

SUPPORTING INFORMATION

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Title: Regio- and Stereoselective Synthesis of Vicinal (Z)-Dihaloalkenylsilanes from Silyl Ethynylarenes

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a) **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. Compounds of trialkylsilyl ethynylarenes were prepared through the cross-coupling between appropriate aryl halide and trialkylsilyl acetylene according to the literature.¹ Column chromatography was carried out with silica gel. HRMS were reported on the basis of TOF (time of flight)-MS, and EB (double-focusing)-MS. ^1H and ^{13}C NMR spectra were recorded with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shifts are reported relative to residual solvent signals [^1H NMR: CHCl_3 (7.26 ppm); ^{13}C NMR: CDCl_3 (77.0 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

b) **Representative procedure for regio- and stereoselective bromochlorination of TIPS-ethynylarenes to give (Z)-(1-bromo-2-chloro-2-(naphthalen-1-yl)vinyl)triisopropylsilane 6 (Table 1, entry 8):** Under an argon atmosphere, to a solution of **1** (154 mg, 0.5 mmol) in anhydrous toluene (2 mL) at 0 °C was added TMSCl (0.75 mL of 1 M in dichloromethane) dropwise over 5 min, and the mixture was stirred for 5 min. Then, NBS (134 mg, 0.75 mmol) in acetonitrile 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 °C with saturated aqueous sodium thiosulfate, and stirred for 10 min, and warmed to ambient temperature. The aqueous phase was extracted with toluene (10 mL \times 3), and the combined organic phases were washed with brine (15 mL), and then dried with sodium sulfate, and concentrated to give 244 mg of crude products. Purification by short-plug column chromatography (eluent; hexane) afforded 205 mg of **6** in 95% yield as a white solid material. Analytical data are listed in the section below. Analytical data are listed in the section below.

c) **Preparation of 1 M TMSX in dichloromethane:** TMSCl (2.6 g) was added to dry dichloromethane (21 mL), TMSBr (3.5 g) was added to dry dichloromethane (20 mL), and TMSI (5 g) was added to dry dichloromethane (25 mL); each was used as a 1 M TMSX solution for our experimental usage. The reactivity of the freshly prepared TMSX solution was maintained at least for two weeks. However, in the case of 1 M toluene solution of TMSX, ^1H NMR spectroscopy revealed the complete decomposition was unfortunately observed only in 24 h.

d) Characterization for (Z)-(1-bromo-2-chloro-2-arylvinyl)triisopropylsilane **2-14**.

(Z)-(1,2-dibromo-2-(naphthalen-1-yl)vinyl)triisopropylsilane, (2): 96% yield, 254 mg as a whitish yellow solid. ^1H NMR (400 MHz, CDCl_3) 8.06 (d, $J = 7.9$ Hz, 1H), 7.85 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 7.56 (dd, $J = 7.6, 6.9$ Hz, 1H), 7.52-7.44 (m, 2H), 7.40 (t, $J = 7.6$ Hz, 1H), 0.96 (d, $J = 7.0$ Hz, 9H), 0.87 (sep, $J = 7.0$ Hz, 3H), 0.82 (d, $J = 7.0$ Hz, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 138.4, 134.0, 133.8, 131.9, 131.3, 130.2, 128.6, 127.2, 126.9, 126.8, 126.5, 125.0, 19.2, 19.0, 13.0 ppm. MS (EI) m/z : 466 (M^+). IR (neat): 2940, 2863, 1558, 1461, 1384, 1228, 1017, 1002 cm^{-1} . HRMS (DI) calcd for $\text{C}_{21}\text{H}_{28}\text{Br}_2\text{Si}$: 466.0327, found 466.0323. Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{Br}_2\text{Si}$: C, 53.85; H, 6.03. Found: C, 53.58; H, 5.83.

1-(1-bromo-2,2-diiodovinyl)naphthalene, (3): 59% yield, 143 mg as a yellowish white solid. ^1H NMR (400 MHz, CDCl_3) 7.91-7.85 (m, 3H), 7.64-7.60 (m, 1H), 7.57-7.44 (m, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 140.0, 134.0, 131.0, 130.0, 129.2, 128.8, 127.4, 126.9, 126.5, 125.8, 125.1, 20.0 ppm. MS (EI) m/z : 484 (M^+), 405 ($[\text{M}-\text{Br}]^+$). IR (neat): 3051, 2926, 2852, 1588, 1502, 1386 cm^{-1} . HRMS (DI) calcd for $\text{C}_{12}\text{H}_7\text{BrI}_2$: 483.7820, found 483.7810.

1,4-bis((Z)-2-bromo-1-chloro-2-(triisopropylsilyl)vinyl)benzene, (4): 82% yield, 410 mg as a yellowish white solid. ^1H NMR (400 MHz, CDCl_3) 7.33 (s, 4H), 1.02 (brs, 42H, *i*Pr-H are overlapped) ppm. ^{13}C NMR (100 MHz, CDCl_3) 142.1, 140.7, 129.2, 126.8, 19.2, 13.1 ppm. IR (neat): 2940, 2865, 1556, 1461, 1216, 1018 cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{46}\text{Br}_2\text{Cl}_2\text{Si}_2$: C, 50.23; H, 6.92. Found: C, 50.23; H, 6.86.

1,4-bis((Z)-1,2-dibromo-2-(triisopropylsilyl)vinyl)benzene, (5): 81% yield, 306 mg as a white solid. ^1H NMR (400 MHz, CDCl_3) 7.23 (s, 4H), 0.99-0.98 (m, 42H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 142.6, 134.4, 129.8, 128.9, 19.2, 13.2 ppm. IR (neat): 2943, 2863, 1600, 1582, 1462, 1251, 1021, 750 cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{46}\text{Br}_4\text{Si}_2$: C, 44.34; H, 6.11. Found: C, 44.37; H, 5.84.

(Z)-(1-bromo-2-chloro-2-(naphthalen-1-yl)vinyl)triisopropylsilane, (6): 95% yield, 205 mg as a white solid. ^1H NMR (400 MHz, CDCl_3) 8.01 (d, $J = 8.3$ Hz, 1H), 7.87 (d, $J = 8.8$ Hz, 1H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.57-7.26 (m, 4H), 0.97 (d, $J = 6.5$ Hz, 9H), 0.90 (sep, $J = 6.5$ Hz, 3H), 0.76 (d, $J = 6.5$ Hz, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 141.2, 136.1, 133.5, 131.2, 130.1, 128.6, 128.3, 127.4, 126.8, 126.4, 125.9, 124.7, 18.9, 18.6, 12.5 ppm. MS (EI) m/z : 422 (M^+). IR (neat): 2942, 1863, 1556, 1505, 1461, 1389 cm^{-1} . HRMS (DI) calcd for $\text{C}_{21}\text{H}_{28}\text{BrClSi}$: 422.0832, found 422.0820.

(Z)-(1,2-dichloro-2-(naphthalen-1-yl)vinyl)triisopropylsilane, (7): 75% yield, 111 mg as a colorless viscous material. ^1H NMR (400 MHz, CDCl_3) 8.01 (d, $J = 8.2$ Hz, 1H), 7.89-7.84 (m, 2H), 7.57-7.39 (m, 4H), 0.97 (d, $J = 7.0$ Hz, 9H), 0.85 (sep, $J = 7.0$ Hz, 3H), 0.75 (d, $J = 7.0$ Hz, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 139.7, 135.7, 135.6, 133.8, 131.8, 130.5, 128.6, 128.2, 126.7, 126.1, 125.0, 19.1, 18.8, 12.4 ppm. MS (EI) m/z : 378 (M^+). IR (neat): 3059, 2943, 2864, 1568, 1463, 1389, 1233, 1171, 1085, 1017 cm^{-1} . Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{Cl}_2\text{Si}$: C, 66.47; H, 7.44. Found: C, 66.76; H, 7.48.

(Z)-(1-bromo-2-chloro-2-(naphthalen-1-yl)vinyl)trimethylsilane, (8): 53% yield, 90 mg as a colorless oil. ^1H NMR (400 MHz, CDCl_3) 7.95 (d, $J = 8.24$ Hz, 1H), 7.88 (dd, $J = 8.24, 8.24$ Hz, 2H), 7.59-7.41 (m, 4H), -0.22 (s, 9H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 139.3, 136.3, 133.5, 131.3, 130.0, 129.8, 128.3,

127.4, 127.0, 126.5, 125.2, 124.9, -0.5 ppm. MS (EI) m/z : 338 (M^+). IR (neat): 3058, 2954, 2896, 1568, 1505, 1390, 1249, 1086, 1045 cm^{-1} . HRMS (DI) calcd for $\text{C}_{15}\text{H}_{16}\text{BrClSi}$: 337.9893, found 337.9875.

(Z)-(1-bromo-2-chloro-2-(4-(2-chloroethoxy)phenyl)vinyl)triisopropylsilane, (9): 92% yield, 10.0 g as whitish yellow solids. ^1H NMR (400 MHz, CDCl_3) 7.30 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 4.25 (t, $J = 5.9$ Hz, 2H), 3.82 (t, $J = 5.9$ Hz, 2H), 1.00 (brs, 21H, *i*Pr-H are over lapped) ppm. ^{13}C NMR (100 MHz, CDCl_3) 159.2, 143.0, 132.7, 131.1, 125.9, 114.3, 68.4, 42.0, 19.2, 12.9 ppm. IR (neat): 3057, 2925, 2854, 1621, 1519, 1466, 1440 cm^{-1} . MS (EI) m/z : 452 (M^+); HRMS (DI) calcd for $\text{C}_{19}\text{H}_{29}\text{BrCl}_2\text{OSi}$: 450.0548, found 450.0540.

(Z)-(1-bromo-2-chloro-2-(4-methoxyphenyl)vinyl)triisopropylsilane, (10): 98% yield, 397 mg as a yellow viscous material. ^1H NMR (400 MHz, CDCl_3) 7.29 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 3.83 (s, 3H), 1.01 (brs, 21H, *i*Pr-H are over lapped) ppm. ^{13}C NMR (100 MHz, CDCl_3) 1160.6, 143.4, 132.0, 131.0, 125.7, 113.6, 55.7, 19.2, 13.0 ppm. MS (EI) m/z : 402 (M^+). IR (neat): 2945, 2865, 1605, 1501, 1462, 1440, 1251, 1108, 1068, 1033, 1020 cm^{-1} . HRMS (DI) calcd for $\text{C}_{18}\text{H}_{28}\text{BrClOSi}$: 402.0781, found 402.0760.

(Z)-(1-bromo-2-chloro-2-(2-methoxyphenyl)vinyl)triisopropylsilane, (11): 88% yield, 356 mg as a yellowish white solid. ^1H NMR (400 MHz, CDCl_3) 7.34 (dd, $J = 6.6, 6.0$ Hz, 1H), 7.21 (d, $J = 6.0$ Hz, 1H), 6.89 (dd, $J = 6.6, 6.0$ Hz, 1H), 6.85 (d, $J = 6.6$ Hz, 1H), 3.82 (s, 3H), 1.00 (m, 21H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 157.6, 140.7, 131.9, 131.8, 128.7, 127.7, 120.7, 111.8, 56.1, 19.7, 19.4, 13.4 ppm. IR (neat): 2942, 2863, 1600, 1582, 1462, 1021, 750 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{BrClOSi}$: C, 53.53; H, 6.99. Found: C, 53.38; H, 6.73.

(Z)-(1-bromo-2-chloro-2-(*o*-tolyl)vinyl)triisopropylsilane, (12): 95% yield, 369 mg as a white solid. ^1H NMR (400 MHz, CDCl_3) 7.28-7.11 (m, 4H), 2.39 (s, 3H), 1.01-0.95 (m, 21H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 142.9, 138.6, 137.1, 130.8, 130.0, 129.9, 127.6, 125.6, 20.1, 19.2, 19.0, 12.9 ppm. MS (EI) m/z : 343 ($[\text{M}-i\text{Pr}]^+$). IR (neat): 2946, 2866, 1556, 1463, 1383, 1219, 1192, 1112, 1070, 1019, 1003 cm^{-1} . Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{BrClSi}$: C, 55.74; H, 7.28. Found: C, 55.79; H, 7.44.

(Z)-(1-bromo-2-chloro-2-(2,6-dimethylphenyl)vinyl)triisopropylsilane, (13): 80% yield, 161 mg as a colorless oil. ^1H NMR (400 MHz, CDCl_3) 7.14 (t, $J = 7.6$ Hz, 1H), 7.00 (d, $J = 7.6$ Hz, 2H), 2.36 (s, 6H), 1.10-0.96 (m, 21H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 141.6, 138.2, 136.9, 129.4, 129.0, 128.0, 20.4, 19.3, 13.1 ppm. IR (neat): 2943, 2865, 1577, 1460, 1381, 1196, 907, 882 cm^{-1} . Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{BrClSi}$: C, 56.78; H, 7.52. Found: C, 56.52; H, 7.42.

(Z)-(1-bromo-2-chloro-2-(thiophen-2-yl)vinyl)triisopropylsilane, (14): 38% yield, 143 mg as a white solid. ^1H NMR (400 MHz, CDCl_3) 7.38 (dd, $J = 5.1, 1.2$ Hz 1H), 7.11 (dd, $J = 4.8, 1.2$ Hz 1H), 6.91 (dd, $J = 5.1, 4.8$ Hz, 1H), 1.12-1.03 (m, 21H) ppm. ^{13}C NMR (100 MHz, CDCl_3) 140.3, 135.7, 130.1, 129.9, 128.6, 126.3, 19.3, 13.2 ppm. MS (EI) m/z : 378 (M^+). IR (neat): 2938, 2863, 1561, 1462, 1228, 1161, 1019 cm^{-1} . HRMS (DI) calcd for $\text{C}_{15}\text{H}_{24}\text{BrClSSi}$: 378.0240, found 378.0252; Anal. Calcd for $\text{C}_{15}\text{H}_{24}\text{BrClSSi}$: C, 47.43; H, 6.37. Found: C, 47.37; H, 6.38.

e) **References.**

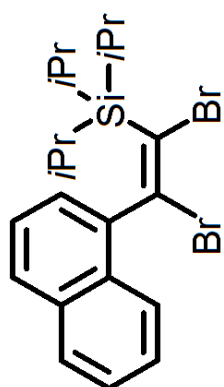
1. Sonogasira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *16*, 4467-4470.

f) ^1H NMR and ^{13}C NMR spectra for compounds **2-14**.

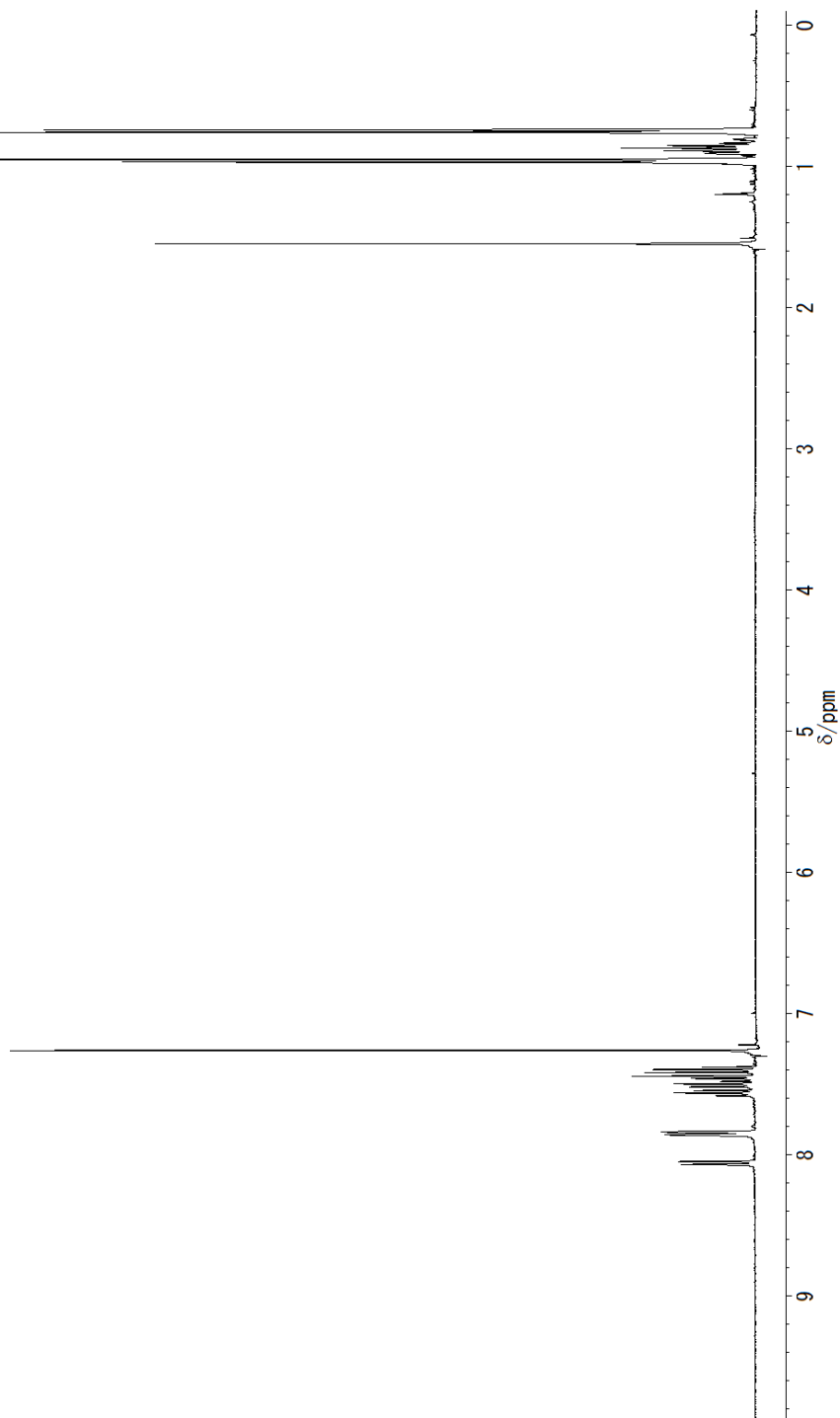
¹H NMR and ¹³C NMR spectra for compounds 2 - 14:

Compound 2

¹H NMR spectrum in CDCl₃

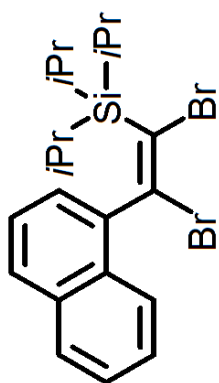


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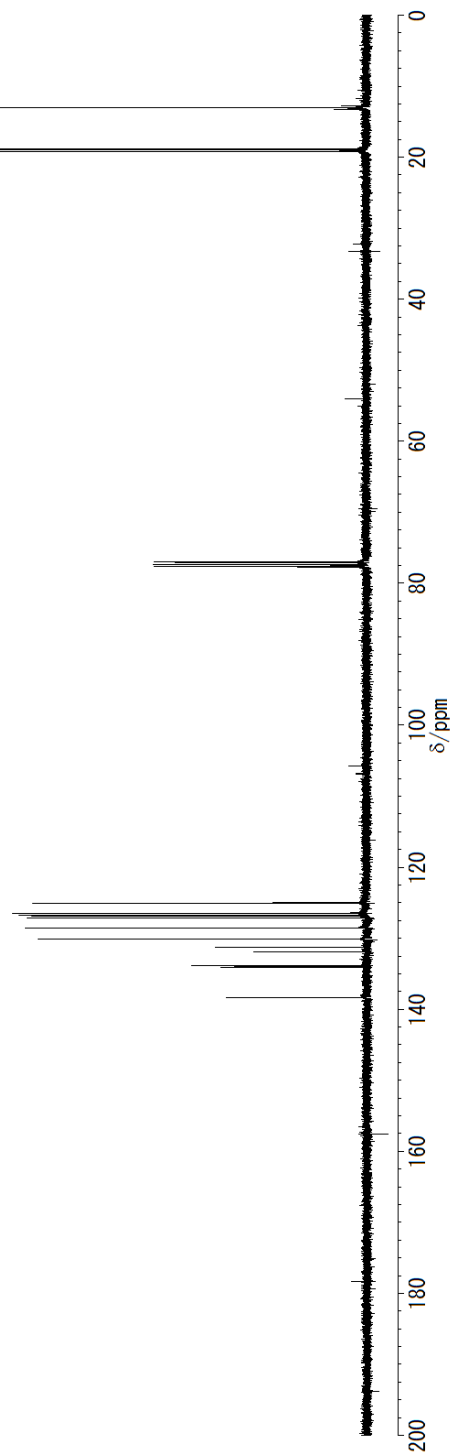


Compound 2

^{13}C NMR spectrum in CDCl_3

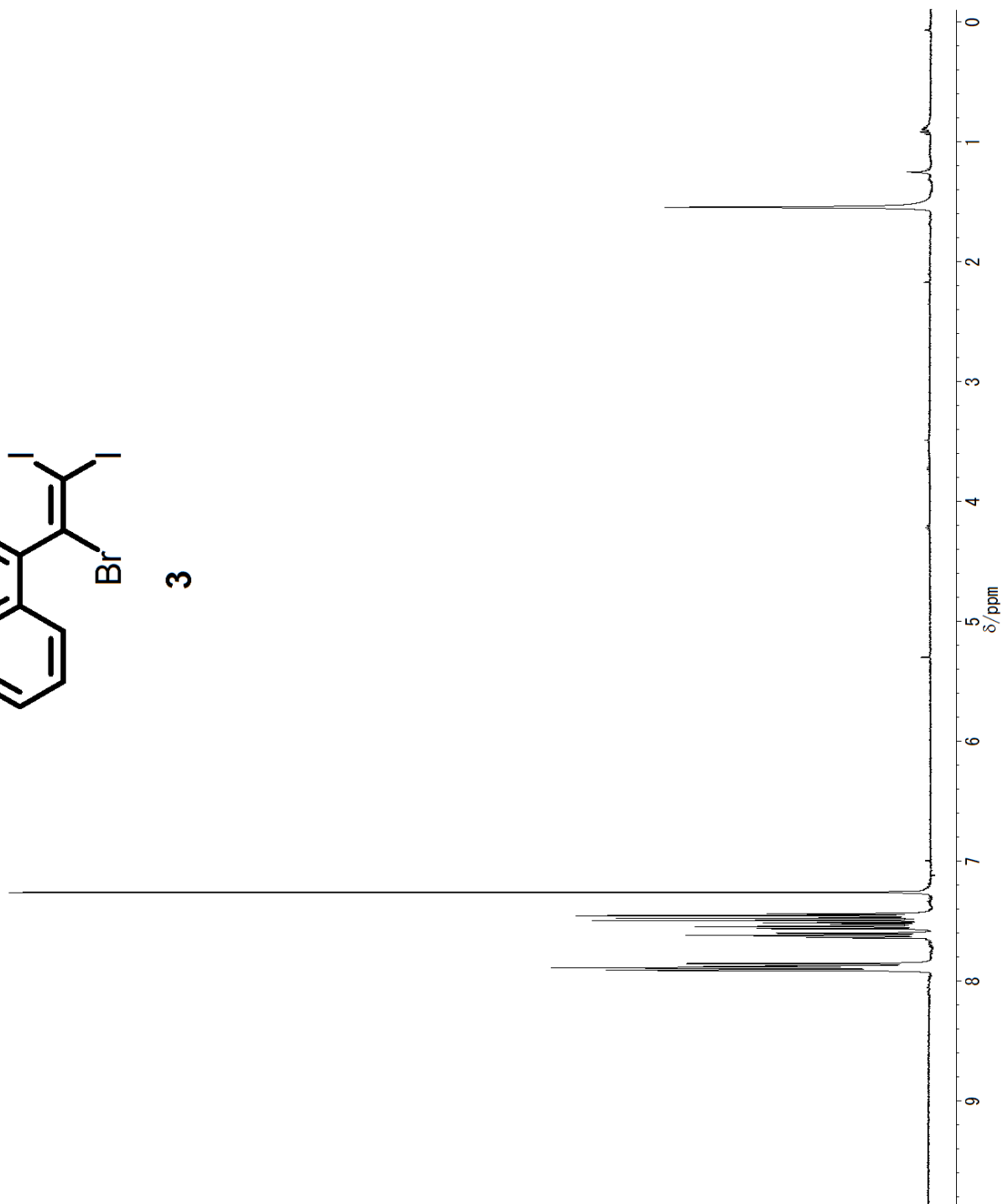
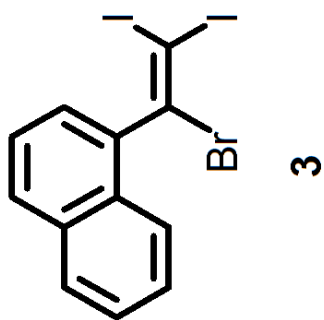


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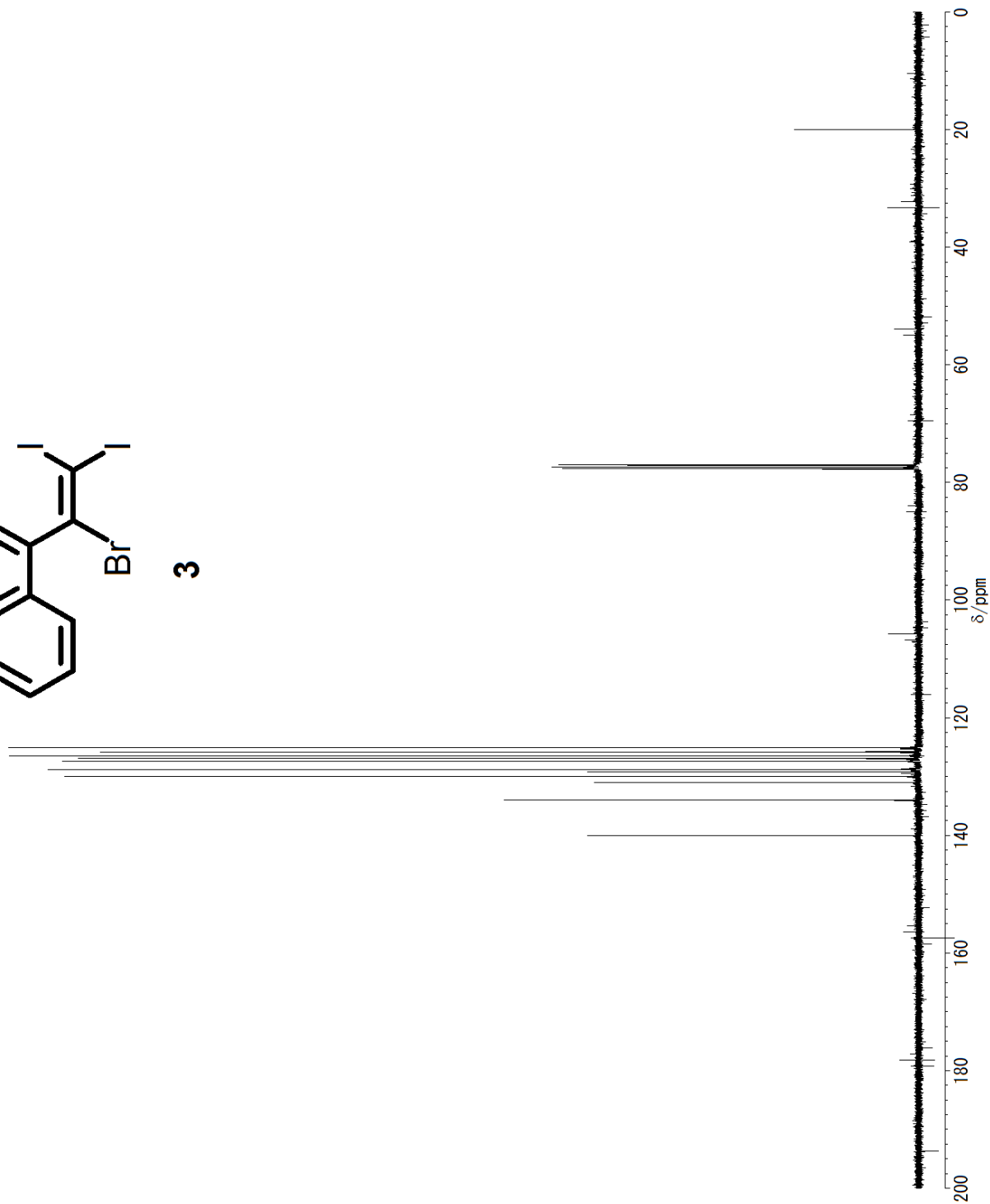
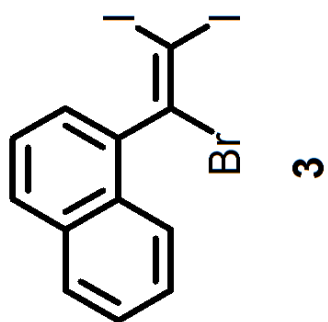
Compound 3

¹H NMR spectrum in CDCl₃



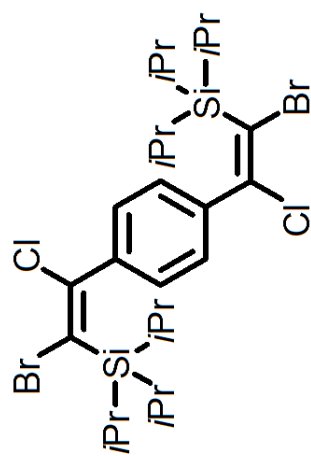
Compound 3

^{13}C NMR spectrum in CDCl_3

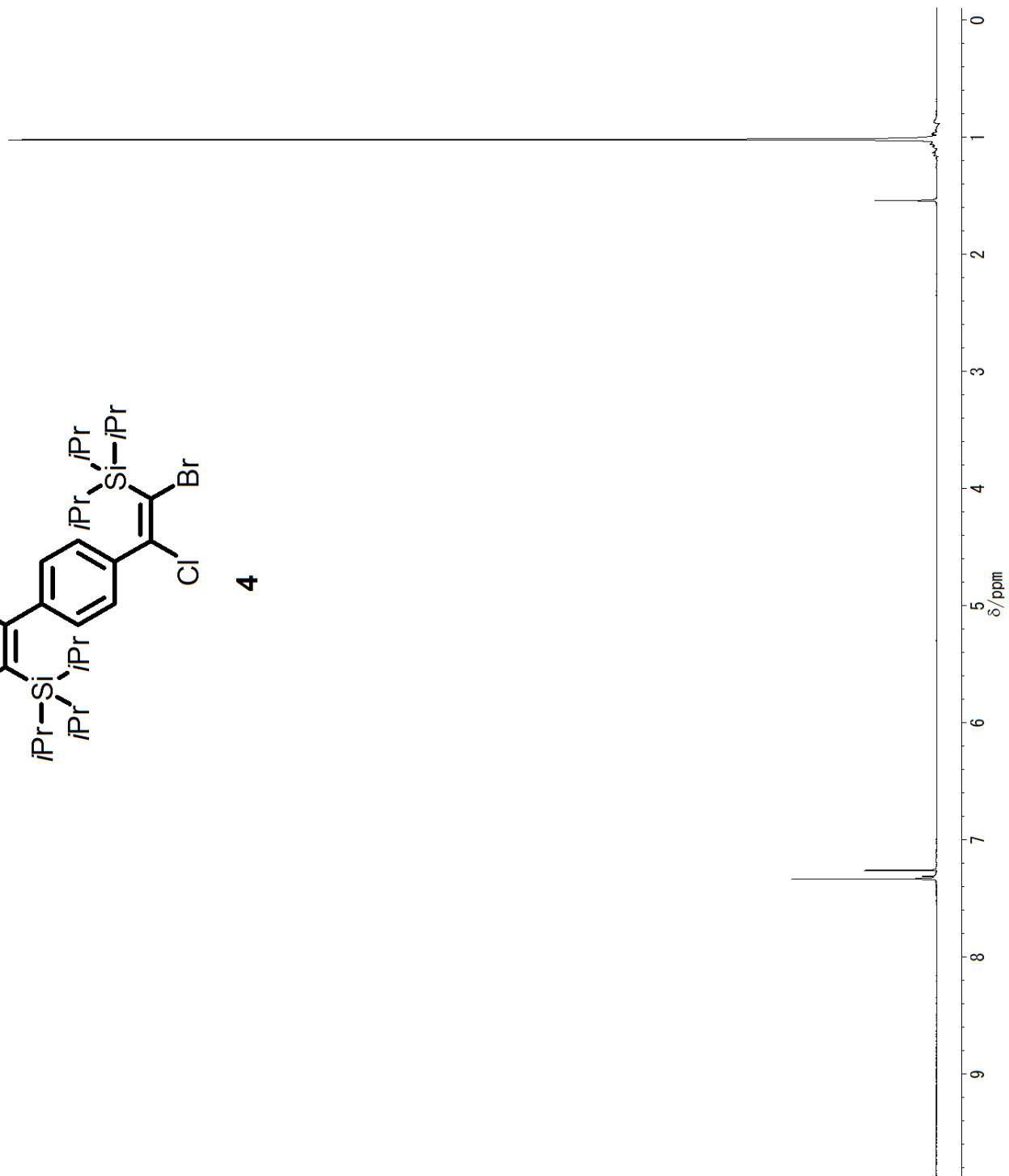


Compound 4

¹H NMR spectrum in CDCl₃

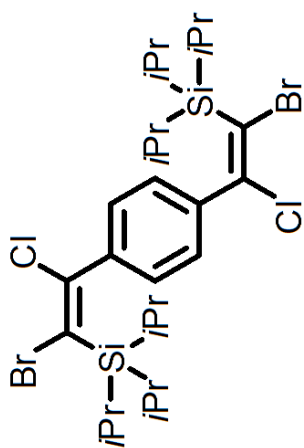


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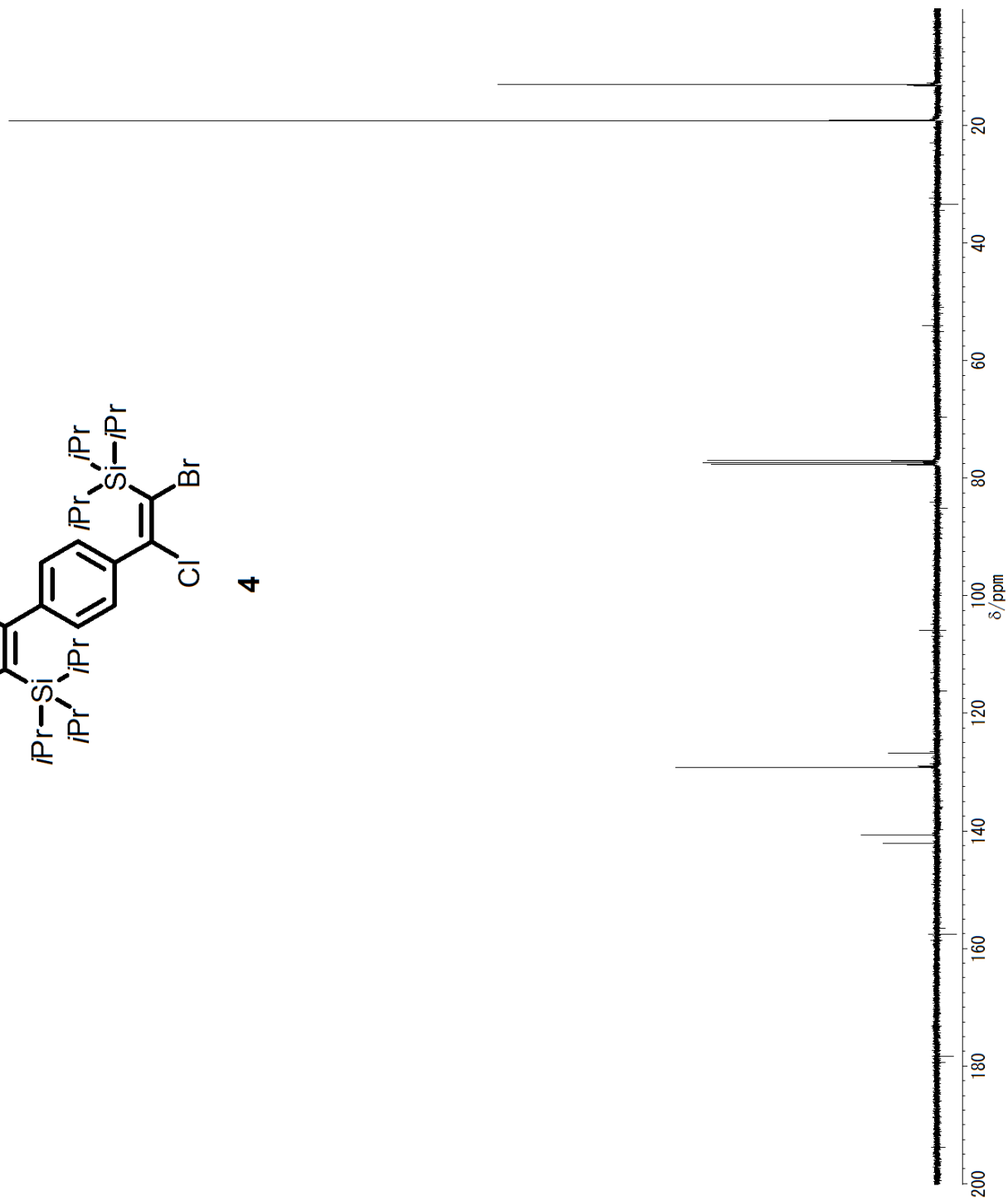


Compound 4

^{13}C NMR spectrum in CDCl_3

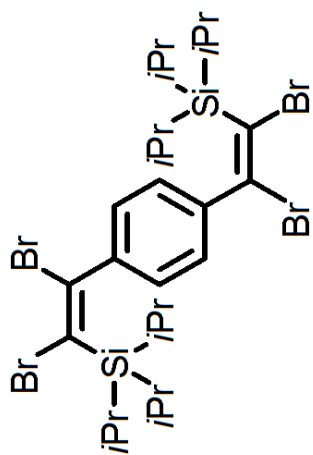


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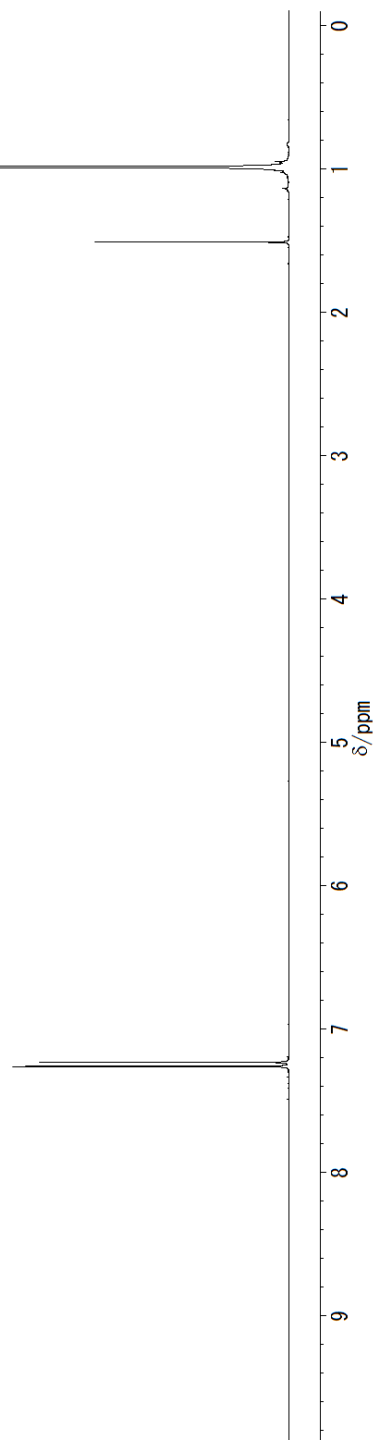


Compound 5

¹H NMR spectrum in CDCl₃

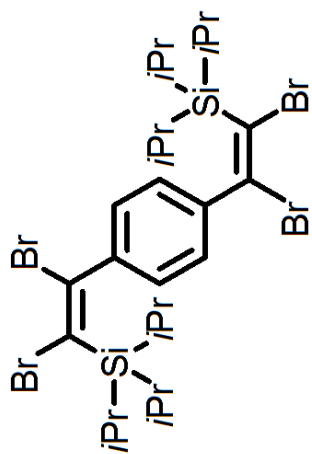


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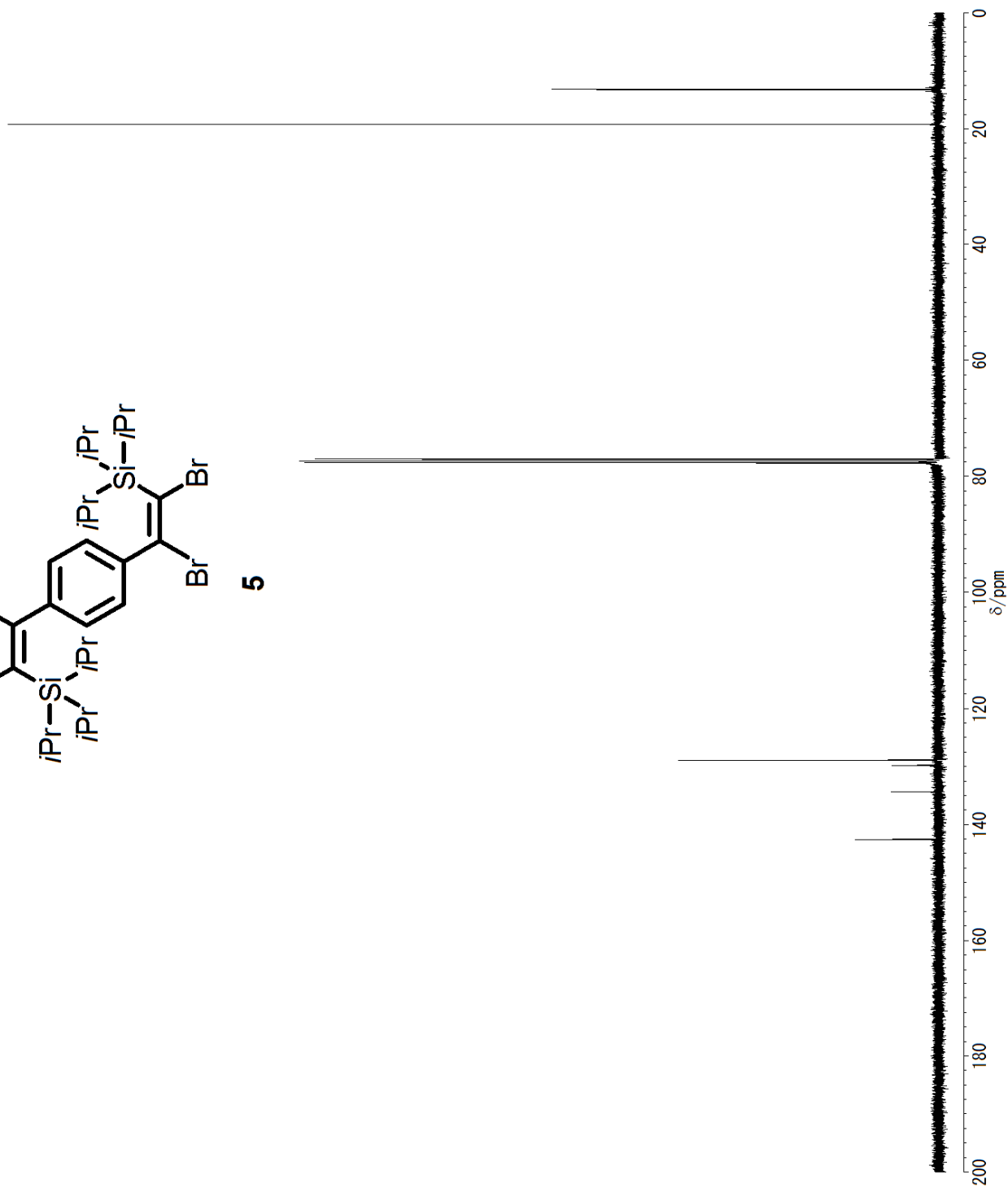


Compound 5

^{13}C NMR spectrum in CDCl_3

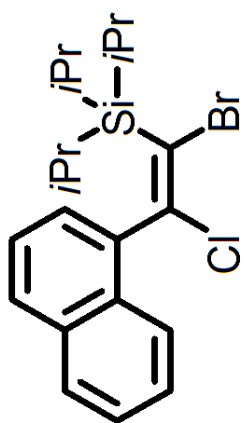


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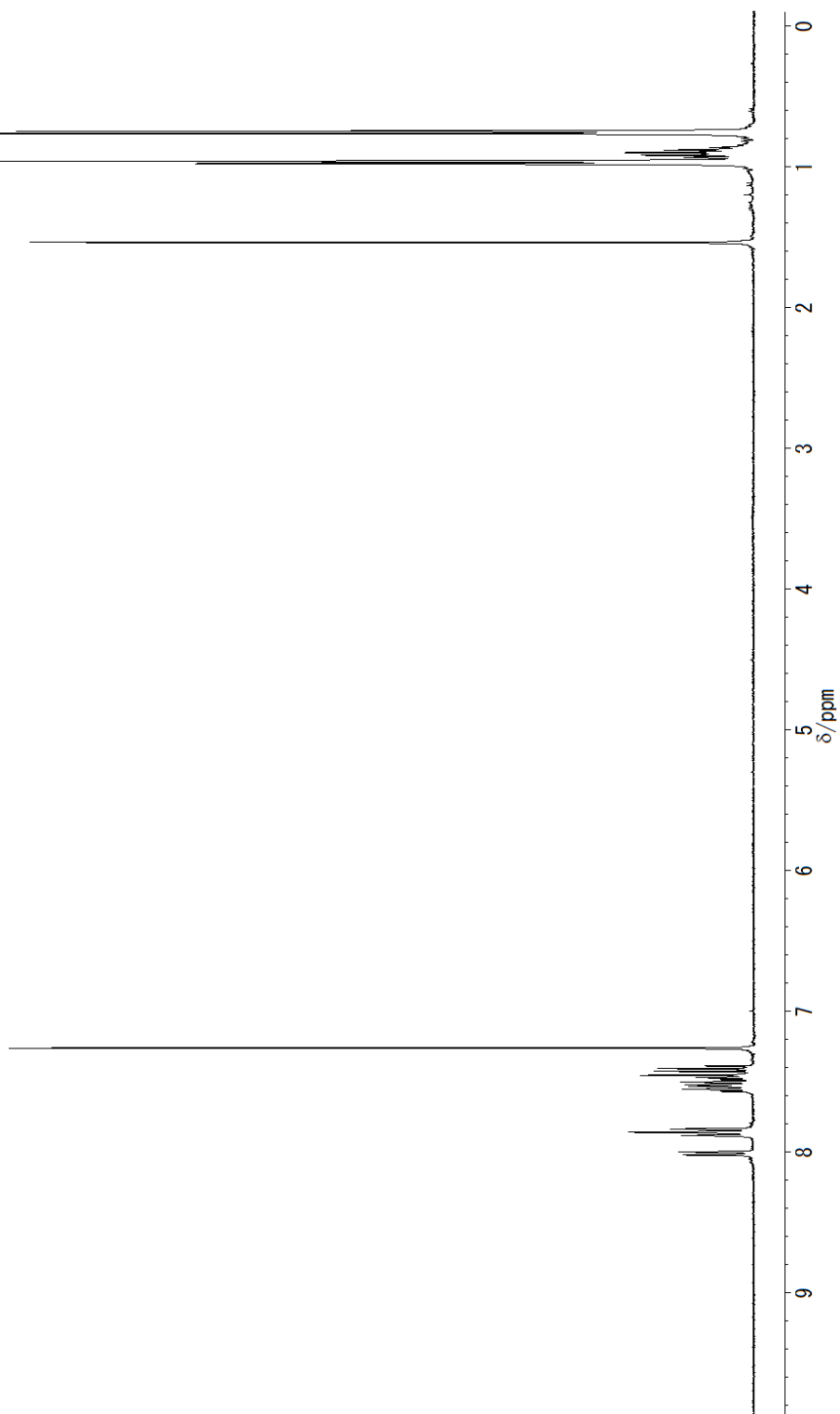


Compound 6

¹H NMR spectrum in CDCl₃

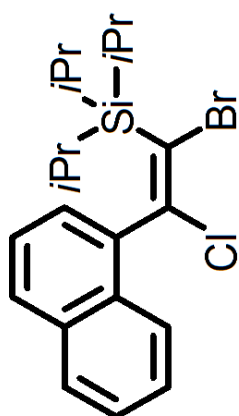


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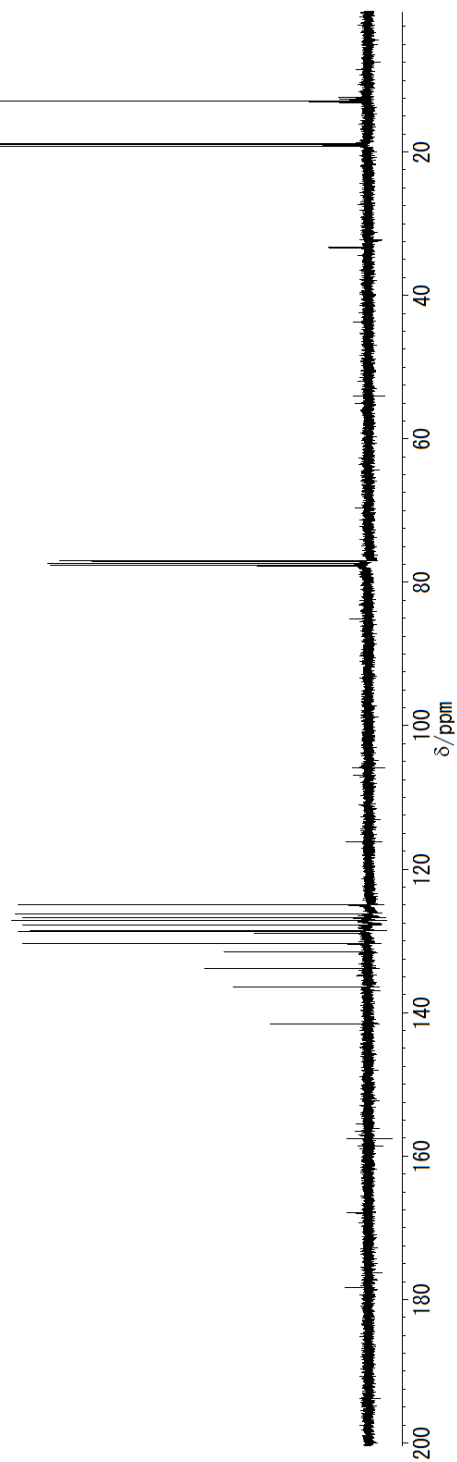


Compound 6

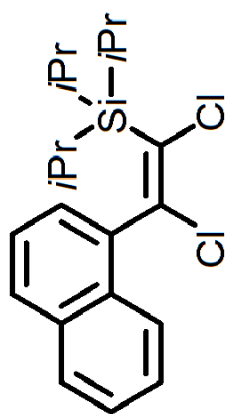
¹³C NMR spectrum in CDCl₃



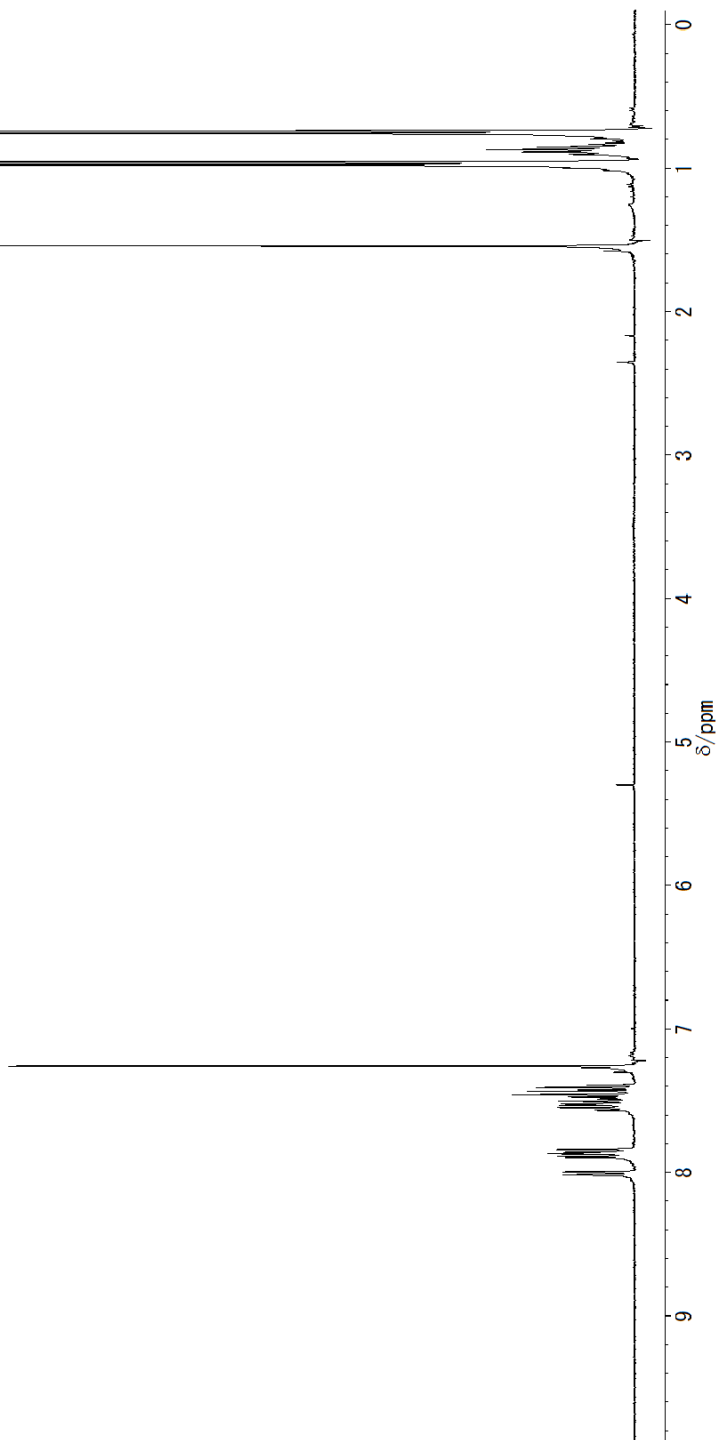
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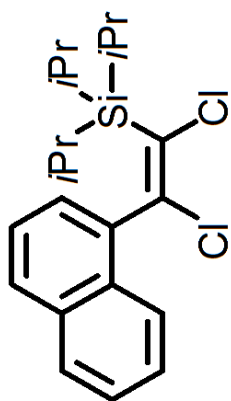
Compound 7
¹H NMR spectrum in CDCl₃



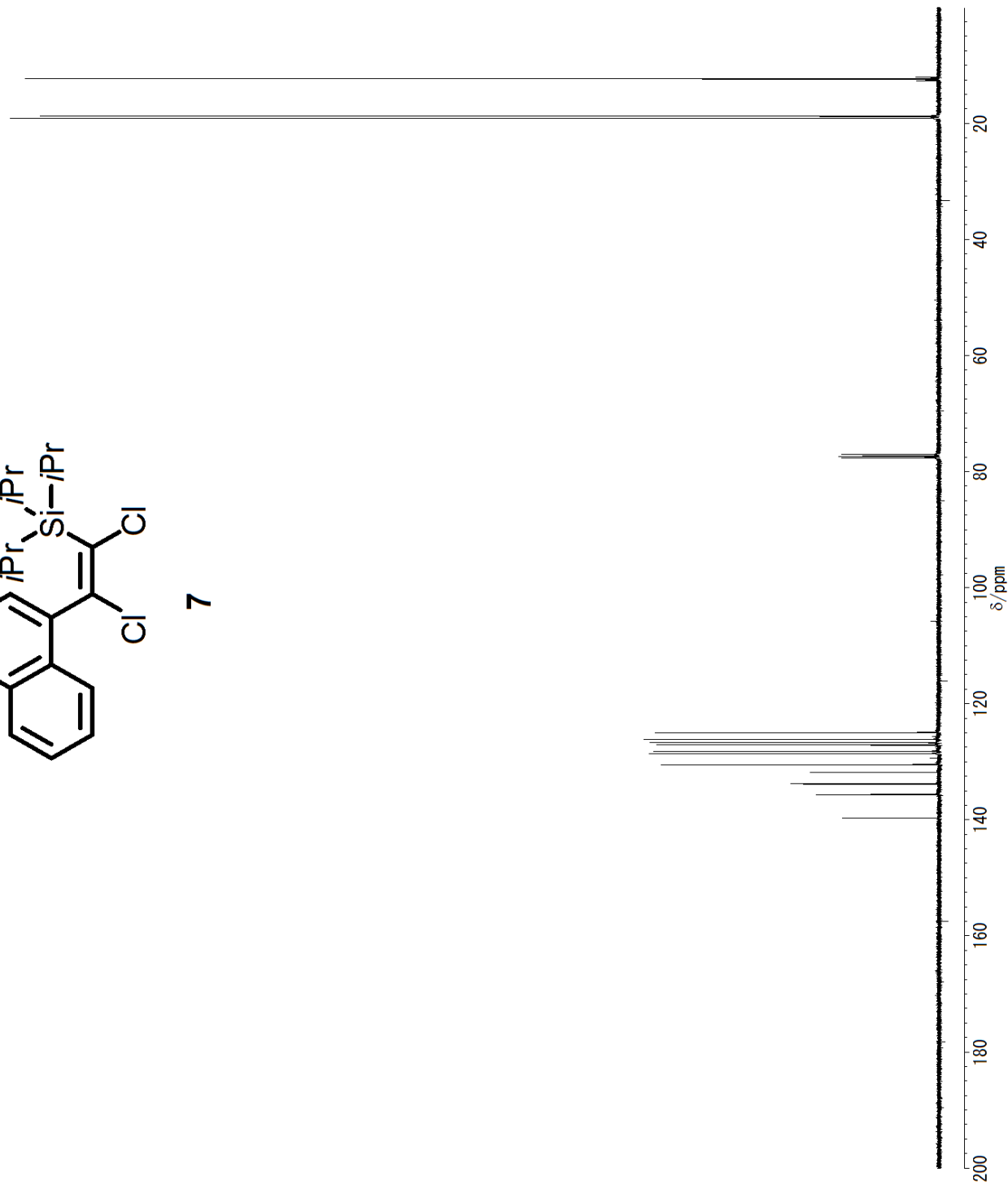
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Compound 7
¹³C NMR spectrum in CDCl₃

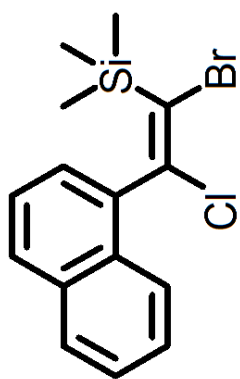


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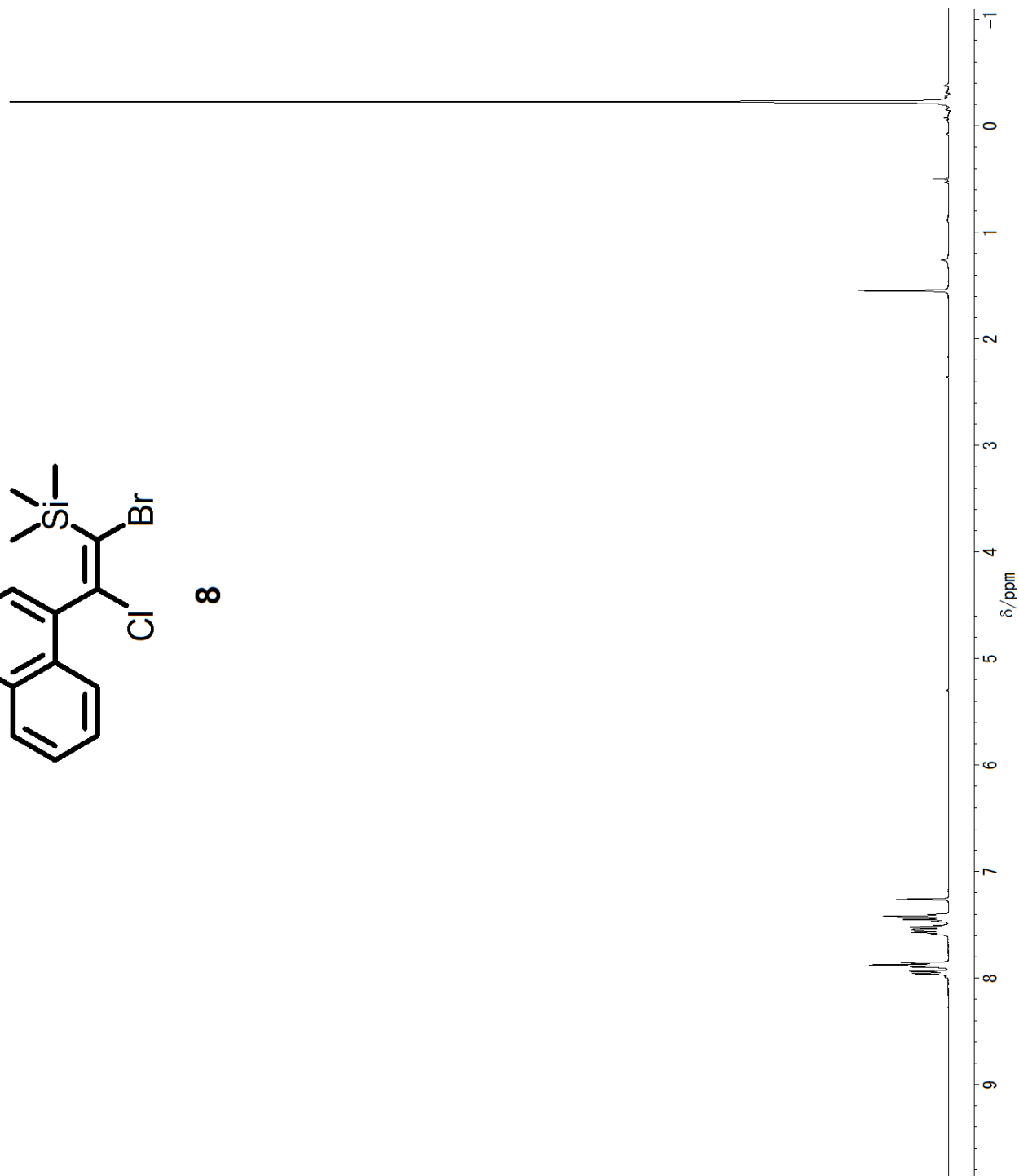


Compound 8

¹H NMR spectrum in CDCl₃

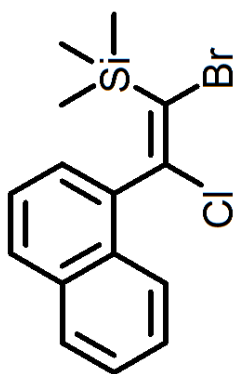


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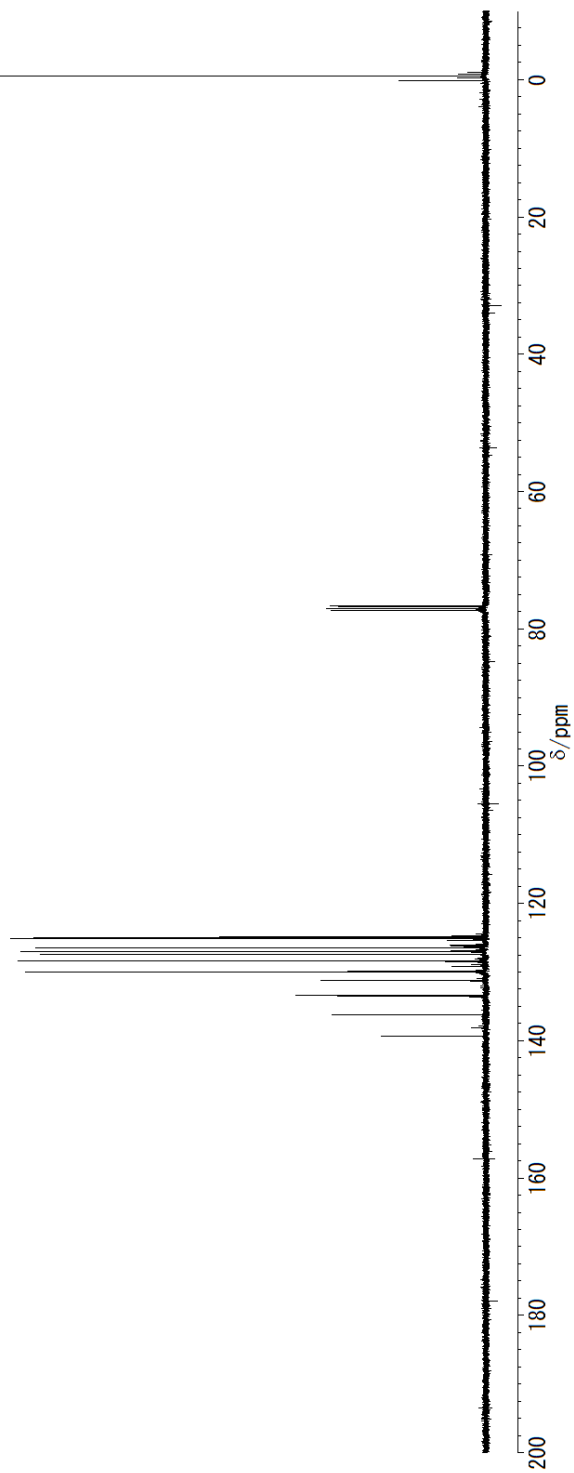


Compound 8

^{13}C NMR spectrum in CDCl_3

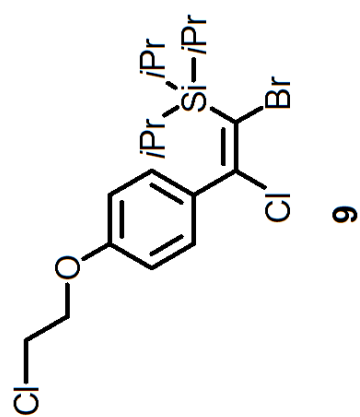


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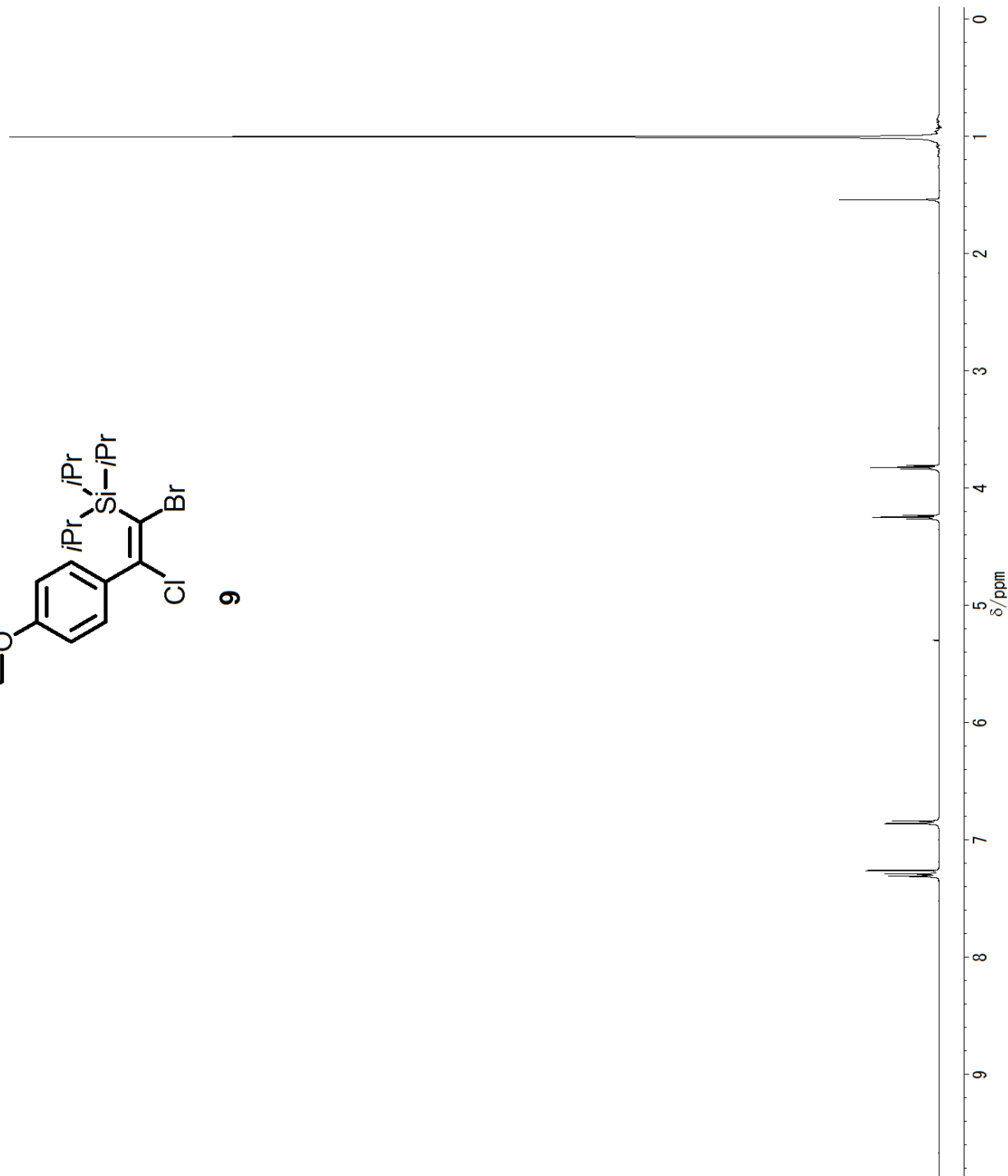


Compound 9

¹H NMR spectrum in CDCl₃

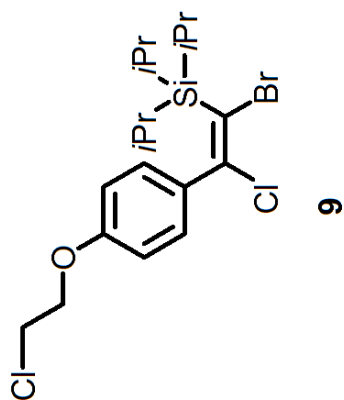


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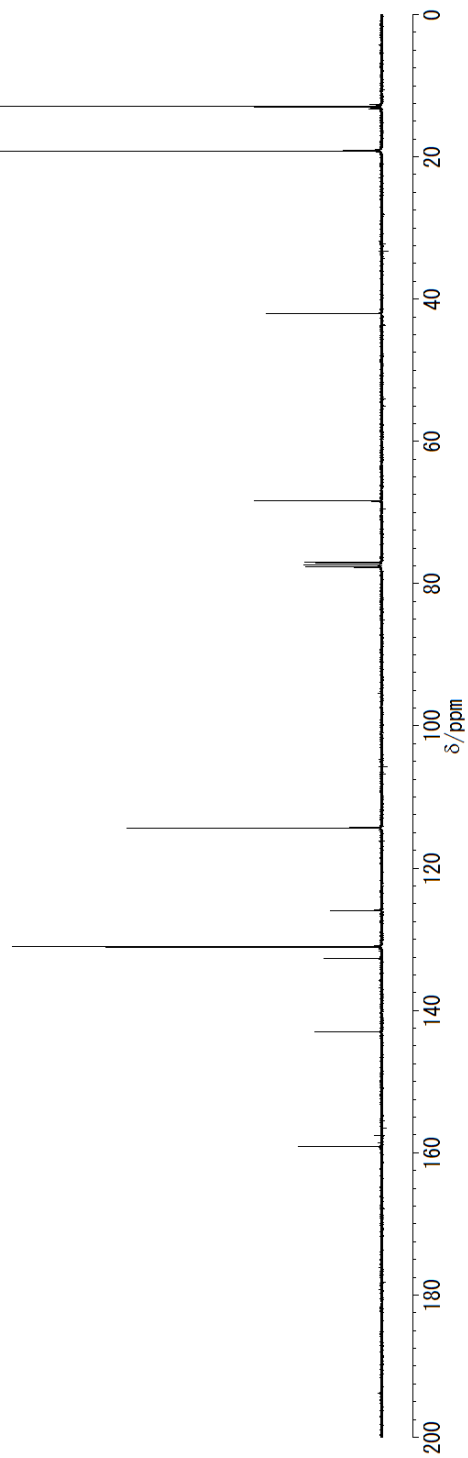


Compound 9

¹³C NMR spectrum in CDCl₃

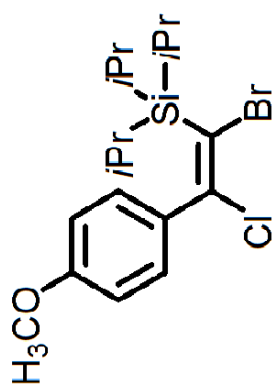


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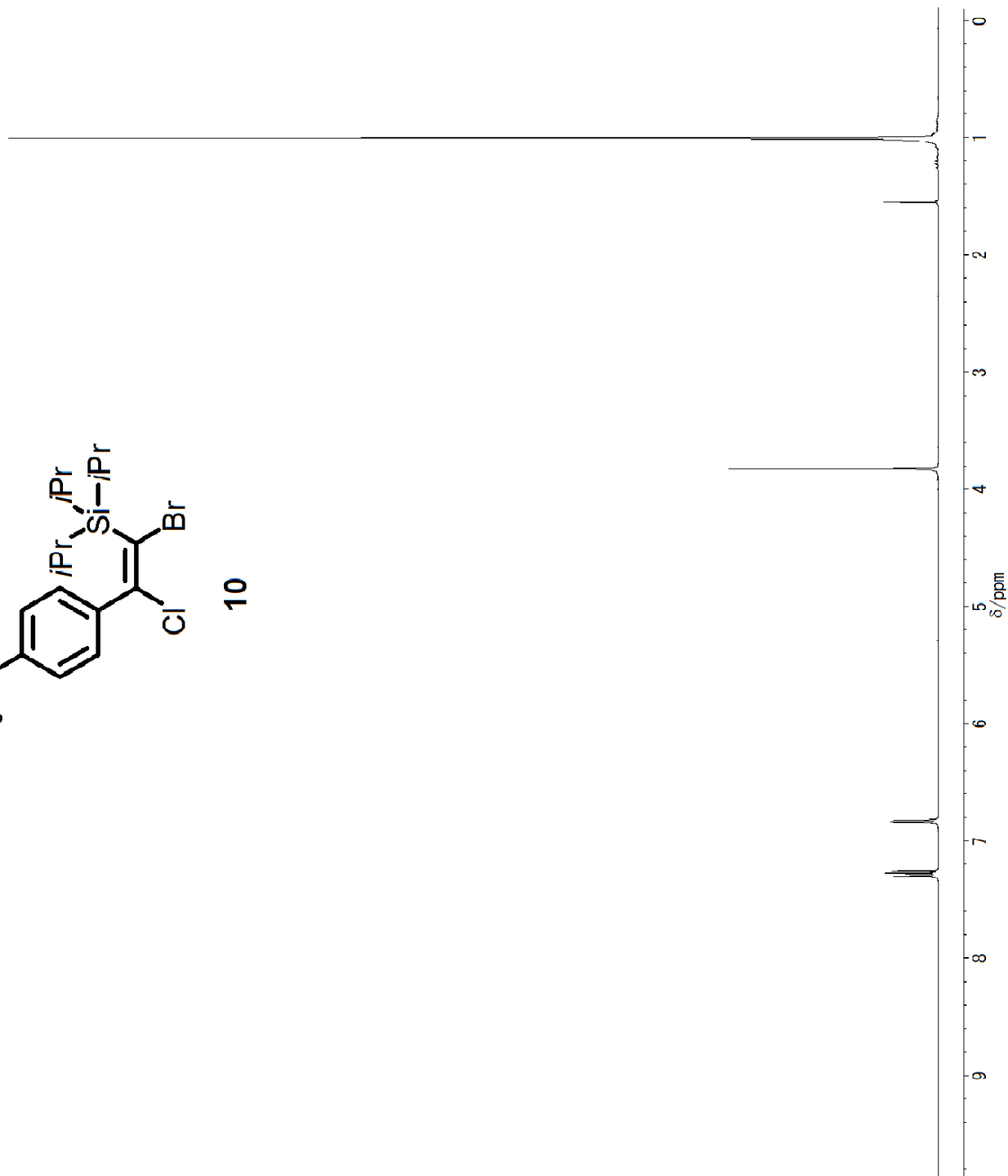


Compound 10

¹H NMR spectrum in CDCl₃

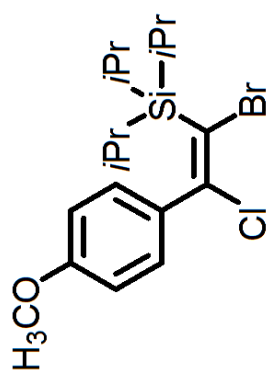


10

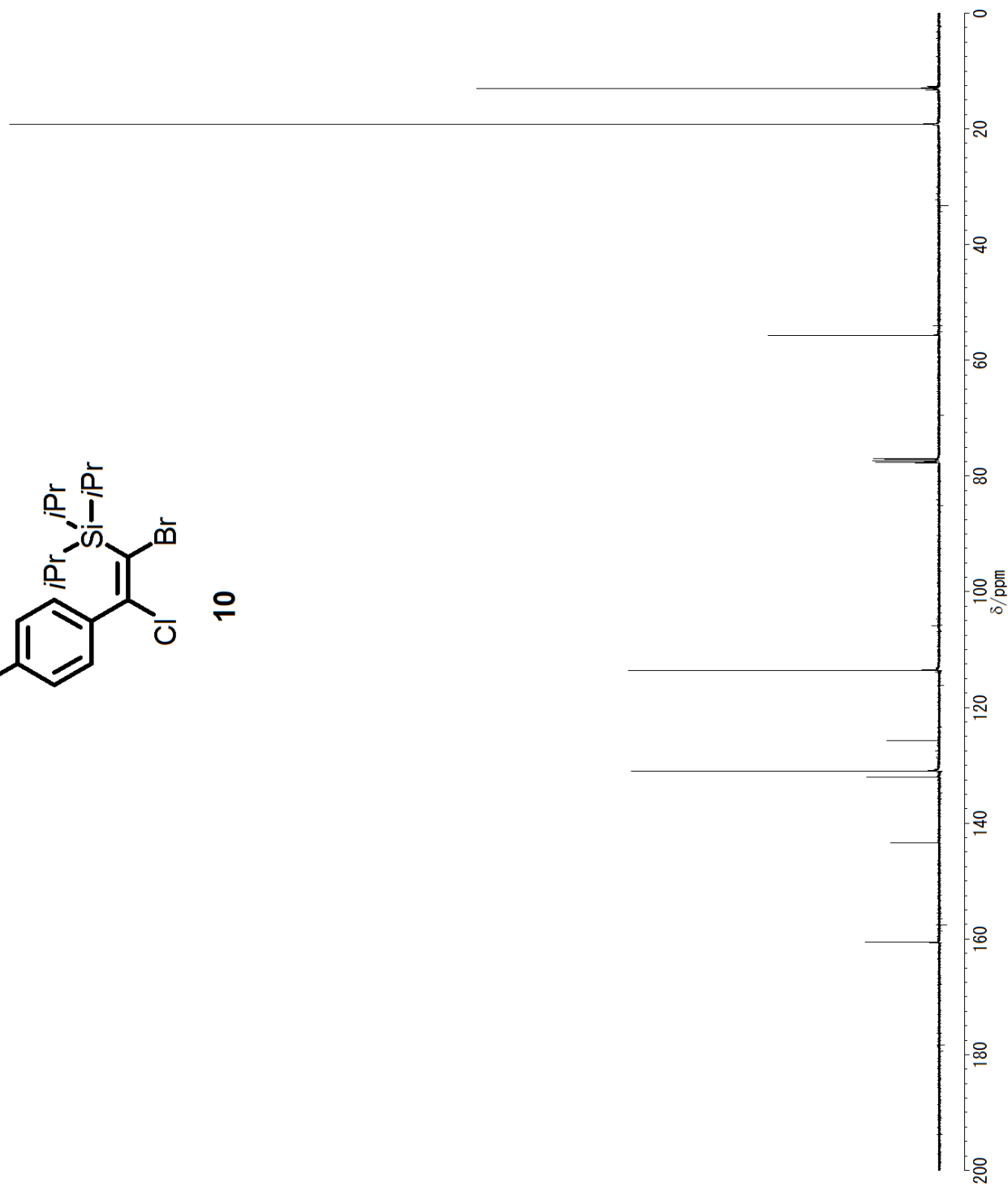


Compound 10

¹³C NMR spectrum in CDCl₃

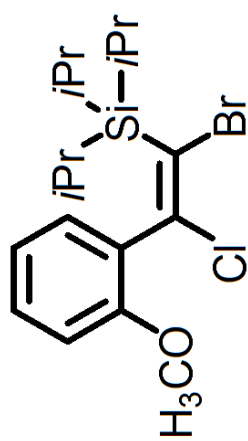


10

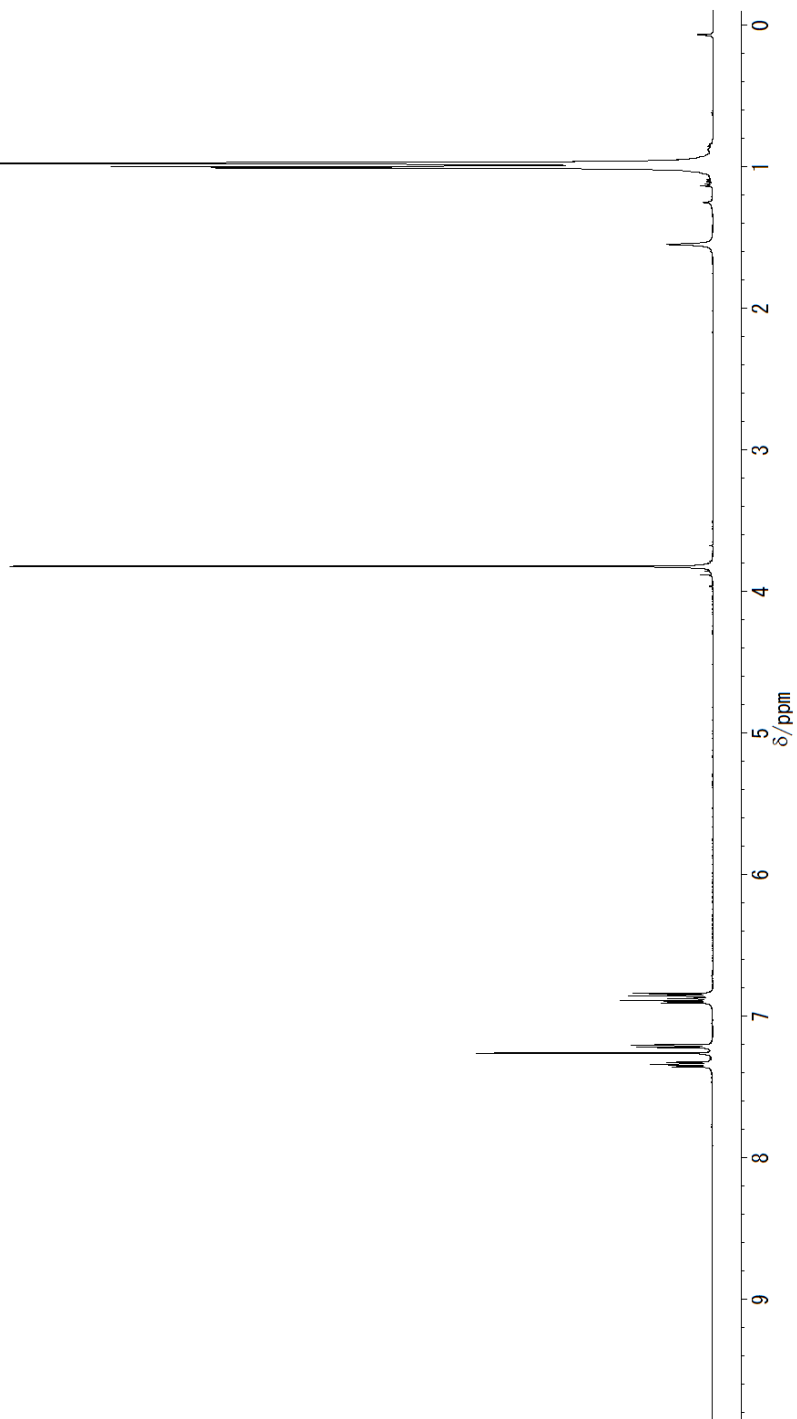


Compound 11

¹H NMR spectrum in CDCl₃

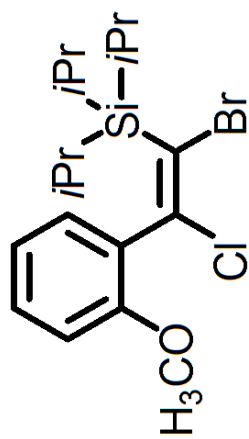


11

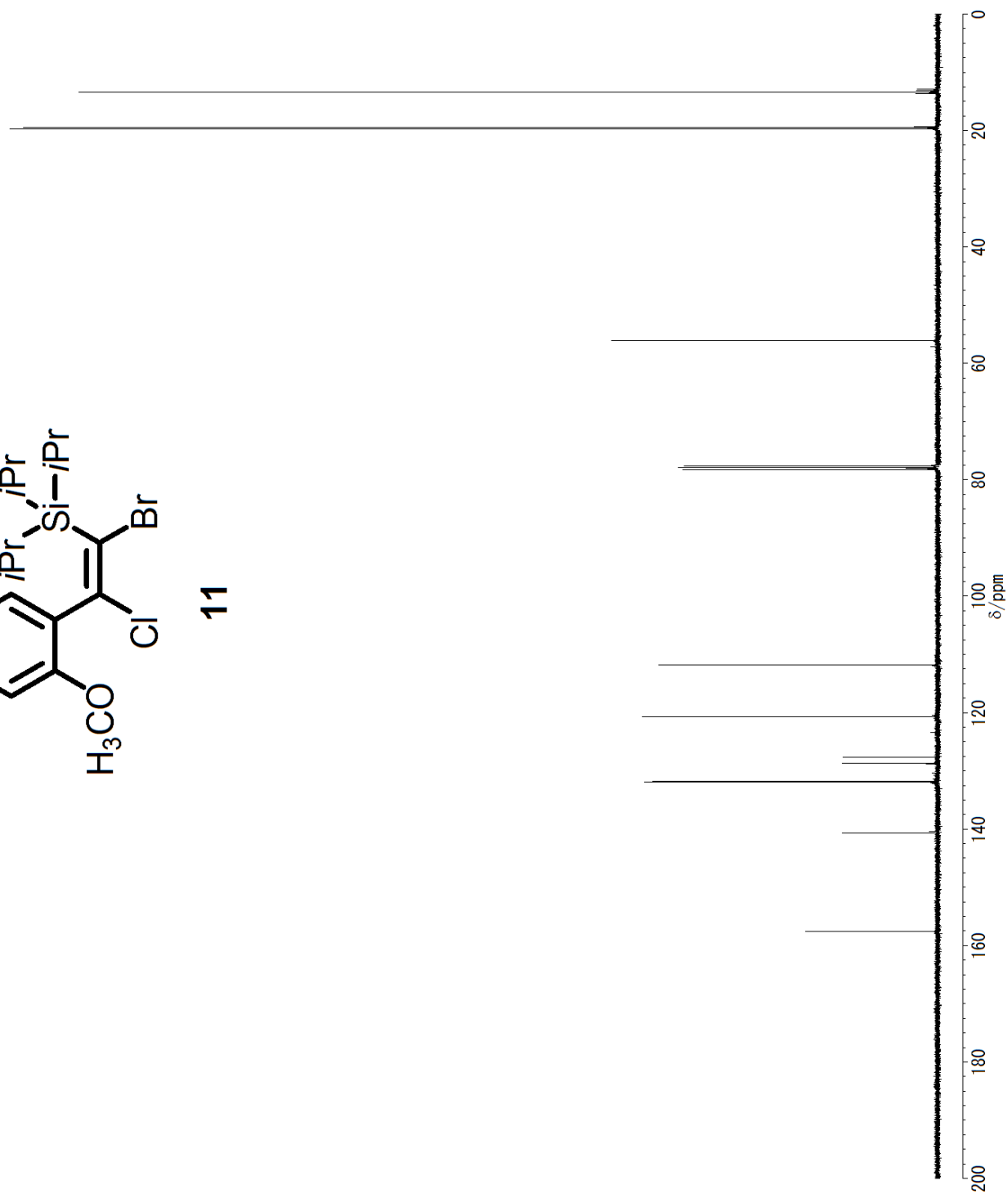


Compound 11

¹³C NMR spectrum in CDCl₃

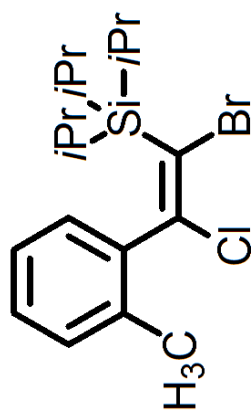


11

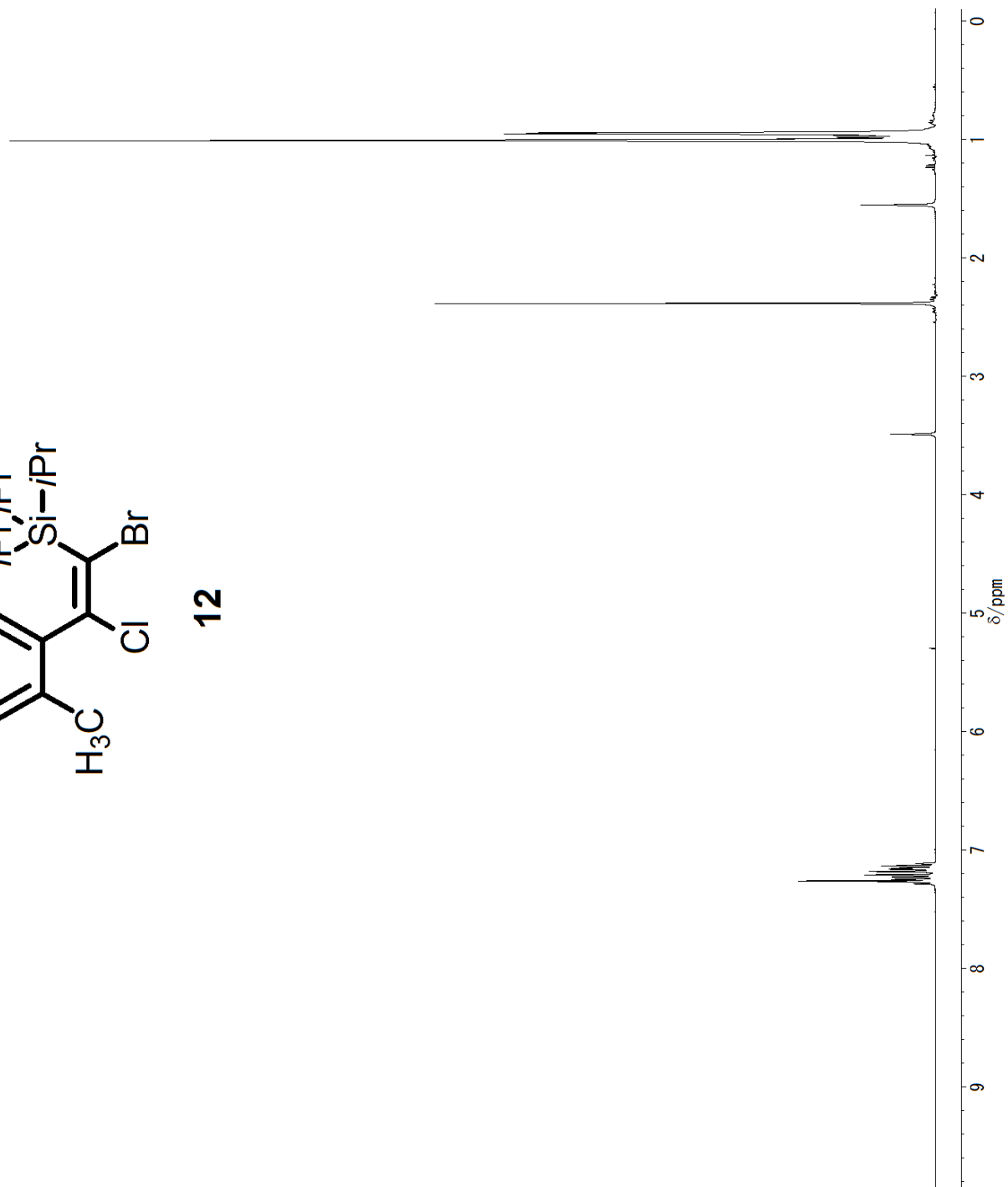


Compound 12

¹H NMR spectrum in CDCl₃

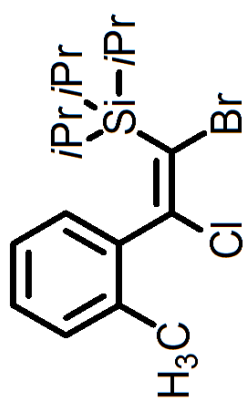


12

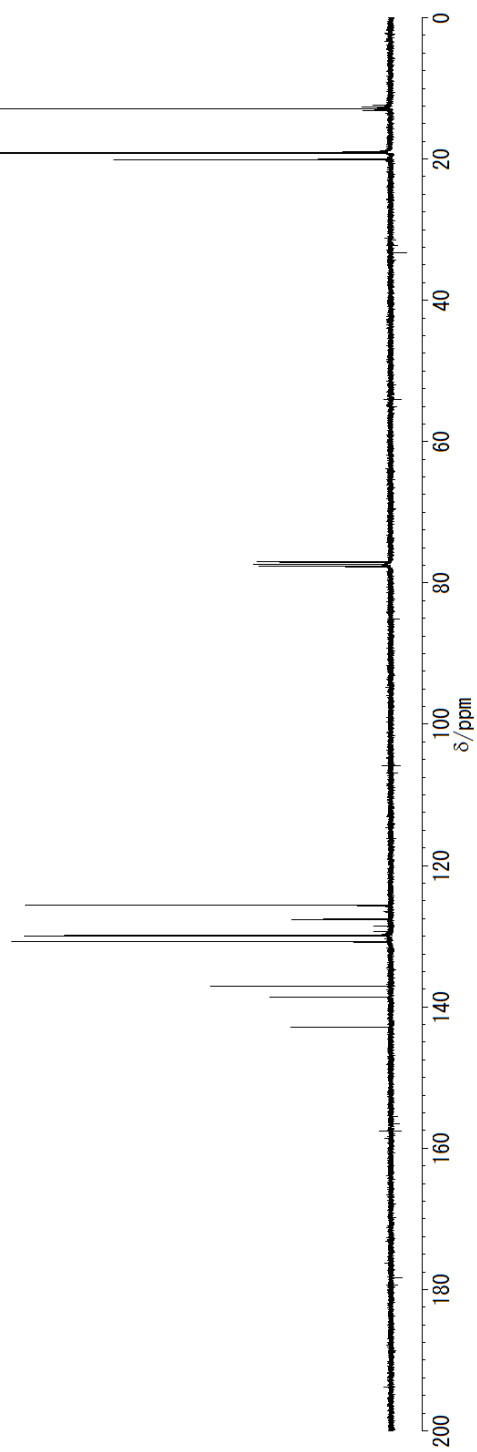


Compound 12

^{13}C NMR spectrum in CDCl_3

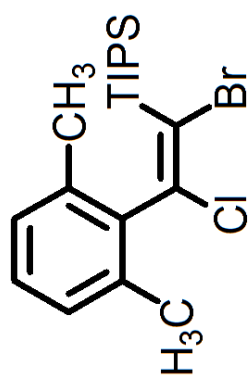


12

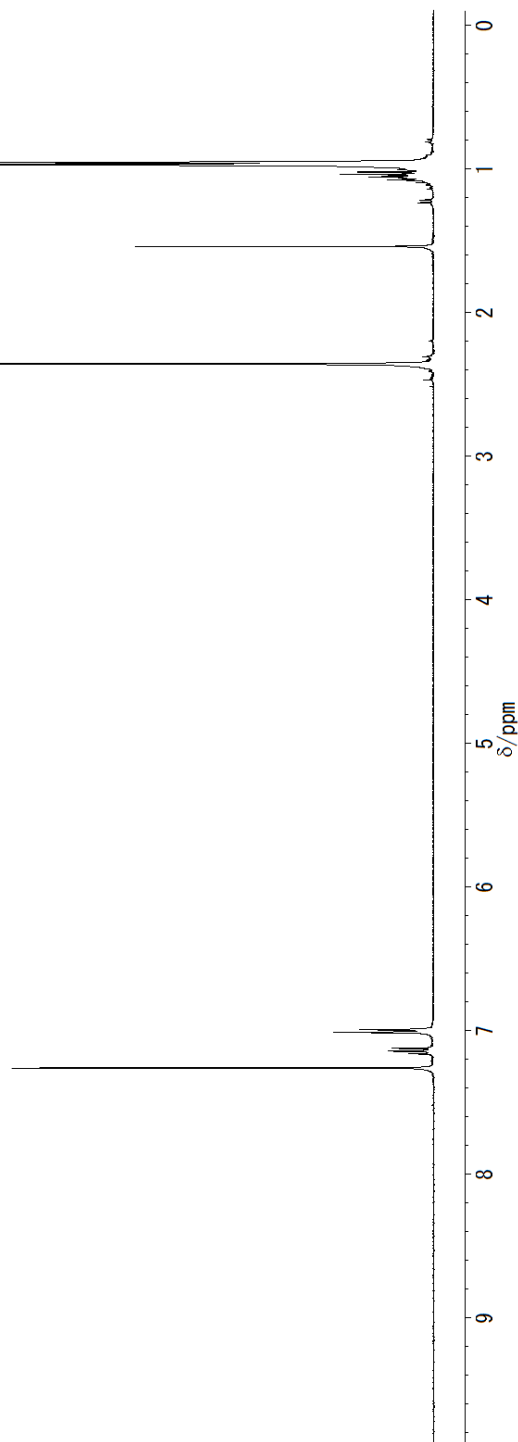


Compound 13

¹H NMR spectrum in CDCl₃

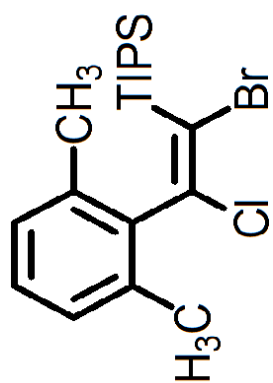


13

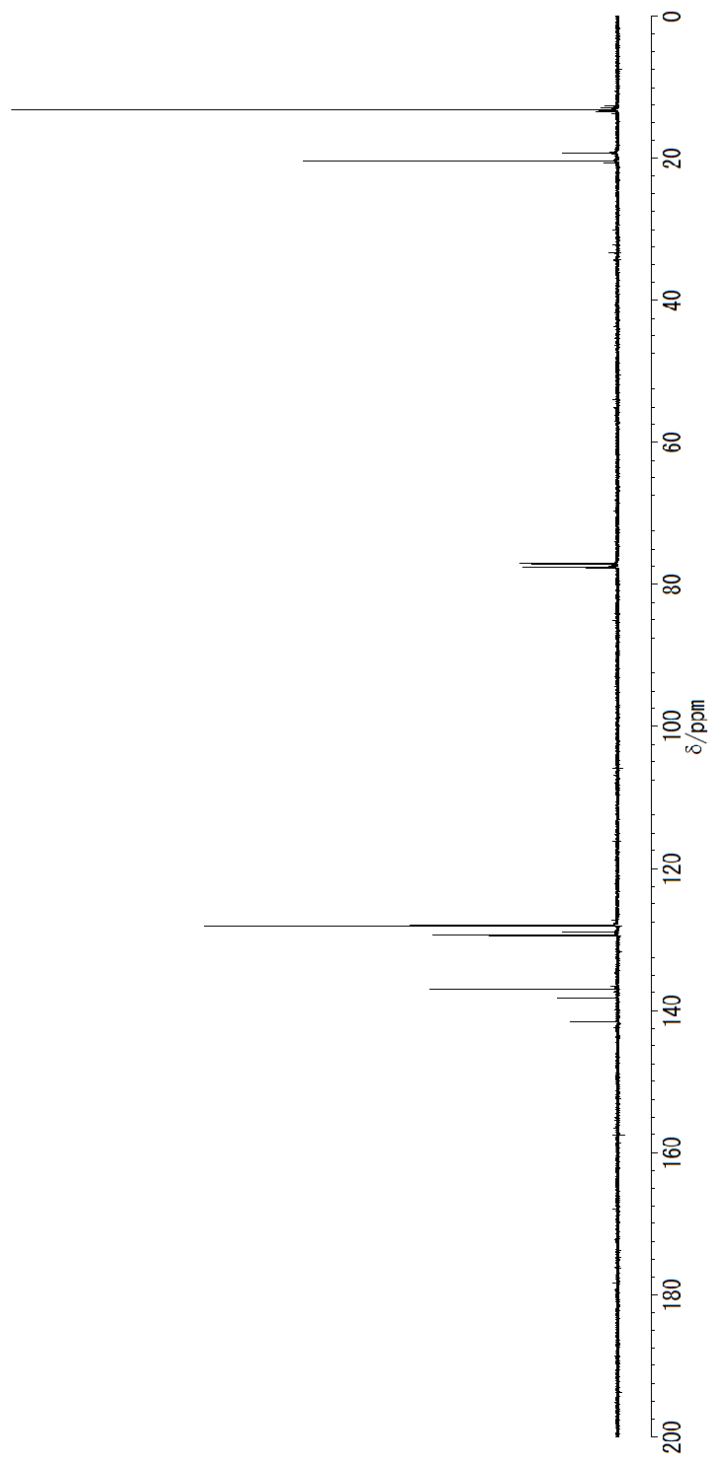


Compound 13

¹³C NMR spectrum in CDCl₃

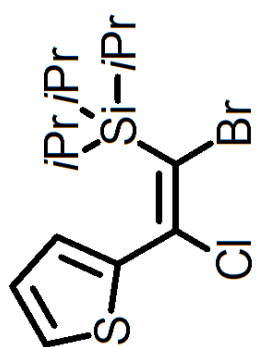


13

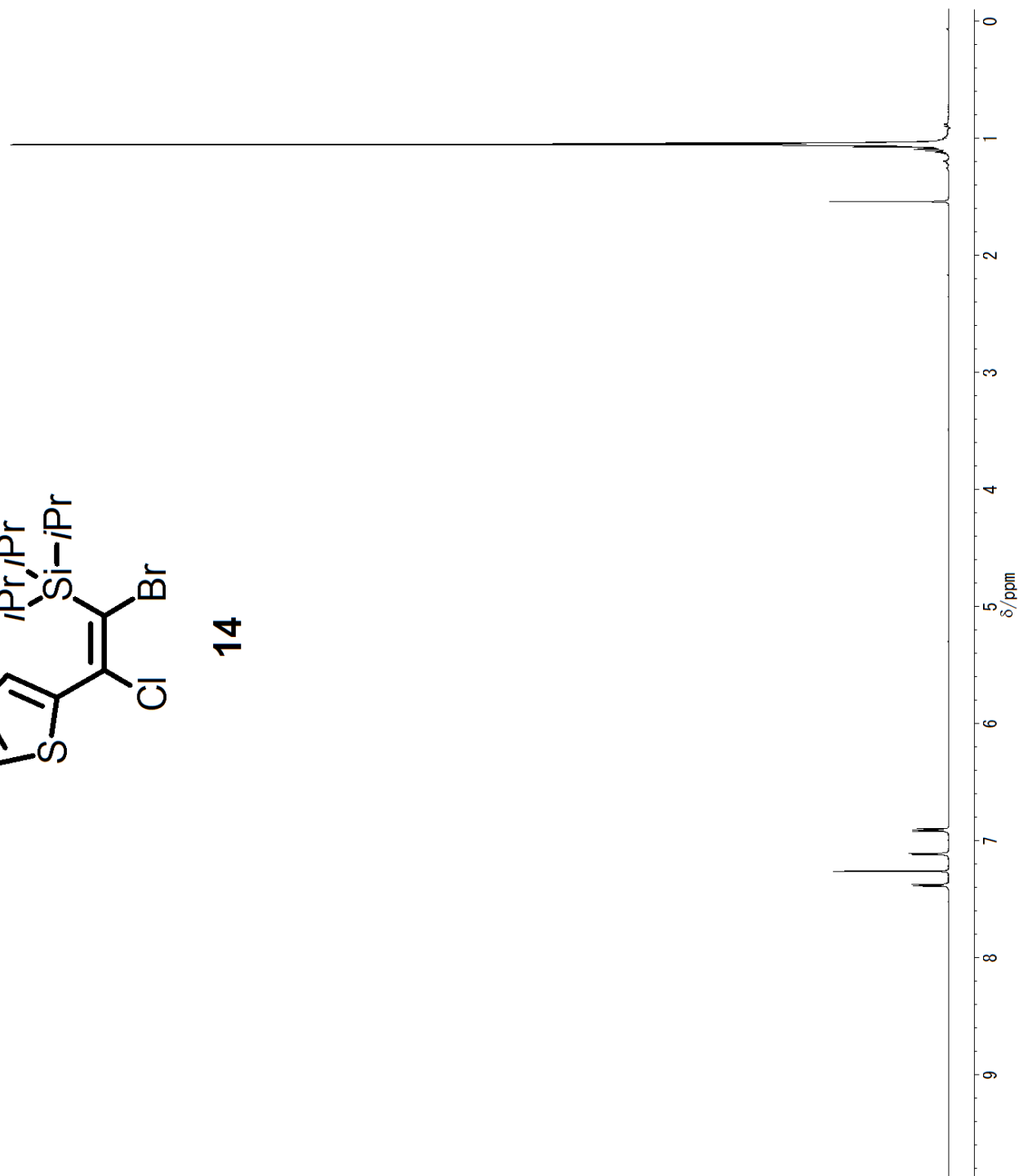


Compound 14

¹H NMR spectrum in CDCl₃

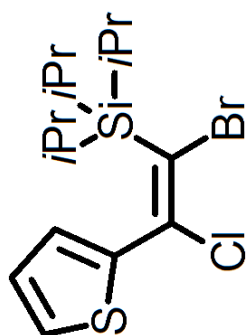


14



Compound 14

¹³C NMR spectrum in CDCl₃



14

