Rhodium-catalyzed asymmetric synthesis of silicon-stereogenic silicon-bridged arylpyridinones

Ryo Shintani,* Ryo Takano, and Kyoko Nozaki*

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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. Mass spectra were recorded on JEOL AccuTOF LC-plus or Bruker Daltonics autoflex speed spectrometers. Optical rotations were recorded on JASCO P-1030, P-2200, or DIP-1000 polarimeters. 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. CD spectra were recorded on JASCO J-820 Spectropolarimeter. Thermogravimetric analyses were performed with SII Exstar TG/DTA6200 under nitrogen atmosphere.

Et_2O, THF, and CH_2Cl_2 were purified by passing through neutral alumina columns under argon. Et_3N was distilled under vacuum over KOH prior to use. *tert*-Butyltrichlorosilane (Aldrich), ethynylbenzene (TCI), phenyl isocyanate (TCI), 4-methoxyphenyl isocyanate (TCI), 4-bromophenyl isocyanate (TCI), 4-iodophenyl isocyanate (Aldrich), benzyl isocyanate (TCI), ethyl 3-isocyanatopropionate (Acros), methyl 4-iodobenzoate (TCI), (*R*)-binap (TCI), (*R*)-dm-segphos (TCI), *n*-BuLi (Kanto Chemical; 1.64 M solution in hexane), NaH (TCI; 60 wt% in mineral oil), CuI (Kanto Chemical), and K_2CO_3 (Wako Chemicals) were used as received. **1a**,[1] **1b**,[1] **1c**,[1] **1j**,[1] 1-bromo-2-trimethylsilylethynylbenzene,[2] $[RhCl(C_2H_4)_2]_2$,[3] $Pd(PPh_3)_4$,[4] (*R*)-H_8-binap,[5] (*R*)-segphos,[6] (*R*)-MeO-mop,[7] (*R*)-**L**,[8] and sodium tetrakis(3,5-bistrifluoromethylphenyl)borate[9] were synthesized following the literature procedures.

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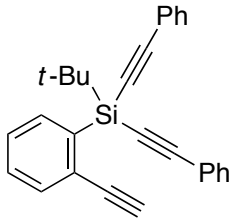
II. Synthesis of Substrates

Representative Procedures for Substrates:
***tert*-Butyl(2-ethynylphenyl)bis(phenylethynyl)silane (1d)**



n-BuLi (6.20 mL, 10.2 mmol; 1.64 M solution in hexane) was added dropwise over 15 min to a solution of 1-bromo-2-trimethylsilylethynylbenzene (2.40 g, 9.48 mmol) in Et_2O (15 mL) at –75 °C and the mixture was stirred for 2 h at –70 °C. The resulting solution was added slowly over 30 min with additional Et_2O (12 mL) to a solution of *tert*-butyltrichlorosilane (2.64 g, 13.8 mmol) in Et_2O (12 mL) at –75 °C. The reaction mixture was stirred for 18 h while gradually raising the temperature to room temperature. The precipitate that formed was filtered off through Celite with Et_2O and the solvent was removed under vacuum. The residue was further dried under vacuum for 1 h at 50 °C to remove excess *tert*-butyltrichlorosilane. Et_2O (30 mL) was then added to the residue and cooled to 0 °C. Phenylethynyllithium [generated by adding *n*-BuLi (17.4 mL, 28.5 mmol; 1.64 M solution in hexane) to ethynylbenzene (3.40 mL, 31.0 mmol) in THF (34 mL) at –60 °C and stirring for 40 min at –55 to –40 °C] was added to it slowly, and the mixture was stirred for 106 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 and then with hexane/Et_2O = 50/1→4/1. The product thus obtained was further purified by GPC with $CHCl_3$ to afford *tert*-butyl(2-trimethylsilylethynylphenyl)bis(phenylethynyl)silane as a white solid (1.60 g, 3.47 mmol, 37% yield).

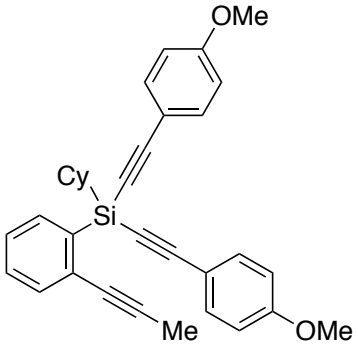
^{1}H NMR ($CDCl_3$): 8.09-8.03 (m, 1H), 7.62-7.53 (m, 5H), 7.41-7.28 (m, 8H), 1.19 (s, 9H), 0.07 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 137.1, 134.3, 133.7, 132.4, 129.8, 129.3, 129.0, 128.3, 127.6, 123.2, 108.2, 106.2, 98.6, 88.5, 27.2, 20.1, –0.2. HRMS (ESI-TOF) calcd for $C_{31}H_{32}Si_2Na$ (M+Na$^+$) 483.1940, found 483.1933.

K_2CO_3 (648 mg, 4.69 mmol) and MeOH (2.0 mL) were added to a solution of *tert*-butyl(2-trimethylsilylethynylphenyl)bis(phenylethynyl)silane (700 mg, 1.52 mmol) in CH_2Cl_2 (2.0 mL) and the mixture was stirred for 4 h at room temperature and for 3 h at 40 °C. The precipitates were filtered off with CH_2Cl_2 and the solvent was removed under vacuum. The residue was chromatographed on silica gel with hexane/EtOAc = 30/1 and then further purified by GPC with $CHCl_3$ to afford compound **1d** as a pale yellow viscous oil (511 mg, 1.32 mmol, 87% yield).

^{1}H NMR ($CDCl_3$): 8.07-8.02 (m, 1H), 7.62-7.54 (m, 5H), 7.43-7.38 (m, 2H), 7.37-7.29 (m, 6H), 3.22 (s, 1H), 1.18 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 137.1, 134.2, 134.1, 132.3, 129.9, 129.0, 128.4, 128.3, 127.9, 123.1, 108.3, 88.2, 85.0, 81.7, 26.9, 20.2. HRMS (ESI-TOF) calcd for $C_{28}H_{24}SiNa$ (M+Na$^+$) 411.1545, found 411.1551.

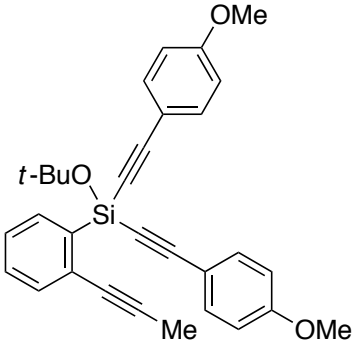
Analytical Data for Other Substrates:

Cyclohexyl(2-(1-propynyl)phenyl)bis(4-methoxyphenylethynyl)silane (1e)



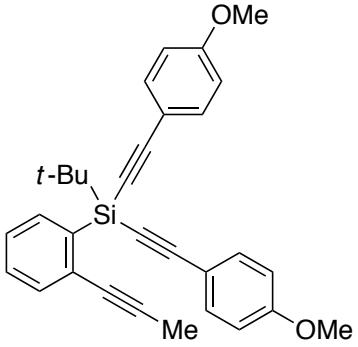
^{1}H NMR ($CDCl_3$): 8.00-7.95 (m, 1H), 7.50 (d, $^3J_{HH}$ = 8.5 Hz, 4H), 7.44-7.39 (m, 1H), 7.37-7.28 (m, 2H), 6.84 (d, $^3J_{HH}$ = 8.6 Hz, 4H), 3.82 (s, 6H), 2.05 (s, 3H), 1.91-1.83 (m, 2H), 1.82-1.68 (m, 3H), 1.48-1.35 (m, 3H), 1.35-1.23 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 160.1, 136.4, 135.0, 133.9, 131.8, 129.8, 129.6, 127.0, 115.3, 113.9, 107.9, 90.7, 86.7, 81.1, 55.4, 28.1, 27.6, 26.9, 25.4, 4.7. HRMS (ESI-TOF) calcd for $C_{33}H_{32}O_2SiNa$ (M+Na$^+$) 511.2069, found 511.2075.

***tert*-Butoxy(2-(1-propynyl)phenyl)bis(4-methoxyphenylethynyl)silane (1f)**



^{1}H NMR ($CDCl_3$): δ 7.98 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.49 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.43 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.35 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.31 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.84 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 3.81 (s, 6H), 2.08 (s, 3H), 1.51 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 160.1, 136.9, 135.3, 133.6, 131.8, 130.1, 129.6, 126.8, 114.9, 113.9, 105.6, 90.7, 89.8, 80.6, 75.2, 55.2, 31.6, 4.7. HRMS (ESI-TOF) calcd for $C_{31}H_{30}O_3SiNa$ (M+Na$^+$) 501.1862, found 501.1847.

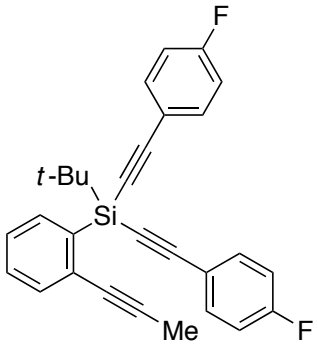
***tert*-Butyl(2-(1-propynyl)phenyl)bis(4-methoxyphenylethynyl)silane (1g)**



^{1}H NMR ($CDCl_3$): δ 8.00 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.51 (d, $^3J_{HH}$ = 8.9 Hz, 4H), 7.43 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.34 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 7.30 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 6.84 (d, $^3J_{HH}$ = 8.9 Hz, 4H), 3.82 (s, 6H), 1.93 (s, 3H), 1.16 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 160.1, 137.0, 134.0, 133.8, 132.5, 130.1, 129.8, 126.7, 115.4,

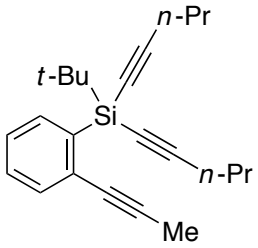
113.9, 107.9, 90.6, 87.0, 81.7, 55.4, 27.0, 20.0, 4.9. HRMS (ESI-TOF) calcd for $C_{31}H_{30}O_2SiNa$ (M+Na$^+$) 485.1913, found 485.1919.

***tert*-Butyl(2-(1-propynyl)phenyl)bis(4-fluorophenylethynyl)silane (1h)**



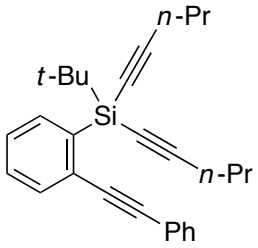
^{1}H NMR ($CDCl_3$): δ 7.97 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.55 (dd, $^3J_{HH}$ = 8.9 Hz and $^4J_{HF}$ = 5.5 Hz, 4H), 7.45 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.36 (td, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.32 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 7.02 (t, ^3J = 8.9 Hz, 4H), 1.93 (s, 3H), 1.16 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 162.9 (d, $^1J_{CF}$ = 250 Hz), 136.9, 134.3 (d, $^3J_{CF}$ = 7.7 Hz), 133.4, 132.6, 130.1, 130.0, 126.8, 119.3 (d, $^4J_{CF}$ = 3.8 Hz), 115.7 (d, $^2J_{CF}$ = 22.0 Hz), 106.7, 90.7, 88.2, 81.6, 26.9, 20.0, 4.8. HRMS (ESI-TOF) calcd for $C_{29}H_{24}F_2SiNa$ (M+Na$^+$) 461.1513, found 461.1507.

***tert*-Butyl(2-(1-propynyl)phenyl)bis(1-pentynyl)silane (1i)**



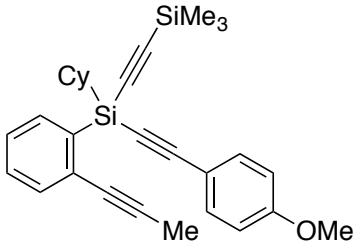
^{1}H NMR ($CDCl_3$): δ 7.91 (dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.39 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.30 (td, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 7.26 (td, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 1.6 Hz, 1H), 2.32 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 2.03 (s, 3H), 1.62 (sext, $^3J_{HH}$ = 7.2 Hz, 4H), 1.041 (s, 9H), 1.039 (t, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 137.0, 134.6, 132.5, 129.9, 129.5, 126.6, 110.0, 90.0, 81.9, 79.2, 26.9, 22.34, 22.26, 19.6, 13.7, 4.8. HRMS (ESI-TOF) calcd for $C_{23}H_{30}SiNa$ (M+Na$^+$) 357.2014, found 357.2014.

***tert*-Butyl(2-(phenylethynyl)phenyl)bis(1-pentynyl)silane (1k)**



^{1}H NMR ($CDCl_3$): δ 7.99 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.64-7.56 (m, 3H), 7.41-7.29 (m, 5H), 2.22 (t, $^3J_{HH}$ = 7.0 Hz, 4H), 1.52 (sext, $^3J_{HH}$ = 7.1 Hz, 4H), 1.12 (s, 9H), 0.96 (t, $^3J_{HH}$ = 7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 137.1, 134.6, 133.2, 131.6, 129.6, 129.1, 128.3, 128.1, 127.2, 124.1, 110.6, 92.7, 91.7, 79.2, 26.9, 22.3, 22.0, 19.6, 13.6. HRMS (ESI-TOF) calcd for $C_{28}H_{32}SiNa$ (M+Na$^+$) 419.2171, found 419.2163.

Cyclohexyl(2-(1-propynyl)phenyl)(4-methoxyphenylethynyl)(trimethylsilylethynyl)silane (1l)



^{1}H NMR ($CDCl_3$): δ 7.91 (dd, $^3J_{HH}$ = 6.8 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.49 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.40 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.36-7.27 (m, 2H), 6.84 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.82 (s, 3H), 2.06 (s, 3H), 1.88-1.66 (m, 5H), 1.43-1.18 (m, 6H), 0.23 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 160.1, 136.4, 134.6, 133.9, 131.8, 129.8, 129.6, 127.0, 117.3, 115.3, 113.9 107.8, 107.2, 90.6, 86.4, 81.1, 55.4, 28.1, 27.5, 27.4, 26.9, 25.1, 4.7, 0.1. HRMS (ESI-TOF) calcd for $C_{29}H_{34}OSi_2Na$ ($M+Na^+$) 477.2046, found 477.2048.

The enantiomers were separated by Daicel Chiralpak IF column with hexane/2-propanol = 100/1 after removal of the trimethylsilyl group. Trimethylsilylation of each enantiomer gave enantiopure (*S*)-(–)-**1l** ($[\alpha]^{20}_D$ –8.4 (*c* 0.96, $CHCl_3$)) and (*R*)-(+)-**1l** ($[\alpha]^{25}_D$ +8.1 (*c* 0.99, $CHCl_3$)), respectively. The absolute configurations were assigned based on the reactivity of rhodium-catalyzed [2 + 2 + 2] cycloaddition with isocyanate **2a** using (*R*)-**L** as the ligand (vide infra).

III. Asymmetric Catalysis, Deprotection, and Polymerization

General Procedure for Table 2 and Equation 4.

A solution of $[RhCl(C_2H_4)_2]_2$ (1.5 mg, 7.7 μmol Rh) and (*R*)-**L** (3.6 mg, 7.5 μmol) in CH_2Cl_2 (0.50 mL) was stirred for 5 min at 25 °C, and a mixture of triyne **1** (0.150 mmol) and $NaBAr^F_4$ (13.3 mg, 15.0 μmol) in CH_2Cl_2 (0.50 mL) was added to it with the aid of additional CH_2Cl_2 (0.50 mL). Isocyanate **2** (0.180 mmol) was then added to it and the reaction mixture was stirred for 16 h at 25 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC to afford compound **3**.

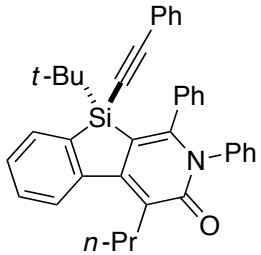


Table 2, Entry 1 (compound 3aa). White solid. 85% yield. The ee was determined on a Daicel Chiralpak IA column with hexane/2-propanol = 95/5, flow = 0.5 mL/min. Retention times: 13.1 min [minor enantiomer], 15.1 min [major enantiomer]. 89% ee. $[\alpha]^{20}_D$ –246 (*c* 0.98, $CHCl_3$). The absolute configuration was determined by X-ray crystallographic analysis after recrystallization from Et_2O/hexane.

^{1}H NMR ($CDCl_3$): δ 8.07 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.84 (dd, $^3J_{HH}$ = 7.3 Hz and $^4J_{HH}$ = 1.2 Hz, 1H), 7.58 (td, $^3J_{HH}$ = 7.7 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.54-7.48 (m, 3H), 7.45 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.40-7.31 (m, 4H), 7.23 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.17-7.10 (m, 2H), 7.08-7.01 (m, 1H), 7.01 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.91 (d, $^3J_{HH}$ = 8.0 Hz, 1H),

6.72-6.60 (m, 1H), 3.15-3.01 (m, 2H), 1.96-1.83 (m, 1H), 1.82-1.69 (m, 1H), 1.15 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.3, 152.2, 150.7, 147.0, 139.7, 139.1, 136.9, 134.5, 132.0, 131.6, 130.7, 130.5, 130.2, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 127.6, 127.5, 127.4, 122.8, 119.0, 110.8, 108.5, 89.6, 30.6, 26.4, 21.0, 18.5, 14.7. HRMS (ESI-TOF) calcd for $C_{38}H_{35}NOSiNa$ (M+Na$^+$) 572.2386, found 572.2385.

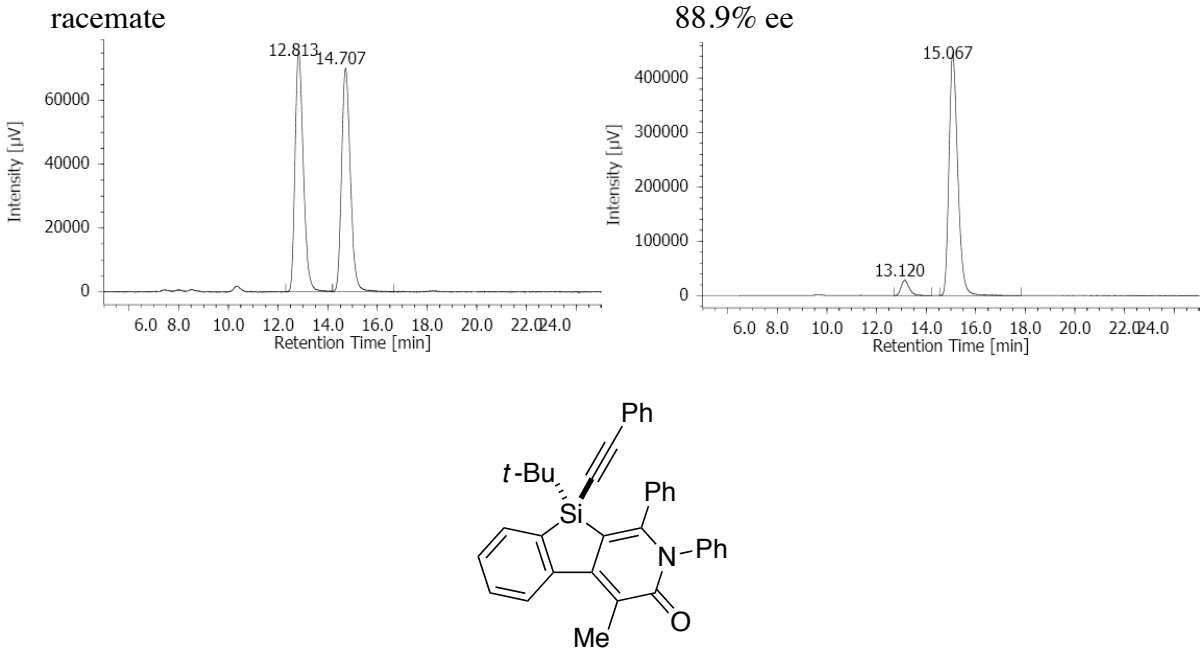
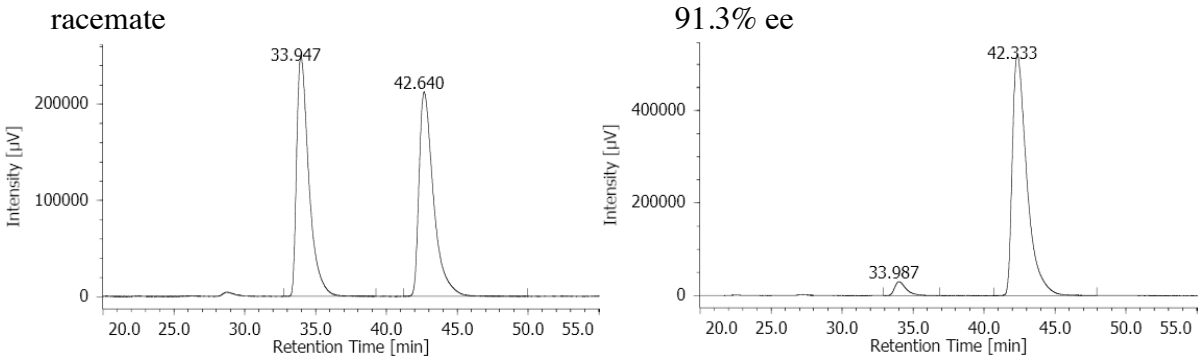


Table 2, Entry 2 (compound 3ba). Pale yellow solid. 84% yield. The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 90/10, flow = 0.5 mL/min. Retention times: 34.0 min [minor enantiomer], 42.3 min [major enantiomer]. 91% ee. $[\alpha]^{25}_D$ – 276 (*c* 1.00, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.24 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.90-7.83 (m, 2H), 7.58 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.53-7.47 (m, 3H), 7.46 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.41-7.32 (m, 4H), 7.23 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.17-7.10 (m, 2H), 7.06 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.02 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.91 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.67 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 2.70 (s, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.4, 152.4, 150.6, 147.7, 139.9, 139.0, 137.0, 134.5, 132.1, 131.6, 130.5, 130.2, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 128.1, 127.6, 127.4, 123.4, 122.8, 110.5, 108.5, 89.5, 26.3, 18.5, 15.4. HRMS (ESI-TOF) calcd for $C_{36}H_{31}NOSiNa$ (M+Na$^+$) 544.2073, found 544.2084.



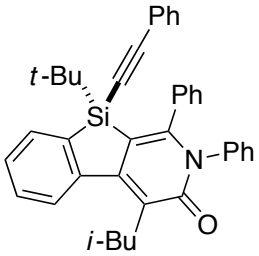
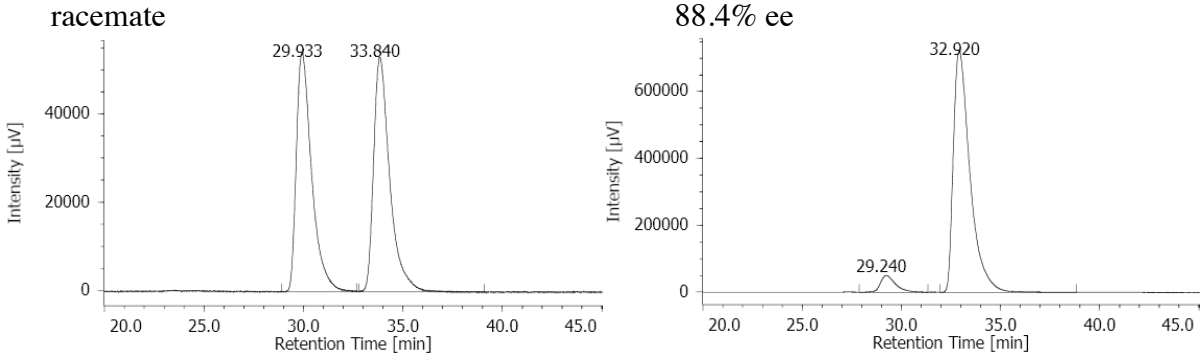


Table 2, Entry 3 (compound 3ca). The reaction was conducted at 35 °C for 37 h. Pale brown solid. 76% yield. The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 95/5, flow = 0.5 mL/min. Retention times: 29.2 min [minor enantiomer], 32.9 min [major enantiomer]. 88% ee. $[\alpha]^{20}_{D}$ –228 (*c* 1.07, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.22 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.89 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.83 (dd, $^3J_{HH}$ = 7.2 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.56 (td, $^3J_{HH}$ = 7.7 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.53-7.46 (m, 3H), 7.44 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.41-7.32 (m, 4H), 7.23 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.11 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.09-7.00 (m, 1H), 7.01 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.92 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.70-6.59 (m, 1H), 3.20 (dd, $^2J_{HH}$ = 14.0 Hz and $^3J_{HH}$ = 7.2 Hz, 1H), 3.16 (dd, $^2J_{HH}$ = 14.1 Hz and $^3J_{HH}$ = 7.2 Hz, 1H), 2.27-2.14 (m, 1H), 1.08 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.03 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.6, 152.5, 150.7, 147.3, 139.9, 139.3, 136.9, 134.5, 132.1, 131.7, 130.6, 130.5, 130.3, 129.1, 128.9, 128.7, 128.5, 128.3, 128.2, 127.9, 127.5, 127.3, 122.9, 119.0, 110.7, 108.5, 89.6, 35.5, 28.2, 26.4, 22.9, 18.5. HRMS (ESI-TOF) calcd for $C_{39}H_{38}NOSi$ ($M+H^+$) 564.2723, found 564.2717.



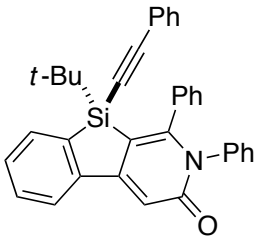
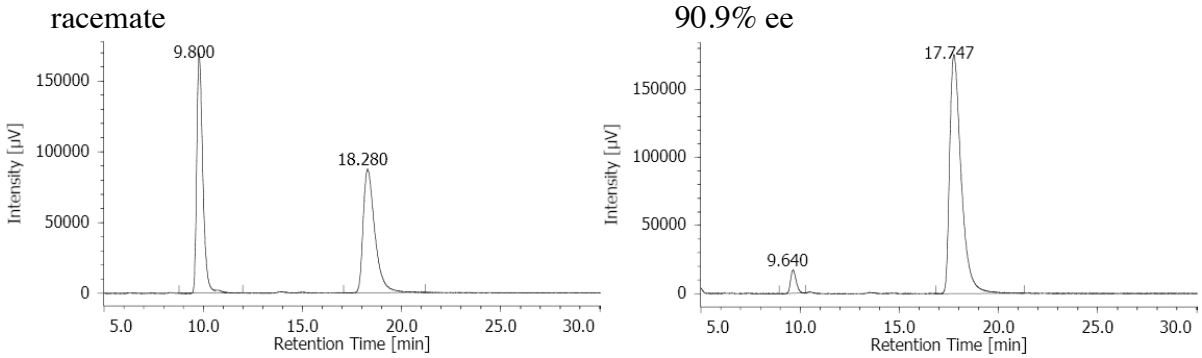


Table 2, Entry 4 (compound 3da). Pale brown solid. 85% yield. The ee was determined on a Daicel Chiralpak IA column with hexane/2-propanol = 80/20, flow = 1.0 mL/min. Retention times: 9.6 min [minor enantiomer], 17.7 min [major enantiomer]. 91% ee. $[\alpha]^{25}_{D}$ –289 (*c* 1.02, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 7.93 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.87 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.80 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 7.56 (td, $^3J_{HH}$ = 7.6 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 7.53-7.44 (m, 4H), 7.42-7.33 (m, 4H), 7.29-7.23 (m, 1H), 7.20-7.13 (m, 3H), 7.10-6.98 (m, 2H), 6.80 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.70 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 0.63 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 164.5, 157.3, 154.8, 145.1, 139.1, 137.7, 137.1, 134.3, 132.1, 131.0, 130.9, 130.2, 130.1, 130.0, 129.3, 129.0,

128.8, 128.6, 128.5, 128.4, 128.3, 127.9, 127.5, 123.1, 122.7, 110.3, 110.0, 108.7, 88.8, 26.2, 18.5. HRMS (ESI-TOF) calcd for $C_{35}H_{29}NOSiNa$ (M+Na$^+$) 530.1916, found 530.1902.



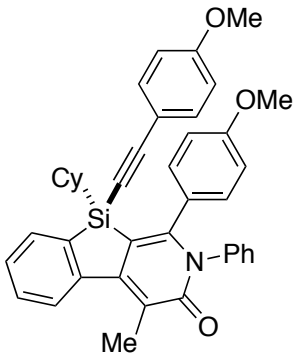
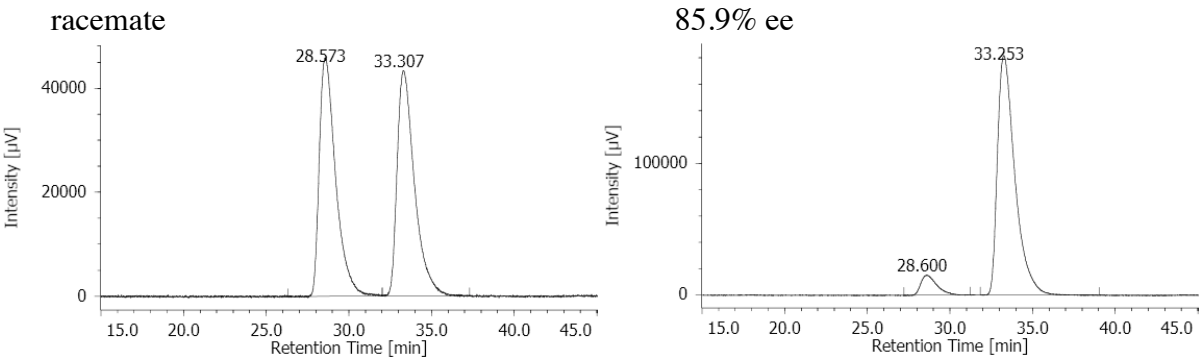


Table 2, Entry 5 (compound 3ea). Pale yellow solid. 83% yield. The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 75/25, flow = 0.5 mL/min. Retention times: 28.6 min [minor enantiomer], 33.3 min [major enantiomer]. 86% ee. $[\alpha]^{20}_{D}$ – 291 (*c* 1.05, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.23 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.80 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.63-7.53 (m, 2H), 7.44 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.39 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 7.35-7.29 (m, 2H), 7.20-7.12 (m, 2H), 6.90-6.81 (m, 2H), 6.83 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 6.72 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 6.62 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 3.82 (s, 3H), 3.73 (s, 3H), 2.67 (s, 3H), 1.75-1.68 (m, 1H), 1.68-1.47 (m, 3H), 1.45-1.38 (m, 1H), 1.29-1.17 (m, 1H), 1.11-0.88 (m, 3H), 0.62-0.50 (m, 1H), 0.48-0.38 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 165.6, 160.1, 159.4, 152.1, 150.0, 147.8, 139.8, 139.2, 134.0, 133.6, 132.1, 130.8, 130.4, 129.6, 129.1, 128.9, 128.8, 128.6, 128.4, 128.1, 127.6, 123.1, 114.9, 113.9, 113.0, 110.7, 108.2, 87.5, 55.4, 55.2, 27.9, 27.6, 26.9, 26.5, 24.4, 15.1. HRMS (ESI-TOF) calcd for $C_{40}H_{37}NO_3SiNa$ (M+Na$^+$) 630.2440, found 630.2450.



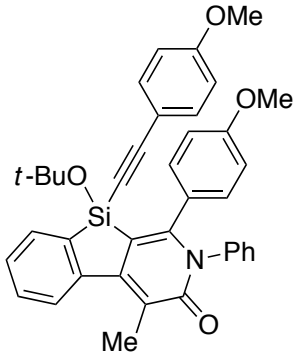
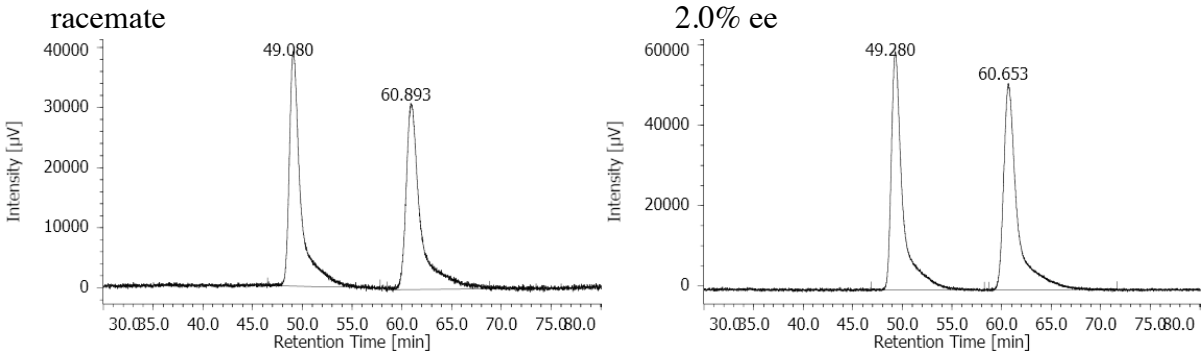


Table 2, Entry 6 (compound 3fa). White solid. 78% yield. The ee was determined on a Daicel Chiralpak IF-3 column with hexane/EtOAc = 70/30, flow = 0.75 mL/min. Retention times: 49.3 min [minor enantiomer], 60.7 min [major enantiomer]. 2% ee. $[\alpha]^{20}_{D}$ –7.4 (*c* 1.01, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 8.22 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.85 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.56 (td, $^3J_{HH}$ = 7.7 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 7.45 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.45-7.06 (m, 8H), 7.00 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 6.80 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.68 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 3.80 (s, 3H), 3.71 (s, 3H), 2.67 (s, 3H), 1.16 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.8, 160.3, 159.3, 150.6, 150.2, 146.4, 140.5, 139.8, 133.6, 133.3, 131.6, 130.8, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 128.1, 127.6, 123.0, 114.6, 113.9, 112.9, 112.1, 106.6, 88.8, 74.9, 55.4, 55.2, 31.6, 15.1. HRMS (ESI-TOF) calcd for $C_{38}H_{36}NO_4Si$ ($M+H^+$) 598.2414, found 598.2403.



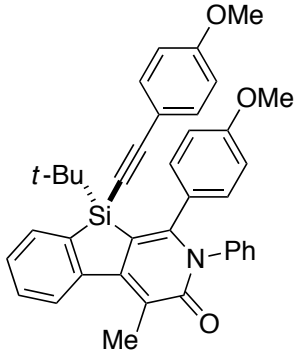
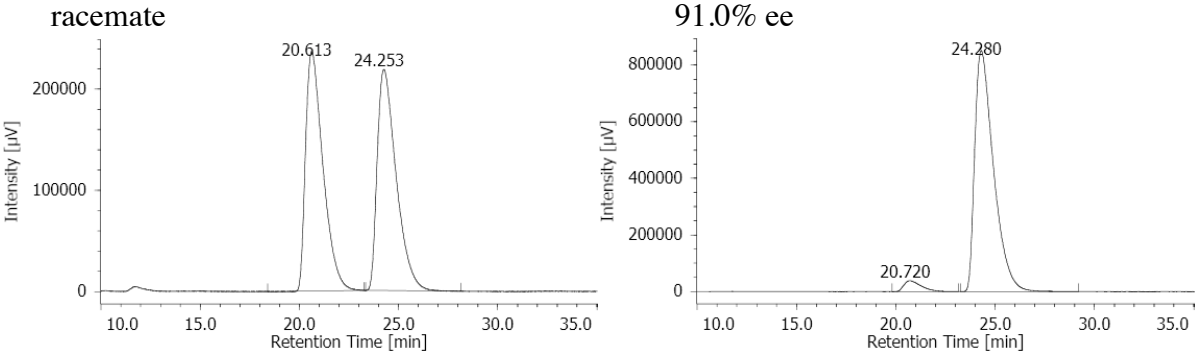


Table 2, Entry 7 (compound 3ga). Pale yellow solid. 94% yield. The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 65/35, flow = 0.5 mL/min. Retention times: 20.7 min [minor enantiomer], 24.3 min [major enantiomer]. 91% ee. $[\alpha]^{20}_{D}$ –383 (*c* 0.98, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.24 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.86 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.81 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.57 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 7.50 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.48-7.42 (m, 3H), 7.38 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.15 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.08 (t, $^3J_{HH}$ = 7.2

Hz, 1H), 6.87 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.83 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 6.72 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 6.67 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 6.55 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 2.70 (s, 3H), 0.68 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.6, 160.3, 159.6, 152.4, 150.4, 147.7, 140.1, 139.3, 134.4, 133.6, 133.1, 131.8, 130.4, 130.2, 129.6, 129.0, 128.7, 128.3, 128.2, 128.1, 127.5, 123.0, 115.0, 114.1, 113.2, 112.9, 110.9, 108.7, 88.0, 55.4, 55.2, 26.4, 18.5, 15.4. HRMS (ESI-TOF) calcd for $C_{38}H_{36}NO_3Si$ ($M+H^+$) 582.2464, found 582.2456.



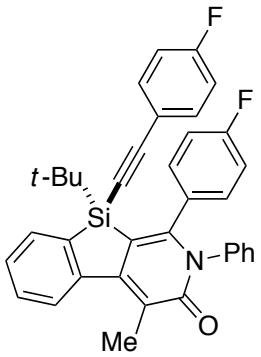
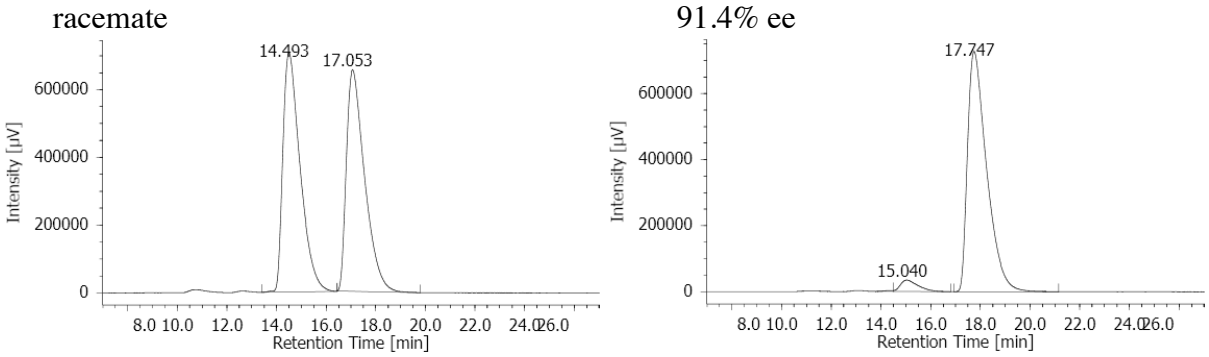


Table 2, Entry 8 (compound 3ha). Pale yellow solid. 90% yield. The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 65/35, flow = 0.5 mL/min. Retention times: 15.0 min [minor enantiomer], 17.7 min [major enantiomer]. 91% ee. $[\alpha]^{20}_D$ – 275 (*c* 1.08, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.24 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.84 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 7.84-7.78 (m, 1H), 7.59 (td, $^3J_{HH}$ = 7.7 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 7.50-7.43 (m, 4H), 7.38 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.17 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.13-7.05 (m, 1H), 7.05 (t, ^3J = 8.7 Hz, 2H), 6.94-6.78 (m, 2H), 6.73 (td, $^3J_{HH}$ = 8.5 Hz and $^4J_{HH}$ = 2.8 Hz, 1H), 6.64 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 2.69 (s, 3H), 0.66 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.4, 163.0 (d, $^1J_{CF}$ = 251 Hz), 162.6 (d, $^1J_{CF}$ = 250 Hz), 152.2, 149.4, 147.6, 139.7, 138.7, 134.4, 134.1 (d, $^3J_{CF}$ = 7.7 Hz), 133.5 (d, $^3J_{CF}$ = 7.7 Hz), 133.1 (d, $^4J_{CF}$ = 2.9 Hz), 132.5 (d, $^3J_{CF}$ = 8.6 Hz), 130.6, 130.1, 129.1, 128.9, 128.4, 128.3, 128.2, 127.8, 123.7, 118.8 (d, $^4J_{CF}$ = 2.9 Hz), 115.9 (d, $^2J_{CF}$ = 23.0 Hz), 114.9 (d, $^2J_{CF}$ = 22.0 Hz), 114.8 (d, $^2J_{CF}$ = 21.1 Hz), 110.7, 107.5, 89.1, 26.4, 18.5, 15.4. HRMS (ESI-TOF) calcd for $C_{36}H_{29}F_2NOSiNa$ ($M+Na^+$) 580.1884, found 580.1898.



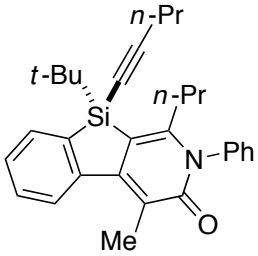
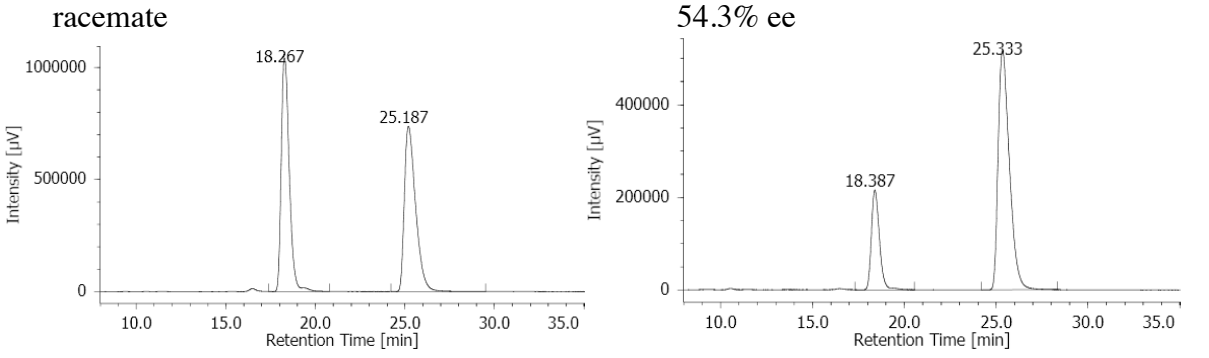


Table 2, Entry 9 (compound 3ia). Pale brown solid. 83% yield. The ee was determined on a Daicel Chiralpak IA column with hexane/2-propanol = 95/5, flow = 0.5 mL/min. Retention times: 18.4 min [minor enantiomer], 25.3 min [major enantiomer]. 54% ee. $[\alpha]^{20}_{D}$ –66.9 (*c* 0.95, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.17 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.81 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 7.55-7.49 (m, 3H), 7.45 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.42 (t, $^3J_{HH}$ = 6.9 Hz, 1H), 7.32-7.24 (m, 2H), 2.67-2.59 (m, 1H), 2.59 (s, 3H), 2.47-2.38 (m, 1H), 2.26 (t, $^3J_{HH}$ = 6.9 Hz, 2H), 1.63-1.51 (m, 3H), 1.36-1.25 (m, 1H), 1.04 (s, 9H), 1.00 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.69 (t, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 166.3, 152.4, 151.0, 147.8, 139.4, 138.9, 133.8, 130.3, 129.4, 129.2, 129.1, 128.6, 128.5, 128.4, 128.0, 121.9, 111.8, 109.0, 77.3, 39.0, 27.2, 23.1, 22.1, 21.9, 19.2, 15.1, 14.1, 13.6. HRMS (ESI-TOF) calcd for $C_{30}H_{35}NOSiNa$ ($M+Na^+$) 476.2386, found 476.2379.



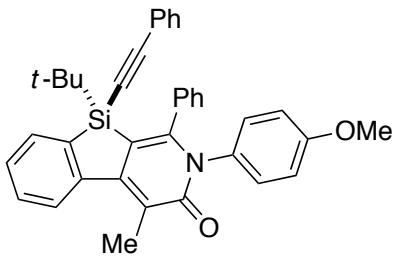
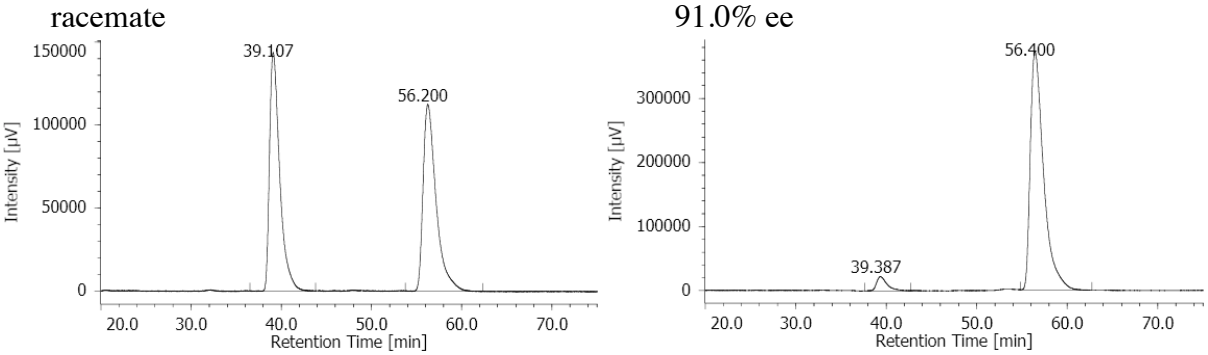


Table 2, Entry 10 (compound 3bb). Pale brown solid. 88% yield (including ca. 3% of inseparable impurity). The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 39.4 min [minor

enantiomer], 56.4 min [major enantiomer]. 91% ee. $[\alpha]^{20}_{D}$ –308 (*c* 1.95, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.24 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.90-7.82 (m, 2H), 7.57 (td, $^3J_{HH}$ = 7.7 Hz and $^4J_{HH}$ = 1.1 Hz, 1H), 7.53-7.48 (m, 2H), 7.45 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.41-7.31 (m, 4H), 7.26-7.20 (m, 1H), 7.16 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.05 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.93 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.88 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 6.61-6.52 (m, 2H), 3.71 (s, 3H), 2.69 (s, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.7, 158.5, 152.3, 151.0, 147.7, 139.0, 137.1, 134.5, 132.6, 132.0, 131.4, 131.0, 130.5, 130.4, 129.3, 129.1, 128.8, 128.7, 128.4, 128.2, 128.1, 127.5, 123.3, 122.8, 114.0, 113.7, 110.4, 108.4, 89.5, 55.4, 26.3, 18.5, 15.5. HRMS (ESI-TOF) calcd for $C_{37}H_{34}NO_2Si$ ($M+H^+$) 552.2359, found 552.2376.



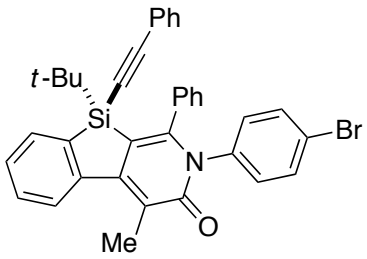
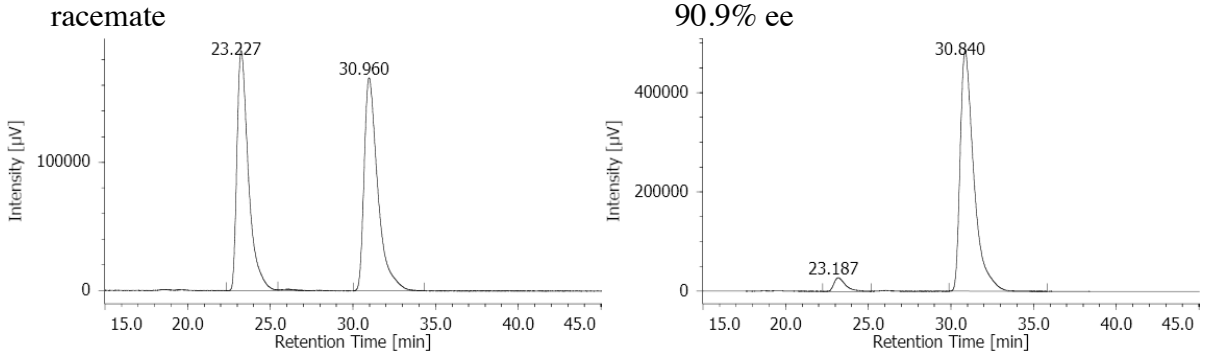


Table 2, Entry 11 (compound 3bc). Pale brown solid. 93% yield. The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 23.2 min [minor enantiomer], 30.8 min [major enantiomer]. 91% ee. $[\alpha]^{25}_{D}$ – 293 (*c* 0.83, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.23 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.90-7.80 (m, 2H), 7.58 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.5 Hz, 1H), 7.54-7.42 (m, 4H), 7.41-7.30 (m, 4H), 7.28-7.22 (m, 1H), 7.22-7.12 (m, 2H), 7.07 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.89 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.53 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 2.68 (s, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.3, 152.6, 150.1, 147.5, 139.0, 138.9, 136.7, 134.5, 132.1, 131.9, 131.5, 130.6, 130.4, 130.0, 129.2, 129.1, 129.0, 128.5, 128.4, 128.2, 127.7, 123.3, 122.8, 121.5, 111.1, 108.6, 89.3, 26.3, 18.5, 15.4. HRMS (ESI-TOF) calcd for $C_{36}H_{31}BrNOSi$ ($M+H^+$) 600.1358, found 600.1379.



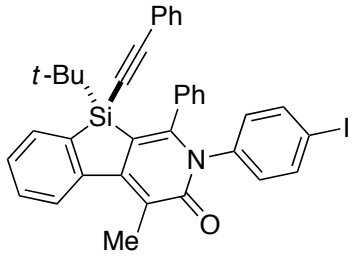
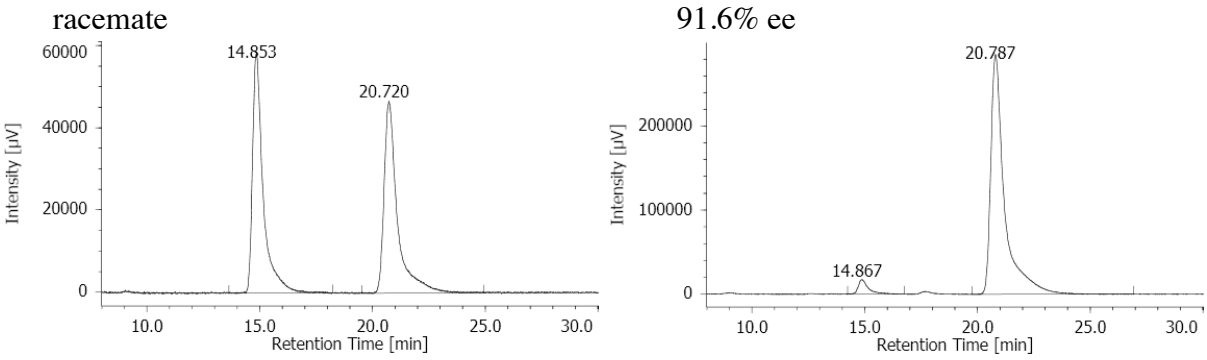


Table 2, Entry 12 (compound 3bd). Pale brown solid. 82% yield. The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 80/20, flow = 0.75 mL/min. Retention times: 14.9 min [minor enantiomer], 20.8 min [major enantiomer]. 92% ee. $[\alpha]^{20}_{D}$ – 275 (*c* 1.00, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.22 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.87 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.85 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.69 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 7.58 (td, $^3J_{HH}$ = 7.8 Hz and $^4J_{HH}$ = 1.3 Hz, 1H), 7.53-7.48 (m, 2H), 7.46 (t, $^3J_{HH}$ = 7.0 Hz, 1H), 7.41-7.32 (m, 4H), 7.28-7.23 (m, 2H), 7.20 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.08 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.89 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.41 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 2.68 (s, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.2, 152.6, 150.1, 147.5, 139.7, 139.0, 138.0, 137.4, 136.7, 134.5, 132.1, 132.0, 131.5, 130.5, 130.4, 130.3, 129.2, 129.0, 128.9, 128.5, 128.4, 128.2, 127.8, 123.3, 122.8, 111.0, 108.6, 93.1, 89.3, 26.3, 18.5, 15.4. HRMS (ESI-TOF) calcd for $C_{36}H_{31}INOSi$ ($M+H^+$) 648.1220, found 648.1225.



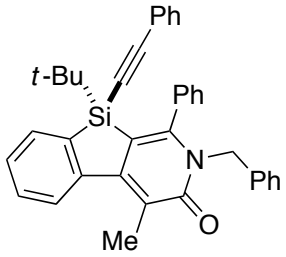
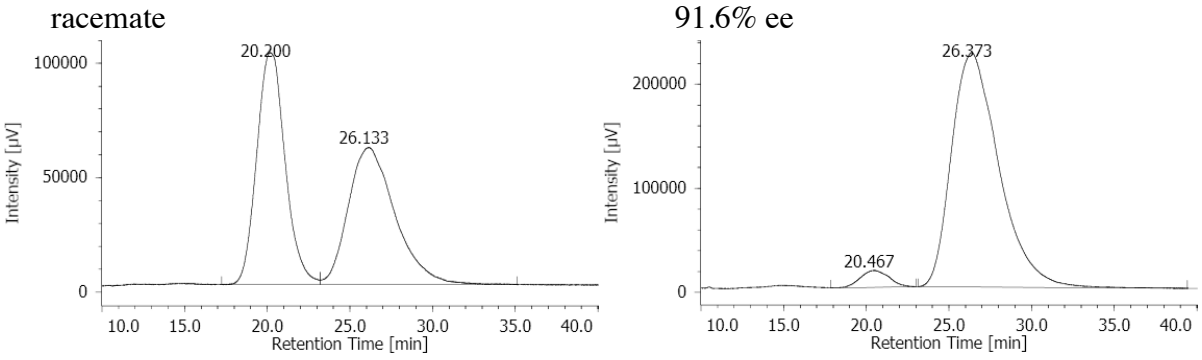


Table 2, Entry 13 (compound 3be). Pale yellow solid. 83% yield. The ee was determined on a Daicel Chiralpak AS-H column with hexane/ethanol = 100/1, flow = 0.8 mL/min. Retention times: 20.5 min [minor enantiomer], 26.4 min [major enantiomer]. 92% ee. $[\alpha]^{20}_{D}$ – 230 (*c* 1.04, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.20 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.81 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 7.61-7.52 (m, 2H), 7.47-7.21 (m, 10H), 7.20-7.12 (m, 3H), 6.92-6.83 (m, 2H), 5.40 (d, $^2J_{HH}$ = 15.2 Hz, 1H), 5.03 (d, $^2J_{HH}$ = 15.1 Hz, 1H), 2.71 (s, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.4, 152.0, 151.0, 147.7, 138.9, 137.7, 136.3, 134.5, 132.0, 131.7, 130.5, 129.6, 129.5, 129.1, 128.8, 128.7, 128.44, 128.36, 128.0, 127.9, 127.04, 126.98, 123.1, 122.8, 111.0, 108.3, 89.2, 49.6, 26.4, 18.4, 15.8. HRMS (ESI-TOF) calcd for $C_{37}H_{34}NOSi$ ($M+H^+$) 536.2410, found 536.2416.



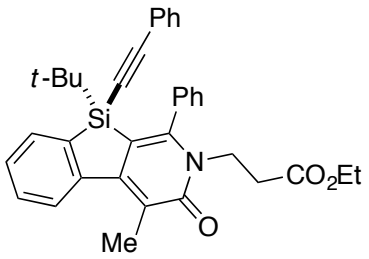
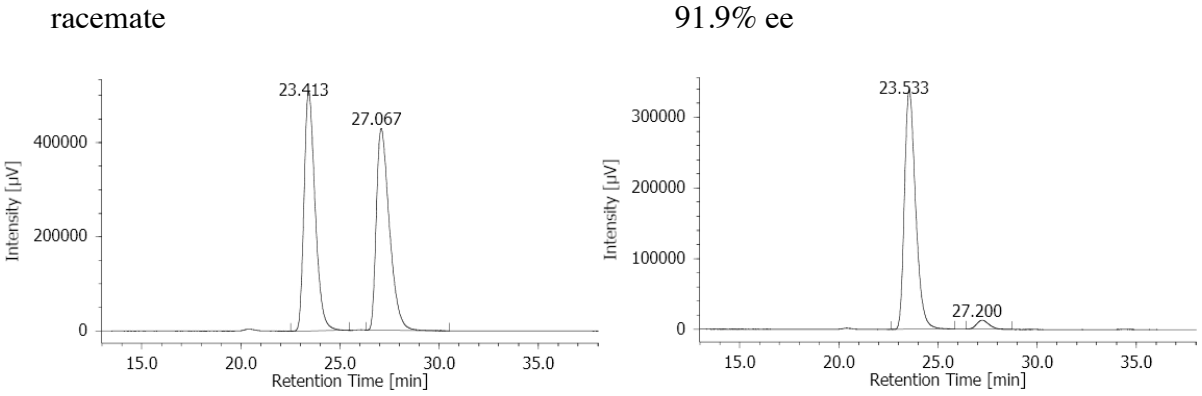
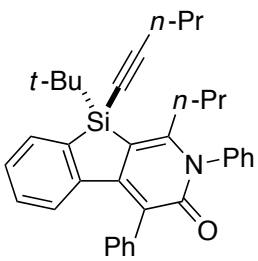


Table 2, Entry 14 (compound 3bf). Yellow solid. 86% yield. The ee was determined on a Daicel Chiralpak IA column with hexane/2-propanol = 95/5, flow = 0.5 mL/min. Retention times: 23.5 min [major enantiomer], 27.2 min [minor enantiomer]. 92% ee. $[\alpha]^{25}_{D}$ –275 (*c* 0.92, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.83-7.76 (m, 2H), 7.54 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.50-7.38 (m, 6H), 7.38-7.30 (m, 4H), 4.23 (ddd, $^2J_{HH}$ = 13.5 Hz and $^3J_{HH}$ = 9.4 and 5.8 Hz, 1H), 4.07 (ddd, $^2J_{HH}$ = 13.5 Hz and $^3J_{HH}$ = 9.2 and 6.6 Hz, 1H), 4.02 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 2.72-2.56 (m, 2H), 2.66 (s, 3H), 1.15 (t, $^3J_{HH}$ = 7.2 Hz, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 171.0, 165.0, 151.9, 150.5, 147.6, 138.8, 136.2, 134.5, 132.0, 131.2, 130.4, 129.8, 129.3, 129.1, 128.7, 128.44, 128.36, 128.0, 122.83, 122.77, 111.1, 108.3, 89.1, 60.6, 42.7, 33.1, 26.4, 18.3, 15.4, 14.1. HRMS (ESI-TOF) calcd for $C_{35}H_{35}NO_3SiNa$ (M+Na$^+$) 568.2284, found 568.2272.

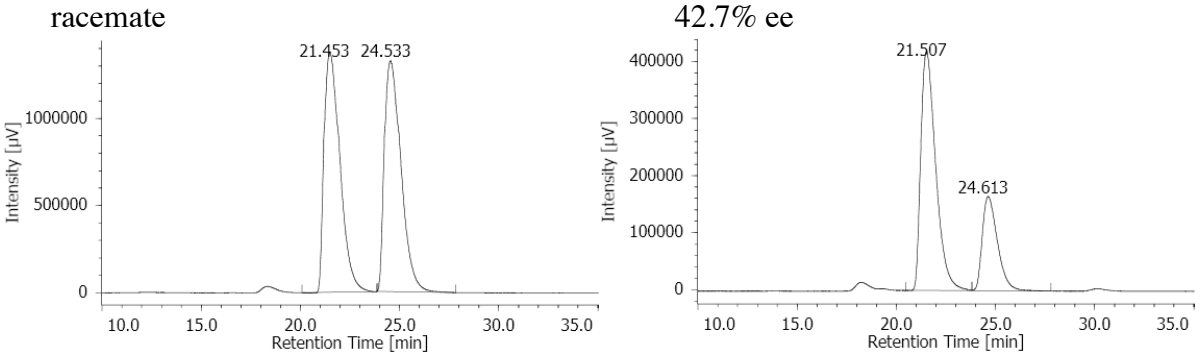




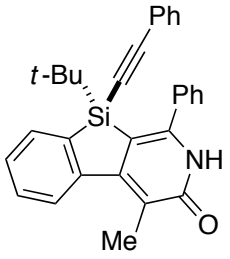
Equation 4 (compound 3ka). Pale yellow solid. 52% yield. The ee was determined on a

Daicel Chiralpak IF-3 column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 21.5 min [major enantiomer], 24.6 min [minor enantiomer]. 43% ee. $[\alpha]^{25}_{D}$ +28.3 (*c* 0.99, $CHCl_3$). The structure was determined by preliminary X-ray crystallographic analysis of the racemic compound. The absolute configuration was assigned by analogy with compound **3aa**.

^{1}H NMR ($CDCl_3$): δ 7.71 (ddd, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.2 Hz, and $^5J_{HH}$ = 0.6 Hz, 1H), 7.52-7.32 (m, 8H), 7.31-7.23 (m, 3H), 7.03 (ddd, $^3J_{HH}$ = 8.2 and 7.3 Hz and $^4J_{HH}$ = 1.4 Hz, 1H), 6.76 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 2.69 (ddd, $^2J_{HH}$ = 13.4 Hz and $^3J_{HH}$ = 11.8 and 5.0 Hz, 1H), 2.49 (ddd, $^2J_{HH}$ = 13.4 Hz and $^3J_{HH}$ = 11.6 and 4.4 Hz, 1H), 2.28 (t, $^3J_{HH}$ = 6.9 Hz, 2H), 1.71-1.52 (m, 3H), 1.46-1.30 (m, 1H), 1.08 (s, 9H), 1.01 (t, $^3J_{HH}$ = 7.3 Hz, 3H), 0.72 (t, $^3J_{HH}$ = 7.3 Hz, 3H). ^{13}C NMR (CD_2Cl_2): δ 165.1, 153.9, 152.9, 146.8, 139.5, 138.3, 133.8, 130.6, 130.5, 130.0, 129.62, 129.56, 129.4, 129.30, 129.26, 129.0, 128.9, 128.8, 128.2, 127.9, 126.2, 112.4, 109.2, 77.3, 39.6, 27.2, 23.3, 22.32, 22.25, 19.3, 14.2, 13.7. HRMS (ESI-TOF) calcd for $C_{35}H_{37}NOSiNa$ (M+Na$^+$) 538.2542, found 538.2543.



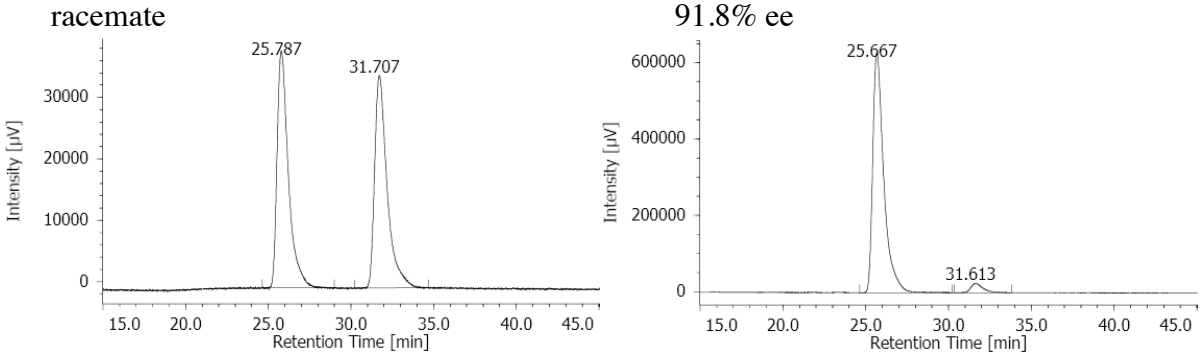
Procedure for Equation 1.



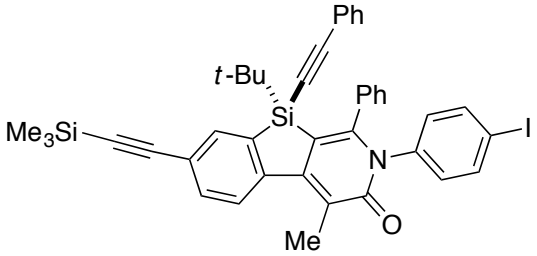
4

A solution of compound **3bf** (91.0 mg, 0.167 mmol; 92% ee) in THF (0.80 mL) was added to a suspension of NaH (13.4 mg, 0.335 mmol; 60 wt% in mineral oil) in THF (0.80 mL) at 0 °C. The mixture was stirred for 3 h at 50 °C and the reaction was quenched with 1 M HClaq (7.5 μL). This was passed through a pad of $MgSO_4$ with Et_2O and then with CH_2Cl_2, and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with CH_2Cl_2/EtOAc = 7/3 to afford compound **4** as a white solid (54.3 mg, 0.122 mmol; 73% yield). The ee was determined on a Daicel Chiralpak IF-3 column with hexane/ethanol = 95/5, flow = 0.8 mL/min. Retention times: 25.7 min [major enantiomer], 31.6 min [minor enantiomer]. 92% ee. $[\alpha]^{25}_{D}$ –193 (*c* 0.99, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 9.57 (bs, 1H), 8.20 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.93-7.87 (m, 2H), 7.85 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.60-7.51 (m, 3H), 7.50-7.42 (m, 4H), 7.41-7.33 (m, 3H), 2.64 (s, 3H), 0.65 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 166.5, 155.1, 149.3, 147.8, 139.1, 137.1, 134.3, 132.1, 130.4, 130.2, 129.5, 129.2, 128.9, 128.8, 128.5, 128.0, 122.8, 122.3, 109.2, 109.0, 89.6, 26.4, 19.0, 14.4. HRMS (ESI-TOF) calcd for $C_{30}H_{27}NOSiNa$ (M+Na$^+$) 468.1760, found 468.1756.



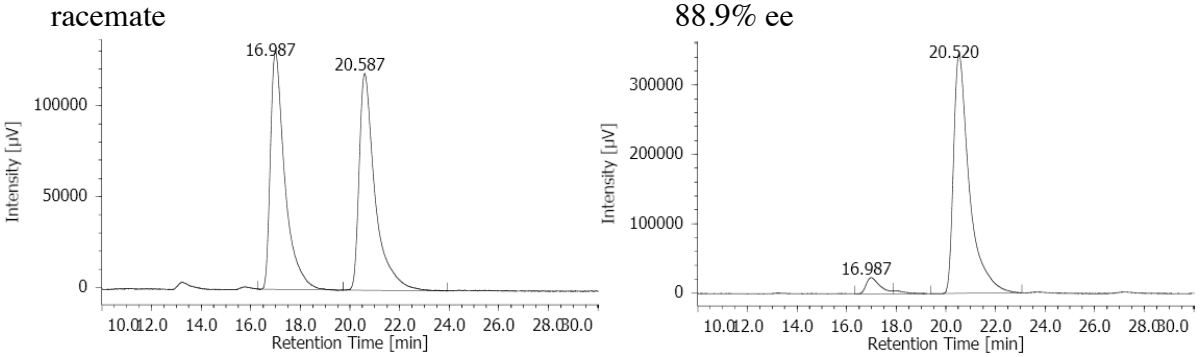
Procedure for Equation 2.

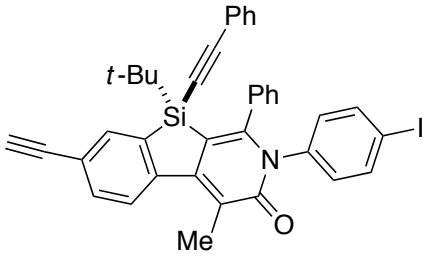


3jd

A solution of $[RhCl(C_2H_4)_2]_2$ (9.8 mg, 50 μmol Rh) and (*R*)-**L** (24.2 mg, 50.1 μmol) in CH_2Cl_2 (3.3 mL) was stirred for 5 min at 25 °C, and a mixture of triyne **1j** (499 mg, 1.00 mmol), isocyanate **2d** (293 mg, 1.20 mmol), and $NaBAr^F_4$ (88.6 mg, 0.100 mmol) in CH_2Cl_2 (4.0 mL) was added to it with the aid of additional CH_2Cl_2 (2.7 mL). The reaction mixture was stirred for 66 h at 30 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2/hexane = 9/1 to afford compound **3jd** as a brown solid (623 mg, 0.837 mmol; 84% yield). The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 80/20, flow = 0.5 mL/min. Retention times: 17.0 min [minor enantiomer], 20.5 min [major enantiomer]. 89% ee. $[\alpha]^{20}_D$ –127 (*c* 1.07, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 8.15 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.89 (d, $^4J_{HH}$ = 1.7 Hz, 1H), 7.85 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.69 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.64 (dd, $^3J_{HH}$ = 8.5 Hz and $^4J_{HH}$ = 1.8 Hz, 1H), 7.55-7.48 (m, 2H), 7.43-7.32 (m, 4H), 7.29-7.22 (m, 2H), 7.19 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.07 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 6.87 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 6.39 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 2.66 (s, 3H), 0.62 (s, 9H), 0.28 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 164.9, 151.6, 150.2, 147.1, 139.4, 139.0, 137.9, 137.5, 137.4, 136.4, 133.9, 132.0, 131.3, 130.2, 129.2, 129.0, 128.4, 128.3, 127.7, 127.6, 123.62, 123.58, 122.5, 110.7, 108.8, 104.9, 96.5, 93.1, 88.8, 26.2, 18.5, 15.4, 0.0. HRMS (ESI-TOF) calcd for $C_{41}H_{38}INOSi_2Na$ ($M+Na^+$) 766.1434, found 766.1413.

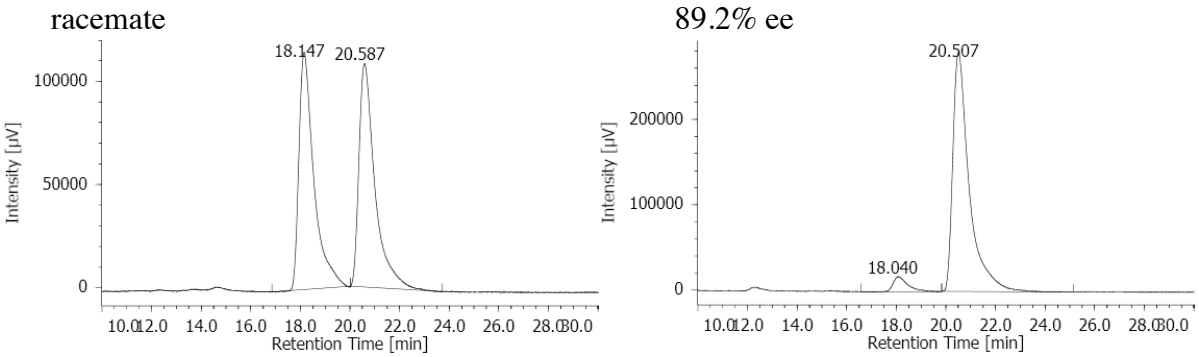




5

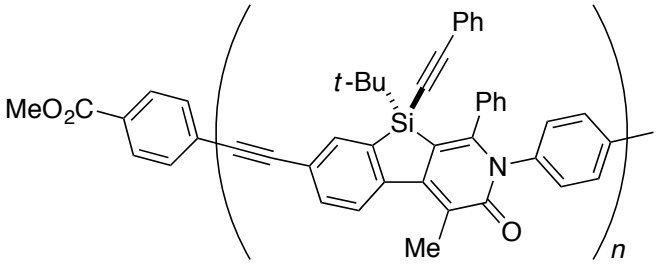
A mixture of compound **3jd** (257 mg, 0.346 mmol; 89% ee) and K_2CO_3 (47.8 mg, 0.346 mmol) in THF (1.4 mL) and MeOH (1.4 mL) was stirred for 1 h at 0 °C. The precipitates were removed by filtration with Et_2O and this was washed with saturated NaClaq. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was chromatographed on silica gel with CH_2Cl_2 to afford compound **5** as a pale yellow solid (222 mg, 0.331 mmol; 96% yield). The ee was determined on a Daicel Chiralpak IF-3 column with hexane/2-propanol = 80/20, flow = 0.75 mL/min. Retention times: 18.0 min [minor enantiomer], 20.5 min [major enantiomer]. 89% ee. $[\alpha]^{25}_D$ –203 (*c* 1.03, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ 8.18 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.94 (d, $^4J_{HH}$ = 1.7 Hz, 1H), 7.86 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.75-7.64 (m, 2H), 7.57-7.48 (m, 2H), 7.44-7.33 (m, 4H), 7.31-7.21 (m, 2H), 7.20 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 7.08 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.88 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 6.47-6.33 (m, 1H), 3.21 (s, 1H), 2.66 (s, 3H), 0.62 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 164.9, 151.5, 150.2, 147.4, 139.4, 139.1, 137.9, 137.7, 137.3, 136.4, 134.0, 132.0, 131.3, 130.2, 129.2, 129.0, 128.4, 128.3, 127.68, 127.66, 123.8, 122.6, 122.4, 110.6, 108.9, 93.1, 88.7, 83.5, 79.3, 26.2, 18.5, 15.4. HRMS (ESI-TOF) calcd for $C_{38}H_{30}INOSiNa$ ($M+Na^+$) 694.1039, found 694.1038.



Recrystallization of compound **5** (200 mg, 0.298 mmol; 89% ee) from MeOH/CH_2Cl_2 preferentially afforded racemic crystals. After removal of the crystals, the mother liquor was concentrated under vacuum (183 mg, 97% ee) and the same recrystallization process was repeated three more times and then this was purified by silica gel preparative TLC with CH_2Cl_2 to afford compound **5** with 99% ee (148 mg, 0.220 mmol; 74% yield). $[\alpha]^{25}_D$ –200 (*c* 1.02, $CHCl_2CHCl_2$).

Procedure for Equation 3.

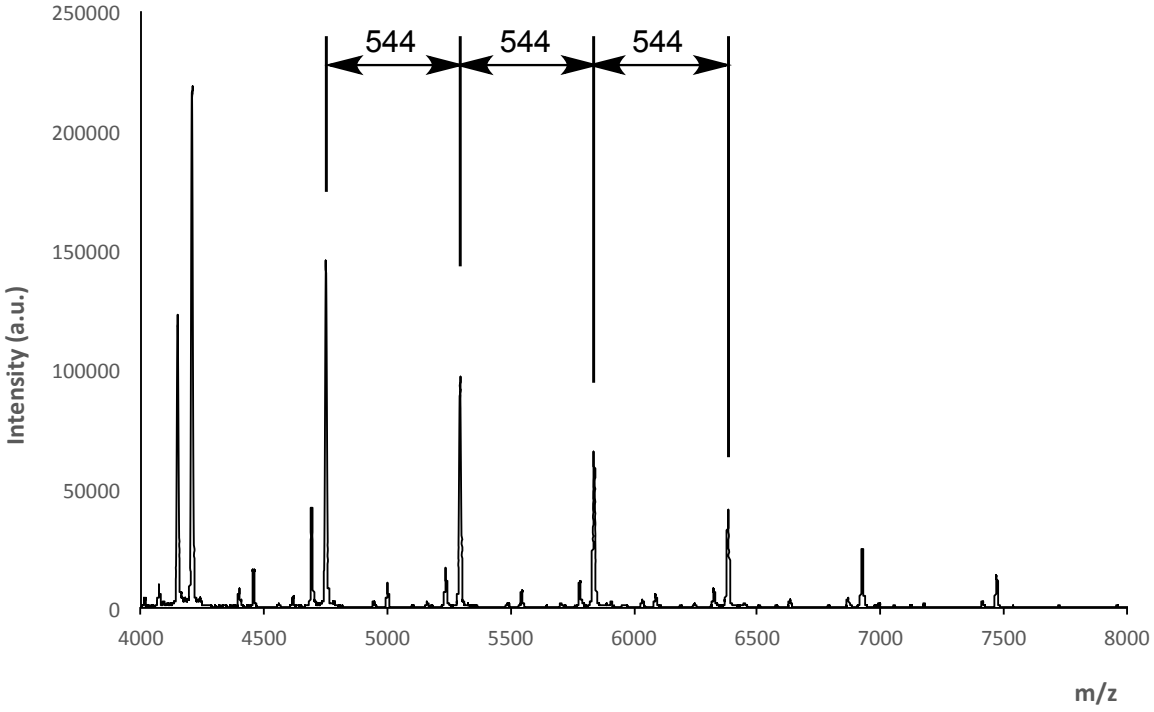


poly-5

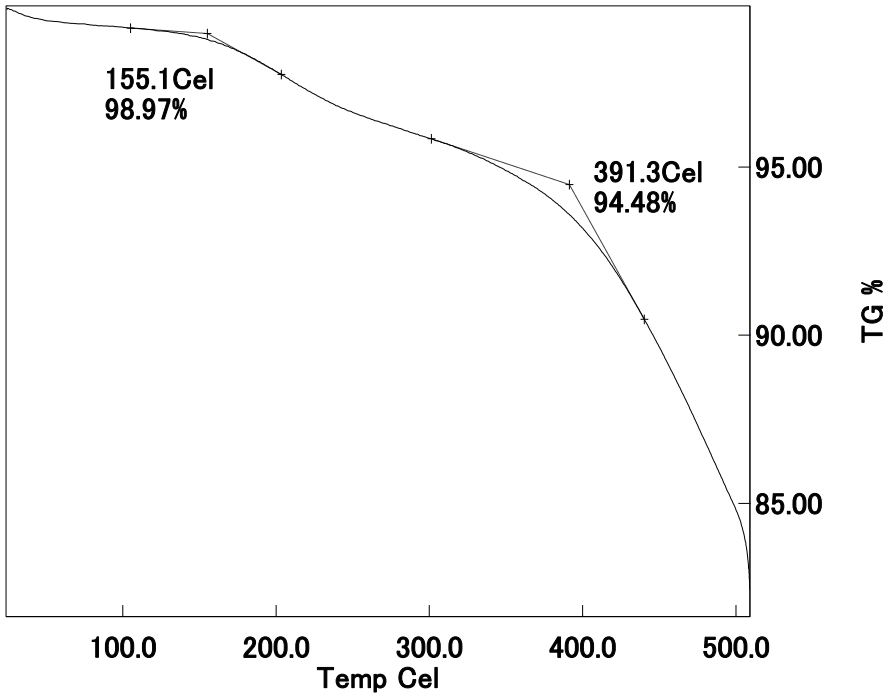
A THF solution (0.50 mL) of methyl 4-iodobenzoate (25.3 mg (96.5 μmol) in 5.0 mL of THF) was added to a mixture of $Pd(PPh_3)_4$ (18.5 mg, 16.0 μmol), CuI (6.2 mg, 33 μmol), and compound **5** (216 mg, 0.322 mmol; 99% ee). Et_3N (180 μL, 1.29 mmol) and THF (1.0 mL) were added to it and the mixture was stirred for 12 h at 60 °C. The reaction mixture was poured into MeOH and the precipitates were collected by filtration. This was dissolved in 1,1,2,2-tetrachloroethane and triturated with MeOH. The precipitates were collected by filtration and washed with hexane to afford **poly-5** as a brown solid (162 mg; 93% yield). $[\alpha]^{25}_{D}$ –282 (*c* 0.76, $CHCl_2CHCl_2$). The degree of polymerization was determined to be 35 (M_n = 19000 g mol^{-1}) by ^1H NMR based on the integration of terminal methyl ester peak versus main chain *tert*-butyl peak.

^1H NMR ($CDCl_2CDCl_2$): δ 8.25 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.00 (s, 1H), 7.90-7.62 (m, 2H), 7.62-7.33 (m, 8H), 7.33-6.83 (m, 5H), 3.99 (s, 0.09H), 2.74 (s, 3H), 0.75 (s, 9H). ^{13}C NMR (major peaks, $CDCl_2CDCl_2$): δ 164.7, 151.3, 150.3, 147.0, 139.9, 139.5, 136.8, 136.5, 133.4, 131.8, 131.5, 130.8, 129.4, 128.9, 128.7, 128.2, 127.7, 127.4, 123.5, 122.7, 122.2, 110.4, 109.0, 90.8, 90.2, 89.0, 26.2, 18.3, 15.1.

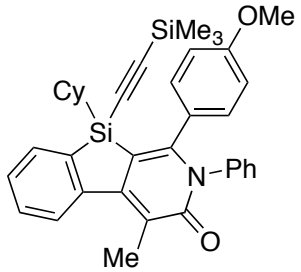
MALDI-TOF MS (DCTB as matrix)



TG (+10 °C/min from 40 °C to 500 °C; 10 min at 500 °C)



Procedure for Equation 5.



3la

A solution of $[RhCl(C_2H_4)_2]_2$ (1.6 mg, 8.2 μmol Rh) and (*R*)-**L** (3.6 mg, 7.5 μmol) in CH_2Cl_2 (0.5 mL) was stirred for 5 min at 25 °C, and a mixture of triyne (±)-**1l** (136 mg, 0.299 mmol) and $NaBAr^F_4$ (13.4 mg, 15.5 μmol) in CH_2Cl_2 (0.50 mL) was added to it with the aid of additional CH_2Cl_2 (0.50 mL). Isocyanate **2a** (16.3 μL, 0.151 mmol) was then added to it and the reaction mixture was stirred for 16 h at 25 °C. This was directly passed through a pad of silica gel with EtOAc and the solvent was removed under vacuum. The residue was purified by silica gel preparative TLC with CH_2Cl_2 to afford compound **3la** as a pale yellow solid (84.0 mg, 0.146 mmol; 97% yield). The ee was determined on a Daicel Chiralpak IA column with hexane/2-propanol = 96/4, flow = 0.75 mL/min. Retention times: 12.6 min, 15.4 min. 0% ee.

^{1}H NMR ($CDCl_3$): δ 8.21 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.75 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.61-7.51 (m, 2H), 7.42 (t, $^3J_{HH}$ = 7.2 Hz, 1H), 7.38-7.29 (m, 2H), 7.23-7.12 (m, 2H), 6.90-6.79 (m, 2H), 6.75 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 6.61 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 3.76 (s, 3H), 2.66 (s, 3H), 1.71-1.43 (m, 4H), 1.40-1.30 (m, 1H), 1.23-0.85 (m, 4H), 0.55-0.42 (m, 1H), 0.38-0.28 (m, 1H), 0.18 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 165.6, 159.4, 152.0, 150.0, 147.8, 139.8, 138.9, 134.0, 132.0, 130.8, 130.4, 129.6, 129.1, 128.9, 128.8, 128.6, 128.4, 128.1, 127.6, 123.0, 117.7, 113.1, 112.9, 110.3, 108.0, 55.2, 27.8, 27.6, 26.7, 26.5, 26.4, 24.1, 15.0, –0.1. HRMS (ESI-TOF) calcd for $C_{36}H_{39}NO_2Si_2Na$ ($M+Na^+$) 596.2417, found 596.2417.

Procedure for Equations 6 and 7.

A solution of $[RhCl(C_2H_4)_2]_2$ (1.9 mg, 9.8 μmol Rh) and (*R*)-**L** (4.8 mg, 9.9 μmol) in CH_2Cl_2 (2.0 mL) was stirred for 10 min at 26 °C. 0.50 mL of this solution was added to a mixture of enantiopure triyne **1l** (45.2 mg, 99.4 μmol), isocyanate **2a** (11.0 μL, 0.102 mmol), $NaBAr^F_4$ (4.4 mg, 5.0 μmol), and 1,3,5-trimethoxybenzene (8.4 mg, 50 μmol; internal standard) in CH_2Cl_2 (5.0 mL) with the aid of additional CH_2Cl_2 (0.50 mL). The resulting mixture was stirred at 26 °C and an aliquot (ca. 0.2 mL) was taken after 6 min. This was immediately quenched with H_2O and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, and concentrated under vacuum. The residue was analyzed by ^1H NMR to determine the reaction progress (production of compound **3la**).

Equation 6 (compound (*R*)-3la). 21% yield. $[\alpha]^{25}_D$ –119 (*c* 1.01, $CHCl_3$). The absolute configuration was assigned by analogy with compound **3aa** based on the reactivity and the sign of optical rotation.

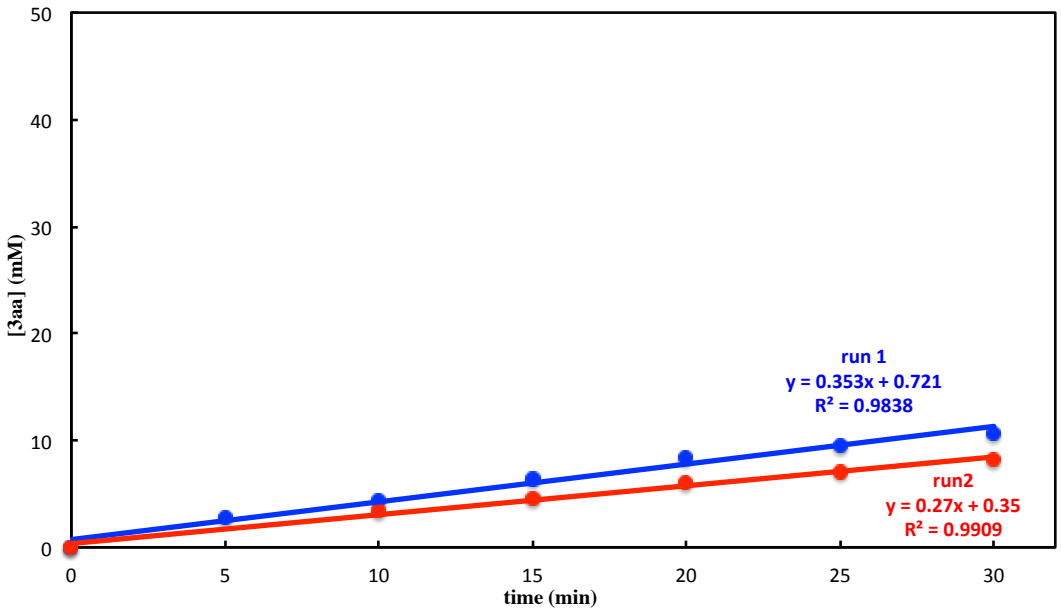
Equation 7 (compound (*S*)-3la). 5% yield. $[\alpha]^{25}_D$ +131 (*c* 1.04, $CHCl_3$).

IV. Kinetic Experiments

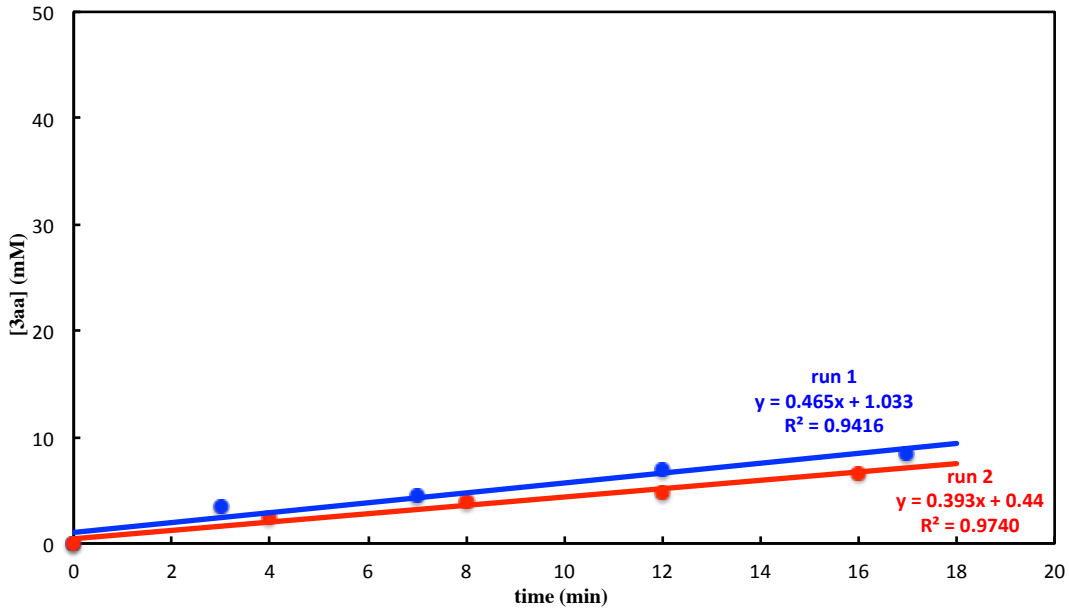
Data Collection for Figure 4.

A solution of $[RhCl(C_2H_4)_2]_2$ (2.1–6.2 μmol Rh), (*R*)-**L** (2.1–6.2 μmol), and 1,3,5-trimethoxybenzene (8.4 mg, 50 μmol; internal standard) in CH_2Cl_2 (2.0 mL) was stirred for 5 min at 28 °C. Triyne **1a** (64.6 mg, 150 μmol) and $NaBAr^F_4$ (4.1–12.3 μmol) were added with the aid of CH_2Cl_2 (0.50 mL), and isocyanate **2a** (16.2 μL, 150 μmol) was subsequently added with additional CH_2Cl_2 (0.50 mL). The resulting mixture was stirred at 28 °C and the aliquots (ca. 0.2 mL each) were taken every few minutes. They were immediately quenched with H_2O and extracted with Et_2O. The organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum. The residues were analyzed by ^1H NMR to determine the reaction progress (production of compound **3aa**). Each experiment was carried out twice.

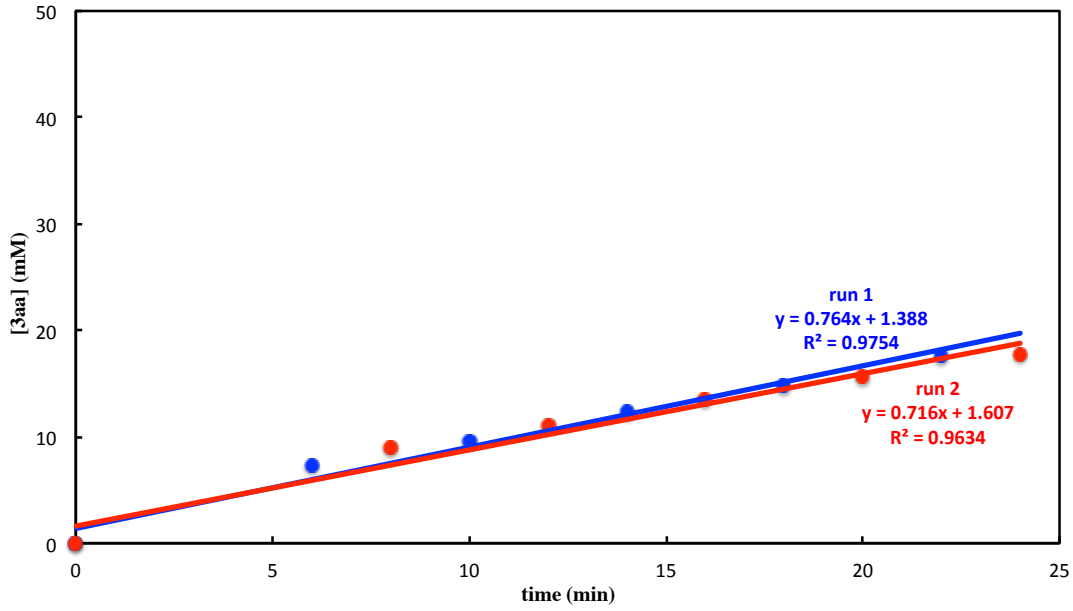
2.1 μmol of Rh: initial rate = 0.312 (mM/min)



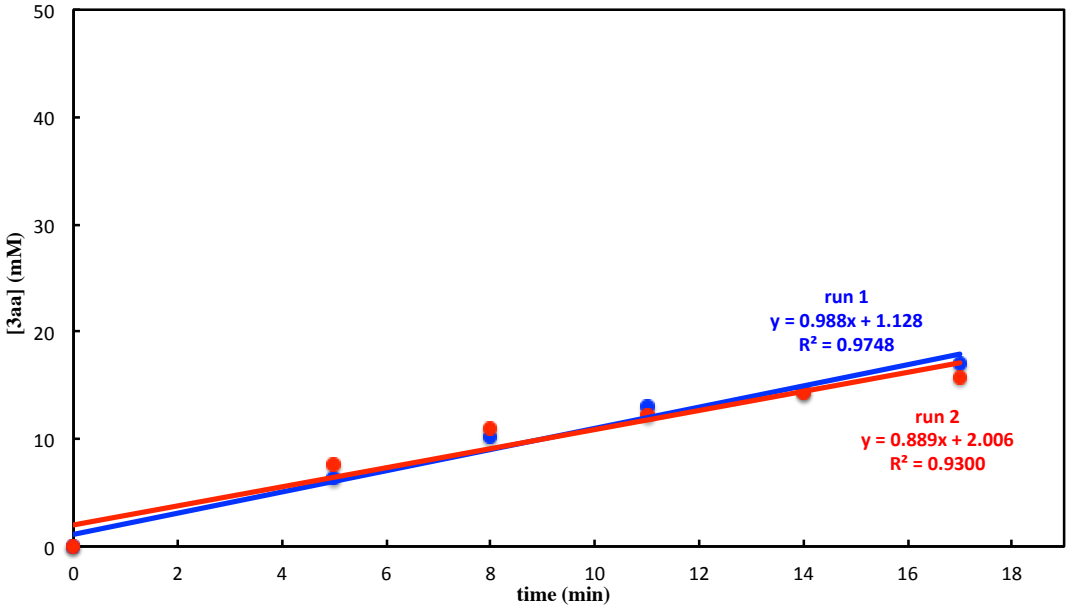
3.1 μmol of Rh: initial rate = 0.429 (mM/min)



4.6 μmol of Rh: initial rate = 0.740 (mM/min)



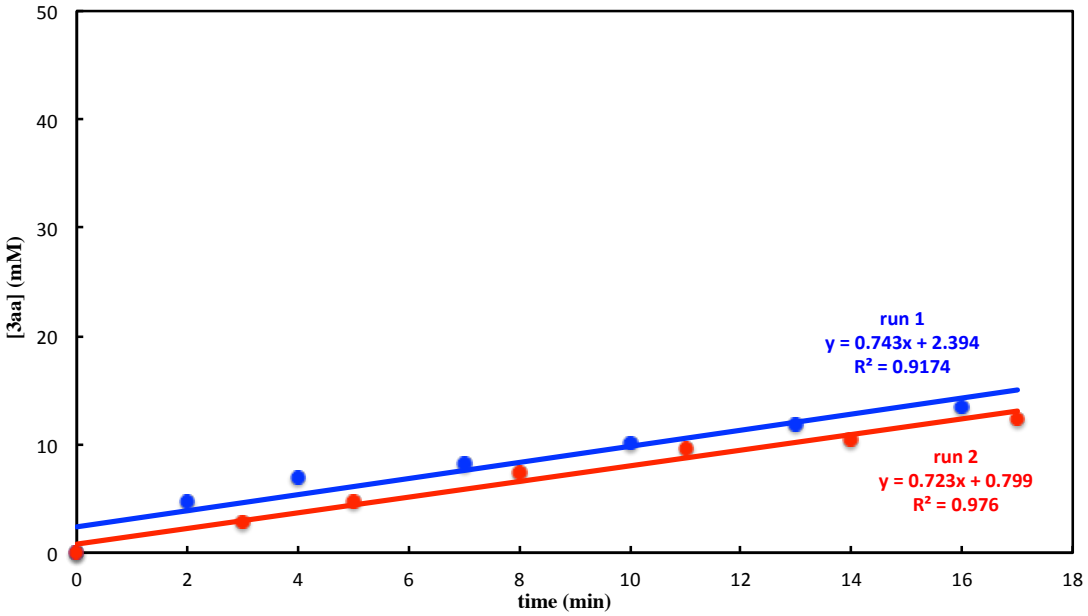
6.2 μmol of Rh: initial rate = 0.939 (mM/min)



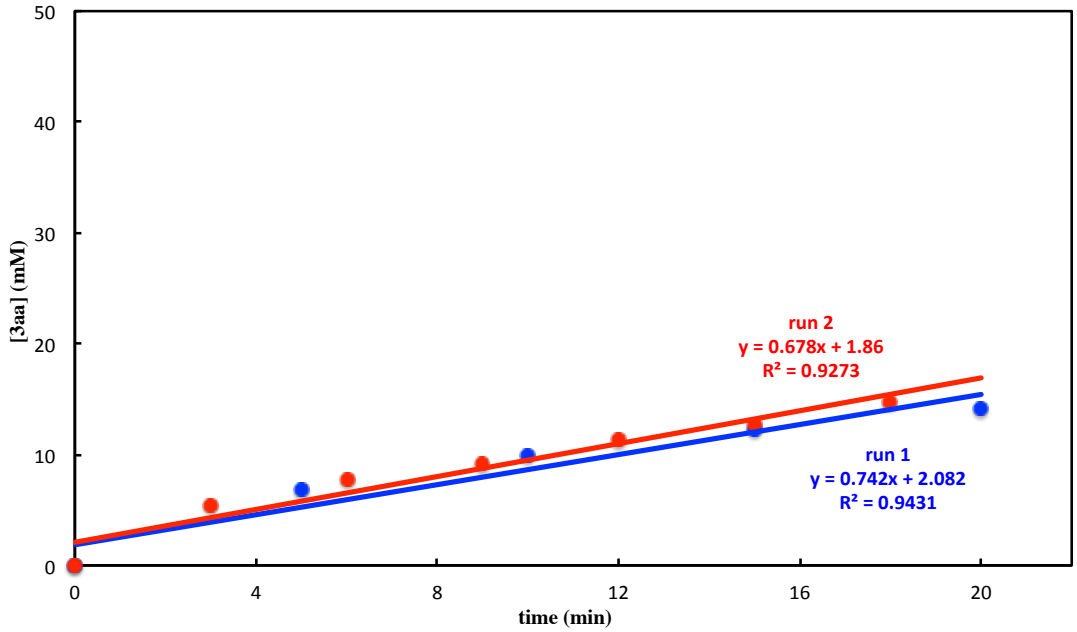
Data Collection for Figure 5.

A solution of $[RhCl(C_2H_4)_2]_2$ (0.9 mg, 4.6 μmol Rh), (*R*)-**L** (2.2 mg, 4.6 μmol), and 1,3,5-trimethoxybenzene (8.4 mg, 50 μmol; internal standard) in CH_2Cl_2 (2.0 mL) was stirred for 5 min at 28 °C. Triyne **1a** (66–150 μmol) and $NaBAr^F_4$ (8.0 mg, 9.0 μmol) were added with the aid of CH_2Cl_2 (0.50 mL), and isocyanate **2a** (16.2 μL, 150 μmol) was subsequently added with additional CH_2Cl_2 (0.50 mL). The resulting mixture was stirred at 28 °C and the aliquots (ca. 0.2 mL each) were taken every few minutes. They were immediately quenched with H_2O and extracted with Et_2O. The organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum. The residues were analyzed by ^1H NMR to determine the reaction progress (production of compound **3aa**). Each experiment was carried out twice.

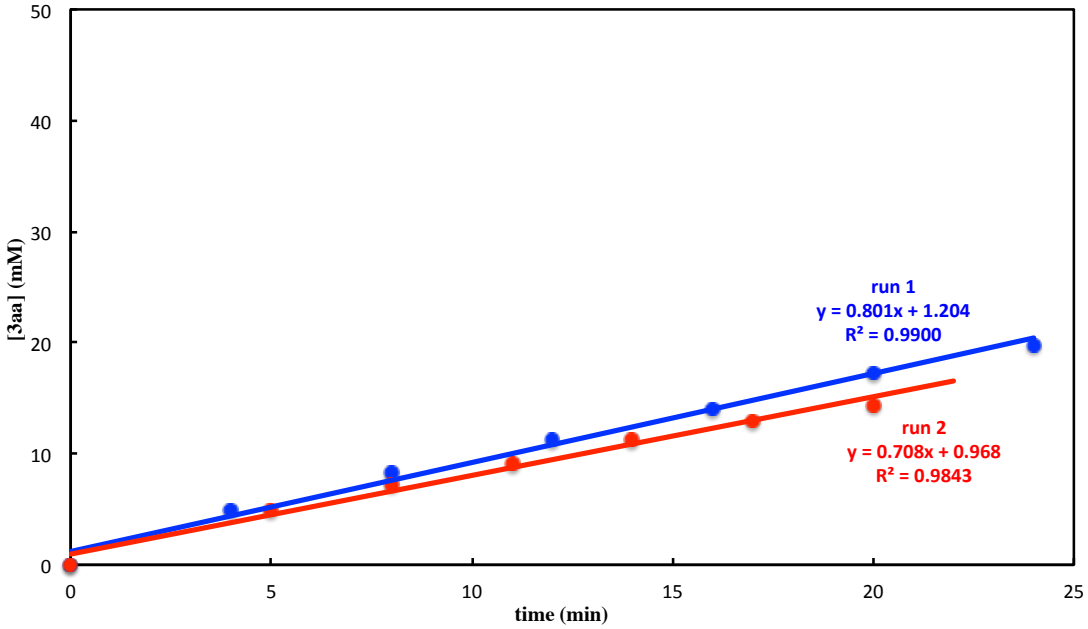
66 μmol of **1a**: initial rate = 0.733 (mM/min)



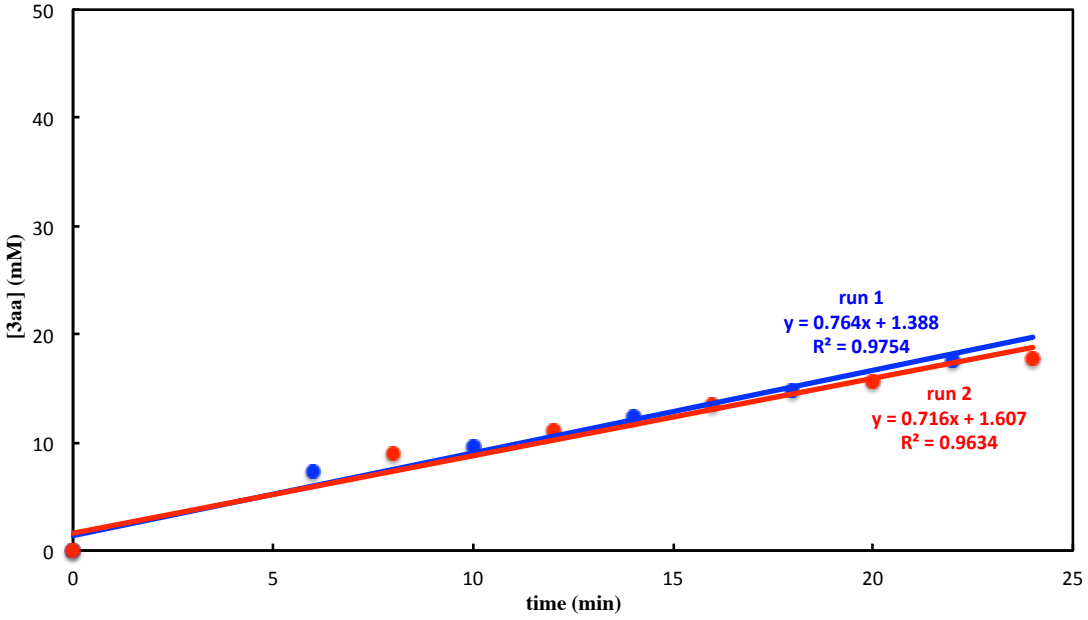
90 μmol of **1a**: initial rate = 0.710 (mM/min)



120 μmol of **1a**: initial rate = 0.755 (mM/min)



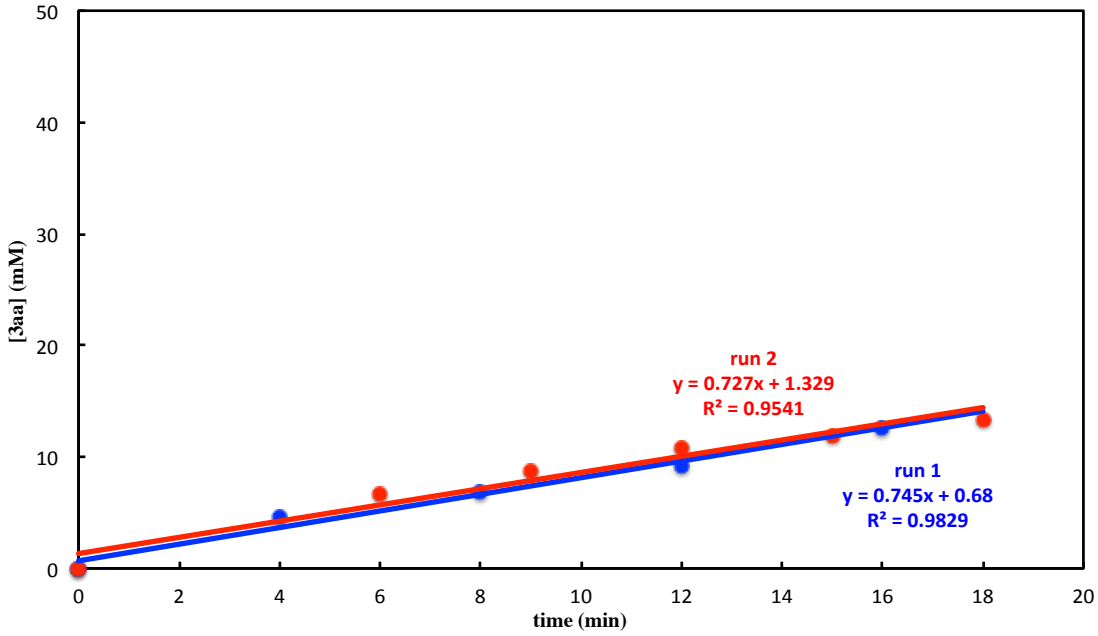
150 μmol of **1a**: initial rate = 0.740 (mM/min)



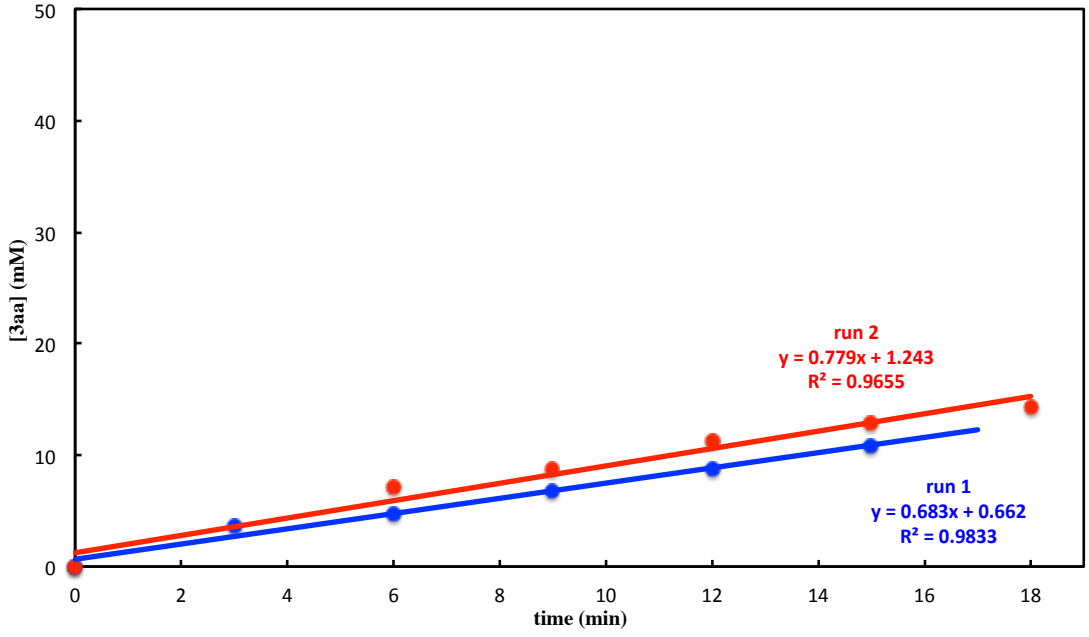
Data Collection for Figure 6.

A solution of $[RhCl(C_2H_4)_2]_2$ (0.9 mg, 4.6 μmol Rh), (*R*)-**L** (2.2 mg, 4.6 μmol), and 1,3,5-trimethoxybenzene (8.4 mg, 50 μmol; internal standard) in CH_2Cl_2 (2.0 mL) was stirred for 5 min at 28 °C. Triyne **1a** (38.8 mg, 90.1 μmol) and $NaBAr^F_4$ (8.0 mg, 9.0 μmol) were added with the aid of CH_2Cl_2 (0.50 mL), and isocyanate **2a** (90–195 μmol) was subsequently added with additional CH_2Cl_2 (0.50 mL). The resulting mixture was stirred at 28 °C and the aliquots (ca. 0.2 mL each) were taken every few minutes. They were immediately quenched with H_2O and extracted with Et_2O. The organic layers were dried over $MgSO_4$, filtered, and concentrated under vacuum. The residues were analyzed by ^1H NMR to determine the reaction progress (production of compound **3aa**). Each experiment was carried out twice.

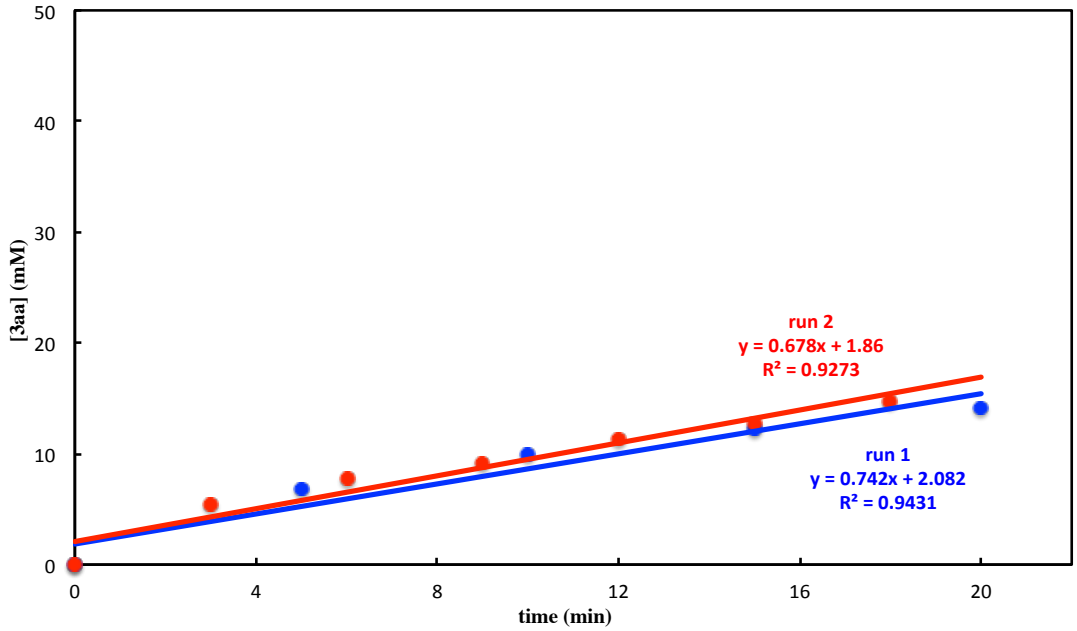
90 μmol of **2a**: initial rate = 0.736 (mM/min)



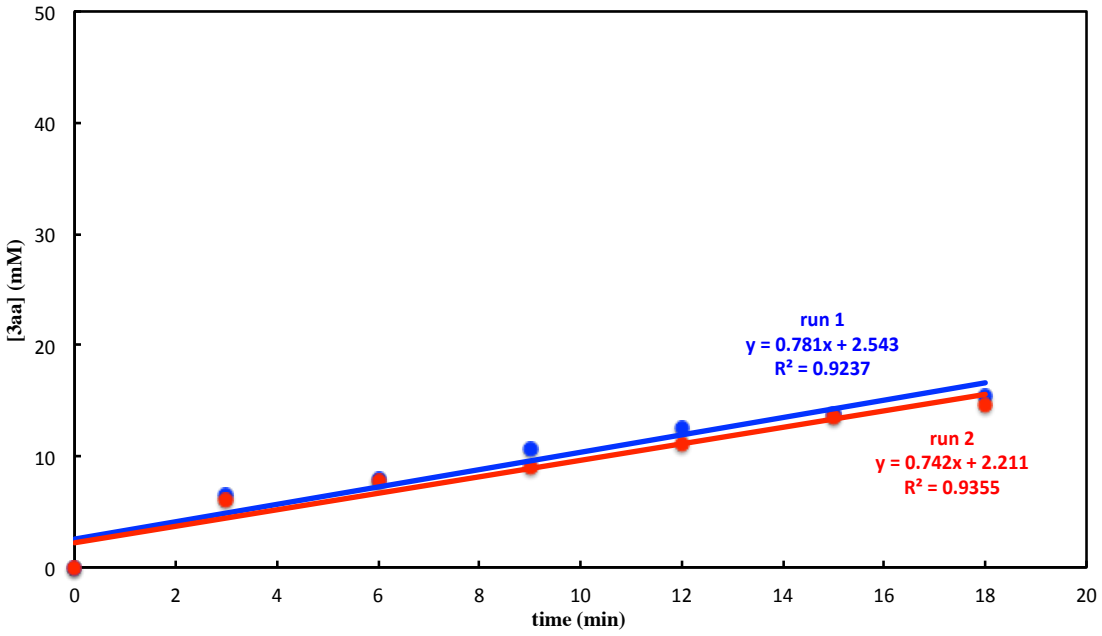
120 μmol of **2a**: initial rate = 0.731 (mM/min)



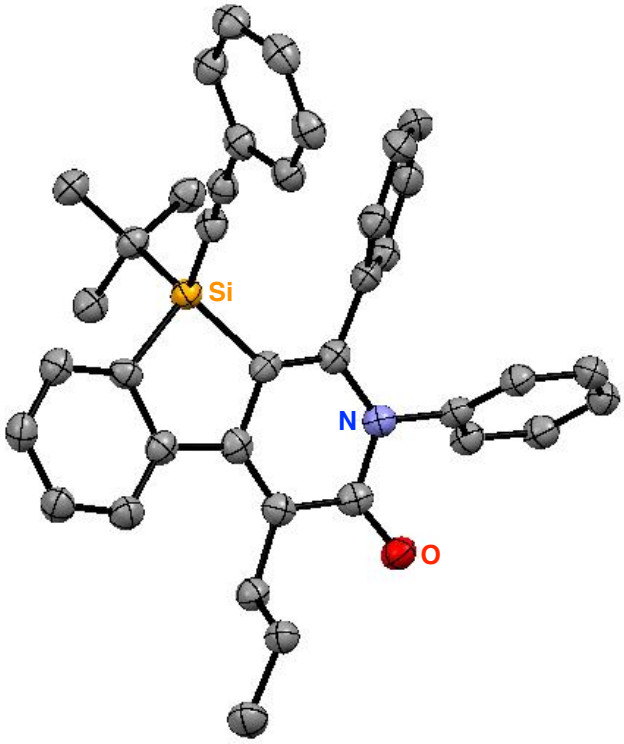
150 μmol of **2a**: initial rate = 0.710 (mM/min)



195 μmol of **2a**: initial rate = 0.762 (mM/min)



V. X-ray Crystal Structure of Compound (*R*)-3aa



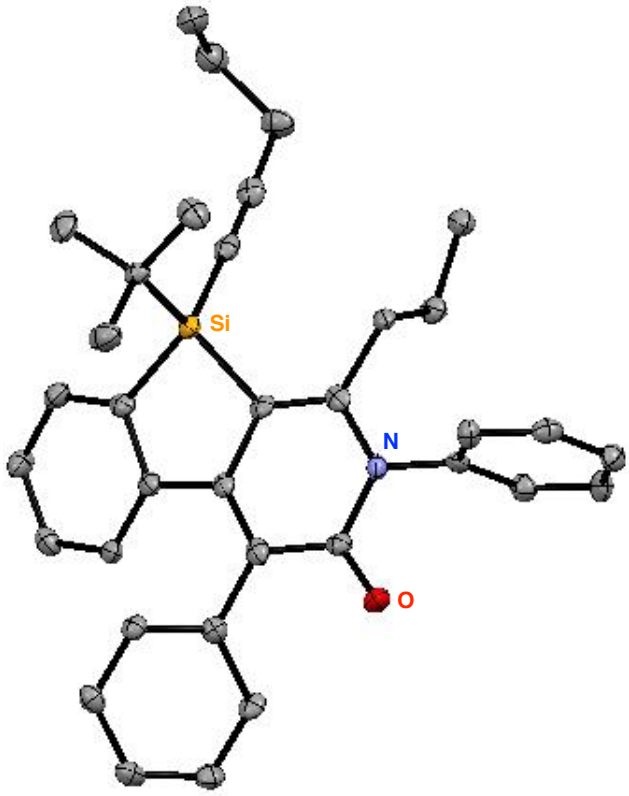
A colorless hexane/Et_2O solution of compound (*R*)-**3aa** was prepared. Crystals suitable for preliminary X-ray analysis were obtained by slow evaporation of the solvent at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 1428796). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

Crystal Data and Structure Refinement.

Empirical Formula	$C_{38}H_{35}NOSi$	
Formula Weight	549.76	
Temperature	93 ± 2 K	
Wavelength	1.54187 Å	
Crystal System	Orthorhombic	
Space Group	$P2_12_12_1$	
Unit Cell Dimensions	a = 9.568(4) Å b = 14.645(4) Å c = 21.564(6) Å	α = 90° β = 90° γ = 90°
Volume	3021.6(17) $Å^3$	
Z Value	4	

Calculated Density	1.208 g/cm^3
Absorption Coefficient	0.912 mm^{-1}
F(000)	1168
Crystal Size	0.21 x 0.07 x 0.06 mm
Theta Range for Data Collection	3.65–74.82°
Index Ranges	$-11 \le h \le 10, -18 \le k \le 18, -26 \le l \le 26$
Reflections Collected	47108
Independent Reflections	6130 [R(int) = 0.0705]
Completeness to Theta = 74.82°	99.3%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	0.9473 and 0.8316
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	6310 / 0 / 374
Goodness-of-Fit on F^2	1.046
Final R Indices [I>2sigma(I)]	R1 = 0.0721, wR2 = 0.1856
R Indices (All Data)	R1 = 0.0735, wR2 = 0.1881
Absolute Structure Parameter	0.04(4)
Largest Diff. Peak and Hole	1.291 and –0.431 e$^-$/Å^3

VI. Preliminary X-ray Crystal Structure of Compound (±)-3ka



A colorless hexane/Et_2O solution of compound (±)-**3ka** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent at room temperature. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 1428797). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.

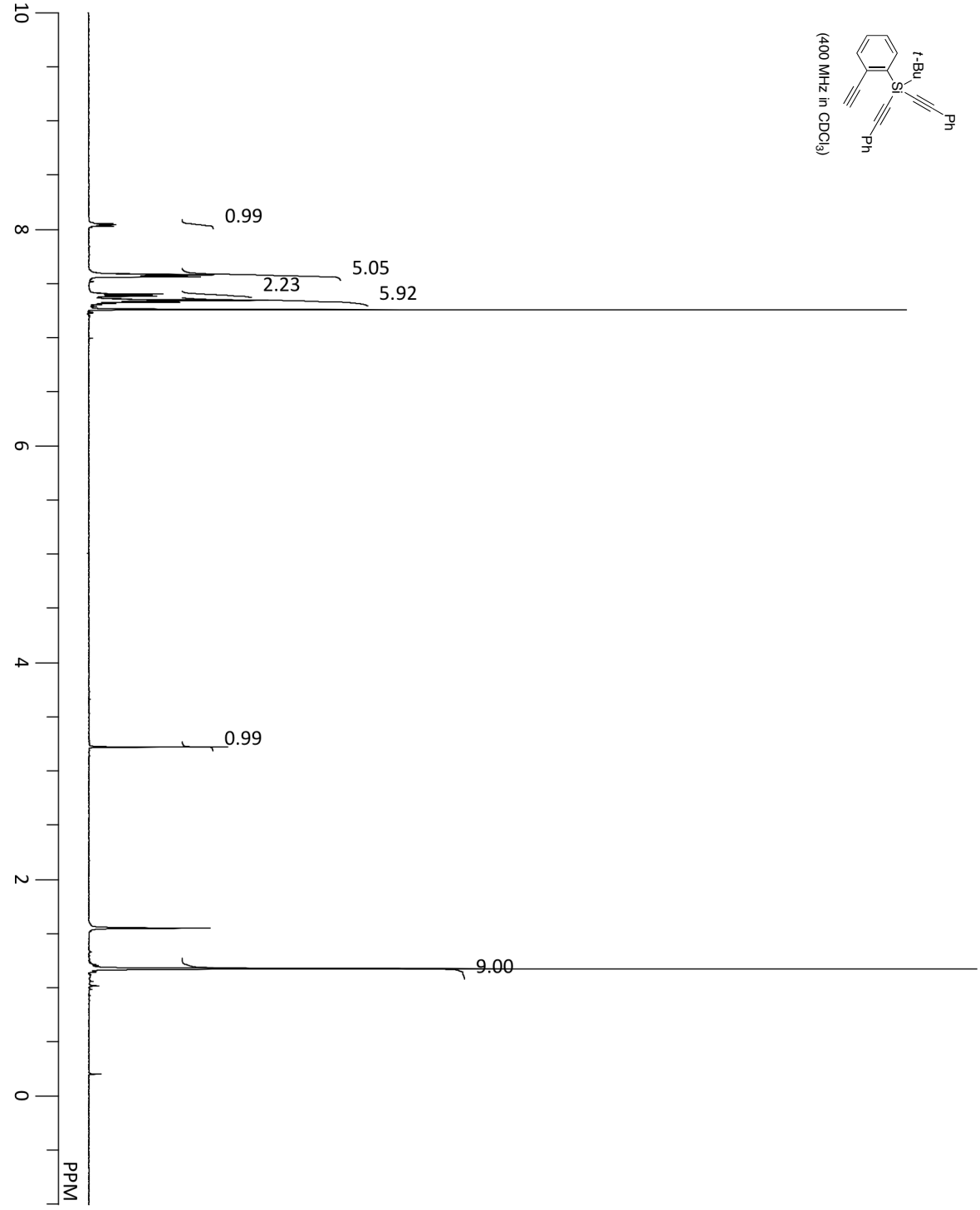
Crystal Data and Structure Refinement.

Empirical Formula	$C_{35}H_{37}NOSi$	
Formula Weight	515.74	
Temperature	93 ± 2 K	
Wavelength	0.71075 Å	
Crystal System	Triclinic	
Space Group	P–1	
Unit Cell Dimensions	a = 10.205(8) Å	α = 80.446(9)°
	b = 14.620(4) Å	β = 84.563(10)°
	c = 21.051(6) Å	γ = 78.321(9)°
Volume	3027.0(15) $Å^3$	

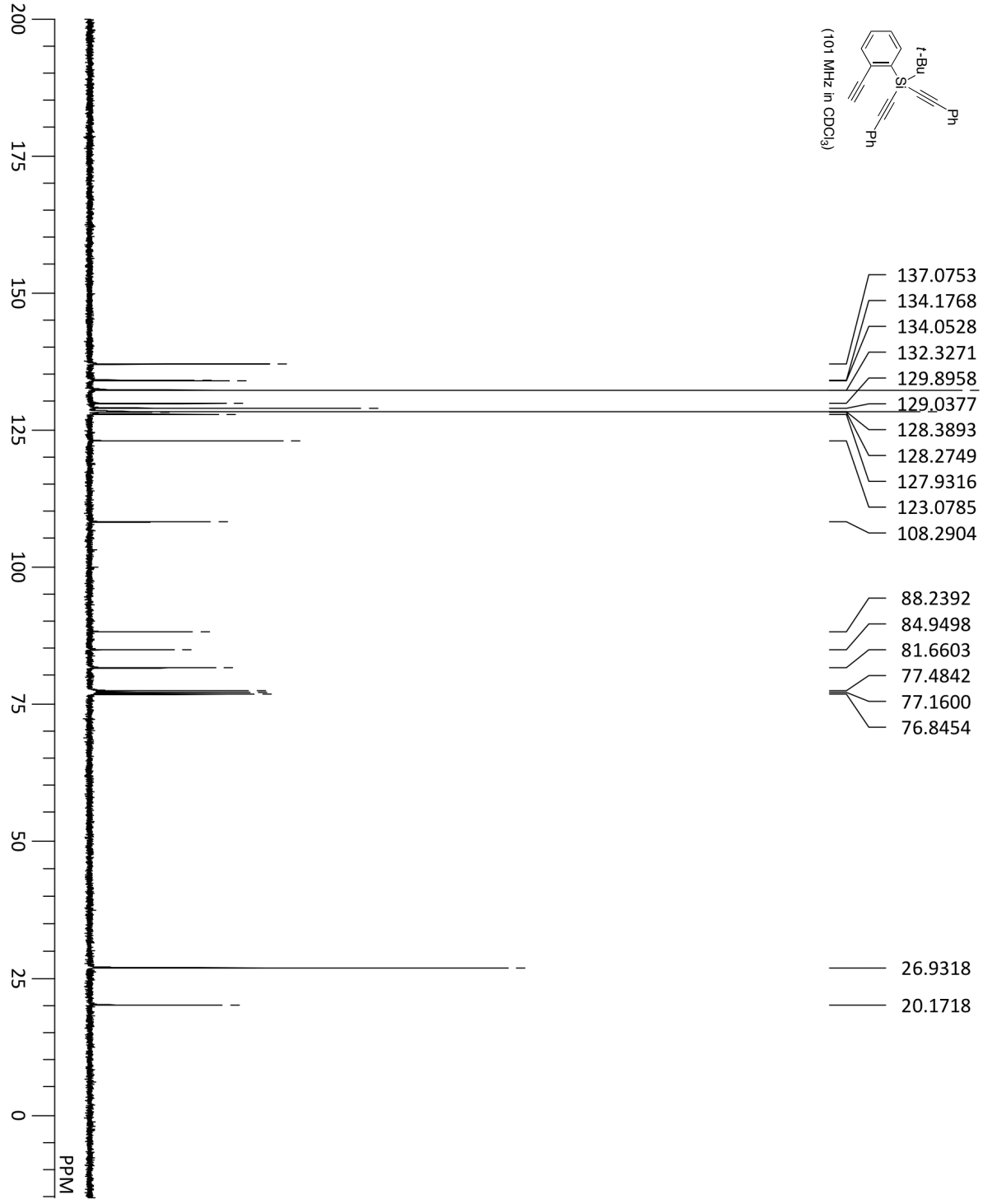
Z Value	4
Calculated Density	1.132 g/cm^3
Absorption Coefficient	0.104 mm^{-1}
F(000)	1100
Crystal Size	0.20 x 0.20 x 0.05 mm
Theta Range for Data Collection	1.861–27.500°
Index Ranges	$-13 \le h \le 9, -18 \le k \le 18, -26 \le l \le 27$
Reflections Collected	17354
Independent Reflections	11417 [R(int) = 0.0511]
Completeness to Theta = 25.242°	86.5%
Absorption Correction	Semi-empirical from equivalents
Max. and Min. Transmission	1.000 and 0.784
Refinement Method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	11417 / 12 / 715
Goodness-of-Fit on F^2	1.148
Final R Indices [I>2sigma(I)]	R1 = 0.0954, wR2 = 0.1940
R Indices (All Data)	R1 = 0.1367, wR2 = 0.2245
Extinction coefficient	n/a
Largest Diff. Peak and Hole	0.404 and –0.500 e$^-$/Å^3

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

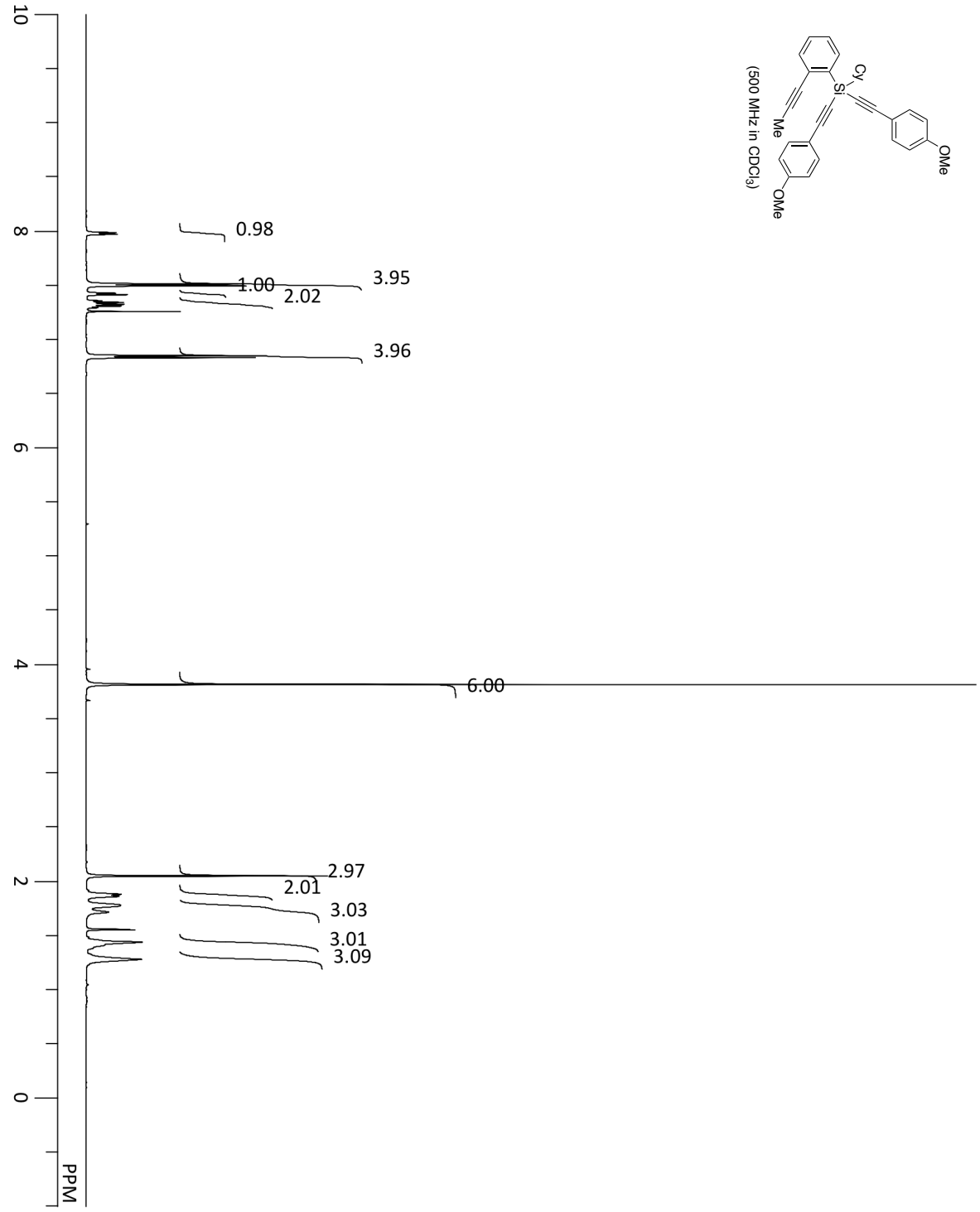
compound **1d**



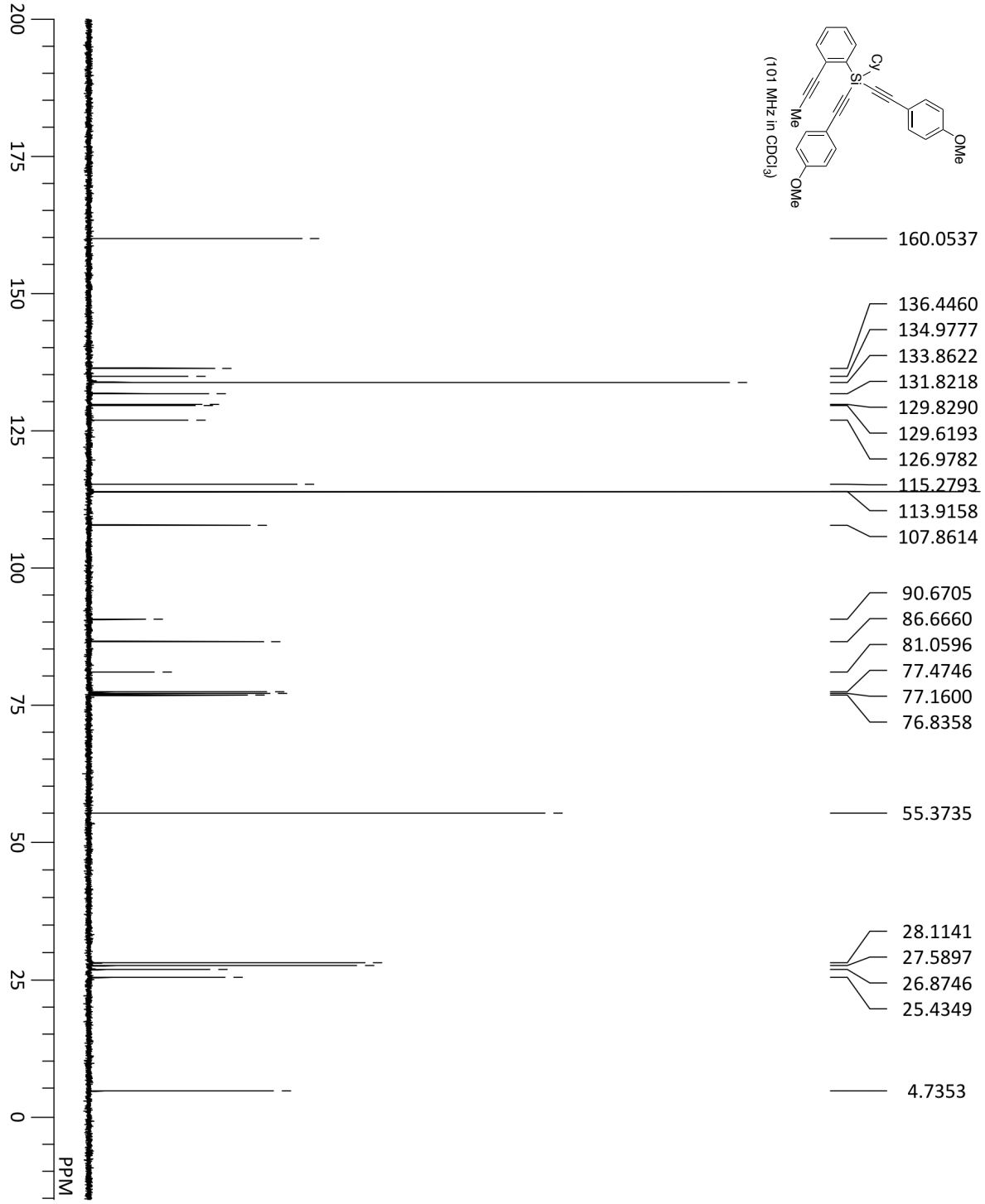
compound **1d**


(101 MHz in CDCl3)
t-Bu
Si
Ph
Ph
137.0753
134.1768
134.0528
132.3271
129.8958
129.0377
128.3893
128.2749
127.9316
123.0785
108.2904
88.2392
84.9498
81.6603
77.4842
77.1600
76.8454
26.9318
20.1718
200
175
150
125
100
75
50
25
0
PPM

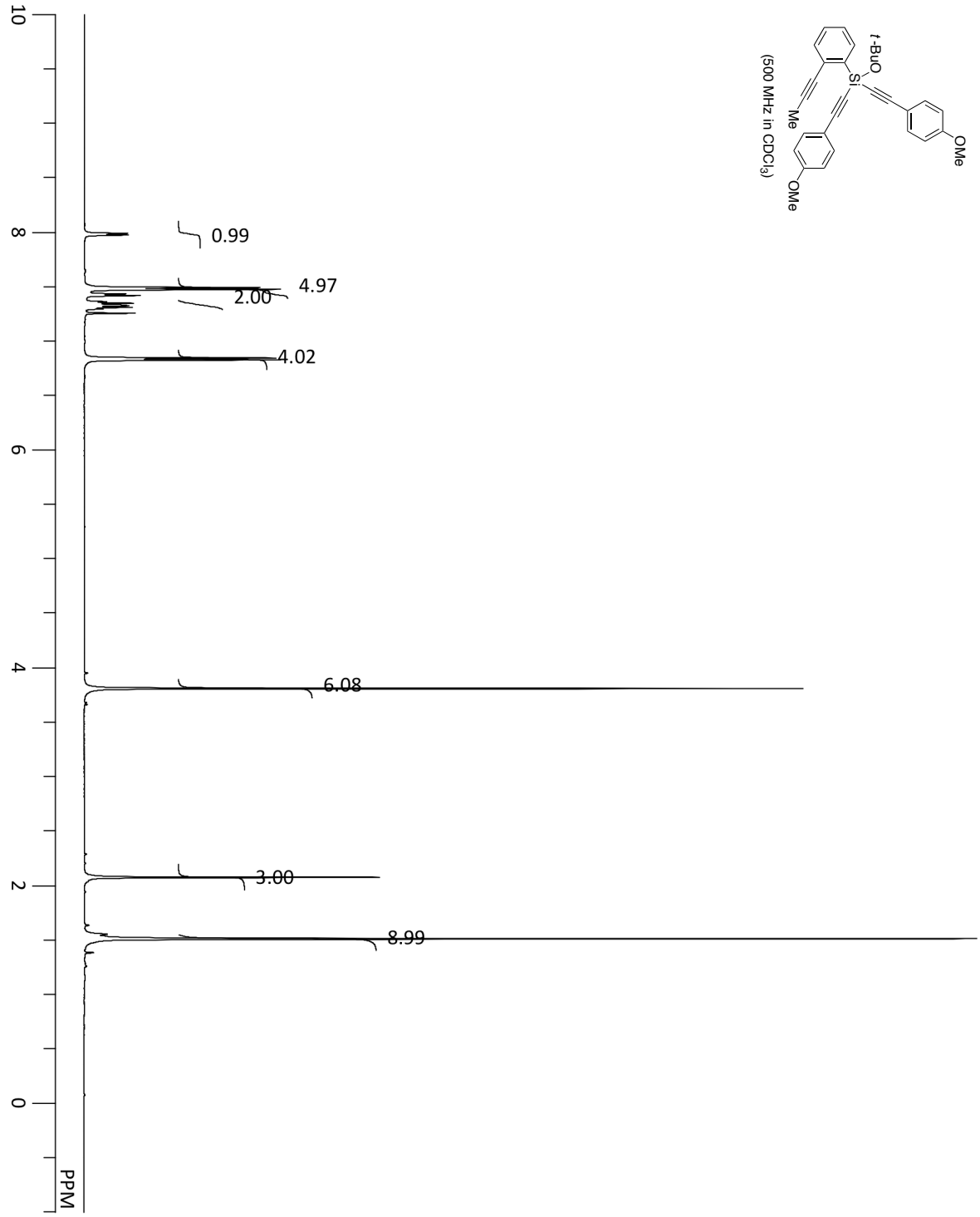
compound **1e**


(500 MHz in CDCl3)
Me
Si
Cy
OMe
OMe
0.98
1.00
3.95
2.02
3.96
6.00
2.97
2.01
3.03
3.01
3.09
PPM

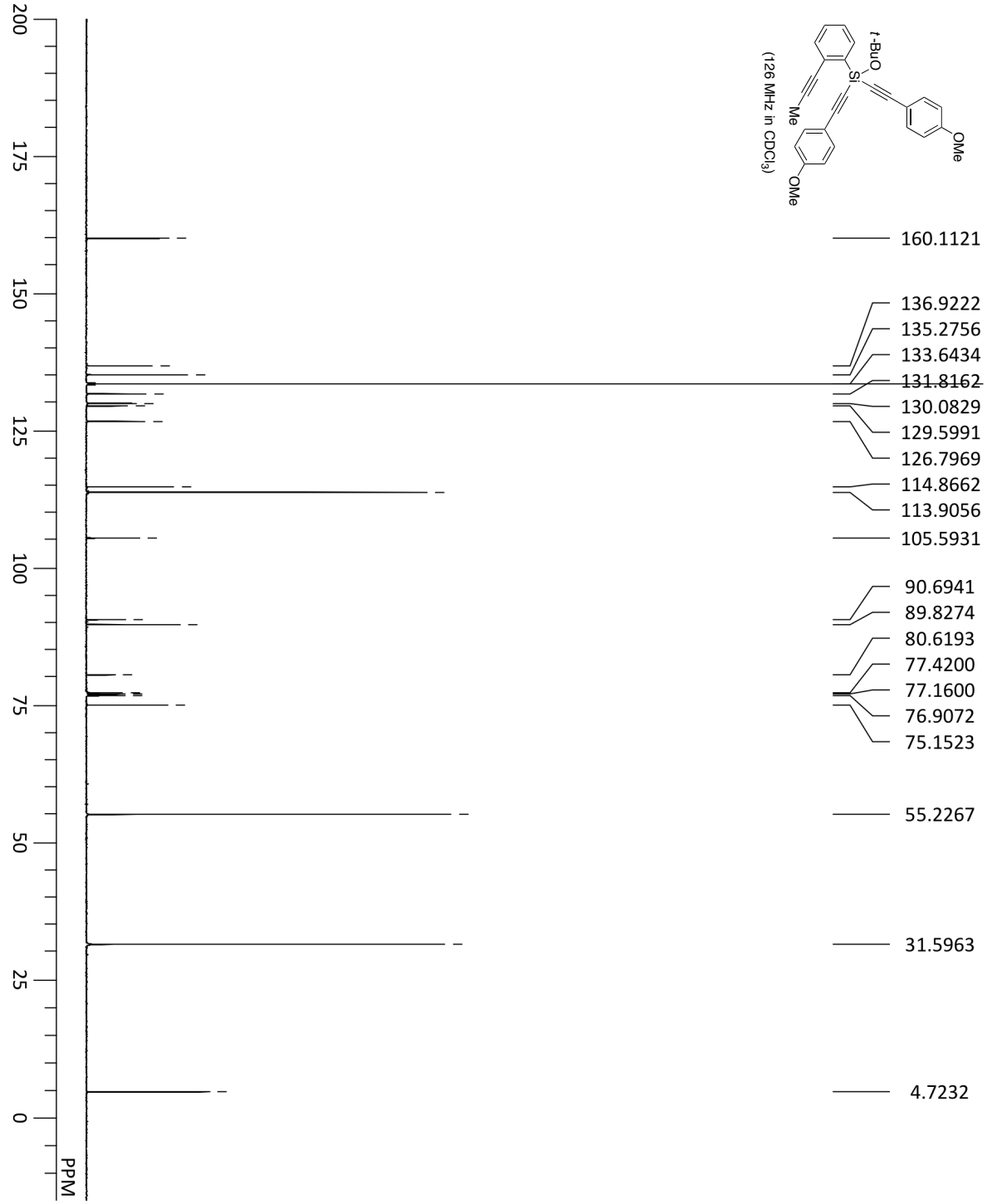
compound **1e**


(101 MHz in CDCl3)
Cy
Si
Me
OMe
OMe
160.0537
136.4460
134.9777
133.8622
131.8218
129.8290
129.6193
126.9782
115.2793
113.9158
107.8614
90.6705
86.6660
81.0596
77.4746
77.1600
76.8358
55.3735
28.1141
27.5897
26.8746
25.4349
4.7353
PPM

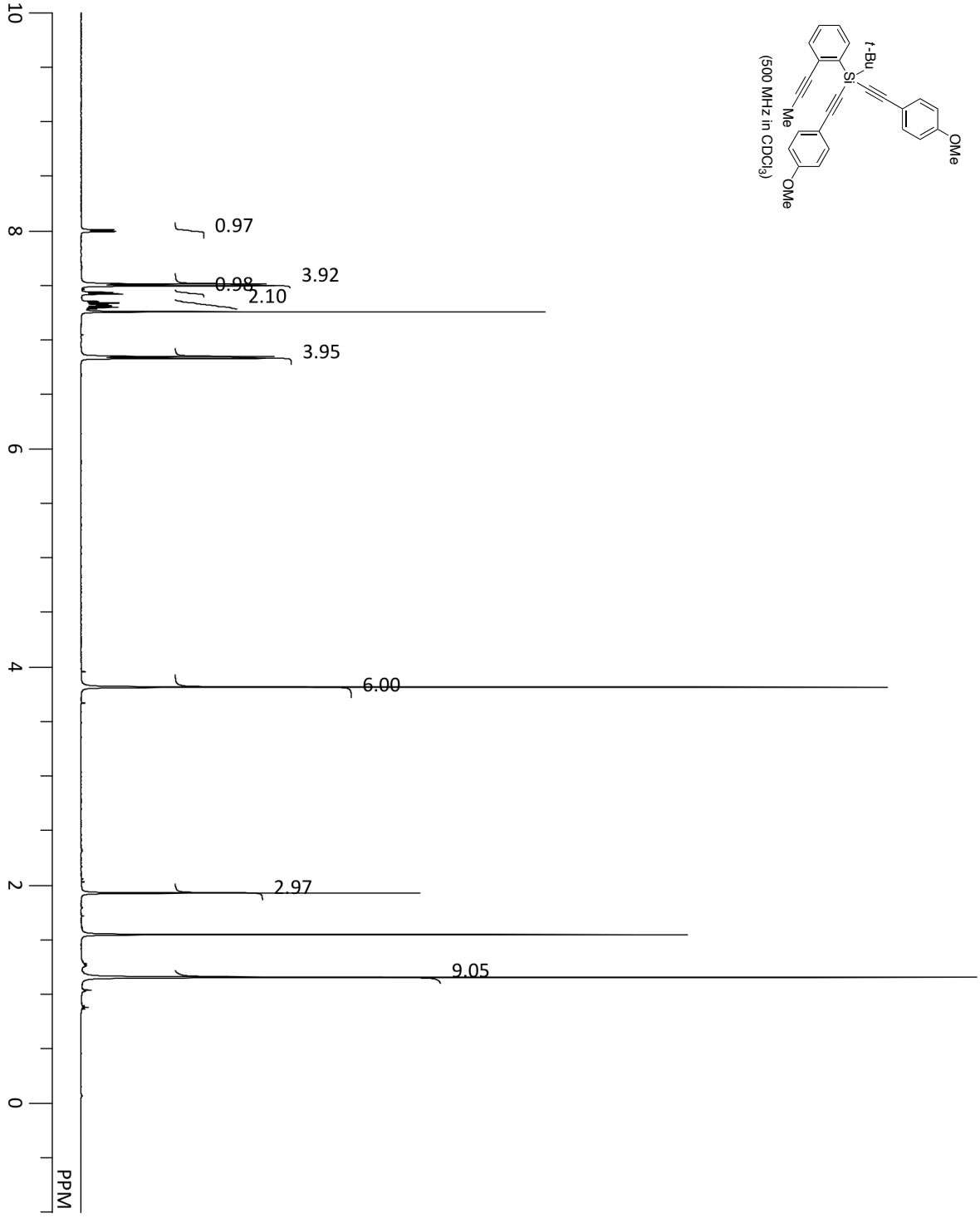
compound **1f**


(500 MHz in CDCl3)
t-BuO
Si
Me
OMe
OMe
0.99
4.97
2.00
4.02
6.08
3.00
8.99
10
8
6
4
2
0
PPM

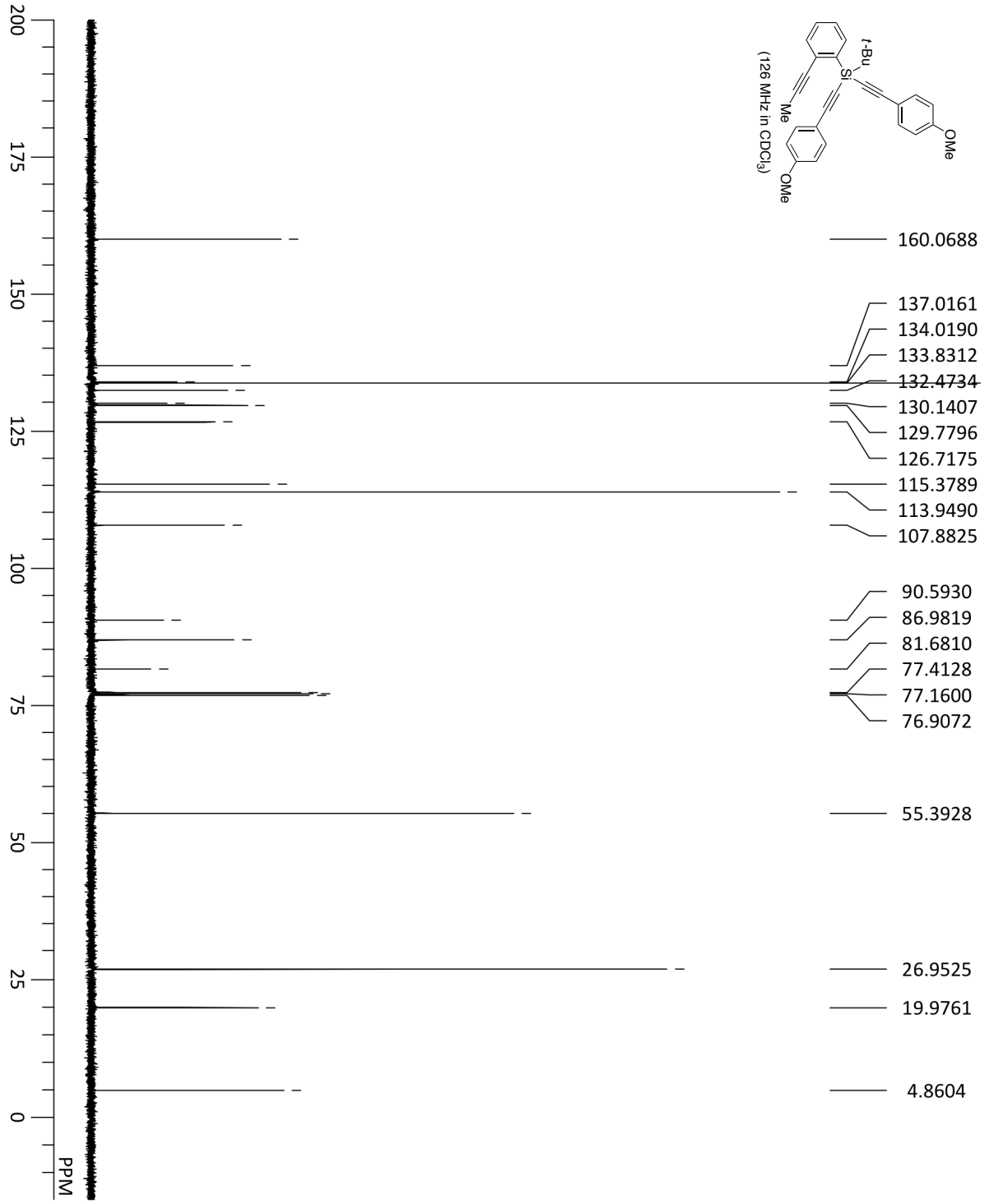
compound **1f**


200
175
150
125
100
75
50
25
0
PPM
(126 MHz in CDCl3)
t-BuO
Si
Me
OMe
OMe
160.1121
136.9222
135.2756
133.6434
131.8162
130.0829
129.5991
126.7969
114.8662
113.9056
105.5931
90.6941
89.8274
80.6193
77.4200
77.1600
76.9072
75.1523
55.2267
31.5963
4.7232

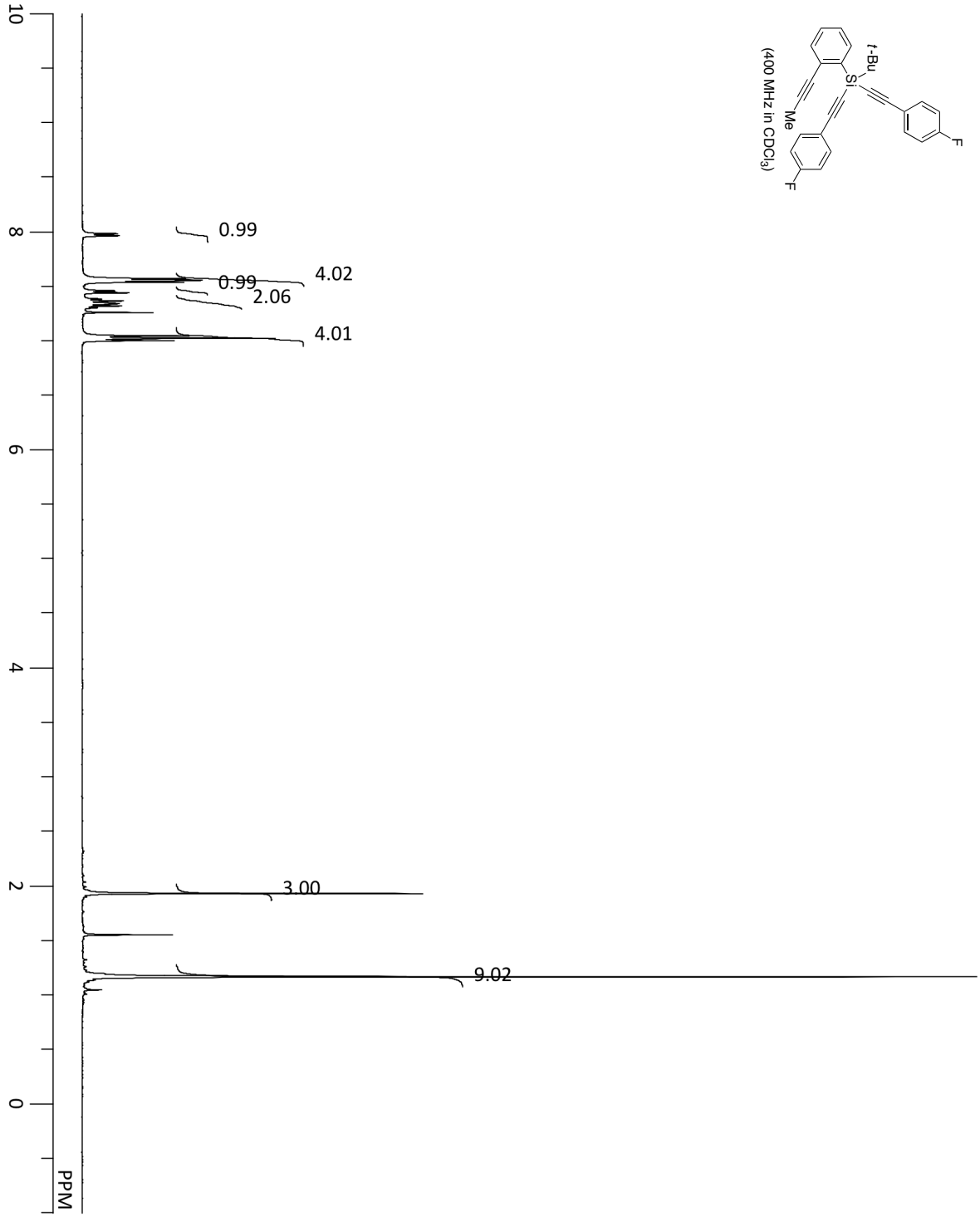
compound **1g**


(500 MHz in $CDCl_3$)
t-Bu
Si
Me
OMe
OMe
0.97
0.98
3.92
2.10
3.95
6.00
2.97
9.05
10
8
6
4
2
0
PPM

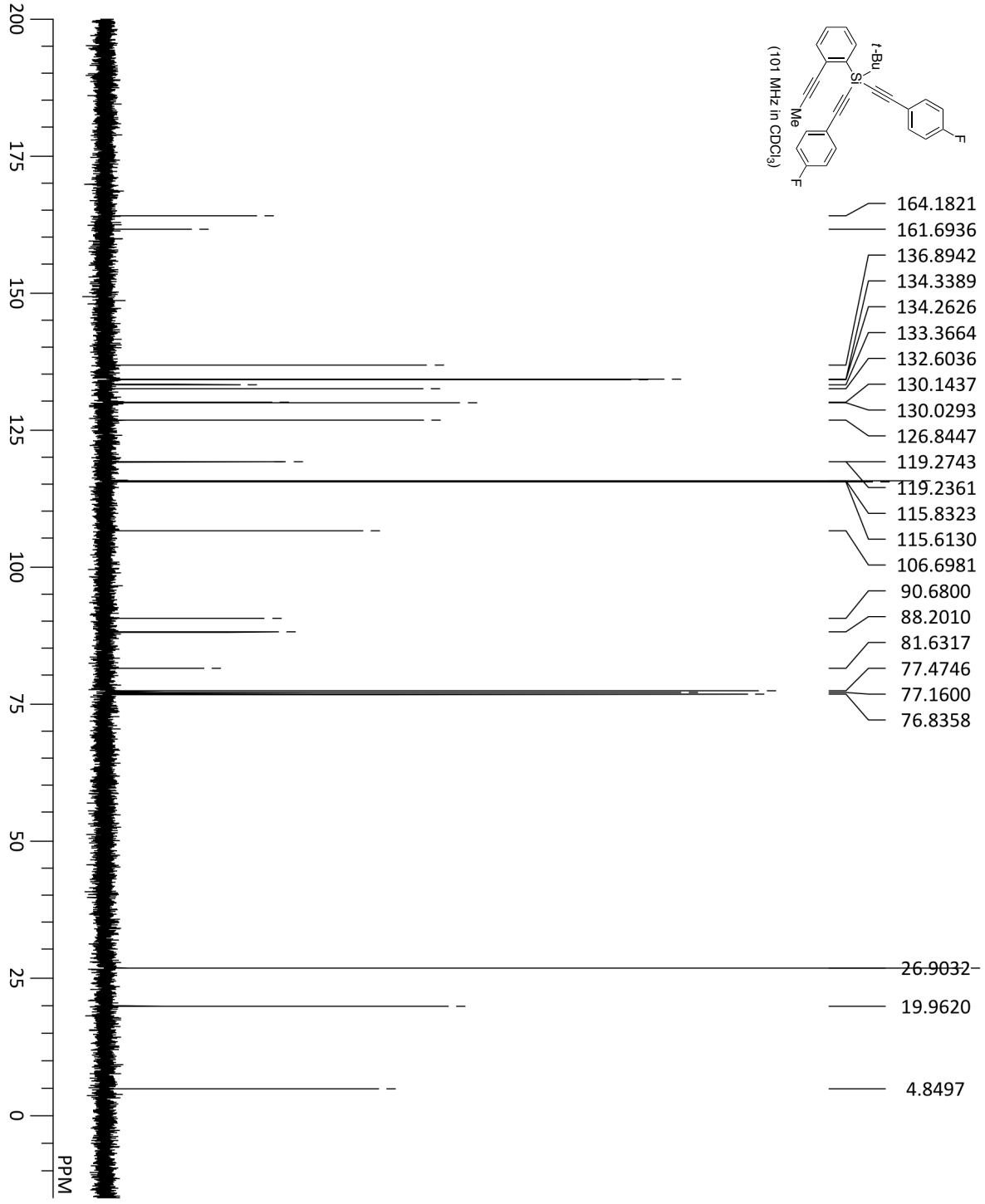
compound **1g**


200
175
150
125
100
75
50
25
0
PPM
(126 MHz in CDCl3)
t-Bu
Si
Me
OMe
OMe
160.0688
137.0161
134.0190
133.8312
132.4734
130.1407
129.7796
126.7175
115.3789
113.9490
107.8825
90.5930
86.9819
81.6810
77.4128
77.1600
76.9072
55.3928
26.9525
19.9761
4.8604

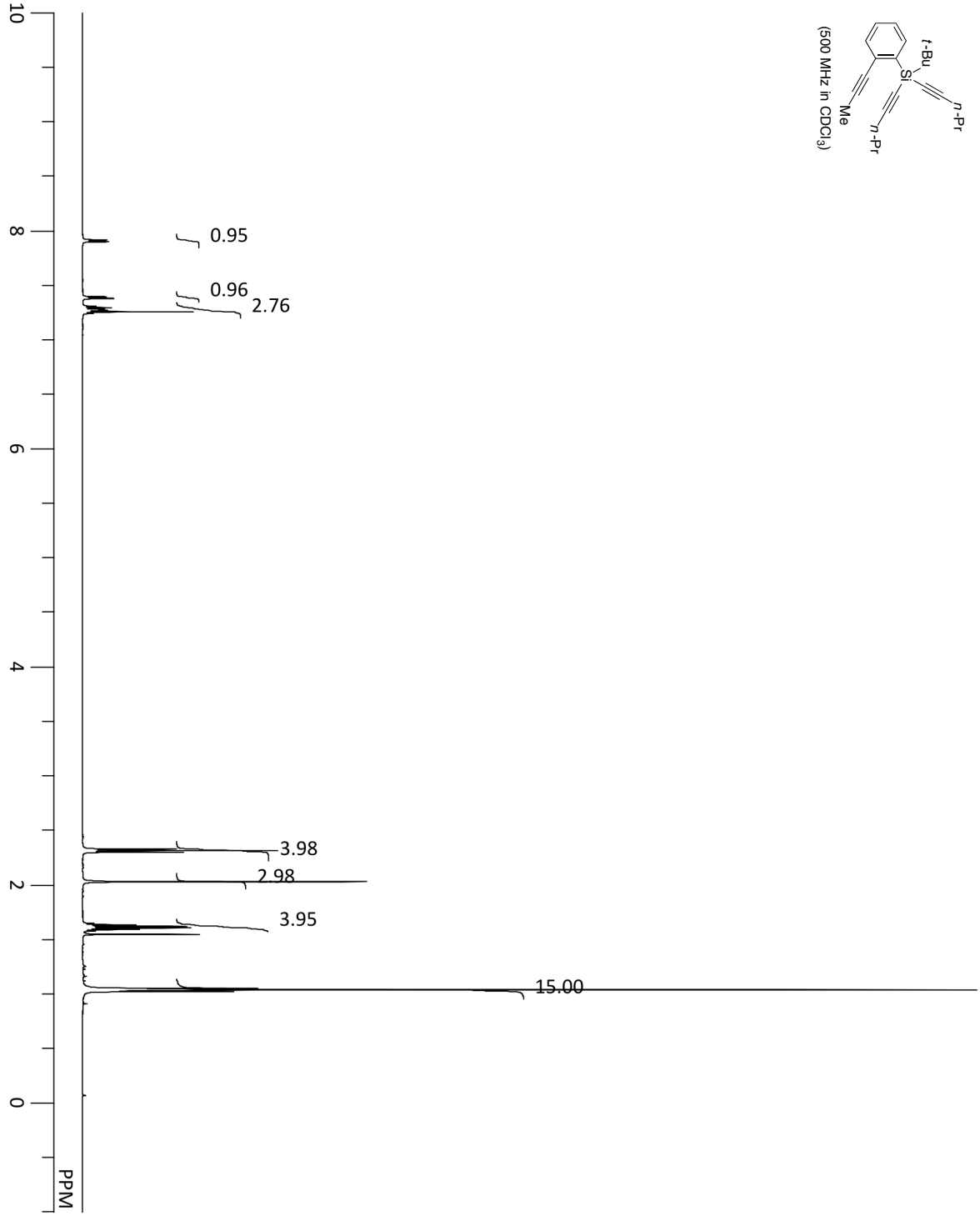
compound **1h**


10
8
6
4
2
0
PPM
0.99
0.99
4.02
2.06
4.01
3.00
9.02
t-Bu
Si
Me
F
F
(400 MHz in CDCl3)

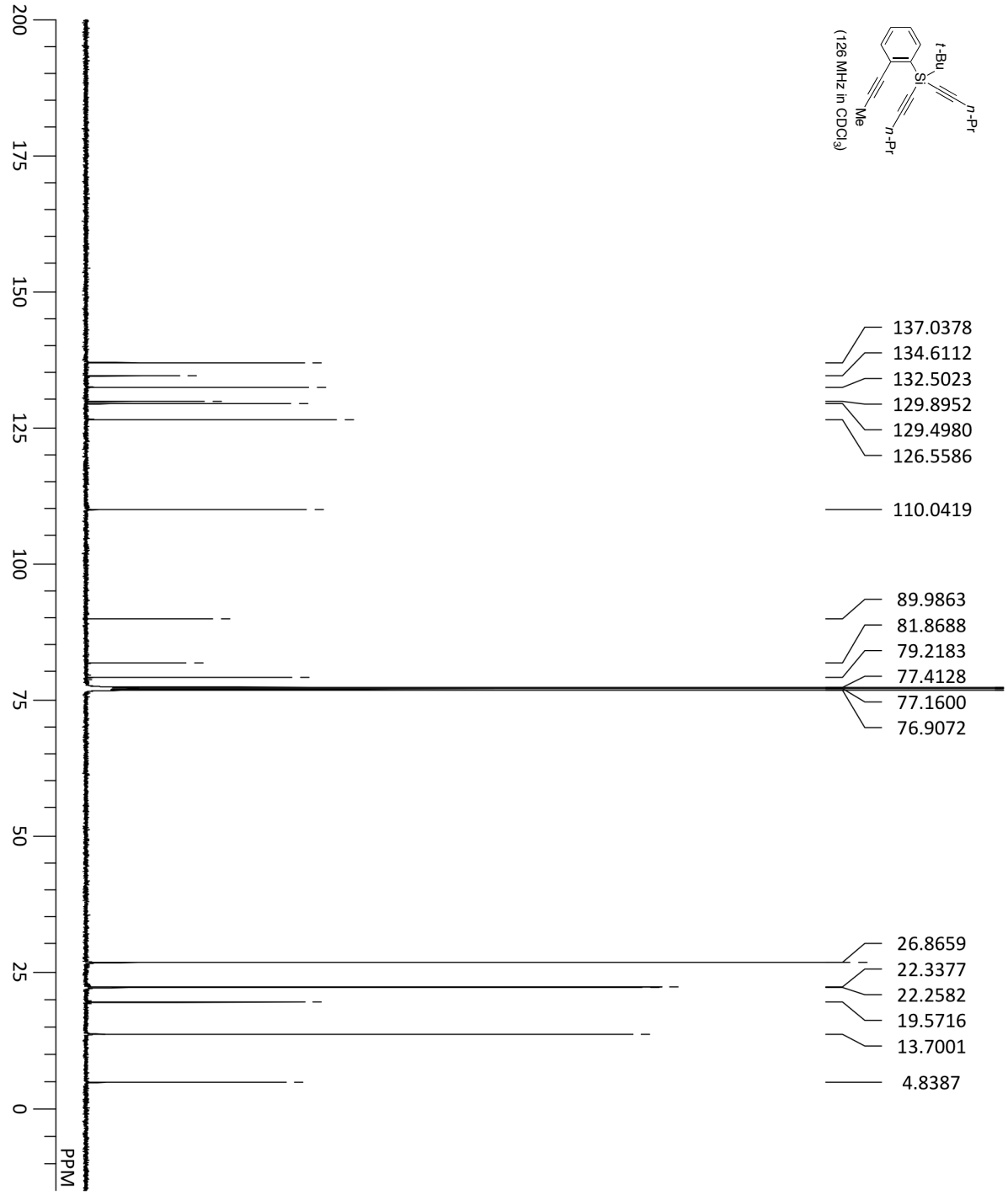
compound **1h**


200
175
150
125
100
75
50
25
0
PPM
(101 MHz in CDCl3)
t-Bu
Si
Me
F
F
164.1821
161.6936
136.8942
134.3389
134.2626
133.3664
132.6036
130.1437
130.0293
126.8447
119.2743
119.2361
115.8323
115.6130
106.6981
90.6800
88.2010
81.6317
77.4746
77.1600
76.8358
26.9032
19.9620
4.8497

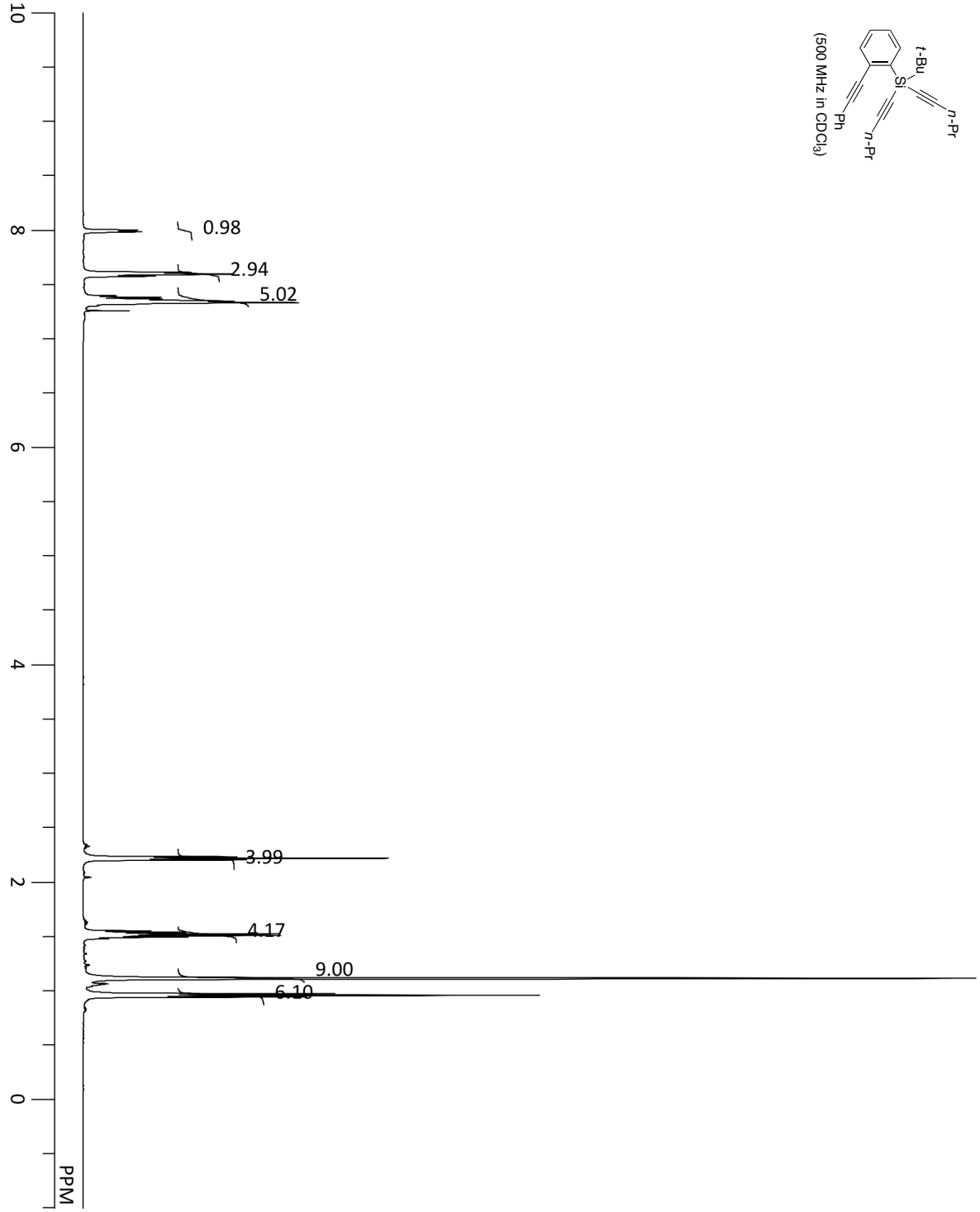
compound **1i**


(500 MHz in $CDCl_3$)
Me
Si
t-Bu
n-Pr
n-Pr
10
8
6
4
2
0
PPM
0.95
0.96
2.76
3.98
2.98
3.95
15.00

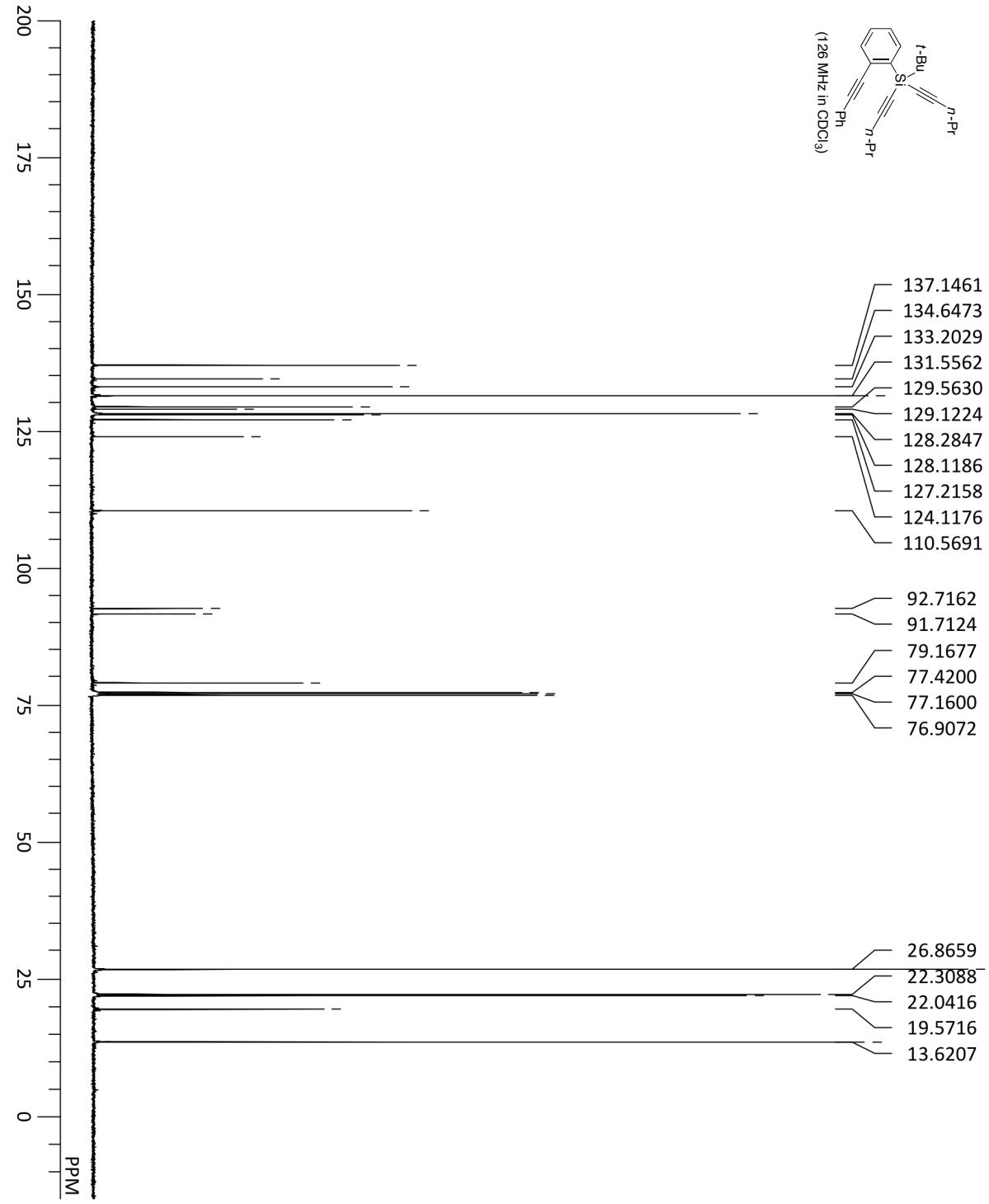
compound **1i**


(126 MHz in CDCl3)
t-Bu
Si
Me
n-Pr
n-Pr
137.0378
134.6112
132.5023
129.8952
129.4980
126.5586
110.0419
89.9863
81.8688
79.2183
77.4128
77.1600
76.9072
26.8659
22.3377
22.2582
19.5716
13.7001
4.8387
PPM

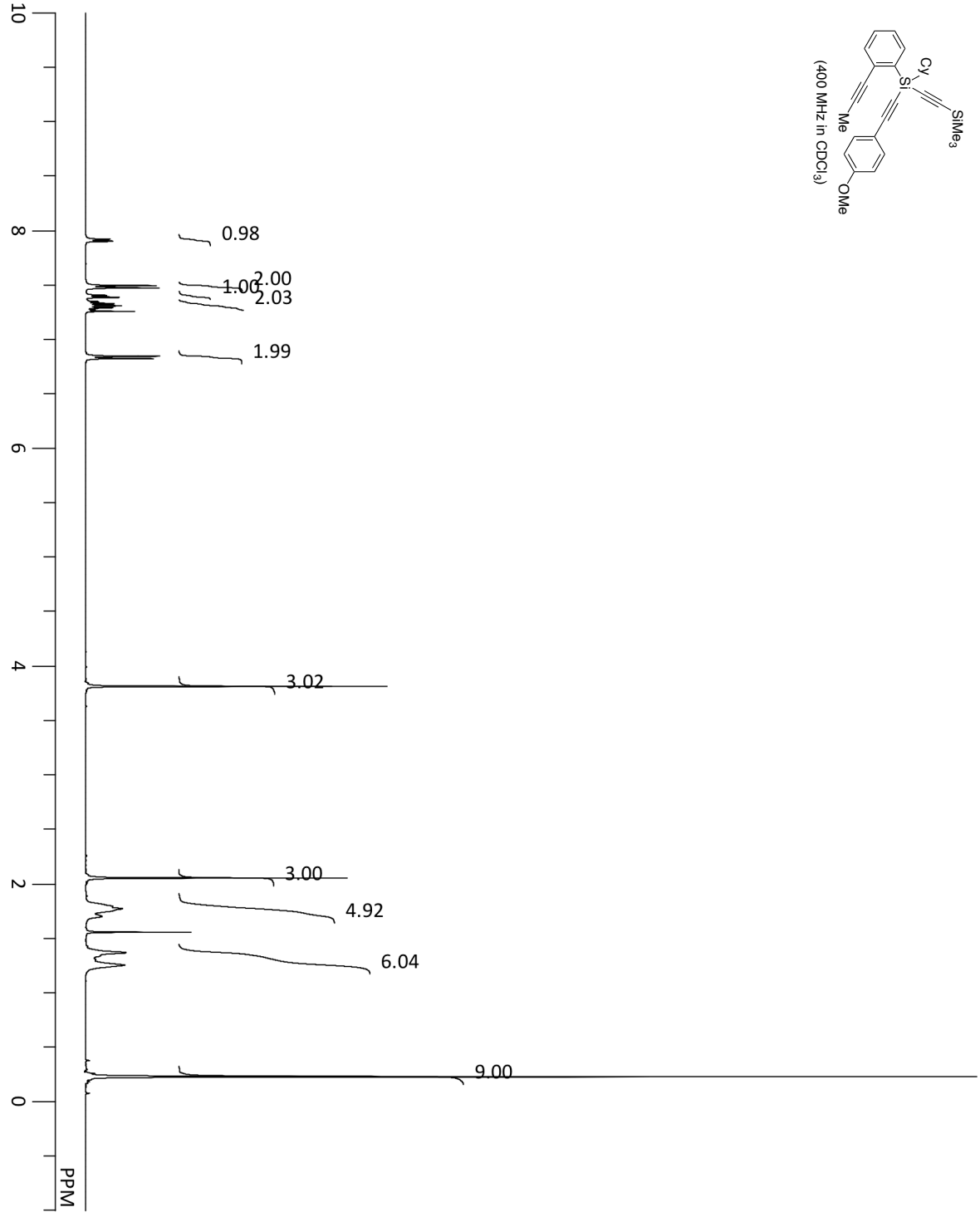
compound **1k**


(500 MHz in CDCl3)
t-Bu
Si
n-Pr
Ph
n-Pr
0.98
2.94
5.02
3.99
4.17
9.00
6.10
PPM

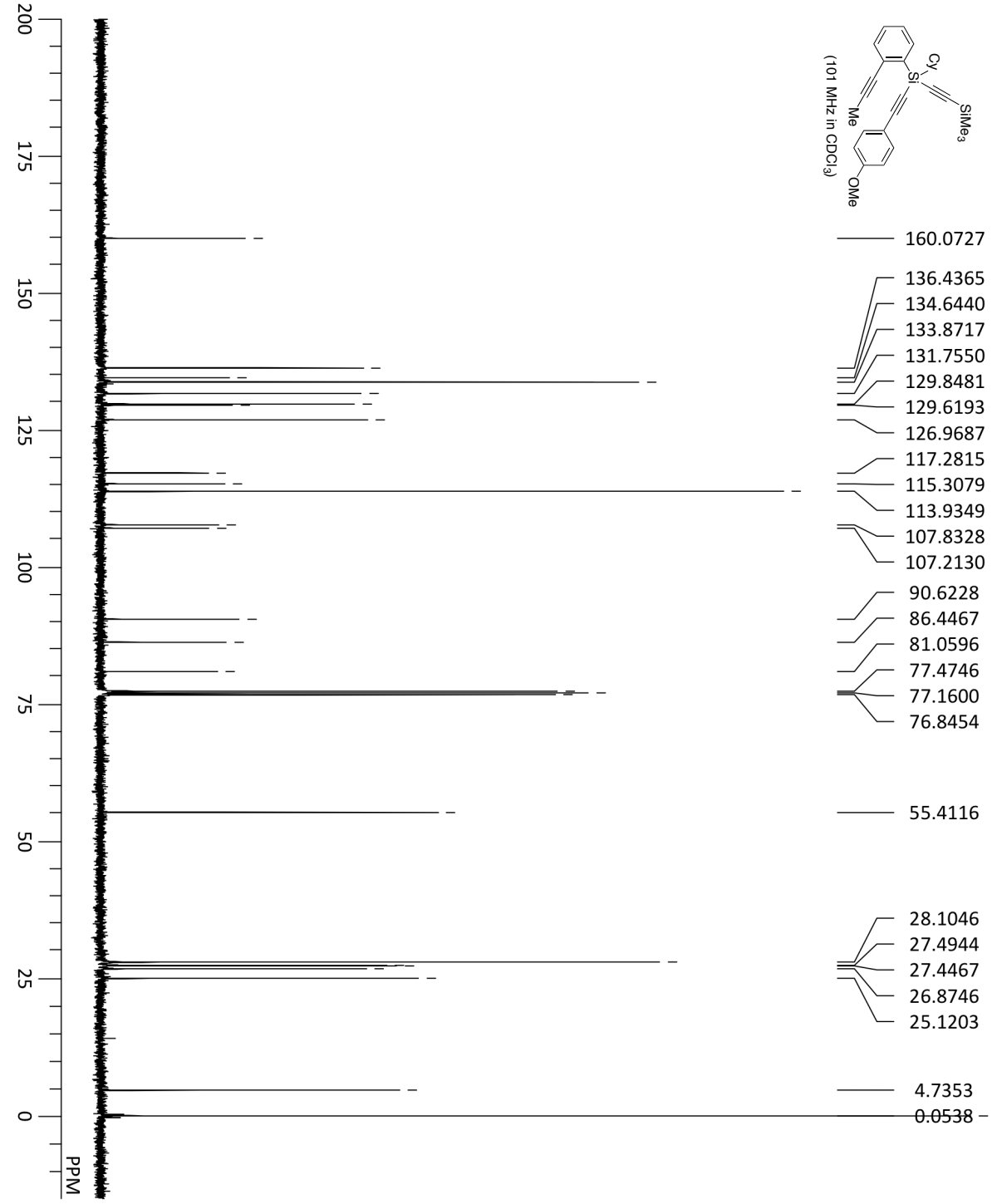
compound **1k**


(126 MHz in CDCl3)
t-Bu
Si
Ph
n-Pr
n-Pr
137.1461
134.6473
133.2029
131.5562
129.5630
129.1224
128.2847
128.1186
127.2158
124.1176
110.5691
92.7162
91.7124
79.1677
77.4200
77.1600
76.9072
26.8659
22.3088
22.0416
19.5716
13.6207
200
175
150
125
100
75
50
25
0
PPM

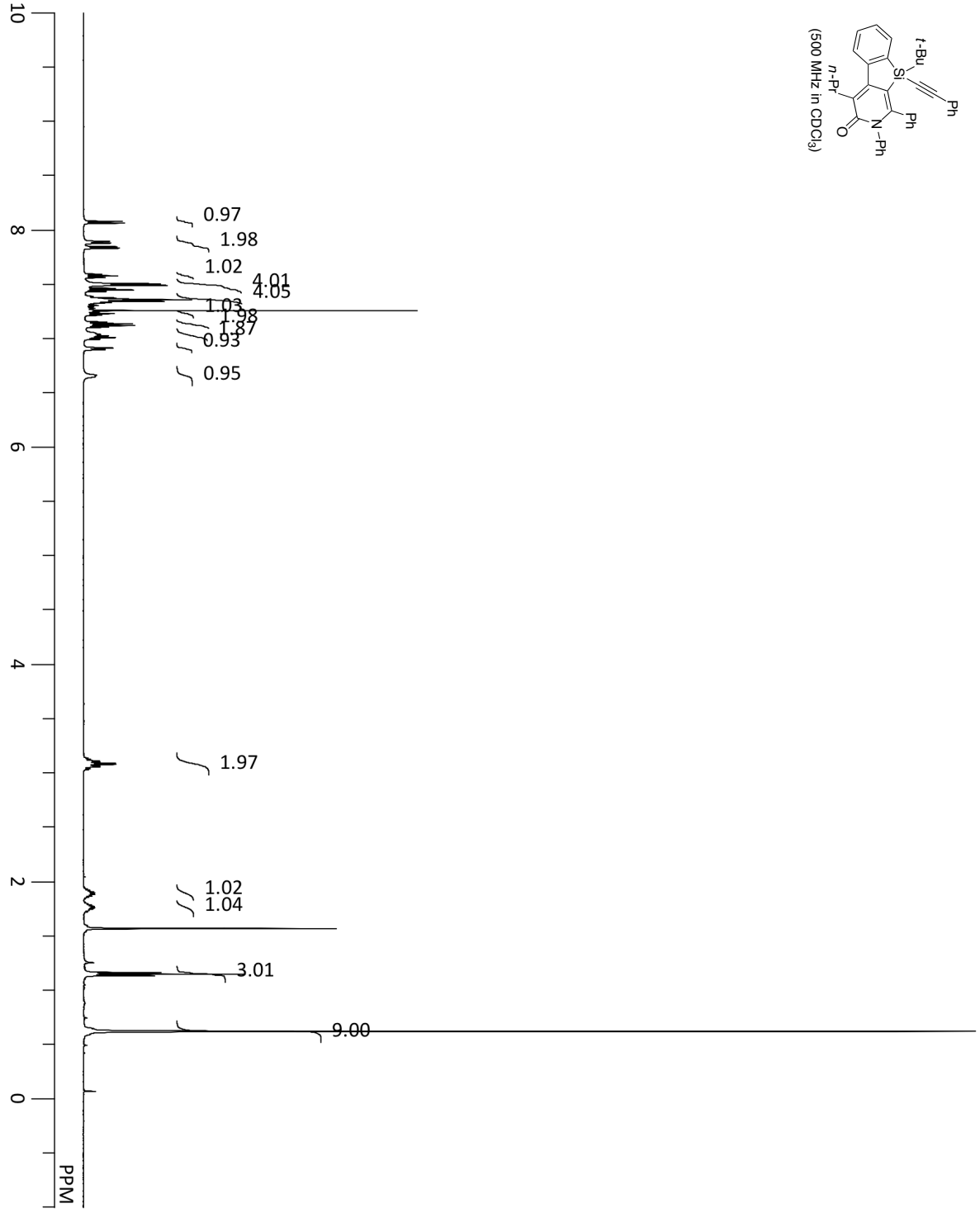
compound **1l**


10
8
6
4
2
0
PPM
0.98
2.00
1.00
2.03
1.99
3.02
3.00
4.92
6.04
9.00
Cy
Si
SiMe3
Me
OMe
(400 MHz in CDCl3)

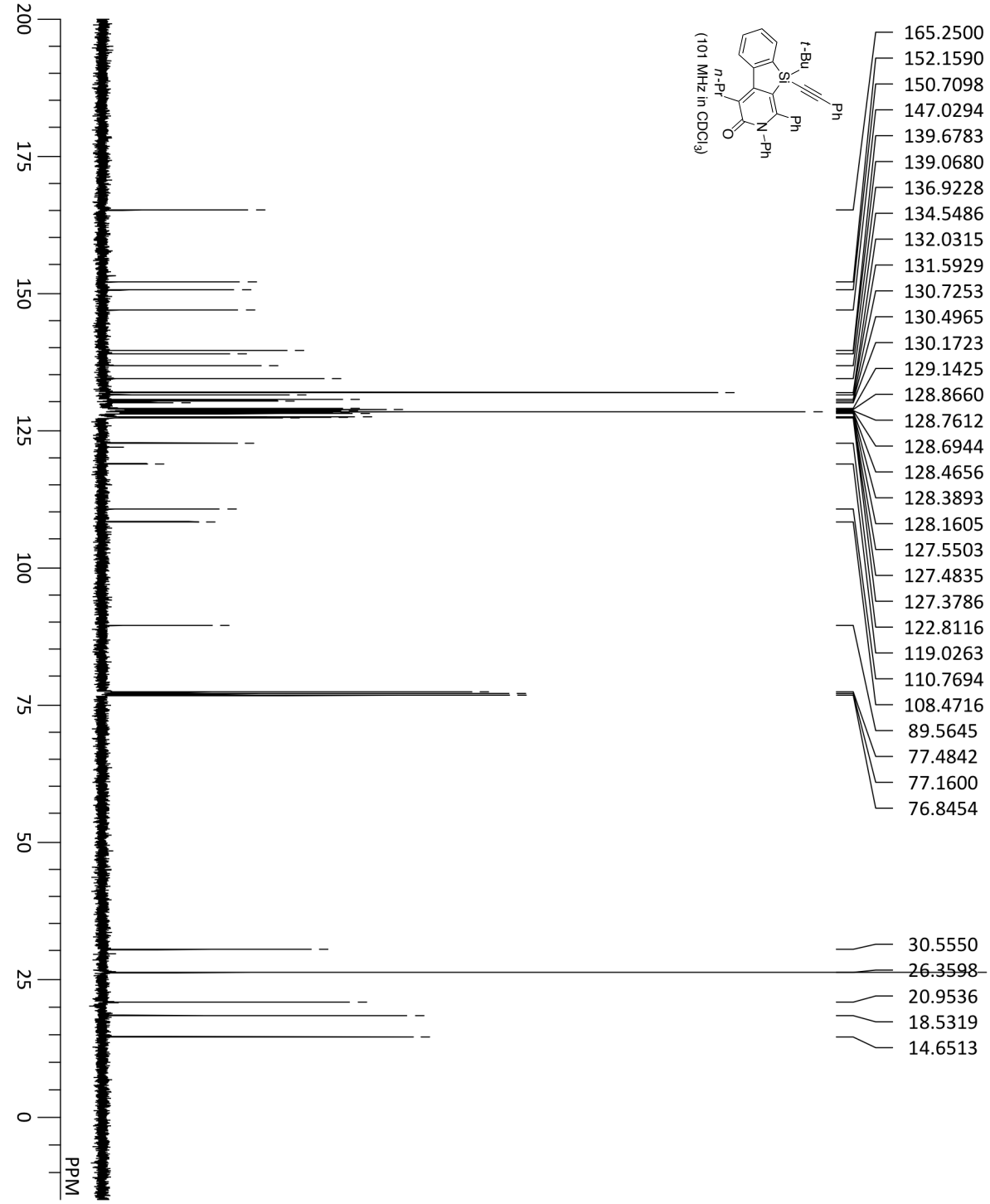
compound **1l**


(101 MHz in CDCl3)
Cy
Si
SiMe3
Me
OMe
160.0727
136.4365
134.6440
133.8717
131.7550
129.8481
129.6193
126.9687
117.2815
115.3079
113.9349
107.8328
107.2130
90.6228
86.4467
81.0596
77.4746
77.1600
76.8454
55.4116
28.1046
27.4944
27.4467
26.8746
25.1203
4.7353
0.0538
PPM

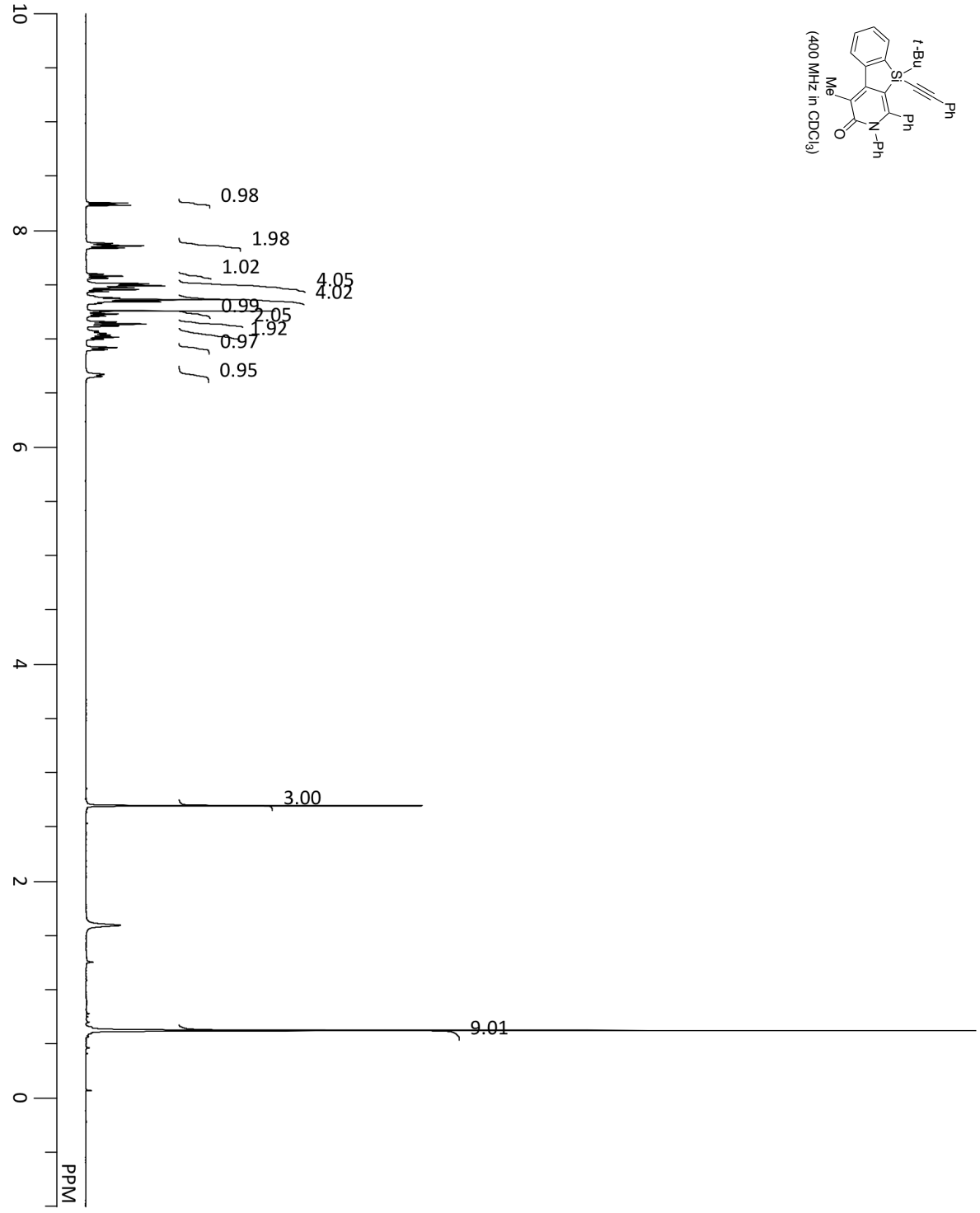
compound **3aa**



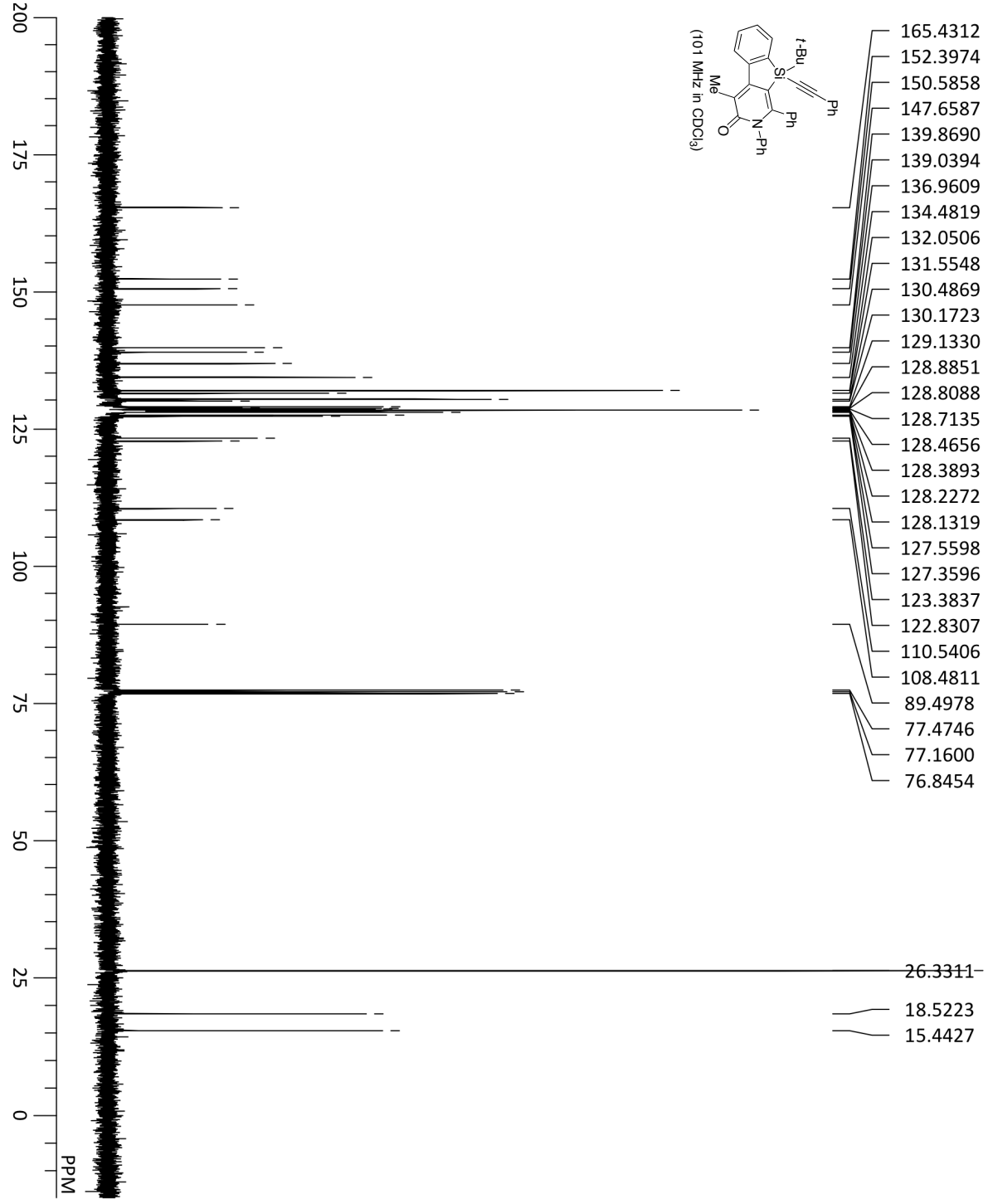
compound **3aa**



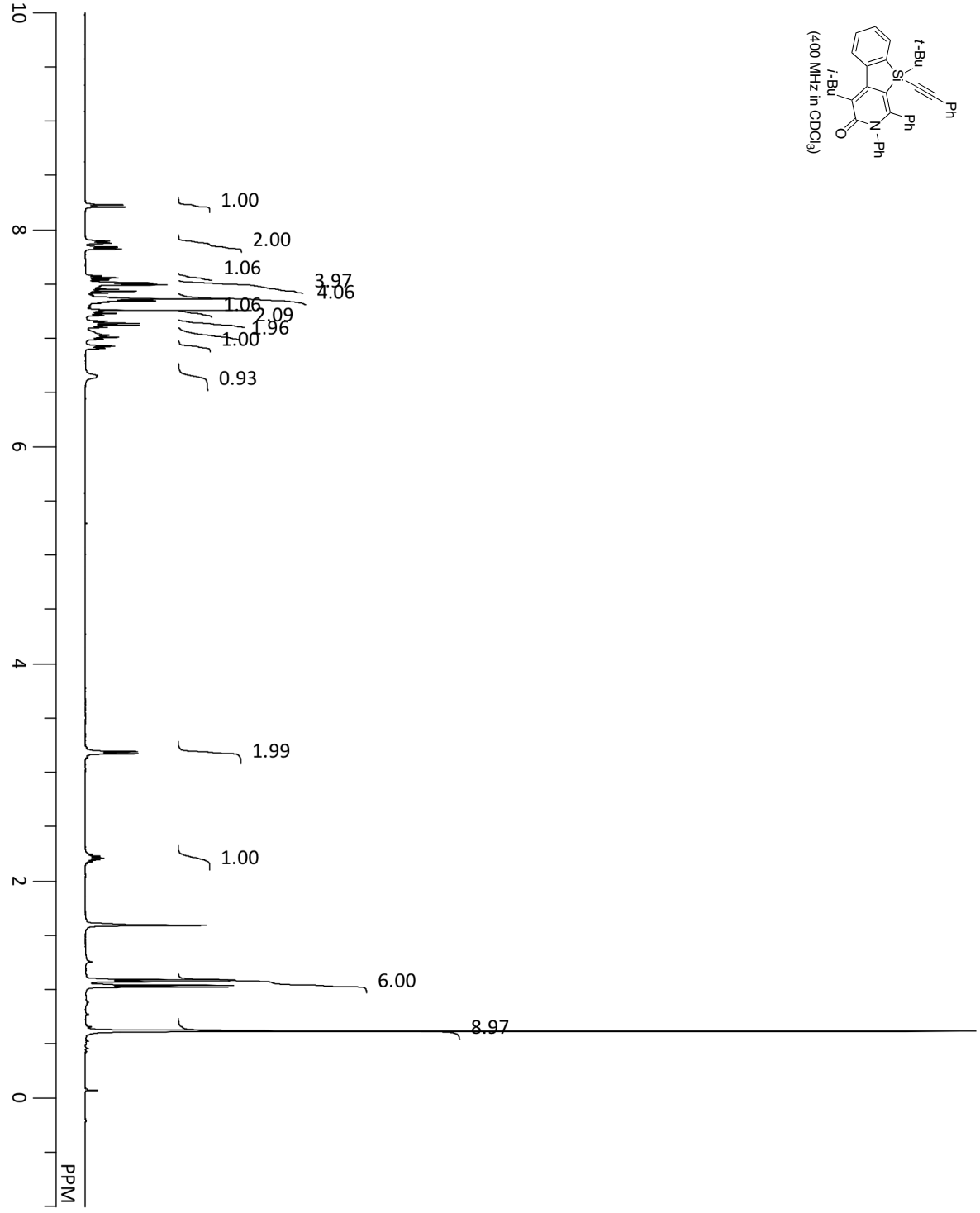
compound **3ba**



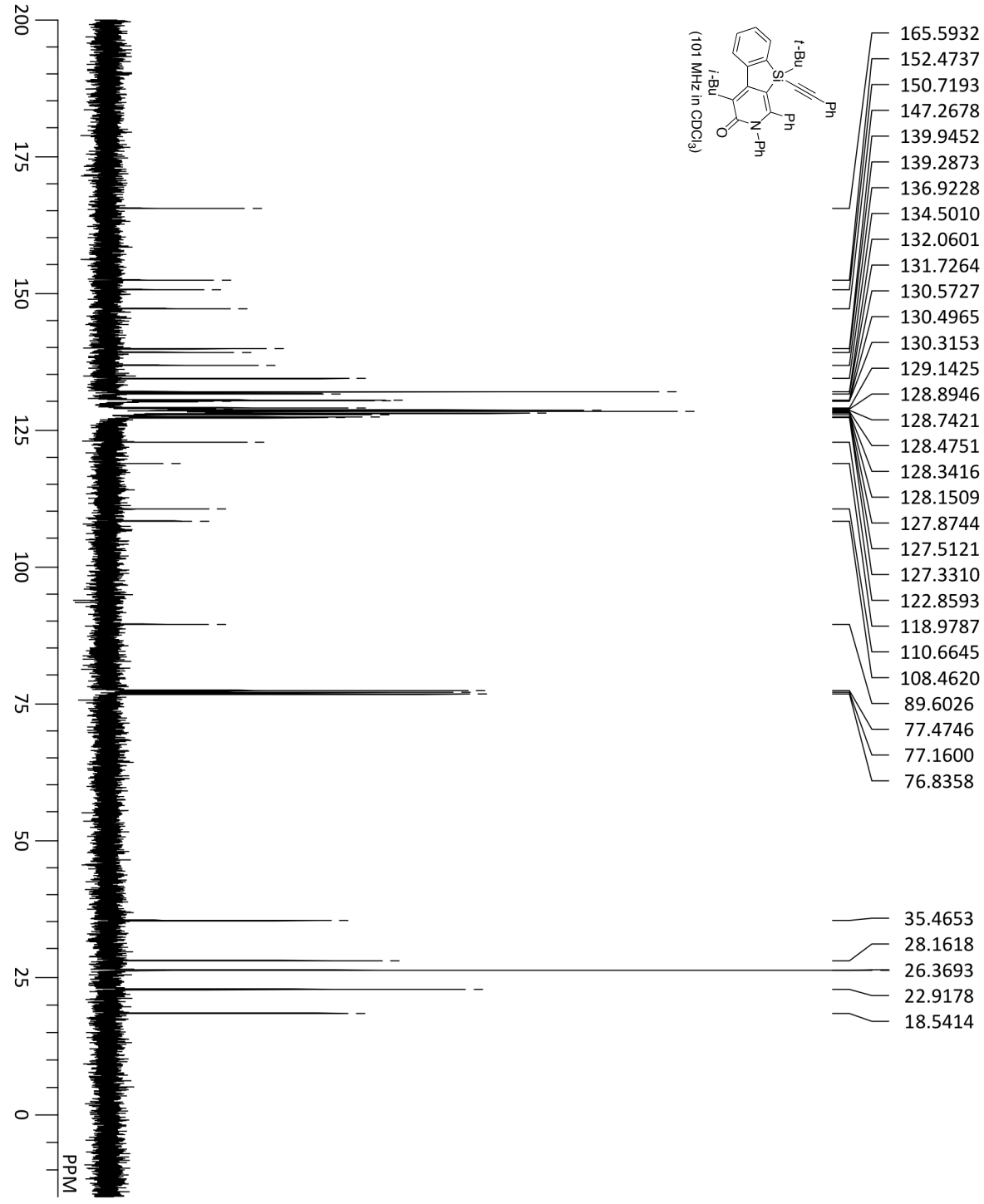
compound **3ba**



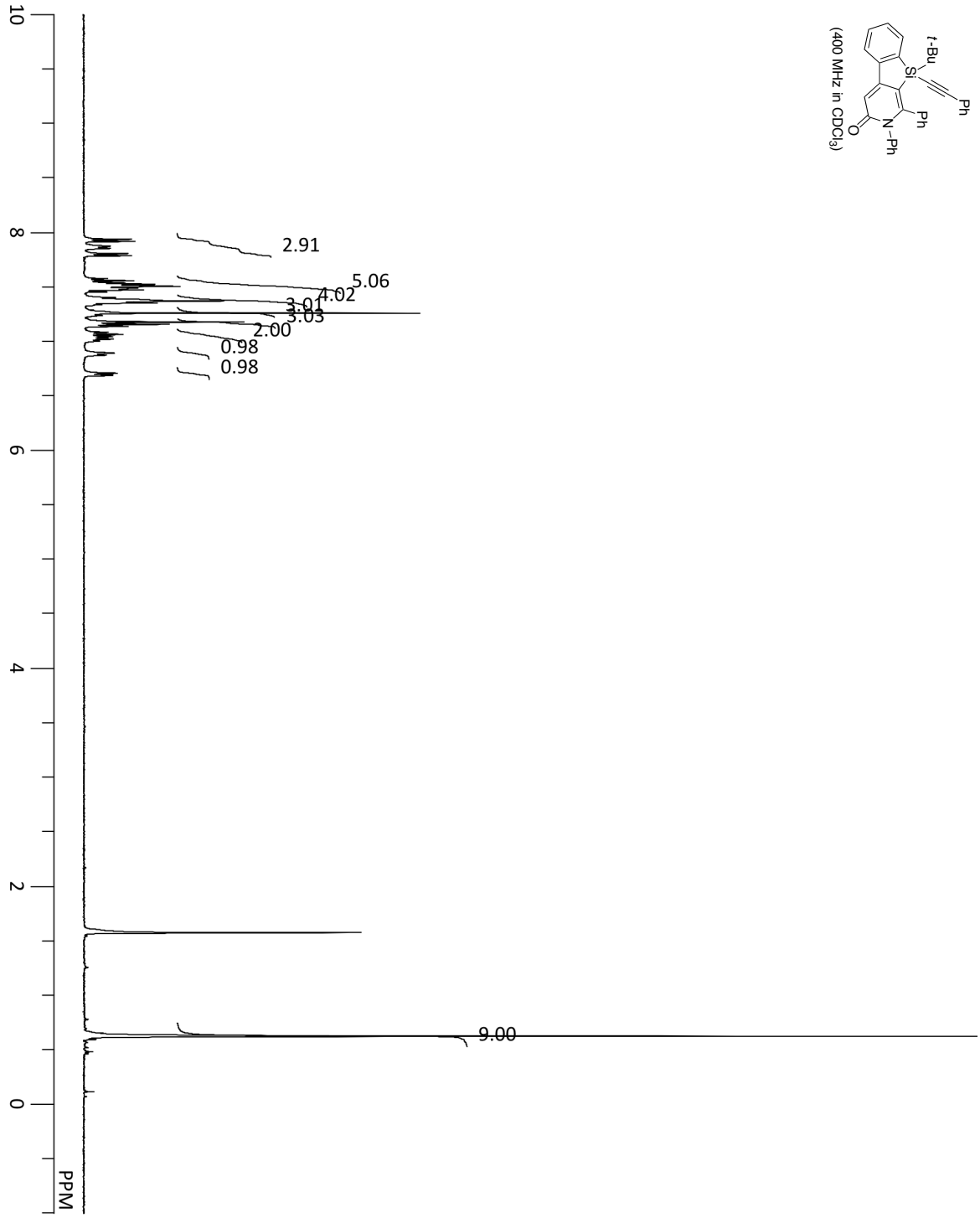
compound **3ca**



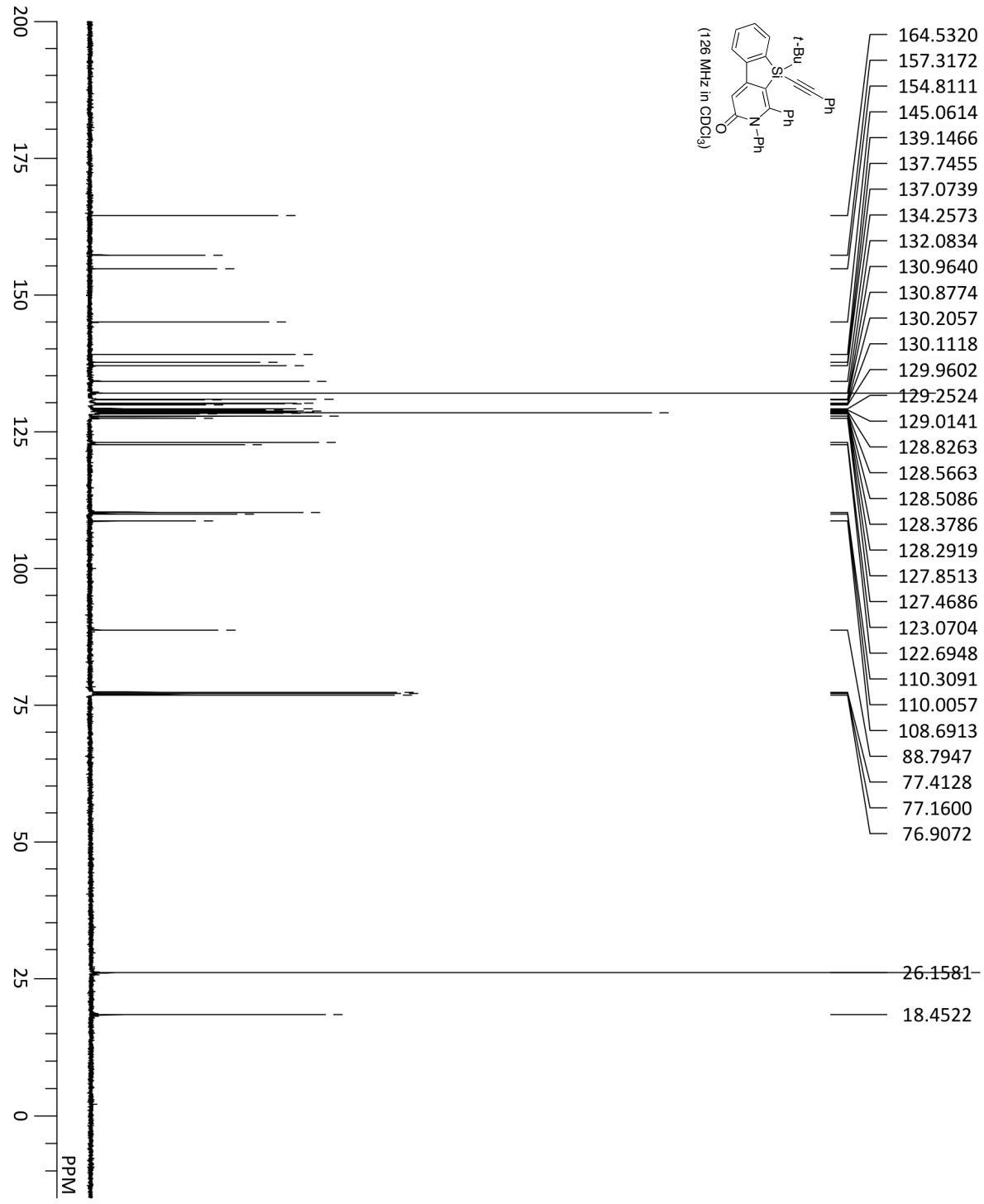
compound **3ca**



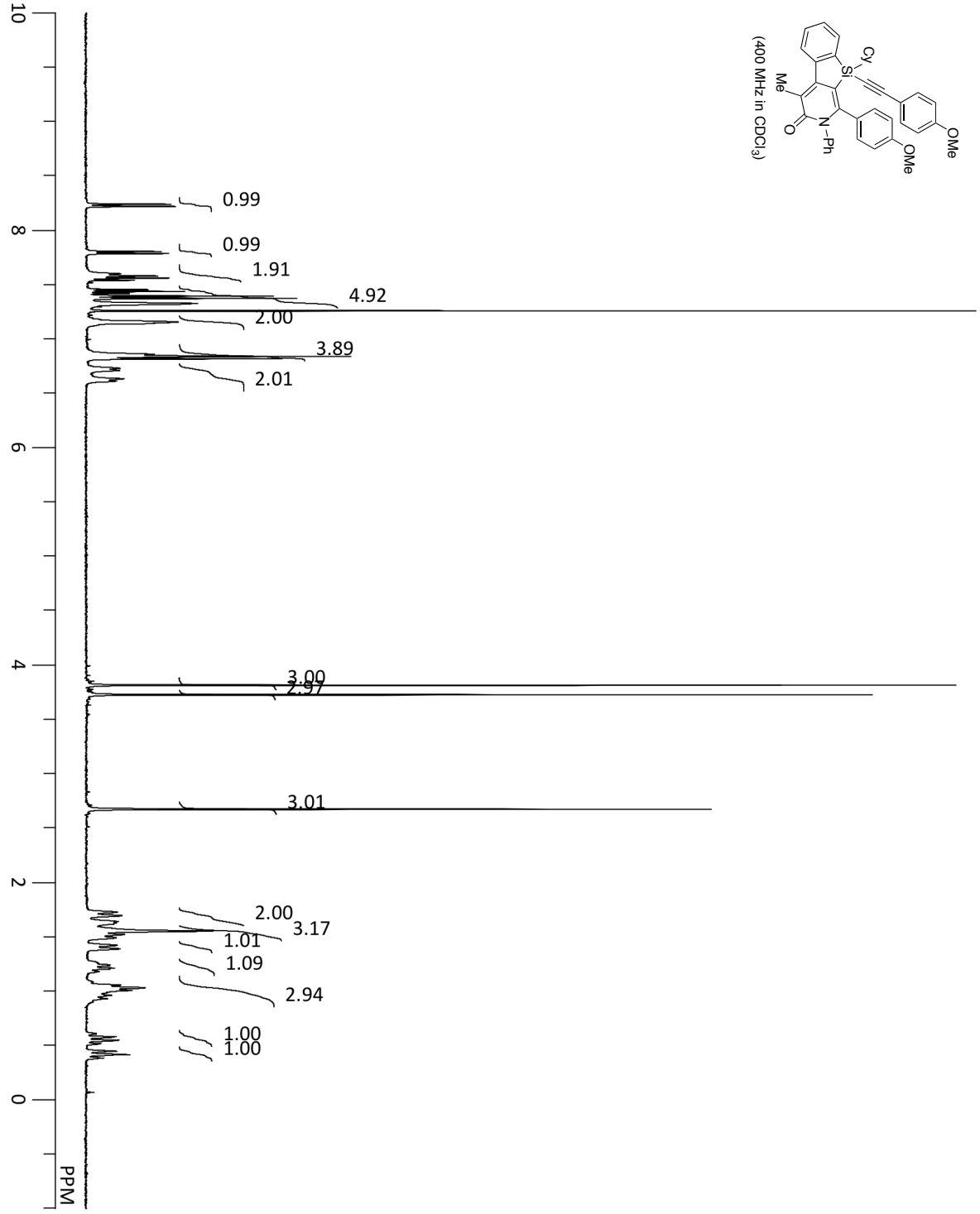
compound **3da**



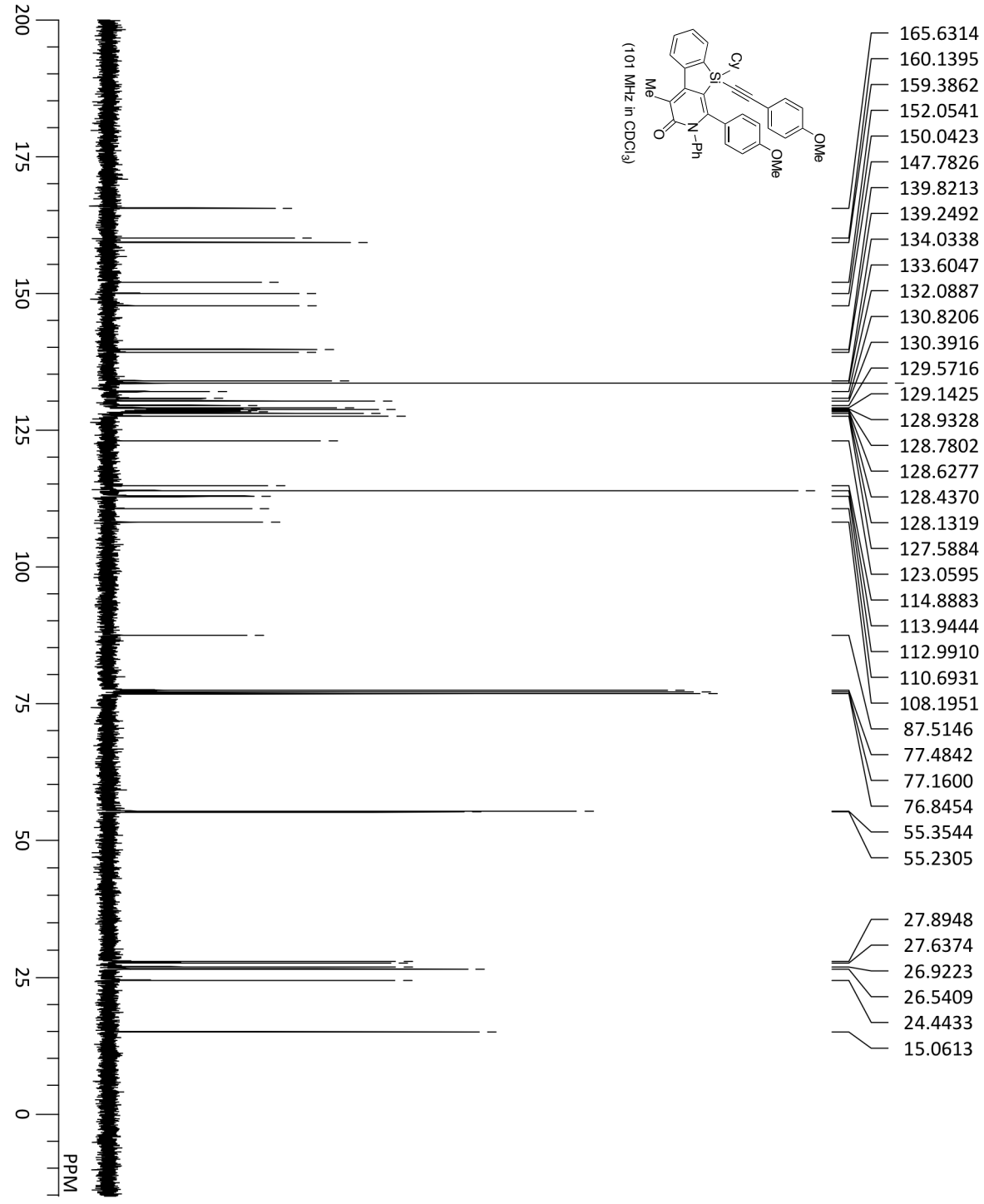
compound **3da**



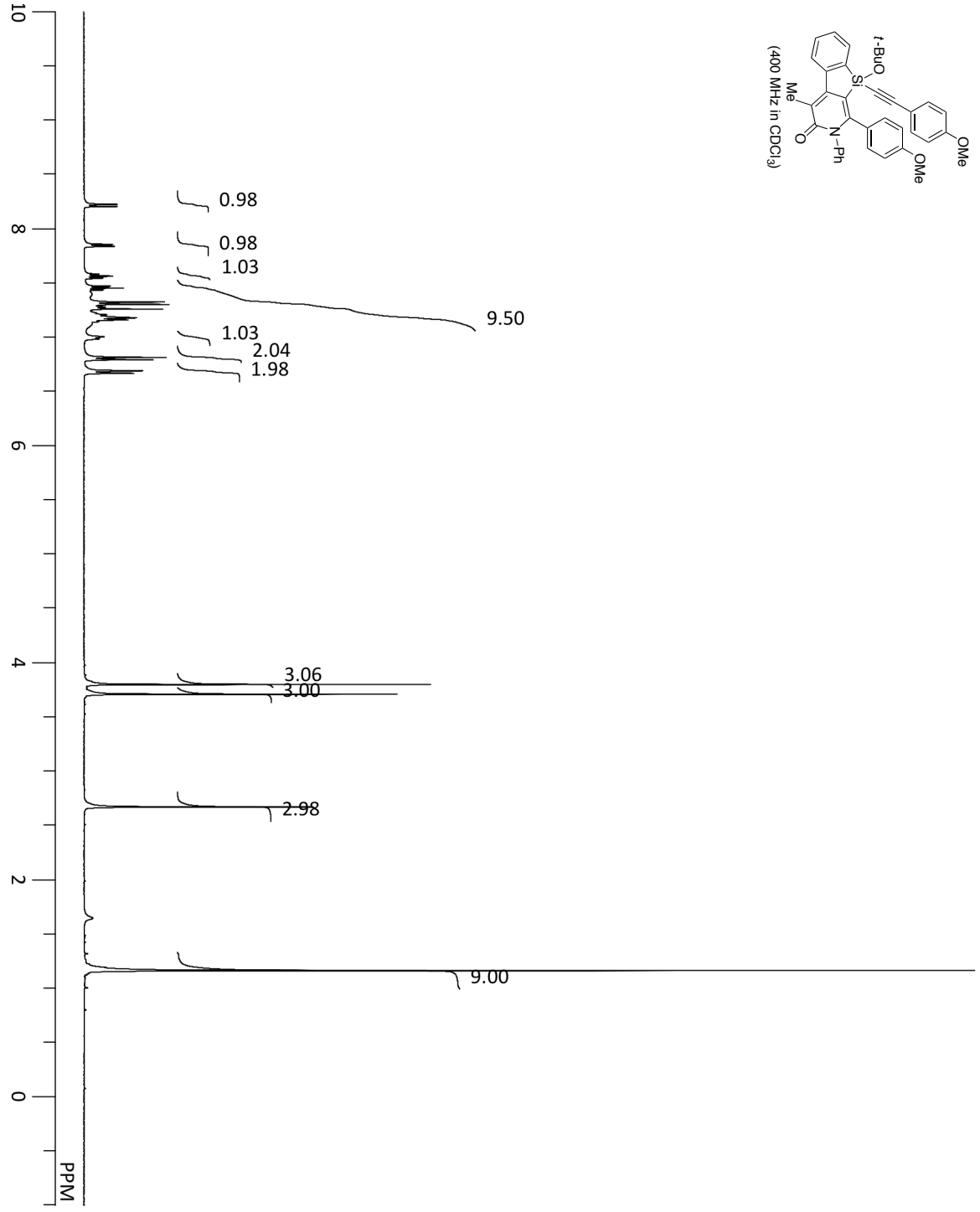
compound **3ea**



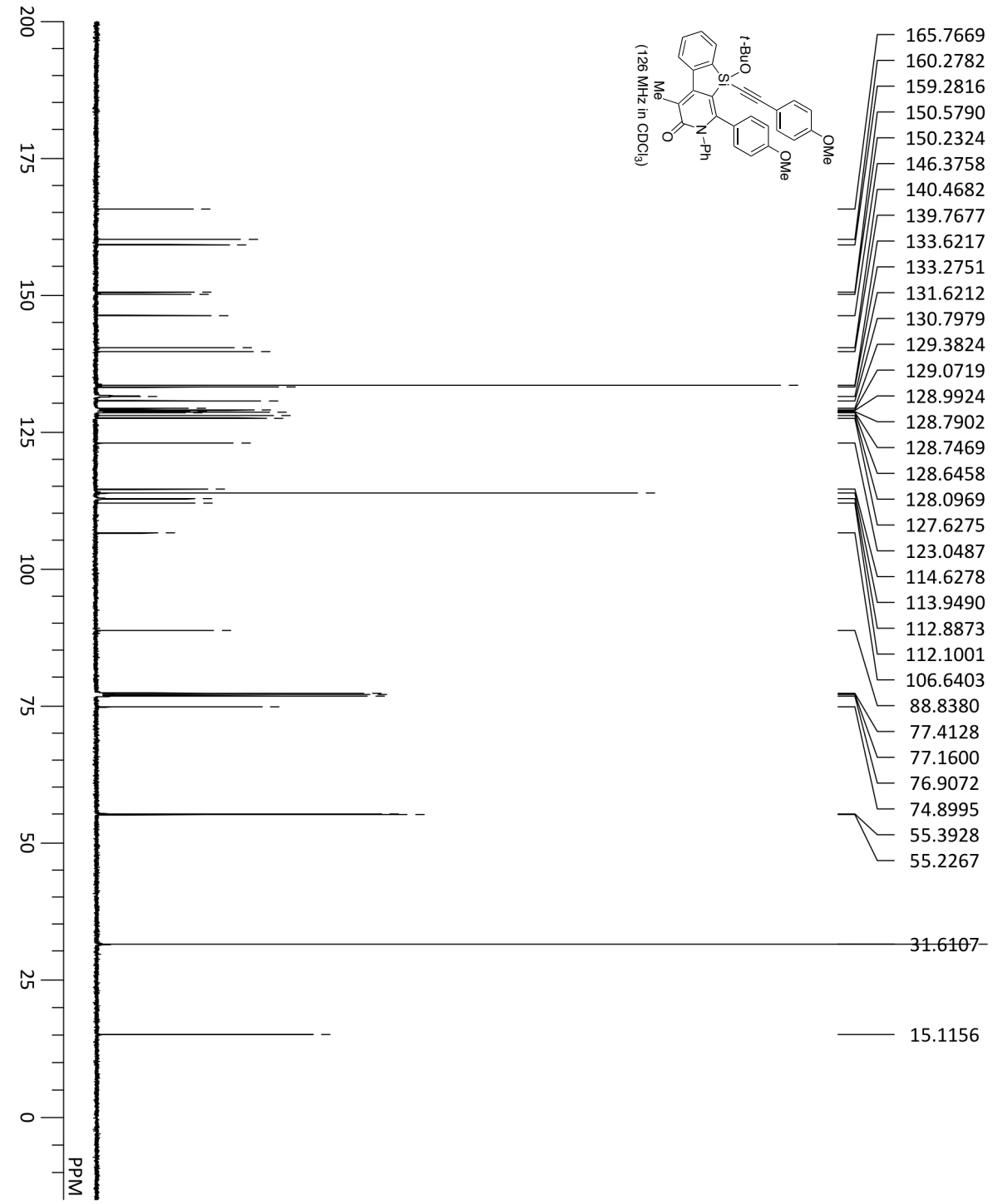
compound **3ea**



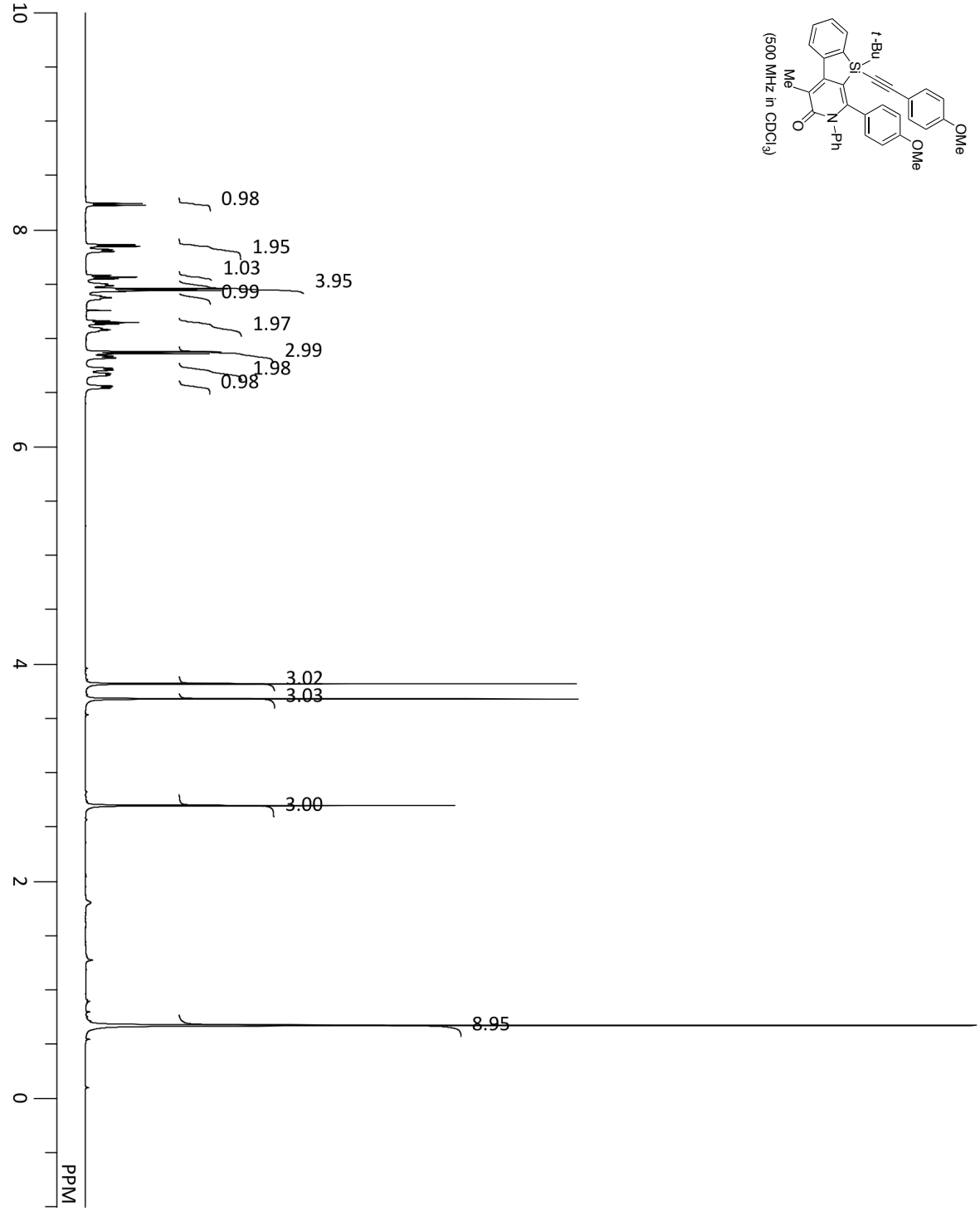
compound **3fa**



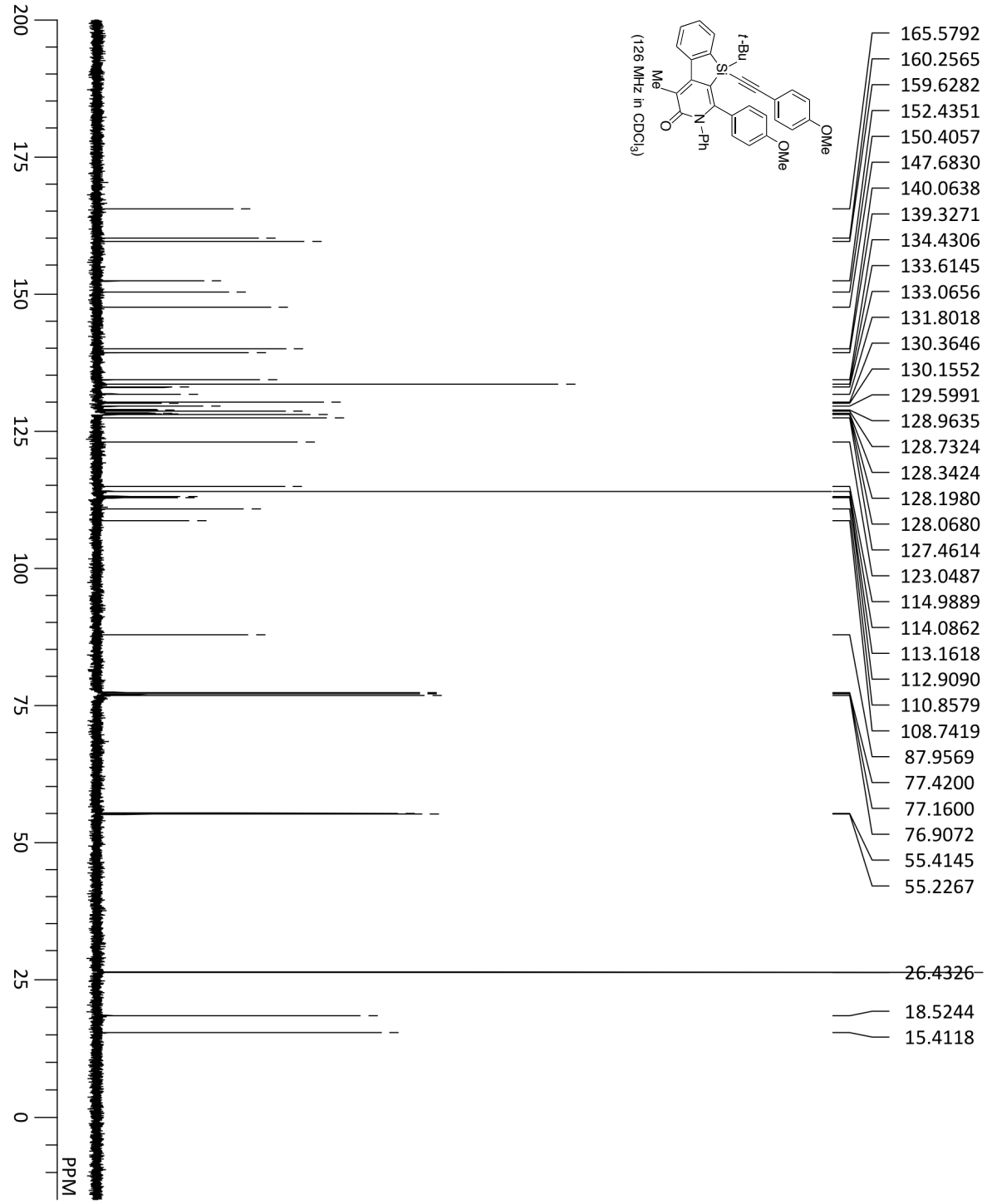
compound **3fa**



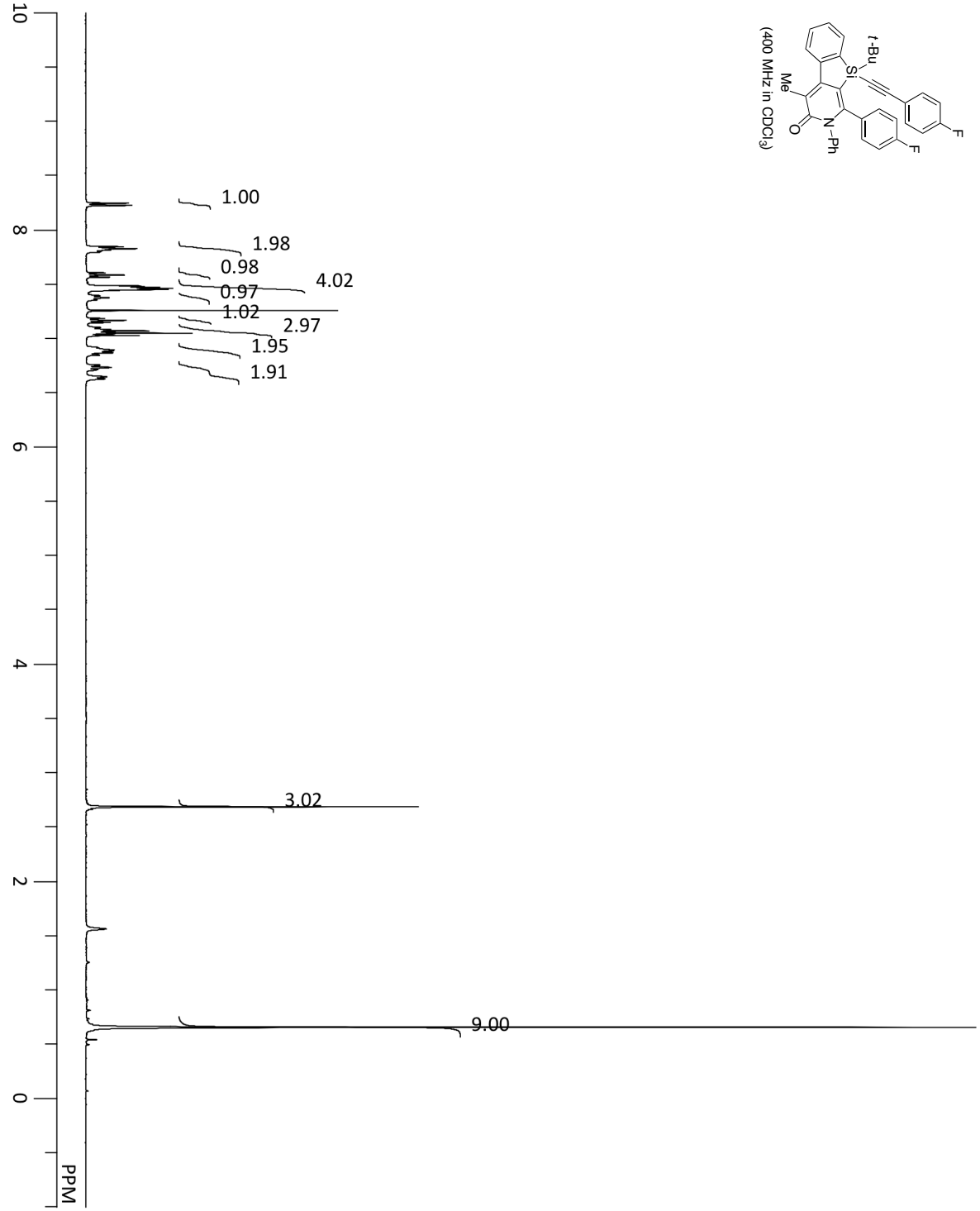
compound **3ga**



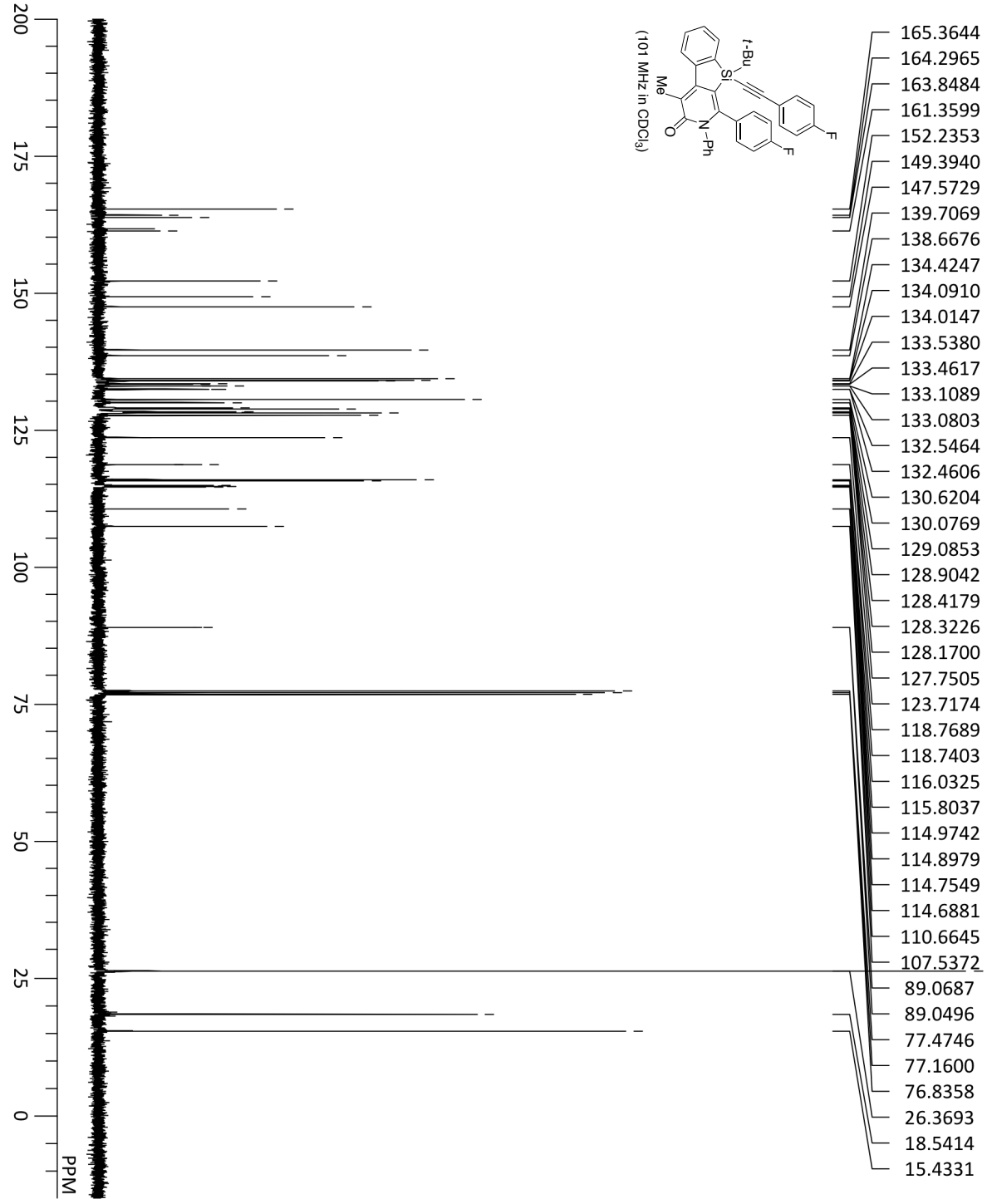
compound **3ga**



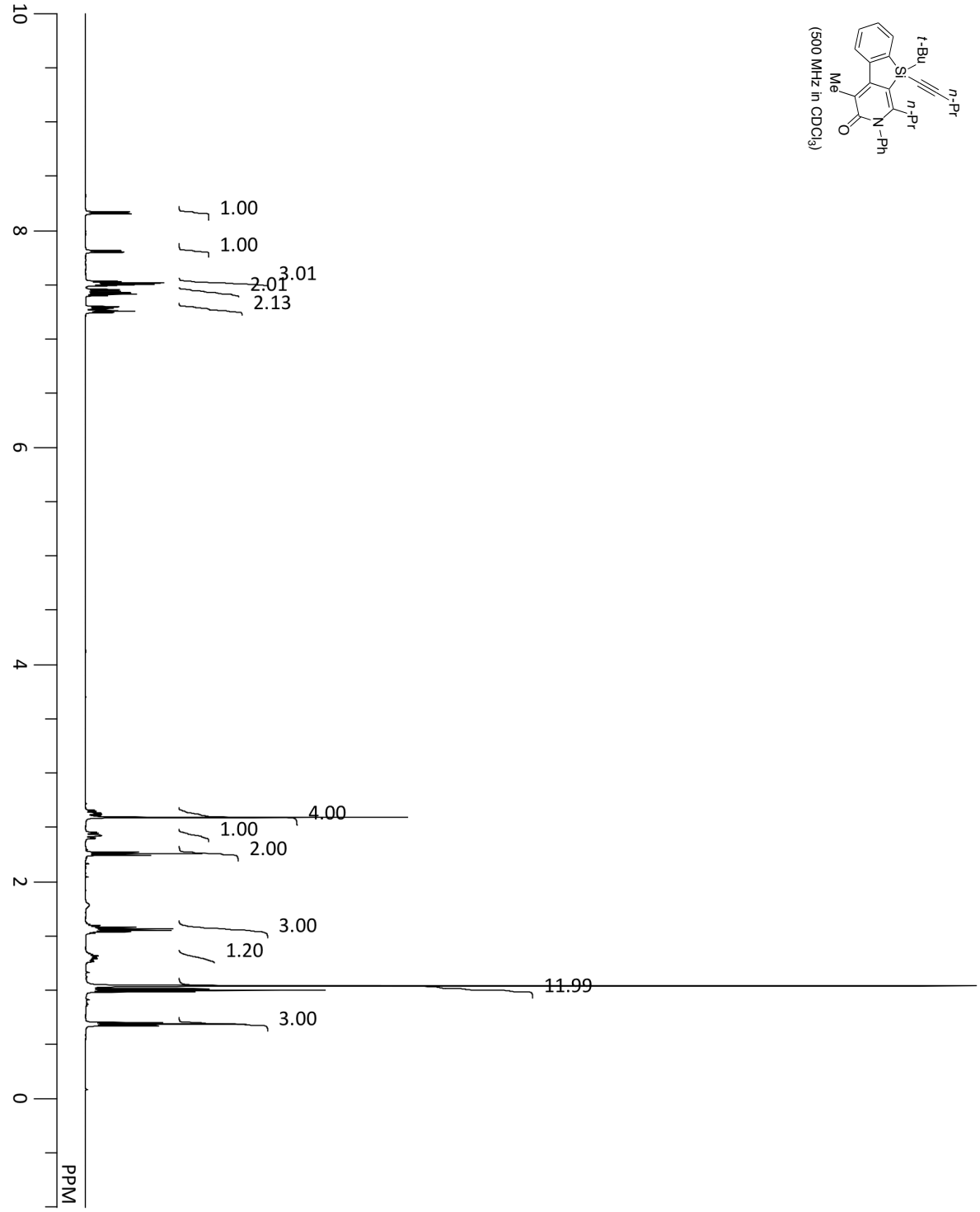
compound **3ha**



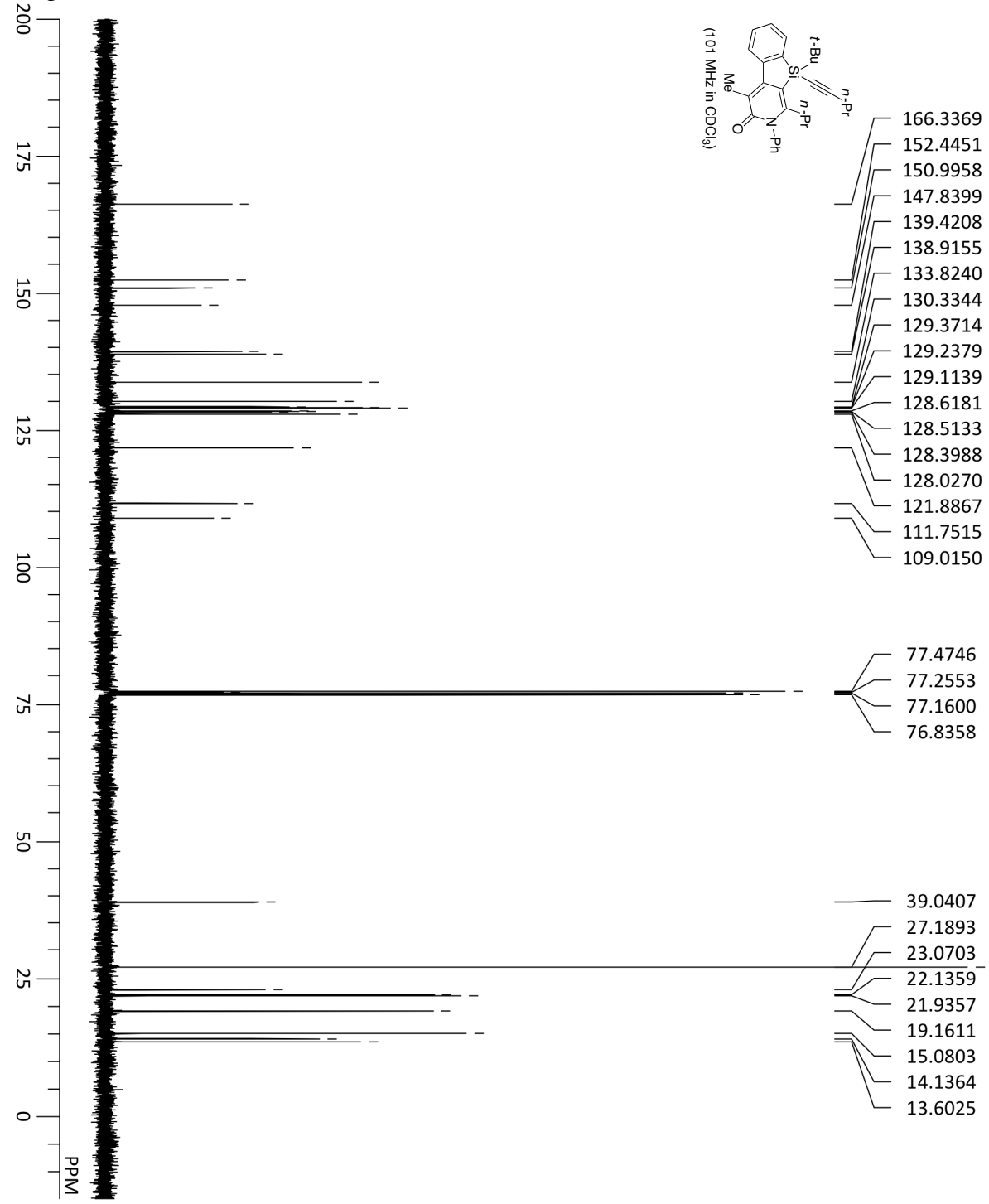
compound **3ha**



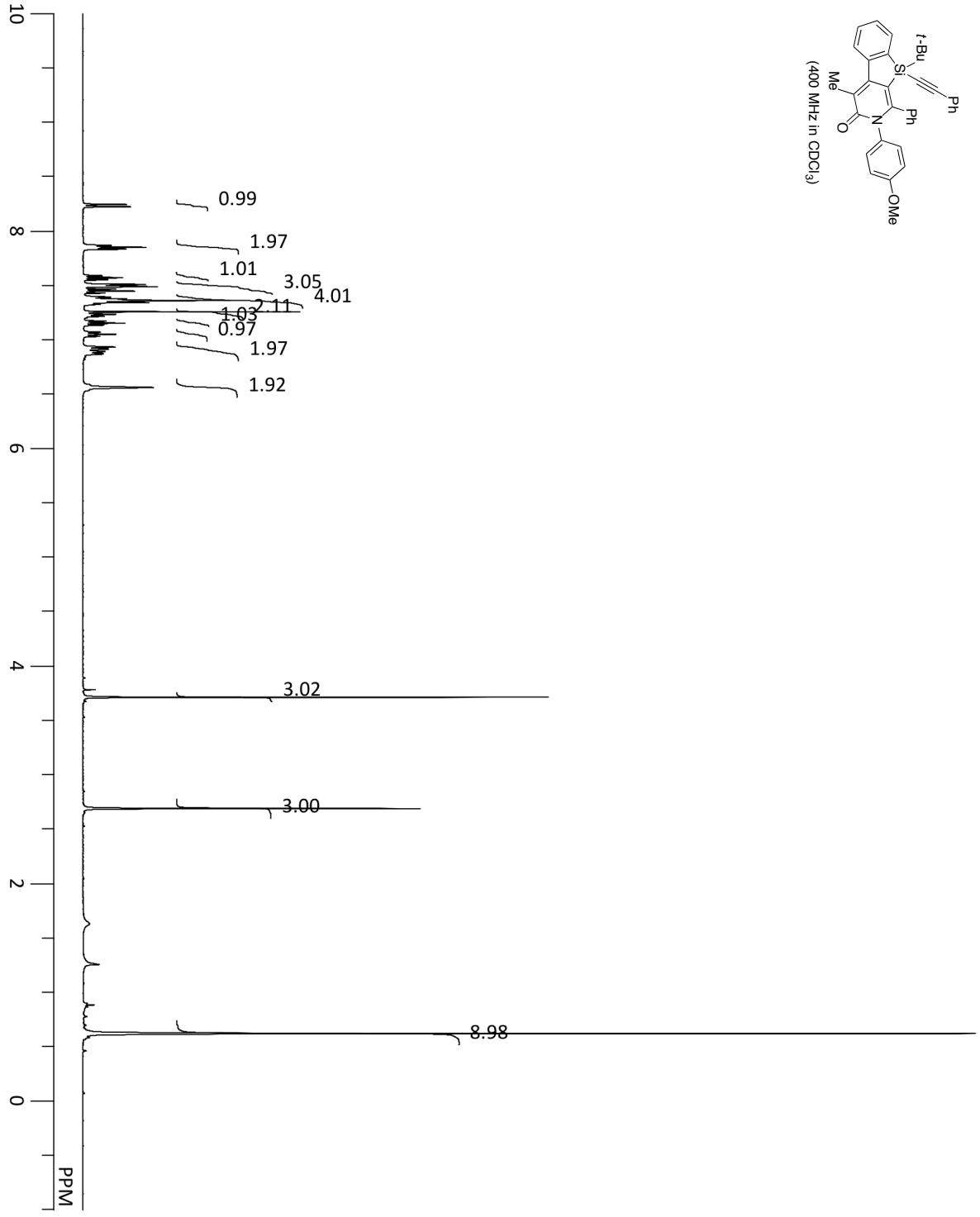
compound **3ia**



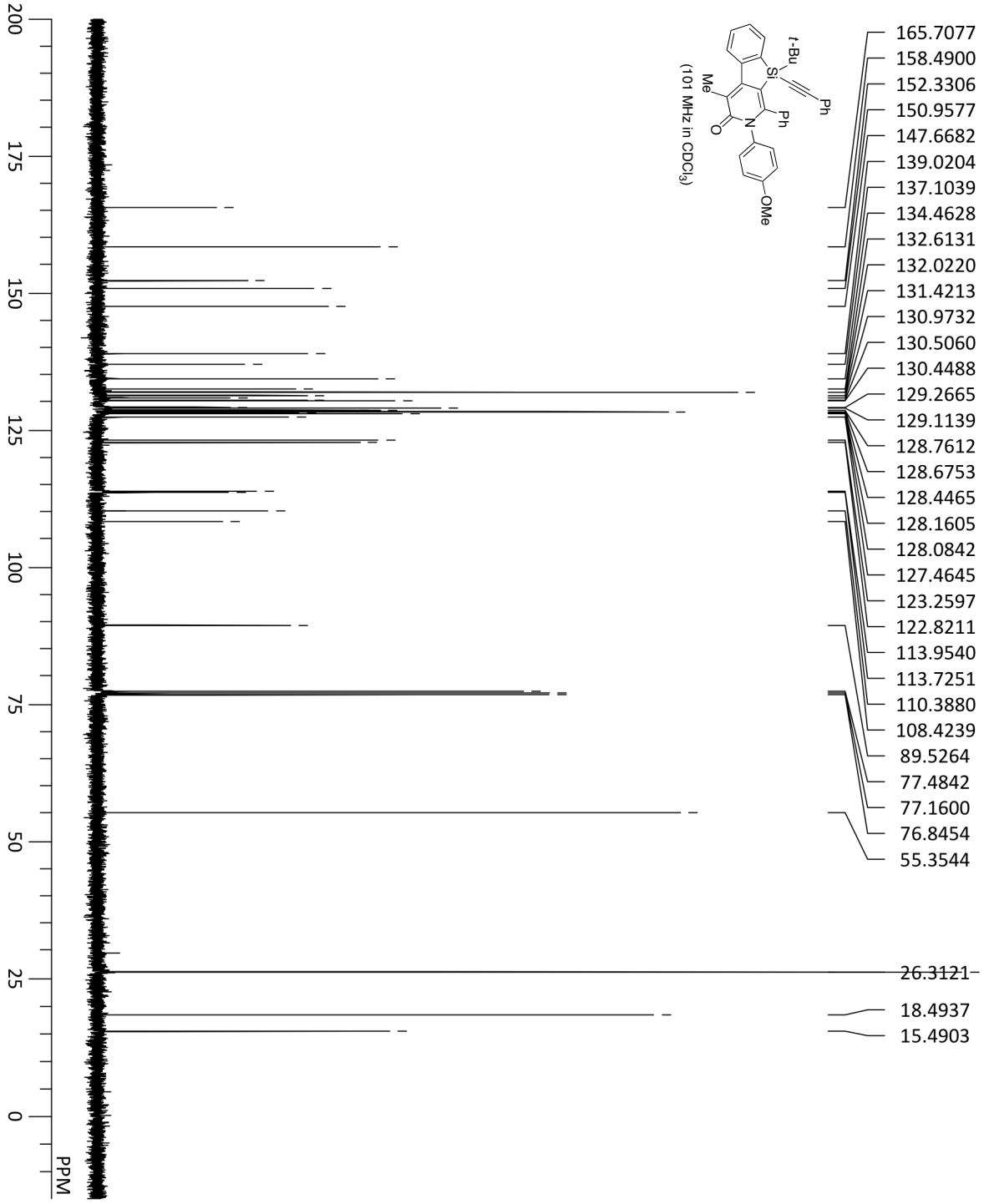
compound **3ia**



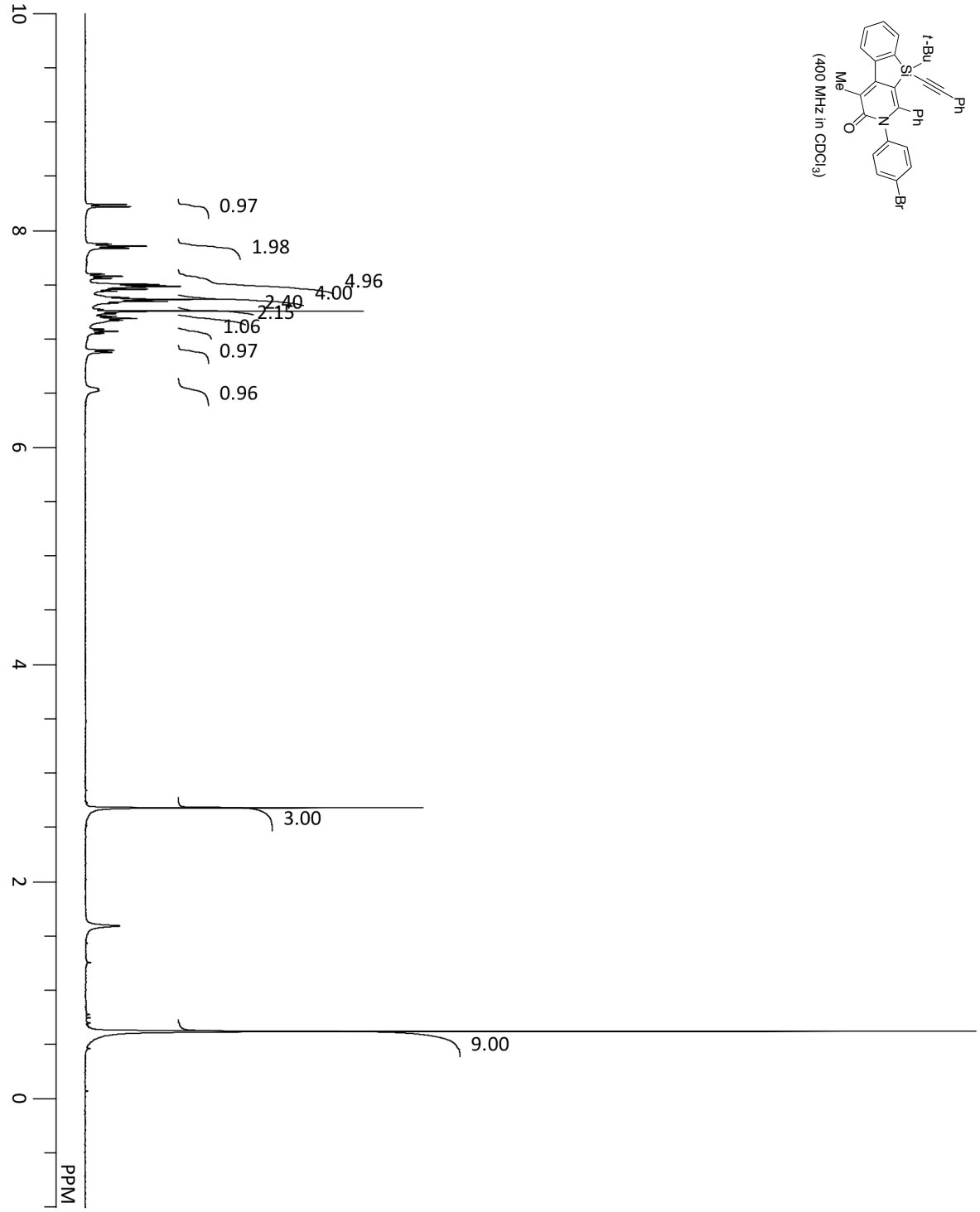
compound **3bb**



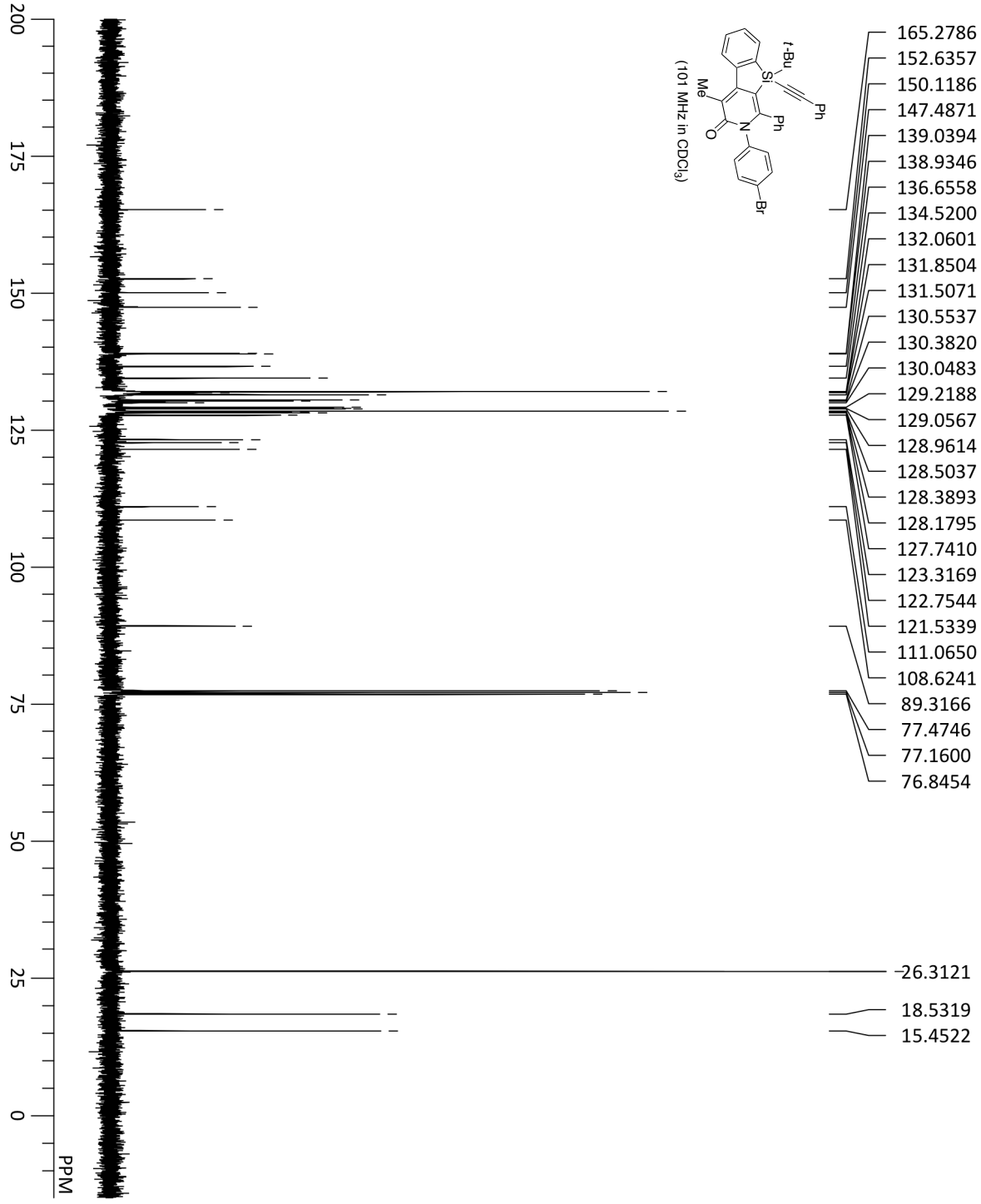
compound **3bb**



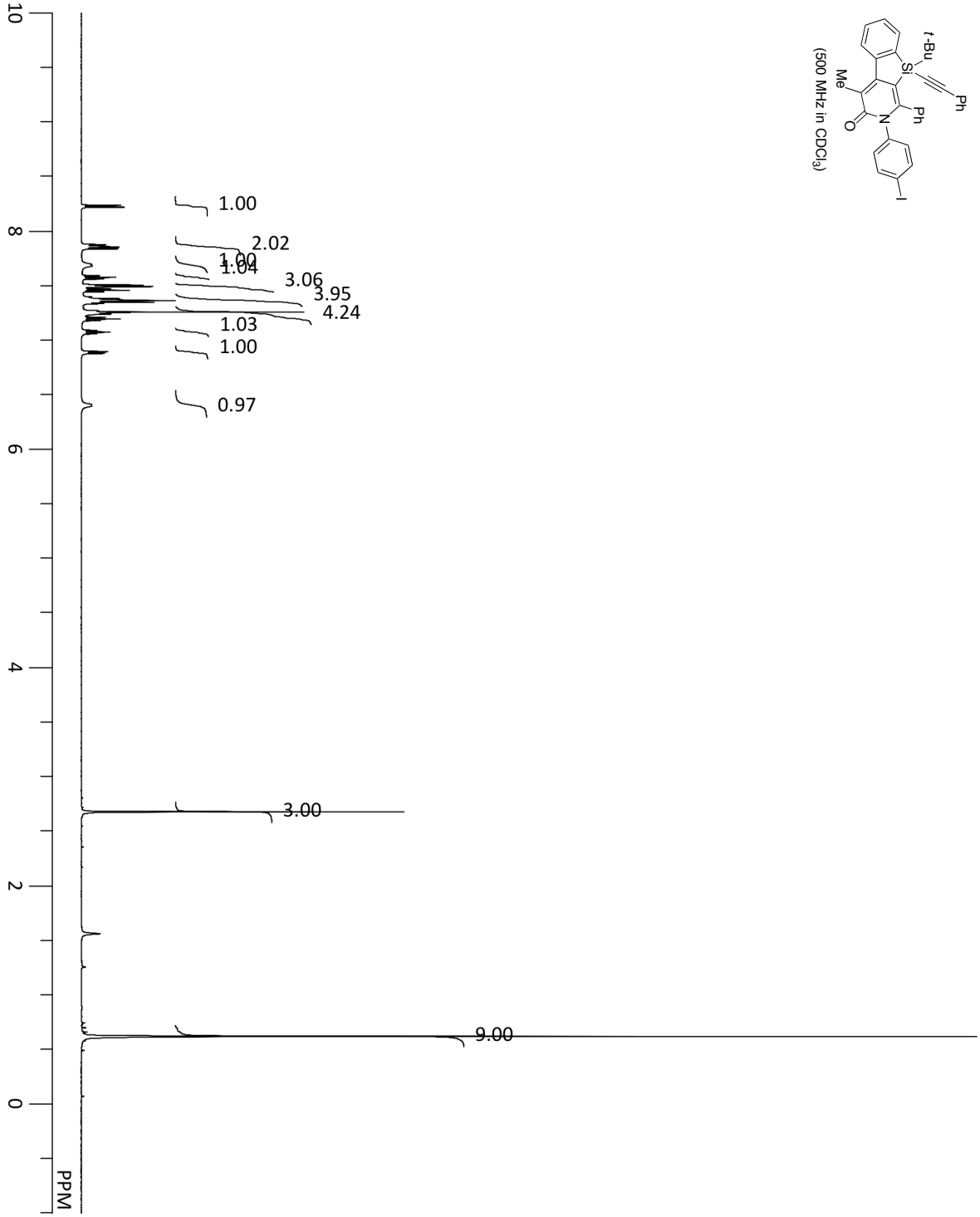
compound **3bc**



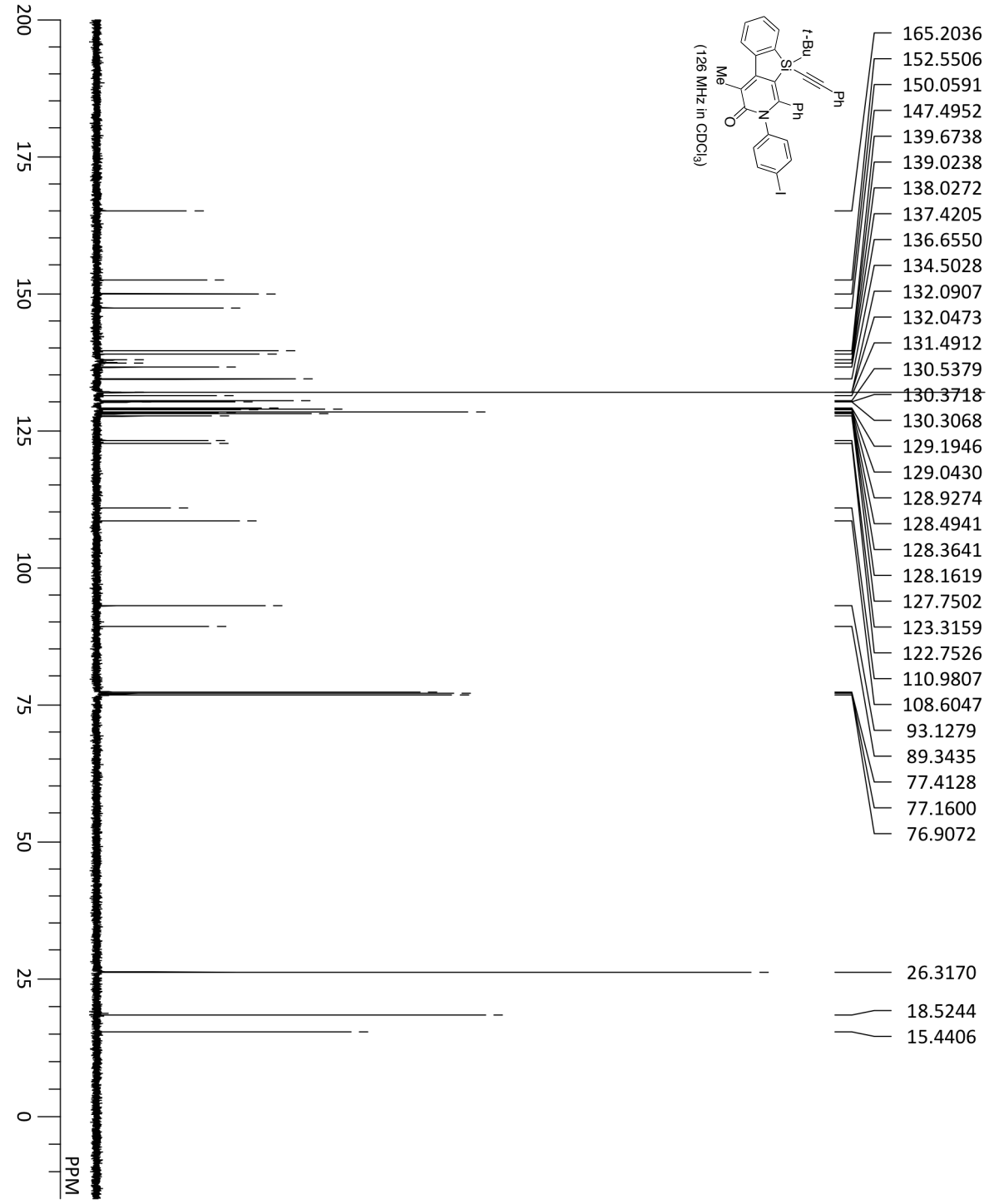
compound **3bc**



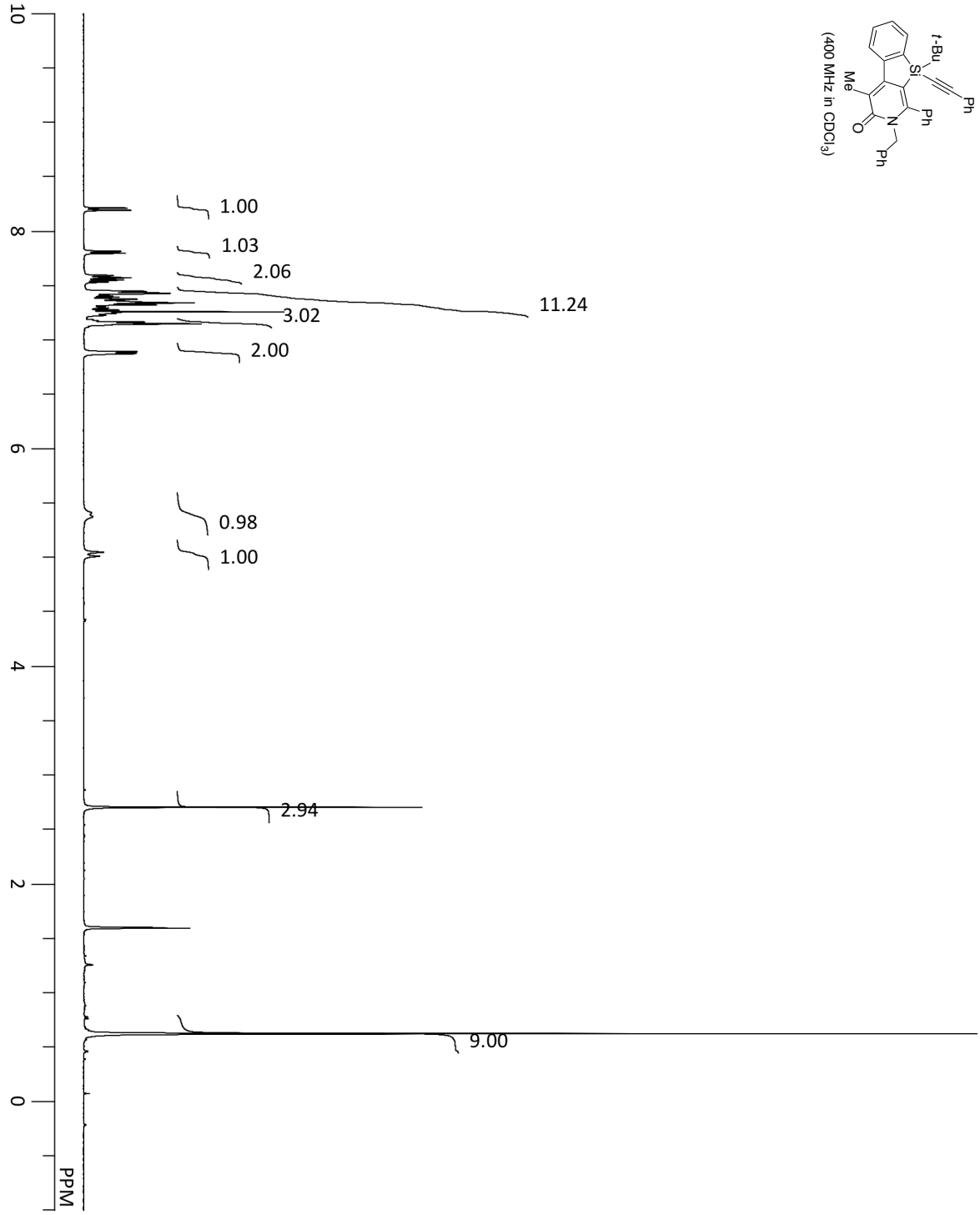
compound **3bd**



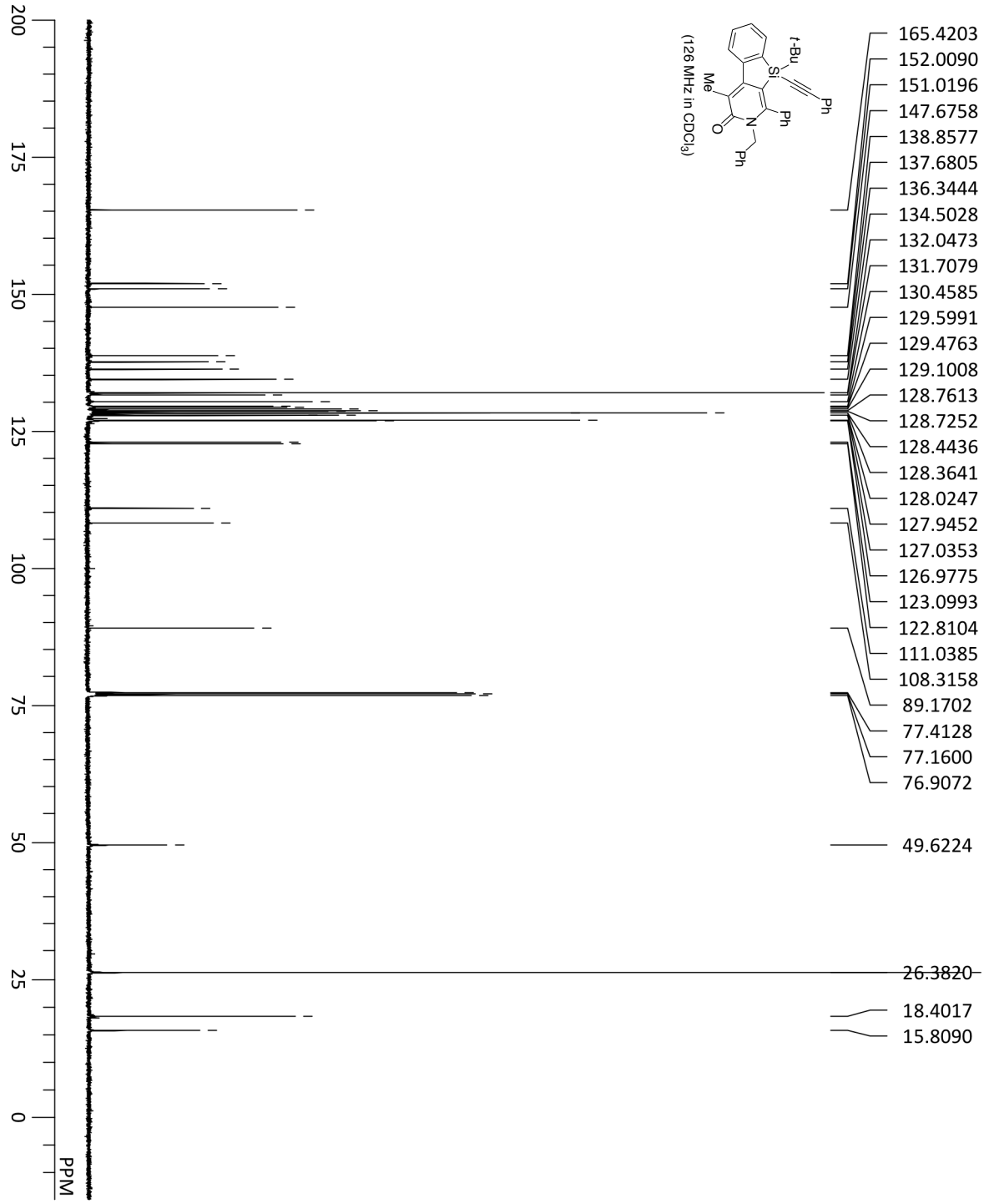
compound **3bd**



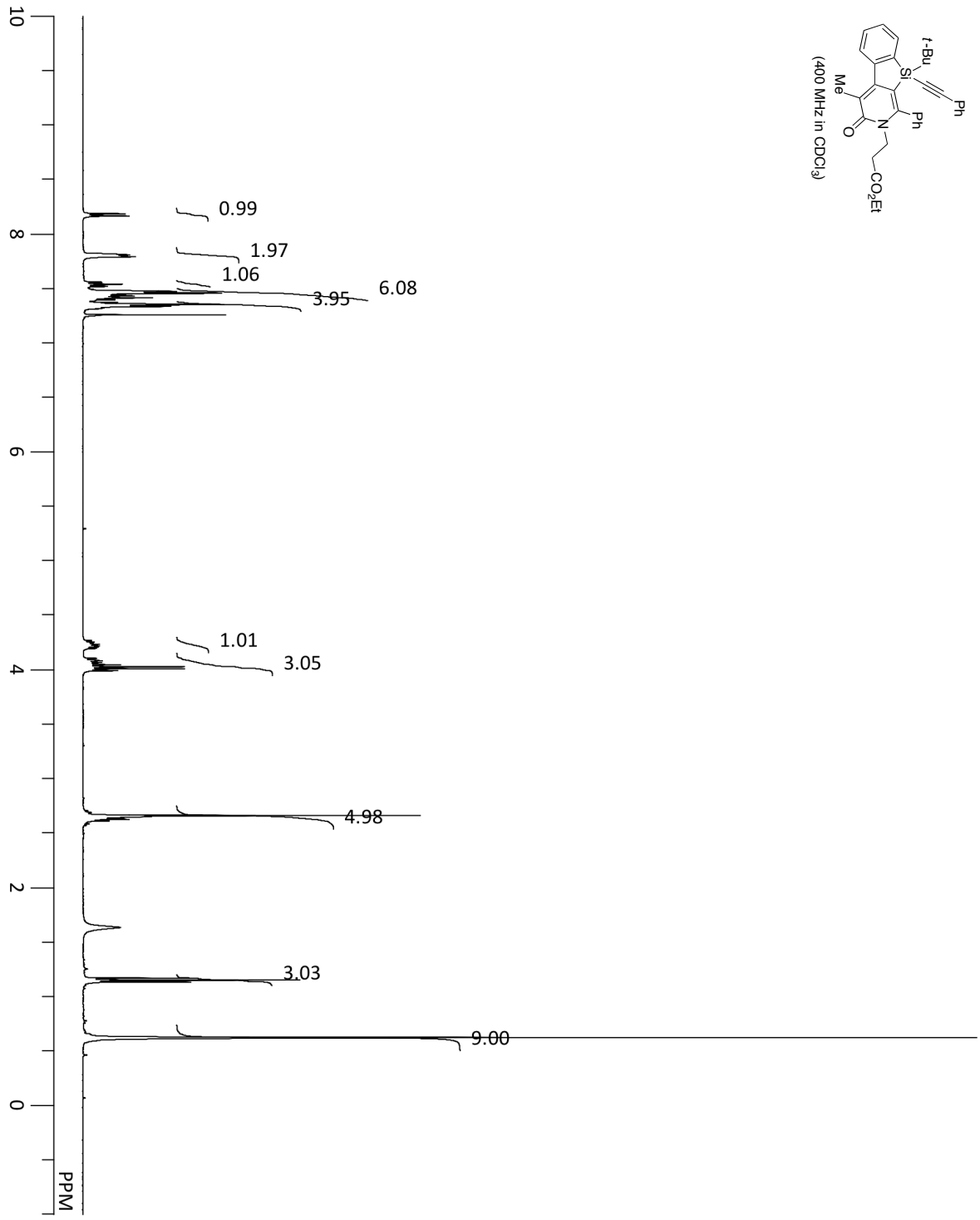
compound **3be**



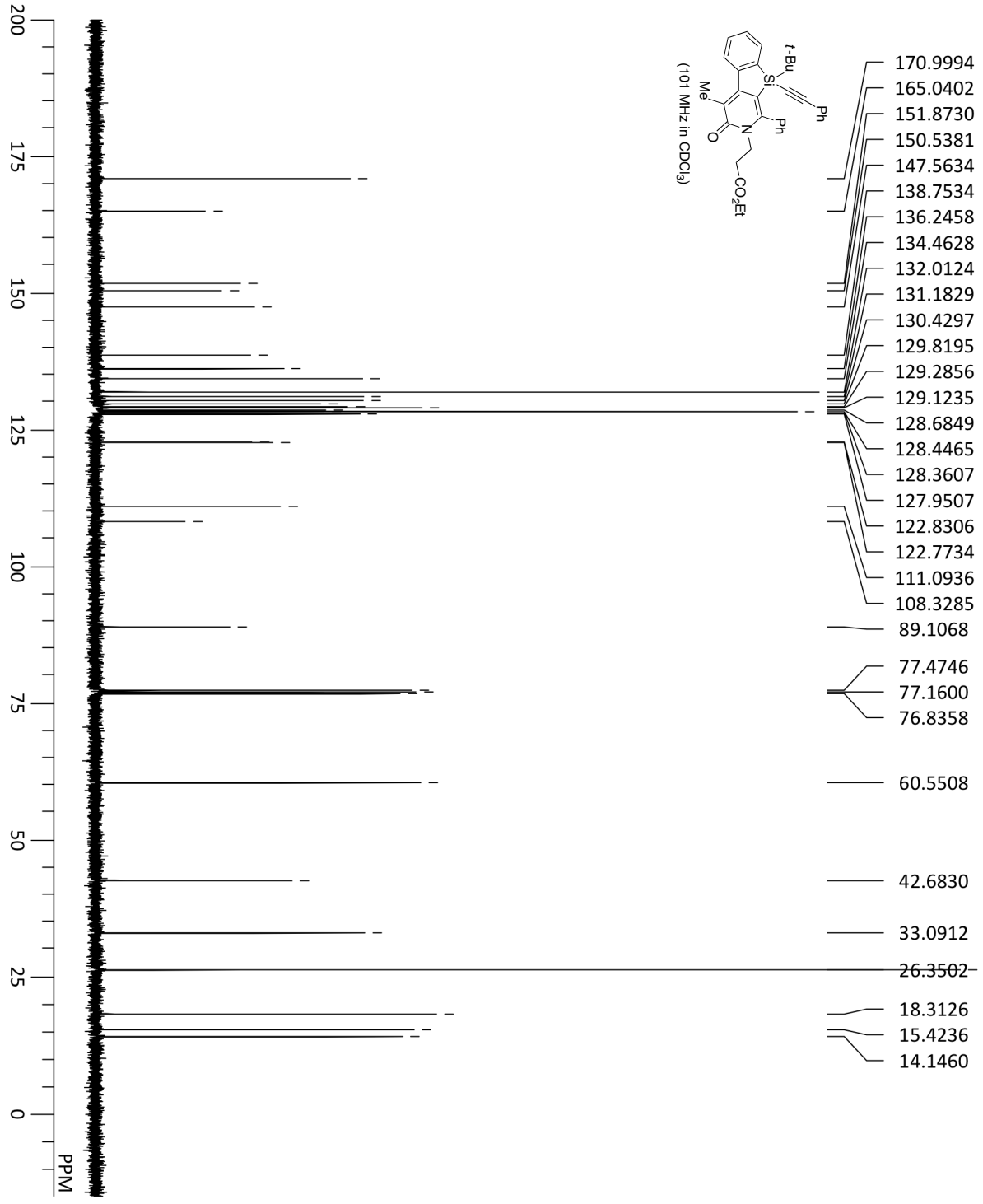
compound **3be**



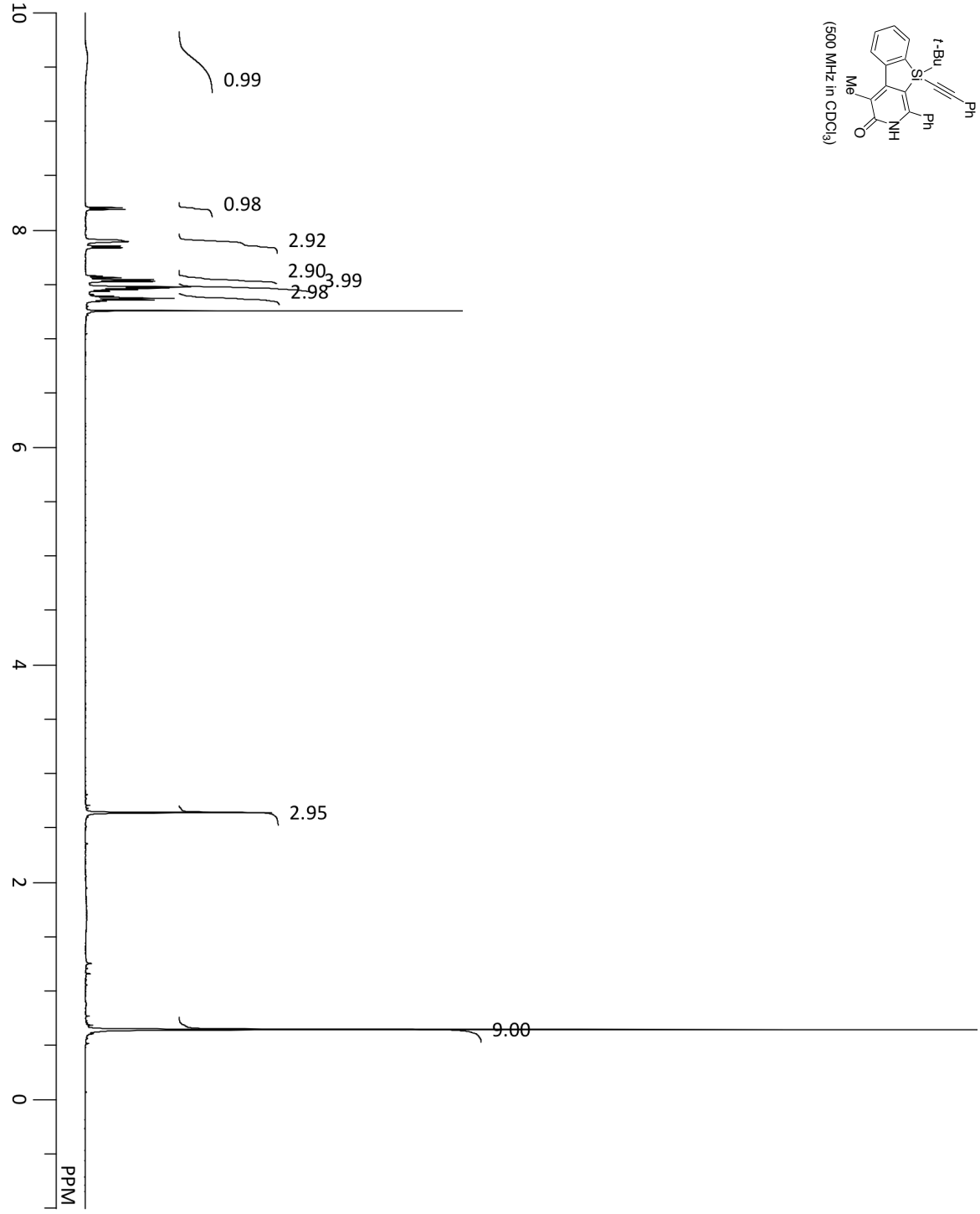
compound **3bf**



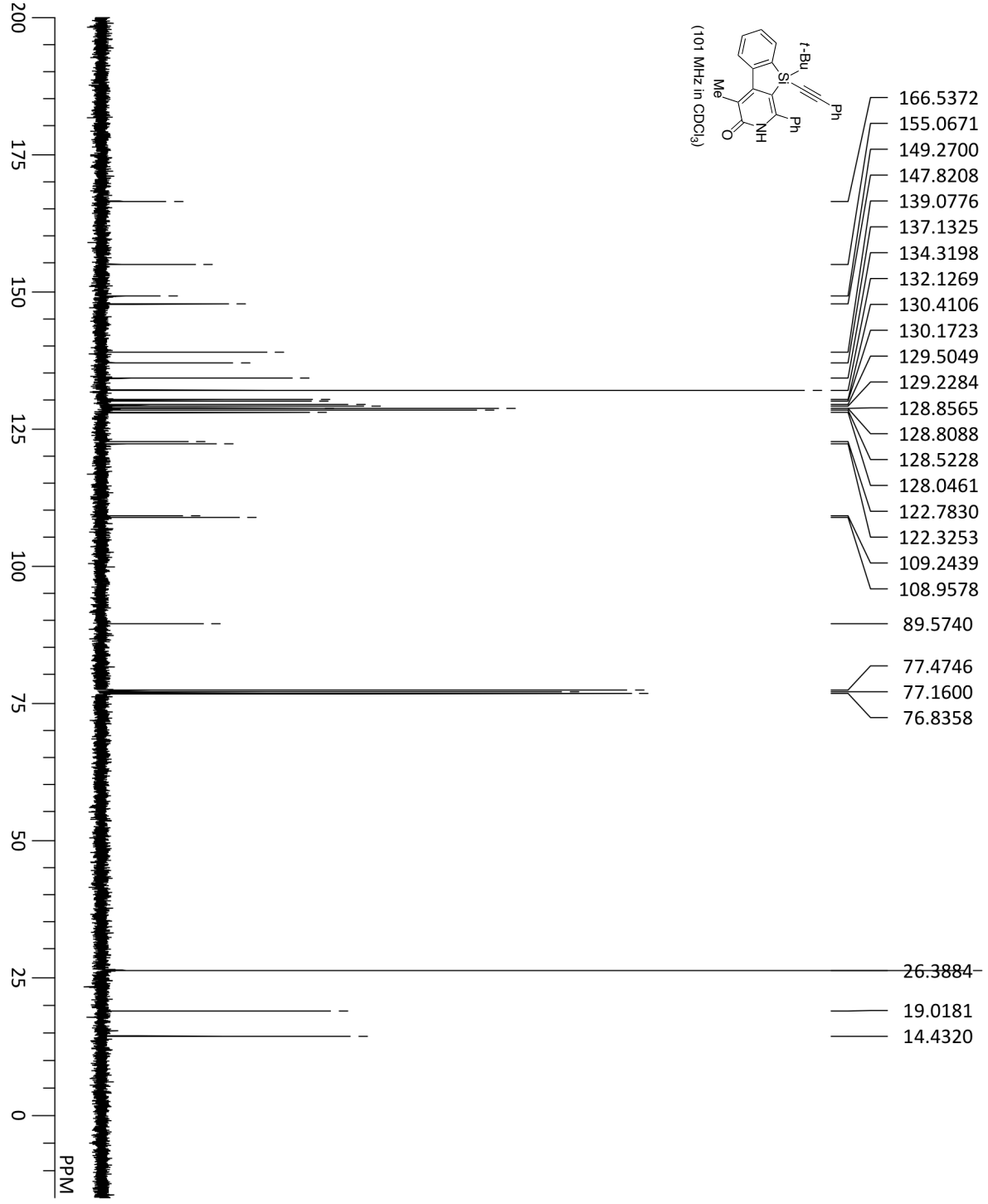
compound **3bf**



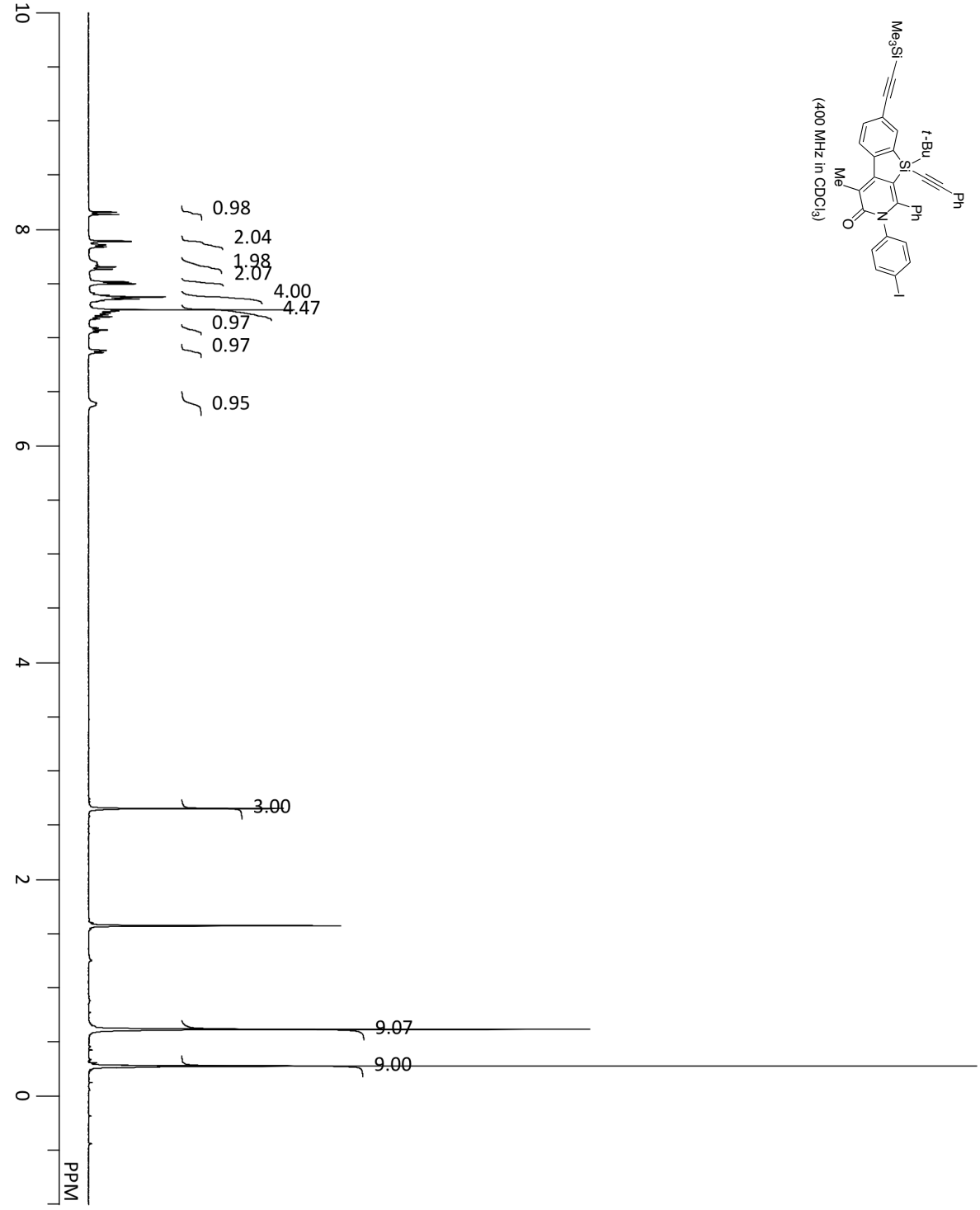
compound **4**


10
8
6
4
2
0
PPM
0.99
0.98
2.92
2.90
3.99
2.98
2.95
9.00
(500 MHz in CDCl3)
t-Bu
Si
Ph
Me
Ph
NH
O

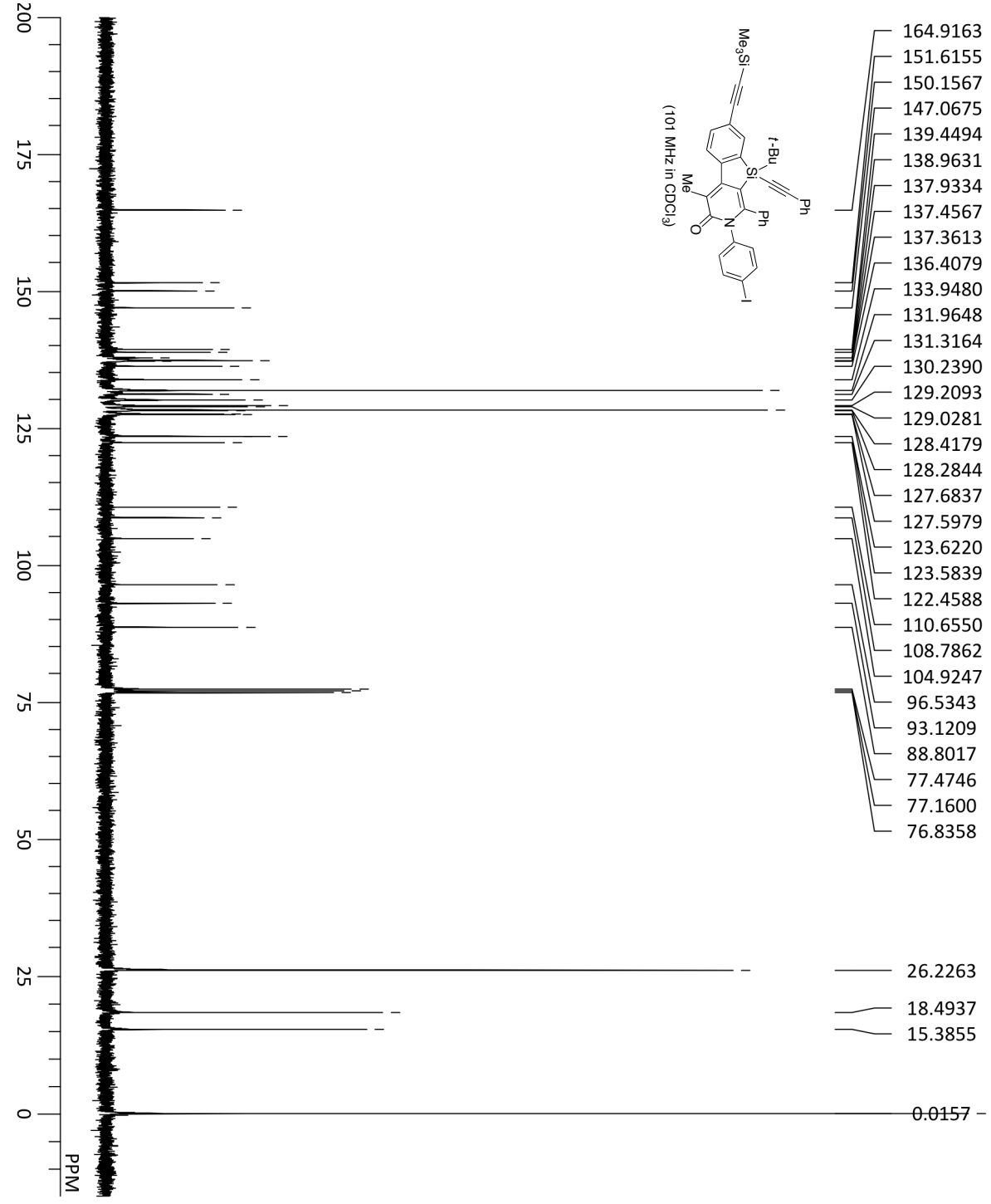
compound **4**


200
175
150
125
100
75
50
25
0
PPM
(101 MHz in CDCl3)
Me
NH
O
Ph
Si
t-Bu
166.5372
155.0671
149.2700
147.8208
139.0776
137.1325
134.3198
132.1269
130.4106
130.1723
129.5049
129.2284
128.8565
128.8088
128.5228
128.0461
122.7830
122.3253
109.2439
108.9578
89.5740
77.4746
77.1600
76.8358
26.3884
19.0181
14.4320

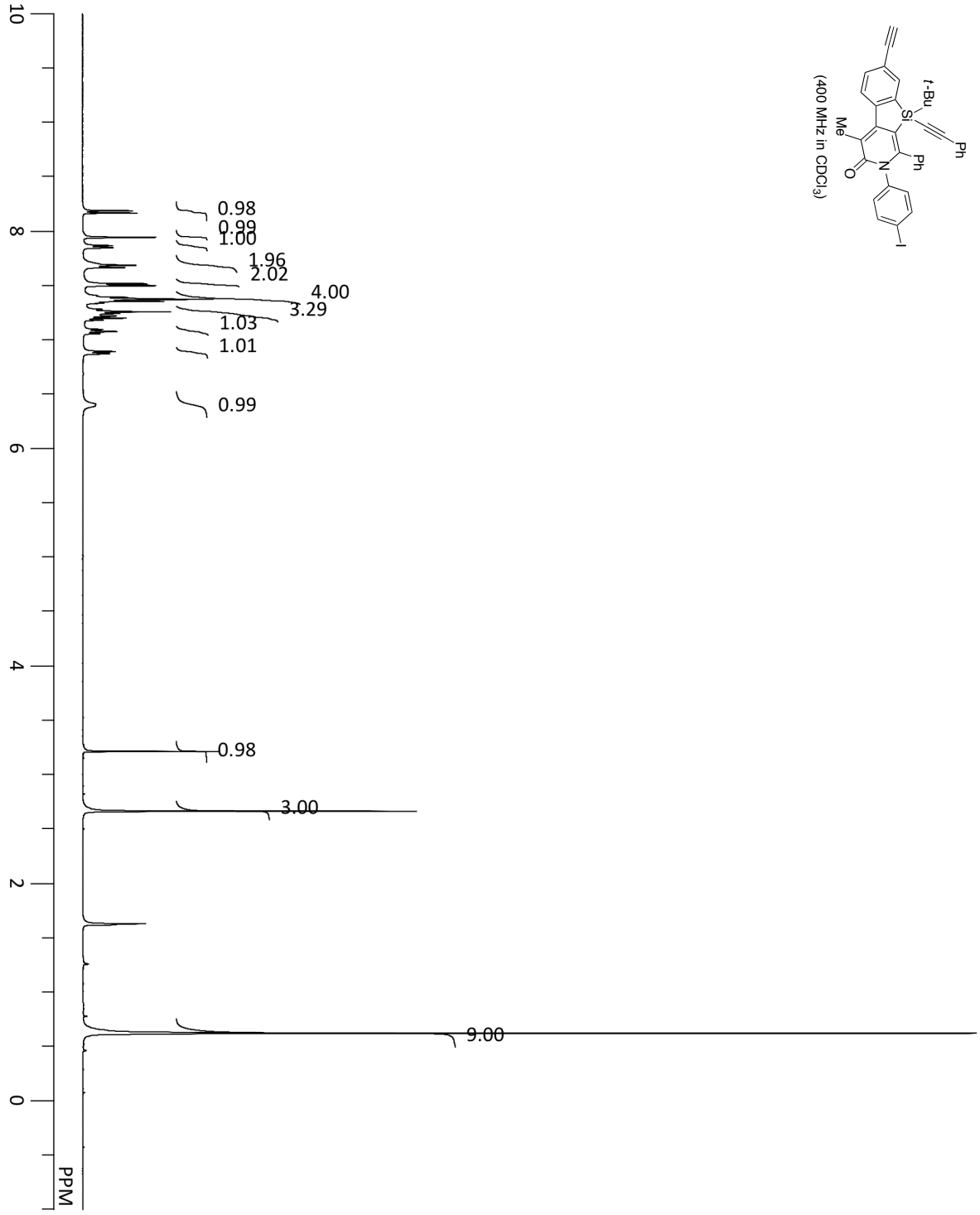
compound **3jd**



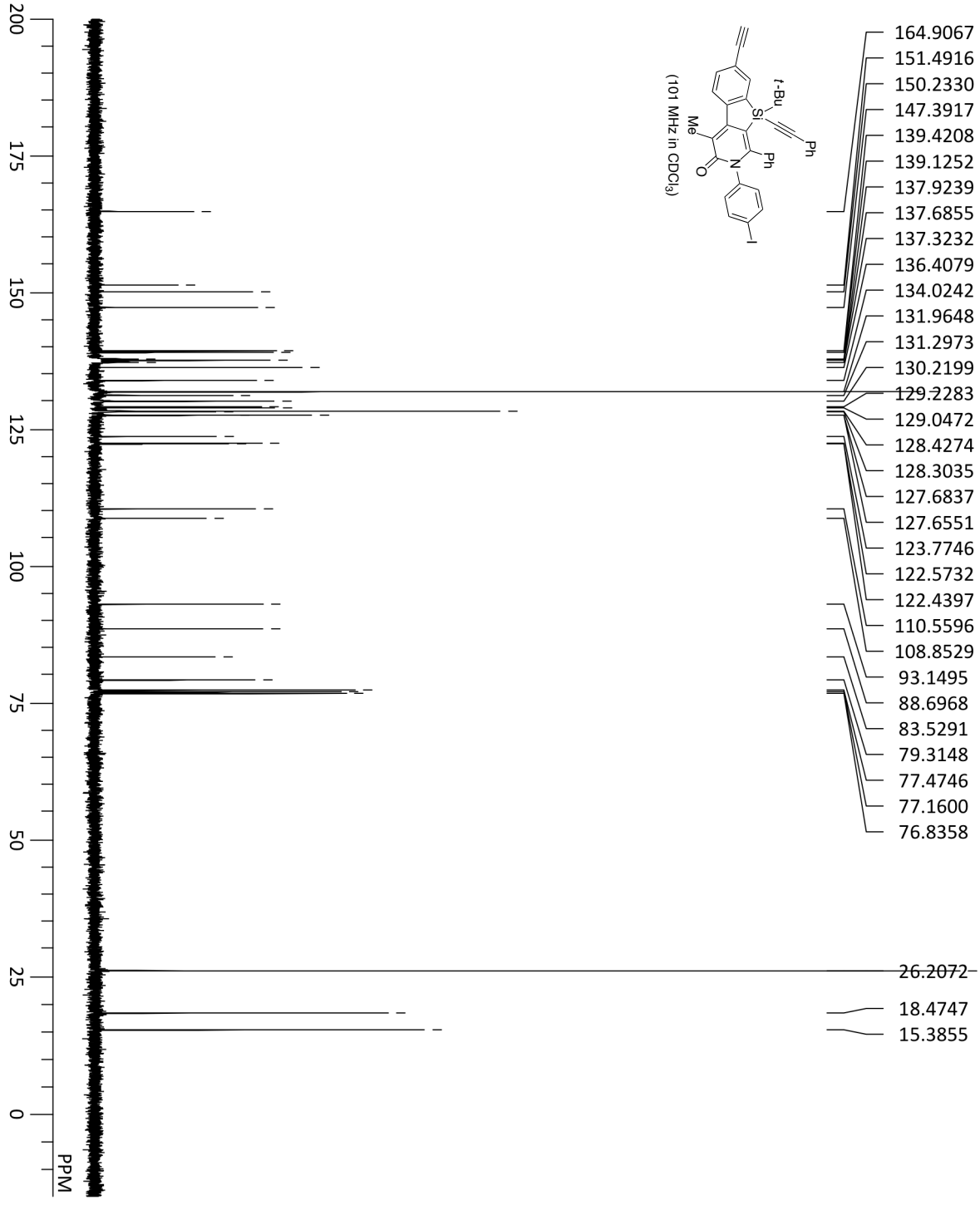
compound **3jd**



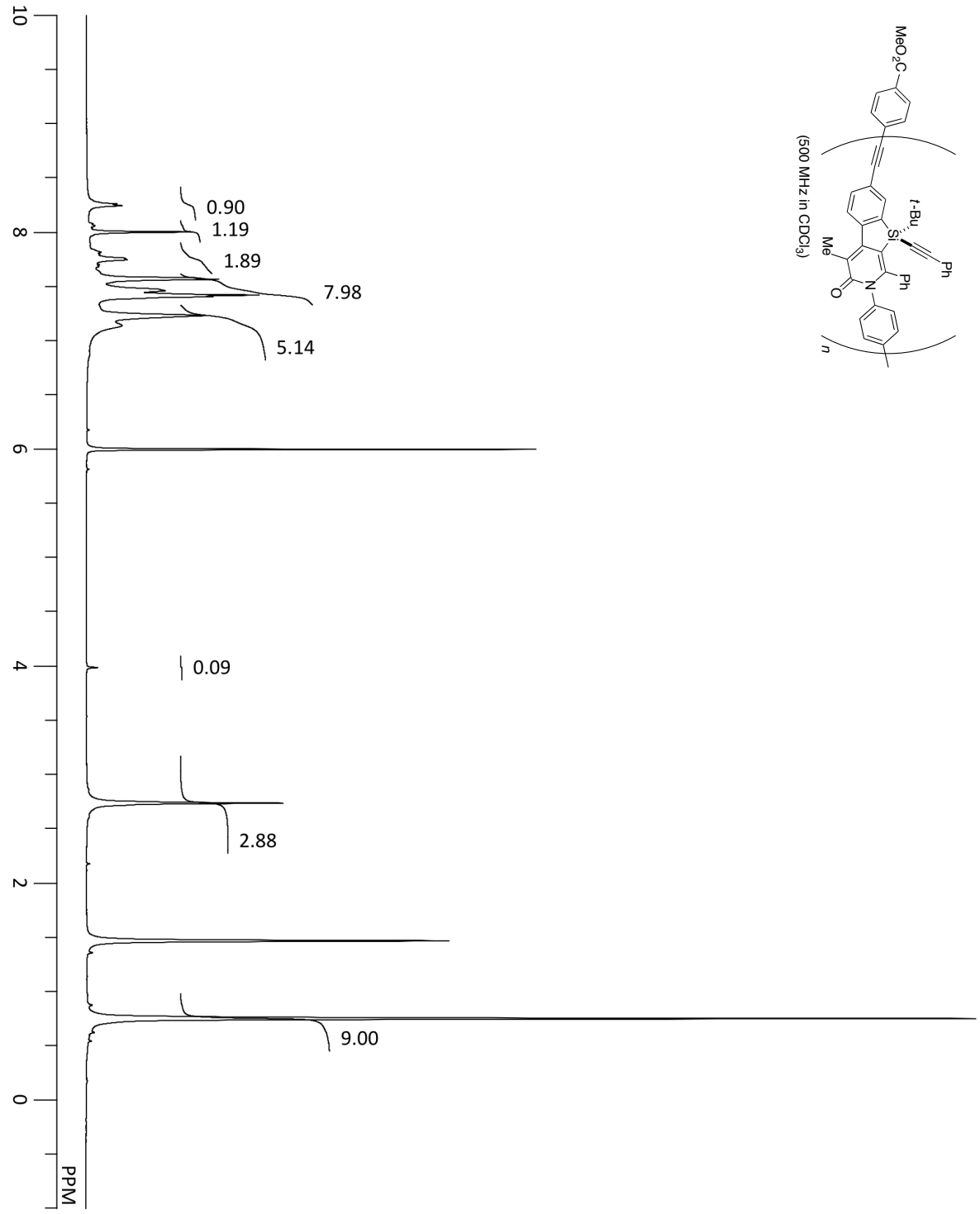
compound **5**


10
8
6
4
2
0
PPM
0.98
0.99
1.00
1.96
2.02
4.00
3.29
1.03
1.01
0.99
0.98
3.00
9.00
(400 MHz in CDCl3)
t-Bu
Si
Ph
Me
Ph
N
O
I

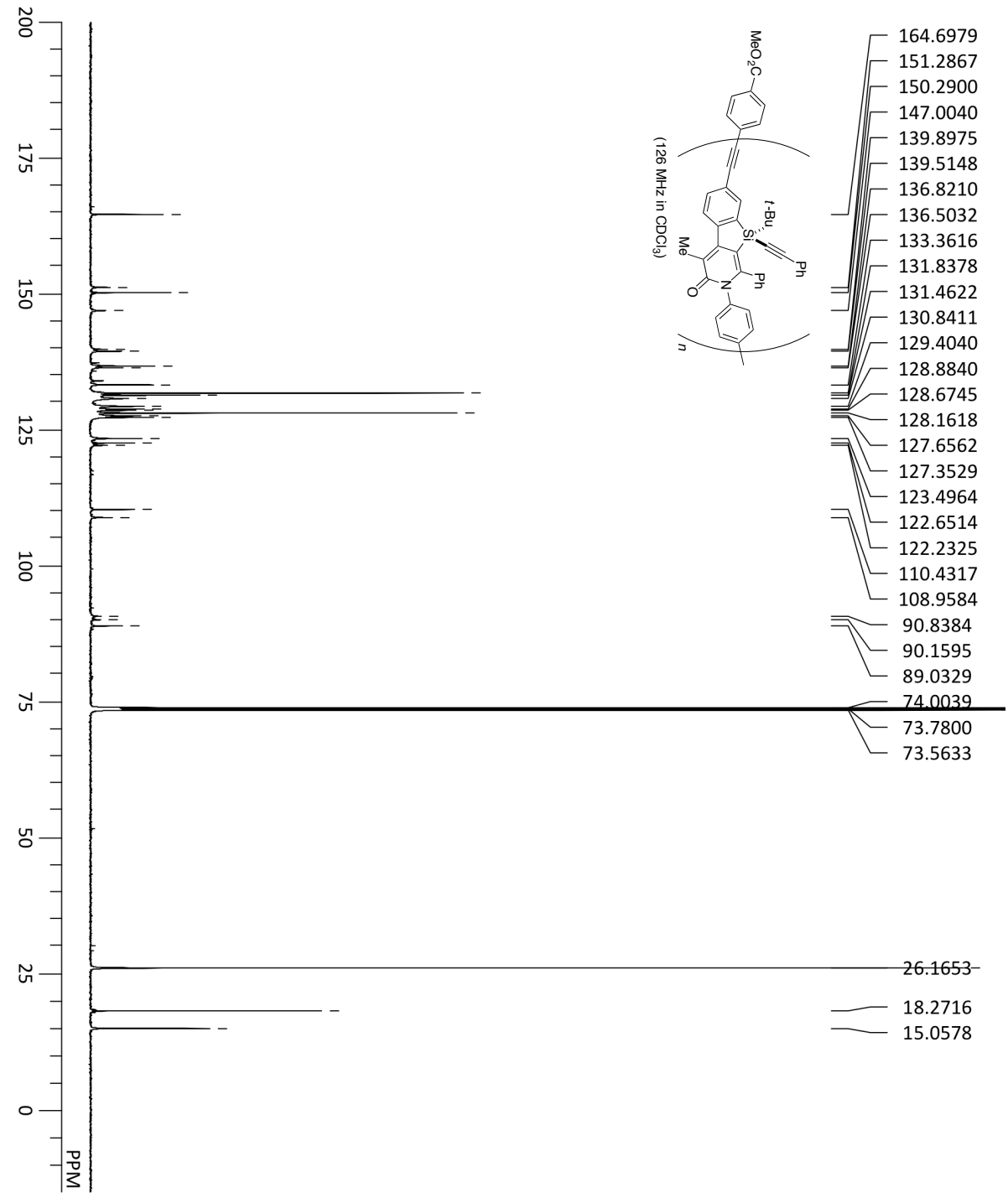
compound **5**


200
175
150
125
100
75
50
25
0
PPM
(101 MHz in CDCl3)
Me
O
N
Ph
Si
t-Bu
Ph
I
164.9067
151.4916
150.2330
147.3917
139.4208
139.1252
137.9239
137.6855
137.3232
136.4079
134.0242
131.9648
131.2973
130.2199
129.2283
129.0472
128.4274
128.3035
127.6837
127.6551
123.7746
122.5732
122.4397
110.5596
108.8529
93.1495
88.6968
83.5291
79.3148
77.4746
77.1600
76.8358
26.2072
18.4747
15.3855

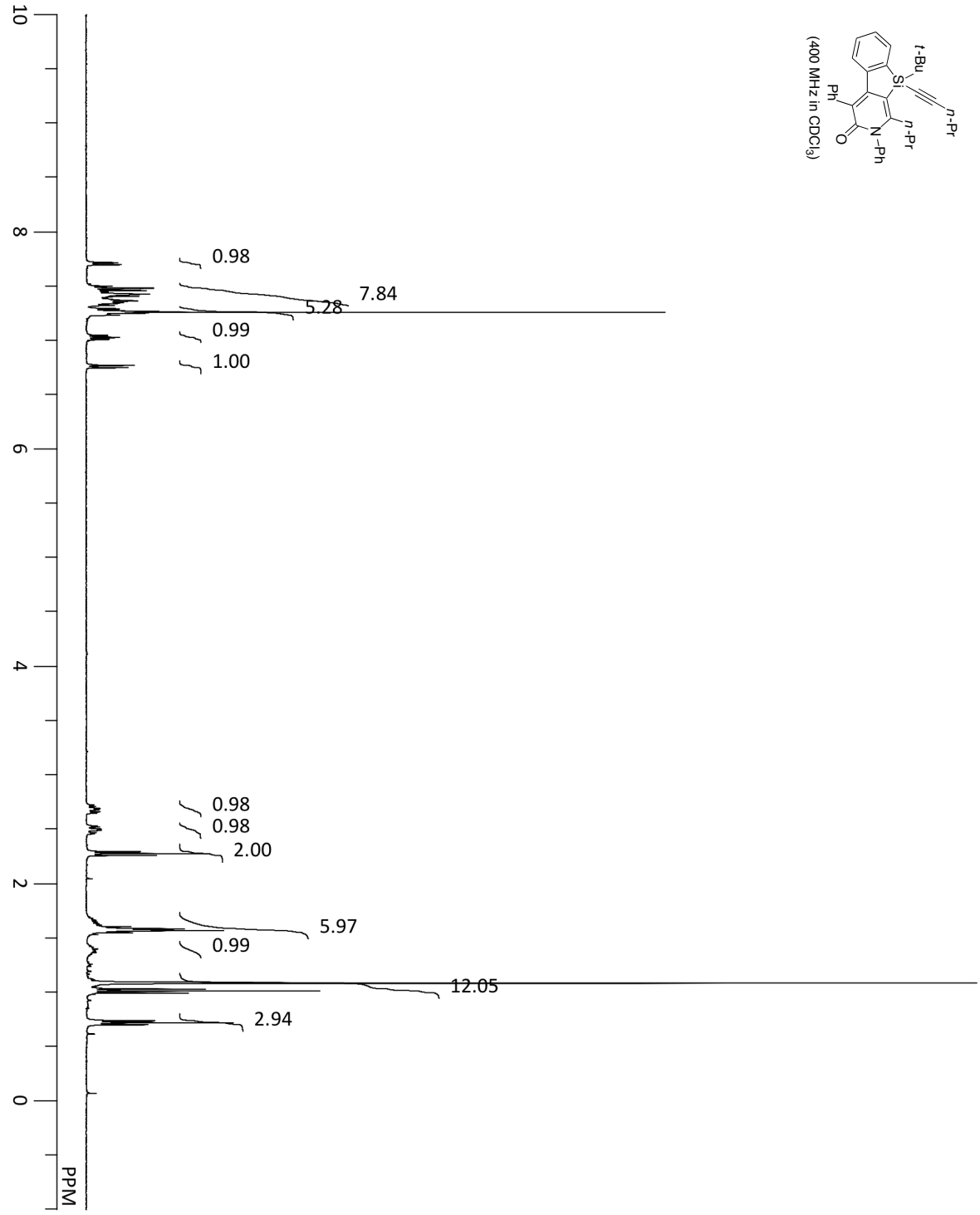
compound **poly-5**



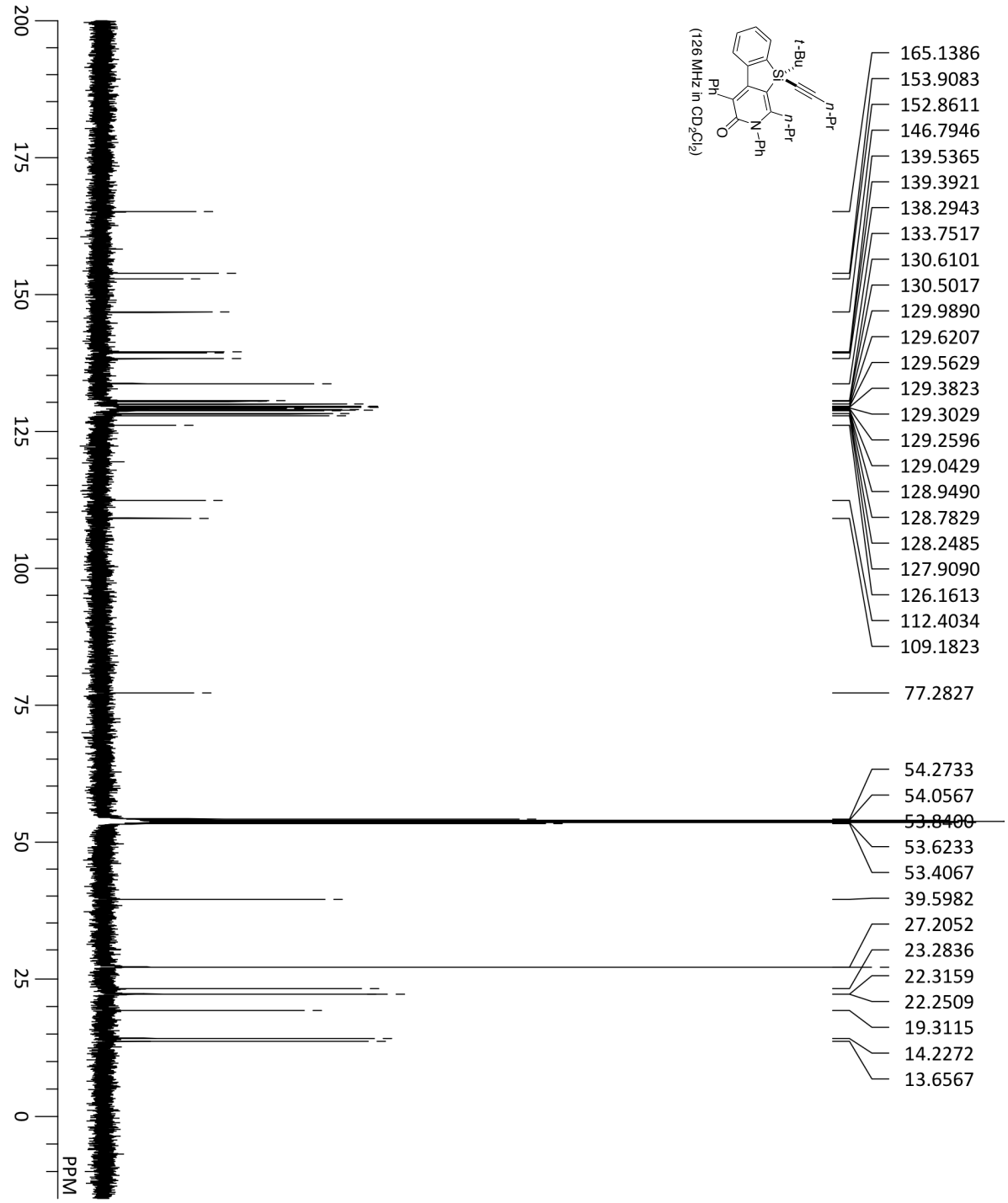
compound **poly-5**



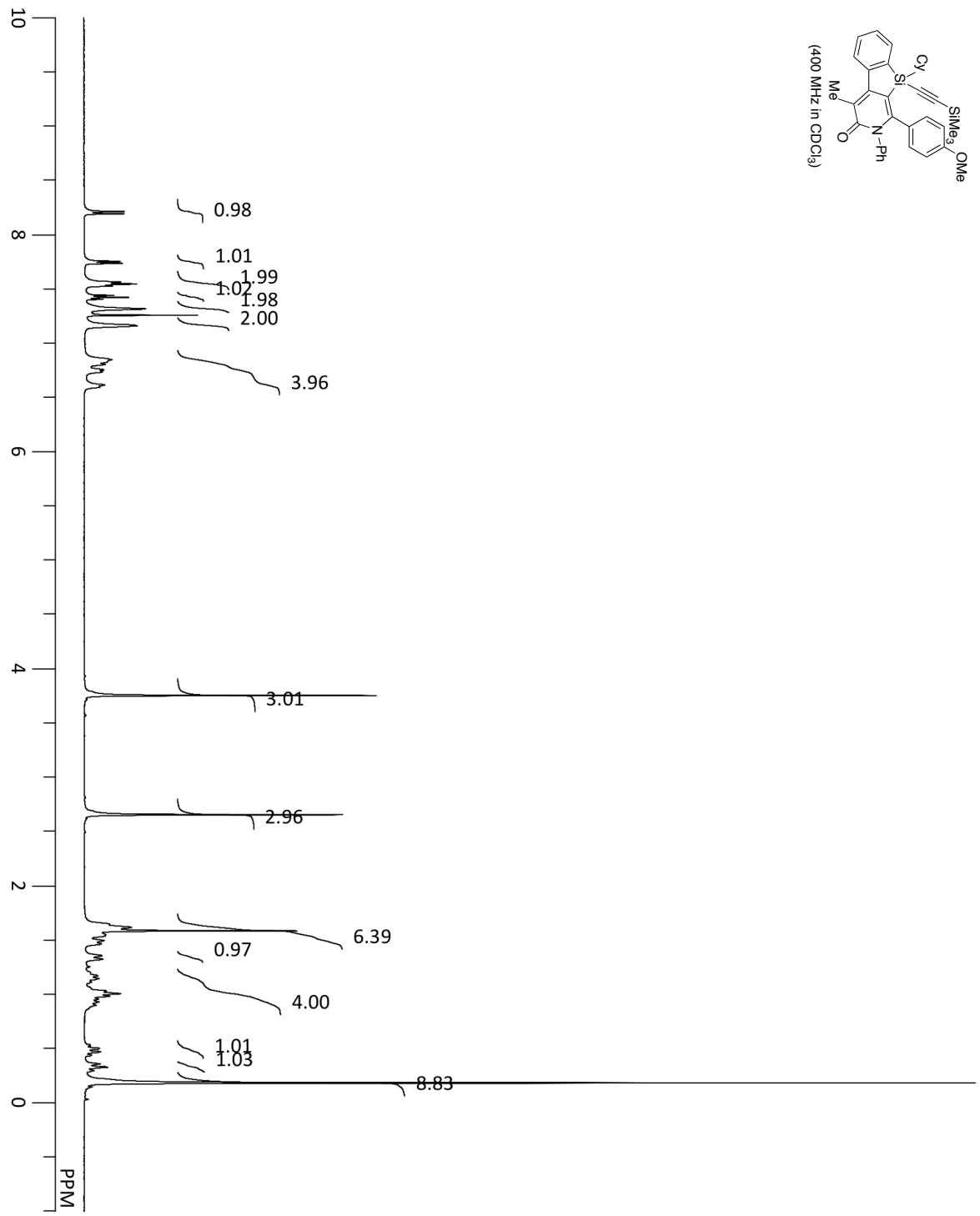
compound **3ka**



compound **3ka**



compound **3la**



compound **3la**