Regio-selective Cyanation of (*Z*)-(1,2-dibromo-2-arylvinyl)triisopropylsilane with Suppression of Halogen Elimination.

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EXPERIMENTAL SECTION

1. General Information: All reactions sensitive to air or moisture were carried out under an argon atmosphere and anhydrous conditions unless otherwise noted. Dry solvents were purchased and used without further purification and dehydration. All reagents were purchased and used without further purification. Analytical thin layer chromatography was carried out on Merck silica 60F_{254}. Column chromatography was carried out with silica gel 60 $_N$ (Kanto Chemical Co.). LRMS were reported on the basis of DI (GC-2010 Plus; Shimadzu). HRMS were reported on the basis of TOF (time of flight)-MS (MADI-TOF or LCMS-IT-TOF; Shimadzu), and DART (Direct Analysis in Real Time)-MS. ^{1}H and ^{13}C NMR spectra were recorded with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in d (ppm) with reference to residual solvent signals [^{1}H NMR: $CHCl_3$ (7.26), C_7H_8 (2.08), C_6H_6 (7.16), CH_2Cl_2 (5.32); ^{13}C NMR: $CDCl_3$ (77.0)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

2. Representative procedure for preparation of **2** ((Z)-(1,2-dibromo-2-(4-methoxyphenyl)vinyl)triisopropylsilane)**:** Under an argon atmosphere, to a solution of triisopropyl((4-methoxyphenyl)ethynyl)silane (2.31 g, 8.0 mmol) in anhydrous toluene (32 mL) at 0 ºC was added TMSBr (12 mL of 1 M in CH_2Cl_2) dropwise over 5 min, and the mixture was stirred for 5 min. Then, NBS (2.14 g, 12 mmol) in CH_3CN (24 mL) was slowly added over 5 min, and the ice-bath was removed to warm to room temperature. After additional stirring for 1 h, the reaction was quenched at 0 ºC with saturated aqueous sodium thiosulfate, and stirred for 10 min, and warmed to ambient

temperature. The aqueous phase was extracted with toluene, and the combined organic phases were washed with brine, and then dried with sodium sulfate, and concentrated to give crude products. The crude products were purified by short-plug column chromatography (eluent; hexane/toluene 19/1), and followed by reprecipitation from CH_2Cl_2/CH_3OH (1/8 v/v), which afforded 2.66 g of **2** in 74% yield as a white solid material. ^{1}H NMR (400 MHz, $CDCl_3$) 7.27 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.04-0.95 (m, 21H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 160.4, 136.0, 134.3, 130.8, 128.9, 113.5, 55.7, 19.2, 13.1 ppm. MS (DART-TOF) *m/z*: 367 $[M(Br79)-Br]^+$. IR (neat): 2936, 2861, 1603, 1561, 1500, 1460, 1295, 1253, 1173, 1030 cm^{-1}. HRMS (DART-TOF) calcd for $C_{18}H_{28}Br(79)OSi$: 367.1087 $[M(Br79)-Br]^+$, Found 367.1069. Anal. Calcd for $C_{18}H_{28}Br_2OSi$: C, 48.22; H, 6.30. Found: C, 48.22; H, 6.29.

3. Characterization for new compounds **5a**, **6a**, **7a**, **8a** and **10a**:

5a: ^{1}H NMR (400 MHz, $CDCl_3$) 7.44-7.36 (m, 5H), 1.10-0.98 (m, 21H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 148.6, 135.1, 131.0, 130.3, 129.5, 128.8, 118.4, 19.0, 13.0 ppm. MS (DART-TOF) *m/z*: 381 $[M(Br79)+NH_4]^+$. IR (neat): 2939, 2867, 1461, 1011, 883, 827 cm^{-1}. HRMS (DART-TOF) calcd for $C_{18}H_{30}Br(79)N_2Si$: 381.1362 $[M(Br79)+NH_4]^+$, Found 381.1335. Anal. Calcd for $C_{18}H_{26}BrNSi$: C, 59.33; H, 7.19; N, 3.84. Found: C, 59.24; H, 7.35; N, 3.87.

6a: ^{1}H NMR (400 MHz, $CDCl_3$) 7.43 (d, *J* = 5.2 Hz, 1H), 7.13 (d, *J* = 3.6 Hz, 1H), 6.99 (dd, *J* = 5.2, 3.6 Hz, 1H), 1.13 (m, 3H), 1.06 (brs, 11H), 1.05 (brs, 7H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 152.2, 135.1, 130.5, 129.0, 127.2, 123.6, 117.8, 19.2, 13.2 ppm. MS (DART-TOF) *m/z*: 387 $[M(Br79)+NH_4]^+$. IR (neat): 2933, 2860, 1461, 1233, 1016, 877, 833 cm^{-1}. HRMS (DART-TOF) calcd for $C_{16}H_{28}Br(79)N_2SSi$: 387.0926 $[M(Br79)+NH_4]^+$, Found 387.0904. Anal. Calcd for $C_{16}H_{24}BrNSSi$: C, 51.88; H, 6.53; N, 3.78. Found: C, 51.65; H, 6.49; N, 3.71.

7a: ^{1}H NMR (400 MHz, $CDCl_3$) 7.97-7.93 (m, 2H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.60 (dd, *J* = 7.6 Hz, 6.9 Hz, 1H), 7.55 (dd, *J* = 7.4Hz, 6.9 Hz, 1H), 7.45-7.43 (m, 2H), 0.98-0.94 (m, 12H), 0.78-0.76 (m, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 150.7, 133.8, 131.9, 131.6, 131.1, 129.5, 128.9, 128.5, 127.7, 127.1, 125.2, 125.0, 117.9, 19.0, 18.7, 12.8 ppm. MS (DART-TOF) *m/z*: 431 $[M(Br79)+NH_4]^+$. IR (neat): 2939, 2867, 1461, 1016, 877, 772 cm^{-1}. HRMS (DART-TOF) calcd for $C_{22}H_{32}Br(79)N_2Si$: 431.1518 $[M(Br79)+NH_4]^+$, Found 431.1507. Anal. Calcd for $C_{22}H_{28}BrNSi$: C, 63.76; H, 6.81; N, 3.38. Found: C, 63.73; H, 6.81; N, 3.33.

8a: ^{1}H NMR (400 MHz, $CDCl_3$) 7.40 (dd, *J* = 8.2 Hz, 7.9 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 6.90 (dd, *J* = 7.9 Hz, 7.4 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H), 1.02 (brs, 21H, $[C\underline{H}(C\underline{H}_3)_2]_3$ are over lapped) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 157.5, 148.2, 132.1, 131.5, 128.0, 123.8, 120.4, 117.8, 111.4, 55.8, 19.0, 18.8, 12.9 ppm. MS (DART-TOF) *m/z*: 411 $[M(79)+NH_4]^+$. IR (neat): 2938, 2867, 1595, 1467, 1255, 1016, 756 cm^{-1}. HRMS (DART-TOF) calcd for $C_{19}H_{32}Br(79)N_2OSi$: 411.1467 $[M(Br79)+NH_4]^+$, Found 411.1455. Anal. Calcd for $C_{19}H_{28}BrNOSi$: C, 57.86; H, 7.16; N, 3.55. Found: C, 57.61; H, 7.12; N, 3.52.

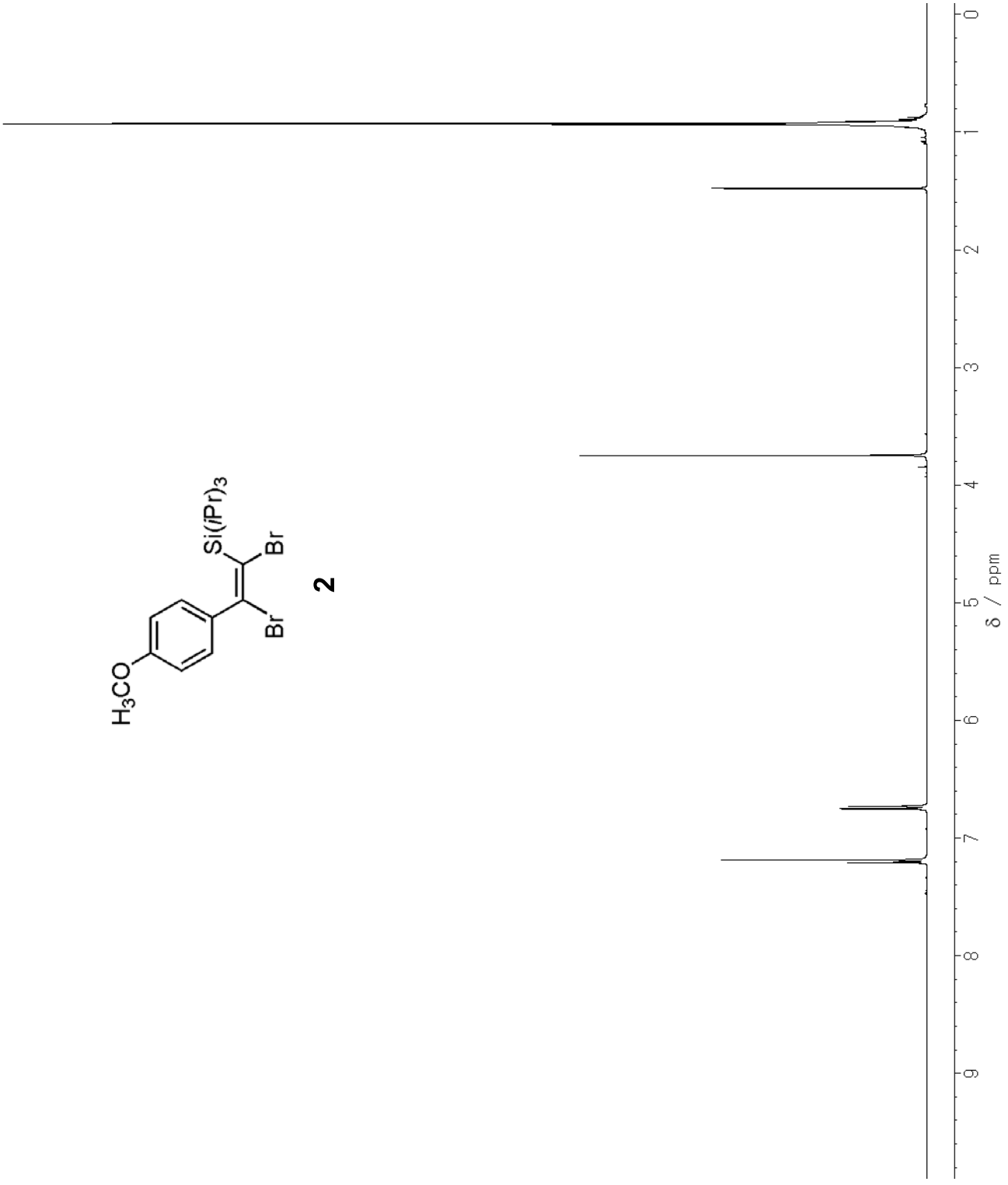
10a: ^{1}H NMR (400 MHz, $CDCl_3$) 7.27 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 1.11-0.99 (m, 21H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) 161.1, 155.2, 131.1, 127.7, 125.9, 117.0, 114.2, 55.7, 19.0, 12.5 ppm. MS (DART-TOF) *m/z*: 350 $[M+H]^+$. IR (neat): 2940, 2866, 1600, 1506, 1456, 1294, 1245, 1177, 827 cm^{-1}. HRMS (DART-TOF) calcd for $C_{19}H_{29}ClNOSi$: 350.1707 $[M+H]^+$, Found 350.1687. Anal. Calcd for $C_{19}H_{28}ClNOSi$: C, 65.21; H, 8.06; N, 4.00. Found: C, 65.20; H, 8.15; N, 4.10.

4. ^{1}H NMR and ^{13}C NMR spectra for all new compounds of **2**, **3**, **5a**, **6a**, **7a**, **8a** and **10a**.

^{1}H NMR and ^{13}C NMR spectra for compounds:

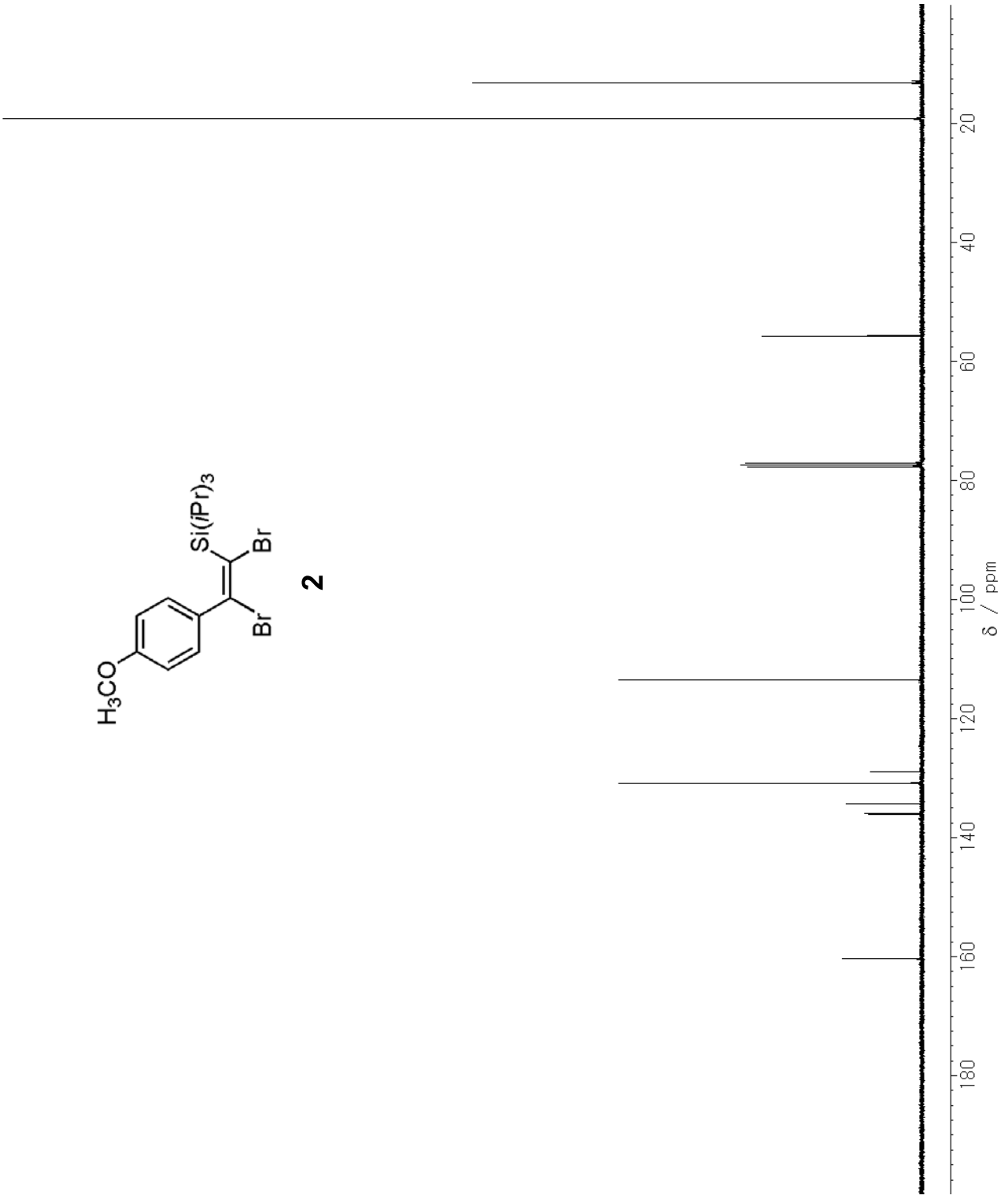
Compound 2

^{1}H NMR spectrum in $CDCl_3$



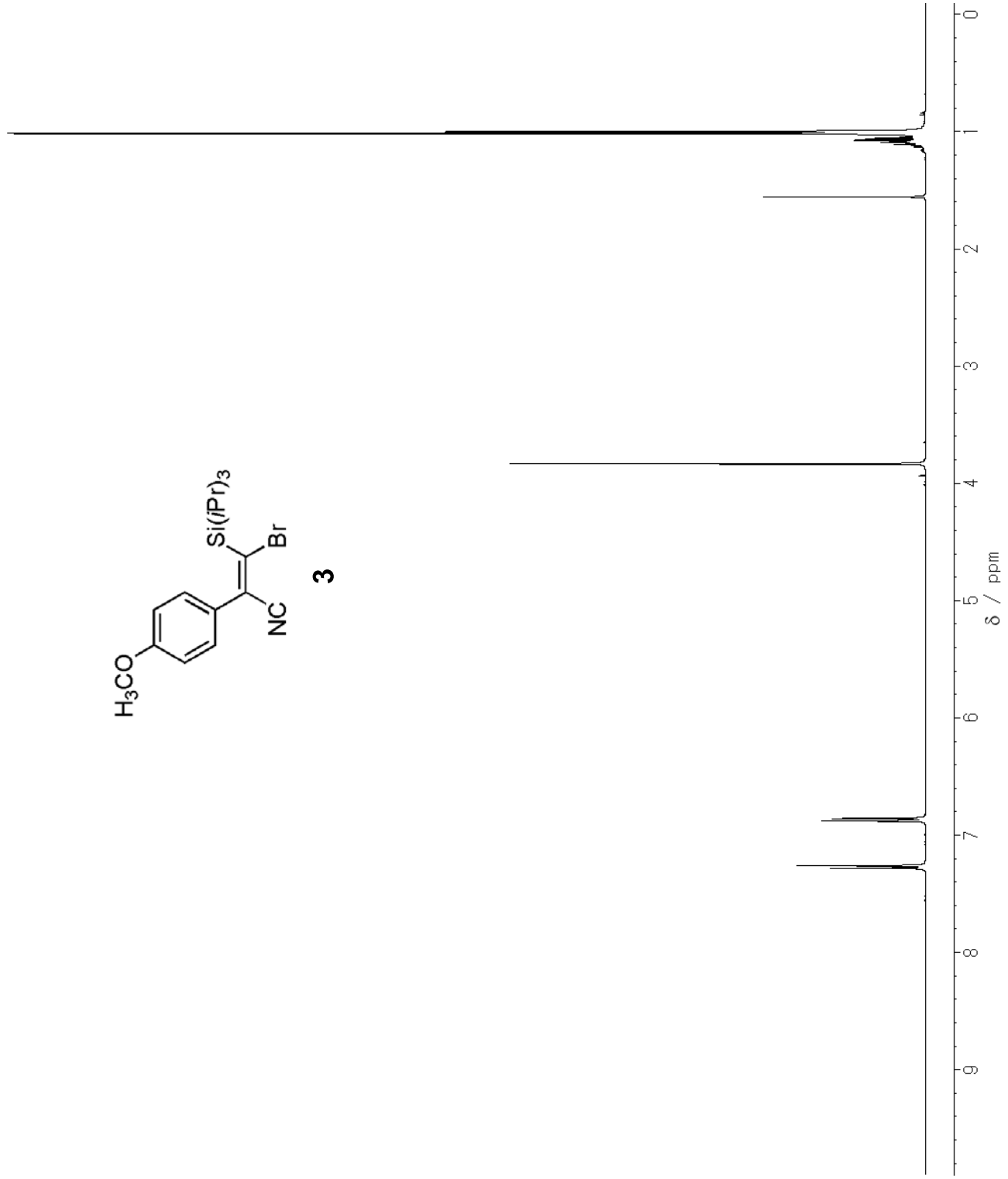
Compound 2

^{13}C NMR spectrum in $CDCl_3$



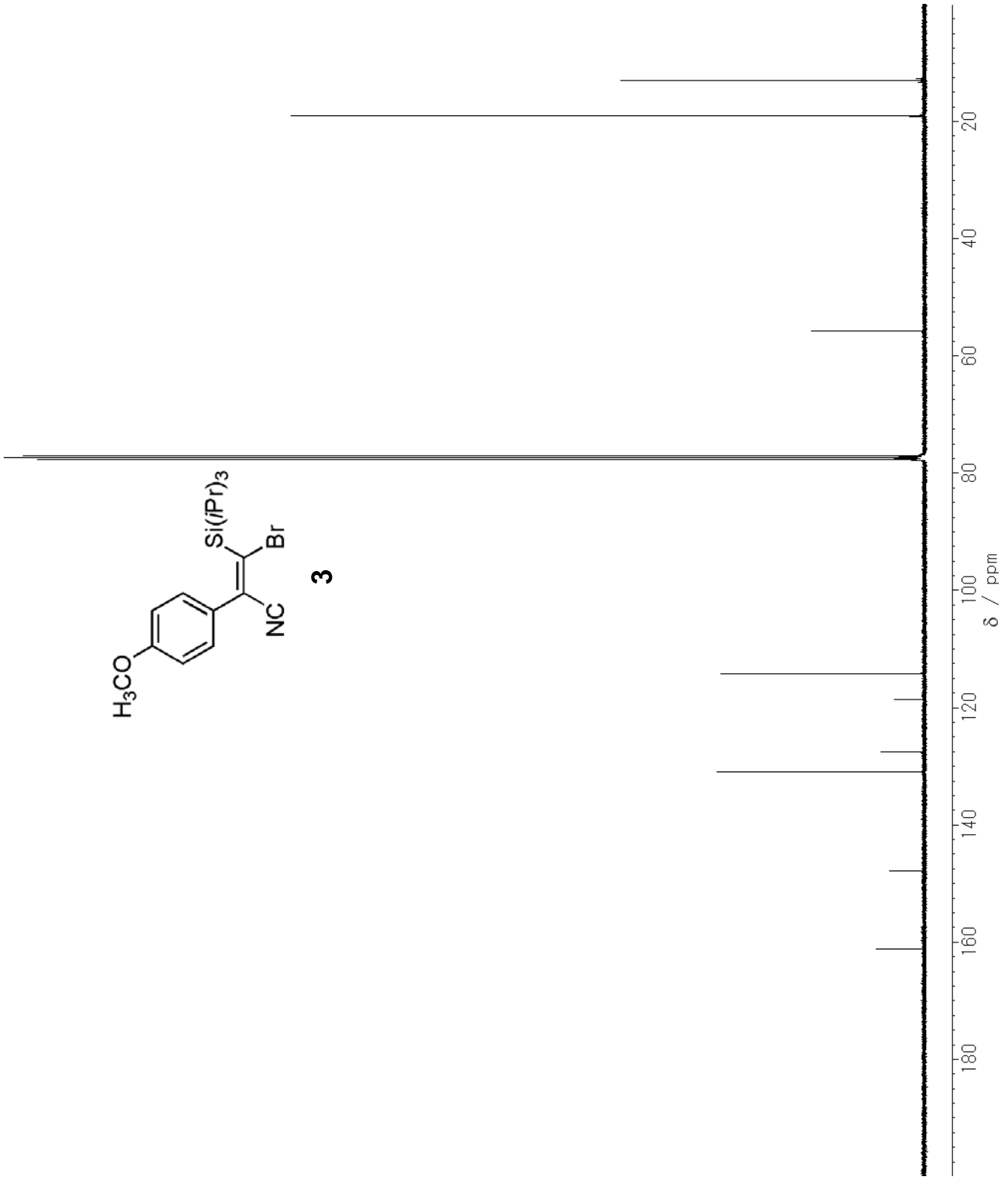
Compound 3

^{1}H NMR spectrum in $CDCl_3$



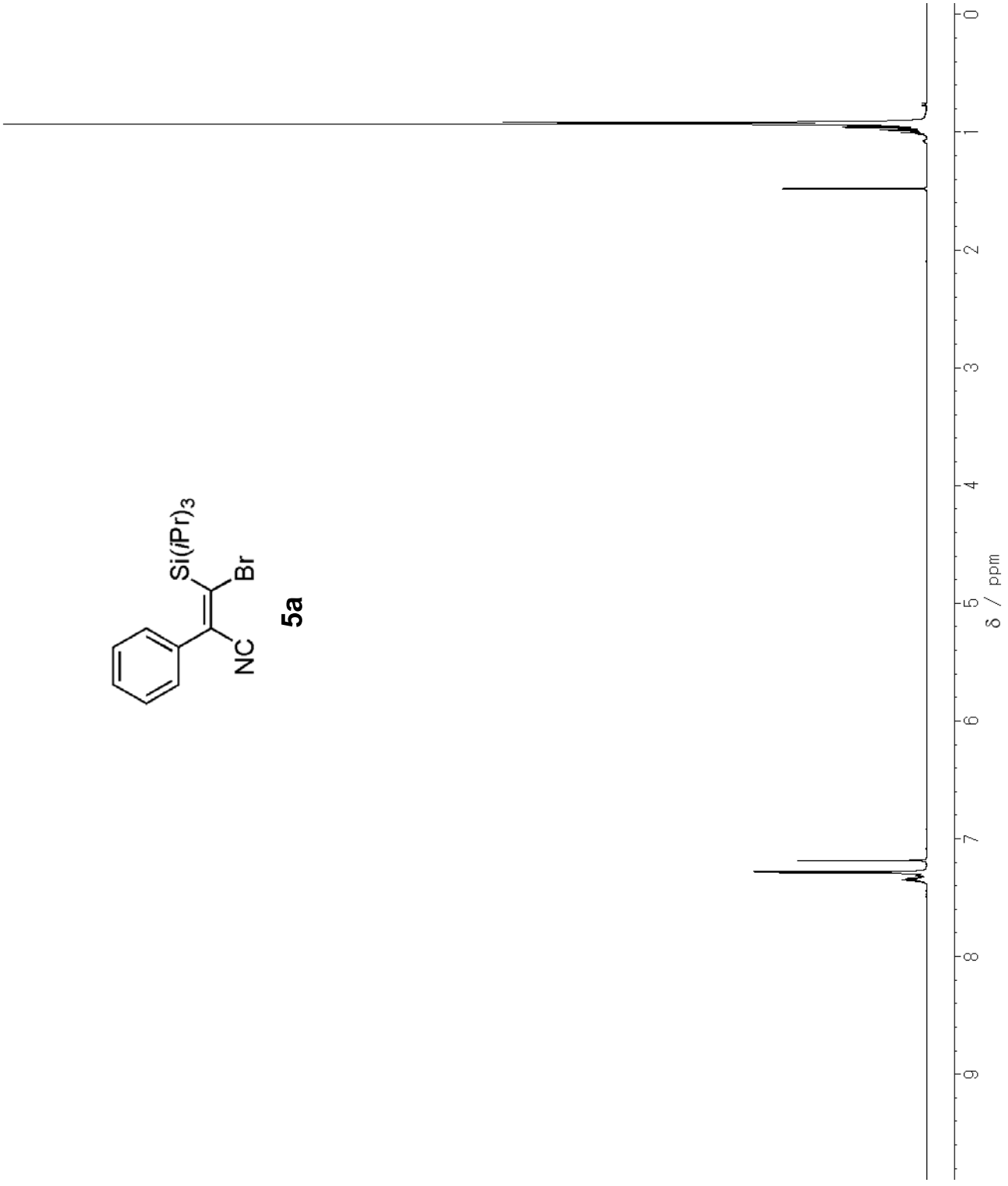
Compound 3

^{13}C NMR spectrum in $CDCl_3$



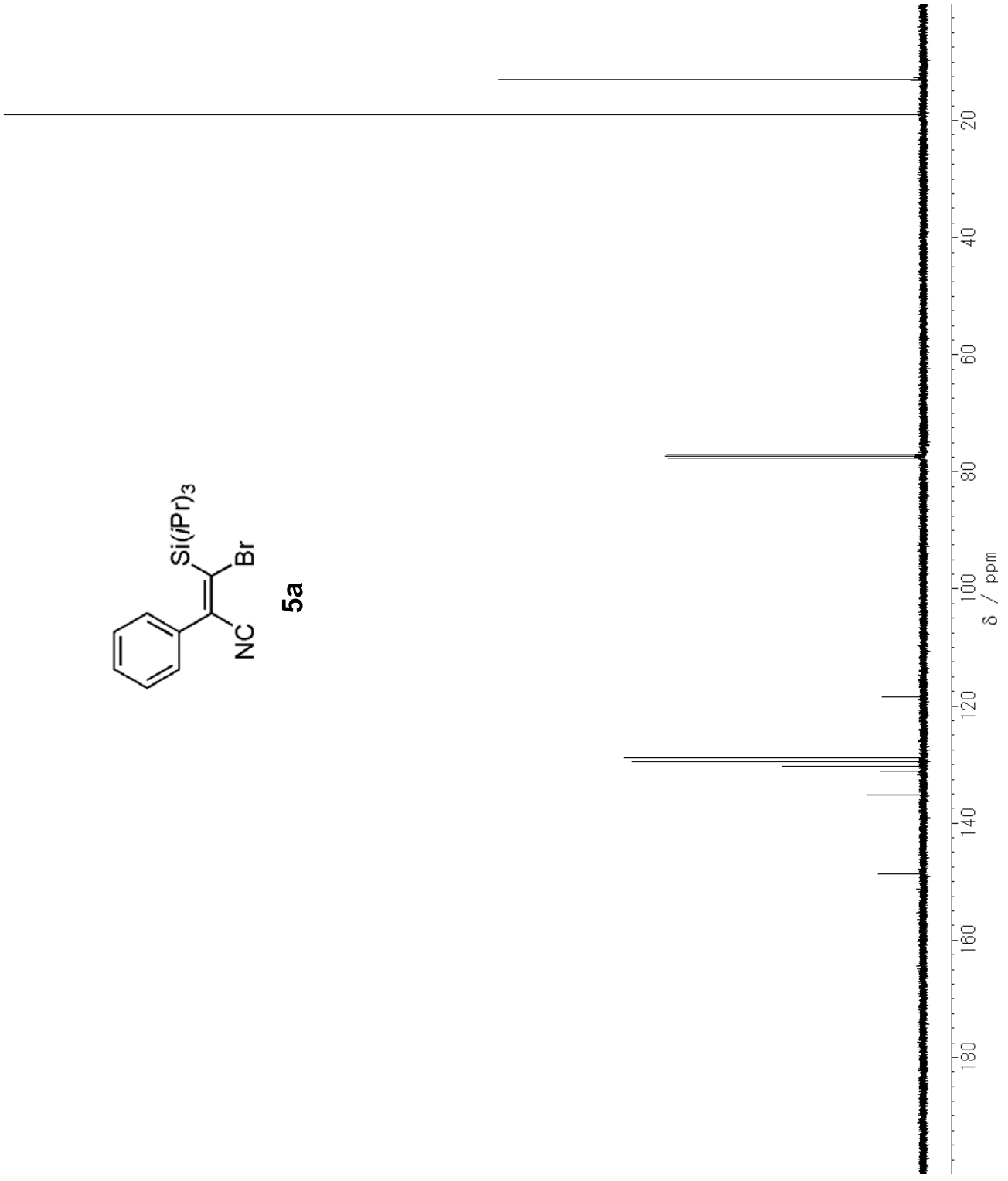
Compound 5a

^{1}H NMR spectrum in $CDCl_3$



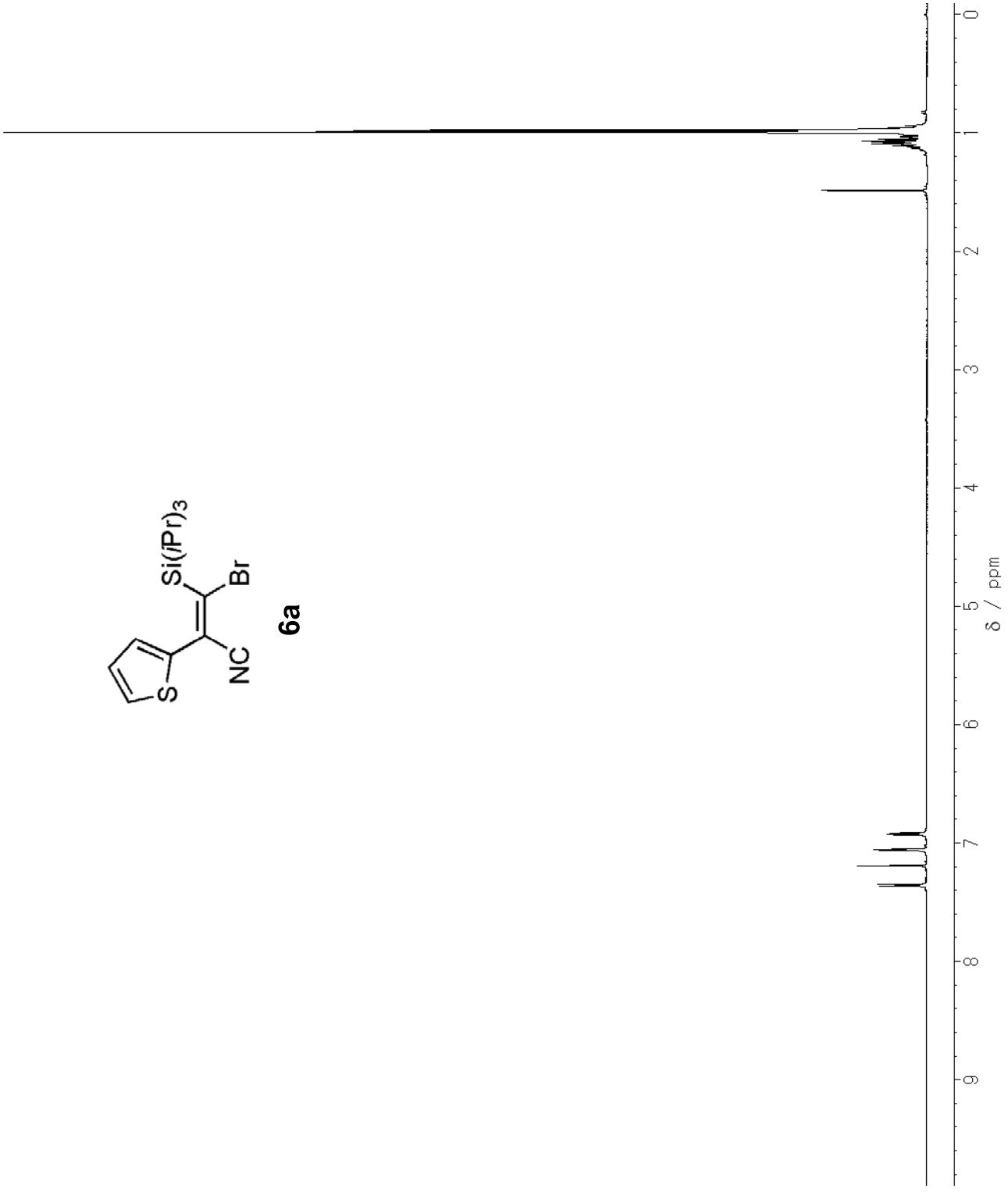
Compound 5a

^{13}C NMR spectrum in $CDCl_3$



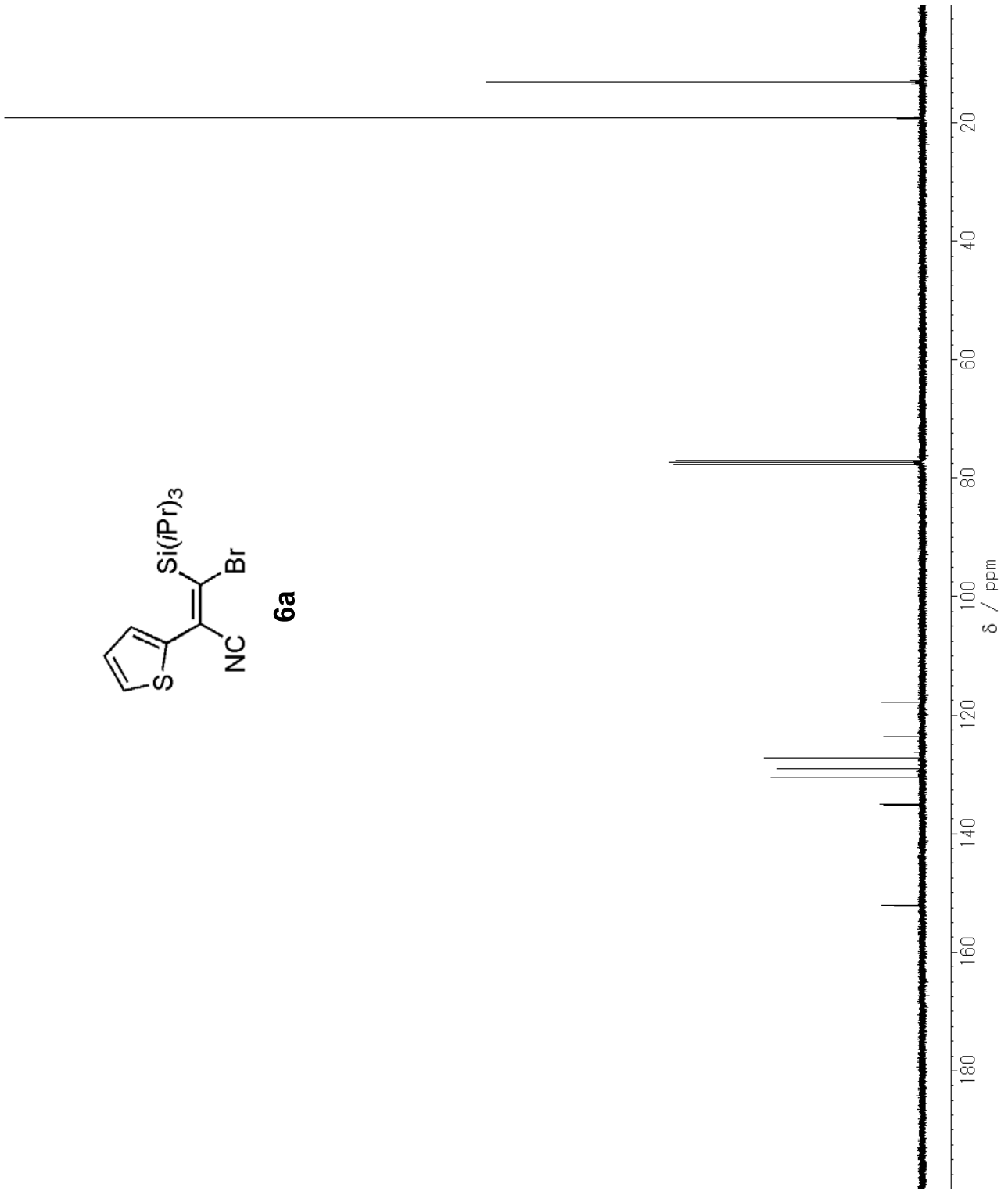
Compound 6a

^{1}H NMR spectrum in $CDCl_3$



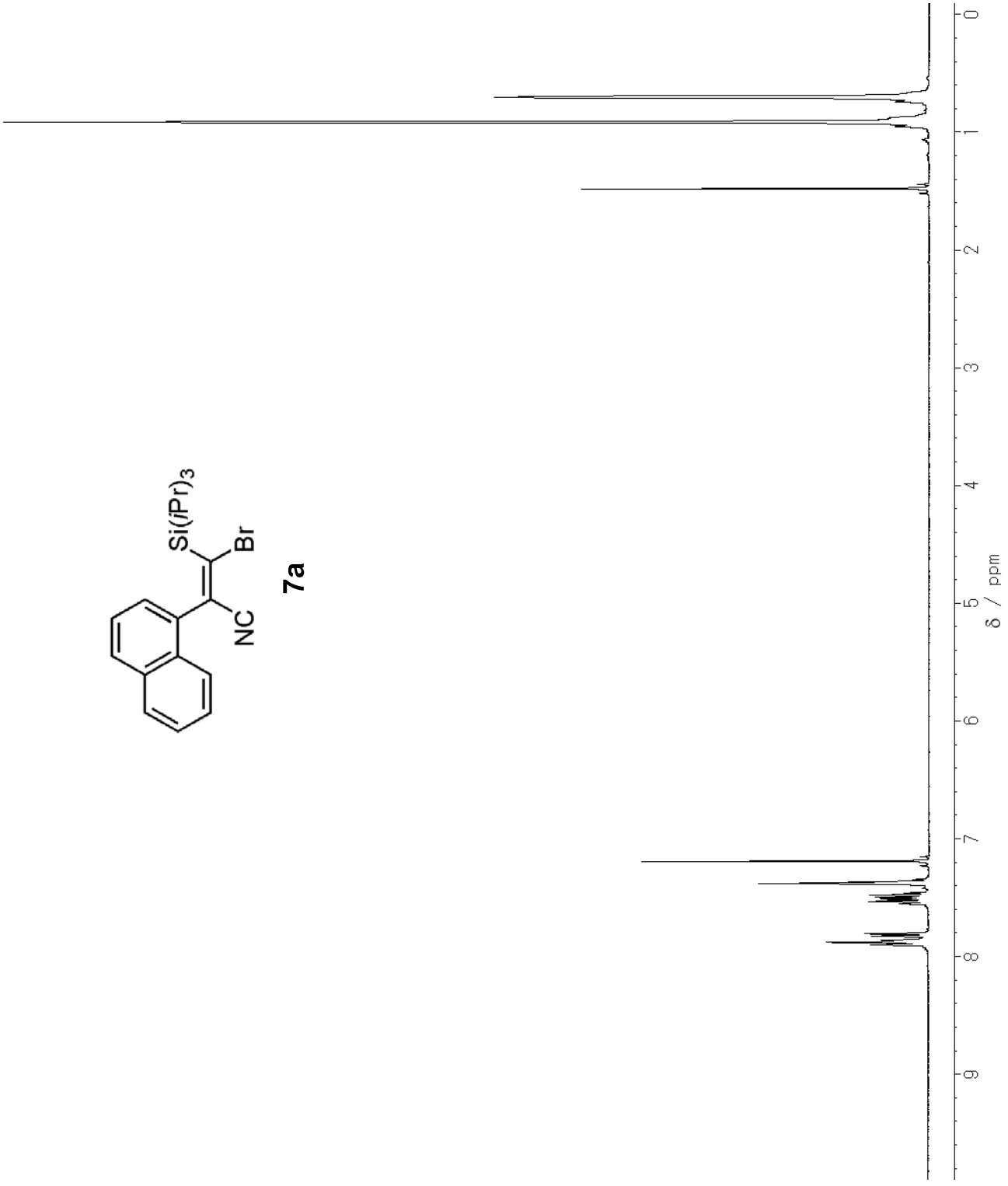
Compound 6a

^{13}C NMR spectrum in $CDCl_3$



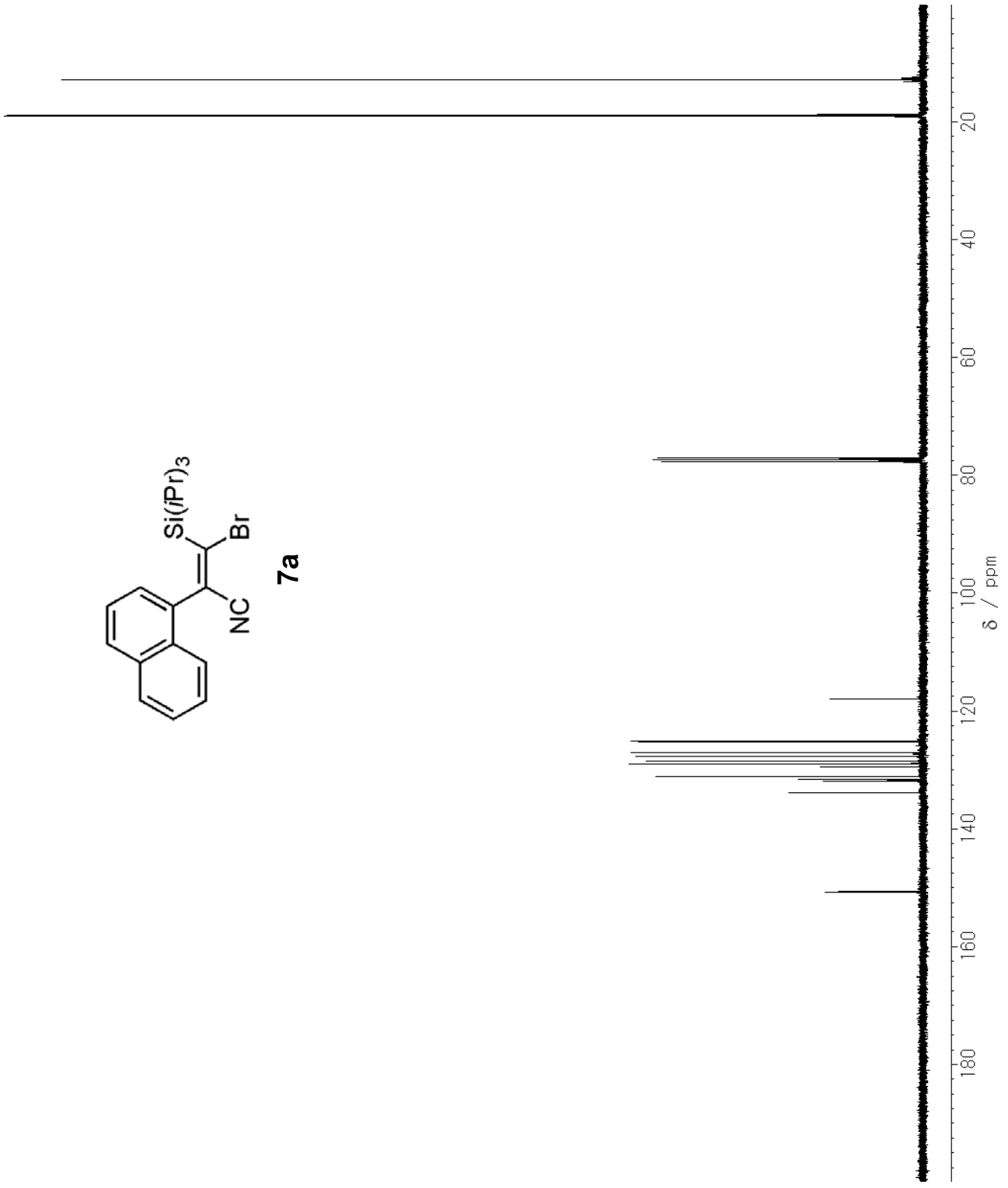
Compound 7a

^{1}H NMR spectrum in $CDCl_3$



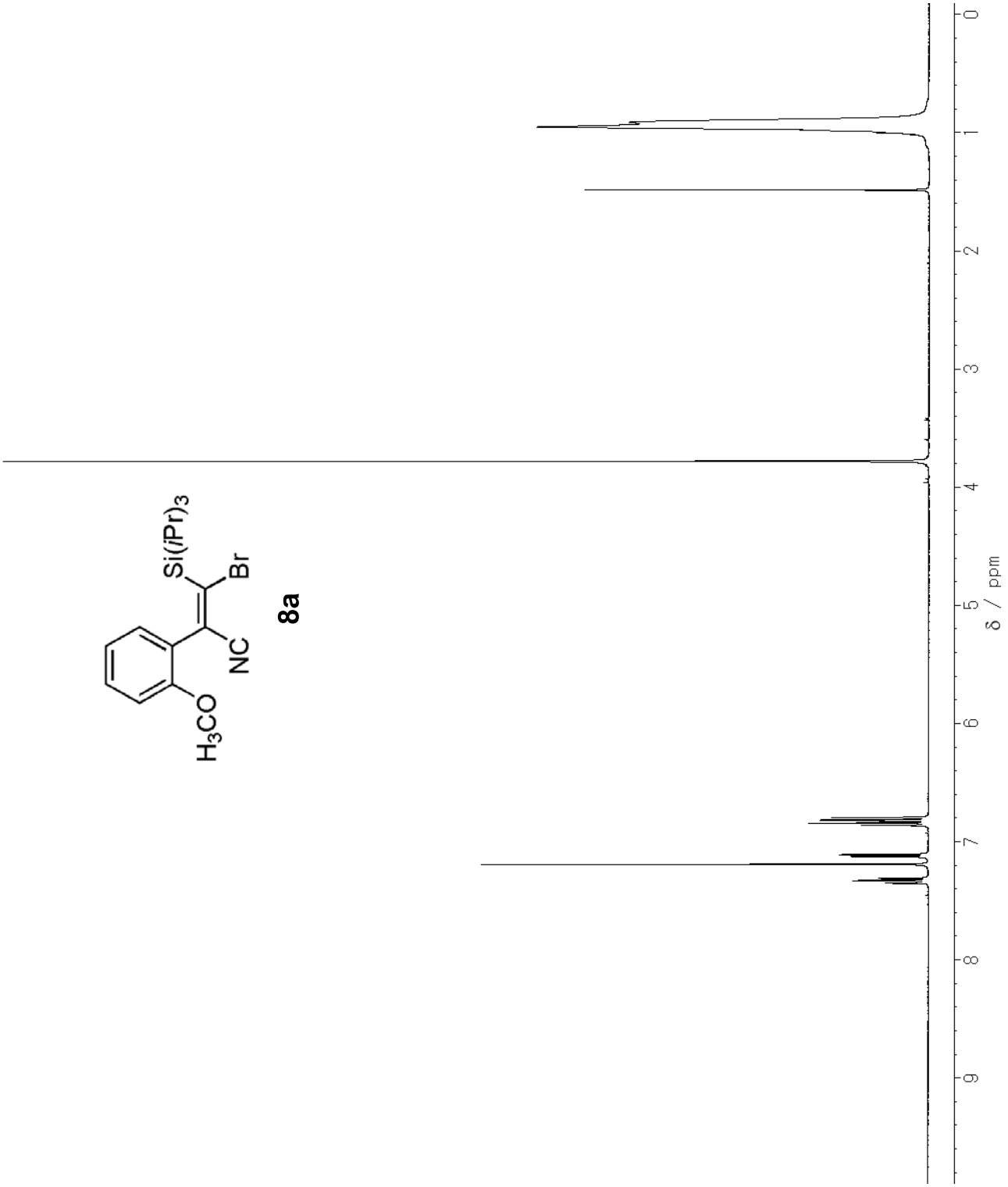
Compound 7a

^{13}C NMR spectrum in $CDCl_3$



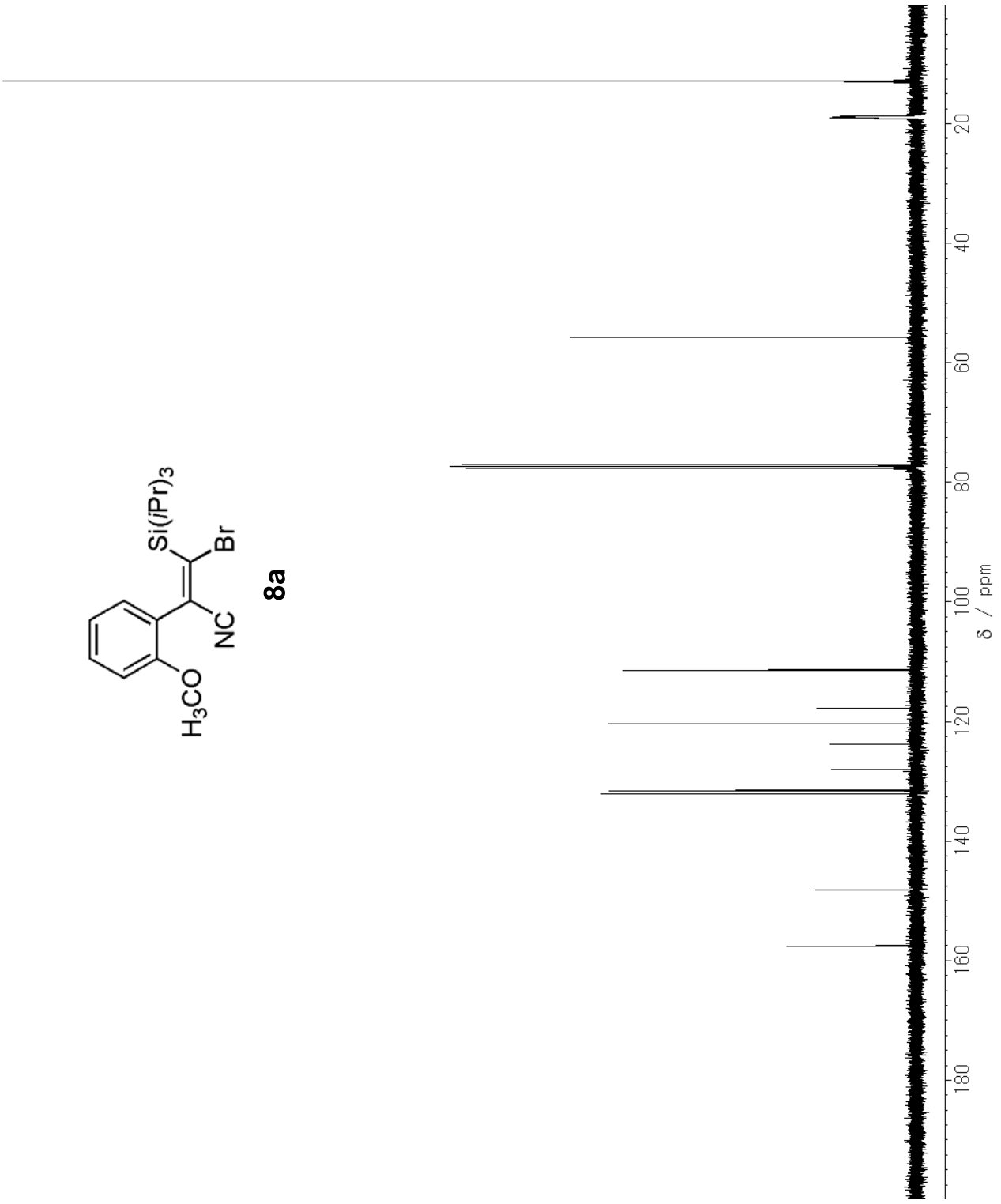
Compound 8a

^{1}H NMR spectrum in $CDCl_3$



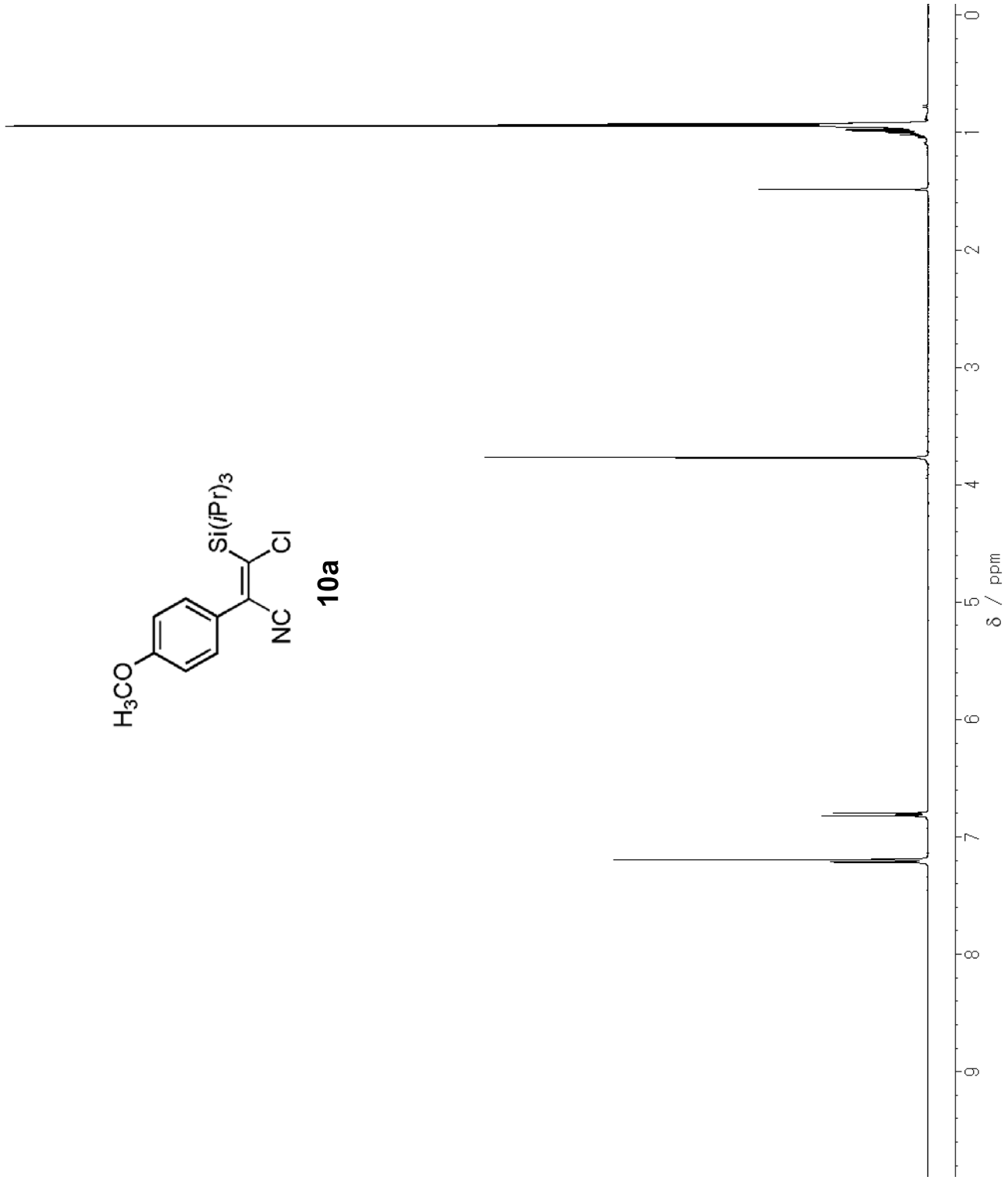
Compound 8

^{13}C NMR spectrum in $CDCl_3$



Compound 10a

^{1}H NMR spectrum in $CDCl_3$



Compound 10a

^{13}C NMR spectrum in $CDCl_3$