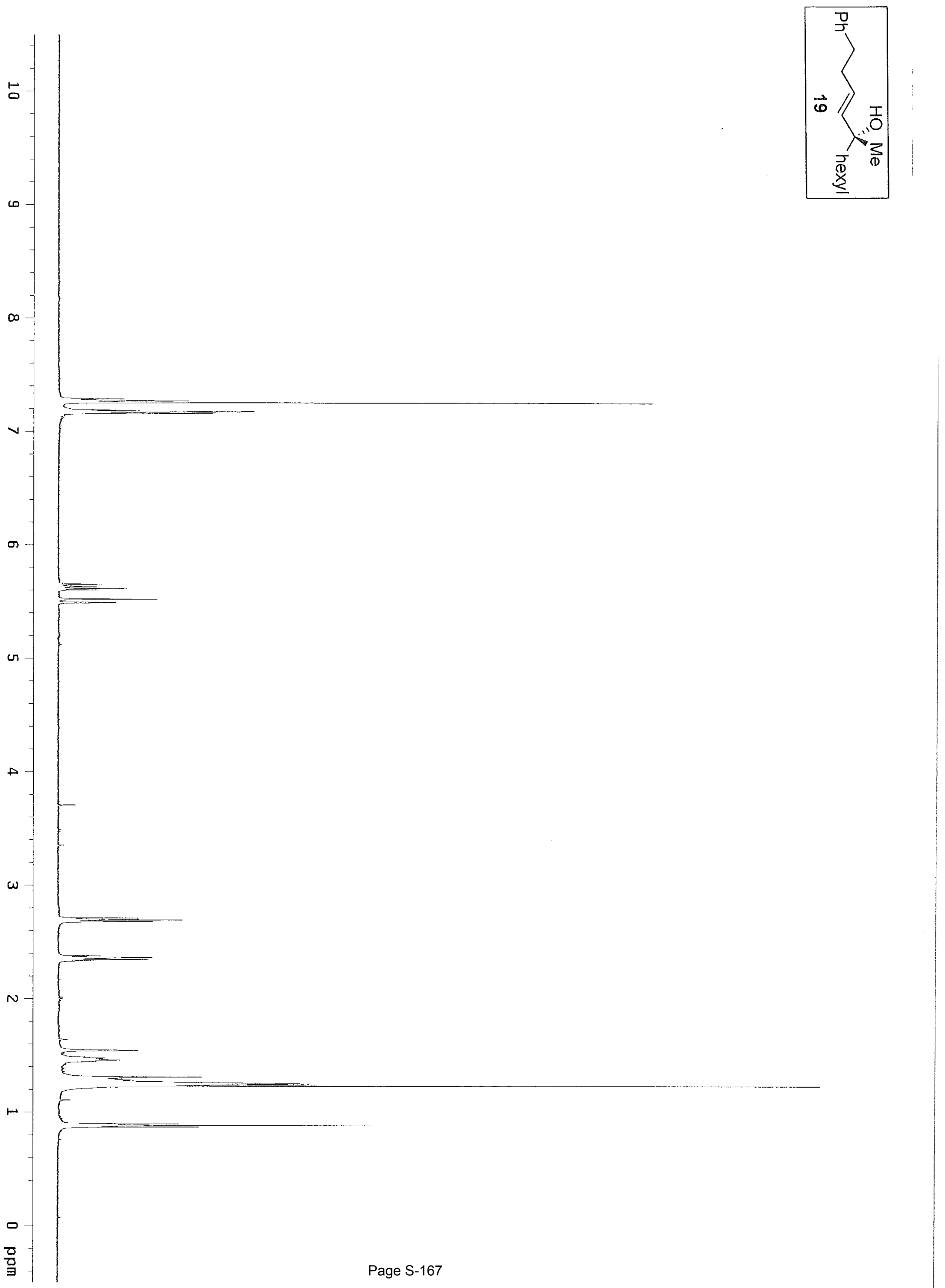

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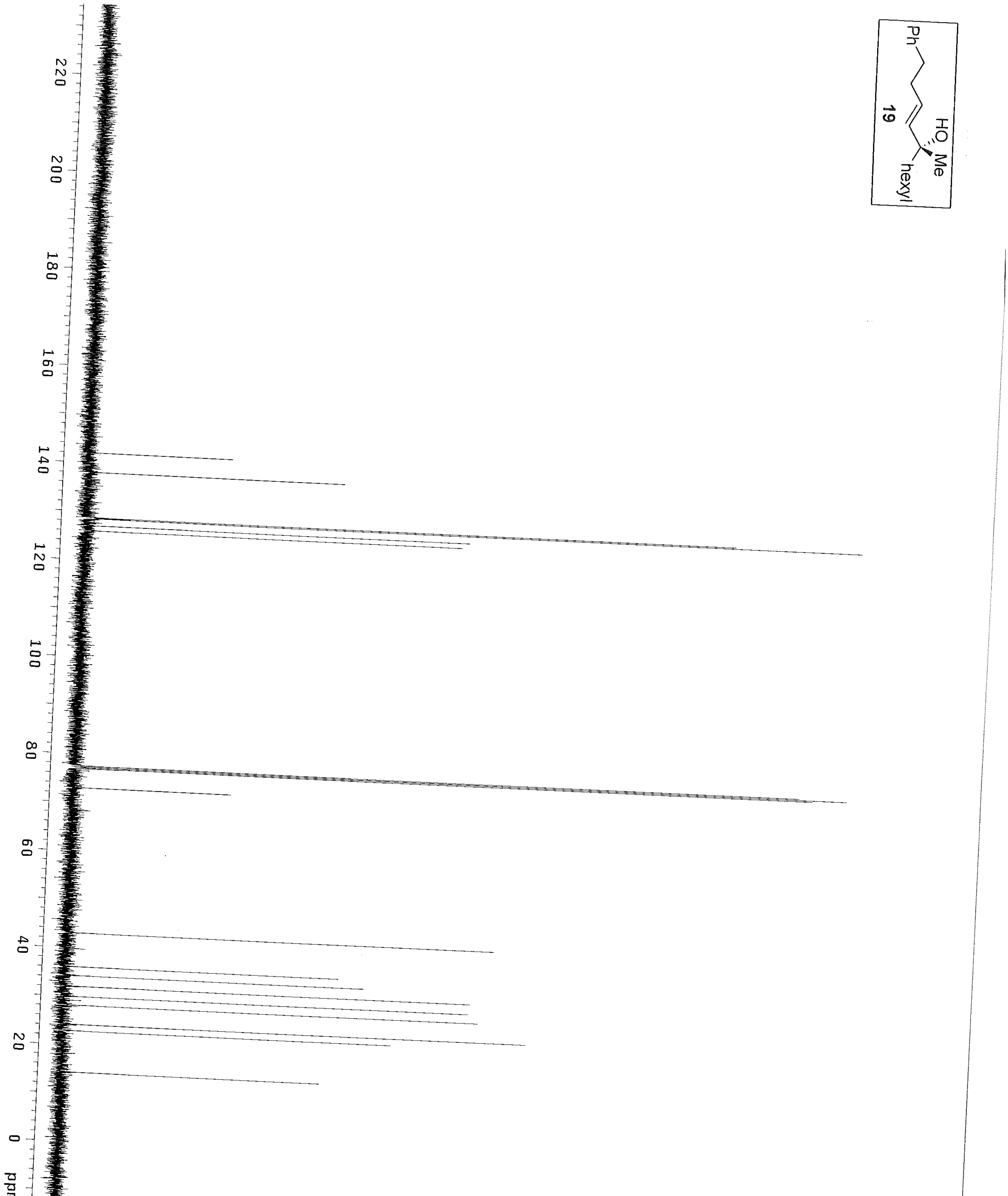
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