Supporting Information

Synthesis and Reactions of 2,2-[60]Fullerenoalkanoyl Chlorides

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(i) General methods

All reactions were performed under argon atmosphere. C₆₀ (≥99.5%) was used as received. Reaction solvents were distilled prior to use. ¹H NMR spectra were recorded on a 300 or 500 MHz instrument. ¹³C NMR spectra were recorded on a 75 or 125 MHz instrument. ¹H and ¹³C chemical shifts are expressed in parts per million using tetramethylsilane or residual undeuterated solvents as an

internal standard. IR spectra were recorded on a FT-IR spectrometer. MALDI-TOF-MS analysis was performed by the positive mode.

(ii) Synthetic procedures and characterization data of **1b**, **1d**, **2b**, **2d**, **3b**, **3d**, **5b**, **5d**, **9a•a–j**, **9c•a**, **9c•b**, **9c•d**, **11a•a–o**, **11c•b**, **11c•e**, and **11c•f**.

***tert*-Butyl 2-Methyl-2-(methylthio)propionate (5b).** The title compound was synthesized from *tert*-butyl 2-bromopropionate (**4b**) through a procedure similar to that for the preparation of **5c** (70% yield). IR (neat) 2977, 2931, 2871, 1724, 1479, 1455, 1392, 1368, 1331, 1275, 1255, 1149, 1089, 1066, 996, 957, 896, 848, 779, 755, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 1.37–1.61 (m, 12H, overlapped with internal H₂O), 2.16 (s, 3H), 3.18–3.25 (m, 1H); ¹³C NMR (CDCl₃) δ 13.85, 16.53, 27.95, 42.94, 81.03, 171.97.

***tert*-Butyl (Methylthio)phenylacetate (5d).** The title compound was synthesized from *tert*-butyl 2-bromo-2-phenylacetate (**4d**) through a procedure similar to that for the preparation of **5c** (96% yield). IR (neat) 2978, 2919, 1729, 1454, 1392, 1368, 1284, 1249, 1219, 1137, 955, 849, 748, 697 cm⁻¹; ¹H NMR (CDCl₃) δ 1.42 (s, 9H), 2.02 (s, 3H), 4.39 (s, 1H), 7.22–7.45 (m, 5H); ¹³C NMR (CDCl₃) δ 14.83, 27.88, 54.54, 81.97, 127.82, 128.37, 128.48, 136.31, 169.77.

***tert*-Butyl 2,2-[60]Fullerenopropionate (3b).** The title compound was synthesized from **5b** through procedures similar to those for the preparation of **3c** (58% yield). IR (KBr) 2973, 2927, 1726, 1455, 1427, 1366, 1285, 1257, 1160, 1135, 1037, 845, 752, 525 cm⁻¹; ¹H NMR (CDCl₃) δ 1.67 (s, 9H), 2.48 (s, 3H); ¹³C NMR (CDCl₃/CS₂ = 1:1, v/v) δ 15.86, 28.04, 45.61, 83.33, 137.76, 137.83, 140.65, 140.83, 141.89, 141.95, 141.97, 142.04, 142.73, 142.78, 142.86, 142.92, 143.00, 143.46, 143.65, 143.98, 144.27, 144.30, 144.44, 144.52, 144.57, 144.67, 144.91, 144.95, 144.97, 145.06, 145.43, 146.31, 147.75, 166.94; MALDI-TOF-MASS (dithranol) for [M]⁺ C₆₇H₁₂O₂ calcd 848.0837, found 848.2483.

***tert*-Butyl [60]Fullerenophenylacetate (3d).** The title compound was synthesized from C₆₀ and **5d** through procedures similar to those for the preparation of **3c** (65% yield). IR (KBr) 2972, 1733, 1447, 1427, 1367, 1280, 1267, 1240, 1185, 1150, 848, 756, 730, 692, 525 cm⁻¹; ¹H NMR (CDCl₃) δ 1.56 (s,

9H), 7.51–7.59 (m, 3H), 8.08–8.11 (m, 2H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2 = 1:1$, v/v) δ 27.87, 57.09, 75.96, 83.69, 128.46, 129.00, 131.95, 132.80, 137.52, 138.04, 140.79, 140.82, 141.94, 142.00, 142.06, 142.21, 142.75, 142.81, 142.83, 142.85, 142.96, 143.55, 143.73, 144.17, 144.25, 144.42, 144.50, 144.55, 144.63, 144.96, 145.02, 145.14, 145.36, 146.32, 147.66, 165.23; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+ \text{C}_{72}\text{H}_{14}\text{O}_2$ calcd 910.0994, found 911.3294.

2,2-[60]Fullerenopropionic Acid (2b). The title compound was synthesized from **3b** through a procedure similar to that for the preparation of **2a** (99% yield). IR (KBr) 3435, 2922, 1707, 1510, 1458, 1427, 1186, 1145, 735, 702, 525 cm^{-1} ; ^1H NMR ($\text{THF}-d_8/\text{CS}_2 = 1:1$, v/v) δ 2.51 (s, 3H), ^{13}C NMR ($\text{THF}-d_8/\text{CS}_2 = 1:1$, v/v) δ 16.10, 45.96, 78.36, 138.77, 139.35, 141.38, 141.66, 142.77, 142.86, 142.91, 143.53, 143.60, 143.69, 143.75, 143.91, 144.31, 144.56, 144.75, 145.08, 145.16, 145.28, 145.39, 145.44, 145.62, 145.72, 145.75, 145.77, 145.80, 146.05, 146.40, 147.56, 149.01, 168.83; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+ \text{C}_{63}\text{H}_4\text{O}_2$ calcd 792.0211, found 792.0476.

[60]Fullerenophenylacetic Acid (2d). The title compound was synthesized from **3d** through a procedure similar to that for the preparation of **2a** (95% yield). IR (KBr) 3435, 2921, 1730, 1540, 1509, 1495, 1464, 1446, 1427, 1259, 1223, 1185, 1093, 1026, 824, 700, 525 cm^{-1} ; ^1H NMR ($\text{THF}-d_8/\text{CS}_2 = 1:1$, v/v) δ 7.16–7.23 (m, 3H), 7.78–7.81 (m, 2H); ^{13}C NMR ($\text{CDCl}_3/\text{DMSO}-d_6/\text{CS}_2 = 1:1:1$, v/v/v) δ 65.54, 75.00, 123.94, 127.29, 127.83, 130.87, 131.63, 136.40, 136.67, 139.41, 139.48, 140.60, 140.69, 140.74, 140.88, 141.47, 141.56, 142.23, 142.44, 142.85, 142.90, 143.15, 143.19, 143.22, 143.36, 143.62, 143.67, 143.92, 144.21, 145.33, 146.77, 166.20; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+ \text{C}_{68}\text{H}_6\text{O}_2$ calcd 854.0367, found 854.2013.

2,2-[60]Fullerenopropionyl Chloride (1b). The title compound was synthesized from **2b** through a procedure similar to that for the preparation of **1c** (99% yield). IR (KBr) 2923, 2852, 1778, 1509, 1458, 1427, 1184, 958, 909, 736, 714, 656, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.66 (s, 3H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2 = 1:1$, v/v) δ 29.77, 52.27, 76.11, 137.67, 138.22, 140.96, 141.08, 141.74, 141.96, 142.03, 142.09, 142.85, 142.92, 142.97, 143.12, 143.49, 143.68, 144.35, 144.56, 144.59, 144.69, 144.75, 145.10, 145.15, 145.70, 167.98; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+ \text{C}_{63}\text{H}_3\text{ClO}$ calcd 809.9872, found 810.1824.

[60]Fullerenophenylacetyl Chloride (1d). The title compound was synthesized from **2d** through a procedure similar to that for the preparation of **1c** (96% yield). IR (KBr) 2922, 1771, 1509, 1446, 1427, 1186, 1046, 947, 906, 870, 810, 751, 727, 701, 651, 526 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.60 (br, 3H), 8.13 (br, 2H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2 = 1:1$, v/v) δ 62.70, 75.08, 128.99, 129.50, 130.16, 132.85, 132.99, 137.76, 138.36, 140.93, 141.03, 141.68, 141.95, 142.04, 142.74, 142.79, 142.87, 142.92, 142.96, 143.51, 143.70, 144.23, 144.41, 144.45, 144.54, 144.59, 144.67, 144.68, 144.71, 145.00, 145.04, 145.11, 145.13, 145.54, 166.40; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{68}\text{H}_5\text{ClO}$ calcd 872.0029, found 872.2001.

2,2-[60]Fullerenoalkanoic Acid Amides (9a•a–j, 9c•a, 9c•b, and 9c•d). The title compounds were synthesized from **1a** or **1c** through a procedure similar to that described in the main text.

9a•a: IR (KBr) 2922, 2851, 1654, 1541, 1452, 1428, 1186, 698, 575, 525 cm^{-1} ; ^1H NMR ($\text{THF}-d_8/\text{CS}_2 = 1:1$, v/v) δ 2.95 (t, 2H, $J = 7.2$ Hz), 3.56–3.69 (m, 9H, overlapped with the signal of internal THF), 4.78 (s, 1H), 7.15–7.27 (m, 5H), 8.07 (br, 1H); ^{13}C NMR ($\text{THF}-d_8/\text{CS}_2 = 1:1$, v/v) δ 36.67, 42.15, 43.12, 73.37, 127.03, 129.19, 129.61, 136.68, 140.06, 141.21, 141.38, 141.68, 142.74, 142.83, 142.94, 143.19, 143.32, 143.55, 143.65, 143.76, 144.03, 144.31, 144.66, 144.75, 144.99, 145.10, 145.20, 145.34, 145.61, 145.67, 145.74, 145.82, 146.15, 146.48, 148.22, 150.18, 164.11; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{70}\text{H}_{11}\text{NO}$ calcd 881.0841, found 881.0324.

9a•b: IR (KBr) 2960, 2923, 1655, 1541, 1457, 1427, 1186, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.44 (s, 9H), 4.60 (s, 1H), 6.13 (br, 1H); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{66}\text{H}_{11}\text{NO}$ calcd 833.0841, found 833.0726.

9a•c: IR (KBr) 2904, 2847, 1655, 1508, 1451, 1427, 1357, 1186, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.22–2.20 (m, 42H, overlapped with the signal of internal H_2O), 4.57 (s, 1H), 5.97 (br, 1H); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{66}\text{H}_{11}\text{NO}$ calcd 833.0841, found 833.0726.

9a•d: IR (KBr) 2966, 2924, 1654, 1510, 1457, 1428, 1257, 1185, 1137, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.30–1.61 (m, 20H, overlapped with the signal of internal H_2O), 3.67 (q, 2H, $J = 6.0$ Hz), 3.98 (q, 2H, $J = 6.0$ Hz), 4.90 (s, 1H); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{66}\text{H}_{11}\text{NO}$ calcd 833.0841, found 833.8675.

9a•e: IR (KBr) 2956, 2912, 2847, 1655, 1509, 1457, 1428, 1225, 1114, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.86–4.17 (m, 8H), 4.90 (s, 1H); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{66}\text{H}_9\text{NO}_2$ calcd 847.0633, found 846.9747.

9a•f: IR (KBr) 2919, 1654, 1509, 1427, 1203, 1186, 1109, 744, 525 cm^{-1} ; ^1H NMR (CDCl_3 , *cis/trans* mixture) δ 3.03 (t, 1H, $J = 5.7$ Hz), 3.20 (t, 2H, $J = 6.0$ Hz), 4.09 (t, 1H, $J = 6.0$ Hz), 4.38 (t, 2H, $J = 5.7$ Hz), 4.97–4.99 (m, 4H), 5.32 (s, 2H); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{71}\text{H}_{11}\text{NO}$ calcd 893.0841, found 893.9194.

9a•g: IR (KBr) 2975, 2927, 1746, 1696, 1460, 1437, 1251, 1217, 1151, 1006, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.20–1.58 (m, 17H, overlapped with the signal of internal H_2O), 3.62 (s, 1H), 4.23–4.38 (m, 2H), 4.70–4.75 (m, 2H), 5.98 (s, 1H), 7.65 (s, 1H); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{69}\text{H}_{13}\text{NO}_5$ calcd 935.0794, found 934.9357.

9a•h: IR (KBr) 2920, 1742, 1654, 1540, 1449, 1429, 1206, 1186, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.64 (d, 3H, $J = 7.2$ Hz), 3.85 (s, 3H), 4.69 (s, 1H), 4.87–4.92 (m, 1H), 7.00 (d, 1H, $J = 5.7$ Hz); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{66}\text{H}_9\text{NO}_3$ calcd 863.0582, found 862.9877.

9a•i: IR (KBr) 2958, 2921, 2850, 1784, 1746, 1697, 1509, 1455, 1428, 1201, 1185, 739, 696, 575, 526 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.48 (s, 3H), 1.71 (s, 3H), 4.57 (s, 1H), 4.71 (s, 1H), 5.23 (s, 2H), 5.71 (d, 1H, $J = 3.9$ Hz), 5.98–6.03 (m, 1H), 7.12 (d, 1H, $J = 9.0$ Hz), 7.39 (s, 5H); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{77}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ calcd 1066.0987, found for 1065.8978.

9a•j: IR (KBr) 2922, 2851, 1750, 1671, 1541, 1511, 1428, 1366, 1220, 1077, 1041, 526 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.08–2.17 (m, 12H), 3.91–3.93 (m, 1H), 4.16–4.21 (m, 1H), 4.30–4.36 (m, 1H), 4.57 (q, 1H, $J = 9.0$ Hz), 4.67 (s, 1H), 5.23 (t, 1H, $J = 9.0$ Hz), 5.38 (t, 1H, $J = 9.0$ Hz), 5.91 (d, 1H, $J = 9.0$ Hz), 6.69 (d, 1H, $J = 9.0$ Hz); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{76}\text{H}_{21}\text{NO}_{10}$ calcd 1107.1165, found 1107.0746.

9c•a: IR (KBr) 2920, 2849, 1652, 1509, 1494, 1453, 1427, 1186, 744, 697, 575, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.26–2.70 (m, 2H), 3.55 (q, 2H, $J = 5.7$ Hz), 4.16 (s, 2H), 5.61 (br, 1H), 7.01–7.03 (m, 2H), 7.13–7.26 (m, 6H, overlapped with the signal of internal CHCl_3), 7.36–7.42 (m, 3H), 7.56–7.58 (m, 2H); ^{13}C NMR (1,2-dichlorobenzene- d_4 /DMSO- d_6 /CS $_2$ = 1:1:1, v/v/v) δ 35.36, 35.62, 41.20, 53.83,

77.49, 125.96, 126.65, 126.80, 128.93, 129.27, 131.31, 136.81, 136.91, 137.08, 137.43, 139.17, 139.95, 140.38, 141.57, 141.62, 141.74, 141.80, 142.18, 142.28, 142.40, 142.44, 142.56, 143.05, 143.29, 143.44, 143.76, 143.86, 143.98, 144.15, 144.28, 144.44, 144.96, 144.52, 145.17, 145.47, 147.04, 149.17, 164.74; MALDI-TOF-MASS (dithranol) for $[M]^+ C_{77}H_{17}NO$ calcd 971.1310, found 971.2957.

9c•b: IR (KBr) 2959, 2921, 1684, 1511, 1452, 1427, 1363, 1213, 1185, 739, 700, 575, 525 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.25 (s, 9H), 4.19 (s, 2H), 5.41 (s, 1H), 7.40–7.50 (m, 3H), 7.64–7.67 (m, 2H); MALDI-TOF-MASS (dithranol) for $[M]^+ C_{73}H_{17}NO$ calcd 923.1310, found 923.3525.

9c•d: IR (KBr) 2966, 2923, 1638, 1509, 1452, 1425, 1185, 753, 695, 573, 525 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.15–1.25 (m, 6H), 3.52–3.57 (m, 2H), 3.67–3.74 (m, 2H), 4.08 (d, 1H, $J = 15$ Hz), 4.34 (d, 1H, $J = 15$ Hz), 7.26–7.46 (m, 6H, overlapped with the signal of internal $CHCl_3$), 7.63–7.66 (m, 2H); ^{13}C NMR ($THF-d_8/CS_2 = 1:1$, v/v) δ 13.32, 13.40, 14.30, 14.32, 36.51, 42.95, 53.29, 79.33, 128.09, 129.42, 130.71, 137.45, 138.37, 138.62, 139.63, 141.47, 141.59, 141.80, 142.82, 143.01, 143.27, 143.57, 143.71, 143.83, 143.88, 143.96, 144.52, 144.64, 144.82, 144.95, 145.11, 145.34, 145.62, 145.77, 145.98, 146.23, 146.79, 147.94, 148.95, 152.85, 164.42; MALDI-TOF-MASS (dithranol) for $[M]^+ C_{73}H_{17}NO$ calcd 923.1310, found 923.3507.

2,2-[60]Fullerenoalkanoic Acid Esters (11a•a–o, 11c•b, 11c•e, and 11c•f). The title compounds were synthesized from **1a** or **1c** through a procedure similar to that described in the main text.

11a•a: IR (KBr) 3435, 2923, 2852, 1748, 1509, 1436, 1198, 1184, 1157, 525 cm^{-1} ; 1H NMR ($CDCl_3/CS_2 = 1:1$, v/v) δ 4.05 (s, 3H), 4.76 (s, 1H); MALDI-TOF-MASS (dithranol) for $[M]^+ C_{63}H_4O_2$ calcd 792.0211, found 791.9718.

11a•b: IR (KBr) 3434, 2921, 2849, 1740, 1509, 1427, 1185, 1155, 1024, 525 cm^{-1} ; 1H NMR (1,2-dichlorobenzene- d_4) δ 1.60 (t, 3H, $J = 7.2$ Hz), 4.63 (q, 2H, $J = 7.2$ Hz), 4.82 (s, 1H); ^{13}C NMR (1,2-dichlorobenzene- d_4) δ 14.59, 39.46, 62.43, 70.98, 136.42, 140.85, 140.91, 141.05, 142.03, 142.10, 142.20, 142.49, 142.82, 142.95, 142.98, 143.08, 143.23, 143.74, 143.95, 144.43, 144.55, 144.63, 144.66, 144.74, 145.07, 145.16, 145.20, 145.22, 145.68, 146.08, 148.40, 165.81; MALDI-TOF-MASS (dithranol) for $[M]^+ C_{64}H_6O_2$ calcd 806.0368, found 806.0502.

11a•c: IR (KBr) 2920, 2848, 1743, 1460, 1428, 1185, 1156, 526 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.88 (t, 3H, $J = 6.9$ Hz), 1.25–1.55 (m, 48H overlapped with the signal of internal H_2O), 1.81–1.89 (m, 2H), 4.46 (t, 2H, $J = 6.9$ Hz), 4.79 (s, 1H); ^{13}C NMR (CDCl_3) δ 14.15, 22.70, 26.09, 28.68, 29.31, 29.37, 29.59, 29.61, 29.67, 29.72, 31.92, 39.10, 66.64, 70.57, 136.33, 140.49, 140.89, 141.09, 142.05, 142.18, 142.38, 142.77, 142.94, 142.97, 143.05, 143.23, 143.69, 143.92, 144.37, 144.56, 144.64, 144.70, 145.05, 145.14, 145.18, 145.22, 145.55, 145.79, 148.27, 166.46; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+ \text{C}_{80}\text{H}_{38}\text{O}_2$ calcd 1030.2872, found 1030.1046.

11a•d: IR (KBr) 3420, 2944, 2845, 1746, 1427, 1183, 1155, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.09 (br, 2H), 4.61 (br, 2H), 4.84 (s, 1H); MALDI-TOF-MASS (dithranol) for $[\text{M}]^+ \text{C}_{64}\text{H}_6\text{O}_3$ calcd 822.0317, found 822.0506.

11a•e: IR (KBr) 2941, 2848, 1737, 1428, 1195, 1186, 1159, 1102, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.48–1.51 (m, 15H, overlapped with the signal of internal H_2O), 4.69 (s, 1H), 5.30–5.35 (m, 1H); ^{13}C NMR(CDCl_3) δ 21.85, 39.23, 39.32, 70.06, 70.52, 136.08, 140.37, 140.67, 140.92, 141.77, 141.84, 141.98, 142.18, 142.55, 142.72, 142.77, 142.84, 143.05, 143.46, 143.71, 144.16, 144.34, 144.37, 144.40, 144.51, 144.83, 144.91, 144.99, 145.31, 145.50, 148.03, 164.85; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+ \text{C}_{65}\text{H}_8\text{O}_2$ calcd 820.0524, found 819.9170.

11a•f: IR (KBr) 2922, 1757, 1503, 1428, 1247, 1185, 1133, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.85 (s, 3H), 4.99 (s, 1H), 6.99 (d, 2H, $J = 9.0$ Hz), 7.31 (d, 2H, $J = 9.0$ Hz); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2 = 1:1$, v/v) δ 38.56, 55.52, 70.25, 114.54, 122.20, 136.44, 140.66, 140.88, 141.11, 141.96, 142.01, 142.13, 142.32, 142.73, 142.90, 142.94, 143.21, 143.65, 143.80, 143.87, 144.40, 144.46, 144.59, 144.62, 144.95, 145.01, 145.12, 145.16, 145.19, 145.22, 145.43, 147.90, 157.60, 164.96; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+ \text{C}_{69}\text{H}_8\text{O}_3$ calcd 884.0473, found 883.8548.

11a•g: IR (KBr) 2923, 2852, 1765, 1508, 1427, 1341, 1197, 1121, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.02 (s, 1H), 7.61 (d, 2H, $J = 9.0$ Hz), 8.39 (d, 2H, $J = 9.0$ Hz); ^{13}C NMR (CDCl_3) δ 67.09, 69.88, 122.51, 125.50, 136.67, 140.67, 141.09, 141.27, 142.01, 142.10, 142.22, 142.38, 142.88, 143.07, 143.30, 143.77, 143.98, 144.62, 144.75, 144.78, 144.79, 144.83, 144.89, 145.17, 145.30, 145.34,

145.36, 145.41, 145.81, 147.54, 154.83, 164.04; MALDI-TOF-MASS (dithranol) for $[M]^+ C_{68}H_5NO_4$ calcd 899.0219, found 898.9030.

11a•h: IR (KBr) 2949, 2918, 2863, 1738, 1512, 1427, 1185, 1159, 525 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.89 (d, 6H, $J = 6.0$ Hz), 0.95–1.30 (m, 6H), 1.55–1.67 (m, 7H, overlapped with the signal of internal H_2O), 1.75–1.81 (m, 3H), 2.11–2.29 (m, 2H), 4.79 (s, 1H), 5.01–5.08 (ddd, 1H, $J_1 = 10.8$ Hz, $J_2 = 10.6$ Hz, $J_3 = 4.2$ Hz); ^{13}C NMR ($CDCl_3$) δ 16.41, 20.88, 22.06, 23.38, 26.37, 31.56, 34.11, 39.50, 41.01, 47.05, 70.74, 136.30, 140.29, 140.30, 140.86, 141.06, 142.05, 142.18, 142.39, 142.78, 142.93, 142.98, 143.05, 143.21, 143.69, 143.91, 144.35, 144.53, 144.60, 144.63, 144.73, 145.05, 145.11, 145.13, 145.17, 145.21, 145.54, 145.57, 145.91, 145.96, 148.34, 165.77; MALDI-TOF-MASS (dithranol) for $[M]^+ C_{72}H_{20}O_2$ calcd 916.1463, found for 916.1508.

11a•i: IR (KBr) 2949, 2871, 1738, 1720, 1511, 1428, 1186, 1154, 525 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.95–2.63 (m, 28H, overlapped with the signal of internal H_2O), 4.83 (s, 1H), 5.27–5.31 (m, 1H); ^{13}C NMR ($CDCl_3/CS_2 = 1:1$, v/v) δ 13.81, 18.83, 19.73, 27.40, 28.19, 36.93, 39.26, 44.87, 48.07, 49.05, 70.66, 82.79, 136.29, 140.41, 140.87, 141.06, 142.01, 142.15, 142.35, 142.75, 142.90, 142.94, 143.03, 143.21, 143.66, 143.89, 144.35, 144.52, 144.58, 144.60, 144.68, 145.01, 145.04, 145.10, 145.15, 145.18, 145.53, 145.73, 145.76, 148.29, 166.62; MALDI-TOF-MASS (dithranol) for $[M]^+ C_{72}H_{18}O_2$ calcd 914.1307, found for 914.1008.

11a•j: IR (KBr) 2918, 2848, 1740, 1428, 1375, 1184, 1154, 525 cm^{-1} ; 1H NMR ($CDCl_3$) δ 1.54 (s, 6H), 1.84 (s, 3H), 4.79 (s, 1H), 4.98 (d, 2H, $J = 6.0$ Hz), 5.05 (br, 2H), 5.13 (br, 2H), 5.59 (q, 1H, $J = 9.0$ Hz), 5.69 (t, 1H, $J = 9.0$ Hz); MALDI-TOF-MASS (dithranol) for $[M]^+ C_{72}H_{18}O_2$ calcd 914.1307, found 914.1487.

11a•k: IR (KBr) 3436, 2863, 2944, 1738, 1157, 1186, 526 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.70–2.17 (m, 124H, overlapped with the signal of internal H_2O), 4.76 (s, 1H), 4.96 (br, 1H), 5.49 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 11.86, 18.70, 19.40, 21.03, 22.56, 22.83, 23.81, 24.28, 27.94, 28.01, 28.23, 31.82, 31.92, 35.79, 36.14, 36.63, 36.99, 38.16, 39.25, 39.48, 39.67, 42.29, 49.94, 56.08, 56.63, 70.68, 123.31, 136.31, 139.17, 140.51, 140.88, 141.08, 142.05, 142.19, 142.40, 142.77, 142.94, 142.97, 143.05, 143.23, 143.69, 143.93, 144.37, 144.55, 144.64, 144.75, 145.04, 145.08, 145.14, 145.18, 145.22,

145.61, 145.82, 145.86, 148.33, 165.78; MALDI-TOF-MASS (dithranol) for $[M + O]^+ C_{88}H_{44}O_3$ calcd 1148.3290, found 1148.2031.

11a•l: IR (KBr) 2921, 1729, 1452, 1427, 1272, 1185, 1157, 1071, 1026, 733, 696, 526 cm^{-1} ; 1H NMR ($CDCl_3$) δ 3.44 (s, 3H), 3.59–3.64 (m, 1H), 3.59–3.72 (m, 1H), 3.97–4.12 (m, 2H), 4.58–5.08 (m, 10H), 7.26–7.38 (m, 16H, overlapped with the signal of internal $CHCl_3$); ^{13}C NMR ($CDCl_3$) δ 38.70, 55.49, 55.53, 64.71, 68.32, 70.36, 73.42, 74.89, 75.69, 79.90, 82.12, 98.24, 127.87, 128.06, 128.43, 128.56, 137.75, 137.95, 138.56, 140.54, 141.14, 141.97, 142.01, 142.05, 142.15, 142.38, 142.78, 142.95, 142.99, 143.24, 143.70, 143.93, 144.40, 144.58, 144.64, 144.66, 144.94, 144.96, 145.07, 145.17, 145.19, 145.24, 145.43, 145.55, 148.10, 165.99; MALDI-TOF-MASS (dithranol) for $[M + Na]^+ C_{90}H_{32}NaO_7$ calcd 1247.2046, found 1247.3272.

11a•m: IR (KBr) 2949, 2925, 2853, 1747, 1692, 1462, 1428, 1272, 1251, 1184, 1156, 1105, 526 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.16 (d, 6H, $J = 5.4$ Hz), 0.94 (s, 9H), 1.98 (s, 3H), 2.25–2.44 (m, 2H), 4.28 (q, 1H, $J = 4.2$ Hz), 4.47–4.52 (m, 1H), 4.65 (d, 2H, $J = 4.8$ Hz), 4.79 (s, 1H), 6.28 (t, 1H, $J = 6.6$ Hz), 7.26–7.33 (m, 9H, overlapped with the signal of internal $CHCl_3$), 8.18 (s, 1H); MALDI-TOF-MASS (dithranol) for $[M]^+ C_{78}H_{28}N_2O_6Si$ calcd 1116.1717, found 1115.9968.

11a•n: IR (KBr) 2948, 2923, 2852, 1732, 1686, 1511, 1459, 1428, 1254, 1183, 1154, 1127, 526 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.19 (s, 6H), 0.97 (s, 9H), 1.96 (s, 3H), 2.27–2.36 (m, 1H), 2.67–2.74 (m, 1H), 4.00–4.09 (m, 2H), 4.44 (s, 1H), 4.82 (s, 1H), 5.64 (d, 1H, $J = 5.7$ Hz), 6.57 (q, 2H, $J = 4.5$ Hz), 7.61 (s, 1H), 8.55 (s, 1H); MALDI-TOF-MASS (dithranol) for $[M + Na]^+ C_{78}H_{28}N_2NaO_6Si$ calcd 1139.1614, found 1139.3863.

11a•o: IR (KBr) 2949, 2926, 2853, 1717, 1698, 1607, 1508, 1458, 1251, 1182, 1156, 1035, 526 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.13 (s, 3H), 0.23 (s, 3H), 0.97 (s, 9H), 3.58–3.62 (m, 1H), 3.68–3.72 (m, 1H), 3.80 (d, 6H, $J = 8.1$ Hz), 4.53–4.54 (m, 1H), 4.73 (t, 1H, $J = 5.1$ Hz), 4.82 (s, 1H), 5.31–5.34 (m, 1H), 5.71 (t, 1H, $J = 4.2$ Hz), 6.18 (d, 1H, $J = 5.4$ Hz), 6.86 (d, 4H, $J = 8.4$ Hz), 7.26–7.42 (m, 30H, overlapped with the signal of internal $CHCl_3$), 7.90 (d, 2H, $J = 8.1$ Hz); MALDI-TOF-MASS (9-nitroanthracene) for $[M]^+ C_{98}H_{44}N_9O_9Si$, calcd 1420.2816, found 1419.9543.

11c•b: IR (KBr) 2971, 2923, 1732, 1494, 1454, 1427, 1364, 1197, 1184, 1128, 1094, 1074, 1020, 753, 737, 696, 575, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.28 (t, 3H, $J = 7.2$ Hz), 4.26 (s, 2H), 4.36 (q, 2H, $J = 7.2$ Hz), 7.33–7.47 (m, 3H), 7.60–7.65 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.23, 35.05, 50.13, 62.48, 75.95, 127.46, 128.91, 129.09, 136.56, 137.95, 138.21, 140.83, 141.12, 142.07, 142.15, 142.19, 142.88, 142.98, 143.05, 143.09, 143.12, 143.21, 143.67, 143.87, 144.28, 144.60, 144.63, 144.66, 144.80, 145.18, 145.24, 145.28, 145.48, 146.45, 147.69, 166.96; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{71}\text{H}_{12}\text{O}_2$ calcd 896.0837, found 896.2389.

11c•e: IR (KBr) 2975, 2924, 1726, 1495, 1452, 1428, 1373, 1205, 1184, 1100, 754, 697, 575, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.24 (d, 6H, $J = 6.3$ Hz), 4.23 (s, 2H), 5.19 (m, 1H), 7.31–7.45 (m, 3H), 7.55–7.64 (m, 2H); ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2 = 1:1$, v/v) δ 21.70, 35.08, 50.13, 70.39, 76.03, 127.39, 128.81, 129.15, 136.49, 137.82, 138.14, 140.78, 141.08, 141.99, 142.03, 142.10, 142.16, 142.84, 142.92, 143.01, 143.15, 143.61, 143.82, 144.22, 144.50, 144.56, 144.60, 144.74, 145.12, 145.18, 145.21, 145.45, 146.45, 146.94, 147.73, 166.26; MALDI-TOF-MASS (dithranol) for $[\text{M}]^+$ $\text{C}_{72}\text{H}_{14}\text{O}_2$ calcd 910.0994, found 910.2902.

11c•f: IR (KBr) 2923, 2828, 1753, 1504, 1455, 1427, 1249, 1187, 1171, 1117, 1098, 1068, 1035, 817, 737, 696, 575, 525 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.78 (s, 3H), 4.35 (s, 2H), 6.83 (s, 4H), 7.36–7.49 (m, 3H), 7.69–7.71 (m, 2H); ^{13}C -NMR (1,2-dichlorobenzene- $d_4/\text{CS}_2 = 1:1$, v/v) δ 35.41, 50.11, 55.09, 75.95, 114.41, 122.26, 127.86, 129.17, 129.49, 136.49, 137.82, 138.35, 140.88, 141.17, 142.05, 142.11, 142.90, 142.94, 143.00, 143.15, 143.61, 143.79, 144.09, 144.32, 144.57, 144.63, 144.73, 145.13, 145.19, 145.36, 146.08, 147.54, 157.68, 165.29; MALDI-TOF-MASS (dithranol) for $\text{C}_{76}\text{H}_{14}\text{O}_3$ calcd 974.0943, found 974.2932.

(iii) ^1H and ^{13}C NMR spectra of *tert*-butyl 2-(methylthio)alkanoates **5b–d**

5b

^1H NMR
(CDCl_3)

^{13}C NMR
(CDCl_3)

5c
(CDCl₃)

¹H NMR
(CDCl₃)

¹³C NMR
(CDCl₃)

5d

^1H NMR
(CDCl_3)

^{13}C NMR
(CDCl_3)

(iv) ^1H and ^{13}C NMR spectra of *tert*-butyl 2,2-[60]fullerenoalkanoates **3a–d**

3a

^1H NMR
($\text{CDCl}_3/\text{CS}_2$)

^{13}C NMR
($\text{CDCl}_3/\text{CS}_2$)

3b

^1H NMR
(CDCl_3)

^{13}C NMR
($\text{CDCl}_3/\text{CS}_2$)

3c

^1H NMR
(CDCl_3)

^{13}C NMR
($\text{CDCl}_3/\text{CS}_2$)

3d

^1H NMR
(CDCl_3)

^{13}C NMR
($\text{CDCl}_3/\text{CS}_2$)

(v) ^1H and ^{13}C NMR spectra of 2,2-[60]fullerenoalkanoic acids **2a–d**

2a

^1H NMR
($\text{THF-}d_8/\text{CS}_2$)

^{13}C NMR
($\text{THF-}d_8/\text{CS}_2$)

2b

^1H NMR
(THF- d_8 /CS $_2$)

^{13}C NMR
(THF- d_8 /CS $_2$)

2c

^1H NMR
(THF- d_8 /CS $_2$)

^{13}C NMR
(THF- d_8 /CS $_2$)

2d

^1H NMR
(THF- d_8 /CS $_2$)

^{13}C NMR
(CDCl $_3$ /
DMSO- d_6 /CS $_2$)

(vi) ^1H and ^{13}C NMR spectra of 2,2-[60]fullerenoalkanoyl chlorides **1a–d**

1a

^1H NMR
($\text{CDCl}_3/\text{CS}_2$)

^{13}C NMR
($\text{THF-}d_8/\text{CS}_2$)

1b

^1H NMR
(CDCl_3)

^{13}C NMR
($\text{CDCl}_3/\text{CS}_2$)

1c

^1H NMR
(CDCl_3)

^{13}C NMR
($\text{CDCl}_3/\text{CS}_2$)

1d

^1H NMR
(CDCl_3)

^{13}C NMR
($\text{CDCl}_3/\text{CS}_2$)

(vii) ^1H and ^{13}C NMR spectra of 2,2-[60]fullerenoalkanoic acid amides **9a•a** and **9c•a**

9a•a

^1H NMR
(THF- d_8 /CS $_2$)

^{13}C NMR
(THF- d_8 /CS $_2$)

9c•a

^1H NMR
(CDCl_3)

^{13}C NMR
(1,2-dichloro-
benzene- d_4 /
 $\text{DMSO}-d_6/\text{CS}_2$)

(viii) ^1H and ^{13}C NMR spectra of 2,2-[60]fullerenoalkanoic acid esters **11a•b** and **11c•b**

11a•b

^1H NMR
(1,2-dichloro- $\text{benzene-}d_4$)

^{13}C NMR
(1,2-dichloro- $\text{benzene-}d_4$)

11c•b

^1H NMR
(CDCl_3)

^{13}C NMR
(CDCl_3)