Supporting Information

Stereospecific Synthesis of Cyclobutylboronates through Copper(I)-Catalyzed Reaction of Homoallylic Sulfonates and a Diboron Derivative

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Experimental Section

General Considerations. Materials were obtained from commercial suppliers and purified by the standard procedure unless otherwise noted. Dry solvents were purchased from commercial suppliers and were degassed via three freeze-pump-thaw cycles and further dried on MS 4A. Phosphine ligands were purchased from commercial suppliers and used without further purification. Bis(pinacolato)diboron was purchased from AllyChem, Co., Ltd. (70,000 JPY/250 g) and purified by recrystallization from hot pentane. Copper(I) chloride (ReagentPlus grade) and THF solution of potassium *tert*-butoxide (1.0 M) were purchased from Aldrich Chemical Co. 1,4-Diisopropylbenzene for the internal standards in GC analysis were distilled from CaH_2 and stored on MS4A under an atmosphere of argon. Recycle gel-permeation chromatography was conducted using JAI LC-9101.

NMR spectra were recorded on Varian Gemini 2000 (^{1}H: 300 MHz and ^{13}C: 75.4 MHz), JEOL EX-270 (^{1}H: 270 MHz) or JEOL JNM-ECA600 (^{1}H: 600 MHz, ^{13}C: 150.9 MHz) spectrometer. The NMR yields were determined by using mesitylene as the internal standard. GLC analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector. IR spectra were recorded on a Perkin-Elmer Spectrum One. Low- and High-resolution mass spectra were recorded on a JEOL JMS-700TZ, JMS-T100L, JMS-T100GC, Thermo Fisher Scientific LTQ-Orbitrap XL, and Thermo Fisher Scientific Exactive mass spectrometer at the Center for Instrumental Analysis, Hokkaido University.

Preparation of Alkenyl Alcohols.

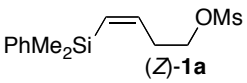
The (*Z*)-alkenyl alcohols having a silyl group for preparation of (*Z*)-**1a**, **1b**, **1c**, **1i**, and **1j** were synthesized by DIBAL reduction of the corresponding silylalkynyl alcohols according to the similar procedure reported by Hosomi et al.[1] The (*E*)-alkenyl alcohols for preparation of (*E*)-**1a**, **1b**, **1c**, **1i**, and **1j** were synthesized by Bu_3SnH-mediated isomerization reaction of the corresponding (*Z*)-alkenyl alcohols.[1] The (*Z*)-alkenyl alcohols for (*Z*)-**1d** and **1e** were prepared according to the reported by Denmark et al.[2] The (*Z*)-alkenyl alcohols for (*Z*)-**1f** was prepared by partial hydrogenation with $Pd/CaCO_3$ catalyst. The (*E*)-alkenyl alcohols for (*E*)-**1d**, **1e**, **1f**, and **1g** were prepared by using stereoselective reduction of the corresponding alkynyl alcohols with Red-Al.[3]

Preparation of Homoallylic Methanesulfonates (1a–1j).

In a 100 mL round bottomed flask, a homoallylic alcohol (12.1 mmol) and pyridine (2.73g, 34.6 mmol) was dissolved in dry CH_2Cl_2 (19 mL), then methanesulfonyl chloride (2.5 g, 21.8 mmol) was added dropwise to the reaction mixture at 0°C with stirring. After 3 h, the reaction mixture was quenched by water, extracted three times with CH_2Cl_2 and the combined organic layer was dried over $MgSO_4$ and filtered. After the solvents were evaporated under reduced pressure, the crude product was

subjected to flash chromatography (SiO_2, hexane/ethyl acetate, typically, 95:5–85:15) and further purified by bulb-to-bulb distillation under reduced pressure to give **1**.

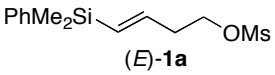
(*Z*)-4-(Dimethyl(phenyl)silyl)but-3-enyl methanesulfonate [(*Z*)-1a].



(*Z*)-**1a**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 95:5–85:15) and bulb-to-bulb distillation (bath temp. 200 °C, 3.0–4.3 Pa). (*Z*)-**1a** was obtained in a 51% yield from (*Z*)-4-(dimethyl(phenyl)silyl)but-3-en-1-ol. GLC analysis showed that the (*Z*)-**1a** contains less than 1% of (*E*)-**1a**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.40 (s, 6H, –SiCH_3), 2.46 (dt, *J* = 6.9, 1.1 Hz, 2H), 2.90 (s, 3H, –OSO_2CH_3), 4.11 (t, *J* = 6.8 Hz, 2H), 5.90 (d, *J* = 14.0 Hz, 1H, SiC*H*=CH), 6.37 (dt, *J* = 14.0, 6.9 Hz, 1H, –SiCH=C*H*–), 7.32–7.39 (m, 3H), 7.51–7.57 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –1.32 (2C, –Si*C*H_3), 32.8 (1C, *C*H_2), 37.1 (1C, –OSO_2*C*H_3), 68.6 (1C, –*C*H_2OSO_2Me), 127.9 (2C, *C*H), 129.1 (1C, *C*H), 131.9 (1C, *C*H), 133.7 (2C, *C*H), 138.9 (1C, *C*), 143.2 (1C, *C*H). IR (neat, cm^{-1}): 2958 (w), 2903 (w), 1610 (m), 1428 (w), 1353 (s), 1249 (m), 1172 (s), 778 (s). HRMS–ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{13}H_{20}NaO_3SSi$, 307.0800; found, 307.0799. Anal. Calcd for $C_{13}H_{20}O_3SSi$: C, 54.89; H, 7.09; S, 11.27. Found: C, 54.64; H, 6.95; S, 11.57.

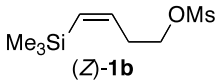
(*E*)-4-(Dimethyl(phenyl)silyl)but-3-enyl methanesulfonate [(*E*)-1a].



(*E*)-**1a**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 98:2–90:10) and bulb-to-bulb distillation (bath temp. 198 °C, 10–14 Pa). The product was obtained in 65% yield from (*E*)-4-(dimethyl(phenyl)silyl)but-3-en-1-ol. GLC analysis showed that the (*E*)-**1a** contains 5% of (*Z*)-**1a**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.34 (s, 6H, –SiCH_3), 2.60 (t, *J* = 6.6 Hz, 2H), 2.96 (s, 3H, –OSO_2CH_3), 4.29 (t, *J* = 6.7 Hz, 2H), 5.95 (d, *J* = 18.7 Hz, 1H, SiC*H*=CH), 6.05 (dt, *J* = 18.7, 5.5 Hz, 1H, SiCH=C*H*), 7.34–7.39 (m, 3H), 7.49–7.51 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –2.94 (2C, –Si*C*H_3), 35.9 (1C, *C*H_2), 37.3 (1C, –OSO_2*C*H_3), 68.6 (1C, –*C*H_2OSO_2Me), 127.8 (2C, *C*H), 129.1 (1C, *C*H), 132.8 (1C, *C*H), 133.8 (2C, *C*H), 138.4 (1C, *C*), 141.8 (1C, *C*H). IR (neat, cm^{-1}): 2957 (w), 2902 (w), 1618 (w), 1428 (m), 1353 (s), 1248 (m), 1171 (s), 820 (s). HRMS–ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{13}H_{20}NaO_3SSi$, 307.0800; found, 307.0795. Anal. Calcd for $C_{13}H_{20}O_3SSi$: C, 54.89; H, 7.09; S, 11.27. Found: C, 54.61; H, 7.06; S, 11.28.

(*Z*)-4-(Trimethylsilyl)but-3-enyl methanesulfonate [(*Z*)-1b].

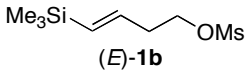


(*Z*)-**1b**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 97:3–91:9) and bulb-to-bulb distillation (bath temp. 135 °C, 9–14 Pa). The product was obtained in 99% yield from (*Z*)-4-(trimethylsilyl)but-3-en-1-ol. GLC analysis showed that the (*Z*)-**1b** contains less than 1% of (*E*)-**1b**.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.14 (s, 9H, –SiC*H*$_3$), 2.59 (dt, *J* = 6.9, 0.8 Hz, 2H), 3.01 (s, 3H, –OSO_2C*H*$_3$), 4.25 (t, *J* = 6.9 Hz, 2H), 5.73 (brd, *J* = 14.3 Hz, 1H, SiC*H*=CH), 6.24 (dt, *J* = 14.1, 7.1 Hz, 1H, SiCH=C*H*). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –0.1 (1C, –Si*C*H$_3$), 32.8 (1C, *C*H$_2$), 37.3 (1C, –OSO_2*C*H$_3$), 68.9 (1C, –*C*H$_2$OSO$_2$Me), 134.1 (1C, *C*H), 141.3 (1C, *C*H). IR (neat, cm^{-1}): 2957 (w), 1610 (w), 1415 (w), 1353 (s), 1249 (m), 1171 (s), 834 (s). HRMS–ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_8H_{18}NaO_3SSi$, 245.0644; found, 245.0642. Anal. Calcd for $C_8H_{18}O_3SSi$: C, 43.21; H, 8.16; S, 14.42 Found: C, 43.27; H, 7.97; S, 14.70.

(*E*)-4-(Trimethylsilyl)but-3-enyl methanesulfonate [(*E*)-1b].

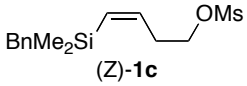


(*E*)-**1b**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 97:3–85:15) and bulb-to-bulb distillation (bath temp. 135 °C, 5–8 Pa). The product was obtained in 99% yield from (*E*)-4-(trimethylsilyl)but-3-en-1-ol. GLC analysis showed that the (*E*)-**1b** contains 4% of (*Z*)-**1b**.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.60 (s, 9H, –SiC*H*$_3$), 2.57 (dq, *J* = 6.9, 1.1 Hz, 2H), 3.01 (s, 3H, –OSO_2C*H*$_3$), 4.28 (t, *J* = 6.9 Hz, 2H), 5.83 (d, *J* = 18.4 Hz, 1H, SiC*H*=CH), 5.98 (dt, *J* = 18.4, 6.9 Hz, 1H, SiCH=C*H*). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –1.6 (3C, –Si*C*H$_3$), 35.9 (1C, *C*H$_2$), 37.3 (1C, –OSO_2*C*H$_3$), 68.8 (1C, –*C*H$_2$OSO$_2$Me), 134.9 (1C, *C*H), 139.8 (1C, *C*H). IR (neat, cm^{-1}): 2956 (m), 1619 (m), 1419 (w), 1353 (s), 1248 (m), 1171 (m), 834 (s). HRMS–ESI (*m*/*z*): [M+Na]$^+$ calcd for $C_8H_{18}NaO_3SSi$, 245.0635; found, 245.0644. Anal. Calcd for $C_8H_{18}O_3SSi$: C, 43.21; H, 8.16; S, 14.42. Found: C, 43.27; H, 8.04; S, 14.40.

(*Z*)-4-(Benzyl(dimethyl)silyl)but-3-enyl methanesulfonate [(*Z*)-1c].

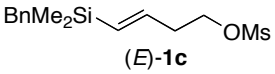


(Z)-**1c**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 97:3–50:50) and bulb-to-bulb distillation (bath temp. 200 °C, 4 Pa). The product was obtained in 79% yield from (*Z*)-4-(benzyldimethylsilyl)but-3-en-1-ol. GLC analysis showed that the (*Z*)-**1c** contains 3% of (*E*)-**1c**.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.13 (s, 6H, –SiCH_3), 2.17 (s, 2H, SiCH_2Ph), 2.42 (dt, J = 6.6, 1.4 Hz, 2H, CH_2CH=CH), 2.98 (s, 3H, –OSO_2CH_3), 4.15 (t, J = 6.6 Hz, 2H, CH_2OMs), 5.69 (dt, J = 14.0, 1.4 Hz, 1H, SiC*H*=CH), 6.27 (dt, J = 14.3, 7.4 Hz, 1H, SiCH=C*H*), 6.95–7.13 (m, 3H, Ar*H*), 7.17–7.25 (m, 2H, Ar*H*). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –2.0 (2C, –Si*C*H_3), 26.2 (1C, *C*H_2), 32.9 (1C, –OSO_2*C*H_3), 37.2 (1C, *C*H_2), 68.7 (1C, –*C*H_2OSO_2Me), 124.2 (1C, *C*H), 128.2 (2C, *C*H), 128.3 (2C, *C*H), 131.8 (1C, *C*H), 139.7 (1C, *C*), 142.6 (1C, *C*H). IR (neat, cm^{-1}): 3025 (w), 2958 (w), 2897 (w), 1600 (m), 1493 (m), 1353 (s), 1249 (m), 1172 (s), 828 (s). HRMS–ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{14}H_{22}NaO_3SSi$, 321.0957; found, 321.0957.

(*E*)-4-(Benzyl(dimethyl)silyl)but-3-enyl methanesulfonate [(*E*)-1c].

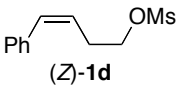


(*E*)-**1c**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 97:3–75:25) and bulb-to-bulb distillation (bath temp. 200 °C, 4 Pa). The product was obtained in 63% yield from (*E*)-4-(benzyldimethylsilyl)but-3-en-1-ol. GLC analysis showed that the (*E*)-**1c** contains 4% of (*Z*)-**1c**.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.04 (s, 6H, –SiCH_3), 2.12 (s, 2H, SiCH_2Ph), 2.54 (q, J = 6.9 Hz, 2H, CH_2CH=CH), 2.96 (s, 3H, –OSO_2CH_3), 4.24 (t, J = 6.9 Hz, 2H, CH_2OMs), 5.78 (d, J = 18.7 Hz, 1H, SiC*H*=CH), 5.93 (dt, J = 18.7, 5.8 Hz, 1H, SiCH=C*H*), 6.95–7.11 (m, 3H), 7.16–7.27 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –3.7 (2C, –Si*C*H_3), 25.8 (1C, *C*H_2), 36.0 (1C, *C*H_2), 37.3 (1C, –OSO_2CH_3), 68.6 (1C, –*C*H_2OSO_2Me), 124.1 (1C, *C*H), 128.2 (2C, *C*H), 128.3 (2C, *C*H), 132.8 (1C, *C*H), 139.8 (1C, *C*), 141.2 (1C, *C*H). IR (neat, cm^{-1}): 3025 (w), 2956 (w), 2897 (w), 1618 (w), 1493 (m), 1354 (s), 1248 (m), 1172 (s), 830 (s). HRMS–ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{14}H_{22}NaO_3SSi$, 321.0957; found, 321.0947. Anal. Calcd for $C_{14}H_{22}O_3SSi$: C, 56.34; H, 7.43; S, 10.74. Found: C, 56.11; H, 7.43; S, 10.90.

(*Z*)-4-Phenylbut-3-enyl methanesulfonate [(*Z*)-1d].

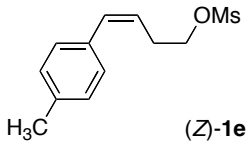


(*Z*)-**1d**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 95:5–0:100) and bulb-to-bulb distillation (bath temp. 205 °C, 4–5 Pa). The product was obtained in 62% yield from (*Z*)-4-phenylbut-3-en-1-ol. NMR analysis shows that the (*Z*)-**1d** contains 4% of (*E*)-**1d**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.79 (dt, J = 6.6, 1.9 Hz, 2H, CH_2CH=CH), 2.99 (s, 3H, –OSO_2CH_3), 4.30 (t, J = 6.6 Hz, 2H, CH_2OMs), 5.66 (dt, J = 11.8, 7.1 Hz, 1H, PhCH=C*H*), 6.62 (d, J = 11.8 Hz, 1H, PhC*H*=CH), 7.24–7.28 (m, 3H), 7.34–7.39 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 28.0 (1C, *C*H_2), 36.8 (1C, –OSO_2*C*H_3), 69.0 (1C, *C*H_2OSO_2Me), 125.6 (1C, *C*H), 126.9 (1C, *C*H), 128.1 (2C, *C*H), 128.4 (2C, *C*H), 132.0 (1C,

*C*H), 136.5 (1C, *C*). IR (neat, cm^{-1}): 3025 (w), 2940 (w), 1600 (w), 1493 (w), 1350 (s), 1213 (w), 1169 (s), 913 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{14}O_3S$, 226.0664; found, 226.0665. Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24; S, 14.17. Found: C, 58.32; H, 6.10; S, 14.45.

(*Z*)-4-(4-Methylphenyl)but-3-enyl methanesulfonate [(*Z*)-1e].

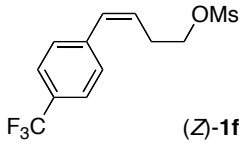


(*Z*)-**1e**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 97:3–80:20) and bulb-to-bulb distillation (bath temp. 200 °C, 10–12 Pa). The product was obtained in 74% yield from (*Z*)-4-(4-methylphenyl)but-3-en-1-ol. GLC analysis shows that the (*Z*)-**1e** contains 13% of (*E*)-**1e**.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.35 (s, 3H, *p*-C*H*$_3$C$_6$H$_4$), 2.78 (dt, *J* = 6.9, 1.7 Hz, 2H, C*H*$_2$CH=CH), 2.99 (s, 3H, –OSO$_2$C*H*$_3$), 4.30 (t, *J* = 6.6 Hz, 2H, C*H*$_2$OMs), 5.60 (dt, *J* = 11.5, 7.1 Hz, 1H, *p*-CH$_3$C$_6$H$_4$CH=C*H*), 6.58 (d, *J* = 11.5 Hz, 1H, *p*-CH$_3$-C$_6$H$_4$C*H*=CH), 7.16 (s, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 20.9 (1C, *p*-*C*H$_3$C$_6$H$_4$), 28.3 (1C, *C*H$_2$), 37.2 (1C, –OSO$_2$*C*H$_3$), 69.1 (1C, *C*H$_2$OSO$_2$Me), 124.9 (1C, *C*H), 128.5 (2C, *C*H), 129.0 (2C, *C*H), 132.2 (1C, *C*H), 133.8 (1C, *C*), 136.9 (1C, *C*). IR (neat, cm^{-1}): 3020 (w), 2940 (w), 1610 (w), 1512 (w), 1350 (s), 1169 (s), 914 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{12}H_{16}O_3S$, 240.0820; found, 240.0821. Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71; S, 13.34. Found: C, 59.80; H, 6.69; S, 13.50.

(*Z*)-4-(4-Trifluoromethylphenyl)but-3-enyl methanesulfonate [(*Z*)-1f].

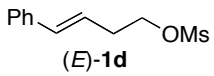


(*Z*)-**1f**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 96:4–75:25) and subsequent bulb-to-bulb distillation (bath temp. 195 °C, 13–17 Pa). The product was obtained in 61% yield from (*Z*)-4-(4-trifluoromethylphenyl)but-3-en-1-ol. GLC analysis shows that the (*Z*)-**1f** contains 12% of (*E*)-**1f**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.77 (dt, *J* = 6.6, 1.7 Hz, 2H, C*H*$_2$CH=CH), 3.01 (s, 3H, –OSO$_2$C*H*$_3$), 4.31 (t, *J* = 6.6 Hz, 2H, C*H*$_2$OMs), 5.78 (dt, *J* = 11.6, 6.6, 1H, *p*-CF$_3$C$_6$H$_4$CH=C*H*), 6.65 (d, *J* = 11.6 Hz, 1H, *p*-CF$_3$-C$_6$H$_4$C*H*=CH), 7.36 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 28.4 (1C, *C*H$_2$), 37.4 (1C, –OSO$_2$*C*H$_3$), 68.6 (1C, *C*H$_2$OSO$_2$Me), 125.4 (q, *J* = 4.0 Hz, 2C, *C*H), 127.7 (q, *J* = 258.8 Hz, 1C, *C*F$_3$), 127.9 (1C, *C*H), 128.9 (2C, CH), 131.3 (1C, *C*H), 140.3 (1C, *C*). IR (neat, cm^{-1}): 3027 (w), 2945 (w), 1617 (w), 1321 (s), 1167 (s), 1110 (s). HRMS–EI

(*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{13}F_3NaO_3S$, 317.04297 found, 317.04297. Anal. Calcd for $C_{12}H_{13}O_3F_3S$: C, 48.97; H, 4.45; S, 10.90. Found: C, 48.79; H, 4.47; S, 11.10.

(*E*)-4-Phenylbut-3-enyl methanesulfonate [(*E*)-1d].

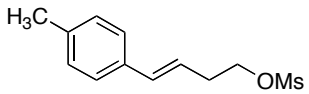


(*E*)-**1d**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 95:5–50:50) and bulb-to-bulb distillation (bath temp. 185 °C, 4 Pa). The product was obtained in 61% yield from (*E*)-4-phenylbut-3-en-1-ol. GLC analysis shows that the (*E*)-**1d** contains less than 3% of (*Z*)-**1d**.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.67 (dt, *J* = 6.9, 1.4 Hz, 2H, CH_2CH=CH), 3.02 (s, 3H, –OSO_2CH_3), 4.34 (t, *J* = 6.6 Hz, 2H, CH_2OMs), 6.16 (dt, *J* = 15.9, 7.1 Hz, 1H, PhC*H*=CH-), 6.53 (d, *J* = 15.9 Hz, 1H, PhC*H*=CH-), 7.20–7.35 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 32.2 (1C, *C*H_2), 36.8 (1C, –OSO_2CH_3), 68.8 (1C, *C*H_2OSO_2Me), 123.6 (1C, *C*H), 125.8 (2C, *C*H), 127.2 (1C, *C*H), 128.2 (2C, *C*H), 133.1 (1C, *C*H), 136.5 (1C, *C*). IR (neat, cm^{-1}): 3027 (w), 2940 (w), 1598 (w), 1494 (w), 1348 (s), 1169 (s), 956 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{11}H_{14}O_3S$, 226.0664; found, 226.0664.

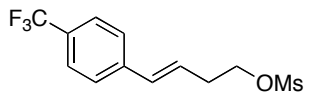
(*E*)-4-(4-Methylphenyl)but-3-enyl methanesulfonate [(*E*)-1e].



(*E*)-**1e**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 98:2–84:16) and and dried under vacuum for 16 h before use. The product was obtained in 97% yield from (*E*)-4-(4-methylphenyl)but-3-en-1-ol. GLC analysis shows that the (*E*)-**1e** contains <1% of (*Z*)-**1e**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.33 (s, 3H, *p*-CH_3-C_6H_4), 2.66 (dt, *J* = 6.9, 1.1 Hz, 2H, CH_2CH=CH), 3.01 (s, 3H, –OSO_2CH_3), 4.33 (t, *J* = 6.6 Hz, 2H, CH_2OMs), 6.10 (dt, *J* = 15.9, 6.9 Hz, 1H, *p*-$CH_3C_6H_4$CH=C*H*), 6.49 (d, *J* = 15.7 Hz, 1H, *p*-$CH_3C_6H_4$C*H*=CH), 7.12 (d, *J* = 8.0 Hz, 2H) 7.25 (d, *J* = 7.1 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 20.9 (1C, *p*-*C*$H_3C_6H_4$), 32.5 (1C, *C*$H_2CH_2OSO_2Me$), 37.1 (1C, –OSO_2CH_3), 69.1 (1C, *C*H_2OSO_2Me), 122.6 (1C, *C*H), 126.0 (2C, *C*H), 129.2 (2C, *C*H), 133.3 (1C, *C*H), 134.0 (1C, *C*), 137.3 (1C, *C*). IR (neat, cm^{-1}): 3022 (w), 2941 (w), 1512 (w), 1330 (s), 1167 (s), 925 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{12}H_{16}O_3S$, 240.0820; found, 240.0818. Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 59.90; H, 6.59.

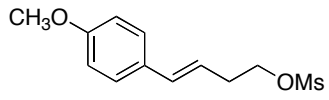
(*E*)-4-(4-Trifluoromethylphenyl)but-3-enyl methanesulfonate [(*E*)-1f].



(*E*)-**1f**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 95:5–85:15) subsequent recycle gel-permeation chromatography (JAI LC-9101, $CHCl_3$) and dried under vacuum for 16 h before use. The product was obtained in 8% yield from (*E*)-4-(4-trifluoromethylphenyl)but-3-en-1-ol. GLC analysis shows that the (*E*)-**1f** contains <1% of (*Z*)-**1f**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.71 (q, J = 6.6 Hz, 2H, CH_2CH=CH), 3.03 (s, 3H, –OSO$_2$CH_3), 4.36 (t, J = 6.6 Hz, 2H, CH_2OMs), 6.28 (dt, J = 15.9, 6.9 Hz, 1H, *p*-$CF_3C_6H_4$CH=C*H*), 6.56 (d, J = 15.7 Hz, 1H, *p*-$CF_3C_6H_4$C*H*=CH), 7.45 (d, J = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 32.7 (1C, *C*H$_2$), 37.4 (1C, –OSO$_2$*C*H$_3$), 68.6 (1C, *C*H$_2$OSO$_2$Me), 125.4 (q, J = 4.0 Hz, 2C, *C*H), 126.0 (q, J = 272.5 Hz, 1C, *C*H), 126.4 (2C, *C*H), 126.8 (1C, *C*H), 132.3 (1C, *C*H), 140.4 (1C, *C*). IR (neat, cm^{-1}): 3030 (w), 2947 (w), 1611 (w), 1323 (s), 1154 (s). HRMS–EI (*m*/*z*): [M+Na]$^+$ calcd for $C_{12}H_{13}F_3NaO_3S$, 317.0430; found, 317.0432. Anal. Calcd for $C_{12}H_{13}F_3O_3S$: C, 48.97; H, 4.45; S, 10.90. Found: C, 49.20; H, 4.40; S, 10.90.

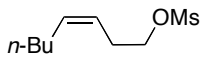
(*E*)-4-(4-Methoxyphenyl)but-3-enyl methanesulfonate [(*E*)-1g].



(*E*)-**1g**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 97:3–80:20), subsequent recycle gel-permeation chromatography (JAI LC-9101, $CHCl_3$) and dried under vacuum for 16 h before use. The product was obtained in 39% yield from (*E*)-4-(4-methoxyphenyl)but-3-en-1-ol. GLC analysis shows that the (*E*)-**1g** contains 3% of (*Z*)-**1g**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 2.64 (dt, J = 6.8, 1.1 Hz, 2H, CH_2CH=CH), 3.01 (s, 3H, –OSO$_2$CH_3), 3.81 (s, 3H, *p*-CH_3OC$_6$H$_4$), 4.32 (t, J = 6.6 Hz, 2H, CH_2OMs), 6.01 (dt, J = 15.9, 7.1 Hz, 1H, *p*-$CH_3OC_6H_4$CH=C*H*), 6.46 (d, J = 16.0 Hz, 1H, *p*-$CH_3OC_6H_4$C*H*=CH), 6.83–6.88 (m, 2H) 7.26–7.31 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 32.6 (1C, *C*H$_2$), 37.3 (1C, –OSO$_2$*C*H$_3$), 55.1 (1C, *p*-*C*H$_3$OC$_6$H$_4$) 69.3 (1C, *C*H$_2$OSO$_2$Me), 114.0 (2C, *C*H), 121.5 (1C, *C*H), 127.3 (2C, *C*H), 129.6 (1C, *C*), 132.9 (1C, *C*H), 159.2 (1C, *C*). IR (neat, cm^{-1}): 3028 (w), 2939 (w), 1510 (w), 1348 (s), 1166 (s), 919 (s). HRMS–EI (*m*/*z*): [M]$^+$ calcd for $C_{12}H_{16}O_4S$, 256.0769; found, 256.0767. Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29; S, 12.51. Found: C, 56.12; H, 6.29; S, 12.23.

(*Z*)-Oct-3-enyl methanesulfonate [(*Z*)-1h].

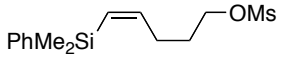


(*Z*)-**1h**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 95:5–50:50) and bulb-to-bulb distillation (bath temp. 155 °C, 4 Pa). The product was obtained in 92% yield from (*Z*)-3-hepten-1-ol. GLC analysis shows that the (*Z*)-**1h** contains less than 1% of (*E*)-**1h**.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.87–0.97 (m, 3H, CH_2CH_3), 1.29–1.40 (m, 4H, $CH_2CH_2CH_3$), 2.05 (dd, *J* = 5.8, 6.9 Hz, 2H, CH_2CH=CH), 2.51 (dd, *J* = 6.6, 0.3 Hz, 2H, CH=CHCH_2CH_2O), 3.01 (s, 3H, –OSO_2CH_3), 4.21 (t, *J* = 6.9 Hz, 2H, CH_2OMs), 5.28–5.39 (m, 1H, *n*-BuCH=C*H*), 5.53–5.62 (m, 1H, *n*-BuC*H*=CH). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 13.6 (1C, CH_3), 22.0 (1C, CH_2), 26.7 (1C, CH_2), 27.0 (1C, CH_2), 31.3 (1C, CH_2), 37.1 (1C, –OSO_2CH_3), 69.2 (1C, CH_2OSO_2Me), 122.6 (1C, *n*-BuCH=*C*H), 134.0 (1C, *n*-Bu*C*H=CH). IR (neat, cm^{-1}): 2958 (m), 2930 (m), 2861 (m), 1655 (w), 1467 (m), 1351 (s), 1171 (s), 952 (s). HRMS–EI (*m*/*z*): [M]$^+$ calcd for $C_9H_{18}O_3S$, 206.0977; found, 206.0981.

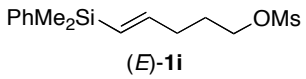
(*Z*)-4-(Dimethyl(phenyl)silyl)pent-3-enyl methanesulfonate [(*Z*)-1i].



(*Z*)-**1i**

This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 98:2–0:100) and bulb-to-bulb distillation (bath temp. 190 °C, 4.2 Pa). The product was obtained in 52% yield. GLC analysis shows that the (*Z*)-**1i** contains 1% of (*E*)-**1i**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.38 (s, 6H), 1.67–1.77 (m, 2H, CH_2), 2.08–2.19 (m, 2H, CH_2), 2.89 (s, 3H, OSO_2CH_3), 4.03 (t, *J* = 6.7 Hz, 2H, CH=CHCH_2CH_2O), 5.74 (dt, *J* = 14.0 Hz, 1H, SiC*H*=CH), 6.37 (dt, *J* = 14.0 Hz, 1H, SiCH=C*H*), 7.31–7.39 (m, 3H), 7.51–7.58 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –1.3 (2C, SiCH_3), 28.6 (1C, CH_2), 29.2 (1C, CH_2), 37.1 (1C, CH_2), 69.2 (1C, CH_2O), 127.9 (2C, *C*H), 128.8 (1C, *C*H), 129.0 (1C, *C*H), 133.7 (2C, *C*H), 139.3 (1C, *C*), 148.1 (1C, *C*H). IR (neat, cm^{-1}): 3022 (m), 2956 (m), 1617 (m), 1352 (s), 1172 (w), 923 (s). HRMS–EI (*m*/*z*): [M]$^+$ calcd for $C_{13}H_{19}O_3SSi$, 283.0824; found, 283.0824. Anal. Calcd for $C_{14}H_{22}O_3SSi$: C, 56.34; H, 7.43; S, 10.74. Found: C, 56.14; H, 7.45; S, 10.99.

(*E*)-4-(Dimethyl(phenyl)silyl)pent-3-enyl methanesulfonate [(*E*)-1i].



(*E*)-**1i**

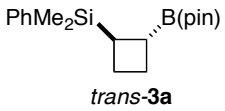
This compound was purified by flash chromatography (SiO_2, hexane/ethyl acetate 94:6–85:15) and bulb-to-bulb distillation (bath temp. 200 °C, 6 Pa). GLC analysis shows that the (*E*)-**1i** contains 5% of (*Z*)-**1i**. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.33 (s, 6H), 1.82–1.93 (m, 2H, CH_2), 2.22–2.32 (m, 2H, CH_2), 2.95 (s, 3H, OSO_2CH_3), 4.22 (t, *J* = 6.5 Hz, 2H, CH=CHCH_2CH_2O), 5.83 (dt, *J* = 18.7, 1.1 Hz, 1H,

SiC*H*=CH), 6.07 (dt, *J* = 18.4, 1.1 Hz, 1H, SiCH=C*H*), 7.32–7.38 (m, 3H), 7.47–7.54 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –2.7 (2C, Si*C*H_3), 27.8 (1C, *C*H_2), 32.2 (1C, *C*H_2), 37.2 (1C, *C*H_2), 69.3 (1C, *C*H_2O), 127.9 (2C, *C*H), 129.1 (1C, *C*H), 129.7 (1C, *C*H), 133.9 (2C, *C*H), 138.9 (1C, *C*), 146.5 (1C, *C*H). IR (neat, cm^{-1}): 3022 (m), 2956 (m), 1617 (m), 1352 (s), 1172 (w), 923 (s). HRMS–EI (*m*/*z*): $[M]^+$ calcd for $C_{13}H_{19}O_3SSi$, 283.0824; found, 283.0823. Anal. Calcd for $C_{14}H_{22}O_3SSi$: C, 56.34; H, 7.43; S, 10.74. Found: C, 56.14; H, 7.40; S, 10.45.

General Procedure for Copper(I)-catalyzed Reaction.

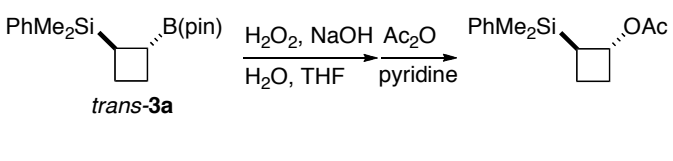
In a reaction vial, CuCl (2.5 mg, 0.025 mmol), dppp (10.3 mg, 0.025 mmol) and bis(pinacolato)diboron (253.9 mg, 1.00 mmol) were placed. After being sealed with a screw cap, the vial was connected to a argon line through a needle. The vial was evacuated and backfilled with argon and THF solution of potassium *tert*-butoxide (1.0 M, 0.5 mL, 0.5 mmol) was then added with stirring. After 30 min, a homoallylic methanesulfonate **1** (0.5 mmol) was added with vigorous stirring at room temperature. The poor stirring or use of a large excess of potassium *tert*-butoxide (>1.5 equiv) caused low trans/cis selectivities of the products. The reaction mixture became viscous after several hours. The completion of the reaction was checked by GC or TLC, the mixture was directly subjected to short column path of silica gel by using hexane/ethyl acetate (80:20) as the eluent. The trans/cis ratio was determined by GLC analylsis of the crude product. After removal of the solvents under reduced pressure, the crude product was purified with flash chromatography (SiO_2, hexane/ethyl acetate, 100:0–96:4) to give the corresponding cyclobutylboronates.

***trans*-1-Dimethyl(phenyl)silyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*trans*-3a).**

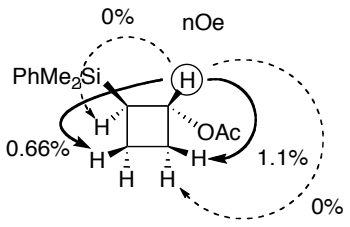


trans-**3a**

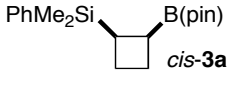
^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.24 (s, 3H, –SiCH_3), 0.25 (s, 3H, –SiCH_3), 1.20 (s, 12H, CH_3), 1.86–2.22 (m, 6H), 7.31–7.34 (m, 3H), 7.49–7.52 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –5.4 (1C, Si*C*H_3), –5.2 (1C, Si*C*H_3), 19.2 (br, 1C, *C*HB), 23.4 (1C, *C*H_2), 23.7 (1C, *C*HSi), 24.0 (1C, *C*H_2), 24.5 (2C, –OC(*C*H_3)$_2$), 24.6 (2C, –OC(*C*H_3)$_2$), 82.8 (2C, –O*C*(CH$_3$)$_2$), 127.6 (2C, *C*H), 128.7 (1C, *C*H), 133.9 (2C, *C*H), 138.9 (1C, *C*). IR (neat, cm^{-1}): 3069 (m), 2957 (m), 2862 (m), 1377 (s), 1314 (s), 1247 (s), 1143 (s), 698 (s). HRMS–EI (*m*/*z*): [M]$^+$ calcd for $C_{18}H_{29}BO_2Si$, 316.2030; found, 316.2027. The stereochemistry of this compound was determined by nOe experiment with the acetate derivative after H_2O_2/NaOH aq. oxidation as shown in the following figure.



trans-**3a**



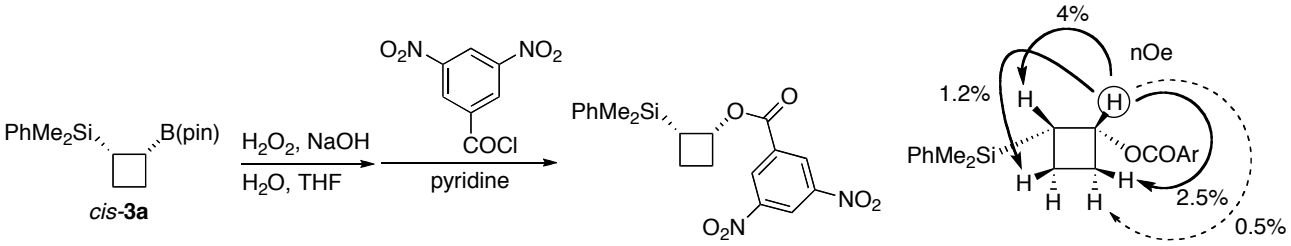
***cis*-1-Dimethyl(phenyl)silyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*cis*-3a).**



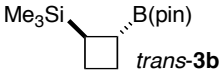
cis-**3a**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.33 (s, 3H, –SiCH_3), 0.36 (s, 3H, –SiCH_3), 1.15 (d, 6H, CCH_3), 1.17 (d, 6H, CCH_3), 1.91–2.06 (m, 2H), 2.09–2.17 (m, 1H), 2.19–2.32 (m, 3H), 7.26–7.32 (m, 3H), 7.47–7.50 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –3.7 (1C, Si*C*H_3), –3.5 (1C, Si*C*H_3), 23.6 (1C, Si*C*H), 24.1 (1C, *C*H_2), 24.2 (1C, *C*H_2), 24.77 (2C, –OC(*C*H_3)$_2$), 24.82 (2C, –OC(*C*H_3)$_2$), 82.9 (2C, –O*C*(CH$_3$)$_2$), 127.6 (2C, *C*H), 128.6 (1C, *C*H), 133.9 (2C, *C*H), 140.2 (1C, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5] IR (neat, cm^{-1}): 3069 (m), 2977 (m), 2865 (m), 1372 (s), 1315 (s), 1246 (s), 1142 (s), 698 (s). HRMS–EI (*m*/*z*): [M–CH_3]$^+$ calcd for $C_{17}H_{26}BO_2Si$, 301.1795; found, 301.1790.

The stereochemistry of this compound was determined by nOe experiment with the 3,5-dinitorobenzoate derivative after H_2O_2/NaOH aq. oxidation as shown in the following figure.

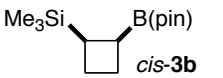


***trans*-1-Trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*trans*-3b).**



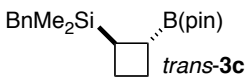
^{1}H NMR (300 MHz, $CDCl_3$, δ): –0.05 (s, 9H, –SiCH_3), 1.24 (s, 12H, CH_3), 1.73–1.83 (m, 2H), 1.92–2.03 (m, 3H), 2.12–2.22 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$, –3.9 (3C, Si*C*H_3), 19.0 (br, 1C, *C*HB), 23.1 (1C, *C*H_2), 23.8 (1C, *C*H_2), 24.55 (2C, –OC(*C*H_3)$_2$) 24.57 (2C, –OC(*C*H_3)$_2$), 24.7 (1C, Si*C*H), 82.8 (2C, –O*C*(CH$_3$)$_2$). IR (neat, cm^{-1}): 2978 (m), 2862 (m), 1372 (s), 1314 (s), 1247 (s), 1144 (s), 833 (s). HRMS–EI (*m*/*z*): [M]$^+$ calcd for $C_{13}H_{27}BO_2Si$, 254.1873; found, 254.1869.

***cis*-1-Trimethylsilyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*cis*-3b).**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.03 (s, 9H, –Si*C*H_3), 1.25 (s, 12H, *C*H_3), 1.79–1.89 (m, 2H), 1.94–2.13 (m, 2H), 2.16–2.36 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –2.4 (3C, Si*C*H_3), 19.5 (br, 1C, *C*HB), 23.84 (1C, *C*H_2), 23.89 (1C, *C*H_2), 24.7 (1C, Si*CH*), 24.9 (2C, –OC(*C*H_3)$_2$), 25.0 (2C, –OC(*C*H_3)$_2$), 82.9 (2C, –O*C*(CH$_3$)$_2$). IR (neat, cm^{-1}): 2952 (m), 2864 (m), 1372 (s), 1310 (s), 1245 (s), 1143 (s), 832 (s). MS–EI (*m*/*z*): [M–CH_3]$^+$ calcd for $C_{12}H_{24}BO_2Si$, 239.2; found, 239.2.

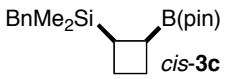
***trans*-1-Benzyl(dimethyl)silyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*trans*-3c).**



trans-**3c**

^{1}H NMR (300 MHz, $CDCl_3$, δ): –0.07 (s, 3H, –SiCH_3), –0.05 (s, 3H, –SiCH_3), 1.25 (s, 12H, CH_3), 1.81–2.05 (m, 5H), 2.06 (s, 2H, –CH_2Ph), 2.13–2.22 (m, 1H), 6.99–7.07 (m, 3H), 7.17–7.21 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –6.1 (1C, Si*C*H_3), –5.8 (1C, Si*C*H_3), 19.0 (br, 1C, *C*HB), 23.1 (1C, *C*H_2), 23.9 (1C, *C*H_2), 24.6 (4C, –OC(*C*H_3)$_2$), 82.9 (2C, –O*C*(CH$_3$)$_2$), 123.8 (1C, *C*H), 128.1 (2C, *C*H), 128.2 (2C, *C*H), 140.6 (1C, *C*). IR (neat, cm^{-1}): 3025 (w), 2977 (m), 1444 (m), 1372 (s), 1316 (m), 1144 (s), 827 (s). HRMS–EI (*m*/*z*): [M+H]$^+$ for $C_{19}H_{32}BO_2Si$, 331.2265; found, 331.2261. [M–CH_3]$^+$ for $C_{18}H_{28}BO_2Si$, 315.1952; found, 315.1949.

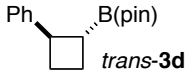
***cis*-1-Benzyl(dimethyl)silyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*cis*-3c).**



cis-**3c**

^{1}H NMR (300 MHz, $CDCl_3$, δ): –0.01 (s, 3H, –SiCH_3), 0.04 (s, 3H, –SiCH_3), 1.27 (s, 12H, CH_3), 1.82–1.92 (m, 2H), 1.94–2.07 (m, 1H), 2.07–2.29 (m, 5H), 6.99–7.07 (m, 3H), 7.17–7.22 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –4.8 (1C, Si*C*H_3), –4.5 (1C, Si*C*H_3), 19.5 (br, 1C, *C*HB), 23.0 (1C, *C*H_2), 23.8 (1C, *C*H_2), 24.1 (1C, *C*H_2), 24.7 (1C, Si*C*H), 24.9 (2C, –OC(*C*H_3)$_2$), 25.0 (2C, –OC(*C*H_3)$_2$), 83.0 (2C, –O*C*(CH$_3$)$_2$), 123.7 (1C, *C*H), 128.1 (2C, *C*H), 128.2 (2C, *C*H), 141.0 (1C, *C*). IR (neat, cm^{-1}): 3060 (w), 2977 (m), 1447 (w), 1379 (s), 1318 (m), 1142 (s), 694 (s). HRMS–ESI (*m*/*z*): [M+Na]$^+$ for $C_{19}H_{31}BNaO_2Si$, 353.20841; found, 353.20786.

***trans*-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*trans*-3d).**



trans-**3d**

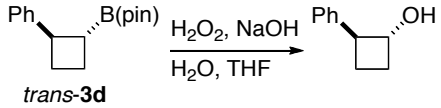
The yield of this product was determined by ^{1}H NMR in the crude mixture (89%). The purification with SiO_2 flash chromatography resulted in partial decomposition of the product with a small amount of impurities (typically < 5%). The further purification was carried out with gel permeation chromatography to afford isomerically pure *trans*-**3d** in 51% yield (trans/cis >99:1).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.26 (s, 12H, CH_3), 1.90–2.10 (m, 3H), 2.23–2.40 (m, 2H), 3.55–3.66 (m, 1H), 7.10–7.31 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 19.7 (1C, *C*H_2), 24.7 (4C, –OC(*C*H_3)$_2$), 29.6 (1C, *C*H_2), 41.4 (1C, *C*HPh), 83.1 (2C, –O*C*(CH$_3$)$_2$), 125.6 (1C, *C*H), 126.2 (2C, *C*H), 128.2 (2C, *C*H), 146.6 (1C, *C*). The carbon directly attached to the boron atom was not detected, likely due to

quadropolar relaxation.[4,5] IR (neat, cm^{-1}): 2976 (m), 2936 (m), 1380 (s), 1314 (s), 1142 (s), 697 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{16}H_{23}BO_2$, 258.1791; found, 258.1783.

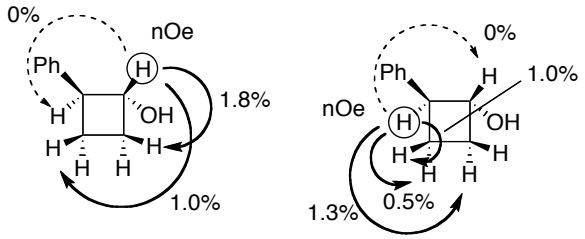
The stereochemistry of *trans*-**3d** was confirmed by stereospecific derivatization to the corresponding alcohol through H_2O_2/NaOH aq. The stereochemical assignments are inconsistent with those reported, where detailed characterization was not shown.[7] Our nOe experiments for *trans*-**3d** represent the stereochemical configuration of them.

***trans*-2-Phenylcyclobutan-1-ol.**

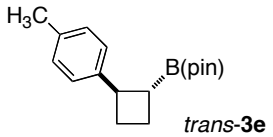


trans-**3d**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.26 (s, 1H, OH), 1.54–1.68 (m, 1H), 1.79–1.94 (m, 1H), 2.00–2.16 (m, 1H), 2.23–2.35 (m, 1H), 3.27 (q, *J* = 9.0 Hz, 1H), 4.29 (q, *J* = 8.6 Hz, 1H), 7.15–7.40 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 18.4 (1C, *C*H_2), 29.5 (1C, *C*H_2), 51.7 (1C, *C*H), 73.6 (1C, *C*HOH), 126.4 (1C, *C*H), 126.7 (2C, *C*H), 128.5 (2C, *C*H), 142.8 (1C, *C*). IR (neat, cm^{-1}): 3304 (br), 3028 (m), 2979 (m), 2945 (m), 1444 (s), 1101 (s), 739 (s), 696 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{10}H_{12}O$, 148.0888; found, 148.0885.



***trans*-1-(4-Methylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*trans*-3e).**

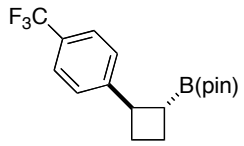


trans-**3e**

The yield of this product was determined by ^{1}H NMR in the crude mixture (76%). In this case, the starting material. The purification with SiO_2 flash chromatography resulted in partial decomposition of the product with a small amount of impurities (typically <5%). The further purification was carried out with recycle gel permeation chromatography (JAI LC-9101, $CHCl_3$) to afford isomerically pure *trans*-**3e** in 55% yield (trans/cis >99:1).^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.25 (s, 12H, CH_3), 1.90–2.07 (m, 3H), 2.19–2.41 (m, 2H), 2.31 (s, 3H, –CH_3), 3.52–3.61 (m, 1H), 7.07–7.15 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 19.7 (1C, *C*H_2), 20.9 (1C, *p*-*C*$H_3C_6H_4$–), 24.6 (4C, –OC(*C*H_3)$_2$), 27.0 (br, 1C, *C*HB), 29.7 (1C, *C*H_2), 41.2 (1C, *C*HPh), 83.0 (2C, –O*C*(CH$_3$)$_2$), 126.1 (2C, *C*H), 128.9 (2C, *C*H), 135.0 (1C, *C*),

143.6 (1C, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5] IR (neat, cm^{-1}): 2975 (m), 2934 (m), 1380 (s), 1314 (s), 1144 (s), 854 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{17}H_{25}BO_2$, 272.1948; found, 272.1951. Anal. Calcd for $C_{17}H_{25}BO_2$: C, 75.01; H, 9.26. Found: C, 75.16; H, 9.42.

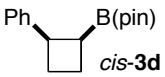
***trans*-1-(4-Trifluoromethyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*trans*-3f).**



trans-**3f**

The yield of this product was determined by ^1H NMR in the crude mixture (28%). The purification with SiO_2 flash chromatography resulted in partial decomposition of the product with a small amount of impurities (typically <5%). ^1H NMR (270 MHz, $CDCl_3$, δ): 1.27 (s, 12H, CH_3), 1.90–2.14 (m, 3H), 2.20–2.42 (m, 2H), 3.55–3.70 (m, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$, δ): 19.8 (1C, *C*H_2), 24.8 (4C, –OC(*C*H_3)$_2$), 27.0 (br, 1C, *C*HB), 29.5 (1C, *C*H_2), 41.3 (1C, *C*HPh), 83.2 (2C, –O*C*(CH$_3$)$_2$), 124.4 (q, *J* = 271.8 Hz, 1C, *C*F_3), 125.1 (q, *J* = 3.5 Hz, 2C, *C*H), 126.4 (2C, *C*H), 127.8 (q, *J* = 33.2 Hz, 1C, *C*), 150.5 (1C, *C*). IR (neat, cm^{-1}): 2979 (m), 1619 (m), 1384 (s), 1325 (s), 1124 (s), 839 (m). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{16}H_{19}BF_3O_2$, 311.1430; found, 311.1429.

***cis*-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*cis*-3d).**



cis-**3d**

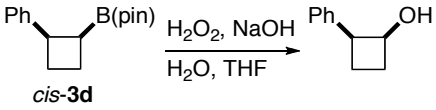
The yield of this product was determined by ^1H NMR in the crude mixture (63%). The purification with SiO_2 flash chromatography resulted in partial decomposition of the product with a small amount of impurities (typically <5%). The further purification was carried out with gel permeation chromatography to afford isomerically pure *cis*-**3d** in 62 % (trans/cis >99:1).

^1H NMR (300 MHz, $CDCl_3$, δ): 0.92 (s, 6H, *C*H_3), 0.95 (s, 6H, *C*H_3), 1.92–2.04 (m, 1H), 2.06–2.19 (m, 1H), 2.24–2.42 (m, 2H), 2.56–2.56 (quint, *J* = 9.6 Hz, 1H), 3.82 (q, *J* = 9.2 Hz, 1H), 7.08–7.14 (m, 1H), 7.22–7.27 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 19.5 (1C, *C*H_2), 24.46 (2C, –OC(*C*H_3)$_2$), 24.52 (2C, –OC(*C*H_3)$_2$), 26.0 (1C, *C*H_2), 40.9 (1C, *C*HPh), 82.6 (2C, –O*C*(CH$_3$)$_2$), 125.5 (1C, *C*H), 126.9 (2C, *C*H), 127.8 (2C, *C*H), 145.0 (1C, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5] IR (neat, cm^{-1}): 2977 (m), 2938 (m), 1379 (s), 1319 (s),

1142 (s), 694 (s). MS–EI (*m*/*z*): $[M]^+$ calcd for $C_{16}H_{23}BO_2$, 258.1791; found, 258.1792. Anal. Calcd for $C_{16}H_{23}BO_2$: C, 74.44; H, 8.98. Found: C, 74.20; H, 9.09.

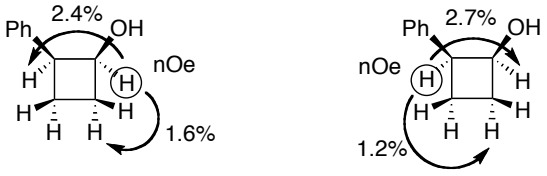
The stereochemistry of *cis*-**3d** was confirmed by stereospecific derivatization to the corresponding alcohol through H_2O_2/NaOH aq. The stereochemical assignments are inconsistent with those reported, where detailed characterization was not shown.[7] Our nOe experiments for *cis*-**3d** represent the stereochemical configuration of them.

***cis*-2-Phenylcyclobutan-1-ol.**

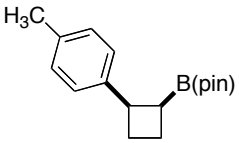


cis-**3d**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.25 (s, 1H, OH), 1.89–2.00 (m, 1H), 2.03–2.15 (m, 1H), 2.23–2.32 (m, 1H), 2.34–2.44(m, 1H), 3.70–3.74 (m, 1H, *C*HPh), 4.41–4.51 (m, 1H, *C*HOH), 7.21–7.28 (m, 3H), 7.33–7.38 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 19.8 (1C, *C*H_2), 30.7 (1C, *C*H_2), 46.8 (1C, *C*H), 69.2 (1C, *C*HOH), 126.6 (1C, *C*H), 128.5 (2C, *C*H), 128.6 (2C, *C*H), 138.4 (1C, *C*). IR (neat, cm^{-1}): 3391 (br), 3027 (m), 2941 (m), 1602 (s), 1494 (s), 1104 (s), 697 (s). HRMS–EI (*m*/*z*): $[M]^+$ calcd for $C_{10}H_{12}O$, 148.0888; found, 148.0885.



***cis*-1-(4-Methylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*cis*-3e).**



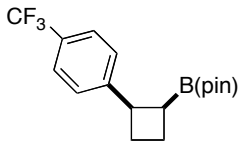
cis-**3e**

The yield of this product was determined by ^{1}H NMR in the crude mixture (70%). The purification with SiO_2 flash chromatography resulted in partial decomposition of the product with a small amount of impurities (typically <5%). The further purification was carried out with gel permeation chromatography to afford isomerically pure *cis*-**3e** (trans/cis 1:>99).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.93 (s, 6H, CH_3), 0.97 (s, 6H, CH_3), 1.93–2.01 (m, 1H), 2.05–2.17 (m, 1H), 2.24–2.33 (m, 2H), 2.28 (s, 3H), 2.52 (quint, 1H), 3.78 (q, *J* = 9.3 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$, δ): 19.5 (1C, *C*H_2), 20.9 (1C, *p*-*C*H_3C$_6$H$_4$–), 24.5 (2C, –OC(*C*H_3)$_2$), 24.6 (2C, –OC(*C*H_3)$_2$), 26.3 (1C, *C*H_2), 40.7 (1C, *C*HPh), 82.7 (2C, –O*C*(CH$_3$)$_2$),

126.9 (2C, *C*H), 128.5 (2C, *C*H), 135.0 (1C, *C*), 142.1 (1C, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5] IR (neat, cm^{-1}): 2976 (m), 2938 (m), 1379 (s), 1318 (s), 1143 (s), 813 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{17}H_{25}BO_2$, 272.1948; found, 272.1948. Anal. Calcd for $C_{17}H_{25}BO_2$: C, 75.01; H, 9.26. Found: C, 74.99; H, 9.48.

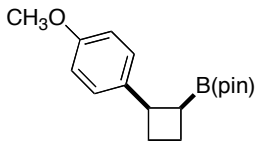
***cis*-1-(4-Trifluoromethyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*cis*-3f).**



cis-**3f**

The yield of this product was determined by ^{1}H NMR in the crude mixture (39%). The further purification was carried out with SiO_2 flash chromatography to afford *cis*-**3f** in 32%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.92 (s, 6H, CH_3), 0.94 (s, 6H, CH_3), 1.95–2.02 (m, 1H), 2.11–2.23 (m, 1H), 2.29–2.44 (m, 2H), 2.56 (quint, J = 9.9 Hz, 1H), 3.86 (q, J = 9.3 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$, δ): 19.7 (1C, CH_2), 24.56 (2C, –OC(CH_3)$_2$), 24.60 (2C, –OC(CH_3)$_2$), 26.1 (1C, CH_2), 40.8 (1C, *C*HPh), 82.9 (2C, –O*C*(CH_3)$_2$), 122.3 (q, J = 271.8 Hz, 1C, CF_3), 124.7 (q, J = 3.5 Hz, 2C, *C*H), 127.2, 128.0, 129.1, 149.3 (1C, *C*). IR (neat, cm^{-1}): 2978 (m), 1618 (m), 1325 (s), 1124 (m). HRMS–EI (*m/z*): $[M–CH_3]^+$ calcd for $C_{16}H_{19}BF_3O_2$, 311.1430; found, 311.1432.

***cis*-1-(4-Methoxylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*cis*-3g).**



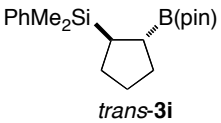
cis-**3g**

The yield of this product was determined by ^{1}H NMR in the crude mixture (60%). The purification with SiO_2 flash chromatography resulted in partial decomposition of the product with a small amount of impurities (typically <5%). The further purification was carried out with gel permeation chromatography to afford pure *cis*-**3g** in 41% yield.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.95 (s, 6H, CH_3), 0.98 (s, 6H, CH_3), 1.93–2.01 (m, 1H), 2.02–2.17 (m, 1H), 2.22–2.38 (m, 2H), 2.51 (q, 10.2 Hz, 1H), 3.71–3.83 (m, 1H), 3.77 (s, 3H), 6.77–6.83 (m, 2H), 7.13–7.20 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 19.4 (1C, CH_2), 24.5 (2C, –OC(CH_3)$_2$), 24.6 (2C, –OC(CH_3)$_2$), 26.4 (1C, CH_2), 40.4 (1C, *C*HPh), 55.3 (1C, *p*-$CH_3OC_6H_4$–), 82.7 (2C, –O*C*(CH_3)$_2$), 113.3 (2C, *C*H), 128.0 (2C, *C*H), 137.4 (1C, *C*), 157.8 (1C, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5] IR (neat, cm^{-1}): 2976 (m), 2937 (m), 1511 (m),

1379 (s), 1318 (s), 1145 (s), 828 (s). HRMS–EI (*m/z*): $[M]^+$ calcd for $C_{17}H_{25}BO_3$, 288.1897; found, 288.1897. Anal. Calcd for $C_{17}H_{25}BO_3$: C, 70.85; H, 8.74. Found: C, 71.01; H, 8.86.

***trans*-1-Dimethyl(phenyl)silyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentane (*trans*-3i).**

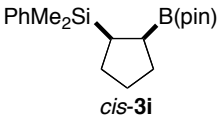


trans-**3i**

The yield of this product was determined by ^{1}H NMR in the crude mixture (68%). The diastereoselectivity was determined by GLC analysis (trans/cis 97:3). The purification with SiO_2 flash chromatography resulted in partial decomposition of the product with a small amount of impurities. The further purification was carried out with gel permeation chromatography to afford *trans*-**3i** in 45%.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.24 (s, 3H, –SiCH_3), 0.25 (s, 3H, –SiCH_3), 1.16 (s, 12H, CH_3), 1.21–1.61 (m, 6H), 1.69–1.82 (m, 2H), 7.31–7.33 (m, 3H), 7.52–7.55 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –4.7 (1C, Si*C*H_3), –4.1 (1C, Si*C*H_3), 24.6 (4C, –OC(*C*H_3)$_2$), 27.0 (1C, *C*HSi), 28.5 (1C, *C*H_2), 29.7 (1C, *C*H_2), 30.9 (1C, *C*H_2), 82.8 (2C, –O*C*(CH$_3$)$_2$), 127.6 (2C, *C*H), 128.7 (1C, *C*H), 134.2 (2C, *C*H), 139.3 (1C, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5] IR (neat, cm^{-1}): 3070 (w), 2976 (m), 2854 (m), 1326 (s), 1312 (s), 1211 (m), 1142 (s), 699 (s). HRMS–EI (m/z): $[M–CH_3]^+$ calcd for $C_{18}H_{28}BO_2Si$, 315.1952; found, 315.1950.

***cis*-1-Dimethyl(phenyl)silyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclobutane (*cis*-3i).**



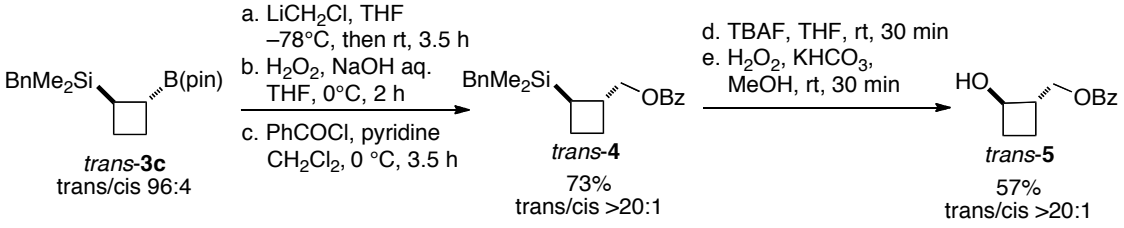
cis-**3i**

The yield of this product was determined by the ^{1}H NMR spectrum of the crude mixture (78%). The diastereoselectivity was determined by GLC analysis (trans/cis 4:96). The purification with SiO_2 flash chromatography resulted in partial decomposition of the product with a small amount of impurities. Repeated flash chromatography purification afforded *cis*-**3i** in 28%.

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.30 (s, 3H, –SiCH_3), 0.34 (s, 3H, –SiCH_3), 1.15 (s, 6H, CCH_3), 1.17 (s, 6H, CCH_3), 1.05–1.20 (m, 1H), 1.20–1.34 (m, 1H), 1.42–1.81 (m, 6H), 7.27–7.37 (m, 3H), 7.51–7.60 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –3.1 (1C, Si*C*H_3), –2.9 (1C, Si*C*H_3), 24.5 (2C, –OC(*C*H_3)$_2$), 24.8 (2C, –OC(*C*H_3)$_2$), 26.0 (1C, *C*H_2), 28.1 (1C, *C*H_2), 29.2 (1C, *C*HSiMe$_2$Ph), 30.0 (1C, *C*H_2), 82.7 (2C, –O*C*(CH$_3$)$_2$), 127.6 (2C, *C*H), 128.4 (1C, *C*H), 133.8 (2C, *C*H), 141.1 (1C, *C*). The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5] IR (neat, cm^{-1}):

3069 (m), 2977 (m), 2866 (m), 1379 (s), 1313 (s), 1246 (s), 1142 (s), 698 (s). HRMS–EI (*m/z*): [M–CH_3]$^+$ calcd for $C_{18}H_{28}BO_2Si$, 315.1952; found, 315.1954.

Stereoselective synthesis of *trans*-1-hydroxy-2-(benzoyloxymethyl)cyclobutane (*trans*-5).

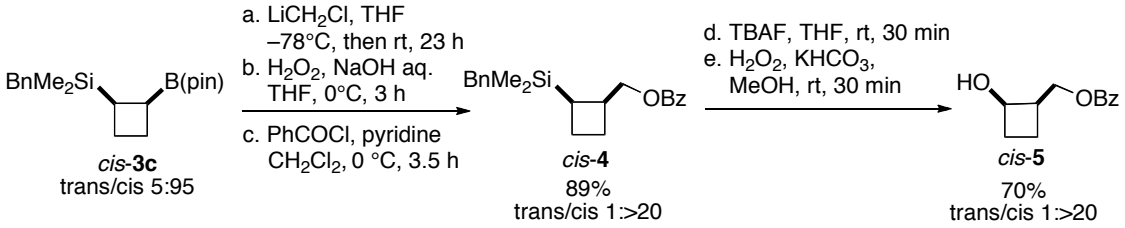


Bromochloromethane (205 mg, 1.58 mmol) and *trans*-**3c** (332 mg, 1.0 mmol) were dissolved in dry THF (8.0 mL) under an argon atmosphere. The mixture was cooled to –78 °C, then *n*-BuLi (1.65 M, 0.8 mL, 1.32 mmol) was added to the mixture with stirring. The mixture was stirred at –78 °C for 10 min, warmed to room temperature, and stirred for 3.5 h. The reaction was quenched with NH_4Cl aq., extracted three times with ethyl acetate, washed with brine, dried over Na_2SO_4, and filtered. The crude product obtained after evaporation was dissolved in THF (2.0 mL) and cooled to 0 °C. 30% H_2O_2 (1.6 mL) and NaOH aq. (3.0 M, 1.6 mL) were added dropwise to the stirred solution. After 2 h, the reaction mixture was diluted by adding water, and saturated Na_2SO_4, extracted three times with CH_2Cl_2, washed with water, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure. The resultant product was subjected to esterification using pyridine (264 mg, 3.34 mmol) and benzoyl chloride (312 mg, 2.22 mmol) in dry CH_2Cl_2 at 0 °C. After 3.5 h, the reaction was quenched by water, extracted three times with CH_2Cl_2, dried over $MgSO_4$, and filtered. After evaporation, the crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 0:100–4:96) to give *trans*-1-(benzyldimethylsilyl)-2-(benzoyloxymethyl)cyclobutane (*trans*-**4**) as a colorless oil (248 mg, 0.73 mmol, 73% for three steps). The diastereomeric ratio was determined by GLC analysis (trans/cis >20:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): –0.01 (s, 3H), 0.00 (s, 3H), 1.55–1.69 (m, 1H), 1.72–1.84 (m, 1H), 1.88–2.20 (m, 3H), 2.09 (s, 2H), 2.55–2.67 (m, 1H), 4.26 (d, *J* = 6.6 Hz, 2H), 6.92–7.10 (m, 3H), 7.14–7.23 (m, 2H), 7.41–7.48 (m, 2H), 7.51–7.60 (m, 1H), 8.00–8.10 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –5.8 (1C, Si*C*H_3), –5.4 (1C, Si*C*H_3), 19.2 (1C, *C*H_2), 23.7 (1C, *C*H), 24.0 (1C, *C*H_2), 24.8 (1C, *C*H_2), 34.9 (1C, *C*H), 69.2 (1C. *C*H_2O), 123.9 (1C, *C*H), 128.0 (2C, *C*H), 128.2 (2C, *C*H), 128.3 (2C, *C*H), 129.6 (2C, *C*H), 130.4 (1C, *C*), 132.8 (1C, *C*H), 140.0 (1C, *C*), 166.8 (1C, *C*). HRMS–ESI (*m/z*): [M+Na]$^+$ calcd for $C_{21}H_{26}NaO_2Si$, 361.15998; found, 361.15989.

A THF solution of tetrabutylammonium fluoride (1.0 M, 0.75 mL, 0.75 mmol) was added to a solution of *trans*-**4** (33.8 mg, 0.10 mmol) in THF (1.6 mL) with stirring at room temperature. After 30

min, methanol (0.7 mL), $KHCO_3$ (38.2 mg, 0.38 mmol), and 30% H_2O_2 (0.4 mL) were successively added to the reaction mixture. After 30 min, the reaction mixture was diluted with water, extracted three times with CH_2Cl_2, washed with water, dried over $MgSO_4$, and filtered. After evaporation, the crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 20:80–100:0) to give *trans*-1-hydroxy-2-(benzoyloxymethyl)cyclobutane (*trans*-**5**) as a colorless oil (11.7 mg, 0.057 mmol, 57%). The diastereomeric ratio was determined by ^{1}H NMR (trans/cis >20:1). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.30–1.41 (m, 1H), 1.72–1.92 (m, 2H), 2.18–2.30 (m, 1H), 2.45–2.30 (m, 1H), 4.09–4.19 (m, 1H), 4.35 (d, J = 5.8 Hz, 1H), 7.40–7.48 (m, 2H), 7.53–7.61 (m, 1H), 8.00–8.08 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 15.0 (1C, *C*H_2), 29.4 (1C, *C*H_2), 45.9 (1C, *C*H), 66.1 (1C, *C*H_2), 69.7 (1C, *C*H), 128.5 (2C, *C*H), 129.7 (2C, *C*H), 130.3 (1C, *C*), 133.1 (1C, *C*H), 167.0 (1C, *C*). HRMS–ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{12}H_{14}NaO_3$, 229.0835; found, 229.0836.

Stereoselective synthesis of *cis*-1-hydroxy-2-(benzoyloxymethyl)cyclobutane (*cis*-5).

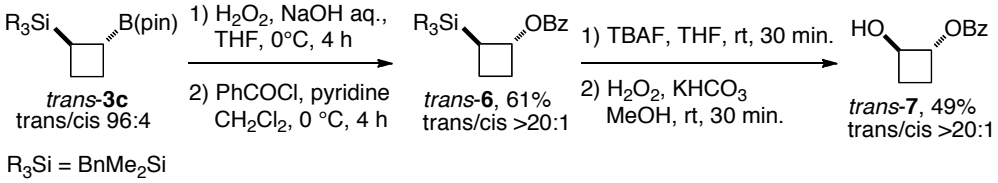


Bromochloromethane (38.6 mg, 0.30 mmol) and *trans*-**3c** (65.7 mg, 0.20 mmol) were dissolved in dry THF (1.6 mL) under an argon atmosphere. The mixture was cooled to –78 °C, then *n*-BuLi (1.57 M, 0.19 mL, 0.30 mmol) was added with stirring. The mixture was stirred at –78 °C for 10 min, warmed to room temperature, and stirred for 5 h. The reaction was quenched with NH_4Cl aq., extracted three times with ethyl acetate, washed with brine, dried over Na_2SO_4, and filtered. The crude product obtained after evaporation was dissolved in THF (0.4 mL) and cooled to 0 °C. 30% H_2O_2 (0.3 mL) and NaOH aq. (3.0 M, 0.3 mL) were then added dropwise to the stirred solution. After 3 h, the reaction mixture was diluted by adding water, and saturated Na_2SO_4, extracted three times with CH_2Cl_2, washed with water, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure. The resultant product was subjected to esterification using pyridine (52.3 mg, 0.66 mmol) and benzoyl chloride (53 mg, 0.38 mmol) in dry CH_2Cl_2 at 0 °C. After 4 h, the reaction was quenched by water, extracted three times with CH_2Cl_2, dried over $MgSO_4$, and filtered. After evaporation, the crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 0:100–4:96) to give *cis*-1-(benzyldimethylsilyl)-2-(benzoyloxymethyl)cyclobutane (*cis*-**4**) as a colorless oil (44.3 mg, 0.0.131 mmol, 66% for three steps). The diastereomeric ratio was determined by GLC analysis (trans/cis 1:>20). ^{1}H NMR (300 MHz, $CDCl_3$,

δ): 0.50 (s, 3H), 0.59 (s, 3H), 1.70–2.20 (m, 3H), 2.20–2.31 (m, 2H), 2.10 (s, 2H), 2.90–3.05 (m, 1H), 4.28–4.45 (m, 2H), 6.95–7.00 (m, 2H), 7.00–7.11 (m, 1H), 7.15–7.24 (m, 2H), 7.39–7.49 (m, 2H), 7.41–7.60 (m, 1H) 7.99–8.10 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): –4.0 (1C, Si*C*H_3), –3.5 (1C, Si*C*H_3), 20.3 (1C, *C*H_2), 23.7 (1C, *C*H), 25.1 (1C, *C*H_2), 25.4 (1C, *C*H_2), 36.1 (1C, *C*H), 67.9 (1C. *C*H_2O), 124.0 (1C, *C*H), 128.1 (2C, *C*H), 128.2 (2C, *C*H), 128.4 (2C, *C*H), 129.56 (1C, *C*H), 129.64 (1C, *C*), 130.4 (1C, *C*), 133.0 (1C, *C*H), 140.1 (1C, *C*), 166.9 (1C, *C*). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{21}H_{26}NaO_2S$, 361.15998; found, 361.15985.

A THF solution of tetrabutylammonium fluoride (1.0 M, 0.5 mL, 0.5 mmol) was added to a solution of *cis*-**4** (22.9 mg, 0.0677 mmol) in THF (0.6 mL) with stirring at room temperature. After 30 min, methanol (0.6 mL), $KHCO_3$ (26.2 mg, 0.26 mmol), and 30% H_2O_2 (0.25 mL) were successively added to the reaction mixture. After 30 min, the reaction mixture was diluted with water, extracted three times with CH_2Cl_2, washed with water, dried over $MgSO_4$, and filtered. After evaporation, the crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 20:80–100:0) to give *cis*-1-hydroxy-2-(benzoyloxymethyl)cyclobutane (*cis*-**5**) as a colorless oil (9.7 mg, 0.047 mmol, 70%). The diastereomeric ratio was determined by ^{1}H NMR (trans/cis 1:>20). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.71–1.92 (m, 2H), 1.93–2.10 (m, 1H), 2.27–2.40 (m, 1H), 2.62 (d, *J* = 4.7 Hz, 1H), 2.78–2.90 (m, 1H), 4.34 (dd, *J* = 11.5, 5.2 Hz, 1H), 4.38–4.45 (m, 1H), 4.76 (dd, *J* = 10.7, 8.2 Hz, 1H), 7.40–7.48 (m, 2H), 7.53–7.61 (m, 1H), 8.00–8.08 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 17.6 (1C, *C*H_2), 29.8 (1C, *C*H_2), 40.5 (1C, *C*H), 64.0 (1C, *C*H_2), 67.8 (1C, *C*H), 127.6 (1C, *C*H), 128.5 (2C, *C*H), 129.7 (2C, *C*), 133.1 (1C, *C*H), 167.0 (1C, *C*). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{12}H_{14}NaO_3$, 229.0835; found, 229.0836.

Stereoselective synthesis of *trans*-1-hydroxy-2-benzoyloxycyclobutane (*trans*-7).

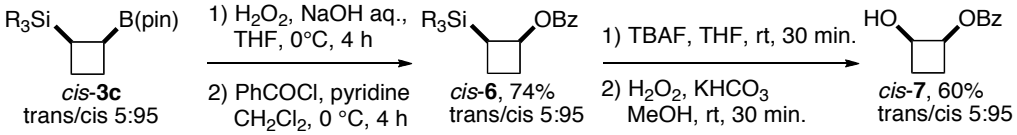


Into a THF (1.2 mL) solution of *trans*-**3c** (160.2 mg, 0.5 mmol), H_2O_2 (30%, 1.0 mL) and aqueous NaOH (3.0 M, 1.0 mL) were added at 0°C with stirring. After 4 h, the reaction mixture was diluted by water and two drops of saturated $Na_2S_2O_3$, extracted with CH_2Cl_2 three times. The combined organic layer was washed with water and dried over $MgSO_4$, filtered and evaporated. The crude mixture was treated by pyridine (117 mg, 1.8 mmol) and benzoyl chloride (141 mg, 1.0 mmol) in CH_2Cl_2 (4.0 mL) at 0°C. After stirred for 4 h, the reaction mixture was quenched by water, extracted with CH_2Cl_2 three

times. The combined organic layer was washed with water and dried over $MgSO_4$, filtered and evaporated. The isomeric ratio of *trans*-**6** (trans/cis >20:1) determined by ^{1}H NMR before purification. The crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 20:80–100:0) to give *trans*-**6** (96 mg, 0.36 mmol, 61%) as a colorless oil.

A THF solution of tetrabutylammonium fluoride (1.0 M, 2.8 mL, 2.8 mmol) was added to a solution of *trans*-**6** (350.4 mg, 1.08 mmol) in THF (2.8 mL) with stirring at room temperature. After 30 min, methanol (2.5 mL), $KHCO_3$ (142 mg, 0.26 mmol), and 30% H_2O_2 (1.5 mL) were successively added to the reaction mixture. After 30 min, the reaction mixture was diluted with water, extracted three times with CH_2Cl_2, washed with water and 1% aqueous $Na_2S_2O_3$, dried over $MgSO_4$, filtered and evaporated. The yield (49%) and isomeric ratio (trans/cis >20:1) of *trans*-**7** determined by ^{1}H NMR before purification. The crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 2:98–12:88) and further purification was carried out with gel permeation chromatography to give *trans*-**7** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.55–1.82 (m, 2H), 2.18–2.31 (m, 2H), 4.18–4.27 (m, 1H), 4.73–4.82 (m, 1H), 7.43–7.50 (m, 2H), 7.56–7.62 (m, 1H), 8.03–8.10 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 19.0 (1C, *C*H_2), 22.0 (1C, *C*H_2), 72.7 (1C, *C*H), 77.2 (1C, *C*H), 128.5 (2C, *C*H), 129.7 (1C, *C*), 129.8 (2C, *C*H), 133.4 (1C, *C*H), 167.6 (1C, *C*). IR (neat, cm^{-1}): 3418 (br), 3064 (w), 2956 (w), 1715 (s), 1700 (s), 1270 (s), 708 (s). HRMS–ESI (*m*/*z*): $[M+Na]^+$ calcd for $C_{11}H_{12}NaO_3$, 215.0679; found, 215.0682.

Stereoselective synthesis of *cis*-1-hydroxy-2-benzoyloxycyclobutane (*cis*-7).

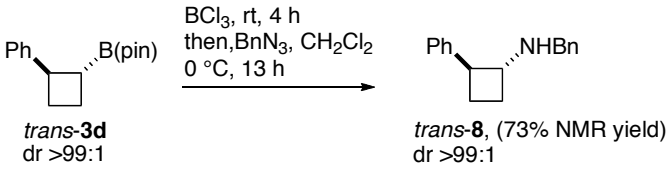


Into a THF (1.2 mL) solution of *cis*-**3c** (161.3 mg, 0.5 mmol), H_2O_2 (30%, 1.0 mL) and aqueous NaOH (3.0 M, 1.0 mL) were added at 0°C with stirring. After 4 h, the reaction mixture was diluted by water and two drops of saturated $Na_2S_2O_3$, extracted with CH_2Cl_2 three times. The combined organic layer was washed with water and dried over $MgSO_4$, filtered and evaporated. The crude mixture was treated by pyridine (53 mg, 1.5 mmol) and benzoyl chloride (141 mg, 1.0 mmol) in CH_2Cl_2 (4.0 mL) at 0°C. After stirred for 4 h, the reaction mixture was quenched by water, extracted with CH_2Cl_2 three times. The combined organic layer was washed with water and dried over MgSO4, filtered and evaporated. The isomeric ratio of the crude product (trans/cis 5:95) was determined by ^{1}H NMR before

purification. The crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 20:80–100:0) to give *cis*-**6** (117 mg, 0.36 mmol, 74%) as a colorless oil.

A THF solution of tetrabutylammonium fluoride (1.0 M, 2.8 mL, 2.8 mmol) was added to a solution of *cis*-**6** (117 mg, 0.36 mmol) in THF (2.8 mL) with stirring at room temperature. After 30 min, methanol (2.5 mL), $KHCO_3$ (142 mg, 0.26 mmol), and 30% H_2O_2 (1.5 mL) were successively added to the reaction mixture. After 30 min, the reaction mixture was diluted with water, extracted three times with CH_2Cl_2, washed with water and 1% aqueous $Na_2S_2O_3$, dried over $MgSO_4$, filtered and evaporated. The yield (60%) and isomeric ratio (trans/cis 5:95) of *cis*-**7** determined by ^1H NMR before purification. The crude product was purified by flash chromatography (SiO_2, ethyl acetate/hexane 2:98–12:88) and further purification was carried out with gel permeation chromatography to give *cis*-**7** as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$, δ): 2.00–2.28 (m, 5H), 4.51–4.64 (m, 1H), 5.20–5.30 (m, 1H), 7.44–7.48 (m, 2H), 7.56–7.62 (m, 1H), 8.06–8.11 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 23.4 (1C, *C*H_2), 27.9 (1C, *C*H_2), 69.0 (1C, *C*H), 73.5 (1C, *C*H), 128.5 (2C, *C*H), 129.8 (2C, *C*H), 129.9 (1C, *C*), 133.3 (1C, *C*H), 166.8 (1C, *C*). IR (neat, cm^{-1}): 3445 (br), 3064 (w), 2951 (w), 1716 (s), 1700 (s), 1272 (s), 711 (s). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{11}H_{12}NaO_3$, 215.0679; found, 215.0683.

Stereoselective synthesis of *trans*-*N*-benzyl-2-phenylcyclobutanamine (*trans*-8).[6]



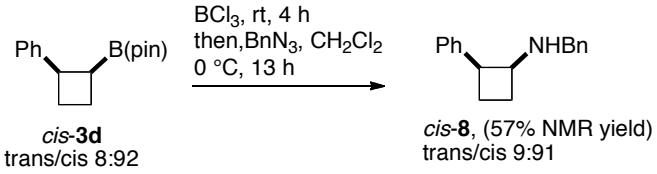
trans-**3d**
dr >99:1

trans-**8**, (73% NMR yield)
dr >99:1

The cyclobutylboronate (*trans*-**3d**, 51 mg, 0.20 mmol, trans/cis >99:1) was placed in a reaction tube and the tube was sealed with a screw cap containing Teflon coated rubber septum. The reaction tube was connected to an argon line through a needle, evacuated and backfilled with argon. A dichloromethane solution of BCl_3 (1.0 M, 1.0 mL, 1.0 mmol) was added to the reaction tube with stirring at room temperature. After 4 h, the volatile materials were removed in vacuo, and dry dichloromethane (1.2 mL) was added to the resultant product. The reaction tube was cooled to 0 °C, and benzylazide (80.0 mg, 0.60 mmol) was added to the mixture. After stirred for 13 h at 0 °C, the reaction mixture was quenched by adding aqueous NaOH , extracted three times with diethyl ether, washed with water, dried over $MgSO_4$, and filtered. The solvents were removed under reduced pressure to give the crude product. The NMR yield of *trans*-**8** was determined by using mesitylene as the internal standard (73%). The diastereoselectivity was determined by GLC analysis (trans/cis >99:1). Further purification

was carried out by flash chromatography to give *trans-N*-benzyl-2-phenylcyclobutanamine (*trans*-**8**) in 44% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.60–1.80 (m, 2H), 2.05–2.30 (m, 2H), 3.18 (dd, *J* = 16.8, 7.9 Hz, 1H), 3.38 (dd, *J* = 15.9, 7.7 Hz, 1H), 3.63–3.78 (m, 2H), 7.15–7.40 (m, 10H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 22.3 (1C, *C*H_2), 27.2 (1C, *C*H_2), 50.1 (1C, *C*H), 50.9 (1C, *C*H_2), 60.7 (1C, *C*H), 126.2 (1C, *C*H), 126.88 (2C, *C*H), 126.90 (1C, *C*H), 128.2 (2C, *C*H), 128.36 (2C, *C*H), 128.38 (2C, *C*H), 140.4 (1C, *C*), 144.2 (1C, *C*). HRMS–EI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{20}N$, 238.1597; found, 238.1597.

Stereoselective synthesis of *cis-N*-benzyl-2-phenylcyclobutanamine (*cis*-8).[6]



cis-**3d**
trans/cis 8:92

cis-**8**, (57% NMR yield)
trans/cis 9:91

The cyclobutylboronate (*cis*-**3d**, 52.2 mg, 0.20 mmol, trans/cis 8:92) was placed in a reaction tube and the tube was sealed with a screw cap containing Teflon coated rubber septum. The reaction tube was connected to an argon line through a needle, evacuated and backfilled with argon. A dichloromethane solution of BCl_3 (1.0 M, 1.0 mL, 1.0 mmol) was added to the reaction tube with stirring at room temperature. After 4 h, the volatile materials were removed in vacuo, and dry dichloromethane (1.2 mL) was added to the resultant product. The reaction tube was cooled to 0 °C, and benzylazide (82.2 mg, 0.60 mmol) was added to the mixture. After stirred for 13 h at 0 °C, the reaction mixture was quenched by adding aqueous NaOH, extracted three times with diethyl ether, washed with water, dried over $MgSO_4$, and filtered. The solvents were removed under reduced pressure to give the crude product. The NMR yield of *cis*-**8** (57%) was determined by using mesitylene as the internal standard. The diastereoselectivity was determined by GLC analysis (trans/cis 9:91). Further purification was carried out by flash chromatography to give *cis-N*-benzyl-2-phenylcyclobutanamine (*cis*-**8**) in 46% as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.93–2.02 (m, 1H), 2.05–2.15 (m, 1H), 2.18–2.28 (m, 1H), 2.32–2.43 (m, 1H), 3.44 (s, 2H), 3.68 (q, *J* = 7.6 Hz, 1H), 3.79–3.87 (m, 1H), 6.95–7.00 (m, 2H), 7.14–7.29 (m, 4H), 7.32–7.38 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 21.5 (1C, *C*H_2), 29.0 (1C, *C*H_2), 46.0 (1C, *C*H), 50.8 (1C, *C*H_2), 55.8 (1C, *C*H), 126.4 (1C, *C*H), 126.9 (1C, *C*H), 128.27 (2C, *C*H), 128.29 (2C, *C*H), 128.49 (2C, *C*H), 128.54 (2C, *C*H), 140.1 (1C, *C*), 140.6 (1C, *C*). IR (neat, cm^{-1}): 3027 (w), 2941 (m), 1494 (m), 1454 (w), 1142 (m), 699 (s). HRMS–EI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{20}N$, 238.1596; found, 238.1599.

References

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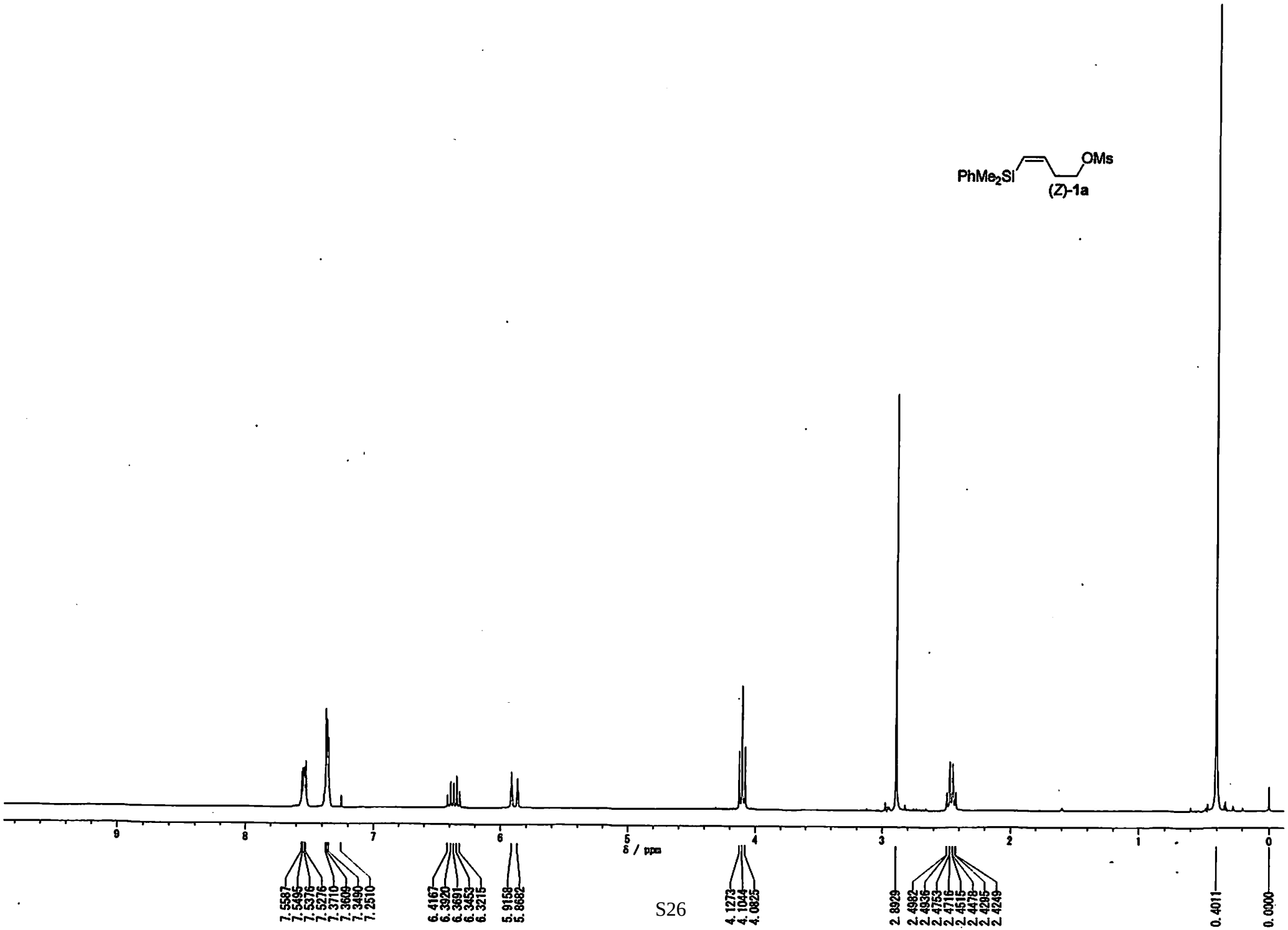
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7.3490
7.2510
6.4167
6.3920
6.3691
6.3453
6.3215
5.9158
5.8682
4.1273
4.1044
4.0825
2.8929
2.4982
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2.4753
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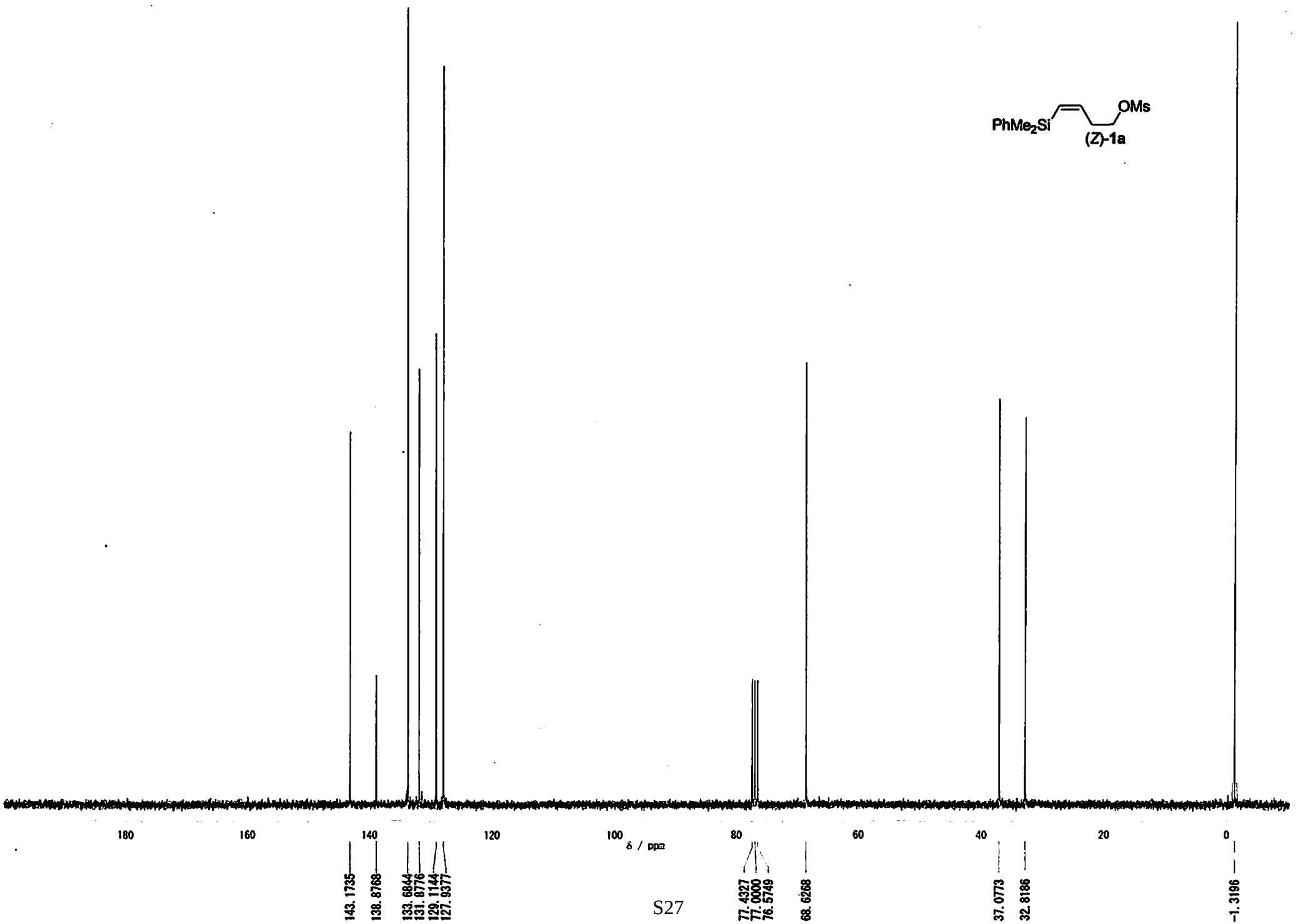
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OMs
(Z)-1a
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160
140
120
100
δ / ppm
80
60
40
20
0
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133.6844
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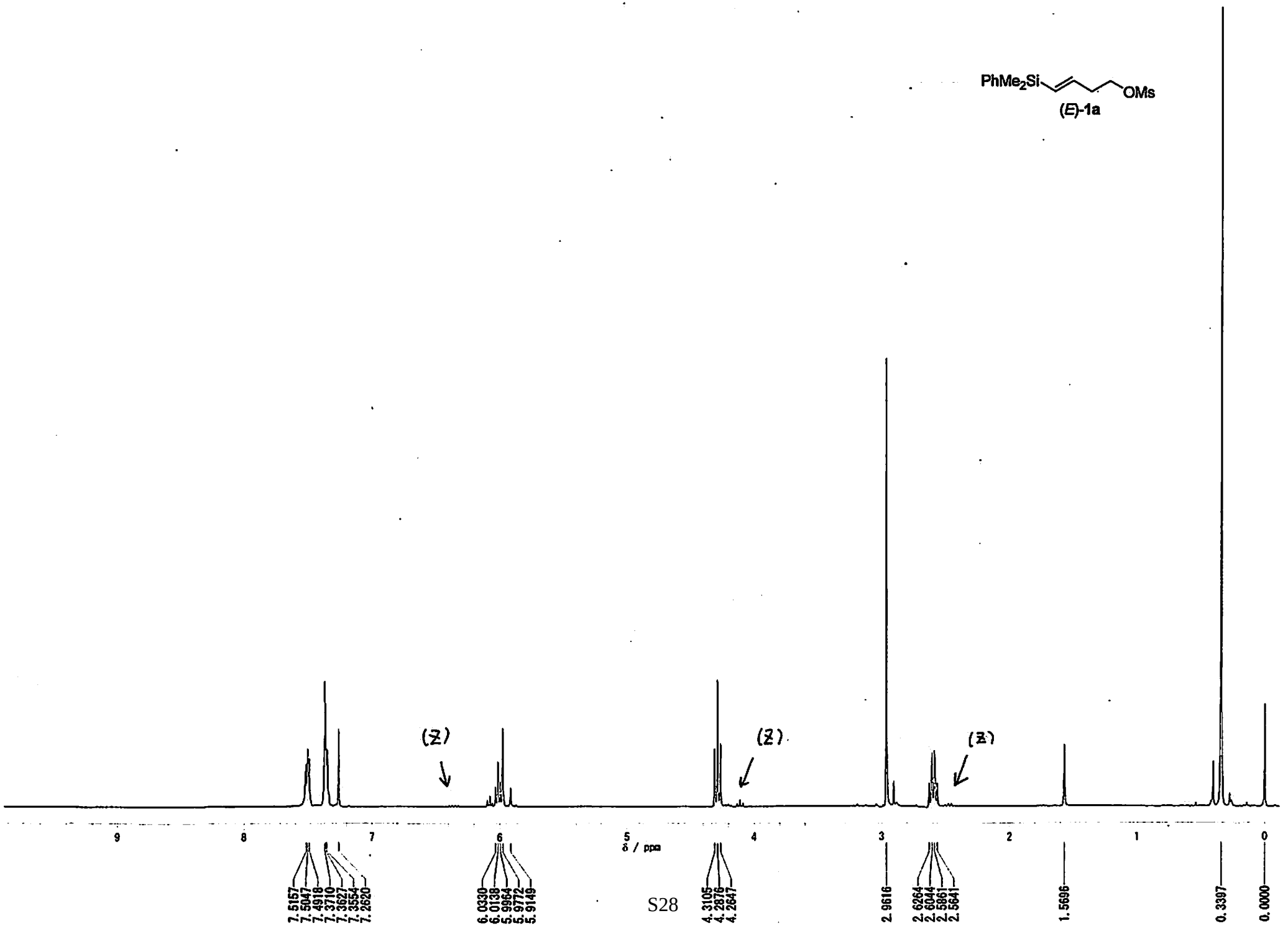
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OMs
(E)-1a
(Z)
(Z)
(Z)
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.5157
7.5047
7.4918
7.3710
7.3627
7.3554
7.2620
6.0330
6.0138
5.9964
5.9772
5.9149
4.3105
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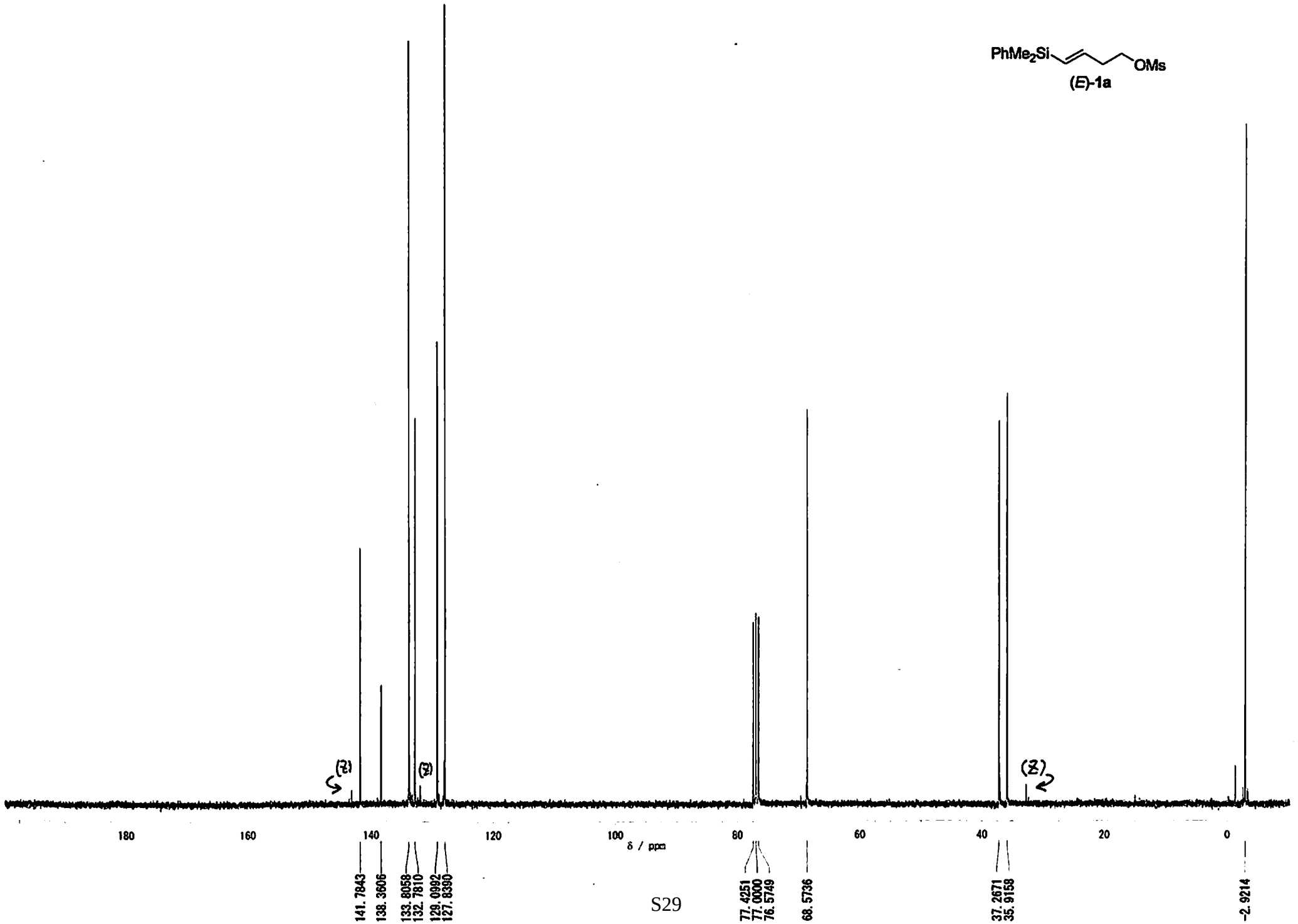
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(E)
(E)
(Z)
180
160
140
120
100
80
60
40
20
0
δ / ppm
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138.3606
133.8058
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76.5749
68.5736
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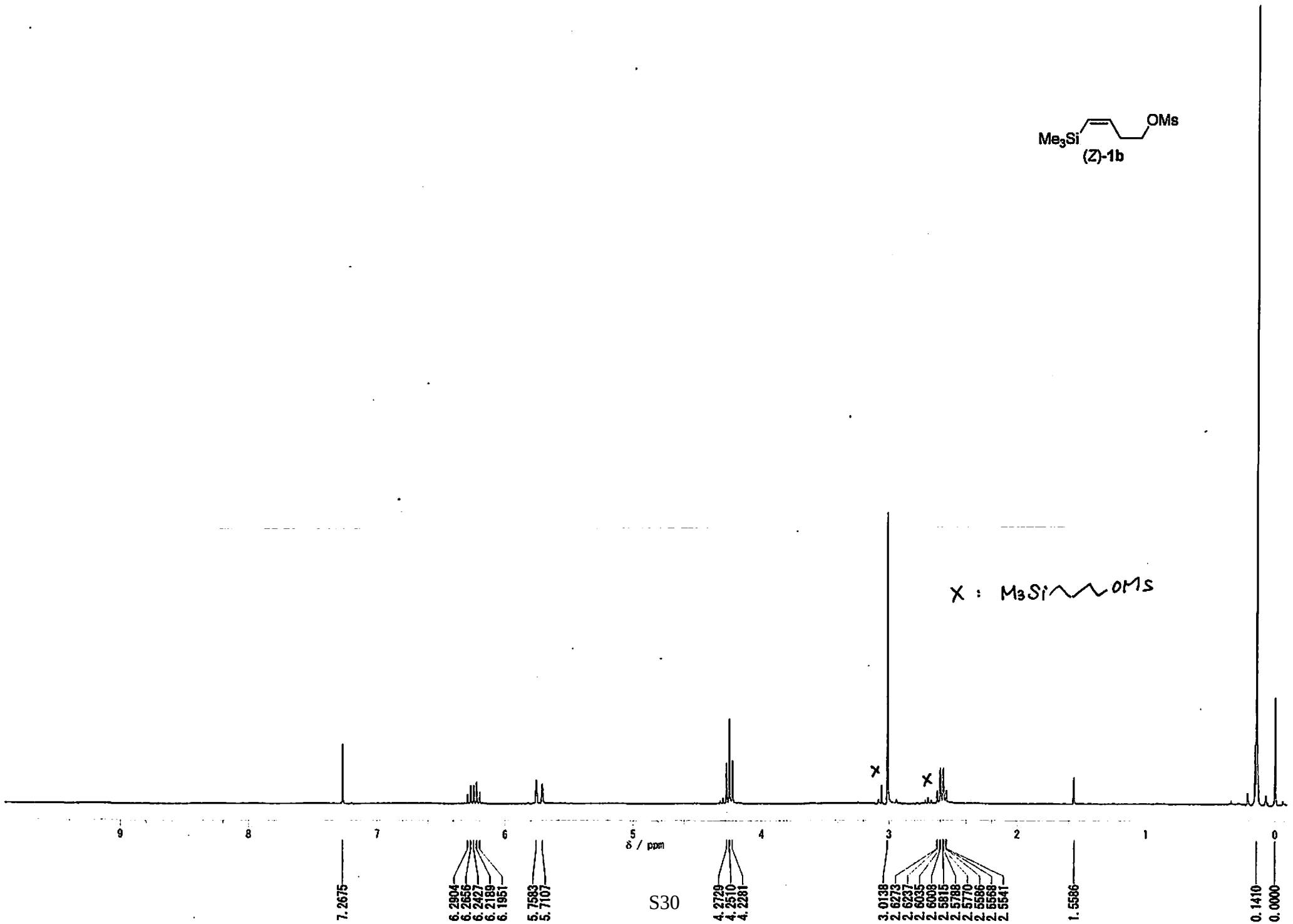
35.9158
-2.9214


Me3Si
OMs
(Z)-1b
X : M3Si OMs
X
X
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8
7
6
5
4
3
2
1
0
δ / ppm
7.2675
6.2904
6.2656
6.2427
6.2189
6.1951
5.7583
5.7107
4.2729
4.2510
4.2281
3.0138
2.6273
2.6237
2.6035
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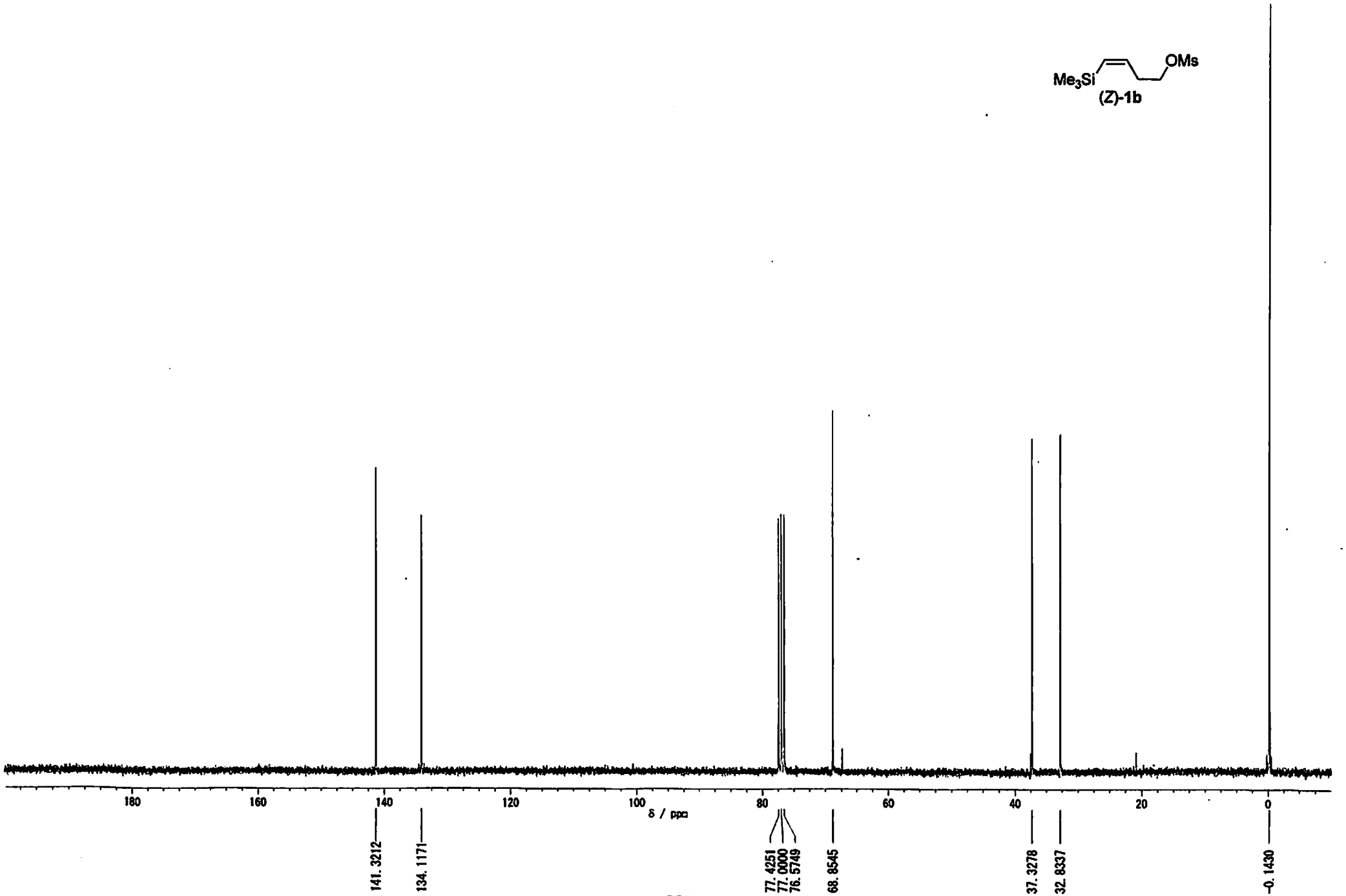
0.0000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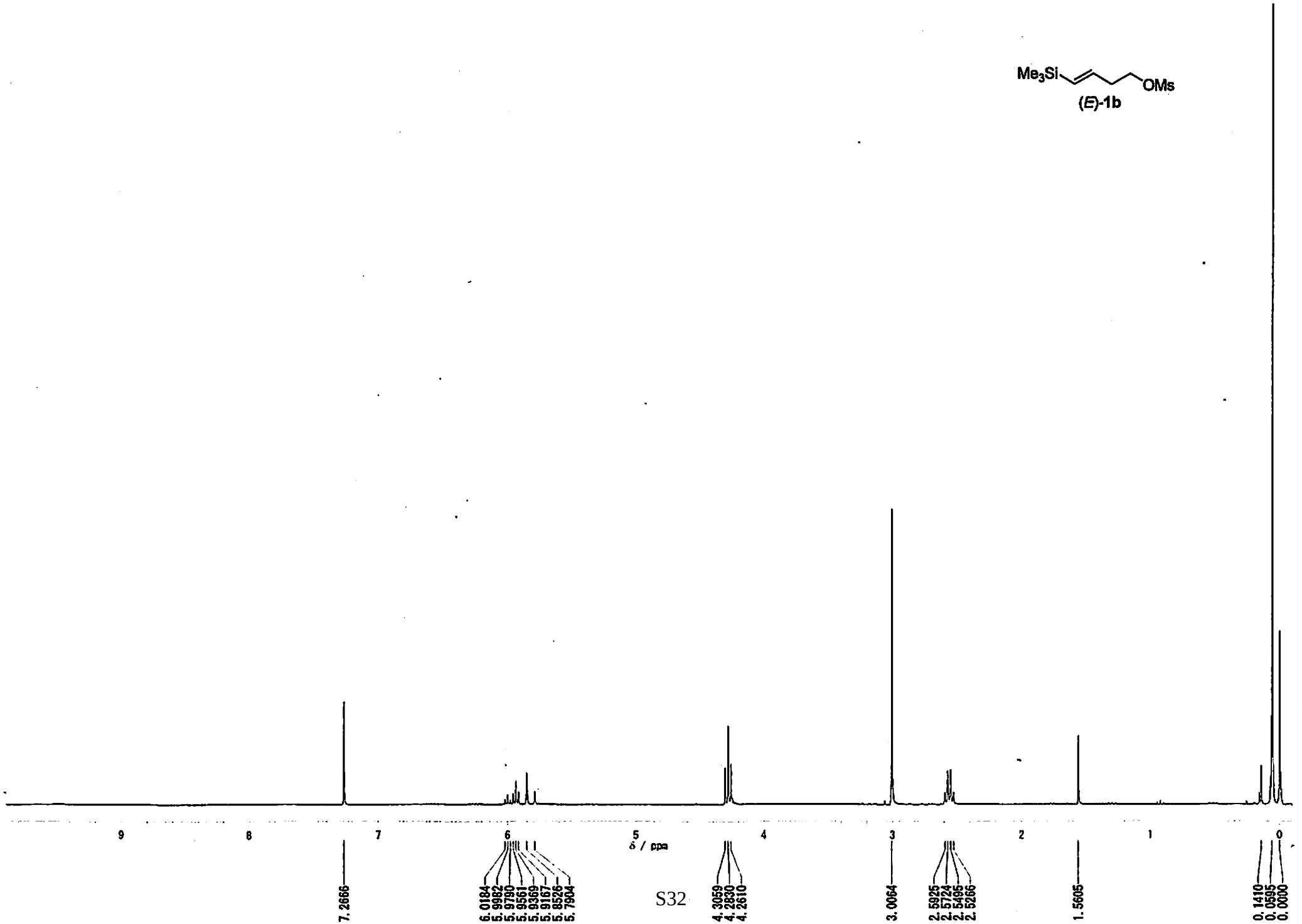
32.8337
-0.1430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δ / ppm
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5.7904
4.3059
4.2830
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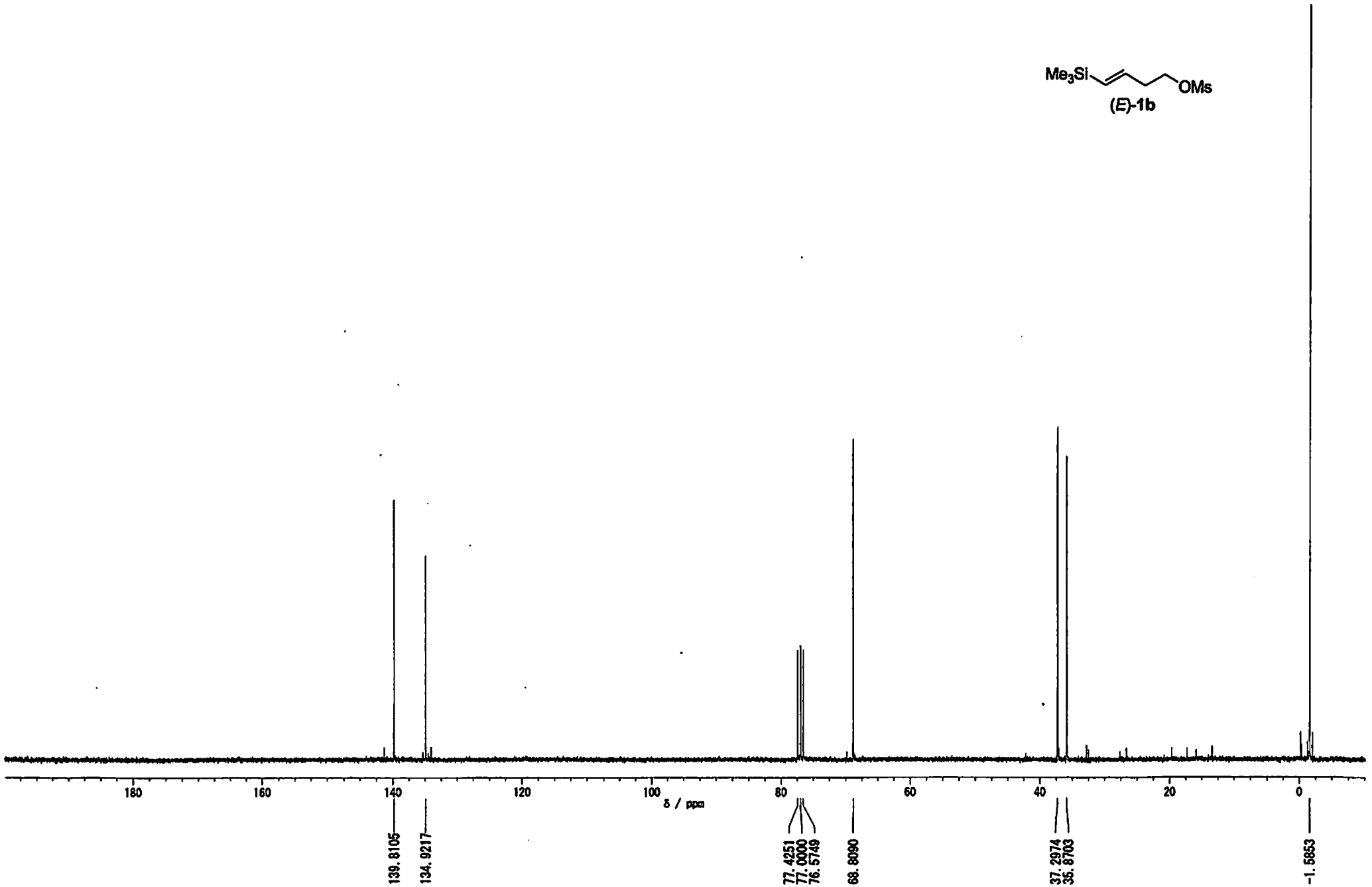
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OMs
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160
140
120
100
80
60
40
20
0
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68.8090
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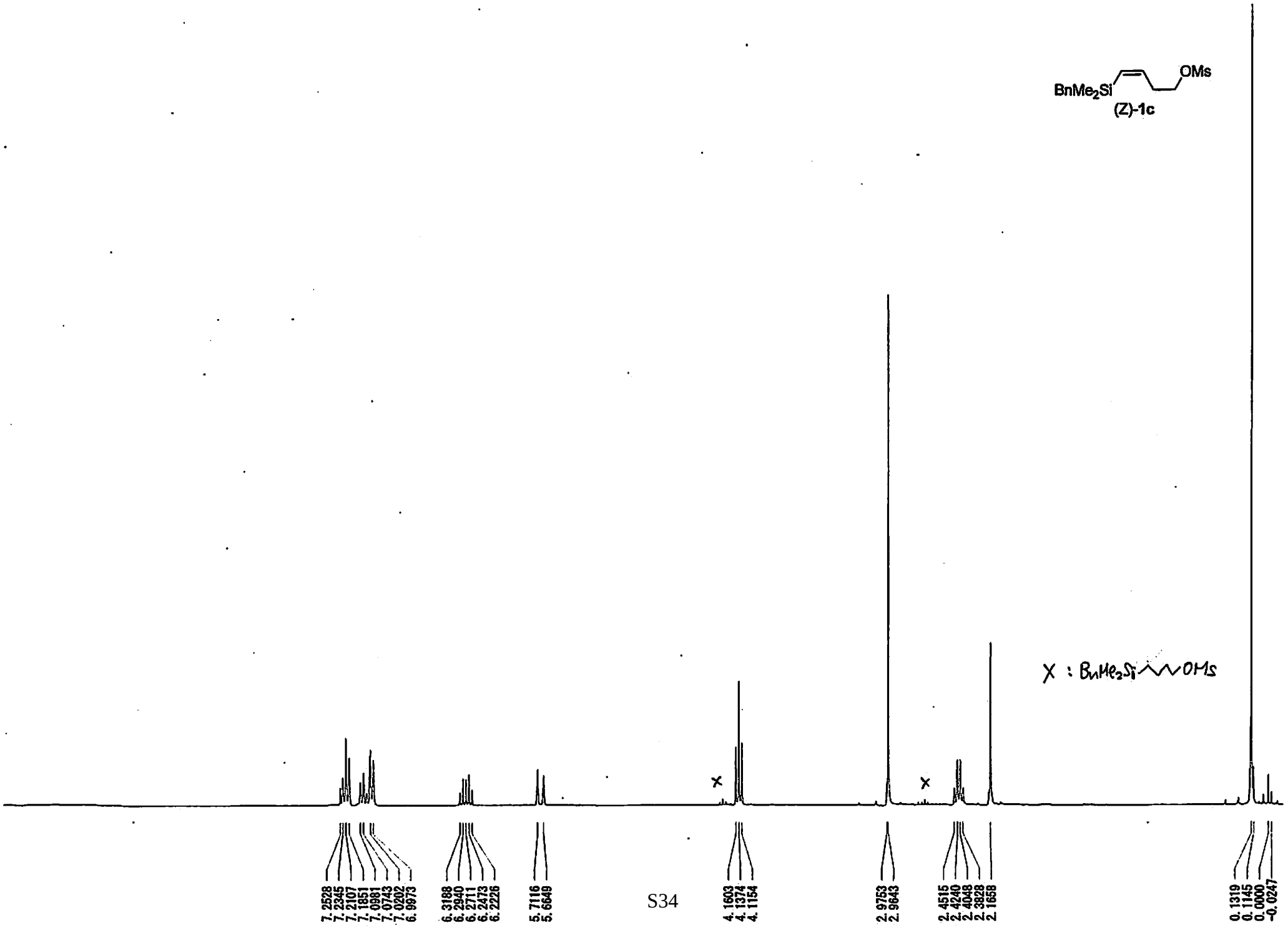
35.8703
-1.5853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OMs
(Z)-1c
X : BnMe2Si OMs
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7.1851
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7.0743
7.0202
6.9973
6.3188
6.2940
6.2711
6.2473
6.2226
5.7116
5.6649
4.1603
4.1374
4.1154
2.9753
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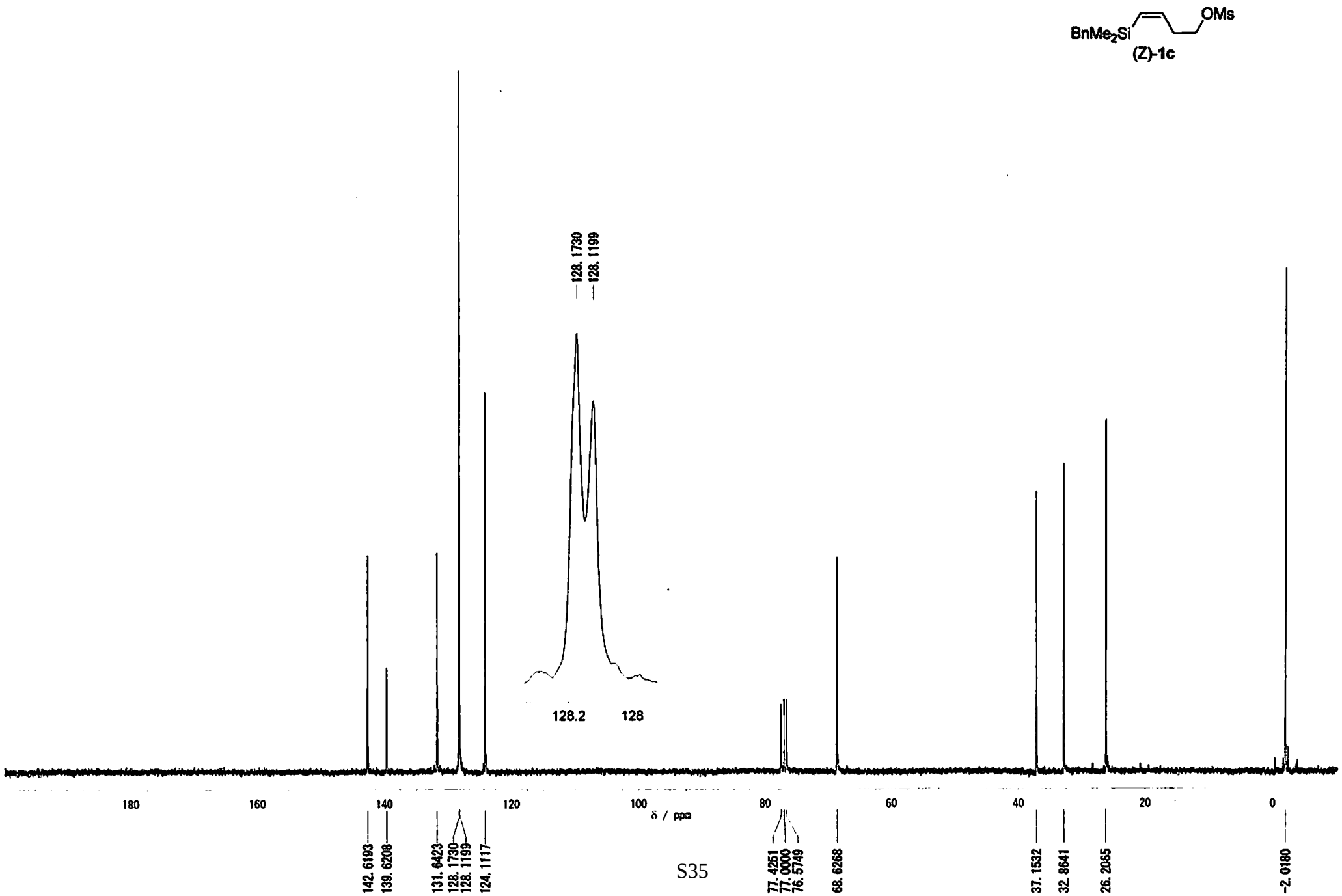
-0.0247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OMs
(Z)-1c
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128.1199
128.2
128
180
160
140
120
100
80
60
40
20
0
δ / ppm
142.6193
139.6208
131.6423
128.1730
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77.0000
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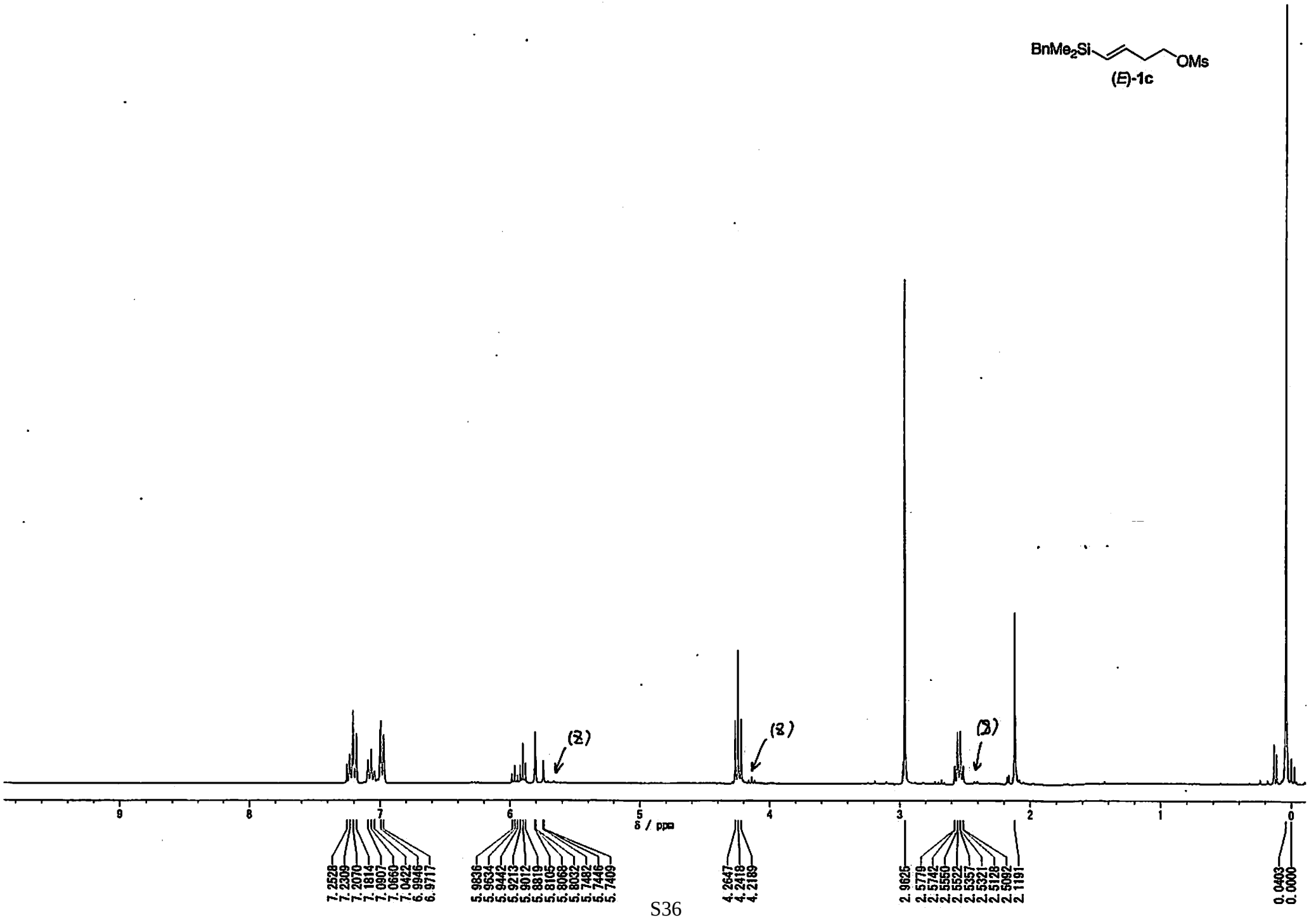
37.1532
32.8641
26.2065
-2.0180


BnMe2Si
OMs
(E)-1c
(2)
(2)
(3)
δ / ppm
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8
7
6
5
4
3
2
1
0
7.2528
7.2309
7.2070
7.1814
7.0907
7.0660
7.0422
6.9946
6.9717
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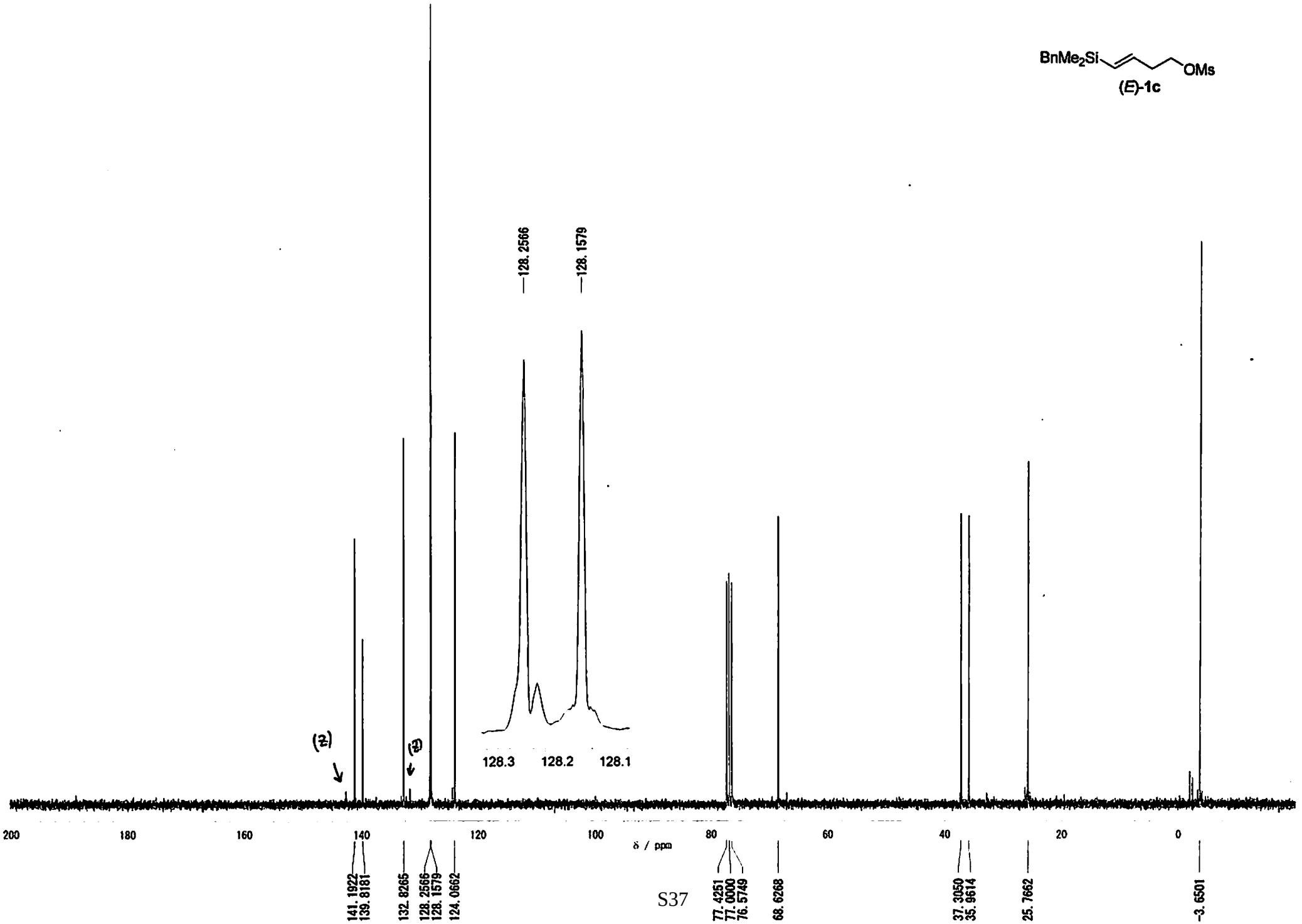
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128.3
128.2
128.1
(Si)
(Si)
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
141.1922
139.8181
132.8265
128.2566
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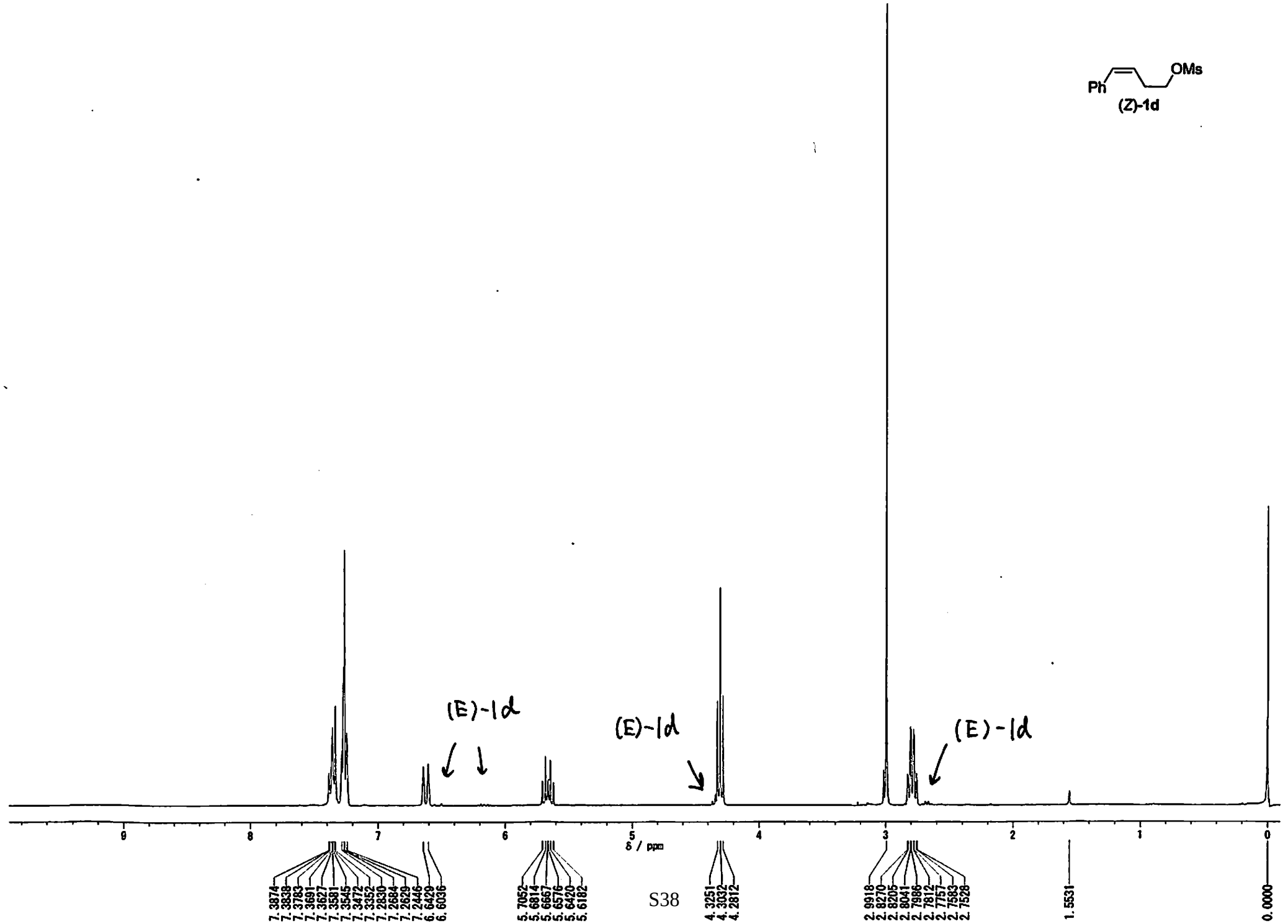
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(E)-1d
(E)-1d
(E)-1d
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7.3691
7.3627
7.3581
7.3545
7.3472
7.3352
7.2830
7.2684
7.2629
7.2446
6.6429
6.6036
5.7052
5.6814
5.6667
5.6576
5.6420
5.6182
4.3251
4.3032
4.2812
2.9918
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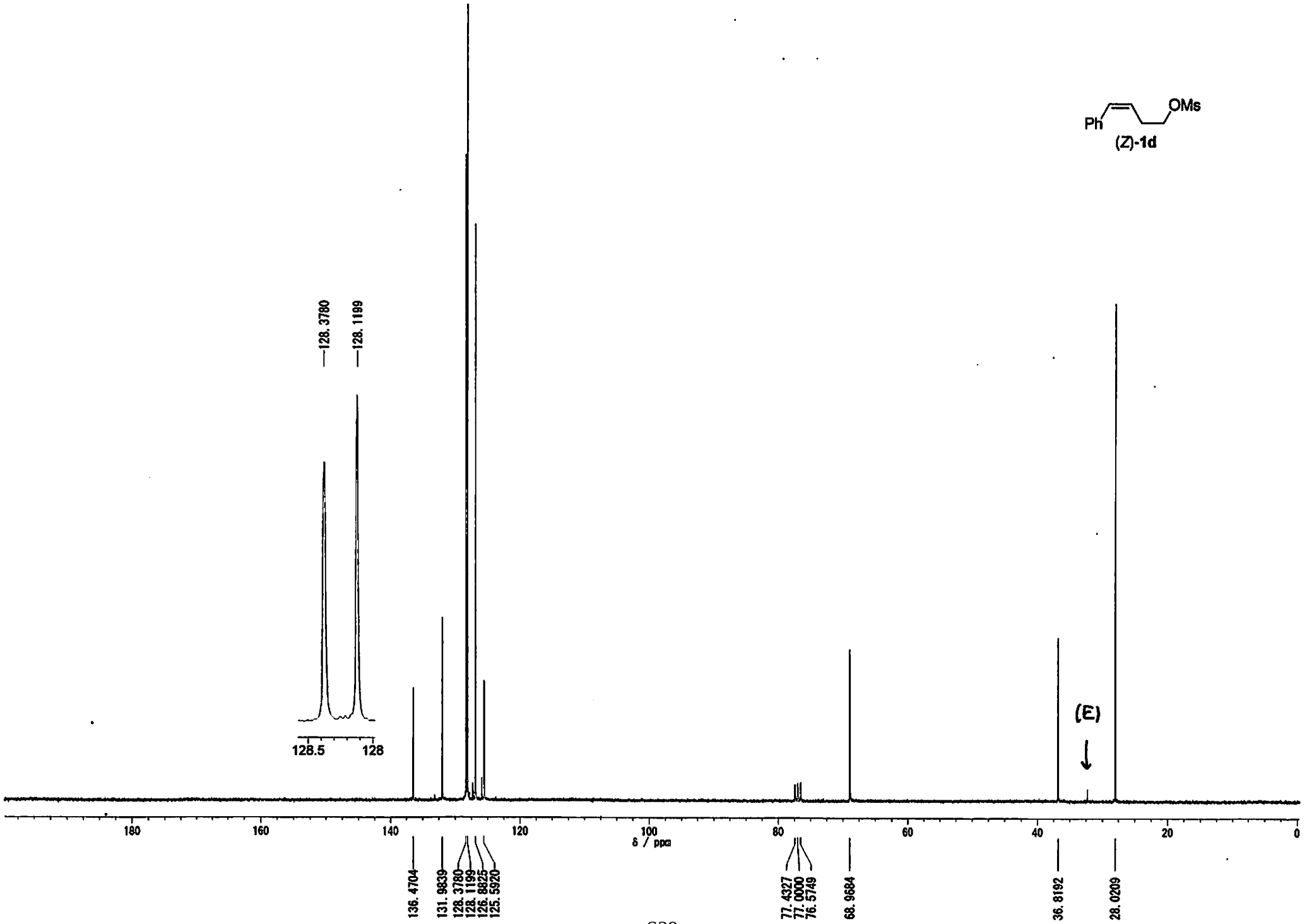
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OMs
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128
(E)
δ / ppm
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160
140
120
100
80
60
40
20
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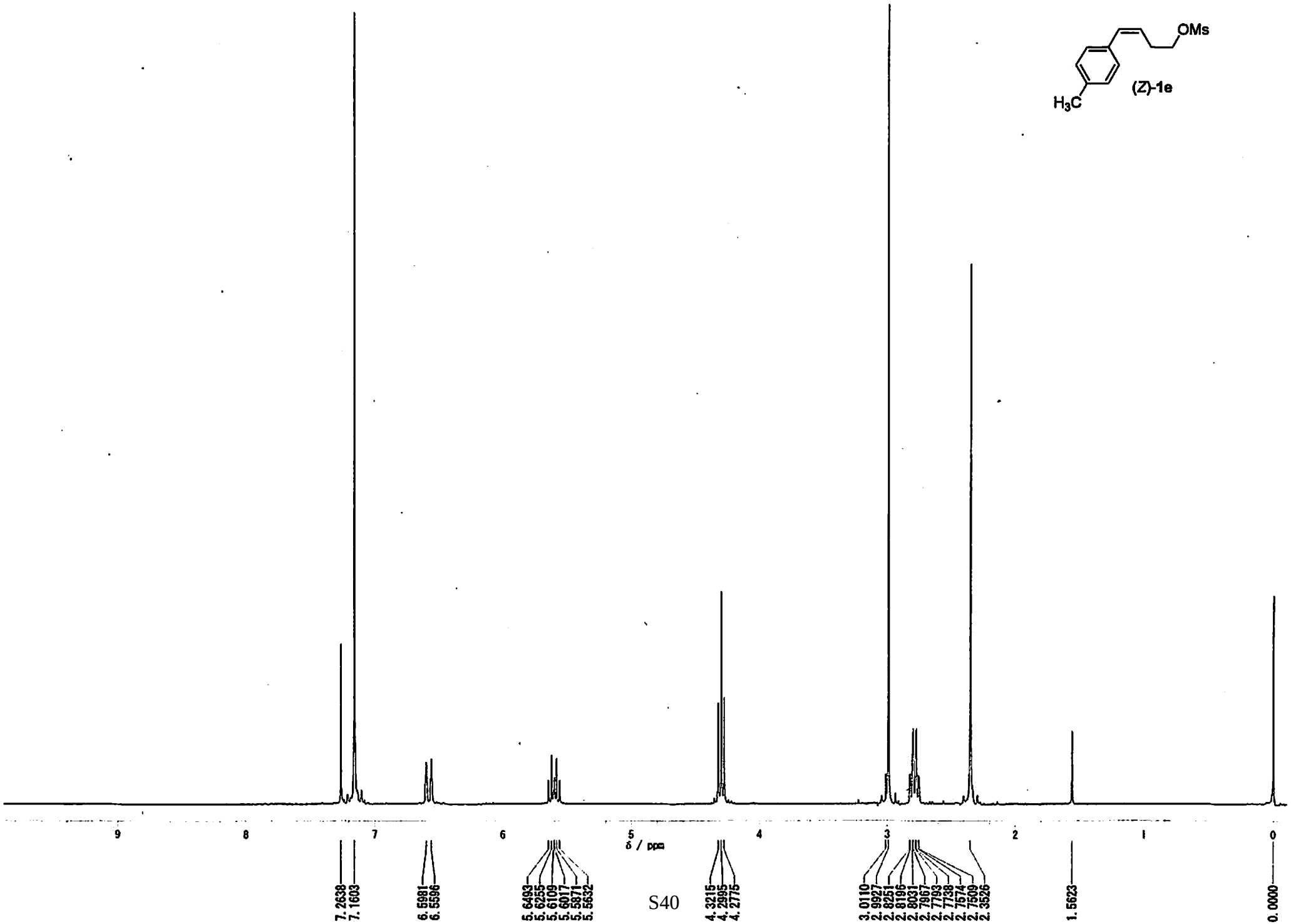
OMs
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H3C
9
8
7
6
5
4
3
2
1
0
δ / ppm
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7.1603
6.5981
6.5596
5.6493
5.6255
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5.5871
5.5632
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4.2995
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3.0110
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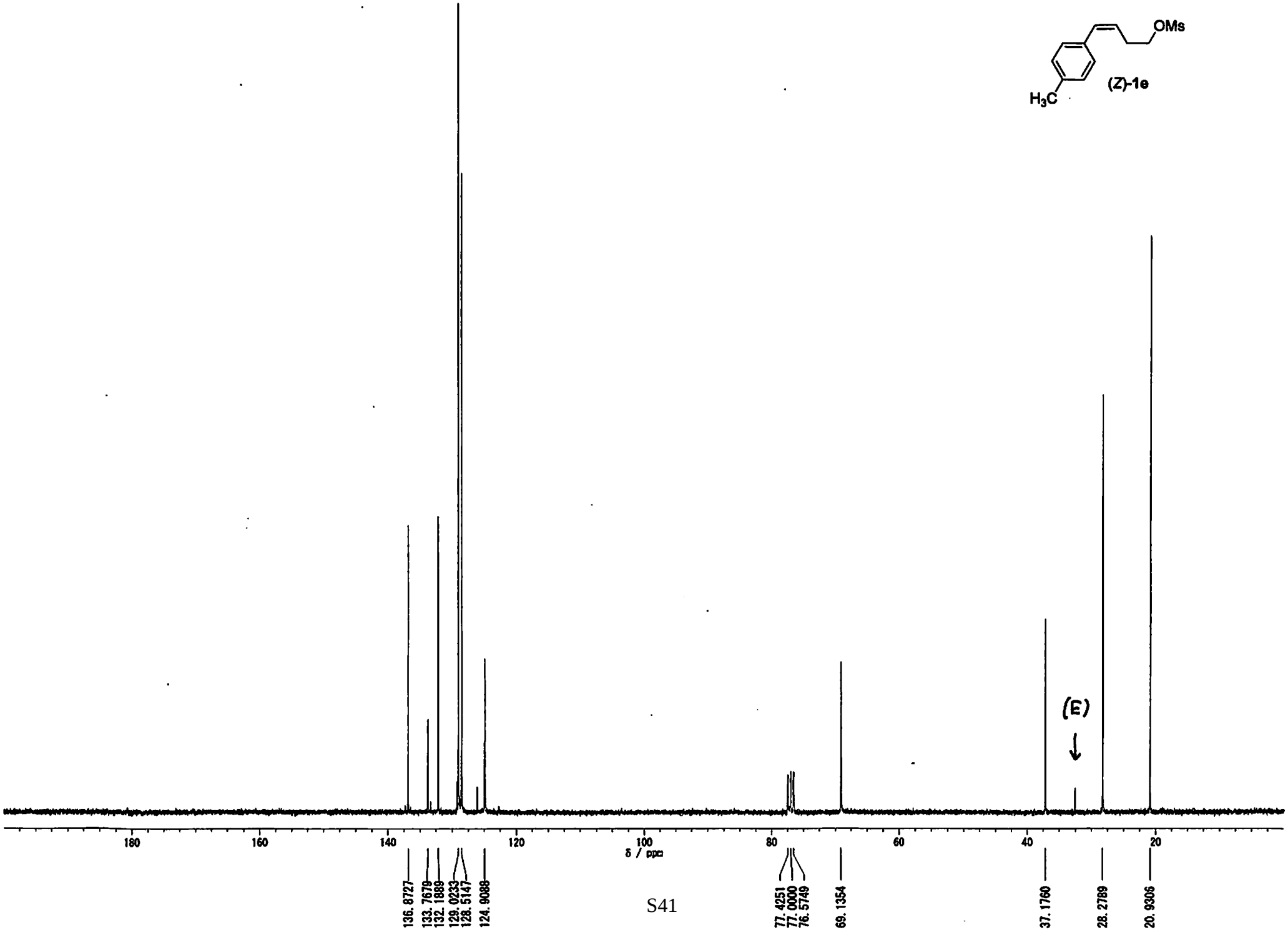
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H_3C
(E)
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100
80
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20
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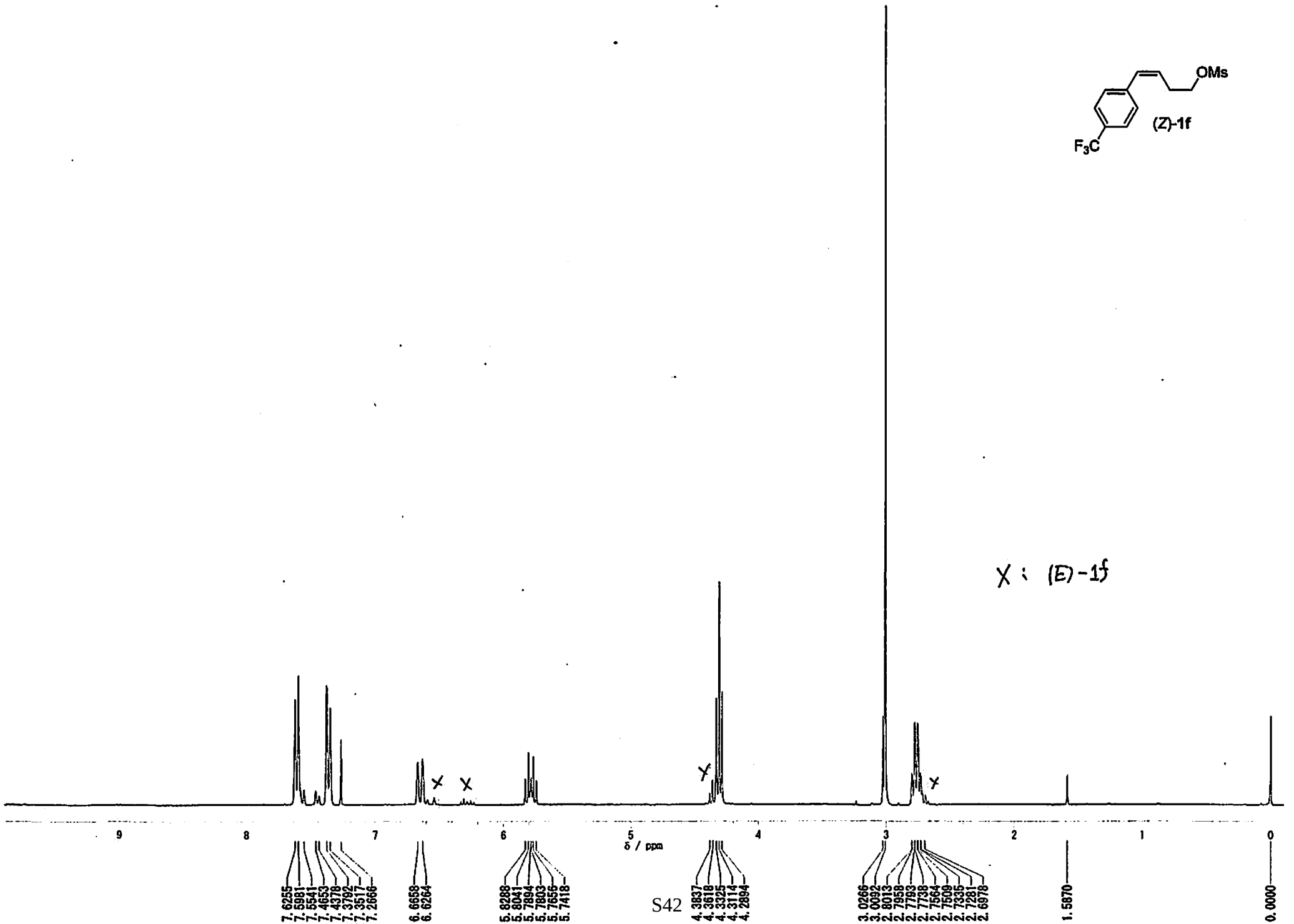
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F3C
X : (E)-1f
9
8
7
6
5
4
3
2
1
0
δ / ppm
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7.5541
7.4653
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4.3325
4.3114
4.2894
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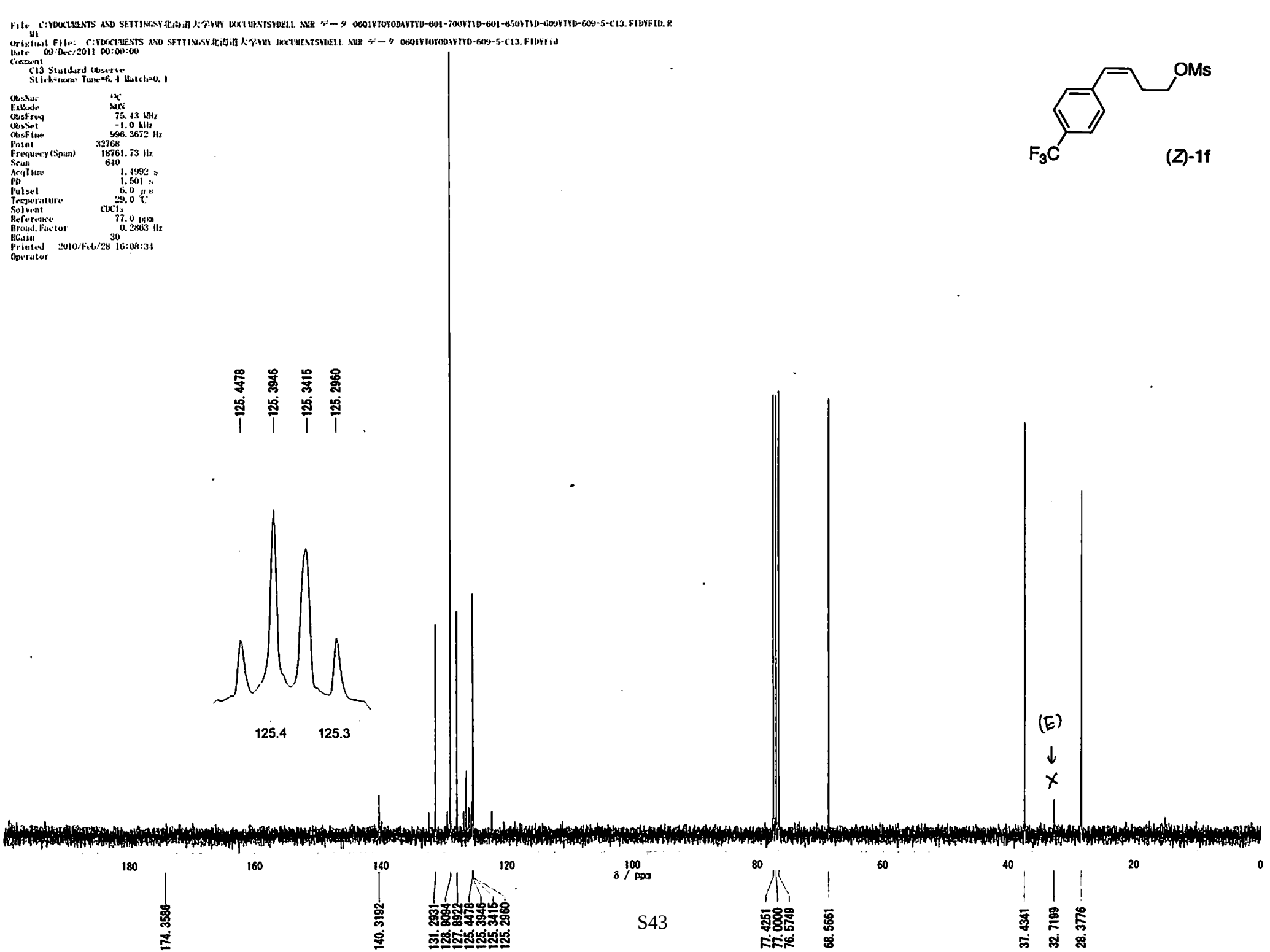
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ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequency(Span) 18761.73 Hz
Scan 640
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PD 1.501 s
Pulse1 6.0 μs
Temperature 29.0 ℃
Solvent CDCl3
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
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Operator
OMs
F3C
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125.3946
125.3415
125.2960
125.4
125.3
(E)
δ / ppm
180
160
140
120
100
80
60
40
20
0
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140.3192
131.2931
128.8094
127.8922
125.4478
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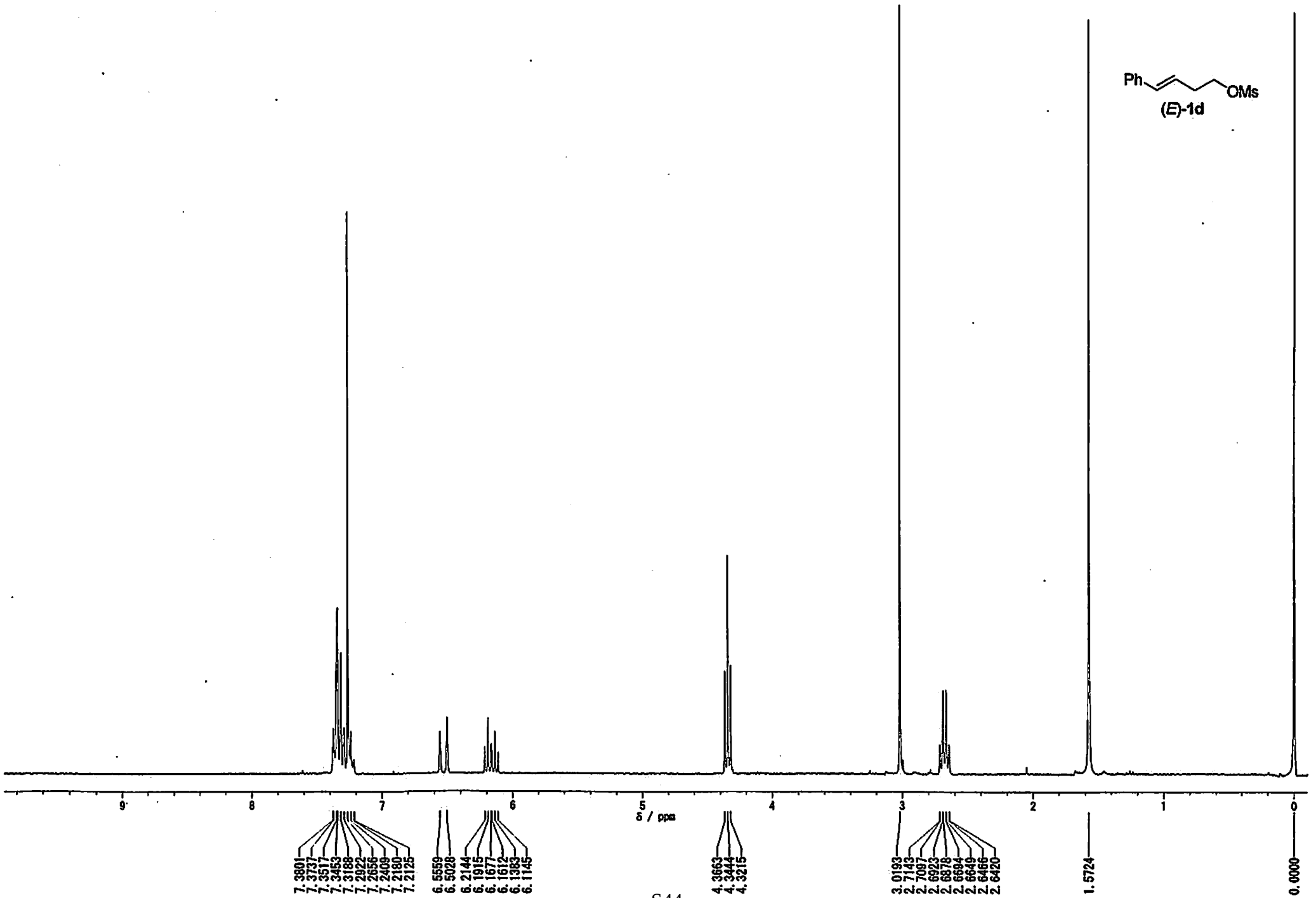
Ph
OMs
(E)-1d
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8
7
6
5
4
3
2
1
0
δ / ppm
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7.3517
7.3453
7.3188
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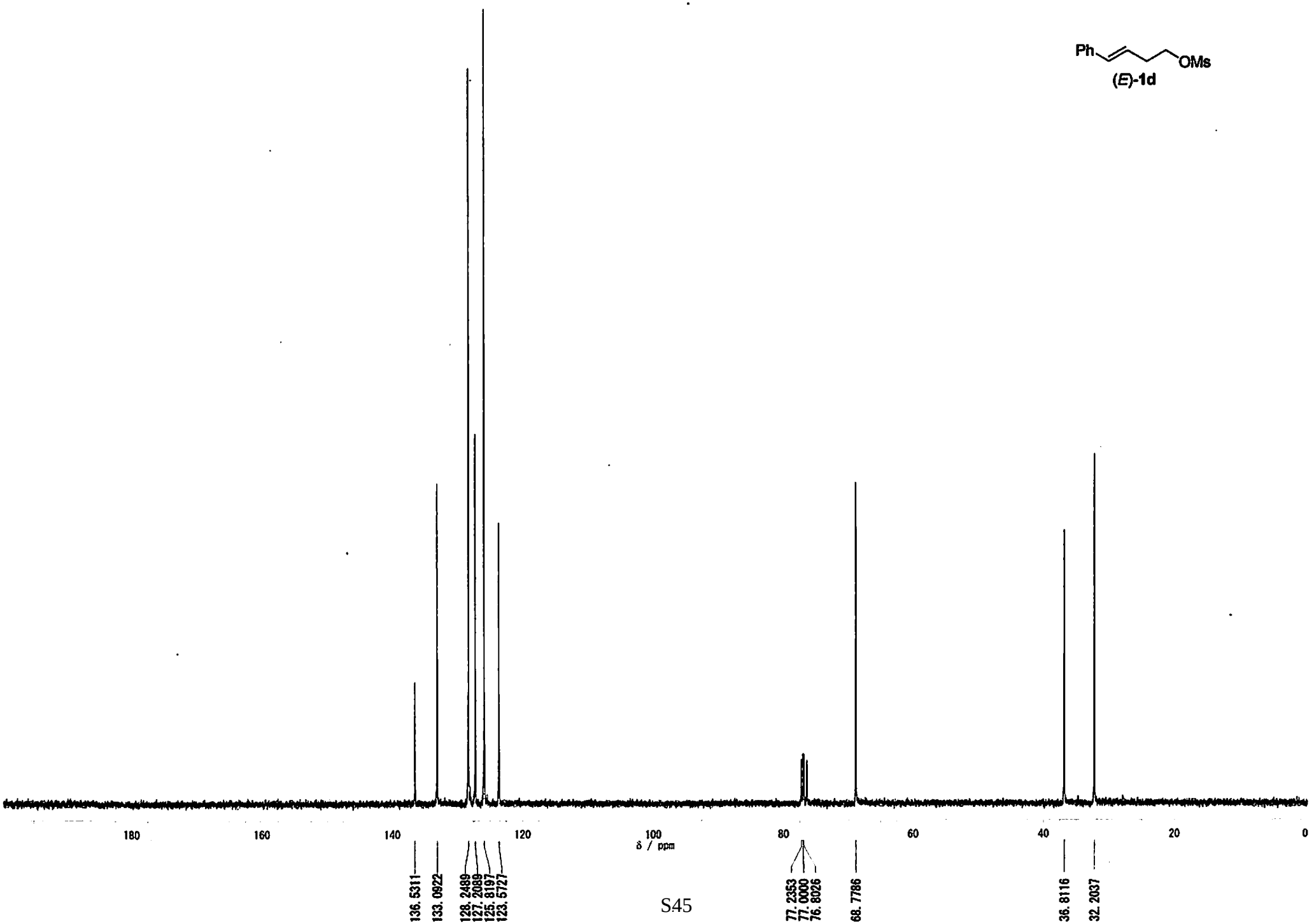
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OMs
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160
140
120
100
80
60
40
20
0
δ / ppm
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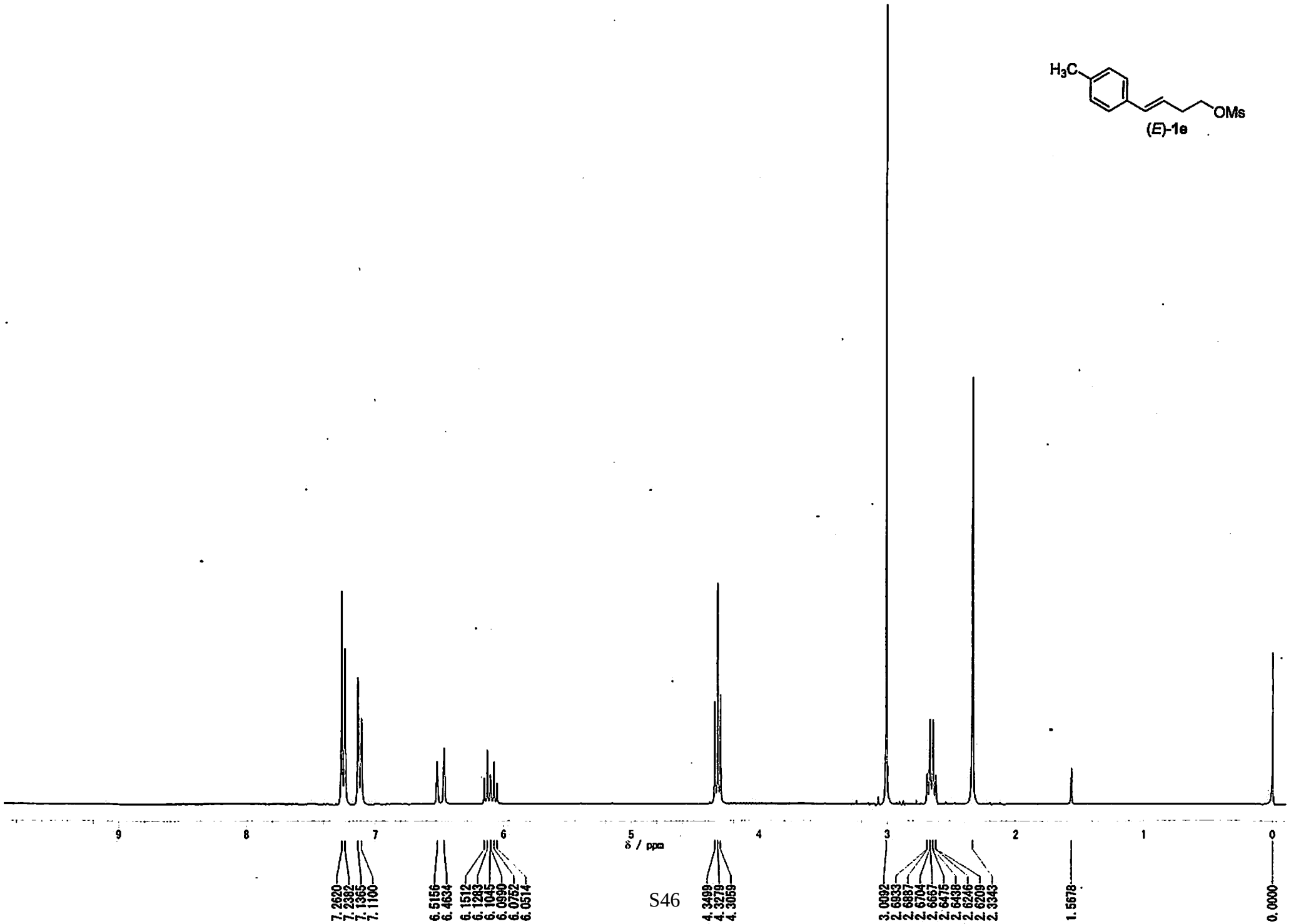
H3C
OMs
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8
7
6
5
4
3
2
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δ / ppm
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7.1365
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6.1283
6.1045
6.0990
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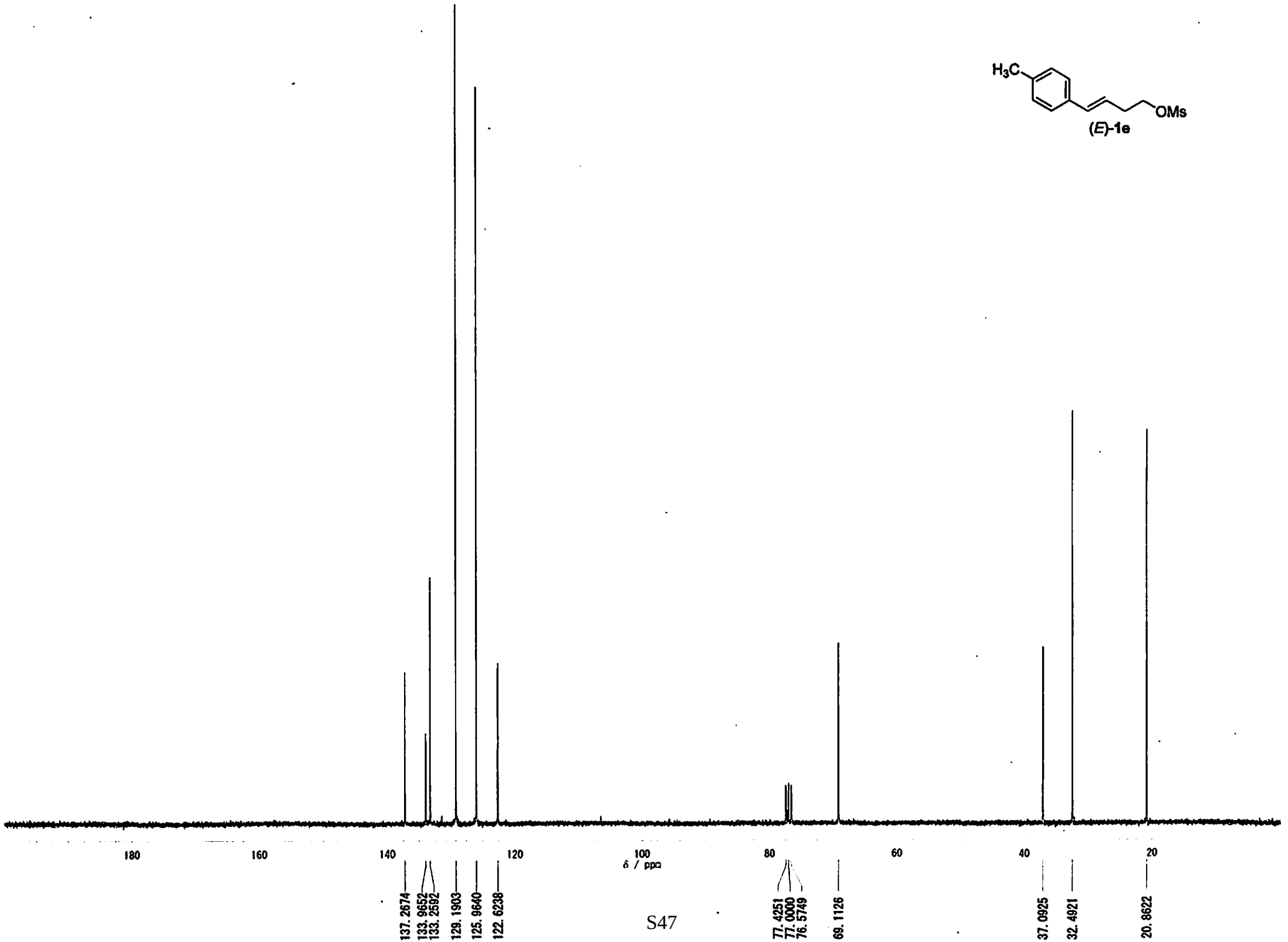
H3C
OMs
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160
140
120
100
δ / ppm
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60
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20
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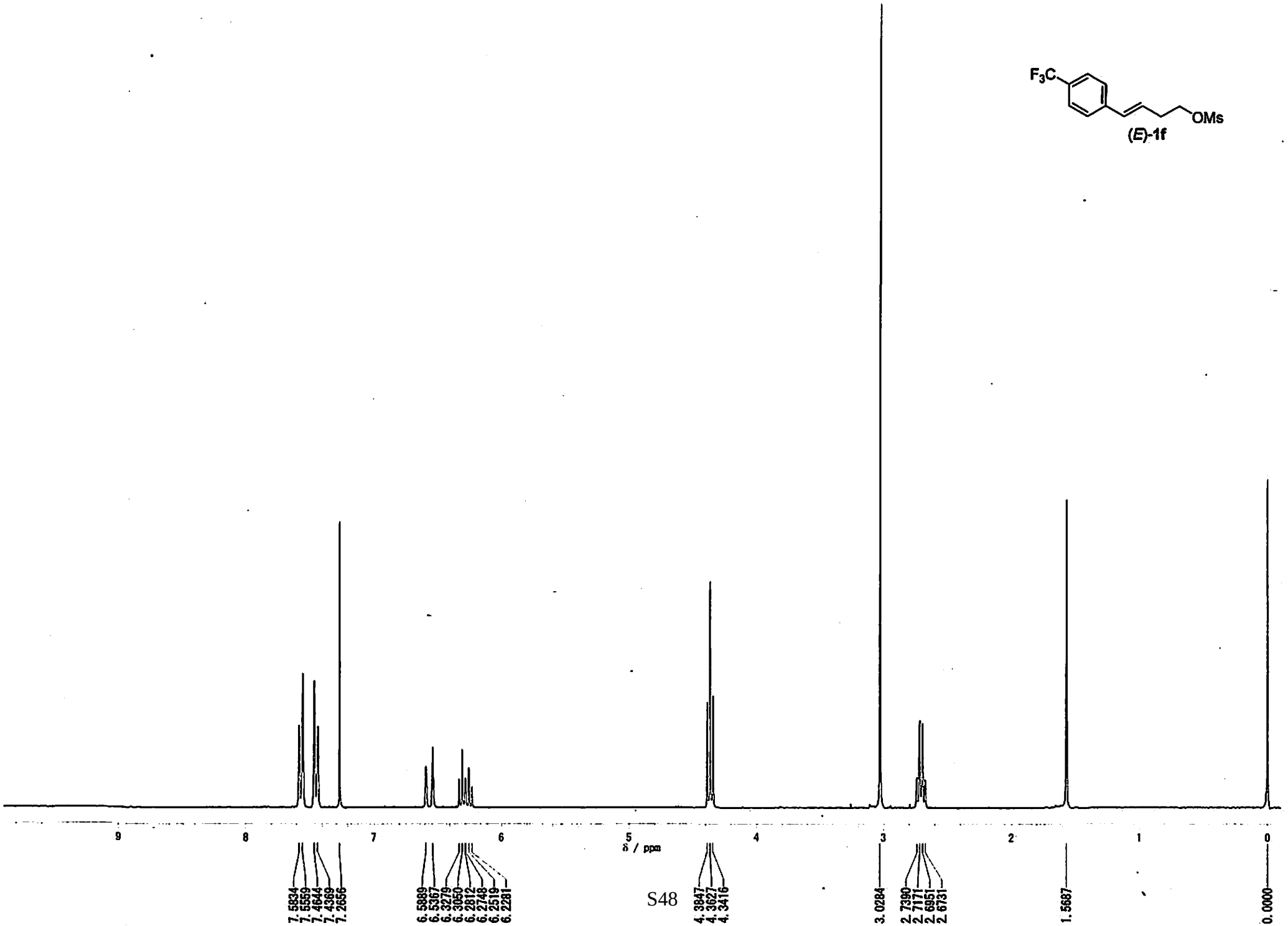
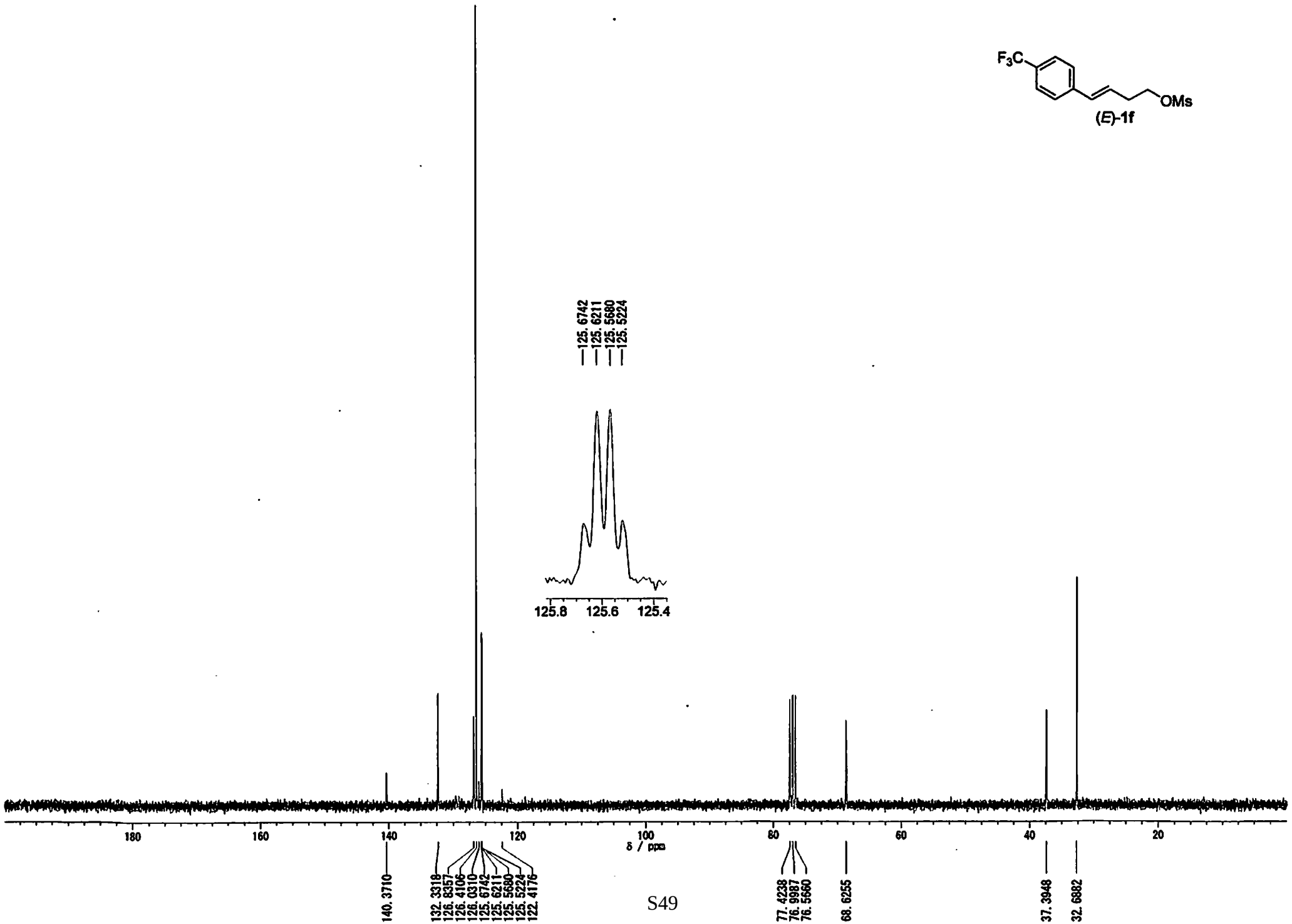
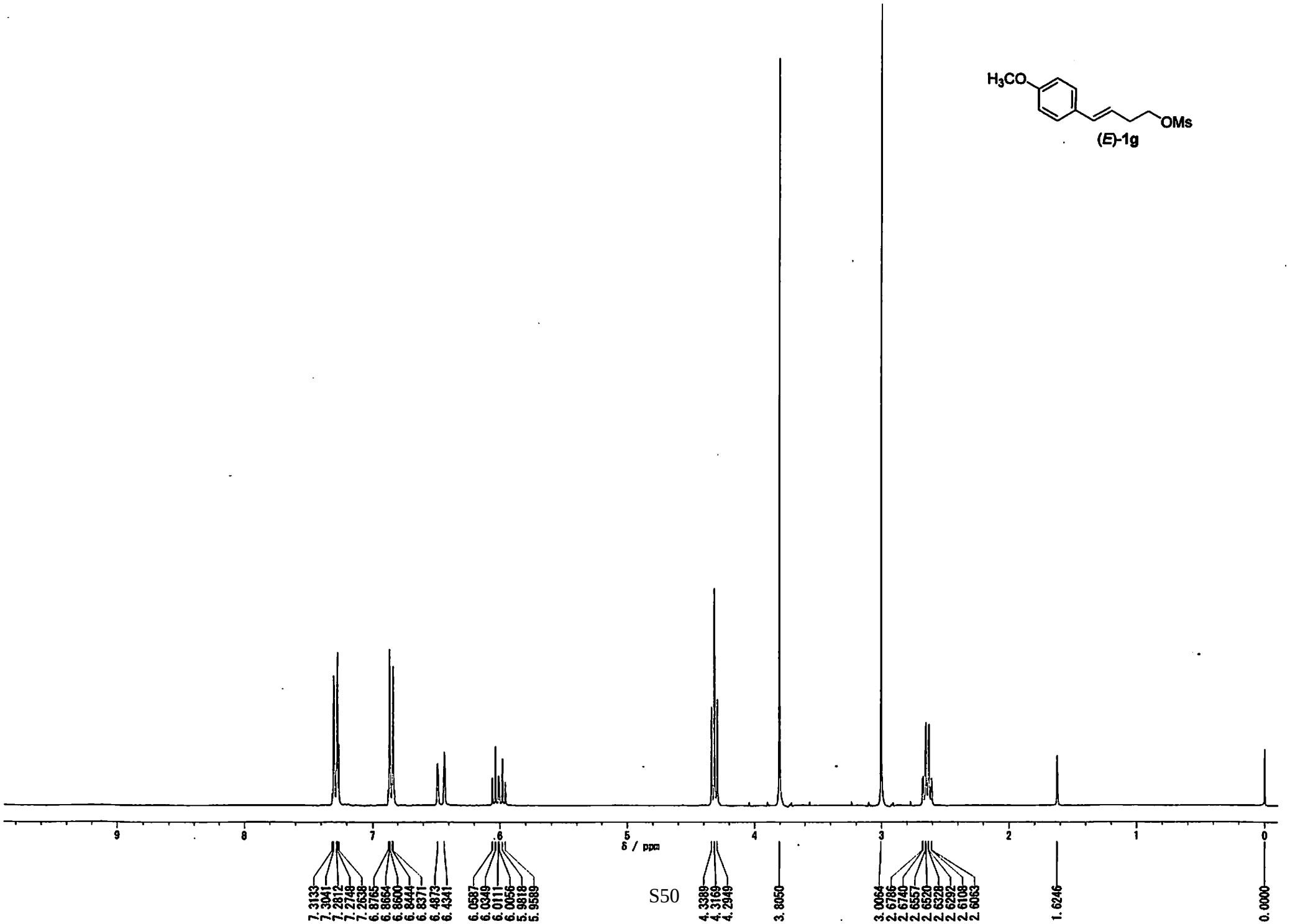
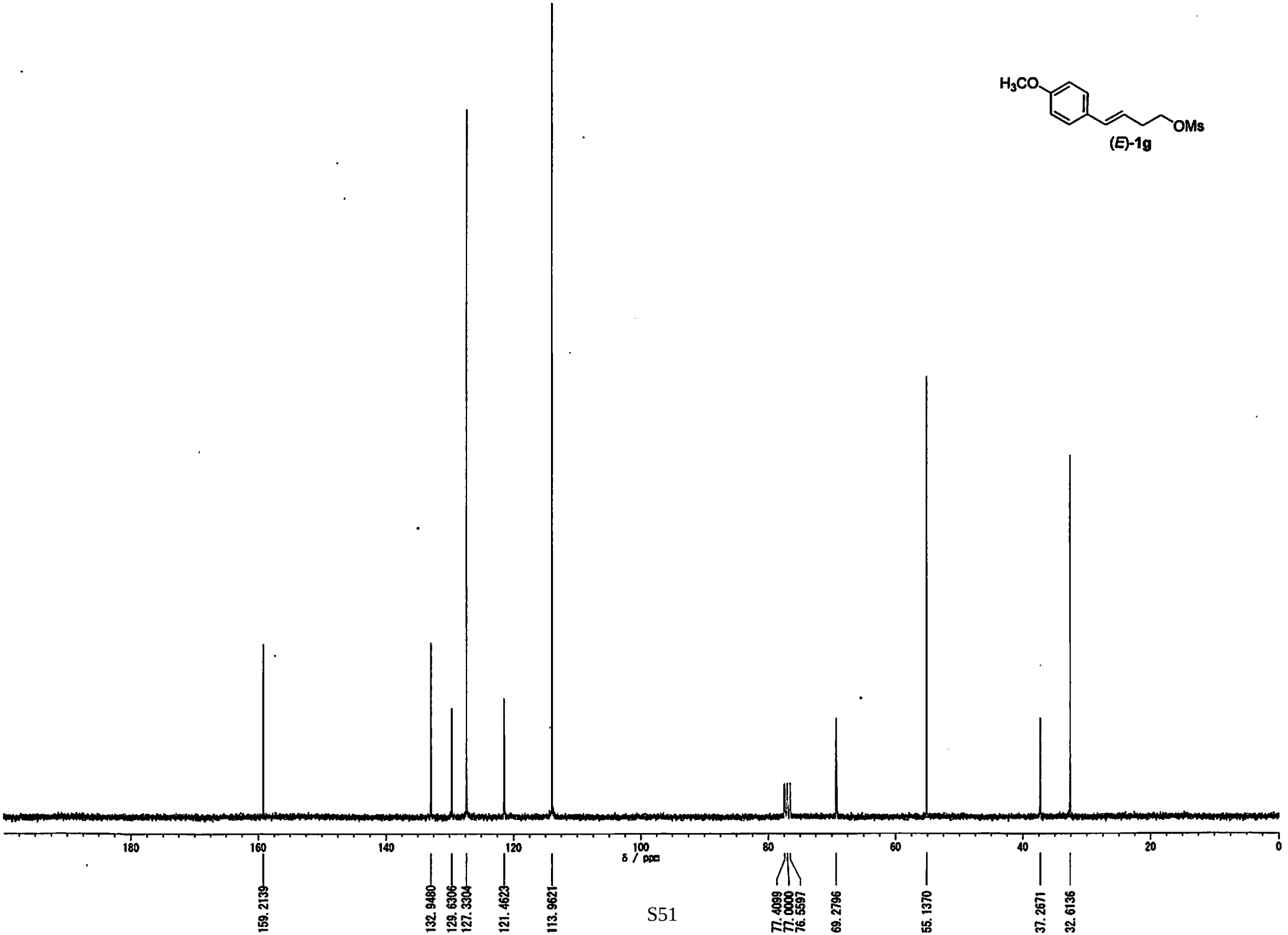
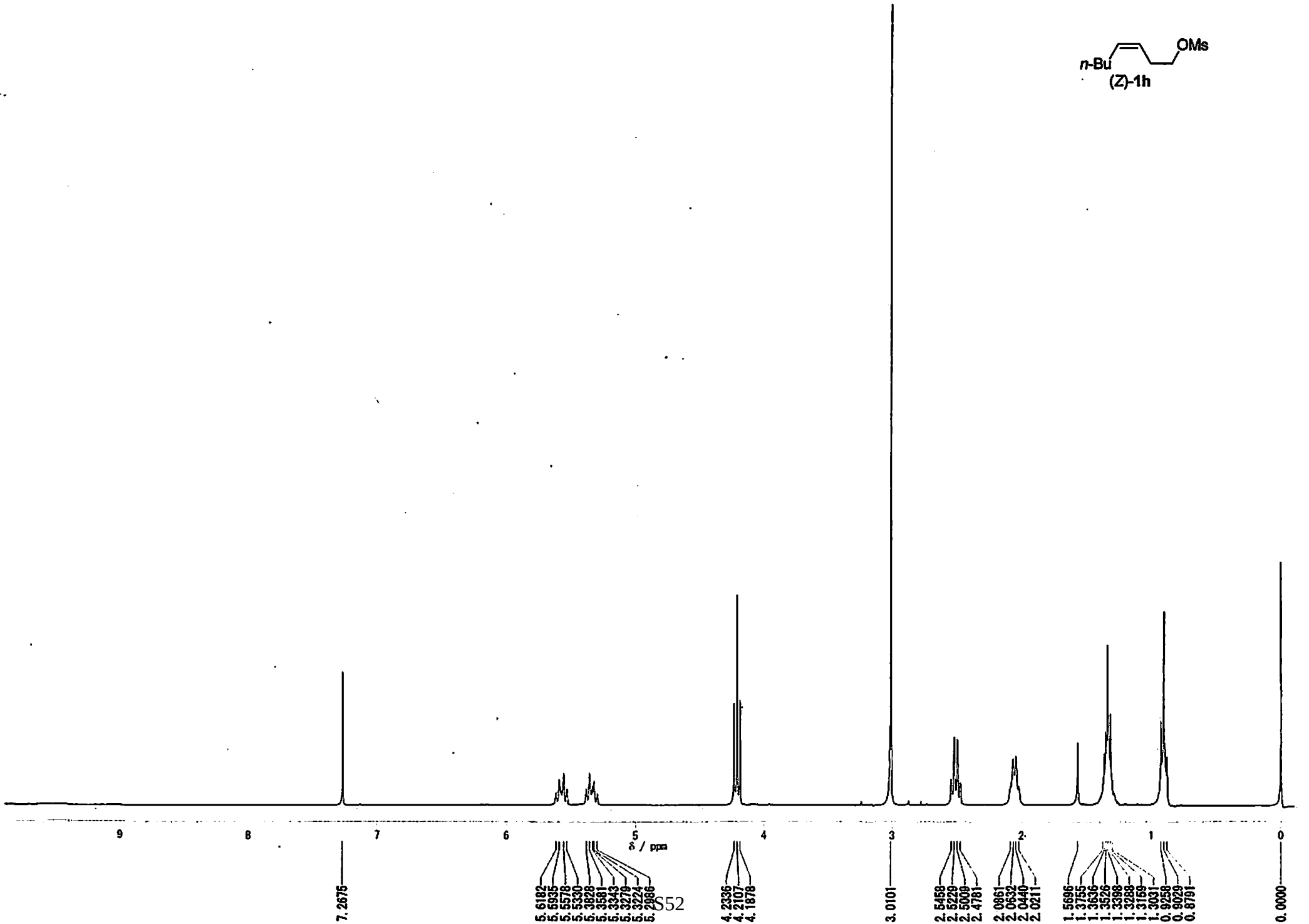
77.0000
76.5749
69.1126
37.0925
32.4921
20.8622

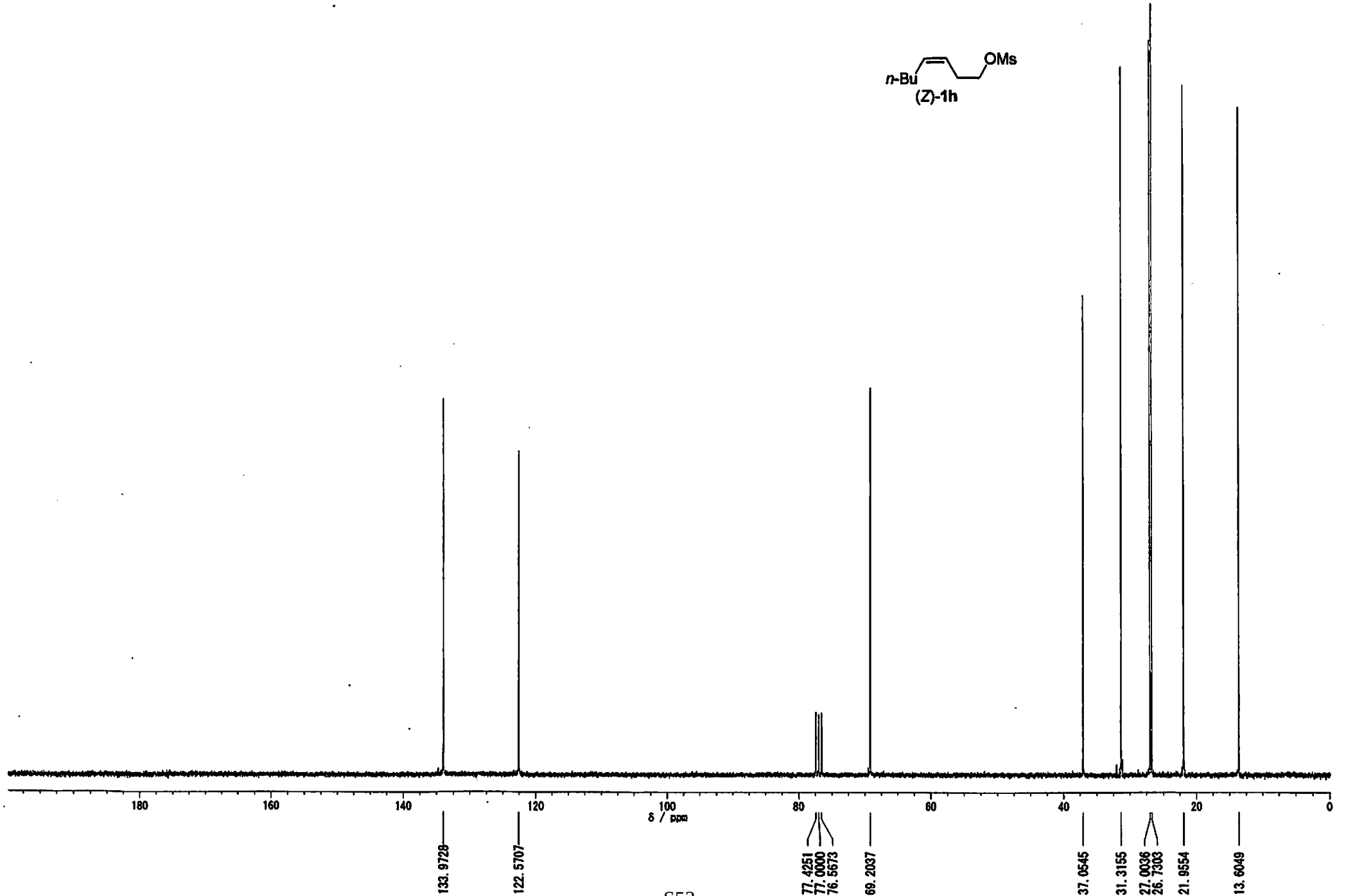

F3C
OMs
(E)-1f
9
8
7
6
5
δ / ppm
4
3
2
1
0
7.5834
7.5559
7.4644
7.4369
7.2656
6.5889
6.5367
6.3279
6.3050
6.2812
6.2748
6.2519
6.2281
4.3847
4.3627
4.3416
3.0284
2.7390
2.7171
2.6951
2.6731
1.5687
0.0000

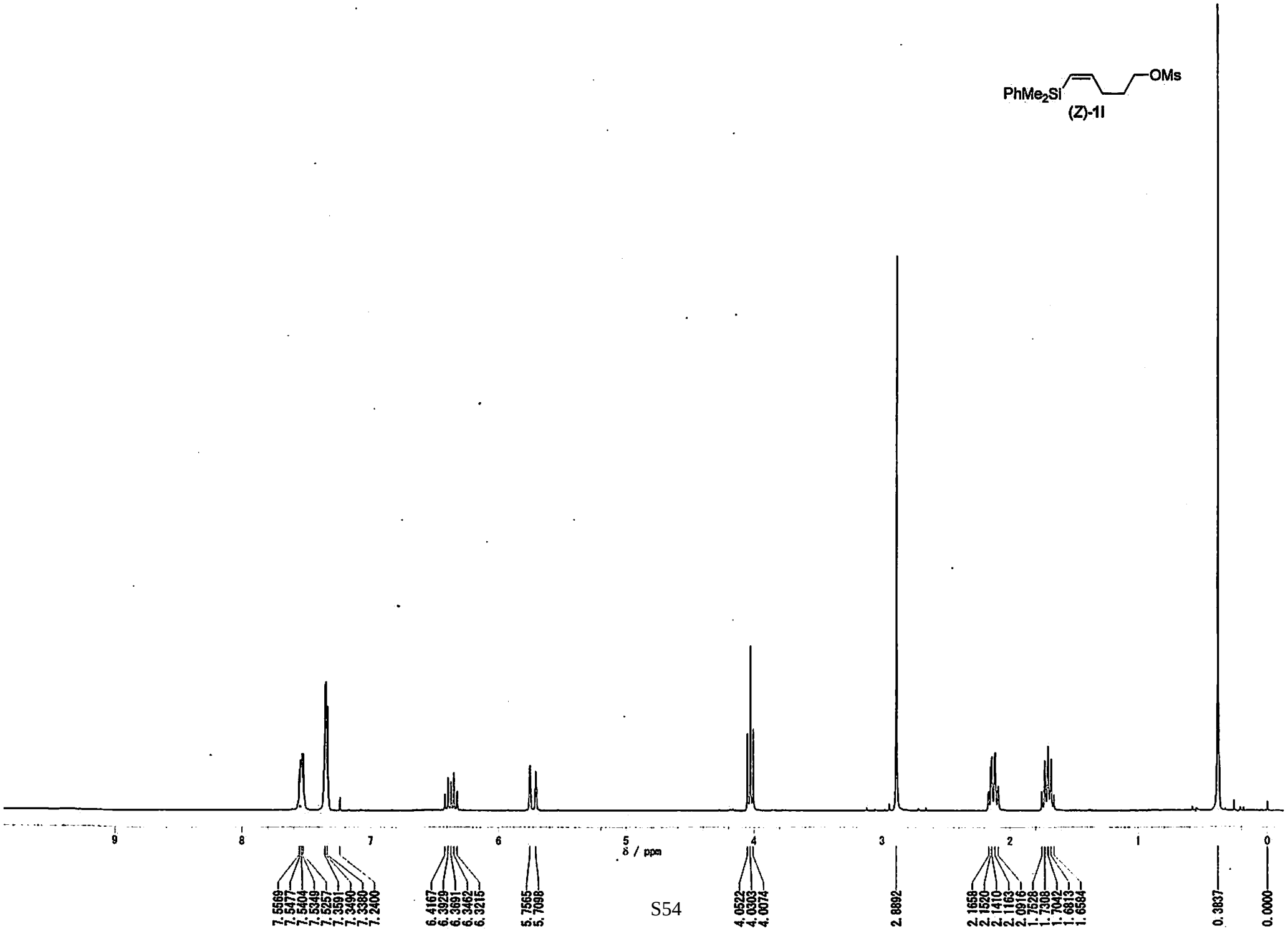

F3C
OMs
(E)-1f
125.6742
125.6211
125.5680
125.5224
125.8
125.6
125.4
180
160
140
120
100
80
60
40
20
δ / ppm
140.3710
132.3318
126.8357
126.4106
126.0310
125.6742
125.6211
125.5680
125.5224
122.4176
77.4238
76.9987
76.5660
68.6255
37.3948
32.6882

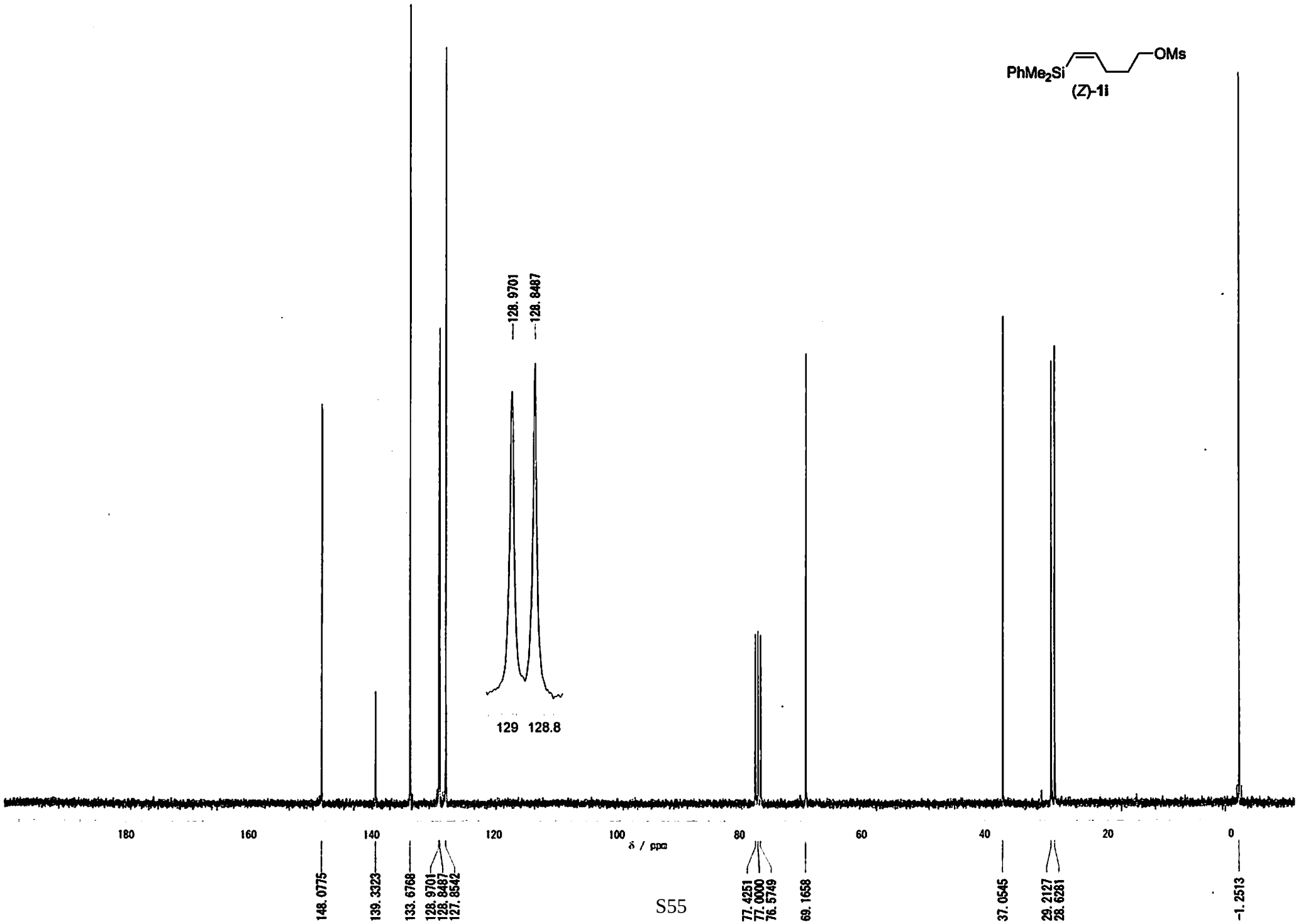

H3CO
OMs
(E)-1g
δ / ppm
7.3133
7.3041
7.2812
7.2748
7.2638
6.8765
6.8664
6.8600
6.8444
6.8371
6.4873
6.4341
6.0587
6.0349
6.0111
6.0056
5.9818
5.9589
4.3389
4.3169
4.2949
3.8050
3.0064
2.6786
2.6740
2.6557
2.6520
2.6328
2.6292
2.6108
2.6063
1.6246
0.0000

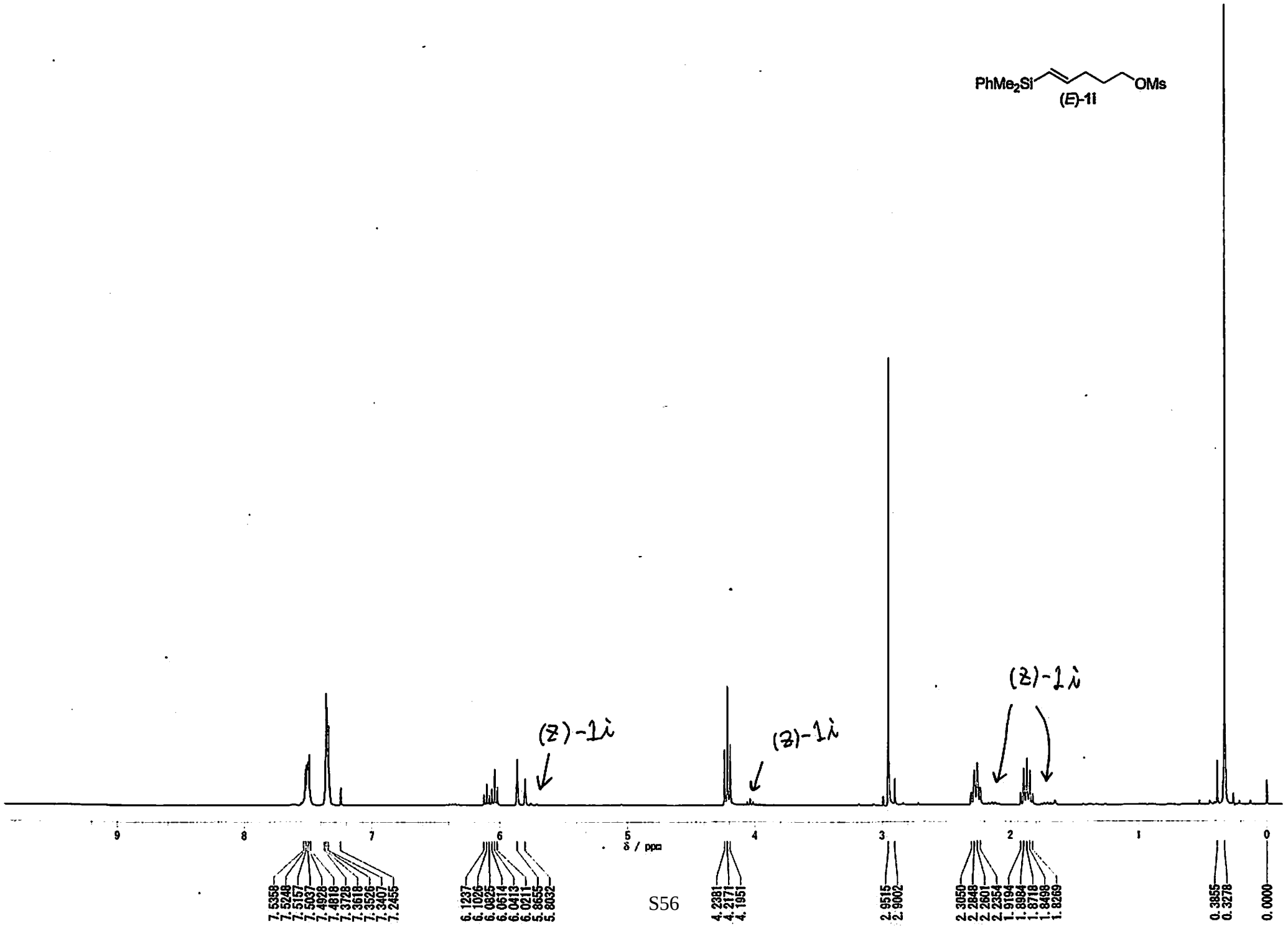

H3CO
OMs
(E)-1g
180
160
140
120
100
80
60
40
20
0
δ / ppm
159.2139
132.9480
129.6306
127.3304
121.4623
113.9621
77.4099
77.0000
76.5597
69.2796
55.1370
37.2671
32.6136

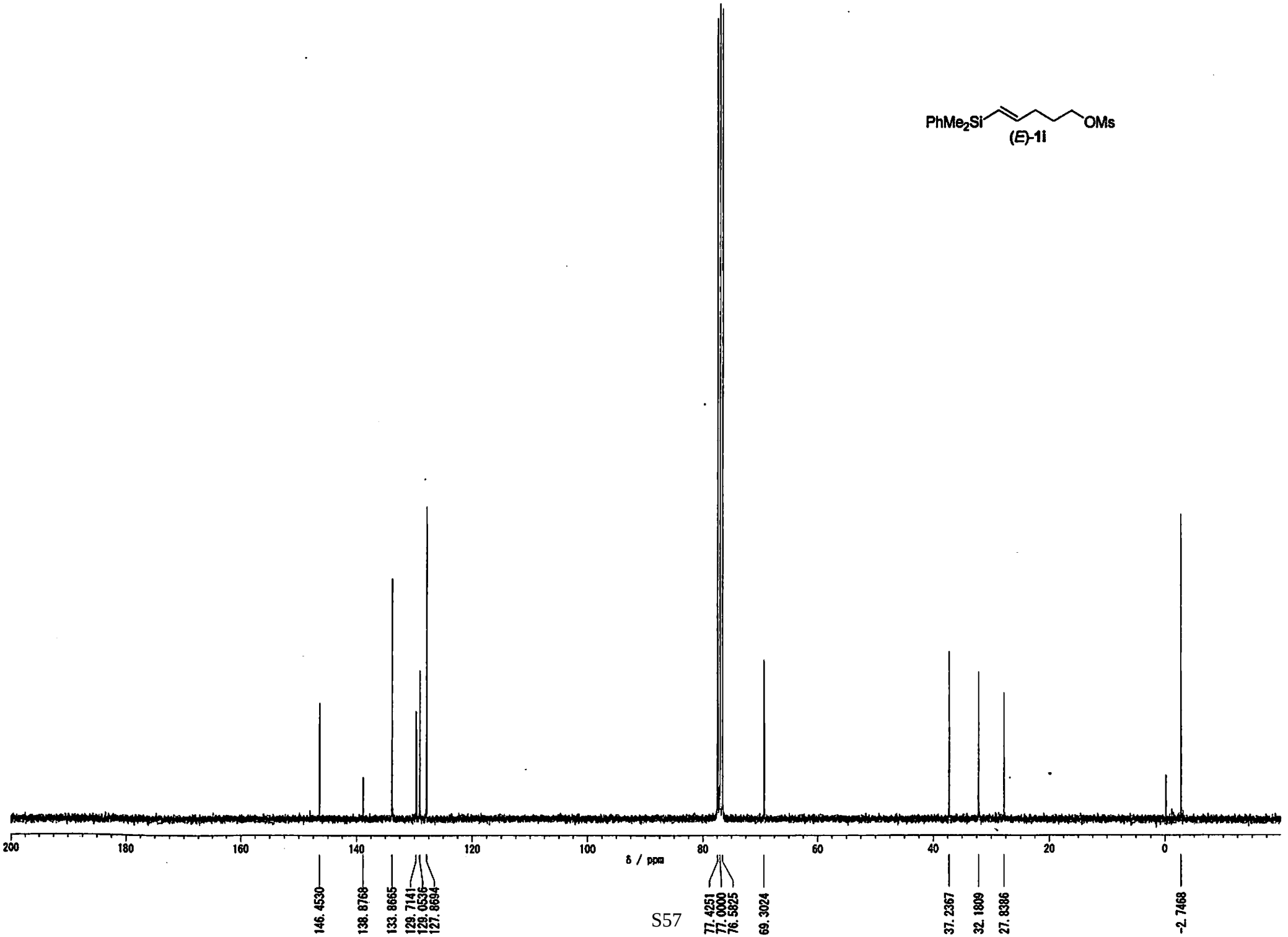

n-Bu
OMs
(Z)-1h
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2675
5.6182
5.5935
5.5578
5.5530
5.3828
5.3581
5.3343
5.3279
5.3224
5.2986
4.2336
4.2107
4.1878
3.0101
2.5458
2.5229
2.5009
2.4781
2.0861
2.0632
2.0440
2.0211
1.5696
1.3755
1.3636
1.3526
1.3398
1.3288
1.3159
1.3031
0.9258
0.9029
0.8791
0.0000

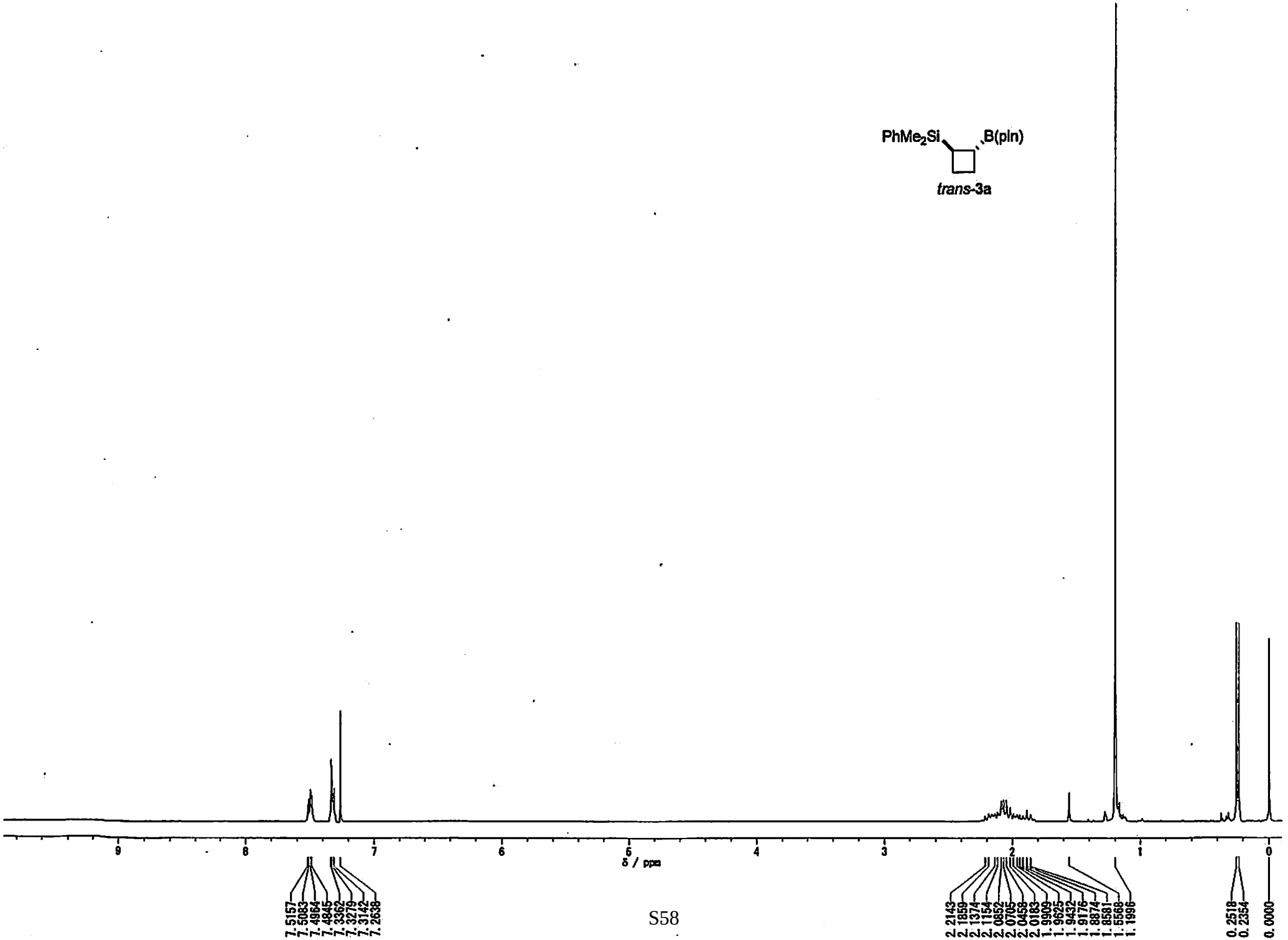

OMs
n-Bu
(Z)-1h
180
160
140
120
100
δ / ppm
80
60
40
20
0
133.9728
122.5707
77.4251
77.0000
76.5673
69.2037
37.0545
31.3155
27.0036
26.7303
21.9554
13.6049

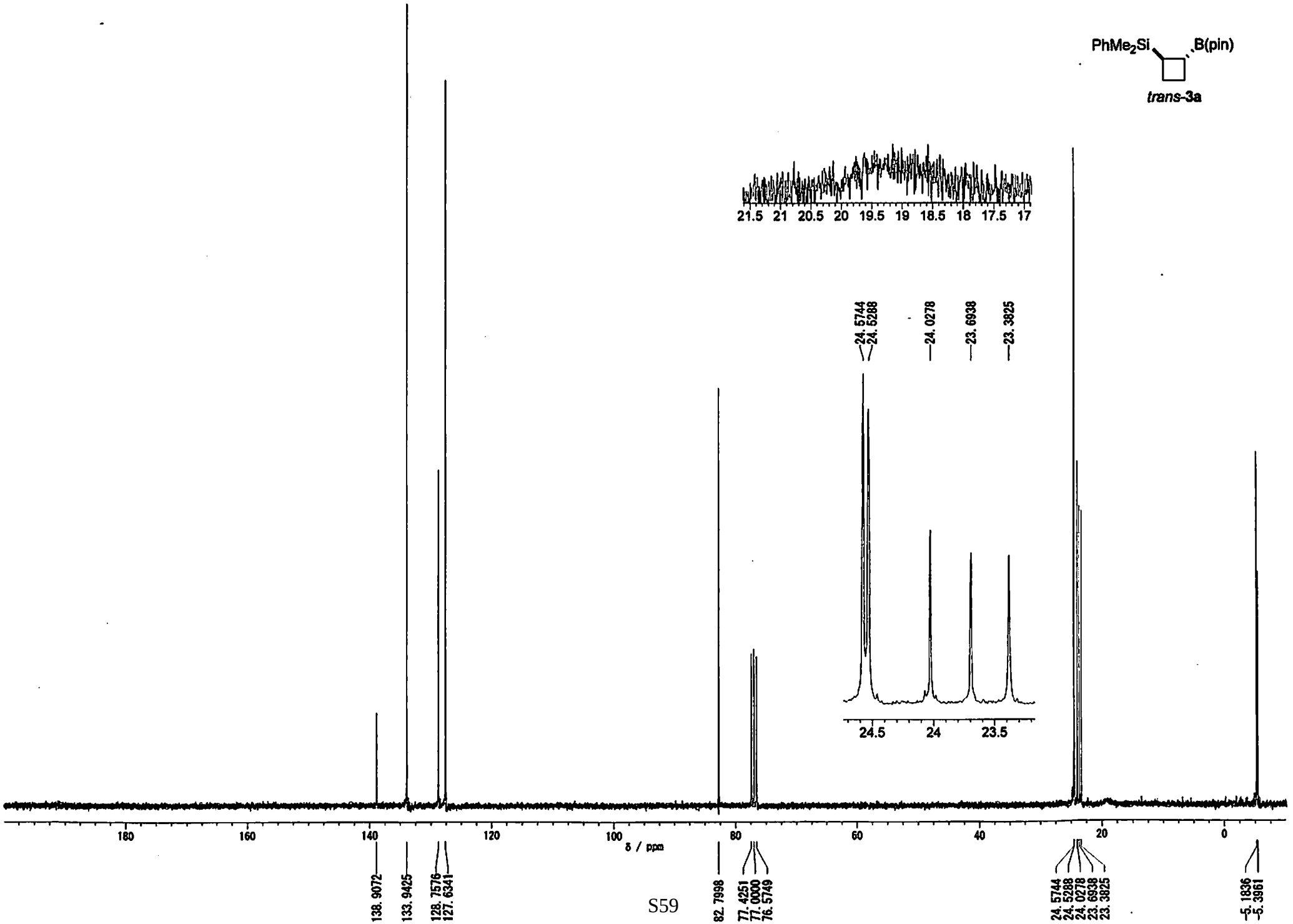

PhMe2Si
OMs
(Z)-1l
9
8
7
6
5
4
3
2
1
0
f1 / ppm
7.5569
7.5477
7.5404
7.5349
7.5257
7.3591
7.3490
7.3380
7.2400
6.4167
6.3929
6.3691
6.3462
6.3215
5.7565
5.7098
4.0522
4.0303
4.0074
2.8892
2.1658
2.1520
2.1410
2.1163
2.0916
1.7528
1.7308
1.7042
1.6813
1.6584
0.3837
0.0000

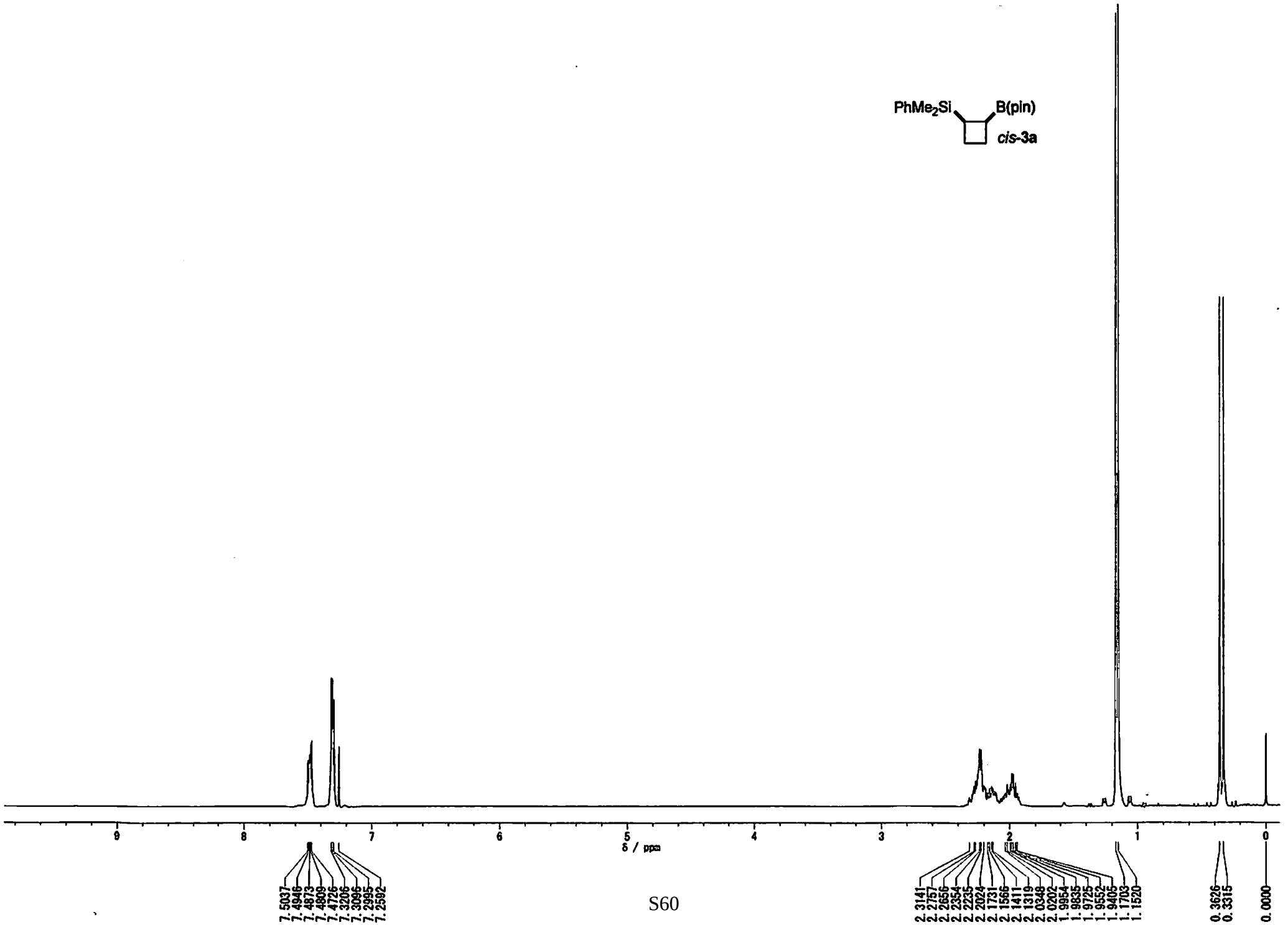

PhMe2Si
OMs
(Z)-1i
128.9701
128.8487
129
128.8
δ / ppm
180
160
140
120
100
80
60
40
20
0
148.0775
139.3323
133.6768
128.9701
128.8487
127.8542
77.4251
77.0000
76.5749
69.1658
37.0545
29.2127
28.6281
-1.2513

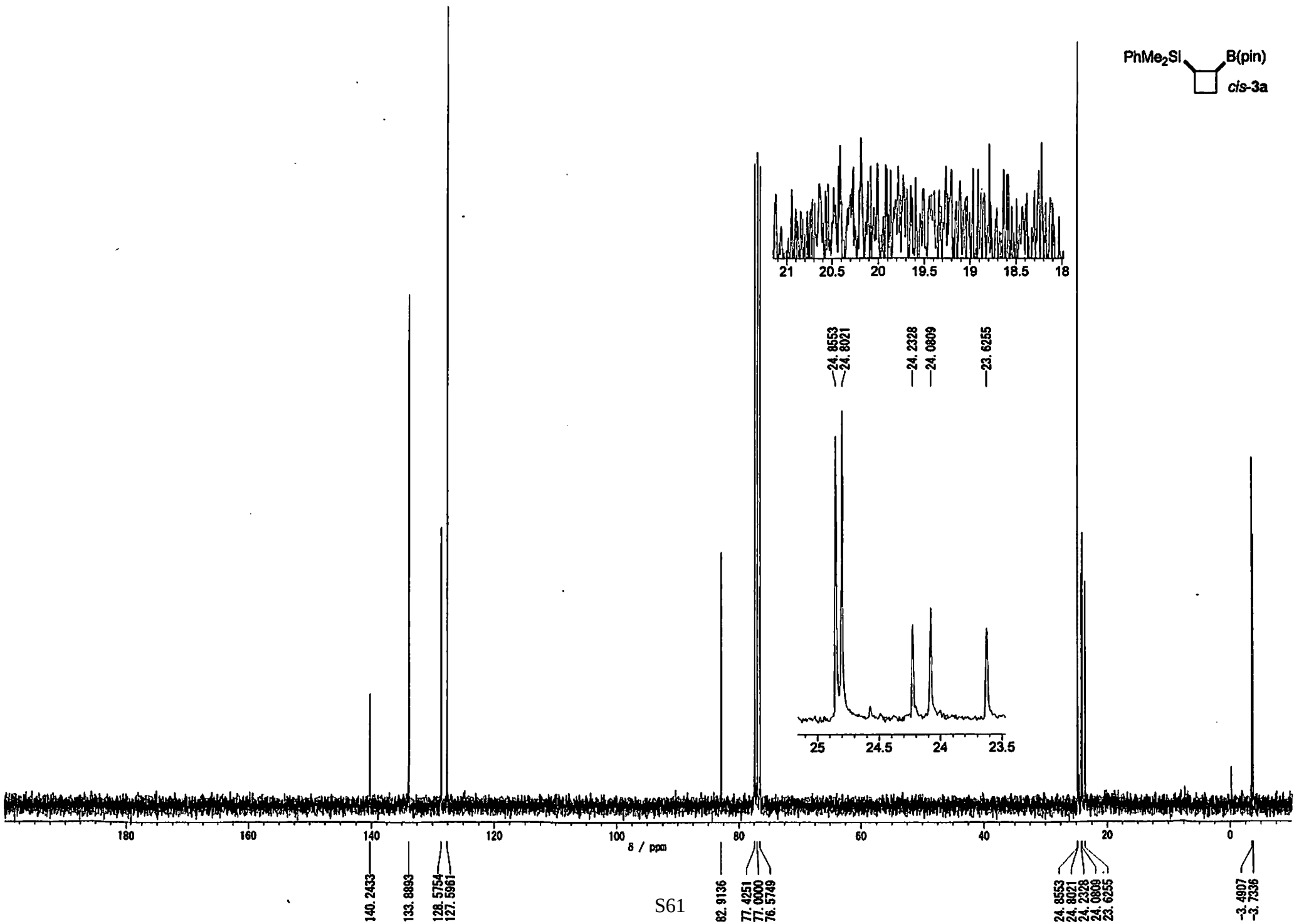

PhMe2Si
OMs
(E)-1i
(Z)-1i
(Z)-1i
(Z)-1i
δ / ppm
9
8
7
6
5
4
3
2
1
0
7.5358
7.5248
7.5157
7.5037
7.4928
7.4818
7.3728
7.3618
7.3526
7.3407
7.2455
6.1237
6.1026
6.0825
6.0614
6.0413
6.0211
5.8655
5.8032
4.2381
4.2171
4.1951
2.9515
2.9002
2.3050
2.2848
2.2601
2.2354
1.9194
1.8984
1.8718
1.8498
1.8269
0.3855
0.3278
0.0000

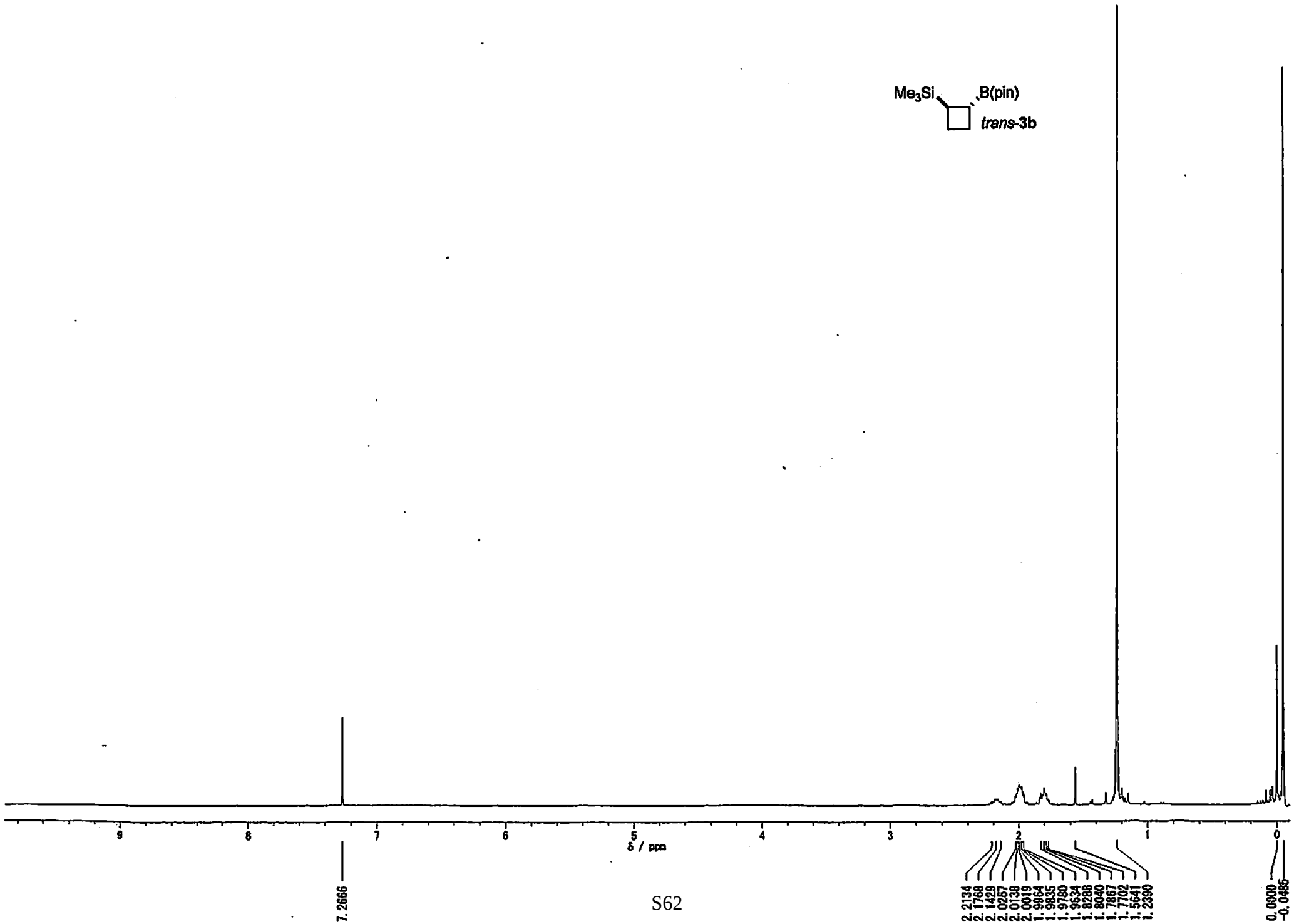

PhMe2Si
OMs
(E)-1i
δ / ppm
146.4530
138.8768
133.8665
129.7141
129.0536
127.8694
77.4251
77.0000
76.5825
69.3024
37.2367
32.1809
27.8386
-2.7468

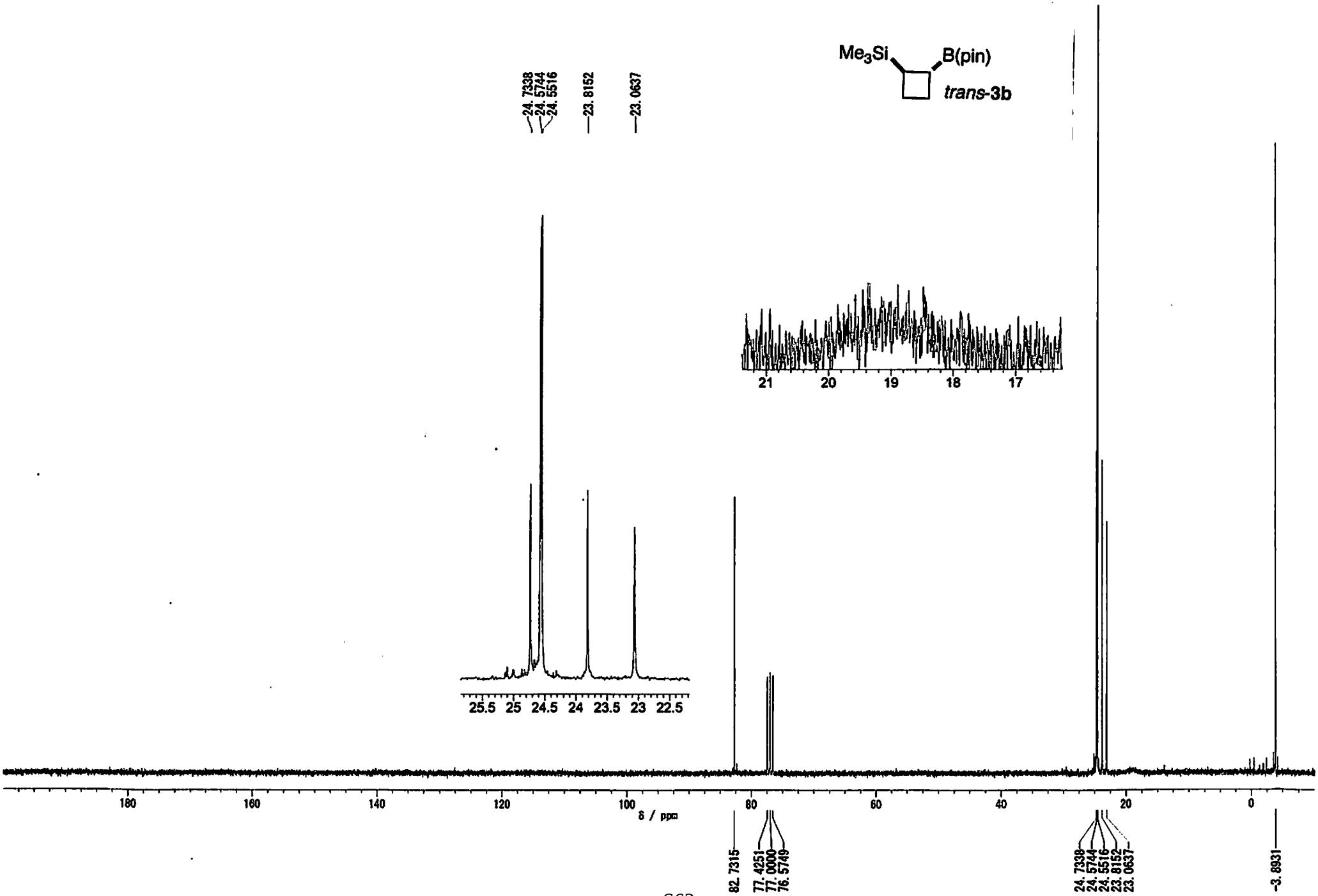

PhMe2Si
B(pin)
trans-3a
δ / ppm
9
8
7
6
5
4
3
2
1
0
7.5157
7.5083
7.4964
7.4845
7.3362
7.3279
7.3142
7.2638
2.2143
2.1859
2.1374
2.1154
2.0852
2.0705
2.0458
2.0183
1.9909
1.9625
1.9432
1.9176
1.8874
1.8581
1.5568
1.1996
0.2518
0.2354
0.0000

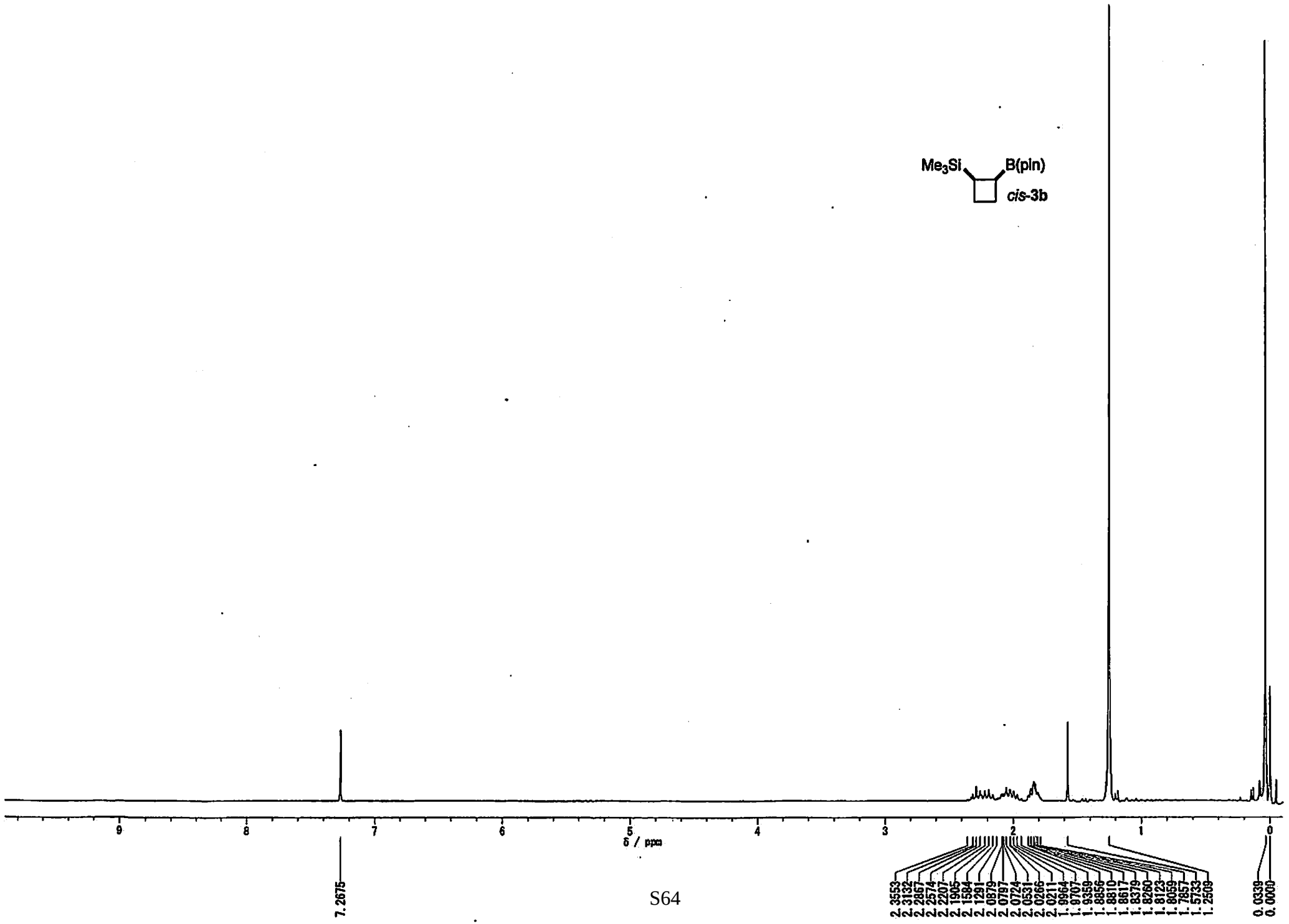

PhMe2Si
B(pin)
trans-3a
21.5 21 20.5 20 19.5 19 18.5 18 17.5 17
24.5744
24.5288
24.0278
23.6938
23.3825
24.5 24 23.5
180 160 140 120 100 80 60 40 20 0
δ / ppm
138.9072
133.9425
128.7576
127.6341
82.7998
77.4251
77.0000
76.5749
24.5744
24.5288
24.0278
23.6938
23.3825
-5.1836
-5.3961

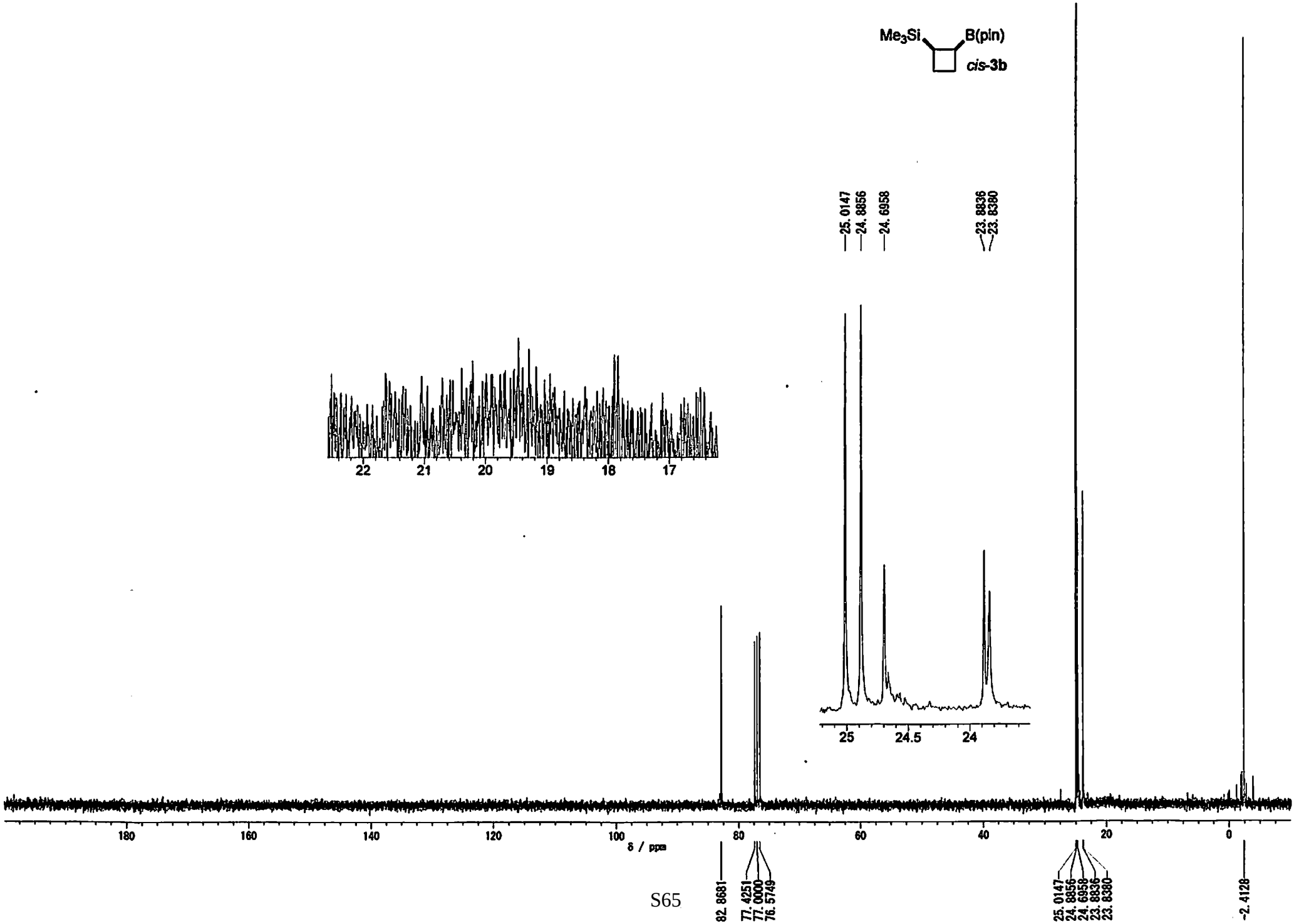

PhMe2Si
B(pin)
cis-3a
δ / ppm
7.5037
7.4946
7.4873
7.4809
7.4726
7.3206
7.3096
7.2995
7.2592
2.3141
2.2757
2.2656
2.2354
2.2235
2.2024
2.1731
2.1566
2.1411
2.1319
2.0348
2.0202
1.9954
1.9835
1.9725
1.9552
1.9405
1.1703
1.1520
0.3626
0.3315
0.0000

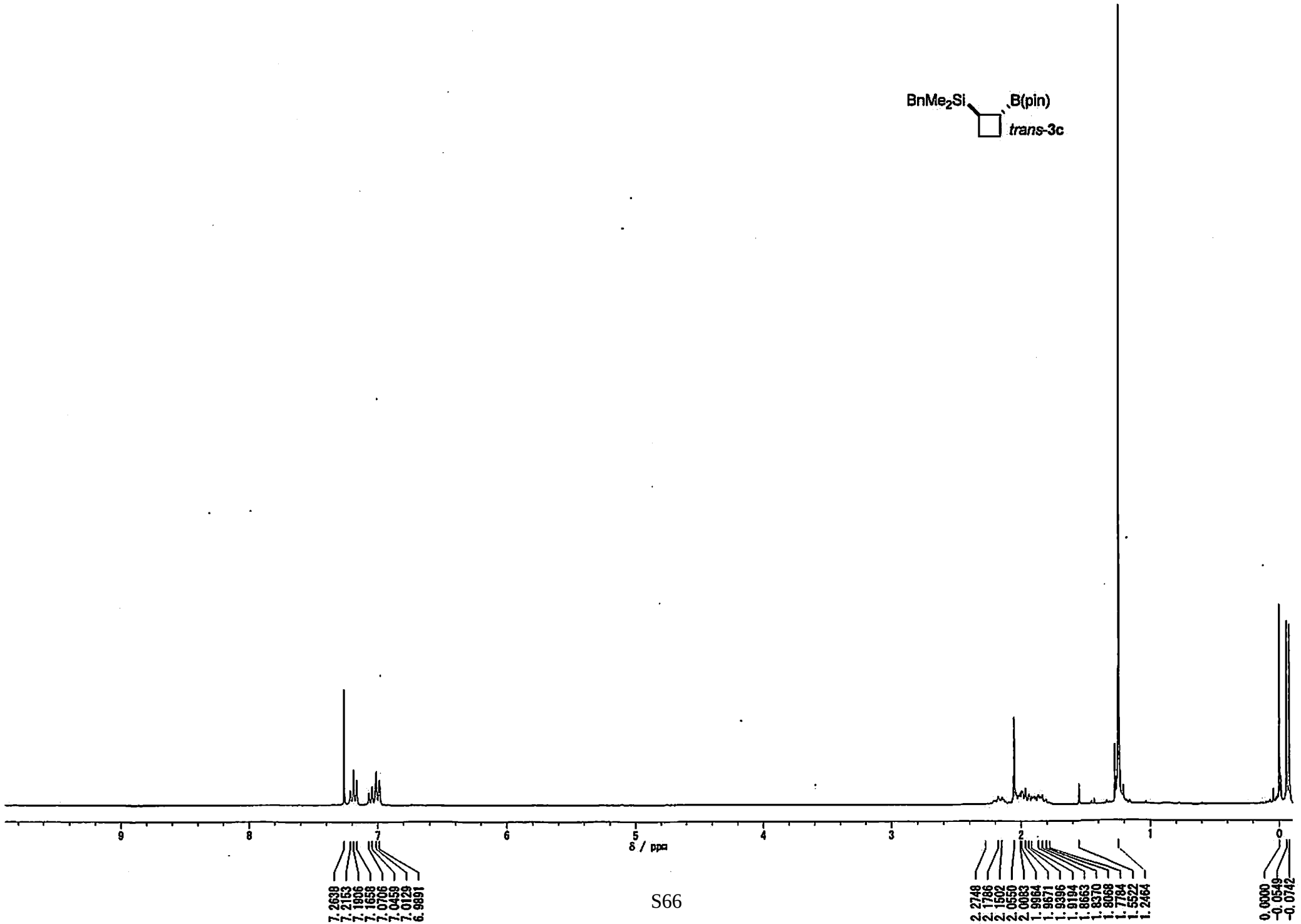

PhMe2Si
B(pin)
cis-3a
δ / ppm
140.2433
133.8893
128.5754
127.5961
82.9136
77.4251
77.0000
76.5749
24.8553
24.8021
24.2328
24.0809
23.6255
-3.4907
-3.7336

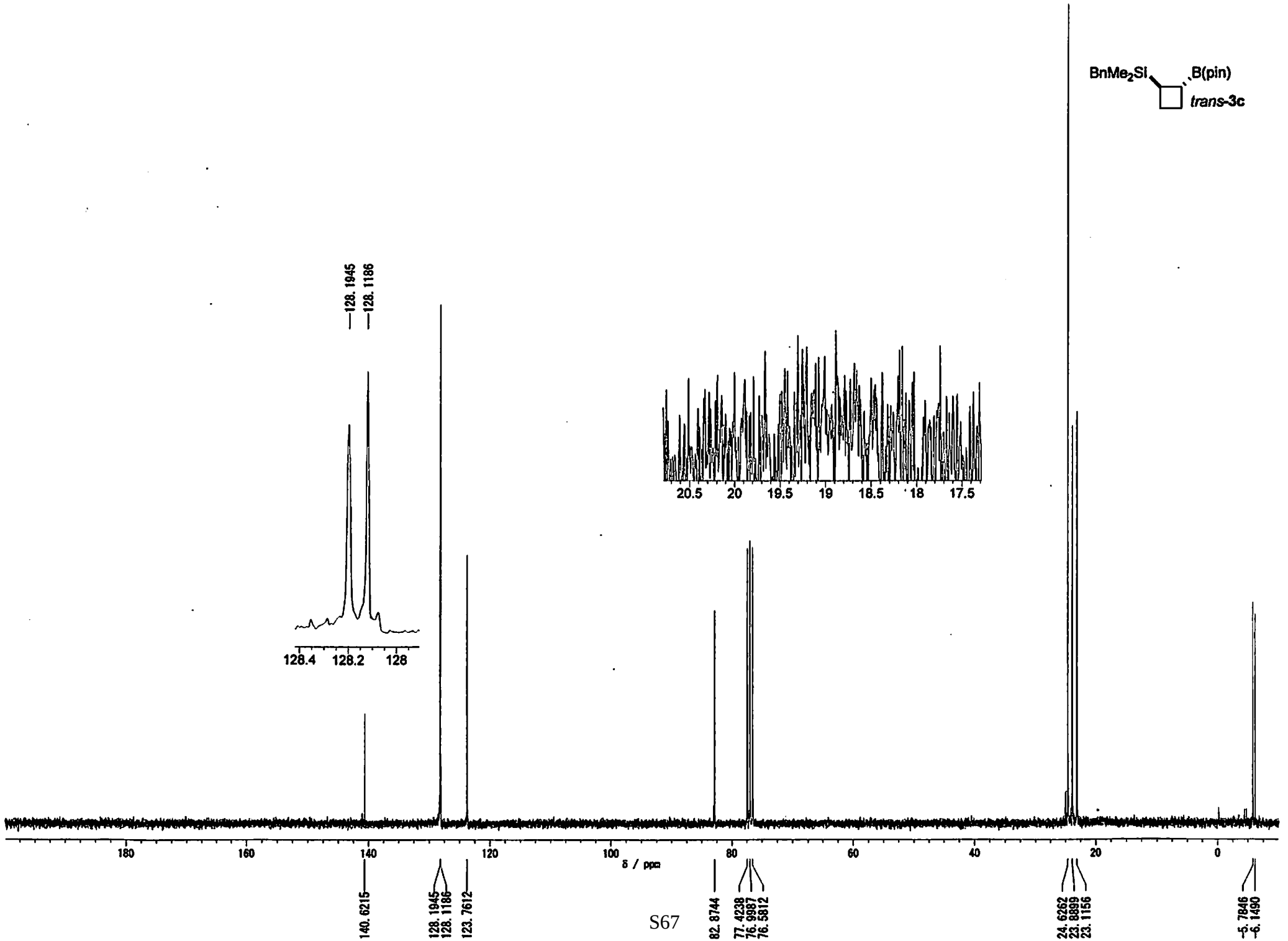

Me3Si
B(pin)
trans-3b
δ / ppm
9
8
7
6
5
4
3
2
1
0
7.2666
2.2134
2.1768
2.1429
2.0257
2.0138
2.0019
1.9964
1.9835
1.9780
1.9534
1.8288
1.8040
1.7867
1.7702
1.5641
1.2390
0.0000
-0.0485

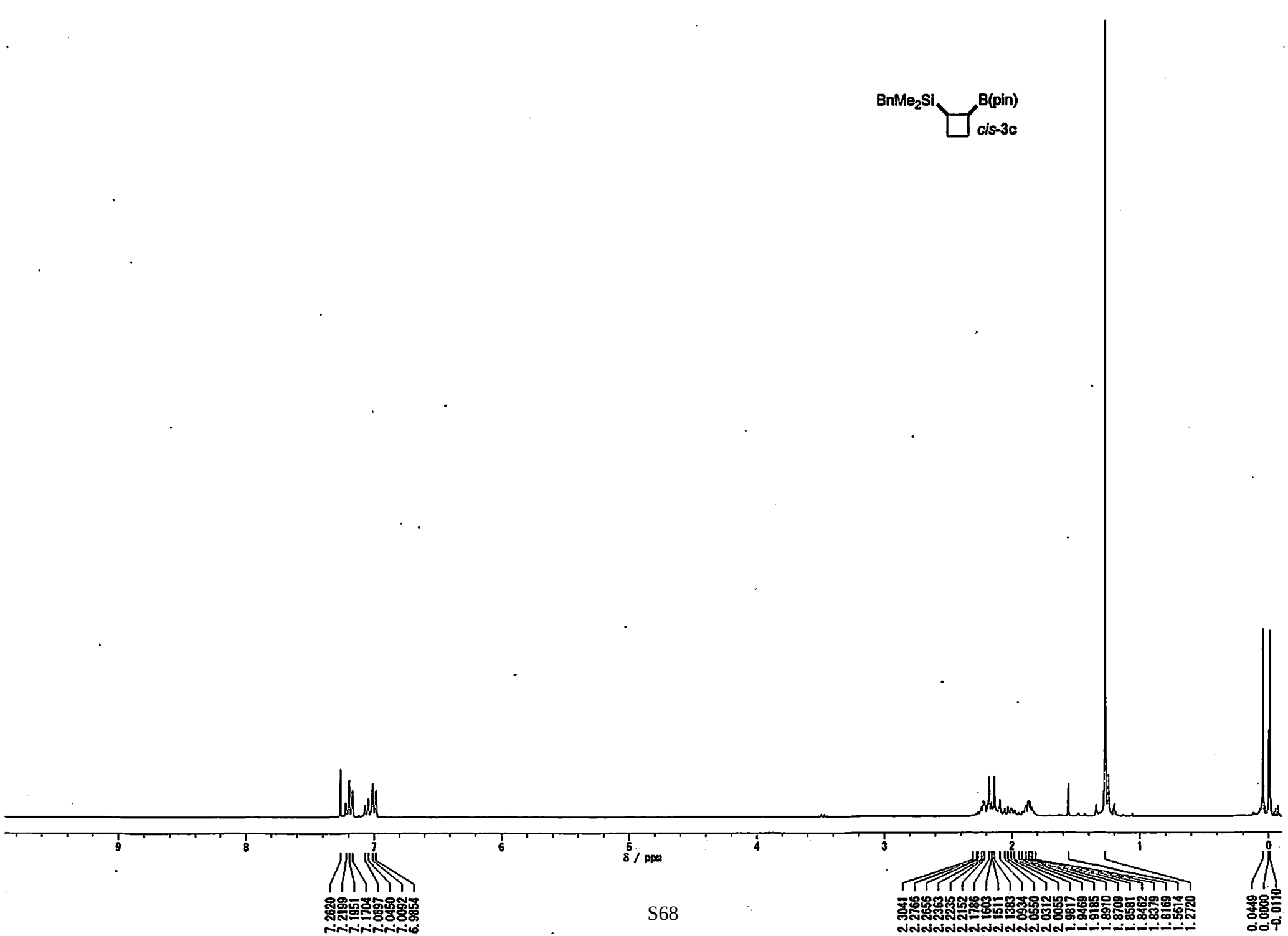

Me3Si
B(pin)
trans-3b
24.7338
24.5744
24.5516
23.8152
23.0637
δ / ppm
82.7315
77.4251
77.0000
76.5749
-3.8931

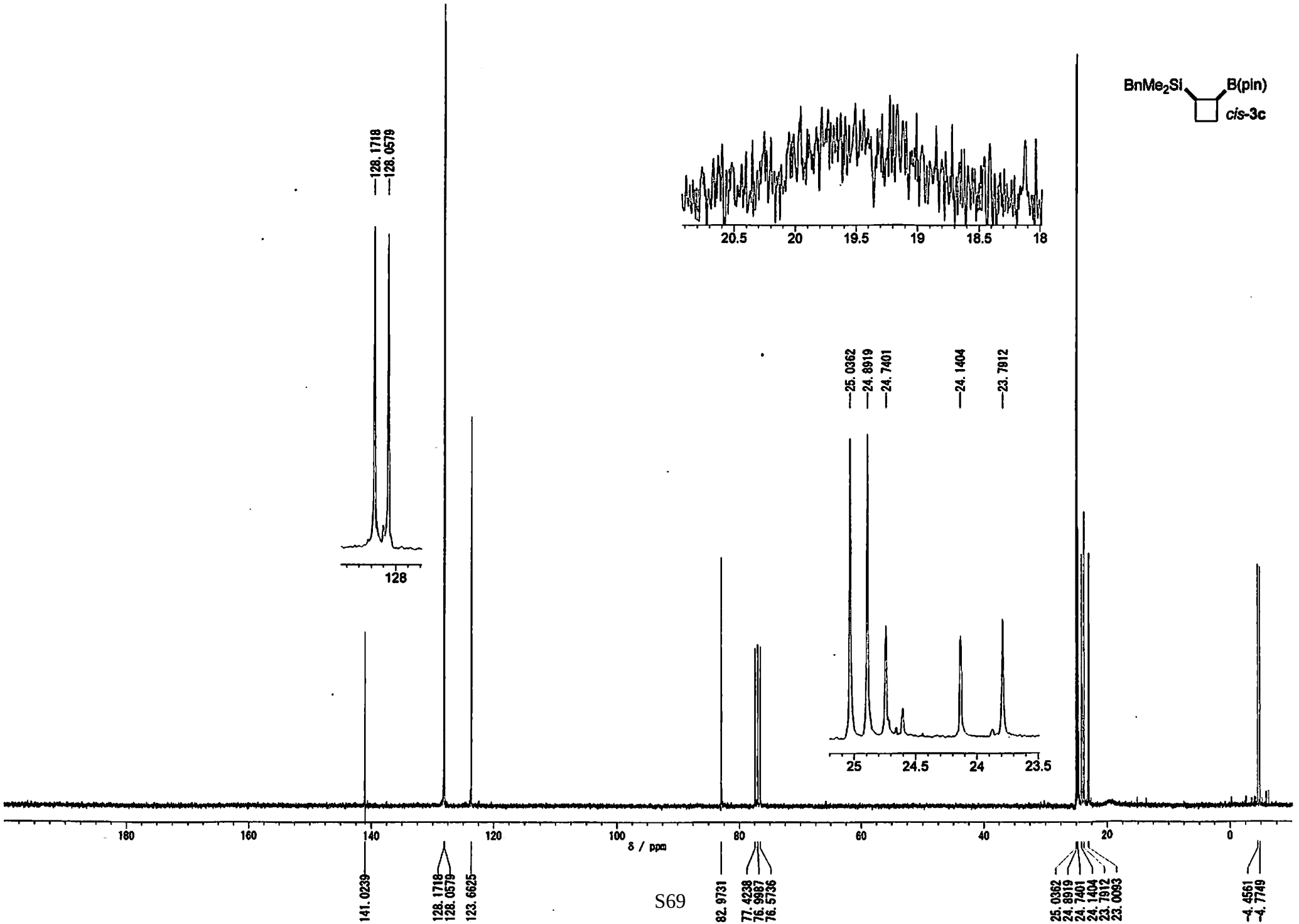

Me3Si
B(pin)
cis-3b
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2675
2.3553
2.3132
2.2867
2.2574
2.2207
2.1905
2.1584
2.1291
2.0879
2.0797
2.0724
2.0531
2.0266
2.0211
1.9964
1.9707
1.9359
1.8856
1.8810
1.8617
1.8379
1.8260
1.8123
1.8059
1.7857
1.5733
1.2509
0.0339
0.0000

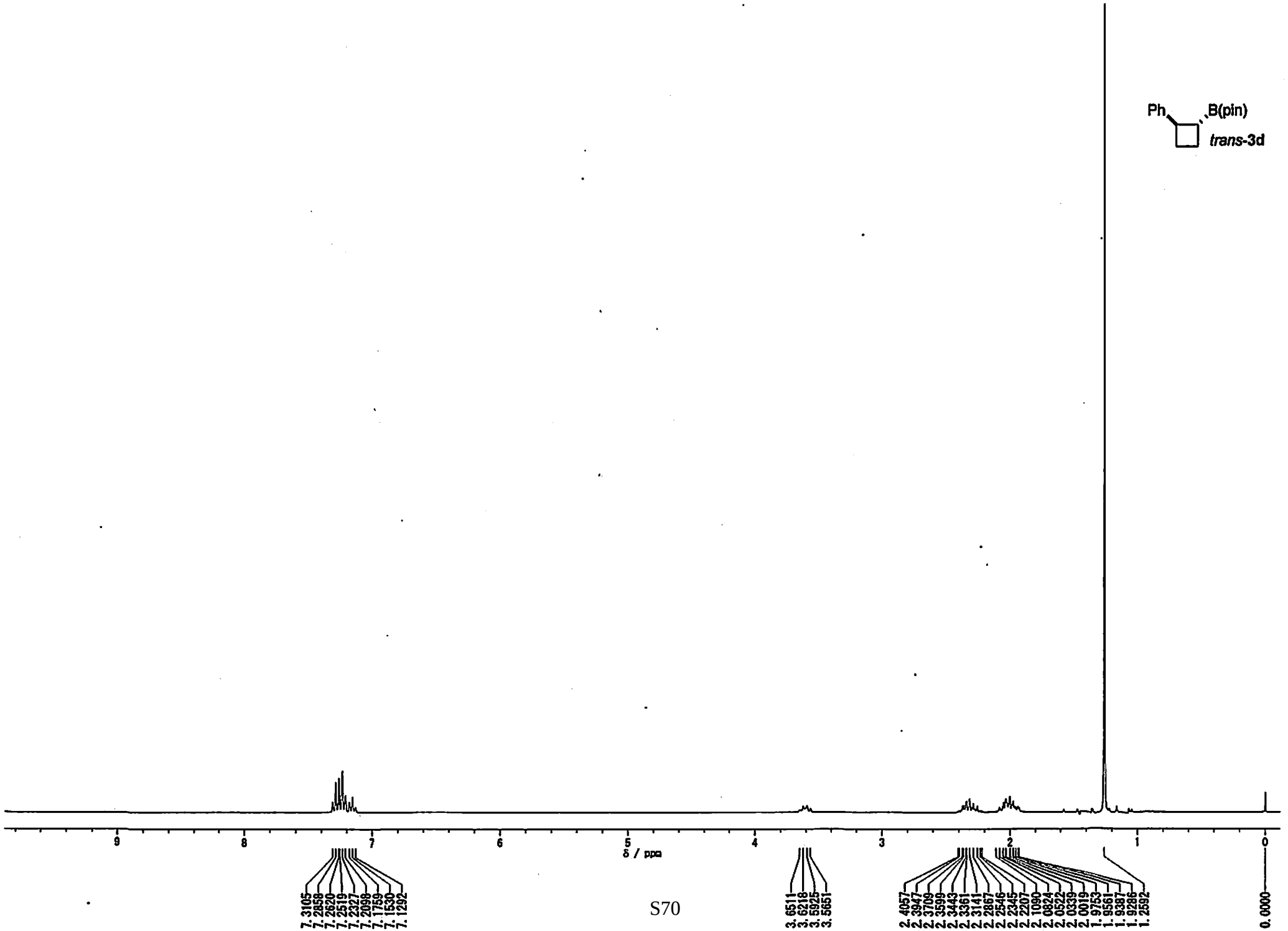

Me3Si
B(pin)
cis-3b
25.0147
24.8856
24.6958
23.8836
23.8380
22
21
20
19
18
17
25
24.5
24
180
160
140
120
100
80
60
40
20
0
δ / ppm
82.8681
77.4251
77.0000
76.5749
25.0147
24.8856
24.6958
23.8836
23.8380
-2.4128

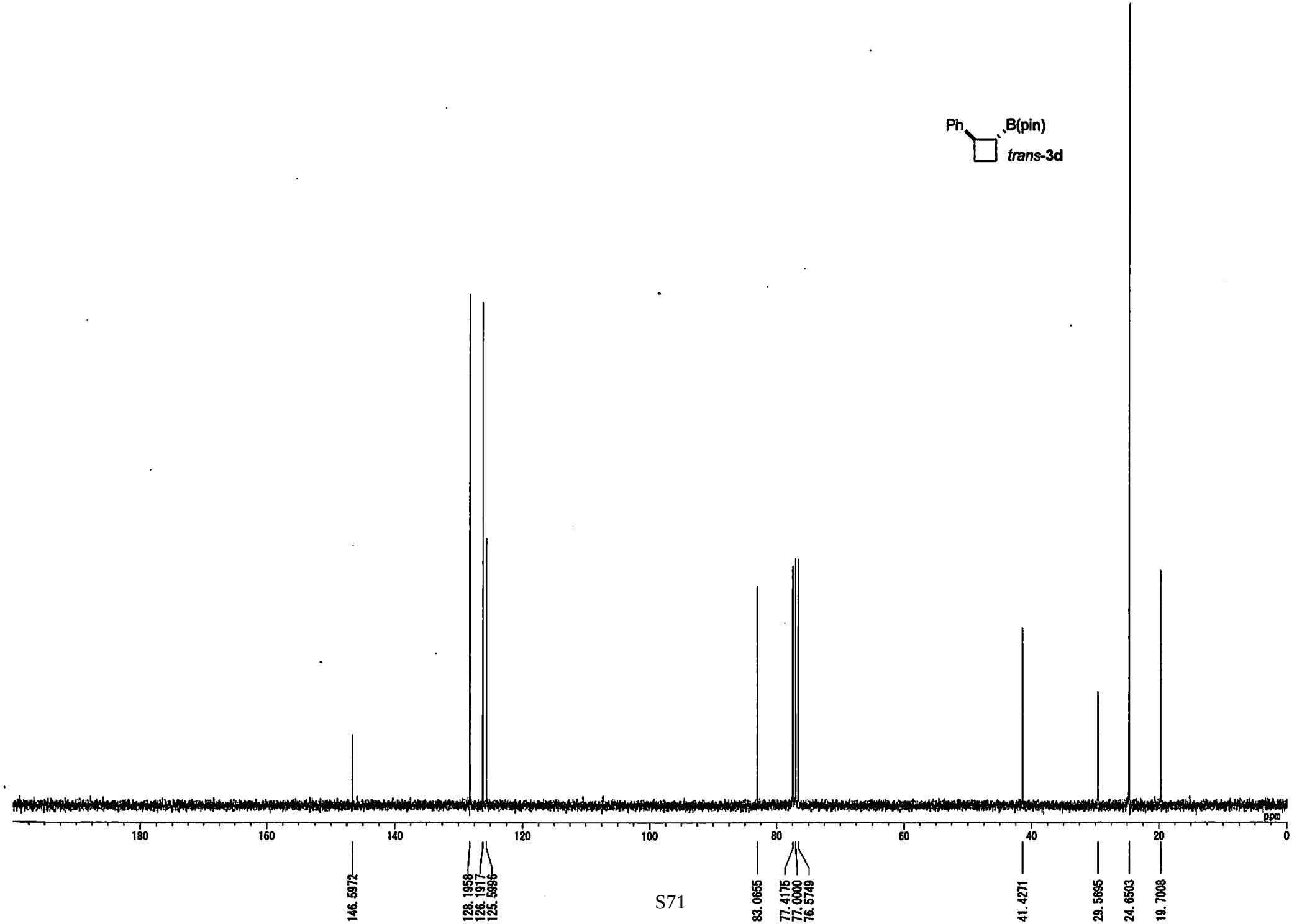

BnMe2Si
B(pin)
trans-3c
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2639
7.2153
7.1906
7.1658
7.0706
7.0459
7.0129
6.9891
2.2748
2.1786
2.1502
2.0550
2.0083
1.9964
1.9671
1.9396
1.9194
1.8663
1.8370
1.8068
1.7784
1.5522
1.2464
0.0000
-0.0549
-0.0742

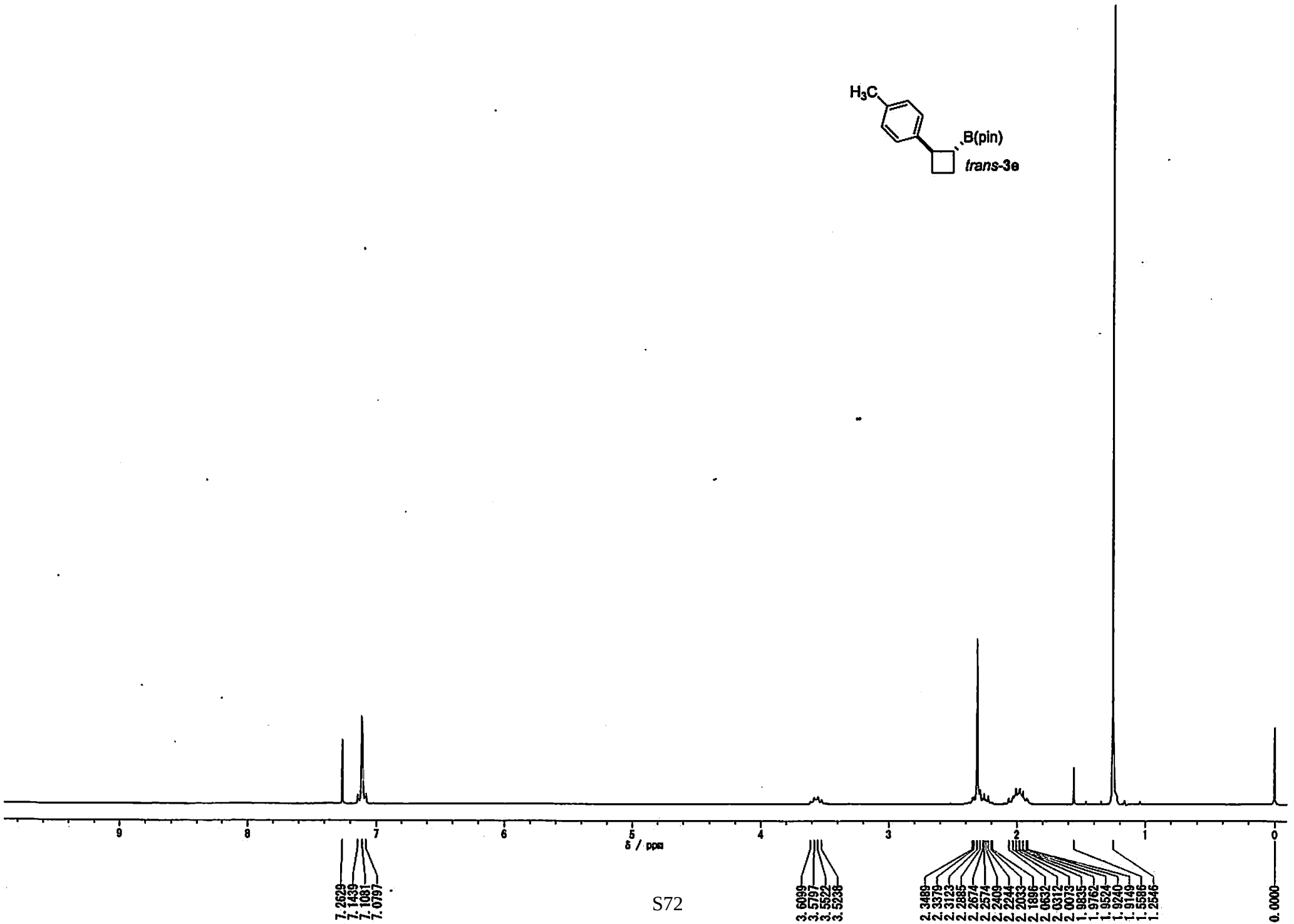

BnMe2Si
B(pin)
trans-3c
128.1945
128.1186
128.4
128.2
128
20.5
20
19.5
19
18.5
18
17.5
180
160
140
120
100
80
60
40
20
0
δ / ppm
140.6215
128.1945
128.1186
123.7612
82.8744
77.4238
76.9987
76.5812
24.6262
23.8899
23.1156
-5.7846
-6.1490

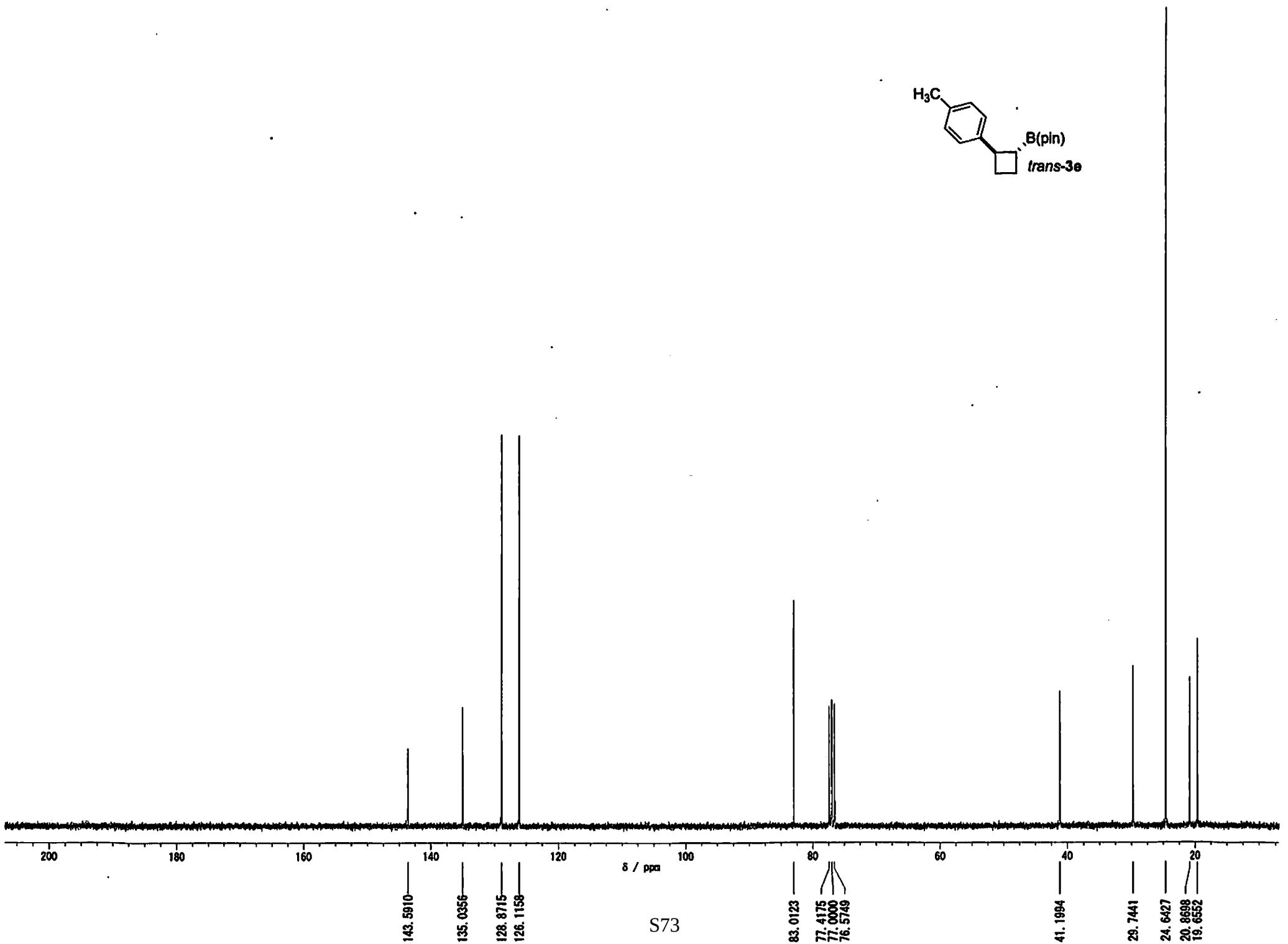

BnMe2Si
B(pin)
cis-3c
δ / ppm
7.2620
7.2199
7.1951
7.1704
7.0697
7.0450
7.0092
6.9854
2.3041
2.2766
2.2656
2.2363
2.2235
2.2152
2.1786
2.1603
2.1511
2.1383
2.0934
2.0550
2.0312
2.0055
1.9817
1.9469
1.9185
1.8910
1.8709
1.8581
1.8462
1.8379
1.8169
1.5614
1.2720
0.0449
0.0000
-0.0110

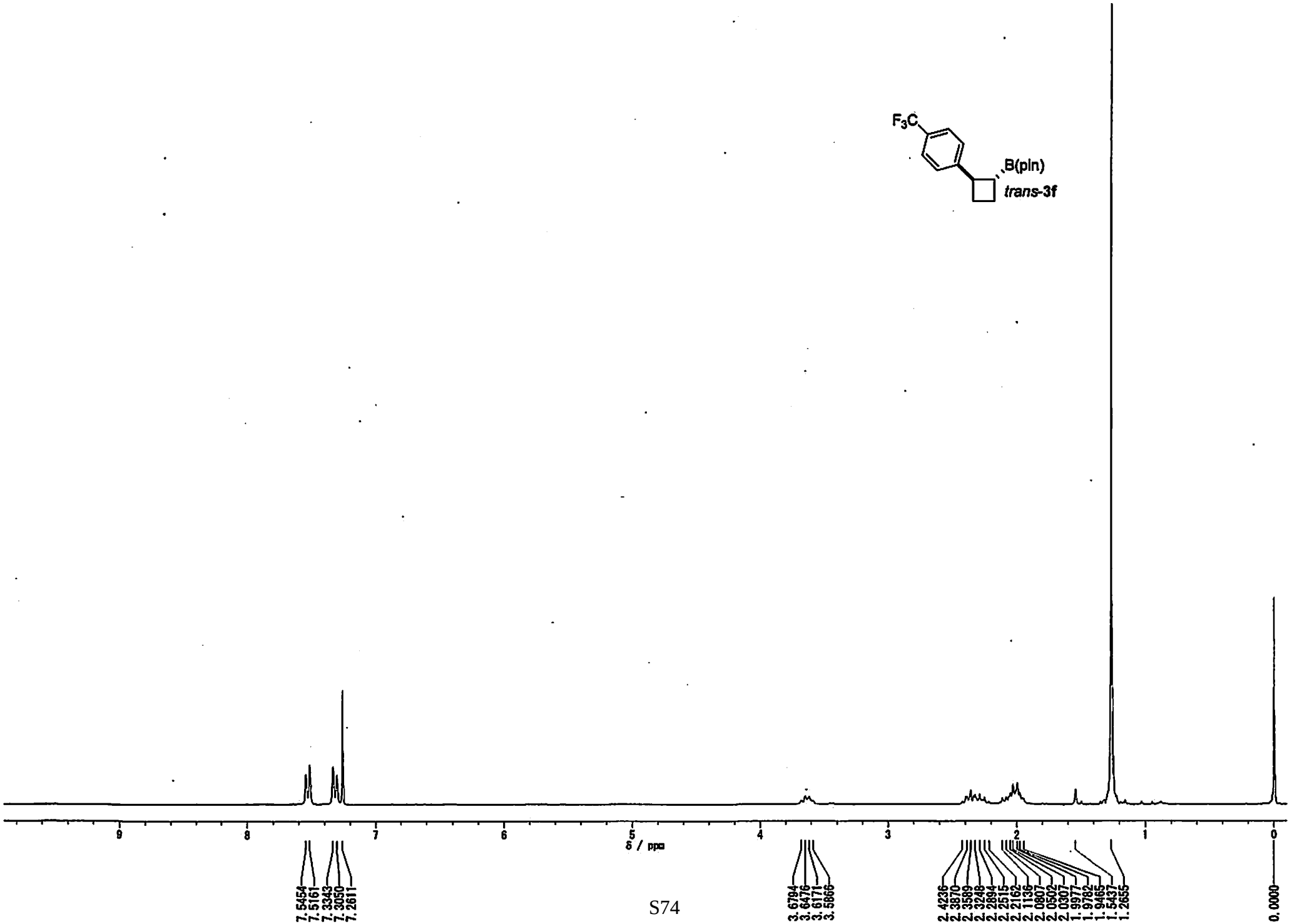

BnMe2Si
B(pin)
cis-3c
128.1718
128.0579
25.0362
24.8919
24.7401
24.1404
23.7912
δ / ppm
141.0239
128.1718
128.0579
123.6625
82.9731
77.4238
76.9987
76.5736
25.0362
24.8919
24.7401
24.1404
23.7912
23.0093
-4.4561
-4.7749

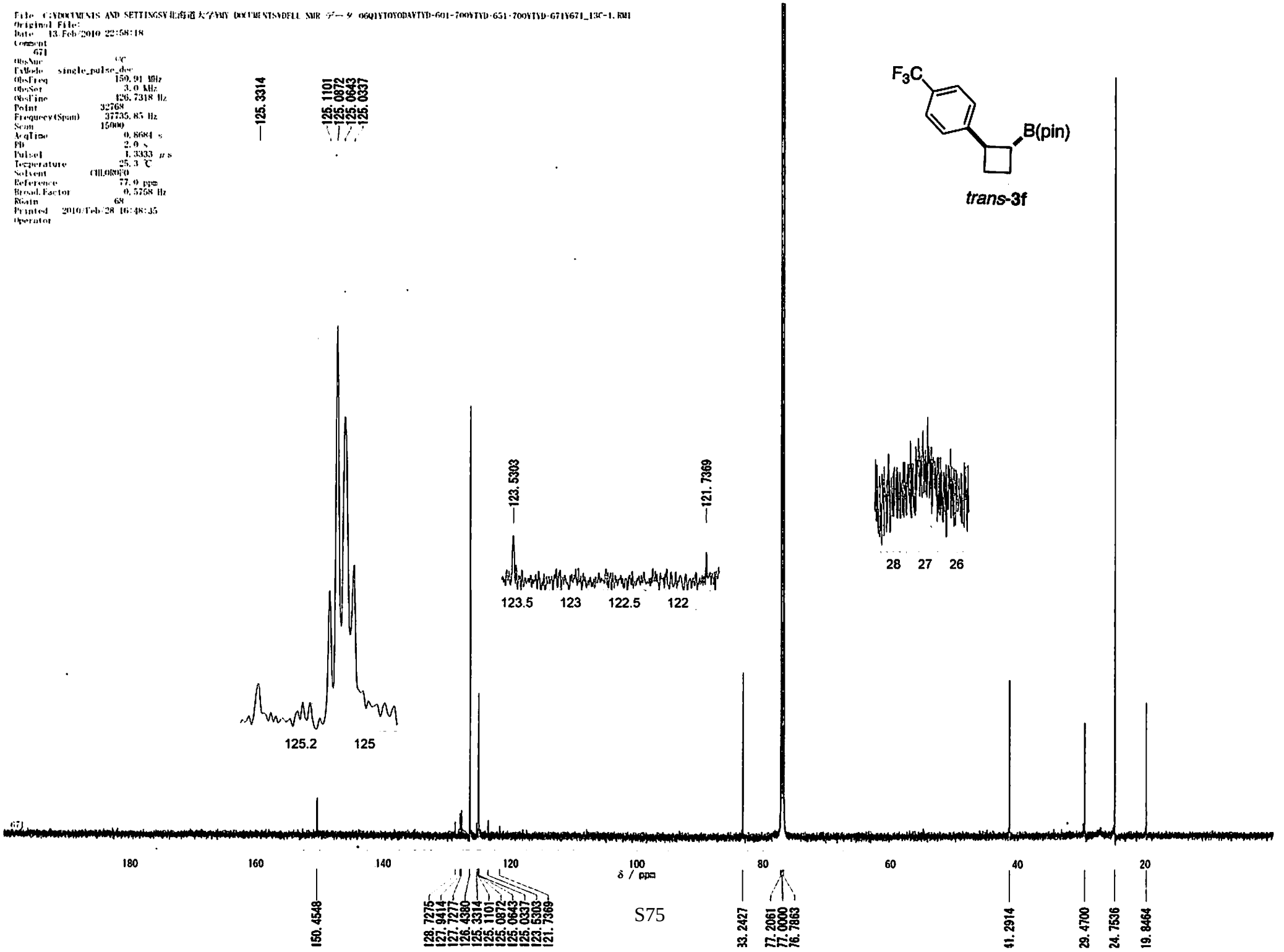

Ph
B(pin)
trans-3d
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.3105
7.2859
7.2620
7.2519
7.2327
7.2098
7.1759
7.1530
7.1292
3.6511
3.6218
3.5925
3.5651
2.4057
2.3947
2.3709
2.3599
2.3443
2.3361
2.3141
2.2867
2.2546
2.2345
2.2207
2.1090
2.0824
2.0522
2.0339
2.0019
1.9753
1.9561
1.9387
1.9286
1.2592
0.0000

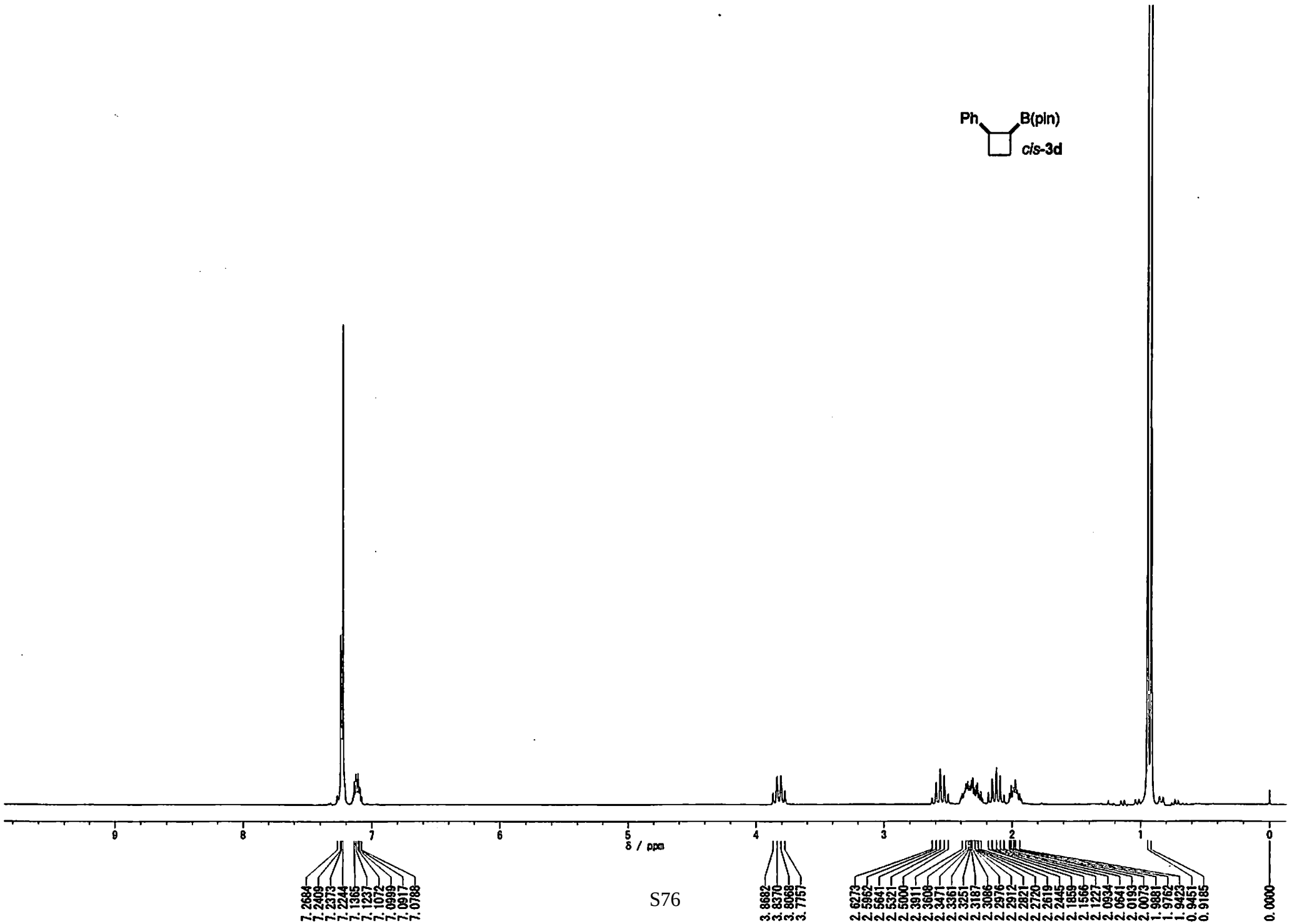

Ph
B(pin)
trans-3d
180
160
140
120
100
80
60
40
20
0
ppm
146.5972
128.1958
126.1917
125.5996
83.0655
77.4175
77.0000
76.5749
41.4271
29.5695
24.6503
19.7008

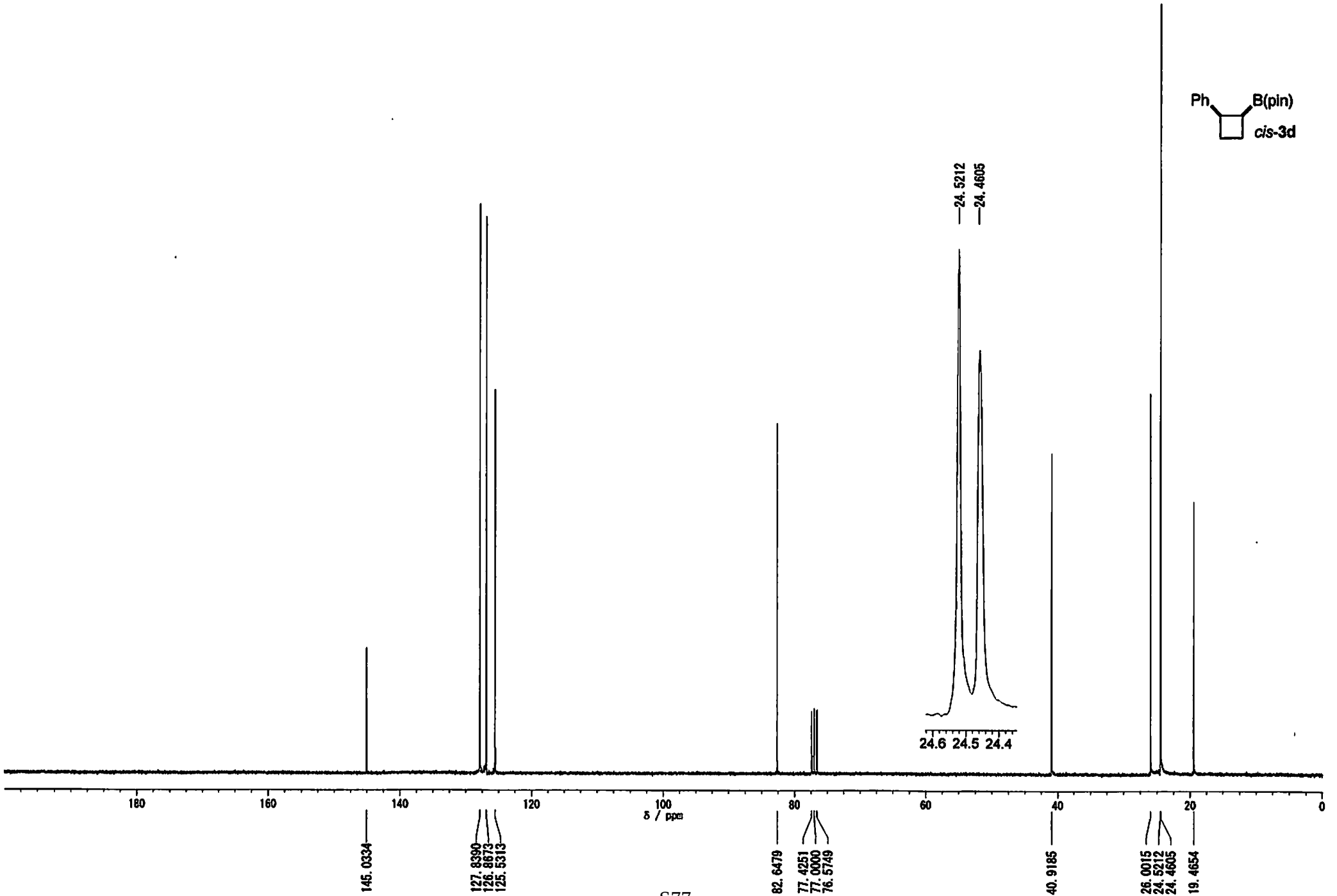

H3C
B(pin)
trans-3e
δ / ppm
9
8
7
6
5
4
3
2
1
0
7.2629
7.1439
7.1081
7.0797
3.6099
3.5797
3.5522
3.5238
2.3489
2.3379
2.3123
2.2885
2.2674
2.2574
2.2409
2.2244
2.2033
2.1896
2.0632
2.0312
2.0073
1.9835
1.9762
1.9524
1.9240
1.9149
1.5586
1.2546
0.0000

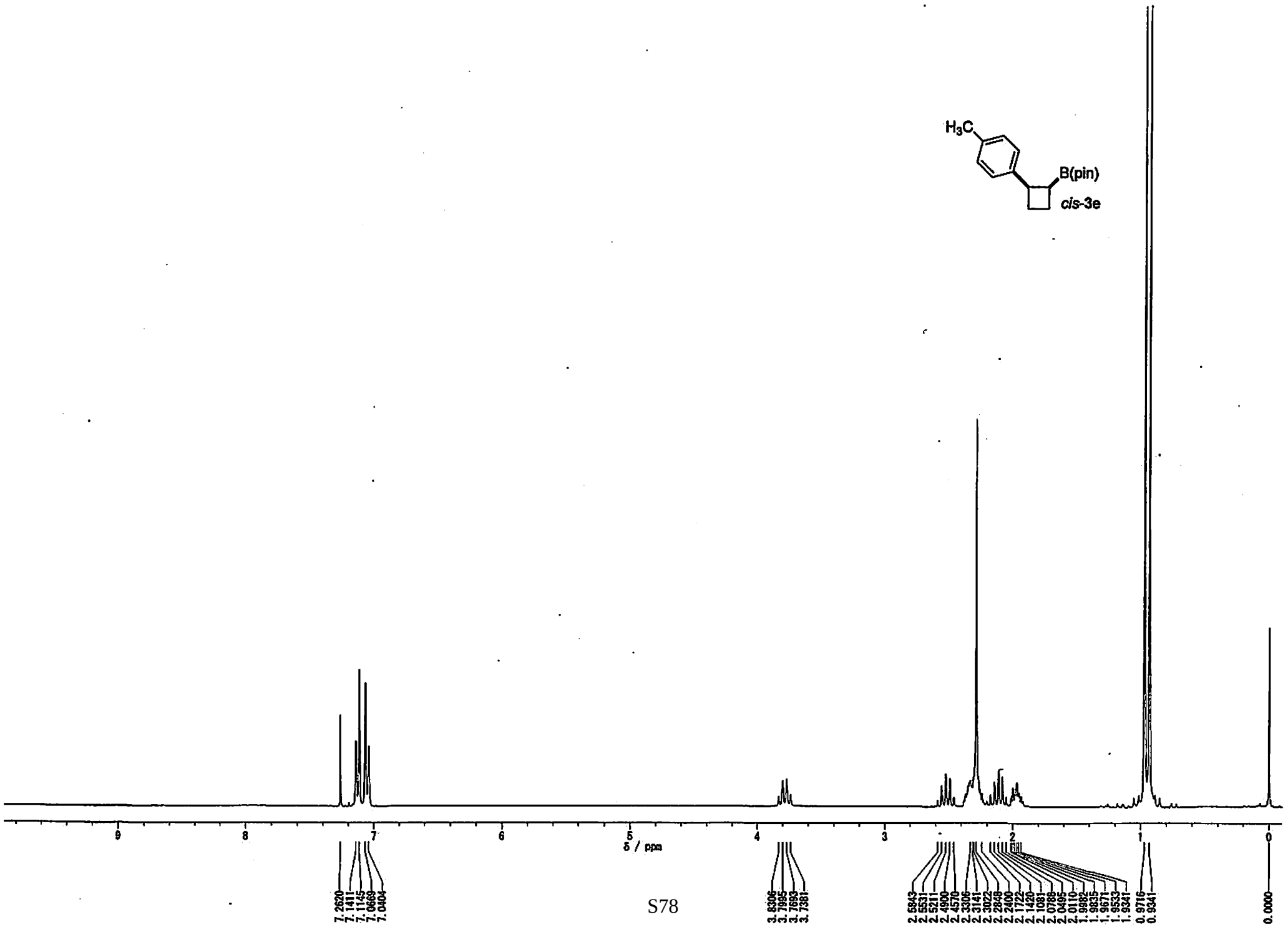

H3C
B(pin)
trans-3e
200
180
160
140
120
100
80
60
40
20
δ / ppm
143.5910
135.0356
128.8715
126.1158
83.0123
77.4175
77.0000
76.5749
41.1994
29.7441
24.6427
20.8698
19.6552

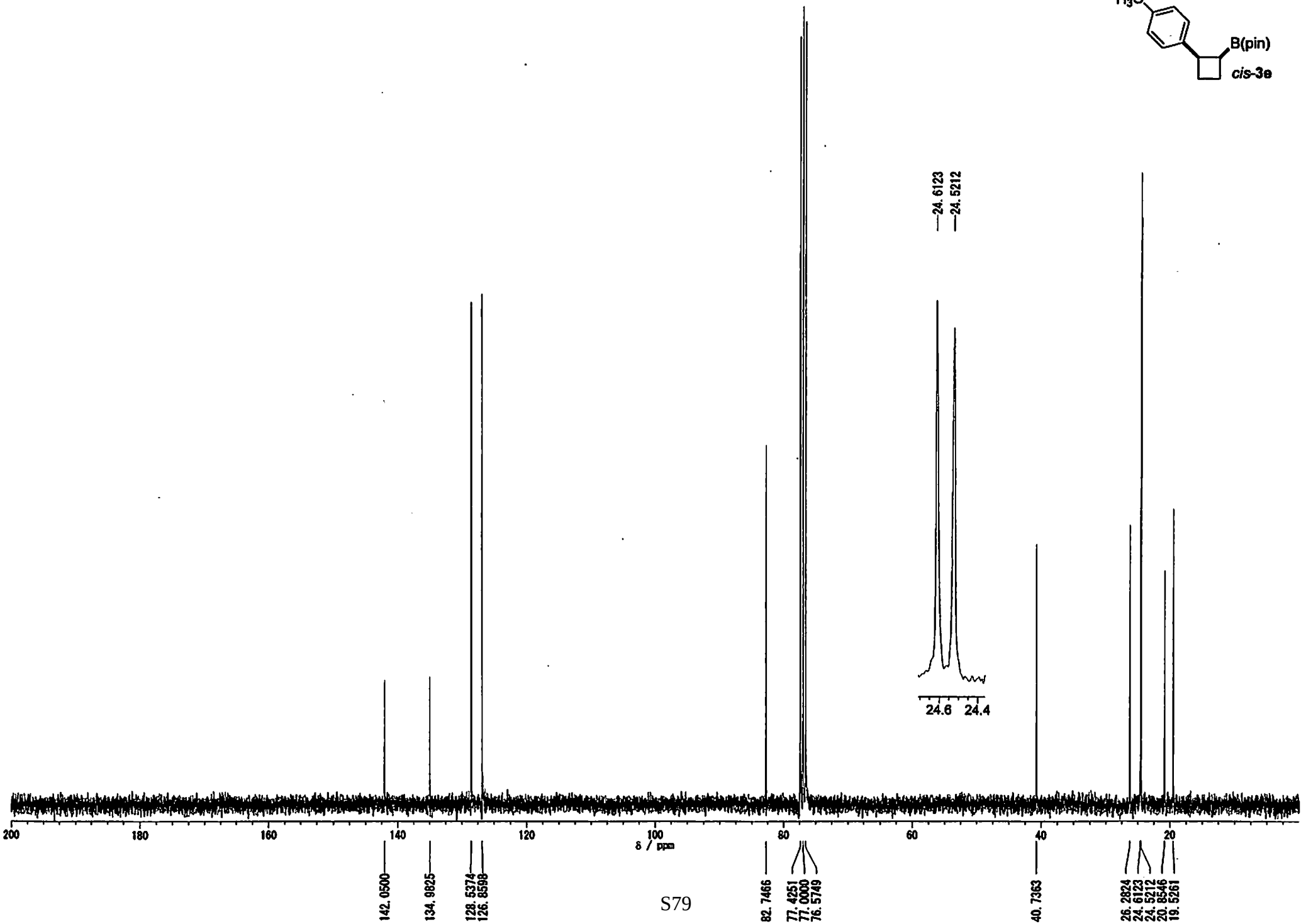

F3C
B(pin)
trans-3f
δ / ppm
7.5454
7.5161
7.3343
7.3050
7.2611
3.6794
3.6476
3.6171
3.5866
2.4236
2.3870
2.3589
2.3248
2.2894
2.2515
2.2162
2.1136
2.0807
2.0502
2.0307
1.9977
1.9782
1.9465
1.5437
1.2655
0.0000

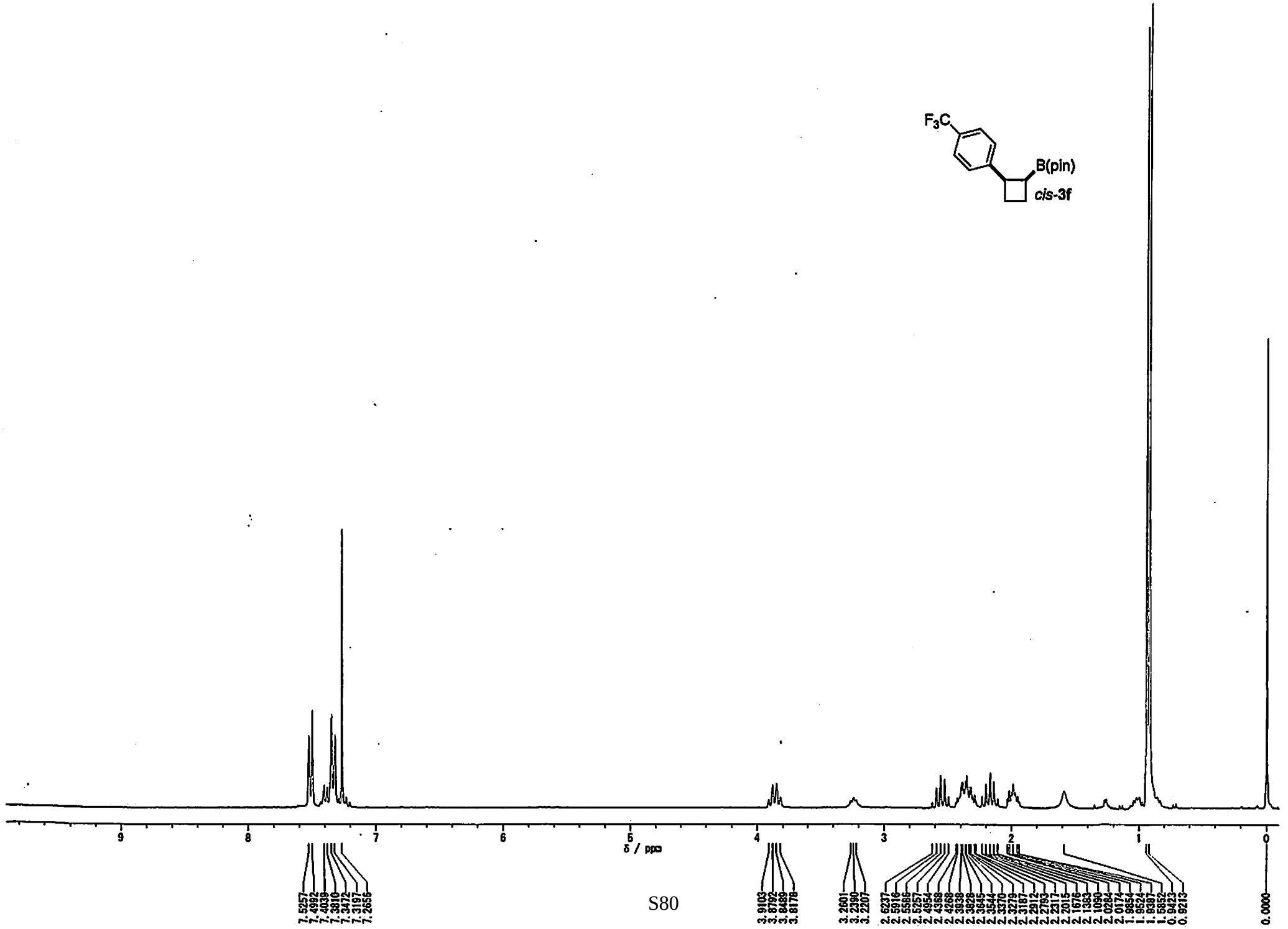

Original File:
Date 13.Feb/2010 22:58:18
Comment
671
ObsNuc 13C
ExMode single_pulse_dec
ObsFreq 150.91 MHz
ObsSor 3.0 kHz
ObsFine 126.7318 Hz
Point 32768
Frequecy(Span) 37735.85 Hz
Scan 15000
AcqTime 0.8684 s
PD 2.0 s
Pulse1 1.3333 μs
Temperature 25.3 ℃
Solvent CHLOROFO
Reference 77.0 ppm
Broad.Factor 0.5758 Hz
Gain 68
Printed 2010/Feb/28 16:48:35
Operator
125.3314
125.1101
125.0872
125.0643
125.0337
F3C
B(pin)
trans-3f
123.5303
121.7369
125.2
125
123.5
123
122.5
122
28
27
26
671
180
160
140
120
100
80
60
40
20
δ / ppm
150.4548
128.7275
127.9414
127.7277
126.4380
125.3314
125.1101
125.0872
125.0643
125.0337
123.5303
121.7369
33.2427
77.2061
77.0000
76.7863
41.2914
29.4700
24.7536
19.8464

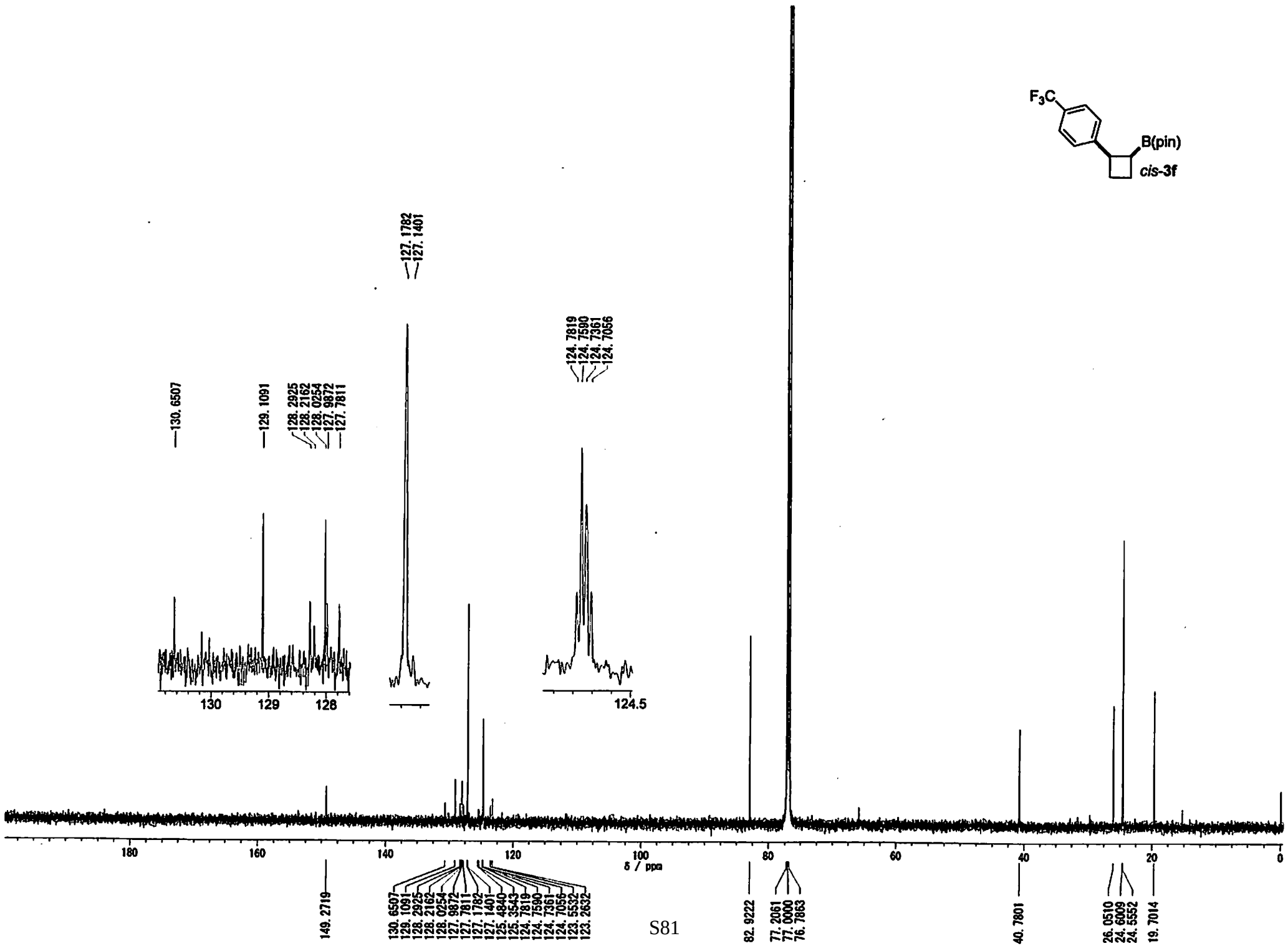

Ph
B(pin)
cis-3d
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2684
7.2409
7.2373
7.2244
7.1365
7.1237
7.1072
7.0999
7.0917
7.0788
3.8682
3.8370
3.8068
3.7757
2.6273
2.5962
2.5641
2.5321
2.5000
2.3911
2.3608
2.3471
2.3361
2.3251
2.3187
2.3086
2.2976
2.2912
2.2821
2.2720
2.2619
2.2445
2.1859
2.1566
2.1227
2.0934
2.0641
2.0193
2.0073
1.9881
1.9762
1.9423
0.9451
0.9185
0.0000

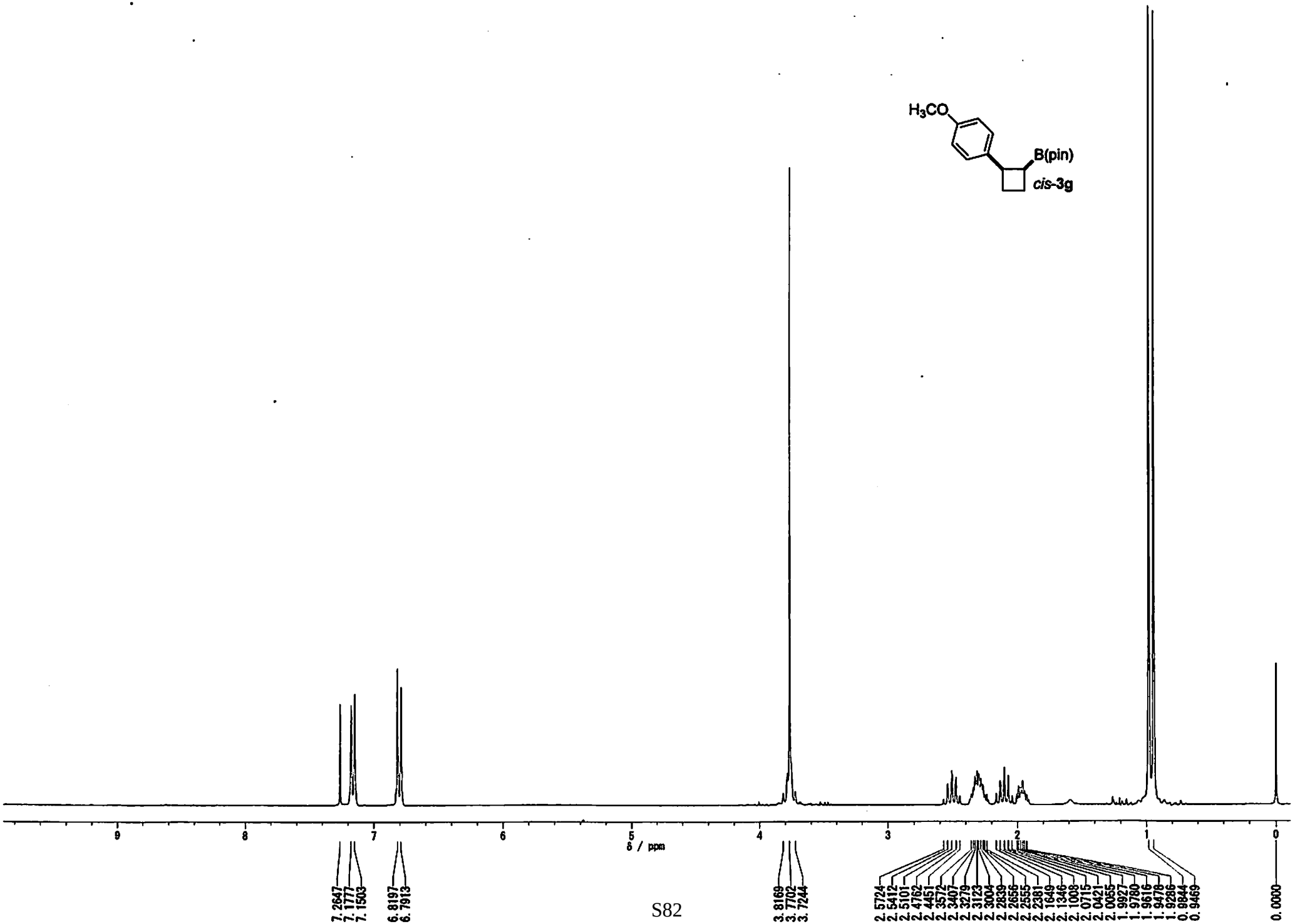

Ph
B(pin)
cis-3d
24.5212
24.4605
24.6 24.5 24.4
180
160
140
120
100
δ / ppm
80
60
40
20
0
145.0334
127.8390
126.8673
125.5313
82.6479
77.4251
77.0000
76.5749
40.9185
26.0015
24.5212
24.4605
19.4654

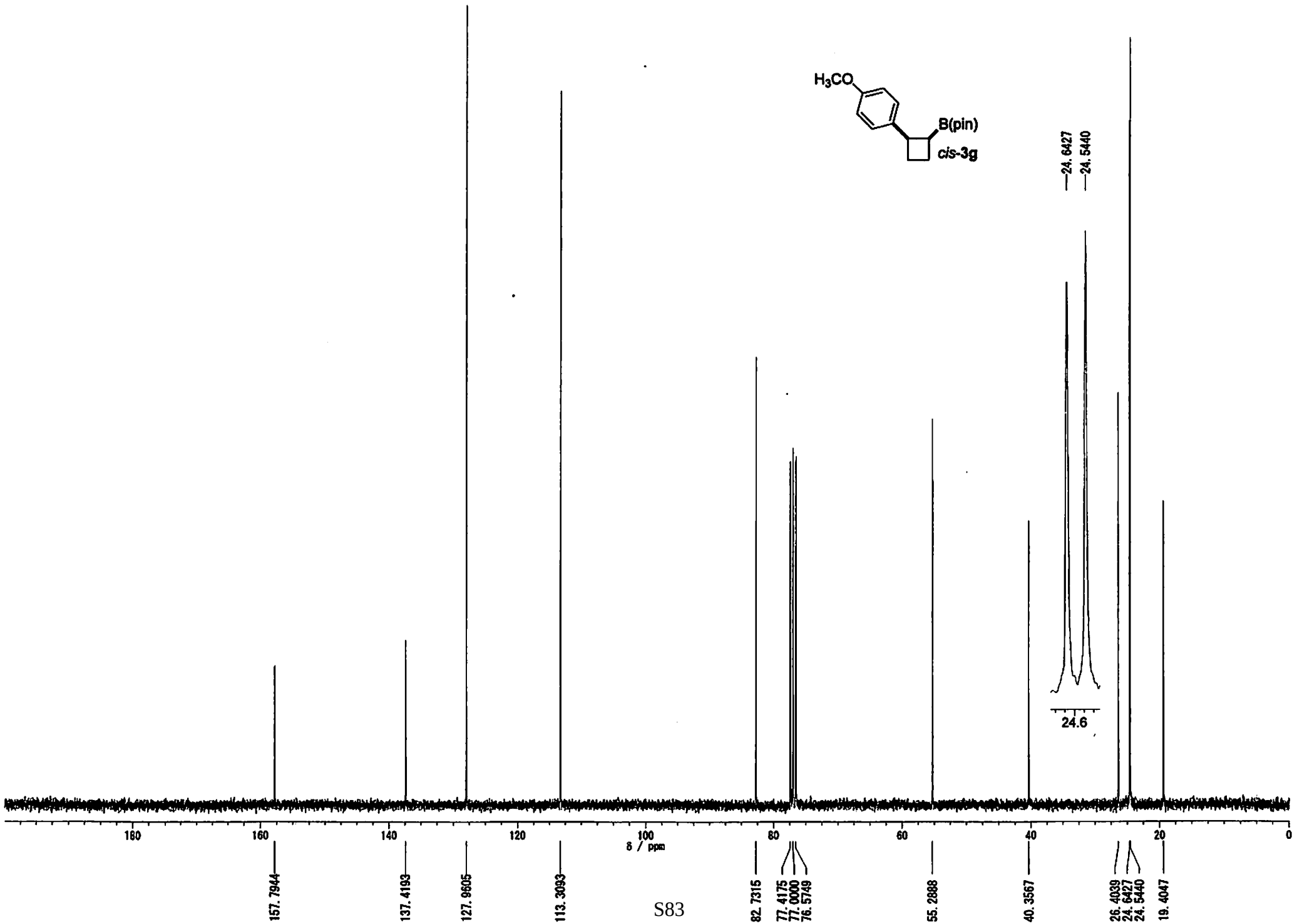

H3C
B(pin)
cis-3e
δ / ppm
9
8
7
6
5
4
3
2
1
0
7.2620
7.1411
7.1145
7.0669
7.0404
3.8306
3.7995
3.7693
3.7381
2.5843
2.5531
2.5211
2.4900
2.4570
2.3306
2.3141
2.3022
2.2848
2.2400
2.1722
2.1420
2.1081
2.0788
2.0495
2.0110
1.9982
1.9835
1.9671
1.9533
1.9341
0.9716
0.9341
0.0000

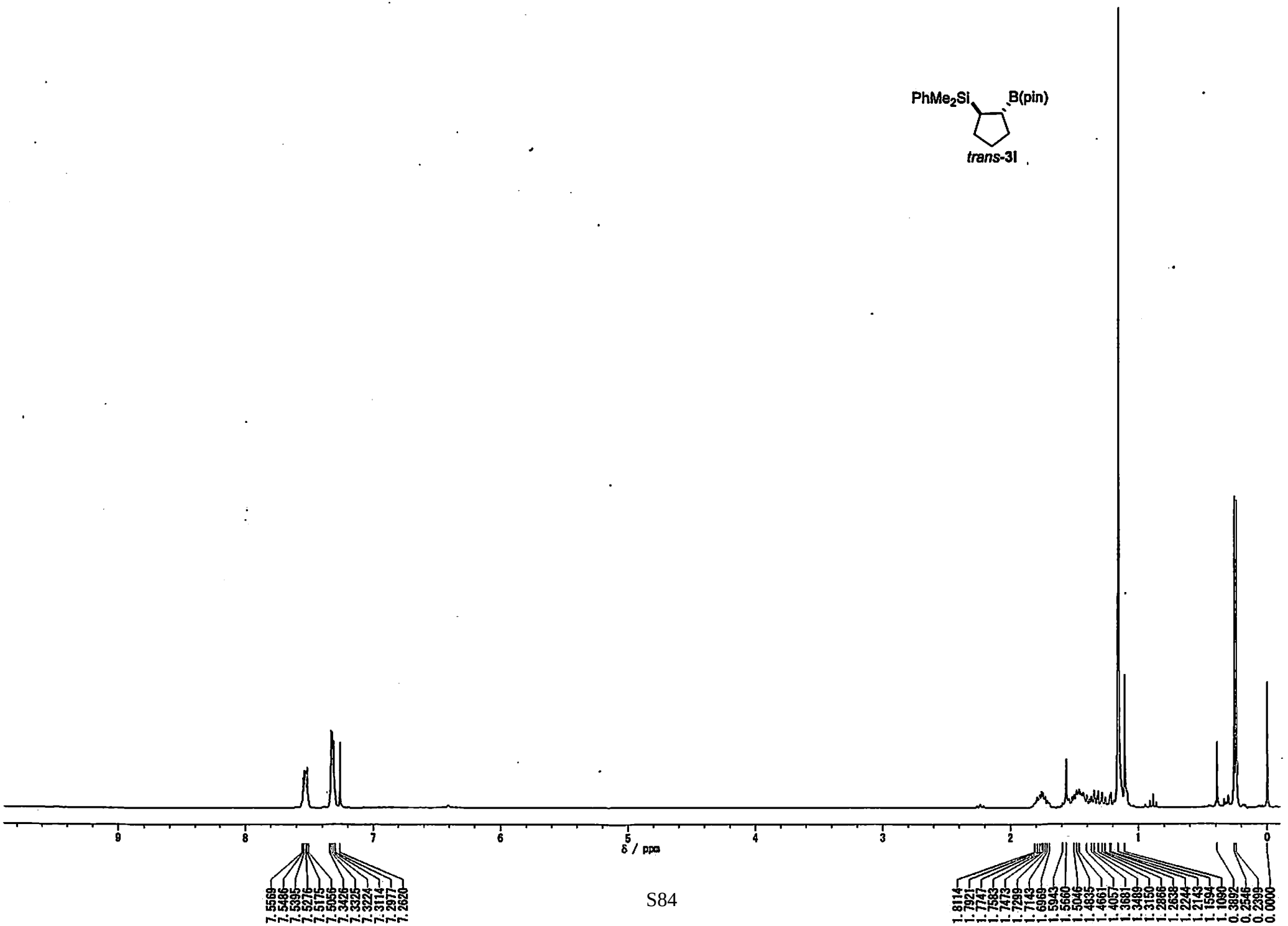

H3C
B(pin)
cis-3e
24.6123
24.5212
24.6
24.4
200
180
160
140
120
100
80
60
40
20
δ / ppm
142.0500
134.9825
128.5374
126.8598
82.7466
77.4251
77.0000
76.5749
40.7363
26.2824
24.6123
24.5212
20.8546
19.5261

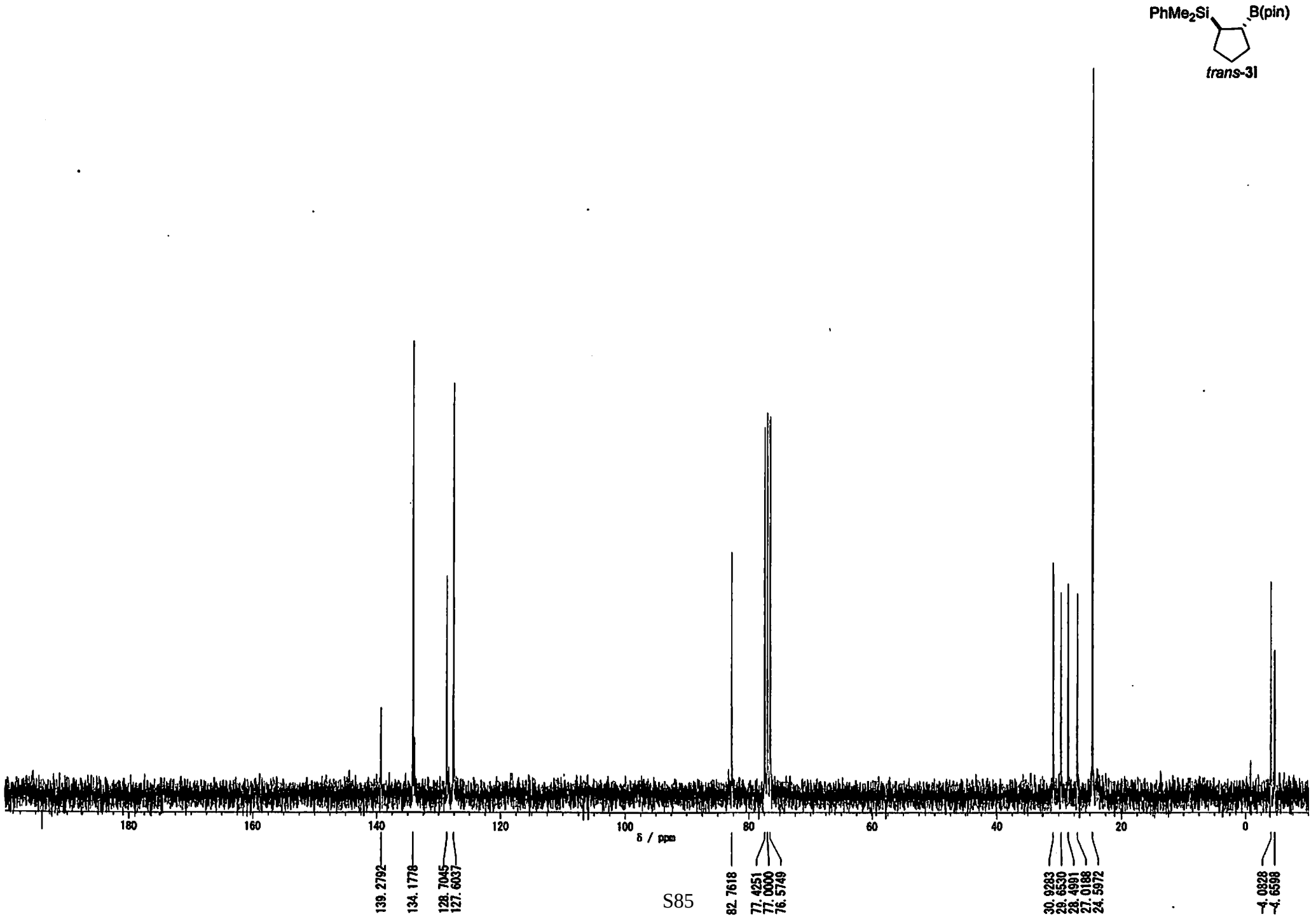

F3C
B(pin)
cis-3f
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.5257
7.4992
7.4039
7.3810
7.3472
7.3197
7.2656
3.9103
3.8792
3.8489
3.8178
3.2601
3.2290
3.2207
2.6237
2.5916
2.5586
2.5257
2.4954
2.4388
2.4268
2.3838
2.3828
2.3545
2.3544
2.3370
2.3279
2.3187
2.2812
2.2783
2.2317
2.2015
2.1676
2.1383
2.1090
2.0284
2.0174
1.9654
1.9524
1.9387
1.5852
0.9423
0.9213
0.0000

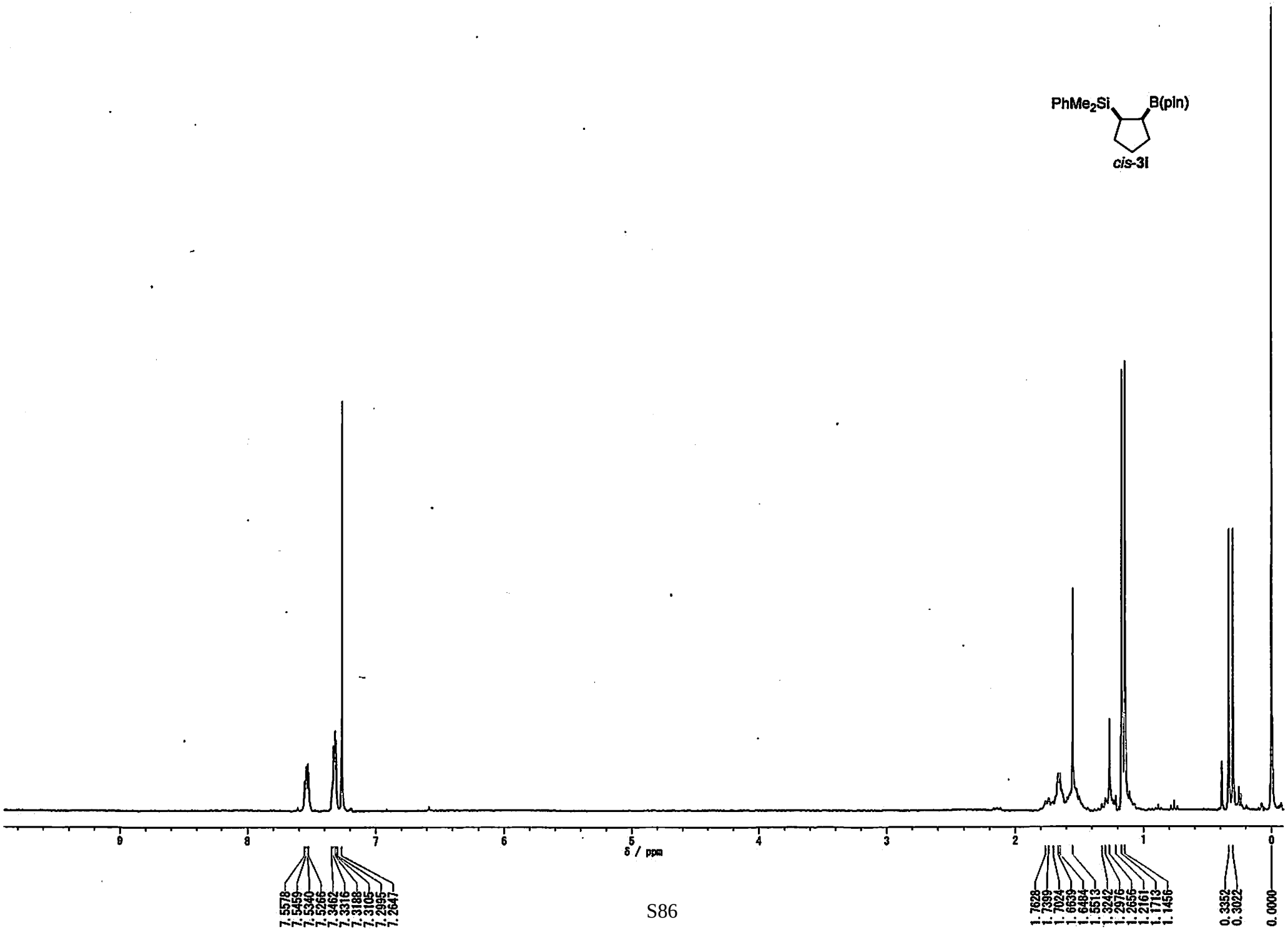

F3C
B(pin)
cis-3f
δ / ppm
149.2719
130.6507
129.1091
128.2925
128.2162
128.0254
127.9872
127.7811
127.1782
127.1401
125.4840
125.3543
124.7819
124.7590
124.7361
124.7056
123.5532
123.2632
82.9222
77.2061
77.0000
76.7863
40.7801
26.0510
24.6009
24.5552
19.7014

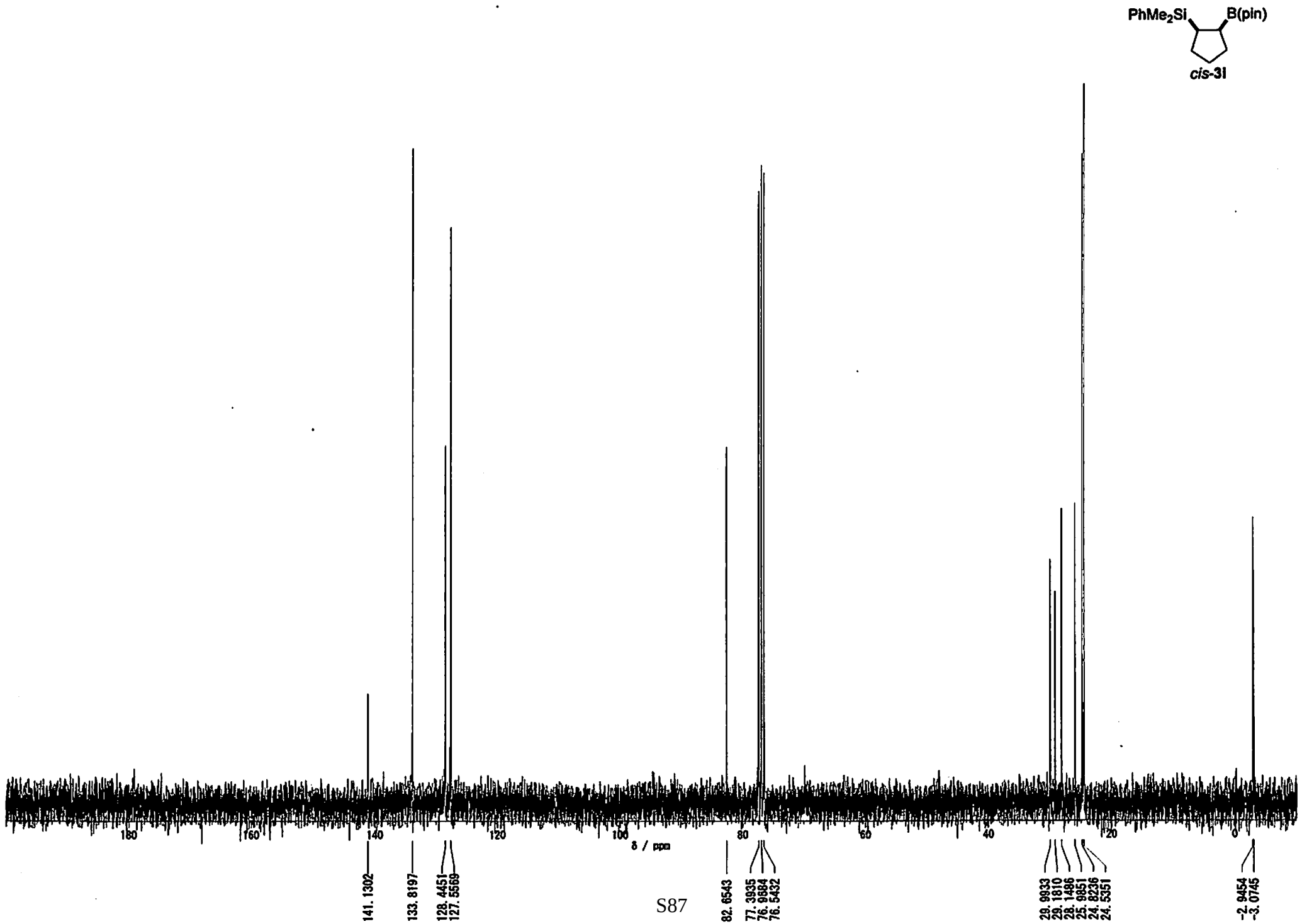

H3CO
B(pin)
cis-3g
δ / ppm
7.2647
7.1777
7.1503
6.8197
6.7913
3.8169
3.7702
3.7244
2.5724
2.5412
2.5101
2.4762
2.4451
2.3572
2.3407
2.3279
2.3123
2.3004
2.2839
2.2656
2.2555
2.2381
2.1649
2.1346
2.1008
2.0715
2.0421
2.0055
1.9927
1.9780
1.9616
1.9478
1.9286
0.9844
0.9469
0.0000

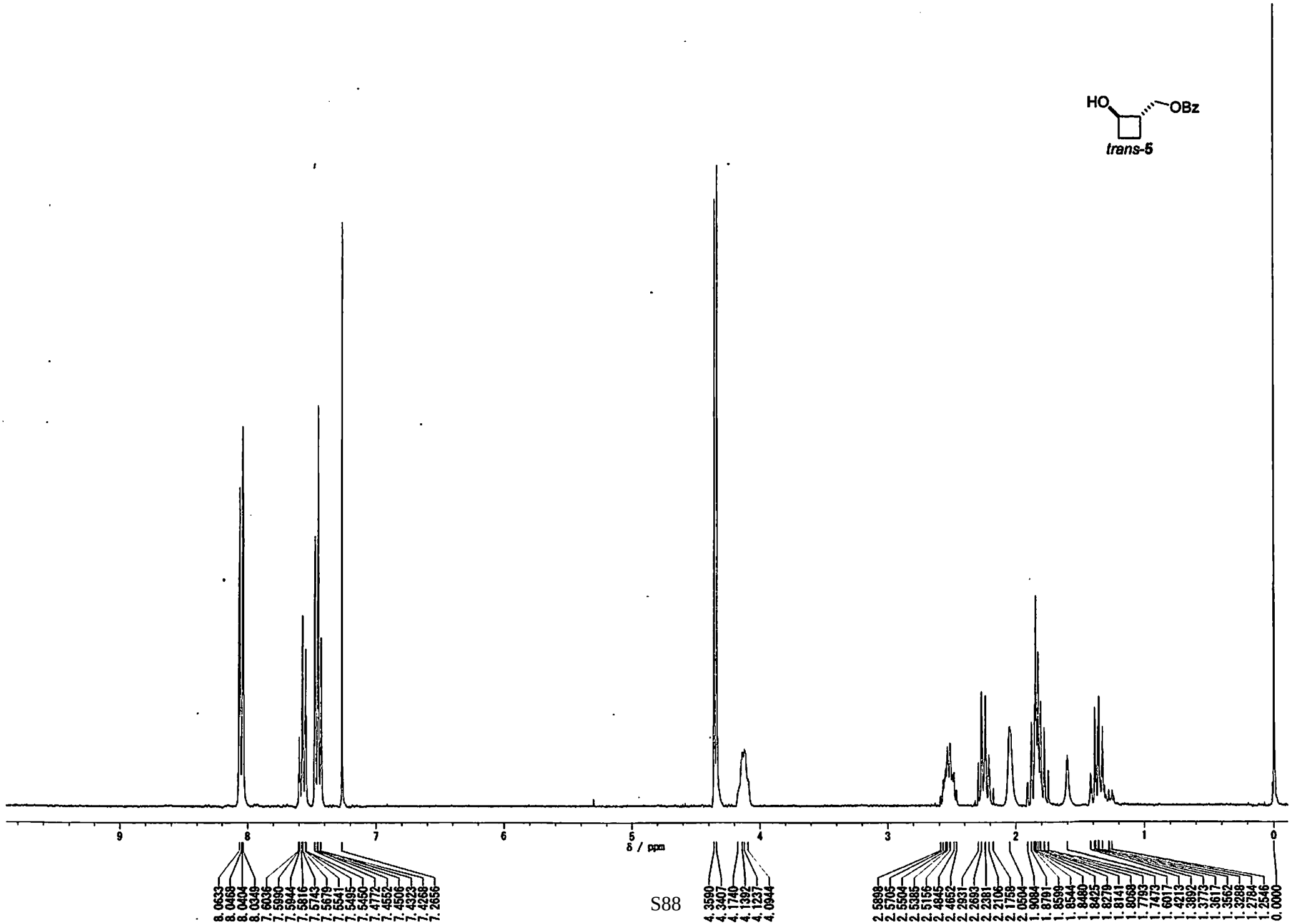

H3CO
B(pin)
cis-3g
24.6427
24.5440
24.6
160
140
120
100
80
60
40
20
0
δ / ppm
157.7944
137.4193
127.9605
113.3093
82.7315
77.4175
77.0000
76.5749
55.2888
40.3567
26.4039
24.6427
24.5440
19.4047

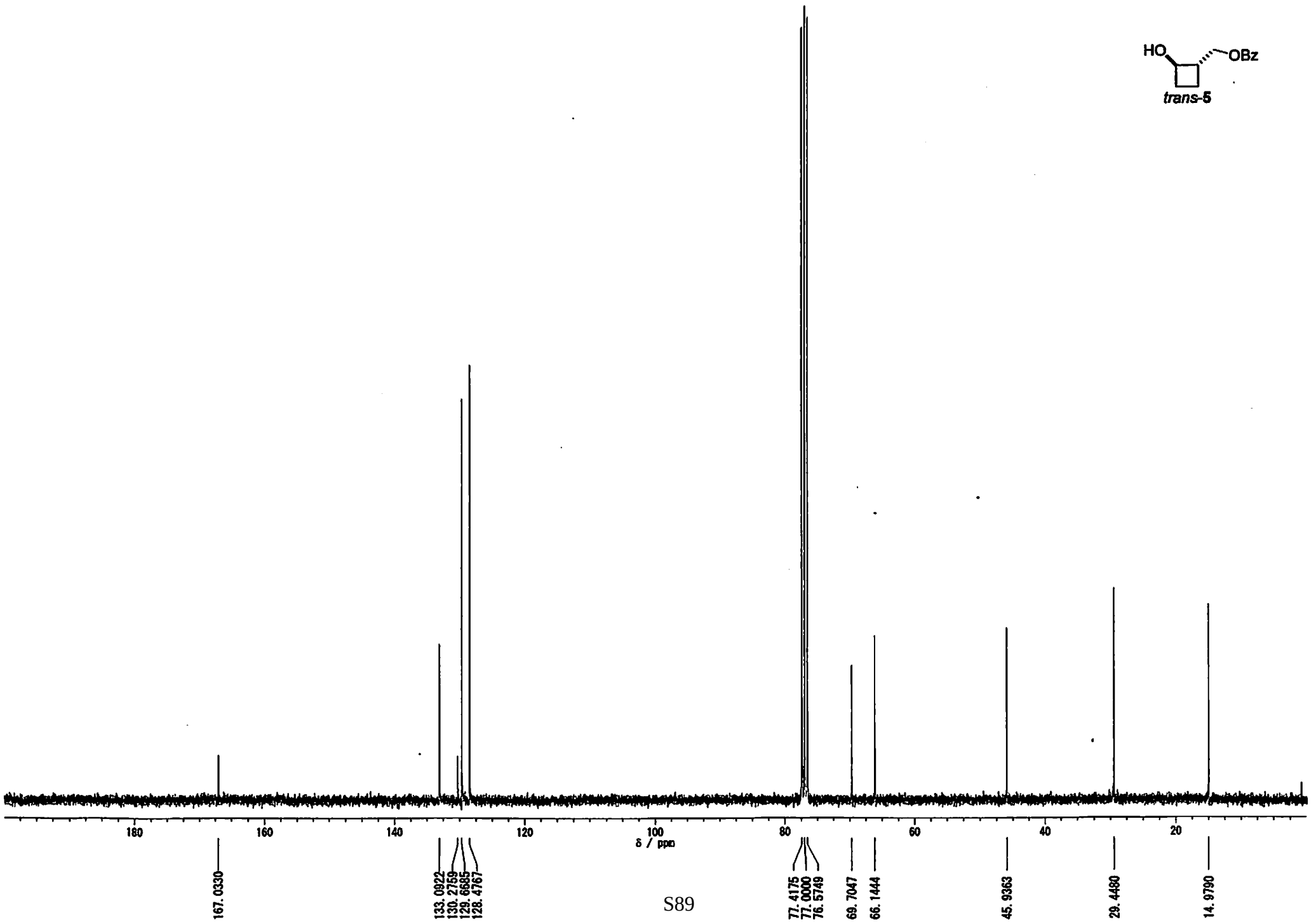

PhMe2Si
B(pin)
trans-3l
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.5569
7.5486
7.5395
7.5276
7.5175
7.5056
7.3426
7.3325
7.3224
7.3114
7.2977
7.2620
1.8114
1.7921
1.7747
1.7583
1.7473
1.7299
1.7143
1.6969
1.5943
1.5560
1.5046
1.4835
1.4661
1.4057
1.3681
1.3489
1.3150
1.2866
1.2638
1.2244
1.2143
1.1594
1.1090
0.3892
0.2546
0.2399
0.0000

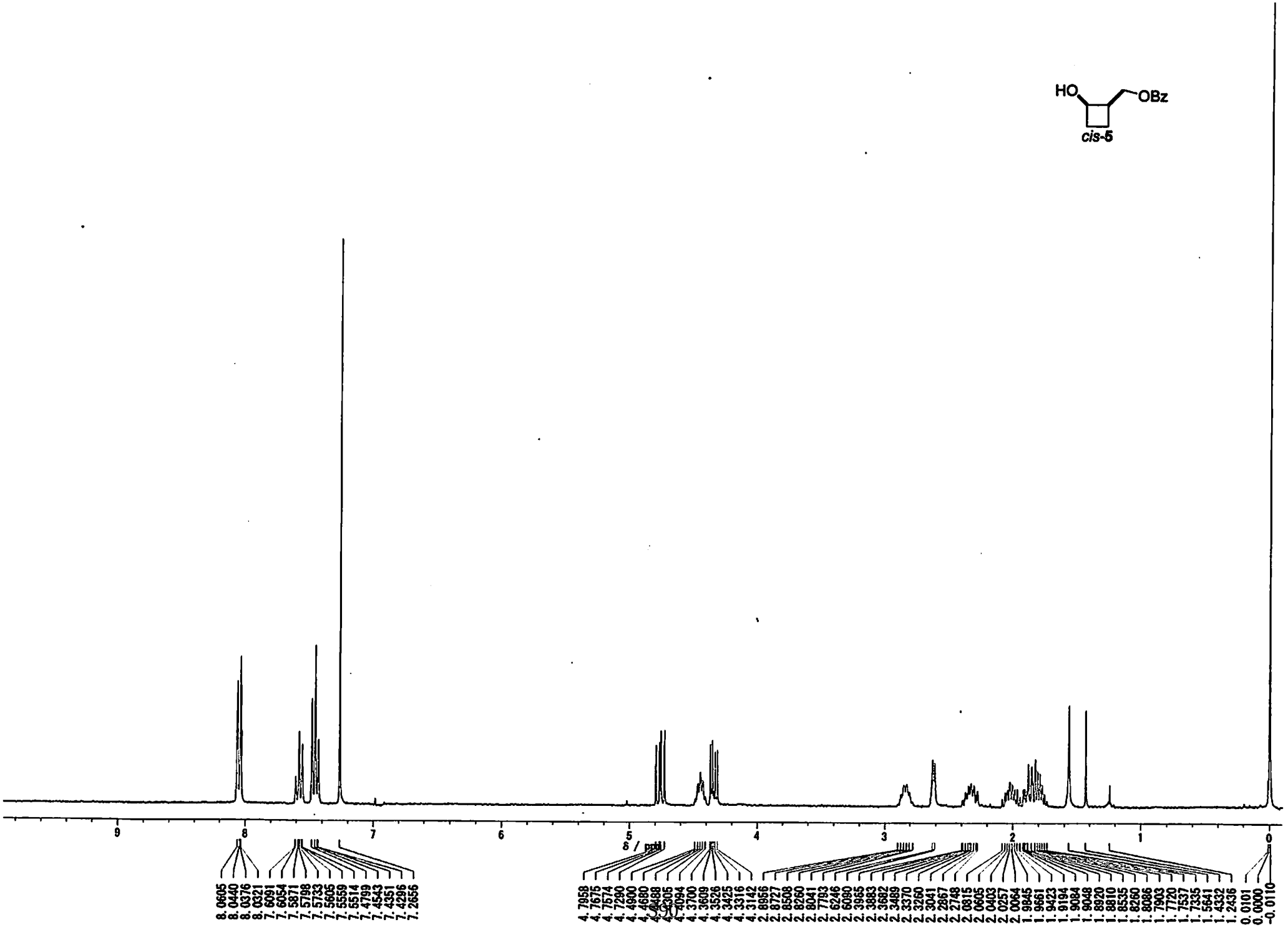

PhMe2Si
B(pin)
trans-3l
180
160
140
120
100
80
60
40
20
0
δ / ppm
139.2792
134.1778
128.7045
127.6037
82.7618
77.4251
77.0000
76.5749
30.9283
28.6530
28.4991
27.0188
24.5972
-4.0328
-4.6598

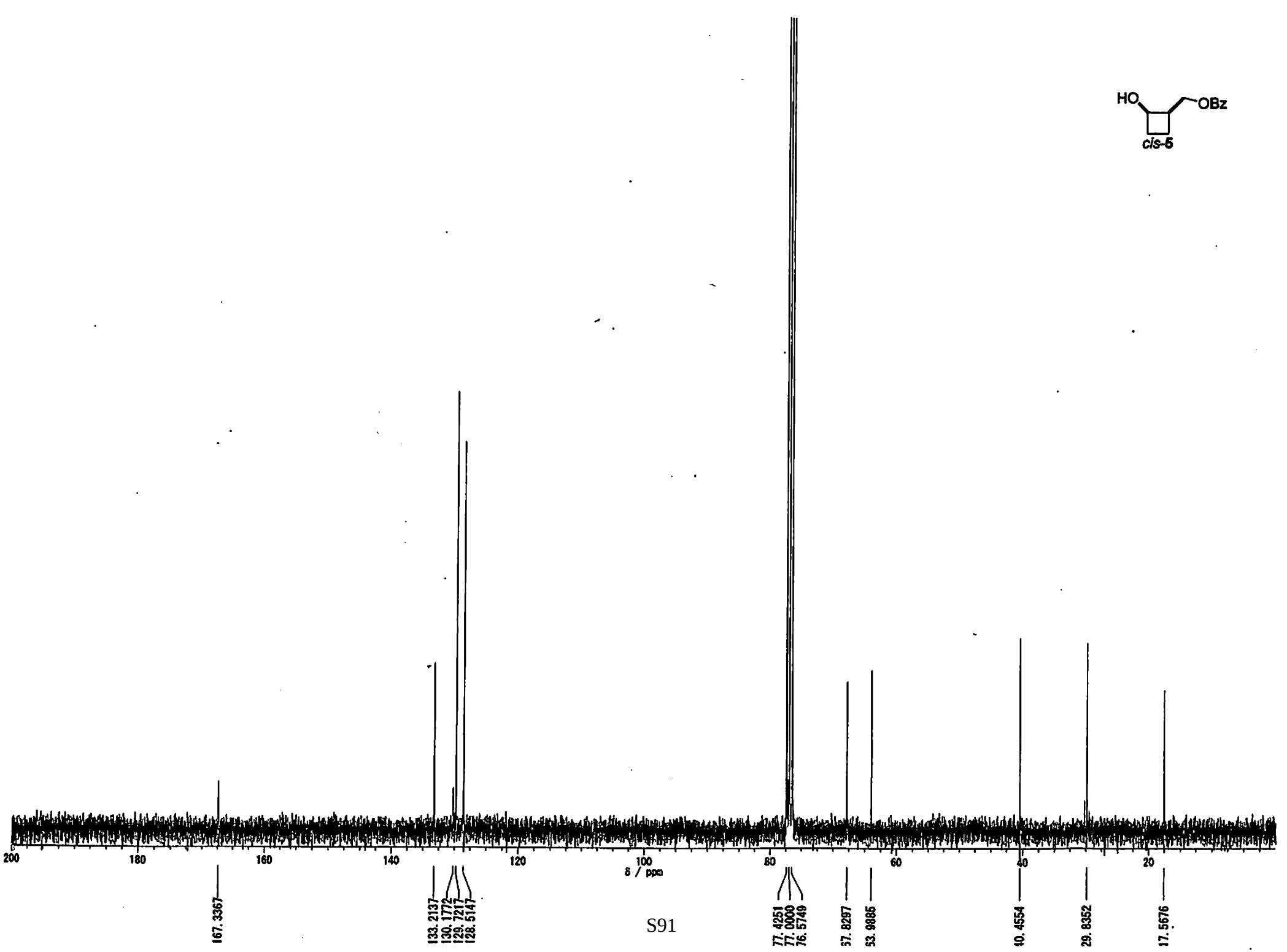

PhMe2Si
B(pin)
cis-3l
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.5578
7.5459
7.5340
7.5266
7.3462
7.3316
7.3188
7.3105
7.2995
7.2647
1.7628
1.7399
1.7024
1.6639
1.6484
1.5513
1.3242
1.2976
1.2656
1.2161
1.1713
1.1456
0.3352
0.3022
0.0000

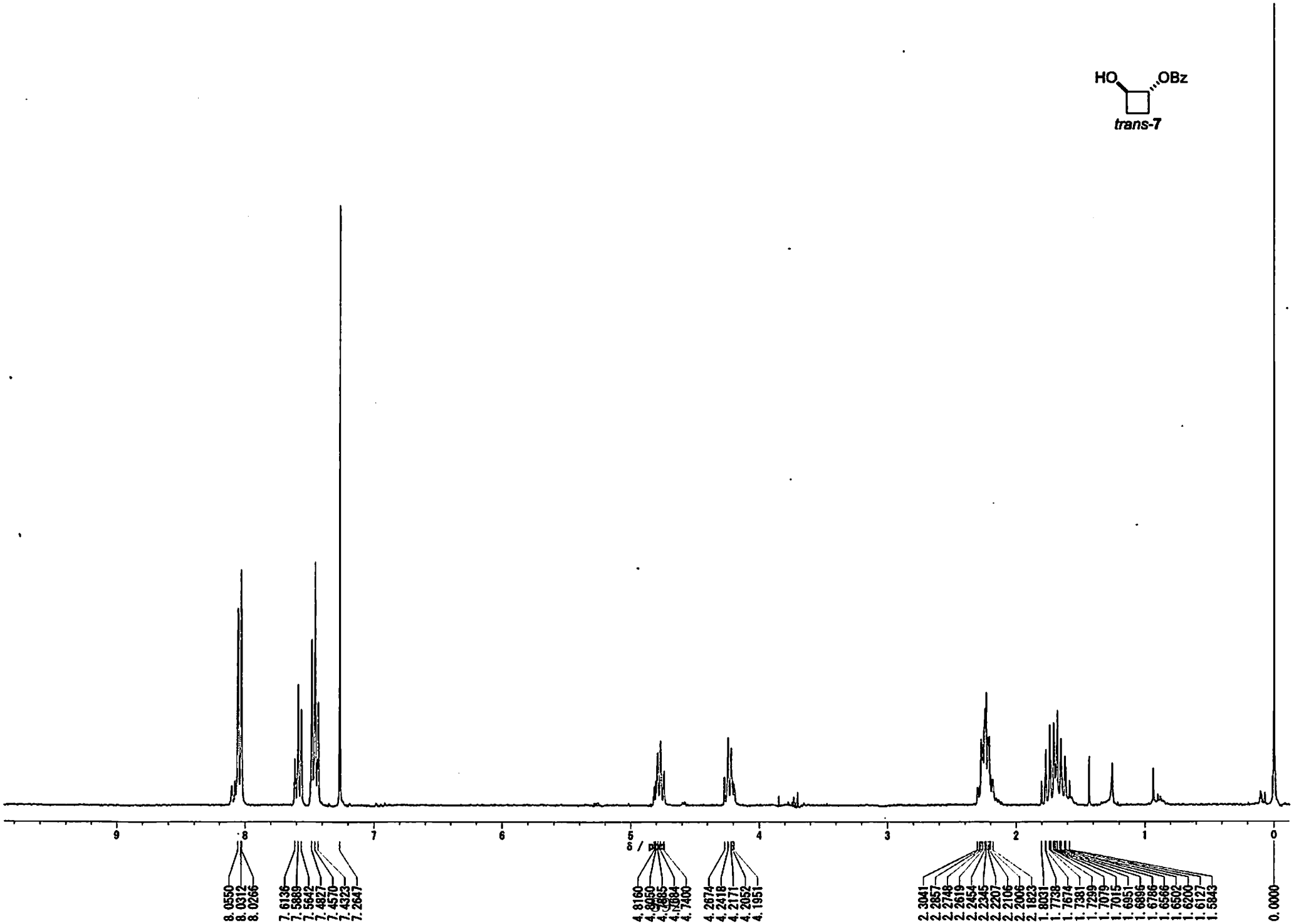

PhMe2Si
B(pin)
cis-3l
δ / ppm
141.1302
133.8197
128.4451
127.5560
82.6543
77.3935
76.9684
76.5432
29.9933
29.1810
28.1486
25.9851
24.8236
24.5351
-2.9454
-3.0745

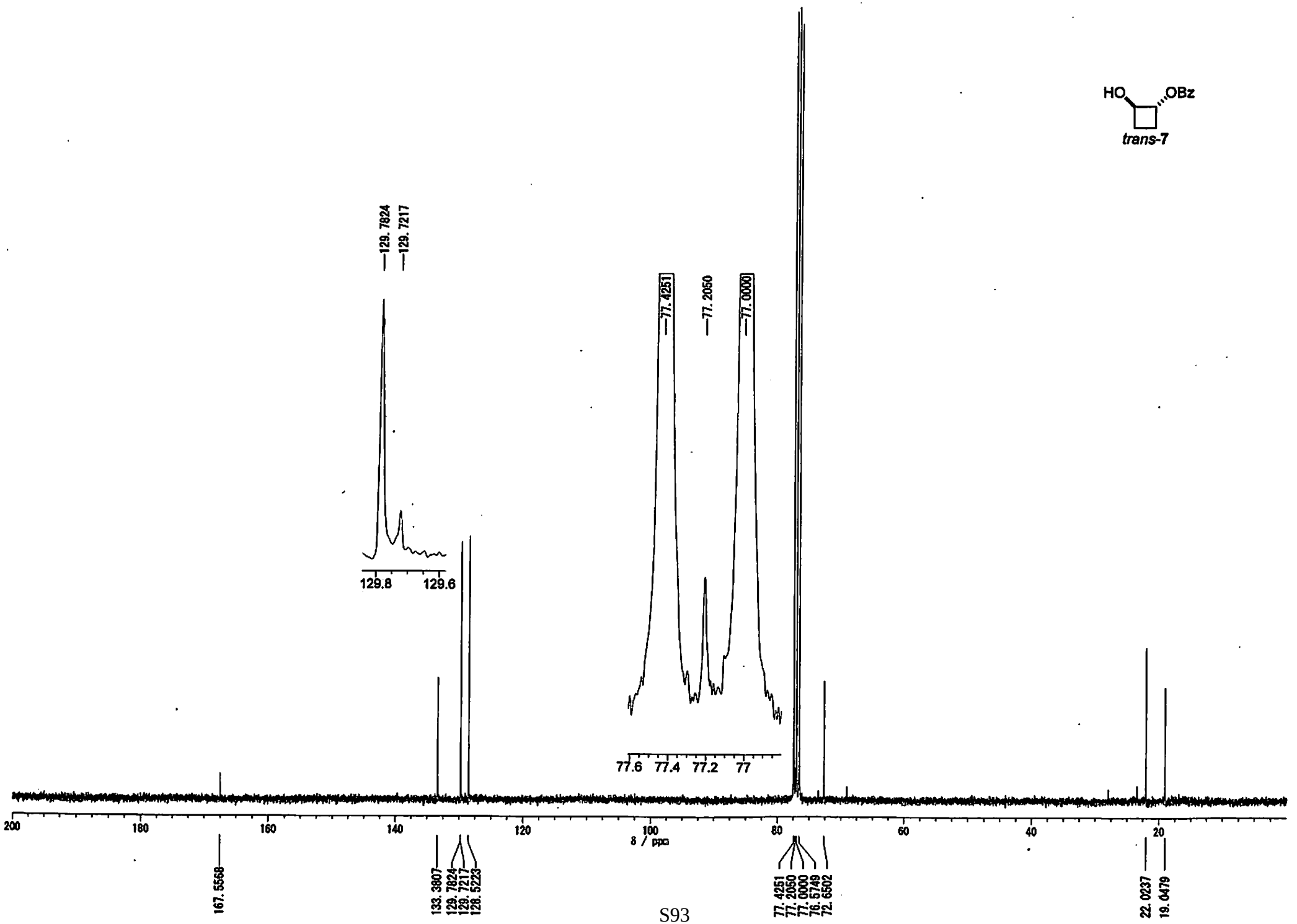

HO
OBz
trans-5
δ / ppm
8.0633
8.0468
8.0404
8.0349
7.6036
7.5990
7.5944
7.5816
7.5743
7.5679
7.5541
7.5495
7.5450
7.4772
7.4552
7.4506
7.4323
7.4268
7.2656
4.3590
4.3407
4.1740
4.1392
4.1237
4.0944
2.5898
2.5705
2.5504
2.5385
2.5156
2.4845
2.4652
2.2931
2.2693
2.2381
2.2106
2.1758
2.0504
1.9084
1.8791
1.8599
1.8544
1.8480
1.8425
1.8279
1.8141
1.8068
1.7793
1.7473
1.6017
1.4213
1.3892
1.3773
1.3617
1.3562
1.3288
1.2784
1.2546
0.0000

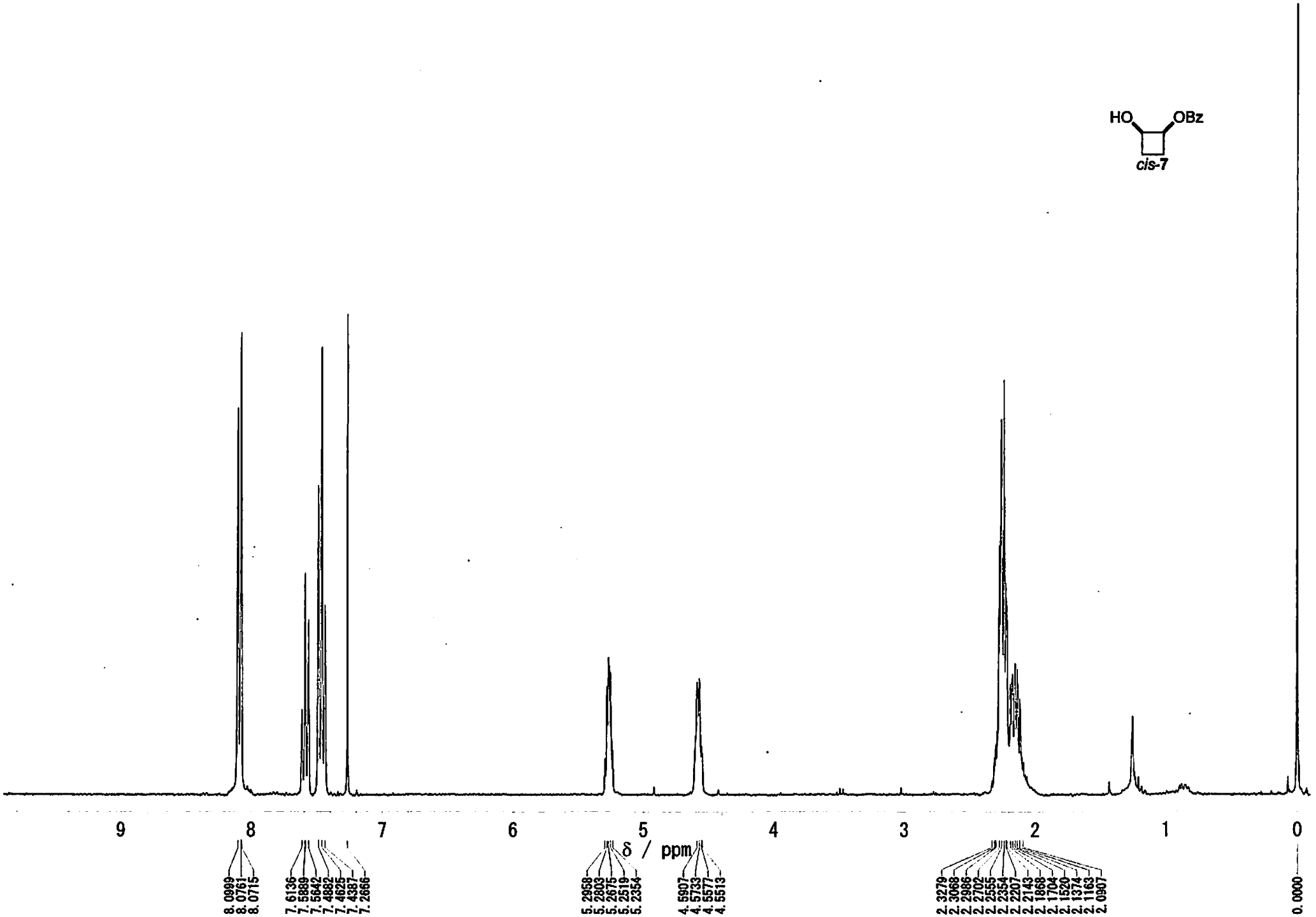

HO
OBz
trans-5
180
160
140
120
100
80
60
40
20
δ / ppm
167.0330
133.0922
130.2759
129.6685
128.4767
77.4175
77.0000
76.5749
69.7047
66.1444
45.9363
29.4480
14.9790

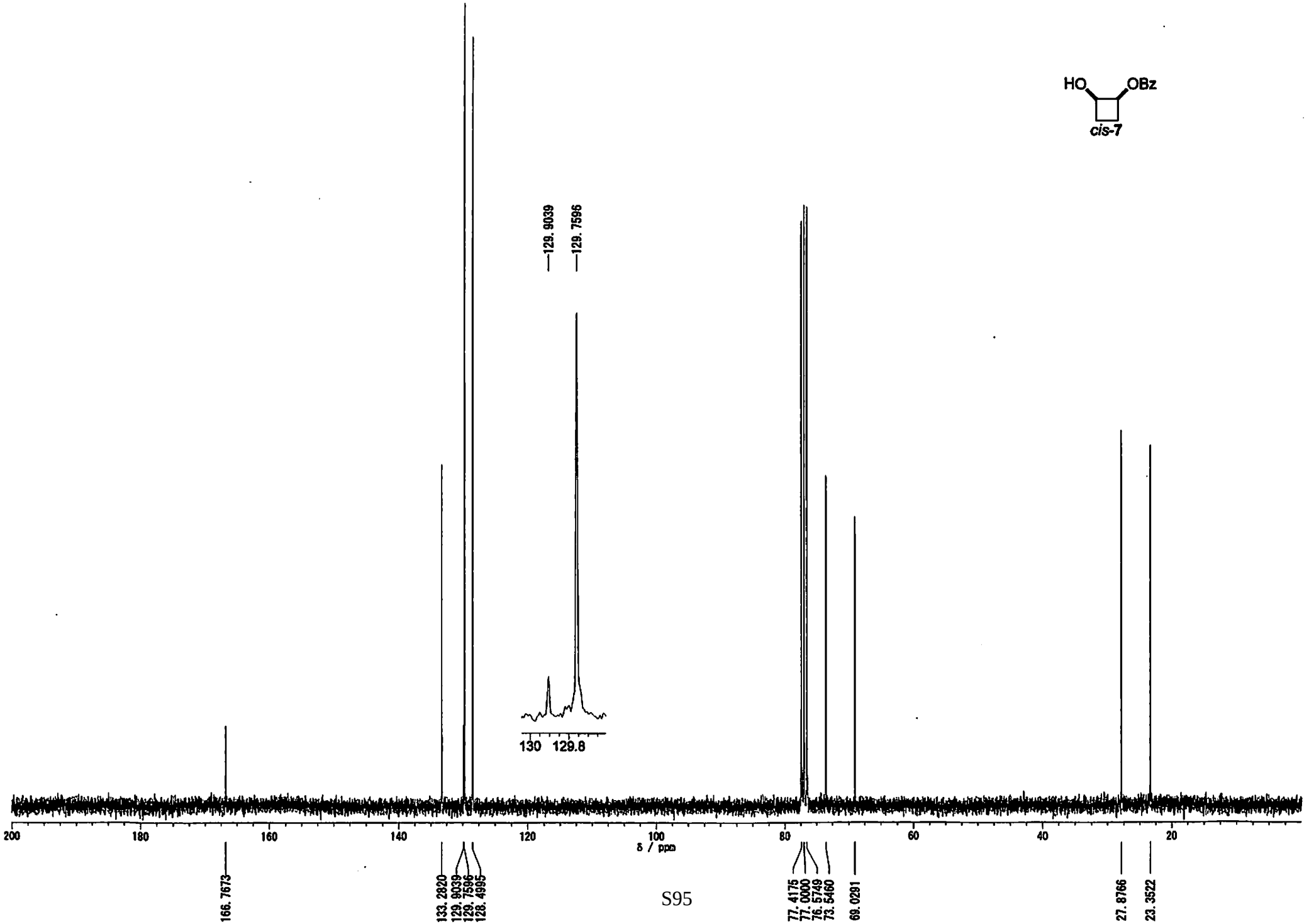

HO
OBz
cis-5
δ / ppm
8.0605
8.0440
8.0376
8.0321
7.6091
7.6054
7.5871
7.5798
7.5733
7.5605
7.5559
7.5514
7.4799
7.4543
7.4351
7.4296
7.2656
4.7958
4.7675
4.7574
4.7290
4.4900
4.4680
4.4488
4.4305
4.4094
4.3700
4.3609
4.3526
4.3425
4.3316
4.3142
2.8956
2.8727
2.8508
2.8260
2.8041
2.7793
2.6246
2.6090
2.3965
2.3883
2.3682
2.3489
2.3370
2.3260
2.3041
2.2867
2.2748
2.0815
2.0605
2.0403
2.0257
2.0064
1.9845
1.9661
1.9423
1.9194
1.9084
1.9048
1.8920
1.8810
1.8535
1.8260
1.8086
1.7903
1.7720
1.7537
1.7335
1.5641
1.4332
1.2436
0.0101
0.0000
-0.0110

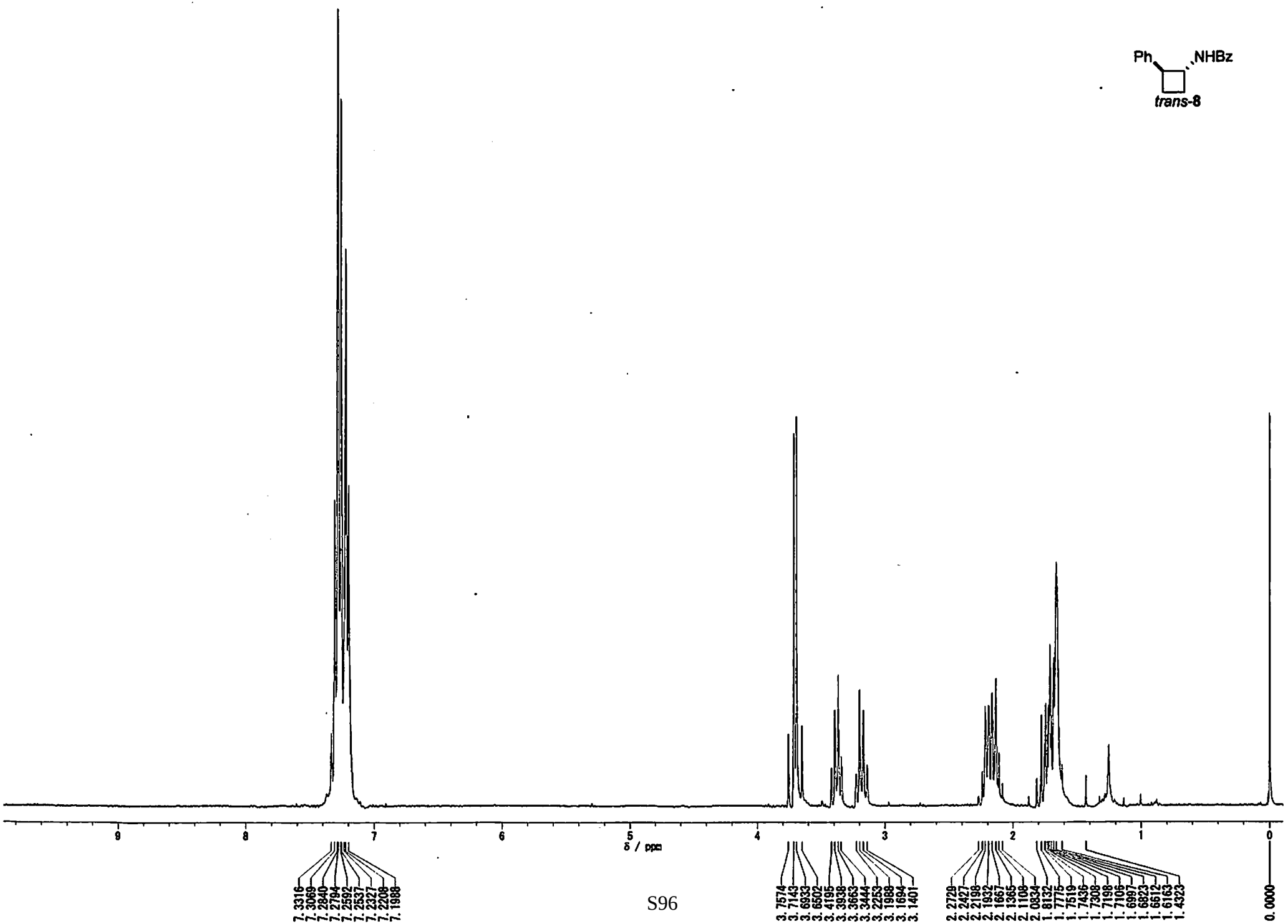

HO
OBz
cis-5
200
180
160
140
120
100
80
60
40
20
δ / ppm
167.3367
133.2137
130.1772
129.7217
128.5147
77.4251
77.0000
76.5749
57.8297
53.9885
40.4554
29.8352
17.5676

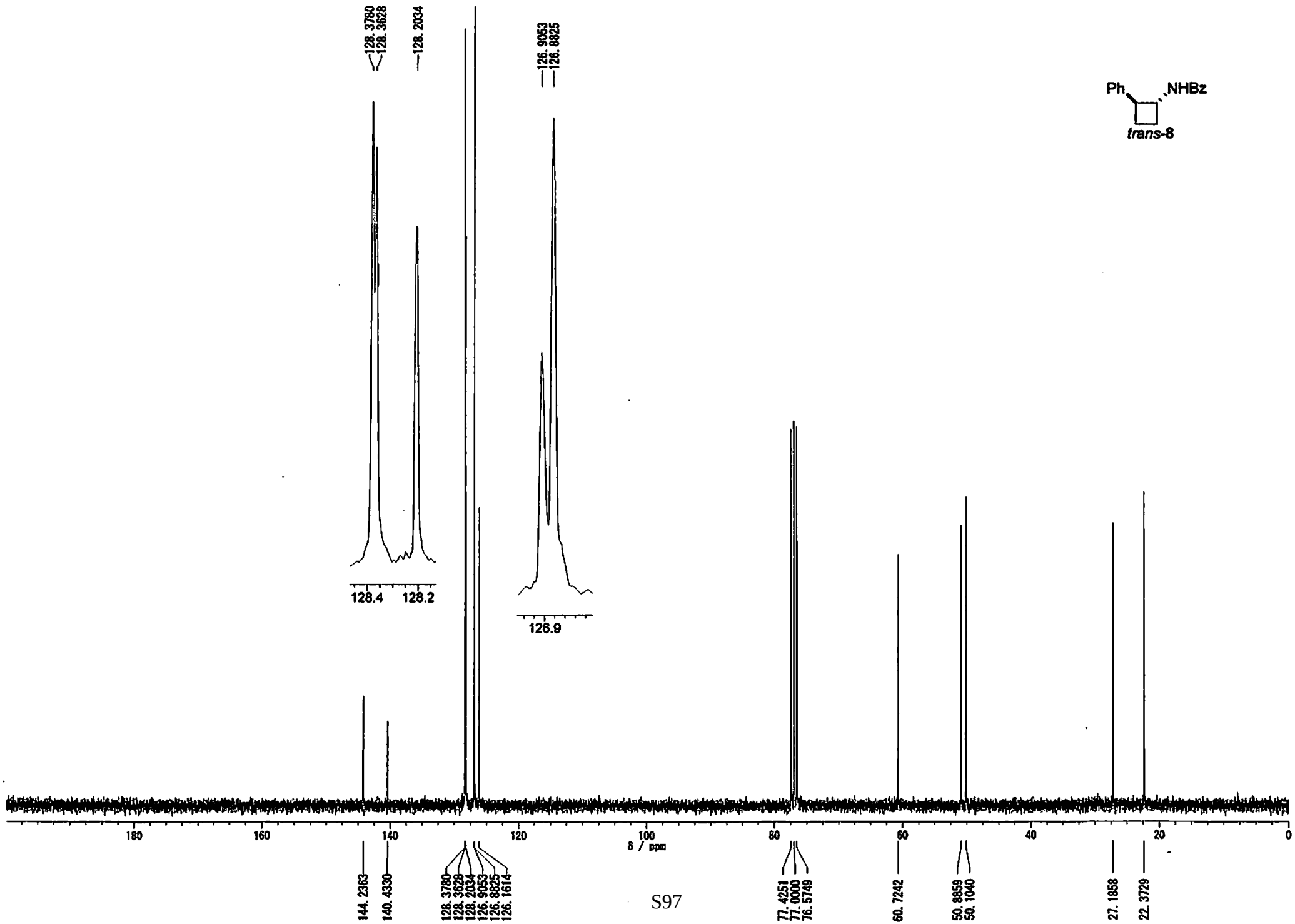

HO
OBz
trans-7
9
8
7
6
5
4
3
2
1
0
δ / ppm
8.0550
8.0312
8.0266
7.6136
7.5889
7.5642
7.4827
7.4570
7.4323
7.2647
4.8160
4.8050
4.7685
4.7384
4.7400
4.2674
4.2418
4.2171
4.2052
4.1951
2.3041
2.2857
2.2748
2.2619
2.2454
2.2345
2.2207
2.2106
2.2006
2.1823
1.8031
1.7738
1.7674
1.7381
1.7299
1.7079
1.7015
1.6951
1.6896
1.6786
1.6566
1.6502
1.6200
1.6127
1.5843
0.0000

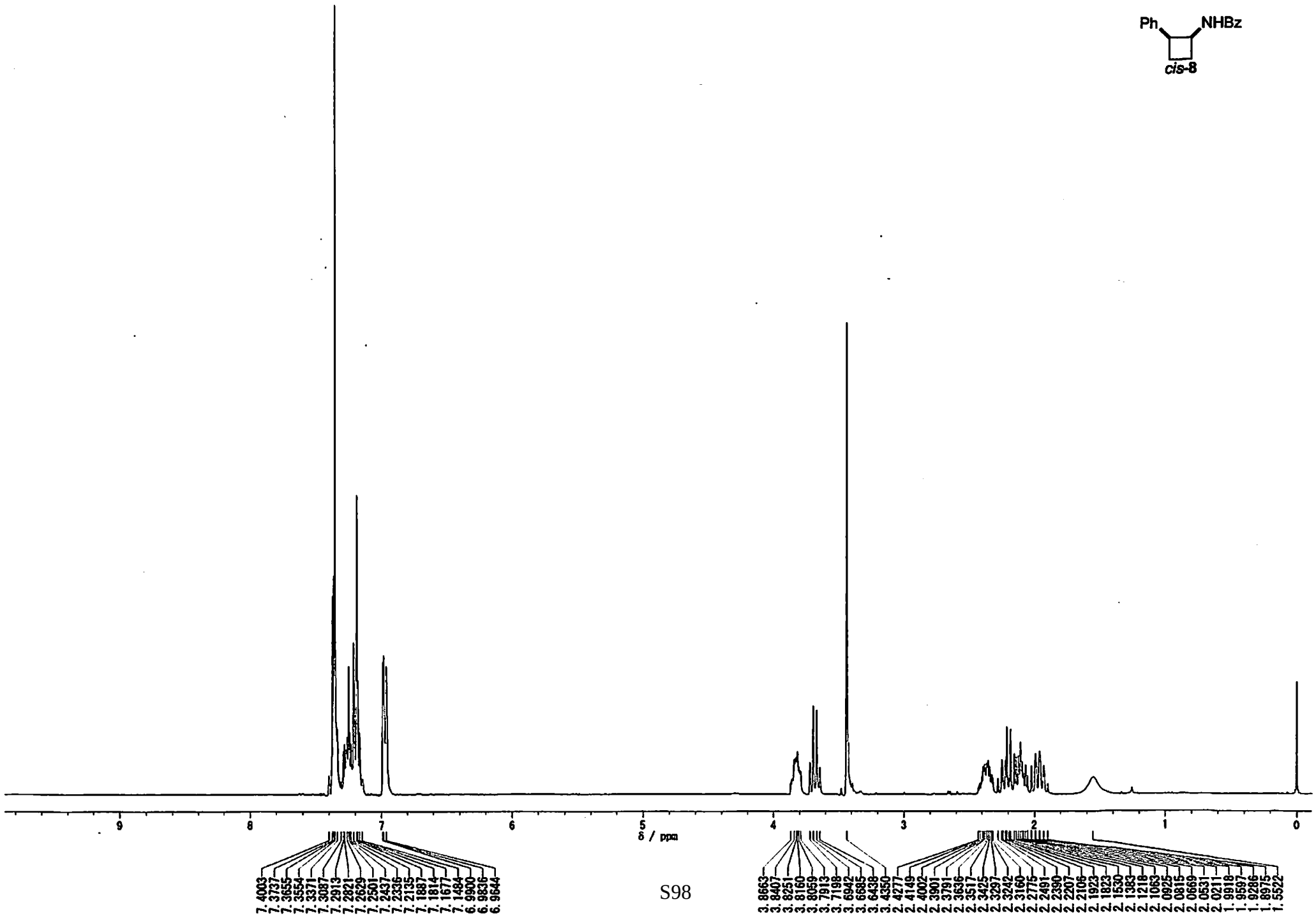

HO
OBz
trans-7
129.7824
129.7217
129.8
129.6
77.4251
77.2050
77.0000
77.6
77.4
77.2
77
200
180
160
140
120
100
80
60
40
20
δ / ppm
167.5568
133.3807
129.7824
129.7217
128.5223
77.4251
77.2050
77.0000
76.5749
72.6502
22.0237
19.0479

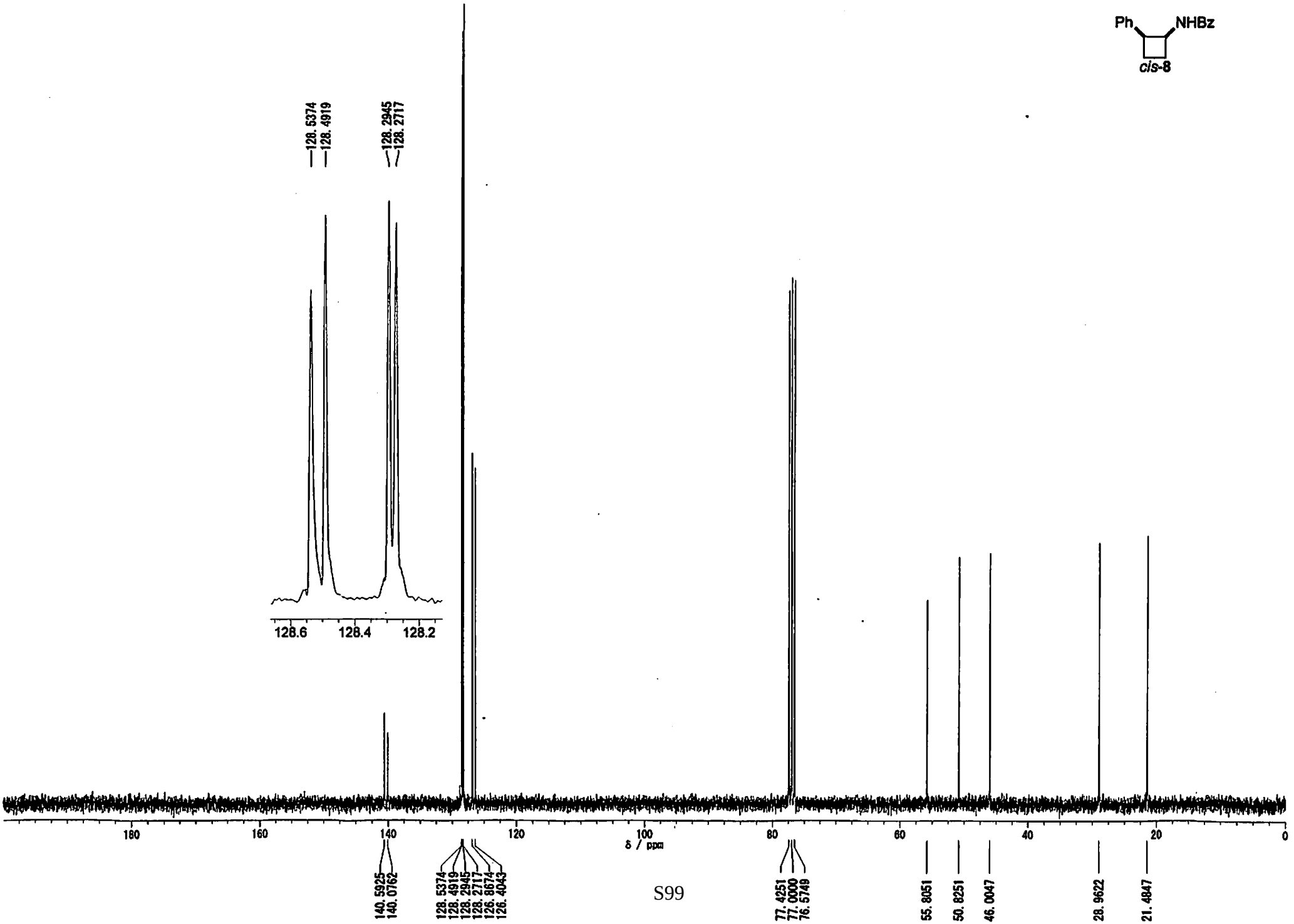

HO
OBz
cis-7
9
8
7
6
5
4
3
2
1
0
δ / ppm
8.0999
8.0761
8.0715
7.6136
7.5889
7.5642
7.4882
7.4625
7.4387
7.2666
5.2958
5.2803
5.2675
5.2519
5.2354
4.5907
4.5733
4.5577
4.5513
2.3279
2.3068
2.2986
2.2702
2.2555
2.2354
2.2207
2.2143
2.1868
2.1704
2.1520
2.1374
2.1163
2.0907
0.0000


HO
OBz
cis-7
129.9039
129.7596
130
129.8
200
180
160
140
120
100
80
60
40
20
δ / ppm
166.7673
133.2820
129.9039
129.7596
128.4995
77.4175
77.0000
76.5749
73.5460
69.0291
27.8766
23.3522


Ph
NHBz
trans-8
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.3316
7.3069
7.2840
7.2794
7.2592
7.2537
7.2327
7.2208
7.1988
3.7574
3.7143
3.6933
3.6502
3.4195
3.3938
3.3663
3.3444
3.2253
3.1988
3.1694
3.1401
2.2729
2.2427
2.2198
2.1932
2.1667
2.1365
2.1109
2.0834
1.8132
1.7775
1.7519
1.7436
1.7308
1.7198
1.7106
1.6997
1.6823
1.6612
1.6163
1.4323
0.0000


128.3780
128.3628
128.2034
126.9053
126.8825
Ph
NHBz
trans-8
128.4
128.2
126.9
δ / ppm
144.2363
140.4330
128.3780
128.3628
128.2034
126.9053
126.8825
126.1614
77.4251
77.0000
76.5749
60.7242
50.8859
50.1040
27.1858
22.3729


Ph
NHBz
cis-8
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.4003
7.3737
7.3655
7.3554
7.3371
7.3087
7.2913
7.2821
7.2629
7.2501
7.2437
7.2336
7.2135
7.1887
7.1814
7.1677
7.1484
6.9900
6.9836
6.9644
3.8663
3.8407
3.8251
3.8160
3.8059
3.7913
3.7198
3.6942
3.6685
3.6438
3.4350
2.4277
2.4149
2.4002
2.3901
2.3791
2.3636
2.3517
2.3425
2.3297
2.3242
2.3160
2.2775
2.2491
2.2390
2.2207
2.2106
2.1923
2.1823
2.1530
2.1383
2.1218
2.1063
2.0925
2.0815
2.0669
2.0531
2.0211
1.9918
1.9597
1.9286
1.8975
1.5522


Ph
NHBz
cis-8
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128.4919
128.2945
128.2717
128.6
128.4
128.2
δ / ppm
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140.0762
128.5374
128.4919
128.2945
128.2717
126.8674
126.4043
77.4251
77.0000
76.5749
55.8051
50.8251
46.0047
28.9622
21.4847