Electronic Supplementary Information
for
Palladium-catalyzed synthesis of 4-sila-4*H*-benzo[*d*][1,3]oxazines by intramolecular Hiyama coupling

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I. General

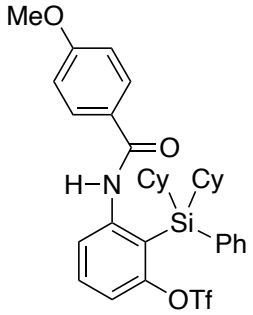
All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen. NMR spectra were recorded on JEOL JNM-ECS400 or Agilent Unity-Inova500 spectrometer. High resolution mass spectra were recorded on JEOL JMS700 spectrometer. X-ray crystallographic analysis was performed by RIGAKU XTaLAB P200 system 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_3N (Wako Chemicals), *i*Pr_2NH (Wako Chemicals), Et_2NH (Wako Chemicals), and 1,2,2,6,6-pentamethylpiperidine (Wako Chemicals) were distilled over KOH under vacuum. THF (Kanto Chemical; dehydrated), 1,2-dichloroethane (Kanto Chemical; dehydrated), CH_2Cl_2 (Kanto Chemical; dehydrated), DMA (Wako Chemicals; dehydrated), DMF (Wako Chemicals; dehydrated), and toluene (Kanto Chemical; dehydrated) were degassed by purging nitrogen. Bromobenzene (Wako Chemicals), 4-methoxybenzoyl chloride (TCI), 4-methylbenzoyl chloride (TCI), bis(trichloromethyl) carbonate (TCI), benzyl alcohol (Nacalai Tesque), *tert*-butyl alcohol (Wako Chemicals), methyl trifluoromethanesulfonate (Wako Chemicals), *N*-phenylbis(trifluoromethanesulfonimide) (Kanto Chemical), imidazole (Nacalai Tesque), dicyclohexyldichlorosilane (Gelest), *tert*-butyldichloro(phenyl)silane (TCI), bis(pinacolato)diboron (Combi-Blocks), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (TCI), PPh_3 (Wako Chemicals), PCy_3•HBF_4 (TCI), P(*t*Bu)$_3$•HBF_4 (TCI), dppf (Wako Chemicals), binap (Wako Chemicals), **L*** (Aldrich), MeLi (Kanto Chemical; 1.37 M solution in cyclopentyl methyl ether), *n*BuLi (Kanto Chemical; 1.57 M solution in hexane), *t*BuLi (Kanto Chemical; 1.60 M solution in pentane), NaH (Kishida Chemical; 60 wt% in mineral oil), Na_2SO_4 (Wako Chemicals), $MgSO_4$ (Wako Chemicals), $Pd(OAc)_2$ (Wako Chemicals), and $[Ir(OMe)(cod)]_2$ (TCI) were used as received. 3-Amino-2-bromophenol,[1] 3-amino-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate,[2] and $Pd(PPh_3)_4$[3] were synthesized following the literature procedures.

II. Synthesis of Substrates

Representative Procedures for Substrates:

2-(Dicyclohexyl(phenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1c)



*t*BuLi (18.9 mL, 30.2 mmol; 1.60 M solution in pentane) was added dropwise over 10 min to a solution of bromobenzene (1.60 mL, 15.1 mmol) in THF (30 mL) at –78 °C and the mixture was stirred for 1.5 h at –78 °C. Dicyclohexyldichlorosilane (3.46 mL, 14.4 mmol) was added to it and the mixture was stirred for 2 h at room temperature. 3-Amino-2-bromophenol (2.26 g, 12.0 mmol) and imidazole (2.04 g, 30.0 mmol) were then added it and the resulting mixture was stirred for 1.5 h at 60 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/CH_2Cl_2 = 2/1 to afford 2-bromo-3-(dicyclohexyl(phenyl)silyloxy)aniline as a colorless oil (5.35 g, 11.7 mmol; 98% yield).

^{1}H NMR ($CDCl_3$): δ 7.68-7.58 (m, 2H), 7.45-7.32 (m, 3H), 6.84 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 6.37 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.21 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 4.13 (bs, 2H), 2.01-1.85 (m, 2H), 1.84-1.58 (m, 8H), 1.39-1.08 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.6, 145.8, 134.8, 134.3, 129.6. 127.8, 109.3, 108.3, 102.6, 28.23, 28.18, 27.4, 27.2, 26.9, 25.3.

*t*BuLi (22.7 mL, 36.3 mmol; 1.60 M solution in pentane) was added dropwise over 10 min to a solution of 2-bromo-3-(dicyclohexyl(phenyl)silyloxy)aniline (5.35 g, 11.7 mmol) in THF (59 mL) at –78 °C, and the mixture was stirred for 30 min at −78 °C and for 40 min at room temperature. The reaction was quenched with H_2O at 0 °C (under nitrogen) 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 resulting solid was washed with hexane to afford 3-amino-2-(dicyclohexyl(phenyl)silyl)phenol as a white solid (3.51 g, 9.24 mmol; 79% yield).

^{1}H NMR ($CDCl_3$): δ 7.67-7.54 (m, 2H), 7.46-7.33 (m, 3H), 7.03 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.15 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.12 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.81 (s, 1H), 3.65 (bs, 2H), 1.97-1.81 (m, 2H), 1.80-1.46 (m, 10H), 1.35-1.01 (m, 8H), 0.99-0.80 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.0, 154.8, 135.8, 134.4, 131.7, 129.6, 128.2, 108.9, 105.3, 102.0, 28.5, 28.3, 27.9, 27.5, 27.0, 23.8.

NaH (739 mg, 18.5 mmol; 60 wt% in mineral oil) was added to a solution of 3-amino-2-(dicyclohexyl(phenyl)silyl)phenol (3.51 g, 9.24 mmol) in THF (46 mL) at 0 °C, and the mixture was stirred for 10 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (3.96 g, 11.1 mmol) was added

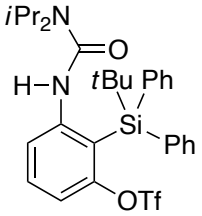
to it and the mixture was stirred for 1.5 h at room temperature. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 20/1 → 5/1 and then with hexane/CH_2Cl_2 = 10/1 → 3/1 to afford 3-amino-2-(dicyclohexyl(phenyl)silyl)phenyl trifluoromethanesulfonate as a white solid (3.86 g, 7.54 mmol; 82% yield).

^{1}H NMR ($CDCl_3$): δ 7.58-7.48 (m, 2H), 7.46-7.33 (m, 3H), 7.20 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 6.77 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.45 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 3.76 (bs, 2H), 1.95-1.52 (m, 12H), 1.40-1.20 (m, 4H), 1.20-0.99 (m, 4H), 0.99-0.80 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.2, 155.3, 135.6, 133.0, 131.9, 129.8, 128.2, 118.8 (q, $^1J_{CF}$ = 321 Hz), 115.0, 107.6 (q, $^5J_{CF}$ = 2.6 Hz), 107.1, 28.2, 28.03, 27.96, 27.5, 26.9, 23.1.

Et_3N (258 μL, 1.85 mmol) and 4-methoxybenzoyl chloride (250 μL, 1.85 mmol) were added to a solution of 3-amino-2-(dicyclohexyl(phenyl)silyl)phenyl trifluoromethanesulfonate (902 mg, 1.76 mmol) in 1,2-dichloroethane (3.5 mL) at room temperature, and the mixture was stirred for 17 h at 60 °C. The reaction was quenched with saturated $NaHCO_3$aq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 5/1 to afford compound **1c** as a white solid (826 mg, 1.28 mmol; 88% yield).

^{1}H NMR ($CDCl_3$): δ 7.97 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.93 (s, 1H), 7.57-7.45 (m, 6H), 7.28-7.23 (m, 1H), 6.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.63 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.82 (s, 3H), 1.89-1.80 (m, 2H), 1.72-1.52 (m, 10H), 1.35-1.16 (m, 4H), 1.10-0.96 (m, 4H), 0.85-0.73 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.0, 162.3, 157.0, 145.6, 135.6, 132.8, 131.8, 130.4, 129.2, 128.6, 126.2, 124.1, 118.7 (q, $^1J_{CF}$ = 320 Hz), 117.2, 115.0 (q, $^5J_{CF}$ = 2.9 Hz), 113.6, 55.4, 28.0, 27.7, 27.4, 27.2, 26.6, 22.6. HRMS (FAB) calcd for $C_{33}H_{39}F_3NO_5SSi$ ($M+H^+$) 646.2265, found 646.2271.

2-(*tert*-Butyldiphenylsilyl)-3-(3,3-diisopropylureido)phenyl trifluoromethanesulfonate (1dd)

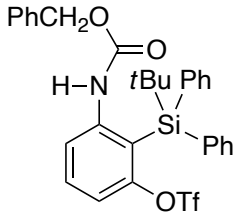


3-Amino-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (528 mg, 1.10 mmol) was added dropwise over 2.5 h to a solution of bis(trichloromethyl) carbonate (163 mg, 0.550 mmol) and Et_3N (15.3 μL, 0.110 mmol) in 1,2-dichloroethane (3.0 mL) at 0 °C. The mixture was stirred for 2 h at room temperature and for 4 h at 85 °C. The volatiles were removed under vacuum and the residue was dissolved in 1,2-dichloroethane (5.5 mL). *i*Pr_2NH (233 μL, 1.65 mmol) was added to the solution and the mixture was stirred for 18 h at 85 °C, and this was concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 → 4/1 to afford compound **1dd** as a yellow

solid (415 mg, 0.680 mmol; 62% yield).

^{1}H NMR ($CDCl_3$): δ 7.68-7.62 (m, 5H), 7.44 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 7.42-7.34 (m, 6H), 7.10 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 6.39 (s, 1H), 2.84 (sept, $^3J_{HH}$ = 6.6 Hz, 2H), 1.25 (s, 9H), 0.99 (d, $^3J_{HH}$ = 6.5 Hz, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.5, 153.5, 147.5, 135.9, 134.9, 131.3, 129.8, 128.5, 124.2, 118.5 (q, $^1J_{CF}$ = 322 Hz), 117.3, 114.1 (q, $^5J_{CF}$ = 1.9 Hz), 46.5, 29.6, 21.2, 20.3. HRMS (FAB) calcd for $C_{30}H_{38}F_3N_2O_4SSi$ ($M+H^+$) 607.2268, found 607.2275.

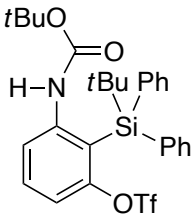
3-(Benzyloxycarbonylamino)-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (1ee)



3-Amino-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (528 mg, 1.10 mmol) was added dropwise over 2.5 h to a solution of bis(trichloromethyl) carbonate (163 mg, 0.550 mmol) and Et_3N (15.3 μL, 0.110 mmol) in 1,2-dichloroethane (3.0 mL) at 0 °C . The mixture was stirred for 2.5 h at room temperature and for 4.5 h at 85 °C. The volatiles were removed under vacuum and the residue was dissolved in 1,2-dichloroethane (5.5 mL). Et_3N (30.7 μL, 0.220 mmol) and benzyl alcohol (140 μL, 1.32 mmol) were added to the solution and the mixture was stirred for 17 h at 85 °C, and this was concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 20/1 → 10/1 to afford compound **1ee** as a yellow viscous oil (576 mg, 0.940 mmol; 85% yield).

^{1}H NMR ($CDCl_3$): δ 7.92 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.68-7.62 (m, 4H), 7.50 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.40-7.29 (m, 9H), 7.23-7.16 (m, 3H), 6.83 (s, 1H), 4.90 (s, 2H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.4, 153.3, 145.8, 136.0, 135.6, 134.4, 132.3, 130.0, 128.7, 128.5, 128.3, 128.2, 121.3, 118.4 (q, $^1J_{CF}$ = 321 Hz), 117.0, 114.5 (q, $^5J_{CF}$ = 2.9 Hz), 66.8, 29.5, 20.1. HRMS (FAB) calcd for $C_{31}H_{31}F_3NO_5SSi$ ($M+H^+$) 614.1639, found 614.1651.

3-(*tert*-Butoxycarbonylamino)-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (1ff)

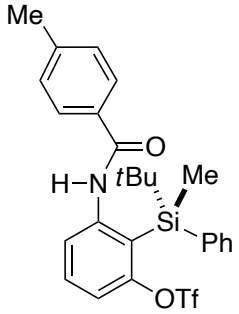


3-Amino-2-(*tert*-butyldiphenylsilyl)phenyl trifluoromethanesulfonate (528 mg, 1.10 mmol) was added dropwise over 2.5 h to a solution of bis(trichloromethyl) carbonate (163 mg, 0.550 mmol) and Et_3N (15.3 μL, 0.110 mmol) in 1,2-dichloroethane (3.0 mL) at 0 °C. The mixture was stirred for 2 h at room temperature and for 4 h at 85 °C. The volatiles were removed under vacuum and the residue was dissolved in *tert*-butyl alcohol (3.00 g, 40.5 mmol). The solution was stirred for 18 h at 85 °C and this

was concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 20/1 to afford compound **1ff** as a white solid (320 mg, 0.551 mmol; 50% yield).

^{1}H NMR ($CDCl_3$): δ 7.90 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.71-7.64 (m, 4H), 7.46 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 7.44-7.34 (m, 6H), 7.13 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.64 (s, 1H), 1.31 (s, 9H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.5, 152.5, 146.4, 135.7, 134.5, 132.1, 130.0, 128.6, 121.0, 118.4 (q, $^1J_{CF}$ = 321 Hz), 116.3, 114.0 (q, $^5J_{CF}$ = 2.6 Hz), 80.4, 29.5, 28.2, 20.2. HRMS (FAB) calcd for $C_{28}H_{32}F_3NO_5SSi$ (M^+) 579.1717, found 579.1718.

(*R*)-2-(*tert*-Butyl(methyl)(phenyl)silyl)-3-(4-methylbenzamido)phenyl trifluoromethanesulfonate (1gg)



MeLi (6.26 mL, 8.57 mmol; 1.37 M solution in cyclopentyl methyl ether) was added dropwise over 15 min to a solution of *tert*-butyldichloro(phenyl)silane (1.80 mL, 8.57 mmol) in THF (34 mL) at –78 °C, and the mixture was stirred for 1.5 h at room temperature. 3-Amino-2-bromophenol (1.46 g, 7.79 mmol) and imidazole (1.35 g, 19.5 mmol) were added to it and the mixture was stirred for 2.5 h at 60 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 5/1 to afford 2-bromo-3-(*tert*-butyl(methyl)(phenyl)silyloxy)aniline as a colorless oil (1.93 g, 5.31 mmol; 68% yield).

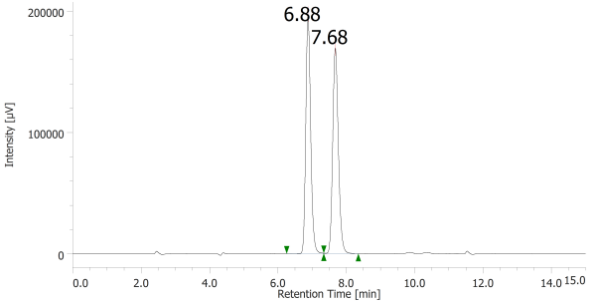
^{1}H NMR ($CDCl_3$): δ 7.63-7.57 (m, 2H), 7.44-7.33 (m, 3H), 6.78 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 6.34 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.06 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 4.13 (bs, 2H), 1.05 (s, 9H), 0.53 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 153.3, 145.9, 134.8, 134.6, 129.9, 127.9, 127.8, 109.1, 108.4, 102.6, 25.9, 18.9, –6.4.

*t*BuLi (10.3 mL, 16.5 mmol; 1.60 M solution in pentane) was added dropwise over 10 min to a solution of 2-bromo-3-(*tert*-butyl(methyl)(phenyl)silyloxy)aniline (1.93 g, 5.31 mmol) in THF (27 mL) at –78 °C, and the mixture was stirred for 1 h at −78 °C and for 2 h at 0 °C. The reaction was quenched with H_2O at 0 °C (under nitrogen) 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 3-amino-2-(*tert*-butyl(methyl)(phenyl)silyl)phenol (compound **S1**) as a colorless oil (1.34 g, 4.71 mmol; 89% yield). The enantiomers were separated by preparative HPLC using Daicel Chiralpak IBN-5 column (2 cm Ø x 25 cm) with hexane/2-propanol = 90/10, flow = 10.0 mL/min. Retention times: 9.8–10.3 min [(*S*)-

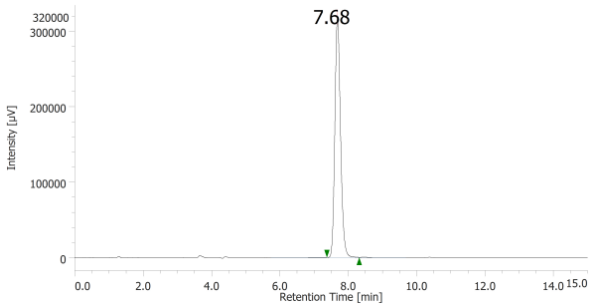
S1], 10.7–11.3 min [(*R*)-**S1**]. The ee of (*R*)-**S1** was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 90/10, flow = 0.7 mL/min. Retention times: 6.9 min [(*S*)-enantiomer], 7.7 min [(*R*)-enantiomer]. >99% ee. $[\alpha]^{23}_{D}$ −87.9 (*c* 0.31, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.78-7.72 (m, 2H), 7.42-7.34 (m, 3H), 7.01 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 6.14-6.08 (m, 2H), 4.78 (s, 1H), 3.64 (bs, 2H), 1.20 (s, 9H), 0.62 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.6, 154.2, 138.9, 134.9, 131.8, 129.4, 128.6, 108.9, 105.5, 104.6, 27.9, 19.9, –0.6.

racemate



>99% ee (*R*)



Et_3N (104 μL, 0.750 mmol) and 4-methylbenzoyl chloride (89.8 μL, 0.680 mmol) were added to a solution of (*R*)-**S1** (194 mg, 0.680 mmol) in 1,2-dichloroethane (1.5 mL) at room temperature, and the mixture was stirred for 14 h at 60 °C. The reaction was quenched with saturated $NaHCO_3$aq and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 3/1 to afford (*R*)-*N*-(2-(*tert*-butyl(methyl)(phenyl)silyl)-3-hydroxyphenyl)-4-methylbenzamide (compound (*R*)-**S2**) as a white solid (237 mg, 0.587 mmol; 86% yield). The absolute configuration was determined by X-ray crystallographic analysis after recrystallization from EtOAc/hexane. $[\alpha]^{25}_{D}$ +2.1 (*c* 0.54, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.77 (bs, 1H), 7.68-7.63 (m, 2H), 7.52-7.43 (m, 2H), 7.38 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.30 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.01 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 6.84 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 6.57 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 5.04 (s, 1H), 2.36 (s, 3H), 1.08 (s, 9H), 0.57 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.8, 162.6, 143.9, 141.9, 138.8, 134.8, 131.6, 131.5, 129.6, 129.3, 129.1, 127.0, 117.4, 113.3, 112.2, 27.6, 21.6, 19.5, 0.0.

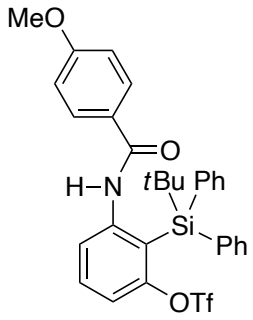
NaH (28.2 mg, 0.705 mmol; 60 wt% in mineral oil) was added to a solution of (*R*)-**S2** (237 mg, 0.587 mmol) in THF (3.0 mL) at 0 °C, and the mixture was stirred for 20 min at 0 °C. *N*-Phenylbis(trifluoromethanesulfonimide) (241 mg, 0.675 mmol) was added to it and the mixture was stirred for 2 h at 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 (*R*)-**1gg** as a yellow oil (267 mg, 0.499 mmol; 85% yield). $[\alpha]^{24}_{D}$ +25.3 (*c* 0.58, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 7.94-7.87 (m, 2H), 7.66-7.60 (m, 2H), 7.56-7.50 (m, 2H), 7.43 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.29 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.01 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 6.76 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 2.37 (s,

3H), 1.06 (s, 9H), 0.65 (s. 3H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 165.4, 156.9, 144.7, 142.4, 136.9, 134.4, 131.8, 130.9, 130.1, 129.7, 129.1, 127.0, 124.3, 119.6, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 115.4, 27.5, 21.5, 19.5, 0.2. HRMS (FAB) calcd for $C_{26}H_{29}F_3NO_4SSi$ ($M+H^+$) 536.1533, found 536.1535.

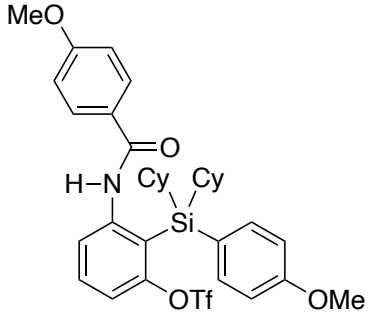
Analytical Data for Other Substrates:

2-(*tert*-Butyldiphenylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1b)



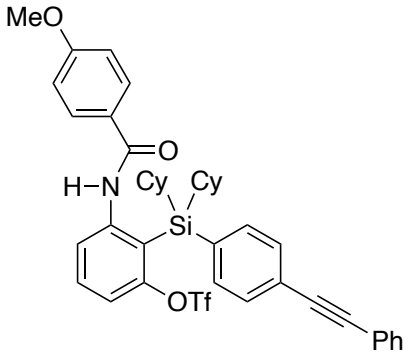
^{1}H NMR ($CDCl_3$): δ 8.04 (dd, $^{3}J_{HH}$ = 8.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 8.01 (bs, 1H), 7.70-7.66 (m, 4H), 7.56 (t, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.44-7.39 (m, 2H), 7.39-7.34 (m, 4H), 7.25 (d, $^{3}J_{HH}$ = 8.5 Hz, 1H), 6.83-6.79 (m, 2H), 6.69-6.64 (m, 2H), 3.82 (s, 3H), 1.23 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 164.9, 162.5, 156.7, 145.4, 135.8, 134.5, 132.0, 130.0, 128.8, 126.1, 124.0, 118.7, 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 115.6 (q, $^{5}J_{CF}$ = 1.9 Hz), 113.6, 55.4, 29.4, 20.4. HRMS (FAB) calcd for $C_{31}H_{31}F_3NO_5SSi$ ($M+H^+$) 614.1639, found 614.1643.

2-(Dicyclohexyl(4-methoxyphenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1d)



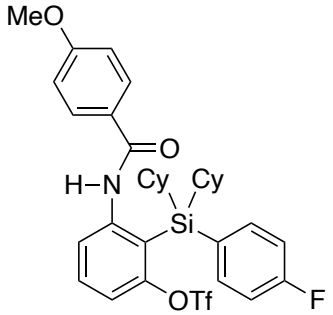
^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 8.00 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.52 (t, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.42 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.23 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.98 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 6.80 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 6.65 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 1.88-1.77 (m, 2H), 1.74-1.50 (m, 10H), 1.36-1.15 (m, 4H), 1.11-0.96 (m, 4H), 0.86-0.71 (m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 165.1, 162.3, 161.6, 157.0, 145.8, 137.1, 131.8, 128.7, 126.5, 123.5, 122.9, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 116.9, 115.0, 114.8 (q, $^{5}J_{CF}$ = 2.6 Hz), 113.5, 55.4, 55.2, 28.0, 27.8, 27.4, 27.3, 26.6, 22.9. HRMS (FAB) calcd for $C_{34}H_{41}F_3NO_6SSi$ ($M+H^+$) 676.2370, found 676.2367.

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



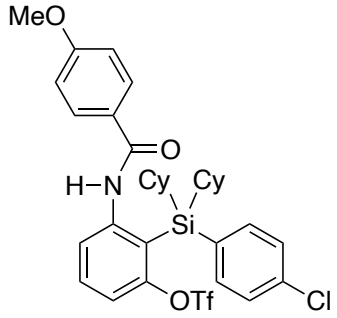
^{1}H NMR ($CDCl_3$): δ 7.95 (dd, $^{3}J_{HH}$ = 8.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.79 (s, 1H), 7.62-7.53 (m, 5H), 7.48 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.43-7.35 (m, 3H), 7.26 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.82 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 6.74 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 3.77 (s, 3H), 1.91-1.79 (m, 2H), 1.75-1.55 (m, 10H), 1.36-1.16 (m, 4H), 1.13-0.98 (m, 4H), 0.88-0.74 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.2, 162.5, 157.0, 145.5, 135.4, 133.2, 132.02, 132.00, 131.8, 128.8, 128.6, 128.5, 126.3, 125.5, 124.0, 122.9, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 116.7, 115.0 (q, $^{5}J_{CF}$ = 2.9 Hz), 113.8, 91.6, 88.8, 55.4, 28.0, 27.7, 27.4, 27.2, 26.6, 22.7. HRMS (FAB) calcd for $C_{41}H_{43}F_3NO_5SSi$ ($M+H^+$) 746.2578, found 746.2579.

2-(Dicyclohexyl(4-fluorophenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1f)



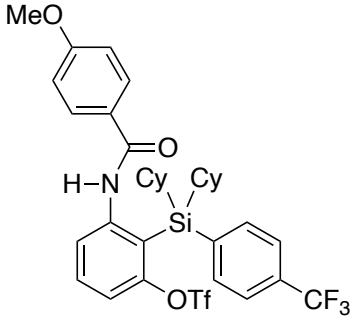
^{1}H NMR ($CDCl_3$): δ 7.95 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.77 (s, 1H), 7.55 (t, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.46 (dd, $^{3}J_{HH}$ = 8.5 Hz and $^{4}J_{HF}$ = 6.1 Hz, 2H), 7.27-7.23 (m, 1H), 7.14 (t, ^{3}J = 8.8 Hz, 2H), 6.84 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H), 6.70 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 3.83 (s, 3H), 1.87-1.78 (m, 2H), 1.75-1.49 (m, 10H), 1.35-1.17 (m, 4H), 1.09-0.97 (m, 4H), 0.85-0.72 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.2, 164.5 (d, $^{1}J_{CF}$ = 252 Hz), 162.5, 156.9, 145.5, 137.5 (d, $^{3}J_{CF}$ = 6.7 Hz), 132.0, 128.4, 128.3 (d, $^{4}J_{CF}$ = 3.8 Hz), 126.4, 124.0, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 116.7, 116.4 (d, $^{2}J_{CF}$ = 20.1 Hz), 115.1 (q, $^{5}J_{CF}$ = 1.9 Hz), 113.7, 55.5, 28.0, 27.7, 27.4, 27.2, 26.6, 22.7. HRMS (FAB) calcd for $C_{33}H_{38}F_4NO_5SSi$ ($M+H^+$) 664.2171, found 664.2181.

2-((4-Chlorophenyl)dicyclohexylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1g)



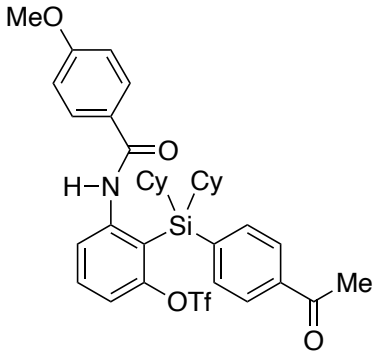
^{1}H NMR ($CDCl_3$): δ 7.93 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.68 (s, 1H), 7.55 (t, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.45-7.37 (m, 4H), 7.25 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H), 6.83 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 6.73 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.85 (s, 3H), 1.89-1.78 (m, 2H), 1.75-1.53 (m, 10H), 1.36-1.15 (m, 4H), 1.12-0.97 (m, 4H), 0.86-0.71 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.2, 162.5, 156.9, 145.4, 136.9, 136.7, 132.1, 131.3, 129.4, 128.4, 126.3, 124.1, 118.6 (q, $^{1}J_{CF}$ = 320 Hz), 116.5, 115.1 (q, $^{5}J_{CF}$ = 2.6 Hz), 113.7, 55.5, 28.0, 27.7, 27.4, 27.2, 26.5, 22.7. HRMS (FAB) calcd for $C_{33}H_{38}ClF_3NO_5SSi$ ($M+H^+$) 680.1875, found 680.1883.

2-(Dicyclohexyl(4-(trifluoromethyl)phenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1h)



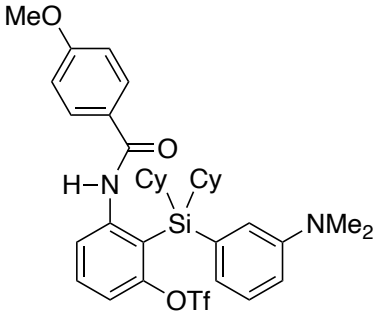
^{1}H NMR ($CDCl_3$): δ 7.89 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.64 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.62-7.53 (m, 3H), 7.45 (s, 1H), 7.28 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 6.80 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 6.66 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.81 (s, 3H), 1.92-1.80 (m, 2H), 1.76-1.53 (m, 10H), 1.38-1.19 (m, 4H), 1.13-0.97 (m, 4H), 0.86-0.72 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.1, 162.6, 156.9, 145.3, 138.3, 135.6, 132.3, 132.1 (q, $^{2}J_{CF}$ = 31.6 Hz), 128.3, 126.1, 125.4 (q, $^{3}J_{CF}$ = 3.5 Hz), 124.6, 124.0 (q, $^{1}J_{CF}$ = 272 Hz), 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 116.7, 115.4 (q, $^{5}J_{CF}$ = 2.6 Hz), 113.7, 55.4, 28.0, 27.7, 27.5, 27.2, 26.5, 22.6. HRMS (FAB) calcd for $C_{34}H_{38}F_6NO_5SSi$ ($M+H^+$) 714.2139, found 714.2139.

2-((4-Acetylphenyl)dicyclohexylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1i)



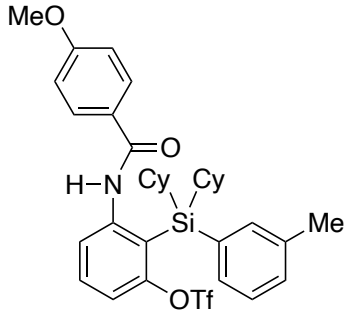
^{1}H NMR ($CDCl_3$): δ 7.92 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.62-7.53 (m, 3H), 7.47 (s, 1H), 7.28 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.81 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.59 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.80 (s, 3H), 2.58 (s, 3H), 1.92-1.79 (m, 2H), 1.76-1.54 (m, 10H), 1.38-1.19 (m, 4H), 1.14-0.97 (m, 4H), 0.89-0.72 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 197.8, 165.0, 162.4, 156.9, 145.3, 139.5, 138.1, 135.5, 132.1, 128.4, 128.1, 126.1, 124.3, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.5, 115.2 (q, $^5J_{CF}$ = 1.9 Hz), 113.6, 55.4, 27.9, 27.63, 27.55, 27.2, 26.6, 26.5, 22.7. HRMS (FAB) calcd for $C_{35}H_{41}F_3NO_6SSi$ ($M+H^+$) 688.2370, found 688.2379.

2-(Dicyclohexyl(3-dimethylaminophenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1j)



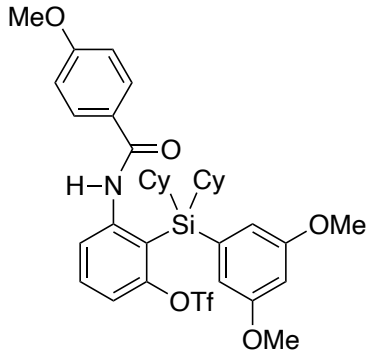
^{1}H NMR ($CDCl_3$): δ 8.19 (s, 1H), 7.94 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.52 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.33 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.24 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.89-6.81 (m, 2H), 6.81-6.75 (m, 3H), 6.64 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.82 (s, 3H), 2.91 (s, 6H), 1.88-1.79 (m, 2H), 1.75-1.50 (m, 10H), 1.37-0.99 (m, 8H), 0.91-0.76 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.1, 162.2, 157.0, 150.7, 145.7, 132.9, 131.6, 130.0, 128.8, 126.3, 124.1, 123.0, 118.71 (q, $^1J_{CF}$ = 320 Hz), 118.69, 117.8, 114.9 (q, $^5J_{CF}$ = 1.9 Hz), 114.1, 113.5, 55.4, 40.5, 28.1, 27.8, 27.44, 27.36, 26.6, 22.9. HRMS (FAB) calcd for $C_{35}H_{44}F_3N_2O_5SSi$ ($M+H^+$) 689.2687, found 689.2694.

2-(Dicyclohexyl(3-tolyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1k)



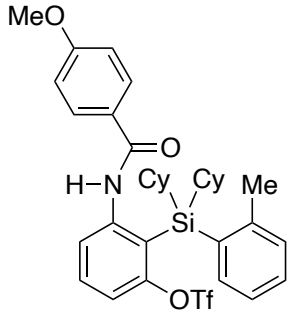
^{1}H NMR ($CDCl_3$): δ 7.98 (s, 1H), 7.95 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.53 (t, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.40-7.22 (m, 5H), 6.71 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 6.64 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.82 (s, 3H), 2.36 (s, 3H), 1.90-1.78 (m, 2H), 1.74-1.50 (m, 10H), 1.37-1.14 (m, 4H), 1.12-0.97 (m, 4H), 0.86-0.71 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.0, 162.3, 157.0, 145.6, 138.7, 135.9, 132.6, 132.5, 131.7, 131.2, 129.1, 128.6, 126.2, 124.0, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 117.3, 114.9 (q, $^{5}J_{CF}$ = 2.9 Hz), 113.5, 55.4, 28.0, 27.7, 27.33, 27.26, 26.6, 22.6, 21.8. HRMS (FAB) calcd for $C_{34}H_{41}F_3NO_5SSi$ ($M+H^+$) 660.2421, found 660.2435.

2-(Dicyclohexyl(3,5-dimethoxyphenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1l)



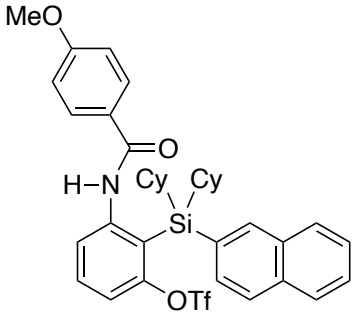
^{1}H NMR ($CDCl_3$): δ 7.920 (s, 1H), 7.916 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.53 (t, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.25 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 6.91 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 6.70 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 6.57 (d, $^{4}J_{HH}$ = 2.3 Hz, 2H), 6.48 (t, $^{4}J_{HH}$ = 2.3 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 6H), 1.89-1.78 (m, 2H), 1.75-1.53 (m, 10H), 1.36-0.99 (m, 8H), 0.93-0.76 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.1, 162.3, 161.3, 156.8, 145.5, 134.8, 131.7, 128.5, 126.2, 124.2, 118.6 (q, $^{1}J_{CF}$ = 320 Hz), 117.2, 114.9 (q, $^{5}J_{CF}$ = 1.9 Hz), 113.4, 112.6, 101.6, 55.29, 55.26, 27.9, 27.7, 27.4, 27.3, 26.5, 22.7. HRMS (FAB) calcd for $C_{35}H_{43}F_3NO_7SSi$ ($M+H^+$) 706.2476, found 706.2482.

2-(Dicyclohexyl(2-tolyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1m)



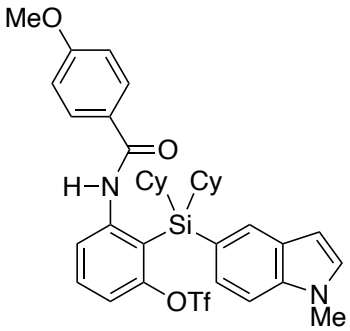
^{1}H NMR ($CDCl_3$): δ 8.18 (s, 1H), 8.05 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.52 (t, $^3J_{HH}$ = 8.5 Hz, 1H), 7.49-7.41 (m, 2H), 7.36-7.20 (m, 3H), 6.71 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.62 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.81 (s, 3H), 2.22 (s, 3H), 1.99-1.86 (m, 2H), 1.80-1.50 (m, 10H), 1.38-1.14 (m, 4H), 1.14-0.94 (m, 4H), 0.94-0.70 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.0, 162.3, 155.9, 145.7, 145.2, 136.6, 132.0, 131.6, 131.1, 130.5, 128.5, 126.1, 123.1, 118.7 (q, $^1J_{CF}$ = 321 Hz), 118.4, 114.9 (q, $^5J_{CF}$ = 2.9 Hz), 113.6, 55.4, 28.1, 27.8, 27.4, 26.5, 24.0, 23.8. HRMS (FAB) calcd for $C_{34}H_{41}F_3NO_5SSi$ ($M+H^+$) 660.2421, found 660.2425.

2-(Dicyclohexyl(2-naphthyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1n)



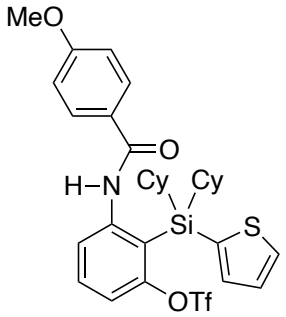
^{1}H NMR ($CDCl_3$): δ 8.01 (s, 1H), 7.98 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.96-7.88 (m, 2H), 7.88-7.80 (m, 2H), 7.67-7.57 (m, 2H), 7.56 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.52 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.29 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.38 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 5.97 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.60 (s, 3H), 1.99-1.86 (m, 2H), 1.86-1.52 (m, 10H), 1.40-0.94 (m, 8H), 0.91-0.76 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.1, 162.0, 157.0, 145.7, 136.6, 134.2, 133.4, 131.9, 131.1, 130.1, 128.72, 128.68, 128.1, 128.0, 127.4, 126.7, 125.9, 123.7, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.8, 114.9 (q, $^5J_{CF}$ = 2.6 Hz), 113.1, 55.1, 28.0, 27.8, 27.4, 26.5, 22.8. HRMS (FAB) calcd for $C_{37}H_{41}F_3NO_5SSi$ ($M+H^+$) 696.2421, found 696.2422.

2-(Dicyclohexyl(1-methyl-1*H*-5-indolyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1o)



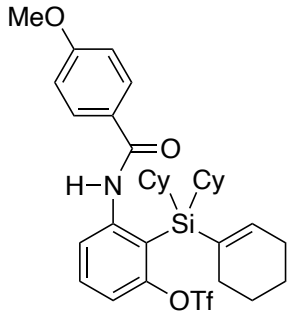
^{1}H NMR ($CDCl_3$): δ 8.29 (s, 1H), 8.05 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.82 (s, 1H), 7.52 (t, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.38 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.29 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H), 7.28-7.22 (m, 1H), 7.16 (d, $^{3}J_{HH}$ = 3.1 Hz, 1H), 6.57 (d, $^{3}J_{HH}$ = 3.1 Hz, 1H), 6.42 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H), 6.18 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H), 3.85 (s, 3H), 3.71 (s, 3H), 1.94-1.84 (m, 2H), 1.75-1.50 (m, 10H), 1.38-1.19 (m, 4H), 1.18-0.96 (m, 4H), 0.87-0.75 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.1, 161.9, 157.1, 146.0, 138.0, 131.6, 129.44, 129.36, 129.2, 128.5, 128.0, 126.2, 123.2, 120.4, 118.7 (q, $^{1}J_{CF}$ = 321 Hz), 117.3, 114.5 (q, $^{5}J_{CF}$ = 2.9 Hz), 113.0, 110.5, 102.0, 55.2, 32.9, 28.1, 27.8, 27.42, 27.39, 26.6, 23.0. HRMS (FAB) calcd for $C_{36}H_{41}F_3N_2O_5SSi$ (M^+) 698.2452, found 698.2438.

2-(Dicyclohexyl(2-thienyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1p)



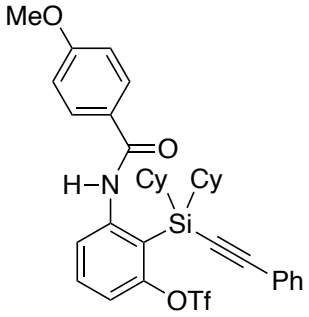
^{1}H NMR ($CDCl_3$): δ 8.27 (s, 1H), 7.96 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.78 (d, $^{3}J_{HH}$ = 5.0 Hz, 1H), 7.53 (t, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.40 (d, $^{3}J_{HH}$ = 3.6 Hz, 1H), 7.33 (dd, $^{3}J_{HH}$ = 5.0 and 3.6 Hz, 1H), 7.23 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 6.89 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 6.71 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 3.84 (s, 3H), 1.87-1.77 (m, 2H), 1.75-1.49 (m, 10H), 1.35-0.99 (m, 8H), 0.90-0.74 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.2, 162.4, 156.3, 145.9, 137.6, 133.1, 132.0, 131.5, 129.5, 128.7, 126.4, 124.1, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 117.0, 114.9 (q, $^{5}J_{CF}$ = 2.2 Hz), 113.6, 55.5, 27.9, 27.70, 27.67, 27.3, 26.6, 23.9. HRMS (FAB) calcd for $C_{31}H_{37}F_3NO_5S_2Si$ ($M+H^+$) 652.1829, found 652.1839.

2-(1-Cyclohexenyldicyclohexylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1q)



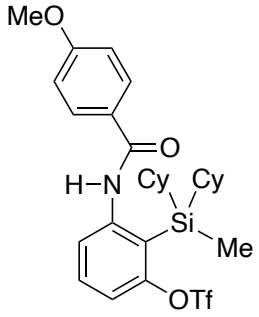
^{1}H NMR ($CDCl_3$): δ 8.84 (s, 1H), 8.09 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.73 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.48 (t, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.16 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 6.26 (s, 1H), 3.88 (s, 3H), 2.12-1.96 (m, 4H), 1.79-1.56 (m, 10H), 1.56-1.36 (m, 6H), 1.33-1.00 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.8, 162.7, 156.6, 145.9, 142.8, 134.4, 131.5, 129.3, 127.4, 122.9, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 117.4, 114.8 (q, $^{5}J_{CF}$ = 2.9 Hz), 114.0, 55.6, 28.7, 28.24, 28.23, 28.0, 27.2, 26.9, 23.6, 22.3, 22.0. HRMS (FAB) calcd for $C_{33}H_{43}F_3NO_5SSi$ ($M+H^+$) 650.2578, found 650.2581.

2-(Dicyclohexyl(phenylethynyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1r)



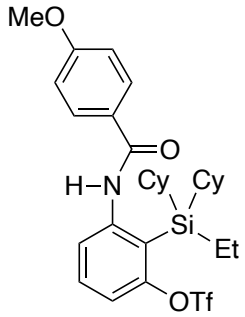
^{1}H NMR ($CDCl_3$): δ 9.93 (s, 1H), 8.21 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.76 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H), 7.50 (t, $^{3}J_{HH}$ = 8.4 Hz, 1H), 7.37 (tt, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.9 Hz, 1H), 7.30-7.24 (m, 2H), 7.23-7.19 (m, 2H), 7.17 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 6.55 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.67 (s, 3H), 1.91-1.81 (m, 2H), 1.77-1.56 (m, 8H), 1.46-1.14 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.4, 162.4, 155.6, 146.3, 132.4, 131.9, 129.5, 128.4, 127.2, 122.7, 121.9, 118.6 (q, $^{1}J_{CF}$ = 320 Hz), 115.5, 114.1 (q, $^{5}J_{CF}$ = 1.9 Hz), 113.8, 113.4, 88.5, 55.3, 28.3, 28.1, 27.9, 27.8, 26.7, 24.7. HRMS (FAB) calcd for $C_{35}H_{39}F_3NO_5SSi$ ($M+H^+$) 670.2265, found 670.2278.

2-(Dicyclohexyl(methyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1s)



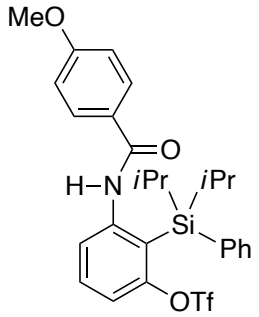
^{1}H NMR ($CDCl_3$): δ 7.87-7.84 (m, 2H), 7.82 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.47 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 7.20 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.02 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.90 (s, 3H), 1.80-1.61 (m, 8H), 1.51-1.43 (m, 2H), 1.24-1.01 (m, 12H), 0.39 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.4, 162.9, 155.9, 144.7, 131.3, 129.1, 126.7, 124.9, 122.4, 118.6 (q, $^1J_{CF}$ = 320 Hz), 116.5 (q, $^5J_{CF}$ = 1.9 Hz), 114.3, 55.6, 28.6, 28.3, 28.2, 28.1, 26.8, 25.4, −6.5. HRMS (FAB) calcd for $C_{28}H_{37}F_3NO_5SSi$ ($M+H^+$) 584.2108, found 584.2116.

2-(Dicyclohexyl(ethyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1t)



^{1}H NMR ($CDCl_3$): δ 7.97 (s, 1H), 7.92 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.82 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.49 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.19 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.01 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.90 (s, 3H), 1.84-1.54 (m, 10H), 1.31-0.95 (m, 17H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.3, 162.9, 156.0, 145.0, 131.5, 129.0, 126.9, 124.4, 120.7, 118.6 (q, $^1J_{CF}$ = 320 Hz), 116.4 (q, $^5J_{CF}$ = 1.9 Hz), 114.3, 55.6, 28.9, 28.8, 28.3, 26.9, 26.0, 8.4, 3.0. HRMS (FAB) calcd for $C_{29}H_{39}F_3NO_5SSi$ ($M+H^+$) 598.2265, found 598.2266.

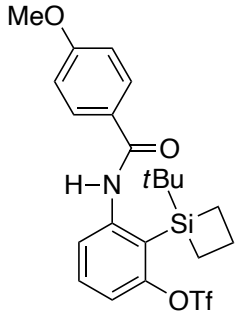
2-(Diisopropyl(phenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1u)



^{1}H NMR ($CDCl_3$): δ 8.01 (s, 1H), 7.97 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.59-7.45 (m,

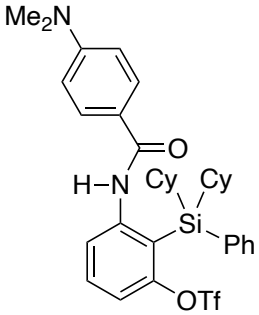
6H), 7.28 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.71 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.64 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.82 (s, 3H), 1.81 (sept, $^3J_{HH}$ = 7.3 Hz, 2H), 1.03 (d, $^3J_{HH}$ = 7.4 Hz, 6H), 0.82 (d, $^3J_{HH}$ = 7.3 Hz, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.9, 162.4, 157.1, 145.6, 135.6, 132.3, 132.0, 130.5, 129.3, 128.7, 126.1, 124.2, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.7, 114.9 (q, $^5J_{CF}$ = 2.6 Hz), 113.6, 55.5, 17.7, 17.6, 11.2. HRMS (FAB) calcd for $C_{27}H_{31}F_3NO_5SSi$ ($M+H^+$) 566.1639, found 566.1627.

2-(1-(*tert*-Butyl)siletan-1-yl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1v)



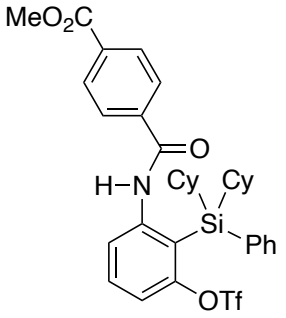
^1H NMR ($CDCl_3$): δ 8.16 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.97 (s, 1H), 7.76 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.52 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.20 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 6.98 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 2.50-2.35 (m, 1H), 2.21-2.04 (m, 1H), 1.62-1.40 (m, 4H), 1.03 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.1, 162.9, 155.0, 144.7, 132.4, 128.9, 126.5, 122.3, 120.1, 118.5 (q, $^1J_{CF}$ = 320 Hz), 114.8 (q, $^5J_{CF}$ = 1.9 Hz), 114.3, 55.6, 26.3, 20.0, 19.3, 13.7, 13.2. HRMS (FAB) calcd for $C_{22}H_{27}F_3NO_5SSi$ ($M+H^+$) 502.1326, found 502.1330.

2-(Dicyclohexyl(phenyl)silyl)-3-(4-(dimethylamino)benzamido)phenyl trifluoromethanesulfonate (1w)



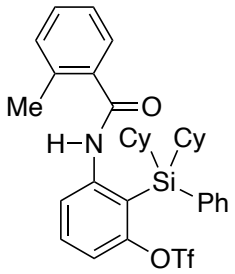
^1H NMR ($CDCl_3$): δ 7.97 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.86 (s, 1H), 7.60-7.45 (m, 6H), 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.62 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.36 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 2.99 (s, 6H), 1.90-1.79 (m, 2H), 1.74-1.50 (m, 10H), 1.37-1.14 (m, 4H), 1.12-0.95 (m, 4H), 0.88-0.73 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 165.4, 157.0, 152.5, 146.0, 135.6, 132.9, 131.7, 130.3, 129.2, 128.3, 124.1, 120.5, 118.7 (q, $^1J_{CF}$ = 321 Hz), 116.9, 114.6 (q, $^5J_{CF}$ = 2.9 Hz), 110.7, 40.1, 28.1, 27.8, 27.33, 27.27, 26.6, 22.6. HRMS (FAB) calcd for $C_{34}H_{42}F_3N_2O_4SSi$ ($M+H^+$) 659.2581, found 659.2589.

Methyl 4-((2-(dicyclohexyl(phenyl)silyl)-3-(trifluoromethylsulfonyloxy)phenyl)carbamoyl)benzoate (1x)



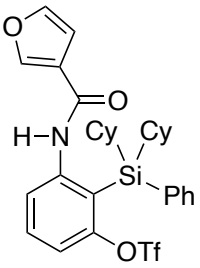
^{1}H NMR ($CDCl_3$): δ 8.09 (s, 1H), 7.99 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.82 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.61-7.53 (m, 2H), 7.51-7.44 (m, 4H), 7.29 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 6.82 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.94 (s, 3H), 1.90-1.78 (m, 2H), 1.74-1.48 (m, 10H), 1.37-1.13 (m, 4H), 1.10-0.96 (m, 4H), 0.85-0.70 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.3, 164.5, 156.9, 144.9, 137.8, 135.5, 132.9, 132.6, 132.0, 130.6, 129.7, 129.3, 126.6, 124.0, 118.7 (q, $^{1}J_{CF}$ = 320 Hz), 117.5, 115.6 (q, $^{5}J_{CF}$ = 1.9 Hz), 52.5, 27.9, 27.7, 27.4, 27.2, 26.5, 22.6. HRMS (FAB) calcd for $C_{34}H_{39}F_3NO_6SSi$ ($M+H^+$) 674.2214, found 674.2220.

2-(Dicyclohexyl(phenyl)silyl)-3-(2-methylbenzamido)phenyl trifluoromethanesulfonate (1y)



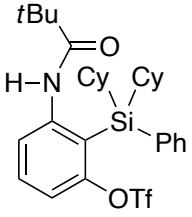
^{1}H NMR ($CDCl_3$): δ 8.11 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.71 (s, 1H), 7.55 (t, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.40-7.33 (m, 3H), 7.30-7.23 (m, 3H), 7.19 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 7.08 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 6.84 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 6.26 (d, $^{3}J_{HH}$ = 7.5 Hz, 1H), 2.27 (s, 3H), 1.88-1.78 (m, 2H), 1.75-1.48 (m, 10H), 1.36-1.17 (m, 4H), 1.14-0.98 (m, 4H), 0.86-0.73 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.6, 156.9, 145.5, 136.9, 135.0, 134.9, 132.04, 131.98, 131.1, 130.3, 130.0, 128.8, 125.8, 125.7, 122.6, 118.7 (q, $^{1}J_{CF}$ = 321 Hz), 116.7, 114.9 (q, $^{5}J_{CF}$ = 2.9 Hz), 27.9, 27.7, 27.5, 27.3, 26.6, 22.7, 19.9. HRMS (FAB) calcd for $C_{33}H_{39}F_3NO_4SSi$ ($M+H^+$) 630.2316, found 630.2325.

2-(Dicyclohexyl(phenyl)silyl)-3-(3-furancarboxamido)phenyl trifluoromethanesulfonate (1z)



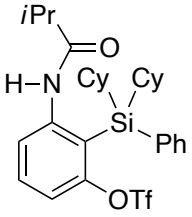
^{1}H NMR ($CDCl_3$): δ 7.99 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.72 (s, 1H), 7.60-7.47 (m, 6H), 7.26 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.20 (t, J_{HH} = 1.6 Hz, 1H), 6.77 (d, J_{HH} = 0.9 Hz, 1H), 5.67 (s, 1H), 1.88-1.78 (m, 2H), 1.74-1.50 (m, 10H), 1.37-1.18 (m, 4H), 1.10-0.95 (m, 4H), 0.87-0.73 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 160.6, 157.0, 144.9, 144.6, 143.6, 135.6, 132.9, 132.0, 130.7, 129.2, 123.8, 122.5, 118.7 (q, $^1J_{CF}$ = 320 Hz), 116.8, 115.3 (q, $^5J_{CF}$ = 2.6 Hz), 108.0, 28.0, 27.7, 27.4, 27.2, 26.6, 22.6. HRMS (FAB) calcd for $C_{30}H_{35}F_3NO_5SSi$ (M+H$^+$) 606.1952, found 606.1949.

2-(Dicyclohexyl(phenyl)silyl)-3-pivalamidophenyl trifluoromethanesulfonate (1aa)



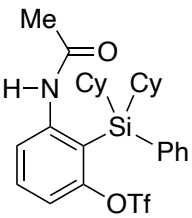
^{1}H NMR ($CDCl_3$): δ 7.80 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.54-7.39 (m, 6H), 7.33 (s, 1H), 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 1.87-1.56 (m, 12H), 1.38-1.20 (m, 4H), 1.12-0.95 (m, 4H), 0.91-0.75 (m, 2H), 0.69 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 177.1, 157.0, 145.8, 135.4, 133.3, 131.5, 130.4, 128.9, 124.9, 118.7 (q, $^1J_{CF}$ = 320 Hz), 117.6, 115.1 (q, $^5J_{CF}$ = 2.6 Hz), 39.3, 28.0, 27.7, 27.4, 26.64, 26.60, 22.9. HRMS (FAB) calcd for $C_{30}H_{41}F_3NO_4SSi$ (M+H$^+$) 596.2472, found 596.2473.

2-(Dicyclohexyl(phenyl)silyl)-3-isobutyramidophenyl trifluoromethanesulfonate (1bb)



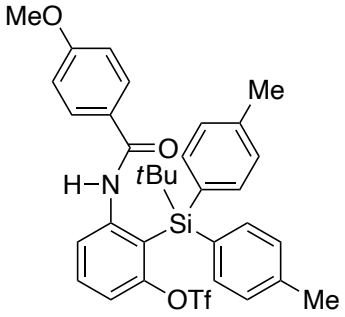
^{1}H NMR ($CDCl_3$): δ 8.10 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.58-7.52 (m, 2H), 7.52-7.43 (m, 4H), 7.29 (s, 1H), 7.19 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 1.90-1.79 (m, 2H), 1.78-1.60 (m, 10H), 1.39-1.24 (m, 4H), 1.17-0.98 (m, 5H), 0.90-0.77 (m, 2H), 0.76 (d, $^3J_{HH}$ = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 175.0, 156.9, 145.8, 135.4, 132.9, 132.0, 130.5, 128.9, 122.0, 118.7 (q, $^1J_{CF}$ = 321 Hz), 115.4, 114.4 (q, $^5J_{CF}$ = 2.6 Hz), 36.4, 28.0, 27.73, 27.70, 27.3, 26.6, 22.8, 19.0. HRMS (FAB) calcd for $C_{29}H_{39}F_3NO_4SSi$ (M+H$^+$) 582.2316, found 582.2329.

3-Acetamido-2-(dicyclohexyl(phenyl)silyl)phenyl trifluoromethanesulfonate (1cc)



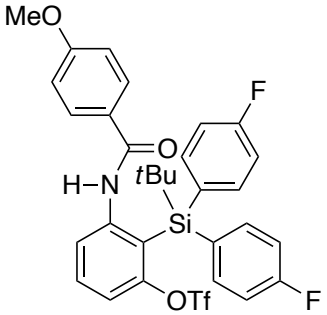
^{1}H NMR ($CDCl_3$): δ 8.02 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.58-7.44 (m, 6H), 7.23 (s, 1H), 7.21 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 1.90-1.80 (m, 2H), 1.78-1.61 (m, 10H), 1.39-1.26 (m, 4H), 1.22 (s, 3H), 1.18-0.98 (m, 4H), 0.90-0.76 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 167.9, 156.8, 145.4, 135.3, 132.9, 132.1, 130.4, 129.0, 122.1, 118.7 (q, $^1J_{CF}$ = 321 Hz), 115.4, 114.6 (q, $^5J_{CF}$ = 1.9 Hz), 28.0, 27.8, 27.7, 27.3, 26.6, 23.6, 22.8. HRMS (FAB) calcd for $C_{27}H_{35}F_3NO_4SSi$ ($M+H^+$) 554.2003, found 554.2015.

2-(*tert*-Butyldi-4-tolylsilyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1hh)



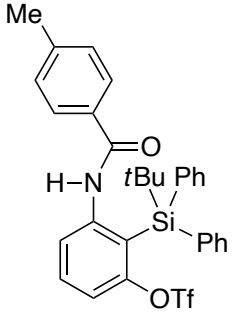
^{1}H NMR ($CDCl_3$): δ 8.10 (s, 1H), 8.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.54 (d, $^3J_{HH}$ = 7.8 Hz, 4H), 7.53 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.23 (d, $^3J_{HH}$ = 8.7 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 7.8 Hz, 4H), 6.84 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.66 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.83 (s, 3H), 2.34 (s, 6H), 1.21 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.1, 162.4, 156.7, 145.5, 140.0, 135.8, 131.9, 131.0, 129.6, 128.9, 126.4, 123.7, 118.9, 118.5 (q, $^1J_{CF}$ = 321 Hz), 115.5 (q, $^5J_{CF}$ = 1.9 Hz), 113.5, 55.5, 29.4, 21.6, 20.4. HRMS (FAB) calcd for $C_{33}H_{35}F_3NO_5SSi$ ($M+H^+$) 642.1952, found 642.1952.

2-(*tert*-Butylbis(4-fluorophenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate (1ii)



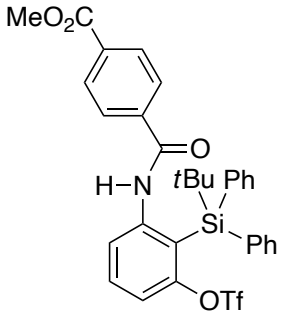
^{1}H NMR ($CDCl_3$): δ 8.01 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.81 (s, 1H), 7.58 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HF}$ = 6.0 Hz, 4H), 7.55 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.02 (t, ^3J = 8.7 Hz, 4H), 6.91 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.70 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.82 (s, 3H), 1.18 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.0, 164.2 (d, $^1J_{CF}$ = 252 Hz), 162.6, 156.4, 145.4, 137.8 (d, $^3J_{CF}$ = 7.7 Hz), 132.3, 129.9 (d, $^4J_{CF}$ = 3.8 Hz), 128.6, 126.2, 124.0, 118.4 (q, $^1J_{CF}$ = 322 Hz), 117.9, 116.1 (d, $^2J_{CF}$ = 20.1 Hz), 115.7 (q, $^5J_{CF}$ = 2.9 Hz), 113.7, 55.4, 29.3, 20.2. HRMS (FAB) calcd for $C_{31}H_{29}F_5NO_5SSi$ ($M+H^+$) 650.1450, found 650.1469.

2-(*tert*-Butyldiphenylsilyl)-3-(4-methylbenzamido)phenyl trifluoromethanesulfonate (1jj)



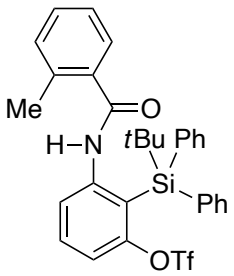
^{1}H NMR ($CDCl_3$): δ 8.07 (s, 1H), 8.05 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.70-7.63 (m, 4H), 7.56 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.44-7.38 (m, 2H), 7.28-7.32 (m, 4H), 7.26 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 6.74 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 2.35 (s, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.3, 156.7, 145.3, 142.3, 135.8, 134.5, 132.1, 131.0, 130.0, 129.1, 128.8, 126.9, 124.0, 118.8, 118.5 (q, $^1J_{CF}$ = 321 Hz), 115.6, 29.4, 21.5, 20.4. HRMS (FAB) calcd for $C_{31}H_{31}F_3NO_4SSi$ ($M+H^+$) 598.1690, found 598.1699.

Methyl 4-((2-(*tert*-butyldiphenylsilyl)-3-(trifluoromethylsulfonyloxy)phenyl)carbamoyl)benzoate (1kk)



^{1}H NMR ($CDCl_3$): δ 8.13 (s, 1H), 8.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.84 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.68-7.62 (m, 4H), 7.59 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 7.44-7.38 (m, 2H), 7.37-7.28 (m, 5H), 6.92 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.95 (s, 3H), 1.22 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.2, 164.4, 156.6, 144.8, 137.7, 135.6, 134.3, 132.9, 132.2, 130.1, 129.6, 128.8, 126.8, 123.9, 119.0, 118.4 (q, $^1J_{CF}$ = 321 Hz), 115.9 (q, $^5J_{CF}$ = 1.9 Hz), 52.4, 29.2, 20.3. HRMS (FAB) calcd for $C_{32}H_{31}F_3NO_6SSi$ ($M+H^+$) 642.1588, found 642.1590.

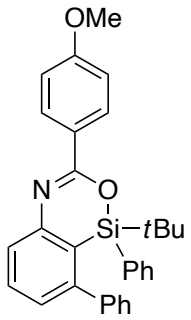
2-(*tert*-Butyldiphenylsilyl)-3-(2-methylbenzamido)phenyl trifluoromethanesulfonate (1ll)



^{1}H NMR ($CDCl_3$): δ 8.15 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.70 (s, 1H), 7.60-7.53 (m, 5H), 7.31-7.17 (m, 8H), 7.09 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.92 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 6.49 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 2.21 (s, 3H), 1.27 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 167.8, 156.6, 145.6, 136.7, 135.4, 135.2, 134.1, 132.3, 131.2, 130.2, 129.9, 128.6, 126.4, 125.8, 122.8, 118.5 (q, $^{1}J_{CF}$ = 321 Hz), 117.8, 115.2 (q, $^{5}J_{CF}$ = 2.9 Hz), 29.3, 20.3, 19.8. HRMS (FAB) calcd for $C_{31}H_{31}F_3NO_4SSi$ ($M+H^+$) 598.1690, found 598.1690.

III. Catalytic Reactions and Derivatization

Procedure for Scheme 1b.

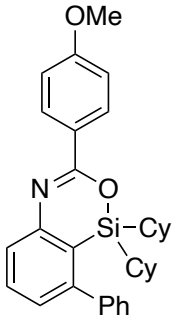


Et_2NH (46.6 μL, 0.450 mmol) and DMA (0.6 mL) were added to a mixture of compound **1b** (92.1 mg, 0.150 mmol) and $Pd(PPh_3)_4$ (17.3 mg, 15.0 μmol), and the resulting solution was stirred for 47 h at 100 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 (containing 2 vol% of Et_3N) to afford compound **3b** as a white amorphous (46.5 mg, 0.100 mmol; 67% yield).

^1H NMR ($CDCl_3$): δ 8.17 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.53-7.45 (m, 4H), 7.44-7.38 (m, 1H), 7.32 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.25 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.12 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.09-7.04 (m, 1H), 7.00 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 6.93 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.85 (s, 3H), 0.82 (s, 9H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 162.1, 154.2, 151.3, 148.7, 143.7, 136.1, 135.2, 131.3, 130.24, 130.20, 130.17, 128.1, 127.97, 127.95, 127.50, 127.47, 127.3, 119.8, 113.6, 55.5, 26.6, 21.1. HRMS (FAB) calcd for $C_{30}H_{30}NO_2Si$ ($M+H^+$) 464.2040, found 464.2042.

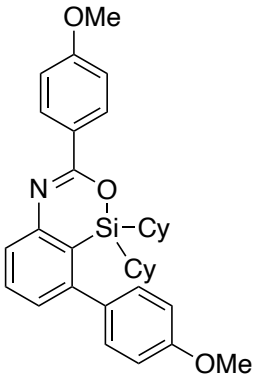
General Procedure for Schemes 2 and 3.

Et_2NH (33.0 μL, 0.320 mmol) and DMF (0.6 mL) were added to a mixture of compound **1** (0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 μmol), and PCy_3•HBF_4 (6.1 mg, 17 μmol), and the resulting solution was stirred for 16 h 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 Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc (containing 2 vol% of Et_3N) to afford compound **3**.



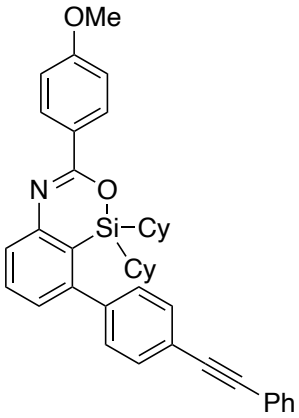
Scheme 2, compound 3c. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 94% yield (69.7 mg). The reaction could be scaled up using 4.26 mmol of **1c** to give **3c** in 83% yield (1.75 g, 3.52 mmol).

^{1}H NMR ($CDCl_3$): δ 8.20 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.50-7.37 (m, 5H), 7.36-7.30 (m, 2H), 7.10 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.98 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 1.74-1.45 (m, 10H), 1.36-1.21 (m, 2H), 1.16-0.97 (m, 6H), 0.91-0.76 (m, 2H), 0.64 (tt, $^{3}J_{HH}$ = 12.8 and 2.7 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 154.6, 151.0, 147.9, 144.2, 130.9, 130.1, 129.0, 128.4, 127.8, 127.5, 126.81, 126.75, 120.5, 113.6, 55.5, 27.92, 27.88, 27.01, 26.97, 26.6. HRMS (FAB) calcd for $C_{32}H_{38}NO_2Si$ ($M+H^+$) 496.2666, found 496.2670.



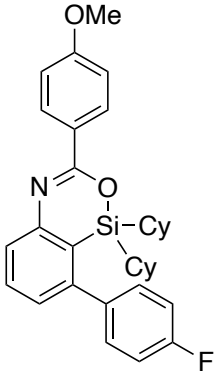
Scheme 2, compound 3d. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 95% yield (74.7 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 7.44 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.36 (dd, $^{3}J_{HH}$ = 8.0 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.24 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H), 7.06 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.00-6.93 (m, 4H), 3.89 (s, 3H), 3.88 (s, 3H), 1.70-1.44 (m, 10H), 1.35-1.21 (m, 2H), 1.15-0.99 (m, 6H), 0.91-0.79 (m, 2H), 0.65 (tt, $^{3}J_{HH}$ = 12.8 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 159.5, 154.5, 151.0, 147.6, 136.6, 130.8, 130.1, 127.5, 127.0, 126.6, 120.7, 113.8, 113.6, 55.6, 55.5, 27.91, 27.89, 27.03, 26.99, 26.7. HRMS (FAB) calcd for $C_{33}H_{40}NO_3Si$ ($M+H^+$) 526.2772, found 526.2784.



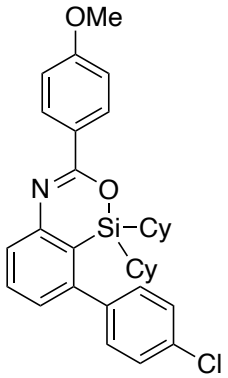
Scheme 2, compound 3e. The reaction was conducted for 40 h. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 65% yield (58.0 mg).

^{1}H NMR ($CDCl_3$): δ 8.19 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.67-7.54 (m, 4H), 7.47 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.44-7.28 (m, 6H), 7.09 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.97 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 1.76-1.43 (m, 10H), 1.38-1.21 (m, 2H), 1.21-0.99 (m, 6H), 0.96-0.79 (m, 2H), 0.66 (t, $^{3}J_{HH}$ = 12.6 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.1, 154.7, 151.1, 147.2, 144.1, 131.8, 131.6, 131.0, 130.2, 129.1, 128.6, 127.4, 127.1, 126.7, 123.3, 122.9, 120.4, 113.7, 90.3, 89.3, 55.5, 27.9, 27.1, 27.0, 26.6. HRMS (FAB) calcd for $C_{40}H_{42}NO_2Si$ ($M+H^+$) 596.2979, found 596.2985.



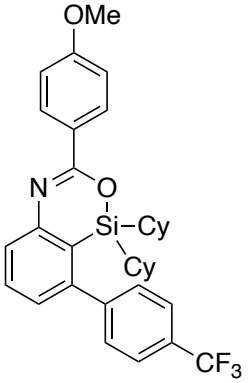
Scheme 2, compound 3f. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 92% yield (71.1 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 7.45 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H), 7.39 (dd, $^{3}J_{HH}$ = 8.0 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 7.29 (dd, $^{3}J_{HH}$ = 8.8 Hz and $^{4}J_{HF}$ = 5.4 Hz, 2H), 7.13 (t, ^{3}J = 8.6 Hz, 2H), 7.05 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.2 Hz, 1H), 6.97 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 3.88 (s, 3H), 1.70-1.43 (m, 10H), 1.34-1.22 (m, 2H), 1.16-0.99 (m, 6H), 0.91-0.80 (m, 2H), 0.62 (tt, $^{3}J_{HH}$ = 12.7 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.7 (d, $^{1}J_{CF}$ = 247 Hz), 162.1, 154.6, 151.1, 146.7, 140.2 (d, $^{4}J_{CF}$ = 2.9 Hz), 130.9, 130.6 (d, $^{3}J_{CF}$ = 8.6 Hz), 130.1, 127.3, 127.0, 126.9, 120.6, 115.2 (d, $^{2}J_{CF}$ = 21.1 Hz), 113.6, 55.5, 27.9, 27.04, 26.97, 26.6. HRMS (FAB) calcd for $C_{32}H_{37}FNO_2Si$ ($M+H^+$) 514.2572, found 514.2579.



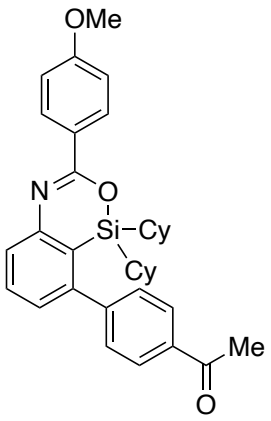
Scheme 2, compound 3g. The reaction was conducted using binap (5.5 mol%) as the ligand. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 86% yield (68.3 mg).

^{1}H NMR ($CDCl_3$): δ 8.17 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.48-7.36 (m, 4H), 7.26 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.04 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 1.73-1.41 (m, 10H), 1.34-1.20 (m, 2H), 1.18-0.97 (m, 6H), 0.91-0.77 (m, 2H), 0.62 (tt, $^3J_{HH}$ = 12.4 and 2.7 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.1, 154.6, 151.1, 146.5, 142.6, 134.0, 131.0, 130.4, 130.2, 128.5, 127.3, 127.2, 126.7, 120.5, 113.7, 55.5, 27.9, 27.1, 27.04, 26.98, 26.6. HRMS (FAB) calcd for $C_{32}H_{37}ClNO_2Si$ ($M+H^+$) 530.2277, found 530.2277.



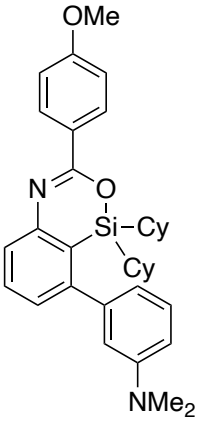
Scheme 2, compound 3h. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 92% yield (78.2 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.72 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.52-7.40 (m, 4H), 7.08 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.88 (s, 3H), 1.71-1.41 (m, 10H), 1.33-1.18 (m, 2H), 1.15-0.96 (m, 6H), 0.88-0.73 (m, 2H), 0.59 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.2, 154.7, 151.2, 147.9, 146.3, 131.1, 130.22 (q, $^2J_{CF}$ = 32.6 Hz), 130.19, 129.4, 127.5, 127.2, 126.5, 125.4 (q, $^3J_{CF}$ = 3.5 Hz), 124.3 (q, $^1J_{CF}$ = 272 Hz), 120.5, 113.7, 55.5, 27.9, 27.8, 27.1, 27.0, 26.9, 26.6. HRMS (FAB) calcd for $C_{33}H_{37}F_3NO_2Si$ ($M+H^+$) 564.2540, found 564.2550.



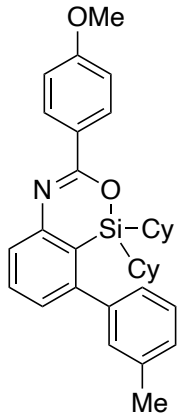
Scheme 2, compound 3i. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 86% yield (69.2 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 8.04 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.52-7.38 (m, 4H), 7.07 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.97 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 2.69 (s, 3H), 1.70-1.40 (m, 10H), 1.35-1.18 (m, 2H), 1.15-0.95 (m, 6H), 0.91-0.77 (m, 2H), 0.60 (tt, $^{3}J_{HH}$ = 12.8 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 197.8, 162.1, 154.6, 151.2, 149.1, 146.6, 136.4, 131.0, 130.1, 129.3, 128.4, 127.4, 127.2, 126.5, 120.3, 113.6, 55.5, 27.83, 27.80, 27.1, 27.04, 26.95, 26.9, 26.5. HRMS (FAB) calcd for $C_{34}H_{40}NO_3Si$ ($M+H^+$) 538.2772, found 538.2775.



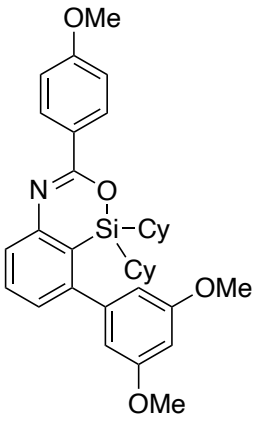
Scheme 2, compound 3j. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 99% yield (79.7 mg).

^{1}H NMR ($CDCl_3$): δ 8.19 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 7.44 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.37 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.27 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.12 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 6.80-6.74 (m, 1H), 6.68-6.63 (m, 2H), 3.88 (s, 3H), 3.00 (s, 6H), 1.69-1.48 (m, 10H), 1.35-1.21 (m, 2H), 1.14-0.97 (m, 6H), 0.93-0.78 (m, 2H), 0.71 (tt, $^{3}J_{HH}$ = 12.6 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 154.7, 150.9, 150.6, 148.9, 144.9, 130.7, 130.1, 129.1, 127.6, 126.6, 126.5, 120.5, 117.4, 113.6, 113.2, 112.0, 55.5, 40.8, 28.0, 27.9, 27.03, 26.97, 26.8, 26.7. HRMS (FAB) calcd for $C_{34}H_{43}N_2O_2Si$ ($M+H^+$) 539.3088, found 539.3102.



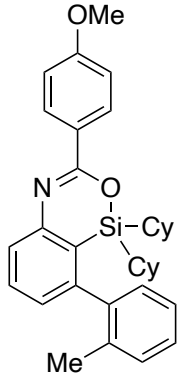
Scheme 2, compound 3k. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 98% yield (74.6 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 7.45 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.38 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.32 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.22 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.15-7.11 (m, 2H), 7.09 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H), 1.70-1.45 (m, 10H), 1.33-1.20 (m, 2H), 1.15-0.98 (m, 6H), 0.87-0.75 (m, 2H), 0.63 (tt,^{3} J_{HH} = 12.8 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 154.6, 151.0, 148.1, 144.0, 137.9, 130.8, 130.1, 129.9, 128.39, 128.37, 127.5, 126.7, 126.6, 126.1, 120.5, 113.6, 55.5, 27.99, 27.97, 27.1, 27.0, 26.9, 26.7, 21.6. HRMS (FAB) calcd for $C_{33}H_{40}NO_2Si$ ($M+H^+$) 510.2823, found 510.2831.



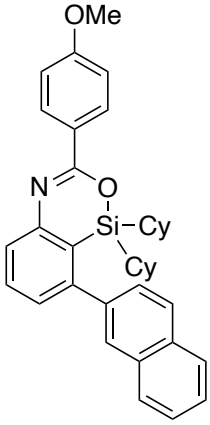
Scheme 2, compound 3l. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 93% yield (77.7 mg).

^{1}H NMR ($CDCl_3$): δ 8.19 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.45 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.39 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.10 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 6.97 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 6.52 (t, $^{4}J_{HH}$ = 2.3 Hz, 1H), 6.48 (d, $^{4}J_{HH}$ = 2.3 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 6H), 1.74-1.48 (m, 10H), 1.38-1.24 (m, 2H), 1.18-0.98 (m, 6H), 0.95-0.81 (m, 2H), 0.74 (tt, $^{3}J_{HH}$ = 12.6 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 160.8, 154.7, 151.0, 147.9, 146.0, 130.8, 130.1, 127.4, 126.9, 126.3, 120.3, 113.6, 107.2, 100.2, 55.6, 55.5, 28.0, 27.1, 27.0, 26.9, 26.7. HRMS (FAB) calcd for $C_{34}H_{42}NO_4Si$ ($M+H^+$) 556.2878, found 556.2879.



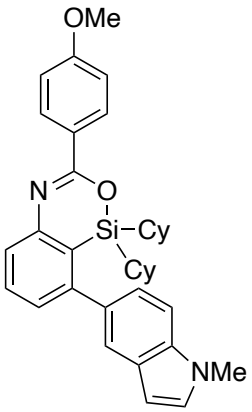
Scheme 2, compound 3m. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 86% yield (65.5 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.44 (td, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.38 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.35-7.20 (m, 3H), 7.15 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 7.01 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 3.88 (s, 3H), 2.19 (s, 3H), 1.78-1.46 (m, 8H), 1.42-0.79 (m, 12H), 0.79-0.64 (m, 1H), 0.35 (tt, $^{3}J_{HH}$ = 12.6 and 2.7 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 154.6, 151.3, 146.7, 142.9, 136.5, 130.53, 130.51, 130.1, 129.4, 128.1, 127.5, 127.3, 126.7, 125.7, 121.0, 113.6, 55.5, 28.0, 27.9, 27.8, 27.7, 27.3, 26.9, 26.8, 26.7, 25.8, 20.4. HRMS (FAB) calcd for $C_{33}H_{40}NO_2Si$ ($M+H^+$) 510.2823, found 510.2827.



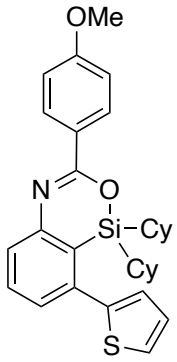
Scheme 2, compound 3n. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 93% yield (76.2 mg).

^{1}H NMR ($CDCl_3$): δ 8.19 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.97-7.80 (m, 3H), 7.76 (s, 1H), 7.60-7.45 (m, 4H), 7.43 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.18 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.97 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 1.63-1.43 (m, 10H), 1.31-1.16 (m, 2H), 1.12-0.90 (m, 6H), 0.87-0.71 (m, 2H), 0.61 (t, $^{3}J_{HH}$ = 12.6 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 154.6, 151.1, 147.9, 141.5, 133.1, 132.8, 130.9, 130.1, 128.1, 128.0, 127.9, 127.7, 127.4, 126.9, 126.8, 126.3, 120.8, 113.6, 55.5, 27.9, 27.8, 27.04, 27.03, 26.9, 26.6. HRMS (FAB) calcd for $C_{36}H_{40}NO_2Si$ ($M+H^+$) 546.2823, found 546.2823.



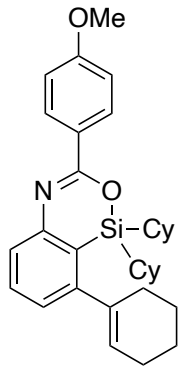
Scheme 2, compound 3o. Hexane/EtOAc = 8/1 was used for silica gel chromatography. White amorphous. 95% yield (78.5 mg).

^{1}H NMR ($CDCl_3$): δ 8.19 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 7.53 (s, 1H), 7.45 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.37 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.36 (d, $^{3}J_{HH}$ = 8.3 Hz, 1H), 7.19 (dd, $^{3}J_{HH}$ = 8.2 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.15 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.13 (d, $^{3}J_{HH}$ = 3.2 Hz, 1H), 6.97 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 6.51 (d, $^{3}J_{HH}$ = 3.2 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 1.63-1.45 (m, 10H), 1.32-1.17 (m, 2H), 1.13-0.93 (m, 6H), 0.87-0.73 (m, 2H), 0.62 (t, $^{3}J_{HH}$ = 12.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.9, 154.5, 150.9, 149.3, 136.4, 135.3, 130.6, 130.1, 129.8, 128.5, 127.7, 127.3, 126.2, 122.9, 121.2, 121.1, 113.6, 108.9, 101.2, 55.5, 33.1, 27.94, 27.88, 27.04, 26.96, 26.7. HRMS (FAB) calcd for $C_{35}H_{41}N_2O_2Si$ ($M+H^+$) 549.2932, found 549.2934.



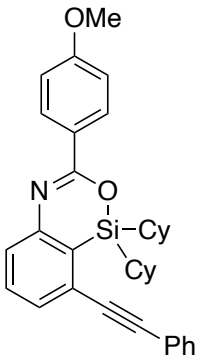
Scheme 2, compound 3p. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 90% yield (68.1 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 7.44 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.39 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.37 (dd, $^{3}J_{HH}$ = 5.0 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.20 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.09 (dd, $^{3}J_{HH}$ = 5.0 and 3.2 Hz, 1H), 7.02-6.88 (m, 3H), 3.88 (s, 3H), 1.78-1.47 (m, 10H), 1.40-1.25 (m, 2H), 1.21-1.01 (m, 6H), 0.98-0.85 (m, 2H), 0.77 (tt, $^{3}J_{HH}$ = 12.4 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.1, 154.8, 151.2, 145.2, 139.7, 130.8, 130.2, 128.1, 127.7, 127.32, 127.26, 126.4, 126.0, 121.8, 113.6, 55.5, 27.9, 27.8, 27.3, 27.1, 27.0, 26.6. HRMS (FAB) calcd for $C_{30}H_{36}NO_2SSi$ ($M+H^+$) 502.2231, found 502.2234.



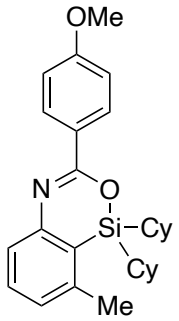
Scheme 2, compound 3q. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 98% yield (73.4 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.37 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.26 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.00 (dd, $^{3}J_{HH}$ = 7.8 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 5.62-5.57 (m, 1H), 3.88 (s, 3H), 2.39-2.31 (m, 2H), 2.24-2.15 (m, 2H), 2.00-1.90 (m, 2H), 1.86-1.51 (m, 12H), 1.51-1.38 (m, 2H), 1.32-1.00 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.9, 154.5, 151.4, 150.2, 141.4, 130.7, 130.1, 127.6, 126.4, 124.6, 119.2, 113.6, 55.5, 30.5, 28.2, 28.0, 27.7, 27.6, 27.5, 26.8, 25.5, 23.2, 22.0. HRMS (FAB) calcd for $C_{32}H_{42}NO_2Si$ ($M+H^+$) 500.2979, found 500.2981.



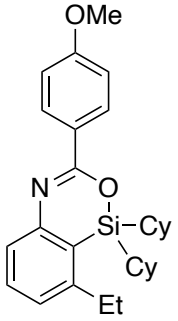
Scheme 2, compound 3r. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 93% yield (72.7 mg).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.57-7.51 (m, 2H), 7.46-7.34 (m, 6H), 6.97 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.88 (s, 3H), 1.97-1.84 (m, 2H), 1.80-1.57 (m, 8H), 1.50-1.10 (m, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.2, 154.9, 151.1, 131.5, 131.2, 130.2, 129.5, 128.7, 128.6, 128.2, 127.5, 127.2, 123.4, 123.3, 113.7, 91.0, 90.8, 55.5, 27.9, 27.2, 26.72, 26.65, 25.6. HRMS (FAB) calcd for $C_{34}H_{38}NO_2Si$ ($M+H^+$) 520.2666, found 520.2670.



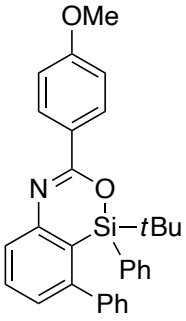
Scheme 2, compound 3s. The reaction was conducted at 100 °C. Hexane/EtOAc = 8/1 was used for silica gel chromatography. White amorphous. 78% yield (50.5 mg).

^{1}H NMR ($CDCl_3$): δ 8.16 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.34 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.22 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.00 (d, $^{3}J_{HH}$ = 7.3 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 3.87 (s, 3H), 2.39 (s, 3H), 1.94-1.85 (m, 2H), 1.79-1.52 (m, 8H), 1.47-1.33 (m, 2H), 1.33-1.10 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 153.8, 151.1, 142.0, 131.2, 130.0, 127.6, 127.0, 125.7, 119.9, 113.6, 55.5, 27.93, 27.88, 27.3, 26.8, 26.7, 26.3, 23.5. HRMS (FAB) calcd for $C_{27}H_{36}NO_2Si$ ($M+H^+$) 434.2510, found 434.2517.

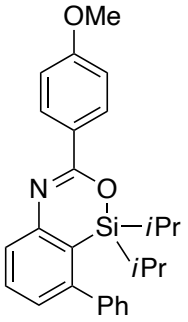


Scheme 2, compound 3t. The reaction was conducted at 100 °C. Hexane/EtOAc = 11/1 was used for silica gel chromatography. White amorphous. 74% yield (49.9 mg).

^{1}H NMR ($CDCl_3$): δ 8.16 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.40 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.23 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.09 (d, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.96 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 3.87 (s, 3H), 2.61 (q, $^{3}J_{HH}$ = 7.5 Hz, 2H), 1.95-1.85 (m, 2H), 1.79-1.53 (m, 8H), 1.46-1.34 (m, 2H), 1.31 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H), 1.34-1.09 (m, 10H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.9, 153.7, 151.0, 148.5, 131.4, 130.0, 127.7, 126.0, 124.9, 119.4, 113.6, 55.5, 30.4, 27.93, 27.89, 27.4, 26.9, 26.7, 15.7. HRMS (FAB) calcd for $C_{28}H_{38}NO_2Si$ ($M+H^+$) 448.2666, found 448.2667.

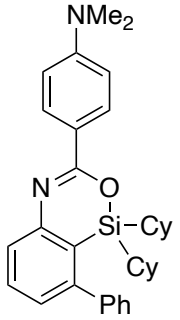


Scheme 2, compound 3b. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 90% yield (62.5 mg).



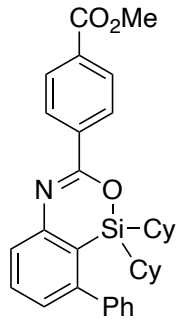
Scheme 2, compound 3u. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 94% yield (58.3 mg).

^{1}H NMR ($CDCl_3$): δ 8.17 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 7.47 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.44-7.32 (m, 6H), 7.11 (dd, $^{3}J_{HH}$ = 7.3 and $^{4}J_{HH}$ = 1.2 Hz, 1H), 6.95 (d, $^{3}J_{HH}$ = 9.0 Hz, 2H), 3.87 (s, 3H), 0.97 (d, $^{3}J_{HH}$ = 7.1 Hz, 6H), 0.95-0.83 (m, 2H), 0.74 (d, J = 7.3 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.1, 154.7, 151.1, 148.1, 144.2, 131.0, 130.1, 129.0, 128.5, 127.9, 127.4, 126.92, 126.87, 120.7, 113.6, 55.5, 17.4, 16.9, 15.3. HRMS (FAB) calcd for $C_{26}H_{30}NO_2Si$ ($M+H^+$) 416.2040, found 416.2037.



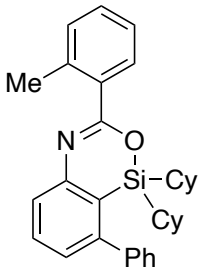
Scheme 3, compound 3w. Hexane/EtOAc = 8/1 was used for silica gel chromatography. White amorphous. 76% yield (58.2 mg).

^{1}H NMR ($CDCl_3$): δ 8.11 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 7.47-7.29 (m, 7H), 7.05 (dd, $^{3}J_{HH}$ = 7.4 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.74 (d, $^{3}J_{HH}$ = 9.2 Hz, 2H), 3.05 (s, 6H), 1.69-1.45 (m, 10H), 1.34-1.21 (m, 2H), 1.15-0.96 (m, 6H), 0.90-0.76 (m, 2H), 0.60 (tt, $^{3}J_{HH}$ = 12.8 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.4, 152.3, 151.5, 147.9, 144.3, 130.7, 129.9, 129.0, 128.4, 127.7, 126.5, 126.1, 122.2, 120.4, 111.3, 40.3, 28.0, 27.9, 27.02, 27.00, 26.96, 26.6. HRMS (FAB) calcd for $C_{33}H_{41}N_2OSi$ ($M+H^+$) 509.2983, found 509.2989.



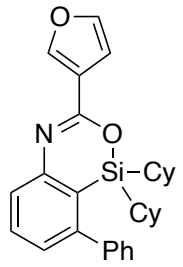
Scheme 3, compound 3x. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 82% yield (64.4 mg).

^{1}H NMR ($CDCl_3$): δ 8.30 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 8.12 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.53-7.40 (m, 5H), 7.35-7.29 (m, 2H), 7.15 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 3.95 (s, 3H), 1.70-1.43 (m, 10H), 1.31-1.19 (m, 2H), 1.14-0.99 (m, 6H), 0.85-0.74 (m, 2H), 0.65 (tt, $^3J_{HH}$ = 12.7 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.9, 153.7, 150.2, 148.1, 143.9, 139.0, 132.1, 131.0, 129.6, 129.0, 128.5, 128.3, 128.0, 127.7, 127.2, 120.8, 52.4, 27.84, 27.82, 27.0, 26.9, 26.6. HRMS (FAB) calcd for $C_{33}H_{38}NO_3Si$ ($M+H^+$) 524.2615, found 524.2625.



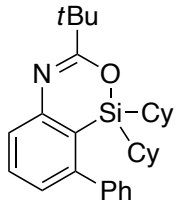
Scheme 3, compound 3y. Hexane/EtOAc = 11/1 was used for silica gel chromatography. White amorphous. 91% yield (65.2 mg).

^{1}H NMR ($CDCl_3$): δ 7.94-7.88 (m, 1H), 7.50-7.37 (m, 5H), 7.36-7.23 (m, 5H), 7.13 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 2.68 (s, 3H), 1.69-1.45 (m, 10H), 1.30-0.98 (m, 8H), 0.94-0.80 (m, 2H), 0.63 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 156.5, 150.7, 148.0, 144.0, 138.2, 135.2, 131.6, 130.9, 129.8, 129.6, 129.1, 128.4, 127.9, 127.3, 127.0, 125.8, 120.2, 27.90, 27.88, 27.0, 26.9, 26.7, 22.3. HRMS (FAB) calcd for $C_{32}H_{38}NOSi$ ($M+H^+$) 480.2717, found 480.2724.



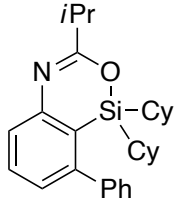
Scheme 3, compound 3z. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 86% yield (59.2 mg).

^{1}H NMR ($CDCl_3$): δ 7.98 (s, 1H), 7.48-7.38 (m, 5H), 7.36-7.28 (m, 3H), 7.10 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 6.92 (d, J_{HH} = 1.8 Hz, 1H), 1.68-1.42 (m, 10H), 1.28-1.15 (m, 2H), 1.14-0.96 (m, 6H), 0.88-0.74 (m, 2H), 0.59 (tt, $^3J_{HH}$ = 12.6 and 2.8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.3, 150.6, 148.0, 145.3, 144.0, 143.6, 130.9, 129.0, 128.4, 127.9, 127.0, 126.6, 124.2, 120.7, 109.9, 27.9, 27.8, 26.93, 26.87, 26.6. HRMS (FAB) calcd for $C_{29}H_{34}NO_2Si$ ($M+H^+$) 456.2353, found 456.2360.



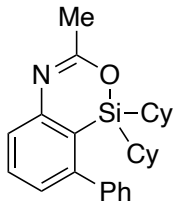
Scheme 2, compound 3aa. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 95% yield (63.5 mg).

^{1}H NMR ($CDCl_3$): δ 7.45-7.36 (m, 4H), 7.32-7.23 (m, 3H), 7.05 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 1.70-1.39 (m, 10H), 1.36-0.97 (m, 8H), 1.31 (s, 9H), 0.87-0.71 (m, 2H), 0.58 (tt, $^3J_{HH}$ = 12.8 and 2.7 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.8, 150.9, 147.8, 144.2, 130.7, 129.1, 128.3, 127.7, 126.9, 126.8, 120.1, 39.0, 28.3, 27.93, 27.91, 27.2, 26.81, 26.79, 26.77. HRMS (FAB) calcd for $C_{29}H_{40}NOSi$ ($M+H^+$) 446.2874, found 446.2876.



Scheme 3, compound 3bb. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 74% yield (47.8 mg).

^{1}H NMR ($CDCl_3$): δ 7.44-7.35 (m, 4H), 7.31-7.21 (m, 3H), 7.05 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 2.70 (sept, $^3J_{HH}$ = 6.8 Hz, 1H), 1.68-1.39 (m, 10H), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.25-0.97 (m, 8H), 0.85-0.70 (m, 2H), 0.58 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.7, 150.7, 147.9, 144.1, 130.8, 129.1, 128.4, 127.8, 126.9, 126.4, 120.2, 36.6, 27.90, 27.88, 27.1, 26.8, 26.7, 20.3. HRMS (FAB) calcd for $C_{28}H_{38}NOSi$ ($M+H^+$) 432.2717, found 432.2719.

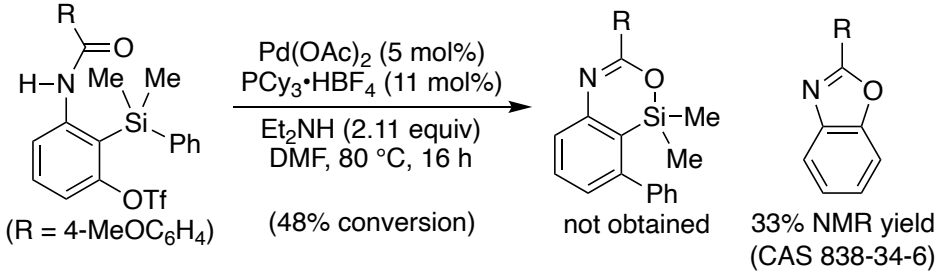


Scheme 3, compound 3cc. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White

amorphous. 62% yield (37.7 mg).

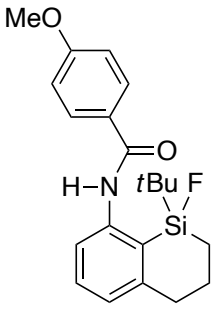
^{1}H NMR ($CDCl_3$): δ 7.45-7.36 (m, 4H), 7.31-7.26 (m, 2H), 7.22 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.08 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 2.22 (s, 3H), 1.69-1.38 (m, 10H), 1.24-0.96 (m, 8H), 0.83-0.68 (m, 2H), 0.62-0.50 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.9, 150.5, 147.9, 144.1, 130.9, 129.0, 128.4, 127.8, 126.9, 125.9, 120.1, 27.89, 27.86, 26.9, 26.8, 26.72, 26.70, 24.1. HRMS (FAB) calcd for $C_{26}H_{34}NOSi$ ($M+H^+$) 404.2404, found 404.2401.

Reaction of 2-(Dimethyl(phenyl)silyl)-3-(4-methoxybenzamido)phenyl trifluoromethanesulfonate to Give 2-(4-Methoxyphenyl)benzo[*d*]oxazole.



^{1}H NMR ($CDCl_3$): δ 8.20 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.77-7.72 (m, 1H), 7.58-7.53 (m, 1H), 7.37-7.28 (m, 2H), 7.04 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 163.3, 162.5, 150.8, 142.4, 129.5, 124.7, 124.6, 119.9, 119.8, 114.5, 110.5, 55.6.

Procedure for Equation 1.

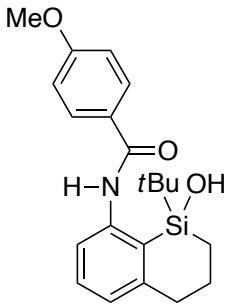


Et_2NH (33.0 µL, 0.320 mmol) and DMF (0.6 mL) were added to a mixture of compound **1v** (75.2 mg, 0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 µmol), and PCy_3•HBF_4 (6.1 mg, 17 µmol), and the resulting solution was stirred for 16 h at 100 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1→6/1 and the resulting solid was washed with hexane to afford compound **4v** as a white solid (23.2 mg, 62.4 µmol; 42% yield). The structure was confirmed by X-ray crystallographic analysis after recrystallization from CH2Cl2/hexane.

^{1}H NMR ($CDCl_3$): δ 8.68-8.57 (m, 1H), 8.16-8.08 (m, 1H), 7.91 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.39 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.03-6.94 (m, 3H), 3.88 (s, 3H), 2.86-2.76 (m, 1H), 2.57-2.46 (m, 1H), 2.21-2.09 (m, 1H), 1.68-1.52 (m, 1H), 1.20-1.09 (m, 2H), 0.90 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 164.6, 162.6,

151.2 (d, $^{3}J_{CF}$ = 3.8 Hz), 144.2 (d, $^{3}J_{CF}$ = 2.9 Hz), 131.4, 129.0, 126.9, 125.2 (d, $^{4}J_{CF}$ = 1.9 Hz), 120.8, 119.9 (d, $^{2}J_{CF}$ = 13.4 Hz), 114.1, 55.6, 35.8, 25.5, 21.8 (d, $^{3}J_{CF}$ = 1.9 Hz), 19.6 (d, $^{2}J_{CF}$ = 14.4 Hz), 9.6 (d, $^{2}J_{CF}$ = 10.5 Hz). ^{19}F NMR ($CDCl_3$): δ –165.9 (s). HRMS (FAB) calcd for $C_{21}H_{27}FNO_2Si$ ($M+H^+$) 372.1790, found 372.1793.

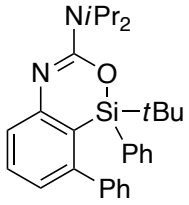
To elucidate the origin of the fluoride on silicon, the reaction of **1v** was also conducted by using free PCy_3 without HBF_4 as the ligand, which gave compound **S3** as the major product in 32% yield with no formation of compound **4v**. This result indicates that the fluoride of compound **4v** comes from BF_4^- of the phosphine ligand salt, although the exact reaction mechanism is unclear at this stage.



S3

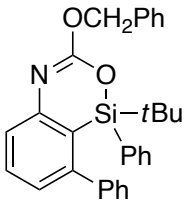
General Procedure for Equations 2 and 3.

1,2,2,6,6-Pentamethylpiperidine (57.0 μL, 0.320 mmol) and DMF (0.6 mL) were added to a mixture of compound **1** (0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 μmol), and PCy_3•HBF_4 (6.1 mg, 17 μmol), and the resulting solution was stirred for 16 h 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 Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc (containing 2 vol% of Et_3N) to afford compound **3** or **5**.



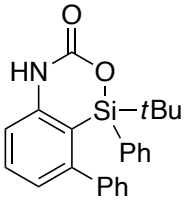
Equation 2, compound 3dd. Hexane/EtOAc = 10/1 was used for silica gel chromatography. Yellow amorphous. 81% yield (55.5 mg).

^{1}H NMR ($CDCl_3$): δ 7.54-7.46 (m, 2H), 7.43-7.37 (m, 1H), 7.37-7.28 (m, 3H), 7.18 (tt, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 7.11-7.02 (m, 3H), 6.99 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H), 6.77 (dd, $^{3}J_{HH}$ = 7.3 Hz and $^{4}J_{HH}$ = 1.4 Hz, 1H), 4.42-3.96 (m, 2H), 1.27 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H), 1.18 (d, $^{3}J_{HH}$ = 6.9 Hz, 6H), 0.79 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.8, 151.4, 148.5, 144.6, 136.5, 135.0, 131.2, 130.04, 129.97, 128.0, 127.9, 127.1, 124.4, 123.3, 115.9, 46.0, 27.1, 21.5, 21.4, 20.6. HRMS (FAB) calcd for $C_{29}H_{37}N_2OSi$ ($M+H^+$) 457.2670, found 457.2673.



Equation 2, compound 3ee. Hexane/EtOAc = 10/1 was used for silica gel chromatography. Yellow viscous oil. 80% yield (55.3 mg).

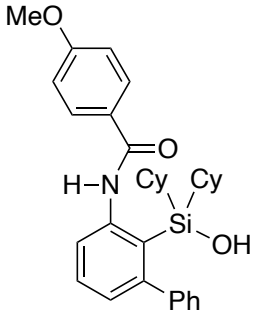
^{1}H NMR ($CDCl_3$): δ 7.49-7.27 (m, 12H), 7.23 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.10 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.01-6.94 (m, 3H), 5.41 (d, $^2J_{HH}$ = 12.4 Hz, 1H), 5.37 (d, $^2J_{HH}$ = 12.4 Hz, 1H), 0.78 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.4, 151.8, 148.8, 143.8, 136.6, 135.4, 135.14, 135.05, 131.4, 130.4, 130.1, 128.5, 128.4, 128.1, 128.0, 127.5, 126.5, 125.5, 117.9, 69.9, 26.6, 20.9. HRMS (FAB) calcd for $C_{30}H_{29}NO_2Si$ (M^+) 463.1968, found 463.1987.



Equation 3, compound 5ff. Hexane/EtOAc = 4/1 → 1/1 was used for silica gel chromatography. White solid. 67% yield (37.8 mg).

^{1}H NMR ($CDCl_3$): δ 8.46 (s, 1H), 7.49-7.36 (m, 4H), 7.33 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 7.28-7.20 (m, 1H), 7.10 (t, $^3J_{HH}$ = 7.6 Hz, 2H), 6.99-6.86 (m, 4H), 0.84 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.1, 149.5, 145.2, 143.0, 135.1, 134.1, 131.8, 130.7, 130.0, 128.2, 128.1, 127.8, 125.6, 115.7, 113.3, 26.6, 20.8. HRMS (FAB) calcd for $C_{23}H_{23}NO_2Si$ (M^+) 373.1498, found 373.1512.

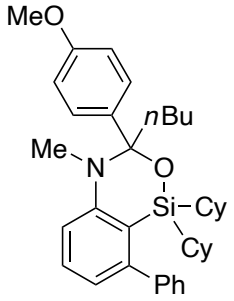
Procedure for Scheme 4a.



H_2O (2 mL) was added to compound **3c** (74.4 mg, 0.150 mmol) and the mixture was stirred for 40 h at 110 °C. After cooled to room temperature, this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 3/1 → 2/1 to afford compound **6** as a white solid (69.5 mg, 0.135 mmol; 90% yield).

^{1}H NMR ($CDCl_3$): δ 10.84 (s, 1H), 8.36 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 8.00 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.45-7.35 (m, 4H), 7.29-7.21 (m, 2H), 7.01-6.91 (m, 3H), 3.88 (s, 3H), 2.31 (bs, 1H), 1.68-1.48 (m, 10H), 1.18-0.91 (m, 10H), 0.17 (t, $^3J_{HH}$ = 12.4 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 165.5, 162.2, 149.3, 145.8, 144.5, 129.6, 129.4, 129.3, 128.10, 128.07, 127.6, 126.1, 123.6, 121.8, 113.8, 55.5, 28.0, 27.9, 27.8, 27.6, 27.0, 26.8. HRMS (FAB) calcd for $C_{32}H_{40}NO_3Si$ ($M+H^+$) 514.2772, found 514.2770.

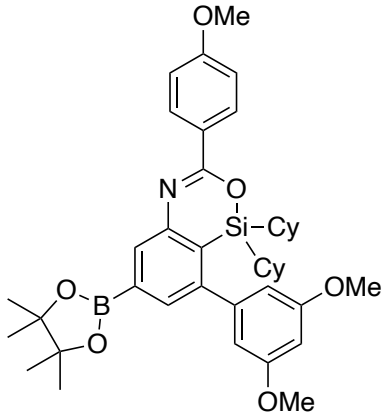
Procedure for Scheme 4b.



Methyl trifluoromethanesulfonate (18.0 μL, 0.165 mmol) was added dropwise to a solution of compound **3c** (74.4 mg, 0.150 mmol) in toluene (1 mL) at room temperature, and the mixture was stirred for 14 h at 90 °C. This was cooled to –78 °C, and *n*BuLi (105 μL, 0.165 mmol; 1.57 M solution in hexane) was added dropwise to it. The resulting mixture was stirred for 1 h at 0 °C and for 5.5 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 Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **7** as a colorless oil (53.2 mg, 93.7 μmol; 62% yield).

^{1}H NMR ($CDCl_3$): δ 7.43-7.34 (m, 5H), 7.33-7.26 (m, 3H), 6.88-6.81 (m, 4H), 3.81 (s, 3H), 2.70 (s, 3H), 2.12 (ddd, $^3J_{HH}$ = 13.3, 12.4, and 4.1 Hz, 1H), 1.82 (ddd, $^3J_{HH}$ = 13.3, 12.4, and 4.1 Hz, 1H), 1.76-1.44 (m, 8H), 1.44-0.86 (m, 16H), 0.80 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.58 (tt, $^3J_{HH}$ = 12.6 and 2.5 Hz, 1H), 0.26 (tt, $^3J_{HH}$ = 12.4 and 2.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.5, 157.0, 147.9, 144.6, 136.0, 129.8, 129.2, 128.4, 128.0, 127.9, 127.3, 123.2, 119.8, 112.9, 91.6, 55.3, 40.6, 38.3, 28.51, 28.49, 28.4, 28.1, 27.9, 27.8, 27.5, 27.1, 27.03, 27.00, 23.0, 14.3. HRMS (FAB) calcd for $C_{37}H_{50}NO_2Si$ ($M+H^+$) 568.3605, found 568.3608.

Procedure for Scheme 4c.[4]



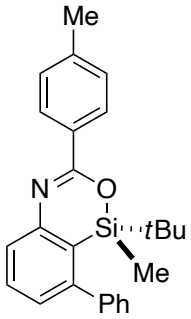
A solution of [Ir(OMe)(cod)]$_2$ (6.2 mg, 19 μmol Ir), 4,4'-di-*tert*-butyl-2,2'-bipyridyl (4.2 mg, 16 μmol), and bis(pinacolato)diboron (70.8 mg, 0.279 mmol) in THF (0.6 mL) was stirred for 10 min at room temperature. Compound **3l** (104 mg, 0.186 mmol) and THF (1.3 mL) were added to it, and this was stirred for 12 h at 70 °C. The reaction mixture was filtered through a pad of silica gel with EtOAc and concentrated under vacuum. The residue was purified by GPC with $CHCl_3$ to afford compound **8** as a pale orange amorphous (111 mg, 0.162 mmol; 87% yield).

^{1}H NMR ($CDCl_3$): δ 8.19 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.85 (d, $^4J_{HH}$ = 0.9 Hz, 1H), 7.53 (d, $^4J_{HH}$ = 0.9 Hz, 1H), 6.96 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 6.53-6.47 (m, 3H), 3.87 (s, 3H), 3.83 (s, 6H), 1.76-1.47 (m, 10H), 1.44-1.18 (m, 2H), 1.35 (s, 12H), 1.18-0.97 (m, 6H), 0.95-0.81 (m, 2H), 0.74 (tt, $^3J_{HH}$ = 12.6 and 2.7 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0, 160.7, 154.4, 150.4, 147.2, 146.0, 133.2, 131.9, 130.1, 127.5, 123.6, 113.6, 107.2, 100.3, 84.0, 55.6, 55.5, 27.9, 27.03, 26.96, 26.8, 26.6, 25.0. HRMS (FAB) calcd for $C_{40}H_{53}BNO_6Si$ ($M+H^+$) 682.3730, found 682.3754.

Procedure for Scheme 5a.

Et_2NH (31.0 μL, 0.300 mmol) and DMF (0.6 mL) were added to a mixture of compound **1b** (46.0 mg, 75.0 μmol), compound **1d** (50.7 mg, 75.0 μmol), $Pd(OAc)_2$ (1.7 mg, 7.5 μmol), and PCy_3•HBF_4 (6.1 mg, 17 μmol), and the mixture was stirred for 16 h 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 Na_2SO_4, filtered, and concentrated under vacuum. The yield of compounds **3b** and **3d** were determined to be 97% yield for both by ^{1}H NMR against an internal standard ($MeNO_2$), and no crossover products were obtained.

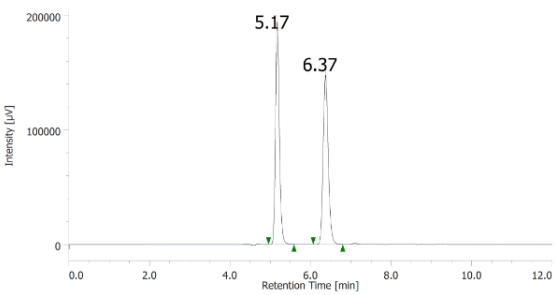
Procedure for Scheme 5b.



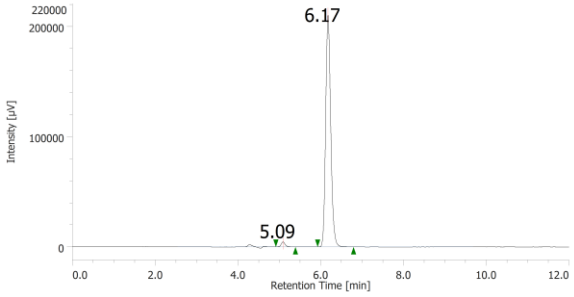
Et_2NH (33.0 µL, 0.320 mmol) and DMF (0.6 mL) were added to a mixture of compound (*R*)-**1gg** (80.3 mg, 0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 µmol), and PCy_3•HBF_4 (6.1 mg, 17 µmol), and the resulting solution was stirred for 22 h at 70 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 10/1 (containing 2 vol% of Et_3N) to afford compound **3gg** as a white amorphous (51.6 mg, 0.134 mmol; 89% yield). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 0.7 mL/min. Retention times: 5.1 min [minor enantiomer], 6.2 min [major enantiomer]. 97% ee. $[\alpha]^{24}_D$ +38.0 (*c* 0.62, $CHCl_3$). The absolute configuration was determined to be *R* by X-ray crystallographic analysis after treatment with TfOH and recrystallization from $CHCl_3$/pentane.

^1H NMR ($CDCl_3$): δ 8.10 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.48 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.44 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.41-7.32 (m, 5H), 7.24 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.10 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 2.41 (s, 3H), 0.62 (s, 9H), 0.40 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.6, 150.9, 148.5, 144.0, 141.3, 132.1, 131.0, 130.1, 129.1, 128.4, 128.0, 127.84, 127.75, 127.4, 121.0, 25.8, 21.7, 20.7, –0.5. HRMS (FAB) calcd for $C_{25}H_{28}NOSi$ ($M+H^+$) 386.1935, found 386.1938.

racemate



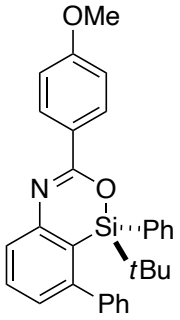
96.5% ee (*R*)



General Procedure for Scheme 7.

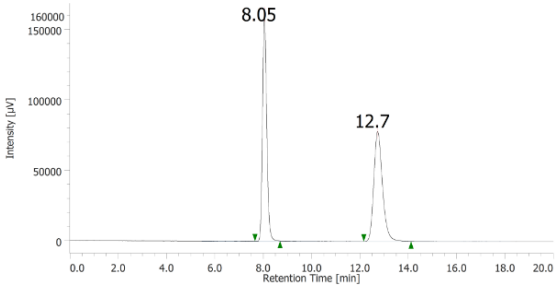
Et_2NH (31.0 µL, 0.300 mmol) and DMA (0.6 mL) were added to a mixture of compound **1** (0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 7.5 µmol), and **L*** (5.0 mg, 8.3 µmol), and the resulting solution was stirred for 40 h at 40 °C. The reaction was quenched with H_2O and this was extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc (containing 2 vol% of Et_3N) to

afford compound **3**.

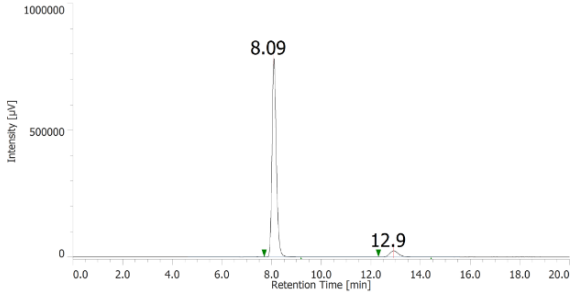


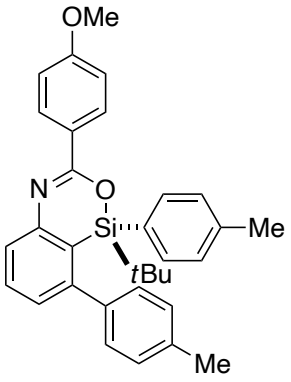
Scheme 7, compound 3b. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 87% yield (60.6 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/1, flow = 0.7 mL/min. Retention times: 8.1 min [major enantiomer], 12.9 min [minor enantiomer]. 88% ee. $[\alpha]^{17}_{D}$ −70.2 (*c* 0.53, $CHCl_3$). The absolute configuration was determined to be *R* by X-ray crystallographic analysis after recrystallization from CH_2Cl_2/hexane.

racemate



87.6% ee (*R*)



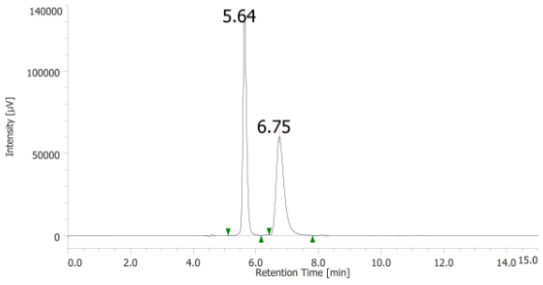


Scheme 7, compound 3hh. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 89% yield (65.6 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 0.7 mL/min. Retention times: 5.6 min [major enantiomer], 6.7 min [minor enantiomer]. 85% ee. $[\alpha]^{22}_{D}$ −19.4 (*c* 0.54, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

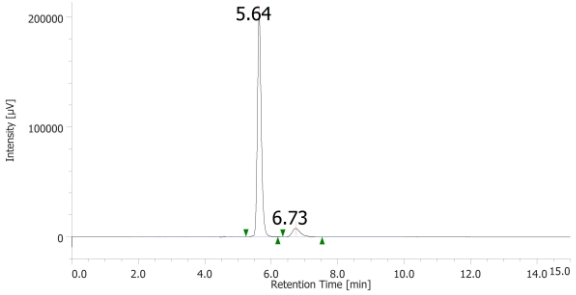
^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^3J_{HH}$ = 9.2 Hz, 2H), 7.54-7.47 (m, 2H), 7.41 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.16 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 7.12-7.05 (m, 1H), 7.01-6.90 (m, 6H), 3.86 (s, 3H), 2.39 (s, 3H), 2.36 (s,

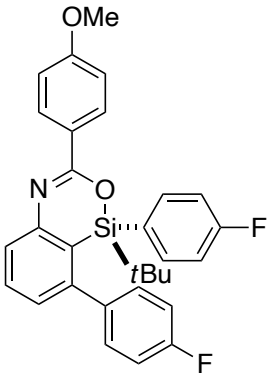
3H), 0.83 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 162.1, 154.2, 151.3, 148.7, 141.0, 140.2, 137.2, 135.2, 132.7, 131.2, 130.2, 130.0, 128.7, 127.9, 127.4, 127.2, 120.2, 113.6, 55.5, 26.7, 21.7, 21.3, 21.0. HRMS (FAB) calcd for $C_{32}H_{34}NO_2Si$ ($M+H^+$) 492.2353, found 492.2358.

racemate



85.2% ee

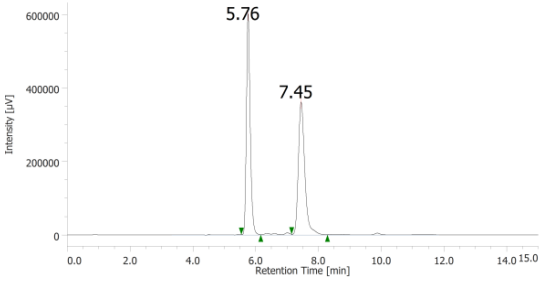




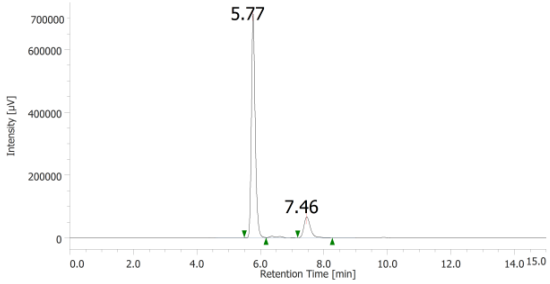
Scheme 7, compound 3ii. Hexane/EtOAc = 9/1 was used for silica gel chromatography. White amorphous. 89% yield (66.8 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 95/5, flow = 0.7 mL/min. Retention times: 5.8 min [major enantiomer], 7.5 min [minor enantiomer]. 73% ee. $[\alpha]^{19}_{D}$ −78.9 (*c* 0.50, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

^{1}H NMR ($CDCl_3$): δ 8.15 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.53-7.48 (m, 2H), 7.44 (dd, $^{3}J_{HH}$ = 8.7 Hz and $^{4}J_{HF}$ = 6.0 Hz, 2H), 7.07-6.99 (m, 3H), 6.97-6.88 (m, 4H), 6.81 (t, $^{3}J_{HH}$ = 8.9 Hz, 2H), 3.86 (s, 3H), 0.85 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 164.4 (d, $^{1}J_{CF}$ = 251 Hz), 162.5 (d, $^{1}J_{CF}$ = 247 Hz), 162.3, 154.2, 151.3, 147.5, 139.6 (d, $^{4}J_{CF}$ = 2.9 Hz), 137.3 (d, $^{3}J_{CF}$ = 8.6 Hz), 131.8 (d, $^{3}J_{CF}$ = 8.6 Hz), 131.4, 131.3 (d, $^{4}J_{CF}$ = 3.8 Hz), 130.2, 128.1, 127.7, 127.1, 119.7, 115.4 (d, $^{2}J_{CF}$ = 19.2 Hz), 114.8 (d, $^{2}J_{CF}$ = 21.1 Hz), 113.8, 55.5, 26.6, 21.2. HRMS (FAB) calcd for $C_{30}H_{28}F_2NO_2Si$ ($M+H^+$) 500.1852, found 500.1868.

racemate

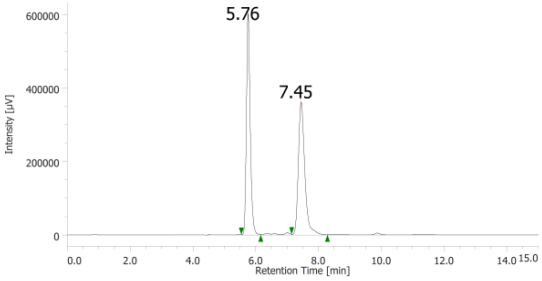


72.9% ee

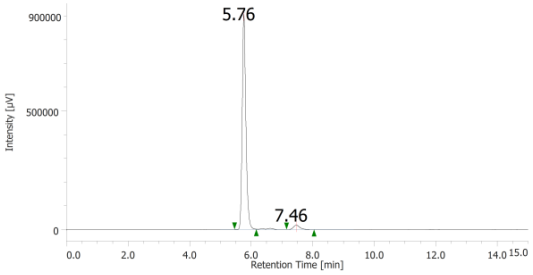


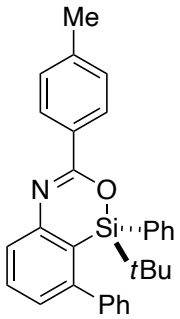
The ee of compound **3ii** could be improved by recrystallisation. Compound **3ii** (40.0 mg, 80.1 μmol; 73% ee) was dissolved in hexane (6.0 mL) at 60 °C, and the solution was slowly cooled to –35 °C to give colorless crystals (28.9 mg, 57.7 μmol; 72% yield, 93% ee).

racemate



93.3% ee

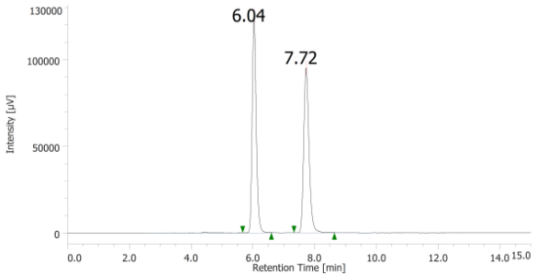




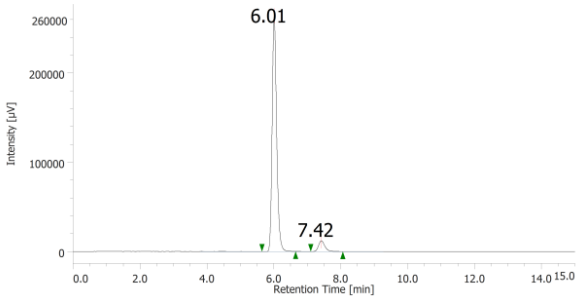
Scheme 7, compound 3jj. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 88% yield (59.4 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/1, flow = 0.7 mL/min. Retention times: 6.0 min [major enantiomer], 7.4 min [minor enantiomer]. 88% ee. $[\alpha]^{23}_{D}$ −66.2 (*c* 0.52, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

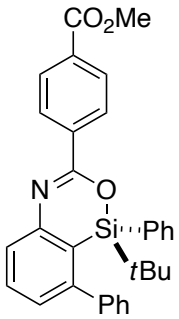
^{1}H NMR ($CDCl_3$): δ 8.11 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.55-7.46 (m, 4H), 7.41 (tt, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 2.1 Hz, 1H), 7.32 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.28-7.20 (m, 3H), 7.17-7.06 (m, 3H), 7.00 (d, $^3J_{HH}$ = 6.8 Hz, 2H), 2.41 (s, 3H), 0.82 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.4, 151.1, 148.7, 143.6, 141.4, 136.0, 135.2, 132.0, 131.3, 130.3, 130.2, 129.1, 128.5, 128.2, 128.1, 128.0, 127.6, 127.5, 120.0, 26.6, 21.7, 21.2. HRMS (FAB) calcd for $C_{30}H_{30}NOSi$ ($M+H^+$) 448.2091, found 448.2098.

racemate



88.1% ee

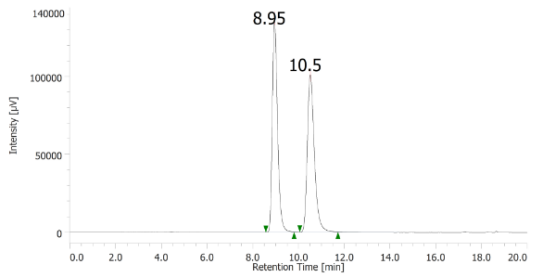




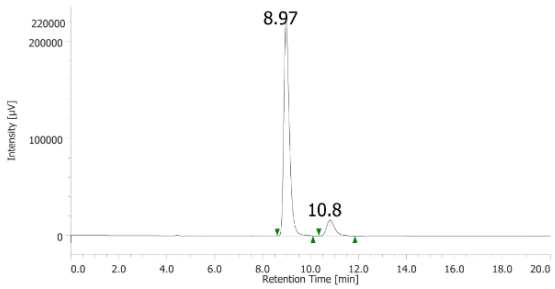
Scheme 7, compound 3kk. Hexane/EtOAc = 8/1 was used for silica gel chromatography. White amorphous. 92% yield (67.5 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/1, flow = 0.7 mL/min. Retention times: 9.0 min [major enantiomer], 10.8 min [minor enantiomer]. 80% ee. $[\alpha]^{19}_{D}$ −48.1 (*c* 0.54, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

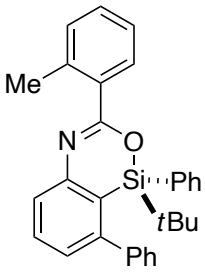
^{1}H NMR ($CDCl_3$): δ 8.27 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 8.08 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.57-7.51 (m, 2H), 7.50-7.45 (m, 2H), 7.43 (tt, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 2.3 Hz, 1H), 7.33 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.28-7.22 (m, 1H), 7.21-7.08 (m, 3H), 6.99 (d, $^3J_{HH}$ = 7.3 Hz, 2H), 3.94 (s, 3H), 0.81 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 166.9, 153.2, 150.6, 148.9, 143.4, 138.9, 135.8, 135.2, 132.1, 131.4, 130.4, 130.2, 129.6, 128.9, 128.3, 128.2, 128.1, 128.0, 127.7, 120.2, 52.4, 26.6, 21.1. HRMS (FAB) calcd for $C_{31}H_{30}NO_3Si$ ($M+H^+$) 492.1989, found 492.1987.

racemate



79.9% ee

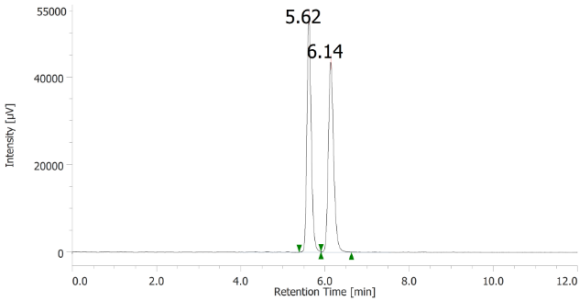




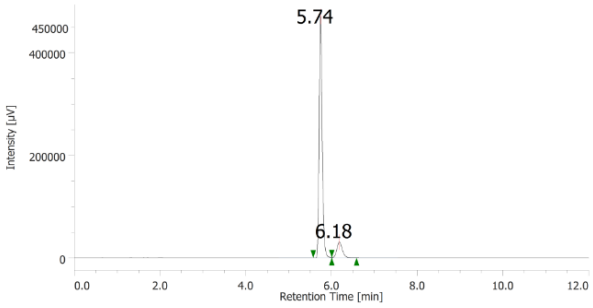
Scheme 7, compound 3ll. The reaction was conducted for 16 h at 60 °C. Hexane/EtOAc = 10/1 was used for silica gel chromatography. White amorphous. 93% yield (62.4 mg). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 100/1, flow = 0.7 mL/min. Retention times: 5.7 min [major enantiomer], 6.2 min [minor enantiomer]. 79% ee. $[\alpha]^{23}_{D}$ +10.0 (*c* 0.55, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3b**.

^{1}H NMR ($CDCl_3$): δ 7.85 (d, $^{3}J_{HH}$ = 6.8 Hz, 1H), 7.56-7.48 (m, 4H), 7.43 (t, $^{3}J_{HH}$ = 6.8 Hz, 1H), 7.34 (t, $^{3}J_{HH}$ = 7.4 Hz, 2H), 7.31-7.18 (m, 4H), 7.15-7.08 (m, 3H), 7.01 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H), 2.61 (s, 3H), 0.80 (s, 9H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 155.9, 151.1, 148.7, 143.7, 138.4, 136.2, 135.1, 134.7, 131.6, 131.3, 130.3, 130.1, 130.0, 129.9, 128.4, 128.2, 128.1, 127.63, 127.59, 125.8, 119.7, 26.7, 22.3, 20.9. HRMS (FAB) calcd for $C_{30}H_{30}NOSi$ ($M+H^+$) 448.2091, found 448.2093.

racemate

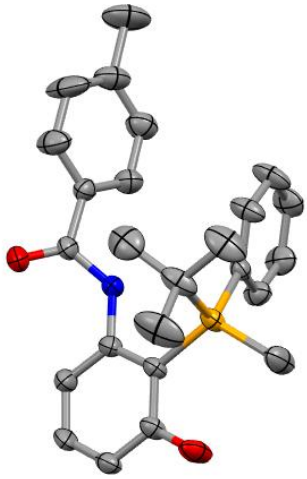


78.8% ee



IV. X-ray Crystal Structure

Compound (*R*)-S2



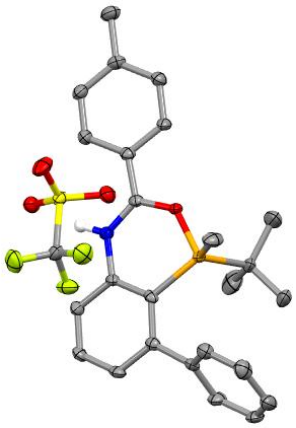
A colorless ethyl acetate solution of compound (*R*)-**S2** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature under hexane atmosphere. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2194996). 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	$C_{27.5}H_{32}NO_2Si$	
Formula Weight	439.65	
Temperature	293 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Orthorhombic	
Space Group	$P2_12_12$	
Unit Cell Dimensions	a = 14.2116(14) Å	α = 90°
	b = 19.3311(19) Å	β = 90°
	c = 9.9202(9) Å	γ = 90°
Volume	2725.3(5) $Å^3$	

Z Value	4
Calculated Density	1.072 g/cm^3
Absorption coefficient	0.108 mm^{-1}
F(000)	948
Crystal size	0.500 x 0.500 x 0.300 mm
Theta Range for Data Collection	3.054–27.546°
Index Ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 25$, $-12 \leq l \leq 11$
Reflections Collected	15527
Independent Reflections	6127 [R(int) = 0.0204]
Completeness to Theta = 25.242°	99.4%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.948 and 0.968
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6127 / 0 / 279
Goodness-of-Fit on F^2	1.025
Final R Indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.1488
R Indices (All Data)	R1 = 0.0722, wR2 = 0.1614
Absolute Structure Parameter	0.07(3)
Largest Diff. Peak and Hole	0.437 and –0.175 e$^-$/Å^3

Compound (*R*)-3gg•HOTf



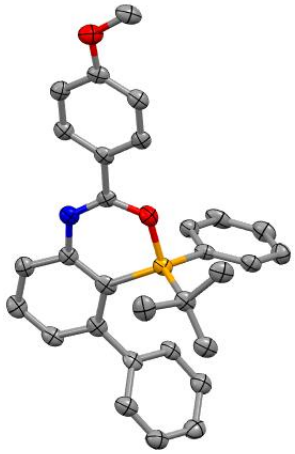
TfOH (6.9 μL, 77.8 μmol) was added to a solution of compound (*R*)-**3gg** (15.0 mg, 38.9 μmol) in 1,2-dichloroethane (0.5 mL) at room temperature. The mixture was concentrated under vacuum and the resulting solid was washed with Et_2O. A colorless $CHCl_3$ solution of this compound was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature under pentane atmosphere. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2194997). 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	$C_{26}H_{28}F_3NO_4SSi$	
Formula Weight	535.64	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Monoclinic	
Space Group	$P2_1$	
Unit Cell Dimensions	a = 9.145(2) Å	α = 90°
	b = 19.109(5) Å	β = 98.006(6)°
	c = 15.052(4) Å	γ = 90°
Volume	2604.7(11) $Å^3$	

Z Value	4
Calculated Density	1.366 g/cm^3
Absorption coefficient	0.225 mm^{-1}
F(000)	1120
Crystal size	0.500 x 0.100 x 0.100 mm
Theta Range for Data Collection	3.099–27.567°
Index Ranges	$-11 \leq h \leq 11$, $-24 \leq k \leq 24$, $-19 \leq l \leq 19$
Reflections Collected	49778
Independent Reflections	11925 [R(int) = 0.0758]
Completeness to Theta = 25.242°	99.7%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.896 and 0.978
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	11925 / 1 / 659
Goodness-of-Fit on F^2	0.989
Final R Indices [I>2sigma(I)]	R1 = 0.0493, wR2 = 0.1167
R Indices (All Data)	R1 = 0.0645, wR2 = 0.1225
Absolute Structure Parameter	–0.02(4)
Largest Diff. Peak and Hole	1.055 and –0.435 e$^-$/Å^3

Compound (*R*)-3b



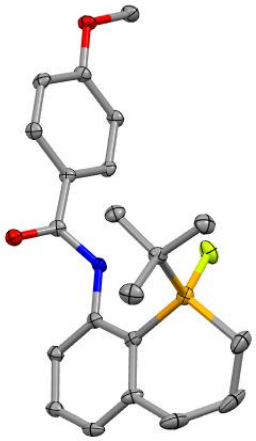
A colorless dichloromethane solution of compound (*R*)-**3b** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature under hexane atmosphere. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2194998). 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	$C_{30}H_{29}NO_2Si$	
Formula Weight	463.63	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Monoclinic	
Space Group	$P2_1$	
Unit Cell Dimensions	a = 9.521(3) Å	α = 90°
	b = 12.367(3) Å	β = 112.719(6)°
	c = 11.509(3) Å	γ = 90°
Volume	1250.0(6) $Å^3$	

Z Value	2
Calculated Density	1.232 g/cm^3
Absorption coefficient	0.121 mm^{-1}
F(000)	492
Crystal size	0.200 x 0.200 x 0.100 mm
Theta Range for Data Collection	3.536–27.480°
Index Ranges	$-12 \leq h \leq 11$, $-16 \leq k \leq 15$, $-14 \leq l \leq 14$
Reflections Collected	22935
Independent Reflections	5645 [R(int) = 0.1207]
Completeness to Theta = 25.242°	99.7%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.976 and 0.988
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	5645 / 1 / 311
Goodness-of-Fit on F^2	0.908
Final R Indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1253
R Indices (All Data)	R1 = 0.0820, wR2 = 0.1305
Absolute Structure Parameter	0.02(12)
Largest Diff. Peak and Hole	0.665 and –0.395 e$^-$/Å^3

Compound 4v



A colorless CH_2Cl_2 solution of compound **4v** was prepared. Crystals suitable for X-ray analysis were obtained by layering hexane and slow diffusion of the solvents at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2247904). The data can be obtained free of charge via the Internet at https://www.ccdc.cam.ac.uk/structures/.

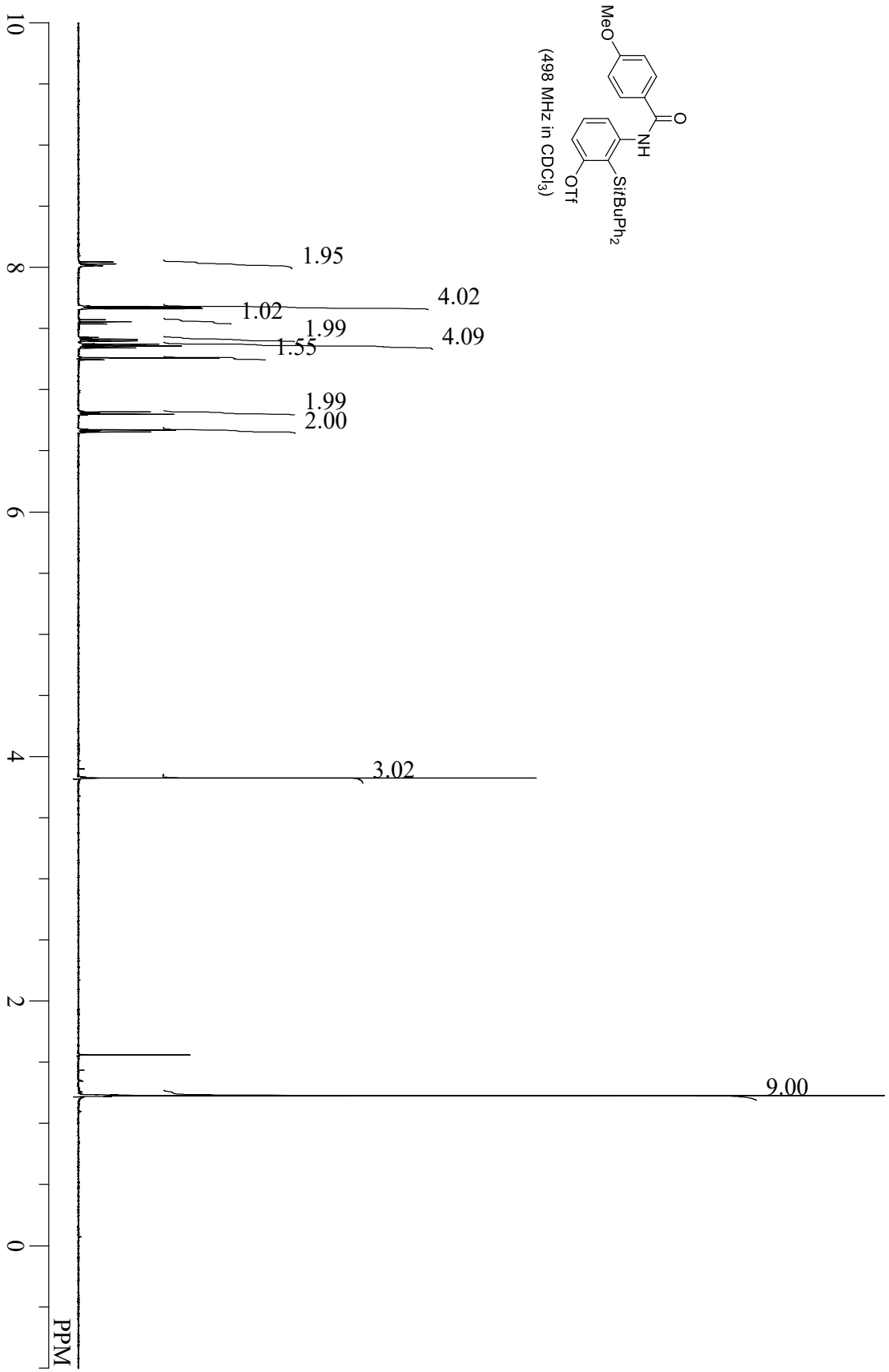
Crystal Data and Structure Refinement.

Empirical Formula	$C_{21}H_{26}FNO_2Si$	
Formula Weight	371.52	
Temperature	113 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Triclinic	
Space Group	P–1	
Unit Cell Dimensions	a = 9.572(3) Å	α = 108.6130(10)°
	b = 12.507(5) Å	β = 90.260(7)°
	c = 17.419(6) Å	γ = 92.4160(10)°
Volume	1974.2(12) $Å^3$	

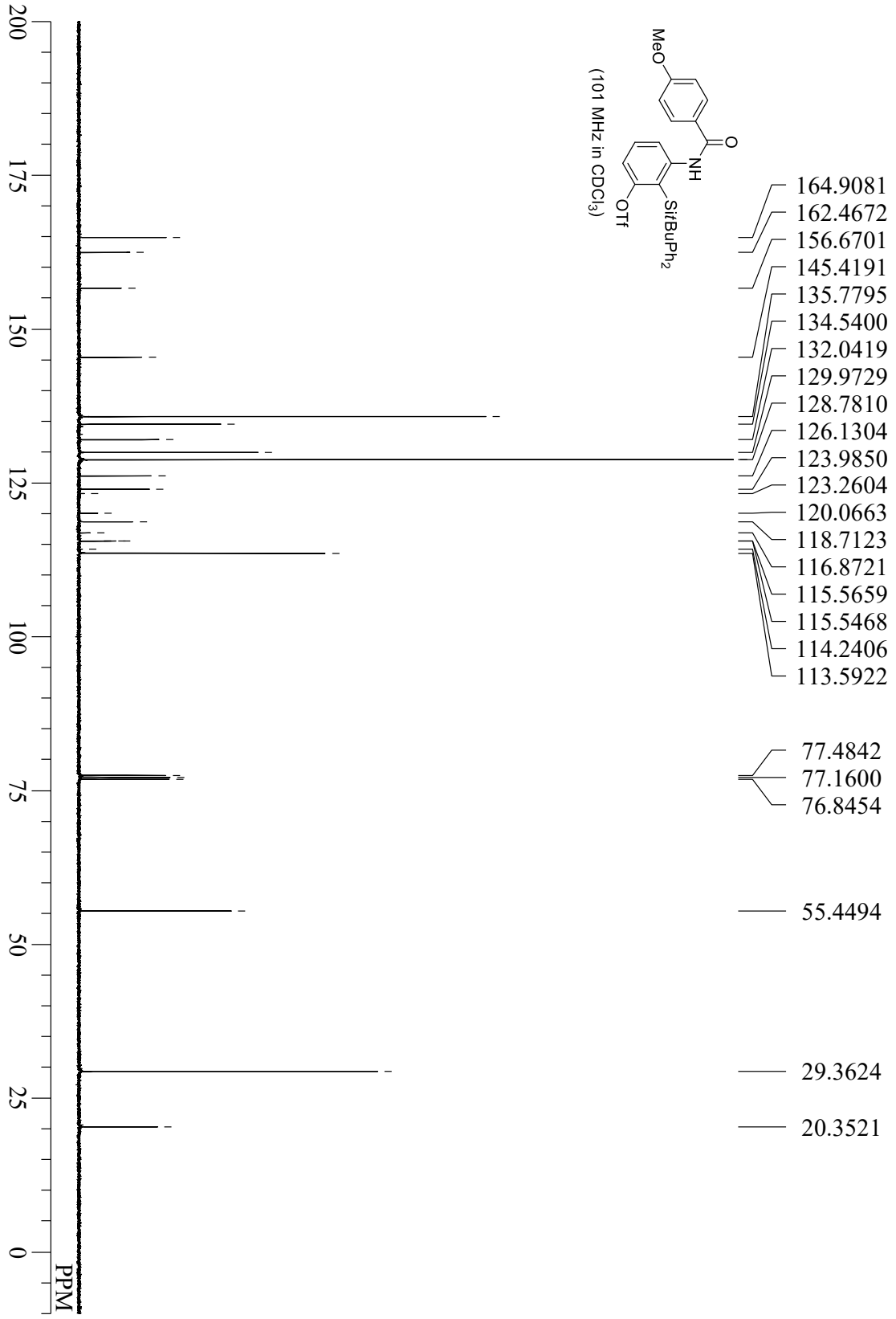
Z Value	4
Calculated Density	1.250 g/cm^3
Absorption coefficient	0.143 mm^{-1}
F(000)	792
Crystal size	0.200 x 0.200 x 0.050 mm
Theta Range for Data Collection	3.153–27.344°
Index Ranges	$-11 \leq h \leq 12$, $-16 \leq k \leq 15$, $-22 \leq l \leq 22$
Reflections Collected	35709
Independent Reflections	8865 [R(int) = 0.1274]
Completeness to Theta = 25.242°	99.8%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.993 and 0.972
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	8865 / 0 / 485
Goodness-of-Fit on F^2	1.045
Final R Indices [I>2sigma(I)]	R1 = 0.0828, wR2 = 0.2023
R Indices (All Data)	R1 = 0.1466, wR2 = 0.2222
Largest Diff. Peak and Hole	0.901 and –0.466 e$^-$/Å^3

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

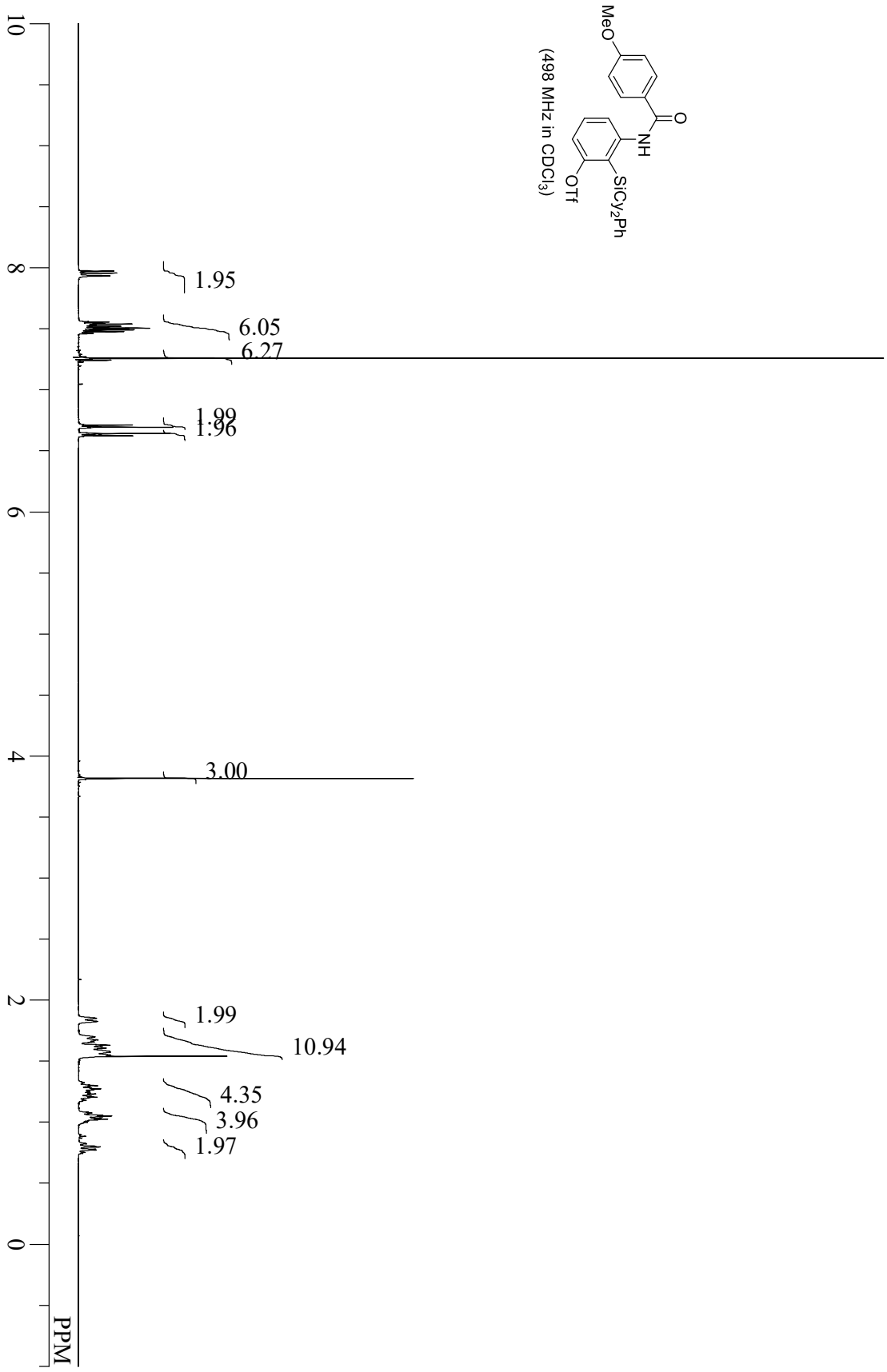
compound **1b**



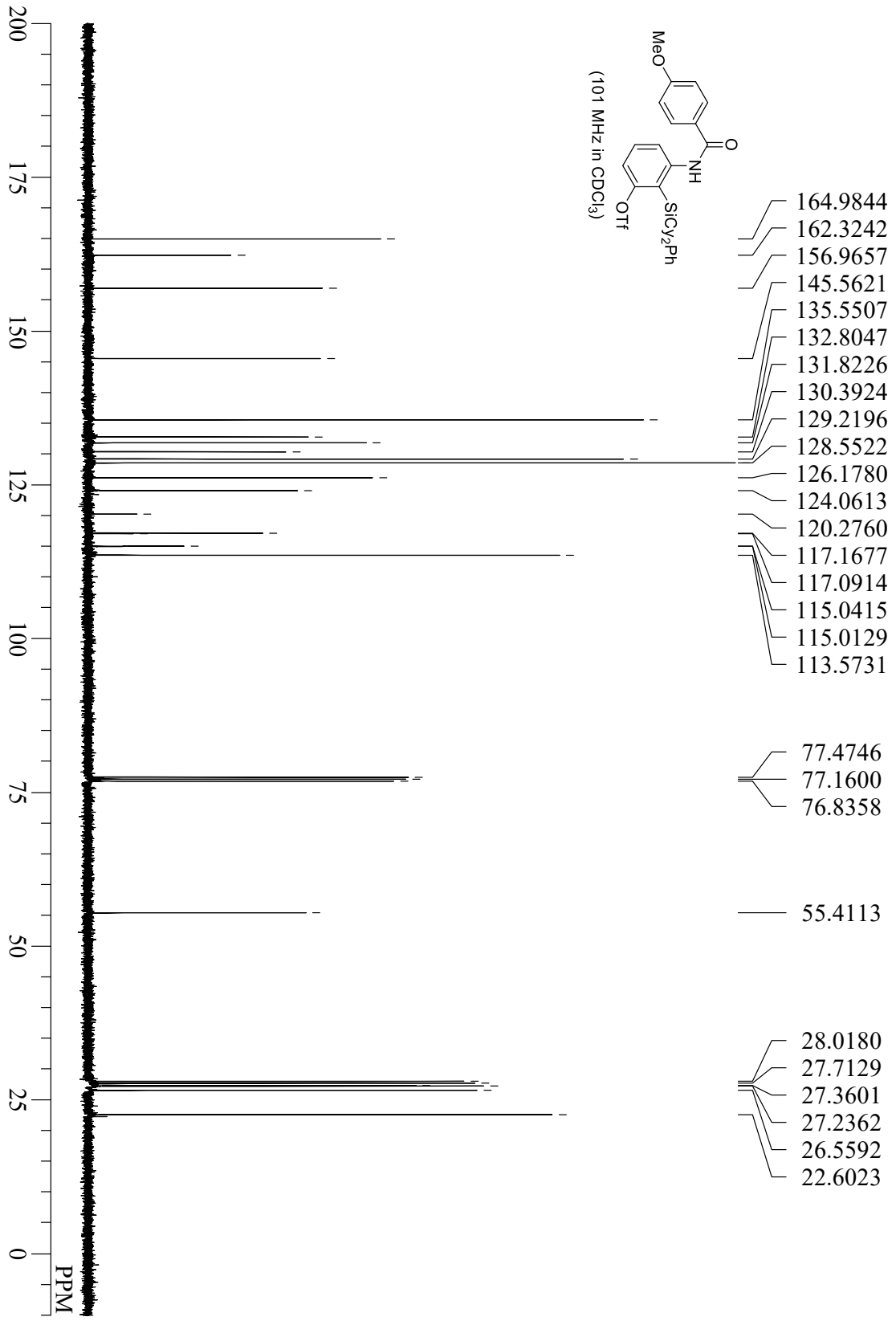
compound **1b**


(101 MHz in CDCl3)
MeO
NH
OTf
SitBuPh2
164.9081
162.4672
156.6701
145.4191
135.7795
134.5400
132.0419
129.9729
128.7810
126.1304
123.9850
123.2604
120.0663
118.7123
116.8721
115.5659
115.5468
114.2406
113.5922
77.4842
77.1600
76.8454
55.4494
29.3624
20.3521
200
175
150
125
100
75
50
25
0
PPM

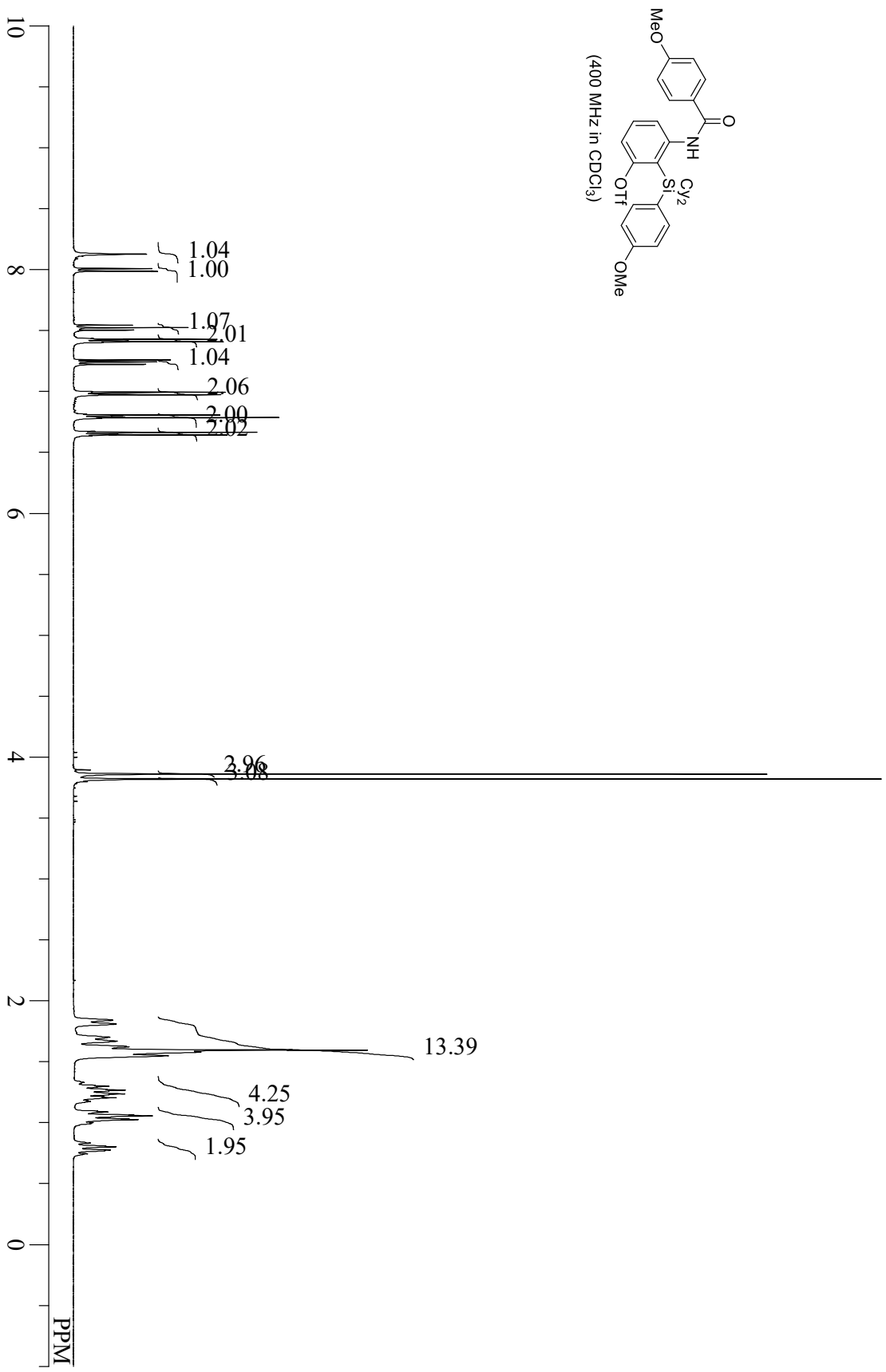
compound **1c**


MeO
O
NH
OTf
SiCy2Ph
(498 MHz in CDCl3)
1.95
6.05
6.27
1.99
1.96
3.00
1.99
10.94
4.35
3.96
1.97
10
8
6
4
2
0
PPM

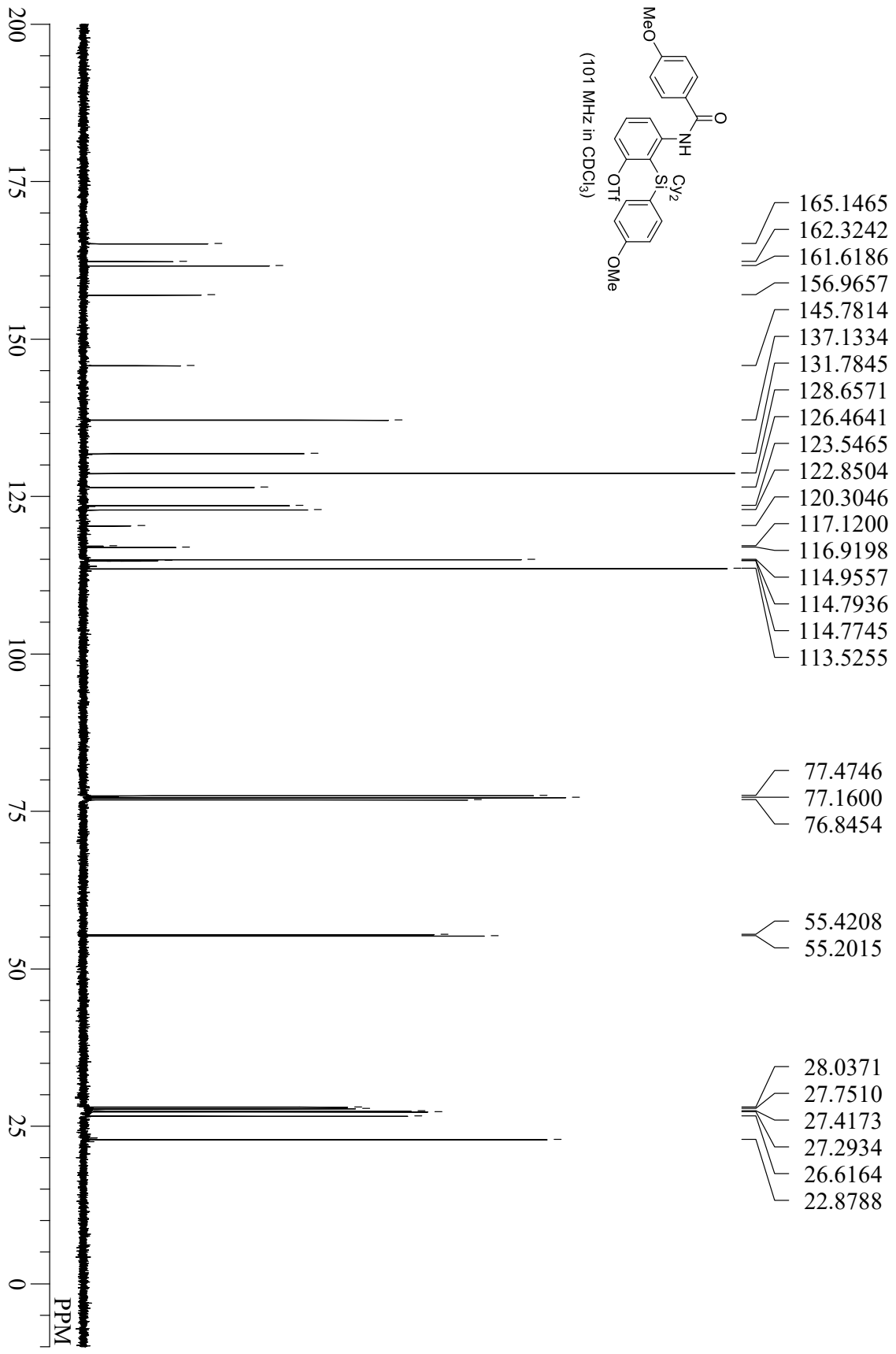
compound **1c**


MeO
O
NH
OTf
SiCy2Ph
(101 MHz in CDCl3)
164.9844
162.3242
156.9657
145.5621
135.5507
132.8047
131.8226
130.3924
129.2196
128.5522
126.1780
124.0613
120.2760
117.1677
117.0914
115.0415
115.0129
113.5731
77.4746
77.1600
76.8358
55.4113
28.0180
27.7129
27.3601
27.2362
26.5592
22.6023
200
175
150
125
100
75
50
25
0
PPM

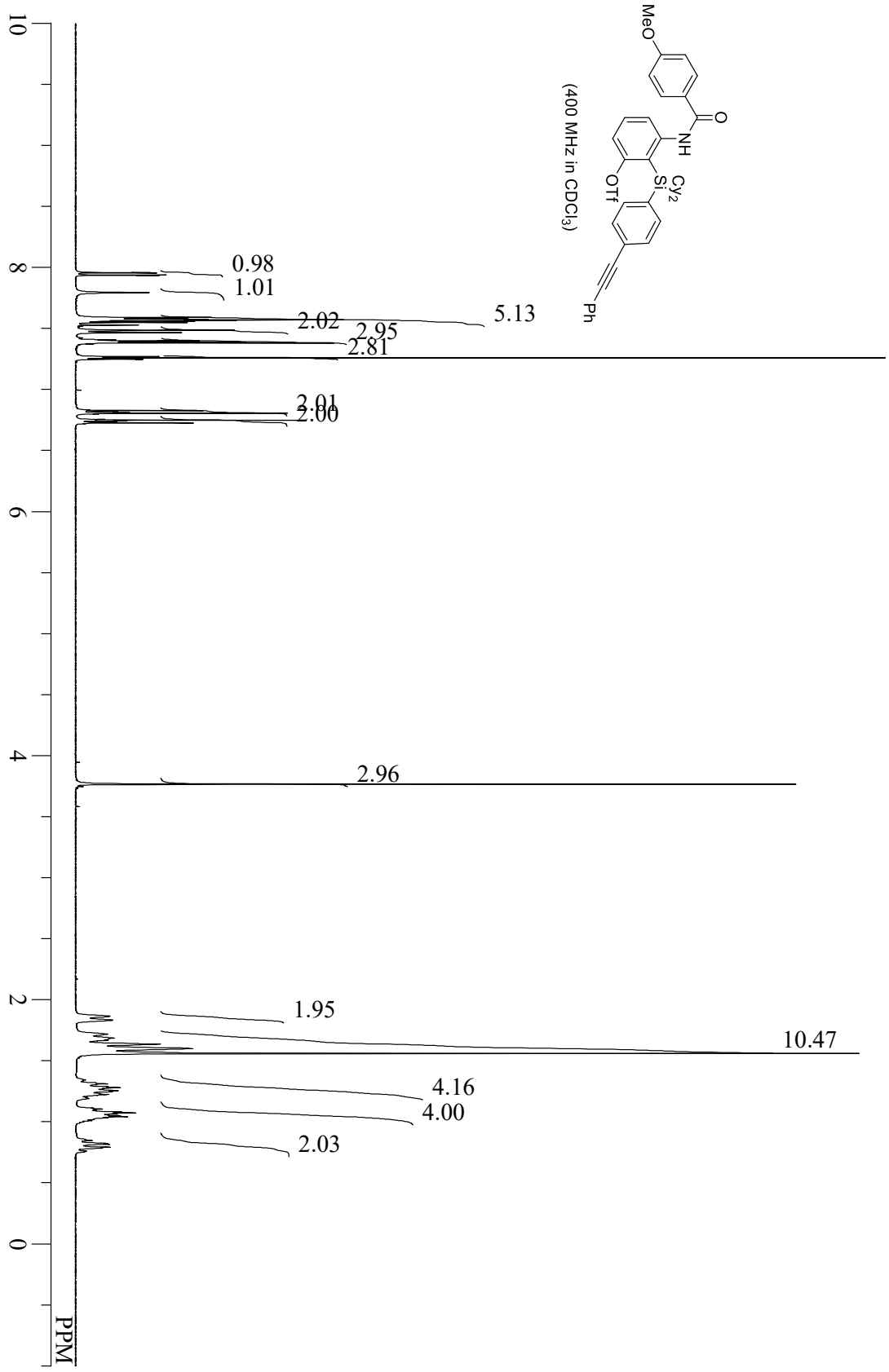
compound **1d**


MeO
O
NH
OTf
Si
Cy2
OMe
(400 MHz in CDCl3)
1.04
1.00
1.07
2.01
1.04
2.06
2.00
2.02
3.96
3.08
13.39
4.25
3.95
1.95
10
8
6
4
2
0
PPM

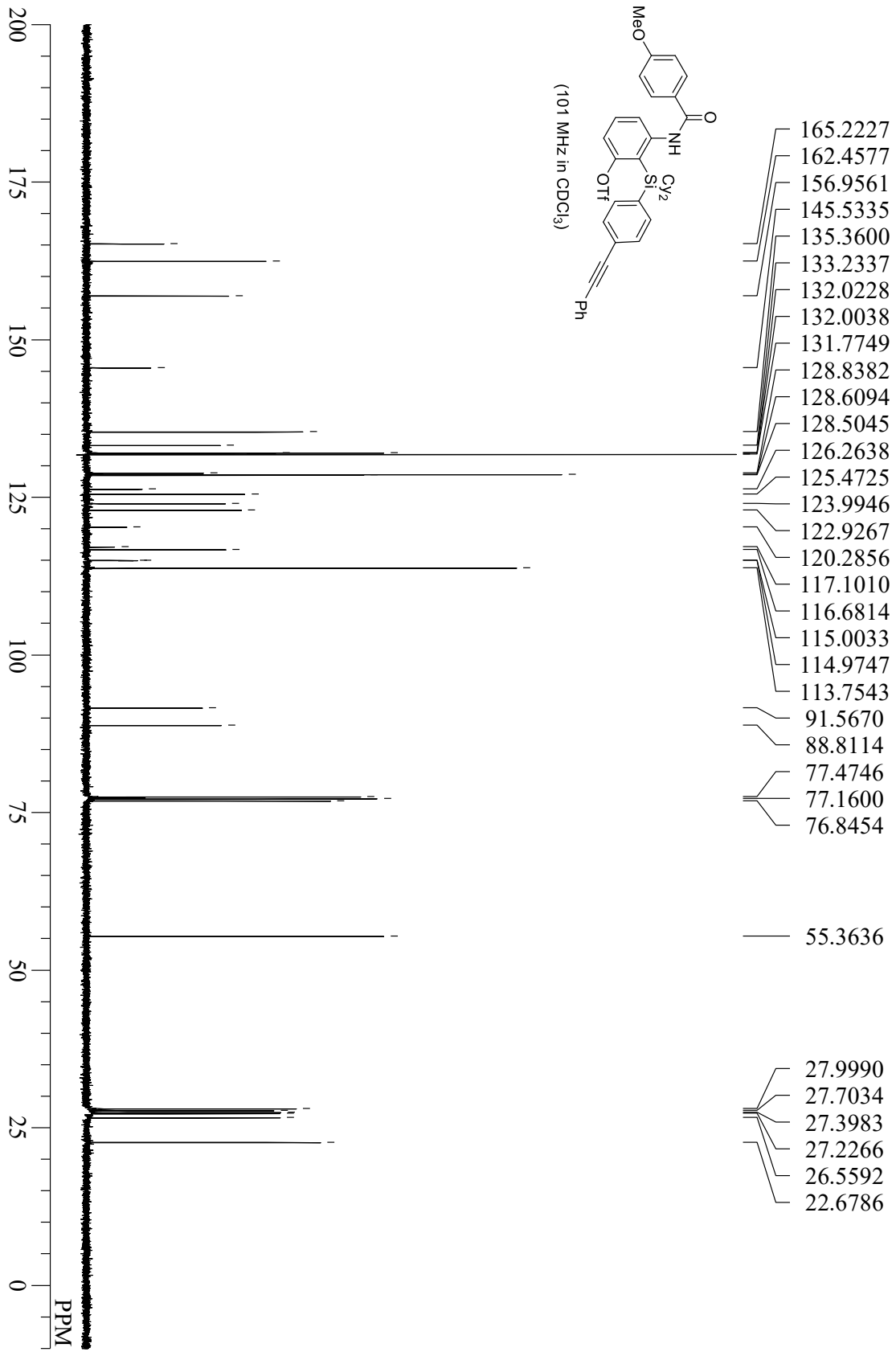
compound **1d**


(101 MHz in CDCl3)
MeO
O
NH
Cy2
Si
OTf
OMe
165.1465
162.3242
161.6186
156.9657
145.7814
137.1334
131.7845
128.6571
126.4641
123.5465
122.8504
120.3046
117.1200
116.9198
114.9557
114.7936
114.7745
113.5255
77.4746
77.1600
76.8454
55.4208
55.2015
28.0371
27.7510
27.4173
27.2934
26.6164
22.8788
200
175
150
125
100
75
50
25
0
PPM

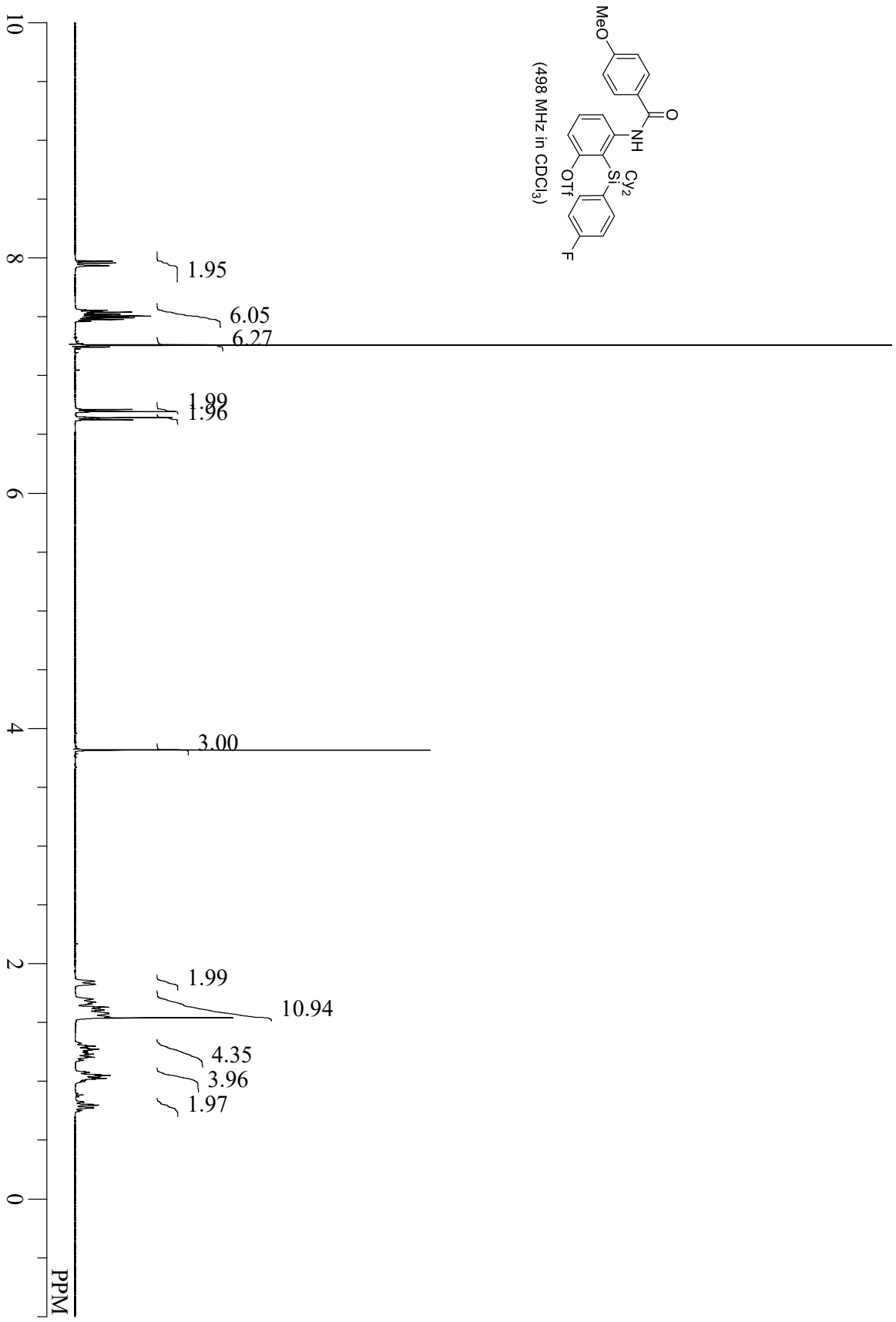
compound **1e**


MeO
O
NH
OTf
Si
Cy2
Ph
(400 MHz in CDCl3)
0.98
1.01
2.02
5.13
2.95
2.81
2.01
2.00
2.96
1.95
10.47
4.16
4.00
2.03
10
8
6
4
2
0
PPM

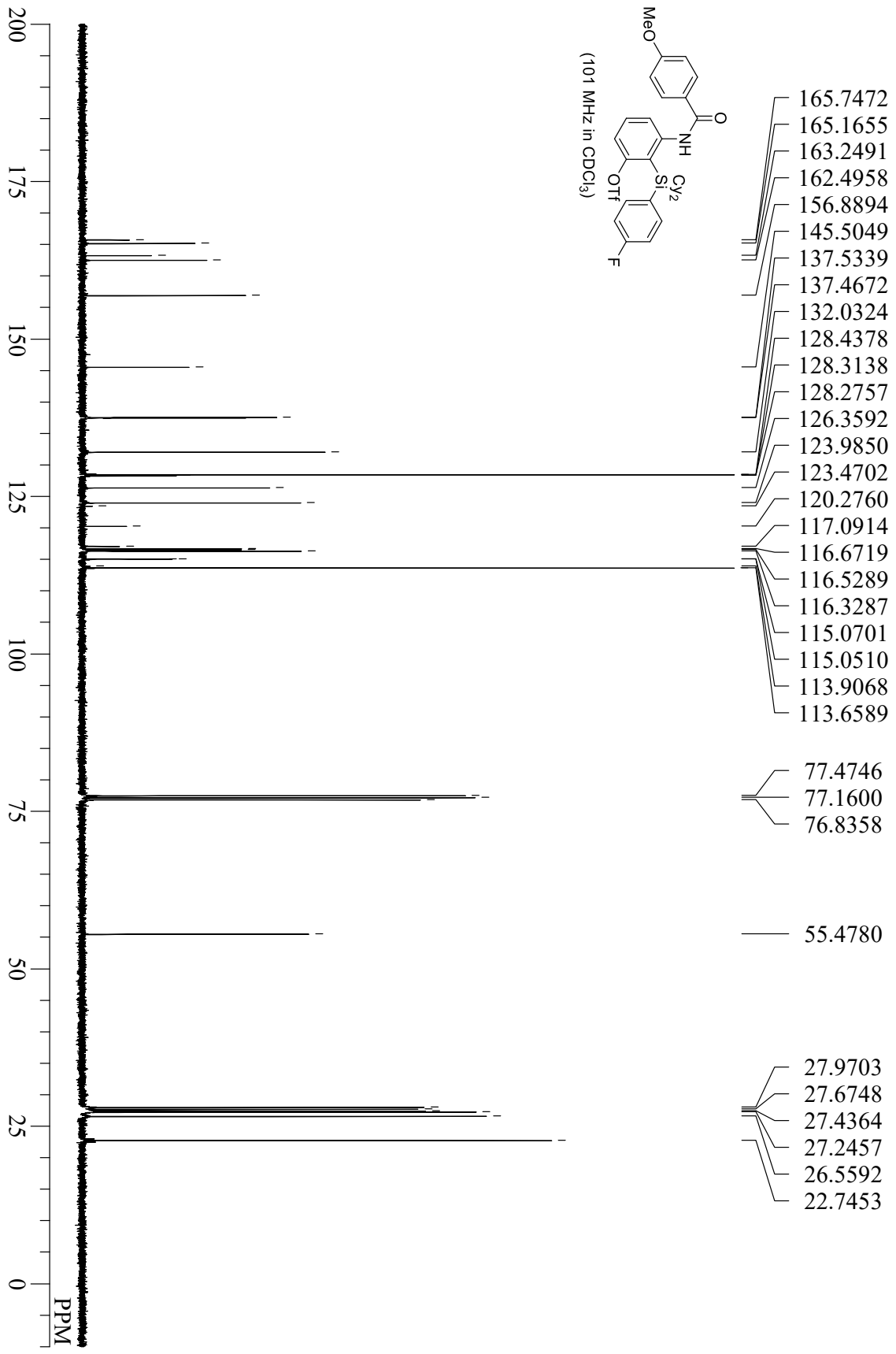
compound **1e**


MeO
O
NH
OTf
Si
Cy2
Ph
(101 MHz in CDCl3)
165.2227
162.4577
156.9561
145.5335
135.3600
133.2337
132.0228
132.0038
131.7749
128.8382
128.6094
128.5045
126.2638
125.4725
123.9946
122.9267
120.2856
117.1010
116.6814
115.0033
114.9747
113.7543
91.5670
88.8114
77.4746
77.1600
76.8454
55.3636
27.9990
27.7034
27.3983
27.2266
26.5592
22.6786
200
175
150
125
100
75
50
25
0
PPM

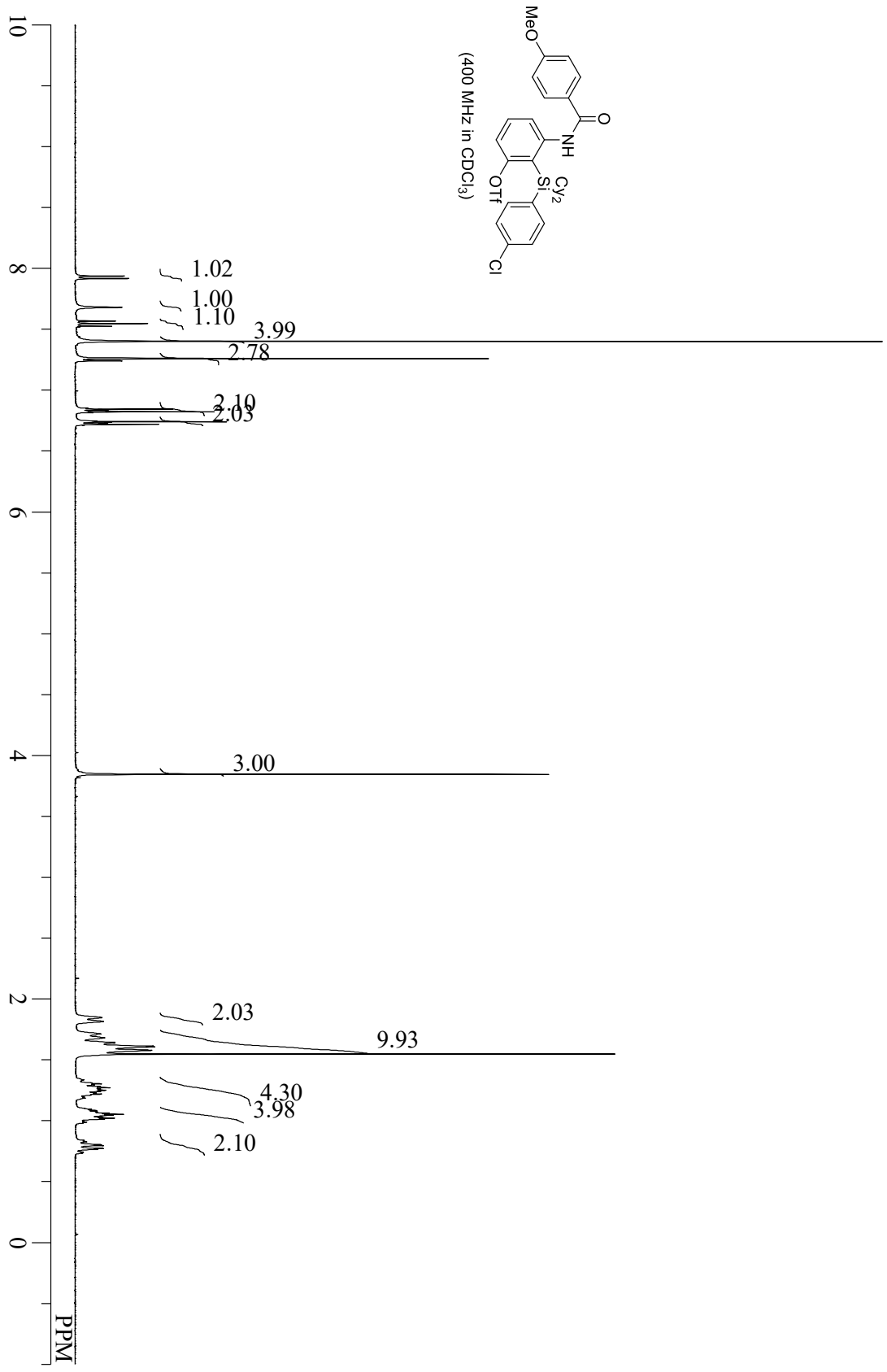
compound **1f**


MeO
O
NH
OTf
Si
Cy2
F
(498 MHz in CDCl3)
1.95
6.05
6.27
1.99
1.96
3.00
1.99
10.94
4.35
3.96
1.97
10
8
6
4
2
0
PPM

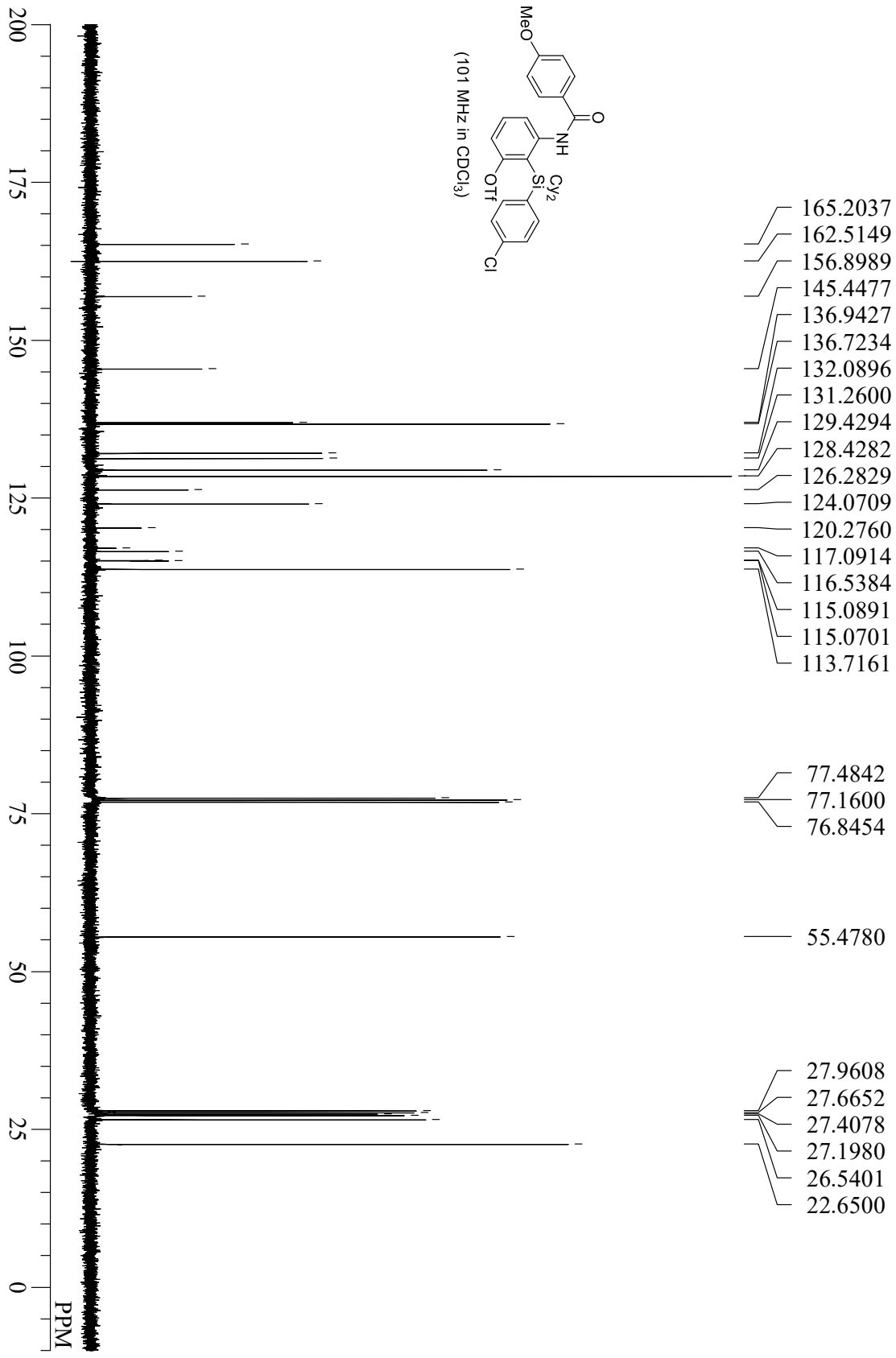
compound **1f**


MeO
O
NH
OTf
Si
Cy2
F
(101 MHz in CDCl3)
165.7472
165.1655
163.2491
162.4958
156.8894
145.5049
137.5339
137.4672
132.0324
128.4378
128.3138
128.2757
126.3592
123.9850
123.4702
120.2760
117.0914
116.6719
116.5289
116.3287
115.0701
115.0510
113.9068
113.6589
77.4746
77.1600
76.8358
55.4780
27.9703
27.6748
27.4364
27.2457
26.5592
22.7453
200
175
150
125
100
75
50
25
0
PPM

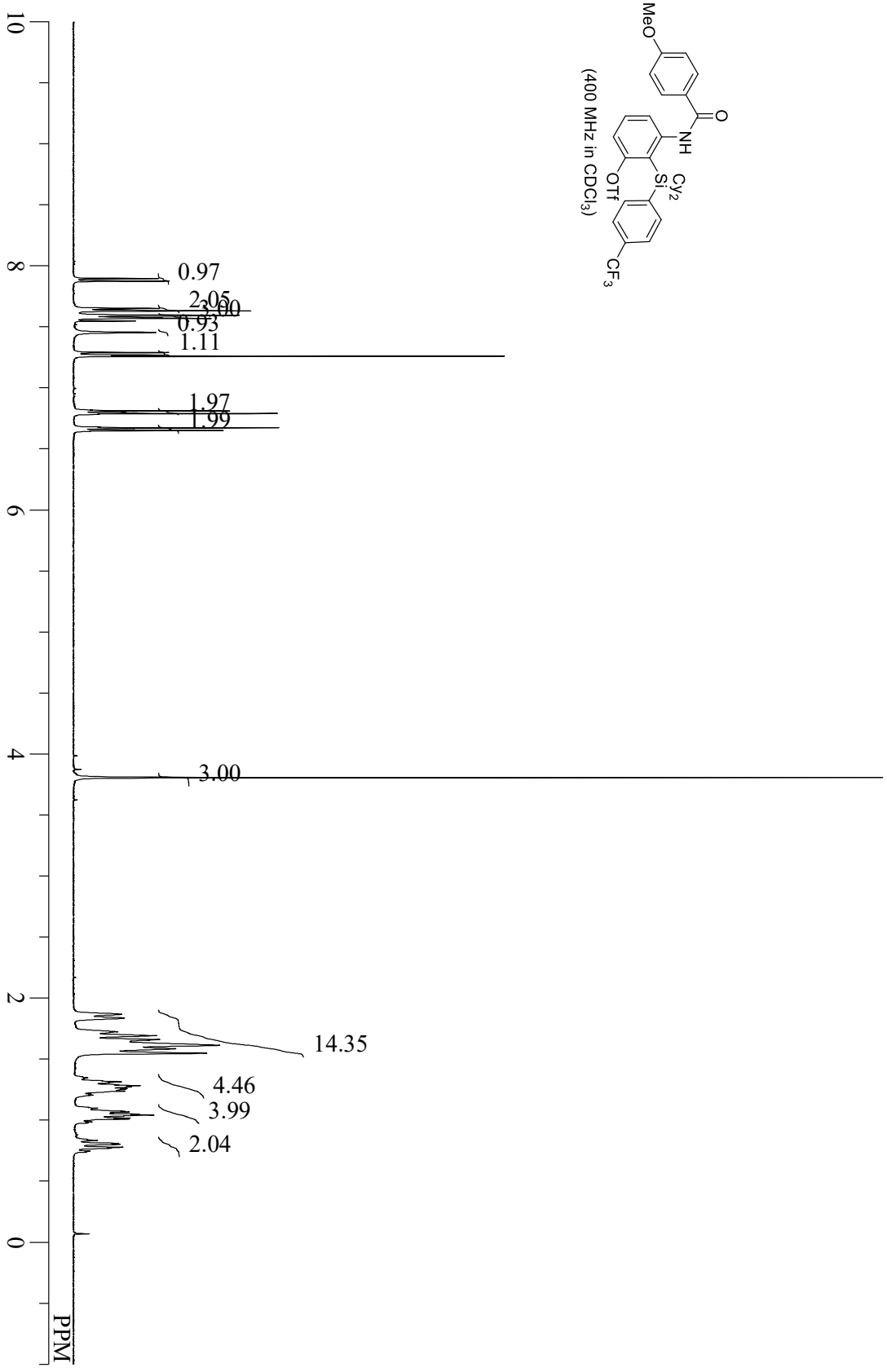
compound **1g**


(400 MHz in CDCl3)
MeO
O
NH
OTf
Si
Cy2
Cl
1.02
1.00
1.10
3.99
2.78
2.10
2.03
3.00
2.03
9.93
4.30
3.98
2.10
10
8
6
4
2
0
PPM

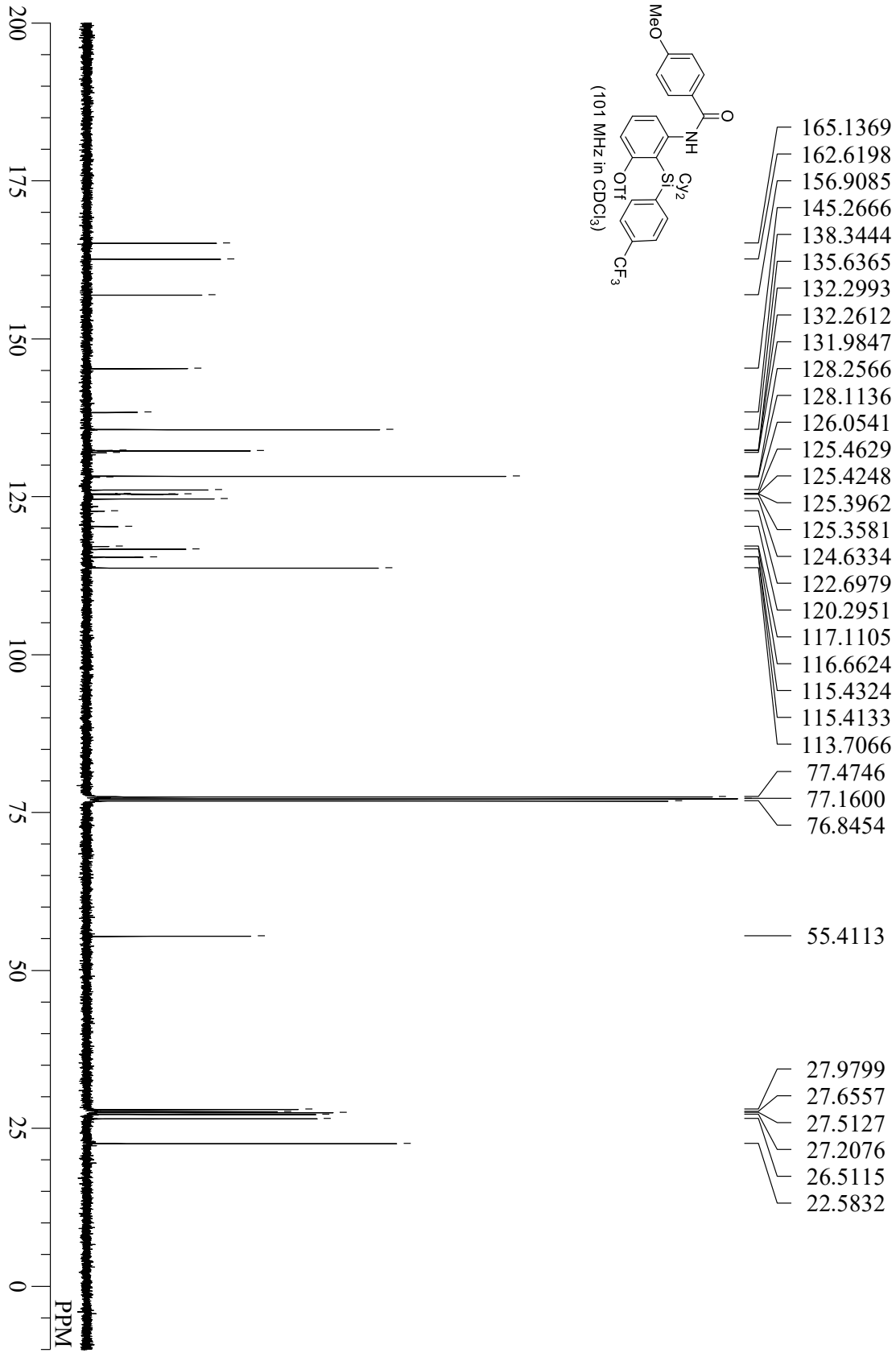
compound **1g**


(101 MHz in CDCl3)
MeO
O
NH
OTf
Cy2
Si
Cl
165.2037
162.5149
156.8989
145.4477
136.9427
136.7234
132.0896
131.2600
129.4294
128.4282
126.2829
124.0709
120.2760
117.0914
116.5384
115.0891
115.0701
113.7161
77.4842
77.1600
76.8454
55.4780
27.9608
27.6652
27.4078
27.1980
26.5401
22.6500
200
175
150
125
100
75
50
25
0
PPM

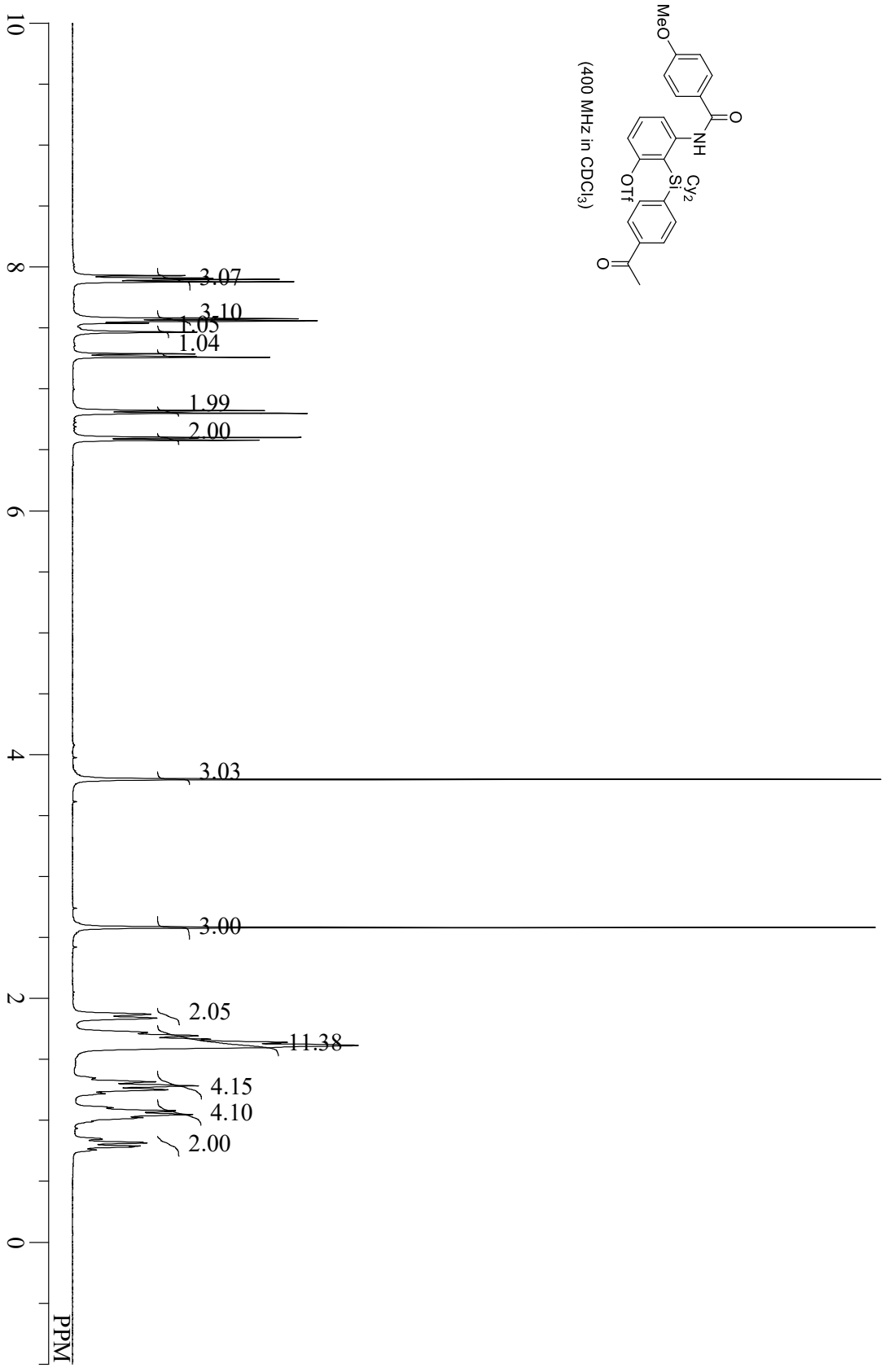
compound **1h**


MeO
O
NH
Cy2
Si
OTf
CF3
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
0.97
2.05
3.00
0.93
1.11
1.97
1.99
3.00
14.35
4.46
3.99
2.04

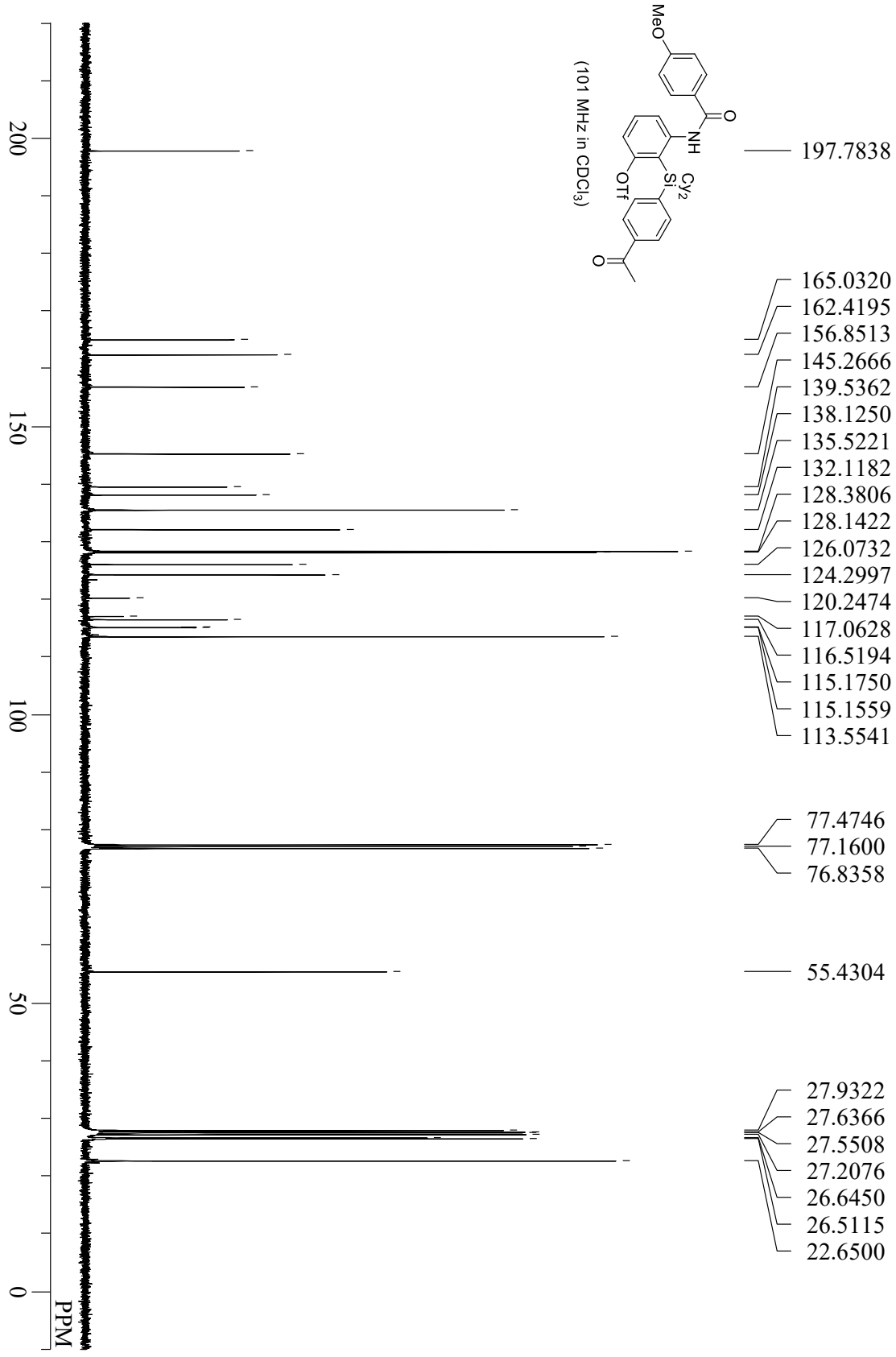
compound **1h**


MeO
O
NH
OTf
Si
Cy2
CF3
(101 MHz in CDCl3)
165.1369
162.6198
156.9085
145.2666
138.3444
135.6365
132.2993
132.2612
131.9847
128.2566
128.1136
126.0541
125.4629
125.4248
125.3962
125.3581
124.6334
122.6979
120.2951
117.1105
116.6624
115.4324
115.4133
113.7066
77.4746
77.1600
76.8454
55.4113
27.9799
27.6557
27.5127
27.2076
26.5115
22.5832
200
175
150
125
100
75
50
25
0
PPM

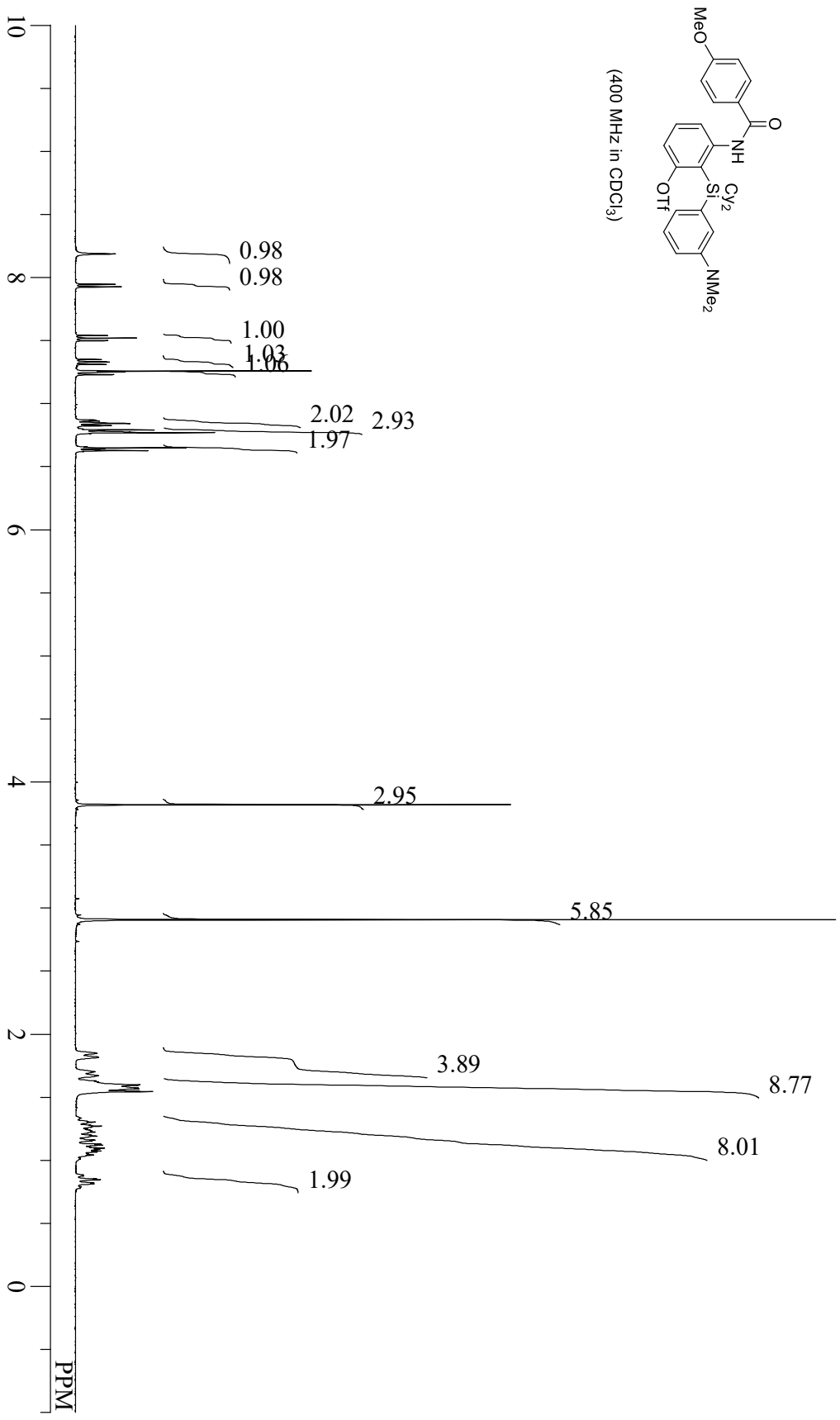
compound **1i**


MeO
O
NH
OTf
Cy2
Si
O
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
3.07
3.10
1.05
1.04
1.99
2.00
3.03
3.00
2.05
11.38
4.15
4.10
2.00

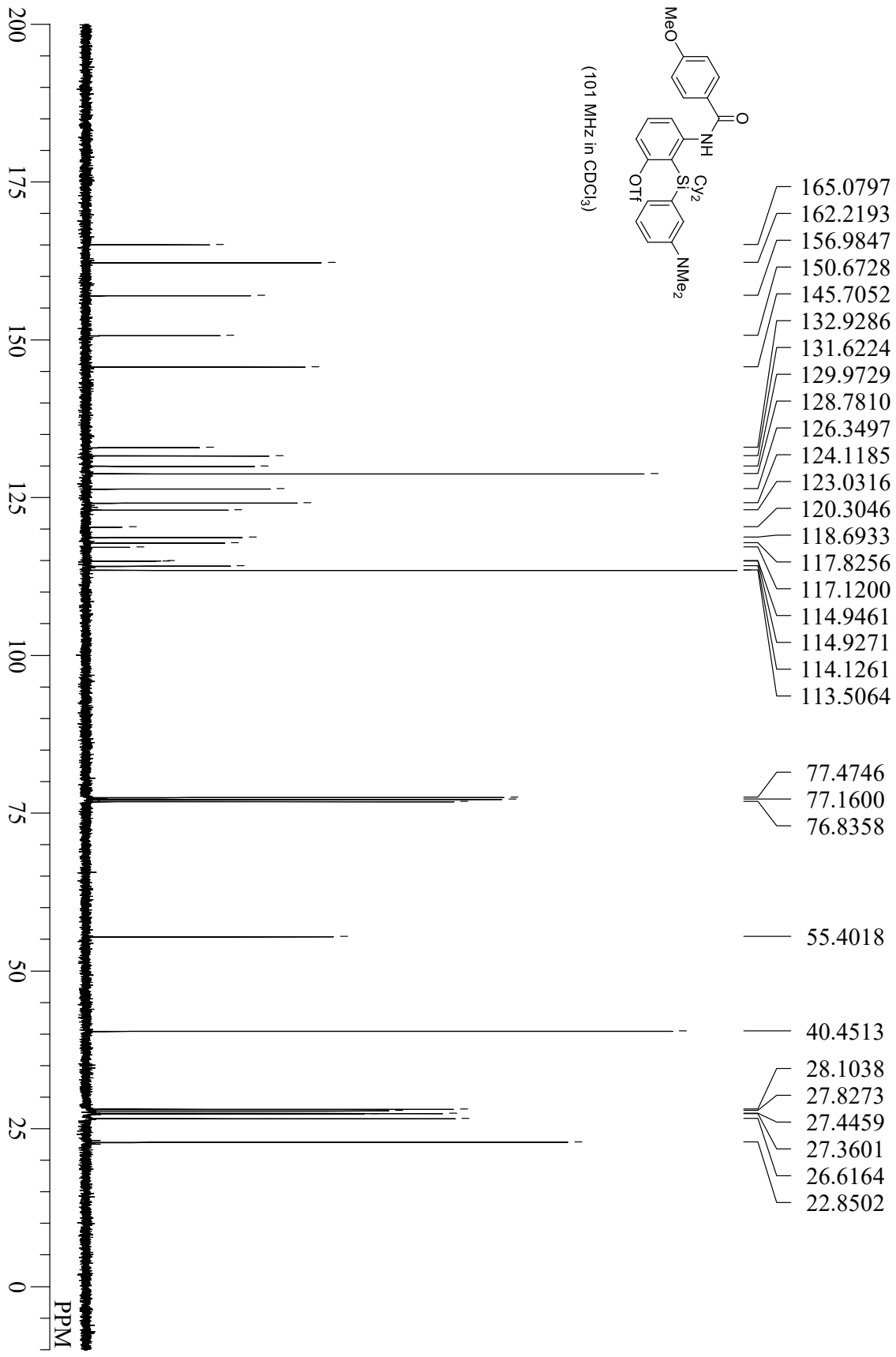
compound **1i**


MeO
O
NH
OTf
Si
Cy2
O
(101 MHz in CDCl3)
197.7838
165.0320
162.4195
156.8513
145.2666
139.5362
138.1250
135.5221
132.1182
128.3806
128.1422
126.0732
124.2997
120.2474
117.0628
116.5194
115.1750
115.1559
113.5541
77.4746
77.1600
76.8358
55.4304
27.9322
27.6366
27.5508
27.2076
26.6450
26.5115
22.6500
200
150
100
50
0
PPM

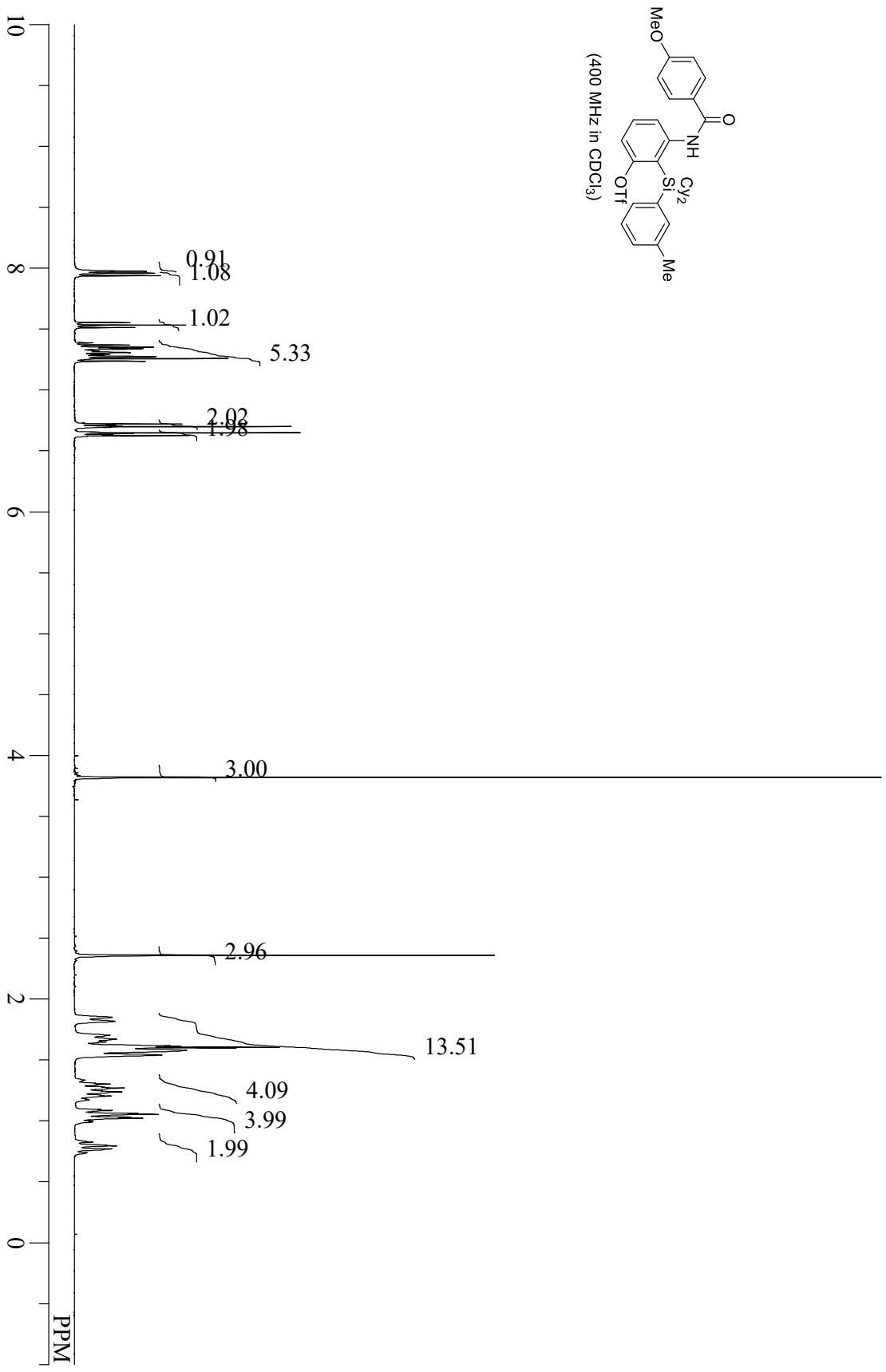
compound **1j**


(400 MHz in CDCl3)
MeO
O
NH
Cy2
Si
OTf
NMe2
0.98
0.98
1.00
1.03
1.06
2.02
2.93
1.97
2.95
5.85
3.89
8.77
8.01
1.99
10
8
6
4
2
0
PPM

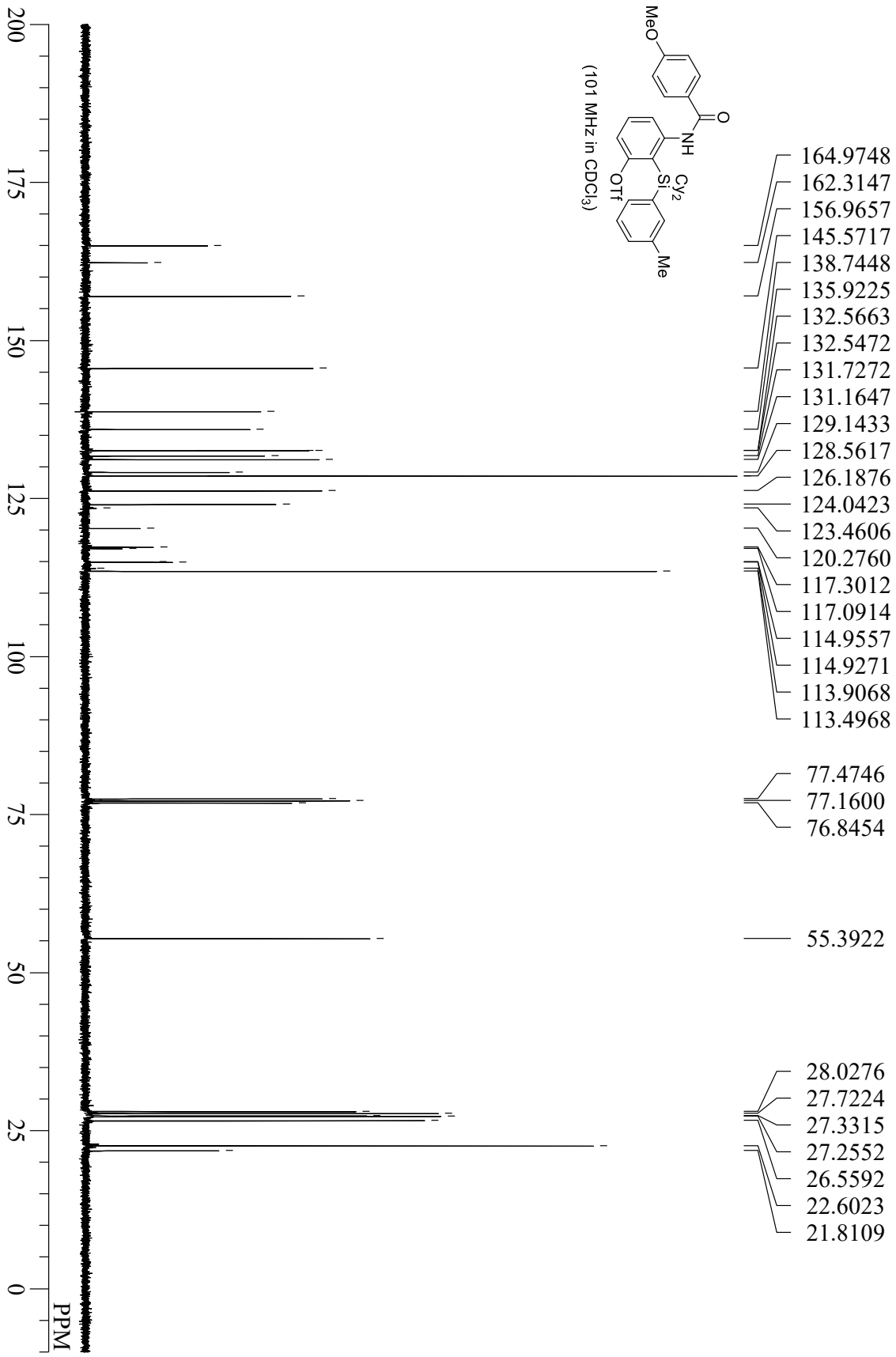
compound **1j**


(101 MHz in CDCl3)
MeO
O
NH
Cy2
Si
OTf
NMe2
165.0797
162.2193
156.9847
150.6728
145.7052
132.9286
131.6224
129.9729
128.7810
126.3497
124.1185
123.0316
120.3046
118.6933
117.8256
117.1200
114.9461
114.9271
114.1261
113.5064
77.4746
77.1600
76.8358
55.4018
40.4513
28.1038
27.8273
27.4459
27.3601
26.6164
22.8502
200
175
150
125
100
75
50
25
0
PPM

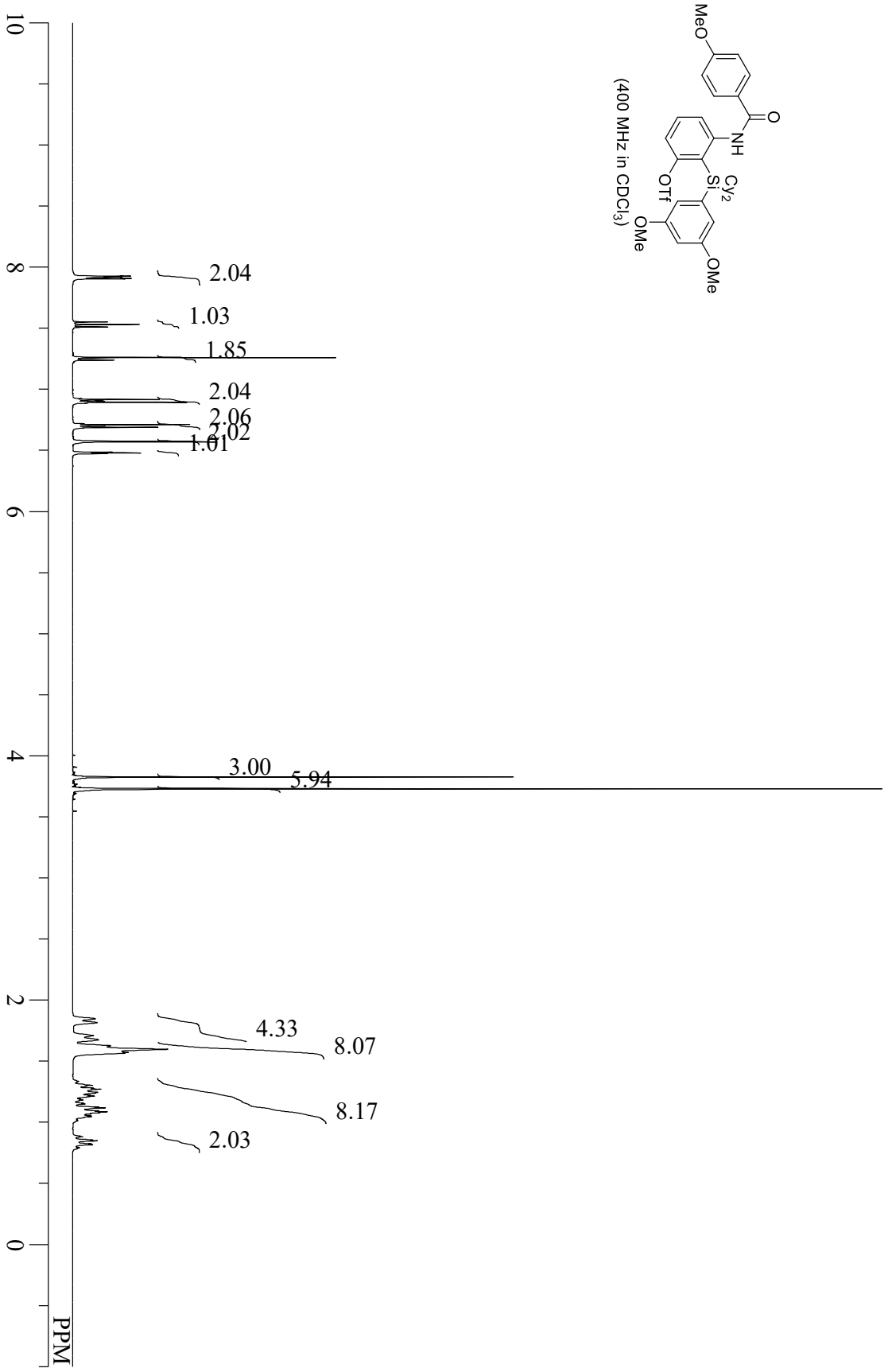
compound **1k**


MeO
O
NH
Cy2
Si
OTf
Me
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
0.91
1.08
1.02
5.33
2.02
1.98
3.00
2.96
13.51
4.09
3.99
1.99

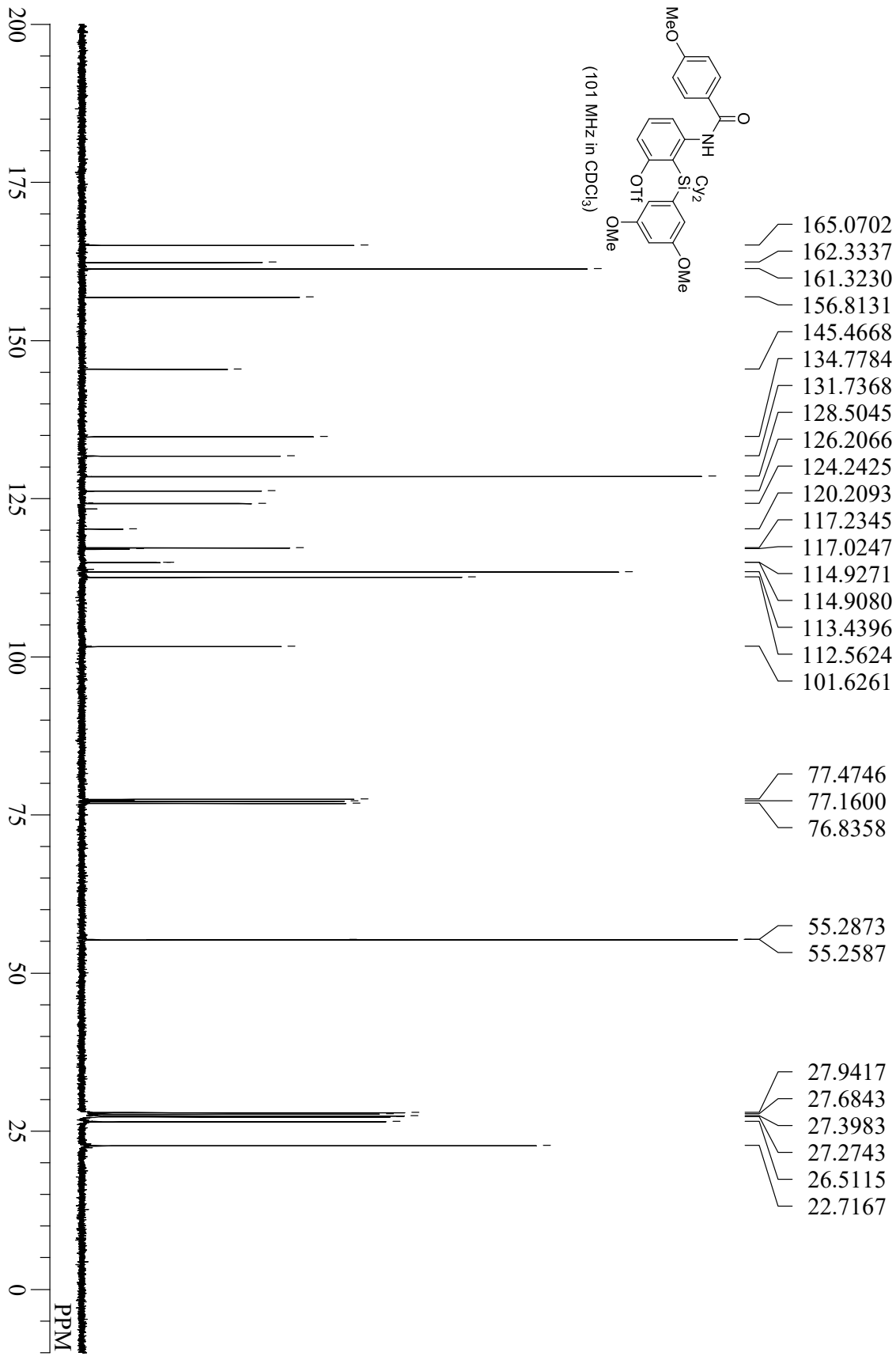
compound **1k**


(101 MHz in CDCl3)
MeO
O
NH
Cy2
Si
OTf
Me
164.9748
162.3147
156.9657
145.5717
138.7448
135.9225
132.5663
132.5472
131.7272
131.1647
129.1433
128.5617
126.1876
124.0423
123.4606
120.2760
117.3012
117.0914
114.9557
114.9271
113.9068
113.4968
77.4746
77.1600
76.8454
55.3922
28.0276
27.7224
27.3315
27.2552
26.5592
22.6023
21.8109
200
175
150
125
100
75
50
25
0
PPM

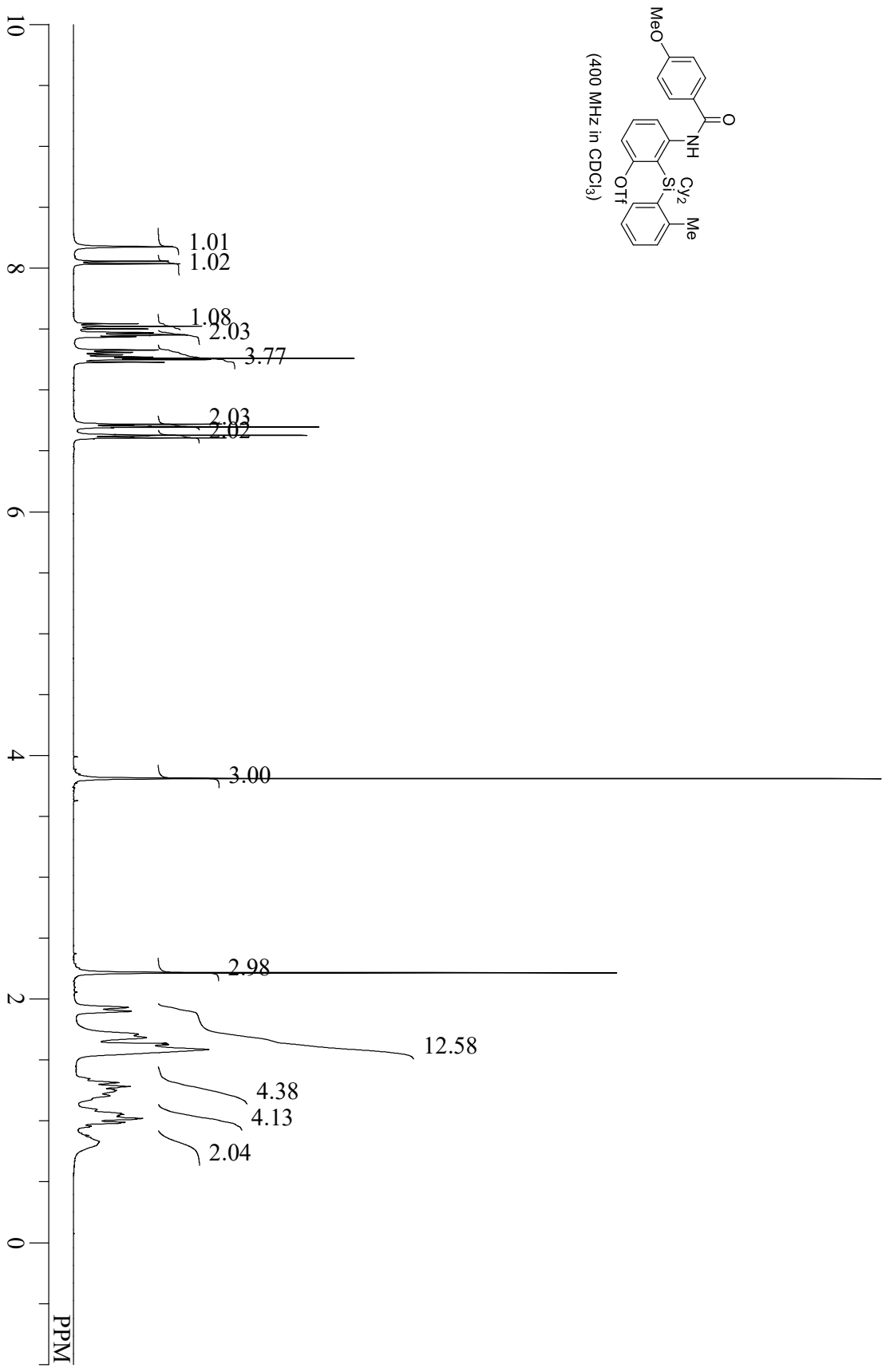
compound **1l**


MeO
O
NH
Cy2
Si
OTf
OMe
OMe
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
2.04
1.03
1.85
2.04
2.06
2.02
1.01
3.00
5.94
4.33
8.07
8.17
2.03

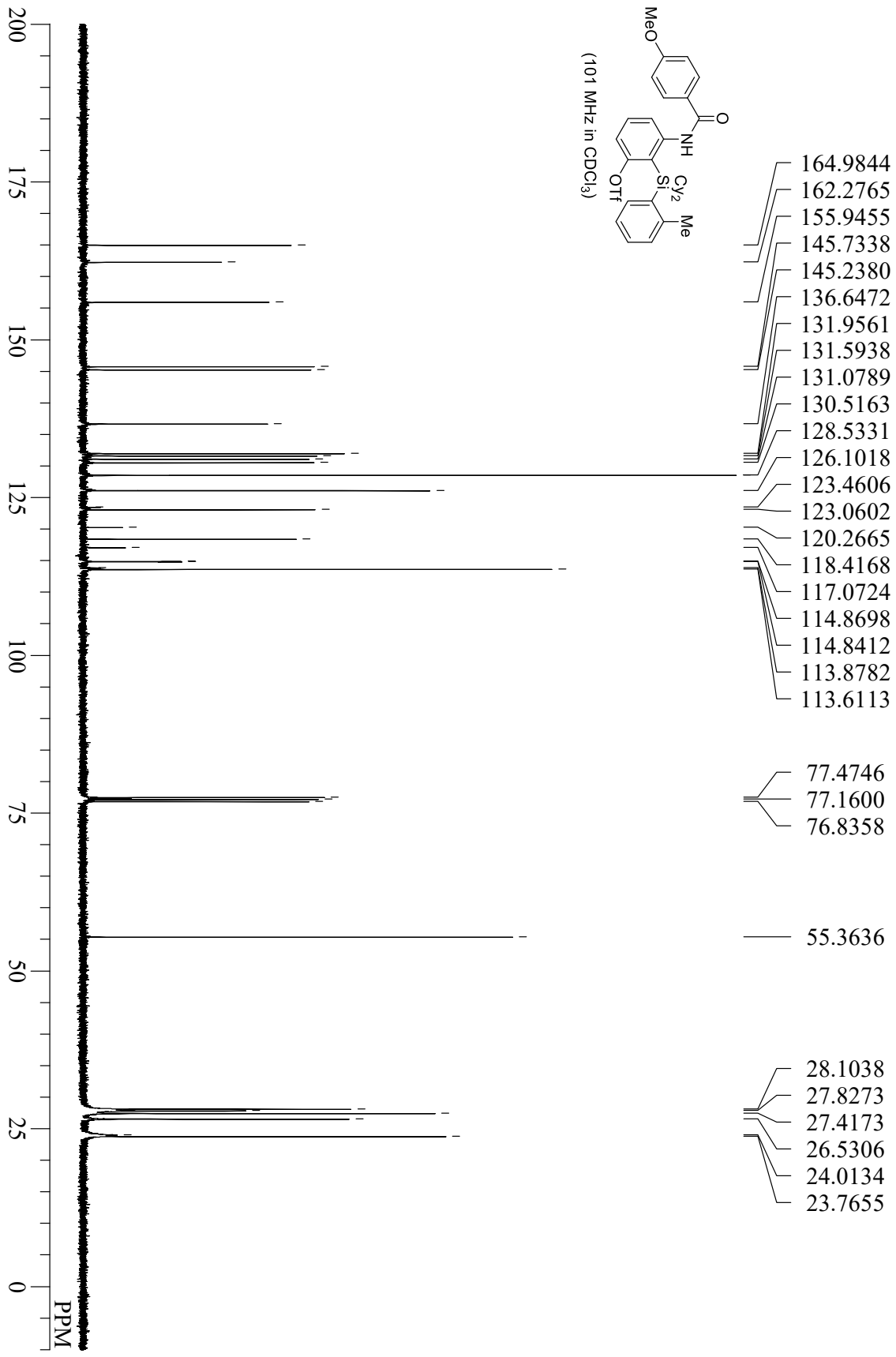
compound **1l**


(101 MHz in CDCl3)
MeO
O
NH
Cy2
Si
OTf
OMe
OMe
165.0702
162.3337
161.3230
156.8131
145.4668
134.7784
131.7368
128.5045
126.2066
124.2425
120.2093
117.2345
117.0247
114.9271
114.9080
113.4396
112.5624
101.6261
77.4746
77.1600
76.8358
55.2873
55.2587
27.9417
27.6843
27.3983
27.2743
26.5115
22.7167
200
175
150
125
100
75
50
25
0
PPM

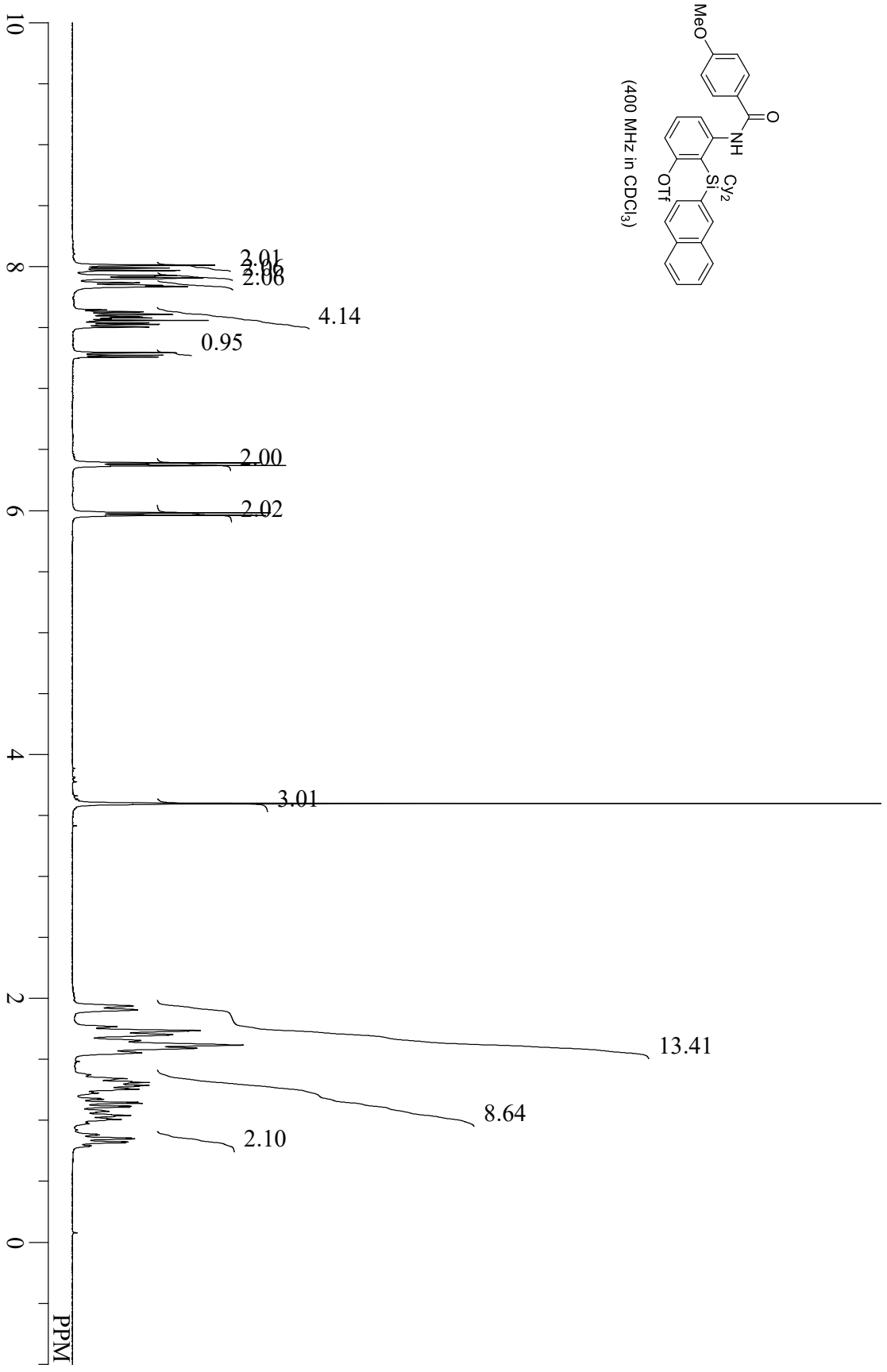
compound **1m**


MeO
O
NH
OTf
Si
Cy2
Me
(400 MHz in CDCl3)
1.01
1.02
1.08
2.03
3.77
2.03
2.02
3.00
2.98
12.58
4.38
4.13
2.04
10
8
6
4
2
0
PPM

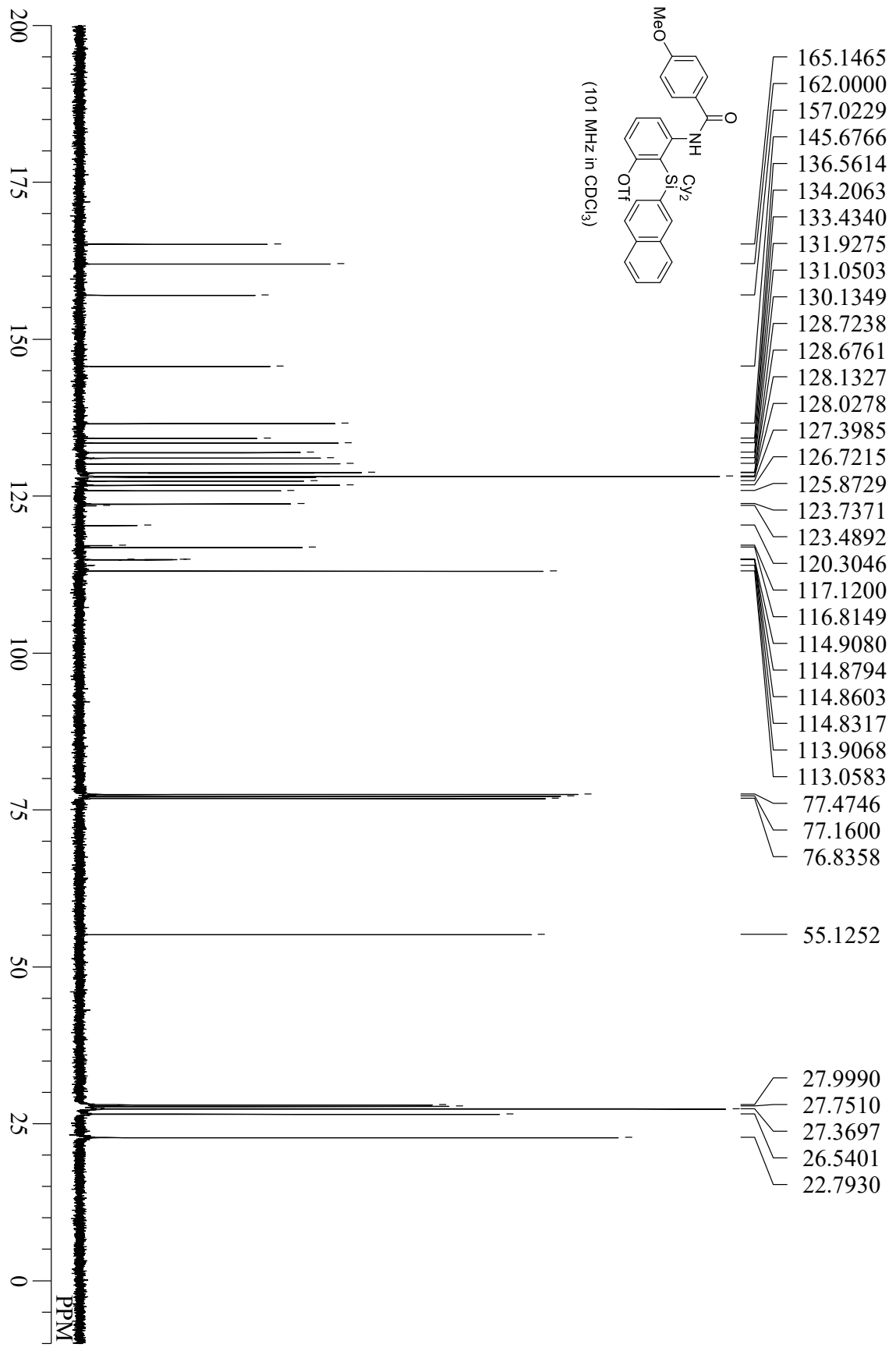
compound **1m**


MeO
O
NH
OTf
Si
Cy2
Me
(101 MHz in CDCl3)
164.9844
162.2765
155.9455
145.7338
145.2380
136.6472
131.9561
131.5938
131.0789
130.5163
128.5331
126.1018
123.4606
123.0602
120.2665
118.4168
117.0724
114.8698
114.8412
113.8782
113.6113
77.4746
77.1600
76.8358
55.3636
28.1038
27.8273
27.4173
26.5306
24.0134
23.7655
200
175
150
125
100
75
50
25
0
PPM

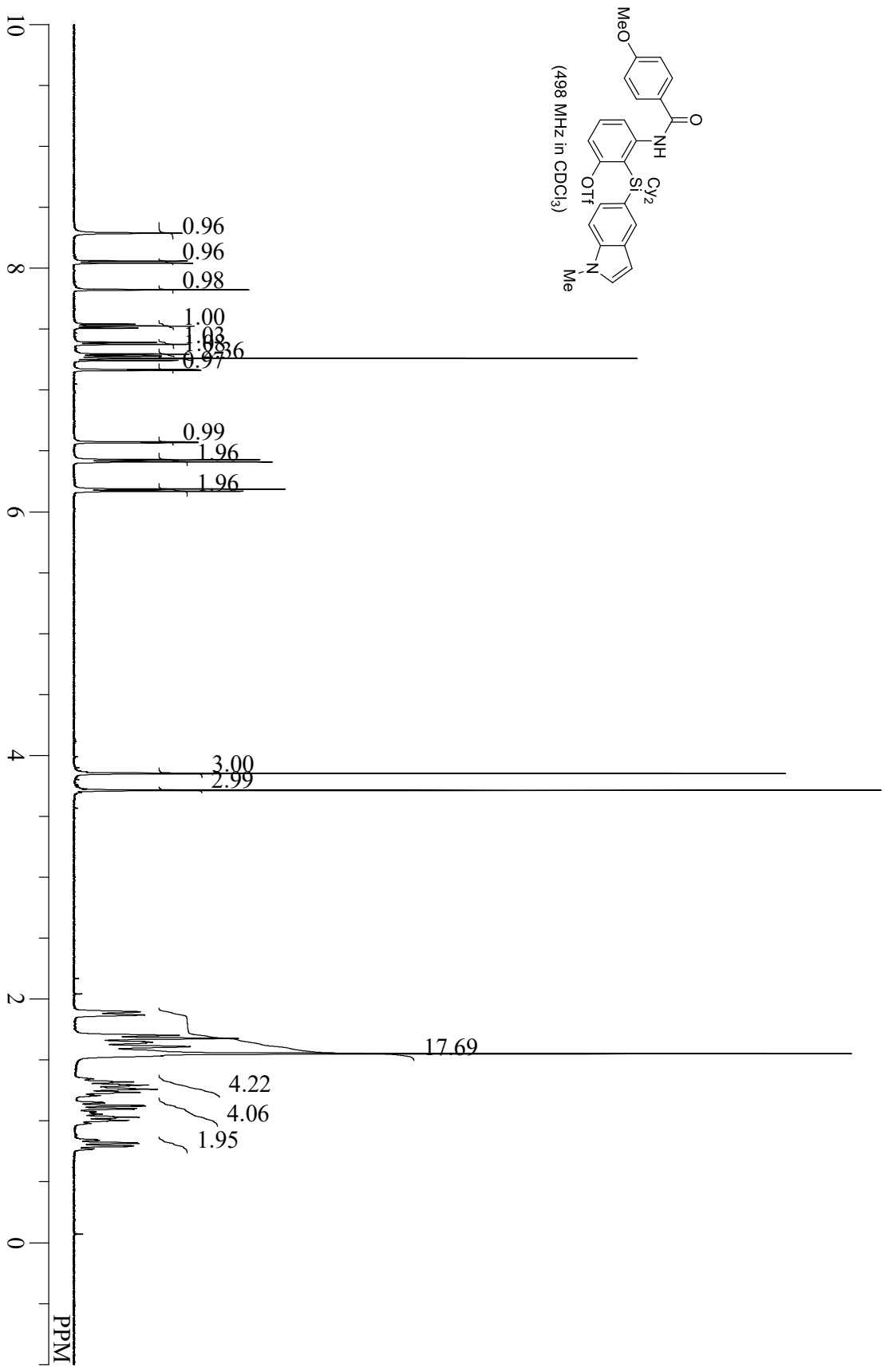
compound **1n**


MeO
O
NH
Cy2
Si
OTf
(400 MHz in CDCl3)
2.01
2.06
2.08
4.14
0.95
2.00
2.02
3.01
13.41
8.64
2.10
10
8
6
4
2
0
PPM

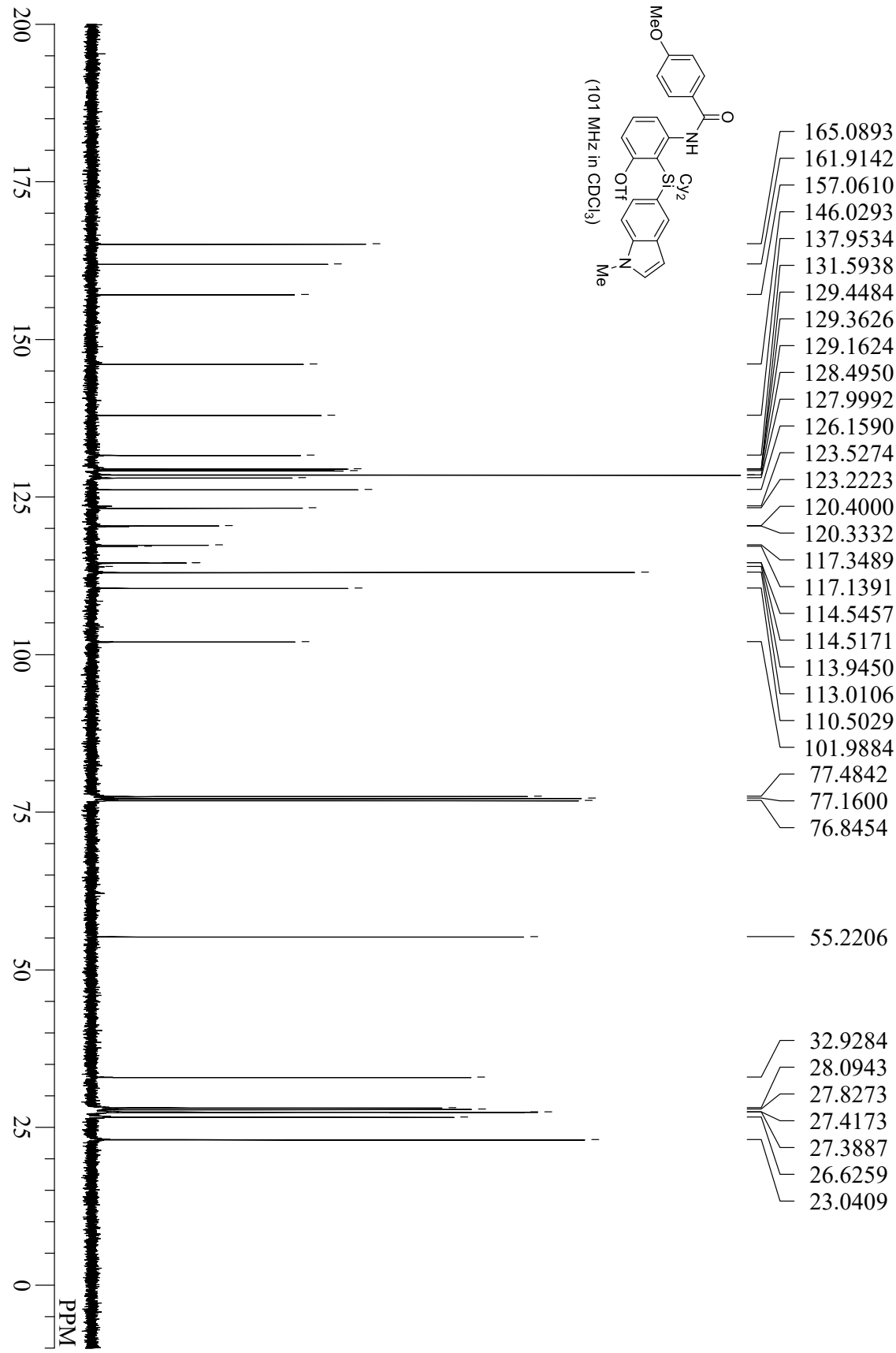
compound **1n**


MeO
O
NH
Cy2
Si
OTf
(101 MHz in CDCl3)
165.1465
162.0000
157.0229
145.6766
136.5614
134.2063
133.4340
131.9275
131.0503
130.1349
128.7238
128.6761
128.1327
128.0278
127.3985
126.7215
125.8729
123.7371
123.4892
120.3046
117.1200
116.8149
114.9080
114.8794
114.8603
114.8317
113.9068
113.0583
77.4746
77.1600
76.8358
55.1252
27.9990
27.7510
27.3697
26.5401
22.7930
200
175
150
125
100
75
50
25
0
PPM

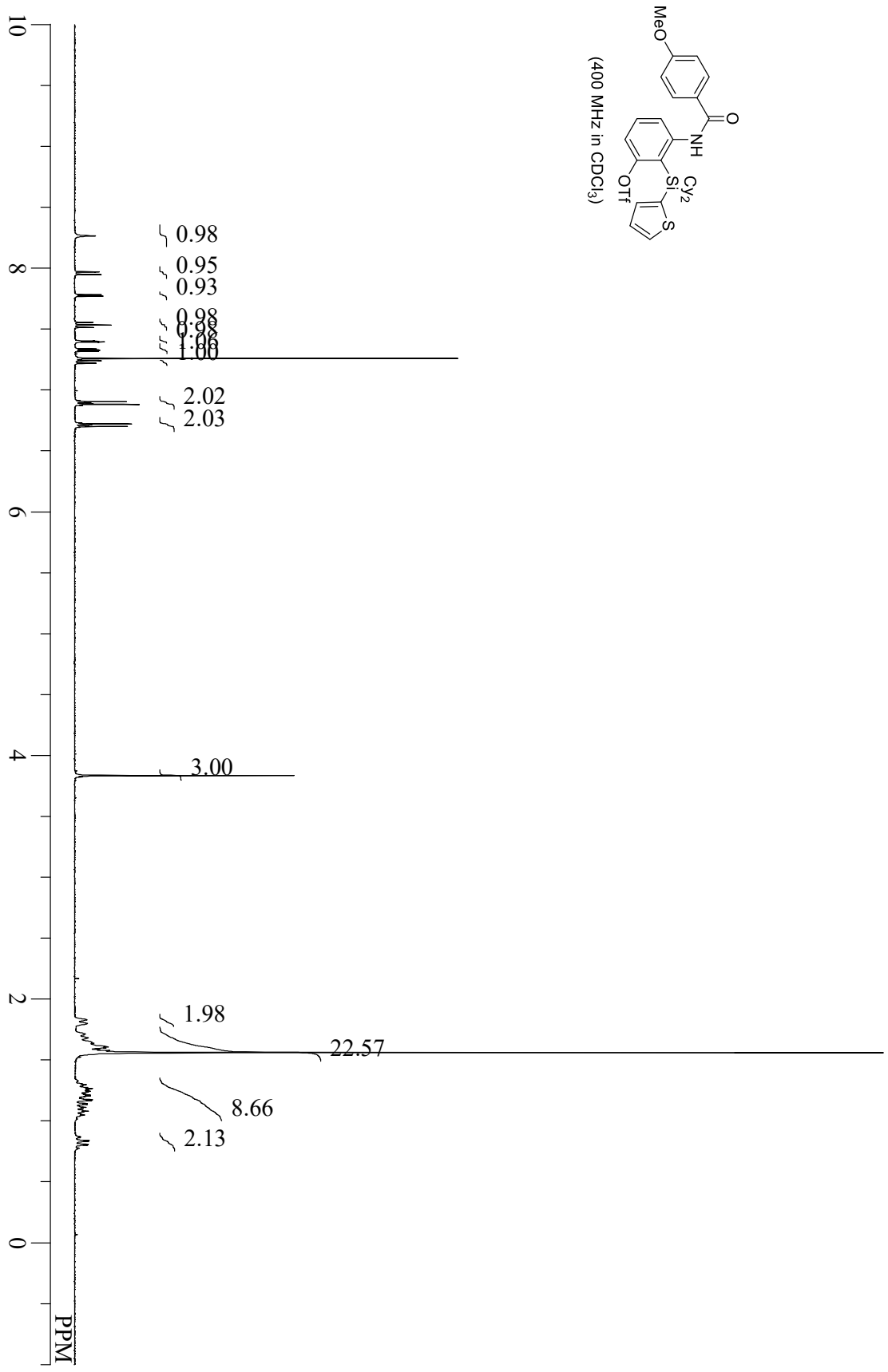
compound **1o**


(498 MHz in CDCl3)
MeO
O
NH
OTf
Si
Cy2
N
Me
0.96
0.96
0.98
1.00
0.97
0.99
1.96
1.96
3.00
2.99
17.69
4.22
4.06
1.95
PPM

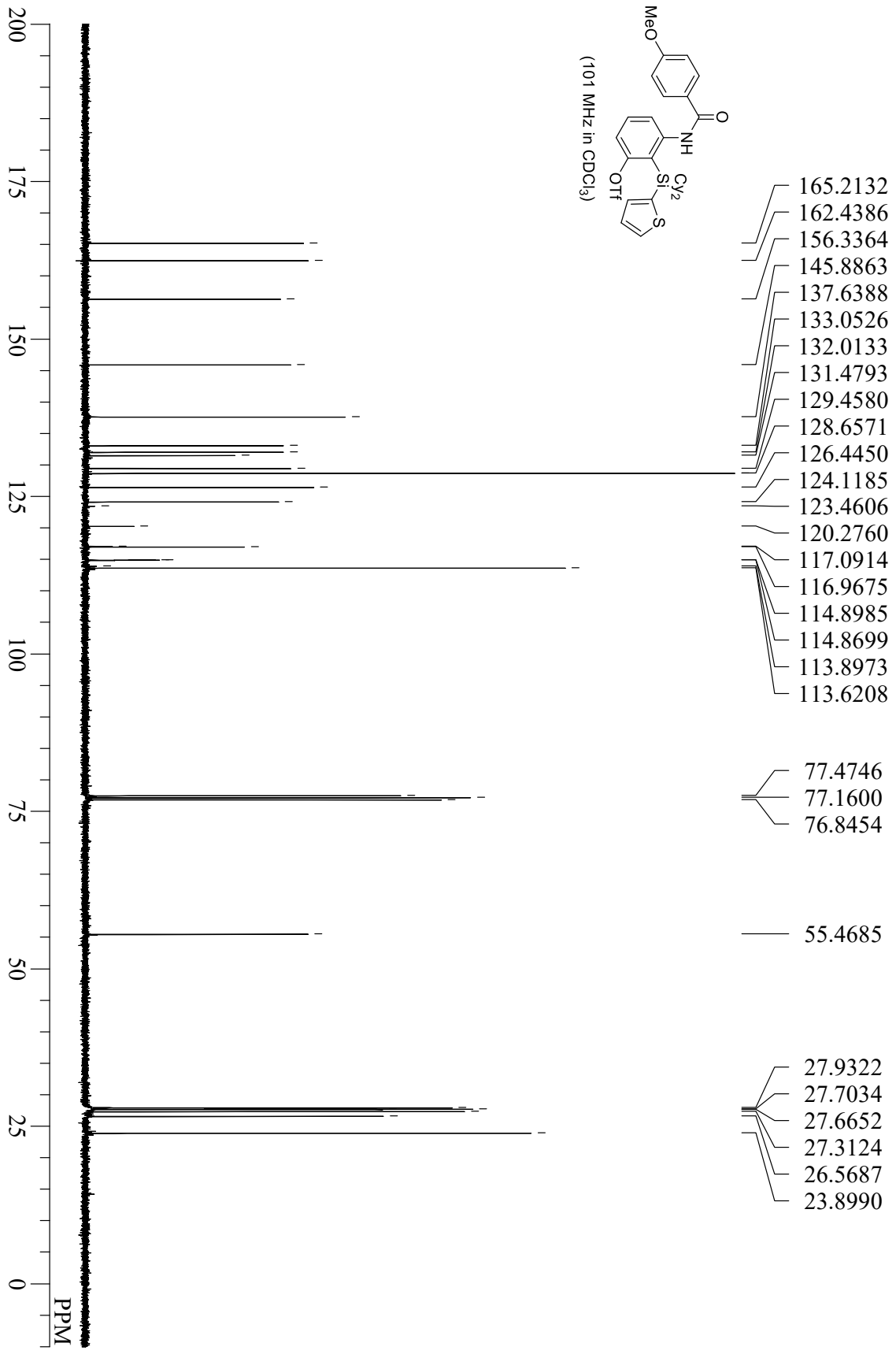
compound **1o**


MeO
O
NH
Cy2
Si
OTf
N
Me
(101 MHz in CDCl3)
165.0893
161.9142
157.0610
146.0293
137.9534
131.5938
129.4484
129.3626
129.1624
128.4950
127.9992
126.1590
123.5274
123.2223
120.4000
120.3332
117.3489
117.1391
114.5457
114.5171
113.9450
113.0106
110.5029
101.9884
77.4842
77.1600
76.8454
55.2206
32.9284
28.0943
27.8273
27.4173
27.3887
26.6259
23.0409
200
175
150
125
100
75
50
25
0
PPM

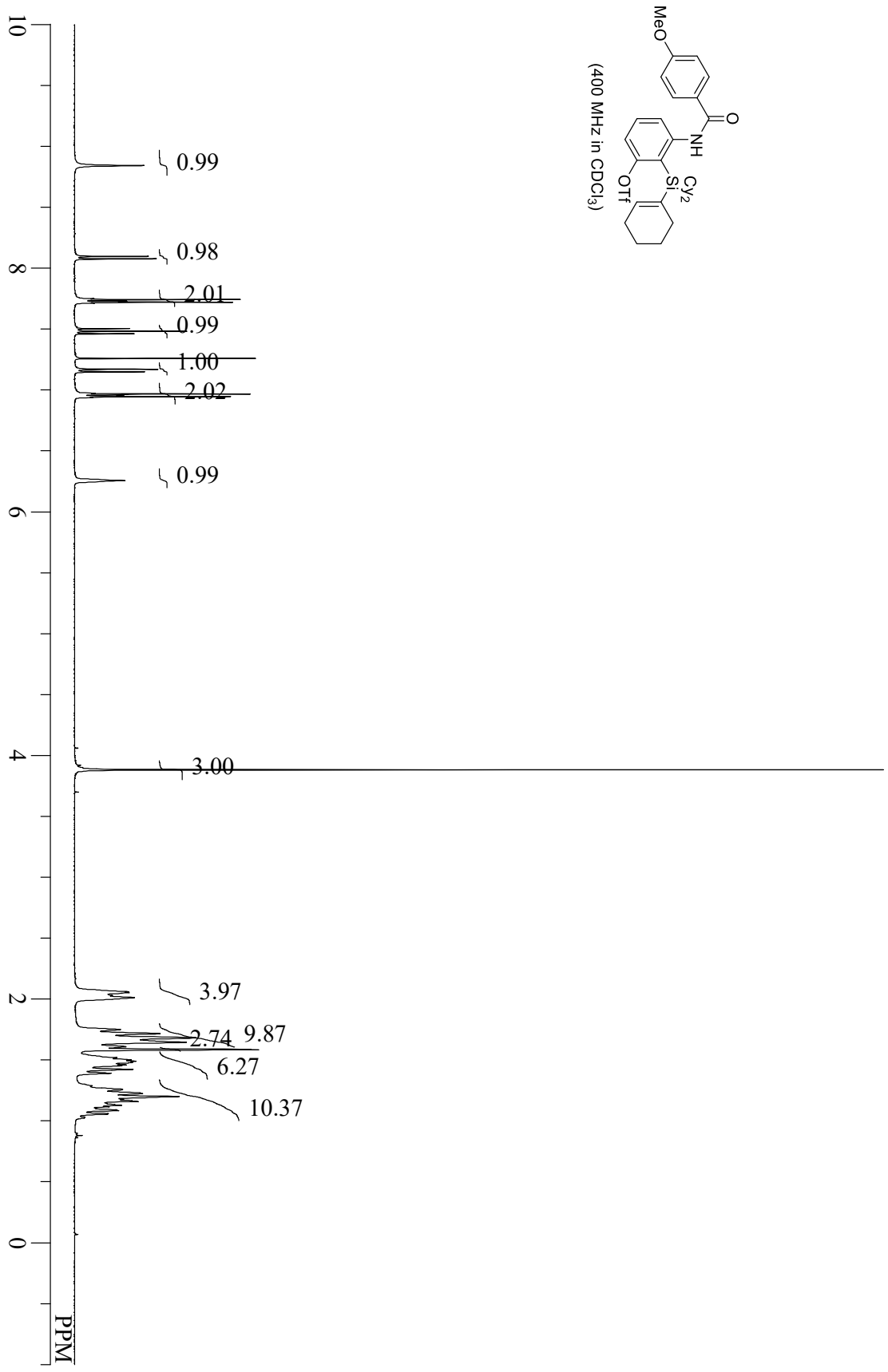
compound **1p**


MeO
O
NH
OTf
Si
Cy2
S
(400 MHz in CDCl3)
0.98
0.95
0.93
0.98
2.02
2.03
3.00
1.98
22.57
8.66
2.13
PPM

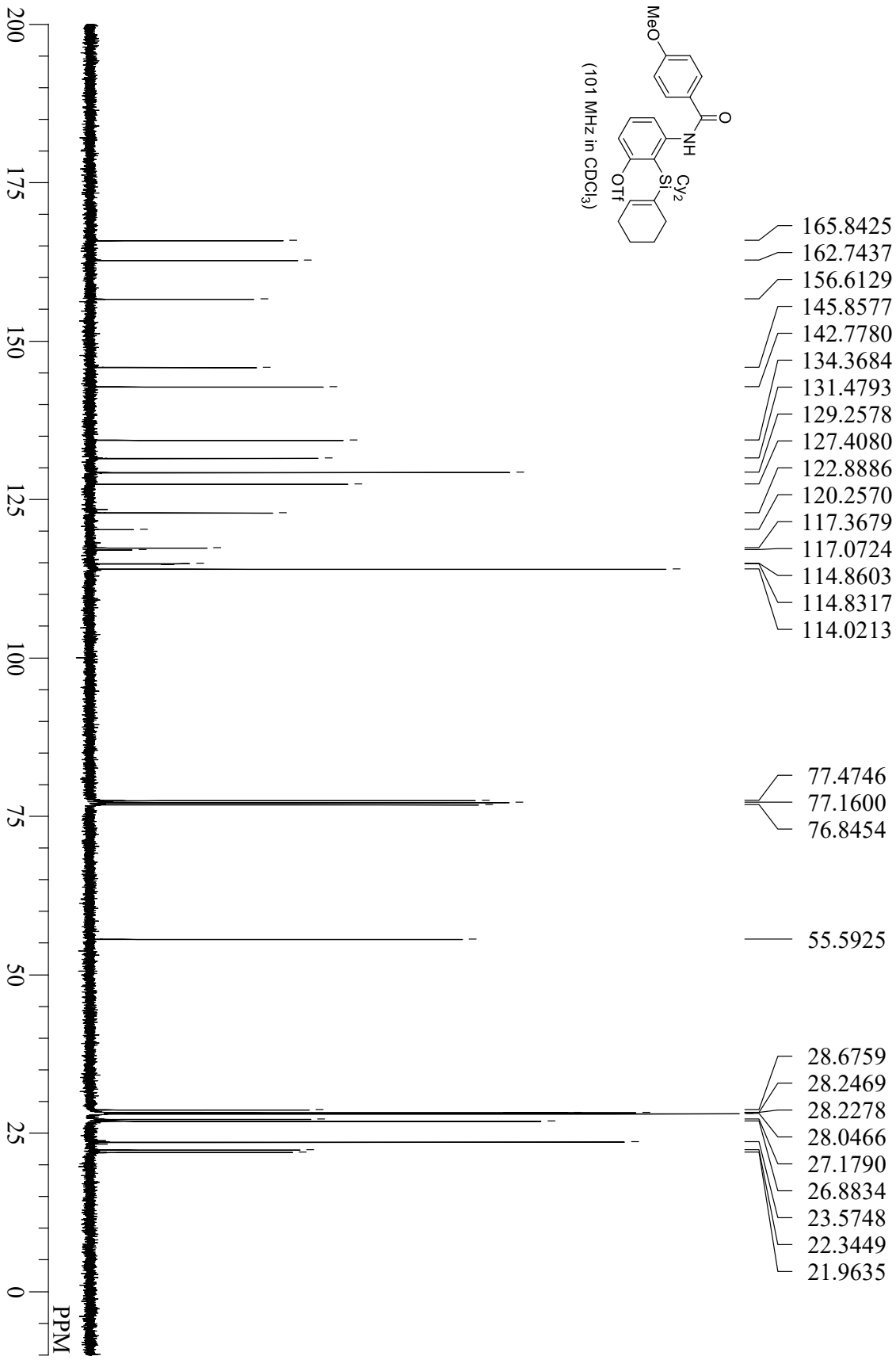
compound **1p**


(101 MHz in CDCl3)
MeO
O
NH
Cy2
Si
OTf
S
165.2132
162.4386
156.3364
145.8863
137.6388
133.0526
132.0133
131.4793
129.4580
128.6571
126.4450
124.1185
123.4606
120.2760
117.0914
116.9675
114.8985
114.8699
113.8973
113.6208
77.4746
77.1600
76.8454
55.4685
27.9322
27.7034
27.6652
27.3124
26.5687
23.8990
200
175
150
125
100
75
50
25
0
PPM

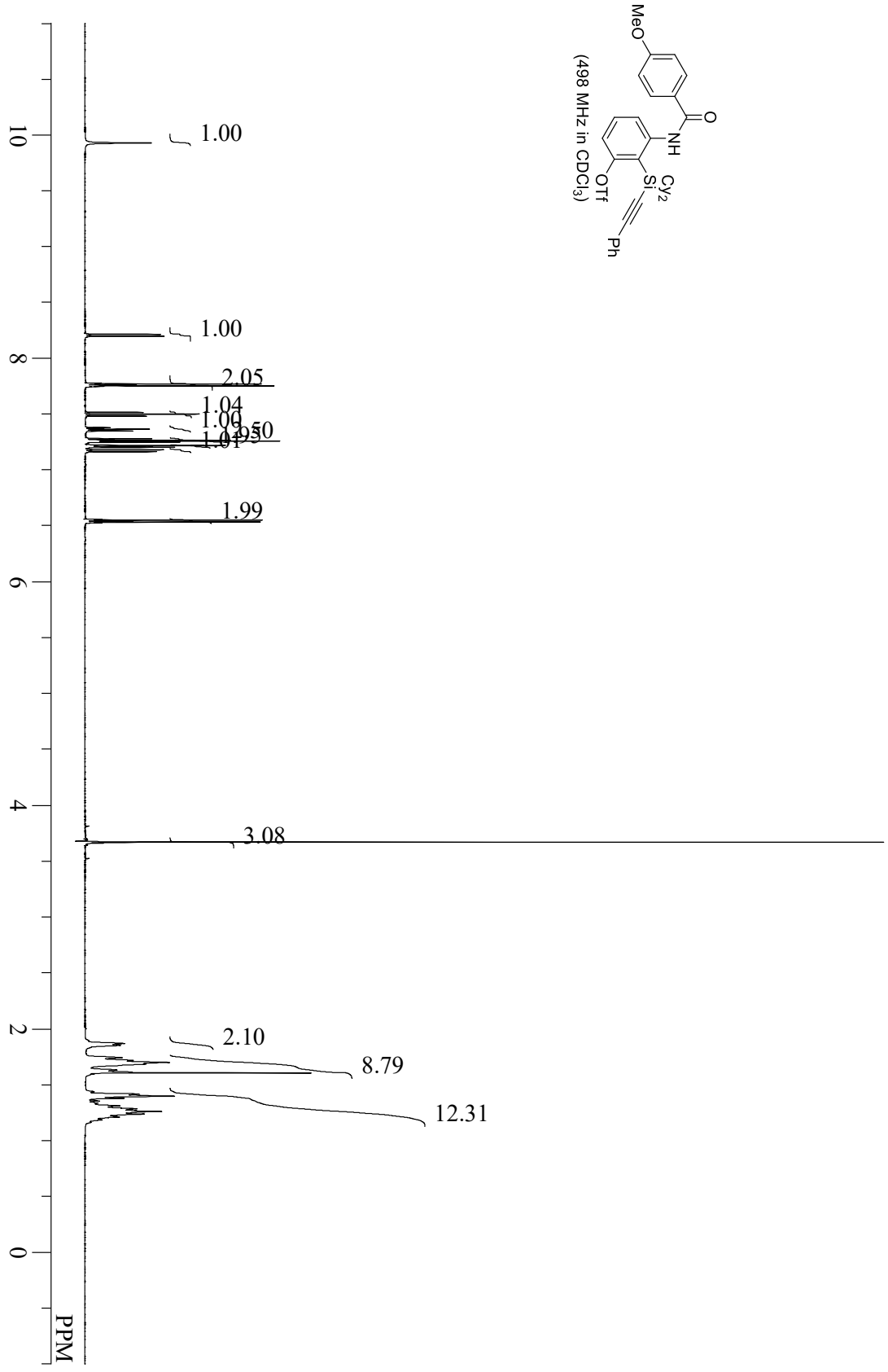
compound **1q**


MeO
O
NH
Cy2
Si
OTf
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
0.99
0.98
2.01
0.99
1.00
2.02
0.99
3.00
3.97
2.74
9.87
6.27
10.37

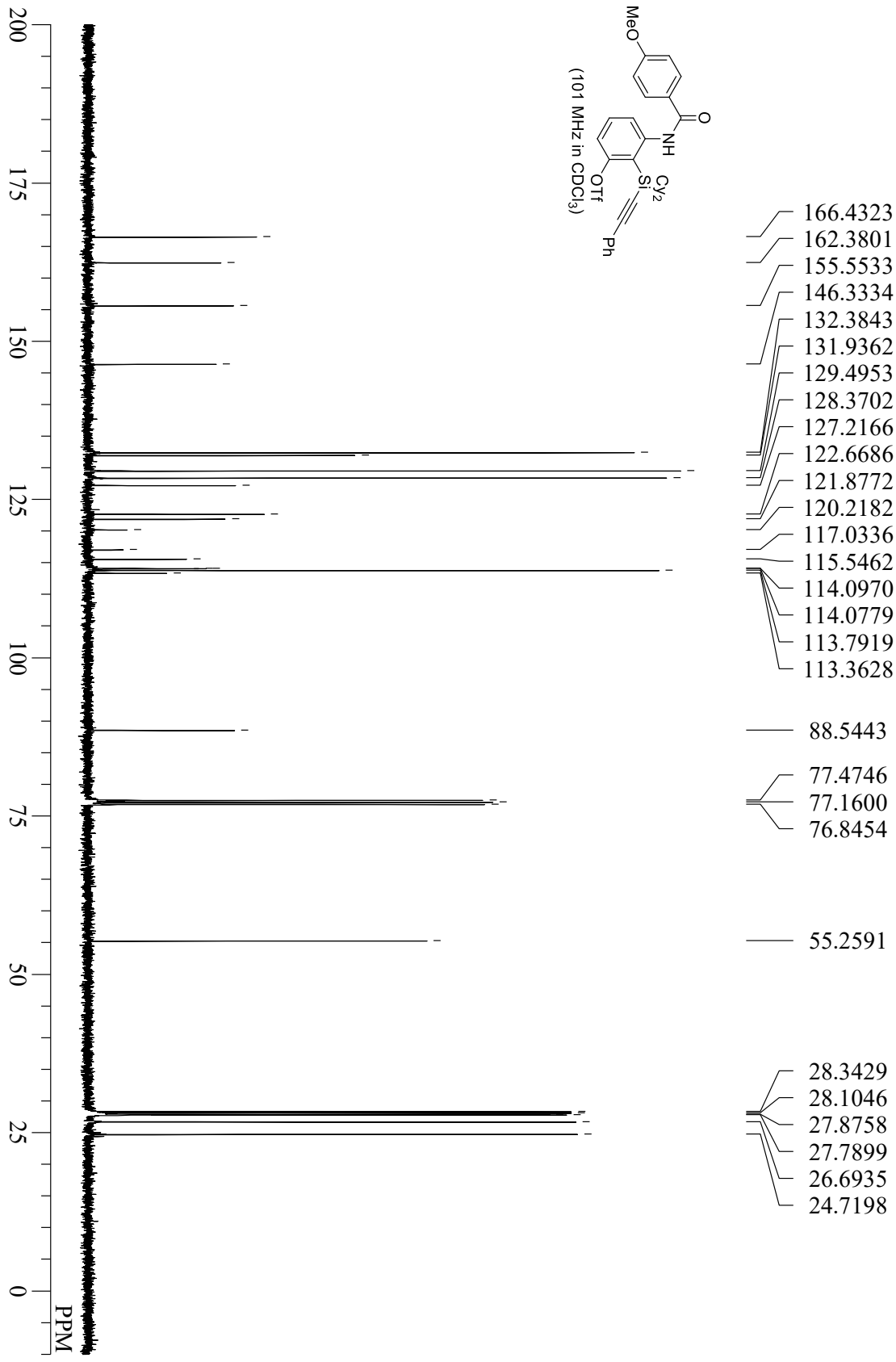
compound **1q**


MeO
O
NH
OTf
Si
Cy2
(101 MHz in CDCl3)
165.8425
162.7437
156.6129
145.8577
142.7780
134.3684
131.4793
129.2578
127.4080
122.8886
120.2570
117.3679
117.0724
114.8603
114.8317
114.0213
77.4746
77.1600
76.8454
55.5925
28.6759
28.2469
28.2278
28.0466
27.1790
26.8834
23.5748
22.3449
21.9635
200
175
150
125
100
75
50
25
0
PPM

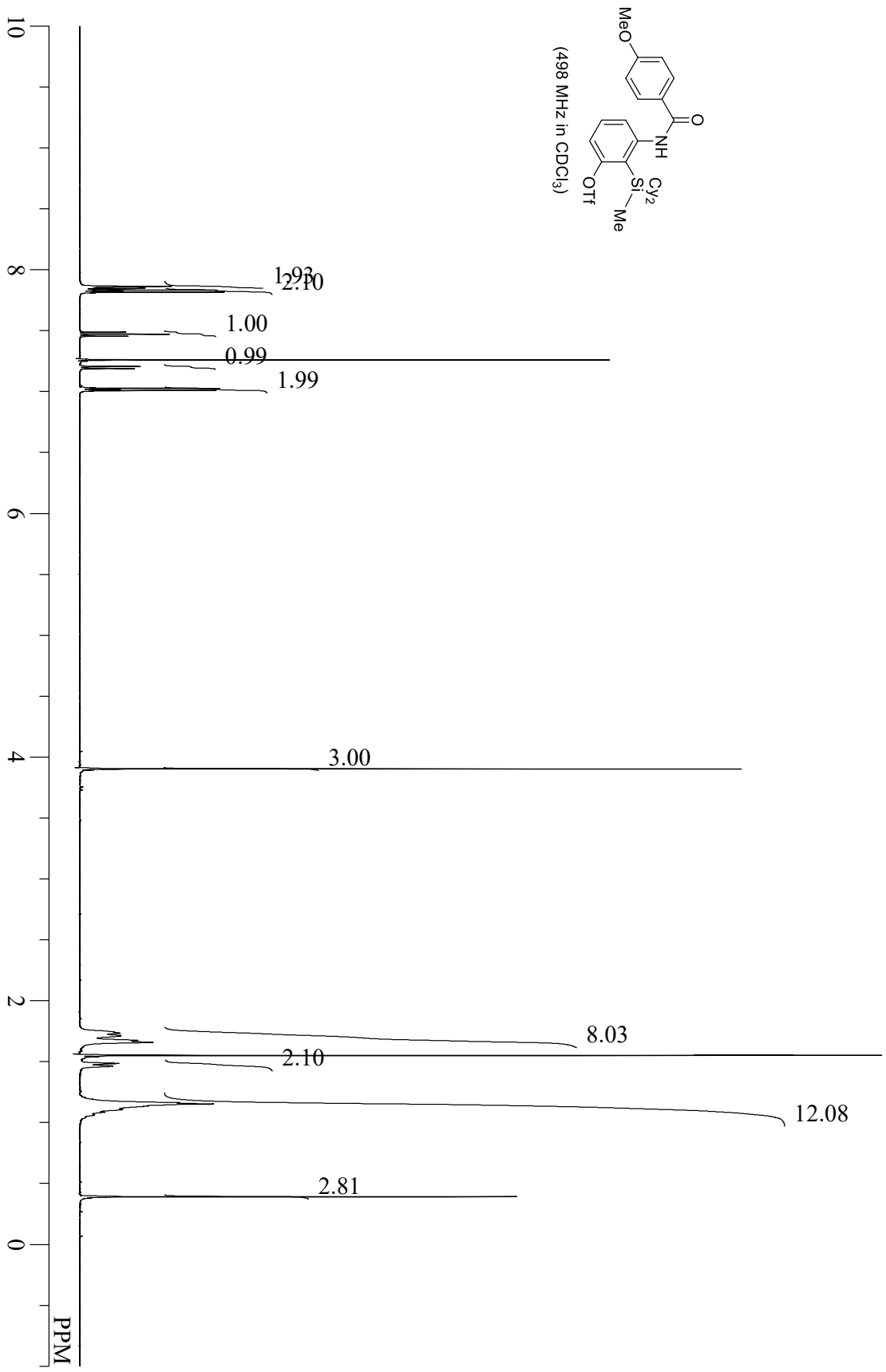
compound **1r**


MeO
O
NH
Cy2
Si
OTf
Ph
(498 MHz in CDCl3)
1.00
1.00
2.05
1.04
1.99
3.08
2.10
8.79
12.31
10
8
6
4
2
0
PPM

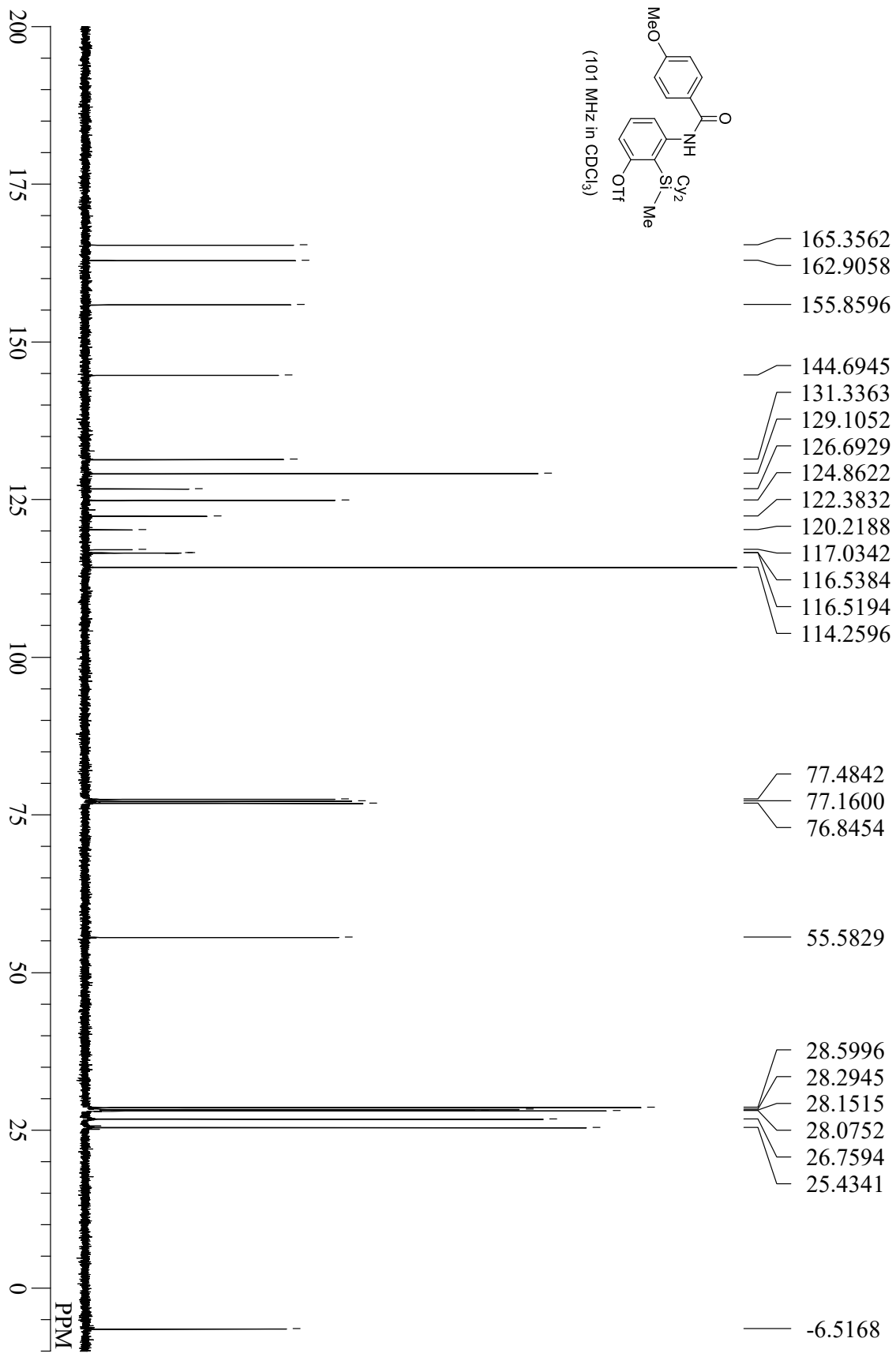
compound **1r**


MeO
O
NH
Cy2
Si
OTf
Ph
(101 MHz in CDCl3)
166.4323
162.3801
155.5533
146.3334
132.3843
131.9362
129.4953
128.3702
127.2166
122.6686
121.8772
120.2182
117.0336
115.5462
114.0970
114.0779
113.7919
113.3628
88.5443
77.4746
77.1600
76.8454
55.2591
28.3429
28.1046
27.8758
27.7899
26.6935
24.7198
200
175
150
125
100
75
50
25
0
PPM

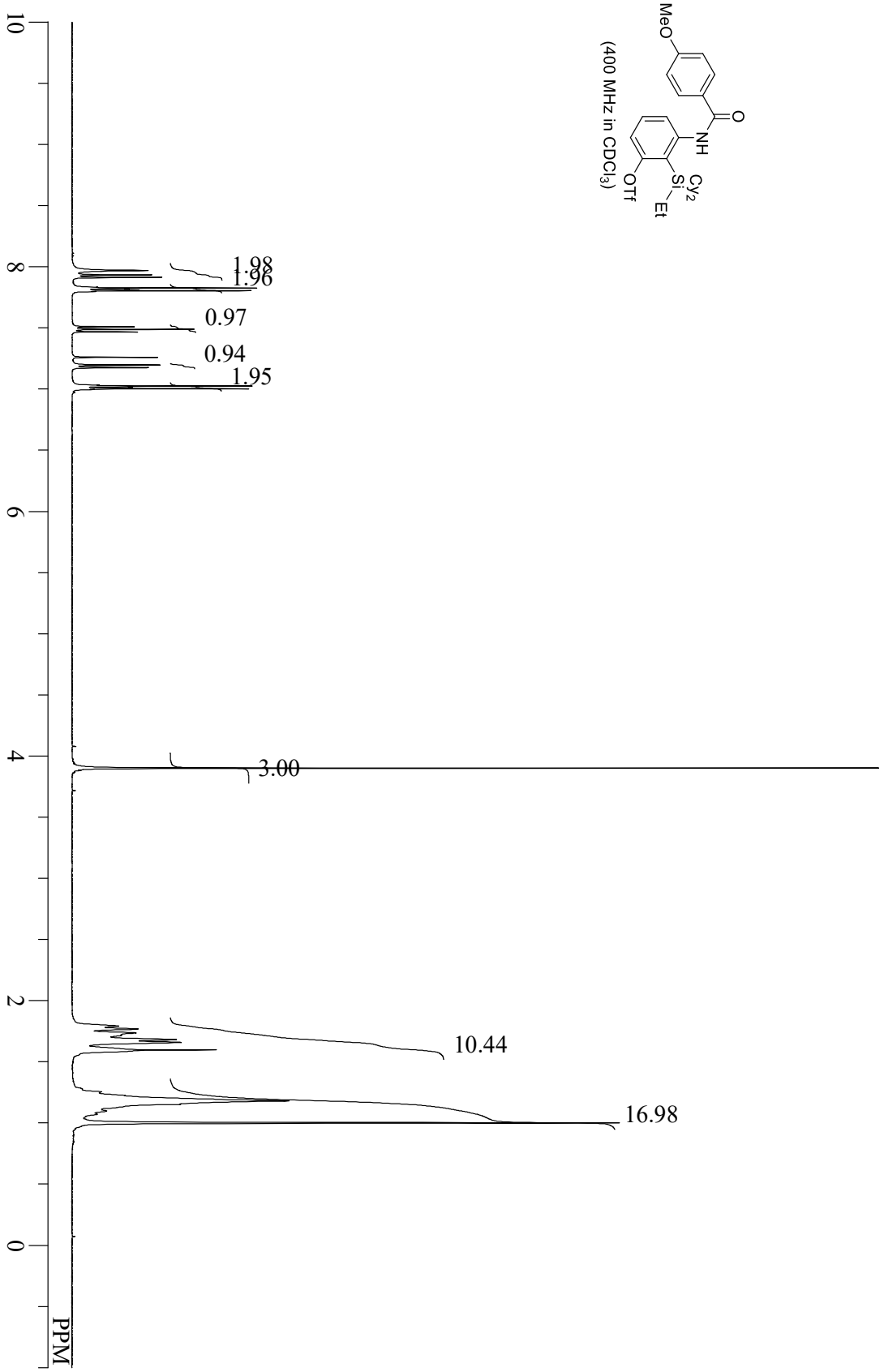
compound **1s**


(498 MHz in CDCl3)
MeO
O
NH
OTf
Si
Cy2
Me
1.93
2.10
1.00
0.99
1.99
3.00
8.03
2.10
12.08
2.81
PPM

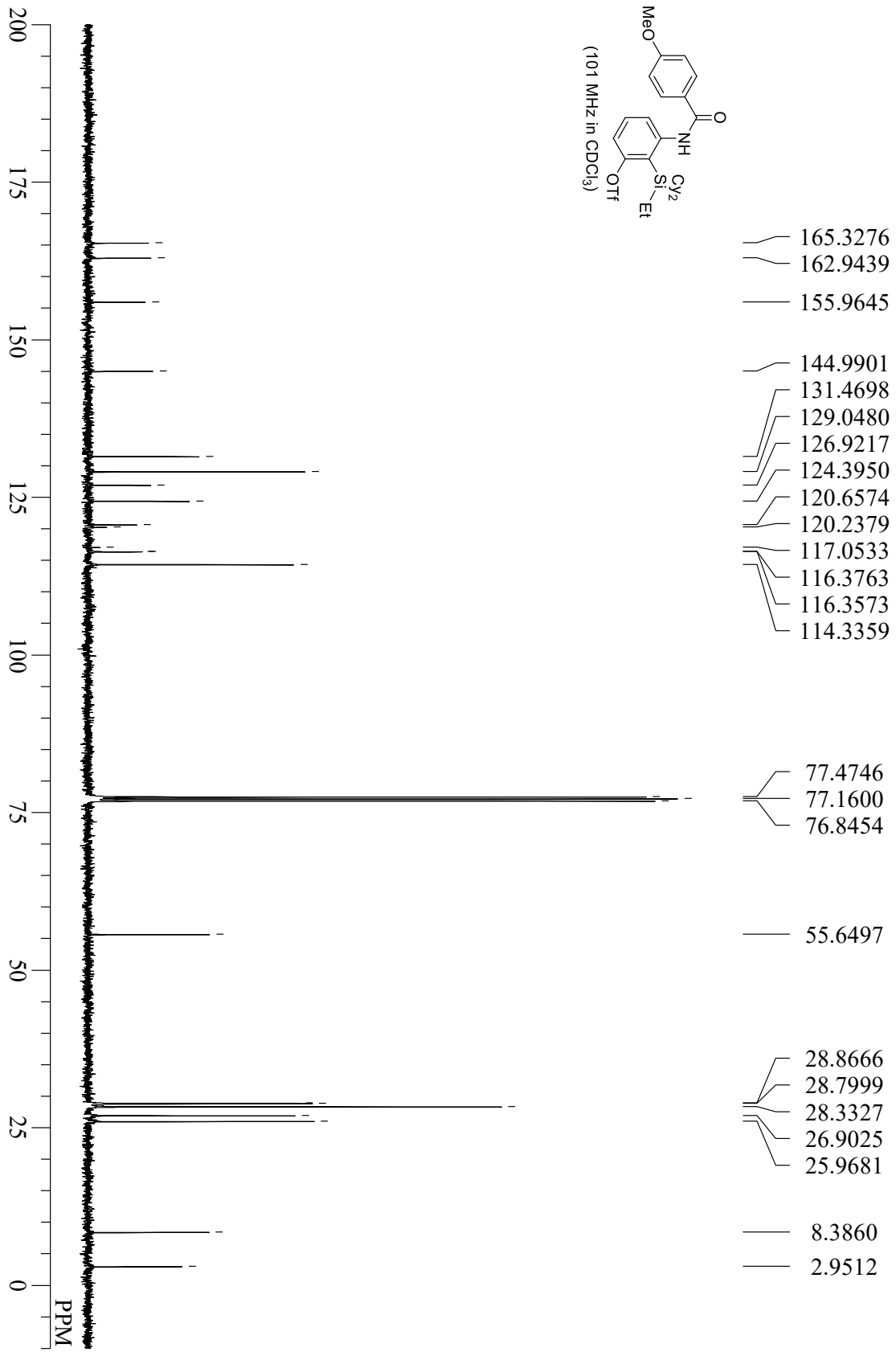
compound **1s**


(101 MHz in CDCl3)
MeO
O
NH
Cy2
Si
Me
OTf
165.3562
162.9058
155.8596
144.6945
131.3363
129.1052
126.6929
124.8622
122.3832
120.2188
117.0342
116.5384
116.5194
114.2596
77.4842
77.1600
76.8454
55.5829
28.5996
28.2945
28.1515
28.0752
26.7594
25.4341
-6.5168
200
175
150
125
100
75
50
25
0
PPM

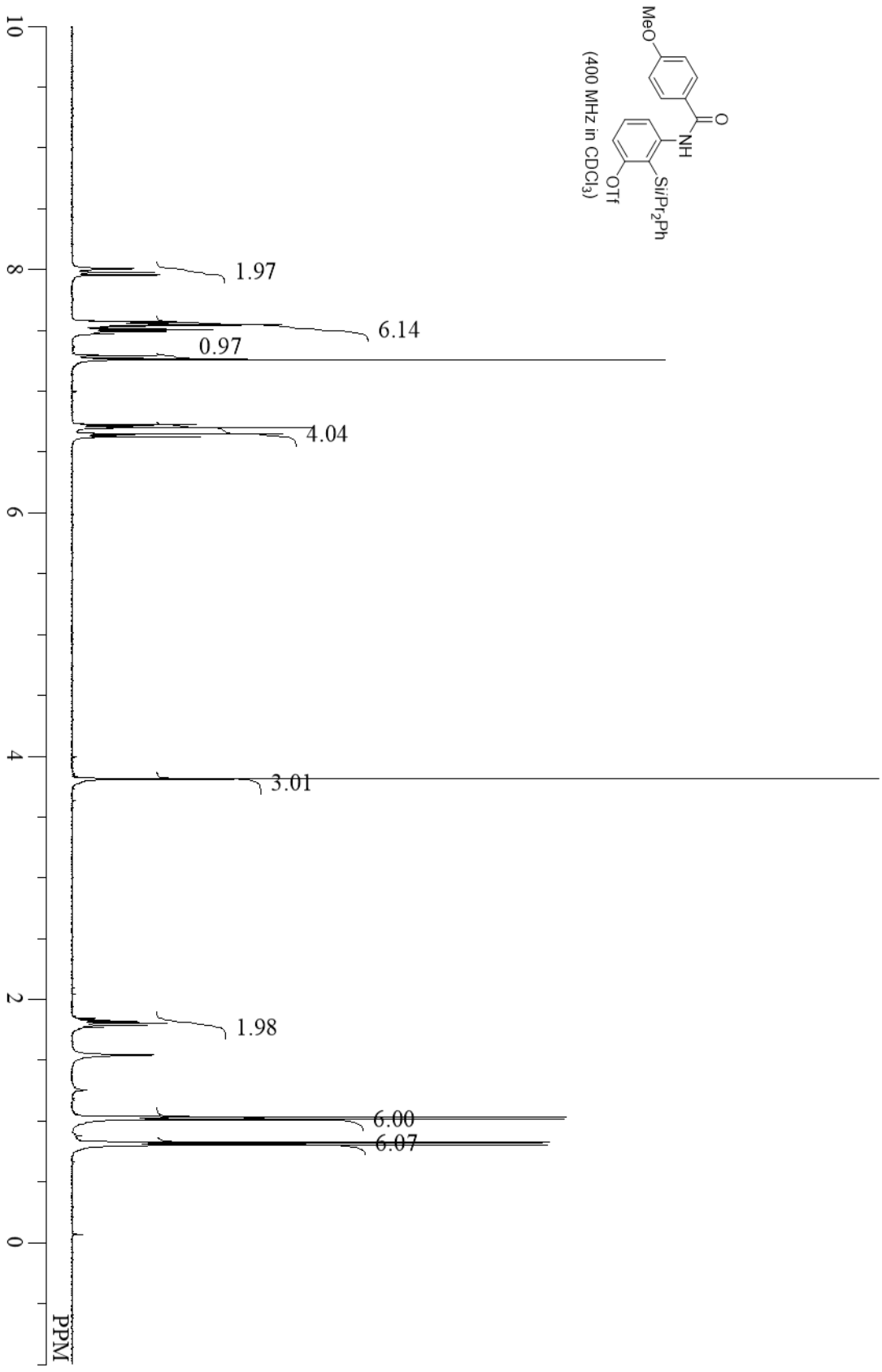
compound **1t**


MeO
O
NH
Cy2
Si
Et
OTf
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
1.98
1.96
0.97
0.94
1.95
3.00
10.44
16.98

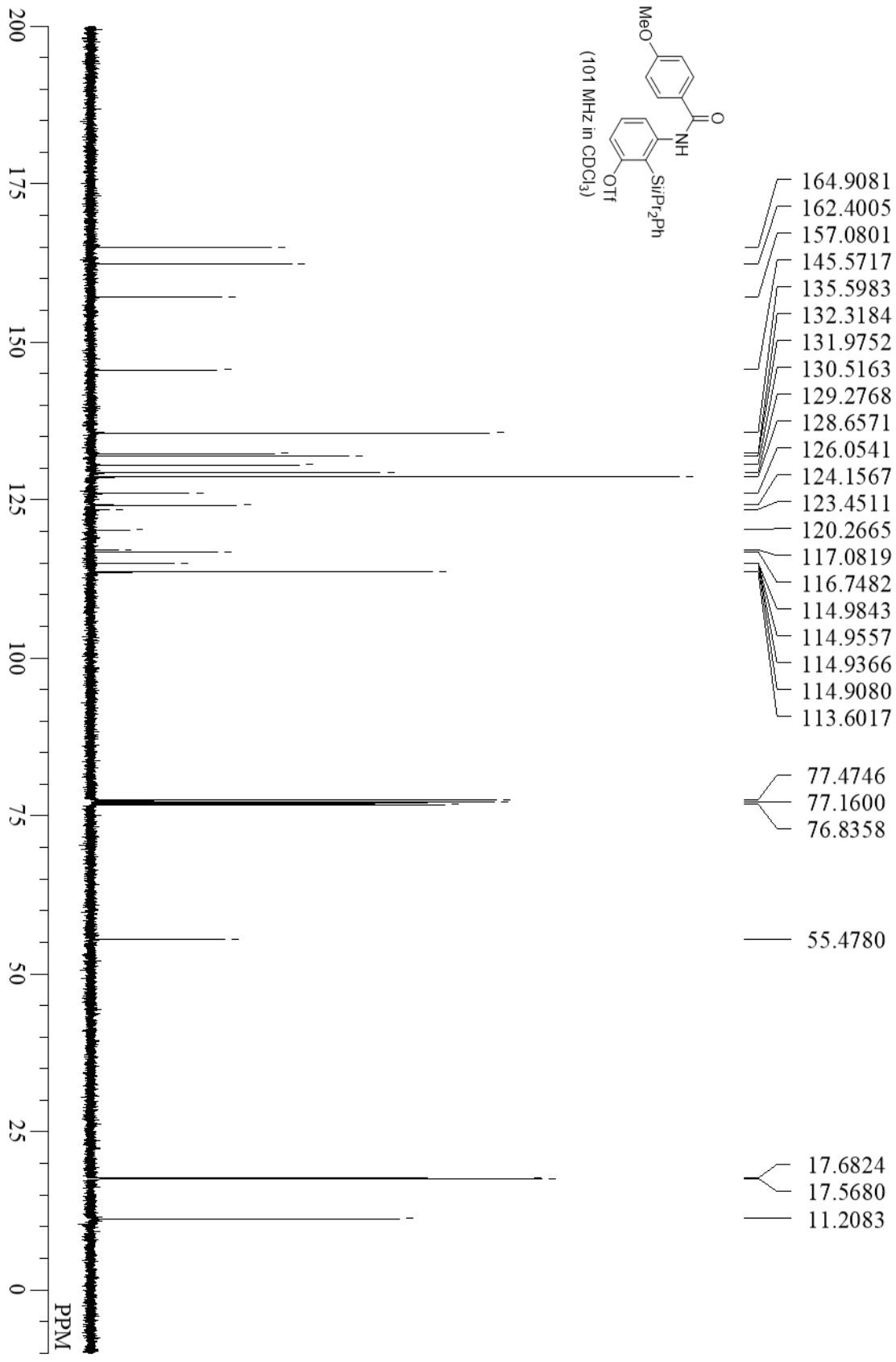
compound **1t**


MeO
O
NH
OTf
Si
Cy2
Et
(101 MHz in CDCl3)
165.3276
162.9439
155.9645
144.9901
131.4698
129.0480
126.9217
124.3950
120.6574
120.2379
117.0533
116.3763
116.3573
114.3359
77.4746
77.1600
76.8454
55.6497
28.8666
28.7999
28.3327
26.9025
25.9681
8.3860
2.9512
200
175
150
125
100
75
50
25
0
PPM

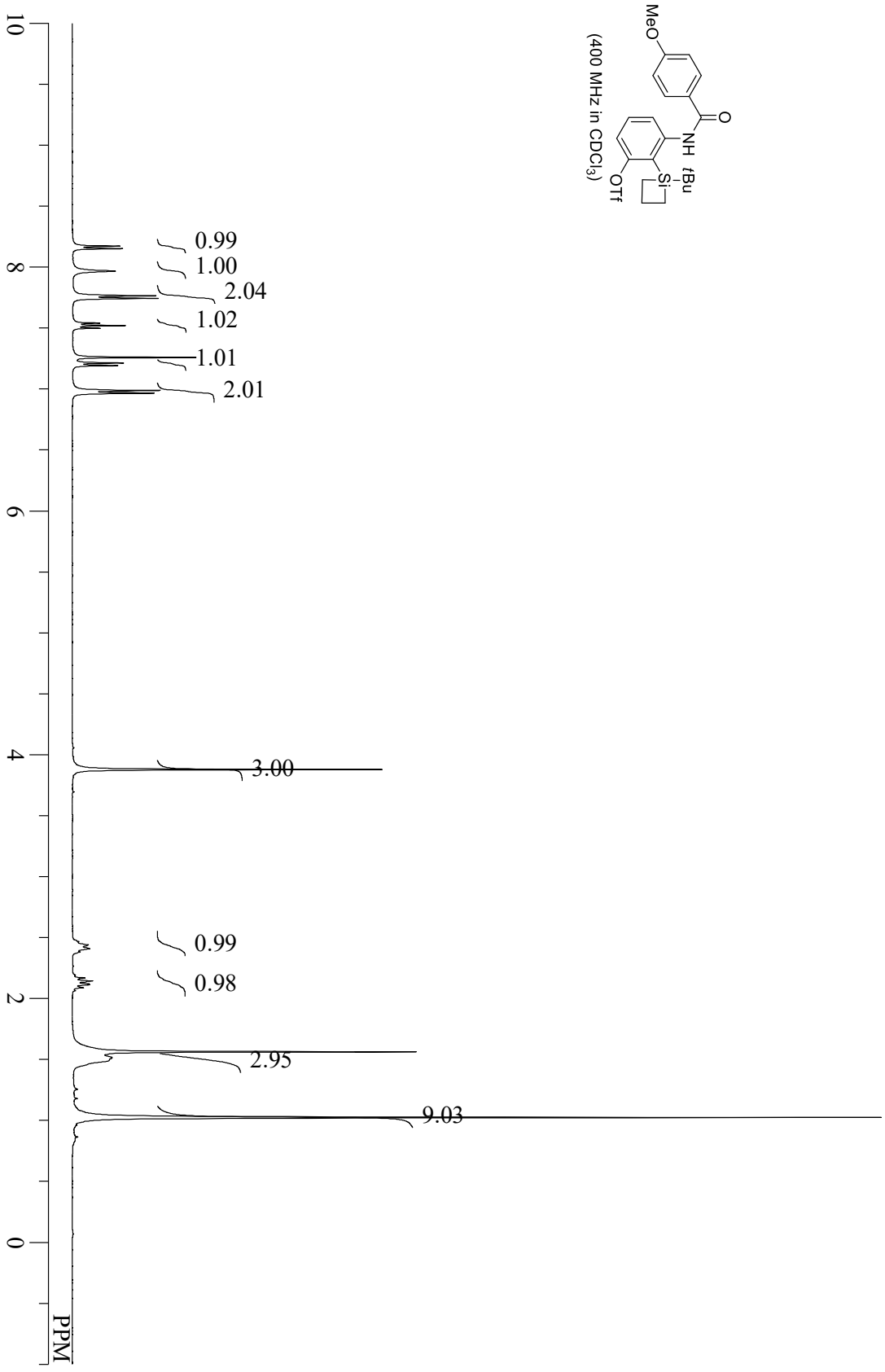
compound **1u**


MeO
O
NH
OTf
SiiPr2Ph
(400 MHz in CDCl3)
1.97
6.14
0.97
4.04
3.01
1.98
6.00
6.07
10
8
6
4
2
0
PPM

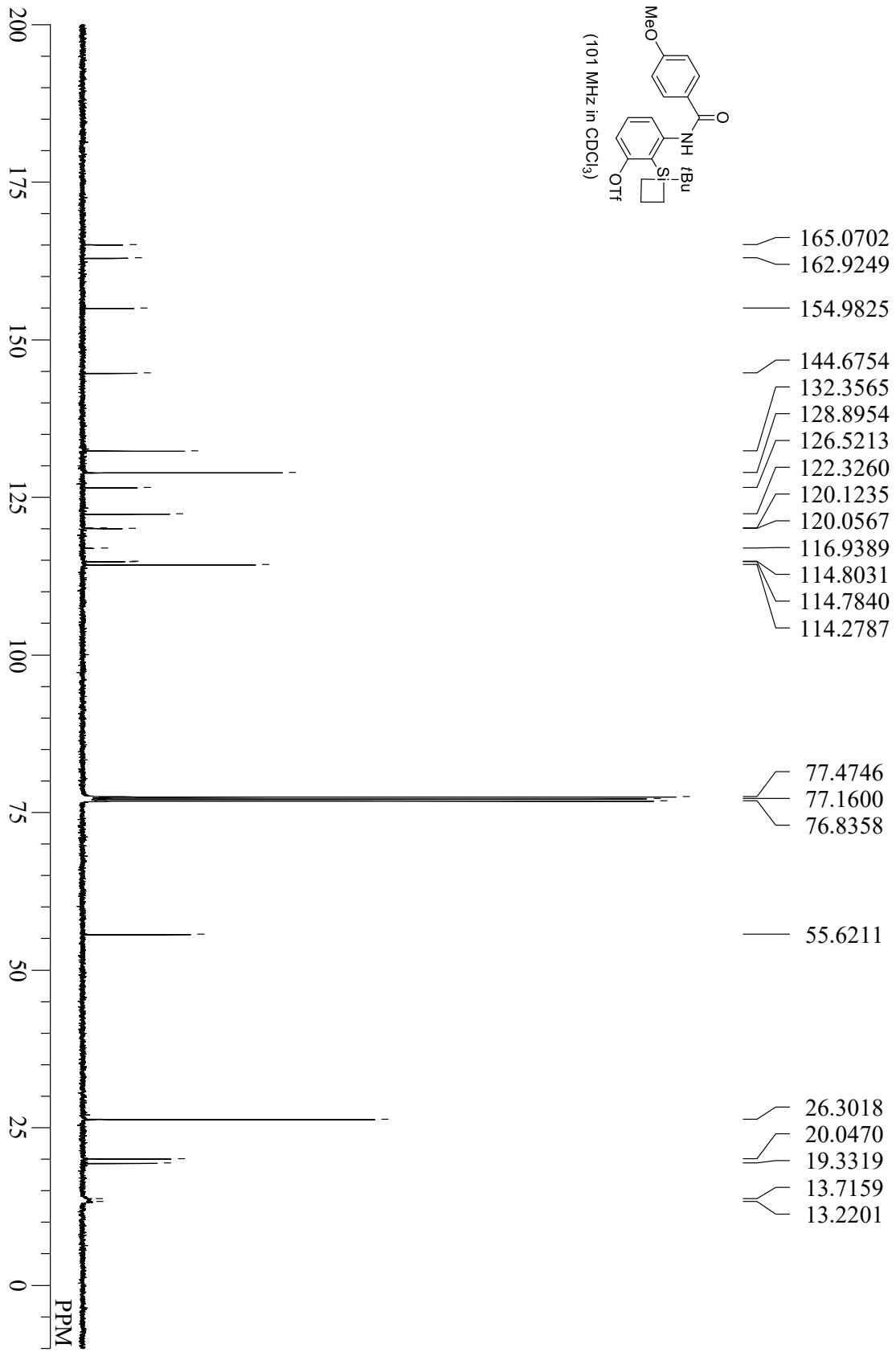
compound **1u**


MeO
O
NH
OTf
SiiPr2Ph
(101 MHz in CDCl3)
164.9081
162.4005
157.0801
145.5717
135.5983
132.3184
131.9752
130.5163
129.2768
128.6571
126.0541
124.1567
123.4511
120.2665
117.0819
116.7482
114.9843
114.9557
114.9366
114.9080
113.6017
77.4746
77.1600
76.8358
55.4780
17.6824
17.5680
11.2083
200
175
150
125
100
75
50
25
0
PPM

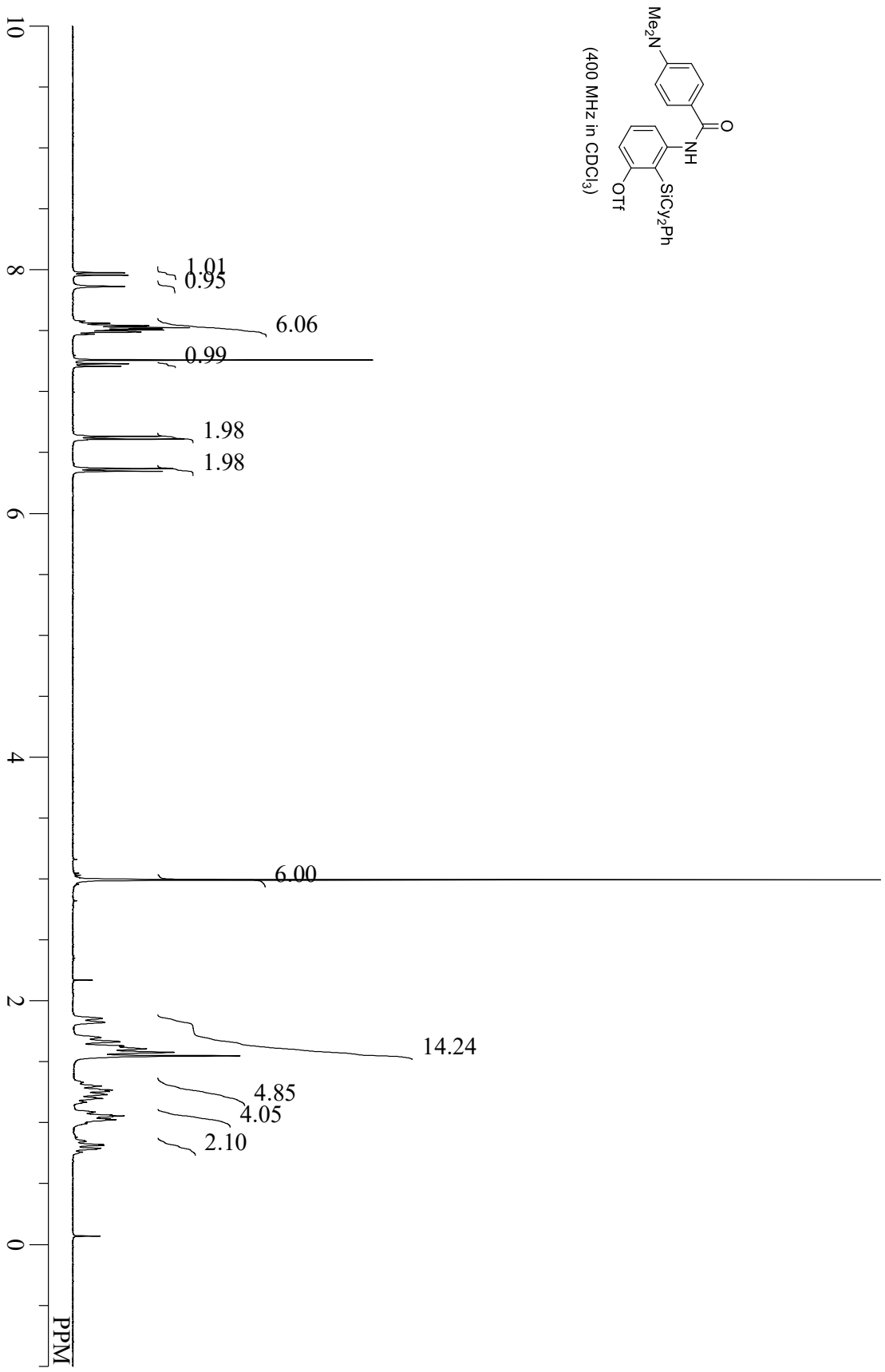
compound **1v**


MeO
O
NH tBu
Si
OTf
(400 MHz in CDCl3)
0.99
1.00
2.04
1.02
1.01
2.01
3.00
0.99
0.98
2.95
9.03
10
8
6
4
2
0
PPM

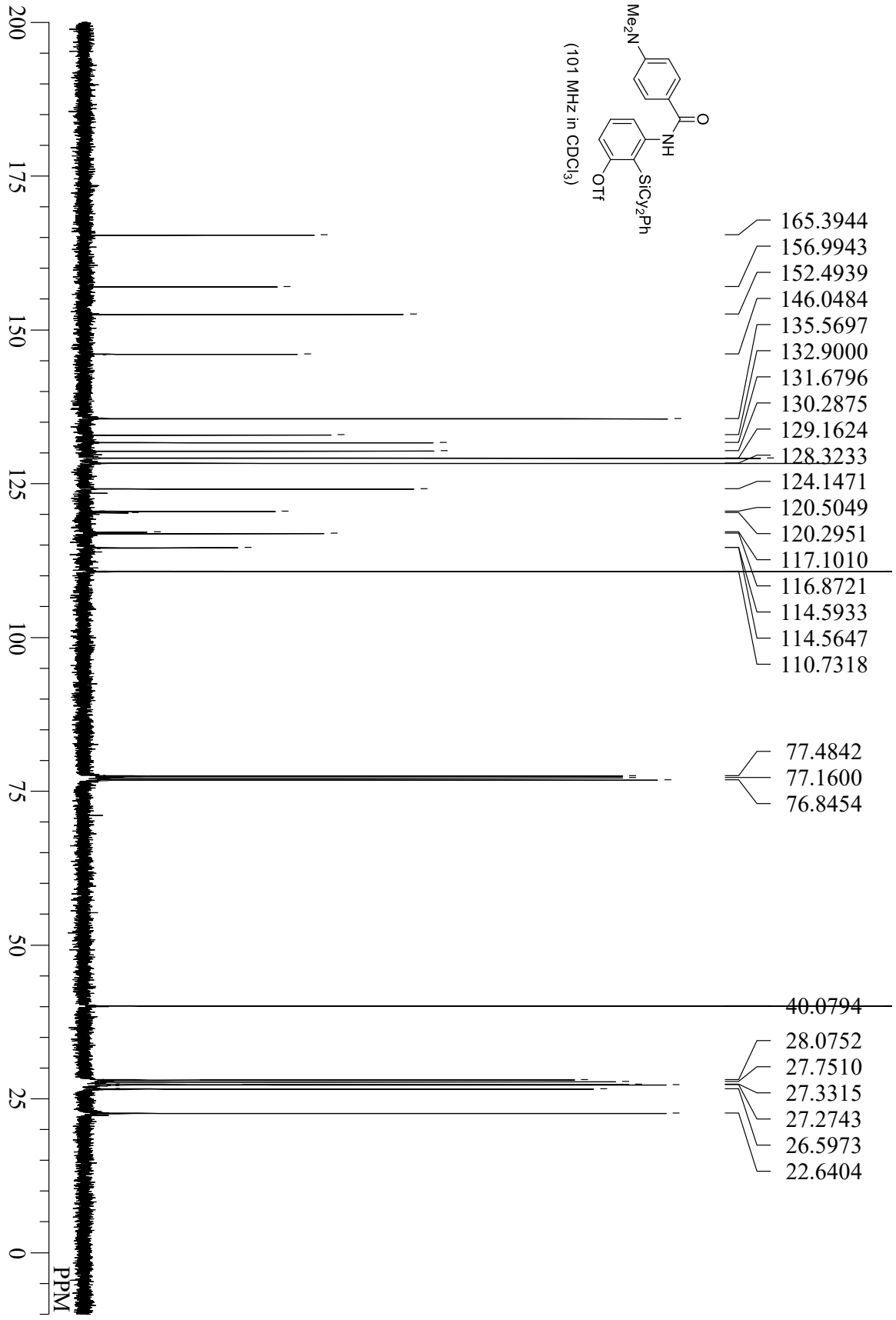
compound **1v**


(101 MHz in CDCl3)
MeO
O
NH
tBu
Si
OTf
165.0702
162.9249
154.9825
144.6754
132.3565
128.8954
126.5213
122.3260
120.1235
120.0567
116.9389
114.8031
114.7840
114.2787
77.4746
77.1600
76.8358
55.6211
26.3018
20.0470
19.3319
13.7159
13.2201
200
175
150
125
100
75
50
25
0
PPM

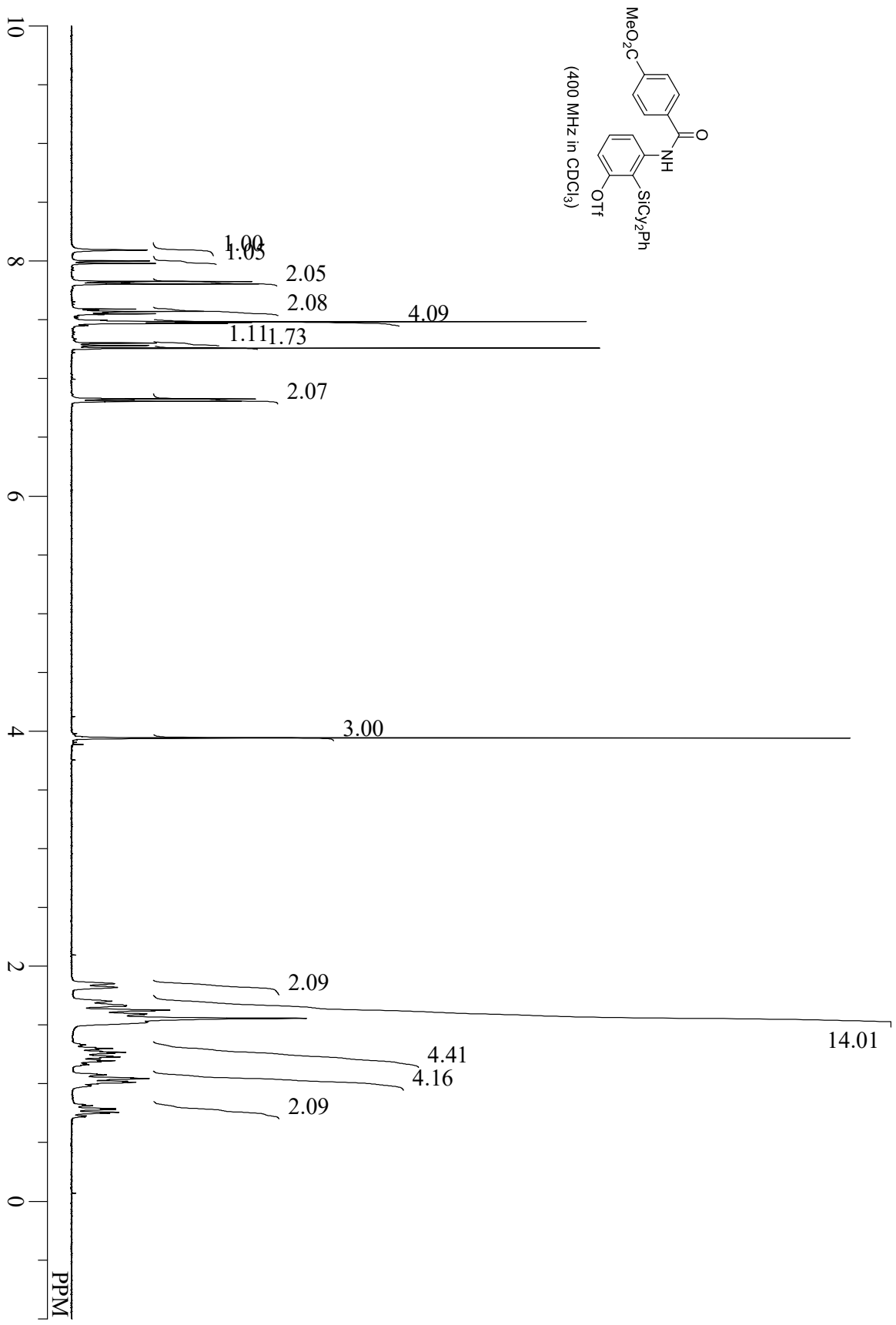
compound **1w**


Me2N
O
NH
OTf
SiCy2Ph
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
1.01
0.95
6.06
0.99
1.98
1.98
6.00
14.24
4.85
4.05
2.10

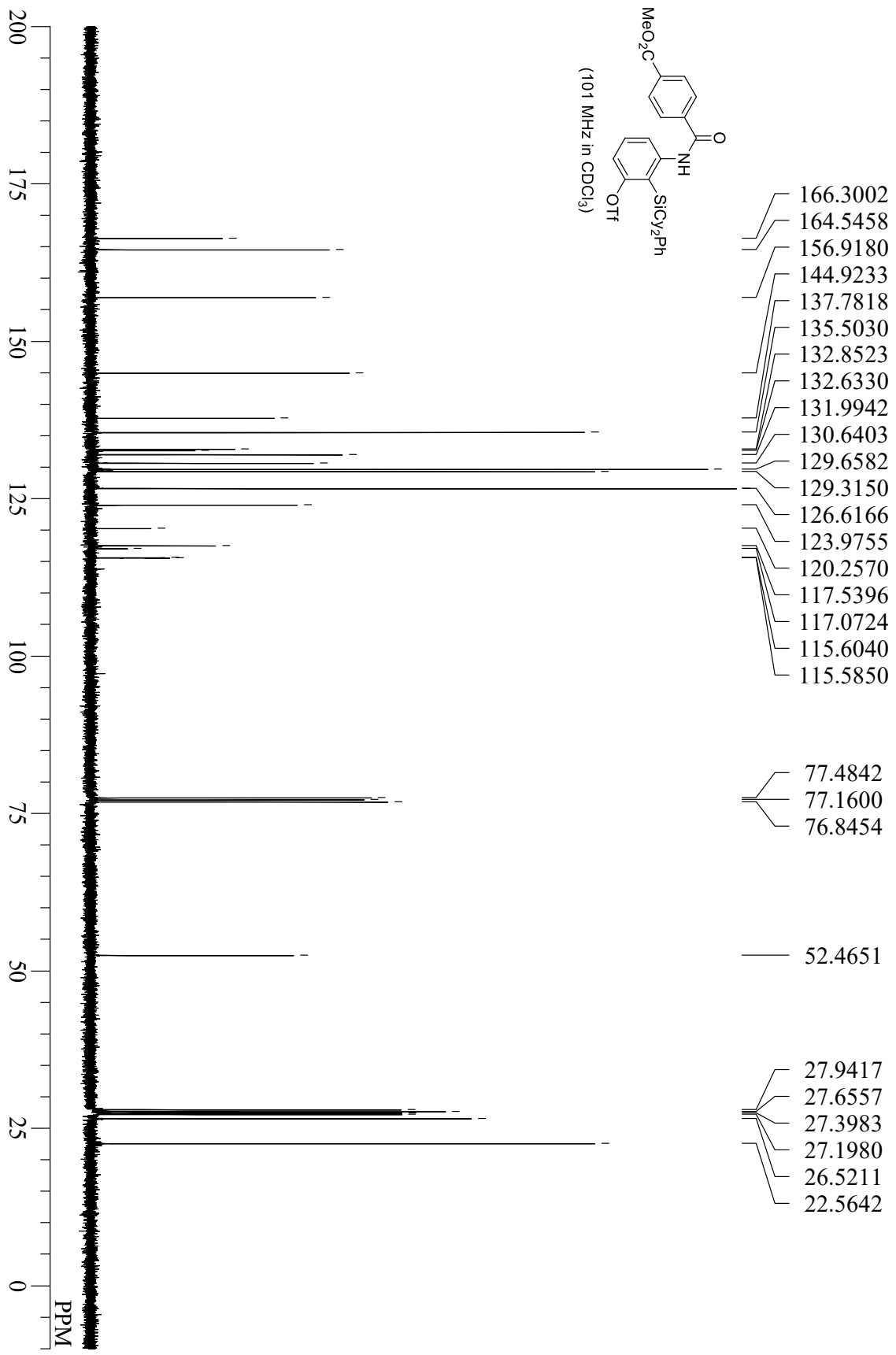
compound **1w**


(101 MHz in CDCl3)
Me2N
O
NH
OTf
SiCy2Ph
165.3944
156.9943
152.4939
146.0484
135.5697
132.9000
131.6796
130.2875
129.1624
128.3233
124.1471
120.5049
120.2951
117.1010
116.8721
114.5933
114.5647
110.7318
77.4842
77.1600
76.8454
40.0794
28.0752
27.7510
27.3315
27.2743
26.5973
22.6404
200
175
150
125
100
75
50
25
0
PPM

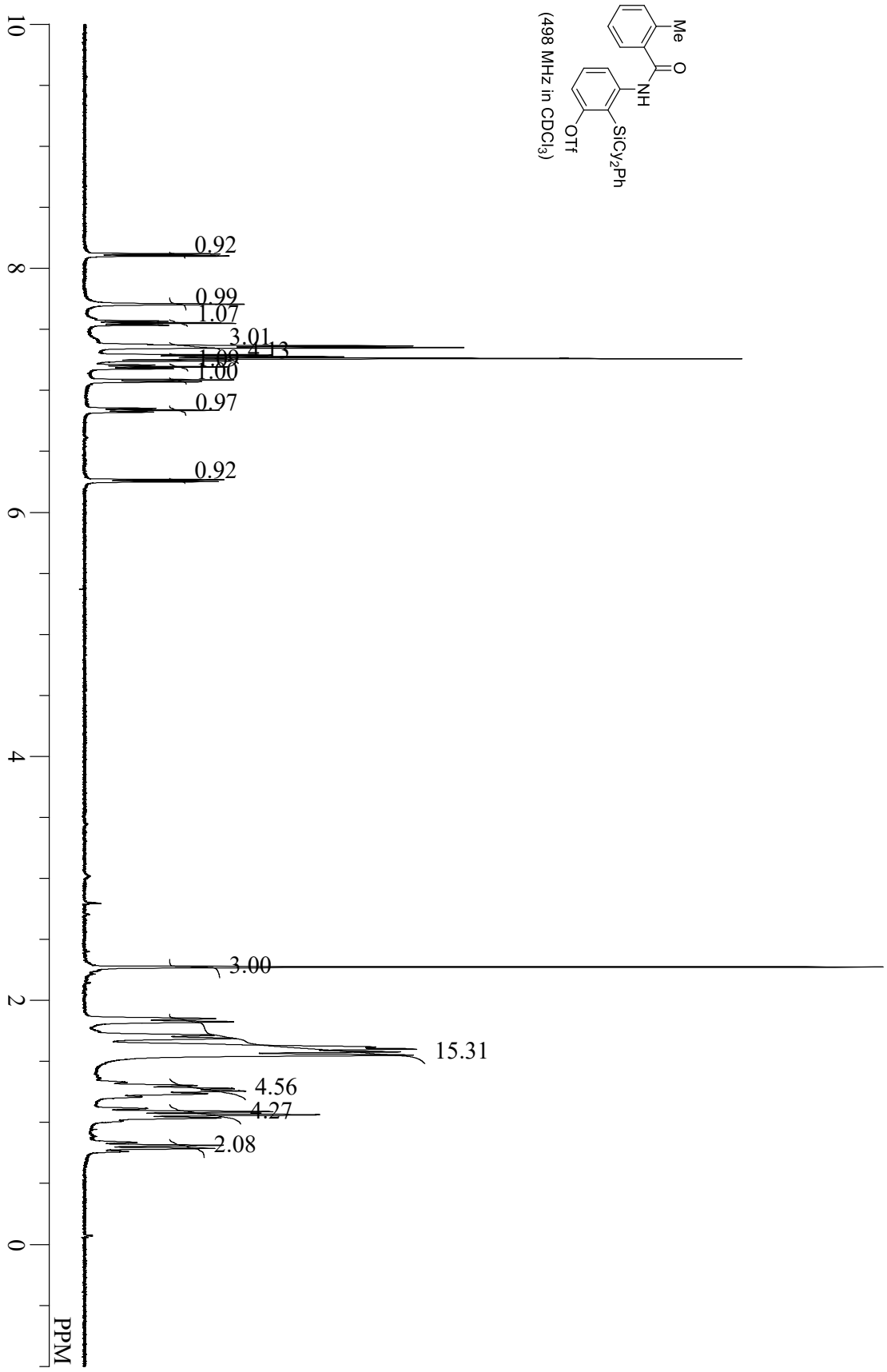
compound **1x**


(400 MHz in CDCl3)
MeO2C
O
NH
OTf
SiCy2Ph
1.00
1.05
2.05
2.08
4.09
1.11
1.73
2.07
3.00
2.09
14.01
4.41
4.16
2.09
10
8
6
4
2
0
PPM

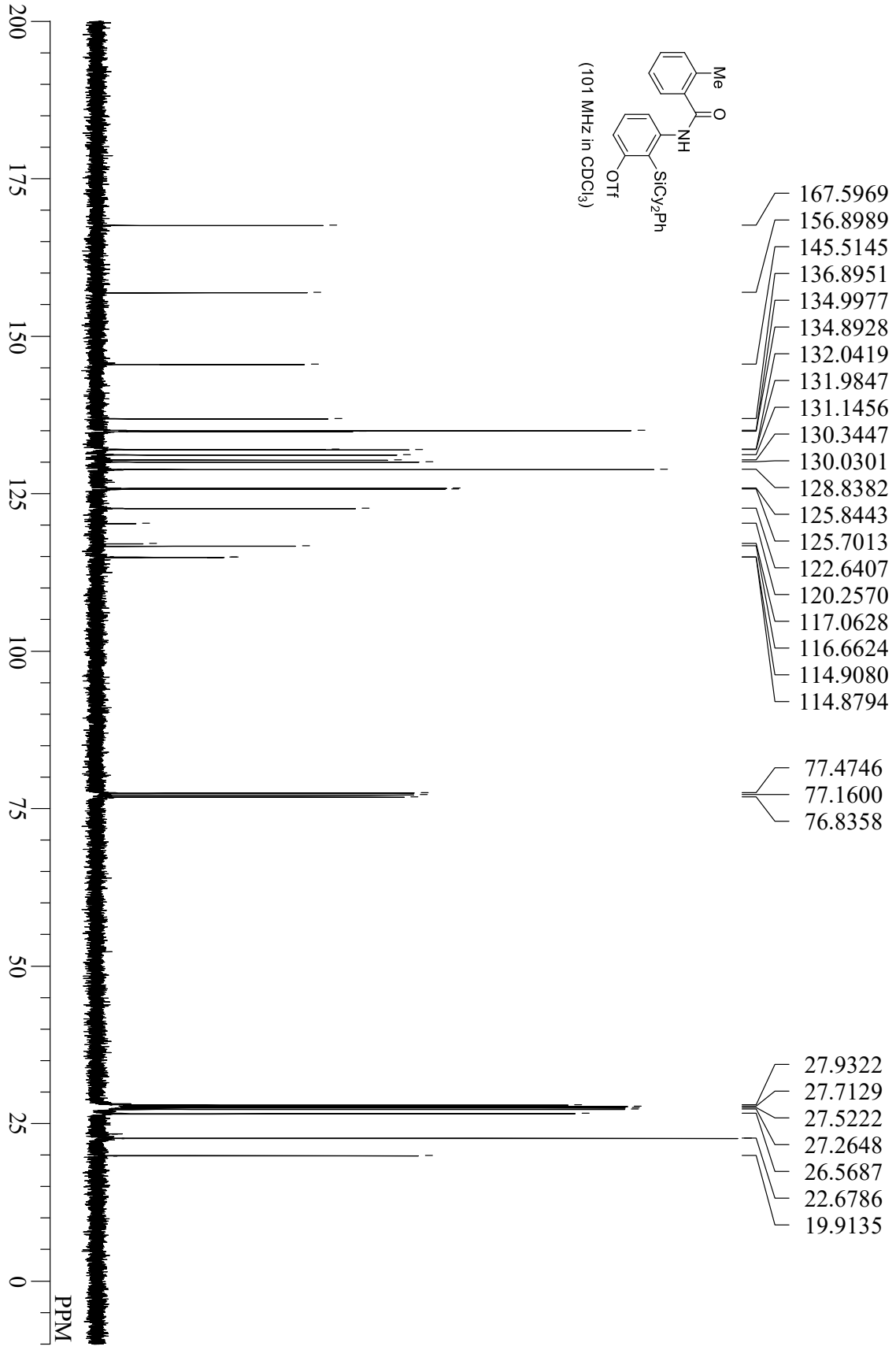
compound **1x**


(101 MHz in CDCl3)
MeO2C
O
NH
OTf
SiCy2Ph
166.3002
164.5458
156.9180
144.9233
137.7818
135.5030
132.8523
132.6330
131.9942
130.6403
129.6582
129.3150
126.6166
123.9755
120.2570
117.5396
117.0724
115.6040
115.5850
77.4842
77.1600
76.8454
52.4651
27.9417
27.6557
27.3983
27.1980
26.5211
22.5642
200
175
150
125
100
75
50
25
0
PPM

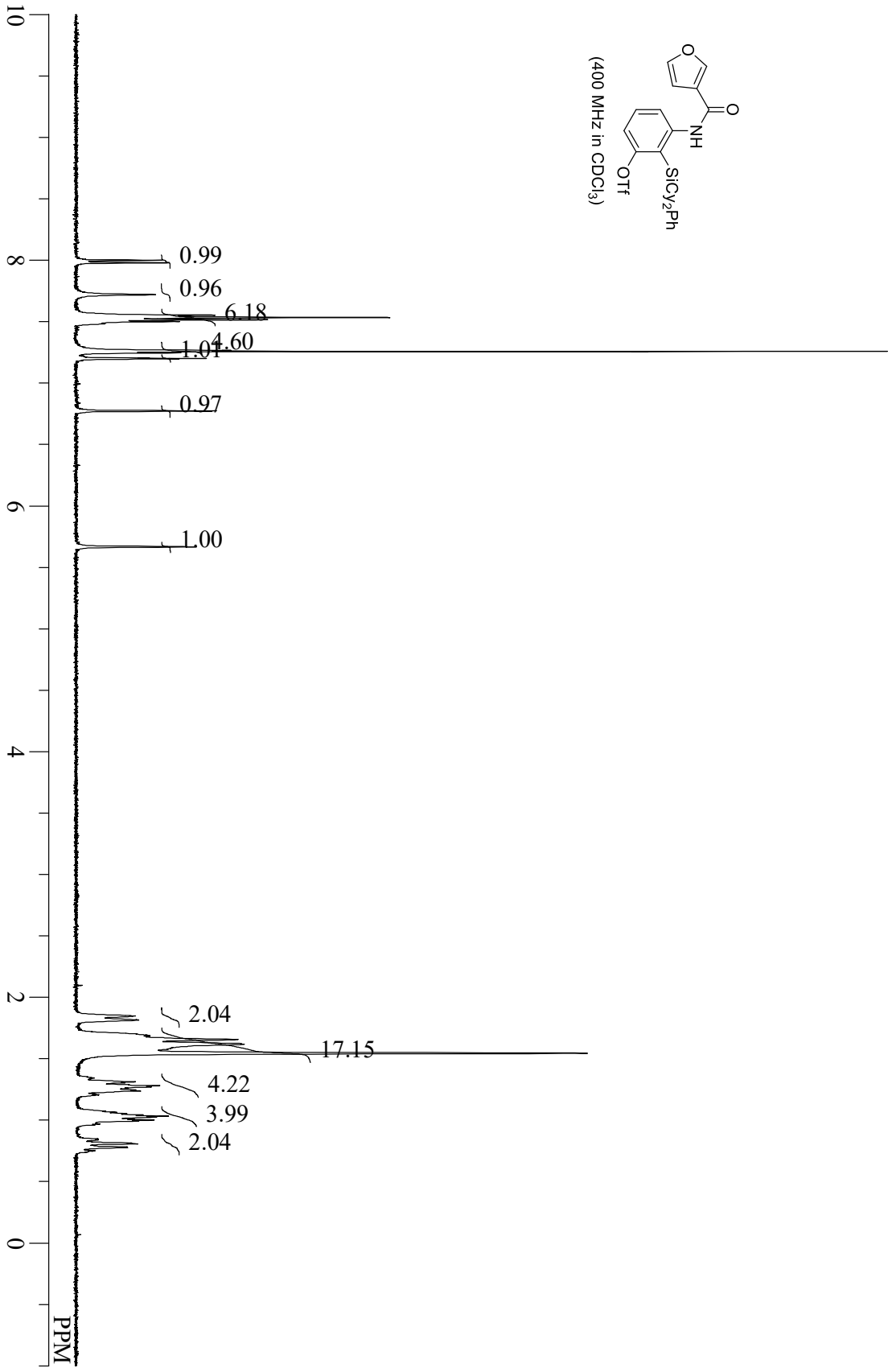
compound **1y**


(498 MHz in CDCl3)
Me
O
NH
OTf
SiCy2Ph
0.92
0.99
1.07
3.01
1.00
0.97
0.92
3.00
15.31
4.56
4.27
2.08
PPM

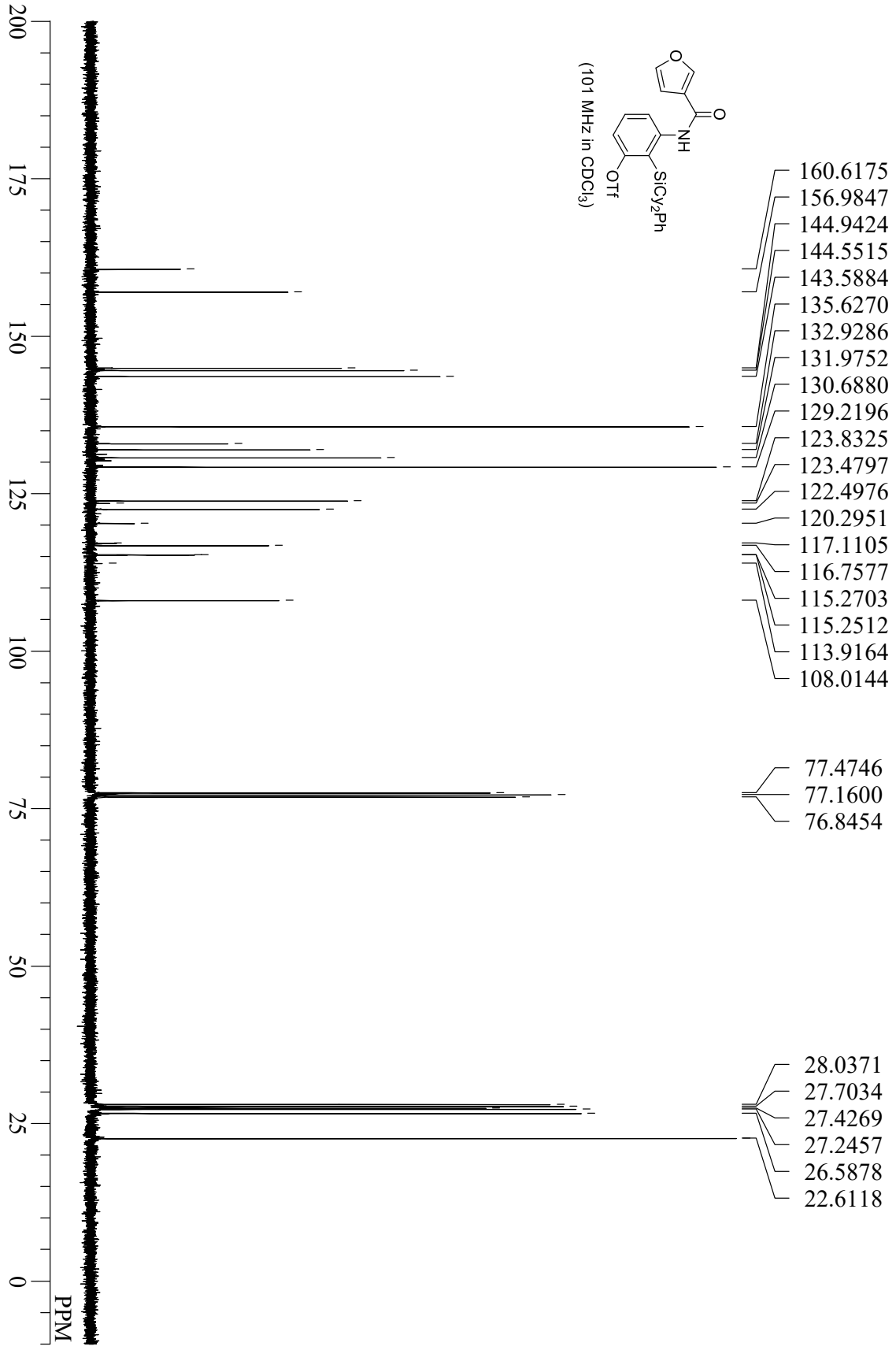
compound **1y**


(101 MHz in CDCl3)
Me
O
NH
SiCy2Ph
OTf
167.5969
156.8989
145.5145
136.8951
134.9977
134.8928
132.0419
131.9847
131.1456
130.3447
130.0301
128.8382
125.8443
125.7013
122.6407
120.2570
117.0628
116.6624
114.9080
114.8794
77.4746
77.1600
76.8358
27.9322
27.7129
27.5222
27.2648
26.5687
22.6786
19.9135
200
175
150
125
100
75
50
25
0
PPM

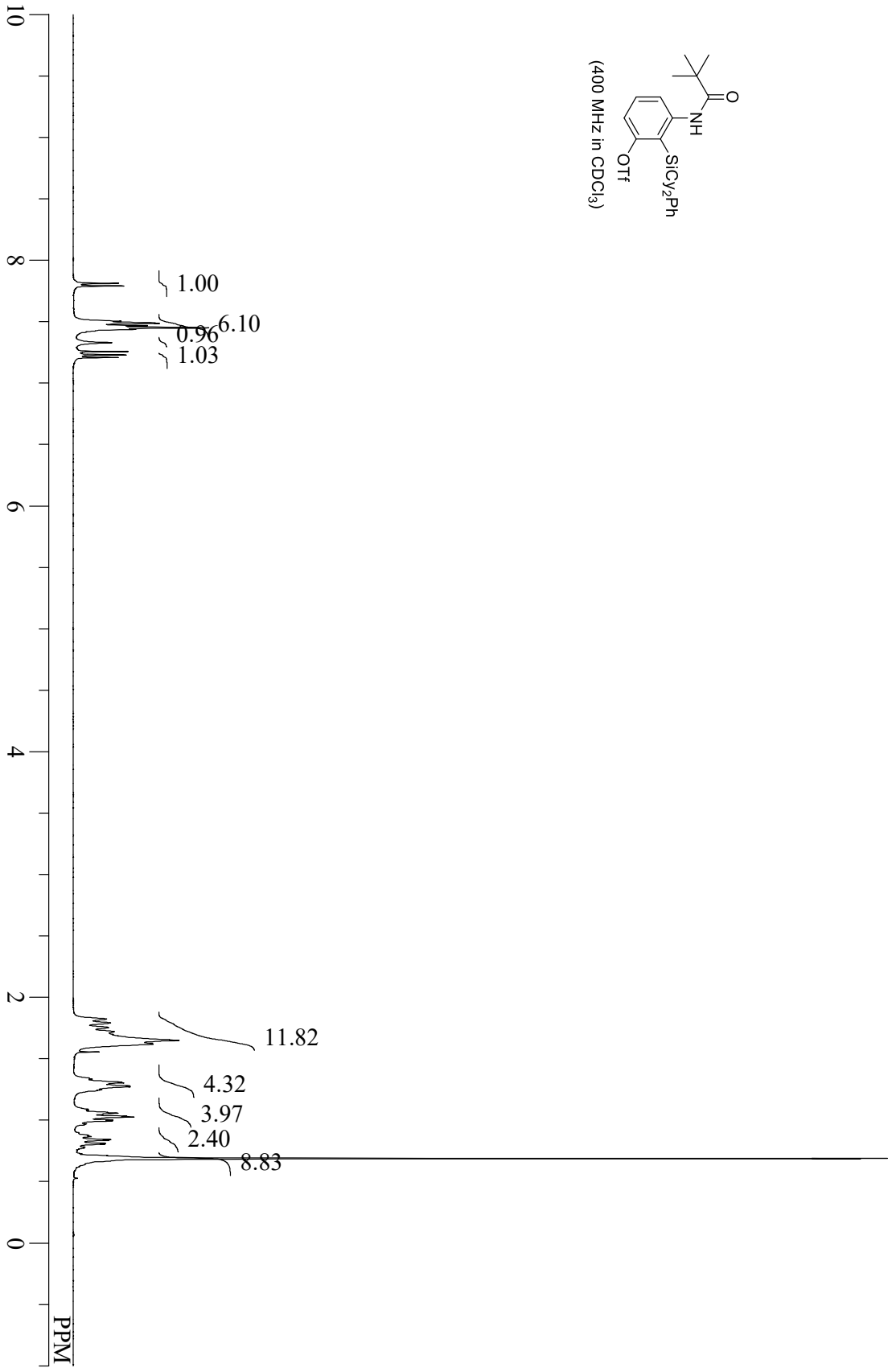
compound **1z**


(400 MHz in CDCl3)
OTf
SiCy2Ph
NH
O
O
0.99
0.96
6.18
4.60
1.01
0.97
1.00
2.04
17.15
4.22
3.99
2.04
PPM
10
8
6
4
2
0

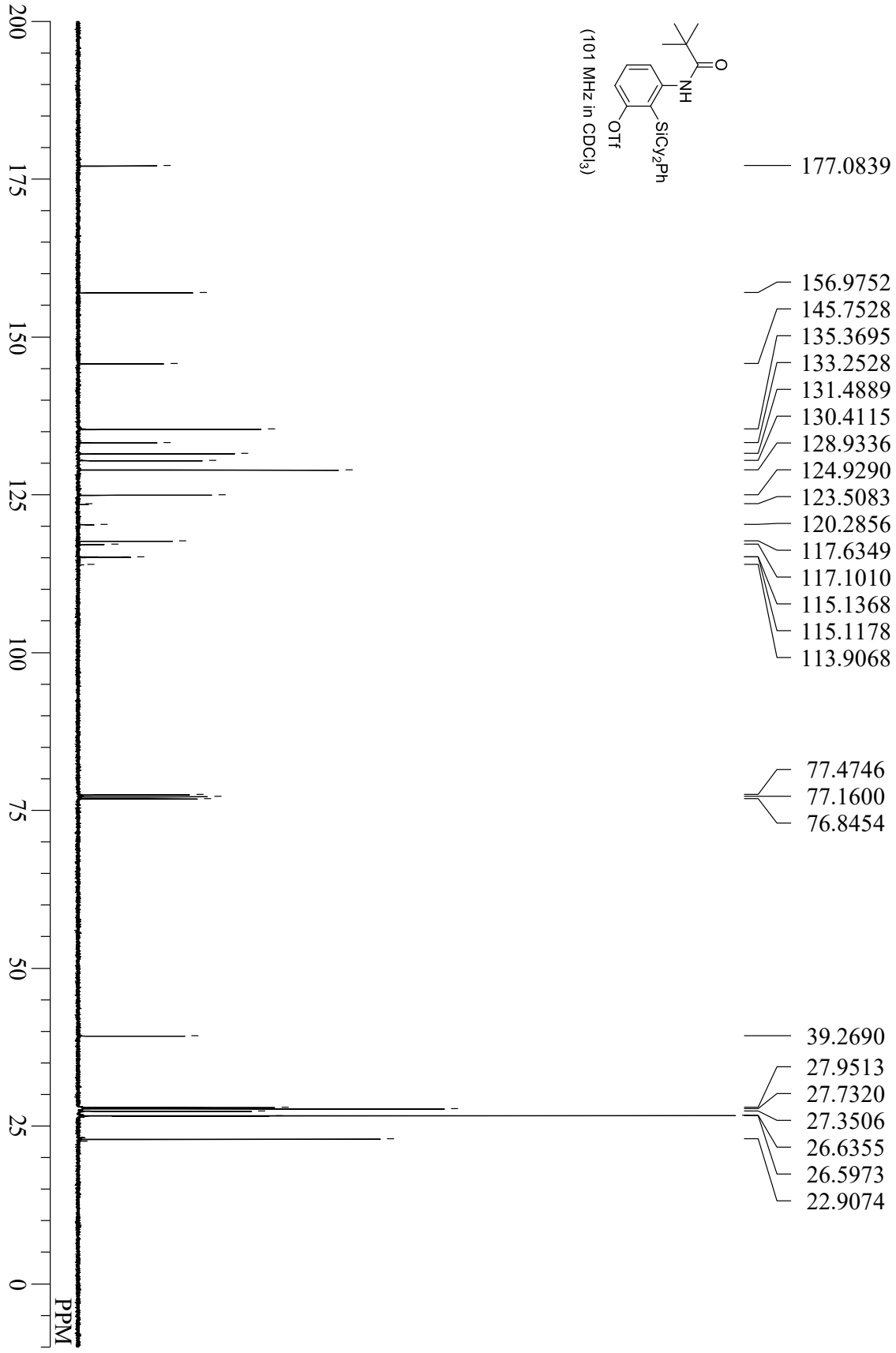
compound **1z**


(101 MHz in CDCl3)
O
NH
O
OTf
SiCy2Ph
160.6175
156.9847
144.9424
144.5515
143.5884
135.6270
132.9286
131.9752
130.6880
129.2196
123.8325
123.4797
122.4976
120.2951
117.1105
116.7577
115.2703
115.2512
113.9164
108.0144
77.4746
77.1600
76.8454
28.0371
27.7034
27.4269
27.2457
26.5878
22.6118
200
175
150
125
100
75
50
25
0
PPM

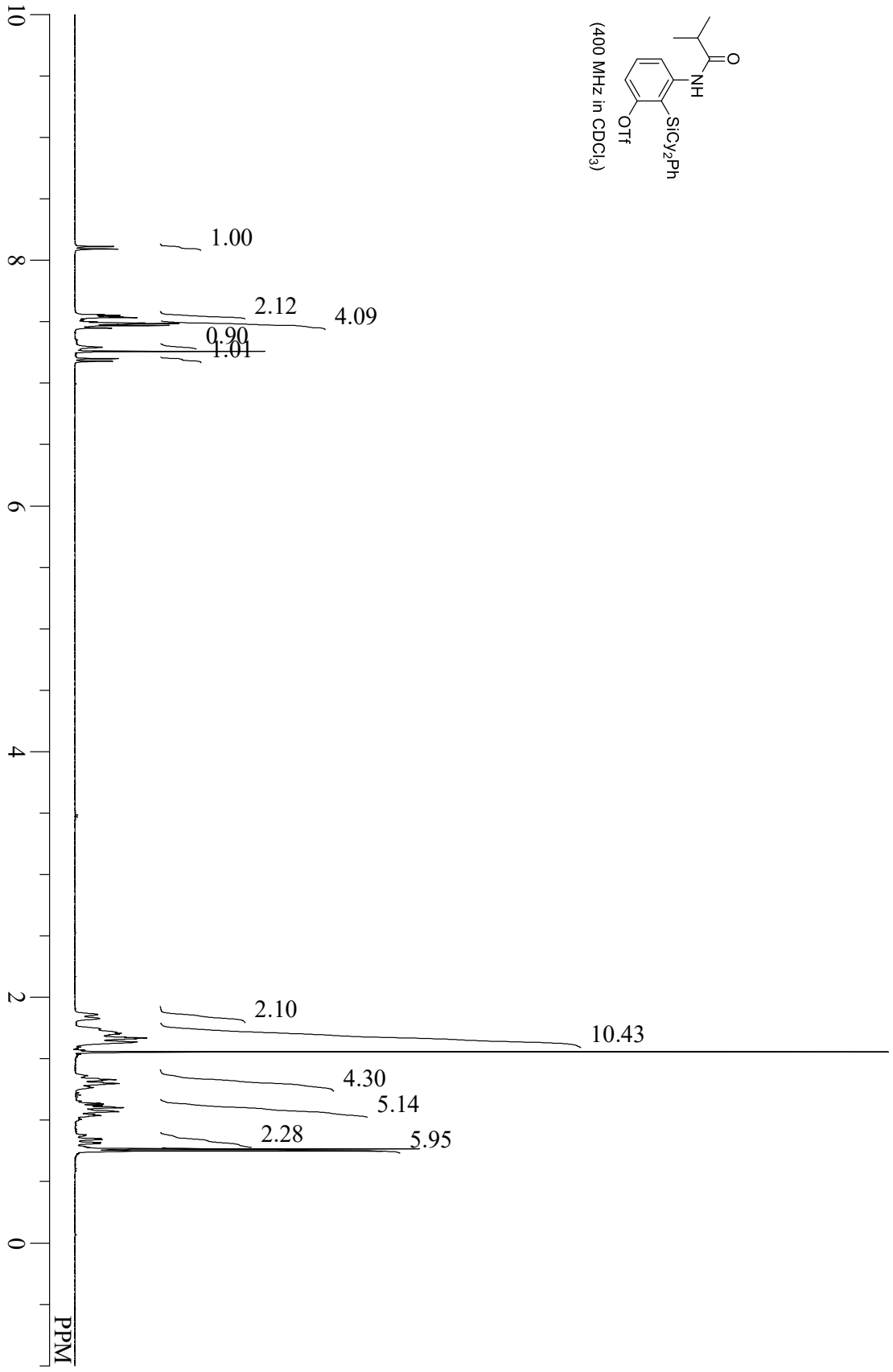
compound **1aa**



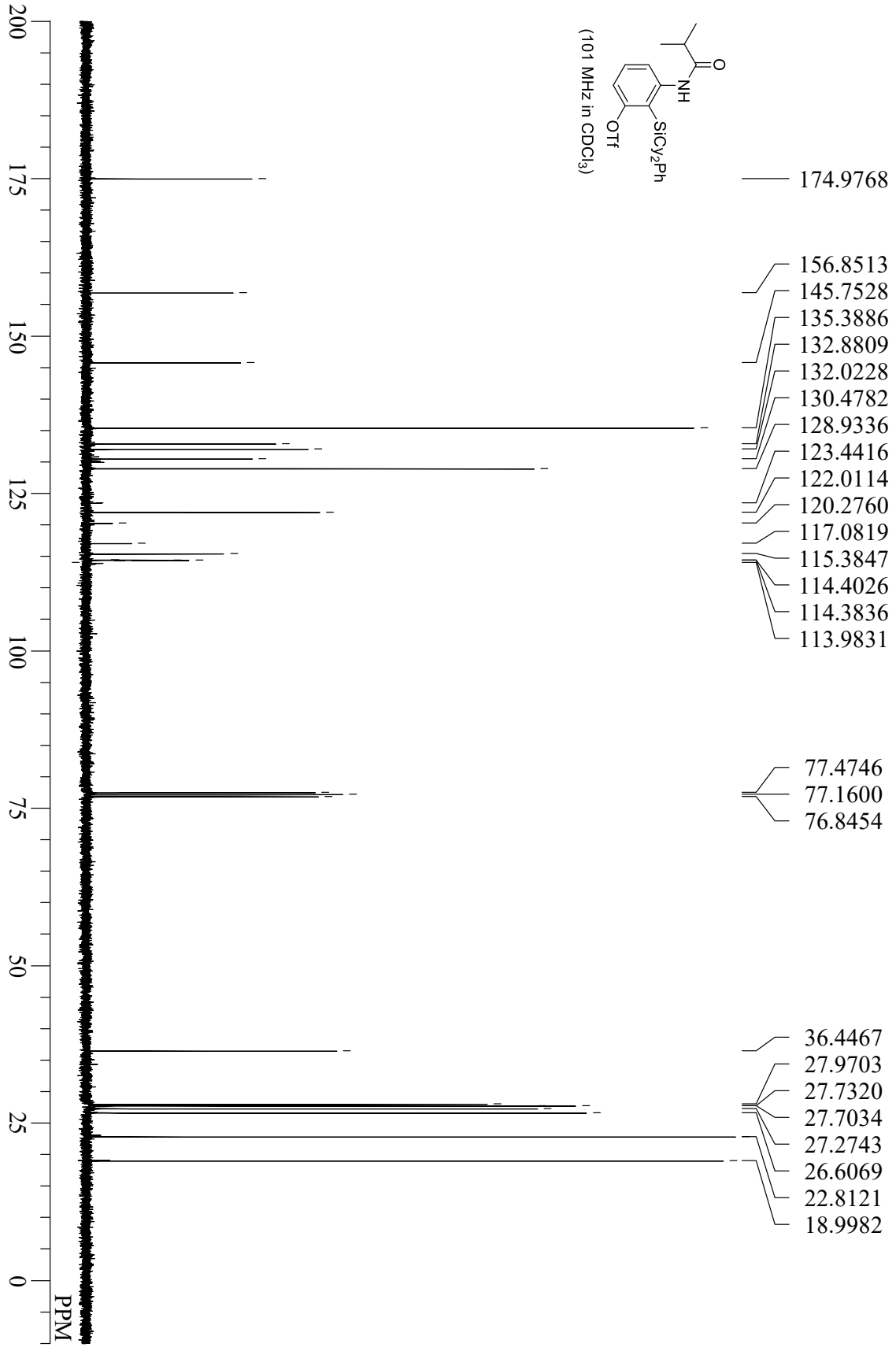
compound **1aa**



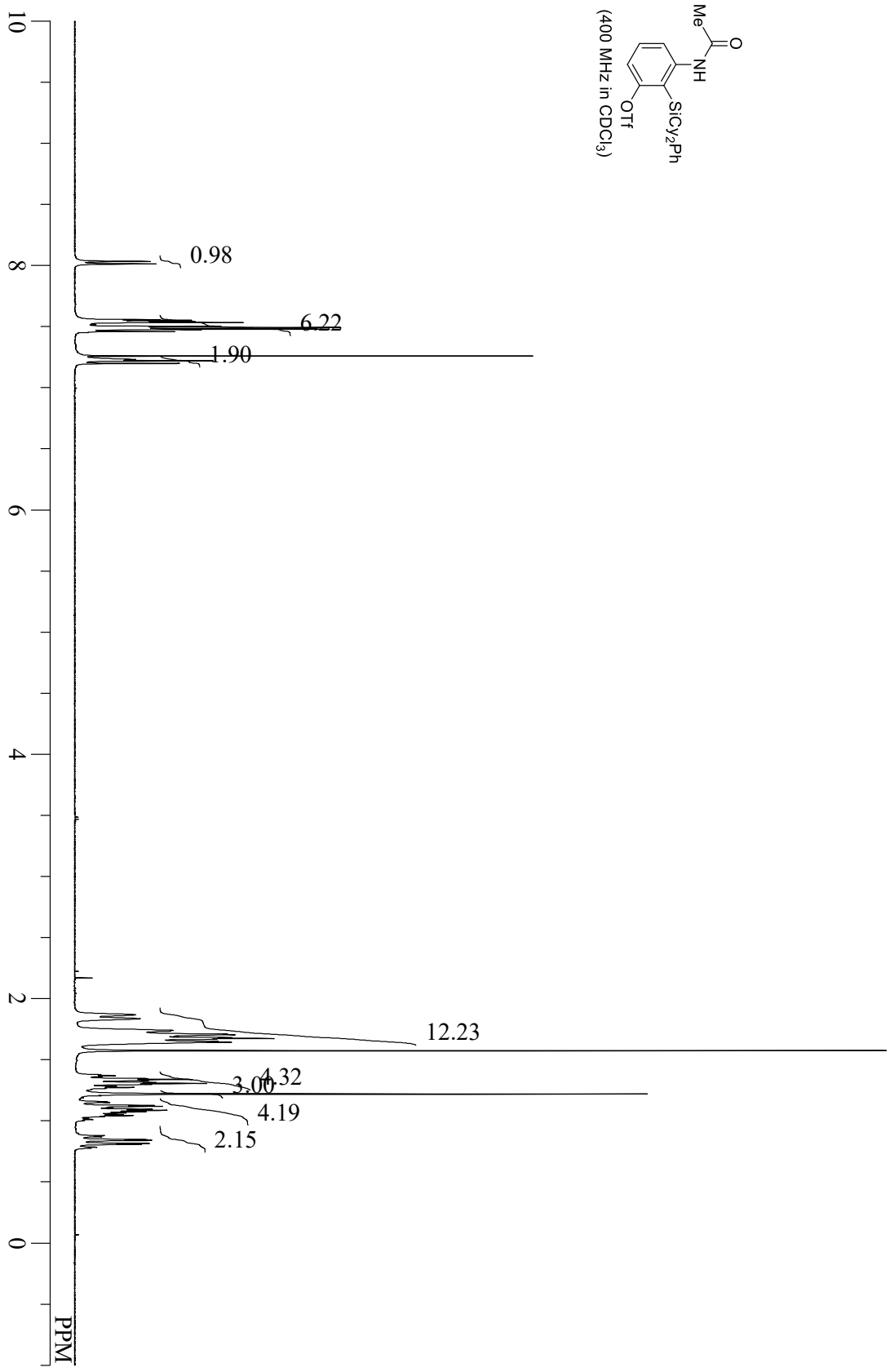
compound **1bb**



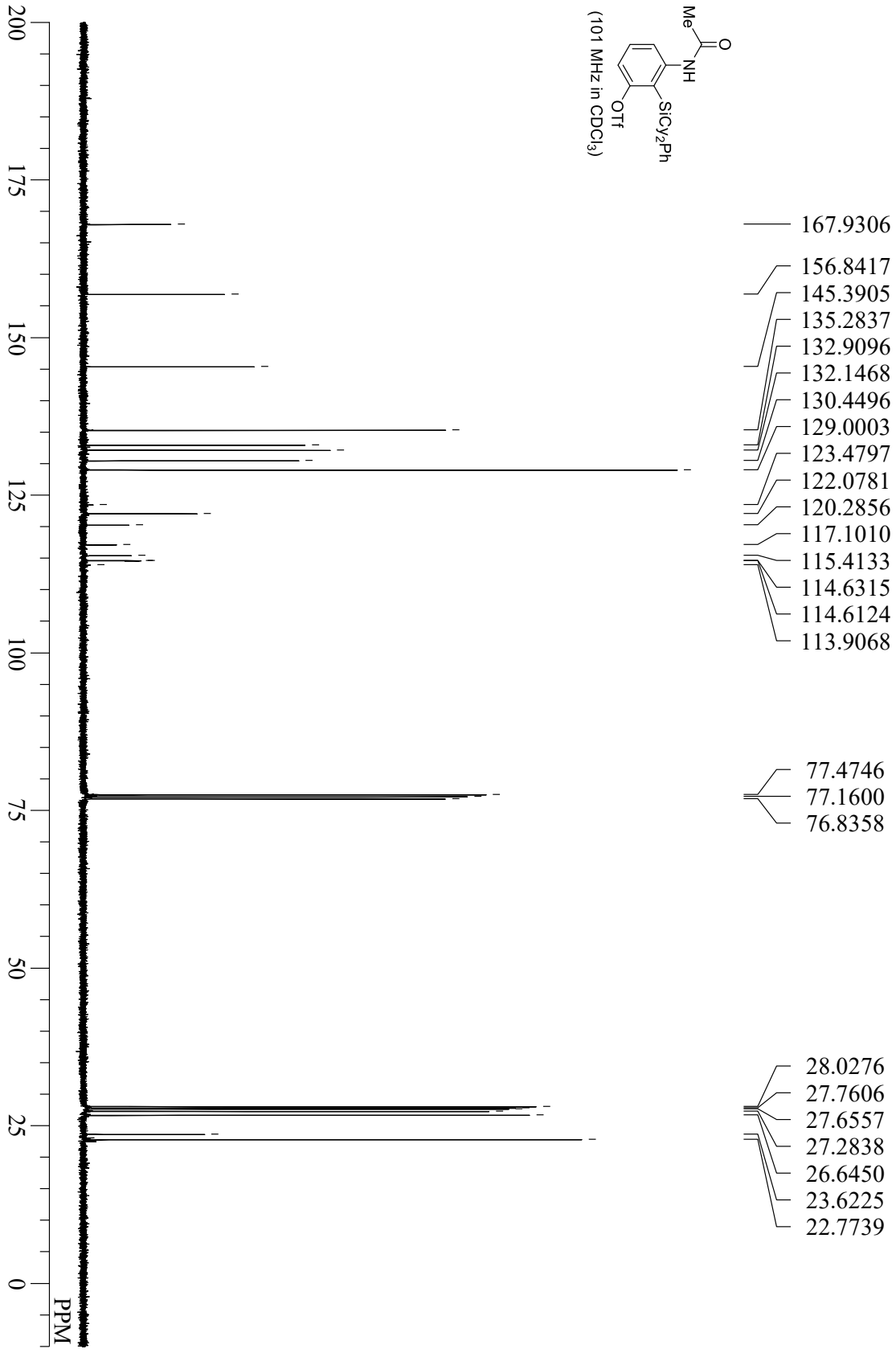
compound **1bb**



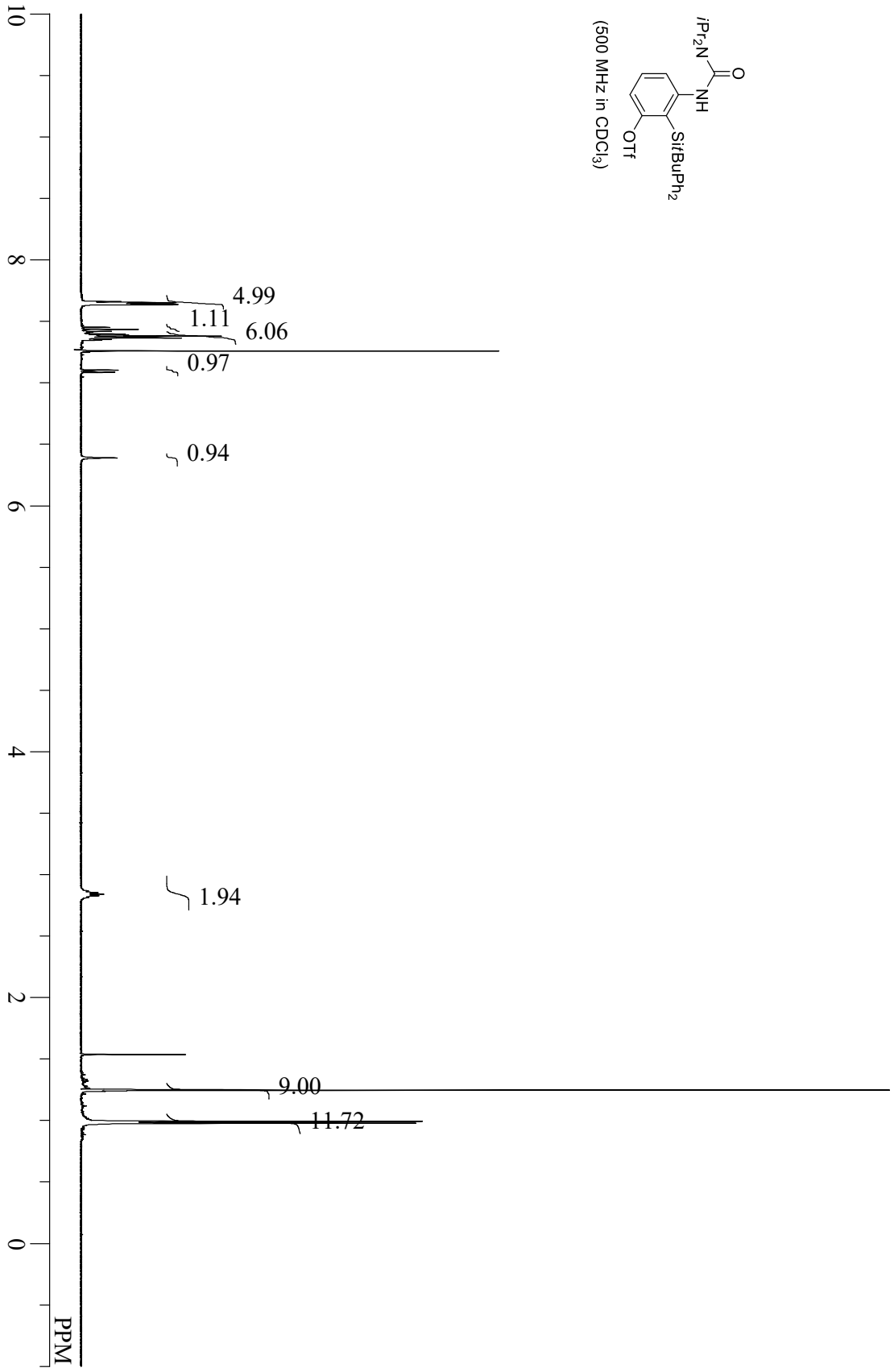
compound **1cc**



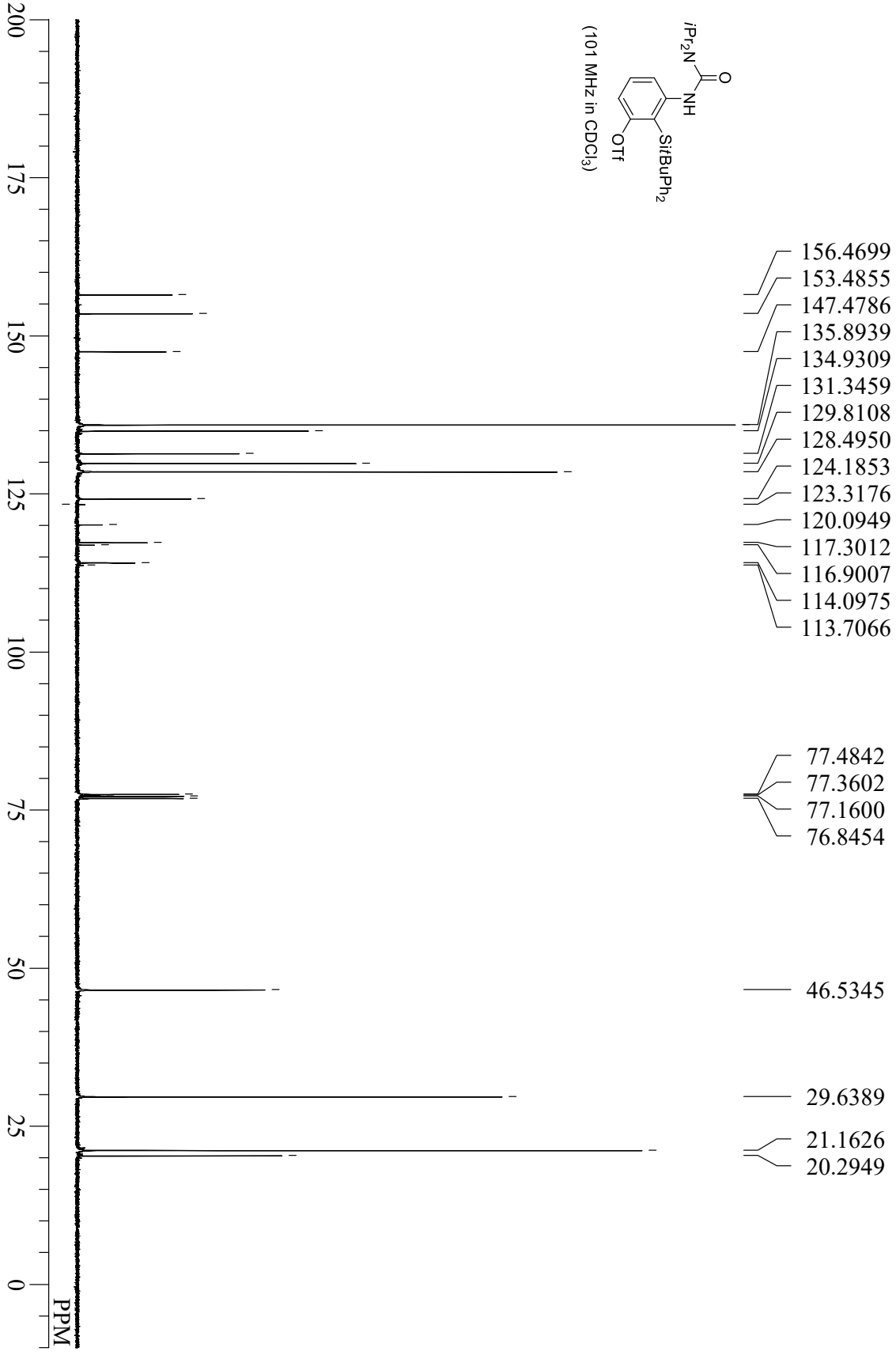
compound **1cc**



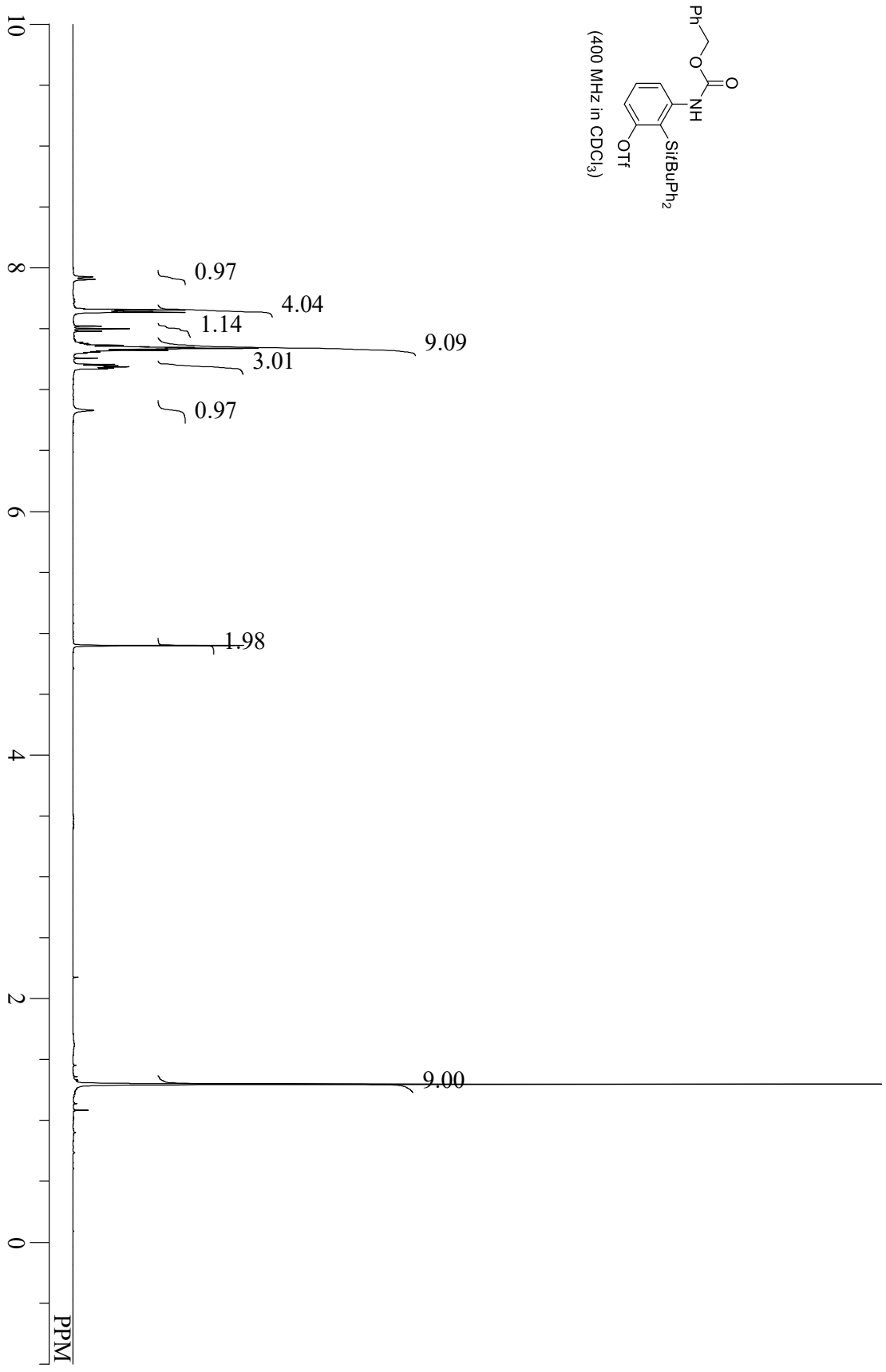
compound **1dd**



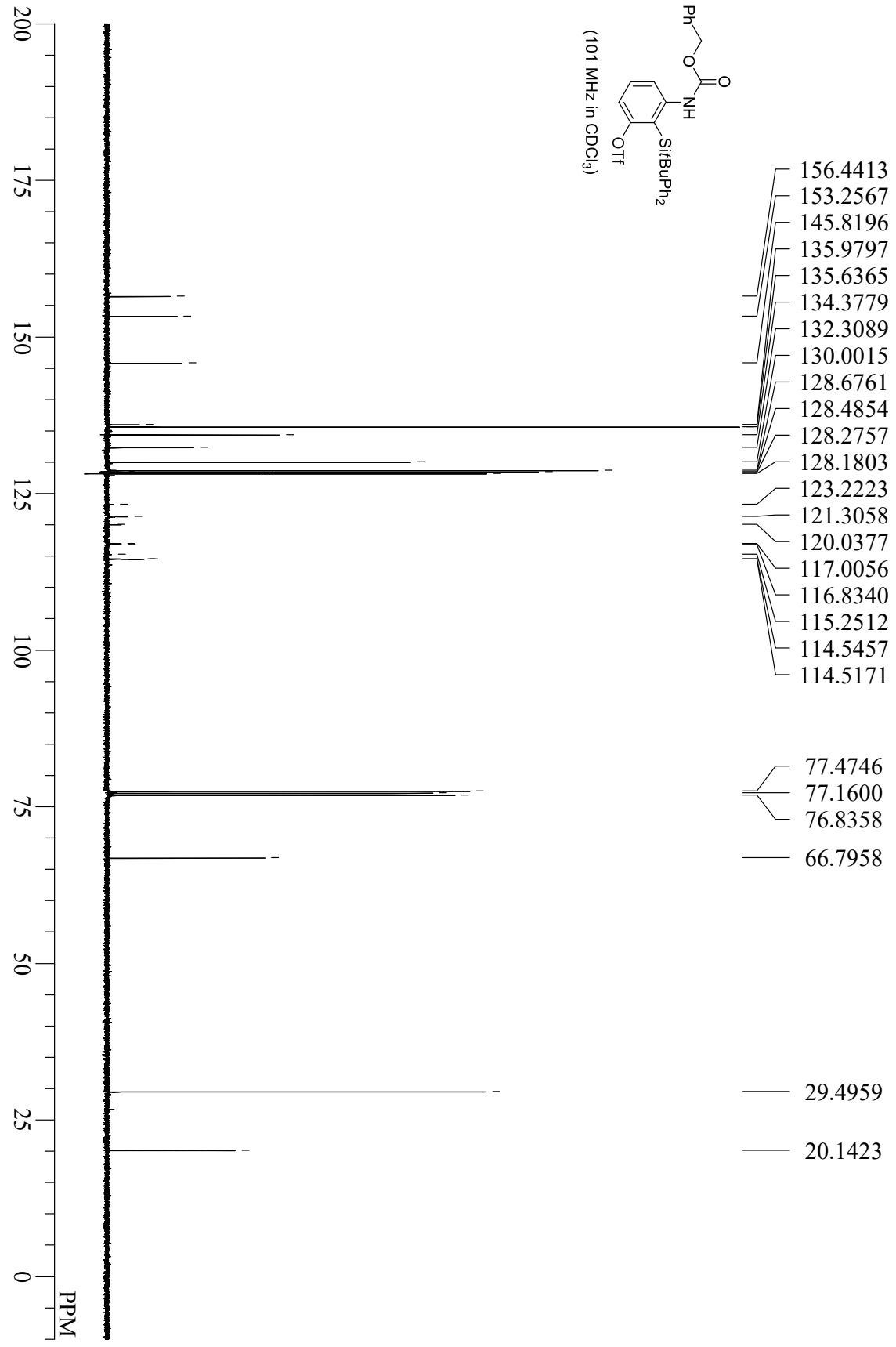
compound **1dd**



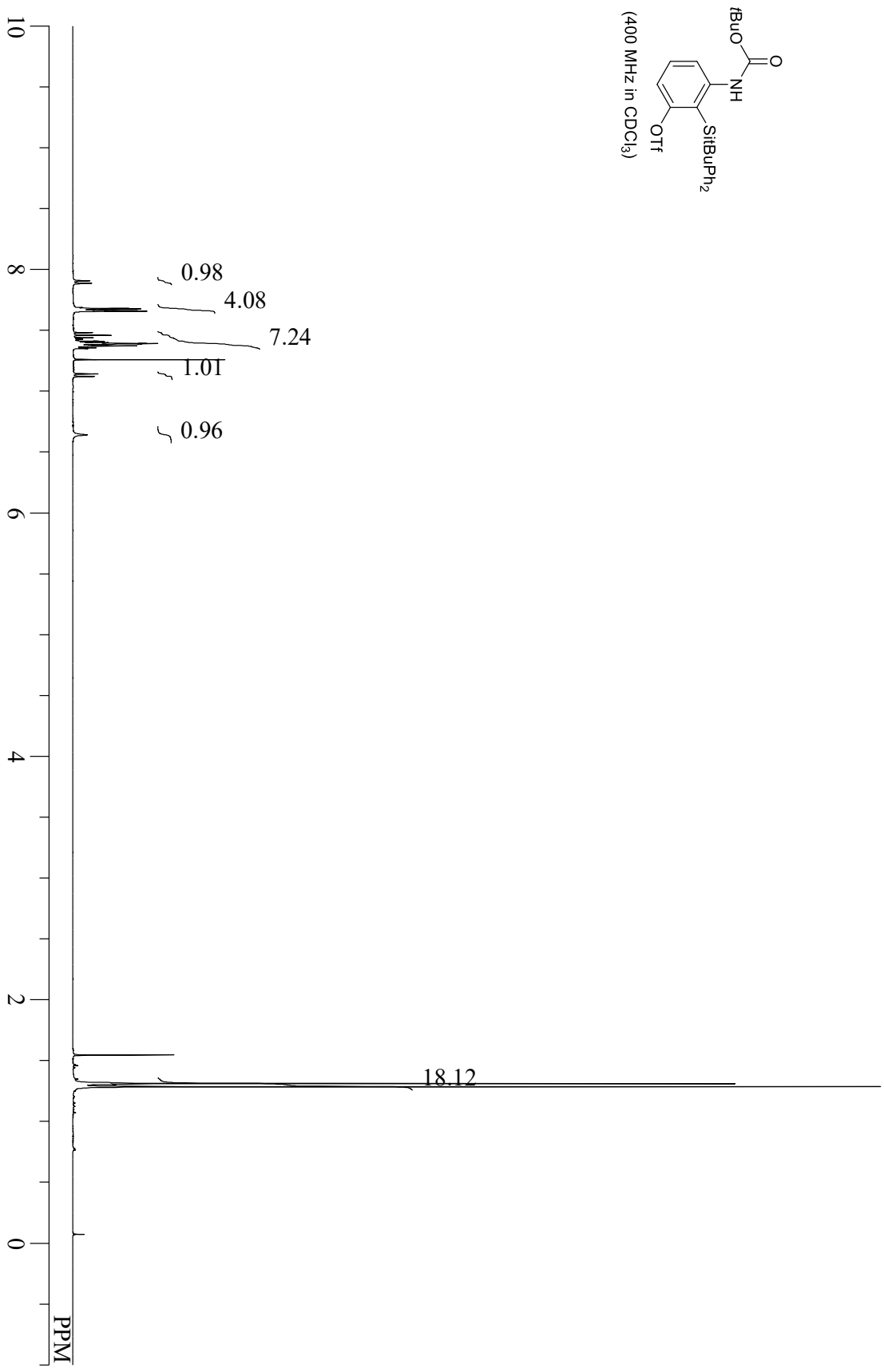
compound **1ee**



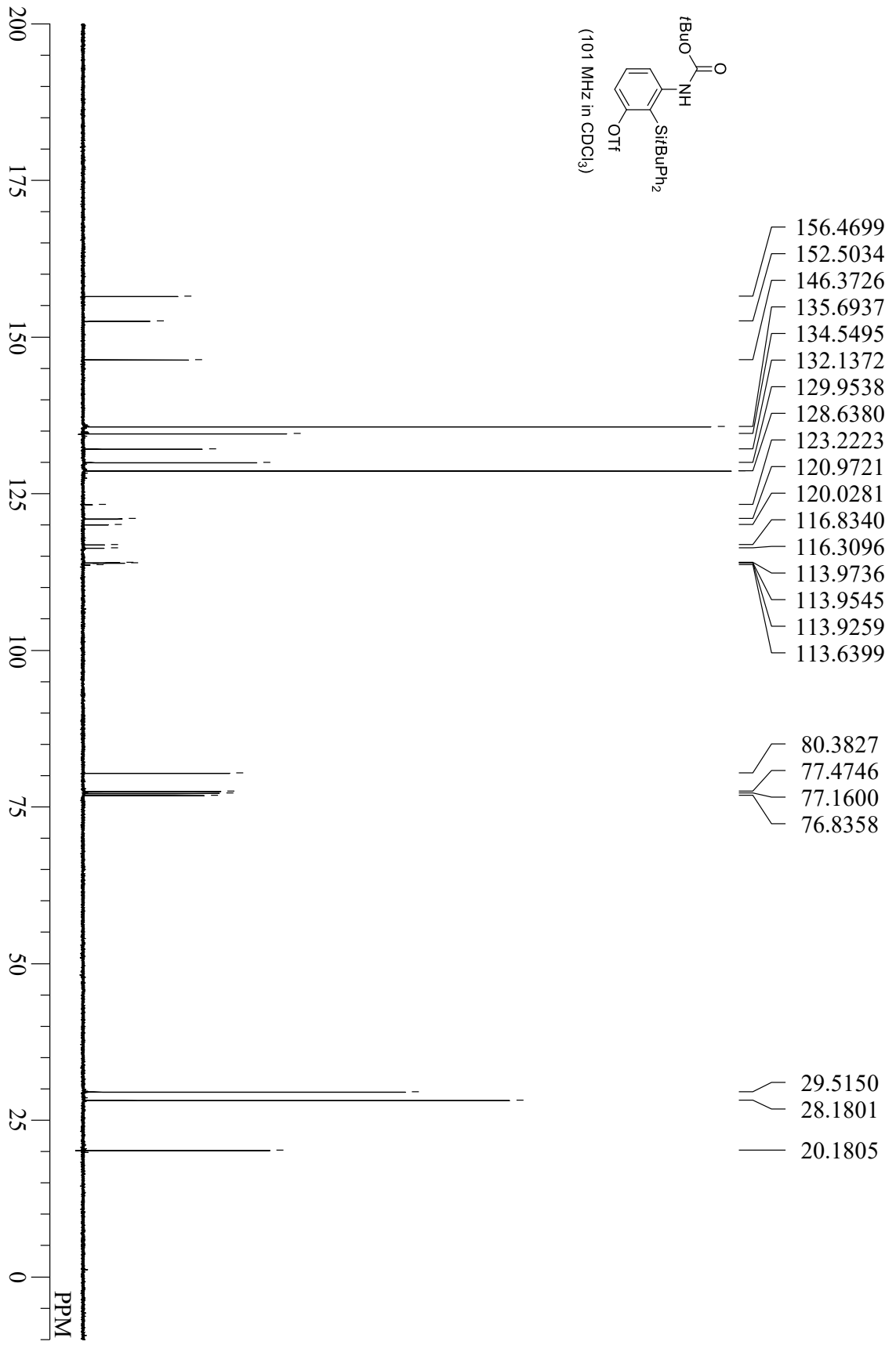
compound **1ee**



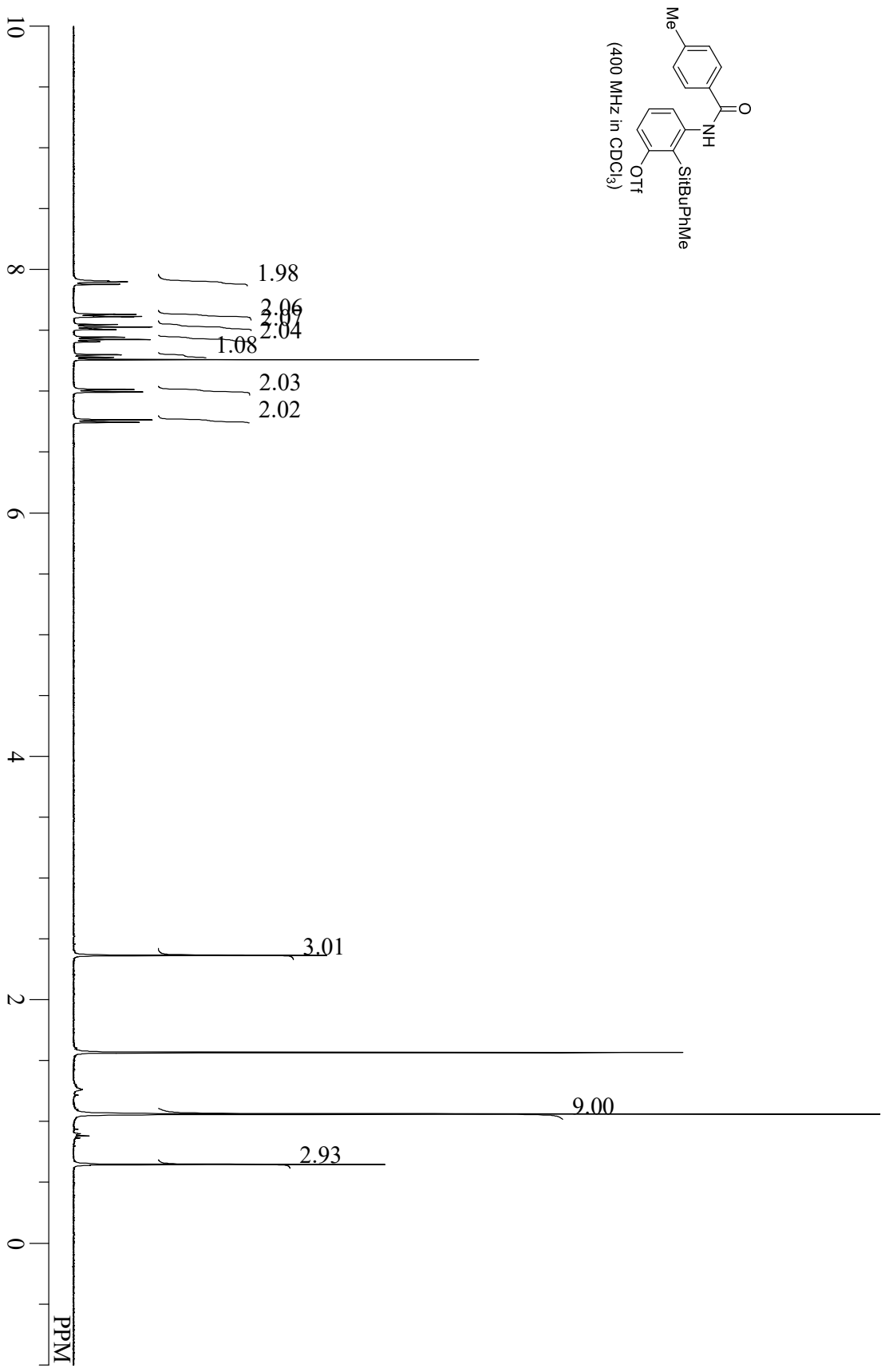
compound **1ff**



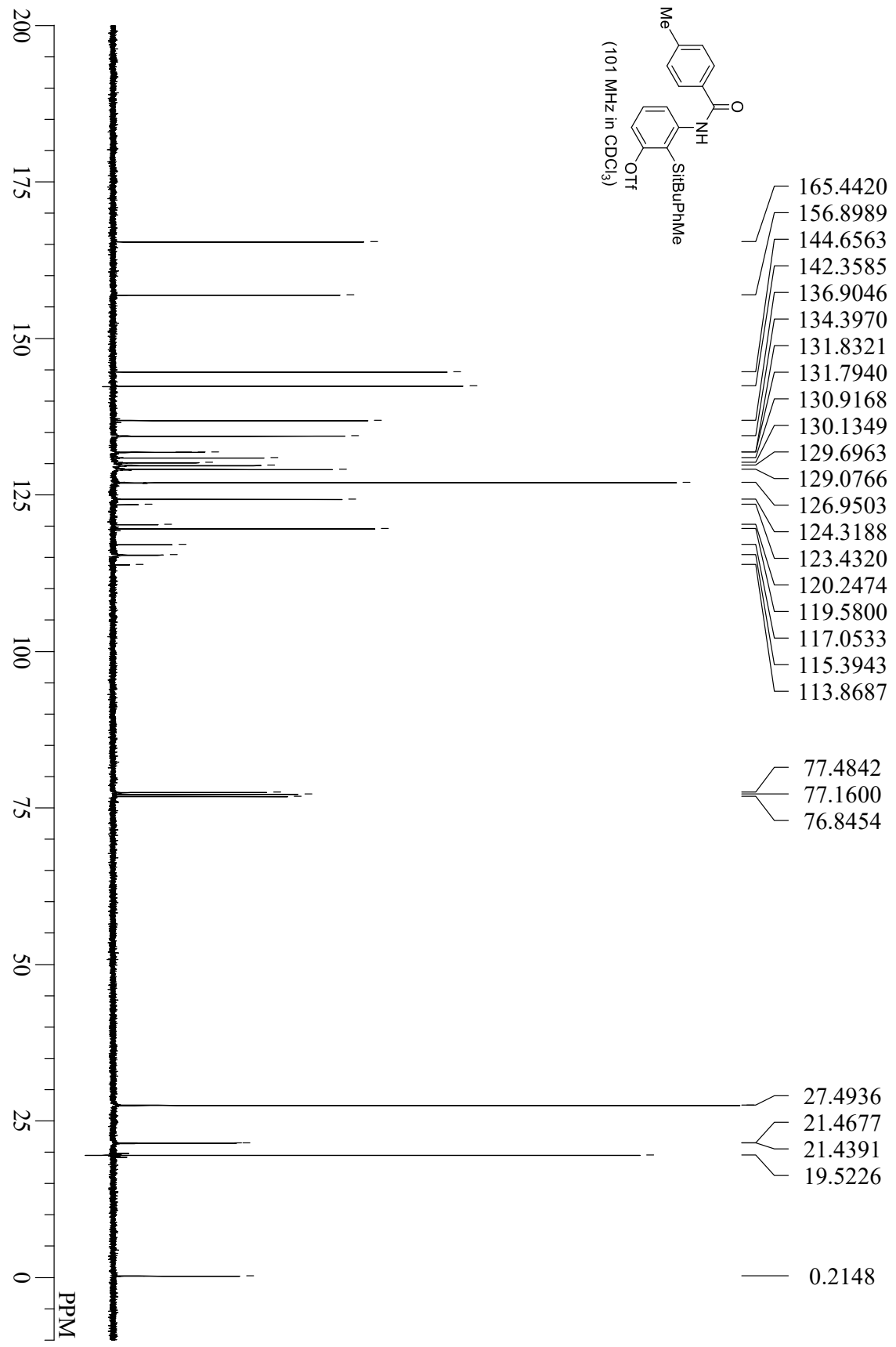
compound **1ff**



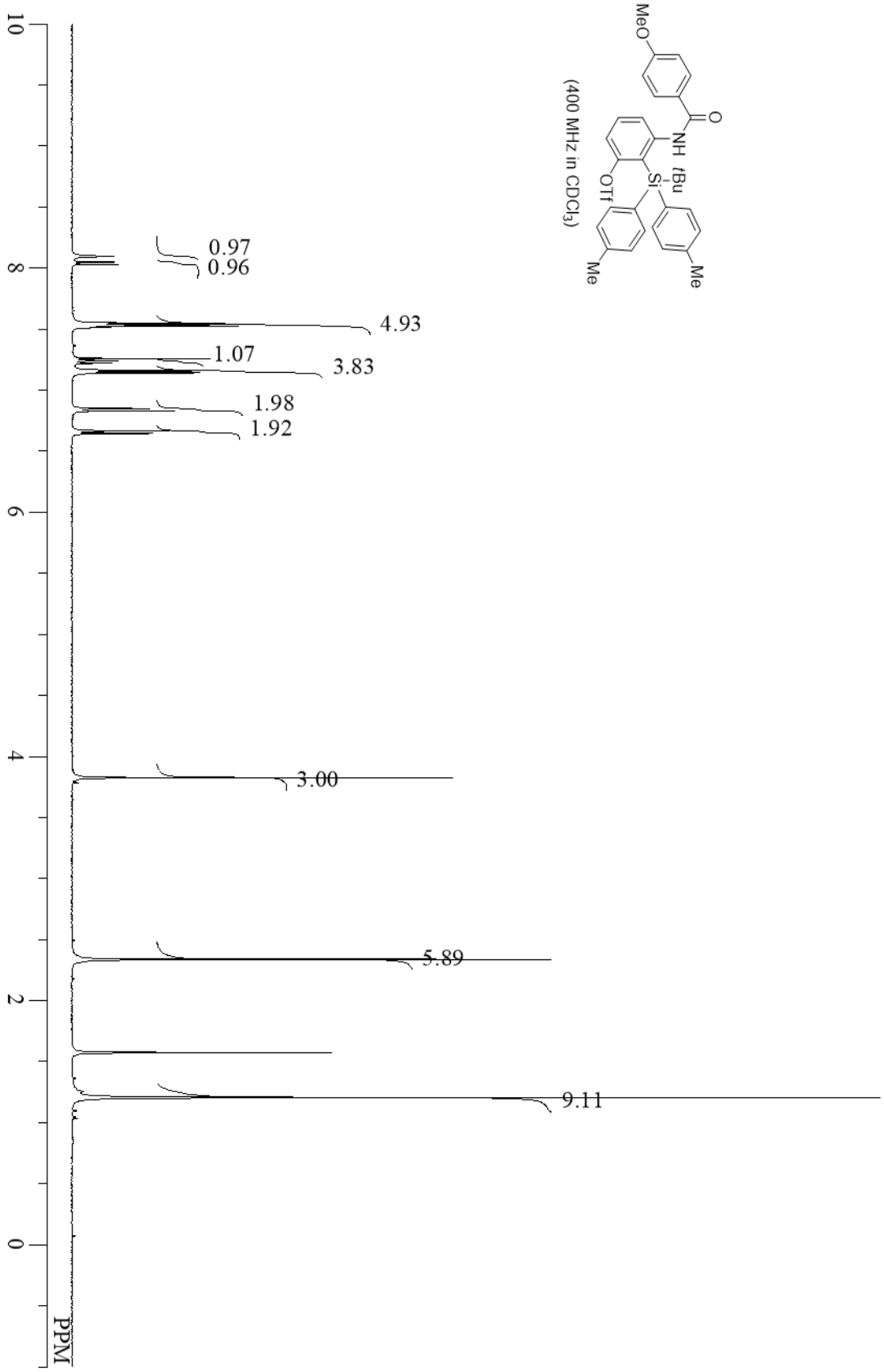
compound **1gg**



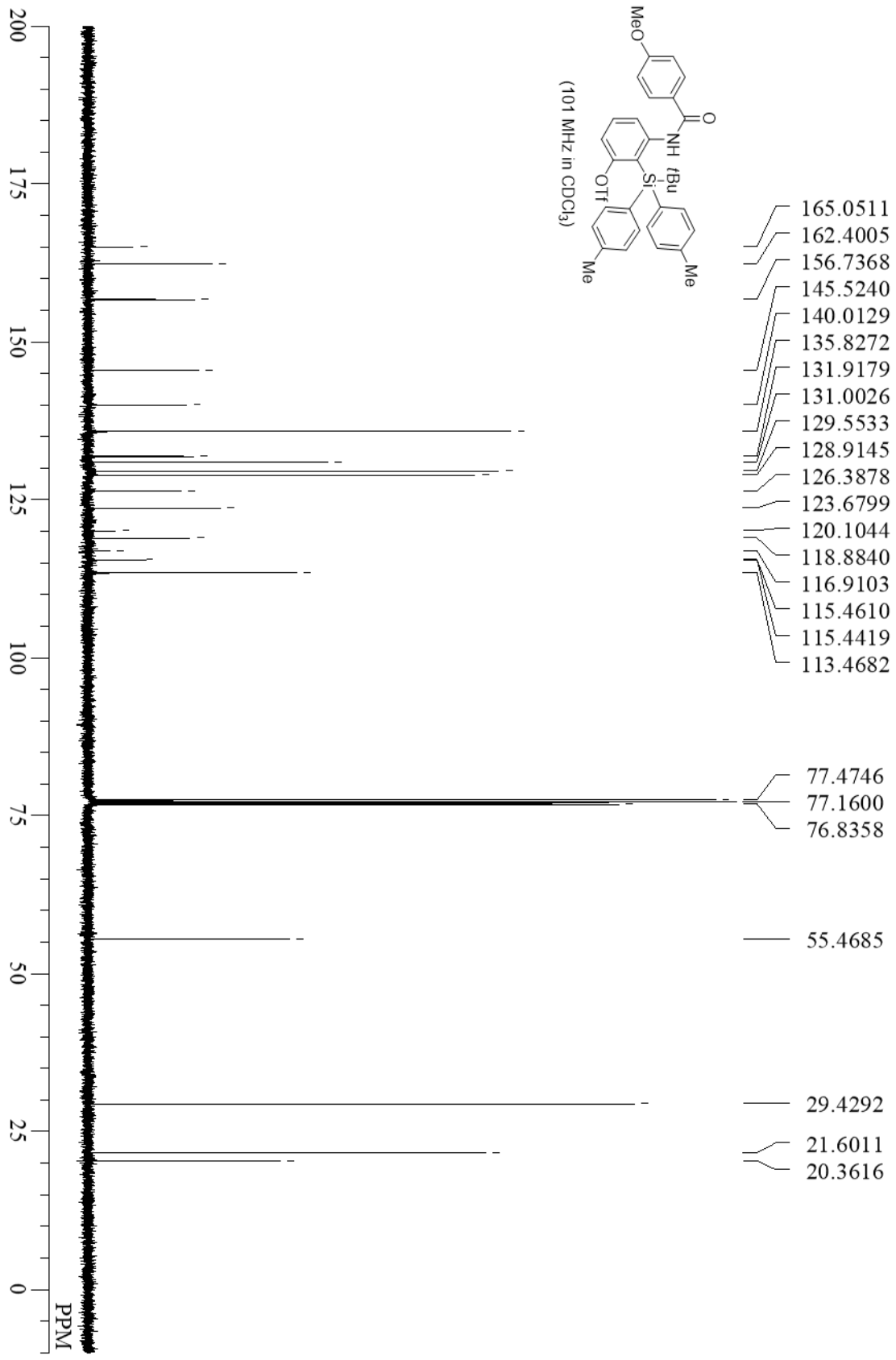
compound **1gg**



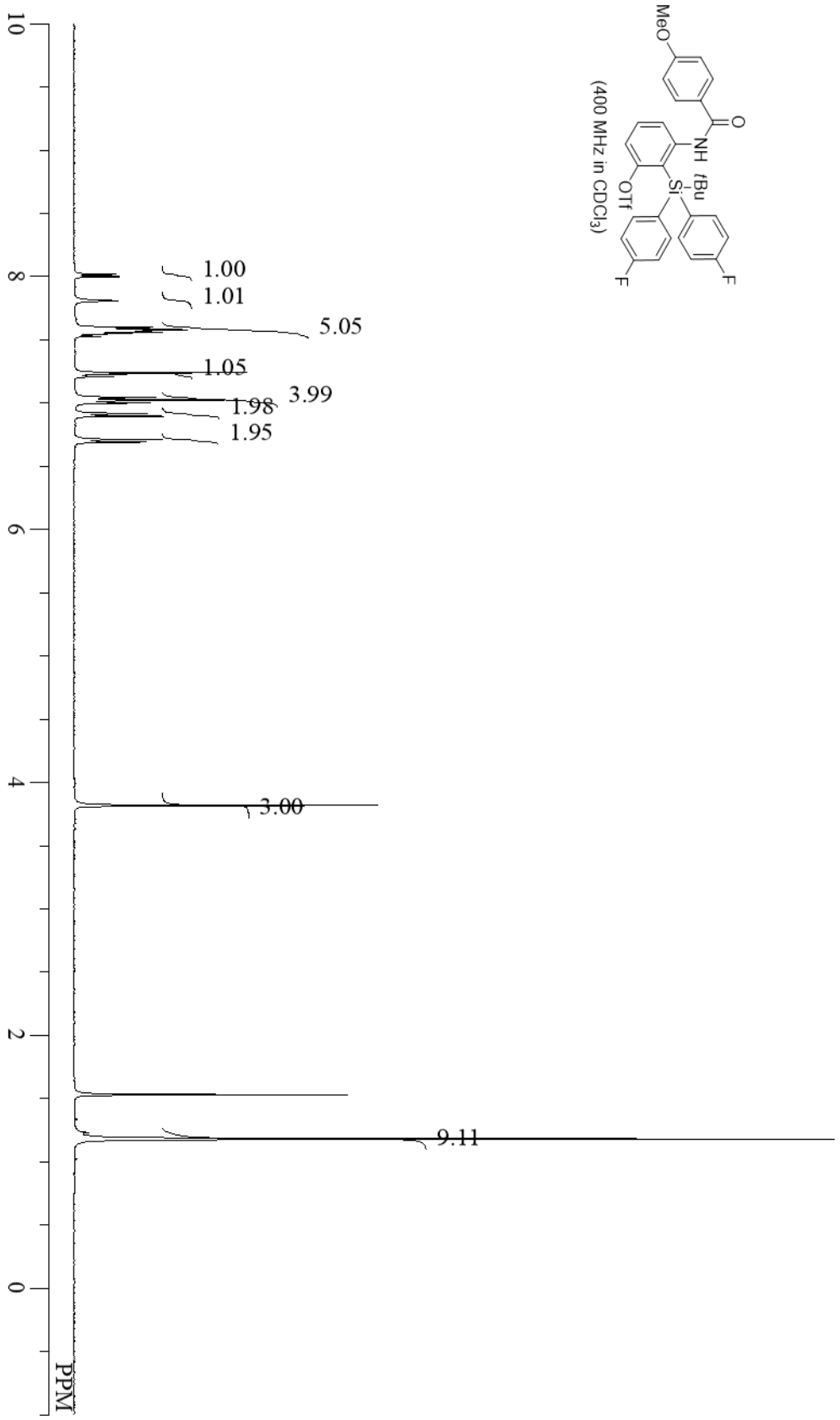
compound **1hh**



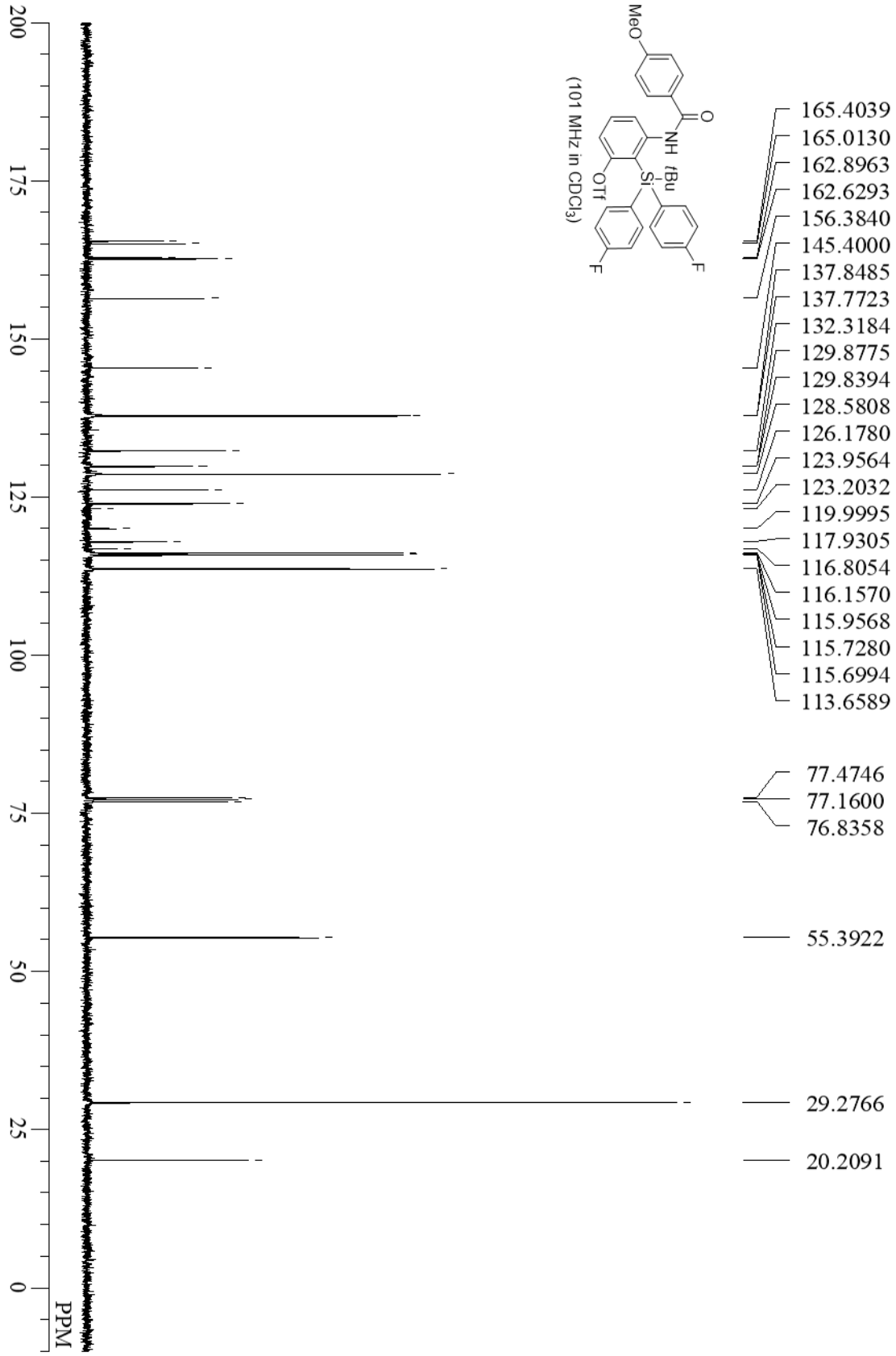
compound **1hh**



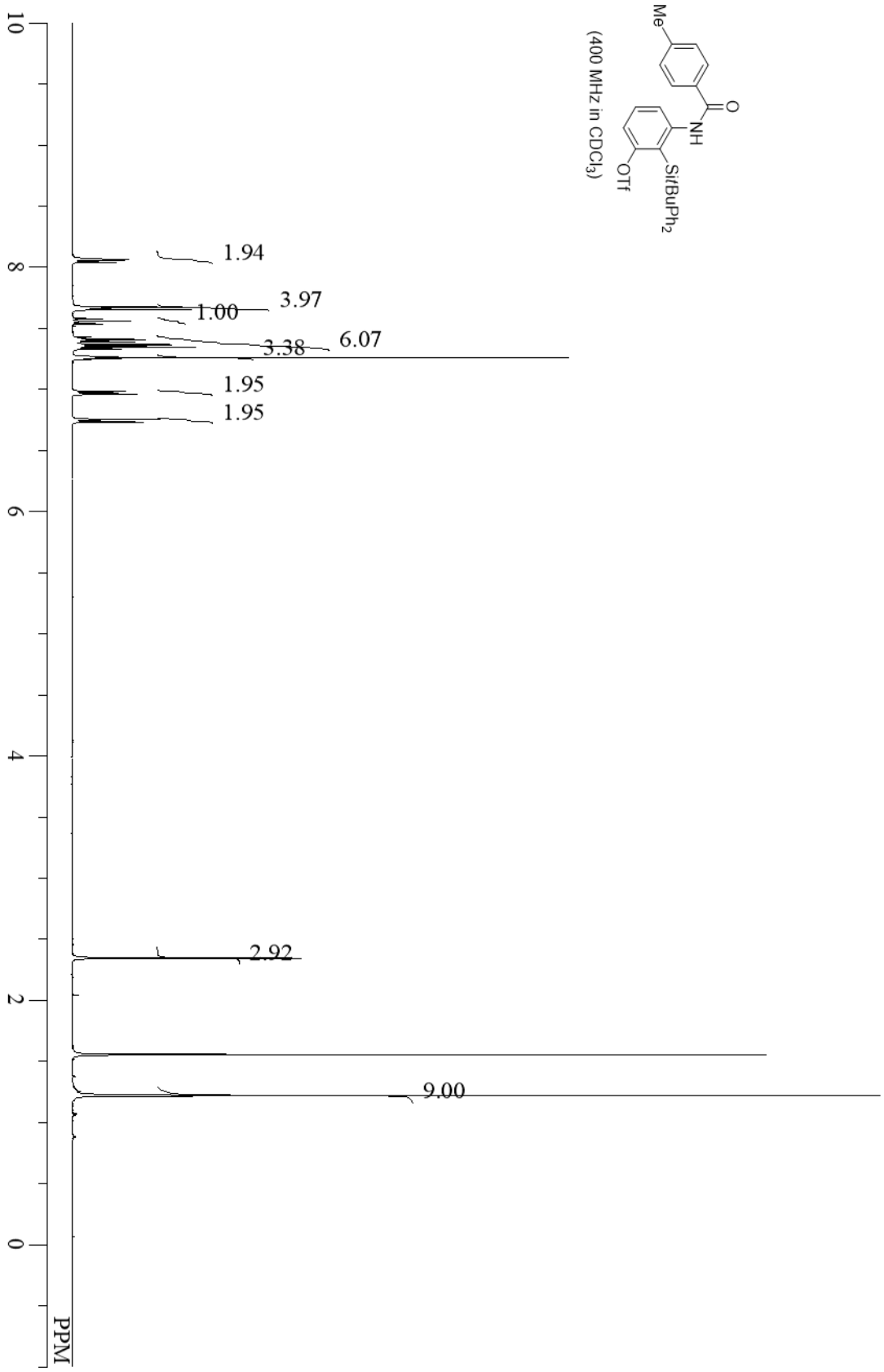
compound **1ii**



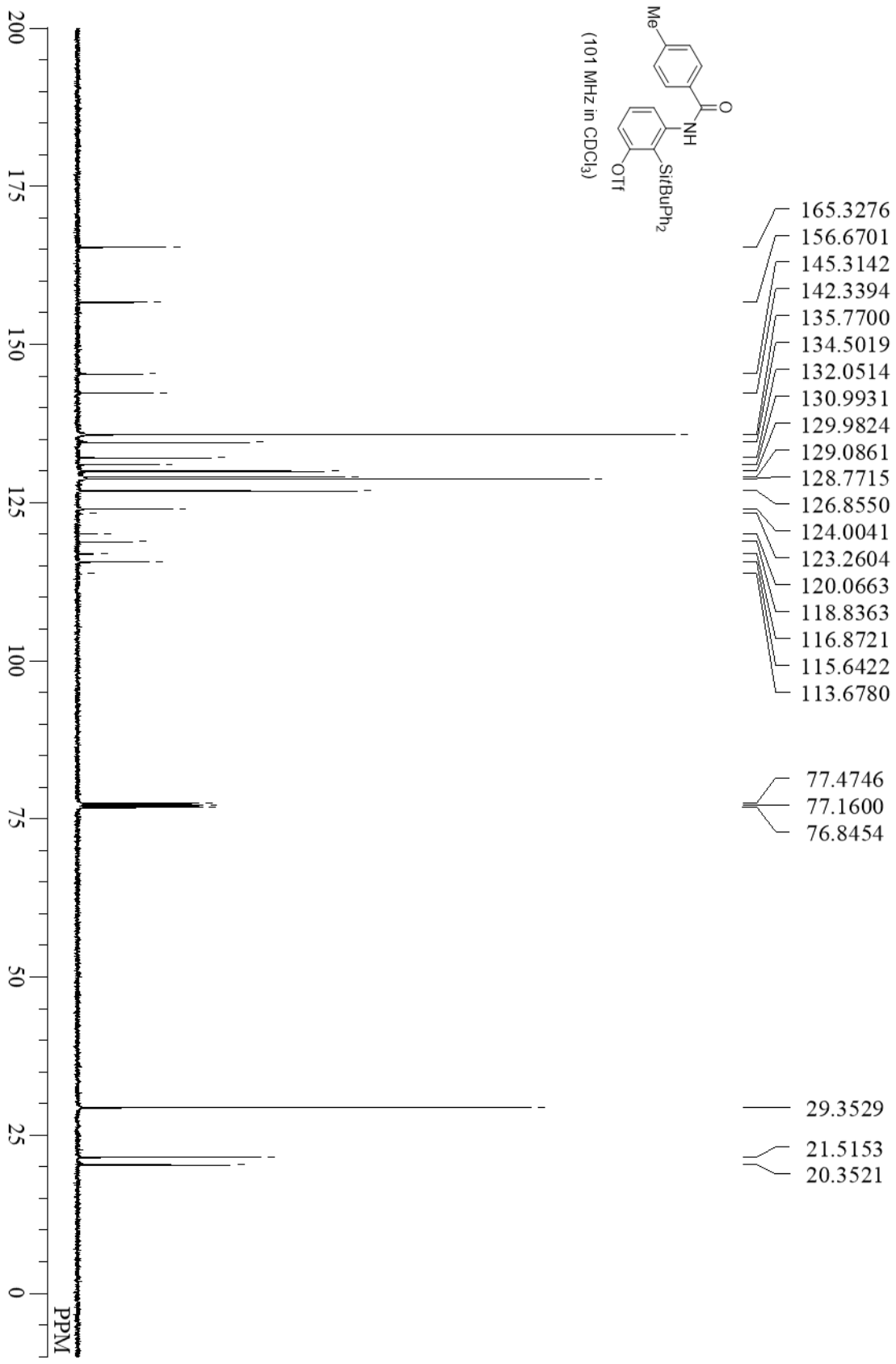
compound **1ii**



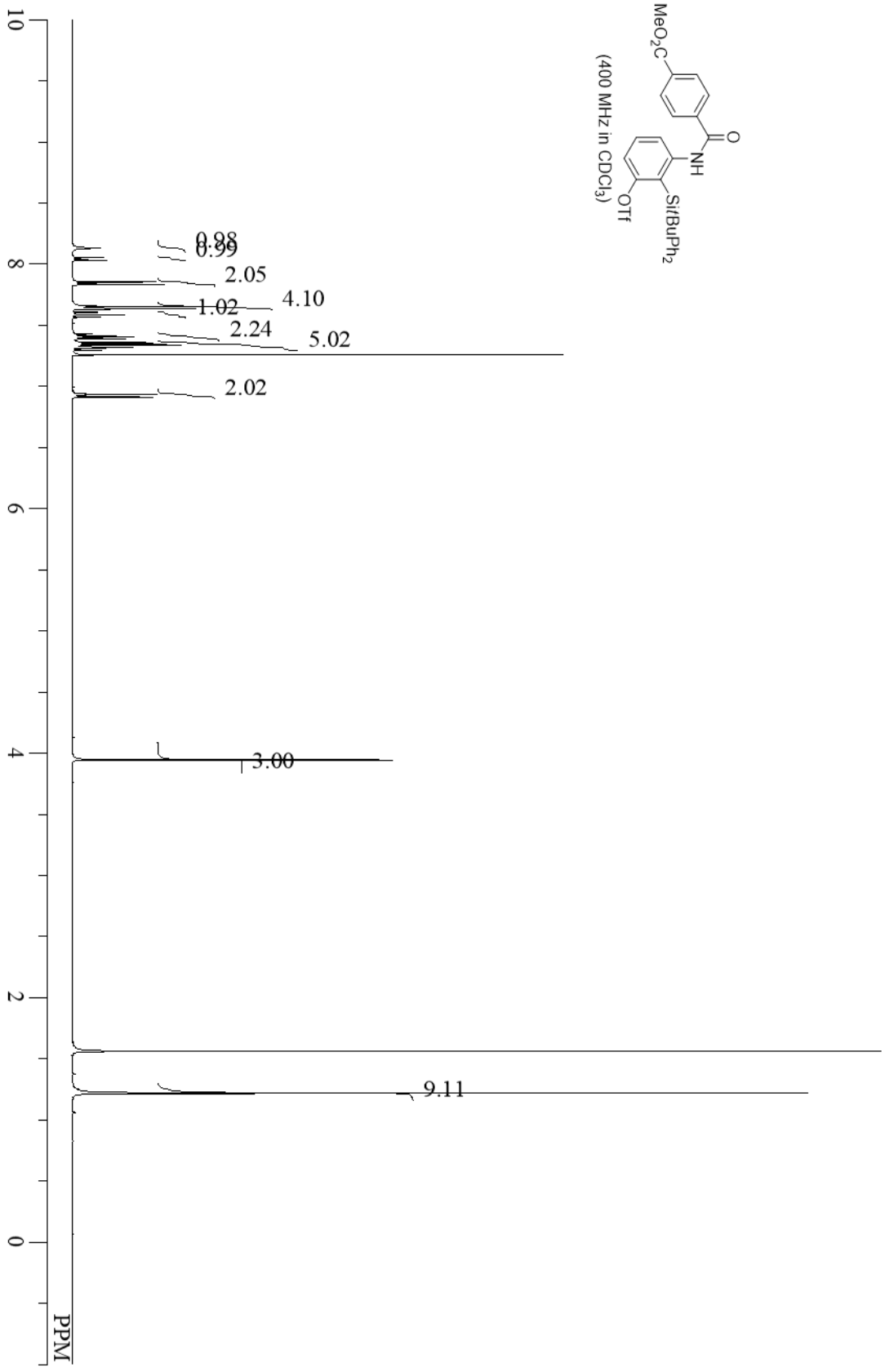
compound **1jj**



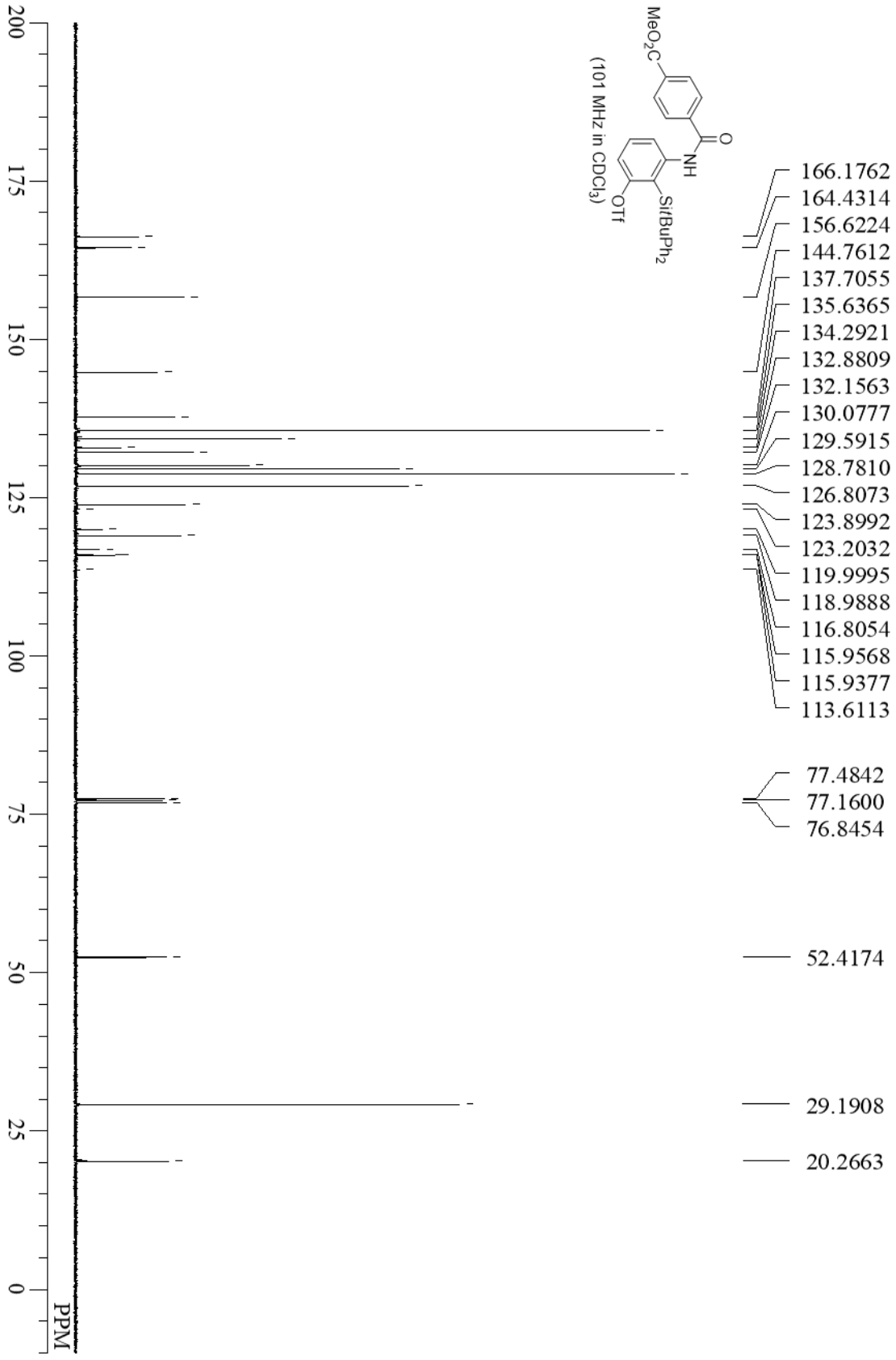
compound **1jj**



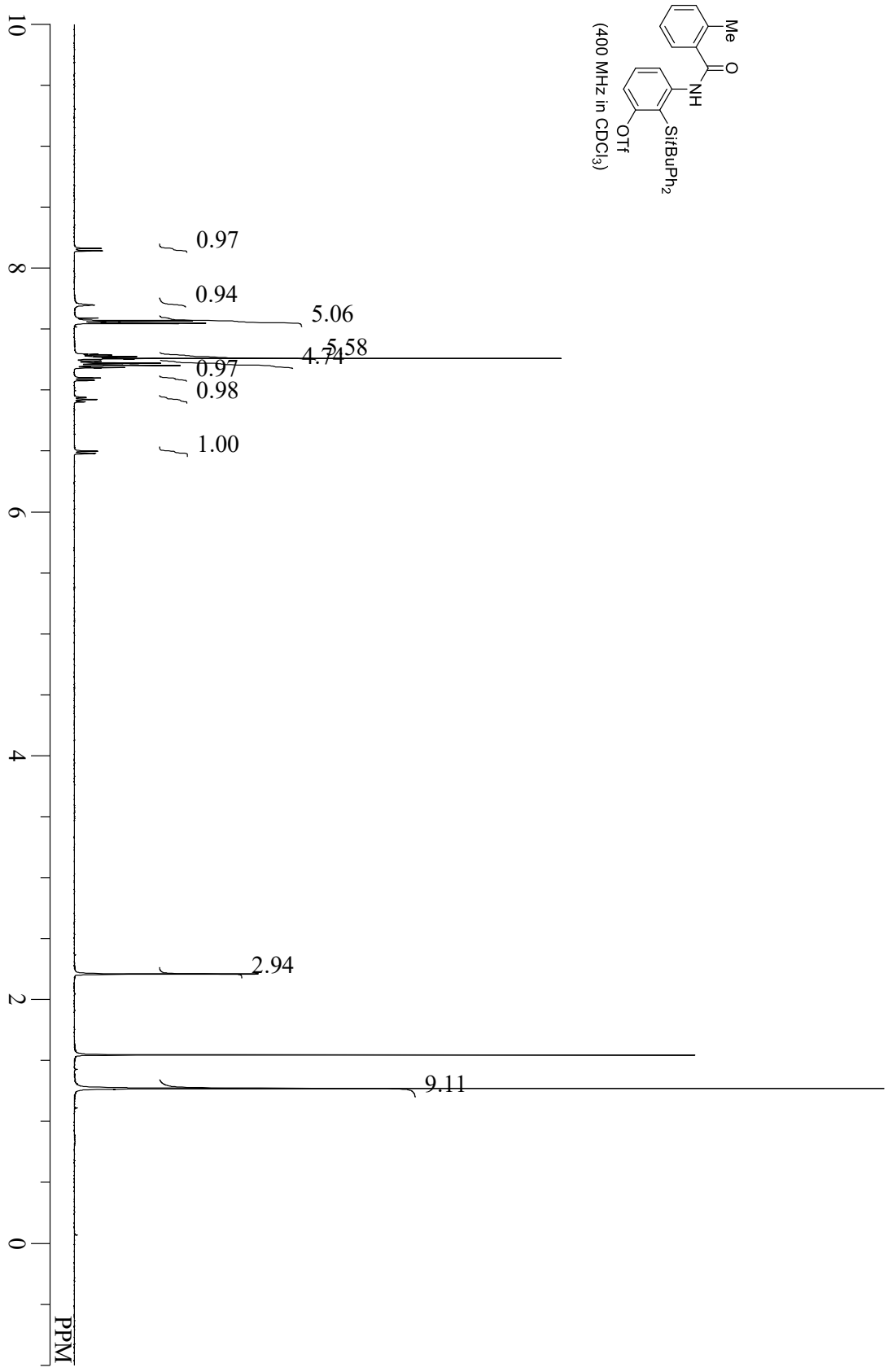
compound **1kk**



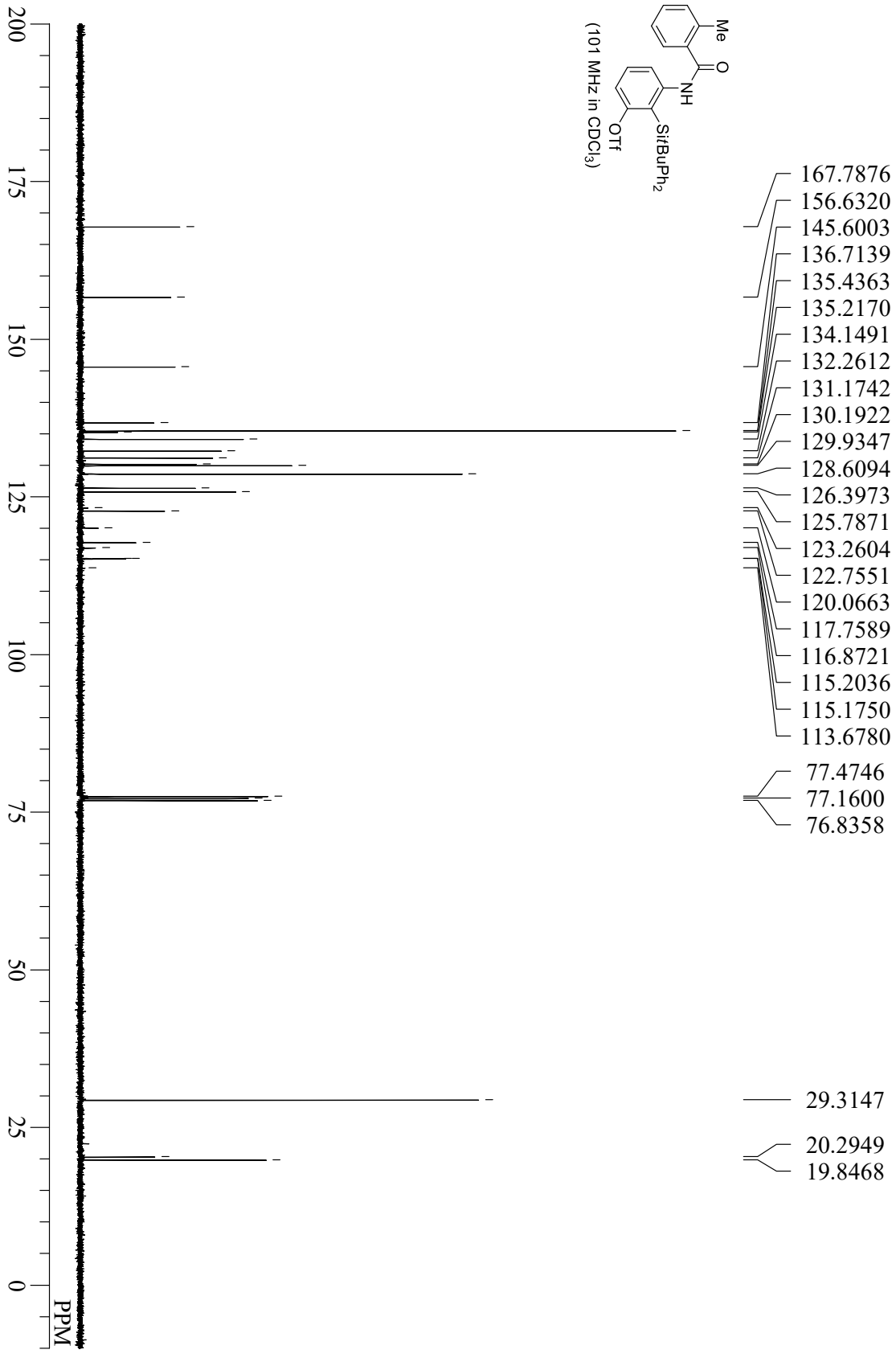
compound **1kk**



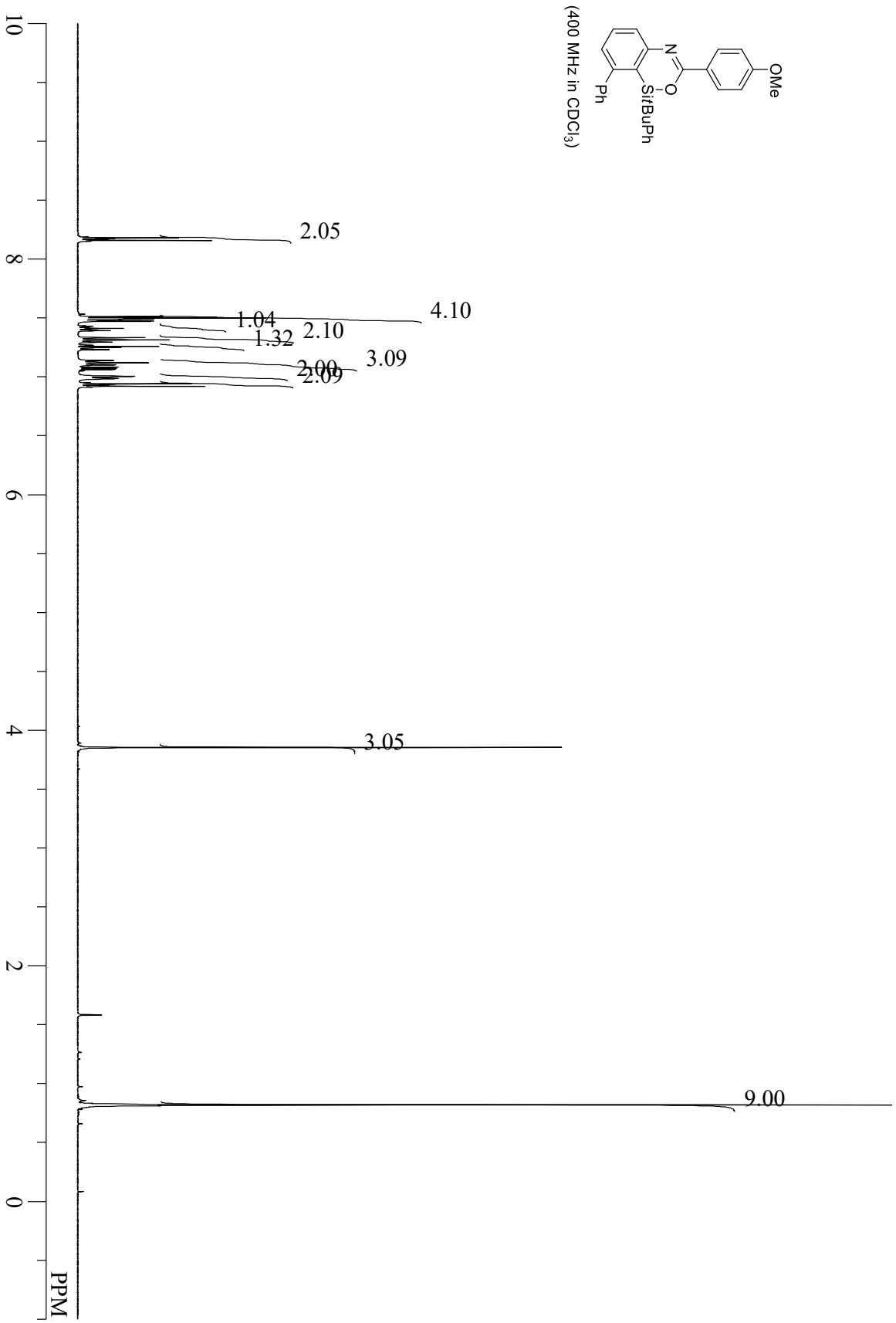
compound **1ll**



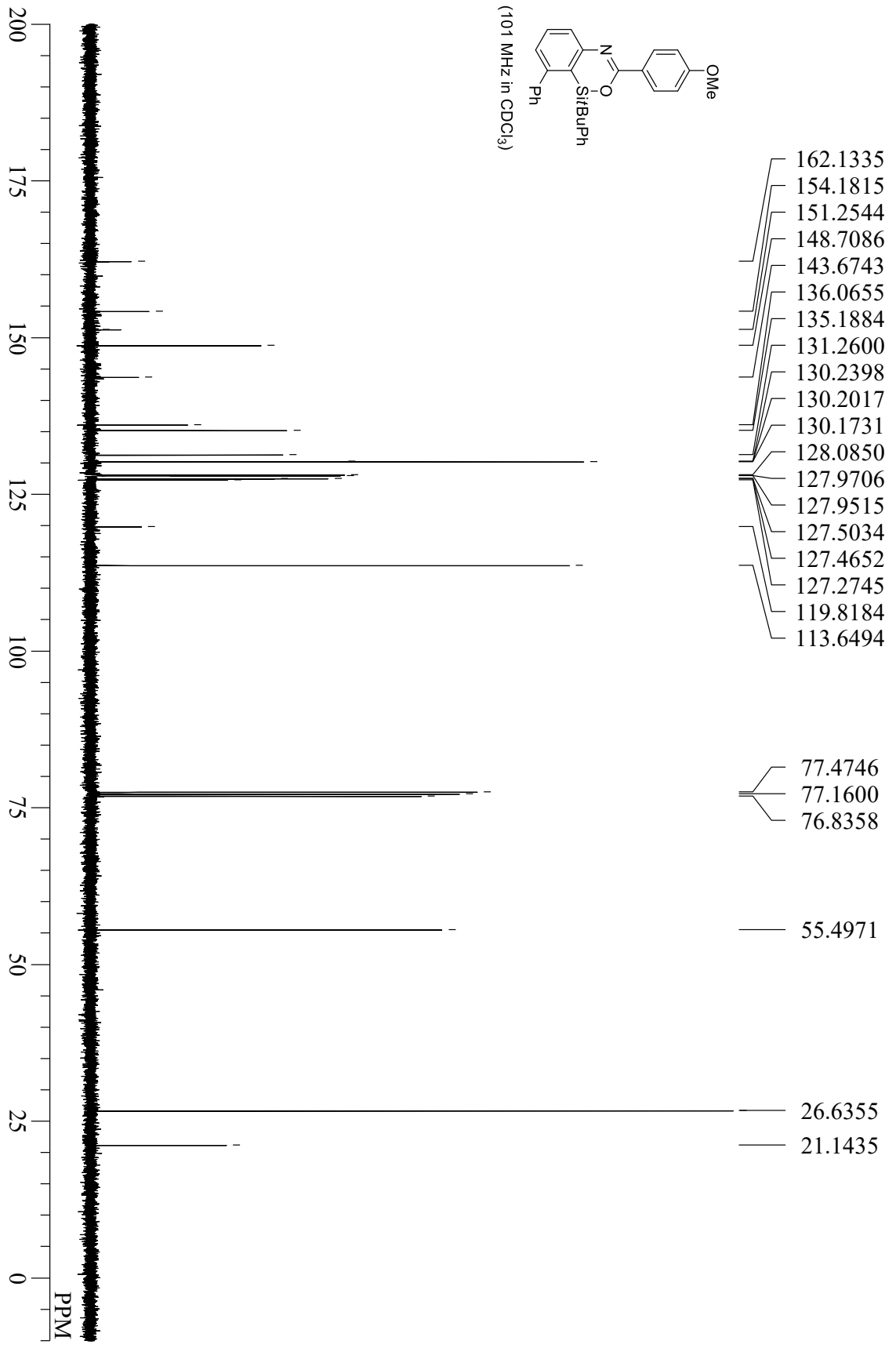
compound **1ll**



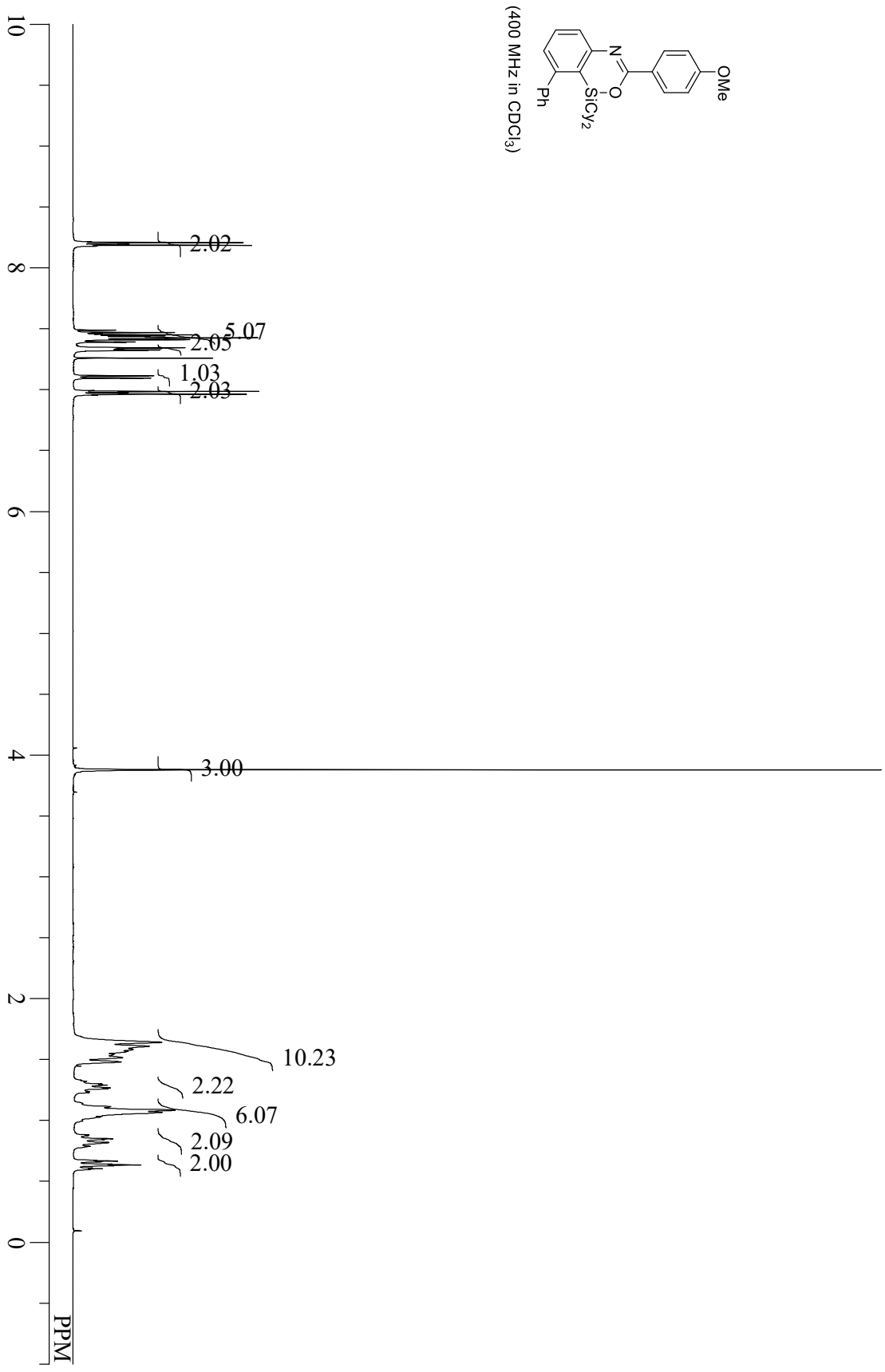
compound **3b**


(400 MHz in CDCl3)
Ph
SitBuPh
N
O
OMe
2.05
4.10
1.04
2.10
1.32
3.09
2.00
2.09
3.05
9.00
10
8
6
4
2
0
PPM

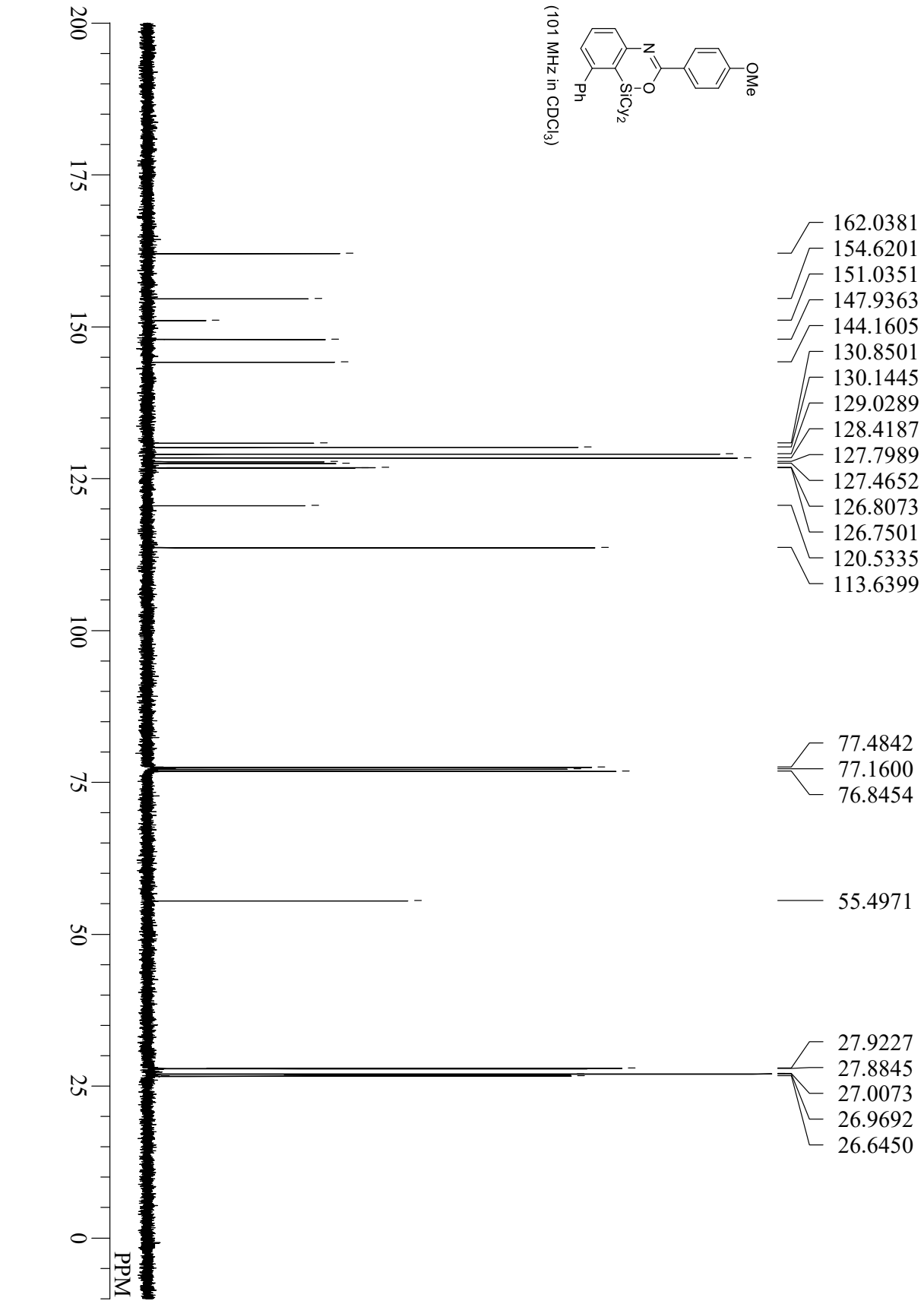
compound **3b**


(101 MHz in CDCl3)
Ph
SitBuPh
OMe
162.1335
154.1815
151.2544
148.7086
143.6743
136.0655
135.1884
131.2600
130.2398
130.2017
130.1731
128.0850
127.9706
127.9515
127.5034
127.4652
127.2745
119.8184
113.6494
77.4746
77.1600
76.8358
55.4971
26.6355
21.1435
200
175
150
125
100
75
50
25
0
PPM

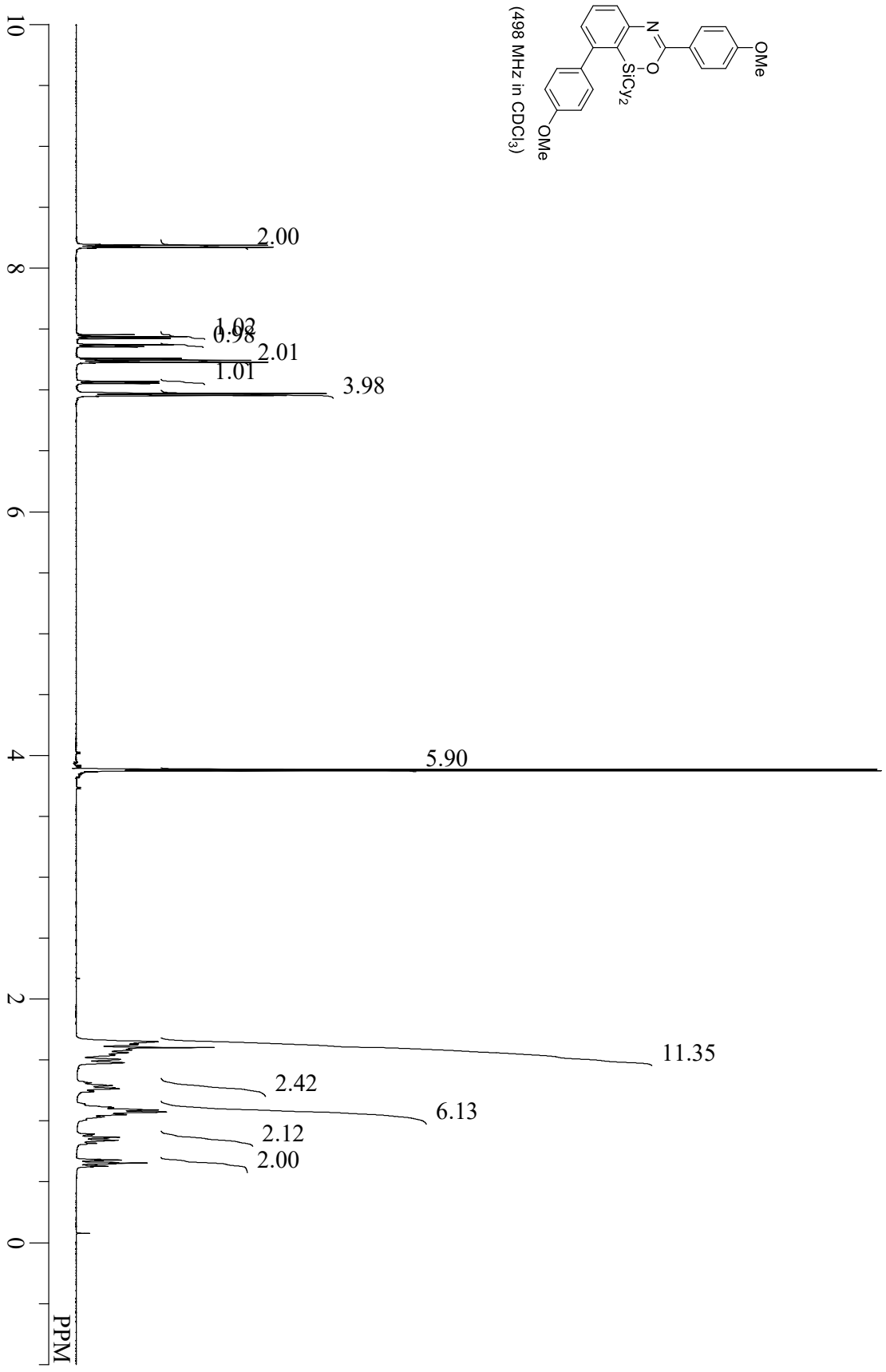
compound **3c**


(400 MHz in CDCl3)
Ph
SiCy2
O
N
OMe
2.02
5.07
2.05
1.03
2.03
3.00
10.23
2.22
6.07
2.09
2.00
PPM

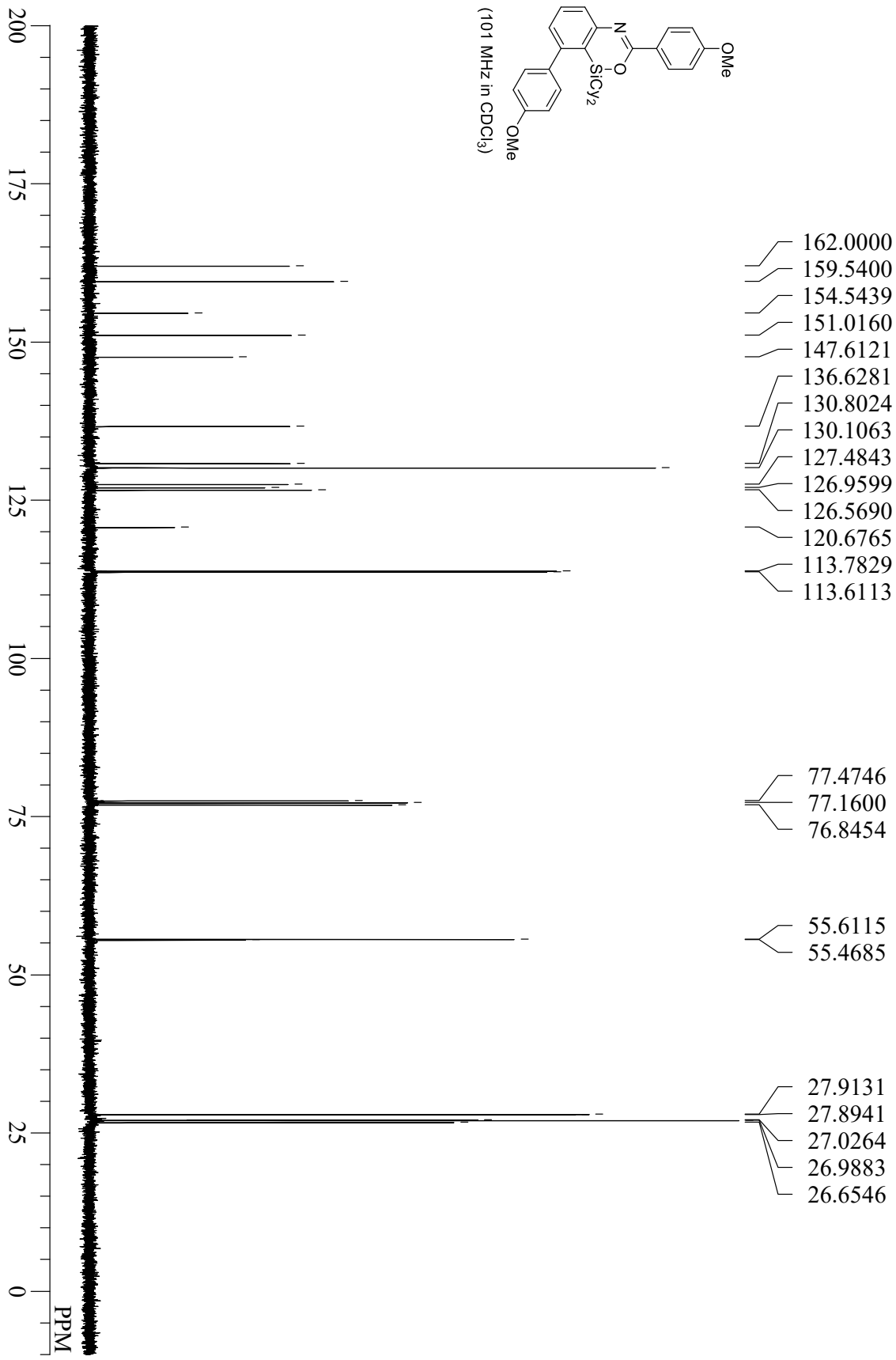
compound **3c**


(101 MHz in CDCl3)
Ph
SiCy2
OMe
162.0381
154.6201
151.0351
147.9363
144.1605
130.8501
130.1445
129.0289
128.4187
127.7989
127.4652
126.8073
126.7501
120.5335
113.6399
77.4842
77.1600
76.8454
55.4971
27.9227
27.8845
27.0073
26.9692
26.6450
200
175
150
125
100
75
50
25
0
PPM

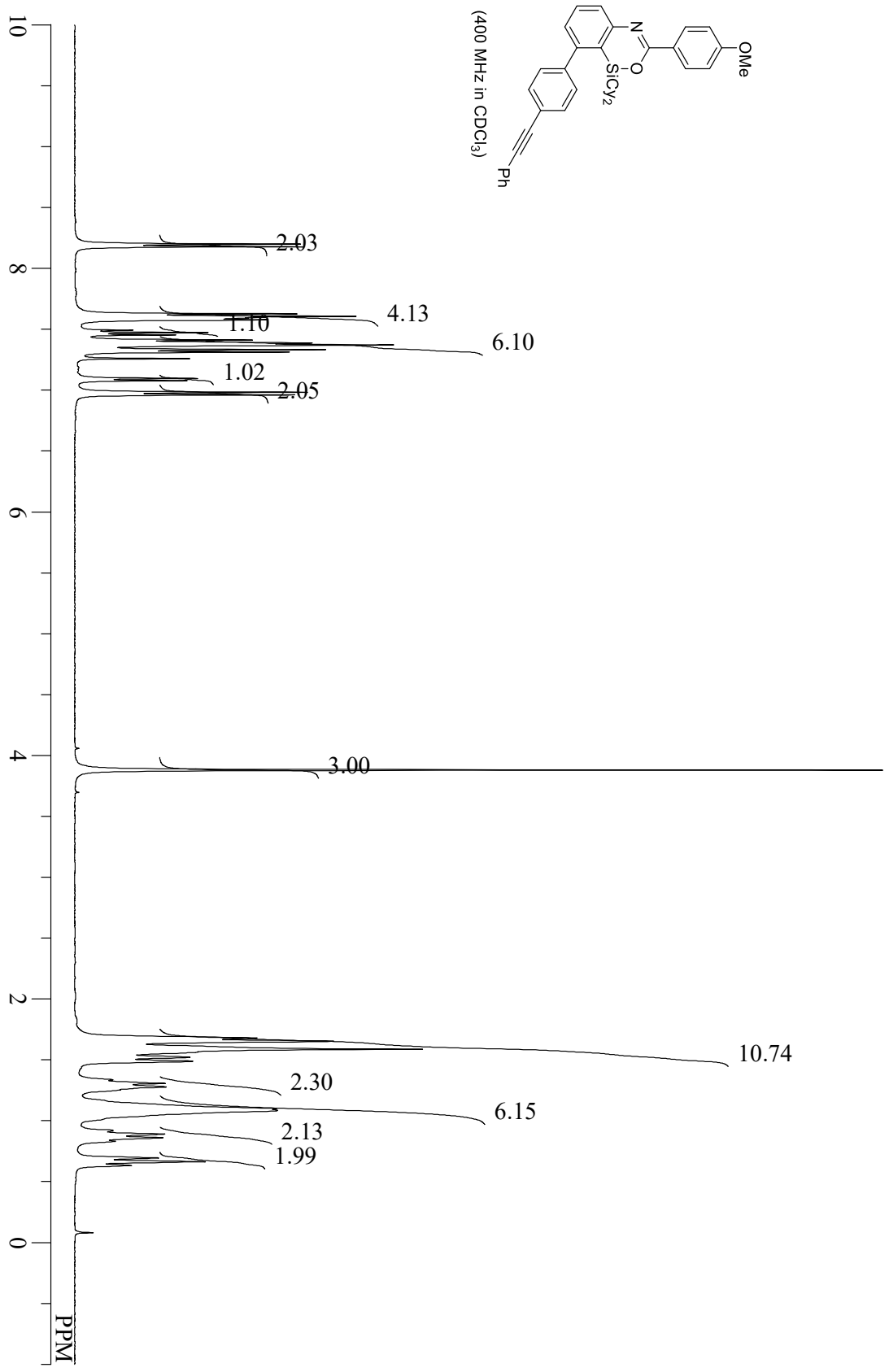
compound **3d**


(498 MHz in CDCl3)
N
O
SiCy2
OMe
OMe
2.00
1.03
0.98
2.01
1.01
3.98
5.90
11.35
2.42
6.13
2.12
2.00
10
8
6
4
2
0
PPM

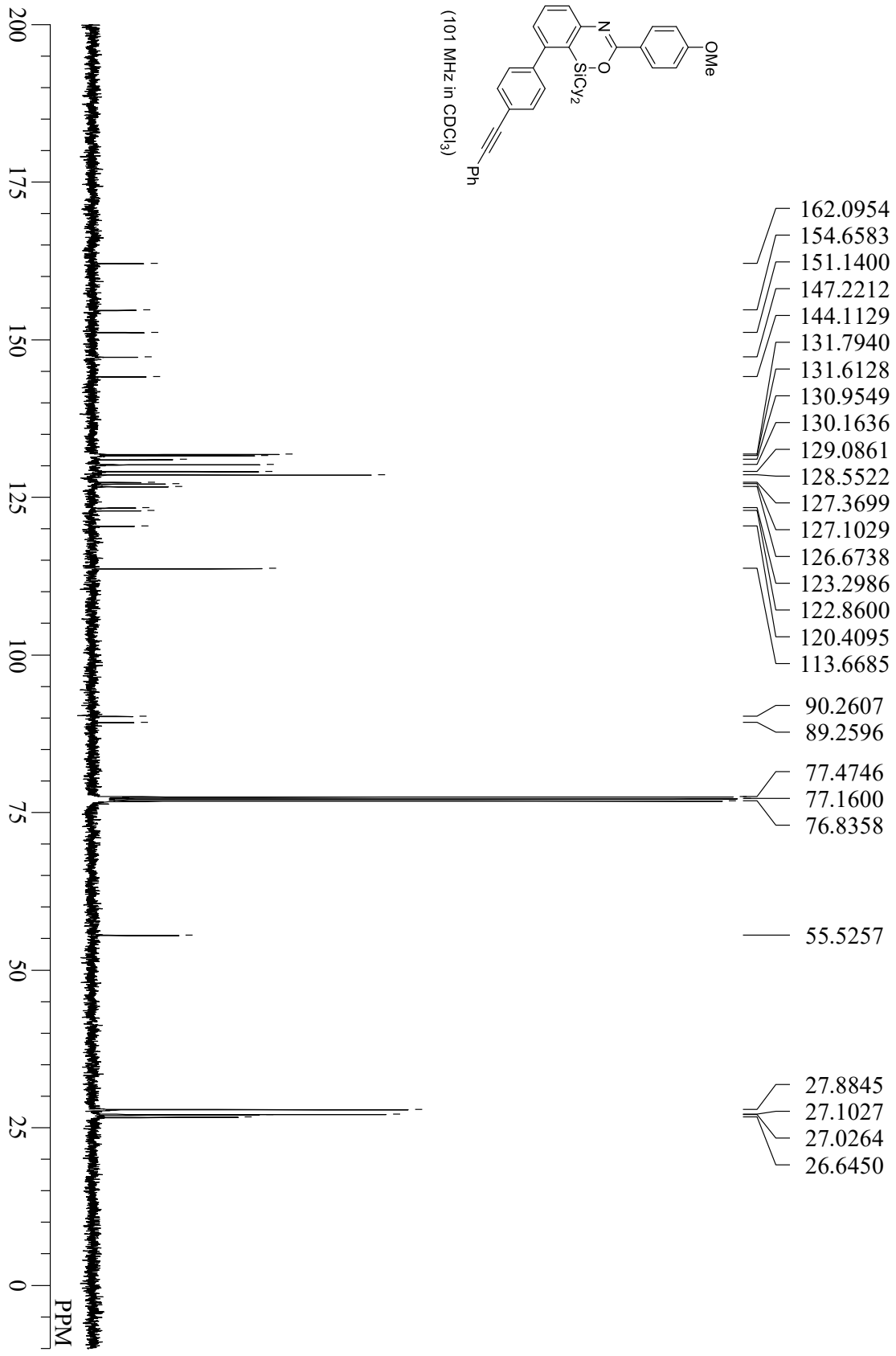
compound **3d**


(101 MHz in CDCl3)
OMe
N
O
SiCy2
OMe
162.0000
159.5400
154.5439
151.0160
147.6121
136.6281
130.8024
130.1063
127.4843
126.9599
126.5690
120.6765
113.7829
113.6113
77.4746
77.1600
76.8454
55.6115
55.4685
27.9131
27.8941
27.0264
26.9883
26.6546
200
175
150
125
100
75
50
25
0
PPM

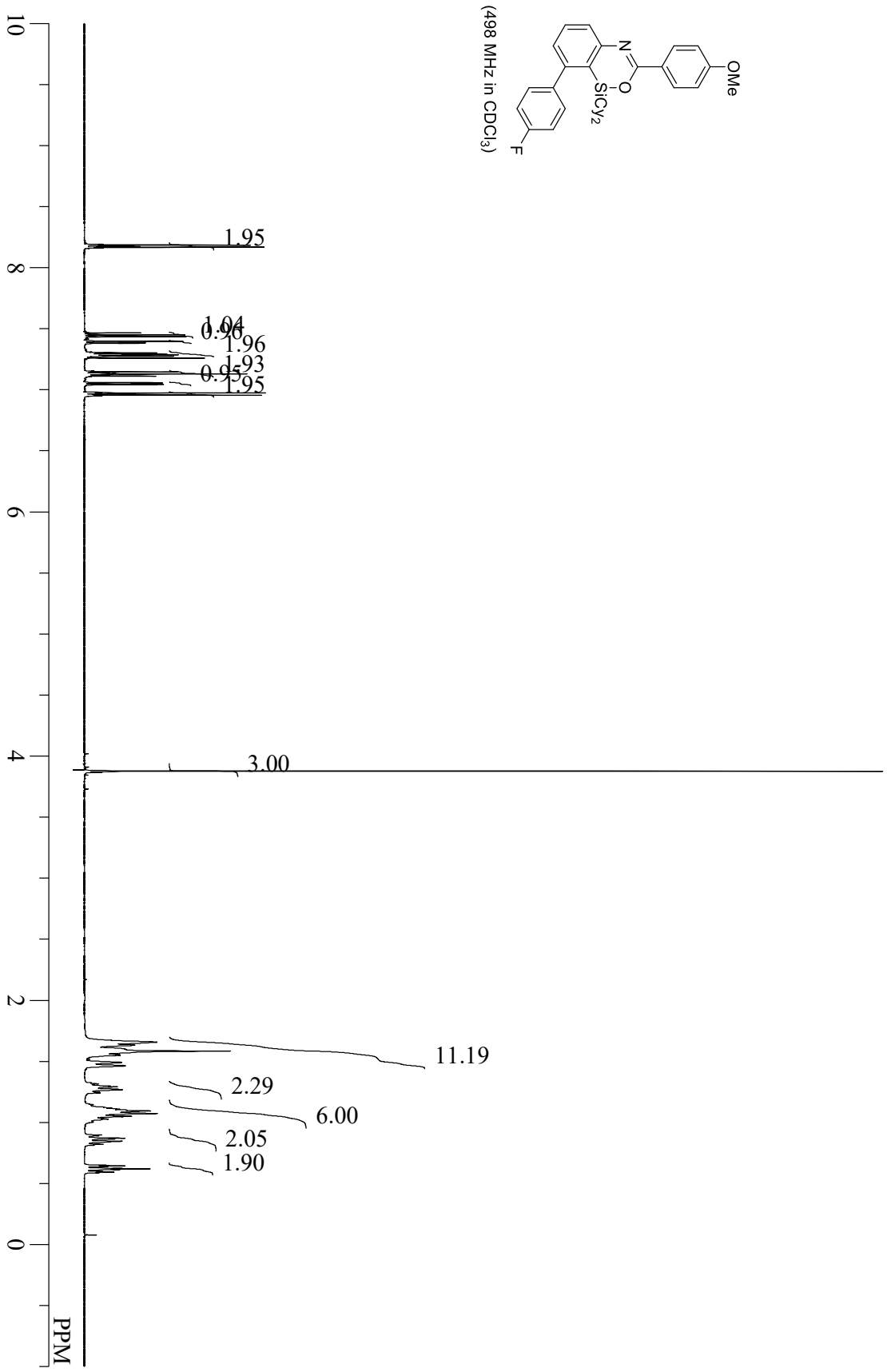
compound **3e**


(400 MHz in CDCl3)
N
O
SiCy2
OMe
Ph
2.03
4.13
1.10
6.10
1.02
2.05
3.00
10.74
2.30
6.15
2.13
1.99
10
8
6
4
2
0
PPM

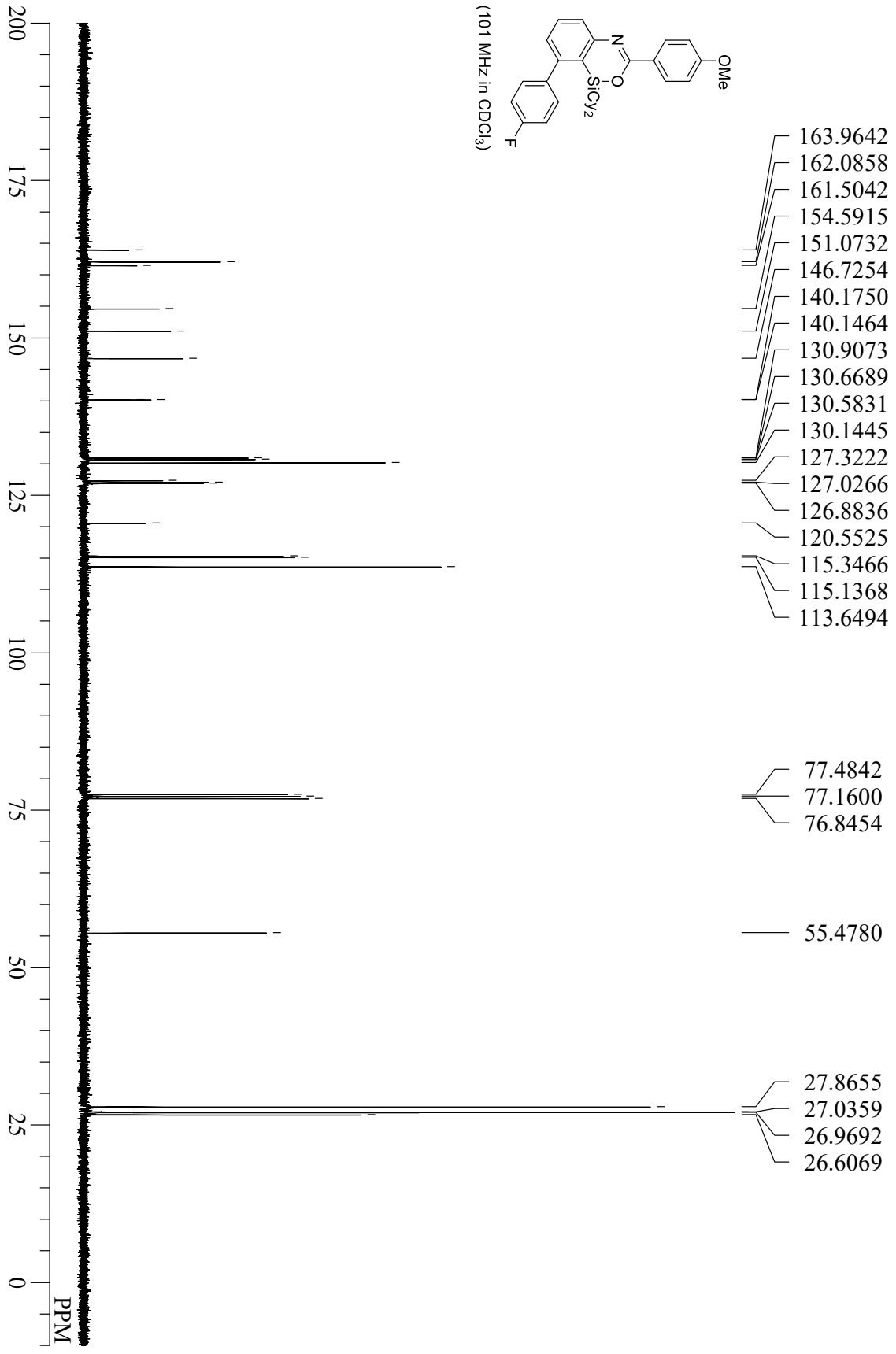
compound **3e**


(101 MHz in CDCl3)
Ph
SiCy2
OMe
162.0954
154.6583
151.1400
147.2212
144.1129
131.7940
131.6128
130.9549
130.1636
129.0861
128.5522
127.3699
127.1029
126.6738
123.2986
122.8600
120.4095
113.6685
90.2607
89.2596
77.4746
77.1600
76.8358
55.5257
27.8845
27.1027
27.0264
26.6450
200
175
150
125
100
75
50
25
0
PPM

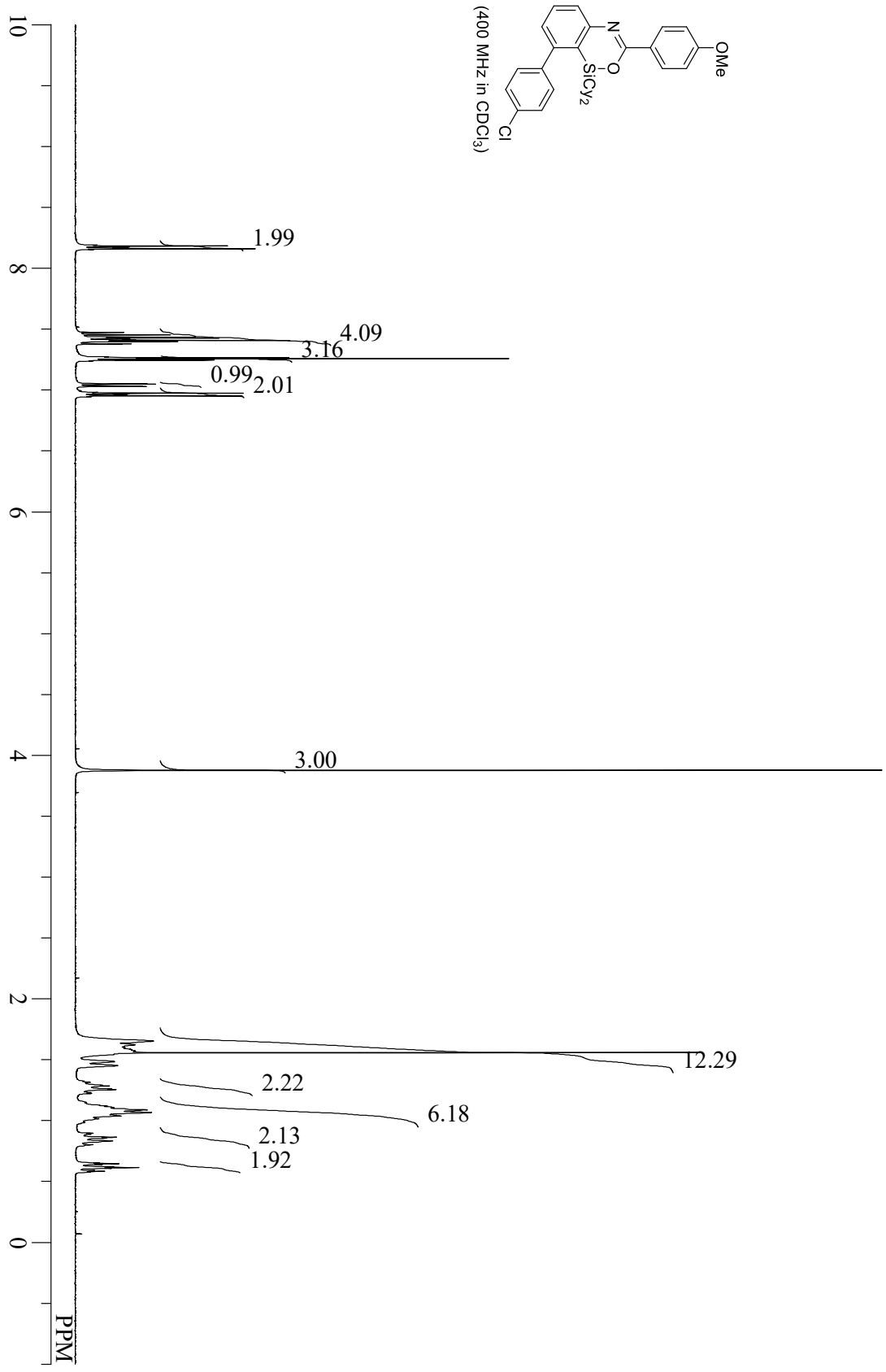
compound **3f**


(498 MHz in CDCl3)
F
SiCy2
N
O
OMe
1.95
1.04
0.96
1.96
1.93
0.95
1.95
3.00
11.19
2.29
6.00
2.05
1.90
10
8
6
4
2
0
PPM

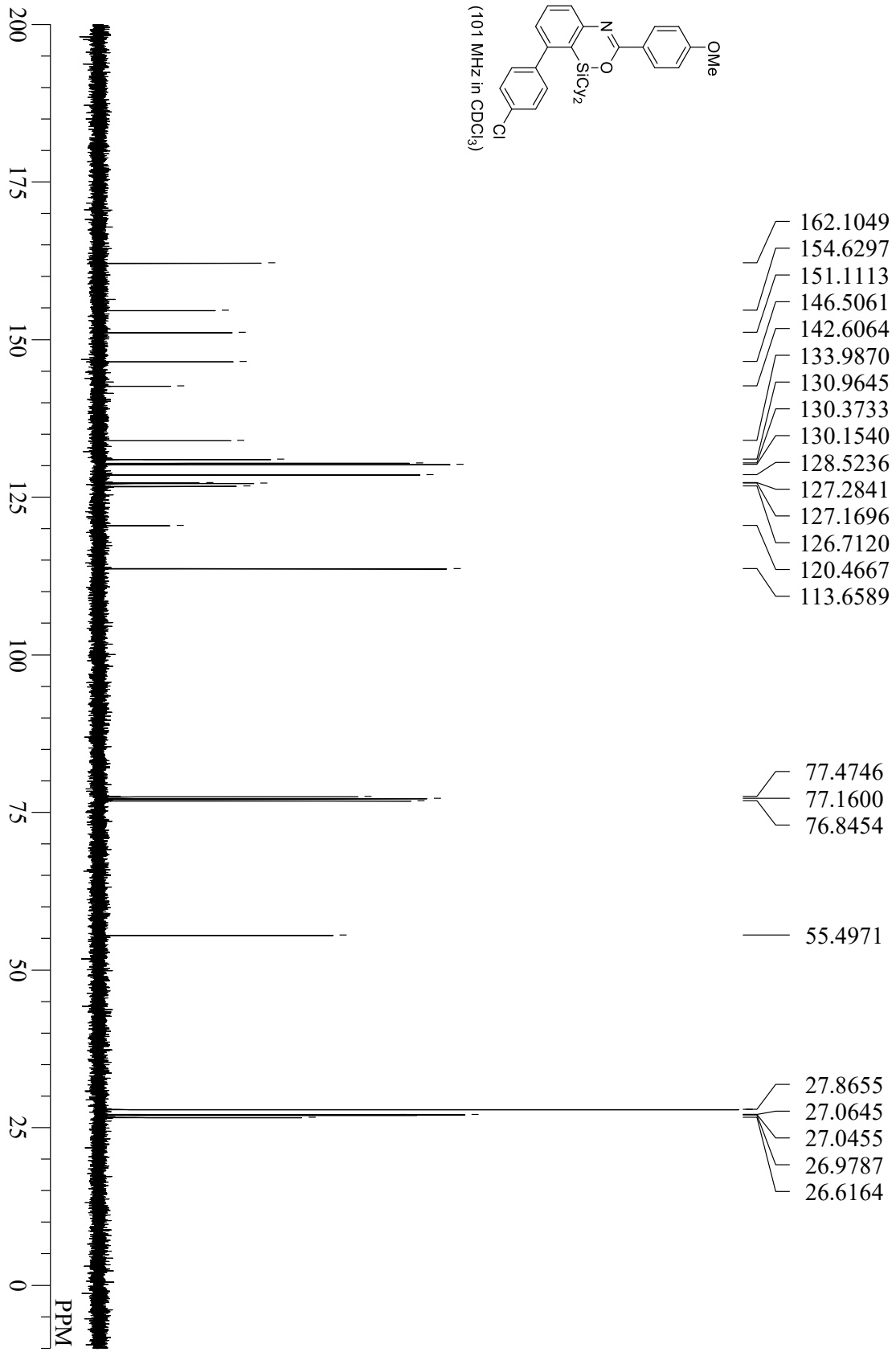
compound **3f**


(101 MHz in CDCl3)
F
SiCy2
N
O
OMe
163.9642
162.0858
161.5042
154.5915
151.0732
146.7254
140.1750
140.1464
130.9073
130.6689
130.5831
130.1445
127.3222
127.0266
126.8836
120.5525
115.3466
115.1368
113.6494
77.4842
77.1600
76.8454
55.4780
27.8655
27.0359
26.9692
26.6069
200
175
150
125
100
75
50
25
0
PPM

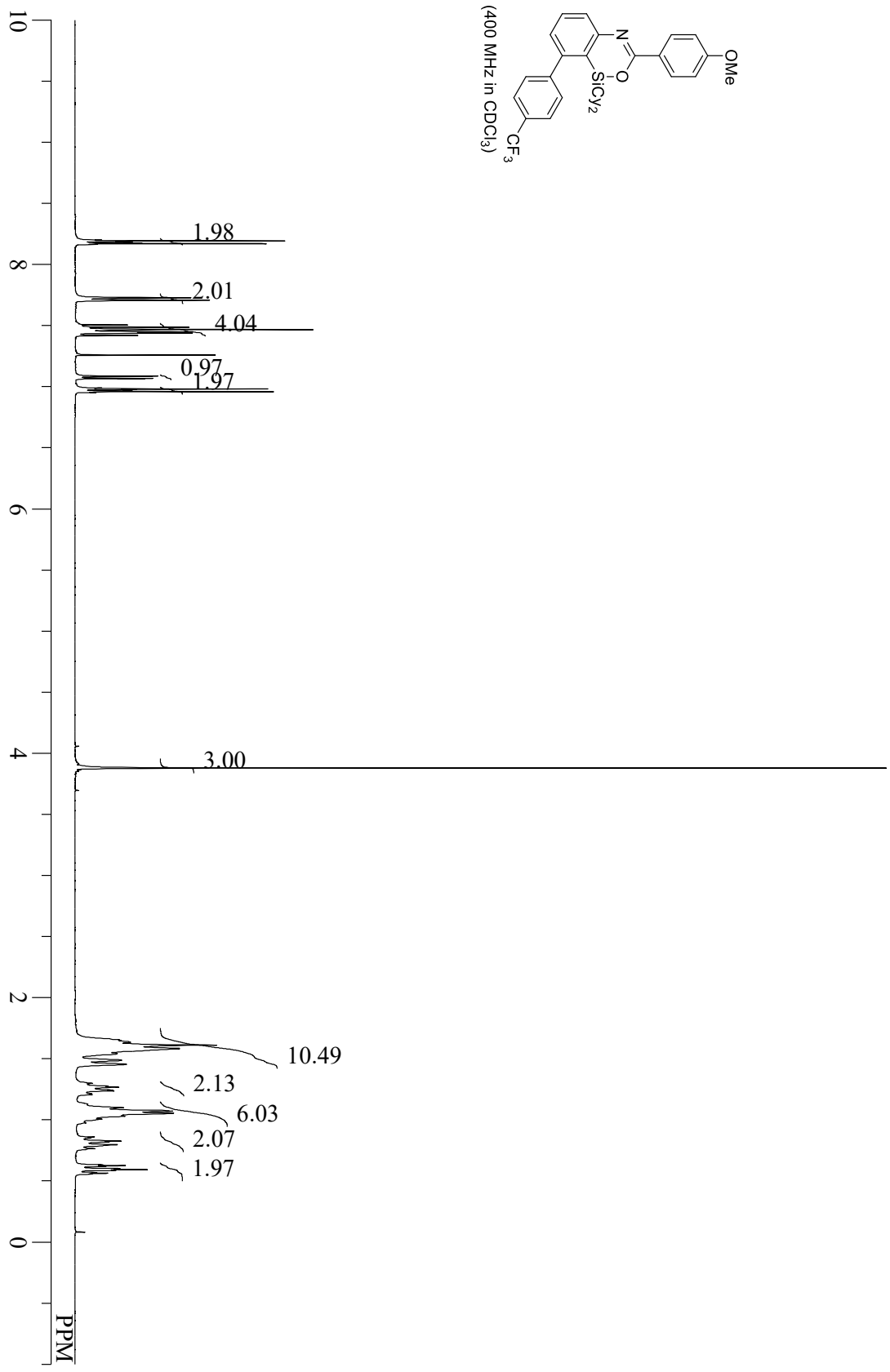
compound **3g**


(400 MHz in CDCl3)
Cl
SiCy2
O
N
OMe
1.99
4.09
3.16
0.99
2.01
3.00
12.29
2.22
6.18
2.13
1.92
10
8
6
4
2
0
PPM

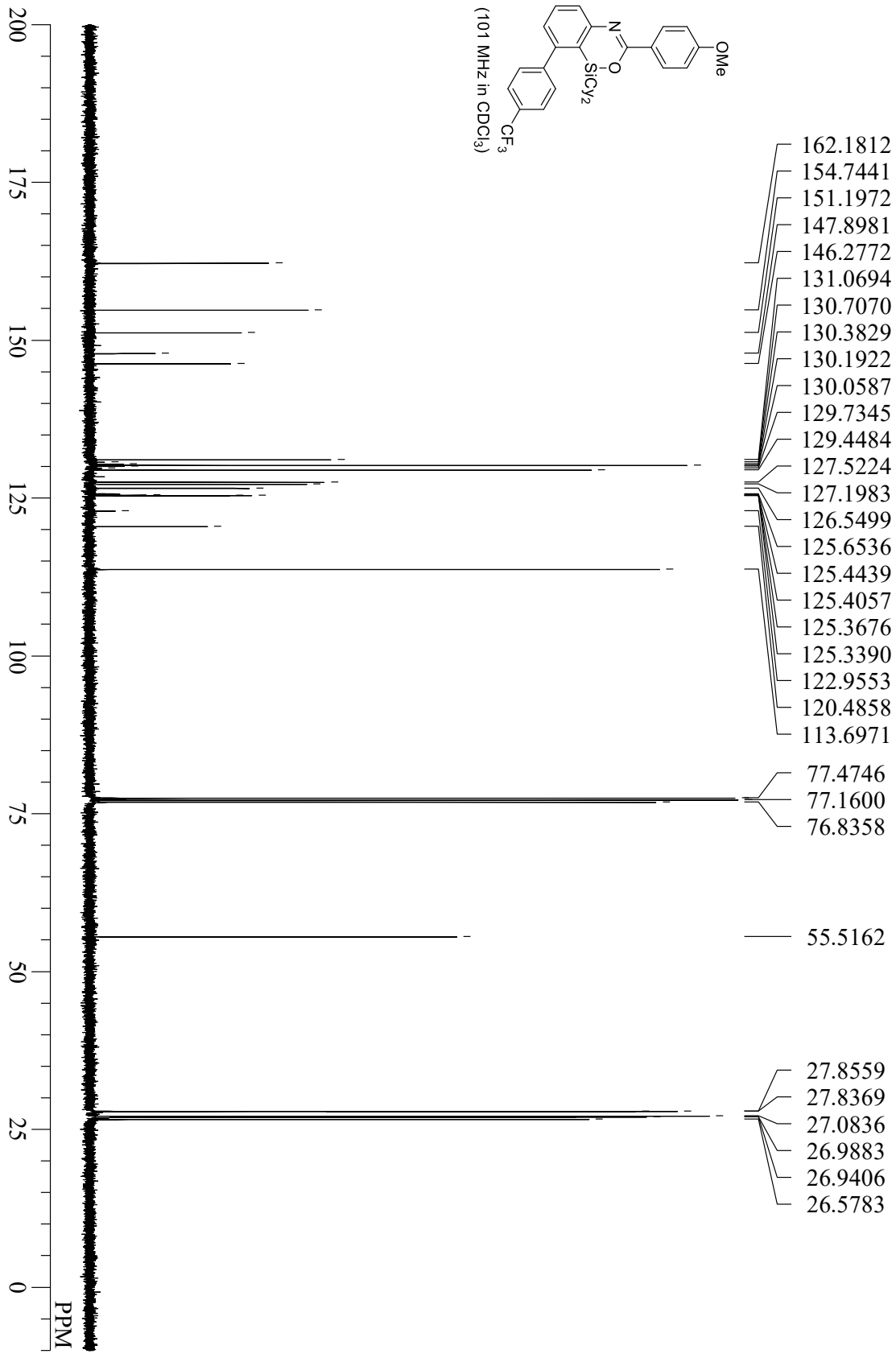
compound **3g**


(101 MHz in CDCl3)
N
O
SiCy2
Cl
OMe
162.1049
154.6297
151.1113
146.5061
142.6064
133.9870
130.9645
130.3733
130.1540
128.5236
127.2841
127.1696
126.7120
120.4667
113.6589
77.4746
77.1600
76.8454
55.4971
27.8655
27.0645
27.0455
26.9787
26.6164
200
175
150
125
100
75
50
25
0
PPM

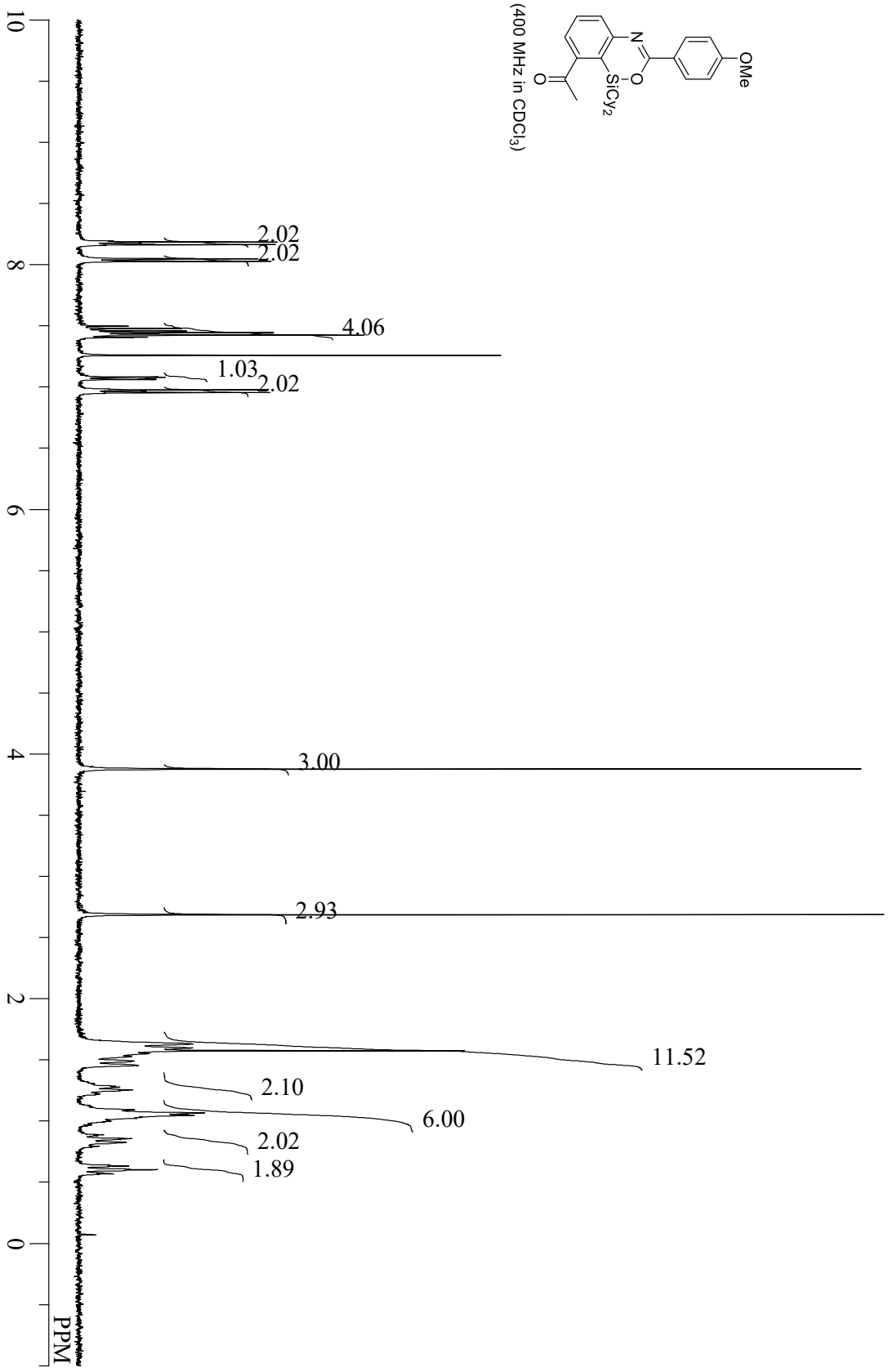
compound **3h**


(400 MHz in CDCl3)
OMe
SiCy2
CF3
1.98
2.01
4.04
0.97
1.97
3.00
10.49
2.13
6.03
2.07
1.97
PPM

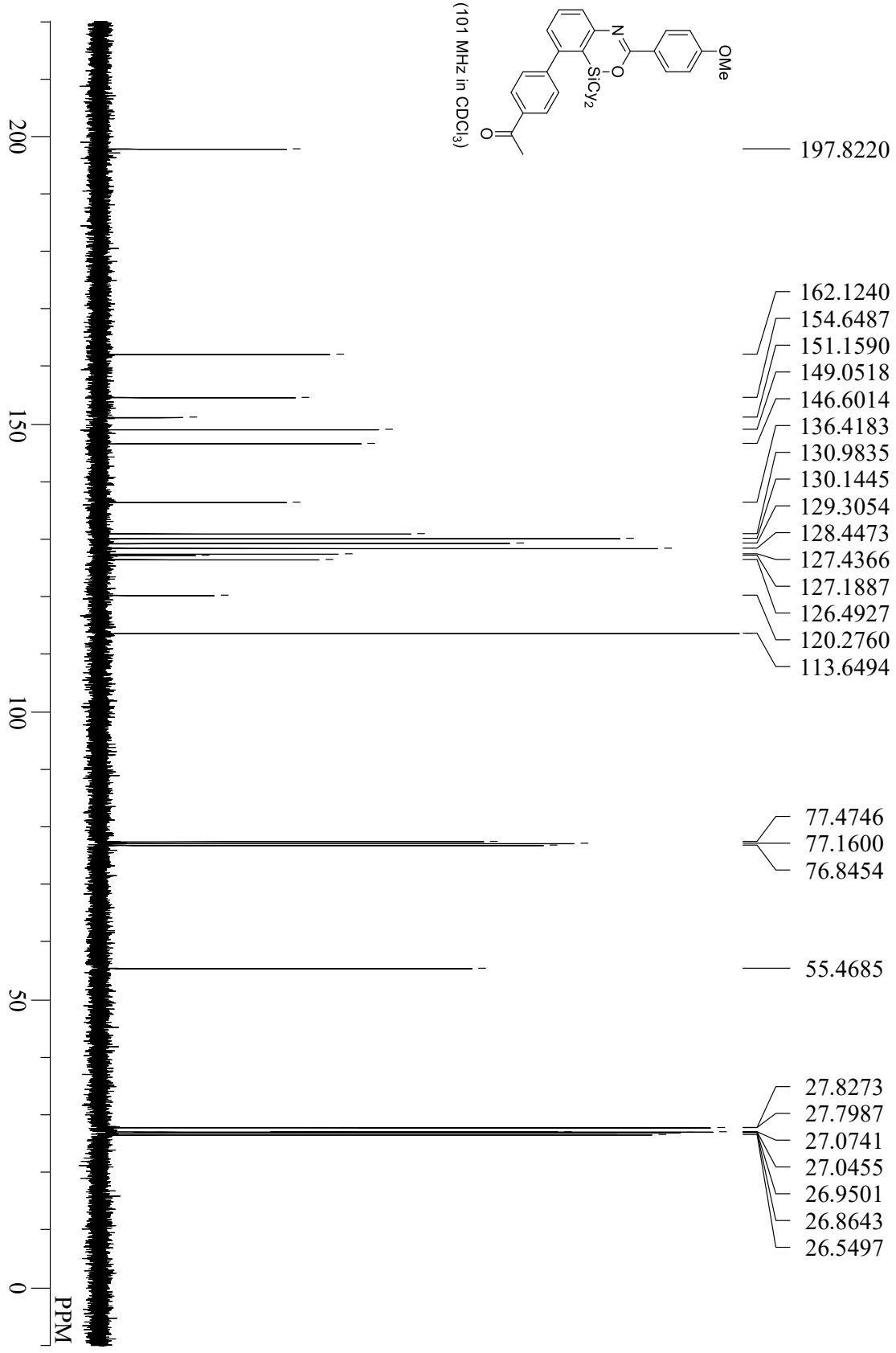
compound **3h**


(101 MHz in CDCl3)
CF3
SiCy2
N
O
OMe
162.1812
154.7441
151.1972
147.8981
146.2772
131.0694
130.7070
130.3829
130.1922
130.0587
129.7345
129.4484
127.5224
127.1983
126.5499
125.6536
125.4439
125.4057
125.3676
125.3390
122.9553
120.4858
113.6971
77.4746
77.1600
76.8358
55.5162
27.8559
27.8369
27.0836
26.9883
26.9406
26.5783
200
175
150
125
100
75
50
25
0
PPM

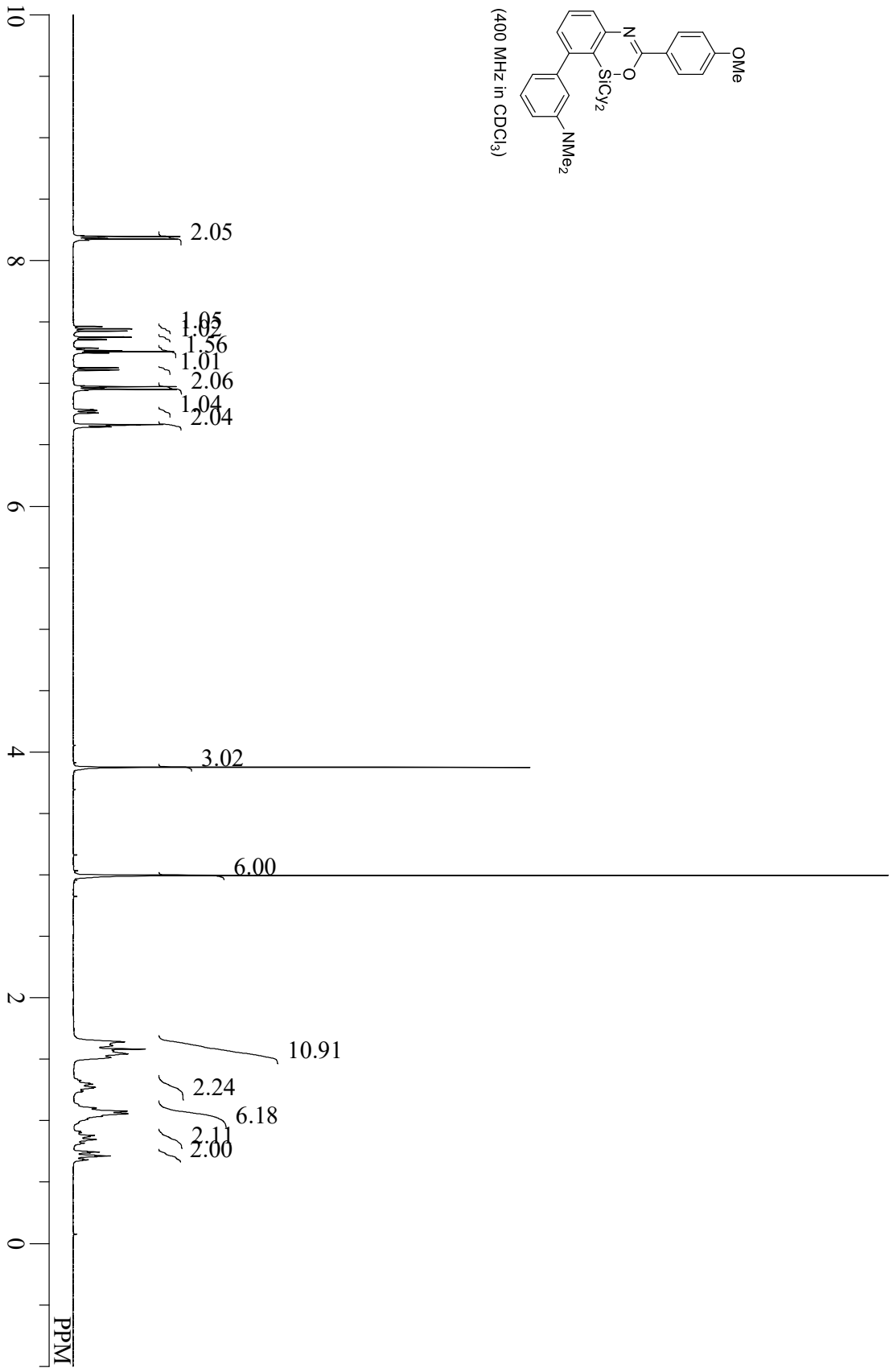
compound **3i**


(400 MHz in CDCl3)
O
N
O
SiCy2
OMe
2.02
2.02
4.06
1.03
2.02
3.00
2.93
11.52
2.10
6.00
2.02
1.89
10
8
6
4
2
0
PPM

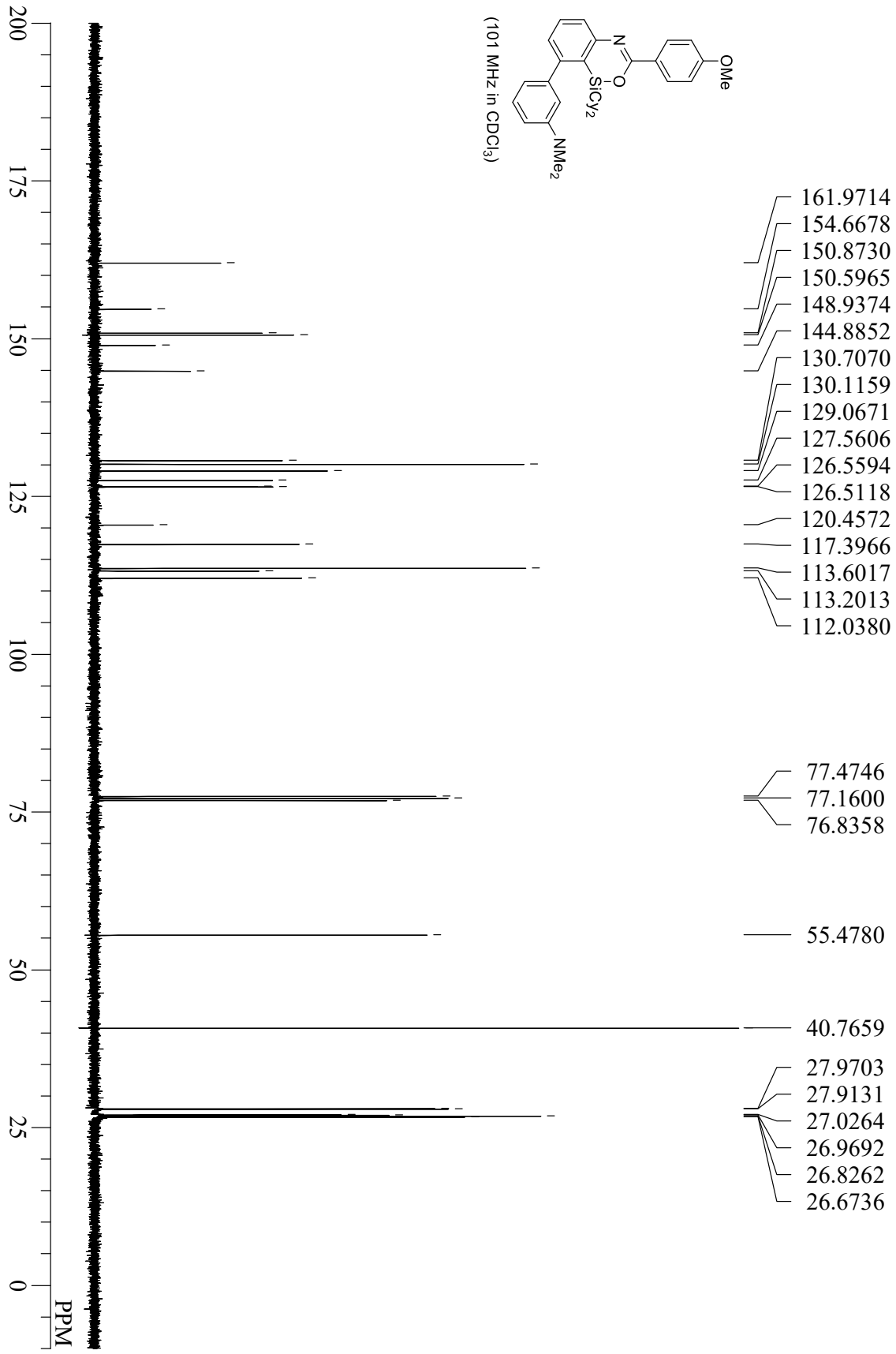
compound **3i**


(101 MHz in CDCl3)
197.8220
162.1240
154.6487
151.1590
149.0518
146.6014
136.4183
130.9835
130.1445
129.3054
128.4473
127.4366
127.1887
126.4927
120.2760
113.6494
77.4746
77.1600
76.8454
55.4685
27.8273
27.7987
27.0741
27.0455
26.9501
26.8643
26.5497
200
150
100
50
0
PPM

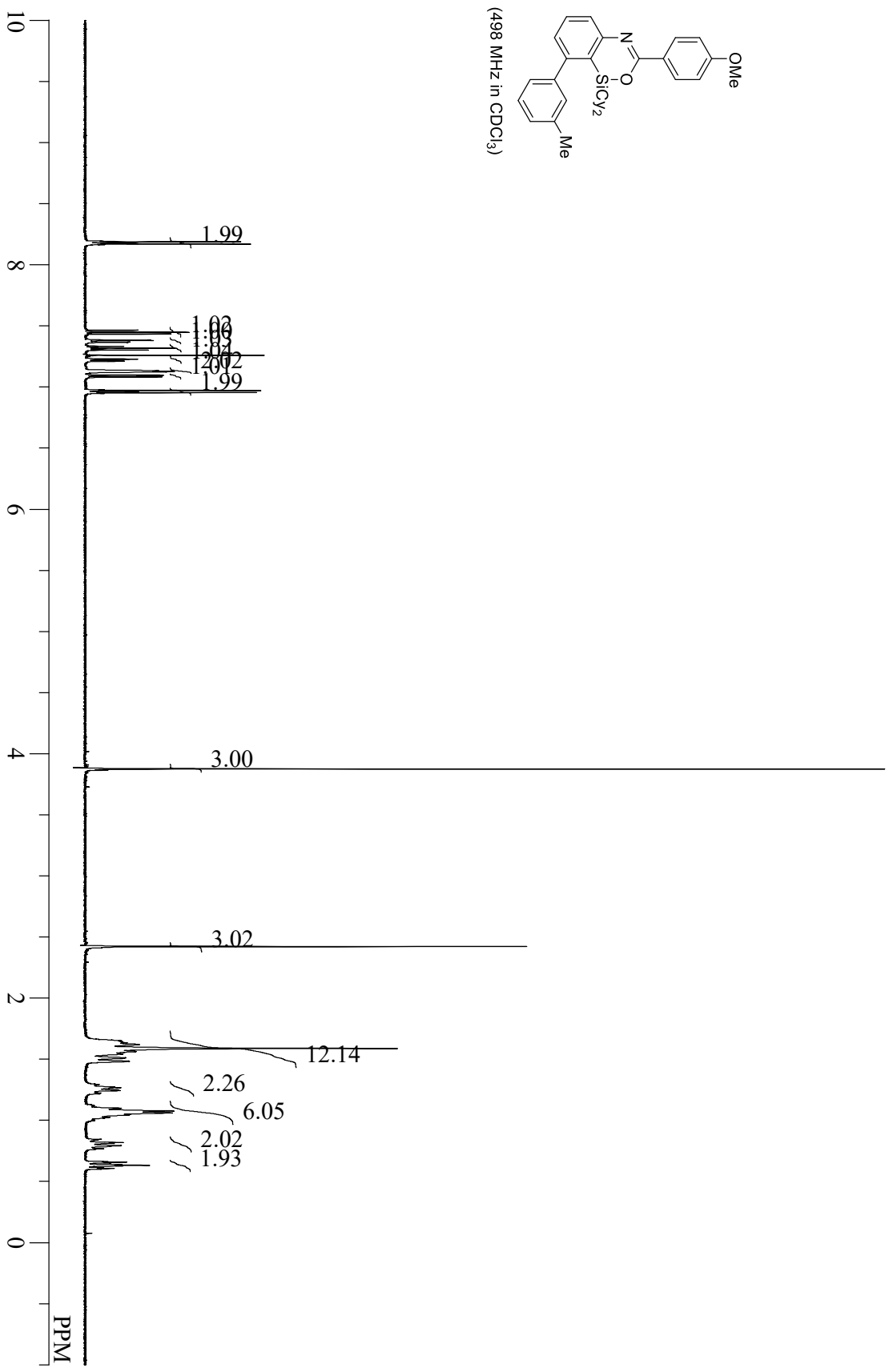
compound **3j**


(400 MHz in CDCl3)
N
O
SiCy2
OMe
NMe2
2.05
1.05
1.02
1.56
1.01
2.06
1.04
2.04
3.02
6.00
10.91
2.24
6.18
2.11
2.00
10
8
6
4
2
0
PPM

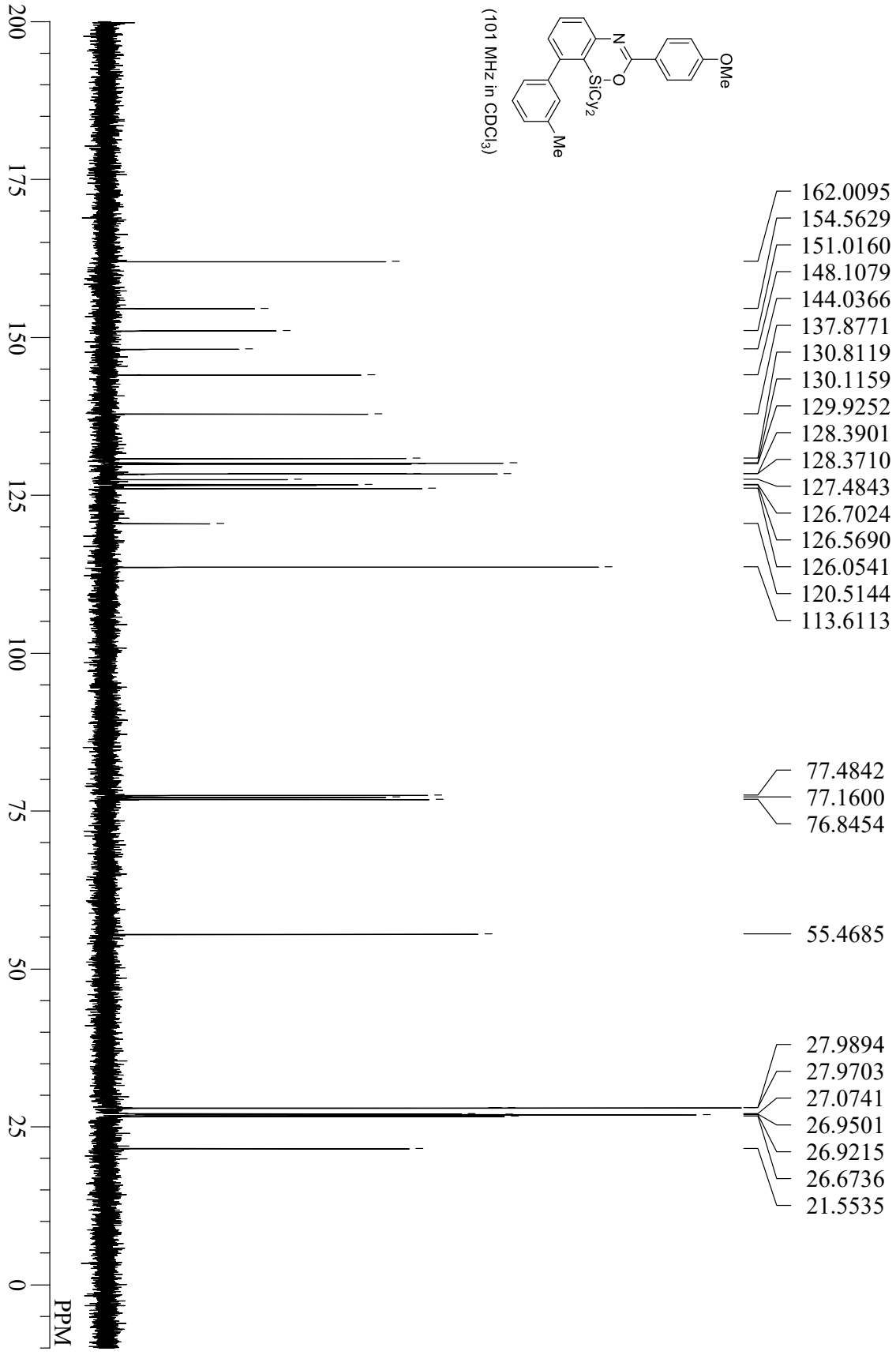
compound **3j**


(101 MHz in CDCl3)
NMe2
SiCy2
N
O
OMe
161.9714
154.6678
150.8730
150.5965
148.9374
144.8852
130.7070
130.1159
129.0671
127.5606
126.5594
126.5118
120.4572
117.3966
113.6017
113.2013
112.0380
77.4746
77.1600
76.8358
55.4780
40.7659
27.9703
27.9131
27.0264
26.9692
26.8262
26.6736
200
175
150
125
100
75
50
25
0
PPM

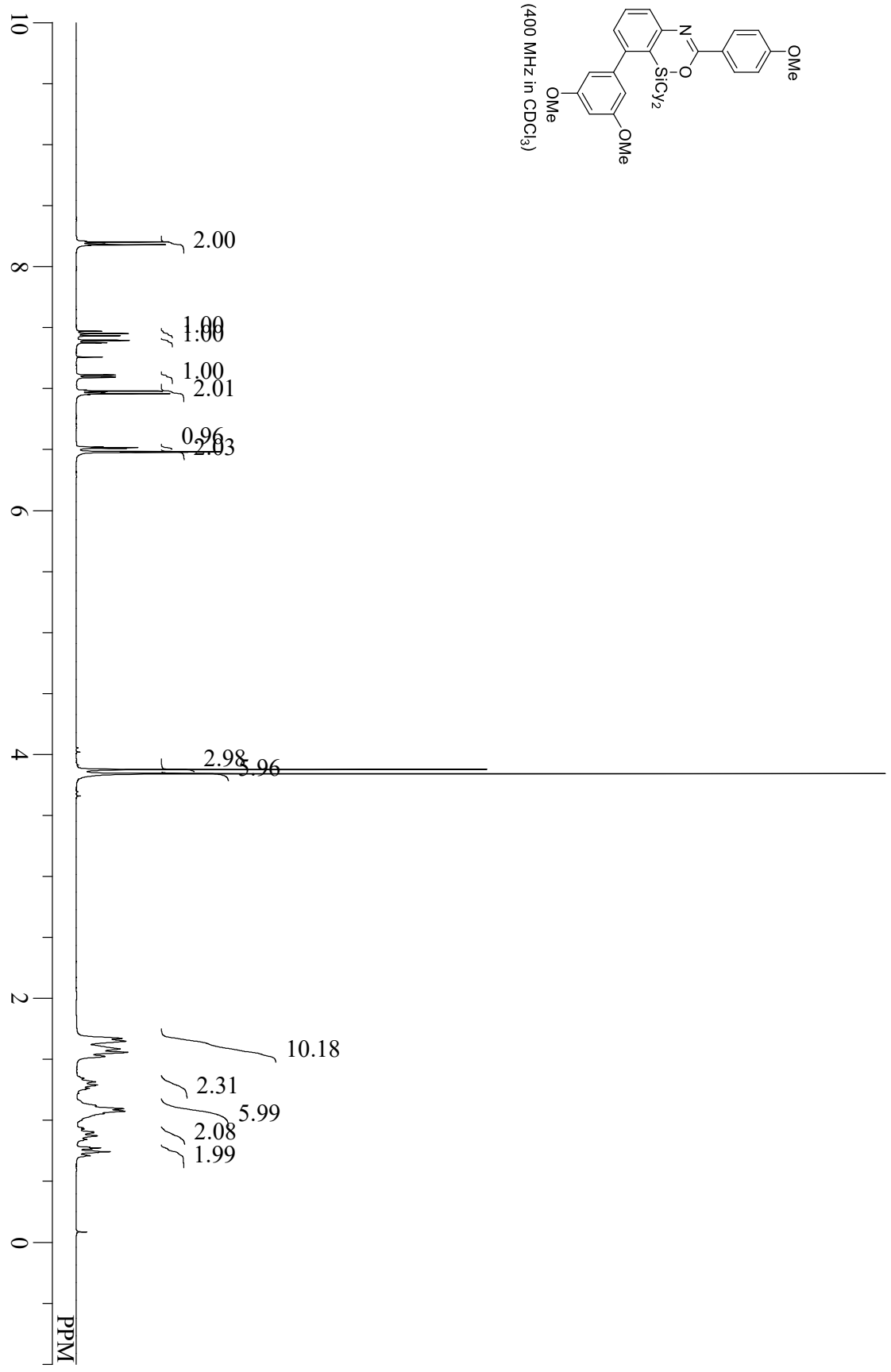
compound **3k**


(498 MHz in CDCl3)
N
O
SiCy2
OMe
Me
1.99
1.02
1.99
3.00
3.02
12.14
2.26
6.05
2.02
1.93
PPM

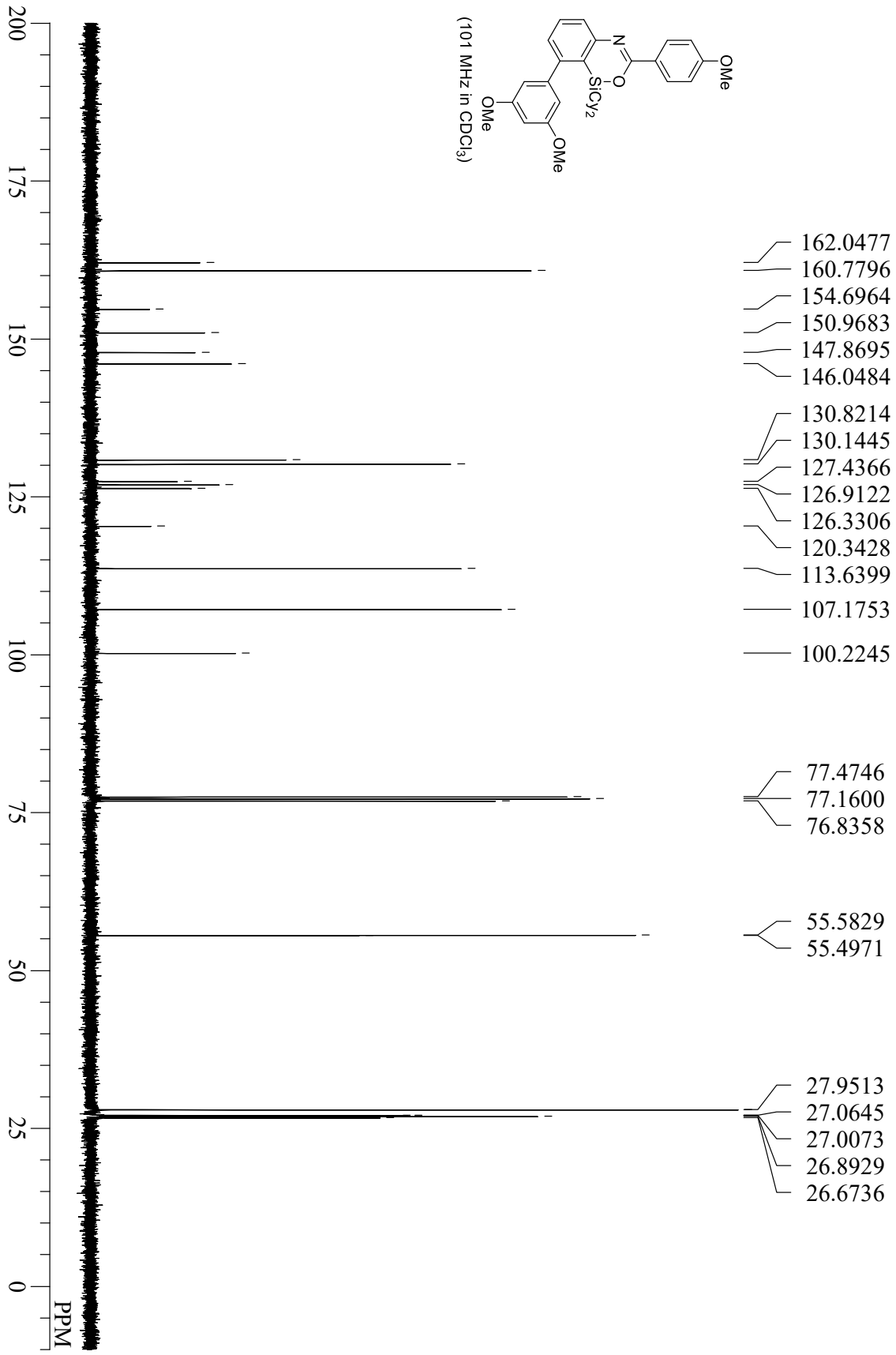
compound **3k**


(101 MHz in CDCl3)
N
O
SiCy2
OMe
Me
162.0095
154.5629
151.0160
148.1079
144.0366
137.8771
130.8119
130.1159
129.9252
128.3901
128.3710
127.4843
126.7024
126.5690
126.0541
120.5144
113.6113
77.4842
77.1600
76.8454
55.4685
27.9894
27.9703
27.0741
26.9501
26.9215
26.6736
21.5535
200
175
150
125
100
75
50
25
0
PPM

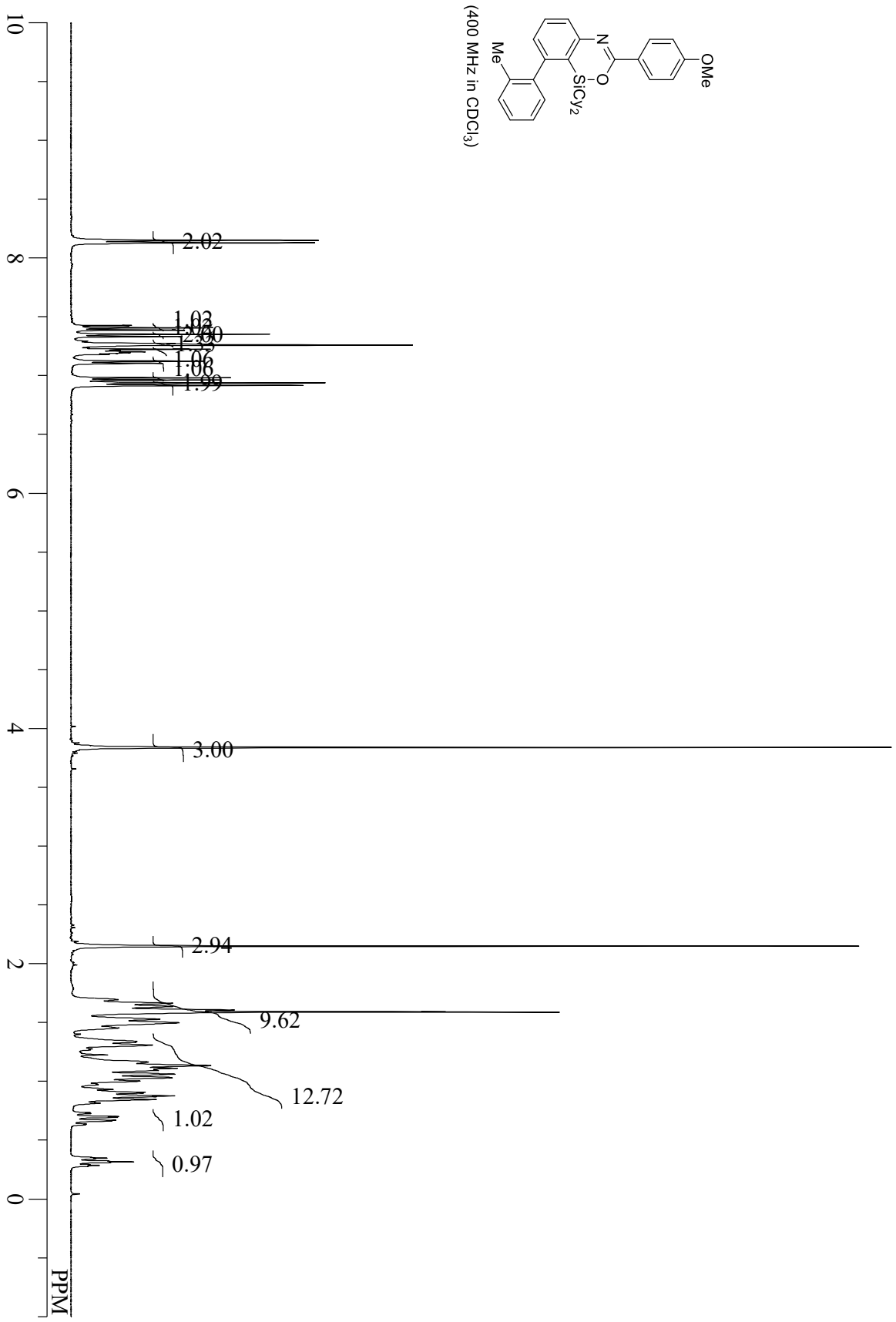
compound **3l**


(400 MHz in CDCl3)
OMe
OMe
OMe
SiCy2
N
O
2.00
1.00
1.00
1.00
2.01
0.96
2.03
2.98
5.96
10.18
2.31
5.99
2.08
1.99
PPM

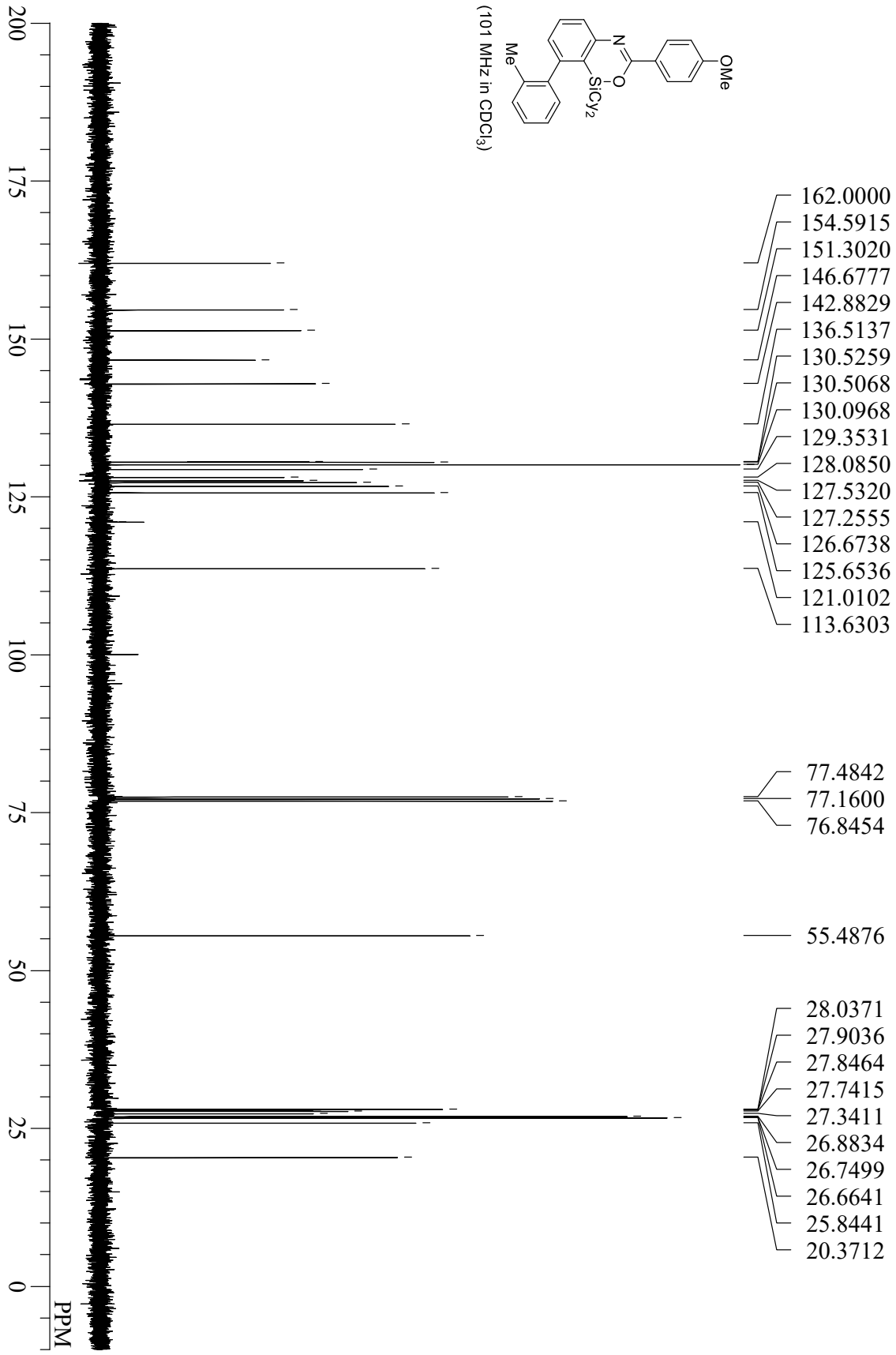
compound **3l**


(101 MHz in CDCl3)
OMe
OMe
SiCy2
N
O
OMe
162.0477
160.7796
154.6964
150.9683
147.8695
146.0484
130.8214
130.1445
127.4366
126.9122
126.3306
120.3428
113.6399
107.1753
100.2245
77.4746
77.1600
76.8358
55.5829
55.4971
27.9513
27.0645
27.0073
26.8929
26.6736
200
175
150
125
100
75
50
25
0
PPM

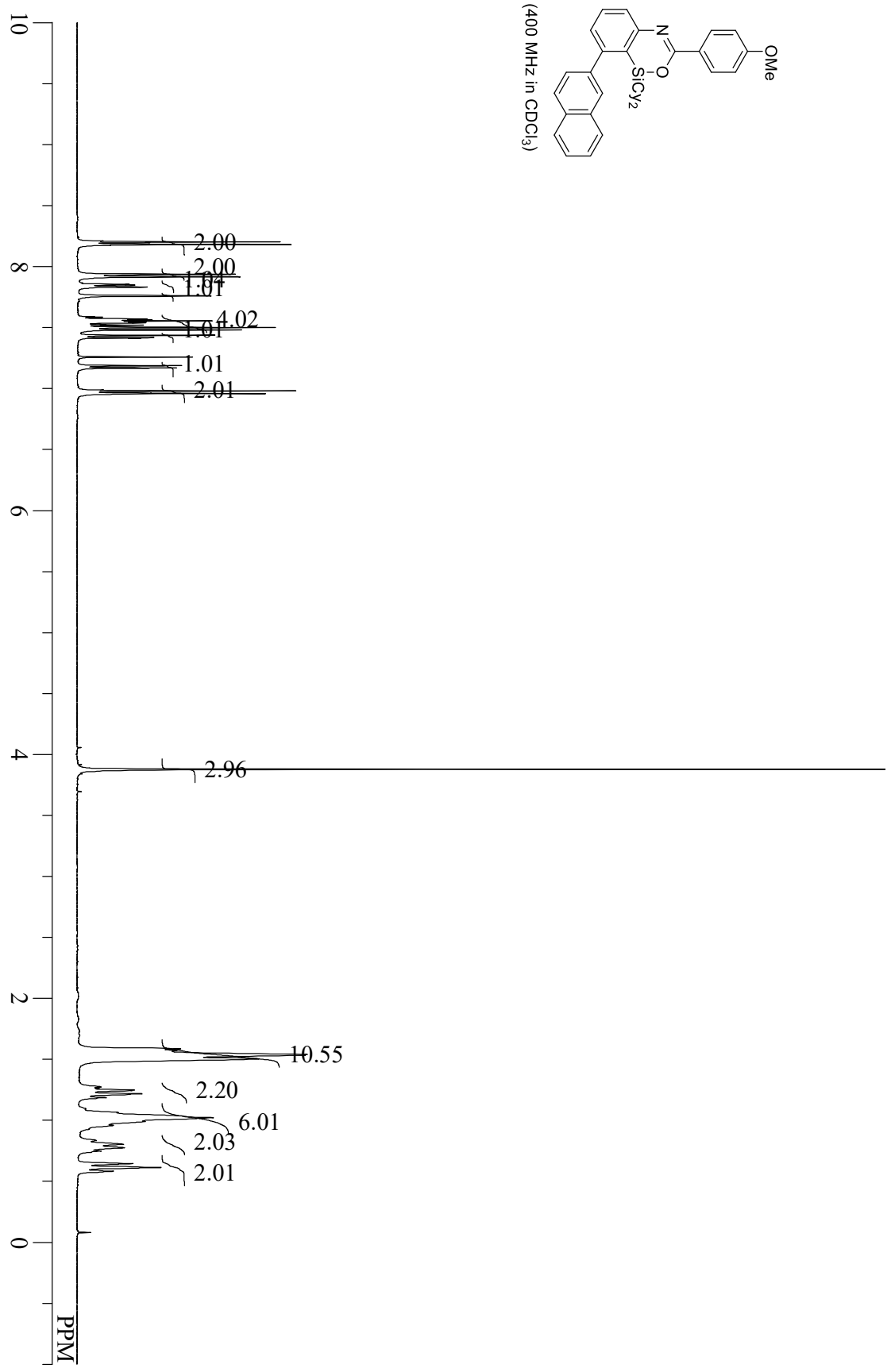
compound **3m**


(400 MHz in CDCl3)
Me
N
O
SiCy2
OMe
2.02
1.03
1.99
3.00
2.94
9.62
12.72
1.02
0.97
10
8
6
4
2
0
PPM

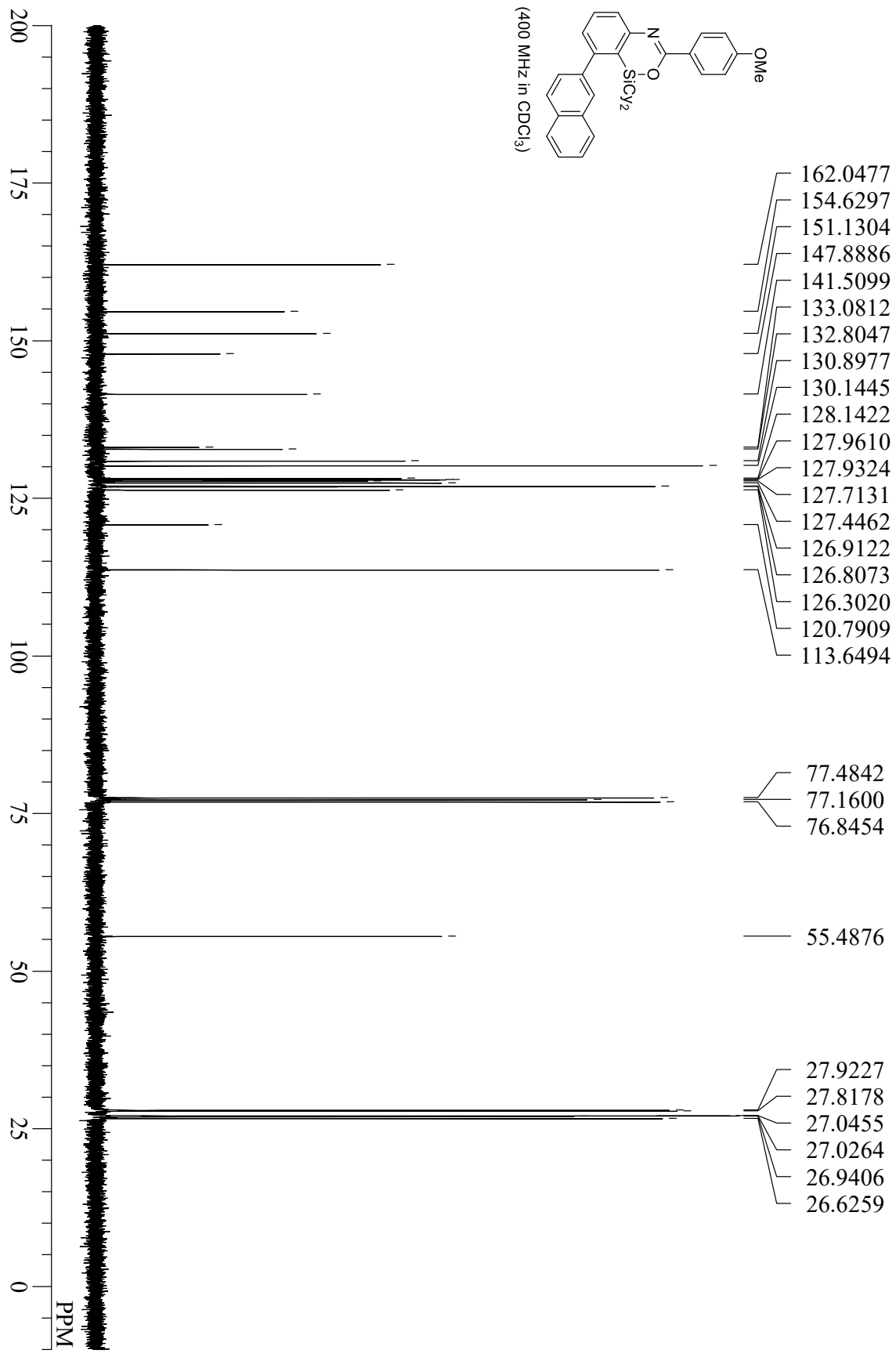
compound **3m**


(101 MHz in CDCl3)
Me
SiCy2
O
N
OMe
162.0000
154.5915
151.3020
146.6777
142.8829
136.5137
130.5259
130.5068
130.0968
129.3531
128.0850
127.5320
127.2555
126.6738
125.6536
121.0102
113.6303
77.4842
77.1600
76.8454
55.4876
28.0371
27.9036
27.8464
27.7415
27.3411
26.8834
26.7499
26.6641
25.8441
20.3712
200
175
150
125
100
75
50
25
0
PPM

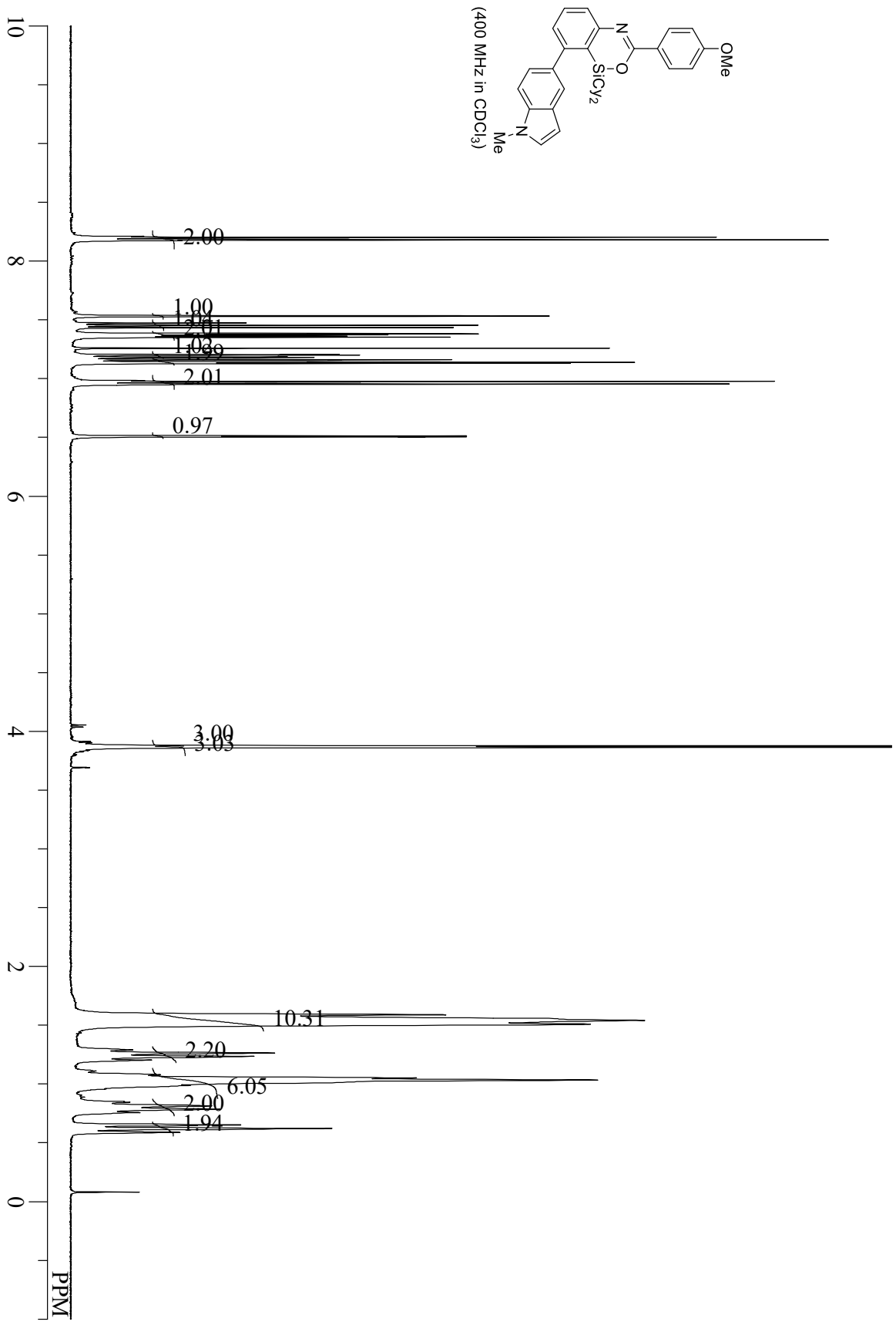
compound **3n**


(400 MHz in CDCl3)
N
O
SiCy2
OMe
10
8
6
4
2
0
PPM
2.00
2.00
1.01
1.01
4.02
1.01
1.01
2.01
2.96
10.55
2.20
6.01
2.03
2.01

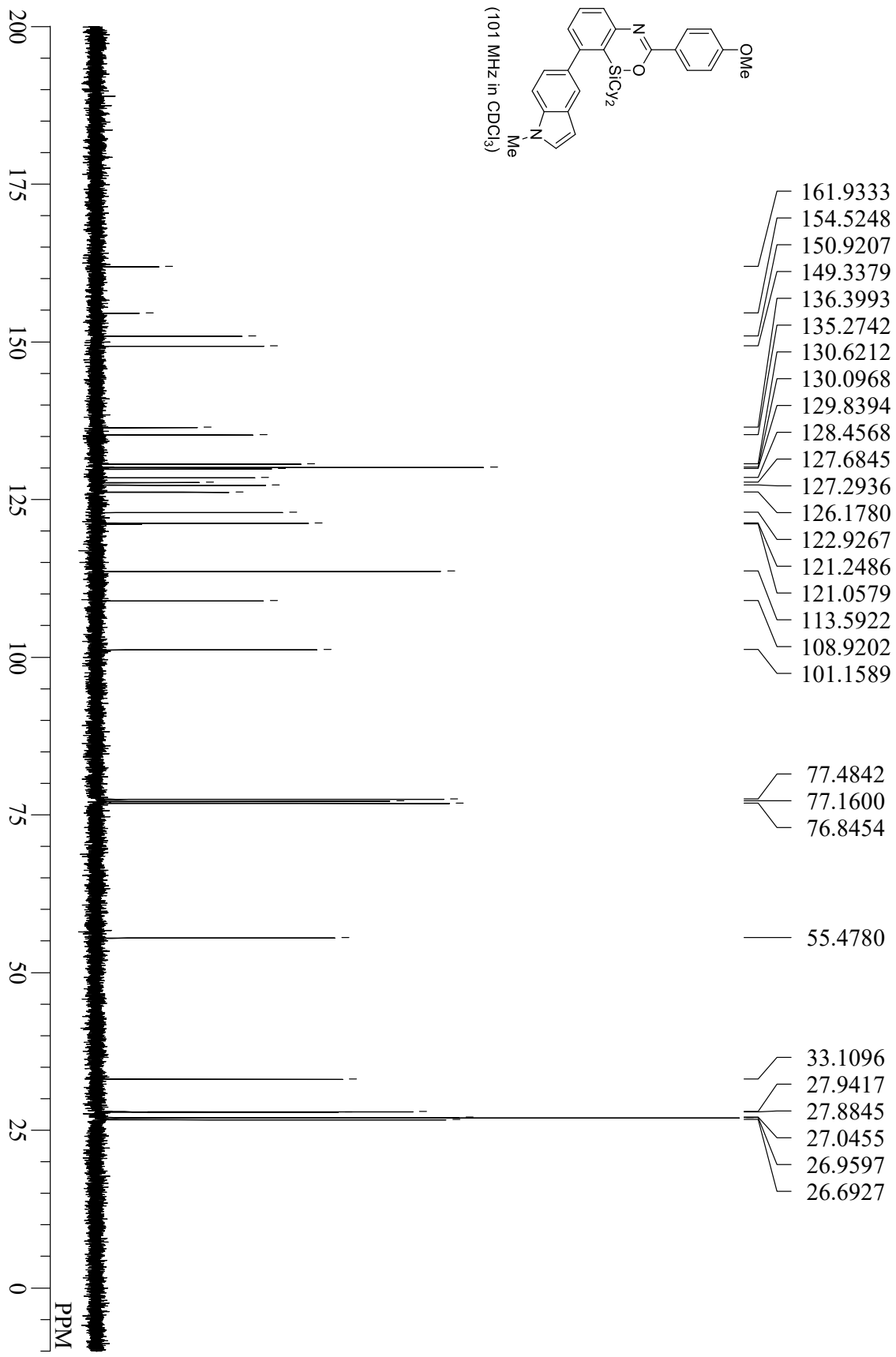
compound **3n**


(400 MHz in CDCl3)
N
O
SiCy2
OMe
162.0477
154.6297
151.1304
147.8886
141.5099
133.0812
132.8047
130.8977
130.1445
128.1422
127.9610
127.9324
127.7131
127.4462
126.9122
126.8073
126.3020
120.7909
113.6494
77.4842
77.1600
76.8454
55.4876
27.9227
27.8178
27.0455
27.0264
26.9406
26.6259
200
175
150
125
100
75
50
25
0
PPM

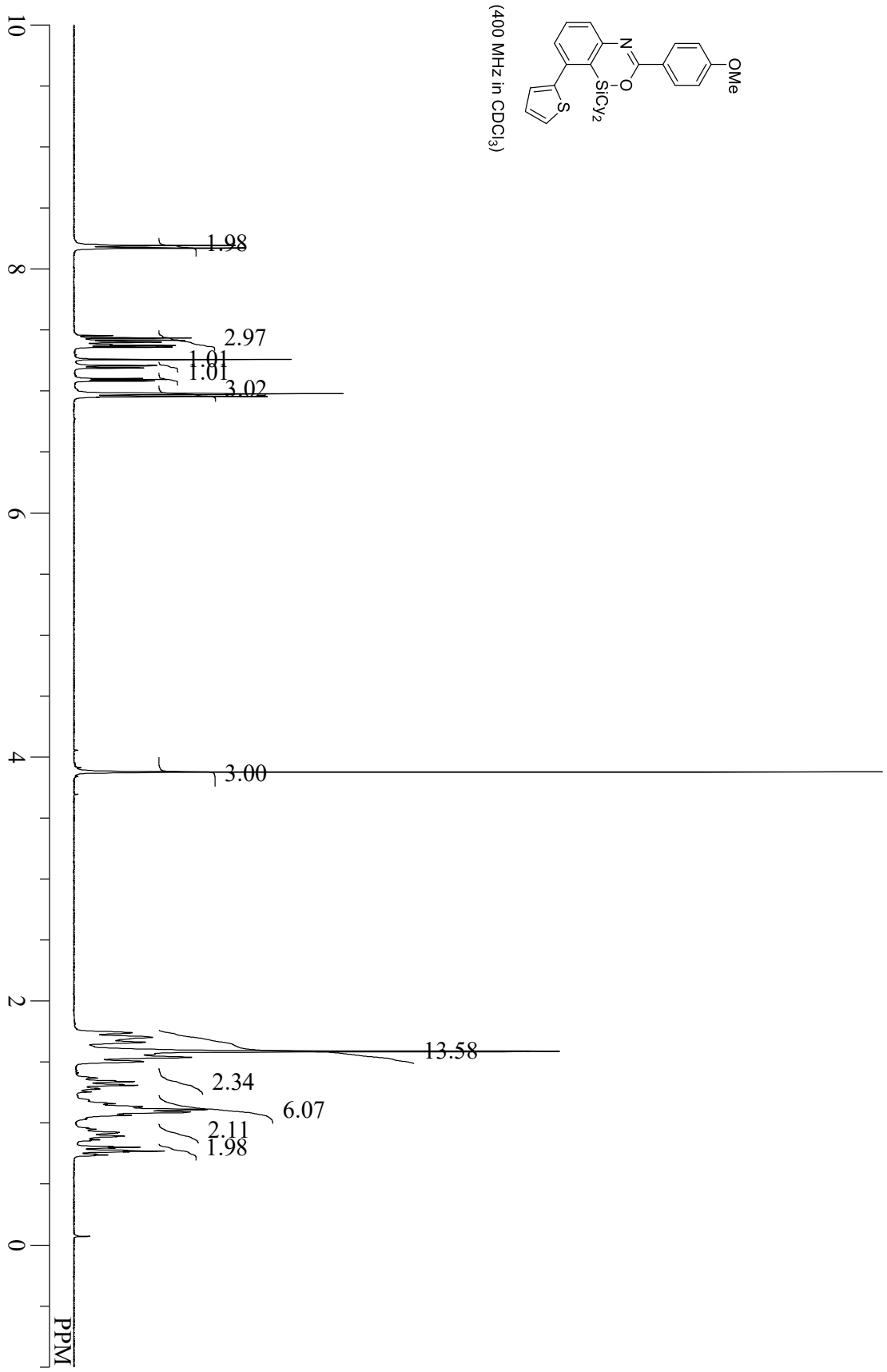
compound **3o**


(400 MHz in CDCl3)
N
O
SiCy2
OMe
N
Me
10
8
6
4
2
0
PPM
2.00
1.00
2.01
0.97
3.00
3.03
10.31
2.20
6.05
2.00
1.94

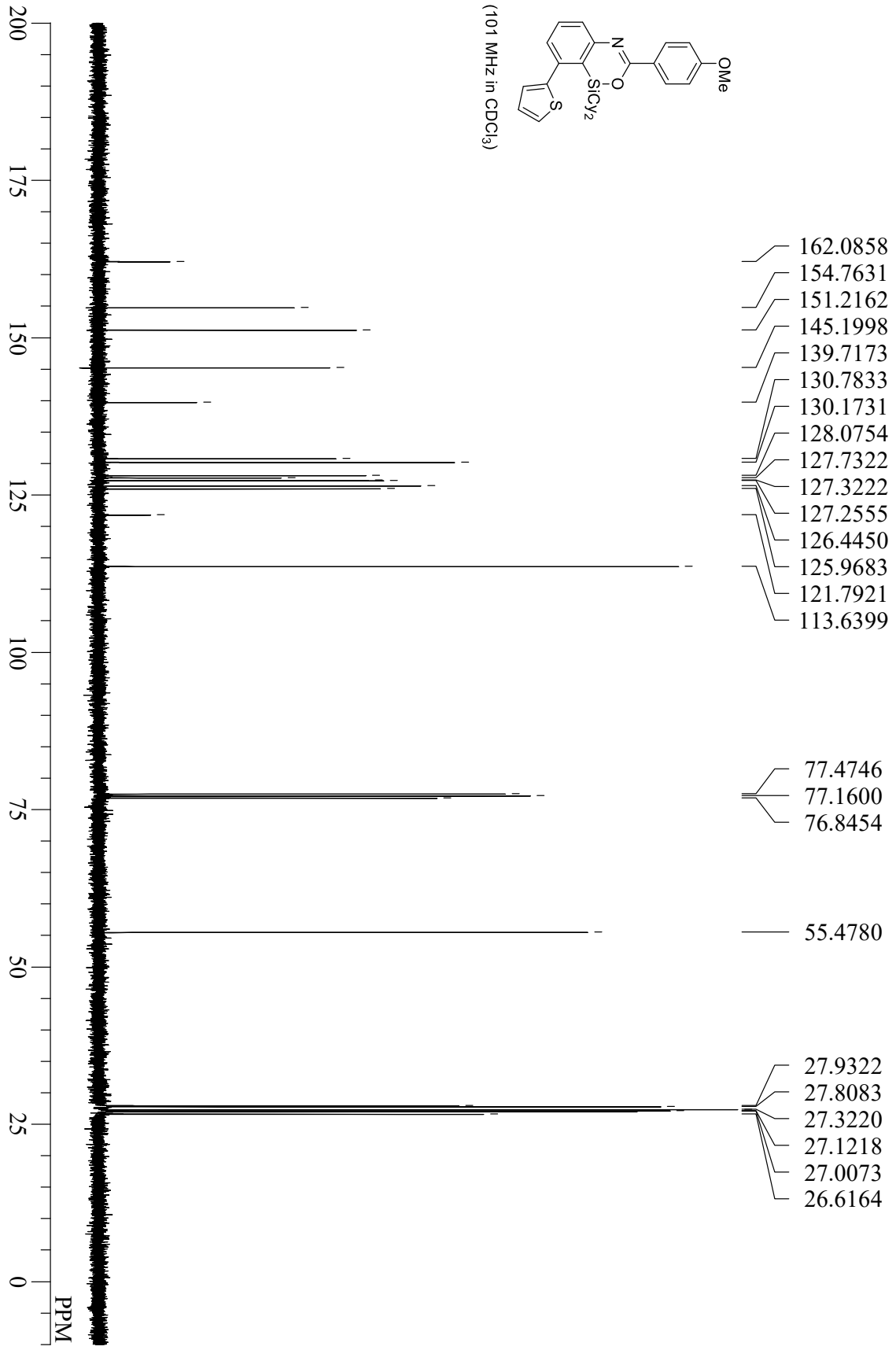
compound **3o**


(101 MHz in CDCl3)
N
O
SiCy2
OMe
Me
161.9333
154.5248
150.9207
149.3379
136.3993
135.2742
130.6212
130.0968
129.8394
128.4568
127.6845
127.2936
126.1780
122.9267
121.2486
121.0579
113.5922
108.9202
101.1589
77.4842
77.1600
76.8454
55.4780
33.1096
27.9417
27.8845
27.0455
26.9597
26.6927
200
175
150
125
100
75
50
25
0
PPM

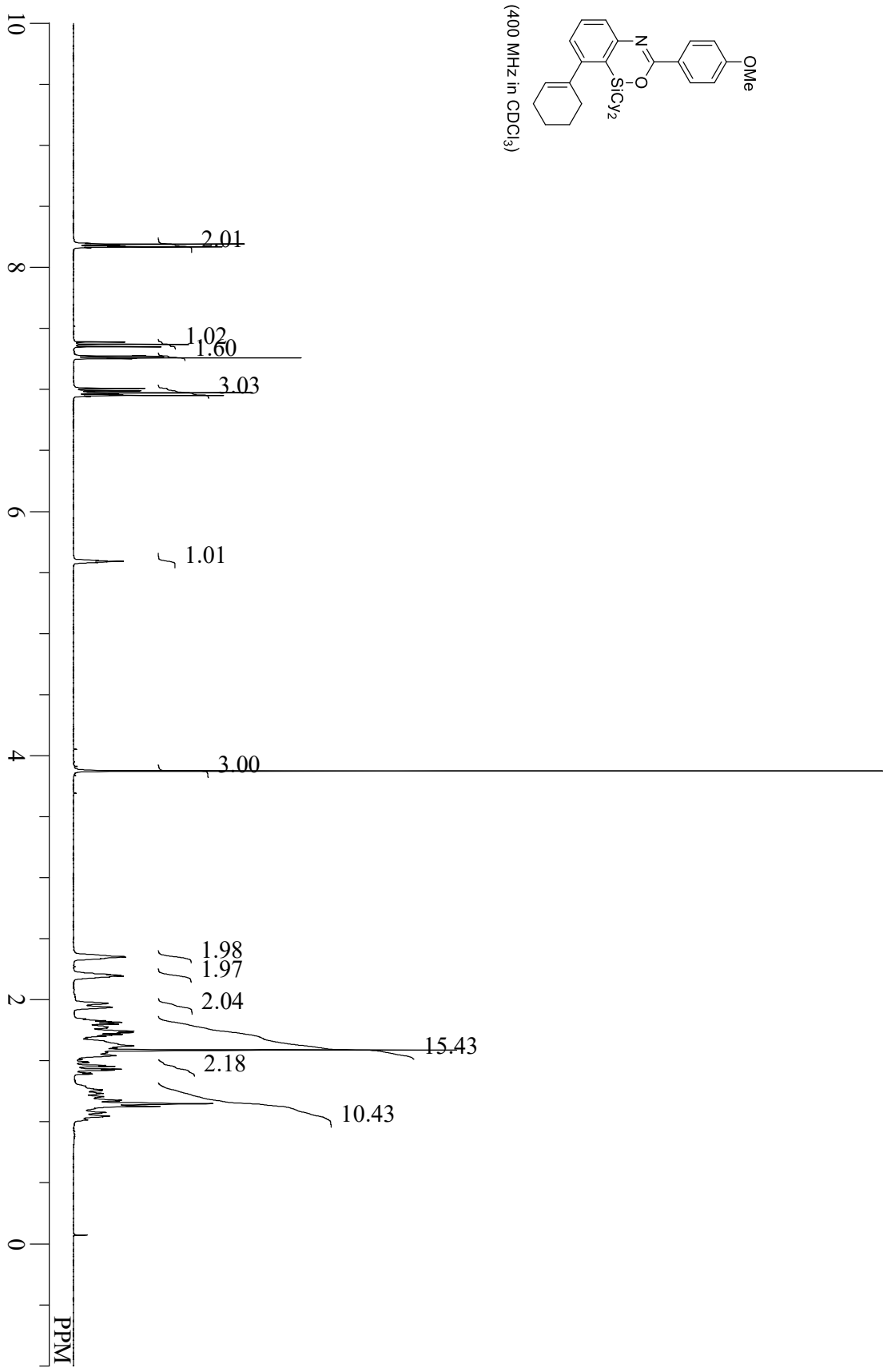
compound **3p**


(400 MHz in CDCl3)
N
O
SiCy2
S
OMe
1.98
2.97
1.01
1.01
3.02
3.00
13.58
2.34
6.07
2.11
1.98
10
8
6
4
2
0
PPM

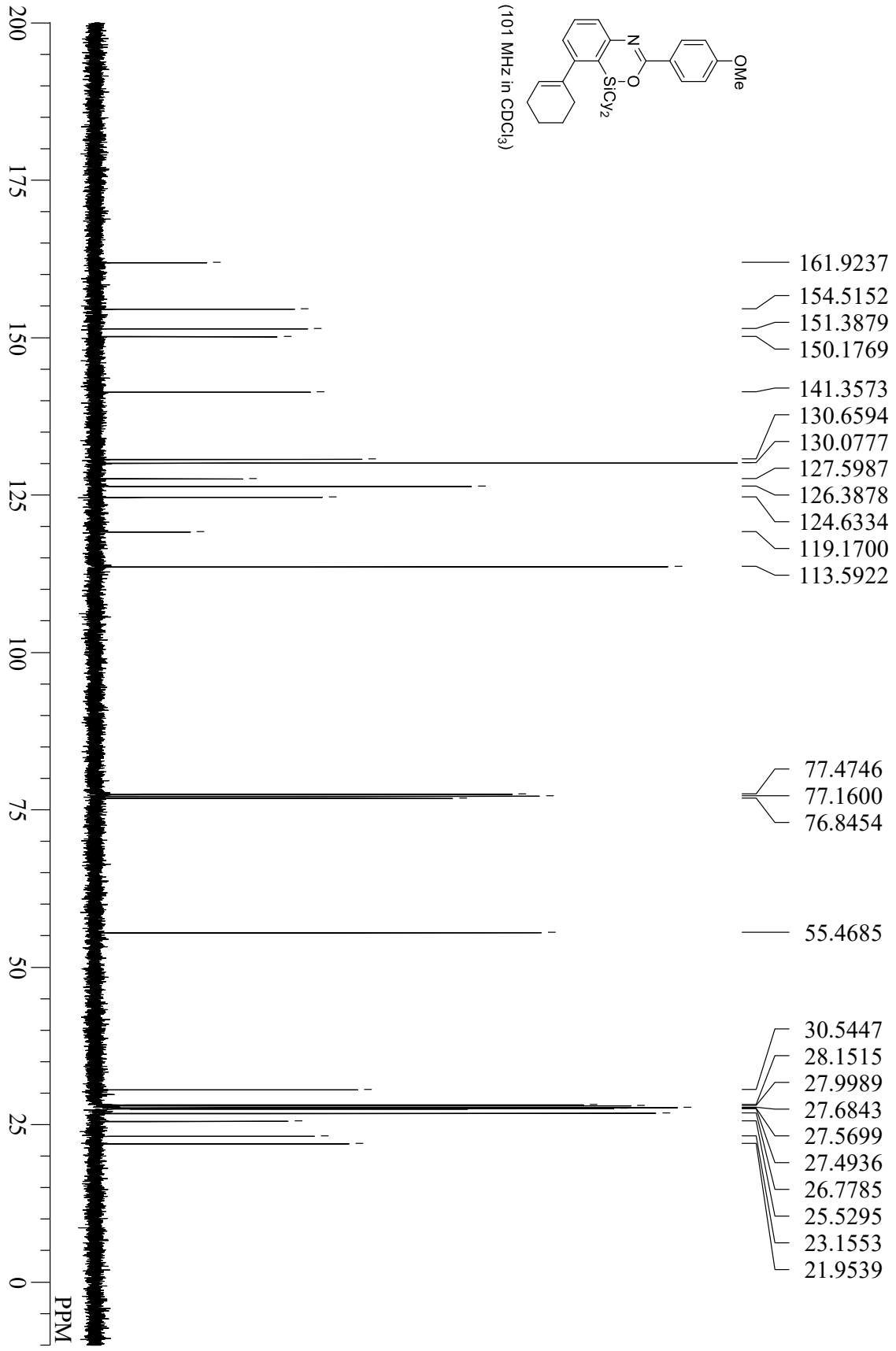
compound **3p**


(101 MHz in CDCl3)
N
O
SiCy2
S
OMe
200
175
150
125
100
75
50
25
0
PPM
162.0858
154.7631
151.2162
145.1998
139.7173
130.7833
130.1731
128.0754
127.7322
127.3222
127.2555
126.4450
125.9683
121.7921
113.6399
77.4746
77.1600
76.8454
55.4780
27.9322
27.8083
27.3220
27.1218
27.0073
26.6164

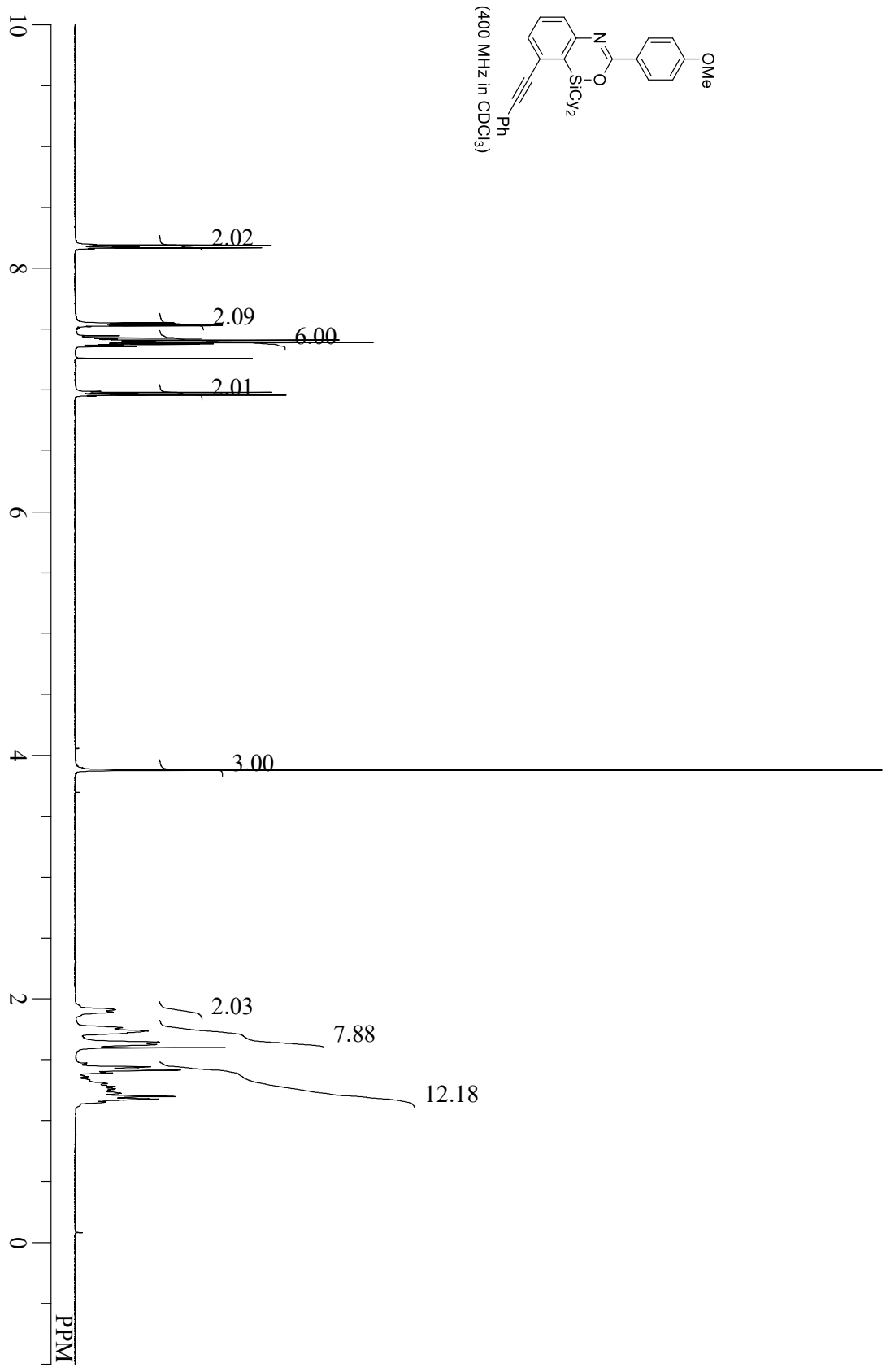
compound **3q**


(400 MHz in CDCl3)
N
O
SiCy2
OMe
10
8
6
4
2
0
PPM
2.01
1.02
1.60
3.03
1.01
3.00
1.98
1.97
2.04
15.43
2.18
10.43

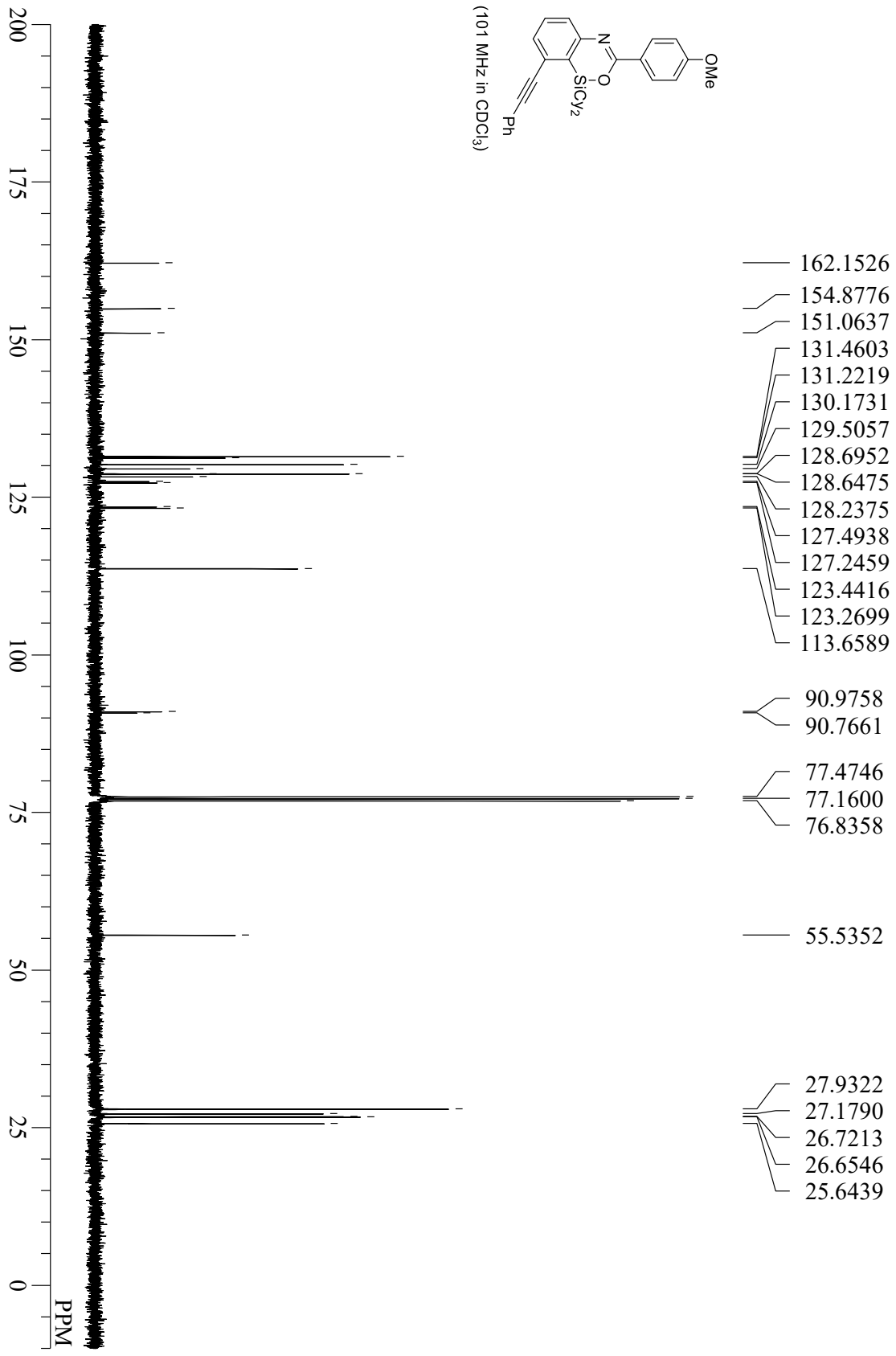
compound **3q**


(101 MHz in CDCl3)
N
O
SiCy2
OMe
161.9237
154.5152
151.3879
150.1769
141.3573
130.6594
130.0777
127.5987
126.3878
124.6334
119.1700
113.5922
77.4746
77.1600
76.8454
55.4685
30.5447
28.1515
27.9989
27.6843
27.5699
27.4936
26.7785
25.5295
23.1553
21.9539
200
175
150
125
100
75
50
25
0
PPM

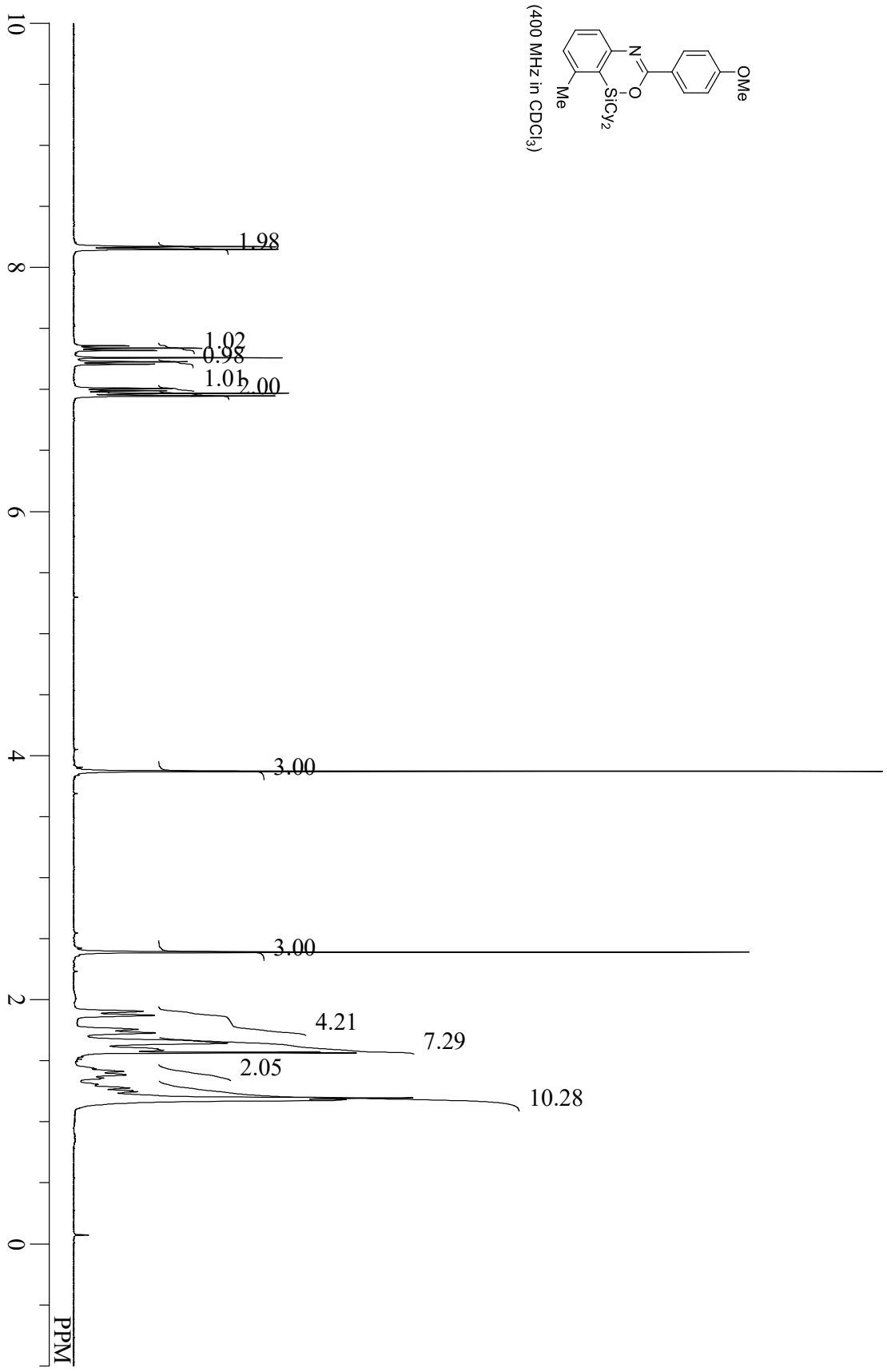
compound **3r**


(400 MHz in CDCl3)
Ph
SiCy2
N
O
OMe
2.02
2.09
6.00
2.01
3.00
2.03
7.88
12.18
10
8
6
4
2
0
PPM

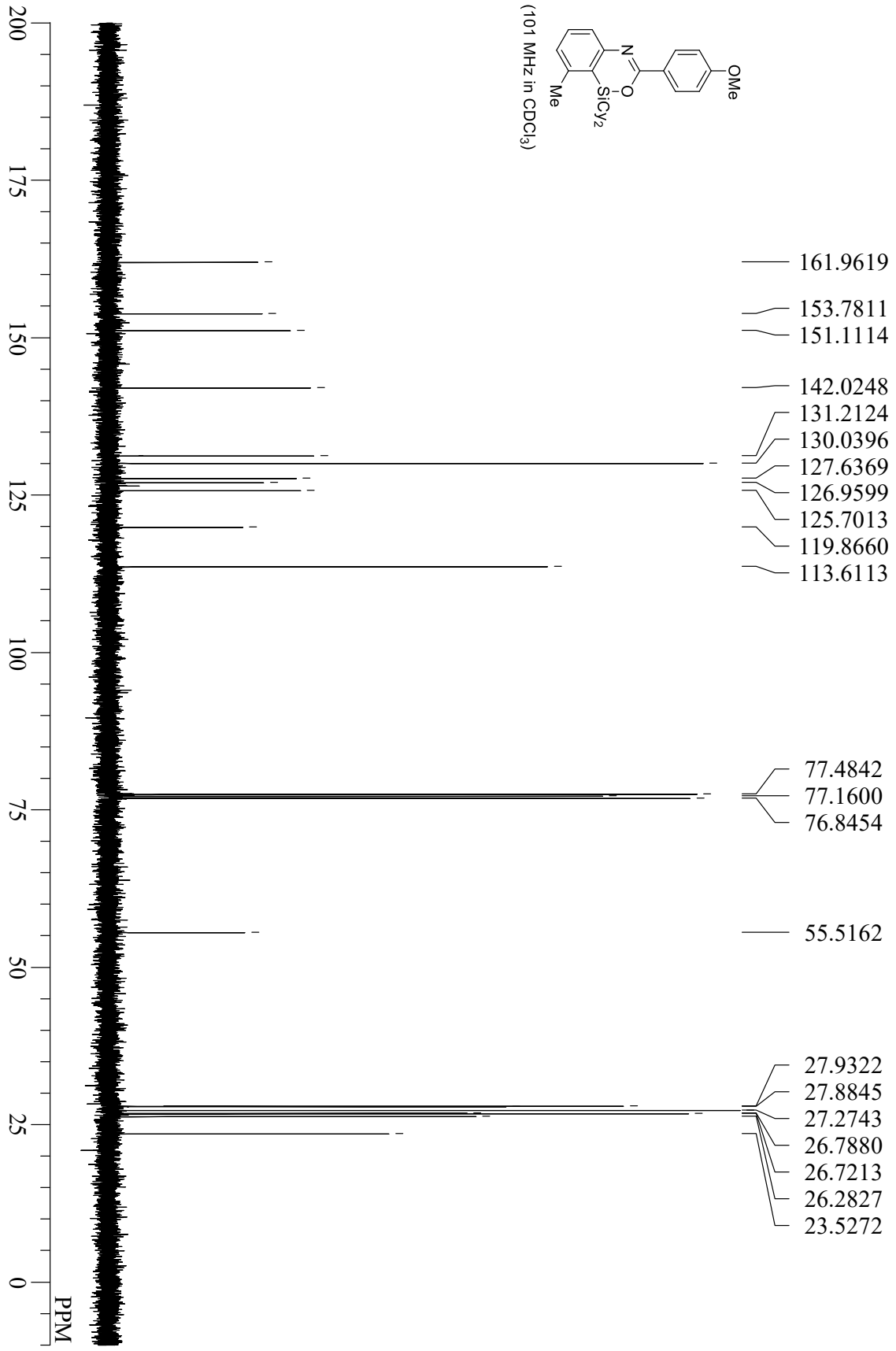
compound **3r**


(101 MHz in CDCl3)
N
O
SiCy2
OMe
Ph
200
175
150
125
100
75
50
25
0
PPM
162.1526
154.8776
151.0637
131.4603
131.2219
130.1731
129.5057
128.6952
128.6475
128.2375
127.4938
127.2459
123.4416
123.2699
113.6589
90.9758
90.7661
77.4746
77.1600
76.8358
55.5352
27.9322
27.1790
26.7213
26.6546
25.6439

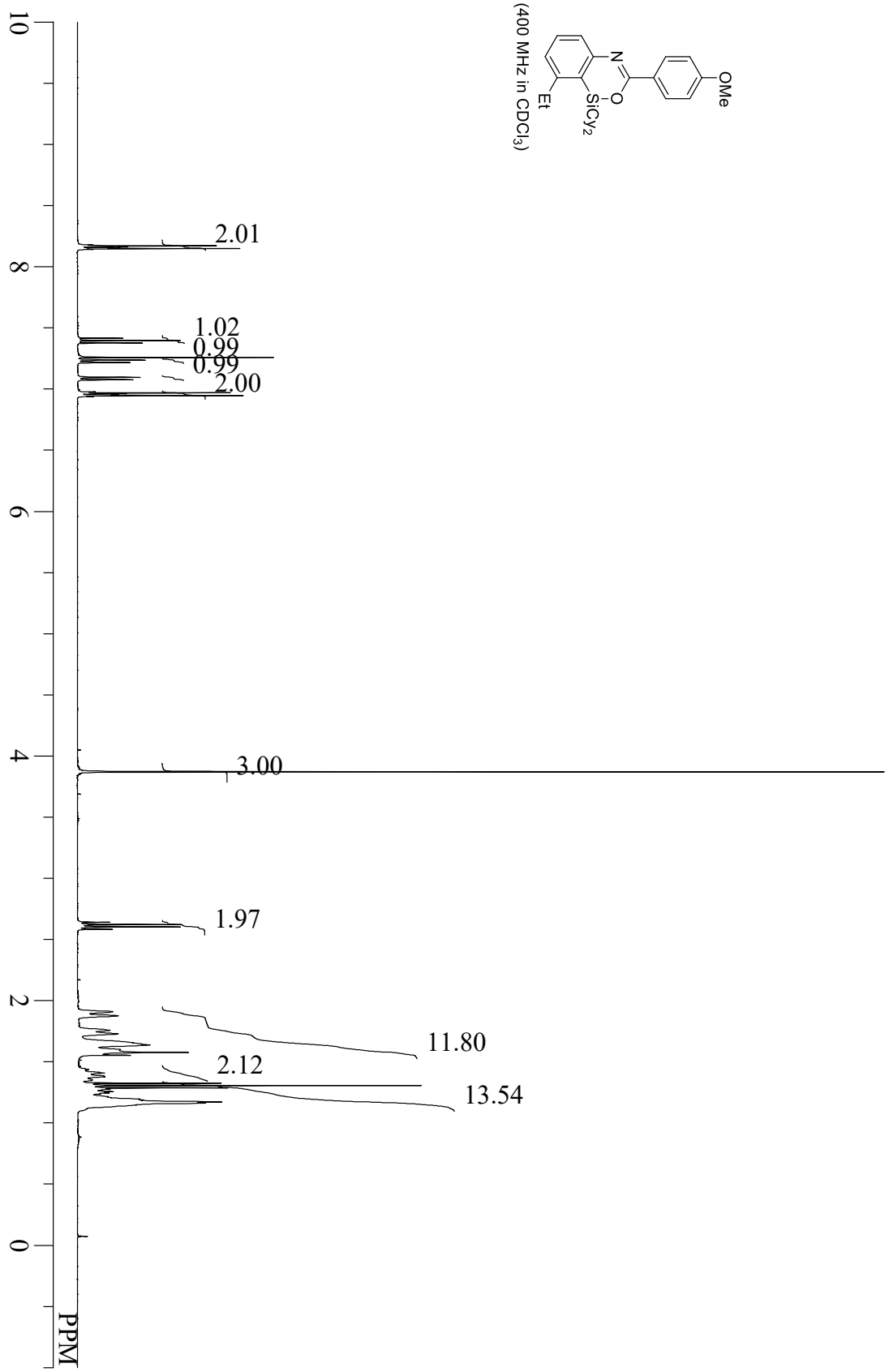
compound **3s**


(400 MHz in CDCl3)
Me
SiCy2
N
O
OMe
1.98
1.02
0.98
1.01
2.00
3.00
3.00
4.21
7.29
2.05
10.28
10
8
6
4
2
0
PPM

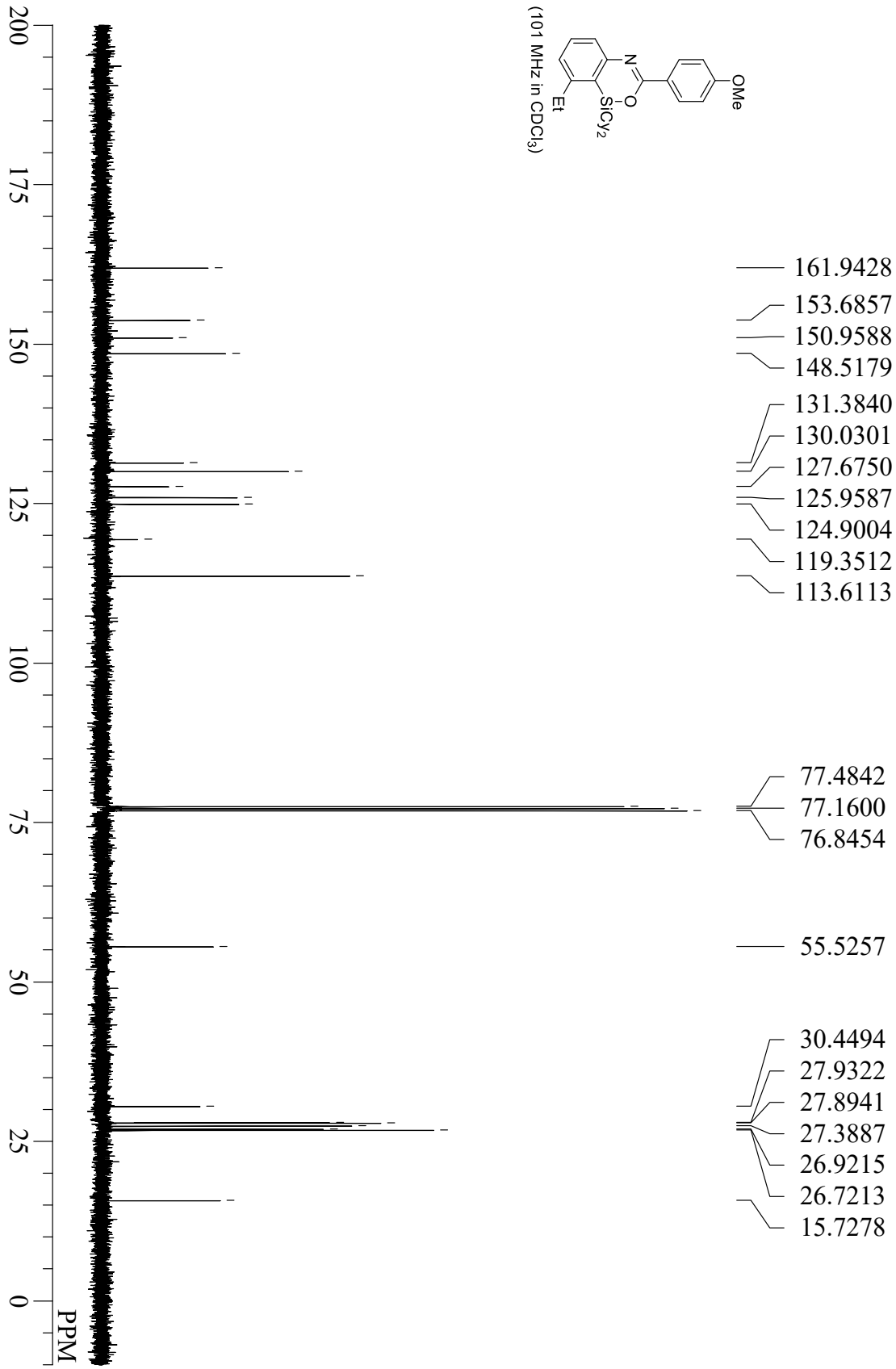
compound **3s**


(101 MHz in CDCl3)
Me
SiCy2
OMe
161.9619
153.7811
151.1114
142.0248
131.2124
130.0396
127.6369
126.9599
125.7013
119.8660
113.6113
77.4842
77.1600
76.8454
55.5162
27.9322
27.8845
27.2743
26.7880
26.7213
26.2827
23.5272
200
175
150
125
100
75
50
25
0
PPM

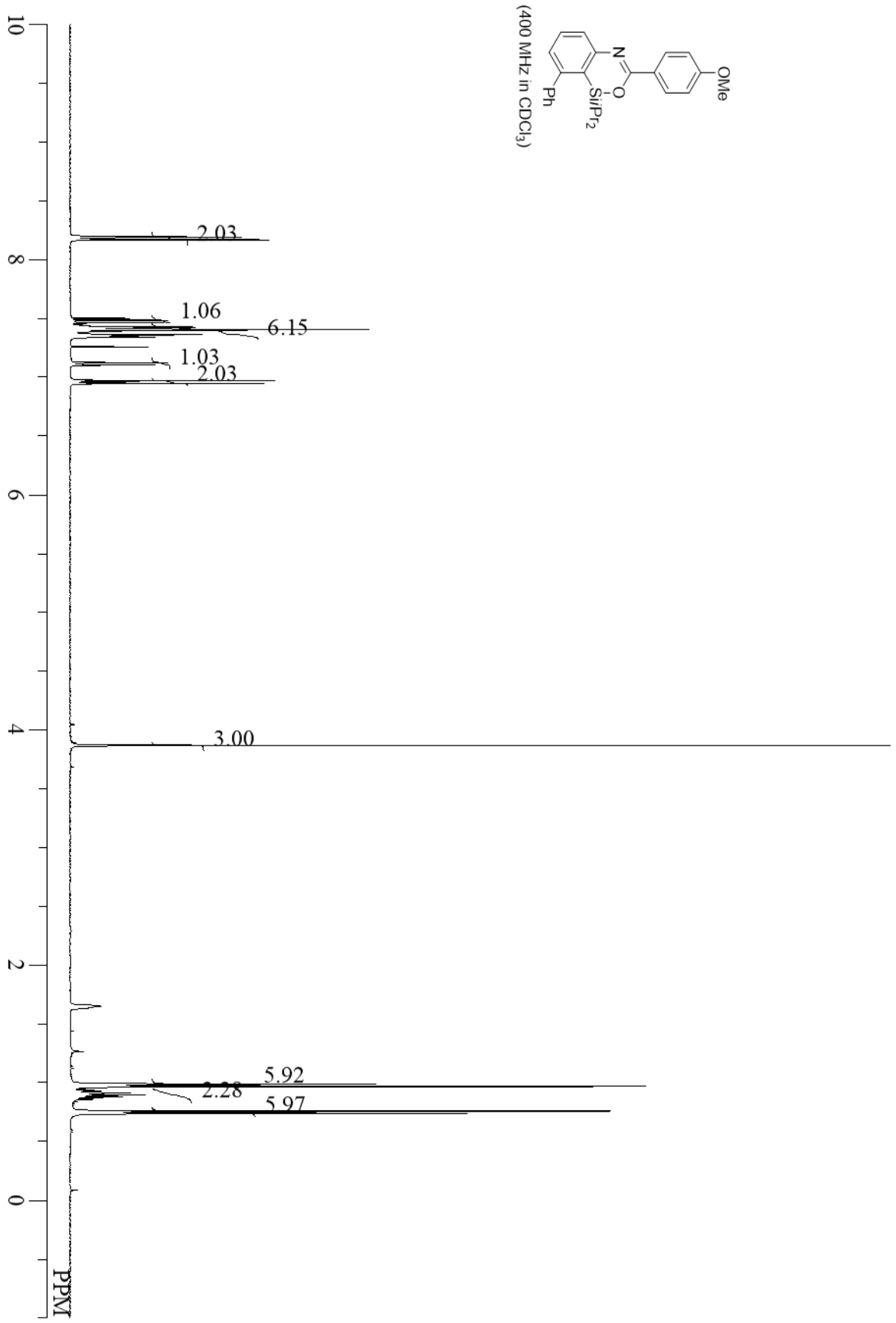
compound **3t**


(400 MHz in CDCl3)
Et
SiCy2
O
N
OMe
2.01
1.02
0.99
0.99
2.00
3.00
1.97
11.80
2.12
13.54
10
8
6
4
2
0
PPM

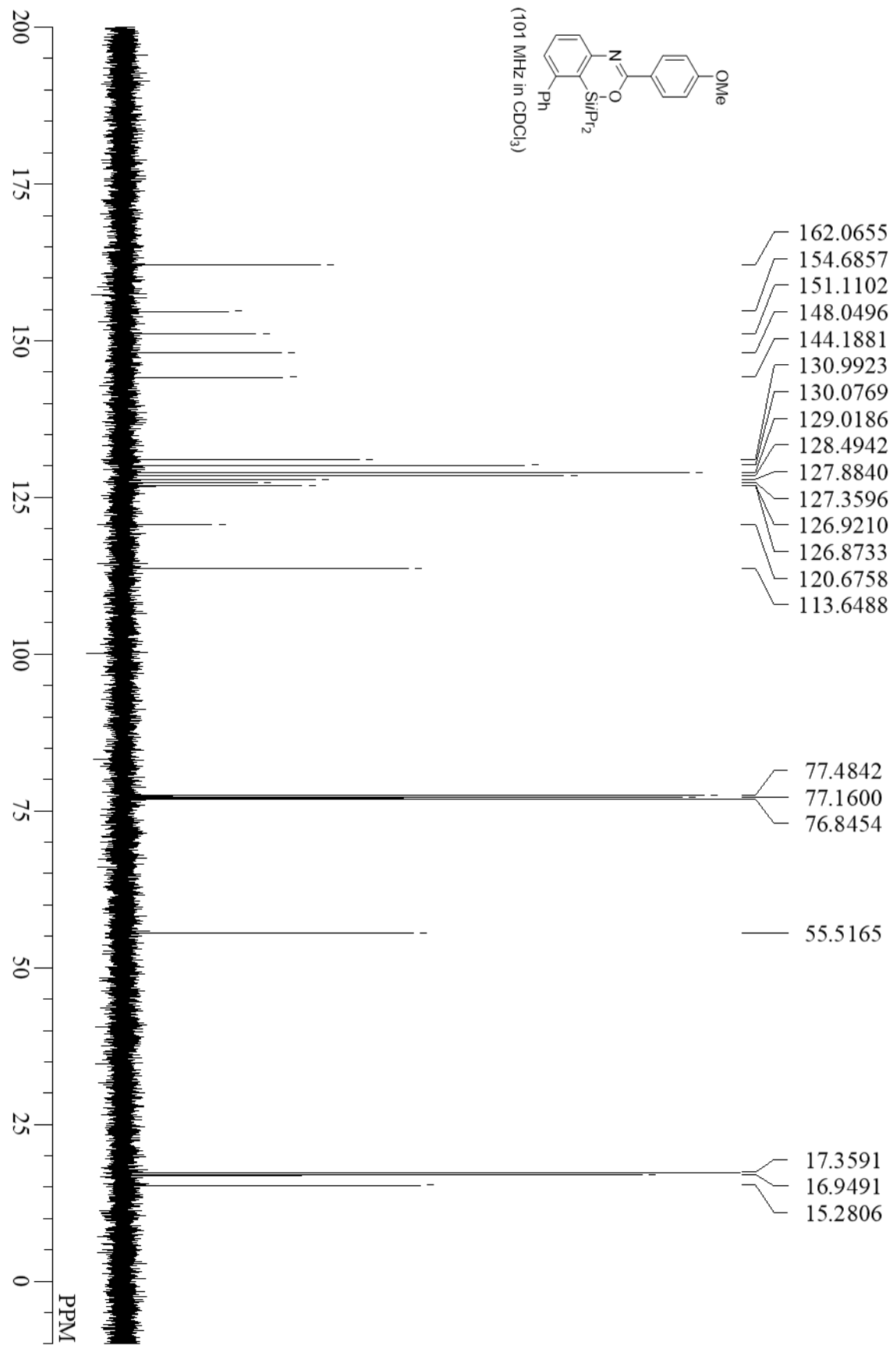
compound **3t**


(101 MHz in CDCl3)
Et
SiCy2
OMe
161.9428
153.6857
150.9588
148.5179
131.3840
130.0301
127.6750
125.9587
124.9004
119.3512
113.6113
77.4842
77.1600
76.8454
55.5257
30.4494
27.9322
27.8941
27.3887
26.9215
26.7213
15.7278
PPM

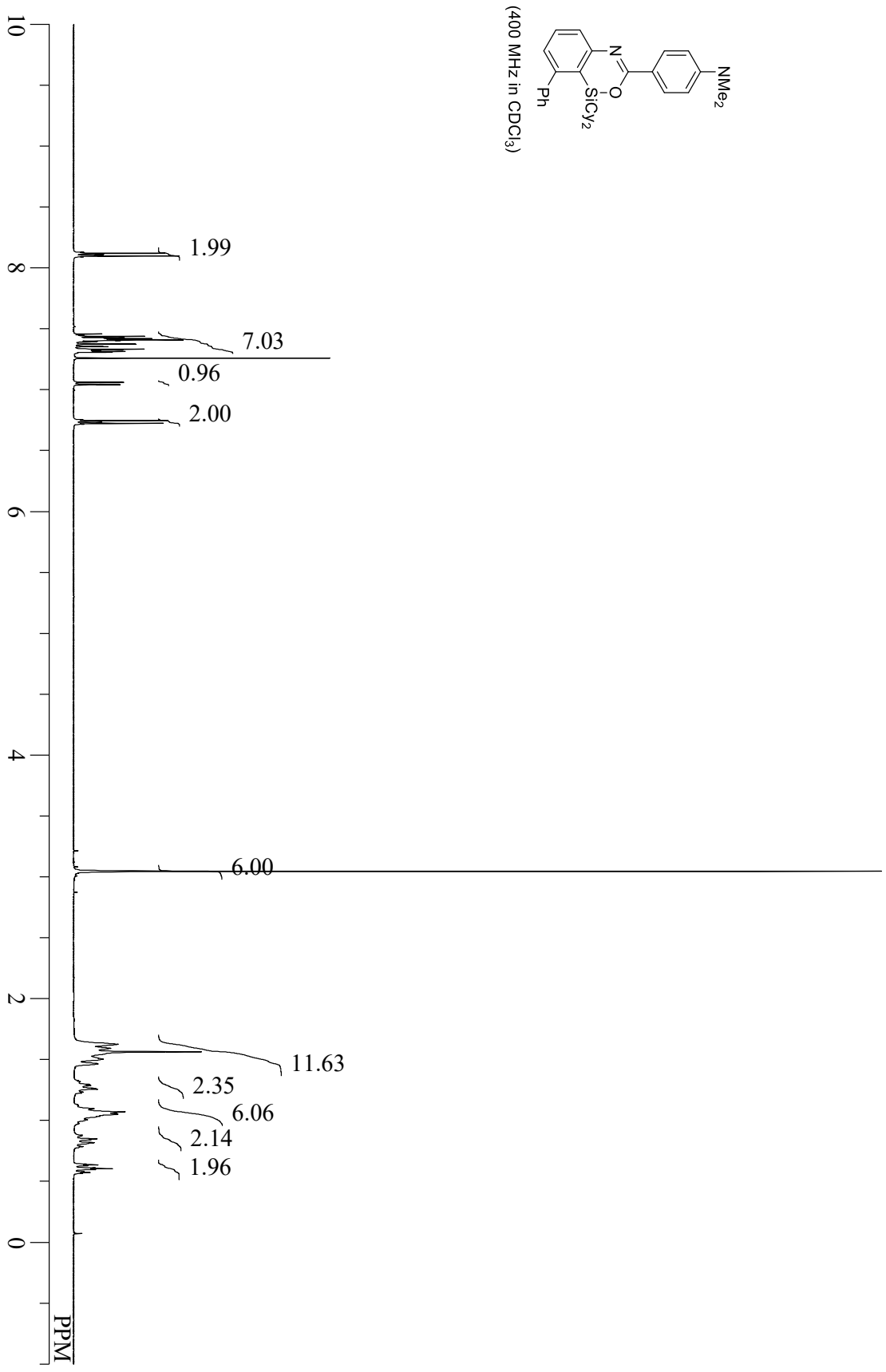
compound **3u**


(400 MHz in CDCl3)
Ph
SiiPr2
OMe
2.03
1.06
6.15
1.03
2.03
3.00
5.92
2.28
5.97
PPM

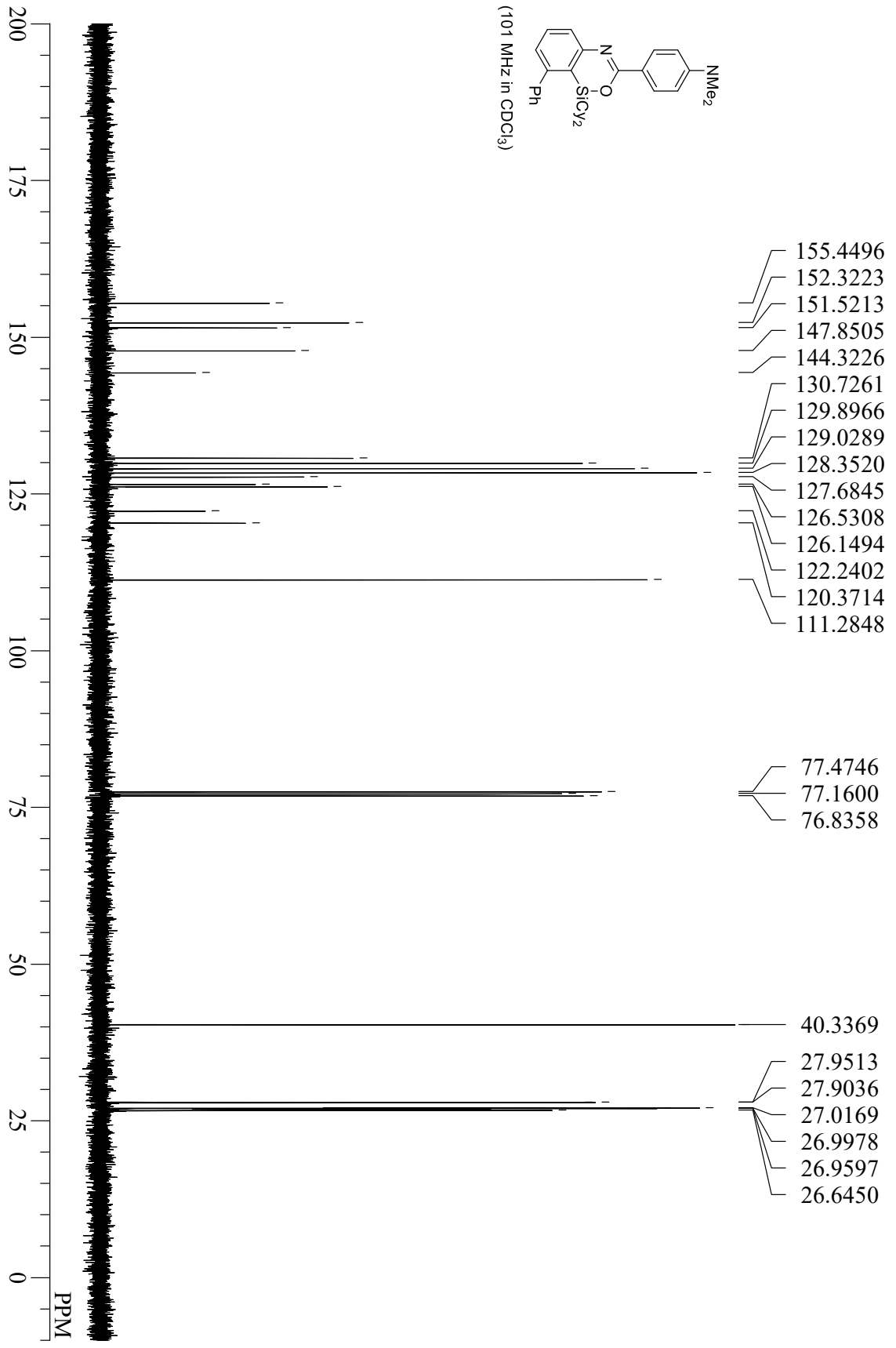
compound **3u**


(101 MHz in CDCl3)
Ph
Si/Pr2
O
N
OMe
162.0655
154.6857
151.1102
148.0496
144.1881
130.9923
130.0769
129.0186
128.4942
127.8840
127.3596
126.9210
126.8733
120.6758
113.6488
77.4842
77.1600
76.8454
55.5165
17.3591
16.9491
15.2806
200
175
150
125
100
75
50
25
0
PPM

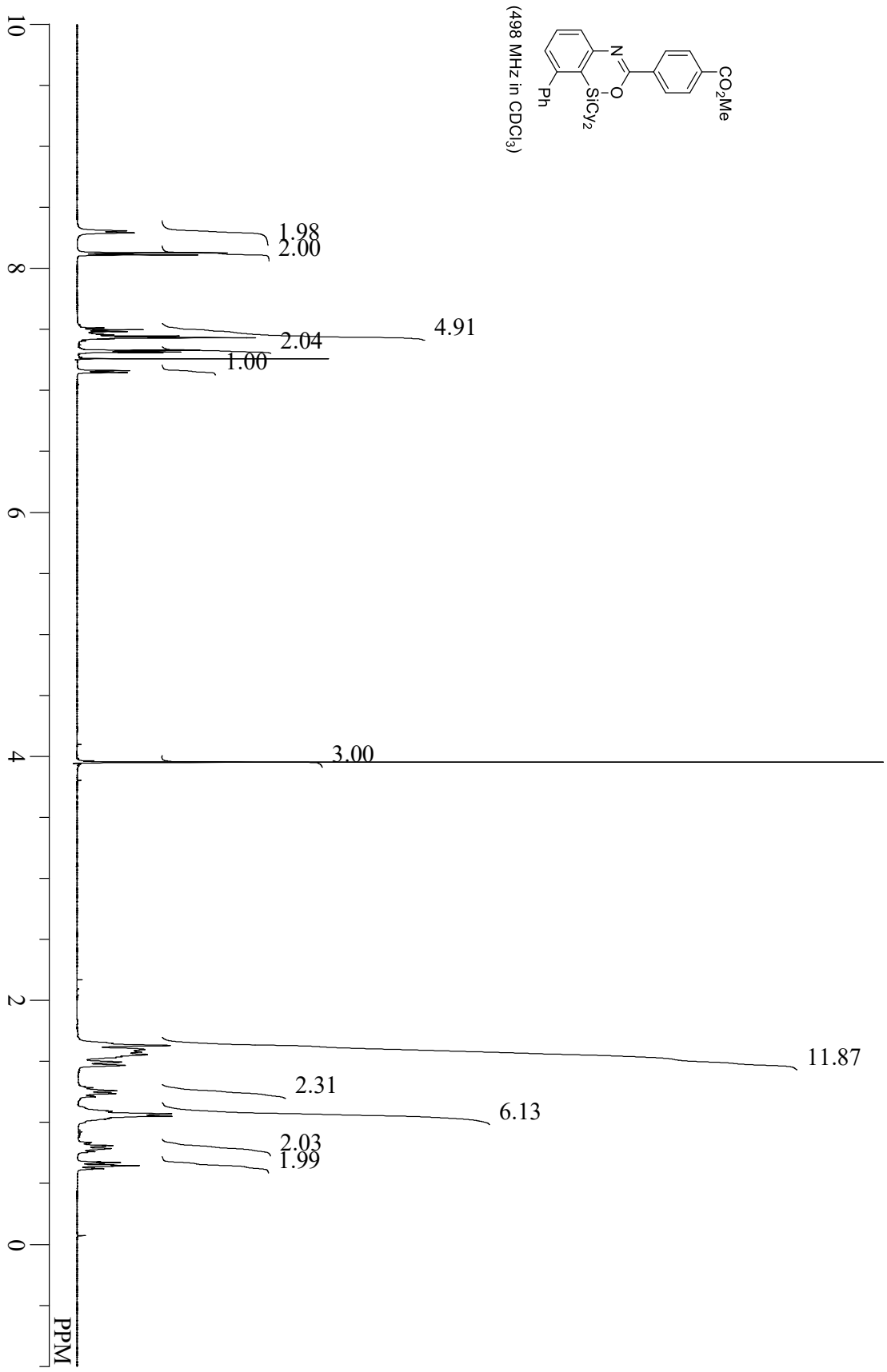
compound **3w**


(400 MHz in CDCl3)
Ph
SiCy2
O
N
NMe2
1.99
7.03
0.96
2.00
6.00
11.63
2.35
6.06
2.14
1.96
10
8
6
4
2
0
PPM

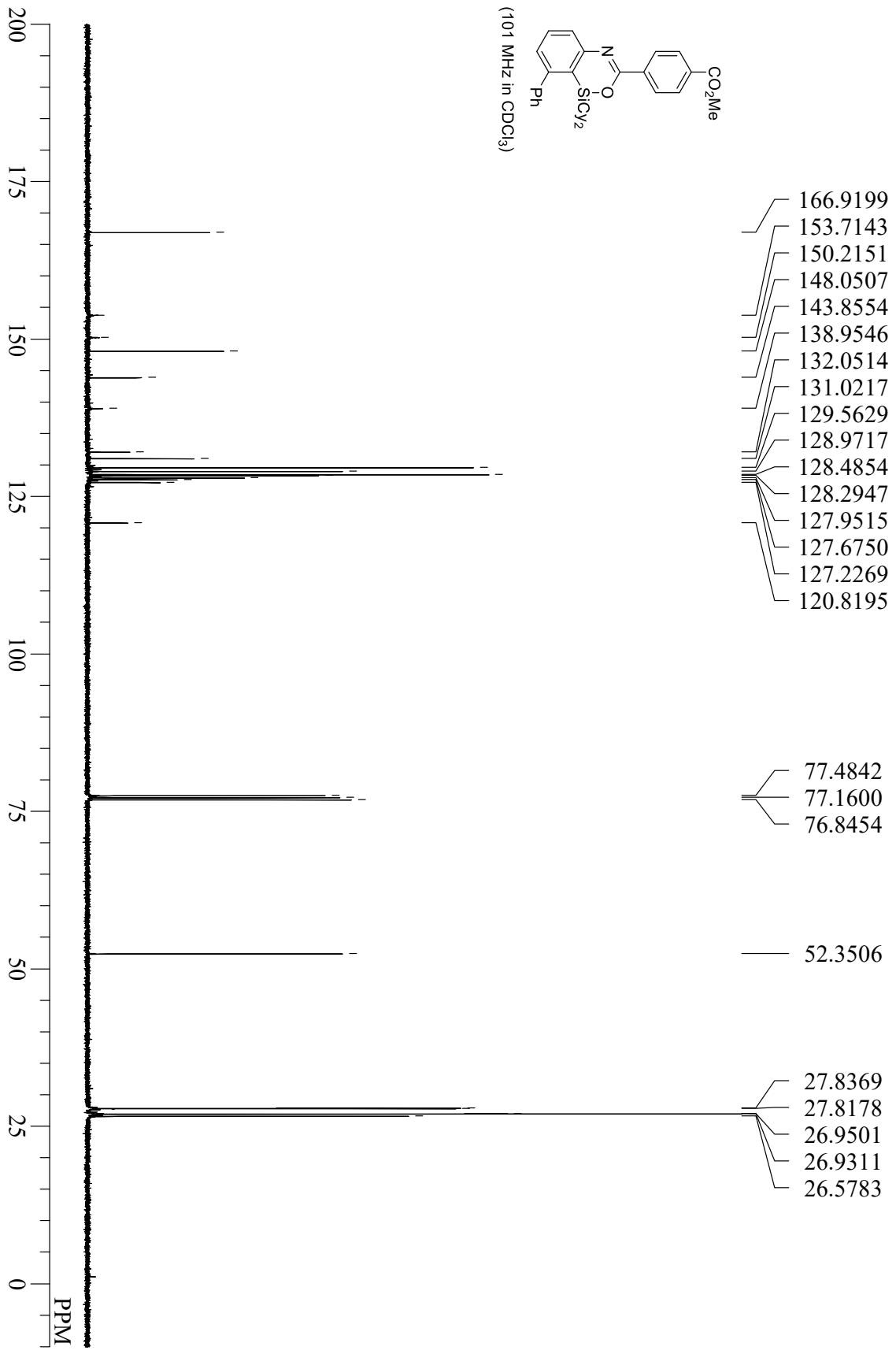
compound **3w**


(101 MHz in CDCl3)
Ph
SiCy2
O
N
NMe2
155.4496
152.3223
151.5213
147.8505
144.3226
130.7261
129.8966
129.0289
128.3520
127.6845
126.5308
126.1494
122.2402
120.3714
111.2848
77.4746
77.1600
76.8358
40.3369
27.9513
27.9036
27.0169
26.9978
26.9597
26.6450
200
175
150
125
100
75
50
25
0
PPM

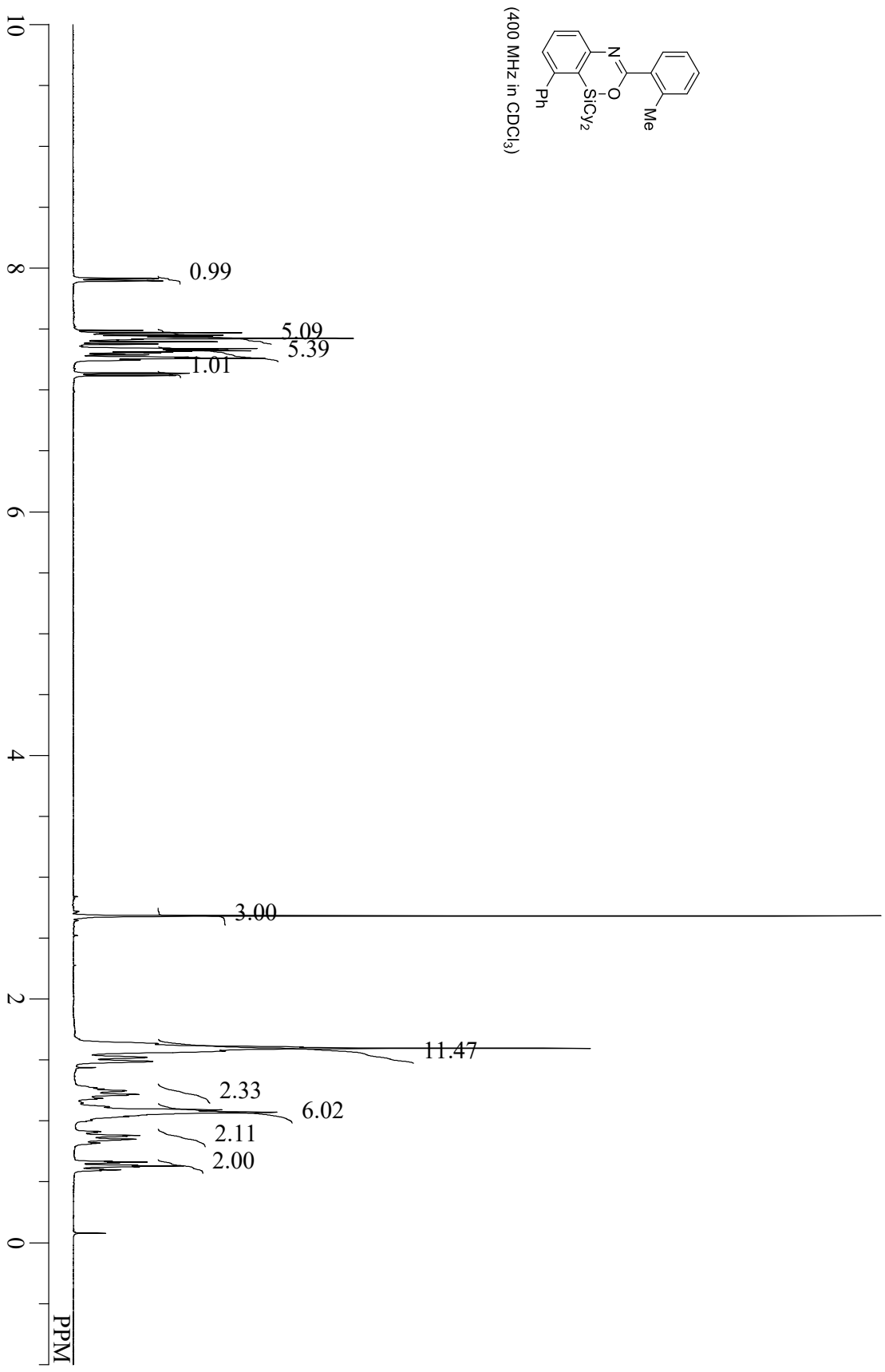
compound **3x**


(498 MHz in CDCl3)
Ph
SiCy2
O
N
CO2Me
1.98
2.00
4.91
2.04
1.00
3.00
11.87
2.31
6.13
2.03
1.99
10
8
6
4
2
0
PPM

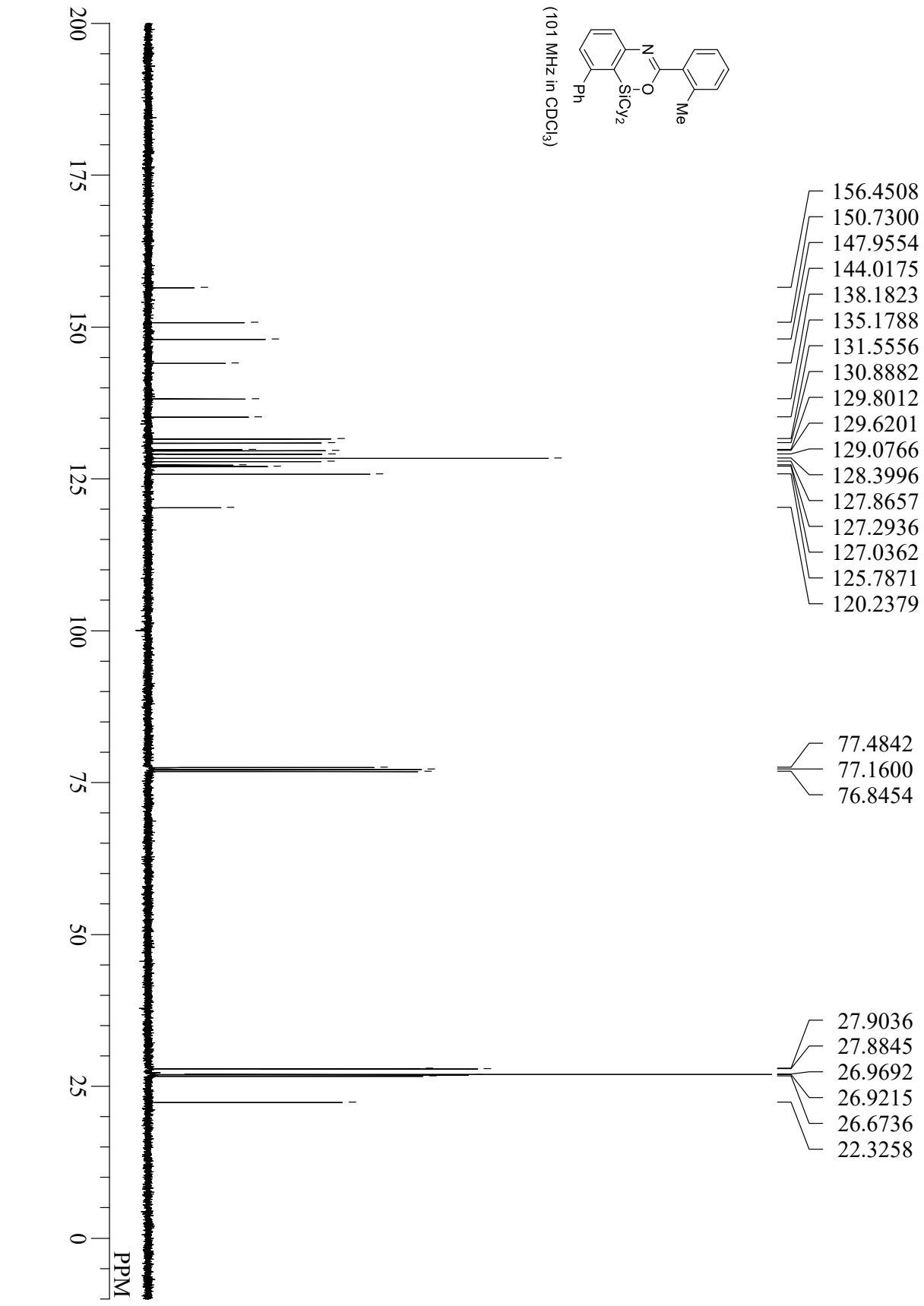
compound **3x**


(101 MHz in CDCl3)
Ph
SiCy2
O
N
CO2Me
166.9199
153.7143
150.2151
148.0507
143.8554
138.9546
132.0514
131.0217
129.5629
128.9717
128.4854
128.2947
127.9515
127.6750
127.2269
120.8195
77.4842
77.1600
76.8454
52.3506
27.8369
27.8178
26.9501
26.9311
26.5783
200
175
150
125
100
75
50
25
0
PPM

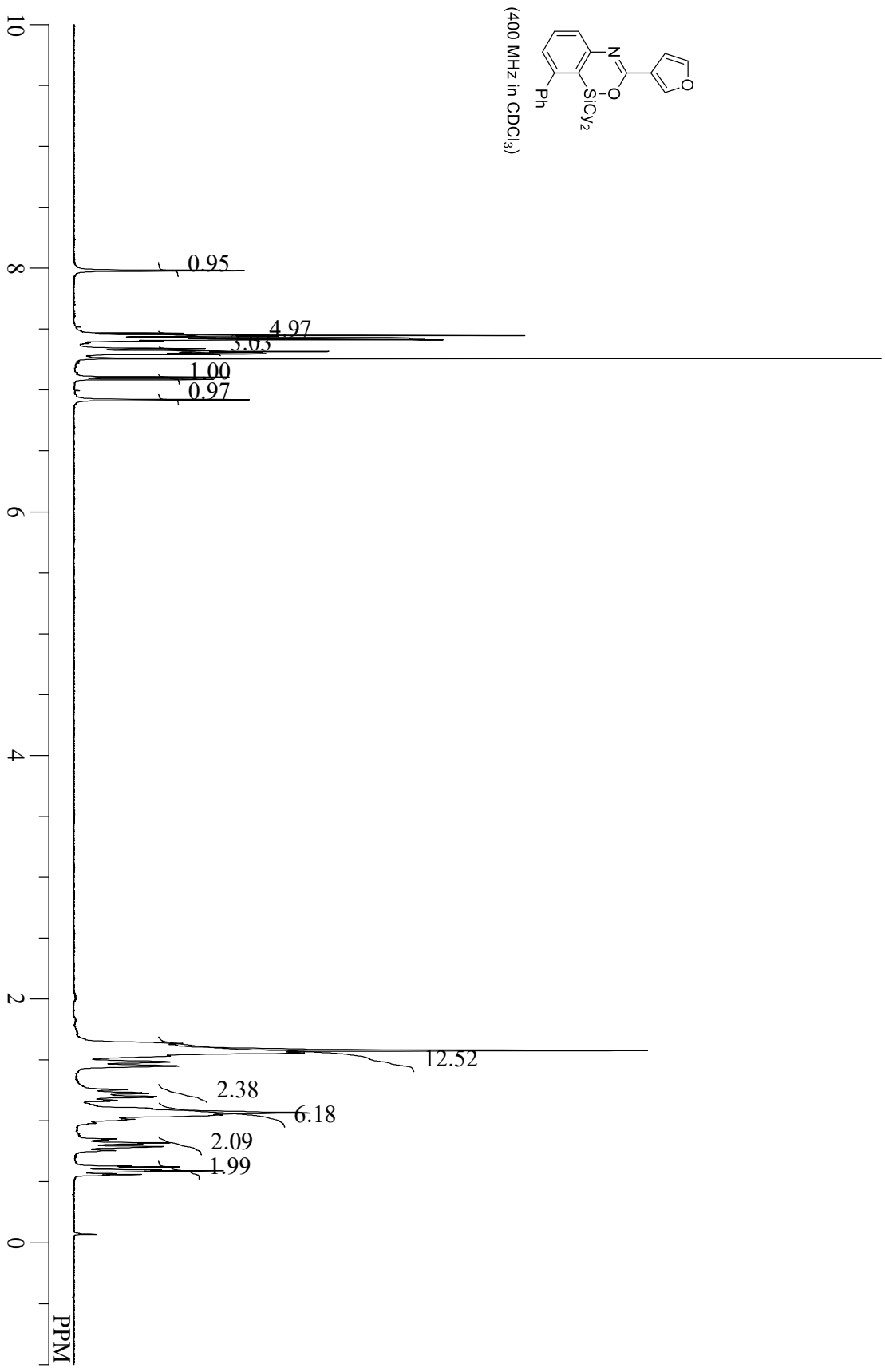
compound **3y**


(400 MHz in CDCl3)
Ph
SiCy2
O
N
Me
0.99
5.09
5.39
1.01
3.00
11.47
2.33
6.02
2.11
2.00
10
8
6
4
2
0
PPM

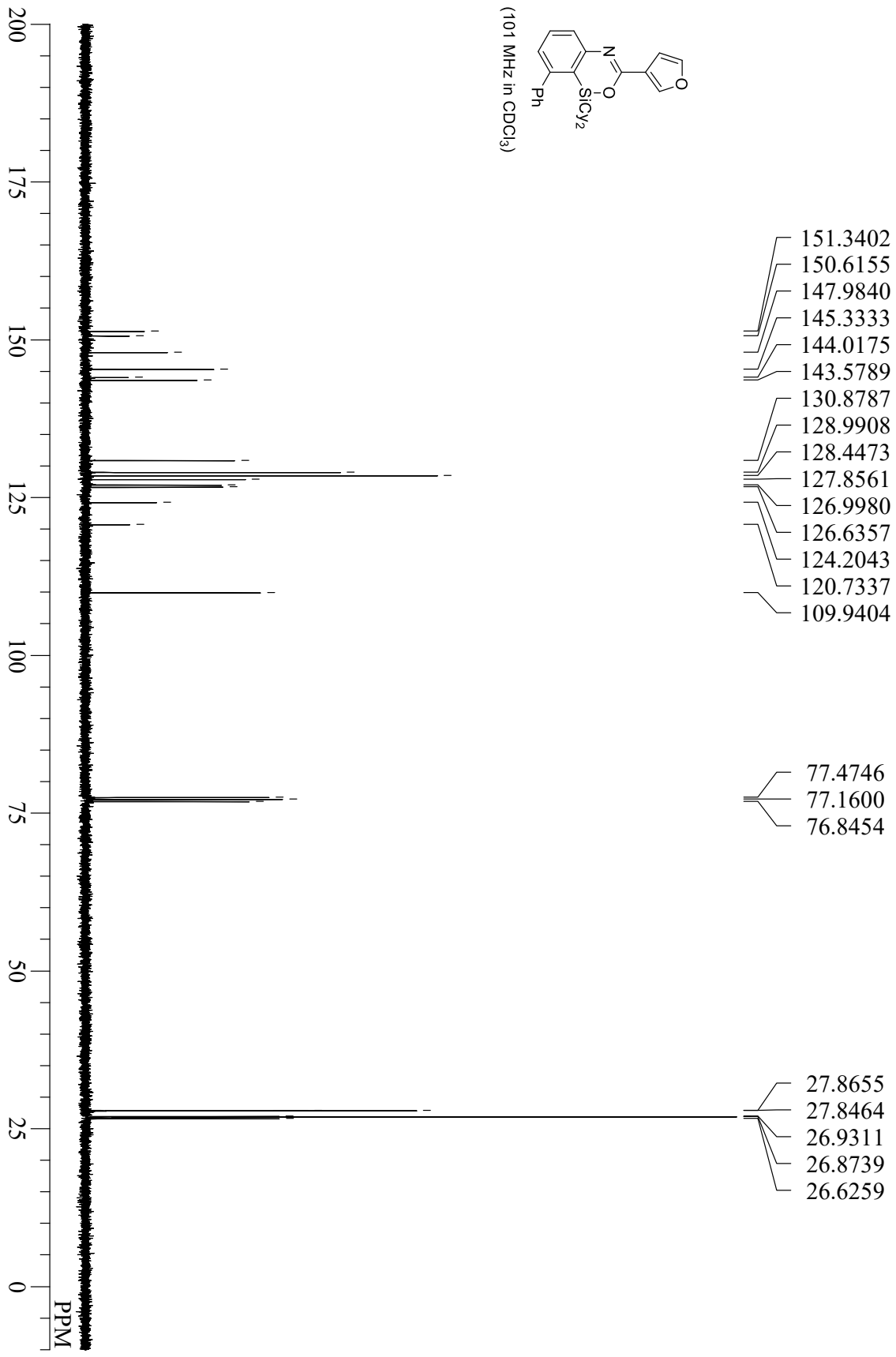
compound **3y**


(101 MHz in CDCl3)
Ph
SiCy2
N
O
Me
156.4508
150.7300
147.9554
144.0175
138.1823
135.1788
131.5556
130.8882
129.8012
129.6201
129.0766
128.3996
127.8657
127.2936
127.0362
125.7871
120.2379
77.4842
77.1600
76.8454
27.9036
27.8845
26.9692
26.9215
26.6736
22.3258
200
175
150
125
100
75
50
25
0
PPM

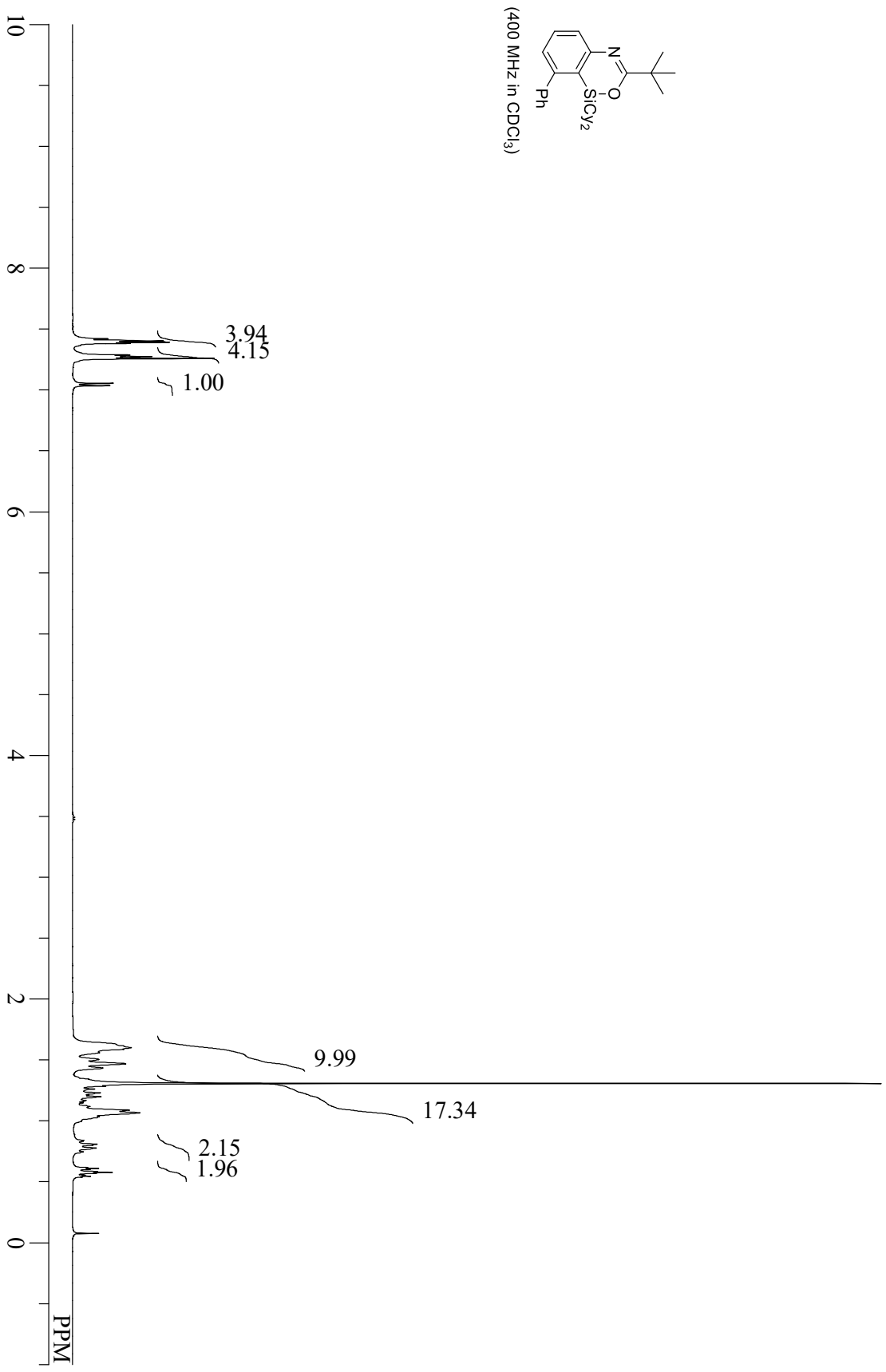
compound **3z**


(400 MHz in CDCl3)
Ph
SiCy2
N
O
O
10
8
6
4
2
0
PPM
0.95
4.97
3.03
1.00
0.97
12.52
2.38
6.18
2.09
1.99

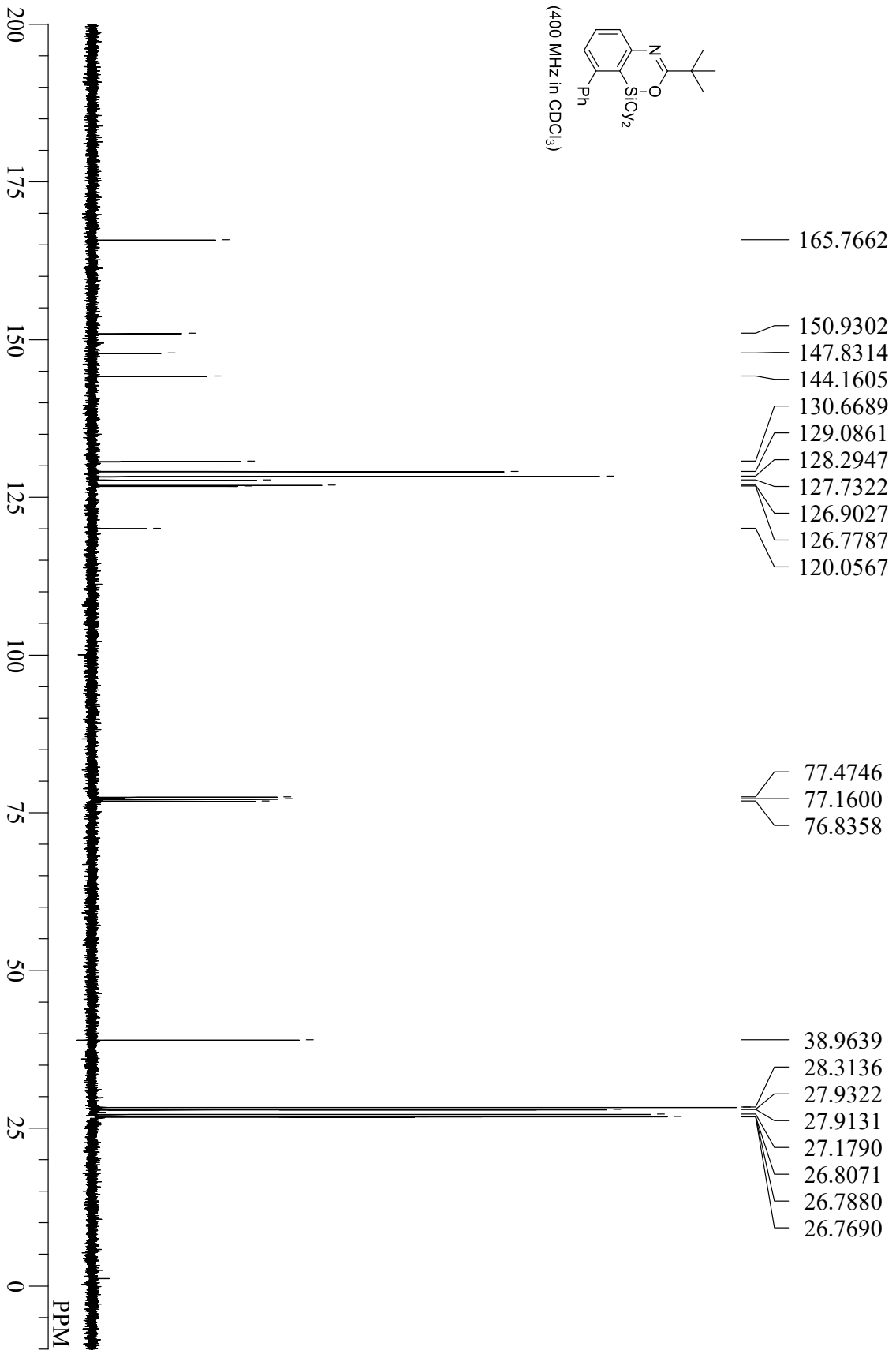
compound **3z**


(101 MHz in CDCl3)
Ph
SiCy2
N
O
O
151.3402
150.6155
147.9840
145.3333
144.0175
143.5789
130.8787
128.9908
128.4473
127.8561
126.9980
126.6357
124.2043
120.7337
109.9404
77.4746
77.1600
76.8454
27.8655
27.8464
26.9311
26.8739
26.6259
200
175
150
125
100
75
50
25
0
PPM

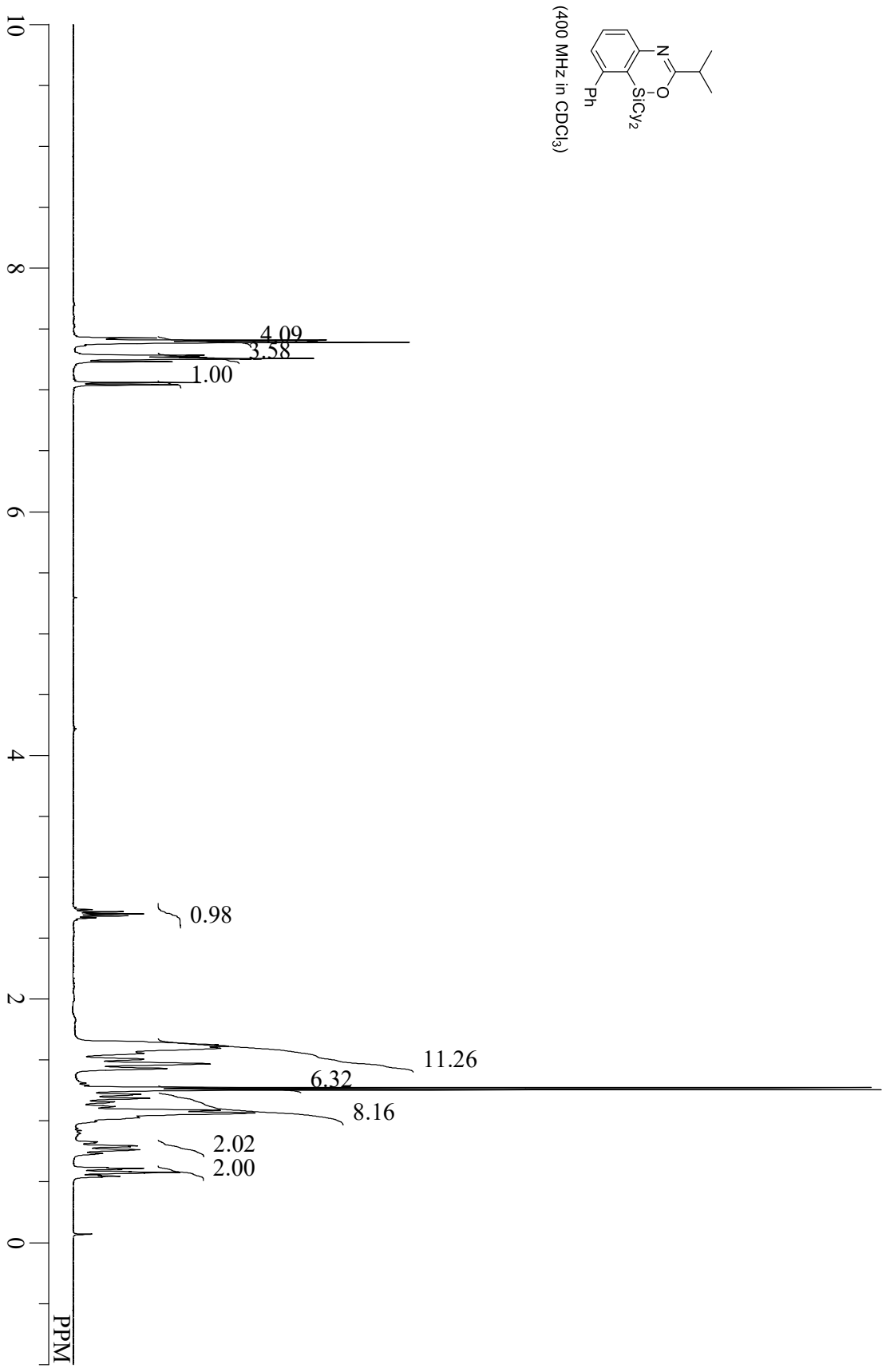
compound **3aa**



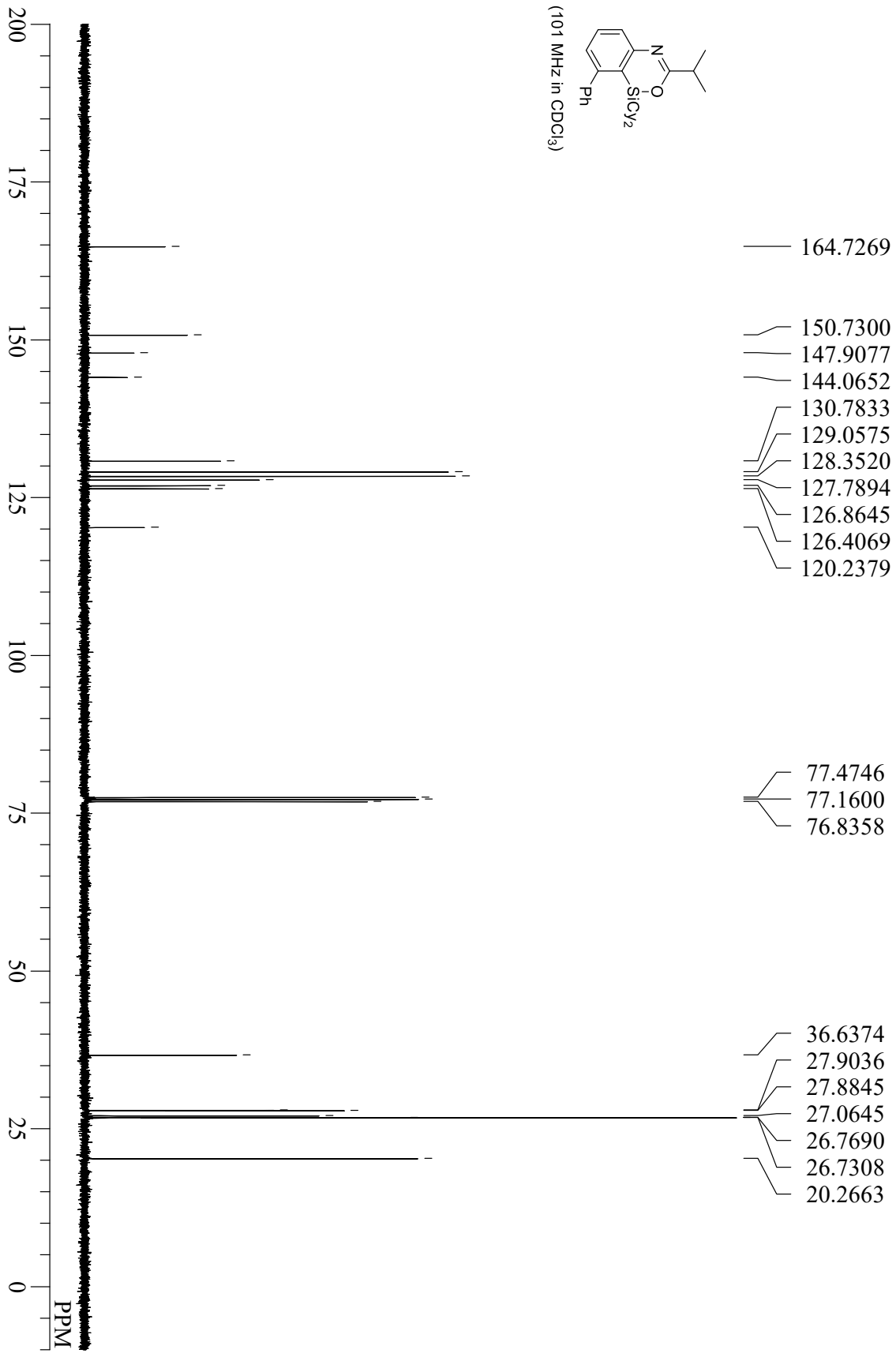
compound **3aa**



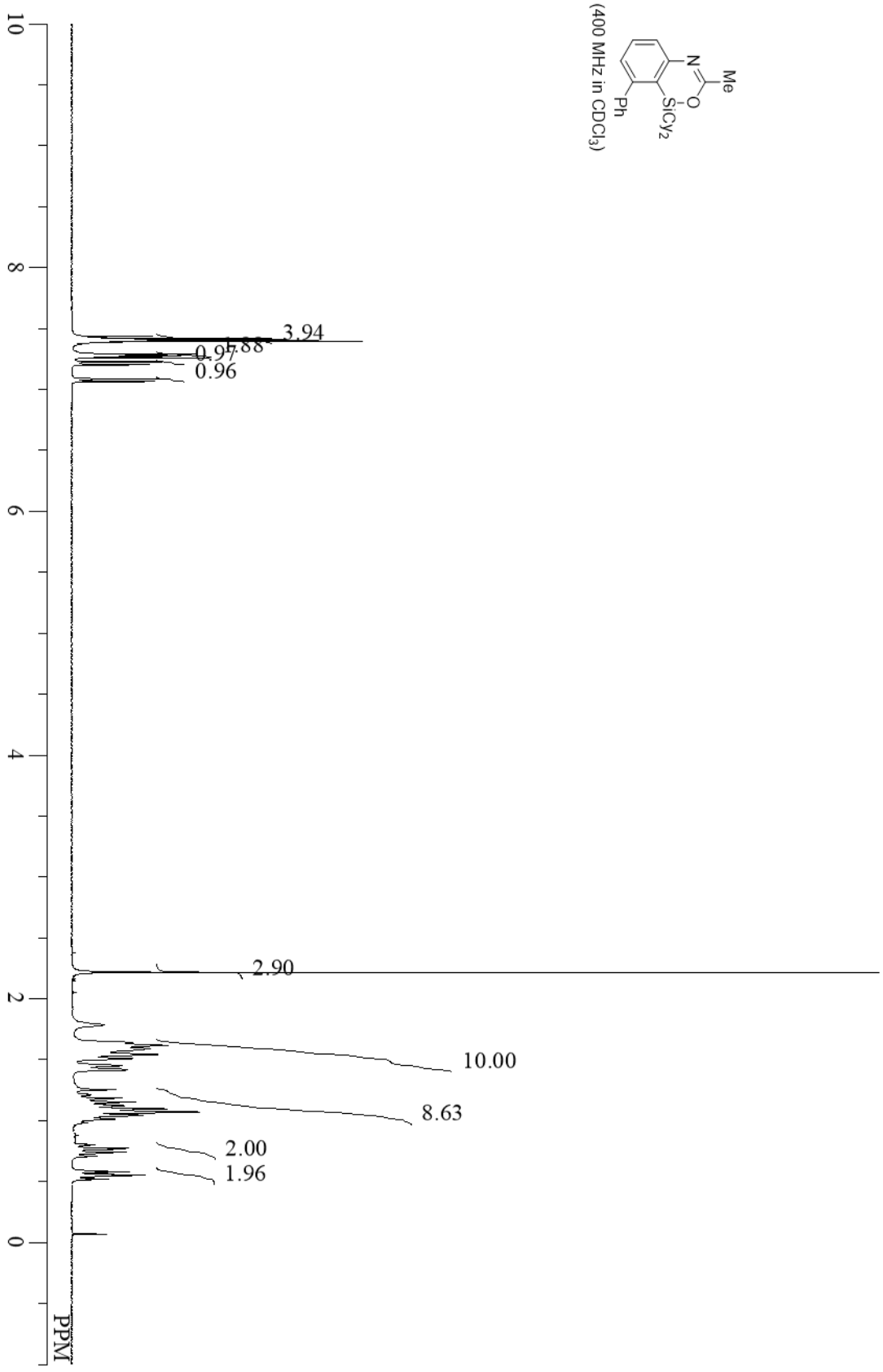
compound **3bb**



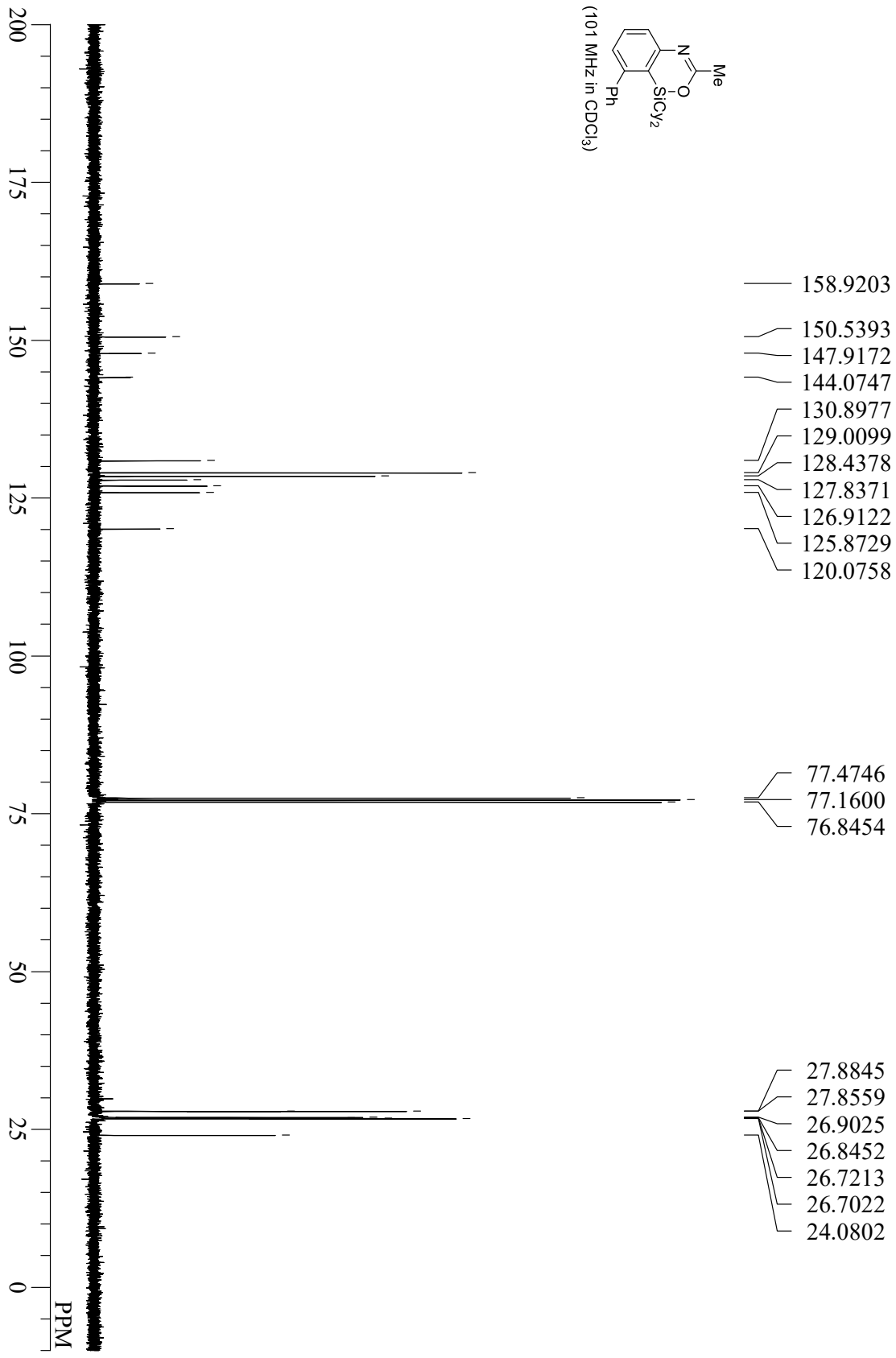
compound **3bb**



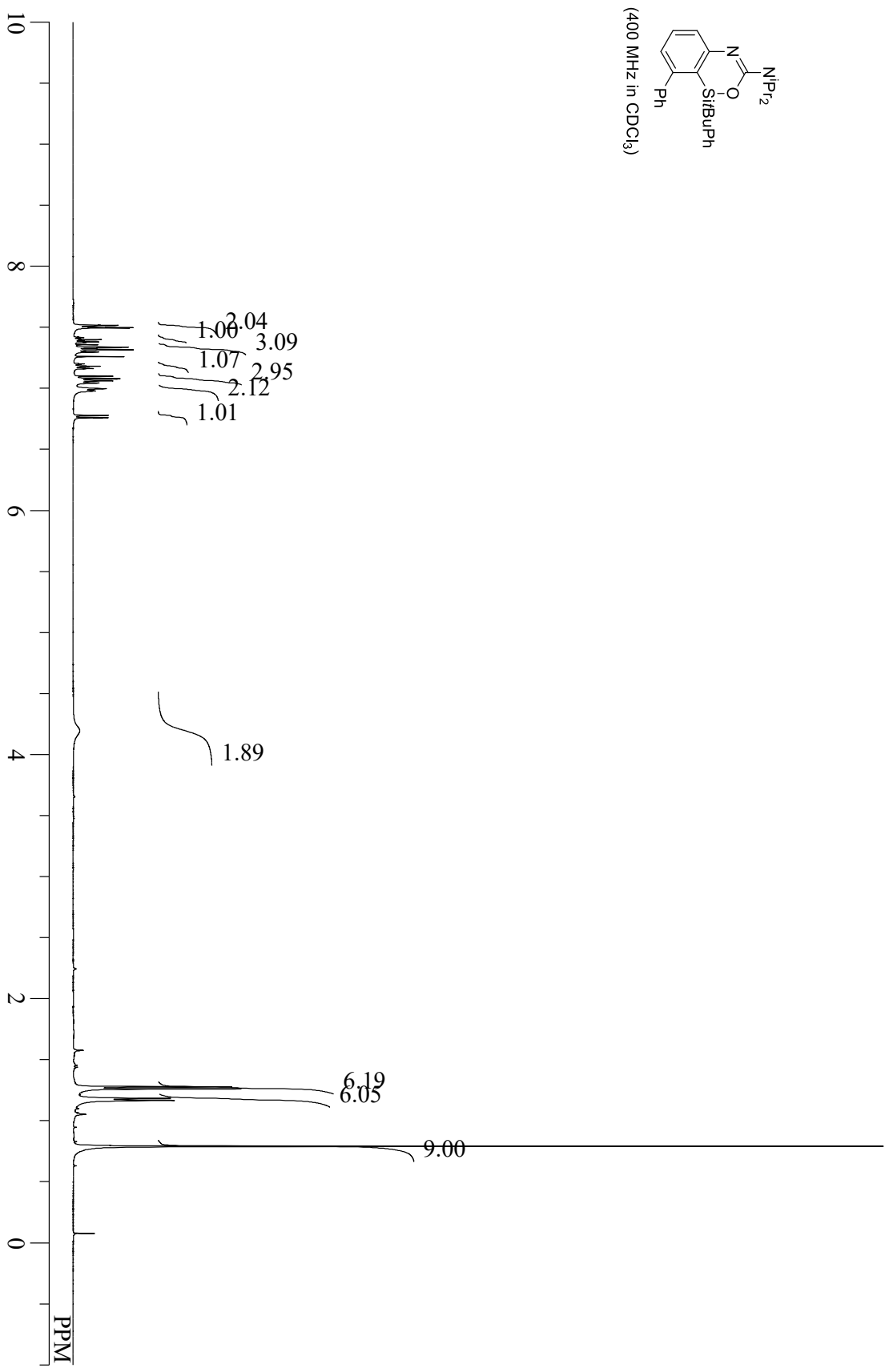
compound **3cc**



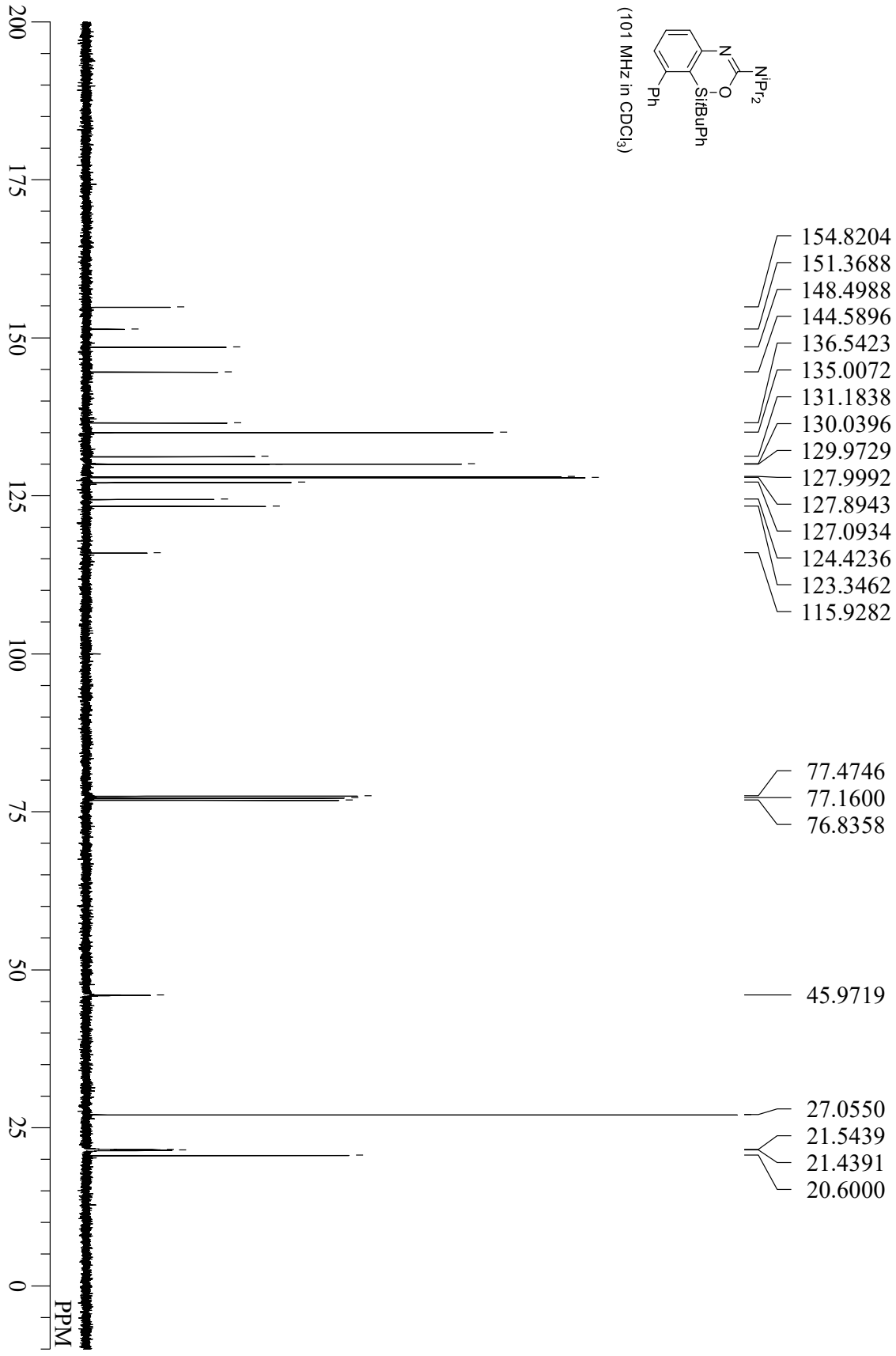
compound **3cc**



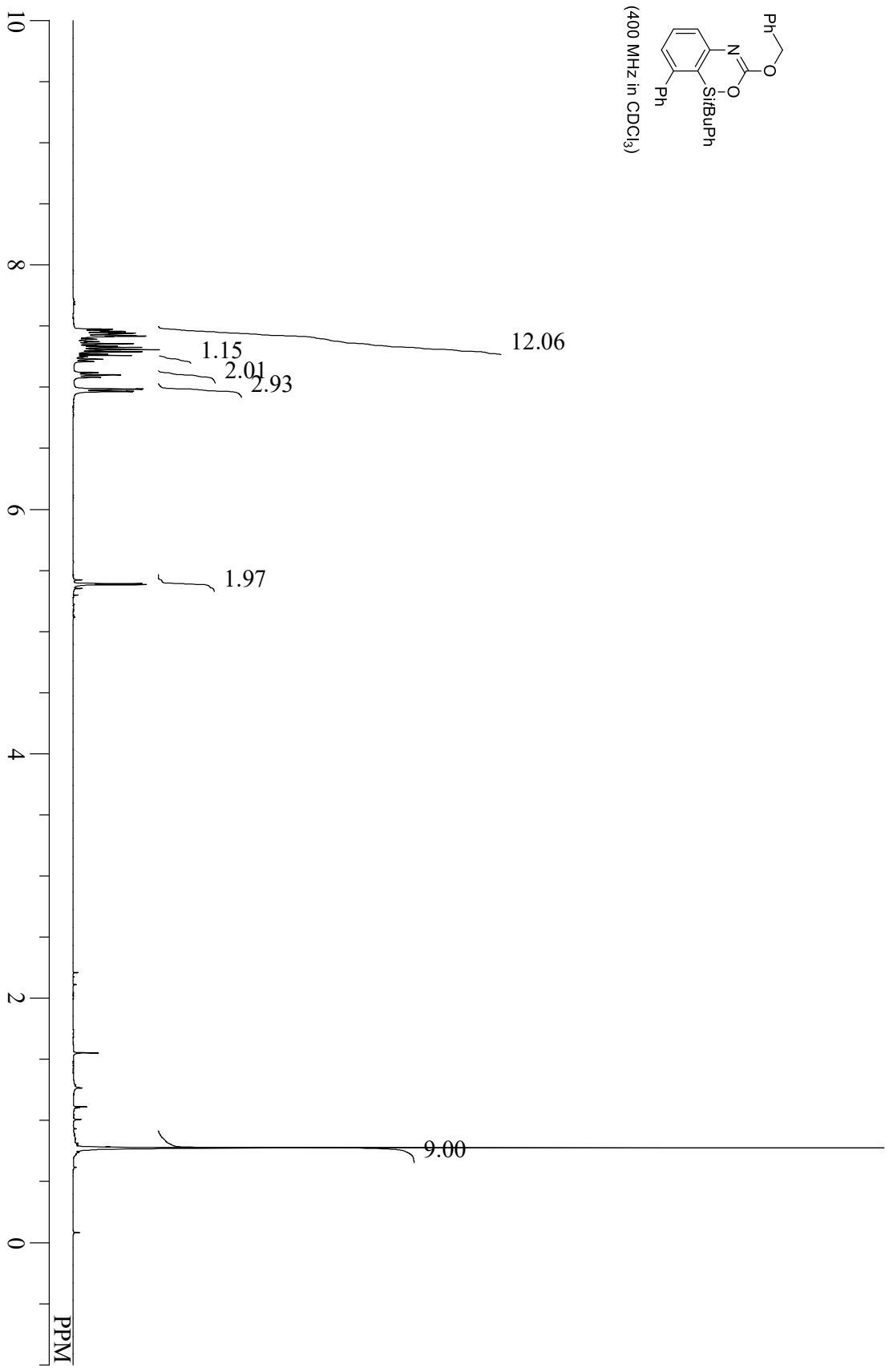
compound **3dd**



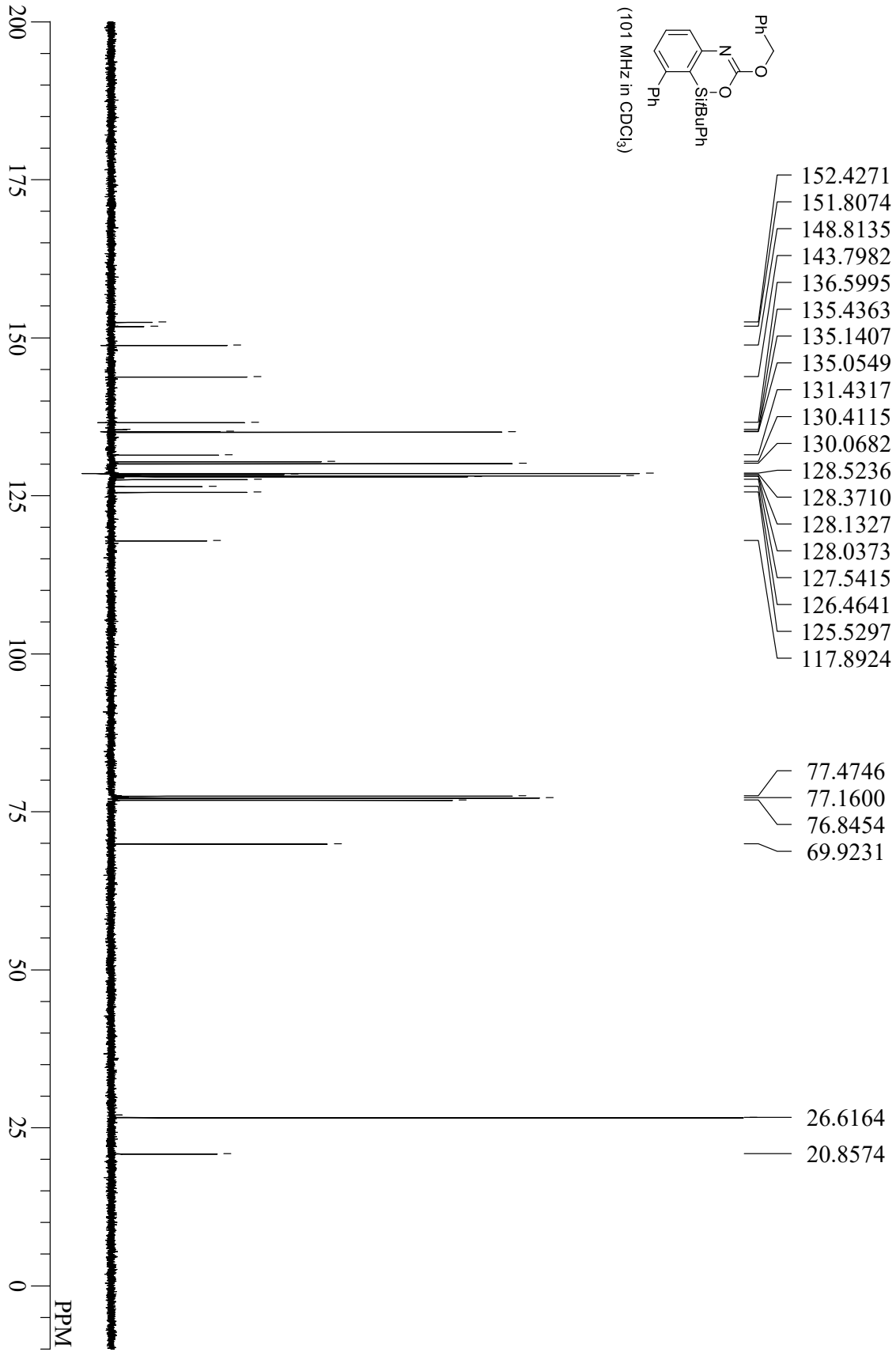
compound **3dd**



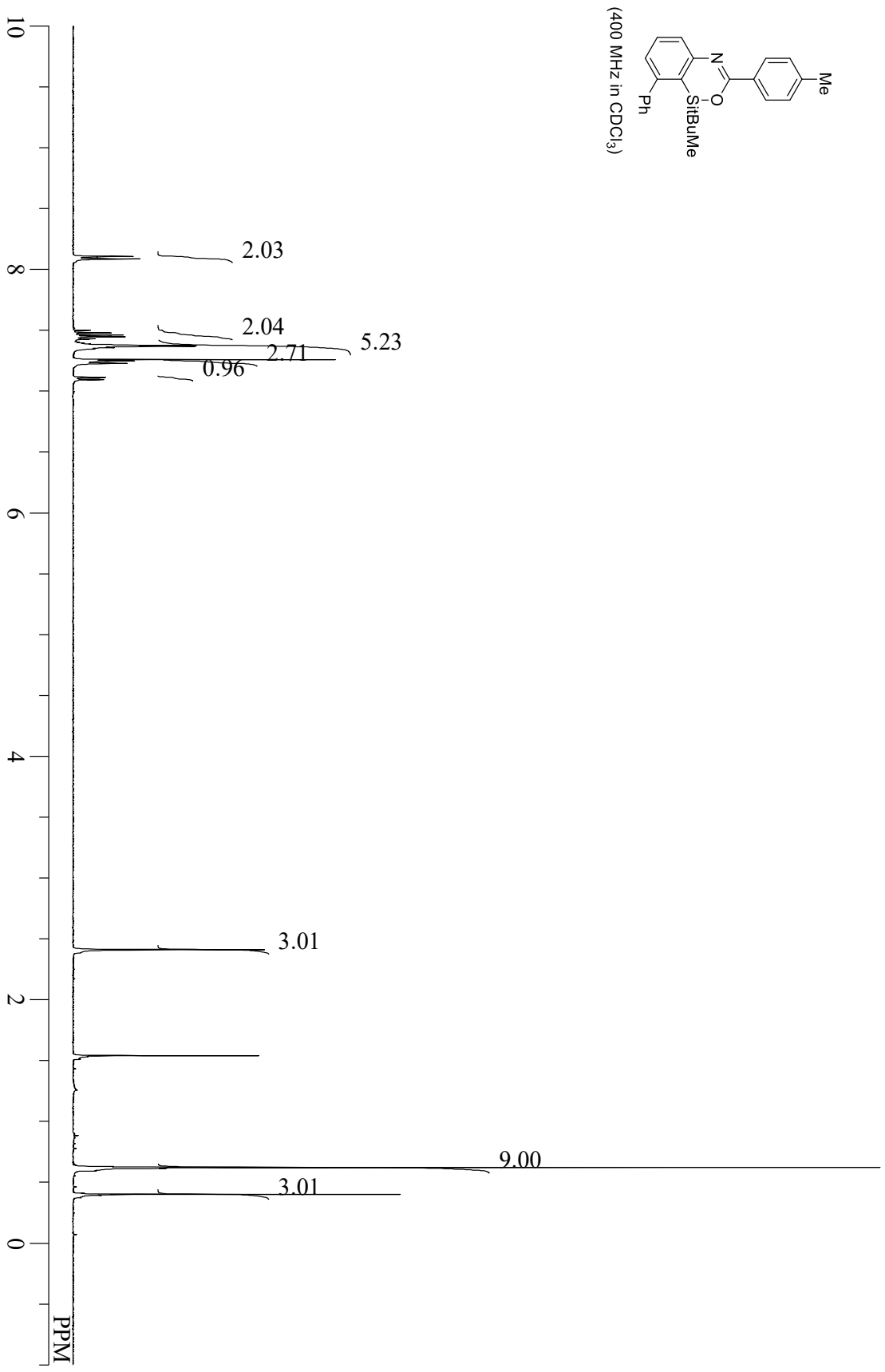
compound **3ee**



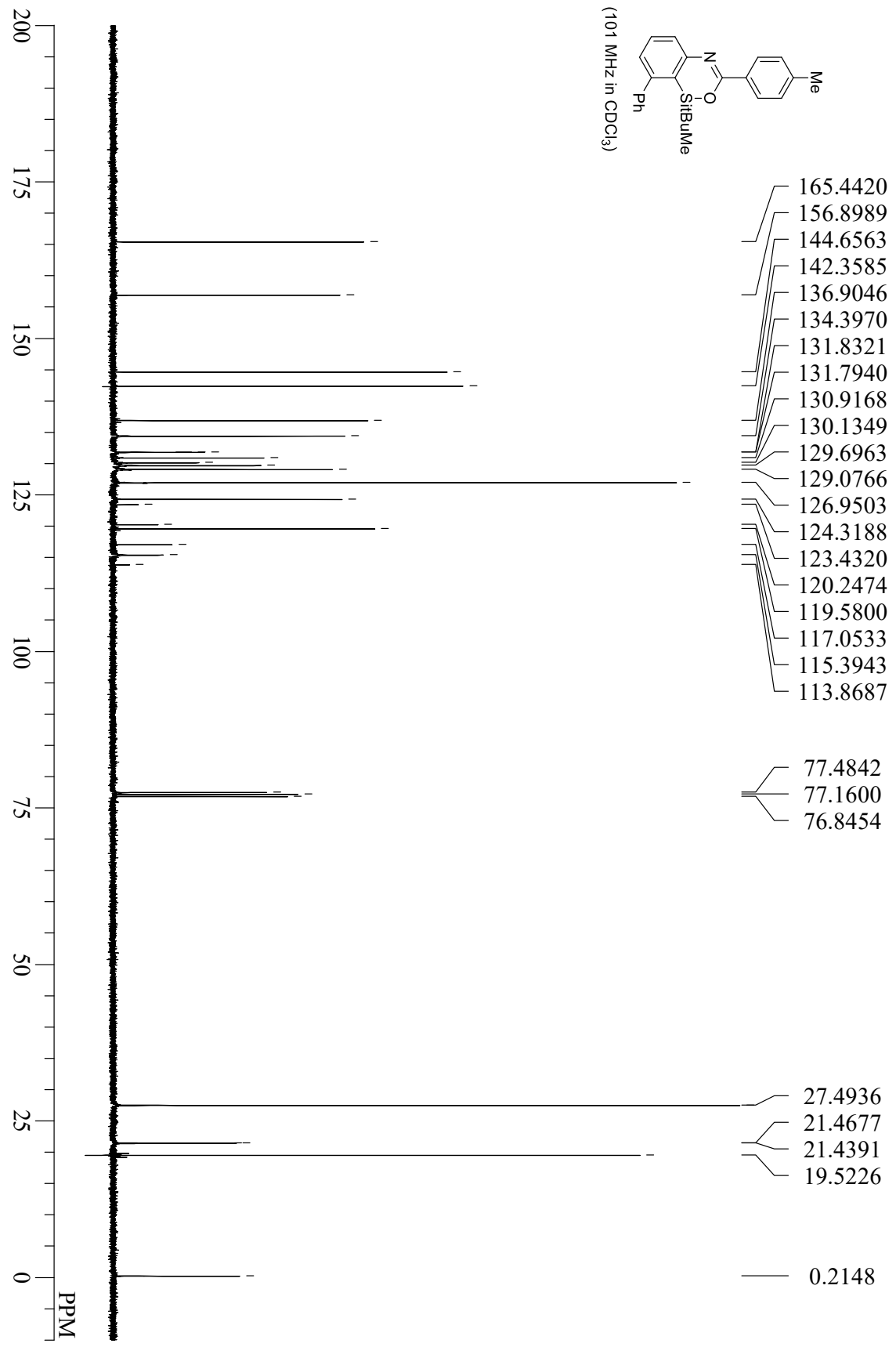
compound **3ee**



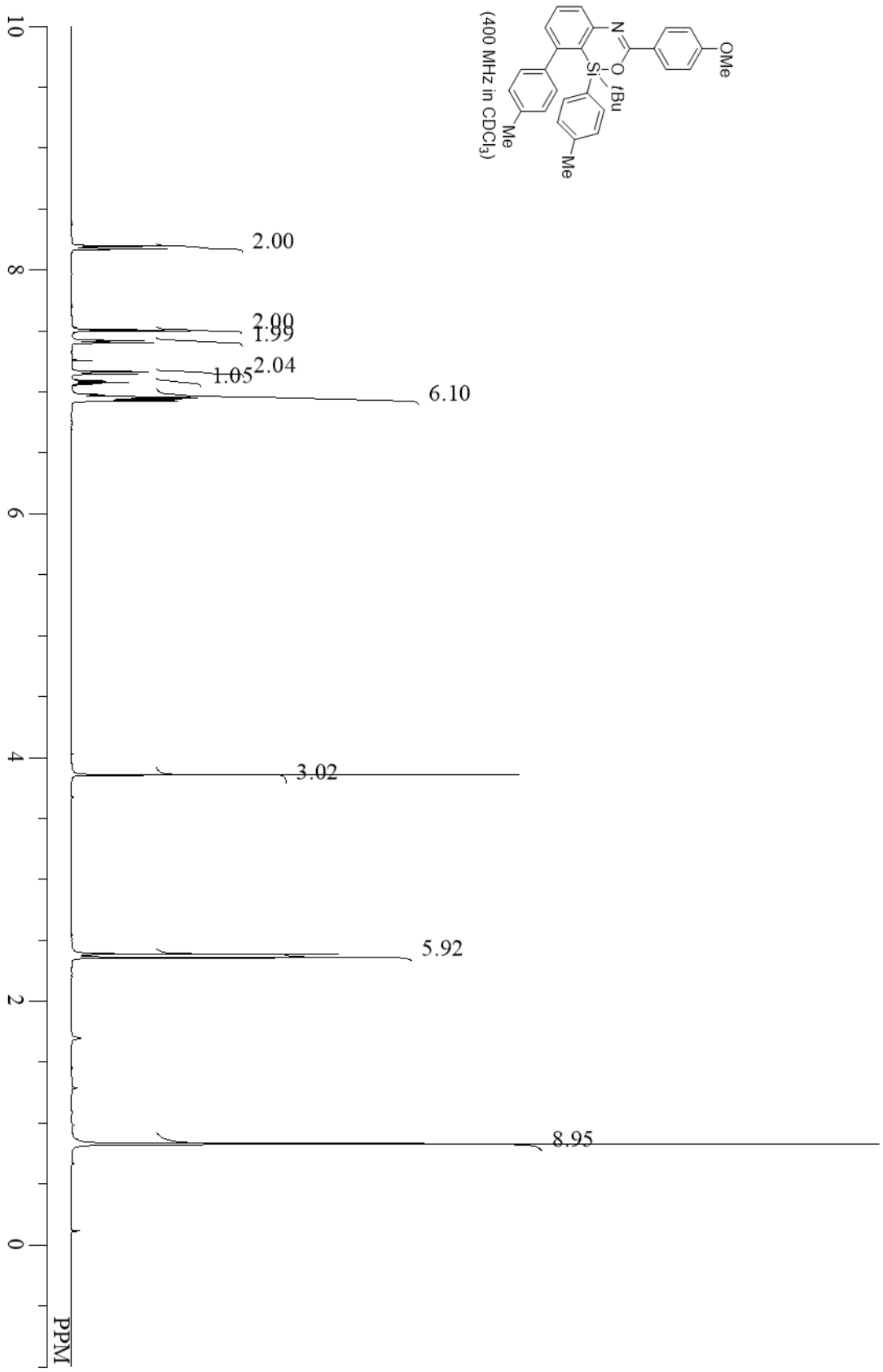
compound **3gg**



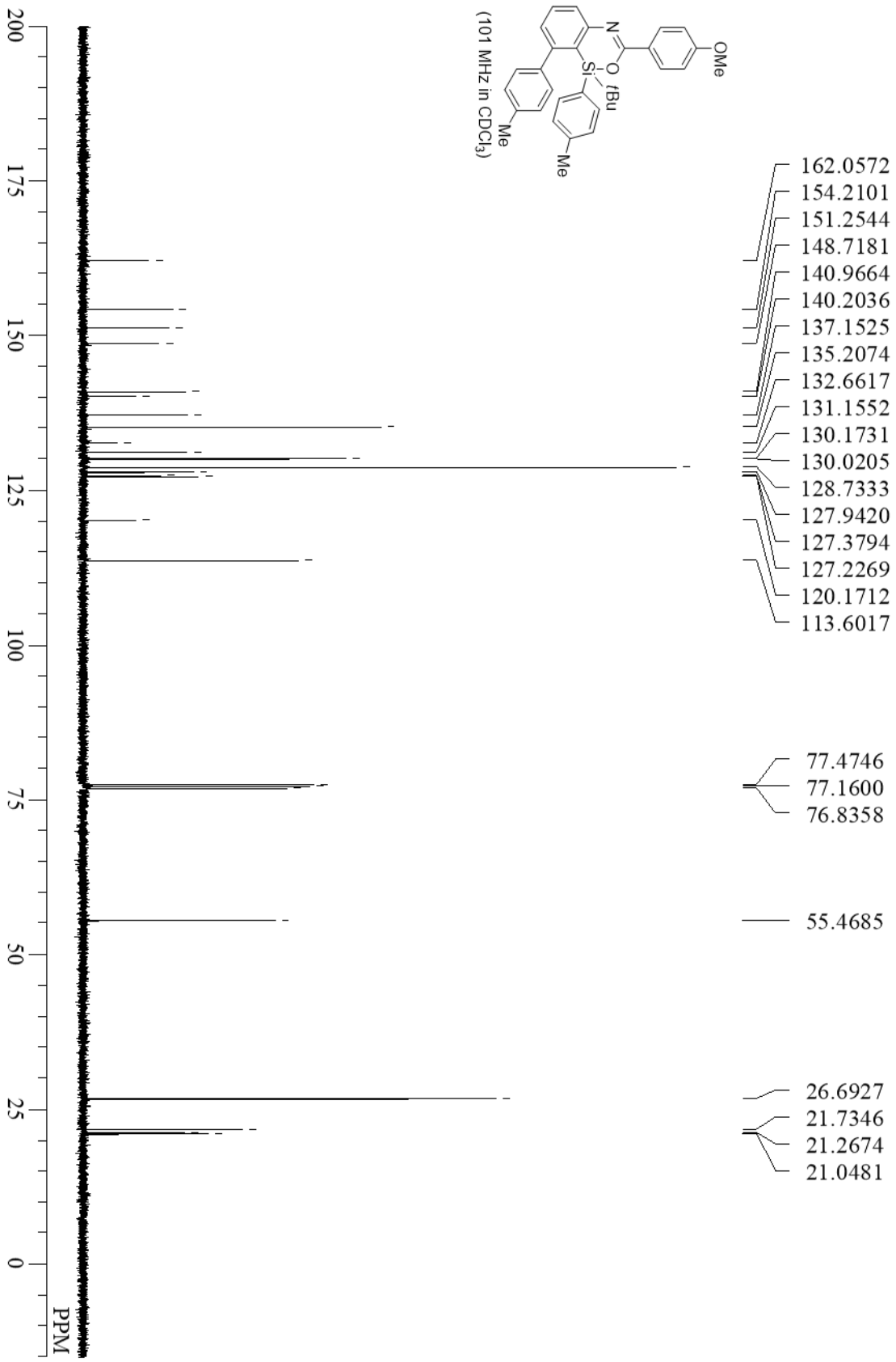
compound **3gg**



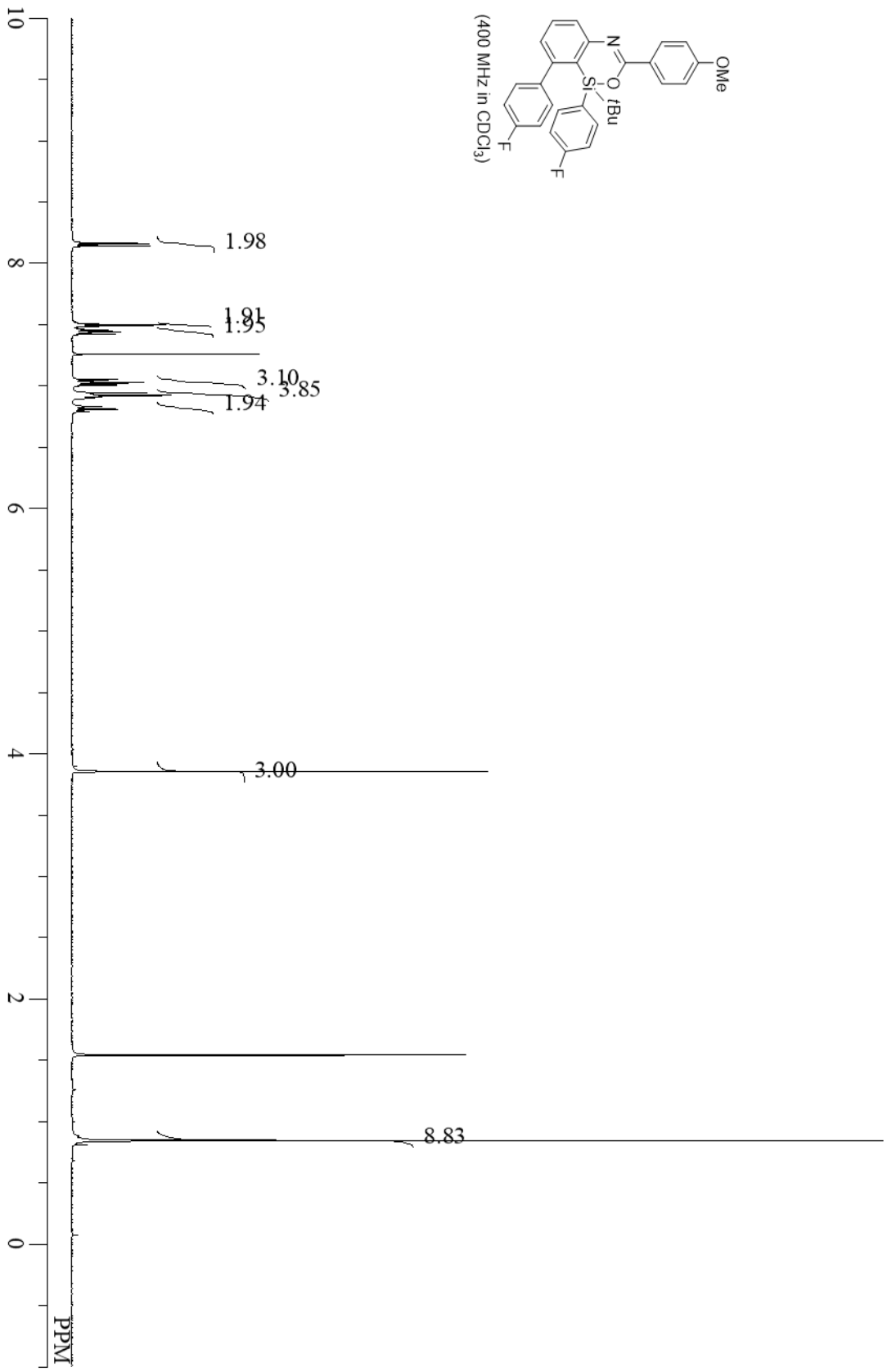
compound **3hh**



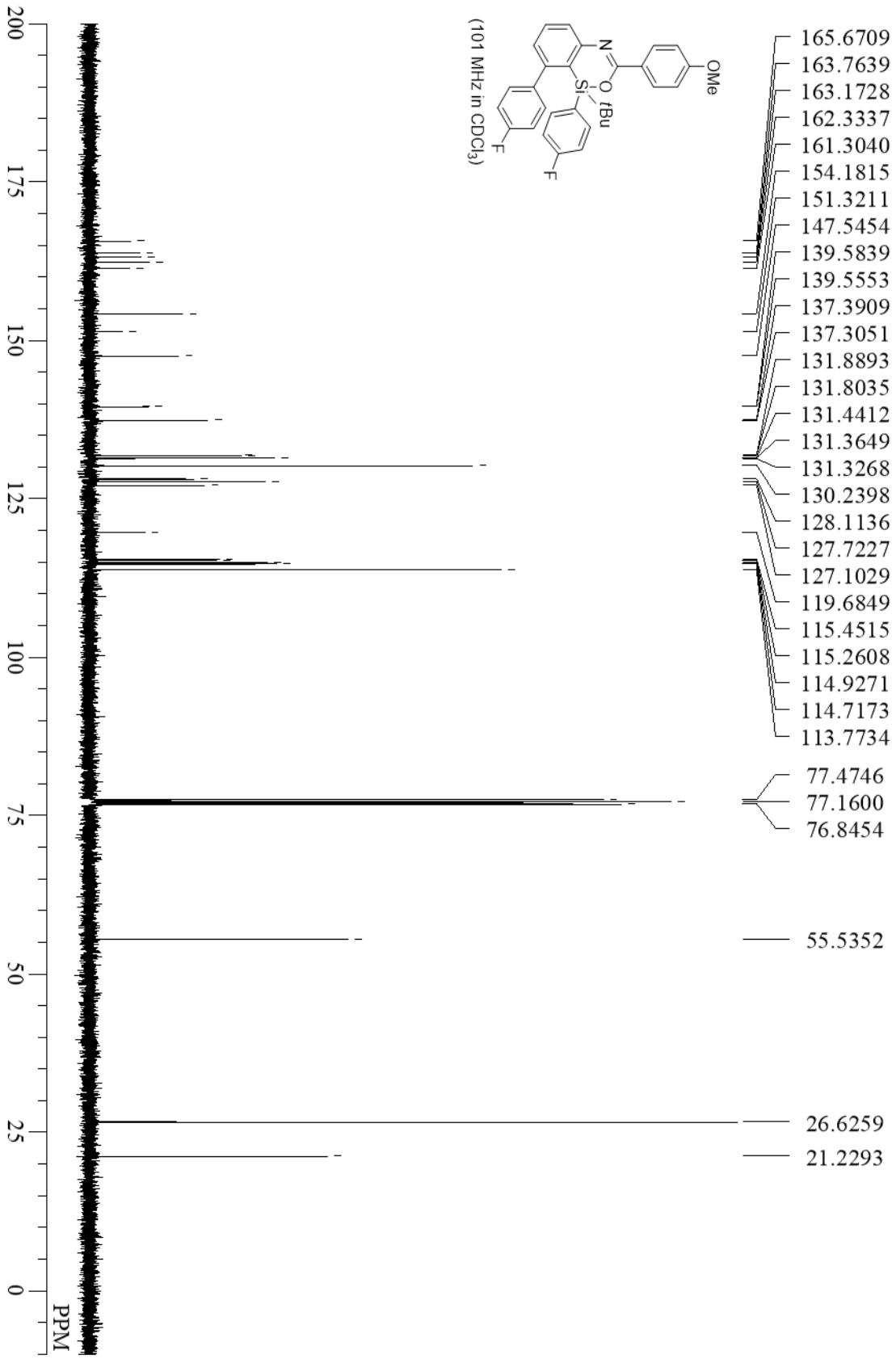
compound **3hh**



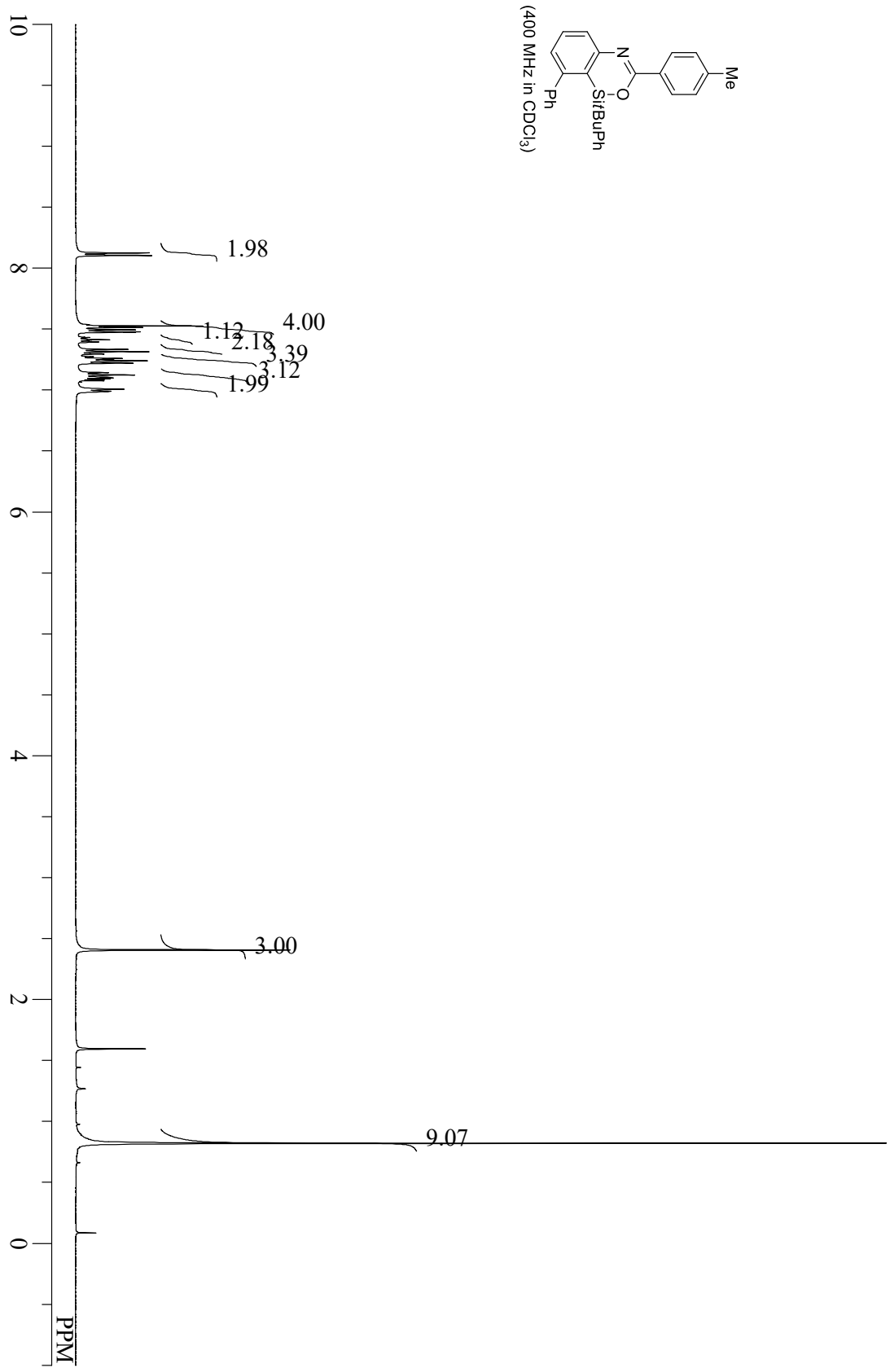
compound **3ii**



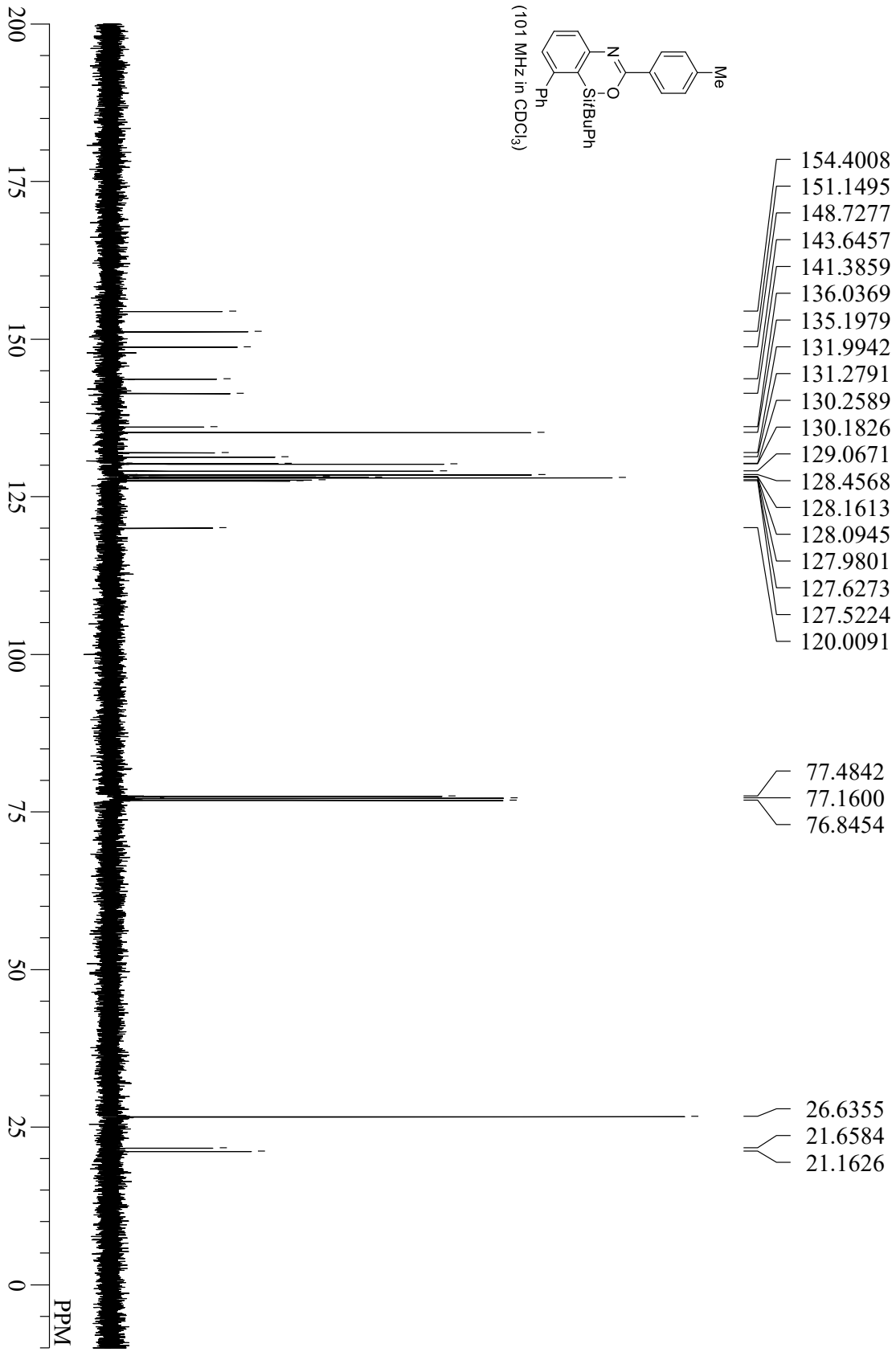
compound **3ii**



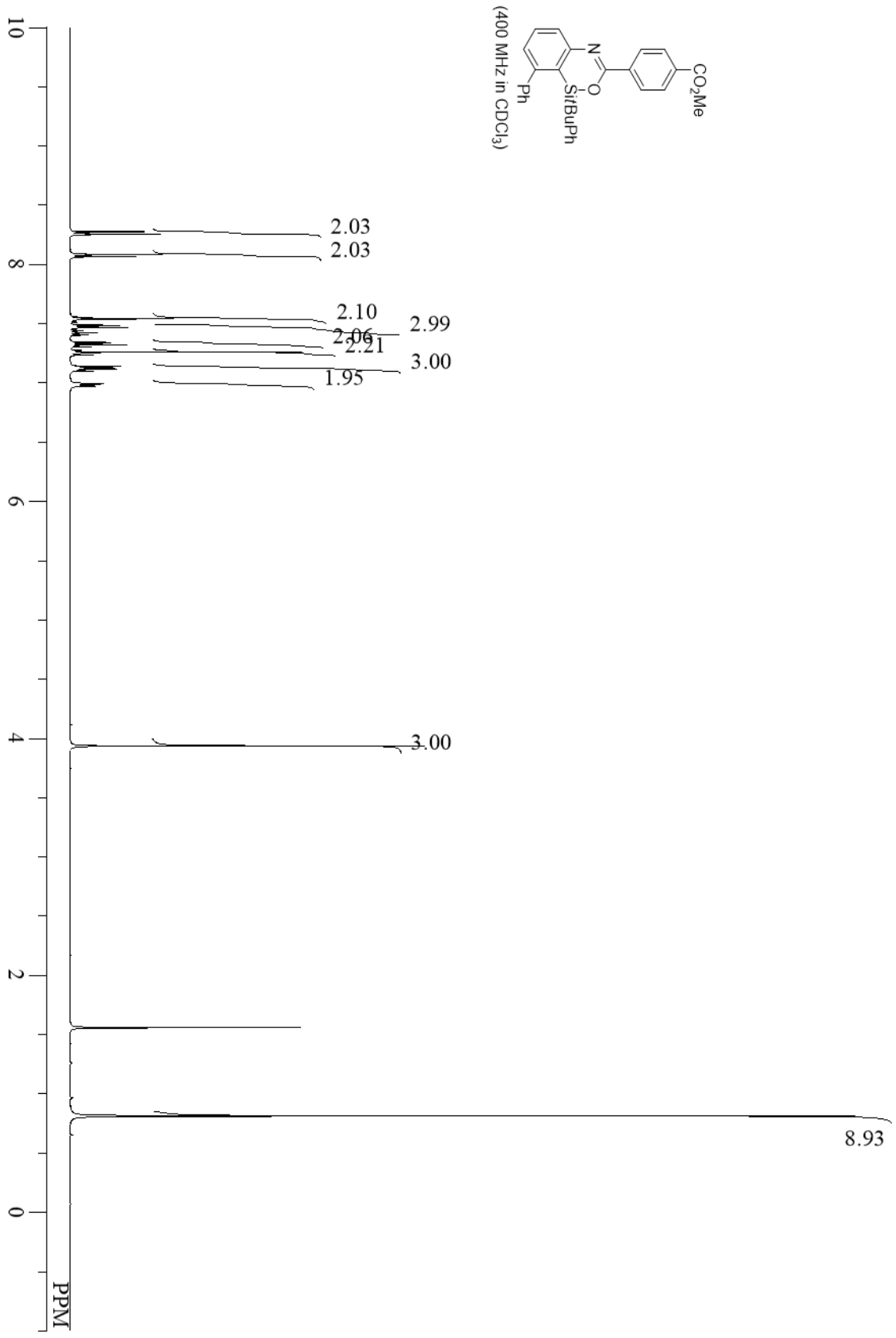
compound **3jj**



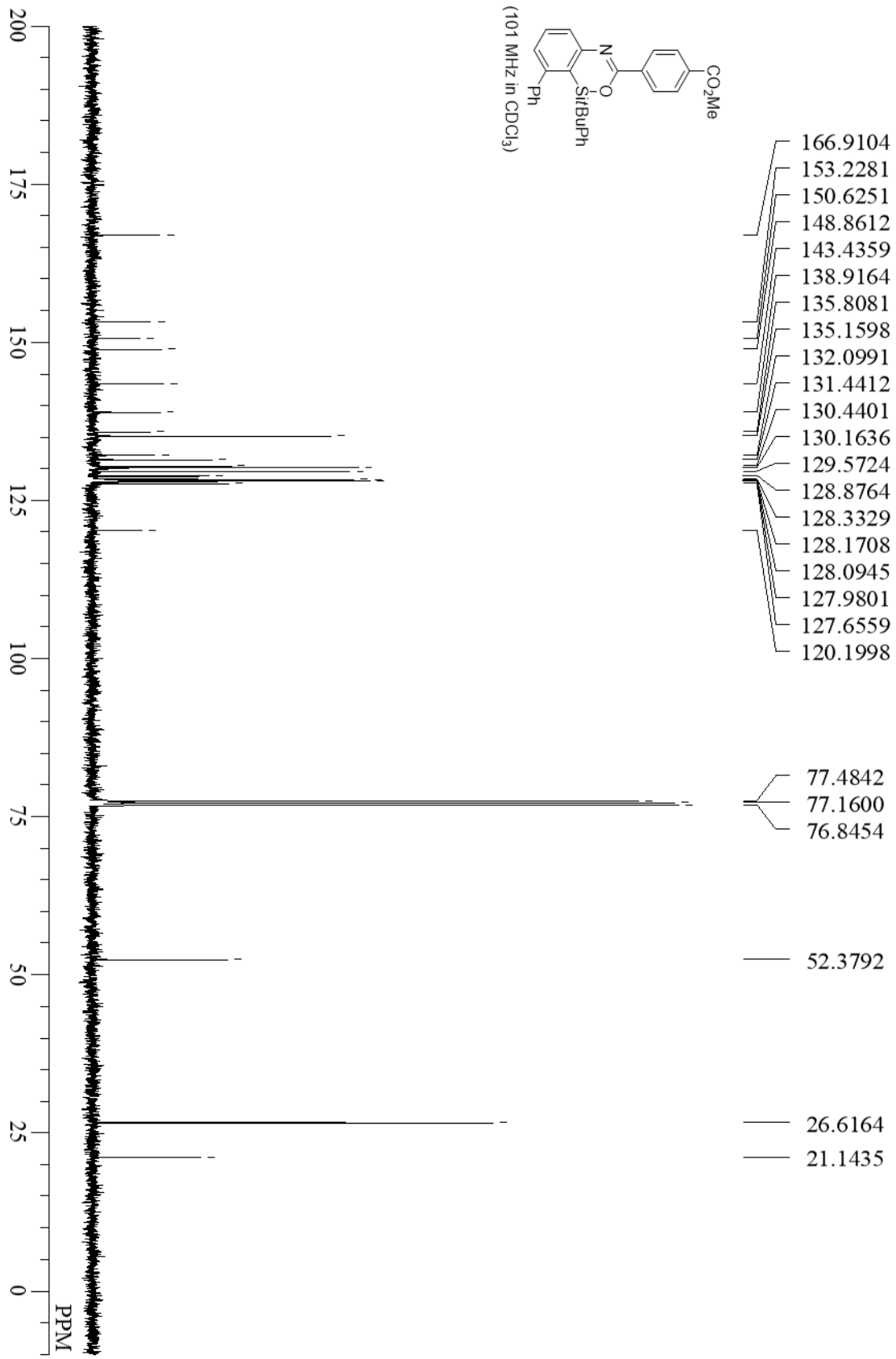
compound **3jj**



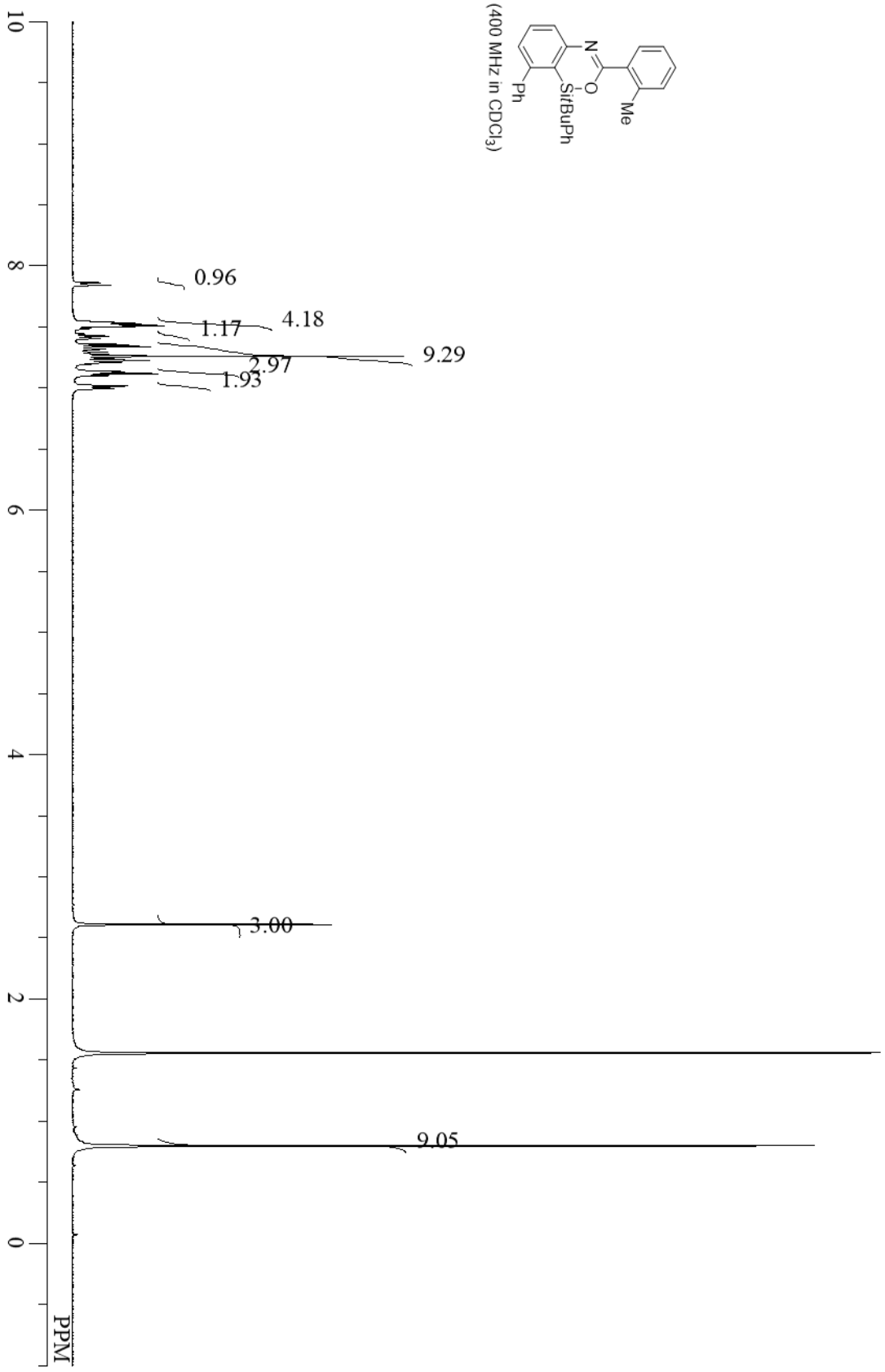
compound **3kk**



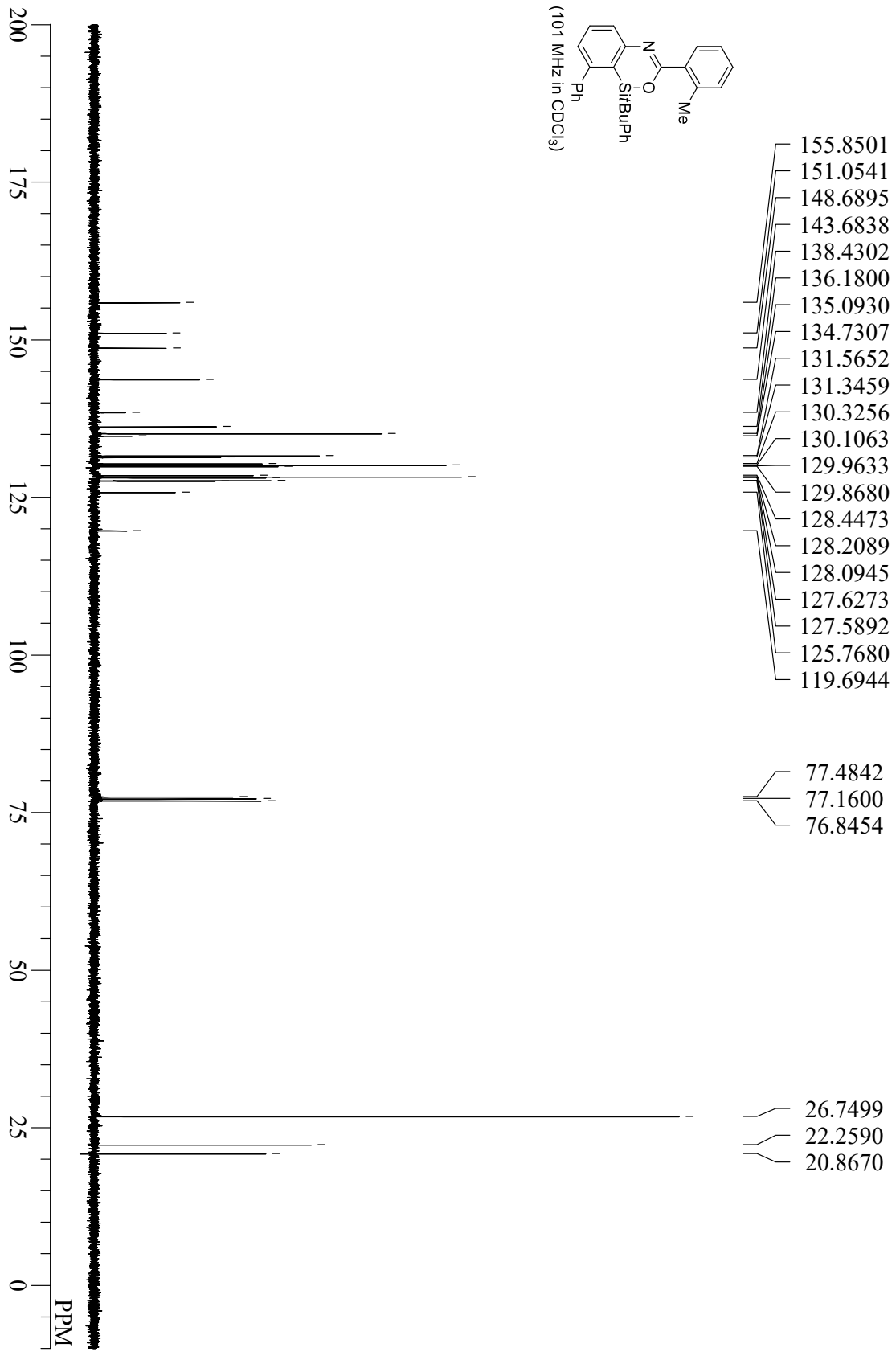
compound **3kk**



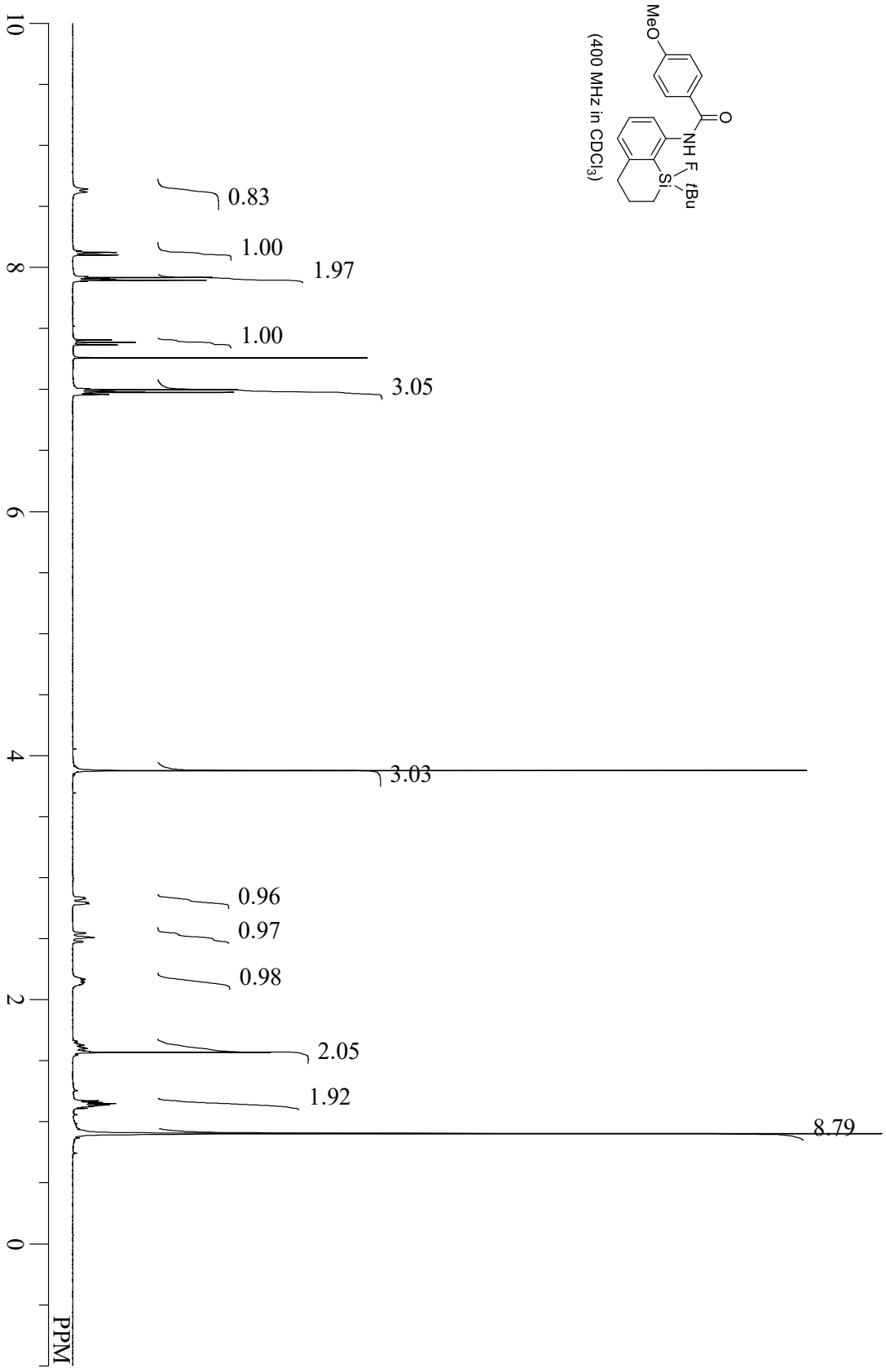
compound **3ll**



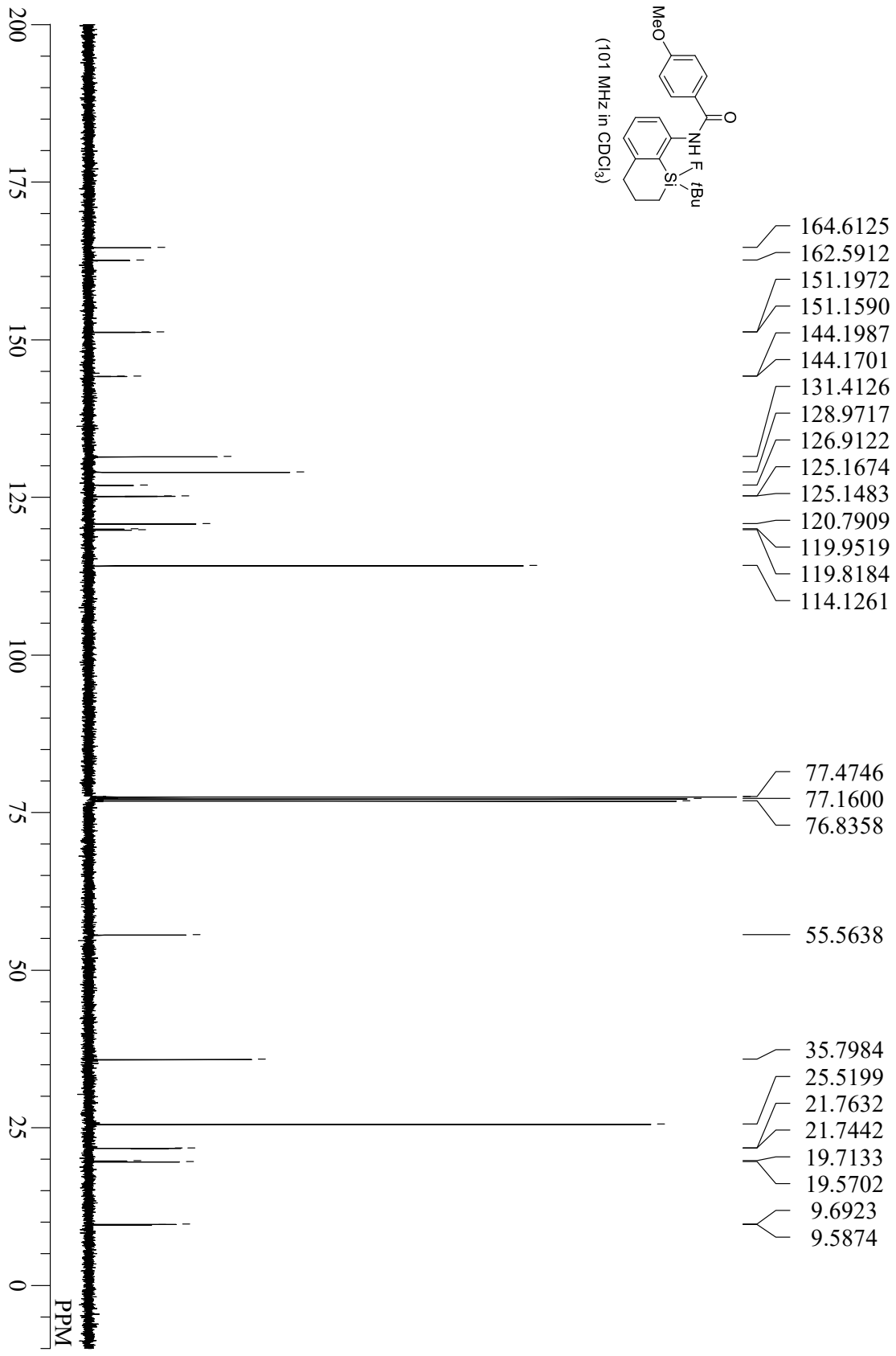
compound **3ll**



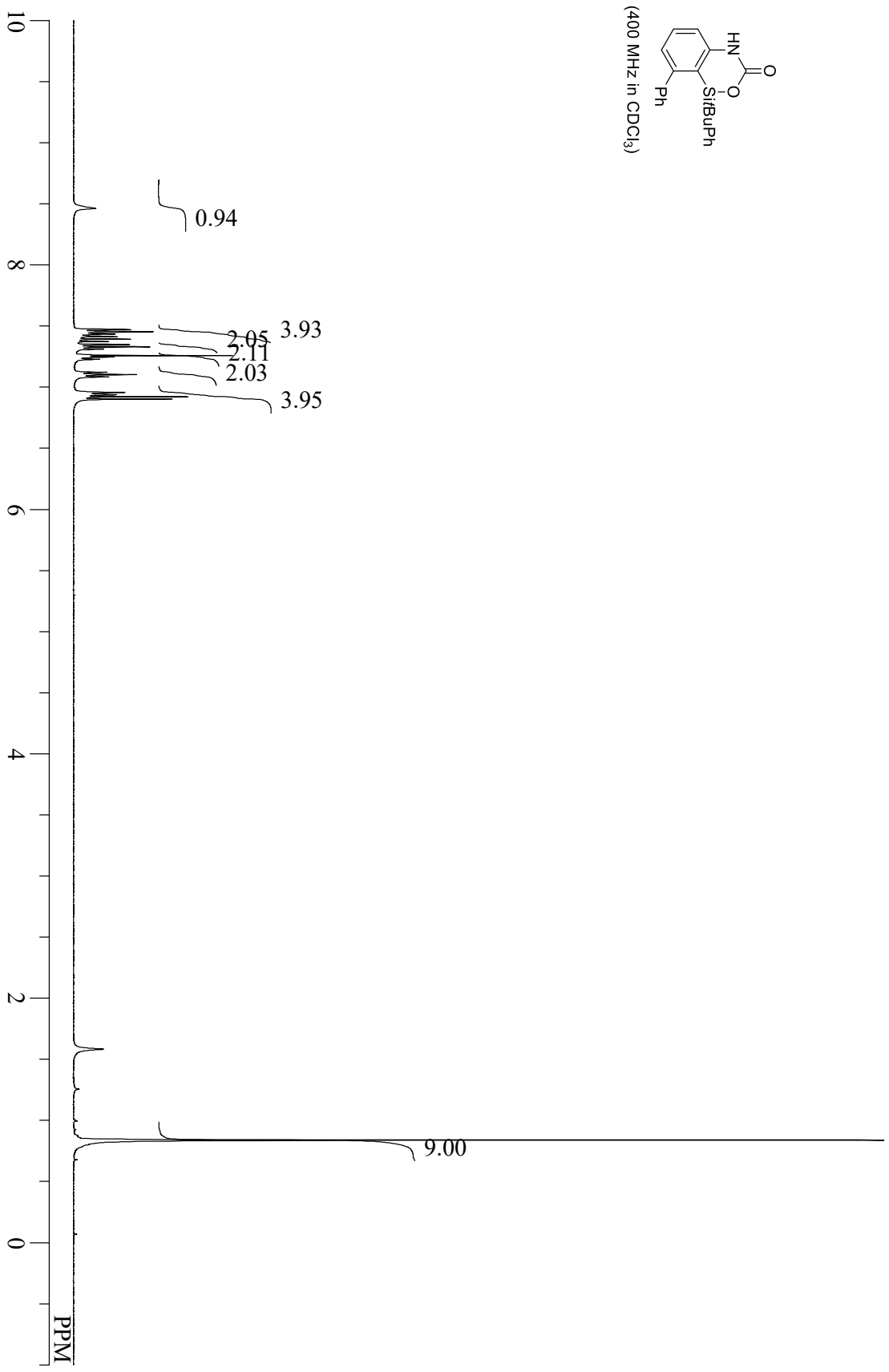
compound **4v**


(400 MHz in CDCl3)
MeO
O
NH F
tBu
Si
0.83
1.00
1.97
1.00
3.05
3.03
0.96
0.97
0.98
2.05
1.92
8.79
10
8
6
4
2
0
PPM

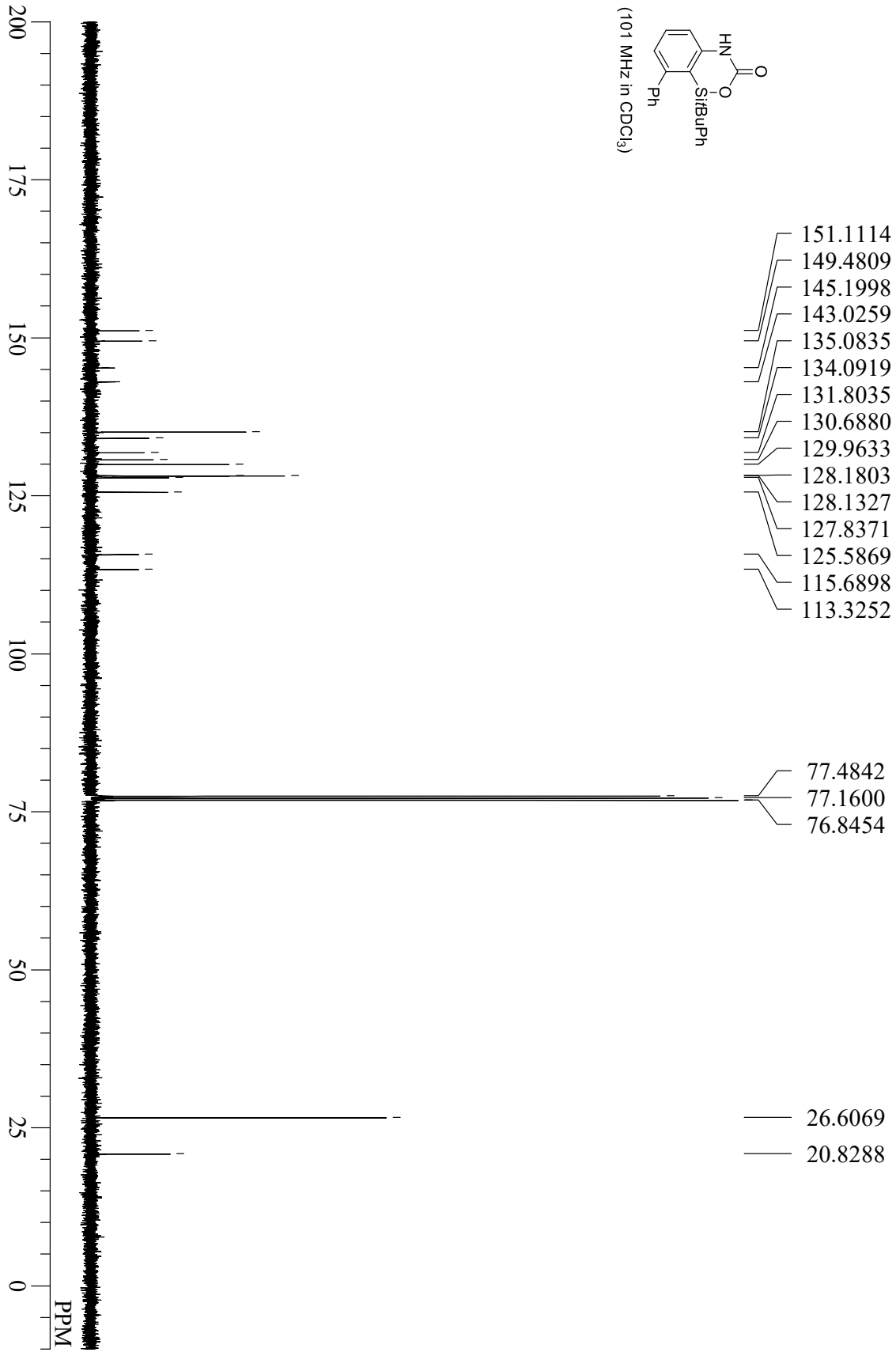
compound **4v**


MeO
O
NH F
tBu
Si
(101 MHz in CDCl3)
164.6125
162.5912
151.1972
151.1590
144.1987
144.1701
131.4126
128.9717
126.9122
125.1674
125.1483
120.7909
119.9519
119.8184
114.1261
77.4746
77.1600
76.8358
55.5638
35.7984
25.5199
21.7632
21.7442
19.7133
19.5702
9.6923
9.5874
200
175
150
125
100
75
50
25
0
PPM

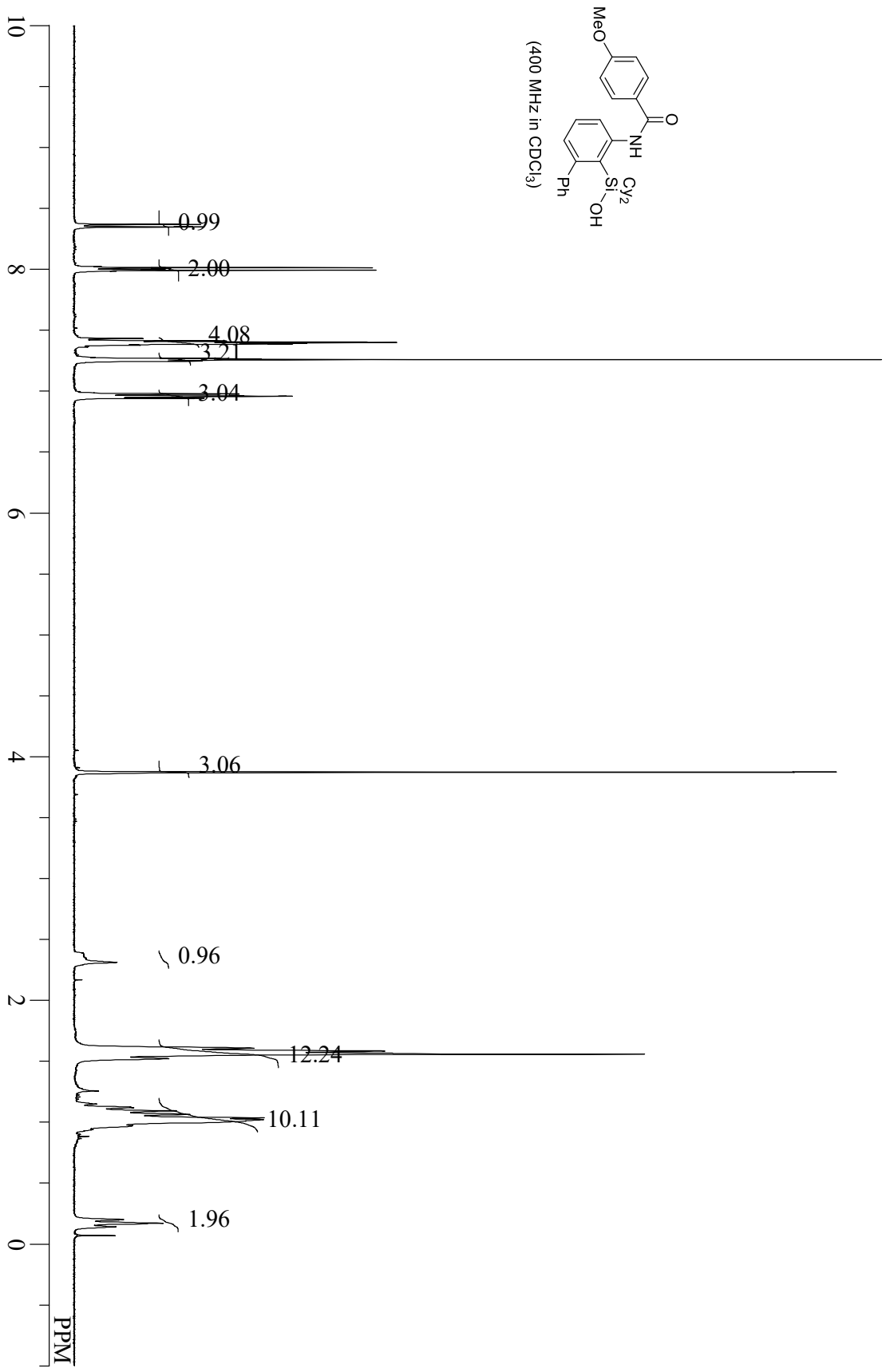
compound **5ff**



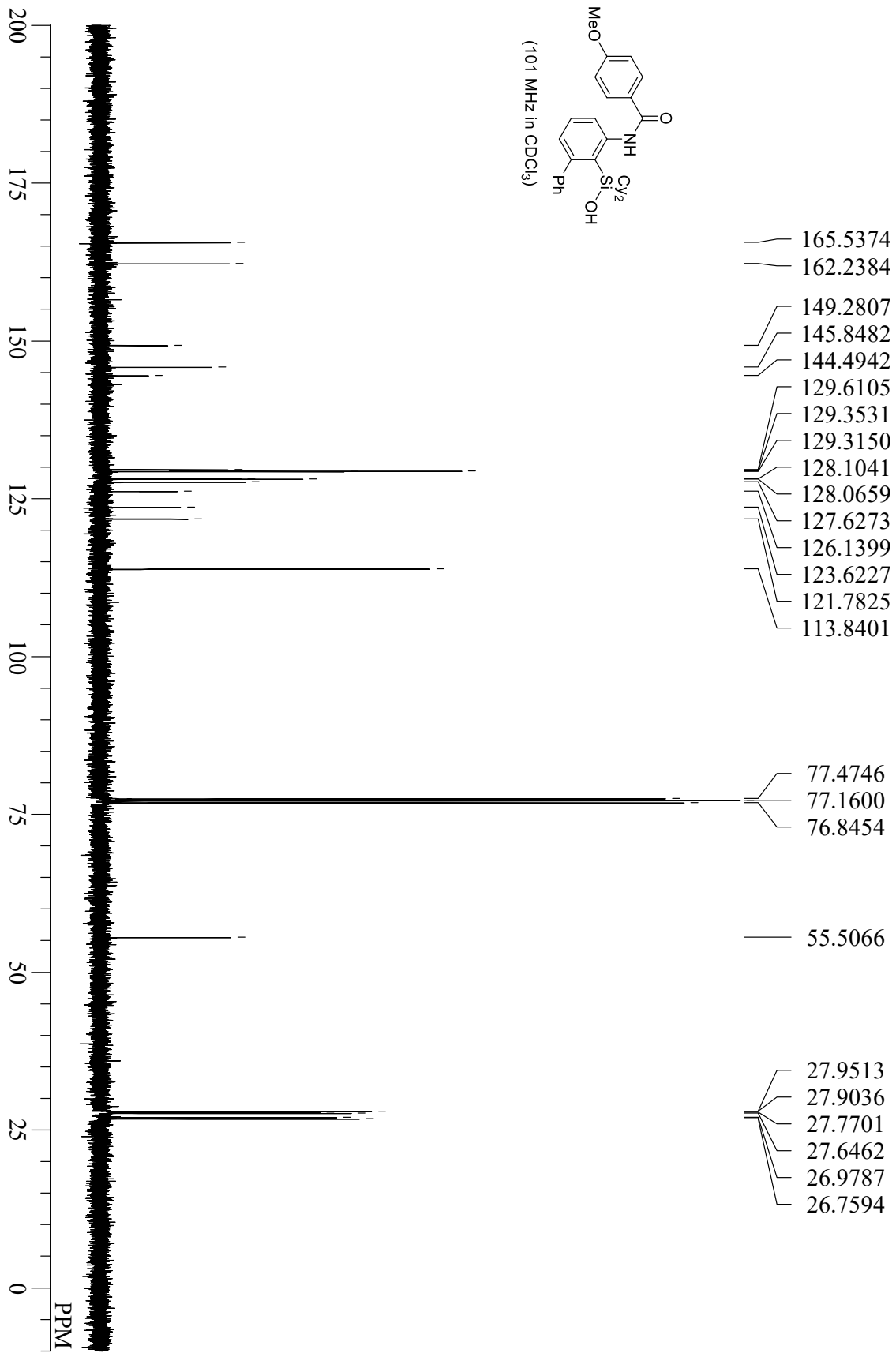
compound **5ff**



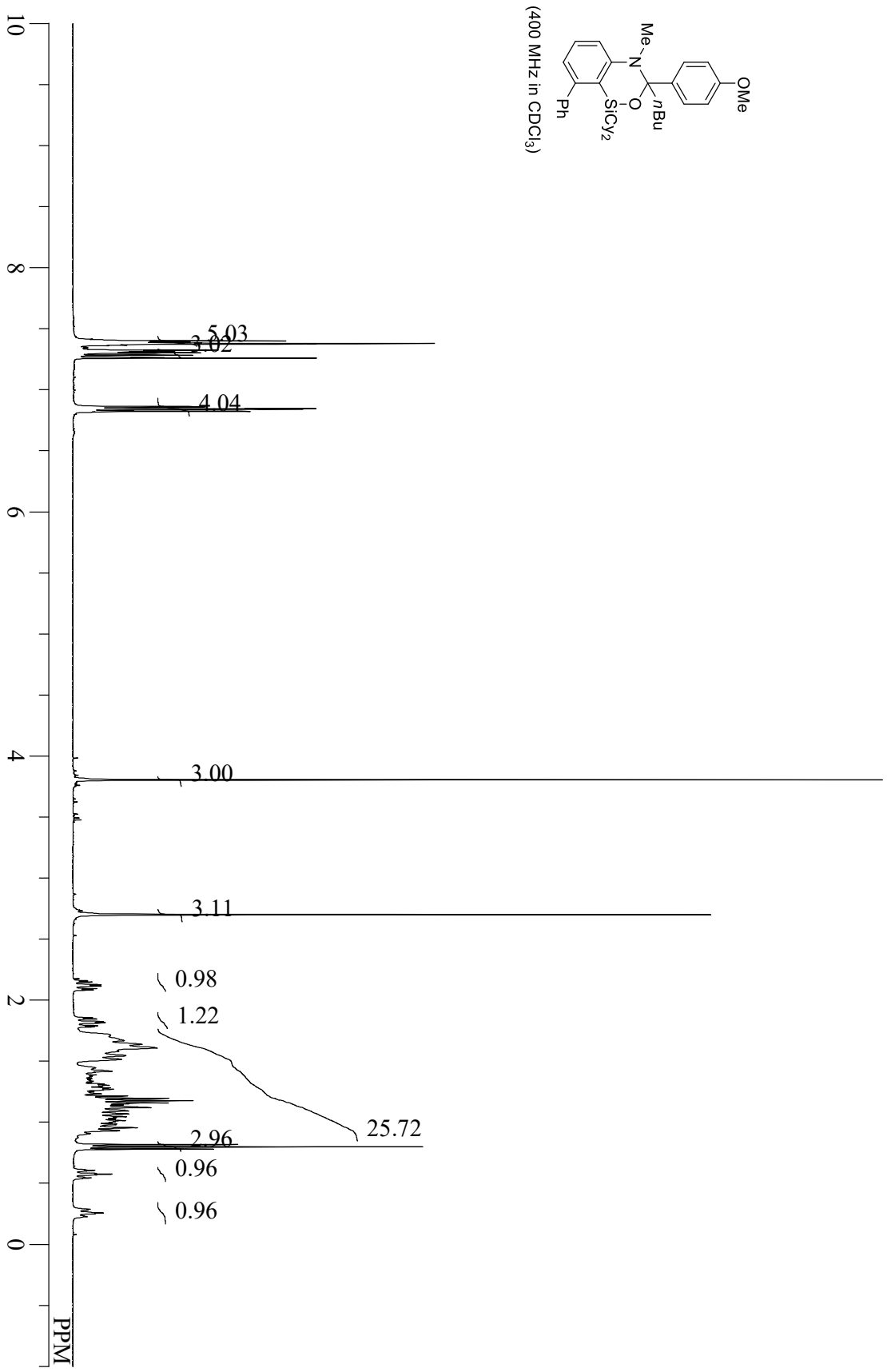
compound **6**


(400 MHz in CDCl3)
MeO
O
NH
Ph
Si
Cy2
OH
10
8
6
4
2
0
PPM
0.99
2.00
4.08
3.21
3.04
3.06
0.96
12.24
10.11
1.96

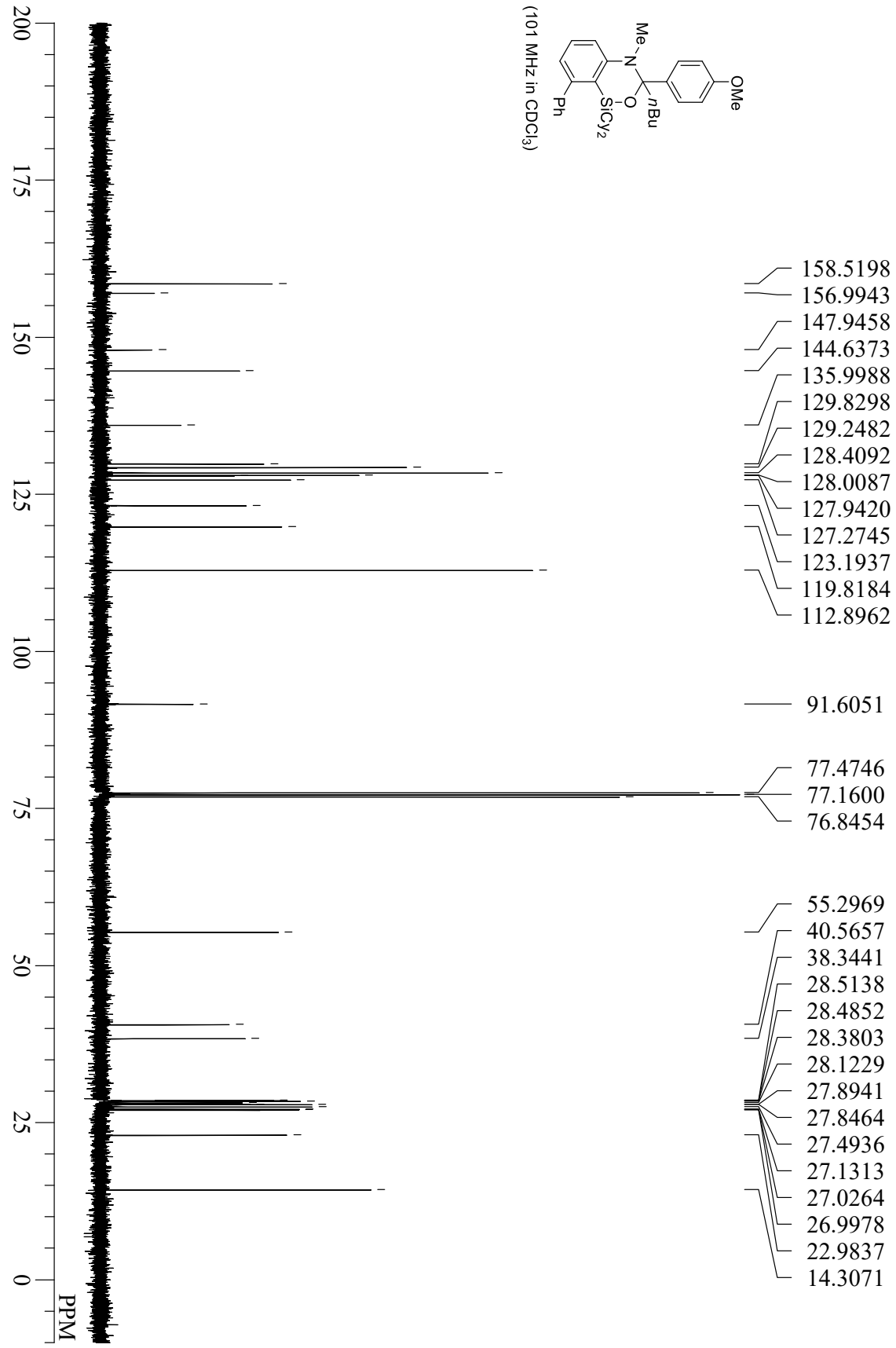
compound **6**


(101 MHz in CDCl3)
MeO
O
NH
Ph
Si
Cy2
OH
165.5374
162.2384
149.2807
145.8482
144.4942
129.6105
129.3531
129.3150
128.1041
128.0659
127.6273
126.1399
123.6227
121.7825
113.8401
77.4746
77.1600
76.8454
55.5066
27.9513
27.9036
27.7701
27.6462
26.9787
26.7594
200
175
150
125
100
75
50
25
0
PPM

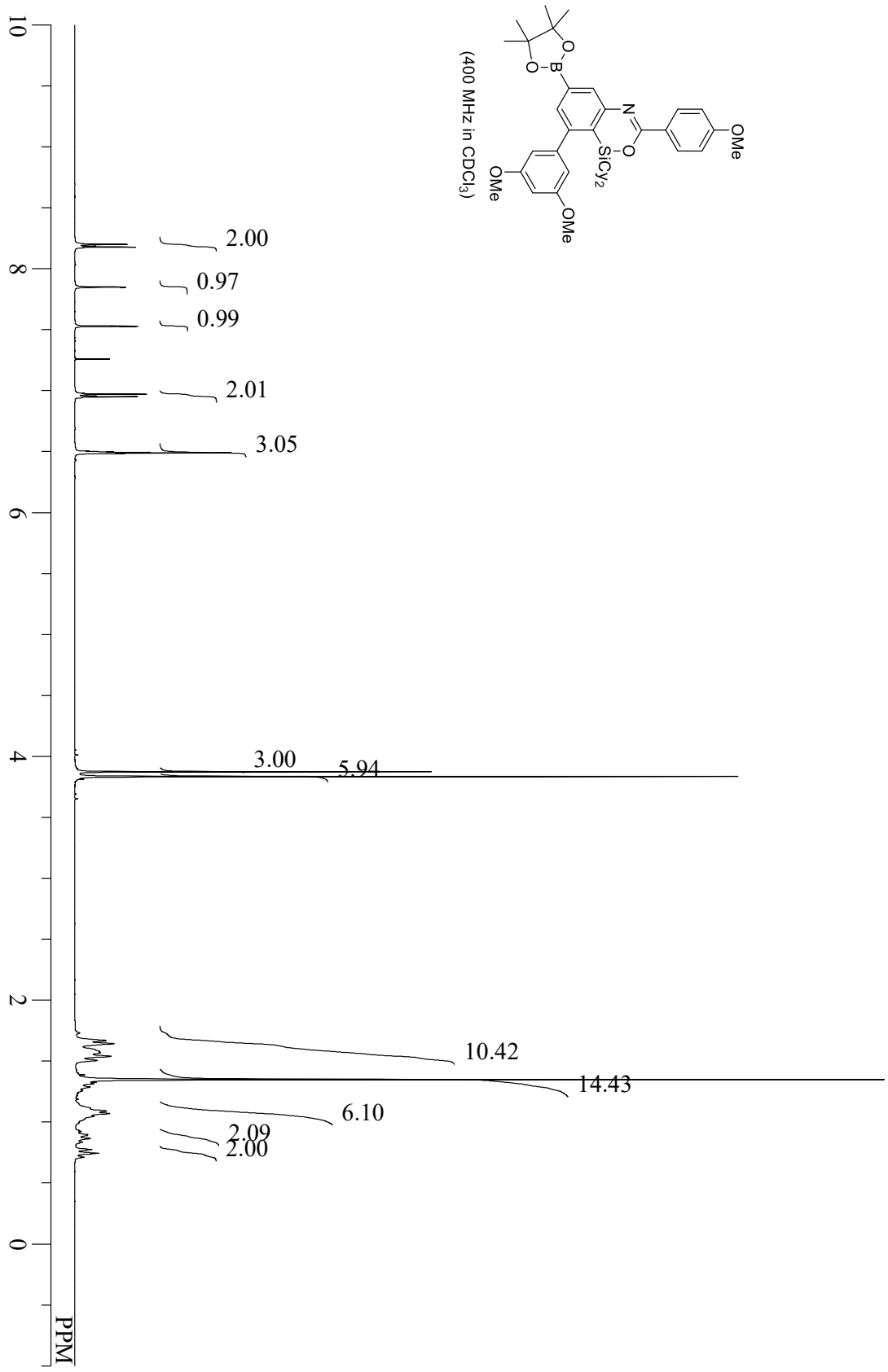
compound **7**


(400 MHz in CDCl3)
Me
N
O
nBu
OMe
SiCy2
Ph
10
8
6
4
2
0
PPM
5.03
3.02
4.04
3.00
3.11
0.98
1.22
25.72
2.96
0.96
0.96

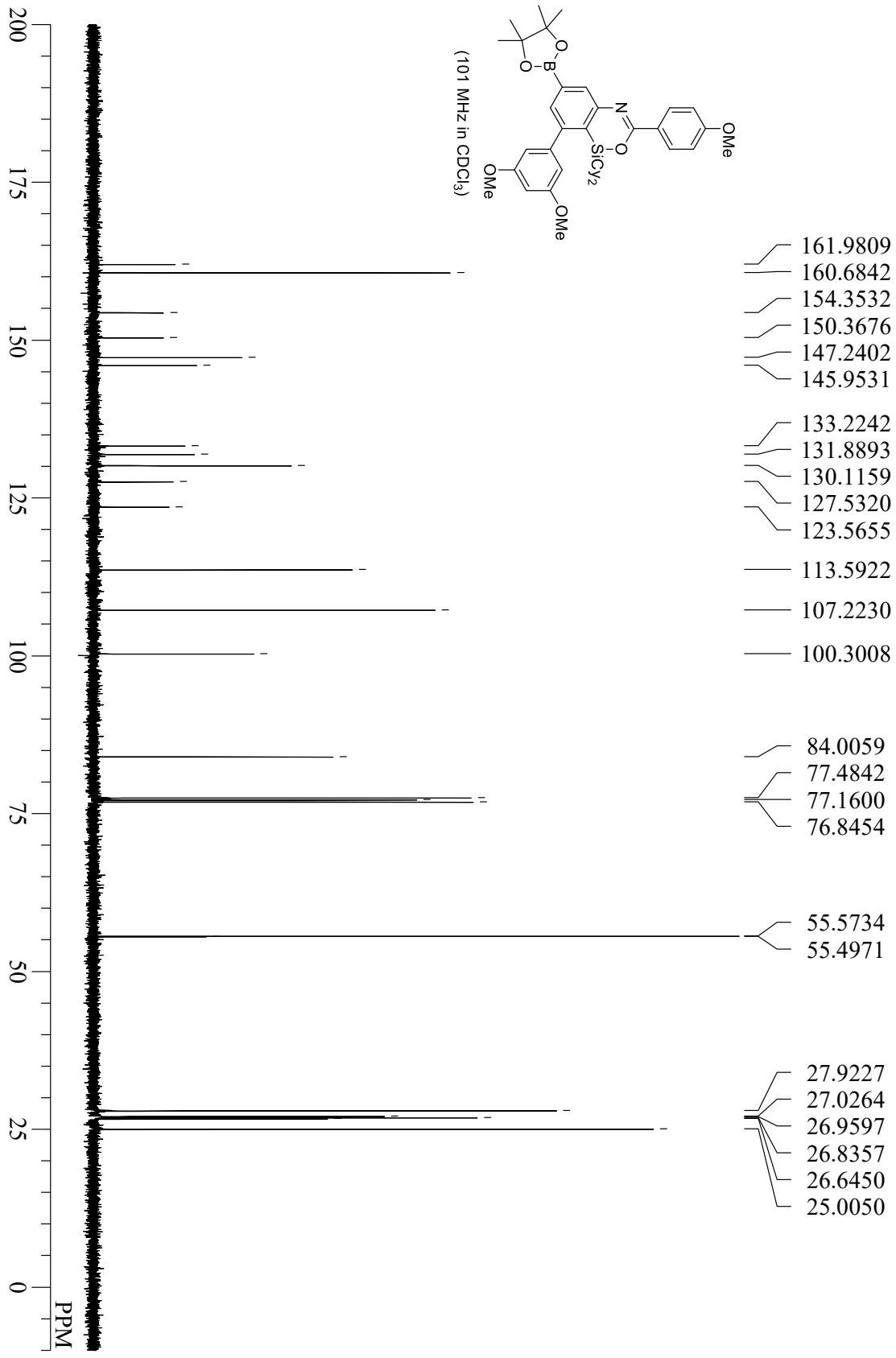
compound **7**


(101 MHz in CDCl3)
Me
N
O
nBu
OMe
SiCy2
Ph
158.5198
156.9943
147.9458
144.6373
135.9988
129.8298
129.2482
128.4092
128.0087
127.9420
127.2745
123.1937
119.8184
112.8962
91.6051
77.4746
77.1600
76.8454
55.2969
40.5657
38.3441
28.5138
28.4852
28.3803
28.1229
27.8941
27.8464
27.4936
27.1313
27.0264
26.9978
22.9837
14.3071
200
175
150
125
100
75
50
25
0
PPM

compound **8**


(400 MHz in CDCl3)
OMe
OMe
OMe
SiCy2
2.00
0.97
0.99
2.01
3.05
3.00
5.94
10.42
14.43
6.10
2.09
2.00
PPM

compound **8**


(101 MHz in CDCl3)
OMe
OMe
OMe
SiCy2
161.9809
160.6842
154.3532
150.3676
147.2402
145.9531
133.2242
131.8893
130.1159
127.5320
123.5655
113.5922
107.2230
100.3008
84.0059
77.4842
77.1600
76.8454
55.5734
55.4971
27.9227
27.0264
26.9597
26.8357
26.6450
25.0050
200
175
150
125
100
75
50
25
0
PPM

VI. References

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2. Y. Sato, C. Takagi, R. Shintani, K. Nozaki, *Angew. Chem. Int. Ed.* **2017**, *56*, 9211.
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