

## Supporting Information

### Mono- and Penta-addition of Enol Silyl Ethers to [60]Fullerene

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### Supplemental Figure and Tables

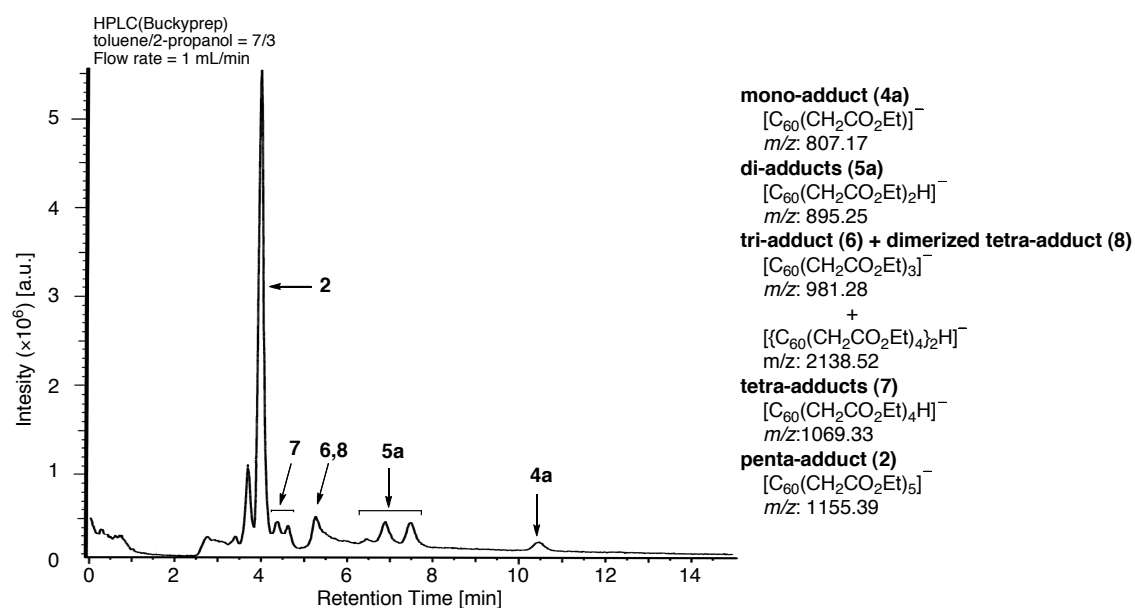


Figure S1. LC-MS Chart of Penta-addition Reaction Measured in Total Ion Current.

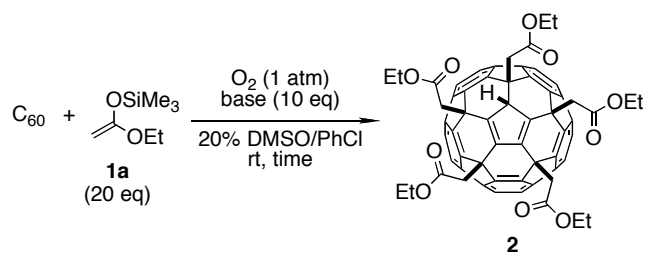
Table S1. Solvent Effect of the Penta-addition Reaction

Reaction scheme showing the penta-addition of enol silyl ether **1a** to [60]fullerene (**C<sub>60</sub>**) under O<sub>2</sub> (1 atm) and K<sub>2</sub>CO<sub>3</sub> (10 eq) in solvent at room temperature (rt) and time, yielding the penta-adduct **2**.

entry	solvent	time (h)	yield <sup>a</sup> (%)	C <sub>60</sub> recovery <sup>a</sup> (%)
1	PhCl	24	0	100
2	10% DMSO/PhCl	1.5	46	15
3	15% DMSO/PhCl	1.5	53	9
4	20% DMSO/PhCl	1.5	72	0
5	25% DMSO/PhCl	1	64	0
6	30% DMSO/PhCl	1	66	0
7	20% HMPA/PhCl	1.5	15	32
8	20% DMPU/PhCl	1.5	<5	72
9	20% DMI/PhCl	1.5	7	30

a) Determined by HPLC using pyrene as an internal standard.

**Table S2.** Effect of Base Adduct



entry	base	time (h)	yield <sup>a</sup> (%)
1	—	3	64
2	pyridine	2.5	41
3	K <sub>2</sub> CO <sub>3</sub>	1.5	72
4	K <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	1.5	15
5	Li <sub>2</sub> CO <sub>3</sub>	2	65
6	Na <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	2	13
7	Cs <sub>2</sub> CO <sub>3</sub> <sup>b</sup>	1.5	23
8	Et <sub>3</sub> N	2	46
9	<sup>i</sup> Pr <sub>2</sub> EtN	2	56
10	DBU	2	0
11	K <sub>3</sub> PO <sub>4</sub>	1.5	0
12	KOH	1.5	7
13	NaOH	1.5	39
14	NaO <sup>t</sup> Bu	1.5	0

a) Determined by HPLC using pyrene as an internal standard.

b) Base reagent was used from the freshly opened reagent bottle. K<sub>2</sub>CO<sub>3</sub> was dried by heating the reagent at 300 °C under vacuum for 12 h.

## Experimental Section

**General.** All manipulations were carried out under nitrogen or argon atmosphere with standard Schlenk techniques unless otherwise noted. All reactions were monitored by HPLC (column, Cosmosil-Buckyprep, 4.6×250 mm, Nacalai Tesque; flow rate, 2.0 mL/min; eluent, toluene/2-propanol (7/3) or flow rate, 1.0 mL/min; eluent, toluene/2-propanol (4/6); detector at 290 nm, Jasco MD-2015PLUS; column temperature at 40 °C). Flash silica-gel column chromatography was performed on silica gel 60N (Kanto, spherical and neutral, 140–325 mesh) as described by Still.<sup>1</sup> Gel permeation column chromatography was performed on a Japan Analytical Industry LC-9201 (eluent: toluene, flow: 3.5 mL/min) with JAIGEL 2H and 3H polystyrene columns. NMR spectra were measured with JEOL ECA-500 (<sup>1</sup>H: 500 MHz; <sup>13</sup>C: 125 MHz), JEOL ECX-400 (<sup>1</sup>H: 400 MHz; <sup>13</sup>C: 100 MHz) or Bruker DRX-500 (<sup>1</sup>H: 500 MHz; <sup>13</sup>C: 125 MHz). NMR spectra are reported in parts per million from internal tetramethylsilane ( $\delta$  0.00 ppm) for <sup>1</sup>H NMR, from solvent carbon ( $\delta$  77.00 ppm for chloroform) for <sup>13</sup>C NMR. IR spectra were recorded on Applied Systems React-IR 1000 equipped with an attenuated total reflection (ATR; neat), and are reported as wavenumbers ( $\nu$ ) in cm<sup>-1</sup>. Mass spectra were obtained on a JEOL JMS-T100LC instrument (APCI-TOF MS).

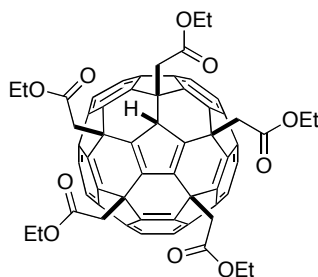
**Materials.** Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and used after appropriate purification before use. Anhydrous ethereal solvents (stabilizer-free) were purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour)<sup>2</sup> equipped with columns of activated alumina and supported copper catalyst (Z-5) prior to use. All other solvents were purified by distillation and stored over molecular sieves 4Å. The water content of solvents was determined with a Karl-Fisher Moisture Titrator (MK-210, Kyoto Electronics Co.) to be less than 40 ppm except for DMSO (88 ppm).

### Synthesis of Ketene Silyl Acetals (1a-d) and Enol Silyl Ethers (1e-g)

Ketene silyl acetals and enol silyl ethers were prepared by following the reported experimental procedures.<sup>3,4</sup>

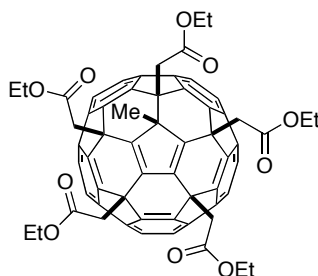
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1. Still, W. C.; Kahn, M.; Mitra, A. J. *Org. Chem.* **1978**, *43*, 2923–2925.
  2. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen R. K.; Timmers F. J. *Organometallics* **1996**, *15*, 1518–1520.
  3. Oisaki, K.; Suto, Y.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 5644–5645.
  4. Bloomfield, J. J.; Nelke, J. M. *Org. Synth.* **1977**, *57*, 1–6.

## Synthesis of $C_{60}(CH_2CO_2Et)_5H$ (**2**)



To a solution of  $C_{60}$  (101 mg, 0.140 mmol) in chlorobenzene (112 mL) was added DMSO (28 mL) under argon at room temperature. The  $O_2$  gas was bubbled through the resulting purple solution for 5 min. Then, potassium bicarbonate (194 mg, 1.40 mmol) and 1-ethoxy-1-[(trimethylsilyl)oxy]ethene **1a** (445 mg, 2.78 mmol) was added, and the solution was stirred under  $O_2$ , where the color change from purple to red solution was immediately observed. The reaction was monitored via HPLC, and quenched with aqueous  $NH_4Cl$  (20 mL) after 1.5 h with 72% HPLC yield using pyrene as an internal standard. The mixture was washed with saturated aqueous  $NH_4Cl$  ( $3 \times 50$  mL). Combined organic layer was dried over  $Na_2SO_4$  and concentrated to give a red solid (243 mg). The crude (237 mg) was purified by toluene GPC to obtain penta-adduct **2** in 21% yield as an analytically pure red solid (34.2 mg). IR (powder) 3232, 1721, 1461, 1372, 1345, 1302, 1250, 1227, 1192, 1185, 1113, 1096, 1065, 1028  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.24 (t,  $J = 7.2$  Hz, 6H), 1.28 (t,  $J = 7.2$  Hz, 6H), 1.29 (t,  $J = 7.2$  Hz, 3H), 3.50 (d,  $J = 14.9$  Hz, 2H), 3.54 (d,  $J = 14.3$  Hz, 2H), 3.61 (d,  $J = 14.3$  Hz, 2H), 3.69 (d,  $J = 14.9$  Hz, 2H), 3.71 (s, 2H), 4.22 (q,  $J = 7.2$  Hz, 4H), 4.25 (q,  $J = 7.2$  Hz, 4H), 4.28 (q,  $J = 7.2$  Hz, 2H), 5.16 (s, 1H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  14.22, 14.26, 44.10, 44.59, 47.43, 51.56, 52.40, 53.80, 57.59, 61.12, 61.16, 61.20, 142.77, 143.58, 143.69, 143.79, 143.85, 143.87, 144.02, 144.13, 144.59, 145.05, 145.14, 145.49, 146.54, 146.86, 146.94, 147.05, 147.64, 147.88, 148.00, 148.05, 148.25, 148.57, 148.59, 148.66, 150.60, 152.17, 153.35, 155.19, 169.88, 170.47, 171.30; HRMS (APCI-)  $m/z$  calcd for  $C_{80}H_{35}O_{10}$   $[M-H]^-$  1155.2230, found 1155.2264. The  $^1H$  and  $^{13}C$  NMR spectra of **2** are shown in Figures S2 and S3.

## $C_{60}(CH_2CO_2Et)_5Me$ (**3**)

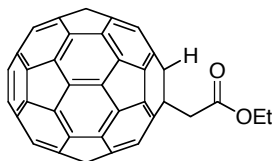


To a solution of  $C_{60}$  (14.5 mg, 0.0201 mmol) in chlorobenzene (16 mL) was added DMSO (4 mL) under argon at room temperature. The  $O_2$  gas was bubbled through the resulting purple solution for 5 min. Then, potassium bicarbonate (27.8 mg, 0.201 mmol) and 1-ethoxy-1-[(trimethylsilyl)oxy]ethene **1a** (66.1 mg, 0.412 mmol) were added, and the solution was stirred under  $O_2$  for 1.5 h. The reaction atmosphere was substituted with argon by bubbling for 5



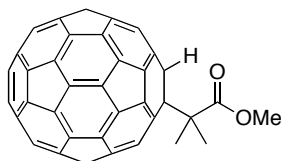
min. Then potassium *tert*-butoxide (1.0 M solution in THF, 40.0  $\mu$ L, 0.0400 mmol) was added to the solution and the mixture was stirred for 1 h, followed by the addition of iodomethane (2.85 g, 20.1 mmol). The reaction was quenched with aqueous  $\text{NH}_4\text{Cl}$  (5 mL) after 7 days, and washed with saturated aqueous  $\text{NH}_4\text{Cl}$  (3  $\times$  5 mL). Combined organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated to give a red solid (72.5 mg). The crude was purified by silica gel column chromatography (17 g, eluent: toluene/ethyl acetate/triethylamine = 90/10/0.5) to obtain product **3** in 51% yield as an analytically pure red solid (12.0 mg). IR (powder) 3245, 2979, 1721, 1461, 1412, 1390, 1372, 1345, 1302, 1248, 1227, 1192, 1185, 1113, 1096, 1028  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24 (t,  $J$  = 7.2 Hz, 6H), 1.27 (t,  $J$  = 7.2 Hz, 6H), 1.30 (t,  $J$  = 7.2 Hz, 3H), 2.31 (s, 3H), 3.49 (d,  $J$  = 14.6 Hz, 2H), 3.55 (d,  $J$  = 14.6 Hz, 2H), 3.62 (d,  $J$  = 14.1 Hz, 2H), 3.72 (d,  $J$  = 14.1 Hz, 2H), 3.73 (s, 2H), 4.21 (q,  $J$  = 7.2 Hz, 4H), 4.25 (q,  $J$  = 7.2 Hz, 4H), 4.26 (q,  $J$  = 7.2 Hz, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  14.16, 14.22, 14.24, 42.21, 44.64, 45.68, 51.08, 53.78, 54.67, 60.69, 61.12, 61.22, 141.81, 142.52, 143.55, 143.70, 143.73, 143.94, 144.00, 144.05, 144.42, 144.80, 145.51, 146.17, 147.03, 147.09, 147.18, 147.75, 147.99, 148.15, 148.31, 148.50, 148.62, 151.39, 152.98, 154.75, 160.94, 170.42, 171.37; HRMS (APCI-)  $m/z$  calcd for  $\text{C}_{81}\text{H}_{38}\text{O}_{10}$   $[\text{M}]^-$  1170.2465, found 1170.2471. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** are shown in Figures S4 and S5.

#### $\text{C}_{60}(\text{CH}_2\text{CO}_2\text{Et})\text{H}$ (**4a**)



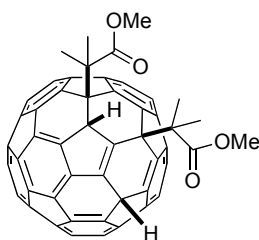
To a solution of  $\text{C}_{60}$  (100 mg, 0.139 mmol) in chlorobenzene (40 mL) was added DMSO (10 mL). To the solution was then added 1-ethoxy-1-[(trimethylsilyl)oxy]ethene **1a** (544  $\mu$ L, 2.78 mmol), and the mixture was stirred under argon at ambient temperature. HPLC analysis of the mixture showed that yield of mono-adduct reached its maximum within 1 h. The mixture was washed with saturated aqueous  $\text{NH}_4\text{Cl}$ . The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. The crude material (132 mg) was purified by a silica gel column chromatography (20 g, eluent: hexane and 50% toluene/hexane) to give  $\text{C}_{60}$  (15.3 mg, 15% recovery) and mono-adduct **4a** (66.5 mg, 62%) as an analytically pure brown powder. IR (powder) 2960, 2929, 2360, 2345, 1735, 1588, 1430, 1345, 1258, 1140, 735  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CS}_2/\text{CDCl}_3$ ; v/v = 1/1)  $\delta$  1.53 (t,  $J$  = 7.2 Hz, 3H), 4.44 (s, 2H), 4.55 (q,  $J$  = 7.2 Hz, 2H), 6.78 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CS}_2/\text{CDCl}_3$ ; v/v = 1/1)  $\delta$  14.51, 49.48, 59.18, 61.07, 61.59, 136.31, 136.62, 140.07, 140.16, 141.53, 141.57, 141.85, 141.99, 142.11, 142.45, 142.49, 143.14, 144.42, 144.70, 145.26, 145.31, 145.33, 145.52, 145.57, 145.74, 146.08, 146.11, 146.27, 146.32, 146.86, 147.18, 147.45, 153.33, 153.95, 170.18; HRMS (APCI-)  $m/z$  calcd for  $\text{C}_{64}\text{H}_7\text{O}_2$   $[\text{M}-\text{H}]^-$  807.0524, found 807.0469. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **4a** are shown in Figures S6 and S7.

**C<sub>60</sub>(CH<sub>3</sub>CH<sub>2</sub>CCO<sub>2</sub>Me)H (4b)**



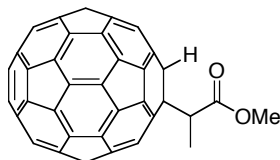
To a solution of C<sub>60</sub> (100 mg, 0.139 mmol) in chlorobenzene (40 mL) was added DMSO (10 mL). To the solution was then added 1-methoxy-2-methyl-1-[(trimethylsilyl)oxy]propene **1b** (116  $\mu$ L, 0.695 mmol), and the mixture was stirred under argon at ambient temperature. HPLC analysis of the mixture showed that yield of mono-adduct reached its maximum within 30 min. The mixture was washed with brine, and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude material (152 mg) was purified by a silica gel column chromatography (20 g, eluent: hexane and 50% toluene/hexane, toluene) to give C<sub>60</sub> (10.6 mg, 11% recovery), mono-adduct **4b** (77.4 mg, 68%) and di-adduct **5b** (12.1 mg, 10%) as an analytically pure brown powder. IR (powder) 2970, 2921, 2846, 2327, 1731, 1560, 1542, 1511, 1460, 1428, 1386, 1366, 1262, 1215, 1183, 1143, 1131, 1060, 983, 896, 844, 799, 768 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>; v/v = 1/1)  $\delta$  2.30 (s, 6H), 4.08 (s, 3H), 6.67 (s, 1H); <sup>13</sup>C NMR (125 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>; v/v = 1/1)  $\delta$  24.03, 52.60, 53.13, 58.10, 70.70, 136.37, 137.05, 138.91, 140.28, 141.36, 141.56, 142.03, 142.08, 142.10, 142.55, 142.58, 143.17, 144.38, 144.69, 145.20, 145.28, 145.38, 145.72, 146.05, 146.11, 146.30, 146.32, 146.82, 147.13, 147.44, 153.93, 176.10; HRMS (APCI-) *m/z* calcd for C<sub>65</sub>H<sub>10</sub>O<sub>2</sub> [M]<sup>-</sup> 822.0881, found 822.0896. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4b** are shown in Figures S8 and S9.

**C<sub>60</sub>(CH<sub>3</sub>CH<sub>2</sub>CCO<sub>2</sub>Me)<sub>2</sub>H<sub>2</sub> (5b)**



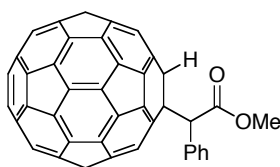
IR (powder) 3434, 2970, 2941, 2353, 1730, 1599, 1514, 1457, 1429, 1387, 1365, 1267, 1184, 1145, 1116, 985, 893, 849, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.89 (s, 3H), 1.91 (s, 3H), 1.92 (s, 3H), 1.95 (s, 3H), 3.82 (s, 3H), 3.96 (s, 3H), 5.51 (d, *J* = 2.1 Hz, 1H), 5.97 (d, *J* = 2.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  22.46, 22.62, 48.42, 48.79, 50.91, 51.86, 52.41, 52.42, 52.65, 52.67, 58.72, 58.73, 61.57, 64.62, 131.75, 133.56, 136.12, 136.73, 137.17, 139.57, 139.87, 141.05, 141.39, 141.71, 141.72, 141.96, 142.77, 143.66, 143.67, 143.71, 144.40, 144.51, 144.59, 144.74, 144.75, 144.88, 145.06, 145.25, 145.27, 145.33, 145.39, 145.58, 145.60, 145.73, 145.84, 146.32, 146.69, 146.75, 146.80, 146.85, 146.87, 147.00, 147.35, 147.69, 147.74, 147.79, 148.72, 149.05, 149.31, 149.65, 149.76, 150.24, 151.24, 153.35, 154.44, 156.57, 157.21, 175.42, 176.51; HRMS (APCI-) *m/z* calcd for C<sub>70</sub>H<sub>20</sub>O<sub>4</sub> [M]<sup>-</sup> 924.1362, found 924.1363. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5b** are shown in Figures S10 and S11.

#### $C_{60}(CH_3CHCO_2Me)H$ (**4c**)



To a solution of  $C_{60}$  (100 mg, 0.139 mmol) in chlorobenzene (40 mL) was added DMSO (10 mL). To the solution was then added 1-methoxy-1-[(trimethylsilyl)oxy]propene **1c** (94.3  $\mu$ L, 0.69 mmol;  $E/Z = 34/66$ ), and the mixture was stirred under argon at ambient temperature. HPLC analysis of the mixture showed that yield of mono-adduct reached its maximum within 1 h. The mixture was washed with saturated aqueous  $NH_4Cl$ . The organic layer was dried over anhydrous  $Na_2SO_4$ , and concentrated *in vacuo*. The crude material (141 mg) was purified by a silica gel column chromatography (20 g, eluent: hexane, 50% toluene/hexane and toluene) to give  $C_{60}$  (13.5 mg, 14% recovery), and mono-adduct **4c** (69.6 mg, 62%) as an analytically pure brown powder. IR (powder) 2921, 2360, 2328, 1734, 1716, 1699, 1684, 1653, 1558, 1541, 1508, 1489, 1473, 1457, 1428, 1396, 1375, 1339, 1195, 1137, 1114, 768  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CS_2/CDCl_3$ ; v/v = 1/1)  $\delta$  2.39 (d,  $J = 7.2$  Hz, 3H), 4.06 (s, 3H), 4.42 (q,  $J = 7.2$  Hz, 1H), 6.94 (s, 1H);  $^{13}C$  NMR (100 MHz,  $CS_2/CDCl_3$ ; v/v = 1/1)  $\delta$  14.95, 51.95, 52.16, 55.98, 66.14, 135.97, 136.16, 136.60, 136.67, 139.88, 140.18, 141.26, 141.38, 141.43, 141.49, 141.57, 141.83, 141.85, 141.92, 141.93, 142.09, 142.17, 142.41, 142.43, 142.45, 143.09, 144.32, 144.58, 144.68, 145.15, 145.18, 145.23, 145.26, 145.27, 145.42, 145.60, 145.63, 145.65, 145.91, 146.01, 146.05, 146.07, 146.20, 146.21, 146.26, 146.82, 146.89, 147.10, 147.40, 153.02, 153.50, 153.73, 153.77, 173.91; HRMS (APCI-)  $m/z$  calcd for  $C_{69}H_{11}O_2 [M-H]^-$  807.0446, found 870.0501. The  $^1H$  and  $^{13}C$  NMR spectra of **4c** are shown in Figures S12 and S13.

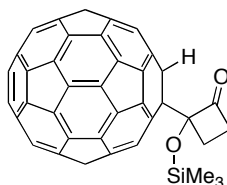
#### $C_{60}(C_6H_5CHCO_2Me)H$ (**4d**)



To a solution of  $C_{60}$  (100 mg, 0.139 mmol) in chlorobenzene (40 mL) was added DMSO (10 mL). To the solution was then added 1-methoxy-1-[(trimethylsilyl)oxy]-2-phenylethene **1d** (144  $\mu$ L, 0.69 mmol;  $E/Z = 56/44$ ), and the mixture was stirred under argon at ambient temperature. HPLC analysis of the mixture showed that yield of mono-adduct reached its maximum within 3 h. The mixture was washed with saturated aqueous  $NH_4Cl$ . The organic layer was dried over anhydrous  $Na_2SO_4$ , and concentrated *in vacuo*. The crude material (152 mg) was purified by a silica gel column chromatography (20 g, eluent: hexane, 50% toluene/hexane) to give  $C_{60}$  (23.3 mg, 23% recovery), and mono-adduct **4d** (66.5 mg, 55%) as an analytically pure

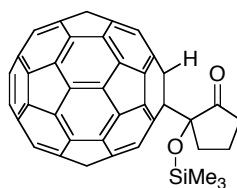
brown powder. IR (powder) 2360, 2342, 1736, 1509, 1452, 1429, 1314, 1201, 1165, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CS}_2/\text{CDCl}_3$ ; v/v = 1/1)  $\delta$  4.04 (s, 3H), 5.61 (s, 1H), 6.95 (s, 1H), 7.47-7.55 (m, 3H), 7.84-7.86 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CS}_2/\text{CDCl}_3$ ; v/v = 1/1)  $\delta$  52.71, 57.61, 63.90, 67.16, 130.49, 133.81, 136.24, 136.42, 136.91, 137.69, 139.47, 139.56, 140.19, 140.26, 141.47, 141.50, 141.52, 141.59, 141.61, 141.96, 141.99, 142.08, 142.19, 142.32, 142.49, 142.56, 142.58, 142.59, 143.17, 143.18, 144.42, 144.46, 144.80, 144.83, 145.26, 145.33, 145.36, 145.42, 145.51, 145.66, 145.77, 146.11, 146.14, 146.16, 146.20, 146.22, 146.31, 146.37, 146.42, 146.44, 146.90, 146.91, 147.25, 147.55, 152.53, 153.31, 153.52, 154.11, 172.27; HRMS (APCI-)  $m/z$  calcd for  $\text{C}_{69}\text{H}_{10}\text{O}_2$  [M-H] $^-$  870.0681, found 870.0705. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **4d** are shown in Figures S14 and S15.

#### $\text{C}_{60}(\text{Me}_3\text{SiOCCCOCH}_2\text{CH}_2)\text{H}$ (**4e**)



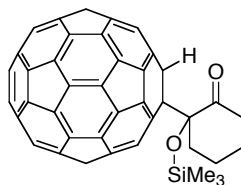
To a solution of  $\text{C}_{60}$  (100 mg, 0.139 mmol) in chlorobenzene (40 mL) was added DMSO (10 mL). To the solution was then added 1,2-bis-[(trimethylsilyl)oxy]cyclobutene **1e** (350  $\mu\text{L}$ , 1.39 mmol), and the mixture was stirred under argon at ambient temperature. HPLC analysis of the mixture showed that yield of mono-adduct reached its maximum within 3 h. The mixture was washed with brine, the organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The crude material (146 mg) was purified with HPLC (Nacalai Tesque, Buckyprep, eluent: toluene/2-propanol = 7/3) to obtain  $\text{C}_{60}$  (15.8 mg, 16% recovery), and mono-adduct **4e** (67.1 mg, 55%) as an analytically pure brown powder. IR (powder) 2919, 2849, 1785, 1459, 1426, 1386, 1250, 1202, 1178, 1058, 998, 974, 930, 892, 842  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.52 (s, 9H), 2.86-2.94 (m, 1H), 3.17-3.35 (m, 2H), 3.69-3.77 (m, 1H), 6.99 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CS}_2/\text{CDCl}_3$ ; v/v = 1/1)  $\delta$  1.77, 26.68, 41.36, 57.24, 70.34, 99.11, 136.14, 137.58, 137.78, 139.62, 139.78, 140.37, 140.41, 141.48, 141.52, 141.57, 141.62, 141.65, 141.72, 142.02, 142.07, 142.11, 142.15, 142.49, 142.54, 142.58, 142.60, 142.66, 142.68, 143.20, 143.24, 144.43, 144.76, 144.86, 145.29, 145.34, 145.53, 145.62, 145.72, 145.83, 146.18, 146.24, 146.25, 146.31, 146.35, 146.41, 146.49, 146.51, 146.82, 146.90, 147.12, 147.21, 147.24, 147.48, 150.78, 150.82, 154.03, 154.20, 209.96; HRMS (APCI-)  $m/z$  calcd for  $\text{C}_{67}\text{H}_{14}\text{O}_2\text{Si}$  [M] $^-$  878.0763, found 878.0795. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **4e** are shown in Figures S16 and S17.

#### $\text{C}_{60}(\text{Me}_3\text{SiOCCCOCH}_2\text{CH}_2\text{CH}_2)\text{H}$ (**4f**)



To a solution of  $C_{60}$  (100 mg, 0.139 mmol) in chlorobenzene (40 mL) was added DMSO (10 mL). To the solution was then added 1,2-bis-[(trimethylsilyl)oxy]cyclopentene **1f** (340  $\mu$ L, 1.39 mmol), and the mixture was stirred under argon at ambient temperature. HPLC analysis of the mixture showed that yield of mono-adduct reached its maximum within 4 h. The mixture was washed with brine, the organic layer was dried over anhydrous  $Na_2SO_4$ , and concentrated *in vacuo*. The crude material (152 mg) was purified with HPLC (Nacalai Tesque, Buckyprep, eluent: toluene/2-propanol = 7/3) to obtain  $C_{60}$  (20.3 mg, 20% recovery), and mono-adduct **4f** (52.6 mg, 42%) as an analytically pure brown powder. IR (powder) 2954, 2890, 1740, 1511, 1461, 1426, 1397, 1358, 1318, 1304, 1248, 1206, 1173, 1138, 1125, 1073, 1040, 1009, 961, 928, 880, 837, 762, 700, 689, 688, 668, 658  $cm^{-1}$ ;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  0.40 (s, 9H), 2.17-2.34 (m, 2H), 2.66-2.79 (m, 3H), 3.59-3.65 (m, 1H), 7.31 (s, 1H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  2.23, 18.34, 36.22, 37.41, 56.67, 72.13, 86.37, 136.02, 137.20, 137.72, 139.10, 139.26, 140.38, 140.46, 141.36, 141.43, 141.50, 141.61, 141.65, 141.72, 142.07, 142.11, 142.48, 142.51, 142.56, 142.62, 142.65, 143.18, 144.31, 144.39, 144.80, 144.86, 145.16, 145.20, 145.30, 145.35, 145.42, 145.48, 145.50, 145.56, 145.82, 145.92, 146.12, 146.20, 146.20, 146.26, 146.30, 146.48, 146.49, 147.13, 147.16, 147.34, 147.46, 147.49, 151.17, 151.66, 154.75, 155.23, 192.53, 217.65; HRMS (APCI-)  $m/z$  calcd for  $C_{68}H_{16}O_2Si$  [M] $^-$  892.0920 found 892.0901. The  $^1H$  and  $^{13}C$  NMR spectra of **4f** are shown in Figures S18 and S19.

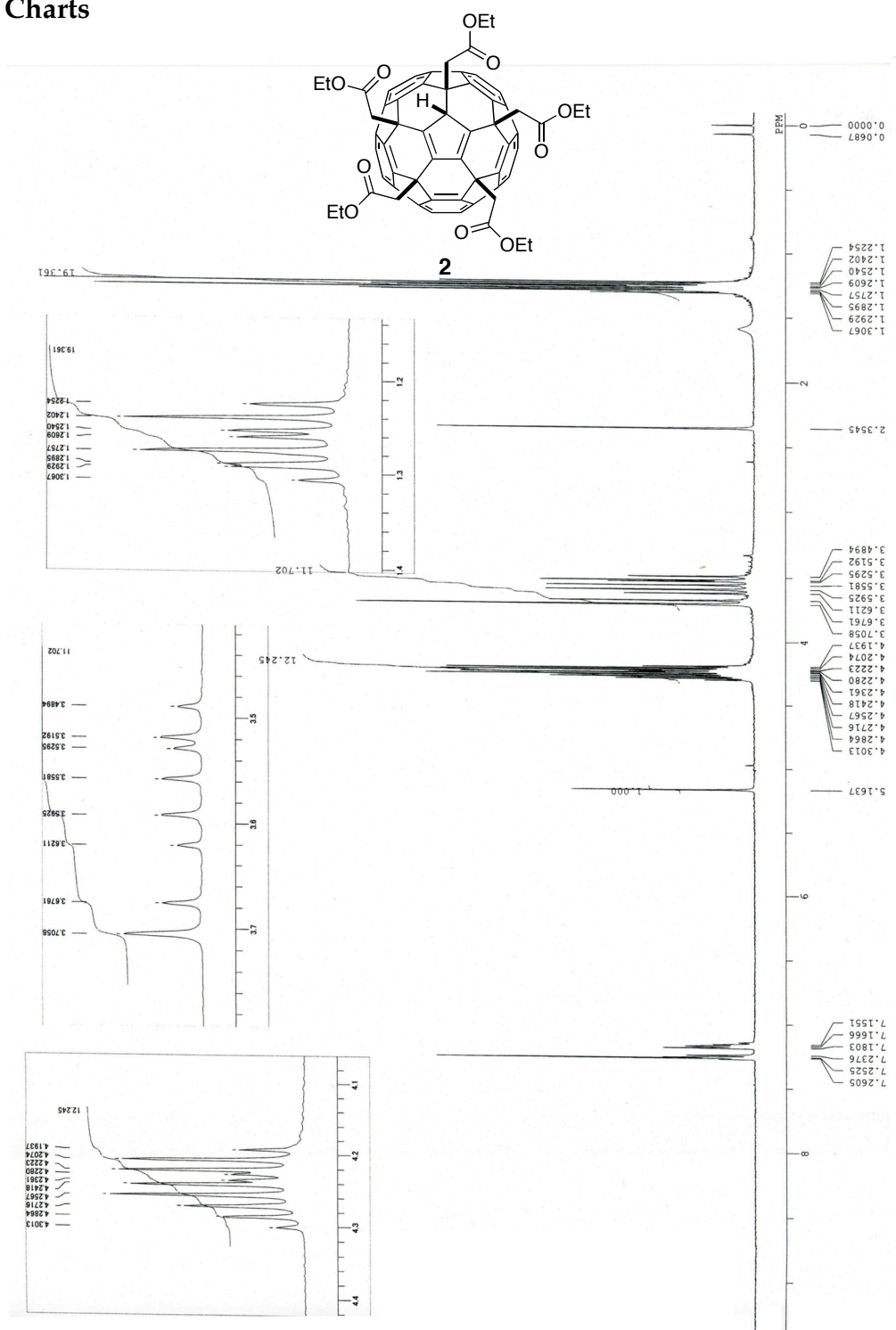
#### $C_{60}(Me_3SiOCCOCH_2CH_2CH_2CH_2)H$ (**4g**)

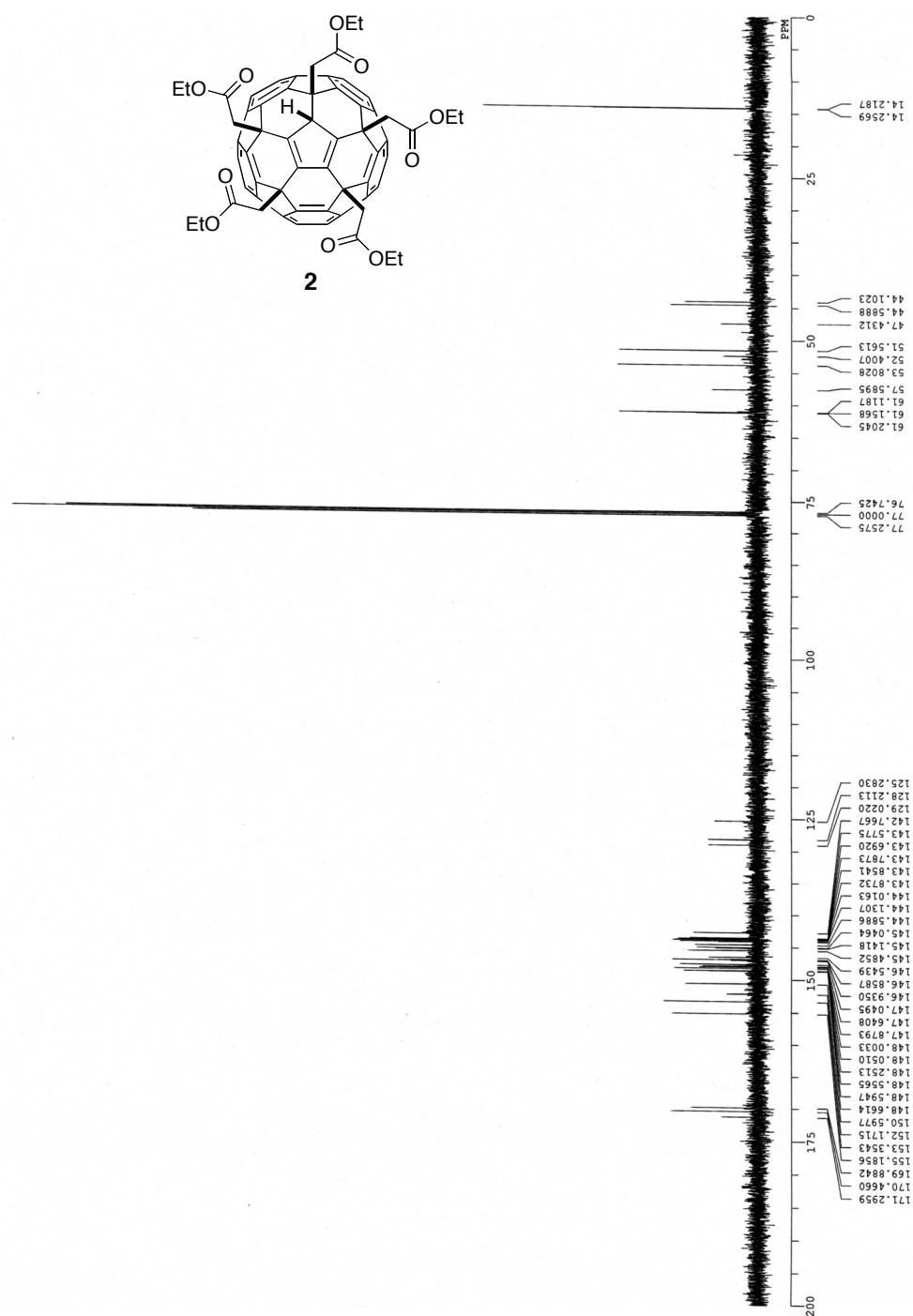


To a solution of  $C_{60}$  (100 mg, 0.139 mmol) in chlorobenzene (40 mL) was added DMSO (10 mL). To the solution was then added 1,2-bis-[(trimethylsilyl)oxy]cyclohexene **1g** (345  $\mu$ L, 1.39 mmol), and the mixture was stirred under argon at ambient temperature. HPLC analysis of the mixture showed that yield of mono-adduct reached its maximum within 6 hours. The mixture was washed with brine, the organic layer was dried over anhydrous  $Na_2SO_4$ , and concentrated *in vacuo*. The crude material (161 mg) was purified with HPLC (Nacalai Tesque, Buckyprep, eluent: toluene/2-propanol = 7/3) to obtain  $C_{60}$  (18.1 mg, 18% recovery), and mono-adduct **4g** (52.0 mg, 42%) as an analytically pure brown powder. IR (powder) 2939, 1715, 1683, 1540, 1507, 1457, 1428, 1250, 1164, 1142, 1129, 1108, 1090, 1071, 1061, 1048, 1028, 978, 965, 949, 936, 920, 903, 864, 834, 809, 761, 726, 712, 700, 689, 673, 654  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  0.47 (s, 9H), 2.16-2.28 (m, 4H), 2.85-2.90 (m, 1H), 3.08-3.13 (m, 1H), 3.19-3.26 (m, 1H), 3.34-3.39 (m, 1H), 6.82 (s, 1H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  3.03, 3.04, 22.77, 37.42, 39.28, 41.43, 57.95, 73.17, 88.64, 136.53, 137.85, 140.33, 140.49, 141.45, 141.50, 141.52, 141.62, 141.76, 142.14, 142.16, 142.34, 142.60, 142.65, 142.67, 142.70, 143.21, 143.22, 144.33, 144.44, 144.85, 144.89, 145.16, 145.30, 145.33, 145.39, 145.42, 145.46, 145.47, 145.81, 145.95, 146.10, 146.15, 146.19, 146.28,

146.44, 147.11, 147.12, 147.42, 147.50, 147.63, 152.27, 152.96, 210.23; HRMS (APCI-)  $m/z$  calcd for  $C_{69}H_{18}O_2Si$   $[M]^-$  906.1076, found 906.1098. The  $^1H$  and  $^{13}C$  NMR spectra of **4g** are shown in Figures S20 and S21.

## NMR Charts

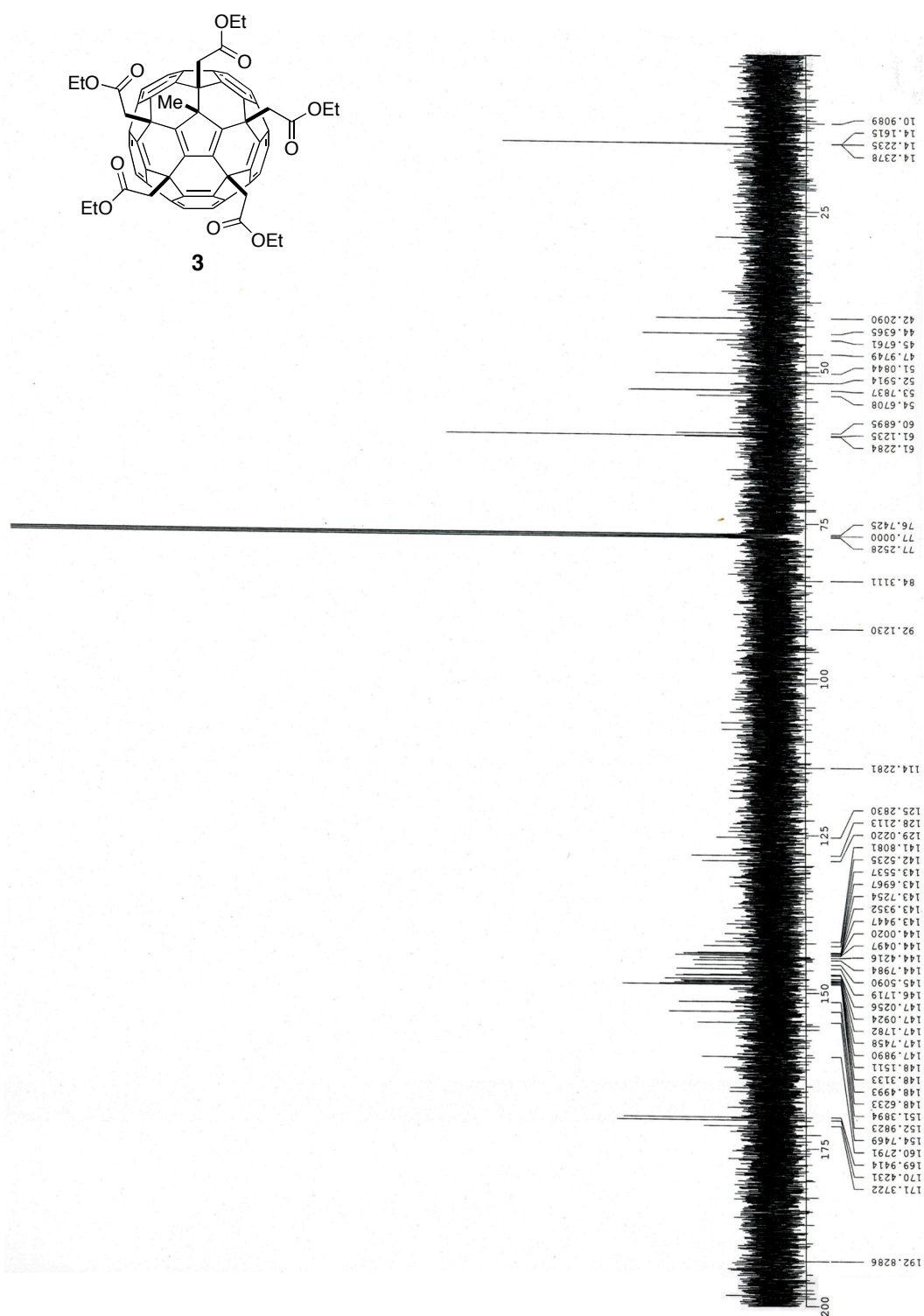




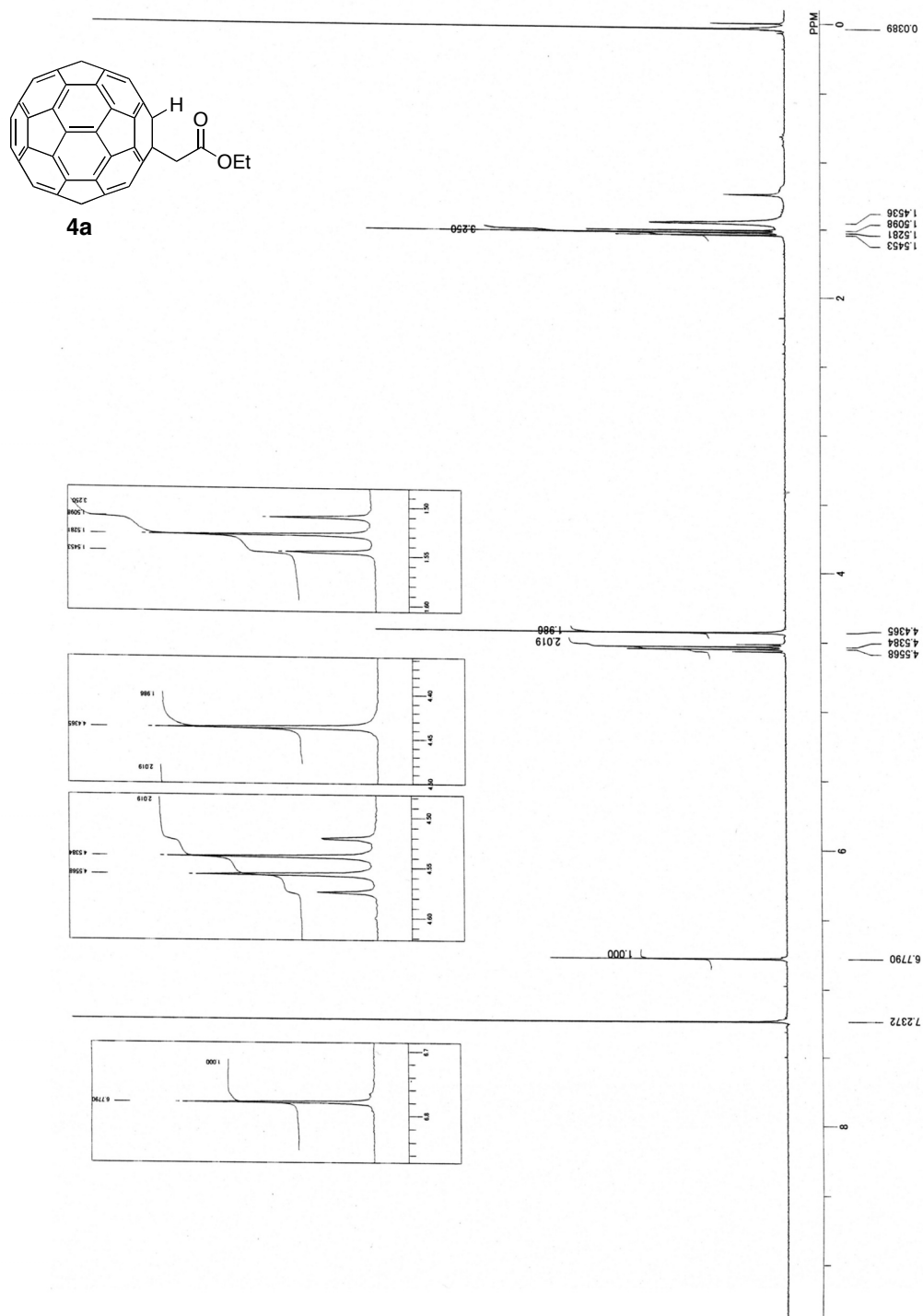
**Figure S3.** A  $^{13}C$  NMR spectrum of  $C_{60}(CH_2CO_2Et)_5H$  (**2**) in  $CDCl_3$



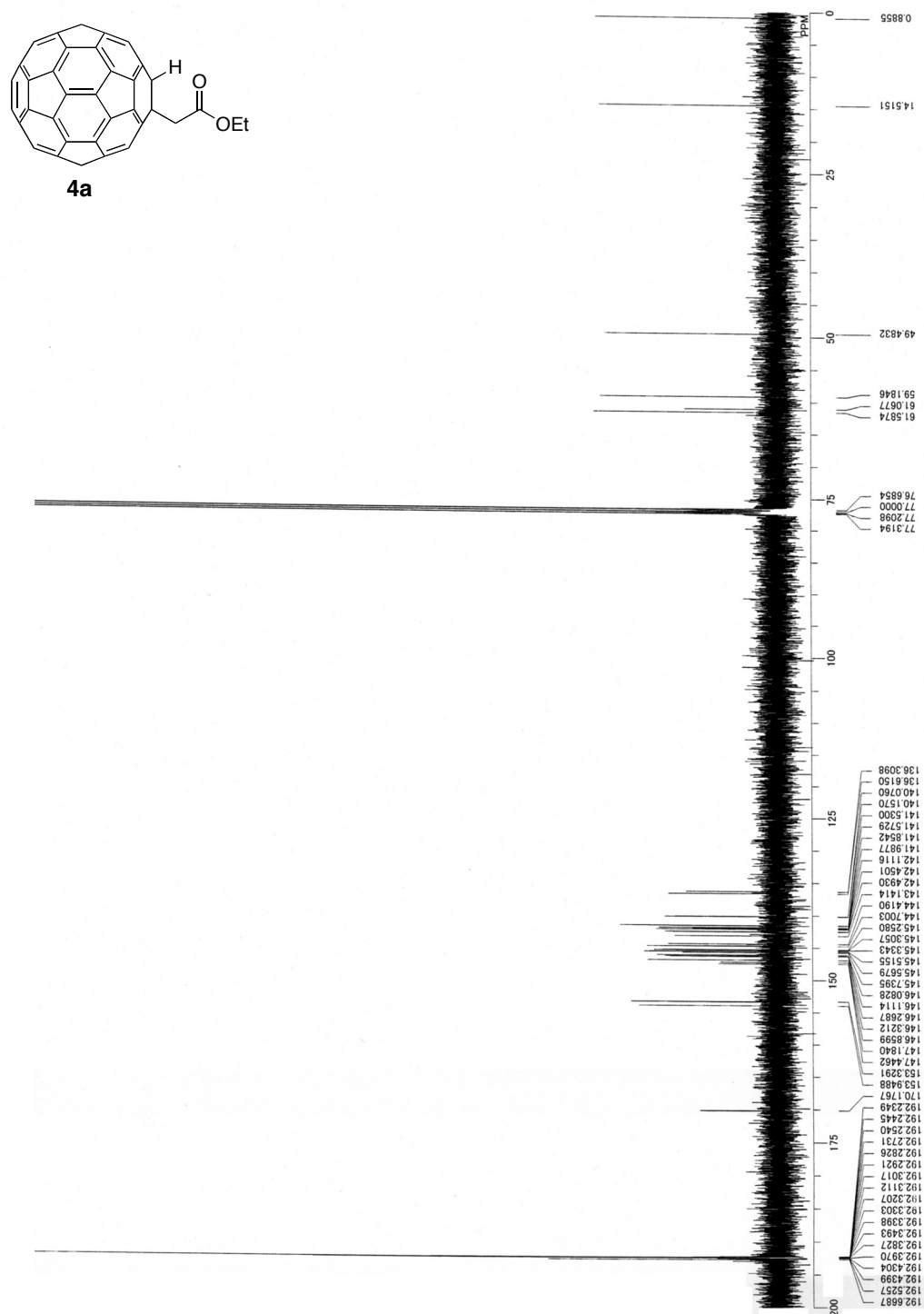




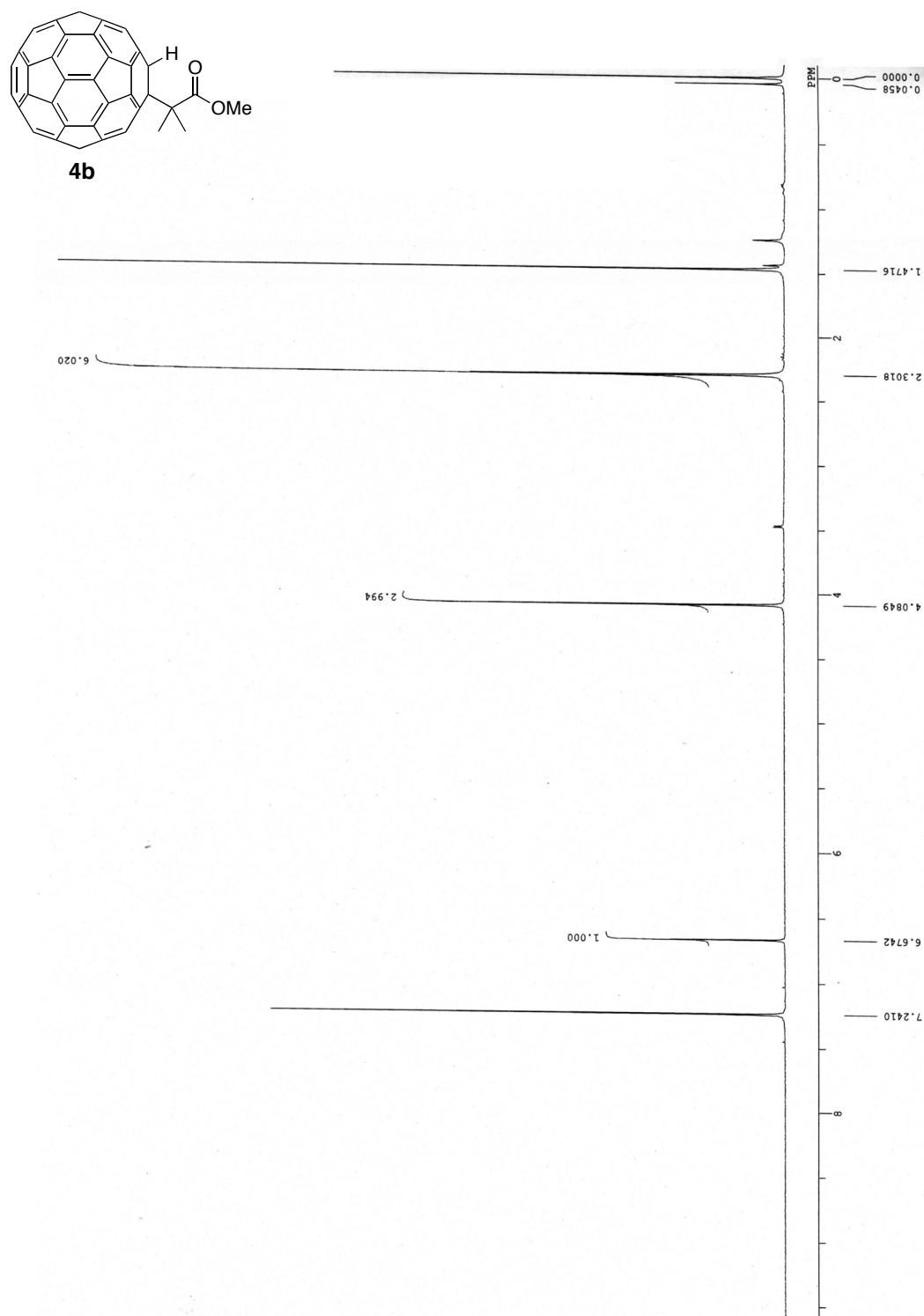
**Figure S5.** A <sup>13</sup>C NMR spectrum of  $C_{60}(CH_2CO_2Et)_5Me$  (**3**) in CDCl<sub>3</sub>



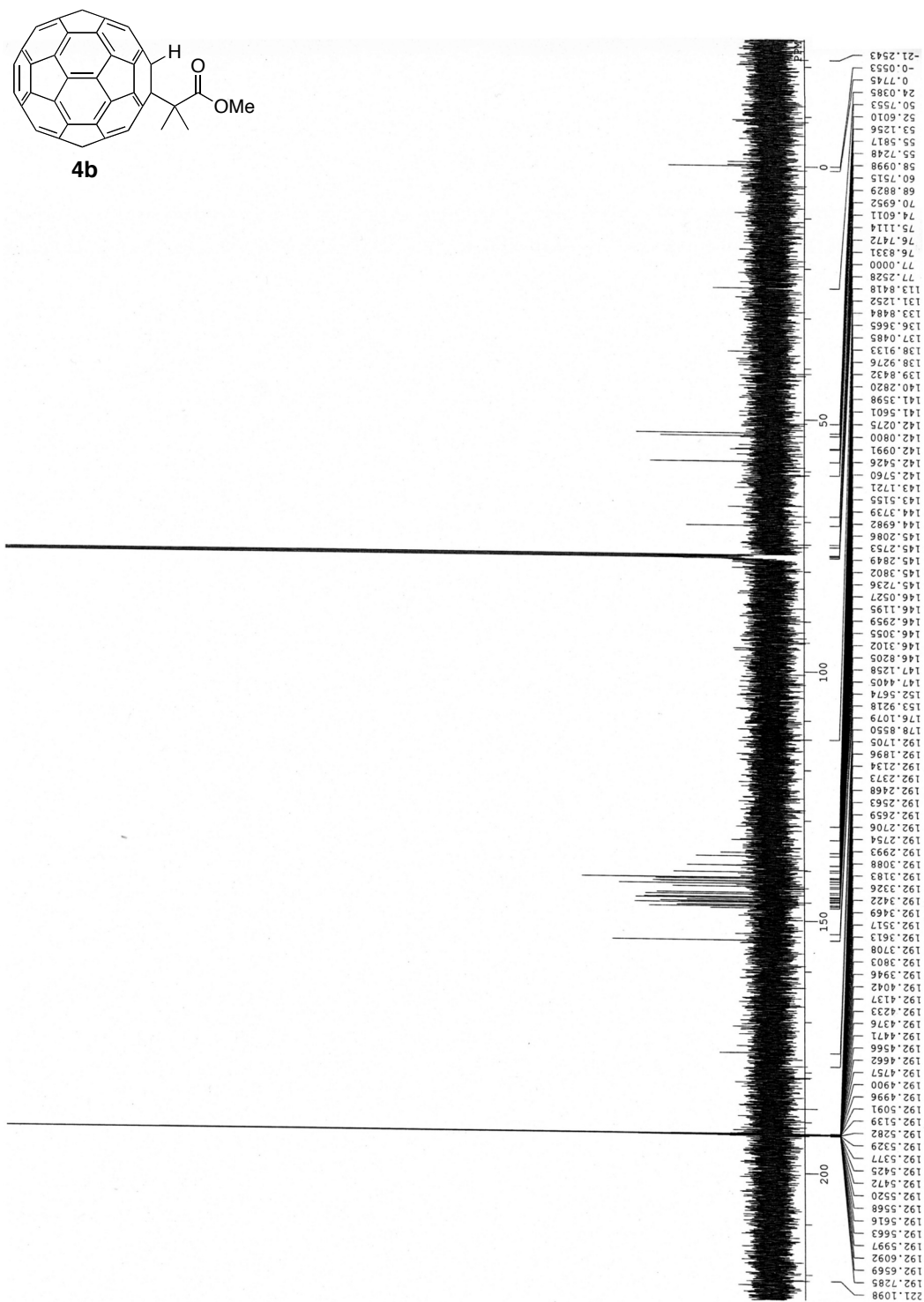
**Figure S6.** A <sup>1</sup>H NMR spectrum of C<sub>60</sub>(CH<sub>2</sub>CO<sub>2</sub>Et)H (**4a**) in CS<sub>2</sub>-CDCl<sub>3</sub>



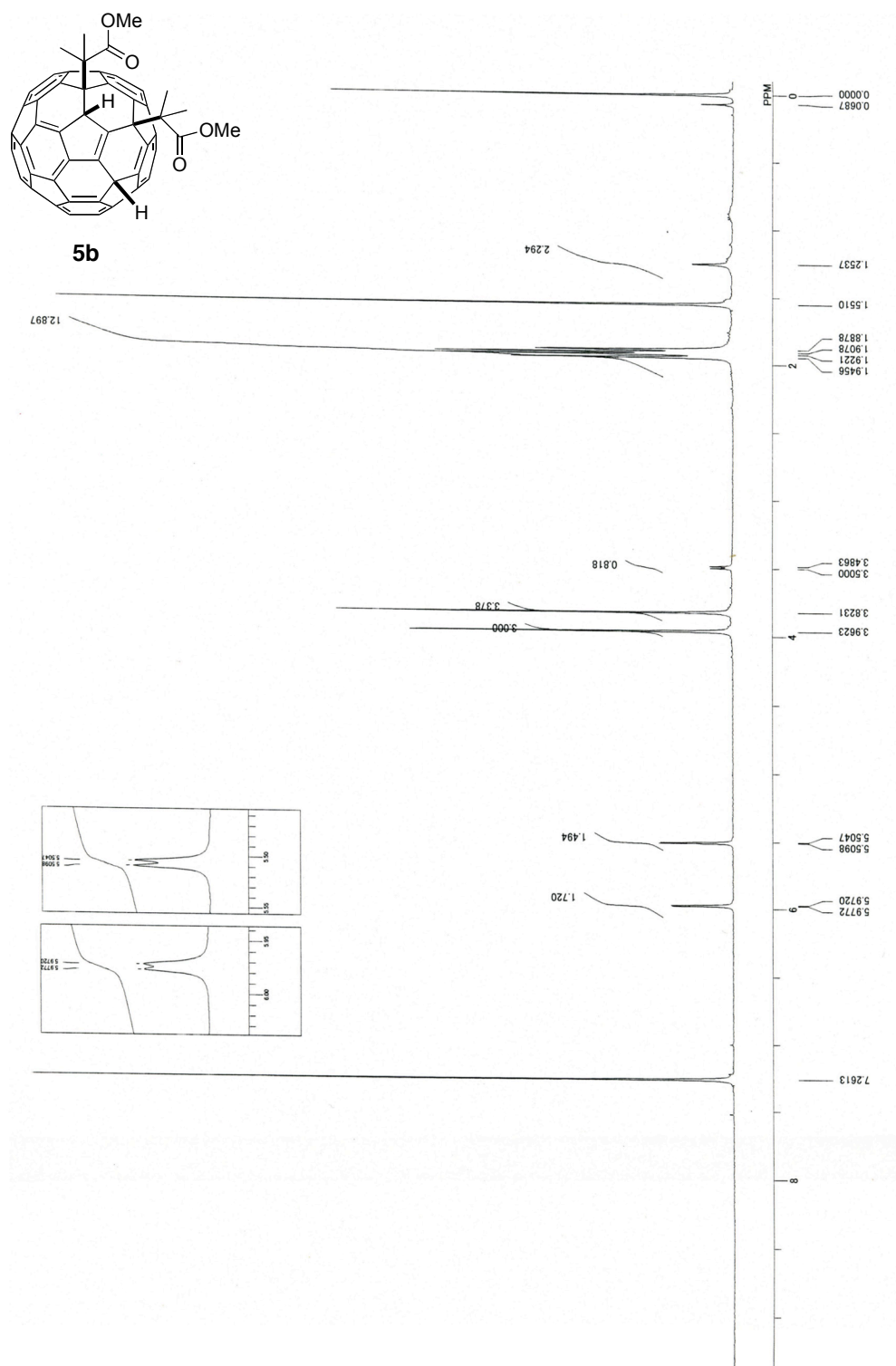
**Figure S7.** A <sup>13</sup>C NMR spectrum of C<sub>60</sub>(CH<sub>2</sub>CO<sub>2</sub>Et)H (**4a**) in CS<sub>2</sub>-CDCl<sub>3</sub>



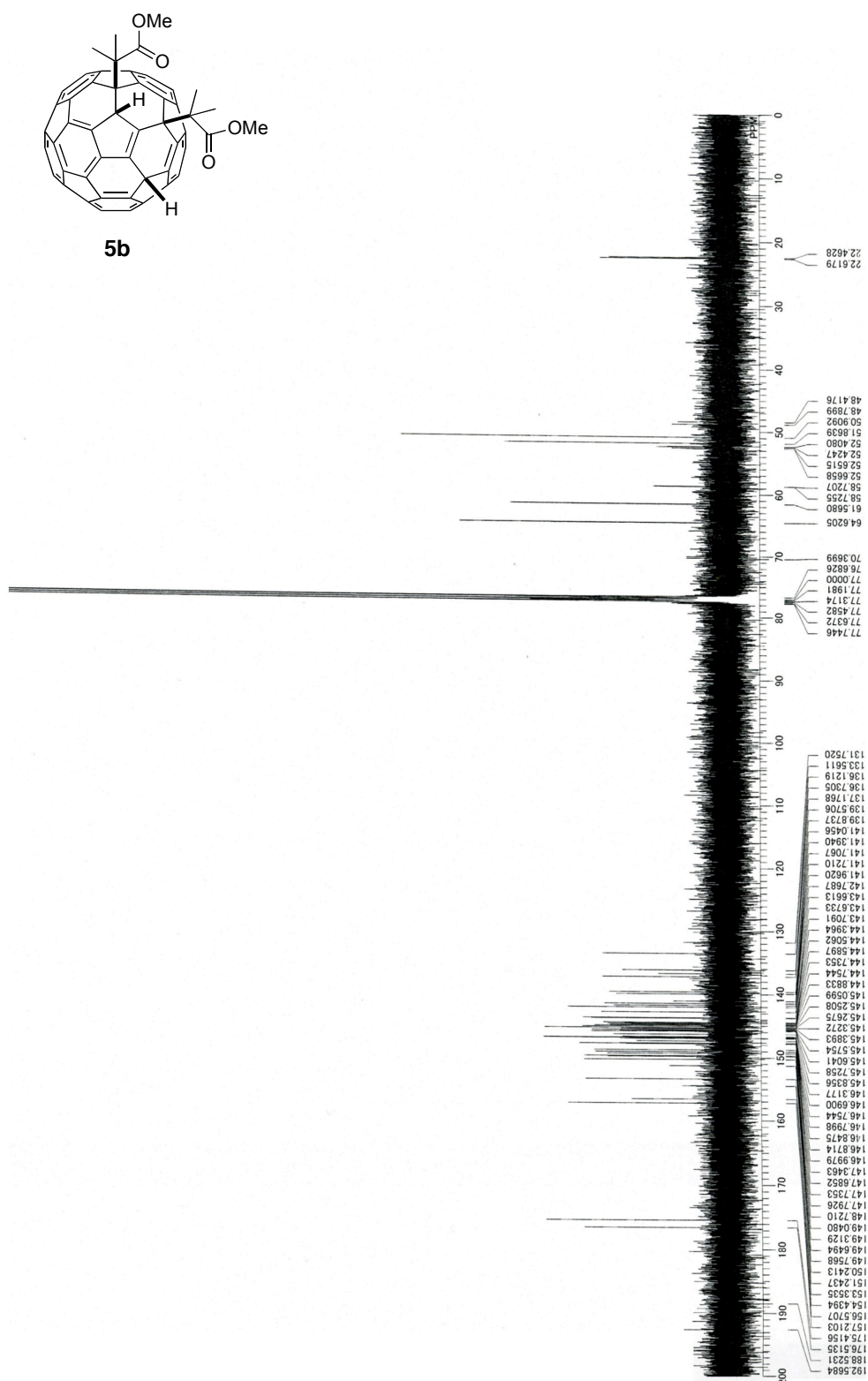
**Figure S8.** A  $^1\text{H}$  NMR spectrum of  $\text{C}_{60}(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})\text{H}$  (**4b**) in  $\text{CS}_2\text{-CDCl}_3$



**Figure S9.** A  $^{13}\text{C}$  NMR spectrum of  $\text{C}_{60}(\text{CH}_3\text{CH}_3\text{CCO}_2\text{Me})\text{H}$  (**4b**) in  $\text{CS}_2\text{-CDCl}_3$

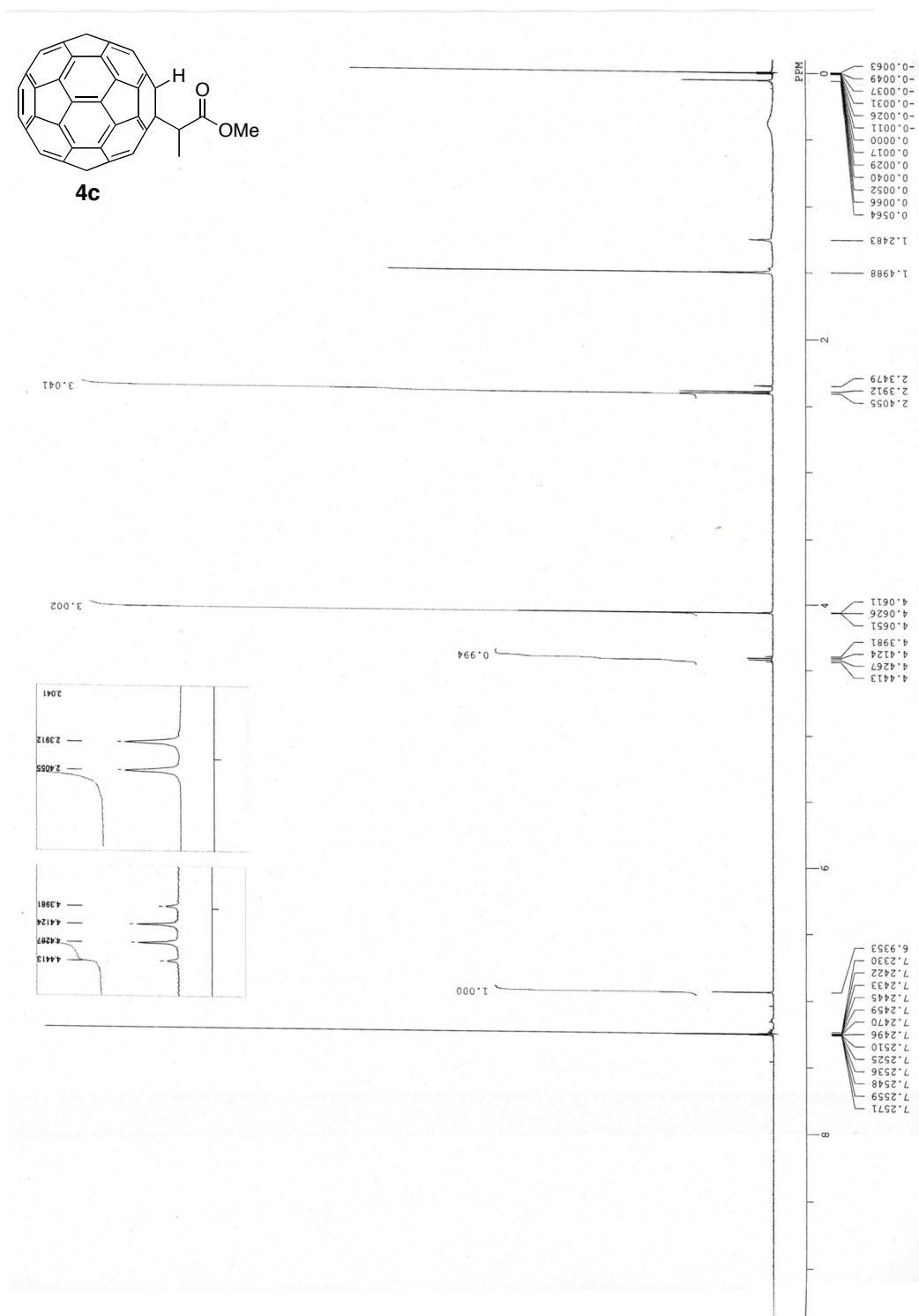


**Figure S10.** A <sup>1</sup>H NMR spectrum of C<sub>60</sub>(CH<sub>3</sub>CH<sub>2</sub>CCO<sub>2</sub>Me)<sub>2</sub>H<sub>2</sub> (**5b**) in CDCl<sub>3</sub>

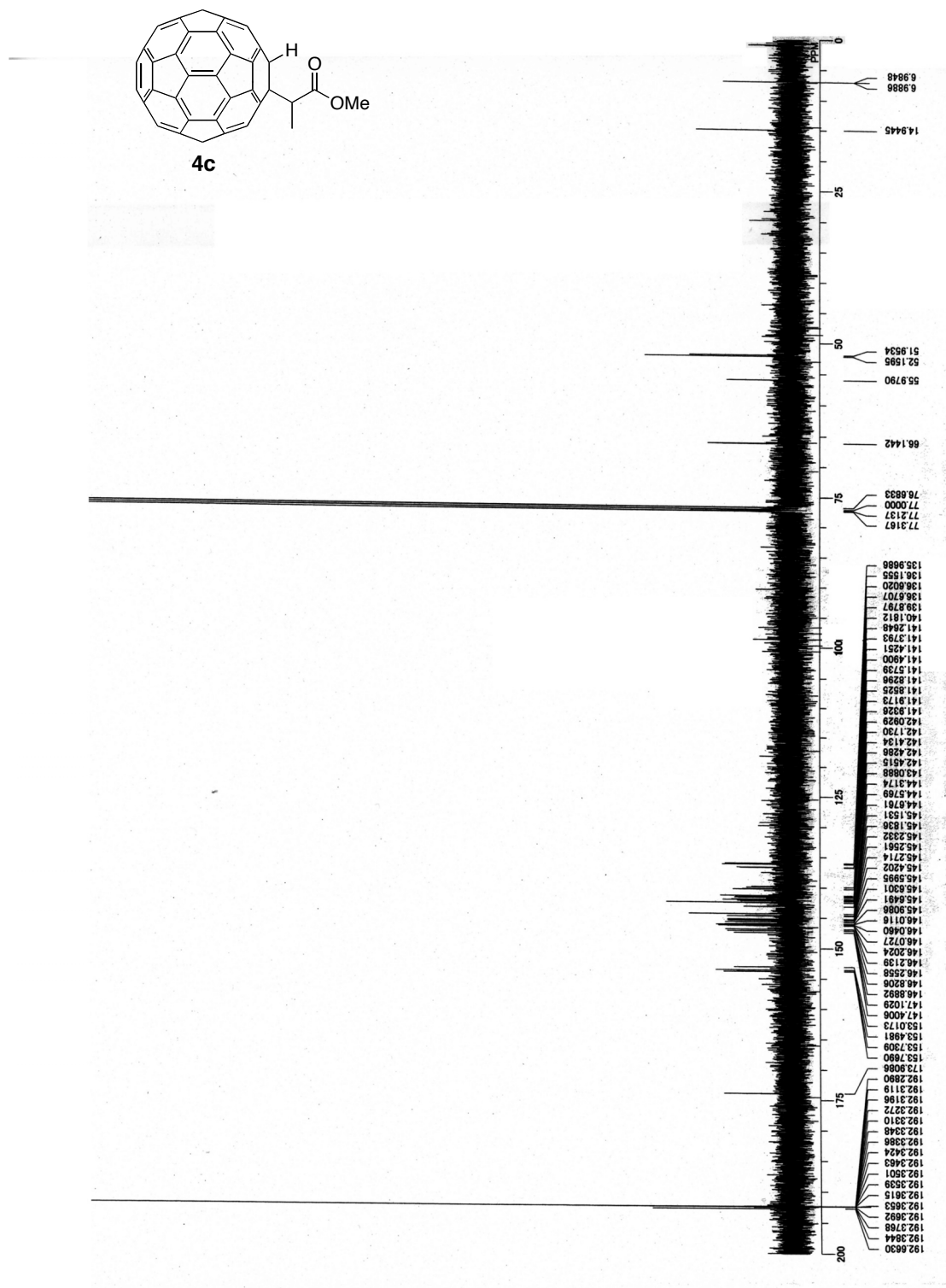


**Figure S11.** A  $^{13}\text{C}$  NMR spectrum of  $\text{C}_{60}(\text{CH}_3\text{CH}_2\text{CCO}_2\text{Me})_2\text{H}_2$  (**5b**) in  $\text{CDCl}_3$

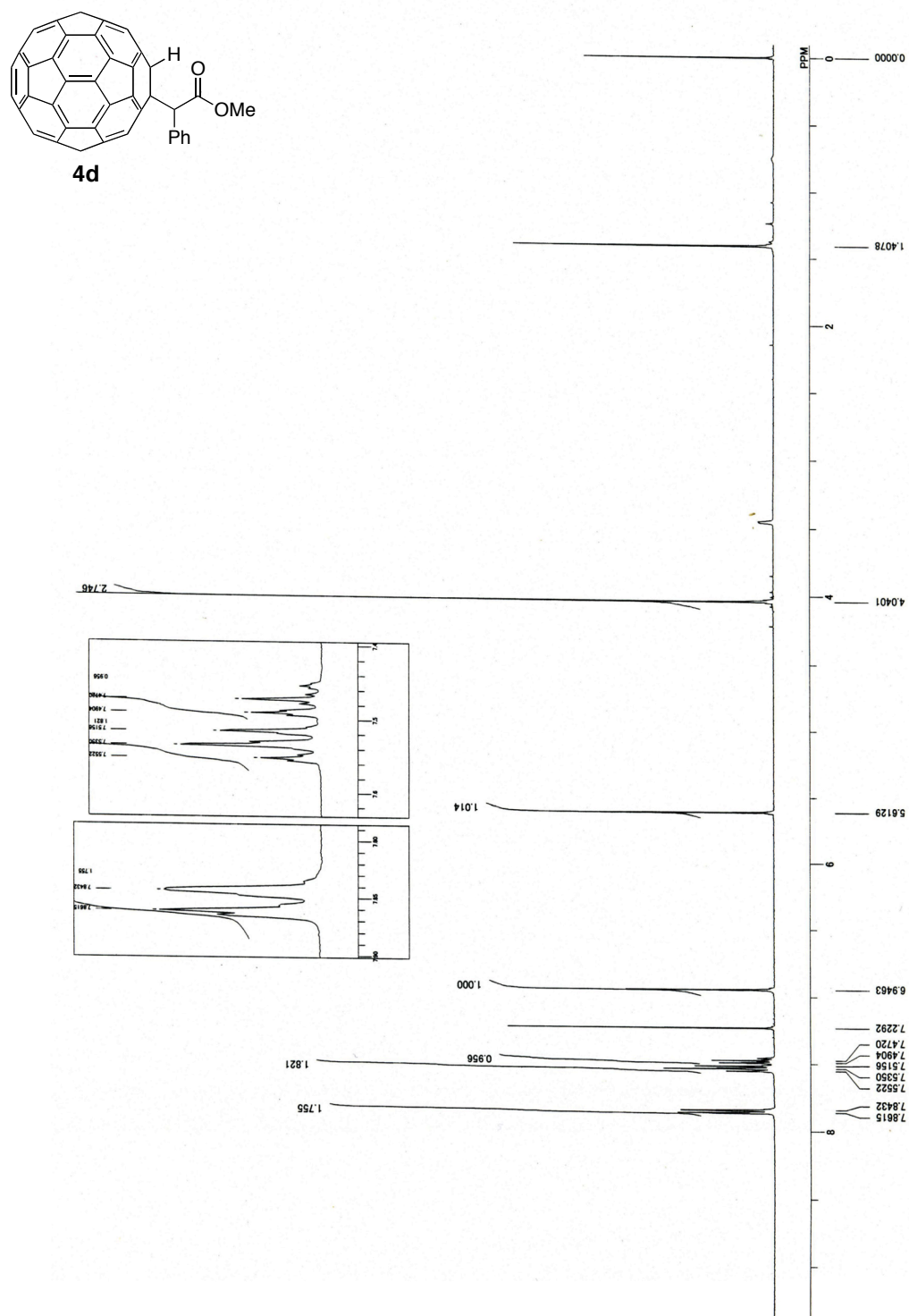




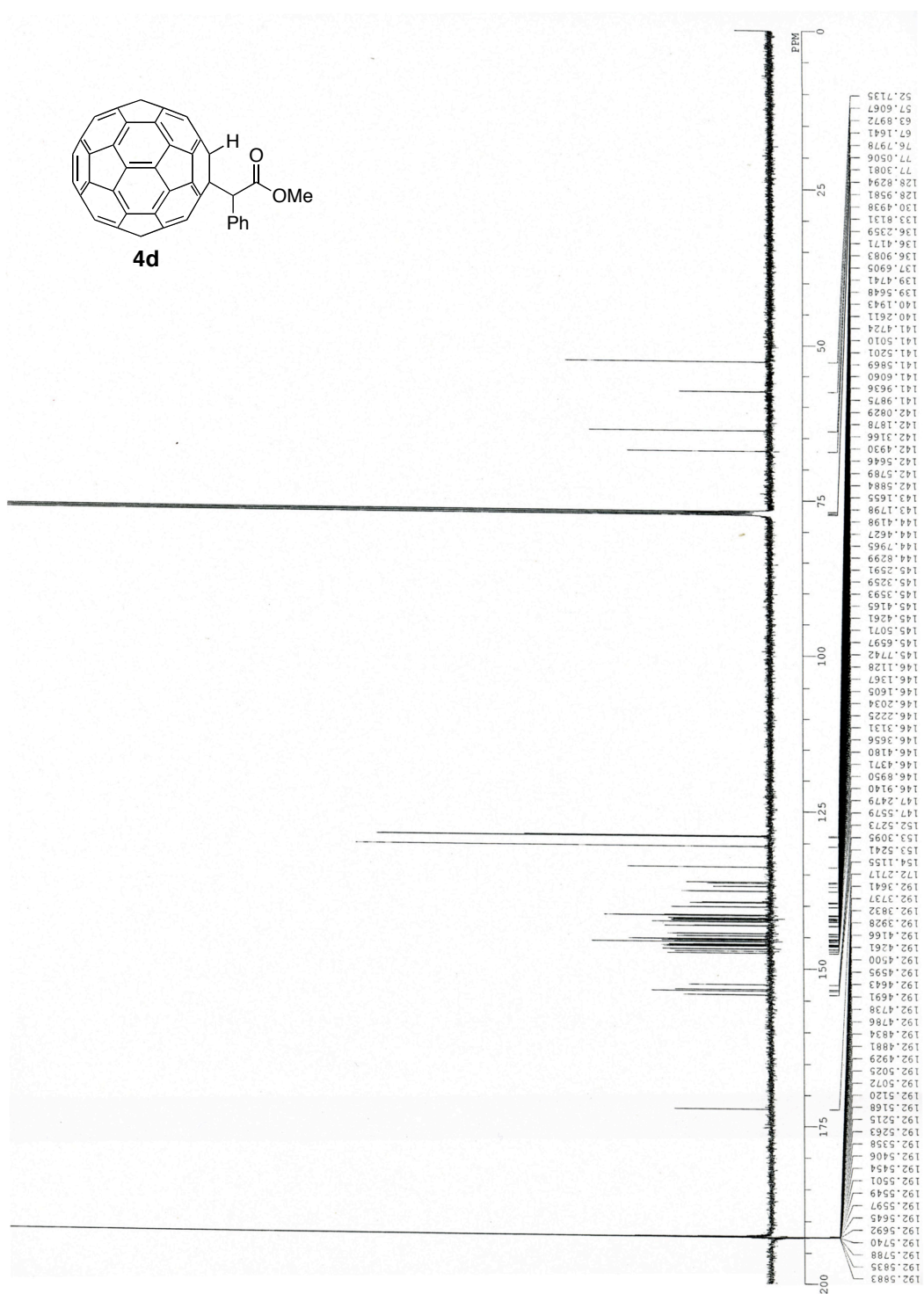
**Figure S12.** A <sup>1</sup>H NMR spectrum of C<sub>60</sub>(CH<sub>3</sub>CHCO<sub>2</sub>Me)H (**4c**) in CS<sub>2</sub>-CDCl<sub>3</sub>



**Figure S13.** A <sup>13</sup>C NMR spectrum of C<sub>60</sub>(CH<sub>3</sub>CHCO<sub>2</sub>Me)H (**4c**) in CS<sub>2</sub>-CDCl<sub>3</sub>

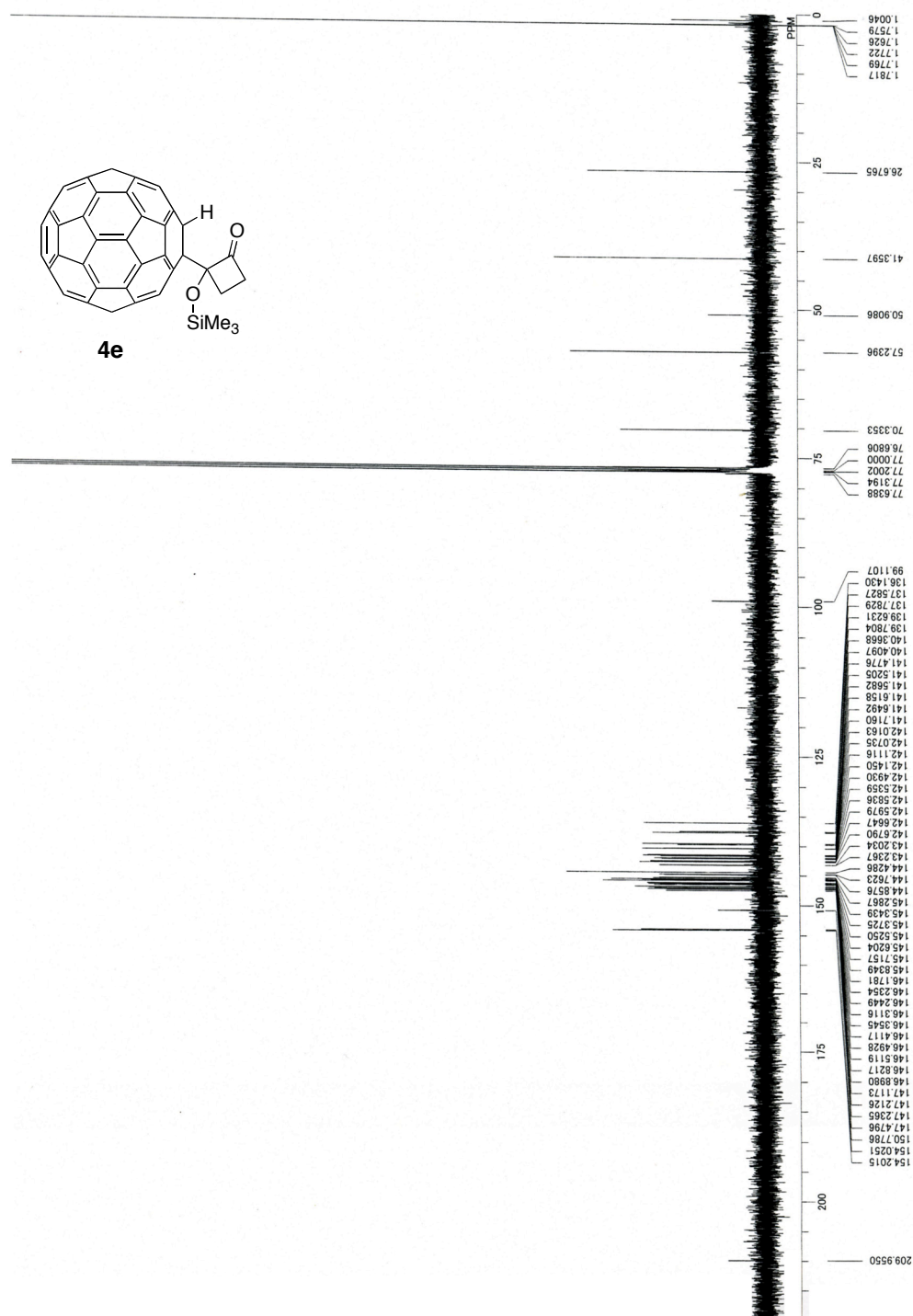


**Figure S14.** A <sup>1</sup>H NMR spectrum of C<sub>60</sub>(C<sub>6</sub>H<sub>5</sub>CHCO<sub>2</sub>Me)H (**4d**) in CS<sub>2</sub>-CDCl<sub>3</sub>





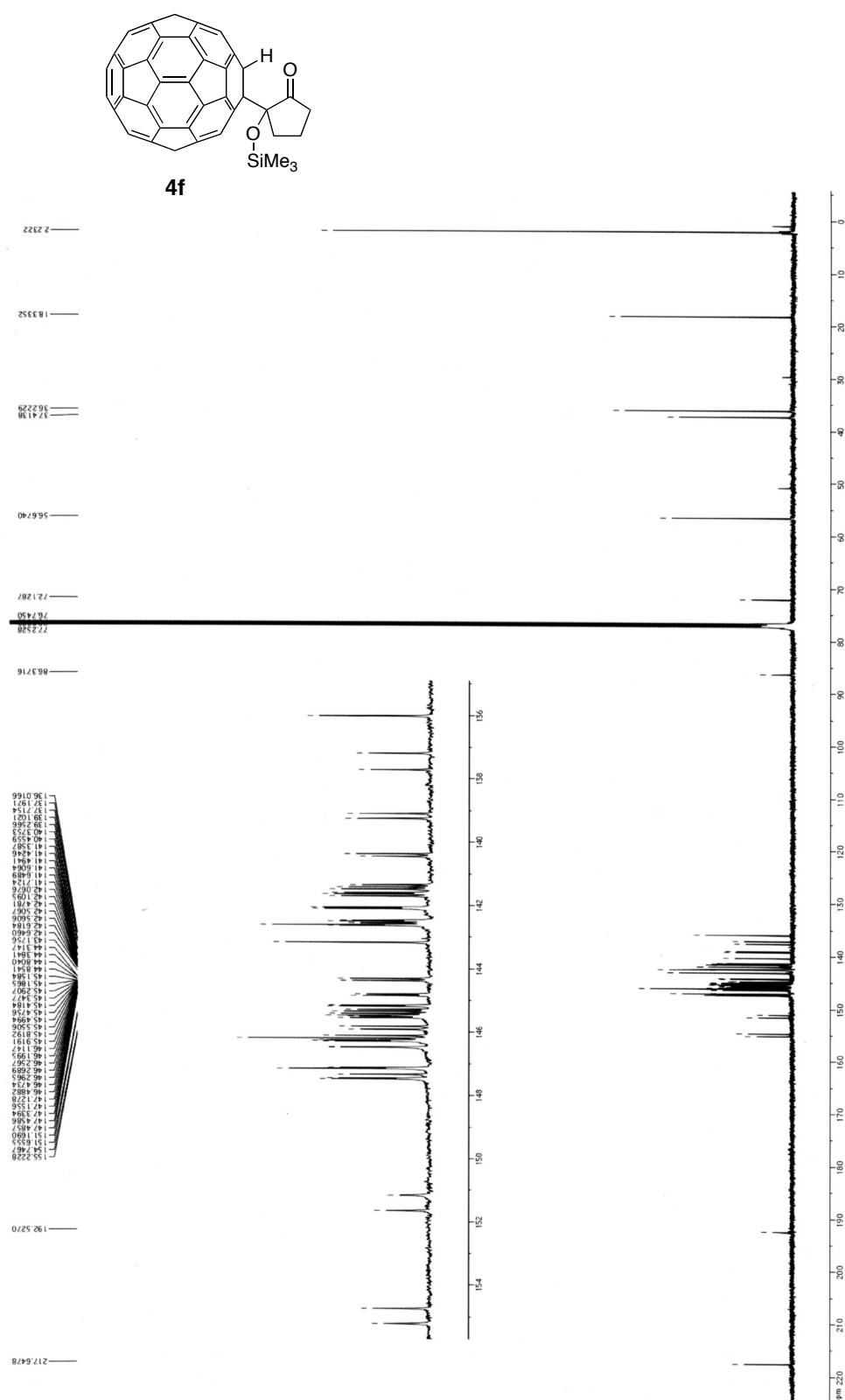




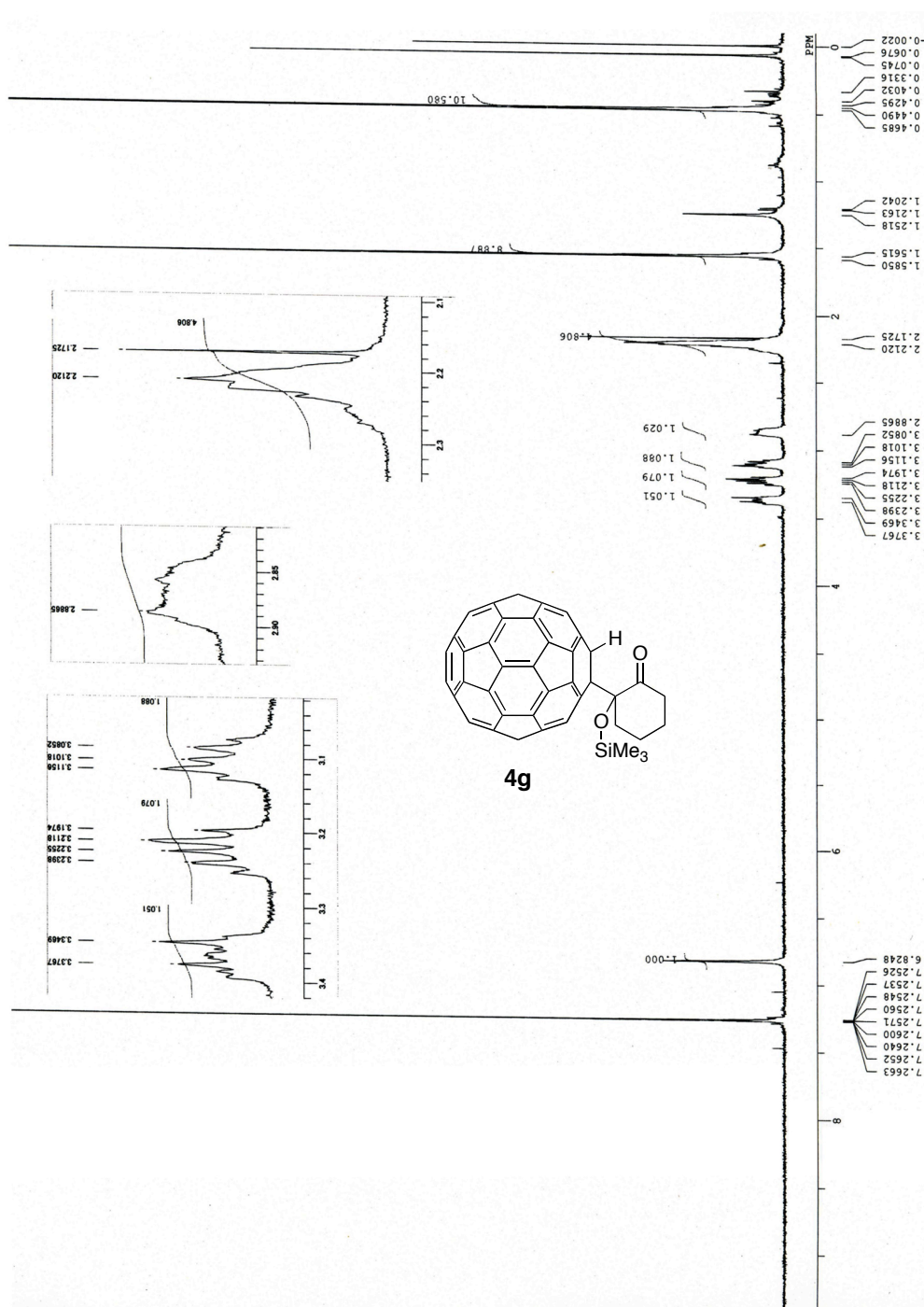
**Figure S17.** A <sup>13</sup>C NMR spectrum of C<sub>60</sub>(Me<sub>3</sub>SiOCCCOCH<sub>2</sub>CH<sub>2</sub>)H (**4e**) in CDCl<sub>3</sub>



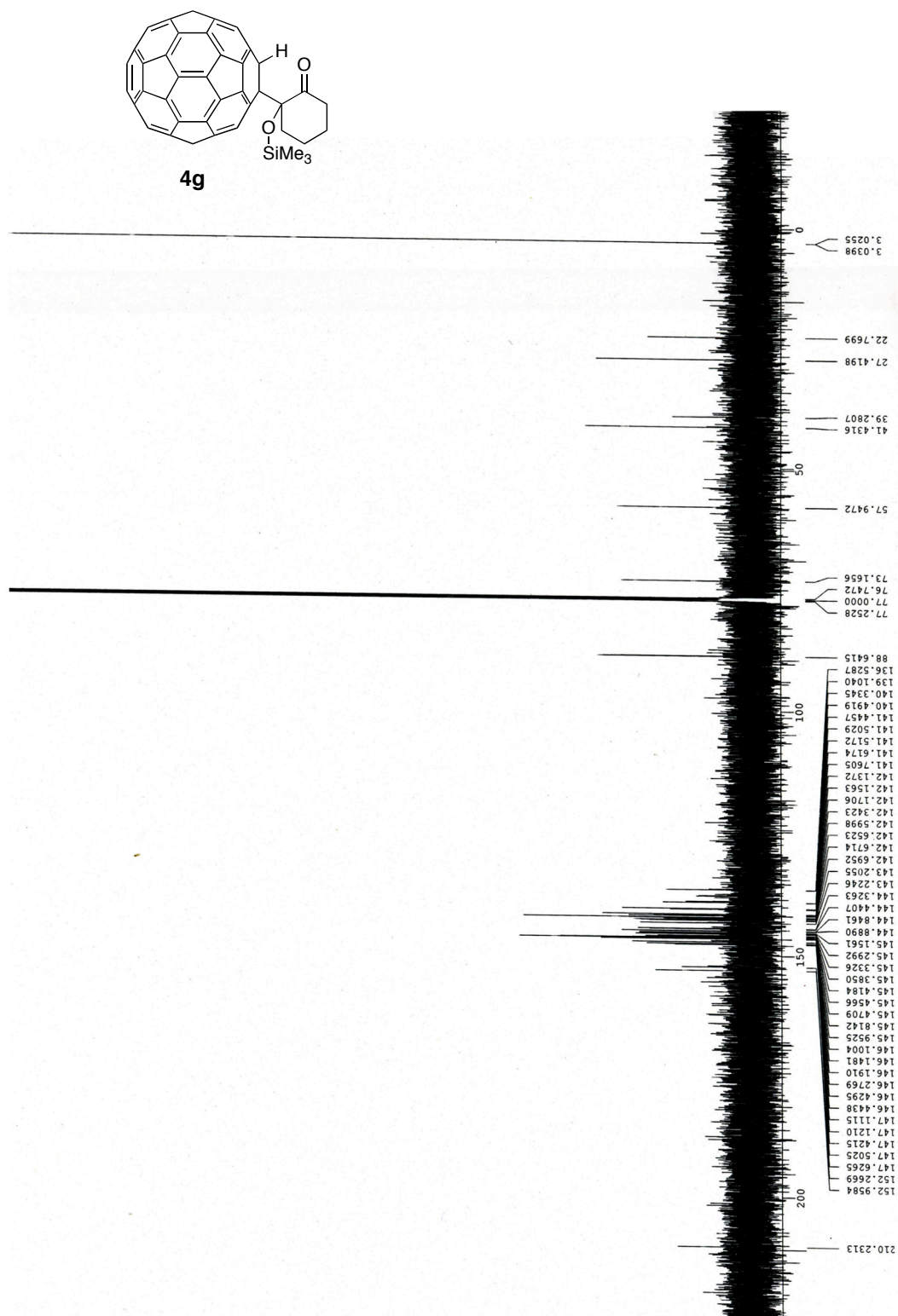
27







**Figure S20.** A  $^1\text{H}$  NMR spectrum of  $\text{C}_{60}(\text{Me}_3\text{SiOCCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{H}$  (**4g**) in  $\text{CDCl}_3$



**Figure S21.**  $^{13}\text{C}$  NMR spectrum of  $\text{C}_{60}(\text{Me}_3\text{SiOCCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{H} (**4g**) in  $\text{CDCl}_3$$