Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information
for
Palladium-catalyzed synthesis of benzosilacyclobutenes via position-selective C(sp^3)–H arylation

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I. General

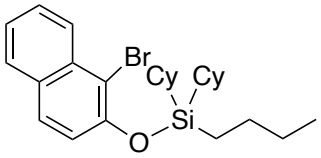
All reactions were carried out with standard Schlenk techniques under nitrogen unless otherwise noted. NMR spectra were recorded on JEOL JNM-ECS400 or Agilent Unity-Inova500 spectrometer. High resolution mass spectra were recorded on JEOL JMS700 or JEOL JMS-T100LP AccuTOF (DART-MS) spectrometer. X-ray crystallographic analysis was performed by RIGAKU XTaLAB P200 with graphite-monochromated Mo-Kα (0.71075 Å) radiation. Preparative GPC was performed with JAI LaboACE LC-5060 equipped with JAIGEL-2HR columns using $CHCl_3$ as an eluent.

Et_2NH (Wako Chemicals) was distilled over KOH under vacuum. CCl_4 (Wako Chemicals) was dried over $MgSO_4$ and degassed by purging nitrogen prior to use. Li turnings were prepared by pounding and cutting Li wire (Kishida Chemical) prior to use. DMF (Wako Chemicals; dehydrated), THF (Kanto Chemical; dehydrated), Et_2O (Wako Chemicals; dehydrated), toluene (Wako Chemicals; dehydrated), 1-bromo-2-naphthol (Aldrich or BLD Pharmatech), 1-iodo-3-phenylpropane (Aldrich), iodomethane-d_3 (CIL), benzaldehyde (Wako Chemicals), cinnamaldehyde (Wako Chemicals), dimethyl acetylenedicarboxylate (Aldrich), diethyl acetylenedicarboxylate (Aldrich), methyl propiolate (TCI), dicyclohexyldichlorosilane (BLD Pharmatech), trichloro(propyl)silane (TCI), dichloro(ethyl)(methyl)silane (Thermo Scientific), imidazole (Nacalai Tesque), *N*-phenylbis(trifluoromethanesulfonimide) (Kanto Chemical, TCI, or Angene), PPh_3 (Wako Chemicals), PCy_3•HBF_4 (TCI), P(*t*Bu)$_3$•HBF_4 (TCI), (±)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl ((±)-binap; Wako Chemicals), 1,1'-bis(diphenylphosphino)ferrocene (dppf; TCI), 1,1'-bis(di-*tert*-butylphosphino)ferrocene (dtbpf; Wako Chemicals), *n*BuLi (Kanto Chemical; 1.52–1.59 M solution in hexane), *t*BuLi (Kanto Chemical; 1.60 M solution in pentane), NaH (Kishida Chemical; 60 wt% in mineral oil), $PdCl_2$ (Tanaka Kikinzoku), $Pd(OAc)_2$ (Wako Chemicals), and $Ni(cod)_2$ (Wako Chemicals) were used as received. 1-Bromo-2-(methoxymethoxy)naphthalene,[1] *tert*-butylchloro(methyl)silane,[2] and $Pd(PPh_3)_4$,[3] were synthesized following the literature procedures.

II. Synthesis of Substrates

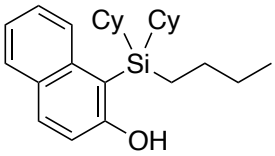
Representative Procedures for Substrates:

1-(Butyldicyclohexylsilyl)-2-naphthyl trifluoromethanesulfonate (1a)



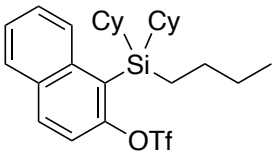
*n*BuLi (2.77 mL, 4.40 mmol; 1.59 M solution in hexane) was added dropwise over 10 min to a solution of dicyclohexyldichlorosilane (1.06 mL, 4.40 mmol) in THF (8.0 mL) at –78 °C. The mixture was stirred for 30 min at –78 °C, warmed to room temperature gradually over 30 min, and further stirred for 1 h at room temperature. 1-Bromo-2-naphthol (898 mg, 4.02 mmol) and imidazole (557 mg, 8.18 mmol) were added to it with the aid of THF (1.5 mL), and the mixture was stirred for 20 h at 35 °C. The reaction was slowly quenched with saturated NH_4Claq at room temperature 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/EtOAc = 50/1 to afford (1-bromo-2-naphthoxy)(butyl)dicyclohexylsilane as a colorless oil (1.82 g, 3.72 mmol; 93% yield).

^{1}H NMR ($CDCl_3$): δ 8.21 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.76 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.68 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.54 (ddd, $^3J_{HH}$ = 8.2 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.38 (ddd, $^3J_{HH}$ = 7.8 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.11 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 1.89-1.78 (m, 4H), 1.78-1.67 (m, 6H), 1.46-1.17 (m, 14H), 1.10 (tt, $^3J_{HH}$ = 12.6 and 2.7 Hz, 2H), 0.93-0.83 (m, 5H).



*n*BuLi (2.34 mL, 3.72 mmol; 1.59 M solution in hexane) was added dropwise over 5 min to a solution of (1-bromo-2-naphthoxy)(butyl)dicyclohexylsilane (1.82 g, 3.72 mmol) in THF (9.4 mL) at –78 °C. The reaction mixture was stirred for 1 h at –78 °C and for 1 h at room temperature. 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 hexane/EtOAc = 5/1 to afford 1-(butyldicyclohexylsilyl)-2-naphthol as a yellow oil (1.57 g, 3.67 mmol; 99% yield).

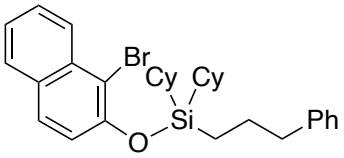
^{1}H NMR ($CDCl_3$): δ 8.03 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 7.76-7.69 (m, 2H), 7.40 (ddd, $^3J_{HH}$ = 8.5 and 6.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.29 (ddd, $^3J_{HH}$ = 8.0 and 6.8 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.93 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 5.28 (s, 1H), 1.94-1.85 (m, 2H), 1.79-1.09 (m, 26H), 0.90 (t, $^3J_{HH}$ = 7.3 Hz, 3H).



NaH (163 mg, 4.07 mmol; 60 wt% in mineral oil) was added to a solution of 1-(butyldicyclohexylsilyl)-2-naphthol (1.57 g, 3.67 mmol) in THF (18 mL) at 0 °C, and the reaction mixture was stirred for 20 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (1.41 g, 3.94 mmol) was added to it, and the mixture was stirred for 5 min at 0 °C and for 1 h at room temperature. 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 hexane to afford compound **1a** as a white solid (1.69 g, 3.20 mmol; 87% yield).

^{1}H NMR ($CDCl_3$): δ ^{1}H NMR ($CDCl_3$): δ 8.27-8.20 (m, 1H), 7.90 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.90-7.83 (m, 1H), 7.58-7.49 (m, 2H), 7.39 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 1.97-1.85 (m, 2H), 1.83-1.07 (m, 26H), 0.89 (d, $^3J_{HH}$ = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.4, 138.7, 132.5, 132.2, 129.03, 129.01, 126.6, 126.4, 126.3, 118.8 (q, $^5J_{CF}$ = 1.9 Hz), 118.7 (q, $^1J_{CF}$ = 320 Hz), 29.2, 28.9, 28.6, 28.5, 27.13, 27.06, 26.9, 26.8, 13.8, 11.9. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 0.9. HRMS (DART) calcd for $C_{27}H_{38}F_3O_3SSi$ ($M+H^+$) 527.2258, found: 527.2271.

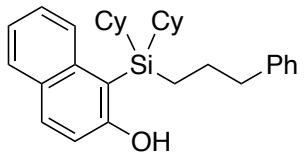
1-(Dicyclohexyl(3-phenylpropyl)silyl)-2-naphthyl trifluoromethanesulfonate (1c)



*t*BuLi (5.50 mL, 8.80 mmol; 1.60 M solution in pentane) was added dropwise over 15 min to a solution of 1-iodo-3-phenylpropane (707 µL, 4.40 mmol) in Et_2O (22 mL) at –78 °C, and the mixture was stirred for 1 h at –78 °C. Dicyclohexyldichlorosilane (1.06 mL, 4.40 mmol) was added to it and the mixture was stirred for 30 min at –78 °C. This was then warmed to room temperature gradually over 30 min and further stirred for 1 h at room temperature. 1-Bromo-2-naphthol (896 mg, 4.01 mmol) and imidazole (566 mg, 8.32 mmol) were added to it with the aid of THF (2.5 mL), and the mixture was stirred for 43 h at 35 °C. The reaction was slowly quenched with saturated NH_4Claq at room temperature 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/EtOAc = 30/1 to afford (1-bromo-2-naphthoxy)dicyclohexyl(3-phenylpropyl)silane as a red oil (2.11 g, 3.93 mmol; 98% yield).

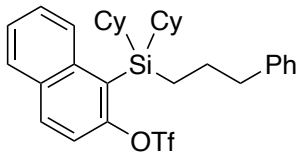
^{1}H NMR ($CDCl_3$): δ 8.23 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.78 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.66 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.56 (ddd, $^3J_{HH}$ = 8.7 and 6.8 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.40 (ddd, $^3J_{HH}$ = 8.2 and 6.9 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.28-7.22 (m, 2H), 7.21-7.15 (m, 1H), 7.15-7.08 (m, 2H), 7.05 (d, $^3J_{HH}$ = 9.2

Hz, 1H), 2.63 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 1.90-1.63 (m, 12H), 1.42-1.16 (m, 10H), 1.11 (tt, $^3J_{HH}$ = 12.4 and 2.7 Hz, 2H), 0.96-0.87 (m, 2H).



*n*BuLi (2.50 mL, 3.93 mmol; 1.57 M solution in hexane) was added dropwise over 5 min to a solution of (1-bromo-2-naphthoxy)dicyclohexyl(3-phenylpropyl)silane (2.11 g, 3.93 mmol) in THF (9.7 mL) at –78 °C. The reaction mixture was stirred for 1 h at –78 °C and for 1 h at room temperature. 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 hexane/EtOAc = 30/1→20/1 and again with hexane/EtOAc = 30/1→20/1→10/1 to afford 1-dicyclohexyl(3-phenylpropyl)silyl-2-naphthol as a pale green oil (761 mg, 1.67 mmol; 42% yield).

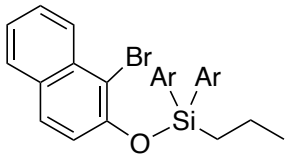
^{1}H NMR ($CDCl_3$): δ 7.99 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.75-7.69 (m, 2H), 7.37 (ddd, $^3J_{HH}$ = 8.5 and 6.8 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.32-7.25 (m, 3H), 7.20-7.13 (m, 3H), 6.89 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 4.98 (s, 1H), 2.68 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 1.89-1.57 (m, 12H), 1.38-1.09 (m, 14H).



NaH (75.5 mg, 1.89 mmol; 60 wt% in mineral oil) was added to a solution of 1-dicyclohexyl(3-phenylpropyl)silyl-2-naphthol (761 mg, 1.67 mmol) in THF (8.5 mL) at 0 °C, and the reaction mixture was stirred for 20 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (655 mg, 1.88 mmol) was added to it, and the mixture was stirred for 5 min at 0 °C and for 1.5 h at room temperature. 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 hexane/EtOAc = 30/1 and again with hexane/EtOAc = 50/1 to afford compound **1c** as a white solid (495 mg, 0.841 mmol; 50% yield).

^{1}H NMR ($CDCl_3$): δ 8.29-8.20 (m, 1H), 7.93 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.92-7.86 (m, 1H), 7.60-7.53 (m, 2H), 7.45 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.32 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.25-7.17 (m, 3H), 2.74 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 2.03-1.89 (m, 2H), 1.87-1.42 (m, 12H), 1.42-1.12 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.4, 142.6, 138.7, 132.7, 132.2, 129.0, 128.9, 128.7, 128.4, 126.7, 126.4, 126.1, 125.8, 118.8 (q, $^5J_{CF}$ = 1.9 Hz), 118.7 (q, $^1J_{CF}$ = 320 Hz), 40.4, 29.1, 28.9, 28.49, 28.46, 27.01, 26.99, 26.7, 12.0. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 0.8. HRMS (DART) calcd for $C_{32}H_{40}F_3O_3SSi$ ($M+H^+$) 589.2414, found: 589.2404.

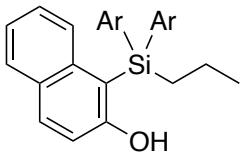
1-(Bis(2-(methoxymethoxy)-1-naphthyl)(propyl)silyl)-2-naphthyl trifluoromethanesulfonate (1h)



(Ar = 2-MeOCH$_2$O-1-naphthyl)

*t*BuLi (36.0 mL, 57.6 mmol; 1.60 M solution in pentane) was added dropwise over 15 min to a solution of 1-bromo-2-(methoxymethoxy)naphthalene (7.82 g, 28.7 mmol) in THF (48 mL) at –78 °C, and the mixture was stirred for 30 min at –78 °C. Trichloro(propyl)silane (2.13 mL, 14.4 mmol) was added to it, and the mixture was stirred for 5 min at –78 °C and for 3.5 h at room temperature. 1-Bromo-2-naphthol (2.69 g, 12.0 mmol) and imidazole (1.64 g, 24.0 mmol) were added to it with the aid of THF (6.0 mL), and the mixture was stirred for 41 h at 35 °C. The reaction was slowly quenched with saturated NH_4Claq at room temperature 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/EtOAc = 10/1→8/1 to afford (1-bromo-2-naphthoxy)di(2-(methoxymethoxy)-1-naphthyl)(propyl)silane as a white amorphous (6.50 g, 9.73 mmol; 81% yield).

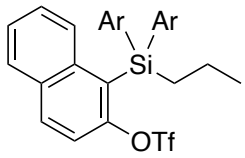
^{1}H NMR ($CDCl_3$): δ 9.06 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 8.23 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.81 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.77 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.62 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.54-7.43 (m, 3H), 7.40-7.29 (m, 4H), 7.27 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.06 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 4.73 (d, $^2J_{HH}$ = 6.9 Hz, 2H), 4.70 (d, $^2J_{HH}$ = 6.9 Hz, 2H), 2.88 (s, 6H), 1.81-1.72 (m, 2H), 1.57-1.45 (m, 2H), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H).



(Ar = 2-MeOCH$_2$O-1-naphthyl)

*n*BuLi (6.20 mL, 9.73 mmol; 1.57 M solution in hexane) was added dropwise over 5 min to a solution of (1-bromo-2-naphthoxy)di(2-(methoxymethoxy)-1-naphthyl)(propyl)silane (6.50 g, 9.73 mmol) in THF (26 mL) at –78 °C. The reaction mixture was stirred for 1 h at –78 °C and for 1 h at room temperature. 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 hexane/EtOAc = 5/1 to afford 1-(bis(2-(methoxymethoxy)-1-naphthyl)(propyl)silyl)-2-naphthol as a white amorphous (5.38 g, 9.13 mmol; 94% yield).

^{1}H NMR ($CDCl_3$): δ 8.21-8.08 (m, 2H), 7.93-7.70 (m, 8H), 7.44-7.13 (m, 5H), 7.08-7.01 (m, 2H), 6.97 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 6.83 (s, 1H), 4.80-4.52 (m, 4H), 2.90 (s, 6H), 2.08-1.94 (m, 1H), 1.90-1.78 (m, 1H), 1.48-1.34 (m, 1H), 1.23-1.09 (m, 1H), 0.88 (t, $^3J_{HH}$ = 7.2 Hz, 3H).

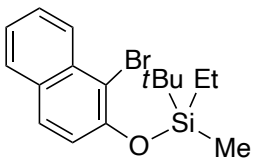


(Ar = 2-MeOCH$_2$O-1-naphthyl)

NaH (400 mg, 9.13 mmol; 60 wt% in mineral oil) was added to a solution of 1-(bis(2-(methoxymethoxy)-1-naphthyl)(propyl)silyl)-2-naphthol (5.38 g, 9.13 mmol) in THF (46 mL) at 0 °C, and the reaction mixture was stirred for 20 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (3.49 g, 9.77 mmol) was added to it, and the mixture was stirred for 5 min at 0 °C and for 3.5 h at room temperature. 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 hexane/EtOAc = 8/1 to afford compound **1h** as a white amorphous (3.77 g, 5.22 mmol; 57% yield).

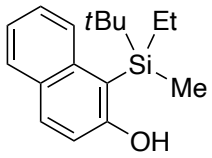
^{1}H NMR ($CDCl_3$): δ 8.08 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.01 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.97 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.93-7.84 (m, 3H), 7.84-7.74 (m, 3H), 7.41-7.33 (m, 4H), 7.30-7.19 (m, 2H), 7.14 (ddd, $^3J_{HH}$ = 8.7 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.03 (ddd, $^3J_{HH}$ = 9.2 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.00 (ddd, $^3J_{HH}$ = 8.7 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 4.52 (d, $^2J_{HH}$ = 7.3 Hz, 1H), 4.42 (d, $^2J_{HH}$ = 7.3 Hz, 1H), 4.40 (d, $^2J_{HH}$ = 6.9 Hz, 1H), 4.35 (d, $^2J_{HH}$ = 7.3 Hz, 1H), 2.83 (s, 3H), 2.81 (s, 3H), 1.91-1.73 (m, 2H), 1.43-1.24 (m, 2H), 0.89 (t, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.73, 161.69, 152.6, 138.6, 138.3, 138.2, 133.0, 132.1, 131.9, 131.4, 130.24, 130.20, 130.0, 129.8, 128.6, 128.5, 128.2, 128.0, 126.1, 126.0, 125.94, 125.85, 123.42, 123.39, 120.02, 119.99, 118.7 (q, $^5J_{CF}$ = 1.9 Hz), 118.3 (q, $^1J_{CF}$ = 320 Hz), 115.3, 115.2, 94.8, 94.6, 55.5, 55.4, 23.2, 19.3, 18.4. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ –19.9. HRMS (FAB) calcd for $C_{38}H_{35}F_3O_7SSi$ (M^+) 720.1825, found: 720.1833.

1-(*tert*-Butyl(ethyl)(methyl)silyl)-2-naphthyl trifluoromethanesulfonate (1s)



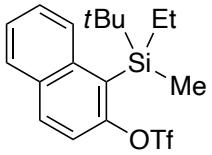
*t*BuLi (5.50 mL, 8.80 mmol; 1.60 M solution in pentane) was added dropwise over 15 min to a solution of dichloro(ethyl)(methyl)silane (592 μL, 4.40 mmol) in Et_2O (3.5 mL) at 0 °C, and the mixture was stirred for 17 h while gradually raising the temperature to room temperature. 1-Bromo-2-naphthol (892 mg, 4.00 mmol) and imidazole (553 mg, 8.12 mmol) were added to it with the aid of THF (2.0 mL), and the mixture was stirred for 4 h at 40 °C. The reaction was quenched with H_2O at room temperature 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/EtOAc = 50/1 to afford (1-bromo-2-naphthoxy)(*tert*-butyl)(ethyl)(methyl)silane as a colorless oil (855 mg, 2.44 mmol; 61% yield).

^{1}H NMR ($CDCl_3$): δ 8.21 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.76 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.69 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.54 (ddd, $^3J_{HH}$ = 8.7 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.38 (ddd, $^3J_{HH}$ = 8.2 and 6.9 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.13 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 1.09 (s, 9H), 1.00 (t, $^3J_{HH}$ = 7.6 Hz, 3H), 0.97-0.76 (m, 2H), 0.32 (s, 3H).



*n*BuLi (1.60 mL, 2.44 mmol; 1.52 M solution in hexane) was added dropwise over 5 min to a solution of (1-bromo-2-naphthoxy)(*tert*-butyl)(ethyl)(methyl)silane (855 mg, 2.44 mmol) in THF (6.1 mL) at –78 °C. The reaction mixture was stirred for 1 h at –78 °C and for 1 h at room temperature. 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 hexane/EtOAc = 5/1 to afford 1-(*tert*-butyl(ethyl)(methyl)silyl)-2-naphthol as a red oil (684 mg, 2.10 mmol; 86% yield).

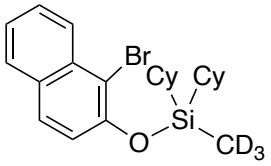
^{1}H NMR ($CDCl_3$): δ 8.05 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.75 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.74 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.40 (ddd, $^3J_{HH}$ = 8.7 and 6.9 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.29 (ddd, $^3J_{HH}$ = 8.2 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.95 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 5.19 (s, 1H), 1.44-1.32 (m, 1H), 1.00 (s, 9H), 0.96-0.79 (m, 4H), 0.58 (s, 3H).



NaH (92.4 mg, 2.31 mmol; 60 wt% in mineral oil) was added to a solution of 1-(*tert*-butyl(ethyl)(methyl)silyl)-2-naphthol (684 mg, 2.10 mmol) in THF (10 mL) at 0 °C, and the reaction mixture was stirred for 20 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (825 mg, 2.31 mmol) was added to it, and the mixture was stirred for 5 min at 0 °C and for 1 h at room temperature. 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 hexane/EtOAc = 100/1 to afford compound **1s** as a white solid (778 mg, 1.92 mmol; 92% yield).

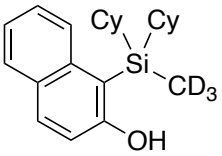
^{1}H NMR ($CDCl_3$): δ 8.28 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.95 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.92-7.84 (m, 1H), 7.60-7.50 (m, 3H), 1.54-1.38 (m, 1H), 1.06 (s, 9H), 0.98-0.86 (m, 4H), 0.65 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.4, 138.6, 133.0, 132.2, 129.8, 129.0, 126.7, 126.2, 125.1, 118.8 (q, $^1J_{CF}$ = 320 Hz), 117.8 (q, $^5J_{CF}$ = 2.4 Hz), 28.0, 19.3, 8.2, 7.6, –1.9. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 7.9. HRMS (FAB) calcd for $C_{18}H_{24}F_3O_3SSi$ ($M+H^+$) 405.1162, found: 405.1165.

1-(Dicyclohexyl(methyl-d_3)silyl)-2-naphthyl trifluoromethanesulfonate (1q-d_3)



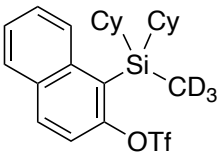
A mixture of Li turnings (134 mg, 20.0 mmol) and iodomethane-d_3 (318 μL, 5.00 mmol) in Et_2O (10 mL) was cooled to 0 °C and sonicated for 1.5 h at 0 °C to give a 0.42 M solution of methyllithium-d_3 (determined by acid–base titration). The resulting mixture (except for unreacted Li) was then added dropwise over 15 min to a solution of dicyclohexyldichlorosilane (1.06 mL, 4.40 mmol) in THF (3.0 mL) at –78 °C. The mixture was stirred for 30 min at –78 °C, warmed to room temperature gradually over 30 min, and further stirred for 1.5 h at room temperature. 1-Bromo-2-naphthol (900 mg, 4.03 mmol) and imidazole (567 mg, 8.18 mmol) were added to it with the aid of THF (3.0 mL), and the mixture was stirred for 16 h at 35 °C. The reaction was slowly quenched with saturated NH_4Claq at room temperature 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/EtOAc = 50/1 to afford (1-bromo-2-naphthoxy)dicyclohexyl(methyl-d_3)silane as a colorless oil (1.52 g, 3.41 mmol; 85% yield).

^{1}H NMR ($CDCl_3$): δ 8.20 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.76 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.68 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.54 (ddd, $^3J_{HH}$ = 8.7 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.38 (ddd, $^3J_{HH}$ = 8.2 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.10 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 1.88-1.65 (m, 10H), 1.42-1.15 (m, 10H), 1.04 (tt, $^3J_{HH}$ = 12.6 and 3.0 Hz, 2H).



*n*BuLi (2.50 mL, 3.93 mmol; 1.57 M solution in hexane) was added dropwise over 5 min to a solution of (1-bromo-2-naphthoxy)dicyclohexyl(methyl-d_3)silane (1.52 g, 3.41 mmol) in THF (8.6 mL) at –78 °C. The reaction mixture was stirred for 1 h at –78 °C and for 1 h at room temperature. 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 hexane/EtOAc = 5/1 to afford 1-dicyclohexyl(methyl-d_3)silyl-2-naphthol as a red oil (1.30 g, 3.38 mmol; 99% yield).

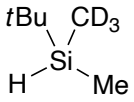
^{1}H NMR ($CDCl_3$): δ 8.02 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.77-7.69 (m, 2H), 7.41 (ddd, $^3J_{HH}$ = 8.7 and 6.9 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.30 (ddd, $^3J_{HH}$ = 8.2 and 6.9 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.93 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 5.30 (s, 1H), 1.94-1.84 (m, 2H), 1.80-1.03 (m, 20H).



NaH (150 mg, 3.75 mmol; 60 wt% in mineral oil) was added to a solution of 1-dicyclohexyl(methyl-d_3)silyl-2-naphthol (1.30 g, 3.38 mmol) in THF (16.6 mL) at 0 °C, and the reaction mixture was stirred for 20 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (1.30 g, 3.64 mmol) was added to it, and the mixture was stirred for 5 min at 0 °C and for 1 h at room temperature. 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 hexane/EtOAc = 50/1 to afford compound **1q-*d*$_3$** as a colorless oil (1.51 g, 3.10 mmol; 92% yield).

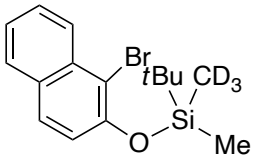
^{1}H NMR ($CDCl_3$): δ 8.21 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.87 (dd, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.61-7.50 (m, 2H), 7.40 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 1.98-1.86 (m, 2H), 1.83-1.49 (m, 6H), 1.46-1.00 (m, 14H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.2, 138.2, 132.5, 132.3, 129.2, 128.9, 127.2, 126.7, 126.4, 119.0, 118.8 (q, $^1J_{CF}$ = 320 Hz), 29.0, 28.34, 28.32, 26.9, 26.6, –5.7-–7.5 (m). HRMS (FAB) calcd for $C_{24}H_{29}D_3F_3O_3SSi$ ($M+H^+$) 448.1976, found: 448.1986.

1-(*tert*-Butyl(methyl)(methyl-*d*$_3$)silyl)-2-naphthyl trifluoromethanesulfonate (1s-*d*$_3$)



A mixture of Li turnings (279 mg, 40.2 mmol) and iodomethane-d_3 (636 μL, 10.0 mmol) in Et_2O (10 mL) was cooled to 0 °C and sonicated for 4 h at 0 °C to give a 0.20 M solution of methyllithium-d_3 (determined by acid–base titration). The resulting mixture (except for unreacted Li) was then added dropwise over 10 min to a solution of *tert*-butylchloro(methyl)silane (600 mg, 4.39 mmol) in Et_2O (3.0 mL) at –78 °C. The mixture was stirred for 30 min at –78 °C, warmed to room temperature, and further stirred for 1 h at room temperature. The mixture was passed through a pad of Celite with Et_2O under nitrogen, and most of the solvent was removed by distillation under atmospheric pressure. The resulting mixture was vacuum-transferred to afford *tert*-butyl(methyl)(methyl-d_3)silane as a colorless oil (1.89 g, 2.37 mmol; 54% yield, 15 wt% in Et_2O).

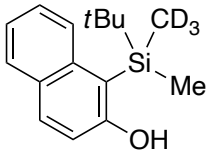
^{1}H NMR ($CDCl_3$): δ 3.62 (q, $^3J_{HH}$ = 3.8 Hz, 1H), 0.91 (s, 9H), 0.02 (d, $^3J_{HH}$ = 3.7 Hz, 3H).



tert-Butyl(methyl)(methyl-d_3)silane (1.89 g, 2.37 mmol; 15 wt% in Et_2O) was added to a suspension of $PdCl_2$ (106 mg, 0.600 mmol) in CCl_4 (2.0 mL) at room temperature. The mixture was

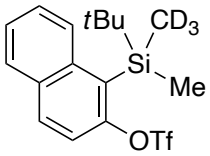
stirred for 5 h at room temperature and passed through a pad of Celite with THF (3.0 mL) under nitrogen. 1-Bromo-2-naphthol (559 mg, 2.51 mmol) and imidazole (350 mg, 5.15 mmol) were added to it and the mixture was stirred for 4 h at 60 °C. The reaction was quenched with H_2O at room temperature and 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 (1-bromo-2-naphthoxy)*tert*-butyl(methyl)(methyl-d_3)silane as a colorless oil (494 mg, 1.52 mmol; 64% yield).

^{1}H NMR ($CDCl_3$): δ 8.21 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.77 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.69 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.55 (ddd, $^3J_{HH}$ = 8.7 and 6.8 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.39 (ddd, $^3J_{HH}$ = 8.2 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.12 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 1.09 (s, 9H), 0.29 (s, 3H).



*n*BuLi (1.00 mL, 1.52 mmol; 1.52 M solution in hexane) was added dropwise over 5 min to a solution of (1-bromo-2-naphthoxy)*tert*-butyl(methyl)(methyl-d_3)silane (494 mg, 1.52 mmol) in THF (4.0 mL) at –78 °C. The reaction mixture was stirred for 1 h at –78 °C and for 1 h at room temperature. 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 hexane/EtOAc = 5/1 to afford 1-(*tert*-butyl(methyl)(methyl-d_3)silyl)-2-naphthol as a red oil (427 mg, 1.38 mmol; 91% yield).

^{1}H NMR ($CDCl_3$): δ 8.03 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.75 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.74 (dd, $^3J_{HH}$ = 8.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.40 (ddd, $^3J_{HH}$ = 8.7 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.29 (ddd, $^3J_{HH}$ = 7.8 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.95 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 5.15 (s, 1H), 1.01 (s, 9H), 0.56 (s, 3H).



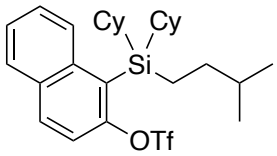
NaH (61.0 mg, 1.53 mmol; 60 wt% in mineral oil) was added to a solution of 1-(*tert*-butyl(methyl)(methyl-d_3)silyl)-2-naphthol (427 mg, 1.38 mmol) in THF (6.0 mL) at 0 °C, and the reaction mixture was stirred for 20 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (546 mg, 1.53 mmol) was added to it, and the mixture was stirred for 5 min at 0 °C and for 1 h at room temperature. 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 hexane to afford compound **1s-*d*$_3$** as a white solid (510 mg, 1.30 mmol; 94% yield).

^{1}H NMR ($CDCl_3$): δ 8.26 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.94 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.91-7.85 (m, 1H),

7.61-7.50 (m, 3H), 1.07 (s, 9H), 0.64 (s, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 155.1, 138.4, 133.0, 132.2, 130.2, 129.0, 126.6, 126.5, 126.2, 118.8 (q, $^{1}J_{CF}$ = 320 Hz), 117.8 (q, $^{5}J_{CF}$ = 2.6 Hz), 27.7, 19.1, 0.5. HRMS (FAB) calcd for $C_{17}H_{19}D_3F_3O_3SSi$ ($M+H^+$) 394.1194, found: 394.1197.

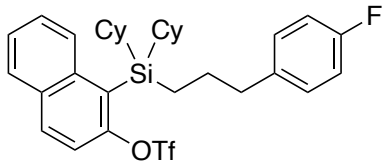
Analytical Data for Other Substrates:

1-(Dicyclohexyl(3-methylbutyl)silyl)-2-naphthyl trifluoromethanesulfonate (1b)



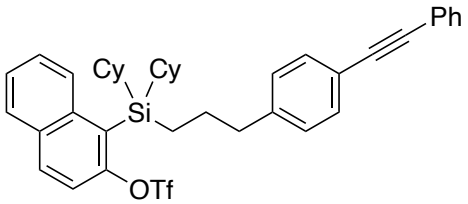
^{1}H NMR ($CDCl_3$): δ 8.30 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.93 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 7.88 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.63-7.51 (m, 2H), 7.45 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H), 2.07-1.93 (m, 2H), 1.89-1.15 (m, 25H), 0.96 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 154.4, 138.8, 132.6, 132.2, 129.1, 129.0, 126.6, 126.4, 126.3, 118.83 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.76 (q, $^{1}J_{CF}$ = 320 Hz), 33.5, 31.7, 29.2, 29.0, 28.6, 28.5, 27.1, 26.8, 22.2, 9.8. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 1.3. HRMS (DART) calcd for $C_{28}H_{40}F_3O_3SSi$ ($M+H^+$) 541.2414, found: 541.2408.

1-(Dicyclohexyl(3-(4-fluorophenyl)propyl)silyl)-2-naphthyl trifluoromethanesulfonate (1d)



^{1}H NMR ($CDCl_3$): δ 8.20-8.13 (m, 1H), 7.90 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 7.90-7.83 (m, 1H), 7.56-7.47 (m, 2H), 7.39 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 7.12-7.03 (m, 2H), 6.98-6.90 (m, 2H), 2.64 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H), 1.95-1.82 (m, 2H), 1.82-1.35 (m, 12H), 1.35-1.05 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 161.4 (d, $^{1}J_{CF}$ = 243 Hz), 154.4, 138.6, 138.2 (d, $^{4}J_{CF}$ = 3.8 Hz), 132.7, 132.2, 130.0 (d, $^{3}J_{CF}$ = 7.7 Hz), 129.1, 128.8, 126.7, 126.4, 126.0, 118.80 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.77 (q, $^{1}J_{CF}$ = 320 Hz), 115.1 (d, $^{2}J_{CF}$ = 21.1 Hz), 39.4, 29.1, 28.9, 28.5, 28.4, 27.1, 27.0, 26.7, 11.8. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 0.8. HRMS (DART) calcd for $C_{32}H_{39}F_4O_3SSi$ ($M+H^+$) 607.2320, found: 607.2330.

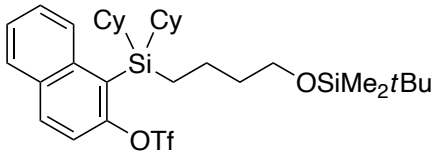
1-(Dicyclohexyl(3-(4-(phenylethynyl)phenyl)propyl)silyl)-2-naphthyl trifluoromethanesulfonate (1e)



^{1}H NMR ($CDCl_3$): δ 8.17 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.96-7.83 (m, 2H), 7.58-7.28 (m, 10H), 7.12 (d,

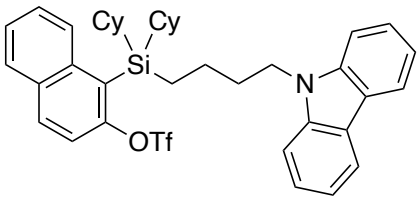
$^{3}J_{HH}$ = 7.8 Hz, 2H), 2.69 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.96-1.82 (m, 2H), 1.82-1.63 (m, 6H), 1.63-1.36 (m, 6H), 1.36-1.05 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 154.4, 143.0, 138.6, 138.2, 132.7, 132.2, 131.7, 129.1, 128.81, 128.77, 128.4, 128.2, 126.7, 126.4, 126.0, 123.6, 120.7, 118.8 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 89.7, 79.0, 40.2, 29.1, 28.9, 28.5, 28.4, 27.0, 26.7, 11.8. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 0.8. HRMS (DART) calcd for $C_{40}H_{44}F_3O_3SSi$ ($M+H^+$) 689.2727, found: 689.2727.

1-((4-(*tert*-Butyldimethylsilyloxy)butyl)dicyclohexylsilyl)-2-naphthyl trifluoromethanesulfonate (1f)



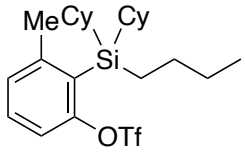
^{1}H NMR ($CDCl_3$): δ 8.25 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.90 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H), 7.87 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 2.3 Hz, 1H), 7.60-7.49 (m, 2H), 7.40 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H), 3.62 (t, $^{3}J_{HH}$ = 6.2 Hz, 2H), 2.00-1.88 (m, 2H), 1.84-1.56 (m, 8H), 1.56-1.08 (m, 18H), 0.87 (s, 9H), 0.02 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 154.3, 138.7, 132.6, 132.2, 129.03, 128.95, 126.6, 126.4, 126.3, 118.8 (q, $^{5}J_{CF}$ = 2.2 Hz), 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 62.8, 37.2, 29.2, 28.9, 28.54, 28.49, 27.0, 26.8, 26.1, 21.1, 18.4, 11.9, –5.2. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 18.3, 1.0. HRMS (DART) calcd for $C_{33}H_{52}F_3O_4SSi_2$ ($M+H^+$) 657.3071, found: 657.3079.

1-((4-(9-Carbazolyl)butyl)dicyclohexylsilyl)-2-naphthyl trifluoromethanesulfonate (1g)



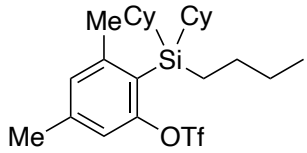
^{1}H NMR ($CDCl_3$): δ 8.13 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 8.08 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H), 7.90 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H), 7.86 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H), 7.53-7.32 (m, 7H), 7.19 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 0.9 Hz, 2H), 4.28 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H), 1.96 (quint, $^{3}J_{HH}$ = 7.3 Hz, 2H), 1.88-1.76 (m, 2H), 1.75-1.30 (m, 12H), 1.30-0.97 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 154.3, 140.5, 138.5, 132.7, 132.1, 129.0, 128.7, 126.6, 126.4, 126.0, 125.6, 123.0, 120.4, 118.8, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 108.8, 42.7, 33.1, 29.1, 28.8, 28.5, 28.4, 26.9, 26.7, 22.8, 11.9. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 0.9. HRMS (DART) calcd for $C_{39}H_{45}F_3NO_3SSi$ ($M+H^+$) 692.2836, found: 692.2843.

2-(Butyldicyclohexylsilyl)-3-methylphenyl trifluoromethanesulfonate (1i)



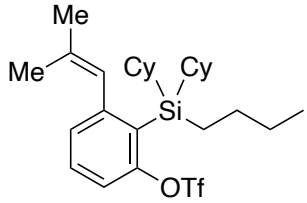
^{1}H NMR ($CDCl_3$): δ 7.29 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.13 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 2.50 (s, 3H), 1.91-1.62 (m, 8H), 1.58-1.47 (m, 2H), 1.46-1.13 (m, 16H), 1.10-0.99 (m, 2H), 0.91 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.7, 147.7, 130.3, 130.2, 128.2, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 117.1 (q, $^{5}J_{CF}$ = 2.2 Hz), 29.0, 28.6, 28.5, 27.3, 27.2, 27.1, 26.4, 24.2, 13.9, 11.7. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 0.9. HRMS (DART) calcd for $C_{24}H_{38}F_3O_3SSi$ ($M+H^+$) 491.2258, found: 491.2272.

2-(Butyldicyclohexylsilyl)-3,5-dimethylphenyl trifluoromethanesulfonate (1j)



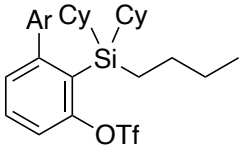
^{1}H NMR ($CDCl_3$): δ 6.98 (s, 1H), 6.96 (s, 1H), 2.47 (s, 3H), 2.33 (s, 3H), 1.93-1.63 (m, 8H), 1.62-1.48 (m, 2H), 1.48-1.13 (m, 16H), 1.11-0.99 (m, 2H), 0.93 (t, $^{3}J_{HH}$ = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.8, 147.3, 140.9, 131.3, 124.4, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 117.8 (q, $^{5}J_{CF}$ = 2.2 Hz), 29.1, 28.7, 28.6, 27.3, 27.24, 27.15, 26.4, 24.1, 21.1, 13.9, 11.7. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 0.6. HRMS (DART) calcd for $C_{25}H_{40}F_3O_3SSi$ ($M+H^+$) 505.2414, found: 505.2428.

2-(Butyldicyclohexylsilyl)-3-(2-methyl-1-propenyl)phenyl trifluoromethanesulfonate (1k)



^{1}H NMR ($CDCl_3$): δ 7.34 (dd, $^{3}J_{HH}$ = 8.3 and 7.8 Hz, 1H), 7.17 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.08 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.39 (s, 1H), 1.91 (d, $^{4}J_{HH}$ = 1.4 Hz, 3H), 1.85-1.58 (m, 8H), 1.70 (d, $^{4}J_{HH}$ = 0.9 Hz, 3H), 1.56-1.43 (m, 2H), 1.43-1.07 (m, 16H), 1.05-0.95 (m, 2H), 0.89 (t, $^{3}J_{HH}$ = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.7, 148.6, 135.4, 130.3, 130.0, 128.1, 127.8, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 117.2 (q, $^{5}J_{CF}$ = 2.2 Hz), 29.00, 28.96, 28.7, 28.6, 27.4, 27.21, 27.16, 26.3, 26.2, 19.4, 14.0, 11.7. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 0.6. HRMS (DART) calcd for $C_{27}H_{42}F_3O_3SSi$ ($M+H^+$) 531.2571, found: 531.2578.

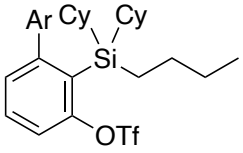
2-(Butyldicyclohexylsilyl)-3-(4-methoxyphenyl)phenyl trifluoromethanesulfonate (1l)



(Ar = 4-$MeOC_6H_4$)

^{1}H NMR ($CDCl_3$): δ 7.38 (dd, $^3J_{HH}$ = 8.2 and 7.3 Hz, 1H), 7.34 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.21 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.16 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.93 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 3.88 (s, 3H), 1.81-1.60 (m, 8H), 1.56-1.45 (m, 2H), 1.33-1.00 (m, 14H), 1.00-0.85 (m, 2H), 0.78 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 0.56-0.42 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 159.5, 157.0, 152.9, 136.3, 130.74, 130.67, 129.9, 127.7, 118.7 (q, $^1J_{CF}$ = 320 Hz), 117.3 (q, $^5J_{CF}$ = 2.2 Hz), 113.3, 55.6, 29.3, 29.2, 28.51, 28.49, 27.14, 27.10, 26.3, 13.8, 11.3. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 1.5. HRMS (DART) calcd for $C_{30}H_{42}F_3O_4SSi$ ($M+H^+$) 583.2520, found: 583.2545.

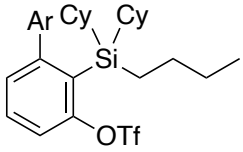
2-(Butyldicyclohexylsilyl)-3-(4-cyanophenyl)phenyl trifluoromethanesulfonate (1m)



(Ar = 4-NCC_6H_4)

^{1}H NMR ($CDCl_3$): δ 7.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.48-7.39 (m, 4H), 7.09 (dd, $^3J_{HH}$ = 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 1.74-1.61 (m, 8H), 1.50-1.41 (m, 2H), 1.25-0.95 (m, 14H), 0.93-0.82 (m, 2H), 0.76 (t, $^3J_{HH}$ = 6.9 Hz, 3H), 0.43-0.32 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.0, 150.6, 148.2, 131.7, 130.40, 130.38, 130.2, 127.7, 118.67 (q, $^1J_{CF}$ = 320 Hz), 118.67, 118.5 (q, $^5J_{CF}$ = 2.2 Hz), 111.8, 29.2, 29.1, 28.4, 27.1, 27.00, 26.95, 26.2, 13.7, 11.4. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 1.8. HRMS (FAB) calcd for $C_{30}H_{39}F_3NO_3SSi$ ($M+H^+$) 578.2367, found: 578.2373.

2-(Butyldicyclohexylsilyl)-3-(3-thienyl)phenyl trifluoromethanesulfonate (1n)

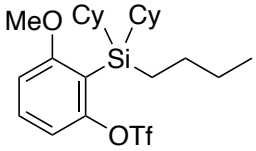


(Ar = 3-thienyl)

^{1}H NMR ($CDCl_3$): δ 7.41-7.31 (m, 3H), 7.19 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.13 (dd, $^4J_{HH}$ = 3.2 and 1.4 Hz, 1H), 7.06 (dd, $^3J_{HH}$ = 5.0 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 1.76-1.58 (m, 8H), 1.53-1.44 (m, 2H), 1.27-1.03 (m, 14H), 0.91-0.77 (m, 5H), 0.63-0.55 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.9, 147.4, 143.9, 130.6, 129.9, 129.7, 128.2, 125.0, 123.8, 118.7 (q, $^1J_{CF}$ = 321 Hz), 118.0 (q, $^5J_{CF}$ = 2.2 Hz), 29.3, 29.2, 28.5, 28.4, 27.3, 27.2, 27.1, 26.2, 13.9, 11.0. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 1.5.

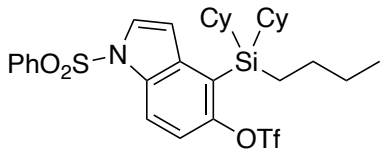
HRMS (FAB) calcd for $C_{27}H_{38}F_3O_3S_2Si$ ($M+H^+$) 559.1978, found: 559.1979.

2-(Butyldicyclohexylsilyl)-3-methoxyphenyl trifluoromethanesulfonate (1o)



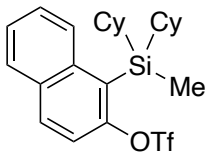
^{1}H NMR ($CDCl_3$): δ 7.37 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 6.95 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.81 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 3.80 (s, 3H), 1.85-1.47 (m, 10H), 1.46-1.10 (m, 16H), 1.04-0.95 (m, 2H), 0.90 (t, $^3J_{HH}$ = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.9, 156.3, 131.7, 118.7 (q, $^1J_{CF}$ = 320 Hz), 117.4, 112.4 (q, $^5J_{CF}$ = 1.9 Hz), 109.0, 55.3, 28.8, 28.70, 28.67, 28.6, 27.3, 27.24, 27.16, 25.4, 14.0, 11.3. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 1.1. HRMS (FAB) calcd for $C_{24}H_{38}F_3O_4SSi$ ($M+H^+$) 507.2207, found: 507.2210.

4-(Butyldicyclohexylsilyl)-1-(phenylsulfonyl)-5-indolyl trifluoromethanesulfonate (1p)



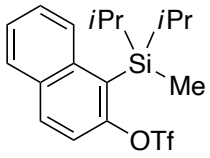
^{1}H NMR ($CDCl_3$): δ 8.04 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.95-7.87 (m, 2H), 7.70 (d, $^3J_{HH}$ = 4.1 Hz, 1H), 7.63-7.56 (m, 1H), 7.50 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.27 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 6.85 (d, $^3J_{HH}$ = 3.2 Hz, 1H), 1.87-1.43 (m, 10H), 1.43-1.02 (m, 18H), 0.87 (t, $^3J_{HH}$ = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.4, 138.2, 137.0, 134.4, 132.7, 129.6, 127.9, 127.1, 122.6, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.5 (q, $^5J_{CF}$ = 1.9 Hz), 115.6, 110.9, 28.7, 28.41, 28.38, 27.2, 27.0, 26.8, 25.6, 13.8, 10.9. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 1.0. HRMS (DART) calcd for $C_{31}H_{41}F_3NO_5S_2Si$ ($M+H^+$) 656.2142, found: 656.2145.

1-(Dicyclohexyl(methyl)silyl)-2-naphthyl trifluoromethanesulfonate (1q)



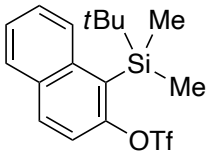
^{1}H NMR ($CDCl_3$): δ 8.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.87 (dd, $^3J_{HH}$ = 7.3 Hz and $^3J_{HH}$ = 1.8 Hz, 1H), 7.62-7.50 (m, 2H), 7.41 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 2.01-1.87 (m, 2H), 1.85-1.49 (m, 6H), 1.48-1.00 (m, 14H), 0.57 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.2, 138.2, 132.5, 132.3, 129.2, 128.9, 127.3, 126.7, 126.4, 119.0 (q, $^5J_{CF}$ = 1.9 Hz), 118.8 (q, $^1J_{CF}$ = 320 Hz), 29.0, 28.3, 27.0, 26.6, –5.9. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 2.7. HRMS (DART) calcd for $C_{24}H_{32}F_3O_3SSi$ ($M+H^+$) 485.1788, found: 485.1797.

1-(Diisopropyl(methyl)silyl)-2-naphthyl trifluoromethanesulfonate (1r)



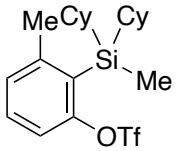
^{1}H NMR ($CDCl_3$): δ 8.29-8.21 (m, 1H), 7.96-7.85 (m, 2H), 7.61-7.51 (m, 2H), 7.46 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 1.64 (sept, $^{3}J_{HH}$ = 7.4 Hz, 2H), 1.19 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H), 0.87 (d, $^{3}J_{HH}$ = 7.4 Hz, 6H), 0.59 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.1, 138.1, 132.6, 132.3, 129.2, 128.9, 127.6, 126.7, 126.4, 119.0 (q, $^{5}J_{CF}$ = 1.9 Hz), 118.8 (q, $^{1}J_{CF}$ = 320 Hz), 18.9, 18.8, 14.5, –7.6. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 8.1. HRMS (DART) calcd for $C_{18}H_{24}F_3O_3SSi$ ($M+H^+$) 405.1162, found: 405.1167.

1-(*tert*-Butyldimethylsilyl)-2-naphthyl trifluoromethanesulfonate (1s)



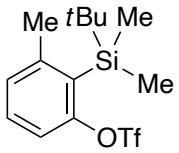
^{1}H NMR ($CDCl_3$): δ 8.26 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.94 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H), 7.88 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.8 Hz 1H), 7.60-7.49 (m, 3H), 1.07 (s, 9H), 0.64 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.1, 138.4, 133.0, 132.2, 130.2, 129.0, 126.6, 126.5, 126.2, 118.8 (q, $^{1}J_{CF}$ = 320 Hz), 117.8 (q, $^{5}J_{CF}$ = 2.4 Hz), 27.7, 19.1, 0.6. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 4.7. HRMS (DART) calcd for $C_{17}H_{22}F_3O_3SSi$ ($M+H^+$) 391.1006, found: 391.1015.

2-(Dicyclohexyl(methyl)silyl)-3-methylphenyl trifluoromethanesulfonate (1u)



^{1}H NMR ($CDCl_3$): δ 7.28 (dd, $^{3}J_{HH}$ = 8.2 and 7.8 Hz, 1H), 7.19 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.12 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 2.49 (s, 3H), 1.93-1.60 (m, 8H), 1.46-1.02 (m, 14H), 0.45 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.6, 147.5, 130.4, 130.1, 128.7, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 116.9 (q, $^{5}J_{CF}$ = 1.9 Hz), 28.9, 28.5, 28.4, 28.3, 27.0, 25.7, 24.8, –5.7. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 2.8. HRMS (DART) calcd for $C_{21}H_{32}F_3O_3SSi$ ($M+H^+$) 449.1788, found: 449.1797.

2-(*tert*-Butyldimethylsilyl)-3-methylphenyl trifluoromethanesulfonate (1v)



^{1}H NMR ($CDCl_3$): δ 7.31 (dd, $^{3}J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.28 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HH}$ = 1.8 Hz, 1H) 7.14 (d, $^{3}J_{HH}$ = 6.4 Hz, 1H), 2.51 (s, 3H), 0.98 (s, 9H), 0.48 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 157.3, 147.7, 130.7, 130.0, 127.7, 118.8 (q, $^{1}J_{CF}$ = 321 Hz), 115.8 (q, $^{5}J_{CF}$ = 2.2 Hz), 27.1, 25.5, 19.2, 0.1. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 4.9. HRMS (DART) calcd for $C_{14}H_{22}F_3O_3SSi$ ($M+H^+$) 355.1006, found: 355.1018.

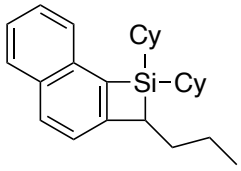
III. Catalytic Reactions and Derivatizations

General Procedure for Compounds 2a–2h in Scheme 2.

Et_2NH (43.4 μL, 0.420 mmol) was added to a mixture of $Pd(OAc)_2$ (2.2 mg, 10 μmol), PCy_3•HBF_4 (7.4 mg, 20 μmol), and compound **1** (0.200 mmol) in DMF (0.80 mL), and the resulting solution was stirred for 18 h at 80 °C. After cooled to room temperature, the reaction mixture was diluted with Et_2O and H_2O was added. 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 purified by silica gel preparative TLC to afford compound **2**.

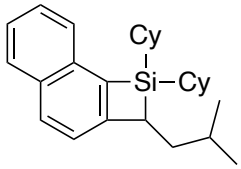
General Procedure for Compounds 2i–2p in Scheme 2.

Et_2NH (43.4 μL, 0.420 mmol) was added to a mixture of $Pd(OAc)_2$ (2.2 mg, 10 μmol), PCy_3•HBF_4 (7.4 mg, 20 μmol), and compound **1** (0.200 mmol) in DMF (4.0 mL), and the resulting solution was stirred for 18 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with Et_2O and H_2O was added. 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 purified by silica gel preparative TLC to afford compound **2**.



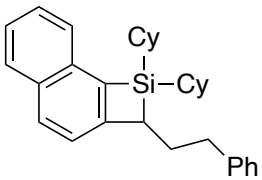
Compound 2a. The reaction was conducted on 0.150 mmol scale. Hexane was used for the preparative TLC. Colorless oil. (45.1 mg, 0.113 mmol; 75% yield, containing ca. 3% impurity). The reaction could be scaled up using 3.05 mmol of **1a** to give **2a** in 75% yield (883 mg, 2.30 mmol; containing ca. 6% impurity).

^1H NMR ($CDCl_3$): δ 7.83-7.77 (m, 2H), 7.68 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.47 (ddd, $^3J_{HH}$ = 7.8 and 6.9 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.41 (ddd, $^3J_{HH}$ = 7.8 and 6.9 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.31 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 2.61 (dd, $^3J_{HH}$ = 10.1 and 6.4 Hz, 1H), 2.02-1.62 (m, 12H), 1.62-1.12 (m, 14H), 1.01 (d, $^3J_{HH}$ = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.0, 140.8, 135.3, 132.6, 131.0, 129.1, 128.5, 126.5, 125.0, 123.7, 33.7, 31.3, 29.1, 28.9, 28.8, 28.4, 28.3, 28.2, 28.1, 27.0, 26.9, 25.0, 24.8, 24.5, 14.5. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ 14.6. IR (neat) 3042, 2919, 2845, 1502, 1445, 1099, 996, 845, 815, 747 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{36}Si$ (M^+) 376.2581, found: 376.2586.



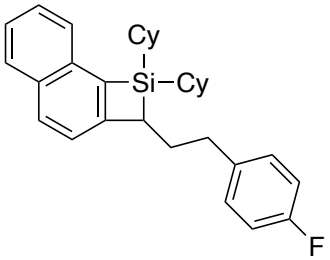
Compound 2b. Hexane was used for the preparative TLC. White solid. (60.5 mg, 0.155 mmol; 78% yield, containing ca. 1% impurity).

^{1}H NMR ($CDCl_3$): δ 7.85-7.80 (m, 2H), 7.72 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.50 (ddd, $^{3}J_{HH}$ = 8.3 and 6.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.43 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.33 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 2.73 (dd, $^{3}J_{HH}$ = 10.1 and 6.9 Hz, 1H), 2.00-1.63 (m, 13H), 1.55-1.13 (m, 12H), 1.05 (d, $^{3}J_{HH}$ = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.1, 140.7, 135.3, 132.6, 131.1, 129.1, 128.5, 126.5, 125.0, 123.6, 40.7, 29.6, 29.3, 29.1, 28.9, 28.8, 28.42, 28.39, 28.3, 28.2, 28.1, 27.0, 26.9, 25.0, 24.5, 23.3, 22.8. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 14.7. IR (KBr) 3044, 2953, 2919, 2844, 1506, 1443, 996, 888, 810, 748 cm^{-1}. HRMS (FAB) calcd for $C_{27}H_{39}Si$ ($M+H^+$) 391.2816, found: 391.2810.



Compound 2c. Hexane/EtOAc = 100/1 → hexane was used for the preparative TLC. Colorless oil (69.6 mg, 0.159 mmol; 79% yield, containing ca. 4% impurity).

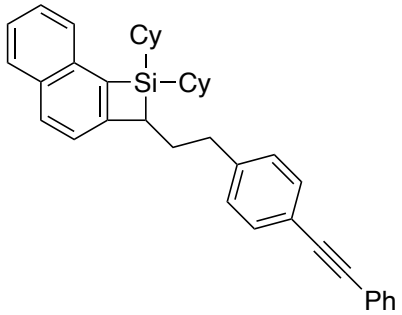
^{1}H NMR ($CDCl_3$): δ 7.86 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.76 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.53 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.47 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.42-7.33 (m, 3H), 7.31 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H), 7.25 (t, $^{3}J_{HH}$ = 7.1 Hz, 1H), 2.98-2.81 (m, 2H), 2.74 (dd, $^{3}J_{HH}$ = 9.6 and 6.0 Hz, 1H), 2.46-2.32 (m, 1H), 2.21-2.06 (m, 1H), 2.06-1.67 (m, 10H), 1.64-1.10 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.5, 142.9, 140.7, 135.3, 132.7, 131.2, 129.1, 128.6, 128.52, 128.49, 126.5, 125.9, 125.1, 123.5, 38.1, 33.7, 31.4, 29.2, 28.94, 28.92, 28.39, 28.37, 28.3, 28.2, 28.1, 27.0, 26.9, 25.0, 24.5. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 14.6. IR (neat) 3026, 2919, 2845, 1496, 1445, 1096, 887, 817, 745, 698 cm^{-1}. HRMS (EI) calcd for $C_{31}H_{38}Si$ (M^+) 438.2737, found: 438.2743.



Compound 2d. Hexane/EtOAc = 50/1 was used for the preparative TLC. Colorless oil (72.1 mg, 0.158 mmol; 79% yield, containing ca. 4% impurity).

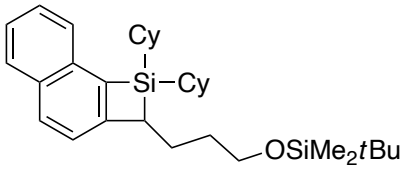
^{1}H NMR ($CDCl_3$): δ 7.88 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.78 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.55 (t, $^{3}J_{HH}$ = 7.6

Hz, 1H), 7.49 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.39 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 2.3 Hz, 1H), 7.31-7.22 (m, 2H), 7.06 (td, ^{3}J = 8.7 Hz and $^{4}J_{HH}$ = 2.3 Hz, 2H), 2.96-2.79 (m, 2H), 2.79-2.69 (m, 1H), 2.44-2.30 (m, 1H), 2.18-2.04 (m, 1H), 2.05-1.67 (m, 10H), 1.65-1.17 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 161.4 (d, $^{1}J_{CF}$ = 243 Hz), 155.3, 140.7, 138.5 (d, $^{4}J_{CF}$ = 2.9 Hz), 135.3, 132.7, 131.2, 129.8 (d, $^{3}J_{CF}$ = 7.7 Hz), 129.1, 128.5, 126.6, 125.2, 123.5, 115.2 (d, $^{2}J_{CF}$ = 21.1 Hz), 37.2, 33.8, 31.2, 29.2, 28.91, 28.89, 28.34, 28.29, 28.1, 28.0, 27.0, 26.8, 25.0, 24.4. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 14.6. IR (neat) 3041, 2919, 2845, 1508, 1445, 1221, 1098, 846, 819, 747 cm^{-1}. HRMS (FAB) calcd for $C_{31}H_{38}FSi$ ($M+H^{+}$) 457.2721, found: 457.2716.



Compound 2e. Hexane/EtOAc = 15/1→50/1 was used for the preparative TLC. White amorphous (60.7 mg, 0.113 mmol; 56% yield).

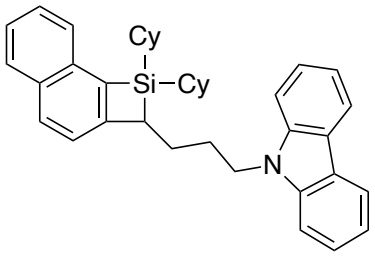
^{1}H NMR ($CDCl_3$): δ 7.82 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.70 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.56-7.45 (m, 5H), 7.42 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.38-7.28 (m, 4H), 7.23 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 2.92-2.75 (m, 2H), 2.67 (dd, $^{3}J_{HH}$ = 10.1 and 6.4 Hz, 1H), 2.38-2.25 (m, 1H), 2.12-1.99 (m, 1H), 1.97-1.61 (m, 10H), 1.53-1.37 (m, 2H), 1.37-1.11 (m, 10H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 155.3, 143.4, 140.7, 135.3, 132.7, 131.8, 131.7, 131.2, 129.1, 128.6, 128.5, 128.2, 126.6, 125.2, 123.6, 123.5, 120.8, 89.7, 89.0, 38.0, 33.5, 31.2, 29.2, 28.91, 28.89, 28.4, 28.3, 28.1, 28.0, 27.0, 26.8, 25.0, 24.4. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 14.5. IR (KBr) 3041, 2918, 2845, 1510, 1444, 996, 816, 753, 689, 510 cm^{-1}. HRMS (FAB) calcd for $C_{39}H_{43}Si$ ($M+H^{+}$) 539.3129, found: 539.3141.



Compound 2f. Hexane/EtOAc = 30/1→50/1 was used for the preparative TLC. Colorless oil (81.2 mg, 0.160 mmol; 80% yield, containing ca. 3% impurity).

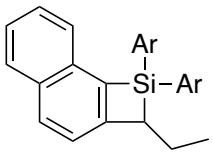
^{1}H NMR ($CDCl_3$): δ 7.82 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.70 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.48 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.42 (ddd, $^{3}J_{HH}$ = 8.2 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.33 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 3.82-3.64 (m, 2H), 2.68-2.56 (m, 1H), 2.08-1.61 (m, 14H), 1.55-1.11 (m, 12H), 0.93 (s, 9H), 0.09 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 155.8, 140.7, 135.3, 132.6, 131.1, 129.1, 128.5, 126.5, 125.1, 123.6, 63.6, 34.9, 31.2, 29.0, 28.9, 28.8, 28.4, 28.34, 28.29, 28.2, 28.1, 27.7, 27.0, 26.9,

26.2, 24.9, 24.4, –5.06, –5.08. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 18.5, 14.6. IR (neat) 3042, 2922, 2848, 1445, 1256, 1099, 1018, 836, 815, 777 cm^{-1}. HRMS (FAB) calcd for $C_{32}H_{51}OSi_2$ ($M+H^+$) 507.3473, found: 507.3480.



Compound 2g. Hexane/EtOAc = 30/1 was used for the preparative TLC. White amorphous (76.4 mg, 0.141 mmol; 70% yield, containing ca. 2% impurity).

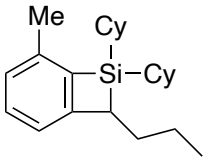
^{1}H NMR ($CDCl_3$): δ 8.14 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.85-7.78 (m, 2H), 7.69 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.56-7.40 (m, 6H), 7.33-7.22 (m, 3H), 4.55-4.34 (m, 2H), 2.63 (dd, $^{3}J_{HH}$ = 9.6 and 5.0 Hz, 1H), 2.25-2.01 (m, 3H), 1.95-1.57 (m, 11H), 1.45-1.02 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.0, 140.7, 140.6, 135.2, 132.6, 131.2, 129.1, 128.4, 126.6, 125.8, 125.2, 123.5, 123.0, 120.5, 118.9, 108.7, 43.3, 31.04, 31.02, 29.3, 29.0, 28.8, 28.4, 28.2, 28.14, 28.08, 28.0, 26.9, 26.8, 24.9, 24.3. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 14.5. IR (KBr) 3045, 2920, 2845, 1597, 1484, 1463, 1451, 1347, 1326, 1243, 1151, 816, 749, 722 cm^{-1}. HRMS (FAB) calcd for $C_{38}H_{43}NSi$ (M^+) 541.3159, found: 541.3168.



(Ar = 2-MeOCH$_2$O-1-naphthyl)

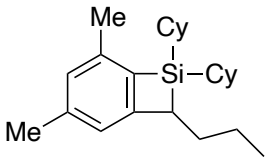
Compound 2h. Hexane/EtOAc = 10/1 and then hexane/EtOAc = 50/1 were used for the preparative TLC. White amorphous (81.9 mg, 0.143 mmol; 72% yield).

^{1}H NMR ($CDCl_3$): δ 8.88 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 8.69 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 8.58 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.89 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.87 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.81 (d, $^{3}J_{HH}$ = 9.2 Hz, 1H), 7.79-7.72 (m, 3H), 7.56 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.53-7.42 (m, 2H), 7.40-7.31 (m, 3H), 7.27 (dd, $^{3}J_{HH}$ = 8.2 and 6.9 Hz, 1H), 7.17 (ddd, $^{3}J_{HH}$ = 8.7 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 4.91 (d, $^{2}J_{HH}$ = 6.9 Hz, 2H), 4.64 (d, $^{2}J_{HH}$ = 6.9 Hz, 2H), 3.67 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 2.85 (s, 3H), 2.59 (s, 3H), 2.06-1.92 (m, 1H), 1.87-1.72 (m, 1H), 1.17 (t, $^{3}J_{HH}$ = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.2, 159.8, 155.9, 142.0, 138.5, 137.9, 135.2, 133.5, 132.1, 131.94, 131.85, 130.3, 129.8, 129.4, 128.7, 128.44, 128.40, 128.3, 126.43, 126.37, 126.1, 125.1, 124.3, 123.7, 123.6, 122.2, 120.7, 115.8, 114.4, 95.0, 94.1, 55.6, 55.2, 39.6, 25.8, 14.8. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 14.5. IR (KBr) 3047, 2956, 2928, 1587, 1505, 1458, 1428, 1322, 1236, 1194, 1148, 1078, 1033, 1013, 987, 921, 888, 822, 777, 748 cm^{-1}. HRMS (FAB) calcd for $C_{37}H_{35}O_4Si$ ($M+H^+$) 571.2299, found: 571.2303.



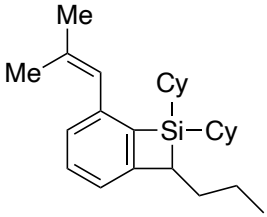
Compound 2i. Hexane was used for the preparative TLC. Colorless oil (49.0 mg, 0.144 mmol; 72% yield, containing ca. 7% impurity). The reaction could be scaled up using 3.18 mmol of **1h** to give **2h** in 79% yield (918 mg, 2.52 mmol; containing ca. 6% impurity).

^{1}H NMR ($CDCl_3$): δ 7.23 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.01 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H), 7.00 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 2.50 (dd, $^{3}J_{HH}$ = 9.6 and 6.9 Hz, 1H), 2.31 (s, 3H), 1.94-1.61 (m, 12H), 1.61-1.10 (m, 14H), 0.99 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.1, 142.4, 141.1, 130.6, 126.8, 121.8, 33.7, 31.2, 29.1, 28.9, 28.8, 28.38, 28.35, 28.3, 28.2, 28.1, 27.0, 26.9, 24.8, 24.7, 24.4, 22.8, 14.5. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 15.2. IR (neat) 3046, 2919, 2846, 1575, 1460, 1445, 1095, 888, 781, 758 cm^{-1}. HRMS (EI) calcd for $C_{23}H_{36}Si$ (M^+) 340.2581, found: 340.2583.



Compound 2j. Hexane was used for the preparative TLC. Colorless oil (55.5 mg, 0.157 mmol; 78% yield, containing ca. 7% impurity).

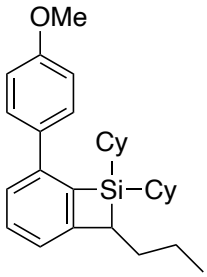
^{1}H NMR ($CDCl_3$): δ 6.86 (s, 1H), 6.84 (s, 1H), 2.46 (dd, $^{3}J_{HH}$ = 9.6 and 6.9 Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 1.93-1.59 (m, 12H), 1.59-1.05 (m, 14H), 0.98 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.2, 141.0, 140.6, 138.6, 128.2, 122.6, 33.7, 30.9, 29.1, 28.9, 28.8, 28.40, 28.38, 28.3, 28.2, 28.1, 27.1, 27.0, 24.9, 24.8, 24.4, 22.7, 22.1, 14.5. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 14.3. IR (neat) 2919, 2846, 1591, 1445, 1097, 995, 888, 846, 815, 732, 608 cm^{-1}. HRMS (FAB) calcd for $C_{24}H_{39}Si$ ($M+H^+$) 355.2816, found: 355.2819.



Compound 2k. Hexane was used for the preparative TLC. Colorless oil (58.6 mg, 0.154 mmol; 77% yield, containing ca. 7% impurity).

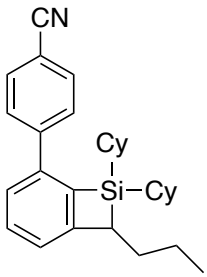
^{1}H NMR ($CDCl_3$): δ 7.29 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.15 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.01 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.17 (s, 1H), 2.52 (dd, $^{3}J_{HH}$ = 9.6 and 6.9 Hz, 1H), 1.97-1.60 (m, 12H), 1.90 (d, $^{4}J_{HH}$ = 0.9 Hz, 3H), 1.85 (d, $^{4}J_{HH}$ = 0.9 Hz, 3H), 1.60-1.12 (m, 14H), 1.00 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.9, 143.0, 141.8, 134.8, 130.1, 126.8, 126.0, 122.2, 33.7, 31.3, 28.9, 28.8, 28.6, 28.4,

28.29, 28.26, 28.2, 28.1, 27.07, 27.06, 27.0, 24.8, 24.7, 24.3, 19.6, 14.5. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 14.8. IR (neat) 3048, 2919, 2846, 1562, 1458, 1445, 1097, 888, 844, 741 cm^{-1}. HRMS (FAB) calcd for $C_{26}H_{41}Si$ ($M+H^+$) 381.2972, found: 381.2981.



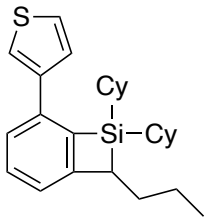
Compound 2l. Hexane/EtOAc = 20/1 was used for the preparative TLC. Yellow oil (78.5 mg, 0.181 mmol; 91% yield, containing ca. 9% impurity).

^{1}H NMR ($CDCl_3$): δ 7.50 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.43-7.35 (m, 2H), 7.14-7.09 (m, 1H), 6.96 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.87 (s, 3H), 2.59 (dd, $^{3}J_{HH}$ = 10.1 and 6.9 Hz, 1H), 2.02-1.43 (m, 14H), 1.40-1.05 (m, 12H), 1.02 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 159.1, 157.4, 143.5, 139.9, 134.7, 131.0, 128.2, 124.2, 122.8, 114.0, 55.4, 33.6, 31.0, 28.9, 28.8, 28.5, 28.2, 28.14, 28.08, 28.02, 28.00, 27.0, 26.9, 24.9, 24.82, 24.80, 14.5. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 14.9. IR (neat) 3047, 2998, 2920, 2846, 1609, 1515, 1456, 1248, 1178, 1037, 785, 833 cm^{-1}. HRMS (FAB) calcd for $C_{29}H_{40}OSi$ (M^+) 432.2843, found: 432.2854.



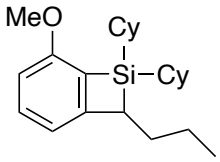
Compound 2m. The purification was performed by column chromatography on silica gel with hexane/EtOAc = 20/1 and by GPC with $CHCl_3$. Yellow oil (62.9 mg, 0.147 mmol; 74% yield, containing ca. 9% impurity).

^{1}H NMR ($CDCl_3$) δ 7.71 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.62 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.44-7.40 (m, 2H), 7.24-7.18 (m, 1H), 2.61 (dd, $^{3}J_{HH}$ = 10.1 and 6.9 Hz, 1H), 2.00-1.87 (m, 1H), 1.85-1.40 (m, 13H), 1.36-1.03 (m, 12H), 1.01 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H).$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 157.7, 146.8, 141.8, 141.3, 132.5, 131.2, 127.7, 125.1, 124.7, 119.2, 110.7, 33.5, 31.1, 28.9, 28.8, 28.3, 28.03, 27.96, 27.9, 26.9, 26.8, 24.8, 24.74, 24.71, 14.5. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 15.2. IR (neat) 2920, 2846, 1606, 1445, 909, 844, 792, 546, 507 cm^{-1}. HRMS (FAB) calcd for $C_{29}H_{38}NSi$ ($M+H^+$) 428.2768, found: 428.2770.



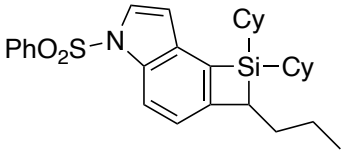
Compound 2n. The purification was performed by column chromatography on silica gel with hexane and by GPC with $CHCl_3$. Colorless oil (54.2 mg, 0.133 mmol; 67% yield, containing ca. 6% impurity).

^{1}H NMR ($CDCl_3$): δ 7.44 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.41-7.31 (m, 4H), 7.11 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 2.58 (dd, $^3J_{HH}$ = 9.6 and 6.9 Hz, 1H), 2.01-1.43 (m, 14H), 1.38-1.07 (m, 12H), 1.02 (t, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.4, 143.6, 139.9, 138.6, 131.0, 126.7, 125.8, 124.3, 123.3, 120.4, 33.5, 30.8, 29.04, 29.00, 28.5, 28.2, 28.1, 27.0, 24.9, 24.7, 14.5. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 15.2. IR (neat) 2919, 2845, 1568, 1459, 1445, 888, 845, 768, 740, 525 cm^{-1}. HRMS (FAB) calcd for $C_{26}H_{36}SSi$ (M^+) 408.2301, found: 408.2314.



Compound 2o. Hexane/EtOAc = 100/1→50/1 was used for the preparative TLC. Colorless oil (44.1 mg, 0.124 mmol; 62% yield, containing ca. 5% impurity).

^{1}H NMR ($CDCl_3$): δ 7.27 (dd, $^3J_{HH}$ = 8.2 and 7.4 Hz, 1H), 6.80 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.66 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 3.77 (s, 3H), 2.53 (dd, $^3J_{HH}$ = 9.6 and 6.4 Hz, 1H), 1.96-1.61 (m, 12H), 1.61-1.06 (m, 14H), 1.00 (t, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.2, 158.2, 132.1, 125.5, 117.4, 110.8, 55.2, 33.5, 31.5, 29.0, 28.7, 28.4, 28.30, 28.28, 28.09, 28.08, 27.0, 26.9, 24.9, 24.8, 24.5, 14.5. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 13.7. IR (neat) 3055, 2920, 2846, 1584, 1561, 1463, 1445, 1255, 1096, 1042, 888, 784 cm^{-1}. HRMS (FAB) calcd for $C_{23}H_{36}OSi$ (M^+) 356.2530, found: 356.2525.



Compound 2p. Hexane/EtOAc = 10/1→30/1 was used for the preparative TLC. This was further purified by recrystallization from CH_2Cl_2/MeOH at room temperature. Colorless solid (27.7 mg, 54.7 μmol; 27% yield).

^{1}H NMR ($CDCl_3$): δ 7.97 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.94-7.87 (m, 2H), 7.60 (d, $^3J_{HH}$ = 3.7 Hz, 1H), 7.57-7.49 (m, 1H), 7.49-7.40 (m, 2H), 7.11 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.51 (d, $^3J_{HH}$ = 3.6 Hz, 1H), 2.58 (dd, $^3J_{HH}$ = 9.6 and 6.4 Hz, 1H), 1.94-1.59 (m, 12H), 1.57-1.08 (m, 14H), 0.98 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.4, 138.8, 135.6, 133.8, 133.3, 132.6, 129.4, 127.0, 126.9, 121.2, 115.8,

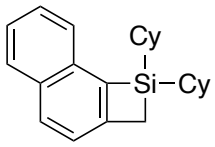
110.1, 34.0, 31.8, 28.7, 28.6, 28.2, 28.04, 27.97, 26.9, 26.8, 24.69, 24.66, 24.2, 14.5. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 14.3. IR (KBr) 2920, 2846, 1447, 1369, 1187, 1165, 1143, 727, 607, 590 cm^{-1}. Mp 172–174 °C. HRMS (FAB) calcd for $C_{30}H_{40}NO_2SSi$ ($M+H^+$) 506.2544, found: 506.2541.

General Procedure for Compounds 2q–2t in Scheme 3.

Et_2NH (41.4 μL, 0.400 mmol) was added to a mixture of $Pd(OAc)_2$ (2.2 mg, 10 μmol), dtbpf (5.2 mg, 11 μmol), and compound **1** (0.200 mmol) in DMF (0.80 mL), and the resulting solution was stirred for 18 h at 80 °C. After cooled to room temperature, the reaction mixture was diluted with Et_2O and H_2O was added. 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 purified by silica gel preparative TLC with hexane to afford compound **2**.

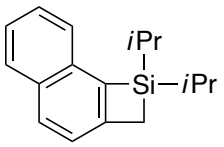
General Procedure for Compounds 2u–2v in Scheme 3.

Et_2NH (41.4 μL, 0.400 mmol) was added to a mixture of $Pd(OAc)_2$ (2.2 mg, 10 μmol), dtbpf (5.2 mg, 11 μmol), and compound **1** (0.200 mmol) in DMF (4.0 mL), and the resulting solution was stirred for 18 h at 100 °C. After cooled to room temperature, the reaction mixture was diluted with Et_2O and H_2O was added. 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 purified by silica gel preparative TLC with hexane to afford compound **2**.



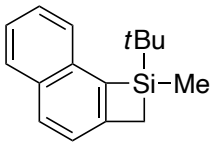
Compound 2q. White solid (56.9 mg, 0.170 mmol; 85% yield). The reaction could be scaled up using 3.01 mmol of **1q** to give **2q** in 82% yield (823 mg, 2.46 mmol).

^{1}H NMR ($CDCl_3$): δ 7.84 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.81 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.71 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.51 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.45 (ddd, $^{3}J_{HH}$ = 8.2 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.28 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 2.18 (s, 2H), 2.00-1.83 (m, 4H), 1.83-1.63 (m, 6H), 1.48-1.15 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 150.9, 142.0, 135.2, 132.3, 130.9, 129.0, 128.3, 126.4, 125.5, 125.0, 28.5, 28.09, 28.06, 28.0, 26.9, 24.4, 14.4. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 15.1. IR (KBr) 3040, 2917, 2844, 1505, 1444, 890, 847, 812, 780, 738, 715, 546 cm^{-1}. HRMS (FAB) calcd for $C_{23}H_{30}Si$ (M^+) 334.2111, found: 334.2112.



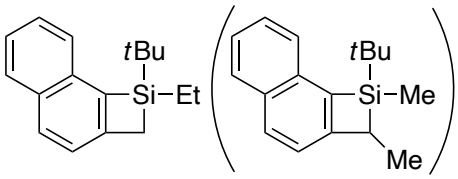
Compound 2r. Colorless oil. (35.4 mg, 0.139 mmol; 70% yield).

^{1}H NMR ($CDCl_3$): δ 7.87-7.79 (m, 2H), 7.70 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.49 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.44 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.29 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 2.18 (s, 2H), 1.40 (sept, $^{3}J_{HH}$ = 7.8 Hz, 2H), 1.18 (d, $^{3}J_{HH}$ = 7.8 Hz, 6H), 1.13 (d, $^{3}J_{HH}$ = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.8, 141.7, 135.2, 132.3, 131.0, 129.0, 128.3, 126.5, 125.5, 125.1, 18.6, 18.2, 14.6, 12.8. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 20.6. IR (neat) 3043, 2939, 2863, 1504, 1461, 879, 814, 781, 738, 696, 614 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{22}Si$ (M^+) 254.1485, found: 254.1492.



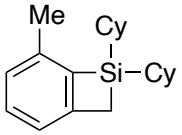
Compound 2s. Colorless oil. (25.2 mg, 0.105 mmol; 52% yield).

^{1}H NMR ($CDCl_3$): δ 7.88-7.80 (m, 2H), 7.70 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.50 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.44 (ddd, $^{3}J_{HH}$ = 8.2 and 6.4 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.30 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 2.31 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H), 2.14 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H), 1.11 (s, 9H), 0.54 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.1, 142.8, 134.9, 132.3, 131.2, 129.1, 128.0, 126.5, 125.6, 125.1, 26.5, 18.2, 17.1, –5.1. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 16.4. IR (neat) 3043, 2950, 2926, 2855, 1504, 1469, 1249, 1071, 829, 778, 761, 741, 593 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{20}Si$ (M^+) 240.1329, found: 240.1334.



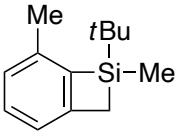
Compound 2t. Colorless oil. (40.8 mg, 0.154 mmol; 77% yield, selectivity = 96/4).

^{1}H NMR ($CDCl_3$): δ 7.84-7.77 (m, 2H), 7.67 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.46 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.41 (ddd, $^{3}J_{HH}$ = 7.8 and 6.9 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.26 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 2.20 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H), 2.15 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H), 1.16-0.95 (m, 14H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.5, 141.8, 135.2, 132.3, 131.0, 129.1, 128.1, 126.5, 125.5, 125.1, 27.0, 18.5, 15.1, 8.2, 3.9. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 20.6. IR (neat) 3043, 2952, 2926, 2855, 1504, 1469, 1361, 1070, 815, 782, 738, 704 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{22}Si$ (M^+) 254.1485, found: 254.1491.



Compound 2u. Colorless oil. (48.9 mg, 0.164 mmol; 82% yield).

^{1}H NMR ($CDCl_3$): δ 7.20 (dd, $^{3}J_{HH}$ = 7.8 and 7.3 Hz, 1H), 6.99 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.92 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 2.30 (s, 3H), 2.01 (s, 2H), 1.88-1.62 (m, 10H), 1.36-1.07 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.7, 143.8, 140.9, 130.6, 126.4, 123.6, 28.5, 28.12, 28.10, 28.0, 26.9, 24.4, 22.7, 14.2. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 15.9. IR (neat) 3045, 2919, 2845, 1576, 1445, 1094, 887, 846, 817, 781, 755 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{30}Si$ (M^+) 298.2111, found: 298.2113.

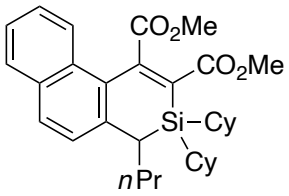


Compound 2v. Colorless oil. (20.4 mg, 0.100 mmol; 50% yield).

^{1}H NMR ($CDCl_3$): δ 7.23 (dd, $^{3}J_{HH}$ = 7.8 and 7.3 Hz, 1H), 7.01 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 2.30 (s, 3H), 2.16 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H), 1.99 (d, $^{2}J_{HH}$ = 16.5 Hz, 1H), 1.03 (s, 9H), 0.43 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.9, 144.7, 140.8, 130.8, 126.5, 123.8, 26.5, 22.3, 18.1, 16.9, –5.4. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 17.5. IR (neat) 3048, 2951, 2926, 2856, 1575, 1461, 1248, 1093, 827, 771, 601 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{20}Si$ (M^+) 204.1329, found: 204.1326.

General Procedure for Scheme 4a.

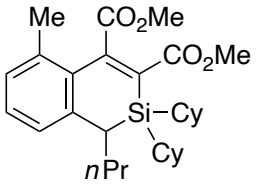
Alkyne **3** (0.225 mmol) was added to a mixture of $Pd(PPh_3)_4$ (8.7 mg, 7.5 μmol) and compound **2** (0.150 mmol) in toluene (375 μL), and the resulting solution was stirred for 15 h at 110 °C. After cooled to room temperature, the mixture was passed through a pad of silica gel with EtOAc. The solvent was removed under vacuum, and the residue was purified by silica gel preparative TLC to afford compound **4**.



Compound 4aa. Hexane/EtOAc = 5/1 was used for the preparative TLC. White amorphous (41.2 mg, 79.4 μmol; 53% yield).

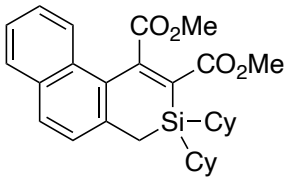
^{1}H NMR ($CDCl_3$): δ 7.82-7.75 (m, 1H), 7.72 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.69-7.61 (m, 1H), 7.42-7.35 (m, 2H), 7.28 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 3.84 (s, 3H), 2.70 (s, 3H), 2.20 (dd, $^{3}J_{HH}$ = 11.4 and 2.7 Hz, 1H), 1.87-1.65 (m, 6H), 1.65-1.16 (m, 13H), 1.16-0.54 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 171.8, 168.9, 142.2, 142.1, 139.8, 132.7, 131.9, 130.0, 129.2, 128.8, 126.3, 125.0, 123.9, 52.5, 52.0, 31.5, 28.9, 28.6,

28.4, 28.3, 28.24, 28.22, 27.8, 27.7, 27.0, 26.6, 22.6, 22.4, 22.1, 14.4. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ –7.9. IR (KBr) 2922, 2848, 1718, 1446, 1433, 1228, 1197, 1179, 1045, 742 cm^{-1}. HRMS (FAB) calcd for $C_{32}H_{42}O_4Si$ (M^+) 518.2847, found: 518.2854.



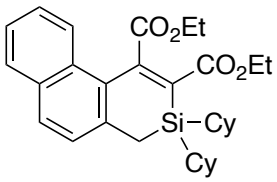
Compound 4ia. Hexane/EtOAc = 5/1 was used for the preparative TLC. Colorless oil (37.9 mg, 78.5 μmol; 52% yield).

^{1}H NMR ($CDCl_3$): δ 7.08 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 6.98 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 2.16 (s, 3H), 2.12-2.01 (m, 1H), 1.84-1.34 (m, 13H), 1.34-1.13 (m, 6H), 1.13-0.52 (m, 10H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 171.6, 168.4, 143.3, 141.0, 140.8, 137.1, 133.1, 129.3, 128.4, 52.4, 51.9, 31.3, 28.6, 28.5, 28.4, 28.34, 28.32, 28.25, 28.22, 27.9, 27.5, 27.0, 26.8, 22.6, 22.3, 22.1, 20.9, 14.3. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ –8.6. IR (neat) 2922, 2848, 1731, 1582, 1446, 1227, 1060, 1011, 891, 742 cm^{-1}. HRMS (FAB) calcd for $C_{29}H_{42}O_4Si$ (M^+) 482.2847, found: 482.2849.



Compound 4qa. Hexane/EtOAc = 5/1 was used for the preparative TLC. White amorphous (70.4 mg, 0.148 mmol; 99% yield).

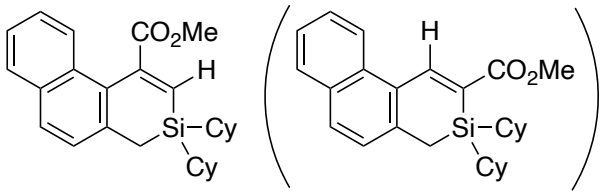
^{1}H NMR ($CDCl_3$): δ 7.82-7.75 (m, 1H), 7.75-7.68 (m, 2H), 7.43-7.36 (m, 2H), 7.33 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.31 (s, 2H), 1.71-1.52 (m, 10H), 1.20-0.87 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 171.5, 169.4, 144.7, 140.7, 136.5, 132.6, 131.8, 129.9, 129.7, 129.4, 128.9, 126.5, 124.9, 123.6, 52.5, 52.1, 28.1, 27.9, 26.7, 22.6, 16.7. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ –7.0. IR (KBr) 2923, 2847, 1736, 1716, 1445, 1228, 1177, 1049, 822, 744 cm^{-1}. HRMS (FAB) calcd for $C_{29}H_{36}O_4Si$ (M^+) 476.2377, found: 476.2381.



Compound 4qb. 0.153 mmol of **2q** was used. Hexane/EtOAc = 6/1 was used for the preparative TLC. White solid (76.0 mg, 0.151 mmol; 99% yield).

^{1}H NMR ($CDCl_3$): δ 7.84-7.74 (m, 2H), 7.70 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.42-7.34 (m, 2H), 7.32 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 4.30 (q, $^{3}J_{HH}$ = 7.2 Hz, 2H), 4.22 (q, $^{3}J_{HH}$ = 7.0 Hz, 2H), 2.31 (s, 2H), 1.72-1.55

(m, 10H), 1.37 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 1.20 (t, $^3J_{HH}$ = 7.1 Hz, 3H), 1.18-0.87 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 171.0, 168.9, 144.8, 140.4, 136.4, 132.6, 131.8, 129.72, 129.67, 128.8, 126.1, 124.7, 124.0, 61.6, 61.0, 28.1, 27.9, 26.7, 22.5, 16.6, 14.4, 13.9. $^{29}Si\{^1H\}$ NMR ($CDCl_3$): δ –7.0. IR (KBr) 2921, 2848, 1721, 1707, 1246, 1224, 1181, 1044, 822, 743 cm^{-1}. HRMS (FAB) calcd for $C_{31}H_{40}O_4Si$ (M^+) 504.2690, found: 504.2696.

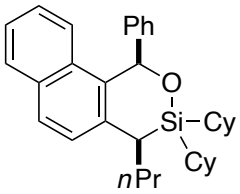


Compound 4qc. Hexane/EtOAc = 8/1 was used for the preparative TLC. Pale yellow oil (18.8 mg, 41.8 μmol; 28% yield, regioselectivity: 82/18).

^1H NMR ($CDCl_3$): δ 9.20 (s, 0.18H), 8.34 (d, $^3J_{HH}$ = 8.7 Hz, 0.18H), 7.85-7.64 (m, 2H), 7.60-7.49 (m, 1H), 7.48-7.31 (m, 2.82H), 7.29 (s, 0.82H), 3.87 (s, 0.54H), 3.71 (s, 2.46H), 2.34 (s, 0.36H), 2.22 (s, 1.64H), 1.83-1.50 (m, 10H), 1.35-0.80 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, major isomer): δ 170.8, 148.1, 138.6, 135.9, 132.5, 131.4, 130.8, 129.9, 128.7, 128.6, 125.8, 124.5, 124.2, 52.2, 28.3, 28.1, 26.8, 22.5, 16.7. IR (KBr) 2918, 2845, 1718, 1594, 1445, 1219, 1070, 1000, 820, 741 cm^{-1}. HRMS (FAB) calcd for $C_{27}H_{34}O_2Si$ (M^+) 418.2323, found: 418.2325.

General Procedure for Scheme 4b.

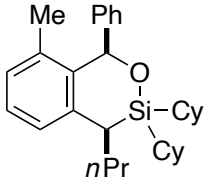
Aldehyde **5** (0.240 mmol) was added to a mixture of $Ni(cod)_2$ (5.5 mg, 20 μmol), PPh_3 (10.5 mg, 40.0 μmol), and compound **2** (0.200 mmol) in toluene (1.2 mL), and the resulting solution was stirred for 20 h at 100 °C. After cooled to room temperature, the mixture was passed through a pad of silica gel with CH_2Cl_2. The solvent was removed under vacuum, and the residue was purified by silica gel preparative TLC and further purified by GPC with $CHCl_3$ to afford compound **6**.



Compound 6aa. Hexane/EtOAc = 100/1 was used for the preparative TLC. Pale yellow amorphous (66.5 mg, 0.138 mmol; 69% yield, dr = 89/11). For analytical purpose, the diastereomers were separated by further purification using silica gel preparative TLC with hexane/EtOAc = 100/1. The relative configuration of the major diastereomer was determined to be *cis* by X-ray crystallographic analysis after recrystallization from CH_2Cl_2/MeOH.

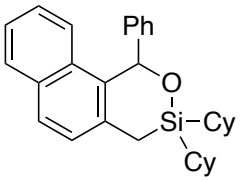
***cis*-6aa:** ^1H NMR ($CDCl_3$): δ 7.89-7.83 (m, 1H), 7.75 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.71 (d, $^3J_{HH}$ = 8.2

Hz, 1H), 7.46-7.36 (m, 2H), 7.30-7.15 (m, 6H), 6.96 (s, 1H), 2.28 (dd, $^{3}J_{HH}$ = 11.9 and 4.1 Hz, 1H), 2.09-1.99 (m, 1H), 1.87-1.66 (m, 4H), 1.62-1.13 (m, 11H), 1.13-0.80 (m, 8H), 0.78-0.67 (m, 1H), 0.66-0.50 (m, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 144.8, 138.4, 134.4, 133.0, 132.2, 132.1, 128.7, 128.0, 127.7, 127.3, 127.1, 126.4, 124.9, 123.6, 74.2, 32.7, 28.4, 28.3, 28.24, 28.21, 28.17, 28.15, 27.4, 27.3, 27.2, 26.8, 25.5, 25.3, 22.2, 14.0. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 5.4. IR (KBr) 3055, 2919, 2846, 1446, 1094, 1069, 935, 818, 741, 697 cm^{-1}. HRMS (FAB) calcd for $C_{33}H_{42}OSi$ (M^+) 482.2999, found: 482.3000.



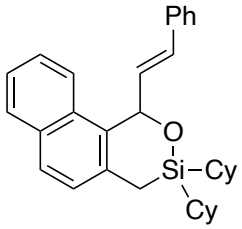
Compound 6ia. The diastereoselectivity was 95/5 before purification. Hexane/EtOAc = 100/1 was used for the preparative TLC. White amorphous (68.0 mg, 0.152 mmol; 76% yield, single diastereomer). The relative configuration was determined to be *cis* by X-ray crystallographic analysis after recrystallization from CH_2Cl_2/MeOH.

***cis*-6ia:** ^{1}H NMR ($CDCl_3$): δ 7.30-7.11 (m, 6H), 7.06 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.98 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.30 (s, 1H), 2.20 (s, 3H), 2.11 (dd, $^{3}J_{HH}$ = 12.4 and 4.1 Hz, 1H), 2.06-1.96 (m, 1H), 1.86-1.64 (m, 4H), 1.62-1.48 (m, 4H), 1.45-0.48 (m, 20H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 144.3, 139.8, 138.3, 135.9, 132.2, 128.0, 127.9, 127.1, 127.0, 126.7, 74.5, 32.4, 28.4, 28.22, 28.20, 28.1, 28.0, 27.7, 27.4, 27.3, 27.1, 27.0, 25.2, 25.3, 21.9, 19.9, 13.8. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 6.2. IR (KBr) 3063, 2919, 2846, 1491, 1460, 1444, 1173, 1094, 1060, 743 cm^{-1}. HRMS (FAB) calcd for $C_{30}H_{42}OSi$ (M^+) 446.2999, found: 446.3008.



Compound 6qa. Hexane/EtOAc = 50/1 and then hexane/EtOAc = 500/1 were used for the preparative TLC. White amorphous (76.6 mg, 0.174 mmol; 87% yield).

^{1}H NMR ($CDCl_3$): δ 7.89-7.82 (m, 1H), 7.82-7.74 (m, 2H), 7.44-7.38 (m, 2H), 7.36 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 7.29-7.16 (m, 5H), 7.01 (s, 1H), 2.08 (d, $^{2}J_{HH}$ = 15.1 Hz, 1H), 1.96 (d, $^{2}J_{HH}$ = 15.6 Hz, 1H), 1.74-1.43 (m, 10H), 1.22-0.62 (m, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 142.8, 134.6, 134.1, 131.9, 131.5, 130.8, 128.8, 128.33, 128.29, 127.9, 127.5, 126.5, 124.6, 122.6, 74.3, 28.10, 28.08, 28.01, 27.99, 27.5, 27.4, 27.0, 26.9, 26.8, 25.44, 25.39, 15.7. $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): δ 8.1. IR (KBr) 3053, 2918, 2845, 1446, 1083, 1065, 937, 815, 741, 699 cm^{-1}. HRMS (FAB) calcd for $C_{30}H_{36}OSi$ (M^+) 440.2530, found: 440.2531.



Compound 6qb. Hexane/EtOAc = 8/1 was used for the preparative TLC. White amorphous (76.7 mg, 0.164 mmol; 82% yield).

^{1}H NMR ($CDCl_3$): δ 7.97 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 7.86 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.75 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.51 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.44 (t, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.33 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.32-7.23 (m, 4H), 7.19 (t, $^{3}J_{HH}$ = 6.9 Hz, 1H), 6.59 (d, $^{3}J_{HH}$ = 5.0 Hz, 1H), 6.53 (dd, $^{3}J_{HH}$ = 15.8 and 5.3 Hz, 1H), 6.32 (d, $^{3}J_{HH}$ = 15.6 Hz, 1H), 2.25 (d, $^{2}J_{HH}$ = 15.6 Hz, 1H), 2.12 (d, $^{2}J_{HH}$ = 15.1 Hz, 1H), 2.04-1.66 (m, 5H), 1.66-1.44 (m, 5H), 1.44-1.17 (m, 5H), 1.17-0.63 (m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.0, 134.0, 133.9, 132.0, 130.95, 130.87, 130.1, 128.9, 128.6, 128.2, 127.6, 126.7, 126.5, 124.7, 122.4, 73.2, 28.20, 28.16, 28.0, 27.9, 27.5, 27.42, 27.37, 27.3, 27.1, 26.8, 25.3, 25.1, 15.3. ^{29}Si{^{1}H} NMR ($CDCl_3$): δ 7.7. IR (neat) 3052, 2918, 2845, 1596, 1509, 1445, 1069, 933, 820, 735cm^{-1}. HRMS (FAB) calcd for $C_{32}H_{38}OSi$ (M^+) 466.2686, found: 466.2696.

Procedure for Scheme 6a.

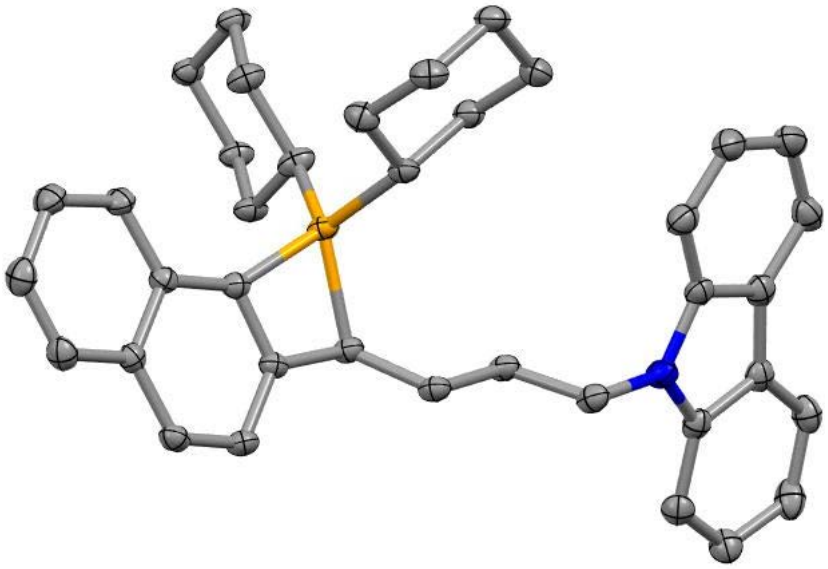
Et_2NH (41.4 μL, 0.400 mmol) was added to a mixture of $Pd(OAc)_2$ (2.2 mg, 10 μmol), dtbpf (5.2 mg, 11 μmol), and compound **1s-*d*$_3$** (78.7 mg, 0.200 mmol) in DMF (0.80 mL), and the resulting solution was stirred for 18 h at 80 °C. After cooled to room temperature, the reaction mixture was diluted with Et_2O and H_2O was added. 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 purified by silica gel preparative TLC with hexane to afford a mixture of compounds **2s-*d*$_3$** and **2s-*d*$_2$** (19.5 mg, 80.1 μmol; 40% yield, **2s-*d*$_3$**/**2s-*d*$_2$** = 7.5/1).

Procedure for Scheme 6b.

Et_2NH (41.4 μL, 0.400 mmol) was added to a mixture of $Pd(OAc)_2$ (2.2 mg, 10 μmol) and dtbpf (5.2 mg, 11 μmol) in DMF (0.30 mL), and the resulting solution was stirred for 20 min at 80 °C. A solution of compound **1q** (48.5 mg, 0.100 mmol) and compound **1q-*d*$_3$** (48.7 mg, 0.100 mmol) in DMF (0.50 mL) was added to it and the resulting solution was stirred for 15 min at 80 °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 purified by silica gel preparative TLC with hexane to afford a mixture of compounds **2q** and **2q-*d*$_2$** (7.5 mg, 22 μmol; 11% yield, **2q**/**2q-*d*$_2$** = 1.2/1).

IV. X-ray Crystal Structures

Compound 2g



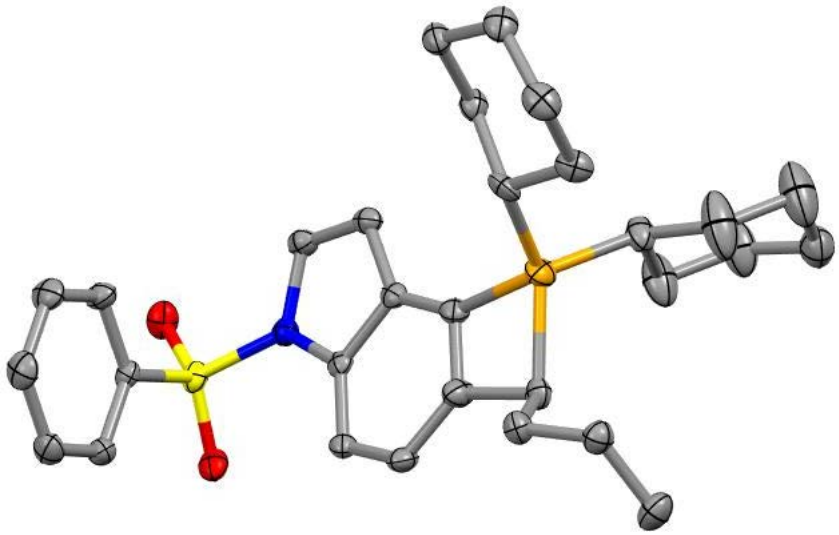
A colorless hexane solution of compound **2g** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2237530). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

Crystal Data and Structure Refinement.

Empirical Formula	$C_{38}H_{43}NSi$	
Formula Weight	541.82	
Temperature	113.15 K	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit Cell Dimensions	a = 22.9951(8) Å	α = 90°
	b = 8.0662(3) Å	β = 106.116(4)°
	c = 35.0695(12) Å	γ = 90°

Volume	6249.2(4) $Å^3$
Z Value	8
Calculated Density	1.152 g/cm^3
Absorption coefficient	0.102 mm^{-1}
F(000)	2336
Crystal size	0.500 x 0.200 x 0.050 mm
Theta Range for Data Collection	2.495–25.325°
Index Ranges	$-27 \leq h \leq 27$, $-9 \leq k \leq 9$, $-42 \leq l \leq 42$
Reflections Collected	59490
Independent Reflections	11450 [R(int) = 0.0788]
Completeness to Theta = 25.242°	99.8%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.00000 and 0.77709
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	11450 / 432 / 850
Goodness-of-Fit on F^2	1.108
Final R Indices [I>2sigma(I)]	R1 = 0.0779, wR2 = 0.1526
R Indices (All Data)	R1 = 0.1274, wR2 = 0.1699
Largest Diff. Peak and Hole	0.395 and –0.589 $e^-/Å^3$

Compound 2p



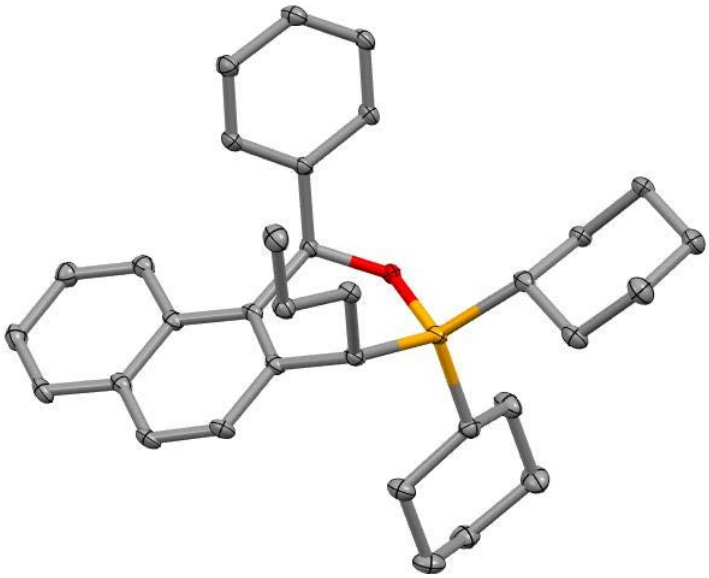
A colorless CH_2Cl_2 solution of compound **2p** was prepared. Crystals suitable for X-ray analysis were obtained by layering MeOH and slow diffusion of the solvents at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2237529). 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	$C_{30}H_{39}NO_2SSi$	
Formula Weight	505.77	
Temperature	113.15 K	
Wavelength	0.71073 Å	
Crystal System	Monoclinic	
Space Group	$P2_1/c$	
Unit Cell Dimensions	a = 18.8834(16) Å	α = 90°
	b = 10.0790(6) Å	β = 111.762(10)°
	c = 15.7187(14) Å	γ = 90°
Volume	2778.5(4) $Å^3$	

Z Value	4
Calculated Density	1.209 g/cm^3
Absorption coefficient	0.187 mm^{-1}
F(000)	1088
Crystal size	0.200 x 0.100 x 0.050 mm
Theta Range for Data Collection	2.321–28.228°
Index Ranges	$-24 \leq h \leq 25$, $-13 \leq k \leq 13$, $-18 \leq l \leq 21$
Reflections Collected	45872
Independent Reflections	7294 [R(int) = 0.0580]
Completeness to Theta = 25.242°	99.9%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.00000 and 0.63788
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	7294 / 463 / 465
Goodness-of-Fit on F^2	1.030
Final R Indices [I>2sigma(I)]	R1 = 0.0590, wR2 = 0.1497
R Indices (All Data)	R1 = 0.0899, wR2 = 0.1651
Largest Diff. Peak and Hole	0.558 and –0.530 e$^-$/Å^3

Compound 6aa



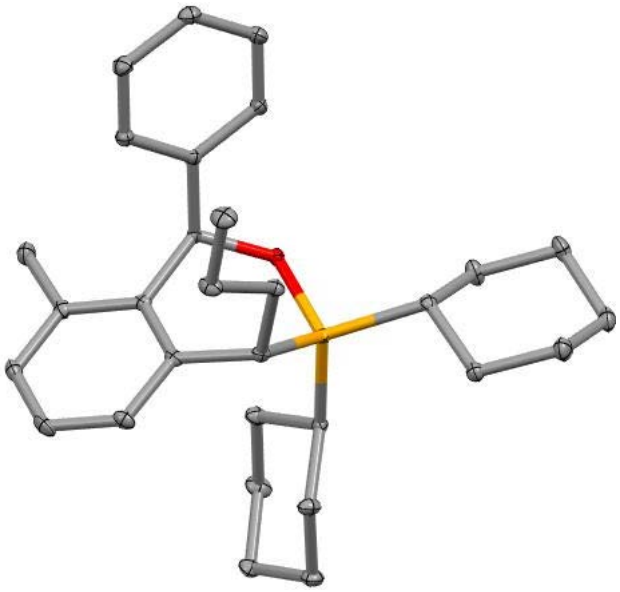
A colorless CH_2Cl_2 solution of compound **6aa** was prepared. Crystals suitable for X-ray analysis were obtained by layering MeOH and slow diffusion of the solvents at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2237531). 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	$C_{33}H_{42}OSi$	
Formula Weight	482.75	
Temperature	113.15 K	
Wavelength	0.71073 Å	
Crystal System	Triclinic	
Space Group	P–1	
Unit Cell Dimensions	a = 10.3545(2) Å	α = 68.423(2)°
	b = 12.0752(2) Å	β = 70.324(2)°
	c = 12.5616(3) Å	γ = 89.9840(10)°
Volume	1361.51(5) $Å^3$	

Z Value	2
Calculated Density	1.178 g/cm^3
Absorption coefficient	0.110 mm^{-1}
F(000)	524
Crystal size	0.190 x 0.160 x 0.160 mm
Theta Range for Data Collection	2.583–29.518°
Index Ranges	$-14 \leq h \leq 14$, $-16 \leq k \leq 14$, $-16 \leq l \leq 17$
Reflections Collected	25360
Independent Reflections	6676 [R(int) = 0.0985]
Completeness to Theta = 25.242°	97.6%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.00000 and 0.52786
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6676 / 625 / 481
Goodness-of-Fit on F^2	1.010
Final R Indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1231
R Indices (All Data)	R1 = 0.0686, wR2 = 0.1258
Largest Diff. Peak and Hole	0.398 and –0.388 e$^-$/Å^3

Compound 6ia



A colorless CH_2Cl_2 solution of compound **6ia** 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 2237532). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

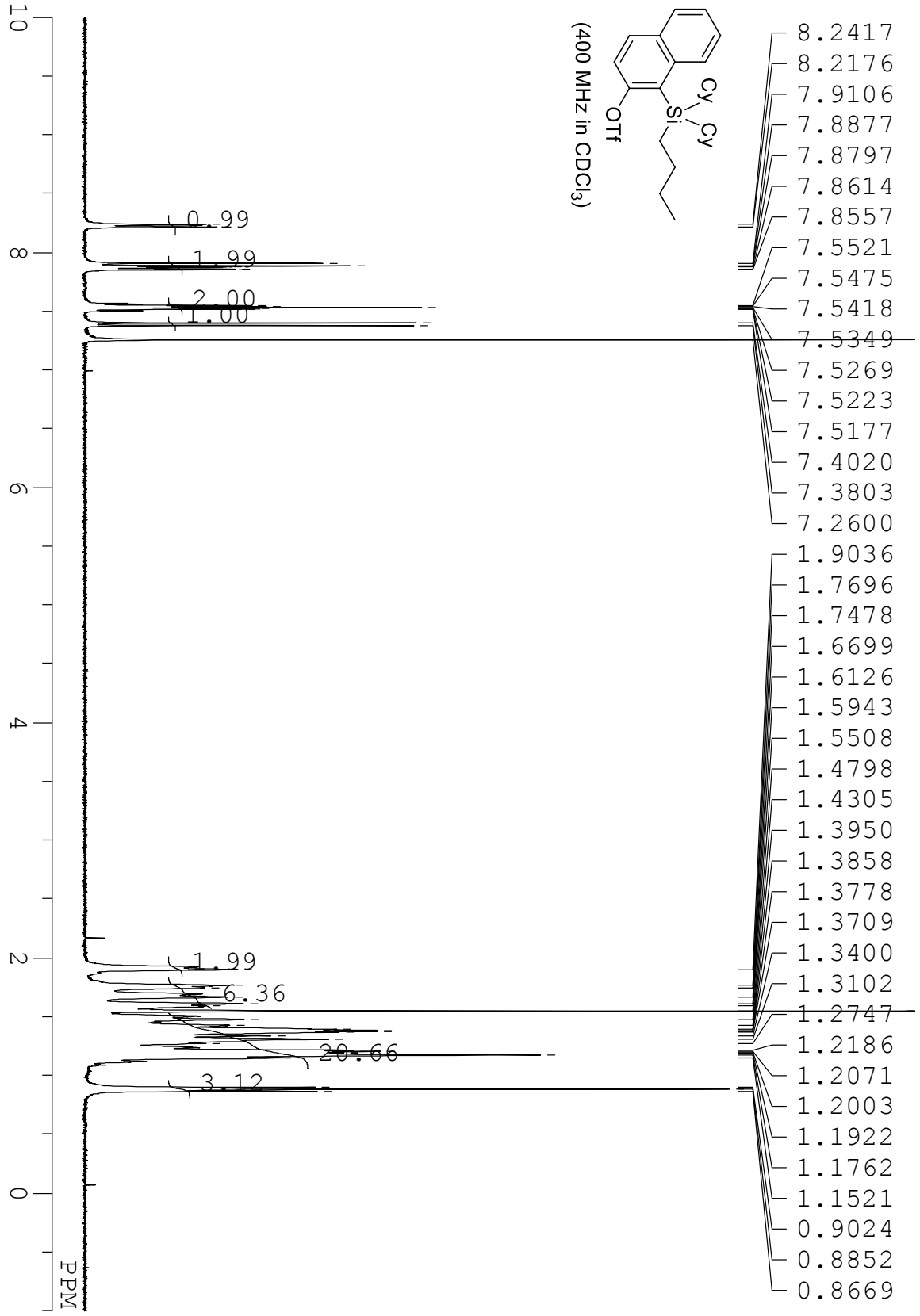
Crystal Data and Structure Refinement.

Empirical Formula	$C_{30}H_{42}OSi$	
Formula Weight	446.72	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Triclinic	
Space Group	P–1	
Unit Cell Dimensions	a = 9.9322(13) Å	α = 72.762(7)°
	b = 10.0147(10) Å	β = 87.903(8)°
	c = 13.5979(14) Å	γ = 82.672(3)°

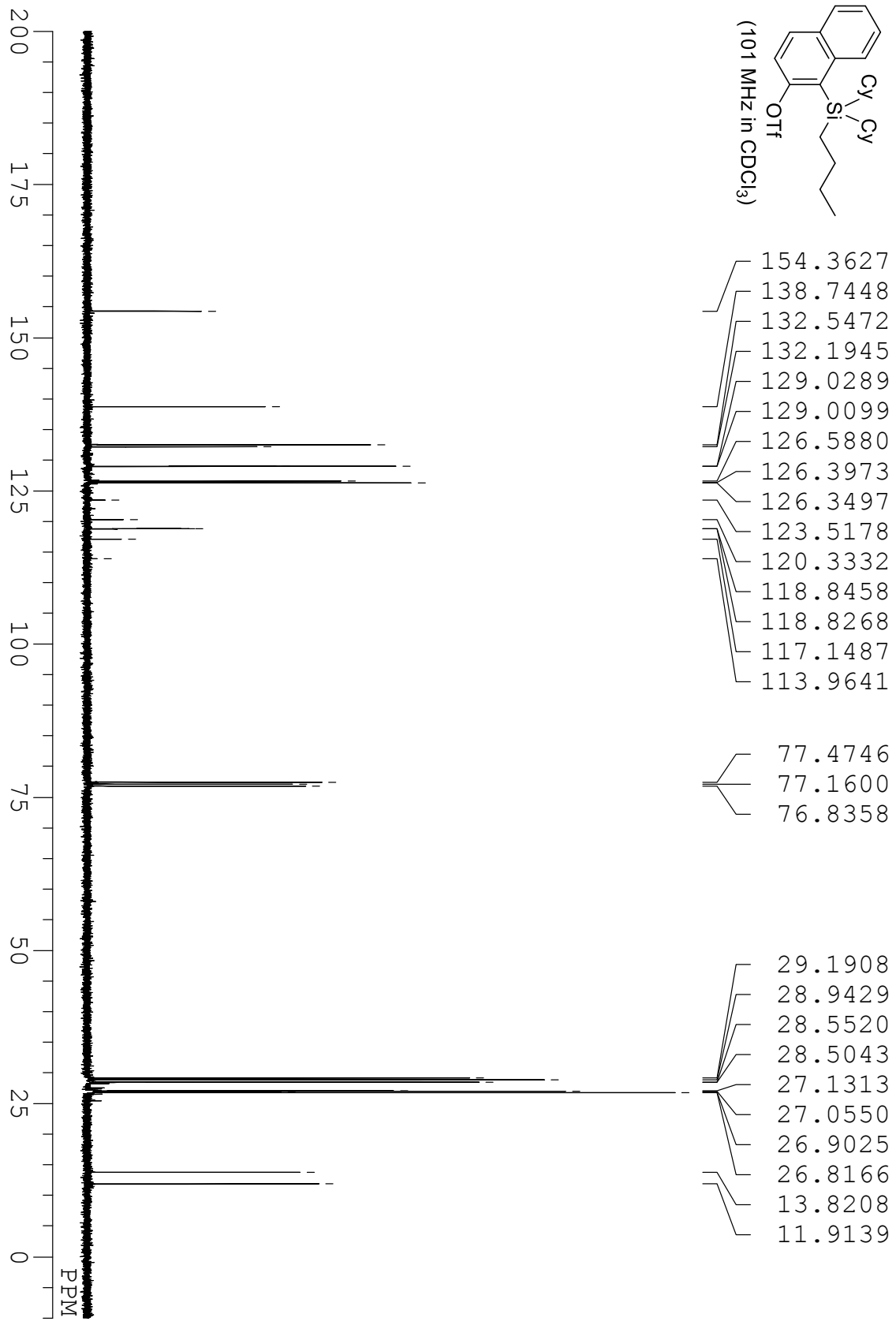
Volume	1281.2(3) $Å^3$
Z Value	2
Calculated Density	1.158 g/cm^3
Absorption coefficient	0.111 mm^{-1}
F(000)	488
Crystal size	0.300 x 0.300 x 0.100 mm
Theta Range for Data Collection	3.1–27.5°
Index Ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-17 \leq l \leq 17$
Reflections Collected	23983
Independent Reflections	5819 [R(int) = 0.0360]
Completeness to Theta = 25.242°	99.7%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.922
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	5819 / 0 / 291
Goodness-of-Fit on F^2	1.016
Final R Indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.1174
R Indices (All Data)	R1 = 0.0463, wR2 = 0.1260
Largest Diff. Peak and Hole	0.348 and –0.422 $e^-/Å^3$

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

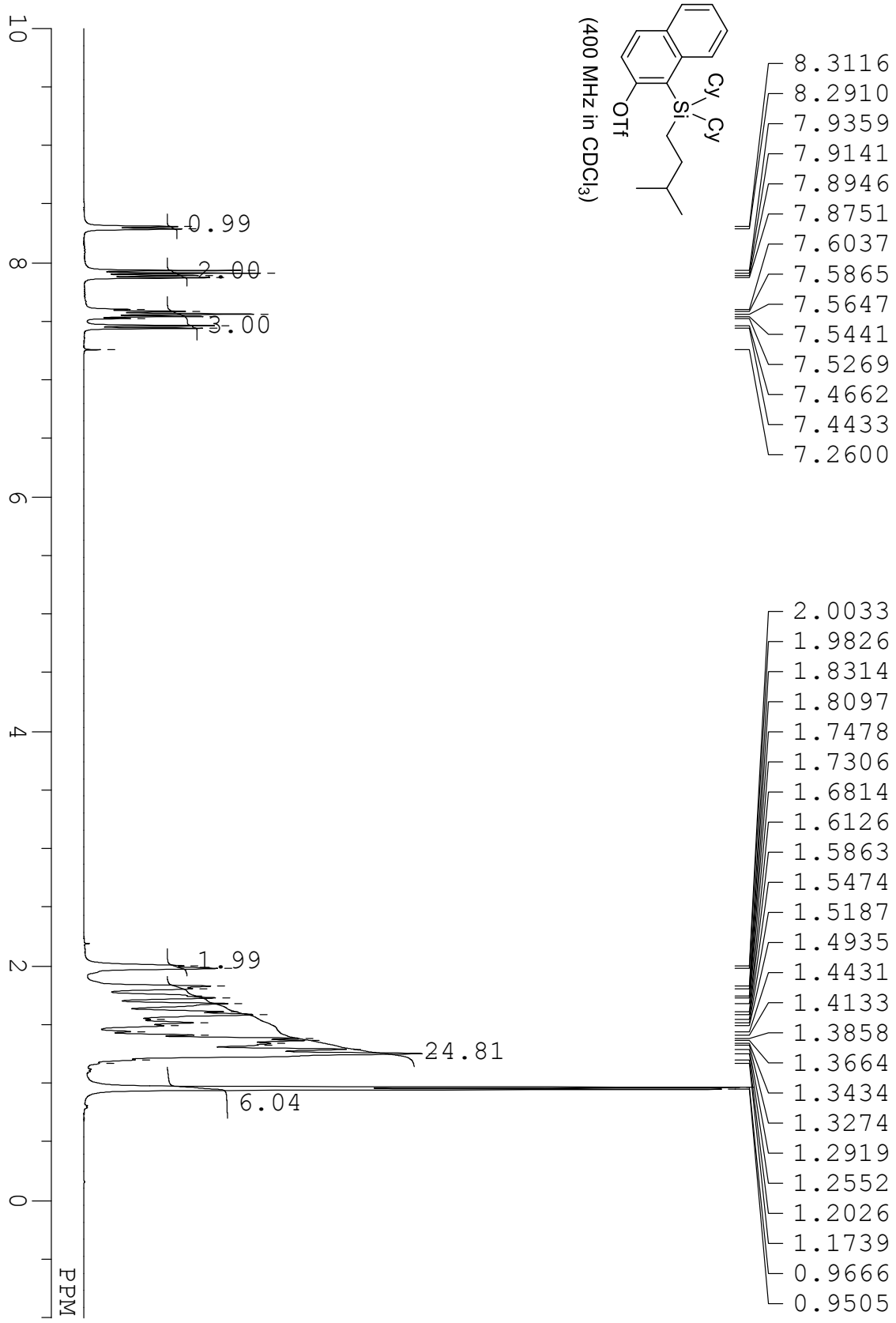
compound **1a**



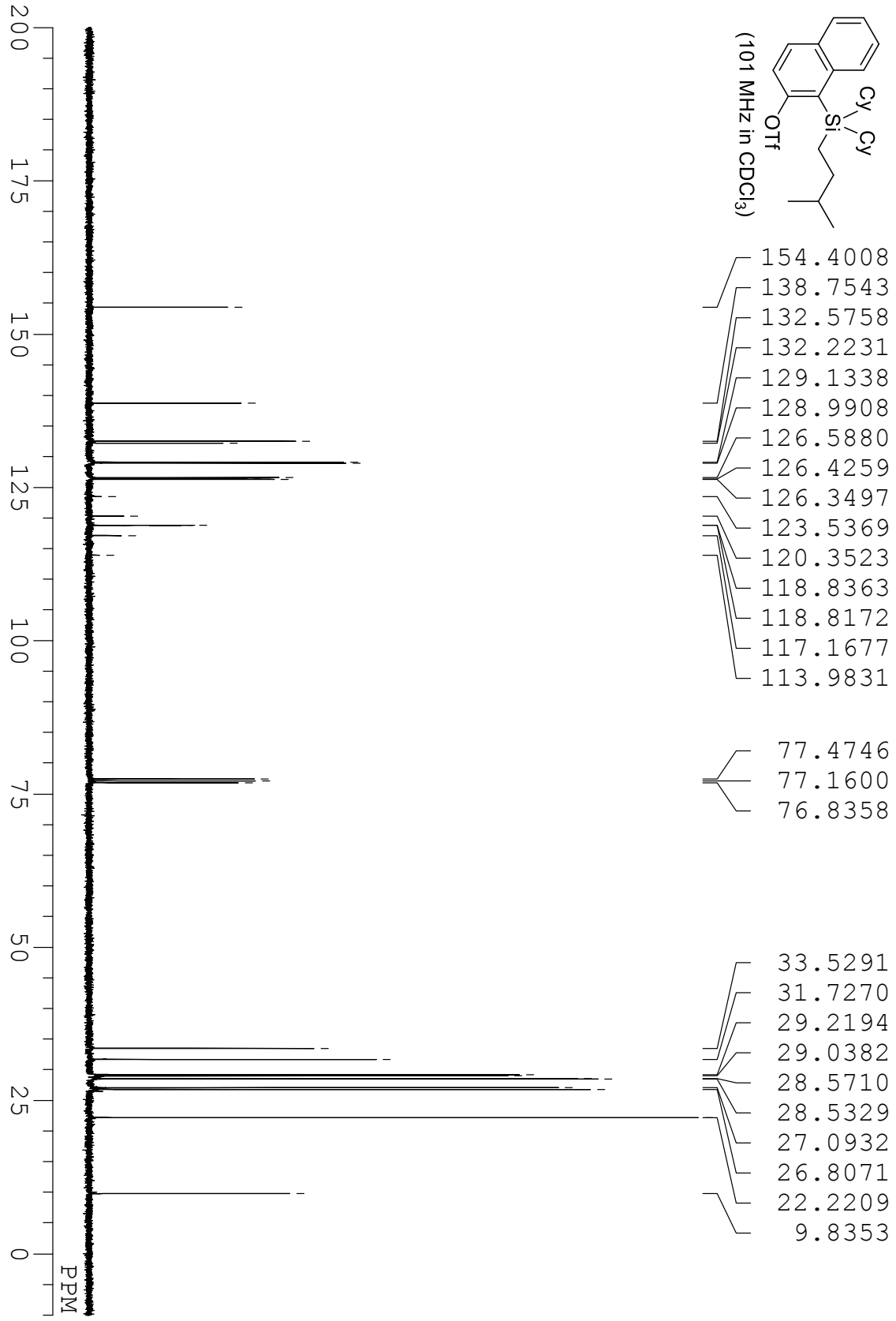
compound **1a**


(101 MHz in CDCl3)
OTf
Si
Cy
Cy
154.3627
138.7448
132.5472
132.1945
129.0289
129.0099
126.5880
126.3973
126.3497
123.5178
120.3332
118.8458
118.8268
117.1487
113.9641
77.4746
77.1600
76.8358
29.1908
28.9429
28.5520
28.5043
27.1313
27.0550
26.9025
26.8166
13.8208
11.9139
200
175
150
125
100
75
50
25
0
PPM

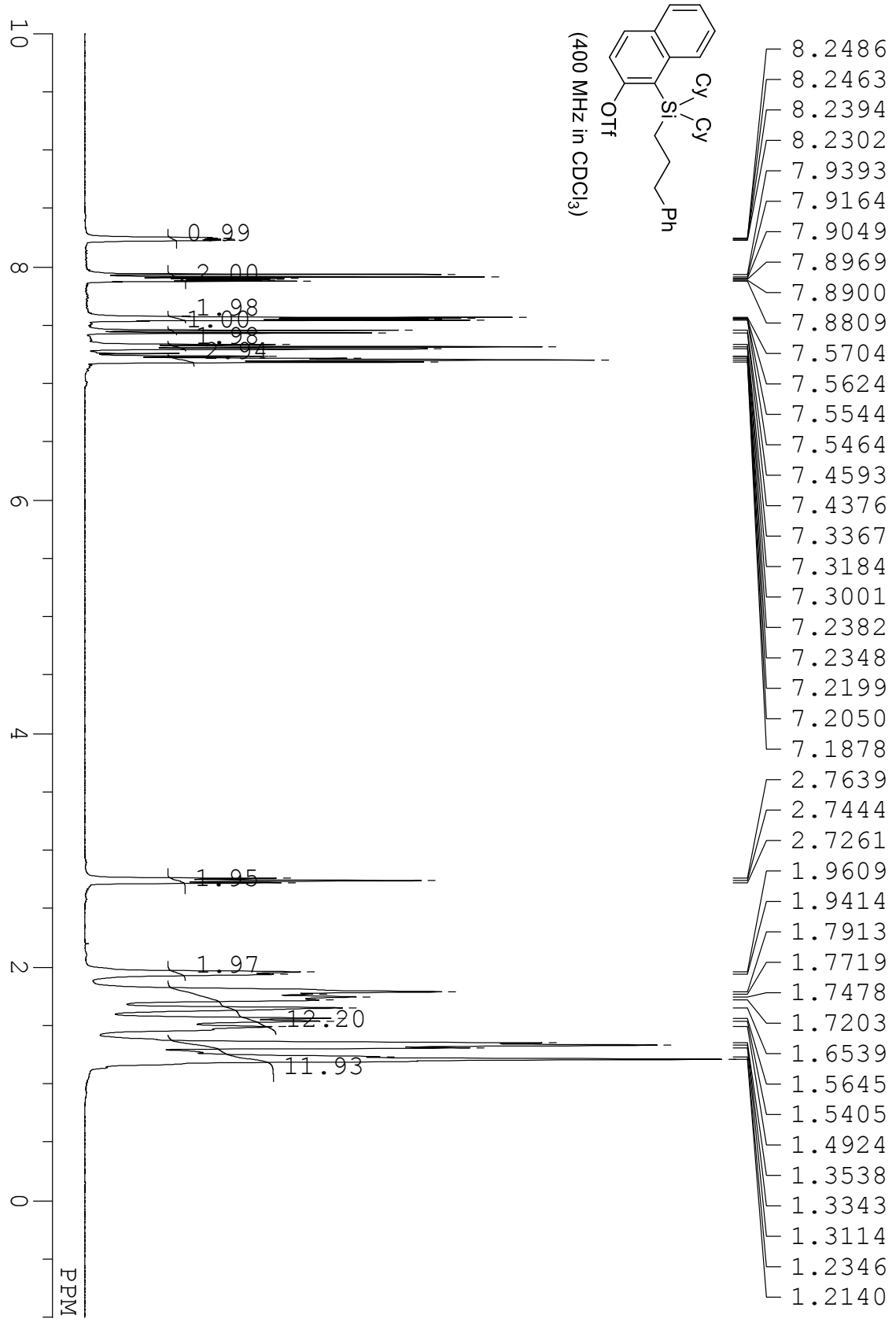
compound **1b**


(400 MHz in CDCl3)
OTf
Si
Cy
Cy
8.3116
8.2910
7.9359
7.9141
7.8946
7.8751
7.6037
7.5865
7.5647
7.5441
7.5269
7.4662
7.4433
7.2600
2.0033
1.9826
1.8314
1.8097
1.7478
1.7306
1.6814
1.6126
1.5863
1.5474
1.5187
1.4935
1.4431
1.4133
1.3858
1.3664
1.3434
1.3274
1.2919
1.2552
1.2026
1.1739
0.9666
0.9505
0.99
2.00
3.00
1.99
24.81
6.04
PPM

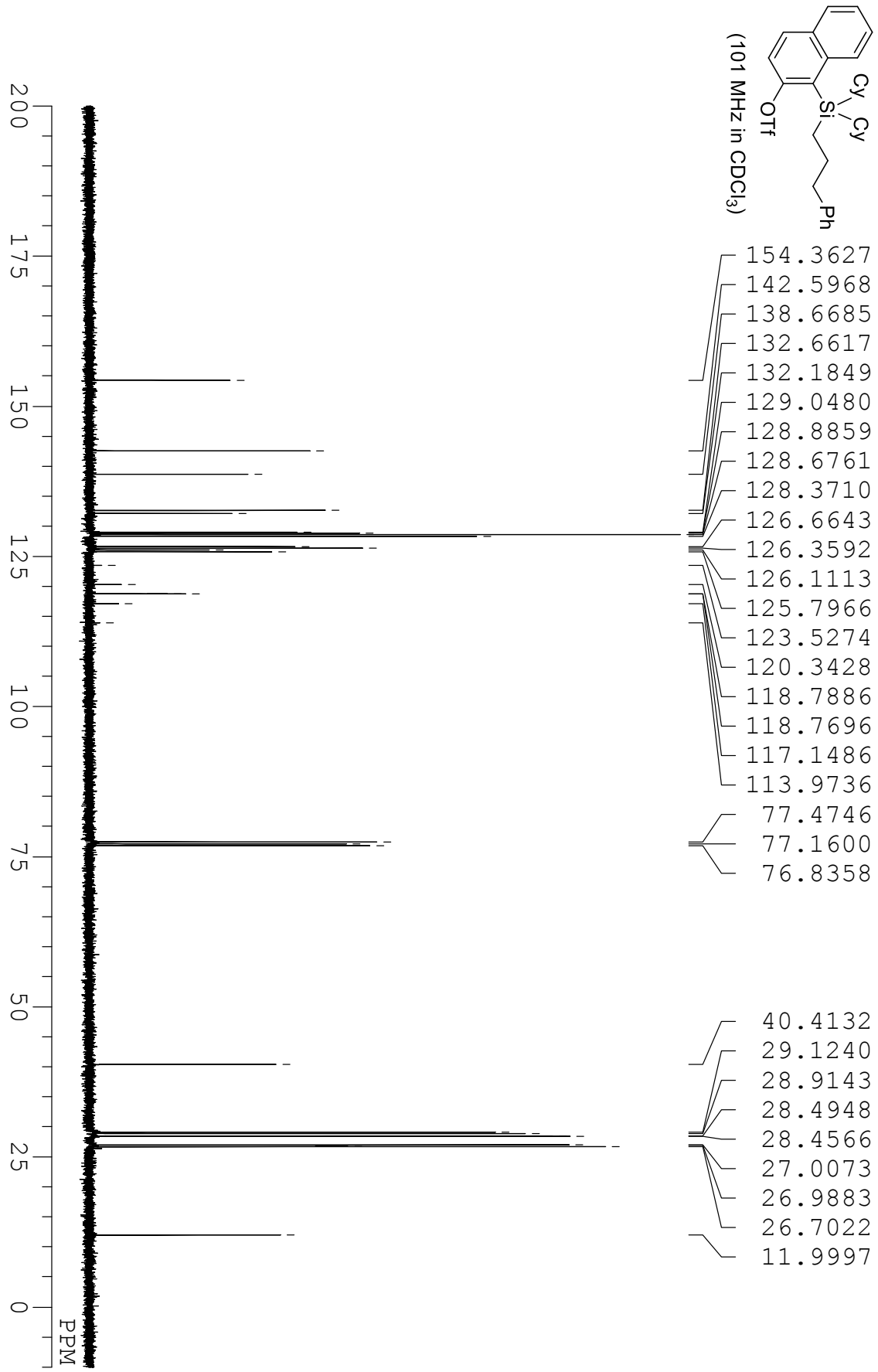
compound **1b**


(101 MHz in CDCl3)
OTf
Si
Cy
Cy
154.4008
138.7543
132.5758
132.2231
129.1338
128.9908
126.5880
126.4259
126.3497
123.5369
120.3523
118.8363
118.8172
117.1677
113.9831
77.4746
77.1600
76.8358
33.5291
31.7270
29.2194
29.0382
28.5710
28.5329
27.0932
26.8071
22.2209
9.8353
200
175
150
125
100
75
50
25
0
PPM

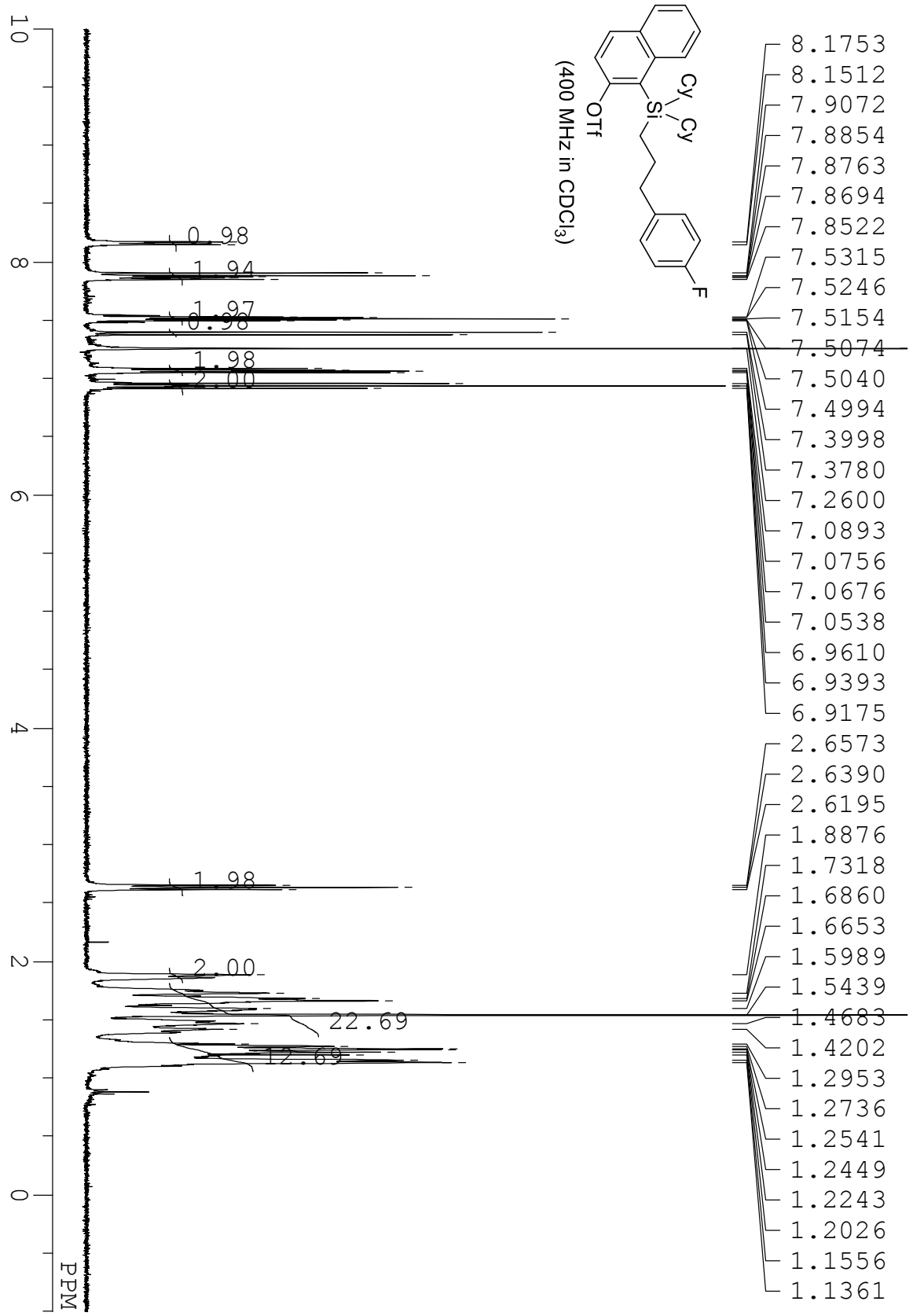
compound **1c**


(400 MHz in CDCl3)
OTf
Si
Cy
Cy
Ph
0.99
2.00
1.98
1.00
1.98
2.04
1.95
1.97
12.20
11.93
PPM
10
8
6
4
2
0
8.2486
8.2463
8.2394
8.2302
7.9393
7.9164
7.9049
7.8969
7.8900
7.8809
7.5704
7.5624
7.5544
7.5464
7.4593
7.4376
7.3367
7.3184
7.3001
7.2382
7.2348
7.2199
7.2050
7.1878
2.7639
2.7444
2.7261
1.9609
1.9414
1.7913
1.7719
1.7478
1.7203
1.6539
1.5645
1.5405
1.4924
1.3538
1.3343
1.3114
1.2346
1.2140

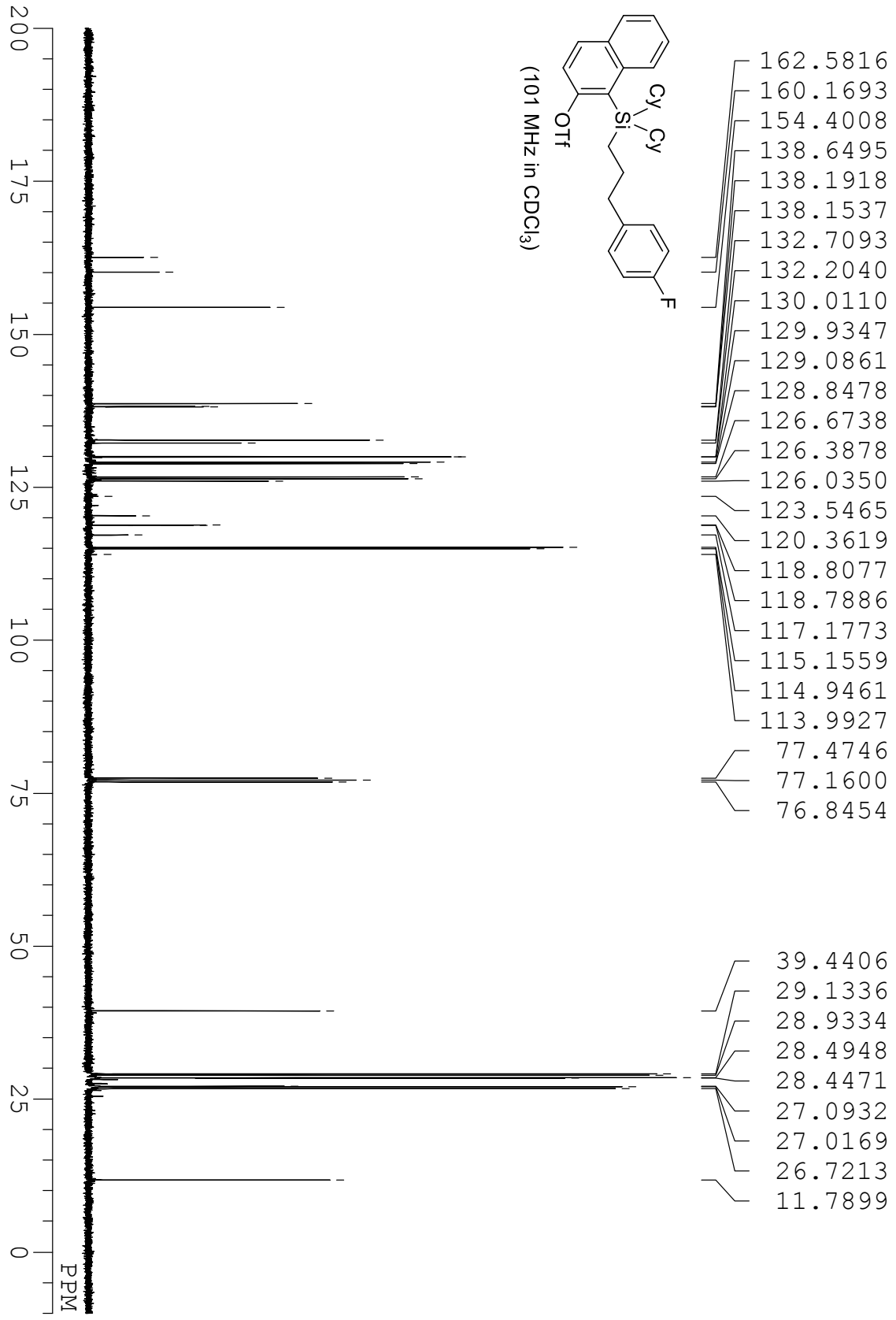
compound **1c**


OTf
Si
Cy
Cy
Ph
(101 MHz in CDCl3)
154.3627
142.5968
138.6685
132.6617
132.1849
129.0480
128.8859
128.6761
128.3710
126.6643
126.3592
126.1113
125.7966
123.5274
120.3428
118.7886
118.7696
117.1486
113.9736
77.4746
77.1600
76.8358
40.4132
29.1240
28.9143
28.4948
28.4566
27.0073
26.9883
26.7022
11.9997
200
175
150
125
100
75
50
25
0
PPM

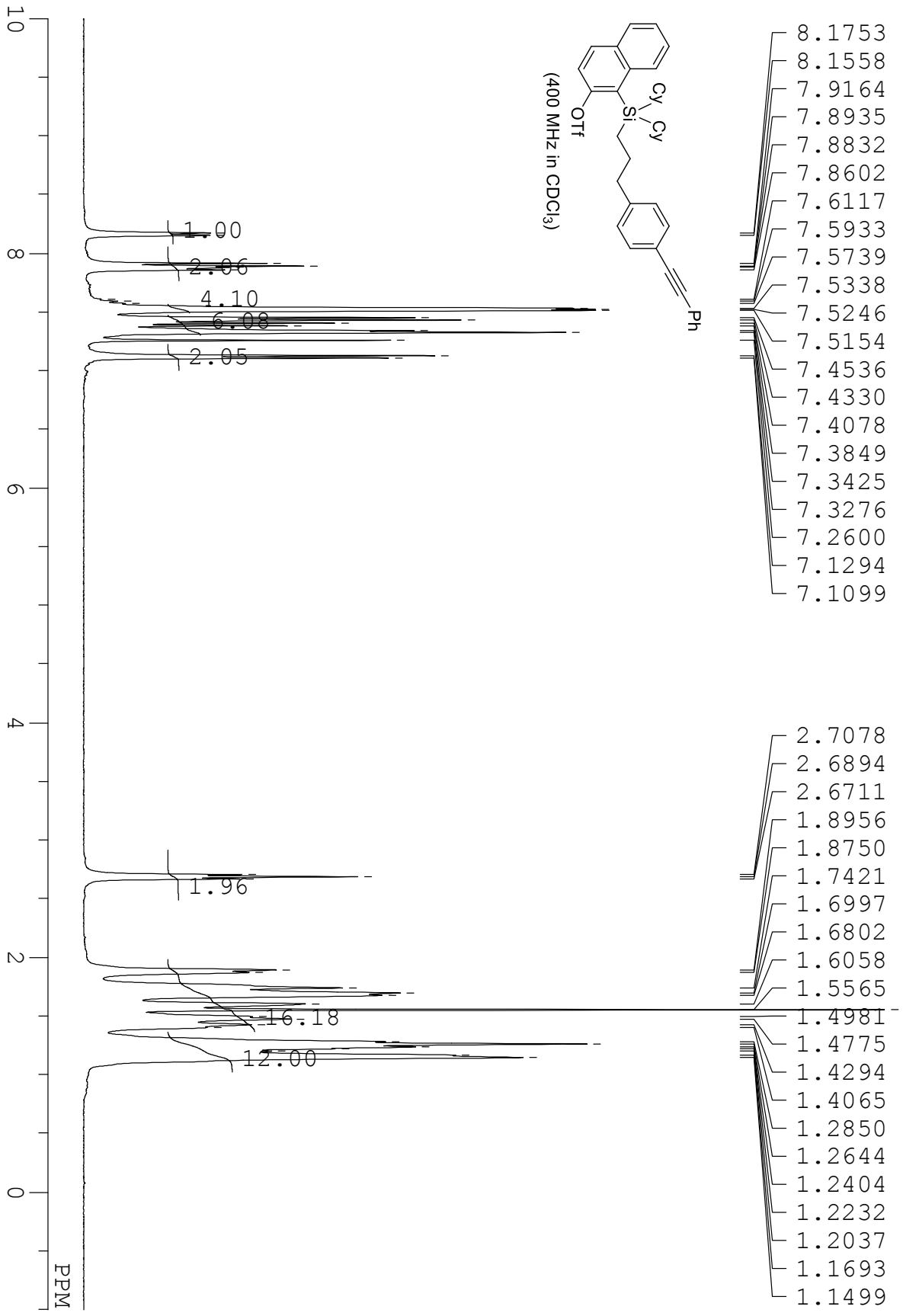
compound **1d**


(400 MHz in CDCl3)
OTf
Si
Cy
Cy
F
0.98
1.94
1.97
0.98
1.98
2.00
1.98
2.00
22.69
12.69
8.1753
8.1512
7.9072
7.8854
7.8763
7.8694
7.8522
7.5315
7.5246
7.5154
7.5074
7.5040
7.4994
7.3998
7.3780
7.2600
7.0893
7.0756
7.0676
7.0538
6.9610
6.9393
6.9175
2.6573
2.6390
2.6195
1.8876
1.7318
1.6860
1.6653
1.5989
1.5439
1.4683
1.4202
1.2953
1.2736
1.2541
1.2449
1.2243
1.2026
1.1556
1.1361
PPM

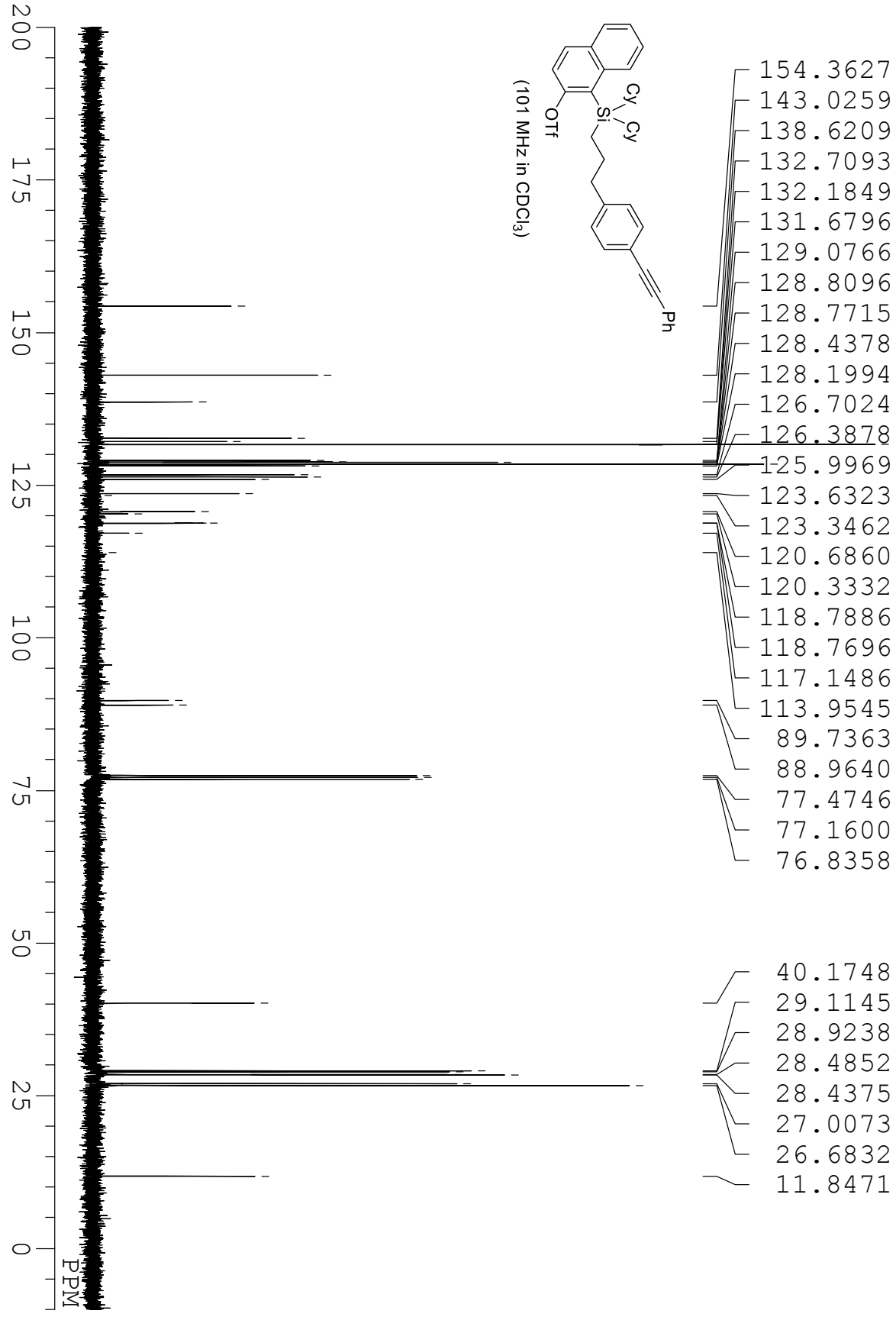
compound **1d**


(101 MHz in CDCl3)
OTf
Si
Cy
Cy
F
162.5816
160.1693
154.4008
138.6495
138.1918
138.1537
132.7093
132.2040
130.0110
129.9347
129.0861
128.8478
126.6738
126.3878
126.0350
123.5465
120.3619
118.8077
118.7886
117.1773
115.1559
114.9461
113.9927
77.4746
77.1600
76.8454
39.4406
29.1336
28.9334
28.4948
28.4471
27.0932
27.0169
26.7213
11.7899
200
175
150
125
100
75
50
25
0
PPM

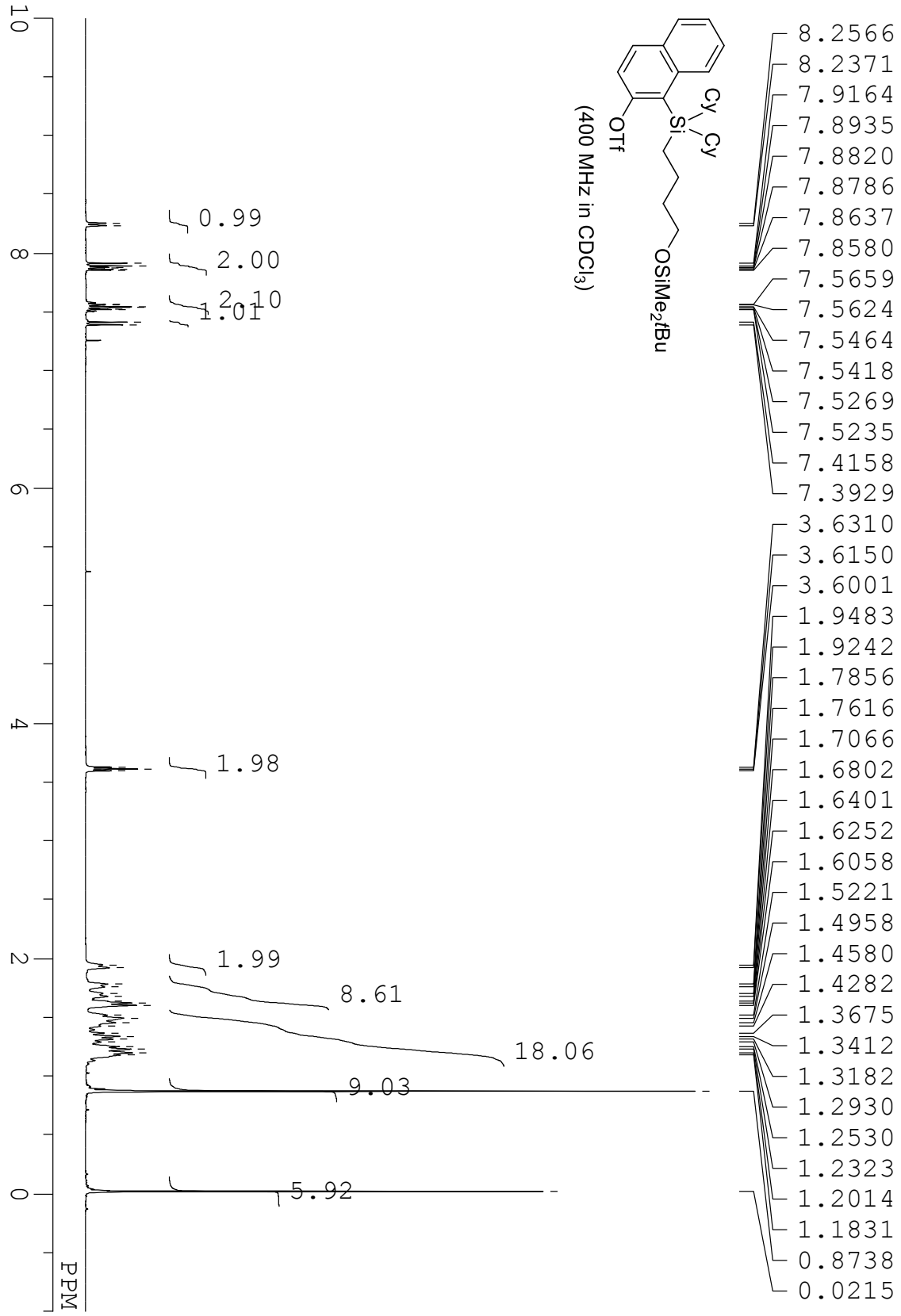
compound **1e**


(400 MHz in CDCl3)
OTf
Si
Cy
Cy
Ph
1.00
2.06
4.10
6.08
2.05
1.96
16.18
12.00
8.1753
8.1558
7.9164
7.8935
7.8832
7.8602
7.6117
7.5933
7.5739
7.5338
7.5246
7.5154
7.4536
7.4330
7.4078
7.3849
7.3425
7.3276
7.2600
7.1294
7.1099
2.7078
2.6894
2.6711
1.8956
1.8750
1.7421
1.6997
1.6802
1.6058
1.5565
1.4981
1.4775
1.4294
1.4065
1.2850
1.2644
1.2404
1.2232
1.2037
1.1693
1.1499
PPM

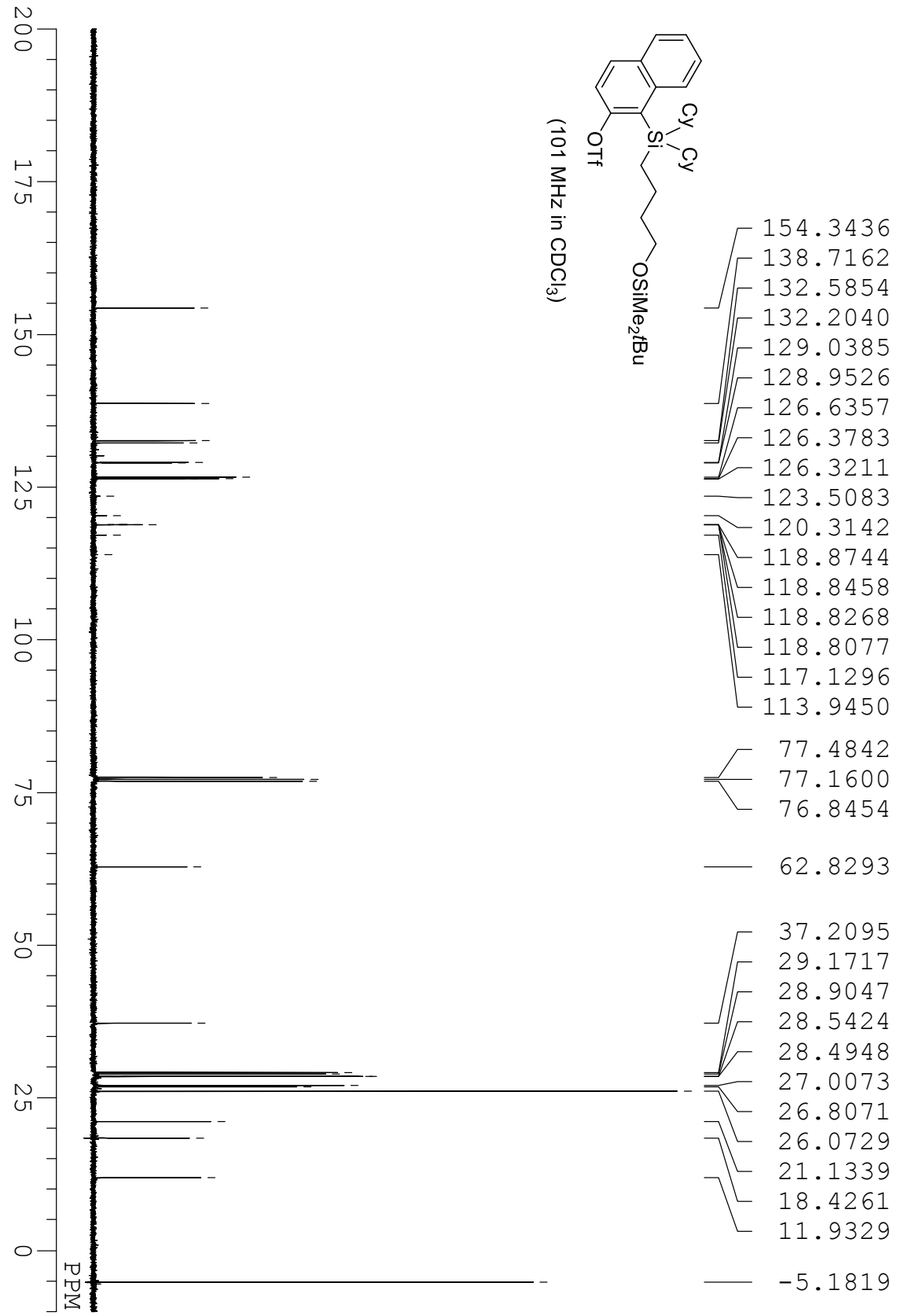
compound **1e**


(101 MHz in CDCl3)
OTf
Si
Cy
Cy
Ph
154.3627
143.0259
138.6209
132.7093
132.1849
131.6796
129.0766
128.8096
128.7715
128.4378
128.1994
126.7024
126.3878
125.9969
123.6323
123.3462
120.6860
120.3332
118.7886
118.7696
117.1486
113.9545
89.7363
88.9640
77.4746
77.1600
76.8358
40.1748
29.1145
28.9238
28.4852
28.4375
27.0073
26.6832
11.8471
200
175
150
125
100
75
50
25
0
PPM

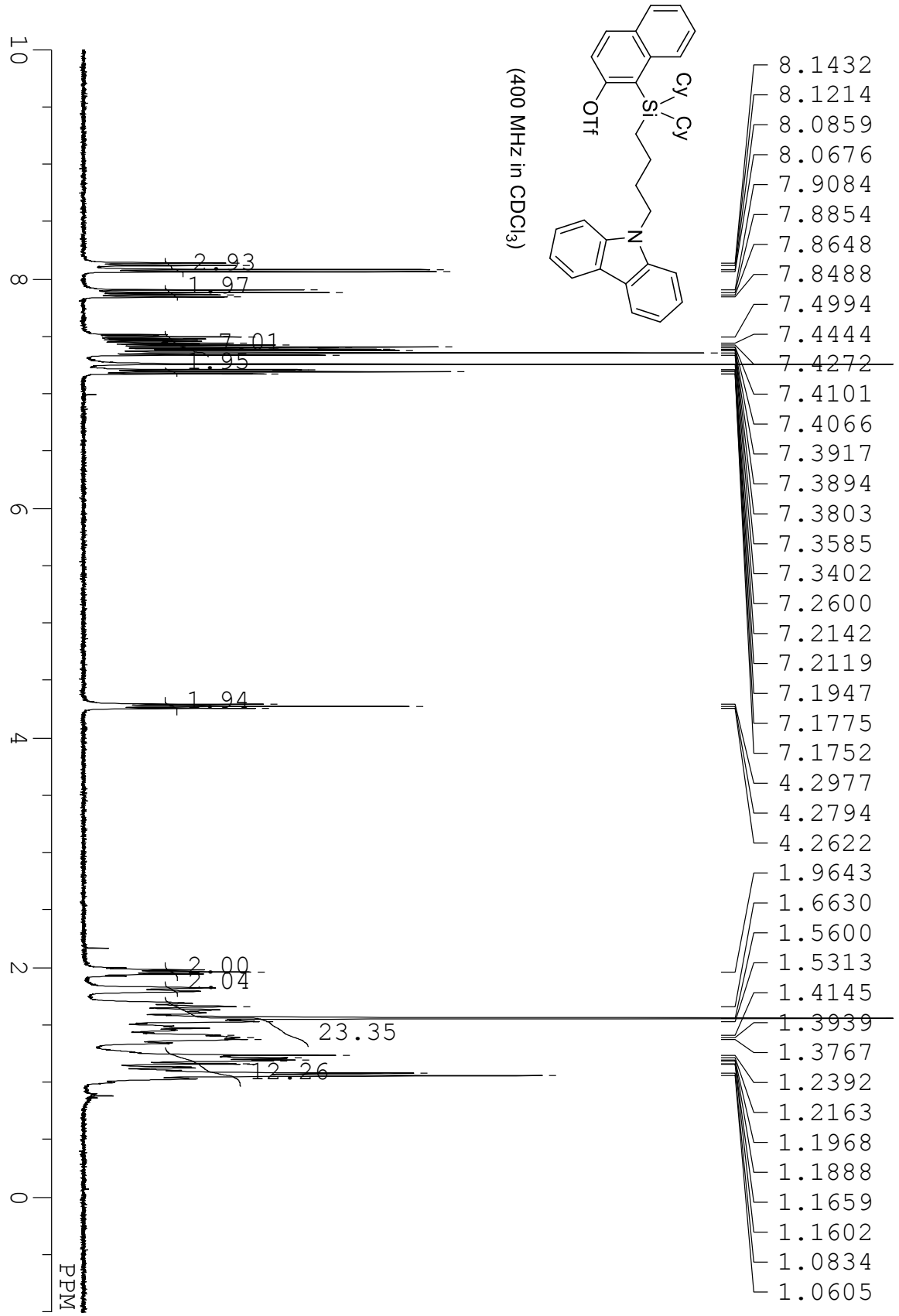
compound **1f**


(400 MHz in CDCl3)
OTf
Si
Cy
Cy
OSiMe2tBu
0.99
2.00
2.10
1.01
1.98
1.99
8.61
18.06
9.03
5.92
PPM
8.2566
8.2371
7.9164
7.8935
7.8820
7.8786
7.8637
7.8580
7.5659
7.5624
7.5464
7.5418
7.5269
7.5235
7.4158
7.3929
3.6310
3.6150
3.6001
1.9483
1.9242
1.7856
1.7616
1.7066
1.6802
1.6401
1.6252
1.6058
1.5221
1.4958
1.4580
1.4282
1.3675
1.3412
1.3182
1.2930
1.2530
1.2323
1.2014
1.1831
0.8738
0.0215

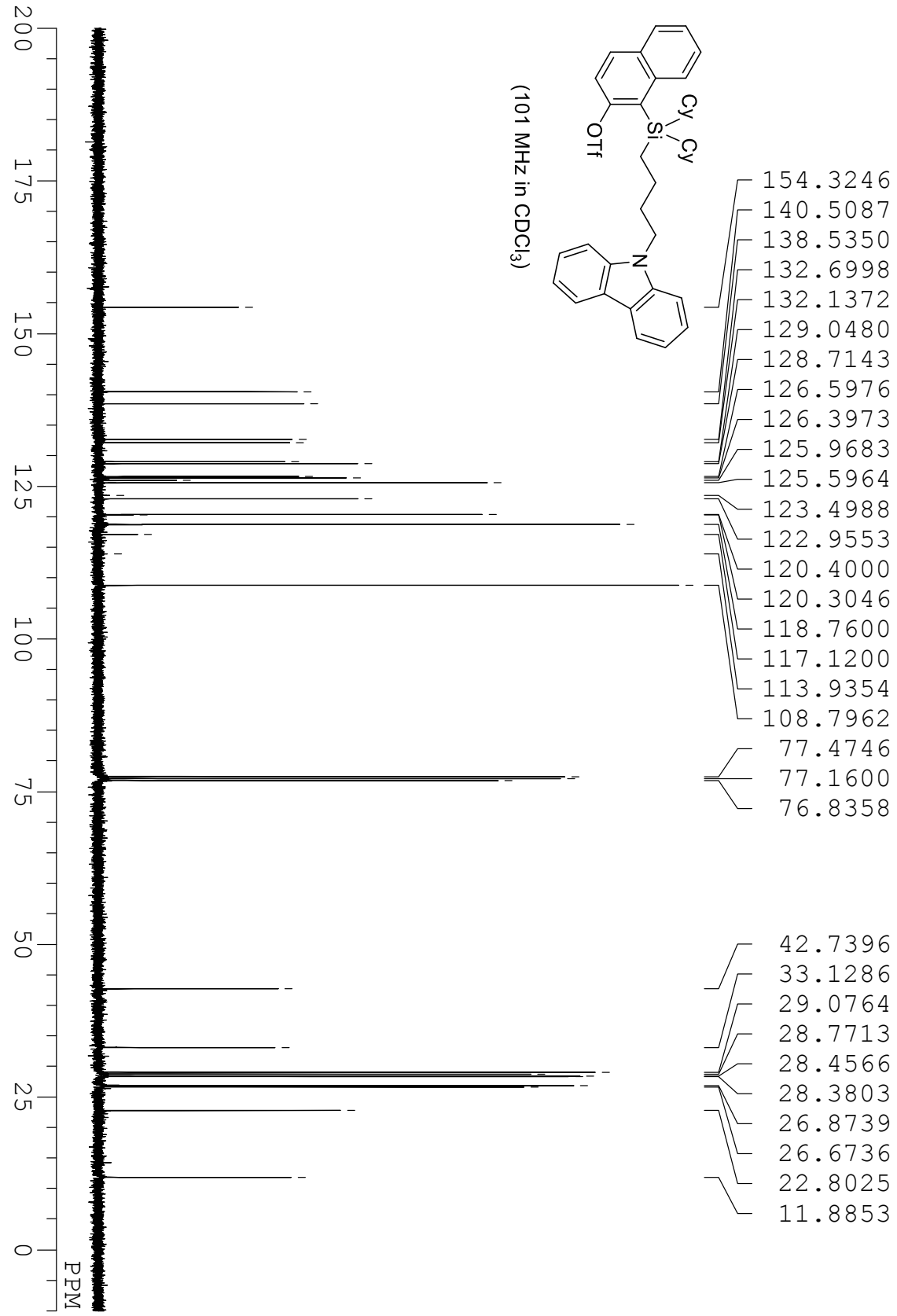
compound **1f**


200
175
150
125
100
75
50
25
0
PPM
(101 MHz in CDCl3)
OTf
Si
Cy
Cy
OSiMe2tBu
154.3436
138.7162
132.5854
132.2040
129.0385
128.9526
126.6357
126.3783
126.3211
123.5083
120.3142
118.8744
118.8458
118.8268
118.8077
117.1296
113.9450
77.4842
77.1600
76.8454
62.8293
37.2095
29.1717
28.9047
28.5424
28.4948
27.0073
26.8071
26.0729
21.1339
18.4261
11.9329
-5.1819

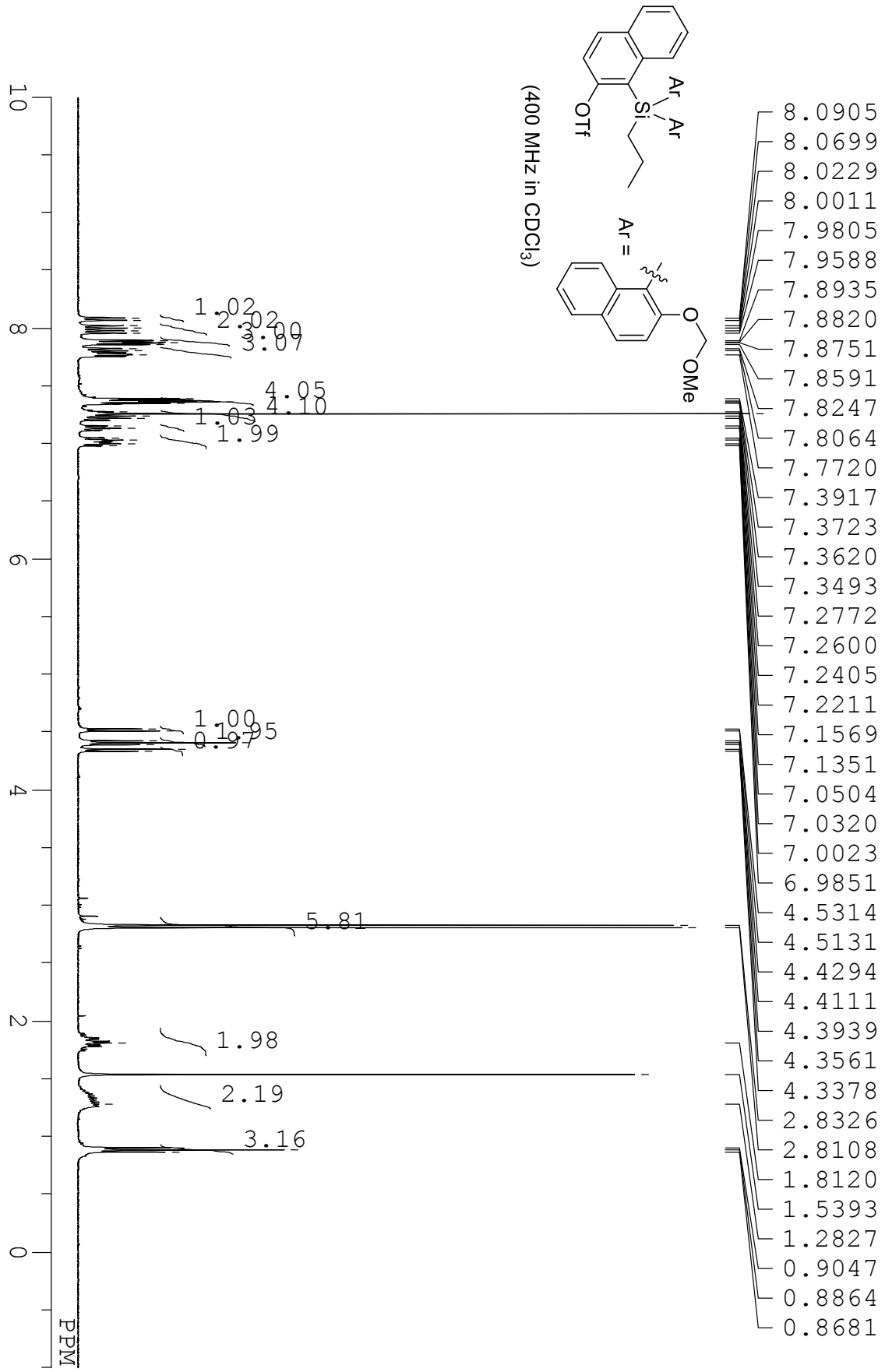
compound **1g**


(400 MHz in CDCl3)
OTf
Si
Cy
Cy
N
8.1432
8.1214
8.0859
8.0676
7.9084
7.8854
7.8648
7.8488
7.4994
7.4444
7.4272
7.4101
7.4066
7.3917
7.3894
7.3803
7.3585
7.3402
7.2600
7.2142
7.2119
7.1947
7.1775
7.1752
4.2977
4.2794
4.2622
1.9643
1.6630
1.5600
1.5313
1.4145
1.3939
1.3767
1.2392
1.2163
1.1968
1.1888
1.1659
1.1602
1.0834
1.0605
2.93
1.97
7.01
1.95
1.94
2.00
2.04
23.35
12.26
PPM

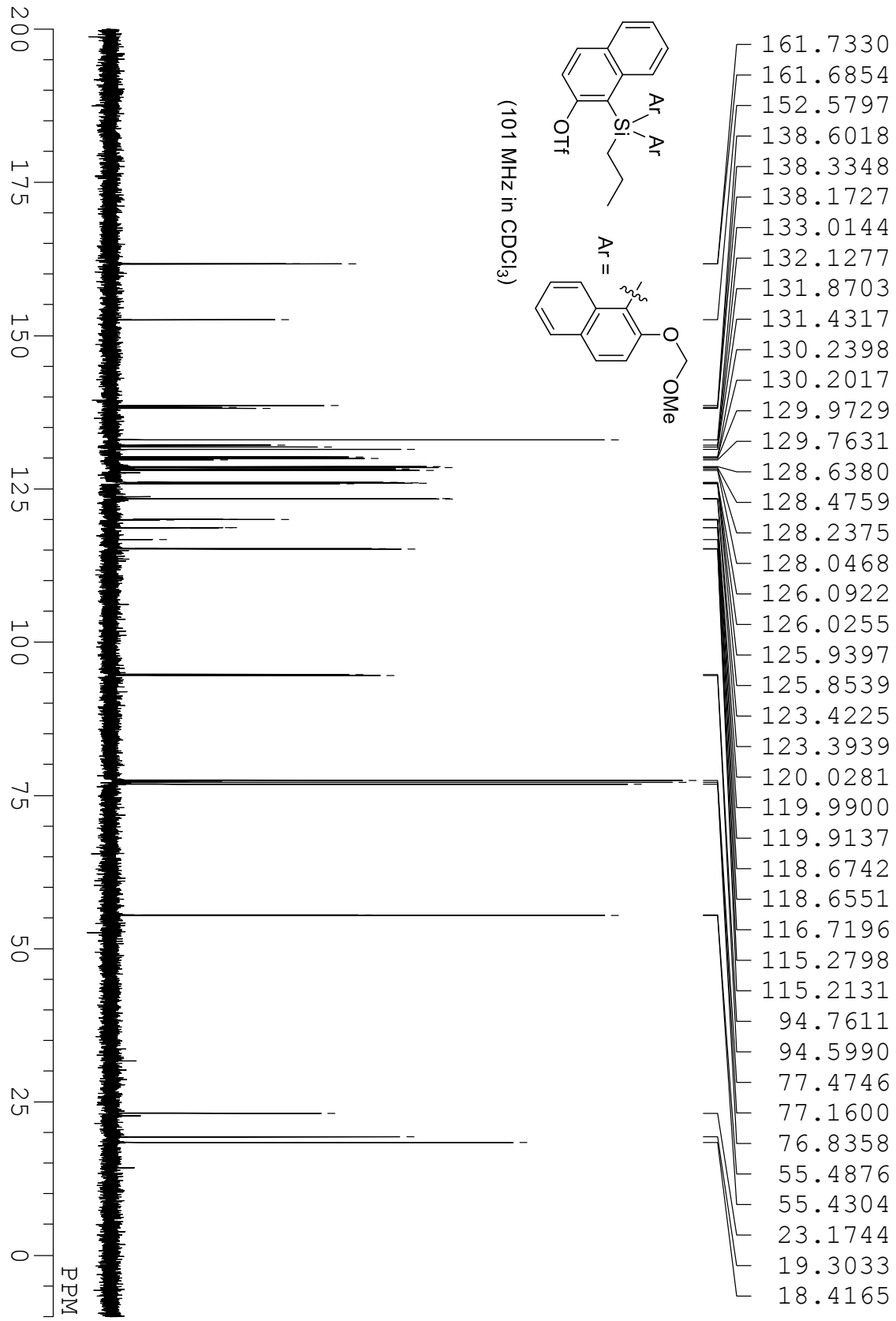
compound **1g**


(101 MHz in CDCl3)
OTf
Si
Cy
Cy
N
154.3246
140.5087
138.5350
132.6998
132.1372
129.0480
128.7143
126.5976
126.3973
125.9683
125.5964
123.4988
122.9553
120.4000
120.3046
118.7600
117.1200
113.9354
108.7962
77.4746
77.1600
76.8358
42.7396
33.1286
29.0764
28.7713
28.4566
28.3803
26.8739
26.6736
22.8025
11.8853
200
175
150
125
100
75
50
25
0
PPM

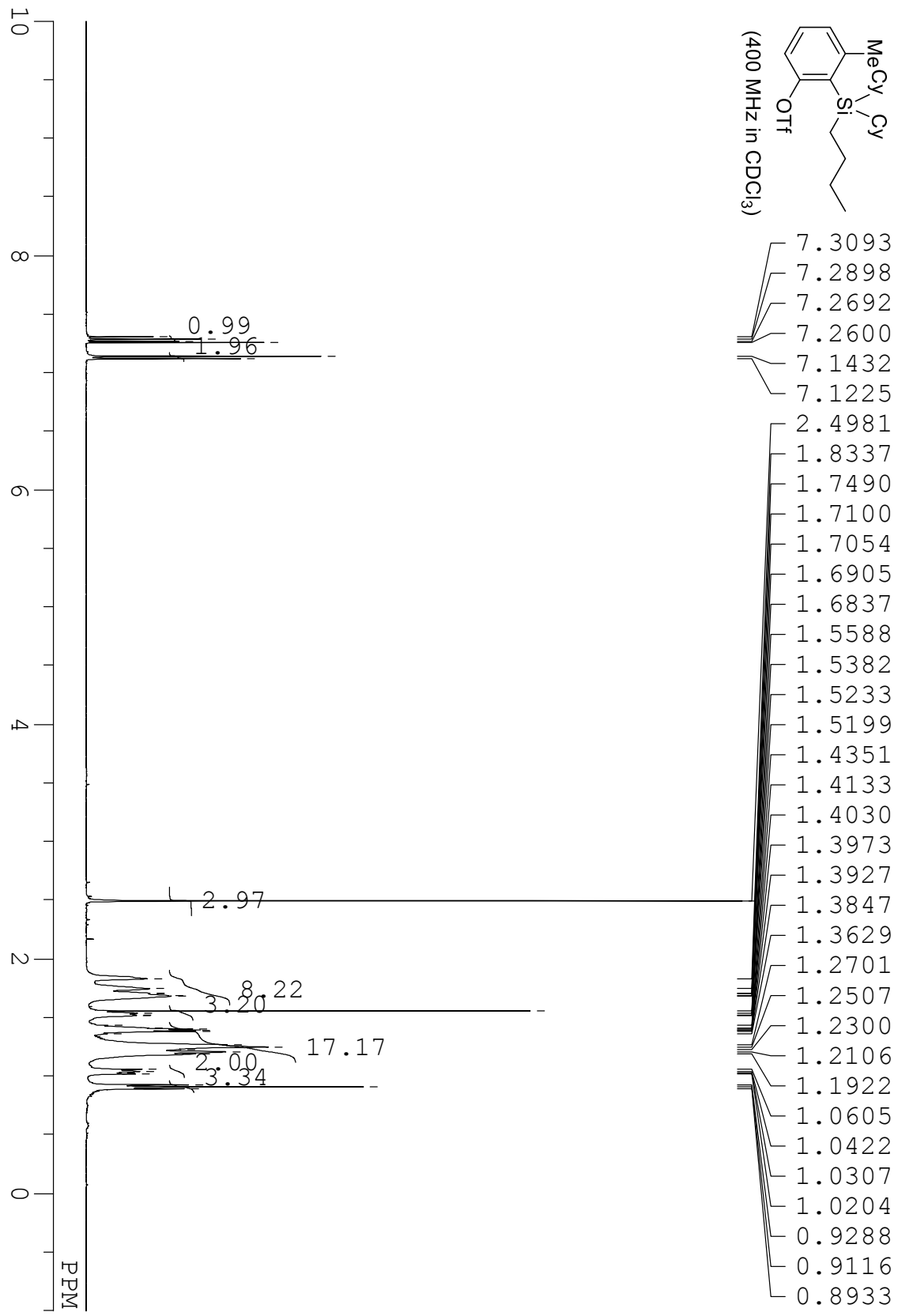
compound **1h**


(400 MHz in CDCl3)
OTf
Si
Ar
Ar
Ar =
O
OMe
1.02
2.02
3.00
3.07
4.05
4.10
1.03
1.99
1.00
1.95
0.97
5.81
1.98
2.19
3.16
PPM
8.0905
8.0699
8.0229
8.0011
7.9805
7.9588
7.8935
7.8820
7.8751
7.8591
7.8247
7.8064
7.7720
7.3917
7.3723
7.3620
7.3493
7.2772
7.2600
7.2405
7.2211
7.1569
7.1351
7.0504
7.0320
7.0023
6.9851
4.5314
4.5131
4.4294
4.4111
4.3939
4.3561
4.3378
2.8326
2.8108
1.8120
1.5393
1.2827
0.9047
0.8864
0.8681

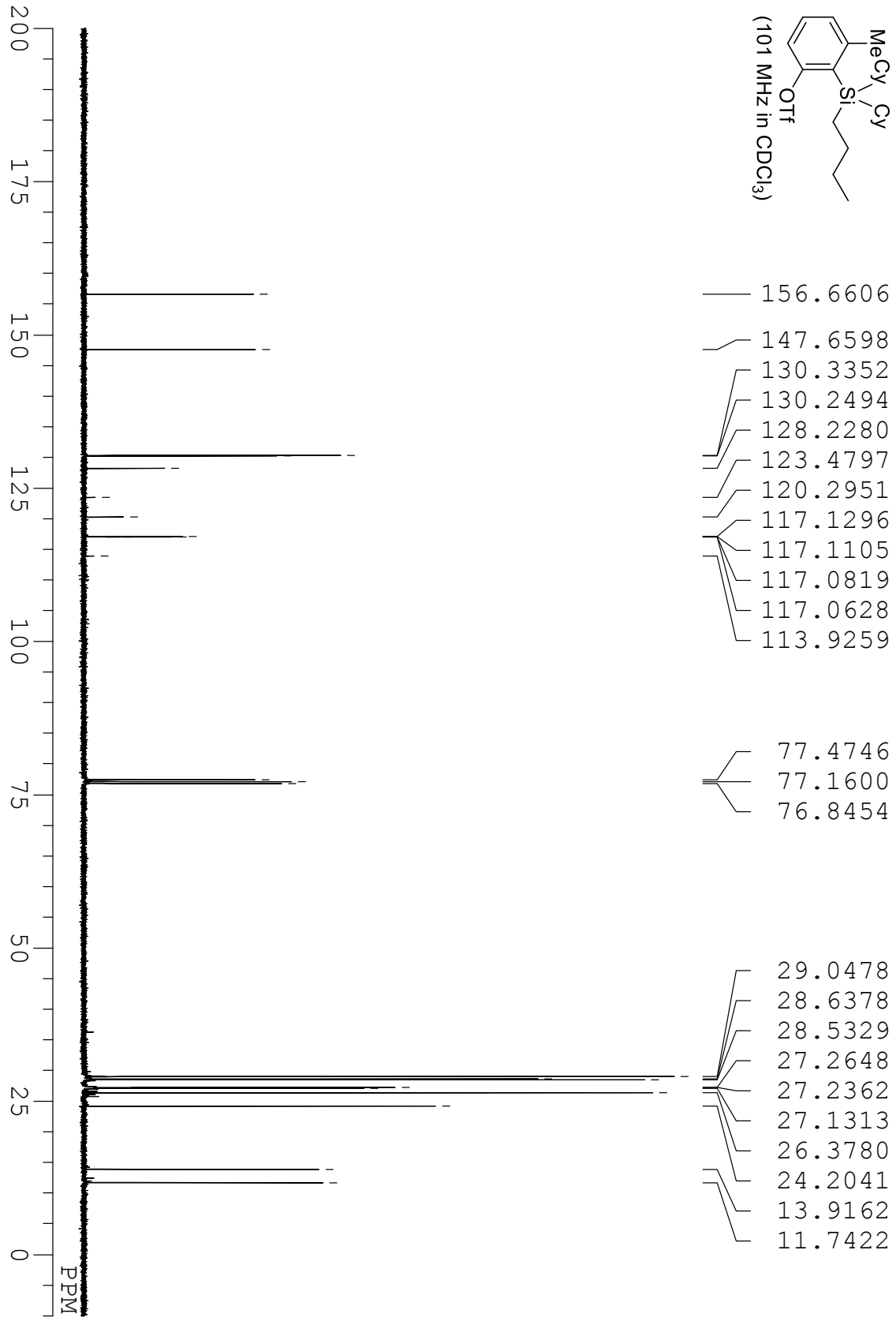
compound **1h**


(101 MHz in CDCl3)
OTf
Si
Ar
Ar
Ar =
O
OMe
200
175
150
125
100
75
50
25
0
PPM
161.7330
161.6854
152.5797
138.6018
138.3348
138.1727
133.0144
132.1277
131.8703
131.4317
130.2398
130.2017
129.9729
129.7631
128.6380
128.4759
128.2375
128.0468
126.0922
126.0255
125.9397
125.8539
123.4225
123.3939
120.0281
119.9900
119.9137
118.6742
118.6551
116.7196
115.2798
115.2131
94.7611
94.5990
77.4746
77.1600
76.8358
55.4876
55.4304
23.1744
19.3033
18.4165

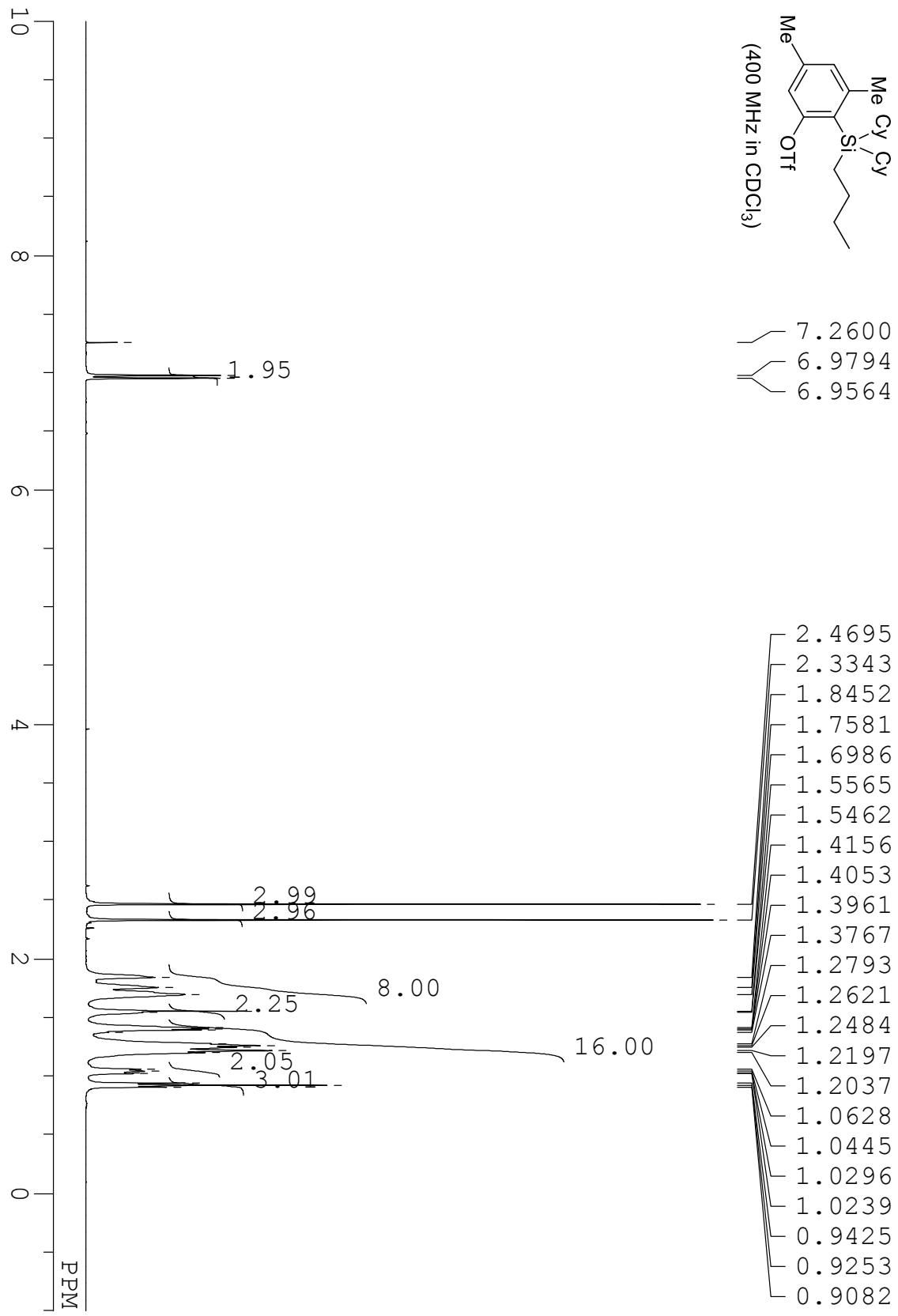
compound **1i**


(400 MHz in CDCl3)
MeCy
Cy
Si
OTf
7.3093
7.2898
7.2692
7.2600
7.1432
7.1225
2.4981
1.8337
1.7490
1.7100
1.7054
1.6905
1.6837
1.5588
1.5382
1.5233
1.5199
1.4351
1.4133
1.4030
1.3973
1.3927
1.3847
1.3629
1.2701
1.2507
1.2300
1.2106
1.1922
1.0605
1.0422
1.0307
1.0204
0.9288
0.9116
0.8933
0.99
1.96
2.97
8.22
3.20
17.17
2.00
3.34
10
8
6
4
2
0
PPM

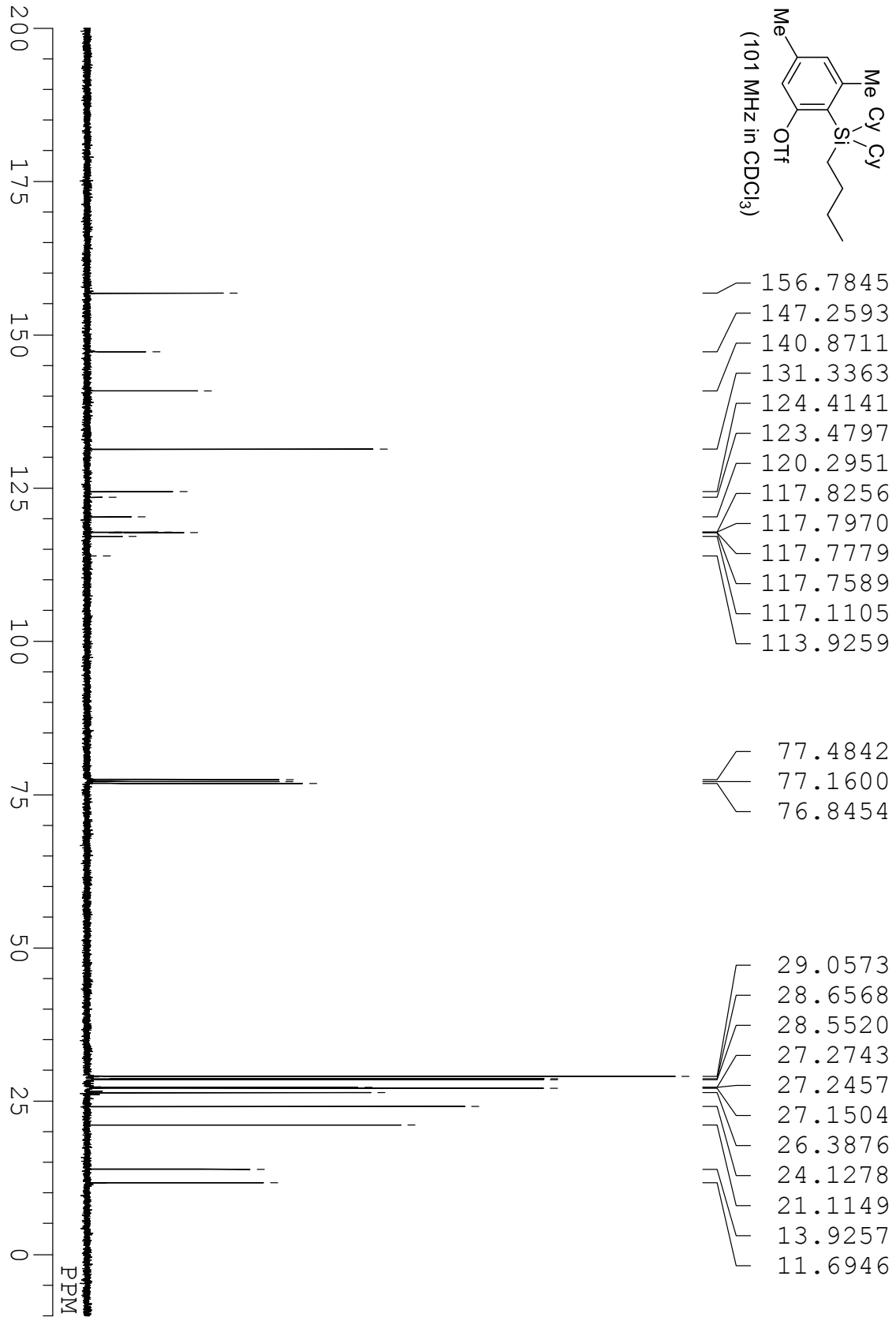
compound **1i**


(101 MHz in CDCl3)
OTf
Si
Cy
MeCy
156.6606
147.6598
130.3352
130.2494
128.2280
123.4797
120.2951
117.1296
117.1105
117.0819
117.0628
113.9259
77.4746
77.1600
76.8454
29.0478
28.6378
28.5329
27.2648
27.2362
27.1313
26.3780
24.2041
13.9162
11.7422
PPM

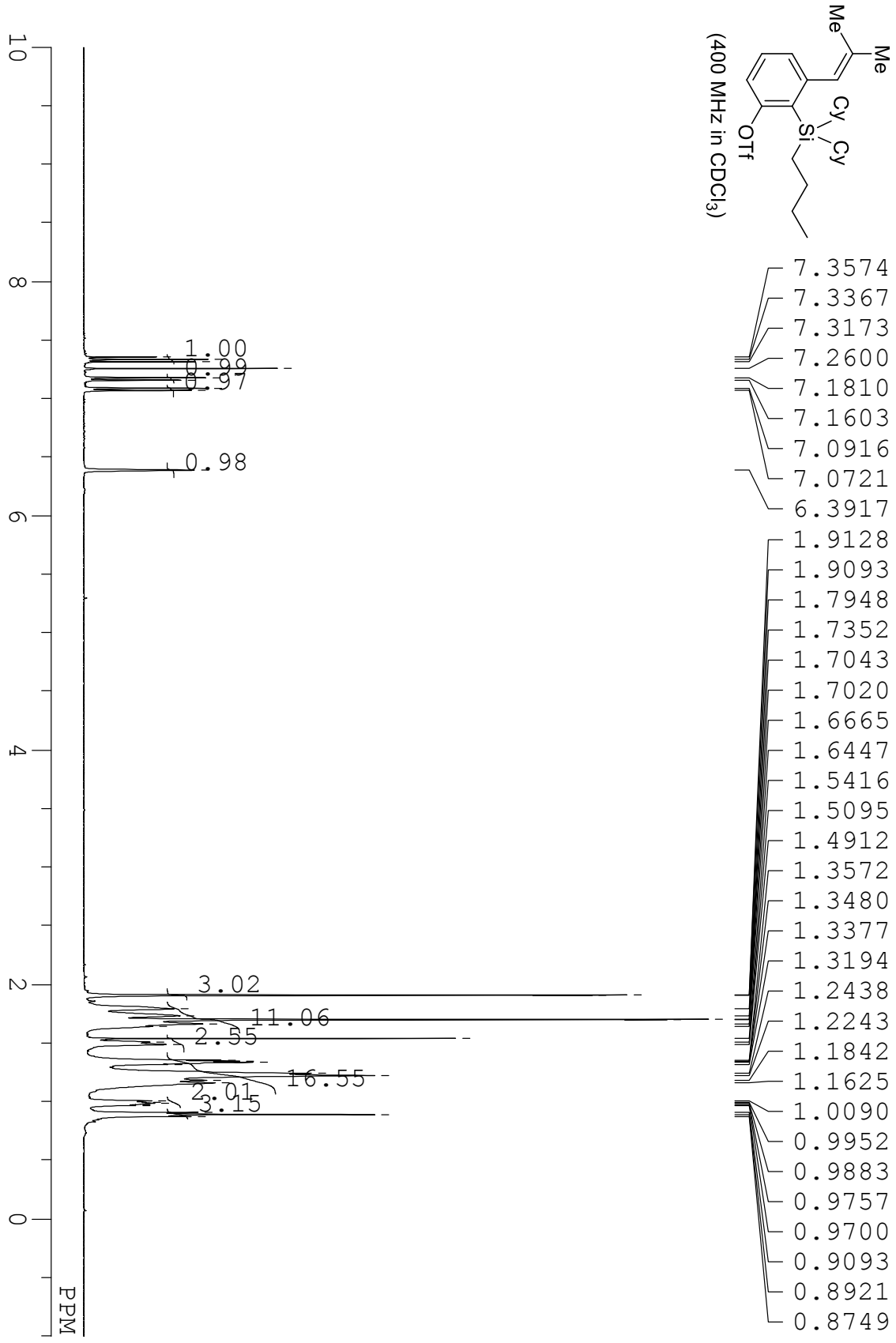
compound **1j**


(400 MHz in CDCl3)
Me
Me
Cy
Cy
Si
OTf
7.2600
6.9794
6.9564
1.95
2.99
2.96
8.00
2.25
16.00
2.05
3.01
2.4695
2.3343
1.8452
1.7581
1.6986
1.5565
1.5462
1.4156
1.4053
1.3961
1.3767
1.2793
1.2621
1.2484
1.2197
1.2037
1.0628
1.0445
1.0296
1.0239
0.9425
0.9253
0.9082
10
8
6
4
2
0
PPM

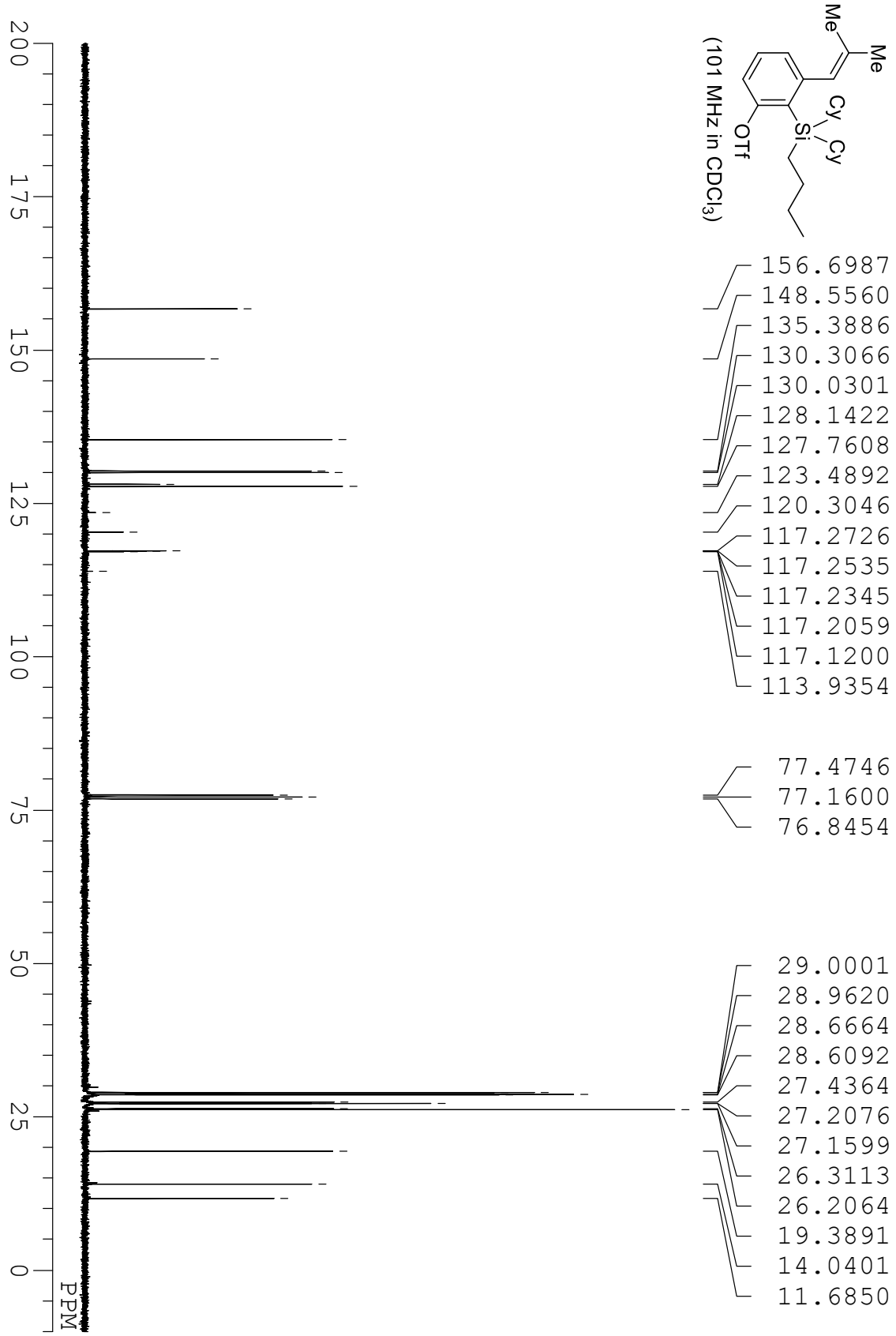
compound **1j**


(101 MHz in CDCl3)
Me
OTf
Si
Cy
Cy
Me
156.7845
147.2593
140.8711
131.3363
124.4141
123.4797
120.2951
117.8256
117.7970
117.7779
117.7589
117.1105
113.9259
77.4842
77.1600
76.8454
29.0573
28.6568
28.5520
27.2743
27.2457
27.1504
26.3876
24.1278
21.1149
13.9257
11.6946
200
175
150
125
100
75
50
25
0
PPM

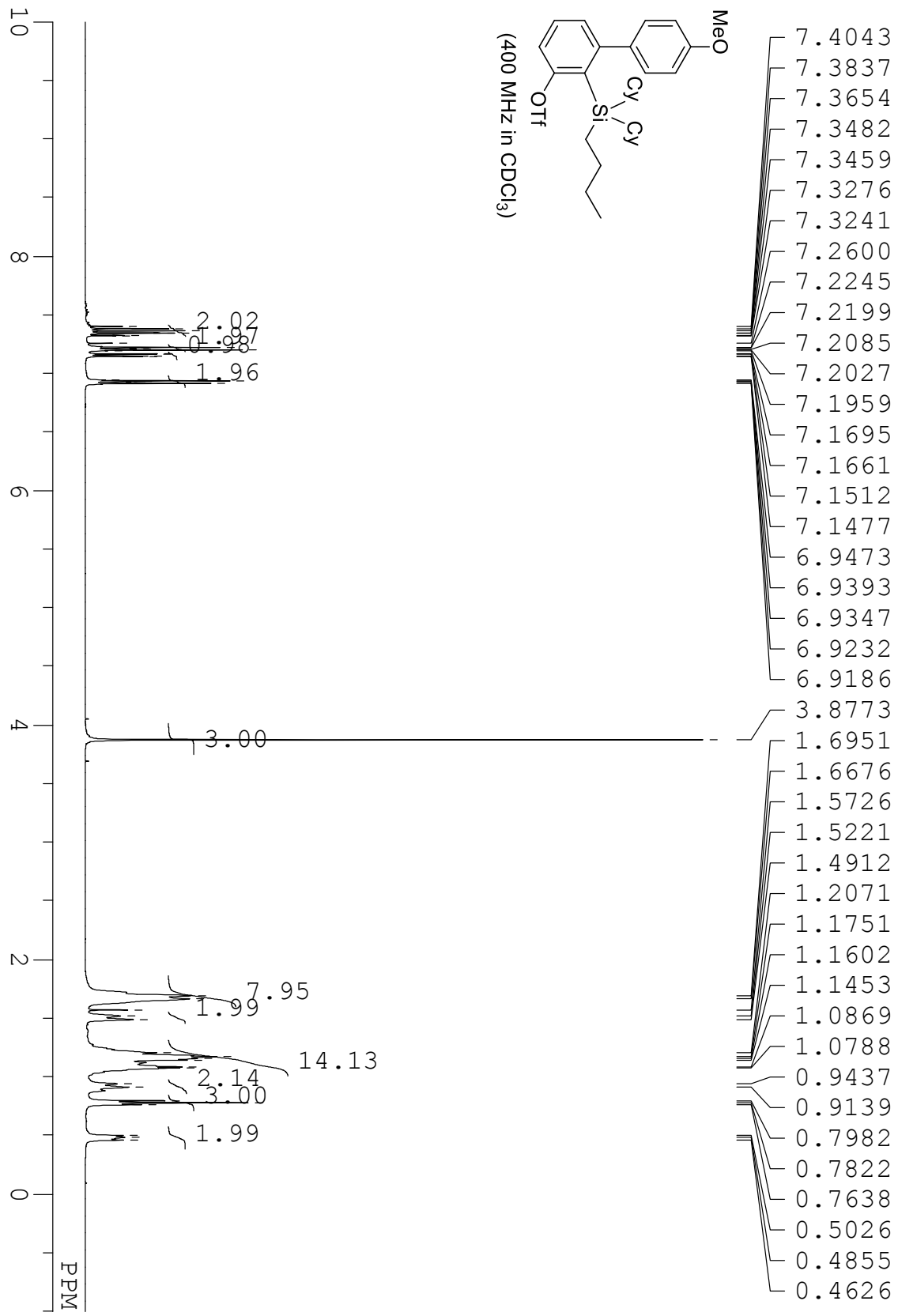
compound **1k**


(400 MHz in CDCl3)
Me
Me
Cy
Cy
Si
OTf
7.3574
7.3367
7.3173
7.2600
7.1810
7.1603
7.0916
7.0721
6.3917
1.9128
1.9093
1.7948
1.7352
1.7043
1.7020
1.6665
1.6447
1.5416
1.5095
1.4912
1.3572
1.3480
1.3377
1.3194
1.2438
1.2243
1.1842
1.1625
1.0090
0.9952
0.9883
0.9757
0.9700
0.9093
0.8921
0.8749
1.00
0.99
0.97
0.98
3.02
11.06
2.55
16.55
2.01
3.15
10
8
6
4
2
0
PPM

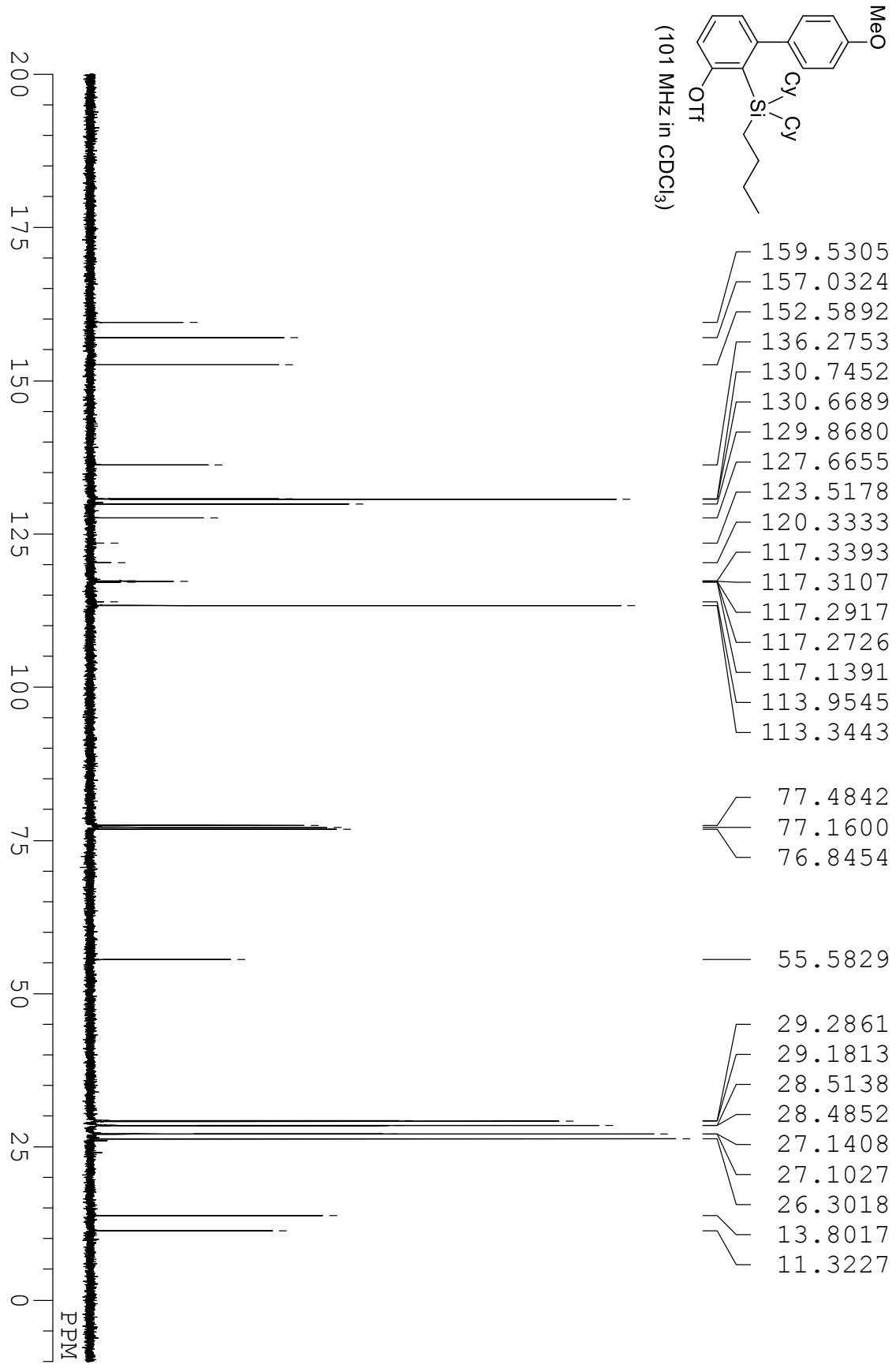
compound **1k**


(101 MHz in CDCl3)
Me
Me
Cy
Cy
Si
OTf
156.6987
148.5560
135.3886
130.3066
130.0301
128.1422
127.7608
123.4892
120.3046
117.2726
117.2535
117.2345
117.2059
117.1200
113.9354
77.4746
77.1600
76.8454
29.0001
28.9620
28.6664
28.6092
27.4364
27.2076
27.1599
26.3113
26.2064
19.3891
14.0401
11.6850
200
175
150
125
100
75
50
25
0
PPM

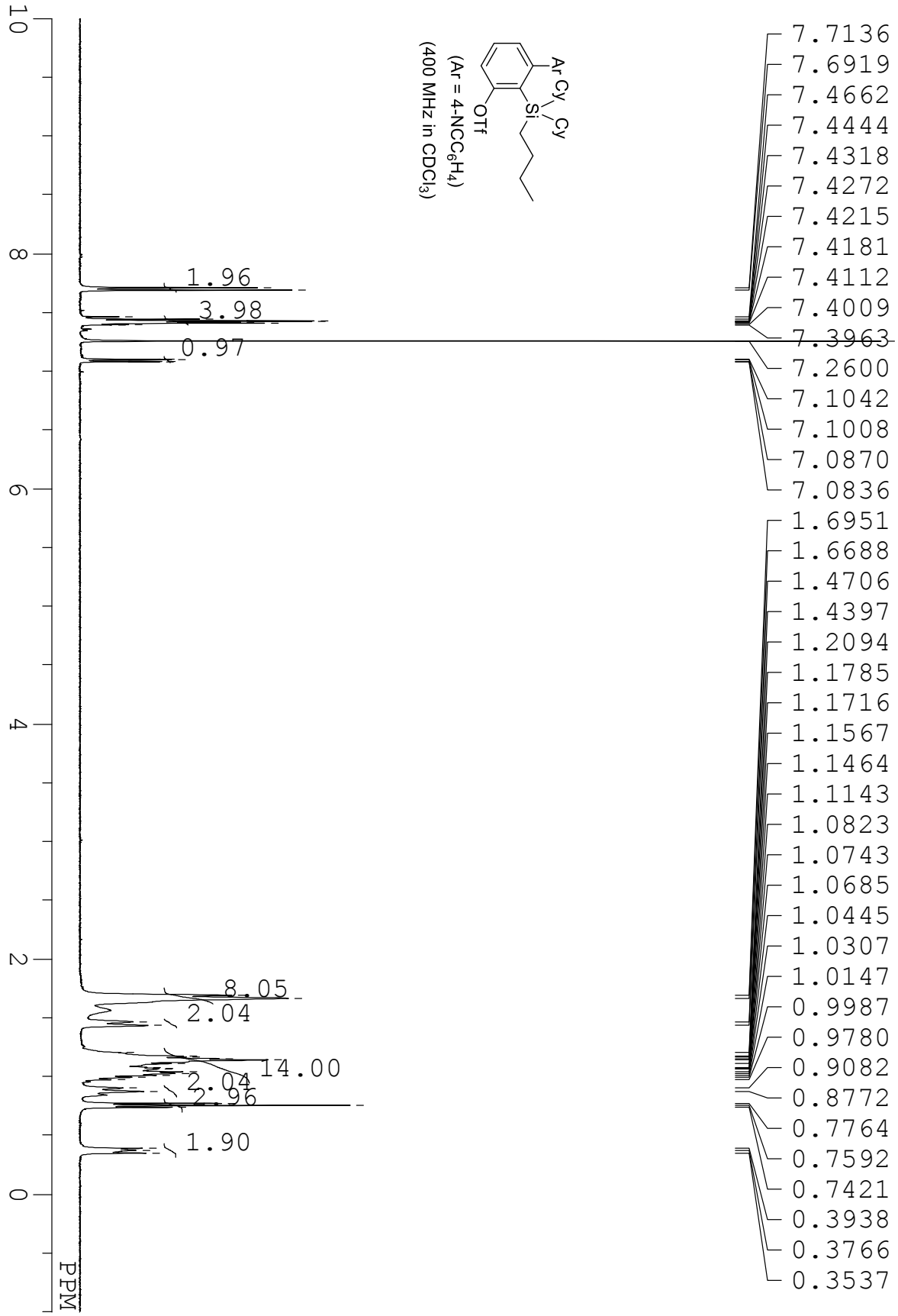
compound **1l**


(400 MHz in CDCl3)
MeO
OTf
Si
Cy
Cy
PPM
10
8
6
4
2
0
2.02
1.87
0.98
1.96
3.00
7.95
1.99
14.13
2.14
3.00
1.99
7.4043
7.3837
7.3654
7.3482
7.3459
7.3276
7.3241
7.2600
7.2245
7.2199
7.2085
7.2027
7.1959
7.1695
7.1661
7.1512
7.1477
6.9473
6.9393
6.9347
6.9232
6.9186
3.8773
1.6951
1.6676
1.5726
1.5221
1.4912
1.2071
1.1751
1.1602
1.1453
1.0869
1.0788
0.9437
0.9139
0.7982
0.7822
0.7638
0.5026
0.4855
0.4626

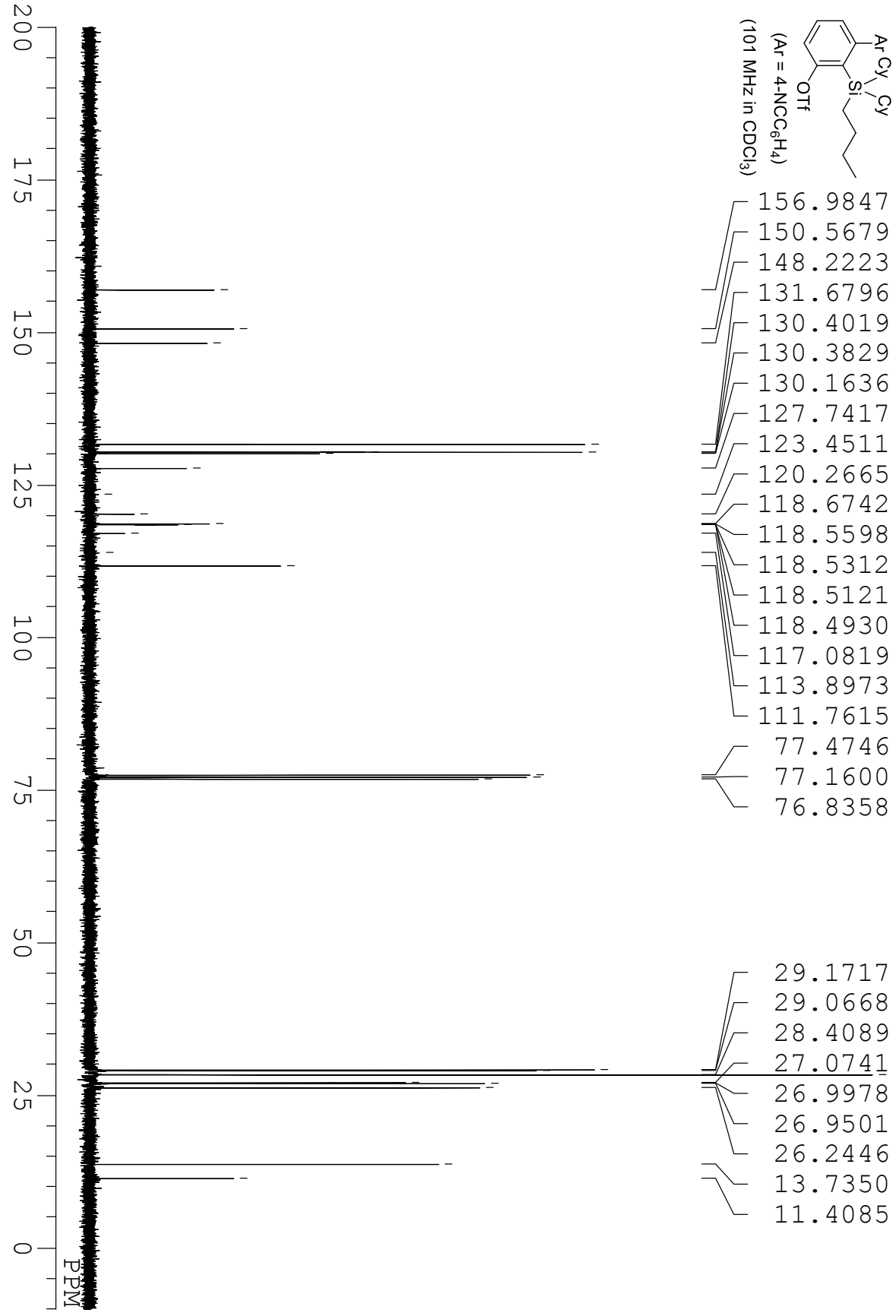
compound **1l**


MeO
Cy
Cy
Si
OTf
(101 MHz in CDCl3)
159.5305
157.0324
152.5892
136.2753
130.7452
130.6689
129.8680
127.6655
123.5178
120.3333
117.3393
117.3107
117.2917
117.2726
117.1391
113.9545
113.3443
77.4842
77.1600
76.8454
55.5829
29.2861
29.1813
28.5138
28.4852
27.1408
27.1027
26.3018
13.8017
11.3227
200
175
150
125
100
75
50
25
0
PPM

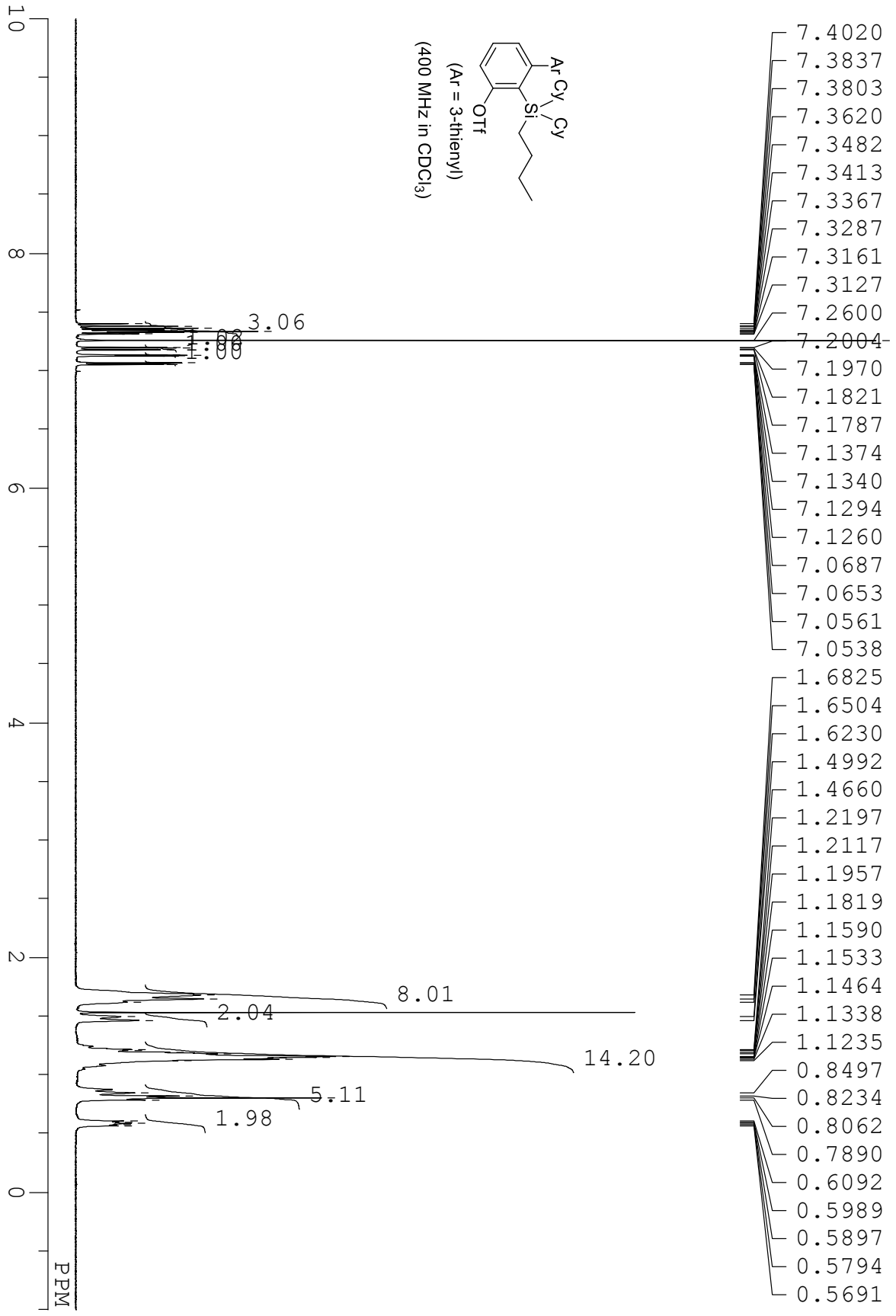
compound **1m**


Ar Cy Cy
Si
OTf
(Ar = 4-NCC6H4)
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
1.96
3.98
0.97
8.05
2.04
14.00
2.04
2.96
1.90
7.7136
7.6919
7.4662
7.4444
7.4318
7.4272
7.4215
7.4181
7.4112
7.4009
7.3963
7.2600
7.1042
7.1008
7.0870
7.0836
1.6951
1.6688
1.4706
1.4397
1.2094
1.1785
1.1716
1.1567
1.1464
1.1143
1.0823
1.0743
1.0685
1.0445
1.0307
1.0147
0.9987
0.9780
0.9082
0.8772
0.7764
0.7592
0.7421
0.3938
0.3766
0.3537

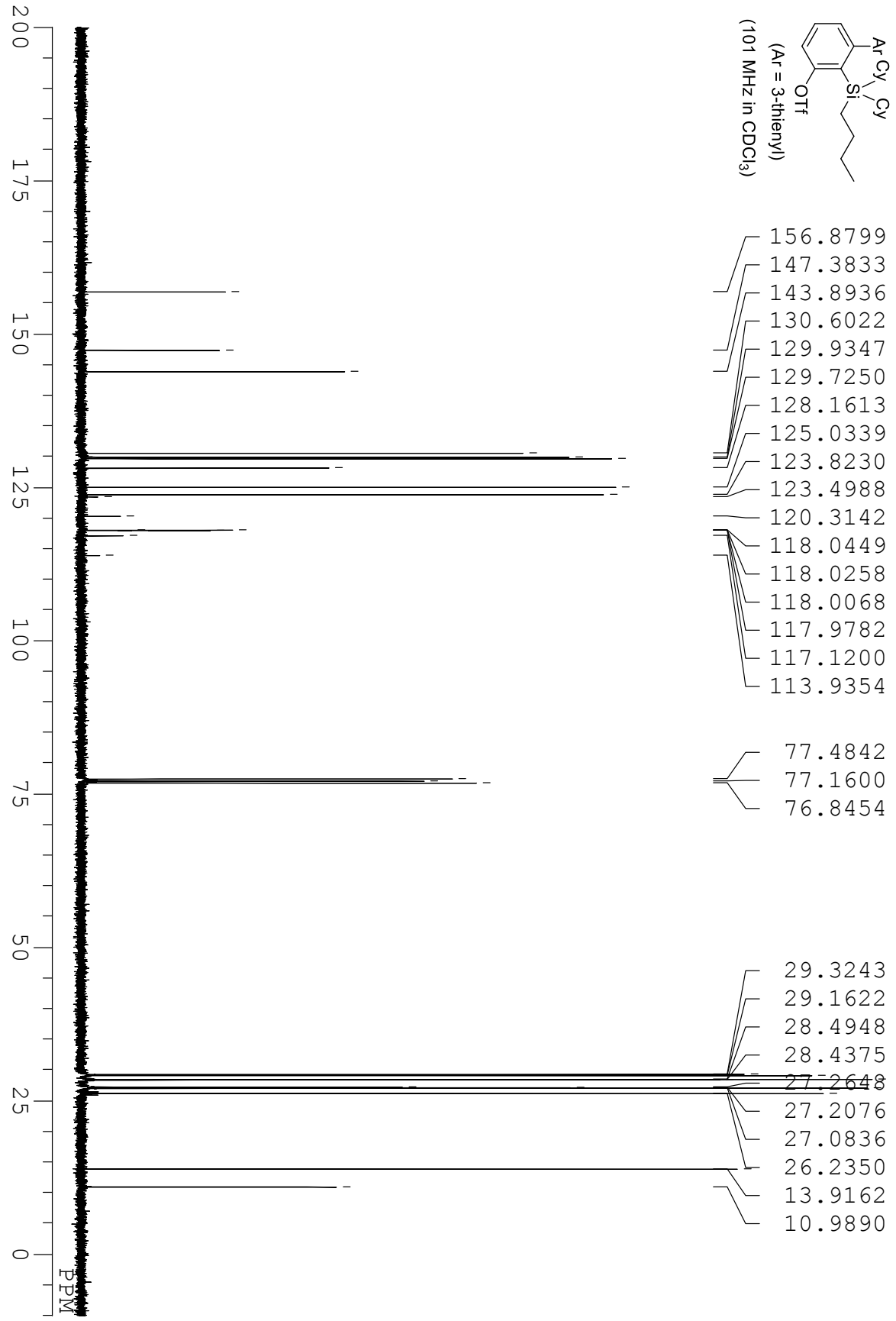
compound **1m**


Ar Cy Cy
Si
OTf
(Ar = 4-NCC6H4)
(101 MHz in CDCl3)
156.9847
150.5679
148.2223
131.6796
130.4019
130.3829
130.1636
127.7417
123.4511
120.2665
118.6742
118.5598
118.5312
118.5121
118.4930
117.0819
113.8973
111.7615
77.4746
77.1600
76.8358
29.1717
29.0668
28.4089
27.0741
26.9978
26.9501
26.2446
13.7350
11.4085
200
175
150
125
100
75
50
25
0
PPM

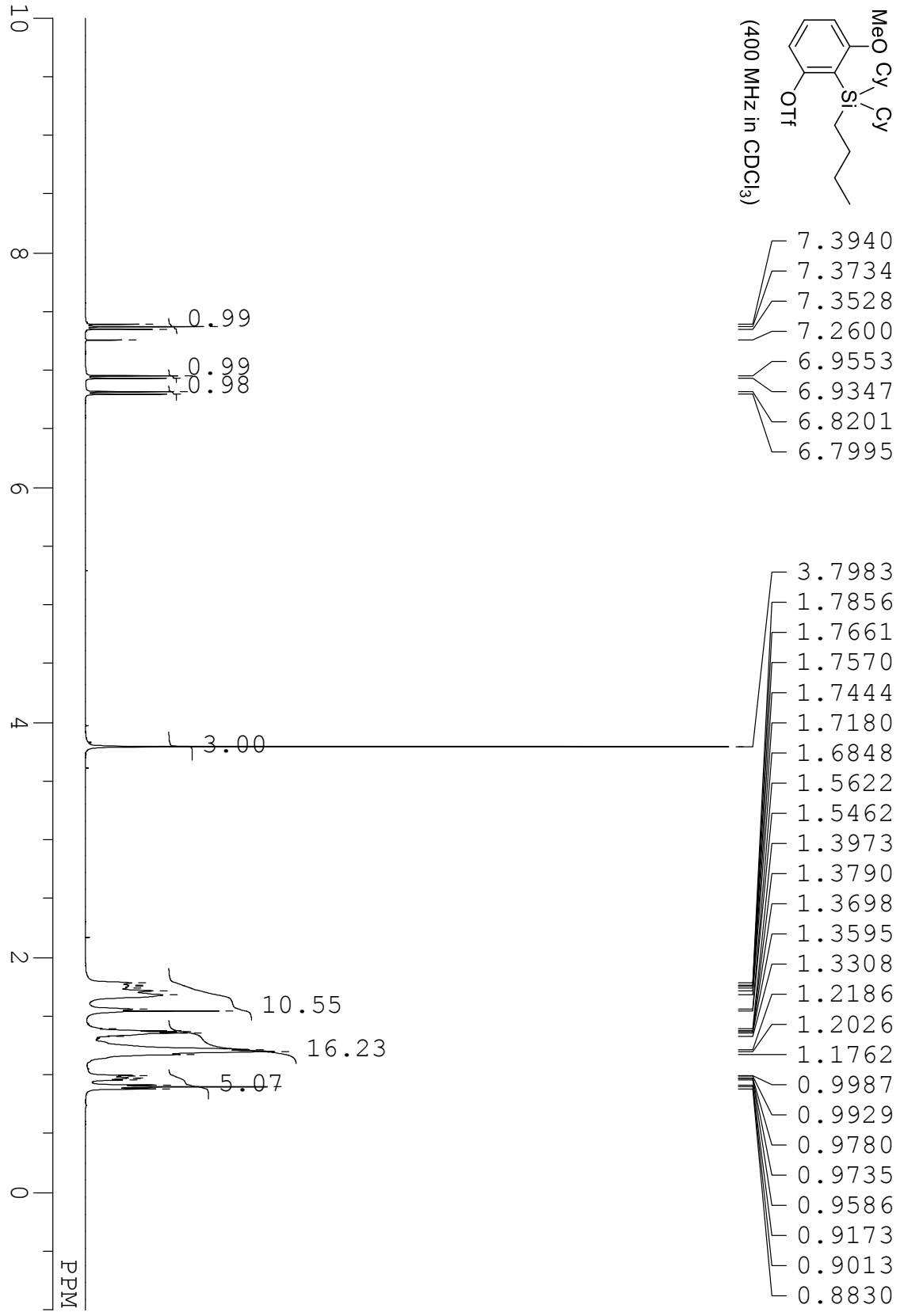
compound **1n**


(Ar = 3-thienyl)
(400 MHz in CDCl3)
Ar Cy Cy
Si
OTf
7.4020
7.3837
7.3803
7.3620
7.3482
7.3413
7.3367
7.3287
7.3161
7.3127
7.2600
7.2004
7.1970
7.1821
7.1787
7.1374
7.1340
7.1294
7.1260
7.0687
7.0653
7.0561
7.0538
1.6825
1.6504
1.6230
1.4992
1.4660
1.2197
1.2117
1.1957
1.1819
1.1590
1.1533
1.1464
1.1338
1.1235
0.8497
0.8234
0.8062
0.7890
0.6092
0.5989
0.5897
0.5794
0.5691
3.06
8.01
2.04
14.20
5.11
1.98
PPM

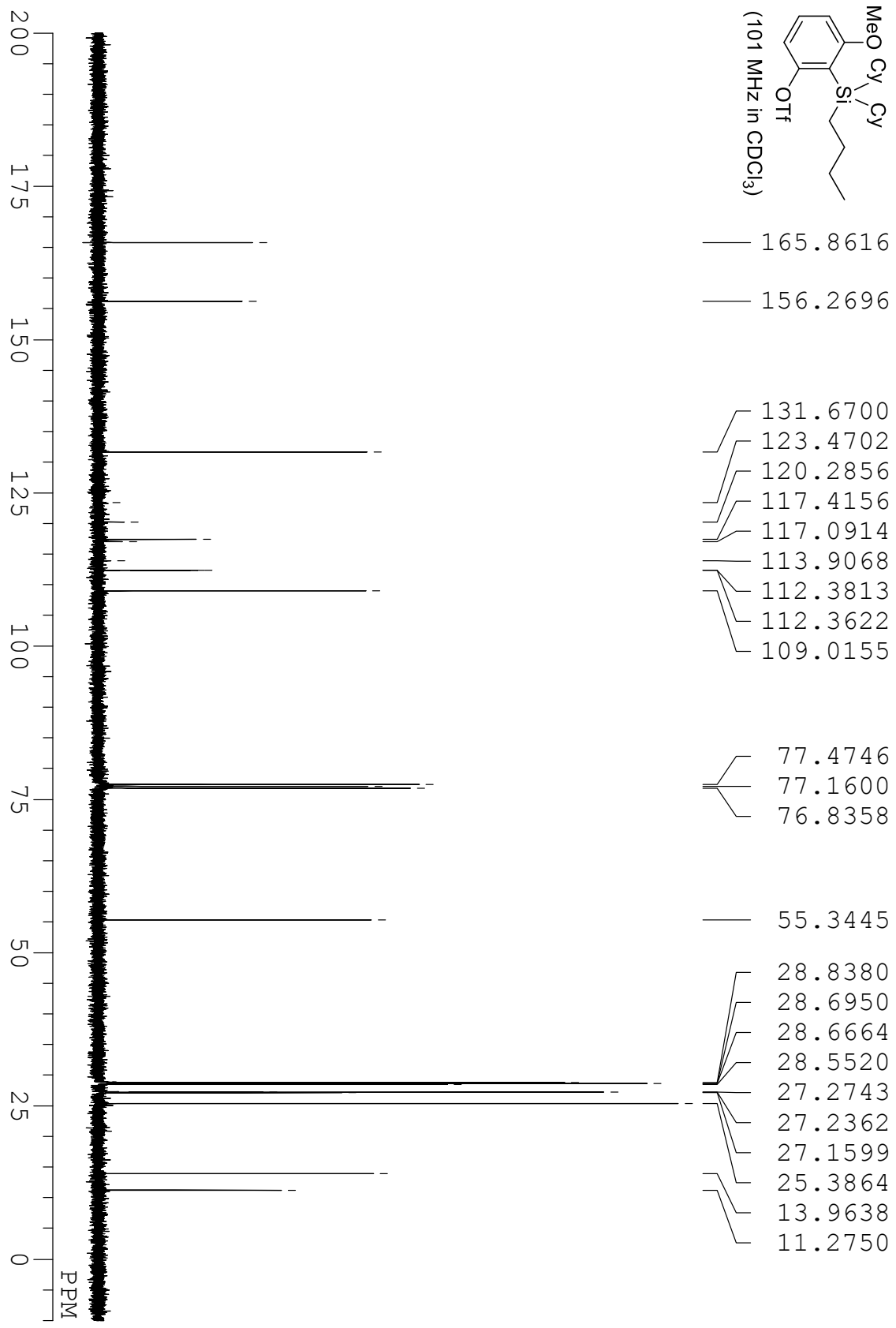
compound **1n**


(101 MHz in CDCl3)
(Ar = 3-thienyl)
OTf
Si
Cy
Cy
Ar
156.8799
147.3833
143.8936
130.6022
129.9347
129.7250
128.1613
125.0339
123.8230
123.4988
120.3142
118.0449
118.0258
118.0068
117.9782
117.1200
113.9354
77.4842
77.1600
76.8454
29.3243
29.1622
28.4948
28.4375
27.2648
27.2076
27.0836
26.2350
13.9162
10.9890
200
175
150
125
100
75
50
25
0
PPM

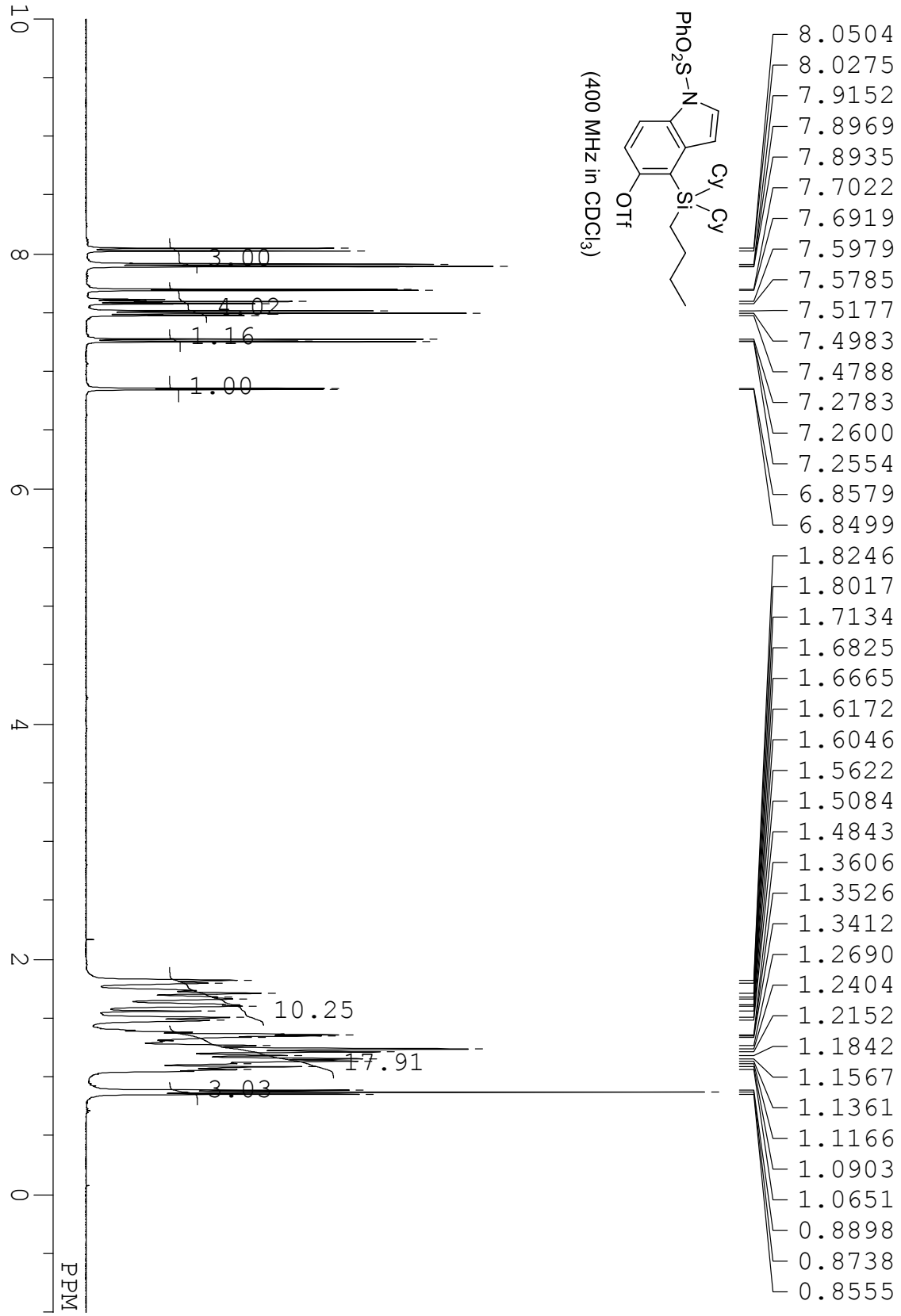
compound **1o**


MeO
Cy
Cy
Si
OTf
(400 MHz in CDCl3)
7.3940
7.3734
7.3528
7.2600
6.9553
6.9347
6.8201
6.7995
3.7983
1.7856
1.7661
1.7570
1.7444
1.7180
1.6848
1.5622
1.5462
1.3973
1.3790
1.3698
1.3595
1.3308
1.2186
1.2026
1.1762
0.9987
0.9929
0.9780
0.9735
0.9586
0.9173
0.9013
0.8830
0.99
0.99
0.98
3.00
10.55
16.23
5.07
10
8
6
4
2
0
PPM

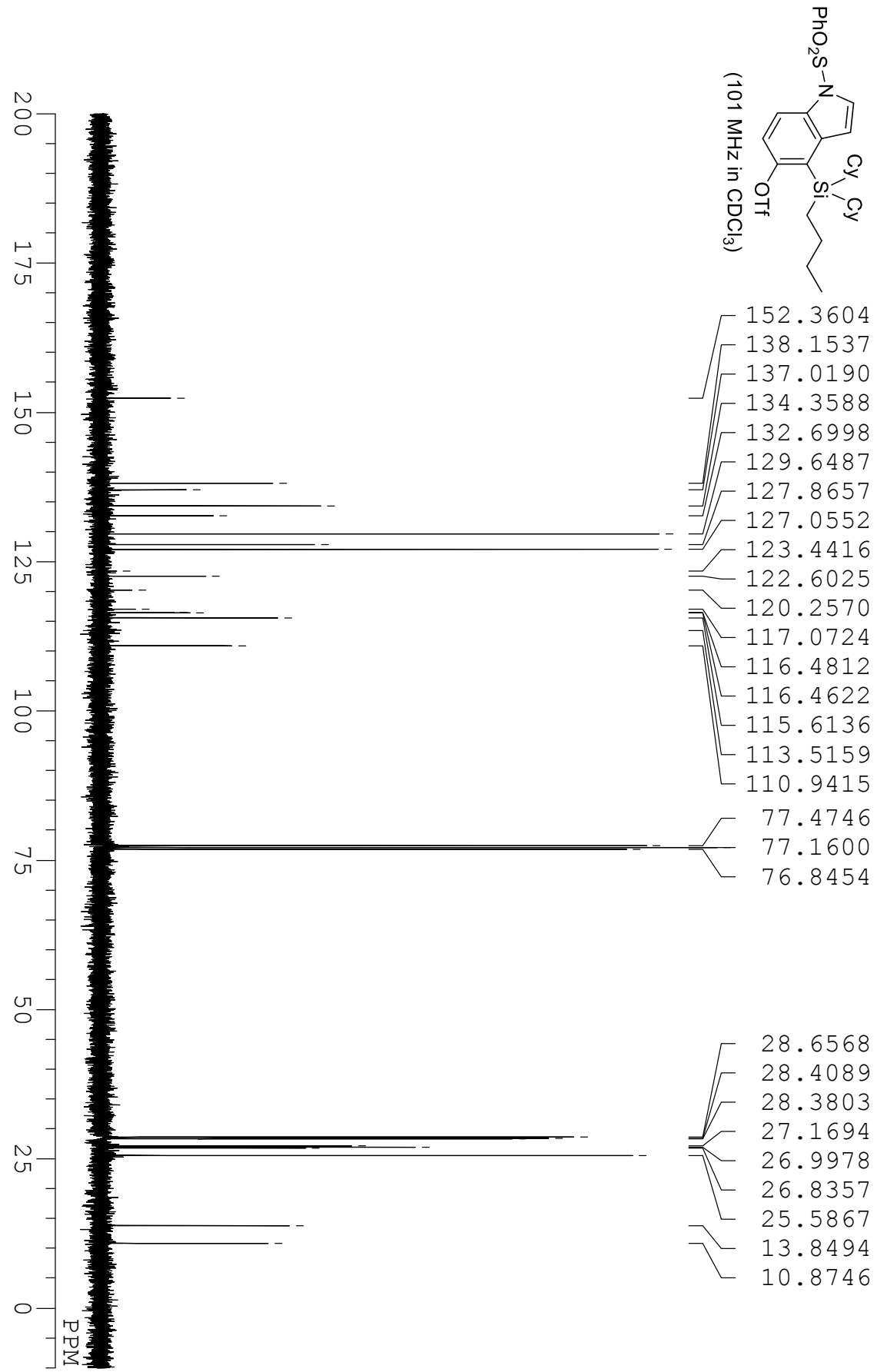
compound **1o**


MeO
Cy
Cy
Si
OTf
(101 MHz in CDCl3)
165.8616
156.2696
131.6700
123.4702
120.2856
117.4156
117.0914
113.9068
112.3813
112.3622
109.0155
77.4746
77.1600
76.8358
55.3445
28.8380
28.6950
28.6664
28.5520
27.2743
27.2362
27.1599
25.3864
13.9638
11.2750
200
175
150
125
100
75
50
25
0
PPM

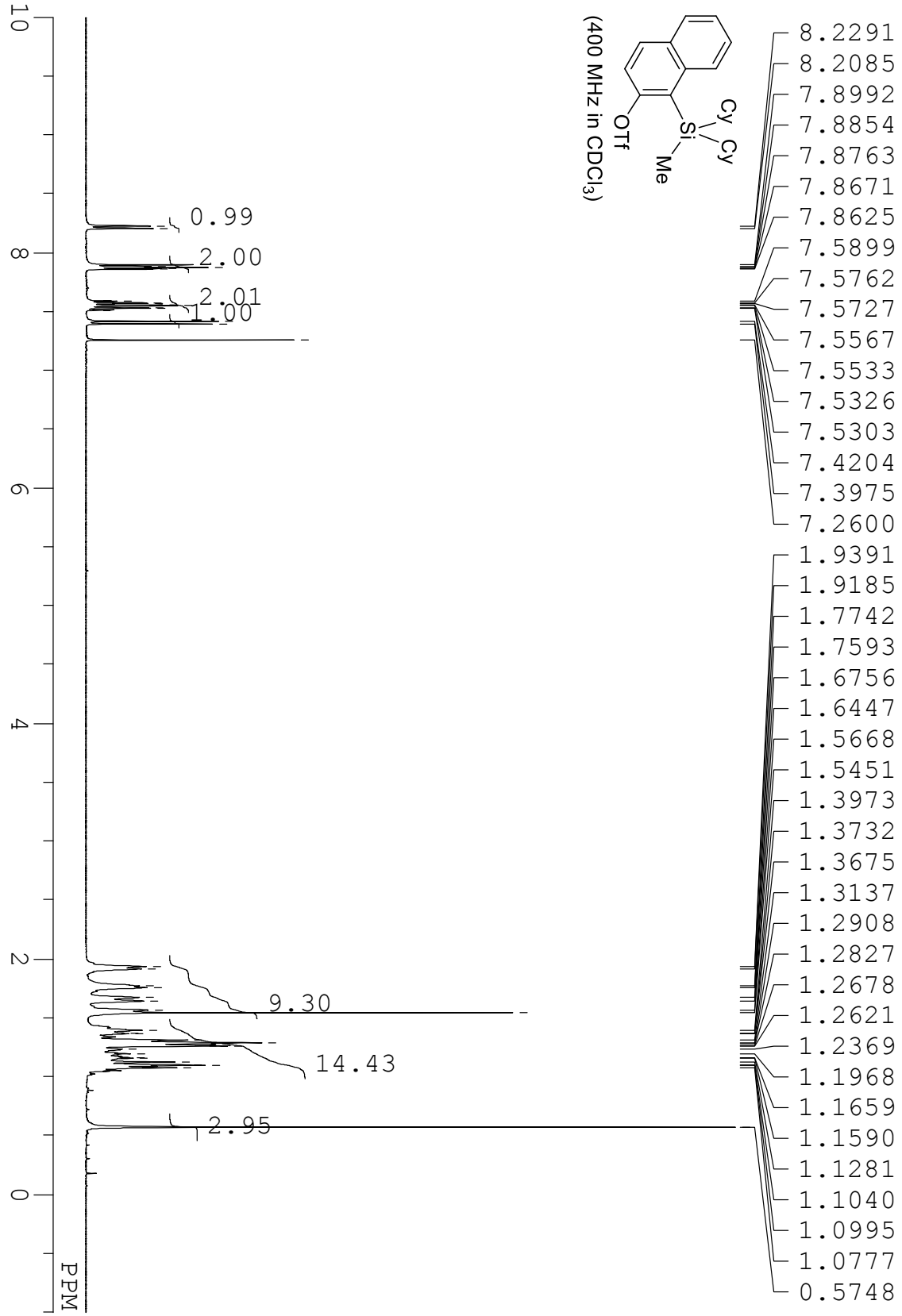
compound **1p**


PhO2S–N
Cy
Cy
Si
OTf
(400 MHz in CDCl3)
8.0504
8.0275
7.9152
7.8969
7.8935
7.7022
7.6919
7.5979
7.5785
7.5177
7.4983
7.4788
7.2783
7.2600
7.2554
6.8579
6.8499
1.8246
1.8017
1.7134
1.6825
1.6665
1.6172
1.6046
1.5622
1.5084
1.4843
1.3606
1.3526
1.3412
1.2690
1.2404
1.2152
1.1842
1.1567
1.1361
1.1166
1.0903
1.0651
0.8898
0.8738
0.8555
3.00
4.02
1.16
1.00
10.25
17.91
3.03
10
8
6
4
2
0
PPM

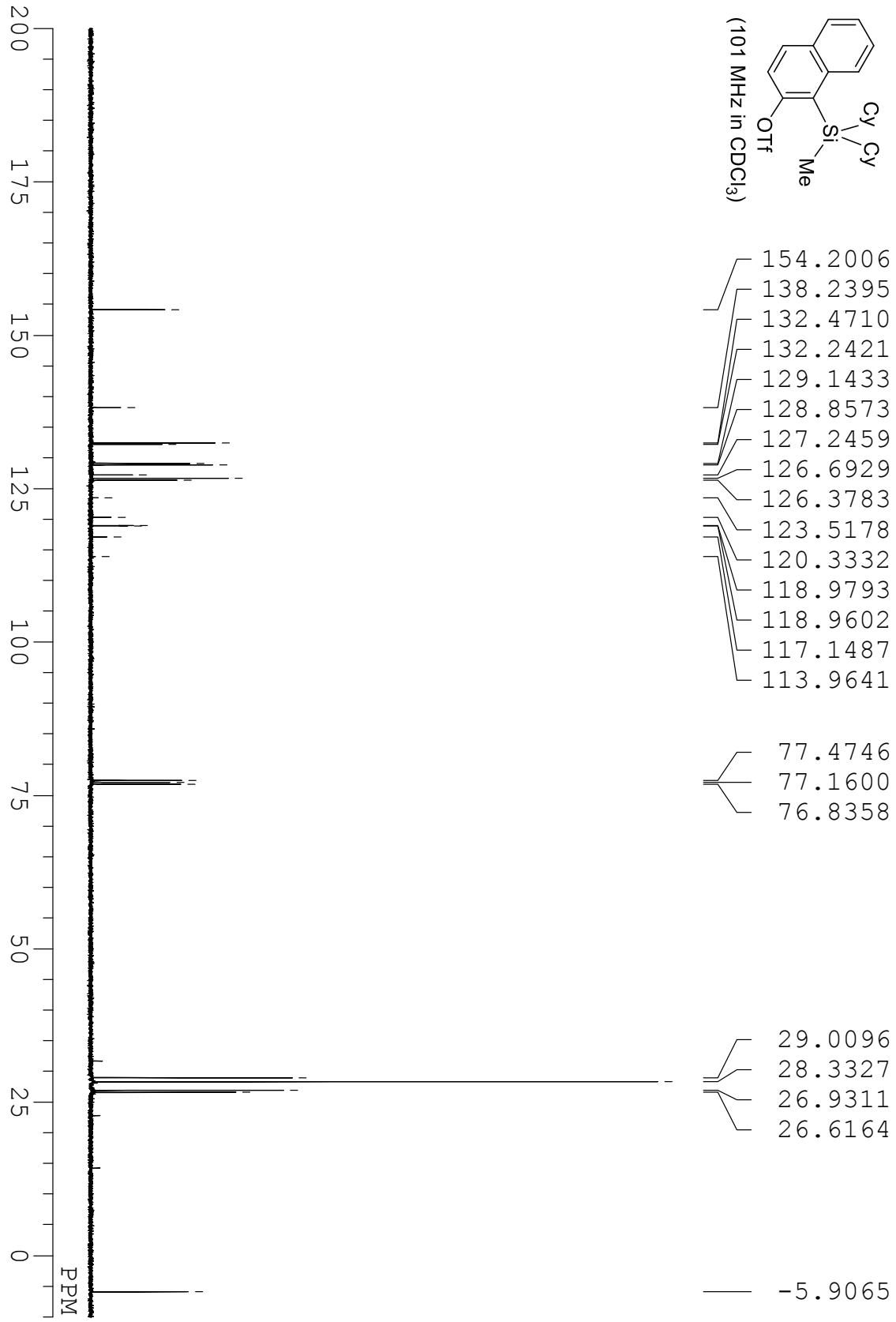
compound **1p**


PhO2S–N
Cy
Cy
Si
OTf
(101 MHz in CDCl3)
152.3604
138.1537
137.0190
134.3588
132.6998
129.6487
127.8657
127.0552
123.4416
122.6025
120.2570
117.0724
116.4812
116.4622
115.6136
113.5159
110.9415
77.4746
77.1600
76.8454
28.6568
28.4089
28.3803
27.1694
26.9978
26.8357
25.5867
13.8494
10.8746
200
175
150
125
100
75
50
25
0
PPM

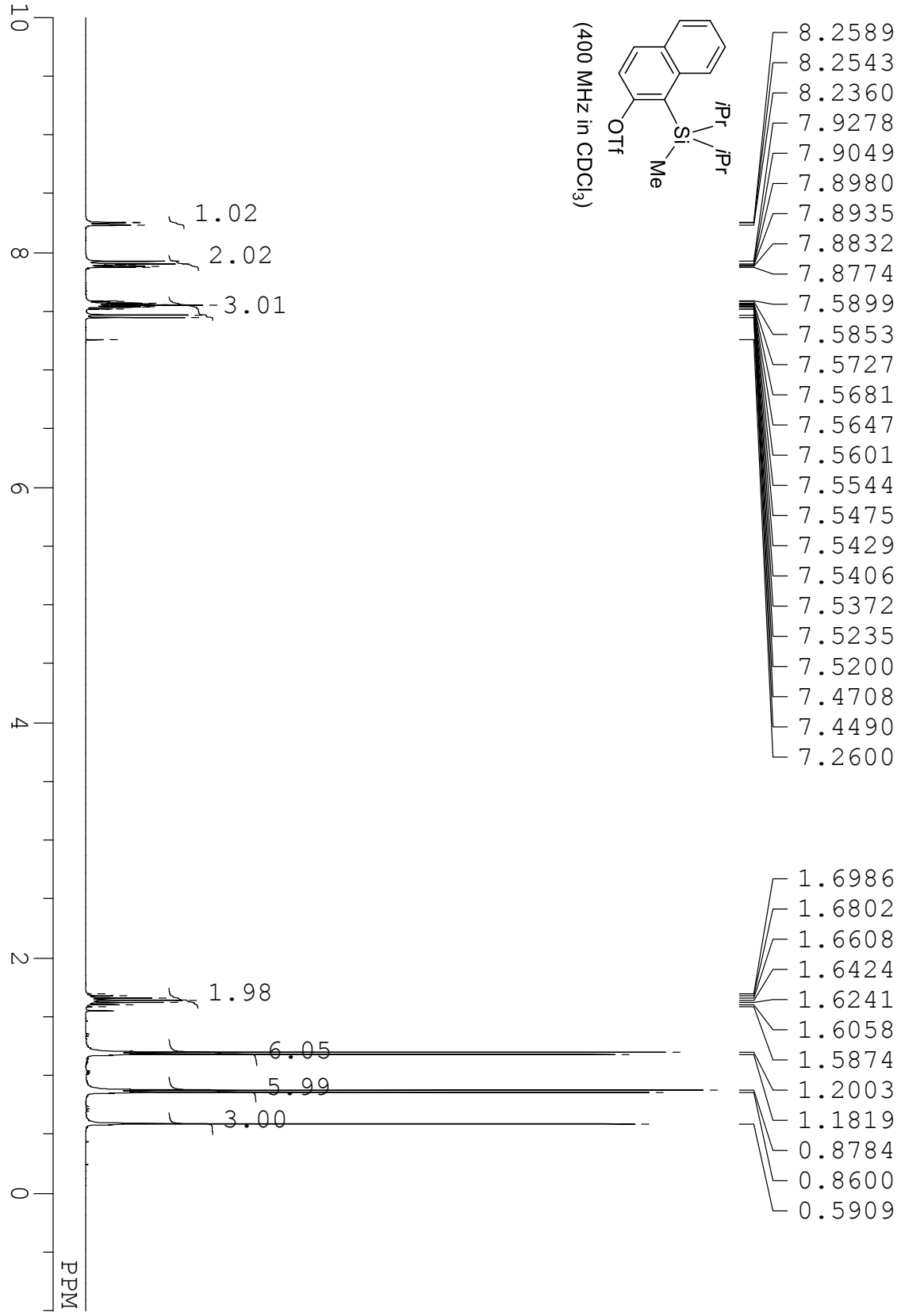
compound **1q**


(400 MHz in CDCl3)
OTf
Si
Cy
Cy
Me
0.99
2.00
2.01
1.00
9.30
14.43
2.95
PPM
8.2291
8.2085
7.8992
7.8854
7.8763
7.8671
7.8625
7.5899
7.5762
7.5727
7.5567
7.5533
7.5326
7.5303
7.4204
7.3975
7.2600
1.9391
1.9185
1.7742
1.7593
1.6756
1.6447
1.5668
1.5451
1.3973
1.3732
1.3675
1.3137
1.2908
1.2827
1.2678
1.2621
1.2369
1.1968
1.1659
1.1590
1.1281
1.1040
1.0995
1.0777
0.5748

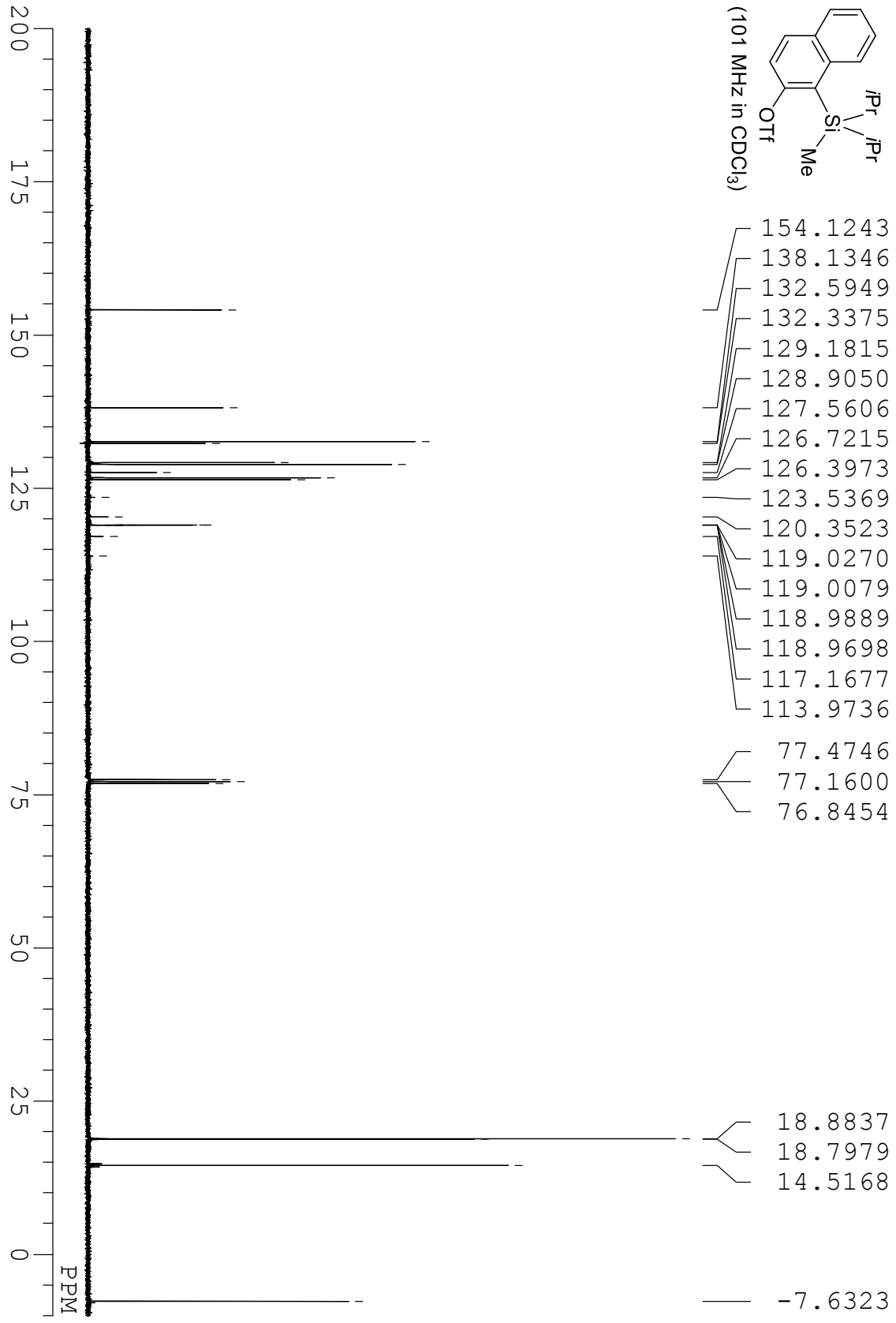
compound **1q**


(101 MHz in CDCl3)
OTf
Si
Me
Cy
Cy
154.2006
138.2395
132.4710
132.2421
129.1433
128.8573
127.2459
126.6929
126.3783
123.5178
120.3332
118.9793
118.9602
117.1487
113.9641
77.4746
77.1600
76.8358
29.0096
28.3327
26.9311
26.6164
-5.9065
PPM
200
175
150
125
100
75
50
25
0

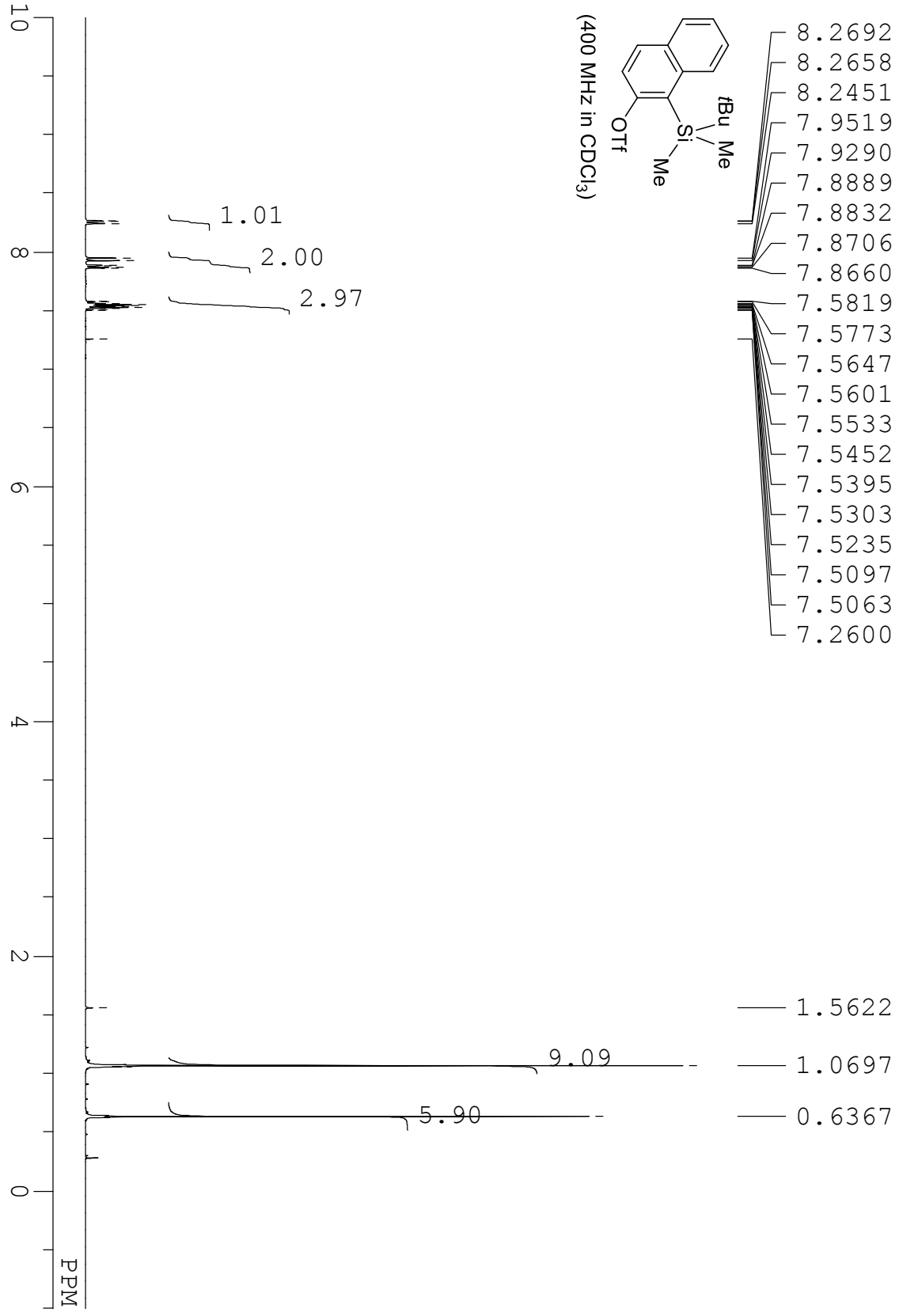
compound **1r**


(400 MHz in CDCl3)
OTf
Si
Me
iPr
iPr
8.2589
8.2543
8.2360
7.9278
7.9049
7.8980
7.8935
7.8832
7.8774
7.5899
7.5853
7.5727
7.5681
7.5647
7.5601
7.5544
7.5475
7.5429
7.5406
7.5372
7.5235
7.5200
7.4708
7.4490
7.2600
1.6986
1.6802
1.6608
1.6424
1.6241
1.6058
1.5874
1.2003
1.1819
0.8784
0.8600
0.5909
1.02
2.02
3.01
1.98
6.05
5.99
3.00
10
8
6
4
2
0
PPM

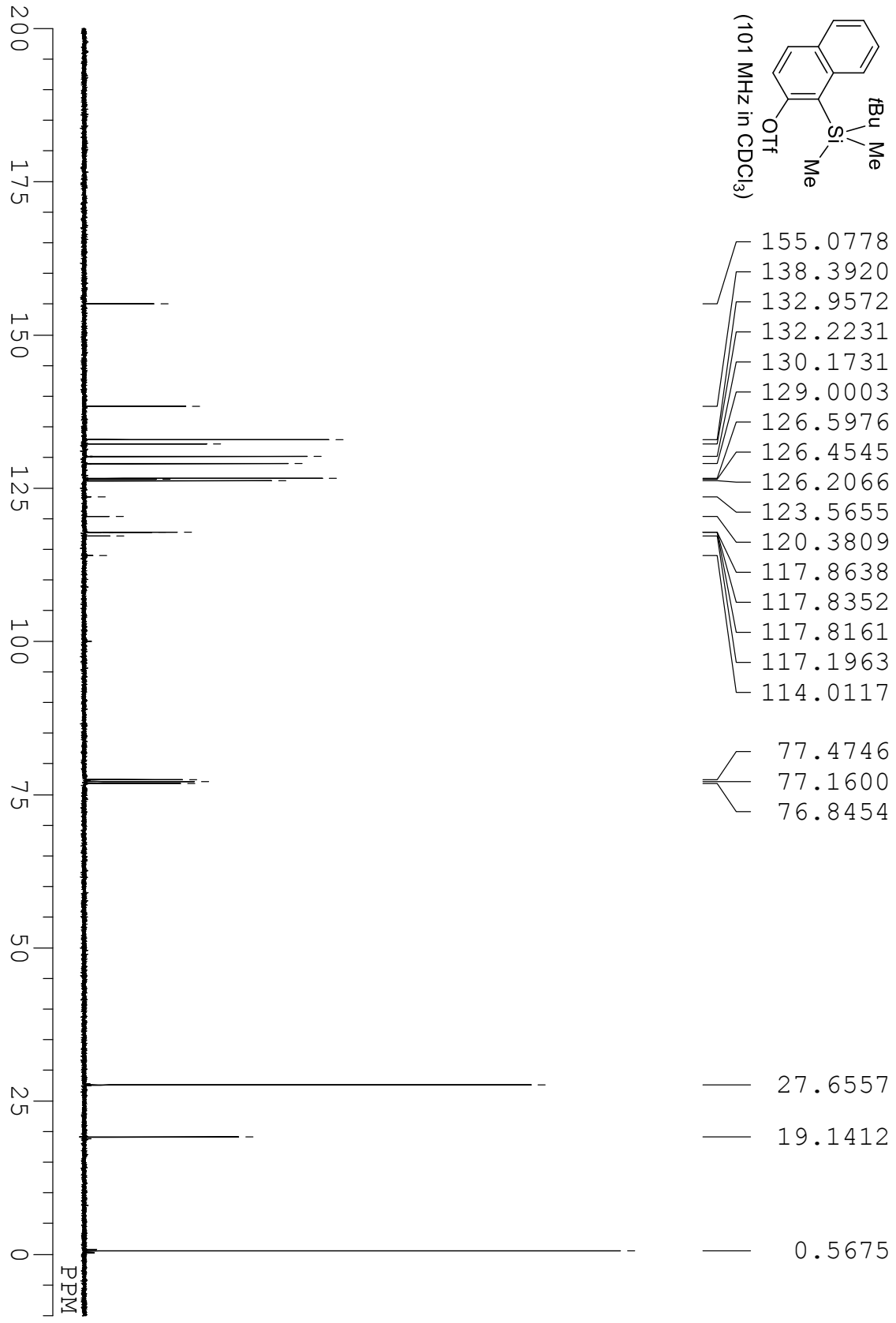
compound **1r**


(101 MHz in CDCl3)
OTf
Si
Me
iPr
iPr
154.1243
138.1346
132.5949
132.3375
129.1815
128.9050
127.5606
126.7215
126.3973
123.5369
120.3523
119.0270
119.0079
118.9889
118.9698
117.1677
113.9736
77.4746
77.1600
76.8454
18.8837
18.7979
14.5168
-7.6323
200
175
150
125
100
75
50
25
0
PPM

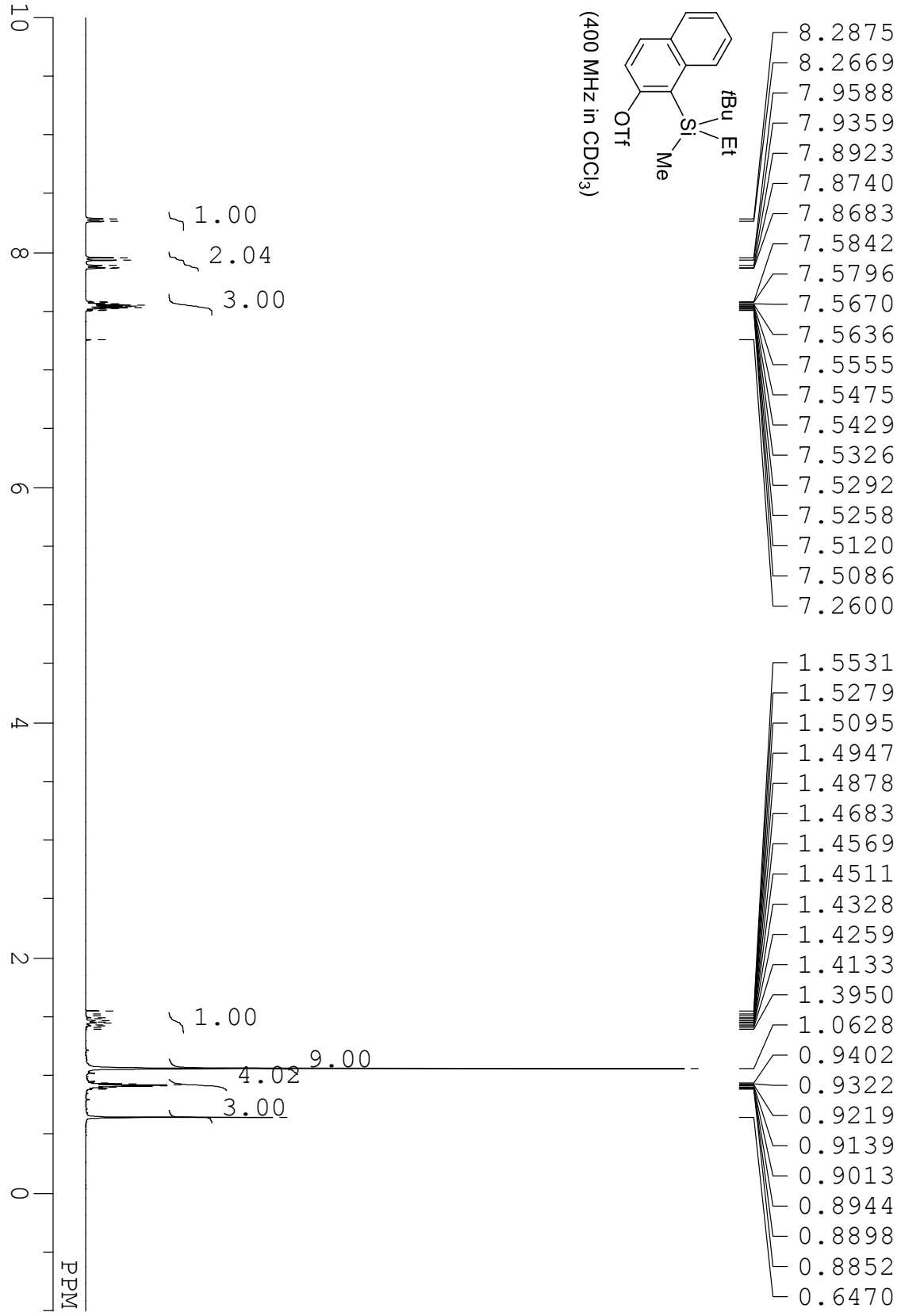
compound **1s**


(400 MHz in CDCl3)
OTf
Si
tBu
Me
Me
8.2692
8.2658
8.2451
7.9519
7.9290
7.8889
7.8832
7.8706
7.8660
7.5819
7.5773
7.5647
7.5601
7.5533
7.5452
7.5395
7.5303
7.5235
7.5097
7.5063
7.2600
1.01
2.00
2.97
9.09
5.90
1.5622
1.0697
0.6367
10
8
6
4
2
0
PPM

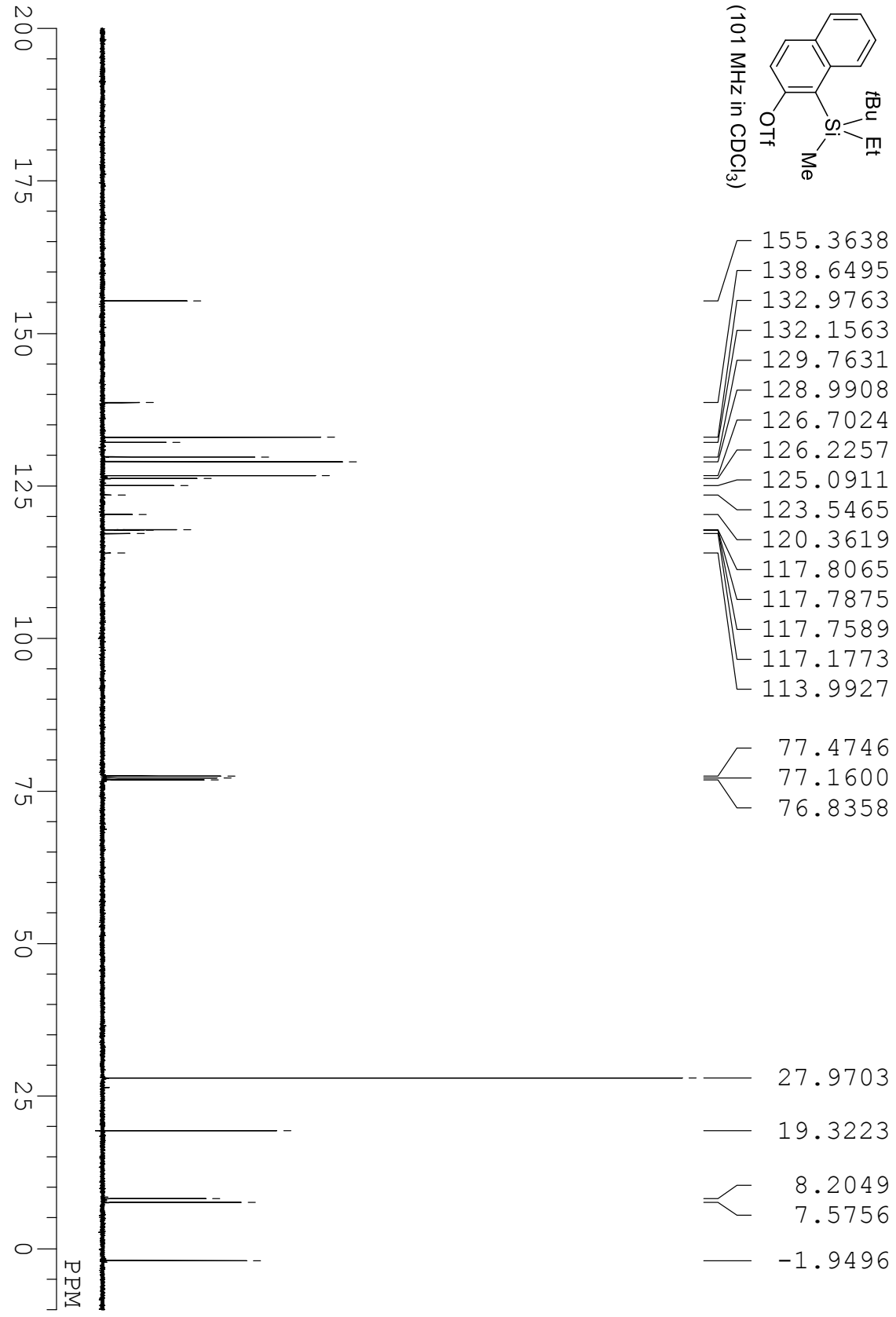
compound **1s**


(101 MHz in CDCl3)
OTf
Si
tBu
Me
Me
155.0778
138.3920
132.9572
132.2231
130.1731
129.0003
126.5976
126.4545
126.2066
123.5655
120.3809
117.8638
117.8352
117.8161
117.1963
114.0117
77.4746
77.1600
76.8454
27.6557
19.1412
0.5675
200
175
150
125
100
75
50
25
0
PPM

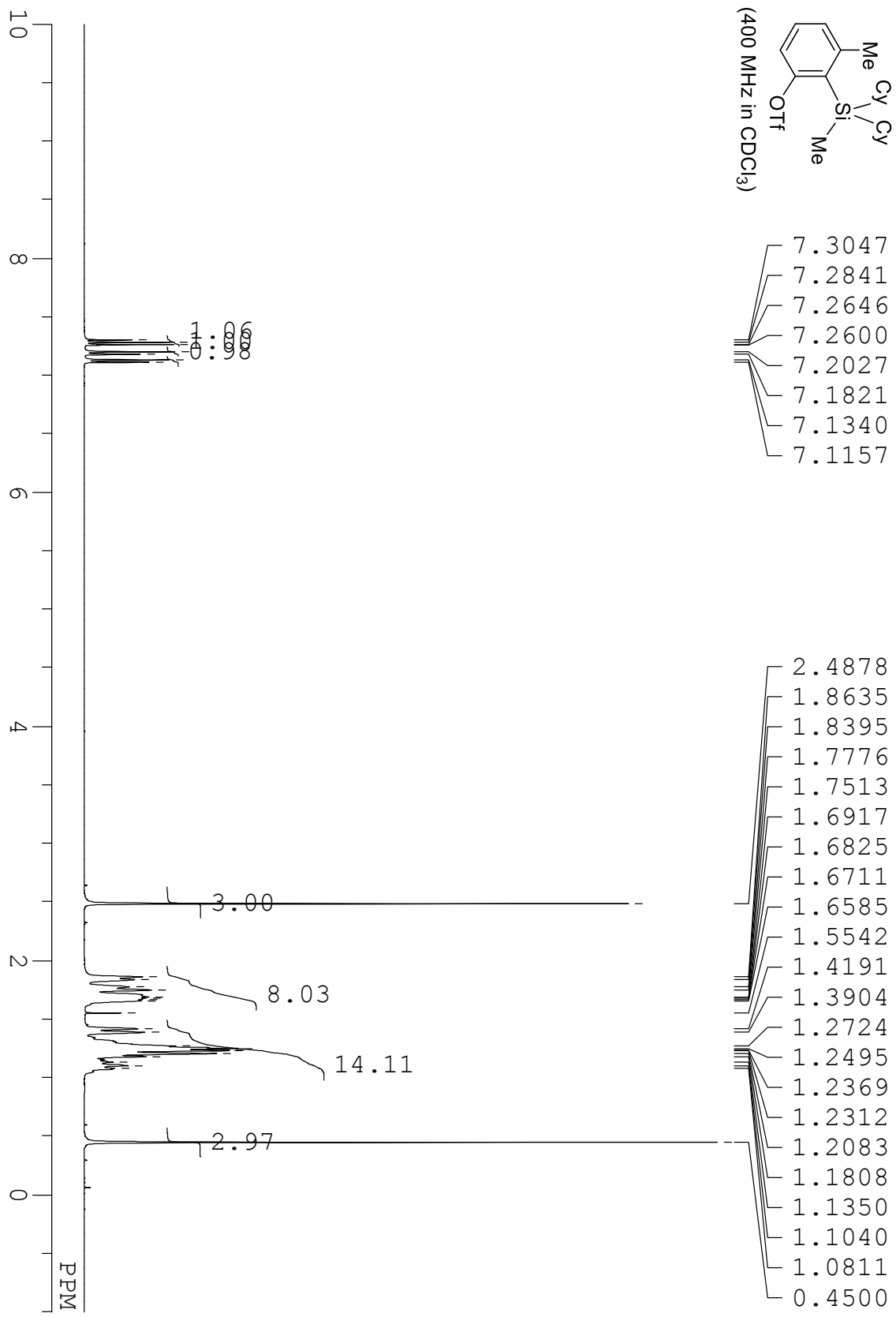
compound **1t**


(400 MHz in CDCl3)
OTf
Si
tBu
Et
Me
8.2875
8.2669
7.9588
7.9359
7.8923
7.8740
7.8683
7.5842
7.5796
7.5670
7.5636
7.5555
7.5475
7.5429
7.5326
7.5292
7.5258
7.5120
7.5086
7.2600
1.5531
1.5279
1.5095
1.4947
1.4878
1.4683
1.4569
1.4511
1.4328
1.4259
1.4133
1.3950
1.0628
0.9402
0.9322
0.9219
0.9139
0.9013
0.8944
0.8898
0.8852
0.6470
1.00
2.04
3.00
1.00
9.00
4.02
3.00
10
8
6
4
2
0
PPM

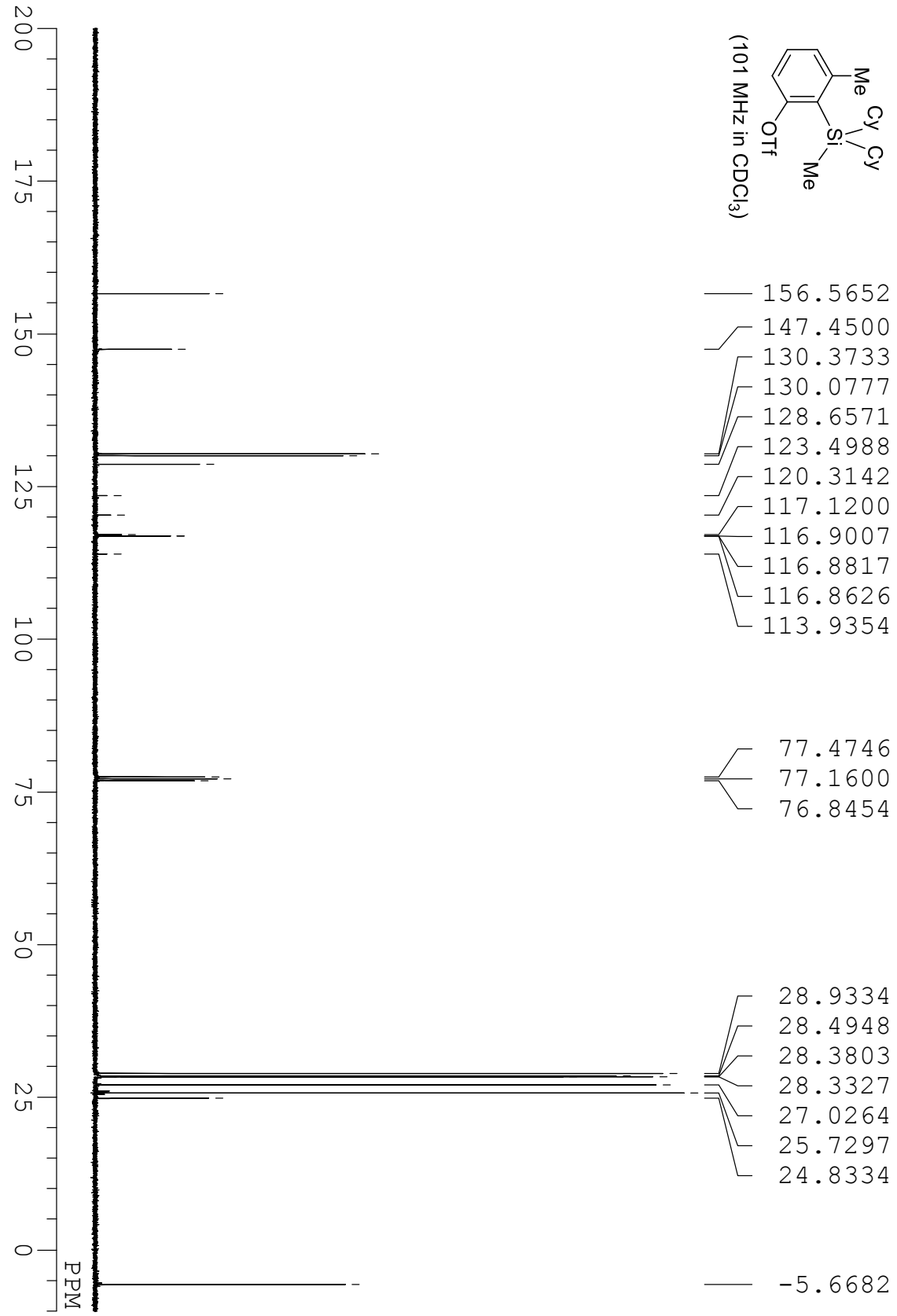
compound **1t**


(101 MHz in CDCl3)
OTf
Si
tBu
Et
Me
155.3638
138.6495
132.9763
132.1563
129.7631
128.9908
126.7024
126.2257
125.0911
123.5465
120.3619
117.8065
117.7875
117.7589
117.1773
113.9927
77.4746
77.1600
76.8358
27.9703
19.3223
8.2049
7.5756
-1.9496
200
175
150
125
100
75
50
25
0
PPM

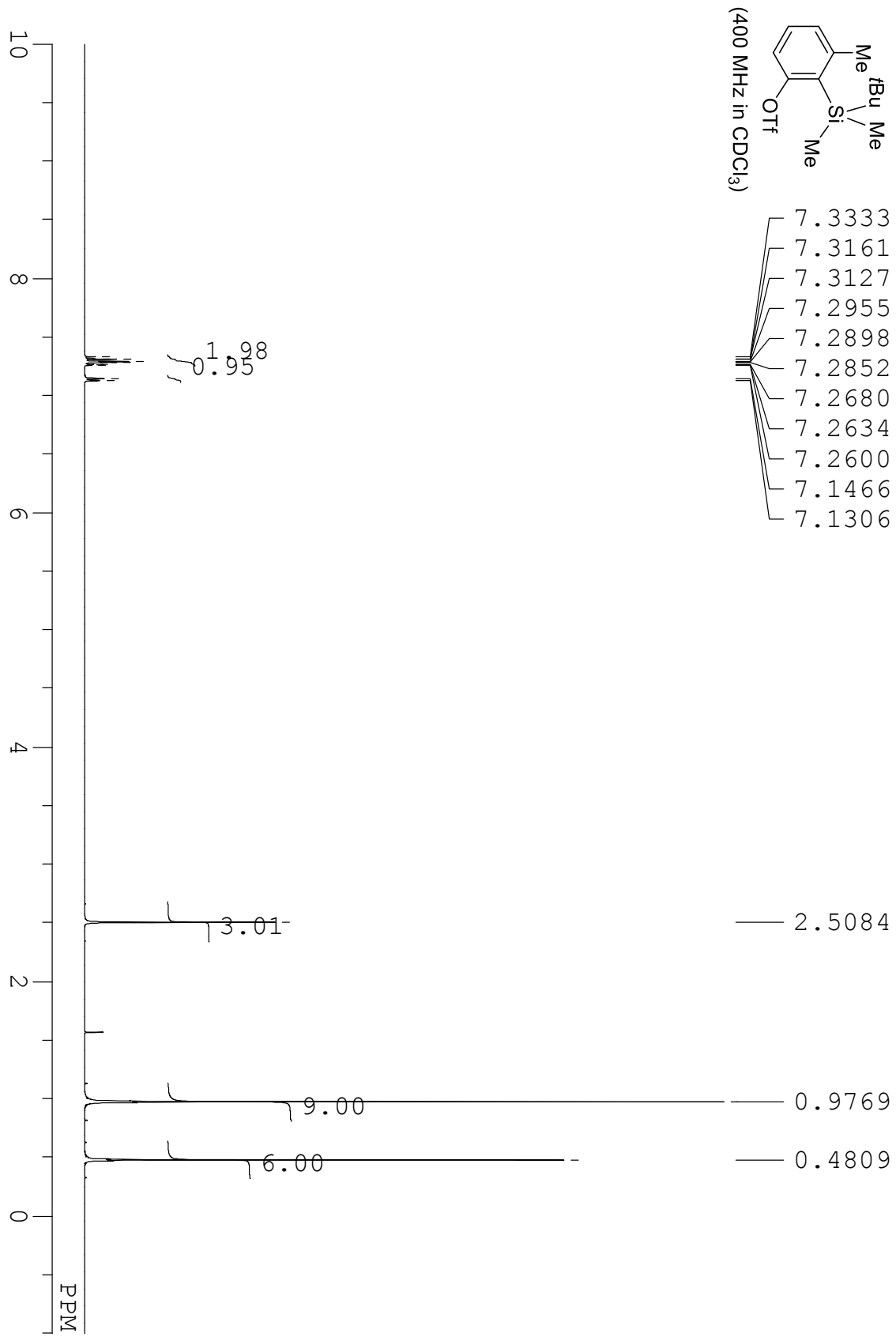
compound **1u**


(400 MHz in CDCl3)
Me
Cy
Cy
Si
Me
OTf
7.3047
7.2841
7.2646
7.2600
7.2027
7.1821
7.1340
7.1157
2.4878
1.8635
1.8395
1.7776
1.7513
1.6917
1.6825
1.6711
1.6585
1.5542
1.4191
1.3904
1.2724
1.2495
1.2369
1.2312
1.2083
1.1808
1.1350
1.1040
1.0811
0.4500
3.00
8.03
14.11
2.97
PPM

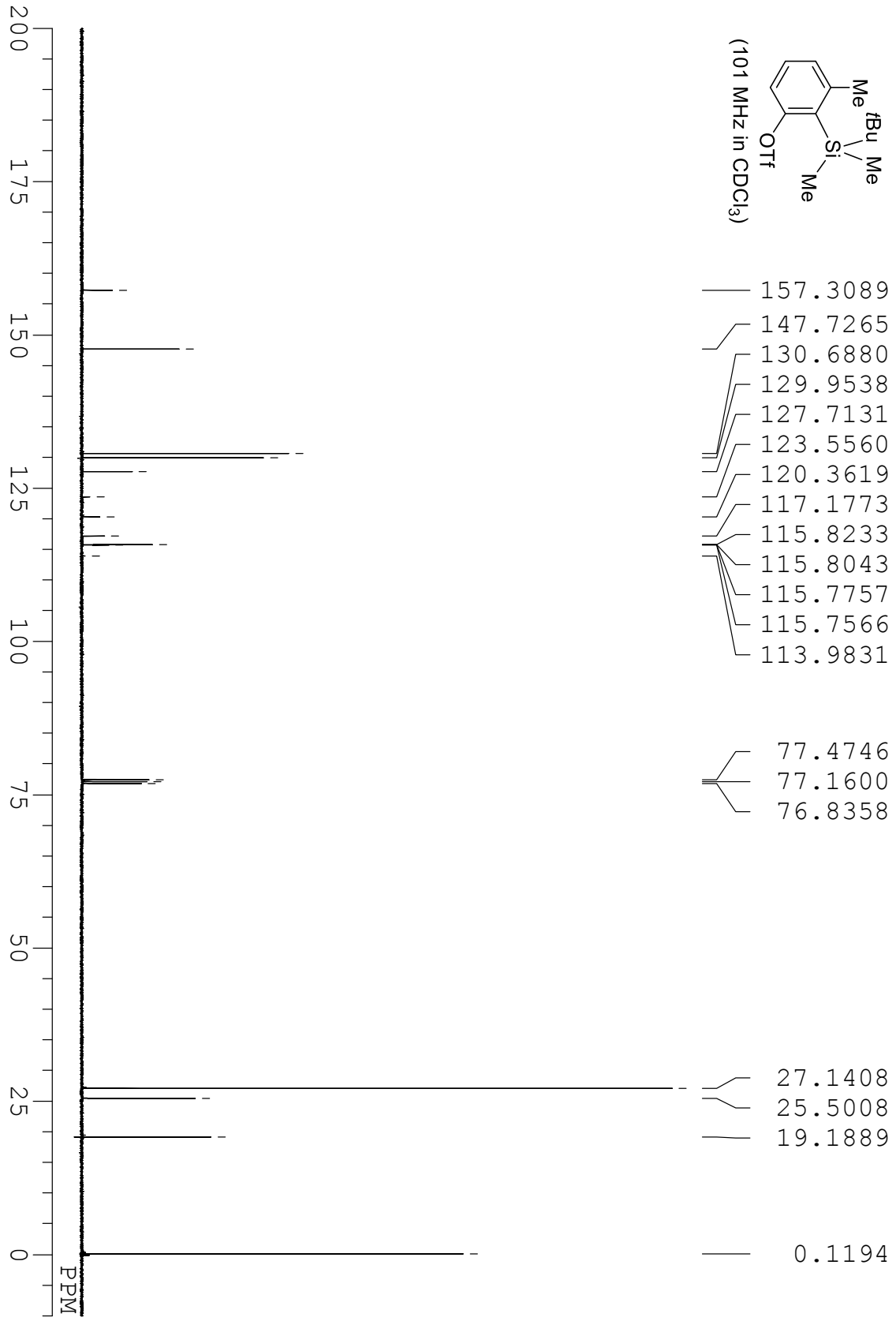
compound **1u**


(101 MHz in CDCl3)
Me
Cy
Cy
Si
Me
OTf
156.5652
147.4500
130.3733
130.0777
128.6571
123.4988
120.3142
117.1200
116.9007
116.8817
116.8626
113.9354
77.4746
77.1600
76.8454
28.9334
28.4948
28.3803
28.3327
27.0264
25.7297
24.8334
-5.6682
200
175
150
125
100
75
50
25
0
PPM

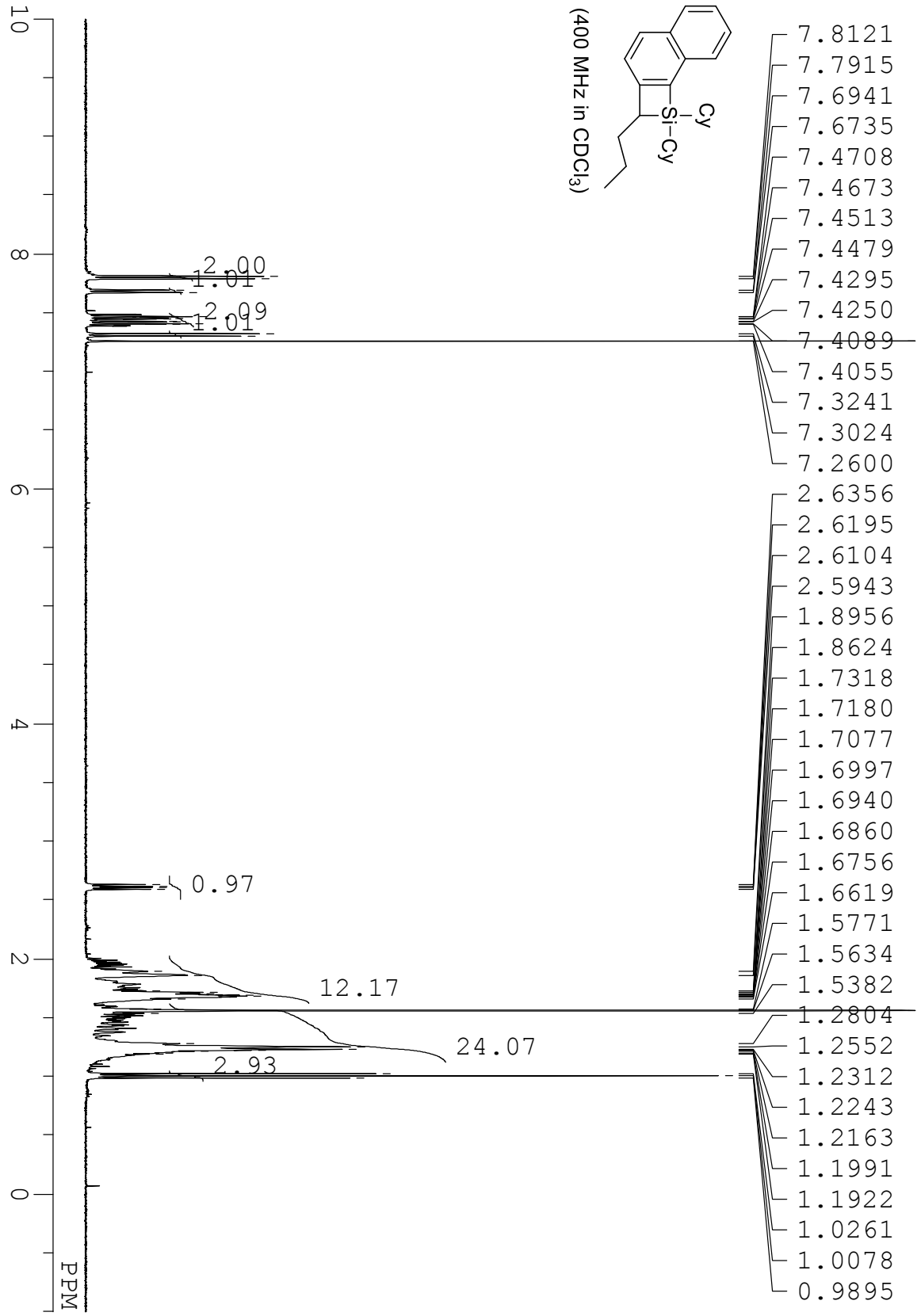
compound **1v**


(400 MHz in CDCl3)
Me
tBu
Me
Si
Me
OTf
7.3333
7.3161
7.3127
7.2955
7.2898
7.2852
7.2680
7.2634
7.2600
7.1466
7.1306
1.98
0.95
3.01
2.5084
9.00
0.9769
6.00
0.4809
PPM

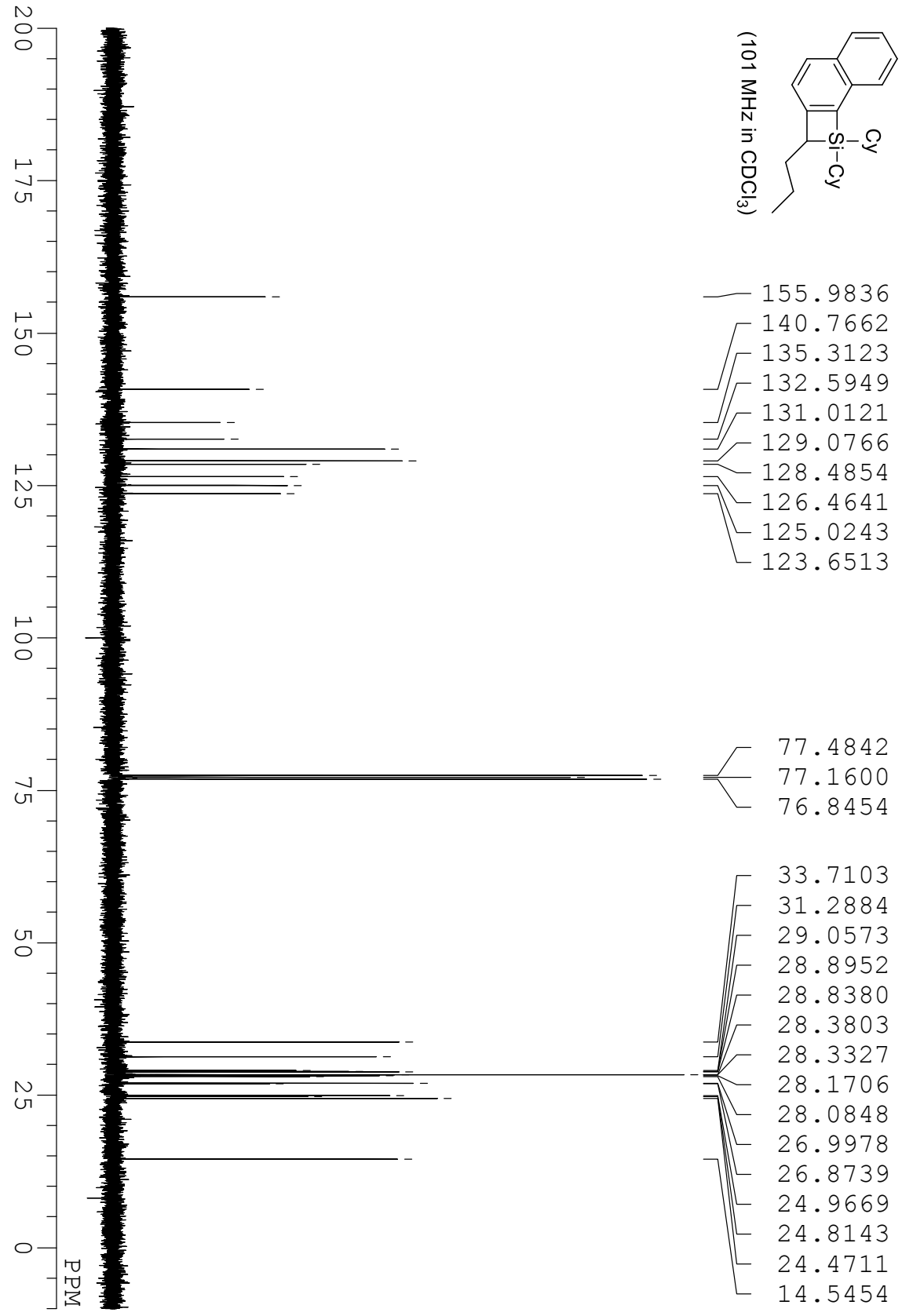
compound **1v**


(101 MHz in CDCl3)
OTf
Me
tBu
Me
Si
Me
157.3089
147.7265
130.6880
129.9538
127.7131
123.5560
120.3619
117.1773
115.8233
115.8043
115.7757
115.7566
113.9831
77.4746
77.1600
76.8358
27.1408
25.5008
19.1889
0.1194
200
175
150
125
100
75
50
25
0
PPM

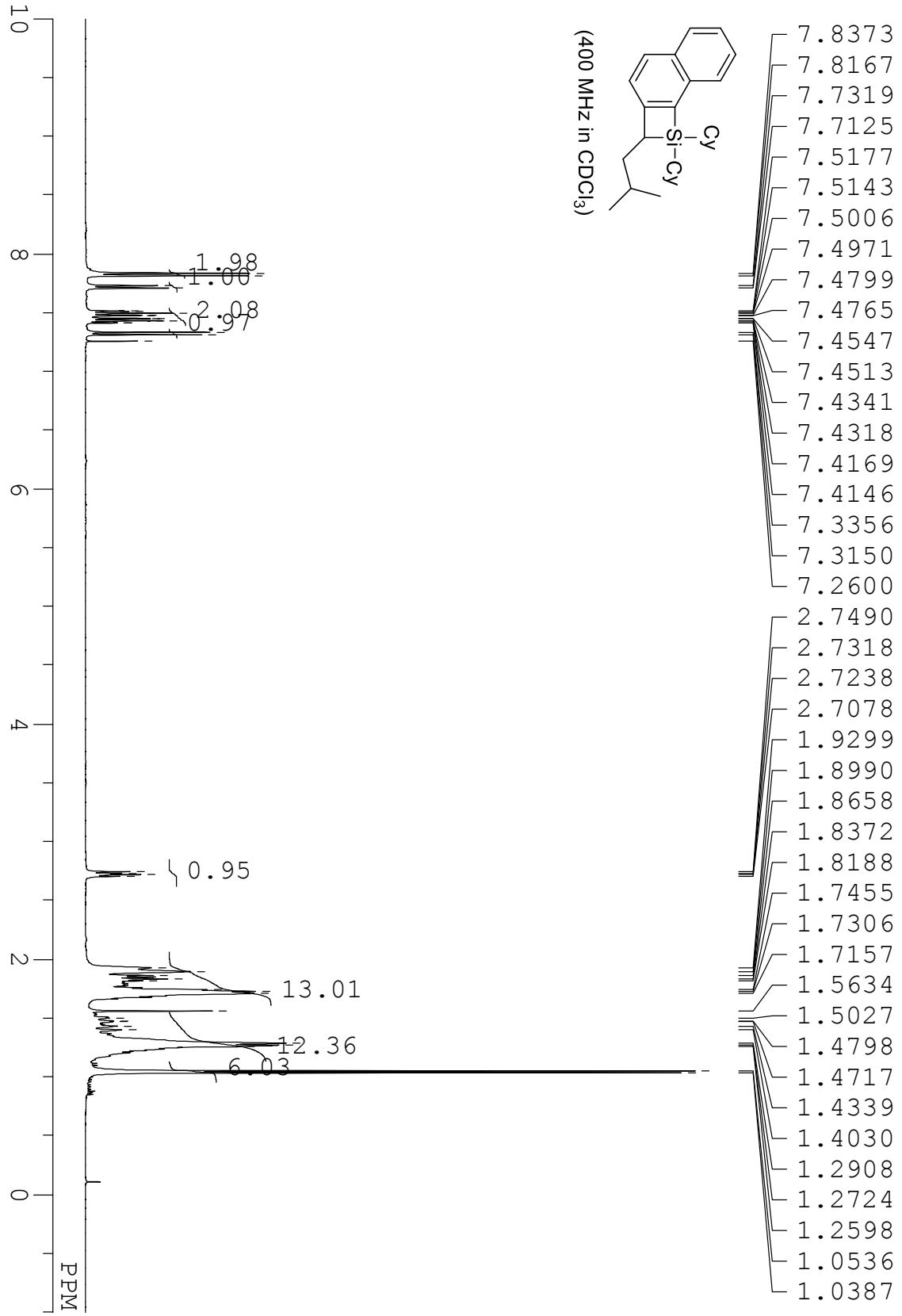
compound **2a** (97% pure)



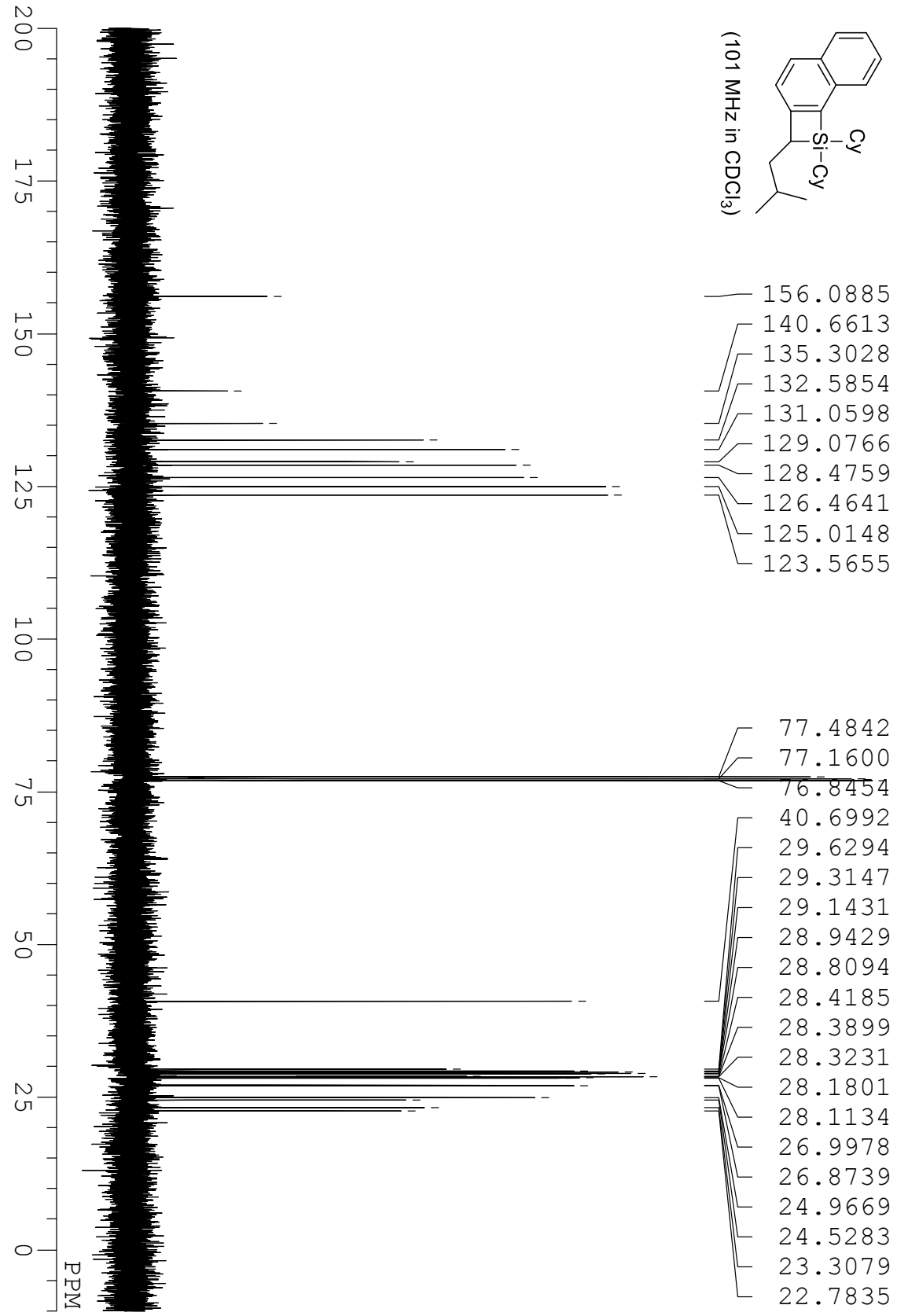
compound **2a** (97% pure)



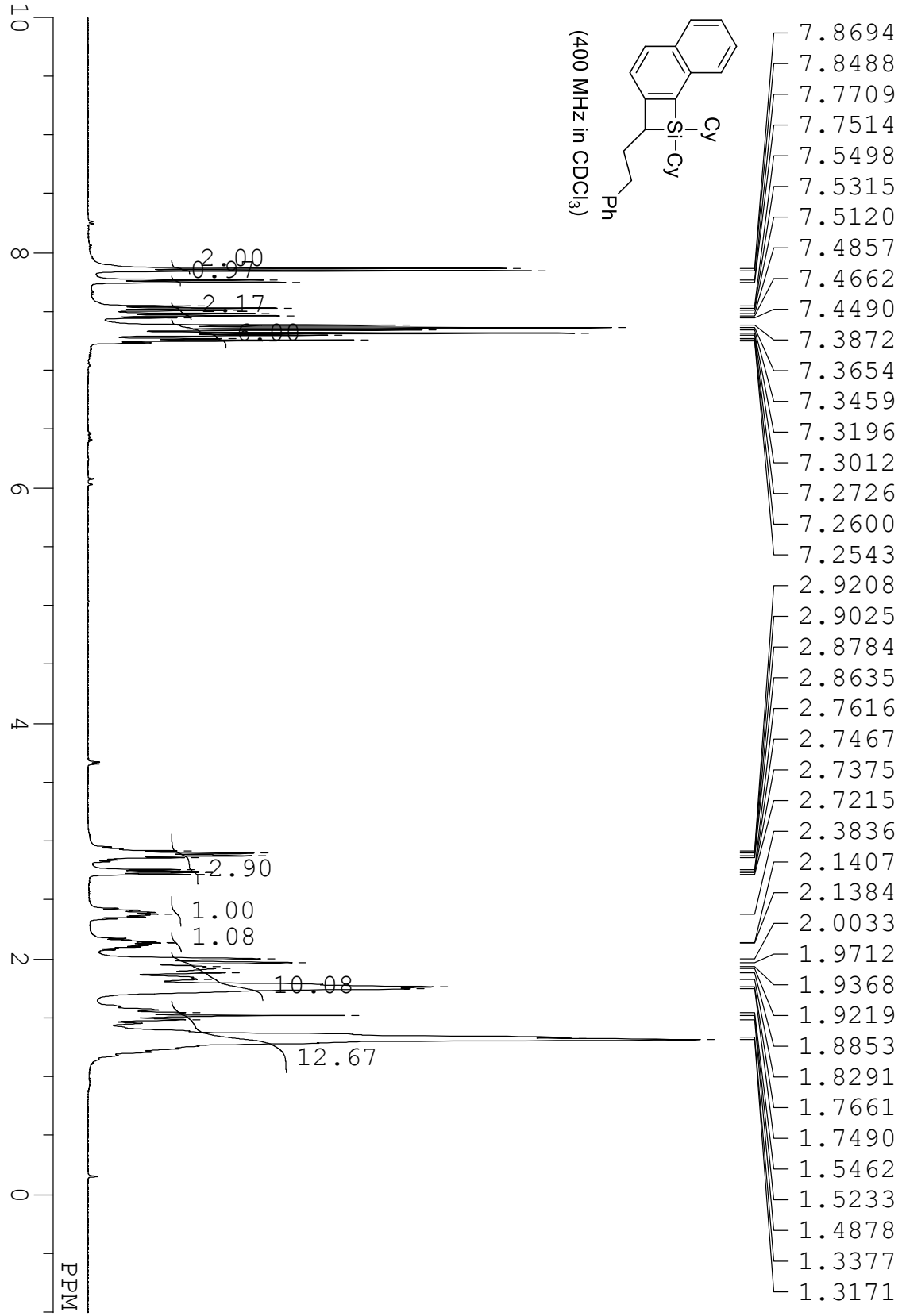
compound **2b** (99% pure)



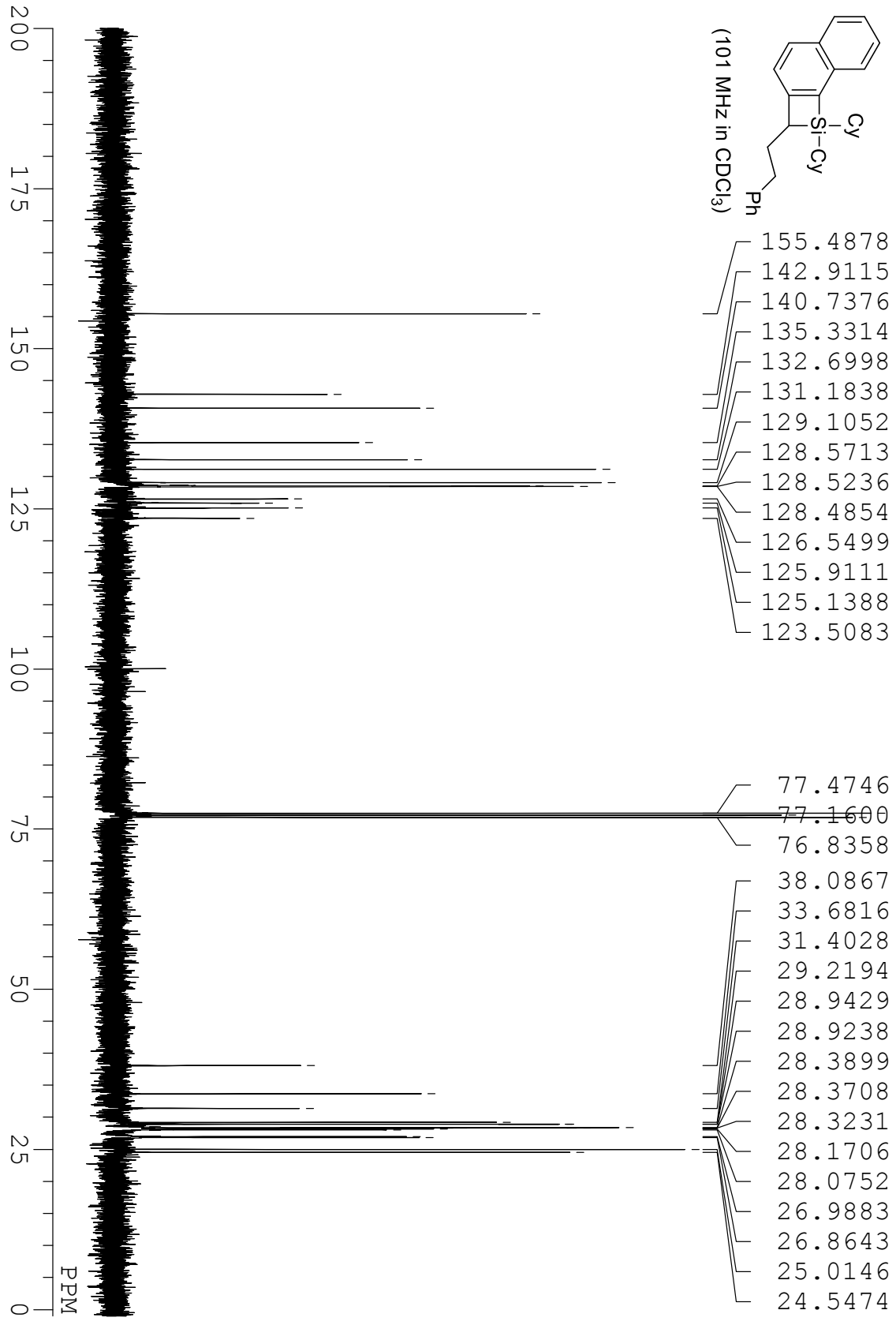
compound **2b** (99% pure)



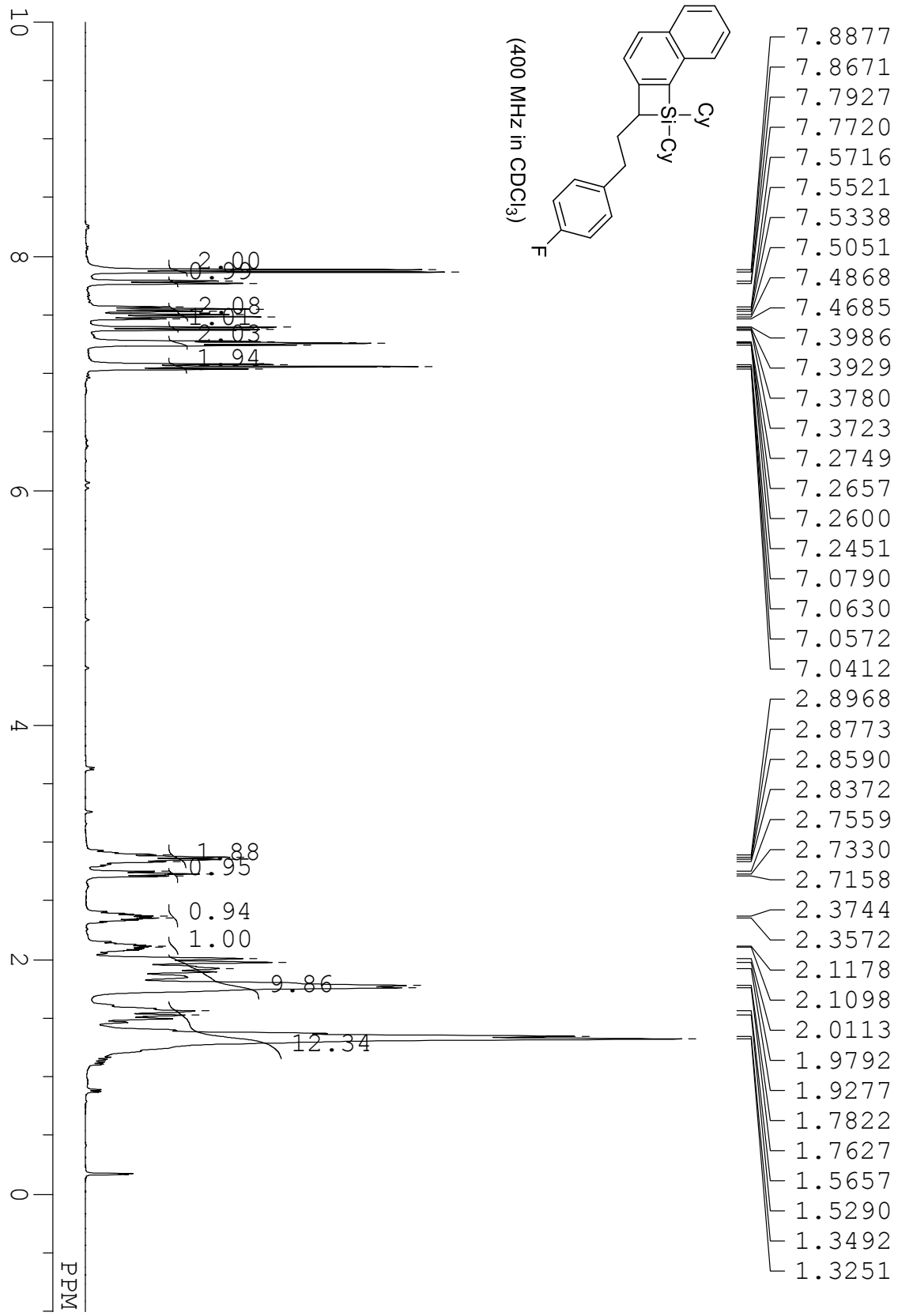
compound **2c** (96% pure)



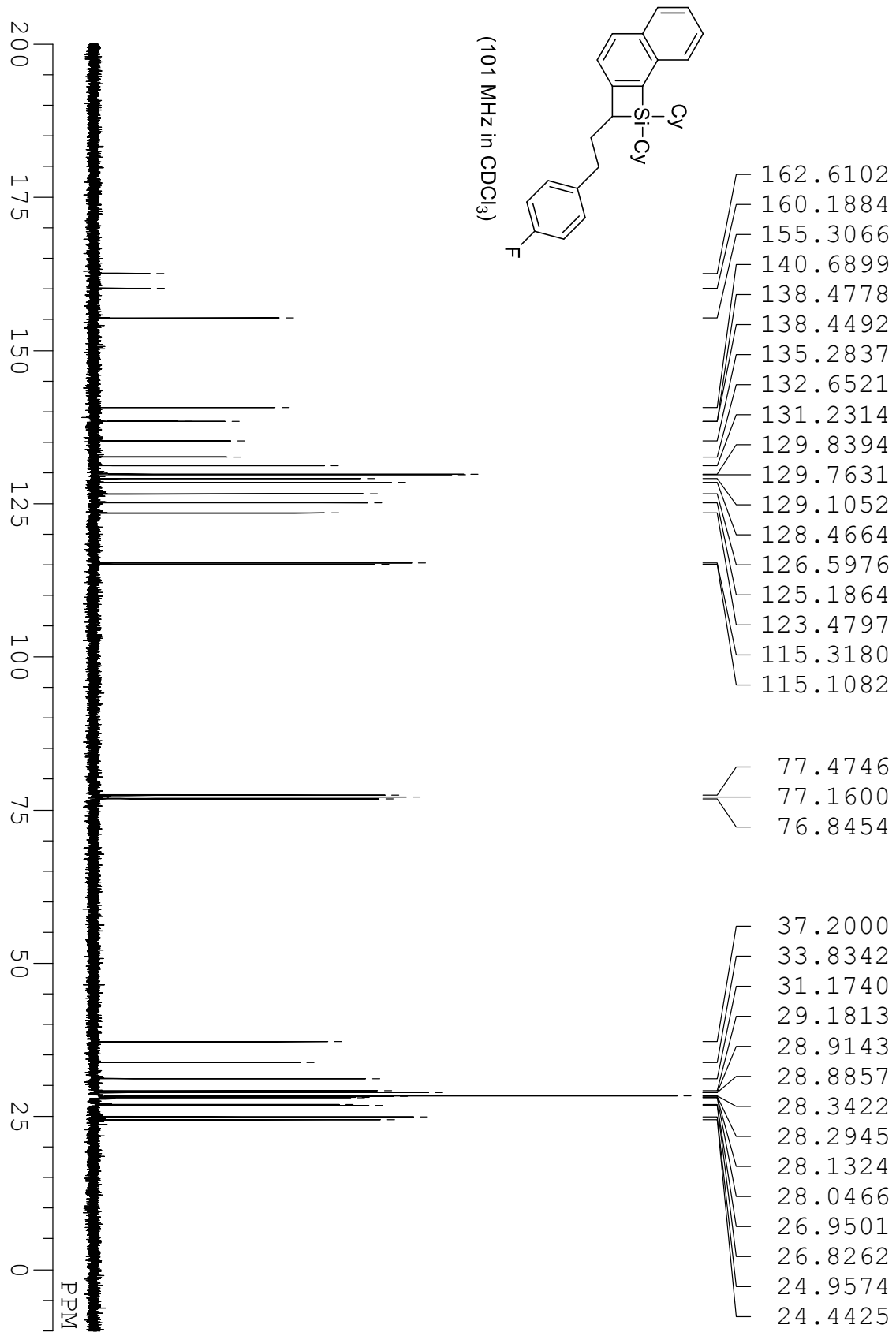
compound **2c** (96% pure)



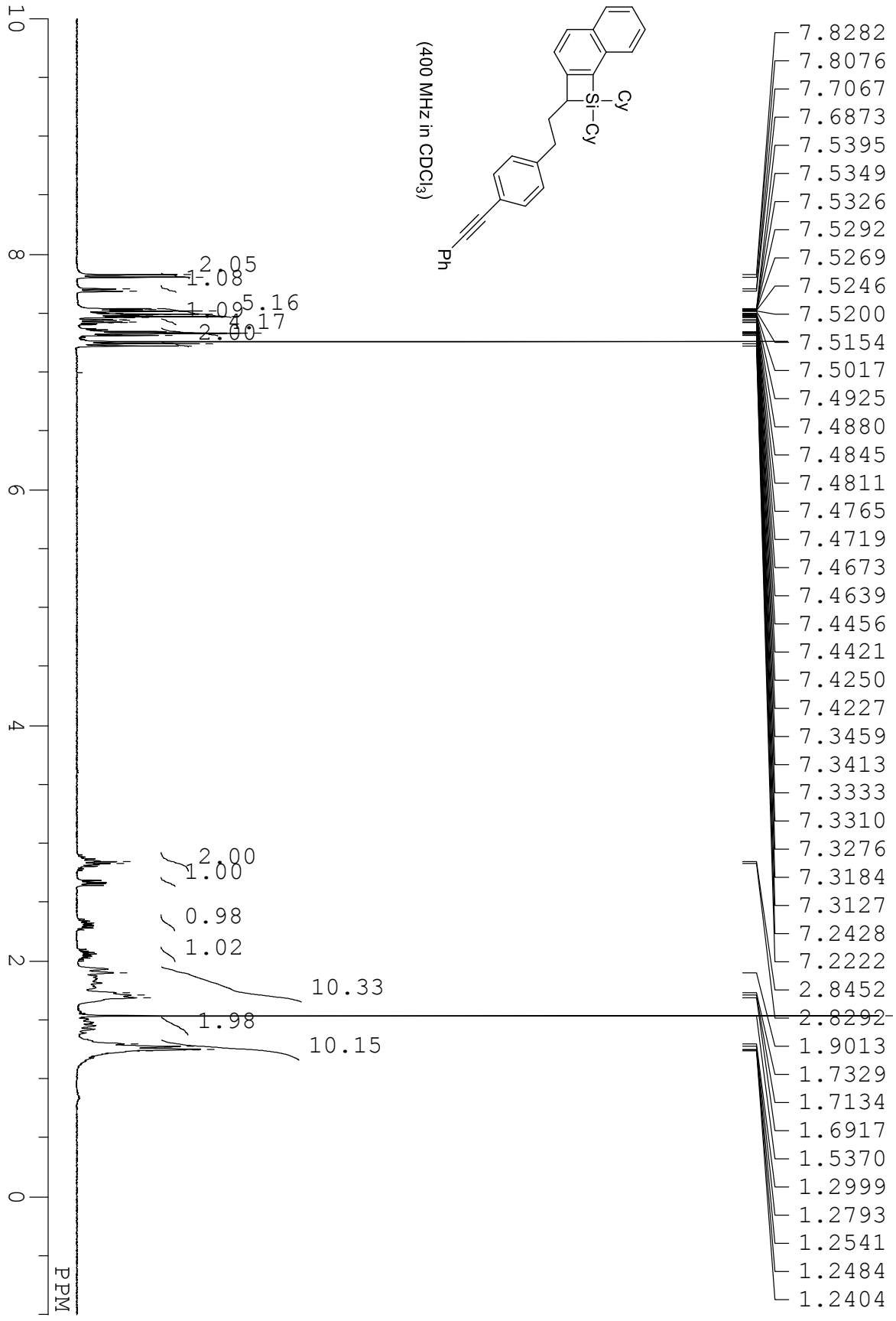
compound **2d** (96% pure)



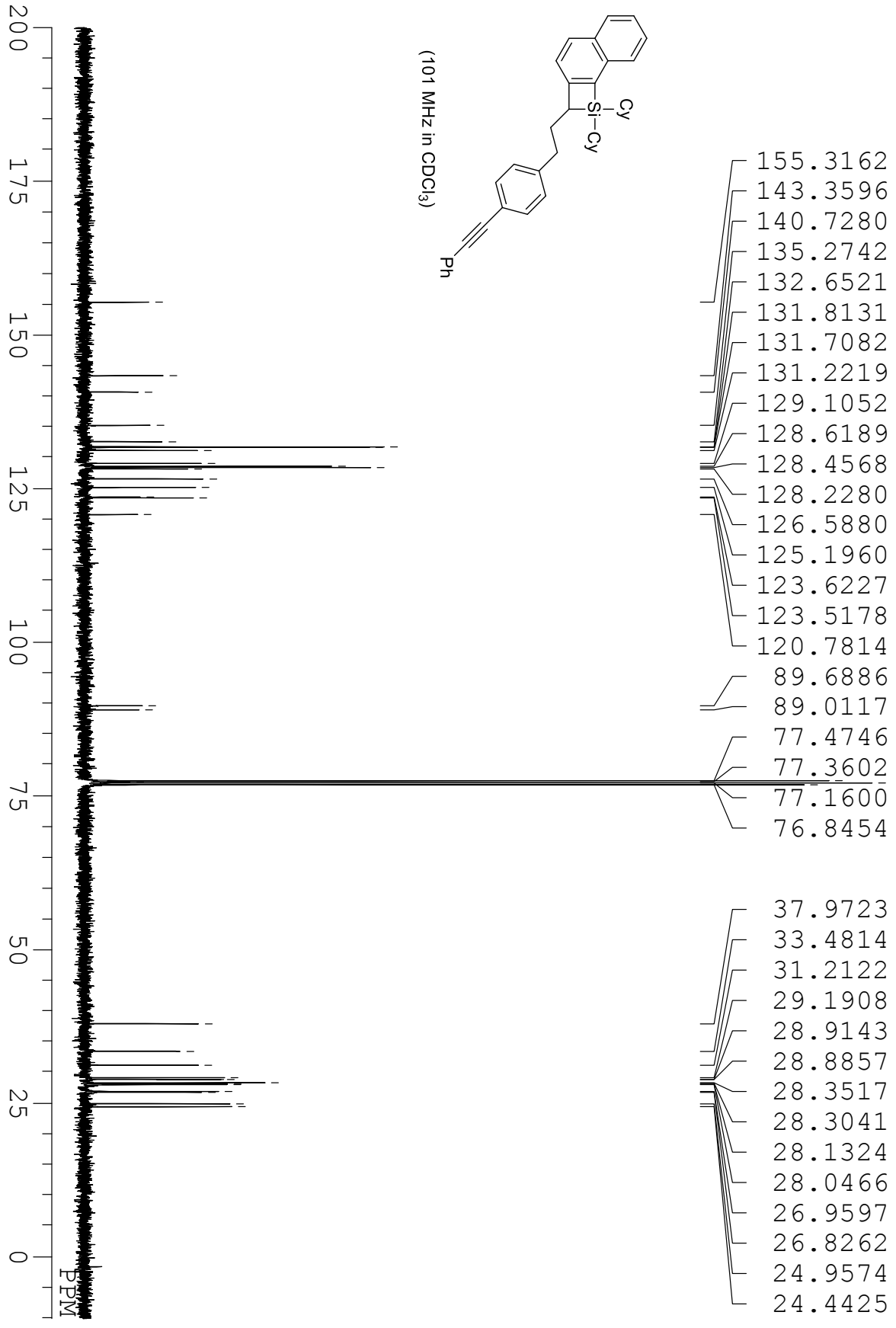
compound **2d** (96% pure)



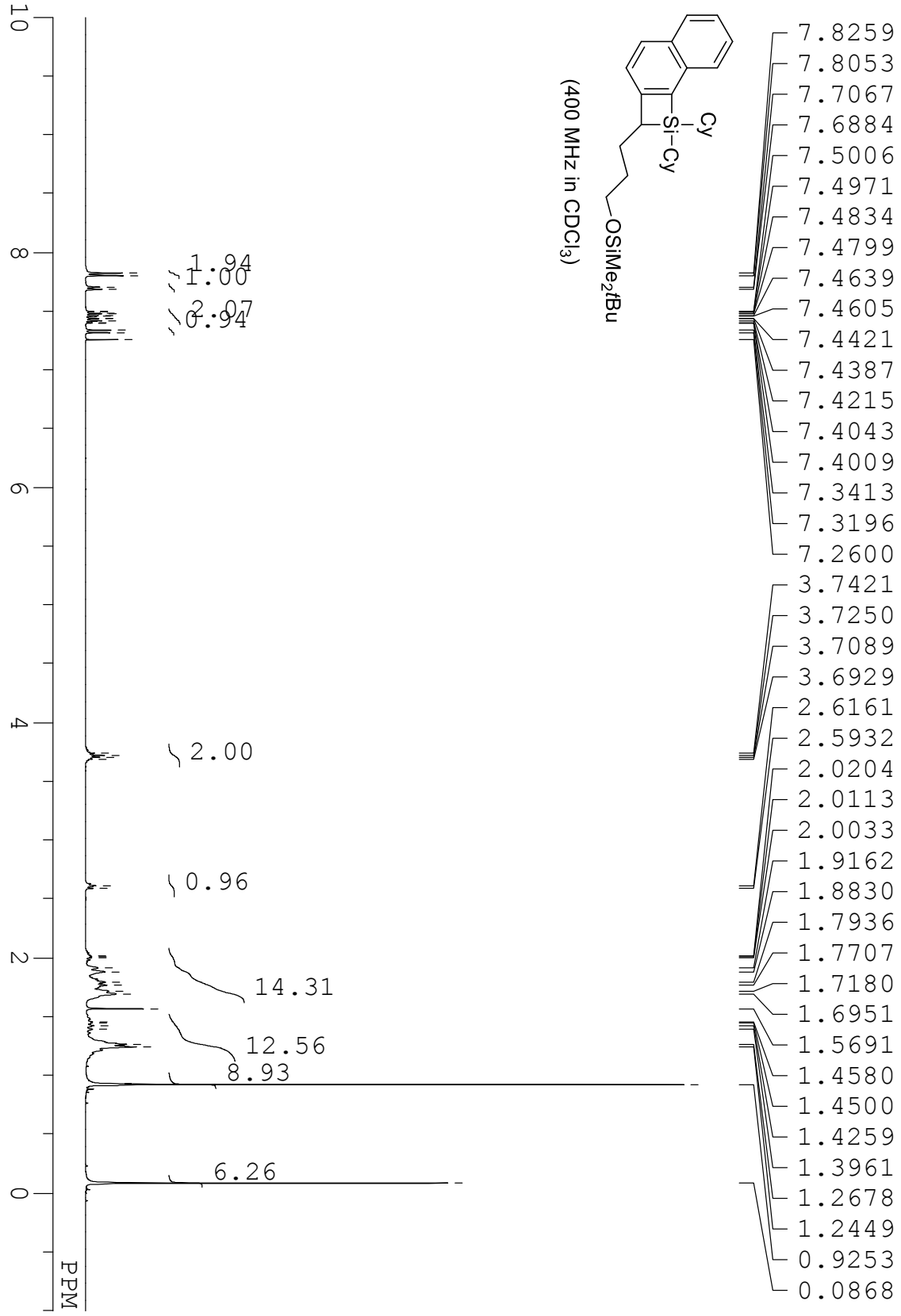
compound **2e**


(400 MHz in CDCl3)
Cy
Si—Cy
Ph
PPM
2.05
1.08
5.16
4.17
2.00
2.00
1.00
0.98
1.02
10.33
1.98
10.15
7.8282
7.8076
7.7067
7.6873
7.5395
7.5349
7.5326
7.5292
7.5269
7.5246
7.5200
7.5154
7.5017
7.4925
7.4880
7.4845
7.4811
7.4765
7.4719
7.4673
7.4639
7.4456
7.4421
7.4250
7.4227
7.3459
7.3413
7.3333
7.3310
7.3276
7.3184
7.3127
7.2428
7.2222
2.8452
2.8292
1.9013
1.7329
1.7134
1.6917
1.5370
1.2999
1.2793
1.2541
1.2484
1.2404

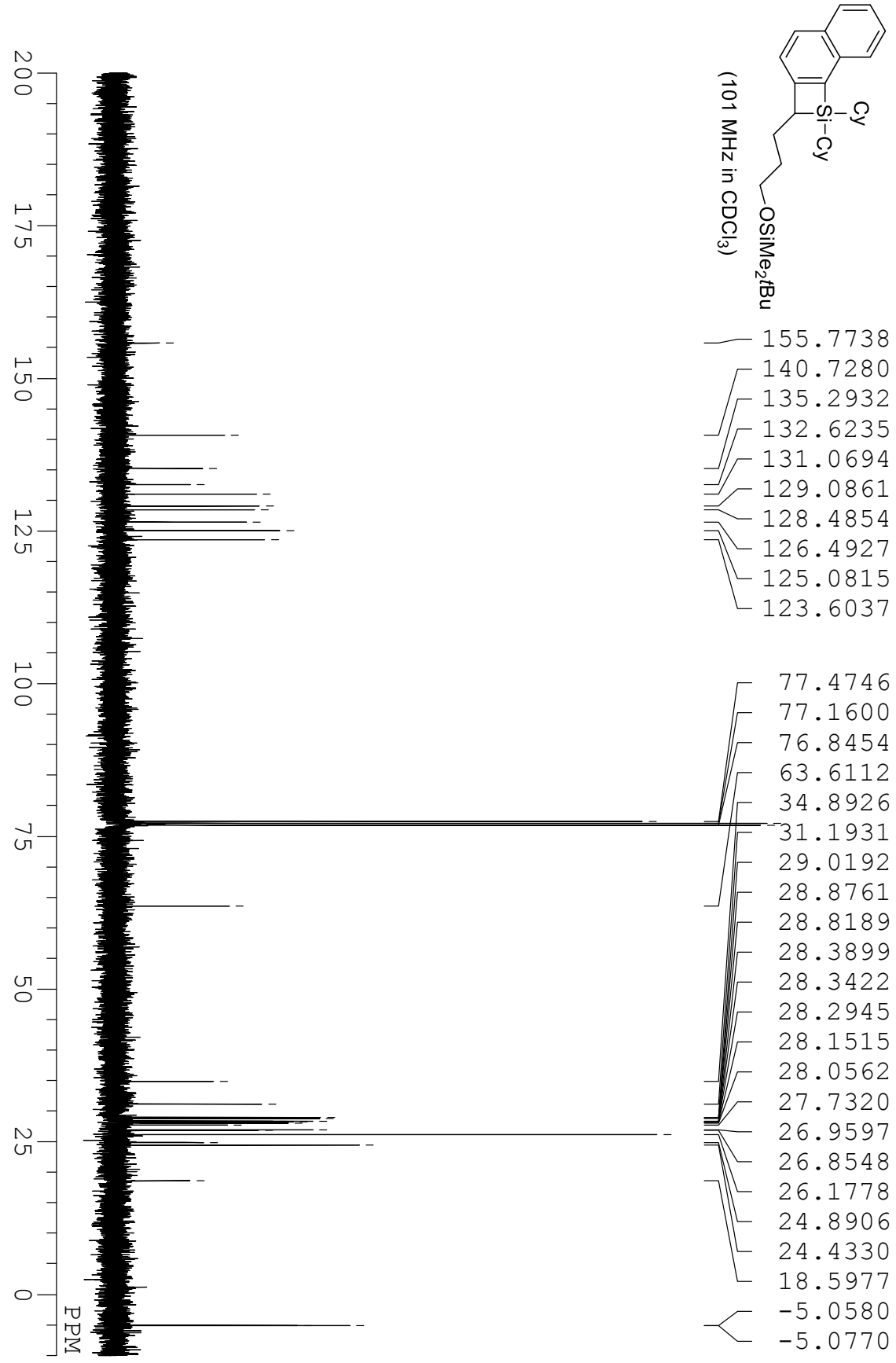
compound **2e**


(101 MHz in CDCl3)
Cy
Si
Cy
Ph
155.3162
143.3596
140.7280
135.2742
132.6521
131.8131
131.7082
131.2219
129.1052
128.6189
128.4568
128.2280
126.5880
125.1960
123.6227
123.5178
120.7814
89.6886
89.0117
77.4746
77.3602
77.1600
76.8454
37.9723
33.4814
31.2122
29.1908
28.9143
28.8857
28.3517
28.3041
28.1324
28.0466
26.9597
26.8262
24.9574
24.4425
200
175
150
125
100
75
50
25
0
PPM

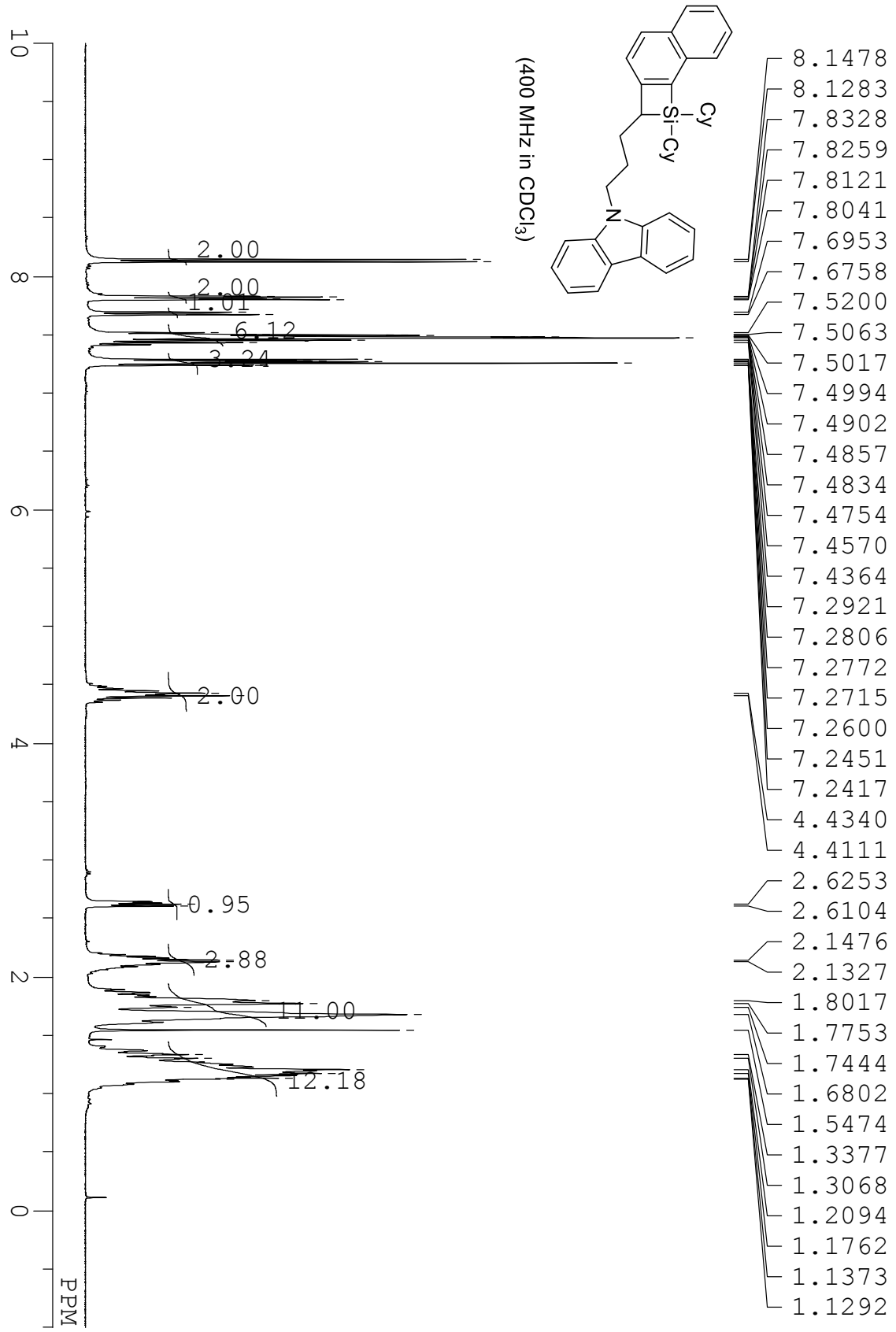
compound **2f** (97% pure)



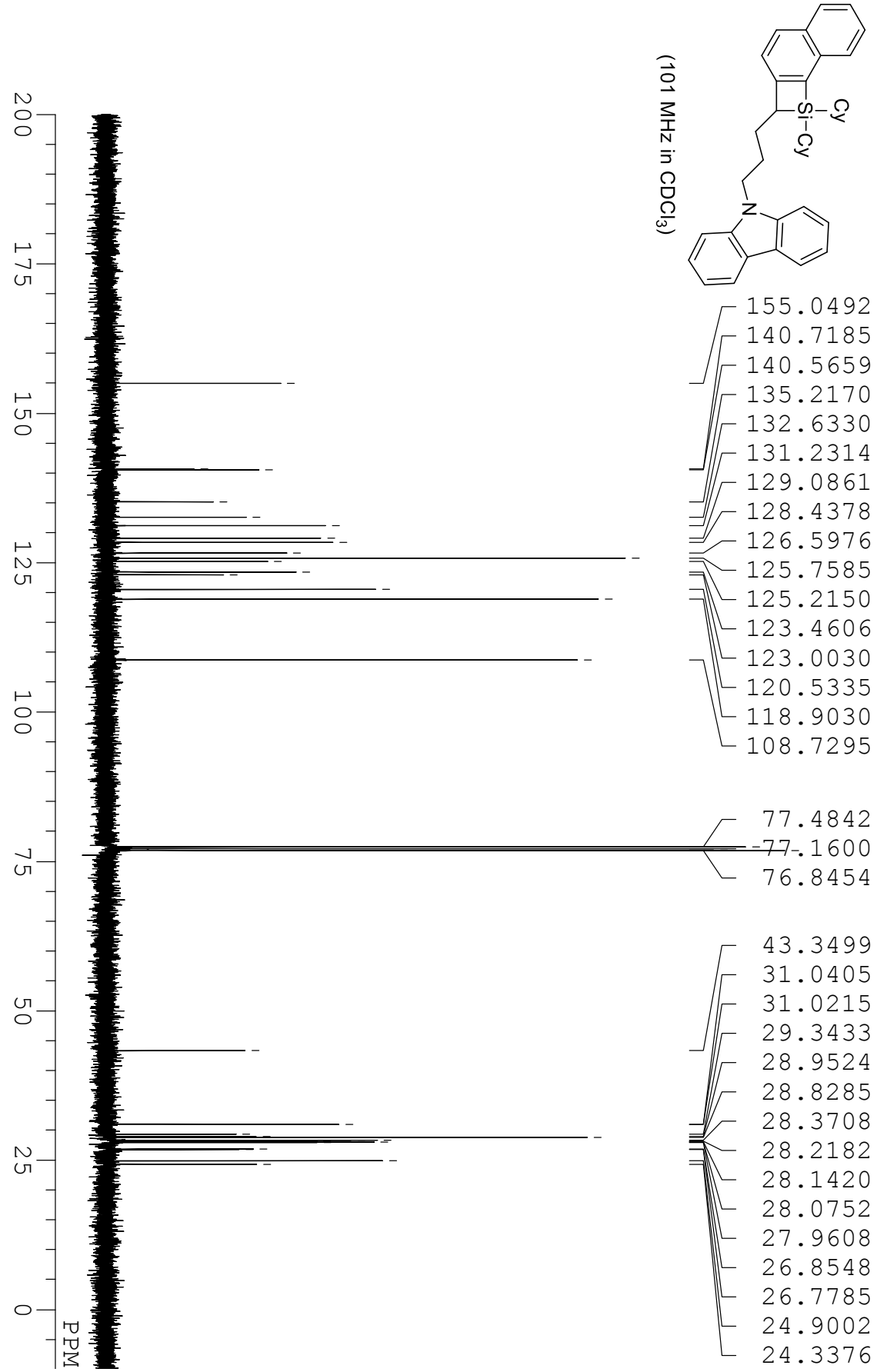
compound **2f** (97% pure)



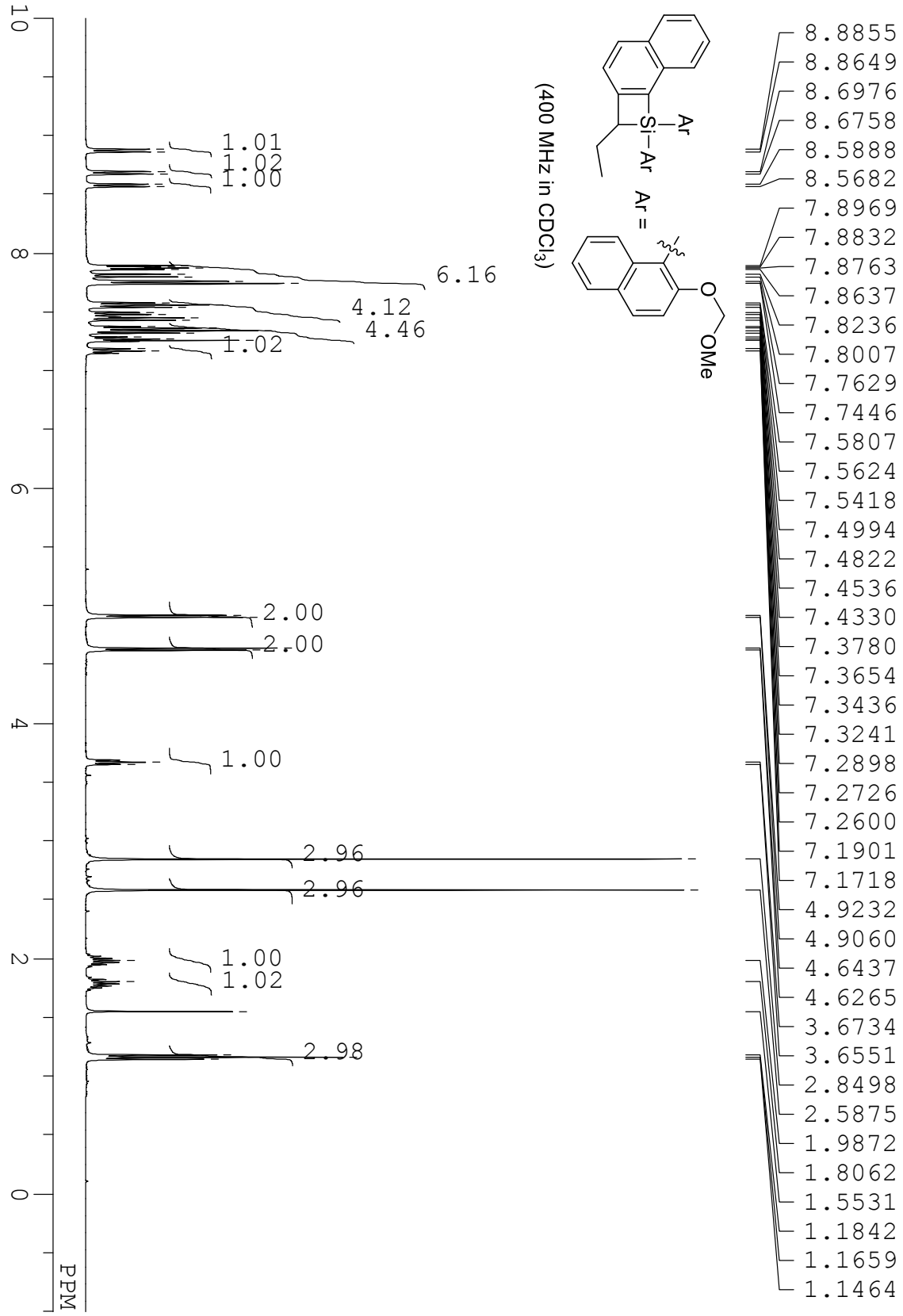
compound **2g** (98% pure)



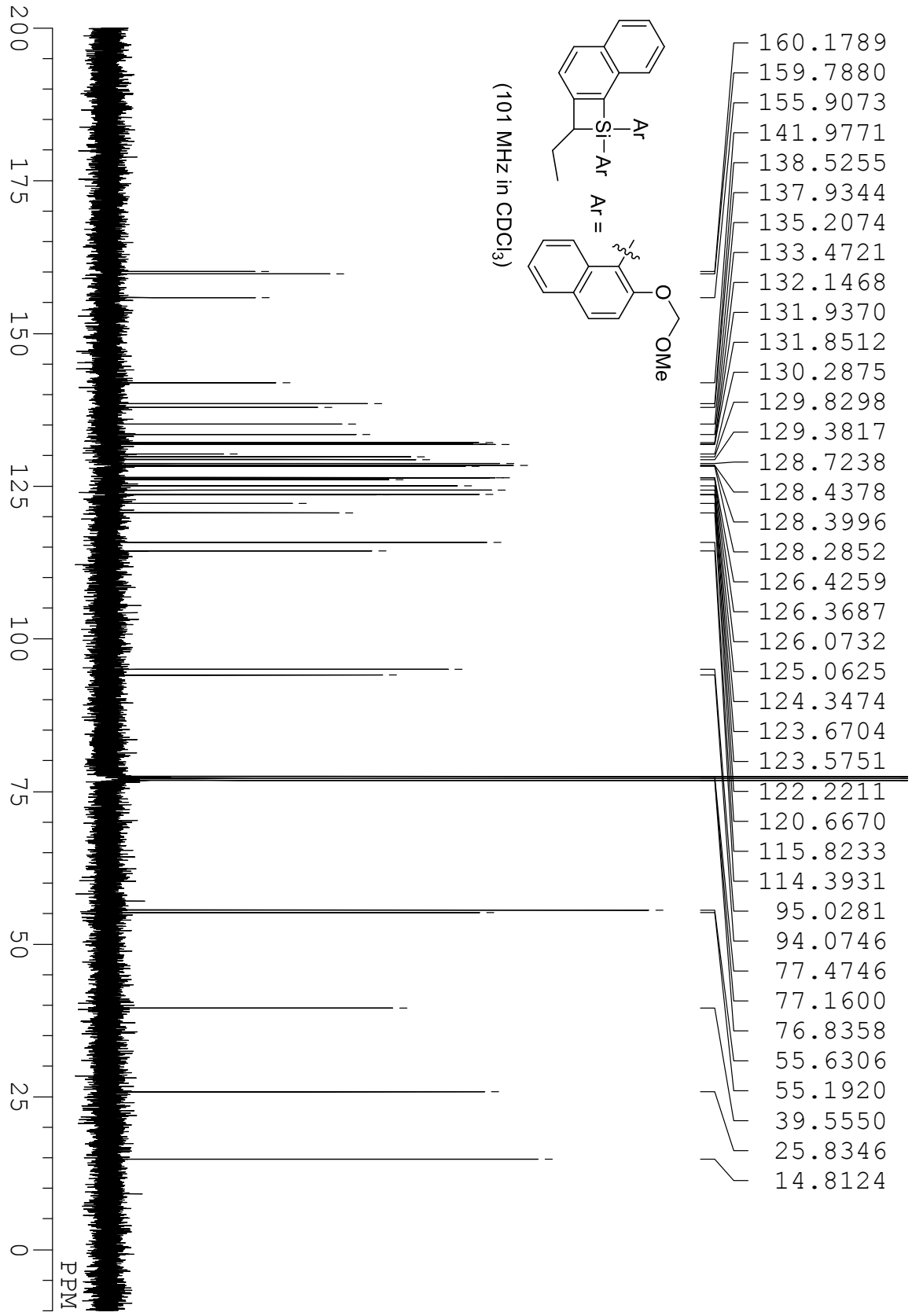
compound **2g** (98% pure)



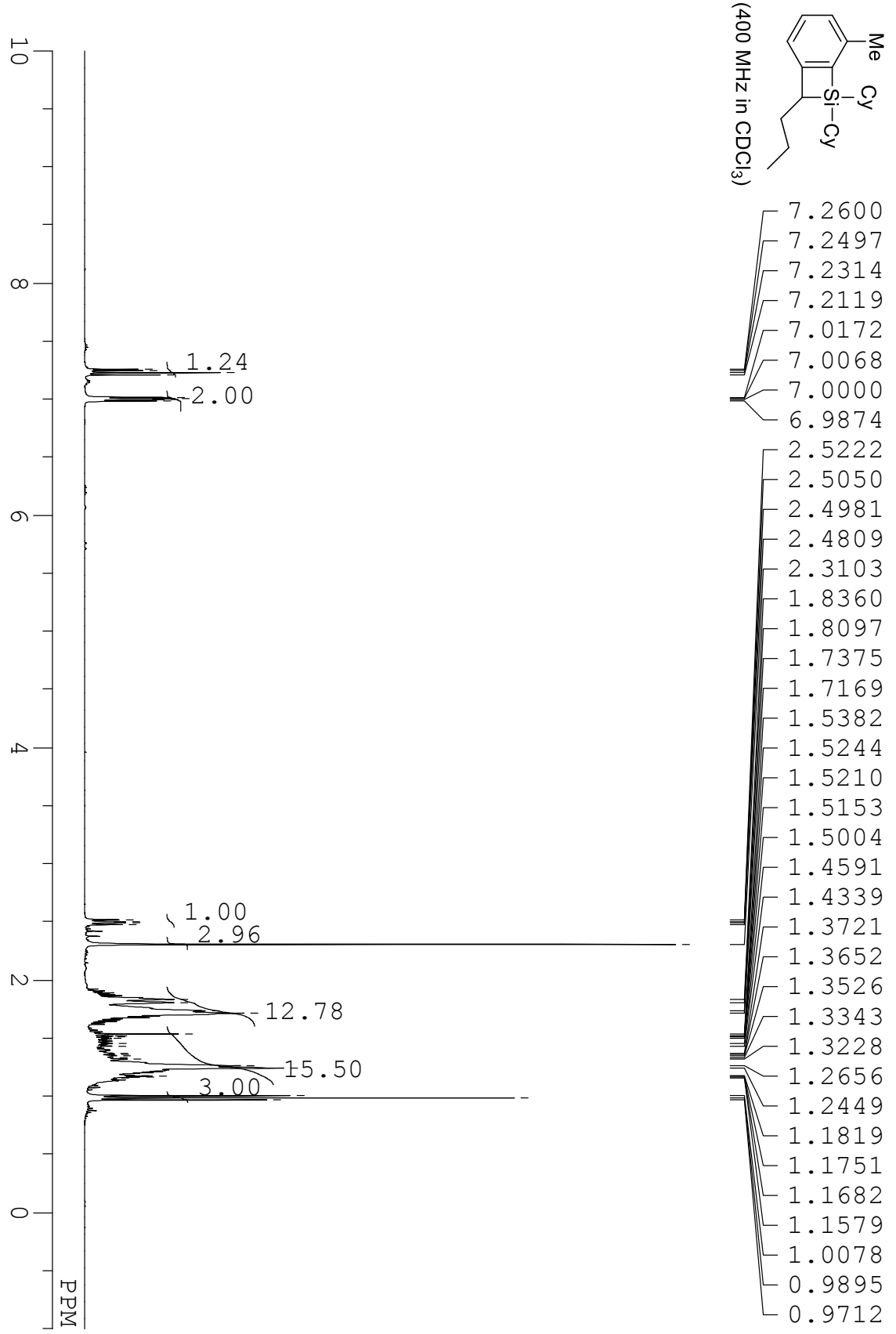
compound **2h**


(400 MHz in CDCl3)
Ar
Si—Ar
Ar =
O
OMe
PPM
10
8
6
4
2
0
1.01
1.02
1.00
6.16
4.12
4.46
1.02
2.00
2.00
1.00
2.96
2.96
1.00
1.02
2.98
8.8855
8.8649
8.6976
8.6758
8.5888
8.5682
7.8969
7.8832
7.8763
7.8637
7.8236
7.8007
7.7629
7.7446
7.5807
7.5624
7.5418
7.4994
7.4822
7.4536
7.4330
7.3780
7.3654
7.3436
7.3241
7.2898
7.2726
7.2600
7.1901
7.1718
4.9232
4.9060
4.6437
4.6265
3.6734
3.6551
2.8498
2.5875
1.9872
1.8062
1.5531
1.1842
1.1659
1.1464

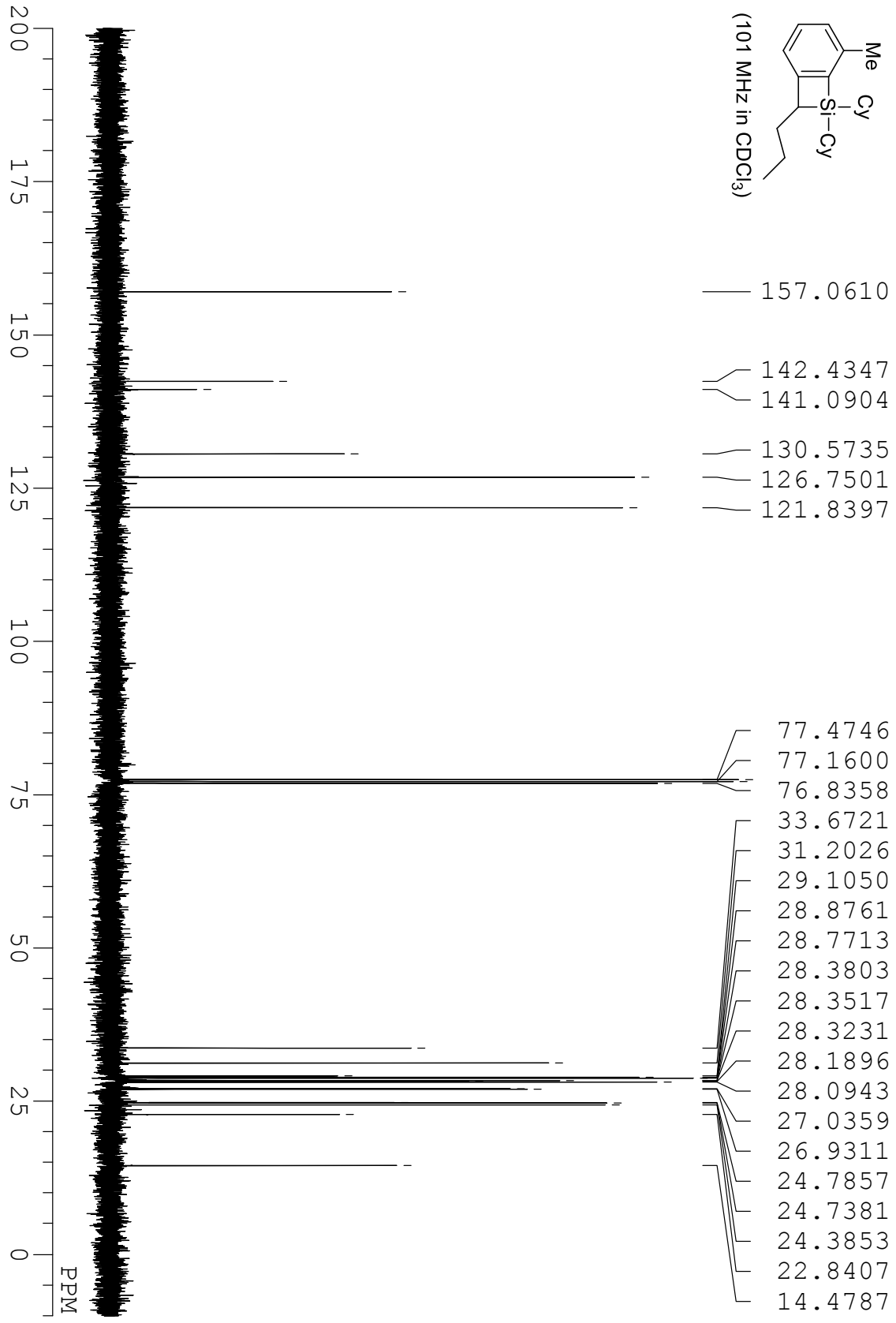
compound **2h**


(101 MHz in CDCl3)
Ar
Si—Ar
Ar =
O
OMe
160.1789
159.7880
155.9073
141.9771
138.5255
137.9344
135.2074
133.4721
132.1468
131.9370
131.8512
130.2875
129.8298
129.3817
128.7238
128.4378
128.3996
128.2852
126.4259
126.3687
126.0732
125.0625
124.3474
123.6704
123.5751
122.2211
120.6670
115.8233
114.3931
95.0281
94.0746
77.4746
77.1600
76.8358
55.6306
55.1920
39.5550
25.8346
14.8124
200
175
150
125
100
75
50
25
0
PPM

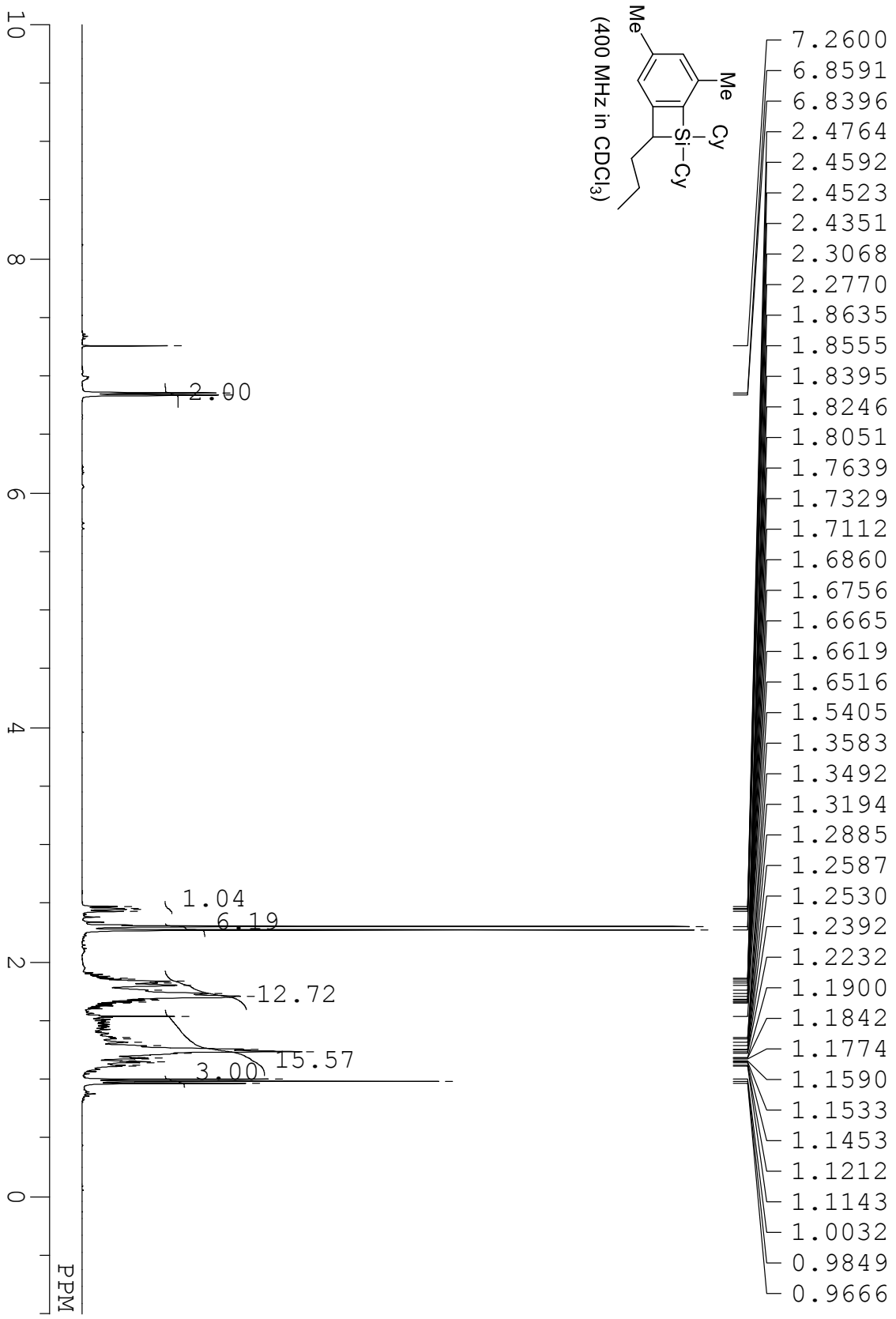
compound **2i** (93% pure)



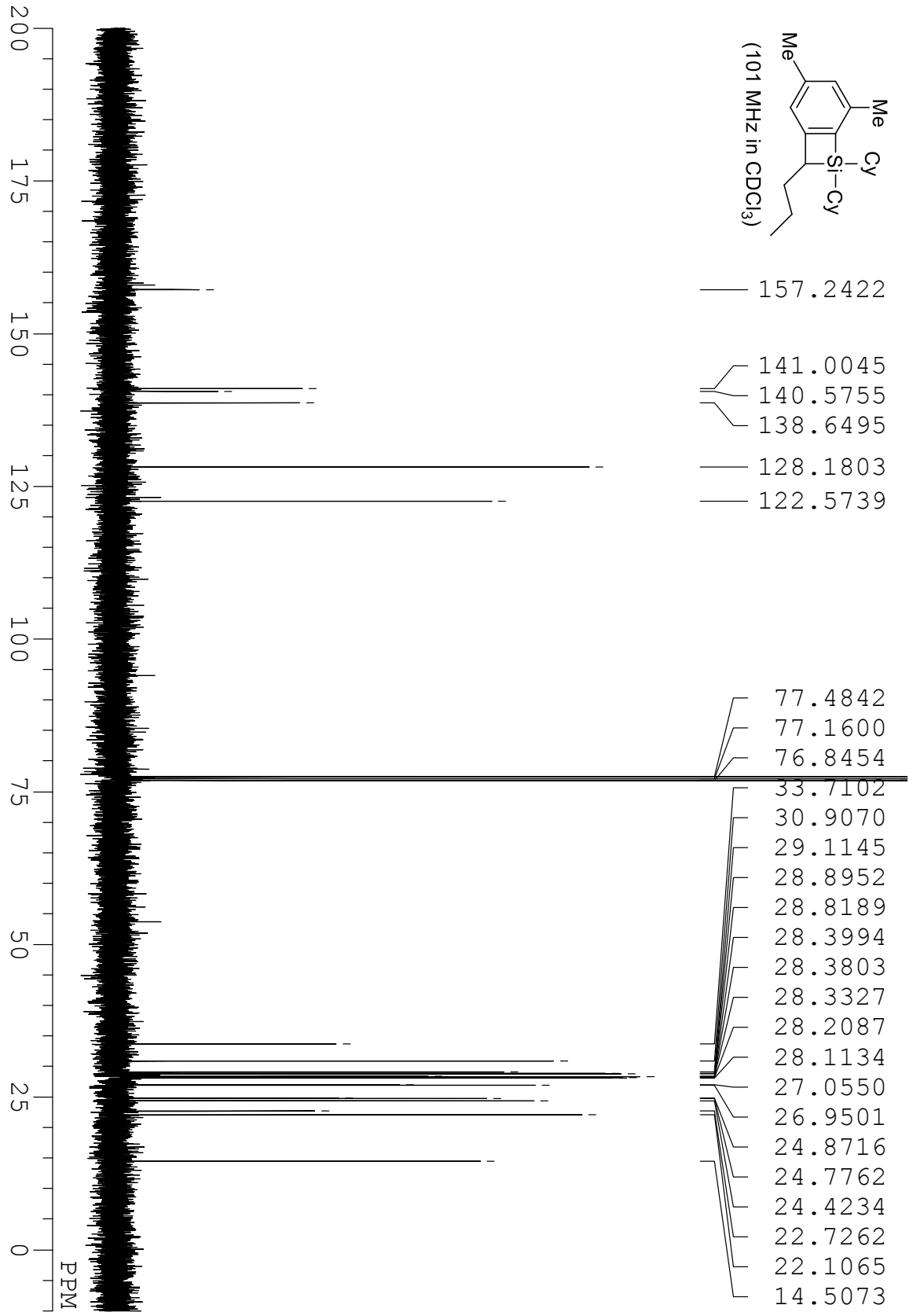
compound **2i** (93% pure)



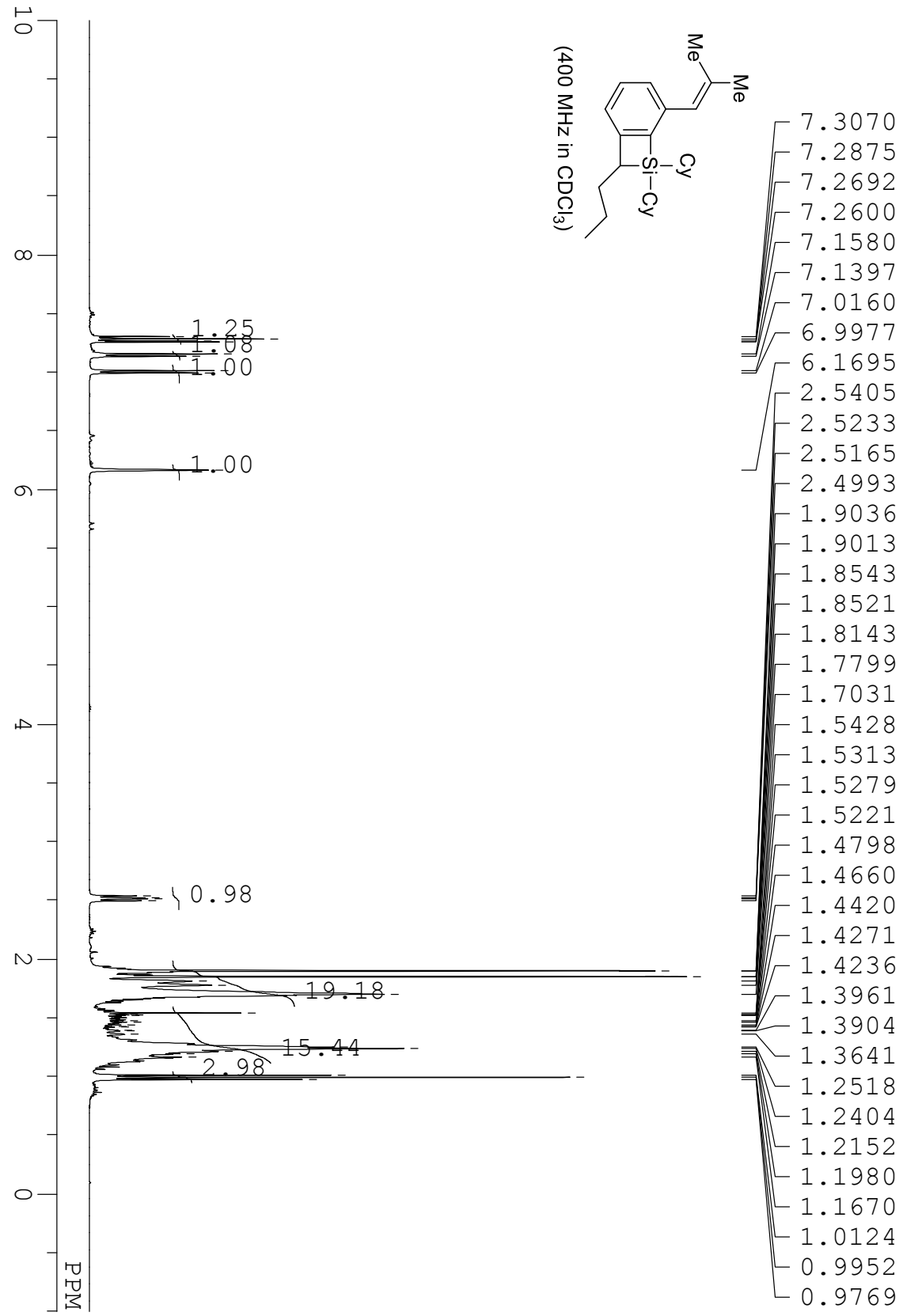
compound **2j** (93% pure)



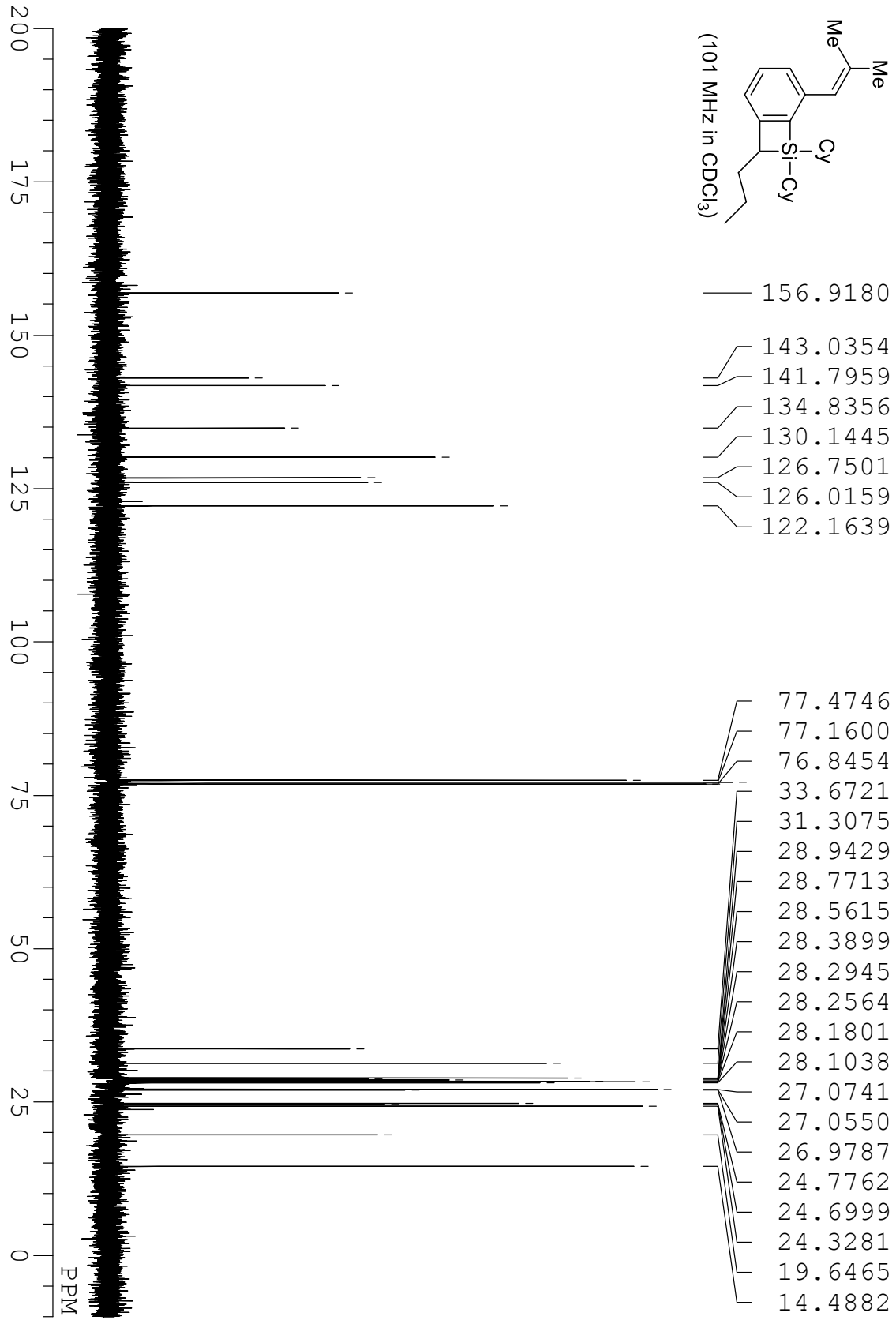
compound **2j** (93% pure)



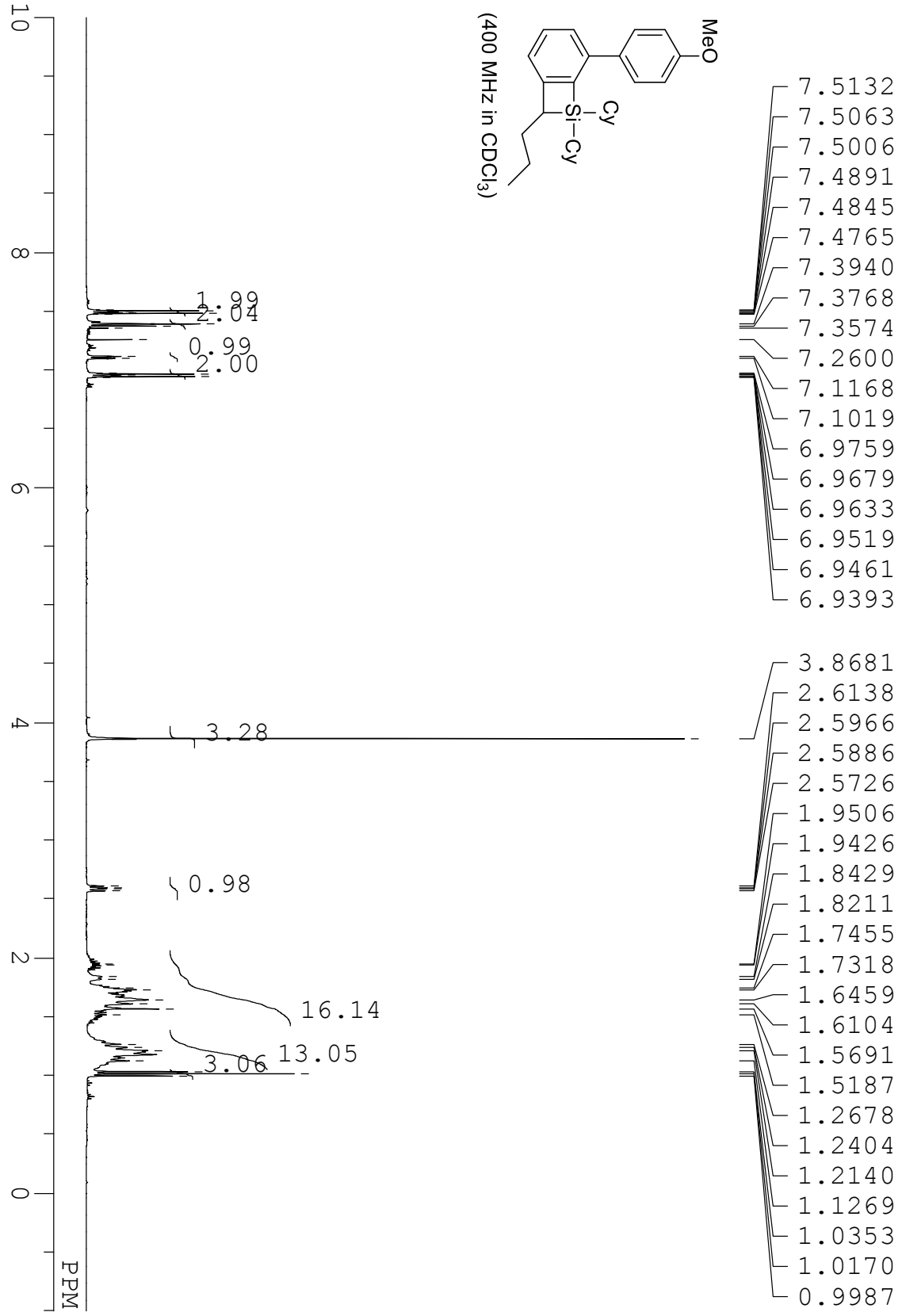
compound **2k** (93% pure)



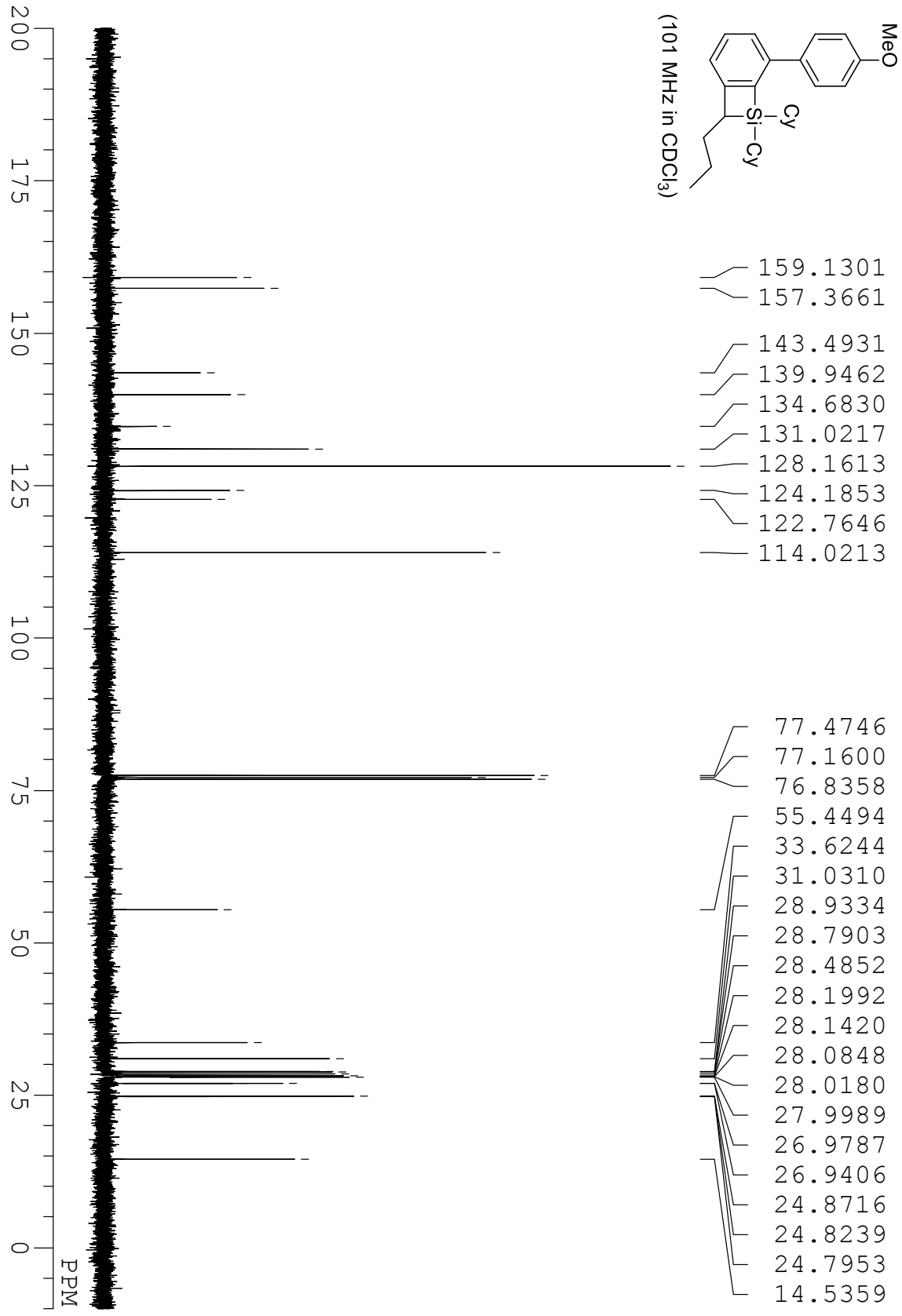
compound **2k** (93% pure)



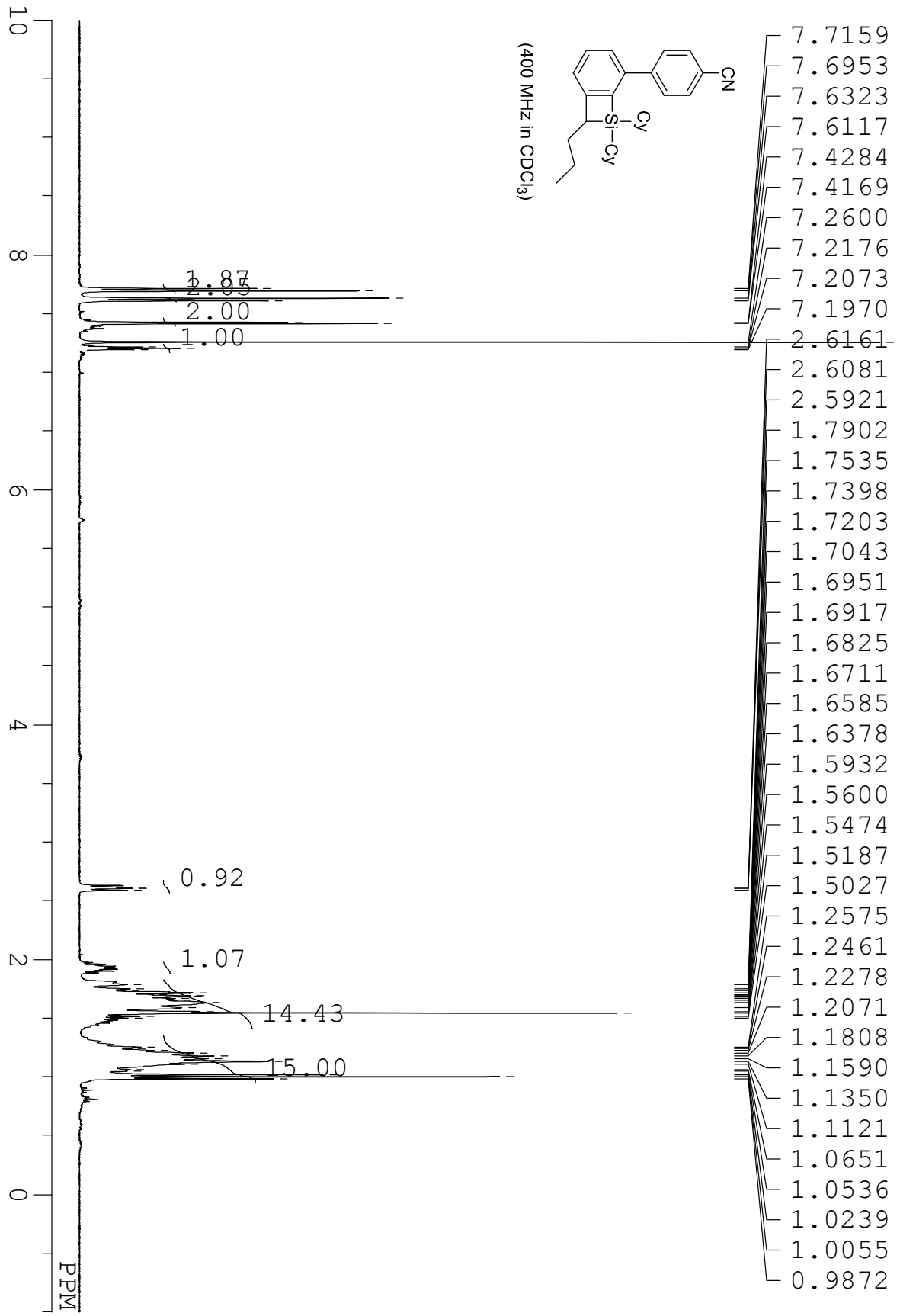
compound **2l** (91% pure)



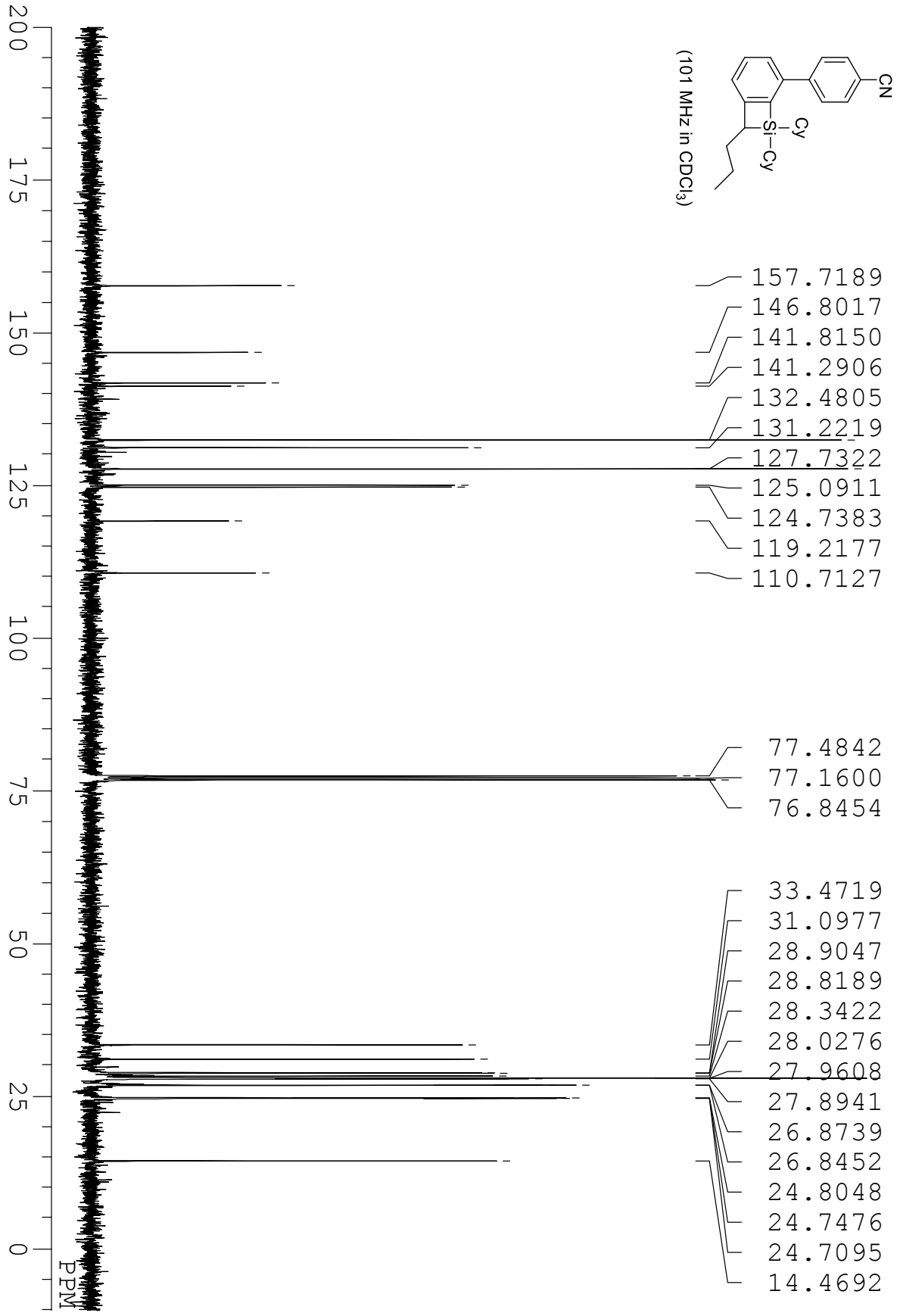
compound **2l** (91% pure)



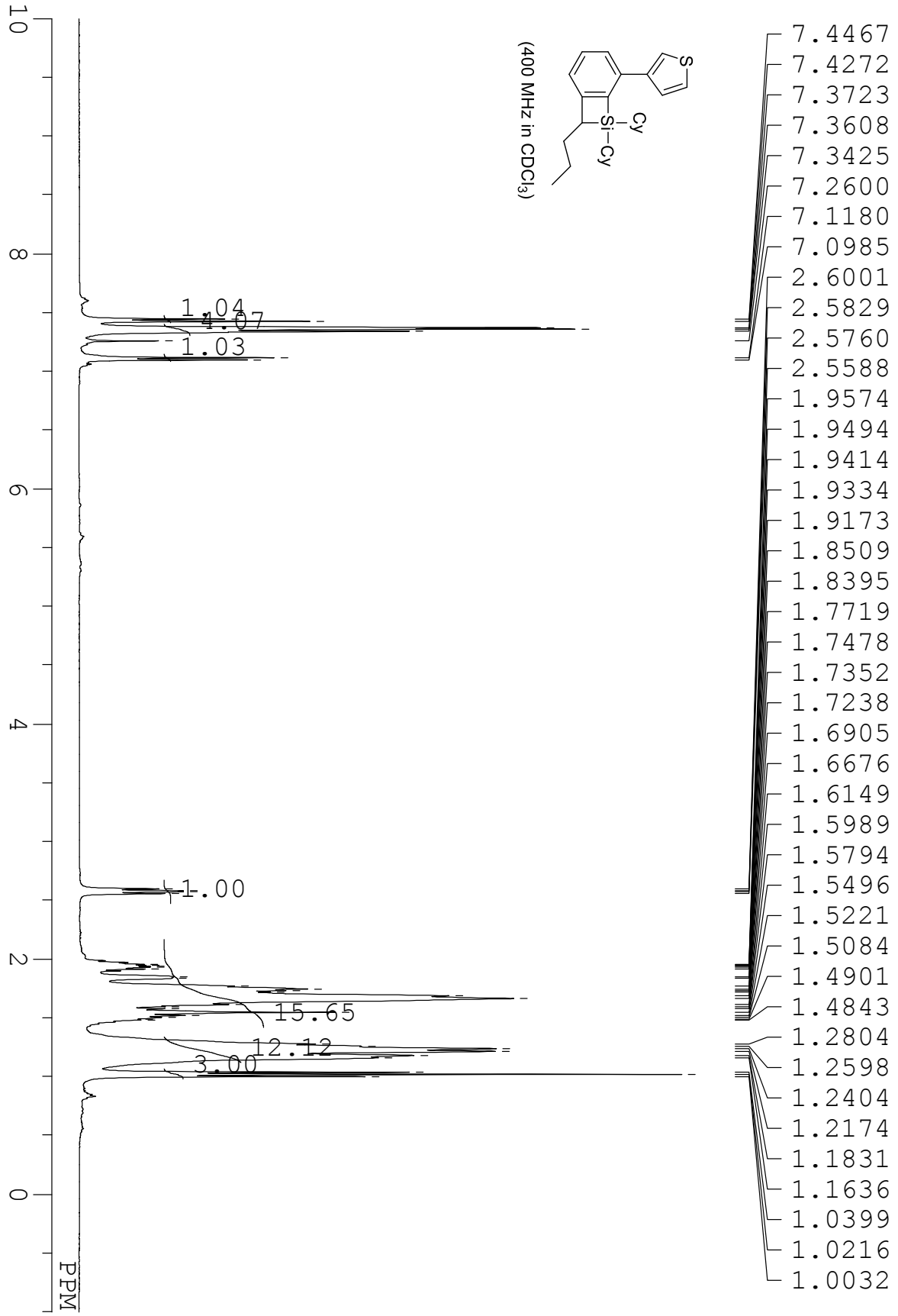
compound **2m** (91% pure)



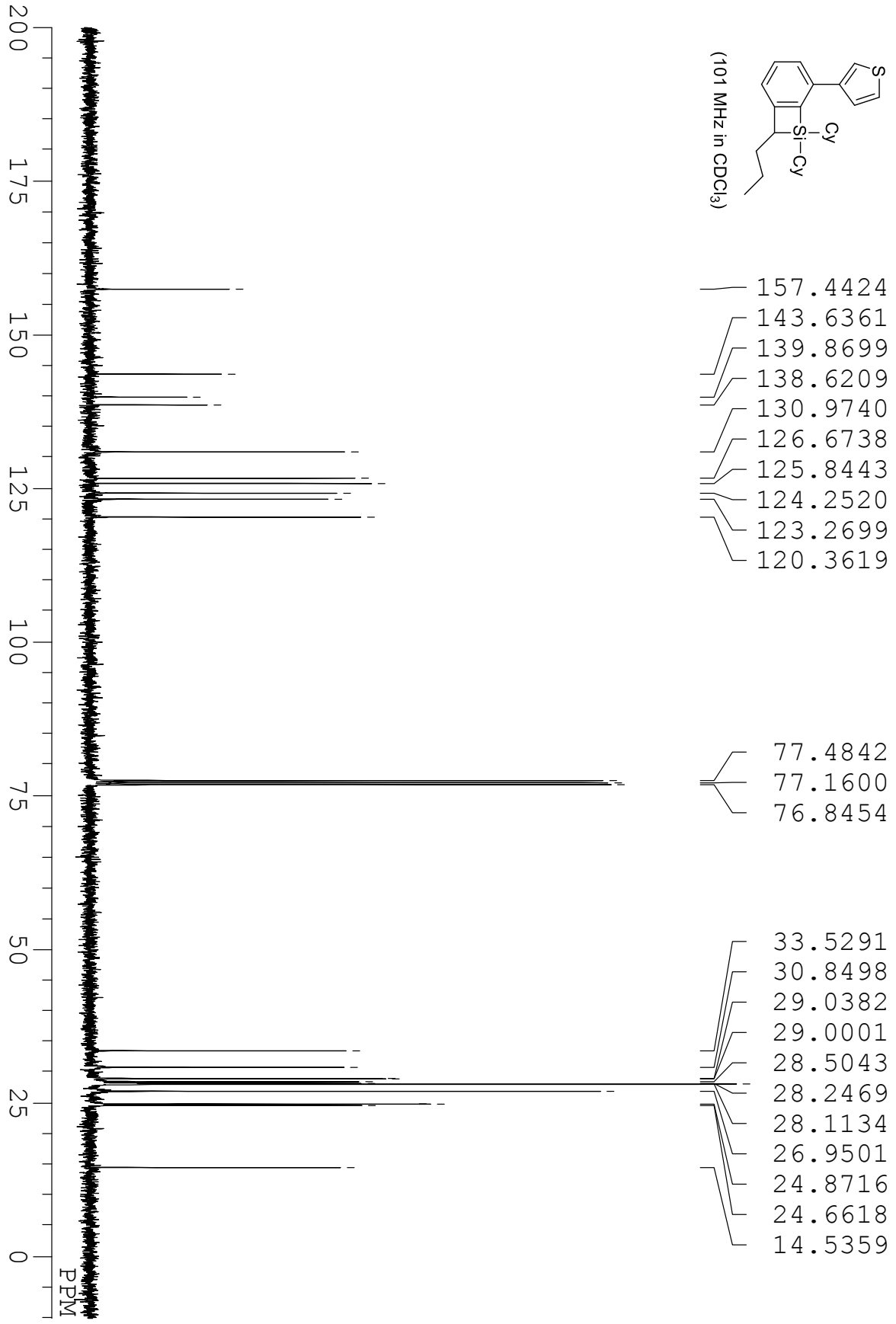
compound **2m** (91% pure)



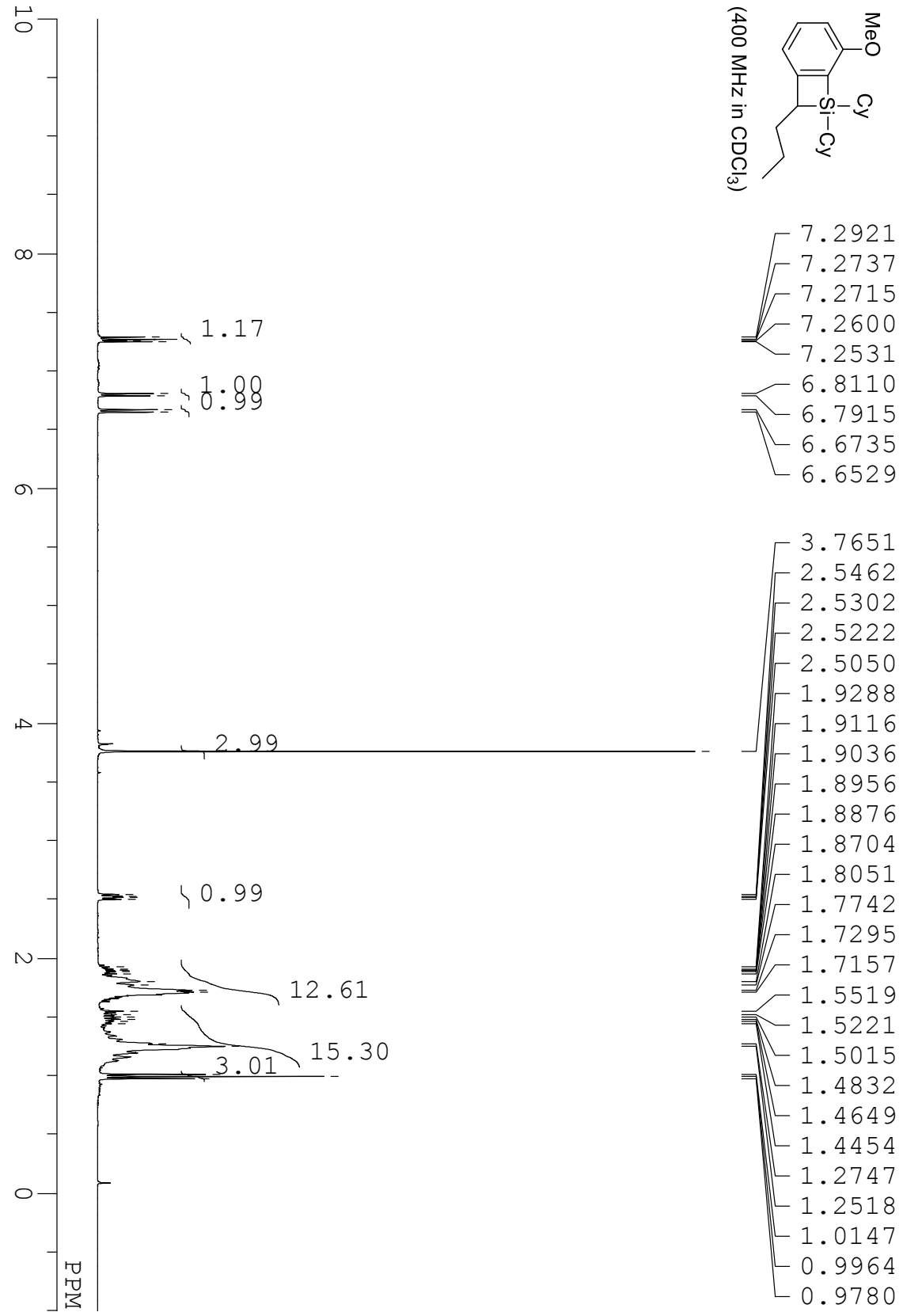
compound **2n** (94% pure)



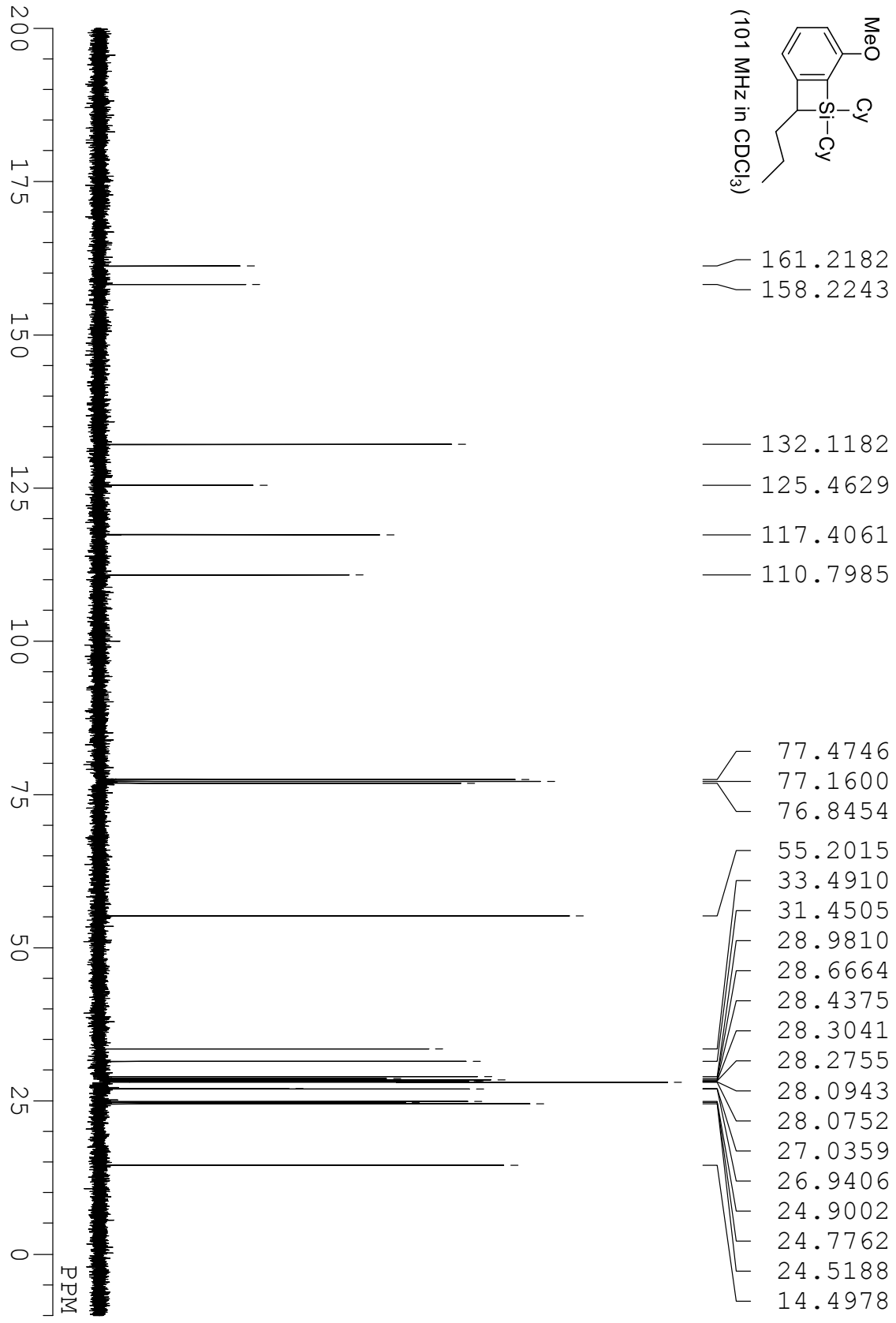
compound **2n** (94% pure)



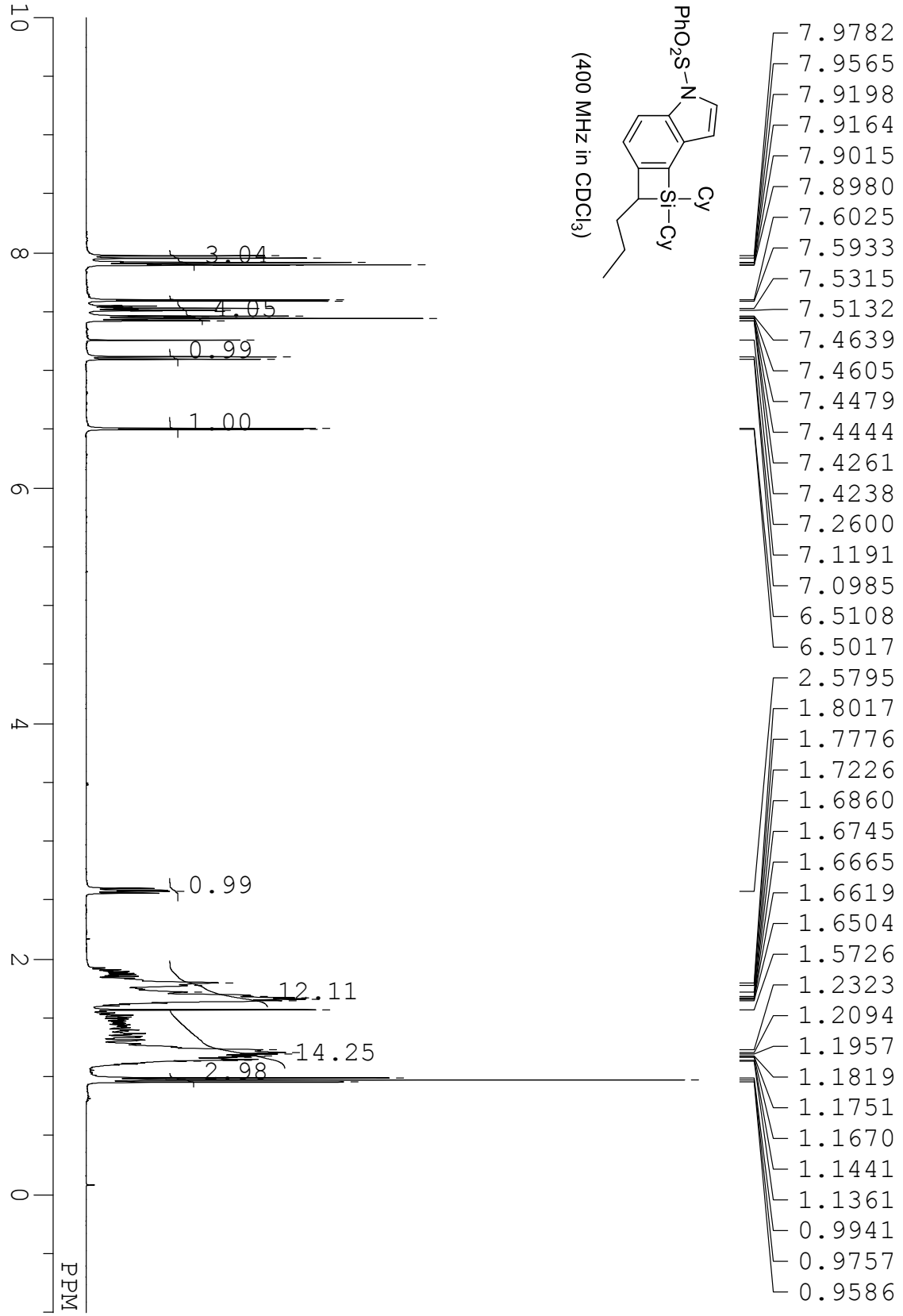
compound **2o** (95% pure)



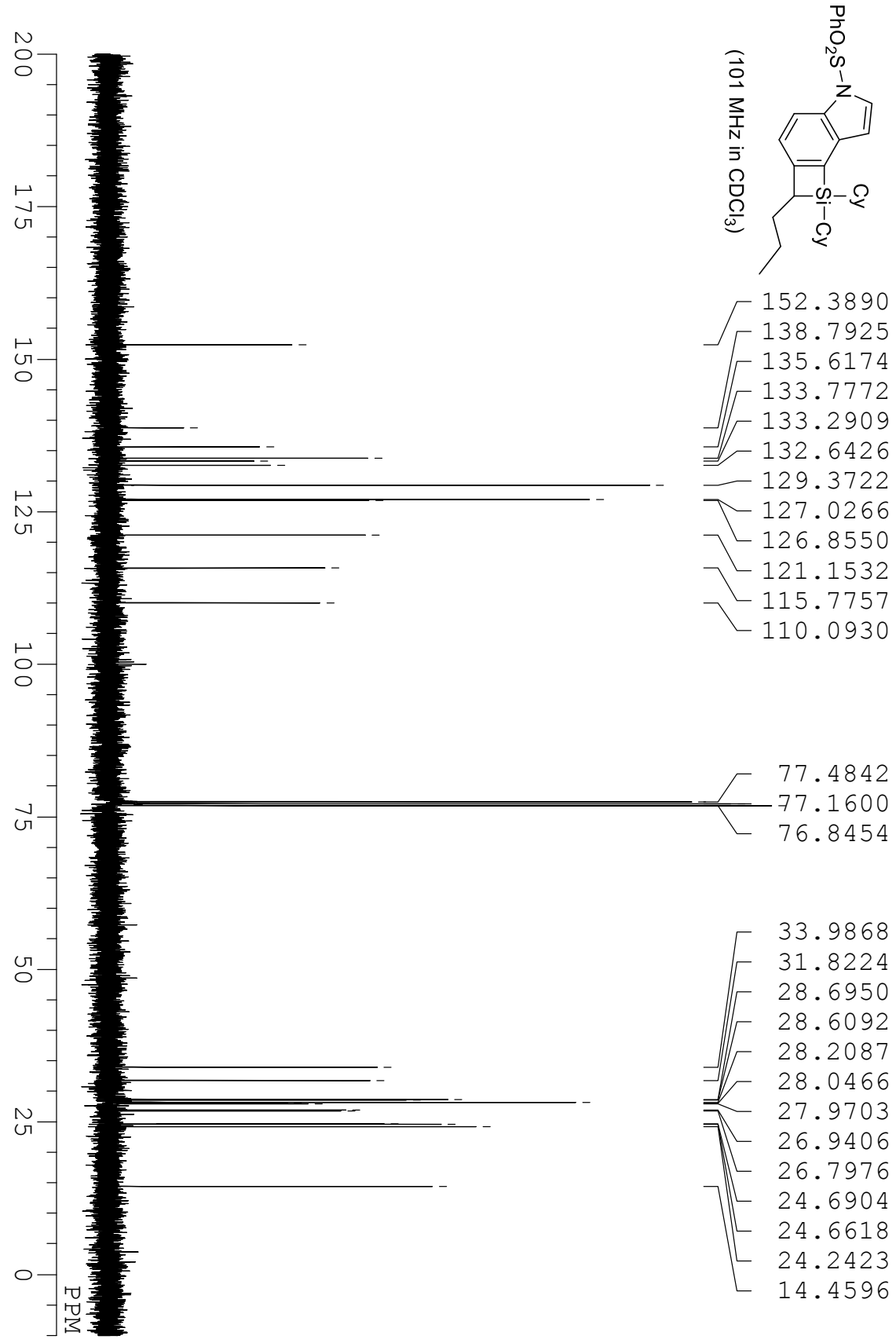
compound **2o** (95% pure)



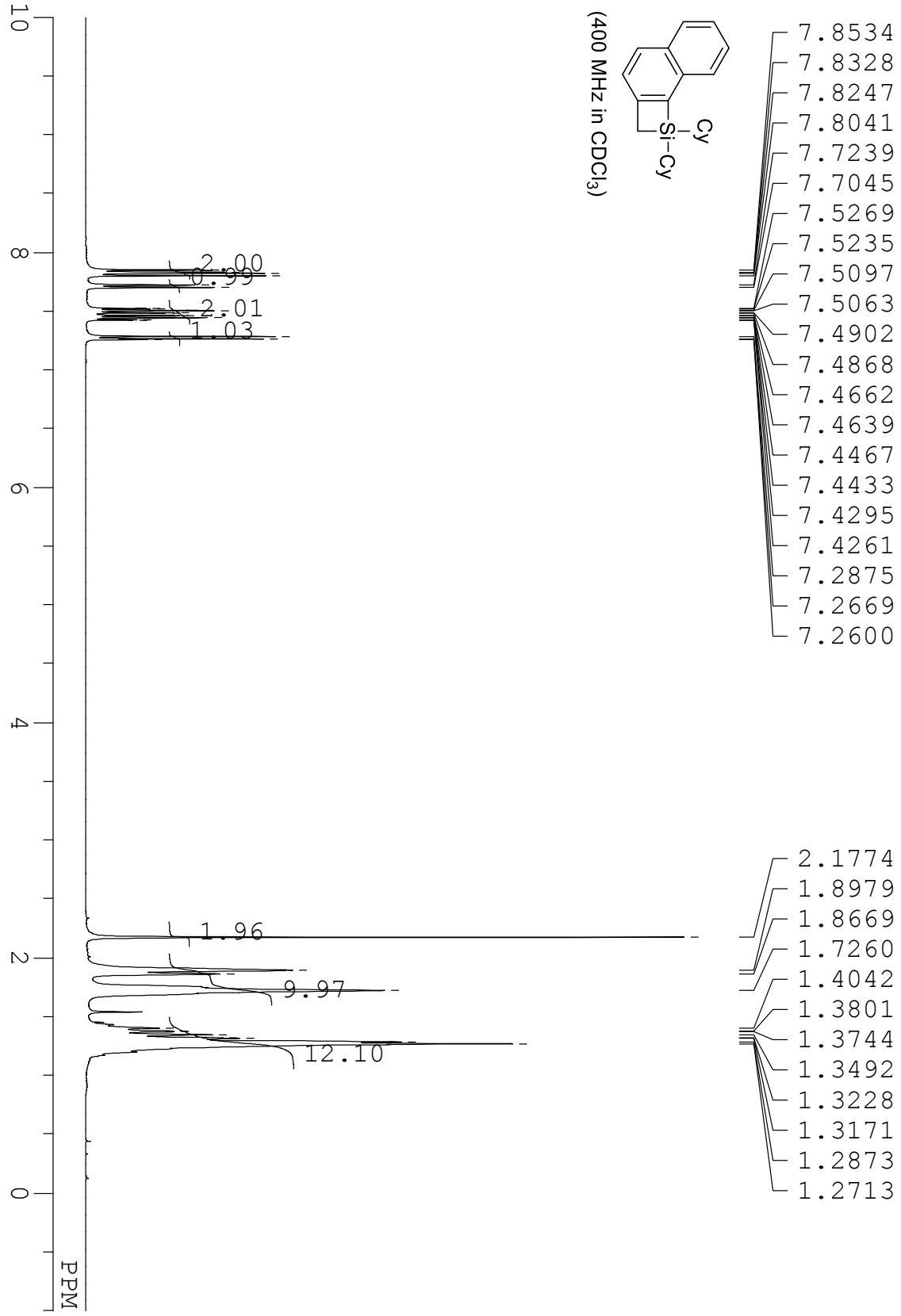
compound **2p**


(400 MHz in CDCl3)
PhO2S–N
Cy
Si–Cy
10
8
6
4
2
0
PPM
3.04
4.05
0.99
1.00
0.99
12.11
14.25
2.98
7.9782
7.9565
7.9198
7.9164
7.9015
7.8980
7.6025
7.5933
7.5315
7.5132
7.4639
7.4605
7.4479
7.4444
7.4261
7.4238
7.2600
7.1191
7.0985
6.5108
6.5017
2.5795
1.8017
1.7776
1.7226
1.6860
1.6745
1.6665
1.6619
1.6504
1.5726
1.2323
1.2094
1.1957
1.1819
1.1751
1.1670
1.1441
1.1361
0.9941
0.9757
0.9586

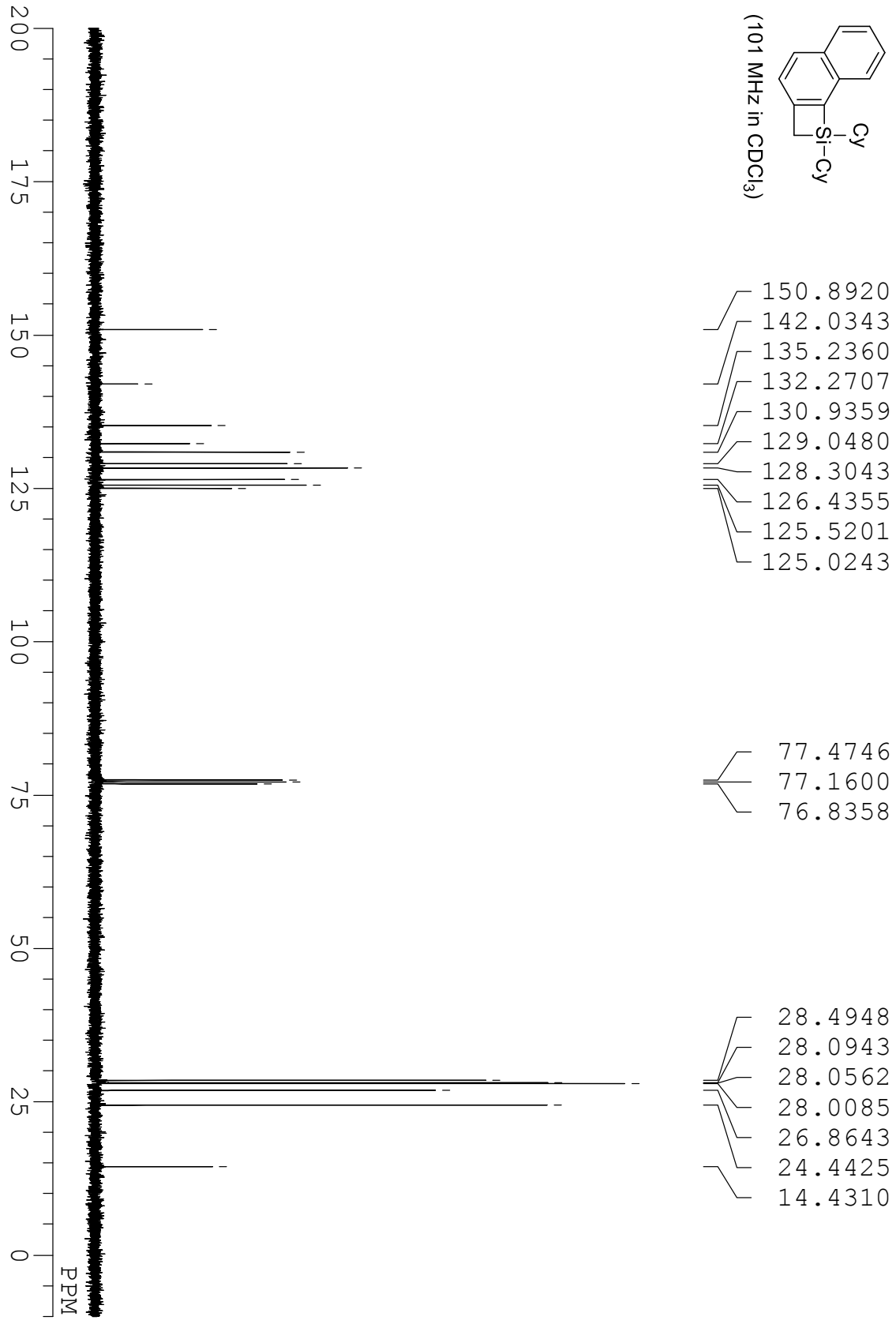
compound **2p**


(101 MHz in CDCl3)
PhO2S–N
Cy
Si–Cy
152.3890
138.7925
135.6174
133.7772
133.2909
132.6426
129.3722
127.0266
126.8550
121.1532
115.7757
110.0930
77.4842
77.1600
76.8454
33.9868
31.8224
28.6950
28.6092
28.2087
28.0466
27.9703
26.9406
26.7976
24.6904
24.6618
24.2423
14.4596
200
175
150
125
100
75
50
25
0
PPM

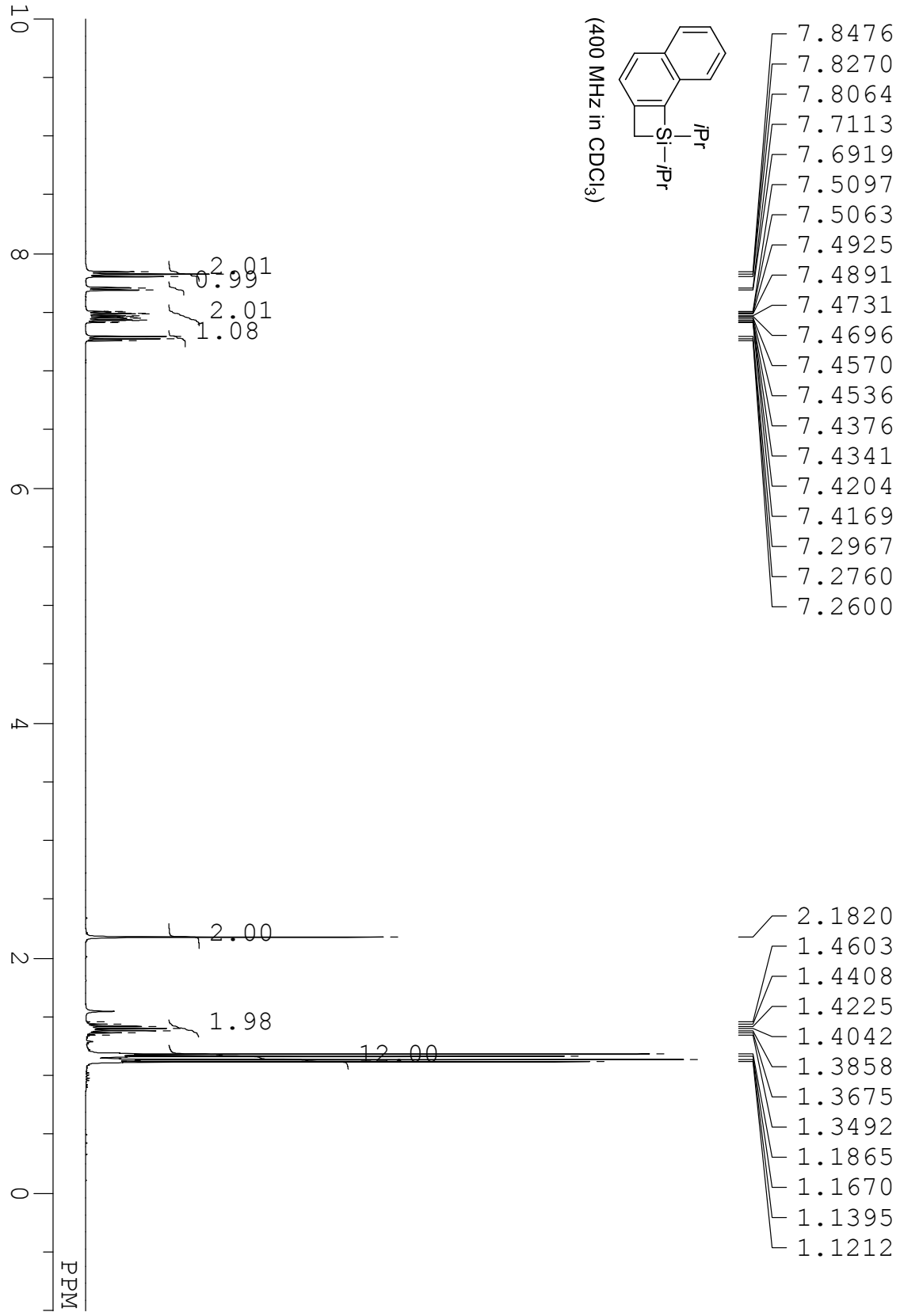
compound **2q**


(400 MHz in CDCl3)
Cy
Si–Cy
7.8534
7.8328
7.8247
7.8041
7.7239
7.7045
7.5269
7.5235
7.5097
7.5063
7.4902
7.4868
7.4662
7.4639
7.4467
7.4433
7.4295
7.4261
7.2875
7.2669
7.2600
2.1774
1.8979
1.8669
1.7260
1.4042
1.3801
1.3744
1.3492
1.3228
1.3171
1.2873
1.2713
2.00
0.99
2.01
1.03
1.96
9.97
12.10
10
8
6
4
2
0
PPM

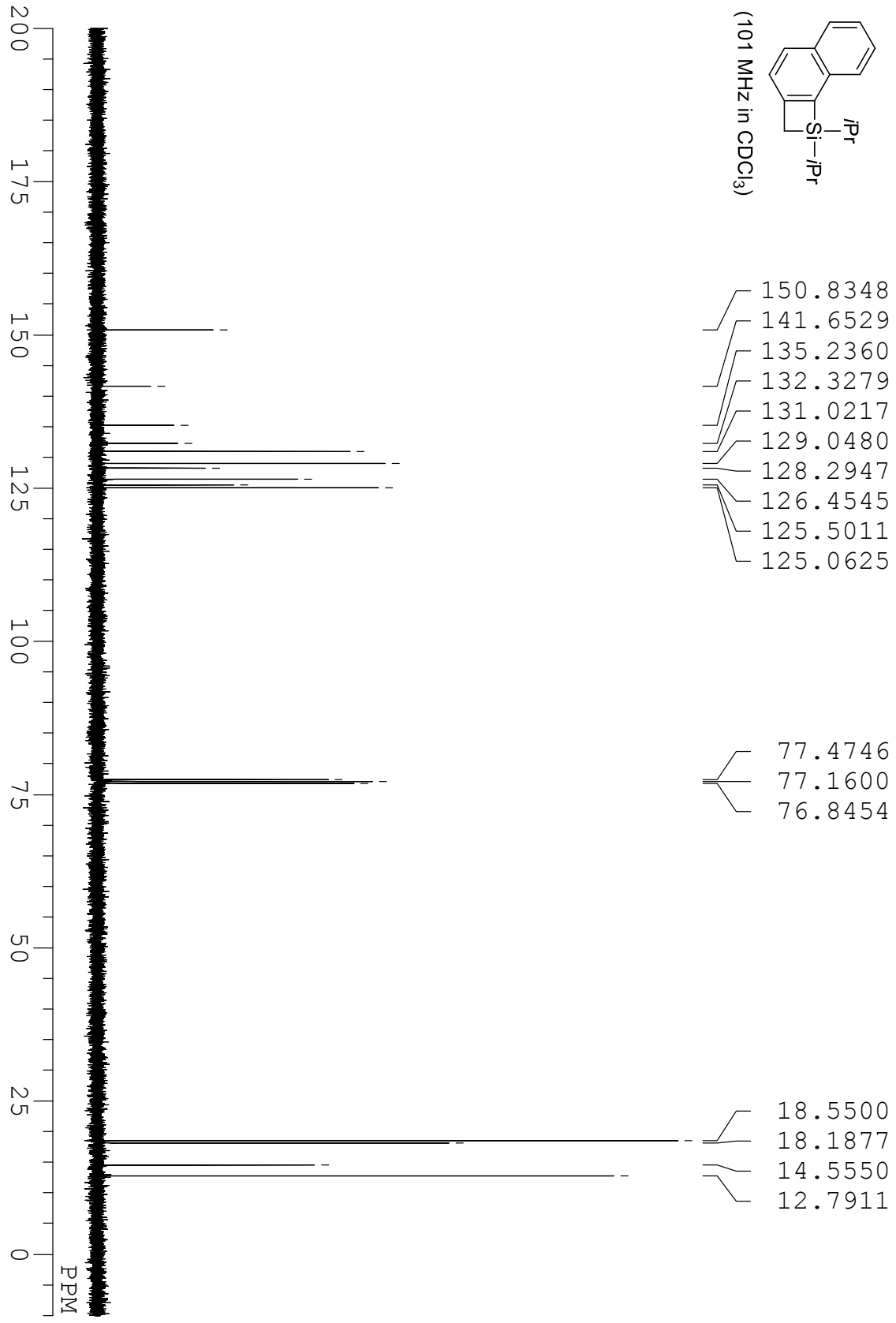
compound **2q**


(101 MHz in CDCl3)
Cy
Si–Cy
150.8920
142.0343
135.2360
132.2707
130.9359
129.0480
128.3043
126.4355
125.5201
125.0243
77.4746
77.1600
76.8358
28.4948
28.0943
28.0562
28.0085
26.8643
24.4425
14.4310
200
175
150
125
100
75
50
25
0
PPM

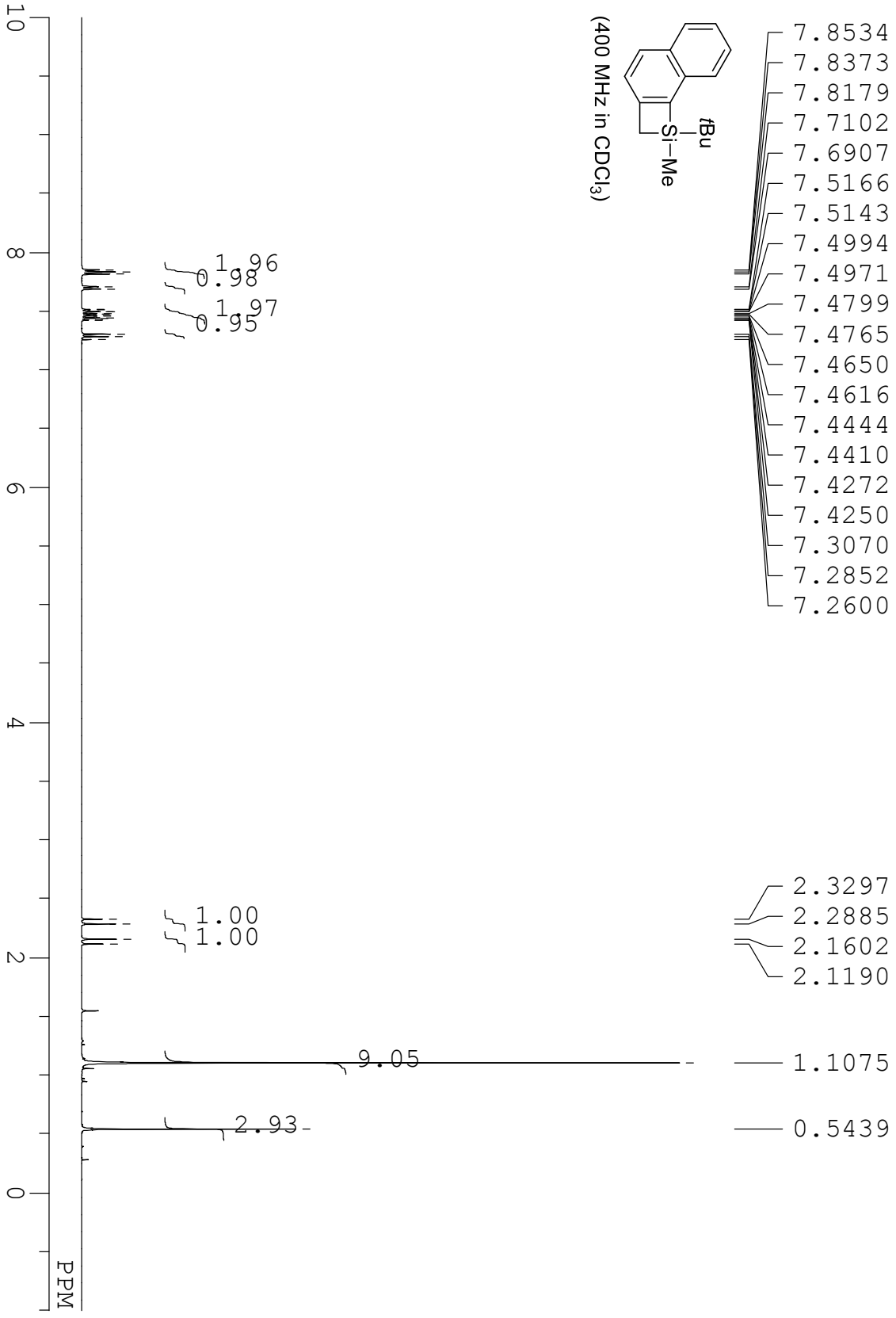
compound **2r**


(400 MHz in CDCl3)
iPr
Si—iPr
7.8476
7.8270
7.8064
7.7113
7.6919
7.5097
7.5063
7.4925
7.4891
7.4731
7.4696
7.4570
7.4536
7.4376
7.4341
7.4204
7.4169
7.2967
7.2760
7.2600
2.1820
1.4603
1.4408
1.4225
1.4042
1.3858
1.3675
1.3492
1.1865
1.1670
1.1395
1.1212
2.01
0.99
2.01
1.08
2.00
1.98
12.00
10
8
6
4
2
0
PPM

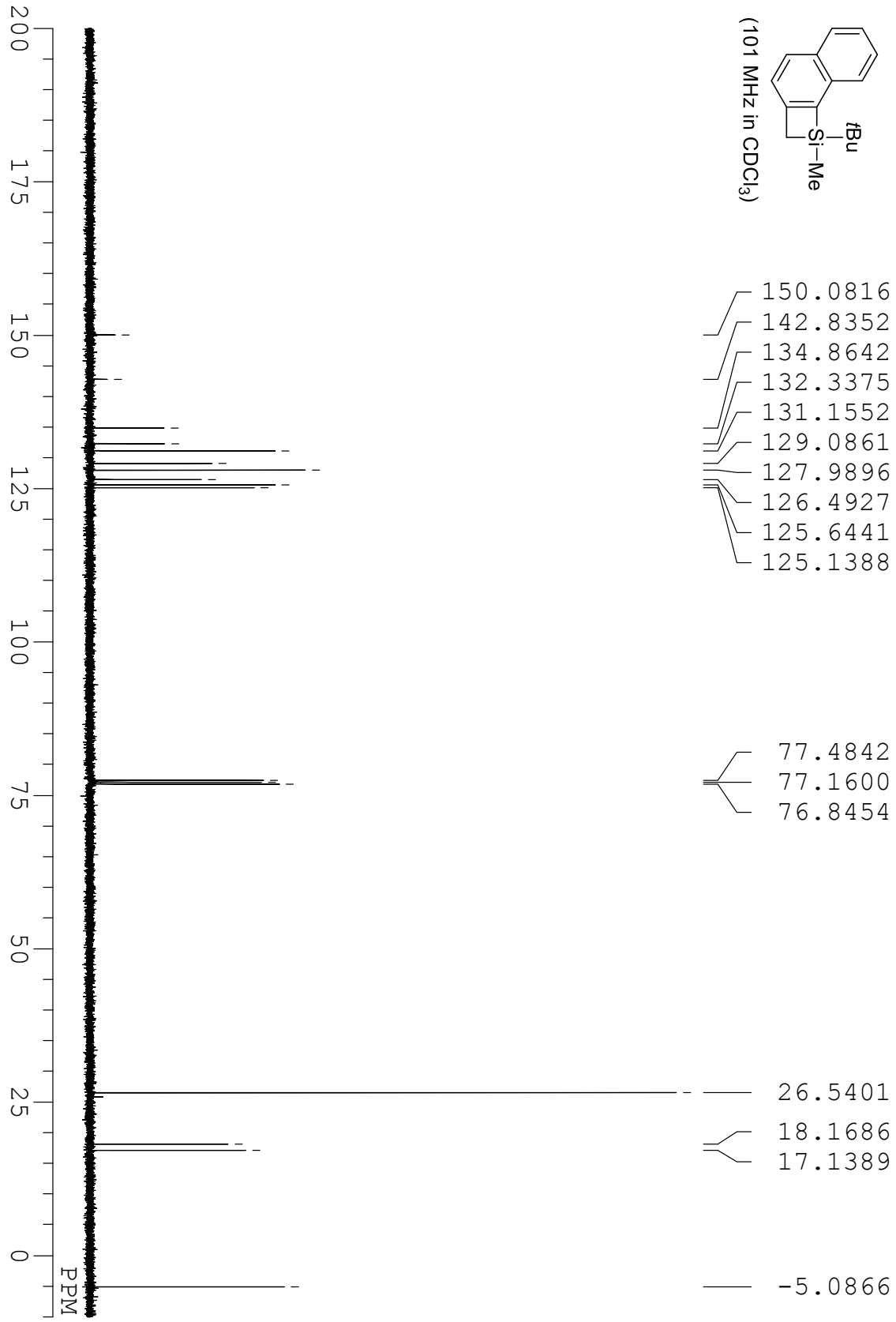
compound **2r**


(101 MHz in CDCl3)
iPr
Si
iPr
150.8348
141.6529
135.2360
132.3279
131.0217
129.0480
128.2947
126.4545
125.5011
125.0625
77.4746
77.1600
76.8454
18.5500
18.1877
14.5550
12.7911
200
175
150
125
100
75
50
25
0
PPM

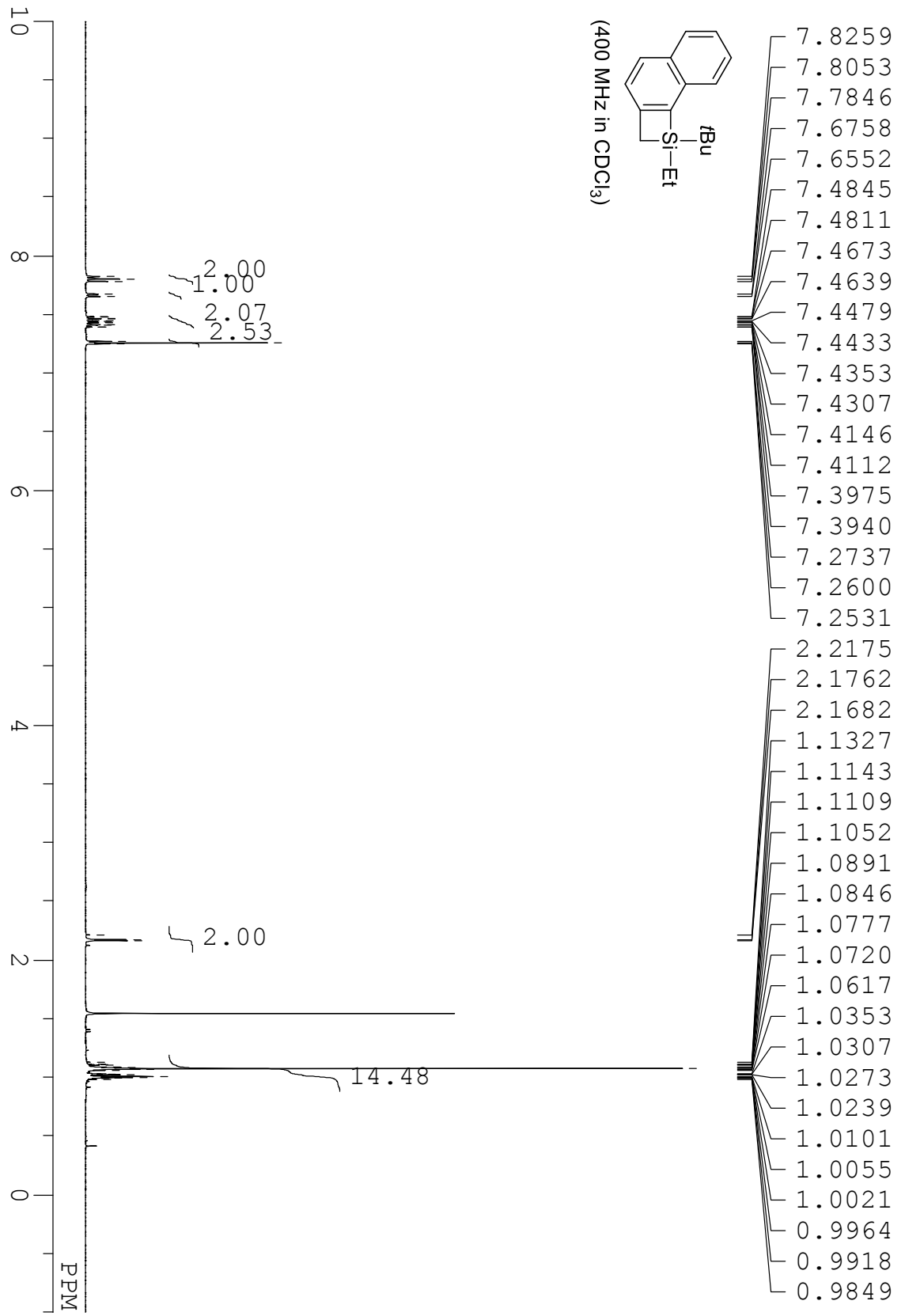
compound **2s**


(400 MHz in CDCl3)
tBu
Si–Me
7.8534
7.8373
7.8179
7.7102
7.6907
7.5166
7.5143
7.4994
7.4971
7.4799
7.4765
7.4650
7.4616
7.4444
7.4410
7.4272
7.4250
7.3070
7.2852
7.2600
2.3297
2.2885
2.1602
2.1190
1.1075
0.5439
1.96
0.98
1.97
0.95
1.00
1.00
9.05
2.93
10
8
6
4
2
0
PPM

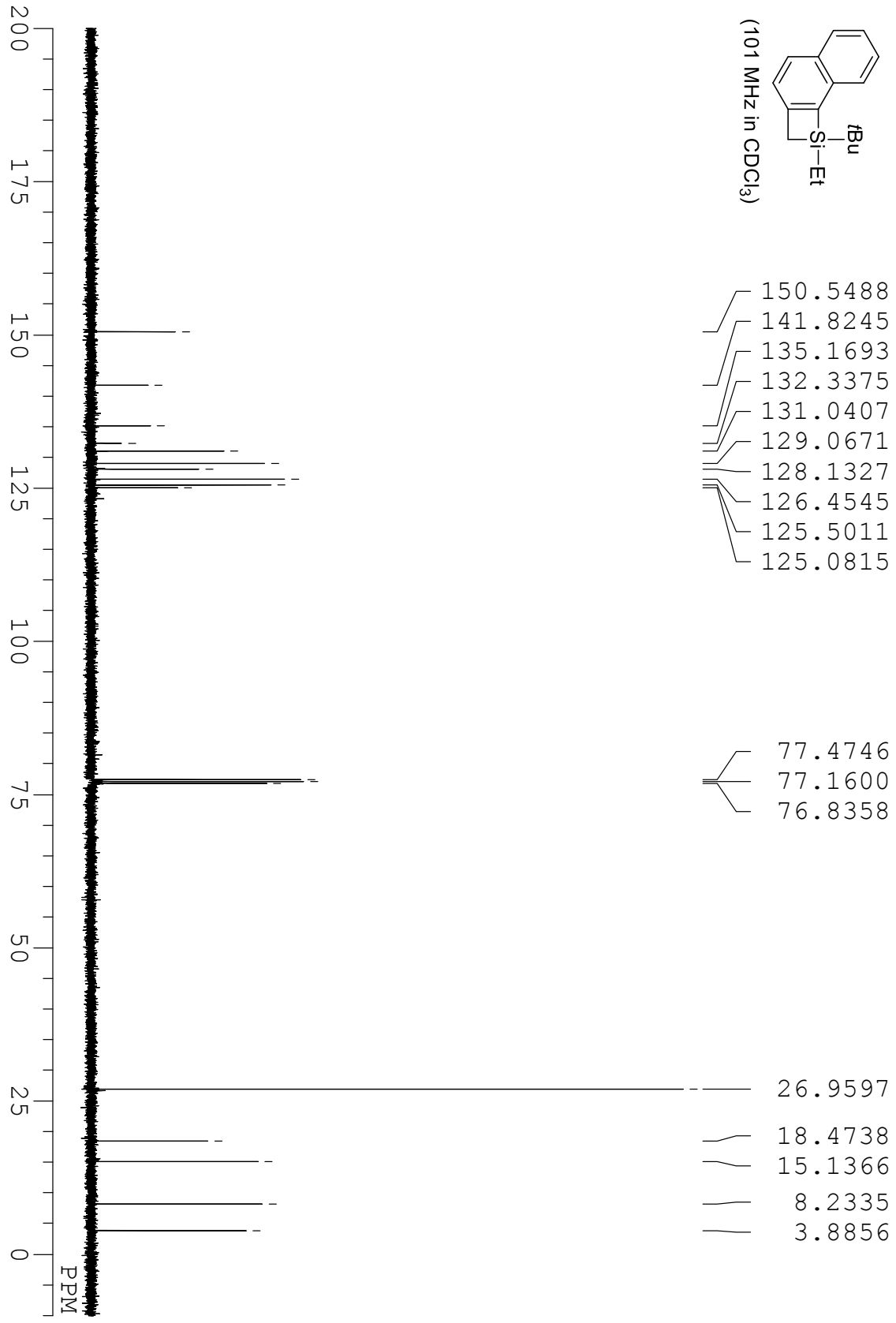
compound **2s**


(101 MHz in CDCl3)
tBu
Si–Me
150.0816
142.8352
134.8642
132.3375
131.1552
129.0861
127.9896
126.4927
125.6441
125.1388
77.4842
77.1600
76.8454
26.5401
18.1686
17.1389
-5.0866
200
175
150
125
100
75
50
25
0
PPM

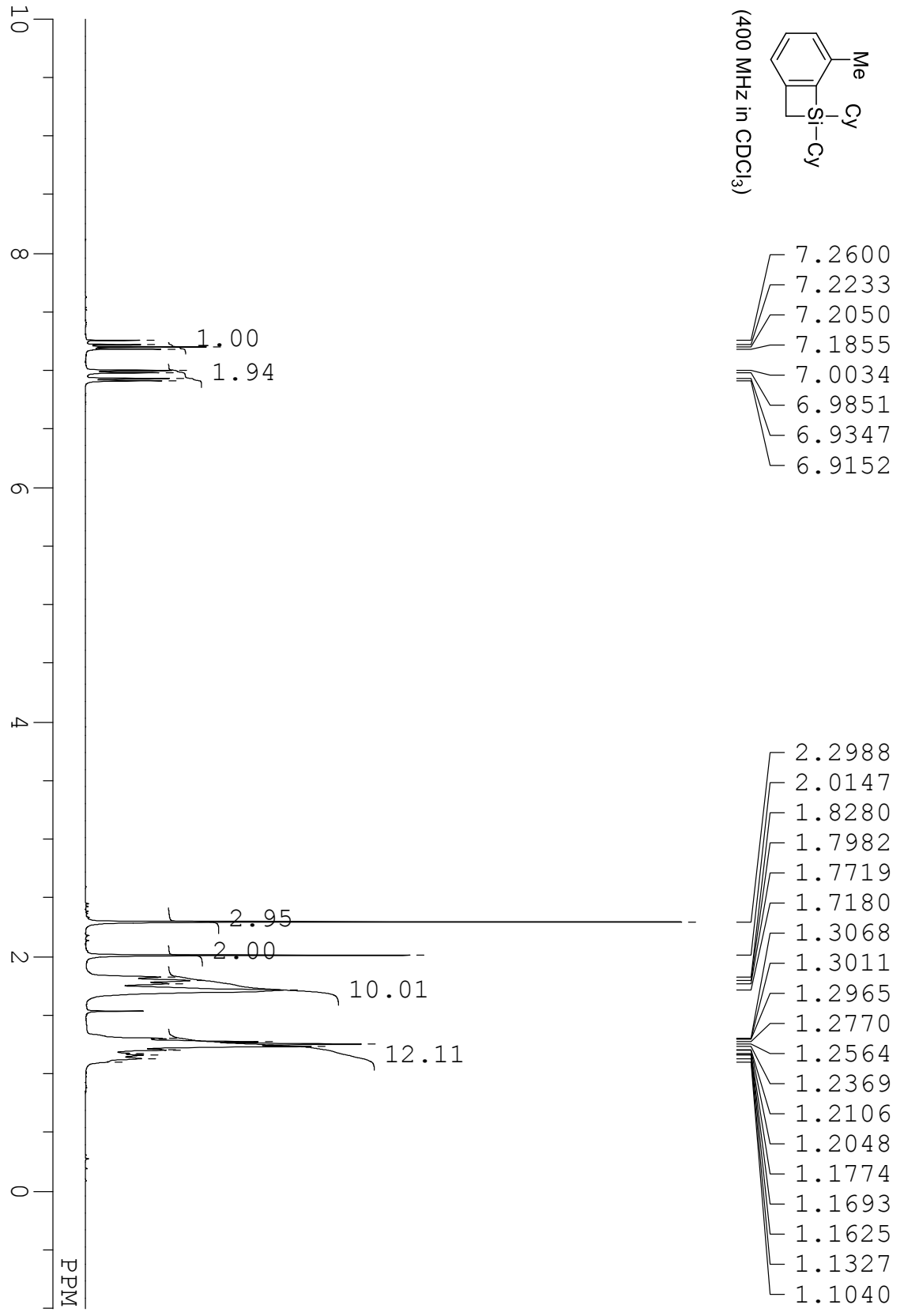
compound **2t** (96% pure)



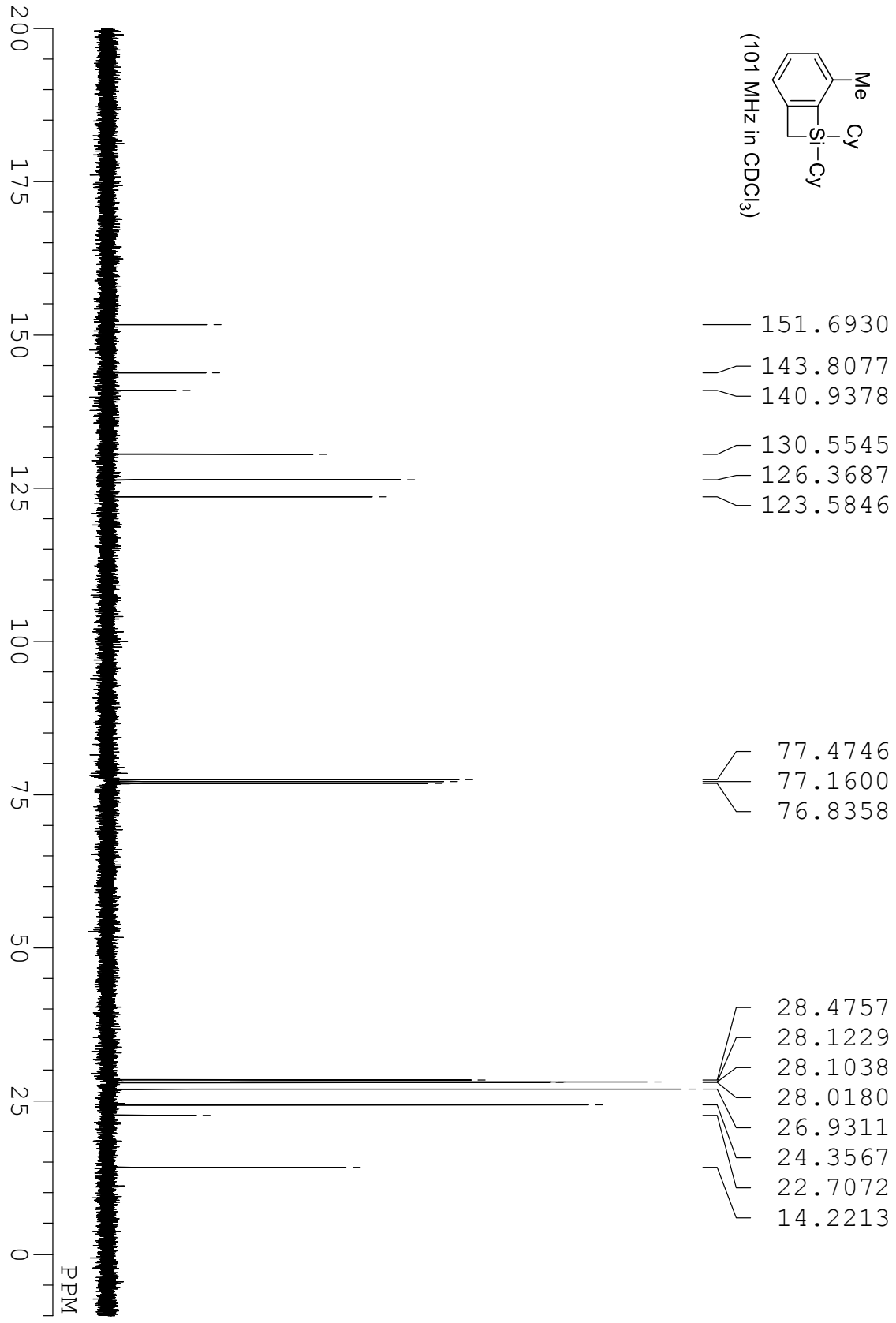
compound **2t** (96% pure)



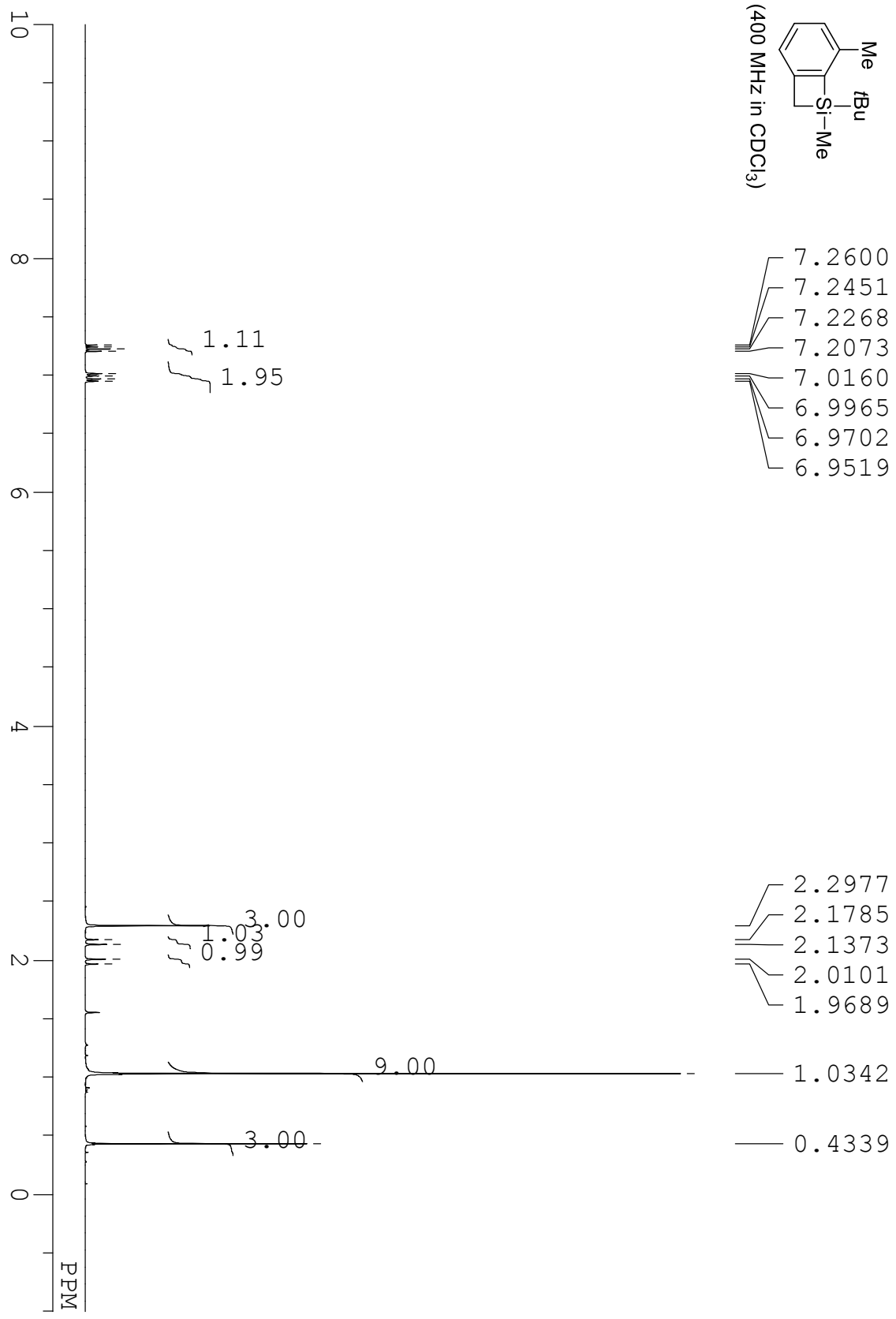
compound **2u**


(400 MHz in CDCl3)
Me
Cy
Si—Cy
7.2600
7.2233
7.2050
7.1855
7.0034
6.9851
6.9347
6.9152
2.2988
2.0147
1.8280
1.7982
1.7719
1.7180
1.3068
1.3011
1.2965
1.2770
1.2564
1.2369
1.2106
1.2048
1.1774
1.1693
1.1625
1.1327
1.1040
1.00
1.94
2.95
2.00
10.01
12.11
10
8
6
4
2
0
PPM

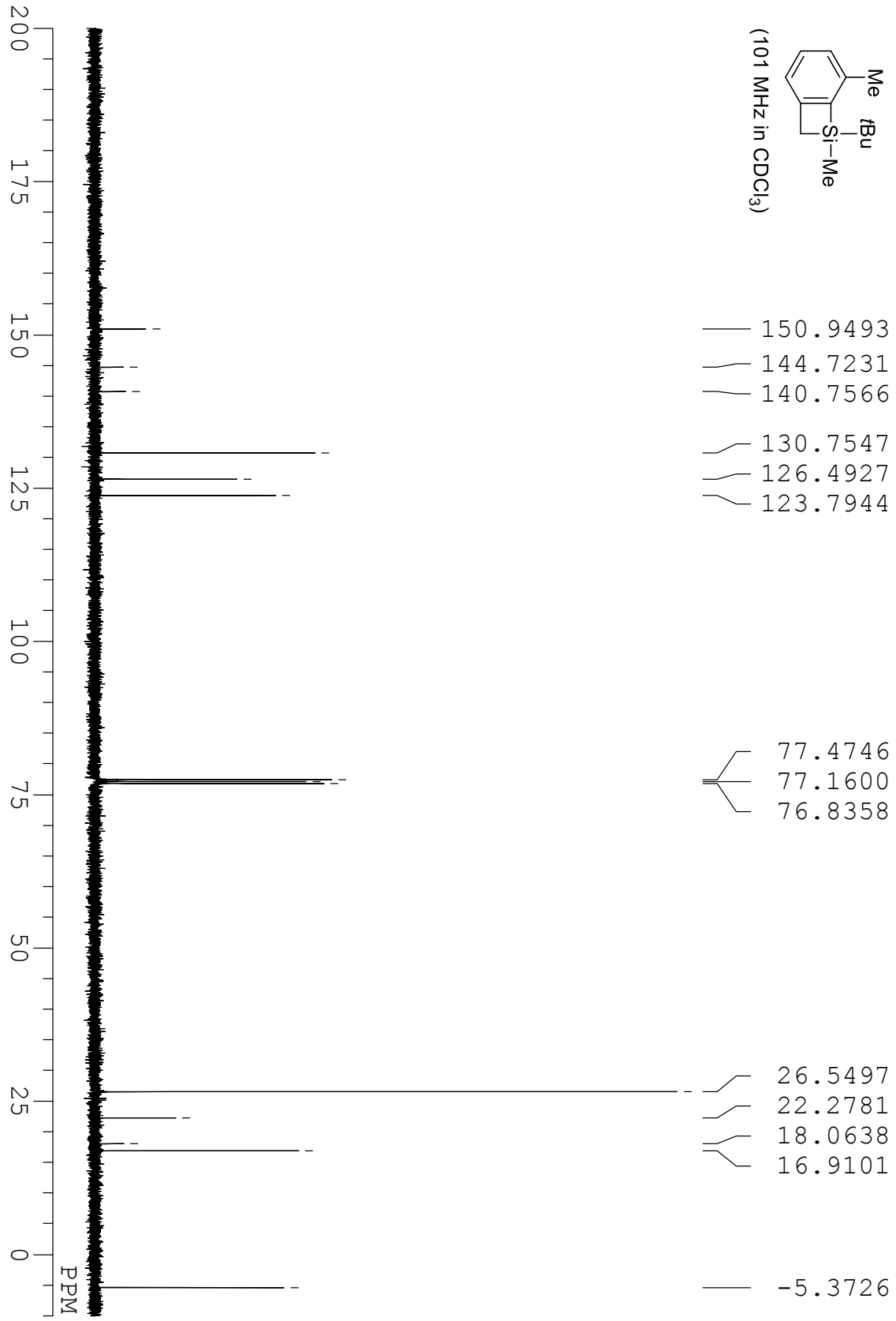
compound **2u**


(101 MHz in CDCl3)
Me
Cy
Si
Cy
151.6930
143.8077
140.9378
130.5545
126.3687
123.5846
77.4746
77.1600
76.8358
28.4757
28.1229
28.1038
28.0180
26.9311
24.3567
22.7072
14.2213
200
175
150
125
100
75
50
25
0
PPM

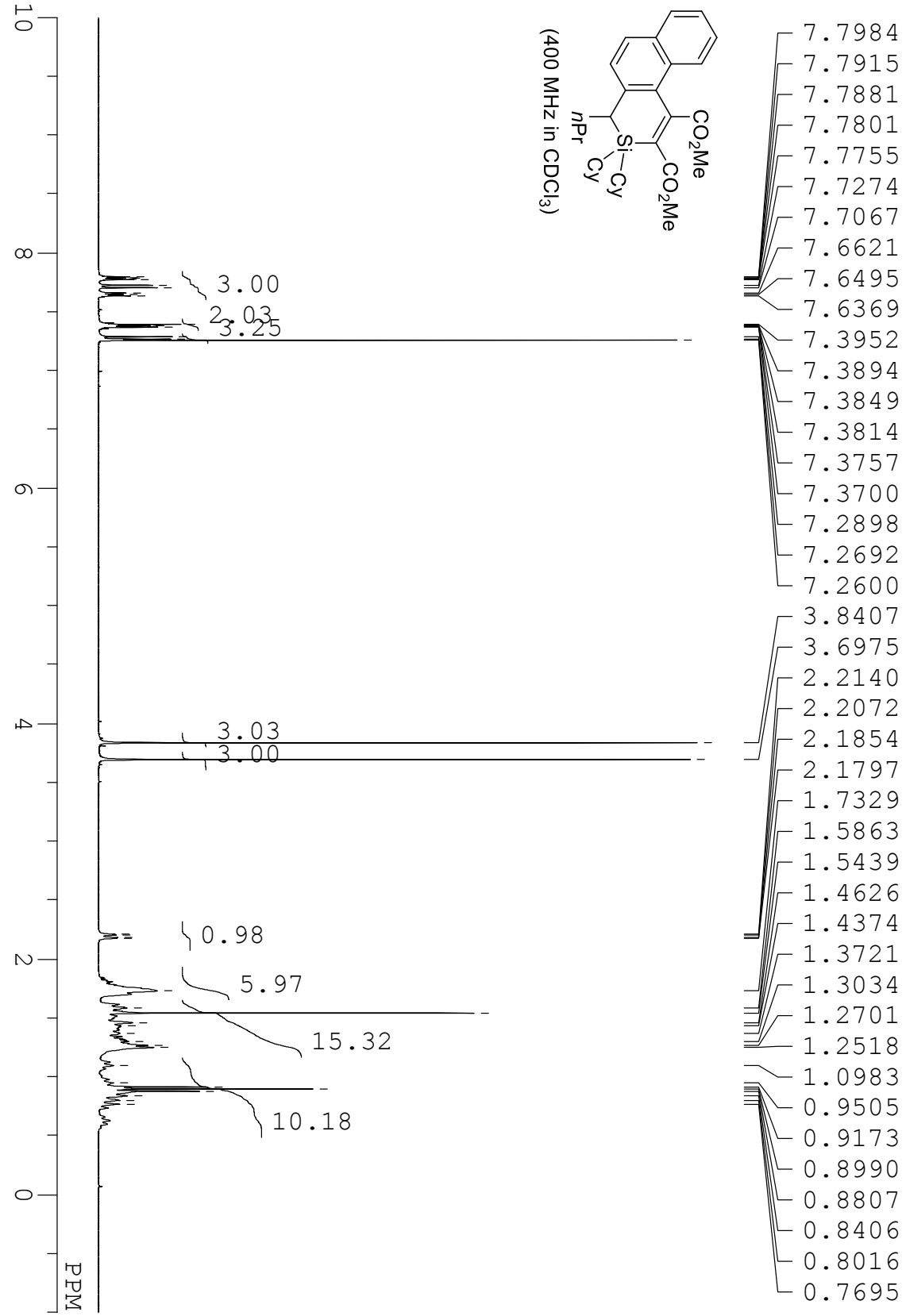
compound **2v**


(400 MHz in CDCl3)
Me
tBu
Si–Me
7.2600
7.2451
7.2268
7.2073
7.0160
6.9965
6.9702
6.9519
1.11
1.95
3.00
1.03
0.99
9.00
3.00
2.2977
2.1785
2.1373
2.0101
1.9689
1.0342
0.4339
10
8
6
4
2
0
PPM

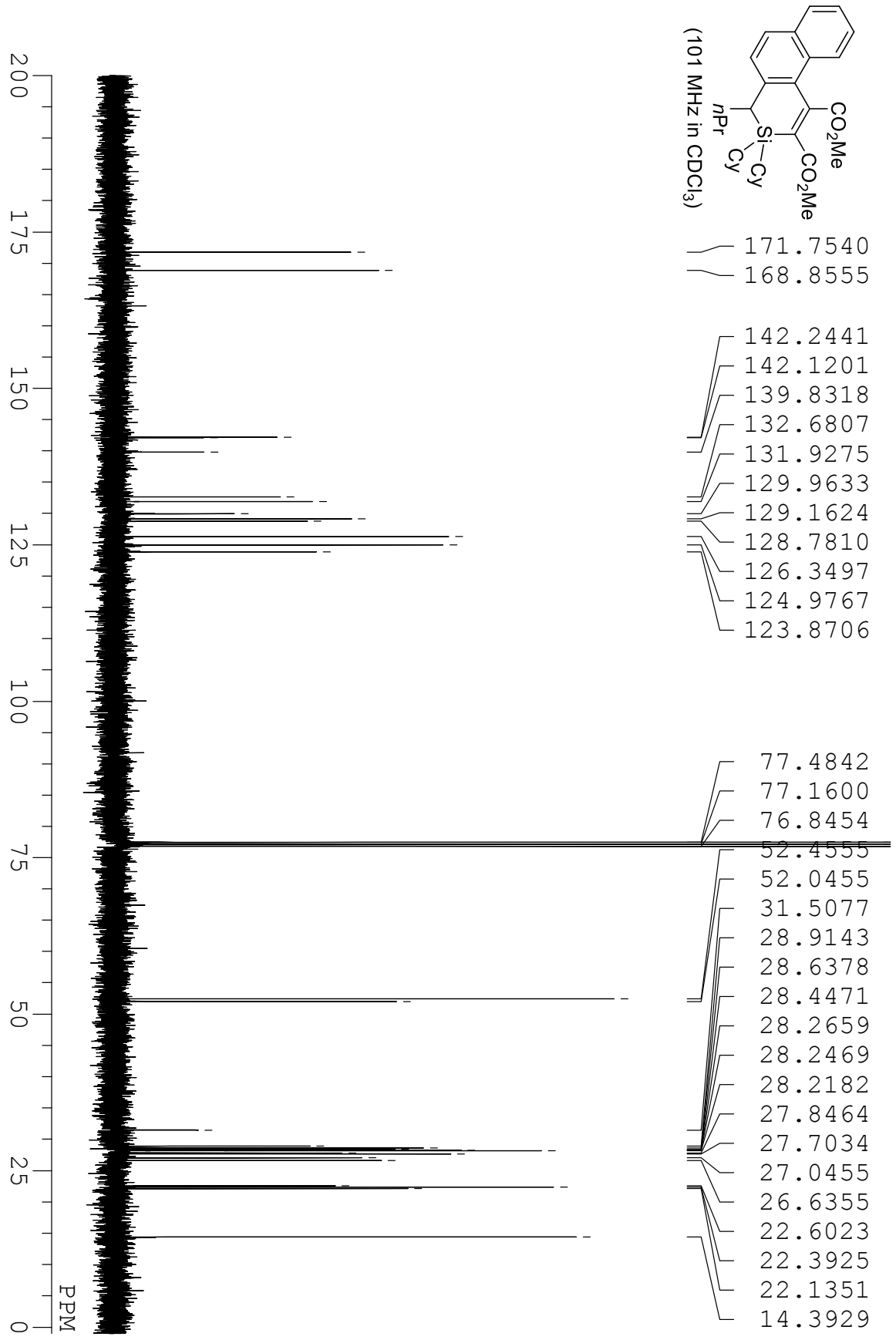
compound **2v**


(101 MHz in CDCl3)
Me
tBu
Si–Me
150.9493
144.7231
140.7566
130.7547
126.4927
123.7944
77.4746
77.1600
76.8358
26.5497
22.2781
18.0638
16.9101
-5.3726
200
175
150
125
100
75
50
25
0
PPM

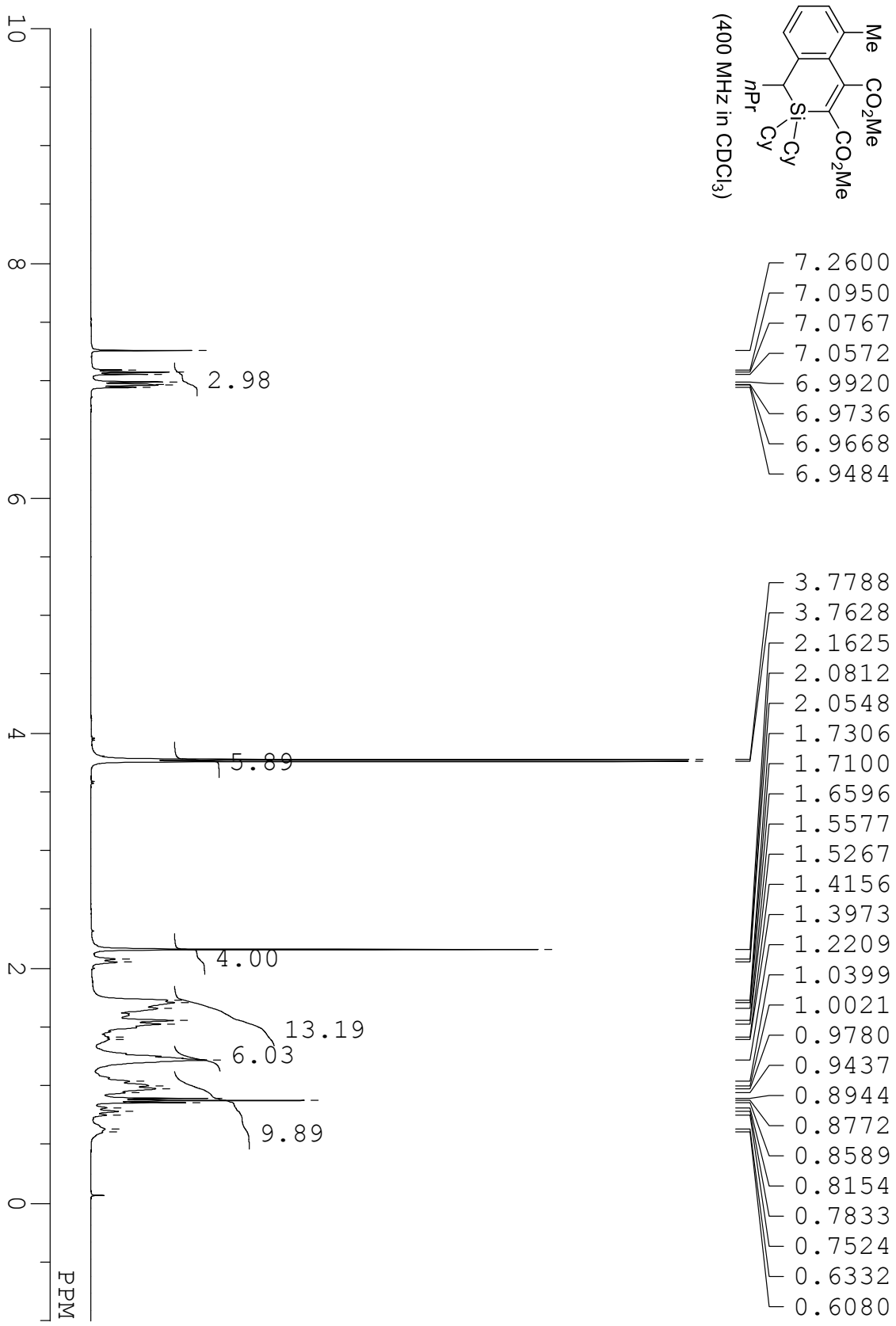
compound **4aa**



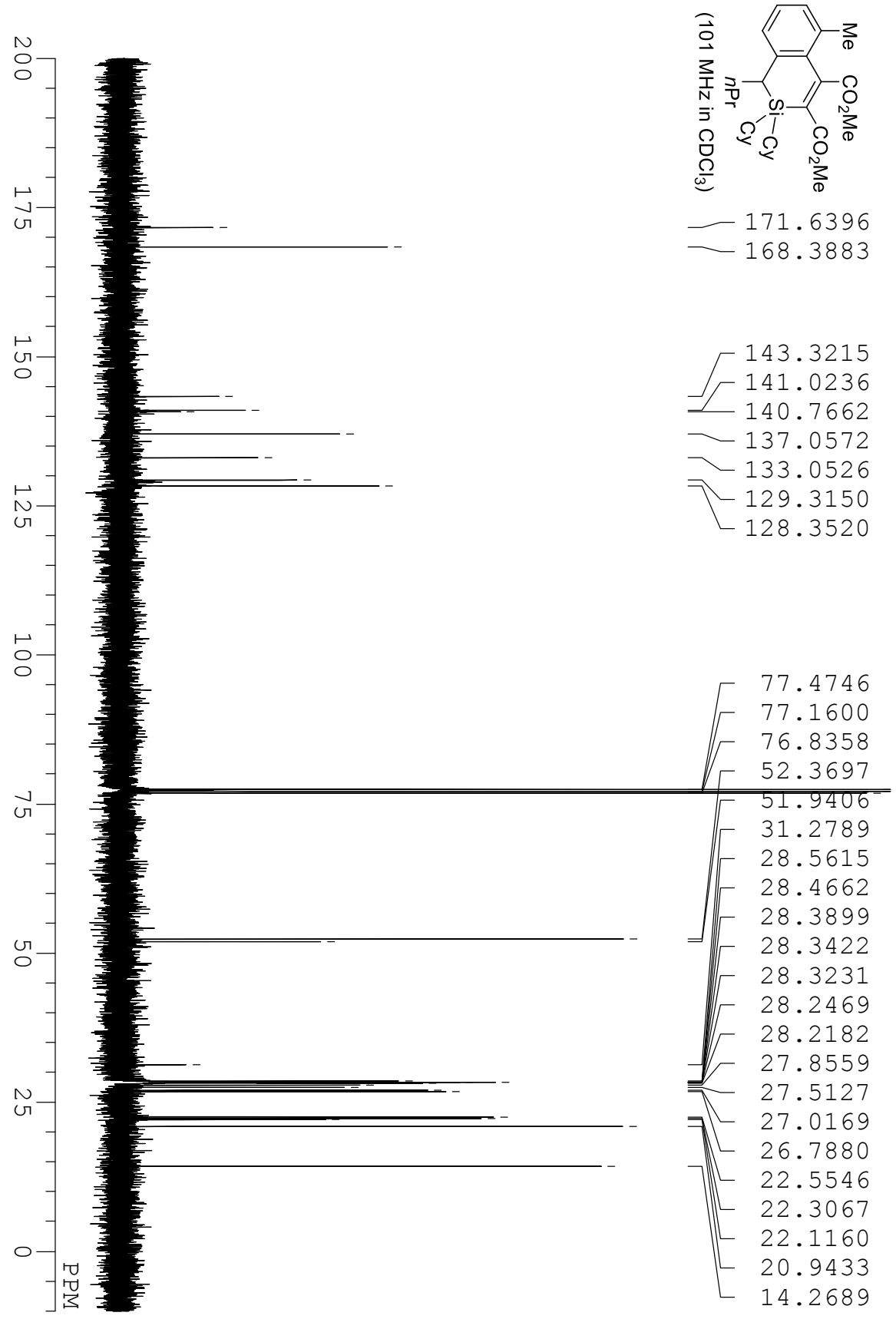
compound **4aa**



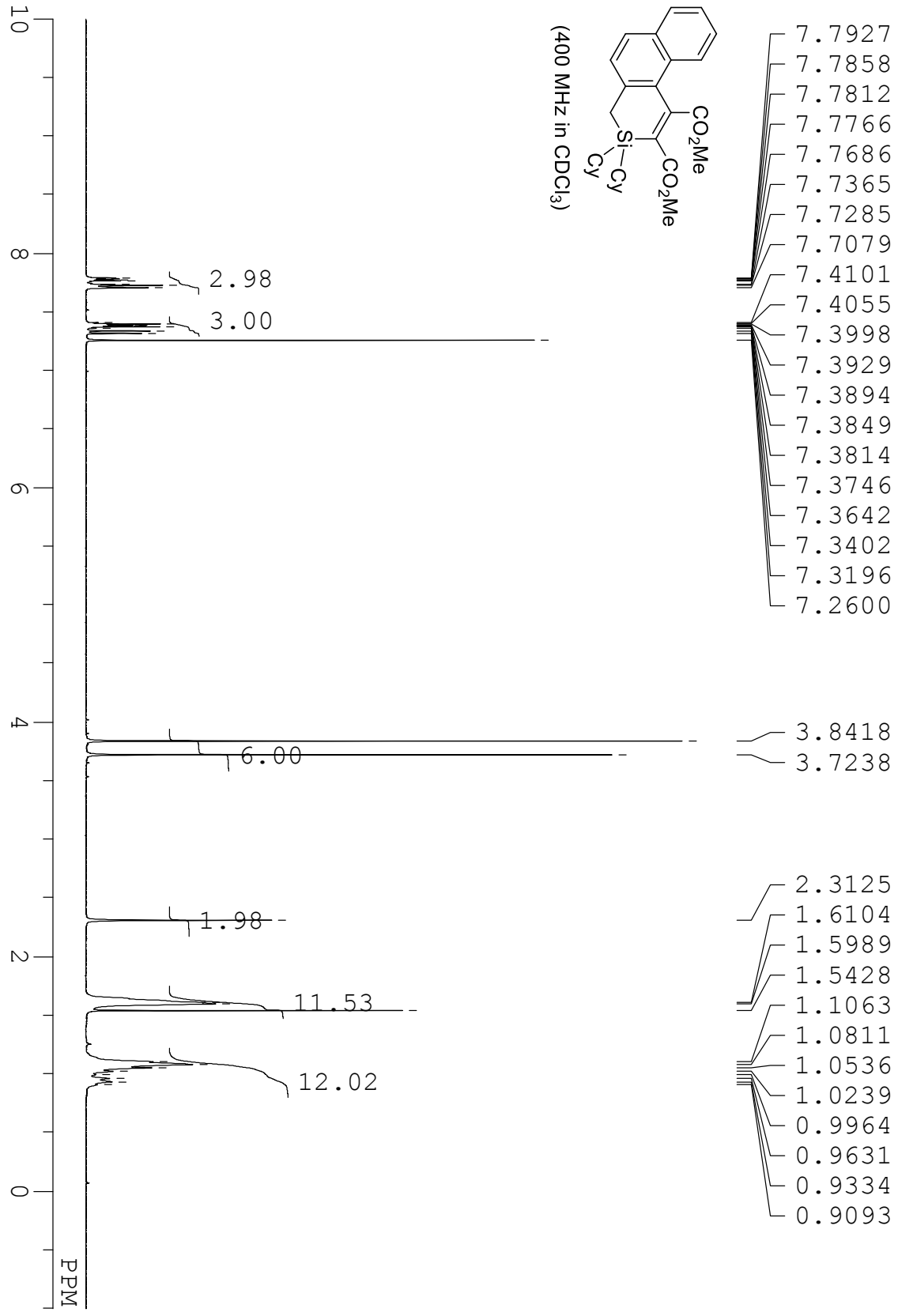
compound **4ia**



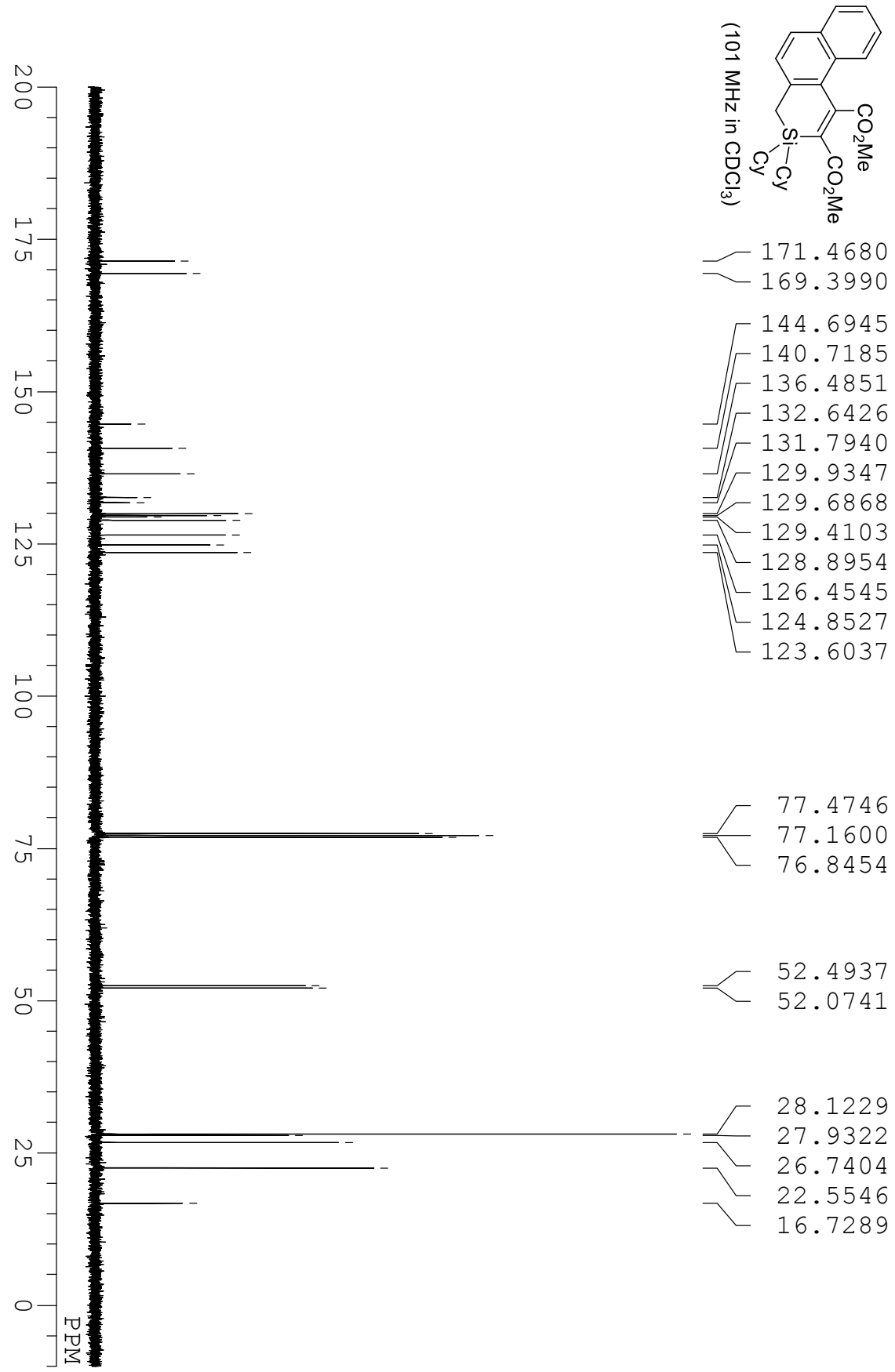
compound **4ia**



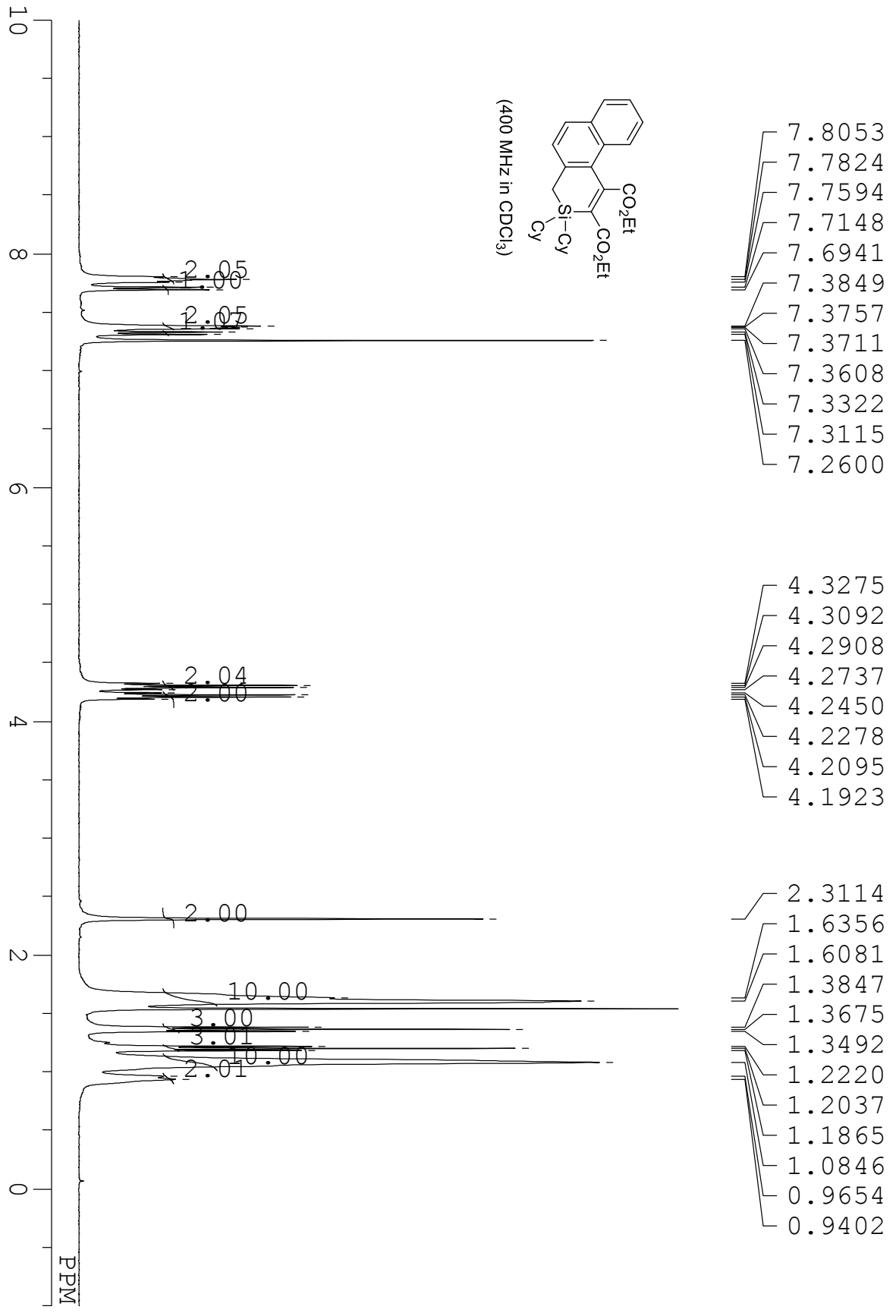
compound **4qa**



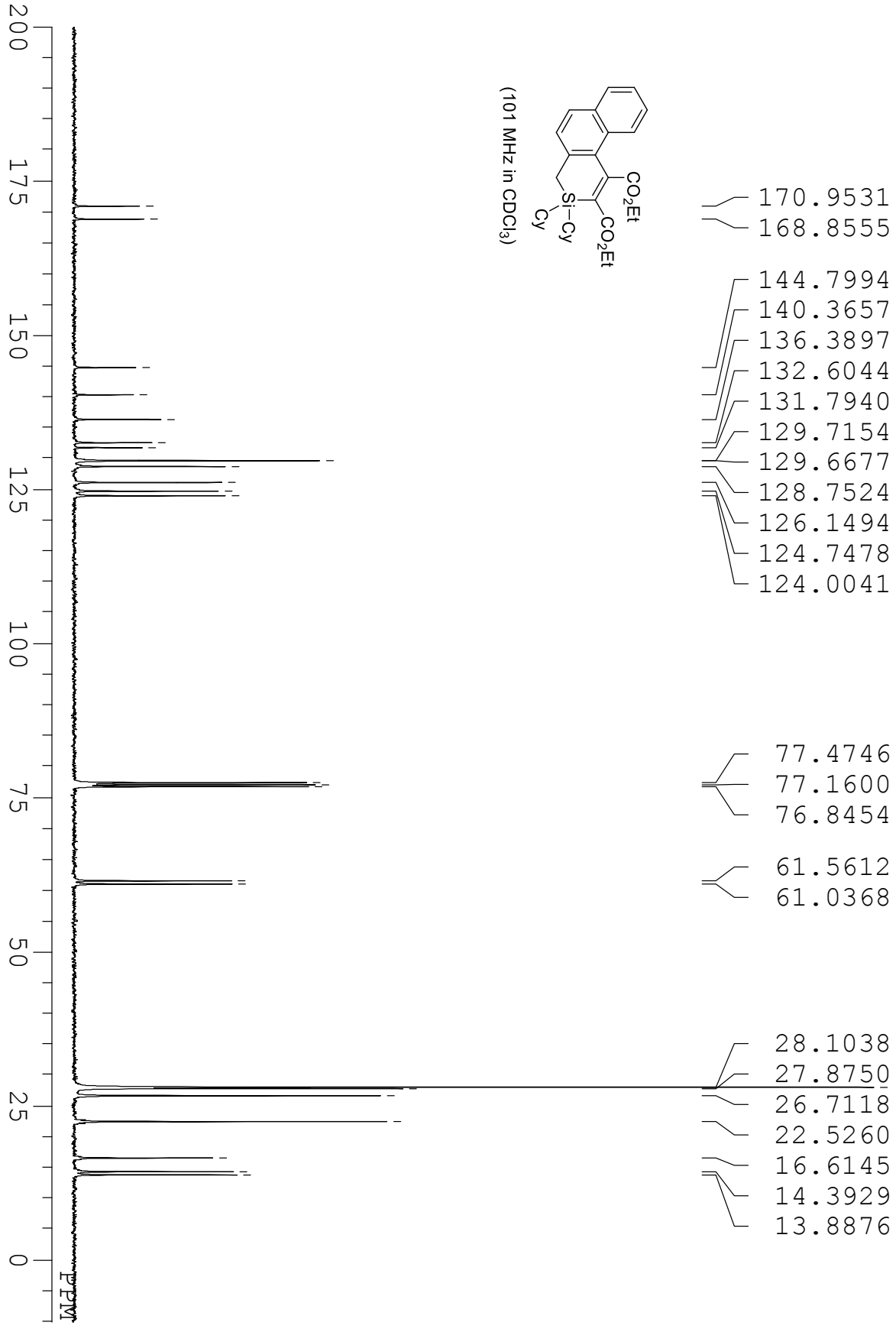
compound **4qa**



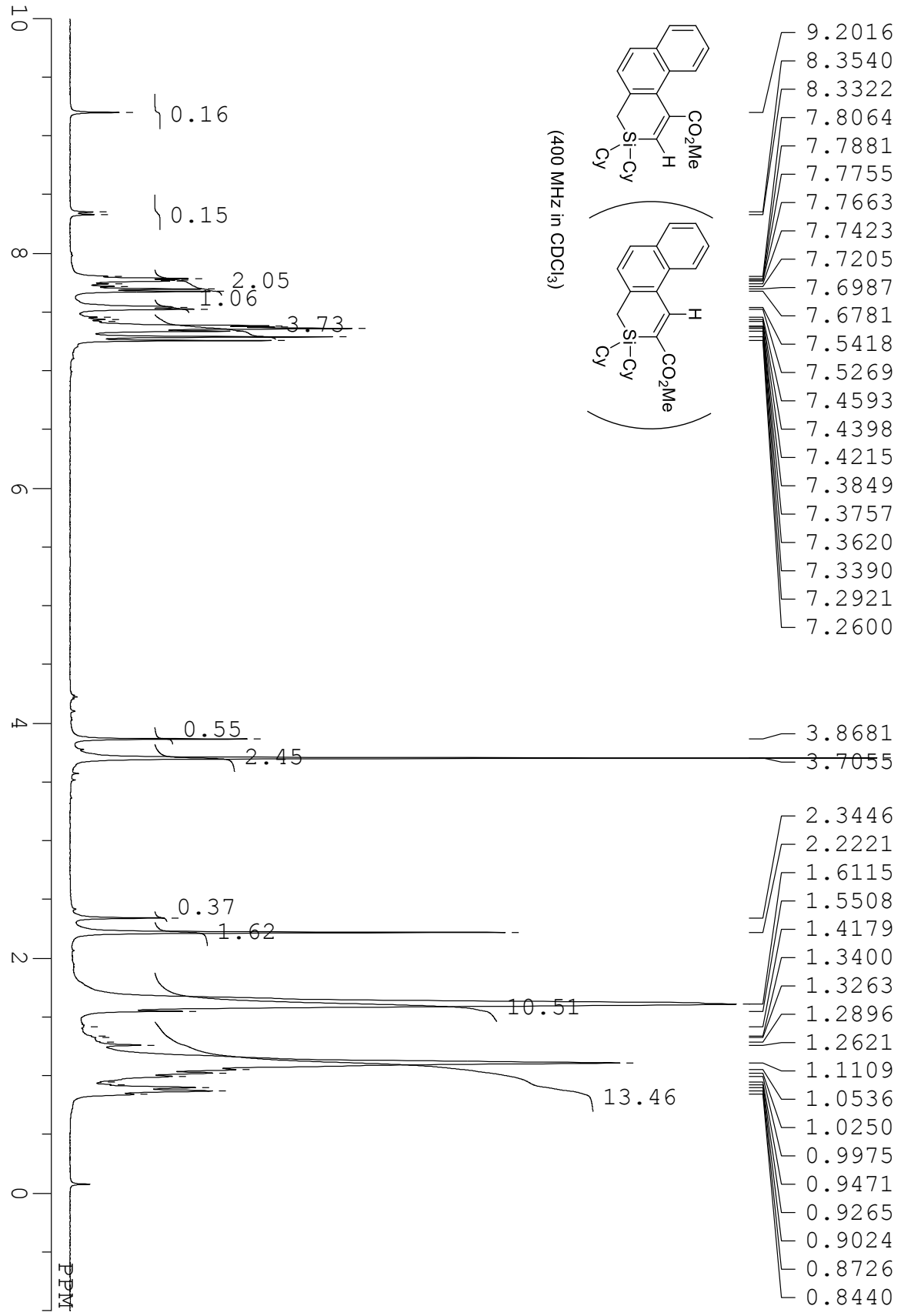
compound **4qb**



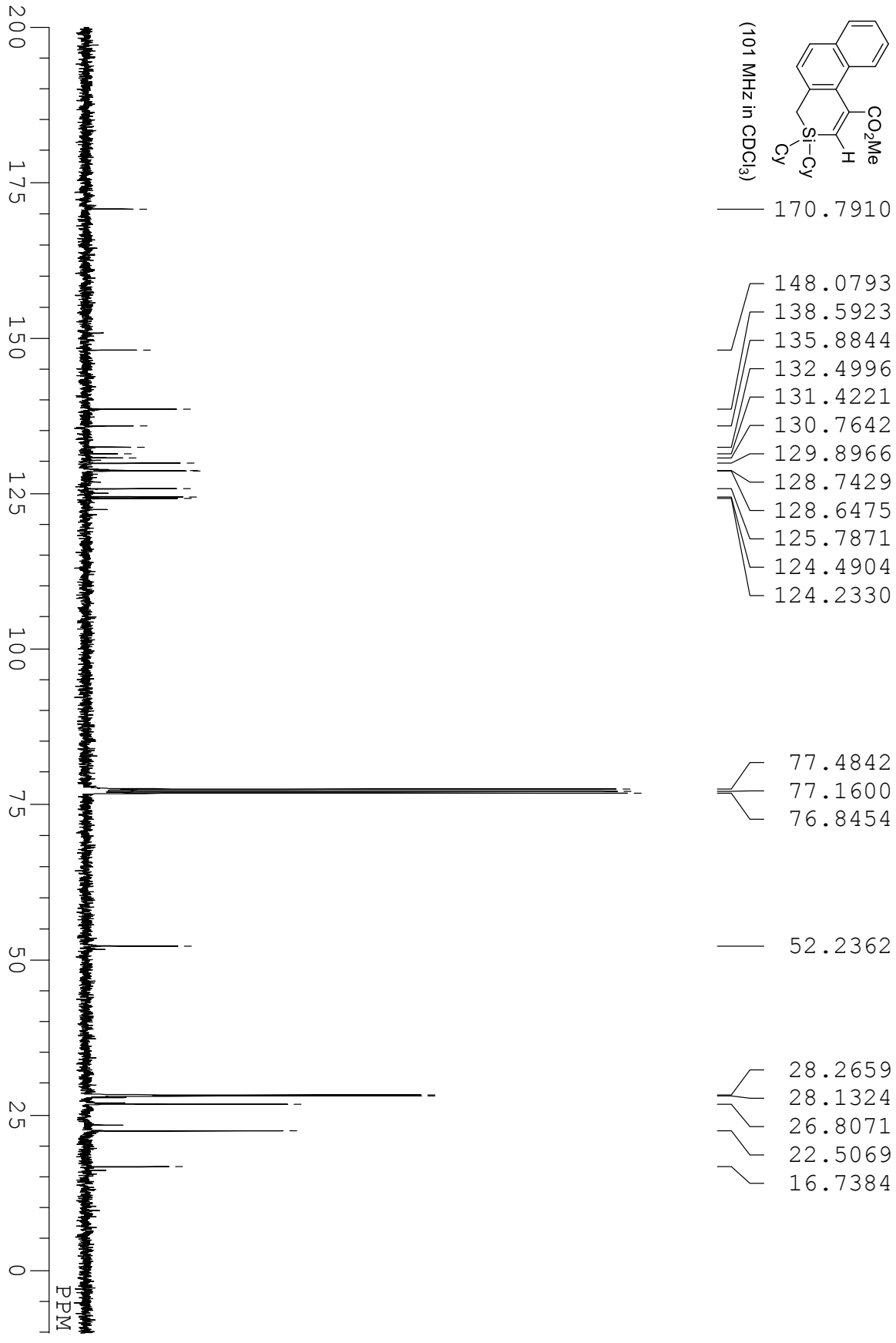
compound **4qb**



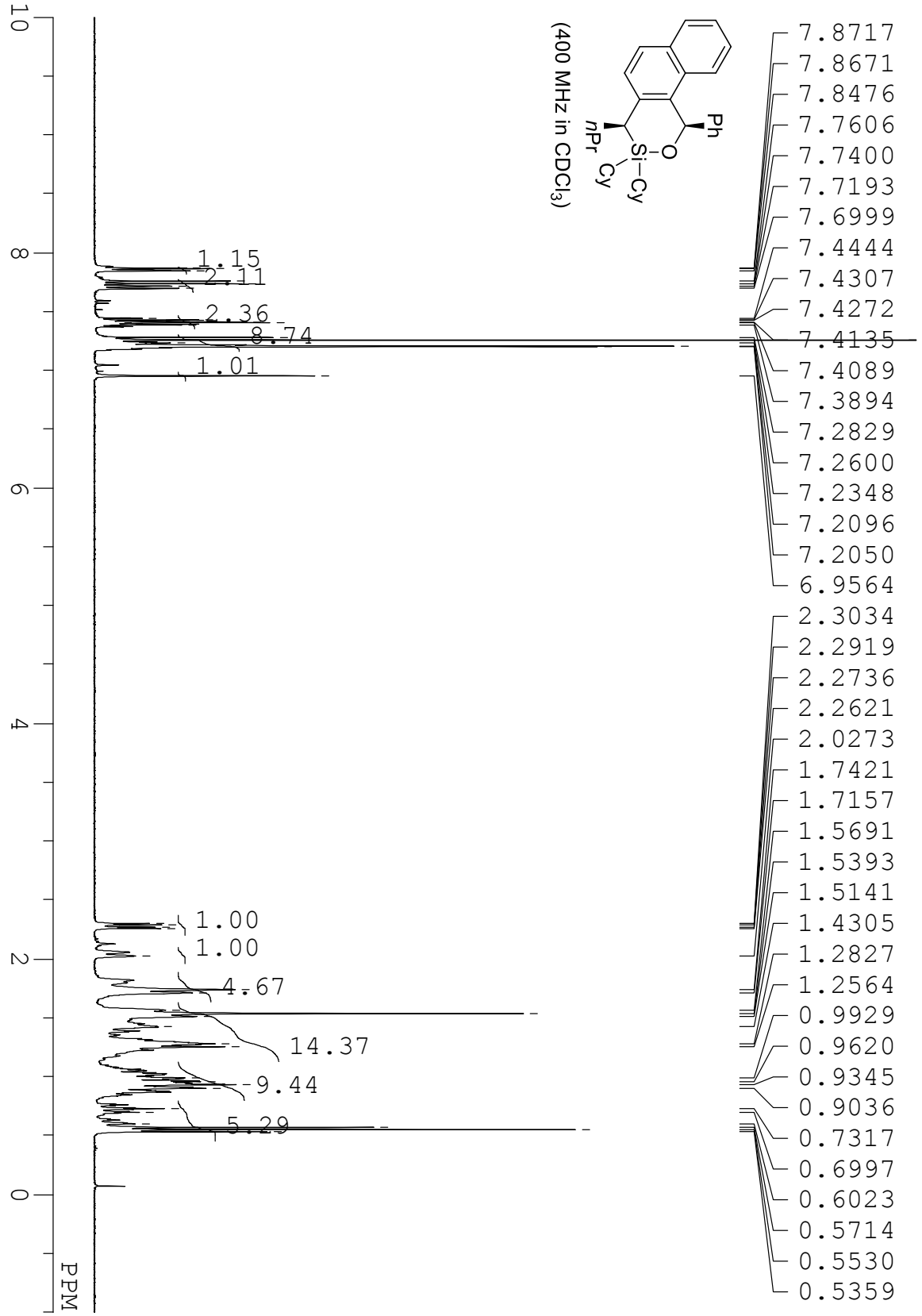
compound **4qc** (regioselectivity: 82/18)



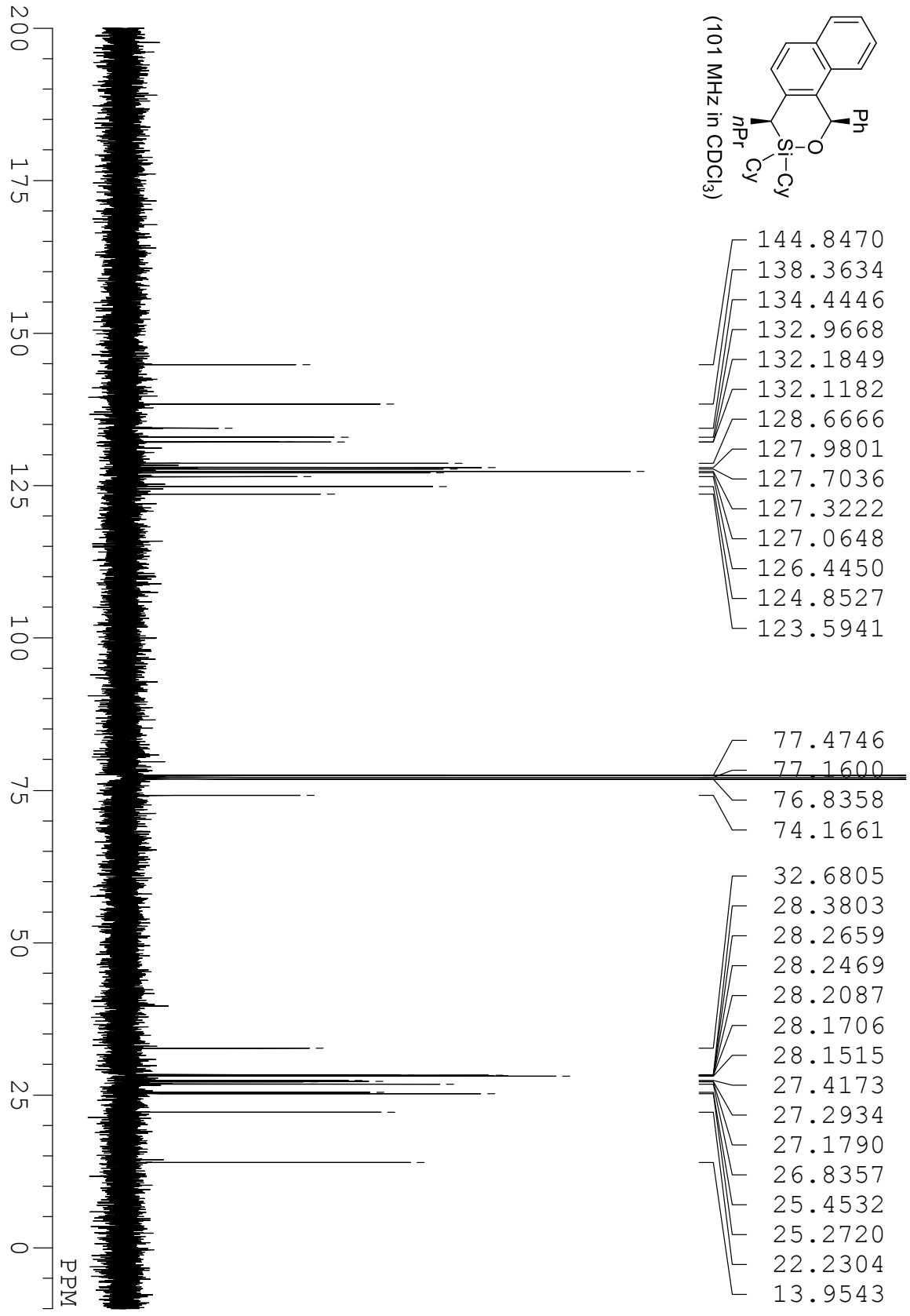
compound **4qc** (regioselectivity: 82/18)



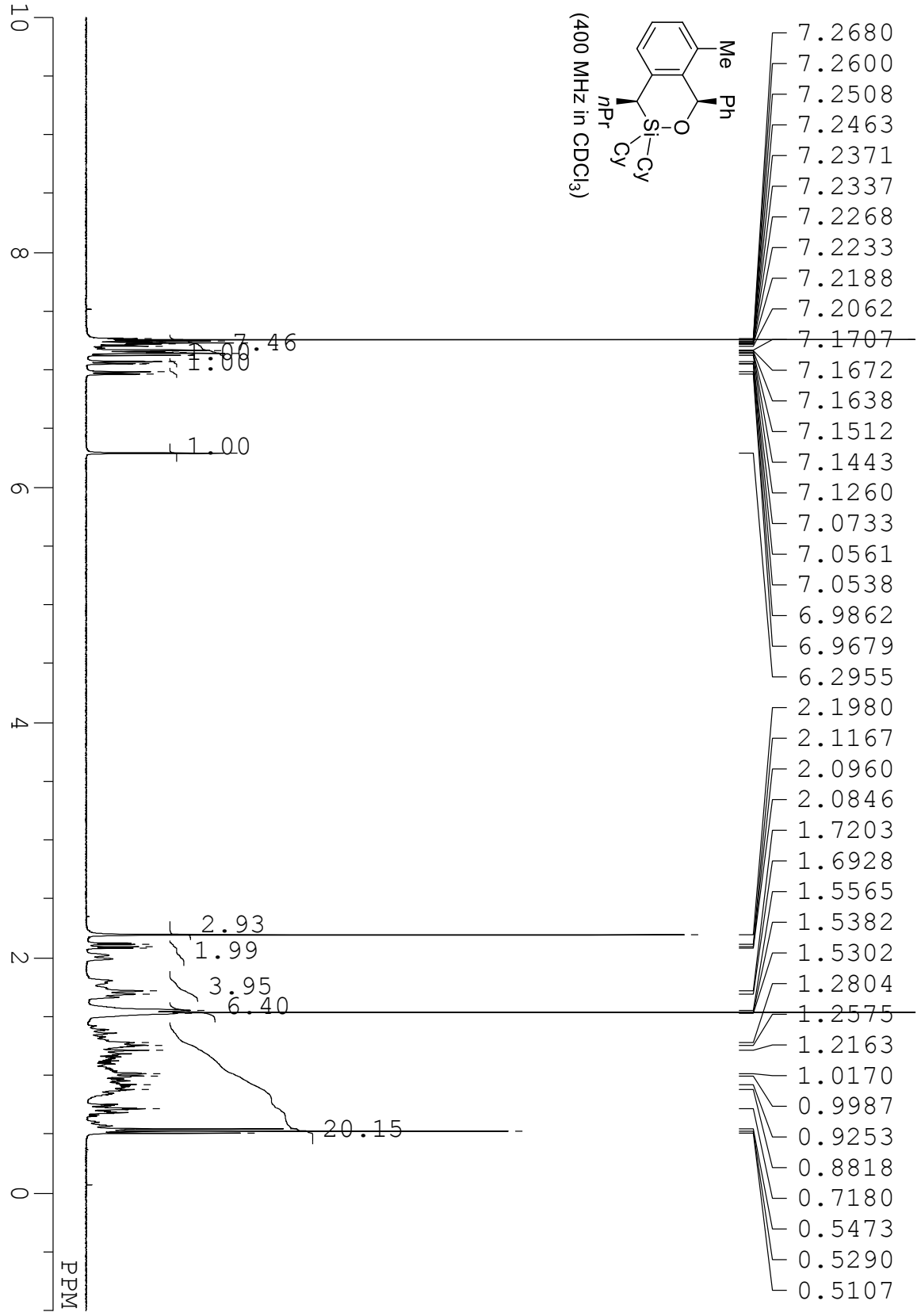
compound **6aa** (*cis*/*trans* = 89/11)



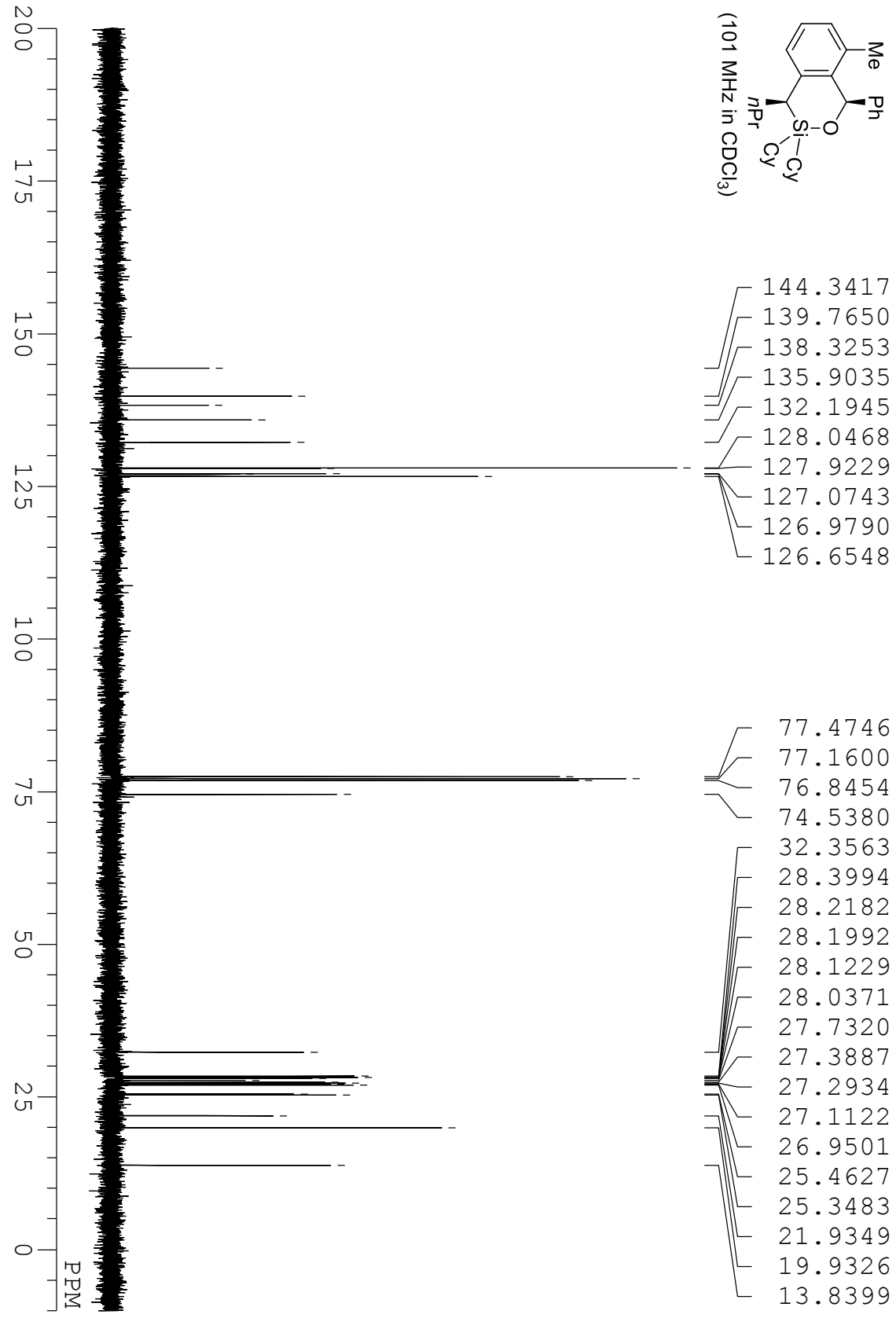
compound **6aa** (*cis*/*trans* = 89/11)



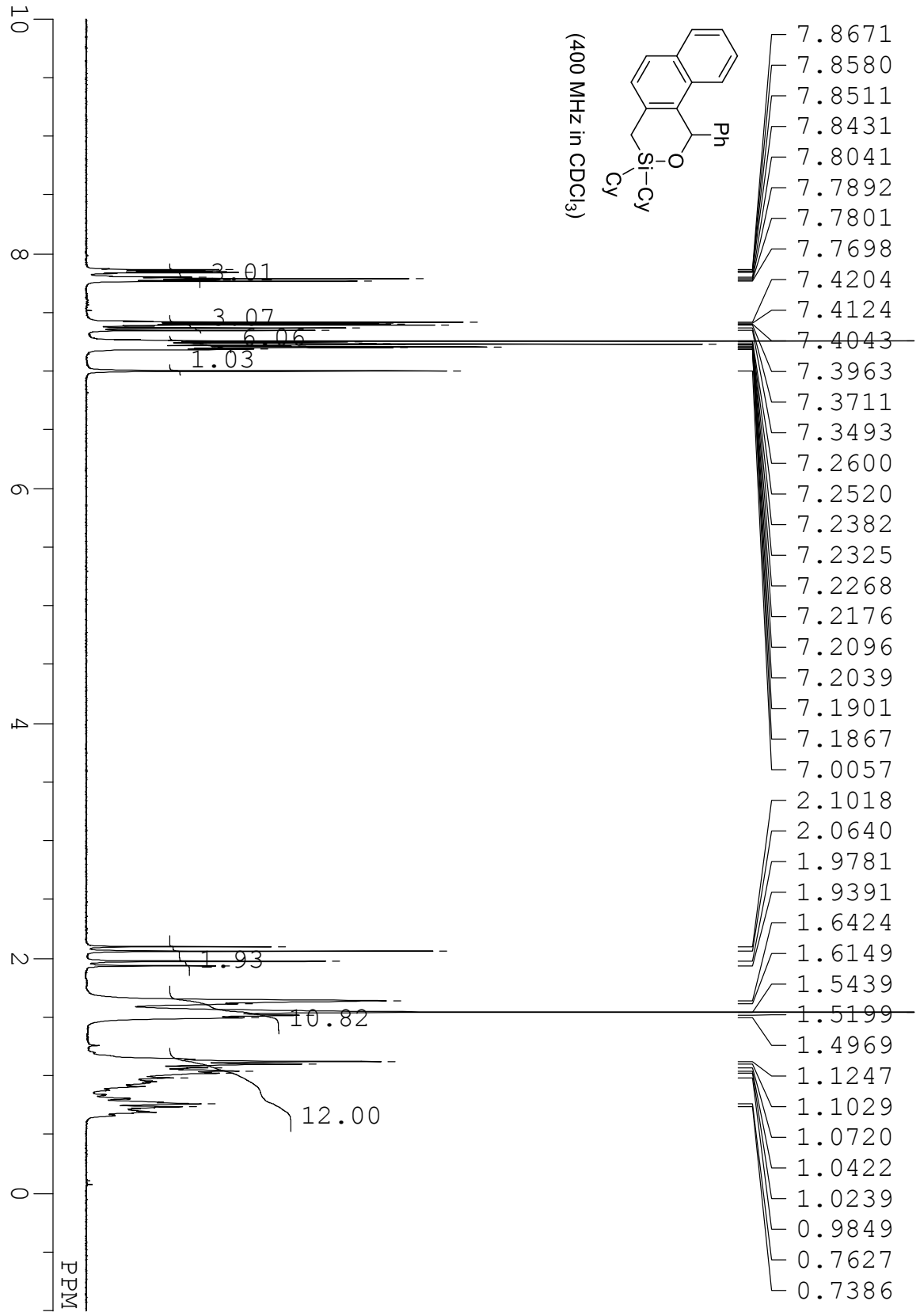
compound **6ia**



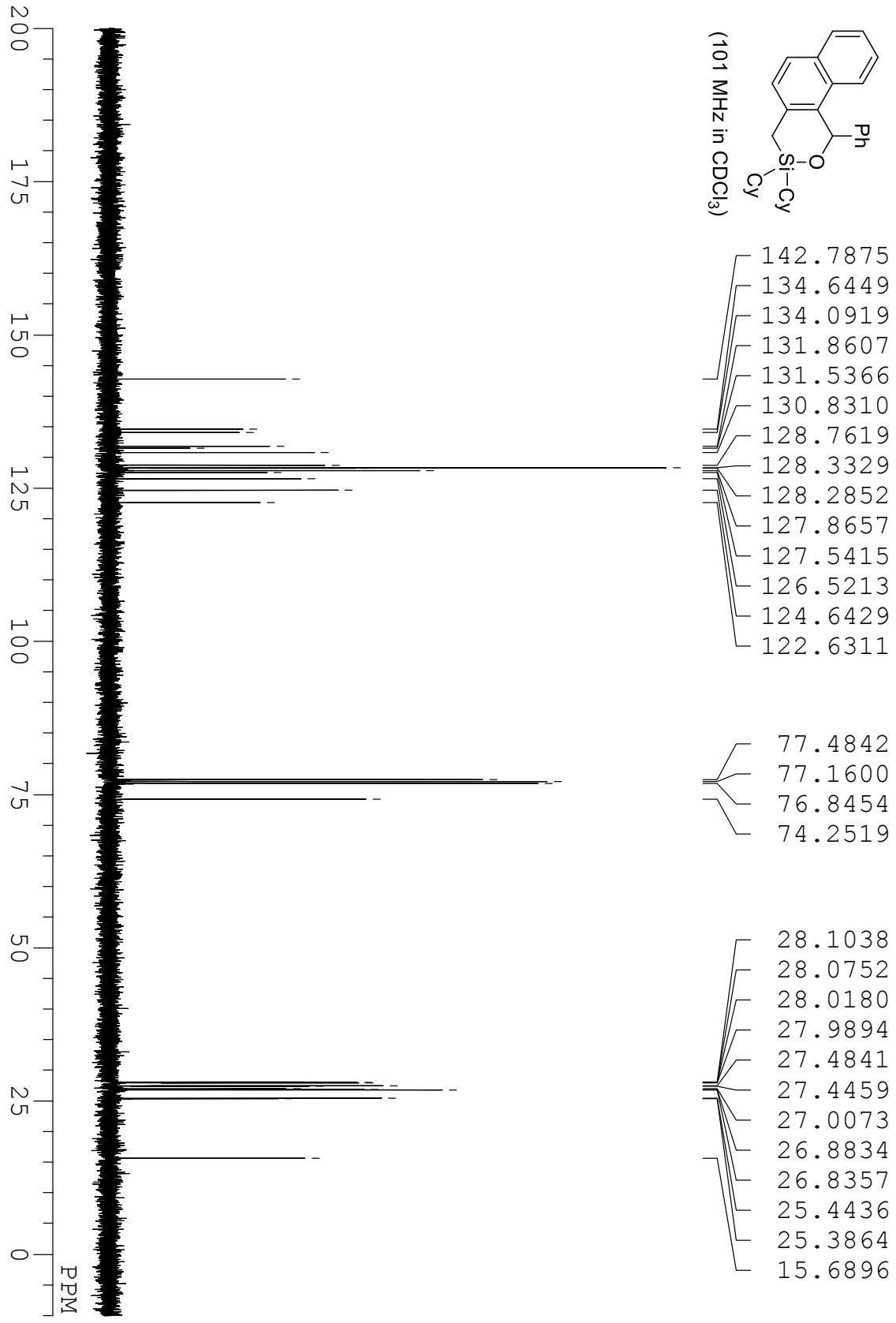
compound **6ia**



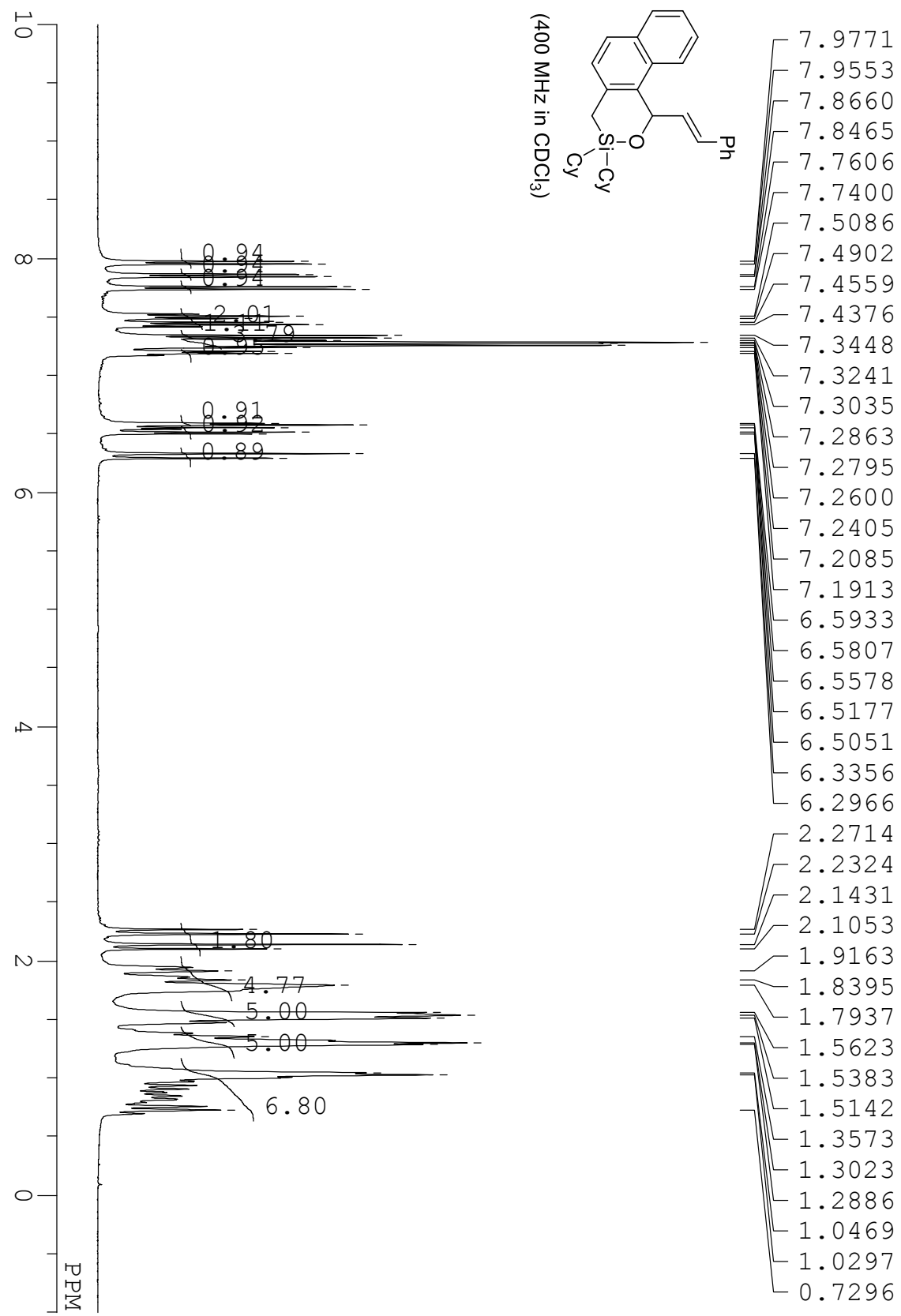
compound **6qa**



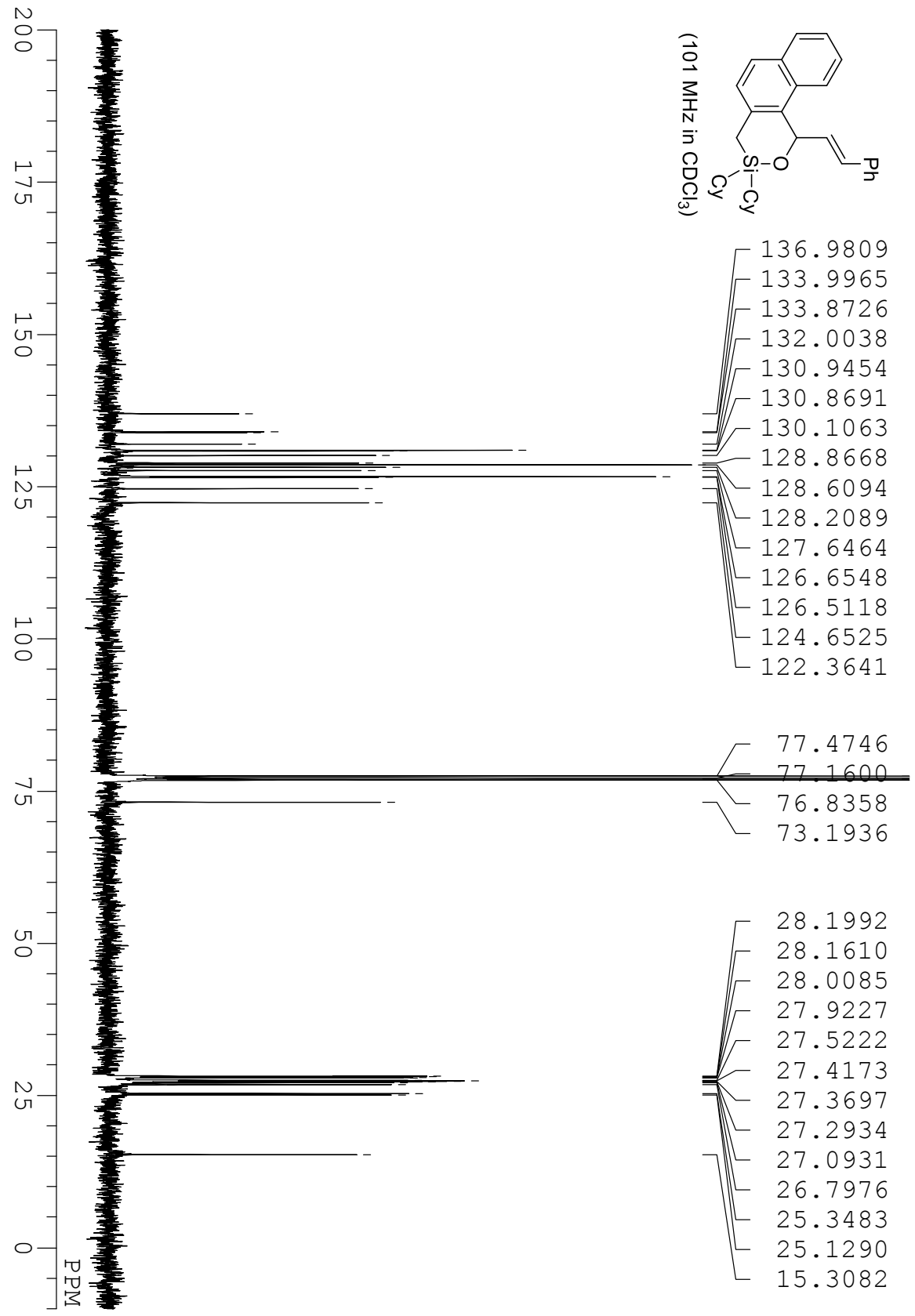
compound **6qa**



compound **6qb**



compound **6qb**



VI. References

1. Li, C.; Qiang, X. Y.; Qi, Z. C.; Cao, B.; Li, J. Y.; Yang, S.-D. *Org. Lett.* **2019**, *21*, 7138.
2. Klare, H. F. T.; Bergander, K.; Oestreich, M. *Angew*. *Chem*., *Int*. *Ed*. **2009**, *48*, 9077.
3. Coulson, D. R.; Satek, L. C.; Grim, S. O. *Inorg*. *Synth*. **1972**, *13*, 121.