Electronic Supplementary Material (ESI) for ChemComm.

Rhodium-Catalyzed Intramolecular Alkynylsilylation of Alkynes

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Electronic Supplementary Information

I. General

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques or in a glove box under argon. NMR spectra were recorded on JEOL JNM-ECS400 or BRUKER Ascend500 spectrometers. Elemental analyses were performed by One-Stop Sharing Facility Center for Future Drug Discoveries, Graduate School of Pharmaceutical Sciences, The University of Tokyo. High resolution mass spectra were recorded on JEOL AccuTOF LC-plus spectrometer. Optical rotations were recorded on JASCO P-2200 polarimeter. UV-VIS spectra were recorded on SHIMADZU UV-3150 spectrometer. Fluorescence spectra were recorded on JASCO FP-8500 Spectrofluorometer. Absolute quantum yields were determined by Hamamatsu C9920-02G Absolute PL Quantum Yields Measurement System. X-ray crystallographic analysis was performed by RIGAKU VariMax Dual with Saturn724 diffractometer.

Et_2O, THF, and CH_2Cl_2 were purified by passing through neutral alumina columns under argon. dichlorodimethylsilane (TCI), phenylacetylene (TCI), 1,4-dimethoxy-2-butyne (Aldrich), MeCN (Kanto Chemical; dehydrated), PPh_3 (Wako Chemicals), $P(4\text{-}MeOC_6H_4)_3$ (TCI), $P(4\text{-}FC_6H_4)_3$ (Alfa Aesar), (*S*)-Ph-phox (Aldrich), and (*R*)-*i*Pr-phox (Strem), 1-propynylmagnesium bromide (Aldrich; 0.5 M solution in THF), *t*-BuLi (Kanto Chemical; 1.63 M solution in pentane), *n*-BuLi (Kanto Chemical; 1.55 M solution in hexane), and $ZnCl_2$ (TCI) were used as received. 1-Bromo-8-iodonaphthalene,[1] $Pd(PPh_3)_4$,[2] $[RhCl(C_2H_4)_2]_2$,[3] (*R*)-MeO-mop,[4] (*S*,*S*,*S*)-phosphoramidite,[5] (*R*,*S*,*S*)-phosphoramidite,[5] and sodium tetrakis(3,5-bistrifluoromethylphenyl)borate[6] were synthesized following the literature procedures.

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[1] Cottet, F.; Castagnetti, E.; Schlosser, M. *Synthesis* **2005**, 798.

[2] Coulson, D. R.; Satek, L. C.; Grim, S. O. *Inorg. Synth.* **1972**, *13*, 121.

[3] Cramer, R.; McCleverty, J. A.; Bray, J. *Inorg. Synth.* **1974**, *15*, 14.

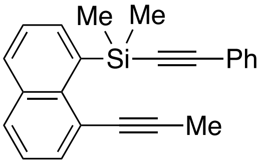
[4] Uozumi, Y.; Tanahashi, A.; Lee, S.-Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945.

[5] Choi, Y. H.; Choi, J. Y.; Yang, H. Y.; Kim, Y. H. *Tetrahedron: Asymmetry* **2002**, *13*, 801.

[6] Reger, D. L.; Wright, T. D.; Little, C. A.; Lamba, J. J. S.; Smith, M. D. *Inorg. Chem.* **2001**, *40*, 3810.

II. Synthesis of Substrates

Representative Procedures for Substrates:
Dimethyl(phenylethynyl)(8-(1-propynyl)-1-naphthyl)silane (1a)



$ZnCl_2$ (1.77 g, 13.0 mmol) was dried under vacuum using a heat gun. THF (10 mL) was added to it and the suspension was cooled to 0 °C. 1-Propynylmagnesium bromide (24.0 mL, 12.0 mmol; 0.5 M solution in THF) was added to it slowly over 8 min and the resulting mixture was stirred for 25 min at 0 °C. $Pd(PPh_3)_4$ (325 mg, 0.281 mmol) and 1-bromo-8-iodonaphthalene (3.46 g, 10.4 mmol) were successively added to it with THF (5 mL) and the mixture was stirred for 12.5 h while gradually raising the temperature to room temperature. The reaction was quenched with 1 M HClaq and diluted with H_2O. After extraction with Et_2O, the organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford 1-bromo-8-(1-propynyl)naphthalene as a yellow oil (1.57 g, 6.40 mmol, 61% yield).

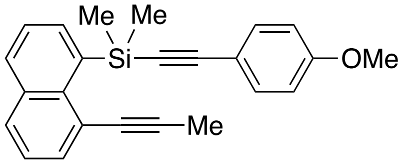
^1H NMR ($CDCl_3$): 7.83 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 7.80-7.72 (m, 3H), 7.38 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.25 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 2.15 (s, 3H).

t-BuLi (6.28 mL, 10.2 mmol; 1.63 M solution in pentane) was added slowly to a solution of 1-bromo-8-(1-propynyl)naphthalene (1.26 g, 5.14 mmol) in Et_2O (17 mL) over 9 min at –75 °C and the mixture was stirred for 50 min at –75 °C. Dichlorodimethylsilane (926 μL, 7.68 mmol) was added to it and the resulting mixture was stirred for 16 h while gradually raising the temperature to room temperature. The volatiles were then removed under vacuum to afford a crude of chlorodimethyl(8-(1-propynyl)-1-naphthyl)silane. Separately, *n*-BuLi (3.30 mL, 5.12 mmol; 1.55 M solution in hexane) was added to a solution of phenylacetylene (590 μL, 5.37 mmol) in Et_2O (10 mL) at –75 °C and the mixture was stirred for 55 min at –75→–60 °C and the cooling bath was removed. This was then added slowly over 7 min with the aid of additional Et_2O (10 mL) to the crude of chlorodimethyl(8-(1-propynyl)-1-naphthyl)silane obtained above in Et_2O (5 mL) at –50 °C. The mixture was stirred for 20 min at –40 °C and for 6 h at room temperature. The reaction was quenched with H_2O, and extracted with Et_2O. The organic layer was washed with saturated NaClaq, dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with hexane to afford compound **1a** as a white solid (1.01 g, 3.11 mmol, 61% yield).

^1H NMR ($CDCl_3$): 8.41 (dd, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 7.89 (dd, $^3J_{HH}$ = 8.1 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 7.81 (dd, $^3J_{HH}$ = 8.1 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 7.76 (dd, $^3J_{HH}$ = 7.2 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.55-7.50 (m, 2H), 7.48 (dd, $^3J_{HH}$ = 8.0 and 7.2 Hz, 1H), 7.41 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.34-7.29 (m, 3H), 2.19 (s, 3H), 0.82 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 138.2, 137.3, 134.5, 134.4, 134.3, 132.0, 131.7, 129.9, 128.5, 128.4, 125.3, 125.0, 123.8, 122.6, 106.4, 96.2, 94.9, 83.8, 6.1, 3.6. Anal. Calcd for $C_{23}H_{20}Si$: C, 85.13; H, 6.21. Found: C, 84.87; H, 6.49.

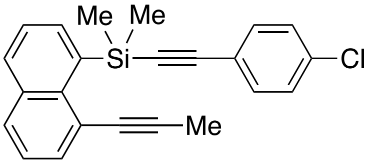
Analytical Data for Other Substrates:

Dimethyl(4-methoxyphenylethynyl)(8-(1-propynyl)-1-naphthyl)silane (1b)



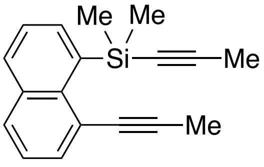
^{1}H NMR (CDCl$_3$): 8.40 (d, $^3J_{\mathrm{HH}}$ = 7.0 Hz, 1H), 7.87 (d, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 1H), 7.80 (d, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 1H), 7.75 (d, $^3J_{\mathrm{HH}}$ = 7.1 Hz, 1H), 7.47 (t, $^3J_{\mathrm{HH}}$ = 7.8 Hz, 1H), 7.45 (d, $^3J_{\mathrm{HH}}$ = 8.4 Hz, 2H), 7.40 (t, $^3J_{\mathrm{HH}}$ = 7.7 Hz, 1H), 6.84 (d, $^3J_{\mathrm{HH}}$ = 8.4 Hz, 2H), 3.81 (s, 3H), 2.18 (s, 3H), 0.80 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 159.7, 138.2, 137.3, 134.4, 133.5, 131.6, 129.8, 125.3, 124.9, 122.6, 116.0, 113.9, 106.5, 94.8, 94.5, 83.8, 55.4, 6.1, 3.7. Anal. Calcd for $C_{24}H_{22}OSi$: C, 81.31; H, 6.26. Found: C, 81.23; H, 6.50.

Dimethyl(4-chlorophenylethynyl)(8-(1-propynyl)-1-naphthyl)silane (1c)



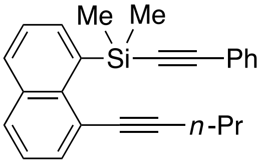
^{1}H NMR (CDCl$_3$): δ 8.38 (dd, $^3J_{\mathrm{HH}}$ = 7.0 Hz and $^4J_{\mathrm{HH}}$ = 1.3 Hz, 1H), 7.91 (dd, $^3J_{\mathrm{HH}}$ = 8.1 Hz and $^4J_{\mathrm{HH}}$ = 1.3 Hz, 1H), 7.83 (dd, $^3J_{\mathrm{HH}}$ = 8.1 Hz and $^4J_{\mathrm{HH}}$ = 1.3 Hz, 1H), 7.78 (dd, $^3J_{\mathrm{HH}}$ = 7.2 Hz and $^4J_{\mathrm{HH}}$ = 1.4 Hz, 1H), 7.50 (dd, $^3J_{\mathrm{HH}}$ = 8.1 and 7.1 Hz, 1H), 7.48-7.44 (m, 2H), 7.43 (dd, $^3J_{\mathrm{HH}}$ = 7.9 and 7.3 Hz, 1H), 7.33-7.29 (m, 2H), 2.20 (s, 3H), 0.82 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 138.2, 137.3, 134.54, 134.45, 134.0, 133.2, 131.8, 129.9, 128.7, 125.3, 125.0, 122.5, 122.3, 105.1, 97.5, 94.9, 83.8, 6.1, 3.6. Anal. Calcd for $C_{23}H_{19}ClSi$: C, 76.96; H, 5.34. Found: C, 76.82; H, 5.41.

Dimethyl(1-propynyl)(8-(1-propynyl)-1-naphthyl)silane (1d)



^{1}H NMR (CDCl$_3$): δ 8.38 (dd, $^3J_{\mathrm{HH}}$ = 6.9 Hz and $^4J_{\mathrm{HH}}$ = 1.3 Hz, 1H), 7.86 (dd, $^3J_{\mathrm{HH}}$ = 8.3 Hz and $^4J_{\mathrm{HH}}$ = 1.2 Hz, 1H), 7.79 (dd, $^3J_{\mathrm{HH}}$ = 8.1 Hz and $^4J_{\mathrm{HH}}$ = 1.2 Hz, 1H), 7.73 (dd, $^3J_{\mathrm{HH}}$ = 7.2 Hz and $^4J_{\mathrm{HH}}$ = 1.3 Hz, 1H), 7.46 (dd, $^3J_{\mathrm{HH}}$ = 8.0 and 7.2 Hz, 1H), 7.38 (t, $^3J_{\mathrm{HH}}$ = 7.6 Hz, 1H), 2.16 (s, 3H), 1.98 (s, 3H), 0.72 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 138.3, 137.3, 134.7, 134.5, 131.5, 129.9, 125.3, 124.9, 122.5, 104.2, 94.6, 85.7, 83.7, 6.0, 5.4, 3.8. HRMS (ESI-TOF) calcd for $C_{18}H_{18}SiCs$ (M+Cs$^+$) 395.0232, found 395.0217.

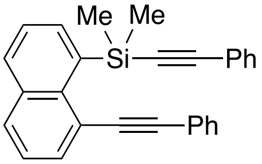
Dimethyl(phenylethynyl)(8-(1-pentynyl)-1-naphthyl)silane (1e)



^{1}H NMR (CDCl$_3$): 8.44 (dd, $^3J_{\mathrm{HH}}$ = 7.0 Hz and $^4J_{\mathrm{HH}}$ = 1.4 Hz, 1H), 7.88 (dd, $^3J_{\mathrm{HH}}$ = 8.2 Hz and $^4J_{\mathrm{HH}}$ = 1.2 Hz, 1H), 7.80 (dd, $^3J_{\mathrm{HH}}$ = 8.1 Hz and $^4J_{\mathrm{HH}}$ = 1.2 Hz, 1H), 7.77 (dd, $^3J_{\mathrm{HH}}$ = 7.2 Hz and $^4J_{\mathrm{HH}}$ = 1.4 Hz, 1H), 7.54-7.49 (m, 2H), 7.47 (dd, $^3J_{\mathrm{HH}}$ = 8.1 and 7.1 Hz, 1H), 7.40 (dd, $^3J_{\mathrm{HH}}$ = 8.1 and 7.3 Hz, 1H), 7.34-7.30 (m, 3H), 2.52 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, 2H), 1.71 (sext, $^3J_{\mathrm{HH}}$ =

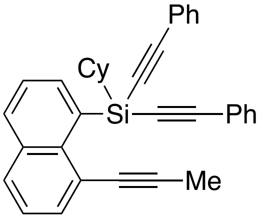
7.3 Hz, 2H), 1.07 (t, ${}^3J_{HH}$ = 7.4 Hz, 3H), 0.81 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 138.3, 137.2, 134.9, 134.44, 134.36, 132.0, 131.6, 129.8, 128.5, 128.3, 125.3, 125.0, 123.8, 122.6, 106.6, 99.2, 96.4, 84.5, 23.0, 22.0, 14.0, 3.9. HRMS (ESI-TOF) calcd for $C_{25}H_{24}SiCs$ (M+Cs$^+$) 485.0702, found 485.0690.

Dimethyl(phenylethynyl)(8-(phenylethynyl)-1-naphthyl)silane (1f)



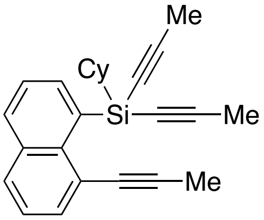
^{1}H NMR ($CDCl_3$): 8.44 (d, ${}^3J_{HH}$ = 7.0 Hz, 1H), 7.93 (d, ${}^3J_{HH}$ = 7.0 Hz, 1H), 7.92 (d, ${}^3J_{HH}$ = 8.0 Hz, 1H), 7.88 (d, ${}^3J_{HH}$ = 8.4 Hz, 1H), 7.69-7.63 (m, 2H), 7.51 (t, ${}^3J_{HH}$ = 7.7 Hz, 1H), 7.47 (t, ${}^3J_{HH}$ = 7.6 Hz, 1H), 7.43-7.32 (m, 5H), 7.31-7.25 (m, 3H), 0.86 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 138.3, 136.8, 135.7, 134.54, 134.48, 132.0, 131.9, 131.7, 130.8, 128.6, 128.5, 128.4, 128.3, 125.5, 125.0, 123.9, 123.7, 121.9, 107.2, 97.3, 96.0, 93.4, 3.8. Anal. Calcd for $C_{28}H_{22}Si$: C, 87.00; H, 5.74. Found: C, 86.73; H, 5.86.

Cyclohexyldi(phenylethynyl)(8-(1-propynyl)-1-naphthyl)silane (1g)



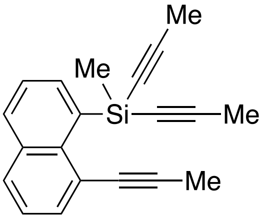
^{1}H NMR ($CDCl_3$): 8.70 (d, ${}^3J_{HH}$ = 7.0 Hz, 1H), 7.91 (d, ${}^3J_{HH}$ = 8.2 Hz, 1H), 7.81 (d, ${}^3J_{HH}$ = 8.2 Hz, 1H), 7.78 (d, ${}^3J_{HH}$ = 6.8 Hz, 1H), 7.60-7.54 (m, 4H), 7.51 (t, ${}^3J_{HH}$ = 7.6 Hz, 1H), 7.42 (t, ${}^3J_{HH}$ = 7.7 Hz, 1H), 7.37-7.28 (m, 6H), 2.24 (s, 3H), 1.98-1.68 (m, 6H), 1.66-1.52 (m, 2H), 1.38-1.23 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 140.5, 137.3, 134.53, 134.46, 132.2, 129.7, 129.2, 128.7, 128.3, 125.3, 125.1, 123.6, 122.7, 107.7, 96.8, 91.7, 83.9, 28.3, 28.1, 27.0, 6.4. Anal. Calcd for $C_{35}H_{30}Si$: C, 87.82; H, 6.32. Found: C, 87.88; H, 6.62.

Cyclohexyldi(1-propynyl)(8-(1-propynyl)-1-naphthyl)silane (1h)



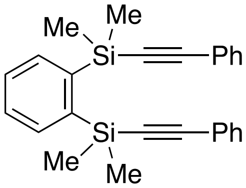
^{1}H NMR ($CDCl_3$): 8.62 (dd, ${}^3J_{HH}$ = 7.0 Hz and ${}^4J_{HH}$ = 0.9 Hz, 1H), 7.86 (d, ${}^3J_{HH}$ = 8.0 Hz, 1H), 7.78 (d, ${}^3J_{HH}$ = 8.0 Hz, 1H), 7.73 (d, ${}^3J_{HH}$ = 7.2 Hz, 1H), 7.46 (t, ${}^3J_{HH}$ = 7.5 Hz, 1H), 7.38 (t, ${}^3J_{HH}$ = 7.7 Hz, 1H), 2.20 (s, 3H), 2.01 (s, 6H), 1.83-1.54 (m, 6H), 1.47-1.33 (m, 2H), 1.30-1.16 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 140.5, 137.2, 134.5, 134.4, 131.9, 129.9, 129.8, 125.2, 124.9, 122.6, 105.5, 96.3, 83.8, 81.4, 28.0, 27.9, 26.9, 6.2, 5.7. HRMS (ESI-TOF) calcd for $C_{25}H_{26}SiCs$ (M+Cs$^+$) 487.0858, found 487.0841.

Methyldi(1-propynyl)(8-(1-propynyl)-1-naphthyl)silane (1i)



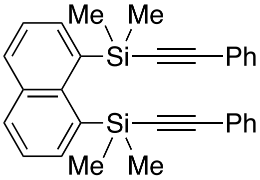
^{1}H NMR (CDCl$_3$): 8.60 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.88 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.78 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.72 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.48 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.39 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 2.20 (s, 3H), 1.99 (s, 6H), 0.82 (s, 3H). ^{13}C NMR (CDCl$_3$): δ 139.4, 137.2, 134.4, 134.1, 132.0, 131.7, 129.6, 125.3, 125.0, 122.5, 104.8, 96.3, 83.5, 83.1, 6.3, 5.6, 4.4. HRMS (ESI-TOF) calcd for $C_{20}H_{18}SiCs$ (M+Cs$^+$) 419.0232, found 419.0238.

1,2-Bis(dimethyl(phenylethynyl)silyl)benzene (1j)



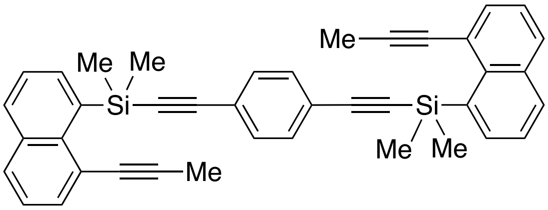
^{1}H NMR (CDCl$_3$): 7.96-7.90 (m, 2H), 7.53-7.46 (m, 4H), 7.44-7.38 (m, 2H), 7.35-7.27 (m, 6H), 0.67 (s, 12H). ^{13}C NMR (CDCl$_3$): δ 143.1, 135.9, 132.0, 128.72, 128.65, 128.4, 123.4, 107.7, 94.8, 2.1. HRMS (ESI-TOF) calcd for $C_{26}H_{26}Si_2Cs$ (M+Cs$^+$) 527.0628, found 527.0614.

1,8-Bis(dimethyl(phenylethynyl)silyl)naphthalene (1k)



^{1}H NMR (CDCl$_3$): 8.11 (dd, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 1.3 Hz, 2H), 7.80 (dd, $^3J_{HH}$ = 7.9 Hz and $^4J_{HH}$ = 1.3 Hz, 2H), 7.48-7.44 (m, 4H), 7.43 (dd, $^3J_{HH}$ = 8.0 and 7.1 Hz, 2H), 7.33-7.26 (m, 6H), 0.61 (s, 12H). ^{13}C NMR (CDCl$_3$): δ 141.5, 138.0, 136.2, 133.5, 131.9, 131.5, 128.6, 128.3, 124.0, 123.6, 107.6, 95.8, 3.4. HRMS (ESI-TOF) calcd for $C_{30}H_{28}Si_2Cs$ (M+Cs$^+$) 577.0784, found 577.0763.

1,4-Bis(dimethyl(8-(1-propynyl)-1-naphthyl)silylethynyl)benzene (4)



^{1}H NMR (CDCl$_3$): 8.37 (dd, $^3J_{HH}$ = 7.0 Hz and $^4J_{HH}$ = 1.3 Hz, 2H), 7.89 (dd, $^3J_{HH}$ = 8.1 Hz and $^4J_{HH}$ = 1.2 Hz, 2H), 7.81 (dd, $^3J_{HH}$ = 8.2 Hz and $^4J_{HH}$ = 1.2 Hz, 2H), 7.76 (dd, $^3J_{HH}$ = 7.1 Hz and $^4J_{HH}$ = 1.2 Hz, 2H), 7.48 (dd, $^3J_{HH}$ = 7.9 and 7.1 Hz, 2H), 7.45 (s, 4H), 7.41 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 2.18 (s, 6H), 0.81 (s, 12H). ^{13}C NMR (CDCl$_3$): δ 138.2, 137.3, 134.5, 134.4, 134.1, 131.8, 131.7, 129.9, 125.3, 125.0, 123.7, 122.5, 105.9, 98.4, 94.9, 83.8, 6.1, 3.6. HRMS (ESI-TOF) calcd for $C_{40}H_{34}Si_2Cs$ (M+Cs$^+$) 703.1254, found 703.1232.

III. Catalytic Reactions

General Procedure for Table 1 and Equations 3–4.

A solution of $[RhCl(C_2H_4)_2]_2$ (3.1 mg, 16 μmol Rh) and PPh_3 (4.2 mg, 16 μmol) in CH_2Cl_2 (0.60 mL) was stirred for 5 min at room temperature and MeCN (10.5 μL, 0.201 mmol) was added to it with additional CH_2Cl_2 (0.10 mL). A mixture of compound **1** (0.200 mmol) and $NaBAr^F_4$ (28.4 mg, 32.0 μmol) in CH_2Cl_2 (0.60 mL) was then added with the aid of additional CH_2Cl_2 (0.70 mL). The reaction mixture was stirred for 16 h at 40 °C, and this was directly passed through a pad of Celite with EtOAc. After removal of the solvent under vacuum, the residue was purified by silica gel preparative TLC to afford compound **3**.

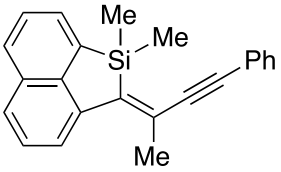


Table 1, Entry 1 (compound 3a). Pale yellow solid. 82% yield.

^{1}H NMR ($CDCl_3$): 7.85 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.78 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.75 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 7.72 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.58-7.49 (m, 4H), 7.42-7.32 (m, 3H), 2.55 (s, 3H), 0.62 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 145.6, 143.2, 141.7, 138.8, 132.5, 131.4, 129.8, 128.6, 128.3, 128.1, 127.5, 126.6, 126.5, 123.64, 123.60, 95.8, 91.2, 23.3, –2.2. HRMS (ESI-TOF) calcd for $C_{23}H_{20}SiCs$ (M+Cs$^+$) 457.0389, found 457.0399.

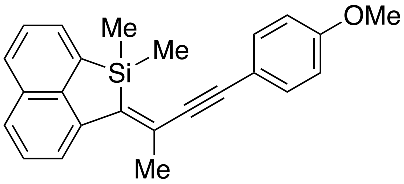


Table 1, Entry 2 (compound 3b). The reaction was conducted at 0.05 M substrate concentration (in 4.0 mL of CH_2Cl_2). Pale yellow solid. 90% yield (*Z*/*E* = 98/2).

^{1}H NMR ($CDCl_3$): 7.84 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.76 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.74 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 7.71 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.57-7.49 (m, 2H), 7.46 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 6.91 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.85 (s, 3H), 2.53 (s, 3H), 0.60 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 159.8, 144.6, 143.2, 141.9, 138.9, 132.9, 132.5, 129.8, 128.0, 127.9, 126.64, 126.62, 126.3, 123.4, 115.8, 114.3, 94.6, 91.3, 55.5, 23.3, –2.1. HRMS (ESI-TOF) calcd for $C_{24}H_{22}OSiCs$ (M+Cs$^+$) 487.0494, found 487.0489.

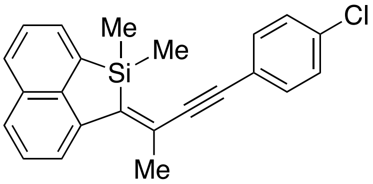


Table 1, Entry 3 (compound 3c). The reaction time was 1 h. Pale yellow solid. 93% yield.

^{1}H NMR ($CDCl_3$): δ 7.85 (dd, $^3J_{HH}$ = 8.1 Hz and $^4J_{HH}$ = 0.9 Hz, 1H), 7.78 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.77-7.72 (m, 2H), 7.58-7.50 (m, 2H), 7.46-7.42 (m, 2H), 7.38-7.33 (m, 2H), 2.53 (s, 3H), 0.59 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 146.2, 143.2, 141.6, 138.6, 134.3, 132.54, 132.49, 129.9, 129.0, 128.1, 127.1, 126.70, 126.69, 126.6, 123.7, 122.2, 96.7, 90.0, 23.2, –2.2. Anal. Calcd for $C_{23}H_{19}ClSi$: C, 76.96; H, 5.34. Found: C, 76.50; H, 5.56.

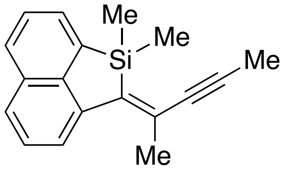


Table 1, Entry 4 (compound 3d). The reaction was conducted at 80 °C in toluene. White solid. 82% yield.

^{1}H NMR (CDCl$_3$): δ 7.82 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.74-7.66 (m, 3H), 7.56-7.47 (m, 2H), 2.41 (s, 3H), 2.09 (s, 3H), 0.52 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 143.6, 143.1, 141.8, 139.1, 132.5, 129.6, 128.3, 128.0, 126.6, 126.5, 126.0, 123.2, 87.9, 86.2, 23.2, 4.6, –2.4. Anal. Calcd for $C_{18}H_{18}Si$: C, 82.38; H, 6.91. Found: C, 82.20; H, 6.91.

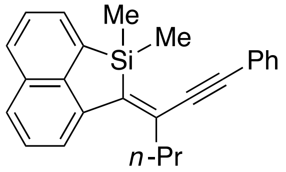


Table 1, Entry 5 (compound 3e). The reaction time was 2 h. Pale yellow solid. 84% yield.

^{1}H NMR (CDCl$_3$): 7.89 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H), 7.83-7.79 (m, 2H), 7.77 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H), 7.62-7.55 (m, 4H), 7.46-7.36 (m, 3H), 2.92 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H), 1.98 (sext, $^{3}J_{HH}$ = 7.5 Hz, 2H), 1.20 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H), 0.69 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 145.2, 143.3, 141.2, 139.0, 133.5, 132.5, 131.4, 129.8, 128.6, 128.3, 128.0, 126.64, 126.59, 126.57, 123.8, 123.4, 94.5, 92.5, 37.1, 21.5, 14.4, –2.0. Anal. Calcd for $C_{25}H_{24}Si$: C, 85.17; H, 6.86. Found: C, 84.91; H, 7.05.

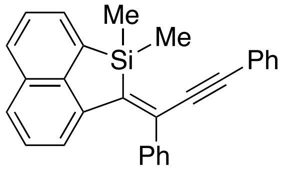


Table 1, Entry 6 (compound 3f). The reaction was conducted at 0.05 M substrate concentration (in 4.0 mL of CH_2Cl_2) with P(4-MeOC$_6$H$_4$)$_3$ instead of PPh$_3$. Yellow solid. 82% yield (*Z*/*E* = 94/6).

^{1}H NMR (CDCl$_3$): 7.81 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H), 7.78 (dd, $^{3}J_{HH}$ = 6.6 Hz and $^{4}J_{HH}$ = 0.9 Hz, 1H), 7.62 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H), 7.57-7.51 (m, 3H), 7.50-7.39 (m, 5H), 7.38-7.30 (m, 3H), 7.13 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 6.89 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H), 0.72 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 146.8, 143.3, 140.7, 140.0, 138.1, 132.5, 131.5, 131.3, 129.9, 129.3, 128.6, 128.44, 128.41, 128.14, 128.09, 127.0, 126.6, 126.3, 123.6, 123.1, 94.1, 93.1, –2.1. HRMS (ESI-TOF) calcd for $C_{28}H_{22}SiCs$ (M+Cs^{+}) 519.0545, found 519.0530.

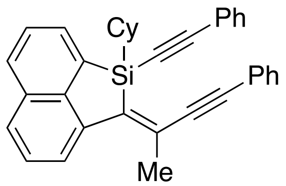


Table 1, Entry 7 (compound 3g). The reaction time was 2 h. Pale yellow solid. 93% yield.

^{1}H NMR (CDCl$_3$): 7.95-7.86 (m, 2H), 7.79 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H), 7.73 (d, $^{3}J_{HH}$ = 8.1 Hz, 1H), 7.67-7.57 (m, 3H), 7.53 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.38-7.29 (m, 5H), 7.28-7.16 (m, 3H), 2.58 (s, 3H), 2.31-2.19 (m, 1H), 1.86-1.48 (m, 6H), 1.35-1.06 (m, 3H), 1.01-0.85 (m, 1H). ^{13}C NMR (CDCl$_3$): δ 144.0, 141.5, 141.1, 133.8, 132.5, 132.3, 131.7, 131.4, 129.3, 128.7, 128.6, 128.5, 128.3, 128.2, 126.8, 126.60, 126.57, 123.9, 123.6, 123.1, 107.8, 96.3, 92.7, 88.6, 28.3, 27.8, 27.6, 27.2, 26.8, 25.3, 23.4. HRMS (ESI-TOF) calcd for $C_{35}H_{30}SiCs$ (M+Cs$^+$) 611.1171, found 611.1169.

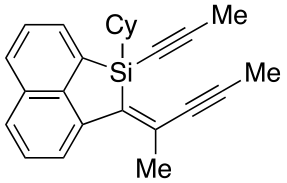


Table 1, Entry 8 (compound 3h). The reaction was conducted for 1 h at 0.05 M substrate concentration (in 4.0 mL of CH_2Cl_2). Yellow solid. 82% yield.

^{1}H NMR ($CDCl_3$): 7.87-7.79 (m, 2H), 7.68 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.67 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.54 (dd, $^3J_{HH}$ = 8.1 and 6.8 Hz, 1H), 7.47 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 2.42 (s, 3H), 2.12 (s, 3H), 2.11-2.02 (m, 1H), 1.94 (s, 3H), 1.85-1.73 (m, 1H), 1.72-1.10 (m, 8H), 0.98-0.82 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 143.7, 141.5, 139.7, 134.6, 132.4, 131.0, 129.7, 128.3, 126.6, 126.4, 126.0, 123.2, 105.3, 89.4, 86.6, 78.0, 28.3, 28.1, 27.5, 27.3, 26.9, 25.3, 23.3, 5.5, 4.9. HRMS (ESI-TOF) calcd for $C_{25}H_{26}SiCs$ (M+Cs$^+$) 487.0858, found 487.0866.

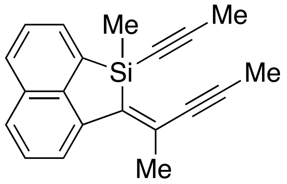
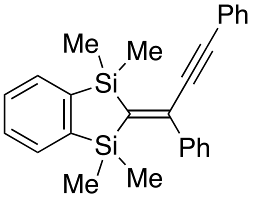


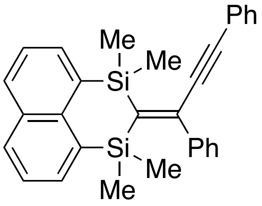
Table 1, Entry 9 (compound 3i). The reaction was conducted at 0.05 M substrate concentration (in 4.0 mL of CH_2Cl_2) with $P(4\text{-}MeOC_6H_4)_3$ instead of PPh_3. White solid. 73% yield.

^{1}H NMR ($CDCl_3$): 7.86-7.81 (m, 2H), 7.72-7.66 (m, 2H), 7.55 (dd, $^3J_{HH}$ = 8.0 and 6.8 Hz, 1H), 7.48 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 2.42 (s, 3H), 2.13 (s, 3H), 1.91 (s, 3H), 0.65 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 143.2, 141.1, 140.8, 136.0, 132.5, 130.2, 129.8, 128.5, 126.7, 126.6, 126.1, 123.3, 104.9, 89.6, 86.3, 79.6, 23.2, 5.4, 4.7, –2.0. HRMS (ESI-TOF) calcd for $C_{20}H_{18}SiCs$ (M+Cs$^+$) 419.0232, found 419.0212.



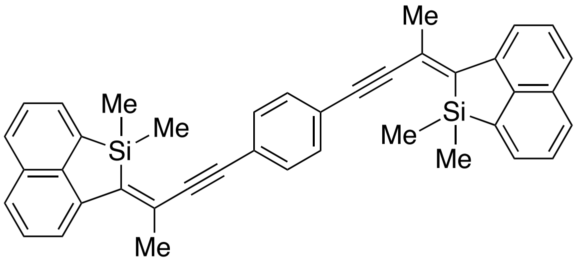
Equation 3 (compound 3j). Yellow oil. 80% yield.

^{1}H NMR ($CDCl_3$): 7.67-7.62 (m, 1H), 7.55-7.46 (m, 5H), 7.43-7.33 (m, 8H), 0.59 (s, 6H), 0.09 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 153.0, 149.6, 149.1, 147.2, 144.0, 132.3, 132.2, 131.6, 129.0, 128.9, 128.7, 128.6, 128.2, 128.1, 127.7, 123.4, 93.3, 92.7, 1.0, –0.7. HRMS (ESI-TOF) calcd for $C_{26}H_{26}Si_2Cs$ (M+Cs$^+$) 527.0628, found 527.0623.



Equation 4 (compound 3k). The reaction time was 2 h. White solid. 95% yield.

^{1}H NMR (CDCl$_3$): 7.90-7.82 (m, 3H), 7.66 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 7.53 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.50-7.38 (m, 8H), 7.38-7.30 (m, 3H), 0.71 (s, 6H), 0.01 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 149.0, 147.7, 144.4, 140.8, 139.5, 139.1, 133.9, 133.4, 133.1, 131.5, 130.4, 130.3, 128.7, 128.5, 128.3, 128.0, 125.10, 125.07, 123.4, 96.8, 93.1, 1.2, 0.5. HRMS (ESI-TOF) calcd for $C_{20}H_{28}Si_2Cs$ (M+Cs$^+$) 577.0784, found 577.0784.



Procedure for Equation 5.

A solution of [RhCl(C$_2$H$_4$)$_2$]$_2$ (1.5 mg, 7.7 μmol Rh) and PPh$_3$ (2.0 mg, 7.6 μmol) in CH$_2$Cl$_2$ (0.60 mL) was stirred for 5 min at room temperature and MeCN (5.2 μL, 0.10 mmol) was added to it with additional CH$_2$Cl$_2$ (0.10 mL). A mixture of compound **4** (57.0 mg, 99.8 μmol) and NaBAr$^F_4$ (14.1 mg, 15.9 μmol) in CH$_2$Cl$_2$ (0.60 mL) was then added with the aid of additional CH$_2$Cl$_2$ (0.70 mL). The reaction mixture was stirred for 16 h at 40 °C, and the precipitates that formed were collected by filtration. The solid was washed with CH$_2$Cl$_2$ to afford compound **5** as a yellow solid (44.2 mg, 77.4 μmol; 78% yield).

^{1}H NMR (CDCl$_3$): 7.86 (dd, $^3J_{HH}$ = 8.1 Hz and $^4J_{HH}$ = 0.9 Hz, 2H), 7.79 (d, $^3J_{HH}$ = 7.4 Hz, 2H), 7.76 (dd, $^3J_{HH}$ = 6.6 Hz and $^4J_{HH}$ = 1.1 Hz, 2H), 7.74 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.59-7.49 (m, 8H), 2.56 (s, 6H), 0.63 (s, 12H). ^{13}C NMR (CDCl$_3$): δ 146.3, 143.3, 141.7, 138.7, 132.5, 131.4, 129.9, 128.1, 127.2, 126.70, 126.66, 123.7, 123.4, 97.8, 91.0, 23.3, –2.1. HRMS (ESI-TOF) calcd for $C_{40}H_{34}Si_2Cs$ (M+Cs$^+$) 703.1254, found 703.1220.

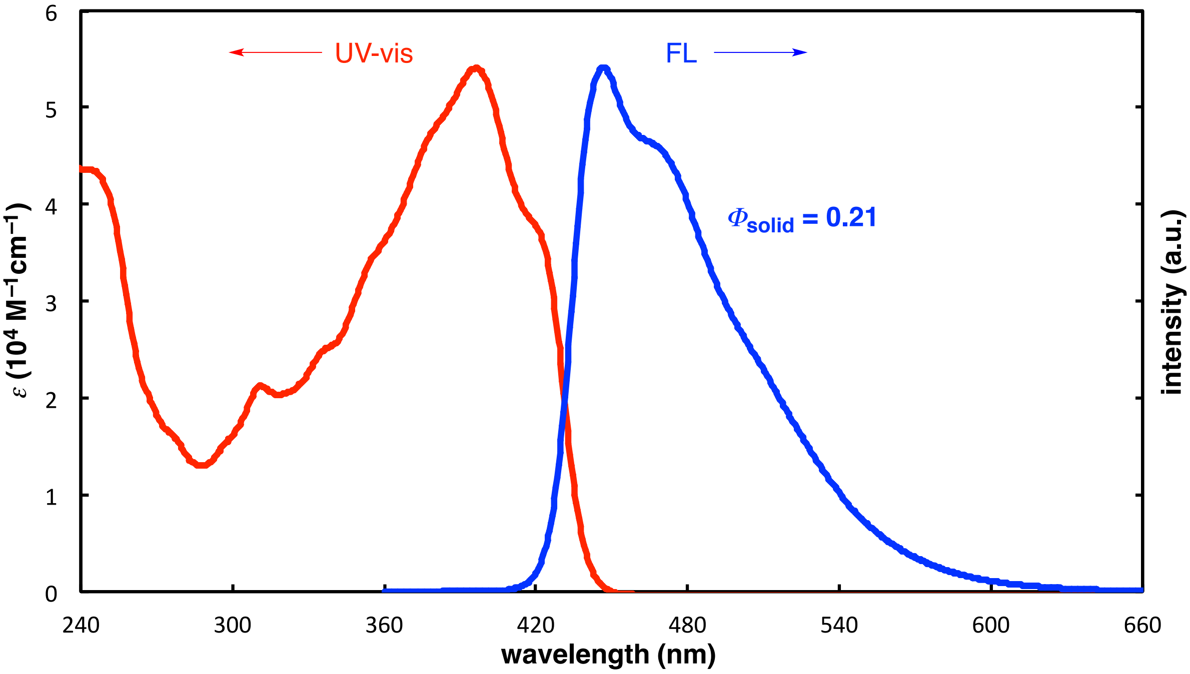
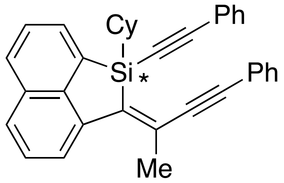
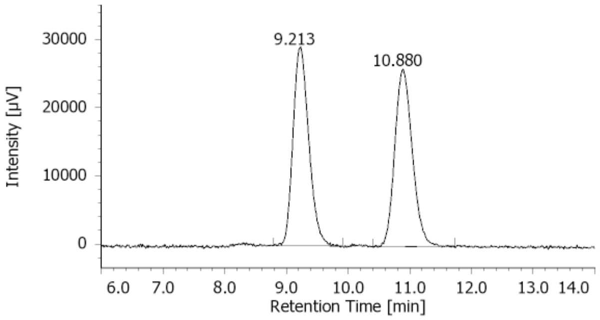


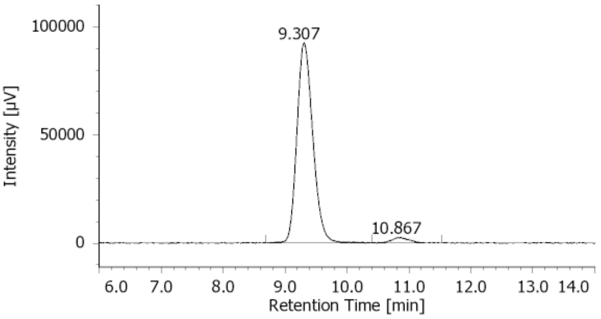
Figure S1. UV-vis (red line; at 1.75 x 10^{-5} M) and fluorescence spectra (blue line; at 1.75 x 10^{-5} M; excited at 350 nm) of compound **5** in CH$_2$Cl$_2$ at 25 °C.



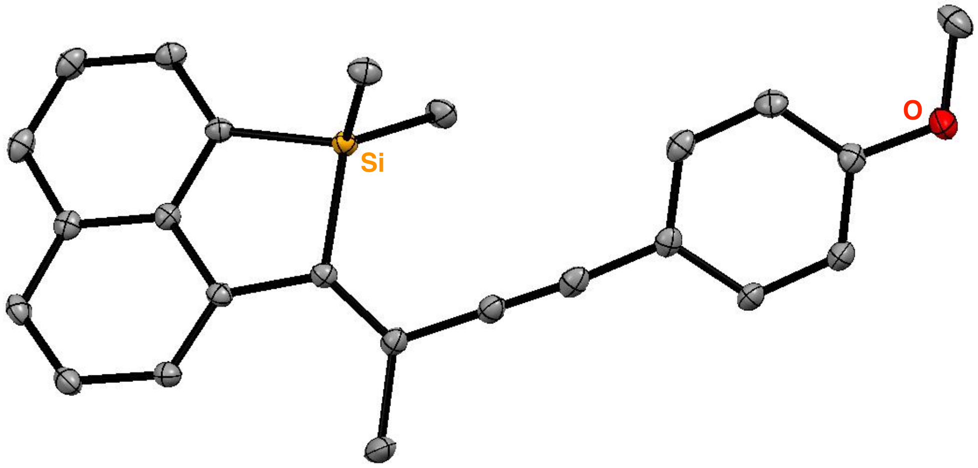
Procedure for Table 3, Entry 7.

A solution of $[RhCl(C_2H_4)_2]_2$ (1.4 mg, 7.2 μmol Rh) and (*R*,*S*,*S*)-phosphoramidite (3.9 mg, 7.3 μmol) in CH_2Cl_2 (0.50 mL) was stirred for 5 min at room temperature and this was diluted with CH_2Cl_2 (1.40 mL). Compound **1g** (34.5 mg, 72.1 μmol) and $NaBAr^F_4$ (12.8 mg, 14.4 μmol) were added to it with additional CH_2Cl_2 (0.50 mL) and the mixture was stirred for 12 h at 40 °C. This was then directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with EtOAc/hexane = 1/200 to afford compound **3g** as a pale yellow oil (20.3 mg, 42.4 μmol; 59% yield). The ee was determined on a Daicel Chiralcel OD-H column with hexane/2-propanol = 98/2, flow = 0.6 mL/min. Retention times: 9.3 min [major enantiomer], 10.9 min [minor enantiomer]. 94% ee. $[\alpha]^{22}_D$ +296 (*c* 0.92, $CHCl_3$).


racemate


94.1% ee

IV. X-ray Crystal Structure of Compound 3b



Data Collection

A colorless MeOH solution of **3b** was prepared at room temperature. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent.

A colorless block crystal of $C_{24}H_{22}OSi$ having approximate dimensions of 0.300 x 0.140 x 0.140 mm was mounted on a glass fiber. All measurements were made on a Rigaku Saturn724 diffractometer using graphite monochromated Mo-Kα radiation.

The crystal-to-detector distance was 44.73 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 8.624(4) Å
b = 15.417(7) Å   β = 104.681(7)°
c = 7.309(3) Å
V = 940.1(7) $Å^3$

For Z = 2 and F.W. = 354.52, the calculated density is 1.252 g/cm^3. Based on the reflection conditions of:

h0l: l ± 2n

packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be:

Pc (#7)

The data were collected at a temperature of –180 ± 1 °C to a maximum 2θ value of 63.2°. A total of 720 oscillation images were collected. A sweep of data was done using ω scans from –110.0 to 70.0° in 0.50° step, at χ = 45.0° and φ = 0.0°. The exposure rate was 2.0 [sec./°]. The detector swing angle was –19.88°. A second sweep was performed using ω scans from –110.0 to 70.0° in 0.50° step, at χ = 45.0° and φ = 90.0°. The exposure rate was 2.0 [sec./°]. The detector swing angle was –19.88°. The crystal-to-detector distance was 44.73 mm. Readout was performed in the 0.141 mm pixel mode.

Data Reduction

Of the 8691 reflections were collected, where 4784 were unique (R_{int} = 0.0403); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).[7]

The linear absorption coefficient, μ, for Mo-Kα radiation is 1.343 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.856 to 0.981. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[8] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[9] on F^2 was based on 4784 observed reflections and 235 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \,||Fo| - |Fc|| / \Sigma\, |Fo| = 0.0413$$

$$wR2 = [\Sigma\,(\,w\,(Fo^2 - Fc^2)^2\,) / \Sigma\, w\,(Fo^2)^2]^{1/2} = 0.1089$$

The goodness of fit[10] was 1.05. Unit weights were used. Plots of $\Sigma w(|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and –0.33 $e^-/Å^3$, respectively. The final Flack parameter[11] was 0.10(8), indicating that the present absolute structure is correct.[12]

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4.[13] Anomalous dispersion effects were included in Fcalc[14]; the values for Δf' and Δf" were those of Creagh and McAuley.[15] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[16] All calculations were performed

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[7] CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998–2014). Tokyo 196-8666, Japan.

[8] SHELXS97: Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.

[9] Least Squares function minimized: (SHELXL2013)

$\Sigma w(F_o^2 - F_c^2)^2$ where w = Least Squares weights.

[10] Goodness of fit is defined as:

$[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$

where: N_o = number of observations, N_v = number of variables

[11] Parsons, S.; Flack, H. *Acta Cryst.* **2004**, *A60*, s61.

[12] Flack, H. D.; Bernardinelli *J. Appl. Cryst.* **2000**, *33*, 114.

[13] International Tables for Crystallography, Vol.C (1992). Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, p. 572.

[14] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

[15] Creagh, D. C.; McAuley, W. J. "International Tables for Crystallography", Vol C (1992), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Boston, Table 4.2.6.8, p. 219.

[16] Creagh, D. C.; Hubbell, J. H. "International Tables for Crystallography", Vol C, (1992), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Boston, Table 4.2.4.3, p. 200.

using the CrystalStructure[17] crystallographic software package except for refinement, which was performed using SHELXL2013.[18]

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 1401151). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

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[17] CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (2000–2014). Tokyo 196-8666, Japan.

[18] SHELXL2013: Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112.

Experimental Details

A. Crystal Data

Empirical Formula	$C_{24}H_{22}OSi$
Formula Weight	354.52
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.300 X 0.140 X 0.140 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 8.624(4) Å b = 15.417(7) Å c = 7.309(3) Å β = 104.681(7) Å V = 940.1(7) Å^3
Space Group	Pc (#7)
Z value	2
D_{calc}	1.252 g/cm^3
F_{000}	376.00
μ(MoKα)	1.343 cm^{-1}

B. Intensity Measurements

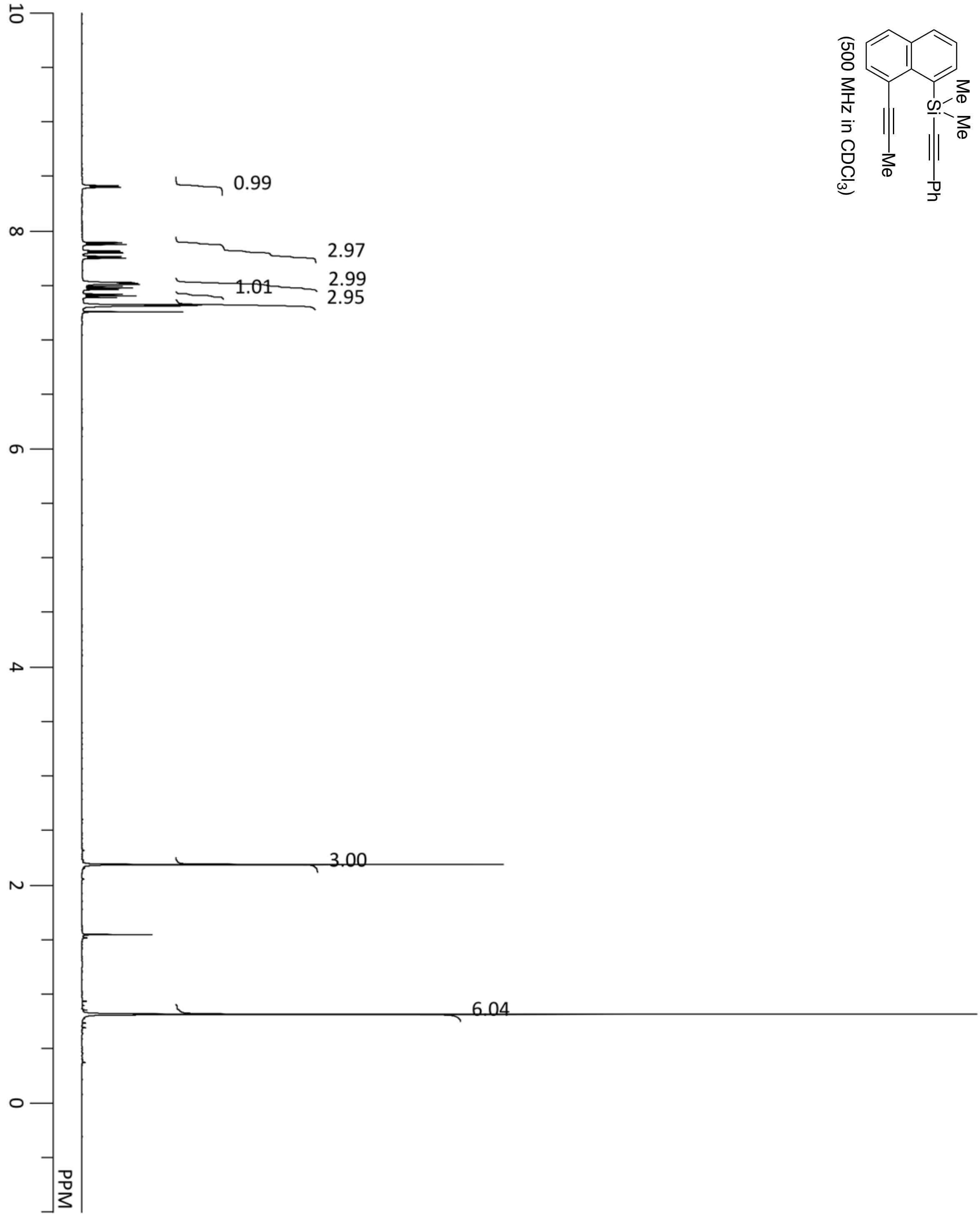
Diffractometer	Saturn724
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50 kV, 24 mA
Temperature	–180.0 °C
Detector Aperture	72.8 mm x 72.8 mm
Data Images	720 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	–110.0 - 70.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	–19.88°
ω oscillation Range (χ=45.0, ϕ=90.0)	–110.0 - 70.0°
Exposure Rate	2.0 sec./°
Detector Swing Angle	–19.88°
Detector Position	44.73 mm
Pixel Size	0.141 mm
$2\theta_{max}$	63.2°
No. of Reflections Measured	Total: 8691 Unique: 4784 (R_{int} = 0.0403) Parsons quotients (Flack x parameter): 1781
Corrections	Lorentz-polarization Absorption (trans. factors: 0.856 - 0.981)

C. Structure Solution and Refinement

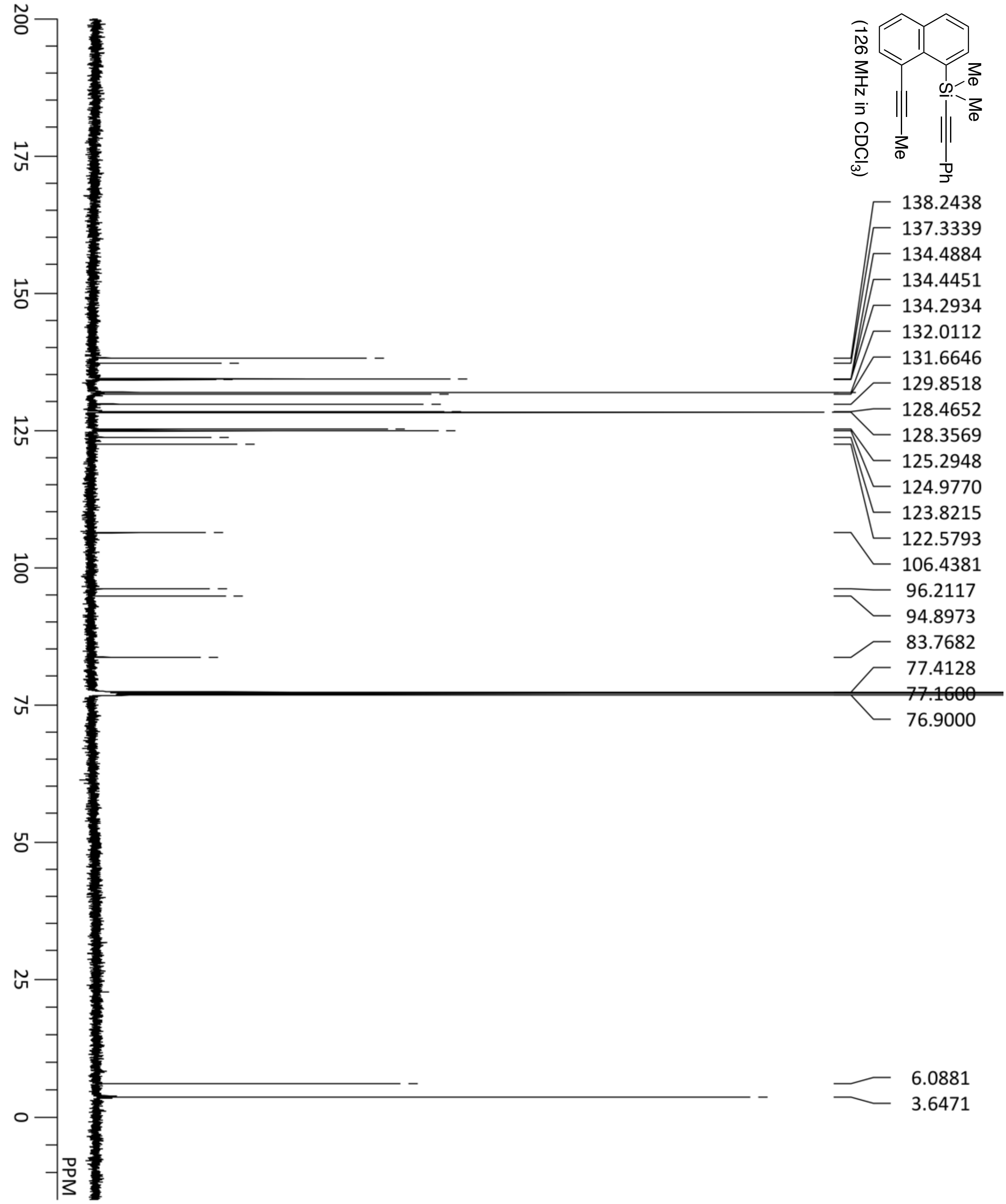
Structure Solution	Direct Methods (SHELXS97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 – Fc^2)^2$
Least Squares Weights	$w = 1/[\sigma^2(Fo^2)+(0.0625P)^2+0.2261P]$ where $P = (Max(Fo^2,0)+2Fc^2)/3$
$2\theta_{max}$ cutoff	63.2°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	4784
No. Variables	235
Reflection/Parameter Ratio	20.36
Residuals: R1 ($I>2.00\sigma(I)$)	0.0413
Residuals: R (All reflections)	0.0430
Residuals: wR2 (All reflections)	0.1089
Goodness of Fit Indicator	1.053
Flack parameter (Parsons' quotients = 1781)	0.10(8)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.29 $e^-/Å^3$
Minimum peak in Final Diff. Map	–0.33 $e^-/Å^3$

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

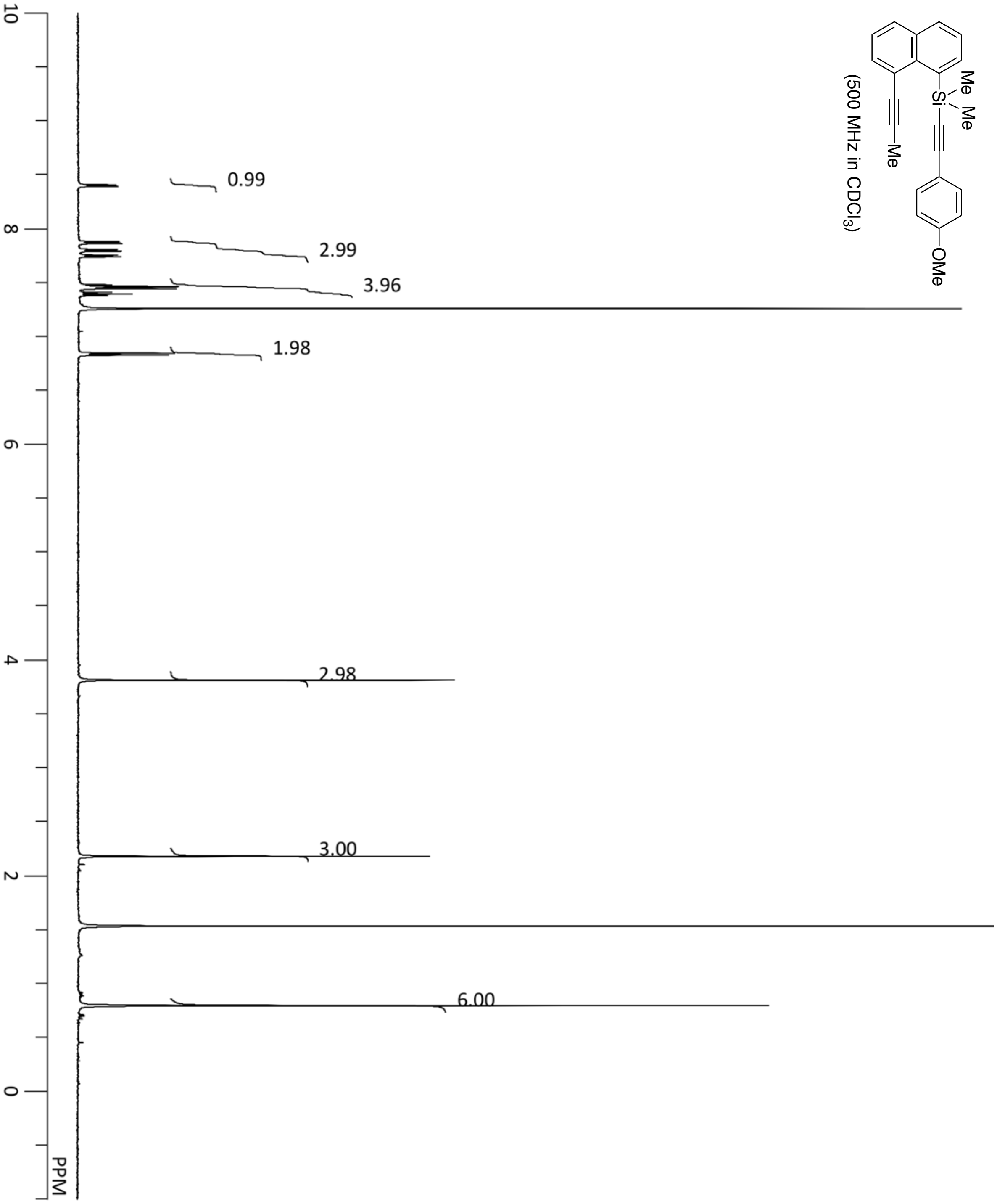
compound **1a**



compound **1a**

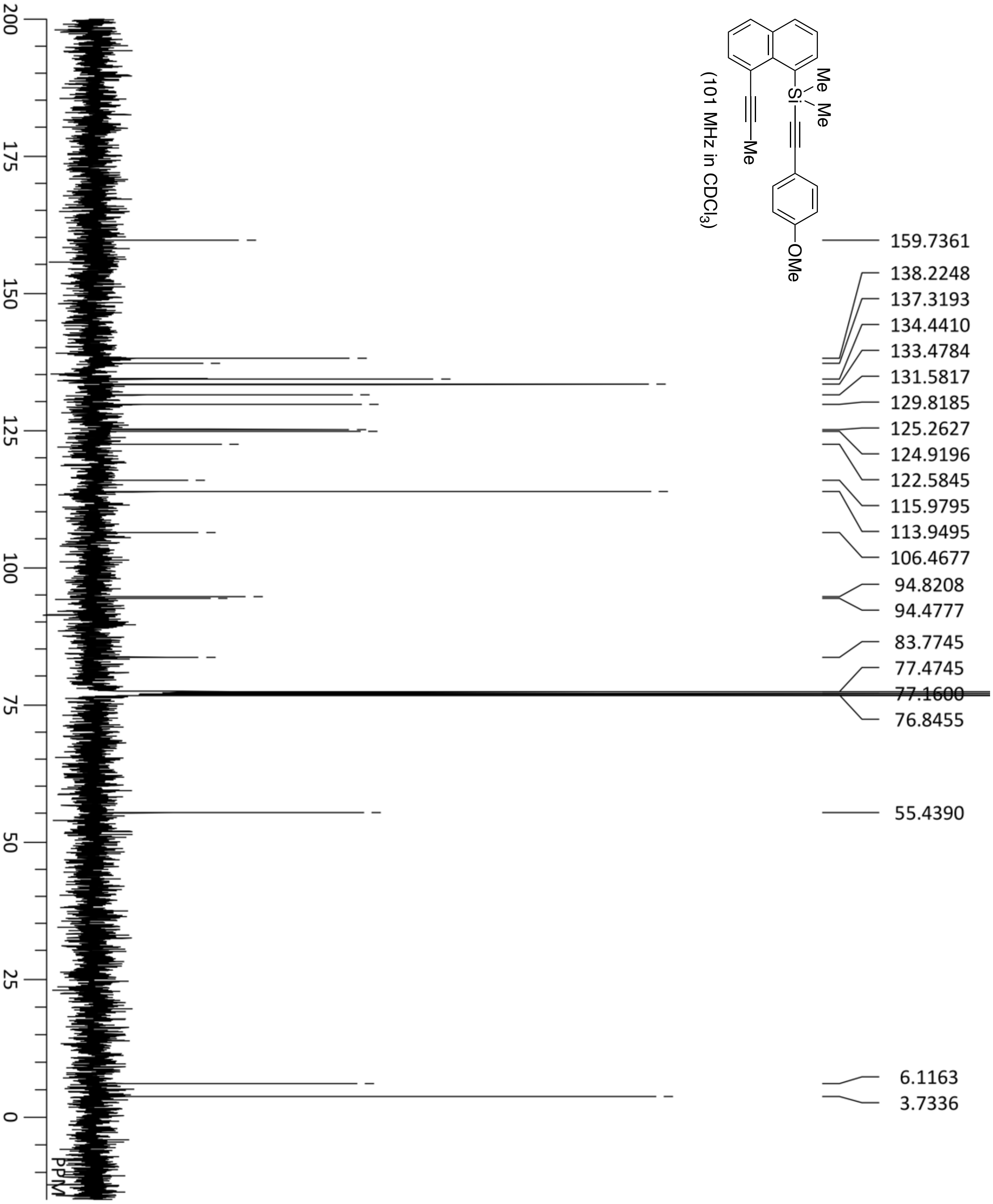

(126 MHz in CDCl$_3$)
Me
Me
Si
Ph
Me
138.2438
137.3339
134.4884
134.4451
134.2934
132.0112
131.6646
129.8518
128.4652
128.3569
125.2948
124.9770
123.8215
122.5793
106.4381
96.2117
94.8973
83.7682
77.4128
77.1600
76.9000
6.0881
3.6471
200
175
150
125
100
75
50
25
0
PPM

compound **1b**

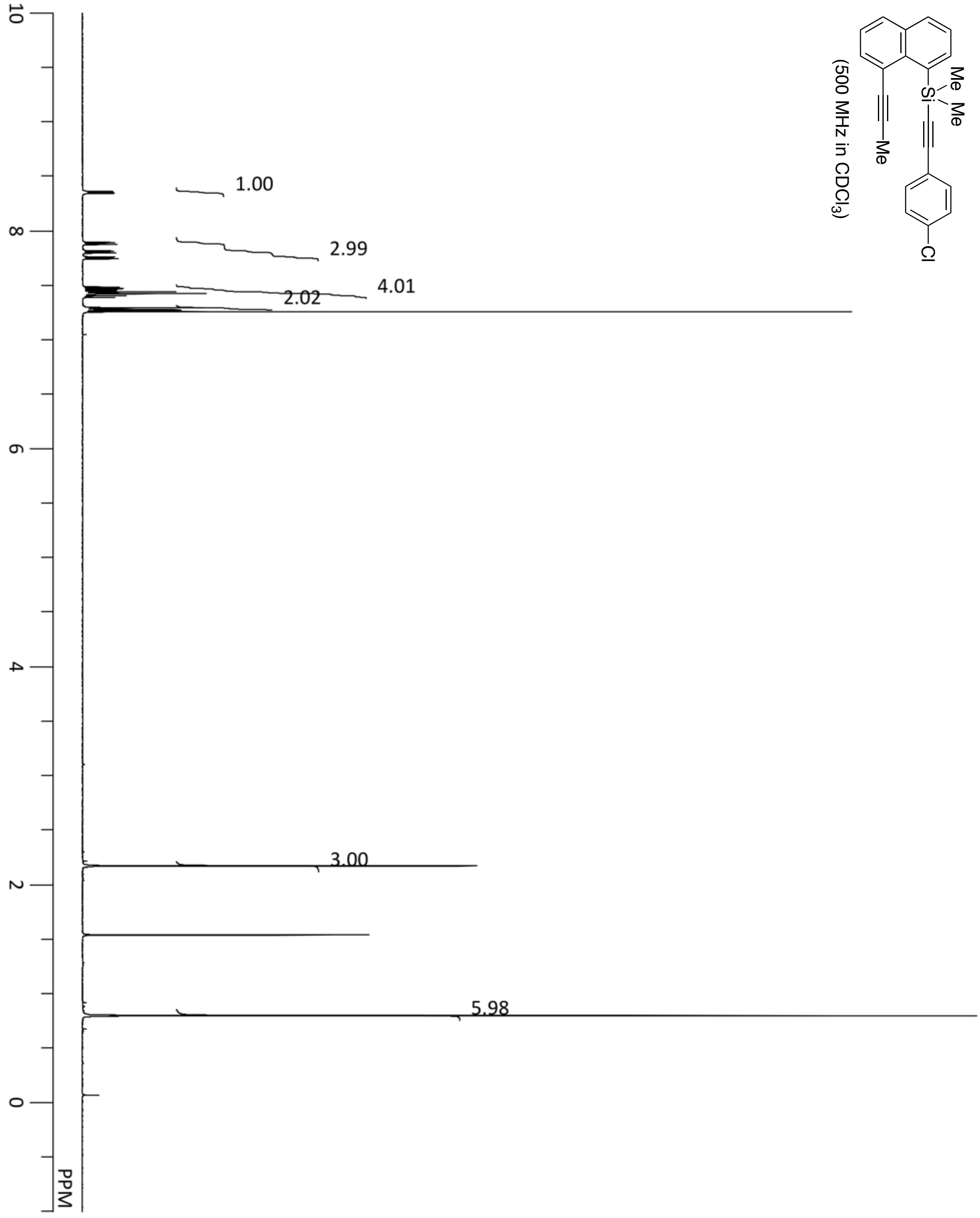


(500 MHz in CDCl$_3$)
Me
Me
Si
Me
OMe
0.99
2.99
3.96
1.98
2.98
3.00
6.00
10
8
6
4
2
0
PPM

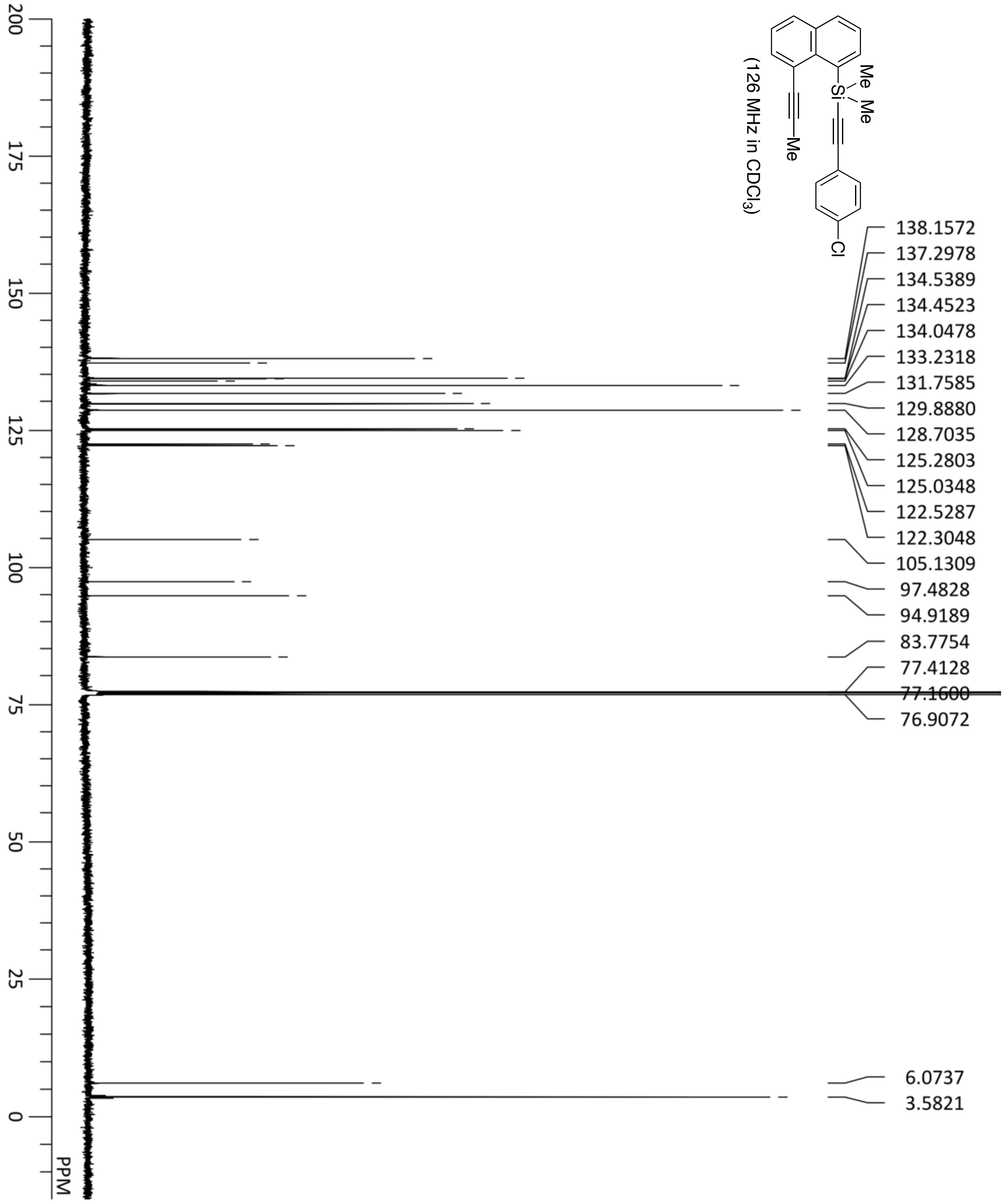
compound **1b**


200
175
150
125
100
75
50
25
0
PPM
Me
Si
Me
Me
OMe
(101 MHz in CDCl$_3$)
159.7361
138.2248
137.3193
134.4410
133.4784
131.5817
129.8185
125.2627
124.9196
122.5845
115.9795
113.9495
106.4677
94.8208
94.4777
83.7745
77.4745
77.1600
76.8455
55.4390
6.1163
3.7336

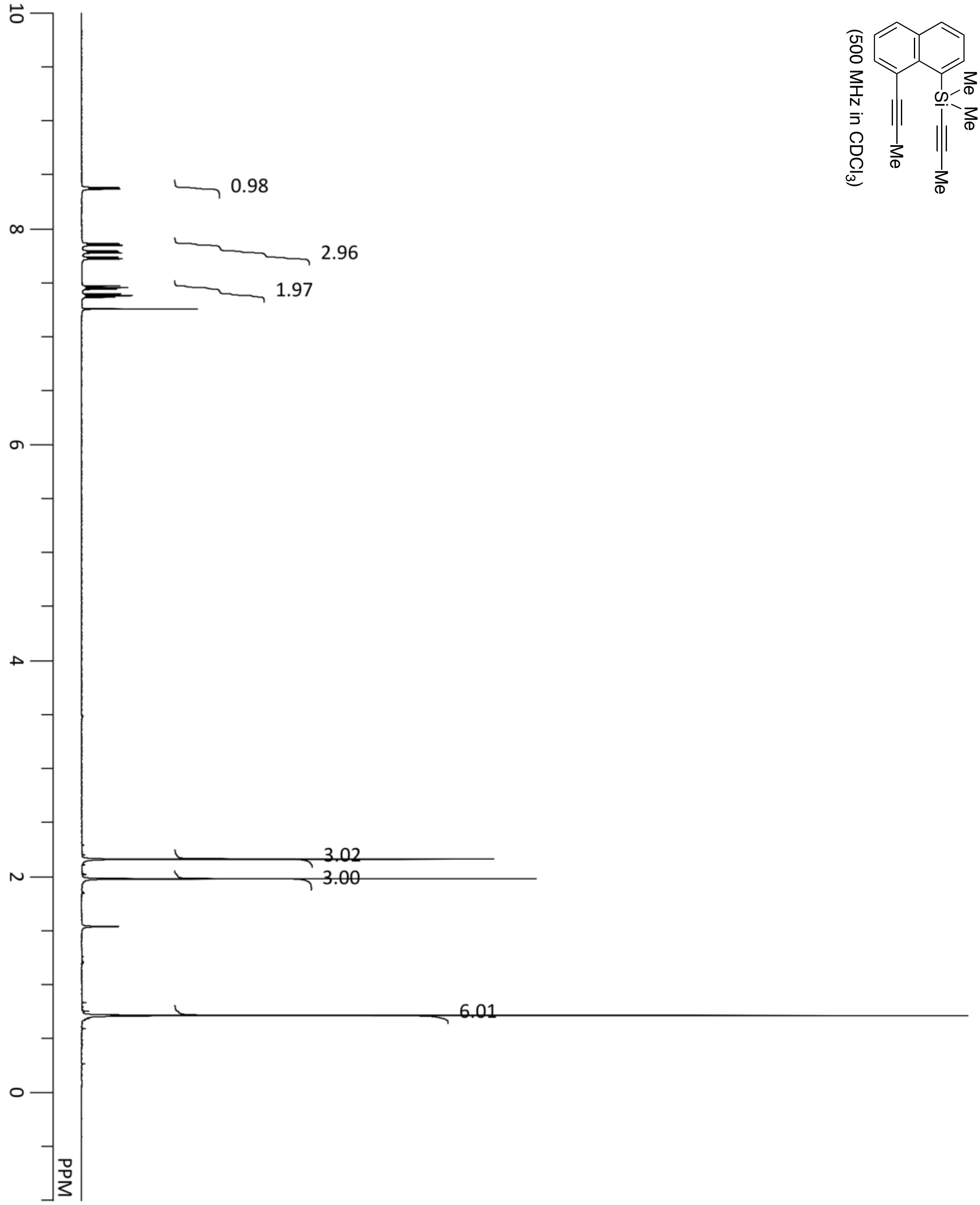
compound **1c**


(500 MHz in CDCl3)
Me
Me
Si
Me
Cl
1.00
2.99
4.01
2.02
3.00
5.98
10
8
6
4
2
0
PPM

compound **1c**

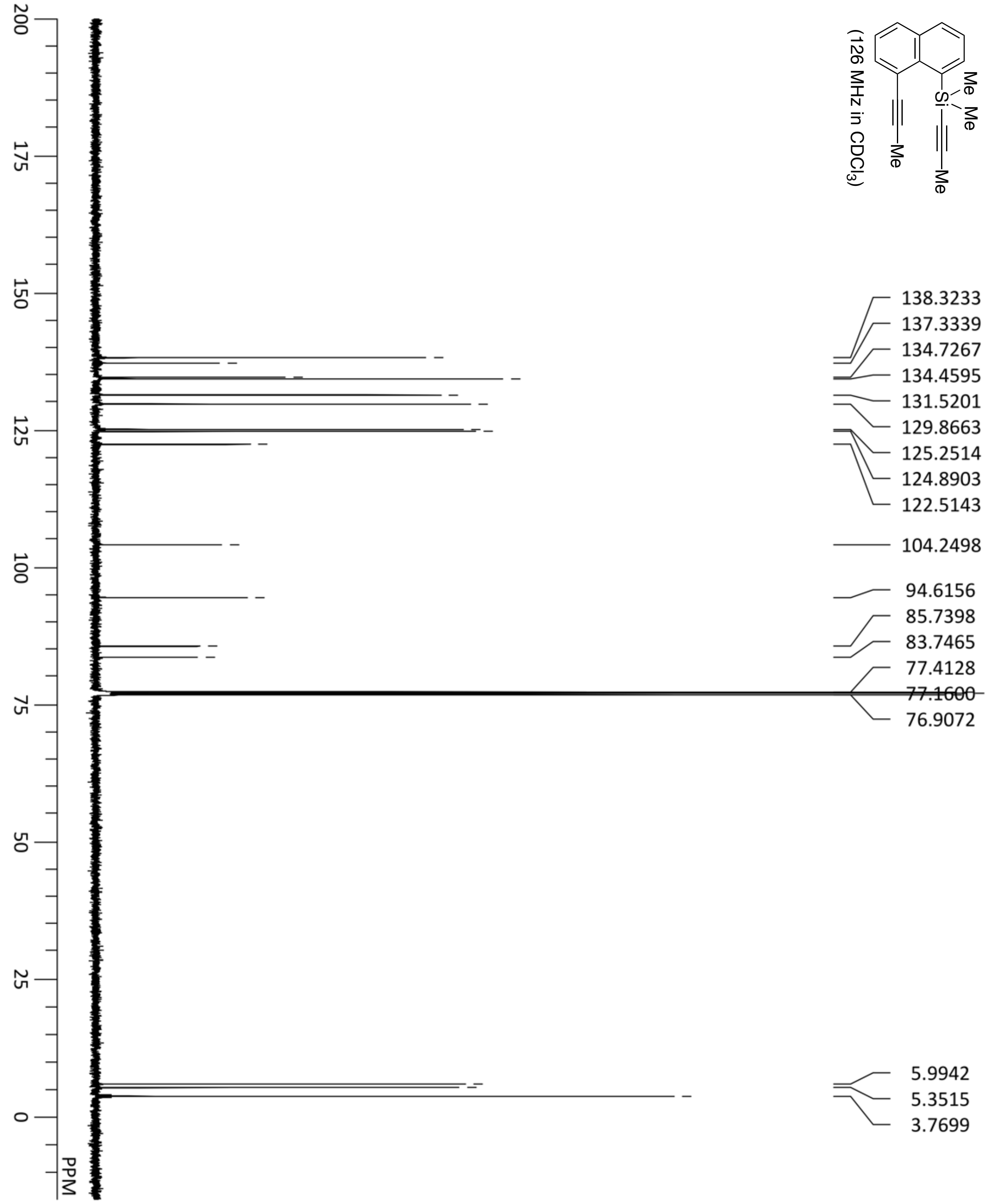

(126 MHz in CDCl$_3$)
Me
Si
Me
Me
Cl
138.1572
137.2978
134.5389
134.4523
134.0478
133.2318
131.7585
129.8880
128.7035
125.2803
125.0348
122.5287
122.3048
105.1309
97.4828
94.9189
83.7754
77.4128
77.1600
76.9072
6.0737
3.5821
200
175
150
125
100
75
50
25
0
PPM

compound **1d**



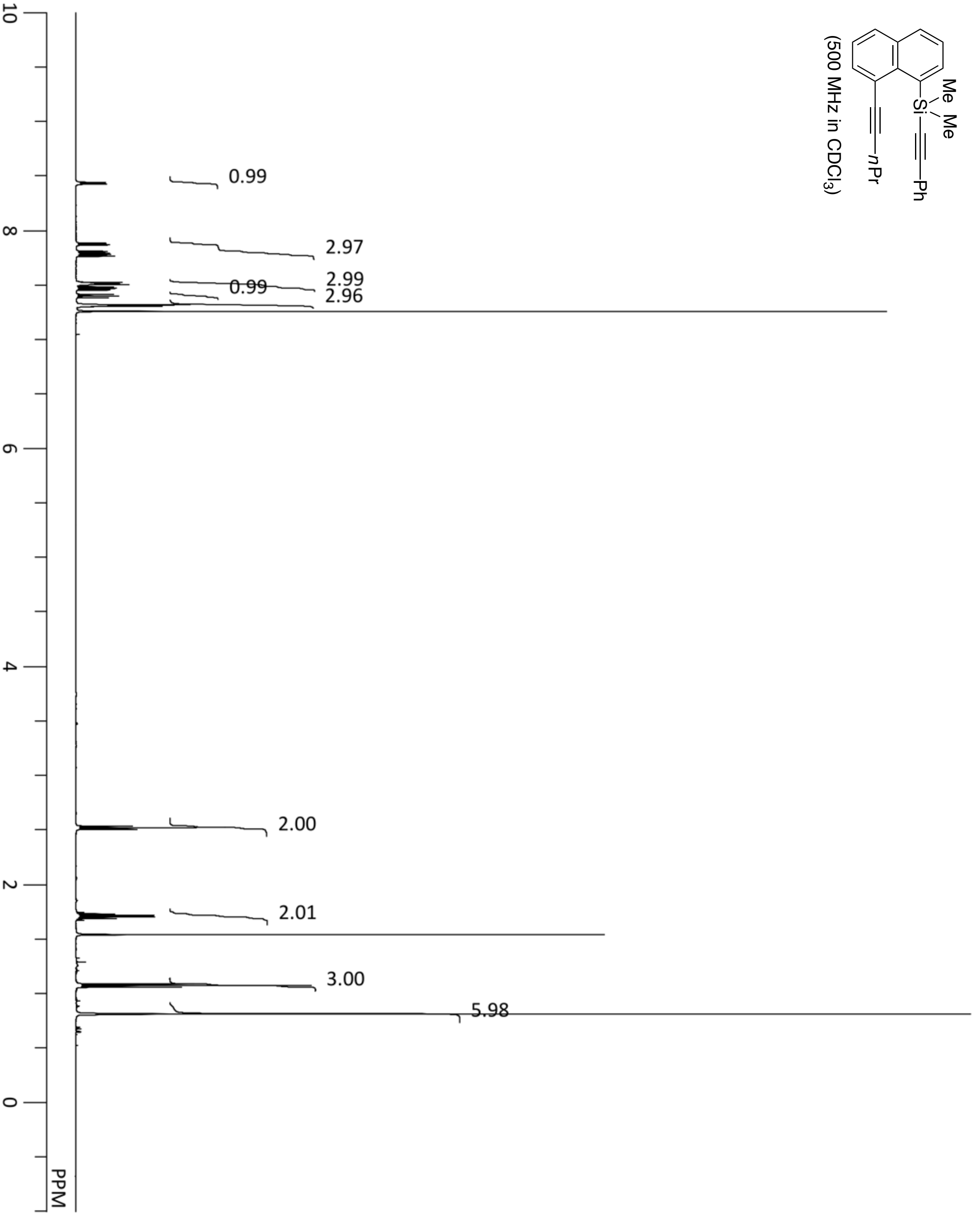
Me
Me
Si
Me
Me
(500 MHz in CDCl$_3$)
0.98
2.96
1.97
3.02
3.00
6.01
10
8
6
4
2
0
PPM

compound **1d**



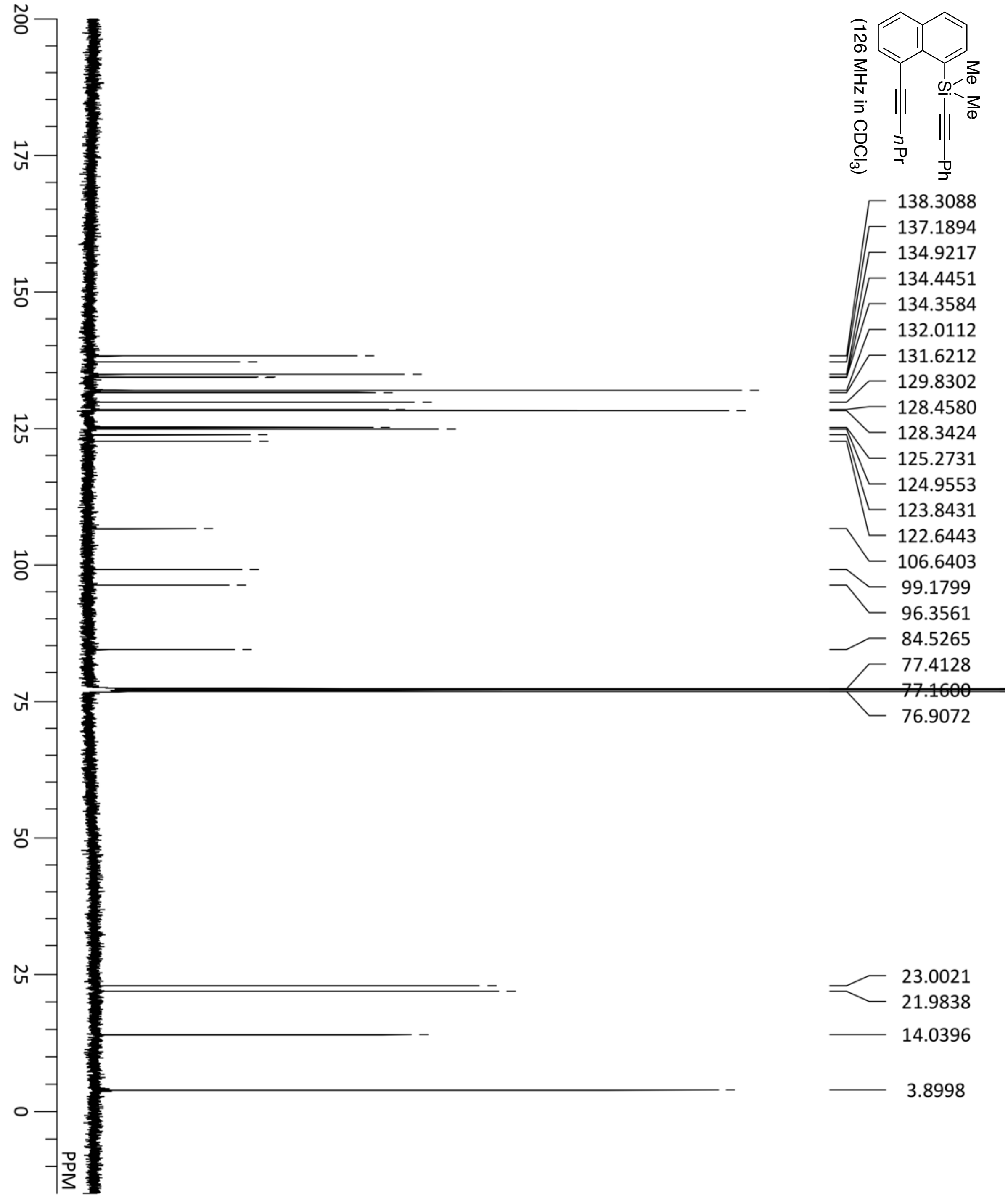
Me
Me
Si
Me
Me
(126 MHz in CDCl$_3$)
200
175
150
125
100
75
50
25
0
PPM
138.3233
137.3339
134.7267
134.4595
131.5201
129.8663
125.2514
124.8903
122.5143
104.2498
94.6156
85.7398
83.7465
77.4128
77.1600
76.9072
5.9942
5.3515
3.7699

compound **1e**

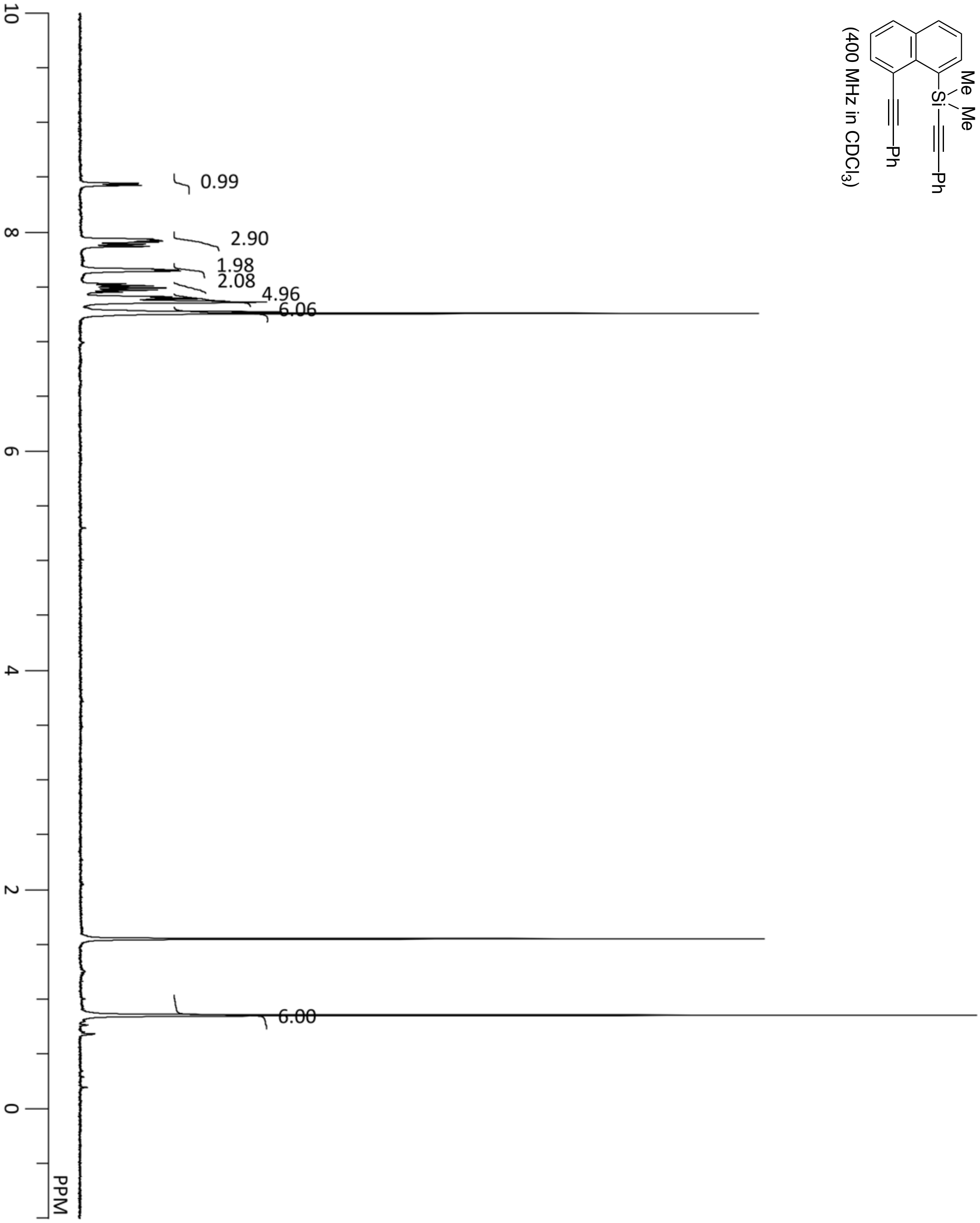


10
8
6
4
2
0
PPM
0.99
2.97
2.99
0.99
2.96
2.00
2.01
3.00
5.98
Me
Me
Si
Ph
*n*Pr
(500 MHz in CDCl$_3$)

compound **1e**

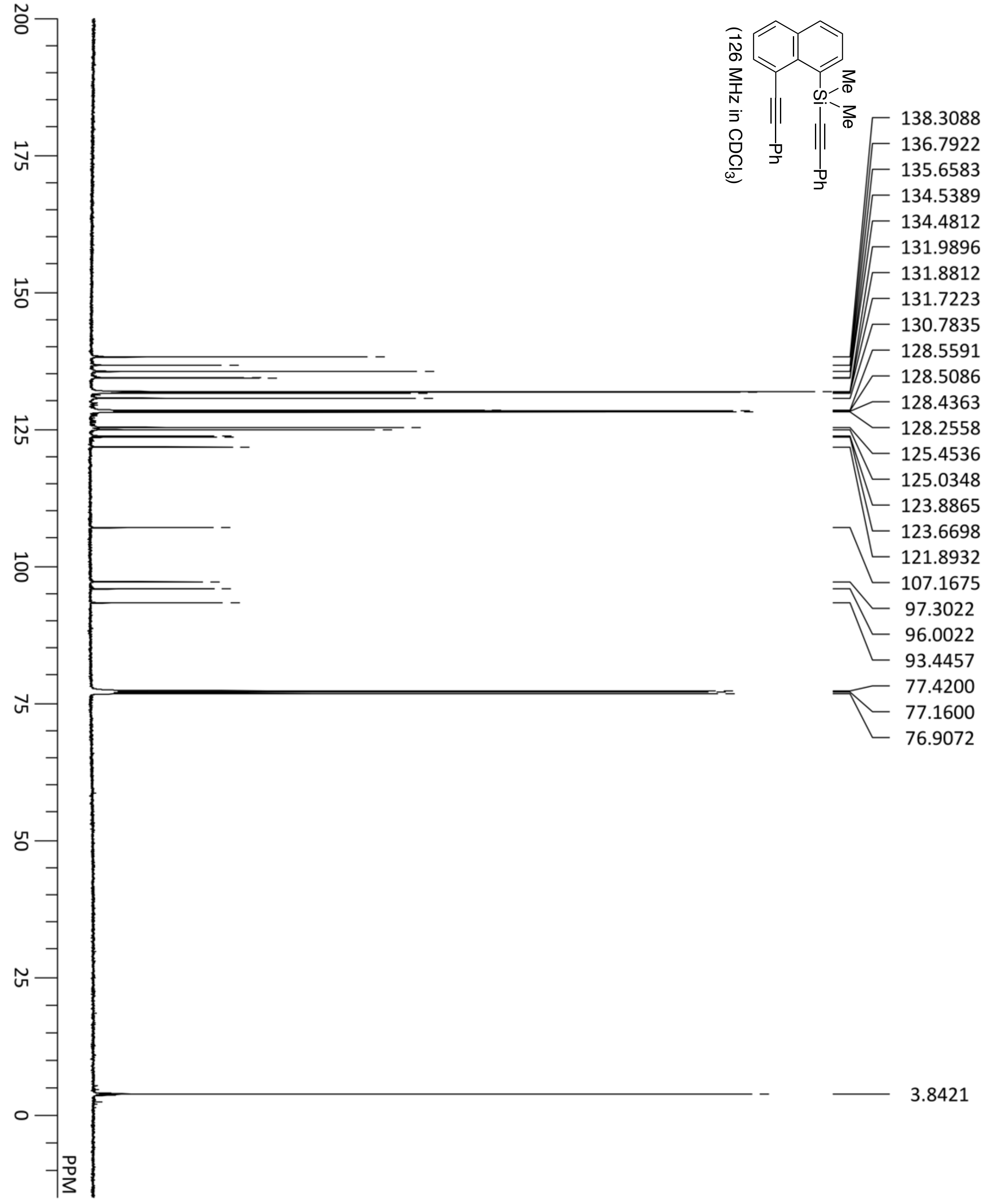

Me
Me
Si
Ph
nPr
(126 MHz in CDCl$_3$)
138.3088
137.1894
134.9217
134.4451
134.3584
132.0112
131.6212
129.8302
128.4580
128.3424
125.2731
124.9553
123.8431
122.6443
106.6403
99.1799
96.3561
84.5265
77.4128
77.1600
76.9072
23.0021
21.9838
14.0396
3.8998
200
175
150
125
100
75
50
25
0
PPM

compound **1f**

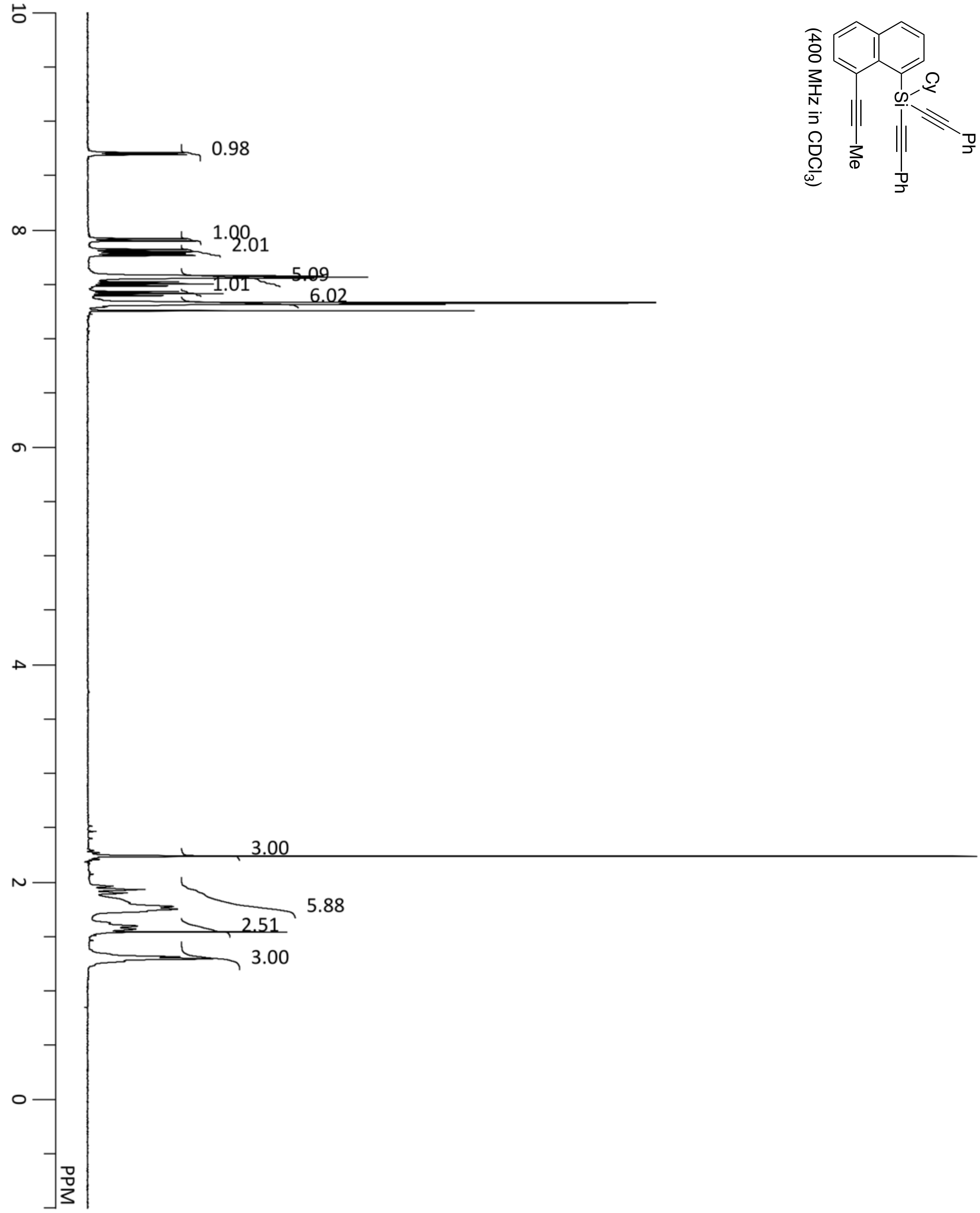


(400 MHz in $CDCl_3$)

compound **1f**

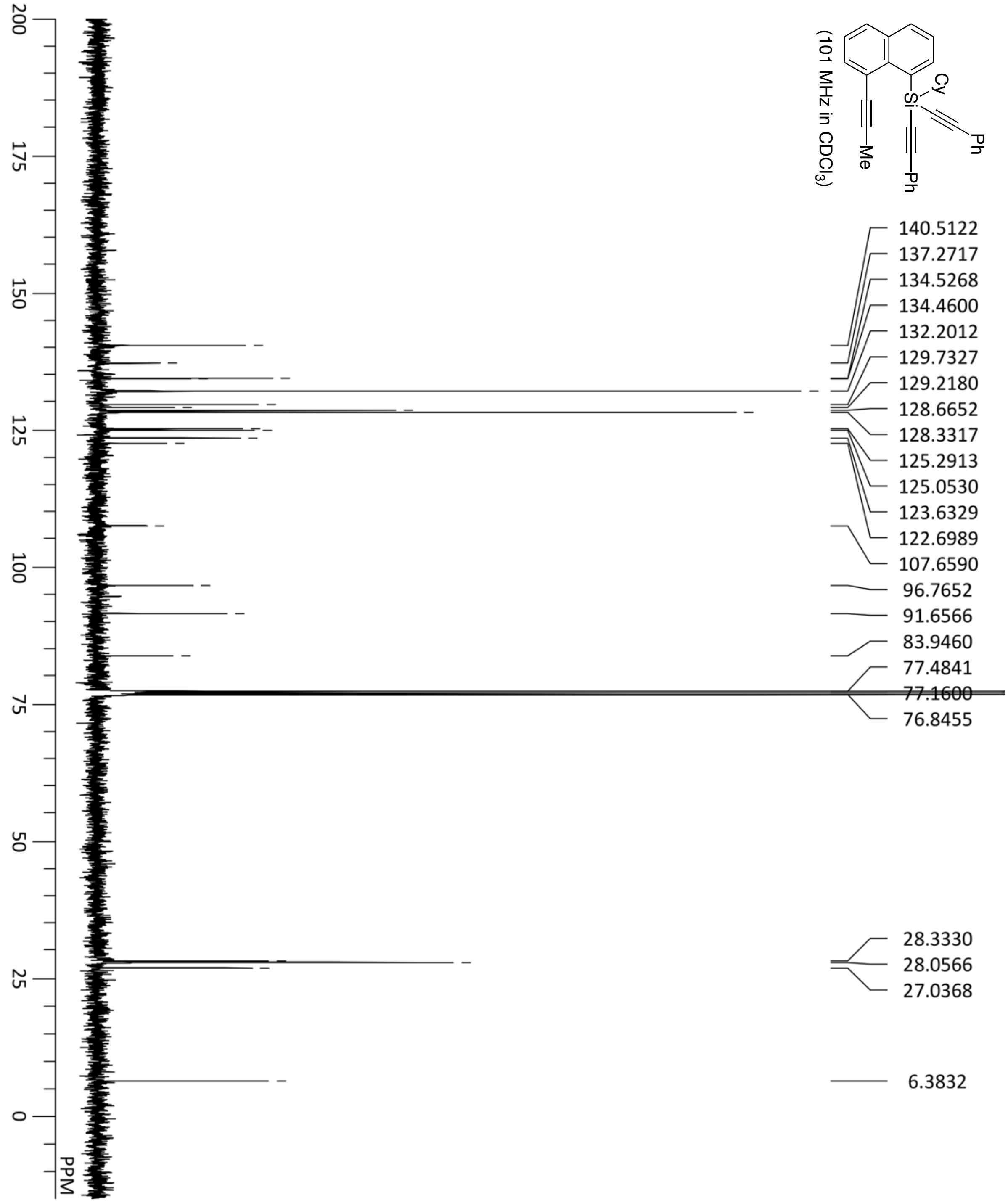

Me
Me
Si
Ph
Ph
(126 MHz in CDCl3)
200
175
150
125
100
75
50
25
0
PPM
138.3088
136.7922
135.6583
134.5389
134.4812
131.9896
131.8812
131.7223
130.7835
128.5591
128.5086
128.4363
128.2558
125.4536
125.0348
123.8865
123.6698
121.8932
107.1675
97.3022
96.0022
93.4457
77.4200
77.1600
76.9072
3.8421

compound **1g**

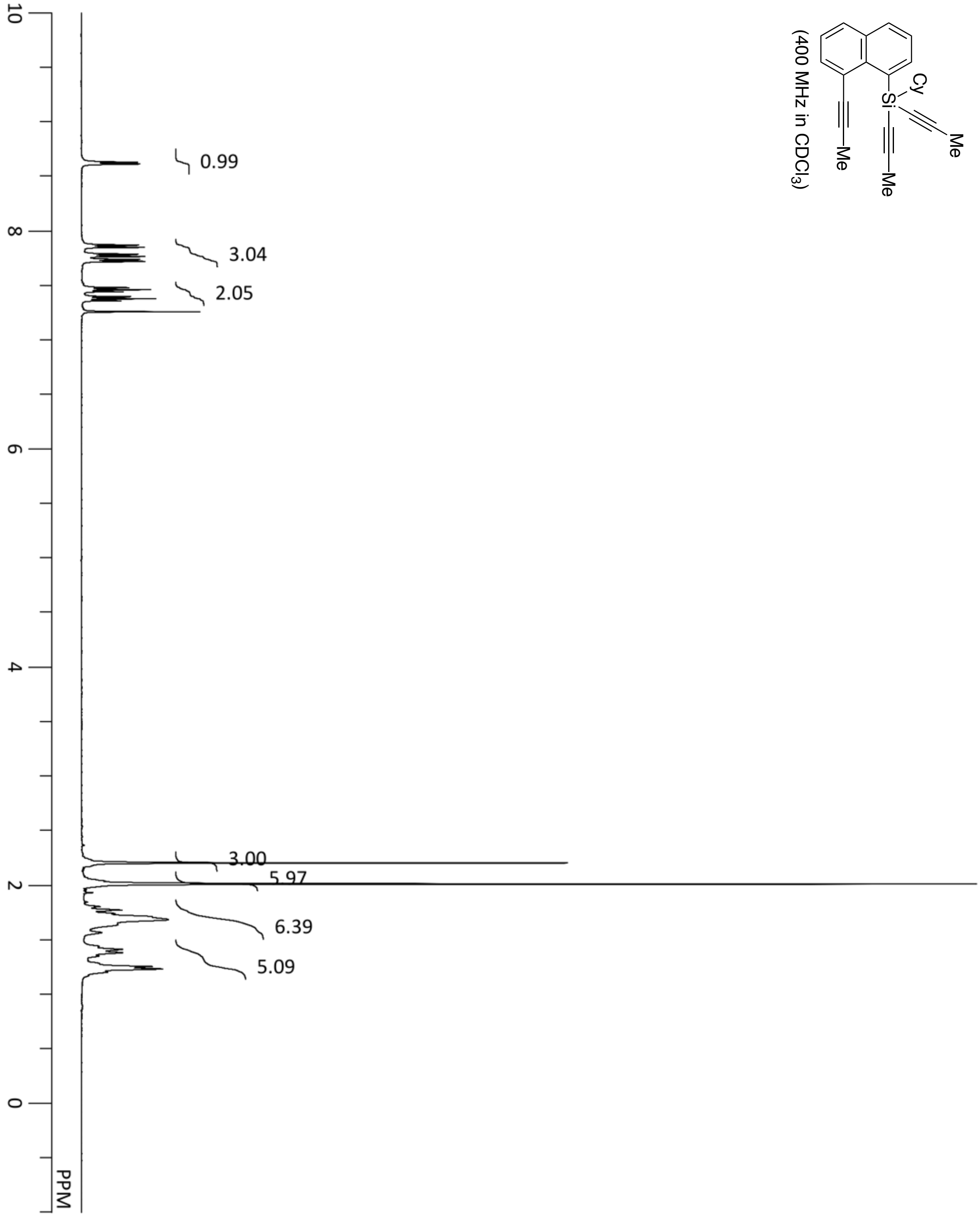


10
8
6
4
2
0
PPM
0.98
1.00
2.01
5.09
1.01
6.02
3.00
5.88
2.51
3.00
Cy
Si
Ph
Ph
Me
(400 MHz in CDCl$_3$)

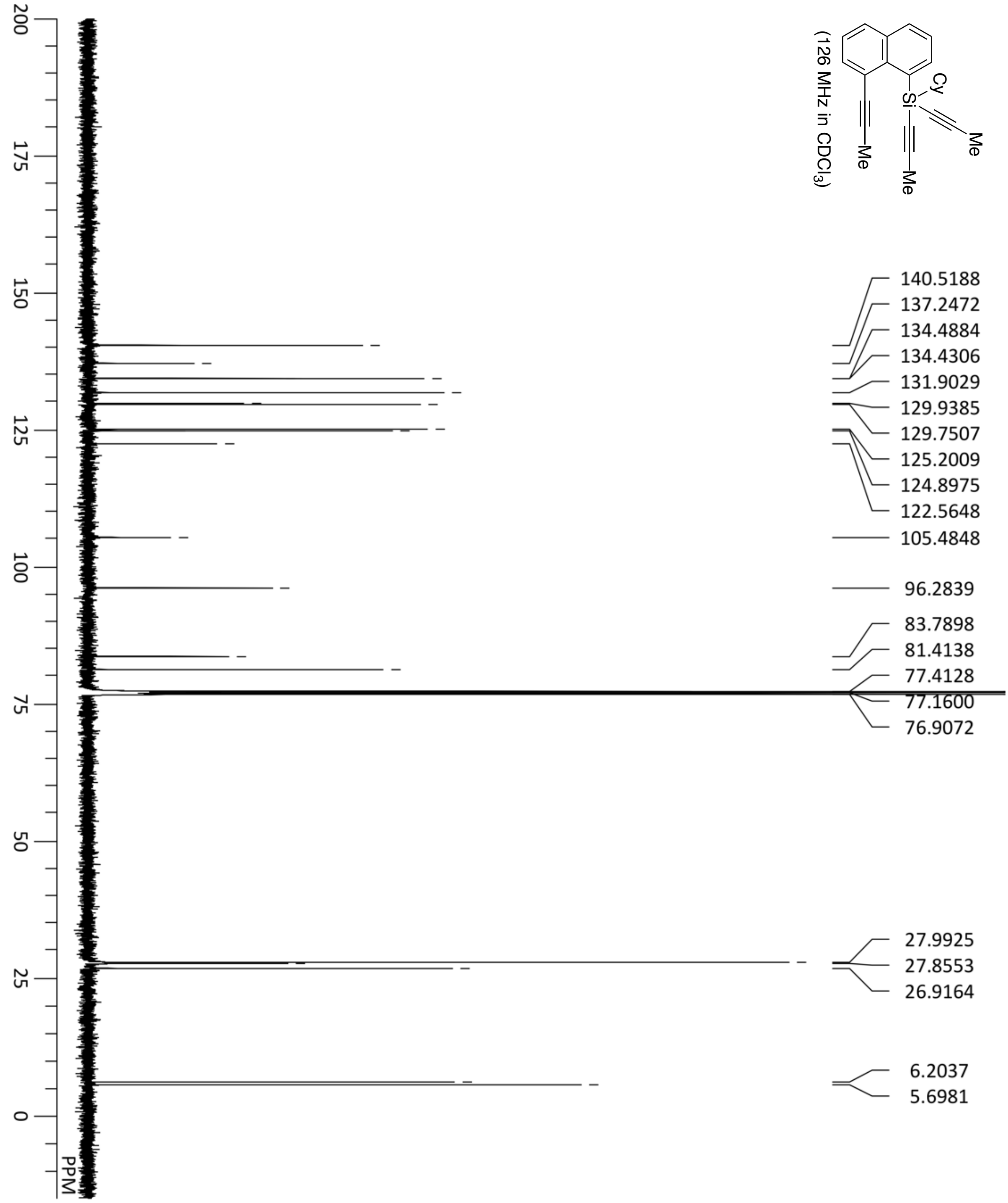
compound **1g**


200
175
150
125
100
75
50
25
0
PPM
(101 MHz in CDCl$_3$)
Cy
Si
Ph
Ph
Me
140.5122
137.2717
134.5268
134.4600
132.2012
129.7327
129.2180
128.6652
128.3317
125.2913
125.0530
123.6329
122.6989
107.6590
96.7652
91.6566
83.9460
77.4841
77.1600
76.8455
28.3330
28.0566
27.0368
6.3832

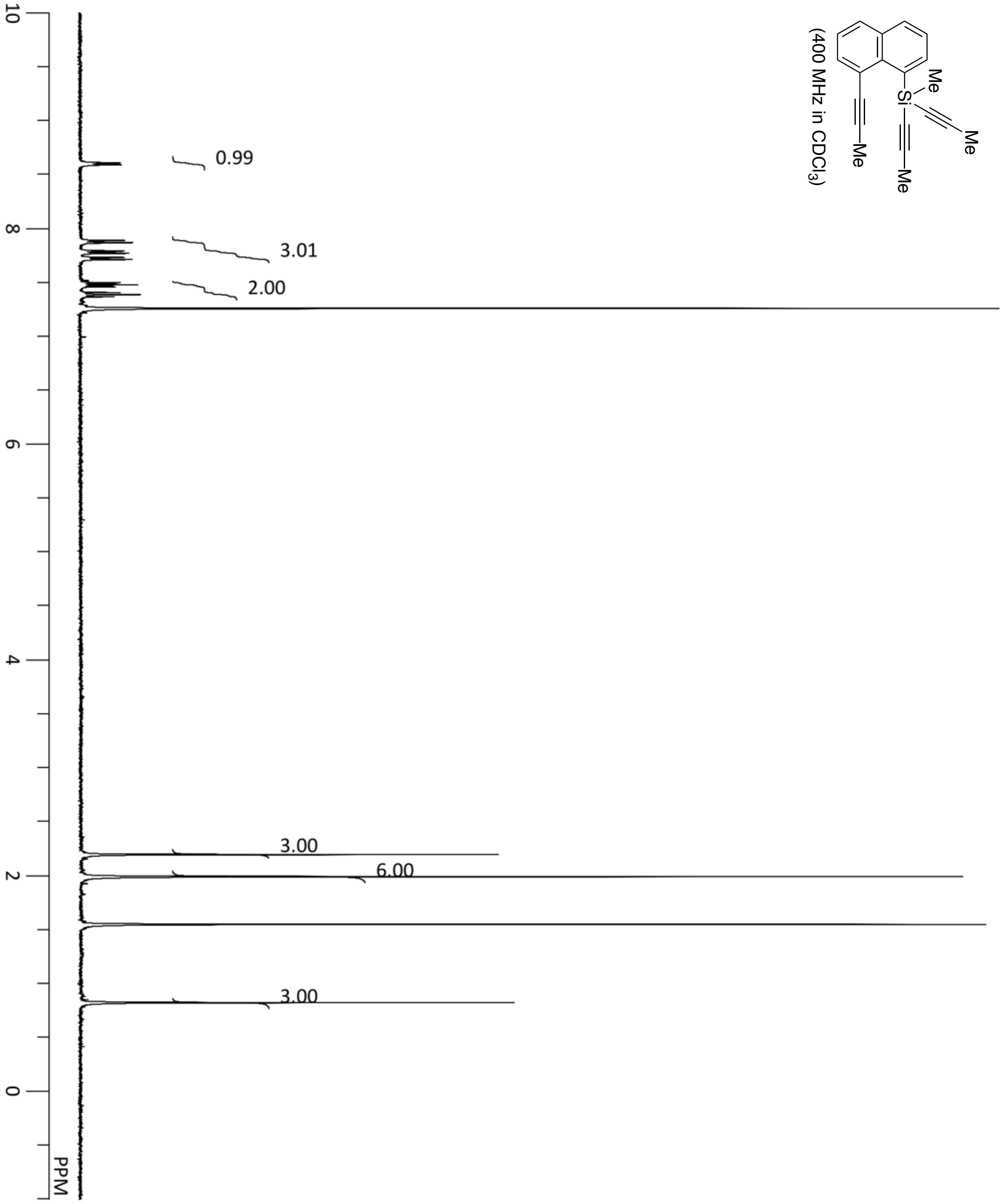
compound **1h**


(400 MHz in CDCl$_3$)
Cy
Si
Me
Me
Me
0.99
3.04
2.05
3.00
5.97
6.39
5.09
10
8
6
4
2
0
PPM

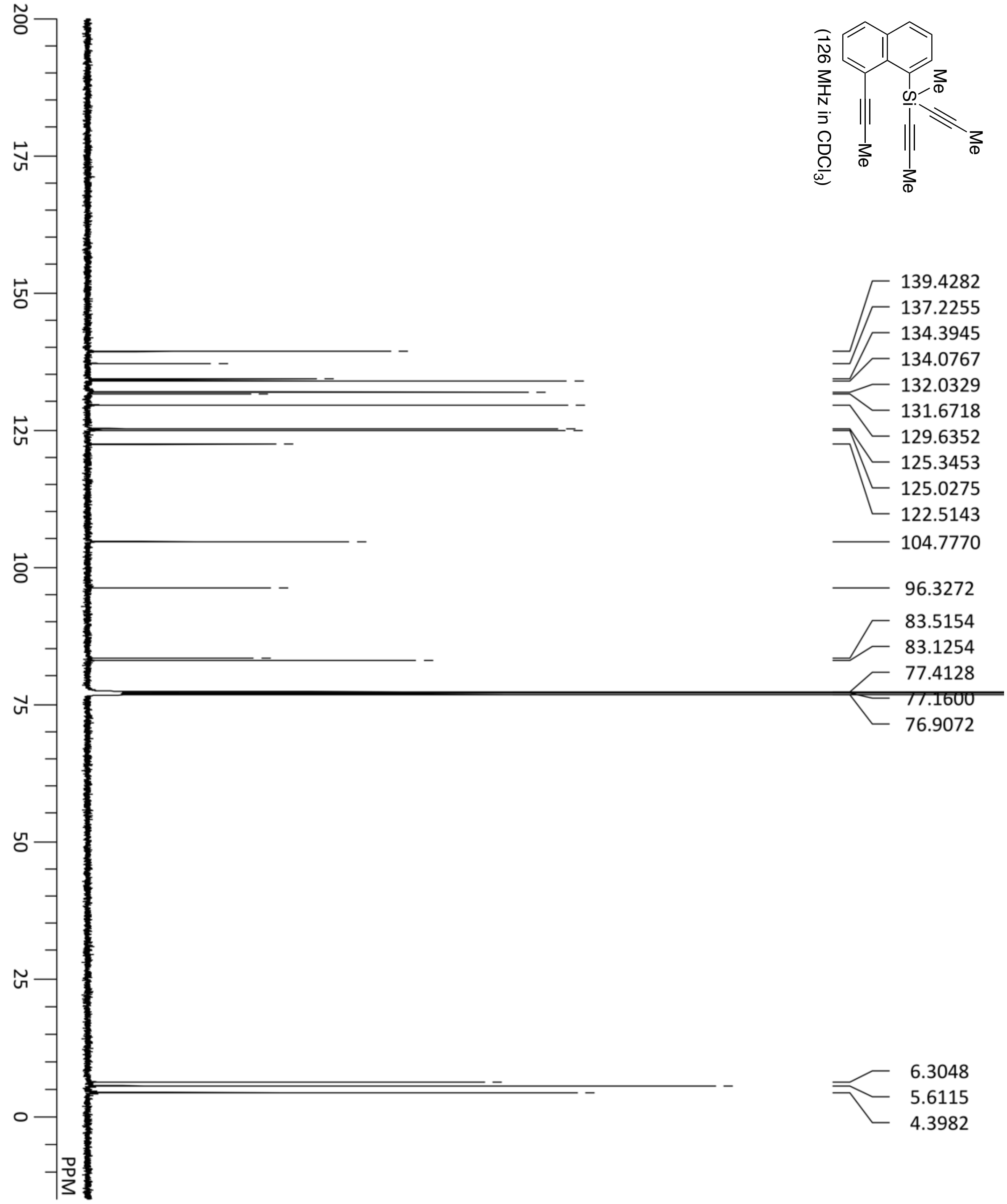
compound **1h**


(126 MHz in CDCl$_3$)
Cy
Si
Me
Me
Me
140.5188
137.2472
134.4884
134.4306
131.9029
129.9385
129.7507
125.2009
124.8975
122.5648
105.4848
96.2839
83.7898
81.4138
77.4128
77.1600
76.9072
27.9925
27.8553
26.9164
6.2037
5.6981
200
175
150
125
100
75
50
25
0
PPM

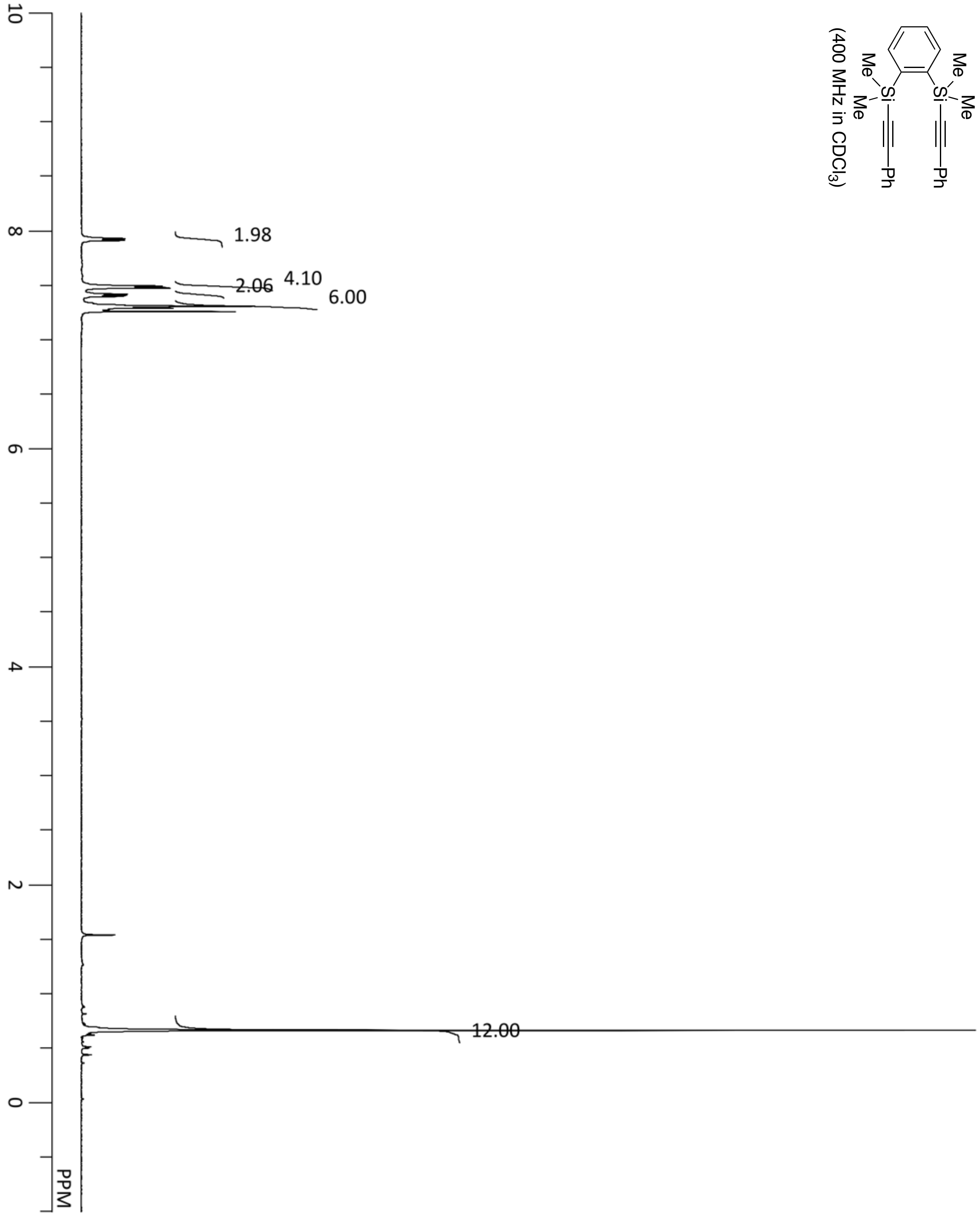
compound **1i**


(400 MHz in CDCl$_3$)
Me
Si
Me
Me
Me
0.99
3.01
2.00
3.00
6.00
3.00
10
8
6
4
2
0
PPM

compound **1i**

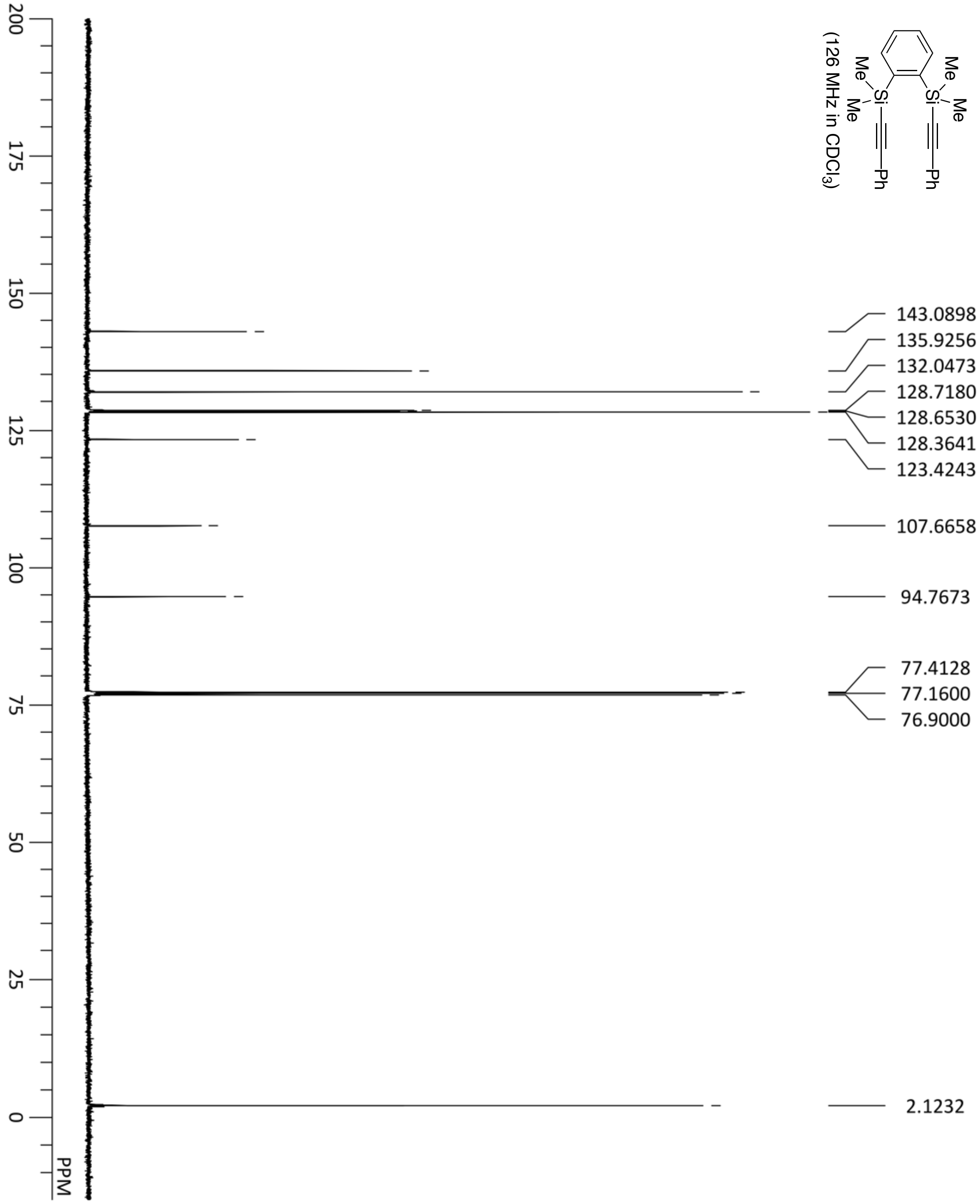

(126 MHz in CDCl3)
Me
Si
Me
Me
Me
139.4282
137.2255
134.3945
134.0767
132.0329
131.6718
129.6352
125.3453
125.0275
122.5143
104.7770
96.3272
83.5154
83.1254
77.4128
77.1600
76.9072
6.3048
5.6115
4.3982
200
175
150
125
100
75
50
25
0
PPM

compound **1j**



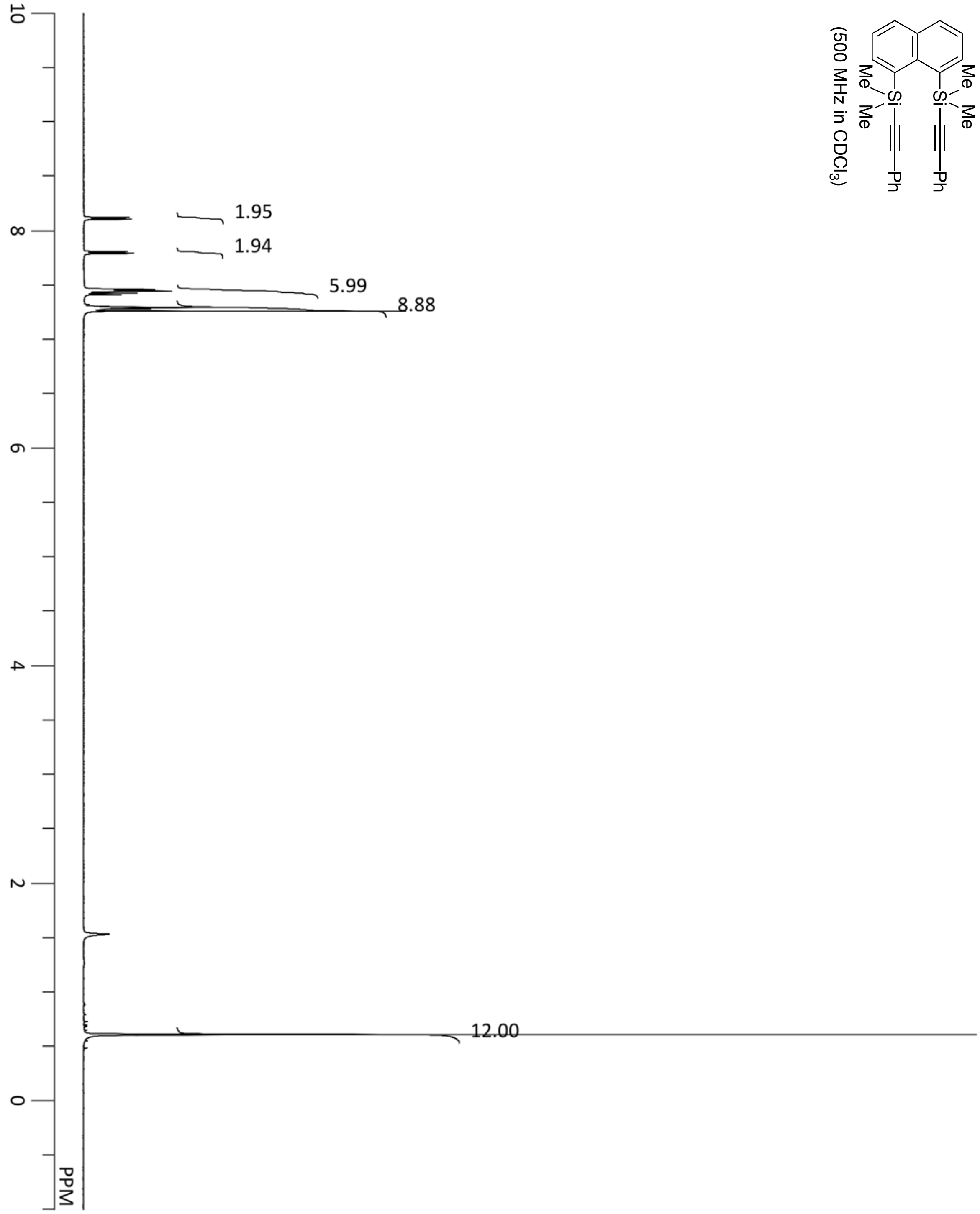
Me
Me
Si
Ph
Me
Me
Si
Ph
(400 MHz in CDCl3)
10
8
6
4
2
0
PPM
1.98
2.06
4.10
6.00
12.00

compound **1j**



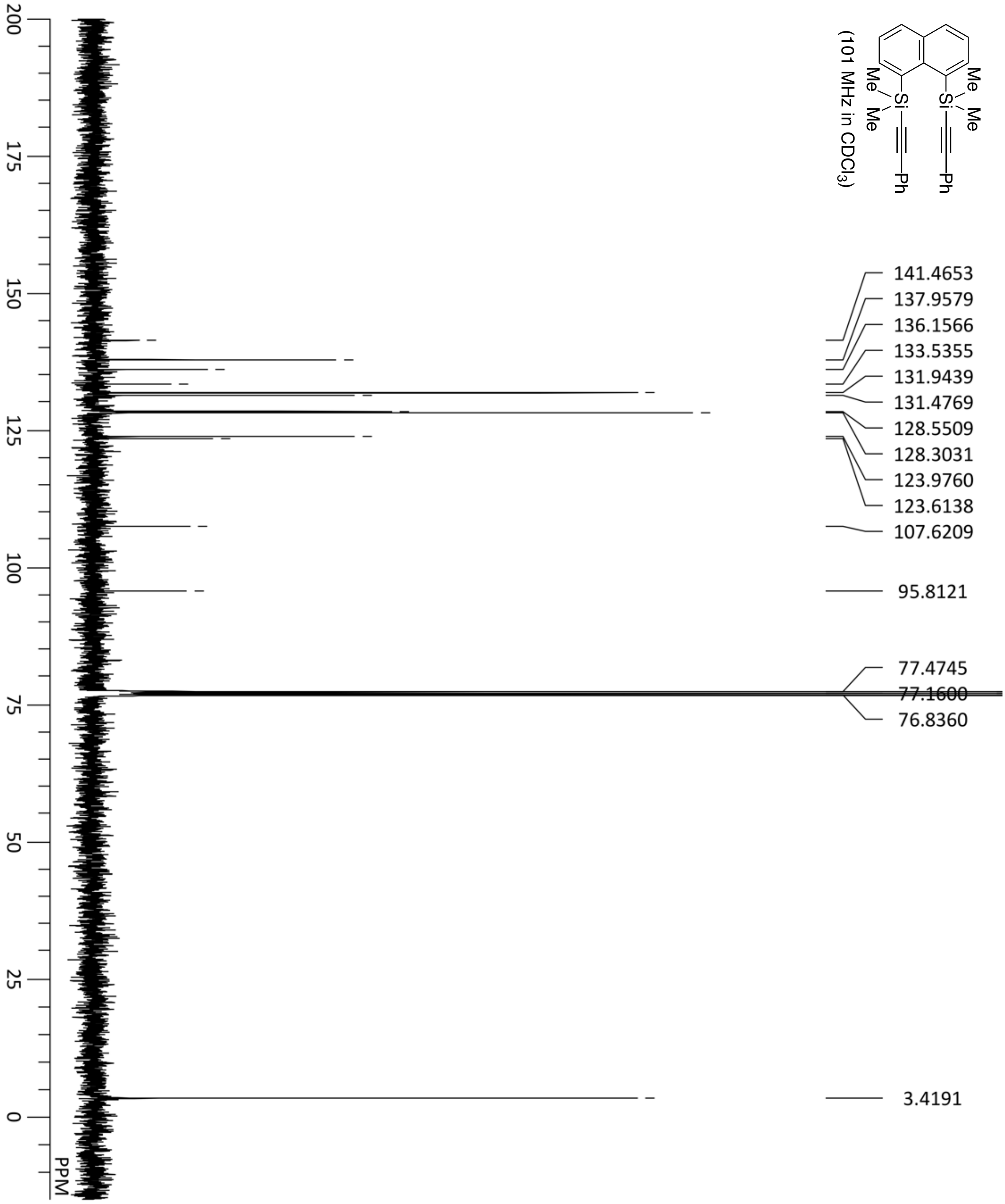
Me
Si
Me
Ph
Me
Si
Me
Ph
(126 MHz in CDCl3)
143.0898
135.9256
132.0473
128.7180
128.6530
128.3641
123.4243
107.6658
94.7673
77.4128
77.1600
76.9000
2.1232
200
175
150
125
100
75
50
25
0
PPM

compound **1k**



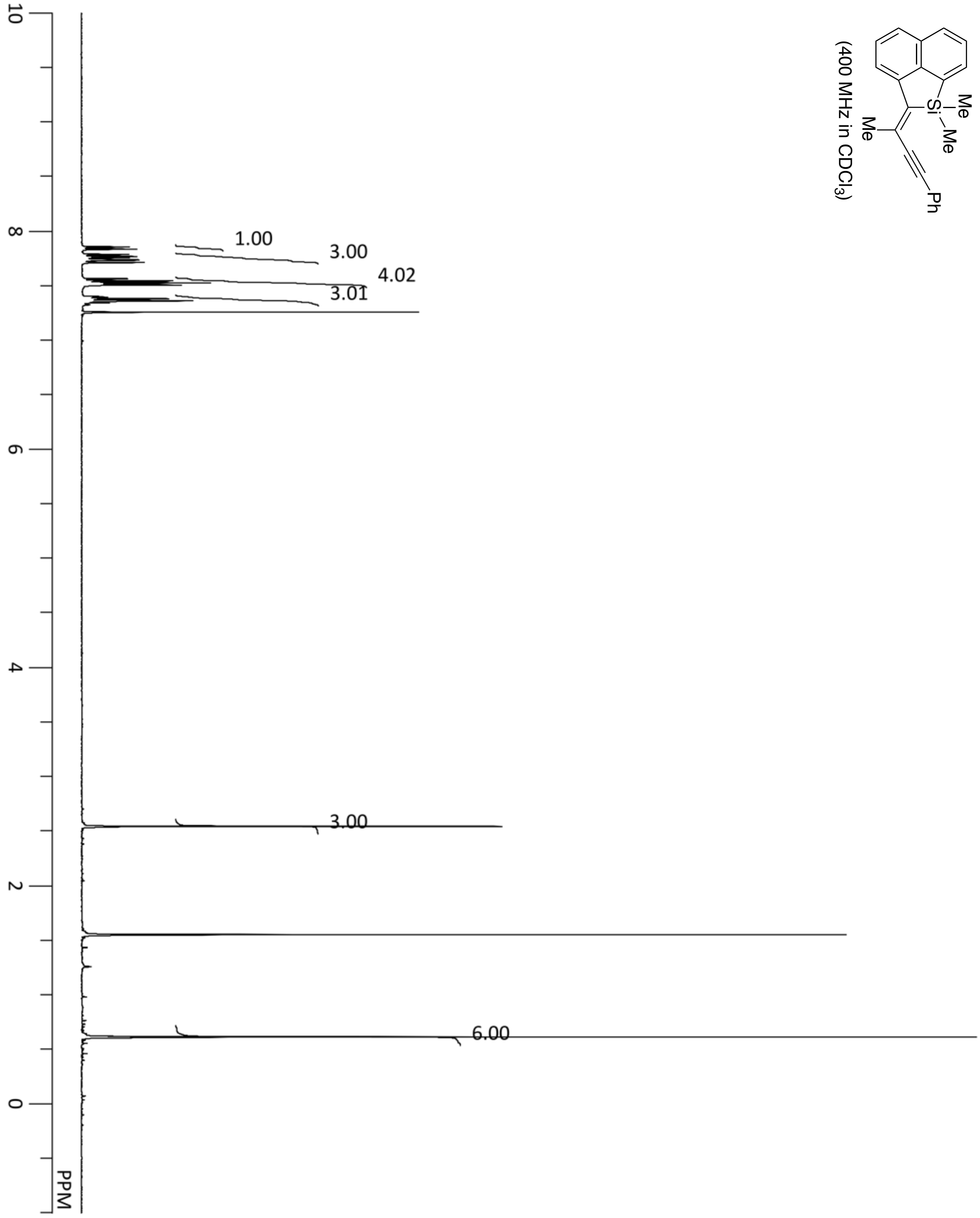
(500 MHz in $CDCl_3$)

compound **1k**

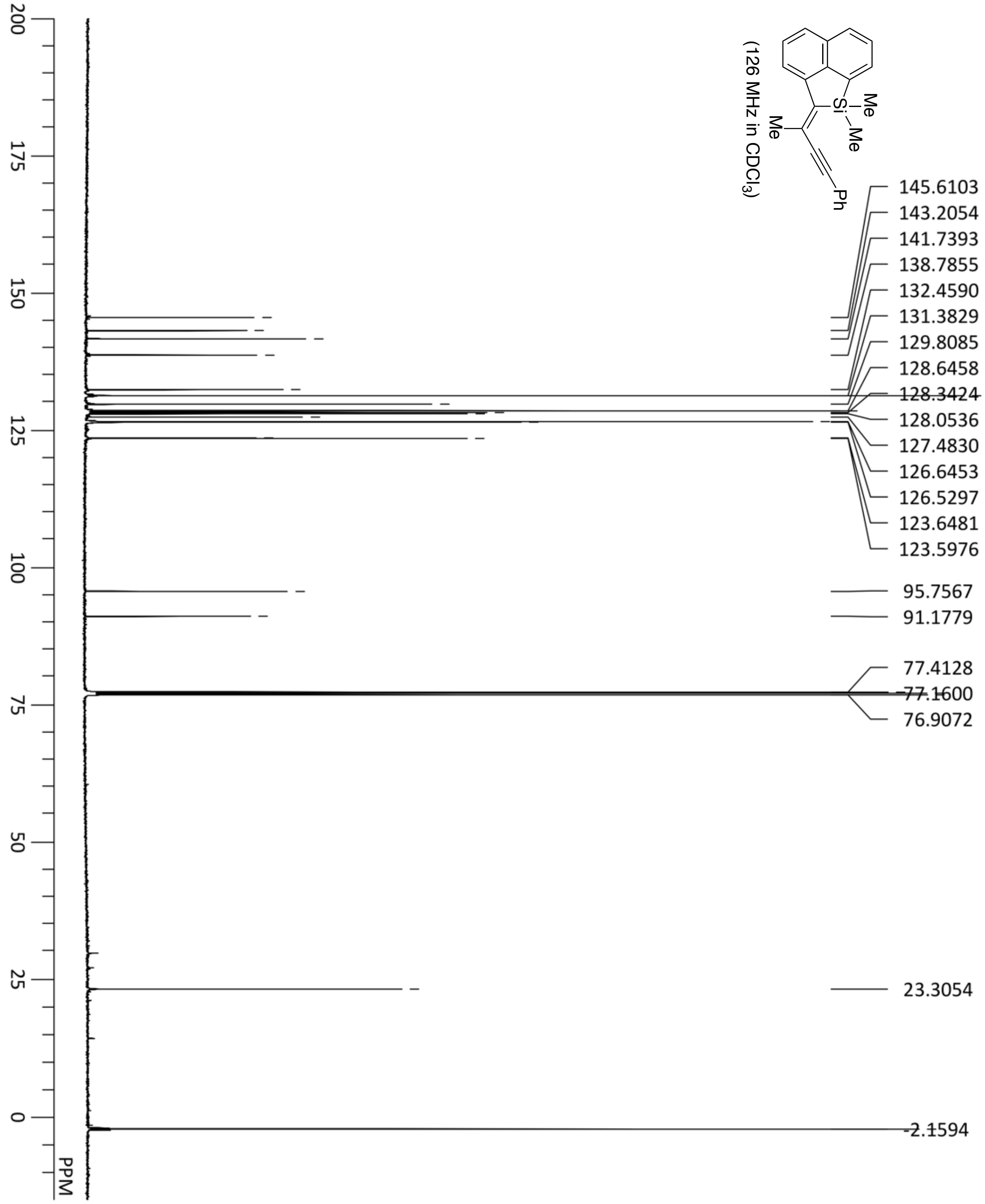


Me
Me
Si
Ph
Me
Me
Si
Ph
(101 MHz in CDCl3)
141.4653
137.9579
136.1566
133.5355
131.9439
131.4769
128.5509
128.3031
123.9760
123.6138
107.6209
95.8121
77.4745
77.1600
76.8360
3.4191
200
175
150
125
100
75
50
25
0
PPM

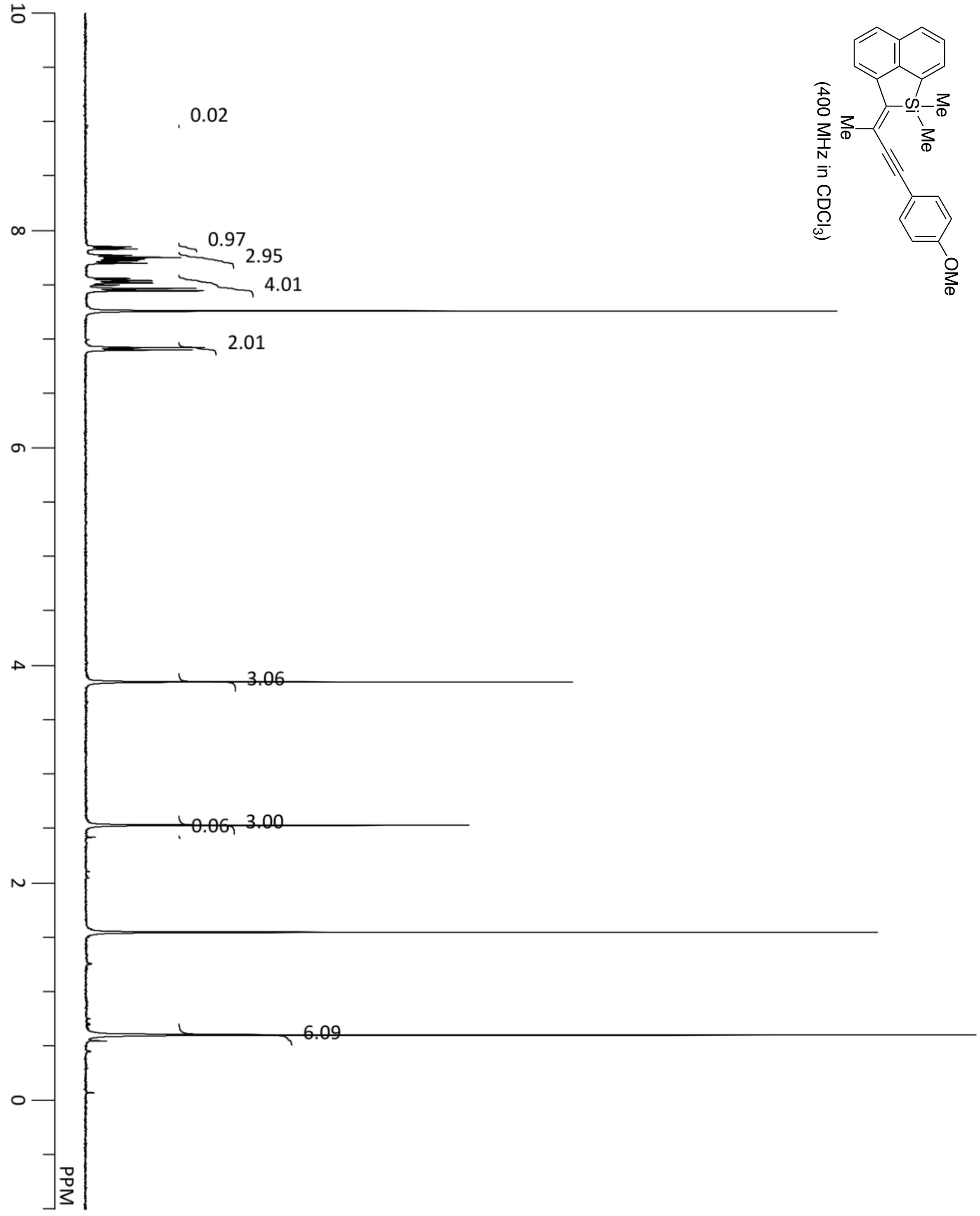
compound **3a**


10
8
6
4
2
0
PPM
1.00
3.00
4.02
3.01
3.00
6.00
Me
Si
Me
Me
Ph
(400 MHz in CDCl3)

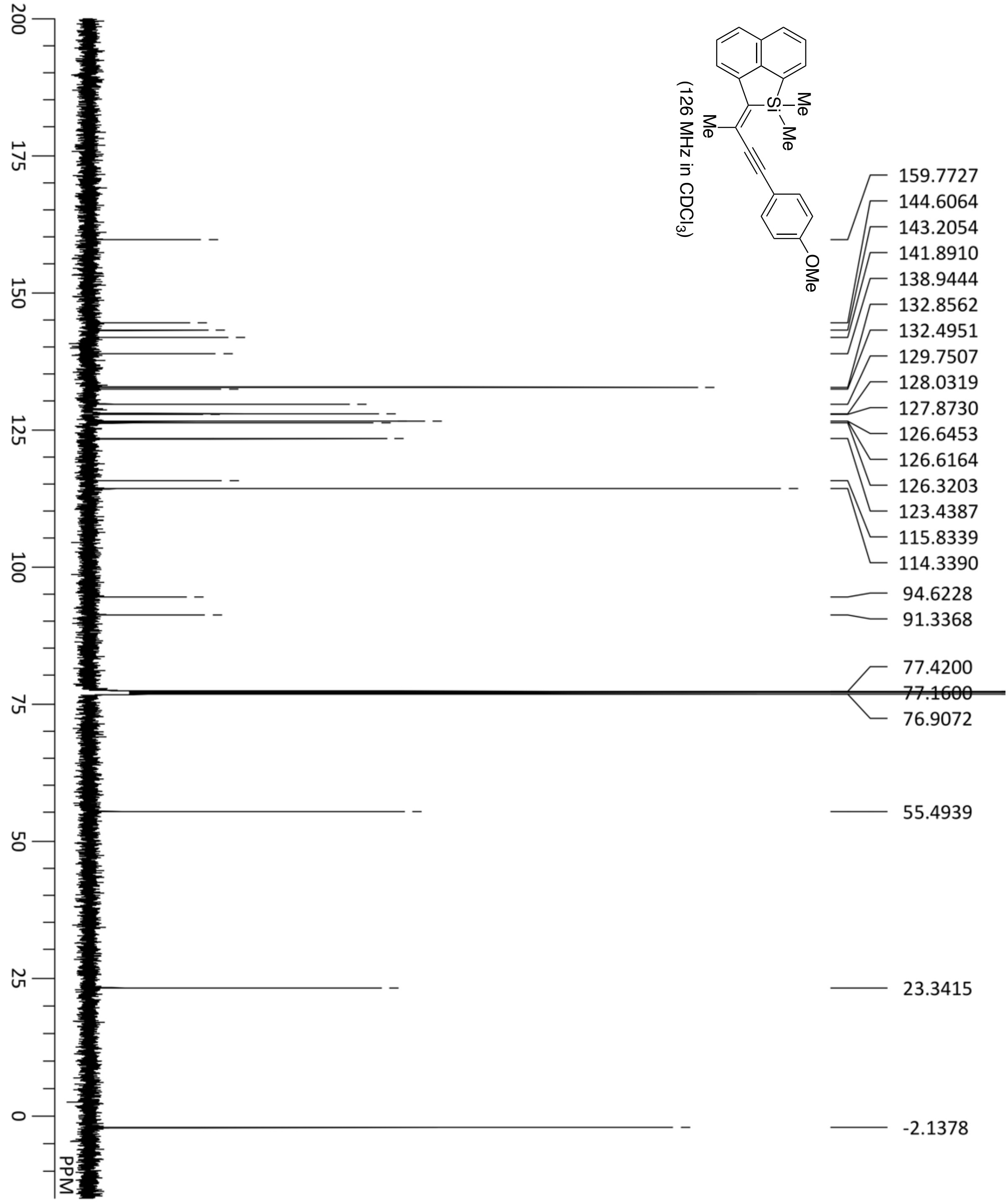
compound **3a**


(126 MHz in CDCl$_3$)
Me
Si
Me
Me
Ph
200
175
150
125
100
75
50
25
0
PPM
145.6103
143.2054
141.7393
138.7855
132.4590
131.3829
129.8085
128.6458
128.3424
128.0536
127.4830
126.6453
126.5297
123.6481
123.5976
95.7567
91.1779
77.4128
77.1600
76.9072
23.3054
-2.1594

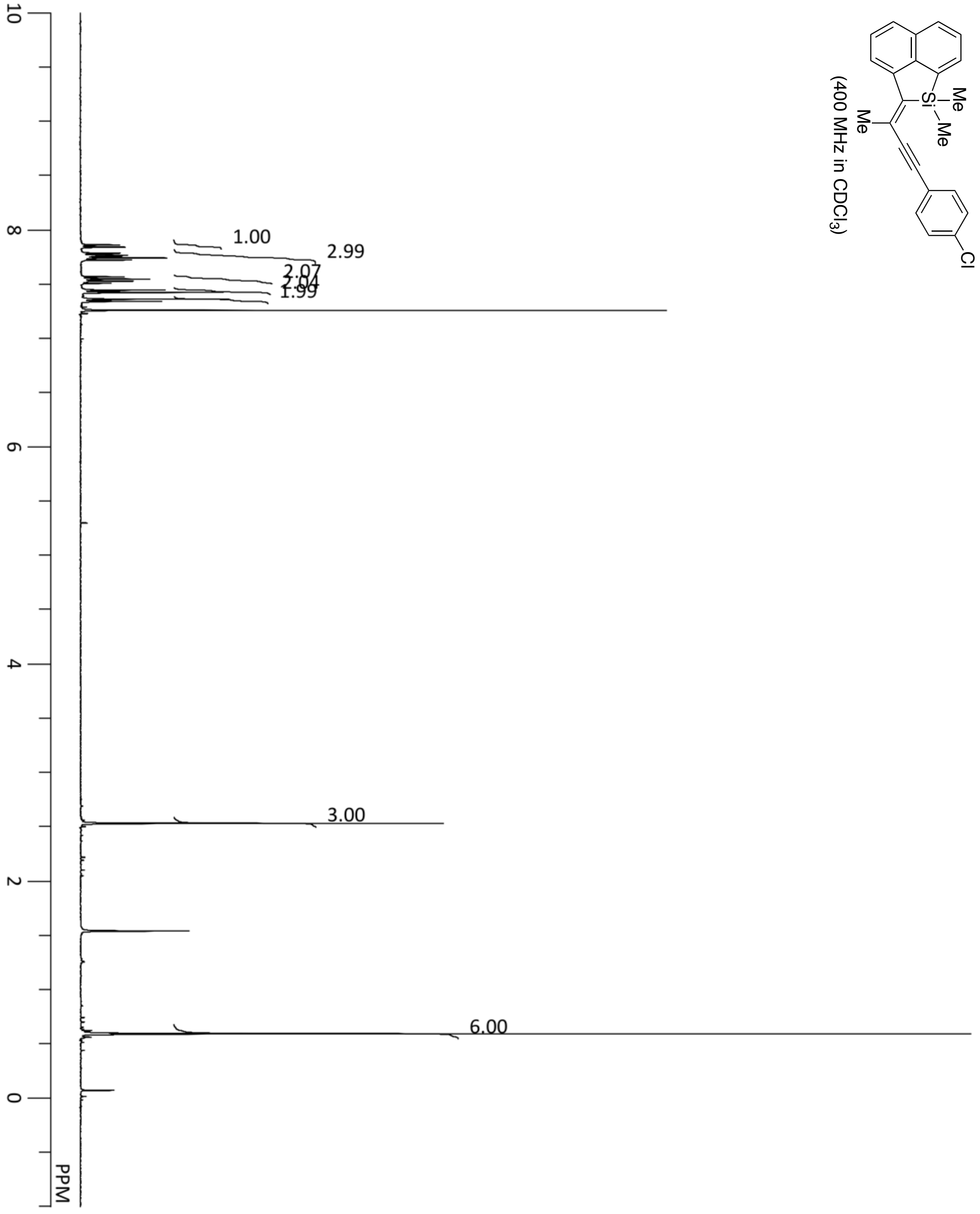
compound **3b** (*Z*/*E* = 98/2)



compound **3b** (*Z*/*E* = 98/2)

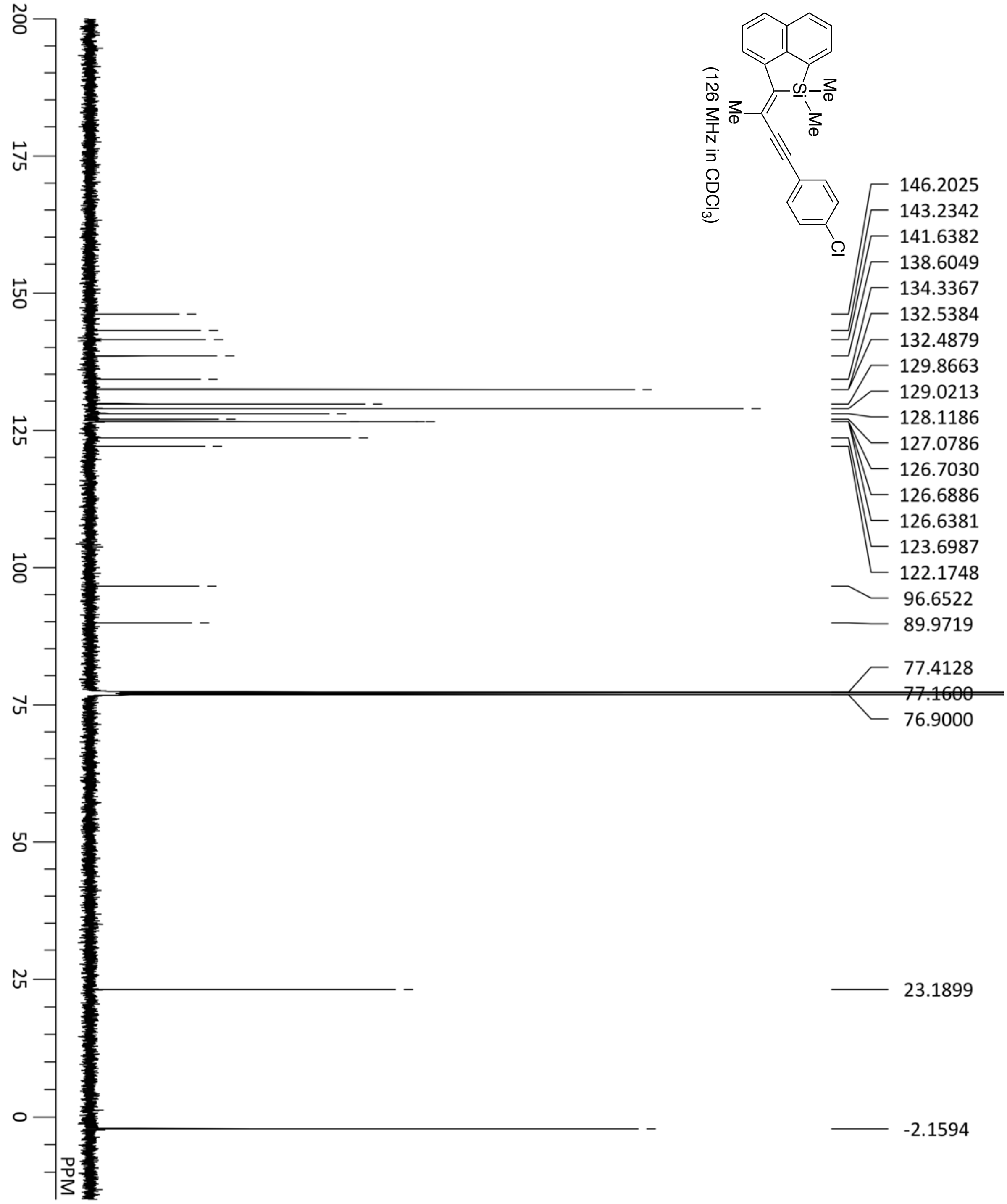


compound **3c**

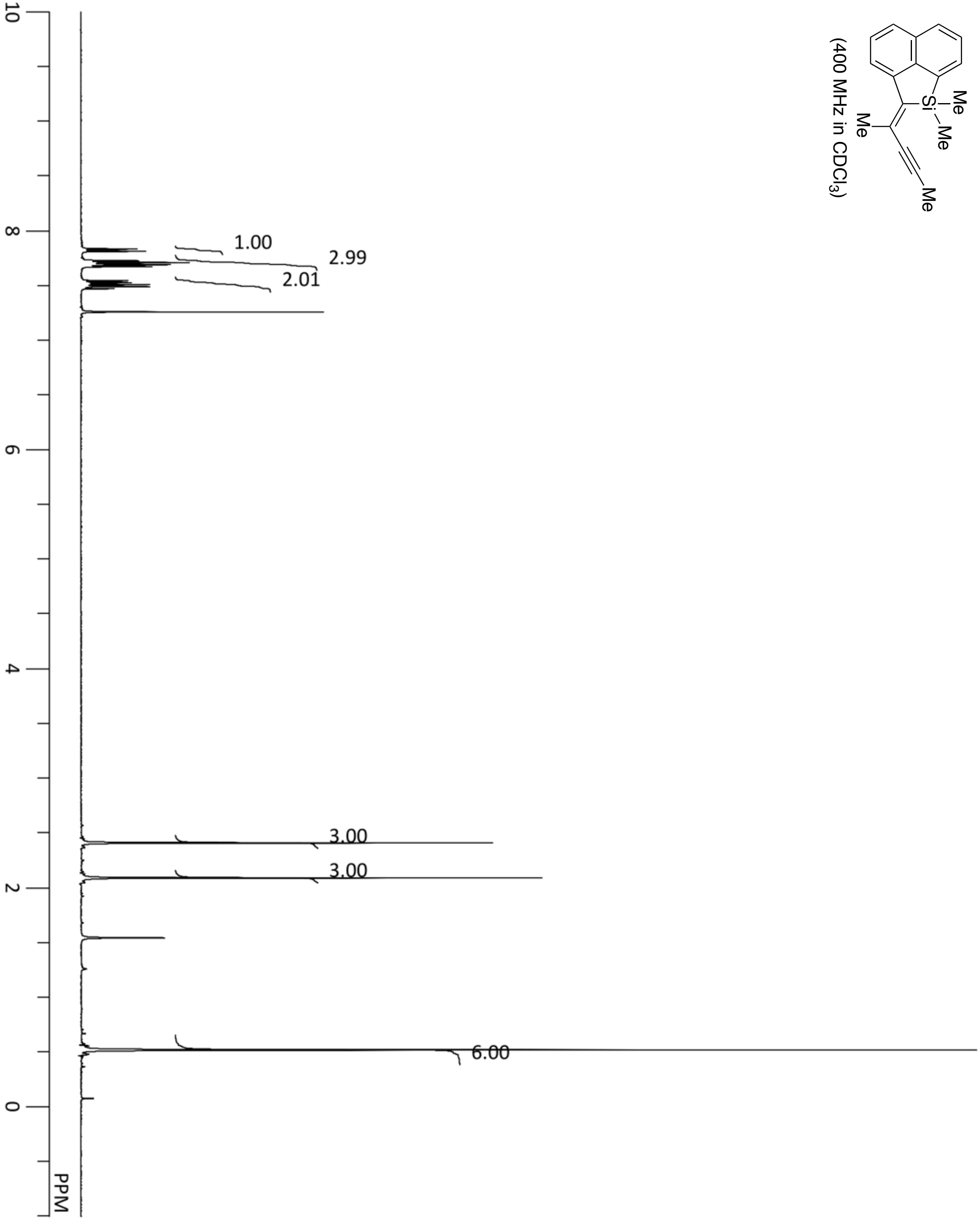


(400 MHz in $CDCl_3$)

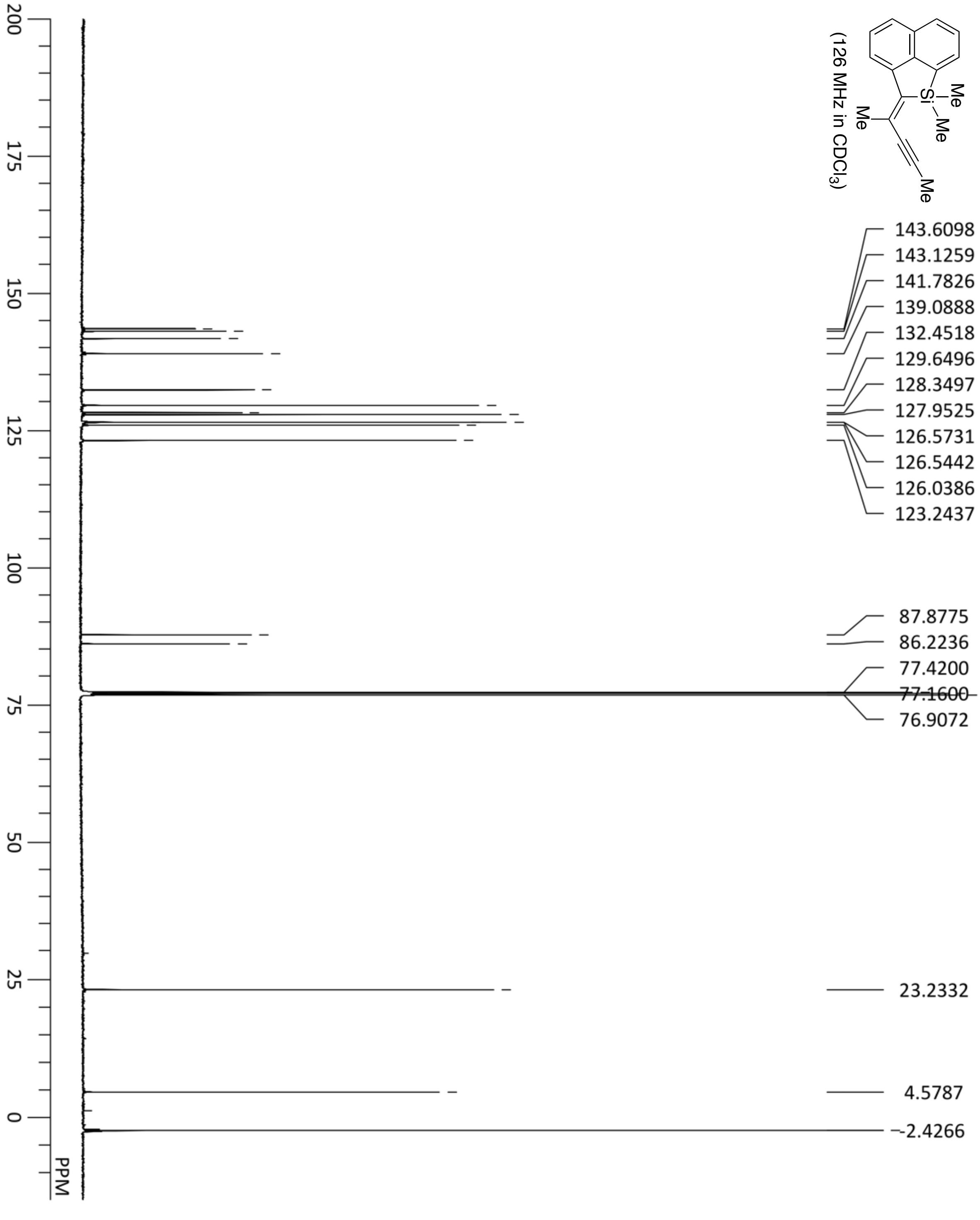
compound **3c**


(126 MHz in CDCl$_3$)
Si
Me
Me
Me
Cl
146.2025
143.2342
141.6382
138.6049
134.3367
132.5384
132.4879
129.8663
129.0213
128.1186
127.0786
126.7030
126.6886
126.6381
123.6987
122.1748
96.6522
89.9719
77.4128
77.1600
76.9000
23.1899
-2.1594
200
175
150
125
100
75
50
25
0
PPM

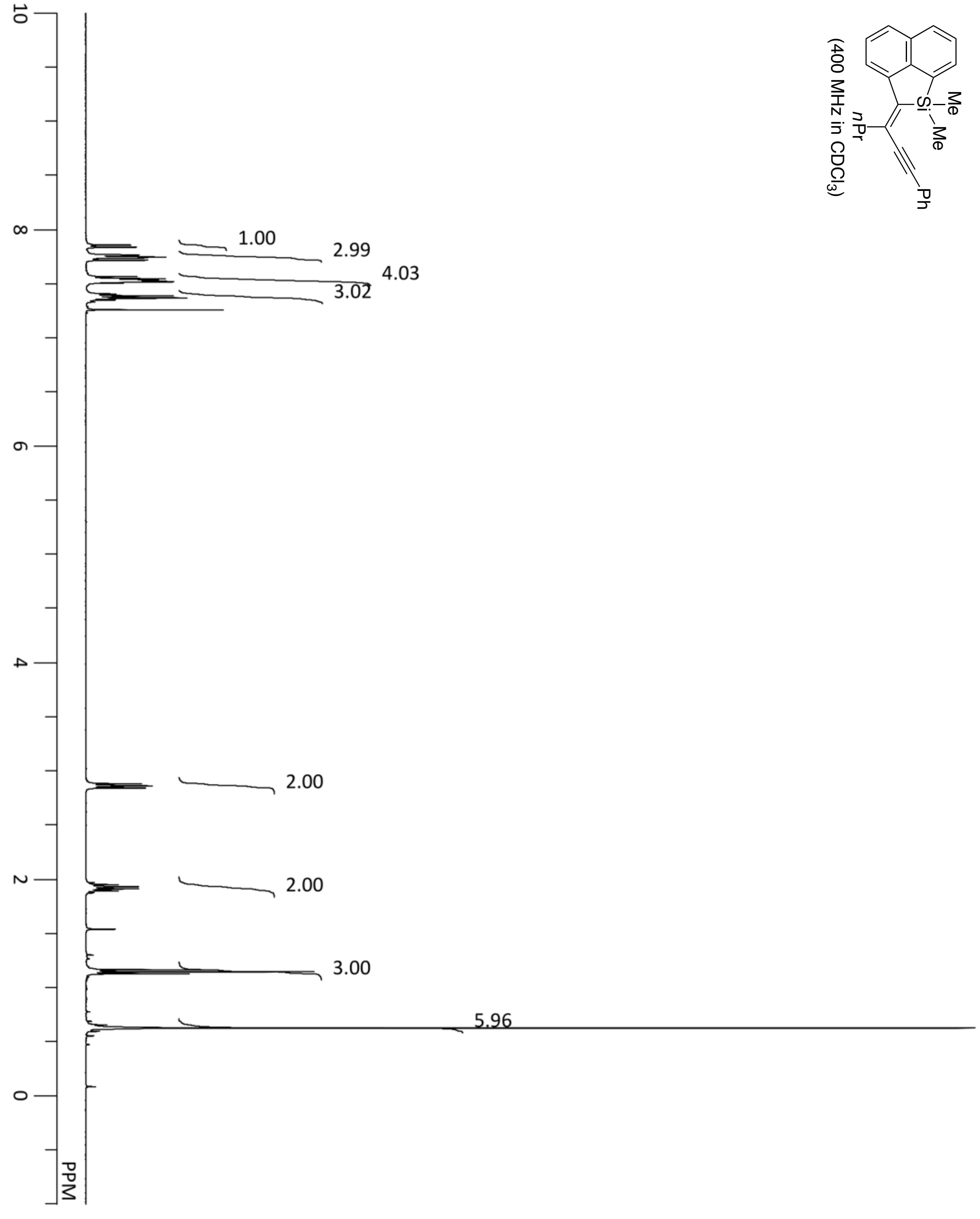
compound **3d**


10
8
6
4
2
0
PPM
1.00
2.99
2.01
3.00
3.00
6.00
Me
Si
Me
Me
Me
(400 MHz in CDCl$_3$)

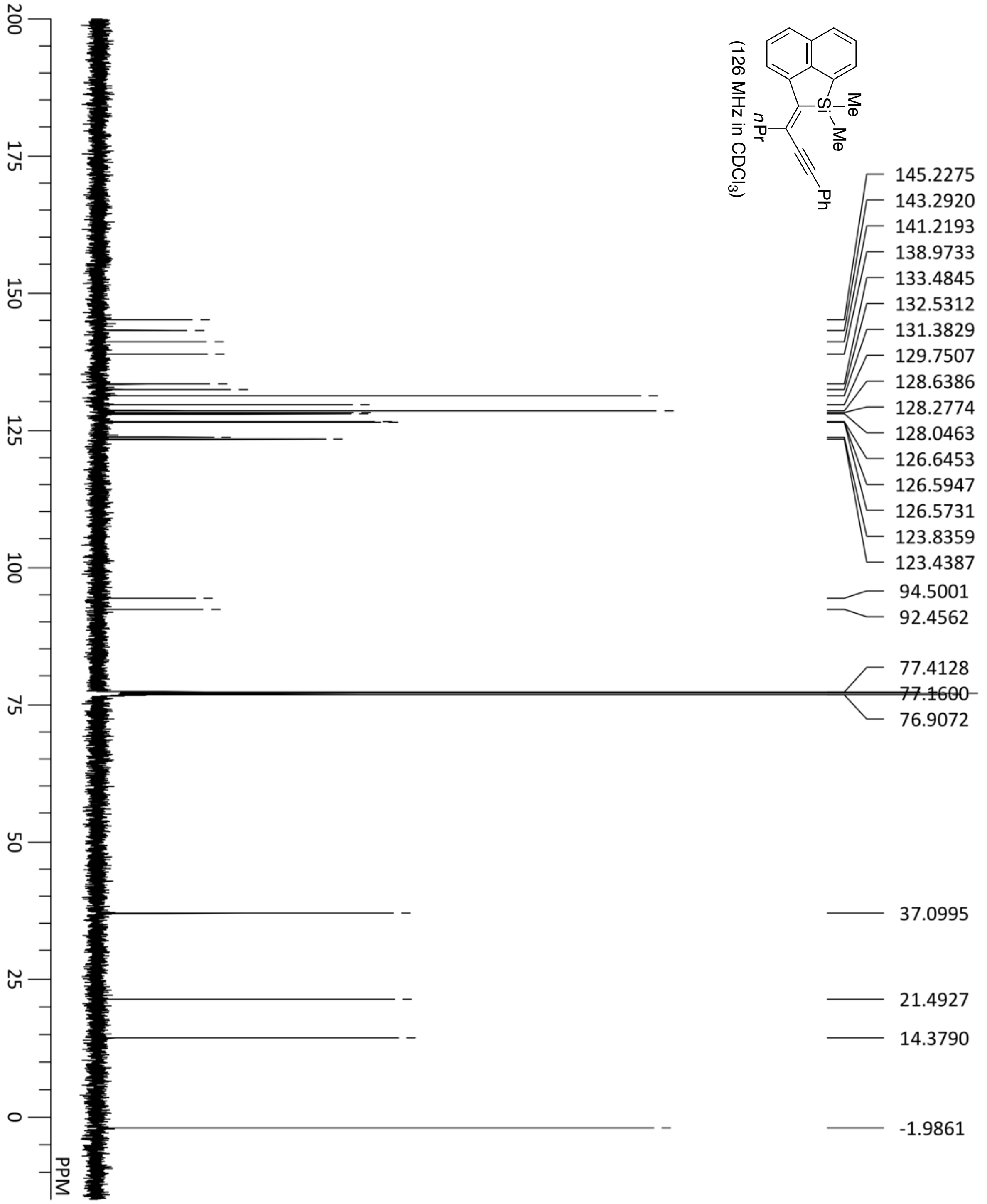
compound **3d**


(126 MHz in CDCl3)
Me
Si
Me
Me
Me
143.6098
143.1259
141.7826
139.0888
132.4518
129.6496
128.3497
127.9525
126.5731
126.5442
126.0386
123.2437
87.8775
86.2236
77.4200
77.1600
76.9072
23.2332
4.5787
−2.4266
200
175
150
125
100
75
50
25
0
PPM

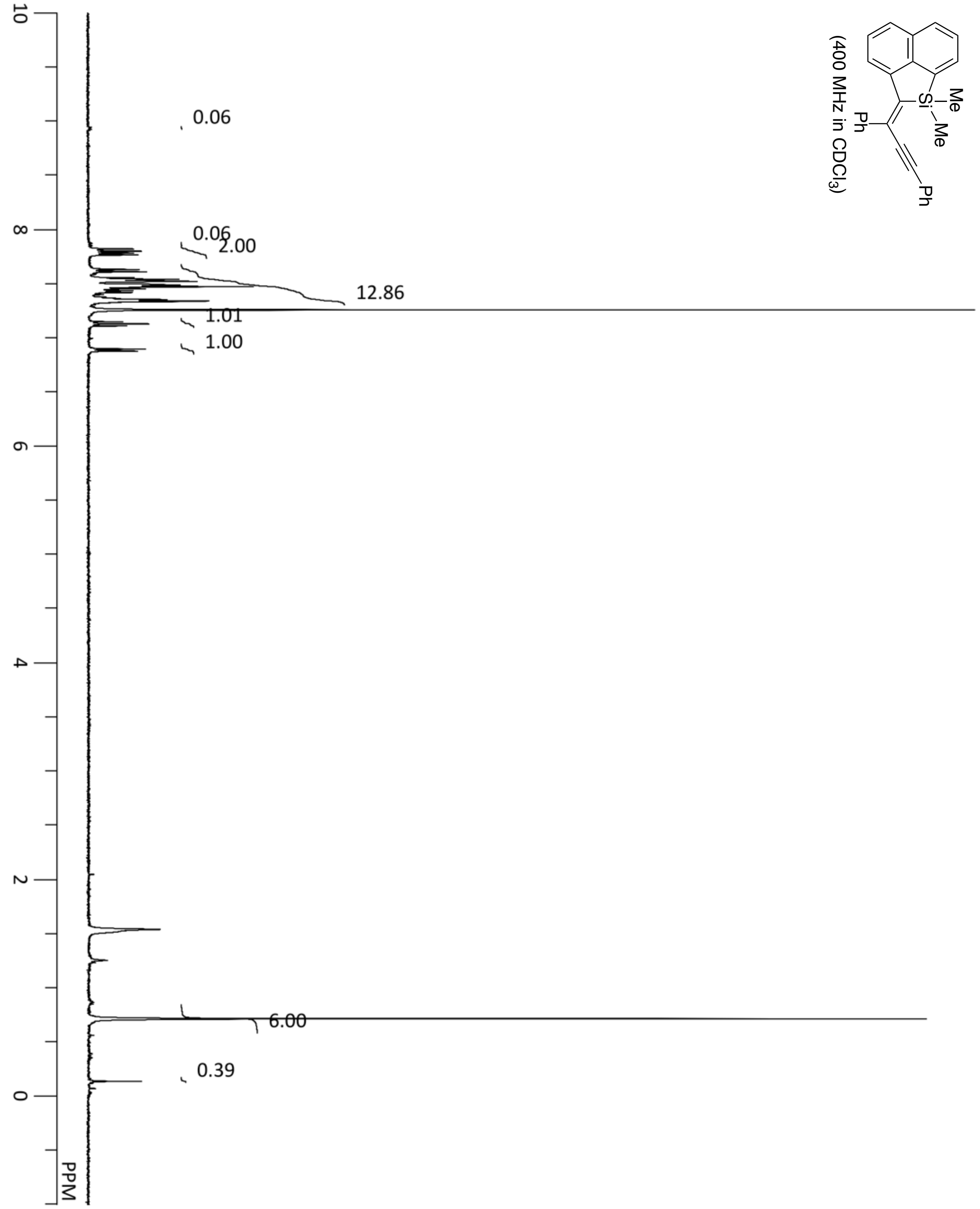
compound **3e**


10
8
6
4
2
0
PPM
1.00
2.99
4.03
3.02
2.00
2.00
3.00
5.96
Me
Si
Me
Ph
nPr
(400 MHz in CDCl3)

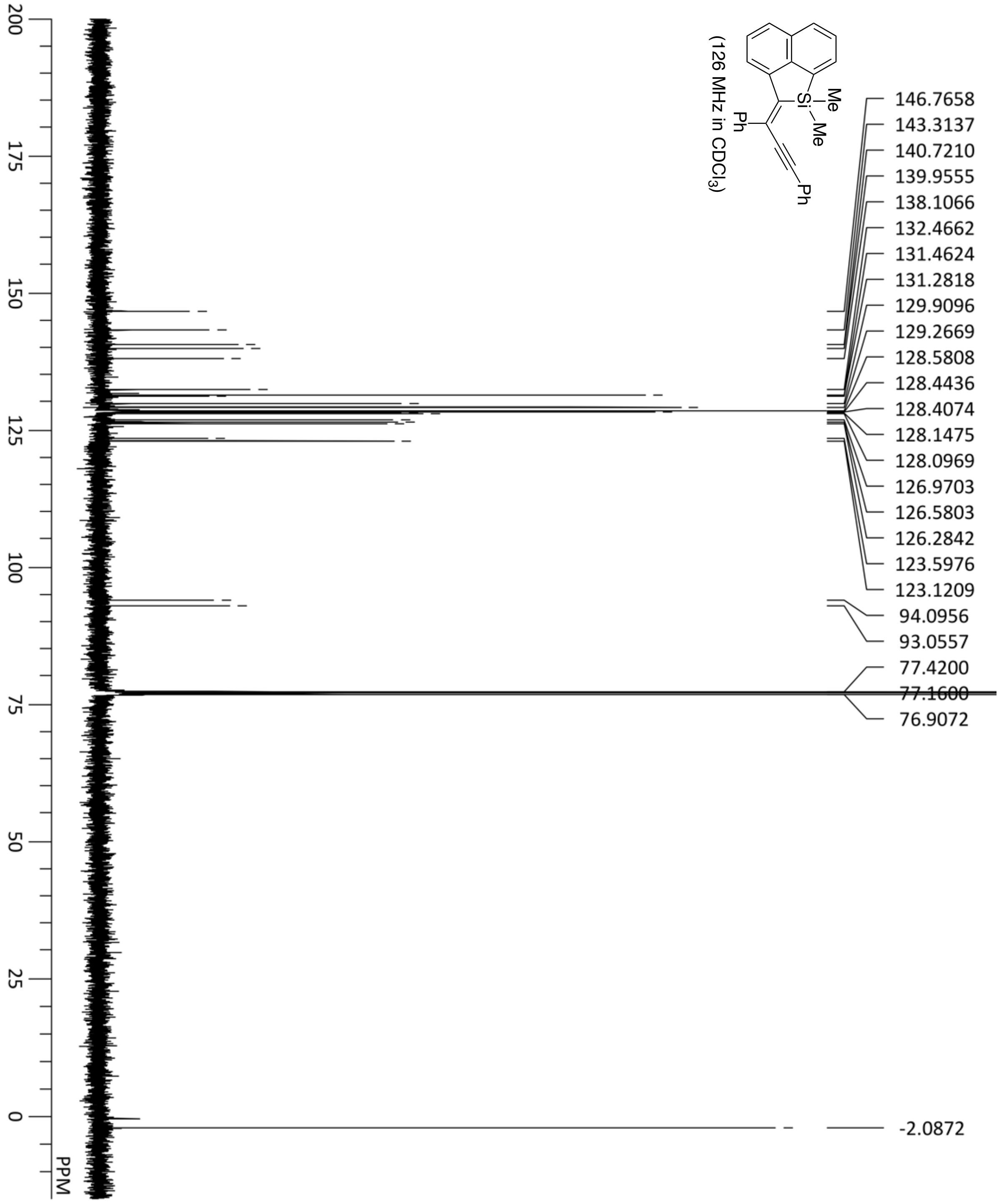
compound **3e**


(126 MHz in CDCl$_3$)
Si
Me
Me
*n*Pr
Ph
145.2275
143.2920
141.2193
138.9733
133.4845
132.5312
131.3829
129.7507
128.6386
128.2774
128.0463
126.6453
126.5947
126.5731
123.8359
123.4387
94.5001
92.4562
77.4128
77.1600
76.9072
37.0995
21.4927
14.3790
-1.9861
200
175
150
125
100
75
50
25
0
PPM

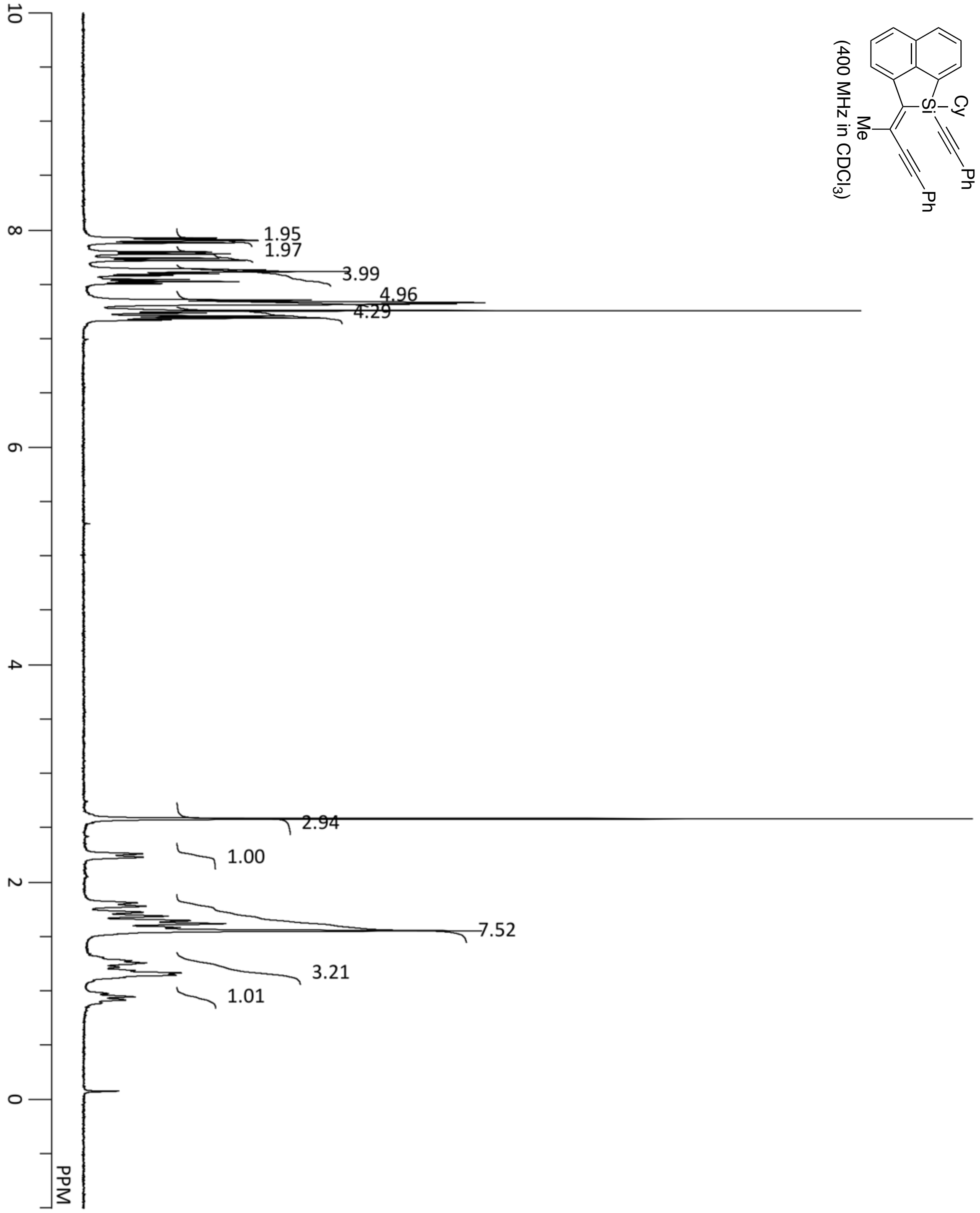
compound **3f** (*Z*/*E* = 94/6)



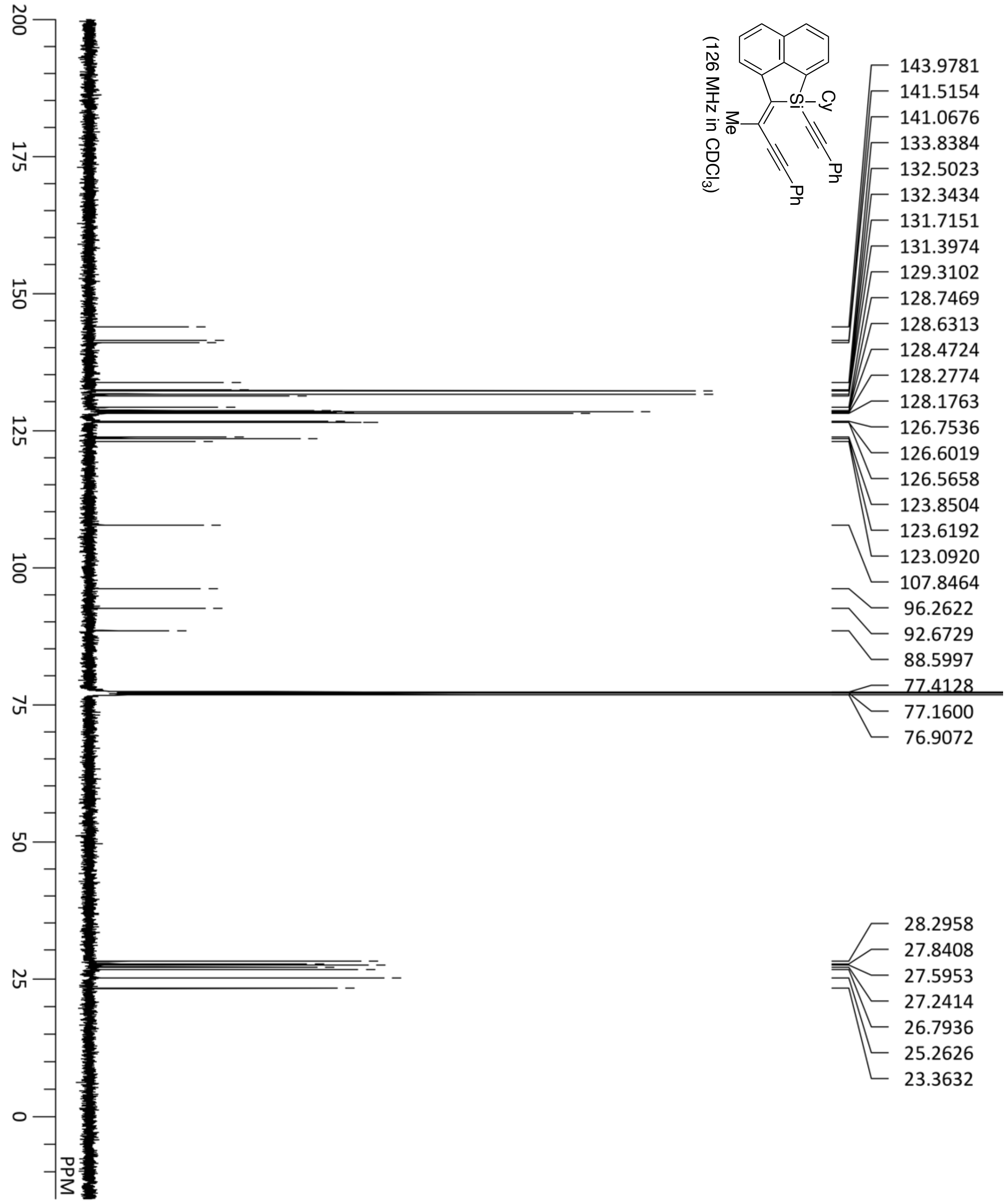
compound **3f** (*Z*/*E* = 94/6)



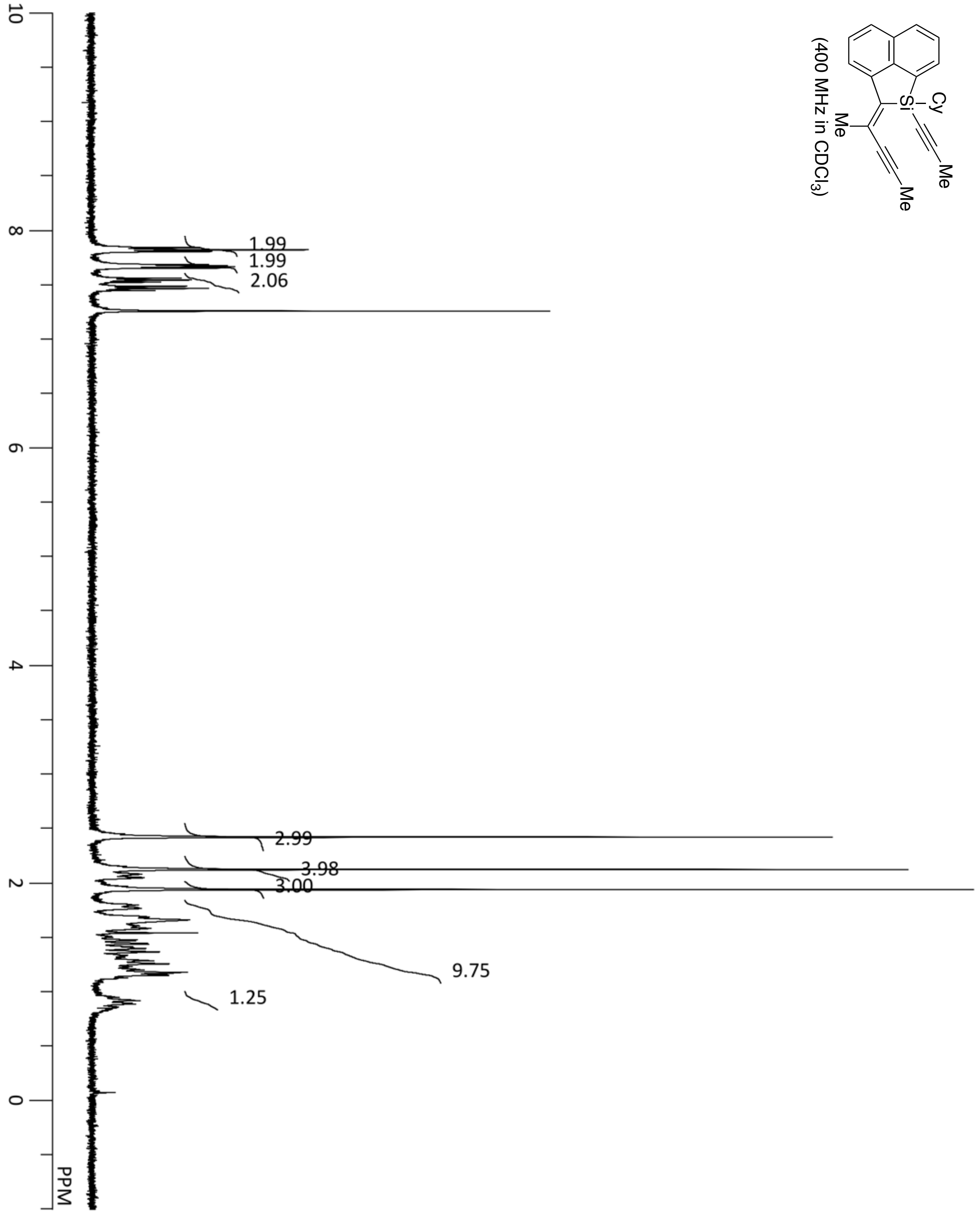
compound **3g**


(400 MHz in CDCl$_3$)
Si
Cy
Me
Ph
Ph
1.95
1.97
3.99
4.96
4.29
2.94
1.00
7.52
3.21
1.01
10
8
6
4
2
0
PPM

compound **3g**

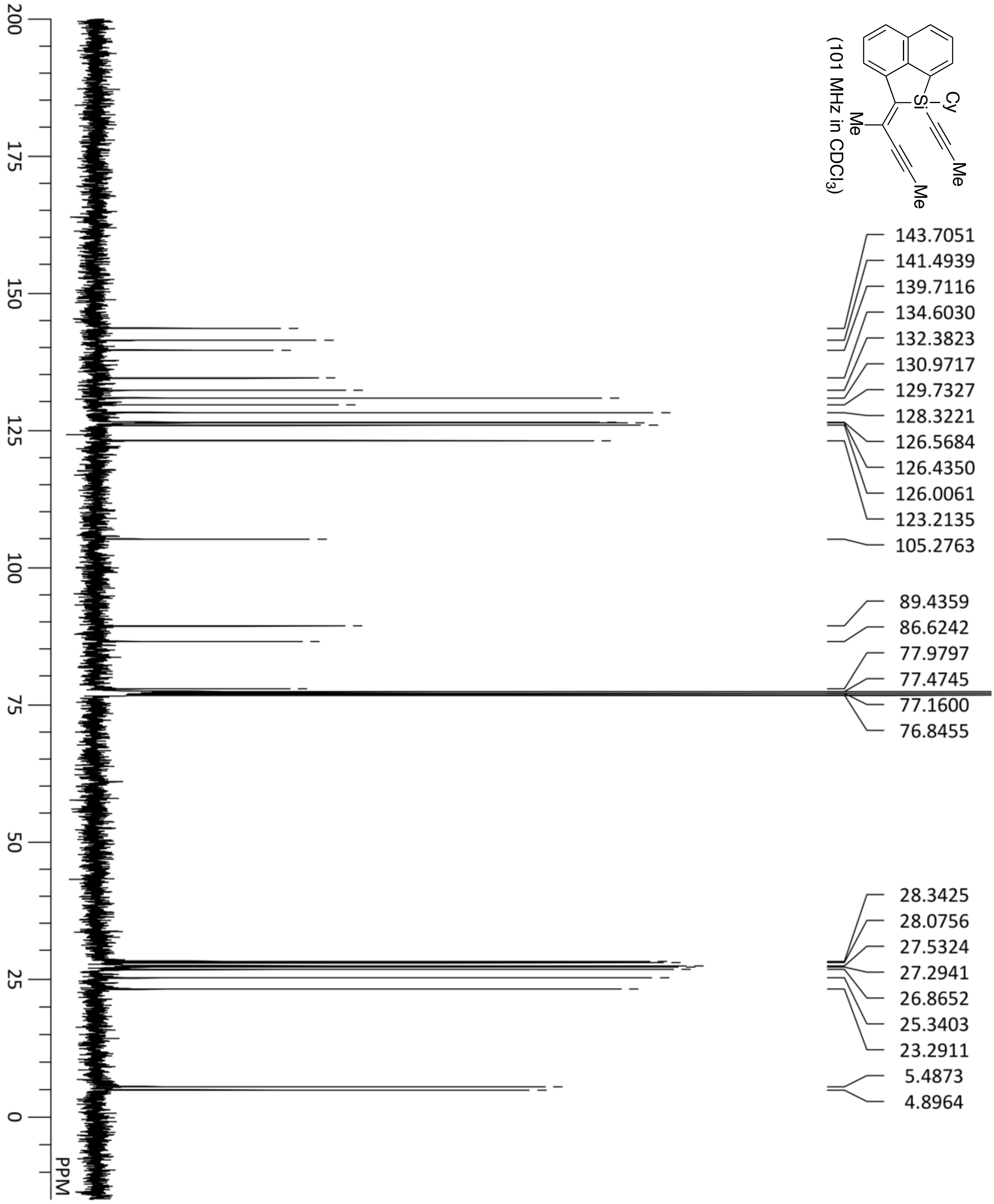

Si
Cy
Ph
Me
Ph
(126 MHz in CDCl$_3$)
200
175
150
125
100
75
50
25
0
PPM
143.9781
141.5154
141.0676
133.8384
132.5023
132.3434
131.7151
131.3974
129.3102
128.7469
128.6313
128.4724
128.2774
128.1763
126.7536
126.6019
126.5658
123.8504
123.6192
123.0920
107.8464
96.2622
92.6729
88.5997
77.4128
77.1600
76.9072
28.2958
27.8408
27.5953
27.2414
26.7936
25.2626
23.3632

compound **3h**

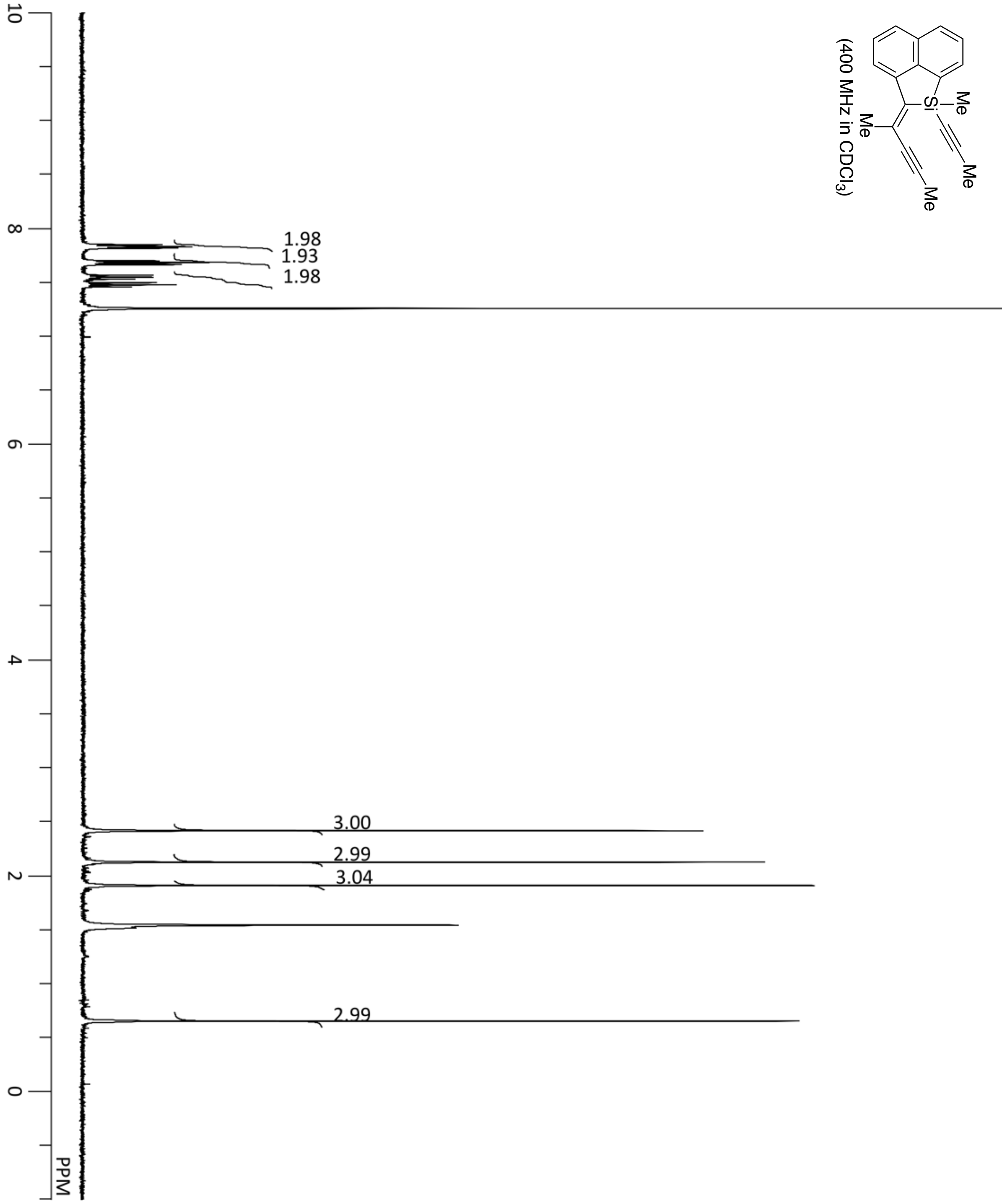


10
8
6
4
2
0
PPM
1.99
1.99
2.06
2.99
3.98
3.00
9.75
1.25
Cy
Si
Me
Me
Me
(400 MHz in CDCl$_3$)

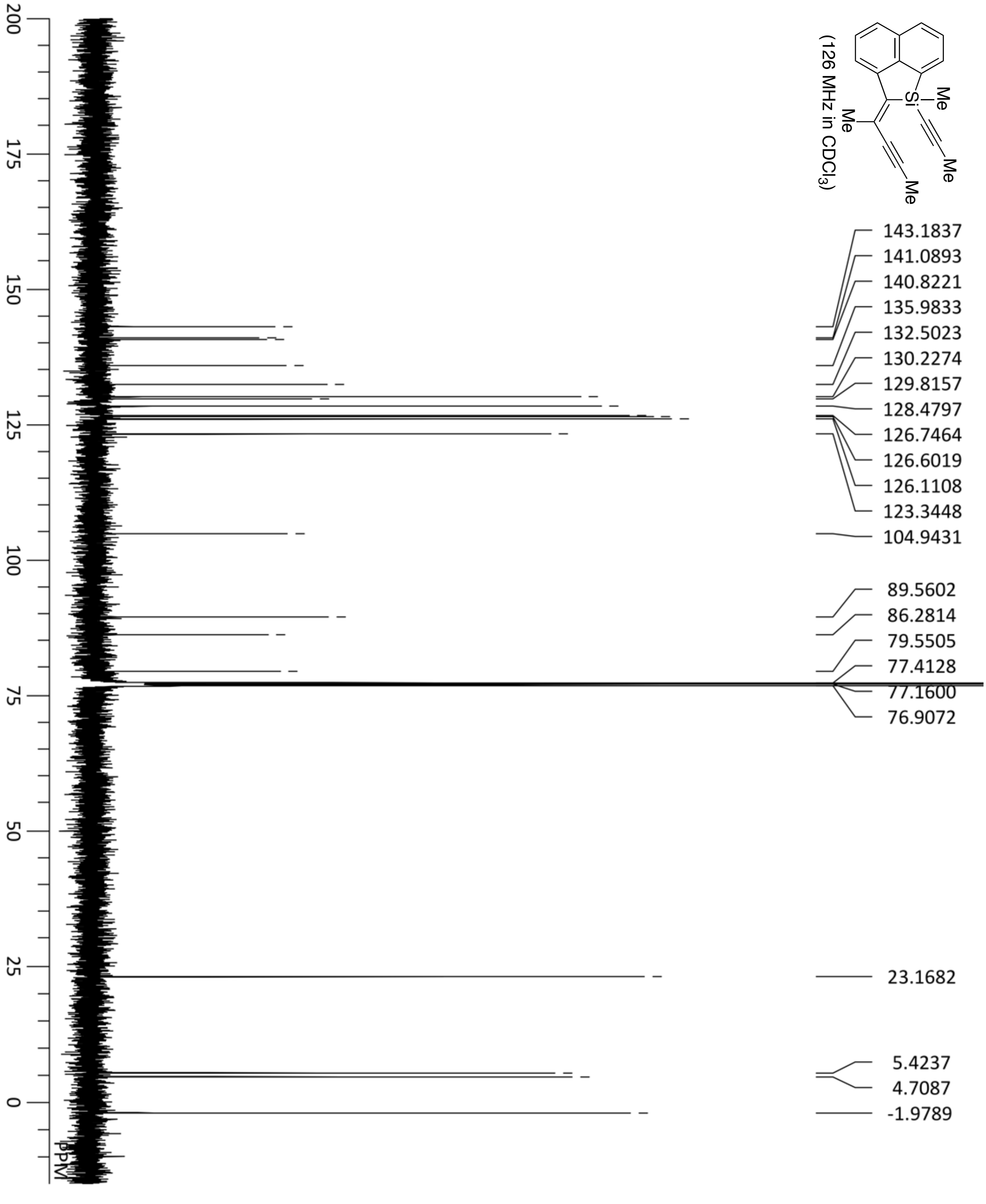
compound **3h**


(101 MHz in CDCl$_3$)
Si
Cy
Me
Me
Me
143.7051
141.4939
139.7116
134.6030
132.3823
130.9717
129.7327
128.3221
126.5684
126.4350
126.0061
123.2135
105.2763
89.4359
86.6242
77.9797
77.4745
77.1600
76.8455
28.3425
28.0756
27.5324
27.2941
26.8652
25.3403
23.2911
5.4873
4.8964
200
175
150
125
100
75
50
25
0
PPM

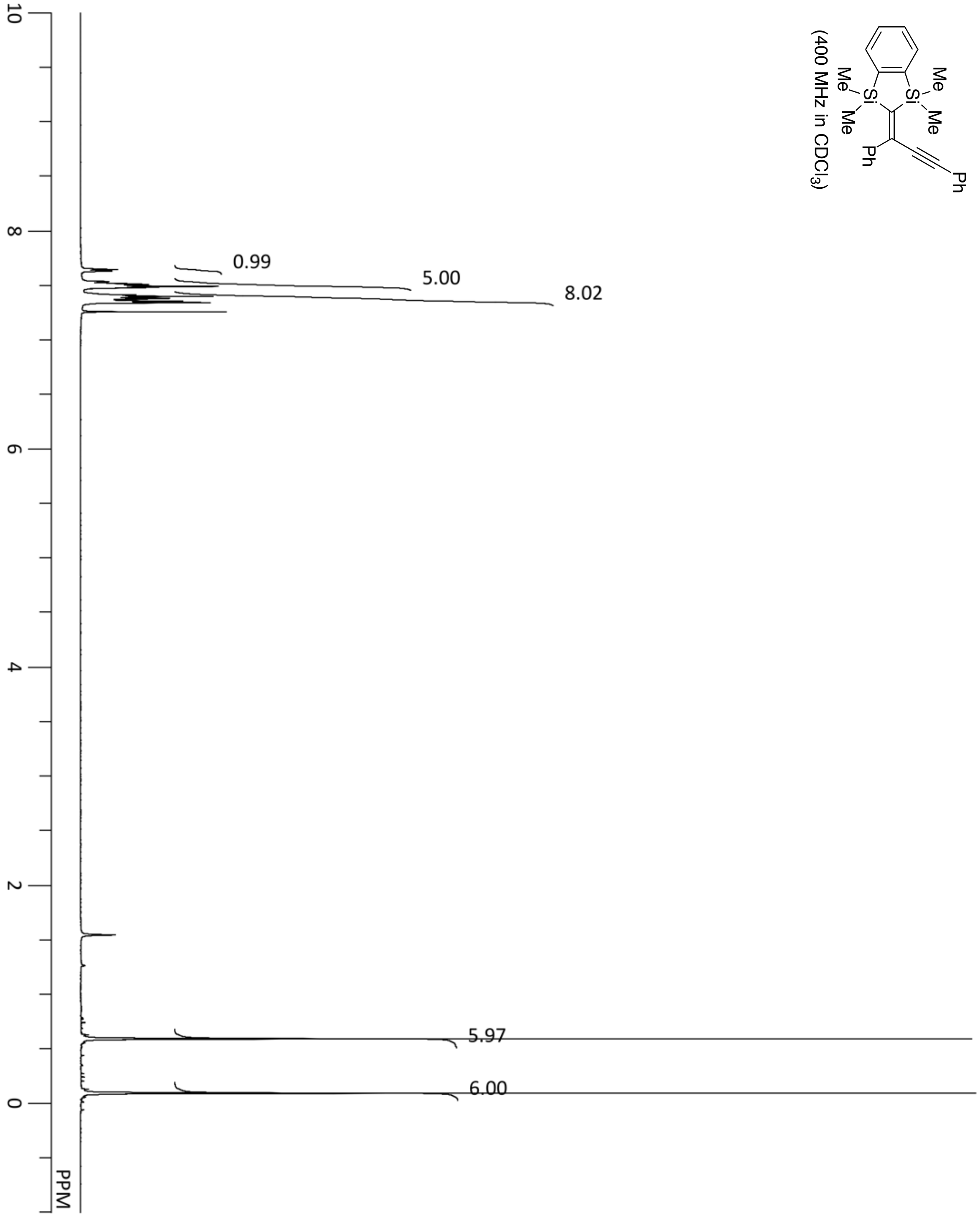
compound **3i**


10
8
6
4
2
0
PPM
1.98
1.93
1.98
3.00
2.99
3.04
2.99
Si
Me
Me
Me
Me
(400 MHz in CDCl3)

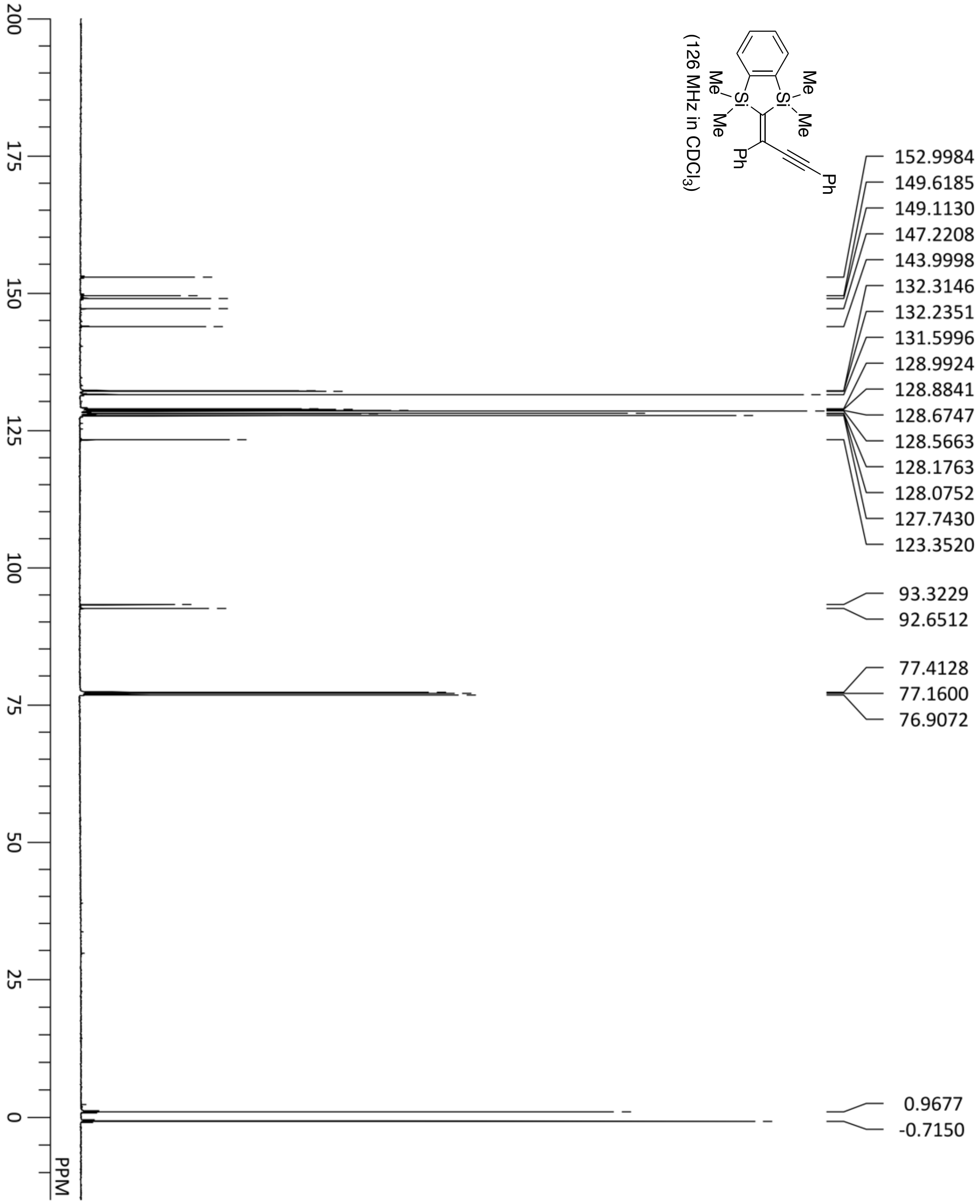
compound **3i**


Me
Si
Me
Me
Me
(126 MHz in CDCl3)
143.1837
141.0893
140.8221
135.9833
132.5023
130.2274
129.8157
128.4797
126.7464
126.6019
126.1108
123.3448
104.9431
89.5602
86.2814
79.5505
77.4128
77.1600
76.9072
23.1682
5.4237
4.7087
-1.9789
200
175
150
125
100
75
50
25
0
PPM

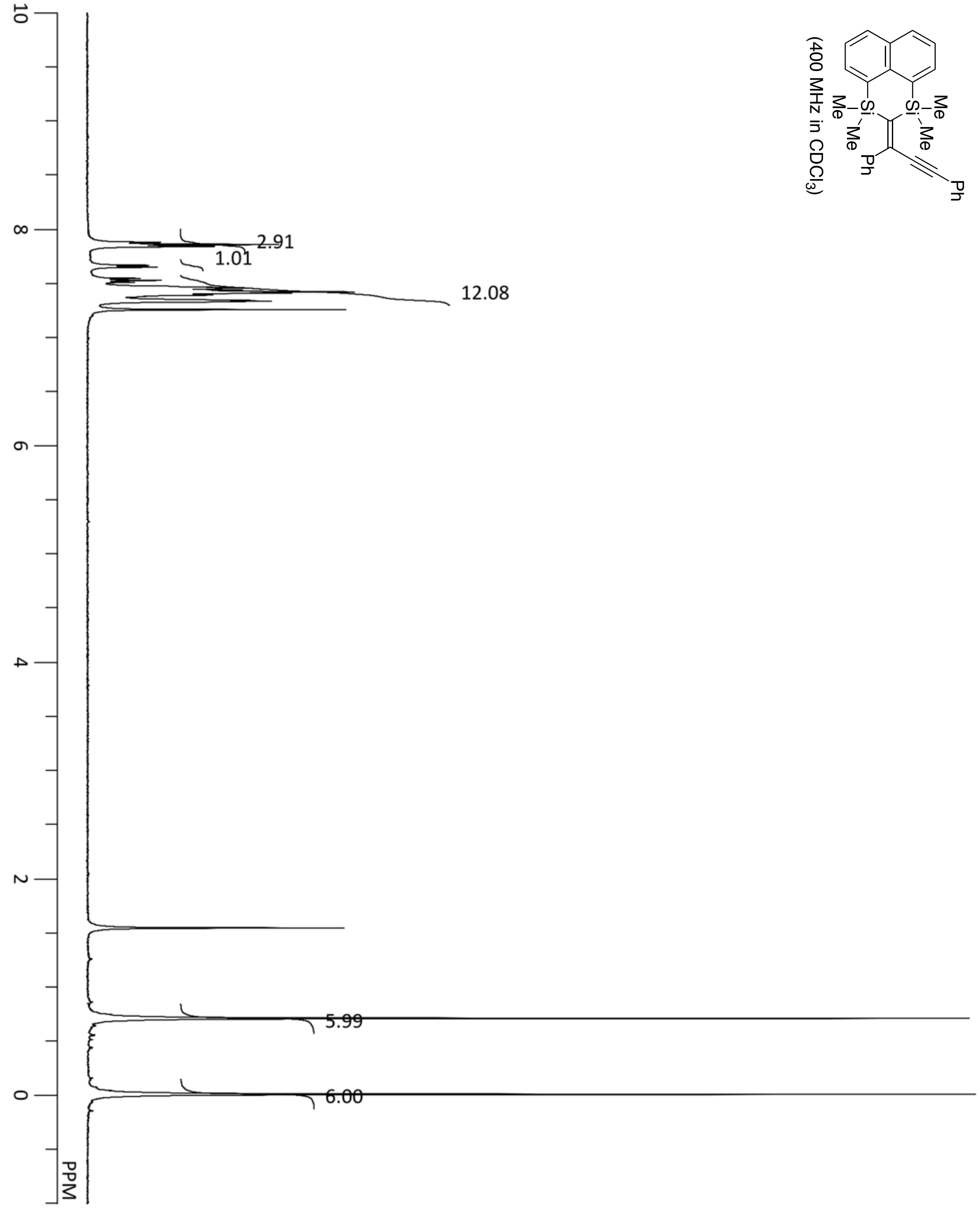
compound **3j**


10
8
6
4
2
0
PPM
0.99
5.00
8.02
5.97
6.00
Me
Si
Me
Me
Si
Me
Ph
Ph
(400 MHz in CDCl3)

compound **3j**

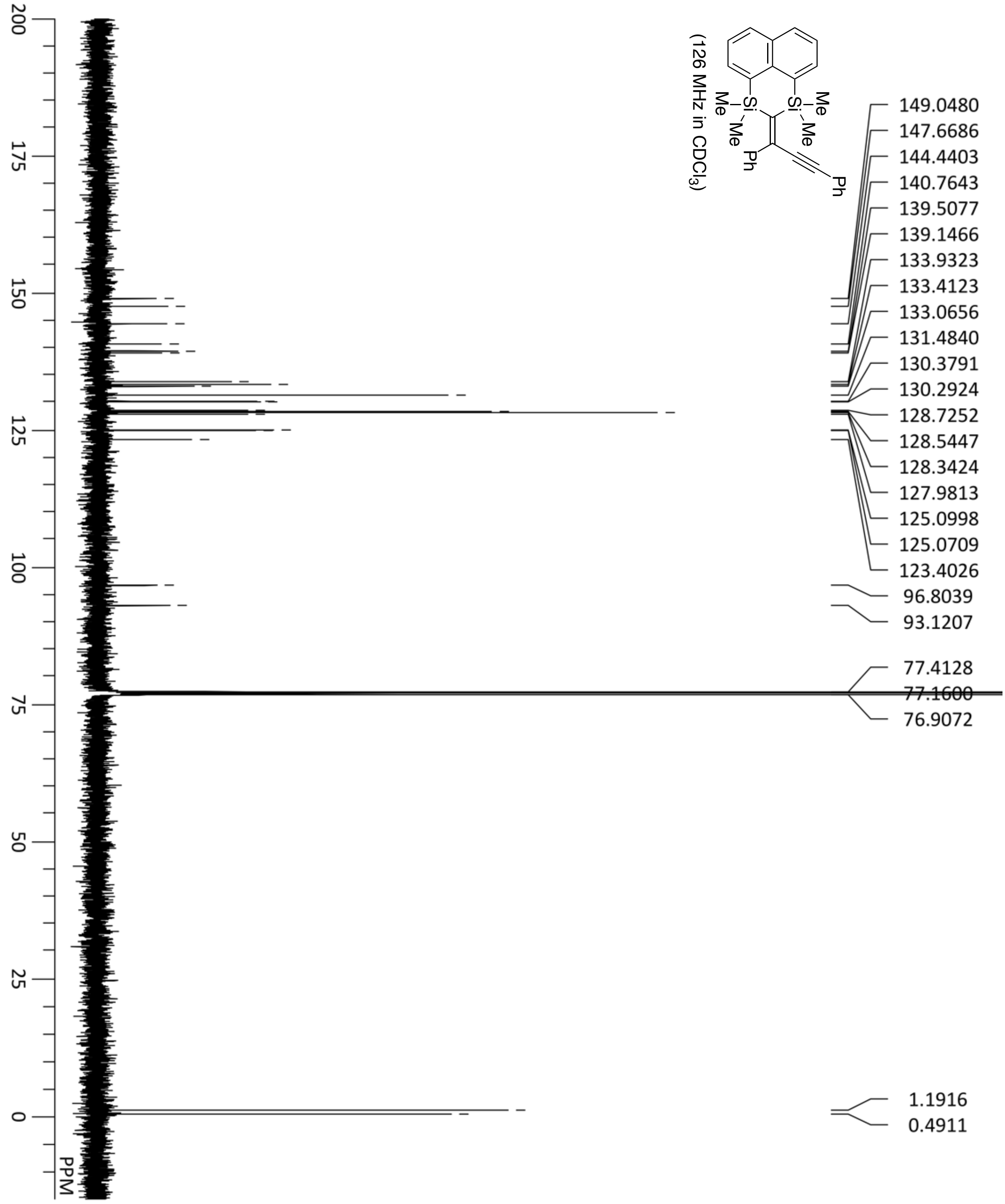

(126 MHz in CDCl3)
Me
Si
Me
Si
Me
Me
Ph
Ph
152.9984
149.6185
149.1130
147.2208
143.9998
132.3146
132.2351
131.5996
128.9924
128.8841
128.6747
128.5663
128.1763
128.0752
127.7430
123.3520
93.3229
92.6512
77.4128
77.1600
76.9072
0.9677
-0.7150
200
175
150
125
100
75
50
25
0
PPM

compound **3k**

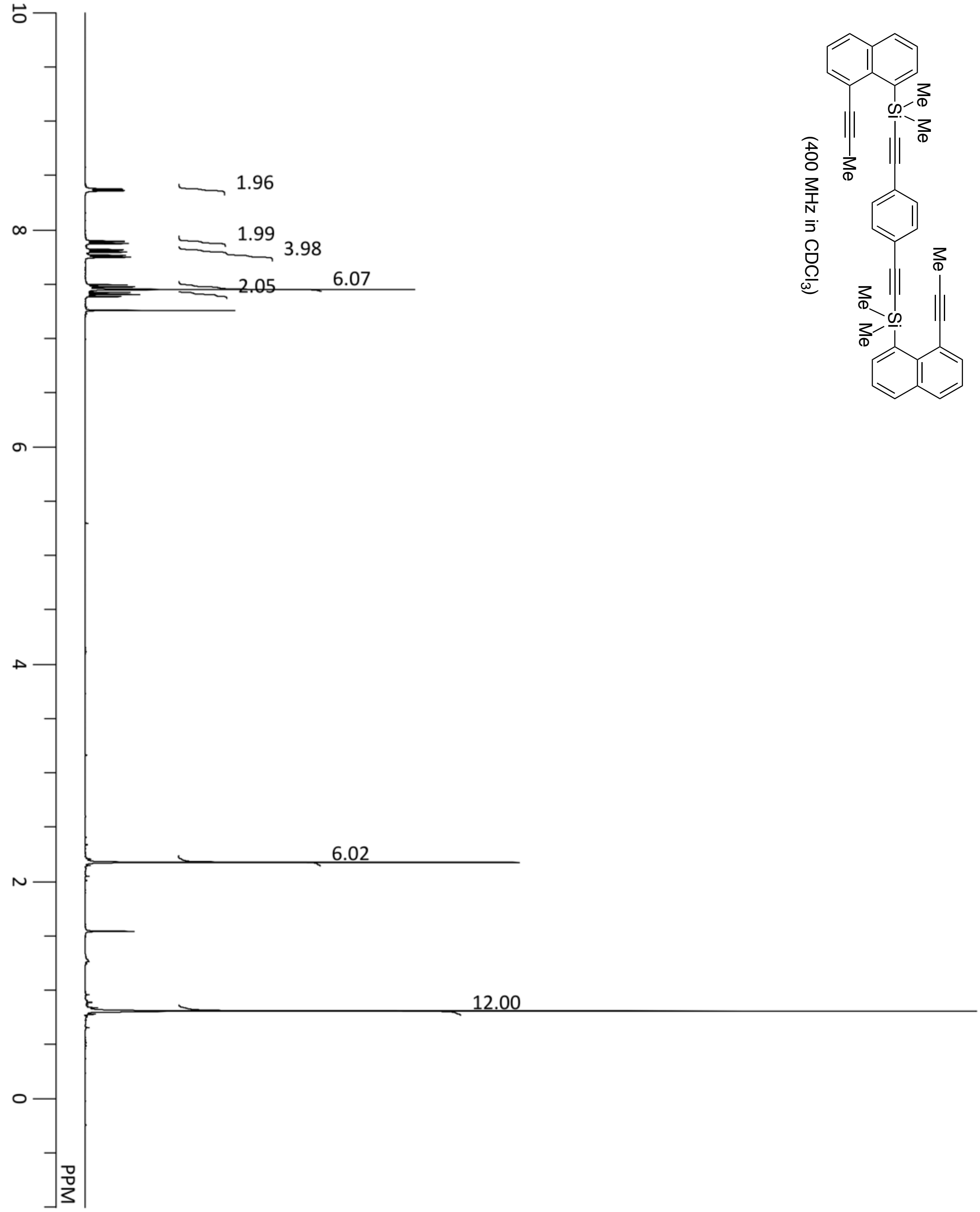


10
8
6
4
2
0
PPM
2.91
1.01
12.08
5.99
6.00
Me
Si
Me
Me
Si
Me
Ph
Ph
(400 MHz in CDCl$_3$)

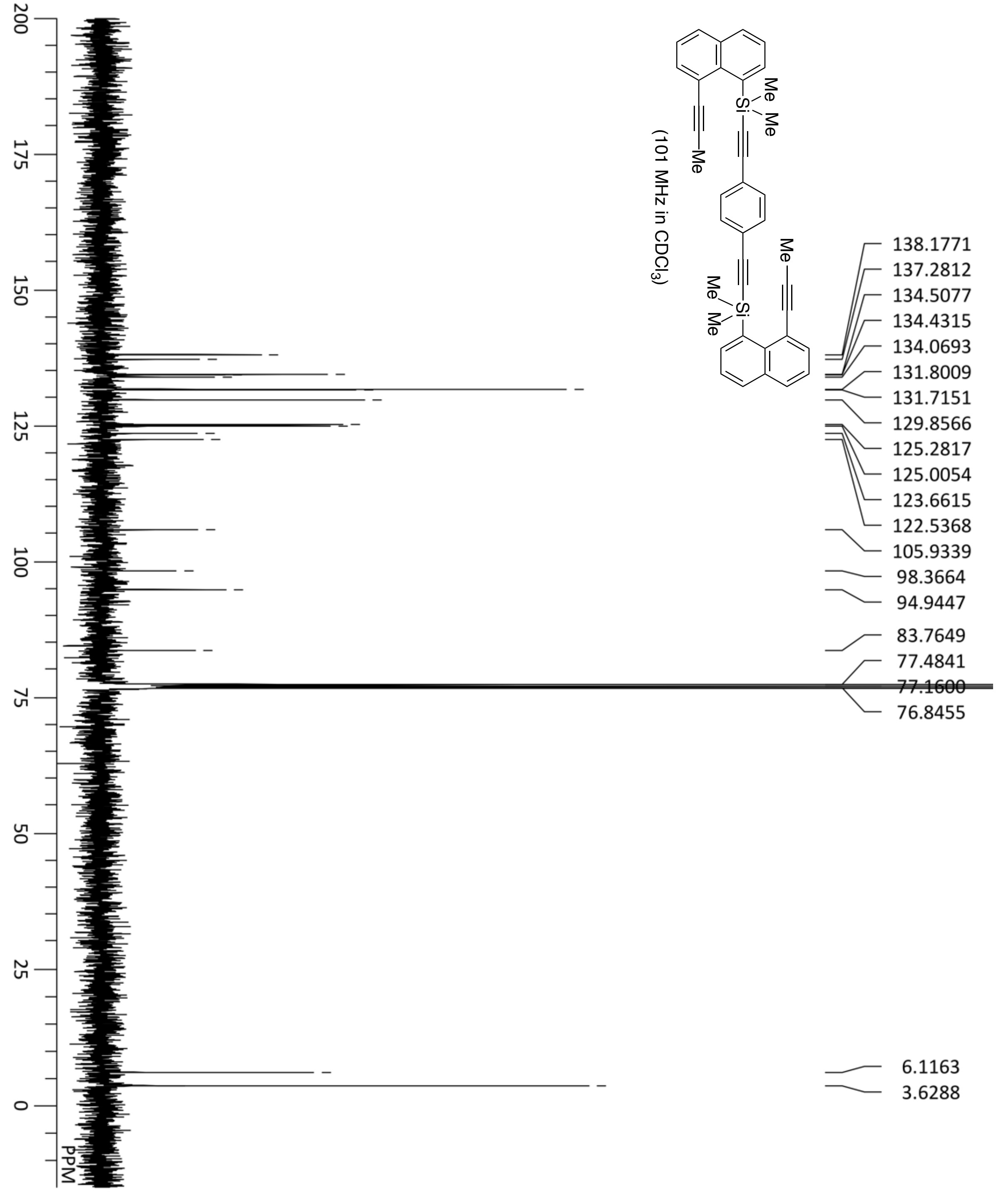
compound **3k**


(126 MHz in CDCl$_3$)

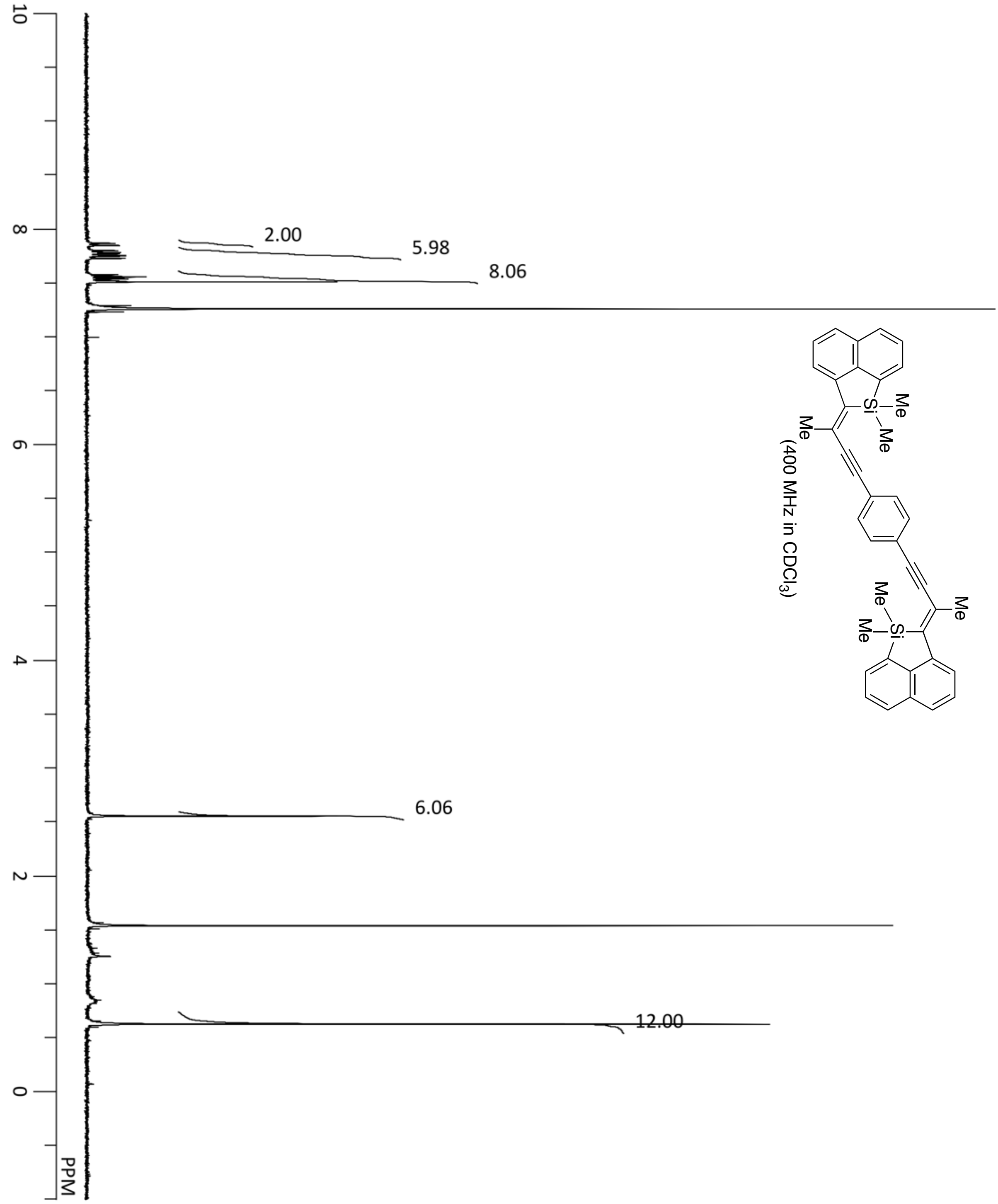
compound **4**


10
8
6
4
2
0
PPM
1.96
1.99
3.98
2.05
6.07
6.02
12.00
Me
Me
Si
Me
Me
Me
Si
Me
Me
(400 MHz in CDCl$_3$)

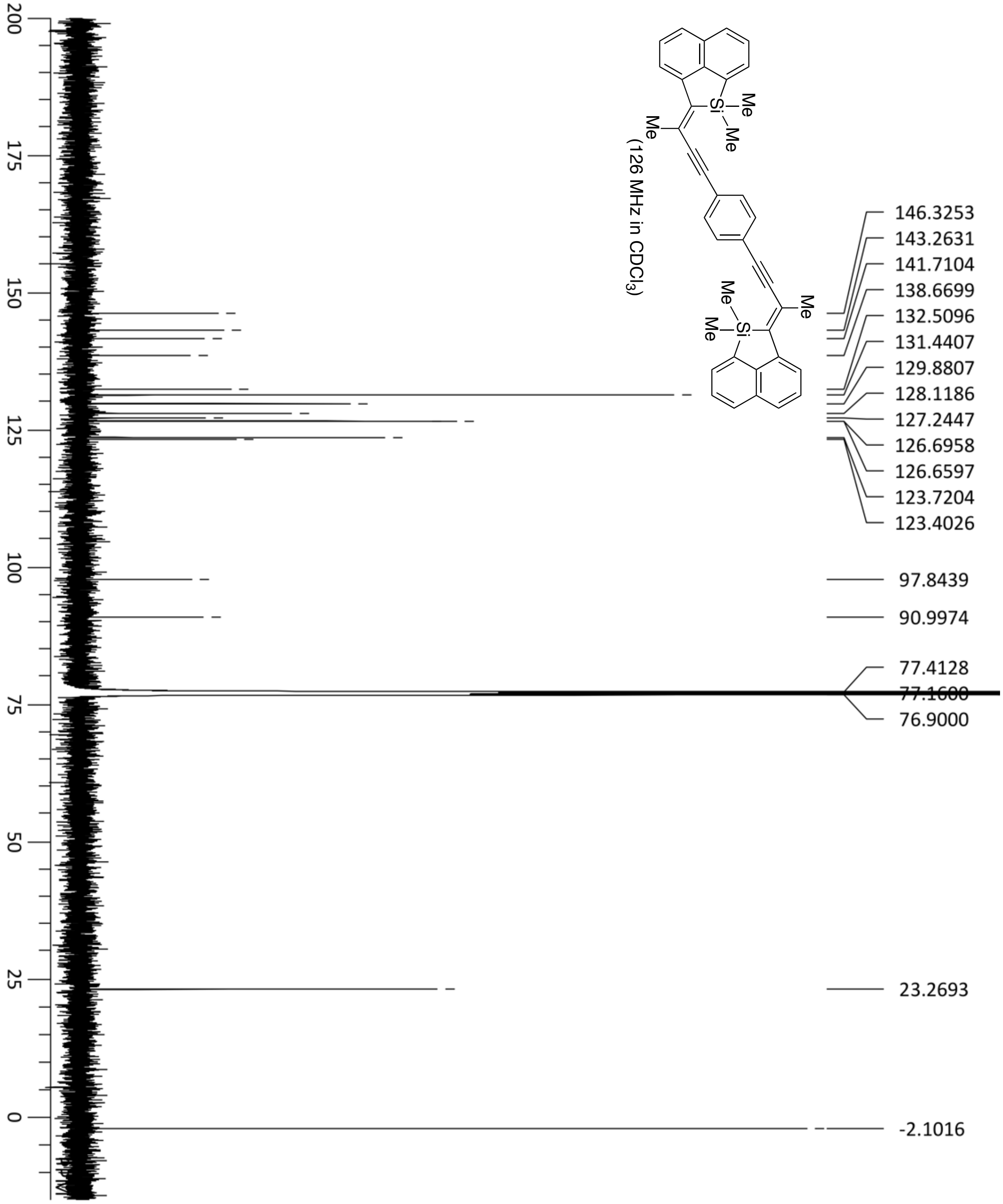
compound **4**


200
175
150
125
100
75
50
25
0
PPM
Me
Me
Si
Me
Me
Me
Si
Me
Me
(101 MHz in CDCl$_3$)
138.1771
137.2812
134.5077
134.4315
134.0693
131.8009
131.7151
129.8566
125.2817
125.0054
123.6615
122.5368
105.9339
98.3664
94.9447
83.7649
77.4841
77.1600
76.8455
6.1163
3.6288

compound **5**


10
8
6
4
2
0
PPM
2.00
5.98
8.06
6.06
12.00
Me
Si
Me
Me
Me
Si
Me
Me
(400 MHz in CDCl$_3$)

compound **5**


(126 MHz in CDCl$_3$)
Si
Me
Me
Me
200
175
150
125
100
75
50
25
0
PPM
146.3253
143.2631
141.7104
138.6699
132.5096
131.4407
129.8807
128.1186
127.2447
126.6958
126.6597
123.7204
123.4026
97.8439
90.9974
77.4128
77.1600
76.9000
23.2693
-2.1016