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Supporting Information

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$AlCl_3$-Mediated Mono-, Di- and Tri-Hydroarylation of [60]fullerene

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Experimental Details and Physical Data: General Considerations and Materials.

All reactions dealing with air- or moisture-sensitive compounds were carried out using standard Schlenk technique or a glove box under an argon or nitrogen atmosphere. HPLC analyses were performed on a Shimadzu LC-10A system equipped with SPD-M10A diode array detector and a Buckyprep column (Nacalai Tesque Inc., 4.6 mm x 250 mm) or an RP-FULLERENE column (Nomura Chemical Co., 4.6 mm x 250 mm). Preparative HPLC was performed on a Buckyprep column (Nacalai Tesque Inc., 20 mm x 250 mm) using toluene/2-propanol (7/3) as eluent (flow rate 18 mL/min, detected at 350 nm with an UV spectrometer, Shimadzu SPD-6A) or an RP-FULLERENE column (Nomura Chemical Co., 20 × 250 mm) using toluene/acetonitrile (4/6) as eluent (flow rate 12 mL/min, detected at 350 nm with an UV spectrophotometric detector, Shimadzu SPD-6A). Flush silica-gel column chromatography was performed on silica gel 60N (Kanto, spherical and neutral, 140–325 mesh) as described by Still.[S1] NMR spectra were measured with a JEOL EX-400 (400 MHz) or a JEOL ECA-500 (500 MHz) spectrometer. Spectra are reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) for ^{1}H NMR, from solvent carbon (e.g. δ 77.00 ppm for chloroform) for ^{13}C NMR. High-resolution mass spectra were measured by APCI using a time-of-flight mass analyzer on JEOL JMS-T100LC (AccuTOF) spectrometer. Unless otherwise noted, materials were purchased from Tokyo Chemical Industry Co., Sigam-Aldrich Co., Kanto Chemical Co., Inc., Wako Pure Chemical Industries, or other commercial suppliers and used after appropriate purification before use. Aluminum(III) chloride (powder) and KO^{t}Bu were purchased from Aldrich Chemical Co. and used as received. $C_{60}(CH_2SiMe_2O^iPr)H$ (**11**) was synthesized according to the literature.[11]

Synthesis.

1-(4-Chlorophenyl)-1,9-dihydro(C_{60}-I_h)[5,6]fullerene (1): To a mixture of C_{60} (72.0 mg, 0.10 mmol) and aluminum(III) chloride (66.7 mg, 0.50 mmol) was added chlorobenzene (20.0 mL) that was prepared to be contained water (1.8 μL, 0.10 mmol). After stirred for 2 hrs at 25 °C, the reaction mixture was quenched with water (0.1 mL). The resulting dark brown solution

was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed by rotary evaporation. The crude product contained the mono adduct **1** and unreacted C_{60} as analyzed by HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 350 nm, eluent: toluene/2-propanol = 7/3) as shown in Figure S1. Purification with a silica-gel column chromatography (eluent: CS_2/hexane = 1/1; the second brown elution following a purple C_{60} elution, R_f = 0.74) gave the title compound $C_{60}(C_6H_4Cl\text{-}4)H$ (32.3 mg, 39%) as a brown powder. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$): δ 2.50 (s, 6H, CH_3), 5.78 (s, 2H, $C_{60}H$), 7.42 (d, 4H, J = 8.0 Hz, C_6H_4), 8.09 (d, 4H, J = 8.0 Hz, C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$): δ 21.17 (2C, CH_3), 56.50 (2C, $C_{60}H$), 63.19 (2C, $C_{60}C_6H_4$), 127.77 (4C, C_6H_4), 130.10 (4C, C_6H_4), 134.42 (2C, C_{60}), 136.28 (2C, C_{60}), 137.16 (2C, C_6H_4), 137.20 (1C, C_{60}), 141.09 (2C, C_{60}), 141.20 (2C, C_{60}), 141.79 (2C, C_{60}), 142.34 (2C, C_{60}), 142.49 (2C+2C, C_{60}), 142.56 (2C, C_{60}), 142.93 (1C, C_{60}), 143.13 (2C, C_{60}), 143.69 (2C, C_{60}), 144.20 (2C, C_{60}), 144.31 (2C, C_{60}), 144.44 (2C, C_{60}), 144.79 (2C, C_{60}), 145.18 (2C, C_{60}), 145.20 (2C, C_{60}), 145.27 (2C, C_{60}), 145.56 (2C, C_6H_4), 146.06 (2C, C_{60}), 146.60 (1C, C_{60}), 147.17 (2C, C_{60}), 147.28 (2C, C_{60}), 148.00 (2C, C_{60}), 148.11 (1C, C_{60}), 148.16 (2C, C_{60}), 149.19 (2C, C_{60}), 149.67 (2C, C_{60}), 151.91 (2C, C_{60}); APCI-HRMS (-): calcd for $C_{74}H_{15}$ ($M\text{-}H^+$), 903.11738; found, 903.11504.

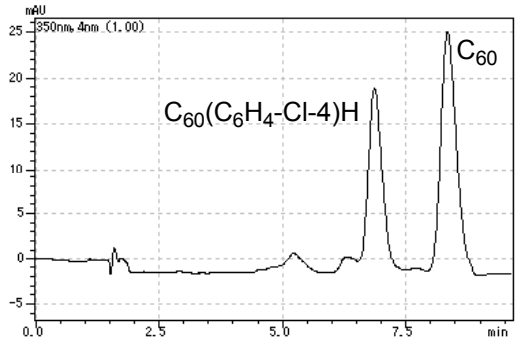

Figure S1. The HPLC chart of **1 (**Buckyprep, flow rate: 2 mL/min).

1-(4-Methoxyphenyl)-1,9-dihydro(C_{60}-I_h)[5,6]fullerene (2): To a mixture of (C_{60}-I_h)[5,6]fullerene (72.0 mg, 0.10 mmol) and aluminum(III) chloride (66.7 mg, 0.50 mmol) was added 1,2-dichlorobenzene (20.0 mL) that was prepared to be contained water (1.8 μL, 0.10 mmol) followed by addition of anisole (109 μL, 1.0 mmol). After stirred for 20 hrs at 80 °C, the reaction mixture was quenched with water (0.1 mL). The resulting dark brown solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed by rotary evaporation. The crude product contained the mono adduct **2** and unreacted C_{60} as analyzed by HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 350 nm, eluent: toluene/2-propanol = 7/3) as shown in Figure S2. Purification with silica-gel column chromatography (eluent: CS_2/hexane = 2/1; the second brown elution following a purple C_{60} elution, R_f = 0.42) gave the title compound $C_{60}(C_6H_4\text{-}OMe\text{-}4)H$ (8.3 mg, 10%) as a brown powder. ^{1}H NMR (400 MHz, $CS_2/CDCl_3$): δ 3.97

(s, 3H, CH_3), 6.71 (s, 1H, $C_{60}H$), 7.24–7.28 (m, 2H, C_6H_4), 8.32–8.36 (m, 2H, C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$): δ 55.21 (1C, CH_3), 63.77 (1C, $C_{60}H$), 67.21 (1C, $C_{60}C$), 115.13 (2C, C_6H_4), 128.62 (2C, C_6H_4), 135.59 (2C, C_{60}), 136.21 (2C, C_{60}), 140.13 (2C, C_{60}), 140.20 (2C, C_{60}), 140.40 (1C, C_6H_4), 141.48 (2C, C_{60}), 141.55 (2C, C_{60}), 141.86 (2C, C_{60}), 141.92 (2C, C_{60}), 141.94 (2C, C_{60}), 142.21 (2C, C_{60}), 142.46 (2C, C_{60}), 142.47 (2C, C_{60}), 143.17 (2C, C_{60}), 144.46 (2C, C_{60}), 144.55 (2C, C_{60}), 145.28 (2C, C_{60}), 145.31 (2C, C_{60}), 145.39 (2C, C_{60}), 145.42 (2C, C_{60}), 145.71 (2C, C_{60}), 145.82 (2C, C_{60}), 146.08 (2C, C_{60}), 146.10 (2C, C_{60}), 146.25 (2C, C_{60}), 146.30 (2C, C_{60}), 146.75 (2C, C_{60}), 147.17 (1C, C_{60}), 147.40 (1C, C_{60}), 152.53 (2C, C_{60}), 154.02 (2C, C_{60}), 159.20 (1C, C_6H_4); APCI-HRMS: m/z calcd for $C_{67}H_7O$ [M-H$^+$], 827.04641, found, 827.04969.

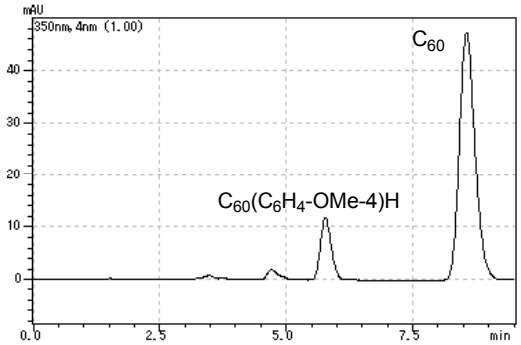

Figure S2. The HPLC chart of **2 (**Buckyprep, flow rate: 2 mL/min).

1,7-Bis(4-methylphenyl)-1,7,8,9-tetrahydro(C_{60}-I_h)[5,6]fullerene (3): To a mixture of C_{60} (72.0 mg, 0.10 mmol) and aluminum(III) chloride (66.7 mg, 0.50 mmol) was added 1,2-dichlorobenzene (100 mL) that was prepared to be contained water (1.8 μL, 0.10 mmol) followed by toluene (92.1 mg, 1.0 mmol) at room temperature. After stirred for 30 min, the reaction mixture was quenched with water (0.1 mL). The resulting solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed with rotary evaporator. The crude product contained mainly the desired bis adduct **3**, small amounts of poly arylated products and a trace amount of unreacted C_{60} as analyzed by HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 350 nm, eluent: toluene/2-propanol = 7/3) as shown in Figure S3. Purification with silica-gel column chromatography (hexane/CS_2 = 3/2; the second brown elution following a purple C_{60} elution, R_f = 0.60) gave the title compound $C_{60}(C_6H_4\text{-Me-4})_2H_2$ as a black powder (50.7 mg, 56%). ^1H NMR (400 MHz, $CS_2/CDCl_3$): δ 2.50 (s, 6H, CH_3), 5.78 (s, 2H, $C_{60}H$), 7.42 (d, 4H, J = 8.0 Hz, C_6H_4), 8.09 (d, 4H, J = 8.0 Hz, C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $CS_2/CDCl_3$): δ 21.17 (2C, CH_3), 56.50 (2C, $C_{60}H$), 63.19 (2C, $C_{60}C_6H_4$), 127.77 (4C, C_6H_4), 130.10 (4C, C_6H_4), 134.42 (2C, C_{60}), 136.28 (2C, C_{60}), 137.16 (2C, C_6H_4), 137.20 (1C, C_{60}), 141.09 (2C, C_{60}), 141.20 (2C, C_{60}), 141.79 (2C, C_{60}), 142.34 (2C, C_{60}), 142.49 (2C, C_{60}), 142.56 (2C, C_{60}), 142.93 (1C, C_{60}), 143.13 (2C,

C_{60}), 143.69 (2C, C_{60}), 144.20 (2C, C_{60}), 144.31 (2C, C_{60}), 144.44 (2C, C_{60}), 144.79 (2C, C_{60}), 145.18 (2C, C_{60}), 145.20 (2C, C_{60}), 145.27 (2C, C_{60}), 145.56 (2C, C_6H_4), 146.06 (2C, C_{60}), 146.60 (1C, C_{60}), 147.17 (2C, C_{60}), 147.28 (2C, C_{60}), 148.00 (2C, C_{60}), 148.11 (1C, C_{60}), 148.16 (2C, C_{60}), 149.19 (2C, C_{60}), 149.67 (2C, C_{60}), 151.91 (2C, C_{60}); APCI-HRMS (-): calcd for $C_{74}H_{15}$ ($M\text{-}H^+$), 903.11738; found, 903.11504.

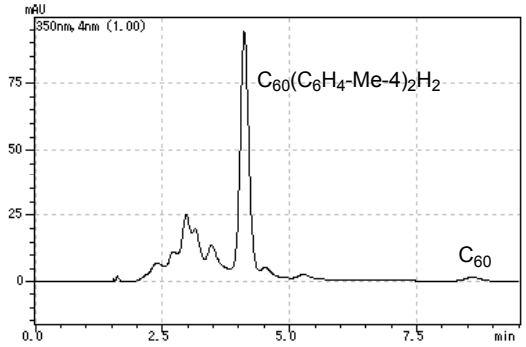

Figure S3. HPLC chart of **3 (**Buckyprep, flow rate: 2 mL/min).

1,7,11-Tris(4-methylphenyl)-1,7,10,11,24,27-hexahydro(C_{60}-I_h)[5,6]fullerene and 1,7,11-tris(4-methylphenyl)-1,7,11,24,25,27-hexahydro(C_{60}-I_h)[5,6]fullerene (4): To a mixture of C_{60} (72.0 mg, 0.10 mmol) and aluminum(III) chloride (66.7 mg, 0.50 mmol) in 1,2-dichlorobenzene (5.0 mL) was added toluene (20 mL) that was prepared to be contained water (1.8 μL, 0.10 mmol). After stirred for 30 min at 25 °C, the reaction mixture was quenched with water (0.1 mL). The crude product contained mainly the desired tris adduct **4** and poly arylated products as analyzed by HPLC (Buckyprep column, Nacalai Tesque Inc., 4.6 mm ID x 250 mm, monitored at 350 nm, eluent: toluene/2-propanol = 7/3) as shown in Figure S4. The following purification process was performed under dark conditions. The resulting dark brown solution was passed through a pad of silica gel (eluent: toluene) and the filtrate was concentrated by rotary evaporation until the volume was about 5 mL. Methanol (30 mL) was added to the brown solution and the resulting brown solid was collected by filtration.

This crude product is purified by open column chromatography (3 cm ID x 20 cm, 50 g of silica gel, eluent CS_2/hexane = 2/1, R_f = 0.52). The first pale brown fraction (ca. 100 mL) contained a small amount of a mono and a bis adduct. The following 60-mL fraction contained the desired tris adducts and the final 30-mL fraction contained a mixture of the desired tris adduct and poly arylated fullerenes. This last fraction was purified again on 50 g of silica gel (3 cm ID x 20 cm, eluent CS_2/hexane = 2/1). The first brown fraction (ca. 50 mL) was collected and combined with the second fraction of the first chromatography. The combined eluent was concentrated under vacuum until the solid just began to appear on the inside wall of the flask. Methanol (30 mL) was added to precipitate the product. The title

compound **4** (55.4 mg, 56%; a 4:1 mixture of **4a** and **4b**) was obtained by filtration as a brown powder, which was >95% pure by ^{1}H NMR analysis. The separation of the two isomers could be carried out with preparative HPLC (RP-FULLERENE, toluene/acetonitrile = 4/6, retention time: 17 min for **4a** and 19 min for **4b**). ^{1}H NMR of **4a** (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 4.90 (dd, 1H, ^5J = 3.6, ^4J = 0.92, $C_{60}H$), 5.43 (d, br, 1H, ^5J = 3.6, $C_{60}H$), 5.56 (d, 1H, br, ^4J = 0.92, $C_{60}H$), 7.15 (2H, d, ^3J = 8 Hz, C_6H_4), 7.27 (d, 2H, ^3J = 8 Hz, C_6H_4), 7.33 (d, 2H, ^3J = 8 Hz, C_6H_4), 7.55 (d, 2H, ^3J = 8 Hz, C_6H_4), 7.76 (d, 2H, ^3J = 8 Hz, C_6H_4), 7.81 (d, 2H, ^3J = 8 Hz, C_6H_4); $^{13}C\{^1H\}$ NMR of **4a** (100 MHz, $CDCl_3$): δ 20.00 (1C, CH_3), 21.17 (1C+1C, CH_3), 44.81 (1C, $C_{60}H$), 46.62 (1C, $C_{60}H$), 58.57 (1C, $C_{60}(C_6H_4)$), 58.76 (1C, $C_{60}H$), 60.74 (1C, $C_{60}(C_6H_4)$), 62.49 (1C, $C_{60}(C_6H_4)$), 126.96 (2C, C_6H_4), 127.11 (2C, C_6H_4), 127.19 (2C, C_6H_4), 129.71 (2C, C_6H_4), 129.83 (2C, C_6H_4), 129.93 (2C, C_6H_4), 137.00 (1C, C_6H_4), 137.28 (1C, C_6H_4), 137.55 (1C, C_6H_4), 137.60 (1C, C_6H_4), 138.13 (1C, C_6H_4), 140.85 (1C, C_6H_4), 142.98 (1C, C_{60}), 142.99 (1C, C_{60}), 143.15 (1C, C_{60}), 143.17 (1C, C_{60}), 143.42 (1C, C_{60}), 143.55 (1C, C_{60}), 144.03 (1C, C_{60}), 144.09 (1C, C_{60}), 144.12 (1C+1C, C_{60}), 144.17 (1C, C_{60}), 144.20 (1C, C_{60}), 144.33 (1C, C_{60}), 144.41 (1C, C_{60}), 144.84 (1C, C_{60}), 145.15 (1C, C_{60}), 145.21 (1C, C_{60}), 145.26 (1C, C_{60}), 145.42 (1C, C_{60}), 145.54 (1C, C_{60}), 145.69 (1C, C_{60}), 145.78 (1C, C_{60}), 146.54 (1C+1C, C_{60}), 146.76 (1C, C_{60}), 146.86 (1C, C_{60}), 146.95 (1C, C_{60}), 146.98 (1C, C_{60}), 147.12 (1C, C_{60}), 147.66 (1C, C_{60}), 147.76 (1C, C_{60}), 147.97 (1C+1C, C_{60}), 148.07 (1C, C_{60}), 148.14 (1C, C_{60}), 148.34 (1C+1C, C_{60}), 148.43 (1C, C_{60}), 148.46 (1C, C_{60}), 148.52 (1C, C_{60}), 148.60 (1C, C_{60}), 148.61 (1C, C_{60}), 148.63 (1C, C_{60}), 148.65 (1C, C_{60}), 148.68 (1C, C_{60}), 148.92 (1C, C_{60}), 148.94 (1C, C_{60}), 149.78 (1C, C_{60}), 152.65 (1C, C_{60}), 152.92 (1C, C_{60}), 153.18 (1C, C_{60}), 153.26 (1C, C_{60}), 153.37 (1C, C_{60}), 157.57 (1C, C_{60}); ^{1}H NMR of **4b** (500 MHz, $CDCl_3$): δ 2.37 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 4.98 (1H, dd, ^3J = 12 Hz, ^4J = 3.5 Hz, $C_{60}H$), 5.29 (1H, d, br, ^3J = 12 Hz, $C_{60}H$), 5.48 (1H, d, ^4J = 3.5 Hz, $C_{60}H$), 7.16 (2H, d, ^3J = 8 Hz, C_6H_4), 7.22 (2H, d, ^3J = 8 Hz, C_6H_4), 7.30 (2H, d, ^3J = 8 Hz, C_6H_4), 7.59 (2H, d, ^3J = 8 Hz, C_6H_4), 7.69 (2H, d, ^3J = 8 Hz, C_6H_4), 7.77 (2H, d, ^3J = 8 Hz, C_6H_4); $^{13}C\{^1H\}$ NMR of **4b** (100 MHz, $CDCl_3$): δ 21.10 (1C, CH_3), 21.16 (1C+1C, CH_3), 44.06 (1C, $C_{60}H$), 44.85 (1C, $C_{60}H$), 51.45 (1C, $C_{60}H$), 58.47 (1C, $C_{60}(C_6H_4)$), 60.46 (1C, $C_{60}(C_6H_4)$), 60.58 (1C, $C_{60}(C_6H_4)$), 126.90 (2C, C_6H_4), 127.40 (2C, C_6H_4), 127.44 (2C, C_6H_4), 129.63 (2C, C_6H_4), 129.70 (2C, C_6H_4), 129.94 (2C, C_6H_4), 137.08 (1C, C_6H_4), 137.33 (1C, C_6H_4), 137.36 (1C, C_6H_4), 137.55 (1C, C_6H_4), 137.73 (1C, C_6H_4), 137.76 (1C, C_6H_4), 141.03 (1C, C_{60}), 143.17 (1C+1C, C_{60}), 143.92 (1C, C_{60}), 144.10 (1C, C_{60}), 144.13 (1C, C_{60}), 144.14 (1C, C_{60}), 144.22 (1C, C_{60}), 144.27 (1C, C_{60}), 144.36 (1C, C_{60}), 144.38 (1C, C_{60}), 144.43 (1C, C_{60}), 144.44 (1C, C_{60}), 144.55 (1C, C_{60}), 144.74 (1C, C_{60}), 144.78 (1C, C_{60}), 144.97 (1C, C_{60}), 145.22 (1C, C_{60}), 145.38 (1C, C_{60}), 145.48 (1C, C_{60}), 146.50 (1C, C_{60}), 146.79 (1C, C_{60}), 146.85 (1C, C_{60}), 146.87 (1C, C_{60}), 146.90 (1C, C_{60}), 146.95 (1C, C_{60}), 146.96 (1C+1C, C_{60}), 147.12 (1C, C_{60}), 147.40 (1C, C_{60}), 147.71 (1C, C_{60}), 147.75 (1C, C_{60}), 147.96 (1C, C_{60}), 148.05 (1C, C_{60}), 148.09 (1C+1C, C_{60}), 148.13 (1C, C_{60}), 148.23 (1C, C_{60}), 148.28 (1C, C_{60}), 148.41 (1C, C_{60}), 148.51 (1C, C_{60}), 148.63 (1C+1C+1C, C_{60}), 148.66 (1C, C_{60}), 149.41 (1C, C_{60}),

149.43 (1C, C_{60}), 149.66 (1C, C_{60}), 150.50 (1C, C_{60}), 151.49 (1C, C_{60}), 152.16 (1C, C_{60}), 152.51 (1C, C_{60}), 156.72 (1C, C_{60}), 156.84 (1C, C_{60}); APCI-HRMS (-): calcd for $C_{81}H_{23}$ ($M\text{-}H^+$), 995.17998; found, 995.18052.

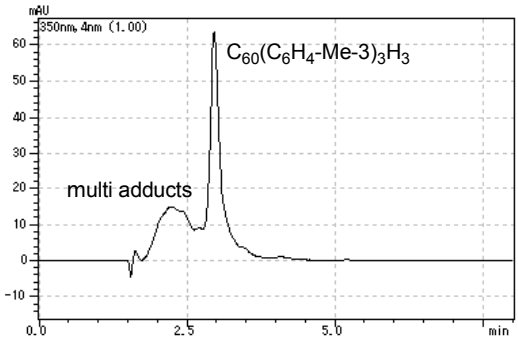

Figure S4. HPLC chart of **4 (**Buckyprep, flow rate: 2 mL/min).

A 1-g scale synthesis of 4: To a mixture of C_{60} (1.00 g, 1.39 mmol) and aluminum(III) chloride (0.923 g, 6.94 mmol) was added toluene (280 mL) that was prepared to be contained water (25.0 μL, 1.39 mmol). After stirred for 80 min at 25 °C, the reaction mixture was quenched with water (2 mL). The following purification process was performed under dark conditions. The resulting dark brown solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed by rotary evaporation. This crude product is purified by open column chromatography (6 cm ID x 25 cm, 350 g of silica gel, eluent CS_2/hexane = 2/1, R_f = 0.52). The first pale brown fraction (ca. 600 mL) contained a small amount of a mono and a bis adduct. The following 400-mL fraction contained the desired tris adducts and the final 200-mL fraction contained a mixture of the desired tris adduct and poly arylated fullerenes. This last fraction was purified again on 70 g of silica gel (3 cm ID x 20 cm, eluent CS_2/hexane = 2/1). The first brown fraction (ca. 50 mL) was collected and combined with the second fraction of the first chromatography. The combined eluent was concentrated under vacuum until the solid just began to appear on the inside wall of the flask. Methanol (200 mL) was added to precipitate the product. The title compound **4** (693 mg, 50%; a 4:1 mixture of **4a** and **4b**) was obtained by filtration as a brown powder, which was >95% pure by ^{1}H NMR analysis.

Dicarbonylchloro-{[(1,2,3,4,5-η)-6,9,12-tris(4-methylphenyl)-6,9,12,15,18-tetrahydro(C_{60}-I_h)[5,6]fulleren-1(*6H*)-yl]ruthenium (5): To a solution of $C_{60}(C_6H_4\text{-Me-}4)_3H_3$ (**4**) (20.0 mg, 0.0201 mmol) in THF (10 mL) was added a solution of KO^{t}Bu (1.0 M, 24 μL, 0.024 mmol) in THF at 0 °C. $[RuCl_2(CO)_3]_2$ (13.4 mg, 0.0261 mmol) was added to the resulting dark brown solution at 0 °C, and the mixture was stirred for 15 min. The solvent was removed under the reduced

pressure to afford a brown solid. Purification with preparative HPLC (Backyprep, eluent: toluene/2-propanol = 7/3, flow rate: 18 mL/min, retention time 11 min) gave the title compound **5** (3.64 mg, 18%) as a brown powder. ^{1}H (400 MHz, $CDCl_3$): δ 2.37 (s, 6H, $C_6H_4CH_3$), 2.43 (s, 3H, $C_6H_4CH_3$), 5.43 (s, 2H, $C_{60}H$), 7.23 (d, 4H, *J* = 7.8 Hz, Ph), 7.34 (d, 2H, *J* = 8.2 Hz, Ph), 7.68 (d, 4H, *J* = 8.2 Hz, Ph), 7.78 (d, 2H, *J* = 7.8 Hz, Ph); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.13 (2C, CH_3), 21.26 (1C, CH_3), 43.72 (2C, $C_{60}H$), 57.88 (1C, $C_{60}(C_6H_4)$), 58.02 (2C, $C_{60}(C_6H_4)$), 100.68 (2C, $C_{60}Ru$), 107.67 (2C, $C_{60}Ru$), 115.13 (1C, $C_{60}Ru$), 127.27 (4C, Ph), 127.41 (2C, Ph), 129.56 (4C, Ph), 129.65 (2C, Ph), 138.05 (2C, Ph), 138.24 (4C, Ph), 139.00 (2C, Ph), 139.77 (4C, Ph), 143.19 (2C, C_{60}), 143.76 (2C, C_{60}), 143.79 (2C, C_{60}), 143.87 (2C, C_{60}), 143.93 (2C, C_{60}), 144.02 (2C, C_{60}), 144.11 (2C, C_{60}), 144.15 (2C, C_{60}), 145.16 (2C, C_{60}), 145.41 (2C, C_{60}), 146.62 (2C, C_{60}), 147.16 (2C, C_{60}), 147.24 (2C, C_{60}), 147.46 (1C, C_{60}), 147.72 (2C, C_{60}), 148.38 (2C, C_{60}), 148.39 (2C, C_{60}), 148.43 (2C, C_{60}), 148.53 (2C, C_{60}), 148.54 (2C, C_{60}), 148.68 (2C, C_{60}), 148.78 (2C, C_{60}), 148.85 (1C, C_{60}), 150.74 (2C, C_{60}), 152.16 (2C, C_{60}), 153.37 (2C, C_{60}), 193.46 (2C, RuCO).

{[(1,2,3,4,5-η)-6,9,12-Tris(4-methylphenyl)-6,9,12,15,18-tetrahydro(C_{60}-*I*$_h$)[5,6]fulleren-1(*6H*)-yl](*η*^{5}-cyclopentadienyl)ruthenium (6): This compound was obtained by using the method described for compound **5**, except $Ru(C_5H_5)(MeCN)_3(PF_6)$ (11.3 mg, 0.0261 mmol) was used as a ruthenium source material. Purification with preparative HPLC (Backyprep, eluent: toluene/2-propanol = 7/3, flow rate: 18 mL/min, retention time 6.4 min) gave the title compound (2.56 mg, 11%) as a brown powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 6H, $C_6H_4CH_3$), 2.43 (s, 3H, $C_6H_4CH_3$), 3.86 (s, 5H, C_5H_5), 5.37 (s, 2H, $C_{60}H$), 7.17 (d, 4H, *J* = 7.8 Hz, C_6H_4), 7.28 (d, 2H, *J* = 8.2 Hz, C_6H_4), 7.72 (d, 2H, *J* = 8.2 Hz, C_6H_4), 7.74 (d, 4H, *J* = 7.8 Hz, C_6Hc_4); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 21.13 (2C+1C, CH_3), 45.19 (2C, $C_{60}H$), 58.18 (1C, $C_{60}(C_6H_4)$), 58.31 (2C, $C_{60}(C_6H_4)$), 90.32 (2C, $C_{60}Ru$), 99.25 (1C, $C_{60}Ru$), 99.41 (2C, $C_{60}Ru$), 127.62 (2C, C_6H_4), 127.64 (4C, C_6H_4), 129.56 (4C, C_6H_4), 129.65 (2C, C_6H_4), 128.59 (4C, C_6H_4), 128.71 (2C, C_6H_4), 136.91 (2C+1C, C_6H_4), 142.90 (2C, C_6H_4), 141.69 (4C, C_6H_4), 143.27 (2C, C_{60}), 143.30 (2C, C_{60}), 143.43 (2C, C_{60}), 143.51 (2C, C_{60}), 143.53 (2C, C_{60}), 144.05 (1C, C_{60}), 144.30 (2C, C_{60}), 144.41 (2C, C_{60}), 145.93 (2C, C_{60}), 147.20 (2C, C_{60}), 147.20 (2C, C_{60}), 147.30 (2C, C_{60}), 148.21 (1C, C_{60}), 148.23 (2C, C_{60}), 148.24 (2C, C_{60}), 148.37 (2C, C_{60}), 148.39 (2C, C_{60}), 148.41 (2C, C_{60}), 148.39 (2C, C_{60}), 148.41 (2C, C_{60}), 148.49 (2C, C_{60}), 149.78 (2C, C_{60}), 151.69 (2C, C_{60}), 153.42 (2C, C_{60}), 153.75 (2C, C_{60}), 154.49 (2C, C_{60}); APCI-HRMS (-): calcd for $C_{86}H_{28}Ru$ ($M\text{-}H^+$), 1161.11562; found, 1161.11849.

Synthesis of 1,7,11-triphenyl-1,7,11,24,25,27-hexahydro(C_{60}-*I*$_h$)[5,6]fullerene (7): To a mixture of C_{60} (72.0 mg, 0.10 mmol) and aluminum(III) chloride (66.7 mg, 0.50 mmol) in 1,2-dichlorobenzene (5.0 mL) was added benzene (20 mL) that was prepared to be contained water (1.8 μL, 0.10 mmol). After stirred for 30 min at 25 °C, the reaction mixture was

quenched with water (0.1 mL). The following purification process was performed under dark conditions. The resulting dark brown solution was passed through a pad of silica gel (eluent: toluene) and the filtrate was heated at 80 °C for 1 h to give a single isomer. The volatiles were removed by rotary evaporation followed by addition of methanol to precipitate the crude product of **7**. Purification with silica-gel column chromatography (eluent: CS_2/hexane = 2/1; R_f = 0.36) was carried out twice as described in the synthesis of compound **4** to remove multi-adducts that elute just after the desired tris adducts. The fraction containing **7** was concentrated on a rotary evaporator until the solid just began to appear on the inside wall of a flask. Methanol (30 mL) was added to the solution to precipitate the product. The title compound (49.1 mg, 51 %) was obtained by filtration as a brown powder, which was >95% pure by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.00 (1H, dd, ^3J = 12 Hz, ^4J = 3.7 Hz, $C_{60}H$), 5.33 (1H, d, br, ^3J = 12 Hz, $C_{60}H$), 5.51 (1H, d, ^4J = 3.7 Hz, $C_{60}H$), 7.31–7.51 (6H, m, Ph), 7.69 (2H, quasi-dd, ^3J = 8.3 Hz, ^4J = 1.8 Hz, C_6H_4), 7.80 (2H, quasi-dd, ^3J = 8.3 Hz, ^4J = 1.8 Hz, C_6H_4), 7.89 (2H, quasi-dd, ^3J = 8.3 Hz, ^4J = 1.8 Hz, C_6H_4); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 44.10 (1C, $C_{60}H$), 44.90 (1C, $C_{60}H$), 51.46 (1C, $C_{60}H$), 58.69 (1C, $C_{60}Ph$), 60.69 (1C, $C_{60}Ph$), 60.84 (1C, $C_{60}Ph$), 127.01 (2C, C_6H_5), 127.48 (2C, C_6H_5), 127.52 (2C, C_6H_5), 127.59 (1C, C_6H_5), 127.65 (1C, C_6H_5), 127.71 (1C, C_6H_5), 128.93 (2C, C_6H_5), 129.02 (2C, C_6H_5), 129.25 (2C, C_6H_5), 139.88 (1C, C_6H_5), 140.56 (1C, C_6H_5), 140.65 (1C, C_6H_5), 141.02 (1C, C_{60}), 143.18 (1C+1C, C_{60}), 143.82 (1C, C_{60}), 144.13 (1C, C_{60}), 144.17 (1C, C_{60}), 144.21 (1C, C_{60}), 144.24 (1C, C_{60}), 144.31 (1C+1C, C_{60}), 144.43 (1C, C_{60}), 144.44 (1C, C_{60}), 144.51 (1C, C_{60}), 144.56 (1C, C_{60}), 144.65 (1C, C_{60}), 144.75 (1C, C_{60}), 144.89 (1C, C_{60}), 145.19 (1C, C_{60}), 145.33 (1C, C_{60}), 145.47 (1C, C_{60}), 146.50 (1C, C_{60}), 146.62 (1C, C_{60}), 146.78 (1C, C_{60}), 146.85 (1C, C_{60}), 146.88 (1C, C_{60}), 146.96 (1C, C_{60}), 147.12 (1C, C_{60}), 147.33 (1C, C_{60}), 147.44 (1C, C_{60}), 147.77 (1C, C_{60}), 147.99 (1C, C_{60}), 148.05 (1C, C_{60}), 148.10 (1C, C_{60}), 148.11 (1C, C_{60}), 148.14 (1C, C_{60}), 148.25 (1C, C_{60}), 148.29 (1C, C_{60}), 148.40 (1C, C_{60}), 148.42 (1C, C_{60}), 148.54 (1C, C_{60}), 148.65 (1C+1C, C_{60}), 148.66 (1C+1C, C_{60}), 148.70 (1C, C_{60}), 149.22 (1C, C_{60}), 149.40 (1C, C_{60}) 149.77 (1C, C_{60}), 150.50 (1C, C_{60}), 151.57 (1C, C_{60}), 152.00 (1C, C_{60}), 152.55 (1C, C_{60}), 156.54 (1C, C_{60}), 156.61 (1C, C_{60}); APCI-HRMS (-): calcd for $C_{78}H_{17}$ (M-H$^+$), 953.13303; found, 953.12872.

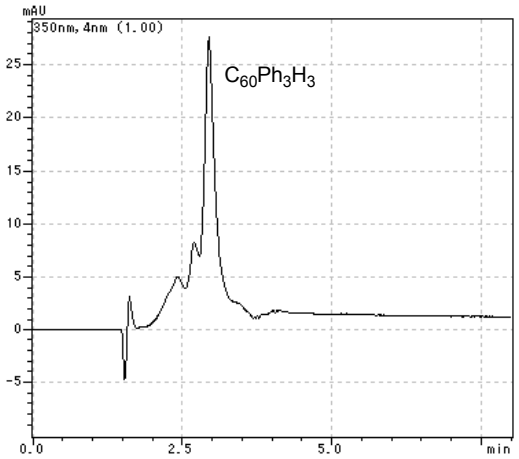

Figure S5. HPLC chart of **7** (Buckyprep, flow rate: 2 mL/min).

1,7,11-Tris(4-(1,1-dimethylethyl)phenyl)-1,7,11,24,25,27-hexahydro(C_{60}-I_h)[5,6]fullerene (8): This compound was obtained by using the method described for compound **7**, except *tert*-butylbenzene (20 mL) was used as a reactant and the time allowed for the reaction was 20 min. Silica-gel column chromatography (eluent: CS_2/hexane = 2/1; the first brown elution, R_f = 0.46) was carried out as described above to remove multi-adducts that elute just after the desired tris adduct. The fraction containing the desired product was concentrated on a rotary evaporator until the solid just begins to appear on the inside wall of a flask. Methanol (30 mL) was added to the solution to precipitate the product. The title compound **8** (18.9 mg, 17 %) was obtained by filtration as a brown powder, which was >95% pure by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.33 (s, 9H, CH_3), 1.36 (s, 9H, CH_3), 1.37 (s, 9H, CH_3), 4.98 (1H, dd, ^3J = 12 Hz, ^4J = 3.4 Hz, $C_{60}H$), 5.29 (1H, d, br, ^3J = 12 Hz, $C_{60}H$), 5.48 (1H, d, ^5J = 3.4 Hz, $C_{60}H$), 7.32 (2H, d, ^3J = 8.6 Hz, C_6H_4), 7.41 (2H, d, ^3J = 8.6 Hz, C_6H_4), 7.50 (2H, d, ^3J = 8.6 Hz, C_6H_4), 7.59 (2H, d, ^3J = 8.6 Hz, C_6H_4), 7.71 (2H, d, ^3J = 8.6 Hz, C_6H_4), 7.79 (2H, d, ^3J = 8.6 Hz, C_6H_4); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 31.31 (3C, CH_3), 31.35 (3C, CH_3), 31.37 (3C, CH_3), 34.50 (1C, *C*CH_3), 34.57 (1C, *C*CH_3), 34.60 (1C, *C*CH_3), 44.11 (1C, $C_{60}H$), 44.91 (1C, $C_{60}H$), 51.46 (1C, $C_{60}H$), 58.42 (1C, $C_{60}(C_6H_4)$), 60.42 (1C, $C_{60}(C_6H_4)$), 60.58 (1C, $C_{60}(C_6H_4)$), 126.68 (2C, C_6H_4), 127.27 (2C, C_6H_4), 127.34 (2C, C_6H_4), 126.68 (2C, C_6H_4), 127.27 (2C, C_6H_4), 127.34 (2C, C_6H_4), 137.01 (1C, C_6H_4), 137.68 (1C, C_6H_4), 137.74 (1C, C_6H_4), 141.03 (1C, C_{60}), 143.18 (1C+1C, C_{60}), 143.92 (1C, C_{60}), 144.13 (1C+1C, C_{60}), 144.18 (1C, C_{60}), 144.27 (1C, C_{60}), 144.30 (1C, C_{60}), 144.40 (1C, C_{60}), 144.41 (1C, C_{60}), 144.45 (1C, C_{60}), 144.56 (1C, C_{60}), 144.66 (1C, C_{60}), 144.92 (1C, C_{60}), 144.99 (1C, C_{60}), 145.22 (1C, C_{60}), 145.36 (1C, C_{60}), 145.42 (1C, C_{60}), 145.60 (1C, C_{60}), 146.52 (1C, C_{60}), 146.81 (1C, C_{60}), 146.84 (1C, C_{60}), 146.87 (1C, C_{60}), 146.89 (1C, C_{60}), 146.94 (1C, C_{60}), 146.97 (1C, C_{60}), 147.12 (1C, C_{60}), 147.41 (1C, C_{60}), 147.76 (1C, C_{60}), 147.78 (1C, C_{60}), 147.78 (1C, C_{60}), 148.07 (1C, C_{60}), 148.10 (1C+1C, C_{60}), 148.11 (1C, C_{60}), 148.13 (1C, C_{60}), 148.25 (1C, C_{60}), 148.29 (1C, C_{60}), 148.44 (1C, C_{60}), 148.53 (1C, C_{60}), 148.63 (1C, C_{60}), 148.65 (1C+1C, C_{60}), 148.68 (1C, C_{60}), 149.40 (1C, C_{60}), 149.45 (1C, C_{60}), 149.93 (1C, C_{60}), 150.51 (1C, C_6H_4), 150.56 (1C,

C_6H_4), 150.70 (1C, C_6H_4), 150.72 (1C, C_{60}), 151.62 (1C, C_{60}), 152.25 (1C, C_{60}), 152.52 (1C, C_{60}), 156.70 (1C, C_{60}), 156.86 (1C, C_{60}); APCI-HRMS (-): calcd for $C_{81}H_{23}$ ($M\text{-}H^+$), 1121.32083; found, 1121.31870.

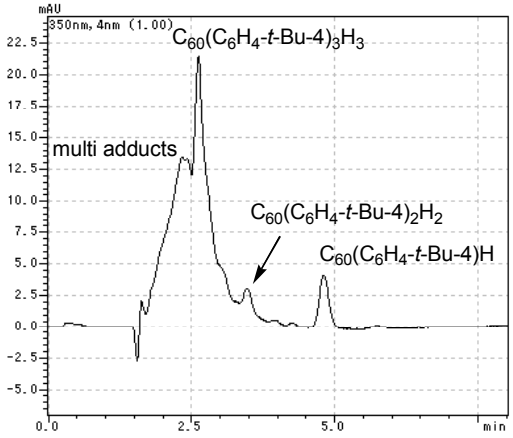

Figure S6. HPLC chart of **8 (**Buckyprep, flow rate: 2 mL/min).

1,7,11-Tris(3,4-dimethylphenyl)-1,7,11,24,25,27-hexahydro(C_{60}-I_h)[5,6]fullerene (9): This compound was obtained by using the method described for compound **7**, except 1,2-dimethylbenzene (212 mg, 2.0 mmol) was used as a reactant and the time allowed for the reaction was 25 min. Purification with silica-gel column chromatography (eluent: CS_2/hexane = 2/1; R_f = 0.48) was carried out twice as described in the synthesis of compound **4** to remove multi-adducts that elute just after the desired tris adduct. The fraction was concentrated on a rotary evaporator until the solid just begins to appear on the inside wall of a flask. Methanol (30 mL) was added to the solution to precipitate the product. The title compound **9** (32.5 mg, 31 %) was obtained by filtration as a brown powder, which was >95% pure by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.16 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 4.99 (dd, 1H, ^3J = 12 Hz, ^5J = 4.6 Hz, C_{60}H), 5.28 (d, 1H, ^3J = 12Hz, C_{60}H), 5.47 (d, 1H, ^5J = 4.6 Hz, C_{60}H), 7.14 (d, 1H, ^3J = 7.8 Hz, Ph), 7.19 (d, 1H, ^3J = 7.8 Hz, C_6H_3), 7.26 (d, 1H, ^3J = 7.8 Hz, C_6H_3), 7.44 (d, 1H, ^4J = 1.8 Hz, C_6H_3), 7.50 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.8 Hz, C_6H_3), 7.52 (d, 1H, ^4J = 1.8 Hz, C_6H_3), 7.57 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.8 Hz, C_6H_3), 7.61 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.8 Hz, C_6H_3),7.62 (d, 1H, ^4J = 1.8 Hz, C_6H_3); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 19.41 (1C, CH_3), 19.44 (1C, CH_3), 19.50 (1C, CH_3), 19.72 (1C, CH_3), 19.78 (1C, CH_3), 20.10 (1C, CH_3), 44.07 (1C, C_{60}H), 44.90 (1C, C_{60}H), 51.53 (1C, C_{60}H), 58.52 (1C, $C_{60}C_6H_3$), 60.49 (1C, $C_{60}C_6H_3$), 60.57 (1C, $C_{60}C_6H_3$), 124.42 (1C, C_6H_3), 124.83 (1C, C_6H_3), 124.97 (1C, C_6H_3), 128.14 (1C, C_6H_3), 129.01 (1C+1C, C_6H_3), 130.12 (1C, C_6H_3), 130.17 (1C, C_6H_3), 136.01 (1C, C_6H_3), 136.06 (1C, C_6H_3), 136.27 (1C, C_6H_3), 137.25 (1C, C_6H_3), 137.35 (1C, C_6H_3), 137.66 (1C, C_6H_3), 137.67 (1C, C_6H_3), 138.17 (1C, C_6H_3), 138.25 (1C, C_6H_3), 141.06 (1C, C_{60}), 146.17 (1C, C_{60}), 143.18 (1C, C_{60}), 143.92 (1C, C_{60}),

144.11 (1C+1C, C_{60}), 144.17 (1C, C_{60}), 144.24 (1C, C_{60}), 144.30 (1C, C_{60}), 144.38 (1C+1C, C_{60}), 144.42 (1C, C_{60}), 144.50 (1C, C_{60}), 144.56 (1C, C_{60}), 144.91 (1C, C_{60}), 144.99 (1C, C_{60}), 145.02 (1C, C_{60}), 145.36 (1C, C_{60}), 145.45 (1C, C_{60}), 145.61 (1C, C_{60}), 146.52 (1C, C_{60}), 146.81 (1C, C_{60}), 146.88 (1C, C_{60}), 146.91 (1C, C_{60}), 146.93 (1C, C_{60}), 146.96 (1C, C_{60}), 146.99 (1C, C_{60}), 147.12 (1C, C_{60}), 147.44 (1C, C_{60}), 147.75 (1C, C_{60}), 147.88 (1C, C_{60}), 147.95 (1C, C_{60}), 148.06 (1C, C_{60}), 148.09 (1C+1C, C_{60}), 148.13 (1C, C_{60}), 148.23 (1C, C_{60}), 148.29 (1C, C_{60}), 148.43 (1C, C_{60}), 148.51 (1C, C_{60}), 148.61 (1C+1C, C_{60}), 148.63 (1C+1C, C_{60}), 148.66 (1C, C_{60}), 149.30 (1C, C_{60}), 149.43 (1C, C_{60}), 149.82 (1C, C_{60}), 150.46 (1C, C_{60}), 151.47 (1C, C_{60}), 152.28 (1C, C_{60}), 152.43 (1C, C_{60}), 156.82 (1C, C_{60}), 156.98 (1C, C_{60}); APCI-HRMS (-): calcd for $C_{84}H_{29}$ ($M\text{-}H^+$), 1037.22693; found, 1037.22977.

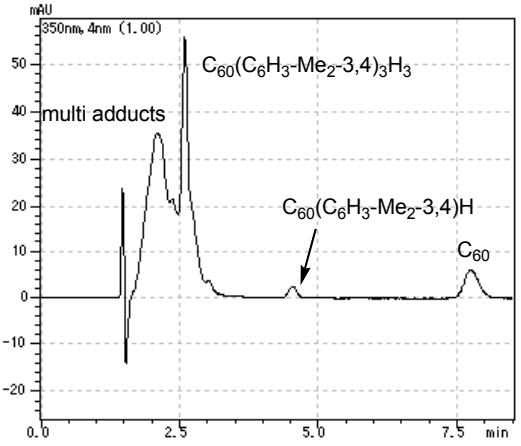

Figure S7. HPLC chart of **9** (Buckyprep, flow rate: 2 mL/min).

1,7,11-Tris(4-phenylphenyl)-1,7,11,24,25,27-hexahydro(C_{60}-I_h)[5,6]fullerene (10): This compound was obtained by using the method described for compound **7**, except biphenyl (1.54 g, 10.0 mmol) was used as a reactant and the time allowed for the reaction was 20 min. Purification with silica-gel column chromatography (eluent: CS_2/hexane = 2/1; R_f = 0.26) was carried out twice as described in the synthesis of compound **4** to remove multi-adducts that elute just after the desired tris adduct. The fraction containing the desired product was concentrated on a rotary evaporator until the solid just begins to appear on the inside wall of a flask. Methanol (30 mL) was added to the solution to precipitate the product. The title compound **10** (32.3 mg, 27 %) was obtained by filtration as a brown powder, which was >95% pure by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.10 (1H, dd, ^3J = 12 Hz, ^4J = 4.0 Hz, $C_{60}H$), 5.39 (1H, d, br, ^3J = 12 Hz, $C_{60}H$), 5.58 (1H, d, ^4J = 4.0Hz, $C_{60}H$), 7.35–7.73 (m, 24H, Ph), 7.81 (d, 1H, J = 8.6 Hz, Ph), 7.91 (d, J = 8.6 Hz, Ph), 7.98 (d, J = 8.6 Hz, Ph); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 44.17 (1C, $C_{60}H$), 44.98 (1C, $C_{60}H$), 51.58 (1C, $C_{60}H$), 60.52 (1C,

$C_{60}C_6H_4$), 60.65 (1C, $C_{60}C_6H_4$), 60.84 (1C, $C_{60}C_6H_4$), 127.12 (2C, Ph), 127.14 (2C, Ph), 127.18 (2C, Ph), 127.49 (2C, Ph), 127.52 (1C, Ph), 127.54 (1C, Ph), 127.56 (1C, Ph), 127.79 (2C, Ph), 127.97 (2C, Ph), 128.03 (2C, Ph), 128.06 (2C, Ph), 128.09 (2C, Ph), 128.85 (2C, Ph), 128.88 (2C, Ph), 128.90 (2C, Ph), 139.00 (1C, Ph), 139.64 (1C, Ph), 139.69 (1C, Ph), 140.41 (1C, Ph), 140.45 (1C, Ph), 140.53 (1C, Ph), 140.67 (1C, Ph), 140.68 (1C, Ph), 140.88 (1C, Ph), 141.21 (1C, C_{60}), 143.27 (1C+1C, C_{60}), 143.87 (1C, C_{60}), 144.20 (1C, C_{60}), 144.24 (1C, C_{60}), 144.28 (1C+1C, C_{60}), 144.39 (1C, C_{60}), 144.42 (1C+1C, C_{60}), 144.50 (1C, C_{60}), 144.52 (1C, C_{60}), 144.58 (1C, C_{60}), 144.66 (1C, C_{60}), 144.82 (1C, C_{60}), 144.84 (1C+1C, C_{60}), 144.96 (1C, C_{60}), 145.23 (1C, C_{60}), 145.39 (1C, C_{60}), 145.50 (1C, C_{60}), 146.56 (1C, C_{60}), 146.62 (1C, C_{60}), 146.85 (1C, C_{60}), 146.91 (1C, C_{60}), 146.94 (1C, C_{60}), 147.02 (1C, C_{60}), 147.19 (1C, C_{60}), 147.40 (1C, C_{60}), 147.45 (1C, C_{60}), 147.85 (1C, C_{60}), 148.07 (1C, C_{60}), 148.12 (1C, C_{60}), 148.19 (1C+1C, C_{60}), 148.21 (1C, C_{60}), 148.31 (1C, C_{60}), 148.36 (1C, C_{60}), 148.49 (1C, C_{60}), 148.61 (1C, C_{60}), 148.72 (1C+1C, C_{60}), 148.73 (1C+1C, C_{60}), 148.76 (1C, C_{60}), 149.16 (1C, C_{60}), 149.50 (1C, C_{60}), 149.82 (1C, C_{60}), 150.60 (1C, C_{60}), 151.74 (1C, C_{60}), 152.07 (1C, C_{60}), 152.63 (1C, C_{60}), 156.60 (1C, C_{60}); APCI-HRMS (-): calcd for $C_{96}H_{29}$ ($M\text{-}H^+$), 1181.22693; found, 1181.23222.

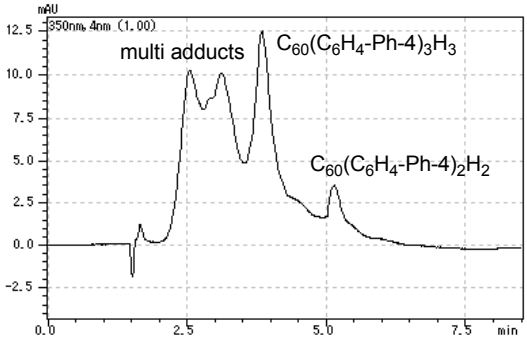

Figure S8. HPLC chart of **10 (**Buckyprep, flow rate: 2 mL/min).

7-(Methoxydimethylsilylmethyl)-1,11-bis(4-methylphenyl)-1,7,11,24,25,27-hexahydro(C_{60}-*I*$_h$)[5,6]fullerene (12): To a mixture of $C_{60}(CH_2SiO^iPrMe_2)H$ (**11**) (85.2 mg, 0.10 mmol) and aluminum(III) chloride (66.7 mg, 0.50 mmol) in 1,2-dichlorobenzene (5.0 mL) was added toluene (20 mL). After stirred for 70 min at 25 °C, the reaction mixture was quenched with methanol (1 mL). The resulting dark brown solution was passed through a pad of silica gel (eluent: toluene) and the volatiles were removed by rotary evaporation. Purification was carried out with silica-gel column chromatography (eluent: toluene/hexane = 3/1 the first brown elution, R_f = 0.46) as described in the synthesis of compound **4**. The title compound was obtained as a brown powder containing regioisomers **12a** and **12b** (57.2 mg, 57%). The separation of the two isomers could be carried out with preparative HPLC (RP-FULLERENE, toluene/acetonitrile = 4/6, retention time: 17 min for one isomer and 19 min for another

isomer). ^{1}H NMR for one isomer (500 MHz, $CS_2/CDCl_3$): δ 0.221 (s, 3H, $SiCH_3$), 0.247 (s, 3H, $SiCH_3$), 2.35 (d, 1H, J = 14 Hz, CH_2Si), 2.42 (s, 3H, $C_6H_4CH_3$), 2.43 (s, 3H, $C_6H_4CH_3$), 2.44 (d, 1H, ^2J = 14 Hz, CH_2Si), 3.44 (s, 2H, OCH_3), 4.99 (dd, 1H, ^3J = 12 Hz, ^5J = 4.0 Hz, $C_{60}H$), 5.27 (d, 1H, ^3J = 12 Hz, $C_{60}H$), 5.42 (d, 1H, ^5J = 4.0 Hz, $C_{60}H$), 7.32 (quasi-d, 2H+2H, J = 7 Hz, C_6H_4), 7.80 (d, 2H, J = 8 Hz, C_6H_4), 7.82 (d, 2H, J = 8 Hz, C_6H_4); ^{1}H NMR for another isomer (500 MHz, $CS_2/CDCl_3$); δ 0.236 (s, 3H, $SiCH_3$), 0.265 (s, 3H, $SiCH_3$), 2.35 (d, 1H, J = 14 Hz, CH_2Si), 2.41 (s, 3H, $C_6H_4CH_3$), 2.42 (m, 3H+1H, $C_6H_4CH_3$, CH_2Si), 3.47 (s, 2H, OCH_3), 4.94 (dd, 1H, ^3J = 12 Hz, ^5J = 4 Hz, $C_{60}H$), 5.23 (d, 1H, ^3J = 12 Hz, $C_{60}H$), 5.40 (d, 1H, ^5J = 4 Hz, $C_{60}H$), 7.29 (quasi-d, 2H+2H, J = 7 Hz, C_6H_4), 7.77–7.79 (d, 2H, J = 8 Hz, C_6H_4), 7.80 (d, 2H, J = 8 Hz, C_6H_4); APCI-HRMS: m/z calcd for $C_{78}H_{27}OSi$ [M-H$^+$], 1007.18312, found, 1007.18533.

X-ray Crystallographic Analysis.

A single crystal of **3** suitable for the X-ray diffraction study was mounted on a RIGAKU RAXIS-RAPID II diffractometer for data collection using MoKα (graphite monochromated, λ = 0.71069) radiation. The ORTEP diagram is shown in Figure S9. The selected bond lengths and angles are listed in Table S1. Crystal data and data statistics are summarized in Table S2. The structure of **3** was solved by the directed method (SHELXS-97).[S2] The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares method, using SHELXL-97.[S3] Hydrogen atoms were placed at calculated positions and refined with riding mode on their corresponding carbon atoms. In the subsequent refinement, the function $\sum\omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR2 = [\sum\omega(F_o^2 - F_c^2)^2 / \sum(\omega F_o^4)]^{1/2}$.

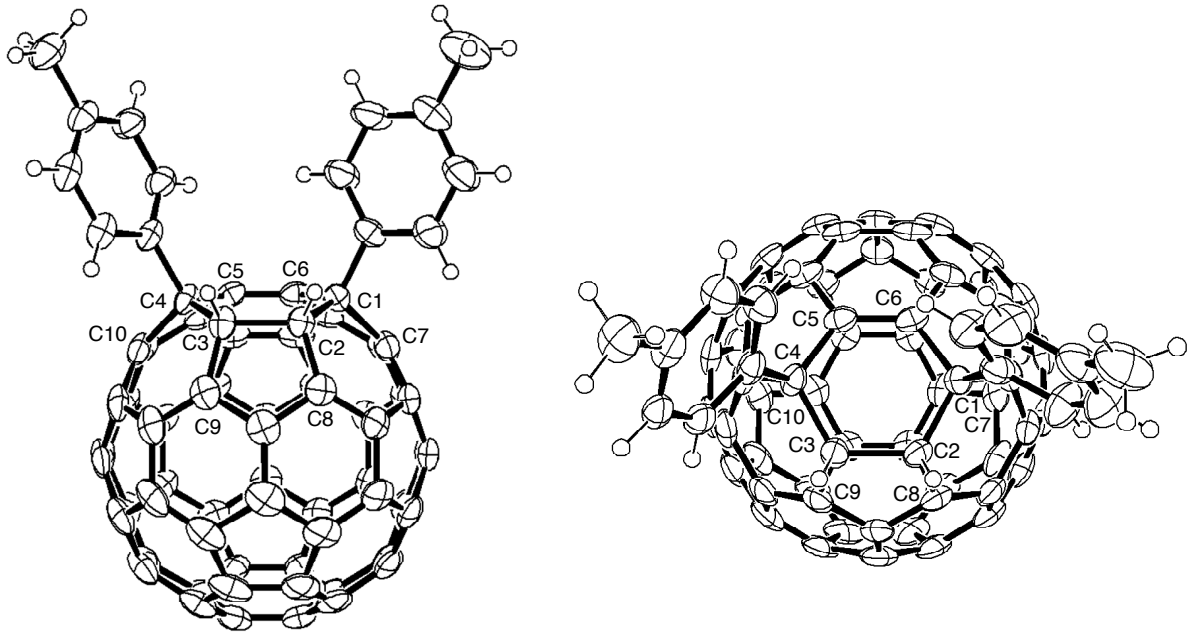

Figure S9. The ORTEP drawing of **3** with 30% probability level ellipsoids.

Table S1. Selected bond lengths (Å) and angles (°).

C1-C2	1.595(4)	C1-C2-C3	118.6(2)
C2-C3	1.594(4)	C1-C2-C8	113.8(3)
C3-C4	1.604(4)	C3-C2-C8	104.9(3)
C4-C5	1.524(4)	C2-C1-C6	114.1(2)
C5-C6	1.376(5)	C6-C1-C7	99.0(2)
C2-C8	1.495(5)	C2-C1-C7	113.2(3)
C1-C7	1.553(5)	C3-C4-C5	113.0(2)
C4-C10	1.544(5)	C5-C4-C10	99.5(3)

Table S2. Crystal data and data statistics of **3**.

formula	$C_{74}H_{16}$
crystal system	trigonal
space group	*R*3*c* (No. 161)
R, *R*w	0.077, 0.2142
*R*1, w*R*2 (all data)	0.082, 0.2212
GOF on F^2	1.092
a, Å	32.427
b, Å	32.427
c, Å	19.412
α, deg	90
β, deg	90
γ, deg	120
Z	6
T, K	180(2)
crystal size, mm	0.60, 0.20, 0.10
D_{calcd}, g/cm^{-3}	1.53
no. refl. measured (Total)	8774
no. refl. measured (Uniq)	7934
no. parameters	668
Δ, eÅ^{-3}	0.844, -0.352

References.

[S1] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem*. **1978**, *43*, 2923–2925.

[S2] G. M. Sheldrick, Program for the Solution of Crystal Structures; University of Göttingen, Germany, **1997**.

[S3] Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Götingen, Germany, **1998**.