

Supporting Information

Synthesis of Imino[60]fullerenes Using Nitriles and Trimethylsilylmethyl Triflate

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General. All experiments were carried out under argon using standard Schlenk techniques. KO^tBu and (trimethylsilyl)methyl triflate were purchased from Aldrich and used as received without further purification. All anhydrous organic solvents were purchased from Kanto chemicals and purified by a solvent purification system (GlassContour) equipped with columns of activated alumina and supported copper catalyst (G-5) before use. Silica gel column chromatography was performed on Kanto Silica gel 60 (spherical, neutral, 140–325 mesh). Mono(organo)[60]fullerenes C₆₀RH as starting materials were prepared according to literature.¹ All ¹H (500 or 400 MHz) and ¹³C (125 or 100 MHz) spectra were recorded on JEOL ECA500 spectrometer or JEOL ECX400 spectrometer, respectively. Spectra were reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ¹H NMR, from solvent carbon (e.g. δ 77.00 ppm for chloroform) for ¹³C NMR. HPLC analyses were performed on Shimadzu LC-10A system equipped with SPD-M10A diode array detector and Cosmosil-Buckyprep column (4.6 x 250 mm, Nacalai Tesque Co.). Gel permeation column chromatography was performed on a Japan Analytical Industry LC-9201 (eluent: toluene) with JAIGEL 2H and 3H polystyrene columns. High-resolution mass spectra were measured on a JEOL JMS-T100LC ESI-TOF mass spectrometer. IR spectra were recorded on Applied Systems Inc. React-IR 1000.

A typical example for the synthesis of C₆₀(CH₂SiMe₃)[C(=NCH₂SiMe₃)Ph] (3a): 1-(Trimethylsilylmethyl)-7-[N-(trimethylsilylmethyl)phenylimino]-1,7-dihydro(C₆₀-I_h)[5,6]fullerene. To a solution of C₆₀(CH₂SiMe₃)H (50.0 mg, 0.0574 mmol) in benzonitrile (25.0 mL) was added a THF solution of KO^tBu (68.9 μL, 1.0 M, 0.0689 mmol) at 25 °C. A dark green solution of potassium salt of C₆₀(CH₂SiMe₃)[−] was obtained immediately. After stirring for 10 min, Me₃SiCH₂OTf (22.9 μL, 0.115 mmol) were added to the solution at 25 °C. Then, the reaction mixture was stirred for 1 hour. The vacuum distillation was performed to remove benzonitrile. The residue was passed through a pad of silica gel to remove potassium salts. The solution was concentrated to obtain a solution (ca. 2–5 mL) containing the product, which was reprecipitated by addition of methanol (ca. 10–50 mL) to obtain dark brown powder. Purification of the

¹ Y. Matsuo, A. Iwashita, Y. Abe, C.-Z. Li, K. Matsuo, M. Hashiguchi, and E. Nakamura, *J. Am. Chem. Soc.* **2008**, *130*, 15429-15436.

product was performed by silica gel column chromatography (eluent: CS₂/hexane = 1/1 to toluene/EtOAc = 10/1 with 1% Et₃N) to obtain the title compound (35.7 mg, 0.0359 mmol, 63% isolated yield) as black crystals.

FTIR (ReactIR diamond probe): 1621, 1326, 1262 (s), 1102 (s), 1019 (s), 854 (s), 800, 694, 669 cm⁻¹; ¹H NMR (500 MHz, CDCl₃/CS₂): δ 0.162 (s, 9H, Si(CH₃)₃), 0.287 (s, 9H, Si(CH₃)₃), 1.88 (d, *J* = 14.3 Hz, 1H, CH₂Si), 2.04 (d, *J* = 14.3 Hz, 1H, CH₂Si), 3.35 (s, 2H, CH₂Si), 7.54–7.61 (m, 5H, ArH); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ -1.88 (3C, NCH₂Si(CH₃)₃), 0.61 (3C, Si(CH₃)₃), 32.30 (C₆₀CH₂), 47.92 (NCH₂), 56.66 (1C, C₆₀CH₂), 68.40 (1C, C₆₀C=N), 125.24, 128.17, 128.50, 128.85, 128.96, 135.59, 137.64, 137.92, 138.65, 138.78, 139.79, 140.53, 141.80, 141.90, 142.02, 142.41, 142.43, 142.56, 142.57, 142.60, 142.82, 142.96, 143.02, 143.08, 143.15, 143.42, 143.61, 143.75, 143.82, 144.00, 144.13, 144.22, 144.25, 144.27, 144.34, 144.41, 144.54, 144.58, 144.76, 144.78, 144.82, 144.91, 145.37, 145.45, 146.74, 146.78, 146.89, 146.92, 146.97, 147.03, 147.07, 147.49, 147.85, 148.45, 148.51, 148.55, 148.57, 148.60, 148.78, 149.10, 154.37, 156.46, 158.22, 167.13 (C=N); APCI-HRMS (-): calcd for C₇₅H₂₇NSi [M]⁻ 997.1682, found 997.1634.

Preparation of C₆₀(CH₂SiMe₂Ph)[C(=NCH₂SiMe₃)Ph] (3b): 1-(Dimethylphenylsilylmethyl)-7-[N-(trimethylsilylmethyl)phenylimino]-1,7-dihydro(C₆₀-I_h)[5,6]fullerene. Synthesis of the title compound was performed by similar condition employing the procedure of **1** described above using C₆₀(CH₂SiMe₂Ph)H as a starting material. The title compound was isolated in 77% yield as black crystals by purification with silica gel column chromatography (eluent: CS₂/hexane = 1/1 to toluene/EtOAc = 10/1 with 1% Et₃N).

FTIR (ReactIR diamond probe): 1630, 1426, 1262, 1246, 1111, 1021, 831, 760, 729, 696 cm⁻¹; ¹H NMR (500 MHz, CDCl₃/CS₂): δ 0.13 (s, 9H, Si(CH₃)₃), 0.573–0.598 (m, 6H, Si(CH₃)₂), 2.22 (d, *J* = 14.3 Hz, 1H, CH₂Si), 2.36 (d, *J* = 14.3 Hz, 1H, CH₂Si), 3.41 (s, 2H, CH₂Si), 7.04–7.621 (m, 6H, ArH), 7.46 (d, *J* = 7.45 Hz, 2H, ArH), 7.58 (d, *J* = 6.35 Hz, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ -1.98 (3C, Si(CH₃)₃), 0.91 (2C, Si(CH₃)₂Ph), 31.08 (C₆₀CH₂), 47.81 (NCH₂), 56.13 (1C, C₆₀CH₂), 68.20 (1C, C₆₀C=N), 127.65, 128.13, 128.40, 128.63, 128.84, 128.90, 129.22, 133.98, 135.41, 137.64, 137.83, 138.05, 138.51, 138.62, 140.43, 141.50, 141.77, 141.90, 142.27, 142.28, 142.32, 142.44, 142.48, 142.50, 142.73, 142.78, 142.91, 142.97, 143.02, 143.32, 143.46, 143.52, 143.54,

143.56, 143.91, 144.01, 144.08, 144.10, 144.13, 144.23, 144.44, 144.47, 144.60, 144.62, 144.76, 144.78, 145.26, 145.32, 146.62, 146.64, 146.76, 146.78, 146.85, 146.94, 147.42, 147.50, 147.65, 148.19, 148.37, 148.42, 148.74, 148.88, 153.95, 156.04, 157.47, 166.75 (C=N); APCI-HRMS (–): calcd for C₈₀H₂₉NSi [M][–] 59.1838, found 1059.1860.

Preparation of C₆₀(C₆H₄-OMe-4)[C(=NCH₂SiMe₃)Ph] (3c): 1-(4-methoxyphenyl)-7-[N-(trimethylsilylmethyl)phenylimino]-1,7-dihydro(C₆₀-I_h)[5,6]fullerene. Synthesis of the title compound was performed by similar condition employing the procedure of **1** described above using C₆₀(C₆H₄-OMe-4)H as a starting material. The title compound was isolated in 78% yield as black crystals by purification with silica gel column chromatography (eluent: CS₂/hexane = 1/1 to toluene/EtOAc = 5/1 with 1% Et₃N).

FTIR (ReactIR diamond probe): 1609, 1507, 1428, 1299, 1248, 1176, 1034, 852, 839, 700 cm^{–1}; ¹H NMR (400 MHz, CDCl₃/CS₂): δ 0.12 (s, 6H, Si(CH₃)₃), 3.38 (s, 2H, CH₂Si), 4.03 (s, 3H, OCH₃), 7.18 (d, *J* = 6.40 Hz, 2H, ArH), 7.41–7.47 (m, 5H, ArH), 8.23 (d, *J* = 6.80 Hz, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃/CS₂): δ –2.09 (3C, Si(CH₃)₃), 47.74 (CH₂), 55.37 (OCH₃), 61.07 (1C, C₆₀CH₂), 68.44 (1C, C₆₀C=N), 114.82, 128.15, 128.28, 128.53, 128.62, 128.94, 133.29, 135.19, 137.13, 138.00, 138.56, 140.74, 142.06, 142.24, 142.47, 142.54, 142.57, 142.61, 142.65, 142.87, 142.98, 143.03, 143.08, 143.11, 143.14, 143.69, 143.76, 143.85, 144.03, 144.06, 144.08, 144.14, 144.16, 144.20, 144.25, 144.31, 144.35, 144.43, 144.56, 144.73, 144.81, 144.91, 145.30, 145.38, 145.41, 145.45, 146.76, 146.78, 146.80, 146.83, 146.89, 146.92, 146.97, 146.99, 147.07, 147.58, 148.39, 148.56, 148.63, 149.32, 150.33, 151.06, 154.91, 157.17, 158.17, 159.34, 166.18 (C=N); APCI-HRMS (–): calcd for C₇₈H₂₃NOSi [M][–] 1017.1548, found 1017.1565.

Preparation of C₆₀(C₆H₄-NMe₂-4)[C(=NCH₂SiMe₃)Ph] (3d): 1-(4-Dimethylaminophenyl)-7-[N-(trimethylsilylmethyl)phenylimino]-1,7-dihydro(C₆₀-I_h)[5,6]fullerene. Synthesis of the title compound was performed by similar condition employing the procedure of **1** described above using C₆₀(C₆H₄-NMe₂-4)H as a starting material. The title compound was isolated in 78% yield as black crystals by purification with silica gel column chromatography (eluent: CS₂/hexane = 1/1 to toluene/EtOAc = 5/1 with 1% Et₃N).

FTIR (ReactIR diamond probe): 1607, 1519 (s), 1430, 1355, 1246, 1189, 1164, 947,

852 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2$): δ 0.054 (s, 6H, $\text{Si}(\text{CH}_3)_3$), 3.08 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.33 (s, 2H, CH_2), 6.93 (dd, $J = 6.40$ Hz, $J = 2.40$ Hz, 2H, ArH), 7.36–7.42 (m, 5H, ArH), 8.09 (dd, $J = 6.40$ Hz, $J = 2.40$ Hz, 2H, ArH); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2$): δ -2.049 (3C, $\text{Si}(\text{CH}_3)_3$), 40.66 (2C, $\text{N}(\text{CH}_3)_2$), 47.78 (CH_2), 61.21 (1C, C_{60}CH_2), 68.39 (1C, $\text{C}_{60}\text{C}=\text{N}$), 113.34, 125.22, 128.14, 128.26, 128.36, 128.57, 128.95, 128.98, 135.28, 137.10, 138.08, 138.34, 138.70, 140.65, 142.06, 142.24, 142.44, 142.55, 142.62, 142.67, 142.79, 142.90, 142.91, 142.98, 143.00, 143.04, 143.06, 143.08, 143.14, 143.66, 143.75, 143.91, 143.95, 144.03, 144.10, 144.25, 144.33, 144.35, 144.38, 144.52, 144.58, 144.76, 144.86, 144.92, 144.94, 144.99, 145.38, 145.41, 145.81, 146.74, 146.77, 146.89, 146.95, 147.02, 147.06, 147.66, 148.45, 148.52, 148.63, 149.49, 150.23, 150.24, 150.38, 151.55, 154.86, 157.50, 166.29 ($\text{C}=\text{N}$); APCI-HRMS (-): calcd for $\text{C}_{79}\text{H}_{26}\text{N}_2\text{Si}$ $[\text{M}]^-$ 1030.1865, found 1030.1889.

Preparation of $\text{C}_{60}(\text{C}_6\text{H}_4\text{-CF}_3\text{-4})[\text{C}(\text{=NCH}_2\text{SiMe}_3)\text{Ph}]$ (3e):
1-(4-trifluoromethylphenyl)-7-[N-(trimethylsilylmethyl)phenylimino]-1,7-dihydro($\text{C}_{60}\text{-I}_h$)[5,6]fullerene. Synthesis of the title compound was performed by similar condition employing the procedure of **1** described above using $\text{C}_{60}(\text{C}_6\text{H}_4\text{-CF}_3\text{-4})\text{H}$ as a starting material. The title compound was isolated in 62% yield as black crystals by purification with silica gel column chromatography (eluent: $\text{CS}_2/\text{hexane} = 1/1$ to toluene/EtOAc = 5/1 with 1% Et_3N).

FTIR (ReactIR diamond probe): 1617, 1428, 1410 (s), 1324 (s), 1260, 1246, 1169, 1127 (s), 1032, 1067 (s), 1019 (s), 847 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3/\text{CS}_2$): δ 0.013 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 3.21 (CH_2), 7.24–7.31 (m, 5H, ArH), 7.76 (d, $J = 8.0$ Hz, 2H, ArH), 8.29 (d, $J = 8.0$ Hz, 2H, ArH); ^{13}C NMR (100 MHz, $\text{CDCl}_3/\text{CS}_2$): δ -2.15 (3C, $\text{Si}(\text{CH}_3)_3$), 47.79 (CH_2), 61.10 (1C, C_{60}CH_2), 68.63 (1C, $\text{C}_{60}\text{C}=\text{N}$), 122.67, 125.23, 126.33, 123.37, 126.40, 127.64, 127.63, 128.22, 128.28, 128.83, 128.96, 130.26, 134.85, 137.19, 137.81, 138.33, 139.08, 140.90, 142.07, 142.09, 142.24, 142.35, 142.51, 142.54, 142.60, 142.70, 142.98, 143.03, 143.12, 143.14, 143.16, 143.18, 143.63, 143.80, 143.92, 143.99, 144.02, 144.12, 144.20, 144.23, 144.28, 144.30, 144.39, 144.56, 144.68, 144.83, 144.90, 145.01, 145.07, 145.50, 145.57, 145.44, 146.44, 146.86, 146.90, 147.00, 147.08, 147.11, 147.39, 148.45, 148.65, 148.70, 148.97, 149.86, 150.18, 155.21, 156.19, 166.22 ($\text{C}=\text{N}$); APCI-HRMS (-): calcd for $\text{C}_{78}\text{H}_{20}\text{F}_3\text{NSi}$ $[\text{M}]^-$ 1055.1317, found 1055.1310.

Preparation of $C_{60}(C_6H_4-OMe-2)[C(=NCH_2SiMe_3)Ph]$ (3f):
1-(2-methoxyphenyl)-7-[N-(trimethylsilylmethyl)phenylimino]-1,7-dihydro($C_{60}-I_h$)[5,6]fullerene. Synthesis of the title compound was performed by similar condition employing the procedure of **1** described above using $C_{60}(C_6H_4-OMe-2)H$ as a starting material. The title compound was isolated in 62% yield as black crystals by purification with silica gel column chromatography (eluent: CS_2 /hexane = 1/1 to toluene/EtOAc = 5/1 with 1% Et_3N).

FTIR (ReactIR diamond probe): 1632, 1488, 1461, 1434, 1246, 1189, 1100, 1027, 897, 852, 804 cm^{-1} ; 1H NMR (100 MHz, $CDCl_3/CS_2$): δ 0.17 (s, 6H, $SiMe_3$), 3.23 (s, 2H, CH_2Si), 4.03 (s, 3H, OCH_3), 7.11–7.18 (m, 2H, ArH), 7.32–7.41 (m, 5H, ArH), 7.45–7.49 (m, 1H, ArH), 8.23 (dd, $J = 8.00$ Hz, $J = 1.60$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$): δ -2.21 (3C, $Si(CH_3)_3$), 47.56 (CH_2), 54.95 (OCH_3), 59.98 (1C, $C_{60}CH_2$), 68.10 (1C, $C_{60}C=N$), 111.43, 112.04, 121.44, 125.20, 128.12, 128.15, 128.19, 128.52, 128.91, 129.42, 129.69, 130.05, 135.27, 137.60, 138.01, 138.38, 138.91, 139.85, 140.11, 140.45, 141.53, 141.61, 142.01, 142.10, 142.23, 142.36, 142.46, 142.50, 142.58, 142.88, 142.91, 142.94, 142.98, 143.17, 143.22, 143.58, 143.63, 143.95, 143.99, 144.07, 144.12, 144.15, 144.28, 144.31, 144.51, 144.57, 144.61, 144.77, 144.82, 144.92, 144.94, 145.27, 145.33, 146.01, 146.40, 146.74, 146.85, 146.89, 147.48, 147.61, 148.44, 148.46, 148.49, 148.80, 150.24, 150.68, 154.98, 155.85, 158.69, 165.73 ($C=N$); APCI-HRMS (–): calcd for $C_{78}H_{23}NOSi [M]^-$ 1017.1548, found 1017.1524.

Preparation of $C_{60}CH_2SiMe_3[C(=NCH_2SiMe_3)Me]$ (3g):
1-(Trimethylsilylmethyl)-7-[N-(trimethylsilylmethyl)methylimino]-1,7-dihydro($C_{60}-I_h$)[5,6]fullerene. Synthesis of the title compound was performed by similar condition employing the procedure of **1** described above using CH_3CN as a solvent. The title compound was isolated in 32% yield as black crystals by purification with GPC (eluent: toluene).

FTIR (ReactIR diamond probe): 1717, 1474, 1422, 1366, 1223, 1094, 854 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3/CS_2$): δ 0.163 (s, 9H, $Si(CH_3)_3$), 0.29 (s, 9H, $Si(CH_3)_3$), 2.35 (s, 2H, CH_2), 2.38 (s, 3H, Me), 2.50 (d, $J = 14.3$ Hz, 1H, CH_2Si), 2.59 (d, $J = 14.3$ Hz, 1H, CH_2Si); APCI-HRMS (–): calcd for $C_{70}H_{25}NSi_2 [M]^-$ 935.1525, found 935.1521. The ^{13}C NMR measurement was failed because of instability of the product.

Electrochemical measurements. Electrochemical measurements were performed on a HOKUTO DENKO electroanalyzer HZ-5000. A glassy-carbon electrode was used as the working electrode and the counter electrode was a platinum coil. All potentials were recorded with vs a Ag/Ag⁺ electrode reference electrode and corrected against Fc/Fc⁺ (Fc: ferrocene). Cyclic voltammetry (CV) was performed at a scan rate of 100 mVs⁻¹. All half-wave potentials are given as $E_{1/2} = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively.

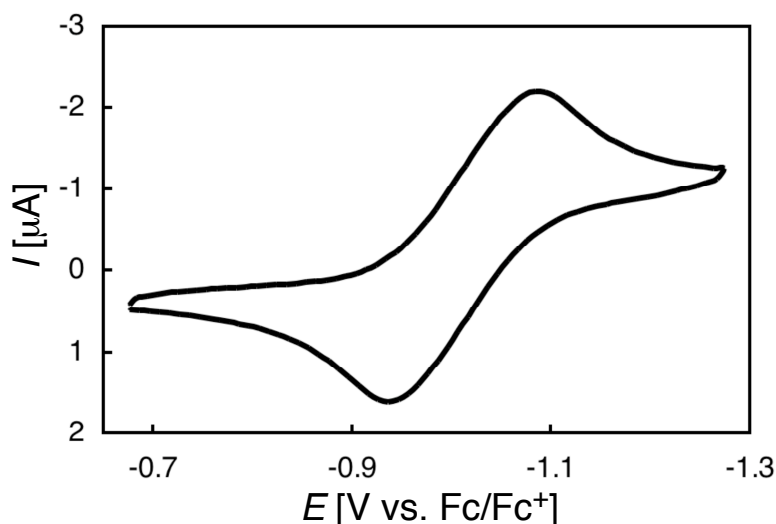
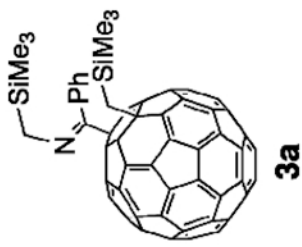
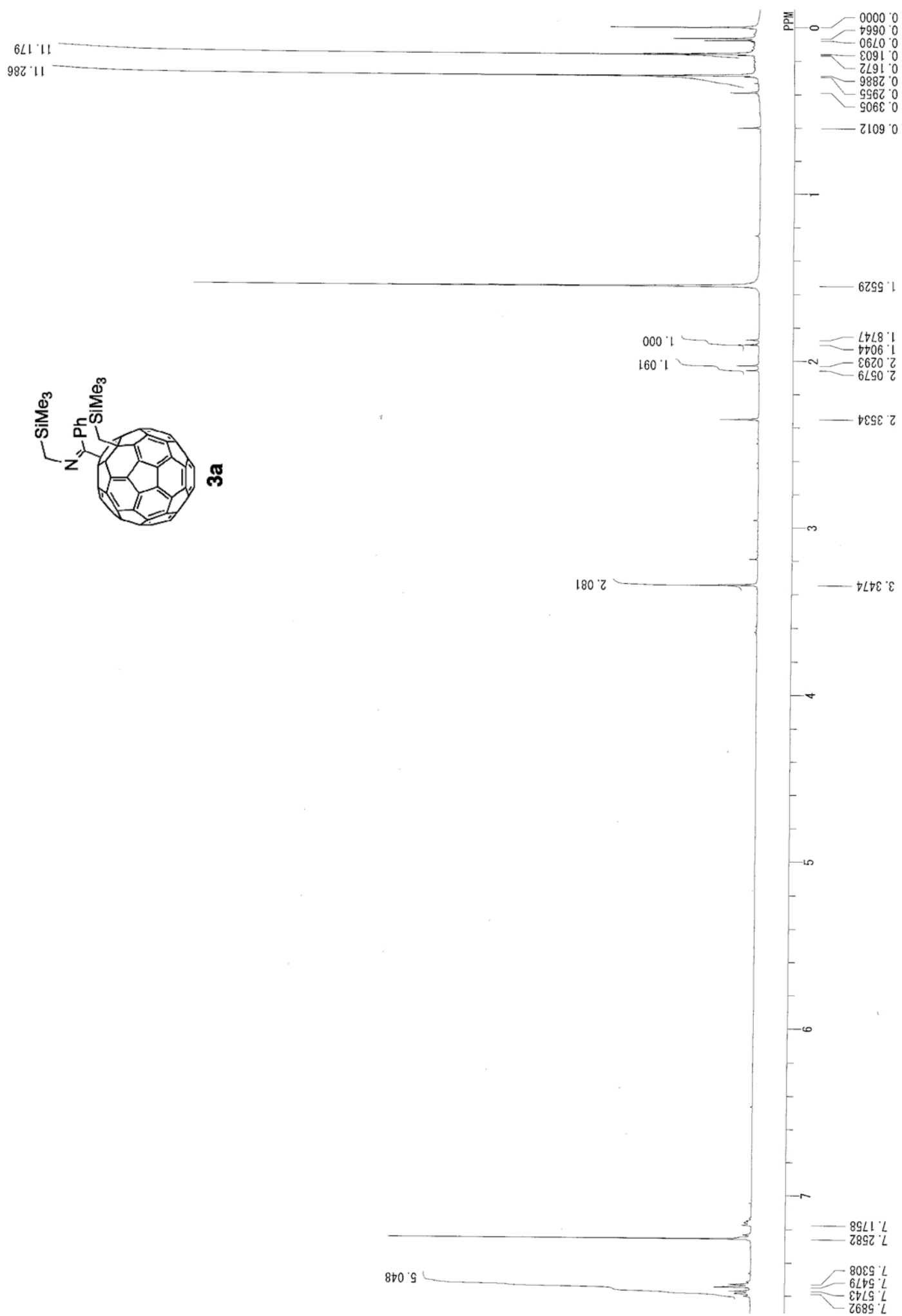
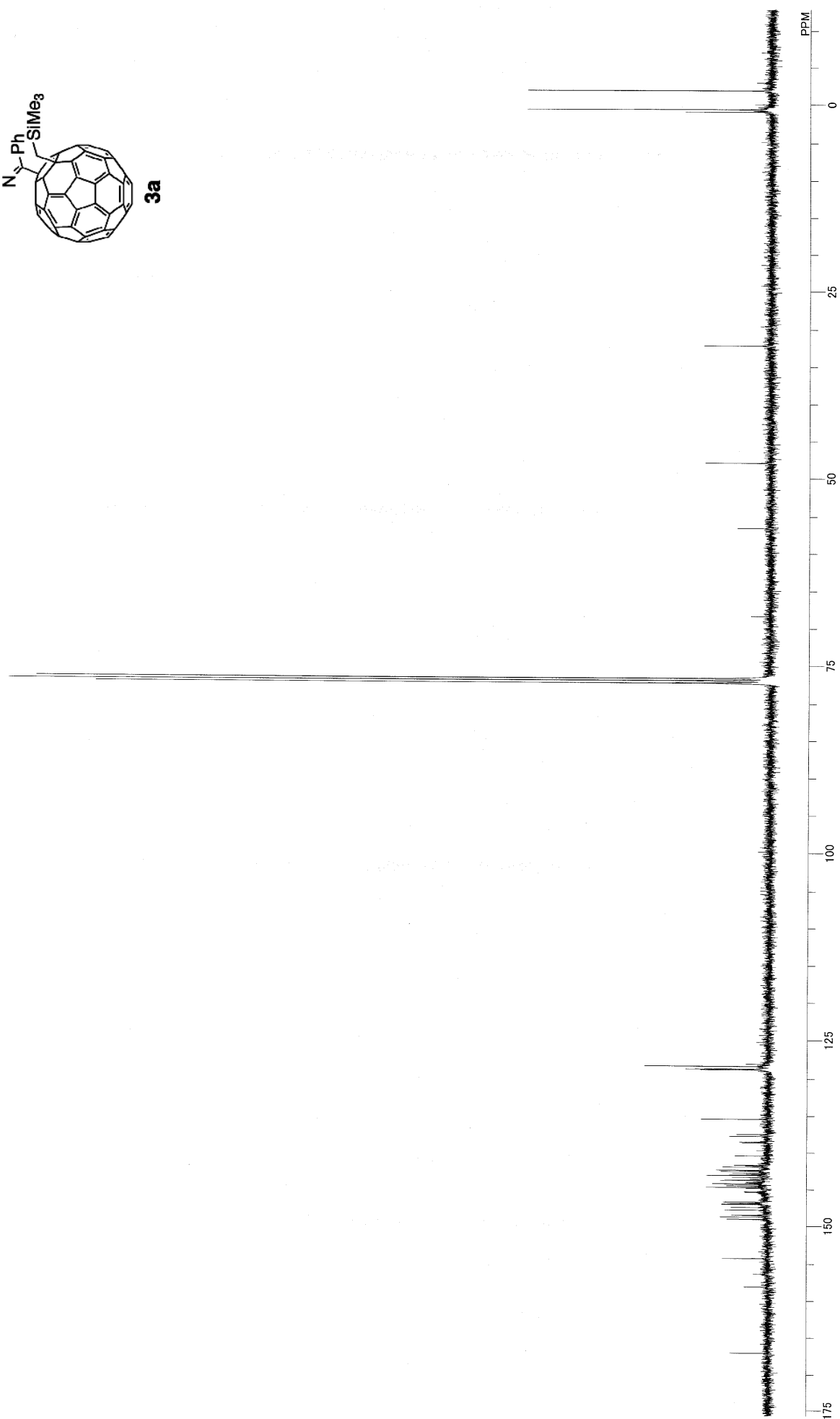
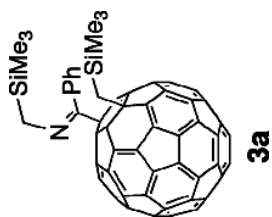
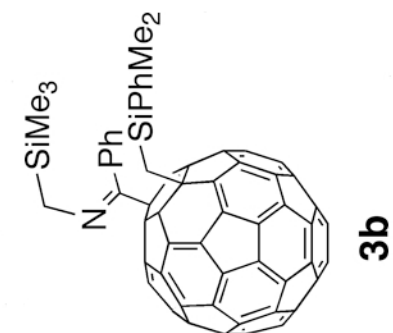
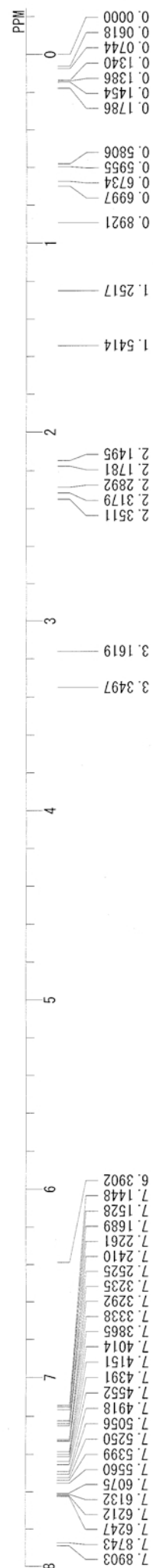


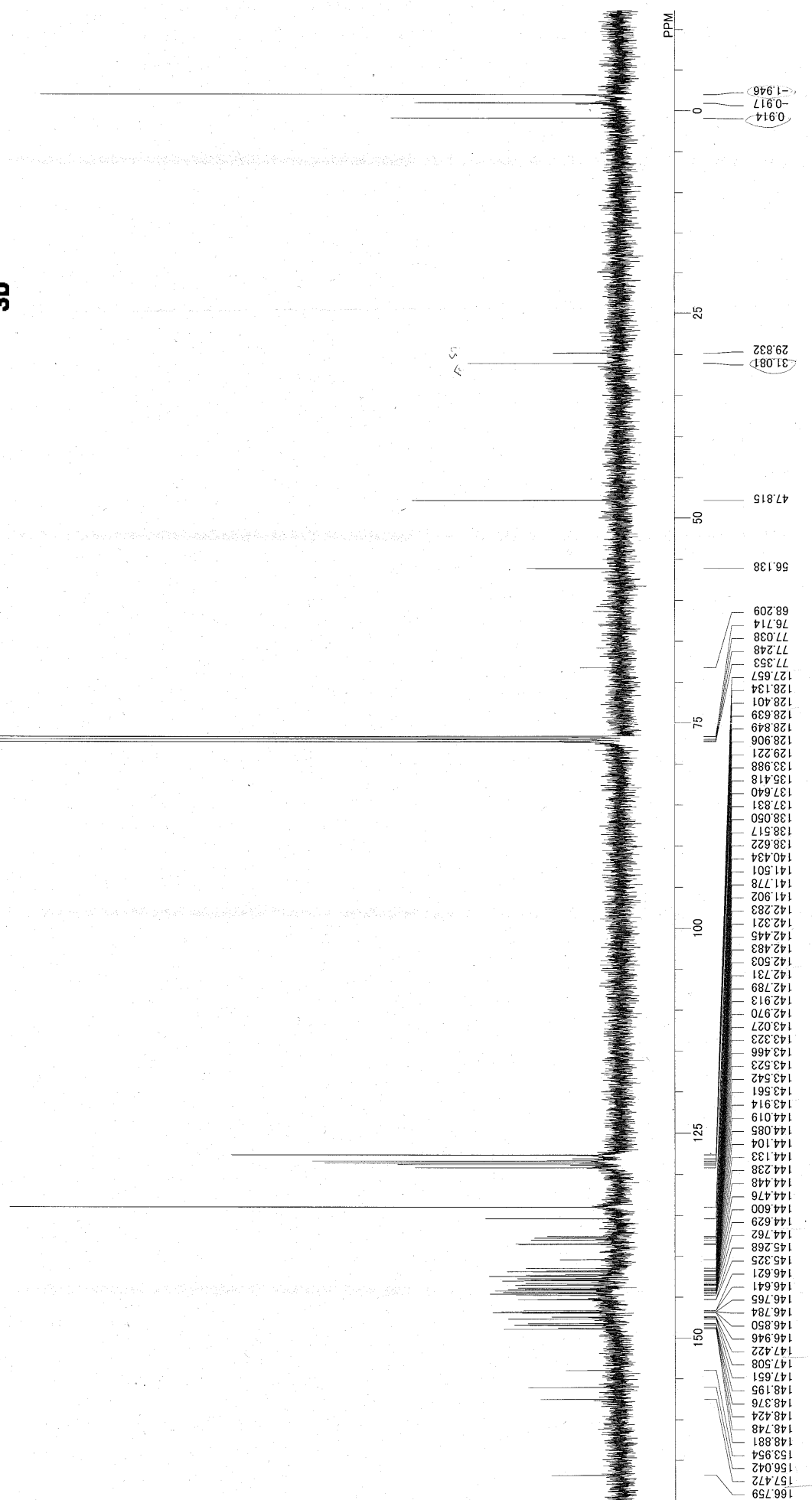
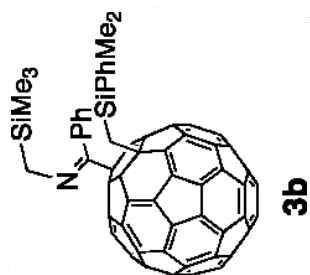
Figure S1. Cyclic voltammograms of **3c**. Measurements were carried out at 25 °C in a THF solution (2.5 mM) containing *n*-Bu₄NClO₄ (0.1 mM) as supporting electrolyte.

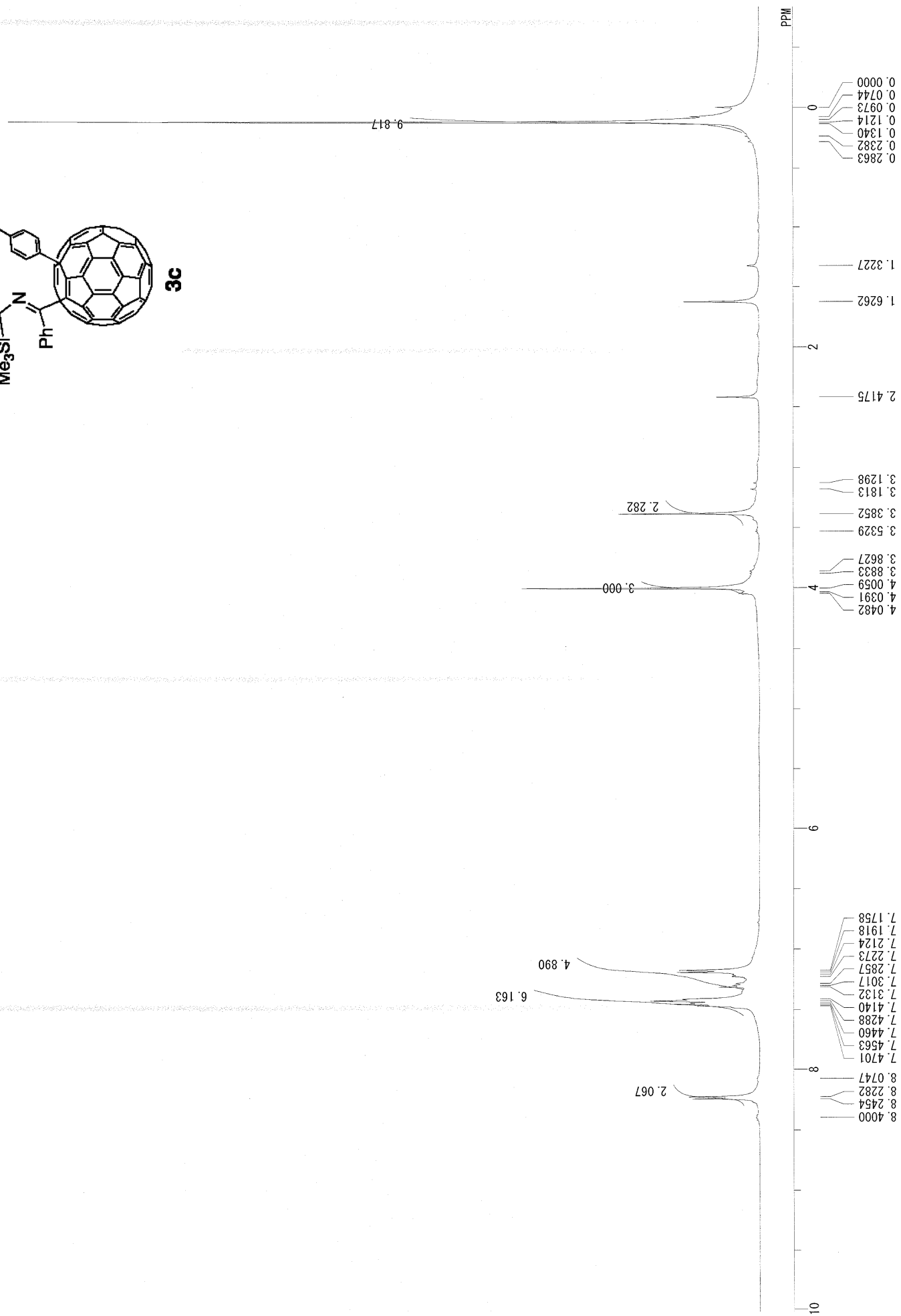
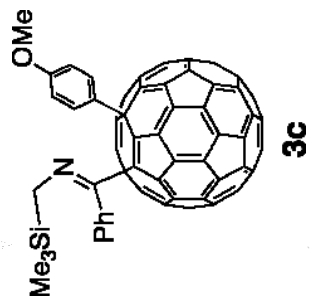
X-ray Crystallographic Analysis. X-ray diffraction data of **3c** was collected on a Rigaku RAXIS-RAPID II imaging plate diffractometer with graphite-monochromated CuK α radiation. The structure of **3c** was solved by the direct method (SIR97). The positional and thermal parameters of non-hydrogen atoms except for several disordered atoms were refined anisotropically on F^2 by the full-matrix least-squares method, using SHELXL-97. Hydrogen atoms were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms.

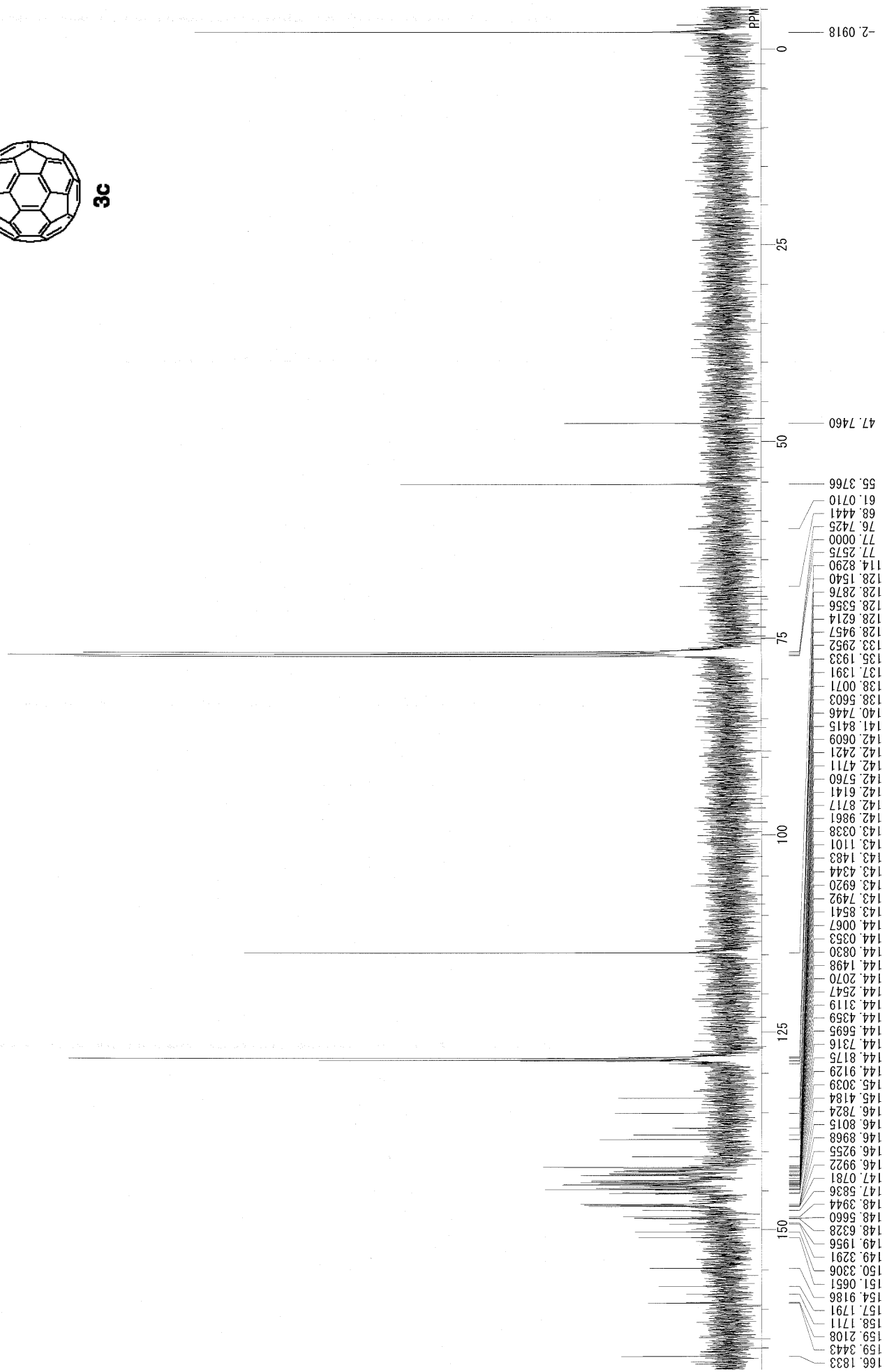
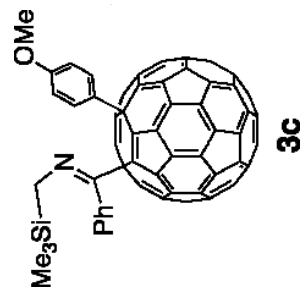


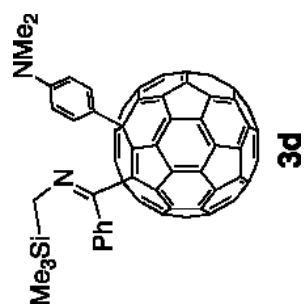




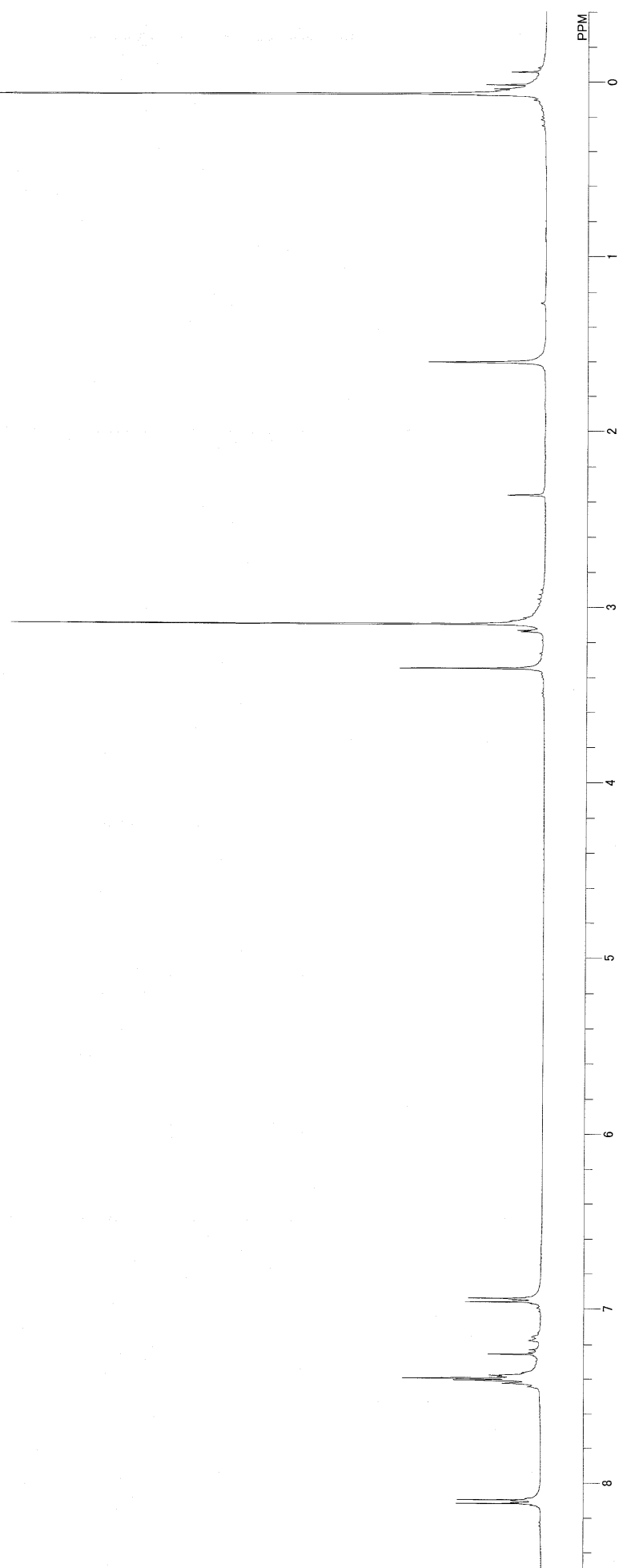


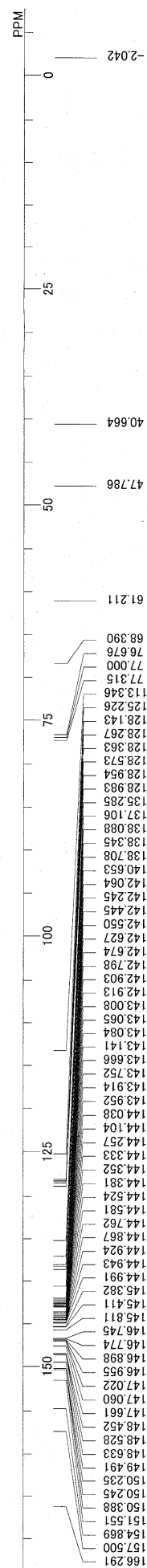
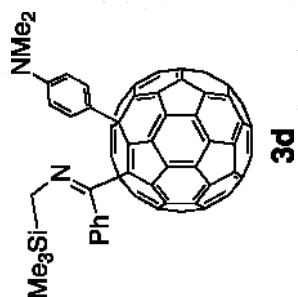


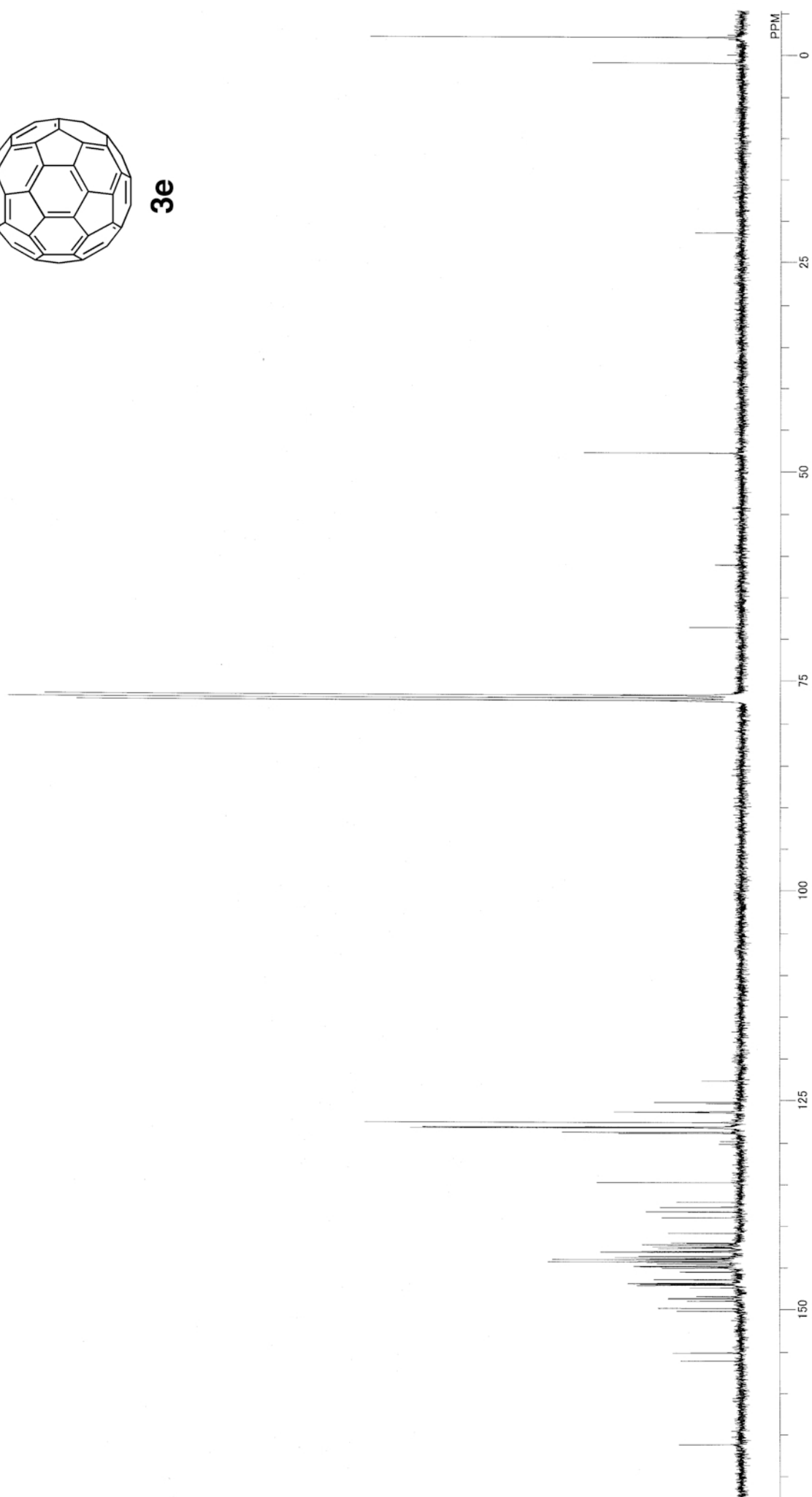
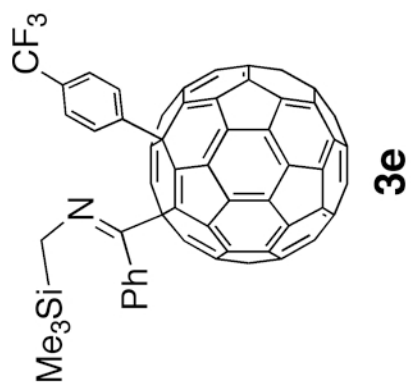


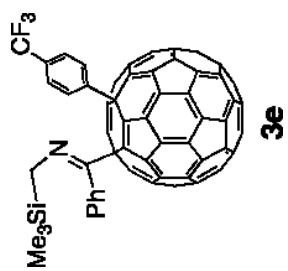


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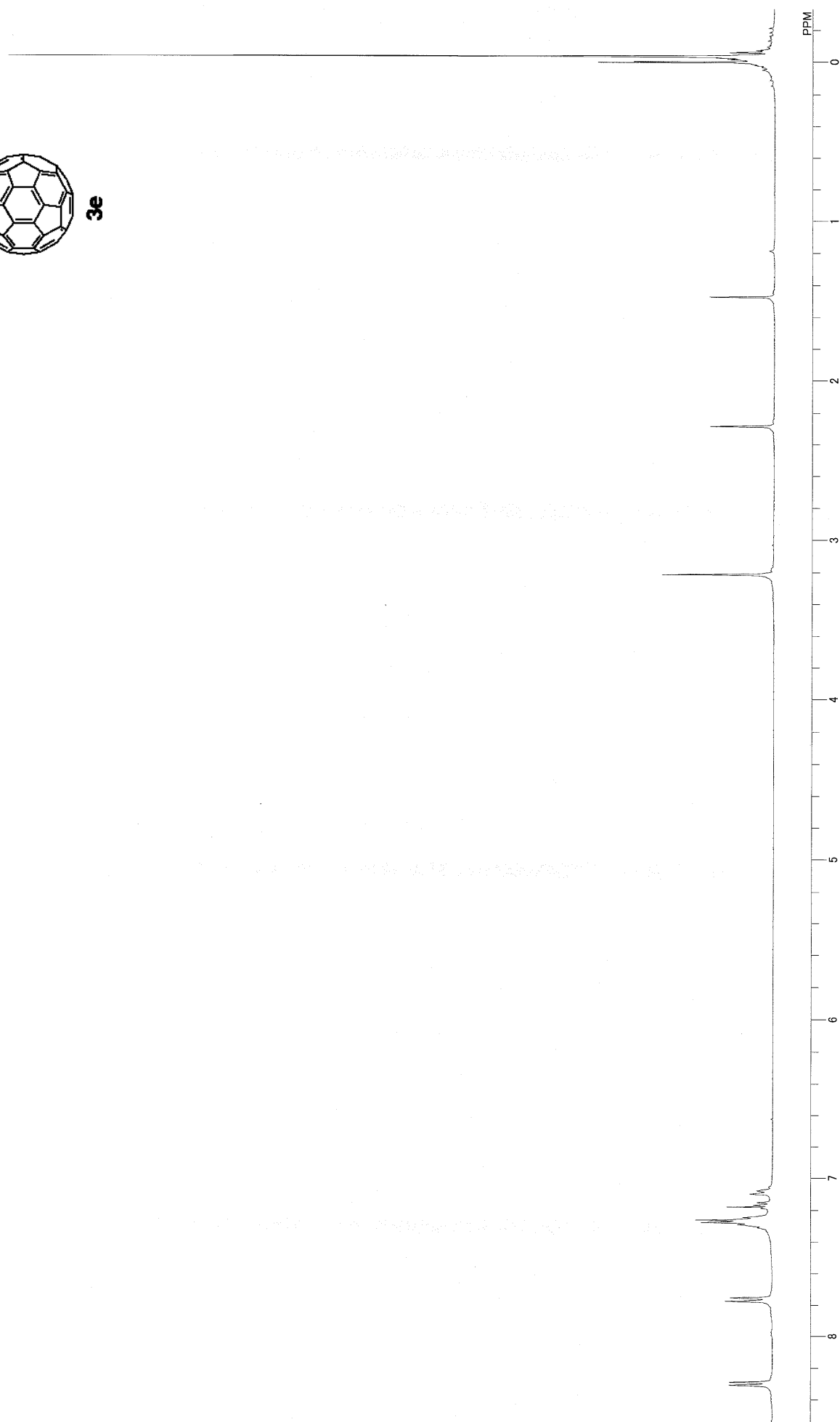


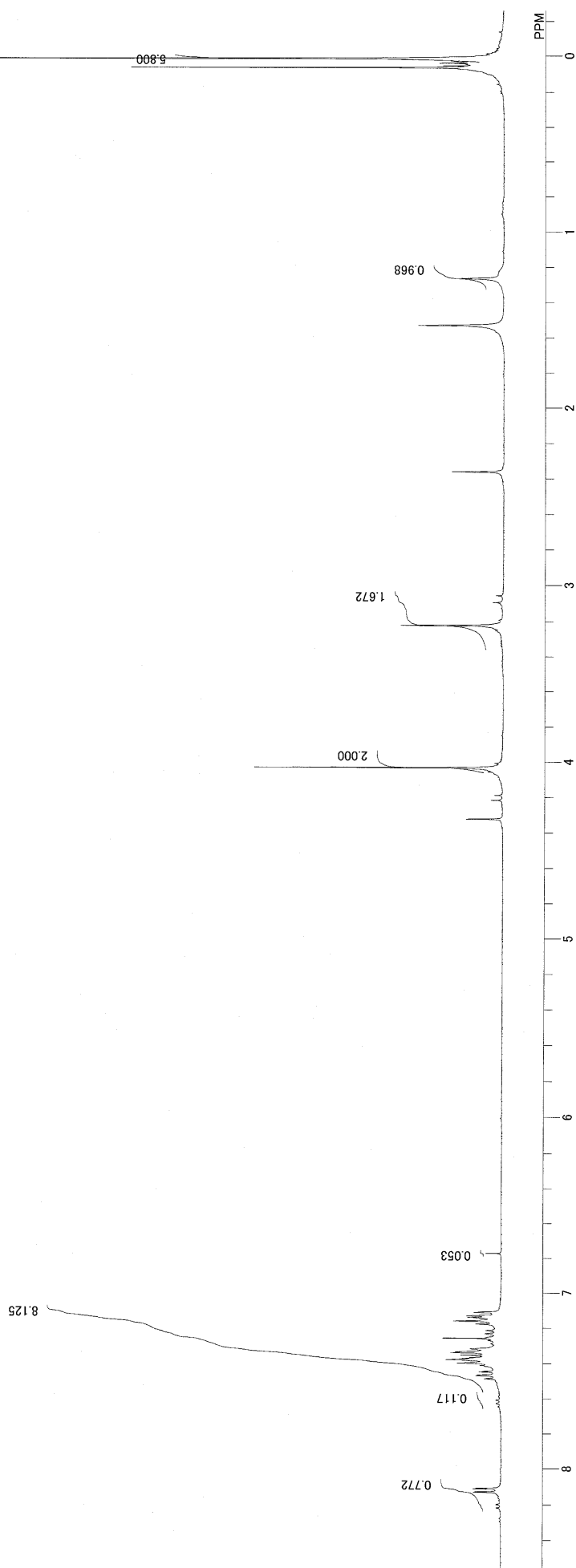
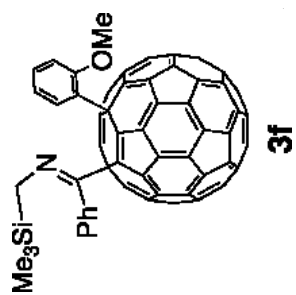


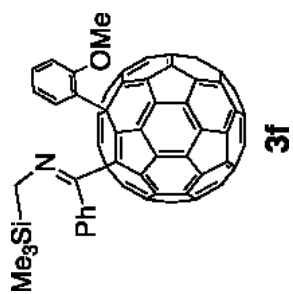




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single_pulse







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