Supporting Information

Harnessing Supported Gold Nanoparticles as a Single-Electron Transfer Catalysts for Decarboxylative Cross-Coupling

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1. General considerations

1-1. Materials

$HAuCl_4 \cdot 3H_2O$ was purchased from KOJIMA CHEMICALS Co., Ltd. Active carbon (Ketjen black carbon ECP) was used as support. ZrO_2 (JRC-ZRO-7), Al_2O_3 (Sumitomo Chemical Co., Ltd, AKP-G015), TiO_2 (rutile, JRC-TIO-16), Nb_2O_5 (JRC-NBO-2),and SiO_2 (JRC-SIO-11) were kindly supplied from the Catalysis Society of Japan. Polyvinyl pyrrolidone (PVP) was purchased from Wako Chemicals. Solvents with super dehydrated grade were used as sold. Disilanes (for **2a**–**2c**) and (bispinacolato)diboron were of analytical grade and used as received without further purification. All redox esters (for **1a**–**1n**) were synthesized according to the procedures described in section 2.

1-2. Physical and analytical measurements

The products of the catalytic runs were analyzed by GC-MS (Shimadzu GCMS-QP2010, CBP-1 capillary column, i.d. 0.25 mm, length 30 m, 50–320 ºC) and gas chromatography (Shimadzu GC-2014, CBP-1 capillary column, i.d. 0.25 mm, length 30 m, 50–320 ºC). NMR spectra were recorded at room temperature on a JMN-ECS400 (FT, 400 MHz (^1H), 100 MHz (^{13}C)) instrument. Chemical shifts (δ) of ^1H and $^{13}C\{^1H\}$ NMR spectra are referenced to $SiMe_4$.

Supported Au catalysts were analyzed by TEM, XRD, nitrogen gas adsorption, temperature-programmed desorption (TPD), and XPS. High angle annular dark field-scanning transmission electron microscope (HADDF-STEM) images were recorded using a JEOL JEM-3200FS transmission electron microscope. The samples were prepared by depositing drops of ethanol suspensions containing small amounts of the powders onto carbon-coated copper grids (JEOL Ltd.) followed by evaporation of the ethanol in air. X-ray powder diffraction analyses were performed using Cu $K\alpha$ radiation and a one-dimensional X-ray detector (XRD: SmartLab, RIGAKU). The samples were scanned from 2Θ=10° to 70° at a scanning rate of 10° min^{-1} and a resolution of 0.01°. The Brunauer-Emmett-Teller (BET) specific surface area was estimated from N_2 isotherms obtained using a BELSORP-mini II (Microtrac MRB, Japan) at 77 K. The analysed samples were evacuated at 573 K for 2 h prior to the measurement. NH_3-TPD were carried out to evaluate the acid property of the supported Au catalysts. TPD was performed on a BELCAT-II (Microtrac MRB) as follows: 0.1 g of the sample was loaded in a quartz reactor and pretreated under a He flow at 500 ^{o}C for 1 h. NH_3 adsorption was carried out over 30 min with NH_3/He at 100 ^{o}C followed by purging with He for 15 min. The temperature was linearly increased from 100–600 ^{o}C (10 ^{o}C min^{-1}). The outlet flow was analyzed by means of a Q-Mass (BELMASS, Microtrac MRB). XPS analysis of the catalysts was performed using a JPS-9010 MX instrument. The spectra were measured using Mg *K*α radiation (15 kV, 400 W) in a chamber at a base pressure of $<10^{-7}$ Pa. All spectra were calibrated using C1s (284.5 eV) as a reference. CV measurements were recorded with ECstats-302 (EC frontier, Japan). Measurements used a glassy carbon working electrode, a Ag/$AgNO_3$ reference electrode, and a Pt wire counter electrode. The concentration of the sample solution was fixed at 20 mM in degassed MeCN/0.1 M $TBAPF_6$ and the sweep rates were set at 50 mV/s. The applied voltage was internally referenced to the redox potential of the ferrocene/ferrocenium ion pair.

2. Experimental procedure

2-1. Preparation of active carbon-supported Au NPs catalysts by a sol-immobilization method[1]

Active carbon-supported Au catalysts were prepared through a sol immobilization method. To an aqueous solution (120 mL) of $HAuCl_4 \cdot 3H_2O$ was added PVP (36 mg), and the solution was cooled to 273 K with an ice bath. Subsequently, 0.1 M aqueous solution of $NaBH_4$ (7.5 mL, $NaBH_4$/metal (mol/mol) = 5) was added rapidly under vigorous stirring. After 0.5 h of colloid generation, 0.97 g of active carbon was added to the colloidal solution. After vigorous stirring overnight at room temperature, the resulting black powder was separated from the suspension by centrifugation, thoroughly washed with distilled water, and dried overnight at 80 °C. The resulting powder was reduced at 400 °C under H_2 flow condition for 2 h to obtain supported Au catalysts. The loading amount of gold was set at 3wt%.

2-2. Preparation of supported Au catalysts by a deposition-precipitation method[2]

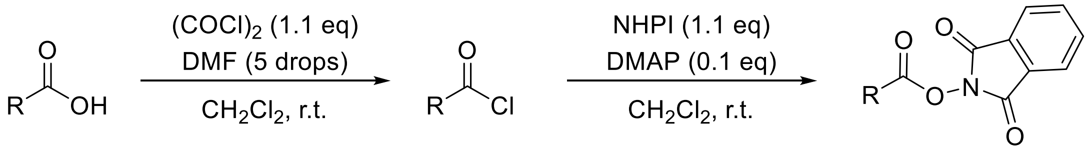
Supported Au catalysts (Au/ZrO_2, Au/Al_2O_3, and Au/TiO_2) were prepared by a deposition-precipitation method with urea as pH adjusting reagent. 0.97 g of support (ZrO_2, Al_2O_3, or TiO_2) was added to 152 mL of an aqueous solution of $HAuCl_4$ (1 mM, the gold concentration in solution corresponds to a theoretical Au loading of 3wt%) and urea (0.1 M). The suspension was heated at 80 °C and stirred vigorously for 16 h (the pH increased from about 3 to 8). The resulting dirty yellow precipitate was separated from the suspension. Prior to their use in catalytic reactions, the catalysts were calcined in air at 573 K for 4 h and reduced in a hydrogen atmosphere at 200 °C for 1 h.

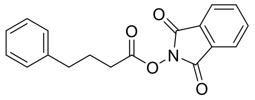
SiO_2- or Nb_2O_5 supported Au catalysts were prepared by a deposition-precipitation method with the use of $Au(en)_2Cl_3$ as an Au precursor. The pH value of an aqueous solution containing 50 mg of $Au(en)_2Cl_3$ was adjusted to 10 by 1M NaOH solution. After 0.99 g of SiO_2 or Nb_2O_5 was added to the solution, the pH value was re-adjusted to 10 with 1M NaOH solution. The suspension was stirred at 343 K for 2 h, separated by centrifugation, and then washed three times with methanol. The resulting powder was dried in vacuo at 343 K for 5 h. Prior to their use in catalytic reactions, the catalysts were calcined in air at 773 K for 1 h and reduced in a hydrogen atmosphere at 423 K for 1 h. The total loading amount of metal was set at 1wt%.

2-3. Preparation of active carbon-supported metal NPs catalysts by an impregnation method

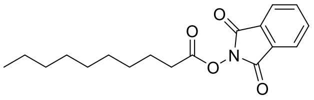
Active carbon-supported metal (Ni, Cu, Rh, Pd, Ag or Pt) catalysts were prepared by an impregnation method with the use of $Ni(NO_3)_2$, $Cu(NO_3)_2$, $RhCl_3$, $PdCl_2$, $AgNO_3$, or H_2PtCl_6 as a metal precursor. ZrO_2 was added to an aqueous solution of the metal precursor, and the suspension was stirred at 80 ^{o}C for 2 h. After the evaporation of water, the resulting powder was reduced at 400 ^{o}C under H_2 flow condition for 2 h to obtain supported metal catalysts. The total loading amount of metal was set at 3wt%.

2-4. Procedure for preparation of redox esters[3]





1a



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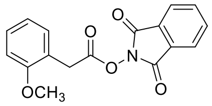

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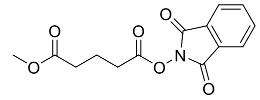

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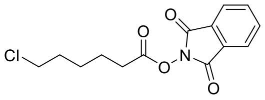

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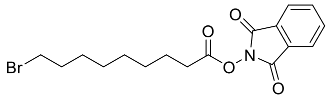

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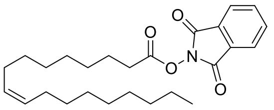

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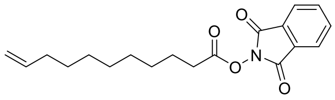

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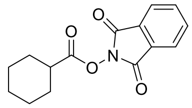

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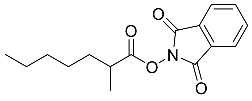

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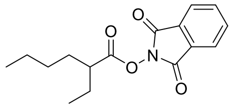

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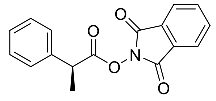

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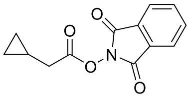

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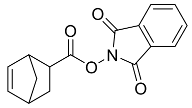
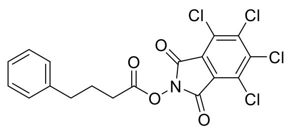
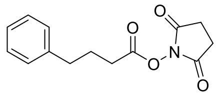


1n



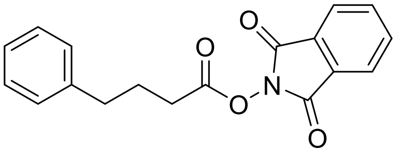
1a-TCNHPI



1a-NHS

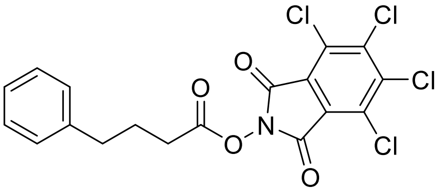
To a solution of carboxylic acid (1.0 equiv.), and *N*,*N*-dimethylformamide (DMF; 5 drops) in CH_2Cl_2 (10 mL), oxalyl chloride (1.1 equiv.) was added dropwise at 0 ºC. Afer the mixture was stirred at room temperature until gas evolution ceased, all volatiles were removed under vacuum to yield the desired acid chloride, which was used in the next step without purification. A solution of the acid chloride in anhydrous CH_2Cl_2 was added to a solution of *N*-hydroxyphthalimide (NHPI; 1.1 equiv) and triethylamine (1.1 equiv.) in anhydrous CH_2Cl_2 (0.2 M for the acid chloride). The resulting solution was stirred overnight at r.t. After the completion of the reaction was confirmed by TLC, the reaction was quenched by the addition of 1N HCl. The organic layer was separated. The resulting mixture was then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The NHPI esters were isolated by silica-gel column chromatography (a mixture of hexane and EtOAc).

1,3-Dioxo-1,3-dihydro-2*H*-isoindol-2-yl 4-phenylbutanoate (**1a-NHPI**; CAS Registry Number 1841512-58-0)[4]



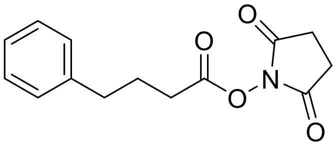
White solid; yield 84%, 1.31 g, (5 mmol scale); hexane/EtOAc = 3/1 (R_f = 0.38); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87-7.91 (m, 2H), 7.77-7.81 (m, 2H), 7.20-7.30 (m, 2H), 7.20-7.26 (m, 3H), 2.78 (t, J =7.6 Hz, 2H), 2.68 (t, J =7.2 Hz, 2H), 2.09-2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 169.4,161.9, 140.6, 134.7, 128.8, 128.5,128.5, 126.2, 123.9, 34.6, 30.2, 26.3.

4,5,6,7-Tetrachloro-1,3-dioxoisoindolin-2-yl 4-phenylbutanoate (**1a-TCNHPI**; CAS Registry Number 2251073-19-3)[5]



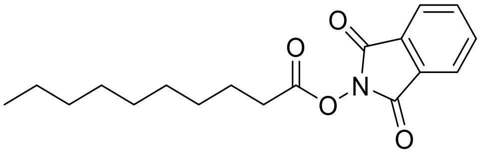
White solid; yield 35%, 796 mg, (5 mmol scale); hexane/EtOAc = 5/1 (R_f = 0.48); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.29-7.33 (m, 2H), 7.20-7.23 (m, 3H), 2.77 (t, J=7.4 Hz, 2H), 2.67 (t, J=7.4 Hz, 2H), 2.08-2.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.9, 157.5, 140.9, 140.4, 130.4, 128.5, 126.2, 124.6, 34.5, 30.0, 26.2.

2,5-dioxopyrrolidin-1-yl 4-phenylbutanoate (**1a-NHS**; CAS Registry Number 88556-26-7)



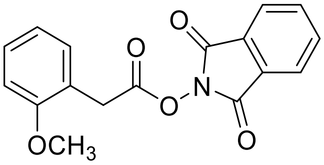
Colorless oil; yield 73%, 0.96 g, (5 mmol scale); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ7.28-7.32 (m, 2H), 7.19-7.23 (m, 3H), 2.85 (s, 2H), 2.84 (s, 2H), 2.74 (t, *J* =7.6 Hz, 2H), 2.61 (t, *J* =7.4 Hz, 2H), 2.08 (quin, *J* =7.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ 169.1, 168.4, 140.6, 128.5, 126.2, 34.5, 30.1, 26.2, 25.6. HRMS (FAB) m/z [M-H]$^+$ calcd for $C_{14}H_{14}NO_4$ 260.0923, found 260.0924.

1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl decanoate (**1b**; CAS Registry Number 94815-91-5)[6]



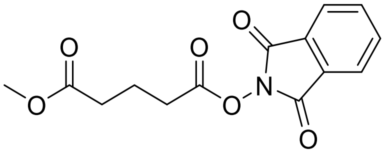
White solid; yield 39%, 620 mg, (5 mmol scale); hexane/EtOAc = 5/1 (R_f = 0.27); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 7.86-7.91 (m, 2H), 7.76-7.80 (m, 2H), 2.66 (t, *J* =7.6 Hz, 2H), 1.75-1.82 (m, 2H), 1.41-1.48 (m, 2H), 1.19-1.36 (m, 10H), 0.89 (t, *J* =7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ 169.6, 162.0, 134.7, 128.9, 123.9, 31.8, 31.0, 29.3, 29.2, 29.1, 28.8, 24.7, 22.7, 14.1.

1,3-dioxoisoindolin-2-yl 2-(2-methoxyphenyl)acetate (**1c**; CAS Registry Number 900634-63-1)[5]



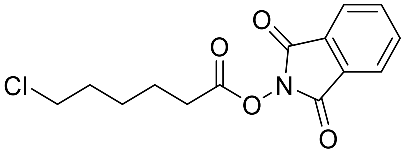
Yellowish solid; (5 mmol scale); hexane/EtOAc = 3/1 (R_f = 0.38); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ7.84-7.89 (m, 2H), 7.75-7.79 (m, 2H), 7.28-7.33 (m, 2H), 6.90-6.97 (m, 2H), 3.97 (s, 2H), 3.90 (s, 3H). ; ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ167.9, 161.8, 157.4, 134.6, 130.7, 129.3, 128.8, 123.8, 120.7, 120.5, 110.4, 55.4, 33.1..

1,3-dioxoisoindolin-2-yl methyl glutarate (**1d**; CAS Registry Number 2228040-39-7)[7]



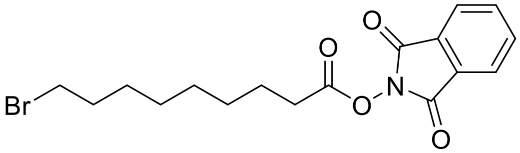
White solid; yield 66%, 1.43 g, (7 mmol scale); hexane/EtOAc = 3/1 (R_f = 0.21); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ7.86-7.89 (m, 2H), 7.78-7.81 (m, 2H), 3.70 (s, 3H), 2.77 (t, *J*=7.4 Hz, 2H), 2.51 (t, *J*=7.2 Hz, 2H), 2.11 (quin, *J*=7.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) 172.9, 169.0, 161.8, 134.8, 128.8, 123.9, 51.7, 32.4, 30.0, 19.8.

1,3-dioxoisoindolin-2-yl 6-chlorohexanoate (**1e**; CAS Registry Number 2360921-48-6)[8]



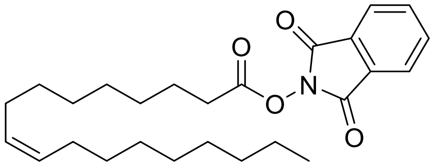
White solid; yield 59%, 0.87 g, (5 mmol scale); hexane/EtOAc = 3/1 (R_f = 0.36); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ7.86-7.89 (m, 2H), 7.78-7.81 (m, 2H), 3.57 (t, *J*=6.4 Hz, 2H), 2.70 (t, *J*=7.4 Hz, 2H), 1.79-1.88 (m, 4H), 1.57-1.65 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ169.3, 161.9, 134.7, 128.8, 123.9, 44.6, 32.0, 30.8, 26.1, 24.0.

1,3-dioxoisoindolin-2-yl 9-bromononanoate (**1f**; CAS Registry Number 2647931-18-6)[9]



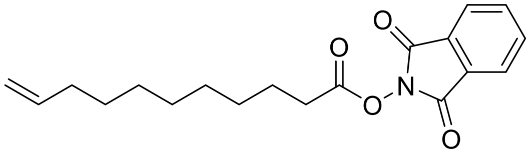
White solid; yield 73%, 0.84 g, (3 mmol scale); hexane/EtOAc = 3/1 (R_f = 0.46); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 7.85-7.89 (m, 2H), 7.76-7.80 (m, 2H), 3.41 (t, *J*=6.8 Hz, 2H), 2.66 (t, *J*=7.2 Hz, 2H), 1.86 (quin, *J*=7.2 Hz, 2H), 1.78 (quin, *J*=7.5 Hz, 2H), 1.34-1.44 (m, 8H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ169.5, 161.9, 134.7, 128.8, 123.9, 34.0, 32.7, 30.9, 28.9, 28.6, 28.4, 28.0, 24.6.

1,3-dioxoisoindolin-2-yl oleate (**1g**; CAS Registry Number 2244772-55-0)[10]



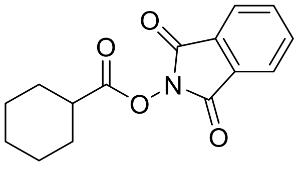
Colorless oil; yield 64%, 1.41 g, (5 mmol scale); hexane/EtOAc = 3/1 ($R_f = 0.47$); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.85-7.89 (m, 2H), 7.75-7.80 (m, 2H), 5.30-5.38 (m, 2H), 2.66 (t, *J*= 7.6 Hz, 2H), 1.99-2.02 (m, 4H), 1.78 (quin, *J*= 7.5 Hz, 2H), 1.26-1.44 (m, 20H), 0.87 (t, *J*= 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ169.5, 161.9, 134.6, 130.0, 129.6, 128.9, 123.9, 31.9, 30.9, 29.7, 29.6, 29.5, 29.3, 29.0, 28.8, 27.2, 27.1, 24.6, 22.7, 14.1.

1,3-dioxoisoindolin-2-yl undec-10-enoate (**1h**; CAS Registry Number 1631179-25-3)[11]



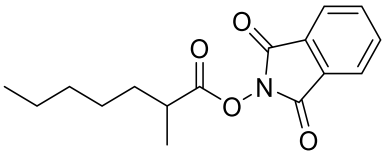
White solid; yield 84%, 1.39 g, (5 mmol scale); hexane/EtOAc = 5/1 ($R_f = 0.20$); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.85-7.90 (m, 2H), 7.77-7.80 (m, 2H), 5.76-5.86 (m, 1H), 4.91-5.02 (m, 2H), 2.66 (t, *J*=7.4 Hz, 2H), 2.04 (q, *J*=6.9 Hz, 2H), 1.78 (quin, *J*=7.5 Hz, 2H), 1.32-1.44 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ169.6, 161.9, 139.1, 134.7, 128.9, 123.9, 114.1, 33.8, 30.9, 29.2, 29.0, 29.0, 28.8, 28.8, 24.6.

1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate (**1i**; CAS Registry Number 126812-30-4)[12]



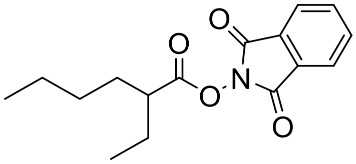
White solid; yield 86%, 1.17 g, (5 mmol scale); hexane/EtOAc = 3/1 ($R_f = 0.56$); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.85-7.89 (m, 2H), 7.75-7.79 (m, 2H), 2.70-2.77 (m, 1H), 2.08-2.12 (m, 2H), 1.81-1.86 (m, 2H), 1.61-1.70 (m, 3H), 1.25-1.43 (m, 3H). ; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 171.8, 162.0, 134.6, 128.9, 123.8, 40.4, 28.8, 25.4, 25.0.

1,3-dioxoisoindolin-2-yl 2-methylheptanoate (**1j**; CAS Registry Number 2152645-22-0)[13]



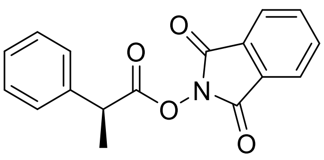
Colorless oil; yield 69%, 1.05 g, (5 mmol scale); hexane/EtOAc = 5/1 (R_f = 0.30); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.86-7.89 (m, 2H), 7.76-7.80 (m, 2H), 2.79-2.88 (m, 1H), 1.78-1.88 (m, 1H), 1.56-1.65 (m, 1H), 1.43-1.50 (m, 2H), 1.33-1.36 (m, 7H), 0.91 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ172.8, 162.0, 134.0, 128.9, 123.9, 37.1, 33.6, 31.5, 26.5, 22.4, 17.0, 14.0.

1,3-dioxoisoindolin-2-yl 2-ethylhexanoate (**1k**; CAS Registry Number 1872262-63-9)[12]



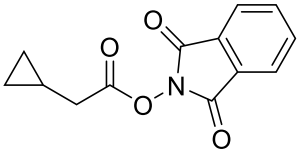
Colorless liquid; yield 65%, 934 mg, (5 mmol scale); hexane/EtOAc = 3/1 (R_f = 0.32); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.84-7.89 (m, 2H), 7.75-7.79 (m, 2H), 2.62-2.69 (m, 1H), 1.59-1.83 (m, 4H), 1.34-1.50 (m, 4H), 1.07 (t, J =7.2 Hz, 3H), 0.94 (t, J =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.4, 162.0, 134.6, 128.9, 123.8, 44.8, 31.7, 29.2, 25.6, 22.5, 13.9, 11.6.

1,3-dioxoisoindolin-2-yl (*S*)-2-phenylpropanoate (**1l**; CAS Registry Number 2248200-52-2)



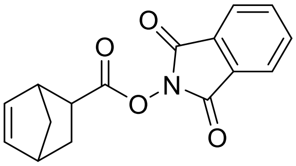
Yellow liquid; yield 79%, 1.30 g, (5 mmol scale); hexane/EtOAc = 5/1 (R_f = 0.22); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.86 (dd, J =5.4, 3.0 Hz, 2H), 7.76-7.79 (m, 2H), 7.39-7.43 (m,4H), 7.31-7.36 (m, 1H), 4.13 (q, J =7.2 Hz, 1H), 1.68 (d, J =7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 170.7, 161.8, 138.3, 134.7, 128.9, 128.8, 127.8, 127.5, 123.9, 42.9, 19.0. HRMS (FAB) m/z $[M-H]^+$ calcd for $C_{17}H_{12}NO_4$ 294.0766, found 294.0769.

1,3-dioxoisoindolin-2-yl 2-cyclopropylacetate (**1m**; CAS Registry Number 2055858-83-6)[14]



White solid; (5 mmol scale); hexane/EtOAc = 3/1 (R_f = 0.33); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ7.86-7.89 (m, 2H), 7.78-7.81 (m, 2H), 2.59 (d, *J*=7.2 Hz, 2H), 1.14-1.23 (m, 1H), 0.65-0.70 (m, 2H), 0.31-0.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ168.9, 161.9, 134.7, 128.9, 123.9, 36.0, 6.5, 4.6.

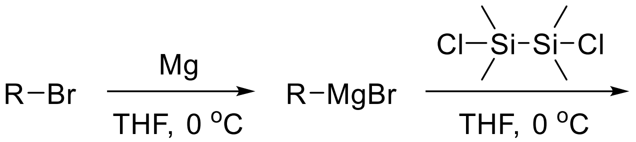
1,3-dioxoisoindolin-2-yl bicyclo[2.2.1]hept-5-ene-2-carboxylate (**1n**; CAS Registry Number 2248324-57-2)[15]

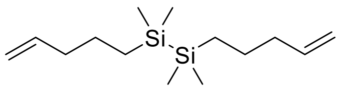


White solid; yield 82%, 1.22 g, (5 mmol scale); hexane/EtOAc = 5/1 (R_f = 0.26); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ7.84-7.90 (m, 2H), 7.75-7.81 (m, 2H), 6.16-6.27 (m, 2H), 3.47 (m, 1H), 3.31 (dt, *J*=9.2, 3.6 Hz, 1H), 3.01 (m, 1H), 2.02-2.09 (m, 1H), 1.52-1.60 (m, 2H), 1.36-1.38 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ170.8, 162.1, 138.1, 134.6, 132.2, 128.9, 123.8, 49.7, 46.5, 42.5, 40.6, 29.6.

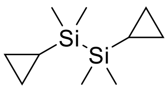
2-5. Procedure for preparation of symmetric disilanes[16,17]

(Method A)

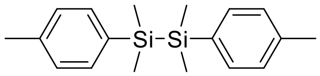




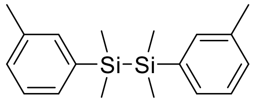
2d



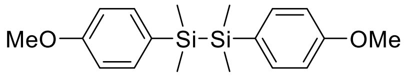
2e



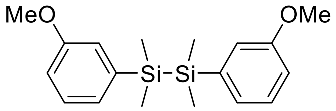
2j



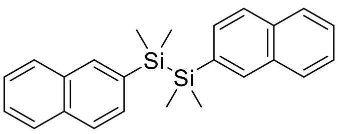
2k



2l



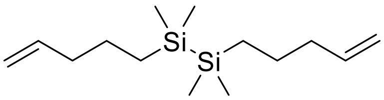
2m



2n

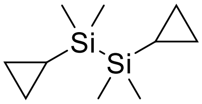
To a 100-mL Schlenk tube containing 10 mL anhydrous tetrahydrofuran (THF) and magnesium tunes (120 mg, 10 mmol), a solution of alkyl/aryl bromide (10 mmol) in 10 mL anhydrous THF was added dropwise at 0 ºC. After stirring for 1 h at 0 ºC, dichlorotetramethyldisilane (5.0 mmol) was added dropwise to the reaction mixture at 0 ºC. After the completion of the reaction was confirmed by GC-MS, the reaction was quenched by the addition of water. The organic layer was separated. The resulting mixture was then extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The target disilanes were isolated by silica-gel column chromatography (hexane).

1,1,2,2-tetramethyl-1,2-di(pent-4-en-1-yl)disilane (**2d**; New compound)



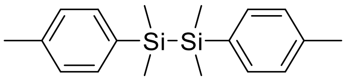
Colorless liquid; yield 89%, 1.12 g, (5 mmol scale); hexane only (R_f = 0.63); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ5.75-5.85 (m, 2H), 4.94-5.03 (m, 4H), 2.05-2.10 (m, 4H), 1.37-1.45 (m, 4H), 0.58-0.62 (m, 4H), 0.04 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ138.9, 114.4, 37.8, 24.1, 14.7, -3.9. HRMS (FAB) m/z $[M-H]^+$ calcd for $C_{14}H_{29}Si_2$ 253.1808, found 253.1799.

1,2-Dicyclopropyl-1,1,2,2-tetramethyldisilane (**2e**; CAS Registry Number 18645-51-7)



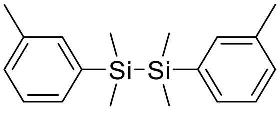
Yellow liquid; yield 43%, 0.43 g, (5 mmol scale); hexane only (R_f = 0.60); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ0.54-0.58 (m, 4H), 0.18-0.22 (m, 4H), -0.03 (s, 12H), -0.38 (tt, *J*=6.8, 9.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ1.3, -5.1, -5.7. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_9H_{19}Si_2$ 183.1025, found 183.1031.

1,1,2,2-tetramethyl-1,2-di-*p*-tolyldisilane (**2j**; CAS Registry Number 5971-96-0)[18]



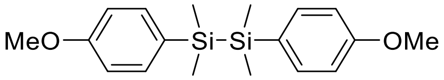
White solid; yield 52%, 777 mg, (5 mmol scale); hexane/EtOAc = 20/1(R_f = 0.56); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.32-7.34 (m, 4H), 7.16-7.18 (m, 4H), 2.38 (s, 6H), 0.34 (s, 12H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ138.1, 135.3, 133.9, 128.5, 21.4, -3.7.

1,1,2,2-tetramethyl-1,2-di-*m*-tolyldisilane (**2k**; CAS Registry Number 684239-25-6)



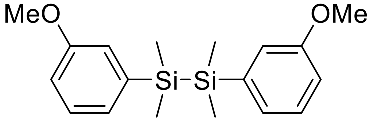
White solid; yield 78%, 2.33 g, (10 mmol scale); hexane/EtOAc = 50/1(R_f = 0.55); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.23-7.28 (m, 4H), 7.17-7.20 (m, 4H), 2.37 (s, 6H), 0.37 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ138.8, 136.8, 134.6, 130.9, 129.2, 127.5, 21.5, -3.9. HRMS (FAB) m/z $[M+H]^+$ calcd for $C_{18}H_{27}Si_2$ 299.1651, found 299.1647.

1,2-bis(4-methoxyphenyl)-1,1,2,2-tetramethyldisilane (**2l**; CAS Registry Number 6009-50-3)



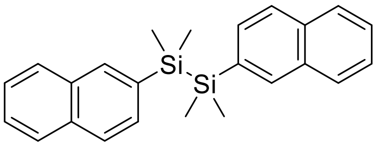
White solid; (5 mmol scale); hexane/EtOAc = 10/1 (R_f = 0.36); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.32-7.35 (m, 4H), 6.88-6.92 (m, 4H), 3.83 (s, 6H), 0.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ159.9, 135.2, 129.7, 113.5, 55.0, -3.6. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{17}H_{23}O_2Si_2$ 315.1237, found 315.1232.

1,2-Bis(3-methoxyphenyl)-1,1,2,2-tetramethyldisilane (**2m**; New compound)



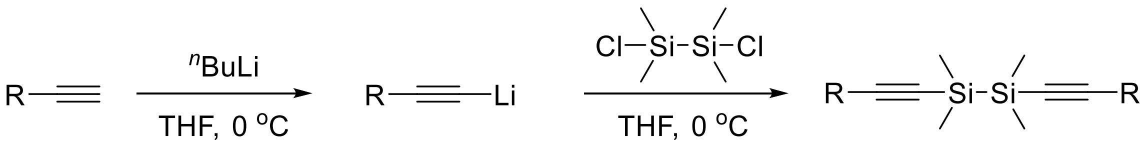
White liquid; yield 43%, 0.67 g, (5 mmol scale); hexane/EtOAc = 20/1 (R_f = 0.25); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.24 (t, J=7.6 Hz, 2H), 6.97 (d, J=7.6 Hz, 2H), 6.83-6.89 (m, 4H), 3.74 (s, 6H), 0.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ158.8, 140.6, 128.8, 126.1, 119.1, 113.8, 55.0, -3.9. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{17}H_{23}O_2Si_2$ 315.1237, found 315.1232.

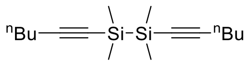
1,1,2,2-tetramethyl-1,2-di(naphthalen-2-yl)disilane (**2n**; CAS Registry Number 130976-50-0)



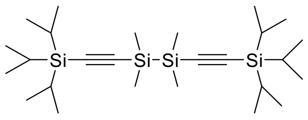
White solid; yield 29%, 0.58 g, (5 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.76-7.98 (m, 8H), 7.46-7.50 (m, 6H), 0.47 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ136.5, 134.3, 133.4, 132.9, 130.4, 127.9, 127.6, 126.8, 126.1, 125.8, -3.8. HRMS (FAB) m/z $[M]^+$ calcd for $C_{24}H_{26}Si_2$ 370.1573, found 370.1575.

(Method B)

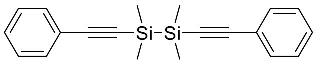




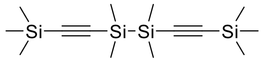
2f



2g



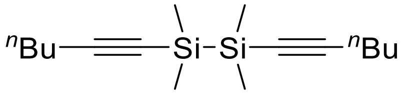
2h



2i

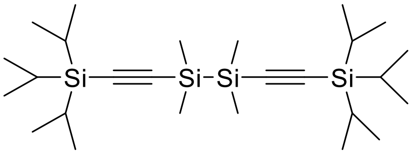
To a solution of terminal alkyne (12 mmol) in THF (20 mL), a hexane solution of *n*-BuLi (1.6 M, 6.25 mL, 10 mmol) was added dropwise at 0 ºC. After stirring for 1 h at 0 ºC, dichlorotetramethyldisilane (5.0 mmol) was added dropwise to the reaction mixture at 0 ºC. After the completion of the reaction was confirmed by GC-MS, the reaction was quenched by the addition of water. The organic layer was separated. The resulting mixture was then extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed in vacuo. The target disilanes were isolated by silica-gel column chromatography (hexane).

1,2-di(hex-1-yn-1-yl)-1,1,2,2-tetramethyldisilane (**2f**; New compound)



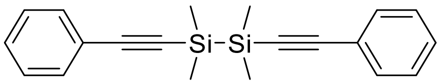
Colorless liquid; yield 66%, 926 mg, (5 mmol scale); hexane ($R_f = 0.31$); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 2.24 (t, *J*=6.8 Hz, 4H), 1.46-1.52 (m, 4H), 1.38-1.44 (m, 4H), 0.91 (t, *J*=7.2 Hz, 6H), 0.23 (s, 12H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 110.0, 82.0, 30.8, 21.8, 19.7, 13.6, -2.8. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{15}H_{27}Si_2$ 263.1651, found 263.1646.

1,1,2,2-tetramethyl-1,2-bis((triisopropylsilyl)ethynyl)disilane (**2g**; New compound)



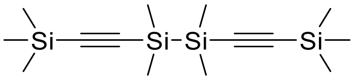
White solid; yield 92%, 2.2 g, (5 mmol scale); hexane only (R_f = 0.45); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ1.02-1.10 (m, 42H), 0.27 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ113.6, 112.8, 18.6, 11.1, -3.1. HRMS (FAB) m/z [M-H]$^+$ calcd for $C_{26}H_{53}Si_4$ 477.3224, found 477.3228.

1,1,2,2-tetramethyl-1,2-bis(phenylethynyl)disilane (**2h**; CAS Registry Number 34627-90-2)



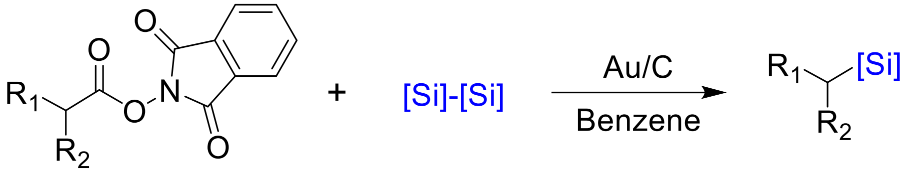
White solid; yield 39%, 0.62 g, (5 mmol scale); hexane only (R_f = 0.23); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.45-7.48 (m, 4H), 7.27-7.32 (m, 6H), 0.41 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ131.9, 128.4, 128.2, 123.2, 107.8, 92.1, -2.9. HRMS (FAB) m/z [M-H]$^+$ calcd for $C_{20}H_{21}Si_2$ 317.1182, found 317.1175.

1,1,2,2-tetramethyl-1,2-bis[(trimethylsilyl)ethynyl]disilane (**2i**; CAS Registry Number 85442-79-1)



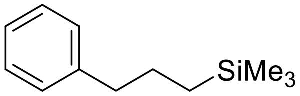
White solid; yield 68%, 1.085 g, (5 mmol scale); hexane/EtOAc = 50/1 (R_f = 0.45); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 0.27 (s, 12H), 0.17 (s, 18H). ; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ116.9, 111.6, 0.0, -3.2. HRMS (FAB) m/z [M-CH_3]$^+$ calcd for $C_{13}H_{27}Si_4$ 295.1192, found 295.1190.

2-6. General procedure for the reaction of NHPI esters with disilanes over Au/C catalyst



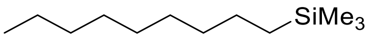
A typical reaction procedure is as follows: NHPI ester (0.30 mmol), hexamethyldisilane (0.90 mmol) and benzene (1.5 mL) were added to a Schlenk tube containing the supported Au catalyst (1 mol% as Au) under an Ar atmosphere. The progress of the reaction was monitored by thin layer chromatography (TLC) and GC analysis. After NHPI ester or disilane was completely consumed, the solid catalyst was removed by passing the mixture through a 0.45 *μ*m polytetrafluoroethylene (PTFE) filter (Millipore Millex LH). The remaining solution was concentrated by rotary evaporation under reduced pressure without heating. The resulting liquid was purified through silica gel column chromatography (a mixture of hexane and EtOAc) to give the product.

[3-(Trimethylsilyl)propyl]benzene (**3aa**; CAS Registry Number 775-24-6)[19]



Colorless liquid; yield 59%, 114.1 mg, (1 mmol scale); hexane only (R_f = 0.48); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 7.30 (t, *J*=7.6 Hz, 2H), 7.19-7.22 (m, 2H), 2.65 (t, *J* =7.6 Hz, 2H), 1.61-1.69 (m, 2H), 0.58 (t, *J* =8.4 Hz, 2H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ 142.7, 128.4, 128.2, 125.6, 40.0, 26.2, 16.6, -1.7.

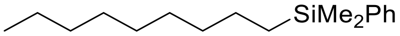
Trimethylnonylsilane (**3ba**; CAS Registry Number 18159-49-4)



Colorless liquid; yield 57%, 34.4 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 1.27 (s, 14H), 0.89 (t, *J* =6.8 Hz, 3H), 0.48 (s, 2H), -0.03 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ 33.7, 31.9, 29.6, 29.4, 23.9, 22.7, 16.7, 14.1, -1.6. HRMS (FAB) m/z [M-CH$_3$]$^+$ calcd for $C_{11}H_{25}Si$

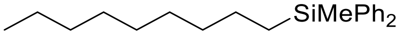
185.1726, found 185.1723.

(Dimethylnonylsilyl)benzene (**3bb**; CAS Registry Number 120059-88-3)[20]



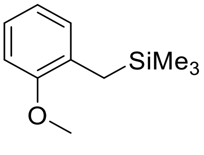
Colorless liquid; yield 53%, 42.3 mg, (0.3 mmol scale); hexane only (R_f = 0.51); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.52-7.54 (m, 2H), 7.35-7.38 (m, 3H), 1.27-1.32 (m, 14H), 0.90 (t, *J*=7.0 Hz, 3H), 0.77 (t, *J*=8.0 Hz, 2H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ139.7, 133.5, 128.7, 127.6, 33.6, 31.9, 29.6, 29.4, 29.3, 23.9, 22.7, 15.7, 14.1, -3.0.

Nonyl(methyl)diphenylsilane (**3bc**; New compound)



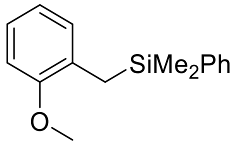
Colorless liquid; yield 49%, 47.9 mg, (0.3 mmol scale); hexane only (R_f = 0.26); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.52-7.55 (m, 4H), 7.34-7.39 (m, 6H), 1.26-1.41 (m, 14H), 1.09 (t, *J*=8.2 Hz, 2H), 0.90 (t, *J*=6.8 Hz, 3H), 0.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ137.5, 134.4, 129.0, 127.7, 33.7, 31.9, 29.5, 29.4, 29.2, 23.8, 22.7, 14.1, -4.4. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{21}H_{29}Si$ 309.2039, found 309.2047.

(2-Methoxybenzyl)trimethylsilane (**3ca**; CAS Registry Number 99522-22-2)[21]



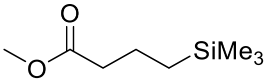
Colorless liquid; yield 21%, 12.3 mg, (0.3 mmol scale); hexane only (R_f = 0.25); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.05-7.09 (m, 1H), 6.86-6.99 (m, 1H), 6.80-6.85 (m, 2H), 3.79 (s, 3H), 2.10 (s, 2H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ156.3, 129.4, 129.2, 124.9, 120.1, 109.7, 54.8, 20.5, -1.6.

(2-Methoxybenzyl)dimethyl(phenyl)silane (**3cb**; New compound)



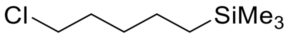
Colorless liquid; yield 45%, 34.4 mg, (0.3 mmol scale); hexane only (R_f = 0.23); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.50-7.52 (m, 2H), 7.35-7.38 (m, 3H), 7.08-7.12 (m, 1H), 6.94-6.96 (m, 1H), 6.78-6.85 (m, 2H), 3.69 (s, 3H), 2.36 (s, 2H), 0.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ156.4, 139.3, 133.6, 129.5, 128.7, 128.4, 127.5, 125.2, 120.1, 109.7, 54.7, 19.7, -3.2. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{15}H_{17}OSi$ 241.1049, found 241.1044.

Methyl 4-(trimethylsilyl)butanoate (**3da**; CAS Registry Number 27798-48-7)



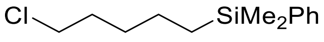
Colorless liquid; yield 40%, 21.1 mg, (0.3 mmol scale); hexane/EtOAc = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ3.67 (s, 3H), 2.33 (t, *J*=7.4 Hz, 2H), 1.59-1.67 (m, 2H), 0.49-0.53 (m, 2H), 0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ174.1, 51.4, 37.8, 19.8, 16.5, -1.8. HRMS (FAB) m/z $[M+H]^+$ calcd for $C_8H_{19}O_2Si$ 175.1154, found 175.1160.

(5-Chloropentyl)trimethylsilane (**3ea**; New compound)



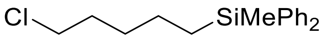
Colorless liquid; yield 39%, 23.1 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ3.53 (t, *J*=6.8 Hz, 2H), 1.78 (quin, *J*=7.1 Hz, 2H), 1.45 (quin, *J*=7.4 Hz, 2H), 1.28-1.36 (m, 2H), 0.48-0.52 (m, 2H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ45.2, 32.4, 30.7, 23.3, 16.5, -1.7. HRMS (FAB) m/z $[M+H]^+$ calcd for $C_8H_{20}ClSi$ 179.1023, found 179.1020.

(5-Chloropentyl)dimethyl(phenyl)silane (**3eb**; CAS Registry Number 133511-88-3)[22]



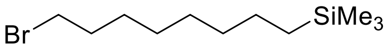
Colorless liquid; yield 30%, 26.0 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δδ7.50-7.54 (m, 2H), 7.36-7.37 (m, 3H), 3.51 (t, *J*=6.8 Hz, 2H), 1.76 (quin, *J*=7.2 Hz, 2H), 1.42-1.50 (m, 2H), 1.32-1.39 (m, 2H), 0.75-0.79 (m, 2H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ139.3, 134.1, 133.5, 128.8, 127.7, 45.1, 32.3, 30.7, 23.2, 15.6, -3.1.

(5-chloropentyl)(methyl)diphenylsilane (**3ec**; New compound)



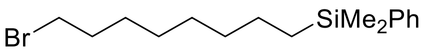
Colorless liquid; yield 27%, 24.2 mg, (0.3 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.49-7.52 (m, 4H), 7.33-7.38 (m, 6H), 3.49 (t, *J*=6.8 Hz, 2H), 1.76 (quin, *J*=7.1 Hz, 2H), 1.37-1.52 (m, 4H), 1.06-1.10 (m, 2H), 0.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm)) δ135.2, 134.4, 129.1, 127.8, 45.1, 32.2, 30.7, 23.2, 14.1, -4.5. HRMS (FAB) m/z $[M-H]^+$ calcd for $C_{18}H_{22}ClSi$ 301.1179, found 301.1170.

Cyclohexyl(methyl)diphenylsilane (**3fa**; New compound)



Colorless liquid; yield 38%, 30.4 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ3.41 (t, *J*=6.8 Hz, 2H), 1.86 (quin, *J*=7.2 Hz, 2H), 1.41-1.44 (m, 2H), 1.26-1.30 (m, 8H), 0.48 (t, *J*=7.8 Hz, 2H), -0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ34.1, 33.5, 32.8, 29.2, 28.7, 28.2, 23.9, 16.7, 1.6. HRMS (FAB) m/z $[M]^+$ calcd for $C_{11}H_{25}BrSi$ 264.0909, found 264.0914.

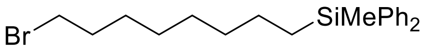
(8-Bromooctyl)dimethyl(phenyl)silane (**3fb**; New compound)



Colorless liquid; yield 33%, 32.3 mg, (0.3 mmol scale); hexane only (R_f = 0.46); ^{1}H NMR (400 MHz,

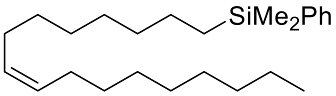
$CDCl_3$, ppm) δ7.51-7.53 (m, 2H), 7.35-7.37 (m, 3H), 3.41 (t, *J*=6.8 Hz, 2H), 1.86 (quin, *J*=7.1 Hz, 2H), 1.29-1.42 (m, 10H), 0.74-0.78 (m, 2H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ139.6, 133.5, 128.7, 127.6, 34.1, 33.6, 33.4, 32.8, 29.2, 29.0, 28.7, 282, 23.8, 15.7, -3.0. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{15}H_{24}BrSi$ 311.0831, found 311.0816.

(8-Bromooctyl)(methyl)diphenylsilane (**3fc**; New compound)



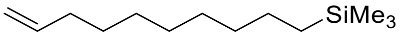
Colorless liquid; yield 35%, 41.0 mg, (0.3 mmol scale); hexane/EtOAc = 50/1 (R_f=0.28); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.51-7.54 (m, 4H), 7.32-7.39 (m, 6H), 3.40 (t, *J*=6.8 Hz, 2H), 1.84 (quin, *J*=7.2 Hz, 2H), 1.28-1.40 (m, 10H), 1.06-1.08 (m, 2H), 0.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ137.4, 134.4, 129.0, 127.7, 34.1, 33.4, 32.8, 29.0, 28.6, 28.1, 23.7, 14.1, -4.5. HRMS (FAB) m/z $[M+H]^+$ calcd for $C_{21}H_{30}BrSi$ 389.1300, found 389.1299.

Heptadec-8-en-1-yldimethyl(phenyl)silane (**3ga**; New compound)



Colorless oil; yield 55%, 62.2 mg, (0.3 mmol scale); hexane only (R_f= 0.52); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.52-7.54 (m, 2H), 7.35-7.37 (m, 3H), 5.35-5.38 (m, 2H), 2.04 (m, 4H), 13.0-13.2 (m, 22H), 0.91 (t, *J*=7.0 Hz, 3H), 0.77 (t, *J*=7.8 Hz, 2H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ139.7, 133.5, 129.9, 129.8, 128.7, 127.6, 33.6, 31.9, 29.8, 29.5, 29.3, 29.2, 29.2, 27.2, 23.9, 22.7, 15.7, 14.1, -3.0. HRMS (FAB) m/z $[M]^+$ calcd for $C_{25}H_{44}Si$ 372.3212, found 372.3220.

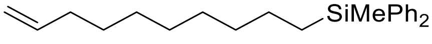
Dec-9-en-1-yltrimethylsilane (**3ha**; CAS Registry Number 846053-32-5)



Colorless liquid; yield 50%, 32.7 mg, (0.3 mmol scale); hexane only (R_f= 0.67); ^{1}H NMR (400 MHz,

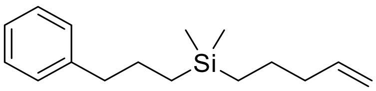
$CDCl_3$, ppm) δ5.77-5.87 (m, 1H), 4.91-5.03 (m, 2H), 2.05 (q, *J*=7.1 Hz, 2H), 1.29-1.41 (m, 12H), 0.48 (t, *J*=7.8 Hz, 2H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ139.2, 114.11, 33.9, 33.6, 29.5, 29.4, 29.2, 29.0, 23.9, 16.7, -1.6. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{12}H_{25}Si$ 197.1726, found 197.1733.

Dec-9-en-1-yl(methyl)diphenylsilane (**3hc**; New compound)



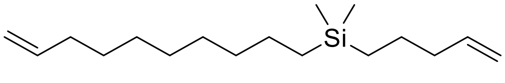
Colorless liquid; yield 54%, 50.0 mg, (0.3 mmol scale); hexane only (R_f = 0.32); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ7.52-7.56 (m, 4H), 7.34-7.41 (m, 6H), 5.78-5.89 (m, 1H), 4.94-5.04 (m, 2H), 2.03-2.08 (m, 22H), 1.28-1.41 (m, 12H), 1.07-1.11 (m, 2H), 0.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ139.2, 137.5, 134.4, 129.0, 127.7, 114.1, 33.8, 33.6, 29.4, 29.2, 28.9, 23.8, 14.2. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{22}H_{29}Si$ 321.2039, found 321.2029.

Dimethyl(pent-4-en-1-yl)(3-phenylpropyl)silane (**3ad**; New compound)



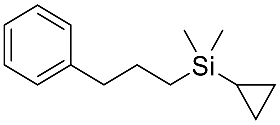
Colorless liquid; yield 54%, 40.6 mg, (0.3 mmol scale); hexane only (R_f= 0.46); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ7.28-7.31 (m, 2H), 7.18-7.21 (m, 3H), 5.76-5.86 (m, 1H), 4.95-5.04 (m, 2H), 2.64 (t, *J*=7.6 Hz, 2H), 2.05-2.10 (m, 2H), 1.59-1.67 (m, 2H), 1.35-1.43 (m, 2H), 0.50- 0 .54 (m, 2H), 0.55-0.59 (m, 2H), -0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ142.7, 139.0, 128.4, 128.2, 125.6, 114.4, 40.0, 37.7, 26.1, 23.4, 15.2, 14.8, -3.4. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{15}H_{23}Si$ 231.1569, found 231.1576.

Dec-9-en-1-yldimethyl(pent-4-en-1-yl)silane (**3hd**; New compound)



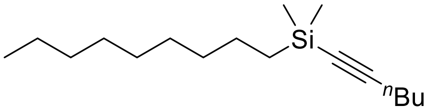
Colorless liquid; yield 43%, 33.6 mg, (0.3 mmol scale); hexane only (R_f =0.62); ^1H NMR (400 MHz, $CDCl_3$, ppm) δ5.75-5.87 (m, 2H), 4.92-5.02 (m, 4H), 2.06 (quin, *J*=7.2 Hz, 4H), 1.28-1.43 (m, 16H), 0.48-0.52 (m, 4H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ139.2, 139.1, 114.3, 114.1, 37.8, 33.8, 33.7, 29.5, 29.3, 29.2, 29.0, 23.9, 23.5, 15.2, 14.9, -3.4. HRMS (FAB) m/z $[M]^+$ calcd for $C_{17}H_{34}Si$ 266.2430, found 266.2429.

Cyclopropyldimethyl(3-phenylpropyl)silane (**3ae**; New compound)



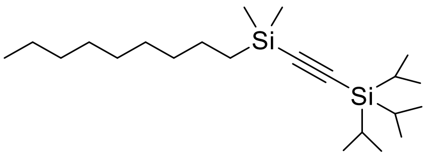
Colorless liquid; yield 37%, 24.0 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.26-7.31 (m, 2H), 7.17-7.21 (m, 3H), 2.65 (t, J=7.6 Hz, 2H), 1.64-1.72 (m, 2H), 0.52-0.56 (m, 2H), 0.56-0.60 (m, 4H), 0.16-0.20 (m, 2H), -0.10 (s, 6H), -0.47--0.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ142.8, 128.4, 128.2, 125.6, 40.0, 26.2, 15.2, 1.0, -4.6, -5.6. HRMS (FAB) m/z $[M]^+$ calcd for $C_{14}H_{22}Si$ 218.1491, found 218.1487.

Hex-1-yn-1-yldimethyl(nonyl)silane (**3bf**; New compound)



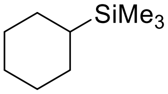
Colorless liquid; yield 32%, 26.1 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ2.23 (t, *J*=7.2 Hz, 2H), 1.27-1.56 (m, 18H), 0.91 (t, *J*=7.2 Hz, 3H), 0.89 (t, *J*=6.8 Hz, 3H), 0.56-0.60 (m, 2H), 0.11 (6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ108.0, 83.5, 33.3, 31.9, 30.8, 29.6, 29.4, 23.8, 22.7, 21.9, 19.6, 16.4, 14.1, 13.6, -1.5. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{16}H_{31}Si$ 251.2195, found 251.2203.

((Dimethyl(nonyl)silyl)ethynyl)triisopropylsilane (**3bg**; New compound)



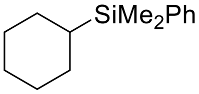
Colorless liquid; yield 36%, 40.4 mg, (0.3 mmol scale); hexane only (R_f= 0.60); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ1.27-1.41 (m, 14H), 1.03-1.10 (m, 21H), 0.89 (t, *J*=6.8 Hz, 3H), 0.59-0.63 (m, 2H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ115.5, 110.4, 33.2, 32.0, 29.6, 29.4, 23.9, 22.7, 18.6, 18.5, 16.2, 14.2, 11.1, -1.6. HRMS (FAB) m/z [M+H]$^+$ calcd for $C_{22}H_{47}Si_2$ 367.3216, found 367.3216.

Cyclohexyltrimethylsilane (**3ia**; CAS Registry Number 10151-74-3)[23]



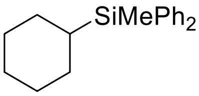
Colorless liquid; yield 17%, 16.7 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ 1.65-1.72 (m, 5H), 1.19-1.26 (m, 4H), 1.05-1.07 (m, 1H), 0.50-0.57 (m, 1H), 0.07 (s, 9H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ28.1, 27.3, 27.0, 26.1, -3.6.

Cyclohexyl(dimethyl)phenylsilane (**3ib**; CAS Registry Number 207687-54-5)[24]



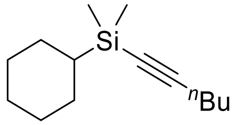
Colorless liquid; yield 53%, 34.5 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ7.49-7.51 (m, 2H), 7.34-7.37 (m, 3H), 1.67-1.73 (m, 5H), 1.05-1.25 (m, 5H), 0.77-0.84 (m, 1H), 0.25 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ138.6, 133.9, 128.6, 127.5, 28.0, 27.4, 26.9, 25.7, -5.2.

Cyclohexyl(methyl)diphenylsilane (**3ic**; CAS Registry Number 139294-82-9)



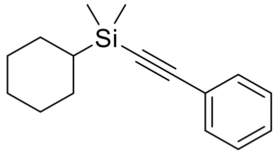
Colorless liquid; yield 57%, 49.0 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ7.52-7.55 (m, 4H), 7.33-7.40 (m, 6H), 1.72-1.78 (m, 5H), 1.16-1.28 (m, 6H), 0.53 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ136.5, 134.8, 128.9, 127.7, 28.1, 27.6, 26.9, 24.4, -6.5. HRMS (FAB) m/z [M-H]$^+$ calcd for $C_{19}H_{23}Si$ 279.1569, found 279.1576.

Cyclohexyl(hex-1-yn-1-yl)dimethylsilane (**3if**; New compound)



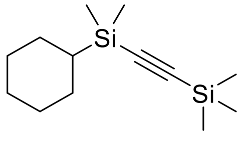
Colorless liquid; yield 28%, 19.0 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ2.23 (t, *J*=7.0 Hz, 2H), 1.72-1.75 (m, 4H), 1.37-1.55 (m, 4H), 1.12-1.27 (m, 6H), 0.92 (t, *J*=7.2 Hz, 3H), 0.59-0.66 (m, 1H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ108.2, 82.7, 30.8, 27.9, 27.3, 27.2, 26.9, 25.8, 21.9, 19.6, 13.6. -3.5. HRMS (FAB) m/z $[M-CH_3]^+$ calcd for $C_{13}H_{23}Si$ 207.1569, found 207.1562.

Cyclohexyldimethyl(phenylethynyl)silane (**3ih**; CAS Registry Number 1422469-24-6)[25]



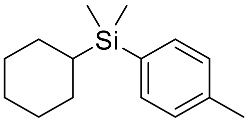
Colorless liquid; yield 17%, 12.4 mg, (0.3 mmol scale); hexane only (R_f = 0.38); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.46-7.48 (m, 2H), 7.28-7.31 (m, 3H), 1.74-1.83 (m, 5H), 1.19-1.26 (m, 5H), 0.72-0.79 (m, 1H), 0.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ132.0, 128.4, 128.1, 123.2, 105.7, 92.8, 27.9, 27.2, 26.9, 25.7, -3.7.

Cyclohexyldimethyl((trimethylsilyl)ethynyl)silane (**3ii**; New compound)



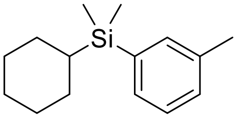
Colorless liquid; yield 12%, 8.9 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ1.72-1.75 (m, 5H), 1.11-1.26 (m, 5H), 0.62-0.70 (m, 1H), 0.17 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ114.6, 112.5, 27.9, 27.1, 26.9, 25.5, 0.0, -3.7. HRMS (FAB) m/z $[M-H]^+$ calcd for $C_{13}H_{25}Si_2$ 237.1495, found 237.1493.

Cyclohexyldimethyl(p-tolyl)silane (**3ij**; New compound)



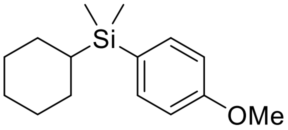
Colorless liquid; yield 27%, 19.0 mg, (0.3 mmol scale); hexane only (R_f = 0.45); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.40 (d, *J*=7.6 Hz, 2H), 7.19 (d, *J*=7.2 Hz, 2H), 2.37 (s, 3H), 1.67-1.70 (m, 5H), 1.04-1.23 (m, 5H), 0.76-0.83 (m, 1H), 0.02 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ138.5, 134.9, 134.0, 128.4, 28.1, 27.4, 26.9, 25.8, 21.5, -5.1. HRMS (FAB) m/z [M-H]$^+$ calcd for $C_{15}H_{23}Si$ 231.1569, found 231.1564.

Cyclohexyldimethyl(*m*-tolyl)silane (**3ik**; New compound)



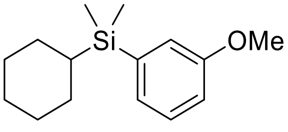
Colorless liquid; yield 29%, 20.7 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.22-7.28 (m, 3H), 7.15-7.17 (m, 1H), 2.36 (s, 3H), 1.65-1.69 (m, 5H), 1.07-1.19 (m, 5H), 0.74-0.82 (m, 1H), 0.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ138.5, 136.8, 134.6, 131.0, 129.5, 127.4, 28.1, 27.4, 26.9, 25.8, 21.6, -5.2. HRMS (FAB) m/z [M]$^+$ calcd for $C_{15}H_{24}Si$ 232.1647, found 232.1637.

Cyclohexyl(4-methoxyphenyl)dimethylsilane (**3il**; New compound)



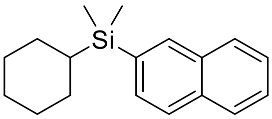
Yellow liquid; yield 19%, 14.1 mg, (0.3 mmol scale); hexane/EtOAc = 10/1 (R_f = 0.40); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.42 (d, *J*=8.4 Hz, 2H), 6.91 (d, *J*=8.4 Hz, 2H), 3.82 (s, 3H), 1.65-1.69 (m, 5H), 1.06-1.22 (m, 5H), 0.72-0.80 (m, 1H), 0.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ160.1, 135.3, 129.4, 113.3, 55.0, 28.1, 27.4, 26.9, 25.9, -5.0. HRMS (FAB) m/z [M+H]$^+$ calcd for $C_{15}H_{25}OSi$ 249.1675, found 249.1663.

Cyclohexyl(3-methoxyphenyl)dimethylsilane (**3im**; New compound)



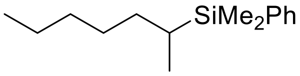
Colorless liquid; yield 23%, 17.5 mg, (0.3 mmol scale); hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.22-7.28(m, 1H), 7.00-7.05 (m, 21H), 6.85-6.99 (m, 1H), 3.79 (s, 3H), 1.63-1.66 (m, 5H), 1.00-1.24 (m, 5H), 0.73-0.80 (m, 1H), 0.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ158.7, 140.4, 128.7, 126.2, 119.7, 113.5, 55.0, 28.0, 27.4, 26.9, 25.7. HRMS (FAB) m/z $[M+H]^+$ calcd for $C_{15}H_{25}OSi$ 249.1675, found 249.1672.

Cyclohexyldimethyl(naphthalen-2-yl)silane (**3in**; New compound)



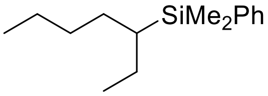
Colorless liquid; yield 46%, 37.2 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.98 (m, 1H), 7.81-7.86 (m, 3H), 7.57-7.59 (m, 1H), 7.46-7.50 (m, 2H), 1.70-1.72 (m, 5H), 1.11-1.27 (m, 5H), 0.84-0.91 (m, 1H), 0.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ136.2, 134.4, 133.5, 132.8, 130.4, 128.0, 127.6, 126.6, 126.1, 125.8, 28.0, 27.5, 26.9, 25.9, -5.1. HRMS (FAB) m/z $[M]^+$ calcd for $C_{18}H_{24}Si$ 268.1647, found 268.1658.

Heptan-2-yldimethyl(phenyl)silane (**3jb**; New compound)



Colorless liquid; yield 53%, 35.4 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.49-7.52 (m, 2H), 7.34-7.37 (m, 3H), 1.09-1.33 (m, 2H), 1.45-1.47 (m, 7H), 0.89 (d, *J*=4.4 Hz, 3H), 0.86 (t, *J*=3.6 Hz, 3H), 0.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ138.9, 133.9, 128.6, 127.5, 31.9, 31.5, 28.2, 22.7, 19.0, 14.1, 14.0, -4.8. HRMS (FAB) m/z $[M-H]^+$ calcd for $C_{15}H_{25}Si$ 233.1726, found 233.1732.

Heptan-3-yldimethyl(phenyl)silane (**3kb**; New compound)



Colorless liquid; yield 22%, 14.7 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.50-7.53 (m, 2H), 7.34-7.35 (m, 3H), 1.19-1.55 (m, 8H), 0.83-0.88 (m, 6H), 0.75-0.79 (m, 1H), 0.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ139.6, 133.8, 128.6, 127.5, 31.3, 28.6, 26.8, 23.0, 22.3, 14.1, 13.7, -3.6, -3.7. HRMS (FAB) m/z $[M-H]^+$ calcd for $C_{15}H_{25}Si$ 233.1726, found 233.1715.

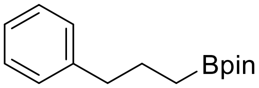
2-7. Procedure for gram-scale decarboxylation silylation over Au/C catalyst

A typical reaction procedure is as follows: NHPI ester **1a** (3.09 g, 10 mmol), hexamethyldisilane (30 mmol) and benzene (50 mL) were added to a Schlenk tube containing Au/C catalyst (1 mol% as Au) under an Ar atmosphere. After the reaction at 70 °C for 1 h, the supported catalyst was removed from the suspension by centrifugation. The solvent was removed in vacuo. The product was isolated by silica-gel column chromatography (hexane) (1.00 g, 52%).

2-8. General procedure for the reaction of NHPI esters and diborons to alkyl boronate over Au/C catalyst

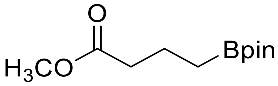
A typical reaction procedure is as follows: NHPI ester (0.30 mmol), hexamethyldisilane (0.60 mmol), (bispinacolato)diboron (0.60 mmol) and benzene (1.5 mL) were added to a Schlenk tube containing the supported Au catalyst (1 mol% as Au) under an Ar atmosphere. The progress of the reaction was monitored by thin layer chromatography (TLC) and GC analysis. After NHPI ester or disilane was completely consumed, the solid catalyst was removed by passing the mixture through a 0.45 μm polytetrafluoroethylene (PTFE) filter (Millipore Millex LH). The remaining solution was concentrated by rotary evaporation under reduced pressure without heating. The resulting liquid was purified through silica gel column chromatography (a mixture of hexane and EtOAc) to give the product.

4,4,5,5-Tetramethyl-2-(3-phenylpropyl)-1,3,2-dioxaborolane (**5a**; CAS Registry Number 329685-40-7)[26]



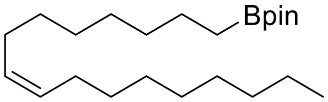
Colorless liquid; yield 43%, 32.0 mg, (0.3 mmol scale); hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.24-7.28 (m, 2H), 7.16-7.18 (m, 3H), 2.61 (t, *J*=7.6 Hz, 2H), 1.74 (quin, *J*=7.8 Hz, 2H), 1.25 (s, 12H), 0.83 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ144.9, 128.2, 127.7, 125.0, 83.2, 24.6, 24.6, 17.1.

Methyl 4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-butanoate (**5d**; CAS Registry Number 2222868-64-4)[27]



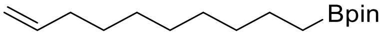
Colorless liquid; yield 36%, 24.7 mg, (0.3 mmol scale); hexane/EtOAc = 5/1 (R_f = 0.32); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ3.65 (s, 3H), 2.32 (t, *J*=7.6 Hz, 2H), 1.74 (quin, *J*=7.7 Hz, 2H), 1.23 (s, 12H), 0.81 (t, *J*=8.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ174.1, 83.0, 51.4, 36.3, 25.0, 24.8, 19.6.

2-(8*Z*)-8-Heptadecen-1-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5g**; CAS Registry Number 2095863-81-1)[13]



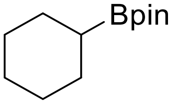
Colorless liquid; yield 40%, 42.6 mg, (0.3 mmol scale); hexane/EtOAc = 20/1 (R_f = 0.30); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ5.30-5.38 (m, 2H), 1.98-2.03 (m, 4H), 1.27-1.40 (m, 22H), 1.24 (s, 12H), 0.88 (t, *J*=6.8 Hz, 3H), 0.77 (t, *J*=7.6 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ129.9, 129.8, 82.8, 32.4, 31.9, 29.8, 29.5, 29.3, 29.3, 27.2, 24.8, 24.0, 22.7, 14.1.

2-(9-Decen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5h**; CAS Registry Number 1361022-68-5)[28]



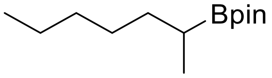
Colorless liquid; yield 29%, 24.3 mg, (0.3 mmol scale); hexane/EtOAc = 20/1 (R_f = 0.34); ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ5.75-5.86 (m, 1H), 4.90-5.01 (m, 2H), 2.03 (q, *J*=7.1 Hz, 2H), 1.24-1.39 (m, 24H), 0.77 (t, *J*=7.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ139.3, 114.0, 82.8, 33.8, 32.4, 29.4, 29.3, 29.1, 28.9, 24.8, 24.0.

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5i**; CAS Registry Number 87100-15-0)[29]



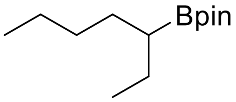
Colorless liquid; yield 35%, 21.8 mg, (0.3 mmol scale); hexane/EtOAc = 10/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.21-7.28 (m, 4H), 7.11-7.15 (m, 1H), 2.44 (q, *J*=7.5 Hz, 1H), 1.34 (d, *J*=7.2 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ144.9, 128.2, 127.7, 125.0, 83.2, 24.6, 24.6, 17.1.

4,4,5,5-Tetramethyl-2-(1-methylhexyl)-1,3,2-dioxaborolane (**5j**; CAS Registry Number 1361022-79-8)[30]



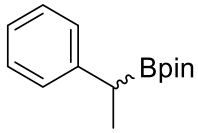
Colorless liquid; yield 48%, 32.0 mg, (0.3 mmol scale); hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ1.42-1.44 (m, 1H), 1.27-1.30 (m, 7H), 1.23 (s, 12H), 0.94-1.00 (m, 4H), 0.87 (t, *J*=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ82.7, 33.2, 32.1, 28.6, 24.7, 24.7, 22.6, 15.5, 14.1.

2-(1-Ethylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5k**; CAS Registry Number 1382358-35-1)[30]



Colorless liquid; yield 49%, 36.7 mg, (0.3 mmol scale); hexane/EtOAc = 20/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ1.26-1.1.43 (m, 9H), 1.24 (s, 12H), 0.89 (t, *J*=7.6 Hz, 3H), 0.87 (t, *J*=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ82.7, 31.5, 30.8, 24.8, 24.3, 23.0, 14.1, 13.7.

4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (**5l**; CAS Registry Number 174090-36-9)[31]



Colorless liquid; yield 43%, 29.8 mg, (0.3 mmol scale); hexane/EtOAc = 20/1 (R_f = 0.32); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.21-7.28 (m, 4H), 7.11-7.15 (m, 1H), 2.44 (q, J=7.5 Hz, 1H), 1.34 (d, J=7.2 Hz, 3H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ144.9, 128.2, 127.7, 125.0, 83.2, 24.6, 24.6, 17.1.

2-9. General procedure for reusing Au/C catalyst toward decarboxylative silylation (Fig. 1).

After the reaction of **1a** and **2a**, the solid was separated from the reaction mixture by centrifugation and completely washed three times with 10 mL of methanol. The resulting solid was dried for 1 h at 80 °C under a reduced pressure (< 0.1 Torr) to give the Au/C catalyst for reuse (Figure S1).

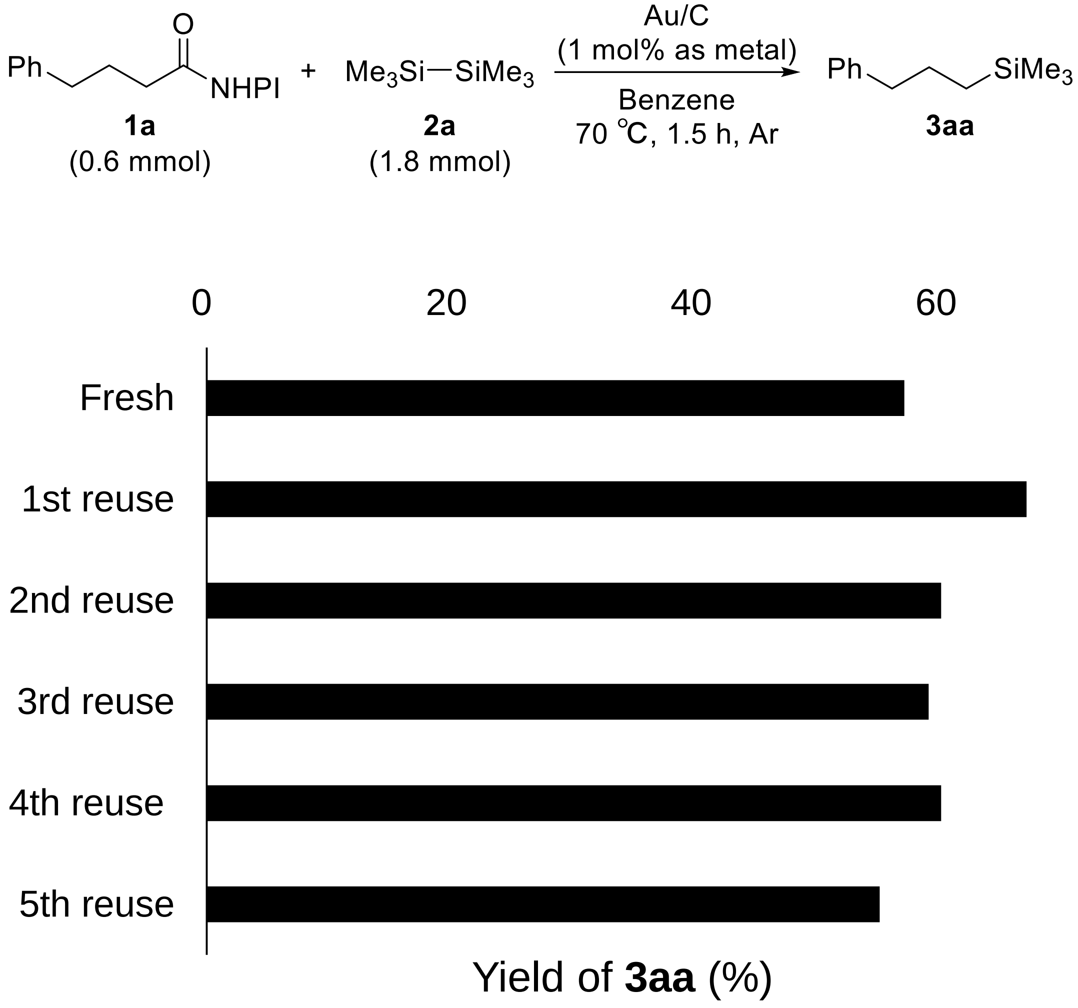
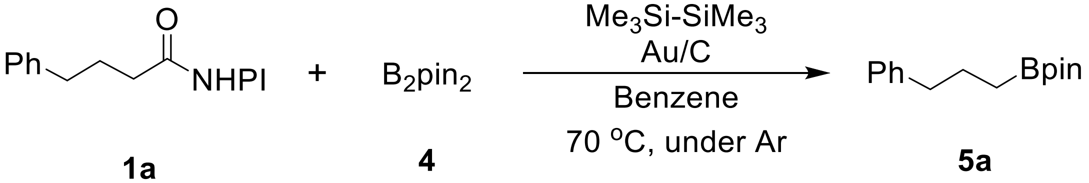


Figure S1. Reuse of Au/C catalyst toward decarboxylative silylation.

2-10. General procedure for reusing Au/C catalyst toward decarboxylative borylation.

After the reaction of **1a** and **4**, the solid was separated from the reaction mixture by centrifugation and completely washed three times with 10 mL of methanol. The resulting solid was dried overnight at 80 °C under a reduced pressure (< 0.1 Torr) to give the Au/C catalyst for reuse (Figure S2).



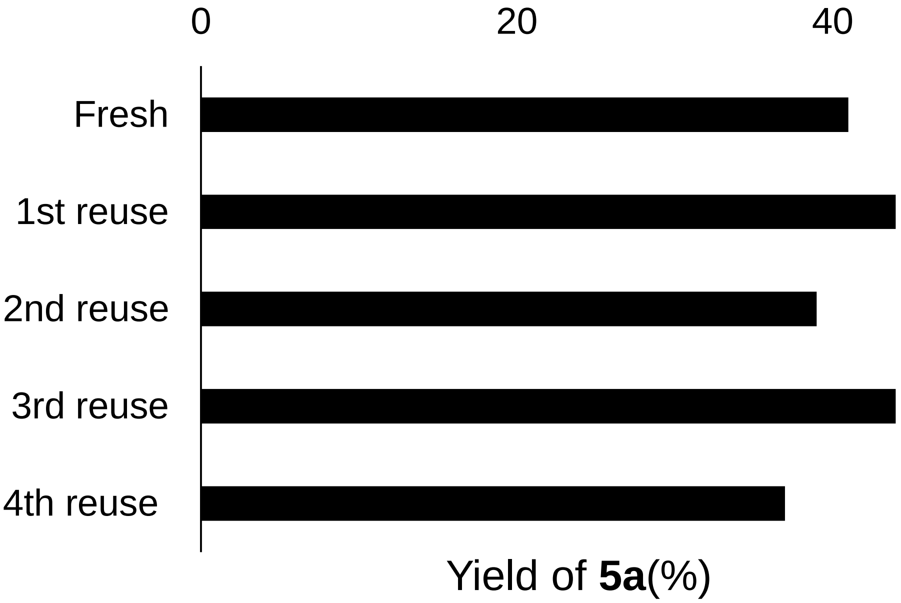
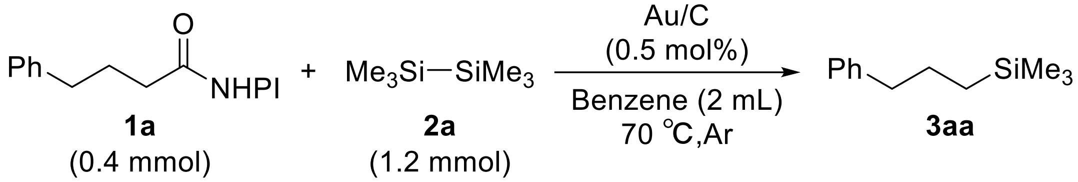


Figure S2. Reuse of Au/C catalyst toward decarboxylative borylation.

3. Hot filtration tests

Figure S3 shows the result of filtration of solid catalyst at 50 min after the reaction started. The reaction was completely stopped by the removal of Au/C. This result clearly indicates that Au/C catalyst worked heterogeneously.



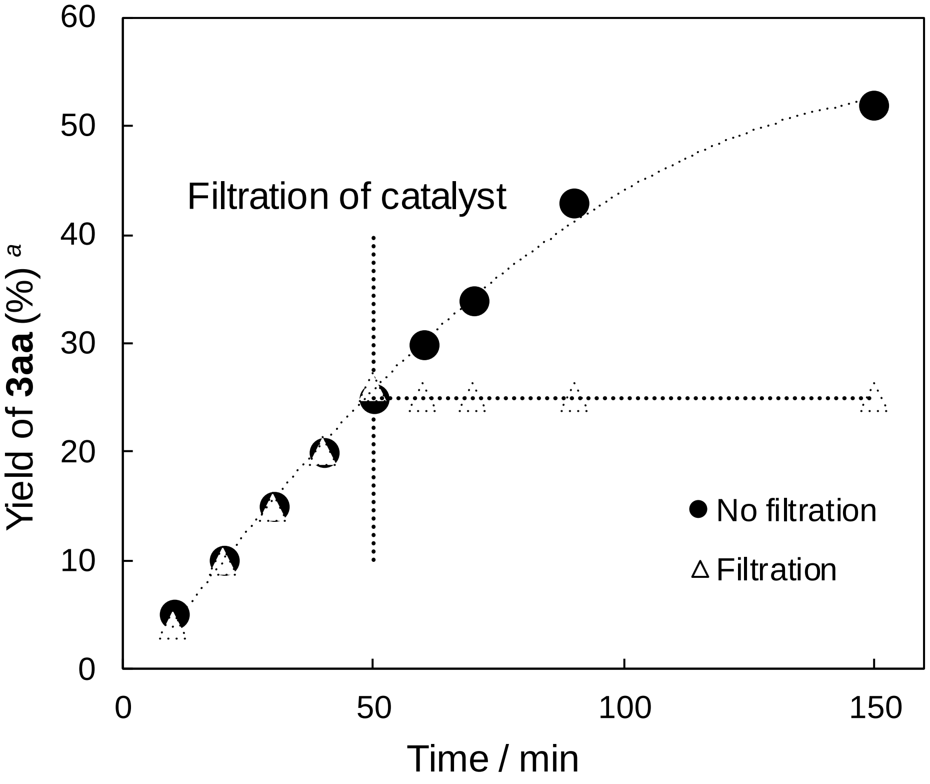
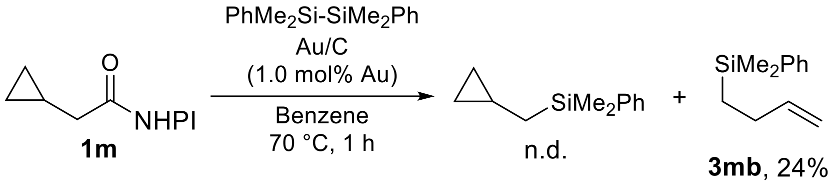


Figure S3. Hot filtration of Au/C catalyst.

4. Studies on reaction mechanism

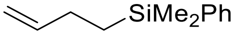
4-1. Radical clock experiments



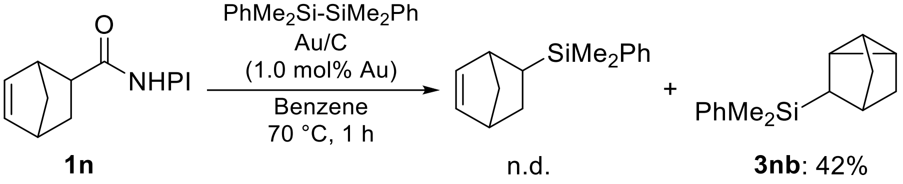
Scheme. S1. Radical clock experiments.

NHPI ester with cyclopropyl group (**1m**, 0.30 mmol), diphenyltetramethyldisilane (**2b**, 0.60 mmol) and benzene (1.5 mL) were added to a Schlenk tube containing Au/C catalyst (1 mol% as Au) under an Ar atmosphere (Scheme S1). The progress of the reaction was monitored by thin layer chromatography (TLC) and GC-MS. After the ester was completely consumed, the solid catalyst was removed by passing the mixture through a 0.45 *μ*m polytetrafluoroethylene (PTFE) filter (Millipore Millex LH). The remaining solution was concentrated by rotary evaporation under reduced pressure without heating. Purification of the resulting liquid through silica gel column chromatography (hexane) gave the product **3mb** in 24%. The fact that cyclopropyl ring opened during the catalytic silylation suggests that the reaction includes the formation of cyclopropylmethyl radical via homolysis of C(sp^3)–C(sp^2) bond by the influence of Au/C catalyst.

But-3-en-1-yldimethyl(phenyl)silane (**3mb**; CAS Registry Number 109790-06-9)[22]



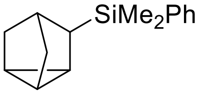
Colorless liquid; yield 24%, 14.2 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.51-7.54 (m, 2H), 7.35-7.37 (m, 3H), 5.88 (ddt, *J*=17.6, 10.0, 6.0 Hz, 1H), 4.88-5.02 (m, 2H), 2.06-2.12 (m, 2H), 0.85-0.89 (m, 2H), 0.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ141.5, 139.2, 133.5, 128.8, 127.7, 112.8, 27.9, 14.8, -3.0.



Scheme. S2. Radical clock experiments.

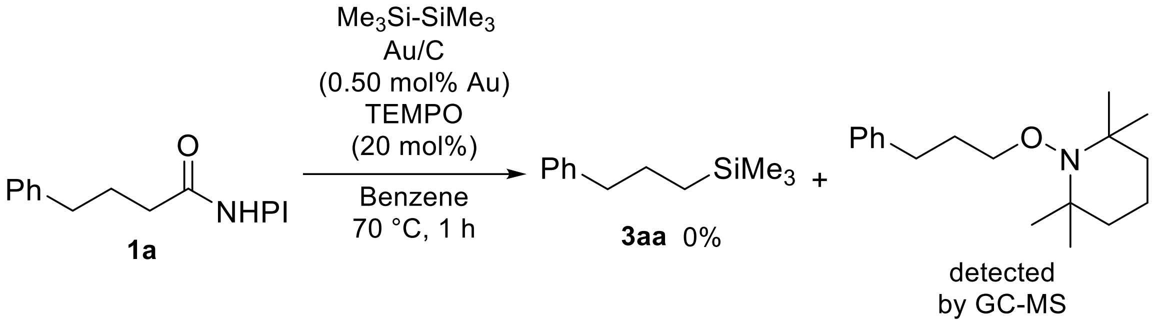
NHPI ester with norbornenyl group (**1n**, 0.30 mmol), diphenyltetramethyldisilane (**2b**, 0.60 mmol) and benzene (1.5 mL) were added to a Schlenk tube containing Au/C catalyst (1 mol% as Au) under an Ar atmosphere (Scheme S2). The progress of the reaction was monitored by thin layer chromatography (TLC) and GC-MS. After the ester was completely consumed, the solid catalyst was removed by passing the mixture through a 0.45 μm polytetrafluoroethylene (PTFE) filter (Millipore Millex LH). The remaining solution was concentrated by rotary evaporation under reduced pressure without heating. Purification of the resulting liquid through silica gel column chromatography (hexane) gave the product **3nb** in 42%.

Dimethyl(phenyl)(tricyclo[2.2.1.0^{2,6}]heptan-3-yl)silane (**3nb**; New compound)



Colorless liquid; yield 42%, 29.8 mg, (0.3 mmol scale); hexane only; ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ7.53-7.55 (m, 2H), 7.33-7.36 (m, 3H), 1.97 (br s, 1H), 1.22-1.28 (m, 1H), 1.17-1.12 (m, 2H), 1.12-1.16 (m, 1H), 1.02-1.06 (m, 2H), 1.00-1.01 (m, 1H), 0.90 (br s, 1H), 0.30, 0.29 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$, ppm) δ139.9, 133.6, 128.6, 127.6, 36.4, 32.8, 32.3, 31.6, 12.9, 10.6, 10.1, -2.6, -3.1. HRMS (FAB) m/z [M-H]$^+$ calcd for $C_{15}H_{19}Si$ 227.1256, found 227.1246.

4-2. Radical trap experiment



Scheme. S3. Radical trap experiment with TEMPO.

NHPI ester (**1a**, 0.40 mmol), hexamethyldisilane (**2a**, 1.2 mmol), 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO; 0.08 mmol), and benzene (2.0 mL) were added to a Schlenk tube containing Au/C catalyst (0.5 mol% as metal) under Ar. The yields of **3aa** after the reaction of 1 h were quantified by GC analysis using biphenyl as an internal standard. The addition of 20 mol% of TEMPO significantly impeded the reaction-rate (Scheme S3). In the case of the reaction in the presence of TEMPO, the formation of alkylated TEMPO was detected by GC-MS analysis (Figure S4). These results clearly indicate that the reaction involves the generation of alkyl radical as a key intermediate for the formation of alkylsilanes.

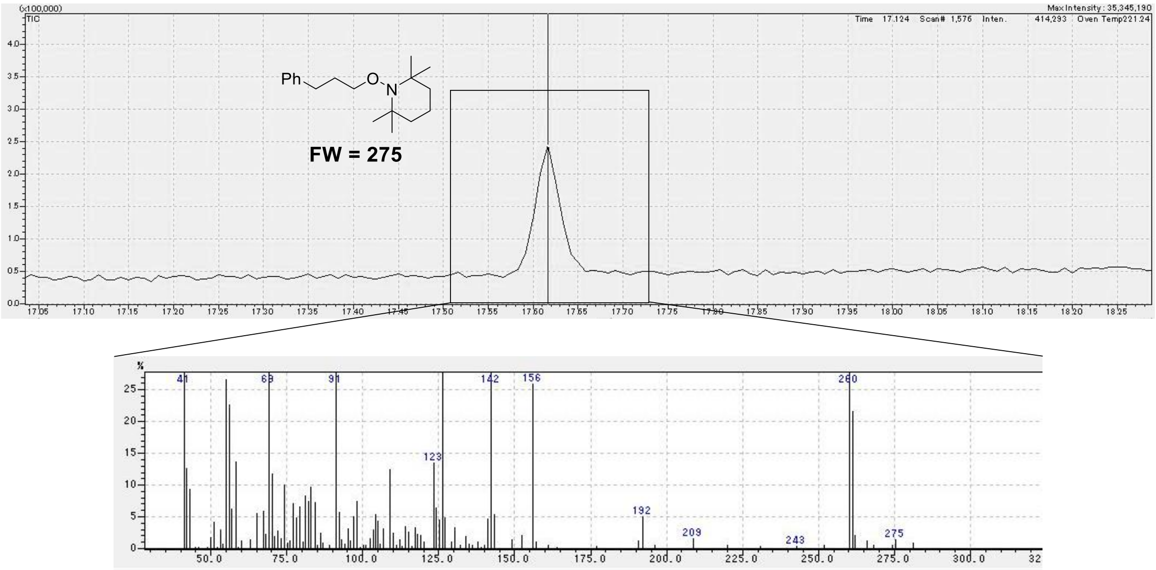
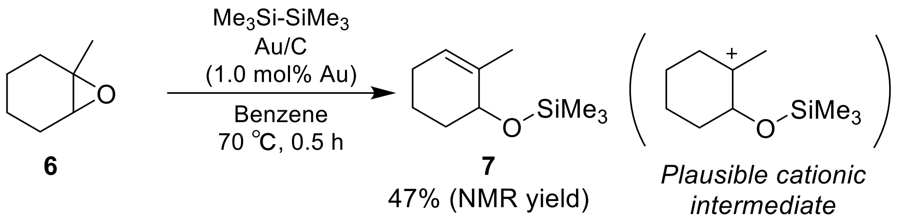


Figure. S4. Mass profile of alkylated-TEMPO.

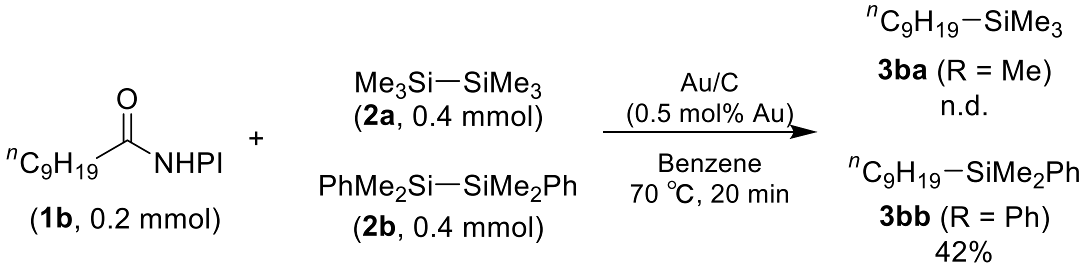
4-3. Control experiments with additives



Scheme. S4. Reaction of epoxide with disilane

1-Methyl-1,2-epoxycyclohexane (**6**, 0.50 mmol), hexamethyldisilane (1.5 mmol) and benzene (1.0 mL) were added to a Schlenk tube containing the silica Au/C catalyst (1 mol% as metal) under an Ar atmosphere (Scheme S4). The yield of the product **7** was quantified by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard.

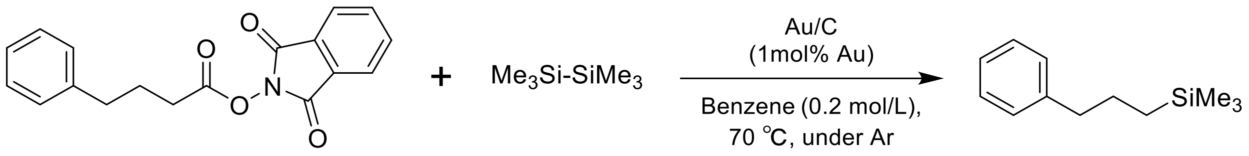
4-4. Control experiments with additives



NHPI ester (**1b**; 0.20 mmol), disilane (**2a** and **2b**; each 0.40 mmol) and benzene (1.0 mL) were added to a Schlenk tube containing Au/C catalyst (0.50 mol% as Au) under an Ar atmosphere. The yield of **3ba** and **3bb** after the reaction of 20 min at 70 ºC were estimated by GC analysis by using biphenyl as an internal standard. As the data is shown in Scheme 4 of main manuscript, the preferential conversion of **2b** whose oxidation potential is lower than that of **2a** implies that the rate-determining step of the reaction would be the single-electron oxidation of disilanes.

5. Kinetic data for decarboxylative C(sp^3)–Si coupling over supported Au catalysts.

5-1. Kinetic data for alkyl–silyl coupling over Au/C catalyst.



1aa **2a** **3aa**

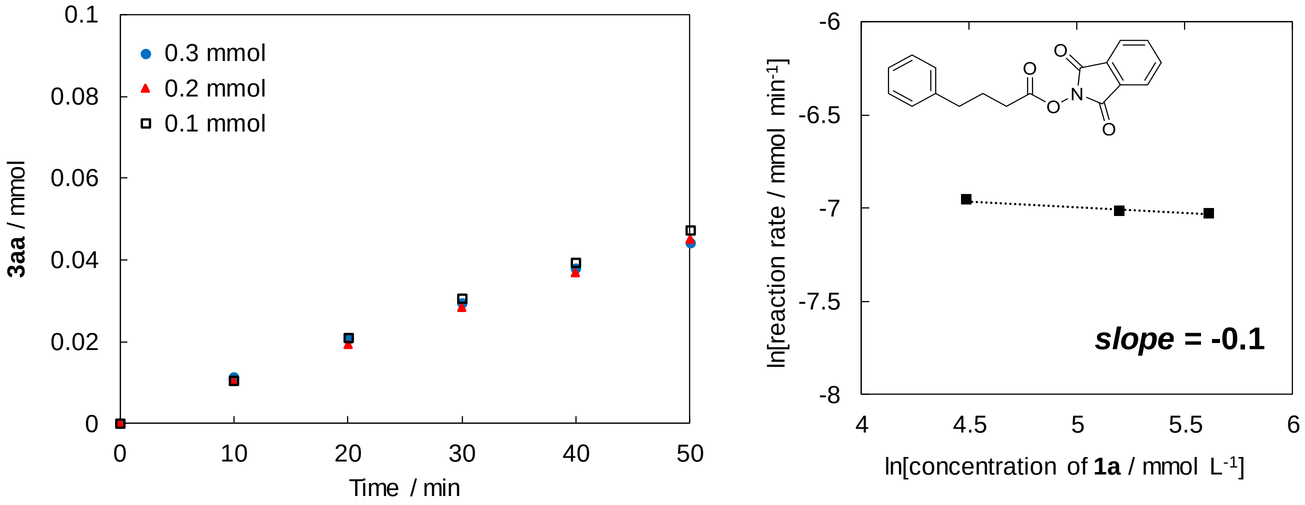


Figure. S5. Effect of concentration of **1a** on alkyl-silyl coupling over Au/C.

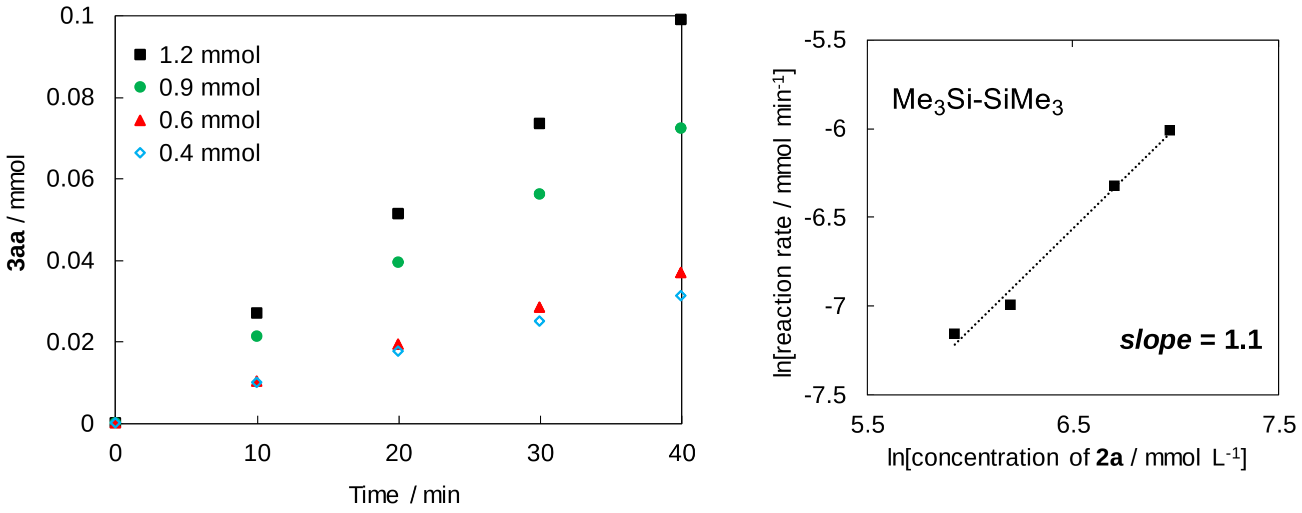
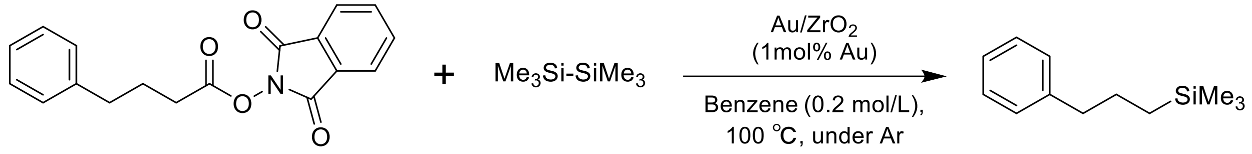


Figure. S6. Effect of concentration of **2a** on alkyl-silyl coupling over Au/C.

5-2. Kinetic data for alkyl–silyl coupling over Au/ZrO$_2$ catalyst.



1aa **2a** **3aa**

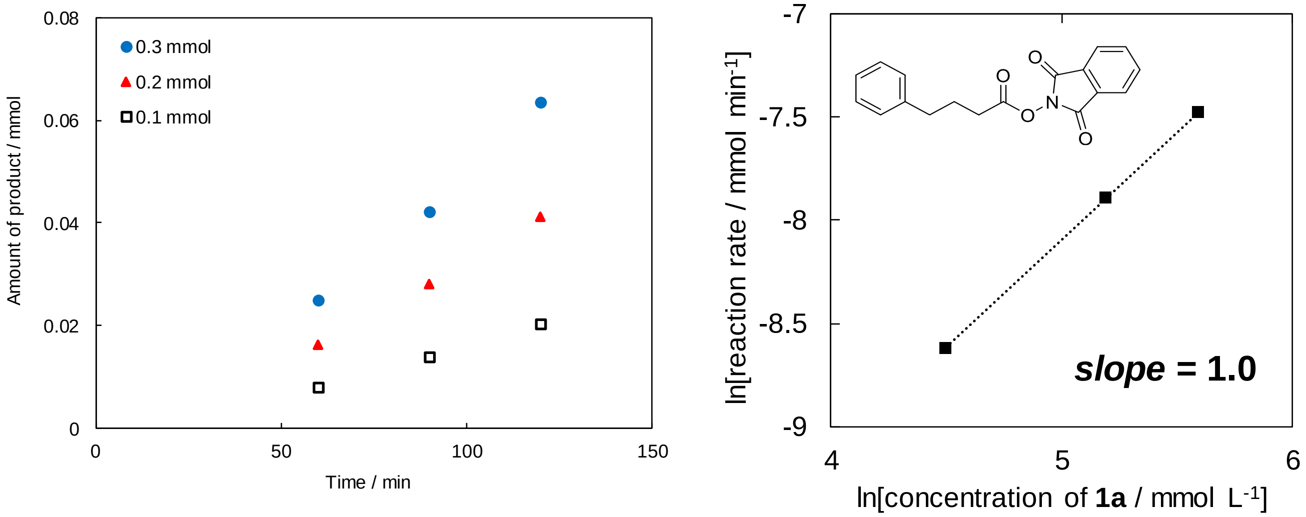


Figure. S7. Effect of concentration of **1a** on alkyl-silyl coupling over Au/ZrO$_2$.

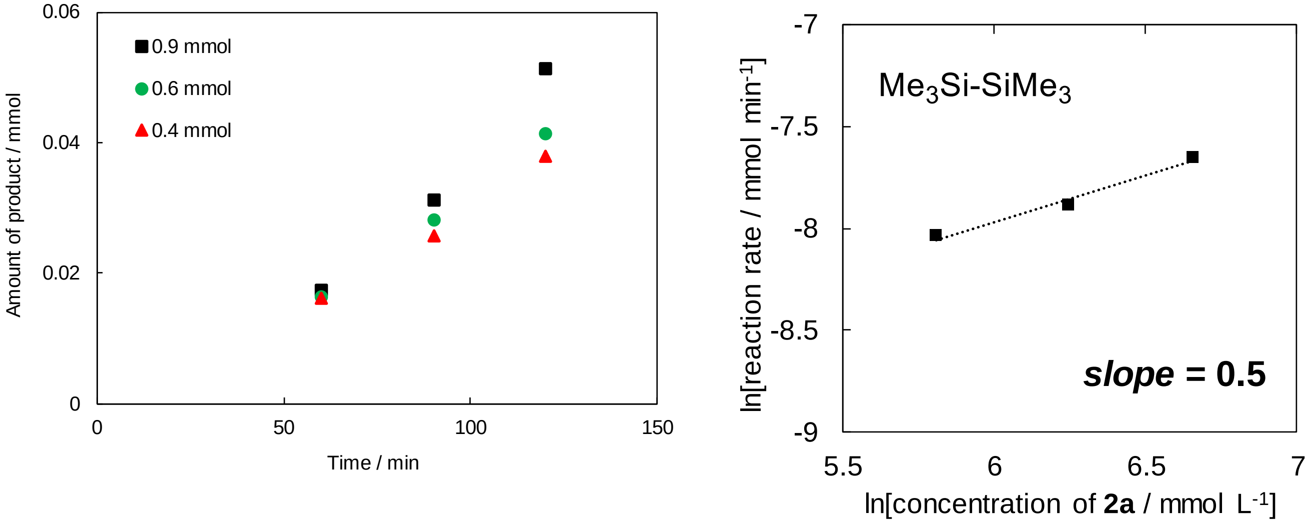


Figure. S8. Effect of concentration of **2a** on alkyl-silyl coupling over Au/ZrO$_2$.

6. Characterization of supported Au catalysts

6-1. XRD pattern of supported Au catalysts

Figure S9 shows the XRD patterns of supported Au catalysts. The pattern mainly displays the peaks due to each metal oxide, and no distinct peaks attributed to Au NPs was identified. This indicates that small Au NPs are highly dispersed on the surface of supports.

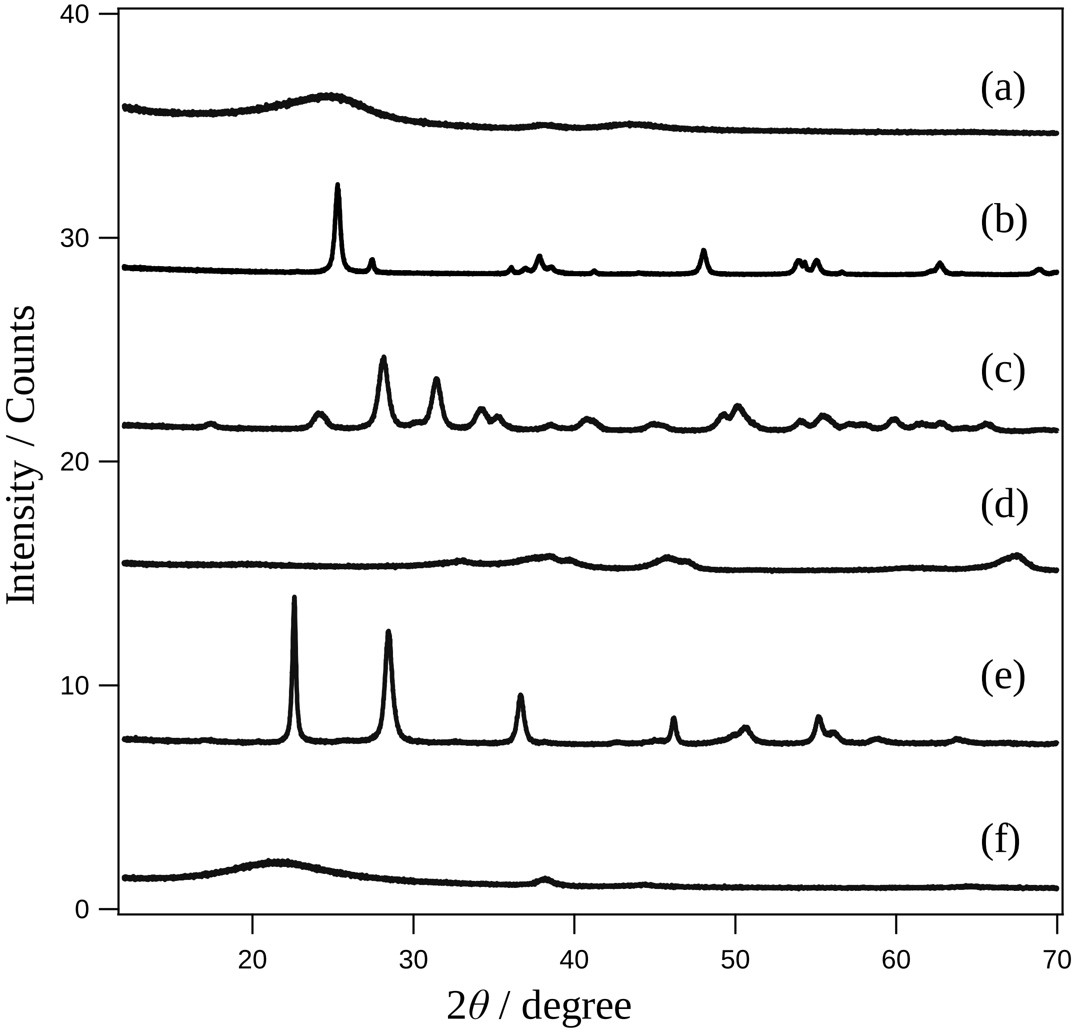


Figure S9. XRD patterns of (a) Au/C, (b) Au/TiO_2, (c) Au/ZrO_2, (d) Au/Al_2O_3, (e) Au/Nb_2O_5, and (f) Au/SiO_2.

6-2. XRD pattern of Au/C catalysts

Figure S10 shows the XRD patterns of Au/C and C. The peaks are attributed to Au (111) were identified at 38°. The crystallite size of is Au NPs indicates that small Au NPs are highly dispersed on the surface of supports.

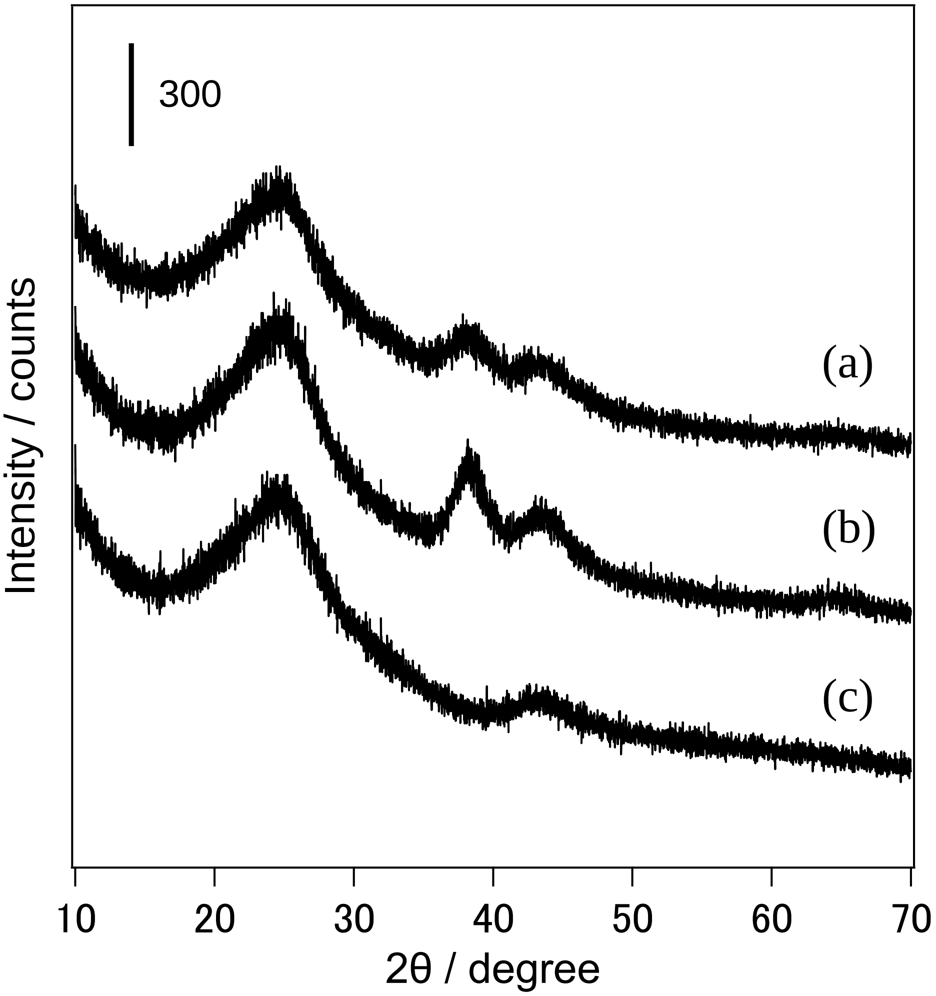


Figure S10. XRD patterns of Au catalysts supported on (a) Au/C (2.1 nm), (b) Au/C (4.8 nm), (c) C.

6-3. HAADF-STEM images of supported Au catalysts.

HAADF-STEM images and the size distribution histograms for fresh supported Au catalyst are shown in Figure S11. Well-dispersed Au NPs with a diameter of ca. 3 nm were found to be mainly present on the surface of each support and noteworthy differences in the mean diameter were not observed. This strongly suggests that remarkable differences in the catalytic activities n were mainly dominated by the factor other than the differences in the particle size of the Au NPs.

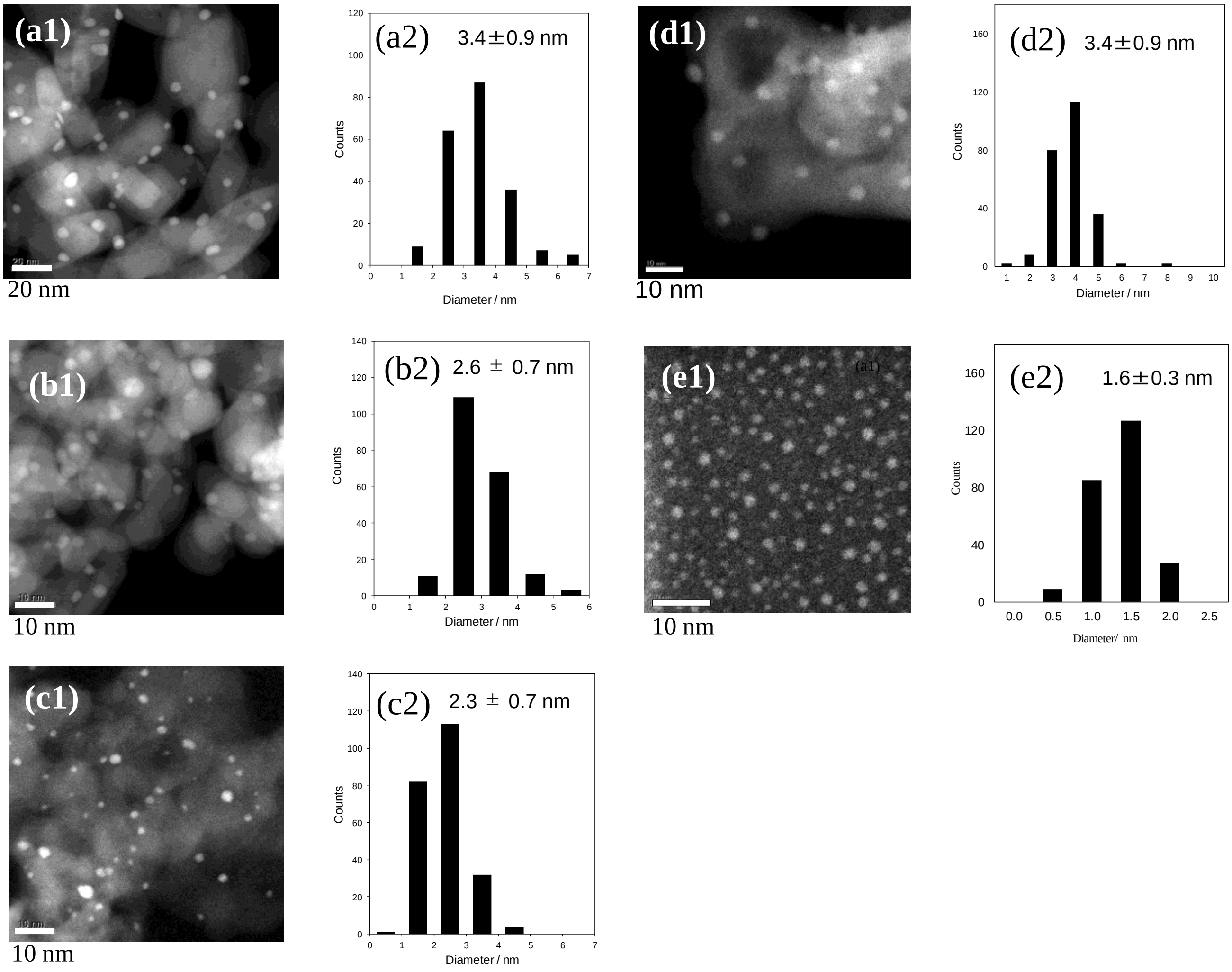


Figure S11. HAADF-STEM images of supported Au catalysts (a1) Au/TiO_2, (b1) Au/ZrO_2, (c1) Au/Al_2O_3, (d1) Au/Nb_2O_5, and (e1) Au/SiO_2, and (a2–e2) their particle size distribution histograms.

6-4. HAADF-STEM images of Au/C catalyst before and after the reaction of 1a with 2a.

HAADF-STEM images and the size distribution histograms for fresh Au/C catalyst and that used for the reaction of **1a** with **2** are shown in Figure S12 (Reaction condition is shown in Table 1.). No remarkable differences in the particle diameters and their standard deviations indicates high stability of Au/C catalysts.

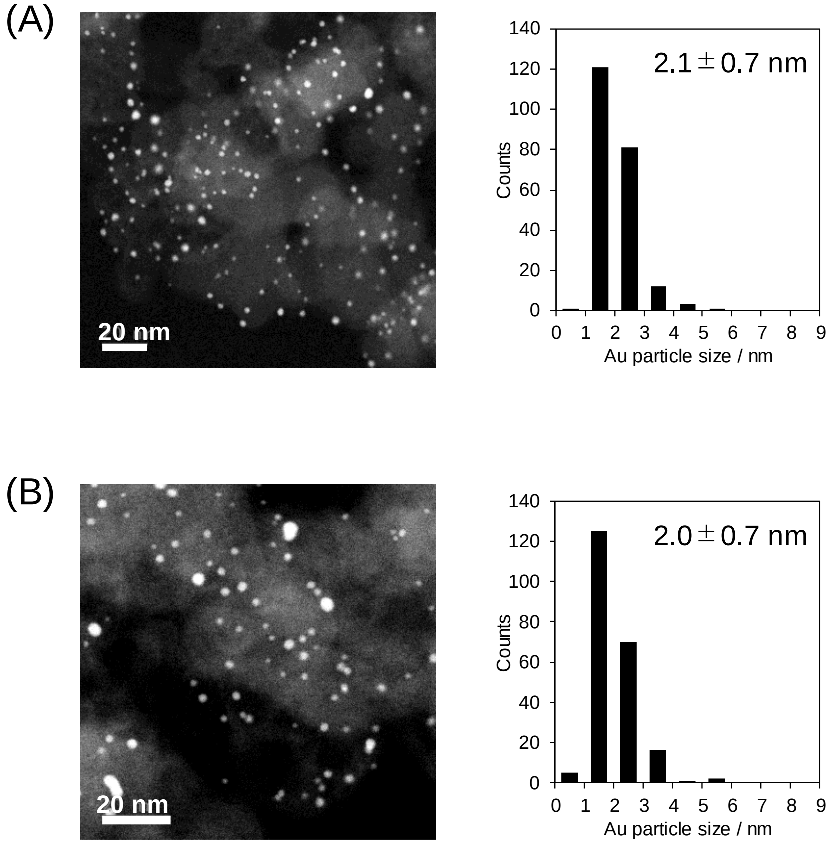
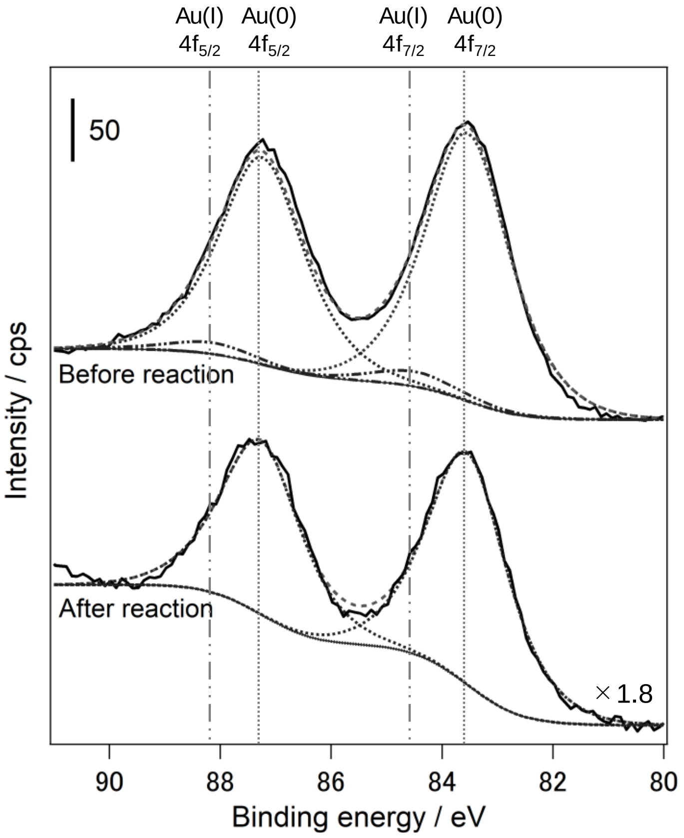


Figure S12. HAADF-STEM images of fresh Au/C catalyst (A1) and that used for the reaction of **1a** with **2a** (B1) and their particle size distribution histograms (A2 and B2).

6-5. XP spectra of Au/C catalyst before and after the reaction of 1a with 2a.

XP spectra of Au/C catalyst before and after the reaction of **1a** and **2a** are shown in Figure S13. The content of Au(I) fraction decreased from 5% to 0%. This implies the electron transfer from organic molecules, probably disilane, to Au NPs during the catalytic reaction.



Catalyst	Au(0) (%)	Au(I) (%)
Au/C (Before reaction)	95	5
Au/C (After reaction)	100	0

Figure S13. XP spectra of Au/C catalyst before and after the reaction of **1a** with **2a**.

6-6. CO_2-TPD profile of Au/C catalyst.

The basic property of supported Au catalysts was estimated by CO_2-temperature-programmed desorption (CO_2-TPD) (Figure S14). Remarkable desorption bands were not identified in the profiles of Au/C catalysts.

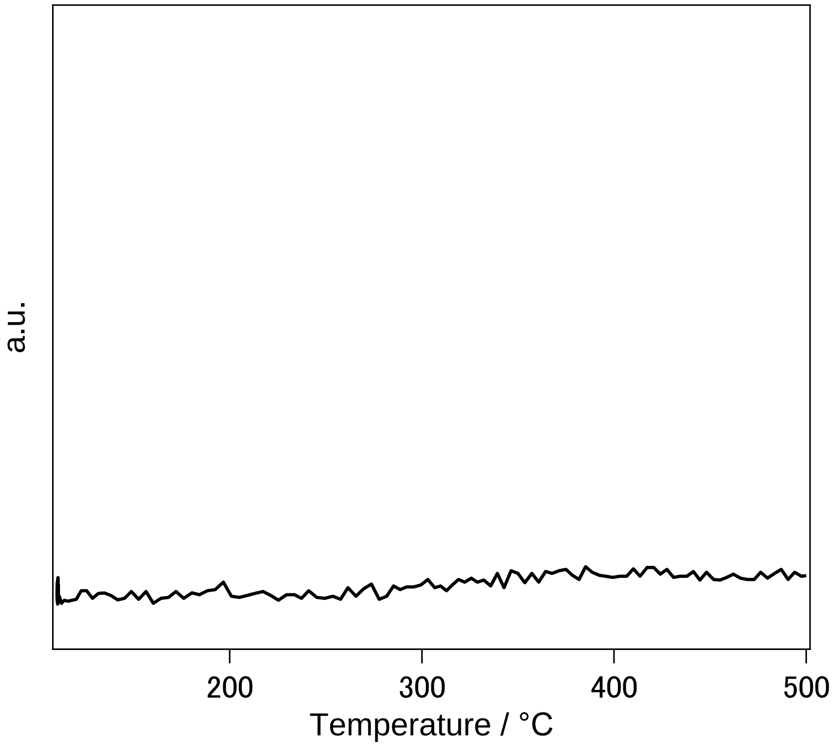


Figure S14. CO_2-TPD profiles of Au/C catalyst

6-7. NH_3-TPD profile of Au/C catalyst.

The acidic property of Au/C catalyst was estimated by NH_3-temperature-programmed desorption (NH_3-TPD) (Figure S15). Remarkable desorption bands were not identified in the profiles of Au/C catalysts.

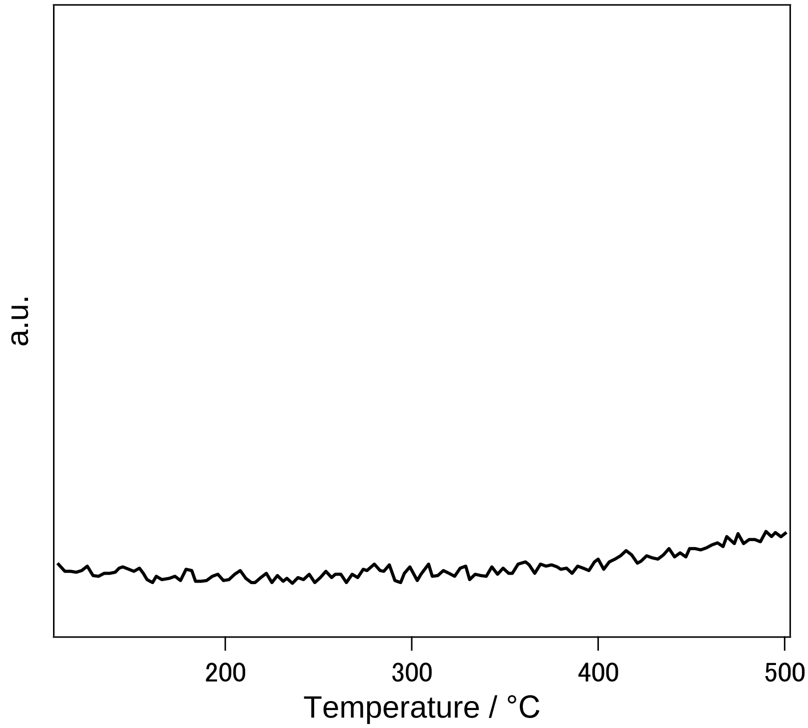


Figure S15. NH_3-TPD profiles of Au/C catalyst

6-8. Surface areas of supported Au catalysts.

Table S1. Summary of physical property of supported Au catalyst

Catalyst	Surface area / $m^2\ g^{-1}$	Yield (%)[a]
Au/C	708	57
Au/ZrO_2	93	6
Au/Al_2O_3	168	0
Au/SiO_2	176	4
Au/TiO_2	52	9
Au/Nb_2O_5	149	0

7. Cyclic voltammetry

Voltammogram of **2a** and **2b** were shown in Figure S16 and S17. Since the potential for Ag/AgNO$_3$ nonaqueous reference electrode is 0.54 V vs. NHE, the oxidation potentials vs. SHE of **2a** and **2b** are 1.78 V and 1.46 V, respectively.

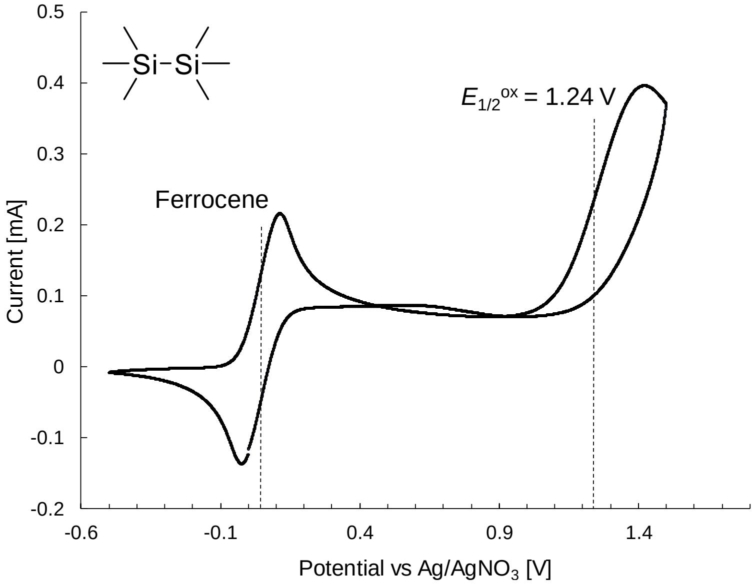


Figure S16. Cyclic voltammogram of **2a**

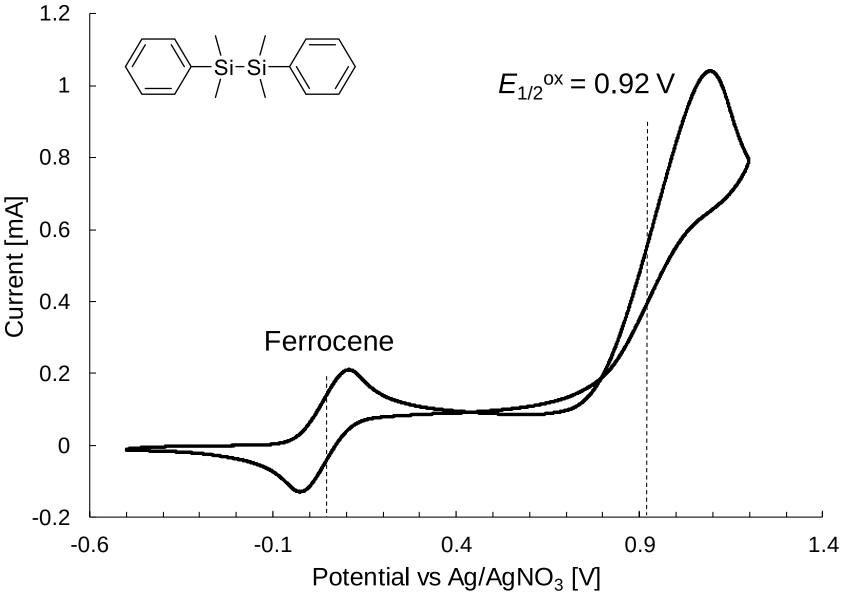


Figure S17. Cyclic voltammogram of **2b**

Voltammogram of **1a-NHPI**, **1a-TCNHPI** and **1a-NHS** were shown in Figure S18 to S20. Since the potential for Ag/AgNO$_3$ nonaqueous reference electrode is 0.54 V vs. NHE, the oxidation potentials vs. SHE of **1a-NHPI**, **1a-TCNHPI** and **1a-NHS** are -1.03 V, -0.79 V and -0.75 V, respectively.

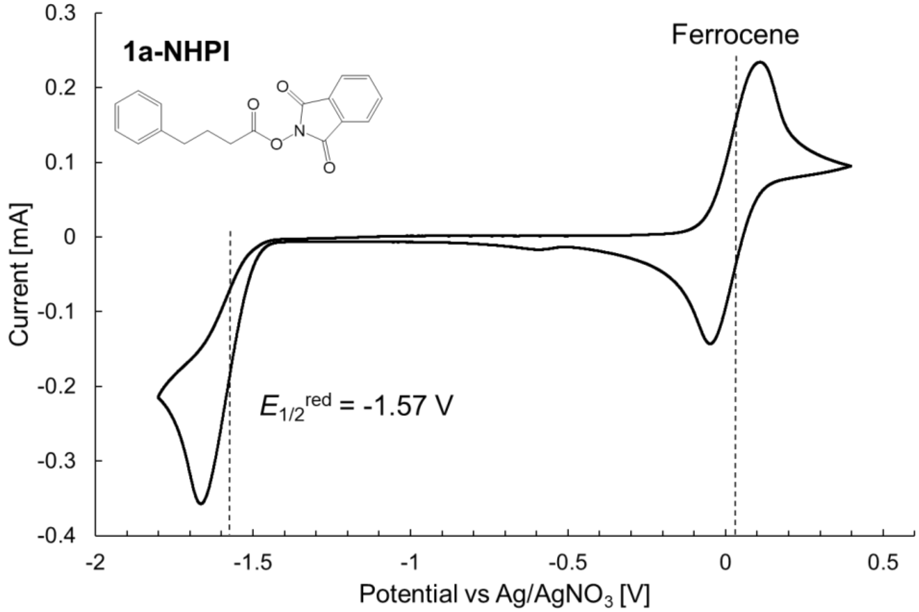


Figure S18. Cyclic voltammogram of **1a-NHPI**

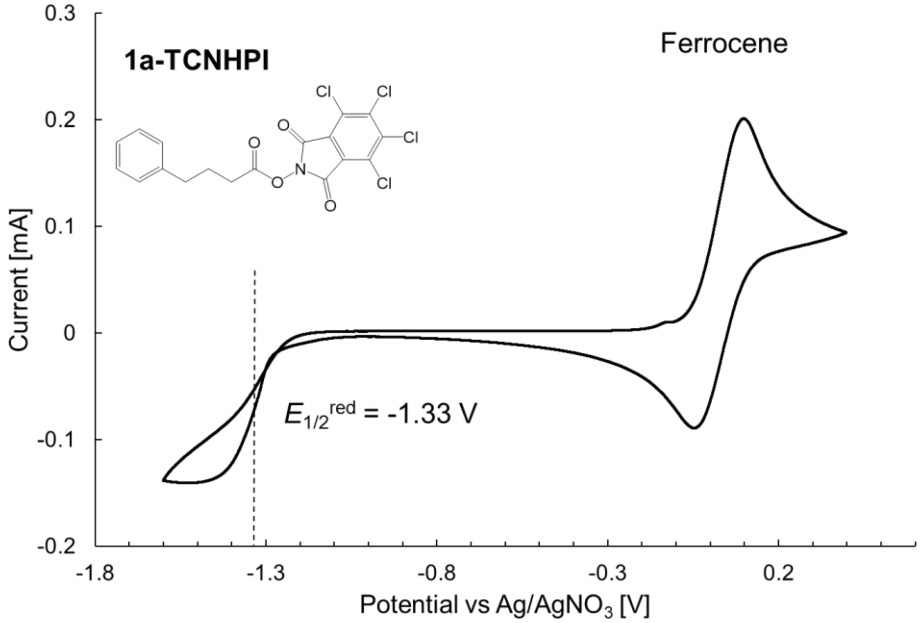


Figure S19. Cyclic voltammogram of **1a-TCNHPI**

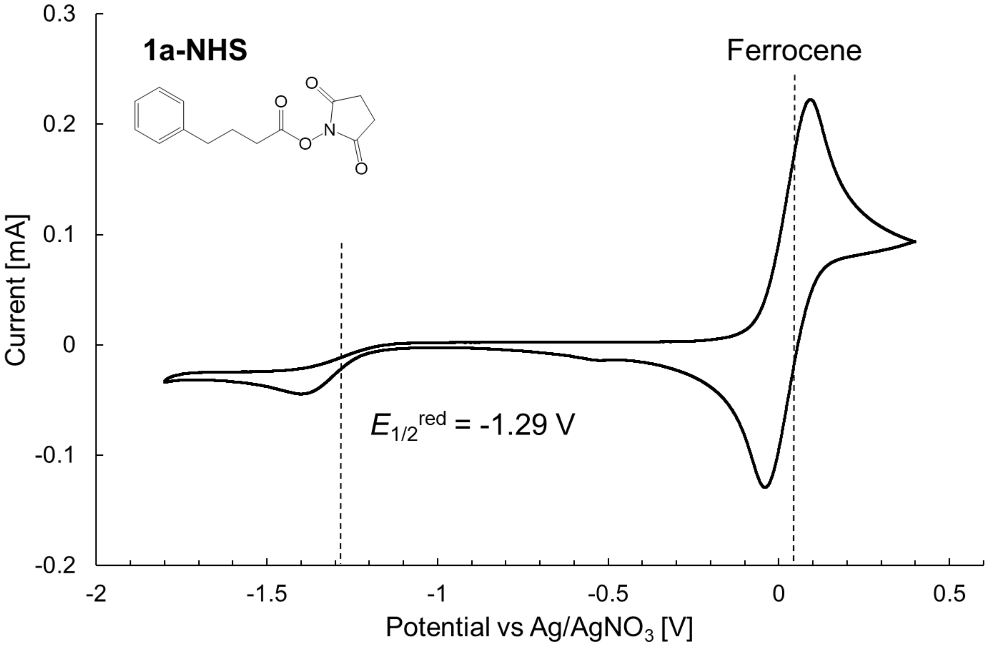


Figure S20. Cyclic voltammogram of **1a-NHS**

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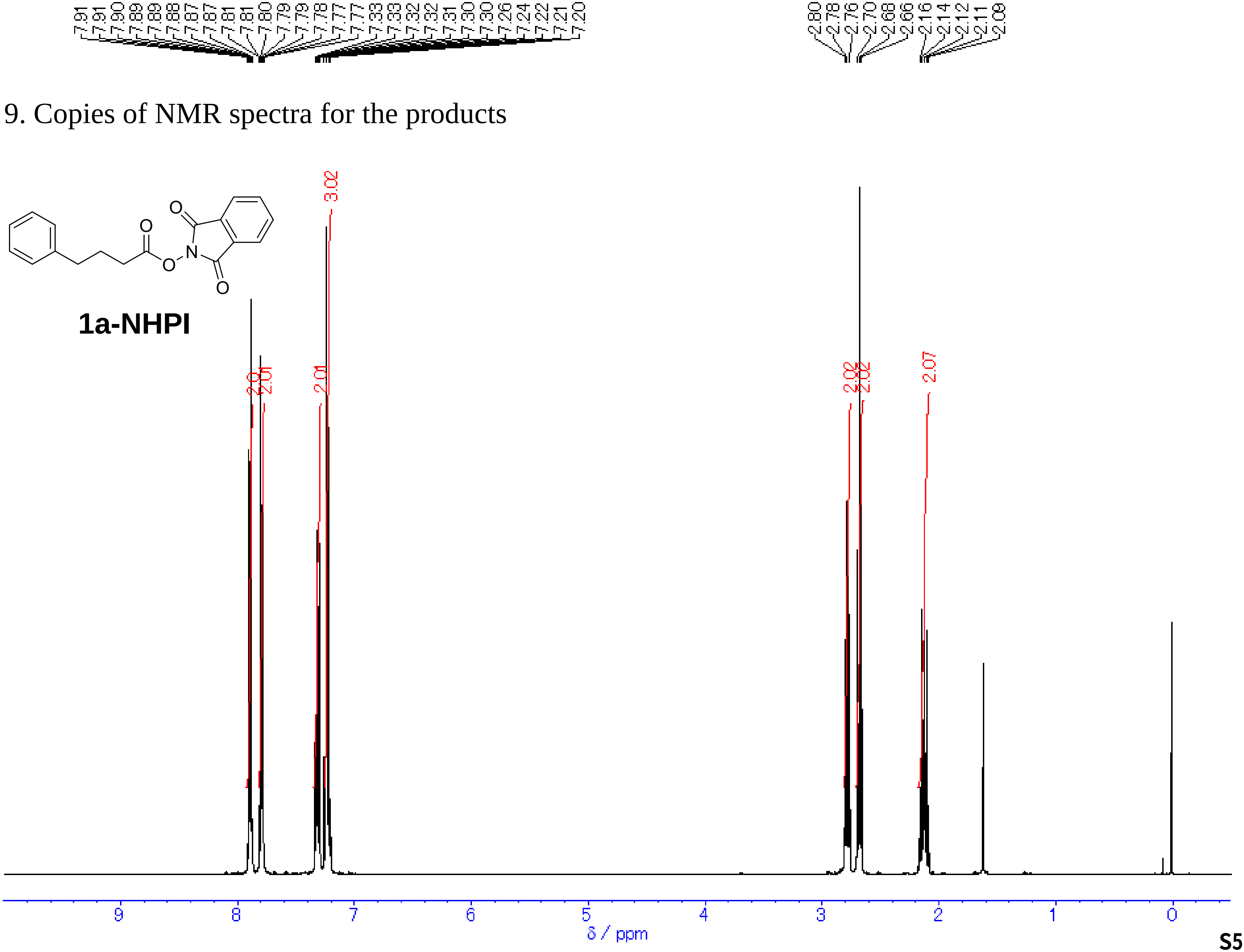
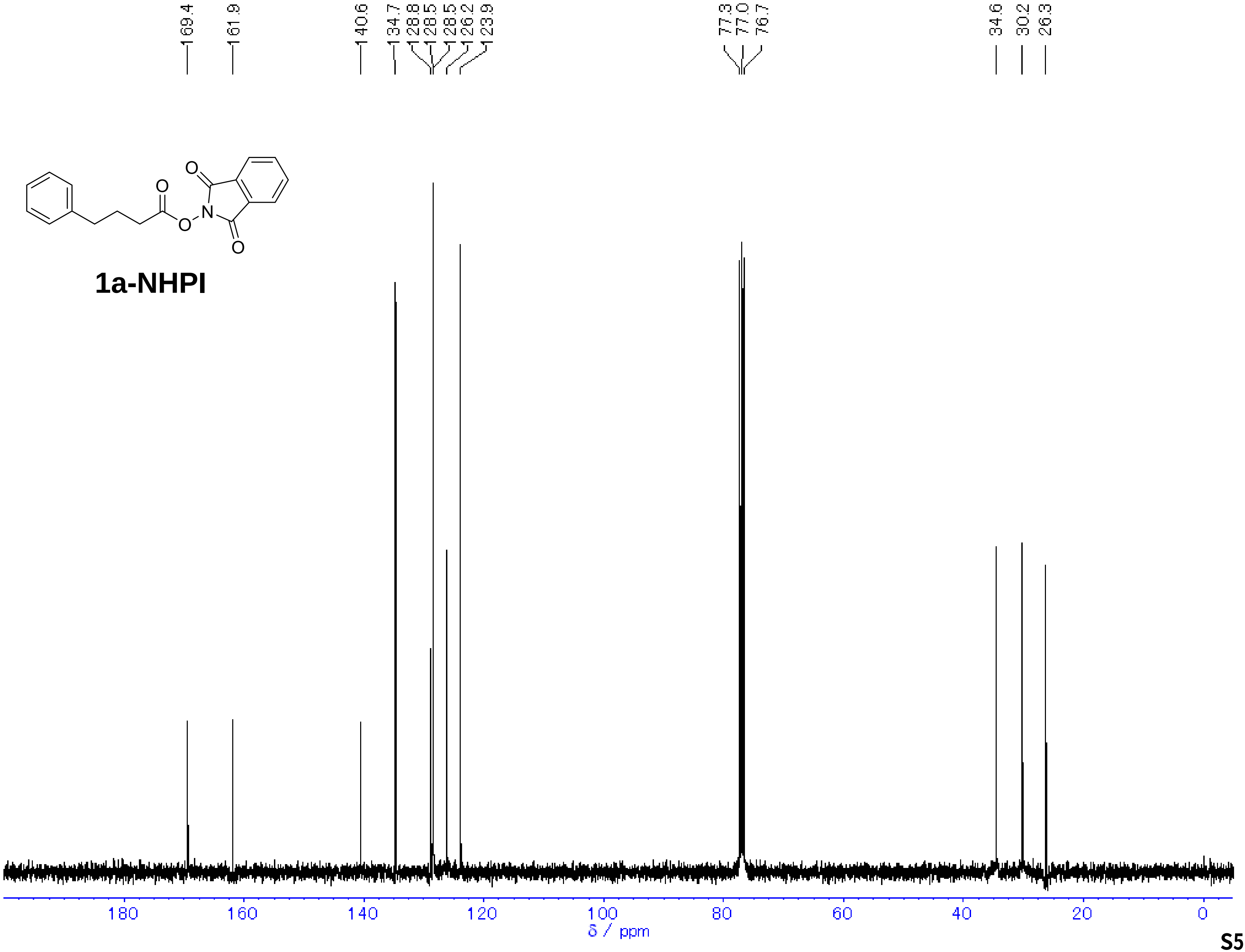
9. Copies of NMR spectra for the products



1a-NHPI



1a-NHPI

169.4
161.9
140.6
134.7
128.8
128.5
128.5
126.2
123.9
77.3
77.0
76.7
34.6
30.2
26.3
O
O
O
N
O
O
180
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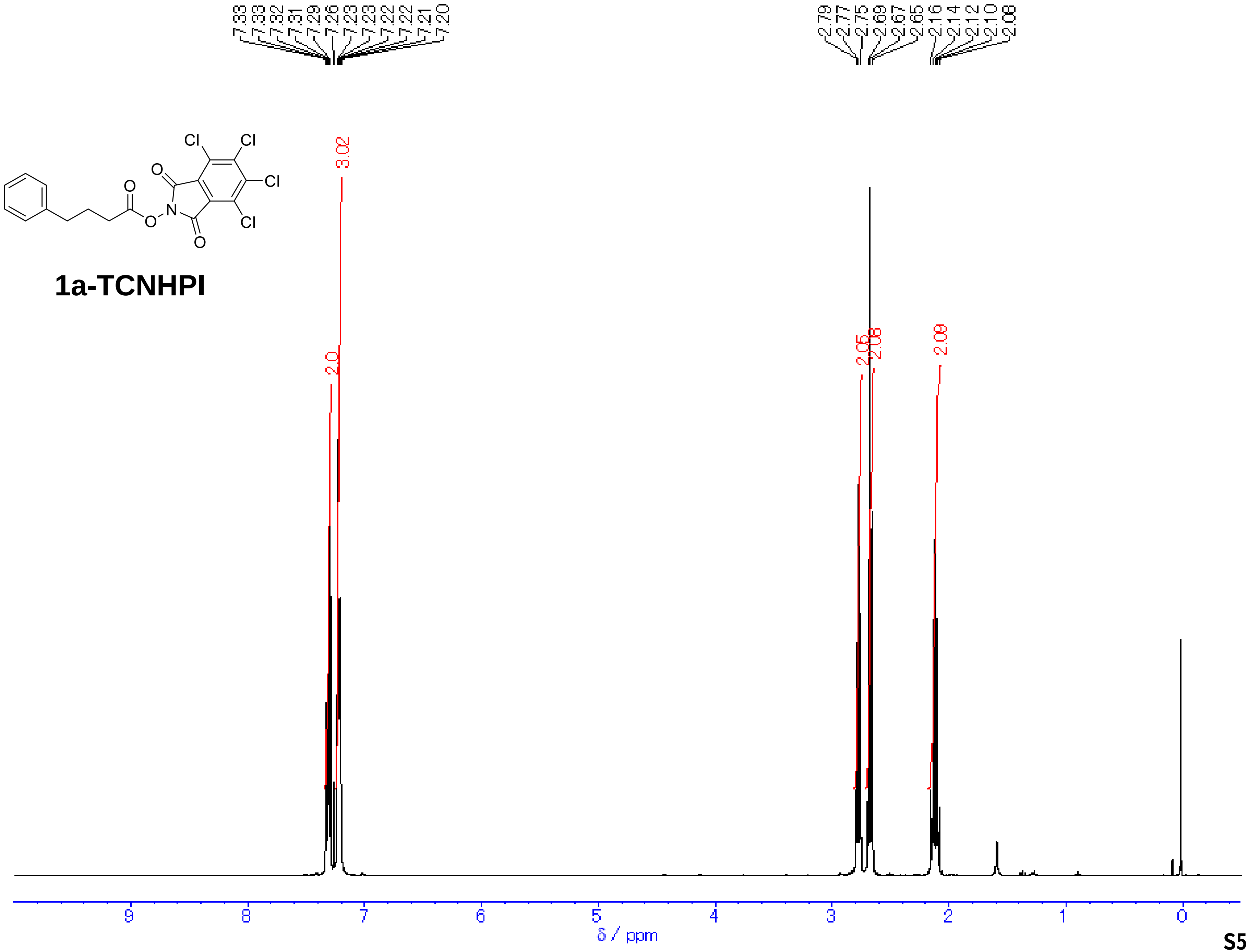
δ / ppm



1a-TCNHPI

7.33
7.33
7.32
7.31
7.29
7.26
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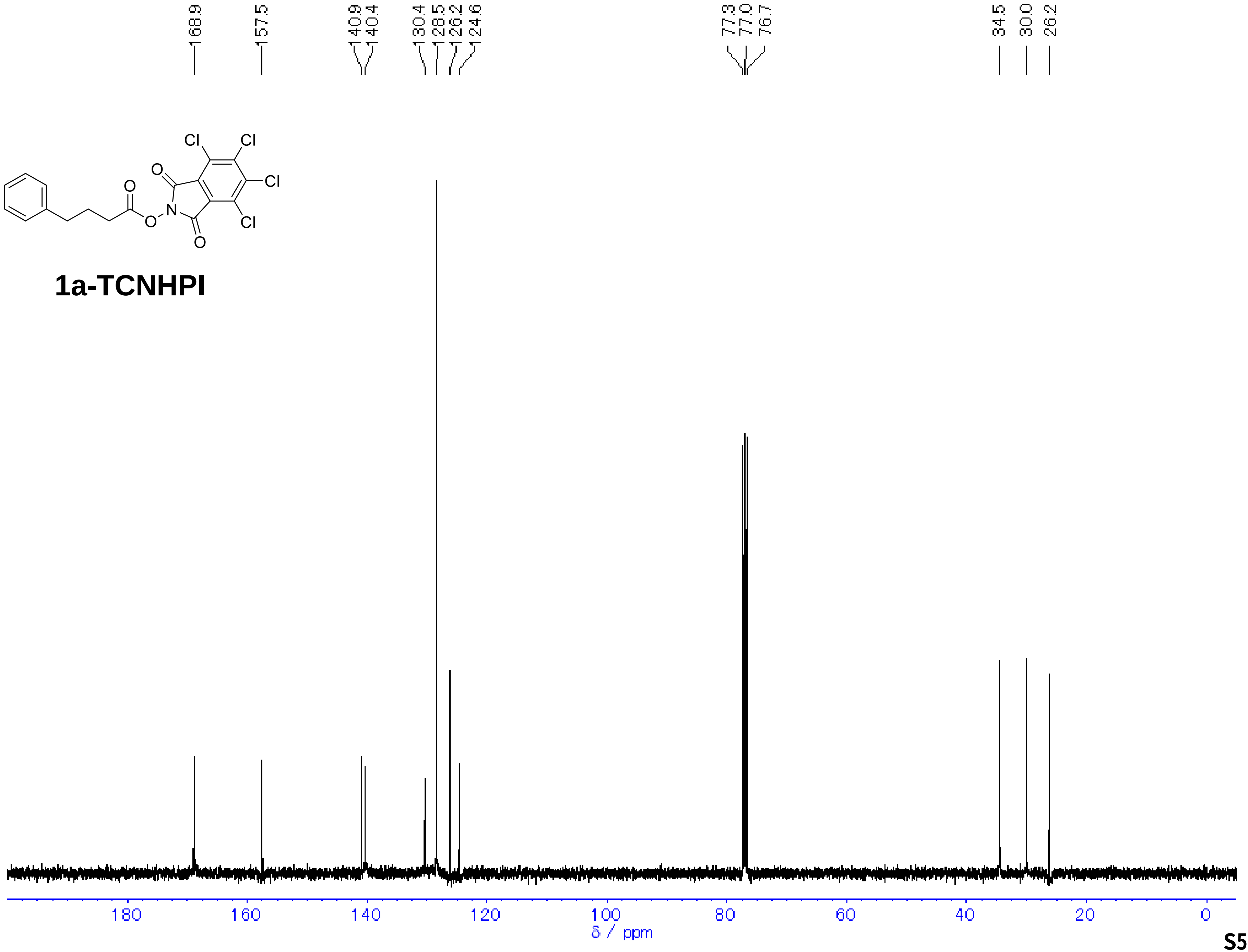
7.23
7.22
7.22
7.21
7.20
2.79
2.77
2.75
2.69
2.67
2.65
2.16
2.14
2.12
2.10
2.08
2.0
3.02
2.05
2.08
2.09
Cl
Cl
Cl
Cl
O
O
O
O
N
9
8
7
6
5
4
3
2
1
0
δ / ppm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124.6
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77.0
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34.5
30.0
26.2
Cl
Cl
Cl
Cl
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O
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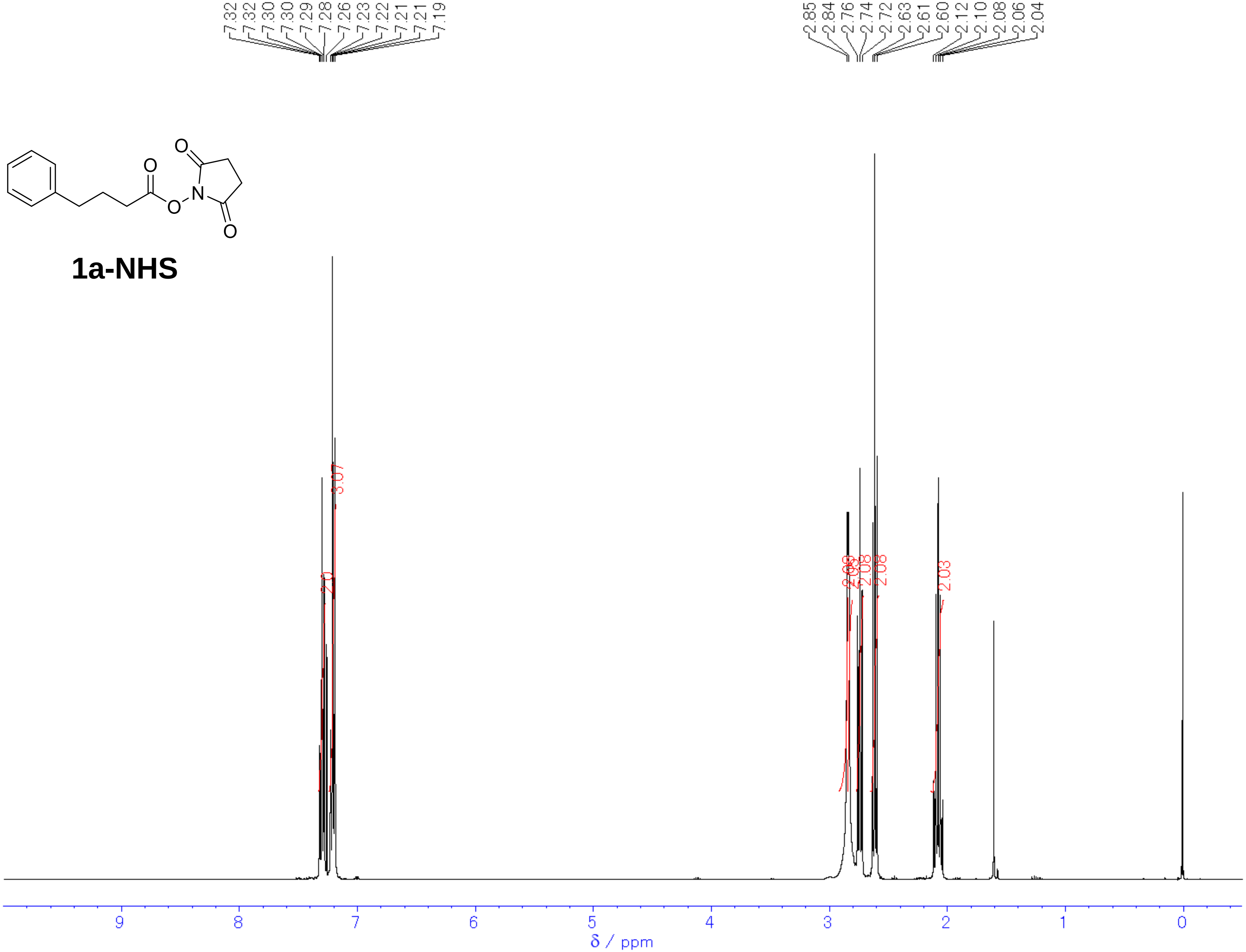
N
O
180
160
140
120
100
80
60
40
20
0
δ / ppm

1a-TCNHPI



1a-NHS

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O
O
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7.32
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7.28
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7.22
7.21
7.21
7.19
2.85
2.84
2.76
2.74
2.72
2.63
2.61
2.60
2.12
2.10
2.08
2.06
2.04
2.0
3.07
2.08
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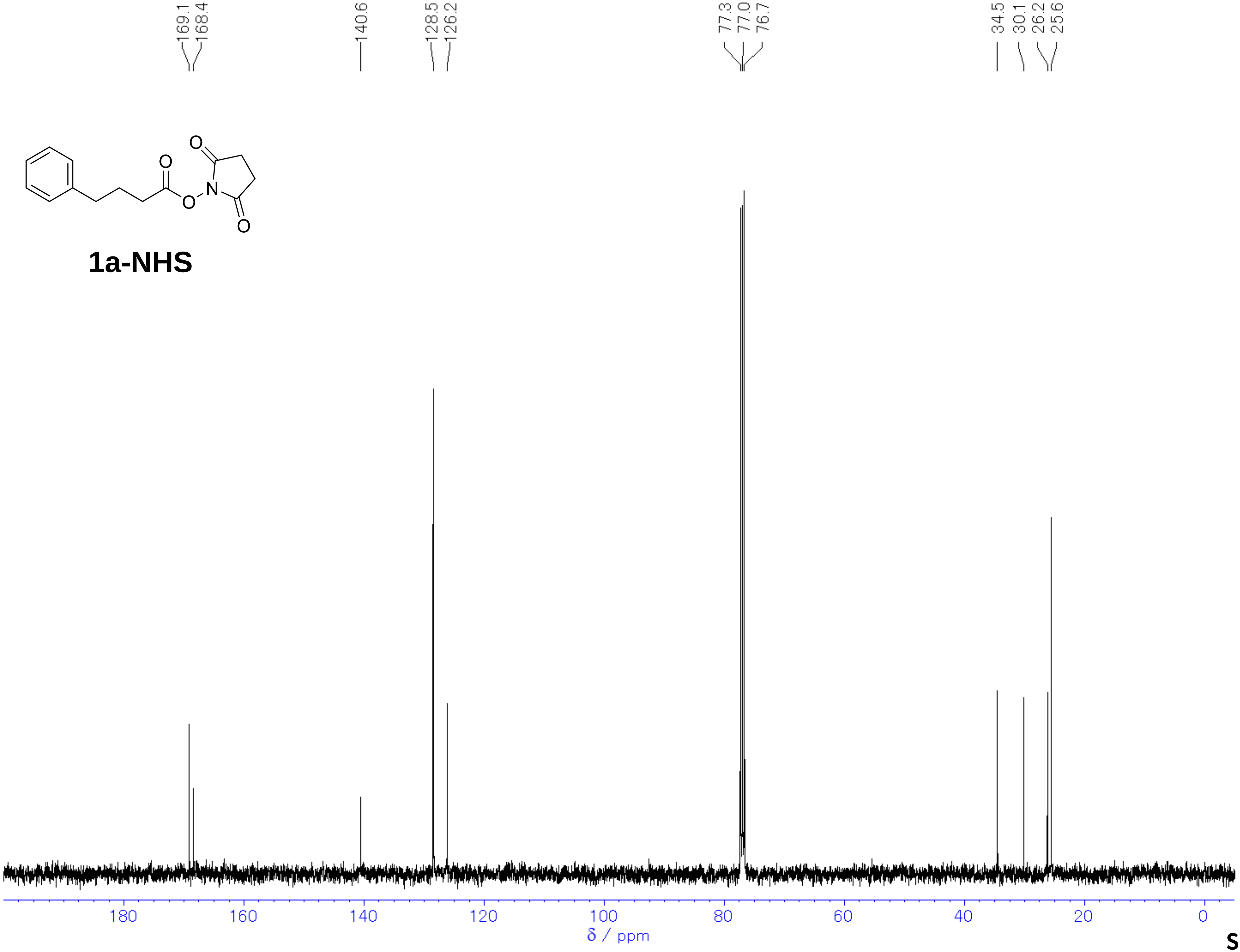
2.08
2.08
2.03
9
8
7
6
5
4
3
2
1
0
δ / ppm



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77.0
76.7
34.5
30.1
26.2
25.6
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O
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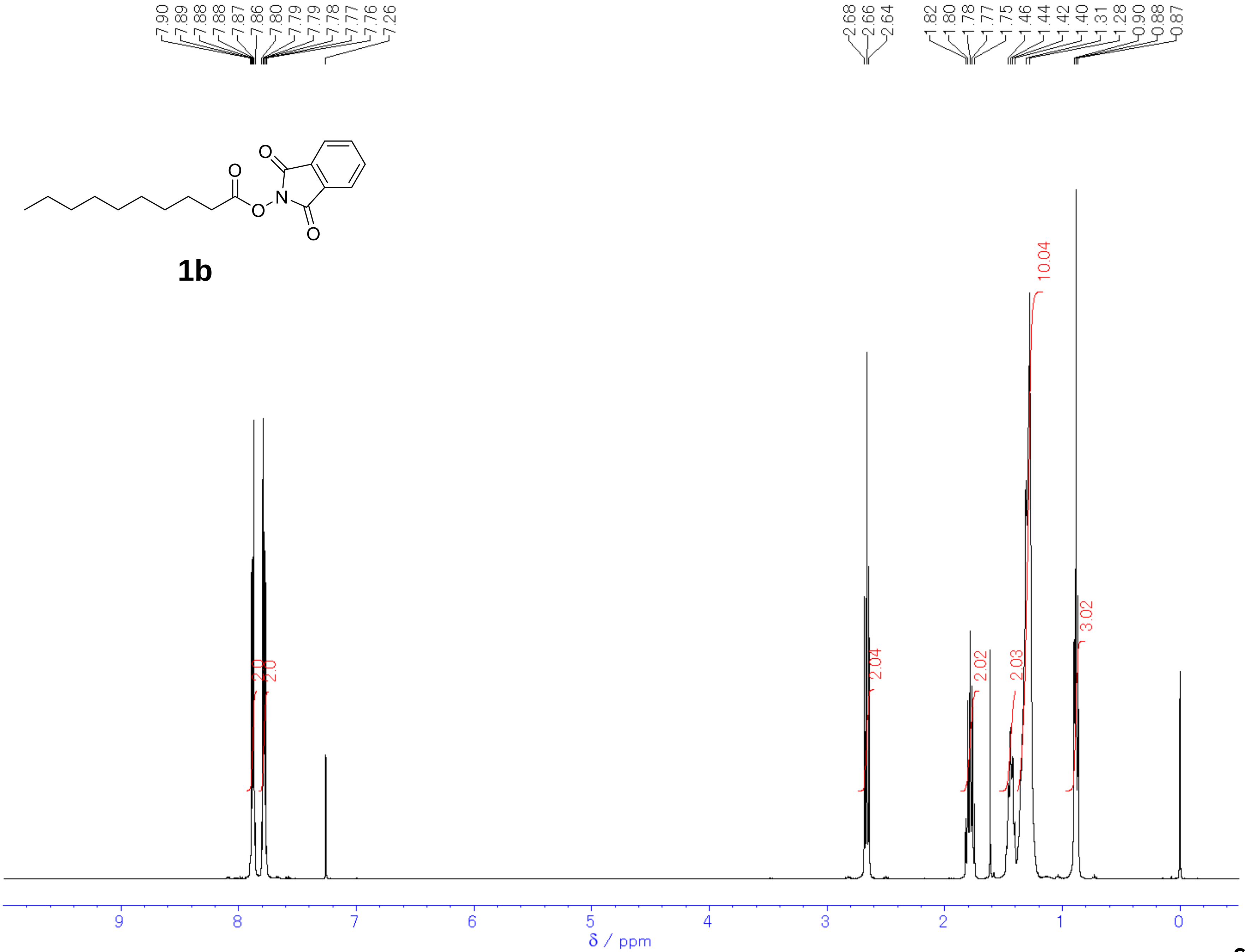
O
O
180
160
140
120
100
80
60
40
20
0
δ / ppm

1a-NHS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7.78
7.77
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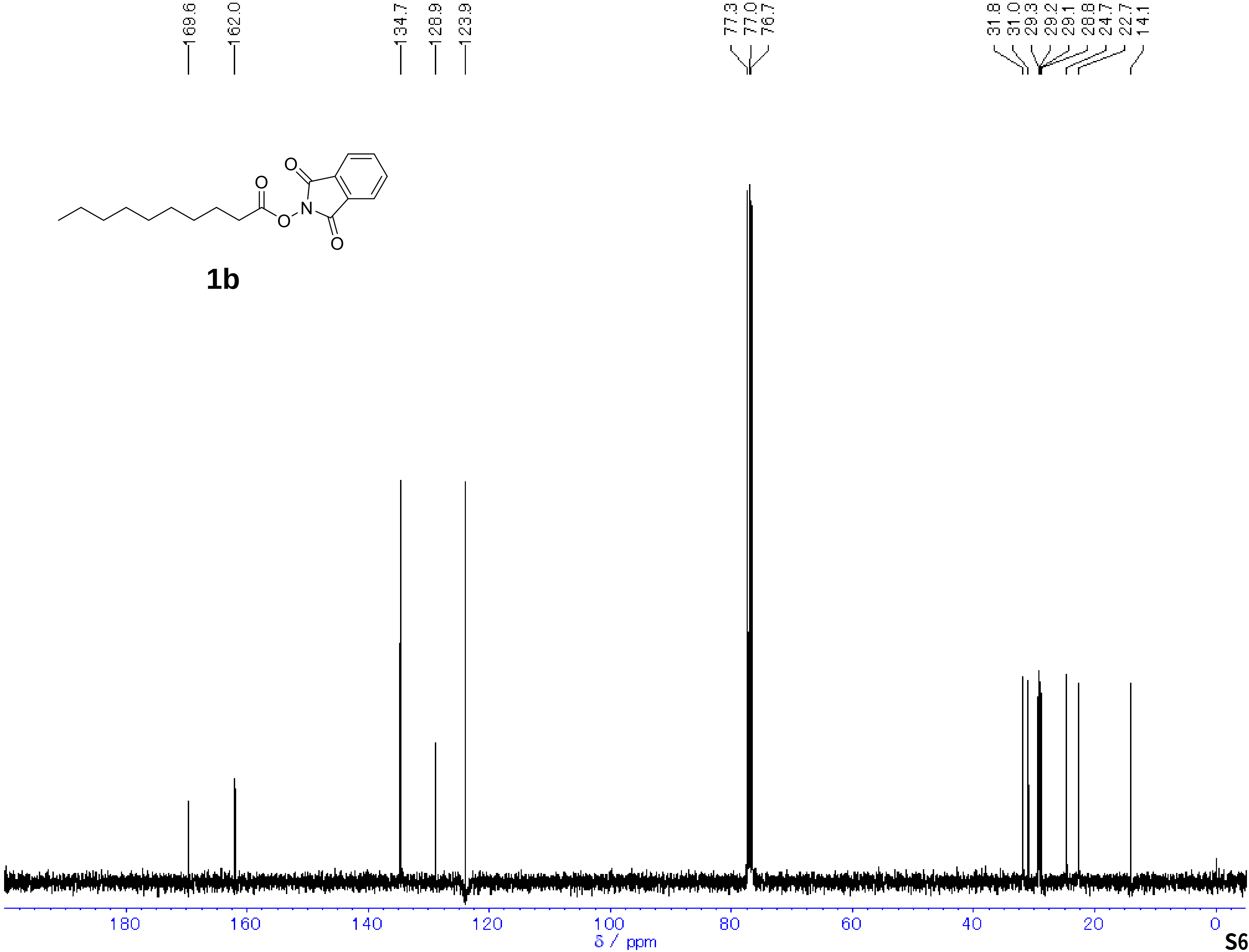
2.66
2.64
1.82
1.80
1.78
1.77
1.75
1.46
1.44
1.42
1.40
1.31
1.28
0.90
0.88
0.87
O
O
N
O
O
2.0
2.0
2.04
2.02
2.03
10.04
3.02
9
8
7
6
5
4
3
2
1
0
δ / ppm

1b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123.9
77.3
77.0
76.7
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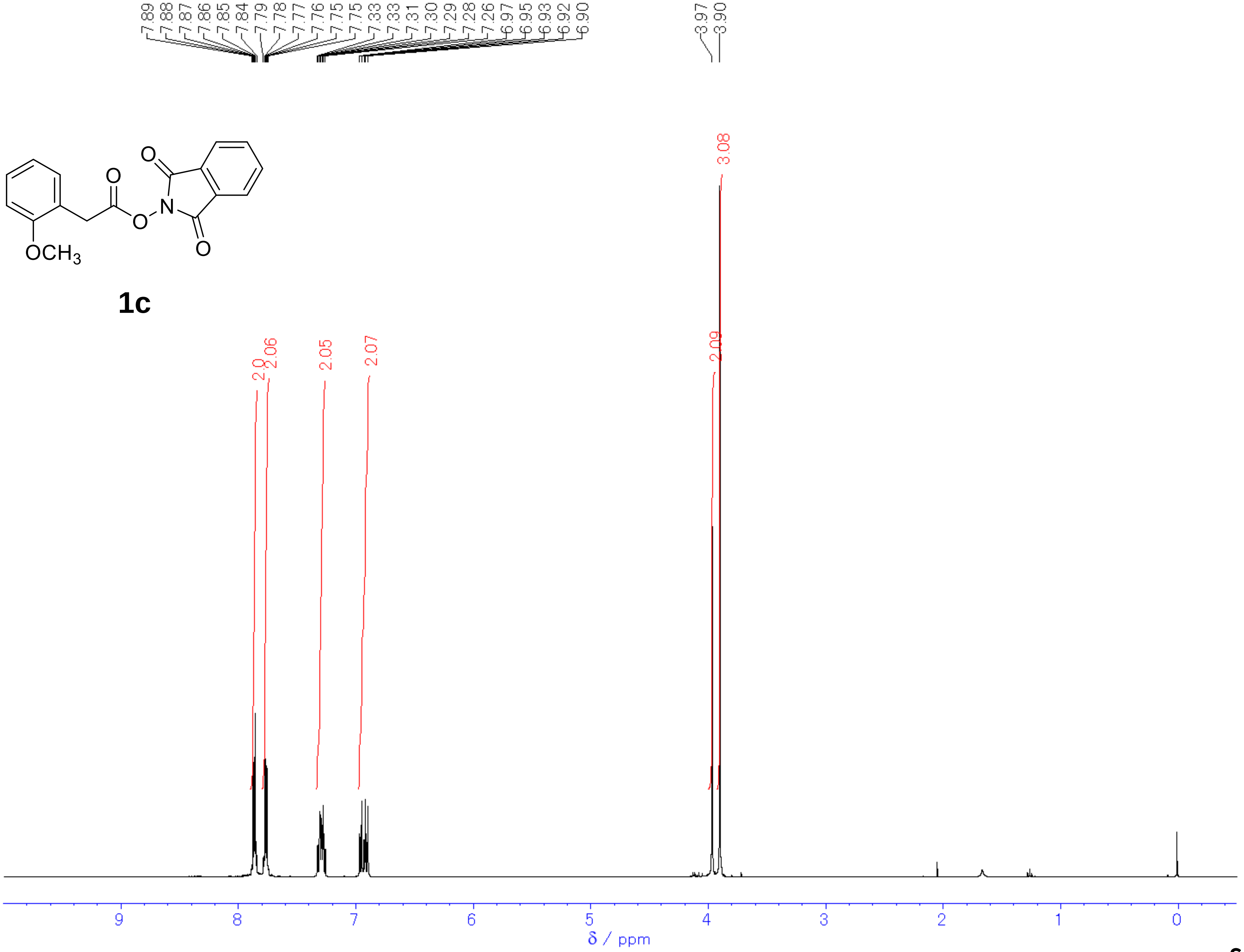
31.0
29.3
29.2
29.1
28.8
24.7
22.7
14.1
O
O
O
N
O
O
180
160
140
120
100
80
60
40
20
0
δ / ppm

1b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7.76
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7.75
7.33
7.33
7.31
7.30
7.29
7.28
7.26
6.97
6.95
6.93
6.92
6.90
3.97
3.90
3.08
2.0
2.06
2.05
2.07
2.09
O
O
N
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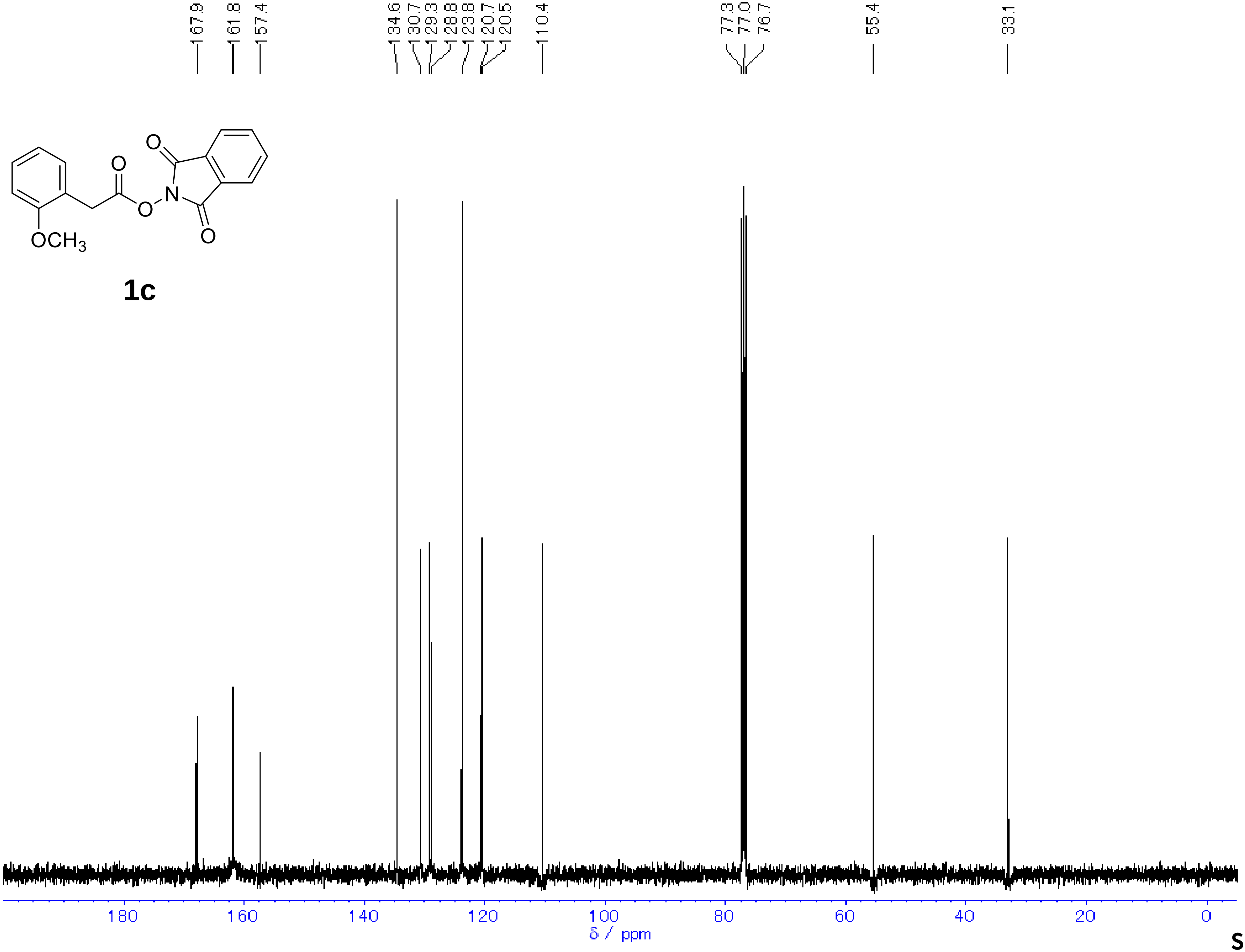
O
O
OCH3
9
8
7
6
5
4
3
2
1
0
δ / ppm

1c

167.9
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77.0
76.7
55.4
33.1
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O
N
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O
OCH$_3$
1c
180
160
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120
100
80
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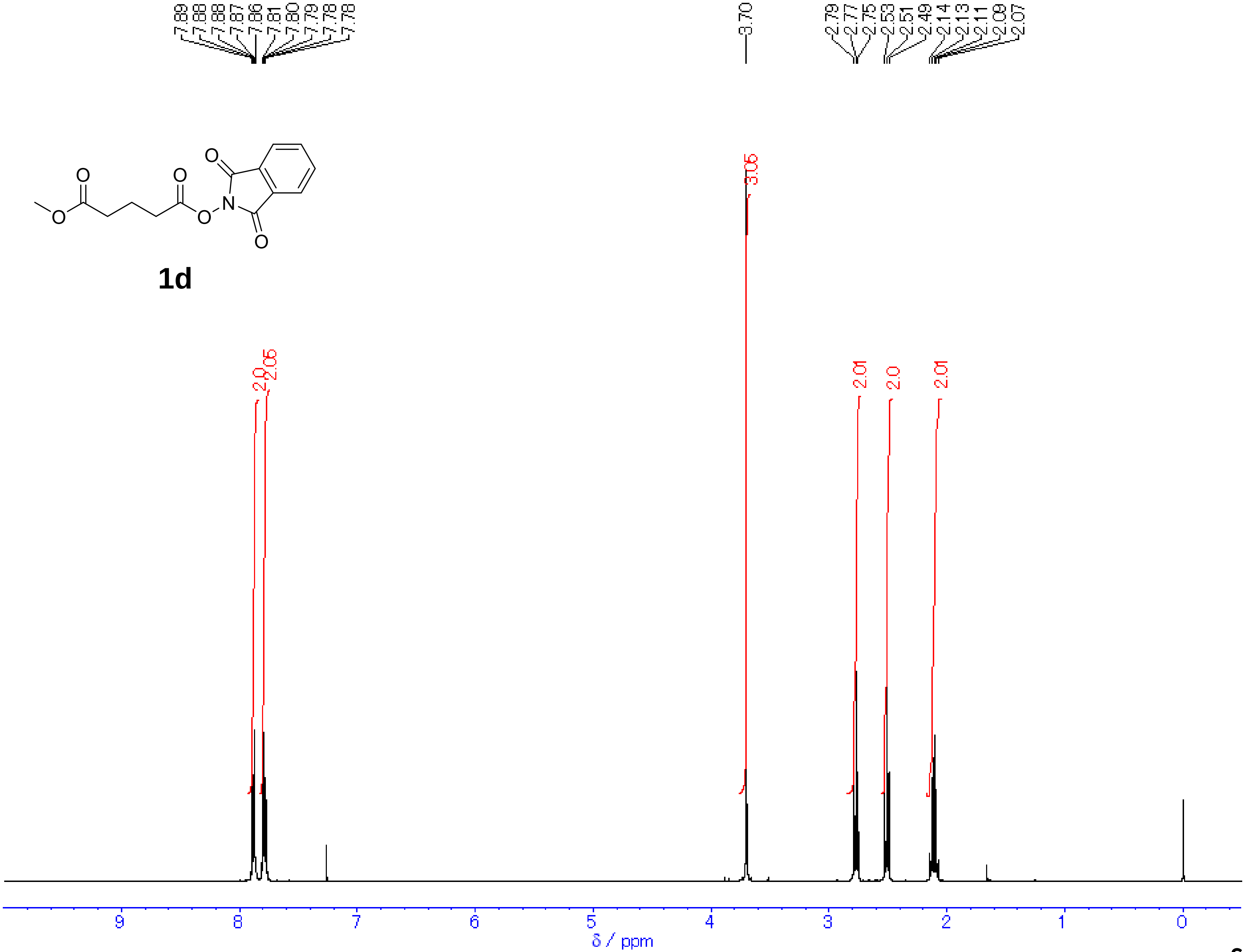
40
20
0
δ / ppm



1d

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7.78
7.78
3.70
2.79
2.77
2.75
2.53
2.51
2.49
2.14
2.13
2.11
2.09
2.07
2.0
2.05
3.05
2.01
2.0
2.01
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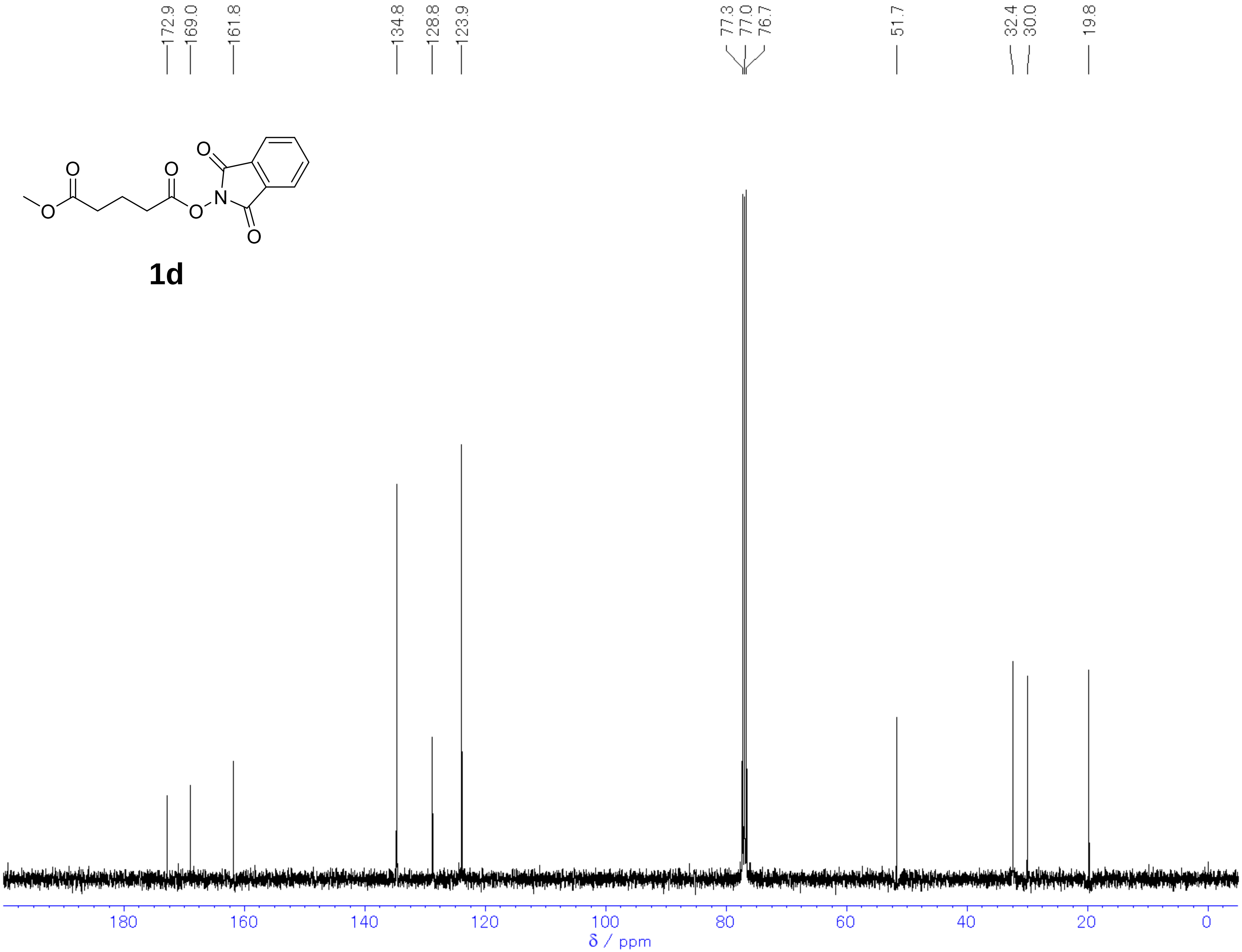
O
O
O
O
O
N
9
8
7
6
5
4
3
2
1
0
δ / ppm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123.9
77.3
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51.7
32.4
30.0
19.8
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O
O
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O
O
O
1d
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100
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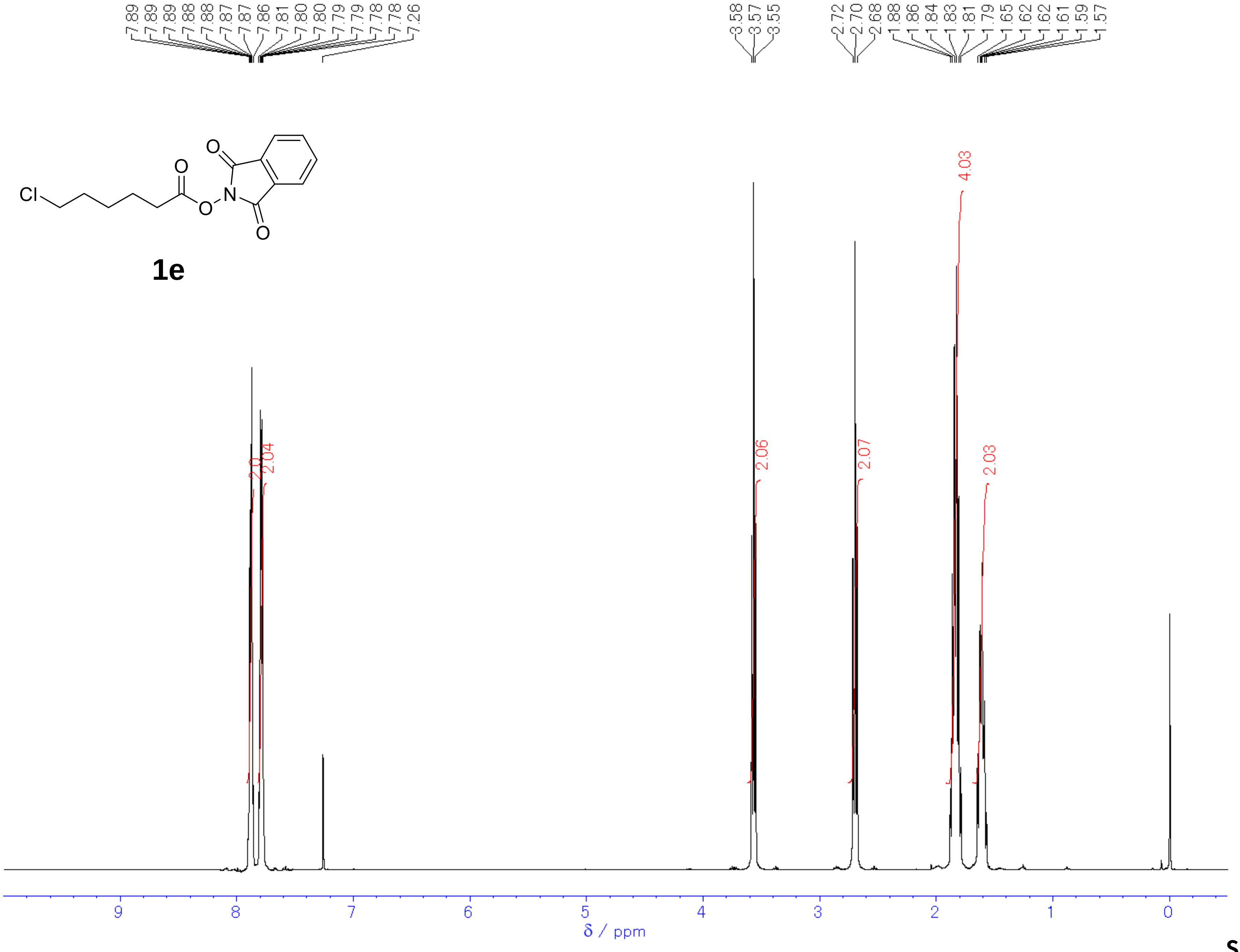
40
20
0
δ / ppm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7.79
7.78
7.78
7.26
3.58
3.57
3.55
2.72
2.70
2.68
1.88
1.86
1.84
1.83
1.81
1.79
1.65
1.62
1.62
1.61
1.59
1.57
Cl
O
O
O
N
O
2.0
2.04
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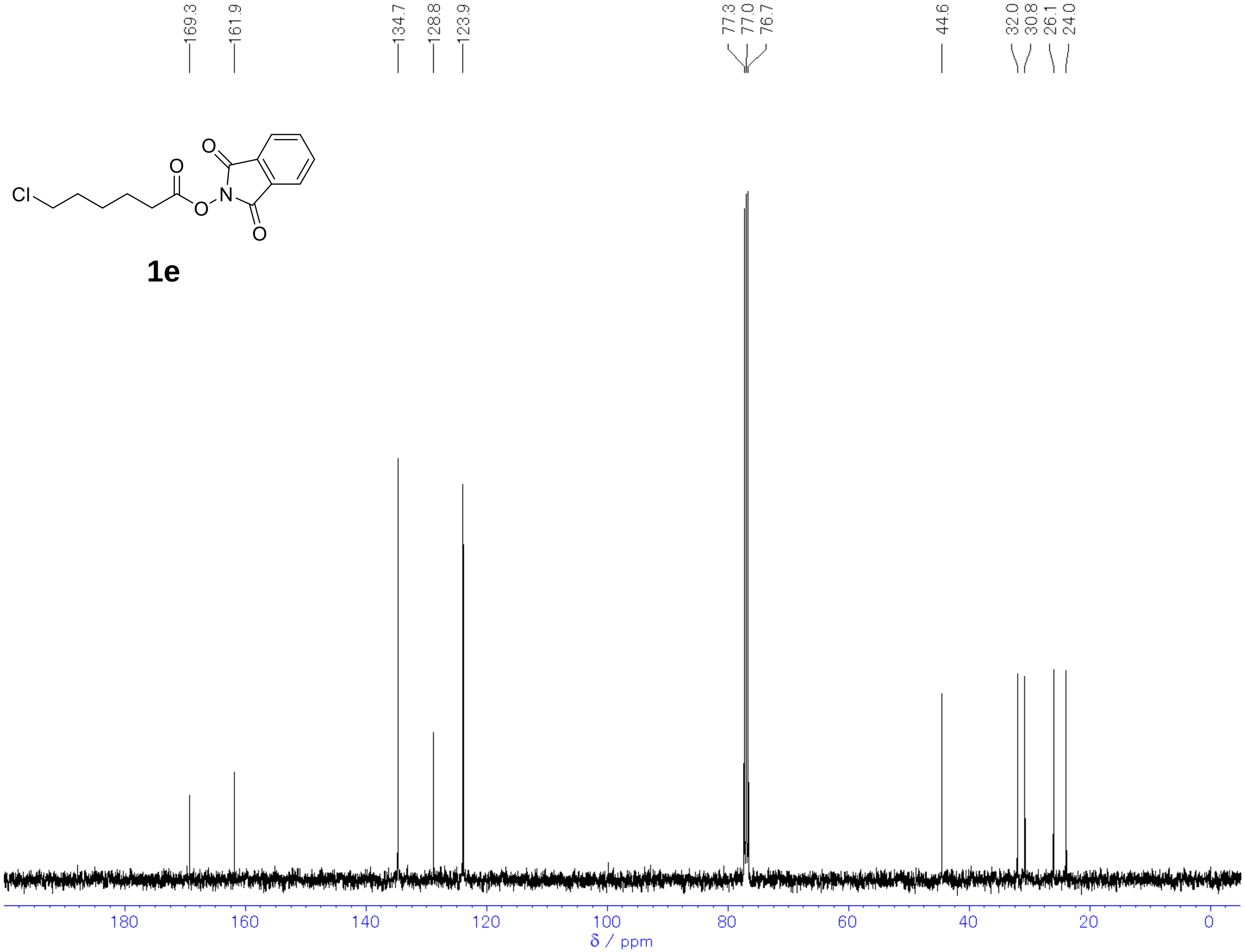
4.03
2.03
9
8
7
6
5
4
3
2
1
0
δ / ppm

1e



1e

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76.7
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32.0
30.8
26.1
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O
N
O
O
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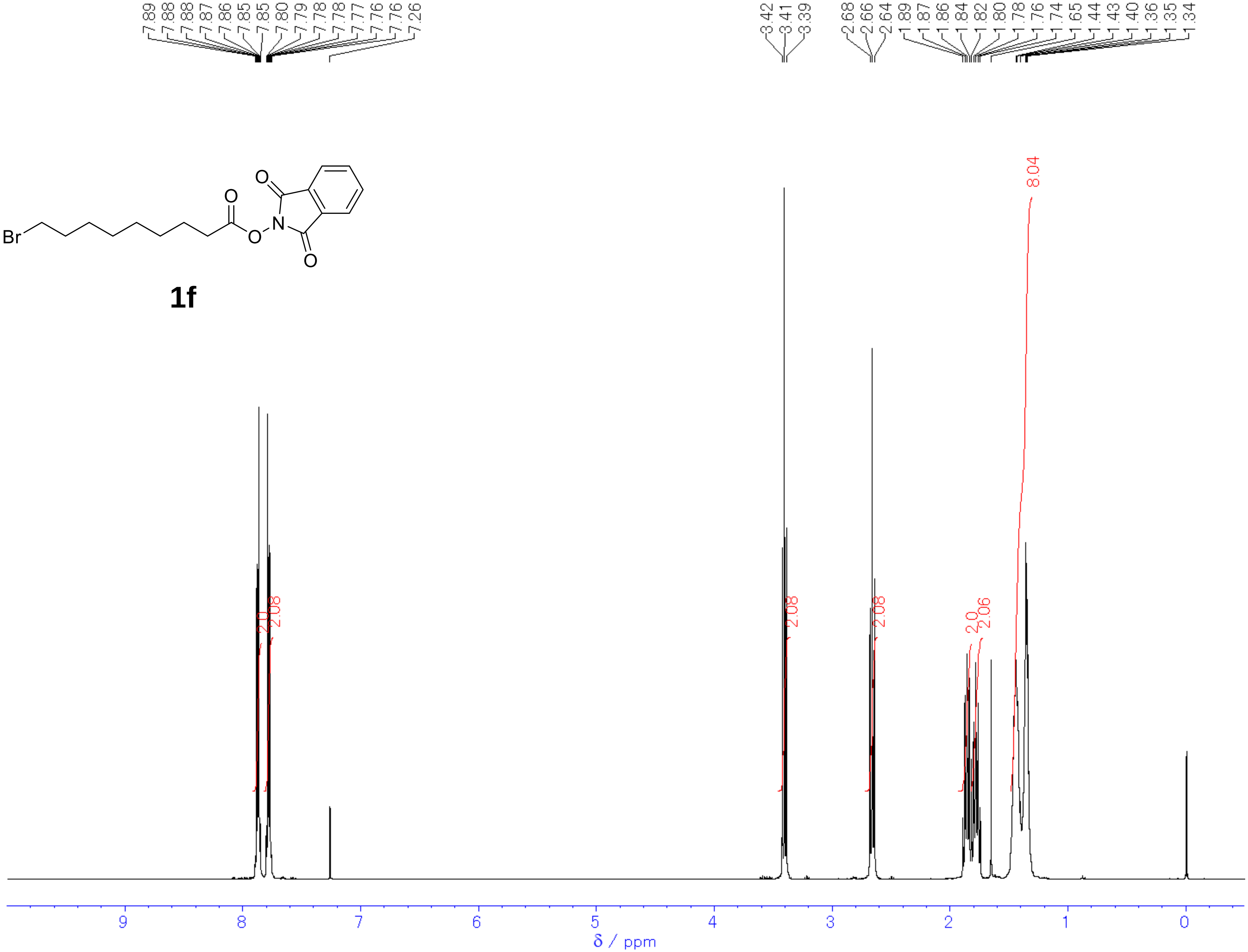
120
100
80
60
40
20
0
δ / ppm



1f

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7.78
7.77
7.76
7.76
7.26
3.42
3.41
3.39
2.68
2.66
2.64
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1.87
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1.80
1.78
1.76
1.74
1.65
1.44
1.43
1.40
1.36
1.35
1.34
8.04
2.0
2.08
2.08
2.08
2.0
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Br
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O
O
N
O
9
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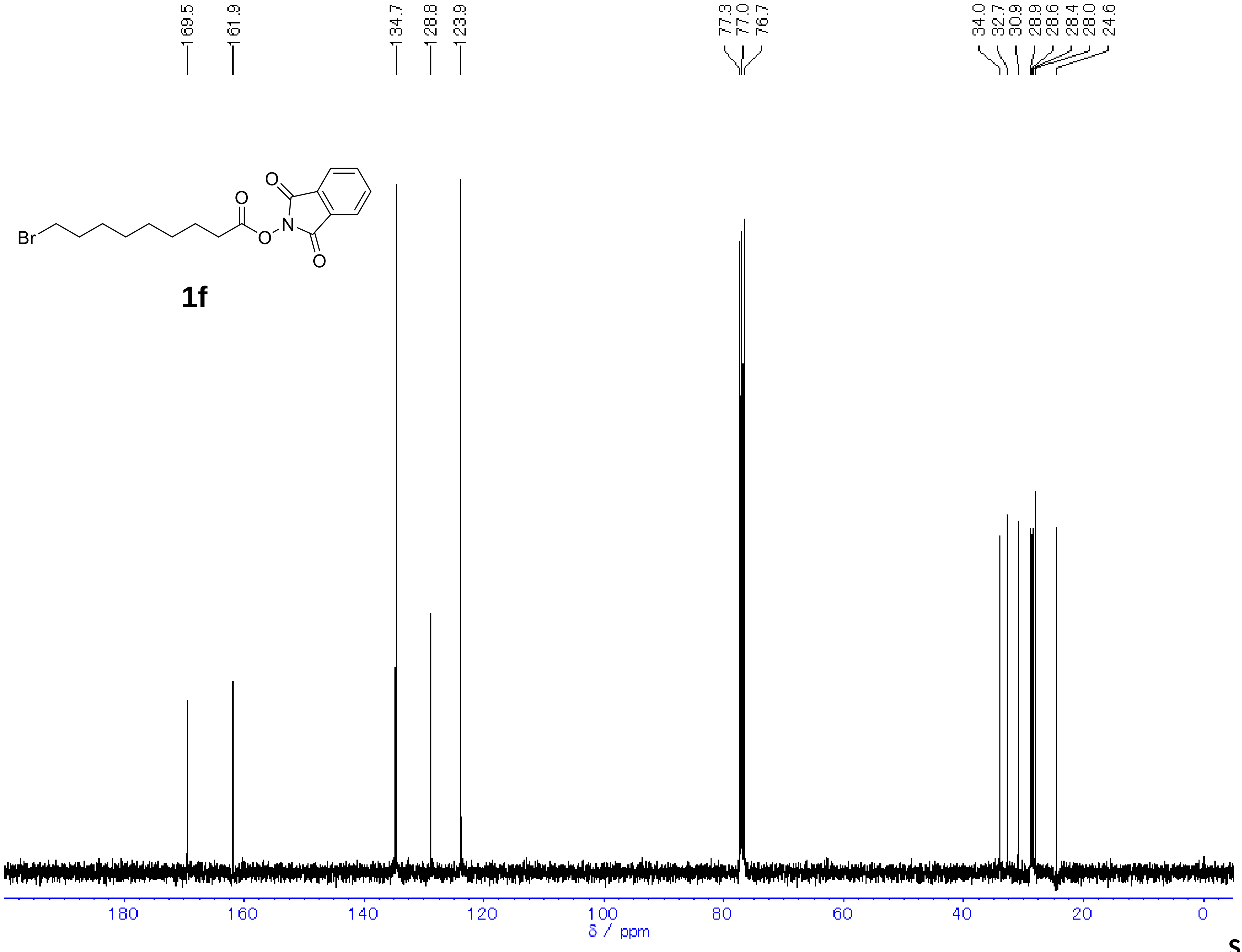
5
4
3
2
1
0
δ / ppm



1f

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28.9
28.6
28.4
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Br
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N
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O
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100
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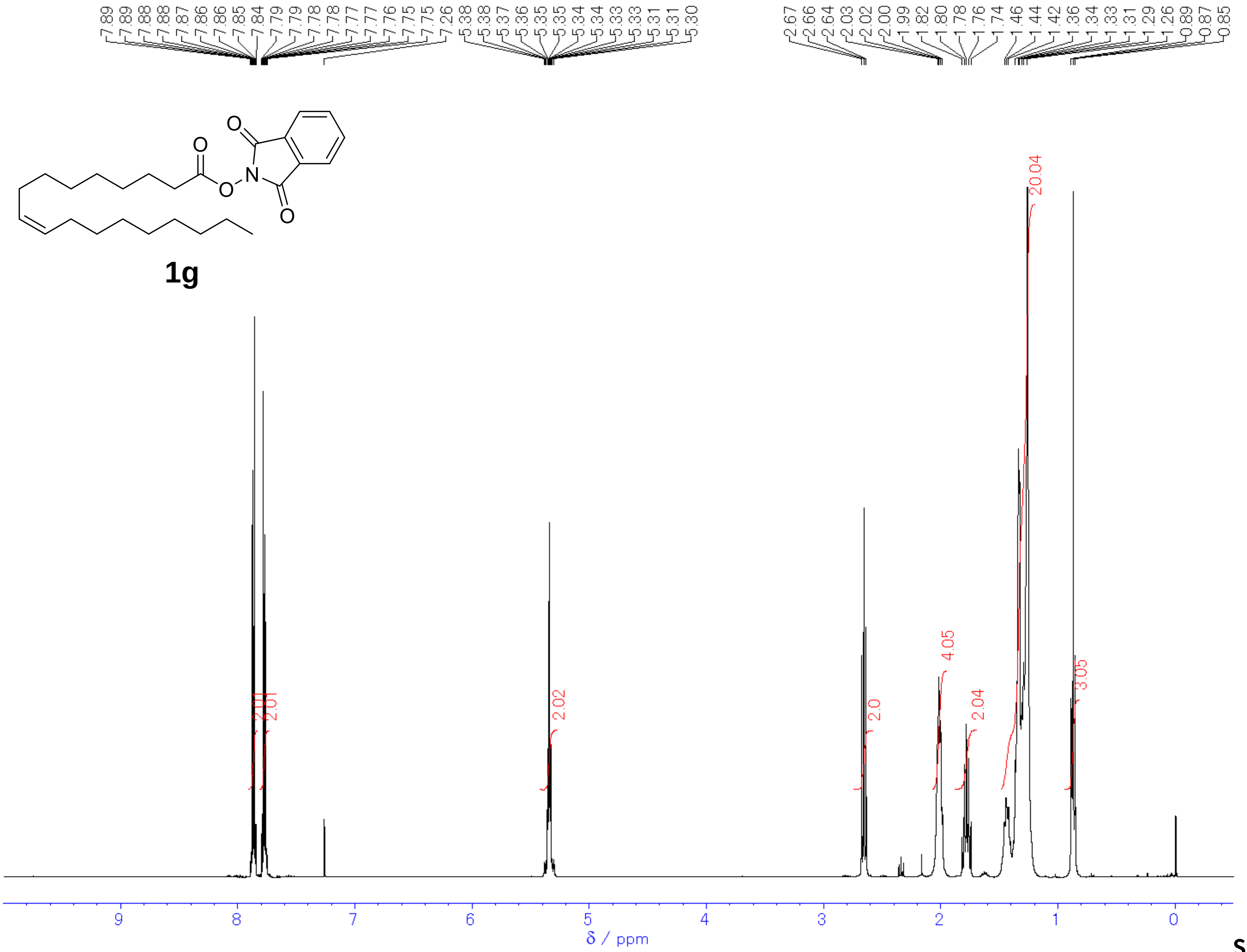
20
0
δ / ppm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7.77
7.76
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5.34
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2.66
2.64
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2.00
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1.80
1.78
1.76
1.74
1.46
1.44
1.42
1.36
1.34
1.33
1.31
1.29
1.26
0.89
0.87
0.85
O
O
N
O
O
20.04
4.05
3.05
2.01
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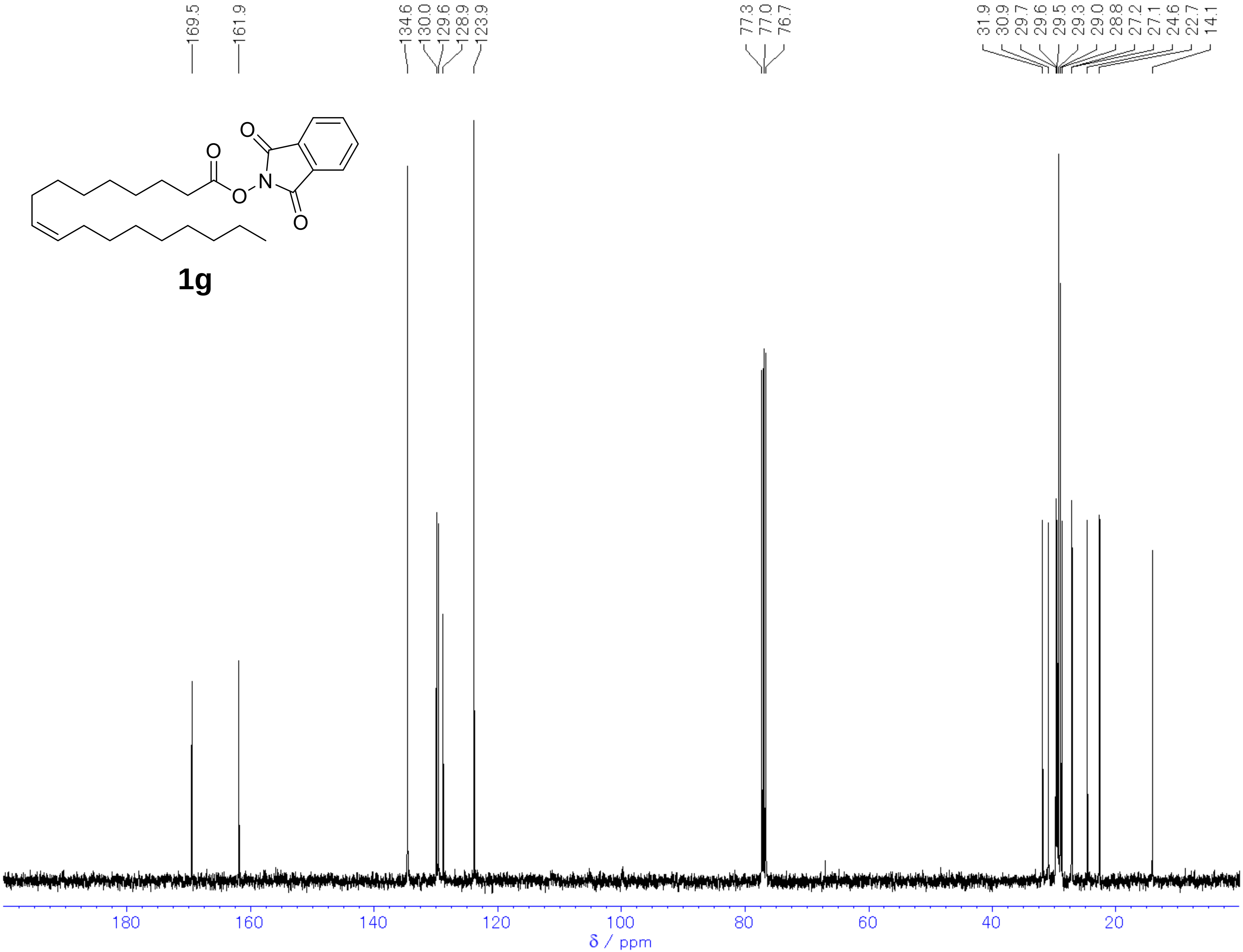
2.0
2.04
9
8
7
6
5
4
3
2
1
0
δ / ppm

1g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123.9
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77.0
76.7
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30.9
29.7
29.6
29.5
29.3
29.0
28.8
27.2
27.1
24.6
22.7
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N
O
O
O
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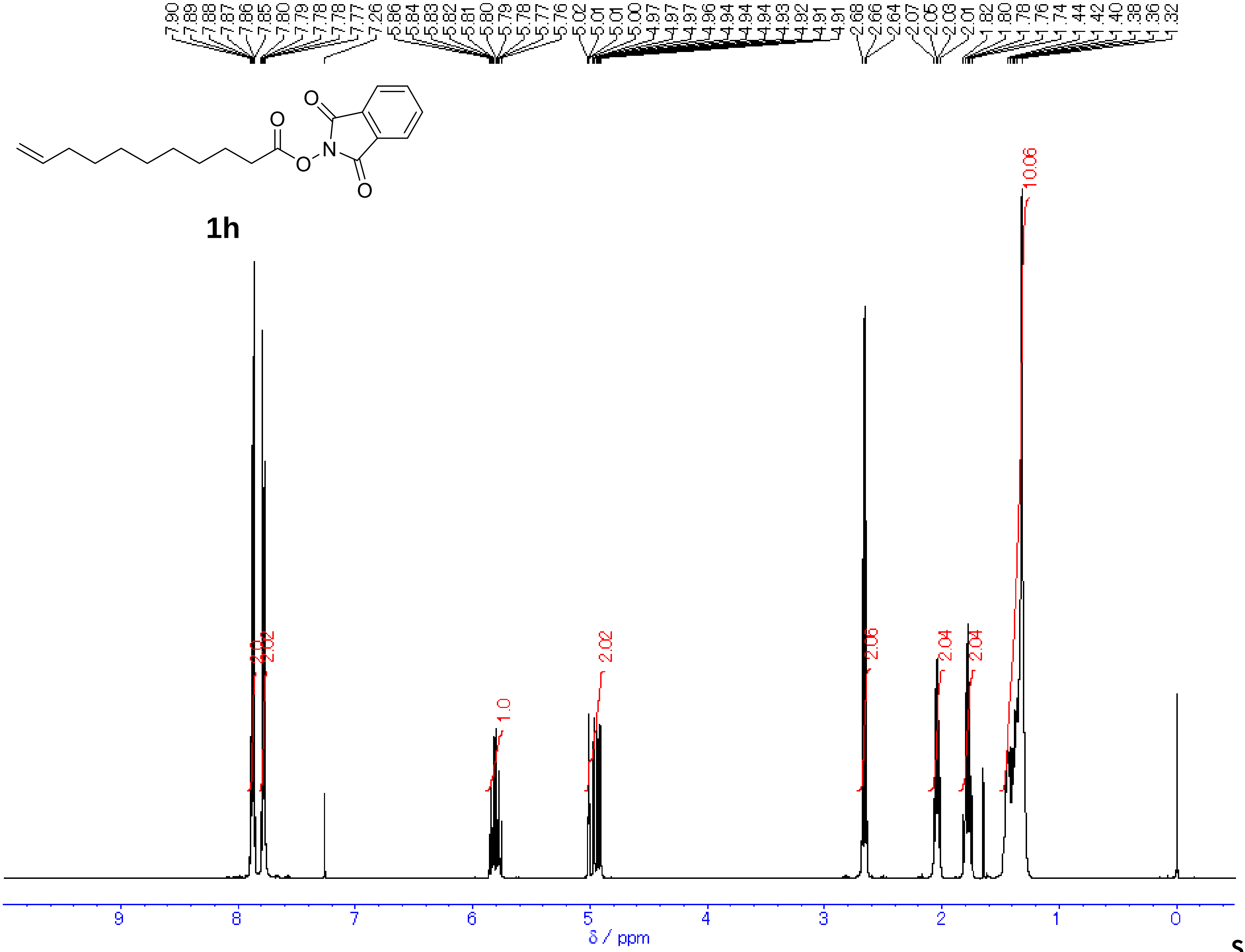
160
140
120
100
80
60
40
20
δ / ppm

1g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5.79
5.78
5.77
5.76
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5.01
5.00
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4.96
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4.92
4.91
4.91
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2.64
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2.05
2.03
2.01
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1.78
1.76
1.74
1.44
1.42
1.40
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1.36
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O
O
O
1h
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2.04
10.06
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5
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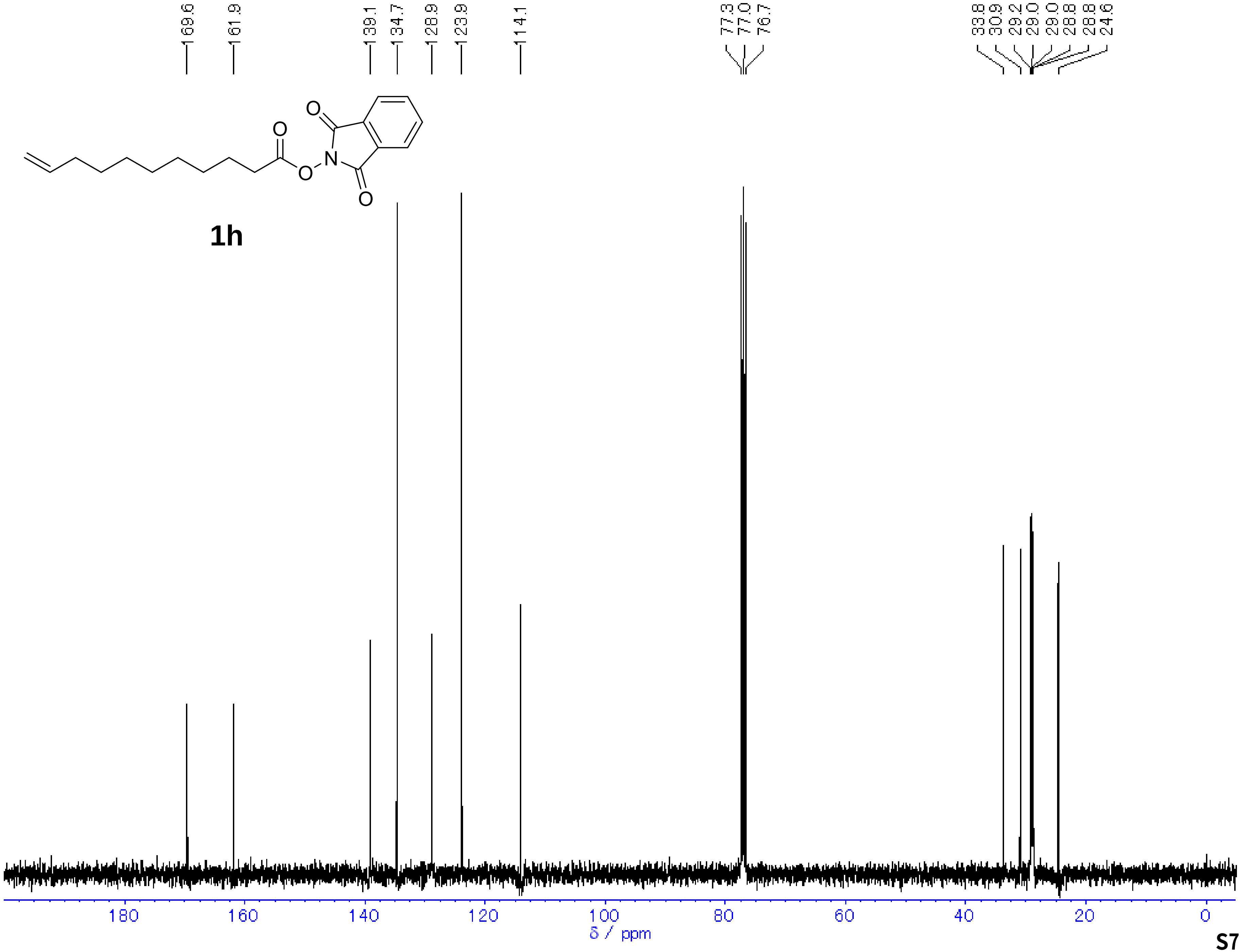
0
δ / ppm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76.7
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29.2
29.0
29.0
28.8
28.8
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O
O
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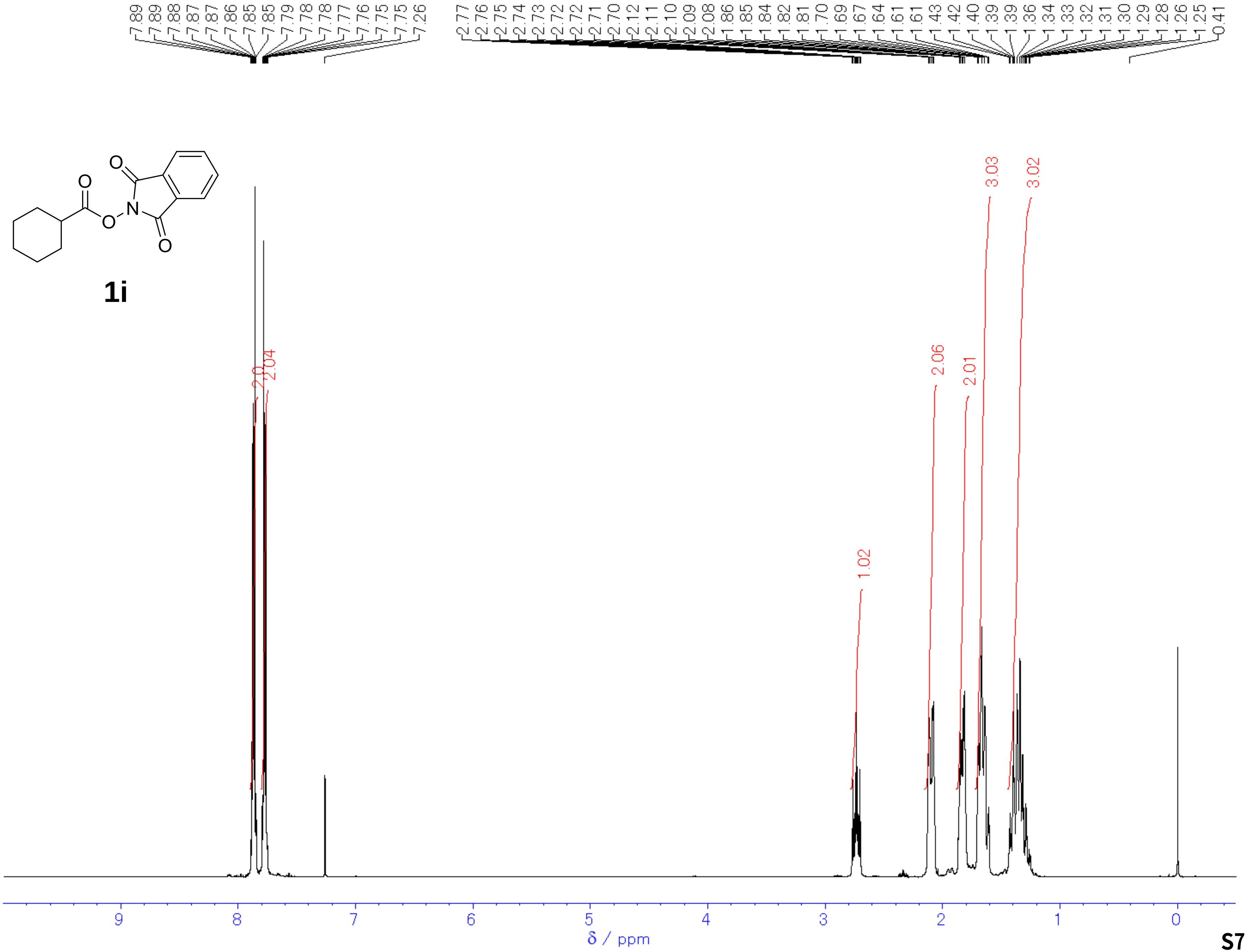
80
60
40
20
0
δ / ppm

1h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2.12
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2.10
2.09
2.08
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1.84
1.82
1.81
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1.67
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1.39
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1.36
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.26
1.25
0.41
O
O
N
O
O
2.0
2.04
1.02
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3.03
3.02
9
8
7
6
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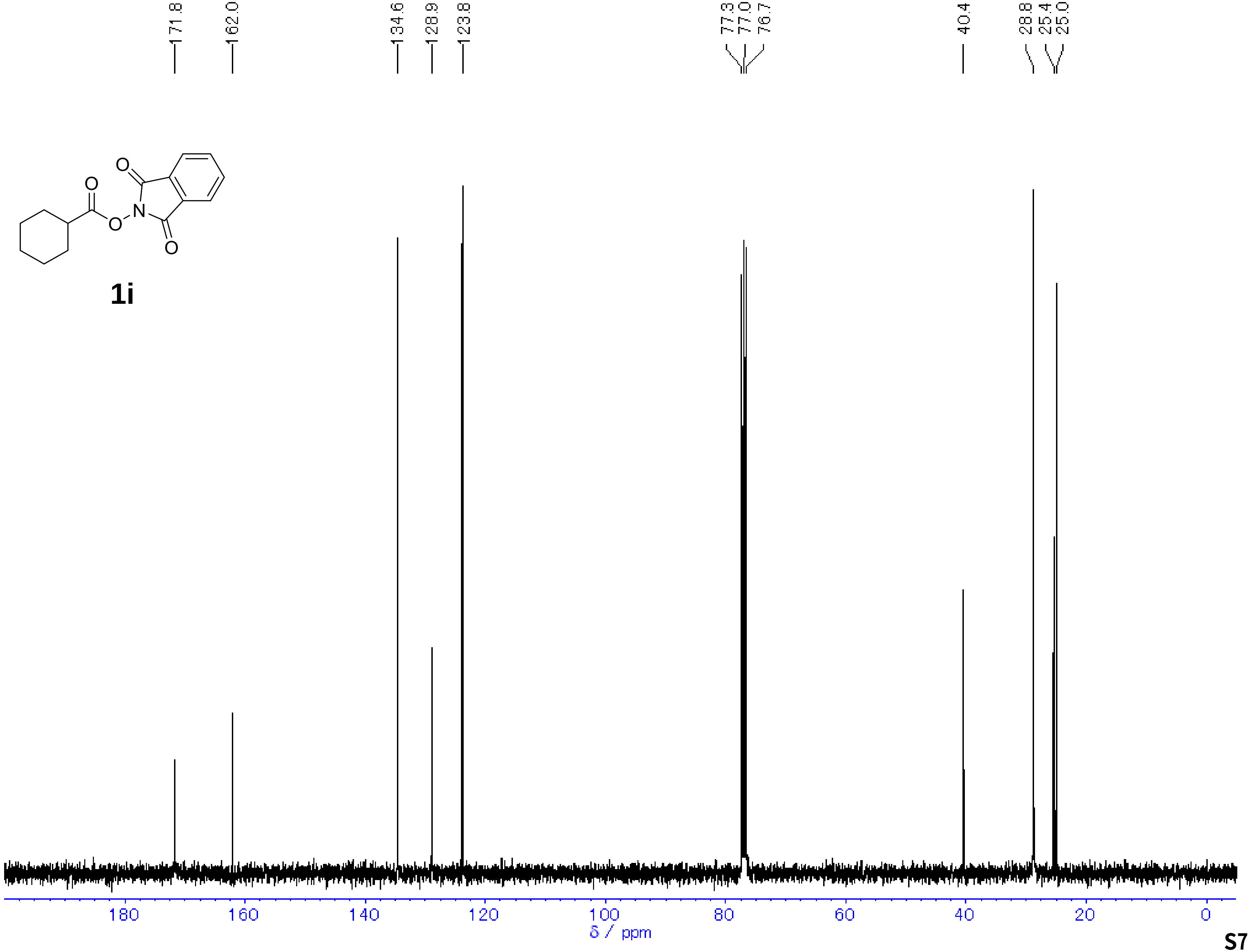
4
3
2
1
0
δ / ppm

1i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77.3
77.0
76.7
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28.8
25.4
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N
O
O
1i
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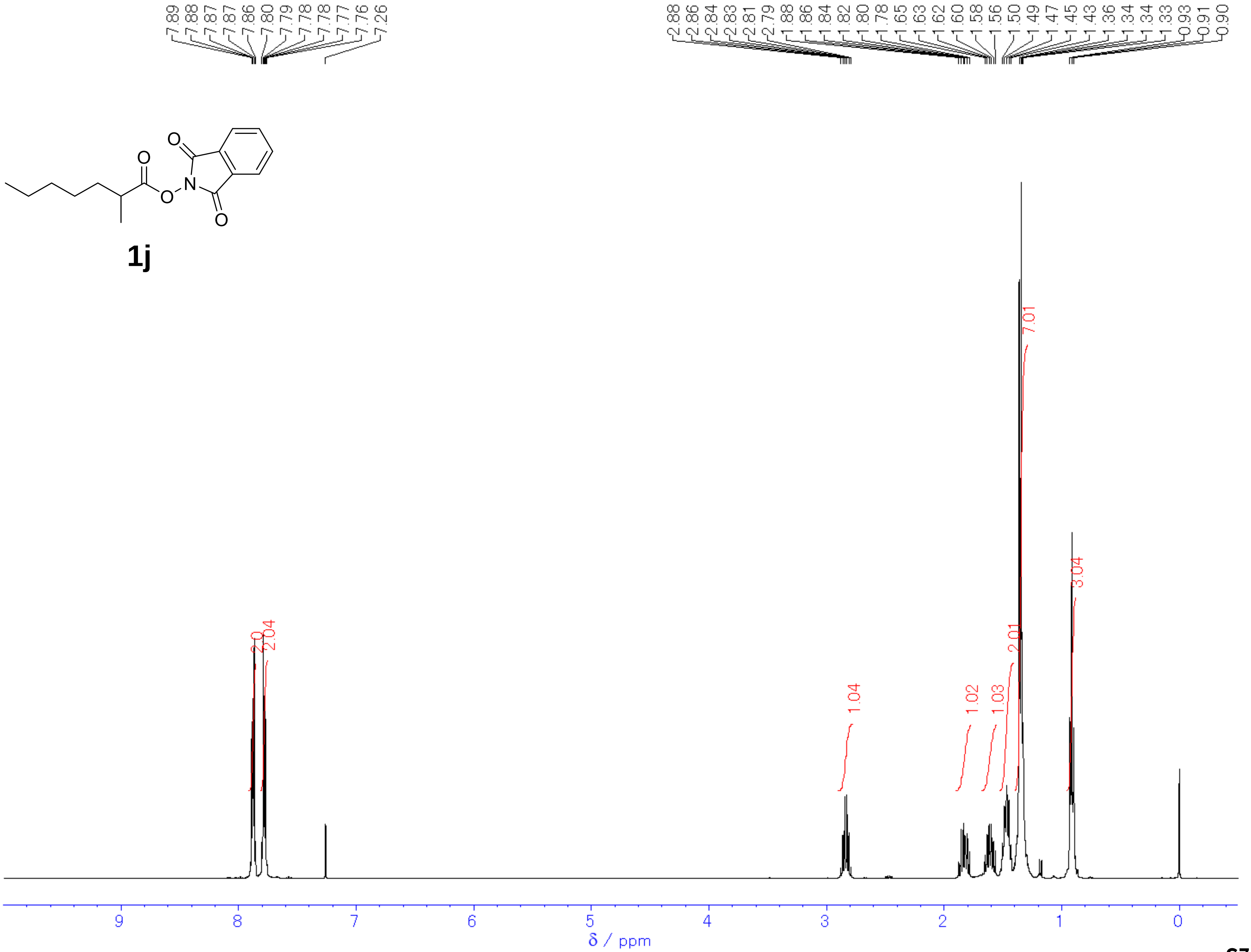
160
140
120
100
80
60
40
20
0
δ / ppm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7.77
7.76
7.26
2.88
2.86
2.84
2.83
2.81
2.79
1.88
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1.84
1.82
1.80
1.78
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1.60
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1.47
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1.43
1.36
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1.33
0.93
0.91
0.90
O
O
N
O
O
2.0
2.04
1.04
1.02
1.03
2.01
7.01
3.04
9
8
7
6
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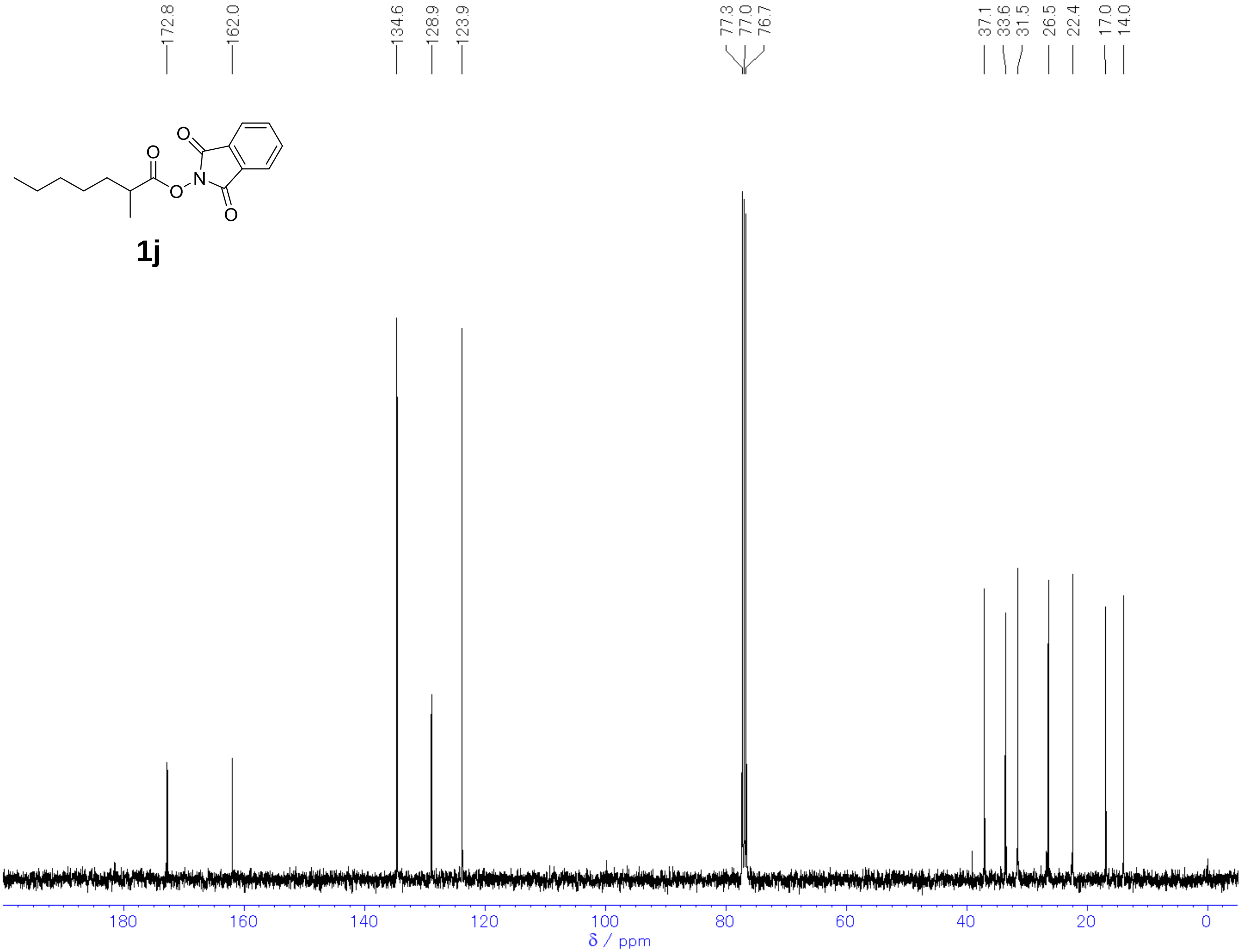
4
3
2
1
0
δ / ppm

1j



1j

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134.6
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123.9
77.3
77.0
76.7
37.1
33.6
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26.5
22.4
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100
80
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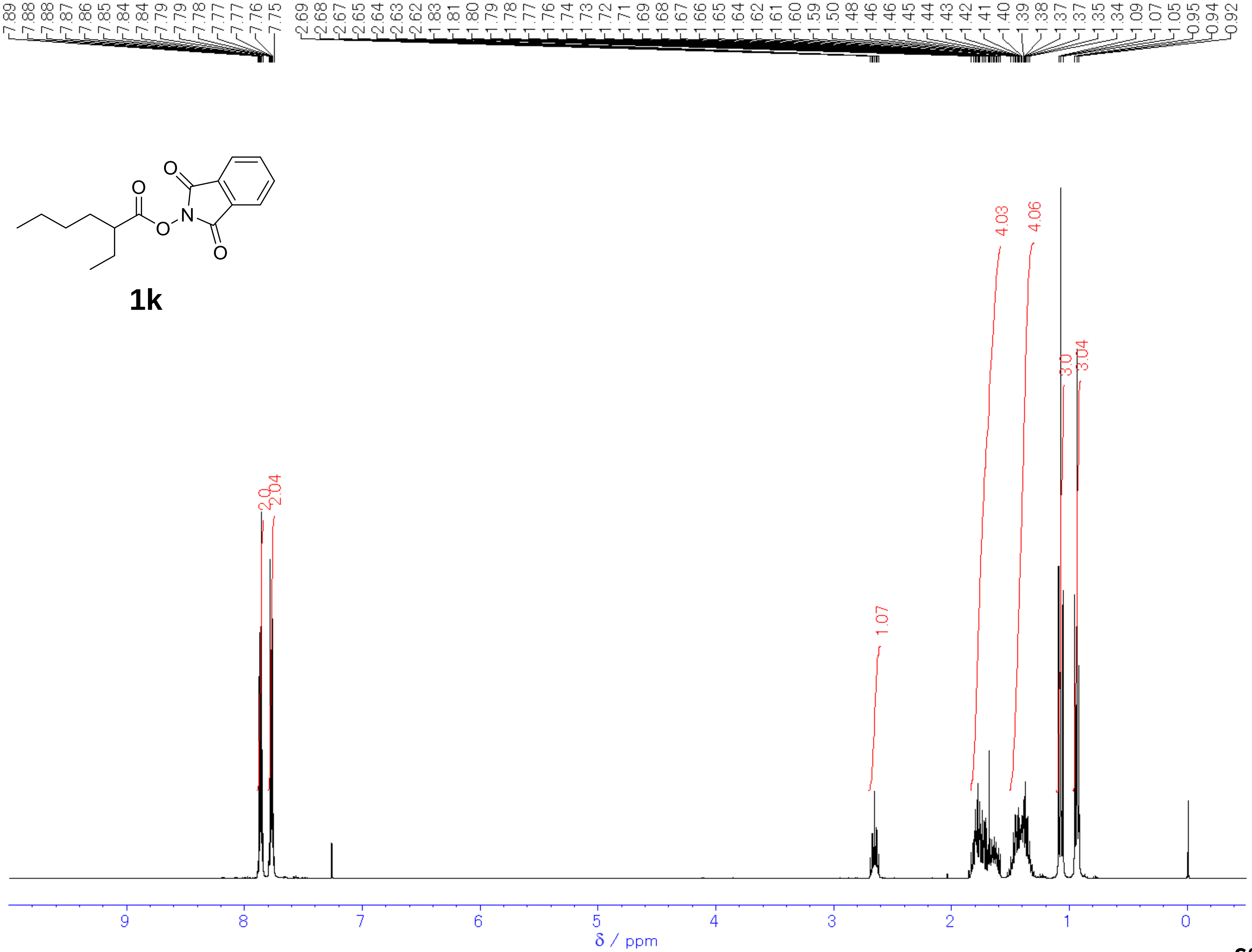
20
0
δ / ppm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7.77
7.76
7.75
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1.78
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1.64
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1.61
1.60
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1.37
1.37
1.35
1.34
1.09
1.07
1.05
0.95
0.94
0.92
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O
O
N
O
1k
2.0
2.04
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3.0
3.04
9
8
7
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5
4
3
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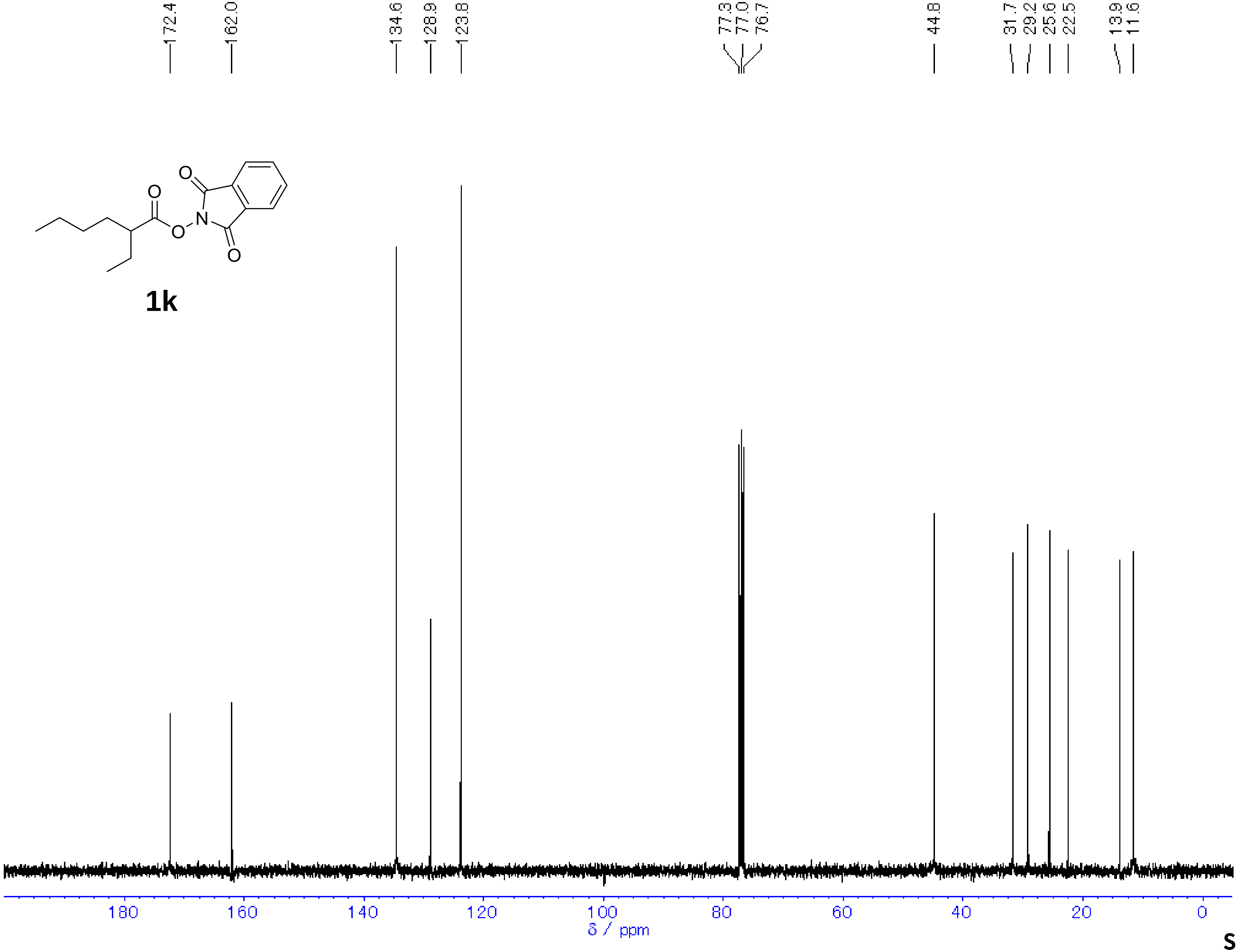
1
0
δ / ppm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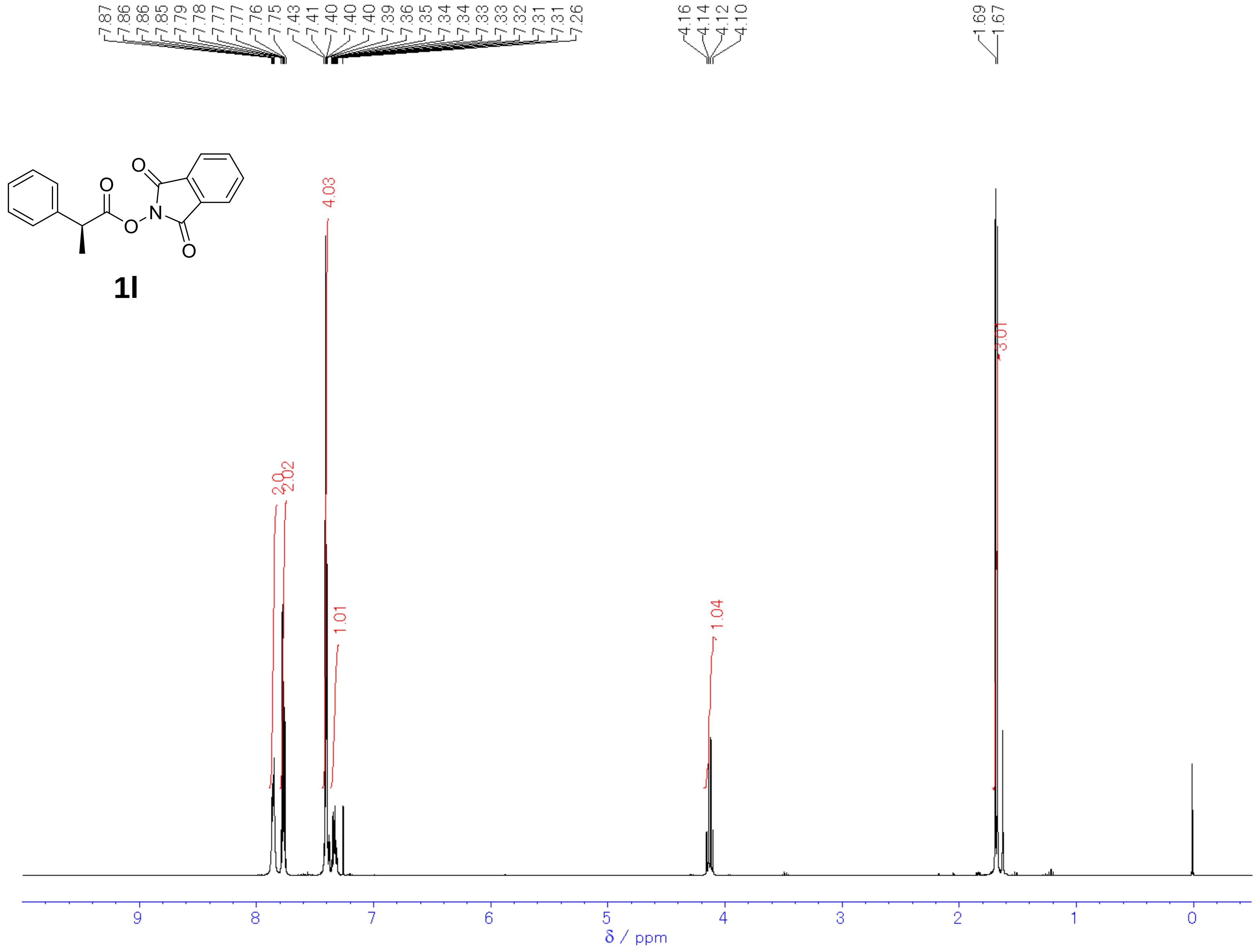
77.0
76.7
44.8
31.7
29.2
25.6
22.5
13.9
11.6
O
O
O
N
O
O
180
160
140
120
100
80
60
40
20
0
δ / ppm

1k



1l

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7.40
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7.31
7.31
7.26
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4.12
4.10
1.69
1.67
2.0
2.02
4.03
1.01
1.04
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O
N
O
O
9
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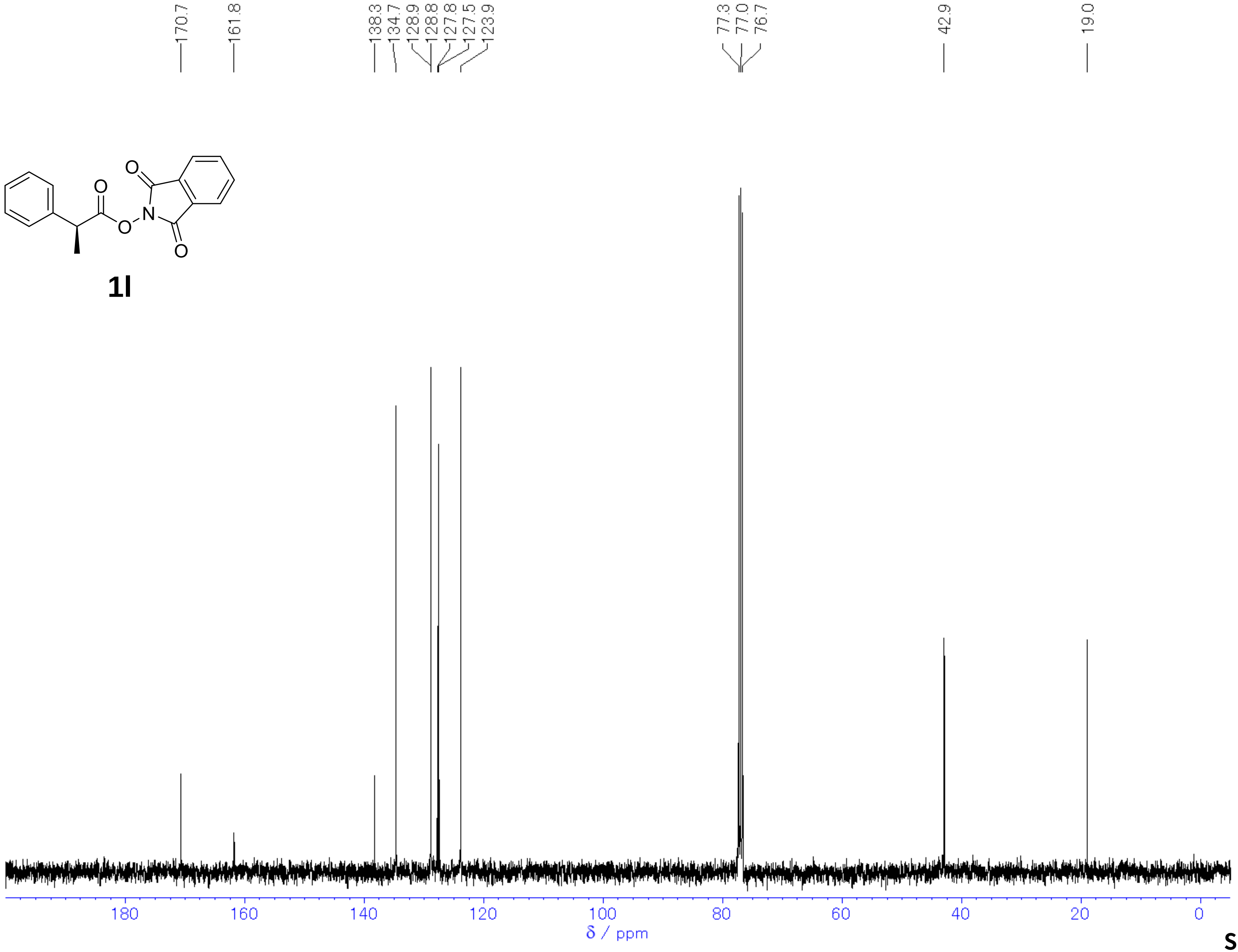
6
5
4
3
2
1
0
δ / ppm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134.7
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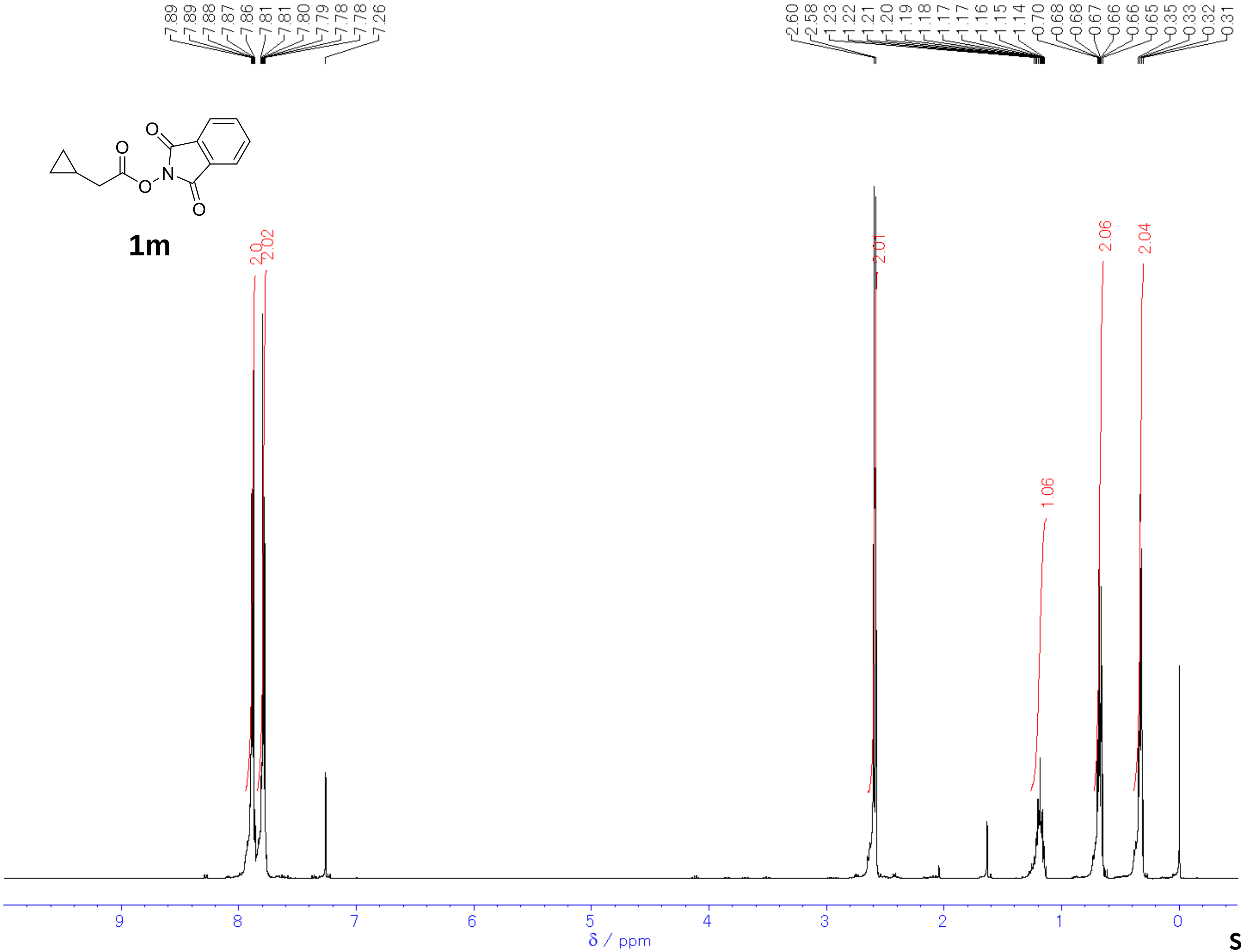
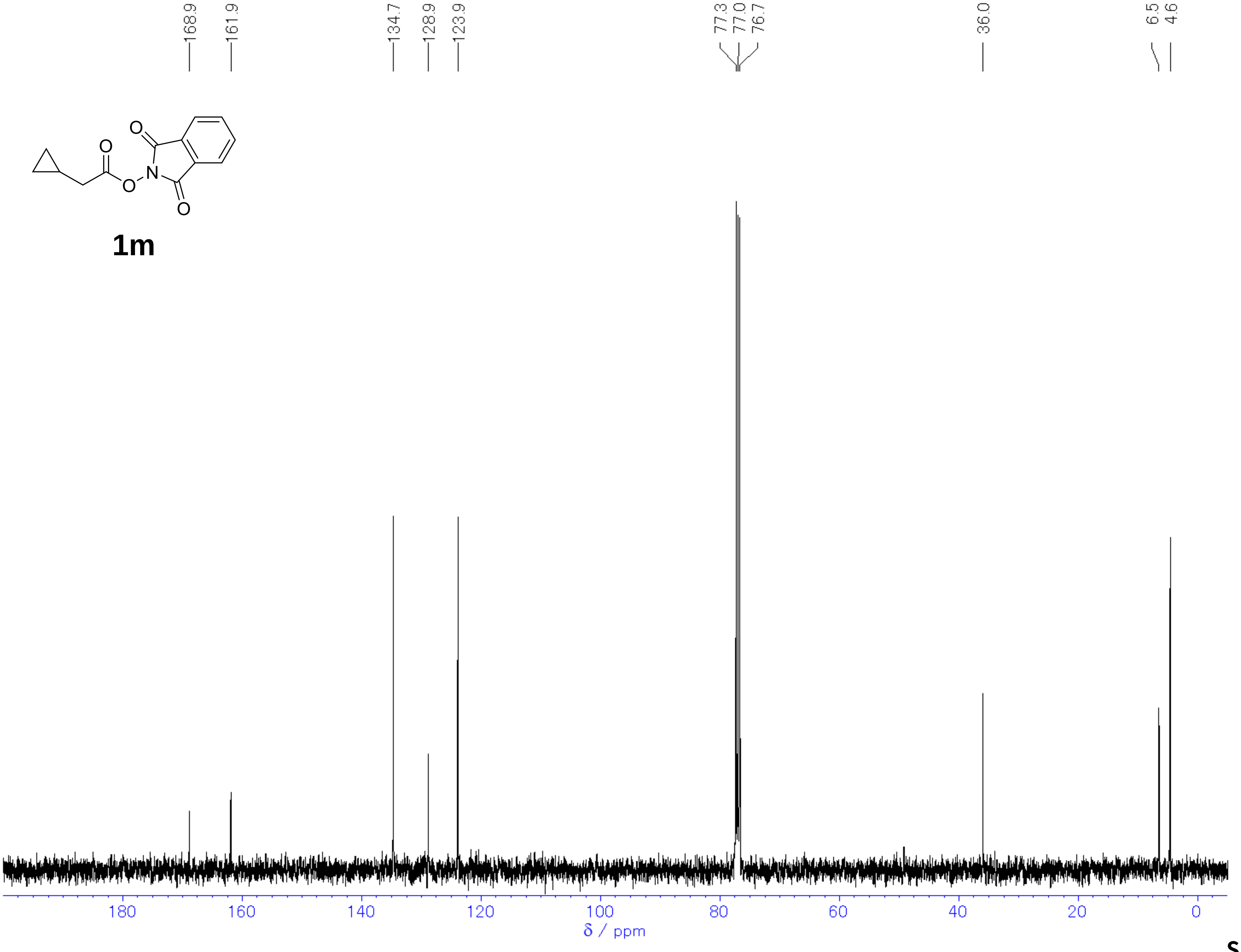
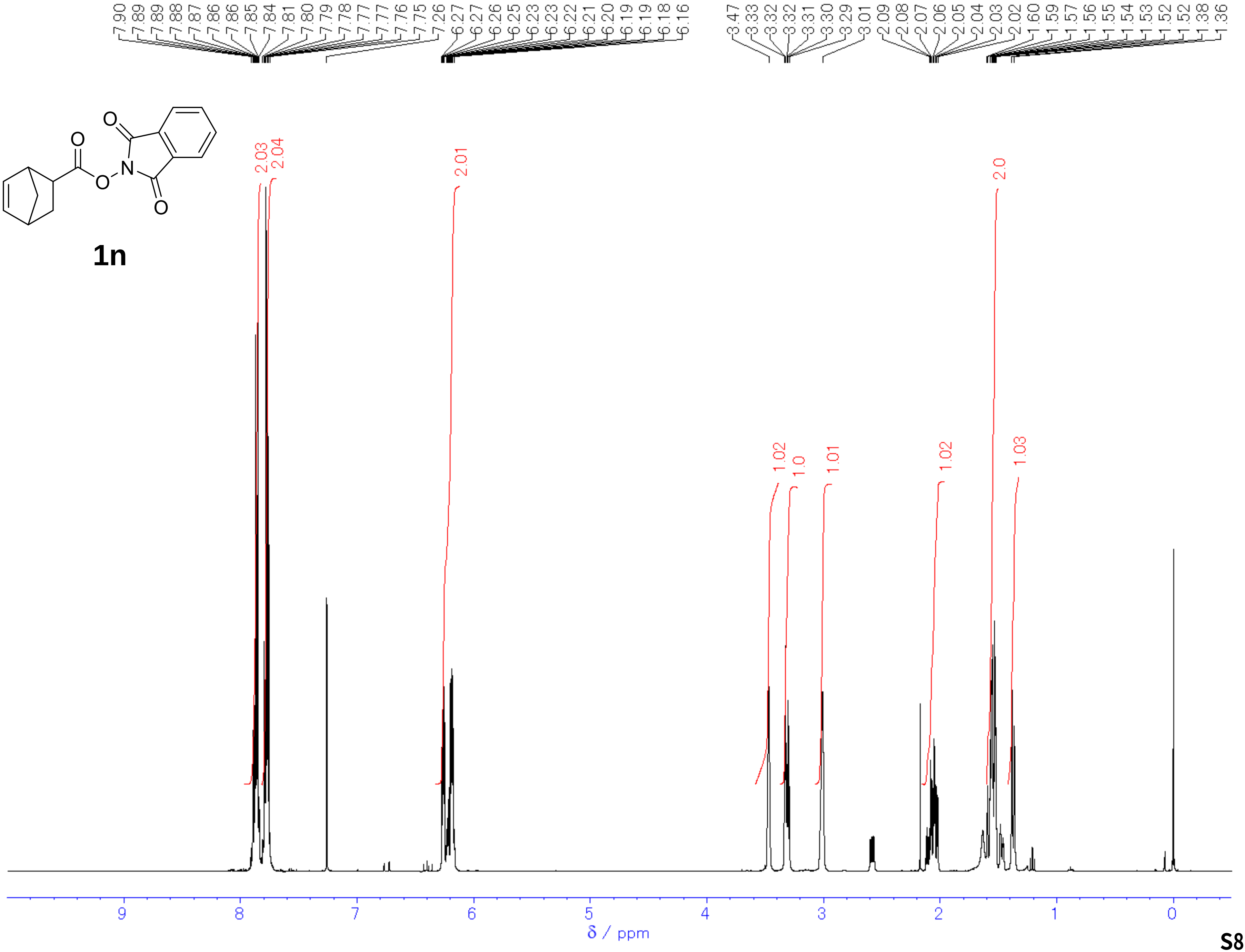
128.8
127.8
127.5
123.9
77.3
77.0
76.7
42.9
19.0
O
O
N
O
O
O
180
160
140
120
100
80
60
40
20
0
δ / ppm

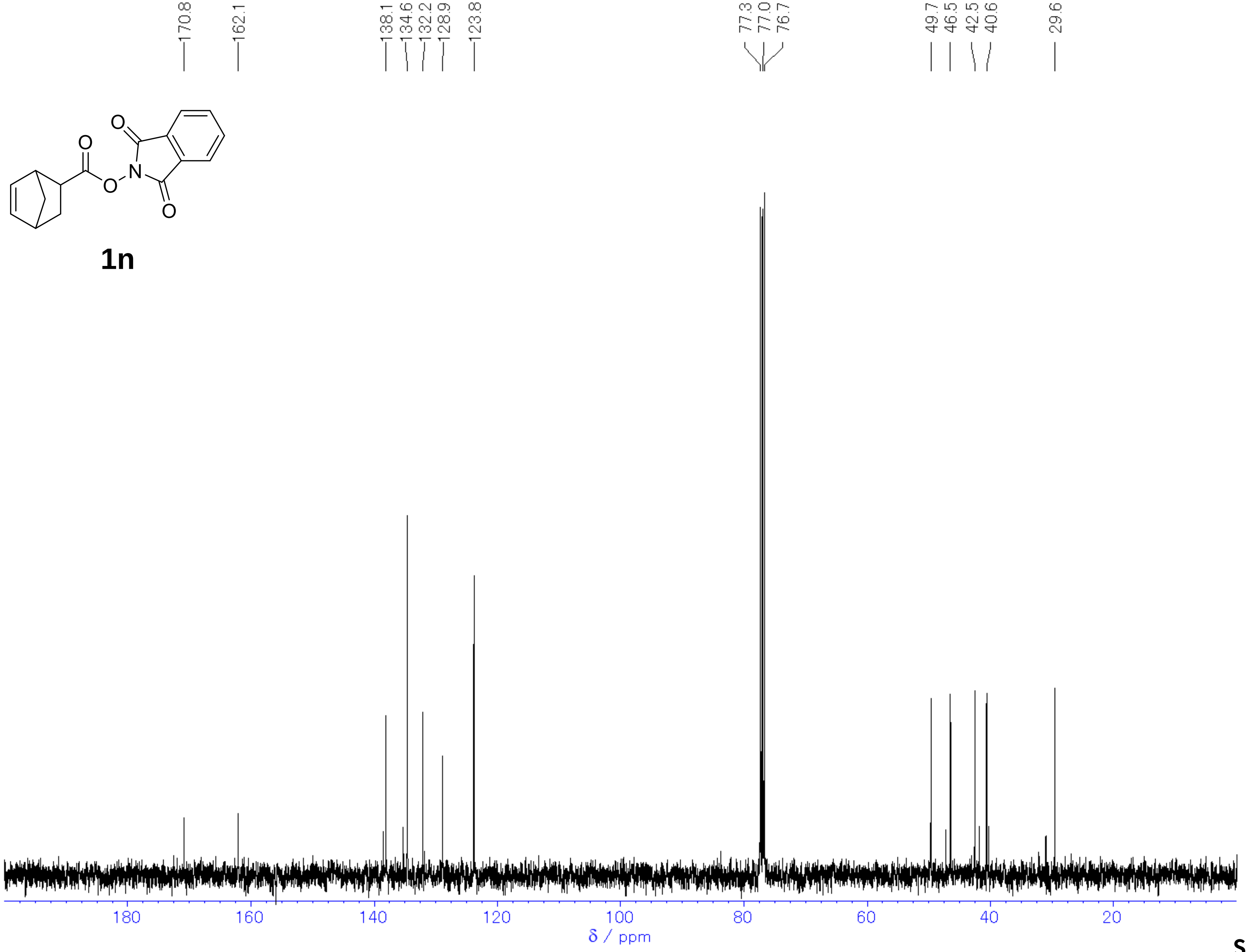
1l


7.89
7.89
7.88
7.87
7.86
7.81
7.81
7.80
7.79
7.78
7.78
7.26
2.60
2.58
1.23
1.22
1.21
1.20
1.19
1.18
1.17
1.17
1.16
1.15
1.14
0.70
0.68
0.68
0.67
0.66
0.66
0.65
0.35
0.33
0.32
0.31
O
O
N
O
O
1m
2.0
2.02
2.01
1.06
2.06
2.04
9
8
7
6
5
4
3
2
1
0
δ / ppm


1m
168.9
161.9
134.7
128.9
123.9
77.3
77.0
76.7
36.0
6.5
4.6
180
160
140
120
100
80
60
40
20
0
δ / ppm

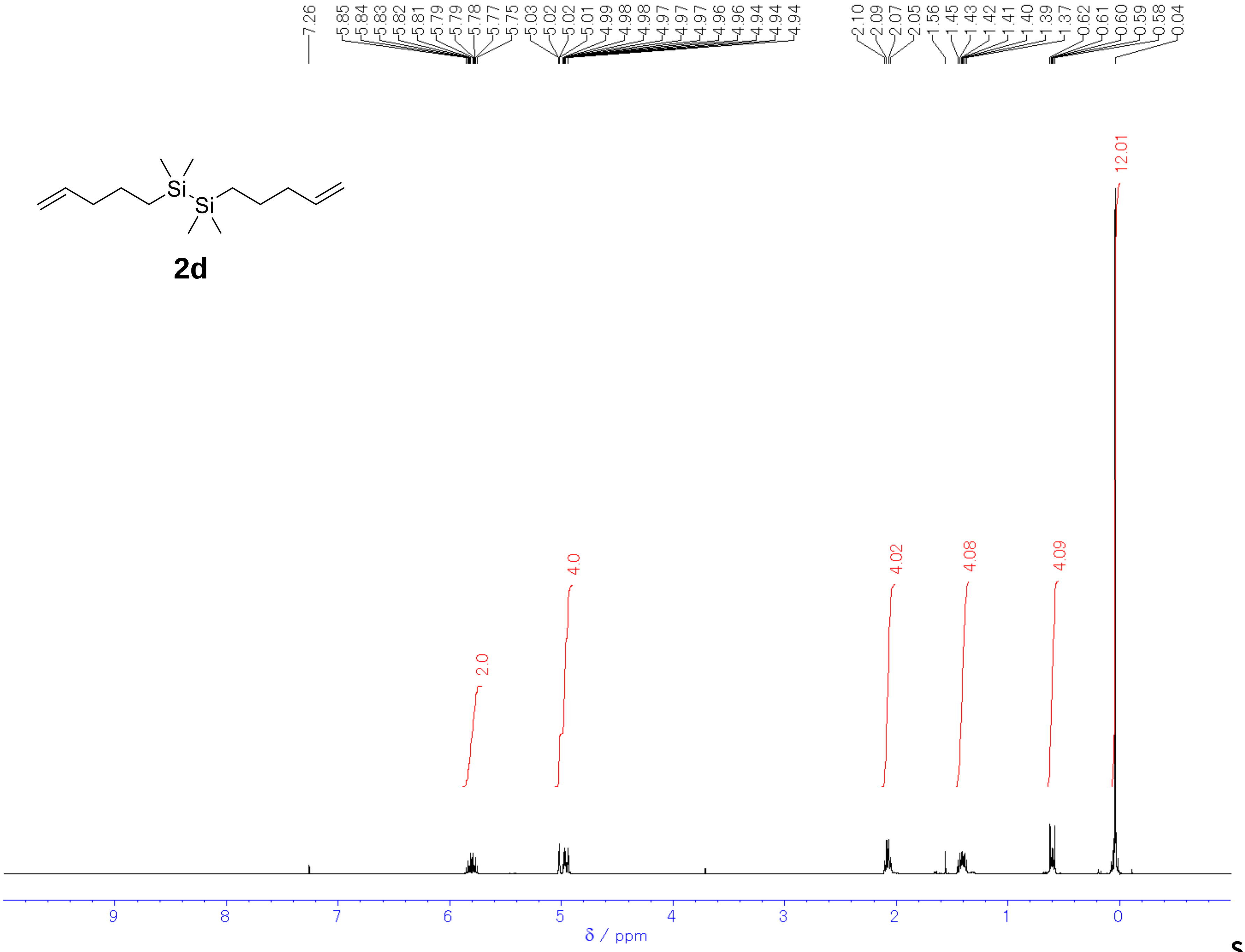

1n

O
O
N
O
O
O
7.90
7.89
7.89
7.88
7.87
7.86
7.86
7.85
7.84
7.81
7.80
7.79
7.78
7.77
7.77
7.76
7.75
7.26
6.27
6.27
6.26
6.25
6.23
6.23
6.22
6.21
6.20
6.19
6.19
6.18
6.16
3.47
3.33
3.32
3.32
3.31
3.30
3.29
3.01
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.02
1.60
1.59
1.57
1.56
1.55
1.54
1.53
1.52
1.52
1.38
1.36
2.03
2.04
2.01
1.02
1.0
1.01
1.02
2.0
1.03
9
8
7
6
5
4
3
2
1
0
δ / ppm



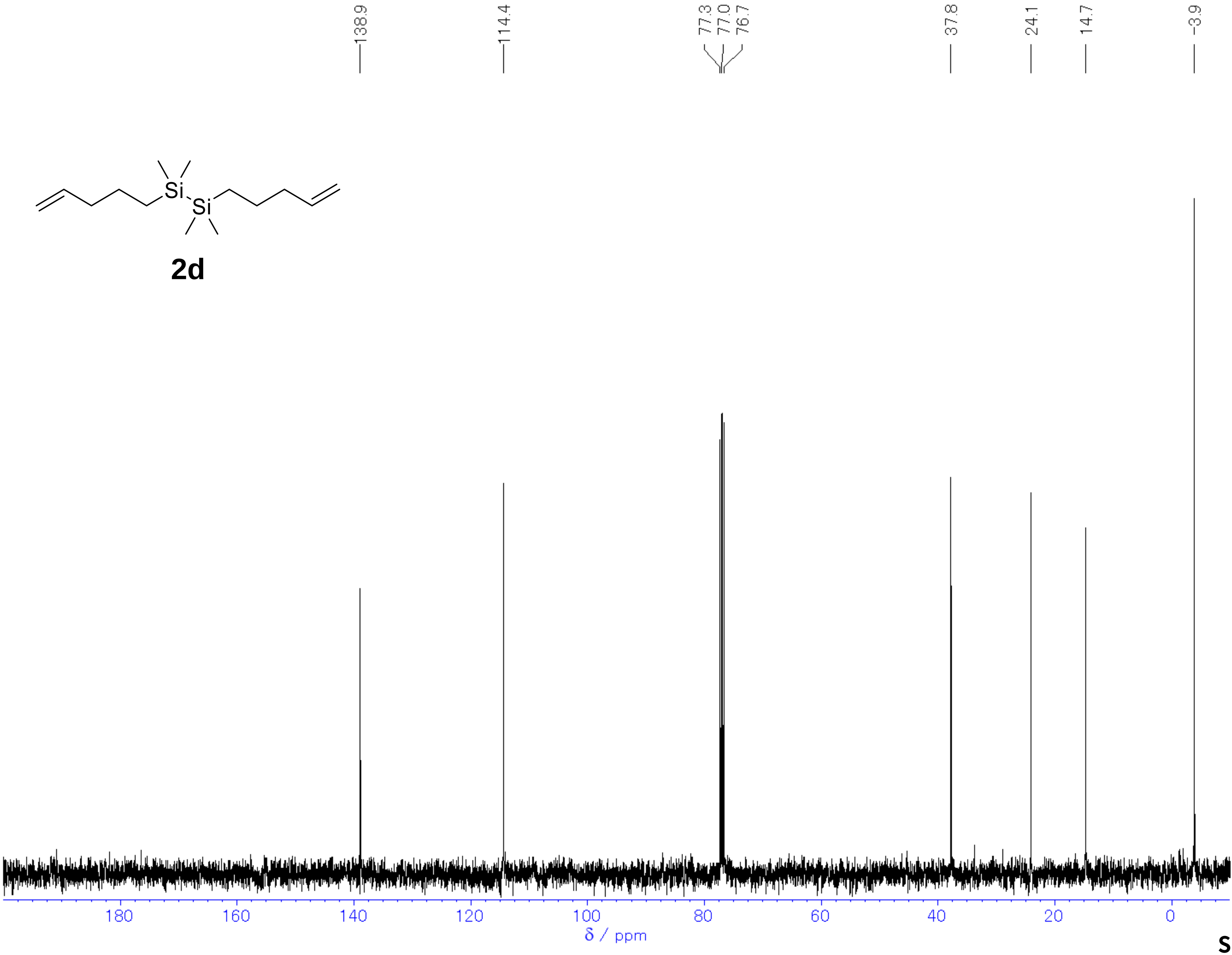
1n

170.8
162.1
138.1
134.6
132.2
128.9
123.8
77.3
77.0
76.7
49.7
46.5
42.5
40.6
29.6
180
160
140
120
100
80
60
40
20
δ / ppm
O
O
O
N
O
O



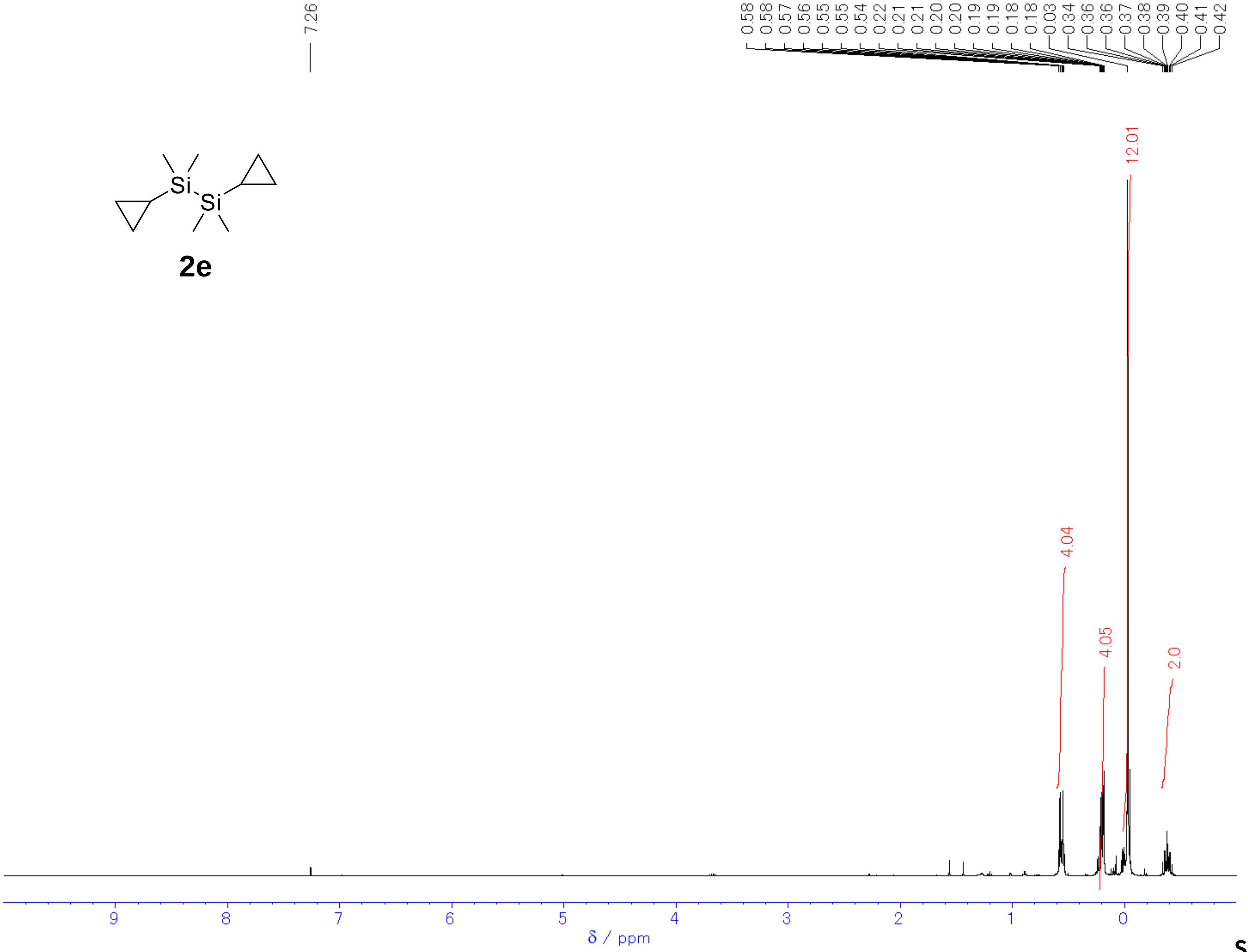
2d

7.26
5.85
5.84
5.83
5.82
5.81
5.79
5.79
5.78
5.77
5.75
5.03
5.02
5.02
5.01
4.99
4.98
4.98
4.97
4.97
4.97
4.96
4.96
4.94
4.94
4.94
2.10
2.09
2.07
2.05
1.56
1.45
1.43
1.42
1.41
1.40
1.39
1.37
0.62
0.61
0.60
0.59
0.58
0.04
12.01
2.0
4.0
4.02
4.08
4.09
9
8
7
6
5
4
3
2
1
0
δ / ppm



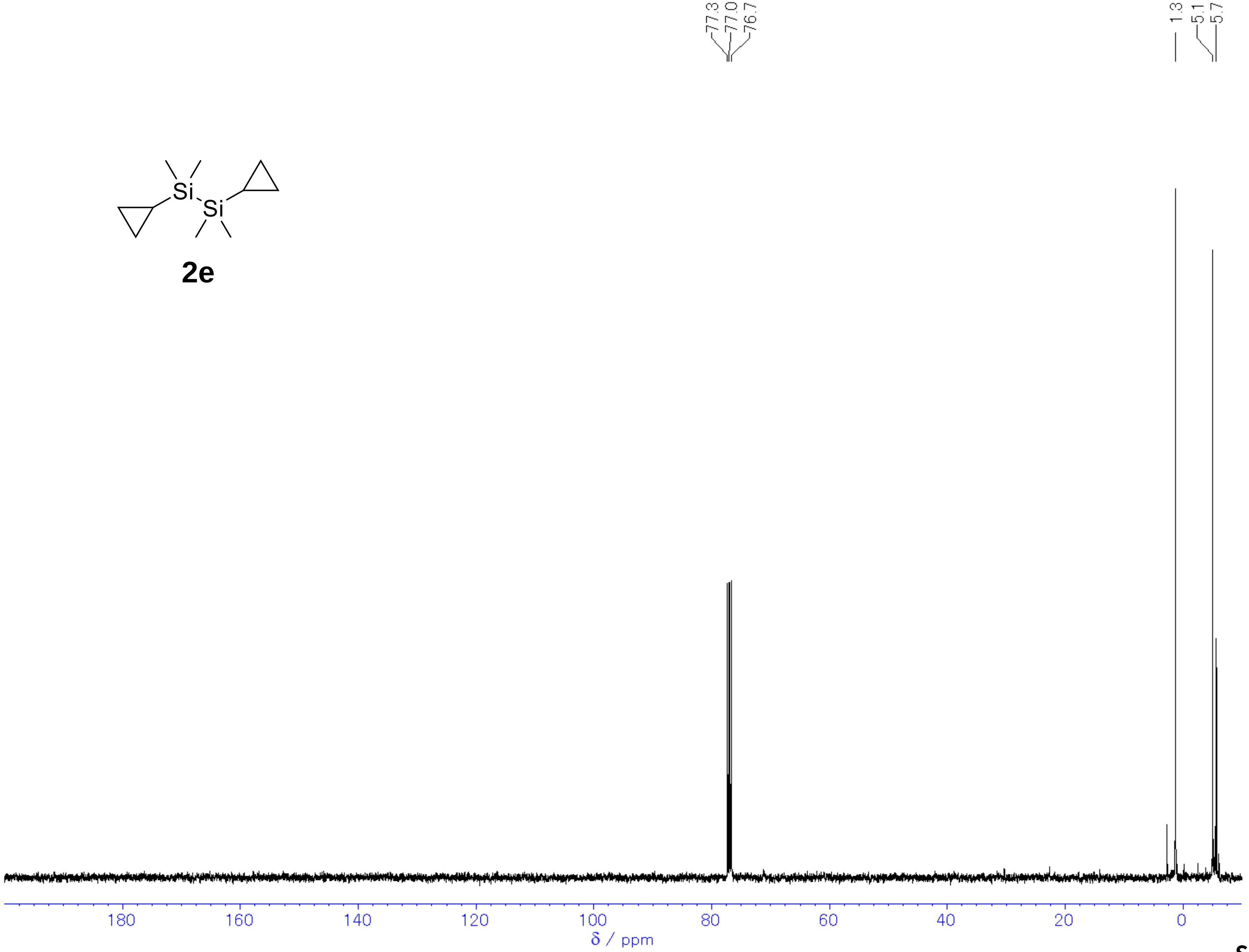
2d

138.9
114.4
77.3
77.0
76.7
37.8
24.1
14.7
-3.9
Si
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm

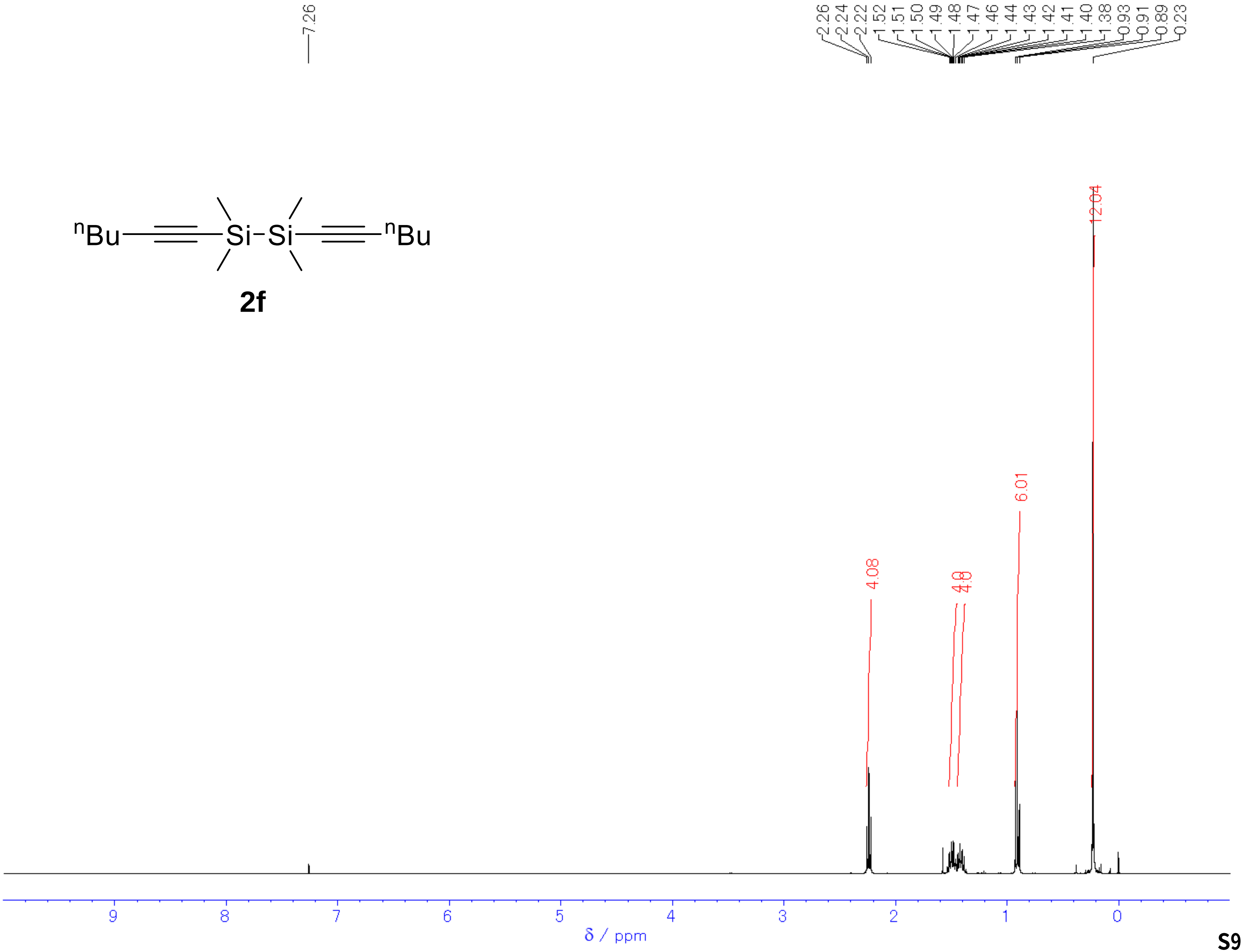


2e

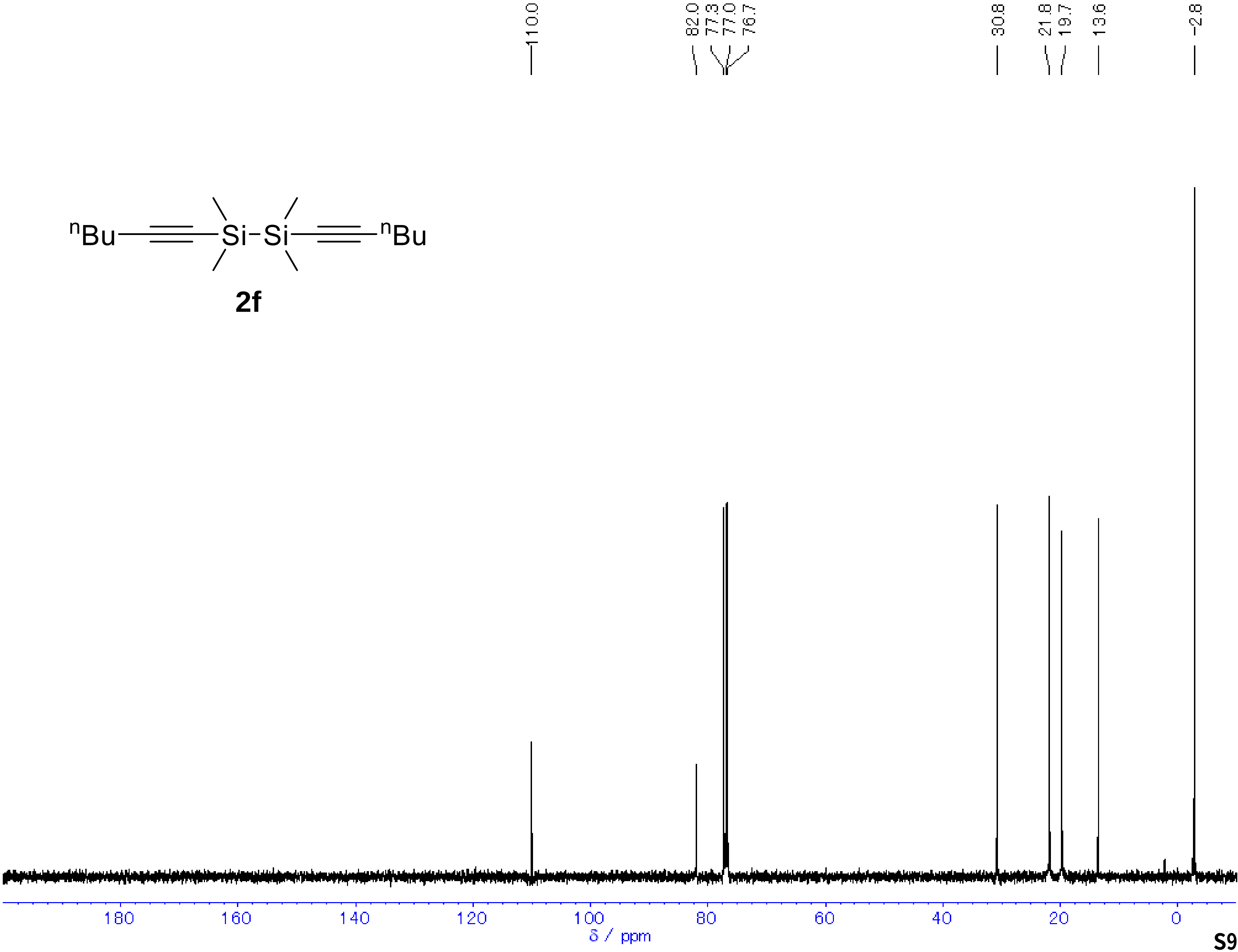
7.26
0.58
0.58
0.57
0.56
0.55
0.55
0.54
0.22
0.21
0.21
0.20
0.20
0.19
0.19
0.18
0.18
0.03
0.34
0.36
0.36
0.37
0.38
0.39
0.40
0.41
0.42
12.01
4.04
4.05
2.0
Si
Si
9
8
7
6
5
4
3
2
1
0
δ / ppm



2e

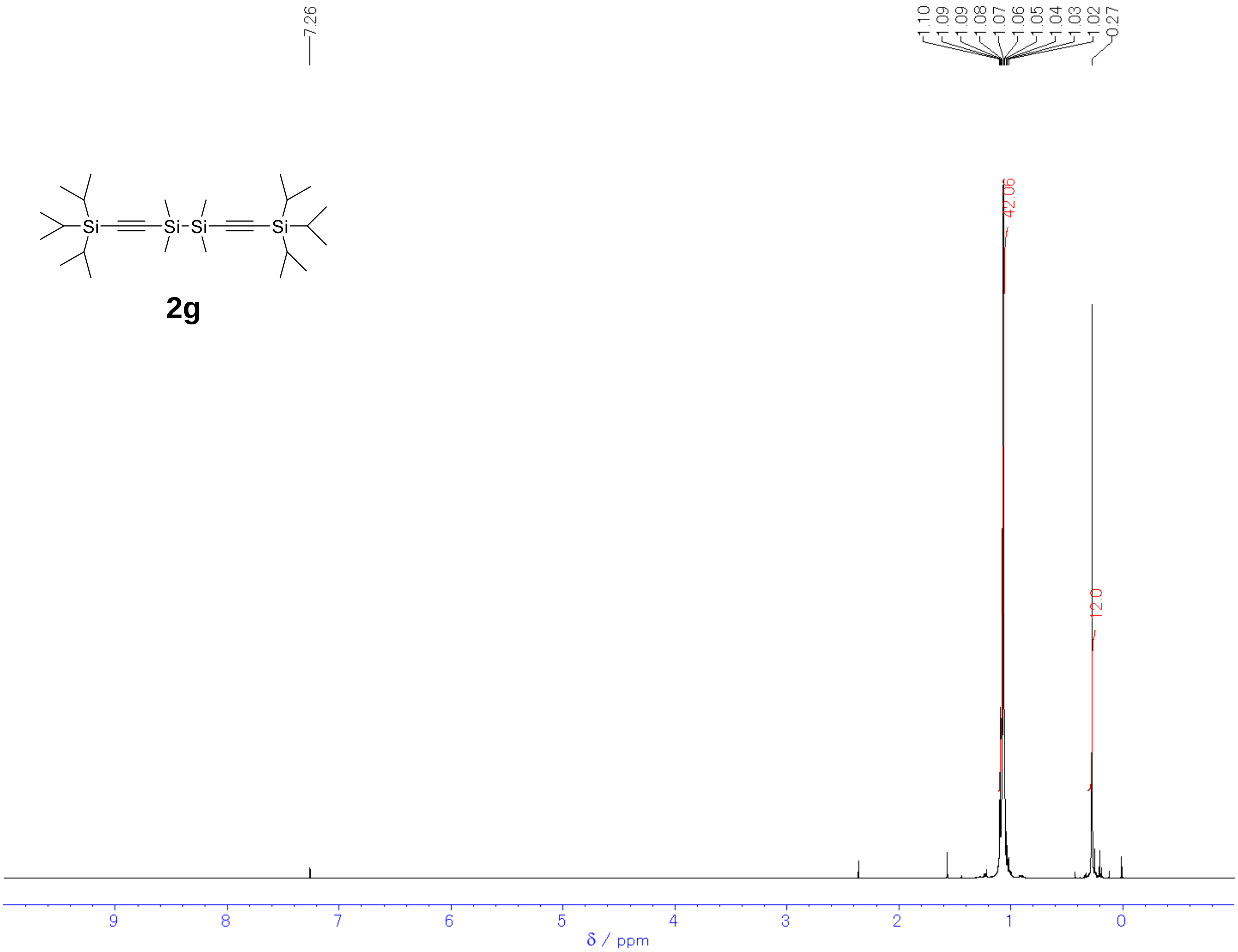
7.26
2.26
2.24
2.22
1.52
1.51
1.50
1.49
1.48
1.47
1.46
1.44
1.43
1.42
1.41
1.40
1.38
0.93
0.91
0.89
0.23
ⁿBu
Si
Si
ⁿBu
12.04
6.01
4.08
4.0
4.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

2f

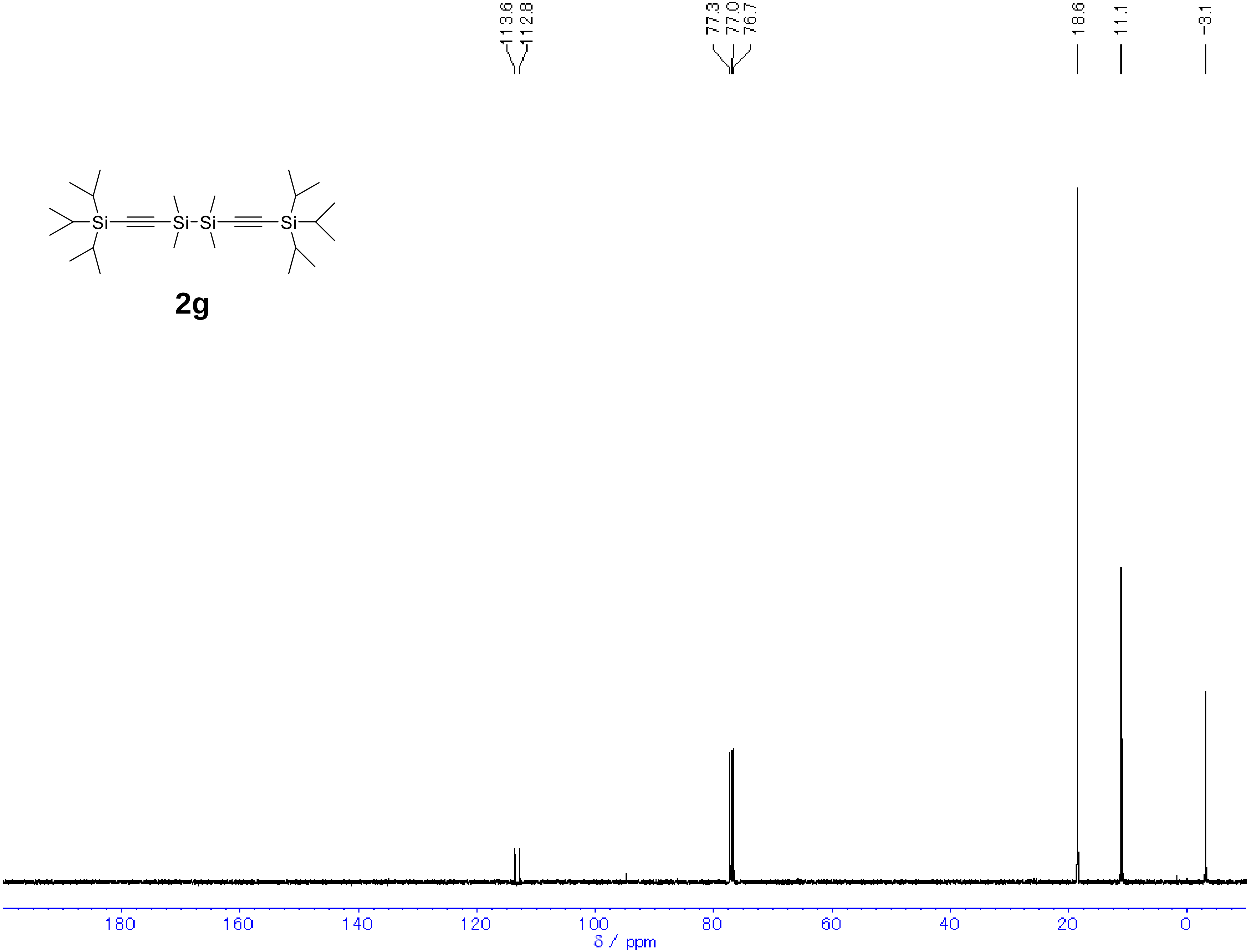


2f

110.0
82.0
77.3
77.0
76.7
30.8
21.8
19.7
13.6
-2.8
^{n}Bu
Si
Si
^{n}Bu
180
160
140
120
100
80
60
40
20
0
δ / ppm

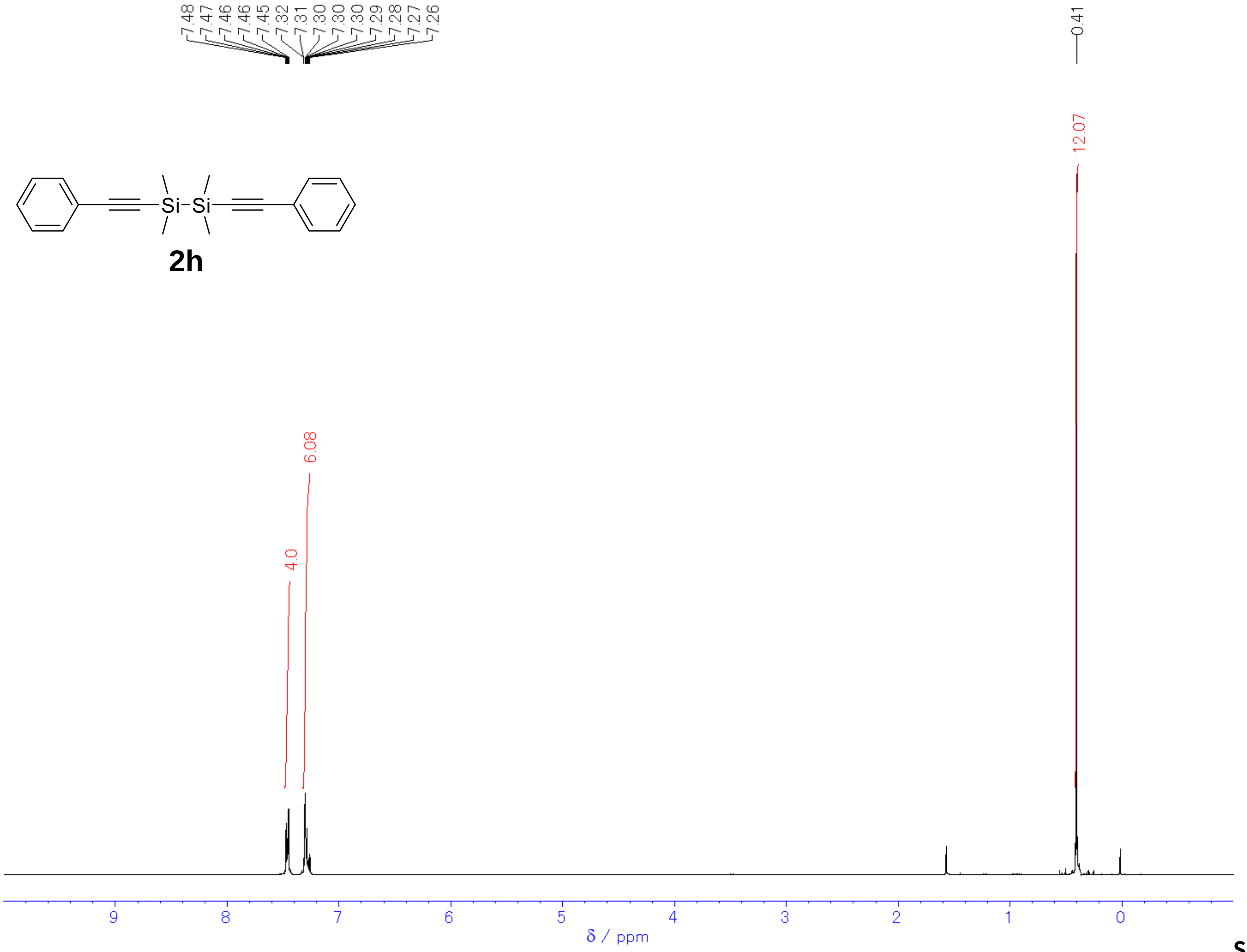

7.26
1.10
1.09
1.09
1.08
1.07
1.06
1.05
1.04
1.03
1.02
0.27
42.06
12.0
Si
Si
Si
Si
9
8
7
6
5
4
3
2
1
0
δ / ppm

2g

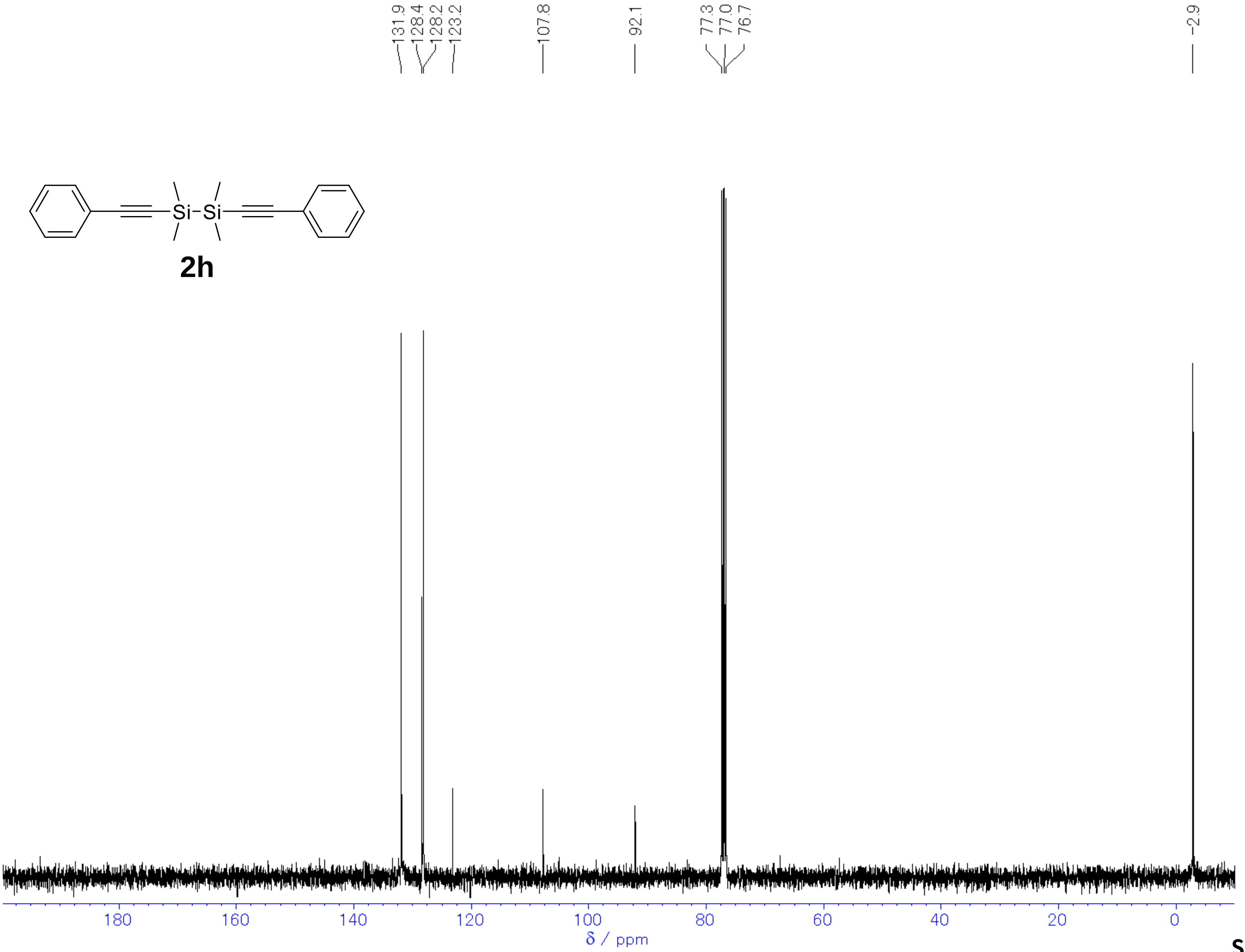


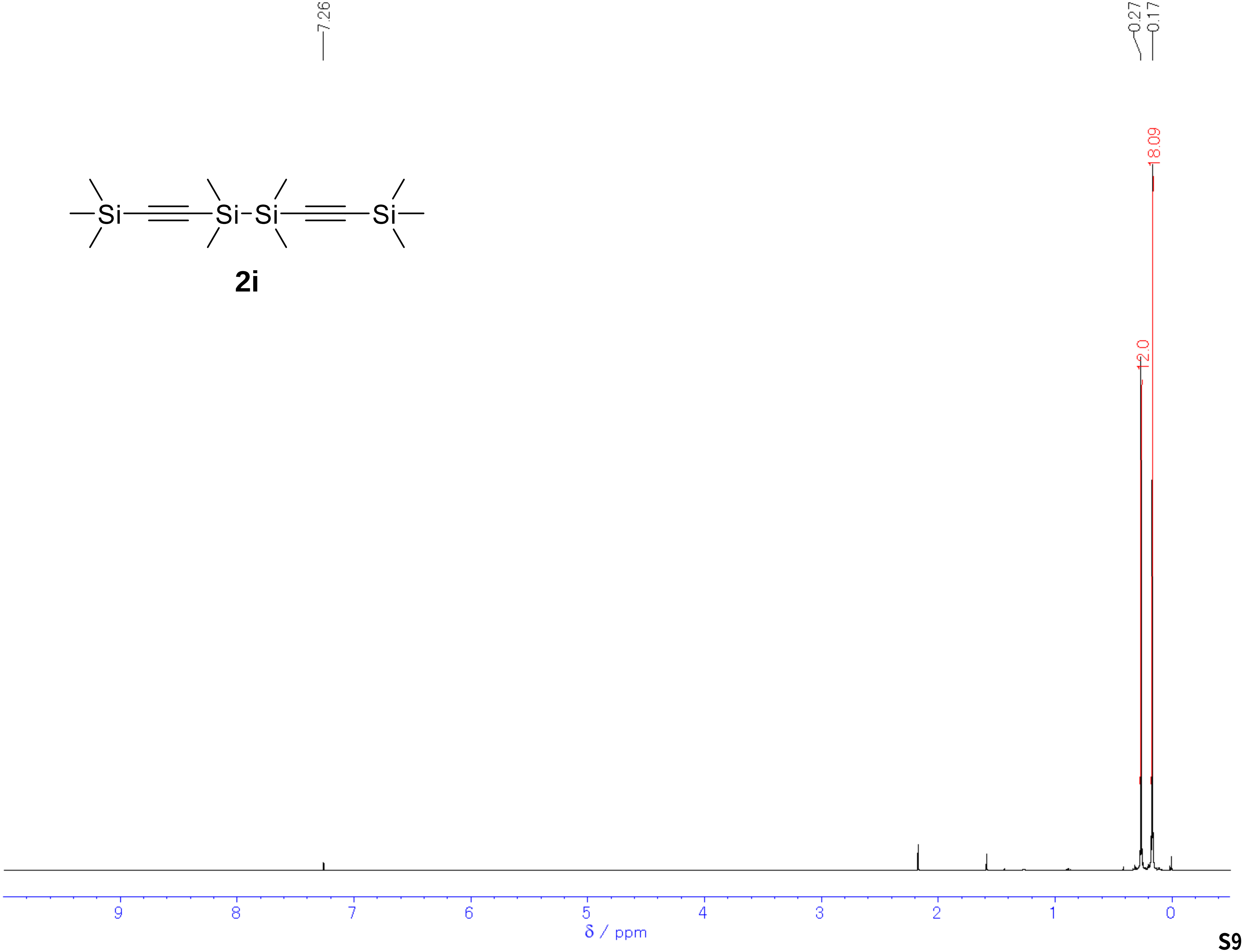
2g

113.6
112.8
77.3
77.0
76.7
18.6
11.1
−3.1
Si
Si
Si
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm

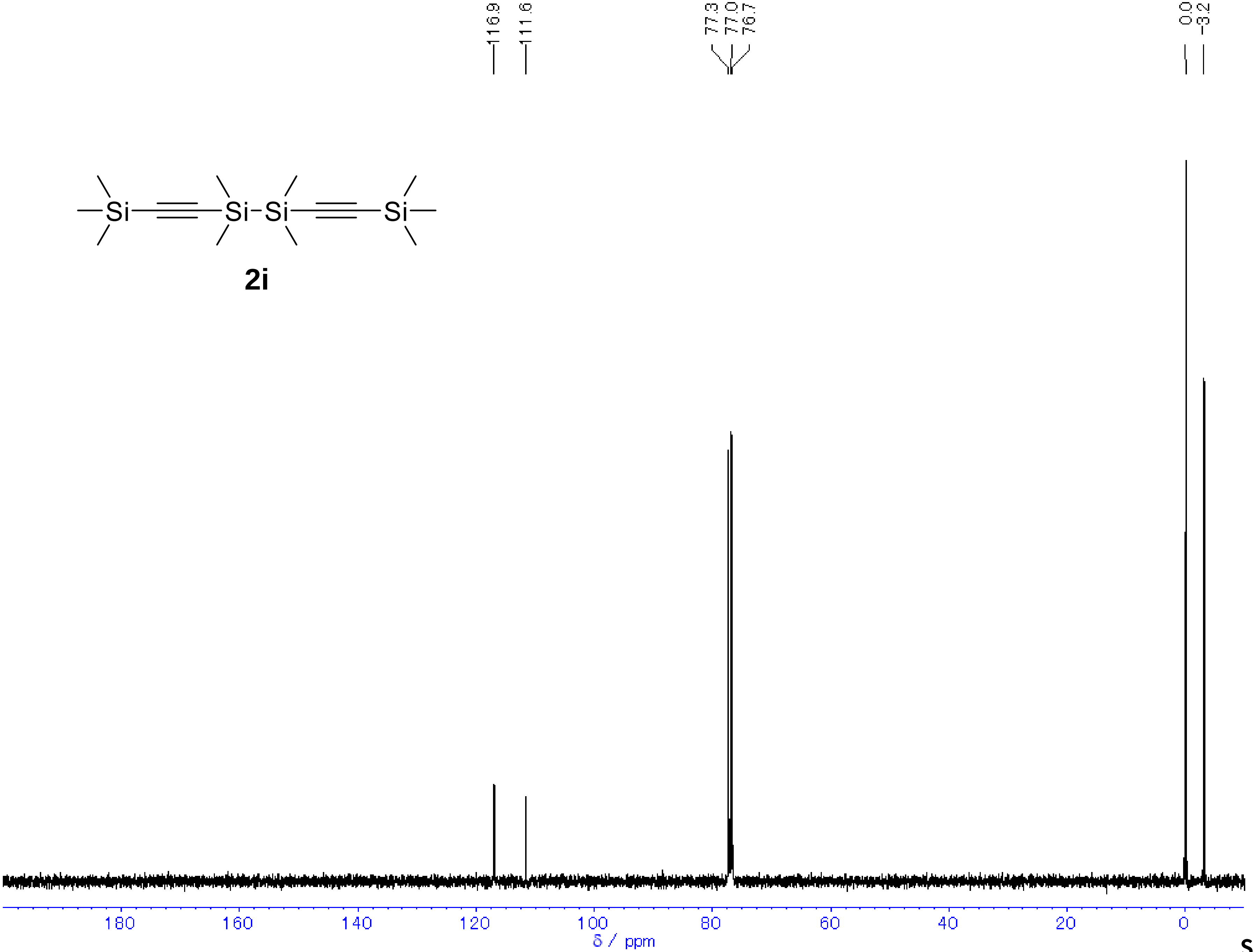

7.48
7.47
7.46
7.46
7.45
7.32
7.31
7.30
7.30
7.30
7.29
7.28
7.27
7.26
0.41
12.07
6.08
4.0
Si
Si
9
8
7
6
5
4
3
2
1
0
δ / ppm

2h


2h
131.9
128.4
128.2
123.2
107.8
92.1
77.3
77.0
76.7
-2.9
180
160
140
120
100
80
60
40
20
0
δ / ppm

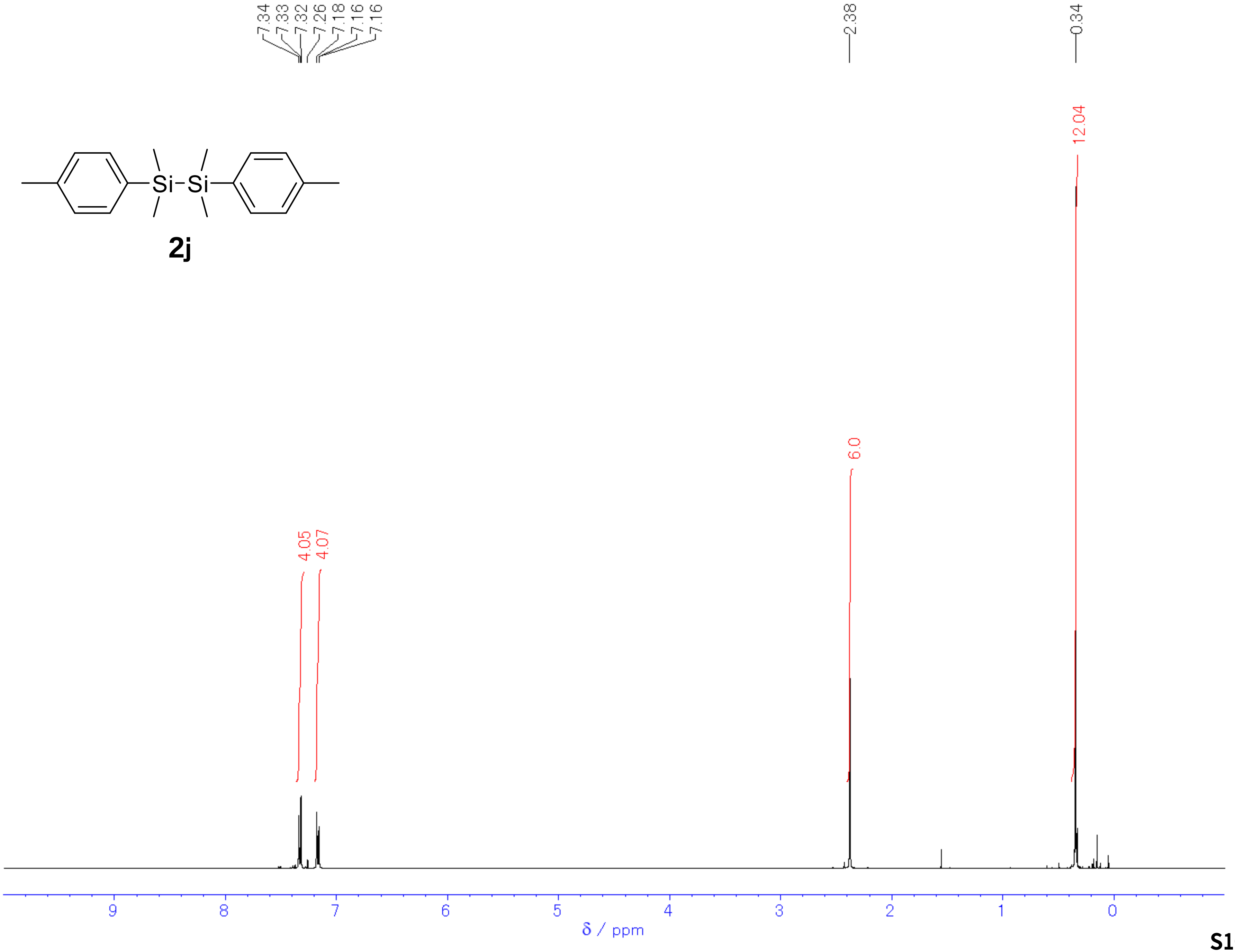


2i

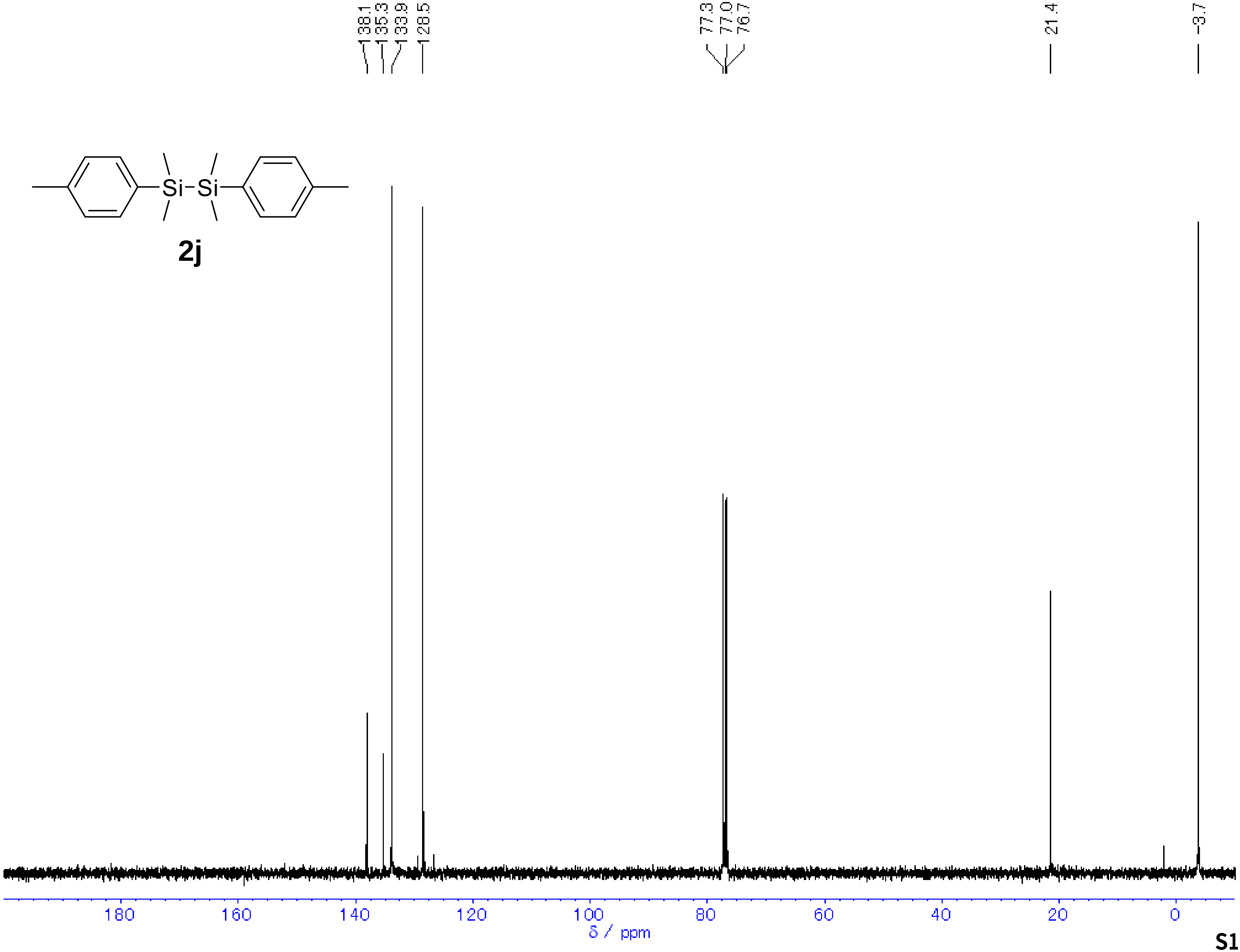


2i

116.9
111.6
77.3
77.0
76.7
0.0
-3.2
Si
Si
Si
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm

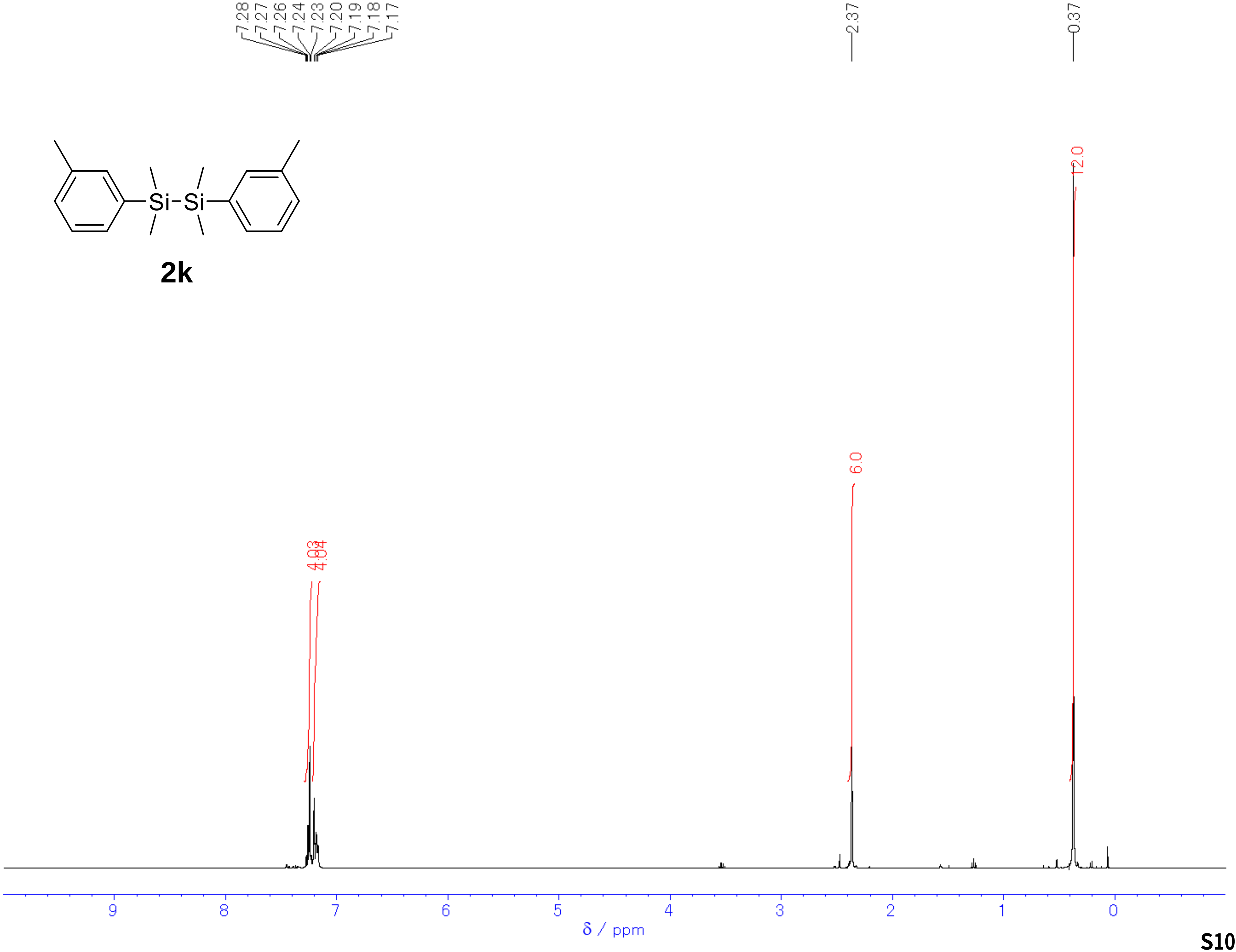

7.34
7.33
7.32
7.26
7.18
7.16
7.16
2.38
0.34
12.04
6.0
4.05
4.07
Si
Si
9
8
7
6
5
4
3
2
1
0
δ / ppm

2j



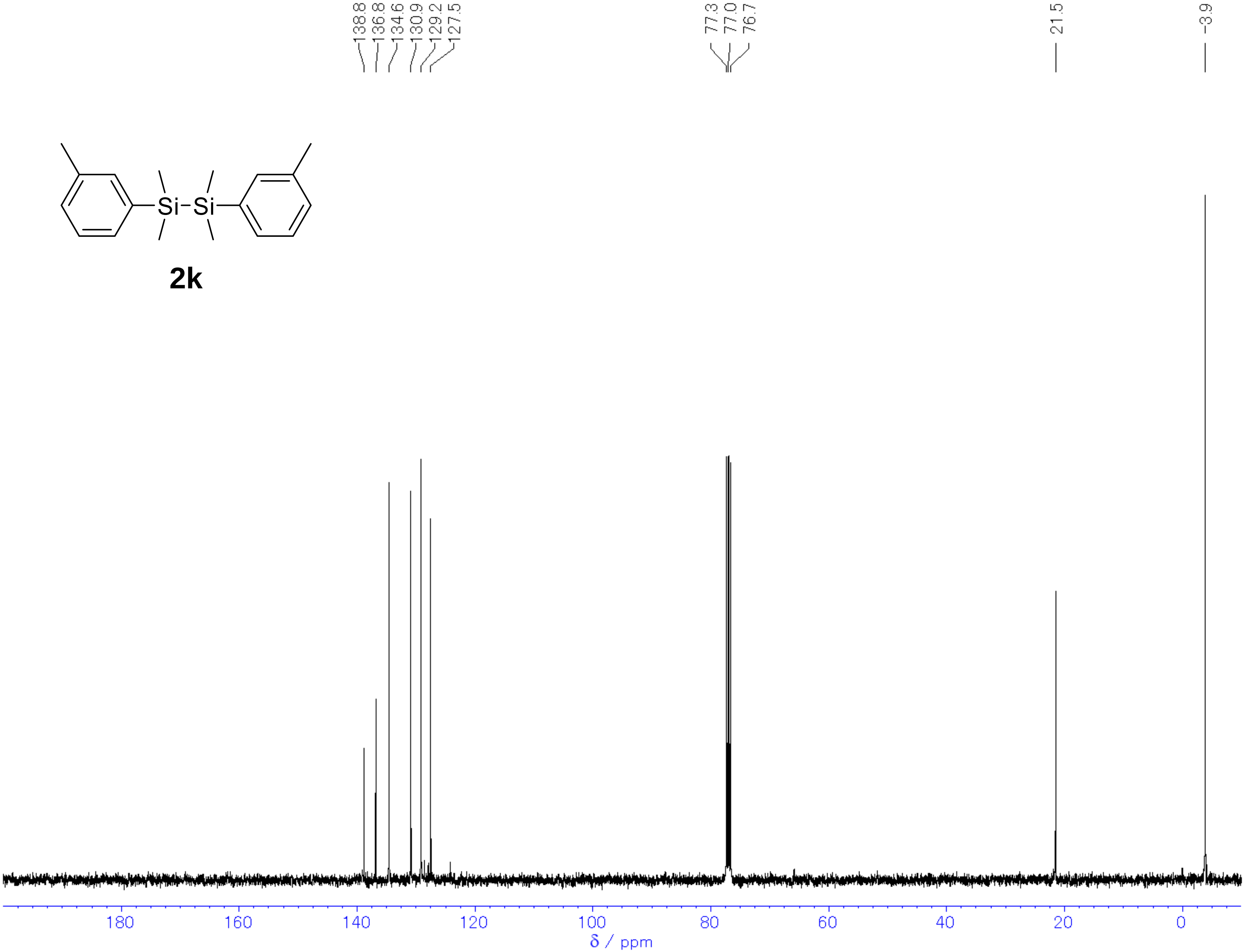
2j

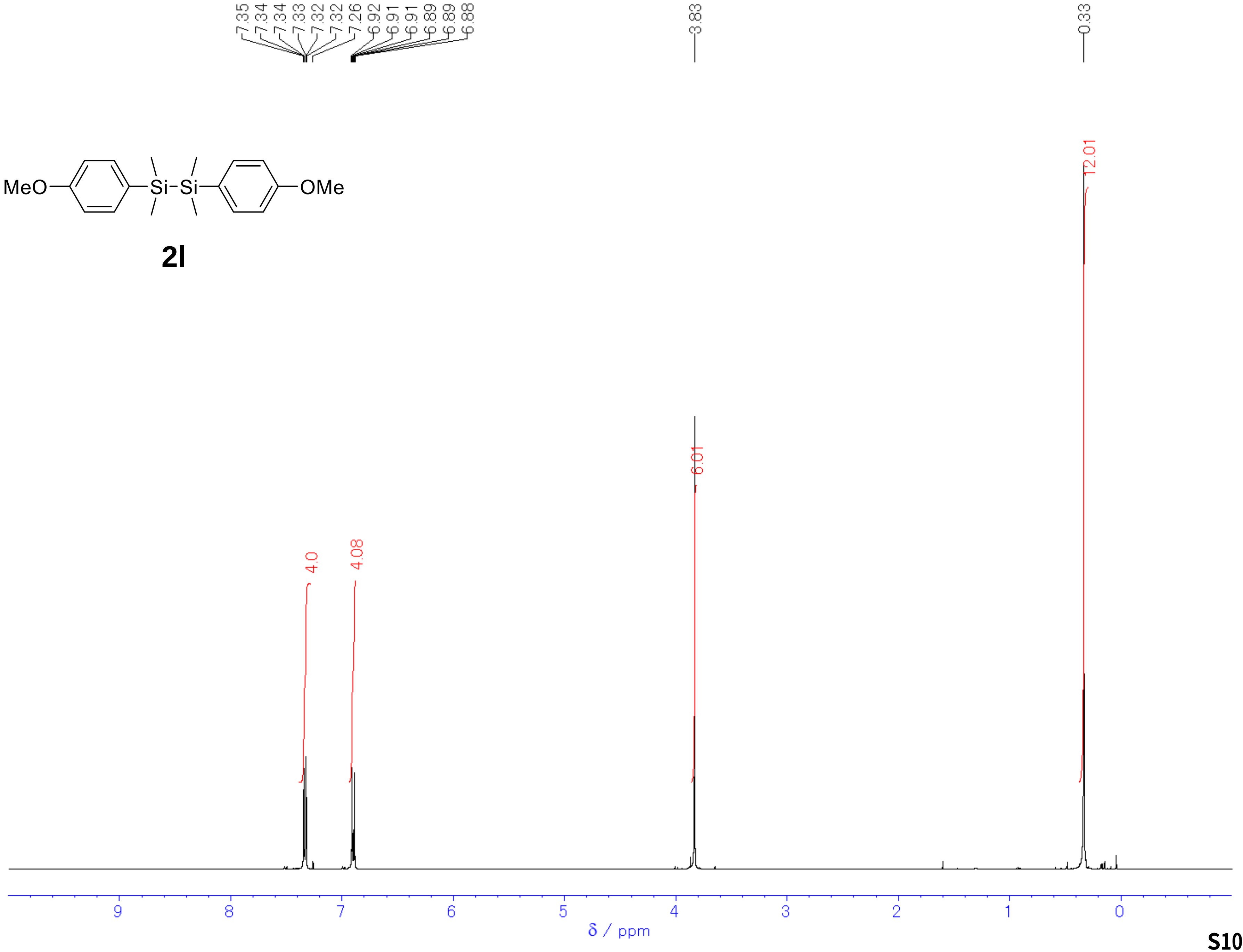
138.1
135.3
133.9
128.5
77.3
77.0
76.7
21.4
-3.7
Si
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm



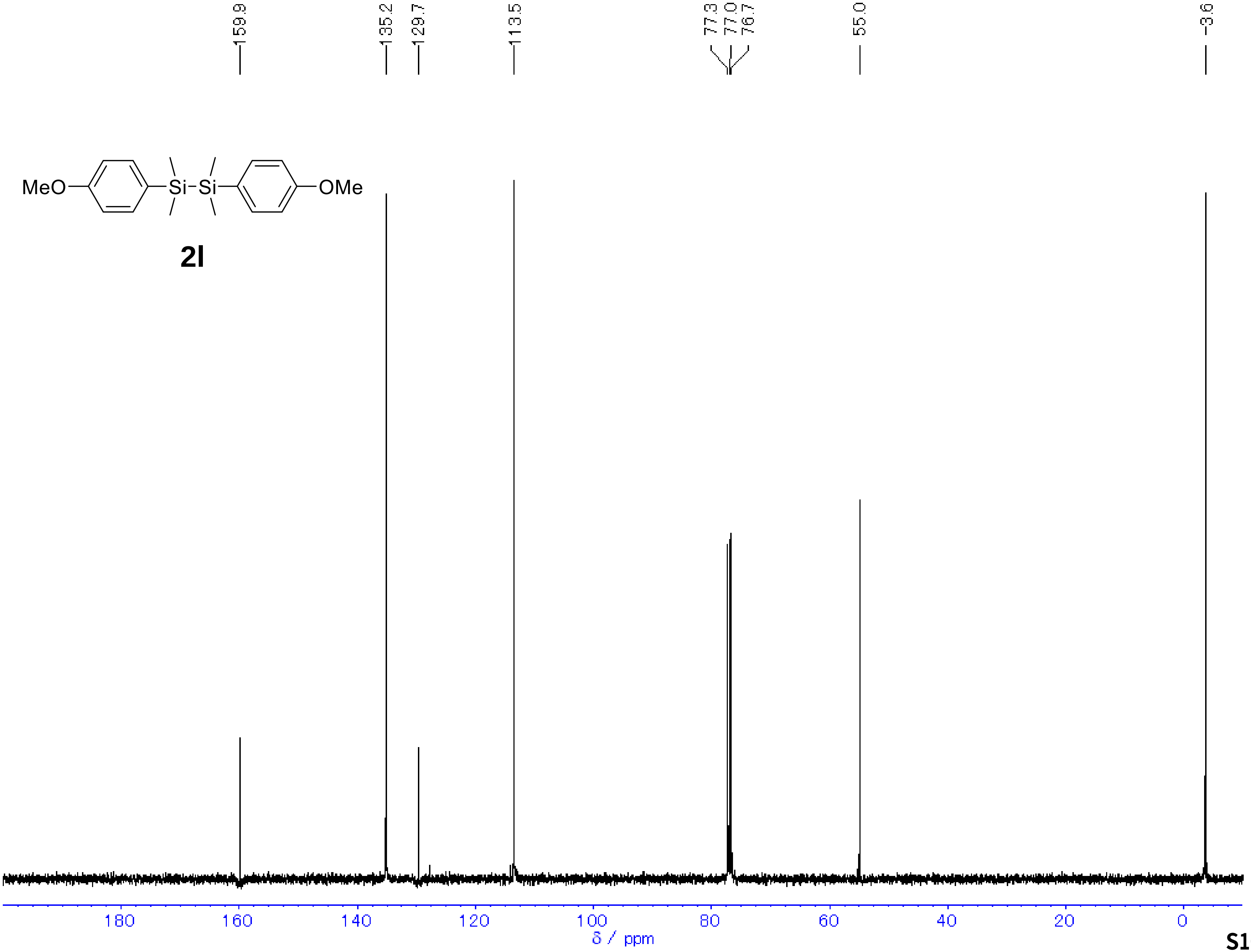
2k

7.28
7.27
7.26
7.24
7.23
7.20
7.19
7.18
7.17
2.37
0.37
12.0
6.0
4.03
4.04
Si
Si
9
8
7
6
5
4
3
2
1
0
δ / ppm


2k
138.8
136.8
134.6
130.9
129.2
127.5
77.3
77.0
76.7
21.5
-3.9
Si
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm


7.35
7.34
7.34
7.33
7.32
7.32
7.26
6.92
6.91
6.91
6.89
6.89
6.88
3.83
0.33
12.01
6.01
4.0
4.08
MeO
Si
Si
OMe
9
8
7
6
5
4
3
2
1
0
δ / ppm

2l

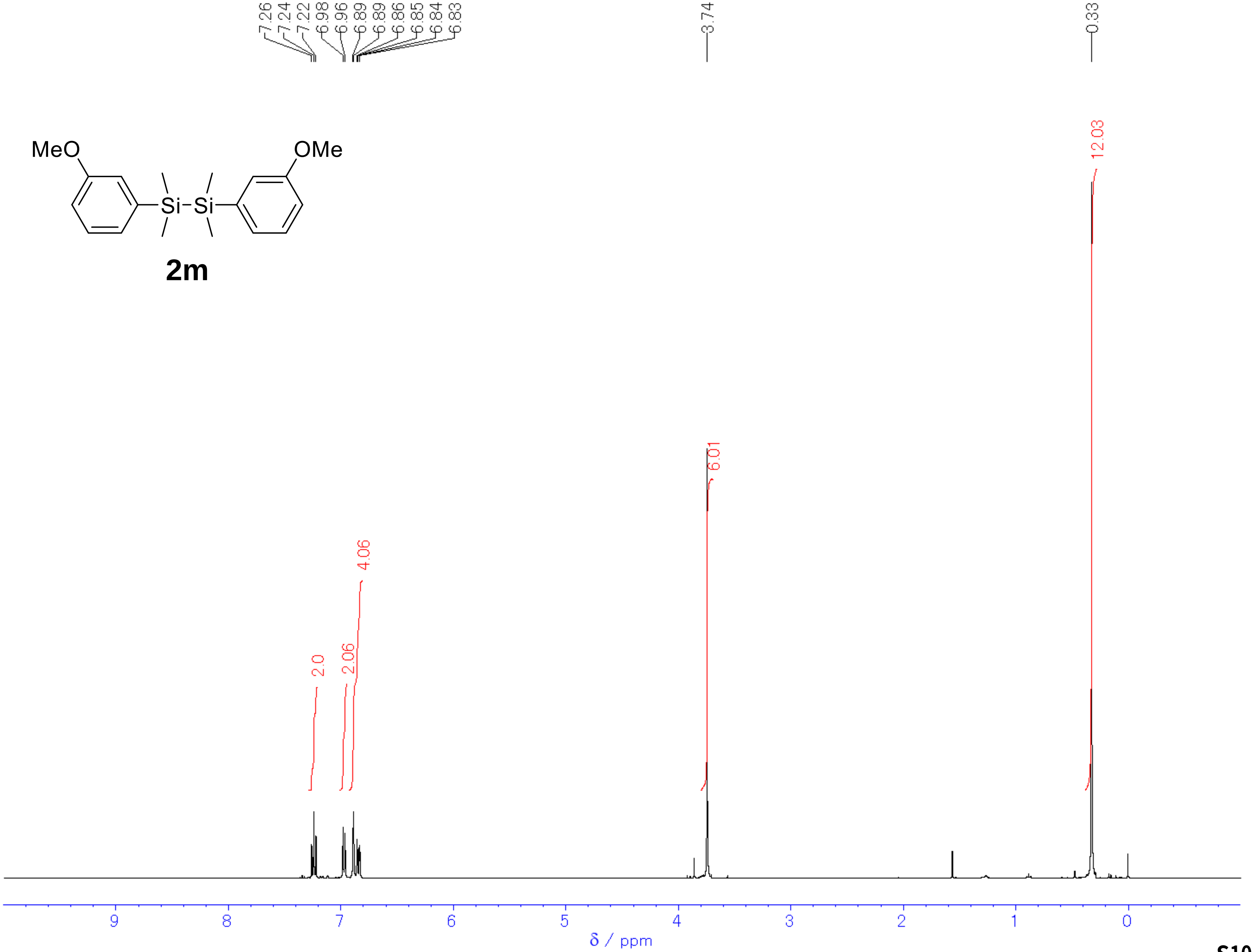


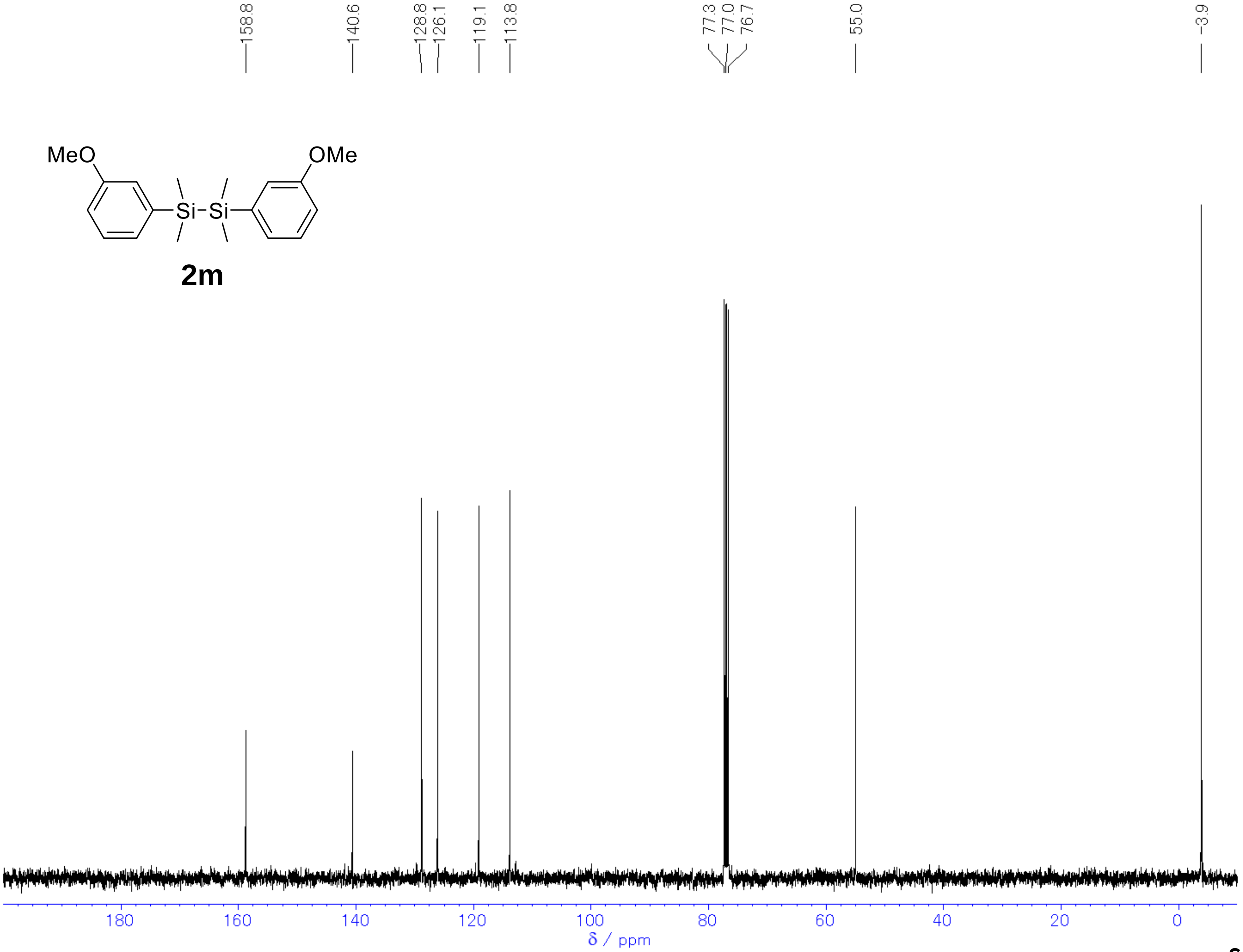
159.9
135.2
129.7
113.5
77.3
77.0
76.7
55.0
-3.6
MeO
Si
Si
OMe
180
160
140
120
100
80
60
40
20
0
δ / ppm

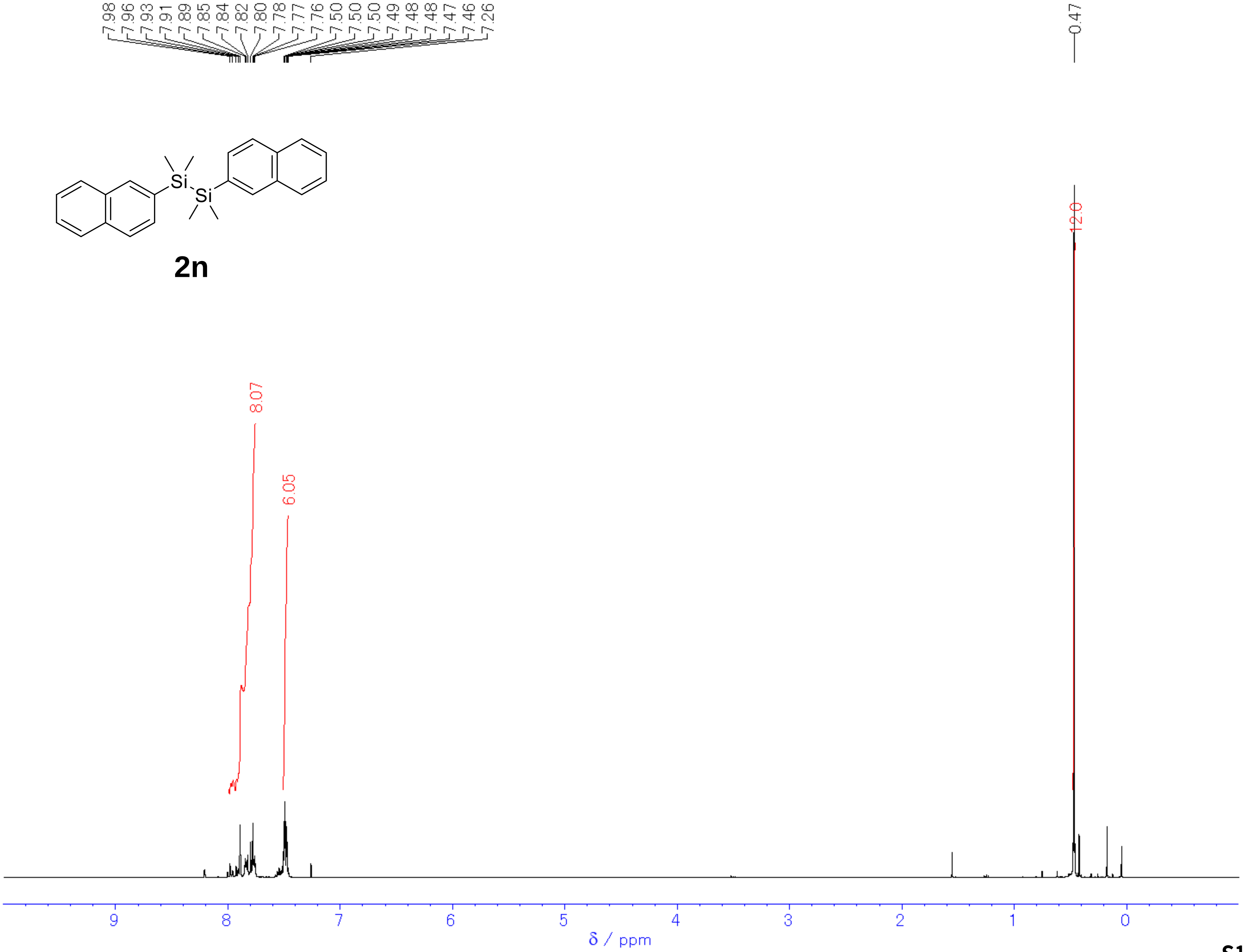
2l

MeO
OMe
Si
Si

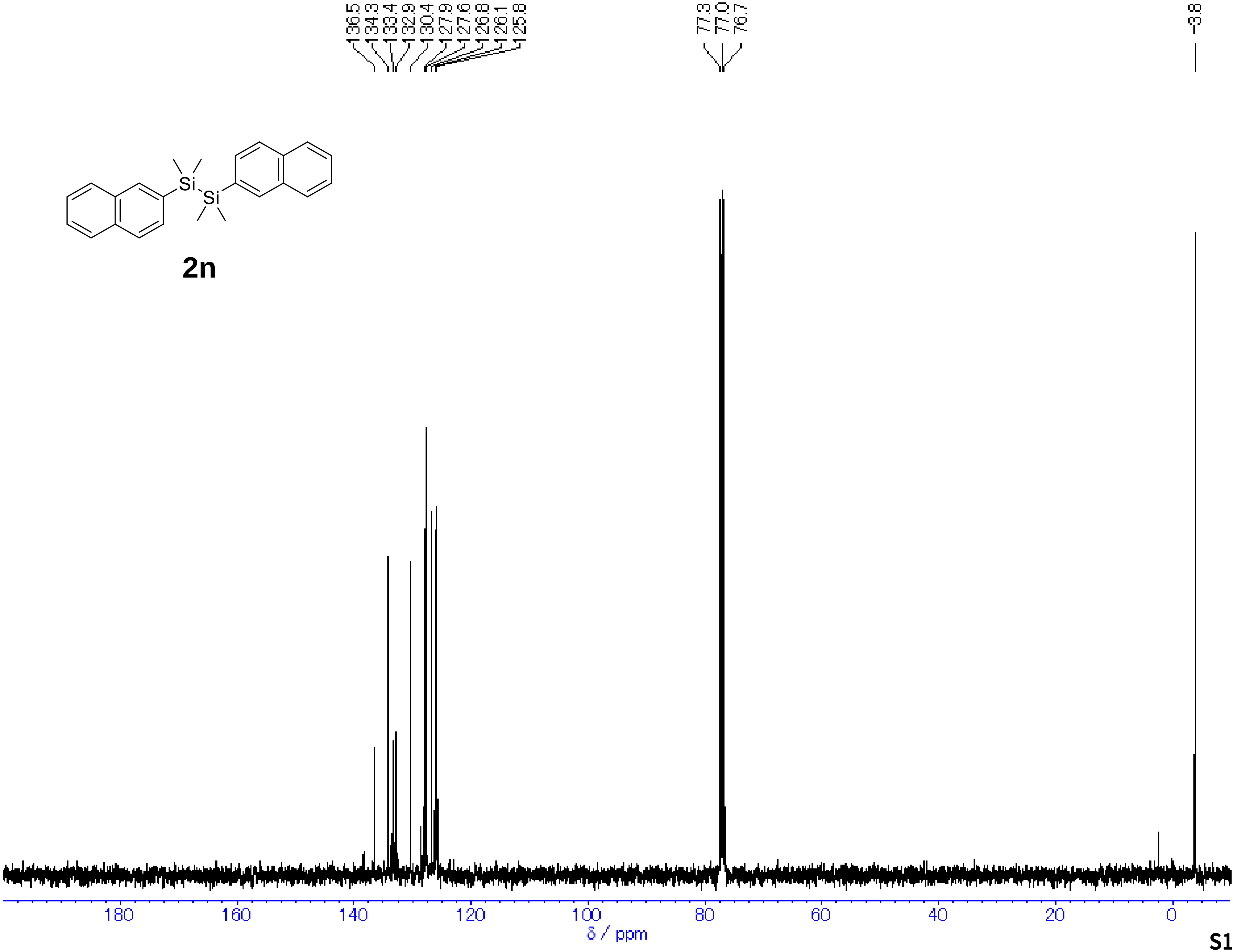
2m


7.26
7.24
7.22
6.98
6.96
6.89
6.89
6.86
6.85
6.84
6.83
3.74
0.33
12.03
6.01
4.06
2.06
2.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

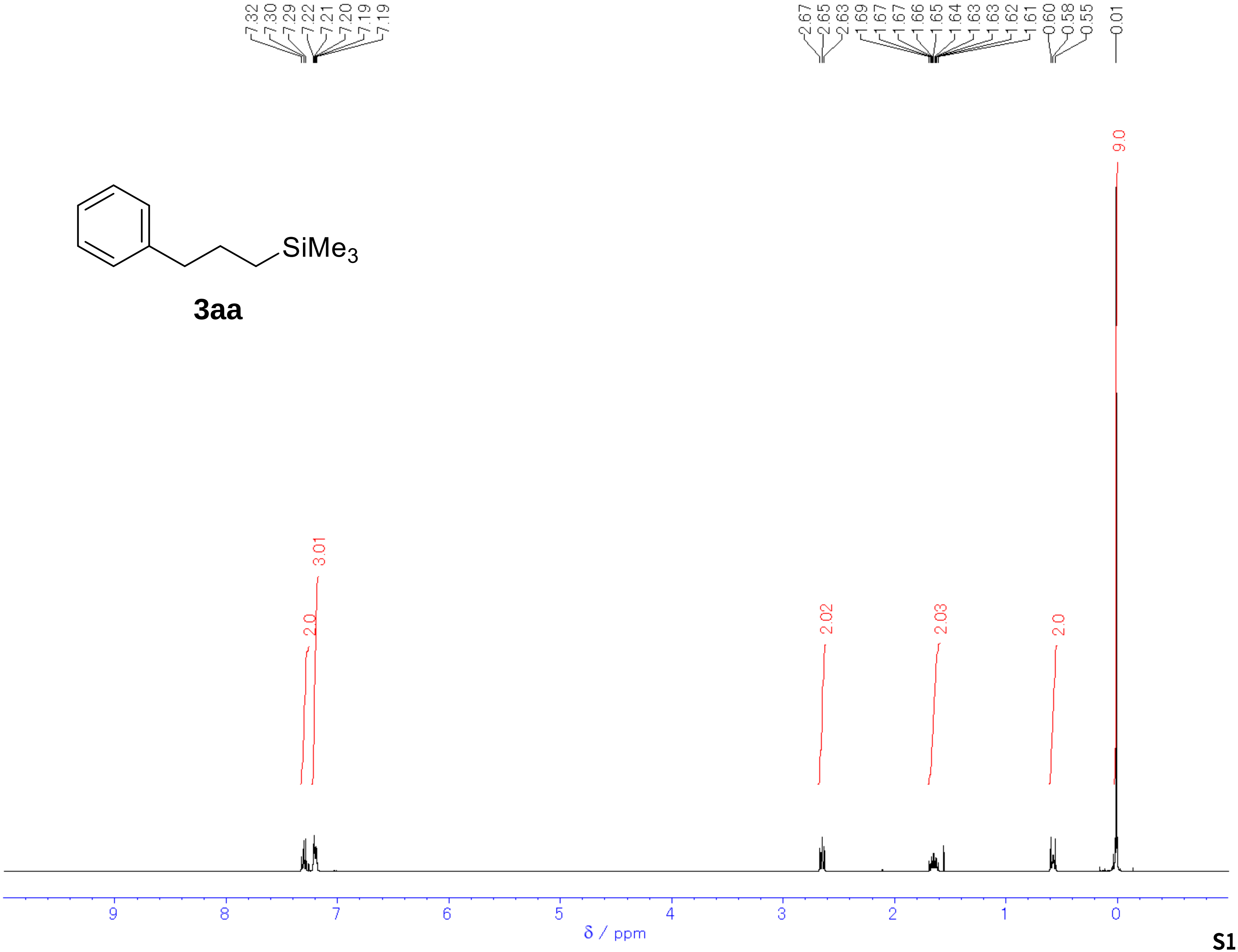

158.8
140.6
128.8
126.1
119.1
113.8
77.3
77.0
76.7
55.0
-3.9
MeO
OMe
Si
Si
2m
180
160
140
120
100
80
60
40
20
0
δ / ppm

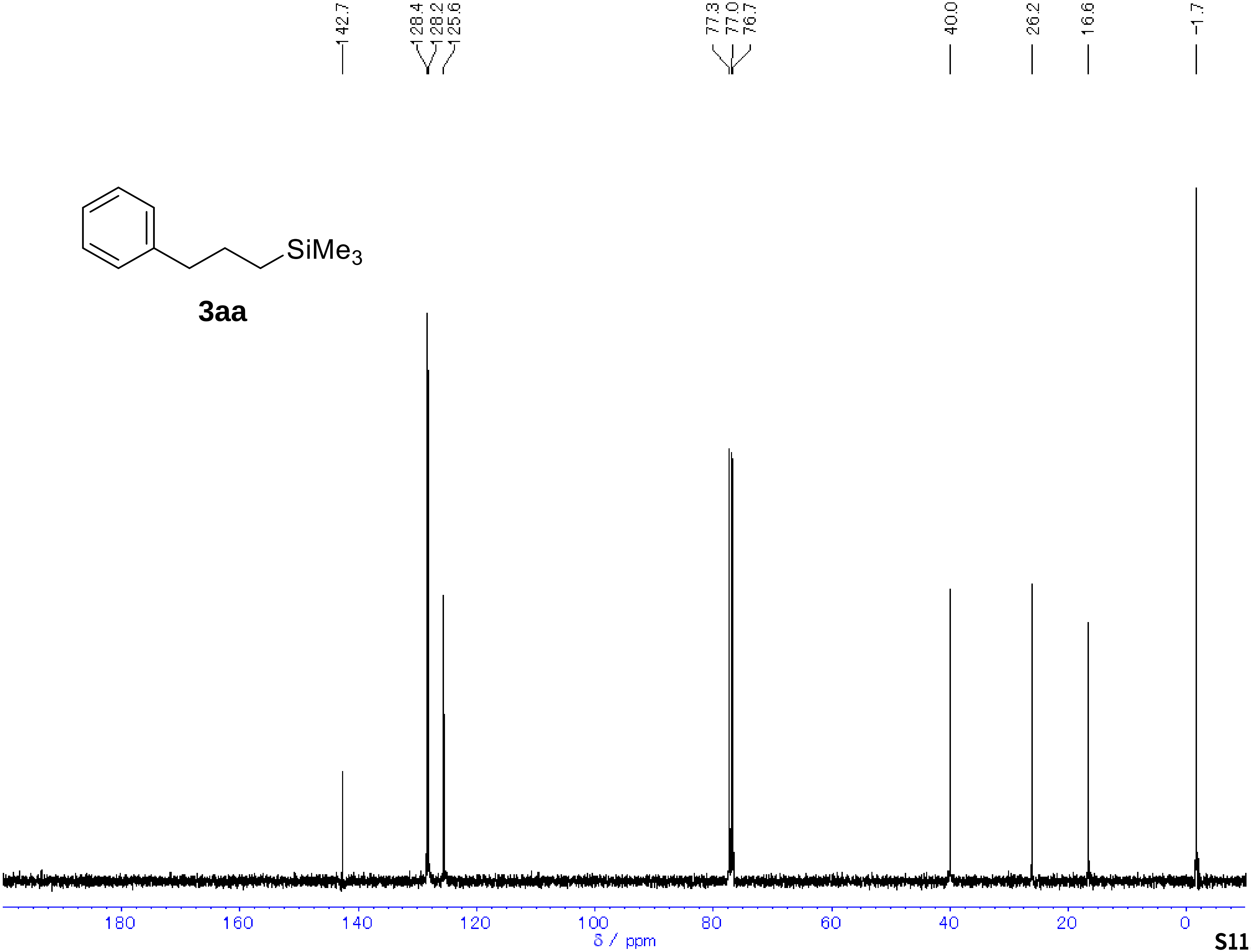

7.98
7.96
7.93
7.91
7.89
7.85
7.84
7.82
7.80
7.78
7.77
7.76
7.50
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.26
0.47
Si
Si
8.07
6.05
12.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

2n


136.5
134.3
133.4
132.9
130.4
127.9
127.6
126.8
126.1
125.8
77.3
77.0
76.7
-3.8
Si
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm

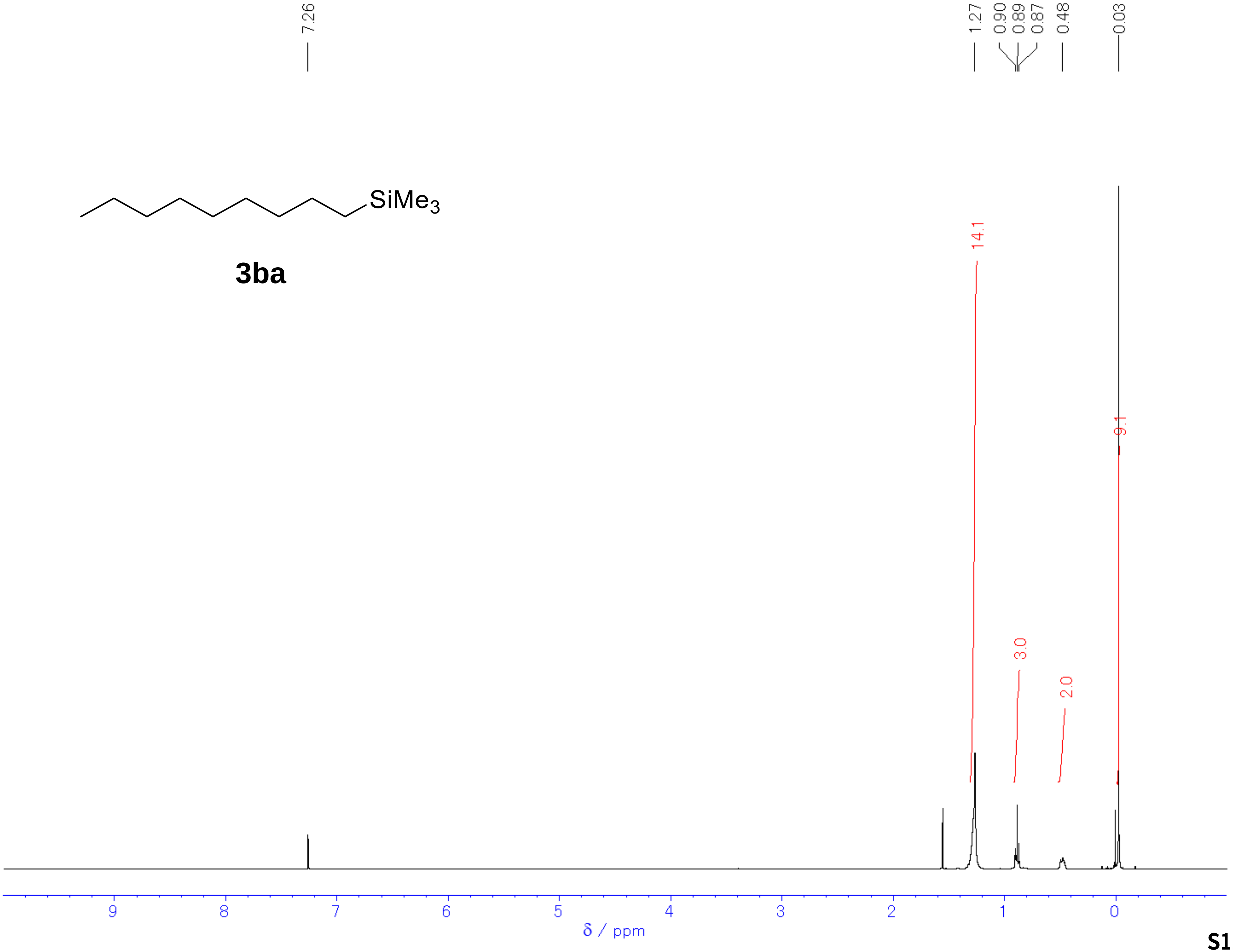
2n


7.32
7.30
7.29
7.22
7.21
7.20
7.19
7.19
2.67
2.65
2.63
1.69
1.67
1.67
1.66
1.65
1.64
1.63
1.63
1.62
1.61
0.60
0.58
0.55
0.01
SiMe3
3aa
9.0
3.01
2.0
2.02
2.03
2.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

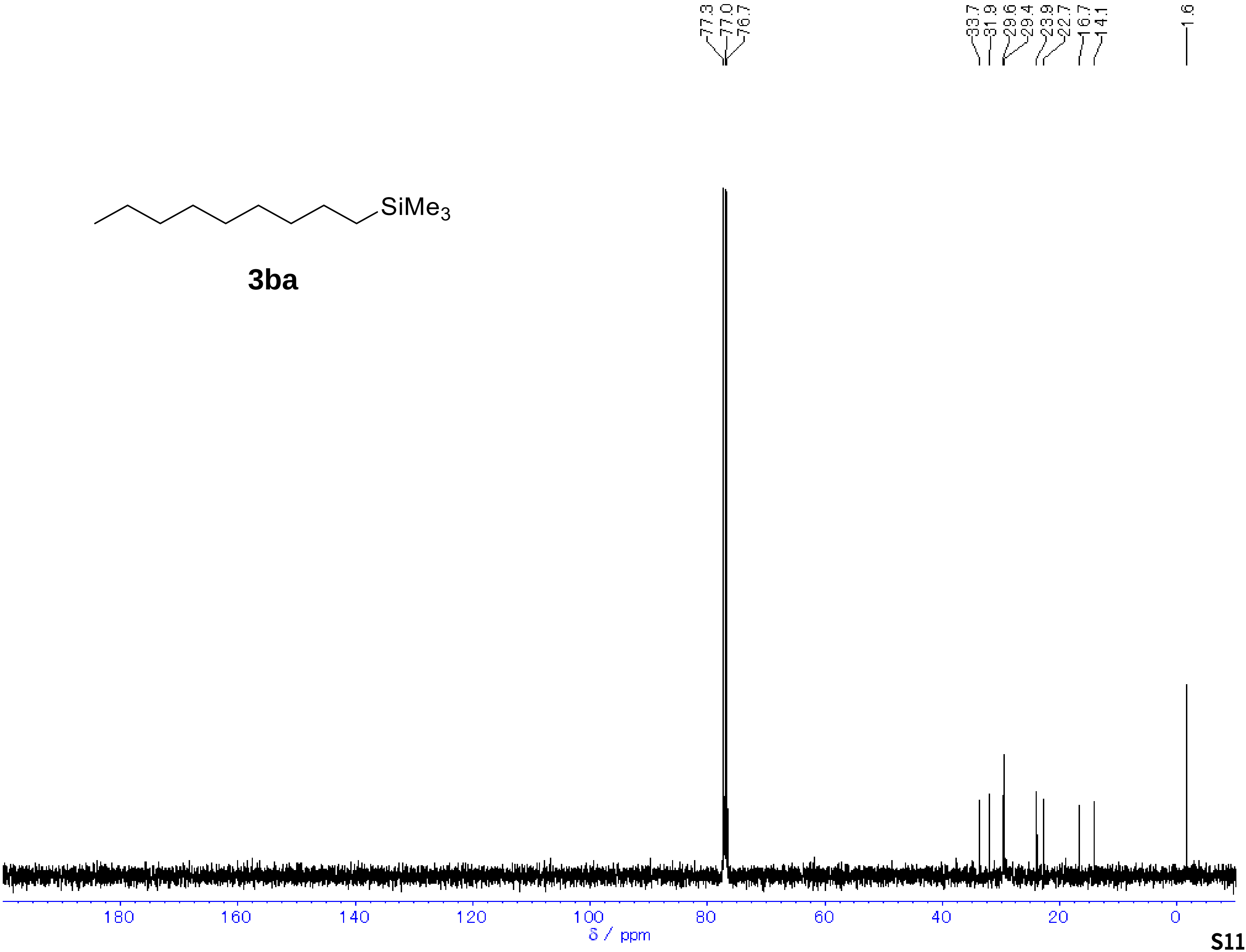


3aa

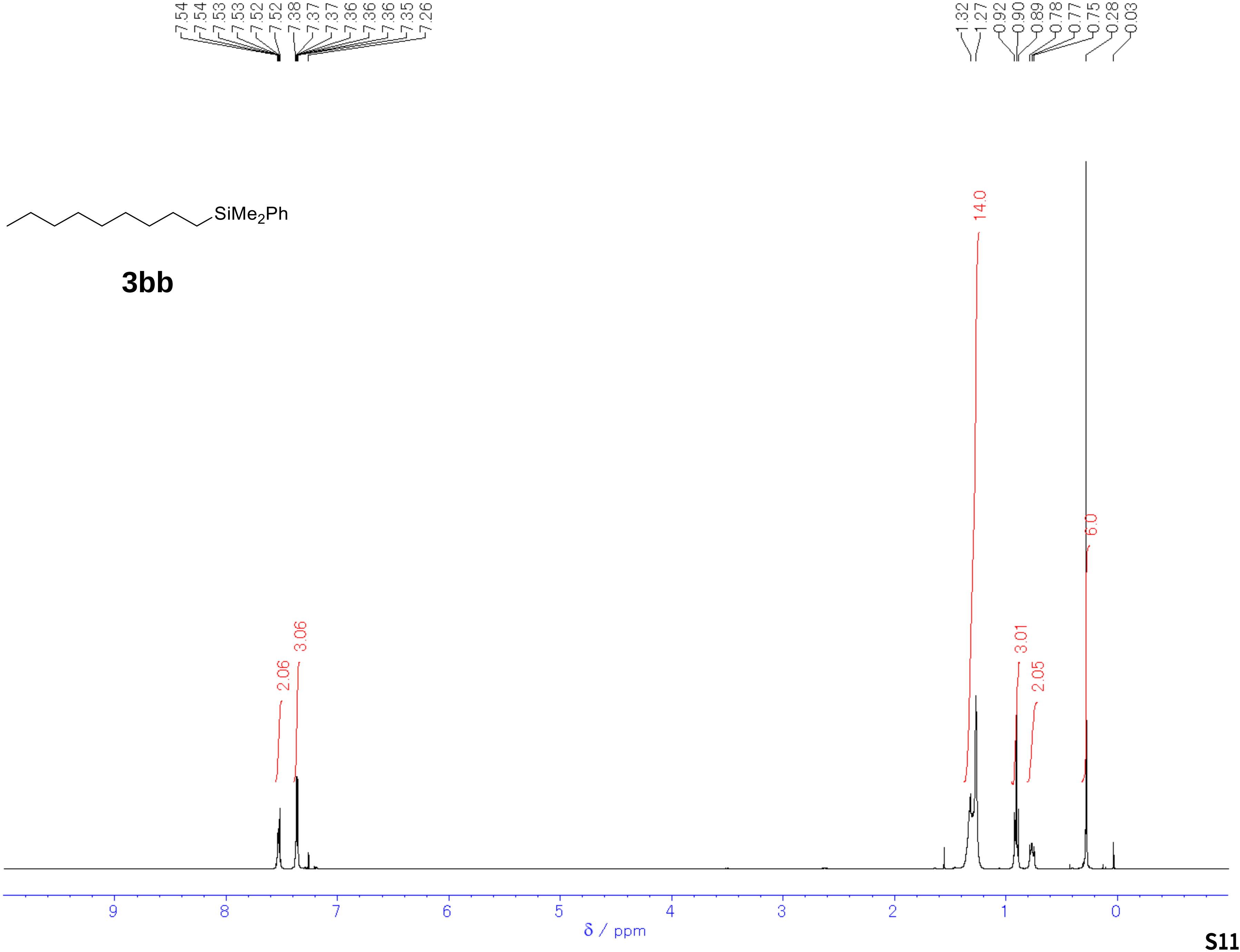
142.7
128.4
128.2
125.6
77.3
77.0
76.7
40.0
26.2
16.6
-1.7
SiMe3
180
160
140
120
100
80
60
40
20
0
δ / ppm



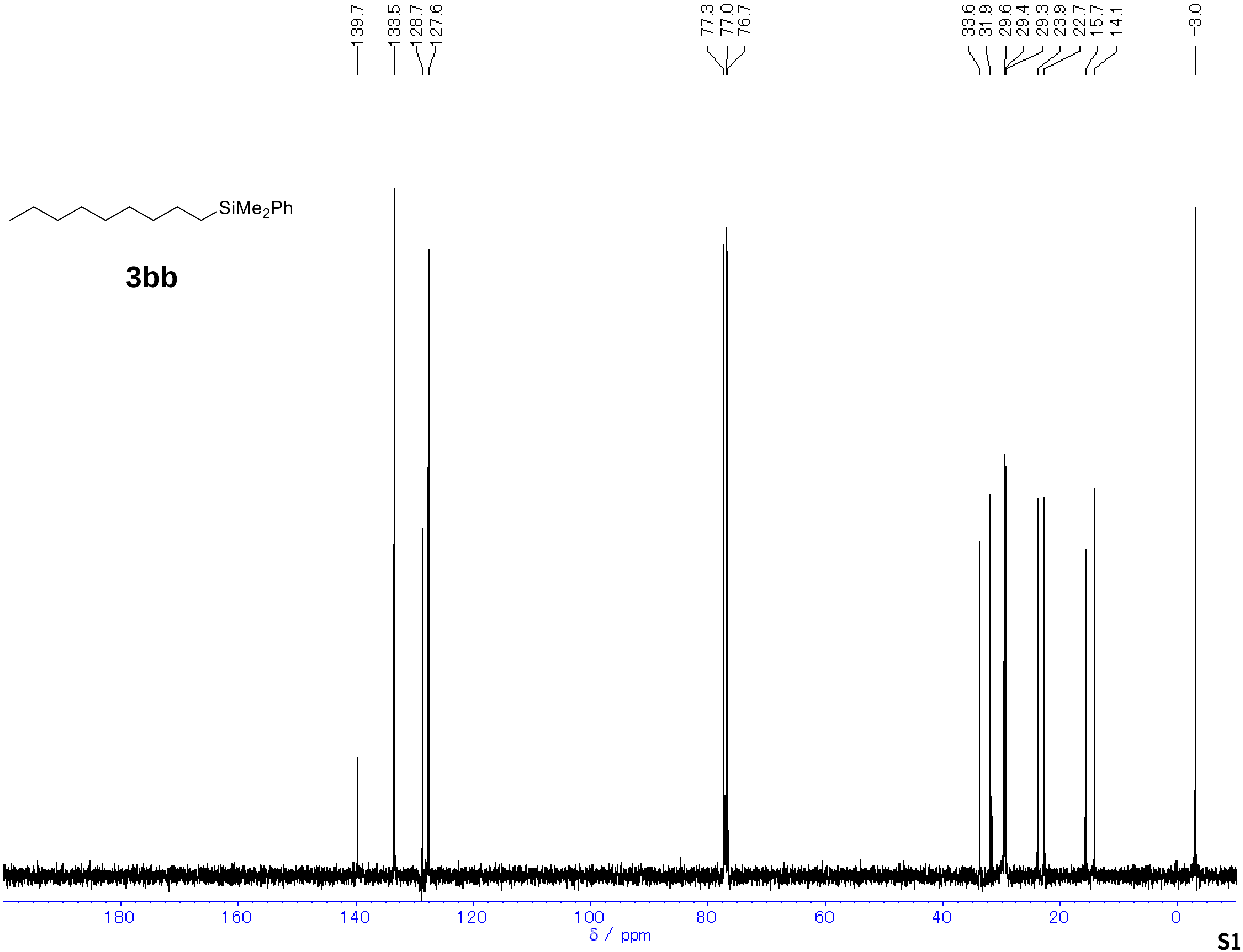
3ba


SiMe$_3$
77.3
77.0
76.7
33.7
31.9
29.6
29.4
23.9
22.7
16.7
14.1
1.6
180
160
140
120
100
80
60
40
20
0
δ / ppm

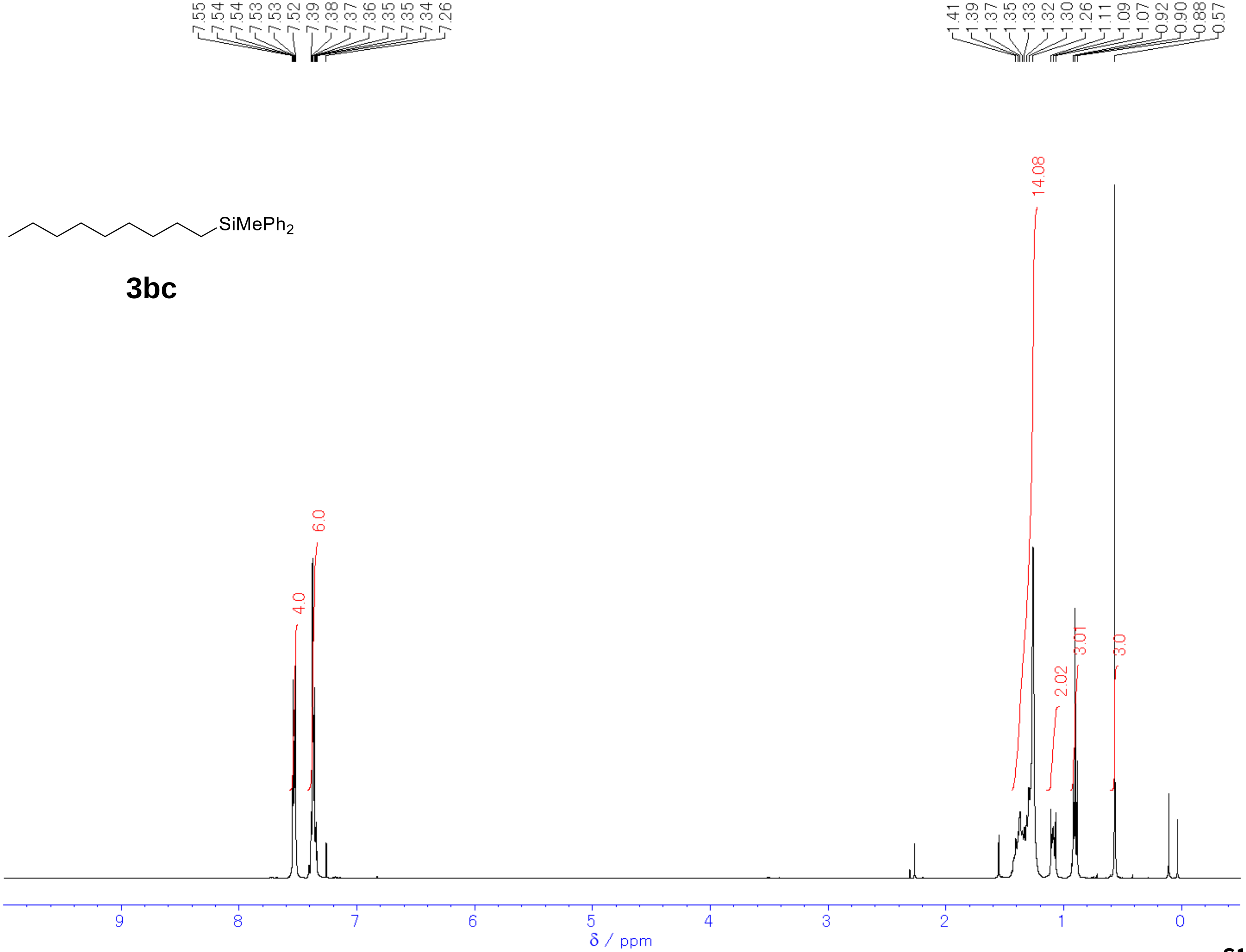
3ba


SiMe2Ph
7.54
7.54
7.53
7.53
7.52
7.52
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.26
1.32
1.27
0.92
0.90
0.89
0.78
0.77
0.75
0.28
0.03
2.06
3.06
14.0
3.01
2.05
6.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

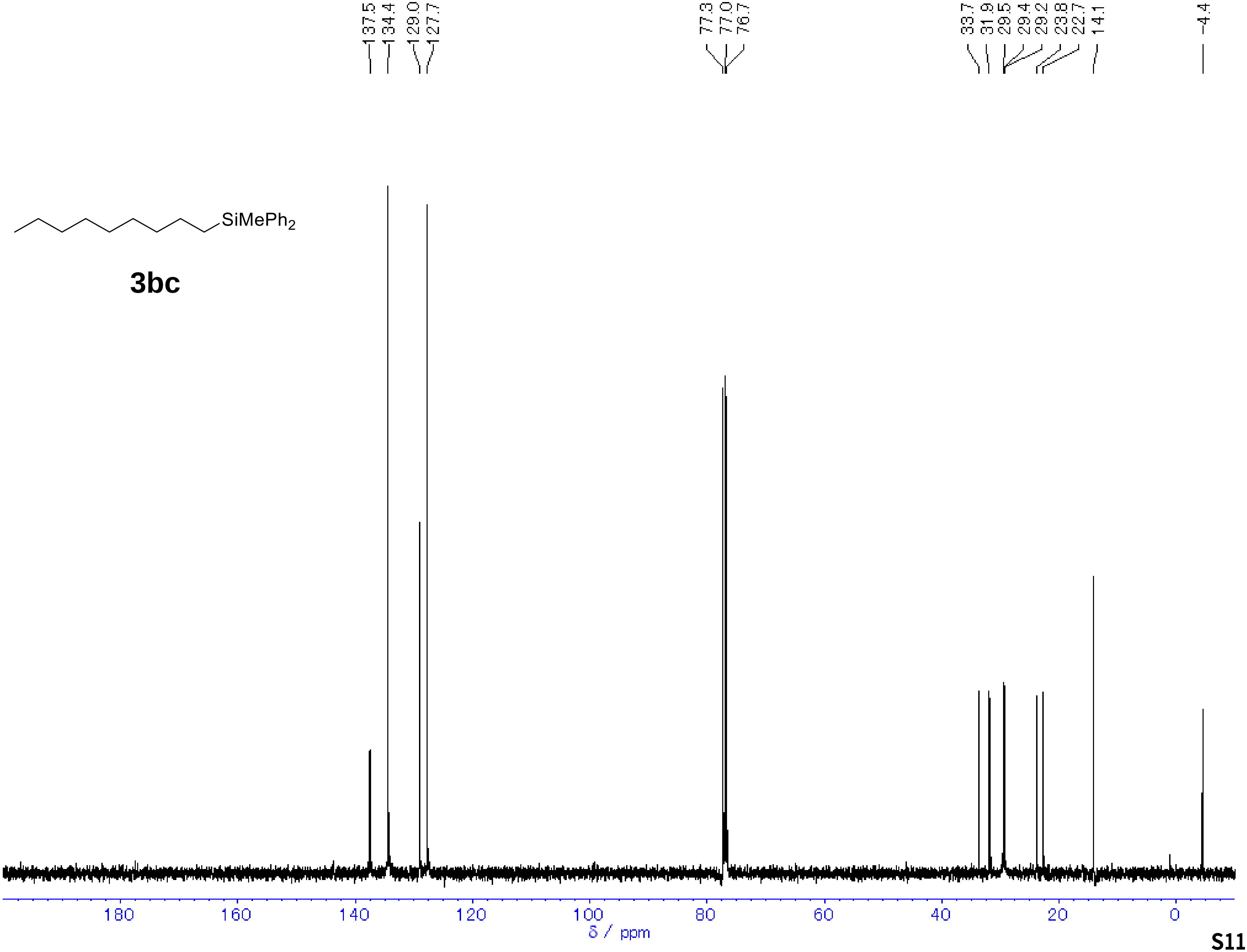
3bb


139.7
133.5
128.7
127.6
77.3
77.0
76.7
33.6
31.9
29.6
29.4
29.3
23.9
22.7
15.7
14.1
-3.0
SiMe$_2$Ph
180
160
140
120
100
80
60
40
20
0
δ / ppm

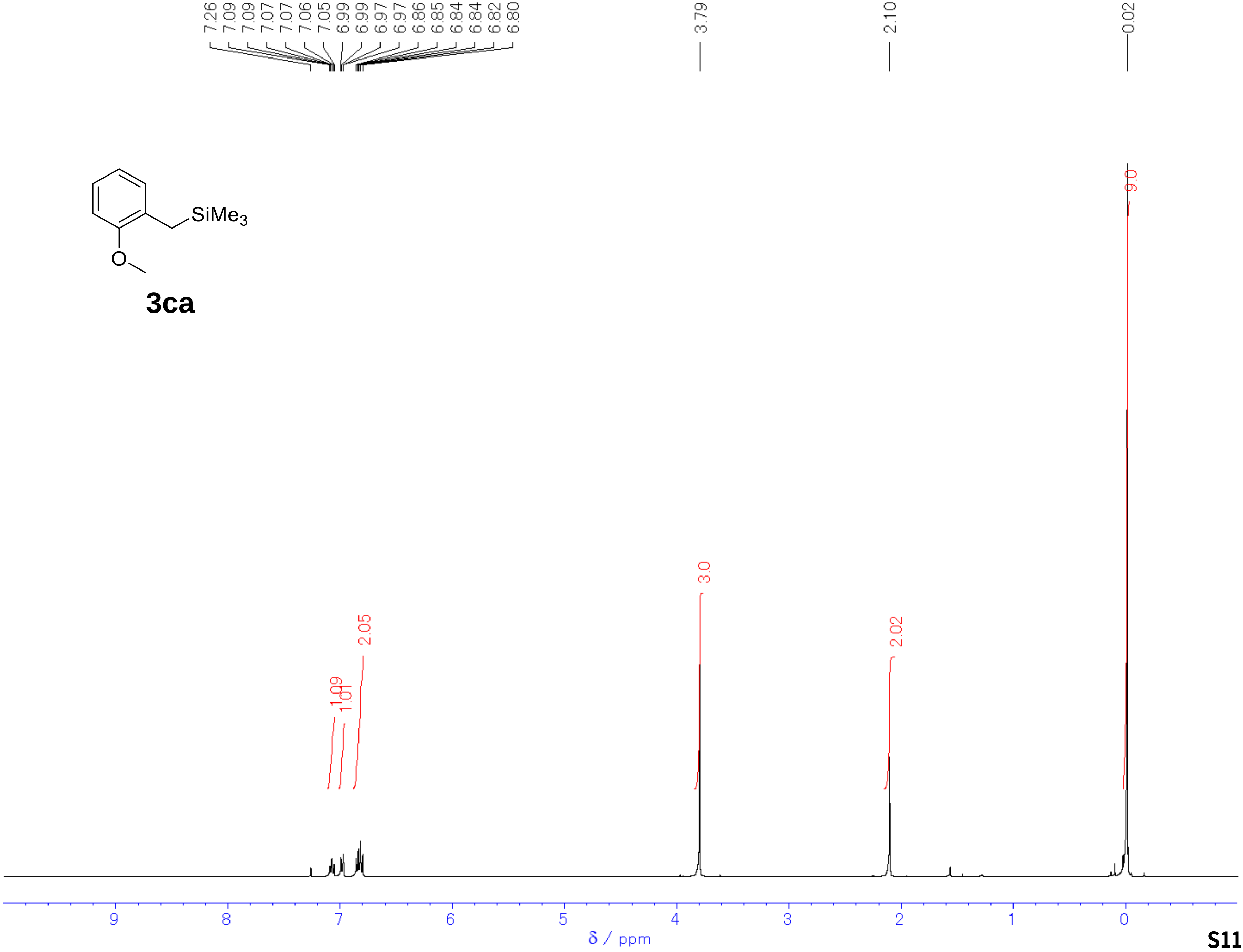
3bb

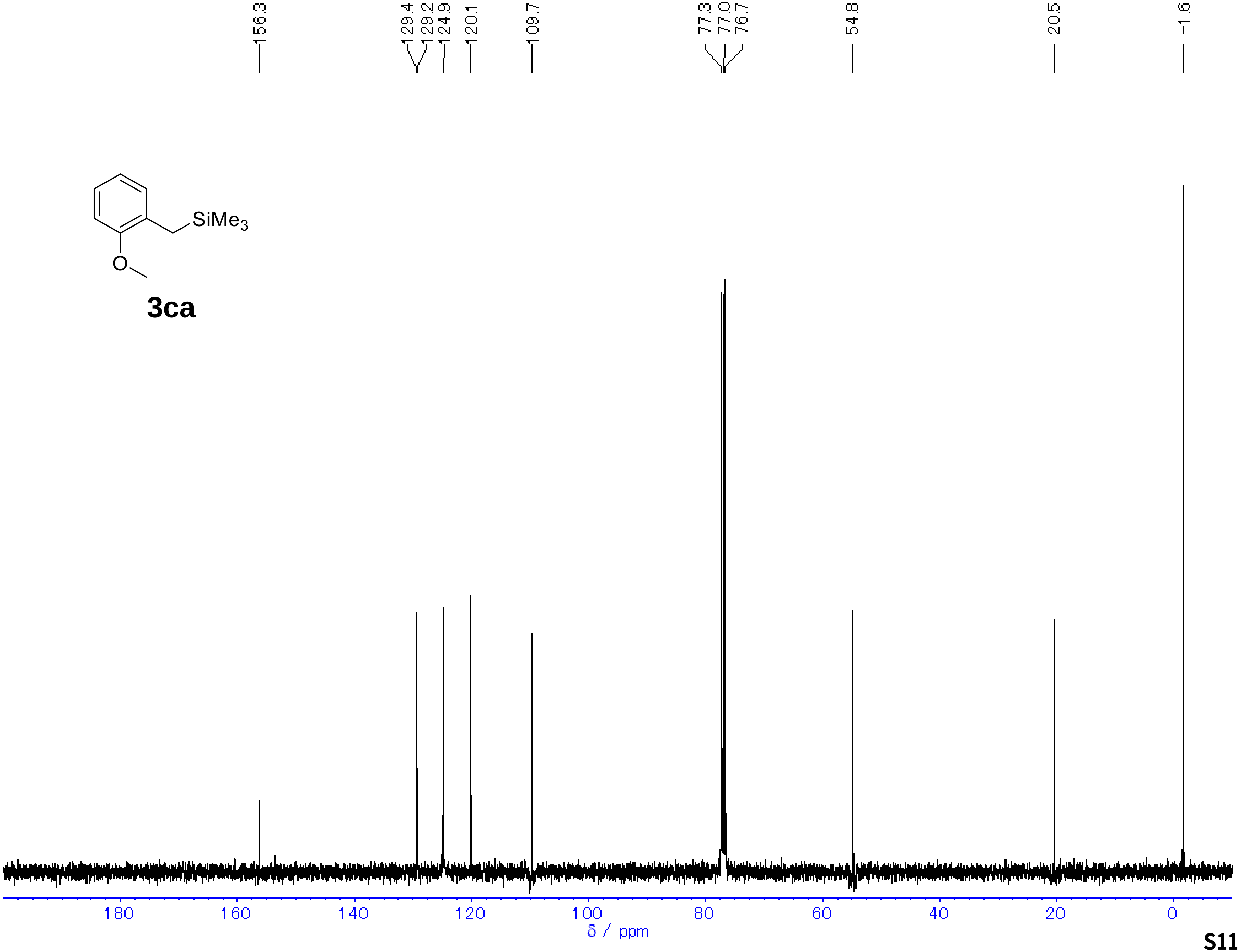

SiMePh$_2$
7.55
7.54
7.54
7.53
7.53
7.52
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.26
1.41
1.39
1.37
1.35
1.33
1.32
1.30
1.26
1.11
1.09
1.07
0.92
0.90
0.88
0.57
4.0
6.0
14.08
2.02
3.01
3.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

3bc

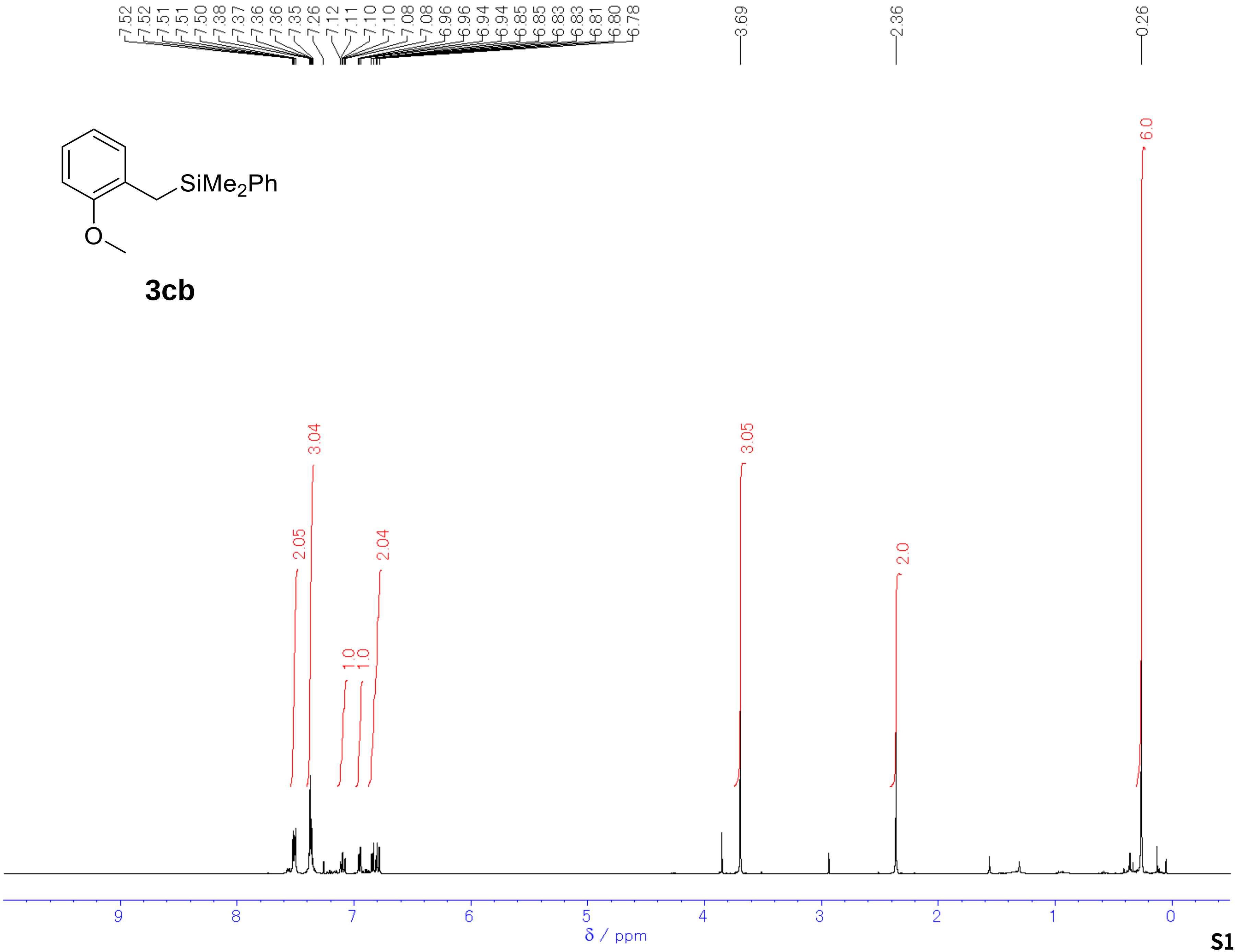

3bc

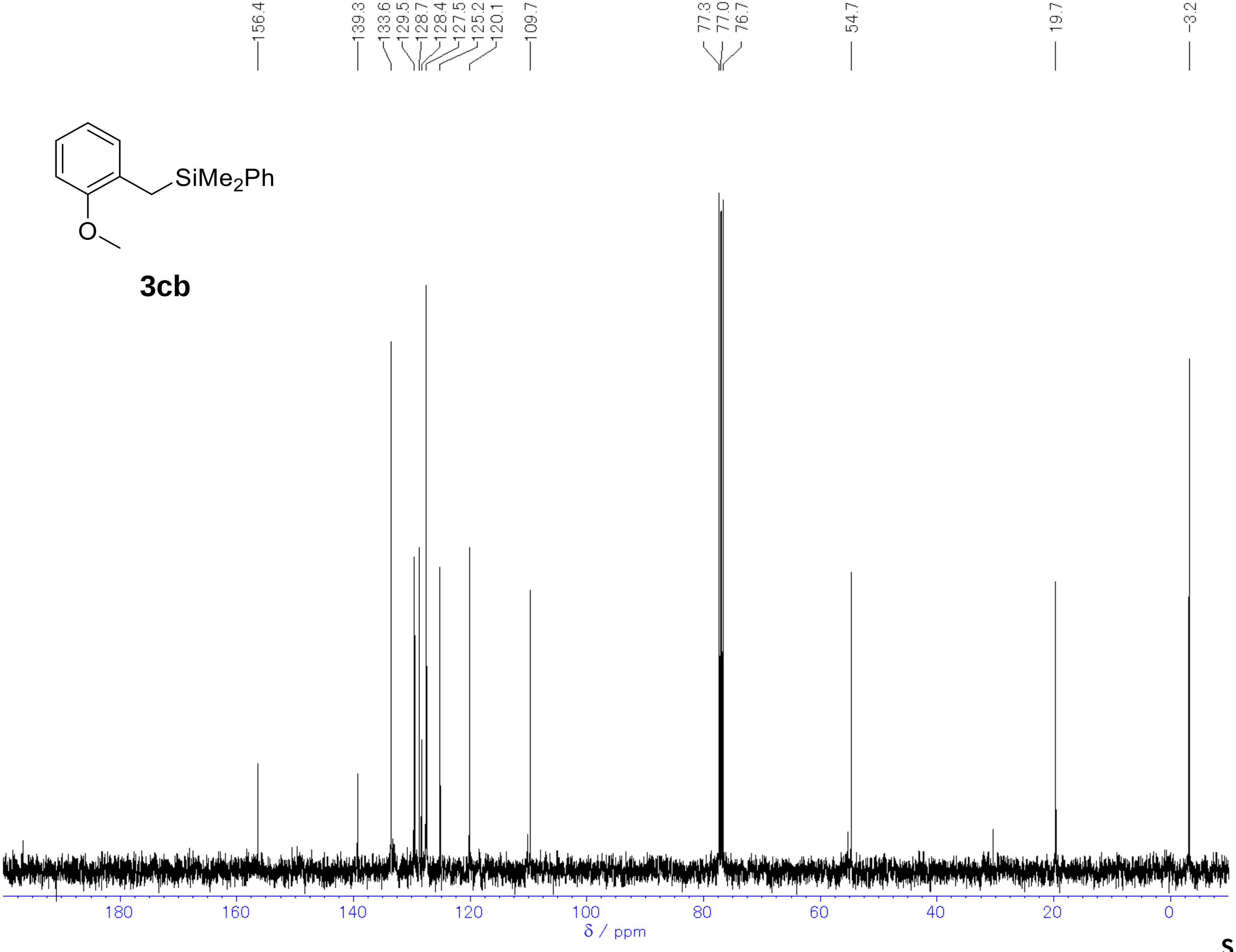
SiMePh$_2$
137.5
134.4
129.0
127.7
77.3
77.0
76.7
33.7
31.9
29.5
29.4
29.2
23.8
22.7
14.1
-4.4
180
160
140
120
100
80
60
40
20
0
δ / ppm


7.26
7.09
7.09
7.07
7.07
7.06
7.05
6.99
6.99
6.97
6.97
6.86
6.85
6.84
6.84
6.82
6.80
3.79
2.10
0.02
SiMe3
O
3ca
1.09
1.01
2.05
3.0
2.02
9.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

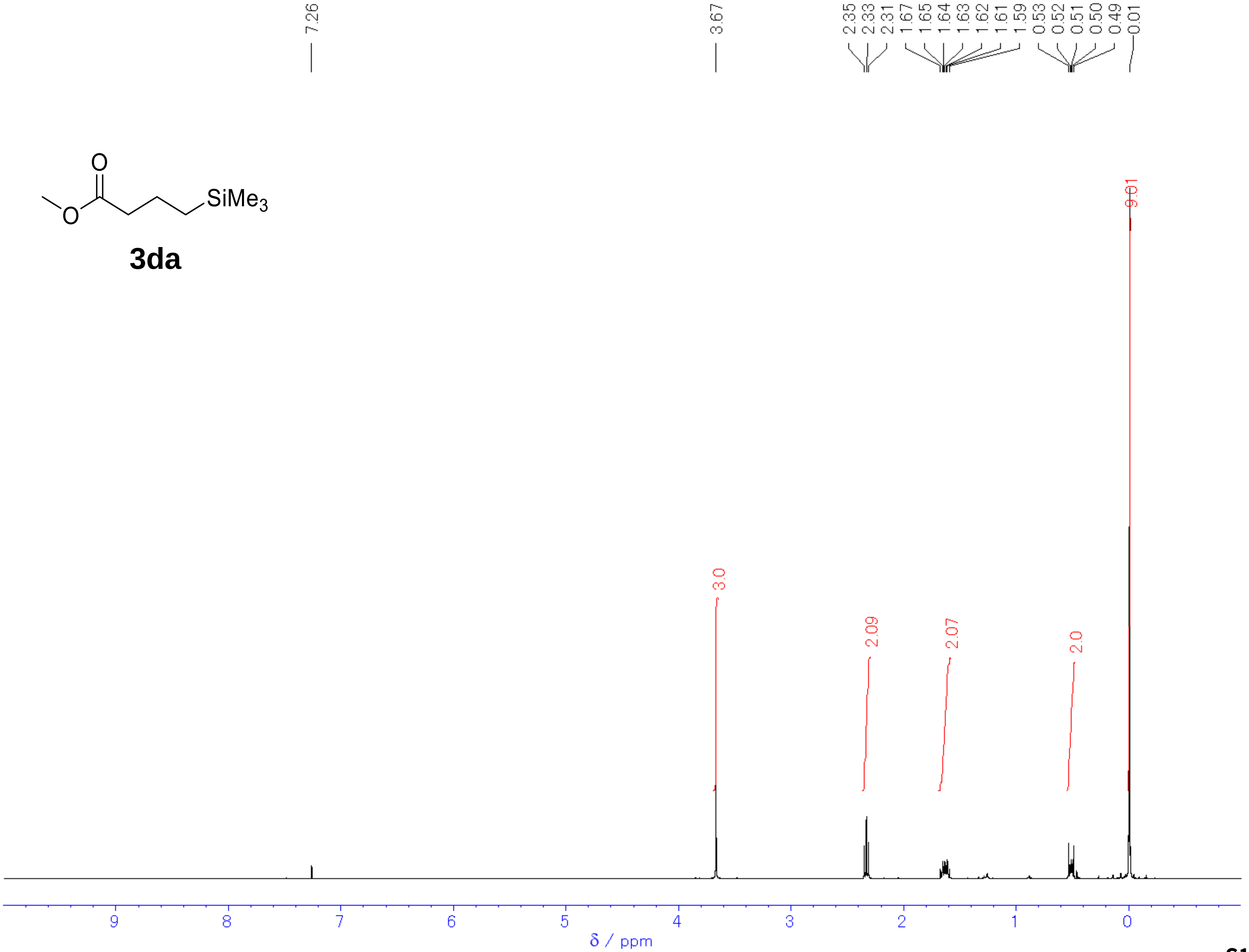

156.3
129.4
129.2
124.9
120.1
109.7
77.3
77.0
76.7
54.8
20.5
-1.6
SiMe3
O
180
160
140
120
100
80
60
40
20
0
δ / ppm

3ca


7.52
7.52
7.51
7.51
7.50
7.38
7.37
7.36
7.36
7.35
7.26
7.12
7.11
7.10
7.10
7.08
7.08
6.96
6.96
6.94
6.94
6.85
6.85
6.83
6.83
6.81
6.80
6.78
3.69
2.36
0.26
SiMe2Ph
O
3cb
2.05
3.04
1.0
1.0
2.04
3.05
2.0
6.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

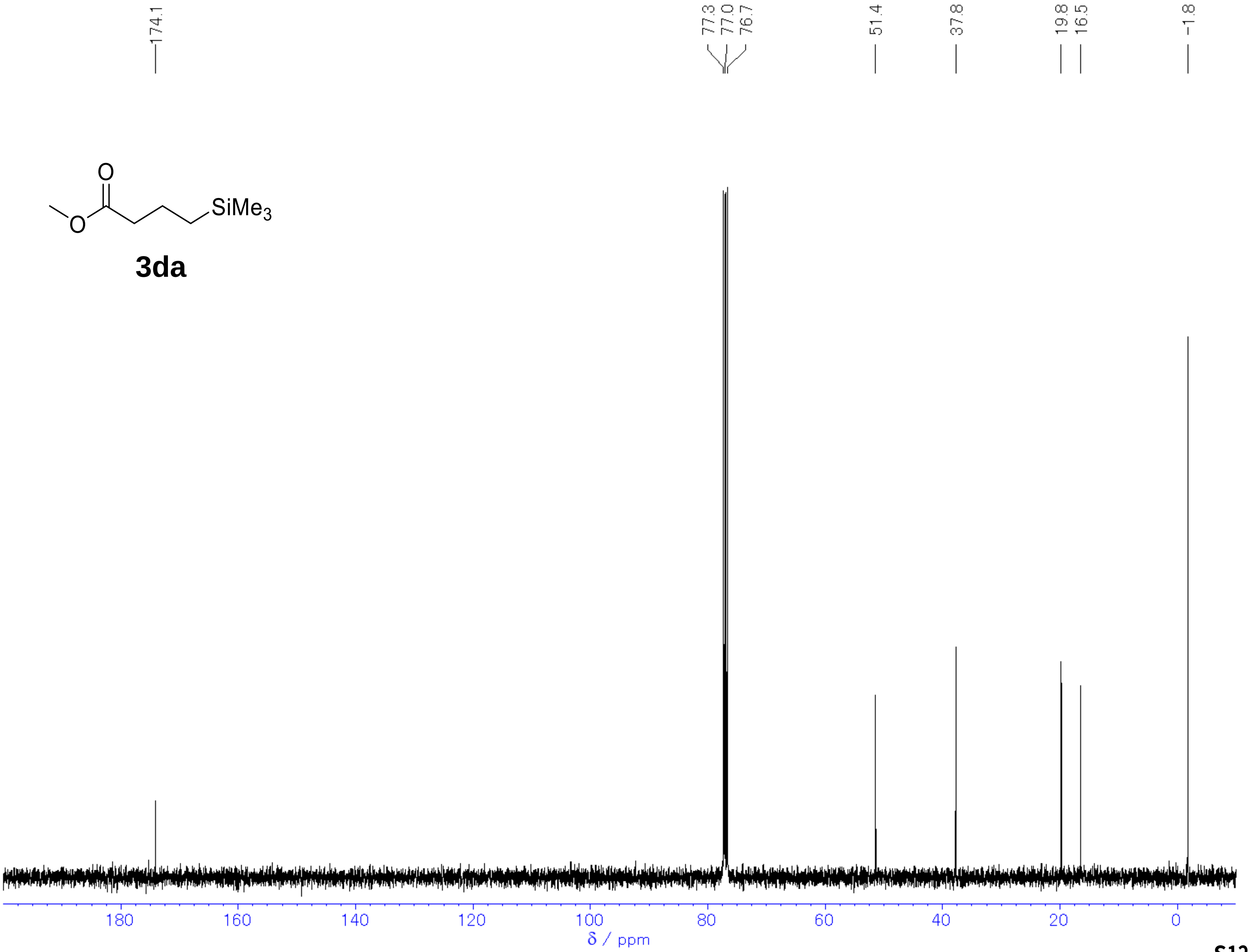

156.4
139.3
133.6
129.5
128.7
128.4
127.5
125.2
120.1
109.7
77.3
77.0
76.7
54.7
19.7
-3.2
SiMe2Ph
O
180
160
140
120
100
80
60
40
20
0
δ / ppm

3cb

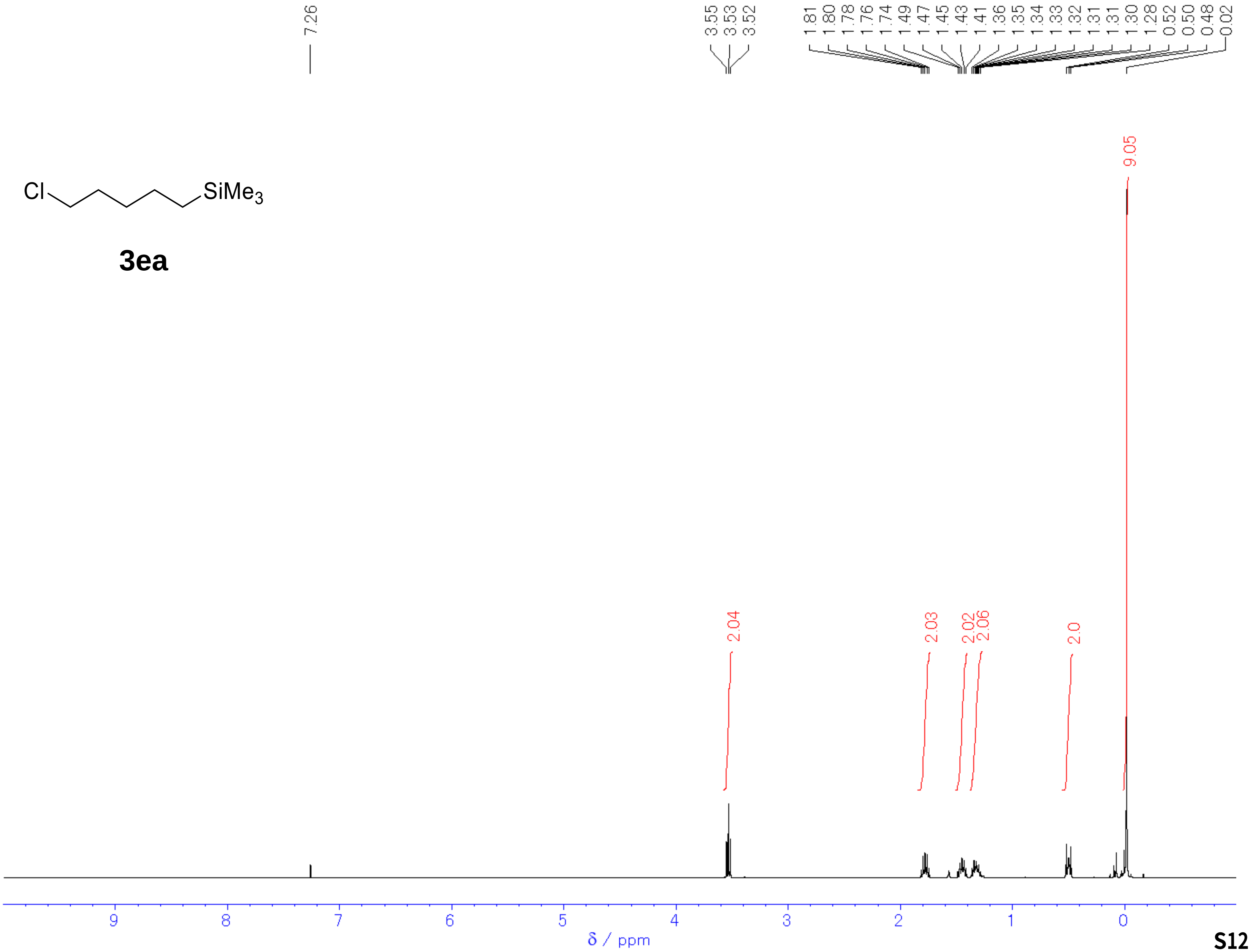


3da

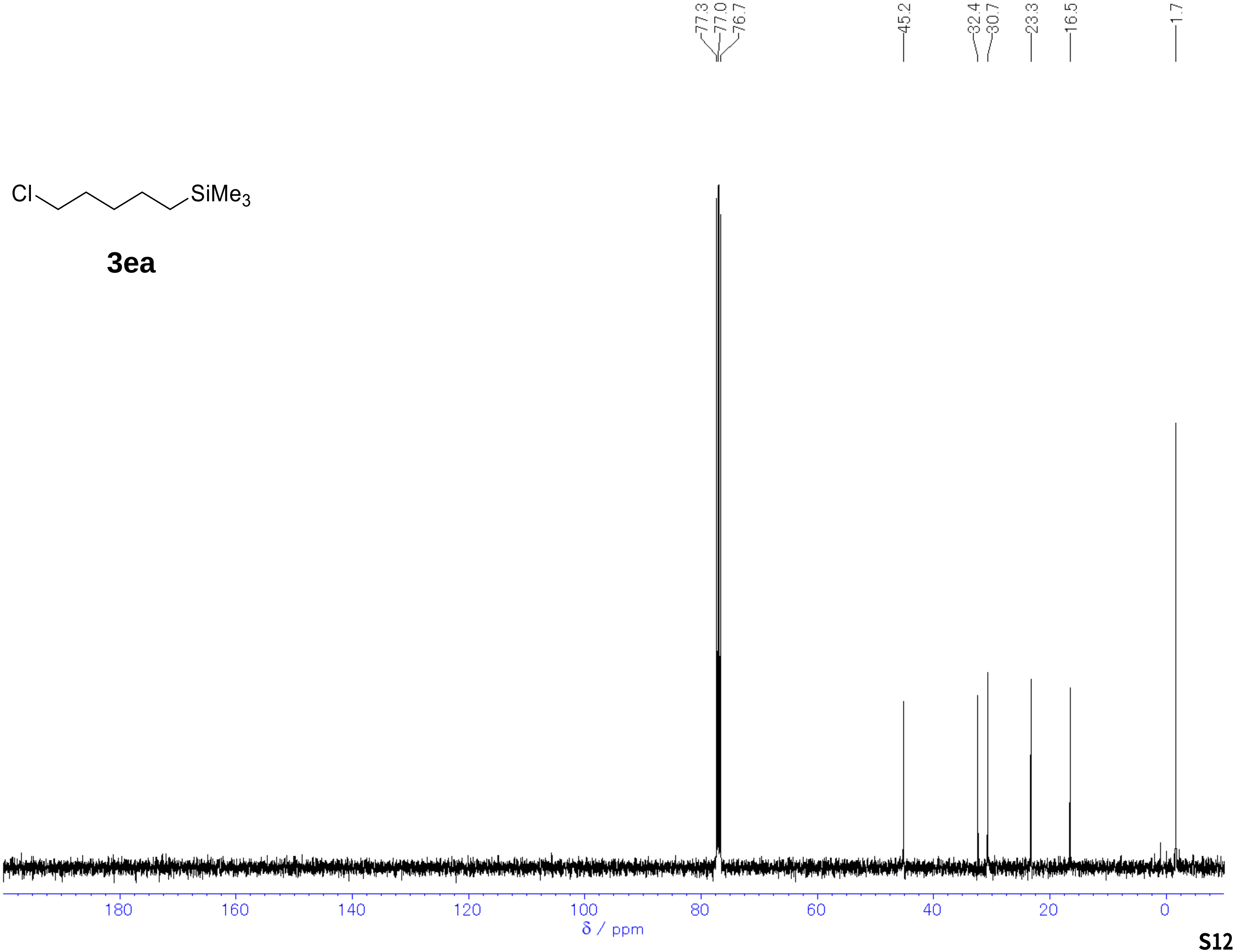
7.26
3.67
2.35
2.33
2.31
1.67
1.65
1.64
1.63
1.62
1.61
1.59
0.53
0.52
0.51
0.50
0.49
0.01
9.01
3.0
2.09
2.07
2.0
O
O
SiMe3
9
8
7
6
5
4
3
2
1
0
δ / ppm


3da

174.1
77.3
77.0
76.7
51.4
37.8
19.8
16.5
-1.8
O
O
SiMe3
180
160
140
120
100
80
60
40
20
0
δ / ppm

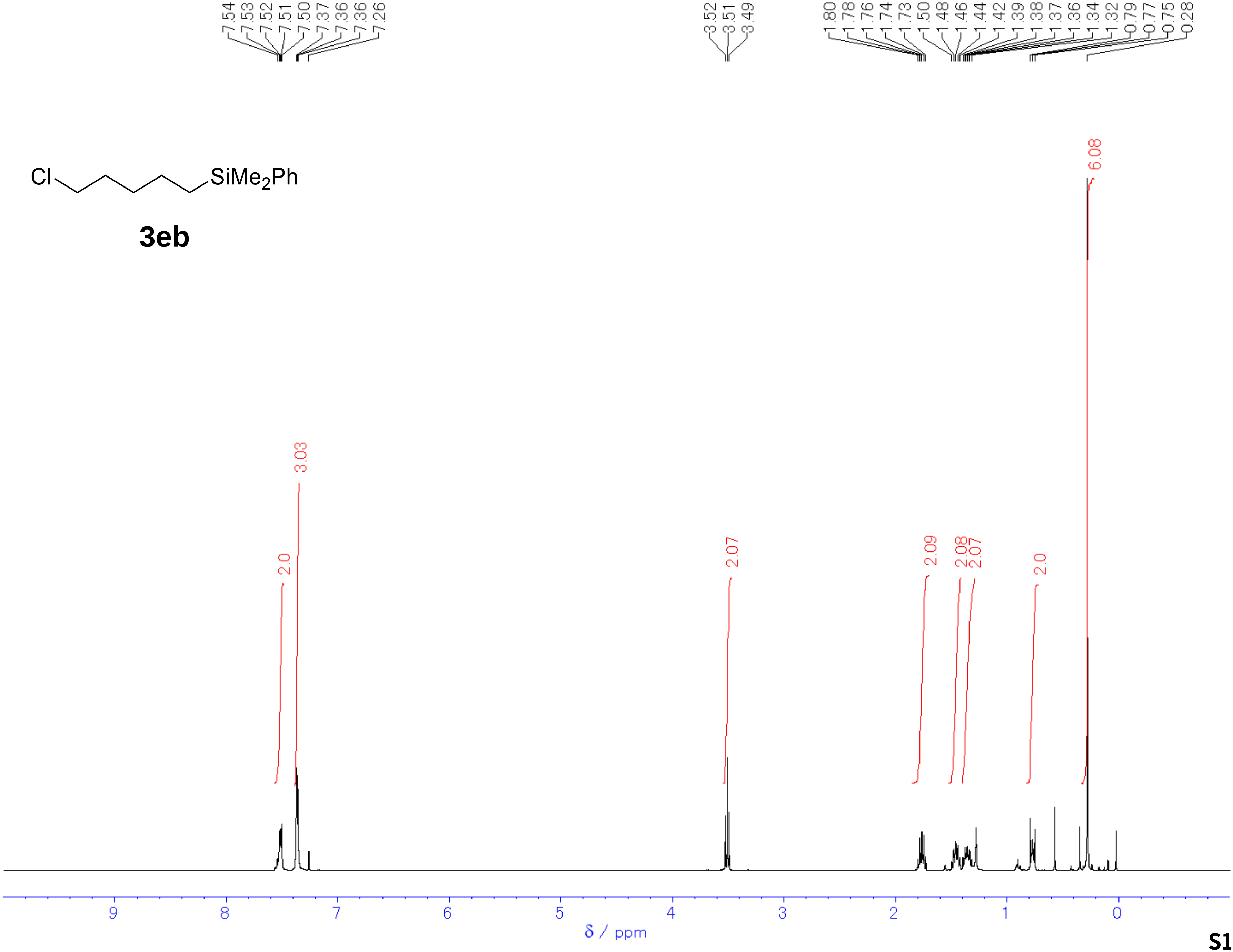

7.26
3.55
3.53
3.53
3.52
1.81
1.80
1.78
1.76
1.74
1.49
1.47
1.45
1.43
1.41
1.36
1.35
1.34
1.33
1.32
1.31
1.31
1.30
1.28
0.52
0.50
0.48
0.02
9.05
2.04
2.03
2.02
2.06
2.0
Cl
SiMe$_3$
9
8
7
6
5
4
3
2
1
0
δ / ppm

3ea

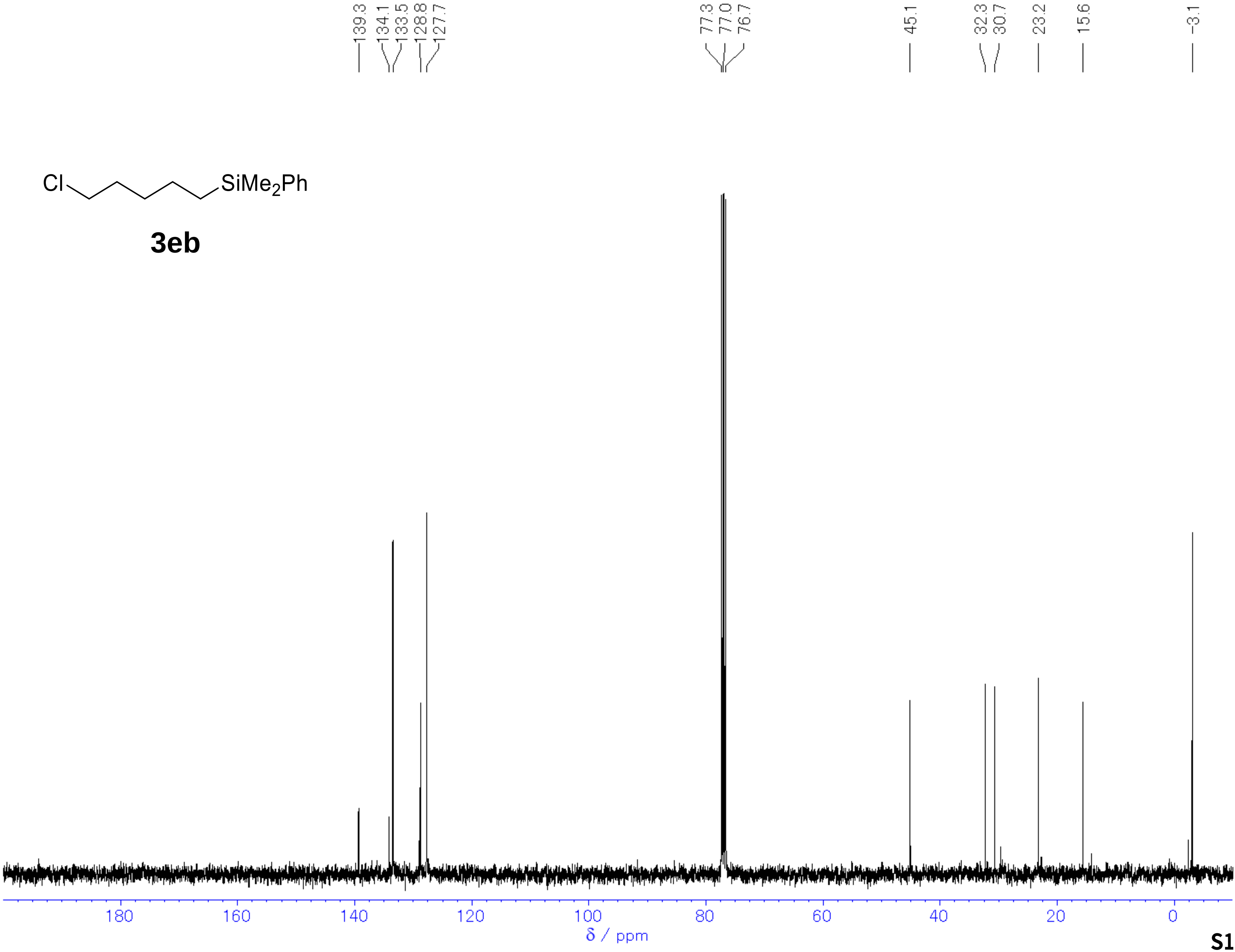


3ea

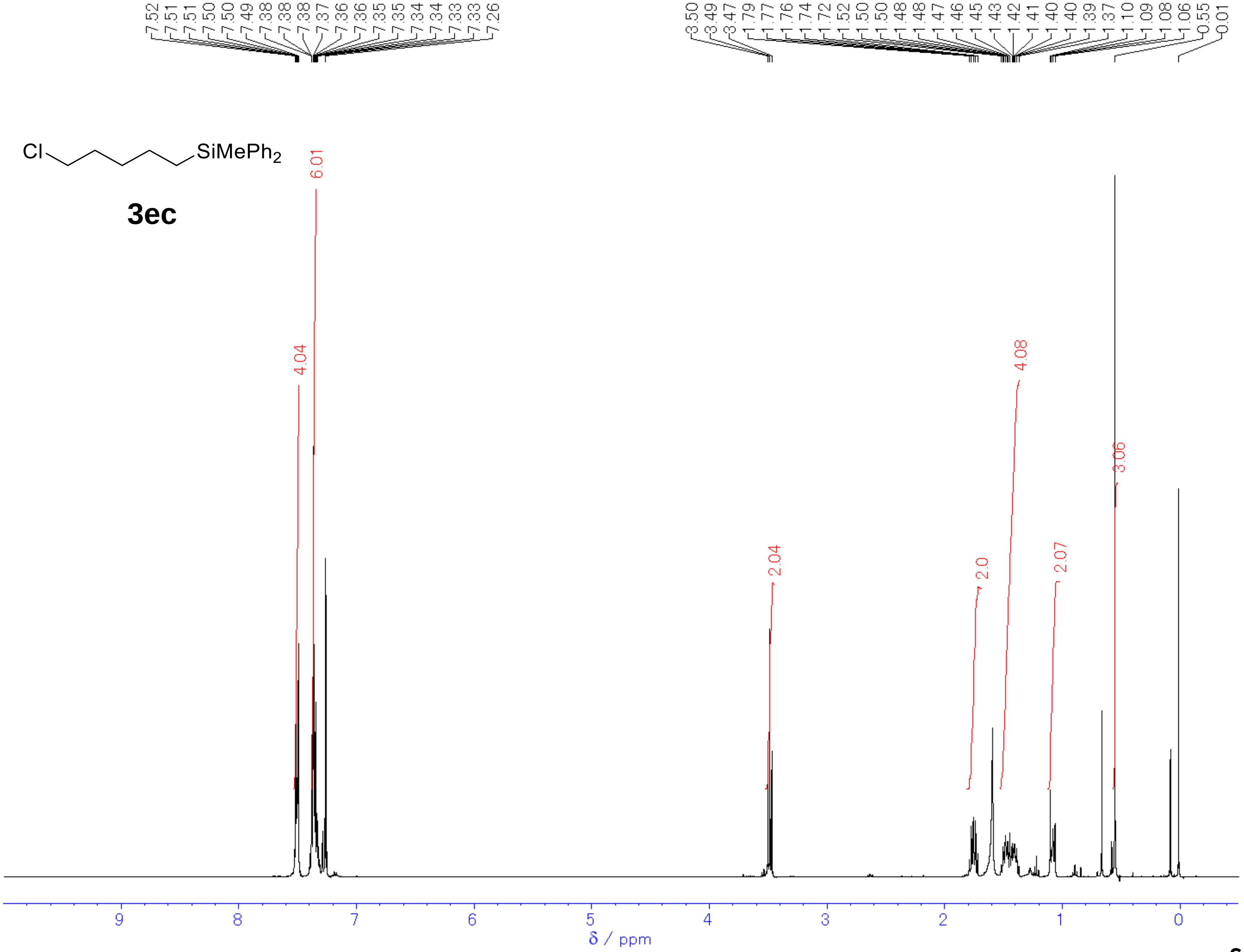
Cl
SiMe3
77.3
77.0
76.7
45.2
32.4
30.7
23.3
16.5
1.7
180
160
140
120
100
80
60
40
20
0
δ / ppm


Cl
SiMe$_2$Ph
7.54
7.53
7.52
7.51
7.50
7.37
7.36
7.36
7.26
3.52
3.51
3.49
1.80
1.78
1.76
1.74
1.73
1.50
1.48
1.46
1.44
1.42
1.39
1.38
1.37
1.36
1.34
1.32
0.79
0.77
0.75
0.28
2.0
3.03
2.07
2.09
2.08
2.07
2.0
6.08
9
8
7
6
5
4
3
2
1
0
δ / ppm

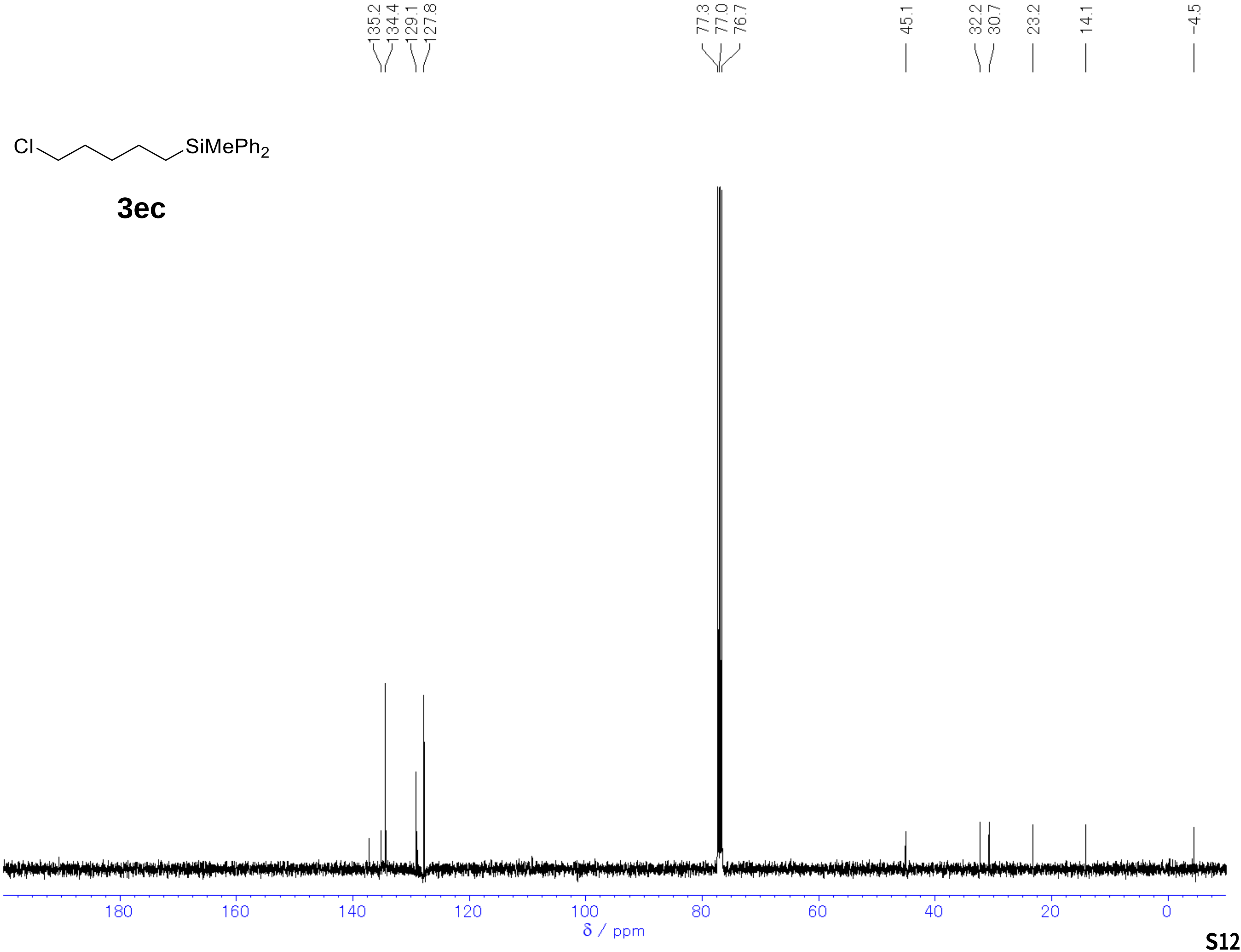
3eb


139.3
134.1
133.5
128.8
127.7
77.3
77.0
76.7
45.1
32.3
30.7
23.2
15.6
−3.1
Cl
SiMe$_2$Ph
180
160
140
120
100
80
60
40
20
0
δ / ppm

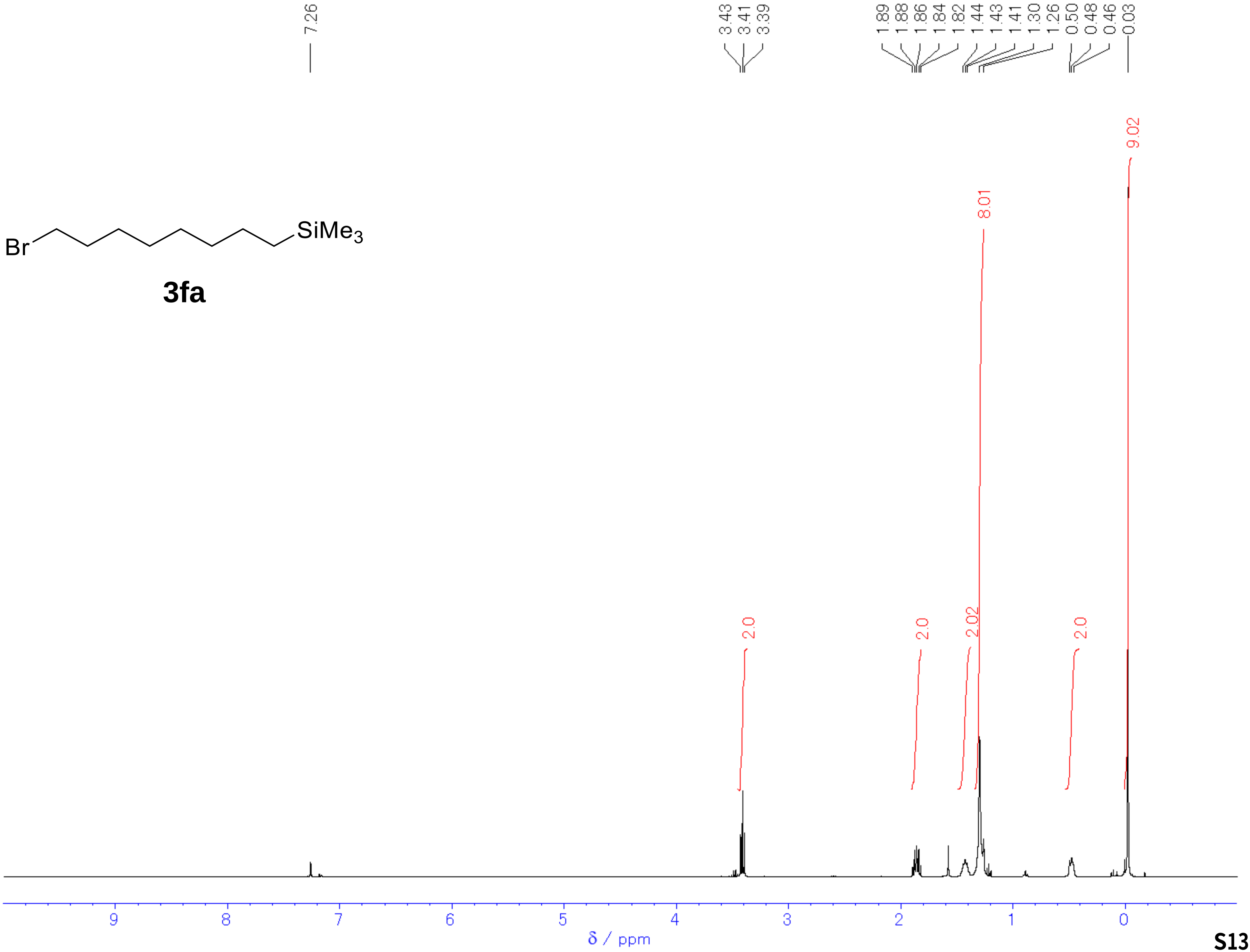
3eb


7.52
7.51
7.51
7.50
7.50
7.49
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.26
3.50
3.49
3.47
1.79
1.77
1.76
1.74
1.72
1.52
1.50
1.50
1.48
1.48
1.47
1.46
1.45
1.43
1.42
1.41
1.40
1.40
1.39
1.37
1.10
1.09
1.08
1.06
0.55
0.01
Cl
SiMePh$_2$
4.04
6.01
2.04
2.0
4.08
2.07
3.06
9
8
7
6
5
4
3
2
1
0
δ / ppm

3ec

135.2
134.4
129.1
127.8
77.3
77.0
76.7
45.1
32.2
30.7
23.2
14.1
-4.5
Cl
SiMePh$_2$
180
160
140
120
100
80
60
40
20
0
δ / ppm

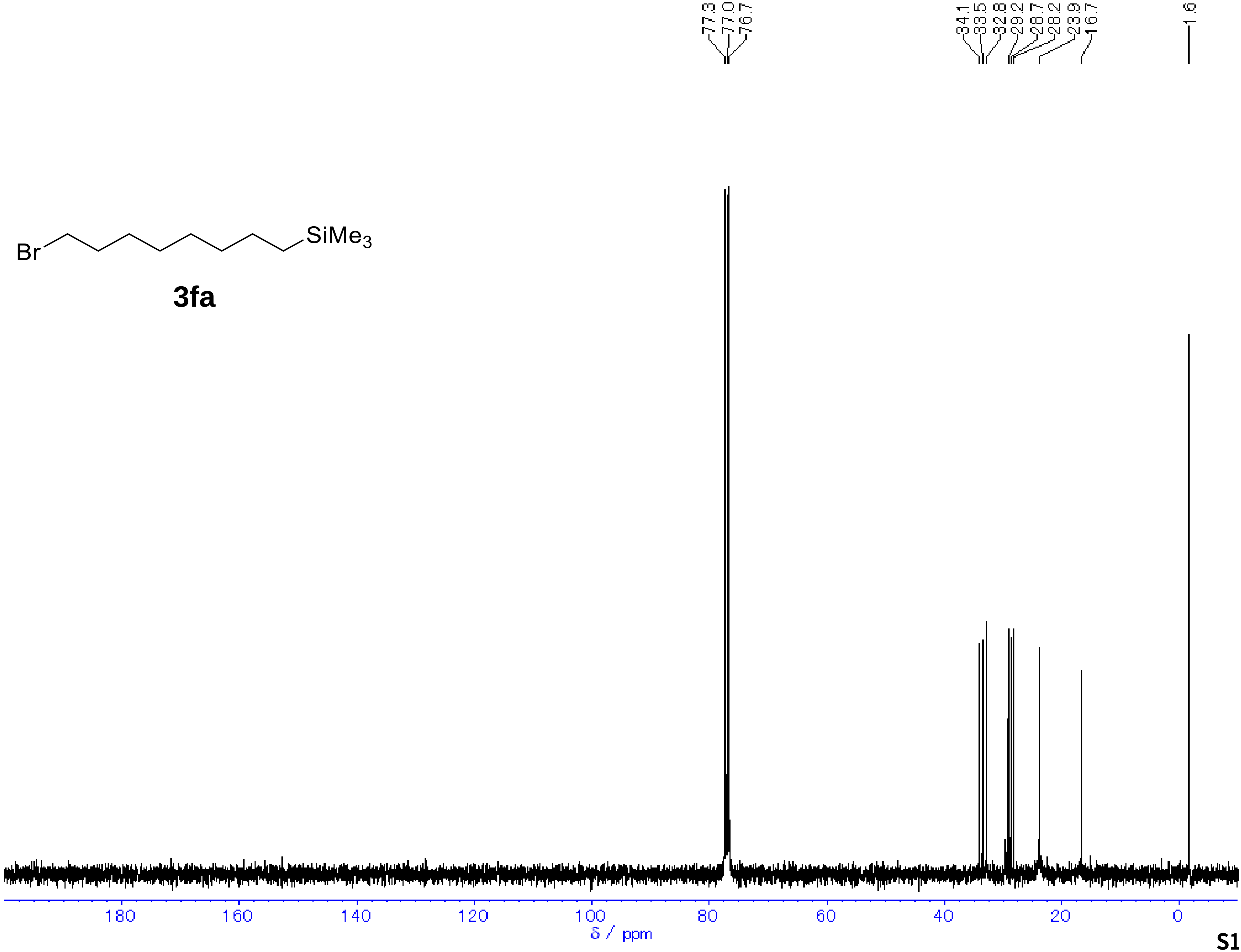
3ec

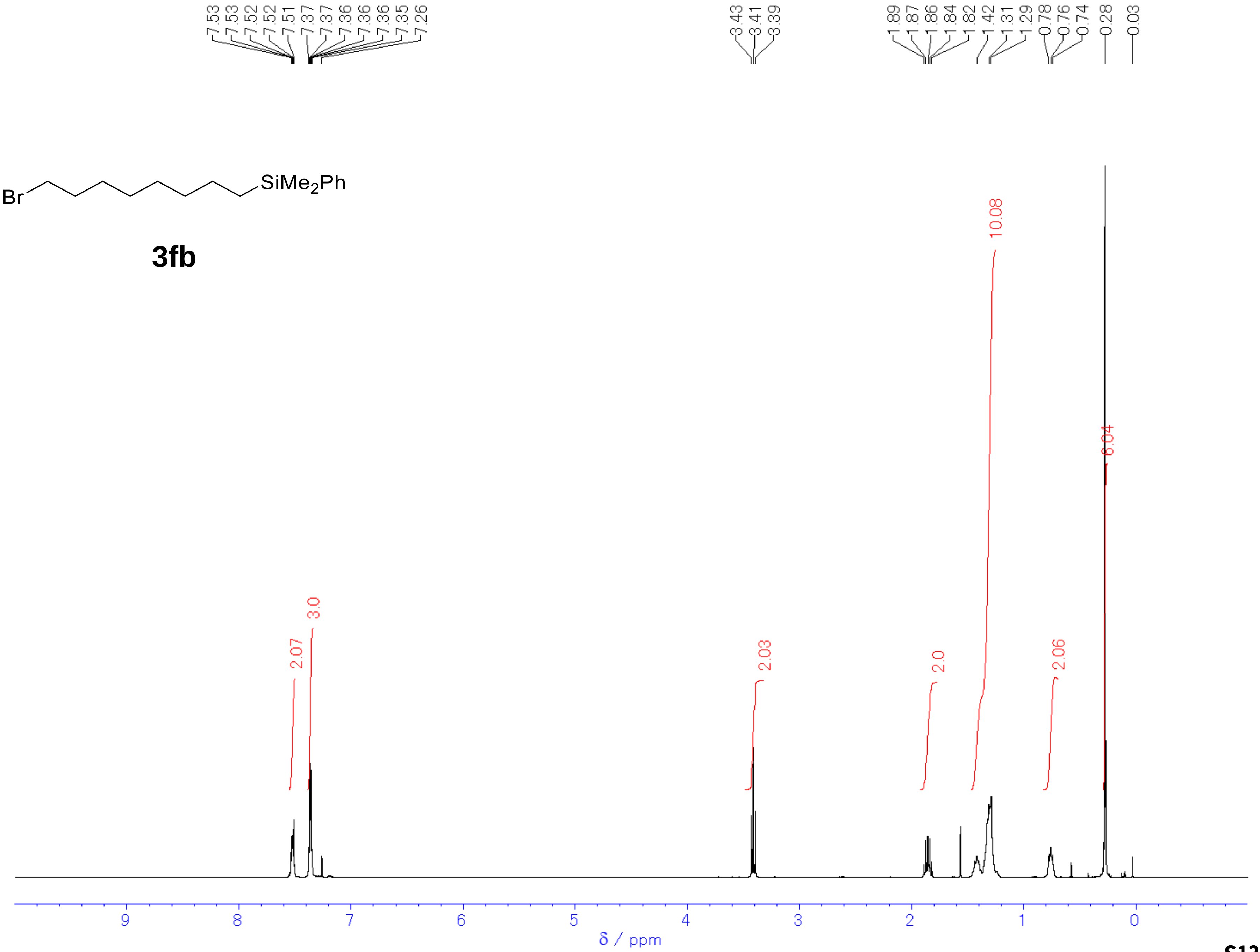

7.26
3.43
3.41
3.39
1.89
1.88
1.86
1.84
1.82
1.44
1.43
1.41
1.30
1.26
0.50
0.48
0.46
0.03
9.02
8.01
2.0
2.0
2.02
2.0
Br
SiMe3
9
8
7
6
5
4
3
2
1
0
δ / ppm

3fa

Br
SiMe3

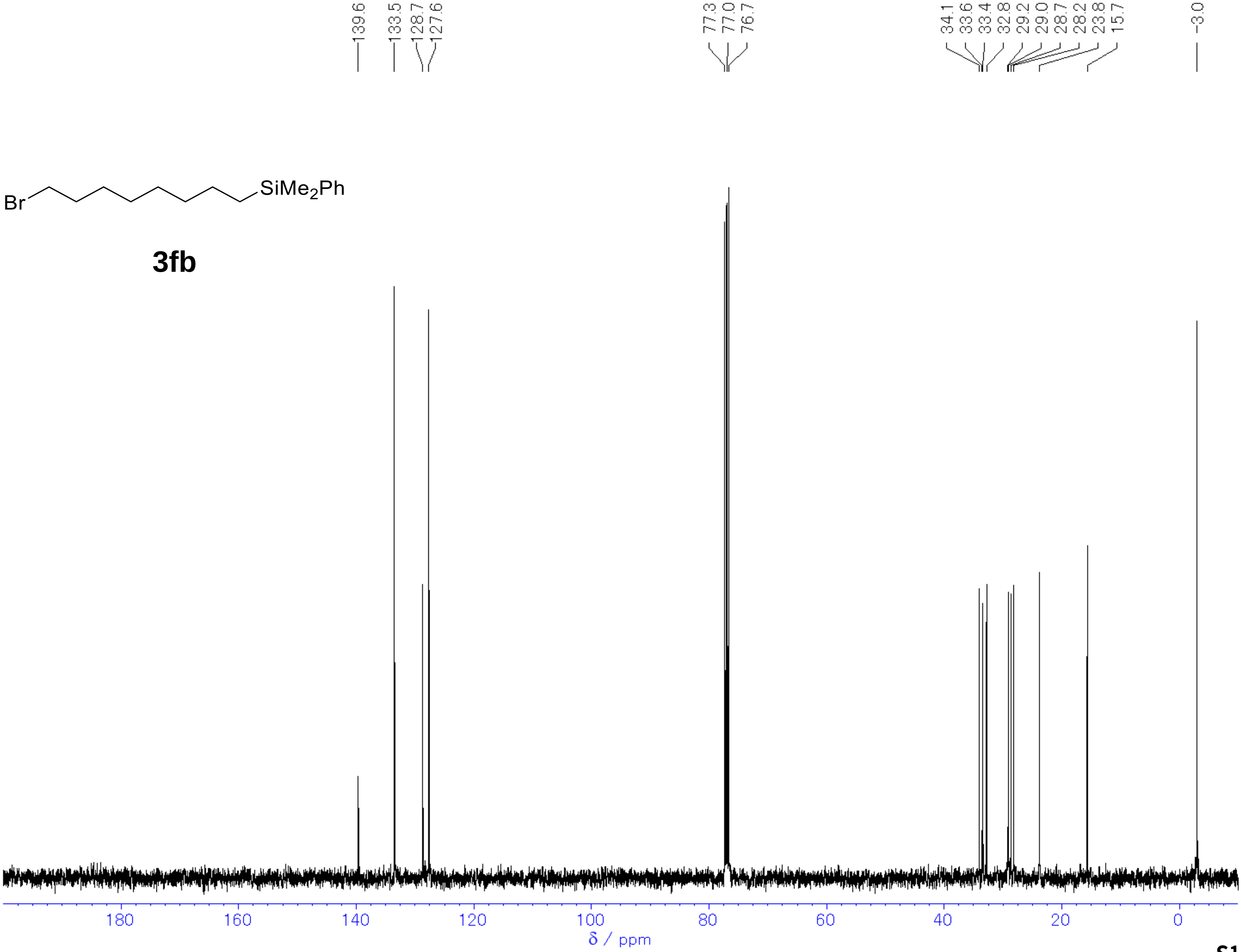
3fa


77.3
77.0
76.7
34.1
33.5
32.8
29.2
28.7
28.2
23.9
16.7
-1.6
180
160
140
120
100
80
60
40
20
0
δ / ppm

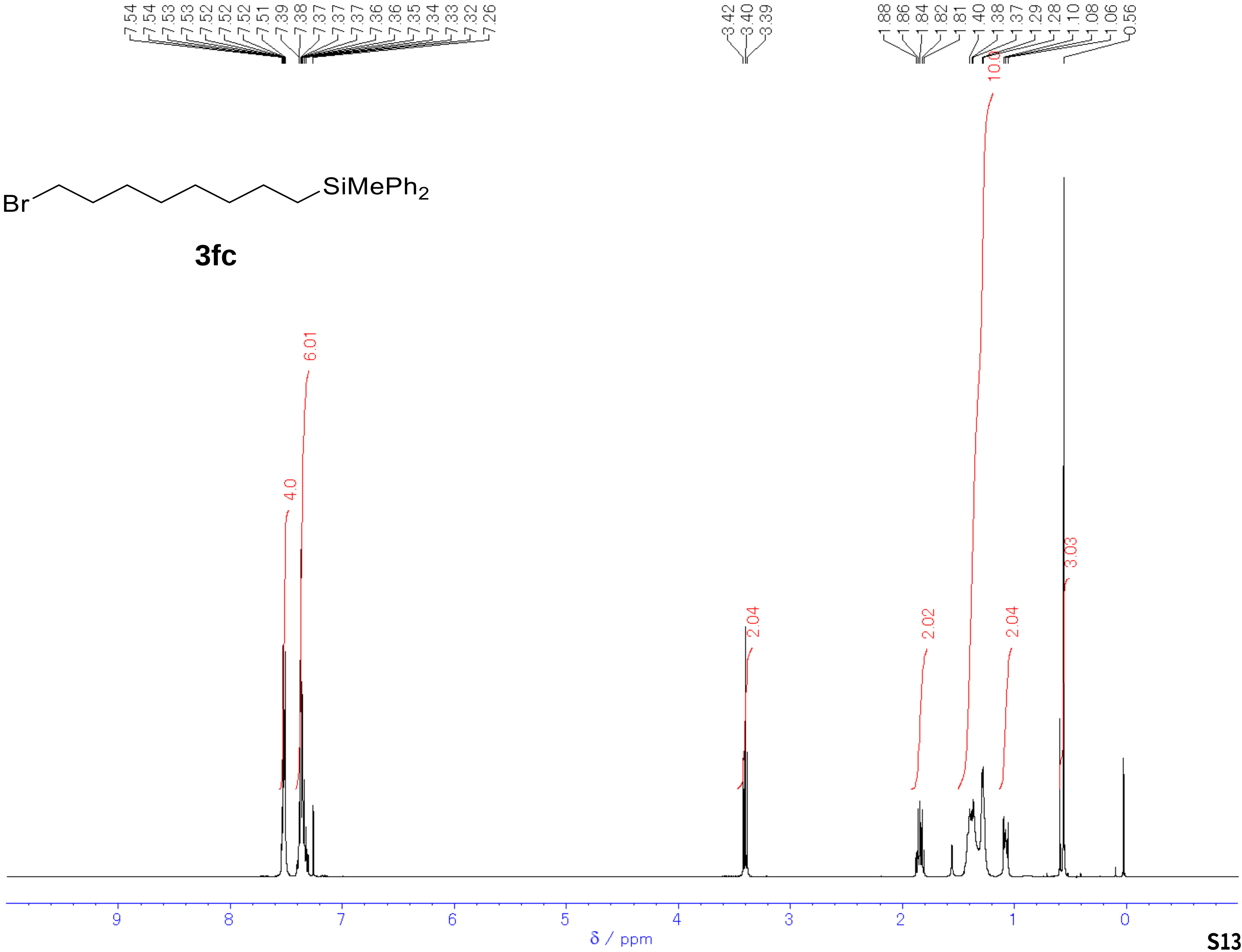


3fb

Br
SiMe$_2$Ph
7.53
7.53
7.52
7.52
7.51
7.37
7.37
7.36
7.36
7.36
7.35
7.26
3.43
3.41
3.39
1.89
1.87
1.86
1.84
1.82
1.42
1.31
1.29
0.78
0.76
0.74
0.28
0.03
2.07
3.0
2.03
2.0
10.08
2.06
6.04
9
8
7
6
5
4
3
2
1
0
δ / ppm

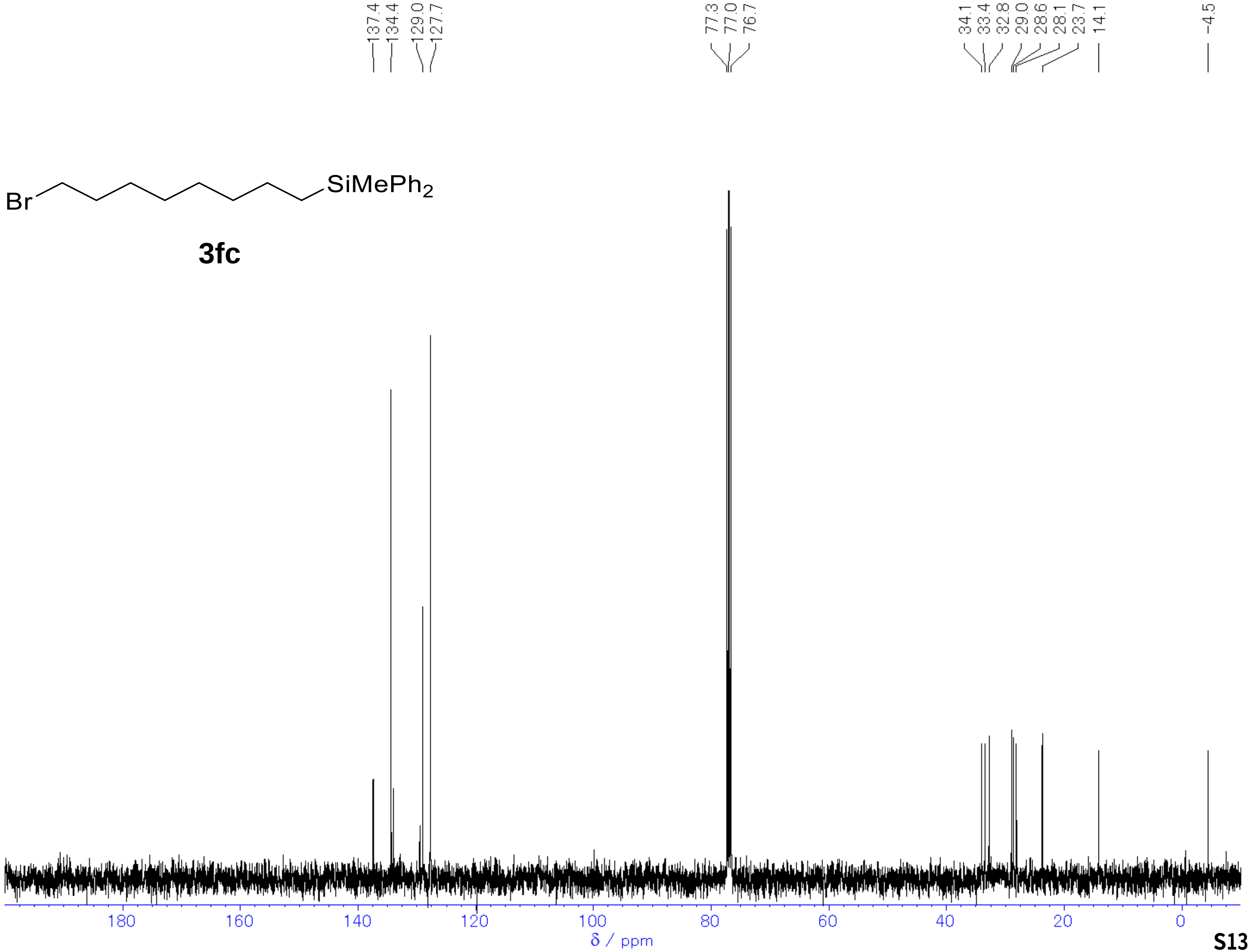

3fb

Br
SiMe$_2$Ph
139.6
133.5
128.7
127.6
77.3
77.0
76.7
34.1
33.6
33.4
32.8
29.2
29.0
28.7
28.2
23.8
15.7
-3.0
180
160
140
120
100
80
60
40
20
0
δ / ppm



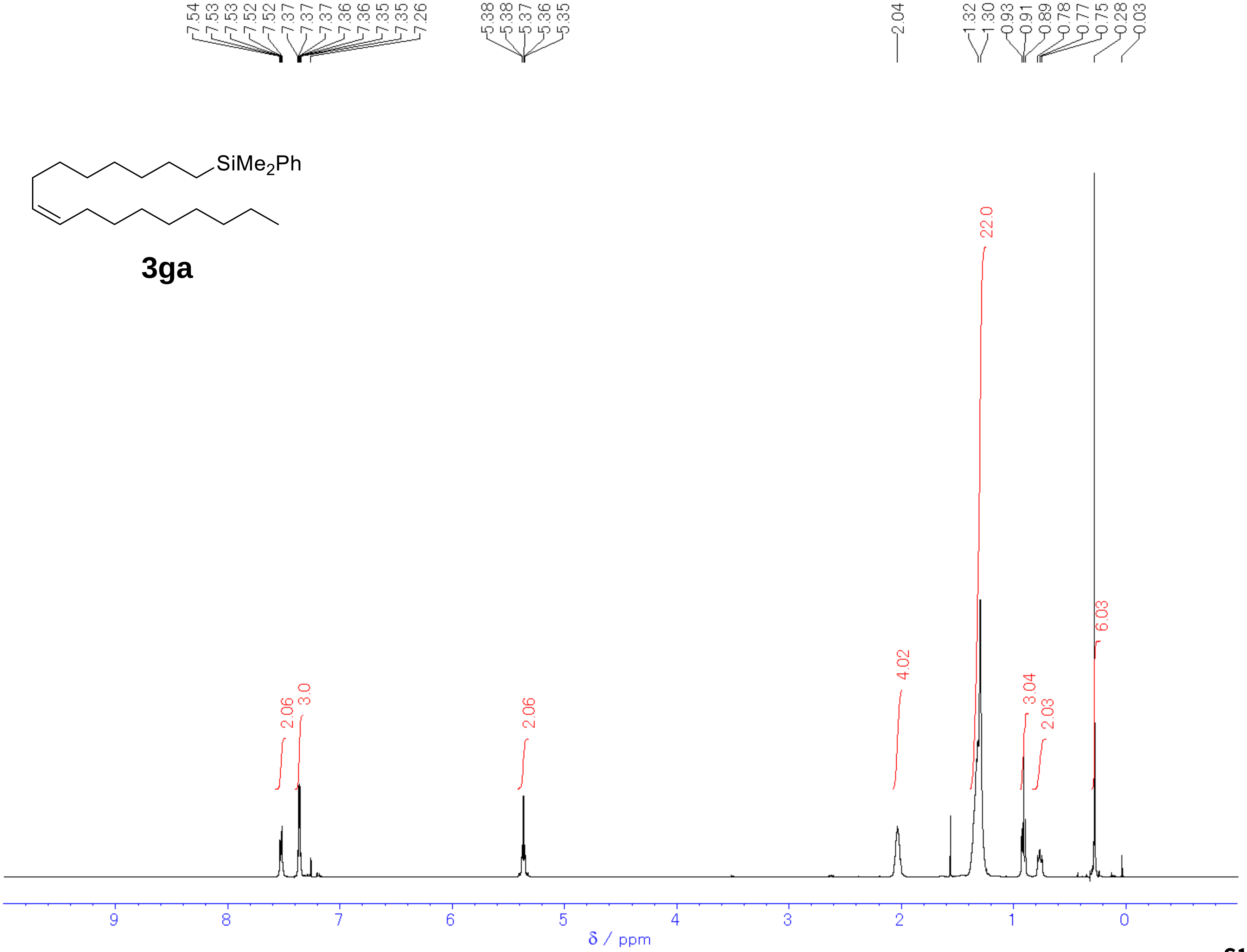
3fc

7.54
7.54
7.53
7.53
7.52
7.52
7.52
7.51
7.39
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.26
3.42
3.40
3.39
1.88
1.86
1.84
1.82
1.81
1.40
1.38
1.37
1.29
1.28
1.10
1.08
1.06
0.56
Br
SiMePh2
4.0
6.01
2.04
2.02
10.0
2.04
3.03
9
8
7
6
5
4
3
2
1
0
δ / ppm

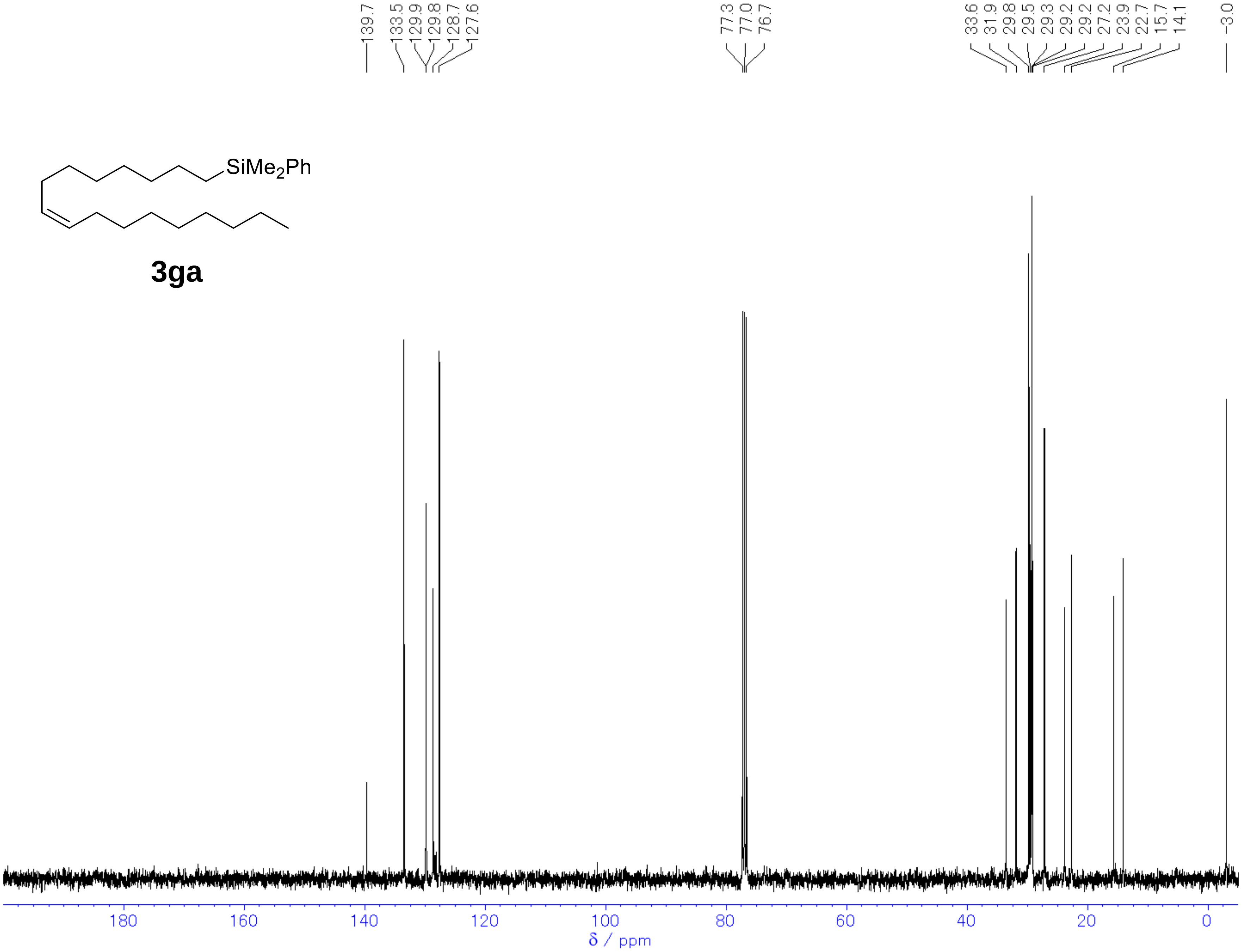


137.4
134.4
129.0
127.7
77.3
77.0
76.7
34.1
33.4
32.8
29.0
28.6
28.1
23.7
14.1
-4.5
Br
SiMePh$_2$
180
160
140
120
100
80
60
40
20
0
δ / ppm

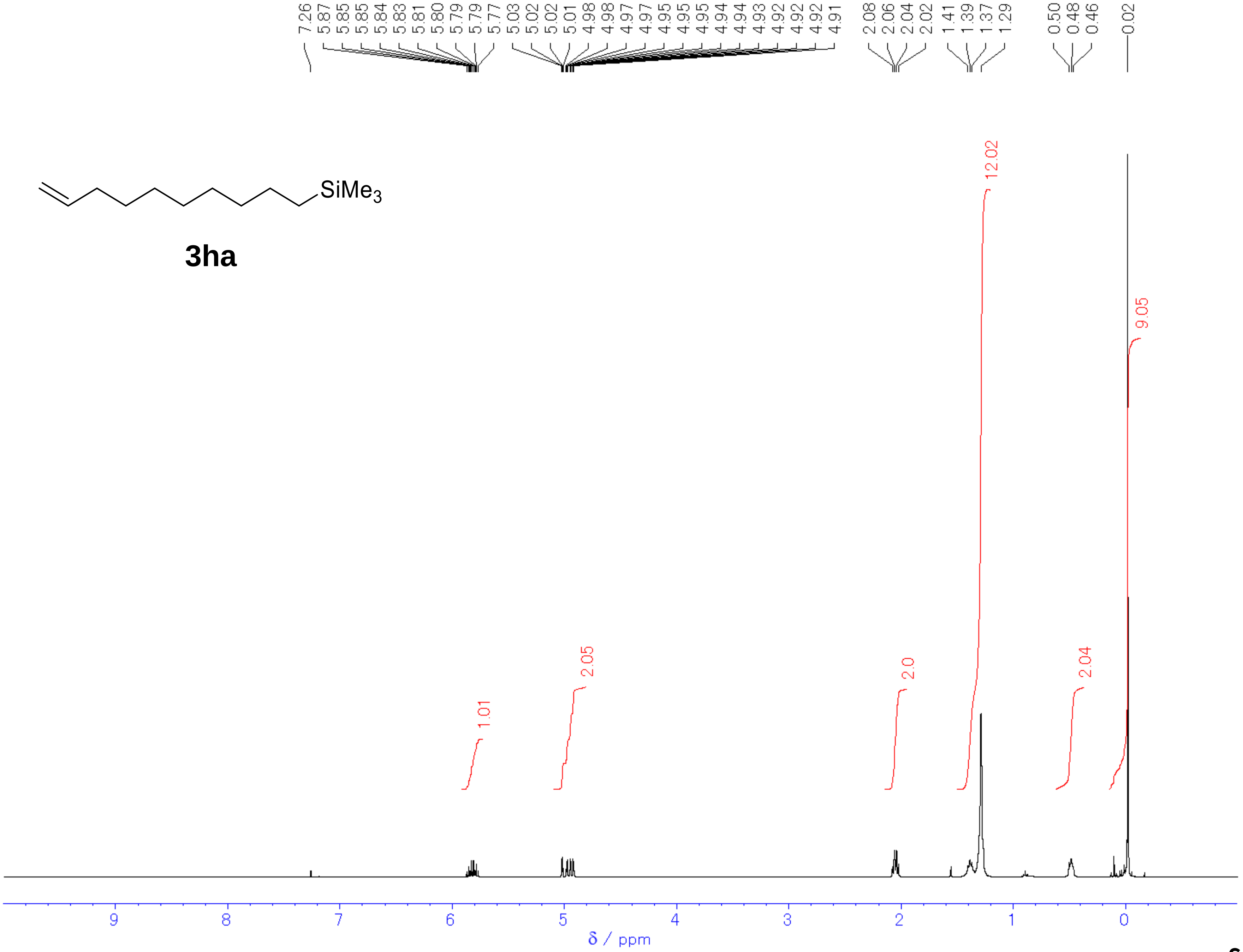
3fc


7.54
7.53
7.53
7.52
7.52
7.37
7.37
7.37
7.36
7.36
7.35
7.35
7.26
5.38
5.38
5.37
5.37
5.36
5.35
2.04
1.32
1.30
0.93
0.91
0.89
0.78
0.77
0.75
0.28
0.03
SiMe$_2$Ph
22.0
6.03
4.02
3.04
2.03
2.06
3.0
2.06
9
8
7
6
5
4
3
2
1
0
δ / ppm

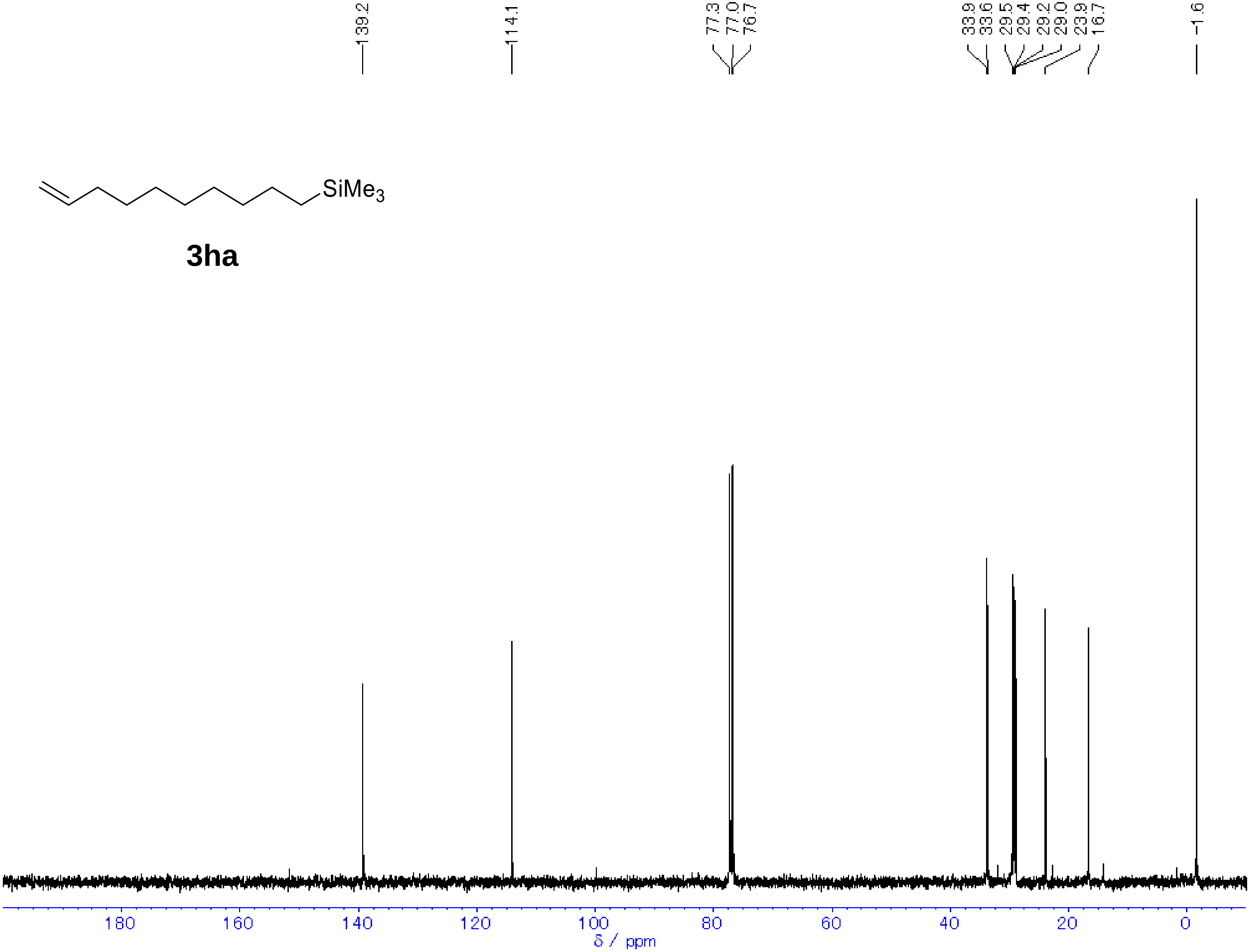
3ga

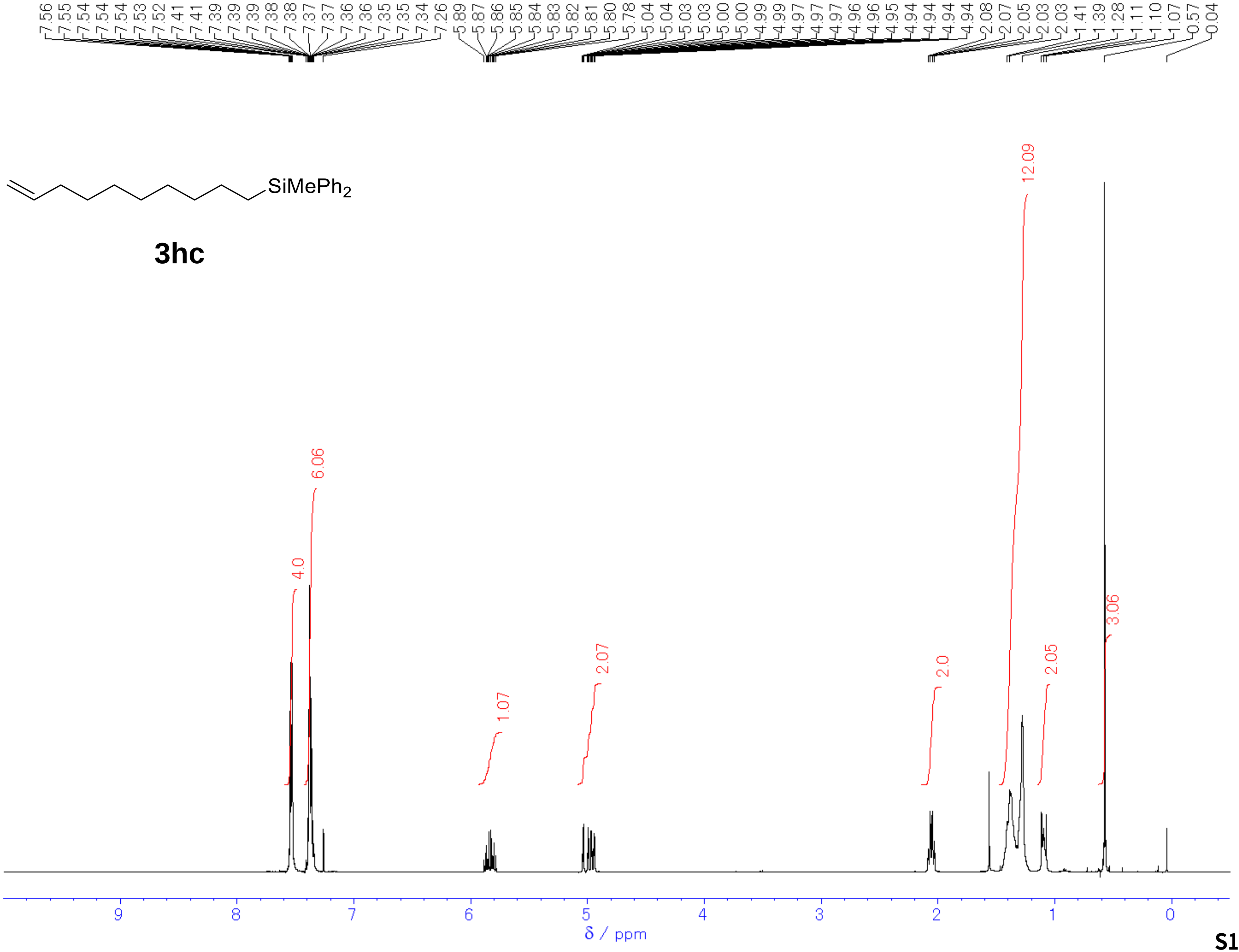

3ga

SiMe$_2$Ph
139.7
133.5
129.9
129.8
128.7
127.6
77.3
77.0
76.7
33.6
31.9
29.8
29.5
29.3
29.2
29.2
27.2
23.9
22.7
15.7
14.1
-3.0
180
160
140
120
100
80
60
40
20
0
δ / ppm

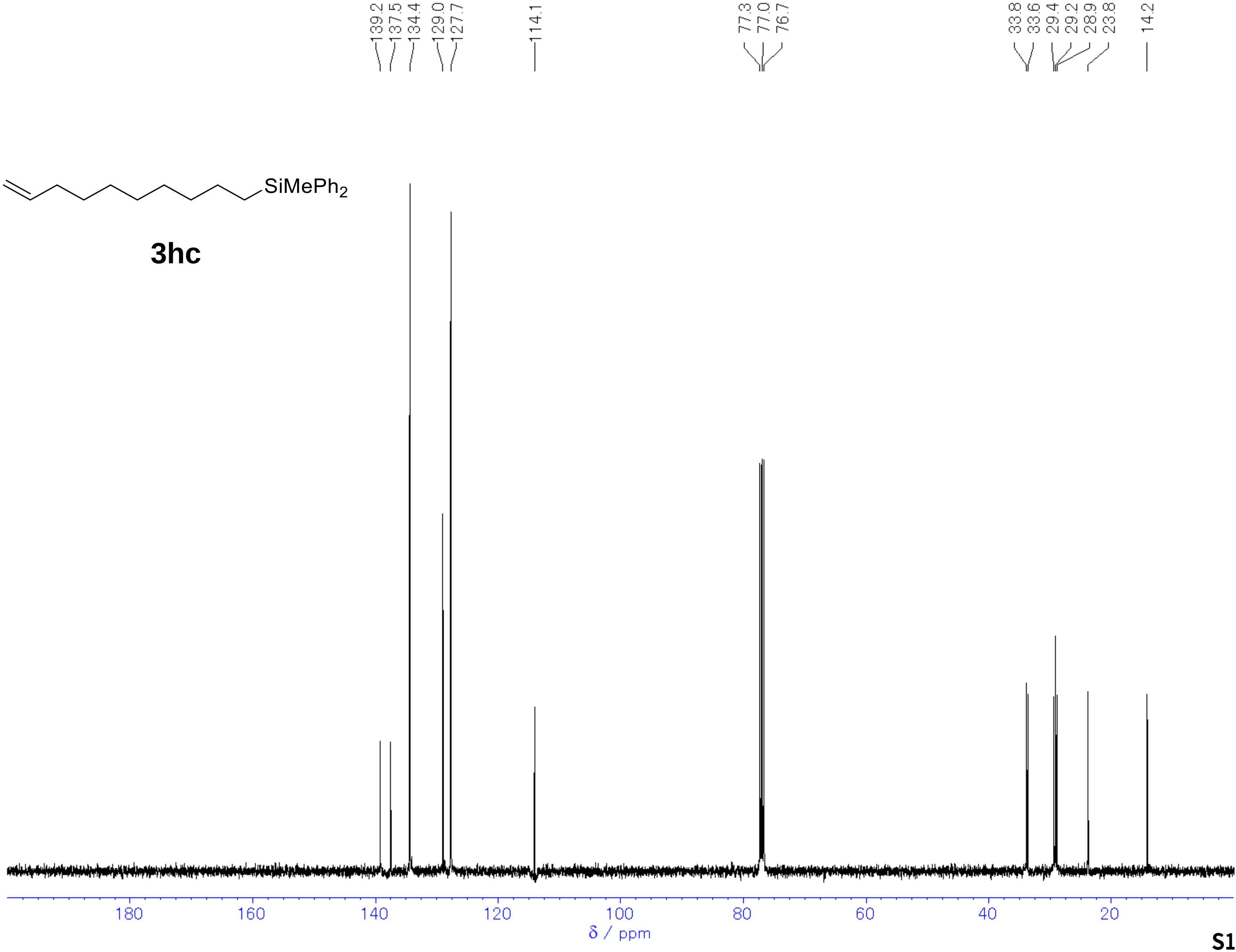

7.26
5.87
5.85
5.85
5.84
5.83
5.81
5.80
5.79
5.79
5.77
5.03
5.02
5.02
5.01
4.98
4.98
4.97
4.97
4.95
4.95
4.95
4.94
4.94
4.93
4.92
4.92
4.92
4.91
2.08
2.06
2.04
2.02
1.41
1.39
1.37
1.29
0.50
0.48
0.46
0.02
SiMe3
12.02
9.05
1.01
2.05
2.0
2.04
9
8
7
6
5
4
3
2
1
0
δ / ppm

3ha


139.2
114.1
77.3
77.0
76.7
33.9
33.6
29.5
29.4
29.2
29.0
23.9
16.7
−1.6
SiMe3
3ha
180
160
140
120
100
80
60
40
20
0
δ / ppm

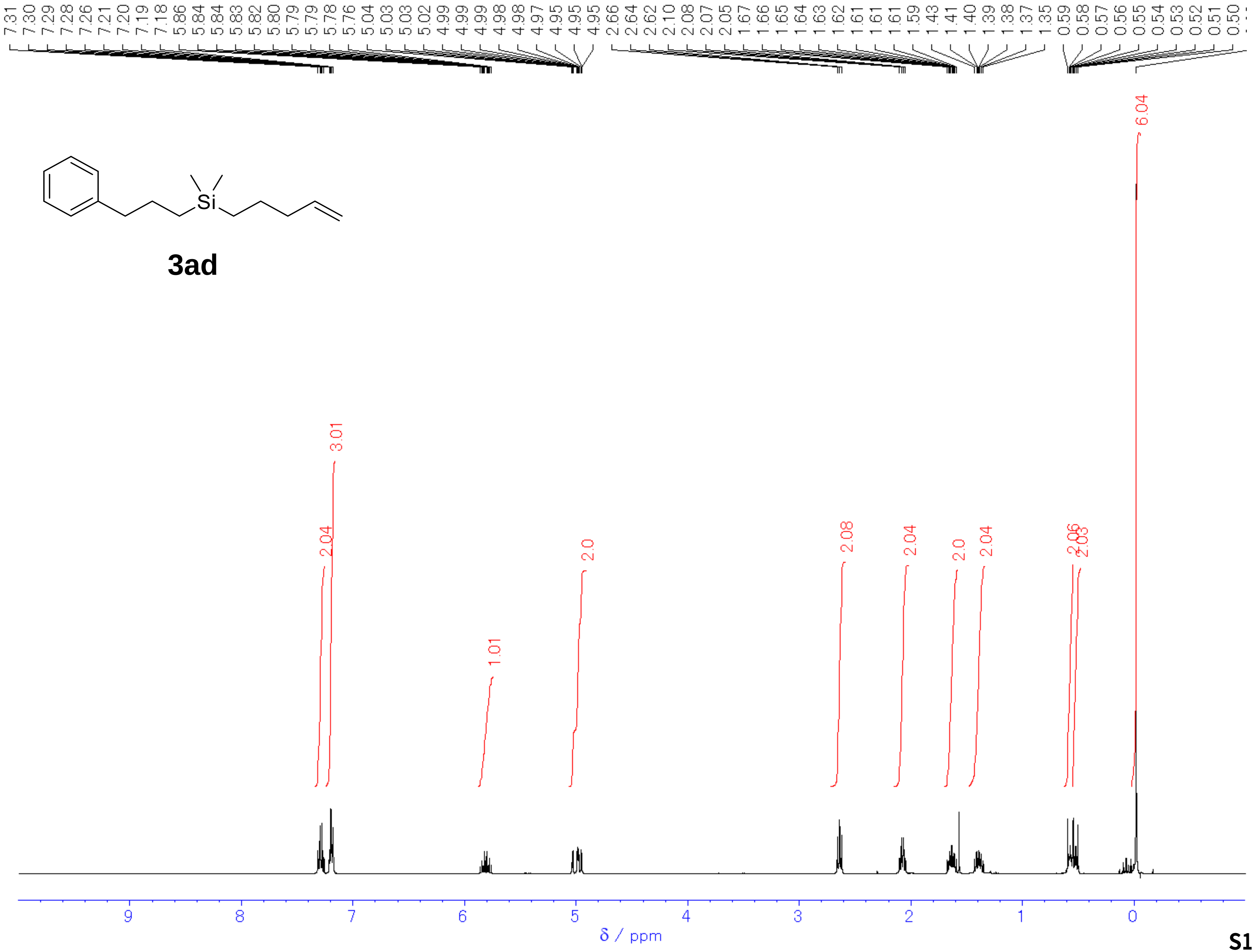

7.56 7.55 7.54 7.54 7.54 7.53 7.52 7.41 7.41 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35 7.35 7.34 7.26 5.89 5.87 5.86 5.85 5.84 5.83 5.82 5.81 5.80 5.78 5.04 5.04 5.03 5.03 5.00 5.00 4.99 4.99 4.97 4.97 4.97 4.96 4.96 4.95 4.94 4.94 4.94 4.94 2.08 2.07 2.05 2.03 2.03 1.41 1.39 1.28 1.11 1.10 1.07 0.57 0.04
SiMePh2
4.0
6.06
1.07
2.07
2.0
12.09
2.05
3.06
9
8
7
6
5
4
3
2
1
0
δ / ppm

3hc



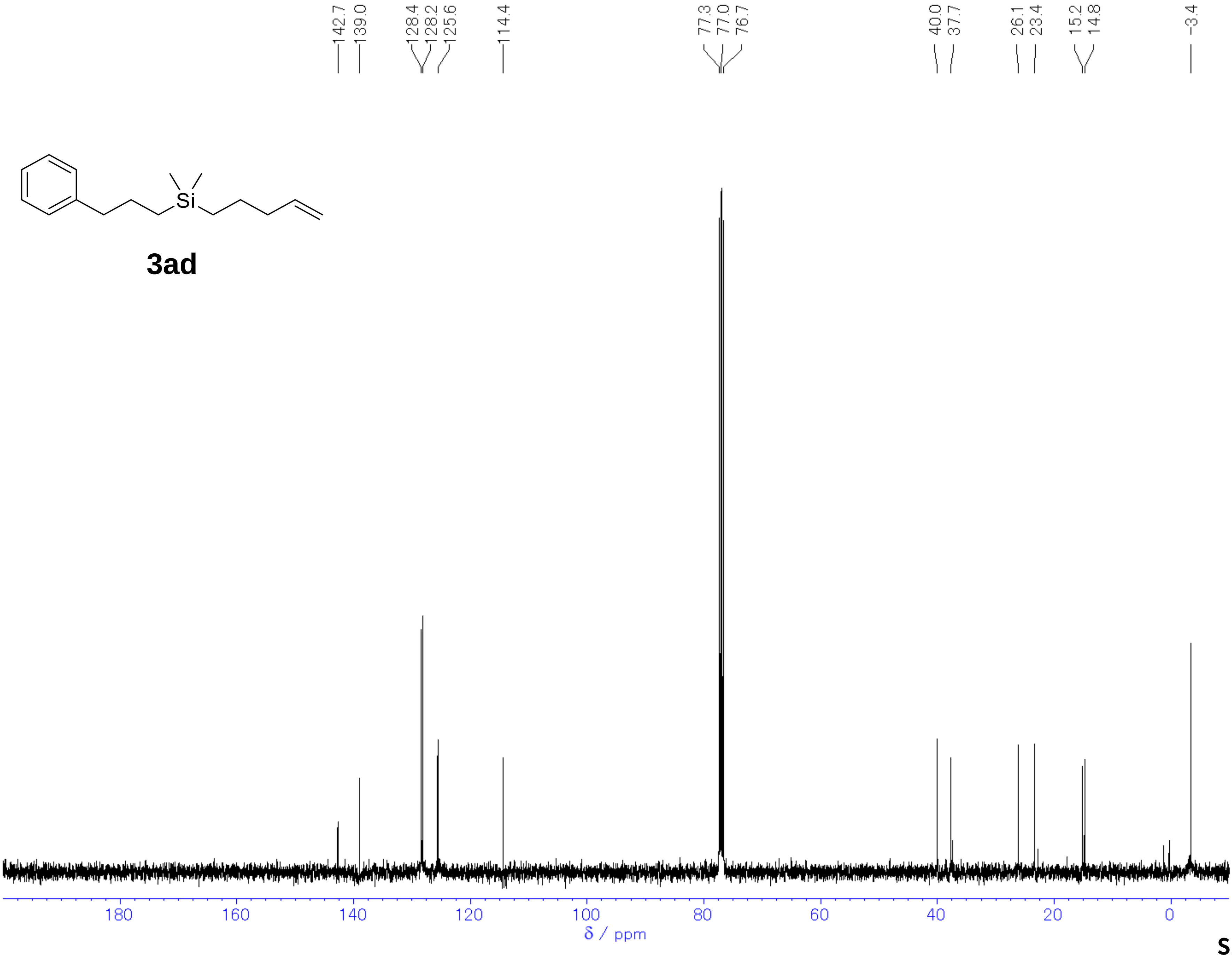
3hc

SiMePh2
139.2
137.5
134.4
129.0
127.7
114.1
77.3
77.0
76.7
33.8
33.6
29.4
29.2
28.9
23.8
14.2
180
160
140
120
100
80
60
40
20
δ / ppm



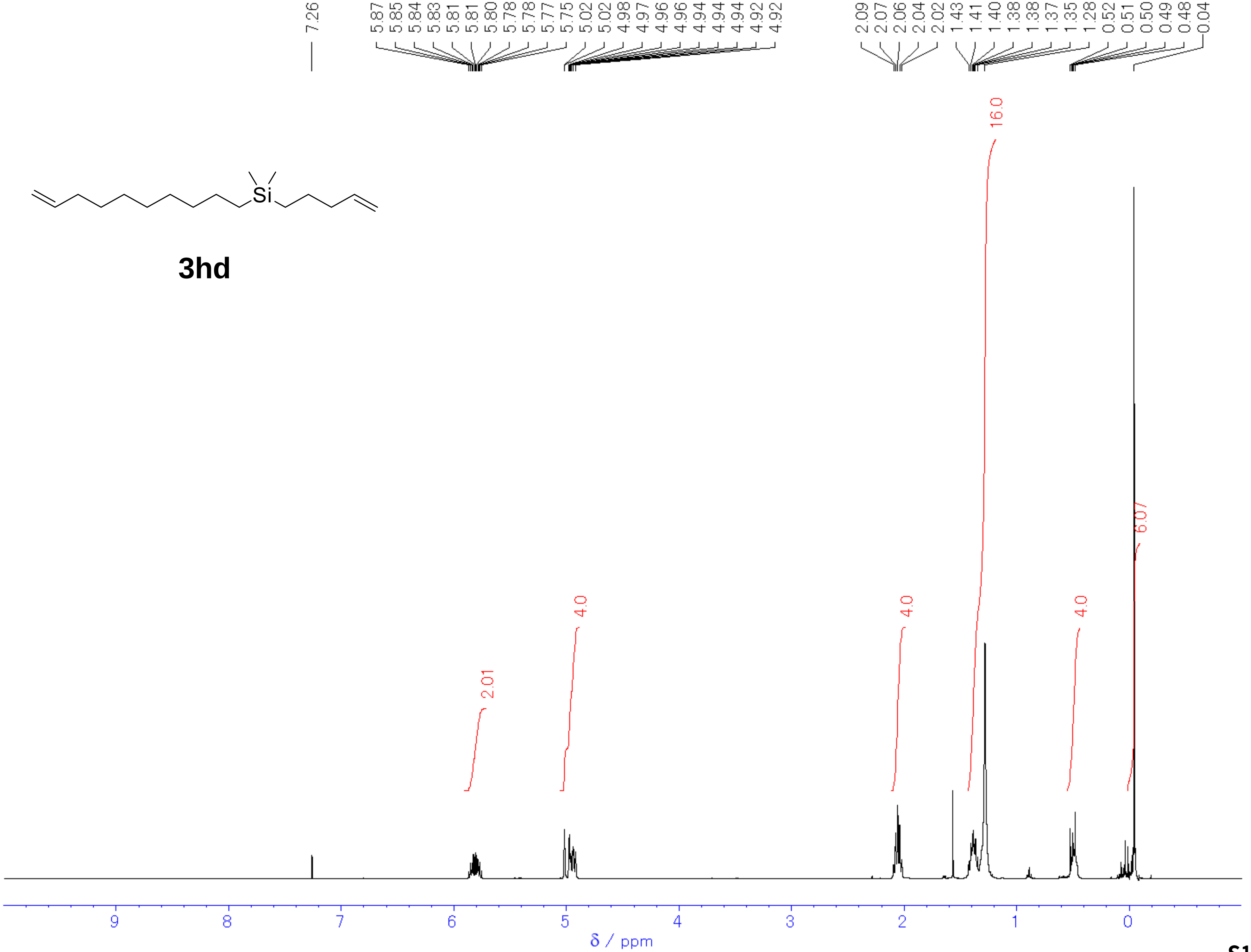
3ad

7.31
7.30
7.29
7.28
7.26
7.21
7.20
7.19
7.18
5.86
5.84
5.84
5.83
5.82
5.80
5.79
5.79
5.78
5.76
5.04
5.03
5.03
5.02
4.99
4.99
4.99
4.98
4.98
4.97
4.95
4.95
4.95
2.66
2.64
2.62
2.10
2.08
2.07
2.05
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.61
1.61
1.59
1.43
1.41
1.40
1.39
1.38
1.37
1.35
0.59
0.58
0.57
0.56
0.55
0.54
0.53
0.52
0.51
0.50
Si
2.04
3.01
1.01
2.0
2.08
2.04
2.0
2.04
2.06
2.03
6.04
9
8
7
6
5
4
3
2
1
0
δ / ppm



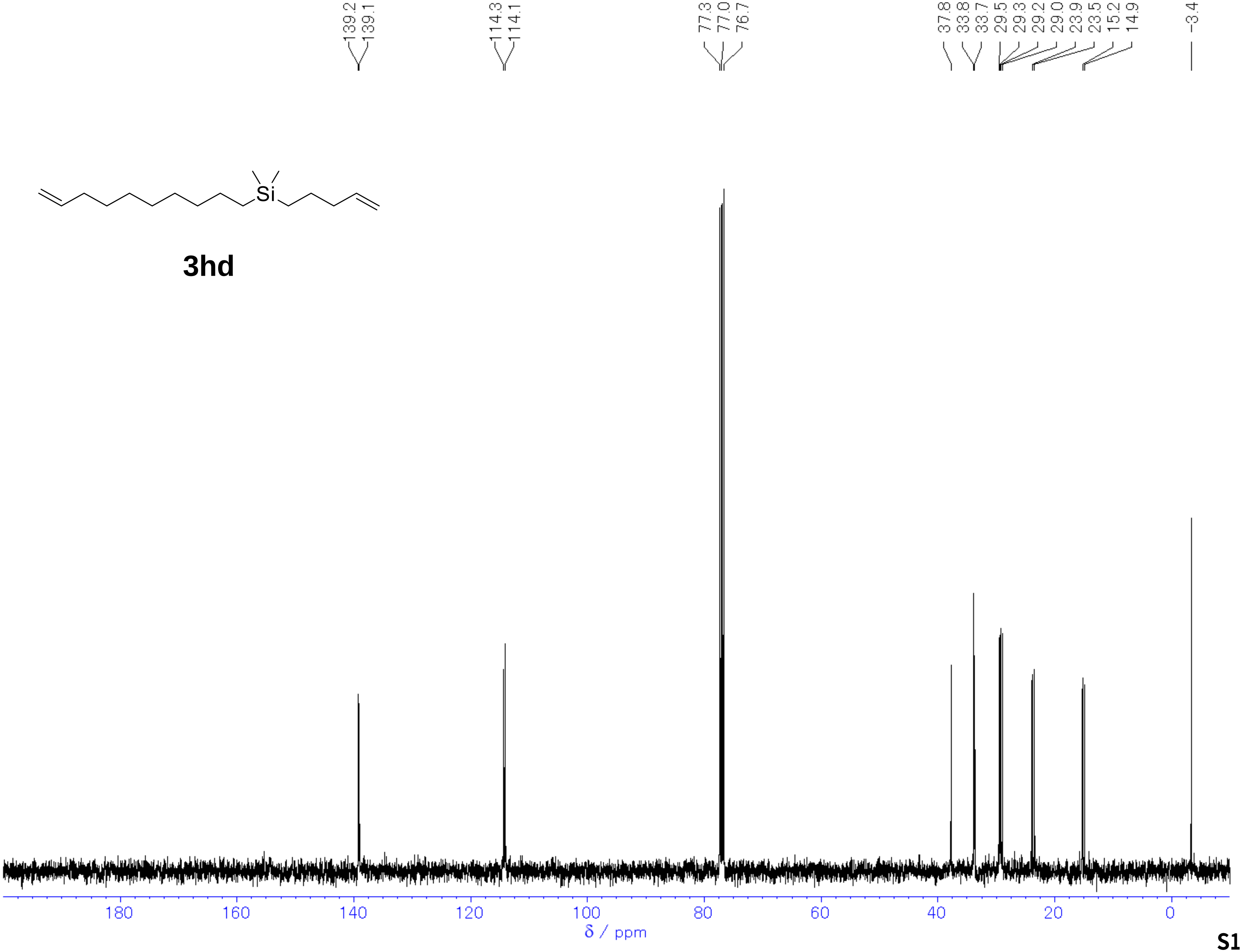
3ad

142.7
139.0
128.4
128.2
125.6
114.4
77.3
77.0
76.7
40.0
37.7
26.1
23.4
15.2
14.8
-3.4
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm



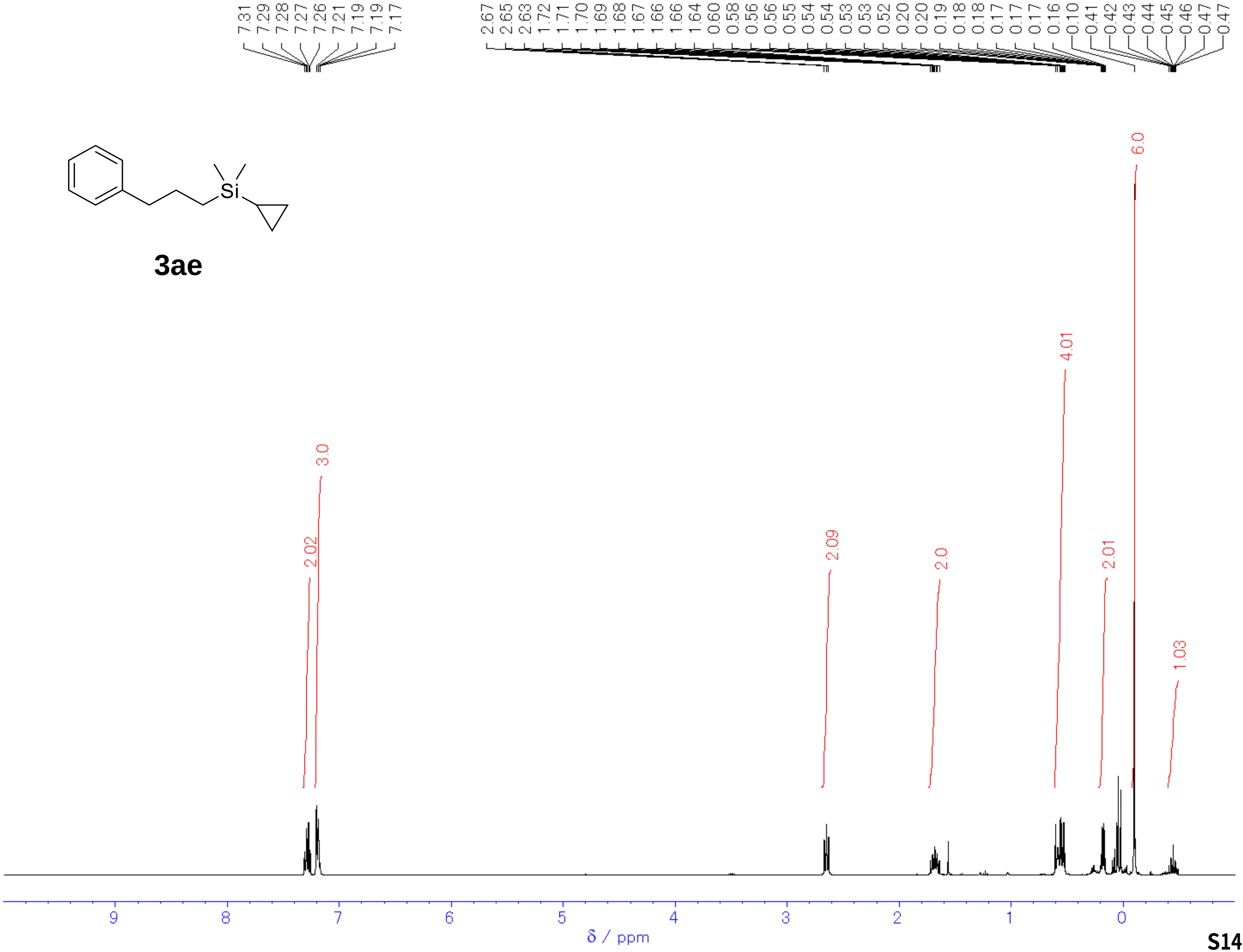
3hd

7.26
5.87
5.85
5.84
5.83
5.81
5.81
5.80
5.78
5.78
5.77
5.75
5.02
5.02
4.98
4.97
4.96
4.96
4.94
4.94
4.94
4.92
4.92
2.09
2.07
2.06
2.04
2.02
1.43
1.41
1.40
1.38
1.38
1.37
1.35
1.28
0.52
0.51
0.50
0.49
0.48
0.04
Si
16.0
6.07
4.0
4.0
2.01
4.0
4.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

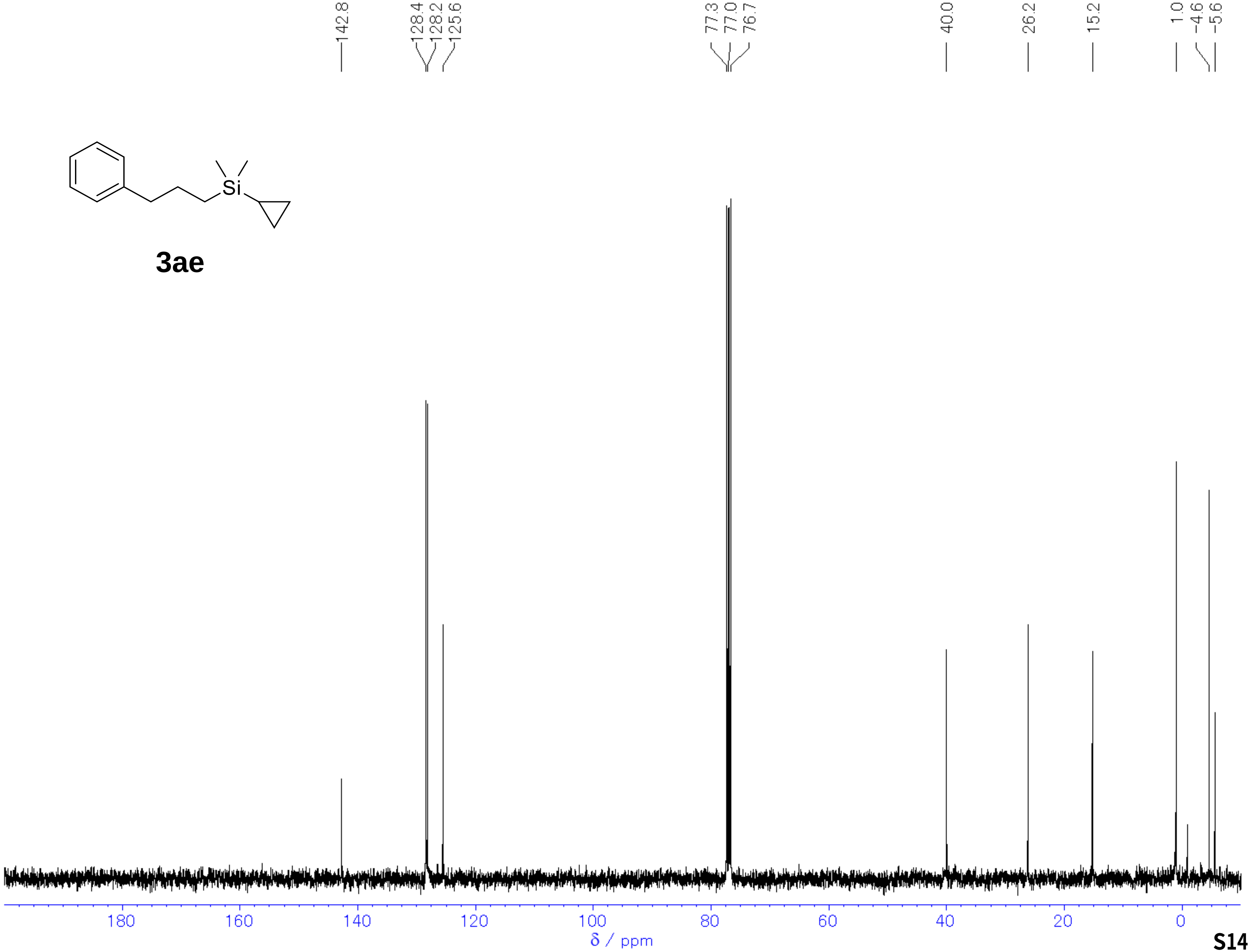


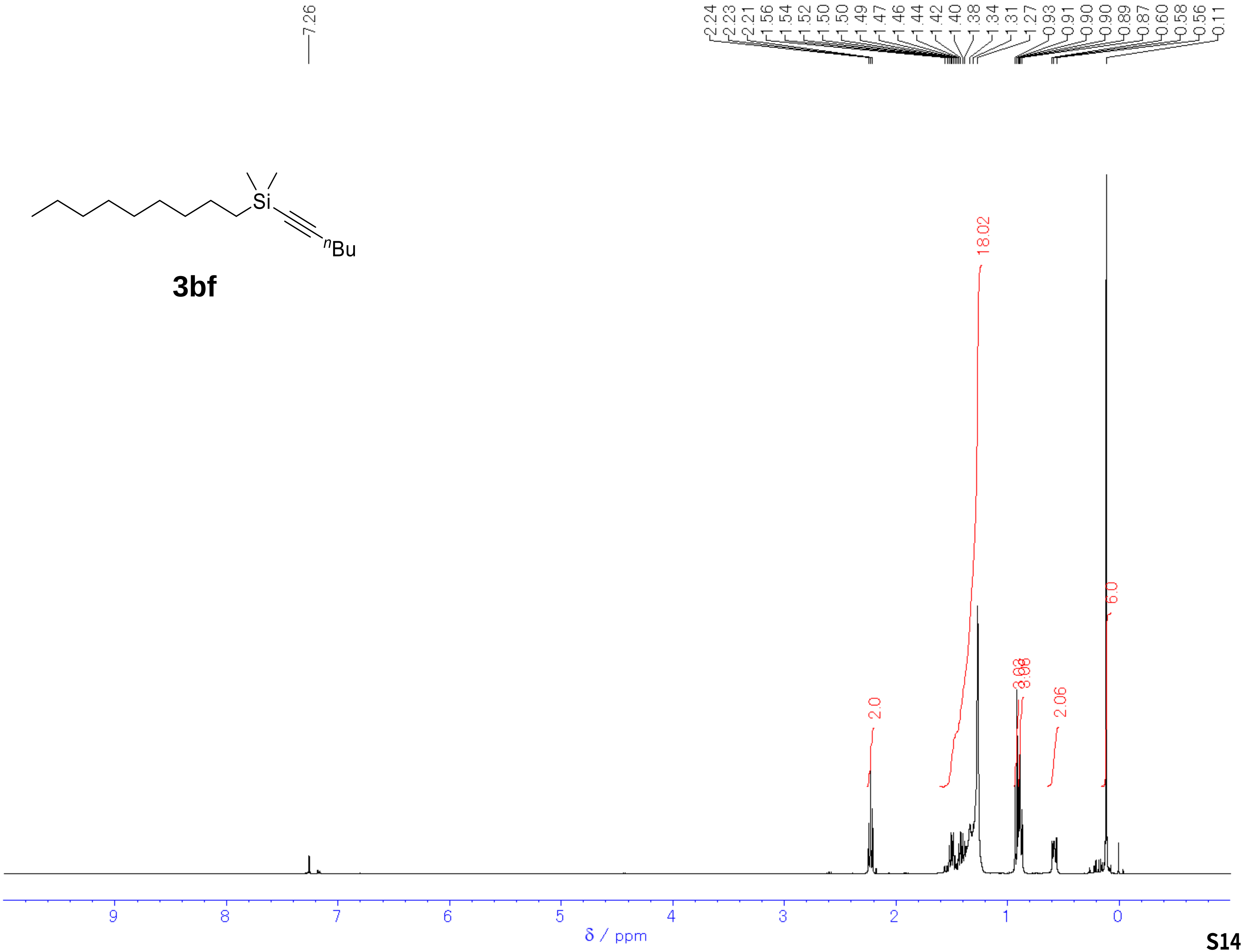
3hd

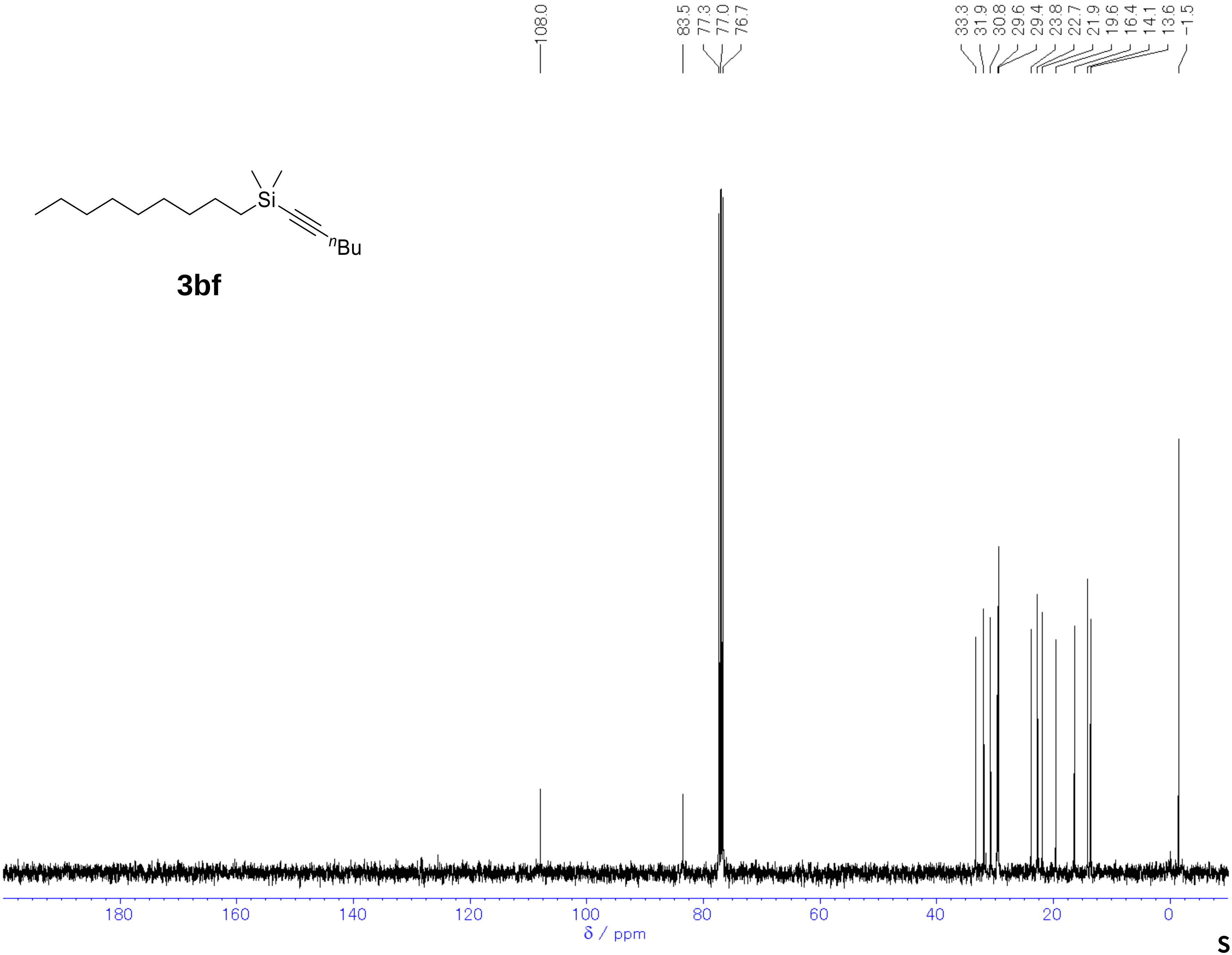
139.2
139.1
114.3
114.1
77.3
77.0
76.7
37.8
33.8
33.7
29.5
29.3
29.2
29.0
23.9
23.5
15.2
14.9
-3.4
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm


3ae

7.31
7.29
7.28
7.27
7.26
7.21
7.19
7.19
7.17
2.67
2.65
2.63
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.66
1.64
0.60
0.58
0.56
0.56
0.55
0.54
0.54
0.53
0.53
0.52
0.20
0.20
0.19
0.18
0.18
0.17
0.17
0.17
0.16
0.10
0.41
0.42
0.43
0.44
0.45
0.46
0.47
0.47
Si
2.02
3.0
2.09
2.0
4.01
2.01
6.0
1.03
9
8
7
6
5
4
3
2
1
0
δ / ppm

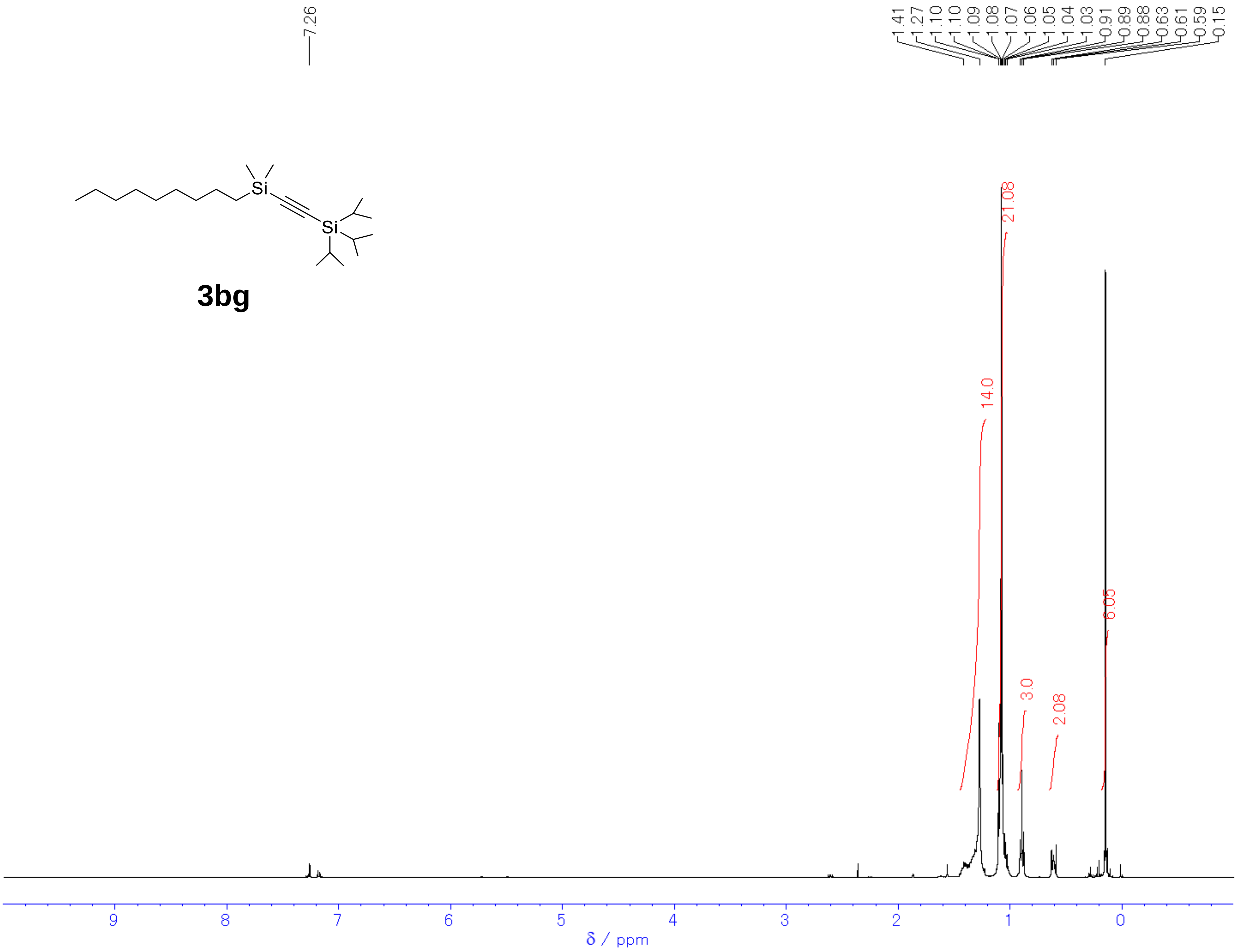

142.8
128.4
128.2
125.6
77.3
77.0
76.7
40.0
26.2
15.2
1.0
-4.6
-5.6
Si
3ae
180
160
140
120
100
80
60
40
20
0
δ / ppm

7.26
2.24
2.23
2.21
1.56
1.54
1.52
1.50
1.50
1.49
1.47
1.46
1.44
1.42
1.40
1.38
1.34
1.31
1.27
0.93
0.91
0.90
0.90
0.89
0.87
0.60
0.58
0.56
0.11
Si
nBu
3bf
18.02
6.0
3.03
3.06
2.0
2.06
9
8
7
6
5
4
3
2
1
0
δ / ppm



3bf

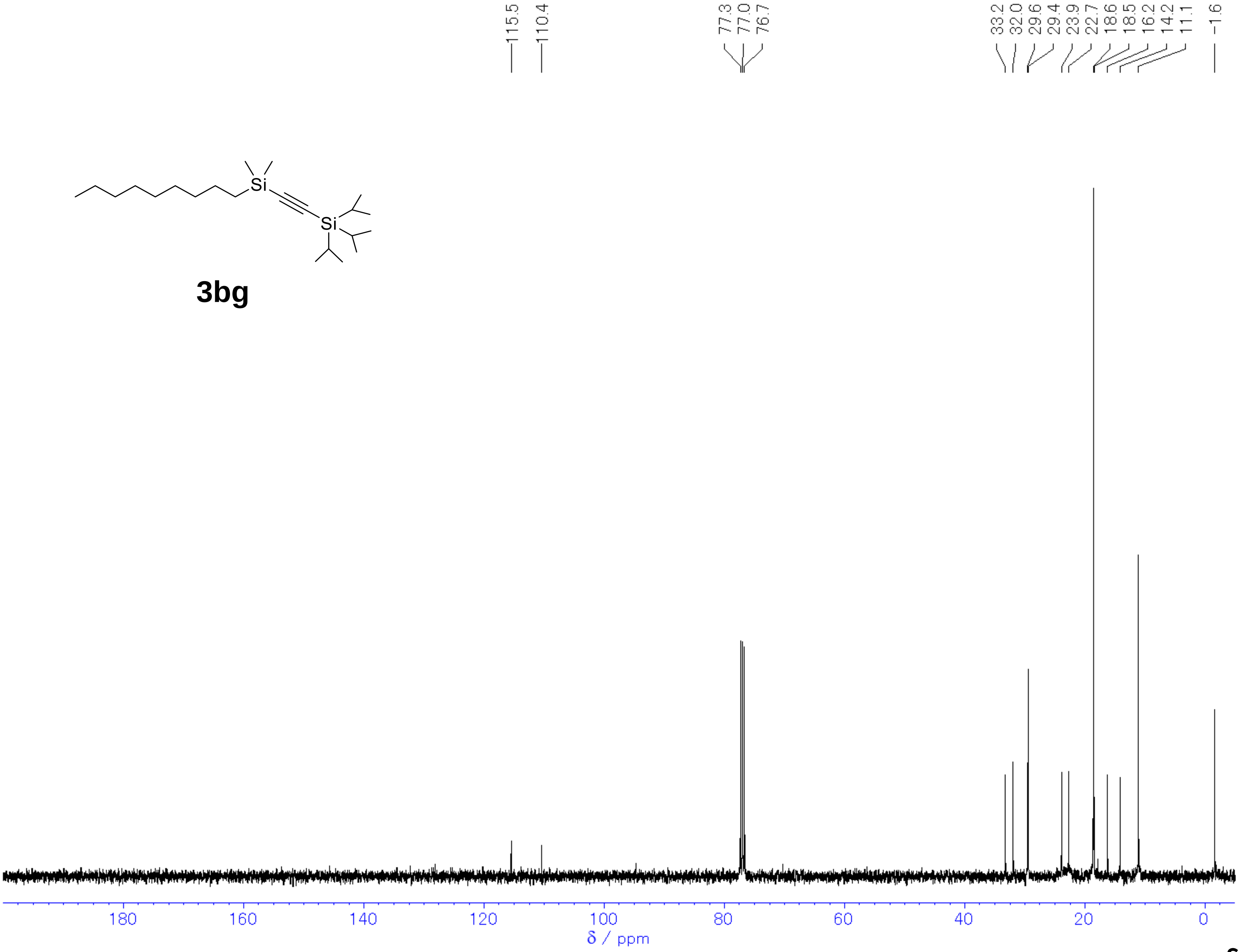
108.0
83.5
77.3
77.0
76.7
33.3
31.9
30.8
29.6
29.4
23.8
22.7
21.9
19.6
16.4
14.1
13.6
–1.5
Si
ⁿBu
180
160
140
120
100
80
60
40
20
0
δ / ppm

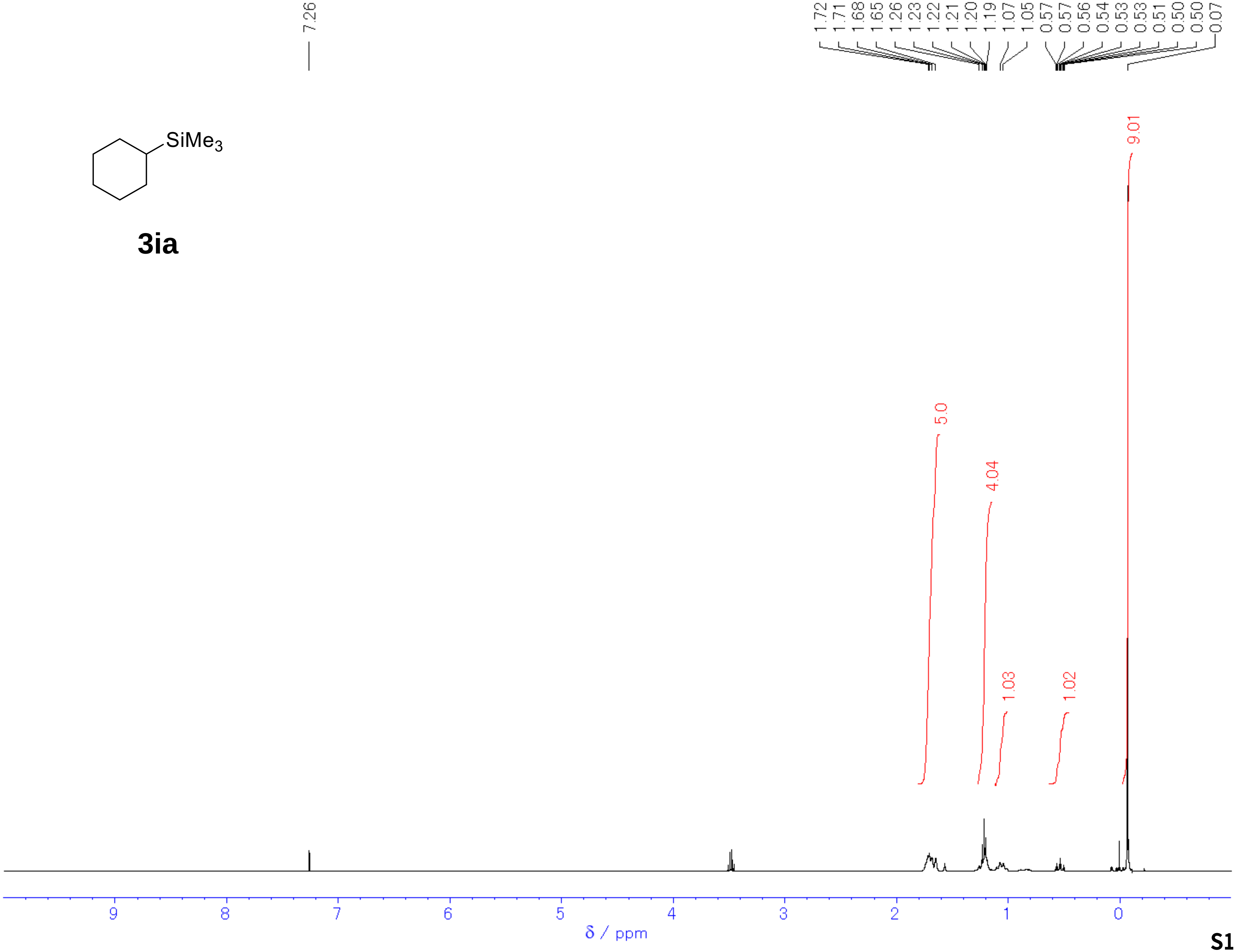
7.26
1.41
1.27
1.10
1.10
1.09
1.08
1.07
1.06
1.05
1.04
1.03
0.91
0.89
0.88
0.63
0.61
0.59
0.15
14.0
21.08
3.0
2.08
6.05
Si
Si
9
8
7
6
5
4
3
2
1
0
δ / ppm

3bg

Si
Si

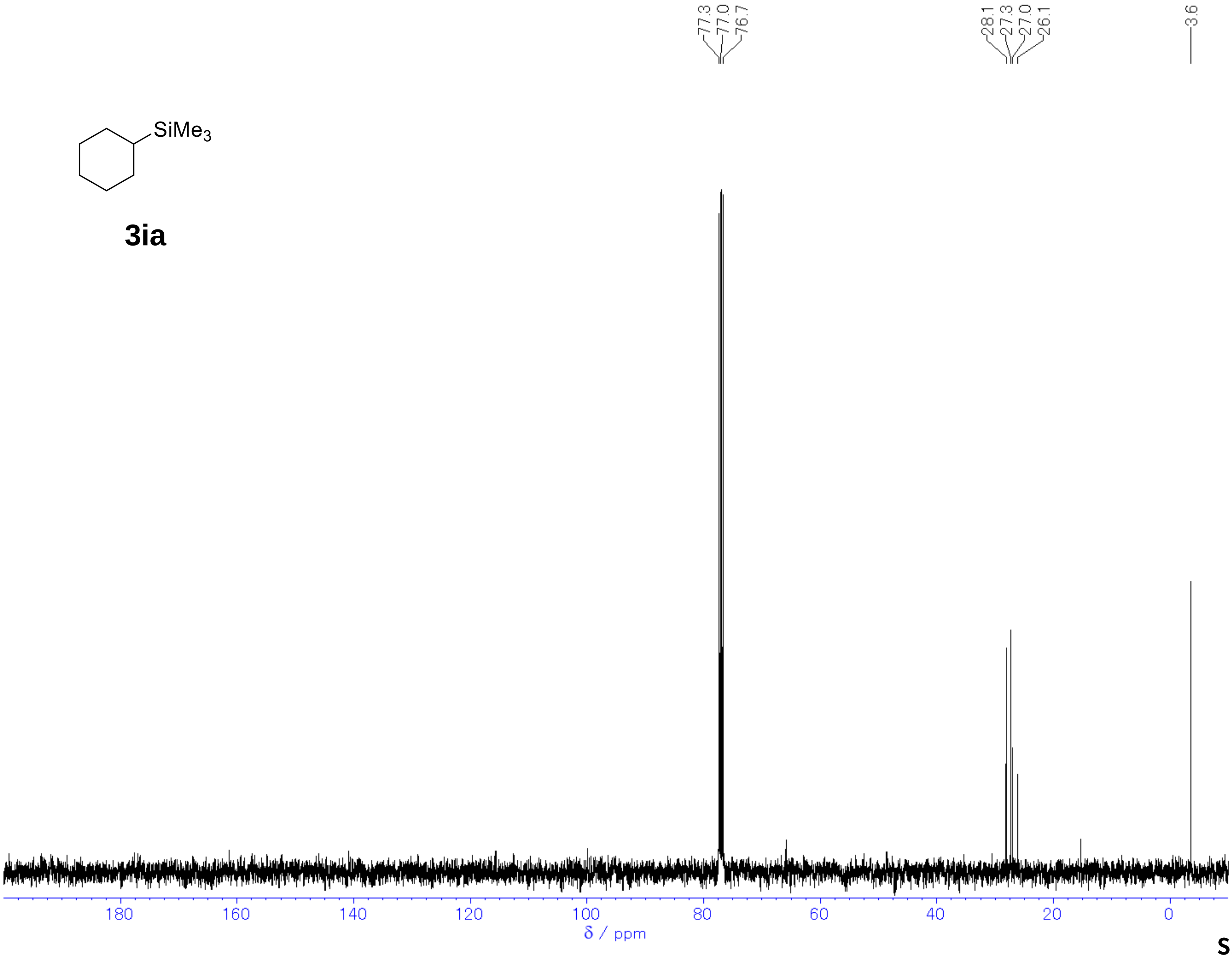
3bg


115.5
110.4
77.3
77.0
76.7
33.2
32.0
29.6
29.4
23.9
22.7
18.6
18.5
16.2
14.2
11.1
−1.6
180
160
140
120
100
80
60
40
20
0
δ / ppm



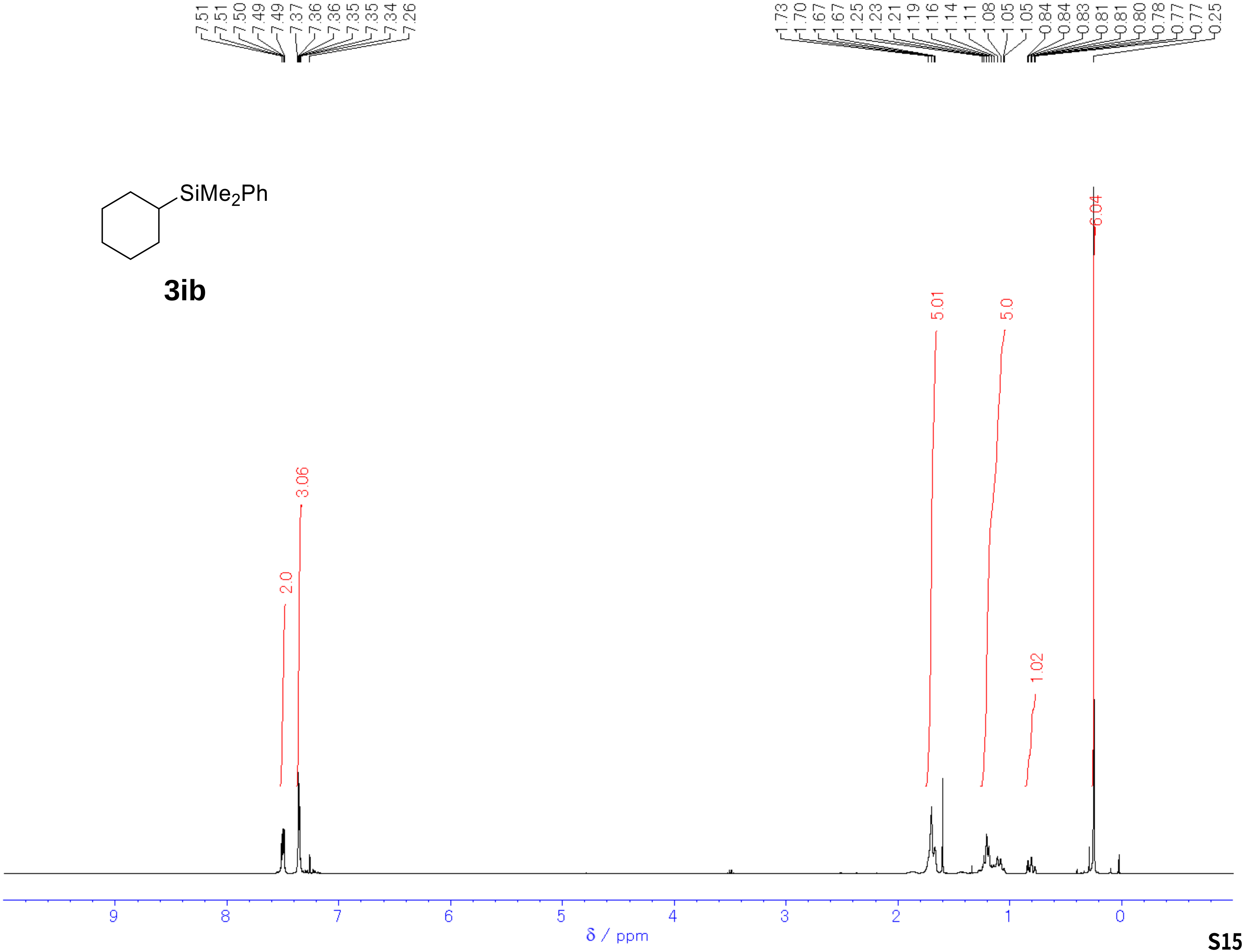
SiMe$_3$
7.26
1.72
1.71
1.68
1.65
1.26
1.23
1.22
1.21
1.20
1.19
1.07
1.05
0.57
0.57
0.56
0.54
0.53
0.53
0.51
0.50
0.50
0.07
5.0
4.04
1.03
1.02
9.01
9
8
7
6
5
4
3
2
1
0
δ / ppm

3ia

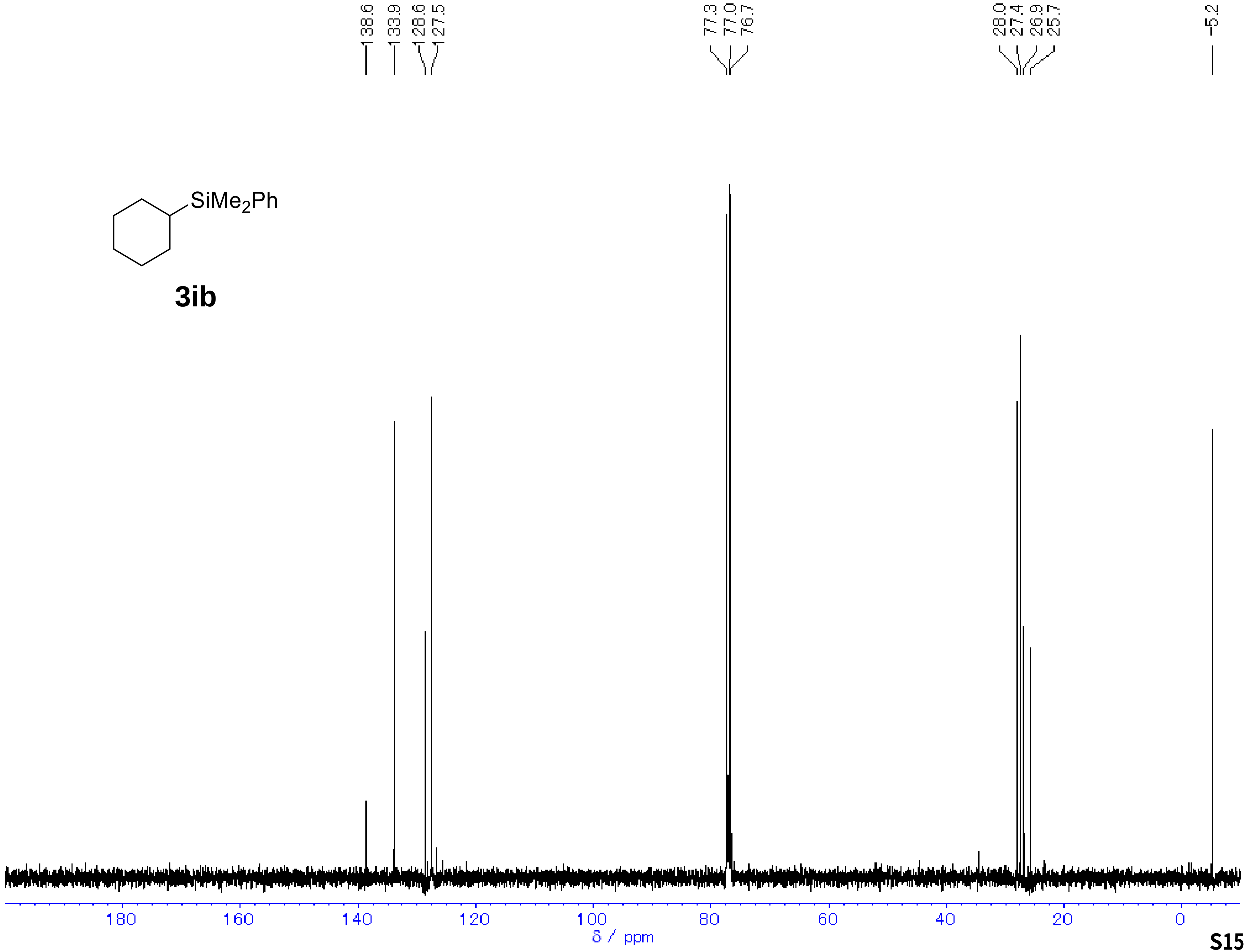


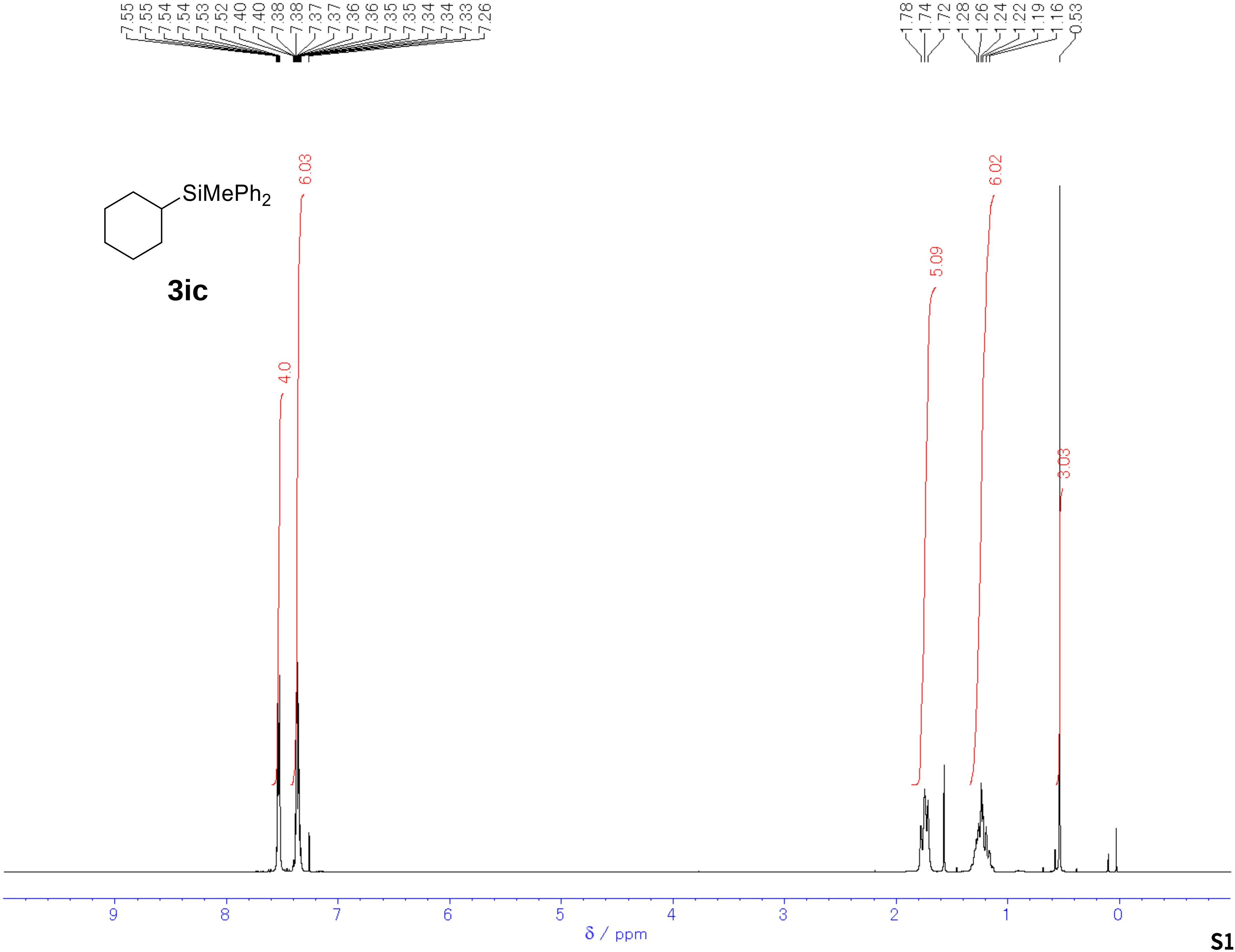
3ia

SiMe3
77.3
77.0
76.7
28.1
27.3
27.0
26.1
3.6
180
160
140
120
100
80
60
40
20
0
δ / ppm

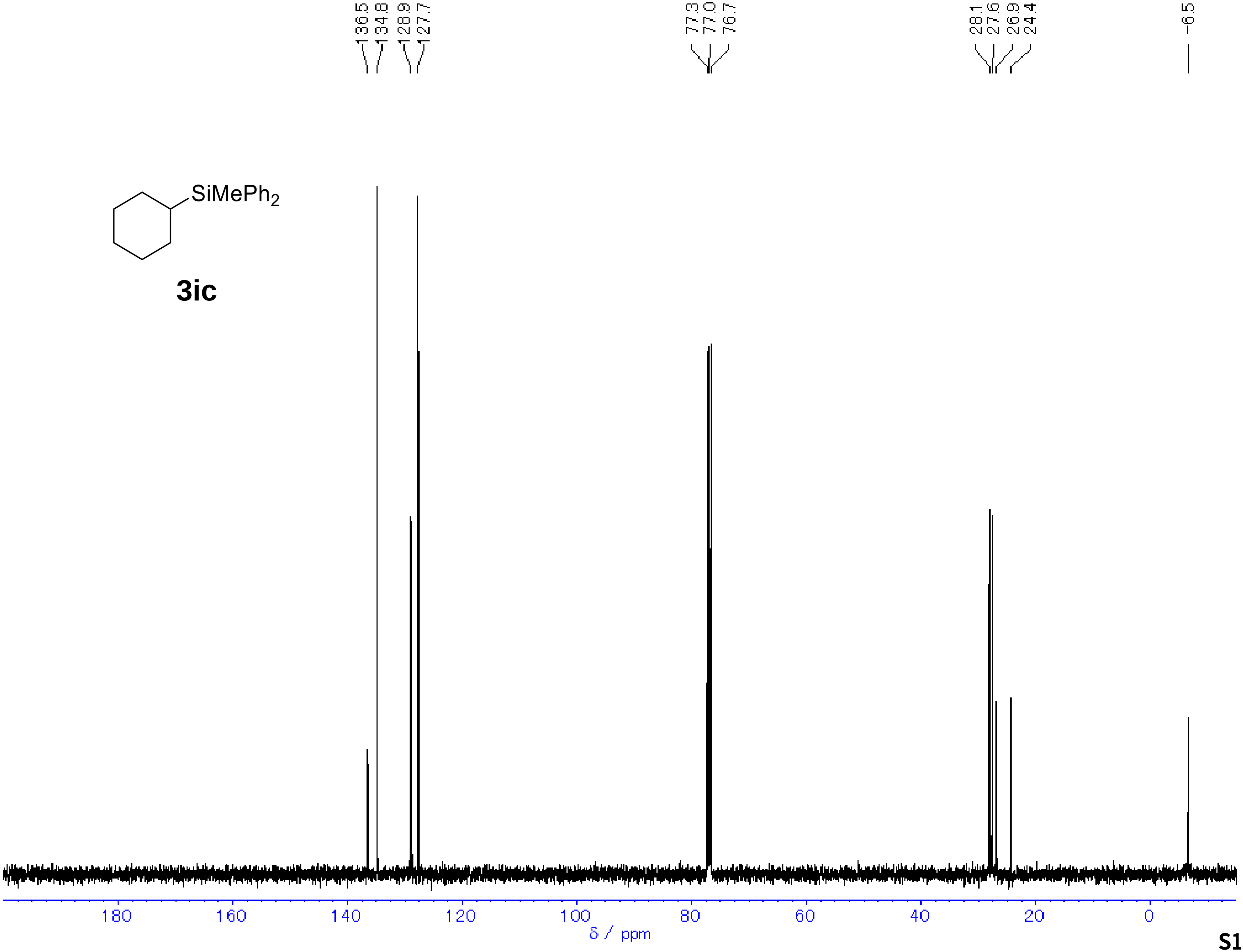

7.51
7.51
7.50
7.49
7.49
7.37
7.36
7.36
7.35
7.35
7.34
7.26
1.73
1.70
1.67
1.67
1.25
1.23
1.21
1.19
1.16
1.14
1.11
1.08
1.05
1.05
0.84
0.84
0.83
0.81
0.81
0.80
0.78
0.77
0.77
0.25
SiMe2Ph
2.0
3.06
5.01
5.0
1.02
6.04
9
8
7
6
5
4
3
2
1
0
δ / ppm

3ib


138.6
133.9
128.6
127.5
77.3
77.0
76.7
28.0
27.4
26.9
25.7
-5.2
SiMe2Ph
3ib
180
160
140
120
100
80
60
40
20
0
δ / ppm


7.55
7.55
7.54
7.54
7.53
7.52
7.40
7.40
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.26
1.78
1.74
1.72
1.28
1.26
1.24
1.22
1.19
1.16
0.53
SiMePh2
4.0
6.03
5.09
6.02
3.03
9
8
7
6
5
4
3
2
1
0
δ / ppm

3ic

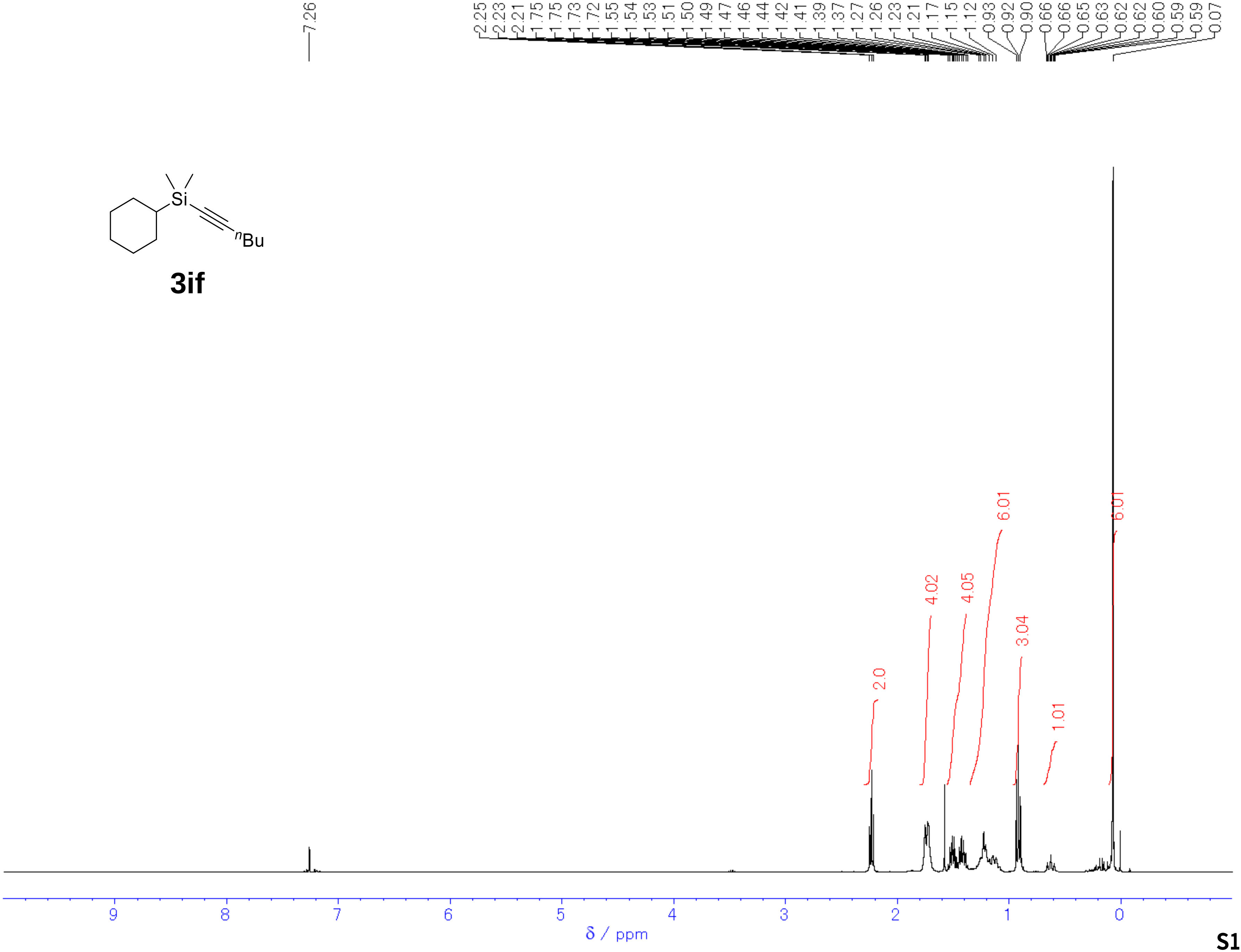


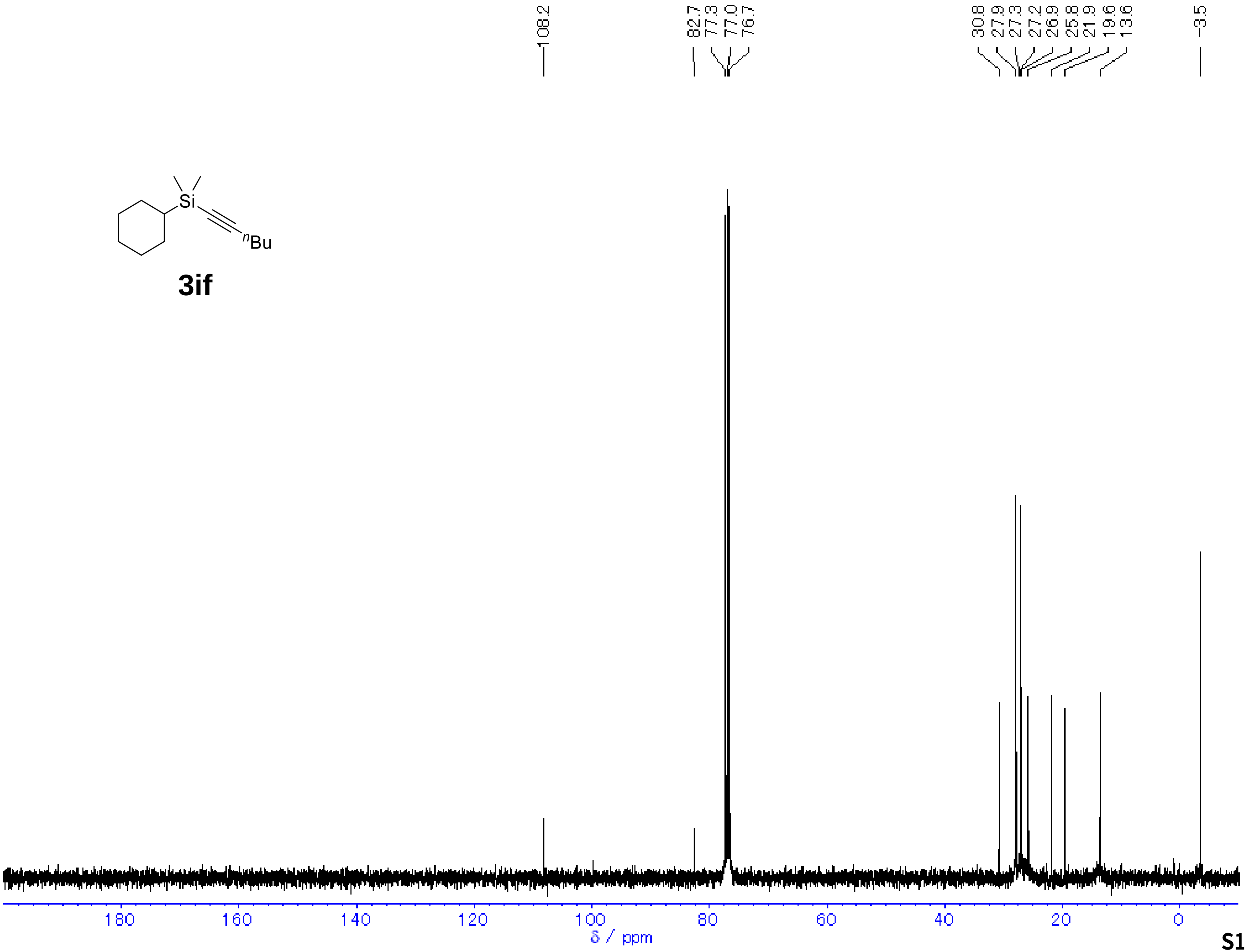
3ic

136.5
134.8
128.9
127.7
77.3
77.0
76.7
28.1
27.6
26.9
24.4
-6.5
180
160
140
120
100
80
60
40
20
0
δ / ppm

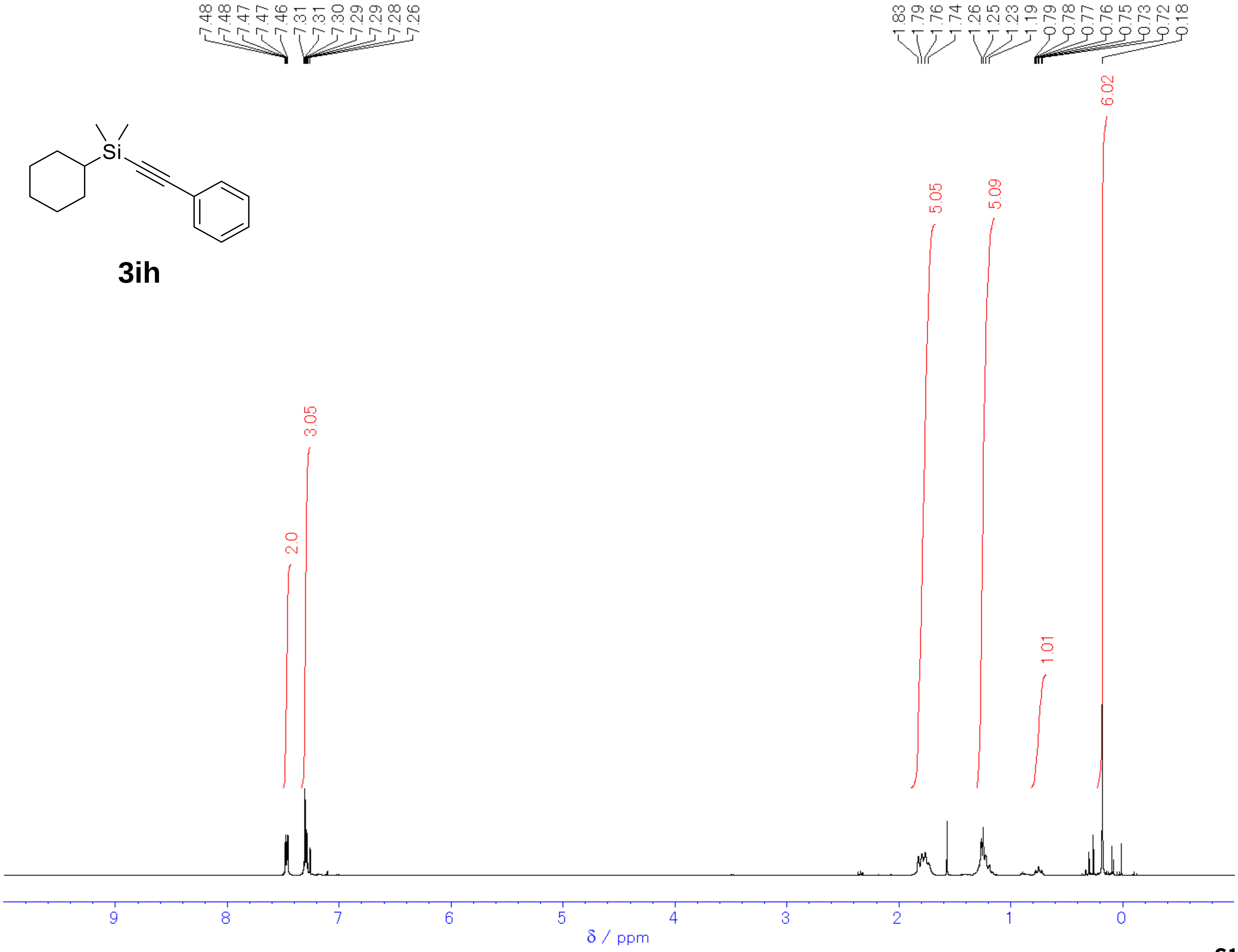
Si
nBu

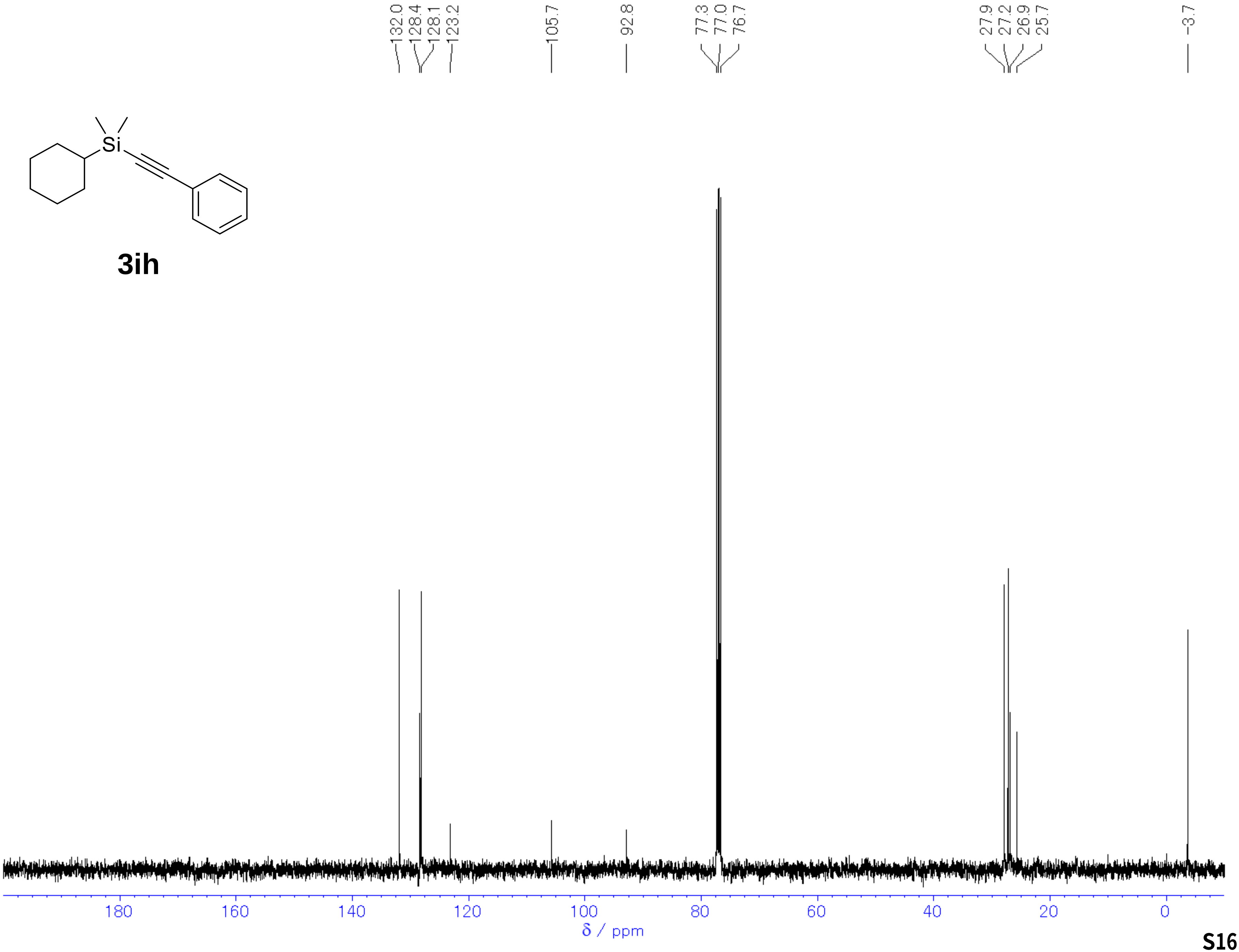
3if


7.26
2.25
2.23
2.21
1.75
1.75
1.73
1.72
1.55
1.54
1.53
1.51
1.50
1.49
1.47
1.46
1.44
1.42
1.41
1.39
1.37
1.27
1.26
1.23
1.21
1.17
1.15
1.12
0.93
0.92
0.90
0.66
0.66
0.65
0.63
0.62
0.62
0.60
0.59
0.59
0.07
2.0
4.02
4.05
6.01
3.04
1.01
6.01
9
8
7
6
5
4
3
2
1
0
δ / ppm

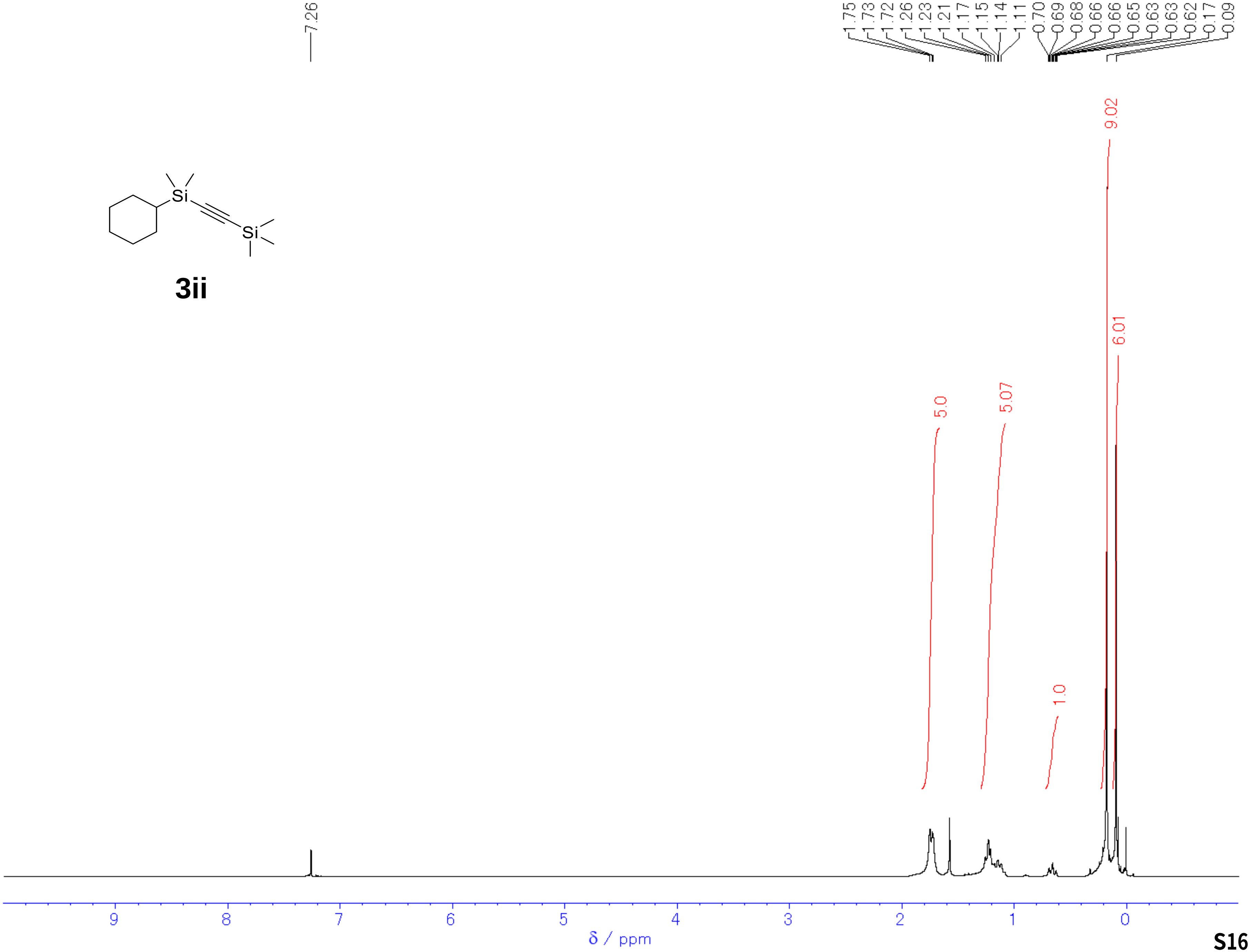

108.2
82.7
77.3
77.0
76.7
30.8
27.9
27.3
27.2
26.9
25.8
21.9
19.6
13.6
-3.5
Si
nBu
180
160
140
120
100
80
60
40
20
0
δ / ppm

3if


7.48
7.48
7.47
7.47
7.46
7.31
7.31
7.30
7.29
7.29
7.28
7.26
1.83
1.79
1.76
1.74
1.26
1.25
1.23
1.19
0.79
0.78
0.77
0.76
0.75
0.73
0.72
0.18
Si
3ih
2.0
3.05
5.05
5.09
1.01
6.02
9
8
7
6
5
4
3
2
1
0
δ / ppm

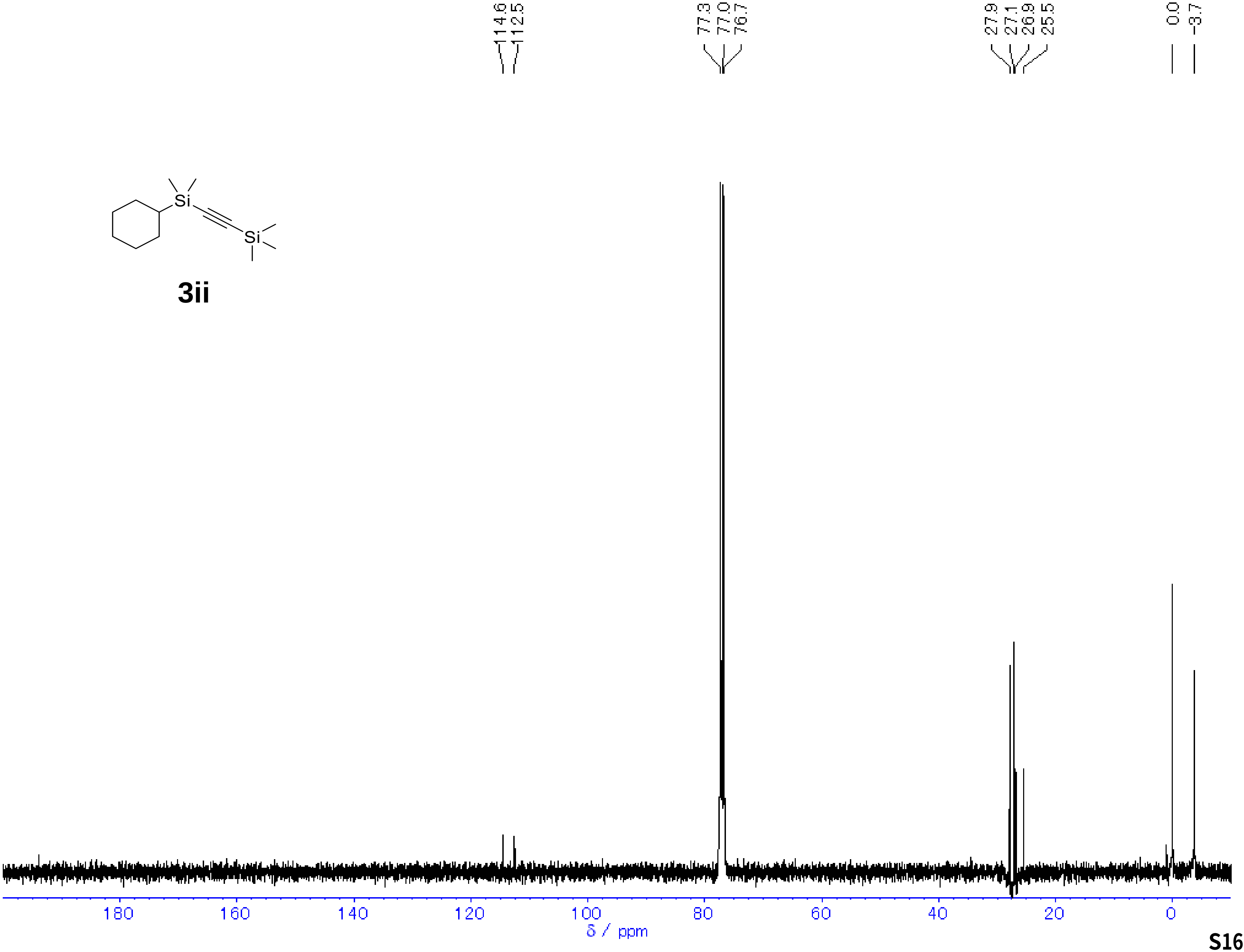

132.0
128.4
128.1
123.2
105.7
92.8
77.3
77.0
76.7
27.9
27.2
26.9
25.7
-3.7
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm

3ih

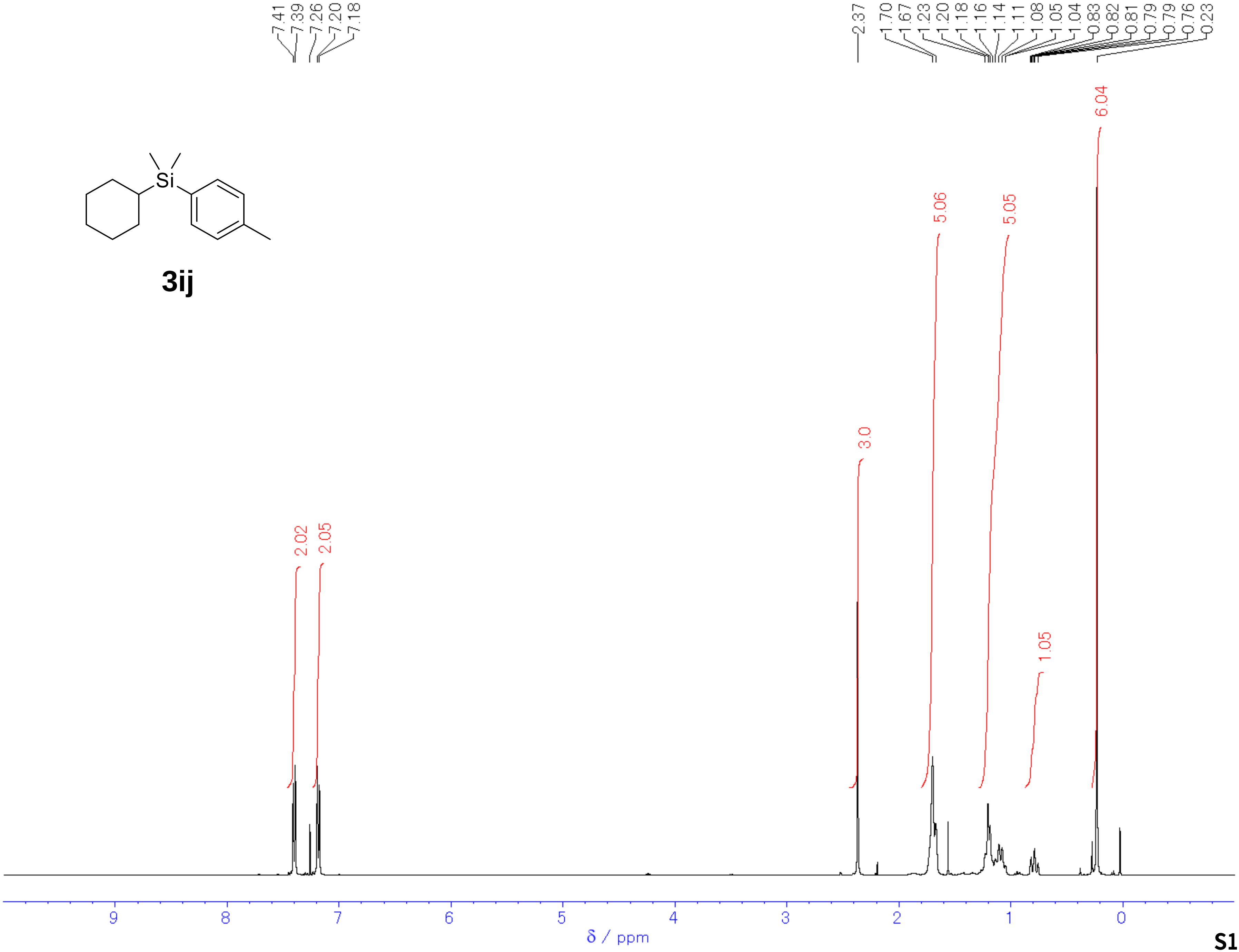


3ii

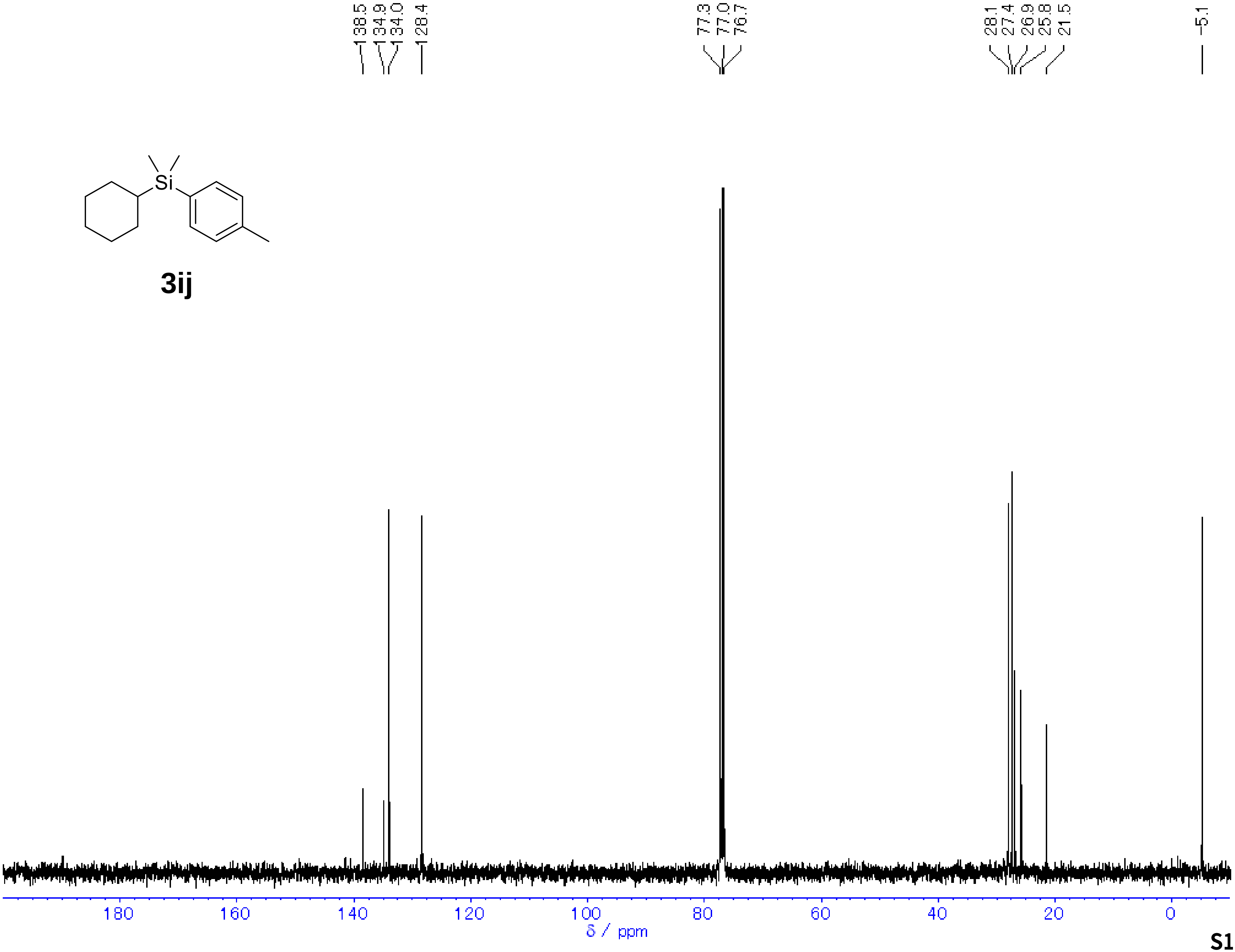
Si
Si
7.26
1.75
1.73
1.72
1.26
1.23
1.21
1.17
1.15
1.14
1.11
0.70
0.69
0.68
0.66
0.66
0.65
0.63
0.63
0.62
0.17
0.09
9.02
6.01
5.0
5.07
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm


114.6
112.5
77.3
77.0
76.7
27.9
27.1
26.9
25.5
0.0
-3.7
Si
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm

3ii

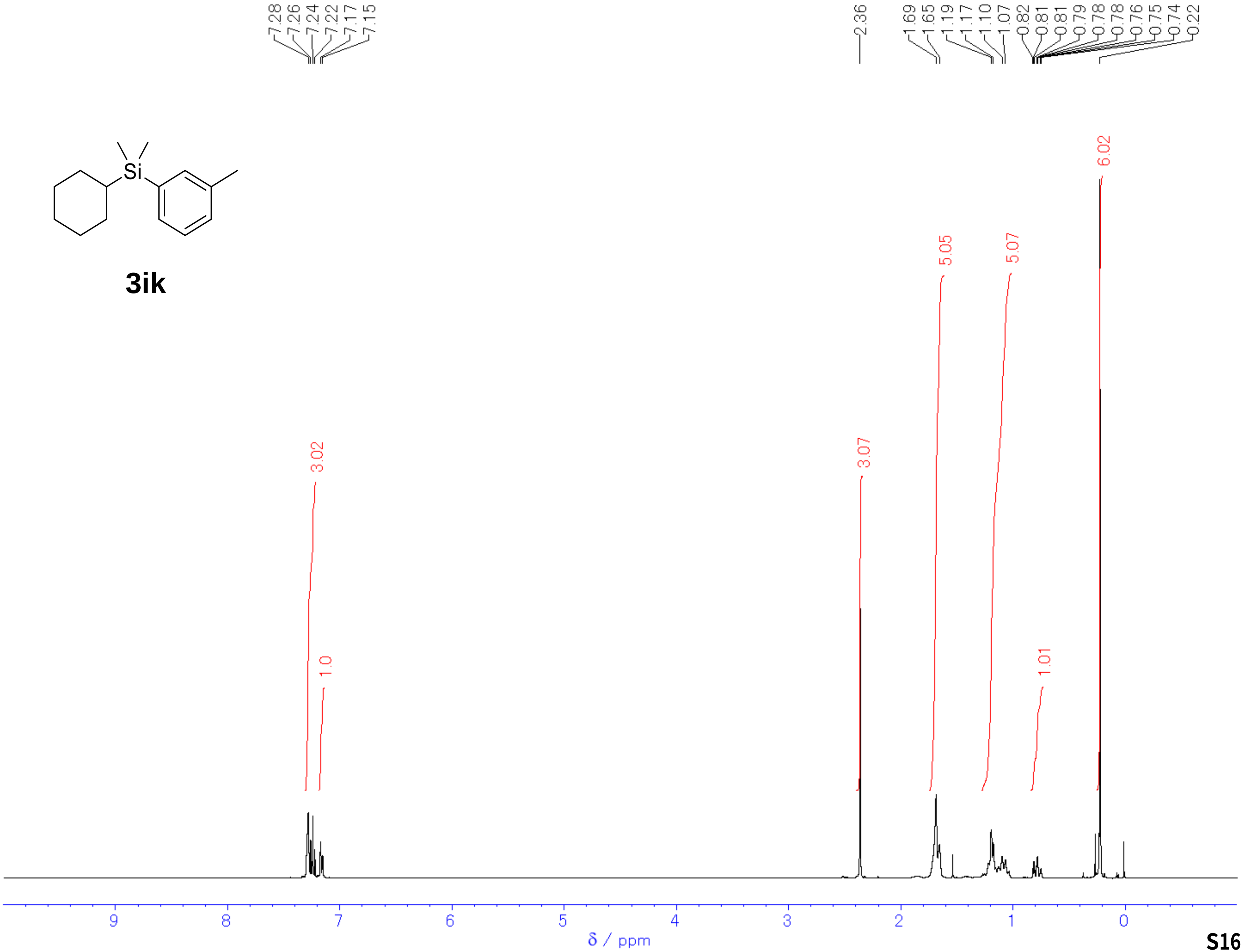

7.41
7.39
7.26
7.20
7.18
2.37
1.70
1.67
1.23
1.20
1.18
1.16
1.14
1.11
1.08
1.05
1.04
0.83
0.82
0.81
0.79
0.79
0.76
0.23
Si
2.02
2.05
3.0
5.06
5.05
1.05
6.04
9
8
7
6
5
4
3
2
1
0
δ / ppm

3ij

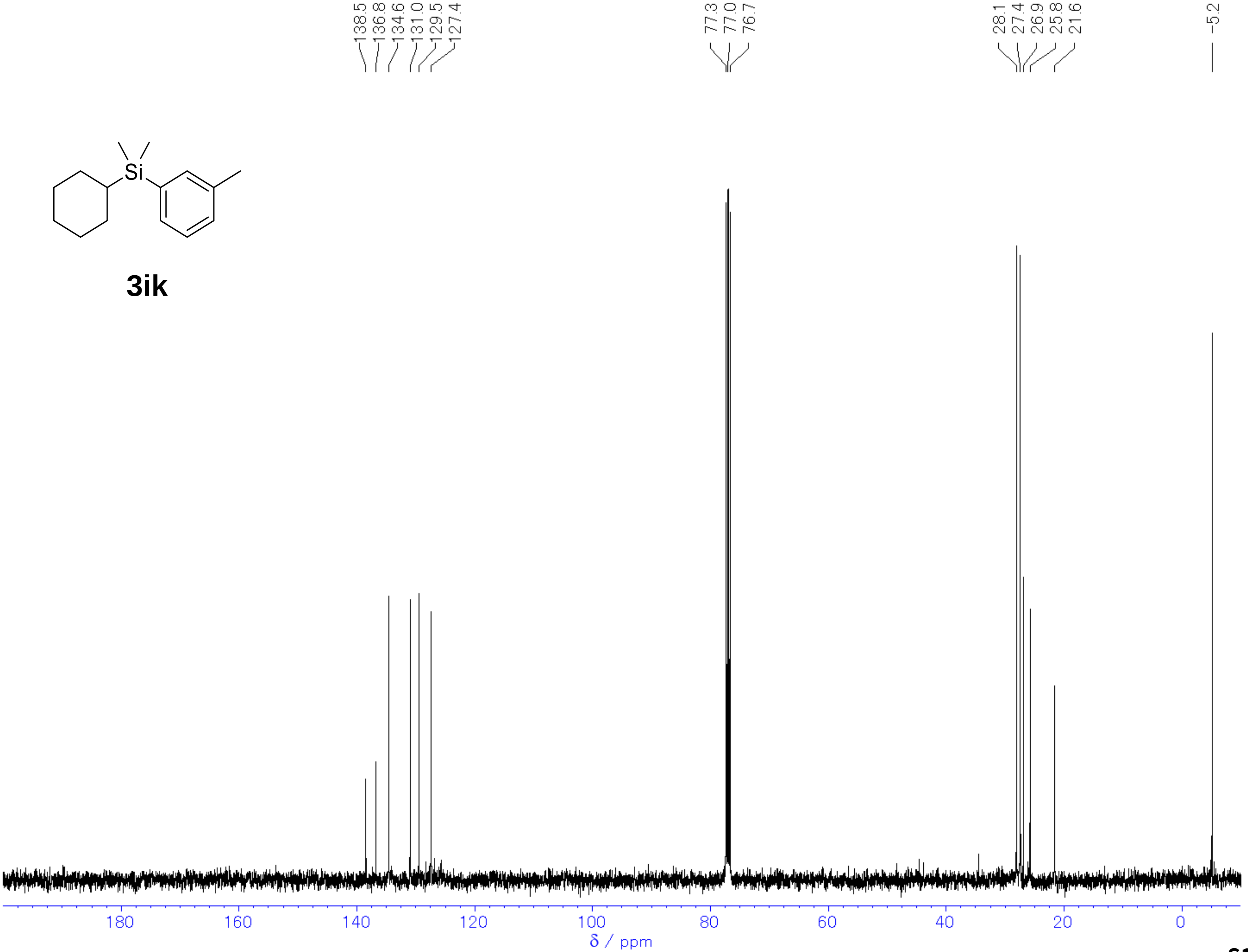


3ij

Si
138.5
134.9
134.0
128.4
77.3
77.0
76.7
28.1
27.4
26.9
25.8
21.5
-5.1
180
160
140
120
100
80
60
40
20
0
δ / ppm

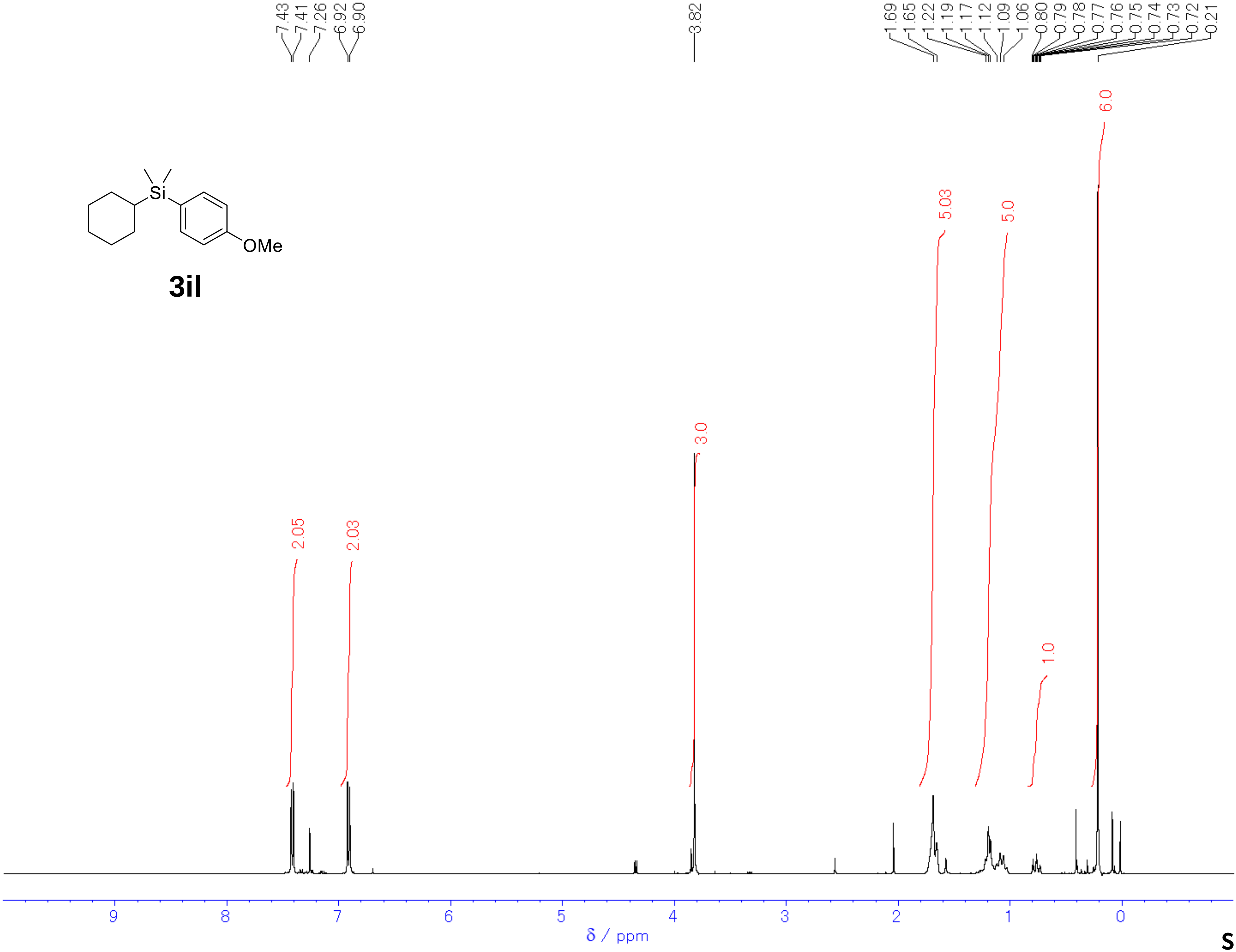

7.28
7.26
7.24
7.22
7.17
7.15
2.36
1.69
1.65
1.19
1.17
1.10
1.07
0.82
0.81
0.81
0.79
0.78
0.78
0.76
0.75
0.74
0.22
Si
3.02
1.0
3.07
5.05
5.07
1.01
6.02
9
8
7
6
5
4
3
2
1
0
δ / ppm

3ik

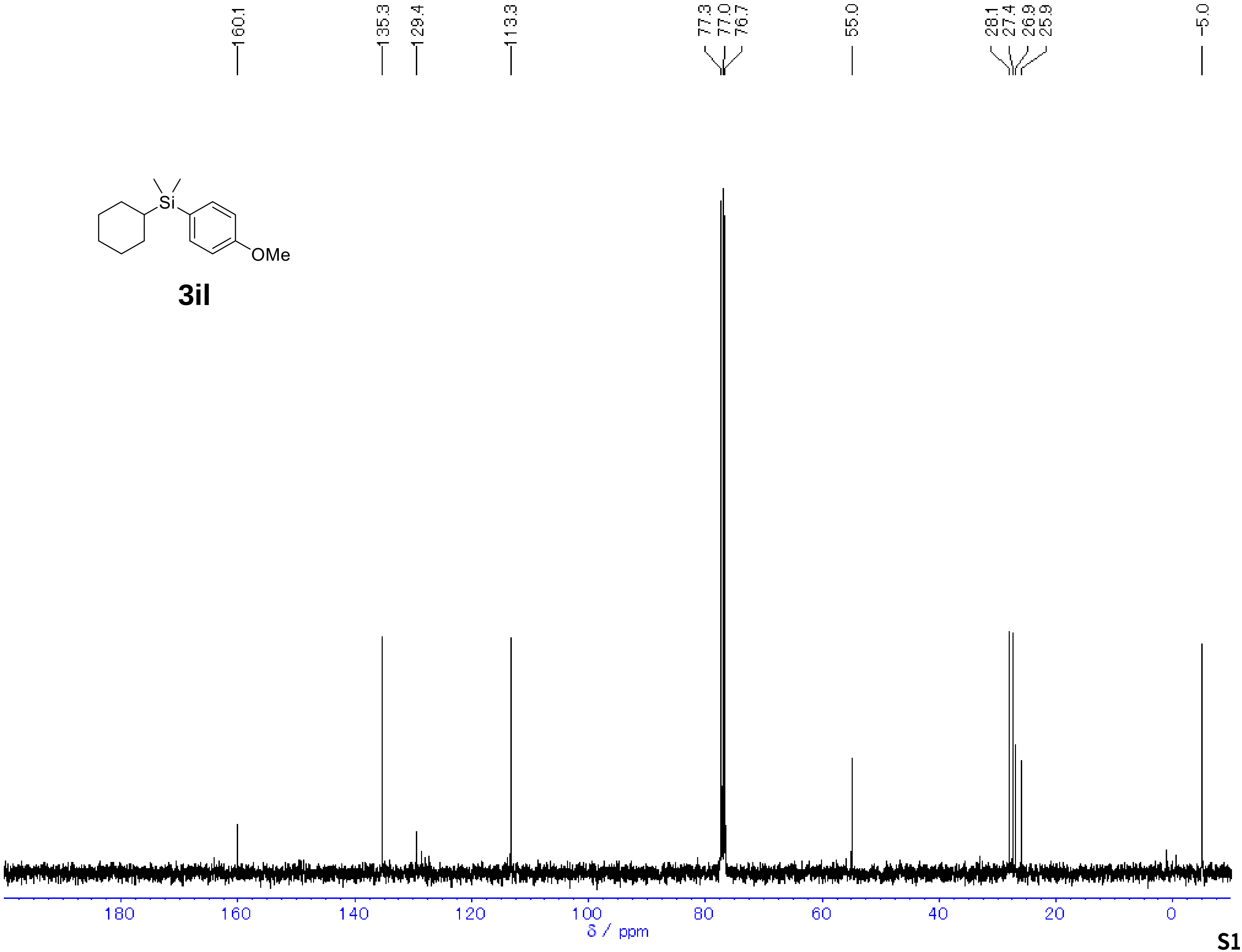


3ik

138.5
136.8
134.6
131.0
129.5
127.4
77.3
77.0
76.7
28.1
27.4
26.9
25.8
21.6
-5.2
Si
180
160
140
120
100
80
60
40
20
0
δ / ppm


7.43
7.41
7.26
6.92
6.90
3.82
1.69
1.65
1.22
1.19
1.17
1.12
1.09
1.06
0.80
0.79
0.78
0.77
0.76
0.75
0.74
0.73
0.72
0.21
Si
OMe
2.05
2.03
3.0
5.03
5.0
1.0
6.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

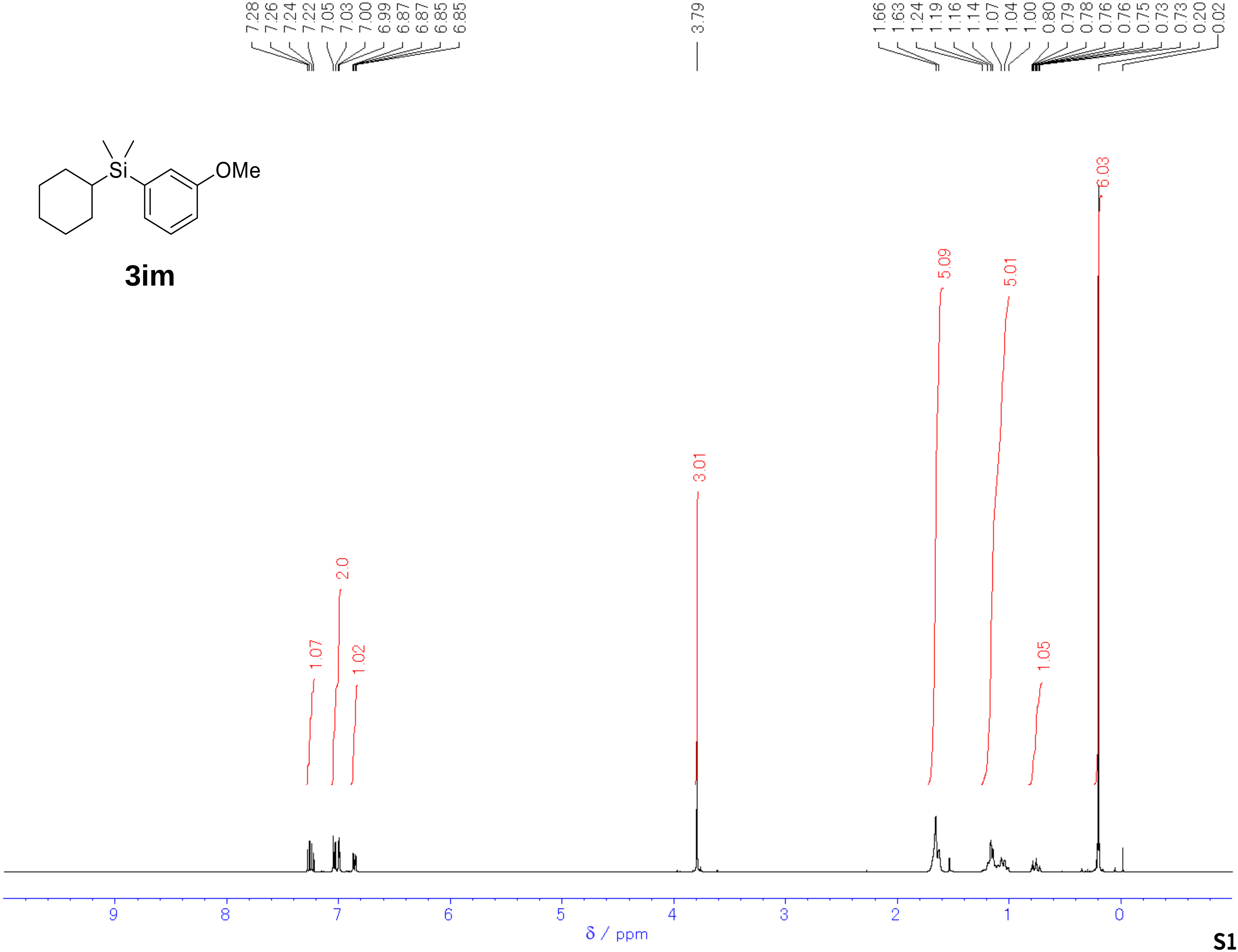
3il

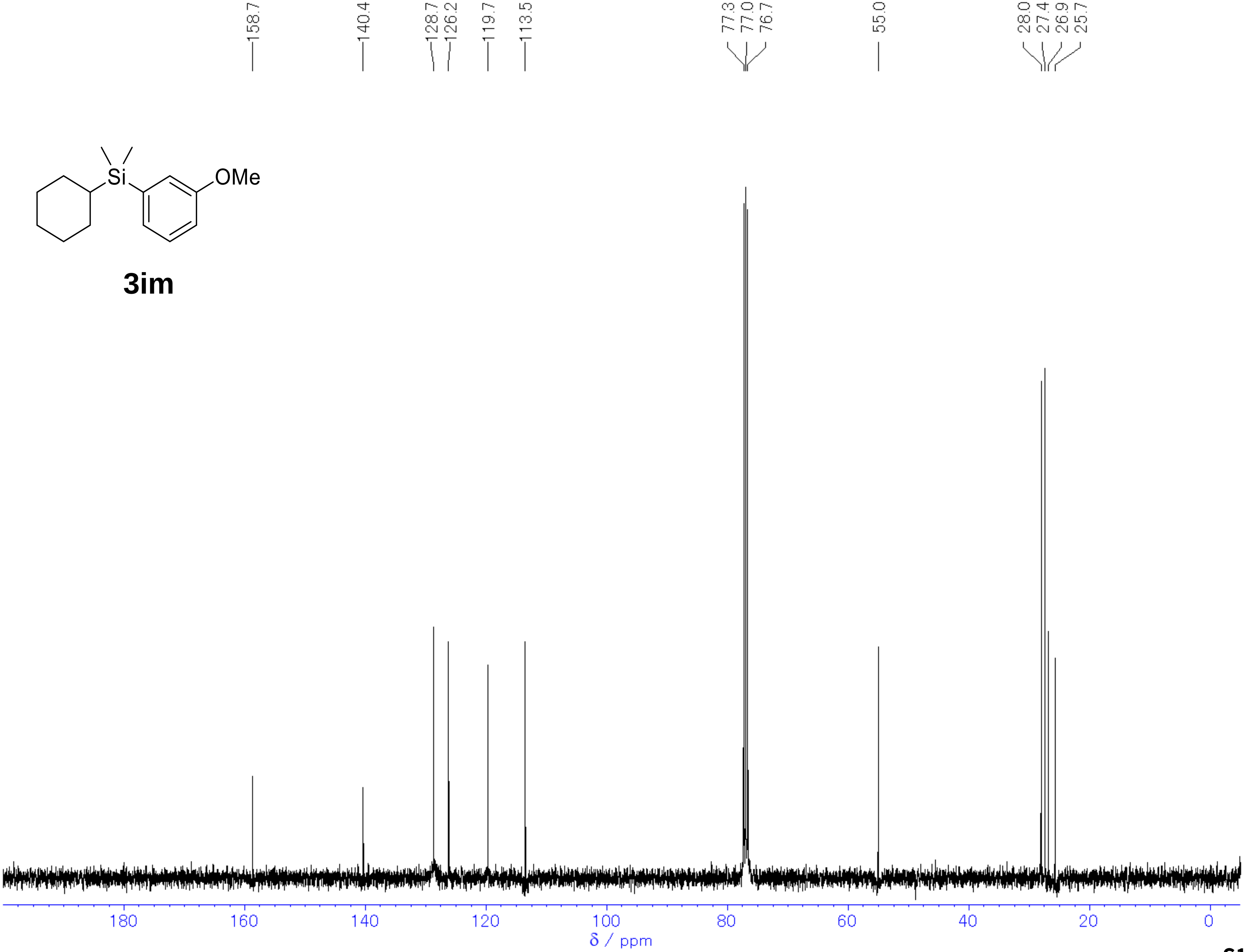

160.1
135.3
129.4
113.3
77.3
77.0
76.7
55.0
28.1
27.4
26.9
25.9
-5.0
Si
OMe
180
160
140
120
100
80
60
40
20
0
δ / ppm

3il

Si
OMe

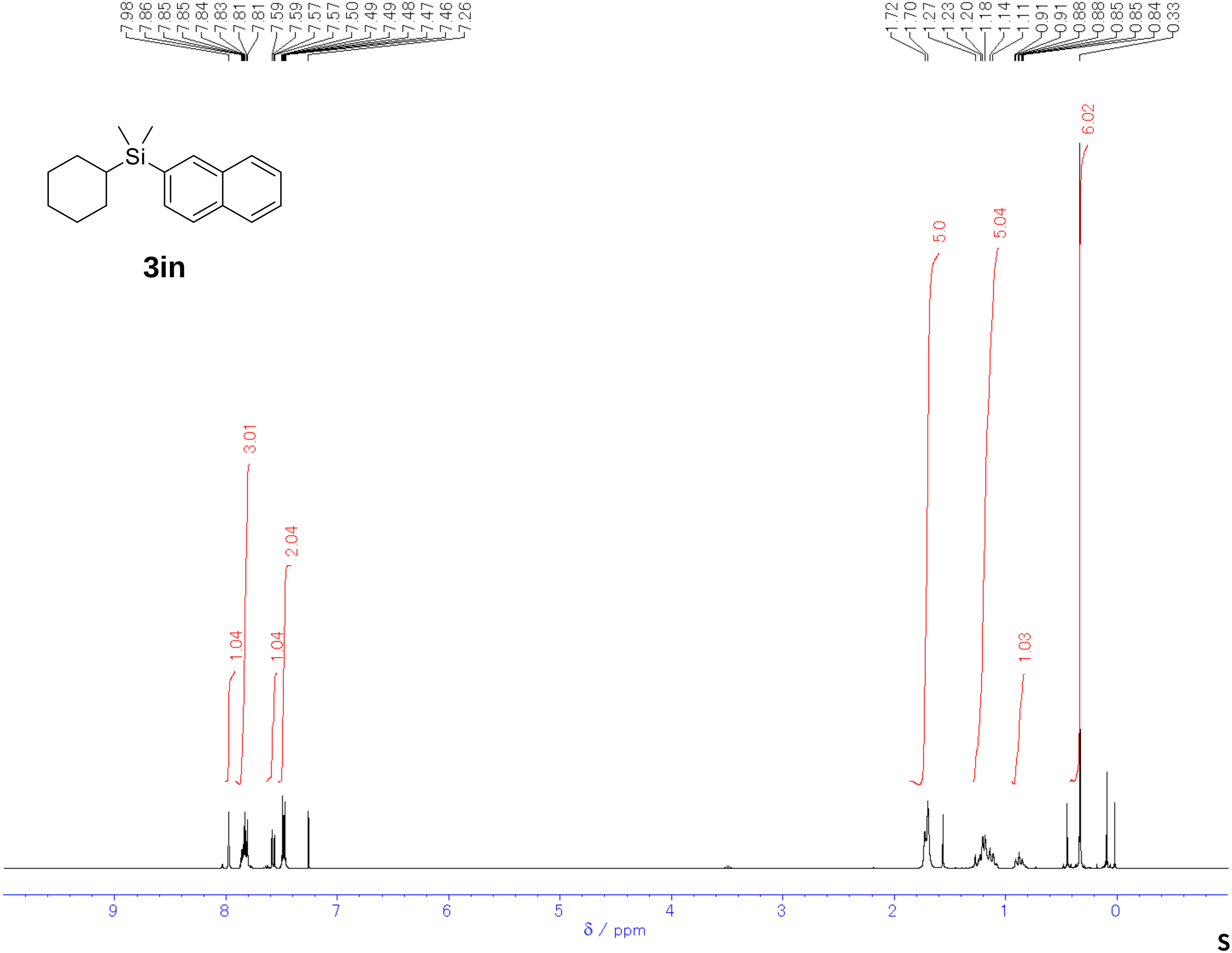
3im


7.28
7.26
7.24
7.22
7.05
7.03
7.00
6.99
6.87
6.87
6.85
6.85
3.79
1.66
1.63
1.24
1.19
1.16
1.14
1.07
1.04
1.00
0.80
0.79
0.78
0.76
0.76
0.75
0.73
0.73
0.20
0.02
1.07
2.0
1.02
3.01
5.09
5.01
1.05
6.03
9
8
7
6
5
4
3
2
1
0
δ / ppm



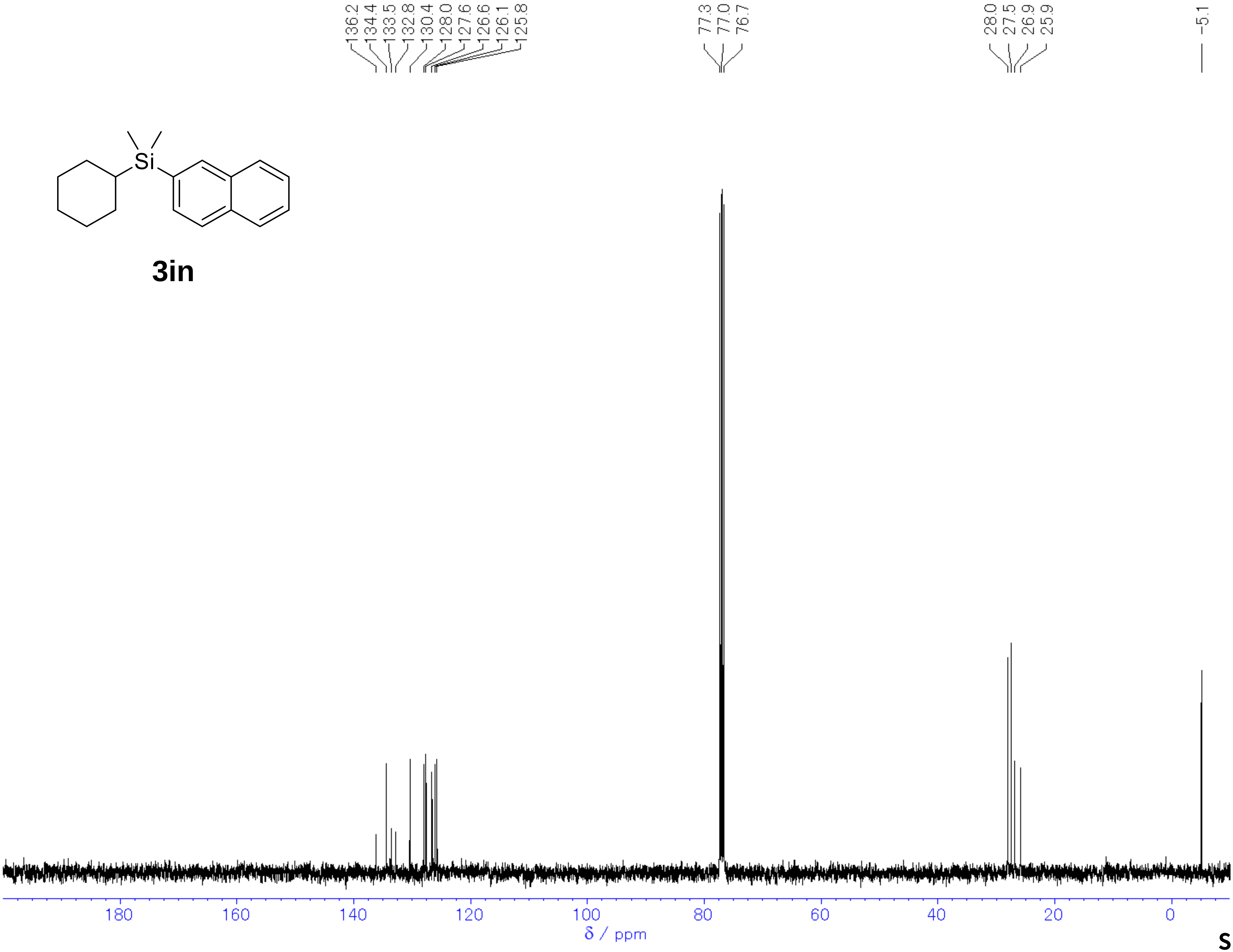
3im

OMe
Si
158.7
140.4
128.7
126.2
119.7
113.5
77.3
77.0
76.7
55.0
28.0
27.4
26.9
25.7
180
160
140
120
100
80
60
40
20
0
δ / ppm



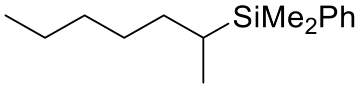
3in

7.98
7.86
7.85
7.85
7.84
7.83
7.81
7.81
7.59
7.59
7.57
7.57
7.50
7.49
7.49
7.48
7.47
7.46
7.26
1.72
1.70
1.27
1.23
1.20
1.18
1.14
1.11
0.91
0.91
0.88
0.88
0.85
0.85
0.84
0.33
1.04
3.01
1.04
2.04
5.0
5.04
1.03
6.02
9
8
7
6
5
4
3
2
1
0
δ / ppm

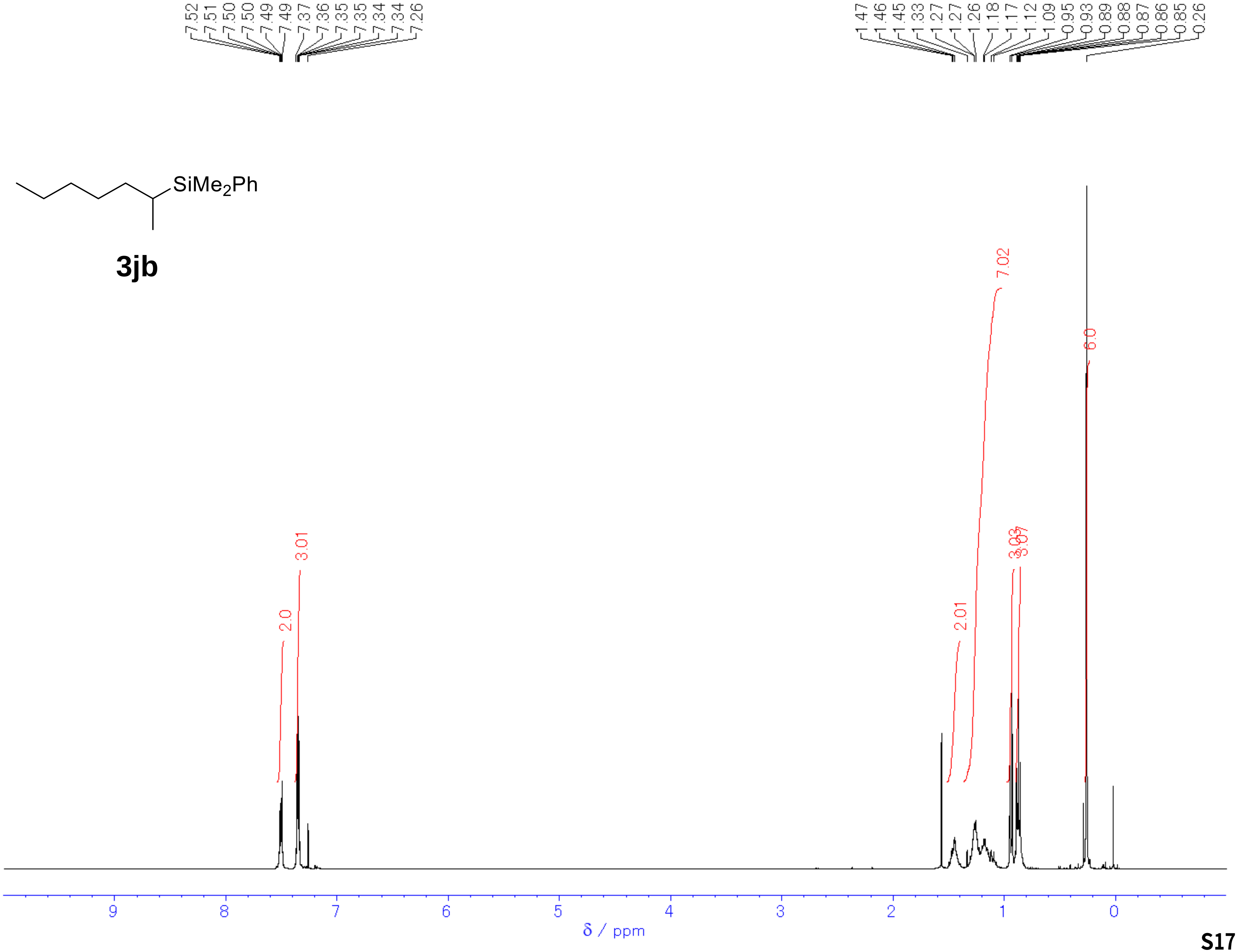


3in

Si
136.2
134.4
133.5
132.8
130.4
128.0
127.6
126.6
126.1
125.8
77.3
77.0
76.7
28.0
27.5
26.9
25.9
-5.1
180
160
140
120
100
80
60
40
20
0
δ / ppm


SiMe2Ph

3jb


7.52
7.51
7.50
7.50
7.49
7.49
7.37
7.36
7.35
7.35
7.34
7.34
7.26
1.47
1.46
1.45
1.33
1.27
1.27
1.26
1.18
1.17
1.12
1.09
0.95
0.93
0.89
0.88
0.87
0.86
0.85
0.26
2.0
3.01
2.01
7.02
3.03
3.07
6.0
9
8
7
6
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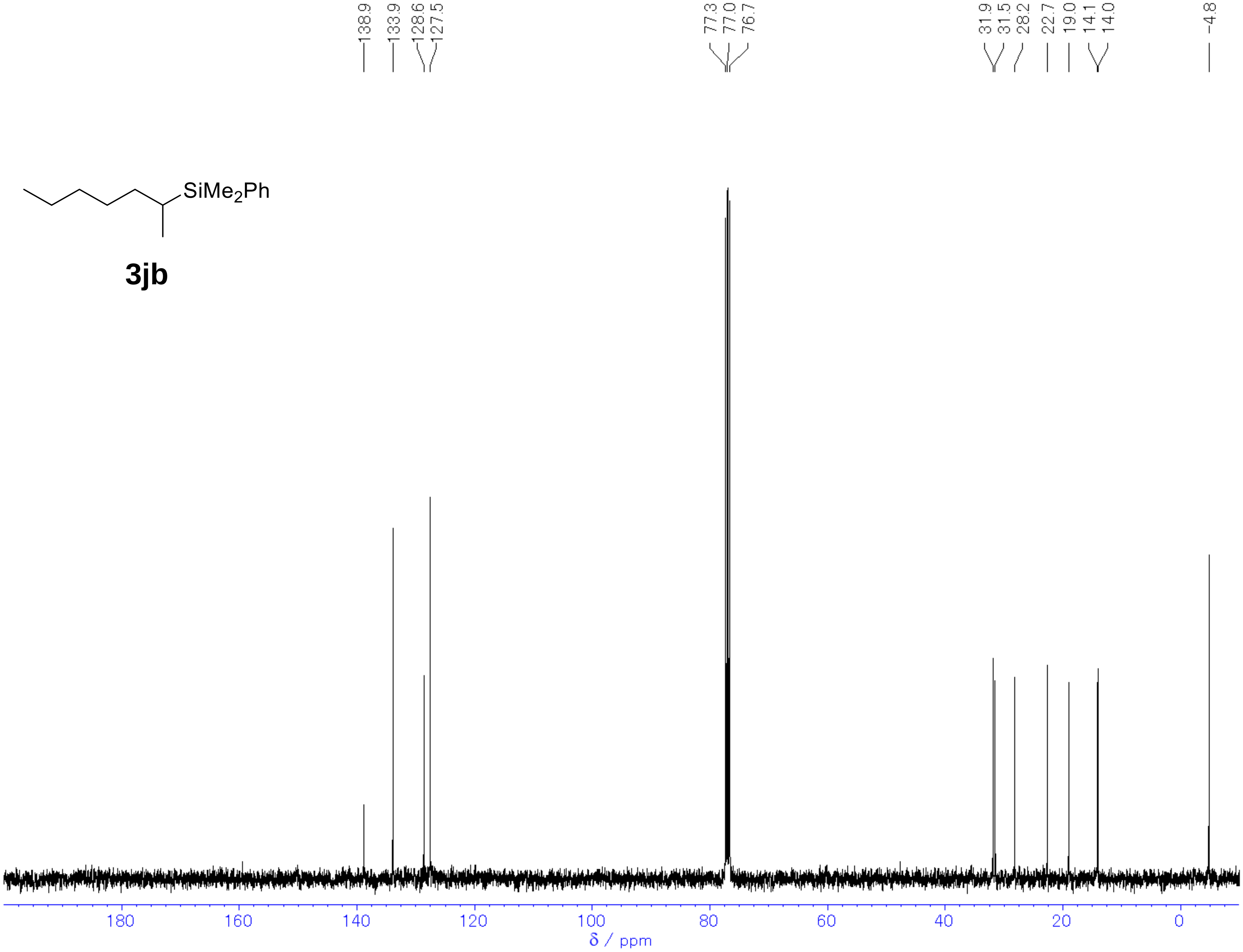
δ / ppm



3jb

SiMe2Ph
138.9
133.9
128.6
127.5
77.3
77.0
76.7
31.9
31.5
28.2
22.7
19.0
14.1
14.0
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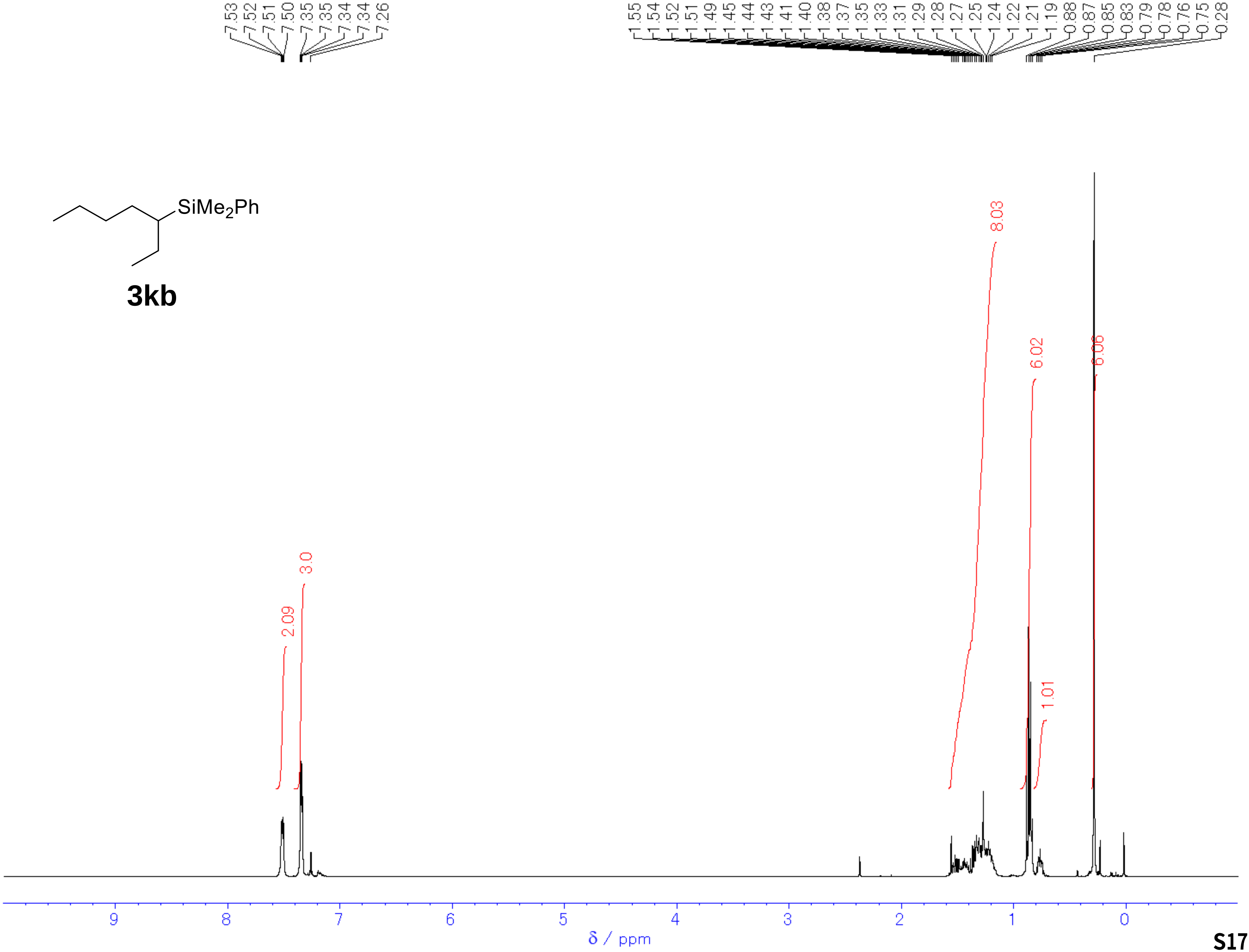
180
160
140
120
100
80
60
40
20
0
δ / ppm

SiMe2Ph

3kb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7.35
7.34
7.34
7.26
1.55
1.54
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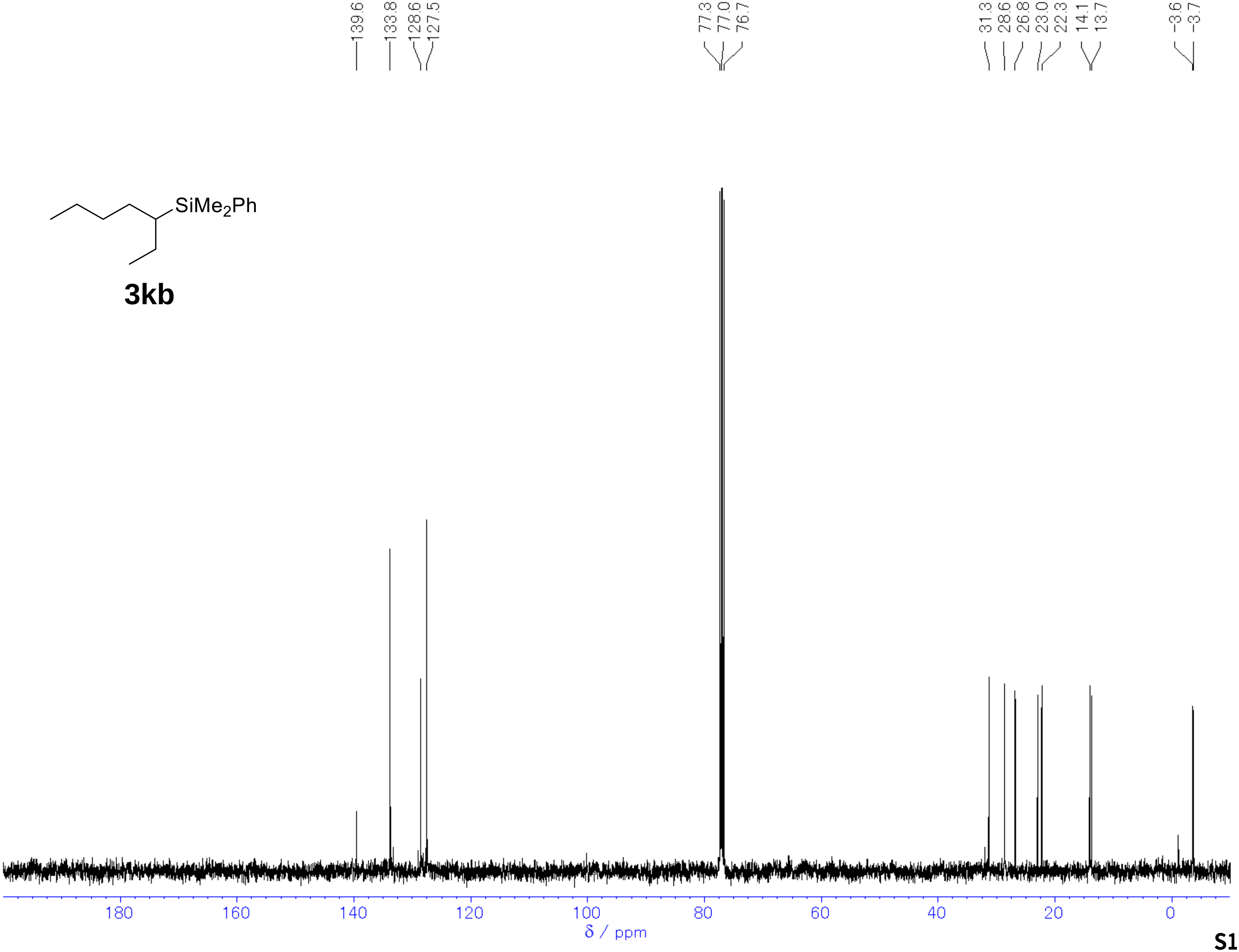
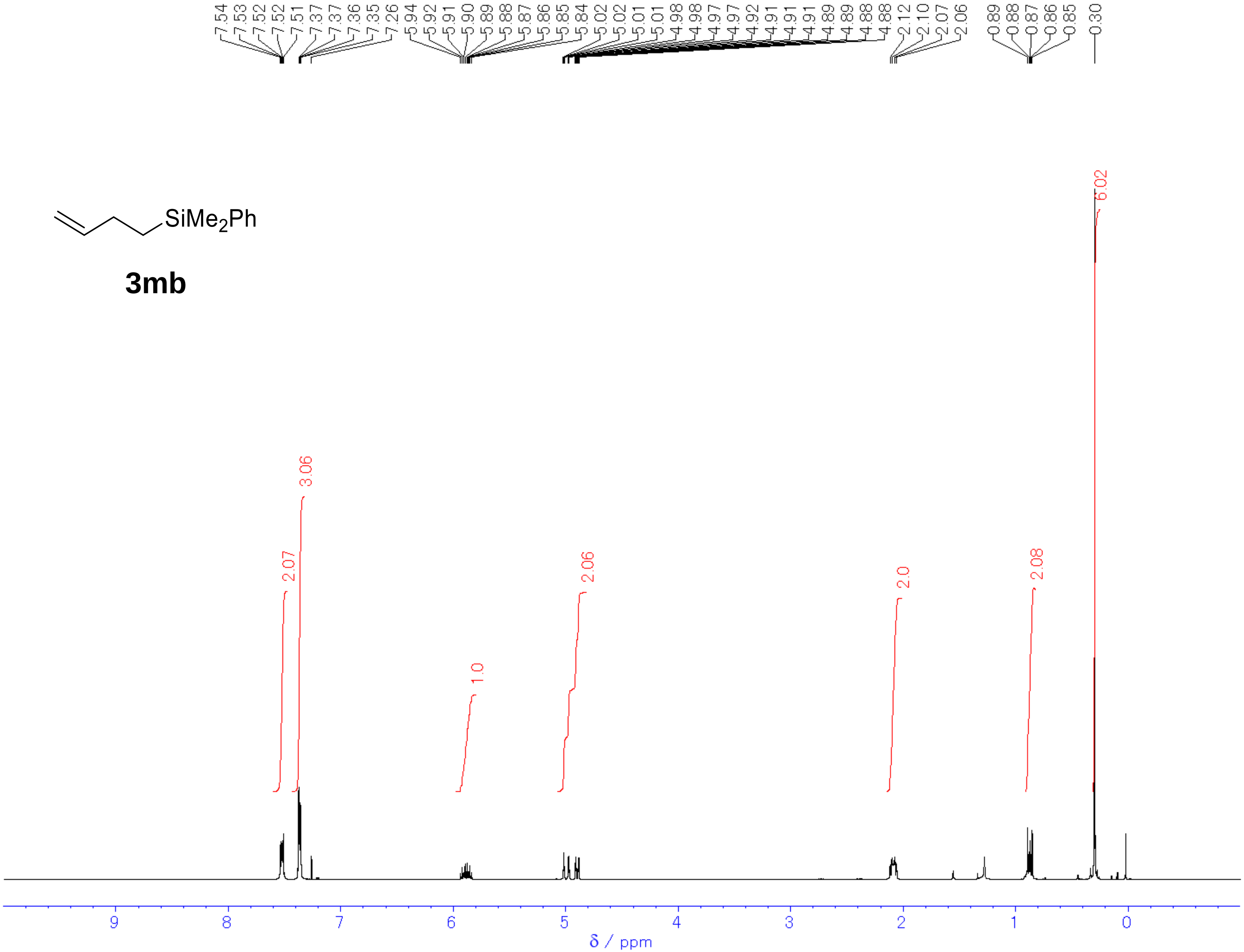
1.51
1.49
1.45
1.44
1.43
1.41
1.40
1.38
1.37
1.35
1.33
1.31
1.29
1.28
1.27
1.25
1.24
1.22
1.21
1.19
0.88
0.87
0.85
0.83
0.79
0.78
0.76
0.75
0.28
2.09
3.0
8.03
6.02
1.01
6.06
9
8
7
6
5
4
3
2
1
0
δ / ppm


3kb

SiMe2Ph
139.6
133.8
128.6
127.5
77.3
77.0
76.7
31.3
28.6
26.8
23.0
22.3
14.1
13.7
-3.6
-3.7
180
160
140
120
100
80
60
40
20
0
δ / ppm


SiMe2Ph
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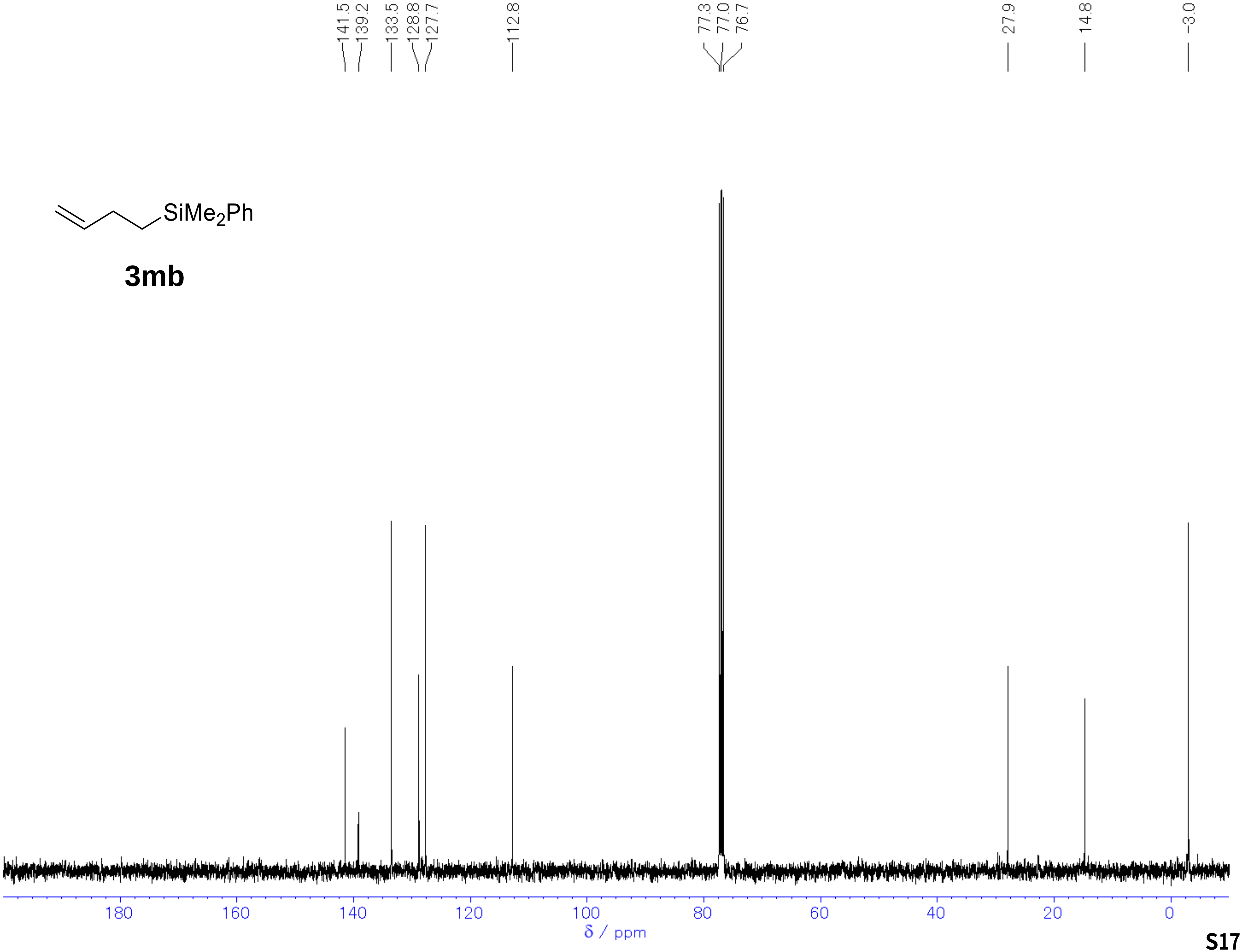
7.51
7.37
7.37
7.36
7.35
7.26
5.94
5.92
5.91
5.90
5.89
5.88
5.87
5.86
5.85
5.84
5.02
5.02
5.01
5.01
4.98
4.98
4.97
4.97
4.92
4.91
4.91
4.91
4.89
4.89
4.88
4.88
2.12
2.10
2.07
2.06
0.89
0.88
0.87
0.86
0.85
0.30
2.07
3.06
1.0
2.06
2.0
2.08
6.02
9
8
7
6
5
4
3
2
1
0
δ / ppm

3mb

SiMe2Ph

3mb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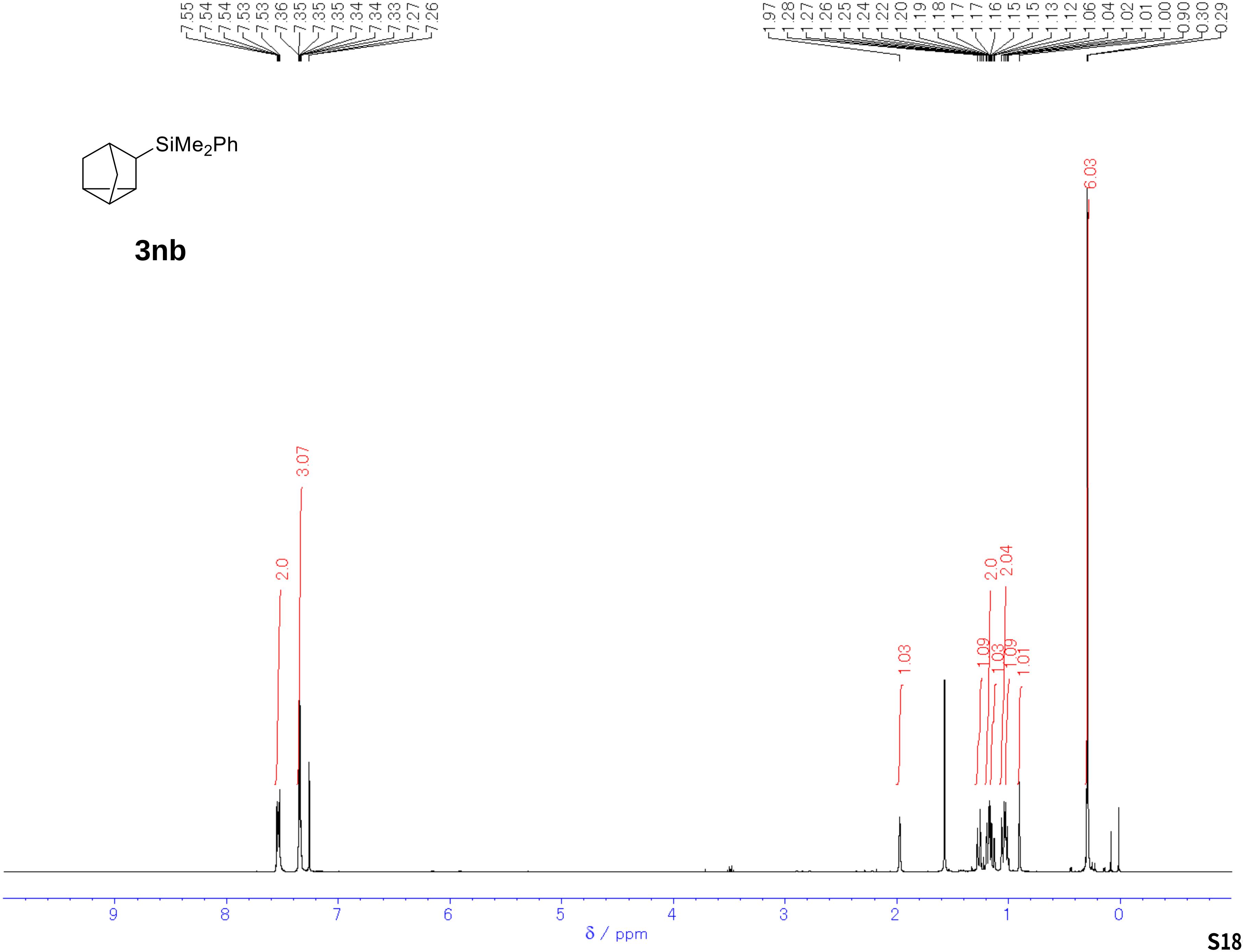
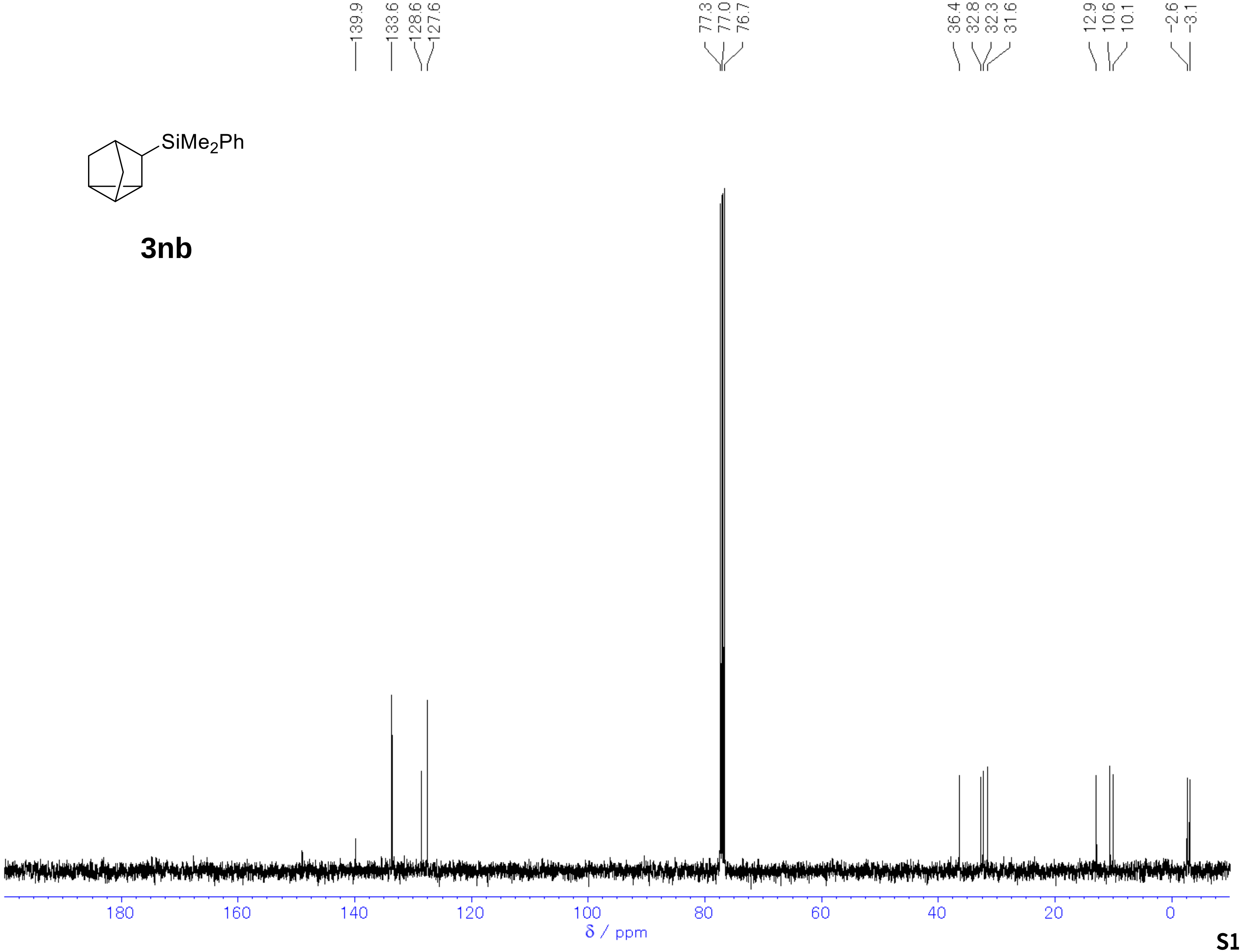
133.5
128.8
127.7
112.8
77.3
77.0
76.7
27.9
14.8
−3.0
180
160
140
120
100
80
60
40
20
0
δ / ppm


7.55
7.54
7.54
7.53
7.53
7.36
7.35
7.35
7.35
7.34
7.34
7.33
7.27
7.26
1.97
1.28
1.27
1.26
1.25
1.24
1.22
1.20
1.19
1.18
1.17
1.17
1.16
1.15
1.15
1.13
1.12
1.06
1.04
1.02
1.01
1.00
0.90
0.30
0.29
SiMe2Ph
3nb
2.0
3.07
1.03
1.09
2.0
1.03
2.04
1.09
1.01
6.03
9
8
7
6
5
4
3
2
1
0
δ / ppm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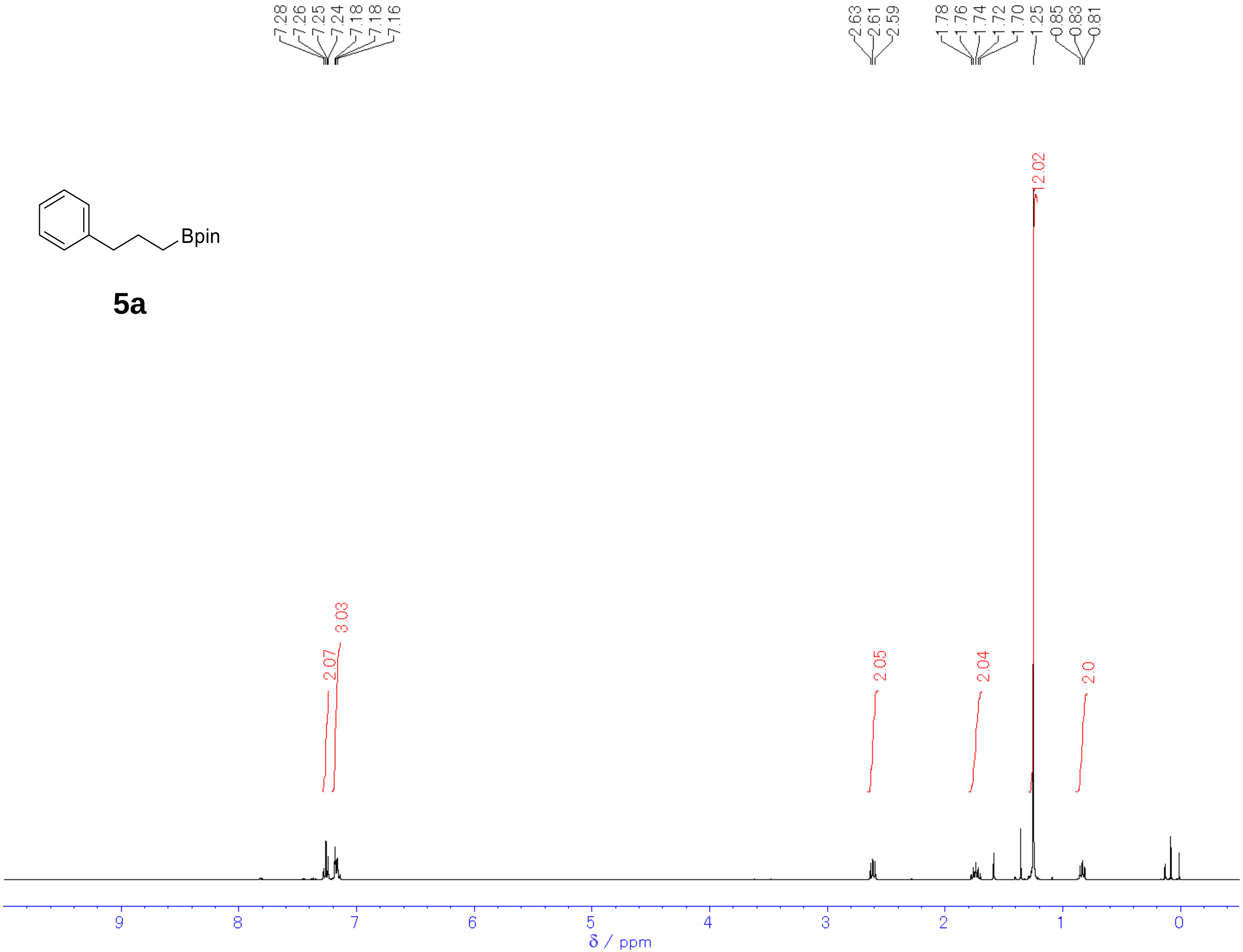
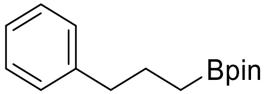
133.6
128.6
127.6
77.3
77.0
76.7
36.4
32.8
32.3
31.6
12.9
10.6
10.1
−2.6
−3.1
SiMe$_2$Ph
180
160
140
120
100
80
60
40
20
0
δ / ppm

3nb

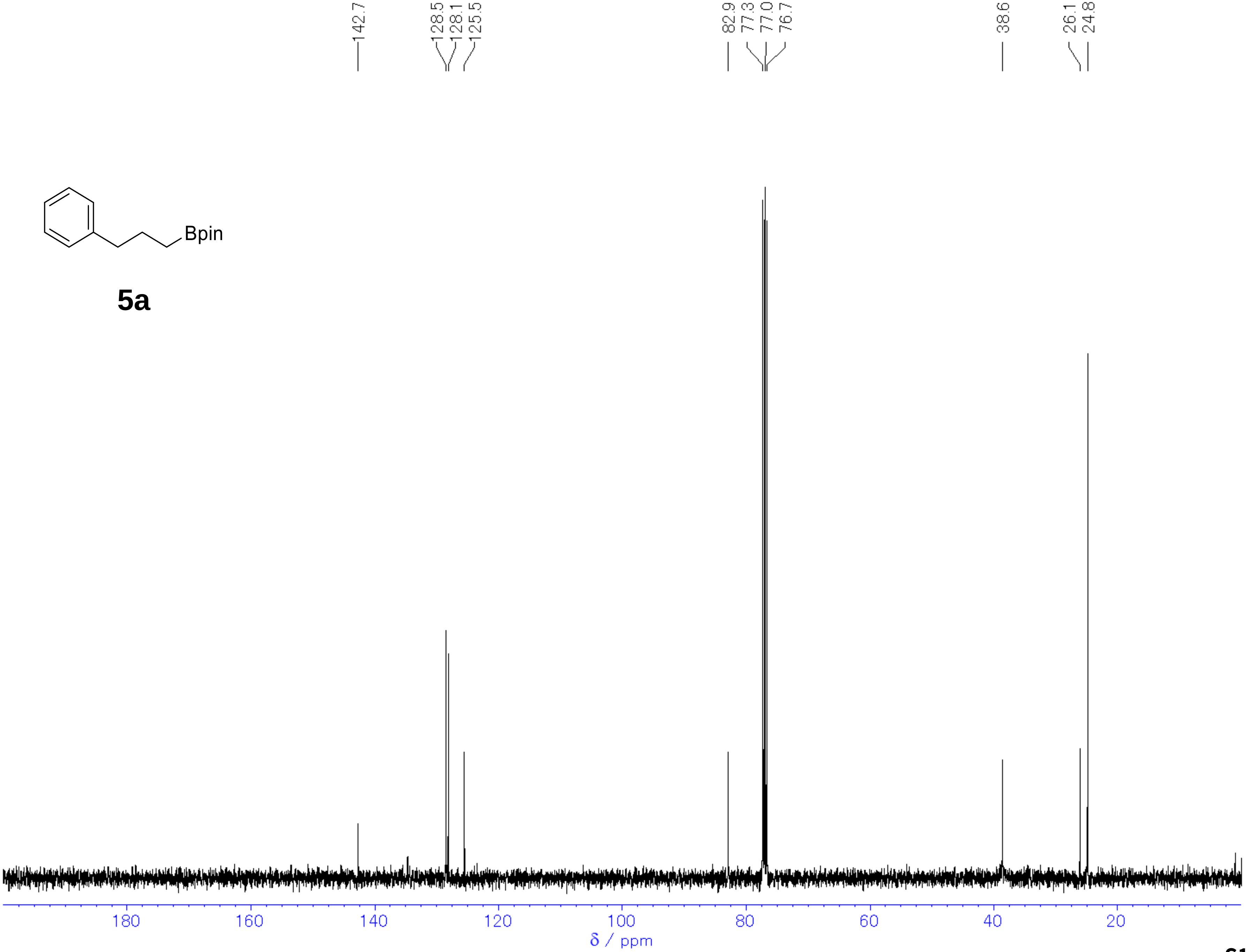


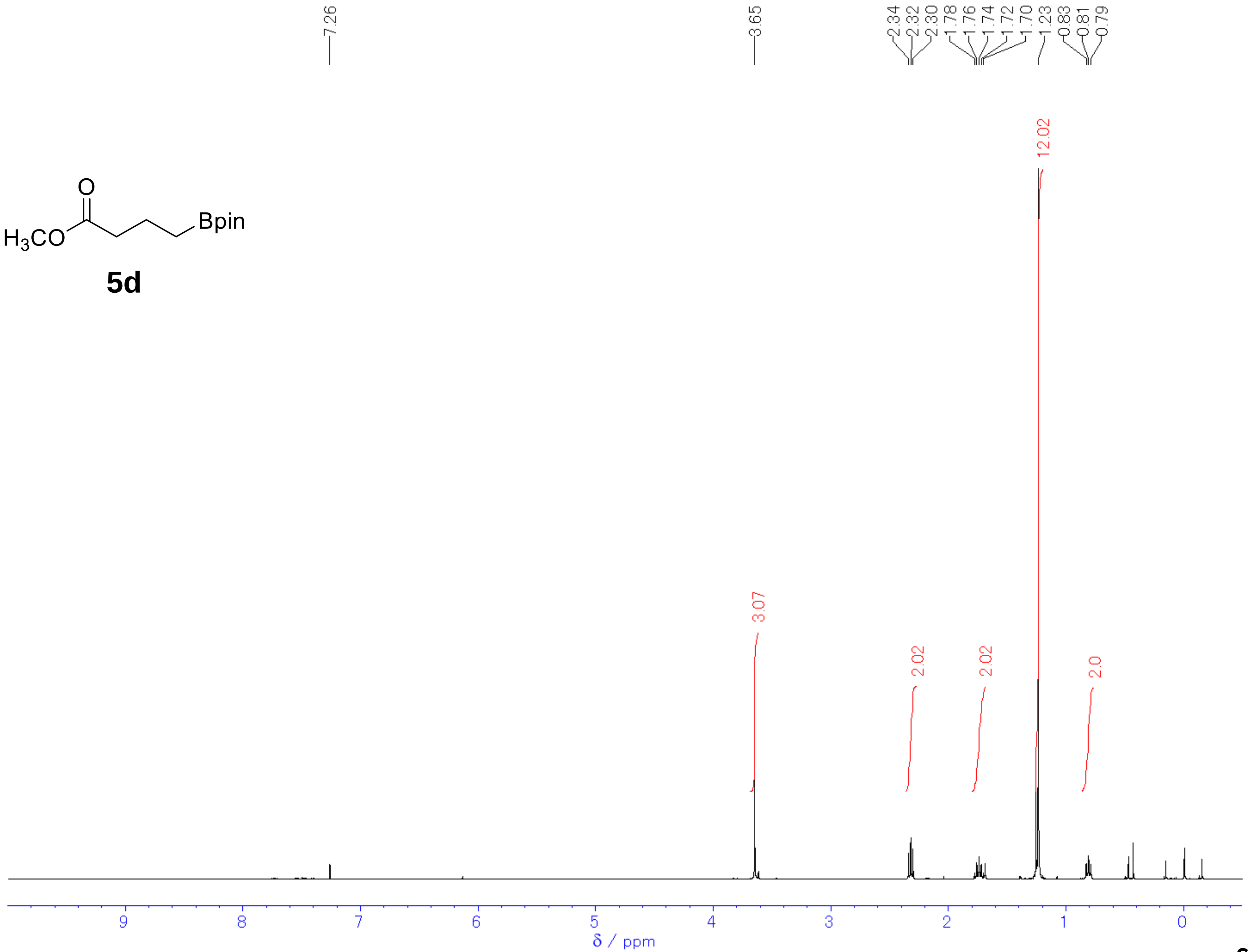
5a

Bpin
7.28
7.26
7.25
7.24
7.18
7.18
7.16
2.63
2.61
2.59
1.78
1.76
1.74
1.72
1.70
1.25
0.85
0.83
0.81
12.02
2.07
3.03
2.05
2.04
2.0
9
8
7
6
5
4
3
2
1
0
δ / ppm


Bpin

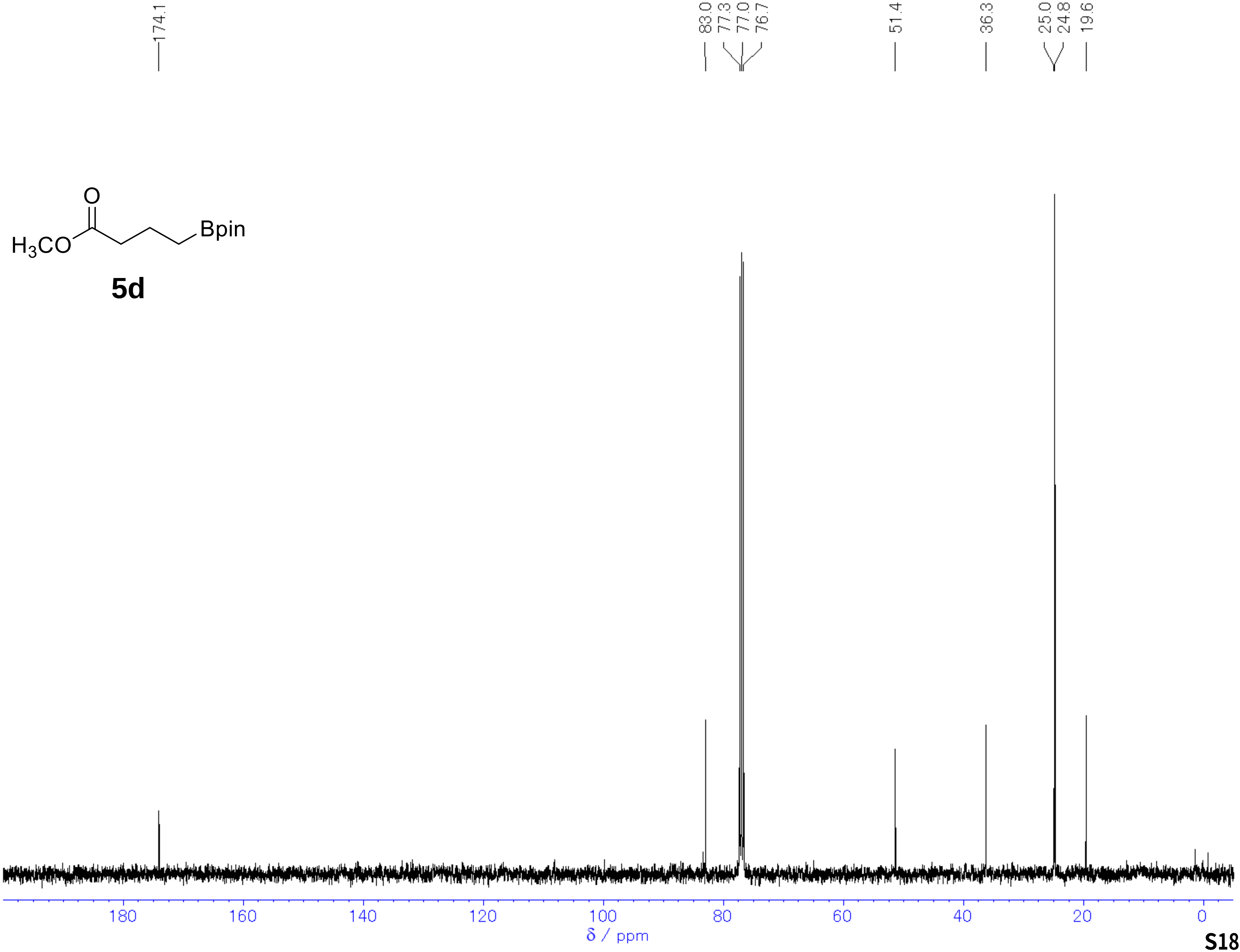
5a


142.7
128.5
128.1
125.5
82.9
77.3
77.0
76.7
38.6
26.1
24.8
180
160
140
120
100
80
60
40
20
δ / ppm

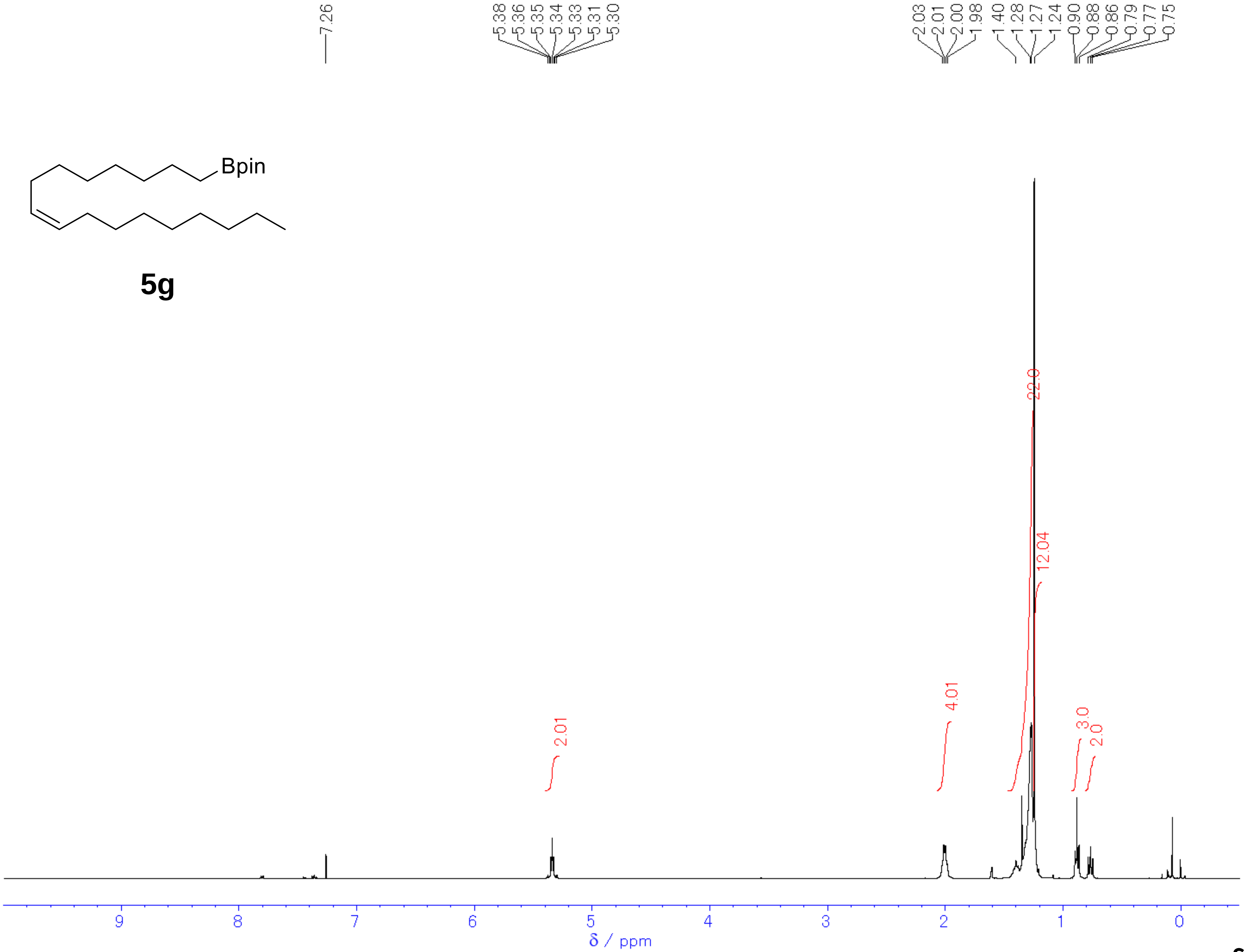


5d

H$_3$CO
O
Bpin
7.26
3.65
2.34
2.32
2.30
1.78
1.76
1.74
1.72
1.70
1.23
0.83
0.81
0.79
12.02
3.07
2.02
2.02
2.0
9
8
7
6
5
4
3
2
1
0
δ / ppm


174.1
83.0
77.3
77.0
76.7
51.4
36.3
25.0
24.8
19.6
O
H_3CO
Bpin
180
160
140
120
100
80
60
40
20
0
δ / ppm

5d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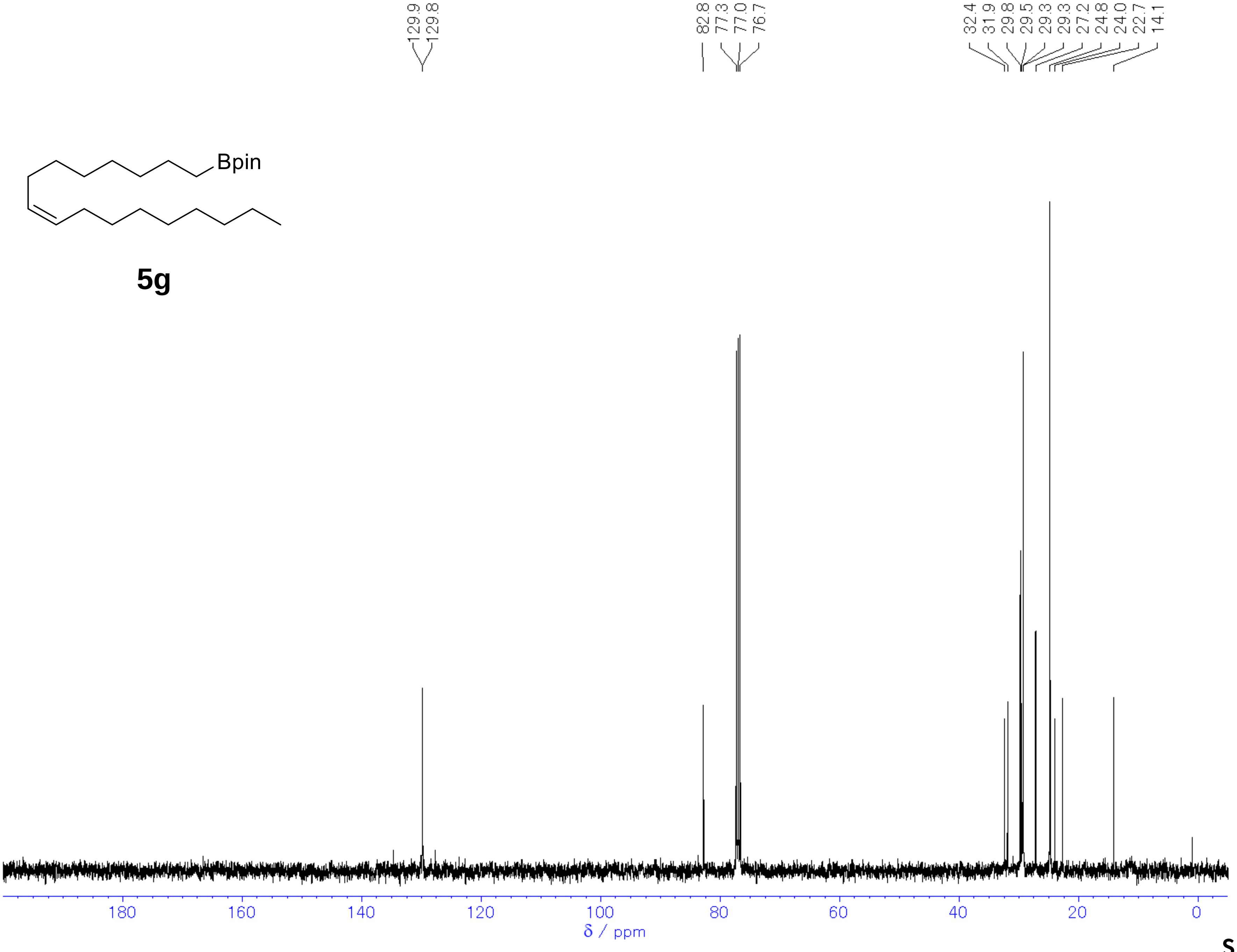
5.38
5.36
5.35
5.34
5.33
5.31
5.30
2.03
2.01
2.00
1.98
1.40
1.28
1.27
1.24
0.90
0.88
0.86
0.79
0.77
0.75
Bpin
2.01
4.01
22.0
12.04
3.0
2.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

5g

Bpin

5g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129.8
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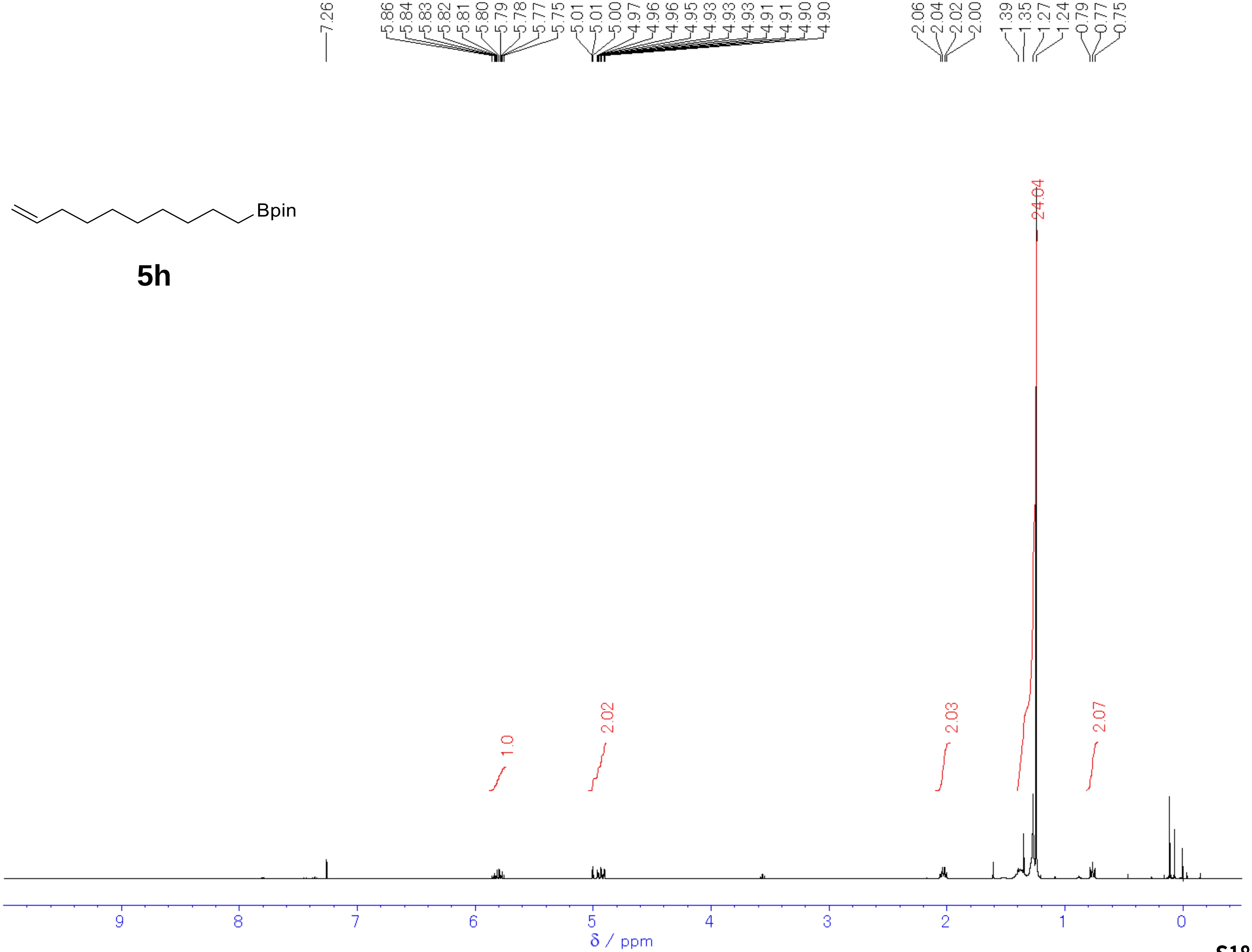
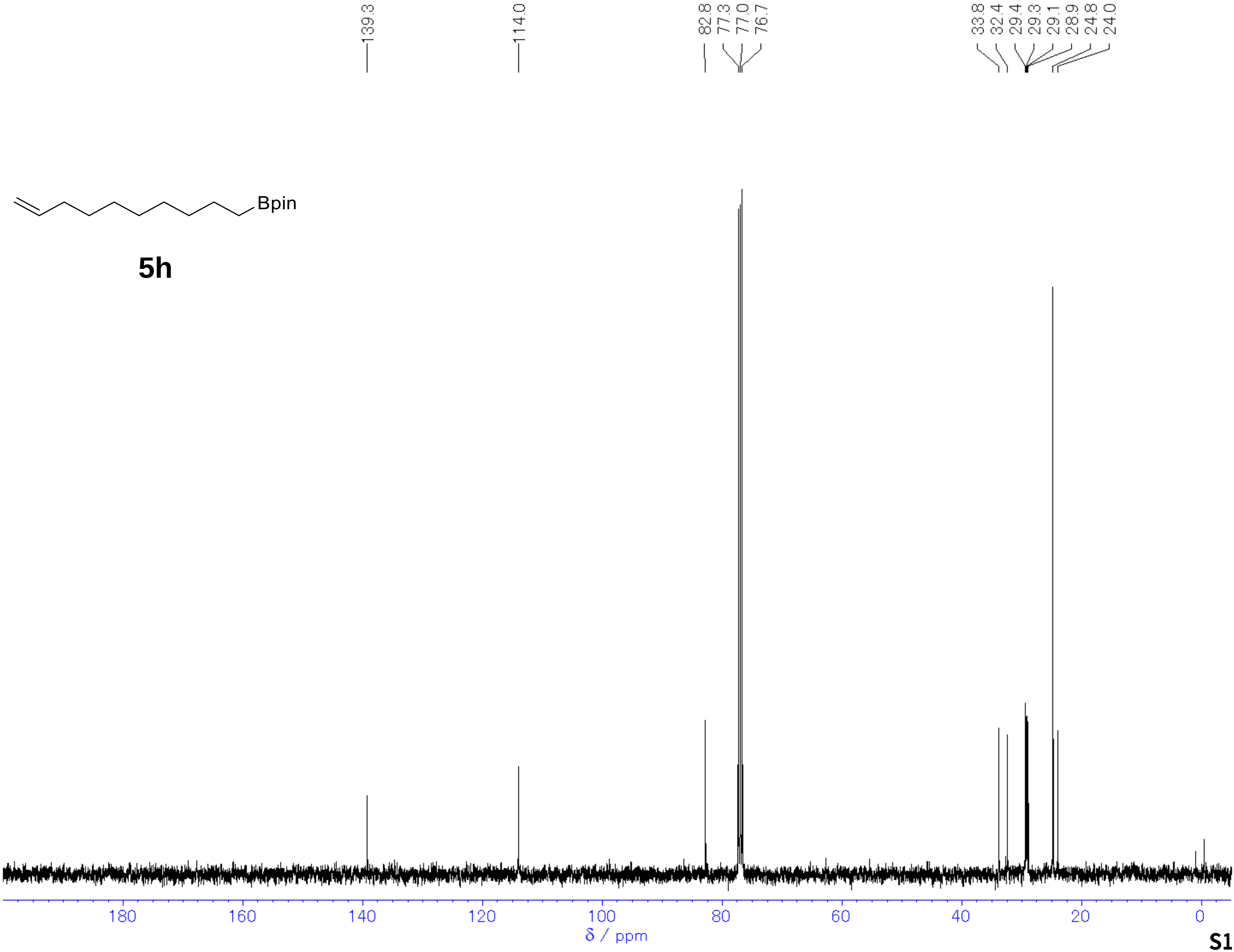
77.3
77.0
76.7
32.4
31.9
29.8
29.5
29.3
29.3
27.2
24.8
24.0
22.7
14.1
180
160
140
120
100
80
60
40
20
0
δ / ppm



5h

Bpin
7.26
5.86
5.84
5.83
5.82
5.81
5.80
5.79
5.78
5.77
5.75
5.01
5.01
5.00
4.97
4.96
4.96
4.95
4.93
4.93
4.93
4.91
4.91
4.90
4.90
2.06
2.04
2.02
2.00
1.39
1.35
1.27
1.24
0.79
0.77
0.75
24.04
1.0
2.02
2.03
2.07
9
8
7
6
5
4
3
2
1
0
δ / ppm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82.8
77.3
77.0
76.7
33.8
32.4
29.4
29.3
29.1
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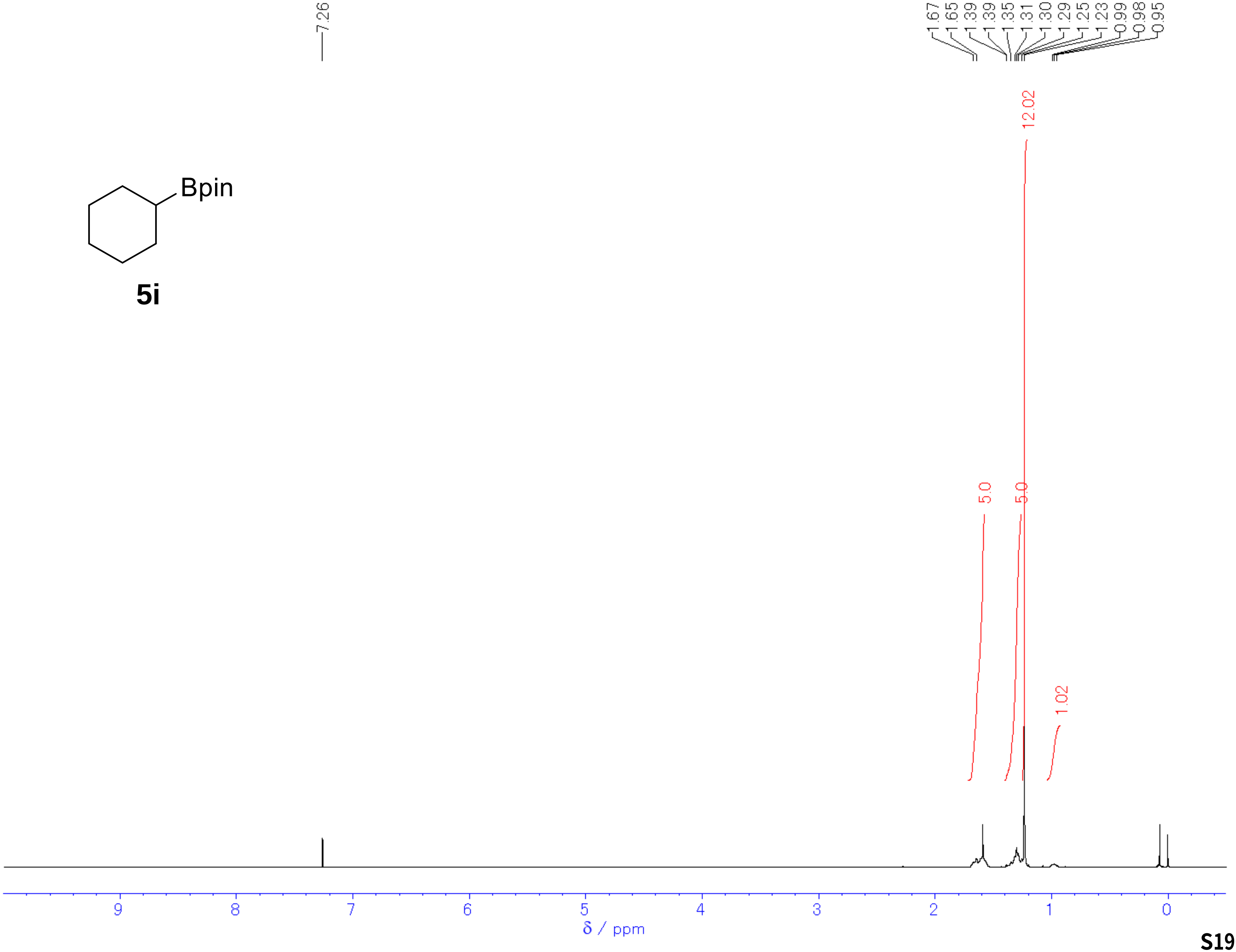
24.8
24.0
Bpin
5h
180
160
140
120
100
80
60
40
20
0
δ / ppm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1.39
1.39
1.35
1.31
1.30
1.29
1.25
1.23
0.99
0.98
0.95
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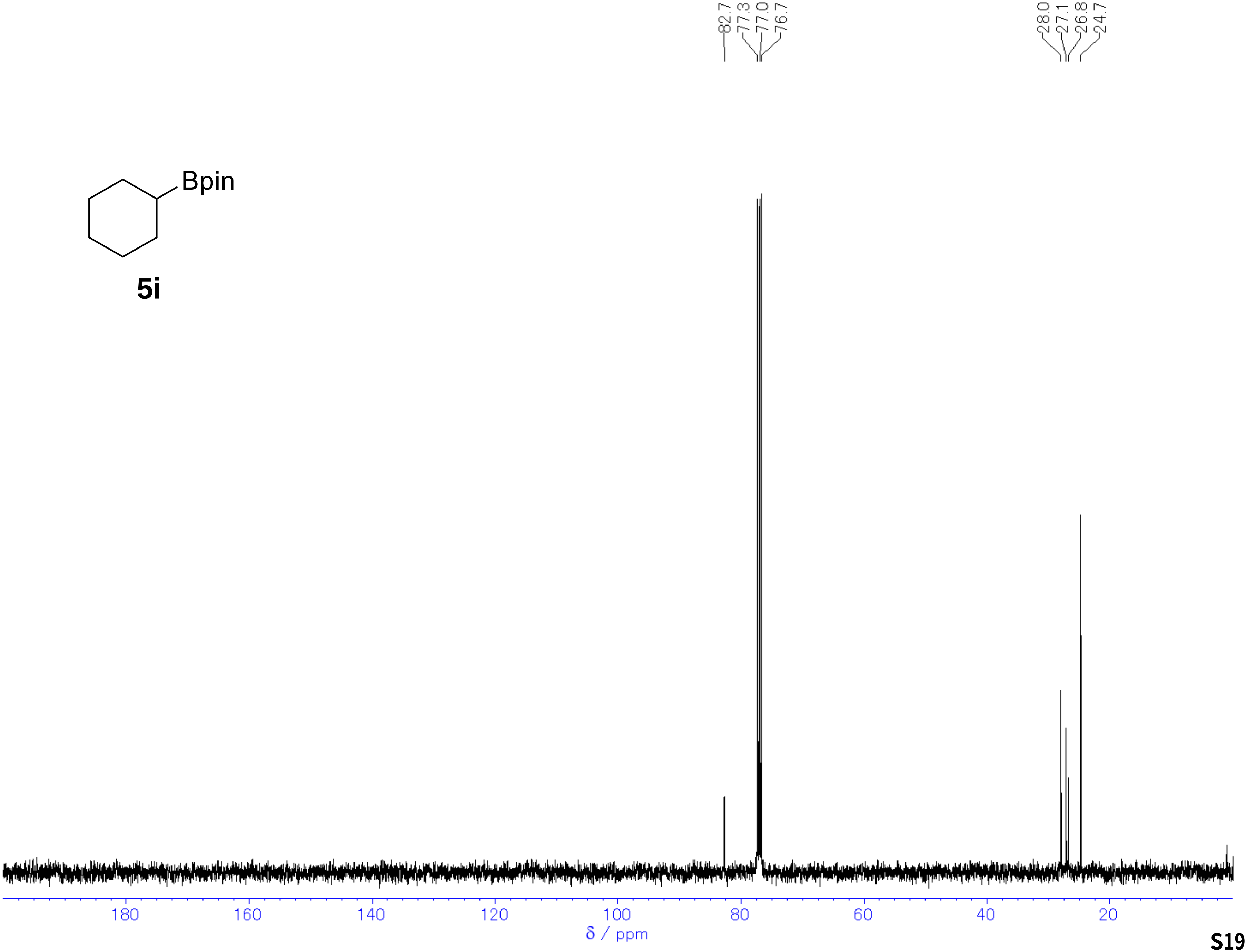
5.0
1.02
9
8
7
6
5
4
3
2
1
0
δ / ppm

5i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77.0
76.7
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24.7
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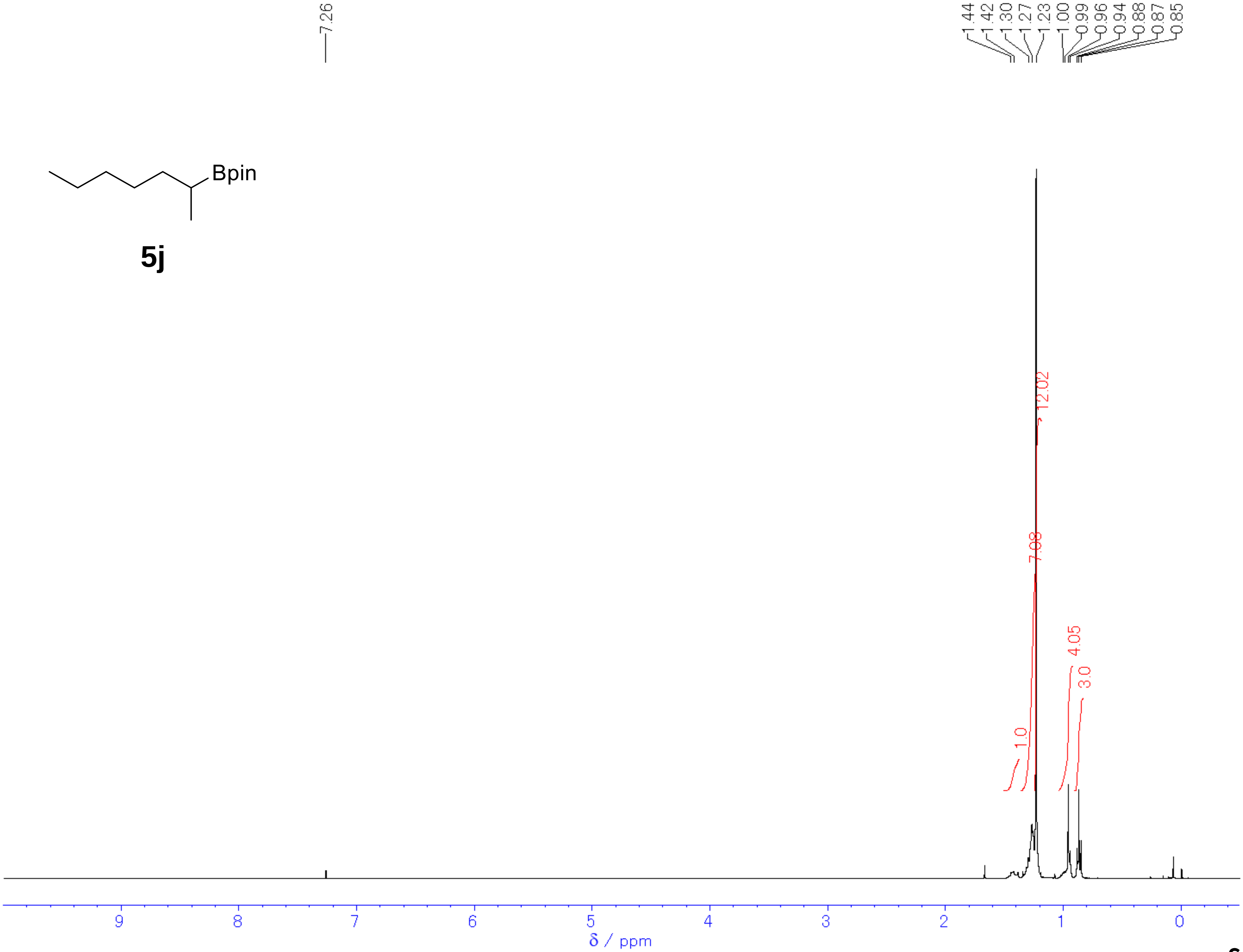
120
100
80
60
40
20
δ / ppm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1.44
1.42
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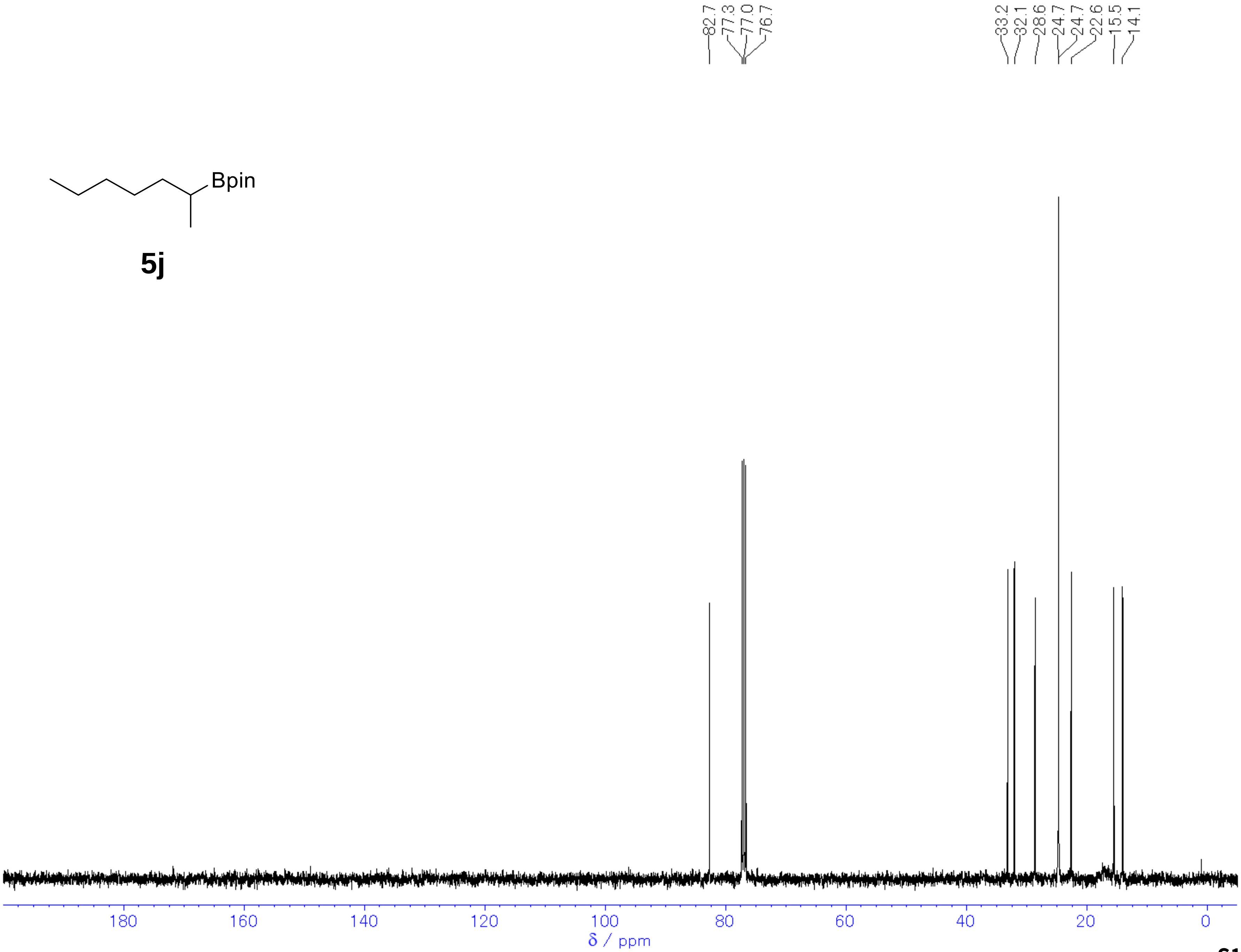
1.27
1.23
1.00
0.99
0.96
0.94
0.88
0.87
0.85
Bpin
12.02
7.08
4.05
3.0
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

5j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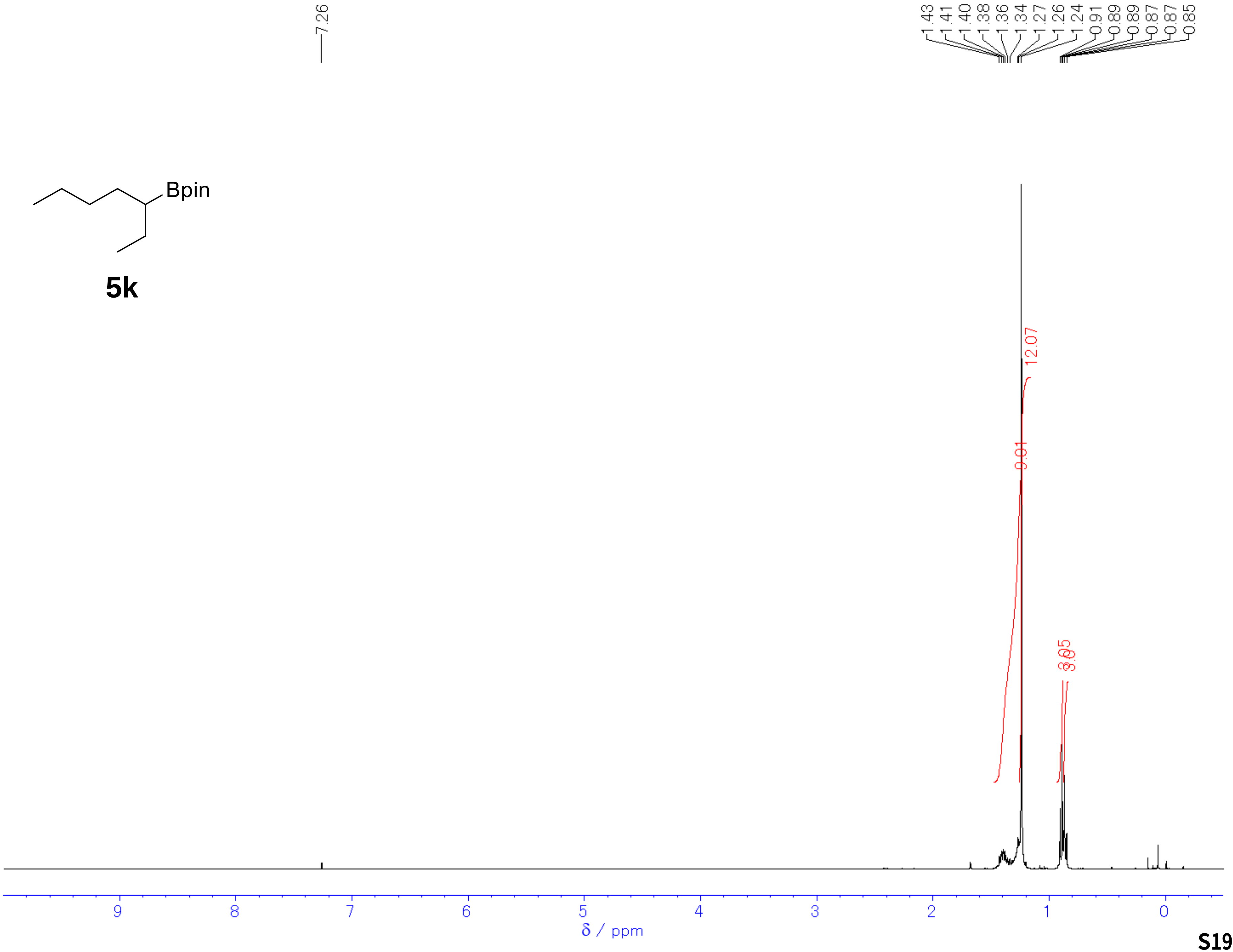
82.7
77.3
77.0
76.7
33.2
32.1
28.6
24.7
24.7
22.6
15.5
14.1
180
160
140
120
100
80
60
40
20
0
δ / ppm

5j


Bpin
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1.38
1.36
1.34
1.27
1.26
1.24
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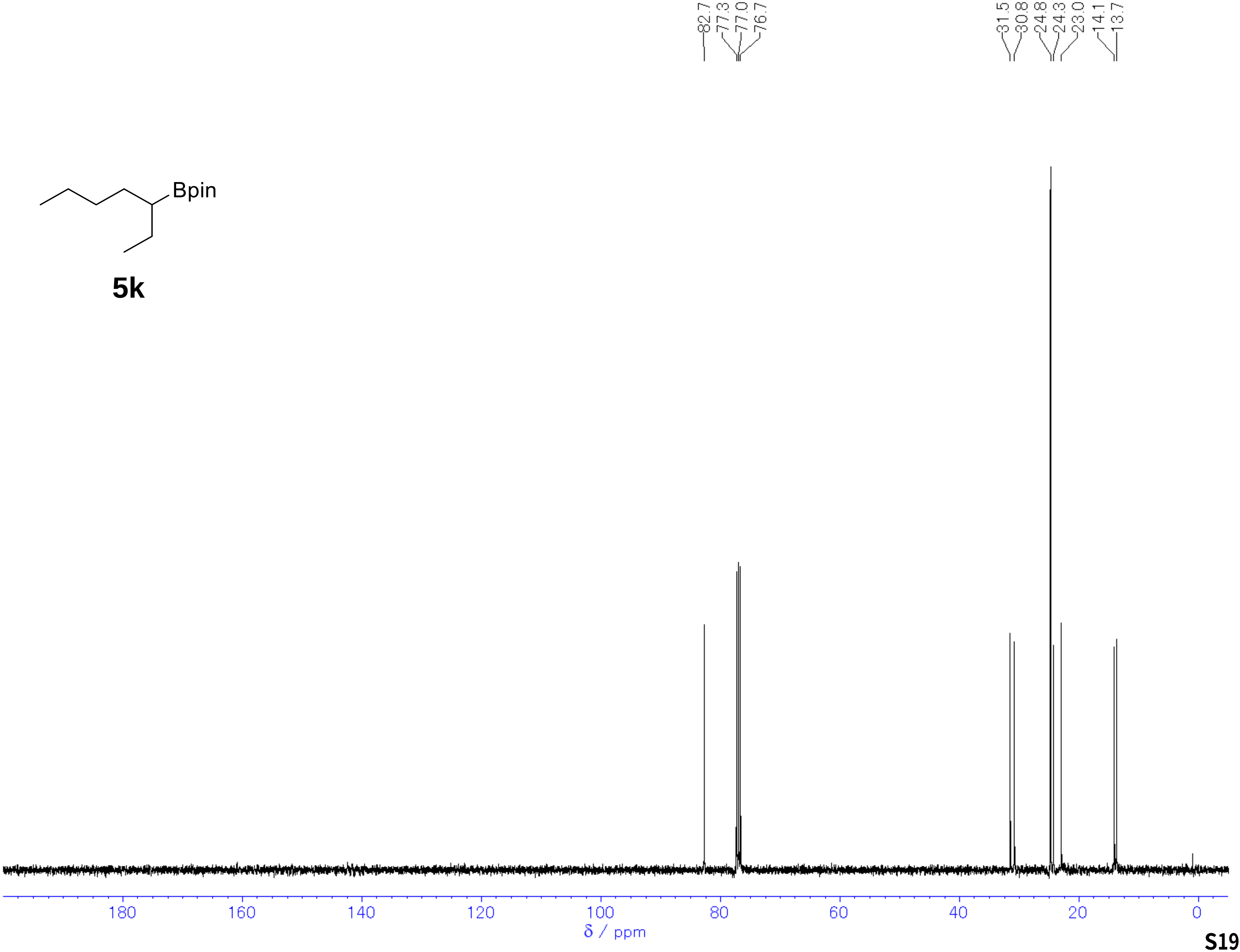
0.89
0.89
0.87
0.87
0.85
12.07
9.01
3.05
3.09
9
8
7
6
5
4
3
2
1
0
δ / ppm

5k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76.7
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30.8
24.8
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13.7
Bpin
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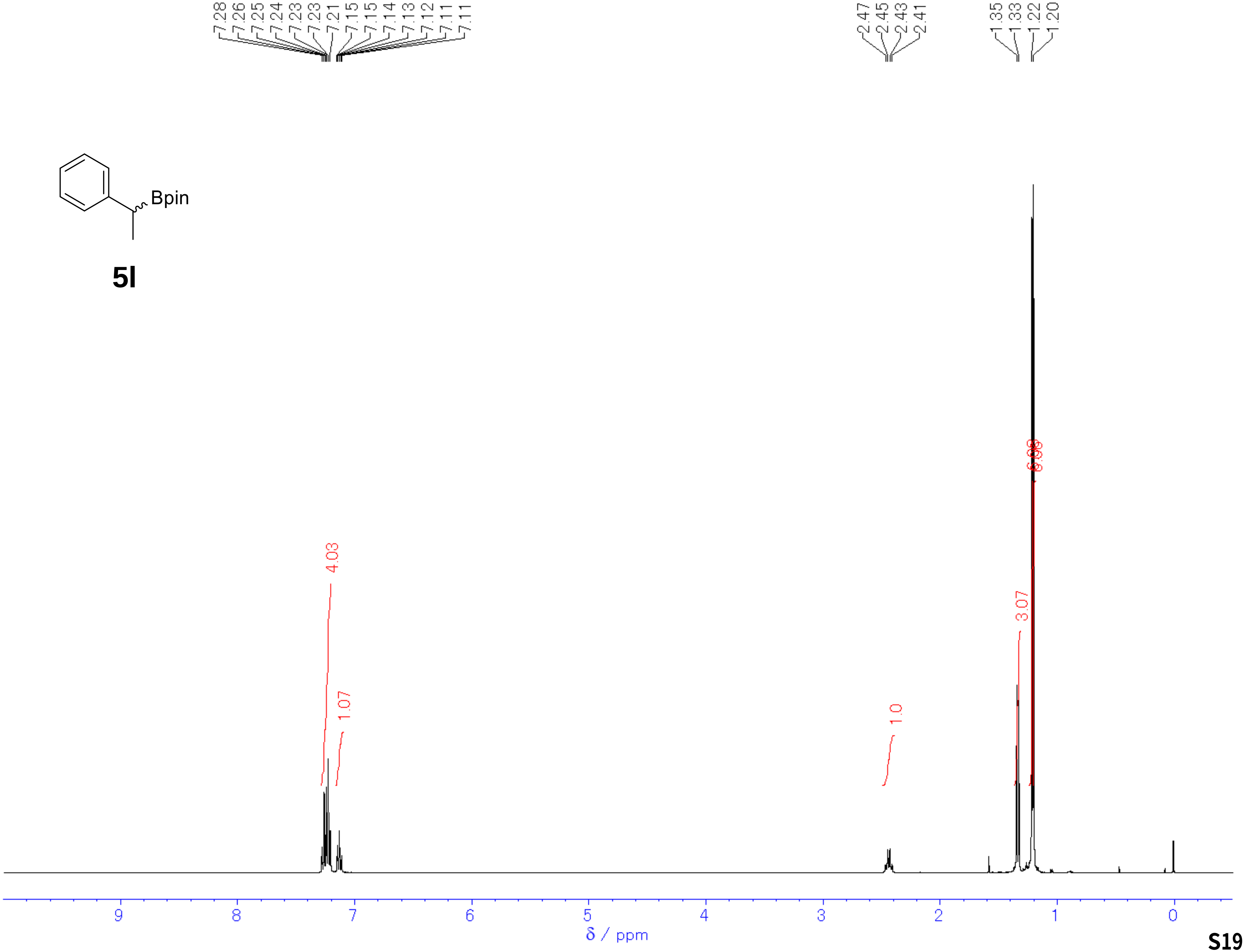
160
140
120
100
80
60
40
20
0
δ / ppm

5k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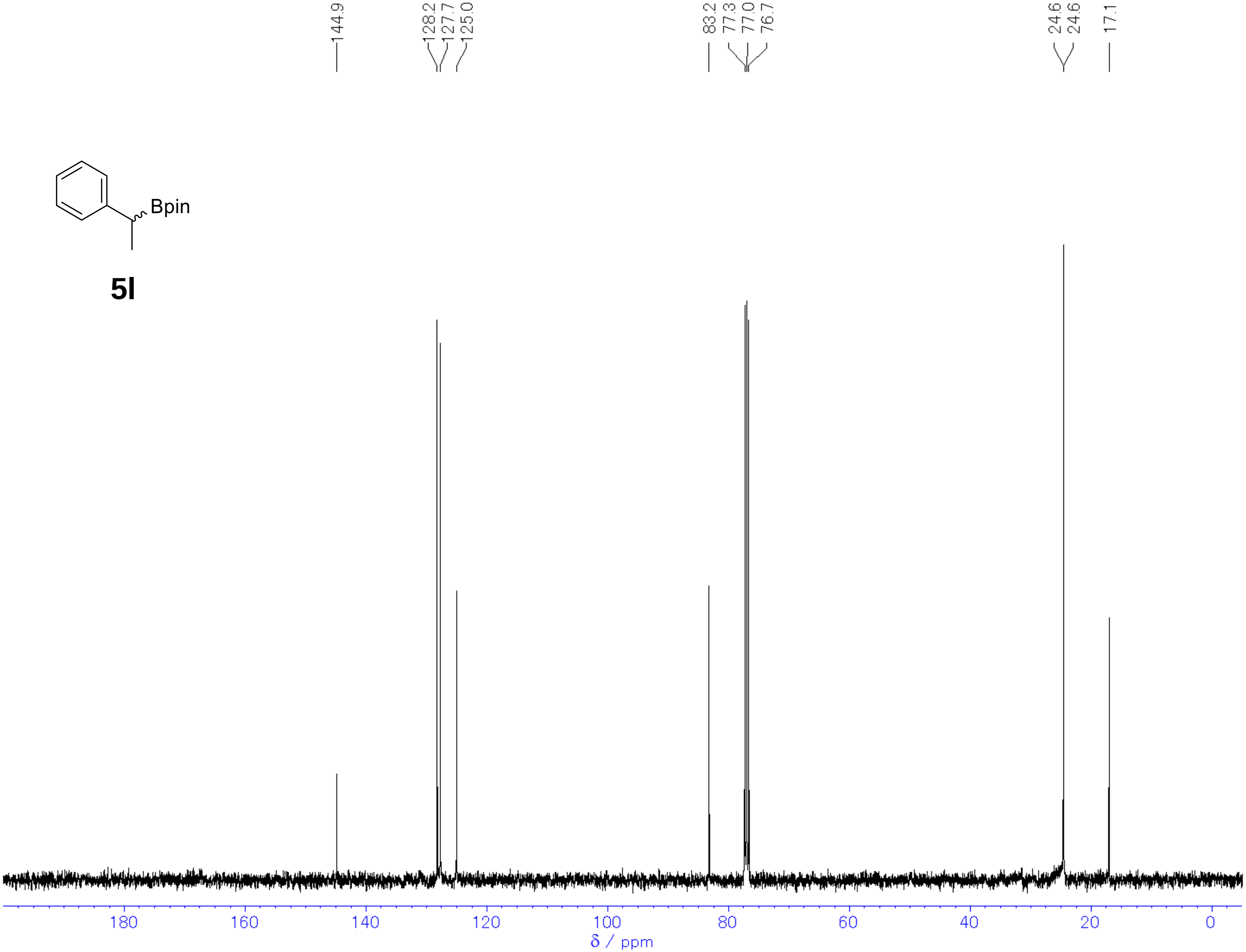
7.13
7.12
7.11
7.11
2.47
2.45
2.43
2.41
1.35
1.33
1.22
1.20
Bpin
5l
4.03
1.07
1.0
3.07
6.08
6.06
9
8
7
6
5
4
3
2
1
0
δ / ppm


Bpin

5l

144.9
128.2
127.7
125.0
83.2
77.3
77.0
76.7
24.6
24.6
17.1
180
160
140
120
100
80
60
40
20
0
δ / ppm