Electronic Supplementary Information
for
Regio- and diastereoselective synthesis of multi-substituted silacyclopentanes by catalytic cyclosilylborylation of styryl(vinyl)silanes

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I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under argon. Preparative GPC was performed with JAI LaboACE LC 5060 equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent. NMR spectra were recorded on JEOL JNM-ECZL400S spectrometer. High resolution mass spectra were recorded on JEOL JMS700 or BRUKER micrOTOF II spectrometer. X-ray crystallographic analysis was performed with Rigaku XtaLAB Synergy R DW HyPix system equipped with a Rigaku GNNP low-temperature device. Elemental analysis was performed with YANACO CHN corder MT-6.

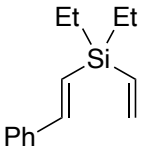
Et_3N (FUJIFILM Wako Chemicals) was distilled over KOH under vacuum. Toluene (Kanto Chemical; dehydrated), CH_2Cl_2 (Kanto Chemical; dehydrated), Et_2O (FUJIFILM Wako Chemicals; dehydrated), THF (Kanto Chemical; dehydrated), DMF (FUJIFILM Wako Chemicals; dehydrated), DMSO (FUJIFILM Wako Chemicals; dehydrated), MeOH (FUJIFILM Wako Chemicals; dehydrated), bromochloromethane (FUJIFILM Wako Chemicals), 1,2-dibromoethane (FUJIFILM Wako Chemicals), β-bromostyrene (TCI), 1-bromo-1-propene (TCI), 1-ethynyl-4-fluorobenzene (TCI), diphenyl disulfide (FUJIFILM Wako Chemicals), chlorodimethylsilane (TCI), chloroldimethylphenylsilane (TCI), chlorodimethylvinylsilane (TCI), dichlorodimethylsilane (TCI), dichlorodiethylsilane (TCI), oxalyl chloride (FUJIFILM Wako Chemicals), (dimethylphenylsilyl)boronic acid pinacol ester (FUJIFILM Wako Chemicals), PPh_3 (FUJIFILM Wako Chemicals), CBr_4 (FUJIFILM Wako Chemicals), H_2O_2 (Kishida Chemical; 35% solution in H_2O), HBF_4•Et_2O (Aldrich), I_2 (FUJIFILM Wako Chemicals), *n*BuLi (Kanto Chemical; 1.51 M solution in hexane), Li*O*tBu (Aldrich), Li wire (Kishida Chemical), $NaN(SiMe_3)_2$ (Chem-Impex International), Na*O*tBu (TCI), NaOEt (TCI), NaOMe (FUJIFILM Wako Chemicals), NaOH (FUJIFILM Wako Chemicals), K*O*tBu (TCI), $KHCO_3$ (FUJIFILM Wako Chemicals), KF (FUJIFILM Wako Chemicals), vinylmagnesium bromide (Aldrich; 1.0 M solution in THF), vinylmagnesium chlororide (FUJIFILM Wako Chemicals; 2.1 M solution in THF), Mg turnings (Nacalai Tesque), and platinum(0)-1,3-divinyltetramethyldisiloxane complex (TCI; 19.0–21.5% Pt in 1,3-divinyltramethylsiloxane) were used as received.

1a,[1] **1d**,[1] **1i**,[1] **2b**,[2] **2c**,[2] (*E*)-1-(2-bromovinyl)-4-methylbenzene,[3] and 2,6-dimethylbenzaldehyde[4] were synthesized following the literature procedures.

II. Synthesis of Substrates

Representative Procedures for Substrates:

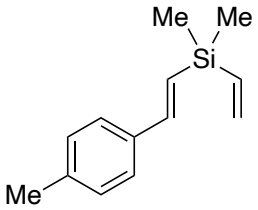
(*E*)-Diethyl(styryl)(vinyl)silane (1b)



I_2 (small pieces) was added to a suspension of Mg turnings (243 mg, 10.0 mmol) in THF (4 mL), and this was stirred for 30 min at room temperature. A solution of β-bromostyrene (1.28 mL, 9.93 mmol) in THF (16 mL) was added to it over 30 min, and the mixture was stirred for 2 h at room temperature. The resulting solution was added over 5 min to a solution of dichlorodiethylsilane (741 μL, 5.00 mmol) in THF (9 mL), and the mixture was stirred for 2 h at room temperature. Vinylmagnesium bromide (6.50 mL, 6.50 mmol; 1.0 M solution in THF) was added over 5 min to the resulting solution and the mixture was stirred for 3.5 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford compound **1b** as a colorless oil (363 mg, 1.68 mmol; 34% yield).

^{1}H NMR ($CDCl_3$): δ 7.49-7.43 (m, 2H), 7.34 (t, $^3J_{HH}$ = 7.5 Hz, 2H), 7.29-7.23 (m, 1H), 6.95 (d, $^3J_{HH}$ = 19.5 Hz, 1H), 6.45 (d, $^3J_{HH}$ = 19.1 Hz, 1H), 6.20 (dd, $^3J_{HH}$ = 20.0 and 14.7 Hz, 1H), 6.10 (dd, $^3J_{HH}$ = 14.6 Hz and $^2J_{HH}$ = 4.4 Hz, 1H), 5.80 (dd, $^3J_{HH}$ = 19.5 Hz and $^2J_{HH}$ = 4.4 Hz, 1H), 1.02 (t, $^3J_{HH}$ = 7.8 Hz, 6H), 0.75 (q, $^3J_{HH}$ = 7.6 Hz, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.9, 138.5, 135.8, 133.6, 128.6, 128.2, 126.5, 124.9, 7.5, 4.2. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 77.45; H, 9.12.

(*E*)-Dimethyl(4-methylstyryl)(vinyl)silane (1e)

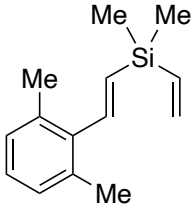


I_2 (small pieces) was added to a suspension of Mg turnings (243 mg, 10.0 mmol) in THF (4 mL), and this was stirred for 30 min at room temperature. A solution of (*E*)-1-(2-bromovinyl)-4-methylbenzene (1.97 g, 10.0 mmol) in THF (16 mL) was added to it over 30 min, and the mixture was stirred for 2 h at room temperature. The resulting solution was added over 2 min to a solution of chlorodimethylvinylsilane (690 μL, 9.59 mmol) in THF (9 mL), and the mixture was stirred for 3 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and

concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford compound **1e** as a colorless oil (634 mg, 3.13 mmol; 62% yield).

^{1}H NMR ($CDCl_3$): δ 7.34 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.14 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 6.88 (d, $^3J_{HH}$ = 19.0 Hz, 1H), 6.39 (d, $^3J_{HH}$ = 19.5 Hz, 1H), 6.23 (dd, $^3J_{HH}$ = 20.0 and 14.7 Hz, 1H), 6.02 (dd, $^3J_{HH}$ = 14.6 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.76 (dd, $^3J_{HH}$ = 20.5 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 2.34 (s, 3H), 0.23 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.9, 138.6, 138.1, 135.7, 132.4, 129.4, 126.5, 126.0, 21.4, –2.8. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 77.12; H, 8.94.

(*E*)-(2,6-Dimethylstyryl)dimethyl(vinyl)silane (1h)



A solution of PPh_3 (2.81 g, 10.7 mmol) in CH_2Cl_2 (8 mL) was added over 10 min to a mixture of 2,6-dimethylbenzaldehyde (552 mg, 4.11 mmol) and CBr_4 (1.80 g, 5.39 mmol) in CH_2Cl_2 (12 mL) at room temperature, and the mixture was stirred for 50 min at room temperature. The precipitates that formed were removed by filtration through Celite and the solvent was removed under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 1/1 to afford 2-(2,2-dibromovinyl)-1,3-dimethylbenzene (CAS 1391469-79-6) as a colorless oil (937 mg, 3.36 mmol; 82% yield).

^{1}H NMR ($CDCl_3$): δ 7.41 (s, 1H), 7.16 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.05 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 2.25 (s, 6H).

*n*BuLi (3.00 mL, 4.53 mmol; 1.51 M solution in hexane) was added over 10 min to a solution of 2-(2,2-dibromovinyl)-1,3-dimethylbenzene (937 mg, 3.23 mmol) in THF (20 mL) at –78 °C, and the mixture was stirred for 20 min at –78 °C and for 4.5 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford 2-ethynyl-1,3-dimethylbenzene (CAS 74331-74-1) as a colorless oil (224 mg, 1.72 mmol; 51% yield).

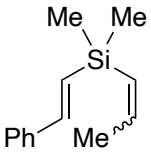
^{1}H NMR ($CDCl_3$): δ 7.14 (dd, $^3J_{HH}$ = 8.3 and 6.8 Hz 1H), 7.05 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 3.51 (s, 1H), 2.46 (s, 6H).

Platinum(0)-1,3-divinyltetramethyldisiloxane complex (14.0 μL, ca. 17.2 μmol; 19.0–21.5% Pt in 1,3-divinyltramethylsiloxane) was added to a solution of chlorodimethylsilane (190 μL, 1.75 mmol) and 2-ethynyl-1,3-dimethylbenzene (224 mg, 1.72 mmol) in toluene (2 mL), and the mixture was stirred for 1.5 h at room temperature. Vinylmagnesium bromide (1.70 mL, 1.70 mmol; 1.0 M solution in THF) was added to it, and the mixture was stirred for 15.5 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was

chromatographed on silica gel with hexane and further purified by GPC with $CHCl_3$ to afford compound **1h** as a colorless oil (179 mg, 0.827 mmol; 48% yield).

^{1}H NMR ($CDCl_3$): δ 7.08-7.00 (m, 3H), 6.93 (d, $^3J_{HH}$ = 19.5 Hz, 1H), 6.25 (dd, $^3J_{HH}$ = 20.5 and 14.6 Hz, 1H), 6.04 (dd, $^3J_{HH}$ = 14.7 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.94 (d, $^3J_{HH}$ = 19.5 Hz, 1H), 5.79 (dd, $^3J_{HH}$ = 20.0 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 2.30 (s, 6H), 0.26 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 143.9, 139.5, 138.5, 135.4, 133.9, 132.4, 127.9, 126.7, 20.9, –2.7. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 77.71; H, 9.26.

Dimethyl(prop-1-en-1-yl)((*E*)-styryl)silane (1m; *E*/*Z* = 13/87)

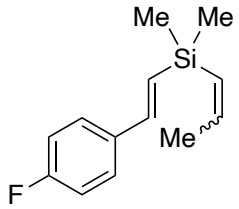


I_2 (small pieces) was added to a suspension of Mg turnings (243 mg, 10.0 mmol) in THF (4 mL), and the mixture was stirred for 30 min at room temperature. A solution of 1-bromo-1-propene (840 μL, 9.93 mmol) in THF (16 mL) was added over 30 min to the resulting mixture, and the mixture was stirred for 4.5 h at room temperature to give a THF solution of 1-propenylmagnesium bromide.

Separately, I_2 (small pieces) was added to a suspension of Mg turnings (243 mg, 10.0 mmol) in THF (4 mL), and the mixture was stirred for 30 min at room temperature. A solution of β-bromostyrene (1.28 mL, 9.93 mmol) in THF (16 mL) was added to it over 30 min, and the mixture was stirred for 3 h at room temperature. This was then added over 5 min to a solution of dichlorodimethylsilane (600 μL, 4.97 mmol) in THF (9 mL), and the mixture was stirred for 1 h at room temperature. The solution of 1-propenylmagnesium bromide obtained above was added to it over 5 min and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford compound **1m** as a colorless oil (237 mg, 1.17 mmol; 24% yield, *E*/*Z* = 13/87).

^{1}H NMR ($CDCl_3$): δ 7.47-7.42 (m, 2H), 7.36-7.30 (m, 2H), 7.28-7.22 (m, 1H), 6.92 (d, $^3J_{HH}$ = 19.1 Hz, 0.87H), 6.89 (d, $^3J_{HH}$ = 19.0 Hz, 0.13H), 6.53 (d, $^3J_{HH}$ = 19.0 Hz, 0.87H), 6.50 (dq, $^3J_{HH}$ = 14.1 and 6.8 Hz, 0.87H), 6.47 (d, $^3J_{HH}$ = 19.1 Hz, 0.13H), 6.15 (dq, $^3J_{HH}$ = 18.5 and 6.1 Hz, 0.13H), 5.72 (dq, $^3J_{HH}$ = 18.5 Hz and $^4J_{HH}$ = 1.6 Hz, 0.13H), 5.58 (dq, $^3J_{HH}$ = 13.7 Hz and $^4J_{HH}$ = 1.5 Hz, 0.87H), 1.85 (dd, $^3J_{HH}$ = 6.4 Hz and $^4J_{HH}$ = 1.4 Hz, 0.39H), 1.82 (dd, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.5 Hz, 2.61H), 0.28 (s, 5.22H), 0.21 (s, 0.78H). ($Z_{propenyl}$)-**1m**: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.8, 144.2, 138.5, 128.64, 128.62, 128.1, 128.0, 126.6, 19.5, –1.1. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 77.35; H, 8.95.

Dimethyl((*E*)-4-fluorostyryl)(prop-1-en-1-yl)silane (1p; *E*/*Z* = 12/88)



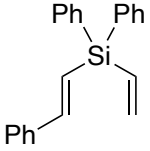
1,2-Dibromoethane (40.0 μL, 0.464 mmol) was added to a suspension of Mg turnings (441 mg, 18.1 mmol) in THF (2 mL), and this was stirred for a while at room temperature until bubbles were observed and ceased. 1-Bromo-1-propene (1.27 mL, 15.0 mmol) was added to it with THF (19 mL) over 35 min and the mixture was stirred for 3 h at room temperature to give a solution of 1-propenylmagnesium bromide (total volume: 22 mL).

Separately, platinum(0)-1,3-divinyltetramethyldisiloxane complex (21.0 μL, ca. 25.8 μmol; 19.0–21.5% Pt in 1,3-divinyltramethylsiloxane) was added to a solution of chlorodimethylsilane (544 μL, 5.00 mmol) and 1-ethynyl-4-fluorobenzene (605 mg, 5.04 mmol) in toluene (5 mL), and the mixture was stirred for 2 h at room temperature. 1-Propenylmagnesium bromide solution obtained above (11 mL, ca. 7.5 mmol) was added to it, and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford compound **1p** as a colorless oil (558 mg, 2.53 mmol; 51% yield, *E*/*Z* = 12/88).

^{1}H NMR ($CDCl_3$): δ 7.47-7.37 (m, 2H), 7.05-6.97 (m, 2H), 6.87 (d, $^3J_{HH}$ = 19.5 Hz, 0.88H), 6.84 (d, $^3J_{HH}$ = 19.0 Hz, 0.12H), 6.50 (dq, $^3J_{HH}$ = 14.1 and 6.8 Hz, 0.88H), 6.42 (d, $^3J_{HH}$ = 19.0 Hz, 0.88H), 6.36 (d, $^3J_{HH}$ = 19.0 Hz, 0.12H), 6.14 (dq, $^3J_{HH}$ = 18.1 and 6.3 Hz, 0.12H), 5.71 (dq, $^3J_{HH}$ = 18.5 Hz and $^4J_{HH}$ = 1.6 Hz, 0.12H), 5.56 (dq, $^3J_{HH}$ = 13.7 Hz and $^4J_{HH}$ = 1.5 Hz, 0.88H), 1.85 (dd, $^3J_{HH}$ = 6.3 Hz and $^4J_{HH}$ = 1.5 Hz, 0.36H), 1.81 (dd, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.5 Hz, 2.64H), 0.27 (s, 5.28H), 0.20 (s, 0.72H). ($Z_{propenyl}$)-**1p**: $^{13}C\{^1H,^{19}F\}$ NMR ($CDCl_3$): δ 162.7, 144.8, 142.9, 134.8, 128.3, 128.1, 127.9, 115.5, 19.5, –1.1. ^{19}F NMR ($CDCl_3$): δ –114.1 (tt, $^3J_{HH}$ = 8.6 Hz and $^4J_{HH}$ = 5.4 Hz). HRMS (FD) calcd for $C_{13}H_{17}FSi$ (M^+) 220.1078, found 220.1088.

Analytical Data for Other Substrates:

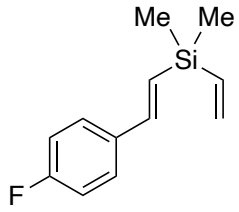
(*E*)-diphenyl(styryl)(vinyl)silane (1c).



^{1}H NMR ($CDCl_3$): δ 7.63-7.57 (m, 4H), 7.51-7.46 (m, 2H), 7.46-7.25 (m, 9H), 7.01 (d, $^3J_{HH}$ = 19.0 Hz, 1H), 6.78 (d, $^3J_{HH}$ = 19.1 Hz, 1H), 6.58 (dd, $^3J_{HH}$ = 20.5 and 14.6 Hz, 1H), 6.31 (dd, $^3J_{HH}$ = 14.6 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.86 (dd, $^3J_{HH}$ = 20.5 Hz and $^2J_{HH}$ = 3.9 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$):

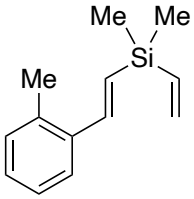
δ 148.8, 138.2, 136.7, 135.7, 134.7, 134.2, 129.7, 128.7, 128.6, 128.1, 126.9, 123.0. Anal. Calcd for $C_{22}H_{20}Si$: C, 84.56; H, 6.45. Found: C, 84.71; H, 6.55.

(*E*)-(4-Ffluorostyryl)dimethyl(vinyl)silane (1f)



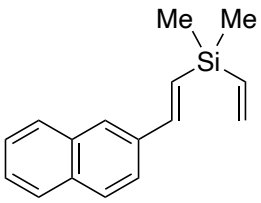
^{1}H NMR ($CDCl_3$): δ 7.41 (dd, $^3J_{HH}$ = 8.8 Hz and $^4J_{HF}$ = 5.4 Hz, 2H), 7.02 (t, ^3J = 8.5 Hz, 2H), 6.86 (d, $^3J_{HH}$ = 19.1 Hz, 1H), 6.36 (d, $^3J_{HH}$ = 19.1 Hz, 1H), 6.22 (dd, $^3J_{HH}$ = 20.5 and 14.7 Hz, 1H), 6.03 (dd, $^3J_{HH}$ = 14.6 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.76 (dd, $^3J_{HH}$ = 20.0 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 0.24 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.8 (d, $^1J_{CF}$ = 247 Hz), 143.6, 138.3, 134.7 (d, $^4J_{CF}$ = 3.0 Hz), 132.6, 128.1 (d, $^3J_{CF}$ = 8.0 Hz), 127.1 (d, $^5J_{CF}$ = 2.0 Hz), 115.5 (d, $^2J_{CF}$ = 22.1 Hz), –2.8. HRMS (APCI) calcd for $C_{12}H_{16}FSi$ ($M+H^+$) 207.1000, found 207.0996.

(*E*)-dimethyl(2-methylstyryl)(vinyl)silane (1g).



^{1}H NMR ($CDCl_3$) δ: 7.56-7.50 (m, 1H), 7.22-7.11 (m, 4H), 6.37 (d, $^3J_{HH}$ = 19.1 Hz, 1H), 6.24 (dd, $^3J_{HH}$ = 20.5 and 14.7 Hz, 1H), 6.04 (dd, $^3J_{HH}$ = 14.7 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.78 (dd, $^3J_{HH}$ = 20.5 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 2.38 (s, 3H), 0.25 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.7, 138.5, 137.7, 135.5, 132.5, 130.5, 129.2, 128.0, 126.2, 125.5, 19.7, –2.7. Anal. Calcd for $C_{13}H_{18}Si$: C, 77.16; H, 8.97. Found: C, 77.24; H, 8.88.

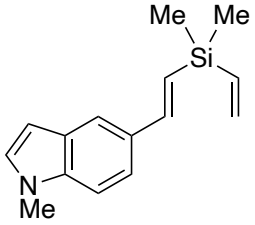
(*E*)-dimethyl(2-(naphthalen-2-yl)vinyl)(vinyl)silane (1j)



^{1}H NMR ($CDCl_3$): δ 7.86-7.76 (m, 4H), 7.69 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 2.0 Hz, 1H), 7.51-7.42 (m, 2H), 7.10 (d, $^3J_{HH}$ = 19.5 Hz, 1H), 6.60 (d, $^3J_{HH}$ = 19.0 Hz, 1H), 6.27 (dd, $^3J_{HH}$ = 20.5 and 14.6 Hz, 1H), 6.06 (dd, $^3J_{HH}$ = 14.6 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.81 (dd, $^3J_{HH}$ = 20.0 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 0.29 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.0, 138.4, 135.8, 133.7, 133.5, 132.6, 128.34, 128.28, 127.9,

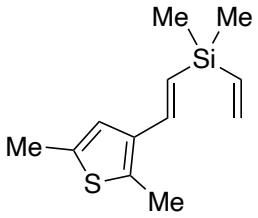
127.8, 126.9, 126.4, 126.1, 123.5, –2.7. Anal. Calcd for $C_{16}H_{18}Si$: C, 80.61; H, 7.61. Found: C, 80.50; H, 7.52.

(*E*)-5-(2-(Dimethyl(vinyl)silyl)vinyl)-1-methyl-1*H*-indole (1k)



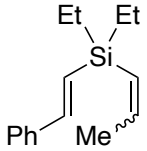
^{1}H NMR ($CDCl_3$): δ 7.68 (d, $^4J_{HH}$ = 1.5 Hz, 1H), 7.42 (dd, $^3J_{HH}$ = 8.8 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.27 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 7.05 (d, $^3J_{HH}$ = 19.0 Hz, 1H), 7.03 (d, $^3J_{HH}$ = 3.4 Hz, 1 H), 6.48 (dd, $^3J_{HH}$ = 2.9 Hz and $^4J_{HH}$ = 1.0 Hz, 1H), 6.38 (d, $^3J_{HH}$ = 19.1 Hz, 1H), 6.27 (dd, $^3J_{HH}$ = 20.5 and 14.6 Hz, 1H), 6.03 (dd, $^3J_{HH}$ = 14.6 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.78 (dd, $^3J_{HH}$ = 20.0 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 3.79 (s, 3H), 0.26 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.3, 139.0, 137.0, 132.1, 130.3, 129.5, 128.7, 123.2, 120.2, 119.9, 109.3, 101.6, 33.1, –2.7. HRMS (APCI) calcd for $C_{15}H_{20}NSi$ ($M+H^+$) 242.1360, found 242.1359.

(*E*)-(2-(2,5-Dimethylthiophen-3-yl)vinyl)dimethyl(vinyl)silane (1l)



^{1}H NMR ($CDCl_3$): δ 6.85 (s, 1H), 6.82 (d, $^3J_{HH}$ = 19.0 Hz, 1H), 6.21 (dd, $^3J_{HH}$ = 20.0 and 14.6 Hz, 1H), 6.06 (d, $^3J_{HH}$ = 18.5 Hz, 1H), 6.01 (dd, $^3J_{HH}$ = 14.7 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.75 (dd, $^3J_{HH}$ = 20.5 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H), 0.21 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.7, 137.0, 136.8, 135.9, 134.3, 132.3, 125.6, 123.2, 15.3, 13.0, –2.7. Anal. Calcd for $C_{12}H_8SSi$: C, 64.80; H, 8.16. Found: C, 64.69; H, 8.07.

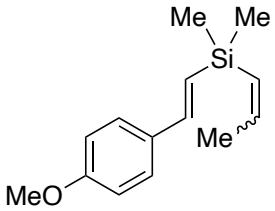
Diethyl(prop-1-en-1-yl)((*E*)-styryl)silane (1n; *E*/*Z* = 16/84)



^{1}H NMR ($CDCl_3$): δ 7.45 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.33 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.25 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.94 (d, $^3J_{HH}$ = 19.0 Hz, 0.84H), 6.91 (d, $^3J_{HH}$ = 19.0 Hz, 0.16H), 6.57 (dq, $^3J_{HH}$ = 14.1 and 6.8 Hz, 0.84H), 6.49 (dd, $^3J_{HH}$ = 19.1 Hz and $^4J_{HH}$ = 1.0 Hz, 0.84H), 6.44 (dd, $^3J_{HH}$ = 18.5 Hz, 0.16H), 6.17 (dqd, $^3J_{HH}$ = 18.5 and 6.4 Hz and $^4J_{HH}$ = 1.0 Hz, 0.16H), 5.73-5.65 (m, 0.16H), 5.58-5.52 (m,

0.84H), 1.88-1.85 (m, 0.48H), 1.83-1.78 (m, 2.52H), 1.05-0.96 (m, 6H), 0.77 (q, $^3J_{HH}$ = 8.0 Hz, 3.36H), 0.70 (q, $^3J_{HH}$ = 7.8 Hz, 0.64H). ($Z_{propenyl}$)-**1n**: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.6, 145.1, 138.7, 128.6, 128.1, 126.5, 126.2, 125.4, 19.9, 7.6, 5.5. HRMS (ESI) calcd for $C_{15}H_{21}Si$ ($M–H^-$) 229.1407, found 229.1411.

Dimethyl((*E*)-4-methoxystyryl)(prop-1-en-1-yl)silane (1o; *E*/*Z* = 14/86)

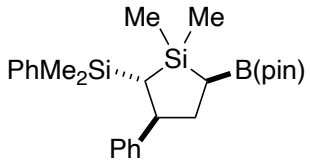


^1H NMR ($CDCl_3$): δ 7.43-7.35 (m, 2H), 6.90-6.83 (m, 3H), 6.49 (dq, $^3J_{HH}$ = 14.1 and 6.8 Hz, 0.86H), 6.34 (d, $^3J_{HH}$ = 19.0 Hz, 0.86H), 6.28 (d, $^3J_{HH}$ = 19.1 Hz, 0.14H), 6.14 (dq, $^3J_{HH}$ = 18.5 and 6.4 Hz, 0.14H), 5.71 (dq, $^3J_{HH}$ = 18.5 Hz and $^4J_{HH}$ = 1.6 Hz, 0.14H), 5.57 (dq, $^3J_{HH}$ = 14.1 Hz and $^4J_{HH}$ = 1.5 Hz, 0.86H), 3.81 (s, 3H), 1.84 (dd, $^3J_{HH}$ = 6.3 Hz and $^4J_{HH}$ = 1.4 Hz, 0.42H), 1.81 (dd, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.4 Hz, 2.58H), 0.26 (s, 5.16H), 0.19 (s, 0.84H). ($Z_{propenyl}$)-**1o**: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 159.7, 144.5, 143.6, 131.6, 128.2, 127.8, 125.7, 114.0, 55.4, 19.5, –1.0. HRMS (FD) calcd for $C_{14}H_{20}OSi$ (M^+) 232.1278, found 232.1287.

III. Catalytic Reactions and Derivatizations

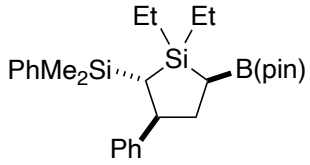
General Procedure for Scheme 2.

Styryl(vinyl)silane **1** (0.200 mmol) and silylboronate **2** (0.240 mmol) were added with the aid of THF (0.7 mL) to a solution of NaO*t*Bu (3.8 mg, 40 μmol) in THF (0.3 mL), and the mixture was stirred for 3 h at 50 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **3**.



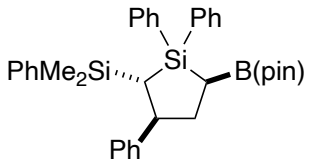
Compound 3aa. The reaction was conducted for 16 h at 10 °C. Colorless oil. 79% yield (71.2 mg, 0.158 mmol; dr = 91/9). The reaction could be scaled up using 2.50 mmol of **1a** to give **3aa** in 89% yield (1.00 g, 2.23 mmol; dr = 91/9).

^{1}H NMR ($CDCl_3$): δ 7.39-7.31 (m, 2H), 7.30-7.16 (m, 7H), 7.15-7.07 (m, 1H), 3.13 (ddd, $^3J_{HH}$ = 11.7, 10.7, and 5.4 Hz, 0.09H), 2.70 (td, $^3J_{HH}$ = 12.7 and 4.4 Hz, 0.91H), 2.25-2.10 (m, 1H), 1.77-1.63 (m, 1H), 1.21 (s, 6.54H), 1.19 (s, 5.46H), 0.72 (dd, $^3J_{HH}$ = 8.8 and 2.9 Hz, 0.09H), 0.59-0.51 (m, 1H), 0.47 (dd, $^3J_{HH}$ = 13.1 and 6.3 Hz, 0.91H), 0.20 (s, 0.27H), 0.17 (s, 2.73H), 0.08 (s, 2.73H), 0.05 (s, 0.27H), 0.02 (s, 0.27H), –0.03 (s, 2.73H), –0.15 (s, 0.27H), –0.18 (s, 2.73H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.0, 140.2, 133.8, 128.6, 128.2, 127.49, 127.47, 126.0, 82.7, 51.0, 41.4, 25.3, 25.0, 23.5, 0.6, –0.2, –0.9, –2.8. HRMS (FAB) calcd for $C_{26}H_{39}BO_2Si_2$ (M^+) 450.2576, found 450.2579.



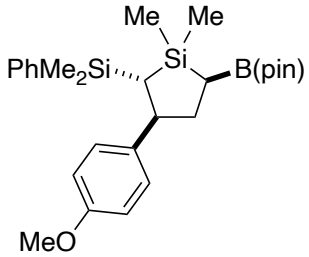
Compound 3ba. Colorless oil. 85% yield (81.4 mg, 0.170 mmol; dr = 87/13). The relative configuration of the major diastereomer was determined by X-ray crystallographic analysis.

^{1}H NMR ($CDCl_3$): δ 7.39-7.32 (m, 2H), 7.27-7.15 (m, 7H), 7.14-7.04 (m, 1H), 3.22 (td, $^3J_{HH}$ = 11.7 and 5.4 Hz, 0.13H), 2.70 (td, $^3J_{HH}$ = 12.4 and 4.4 Hz, 0.87H), 2.22-2.11 (m, 1H), 1.73-1.59 (m, 1H), 1.23 (s, 0.78H), 1.22 (s, 6H), 1.19 (s, 5.22H), 0.96 (t, $^3J_{HH}$ = 8.0 Hz, 3H), 0.92 (t, $^3J_{HH}$ = 7.8 Hz, 2.61H), 0.86 (t, $^3J_{HH}$ = 8.0 Hz, 0.39H), 0.75-0.26 (m, 6H), 0.19 (s, 0.39H), 0.16 (s, 2.61H), –0.14 (s, 2.61H), –0.15 (s, 0.39H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.3, 140.4, 133.7, 128.5, 128.2, 127.5, 126.0, 82.6, 51.2, 42.1, 25.4, 24.8, 19.8, 8.0, 7.8, 7.2, 5.6, –0.8, –2.2. HRMS (FAB) calcd for $C_{28}H_{43}BO_2Si_2$ (M^+) 478.2889, found 478.2894.



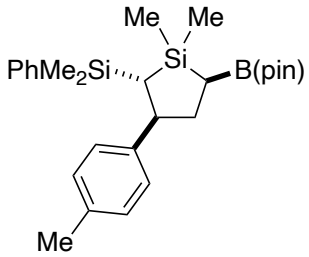
Compound 3ca. Colorless oil. 76% yield (87.4 mg, 0.152 mmol; dr = 89/11).

^{1}H NMR ($CDCl_3$): δ 7.73-7.67 (m, 1.78H), 7.61 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 0.22H), 7.46-7.34 (m, 6H), 7.33-7.06 (m, 8.22H), 7.03-6.94 (m, 2H), 6.88 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1.78H), 3.63-3.55 (m, 0.11H), 2.96 (td, $^3J_{HH}$ = 12.9 and 4.9 Hz, 0.89H), 2.50 (ddd, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 7.3 and 6.4 Hz, 0.11H), 2.38 (ddd, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 7.3 and 4.9 Hz, 0.89H), 2.06-1.86 (m, 1H), 1.41 (d, $^3J_{HH}$ = 12.7 Hz, 0.89H), 1.33-1.23 (m, 1.11H), 1.11 (s, 0.66H), 0.90 (m, 5.34H), 0.88 (s, 0.66H), 0.80 (s, 5.34H), 0.01 (s, 0.33H), –0.03 (s, 0.33H), –0.23 (s, 2.67H), –0.36 (s, 2.67H). Major diastereomer: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.3, 139.7, 136.6, 136.2, 135.23, 135.18, 133.8, 129.6, 129.5, 128.2, 128.1, 127.64, 127.60, 127.1, 126.2, 82.6, 50.9, 42.1, 24.9, 24.8, 21.2, –1.4, –2.4. HRMS (FAB) calcd for $C_{36}H_{43}BO_2Si_2$ (M^+) 574.2889, found 574.2905.



Compound 3da. The reaction was conducted for 16 h. Colorless oil. 85% yield (83.5 mg, 0.170 mmol; dr = 88/12).

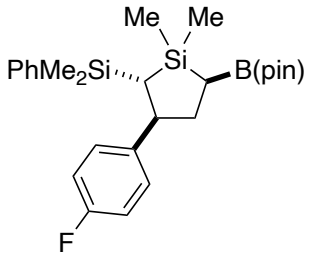
^{1}H NMR ($CDCl_3$): δ 7.38-7.29 (m, 2H), 7.29-7.20 (m, 3H), 7.12-7.05 (m, 2H), 6.77-6.69 (m, 2H), 3.77 (s, 3H), 3.09 (td, $^3J_{HH}$ = 11.2 and 5.4 Hz, 0.12H), 2.66 (td, $^3J_{HH}$ = 12.4 and 4.4 Hz, 0.88H), 2.21-2.07 (m, 1H), 1.72-1.58 (m, 1H), 1.21 (s, 6.72H), 1.19 (s, 5.28H), 0.71 (dd, $^3J_{HH}$ = 8.3 and 2.9 Hz, 0.12H), 0.53-0.40 (m, 1.88H), 0.20 (s, 0.36H), 0.17 (s, 2.64H), 0.08 (s, 2.64H), 0.05 (s, 0.36H), 0.02 (s, 0.36H), –0.02 (s, 2.64H), –0.11 (s, 0.36H), –0.14 (s, 2.64H). Major diastereomer: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.9, 140.3, 139.1, 133.7, 128.5, 128.2, 127.4, 113.5, 82.7, 55.3, 50.2, 41.5, 25.3, 25.0, 23.7, 0.6, –0.2, –1.0, –2.7. HRMS (FAB) calcd for $C_{27}H_{41}BO_3Si_2$ (M^+) 480.2682, found 480.2678.



Compound 3ea. The reaction was conducted for 16 h at 10 °C. Colorless oil. 82% yield (73.6 mg,

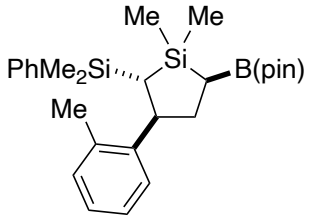
0.164 mmol; dr = 89/11).

^{1}H NMR ($CDCl_3$): δ 7.38-7.31 (m, 2H), 7.30-7.21 (m, 3H), 7.11-7.05 (m, 2H), 7.04-6.96 (m, 2H), 3.11 (td, $^3J_{HH}$ = 11.0 and 5.9 Hz, 0.11H), 2.67 (td, $^3J_{HH}$ = 12.7 and 4.4 Hz, 0.89H), 2.30 (s, 0.33H), 2.29, (s, 2.67H), 2.21-2.08 (m, 1H), 1.75-1.62 (m, 1H), 1.21 (s, 6H), 1.20 (s, 0.66H), 1.19 (s, 5.34H), 0.71 (dd, $^3J_{HH}$ = 8.3 and 3.4 Hz, 0.11H), 0.54 (d, $^3J_{HH}$ = 12.2 Hz, 0.11H), 0.53 (d, $^3J_{HH}$ = 12.7 Hz, 0.89H), 0.46 (dd, $^3J_{HH}$ = 13.2 and 6.8 Hz, 0.89H), 0.21 (s, 0.33H), 0.17 (s, 2.67H), 0.07 (s, 2.67H), 0.05 (s, 0.33H), 0.02 (s, 0.33H), –0.02 (s, 2.67H), –0.13 (s, 0.33H), –0.16 (s, 2.67H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ146.4, 140.3, 133.8, 128.5, 128.1, 128.0, 127.5, 126.0, 82.7, 57.6, 46.8, 25.4, 25.3, 24.7, 21.9, 0.4, –0.2, –1.1, –3.0. HRMS (FAB) calcd for $C_{27}H_{41}BO_2Si_2$ (M^+) 464.2733, found 464.2743.



Compound 3fa. Colorless oil. 87% yield (81.5 mg, 0.174 mmol; dr = 89/11).

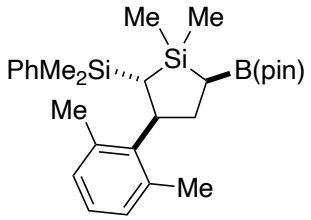
^{1}H NMR ($CDCl_3$): δ 7.34-7.19 (m, 5H), 7.13-7.07 (m, 2H), 6.88-6.80 (m, 2H), 3.09 (td, $^3J_{HH}$ = 11.5 and 5.8 Hz, 0.11H), 2.68 (td, $^3J_{HH}$ = 12.7 and 4.4 Hz, 0.89H), 2.20-2.08 (m, 1H), 1.69-1.56 (m, 1H), 1.222 (s, 0.66H), 1.216 (s, 5.34H), 1.21 (s, 0.66H), 1.19 (s, 5.34H), 0.72 (dd, $^3J_{HH}$ = 8.8 and 2.9 Hz, 0.11H), 0.52-0.43 (m, 1.89H), 0.20 (s, 0.33H), 0.17 (s, 2.67H), 0.10 (s, 2.67H), 0.07 (s, 0.33H), 0.05 (s, 0.33H), 0.00 (s, 2.67H), –0.09 (s, 0.33H), –0.11 (s, 2.67H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.4 (d, $^1J_{CF}$ = 242 Hz), 142.6 (d, $^4J_{CF}$ = 3.0 Hz), 140.0, 133.7, 128.7 (d, $^3J_{CF}$ = 8.1 Hz), 128.5, 127.5, 114.8 (d, $^2J_{CF}$ = 21.1 Hz), 82.8, 50.2, 41.5, 25.3, 25.0, 23.8, 0.6, –0.2, –1.3, –2.5. HRMS (FAB) calcd for $C_{26}H_{39}BFO_2Si_2$ ($M+H^+$) 469.2560, found 469.2570.



Compound 3ga. Colorless oil. 82% yield (73.6 mg, 0.164 mmol; dr = 94/6).

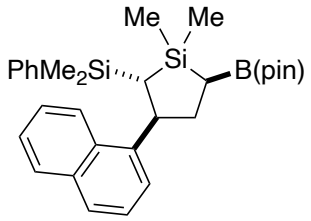
^{1}H NMR ($CDCl_3$): δ 7.38-7.30 (m, 2H), 7.30-7.18 (m, 4H), 7.10-6.96 (m, 3H), 3.45 (td, $^3J_{HH}$ = 11.7 and 4.9 Hz, 0.06H), 2.99 (td, $^3J_{HH}$ = 12.4 and 4.4 Hz, 0.94H), 2.37 (s, 0.18H), 2.27 (s, 2.82H), 2.13 (ddd, $^2J_{HH}$ = 12.7 Hz and $^3J_{HH}$ = 6.4 and 4.4 Hz, 1H), 1.58-1.41 (m, 1H), 1.23 (s, 0.36H), 1.22 (s, 0.36H), 1.21 (s, 5.64H), 1.18 (s, 5.64H), 0.73-0.64 (m, 1.06H), 0.48 (dd, $^3J_{HH}$ = 13.7 and 6.8 Hz, 0.94H), 0.21 (s, 0.18H), 0.19 (s, 2.82H), 0.114 (s, 2.82H), 0.106 (s, 0.18H), 0.05 (s, 0.18H), 0.01 (s,

2.82H), –0.13 (s, 3H). Major diastereomer: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ. 144.7, 140.1, 134.7, 133.7, 130.0, 128.6, 127.5, 126.4, 125.9, 125.5, 82.7, 45.0, 40.8, 25.3, 25.0, 21.8, 19.8, 0.7, –0.0, –0.7, –2.3. HRMS (FAB) calcd for $C_{27}H_{41}BO_2Si_2$ (M^+) 464.2733, found 464.2726.



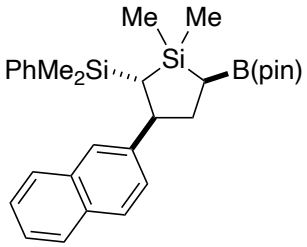
Compound 3ha. The reaction was conducted for 16 h. Colorless oil. 73% yield (67.5 mg, 0.146 mmol; dr = 94/6).

^{1}H NMR ($CDCl_3$): δ 7.34-7.29 (m, 2H), 7.29-7.19 (m, 3H), 6.95-6.86 (m, 2H), 6.84-6.78 (m, 1H), 3.60 (td, $^{3}J_{HH}$ = 13.2 and 5.8 Hz, 0.06H), 3.22 (dt, $^{3}J_{HH}$ = 13.7 and 8.8 Hz, 0.94H), 2.41 (s, 3H), 2.37 (s, 0.18H), 2.27 (s, 2.82H), 2.12-1.95 (m, 2H), 1.25 (s, 0.36H), 1.23 (s, 0.36H), 1.21 (s, 5.64H), 1.19 (s, 5.64H), 1.16-1.06 (m, 1H), 0.71 (d, $^{3}J_{HH}$ = 6.8 Hz, 0.06H), 0.48 (t, $^{3}J_{HH}$ = 9.8 Hz, 0.94H), 0.26 (s, 0.18H), 0.23 (s, 2.82H), 0.13 (s, 2.82H), 0.08 (s, 0.18H), 0.04 (s, 0.18H), –0.01 (s, 2.82H), –0.14 (s, 2.82H), –0.19 (s, 0.18H). Major diastereomer: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 141.7, 140.2, 136.6, 135.9, 133.6, 130.6, 128.5, 128.4, 127.5, 125.6, 82.7, 45.8, 35.0, 25.3, 25.0, 22.3, 21.8, 17.9, 0.6, 0.3, –1.2, –2.7. HRMS (FAB) calcd for $C_{28}H_{43}BO_2Si_2$ (M^+) 478.2889, found 478.2892.



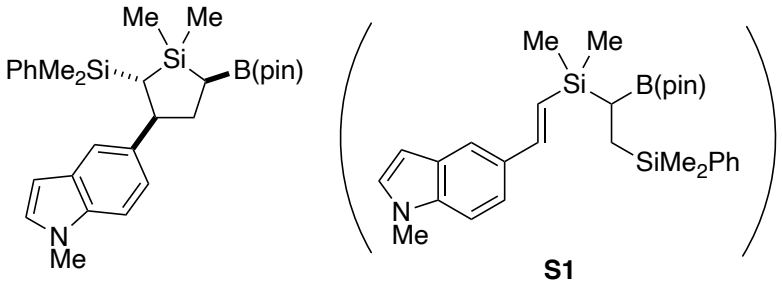
Compound 3ia. Colorless oil. 79% yield (79.1 mg, 0.158 mmol; dr = 93/7).

^{1}H NMR ($CDCl_3$): δ 8.52 (d, $^{3}J_{HH}$ = 8.3 Hz, 0.07H), 8.15 (d, $^{3}J_{HH}$ = 8.3 Hz, 0.93H), 7.88-7.80 (m, 1H), 7.68-7.60 (m, 1H), 7.56-7.40 (m, 3H), 7.35-7.13 (m, 6H), 4.17 (td, $^{3}J_{HH}$ = 11.5 and 3.9 Hz, 0.07H), 3.70 (td, $^{3}J_{HH}$ = 12.4 and 4.4 Hz, 0.93H), 2.35 (ddd, $^{2}J_{HH}$ = 12.7 Hz and $^{3}J_{HH}$ = 6.4 and 4.4 Hz, 1H), 1.69 (q, J_{HH} = 12.8 Hz, 1H), 1.30 (s, 0.84H), 1.23 (s, 5.58H), 1.20 (s, 5.58H), 0.95-0.83 (m, 1H), 0.78 (d, $^{3}J_{HH}$ = 6.8 Hz, 0.07H), 0.63 (dd, $^{3}J_{HH}$ = 13.2 and 6.8 Hz, 0.93H), 0.20 (s, 3H), 0.17 (s, 0.21H), 0.16 (s, 2.79H), 0.12 (s, 0.21H), 0.10 (s, 2.79H), –0.11 (s, 0.21H), –0.18 (s, 2.79H). Major diastereomer: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 142.6, 140.0, 133.9, 133.7, 131.7, 129.0, 128.5, 127.4, 126.2, 125.6, 125.4, 125.1, 124.0, 122.9, 82.7, 43.8, 41.7, 25.3, 25.0, 22.3, 0.8, 0.0, –0.9, –2.2. HRMS (FAB) calcd for $C_{30}H_{41}BO_2Si_2$ (M^+) 500.2733, found 500.2750.



Compound 3ja. The reaction was conducted at 0.07 M. Colorless oil. 50% yield (50.6 mg, 0.100 mmol; dr = 88/12).

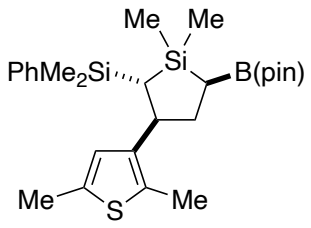
^{1}H NMR ($CDCl_3$): δ 7.81-7.71 (m, 2H), 7.69 (d, $^3J_{HH}$ = 8.8 Hz, 0.12H), 7.68 (d, $^3J_{HH}$ = 8.3 Hz, 0.88H), 7.62 (s, 0.12H), 7.60 (s, 0.88H), 7.47-7.28 (m, 5H), 7.23-7.12 (m, 3H), 3.33 (td, $^3J_{HH}$ = 11.0 and 5.4 Hz, 0.12H), 2.91 (td, $^3J_{HH}$ = 12.4 and 4.4 Hz, 0.88H), 2.31-2.18 (m, 1H), 1.99-1.75 (m, 1H), 1.261 (s, 0.72H), 1.257 (s, 0.72H), 1.25 (s, 5.28H), 1.22 (s, 5.28H), 0.80 (dd, $^3J_{HH}$ = 8.3 and 2.9 Hz, 0.12H), 0.70 (d, $^3J_{HH}$ = 11.2 Hz, 0.12H), 0.68 (d, $^3J_{HH}$ = 12.7 Hz, 0.88H), 0.56 (dd, $^3J_{HH}$ = 13.2 and 6.8 Hz, 0.88H), 0.24 (s, 0.36H), 0.20 (s, 2.64H), 0.16 (s, 2.64H), 0.14 (s, 0.36H), 0.11 (s, 0.36H), 0.07 (s, 2.64H), –0.11 (s, 0.36H), –0.15 (s, 2.64H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.4, 140.0, 133.7, 133.6, 132.5, 128.5, 127.74, 127.66, 127.6, 127.4, 126.0, 125.9, 125.7, 125.0, 82.7, 51.1, 41.3, 25.3, 25.0, 23.5, 0.6, –0.1, –1.0, –2.6. HRMS (FAB) calcd for $C_{30}H_{41}BO_2Si_2$ (M^+) 500.2733, found 500.2729.



S1

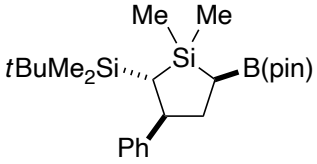
Compound 3ka. The reaction was conducted at 0.07 M for 16 h at 70 °C in the presence of 40 mol% of NaO*t*Bu. Yellow oil. 64% yield (64.5 mg, 0.128 mmol; dr = 86/14 (94% pure with inseparable **S1**)).

^{1}H NMR ($CDCl_3$): δ 7.47 (d, $^4J_{HH}$ = 1.5 Hz, 0.14H), 7.46 (d, $^4J_{HH}$ = 1.0 Hz, 0.86H), 7.42-7.31 (m, 2H), 7.28-7.09 (m, 5H), 7.04-6.98 (m, 1H), 6.43-6.38 (m, 1H), 3.76 (s, 3H), 3.28 (td, $^3J_{HH}$ = 11.0 and 5.9 Hz, 0.14H), 2.83 (td, $^3J_{HH}$ = 12.7 and 4.4 Hz, 0.86H), 2.27-2.15 (m, 1H), 1.86-1.73 (m, 1H), 1.24 (s, 0.84H), 1.23 (s, 5.16H), 1.22 (s, 0.84H), 1.20 (s, 5.16H), 0.75 (dd, $^3J_{HH}$ = 8.8 and 3.4 Hz, 0.14H), 0.68-0.59 (m, 1H), 0.50 (dd, $^3J_{HH}$ = 13.2 and 6.8 Hz, 0.86H), 0.23 (s, 0.42H), 0.19 (s, 2.58H), 0.08 (s, 3H), 0.03 (s, 0.42H), –0.01 (s, 2.58H), –0.19 (s, 0.42H), –0.25 (s, 2.58H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.6, 137.8, 135.8, 133.8, 128.7, 128.6, 128.4, 127.3, 121.5, 119.3, 108.8, 100.6, 82.6, 51.2, 41.9, 33.0, 25.3, 25.0, 24.0, 0.6, –0.1, –0.7, –2.9. HRMS (FAB) calcd for $C_{29}H_{42}BNO_2Si_2$ (M^+) 503.2842, found 503.2843.



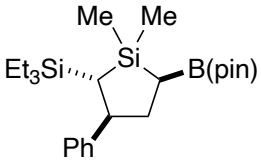
Compound 3la. The reaction was conducted for 16 h at 70 °C in the presence of 40 mol% of NaO*t*Bu. Yellow oil. 73% yield (70.8 mg, 0.146 mmol; dr = 89/11).

^{1}H NMR ($CDCl_3$): δ 7.37-7.29 (m, 2H), 7.29-7.21 (m, 3H), 6.40 (s, 0.89H), 6.34 (s, 0.11H), 3.19 (td, $^3J_{HH}$ = 11.7 and 4.9 Hz, 0.11H), 2.72 (td, $^3J_{HH}$ = 12.4 and 4.4 Hz, 0.89H), 2.28 (s, 0.66H), 2.26 (s, 2.67H), 2.22 (s, 2.67H), 2.03 (ddd, $^2J_{HH}$ = 13.1 Hz and $^3J_{HH}$ = 6.8 and 4.4 Hz, 1H), 1.62-1.47 (m, 1H), 1.23 (s, 0.66H), 1.21 (s, 6H), 1.18 (s, 5.34H), 0.67 (dd, $^3J_{HH}$ = 7.8 and 2.4 Hz, 0.11H), 0.48-0.38 (m, 1.89H), 0.22 (s, 0.33H), 0.21 (s, 2.67H), 0.11 (s, 2.67H), 0.08 (s, 0.33H), 0.05 (s, 0.33H), –0.006 (s, 2.67H), –0.011 (s, 0.33H), –0.02 (s, 2.67H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.3, 140.3, 134.7, 133.6, 128.44, 128.41, 127.4, 125.0, 82.7, 43.1, 40.0, 25.3, 25.0, 23.0, 15.3, 12.9, 0.6, –0.1, –1.8, –2.4. HRMS (FAB) calcd for $C_{26}H_{41}BO_2SSi_2$ (M^+) 484.2453, found 484.2466.



Compound 3ab. Colorless oil. 55% yield (47.4 mg, 0.110 mmol; dr = 83/17).

^{1}H NMR ($CDCl_3$): δ 7.25-7.16 (m, 4H), 7.16-7.09 (m, 1H), 3.36 (q, $^3J_{HH}$ = 6.4 Hz, 0.17H), 2.71 (td, $^3J_{HH}$ = 12.2 and 4.9 Hz, 0.83H), 2.16 (ddd, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 6.4 and 4.9 Hz, 0.83H), 2.10 (ddd, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 9.3 and 6.4 Hz, 0.17H), 1.7 (dt, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 5.9 Hz, 0.17H), 1.59 (td, J_{HH} = 13.7 Hz and $^3J_{HH}$ = 12.2 Hz, 0.83H), 1.23 (s, 4.98H), 1.22 (s, 1.02H), 1.20 (s, 6H), 0.73 (s, 1.53H), 0.70 (s, 7.47H), 0.63 (dd, $^3J_{HH}$ = 9.3 and 6.4 Hz, 0.17H), 0.56-0.45 (m, 1.83H), 0.37 (s, 0.51H), 0.33 (s, 2.49H), 0.27 (s, 2.49H), 0.23 (s, 0.51H), –0.03 (s, 0.51H), –0.09 (s, 2.49H), –0.17 (s, 0.51H), –0.45 (s, 2.49H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.1, 128.1, 127.5, 125.9, 82.7, 51.5, 42.6, 27.4, 25.3, 25.0, 18.6, 17.7, 2.0, 0.6, –3.8, –4.0. HRMS (FAB) calcd for $C_{24}H_{44}BO_2Si_2$ (M+H^+) 431.2967, found 431.2961.



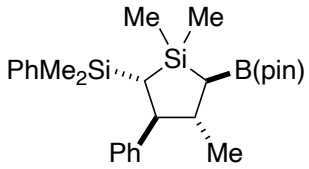
Compound 3ac. The reaction was conducted for 16 h. Colorless oil. 71% yield (60.8 mg, 0.142 mmol; dr = 88/12).

^{1}H NMR ($CDCl_3$): δ 7.25-7.18 (m, 4H), 7.17-7.10 (m, 1H), 3.13 (td, $^3J_{HH}$ = 11.0 and 5.4 Hz, 0.12H),

2.68 (td, $^3J_{HH}$ = 12.4 and 4.4 Hz, 0.88H), 2.20-2.08 (m, 1H), 1.74-1.60 (m, 1H), 1.23 (s, 6H), 1.22 (s, 0.72H), 1.21 (s, 5.28H), 0.90-0.70 (m, 9.12H), 0.49 (dd, $^3J_{HH}$ = 13.7 and 6.3 Hz, 0.88H), 0.43-0.17 (m, 13H). Major diastereomer: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 147.6, 128.1, 127.4, 126.0, 82.7, 50.9, 41.6, 25.3, 25.0, 20.1, 7.9, 4.4, 1.1, 0.3. HRMS (FAB) calcd for $C_{24}H_{43}BO_2Si_2$ (M^+) 430.2889, found 430.2906.

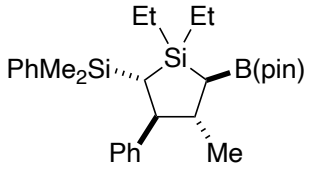
General Procedure for Scheme 3a.

Styryl(1-propenyl)silane **1** (0.200 mmol) and silylboronate **2a** (65.4 μL, 0.240 mmol) were added with the aid of THF (3.5 mL) to a solution of NaO*t*Bu (7.7 mg, 80 μmol) in THF (1.5 mL), and the mixture was stirred for 16–23 h at 50 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **3**.



Compound 3ma. The reaction was conducted for 16 h. Colorless oil. 83% yield (67.1 mg, 0.166 mmol; dr = 84/16).

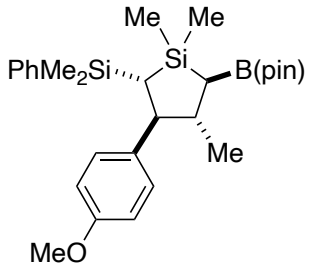
^1H NMR ($CDCl_3$): δ 7.41-7.37 (m, 0.32H), 7.36-7.31 (m, 1.68H), 7.29-7.06 (m, 8H), 3.29 (t, $^3J_{HH}$ = 6.6 Hz, 0.16H), 2.38-2.27 (m, 0.16H), 2.26 (dd, $^3J_{HH}$ = 12.7 and 10.7 Hz, 0.84H), 2.08-1.94 (m, 0.84H), 1.23 (s, 5.04H), 1.212 (s, 0.96H), 1.207 (s, 0.96H), 1.20 (s, 5.04H), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 0.16H), 0.76-0.65 (m, 3.84H), 0.61 (d, $^3J_{HH}$ = 9.3 Hz, 0.16H), 0.26 (s, 0.48H), 0.241 (s, 0.48H), 0.235 (d, $^3J_{HH}$ = 12.2 Hz, 0.84H), 0.16 (s, 2.52H), 0.12 (s, 0.48H), 0.04 (s, 2.52H), 0.03 (s, 0.48H), –0.05 (s, 2.52H), –0.26 (s, 2.52H). Major diastereomer: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 146.4, 140.3, 133.7, 128.5, 128.1, 128.0, 127.5, 126.0, 82.7, 57.6, 46.8, 25.4, 24.7, 21.9, 0.4, –0.2, –1.1, –3.1. HRMS (FAB) calcd for $C_{27}H_{40}BO_2Si_2$ ($M–H^–$) 463.2654, found 463.2662.



Compound 3na. The reaction was conducted for 16 h. Colorless oil. 74% yield (70.8 mg, 0.148 mmol; dr = 82/18). The relative configuration of the major diastereomer was determined by X-ray crystallographic analysis.

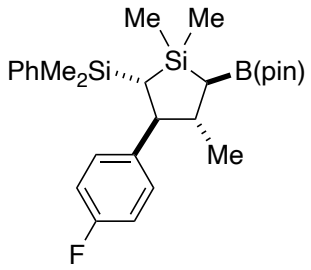
^1H NMR ($CDCl_3$): δ 7.39-7.29 (m, 2H), 7.29-7.03 (m, 8H), 3.32 (dd, $^3J_{HH}$ = 7.8 and 6.4 Hz, 0.18H), 2.38-2.27 (m, 0.18H), 2.25 (dd, $^3J_{HH}$ = 12.7 and 10.7 Hz, 0.82H), 2.05-1.92 (m, 0.82H), 1.23 (s, 6H), 1.22 (s, 1.08H), 1.20 (s, 4.92H), 1.00 (t, $^3J_{HH}$ = 7.8 Hz, 0.54H), 0.99 (t, $^3J_{HH}$ = 7.8 Hz, 2.46H), 0.90 (t, $^3J_{HH}$ = 8.0 Hz, 2.46H), 0.89 (t, $^3J_{HH}$ = 8.3 Hz, 0.54H), 0.85 (d, $^3J_{HH}$ = 12.7 Hz, 0.82H), 0.80-0.46 (m,

6.54H), 0.36-0.24 (m, 2.18H), 0.14 (s, 2.46H), 0.11 (s, 0.54H), –0.22 (s, 2.46H). Major diastereomer: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 146.7, 140.5, 133.7, 128.5, 128.1, 128.0, 127.4, 126.0, 82.6, 57.8, 47.2, 25.5, 24.5, 21.9, 21.5, 7.9, 7.8, 7.2, 5.5, –0.9, –2.5. HRMS (FAB) calcd for $C_{29}H_{45}BO_2Si_2$ (M^+) 492.3046, found 492.3043.



Compound 3oa. The reaction was conducted for 23 h. Colorless oil. 83% yield (81.8 mg, 0.165 mmol; dr = 82/18).

^{1}H NMR ($CDCl_3$): δ 7.40-7.36 (m, 0.36H), 7.33-7.18 (m, 1.64H), 7.27-7.19 (m, 3H), 7.02 (d, $^{3}J_{HH}$ = 8.3 Hz, 1.64H), 6.99 (t, $^{3}J_{HH}$ = 8.3 Hz, 0.36H), 6.75-6.68 (m, 2H), 3.774 (s, 0.54H), 3.767 (s, 2.46H), 3.24 (dd, $^{3}J_{HH}$ = 7.3 and 5.9 Hz, 0.18H), 2.28 (dd, $^{3}J_{HH}$ = 8.3 and 5.9 Hz, 0.18H), 2.21 (dd, $^{3}J_{HH}$ = 12.7 and 10.7 Hz, 0.82H), 2.01-1.87 (m, 0.82H), 1.22 (s, 4.92H), 1.21 (s, 1.08H), 1.20 (s, 1.08H), 1.19 (s, 4.92H), 0.82 (d, $^{3}J_{HH}$ = 7.3 Hz, 0.18H), 0.72 (d, $^{3}J_{HH}$ = 6.4 Hz, 2.46H), 0.67 (d, $^{3}J_{HH}$ = 6.8 Hz, 0.54H), 0.63 (d, $^{3}J_{HH}$ = 12.7 Hz, 0.82H), 0.57 (d, $^{3}J_{HH}$ = 9.3 Hz, 0.18H), 0.26-0.17 (m, 1.9H), 0.16 (s, 2.46H), 0.12 (s, 0.54H), 0.04 (s, 2.46H), 0.02 (s, 0.54H), –0.04 (s, 2.46H), –0.21 (s, 2.46H). Major diastereomer: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 157.9, 140.4, 138.4, 133.7, 128.7, 128.4, 127.4, 113.5, 82.7, 56.8, 55.3, 46.8, 25.4, 24.8, 21.9, 0.5, –0.1, –1.2, –2.8. HRMS (FD) calcd for $C_{28}H_{43}BO_3Si_2$ (M^+) 494.2838, found 494.2843.

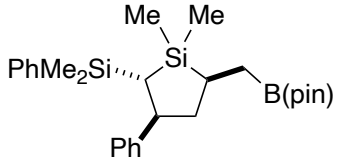


Compound 3pa. The reaction was conducted for 23 h. Colorless oil. 68% yield (65.9 mg, 0.137 mmol; dr = 84/16).

^{1}H NMR ($CDCl_3$): δ 7.37-7.33 (m, 0.32H), 7.31-7.18 (m, 4.68H), 7.08-7.02 (m, 1.68H), 7.02-6.97 (m, 0.32H), 6.87-6.79 (m, 2H), 3.27 (dd, $^{3}J_{HH}$ = 7.8 and 5.8 Hz, 0.16H), 2.34-2.25 (m, 0.16H), 2.24 (dd, $^{3}J_{HH}$ = 12.7 and 10.7 Hz, 0.84H), 2.00-1.87 (m, 0.84H), 1.23 (s, 5.04H), 1.22 (s, 0.96H), 1.21 (s, 0.96H), 1.20 (s, 5.04H), 0.80 (d, $^{3}J_{HH}$ = 7.8 Hz, 0.16H), 0.71 (d, $^{3}J_{HH}$ = 6.4 Hz, 2.52H), 0.65 (d, $^{3}J_{HH}$ = 6.8 Hz, 0.48H), 0.62 (d, $^{3}J_{HH}$ = 12.7 Hz, 0.84H), 0.56 (d, $^{3}J_{HH}$ = 8.3 Hz, 0.16H), 0.27-0.20 (m, 1.8H), 0.16 (s, 2.52H), 0.13 (s, 0.48H), 0.07 (s, 2.52H), 0.05 (s, 0.48H), –0.01 (s, 2.52H), –0.17 (s, 2.52H).

Major diastereomer: $^{13}C\{^{1}H,^{19}F\}$ NMR ($CDCl_3$): δ 161.4, 141.9, 140.1, 133.6, 129.1, 128.5, 127.5, 114.8, 82.7, 56.8, 46.9, 25.4, 24.8, 21.8, 0.5, –0.1, –1.4, –2.7. ^{19}F NMR ($CDCl_3$): δ –117.9 (tt, $^{3}J_{HH}$ = 8.8 Hz and $^{4}J_{HH}$ = 5.4 Hz). HRMS (FD) calcd for $C_{27}H_{40}BFO_2Si_2$ (M^+) 482.2638, found 482.2645.

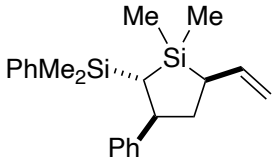
Procedure for Scheme 3b, Compound 4.



*n*BuLi (400 μL, 0.604 mmol; 1.51 M solution in hexane) was added slowly over 10 min to a solution of compound **3aa** (135 mg, 0.300 mmol; dr = 91/9) and bromochloromethane (39.0 μL, 0.600 mmol) in Et_2O (0.8 mL) at –78 °C, and the mixture was stirred for 1 h at –78 °C and for 21 h at room temperature. The reaction was quenched with saturated NH_4Claq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/40 to afford compound **4** as a colorless oil (121 mg, 0.259 mmol; 86% yield, dr = 92/8).

^{1}H NMR ($CDCl_3$): δ 7.37-7.31 (m, 2H), 7.29-7.08 (m, 8H), 2.97 (td, $^{3}J_{HH}$ = 11.5 and 4.9 Hz, 0.08H), 2.74 (td, $^{3}J_{HH}$ = 12.4 and 3.9 Hz, 0.92H), 2.20 (ddd, $^{2}J_{HH}$ = 12.2 Hz and $^{3}J_{HH}$ = 6.9 and 4.4 Hz, 0.92H), 1.88 (ddd, $^{2}J_{HH}$ = 13.1 Hz and $^{3}J_{HH}$ = 11.7 and 7.8 Hz, 0.08H), 1.74 (ddd, $^{2}J_{HH}$ = 13.2 Hz and $^{3}J_{HH}$ = 4.9 and 2.4 Hz, 0.08H), 1.37-1.14 (m, 12.92H), 1.06-0.72 (m, 3H), 0.58-0.50 (m, 1H), 0.18 (s, 0.24H), 0.14 (s, 2.76H), 0.01 (s, 3H), –0.06 (s, 0.24H), –0.11 (s, 2.76H), –0.19 (s, 0.24H), –0.23 (s, 2.76H). Major diastereomer: $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 147.5, 140.4, 133.7, 128.5, 128.2, 127.4, 127.3, 126.0, 83.0, 49.5, 48.2, 25.03, 24.99, 24.0, 22.8, –0.8, –0.9, –2.7, –2.8. HRMS (FAB) calcd for $C_{27}H_{41}BO_2Si_2$ (M^+) 464.2733, found 464.2739.

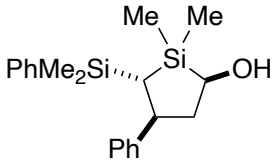
Procedure for Scheme 3b, Compound 5.



Vinylmagnesium chlororide (571 μL, 1.20 mmol; 2.1 M solution in THF) was added over 10 min to a solution of compound **3aa** (135 mg, 0.300 mmol; dr = 91/9) in THF (2.4 mL) at 0 °C, and the mixture was stirred for 4 h at 0 °C. A solution of I_2 (307 mg, 1.20 mmol) in MeOH (2.4 mL) was added to it and the resulting mixture was stirred for 2.5 h at 0 °C. The reaction was quenched with 5% Na_2SO_3aq and the volatiles were removed under vacuum. This was extracted with Et_2O and the organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel hexane to afford compound **5** as a colorless oil (44.9 mg, 0.128 mmol; 43% yield, dr = 90/10).

^{1}H NMR ($CDCl_3$): δ 7.42-7.35 (m, 2H), 7.35-7.13 (m, 8H), 5.90-5.77 (m, 1H), 4.91-4.75 (m, 2H), 3.11 (td, $^3J_{HH}$ = 11.5 and 4.9 Hz, 0.1H), 2.84 (td, $^3J_{HH}$ = 12.4 and 4.4 Hz, 0.9H), 2.23-2.02 (m, 1.1H), 1.93-1.78 (m, 1H), 1.66 (q, J_{HH} = 12.4 Hz, 0.9H), 0.69-0.62 (m, 1H), 0.23 (s, 0.3H), 0.20 (s, 2.7H), 0.06 (s, 0.3H), 0.04 (s, 2.7H), –0.03 (s, 0.3H), –0.06 (s, 2.7H), –0.12 (s, 0.3H), –0.16 (s, 2.7H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.9, 140.3, 140.0, 133.7, 128.7, 128.4, 127.6, 127.3, 126.3, 109.5, 48.2, 44.7, 36.1, 23.5, –0.9, –1.2, –2.1, –2.8. HRMS (FAB) calcd for $C_{22}H_{31}Si_2$ ($M+H^+$) 351.1959, found 351.1971.

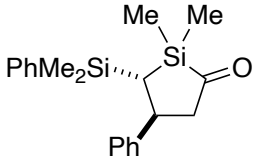
Procedure for Scheme 3b, Compound 6.



3 M NaOHaq (400 μL, 1.20 mmol) and H_2O_2 (389 mg, 4.00 mmol; 35% solution in H_2O) were added to a solution of compound **3aa** (90.1 mg, 0.200 mmol; dr = 91/9) in THF (1.0 mL) and the mixture was stirred for 5 h at room temperature. The reaction mixture was diluted with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/8 → 1/5 to afford compound **6** as a colorless oil (66.8 mg, 0.196 mmol; 98% yield, dr = 92/8).

^{1}H NMR ($CDCl_3$): δ 7.40-7.13 (m, 10H), 3.81 (dd, $^3J_{HH}$ = 4.9 and 1.4 Hz, 0.08H), 3.74 (dd, $^3J_{HH}$ = 10.7 and 8.3 Hz, 0.92H), 3.24 (td, $^3J_{HH}$ = 12.7 and 4.4 Hz, 0.08H), 2.73 (td, $^3J_{HH}$ = 12.7 and 4.4 Hz, 0.92H), 2.49 (ddd, $^2J_{HH}$ = 12.2 Hz and $^3J_{HH}$ = 8.3 and 4.4 Hz, 0.92H), 2.16 (ddd, $^2J_{HH}$ = 14.1 Hz and $^3J_{HH}$ = 4.4 and 2.0 Hz, 0.08H), 1.84-1.68 (m, 1H), 1.29 (bs, 1H), 0.74 (d, $^3J_{HH}$ = 12.7 Hz, 0.92H), 0.52 (d, $^3J_{HH}$ = 12.7 Hz, 0.08H), 0.23 (s, 0.24H), 0.18 (s, 2.76H), 0.08 (s, 0.24H), 0.06 (s, 2.76H), 0.03 (s, 2.76H), 0.02 (s, 0.24H), –0.20 (s, 0.24H), –0.22 (s, 2.76H). Major diastereomer: ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.4, 139.9, 133.7, 128.7, 128.5, 127.6, 127.3, 126.4, 67.3, 49.1, 43.9, 23.4, –0.9, –2.0, –3.0, –3.6. HRMS (FAB) calcd for $C_{20}H_{27}OSi_2$ ($M–H^–$) 339.1595, found 339.1613.

Procedure for Scheme 3b, Compound 7.

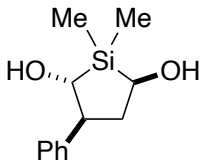


A solution of DMSO (34.0 μL, 0.480 mmol) in CH_2Cl_2 (1.0 mL) was added to a solution of oxalyl chloride (19.0 μL, 0.220 mmol) in CH_2Cl_2 (0.4 mL) at –78 °C and the mixture was stirred for 3 min at –78 °C. Compound **6** (63.7 mg, 0.187 mmol; dr = 92/8) and Et_3N (140 μL, 1.01 mmol) were added to it with the aid of CH_2Cl_2 (0.6 mL), and the mixture was stirred for 3.5 h at –78 °C. The reaction was

quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/5 to afford compound **7** as a colorless oil (33.7 mg, 0.100 mmol; 53% yield).

^{1}H NMR ($CDCl_3$): δ 7.40-7.35 (m, 2H), 7.35-7.18 (m, 8H), 3.26 (td, $^3J_{HH}$ = 12.9 and 5.4 Hz, 1H), 2.57 (dd, $^2J_{HH}$ = 17.1 Hz and $^3J_{HH}$ = 5.4 Hz, 1H), 2.22 (dd, $^2J_{HH}$ = 17.1 Hz and $^3J_{HH}$ = 12.7 Hz, 1H), 1.10 (d, $^3J_{HH}$ = 13.1 Hz, 1H), 0.29 (s, 3H), 0.11 (s, 3H), –0.15 (s, 3H), –0.18 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 145.1, 139.1, 133.6, 129.2, 128.8, 127.9, 127.4, 126.9, 59.8, 42.2, 24.8, –1.0, –3.2, –3.9, –5.2. HRMS (FAB) calcd for $C_{20}H_{27}OSi_2$ ($M+H^+$) 339.1595, found 339.1602.

Procedure for Scheme 3b, Compound 8.



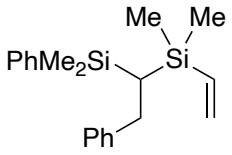
HBF_4•Et_2O (559 mg, 1.86 mmol) was added over 5 min to a solution of compound **6** (68.1 mg, 0.200 mmol; dr = 92/8) in CH_2Cl_2 (1.0 mL) at 0 ℃, and the mixture was stirred for 5 h at room temperature. The reaction was quenched with saturated $NaHCO_3$aq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was dissolved in THF (1.0 mL) and MeOH (1.0 mL), and KF (26.7 mg, 0.460 mmol), $KHCO_3$ (220 mg, 2.20 mmol) and H_2O_2 (363 mg, 3.73 mmol; 35% solution in H_2O) were added to it at 0 ℃, and the mixture was stirred for 30 min at 0 ℃ and for 2 h at 60 ℃. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with EtOAc/hexane = 1/3 → 1/1 to afford compound **8** as a colorless oil (39.1 mg, 0.176 mmol; 88% yield, dr = 92/8).

^{1}H NMR ($CDCl_3$): δ 7.38-7.31 (m, 2H), 7.30-7.22 (m, 3H), 3.87 (dd, $^3J_{HH}$ = 11.2 and 8.8 Hz, 0.92H), 3.81 (dd, $^3J_{HH}$ = 4.4 and 1.5 Hz, 0.08H), 3.62 (d, $^3J_{HH}$ = 11.2 Hz, 0.92H), 3.53 (d, $^3J_{HH}$ = 10.7 Hz, 0.08H), 3.24 (ddd, $^3J_{HH}$ = 13.7, 11.2, and 4.9 Hz, 0.08H), 2.70 (ddd, $^3J_{HH}$ = 13.7, 11.2, and 4.4 Hz, 0.92H), 2.42 (ddd, $^3J_{HH}$ = 12.2, 8.8, and 4.4 Hz, 0.92H), 2.08 (ddd, $^3J_{HH}$ = 14.1, 4.4, and 2.0 Hz, 0.08H), 1.91-71 (m, 1H), 1.52-1.30 (br, 2H), 0.35 (s, 0.24H), 0.32 (m, 2.76H), 0.31 (m, 2.76H), 0.27 (s, 0.24H). Major diastereomer: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 142.8, 129.0, 127.4, 127.0, 72.3, 65.0, 49.9, 40.2, –6.0, –6.3. HRMS (FAB) calcd for $C_{12}H_{17}O_2Si$ ($M–H^–$) 221.0992, found 221.0994.

Procedure for Scheme 5a.

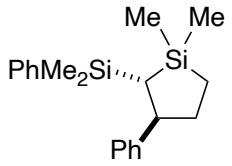
Li wire (27.7 mg. 3.99 mmol; cut in small pieces) in THF (2.0 mL) was sonicated for 1.5 h at 0 ℃. Chloroldimethylphenylsilane (170 μL, 1.03 mmol) was added to it slowly over 5 min at 0 ℃, and the resulting mixture was stirred for 1 h at 0 ℃ and for 14.5 h at room temperature to give a solution of

dimethylphenylsilyllithium in THF. A solution of compound **1a** (37.7 mg, 0.200 mmol) in THF (1.0 mL) was added to the generated dimethylphenylsilyllithium (750 μL, 0.300 mmol; 0.40 M solution in THF) at –78 ℃, and the mixture was stirred for 0.5–7 h at –78 ℃. MeOH (12.2 μL, 0.300 mmol) was added to it, and the mixture was stirred for 10 min at –78 ℃ and for 10 min at room temperature. This was passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was analyzed by ^{1}H NMR to determine the yields of **9aa** and **10aa** against an internal standard (dimethyl terephthalate).



Compound 9aa. Colorless oil.

^{1}H NMR ($CDCl_3$): δ 7.54-7.46 (m, 2H), 7.37-7.29 (m, 3H), 7.23-7.16 (m, 2H), 7.15-7.05 (m, 3H), 6.01 (dd, $^3J_{HH}$ = 20.0 and 14.6 Hz, 1H), 5.86 (dd, $^3J_{HH}$ = 14.7 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 5.58 (dd, $^3J_{HH}$ = 20.0 Hz and $^2J_{HH}$ = 3.9 Hz, 1H), 2.84 (dd, $^2J_{HH}$ = 14.6 Hz and $^3J_{HH}$ = 6.4 Hz, 1H), 2.78 (dd, $^2J_{HH}$ = 14.6 Hz and $^3J_{HH}$ = 7.8 Hz, 1H), 0.67 (dd, $^3J_{HH}$ = 7.8 and 6.4 Hz, 1H), 0.33 (s, 3H), 0.27 (s, 3H), –0.079 (s, 3H), –0.084 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 144.3, 140.14, 140.06, 133.9, 131.2, 128.8, 128.6, 128.2, 127.8, 125.7, 32.0, 14.9, –1.1, –1.68, –1.72, –1.8. HRMS (FAB) calcd for $C_{20}H_{27}Si_2$ ($M–H^–$) 323.1646, found 323.1656.



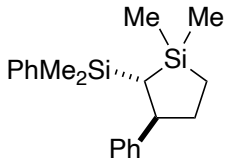
Compound 10aa. Colorless oil.

^{1}H NMR ($CDCl_3$): δ 7.38-7.32 (m, 2H), 7.30-7.10 (m, 8H), 2.73 (td, $^3J_{HH}$ = 12.4 and 4.4 Hz, 1H), 2.13 (dddd, $^2J_{HH}$ = 12.7 Hz and $^3J_{HH}$ = 8.3, 4.4, and 1.4 Hz, 1H), 1.49 (qd, J_{HH} = 12.5 Hz and $^3J_{HH}$ = 7.3 Hz, 1H), 0.86 (ddd, $^2J_{HH}$ = 14.7 Hz and $^3J_{HH}$ = 7.3 and 1.5 Hz, 1H), 0.52 (ddd, $^2J_{HH}$ = 14.7 Hz and $^3J_{HH}$ = 12.7 and 8.3 Hz, 1H), 0.47 (d, $^3J_{HH}$ = 12.7 Hz, 1H), 0.17 (s, 3H), 0.01 (s, 3H), –0.02 (s, 3H), –0.19 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.5, 140.4, 133.7, 128.5, 128.3, 127.5, 127.3, 126.1, 50.2, 38.8, 23.3, 13.9, –0.0, –0.2, –0.9, –2.7. HRMS (FAB) calcd for $C_{20}H_{27}Si_2$ ($M–H^–$) 323.1646, found 323.1654.

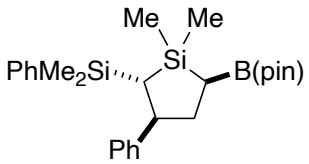
General Procedure for Scheme 5b.

Li wire (27.7 mg. 3.99 mmol; cut in small pieces) in THF (2.0 mL) was sonicated for 1.5 h at 0 ℃. Chloroldimethylphenylsilane (170 μL, 1.03 mmol) was added to it slowly over 5 min at 0 ℃, and the resulting mixture was stirred for 1 h at 0 ℃ and for 14.5 h at room temperature to give a solution of

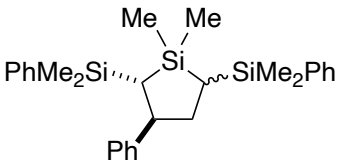
dimethylphenylsilyllithium in THF. A solution of compound **1a** (37.7 mg, 0.200 mmol) in THF (1.0 mL) was added to the generated dimethylphenylsilyllithium (750 μL, 0.300 mmol; 0.40 M solution in THF) at –78 ℃, and the mixture was stirred for 7 h at –78 ℃. An electrophile (0.300 mmol) was added to it, and the mixture was stirred for 16 h at –50 ℃. This was passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **10**.



Compound 10aa. MeOH was used as the electrophile. Colorless oil. 70% yield (45.3 mg, 0.139 mmol).

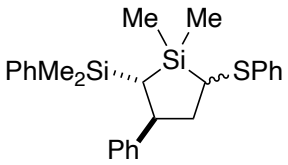


Compound 10ab (= 3aa). $B(OMe)_3$ was used as the electrophile, and pinacol (0.300 mmol) was added after the reaction. 65% yield (58.7 mg, 0.130 mmol; dr = 87/13).



Compound 10ac. Chloroldimethylphenylsilane was used as the electrophile. Colorless oil. 70% yield (63.9 mg, 0.139 mmol; dr = 55/45).

^{1}H NMR ($CDCl_3$): δ 7.52-7.45 (m, 2H), 7.38-7.10 (m, 13H), 2.87 (td, $^3J_{HH}$ = 11.0 and 6.4 Hz, 0.55H), 2.74 (td, $^3J_{HH}$ = 12.2 and 4.4 Hz, 0.45H), 2.21-2.04 (m, 1H), 1.92 (dt, $^2J_{HH}$ = 13.2 Hz and $^3J_{HH}$ = 10.2 Hz, 0.55H), 1.48 (dt, $^2J_{HH}$ = 13.7 Hz and $^3J_{HH}$ 12.2 Hz, 0.45H), 0.63-0.47 (m, 1.55H), 0.292 (s, 1.35H), 0.287 (s, 1.65H) 0.28 (s, 3H), 0.28-0.21 (m, 0.45H), 0.17 (s, 1.65H) 0.16 (s, 1.35H) –0.02 (s, 1.65H), –0.07 (s, 4.35H), –0.16 (s, 1.65H), –0.17 (s, 1.35H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.4, 147.1, 140.6, 140.4, 140.3, 140.1, 133.8, 133.72, 133.67, 133.66, 128.78, 128.76, 128.6, 128.5, 128.33, 128.29, 127.8, 127.7, 127.52, 127.48, 127.34, 127.32, 126.2, 126.1, 51.6, 49.1, 41.9, 40.0, 24.0, 23.3, 16.7, 11.8, 1.3, 0.9, 0.7, –0.2, –1.0, –1.1, –1.7, –1.9, –2.3, –2.4, –2.7, –2.8. HRMS (FAB) calcd for $C_{28}H_{38}Si_3$ (M^+) 458.2276, found 458.2294.

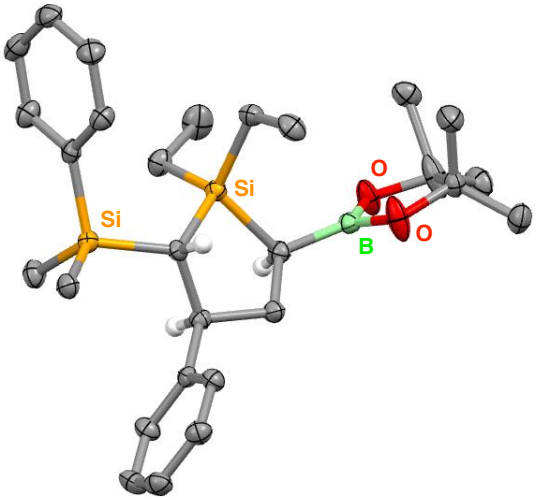


Compound 10ad. Diphenyl disulfide was used as the electrophile. Colorless oil. 74% yield (61.7 mg, 0.148 mmol; dr = 56/44).

^{1}H NMR ($CDCl_3$): δ 7.41-7.07 (m, 15H), 3.26 (td, $^{3}J_{HH}$ = 12.4 and 4.9 Hz, 0.56H), 2.98 (d, $^{3}J_{HH}$ = 5.4 Hz, 0.56H), 2.82 (td, $^{3}J_{HH}$ = 12.9 and 4.4 Hz, 0.44H), 2.72-2.58 (m, 0.88H), 2.13 (ddd, $^{2}J_{HH}$ = 13.7 Hz and $^{3}J_{HH}$ = 4.9 and 1.4 Hz, 0.56H), 2.00 (ddd, $^{2}J_{HH}$ = 13.7 Hz and $^{3}J_{HH}$ = 12.2 and 6.8 Hz, 0.56H), 1.67 (q, J_{HH} = 11.9 Hz, 0.44H), 0.74 (d, $^{3}J_{HH}$ = 13.2 Hz, 0.44H), 0.68 (d, $^{3}J_{HH}$ = 12.7 Hz, 0.56H), 0.30 (s, 1.68H), 0.21 (s, 1.32H), 0.17 (s, 1.68H), 0.14 (s, 1.32H), 0.114 (s, 1.68H), 0.105 (s, 1.32H), –0.18 (s, 1.32H), –0.20 (s, 1.68H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.1, 145.9, 140.0, 139.6, 138.5, 138.2, 133.7, 133.6, 128.9, 128.82, 128.78, 128.7, 128.5, 128.4, 128.1, 127.7, 127.5, 127.3, 126.5, 126.4, 125.6, 125.3, 48.2, 47.7, 46.2, 45.6, 30.9, 29.4, 23.7, 23.5, 0.3, –0.7, –0.9, –1.0, –2.4, –3.0, –3.15, –3.19. HRMS (FAB) calcd for $C_{26}H_{32}SSi_2$ (M^+) 432.1758, found 432.1757.

IV. X-ray Crystal Structures

Compound 3ba



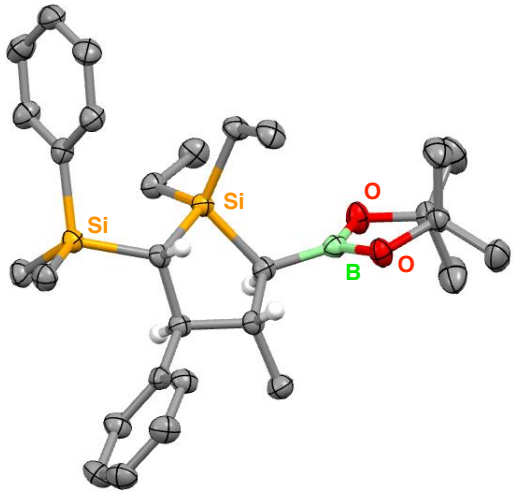
A colorless CH_2Cl_2 solution of compound **3ba** was prepared. Crystals suitable for X-ray analysis were obtained by layering MeOH and slow diffusion of the solvents at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2524632). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

Crystal Data and Structure Refinement.

Empirical Formula	$C_{28}H_{43}BO_2Si_2$	
Formula Weight	478.63	
Temperature	113 ± 2 K	
Wavelength	1.54184 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit Cell Dimensions	a = 16.5182(3) Å	α = 90°
	b = 13.8191(2) Å	β = 113.011(2)°
	c = 13.2866(2) Å	γ = 90°

Volume	2791.57(9) $Å^3$
Z Value	4
Calculated Density	1.170 g/cm^3
Absorption coefficient	1.306 mm^{-1}
F(000)	1048
Crystal size	0.290 x 0.190 x 0.100 mm
Theta Range for Data Collection	2.906–76.195°
Index Ranges	$-20 \leq h \leq 19$, $-16 \leq k \leq 16$, $-16 \leq l \leq 16$
Reflections Collected	18802
Independent Reflections	5606 [R(int) = 0.0279]
Completeness to Theta = 67.684°	99.9%
Absorption Correction	Semi-empirical from equivalents
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	5606 / 8 / 351
Goodness-of-Fit on F^2	1.034
Final R Indices [I>2sigma(I)]	R1 = 0.0354, wR2 = 0.0923
R Indices (All Data)	R1 = 0.0399, wR2 = 0.0953
Largest Diff. Peak and Hole	0.447 and –0.392 $e^-/Å^3$

Compound 3na



A colorless CH_2Cl_2 solution of compound **3na** was prepared. Crystals suitable for X-ray analysis were obtained by layering MeOH and slow diffusion of the solvents at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2524633). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

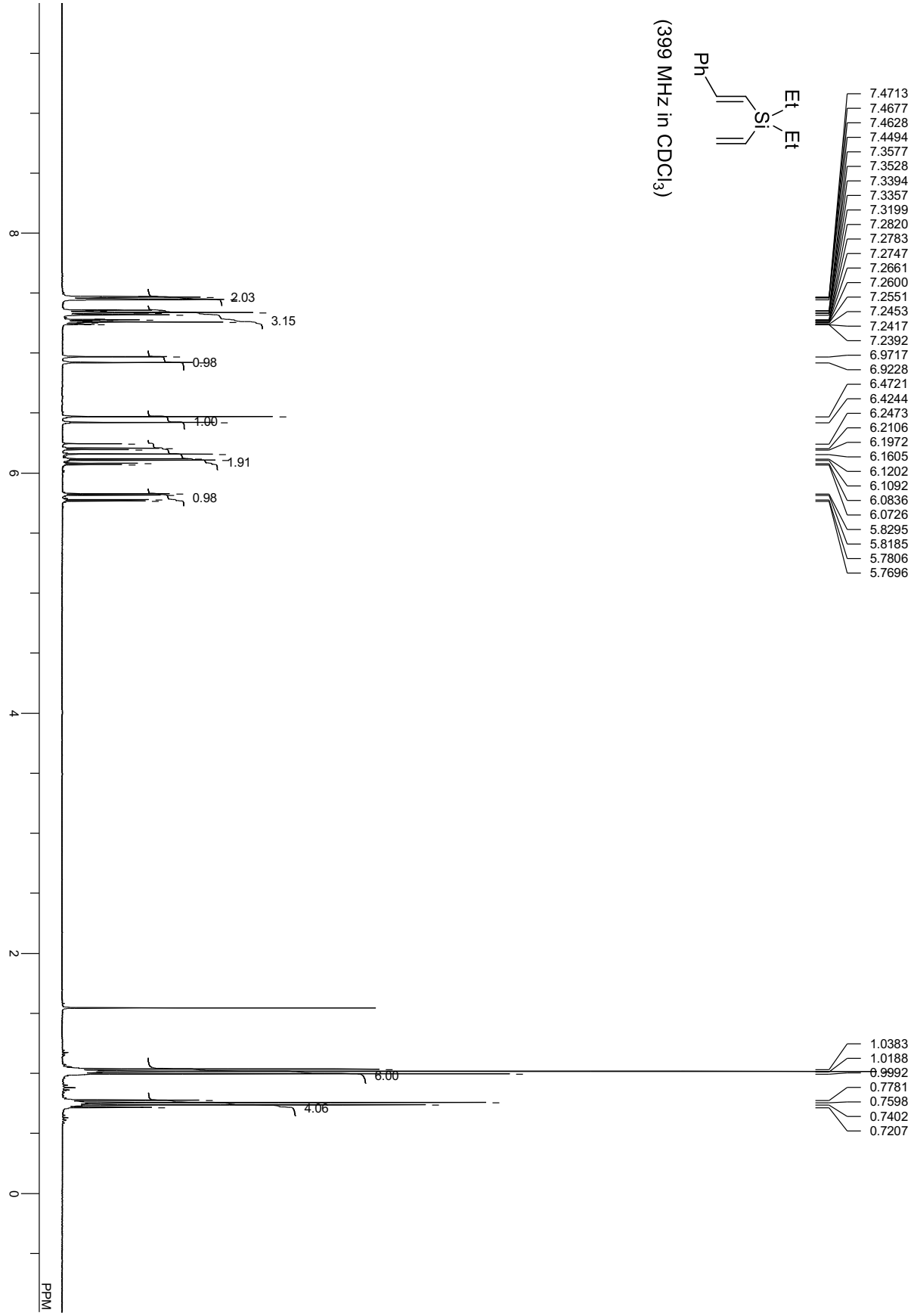
Crystal Data and Structure Refinement.

Empirical Formula	$C_{29}H_{45}BO_2Si_2$	
Formula Weight	492.64	
Temperature	113 ± 2 K	
Wavelength	1.54184 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit Cell Dimensions	a = 15.2241(2) Å	α = 90°
	b = 14.3979(2) Å	β = 92.7620(10)°
	c = 13.2285(2) Å	γ = 90°
Volume	2896.25(7) $Å^3$	

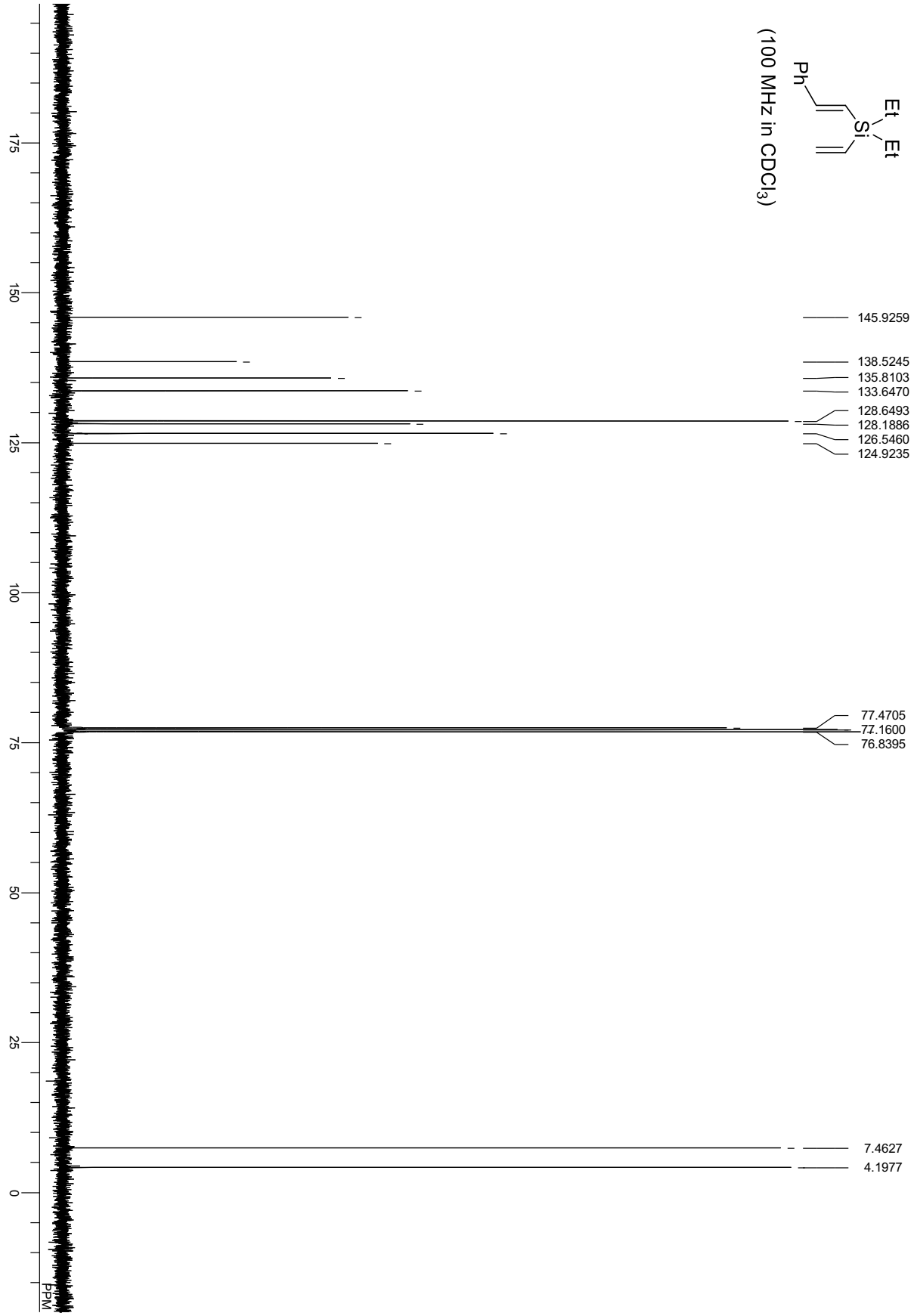
Z Value	4
Calculated Density	1.130 g/cm^3
Absorption coefficient	1.274 mm^{-1}
F(000)	1072
Crystal size	0.649 x 0.130 x 0.103 mm
Theta Range for Data Collection	2.906–76.127°
Index Ranges	$-18 \leq h \leq 18$, $-13 \leq k \leq 18$, $-16 \leq l \leq 16$
Reflections Collected	21625
Independent Reflections	5818 [R(int) = 0.0420]
Completeness to Theta = 67.684°	100%
Absorption Correction	Semi-empirical from equivalents
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	5818 / 0 / 316
Goodness-of-Fit on F^2	1.039
Final R Indices [I>2sigma(I)]	R1 = 0.0495, wR2 = 0.1356
R Indices (All Data)	R1 = 0.0526, wR2 = 0.1413
Largest Diff. Peak and Hole	0.776 and –0.513 e$^-$/Å^3

V. ^{1}H and ^{13}C NMR Spectra

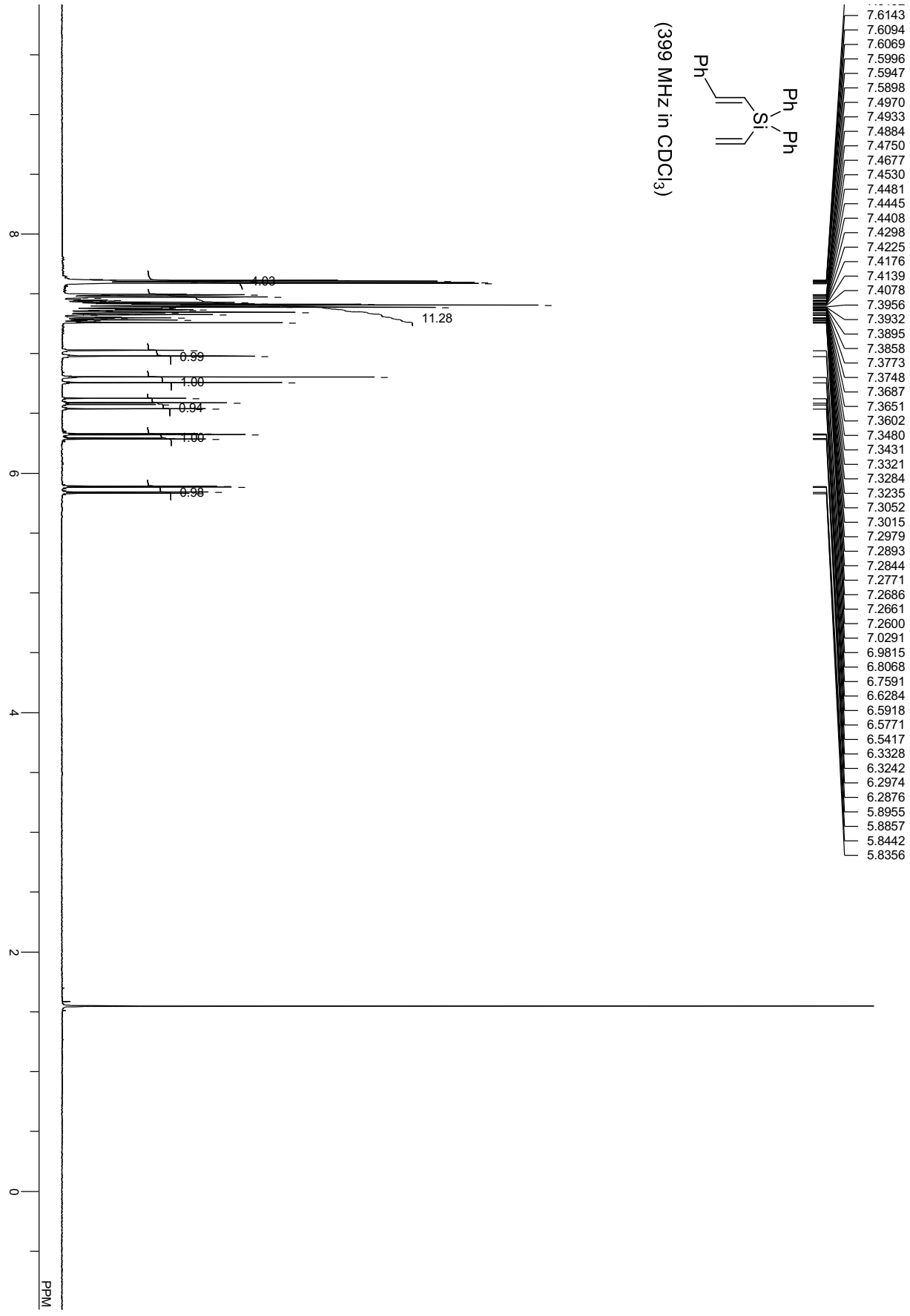
compound **1b**



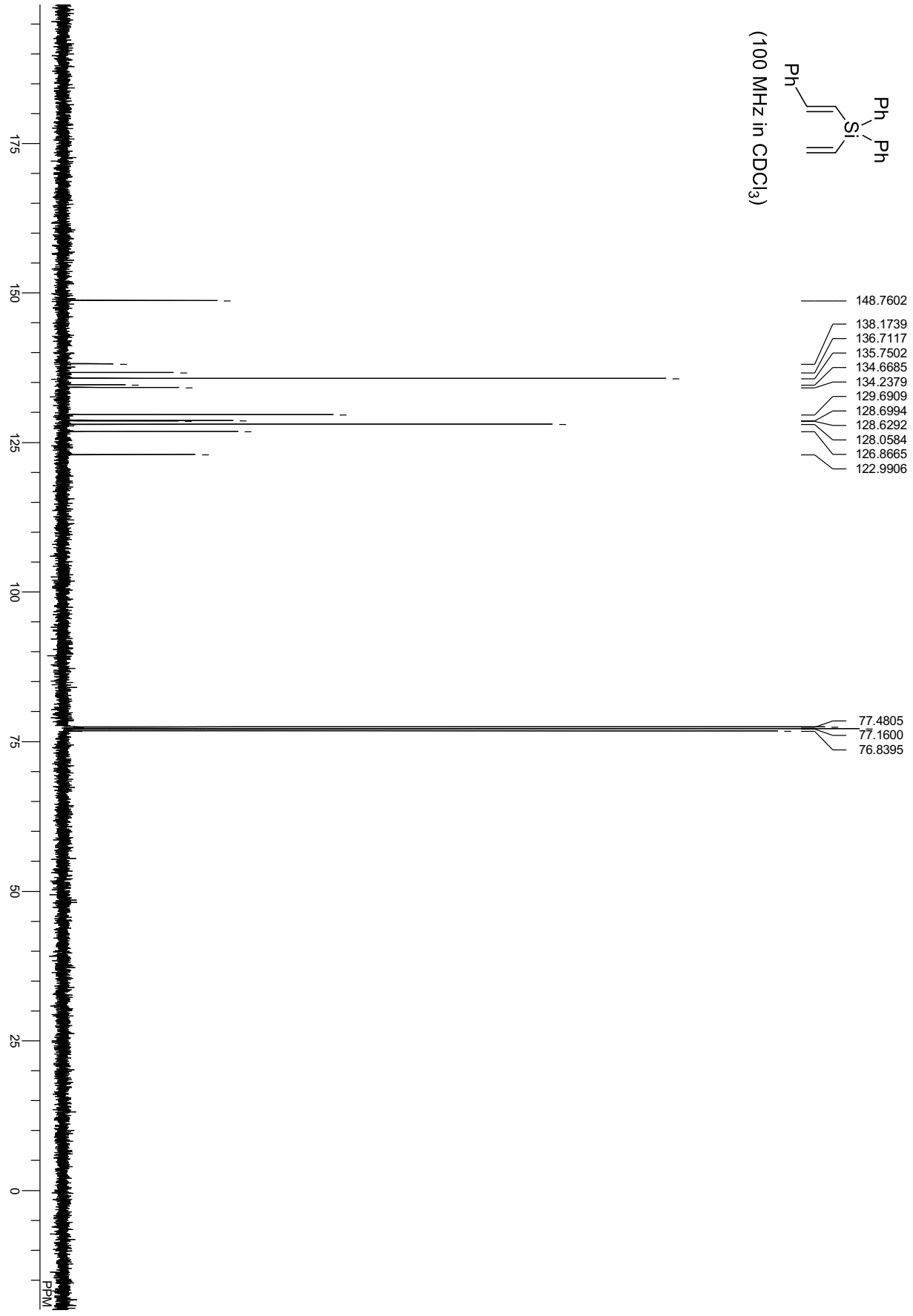
compound **1b**


(100 MHz in CDCl3)
Ph
Si
Et
Et
145.9259
138.5245
135.8103
133.6470
128.6493
128.1886
126.5460
124.9235
77.4705
77.1600
76.8395
7.4627
4.1977
175
150
125
100
75
50
25
0
PPM

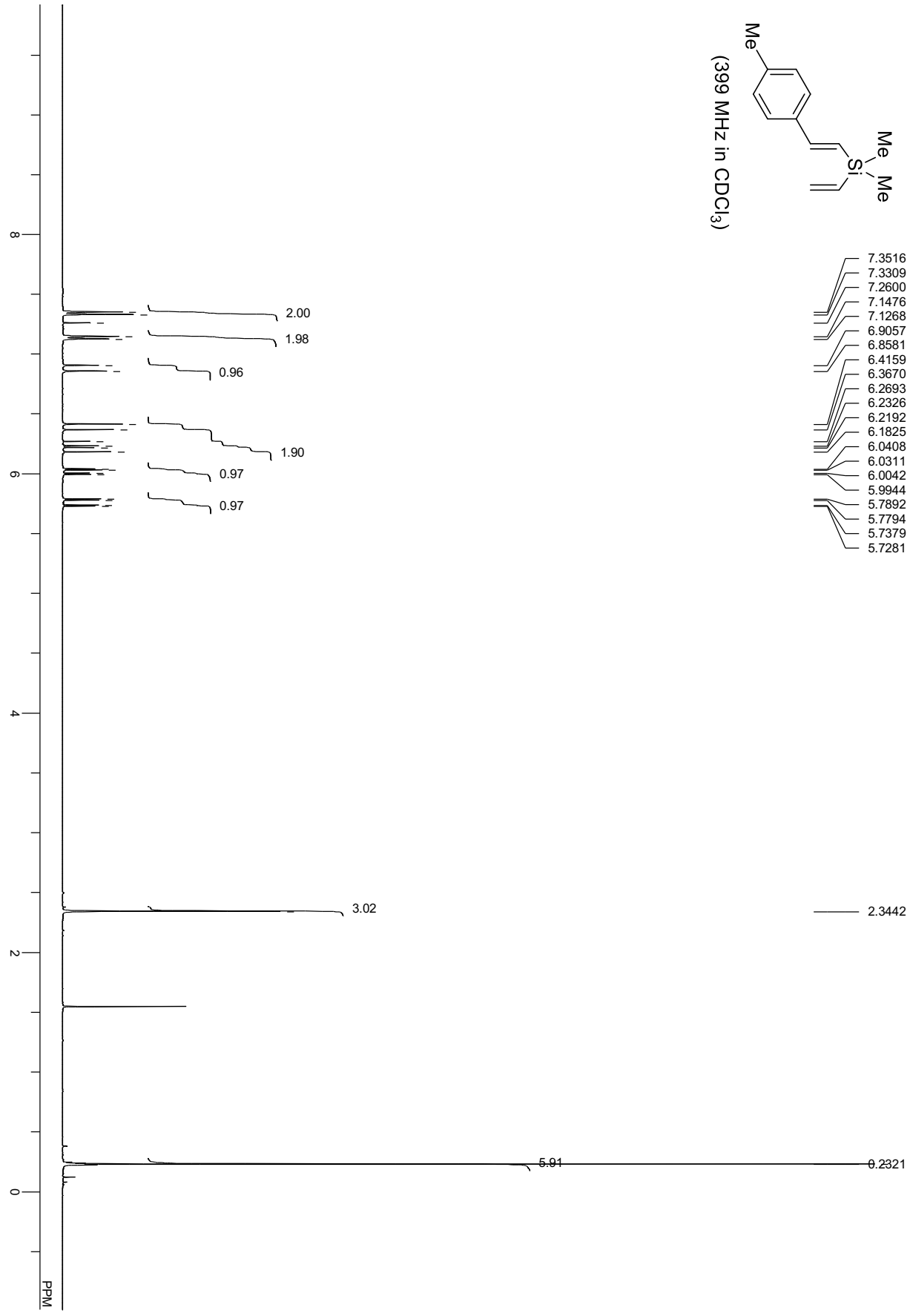
compound **1c**


(399 MHz in CDCl3)
Ph
Si
Ph
Ph
7.6143
7.6094
7.6069
7.5996
7.5947
7.5898
7.4970
7.4933
7.4884
7.4750
7.4677
7.4530
7.4481
7.4445
7.4408
7.4298
7.4225
7.4176
7.4139
7.4078
7.3956
7.3932
7.3895
7.3858
7.3773
7.3748
7.3687
7.3651
7.3602
7.3480
7.3431
7.3321
7.3284
7.3235
7.3052
7.3015
7.2979
7.2893
7.2844
7.2771
7.2686
7.2661
7.2600
7.0291
6.9815
6.8068
6.7591
6.6284
6.5918
6.5771
6.5417
6.3328
6.3242
6.2974
6.2876
5.8955
5.8857
5.8442
5.8356
4.03
11.28
0.59
1.00
0.94
1.00
0.98
8
6
4
2
0
PPM

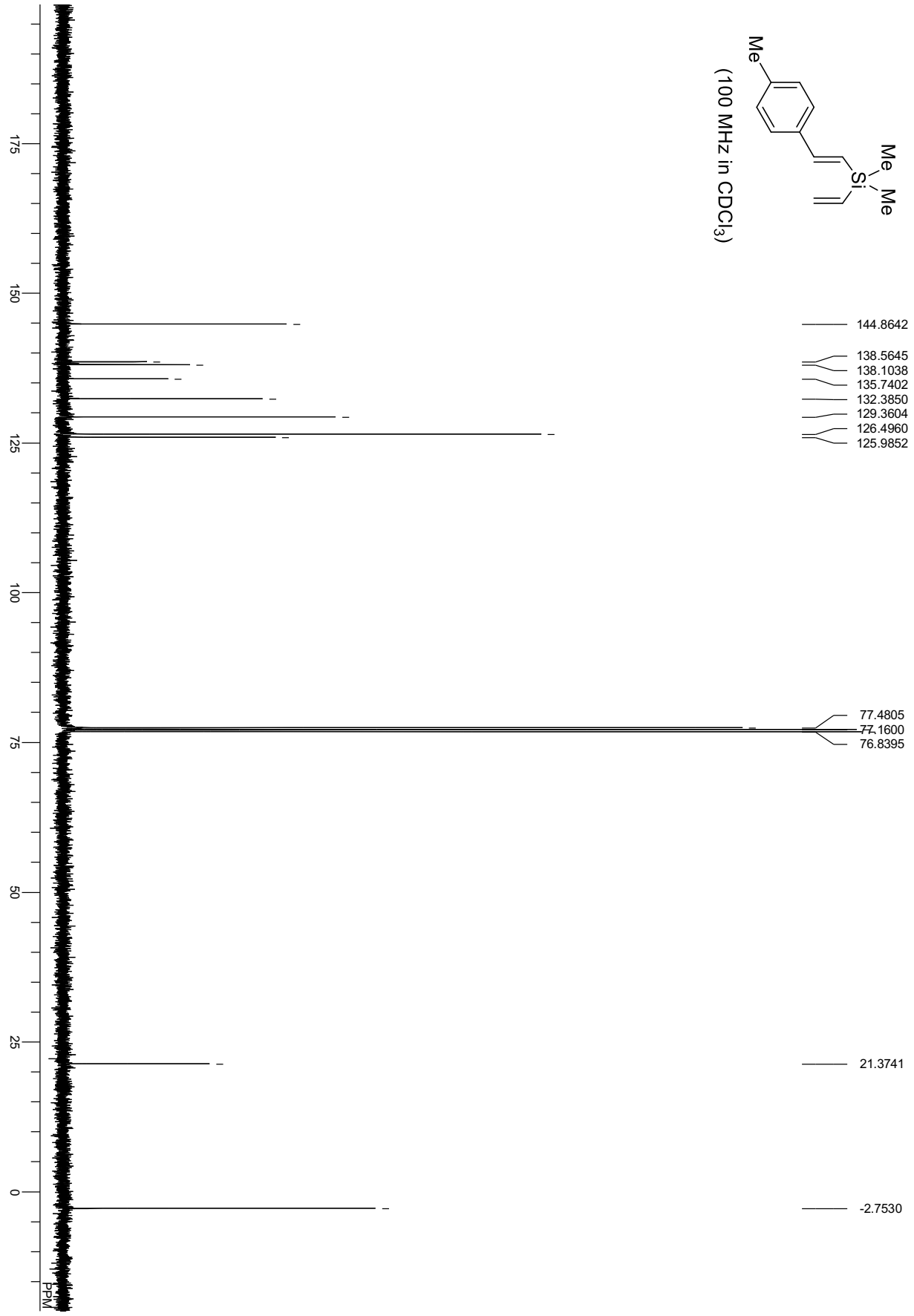
compound **1c**


(100 MHz in CDCl3)
Ph
Si
Ph
Ph
148.7602
138.1739
136.7117
135.7502
134.6685
134.2379
129.6909
128.6994
128.6292
128.0584
126.8665
122.9906
77.4805
77.1600
76.8395
175
150
125
100
75
50
25
0
PPM

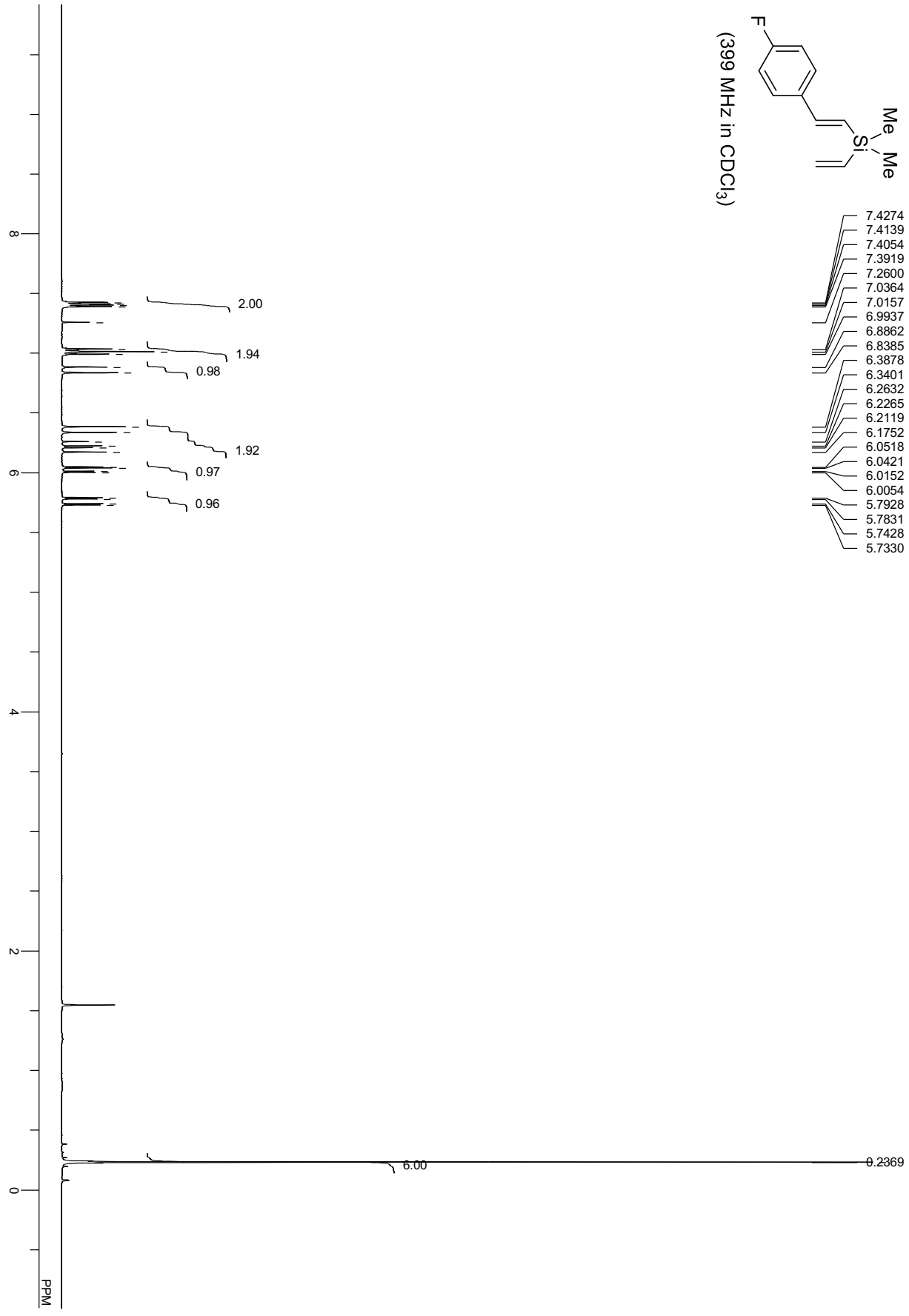
compound **1e**


Me
Me
Si
Me
(399 MHz in CDCl3)
7.3516
7.3309
7.2600
7.1476
7.1268
6.9057
6.8581
6.4159
6.3670
6.2693
6.2326
6.2192
6.1825
6.0408
6.0311
6.0042
5.9944
5.7892
5.7794
5.7379
5.7281
2.3442
0.2321
2.00
1.98
0.96
1.90
0.97
0.97
3.02
5.91
8
6
4
2
0
PPM

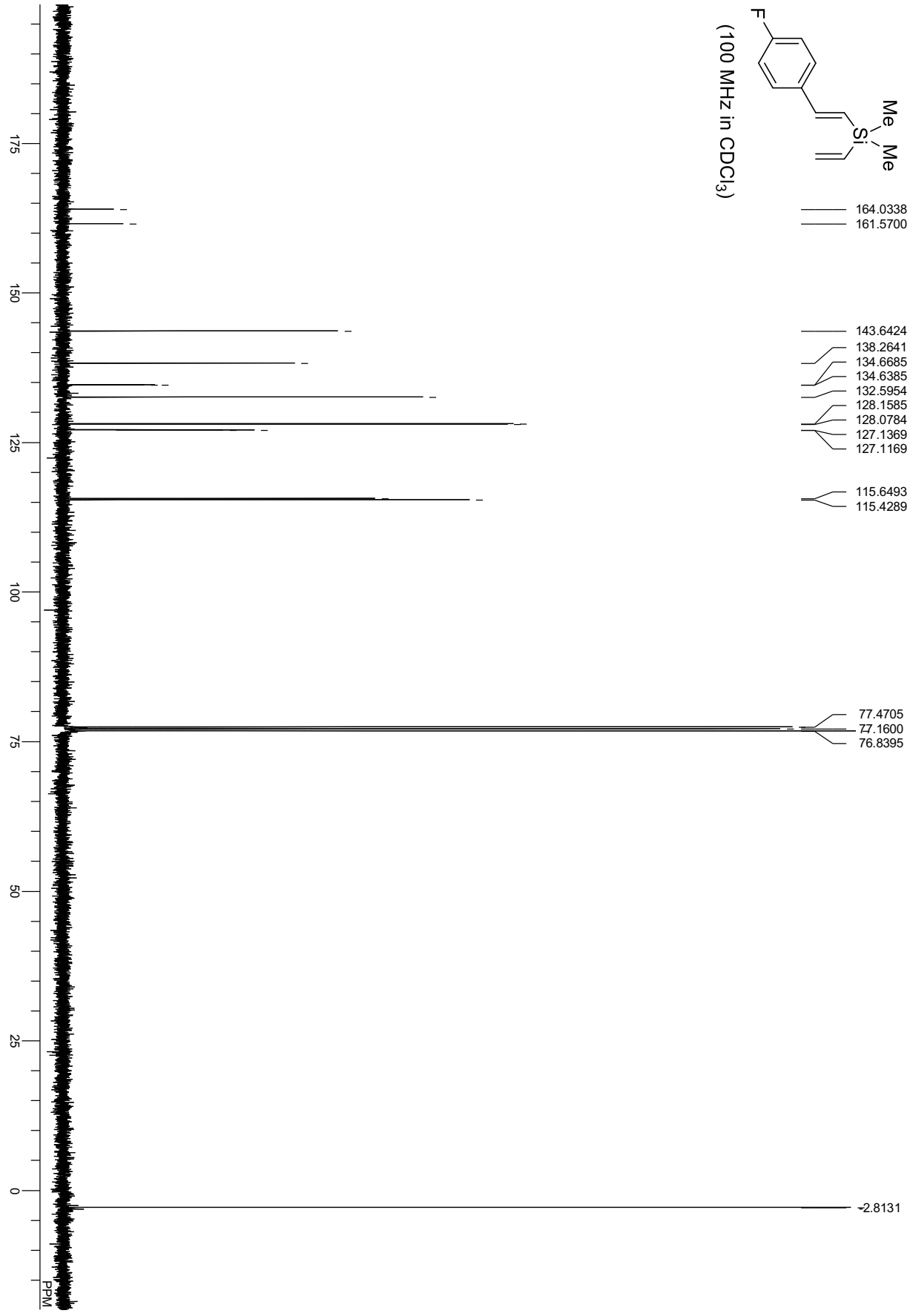
compound **1e**


Me
Me Me
Si
(100 MHz in CDCl3)
144.8642
138.5645
138.1038
135.7402
132.3850
129.3604
126.4960
125.9852
77.4805
77.1600
76.8395
21.3741
-2.7530
PPM

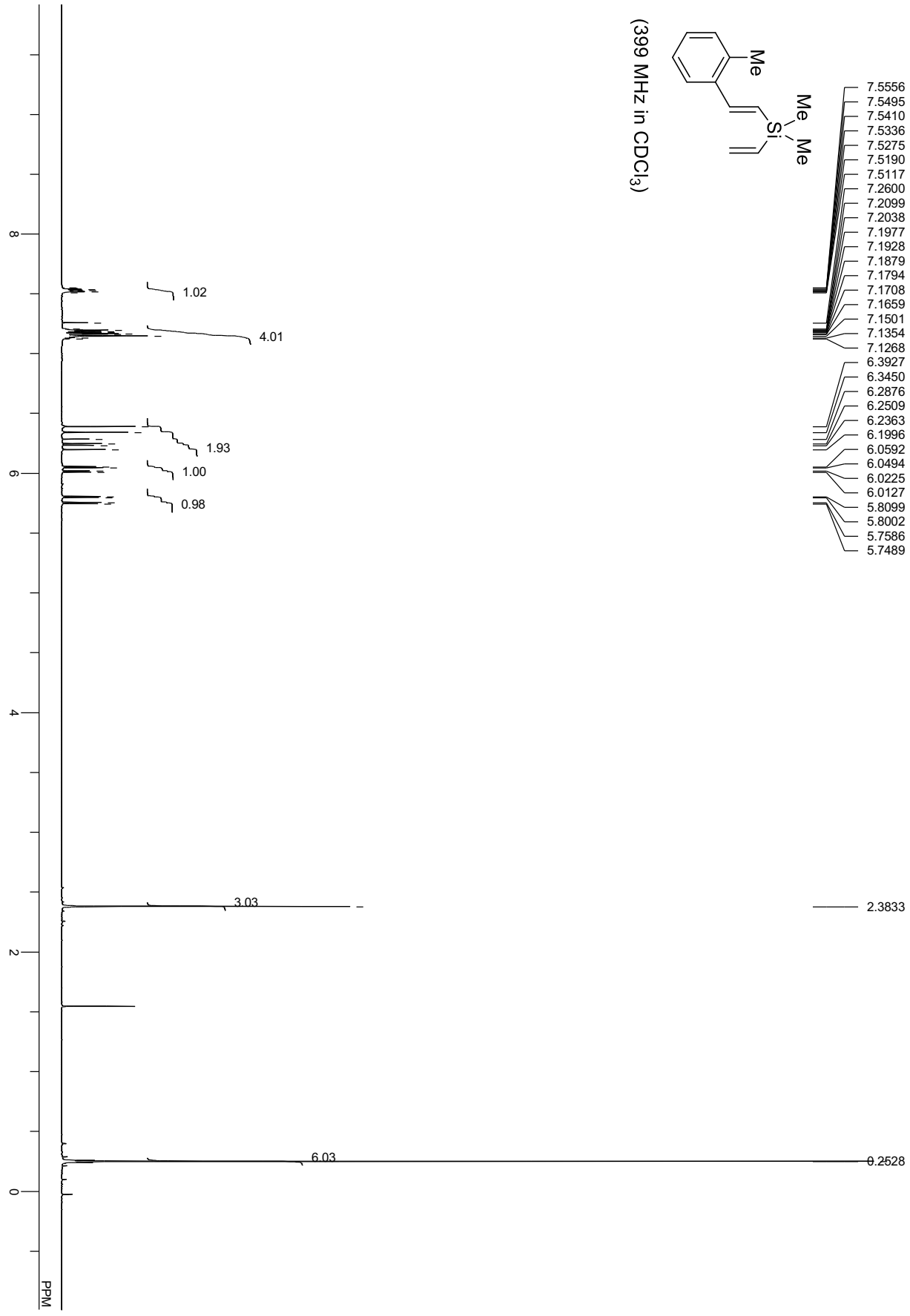
compound **1f**


(399 MHz in CDCl3)
F
Me
Si
Me
7.4274
7.4139
7.4054
7.3919
7.2600
7.0364
7.0157
6.9937
6.8862
6.8385
6.3878
6.3401
6.2632
6.2265
6.2119
6.1752
6.0518
6.0421
6.0152
6.0054
5.7928
5.7831
5.7428
5.7330
2.00
1.94
0.98
1.92
0.97
0.96
6.00
0.2369
8
6
4
2
0
PPM

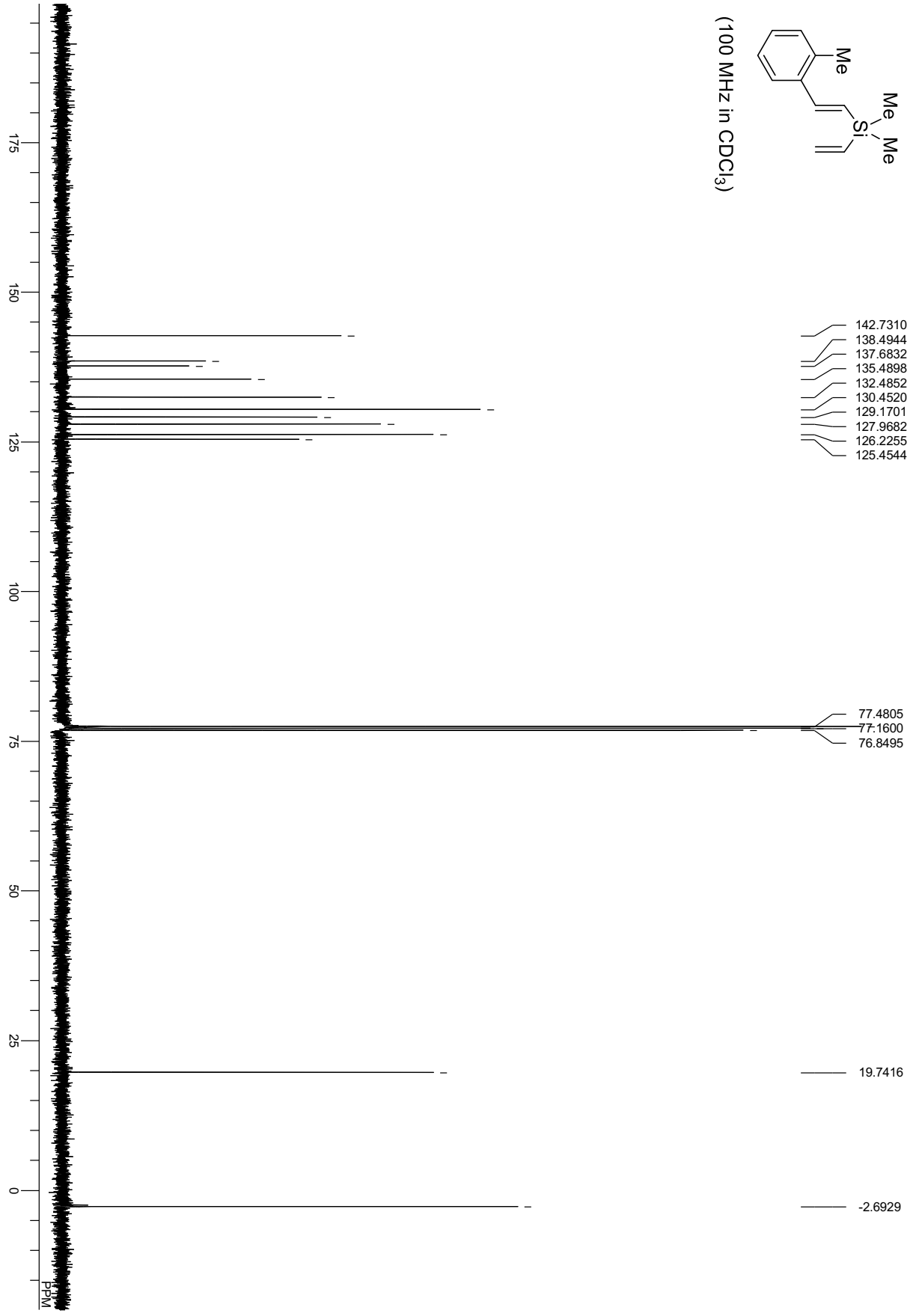
compound **1f**


(100 MHz in CDCl3)
F
Si
Me
Me
164.0338
161.5700
143.6424
138.2641
134.6685
134.6385
132.5954
128.1585
128.0784
127.1369
127.1169
115.6493
115.4289
77.4705
77.1600
76.8395
-2.8131
PPM

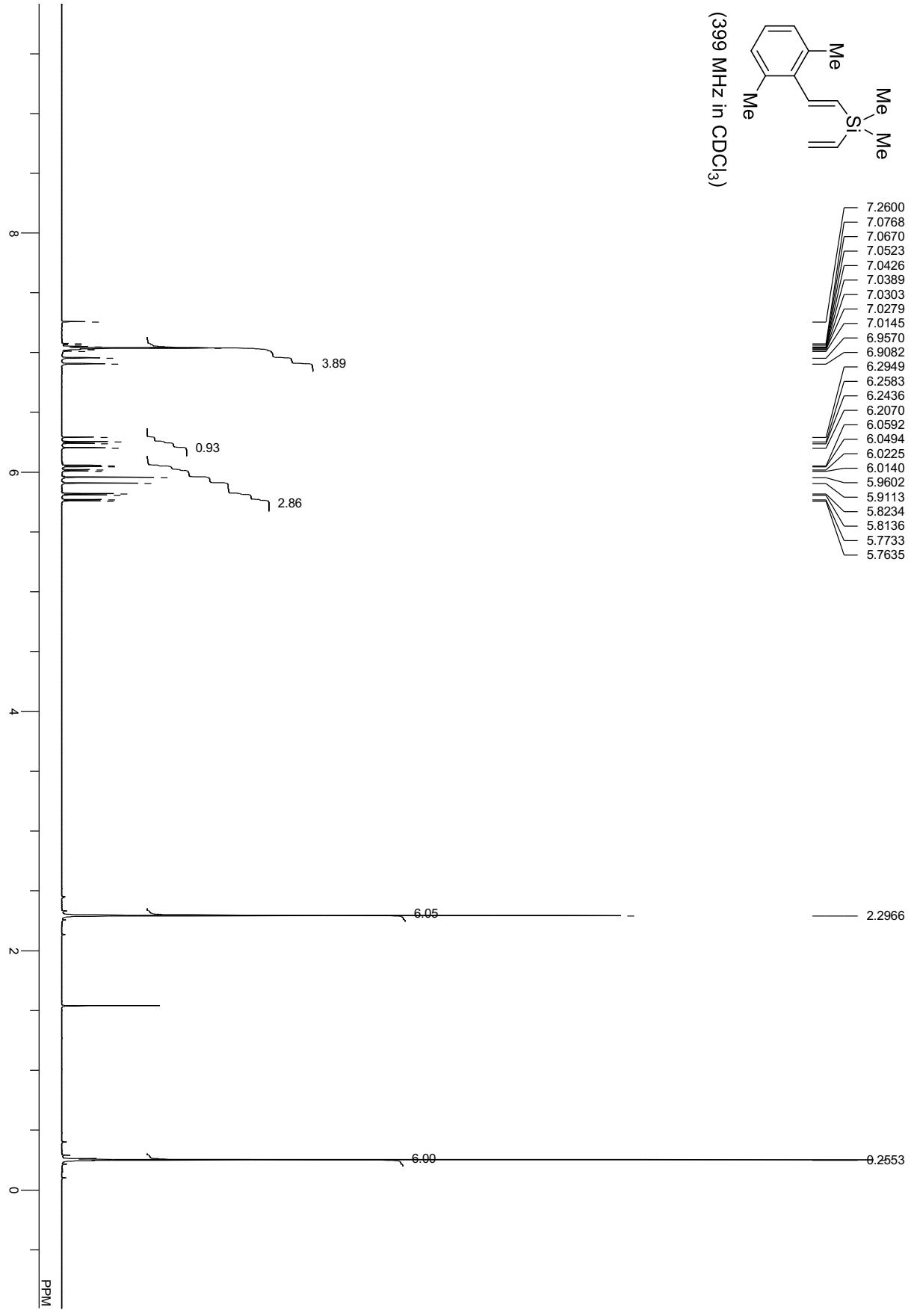
compound **1g**


(399 MHz in CDCl3)
Me
Si
Me
Me
7.5556
7.5495
7.5410
7.5336
7.5275
7.5190
7.5117
7.2600
7.2099
7.2038
7.1977
7.1928
7.1879
7.1794
7.1708
7.1659
7.1501
7.1354
7.1268
6.3927
6.3450
6.2876
6.2509
6.2363
6.1996
6.0592
6.0494
6.0225
6.0127
5.8099
5.8002
5.7586
5.7489
2.3833
0.2528
1.02
4.01
1.93
1.00
0.98
3.03
6.03
8
6
4
2
0
PPM

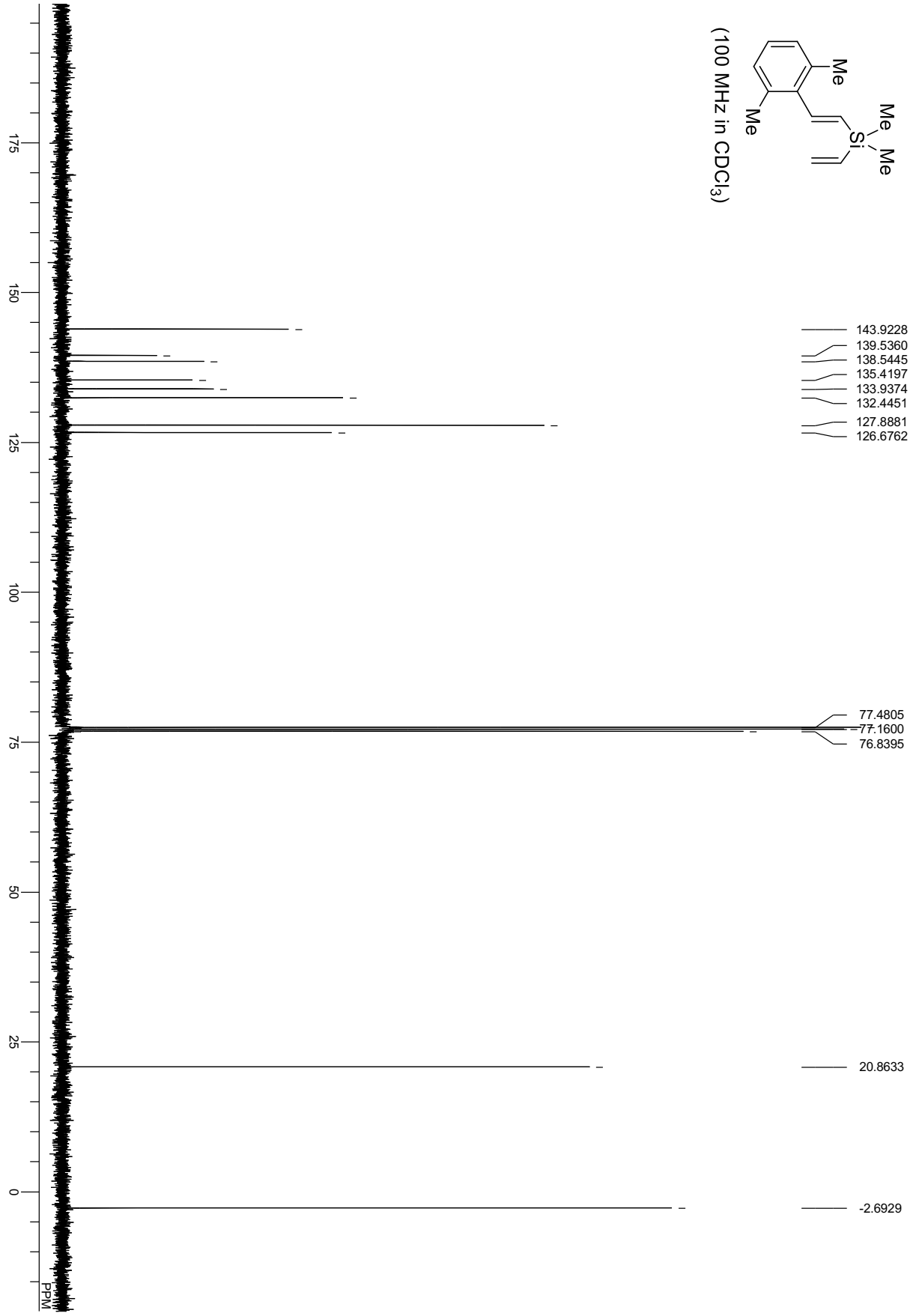
compound **1g**


(100 MHz in CDCl3)
Me
Me
Me
Si
142.7310
138.4944
137.6832
135.4898
132.4852
130.4520
129.1701
127.9682
126.2255
125.4544
77.4805
77.1600
76.8495
19.7416
-2.6929
PPM

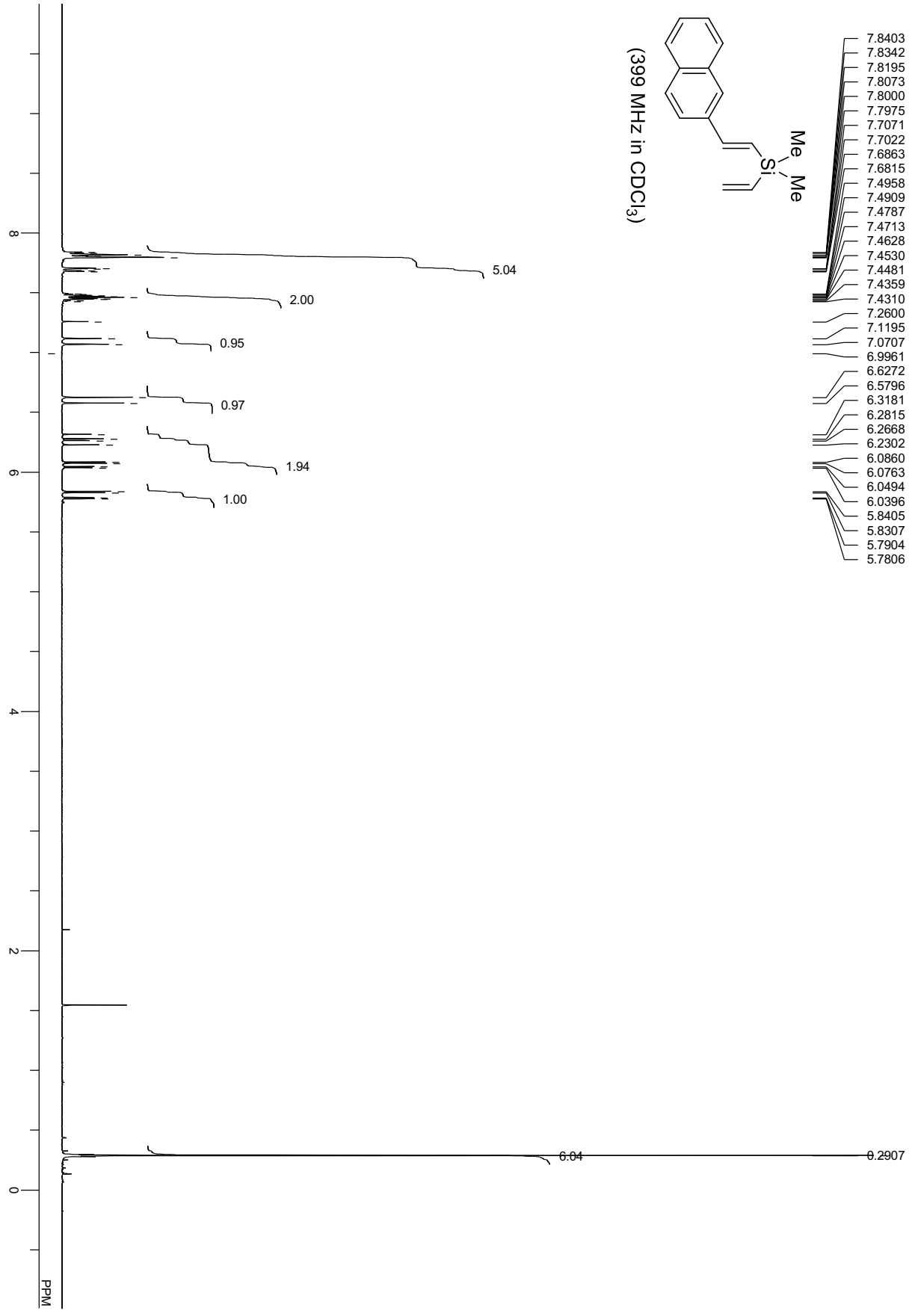
compound **1h**


(399 MHz in CDCl3)
Me
Me
Si
Me
Me
7.2600
7.0768
7.0670
7.0523
7.0426
7.0389
7.0303
7.0279
7.0145
6.9570
6.9082
6.2949
6.2583
6.2436
6.2070
6.0592
6.0494
6.0225
6.0140
5.9602
5.9113
5.8234
5.8136
5.7733
5.7635
3.89
0.93
2.86
6.05
2.2966
6.00
0.2553
8
6
4
2
0
PPM

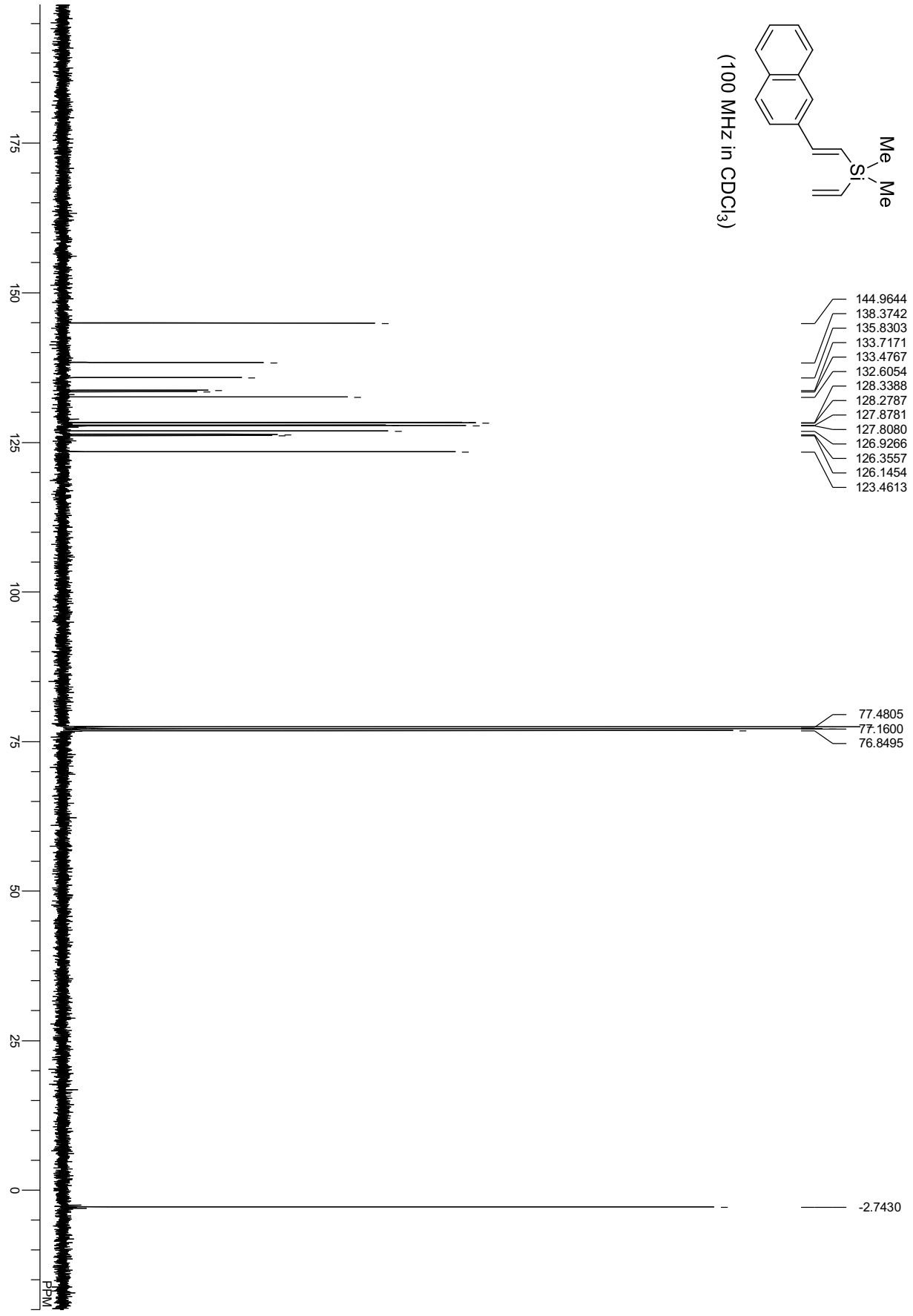
compound **1h**


(100 MHz in CDCl3)
Me
Me
Si
Me
Me
143.9228
139.5360
138.5445
135.4197
133.9374
132.4451
127.8881
126.6762
77.4805
77.1600
76.8395
20.8633
-2.6929
PPM

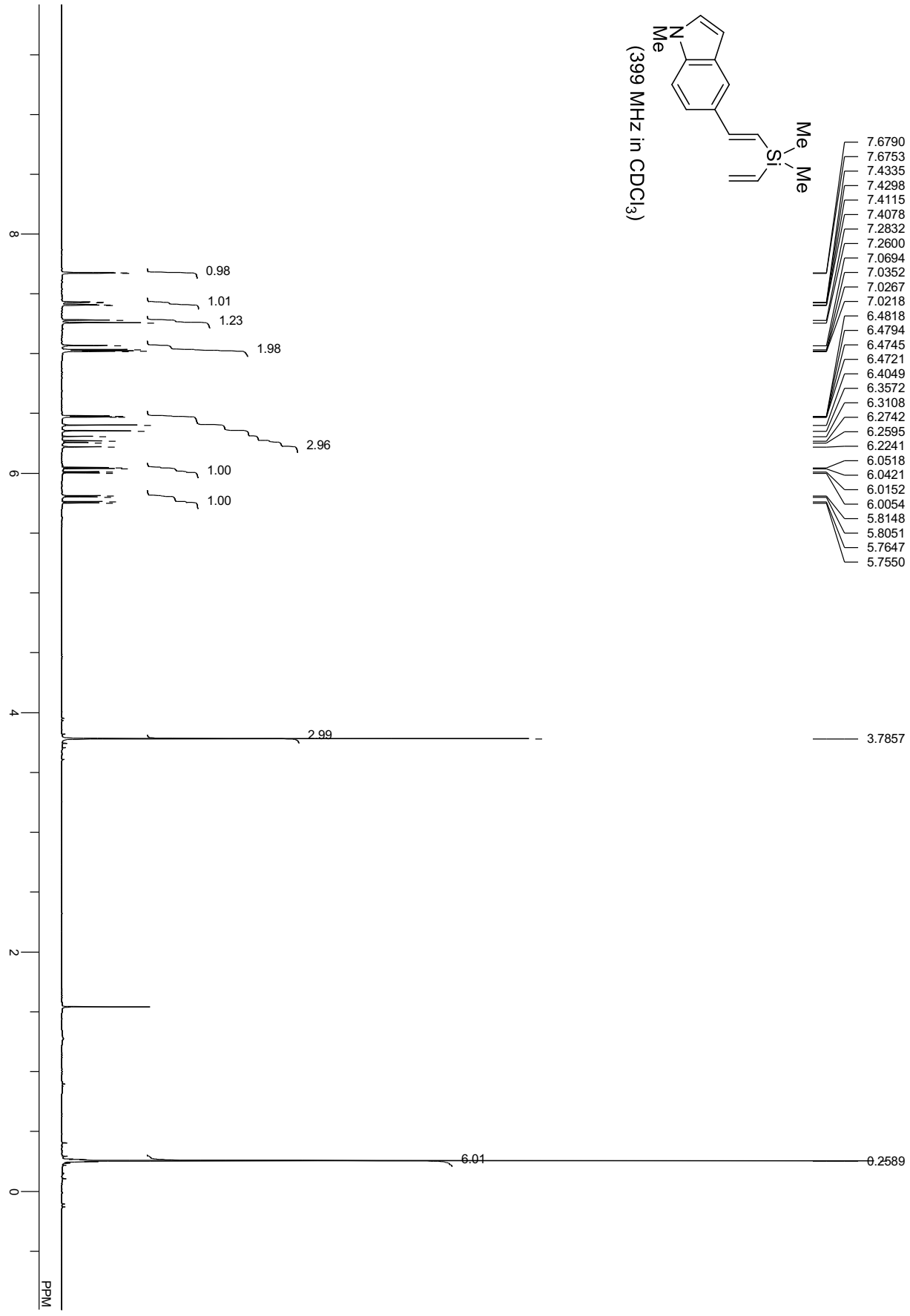
compound **1j**


(399 MHz in CDCl3)
Si
Me
Me
7.8403
7.8342
7.8195
7.8073
7.8000
7.7975
7.7071
7.7022
7.6863
7.6815
7.4958
7.4909
7.4787
7.4713
7.4628
7.4530
7.4481
7.4359
7.4310
7.2600
7.1195
7.0707
6.9961
6.6272
6.5796
6.3181
6.2815
6.2668
6.2302
6.0860
6.0763
6.0494
6.0396
5.8405
5.8307
5.7904
5.7806
5.04
2.00
0.95
0.97
1.94
1.00
6.04
0.2907
8
6
4
2
0
PPM

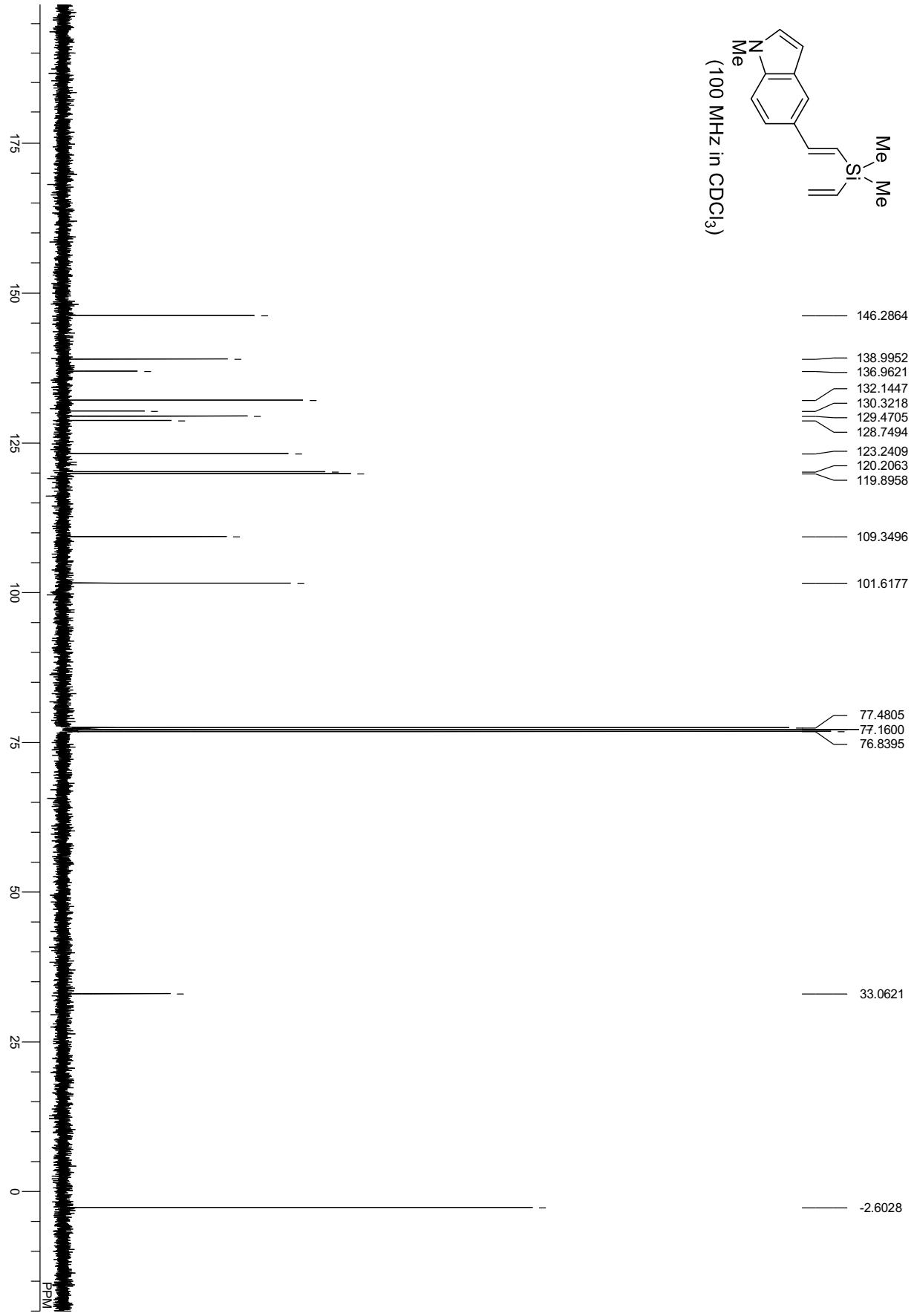
compound **1j**


(100 MHz in CDCl3)
Me
Si
Me
144.9644
138.3742
135.8303
133.7171
133.4767
132.6054
128.3388
128.2787
127.8781
127.8080
126.9266
126.3557
126.1454
123.4613
77.4805
77.1600
76.8495
-2.7430
175
150
125
100
75
50
25
0
PPM

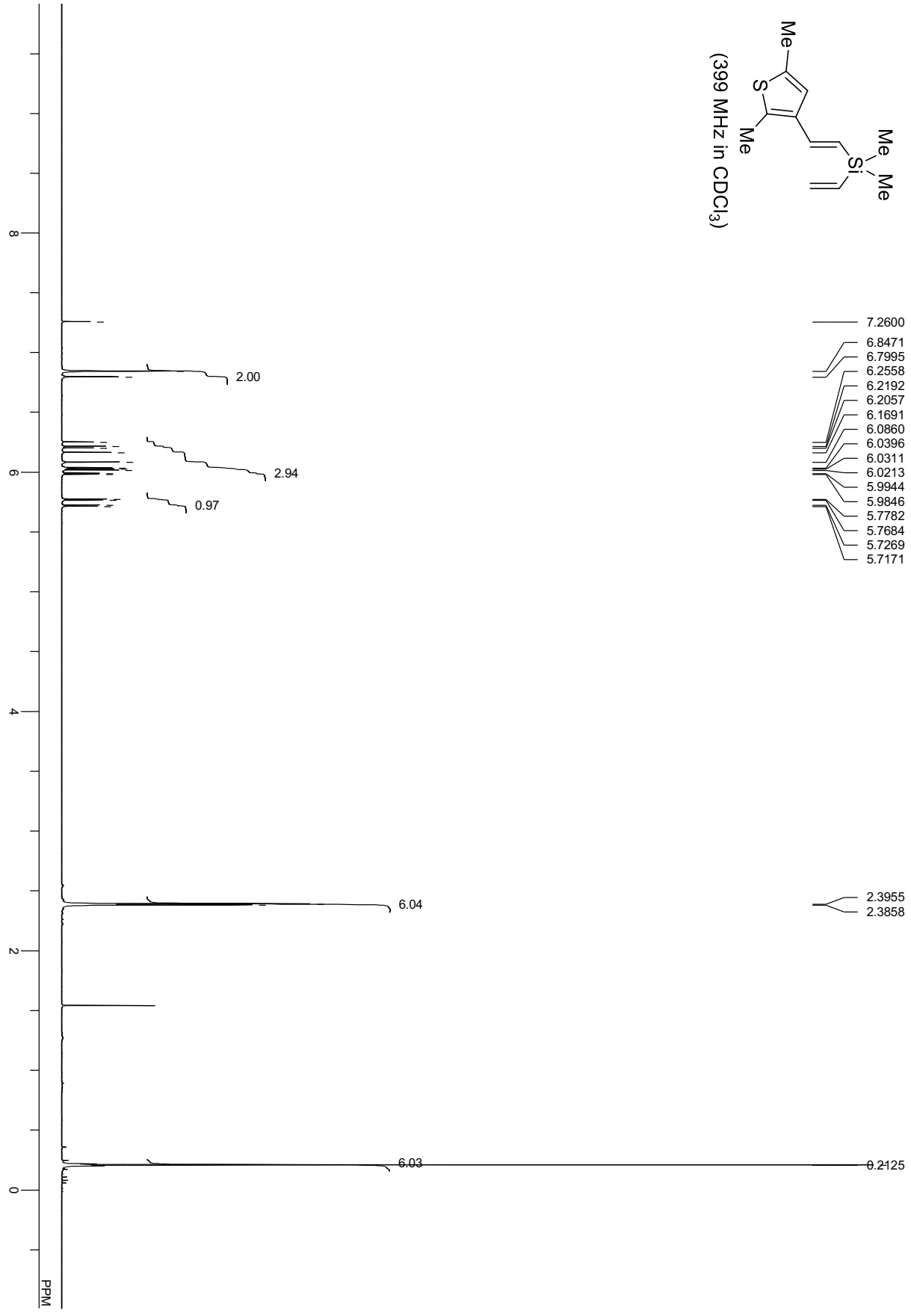
compound **1k**


N
Me
(399 MHz in CDCl3)
Me Me
Si
7.6790
7.6753
7.4335
7.4298
7.4115
7.4078
7.2832
7.2600
7.0694
7.0352
7.0267
7.0218
6.4818
6.4794
6.4745
6.4721
6.4049
6.3572
6.3108
6.2742
6.2595
6.2241
6.0518
6.0421
6.0152
6.0054
5.8148
5.8051
5.7647
5.7550
3.7857
0.2589
0.98
1.01
1.23
1.98
2.96
1.00
1.00
2.99
6.01
8
6
4
2
0
PPM

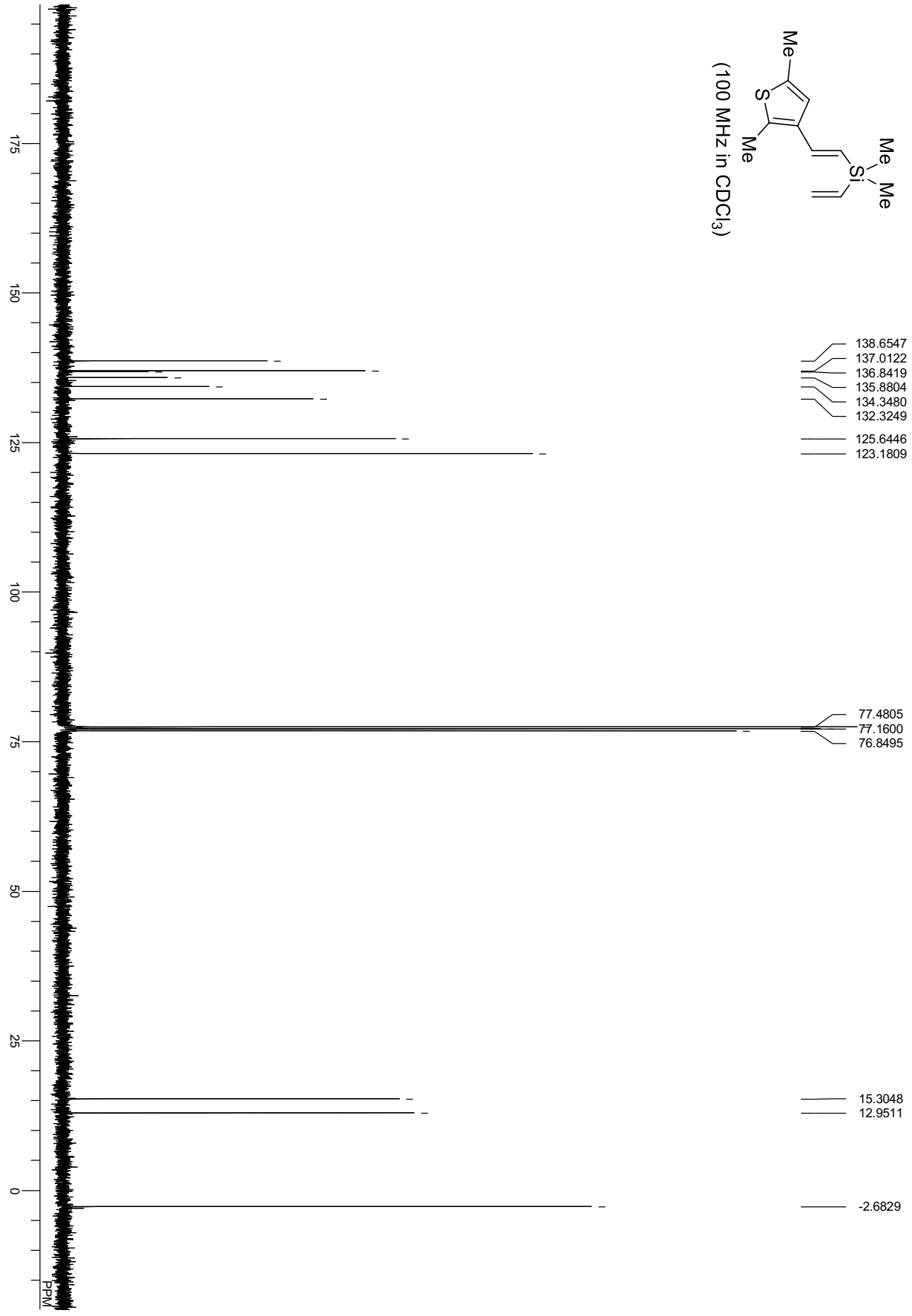
compound **1k**


N
Me
Si
Me
Me
(100 MHz in CDCl3)
146.2864
138.9952
136.9621
132.1447
130.3218
129.4705
128.7494
123.2409
120.2063
119.8958
109.3496
101.6177
77.4805
77.1600
76.8395
33.0621
-2.6028
PPM

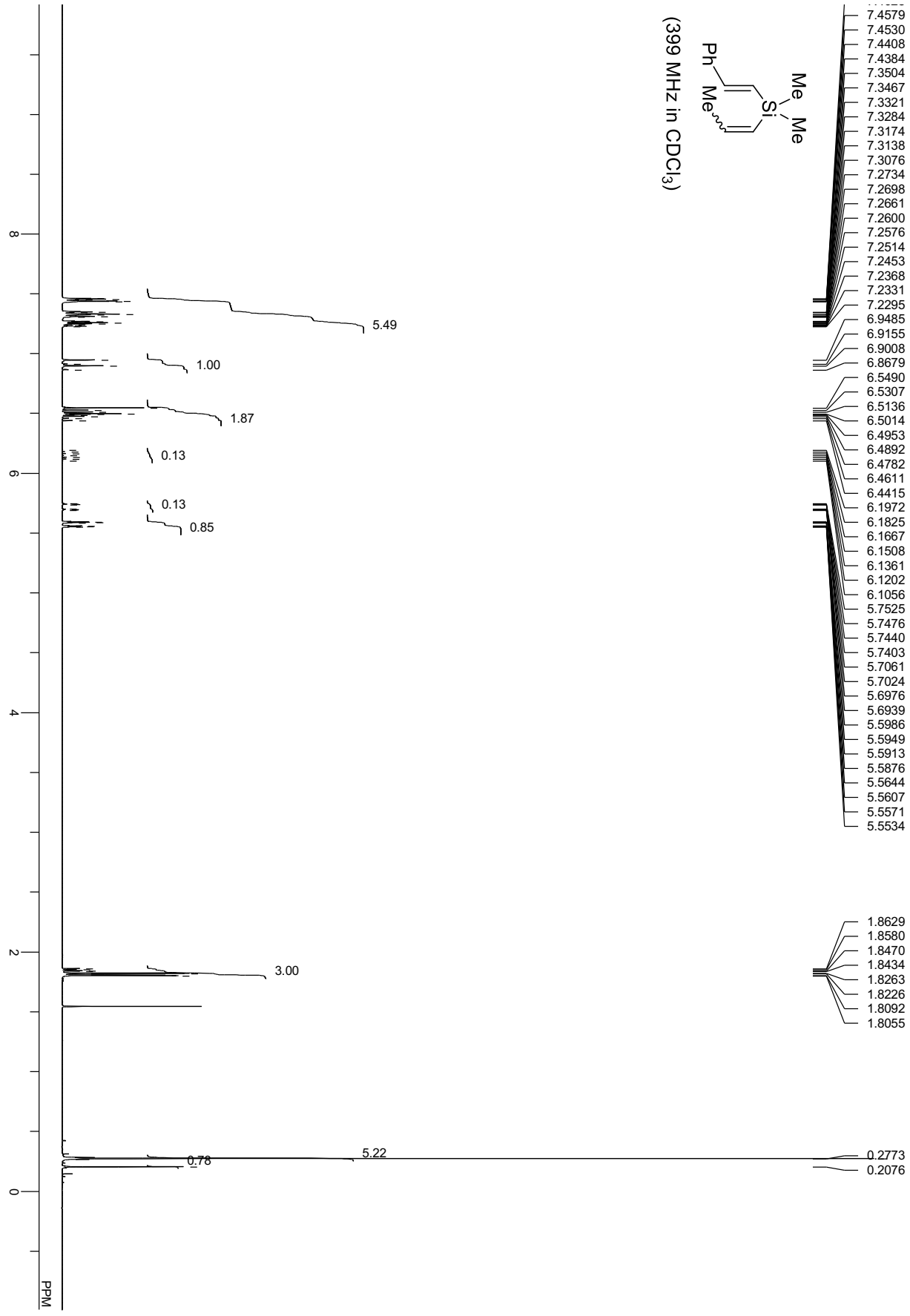
compound **1l**


(399 MHz in CDCl3)
Me
S
Me
Si
Me
Me
7.2600
6.8471
6.7995
6.2558
6.2192
6.2057
6.1691
6.0860
6.0396
6.0311
6.0213
5.9944
5.9846
5.7782
5.7684
5.7269
5.7171
2.3955
2.3858
0.2125
2.00
2.94
0.97
6.04
6.03
8
6
4
2
0
PPM

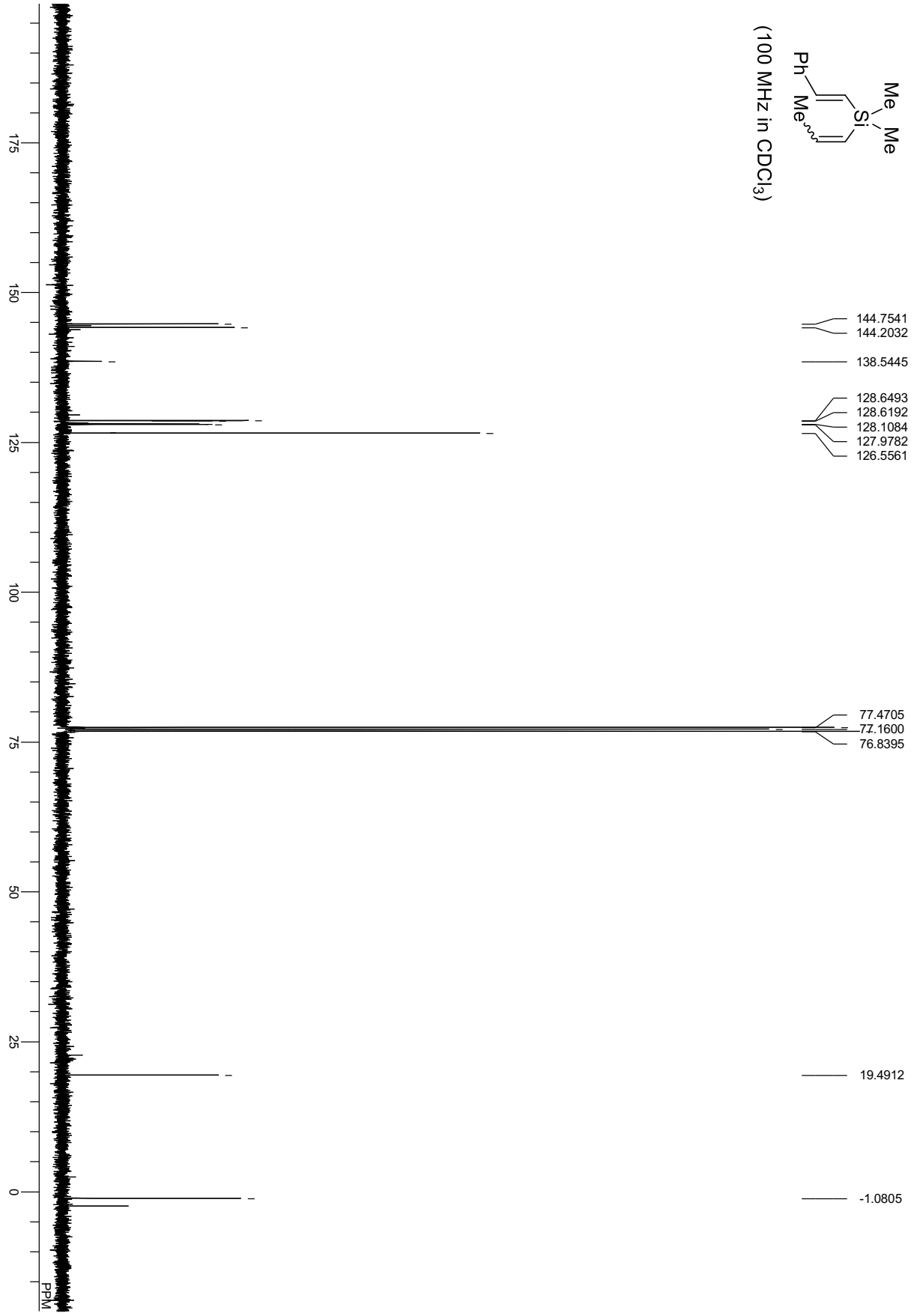
compound **1l**


Me
S
Me
Me
Si
Me
(100 MHz in CDCl3)
138.6547
137.0122
136.8419
135.8804
134.3480
132.3249
125.6446
123.1809
77.4805
77.1600
76.8495
15.3048
12.9511
-2.6829
PPM

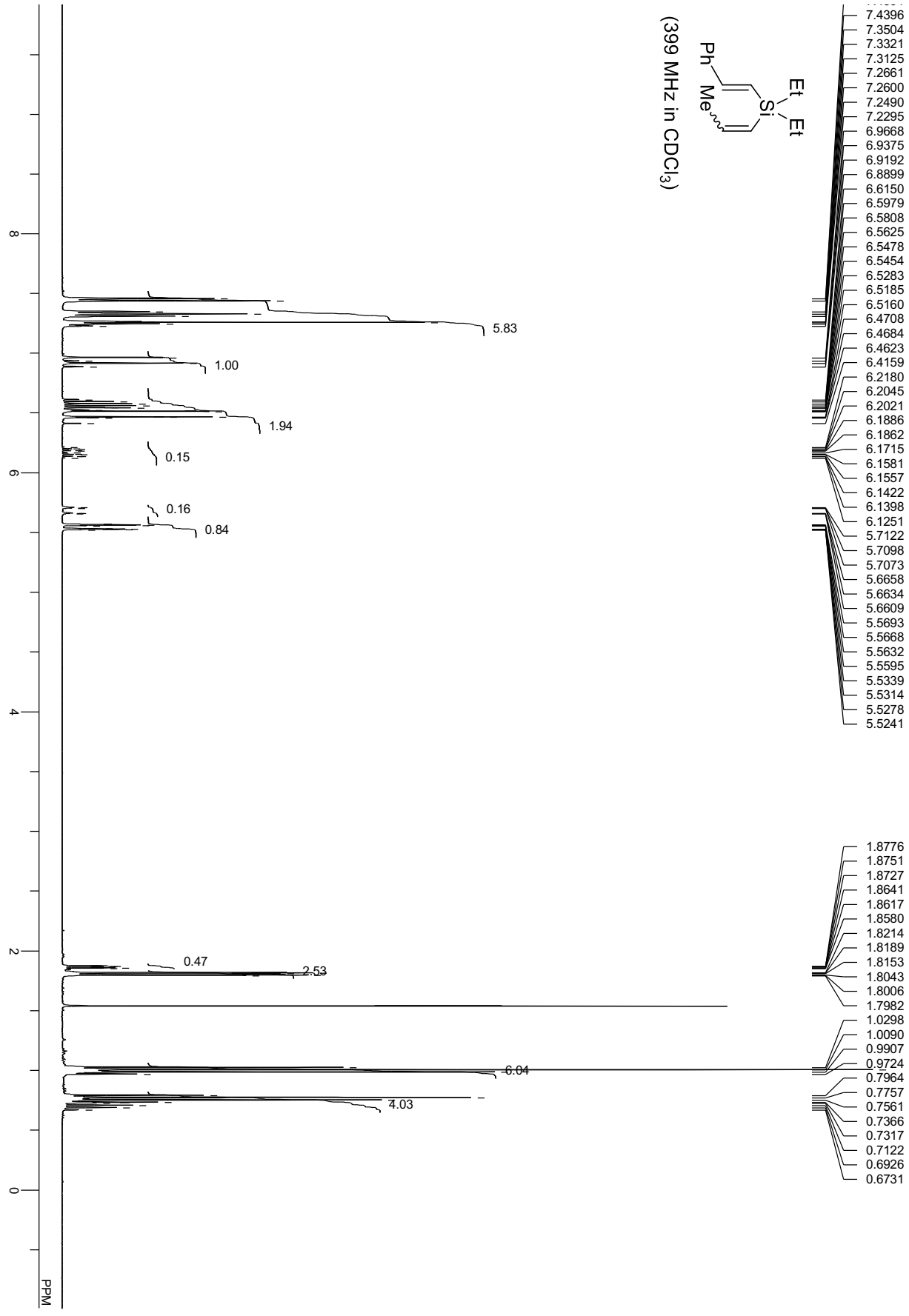
compound **1m** (*Z*/*E* = 87/13)



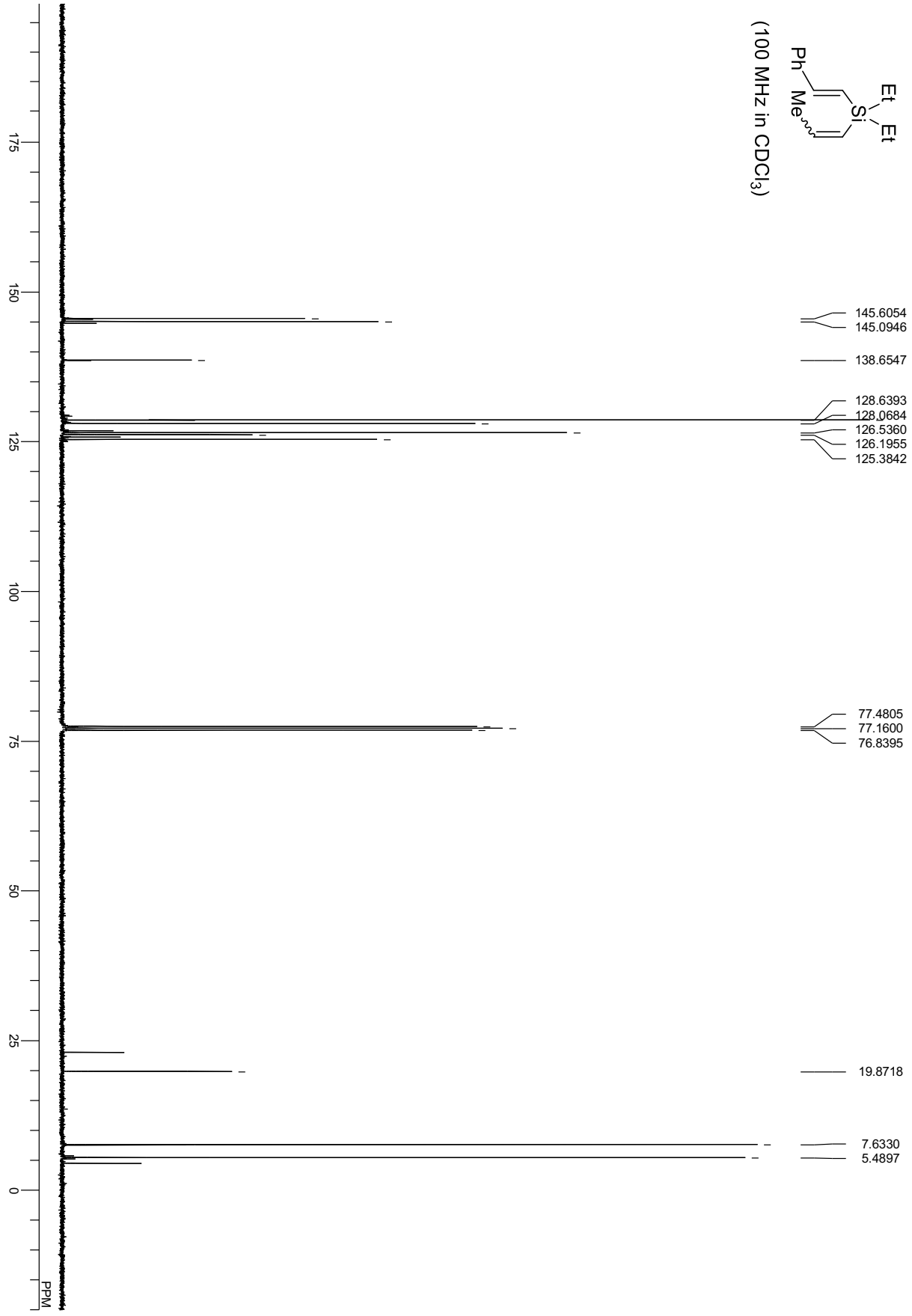
compound **1m** (*Z*/*E* = 87/13)



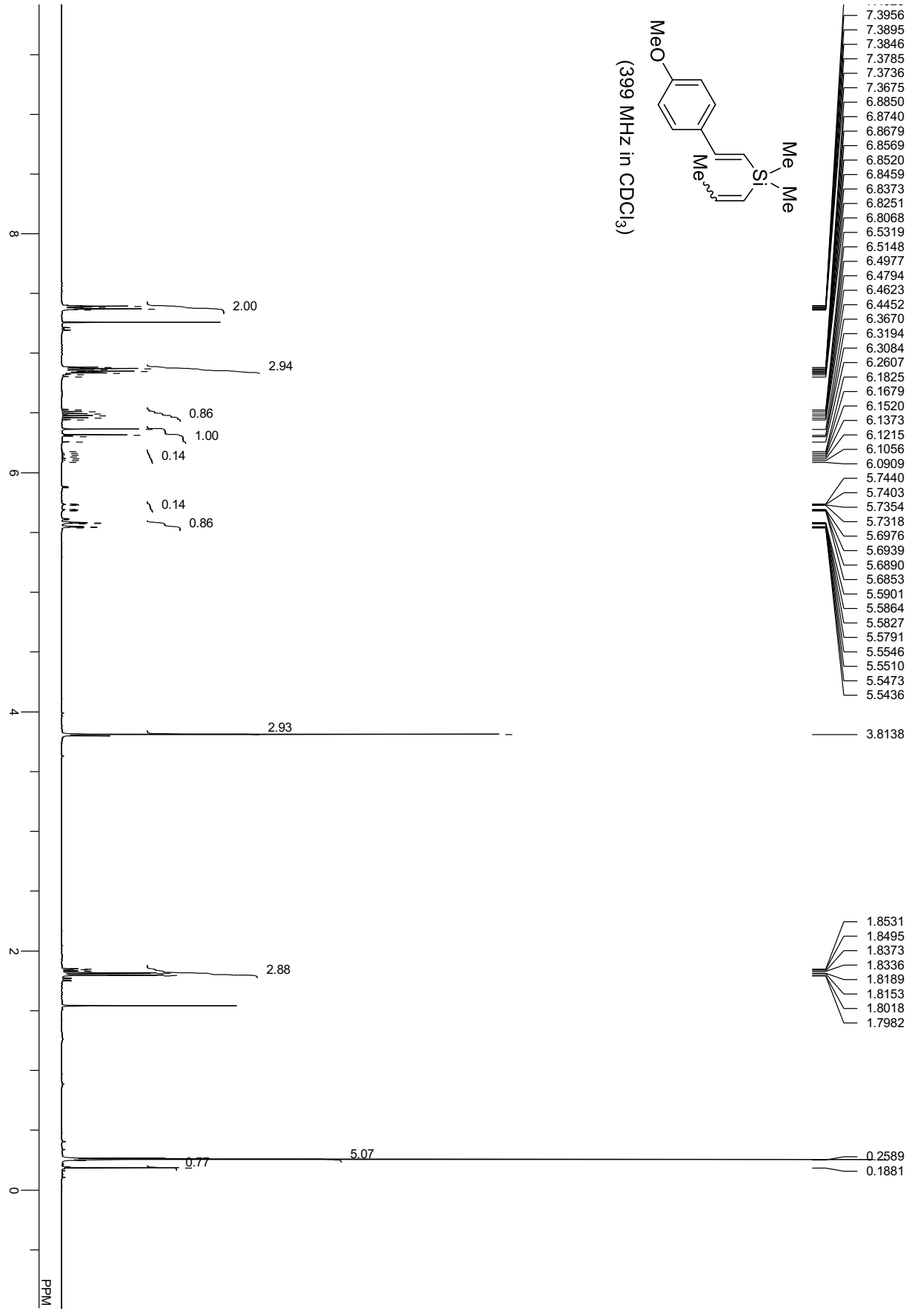
compound **1n** (*Z*/*E* = 84/16)



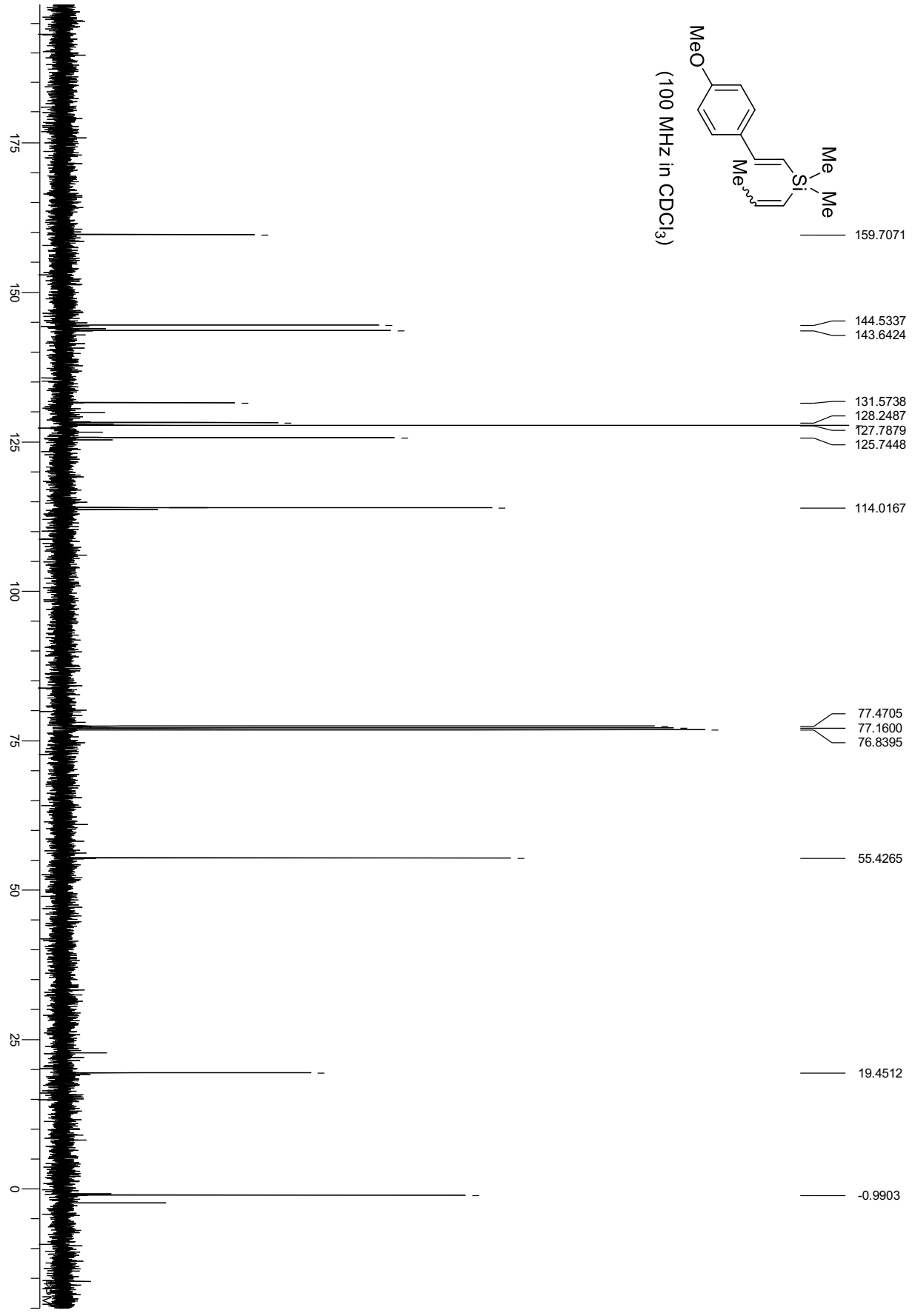
compound **1n** (*Z*/*E* = 84/16)



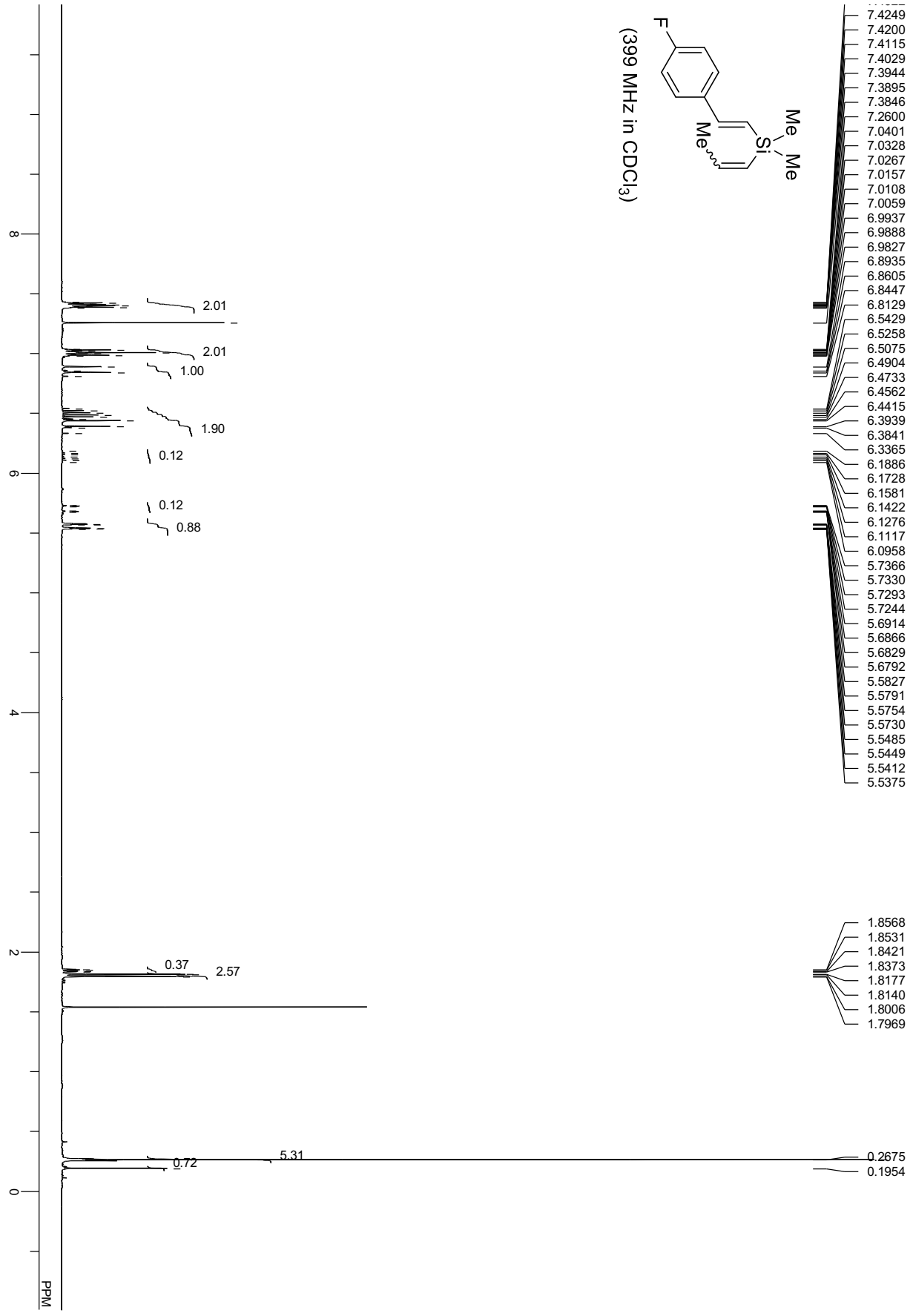
compound **1o** (*Z*/*E* = 86/14; 91% pure)



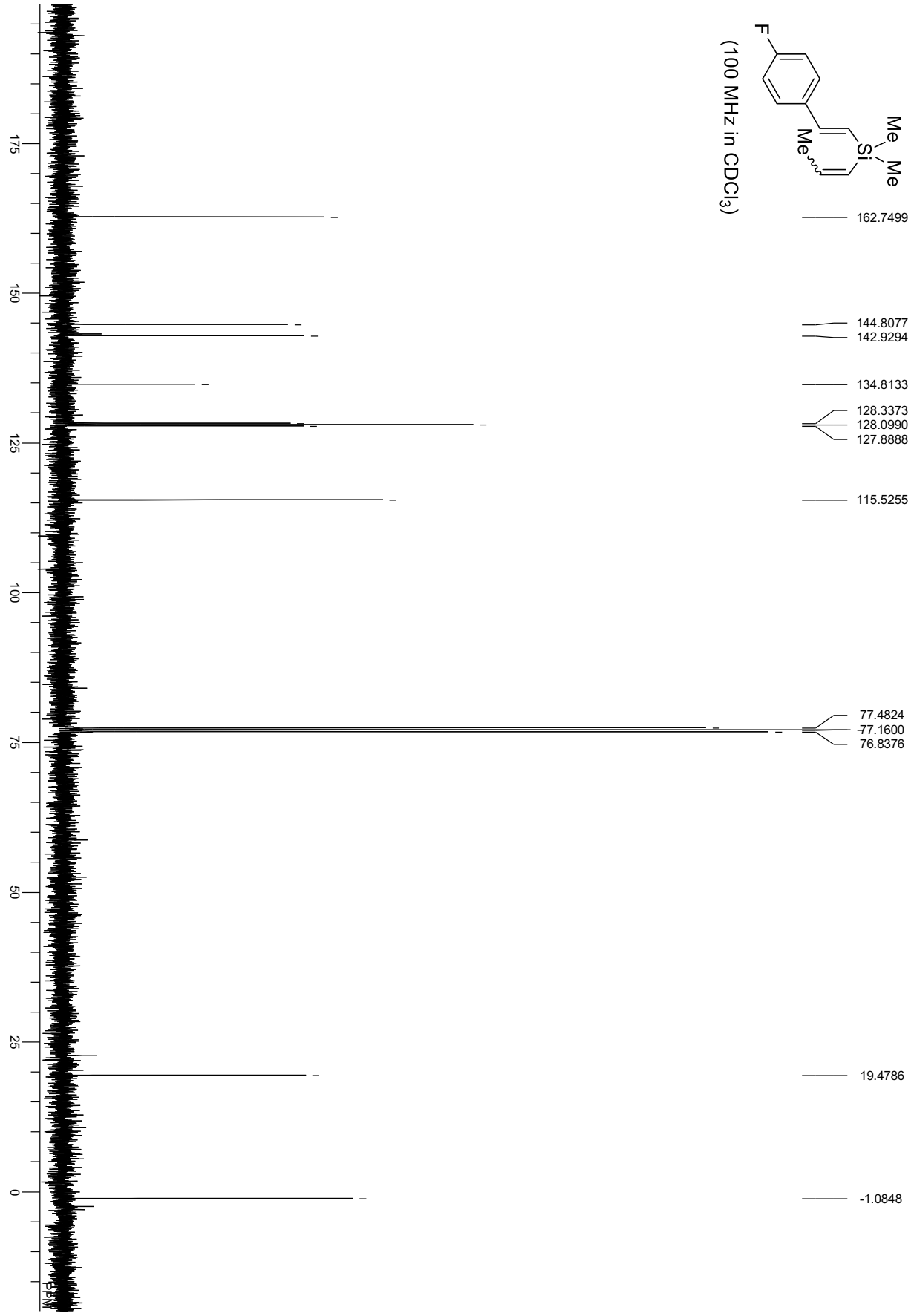
compound **1o** (*Z*/*E* = 86/14; 91% pure)



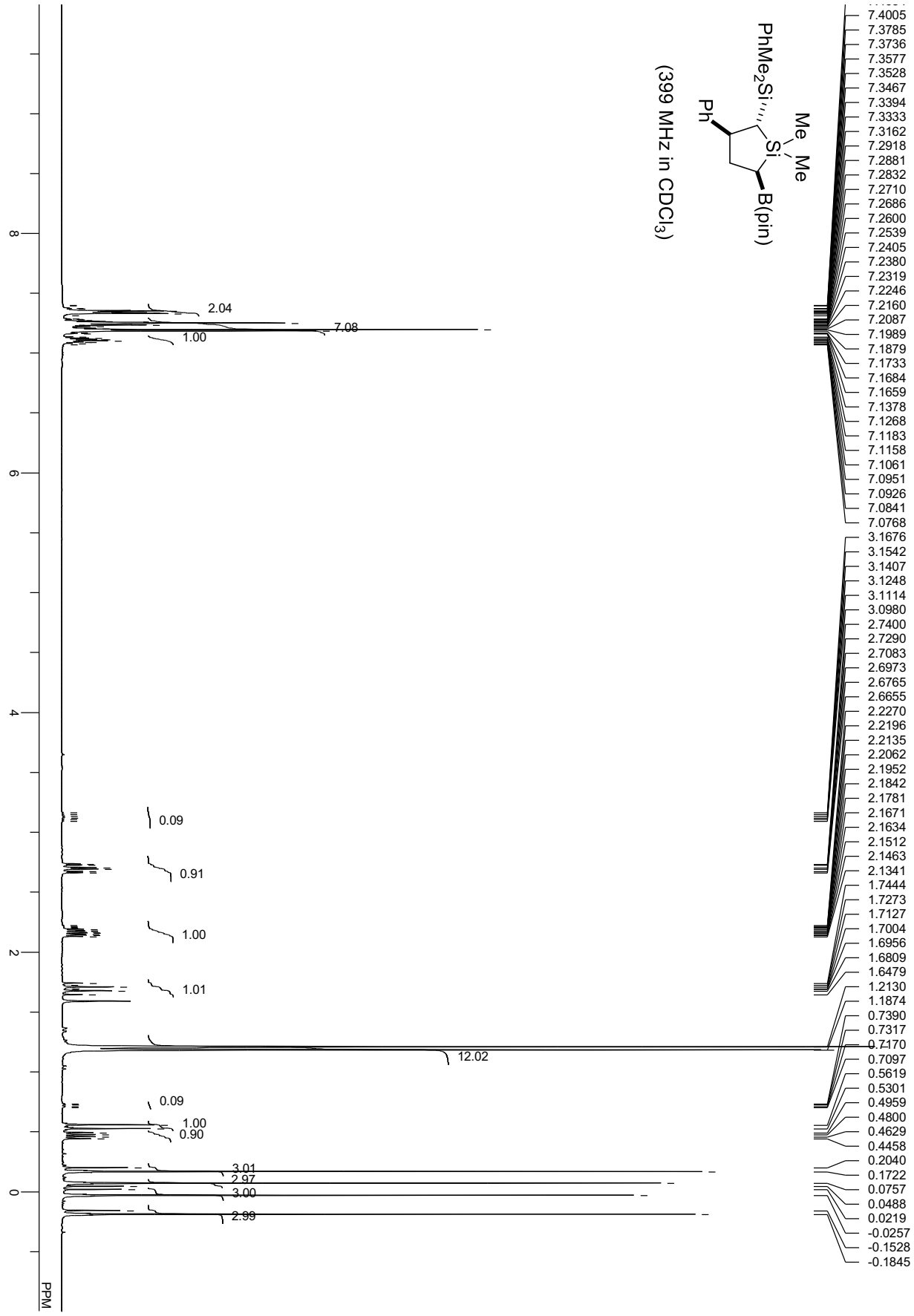
compound **1p** (*Z*/*E* = 88/12; 97% pure)



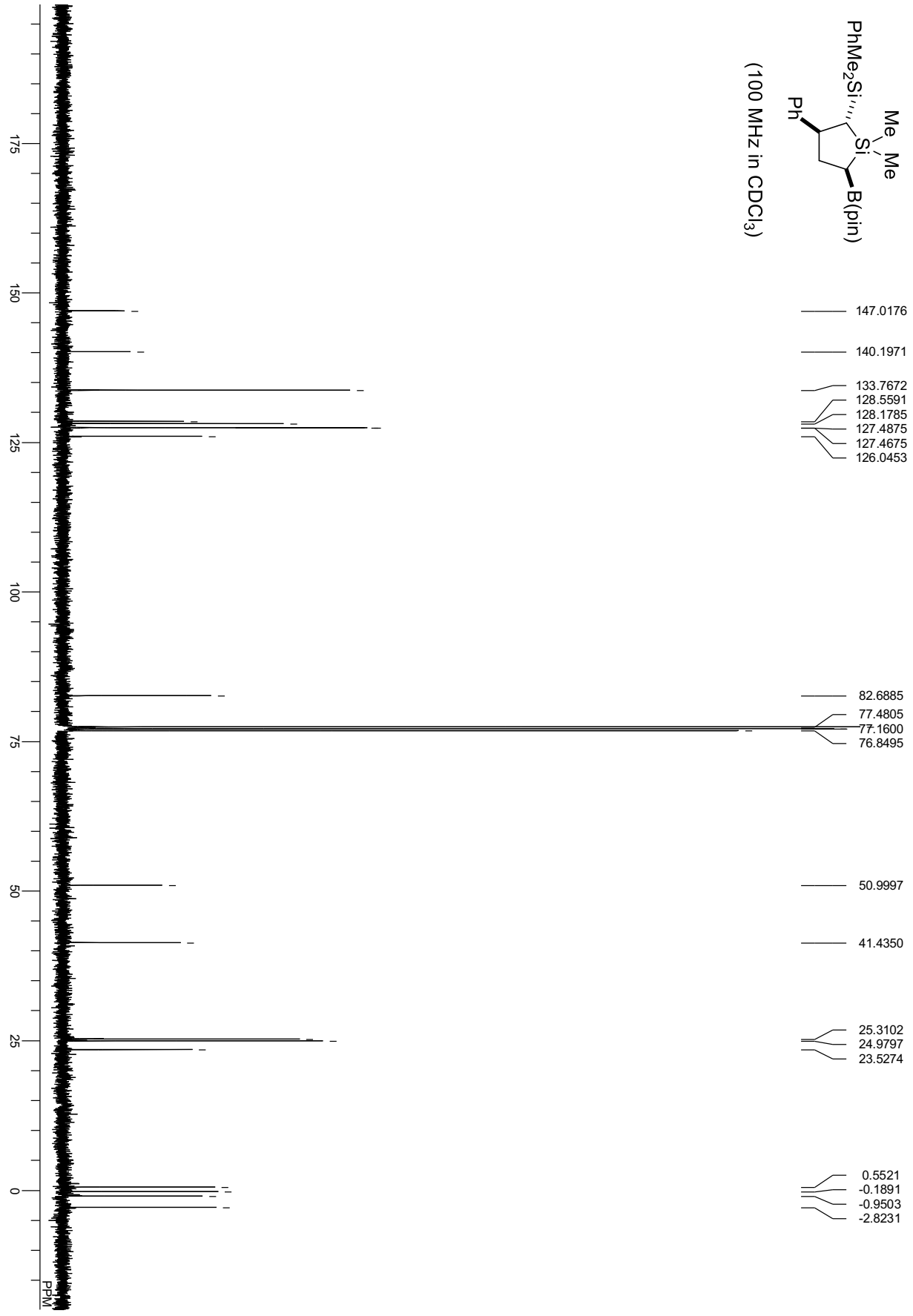
compound **1p** (*Z*/*E* = 88/12; 97% pure)



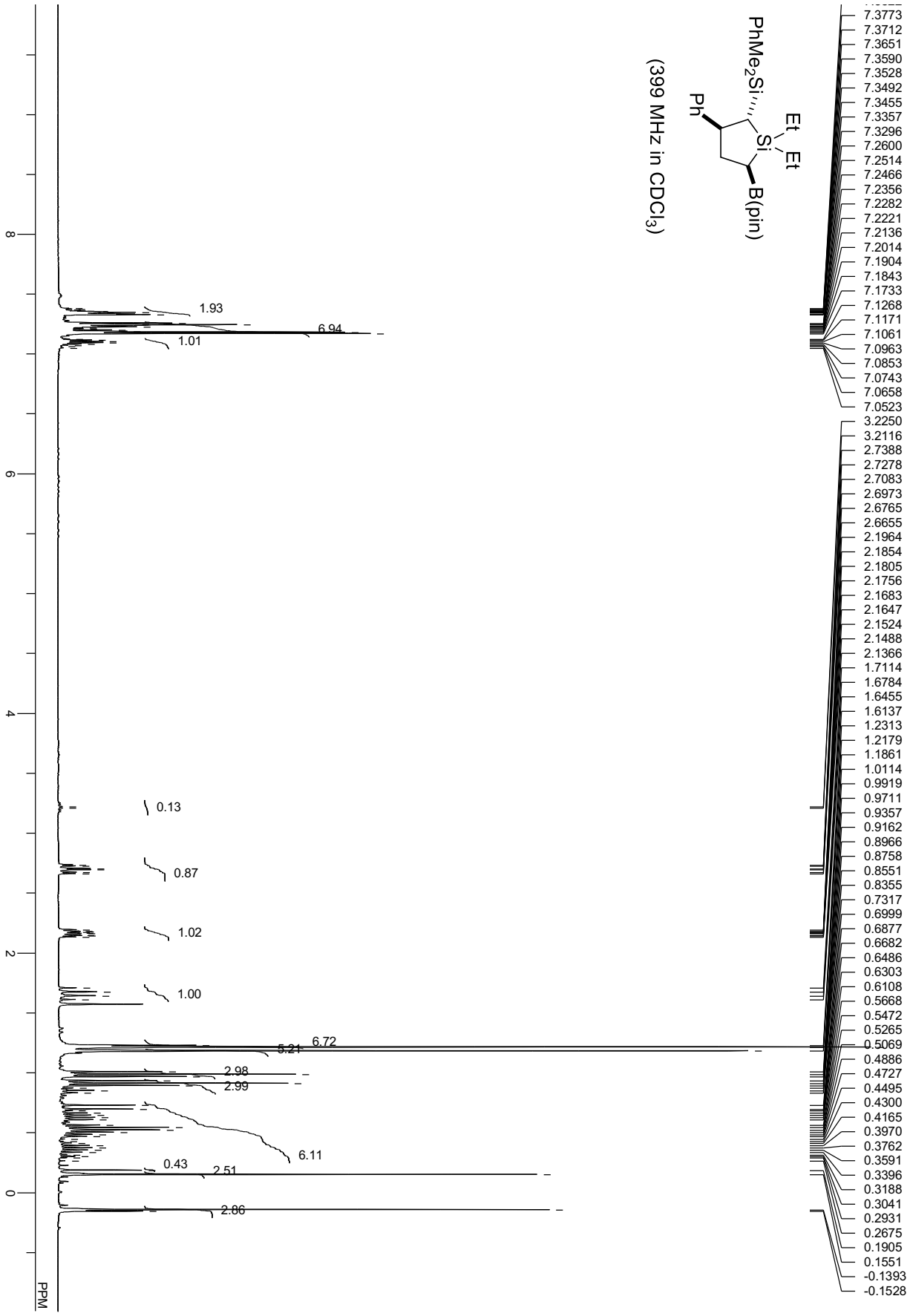
compound **3aa** (dr = 91/9)



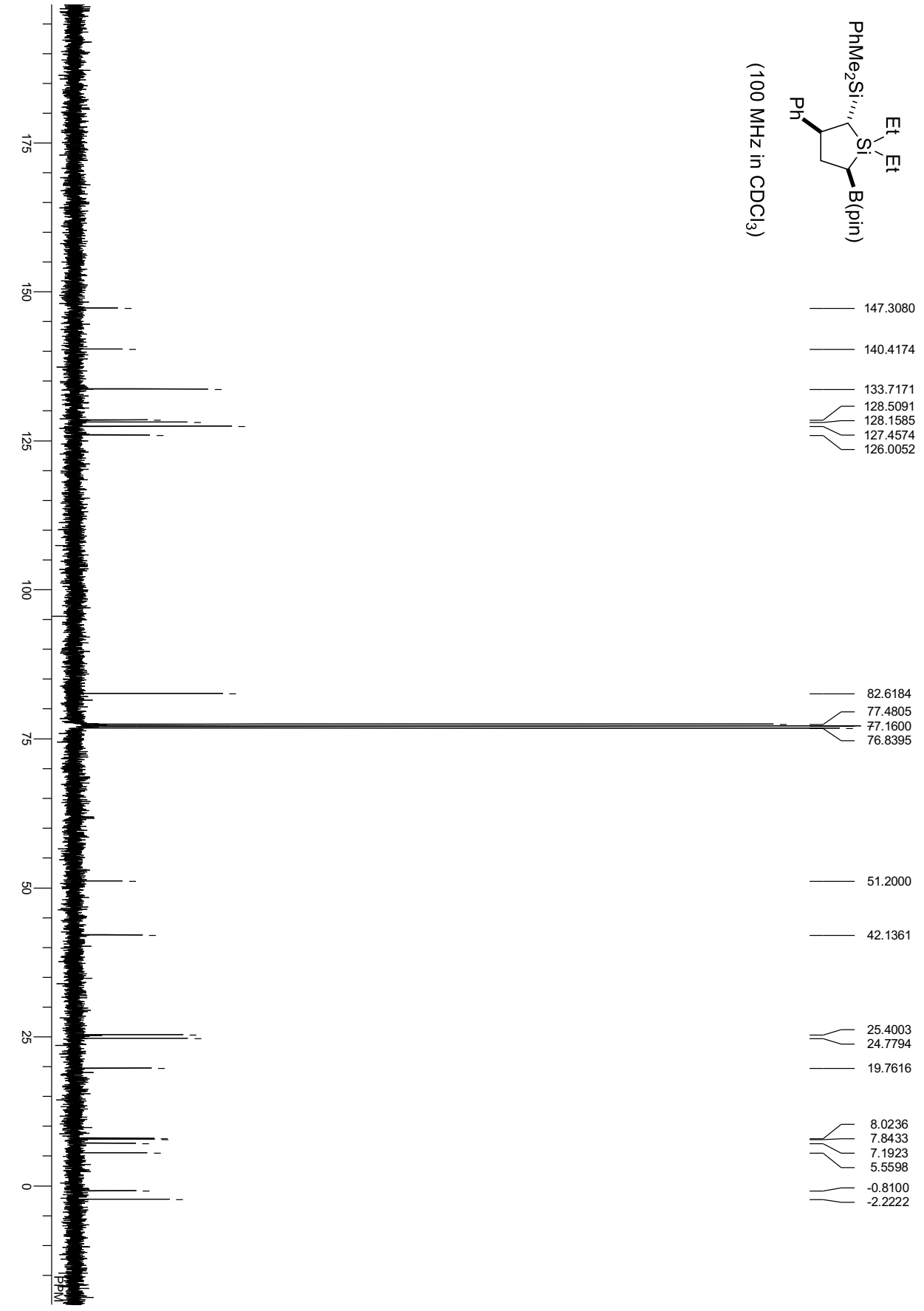
compound **3aa** (dr = 91/9)



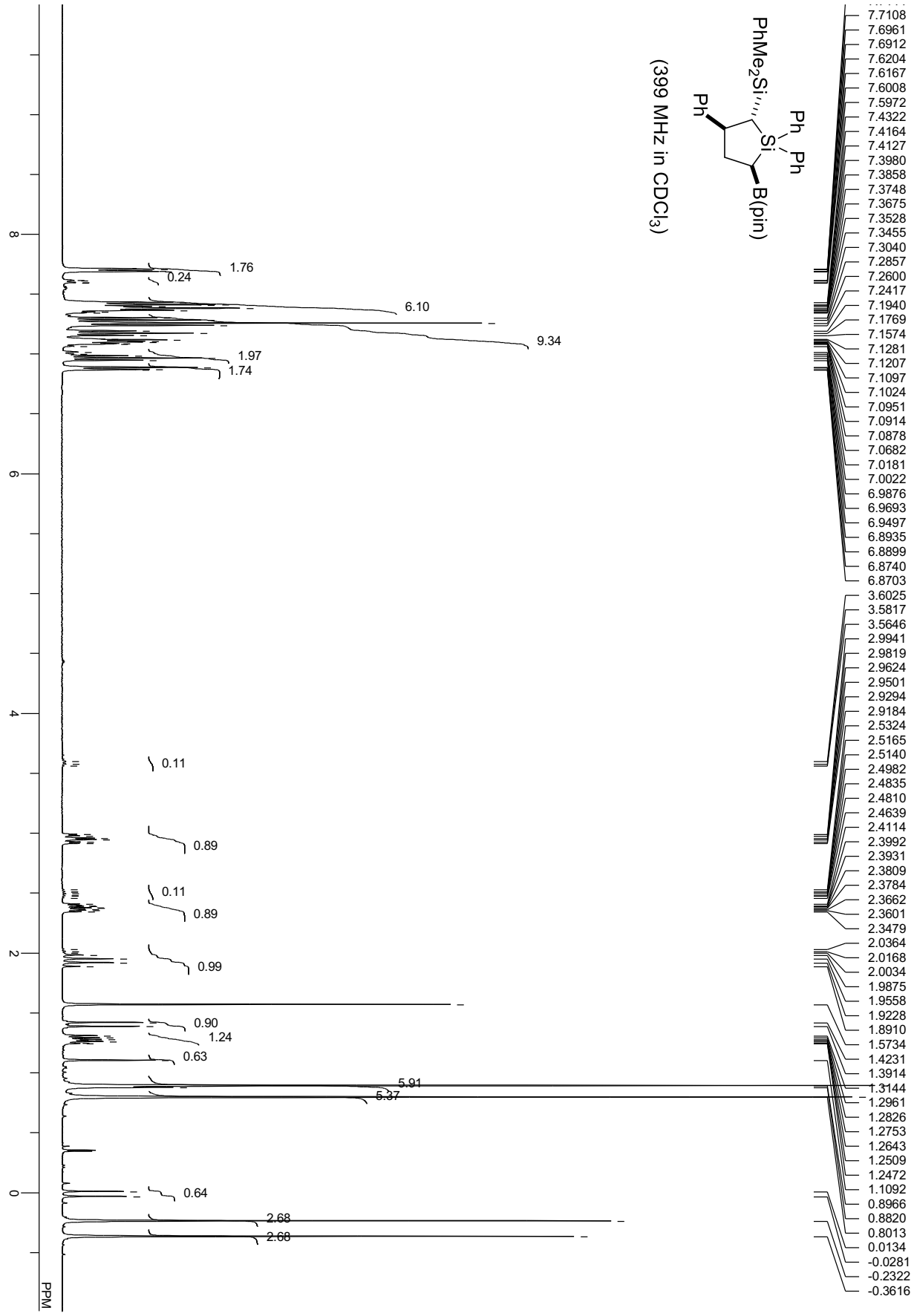
compound **3ba** (dr = 87/13)



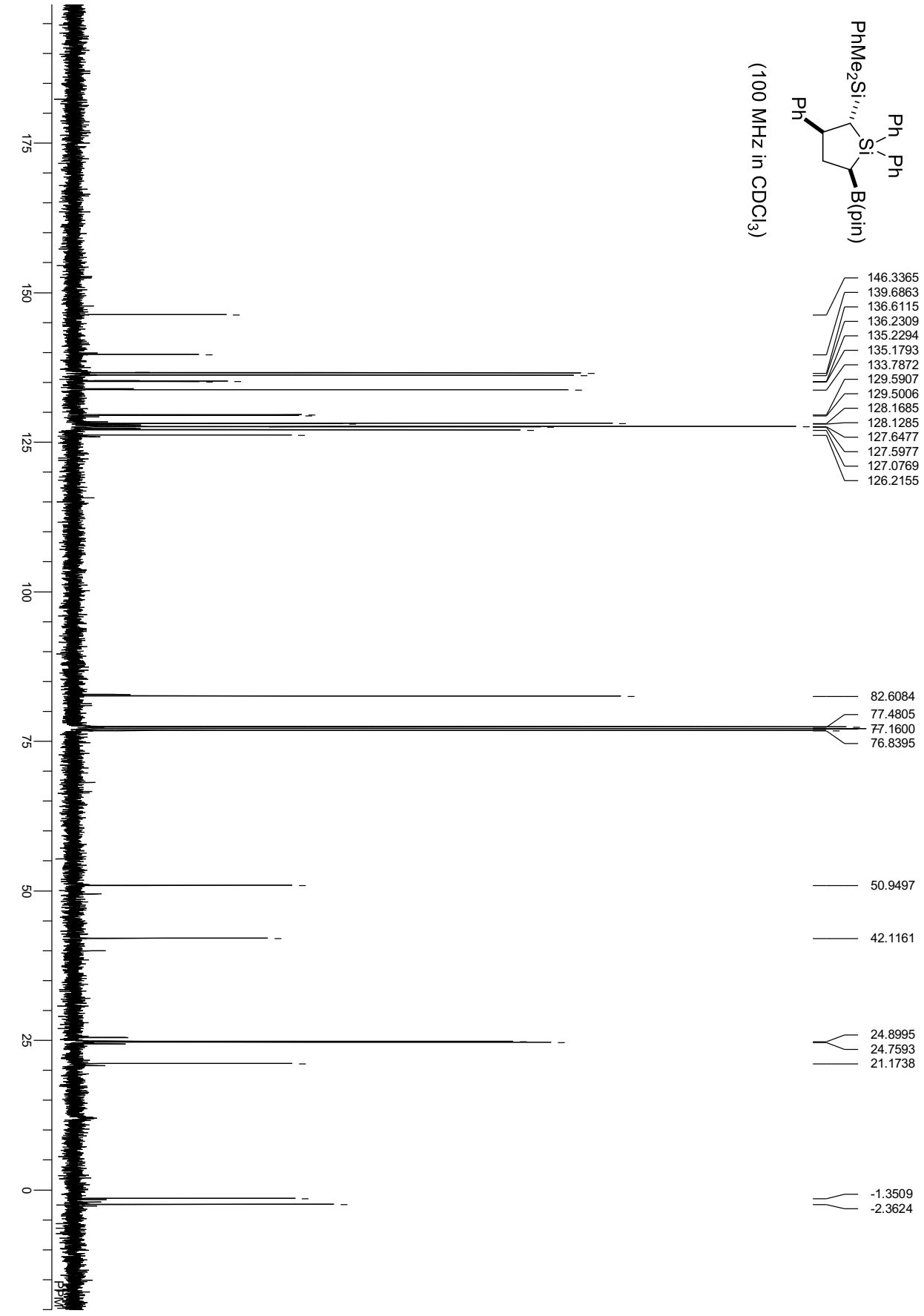
compound **3ba** (dr = 87/13)



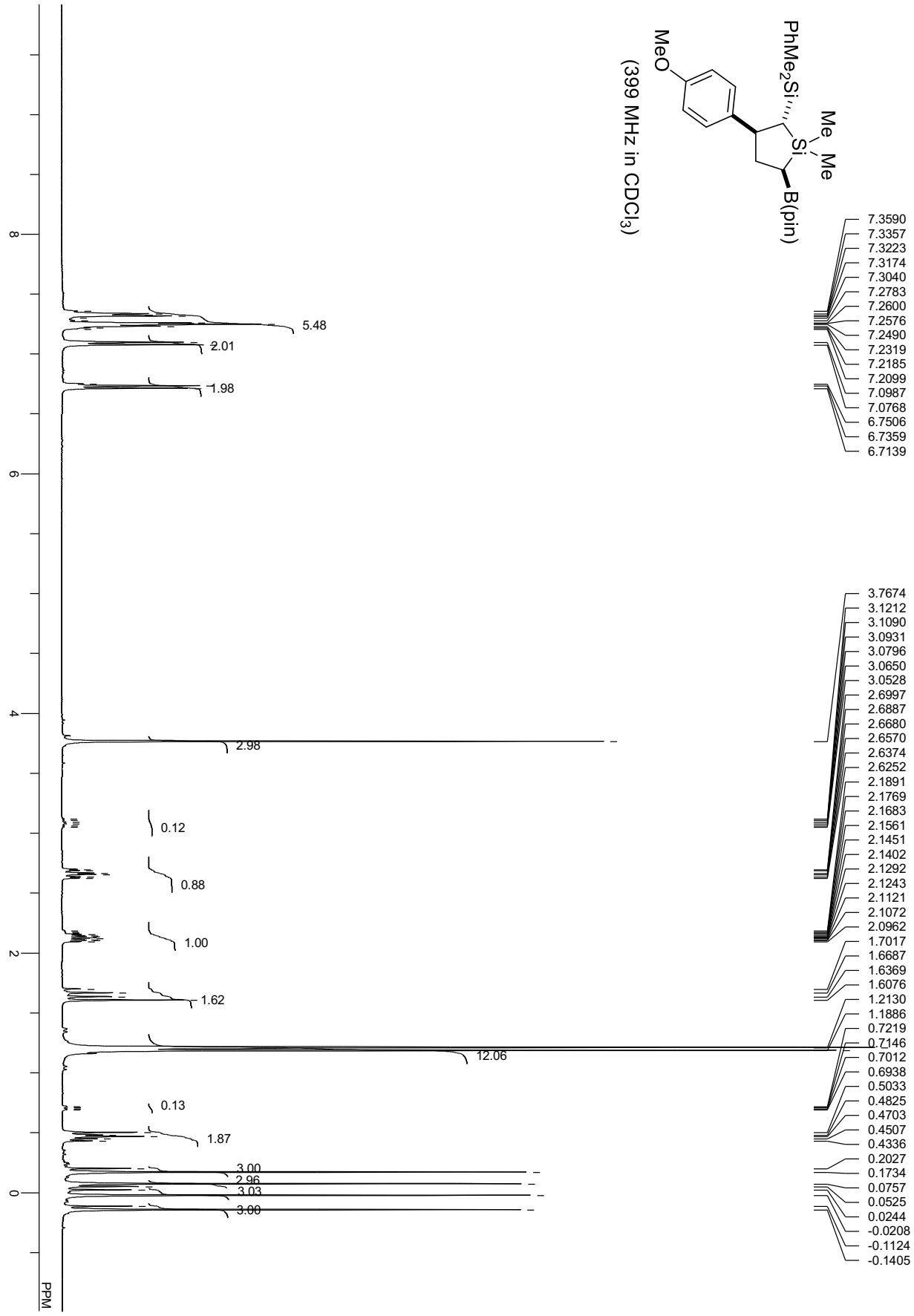
compound **3ca** (dr = 89/11)



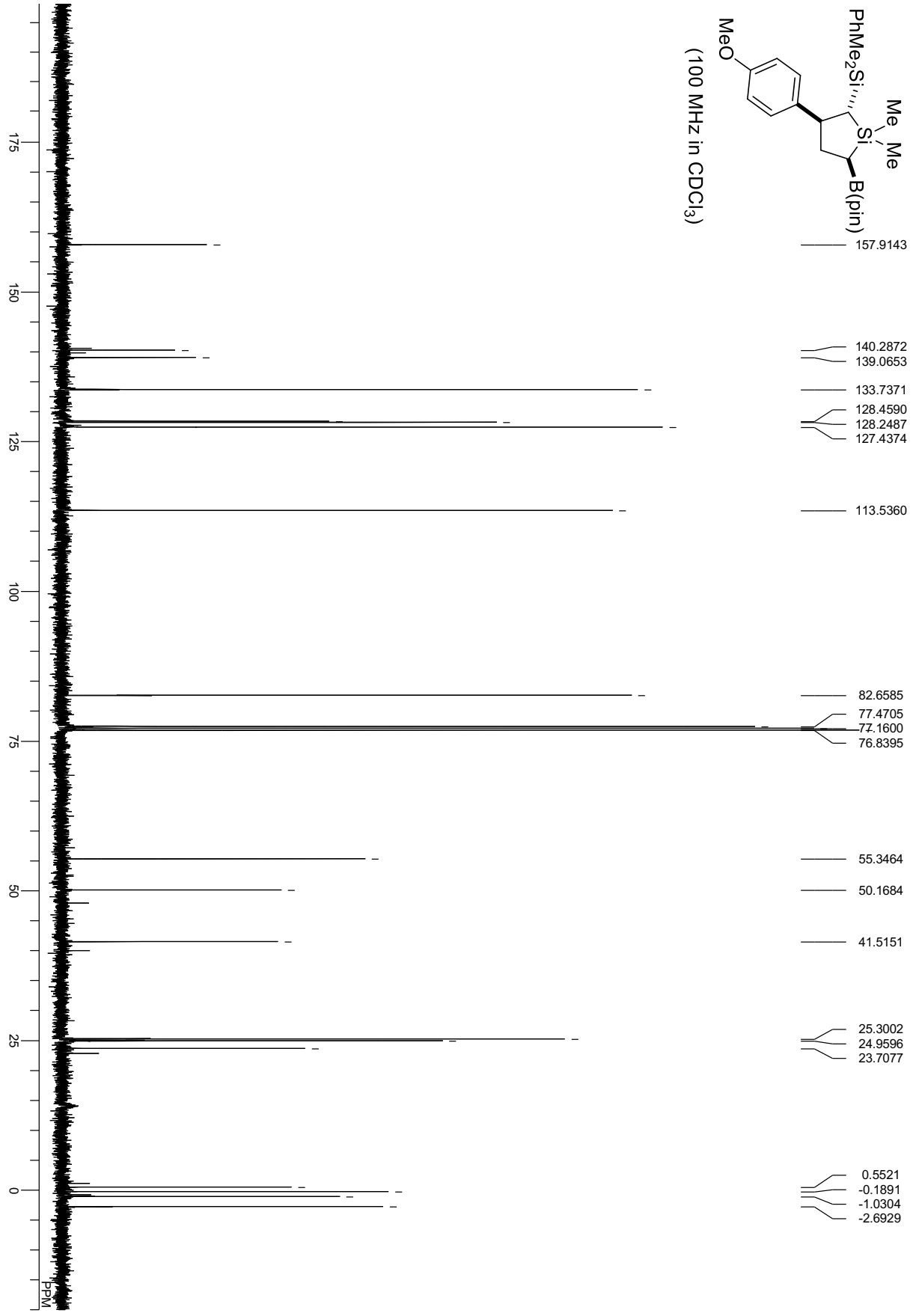
compound **3ca** (dr = 89/11)



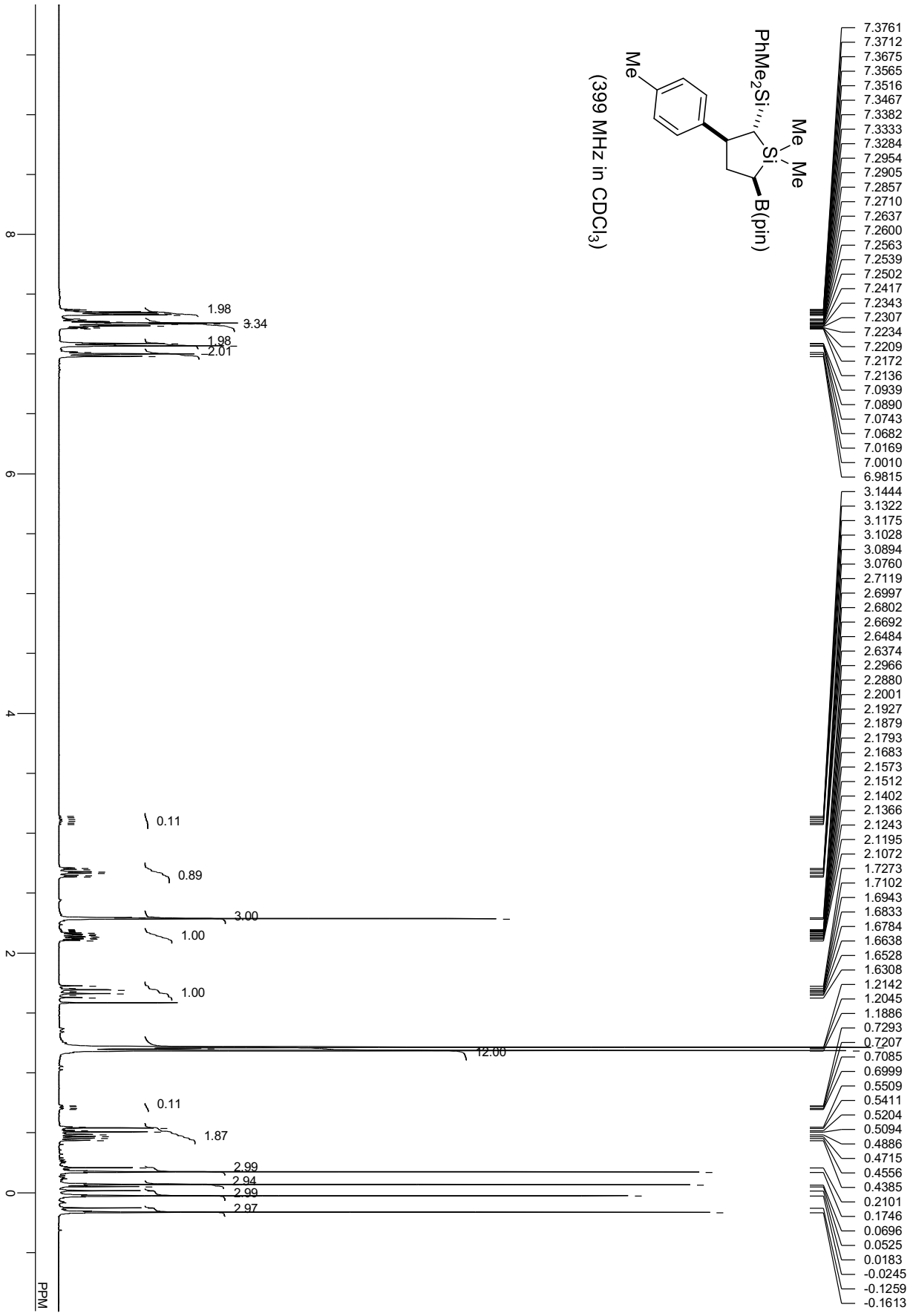
compound **3da** (dr = 88/12)



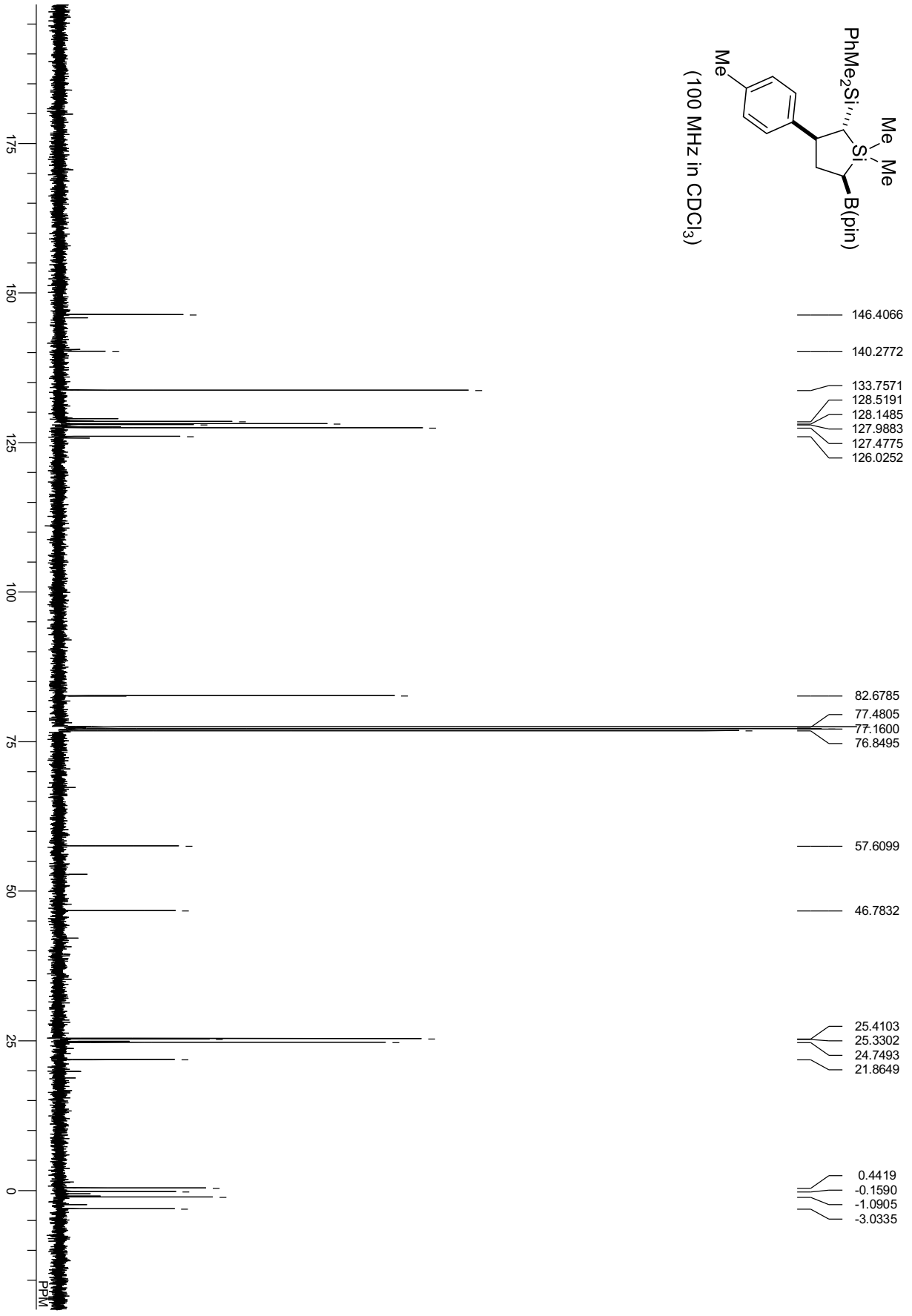
compound **3da** (dr = 88/12)



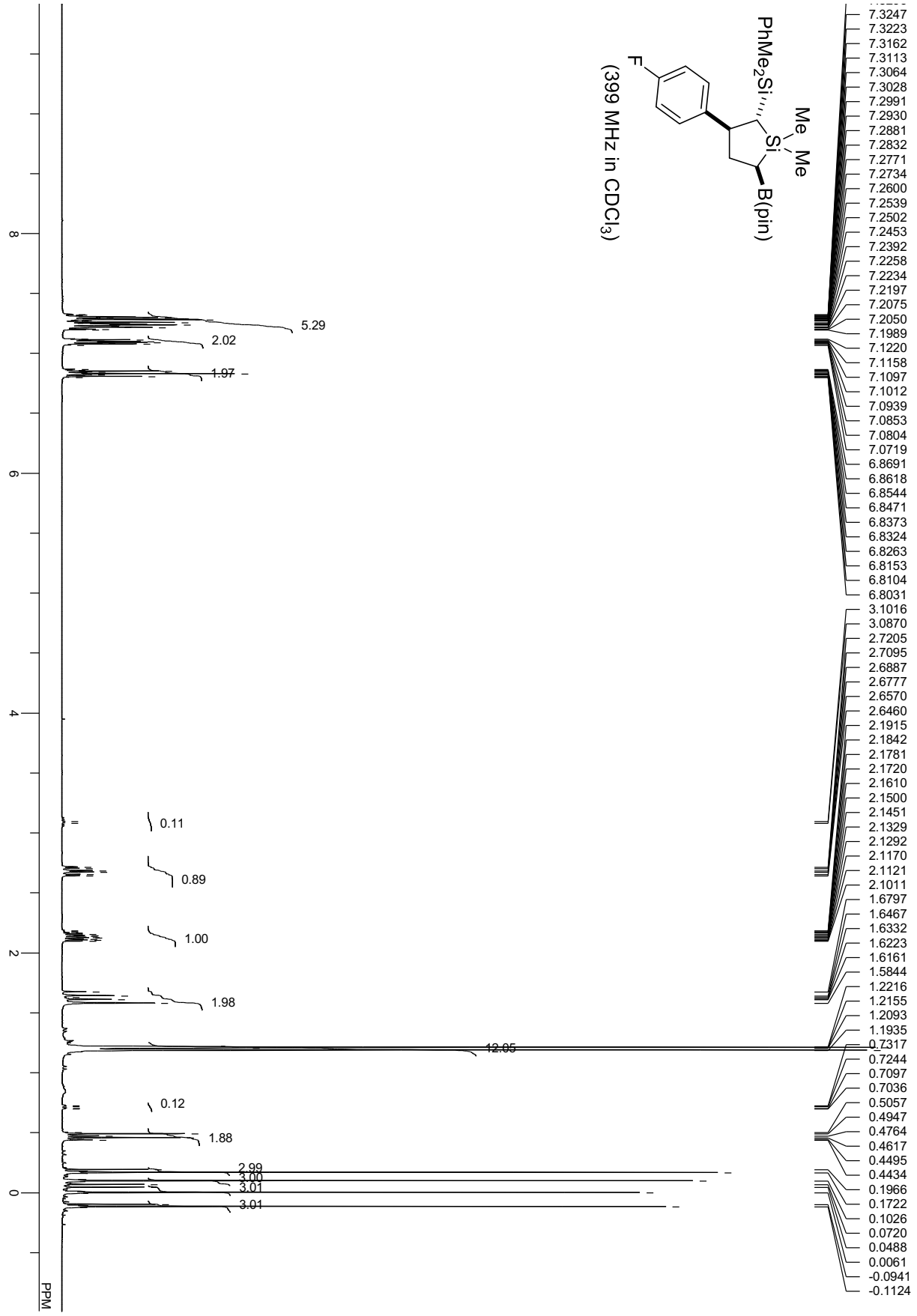
compound **3ea** (dr = 89/11)



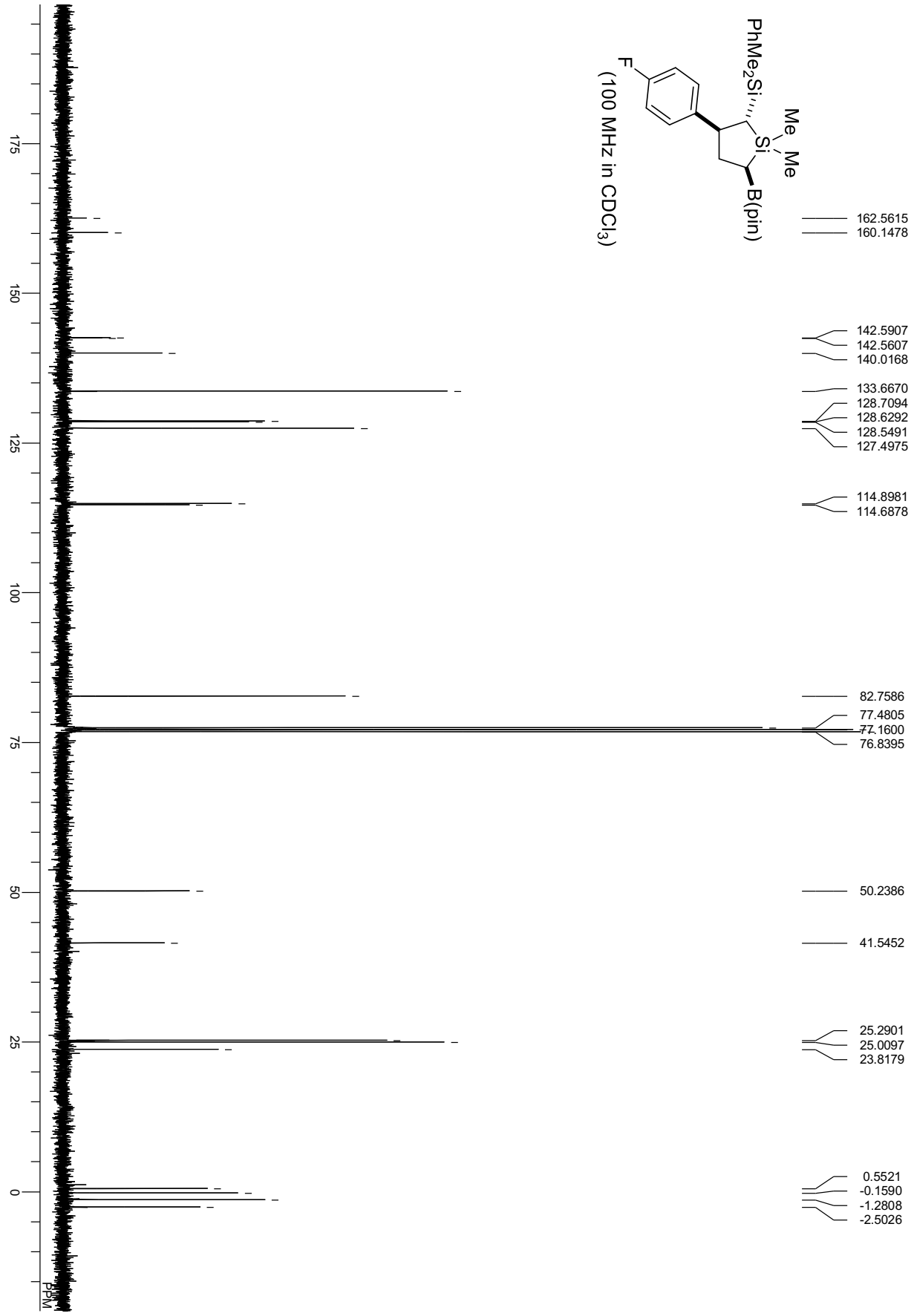
compound **3ea** (dr = 89/11)



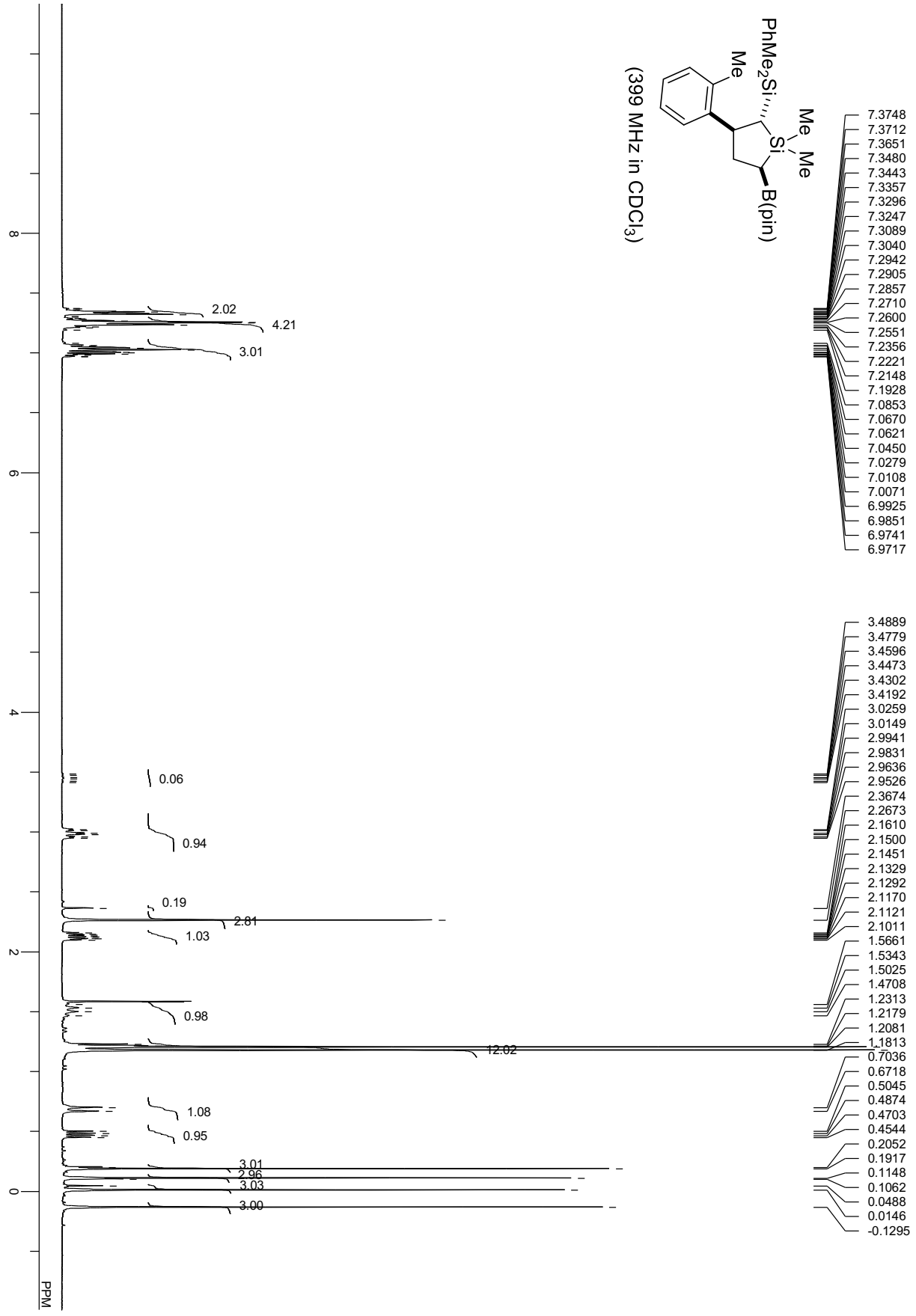
compound **3fa** (dr = 89/11)



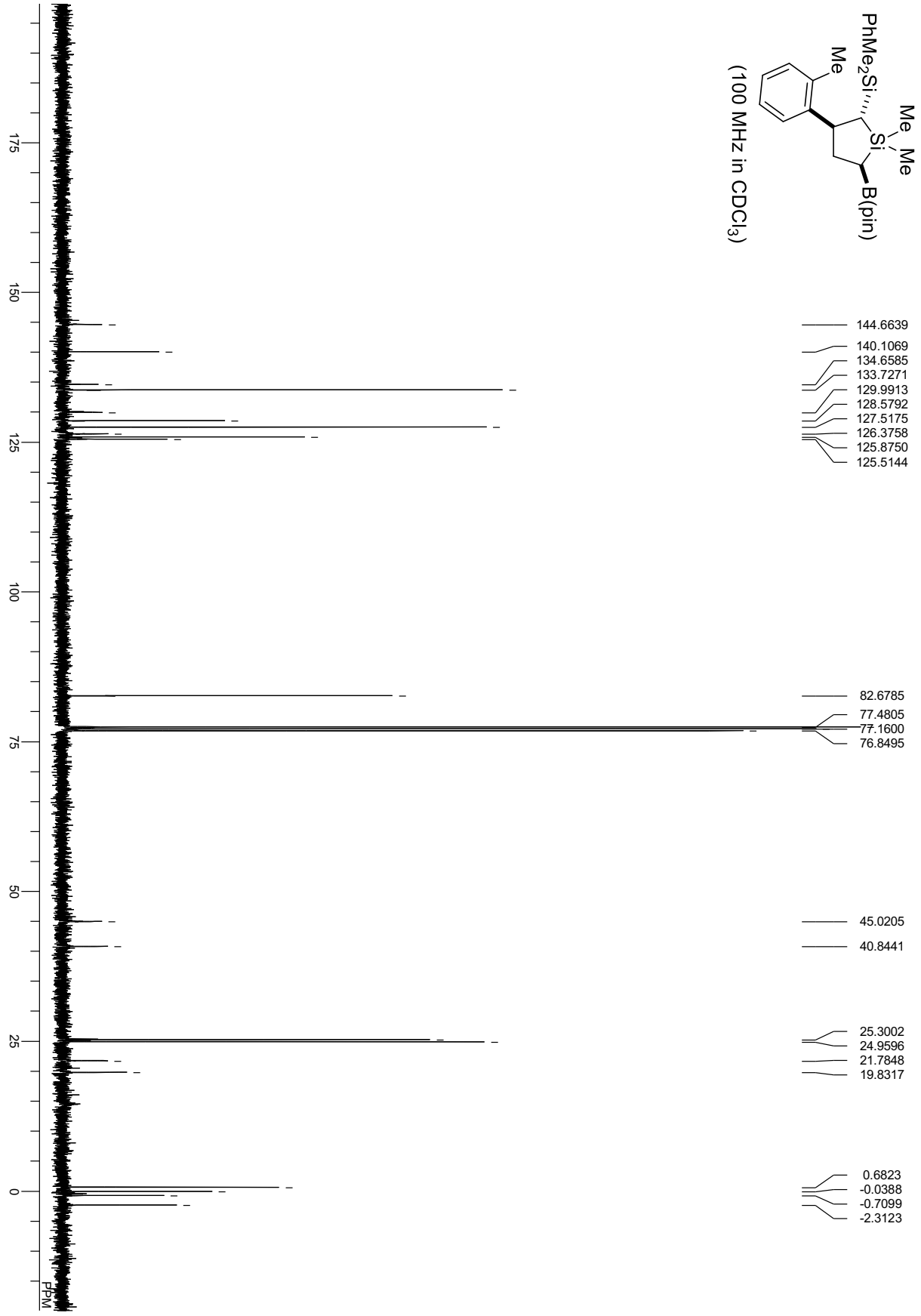
compound **3fa** (dr = 89/11)



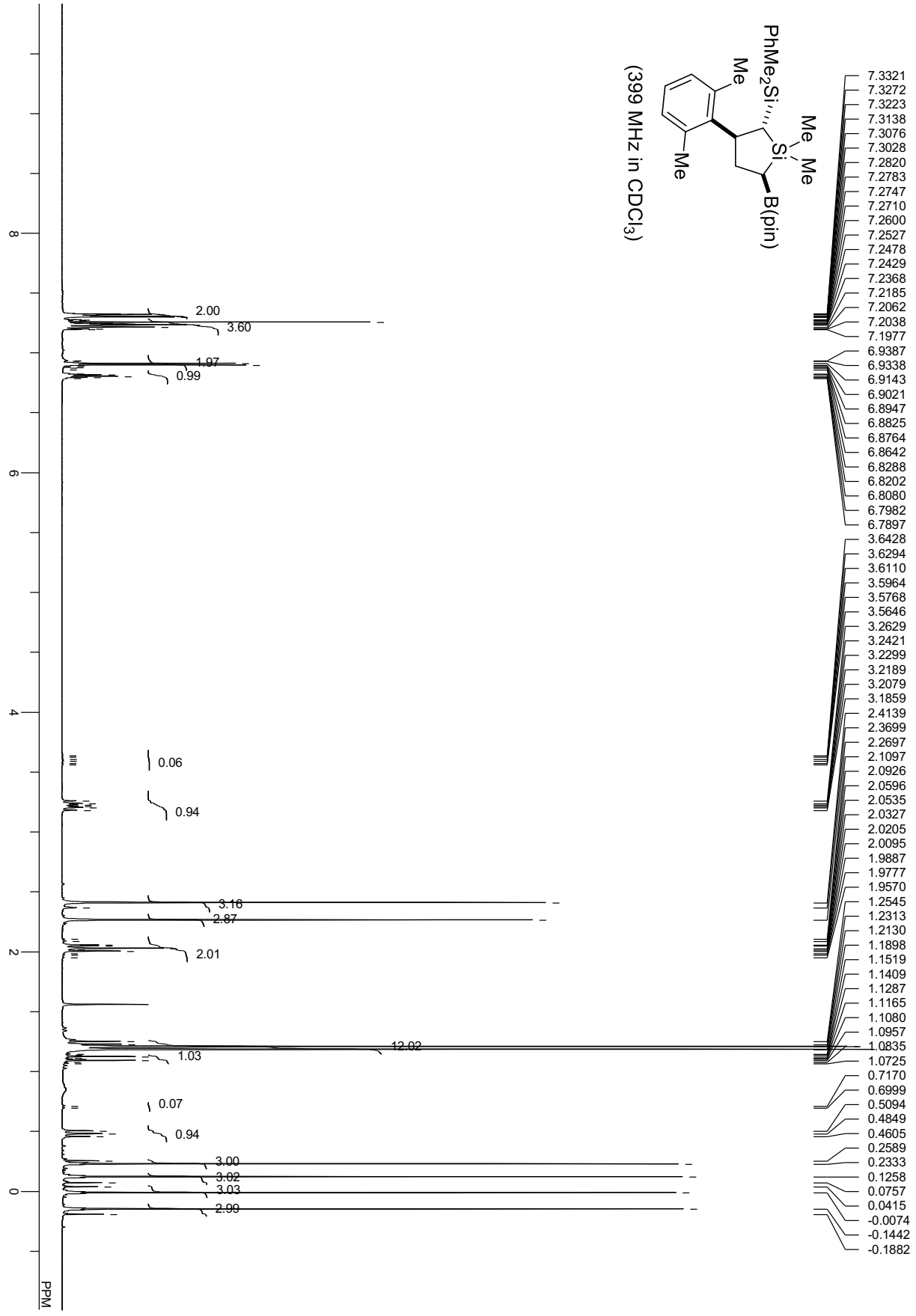
compound **3ga** (dr = 94/6)



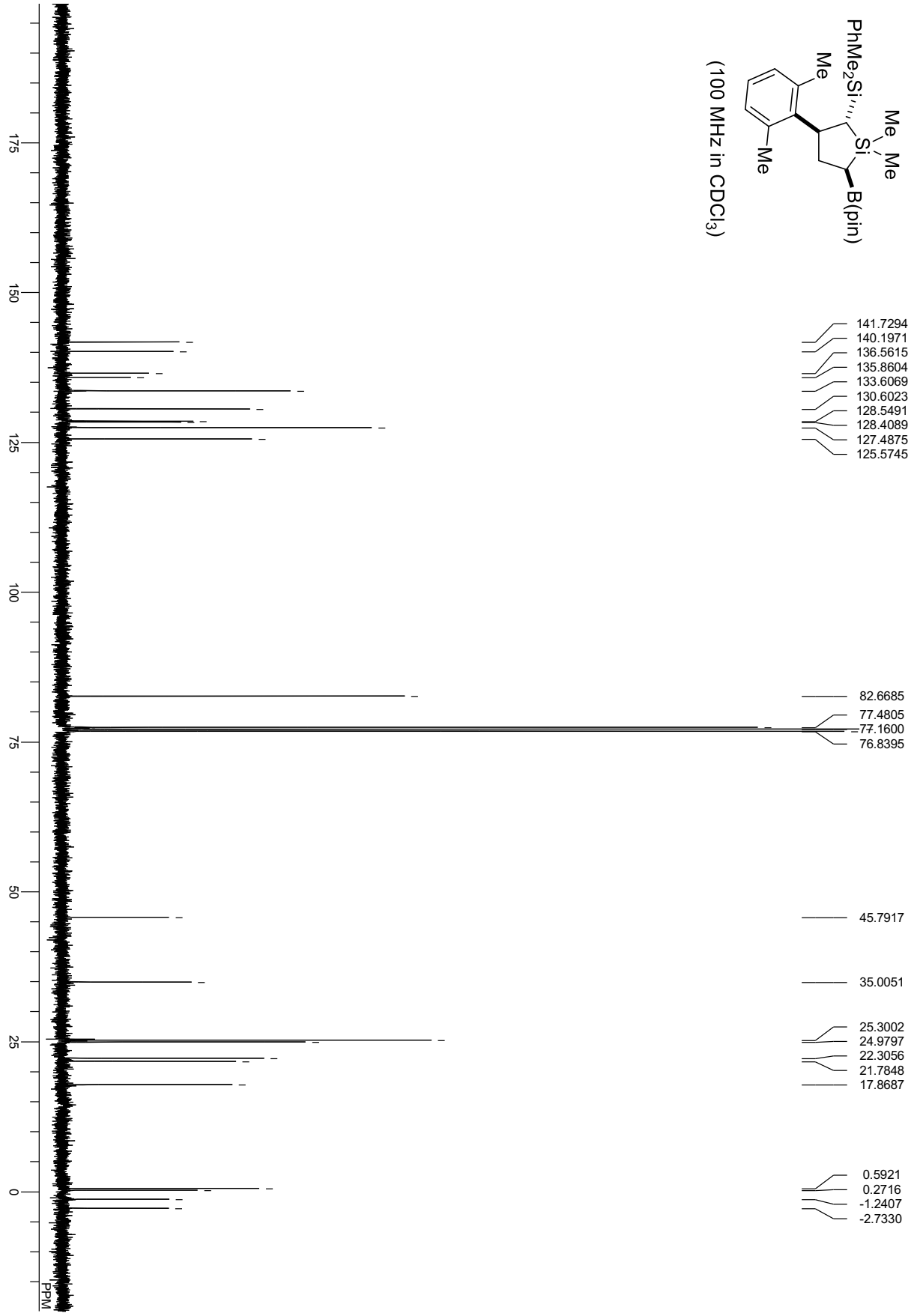
compound **3ga** (dr = 94/6)



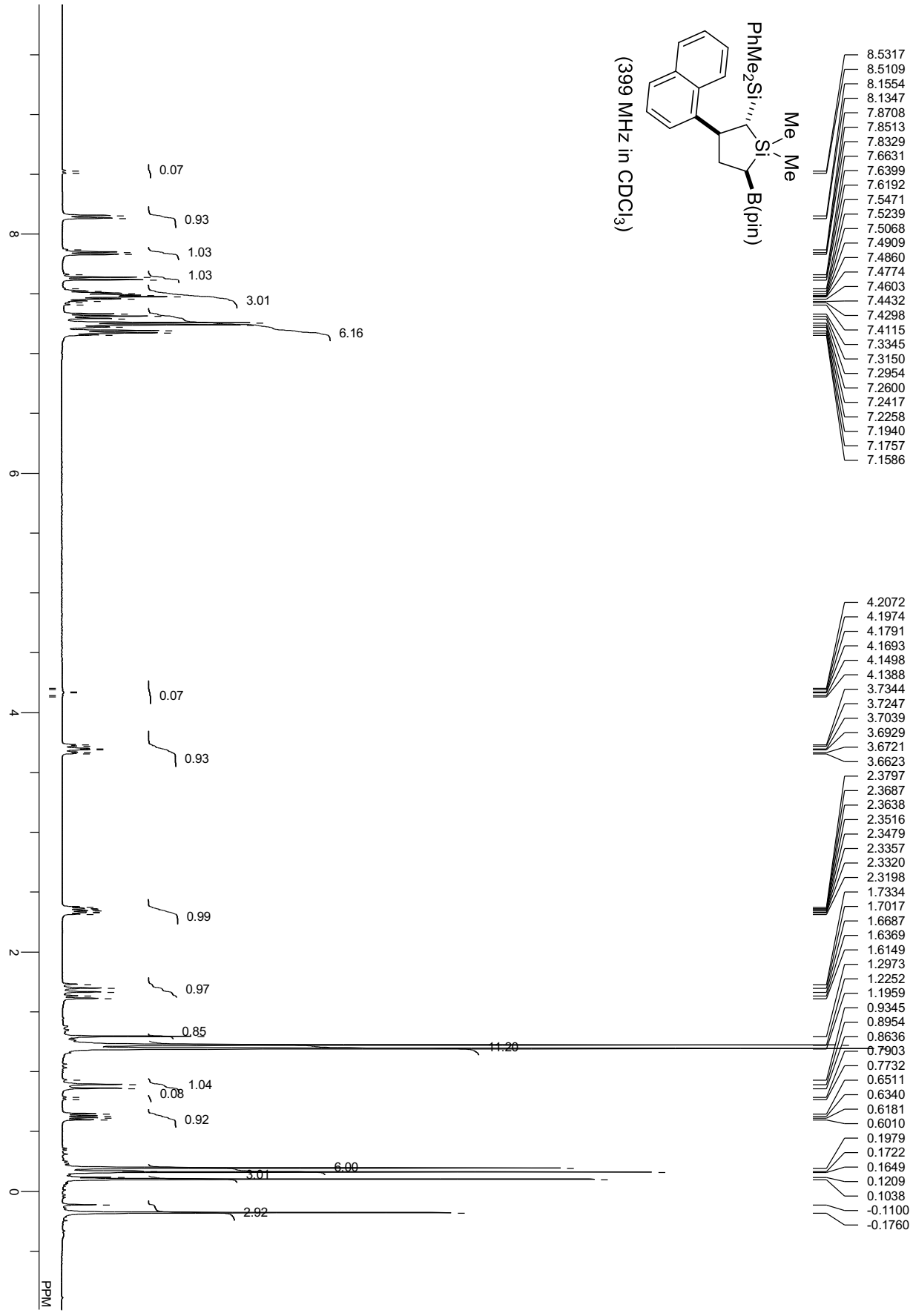
compound **3ha** (dr = 94/6)



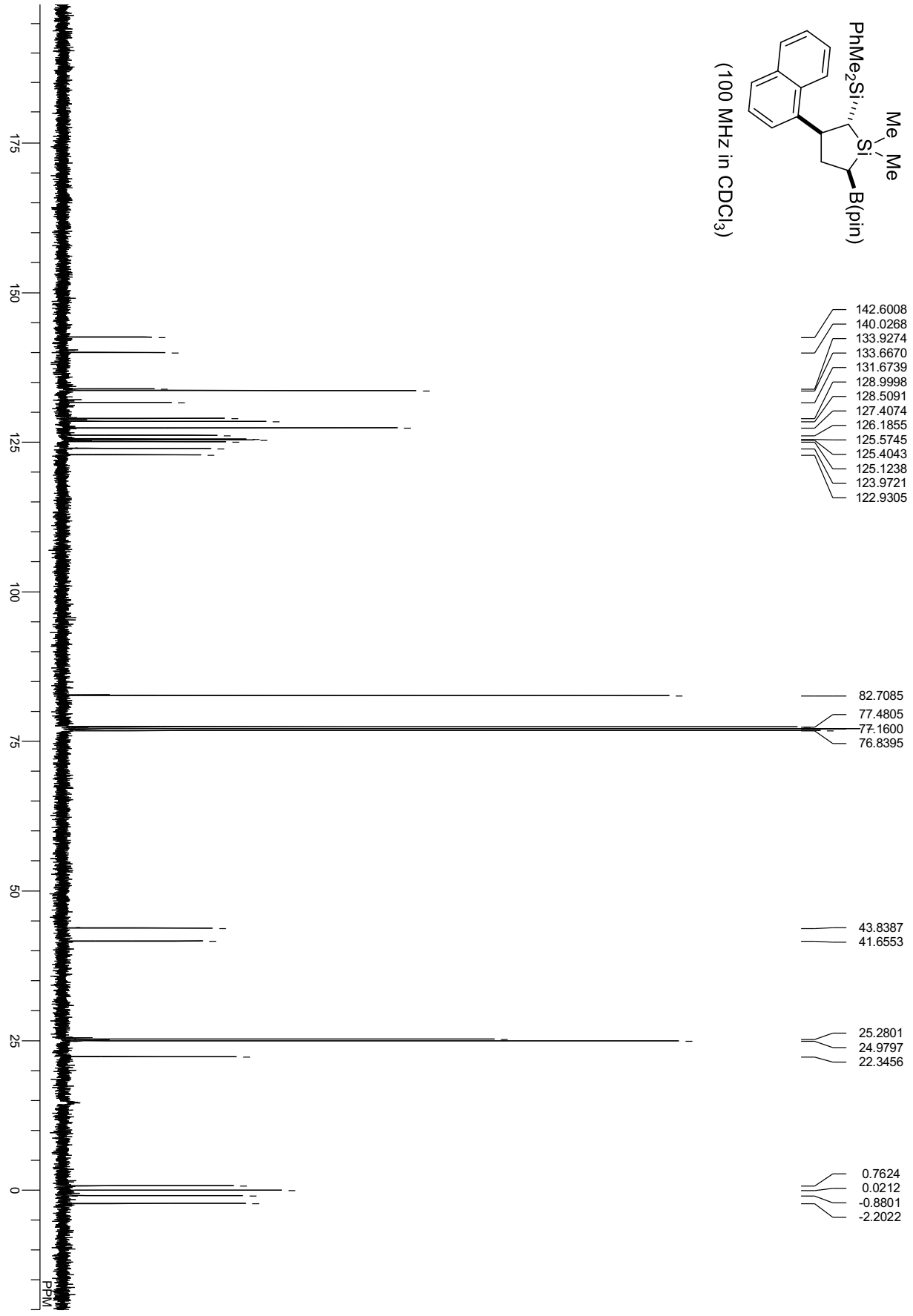
compound **3ha** (dr = 94/6)



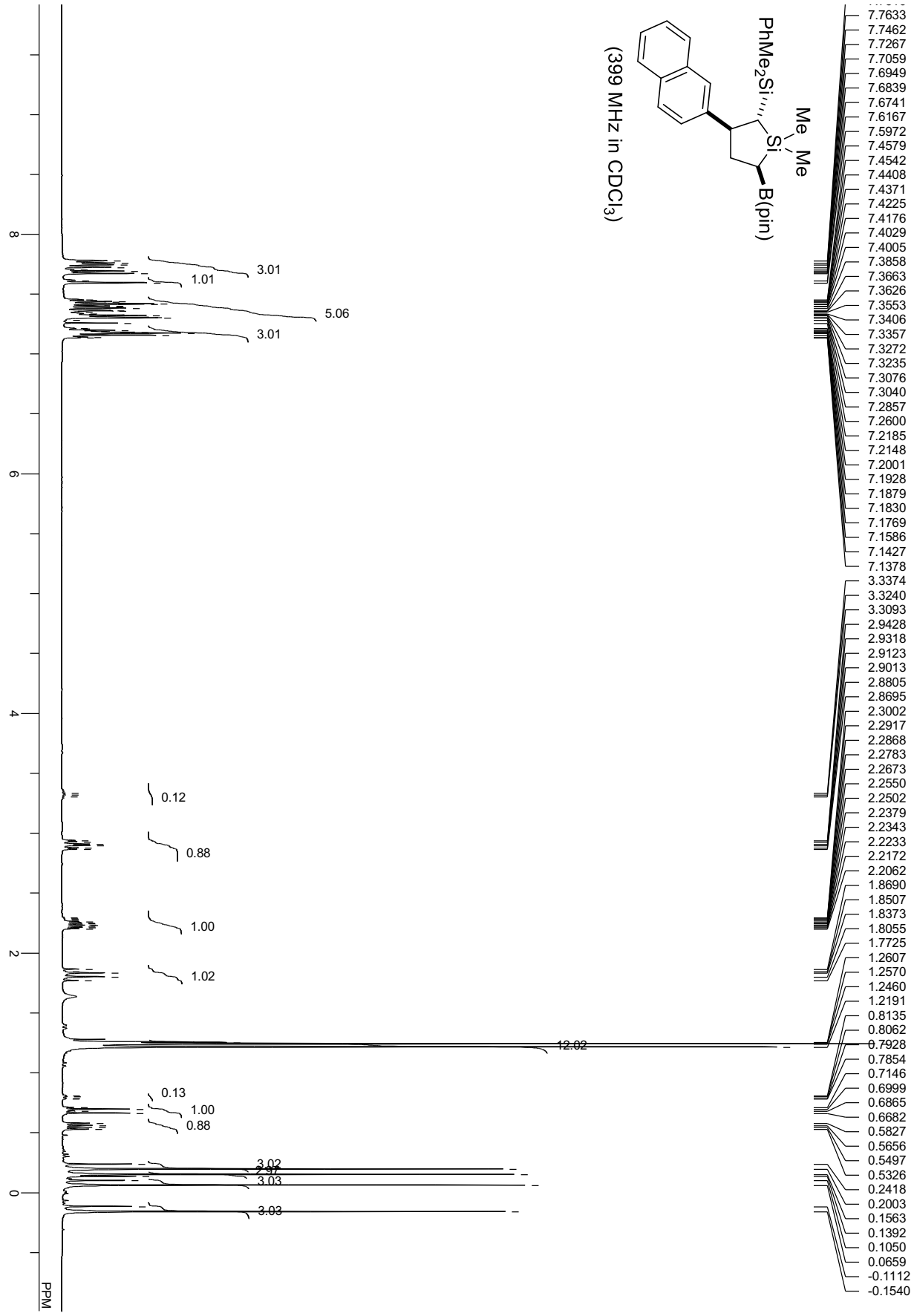
compound **3ia** (dr = 93/7)



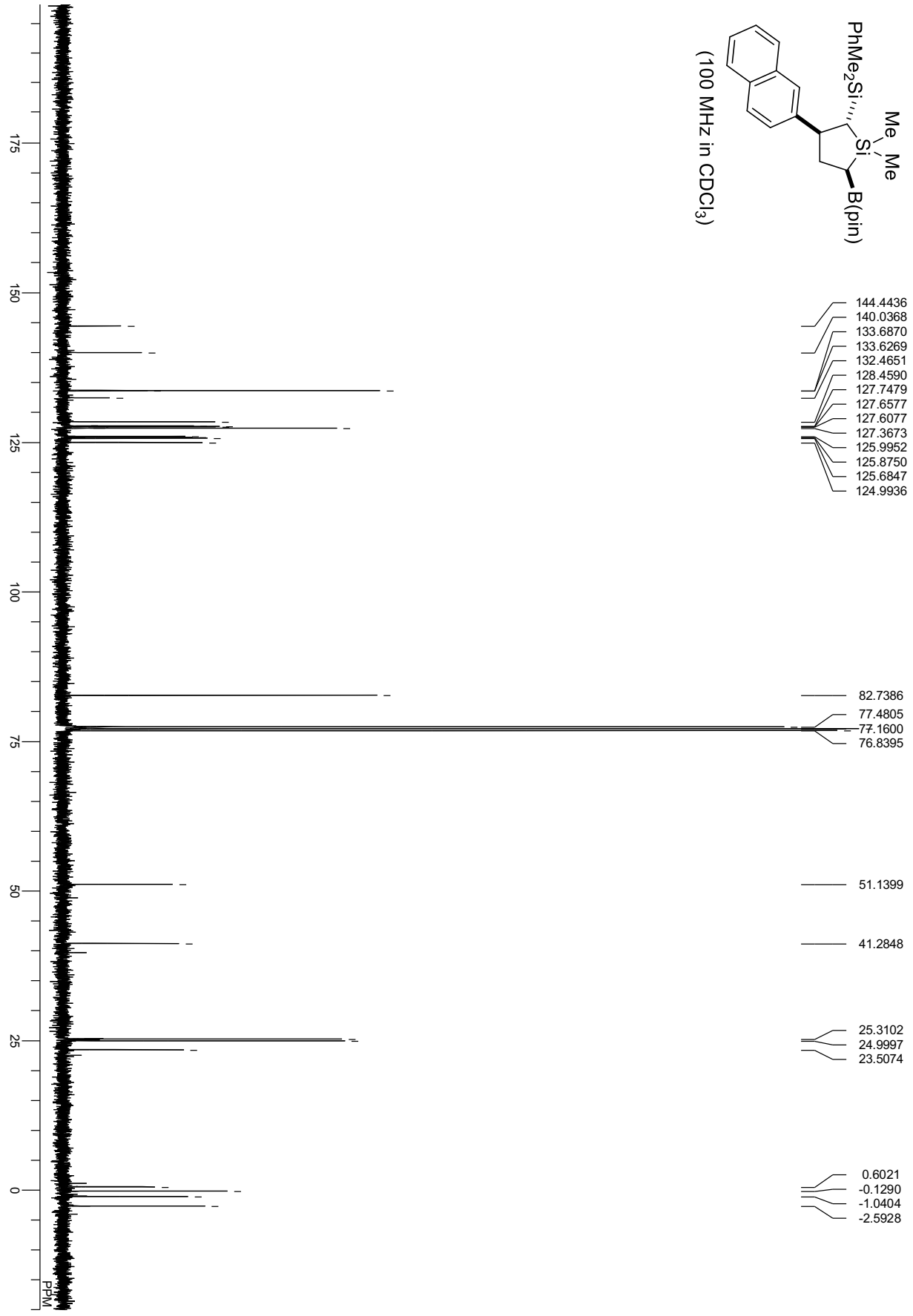
compound **3ia** (dr = 93/7)



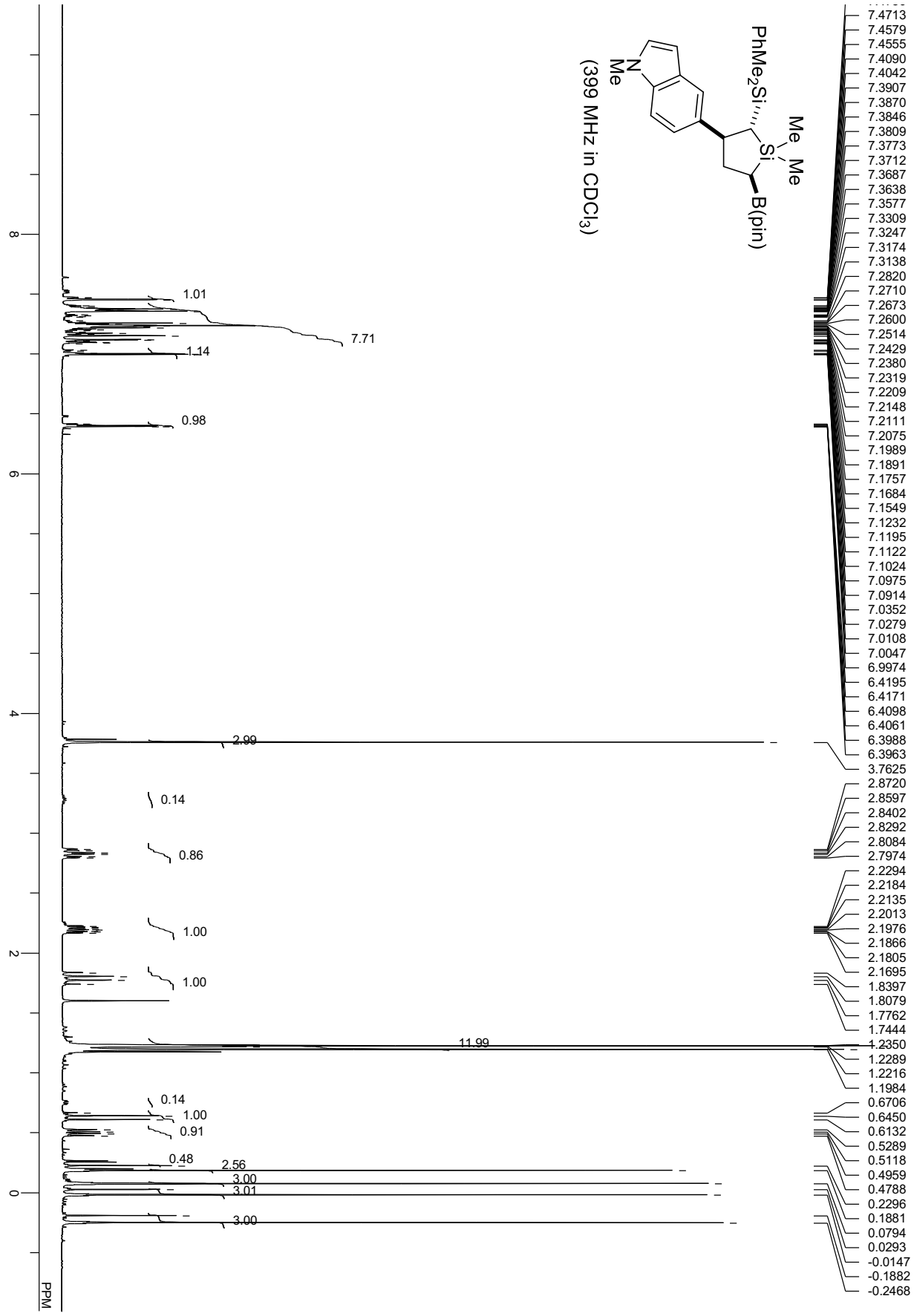
compound **3ja** (dr = 88/12)



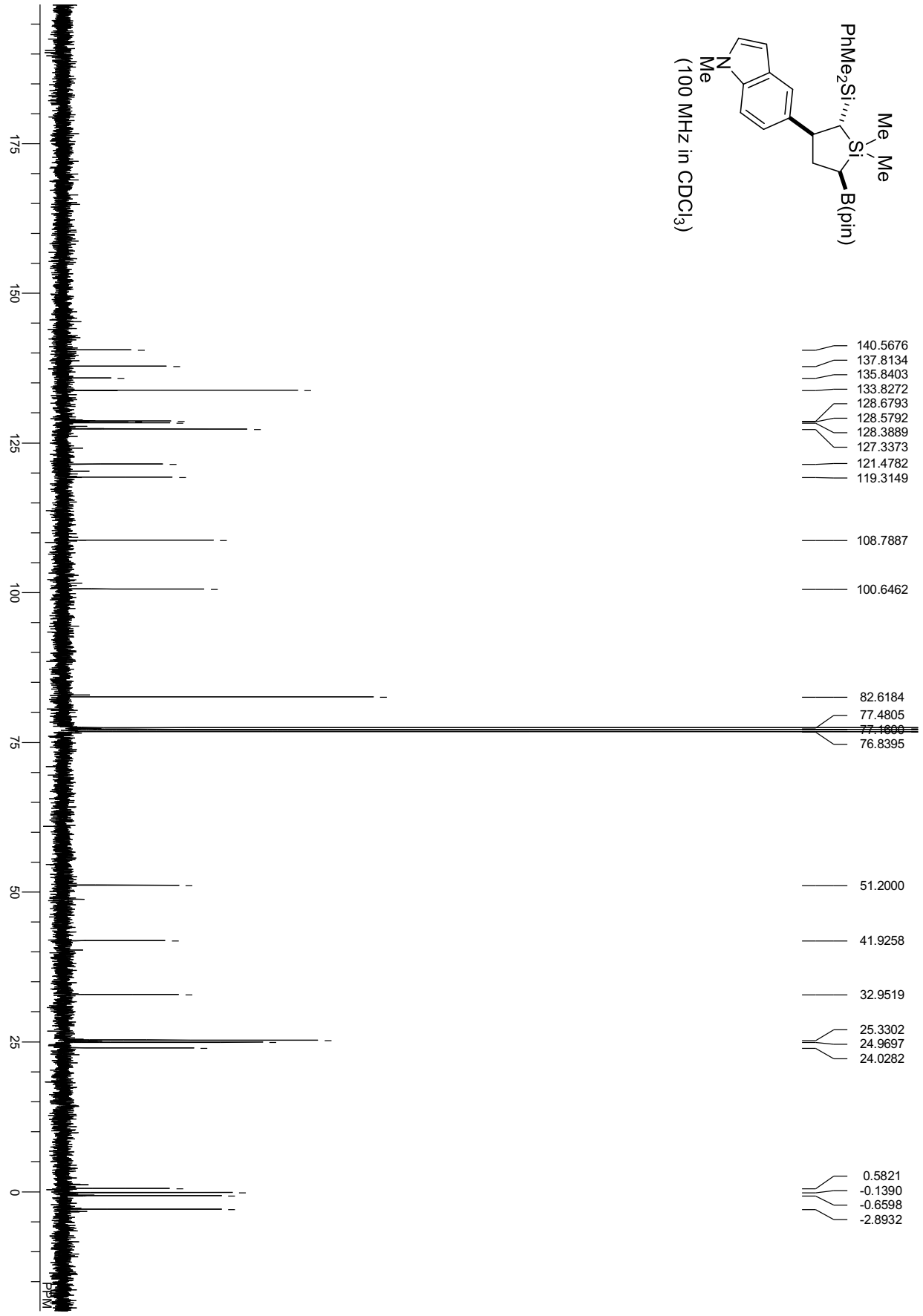
compound **3ja** (dr = 88/12)



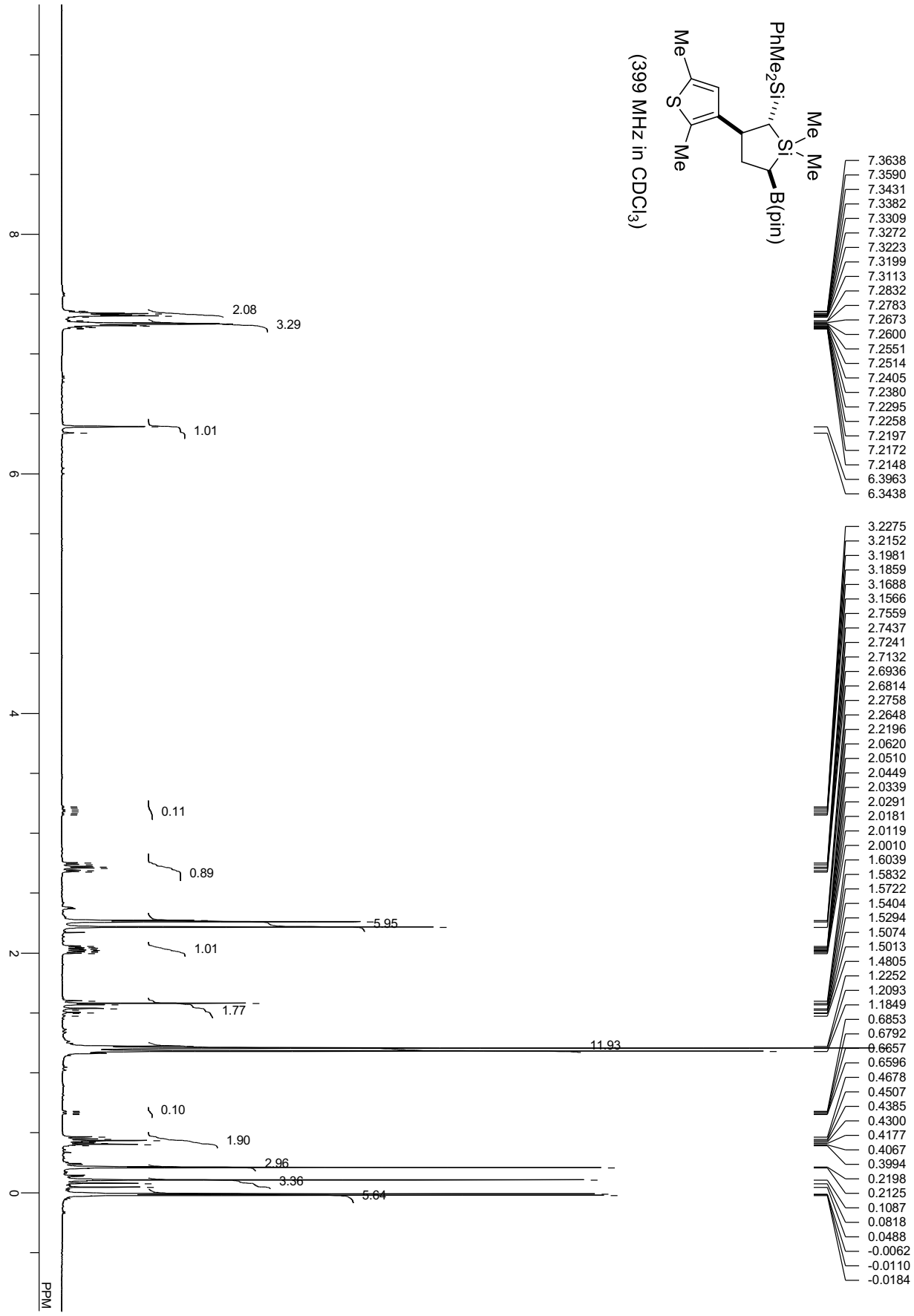
compound **3ka** (dr = 86/14)



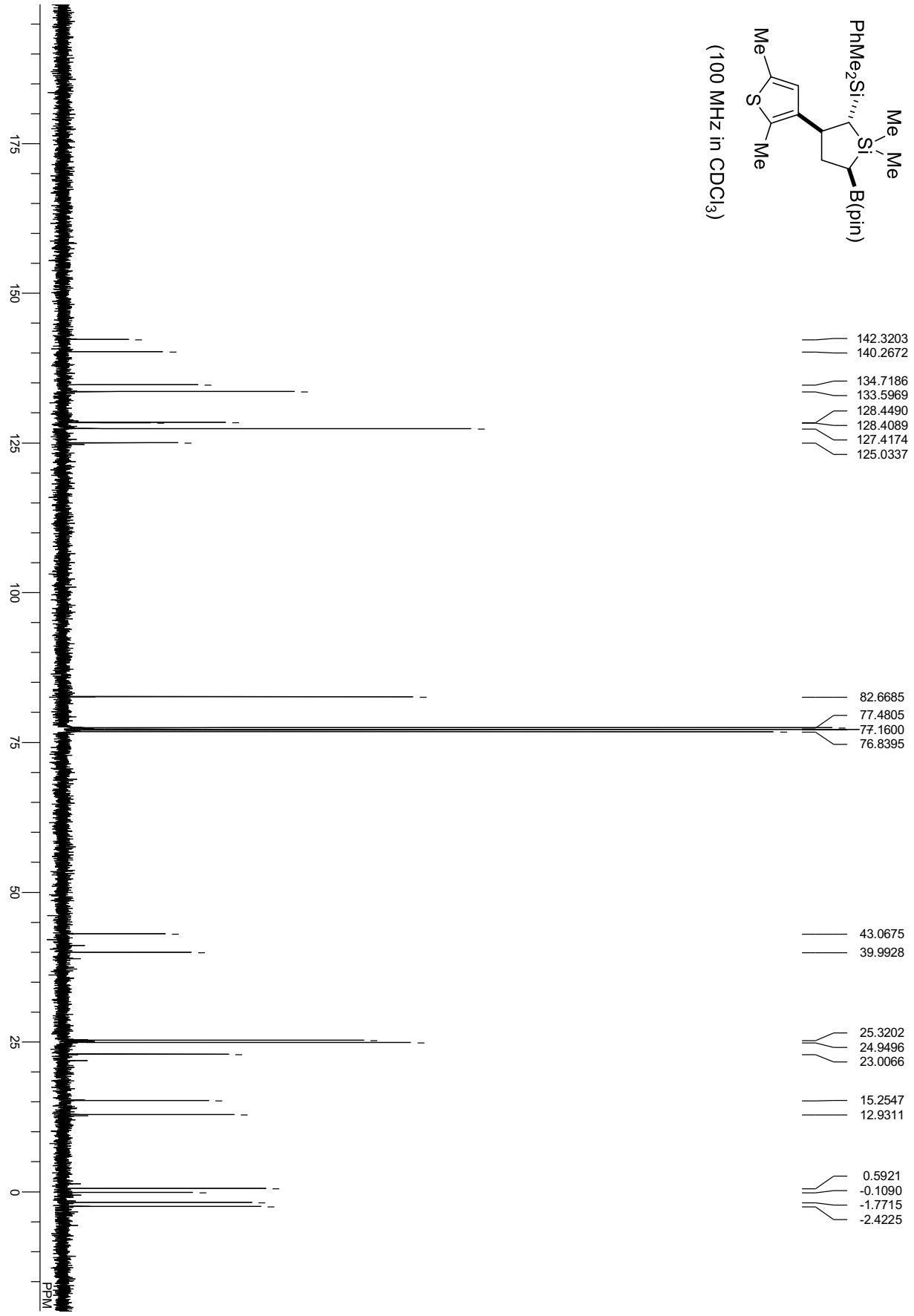
compound **3ka** (dr = 86/14)



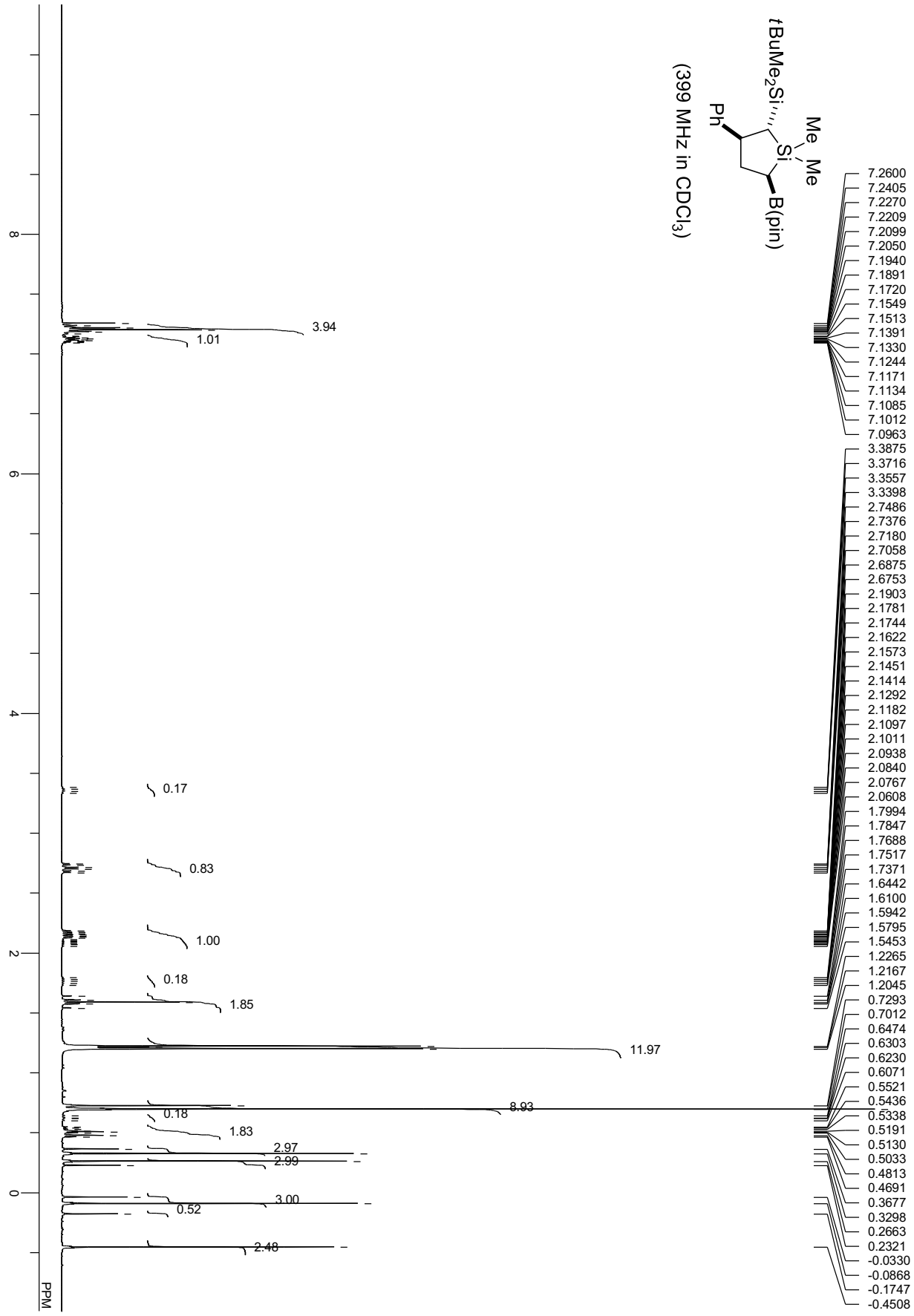
compound **3la** (dr = 89/11)



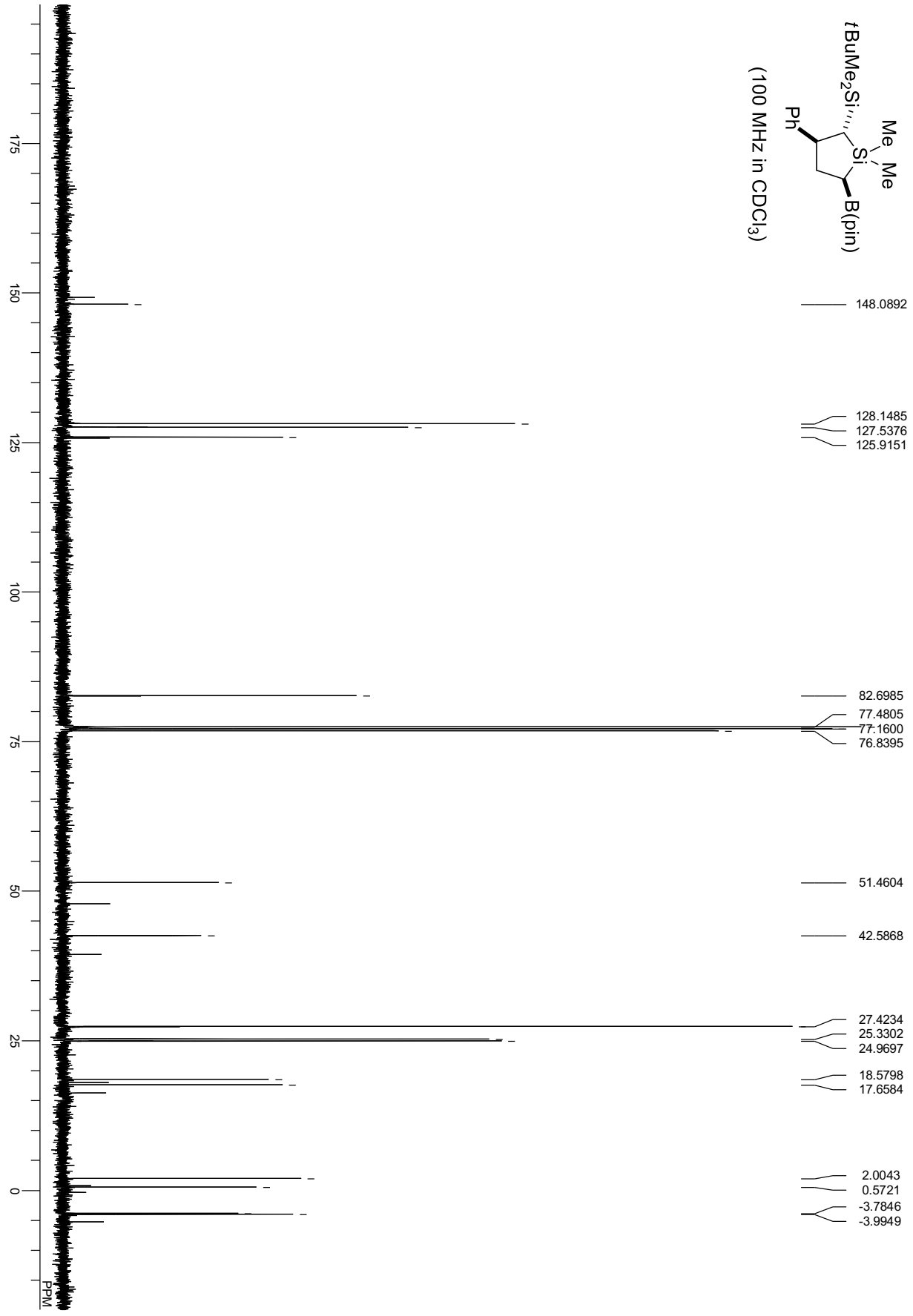
compound **3la** (dr = 89/11)



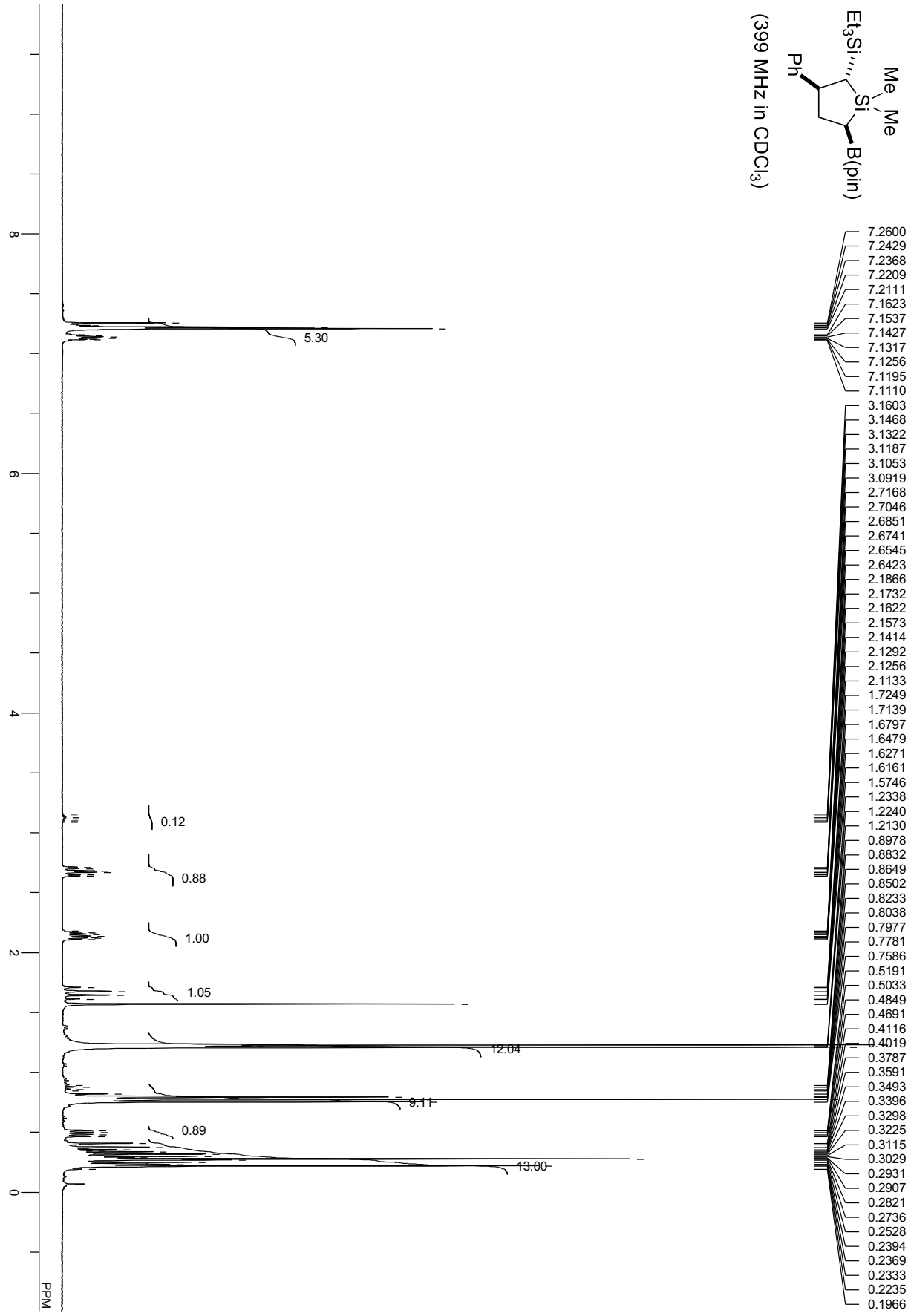
compound **3ab** (dr = 83/17)



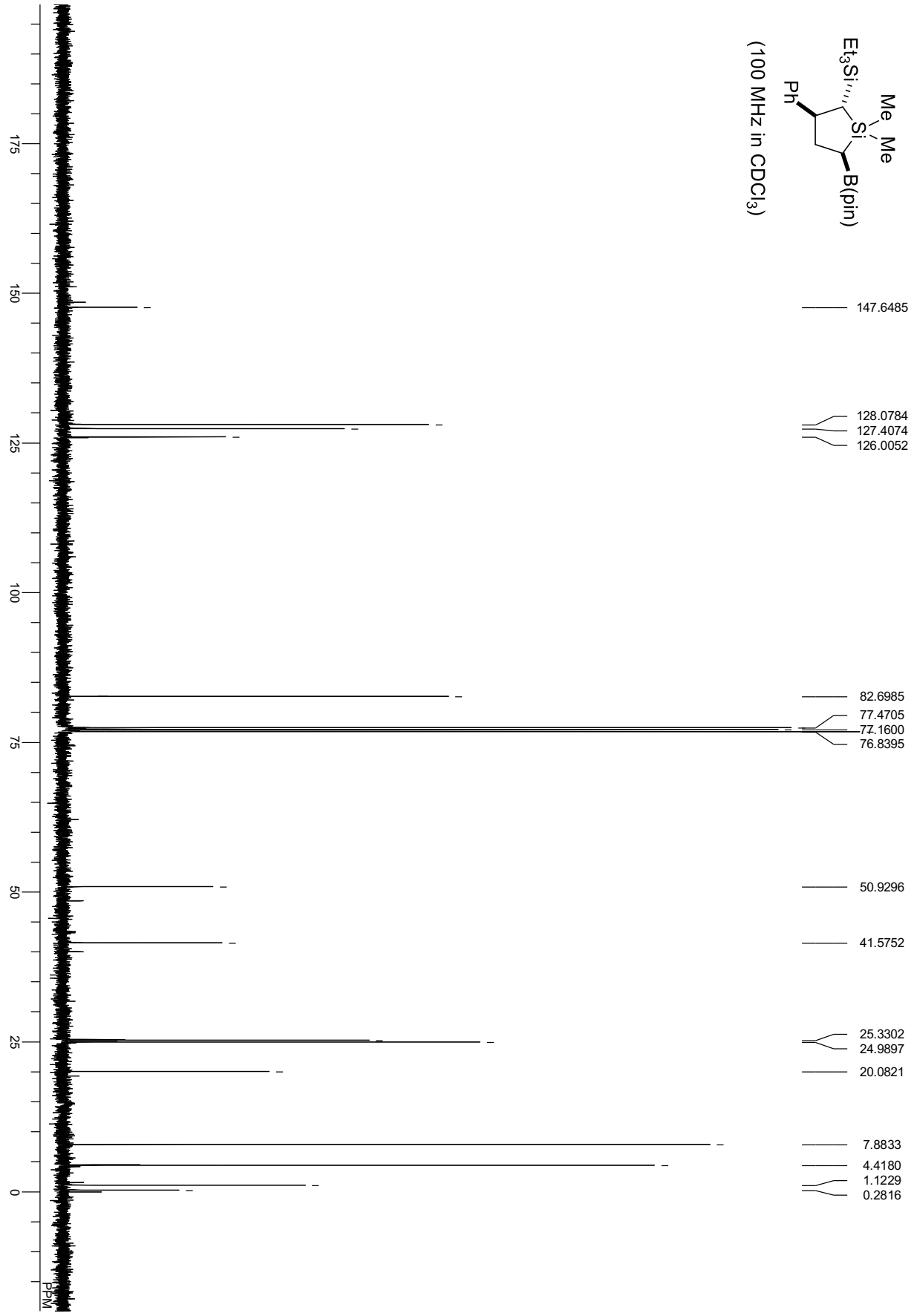
compound **3ab** (dr = 83/17)



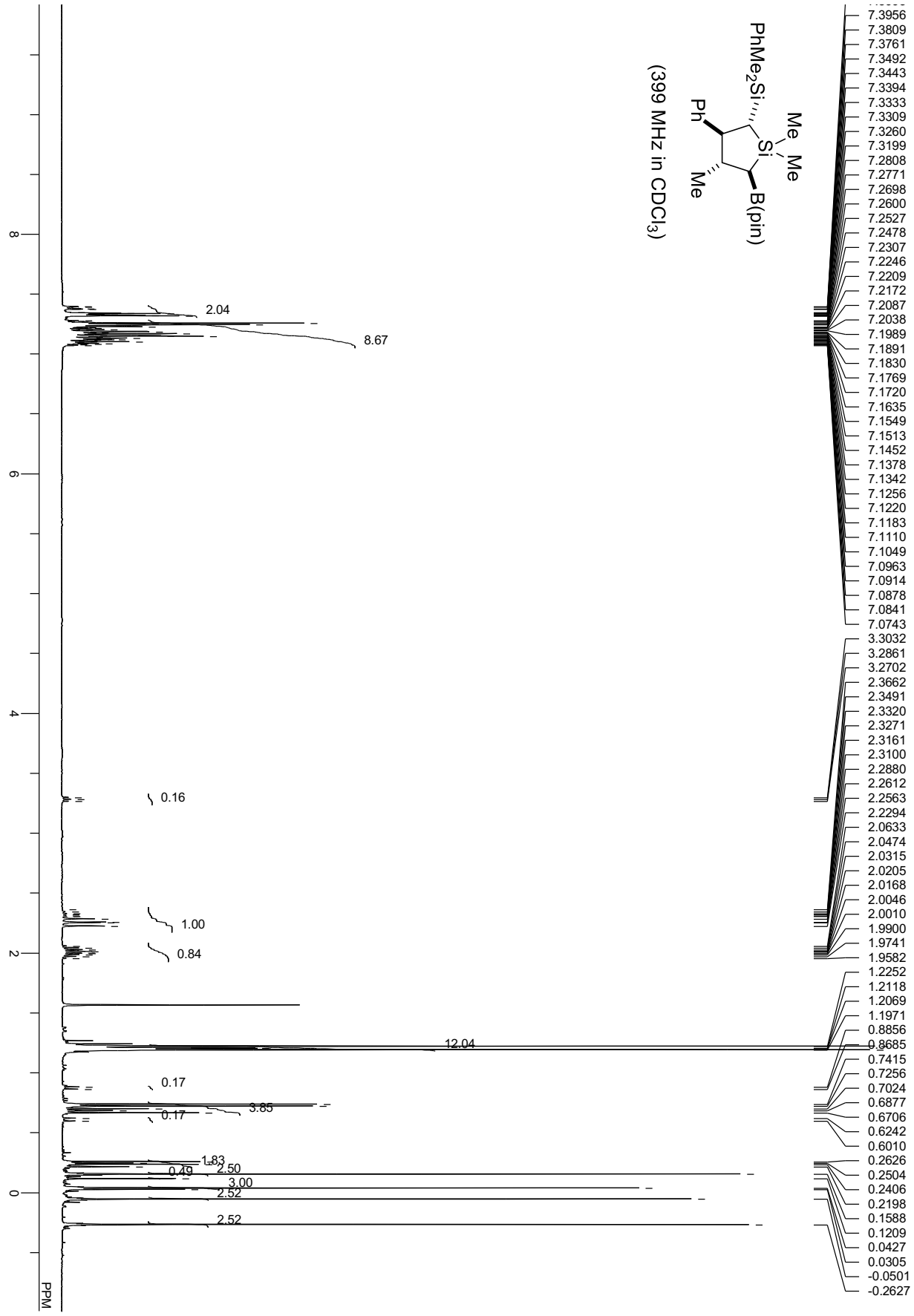
compound **3ac** (dr = 88/12)



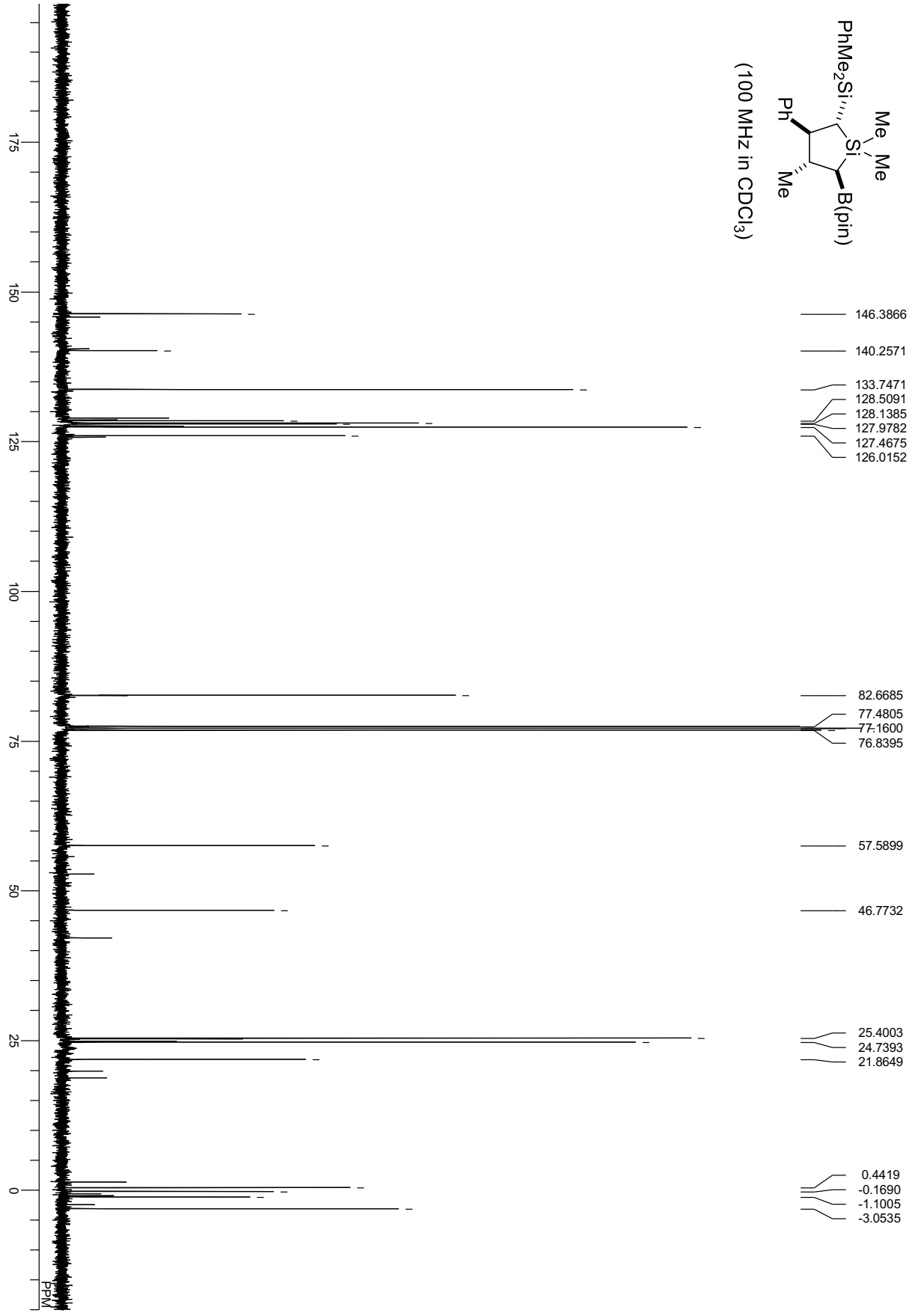
compound **3ac** (dr = 88/12)



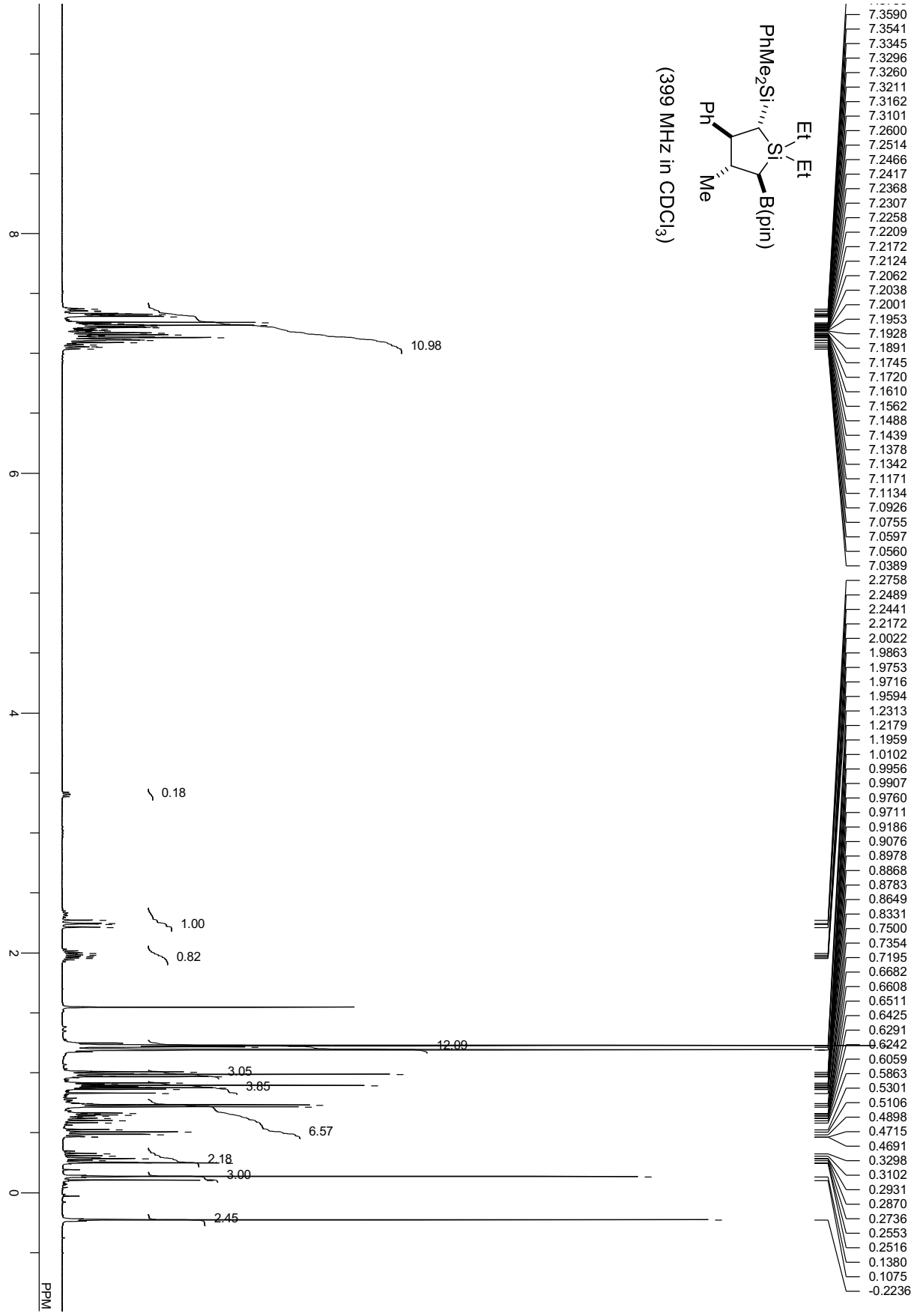
compound **3ma** (dr = 84/16)



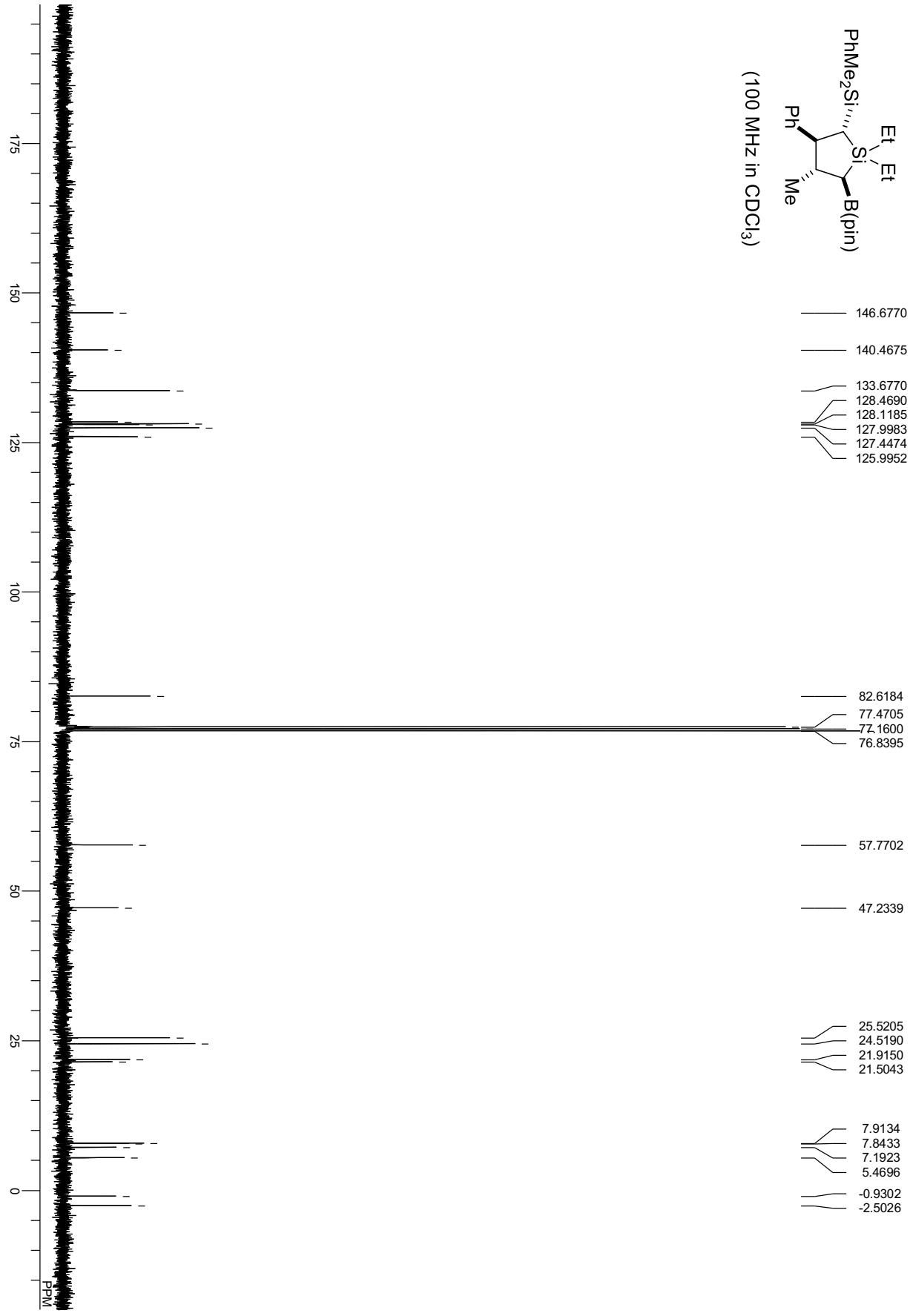
compound **3ma** (dr = 84/16)



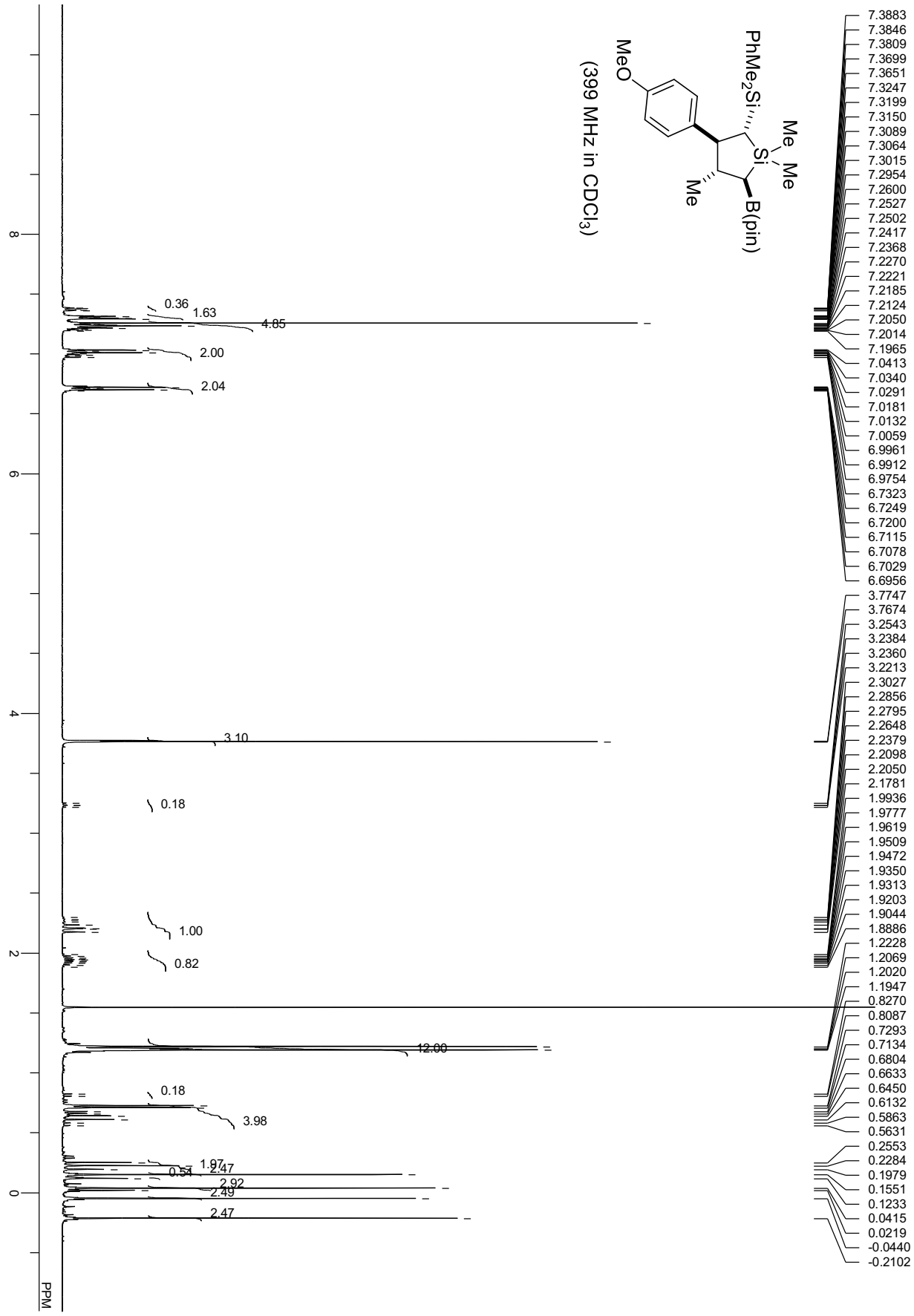
compound **3na** (dr = 82/18)



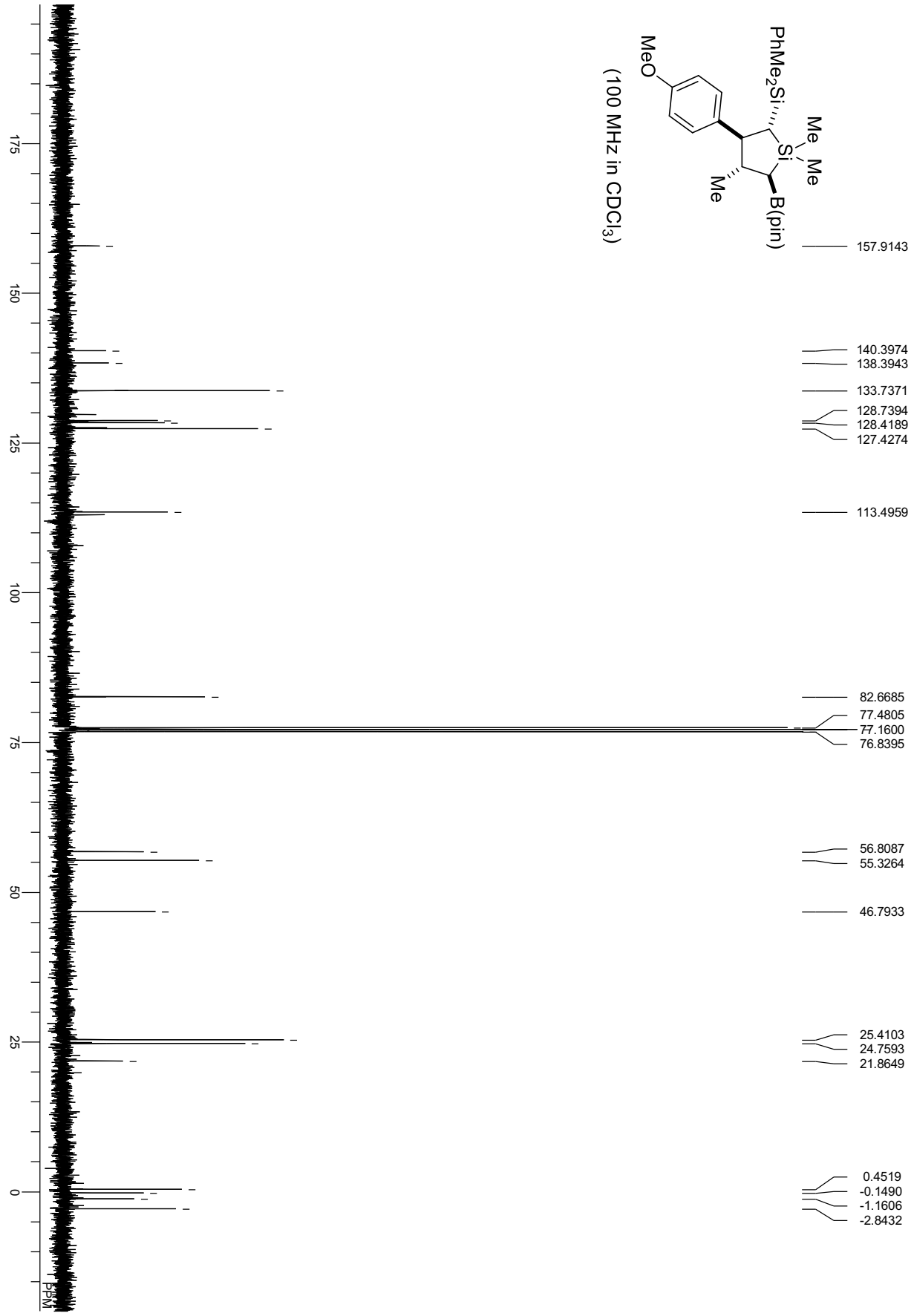
compound **3na** (dr = 82/18)



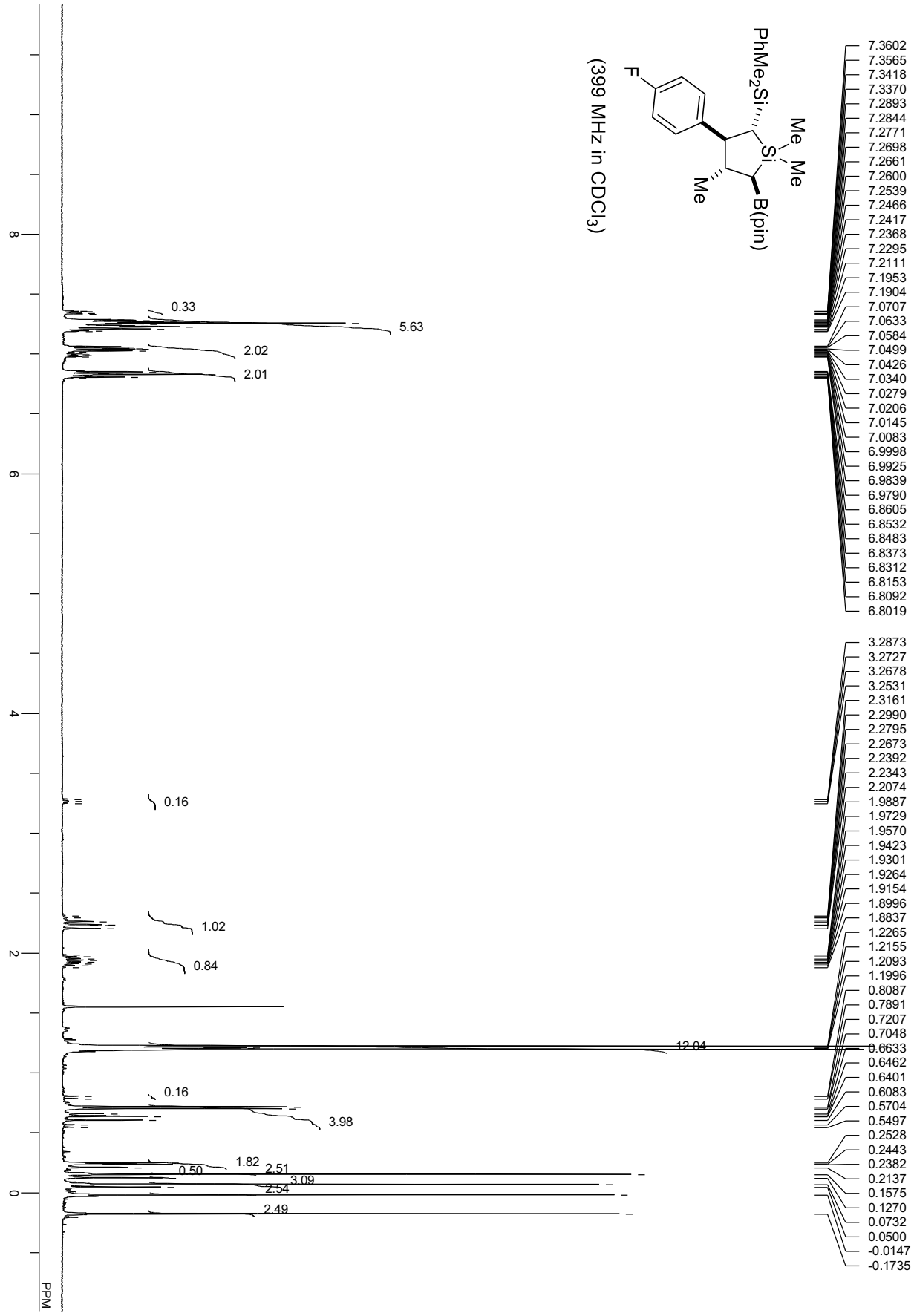
compound **3oa** (dr = 82/18)



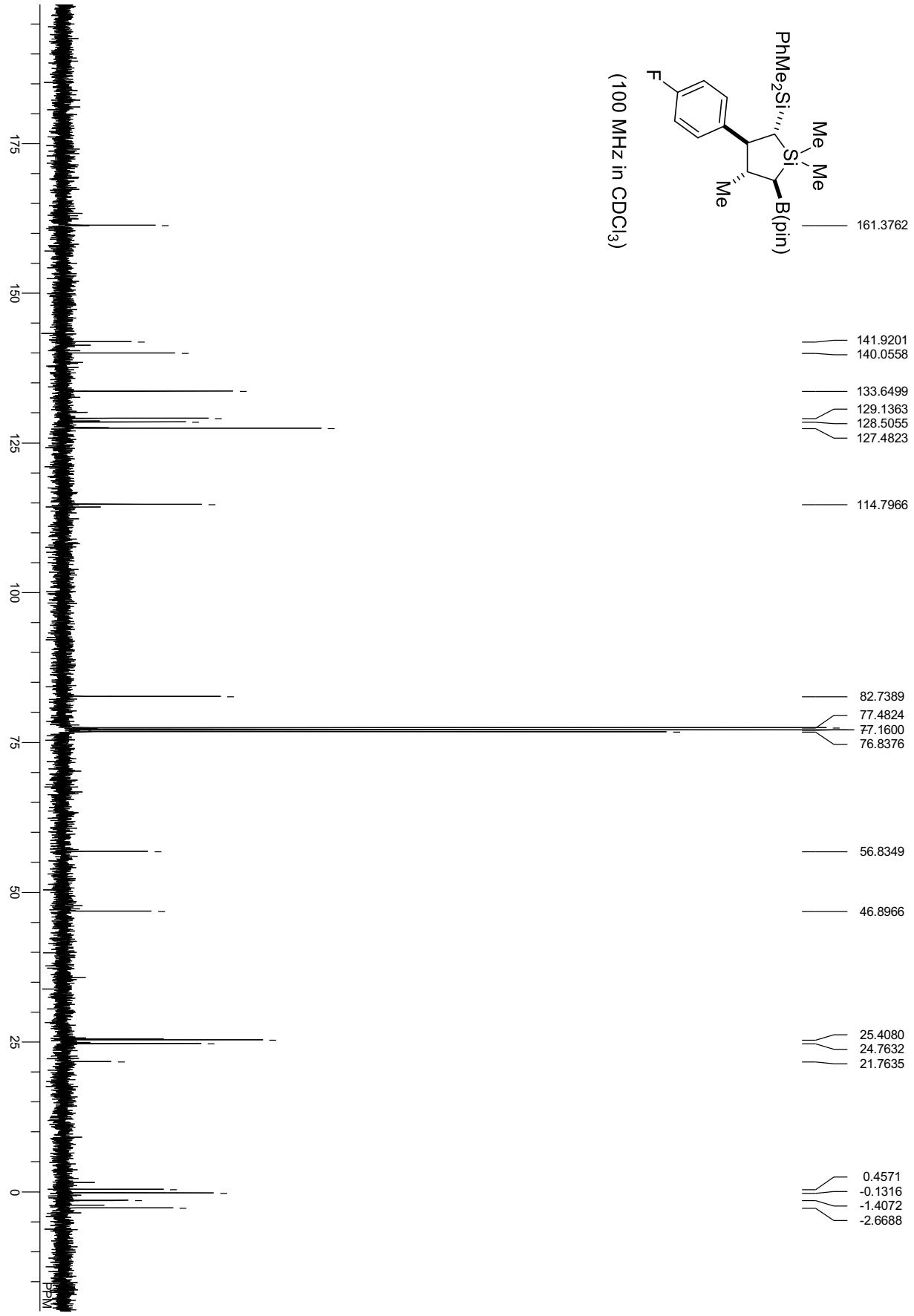
compound **3oa** (dr = 82/18)



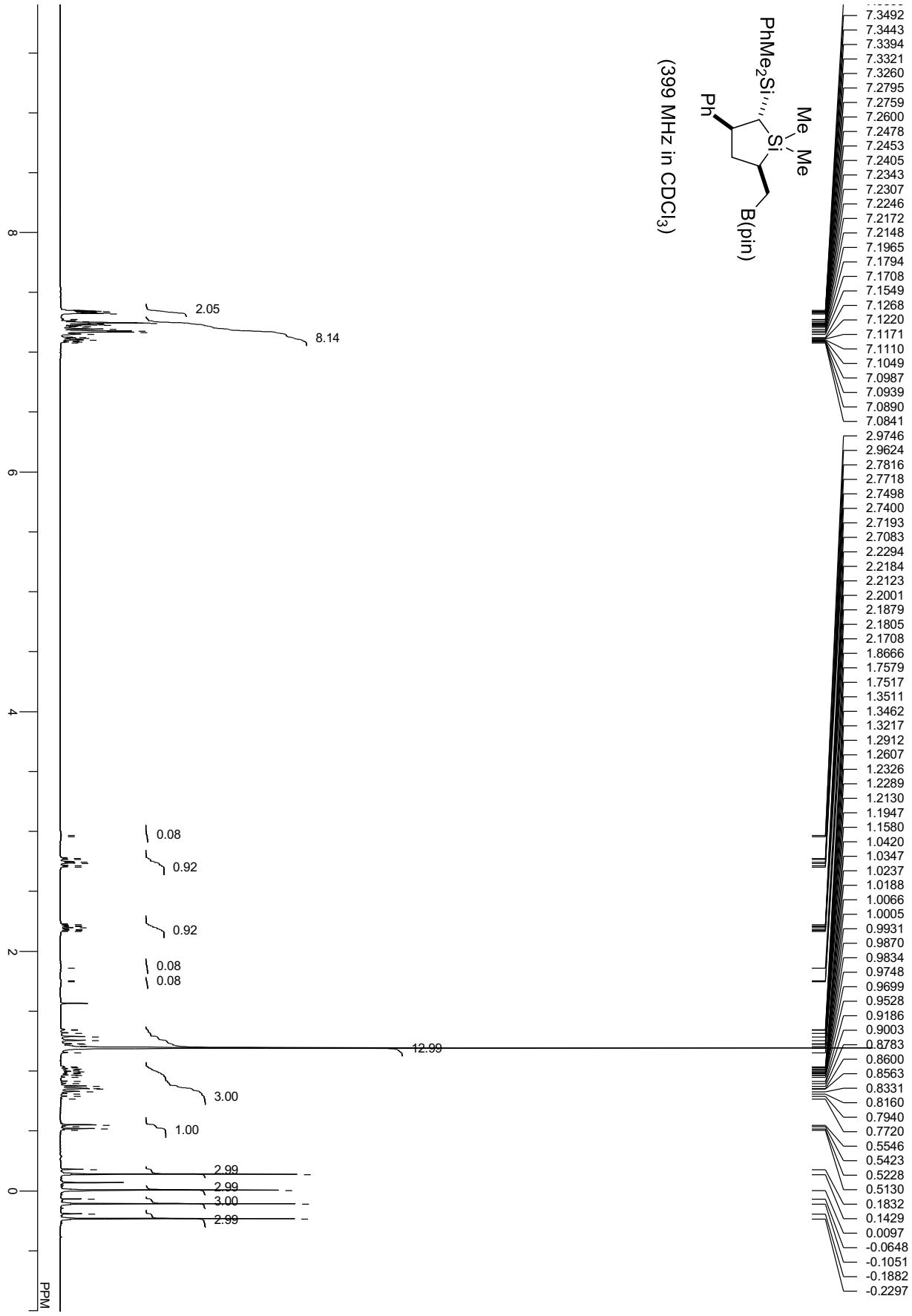
compound **3pa** (dr = 84/16)



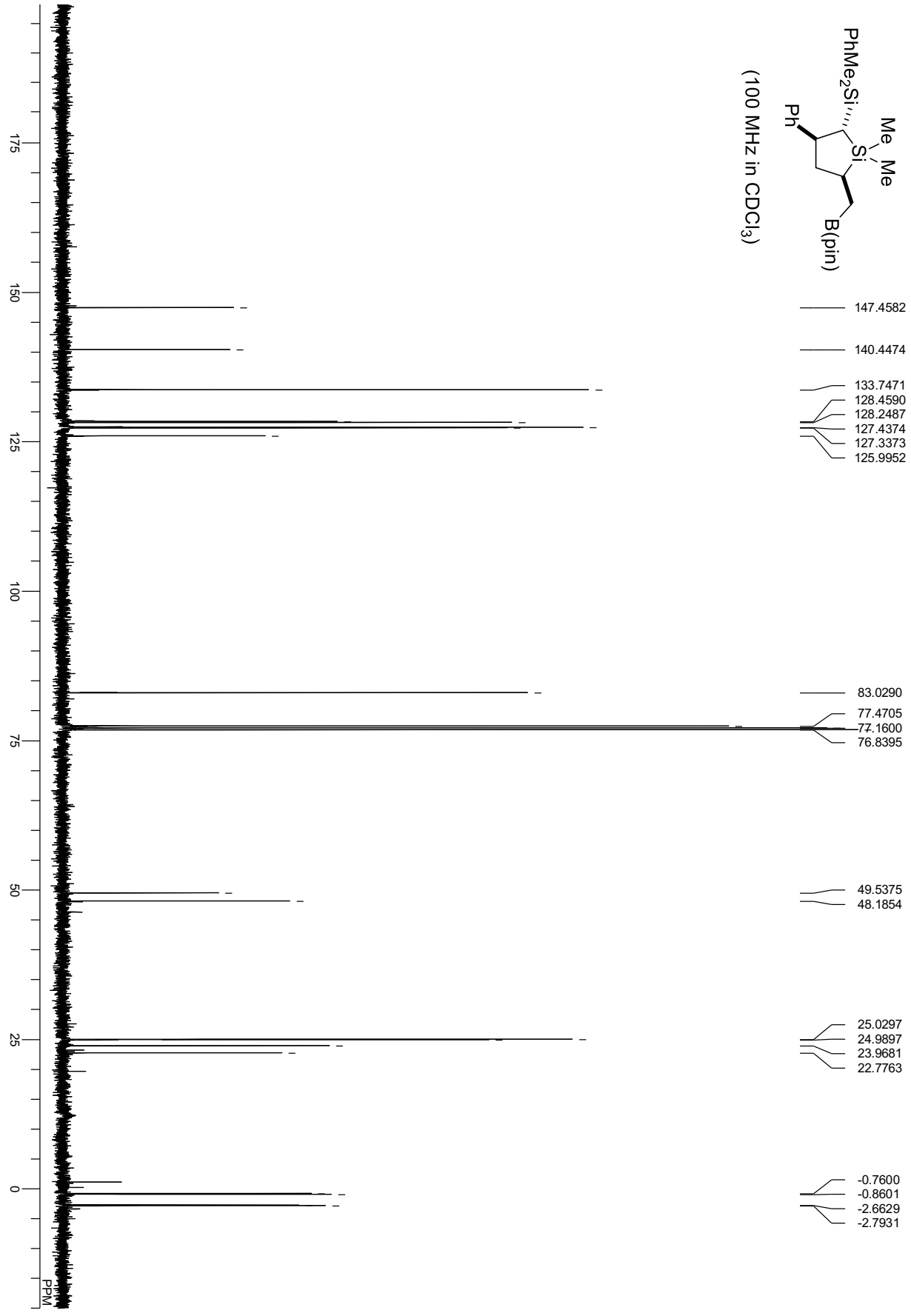
compound **3pa** (dr = 84/16)



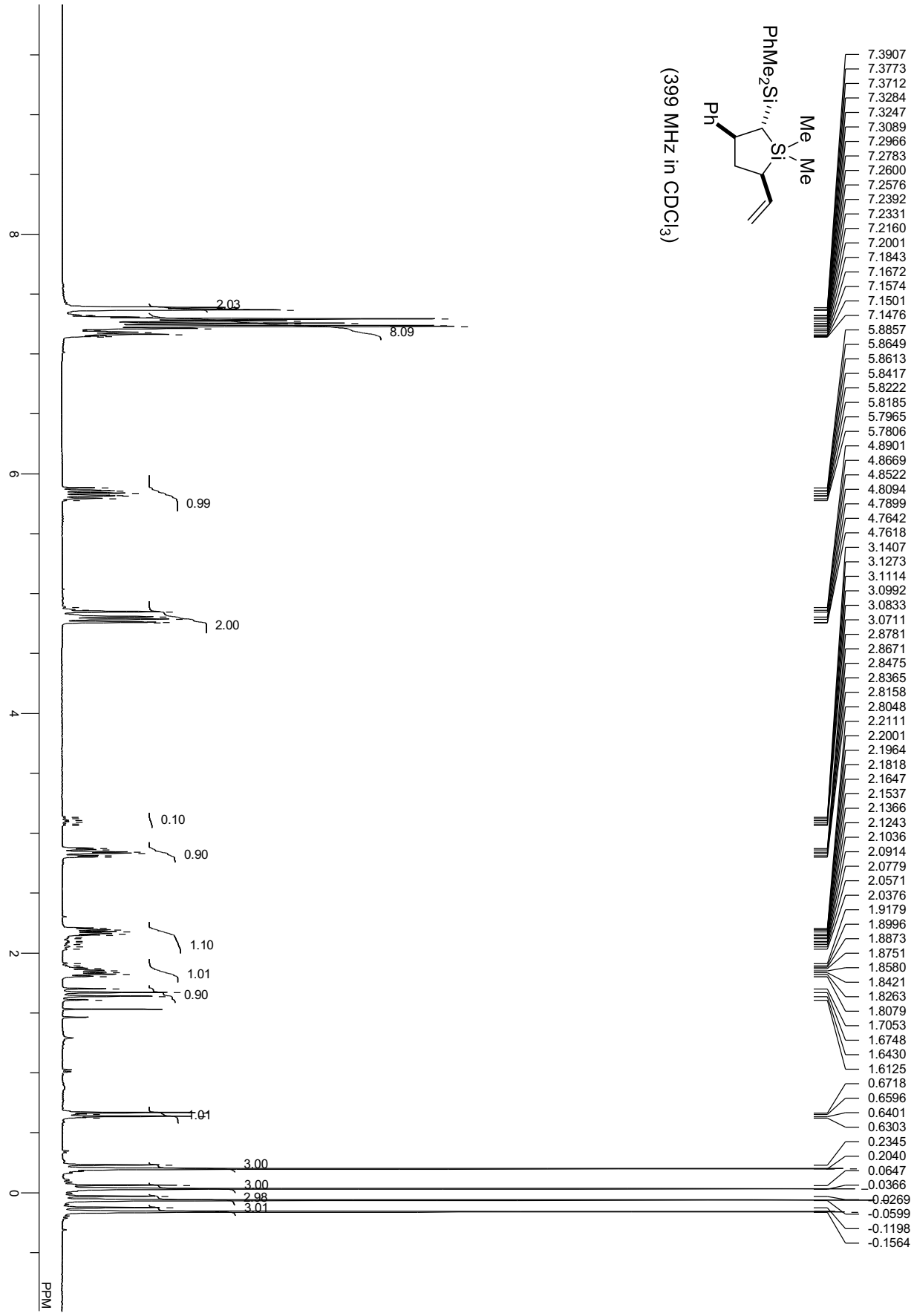
compound **4** (dr = 92/8)



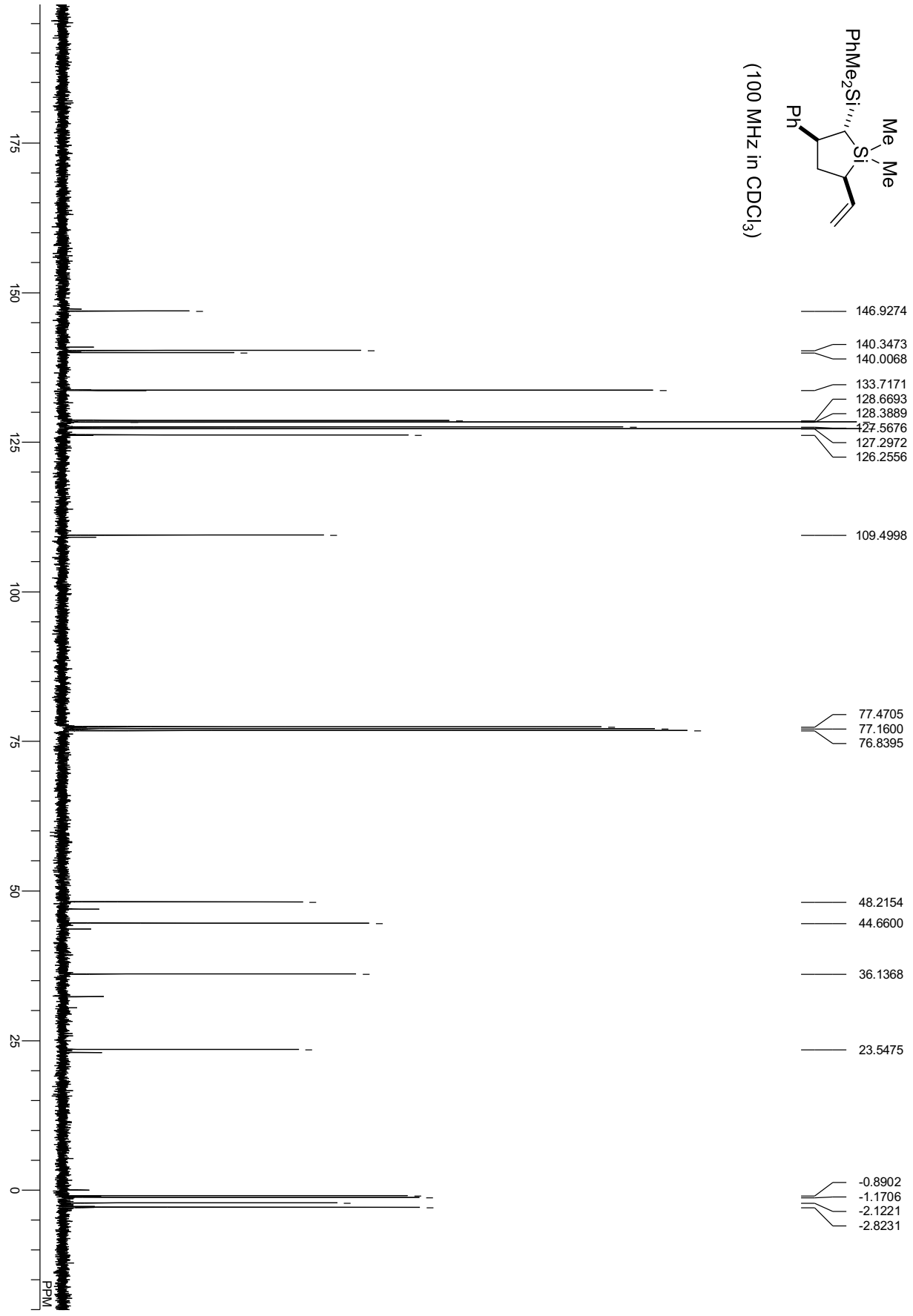
compound **4** (dr = 92/8)



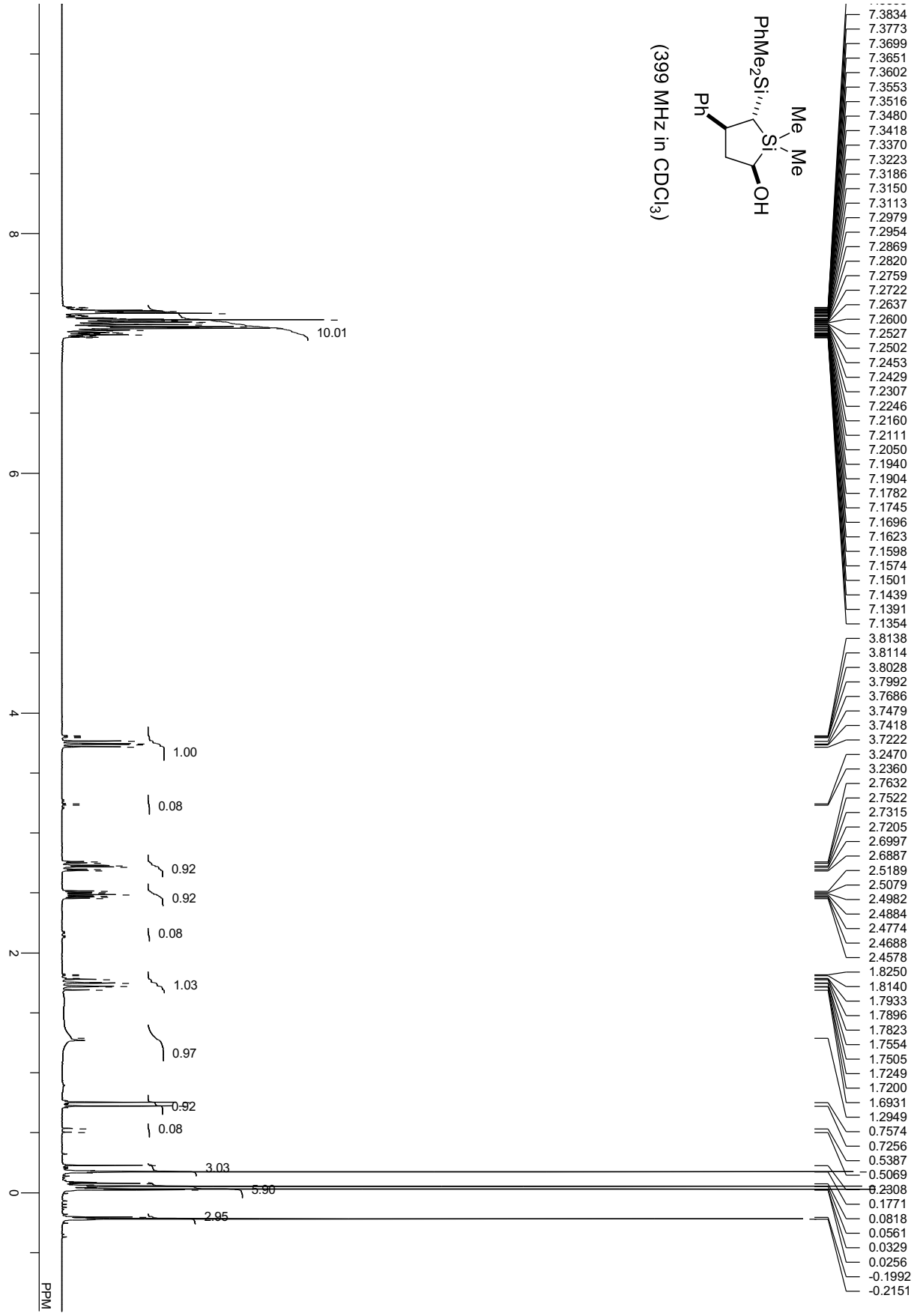
compound **5** (dr = 90/10)



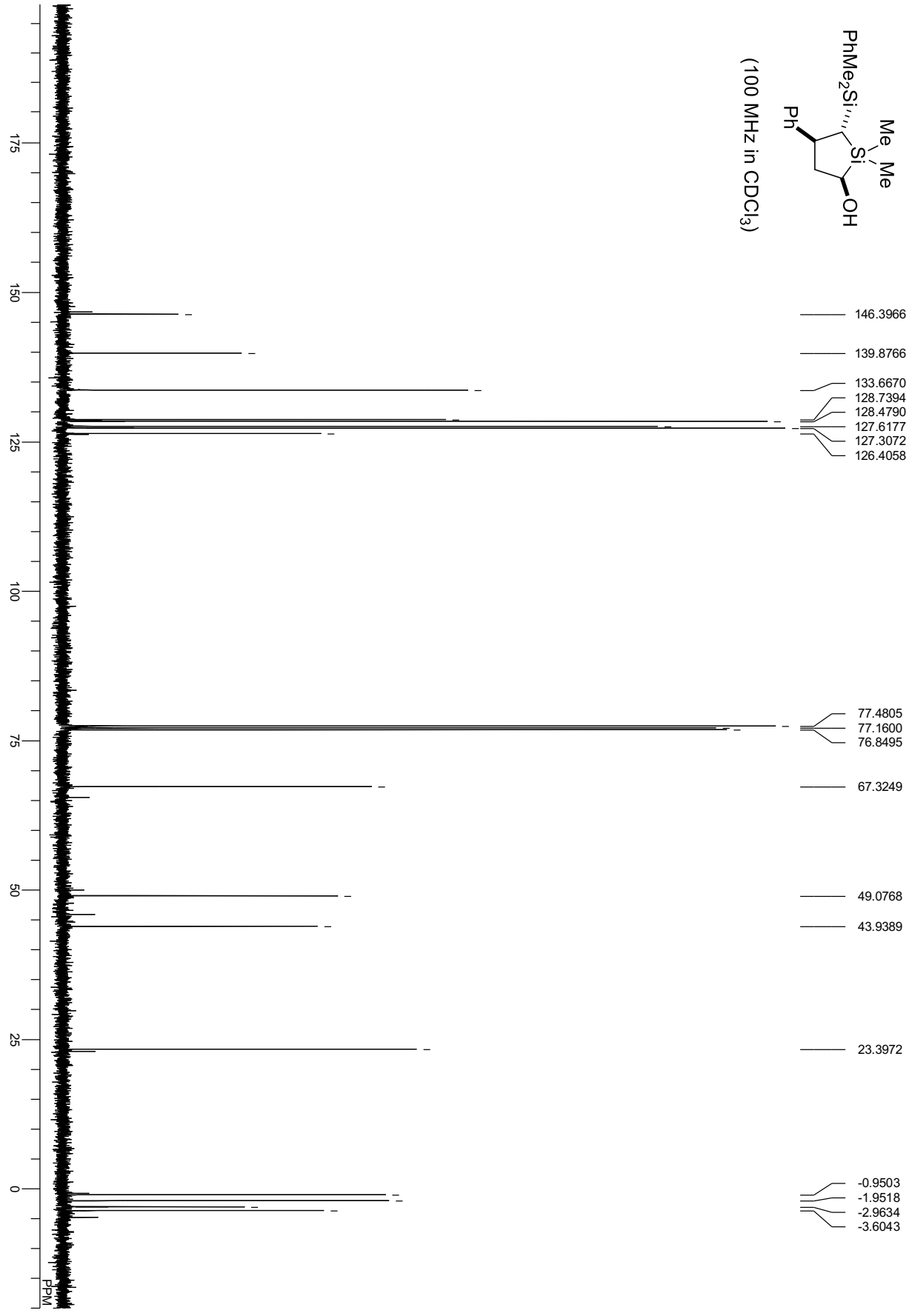
compound **5** (dr = 90/10)



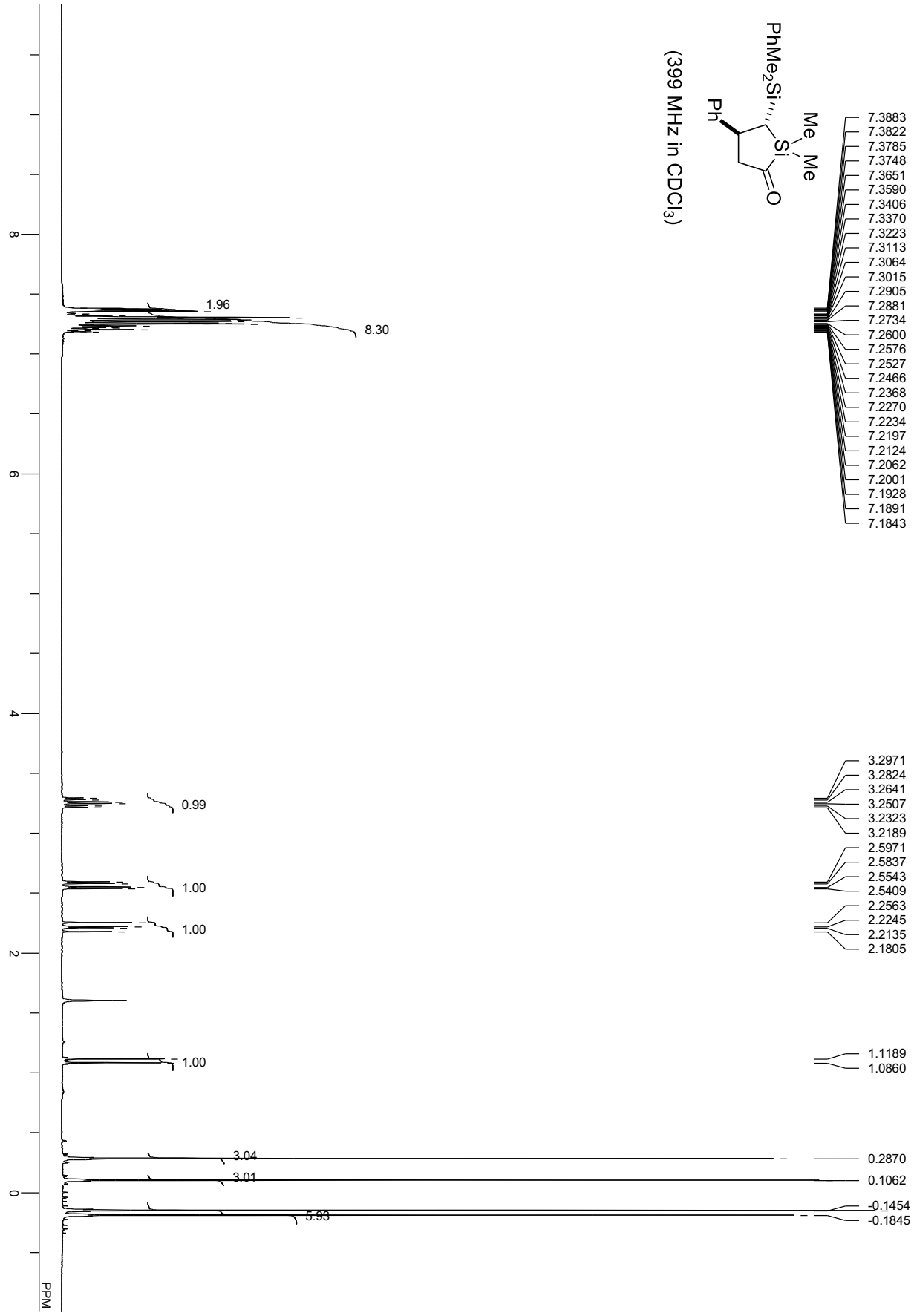
compound **6** (dr = 92/8)



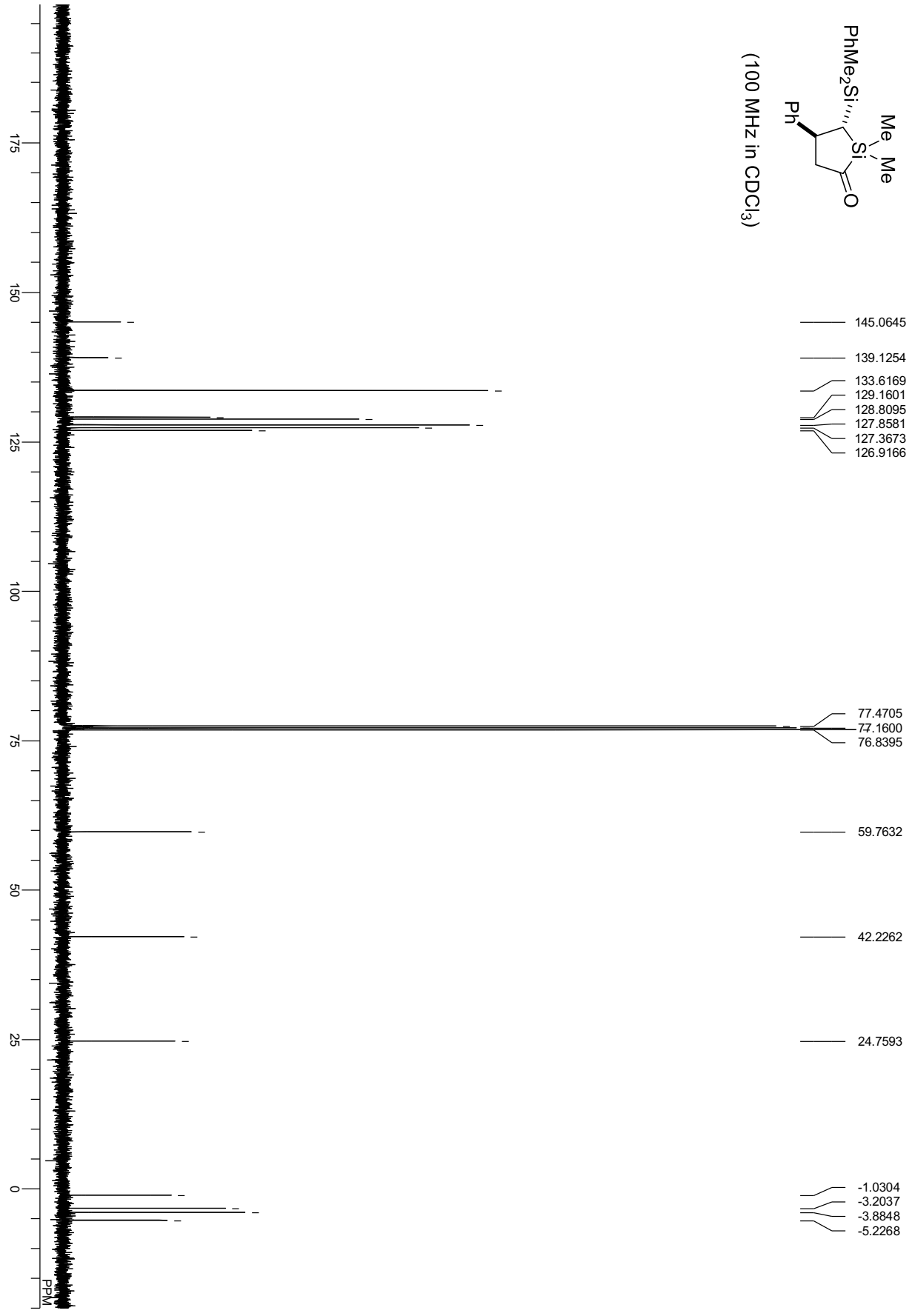
compound **6** (dr = 92/8)



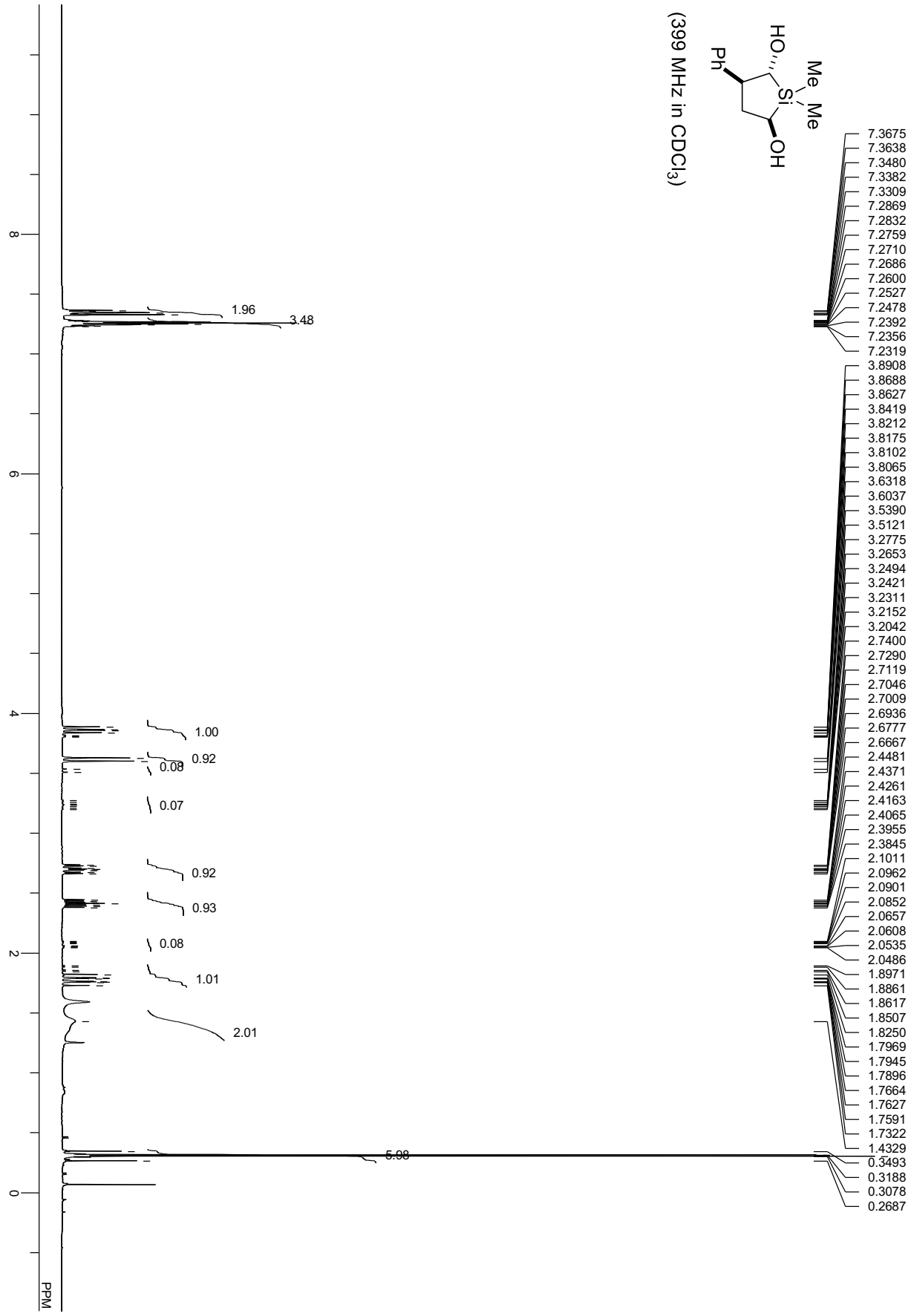
compound **7**


(399 MHz in CDCl3)
PhMe2Si
Ph
Si
Me Me
O
7.3883
7.3822
7.3785
7.3748
7.3651
7.3590
7.3406
7.3370
7.3223
7.3113
7.3064
7.3015
7.2905
7.2881
7.2734
7.2600
7.2576
7.2527
7.2466
7.2368
7.2270
7.2234
7.2197
7.2124
7.2062
7.2001
7.1928
7.1891
7.1843
3.2971
3.2824
3.2641
3.2507
3.2323
3.2189
2.5971
2.5837
2.5543
2.5409
2.2563
2.2245
2.2135
2.1805
1.1189
1.0860
0.2870
0.1062
-0.1454
-0.1845
1.96
8.30
0.99
1.00
1.00
1.00
3.04
3.01
5.93
8
6
4
2
0
PPM

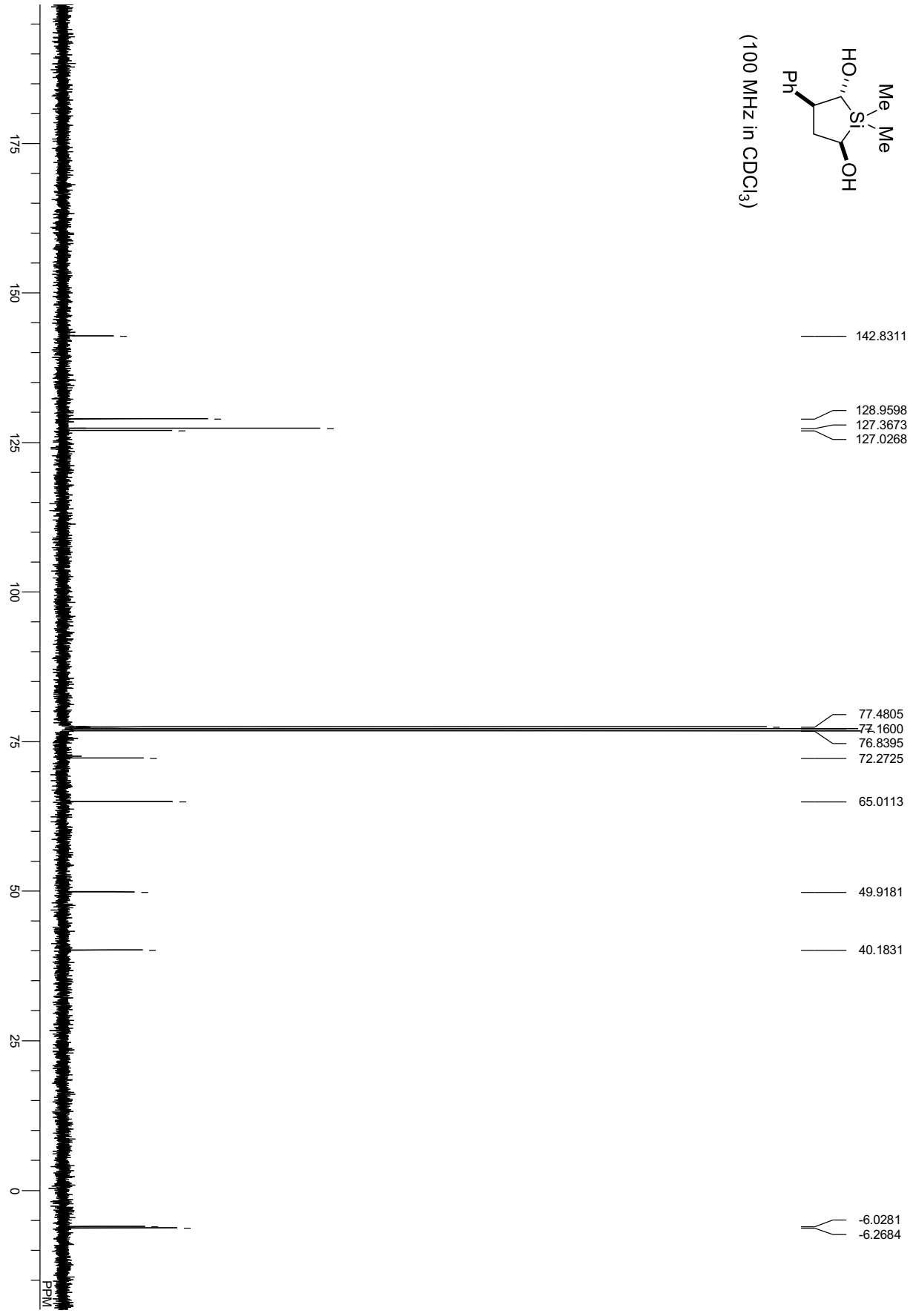
compound **7**


(100 MHz in CDCl3)
PhMe2Si
Ph
Si
Me
Me
O
145.0645
139.1254
133.6169
129.1601
128.8095
127.8581
127.3673
126.9166
77.4705
77.1600
76.8395
59.7632
42.2262
24.7593
-1.0304
-3.2037
-3.8848
-5.2268
PPM

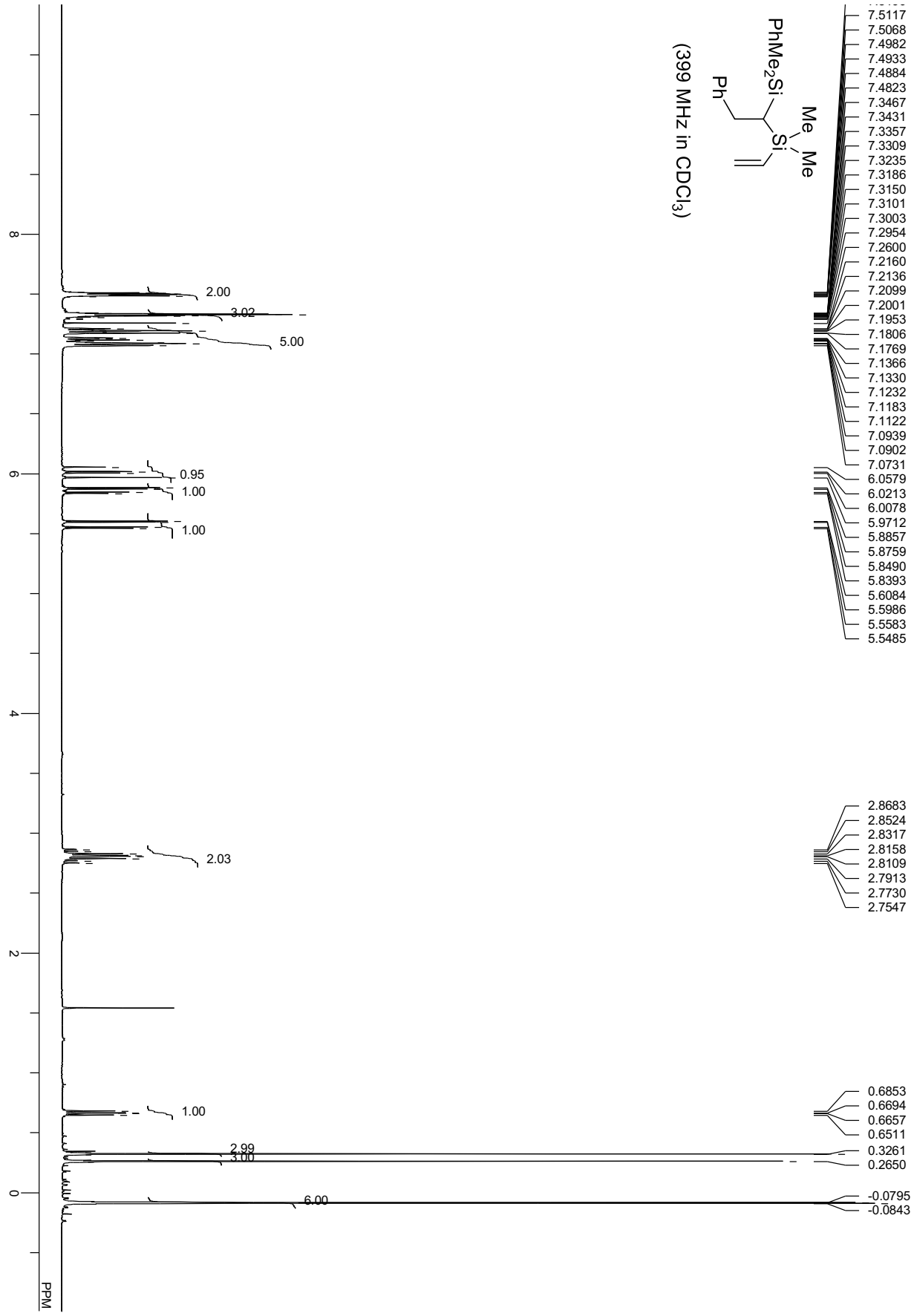
compound **8** (dr = 92/8)



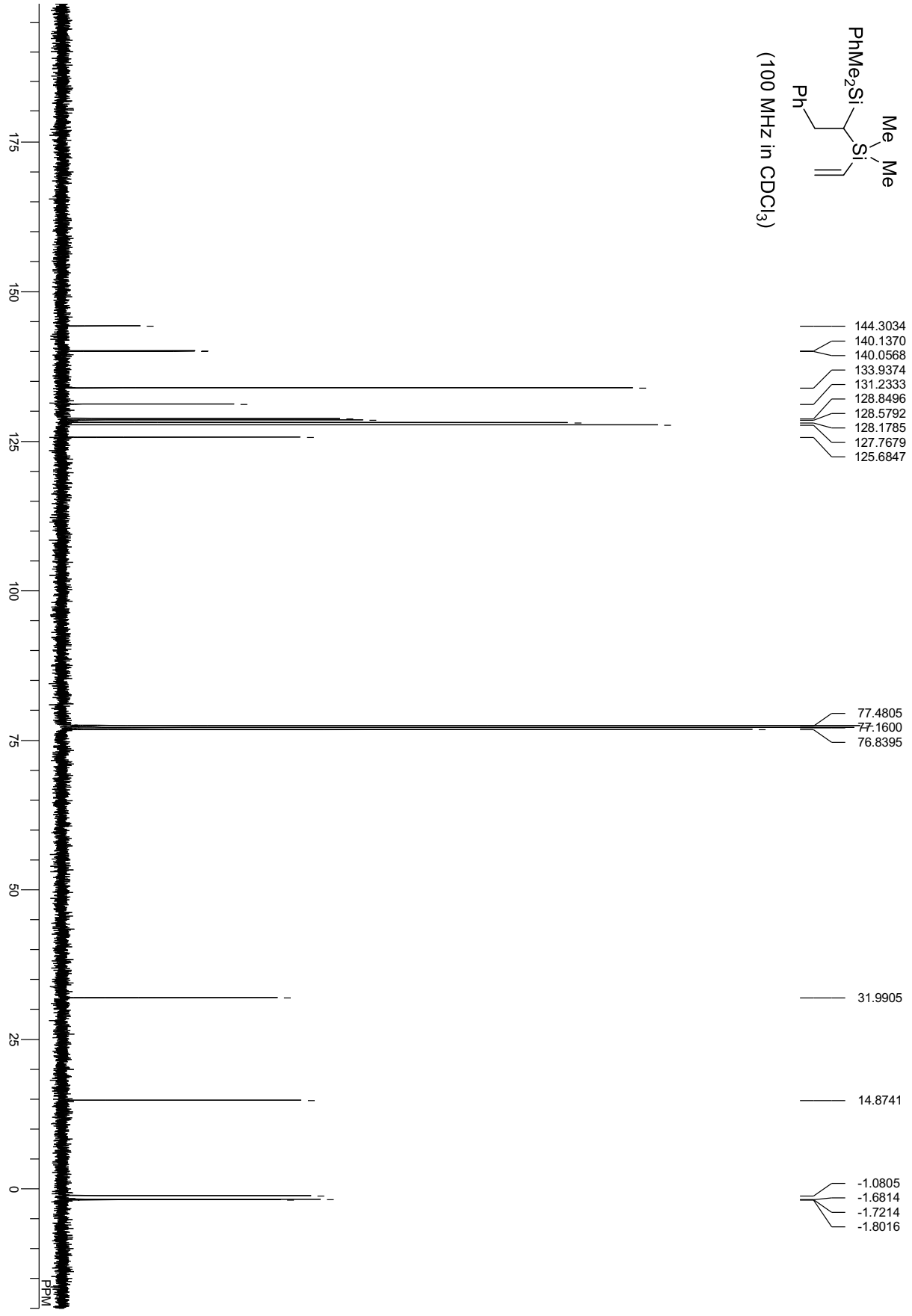
compound **8** (dr = 92/8)



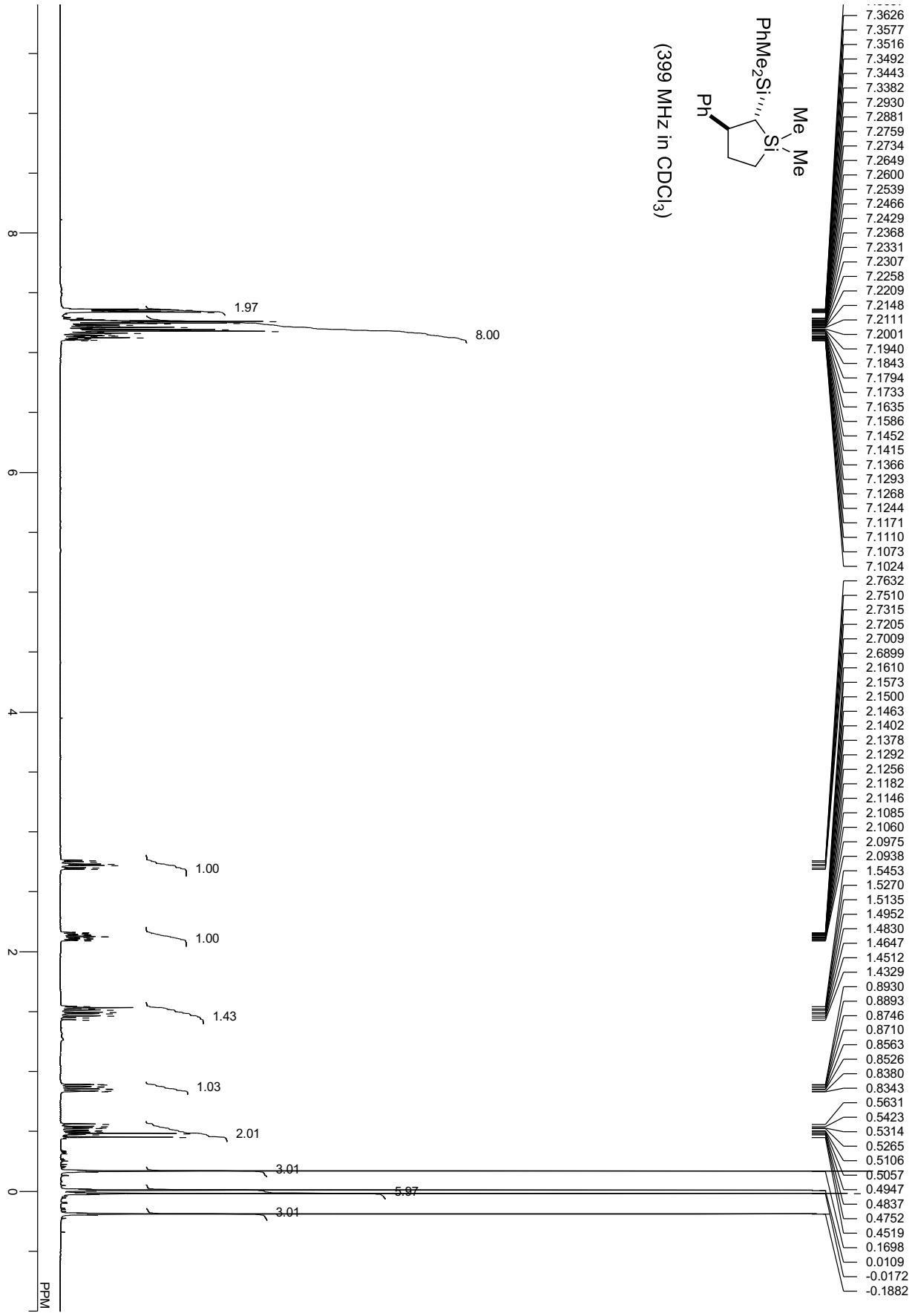
compound **9aa**



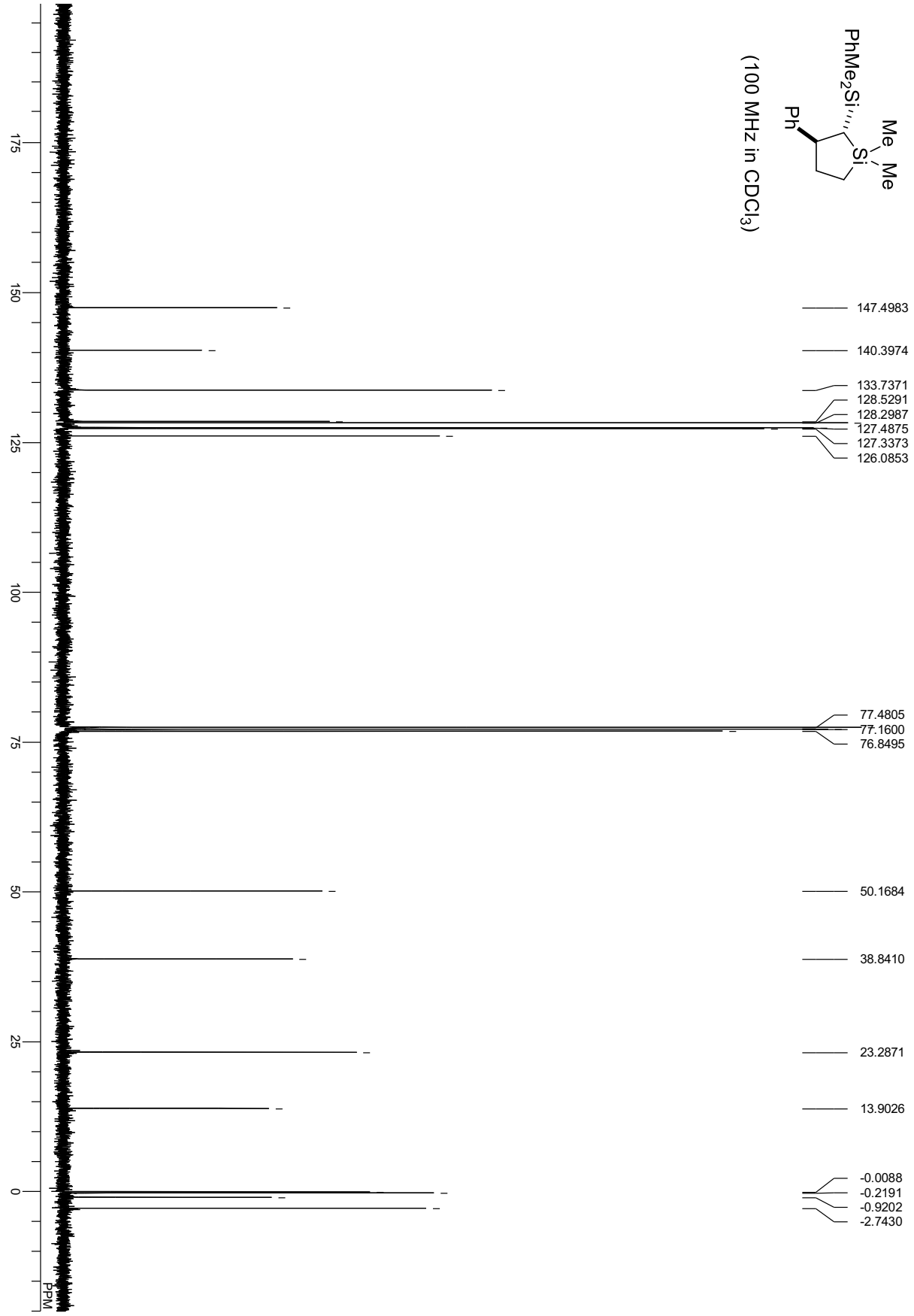
compound **9aa**



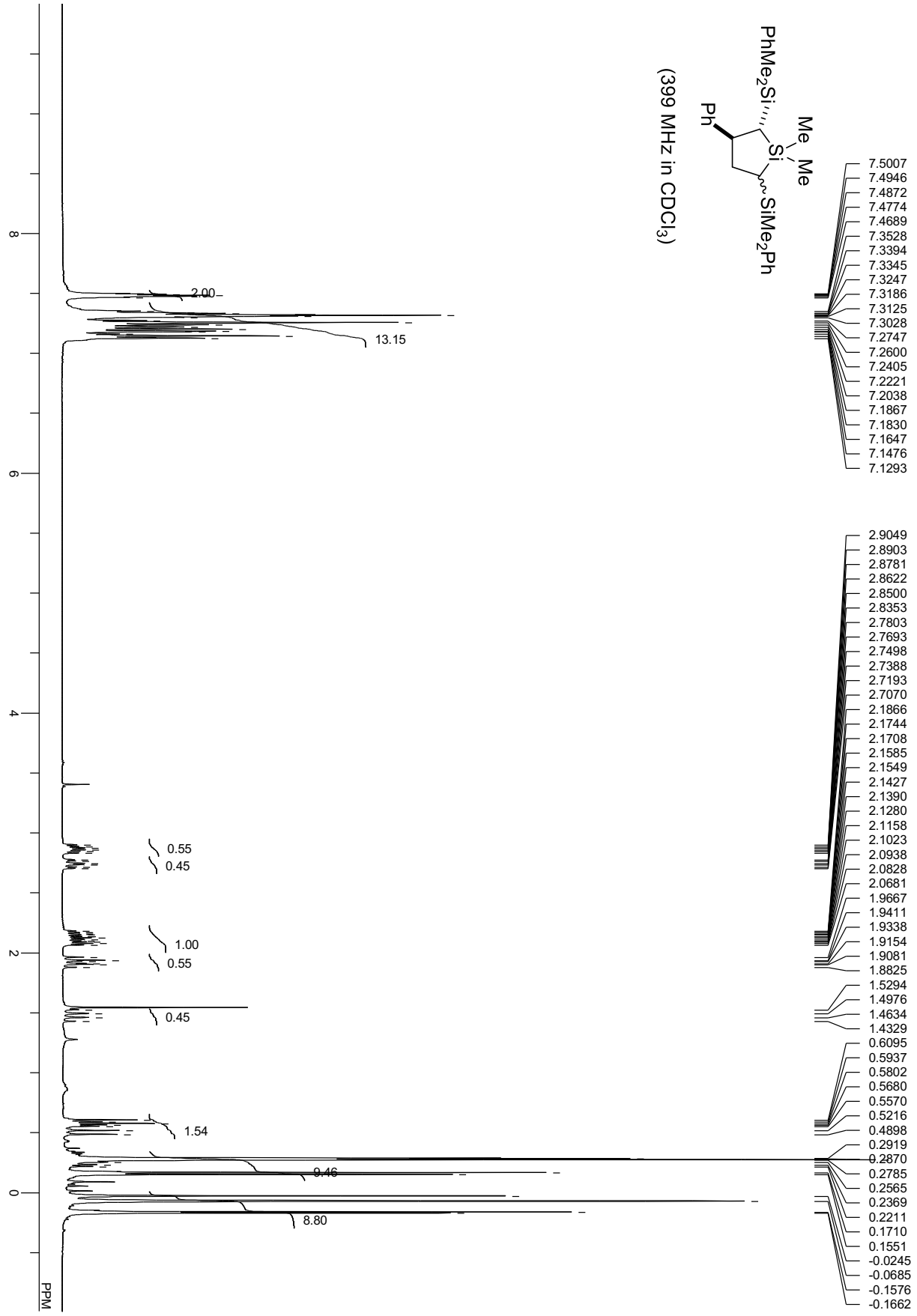
compound **10aa**



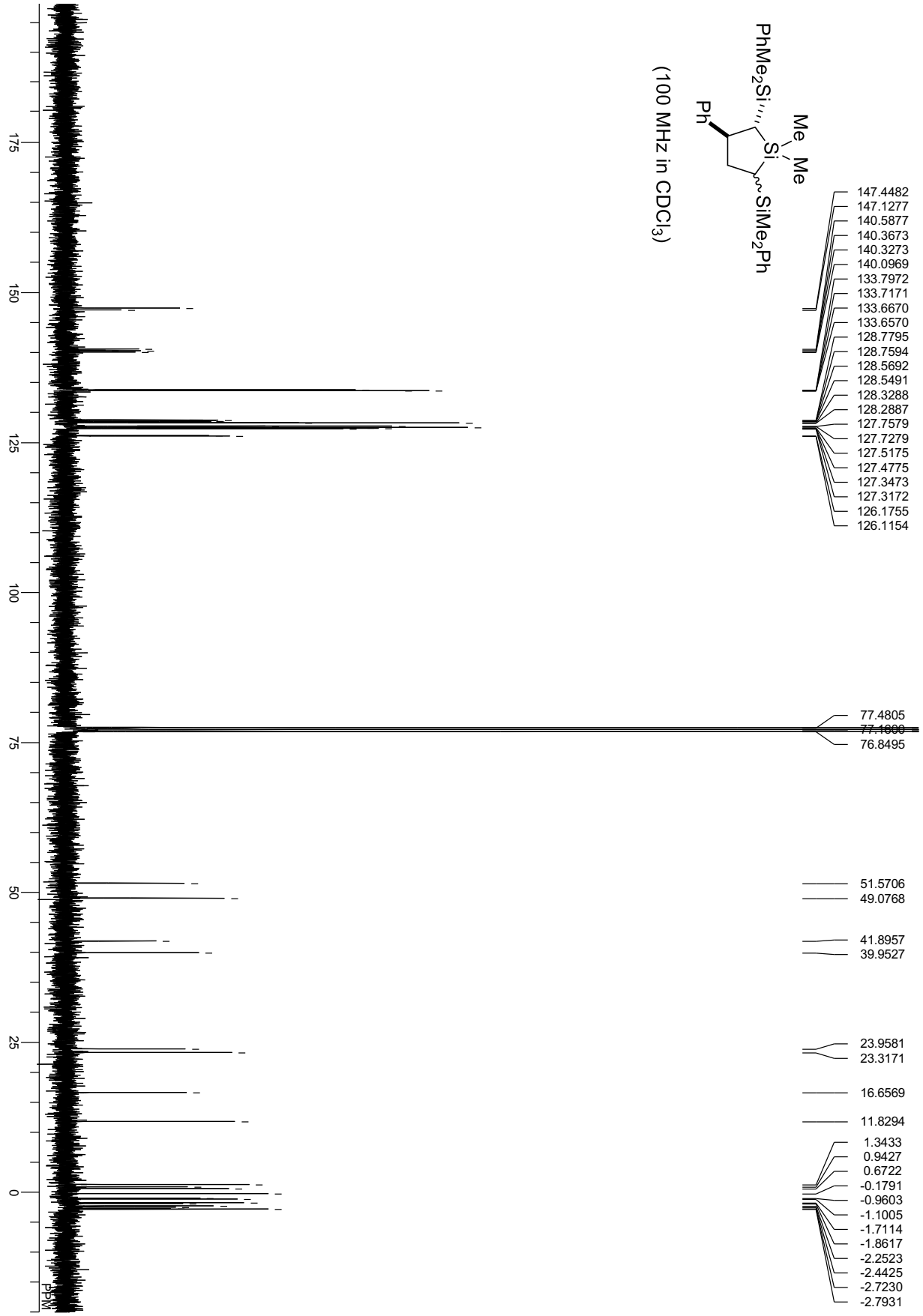
compound **10aa**



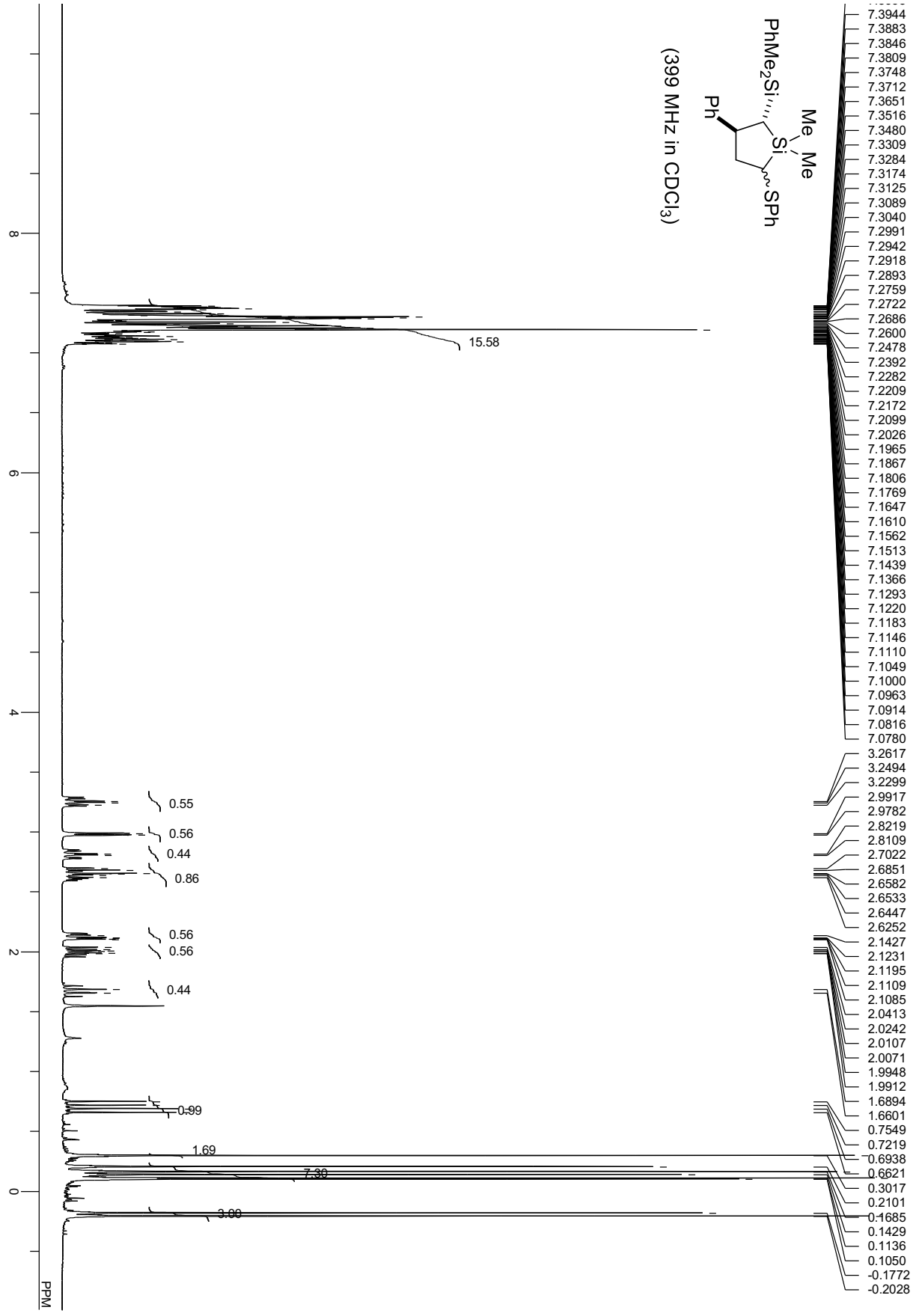
compound **10ac** (dr = 55/45)



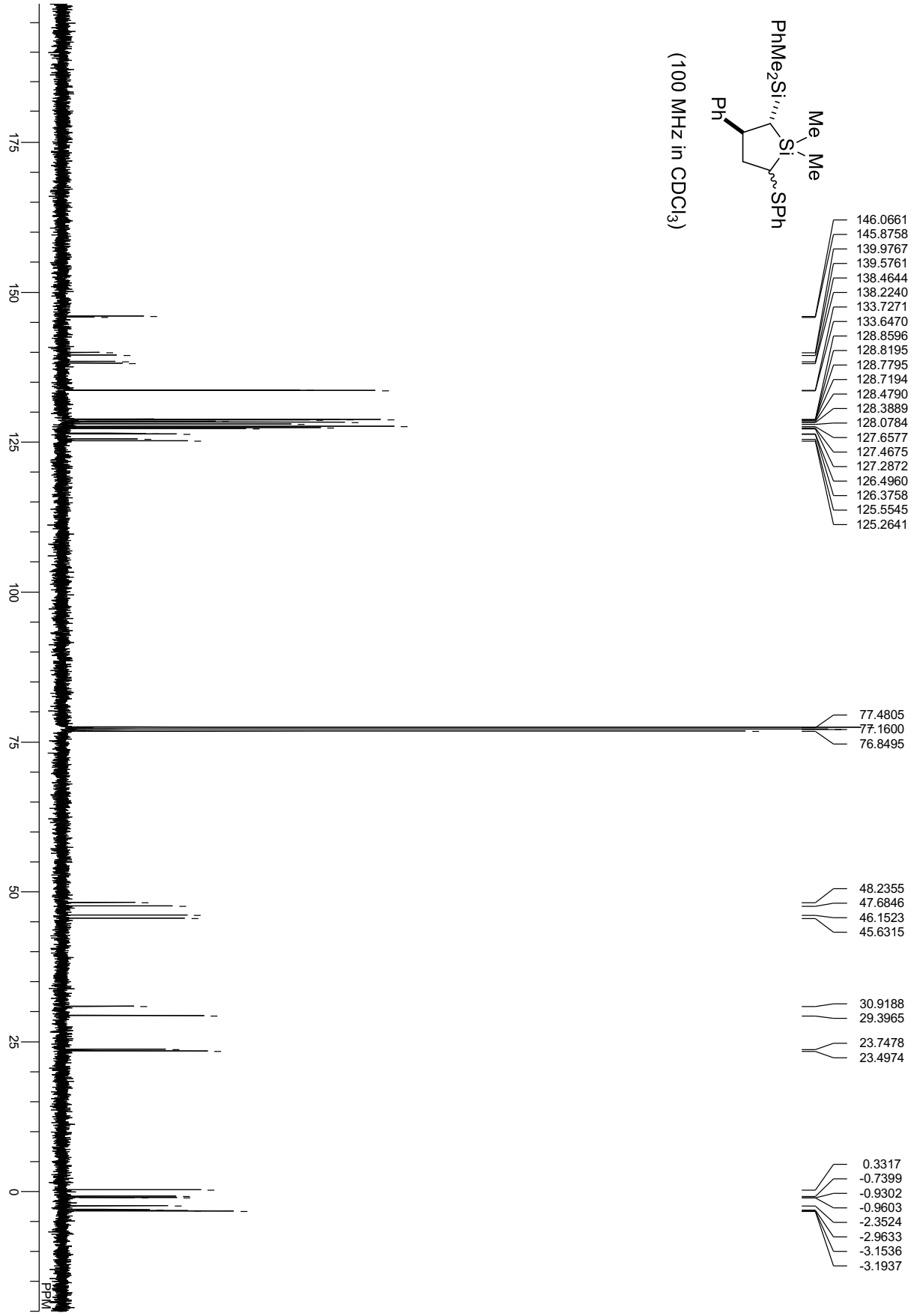
compound **10ac** (dr = 55/45)



compound **10ad** (dr = 56/44)



compound **10ad** (dr = 56/44)



VI. References

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