

## **Supporting Information**

### **Methanofullerenes, C<sub>60</sub>(CH<sub>2</sub>)<sub>n</sub> (n = 1, 2, 3), as building blocks for high-performance acceptors used in organic solar cells**

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## 1. General characterization

All reagents were purchased from Alfa Aesar Co., Aladdin Co., Acros Co. and other commercial suppliers. NMR spectra were measured with a Bruker Avance-400, a Bruker Avance-500, or a Bruker Avance-600 spectrometer. MALDI-TOF mass spectra and high resolution ESI mass spectra were measured on a Bruker Apex IV FTMS spectrometer. HPLC experiments were performed on a Gilson Analytical HPLC System equipped with a UV detector and a COSMOSIL Buckyprep packed column (Nacalai Tesque, 4.6 mm I.D.  $\times$  250 mm) using toluene as eluent (1 mL/min). Absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. Cyclic voltammetry (CV) was conducted on a Shanghai Chenhua CHI620D voltammetric analyzer. All measurements were carried out in a one-compartment cell under Ar gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag/Ag<sup>+</sup> reference electrode. Measurements were performed in ODCB/CH<sub>3</sub>CN (9:1) solution containing tetrabutylammonium hexafluorophosphate (0.1 M) as a supporting electrolyte at 25 °C (scan rate 0.1 V/s). All potentials were corrected against Fc/Fc<sup>+</sup>.

## 2. Device fabrication and measurements

### Solar cells

Patterned ITO glass with a sheet resistance of 15  $\Omega$  sq<sup>-1</sup> was ultrasonically cleaned using detergent, distilled water, acetone, isopropanol sequentially and then given UV-ozone treatment. A 30 nm thick poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate (PEDOT:PSS, Clevios™ P VP Al 4083) layer was formed on ITO substrates by spin coating an aqueous dispersion onto ITO glass (4000 rpm for 30 s). PEDOT:PSS coated substrates were dried at 150 °C for 10 min. A P3HT:fullerene (w/w, 1:0.6) blend in ODCB (24 mg/mL) was spin-coated onto PEDOT:PSS layer (1200 rpm for 60 s). Then the films were annealed at 150 °C for 10 min (90 °C for P3HT:OQTMF film). The thicknesses of the active layers (~100 nm) were measured

by a KLA Tencor D-120 profilometer. Finally, Ca (~10 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca.  $10^{-4}$  Pa). The effective area for the devices is 4 mm<sup>2</sup>. *J-V* curves were measured with a computerized Keithley 2420 SourceMeter. Device characterization was done in air using a Xenon-lamp-based solar simulator (Newport, 91159A, AM 1.5G, 100 mW/cm<sup>2</sup>). Solar simulator illumination intensity was determined using a monocrystalline silicon cell (Oriel 91150, 2 × 2 cm) calibrated by NREL. The external quantum efficiency (EQE) was measured using a QE-R3011 measurement system (Enli Technology, Inc.).

### **Electron-only devices**

The structure for electron-only devices is Al/active layer/Ca/Al. Al (~80 nm) was firstly evaporated onto a glass substrate. A P3HT:fullerene (w/w, 1:0.6) blend in ODCB (24 mg/mL) was spin-coated onto Al (1200 rpm for 60 s). The films were annealed at 150 °C for 10 min (90 °C for P3HT:OQTMF film). Ca (~5 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca.  $10^{-4}$  Pa). *J-V* curves were measured using a computerized Keithley 2420 SourceMeter in the dark.

## **3. Synthetic procedures and spectral data**

**Di-ter-butyl-2-bromomalonate.** To a solution of di-tert-butyl malonate (3.00 g, 13.9 mmol) in anhydrous THF (200 mL) was added DBU (2.11 g, 13.9 mmol) at 0 °C under N<sub>2</sub>. The mixture was stirred at room temperature for 1 h and then cooled to -78 °C. To the solution was added CBr<sub>4</sub> (7.93 g, 23.9 mmol). The mixture was stirred at -78 °C for 3 h and quenched with saturated aqueous NH<sub>4</sub>Cl. Hexane was added to extract the product. The organic layer was collected and washed with brine. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> twice. The combined organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent, the crude product was purified through a silica gel column with ether/hexane (1:8) to give

di-ter-butyl-2-bromomalonate (3.12 g, 76%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 4.66 (s, 1H, *CH*), 1.49 (s, 18H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 163.55, 82.79, 45.59, 27.64.

**Compound 1.** To a solution of  $\text{C}_{60}$  (1.00 g, 1.39 mmol) and di-ter-butyl-2-bromomalonate (410 mg, 1.39 mmol) in ODCB (100 mL) was added DBU (212 mg, 1.39 mmol). The mixture was stirred at room temperature for 1 h. The solution was directly submitted to a silica gel column with  $\text{CS}_2$  as the eluent. The major purple-red band was collected to give compound **1** (856 mg, 66%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.70 (s, 18H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 160.59, 143.87, 143.48, 143.33, 143.25, 142.90, 142.79, 142.62, 141.99, 141.20, 141.11, 141.09, 140.35, 140.07, 139.00, 137.05, 82.83, 70.36, 52.29, 26.26. ESI-HRMS (+):  $\text{C}_{71}\text{H}_{18}\text{O}_4$  [ $\text{M}^+$ ] calc. 934.1205, found 934.1211.

**Compound 2.** A solution of compound **1** (1.50 g, 1.61 mmol) in ODCB (100 mL) was heated to reflux for 6 h. The solution was cooled to room temperature and poured into hexane. The precipitate was collected and dried under vacuum overnight to give compound **2** (1.25 g, 100%).  $^1\text{H}$  NMR (400 MHz,  $\text{ODCB-d}_4/\text{THF-d}_8$ ):  $\delta$  (ppm) 10.91 (s, 1H, *COOH*), 4.97 (s, 1H, *CH*).  $^{13}\text{C}$  NMR (100 MHz,  $\text{ODCB-d}_4/\text{THF-d}_8$ ):  $\delta$  (ppm) 167.51, 149.90, 147.61, 146.58, 146.10, 145.91, 145.86, 145.83, 145.75, 145.58, 145.47, 145.37, 145.35, 145.28, 145.16, 144.99, 144.69, 144.46, 143.98, 143.80, 143.70, 143.64, 143.52, 143.28, 142.94, 142.85, 141.75, 141.53, 141.49, 137.21, 72.54, 40.62. ESI-HRMS (-):  $\text{C}_{62}\text{HO}_2$  [ $\text{M} - \text{H}^+$ ] calc. 776.9977, found 776.9983.

**1,2-Dihydromethano[60]fullerene ( $\text{C}_{60}\text{CH}_2$ ).** To a suspension of compound **2** (500 mg, 0.64 mmol) in ODCB (100 mL) were added 1,10-phenanthroline (116 mg, 0.64 mmol) and  $\text{Ag}_2\text{CO}_3$  (88 mg, 0.32 mmol). The mixture was heated to reflux and irradiated by four lamps (13 W) for 8 h. The reaction mixture was cooled to room temperature and poured into methanol. The crude product was collected by filtration and purified through a silica gel column with hexane/ $\text{CS}_2$  (1:1) as the eluent. The first

purple-red band was collected to give C<sub>60</sub>CH<sub>2</sub> (210 mg, 45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>): δ (ppm) 3.92 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, ODCB-d<sub>4</sub>/CDCl<sub>3</sub>): δ (ppm) 150.81, 146.44, 145.91, 145.82, 145.52, 145.45, 145.08, 144.96, 144.45, 143.86, 143.72, 143.55, 142.94, 141.69, 137.46, 72.48, 28.91. MALDI-TOF-MS (+) for C<sub>61</sub>H<sub>2</sub> [M<sup>+</sup>]: 734.04.

**Compound 3.** To a solution of C<sub>60</sub> (2.00 g, 2.78 mmol) and di-ter-butyl-2-bromomalonate (1.64 g, 5.56 mmol) in ODCB (135 mL) was added DBU (846 mg, 5.56 mmol). The mixture was stirred at room temperature for 1.5 h. The solution was directly submitted to a silica gel column with toluene/CS<sub>2</sub> (1:1) as the eluent. The major brown-red band was collected to give compound **3** (2.20 g, 69%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 1.55-1.71 (m, 36H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 161.55, 161.51, 161.49, 161.44, 161.41, 161.38, 147.07, 146.99, 146.35, 146.15, 146.09, 145.84, 145.79, 145.57, 145.48, 145.42, 145.39, 145.35, 145.33, 145.25, 145.20, 145.01, 144.86, 144.67, 144.52, 144.44, 144.35, 144.28, 144.23, 144.16, 144.07, 144.01, 143.90, 143.80, 143.65, 143.57, 143.54, 143.34, 143.11, 143.07, 142.98, 142.87, 142.79, 142.74, 142.66, 142.45, 142.34, 142.24, 142.20, 142.11, 142.06, 141.93, 141.81, 141.62, 141.59, 141.41, 141.23, 141.10, 141.05, 141.00, 140.91, 140.84, 140.70, 140.65, 140.62, 140.59, 140.45, 139.85, 139.64, 139.33, 137.96, 137.78, 137.57, 137.49, 137.43, 137.27, 134.61, 83.58, 83.49, 83.46, 83.44, 83.42, 83.30, 71.36, 71.20, 70.90, 70.66, 70.35, 69.99, 54.48, 52.55, 52.19, 51.03, 27.15, 27.11, 27.06. ESI-HRMS (+): C<sub>82</sub>H<sub>36</sub>O<sub>8</sub> [M<sup>+</sup>] calc. 1148.2410, found 1148.2399.

**Compound 4.** A solution of compound **3** (1.10 g, 0.96 mmol) in ODCB (55 mL) was heated to reflux for 16 h. The reaction solution was cooled to room temperature and poured into hexane. The precipitate was collected and dried under vacuum overnight to give compound **4** (772 mg). <sup>1</sup>H NMR (400 MHz, ODCB-d<sub>4</sub>/THF-d<sub>8</sub>): δ (ppm) 10.84 (br, COOH), 4.59-4.99 (m, CH). <sup>13</sup>C NMR (150 MHz, ODCB-d<sub>4</sub>/THF-d<sub>8</sub>): δ (ppm) 167.48, 151.24, 150.73, 149.95, 149.81, 149.01, 148.79, 148.55, 148.32,

147.82, 147.56, 147.24, 147.12, 146.95, 146.69, 146.23, 145.83, 145.62, 145.35, 145.07, 144.88, 144.63, 144.24, 144.13, 144.02, 143.77, 143.41, 143.04, 142.89, 142.57, 141.92, 141.56, 140.43, 140.20, 139.47, 137.46, 137.30, 136.84, 73.10, 72.91, 72.61, 72.28, 42.15, 41.57, 40.06, 39.99, 39.88, 38.31.

**Bis-methano[60]fullerene ( $C_{60}(CH_2)_2$ ).** To a suspension of compound **4** (772 mg) in ODCB (155 mL) were added 1,10-phenanthroline (518 mg, 2.88 mmol) and  $Ag_2CO_3$  (397 mg, 1.44 mmol). The mixture was heated to reflux and irradiated by four lamps (13 W) for 15 h. The reaction mixture was cooled to room temperature and poured into methanol. The crude product was collected by filtration and purified through a silica gel column with hexane/ $CS_2$  (1:1) as the eluent. The first purple-red band was collected to give  $C_{60}(CH_2)_2$  (198 mg, 28% yield from **3**).  $^1H$  NMR (400 MHz, ODCB- $d_4$ / $CS_2$ ):  $\delta$  (ppm) 3.52-3.81 (m, 4H,  $CH_2$ ).  $^{13}C$  NMR (150 MHz, ODCB- $d_4$ / $CS_2$ ):  $\delta$  (ppm) 150.63, 149.93, 149.32, 148.99, 147.70, 147.48, 147.38, 146.41, 145.81, 145.33, 145.26, 144.94, 144.53, 144.18, 143.91, 143.60, 143.08, 143.02, 142.90, 142.64, 142.53, 142.07, 142.02, 141.82, 141.43, 141.10, 140.51, 140.44, 140.02, 139.30, 138.83, 138.46, 138.19, 138.02, 135.59, 135.45, 135.30, 134.98, 71.49, 71.12, 70.44, 70.01, 69.90, 68.92, 68.60, 28.05, 26.95, 26.10, 26.00, 24.67. MALDI-TOF-MS (+) for  $C_{62}H_4 [M^+]$ : 748.05.

**Compound 5.** To a solution of  $C_{60}$  (2.50 g, 3.47 mmol) and di-ter-butyl-2-bromomalonate (3.08 g, 10.4 mmol) in ODCB (170 mL) was added DBU (1.59 g, 10.4 mmol). The mixture was stirred at room temperature for 1.5 h. The solution was directly submitted to a silica gel column with toluene as the eluent. The major brown band was collected to give compound **5** (3.30 g, 70%). A small amount of di-ter-butyl-2-bromomalonate existed in compound **5**, but it didn't affect succeeding reaction.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 1.51-1.71 (m, 54H,  $CH_3$ ).  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 164.48, 163.96, 163.83, 163.76, 163.64, 163.56, 163.43, 163.35, 163.30, 163.21, 150.53, 150.37, 149.95, 149.78, 149.32, 149.20, 148.79, 148.42, 148.07, 147.79, 147.61, 147.42, 147.31, 147.08, 146.92,

146.70, 146.32, 146.09, 145.88, 145.76, 145.42, 144.98, 144.76, 144.63, 144.49, 144.22, 144.04, 143.87, 143.51, 143.42, 143.12, 142.92, 142.77, 142.64, 142.47, 142.19, 142.07, 141.93, 141.62, 141.02, 140.89, 140.48, 140.07, 139.75, 139.49, 139.33, 139.16, 138.56, 138.27, 137.95, 137.73, 136.34, 136.04, 133.74, 131.45, 129.44, 129.00, 128.65, 85.44, 85.19, 85.13, 85.08, 84.94, 84.47, 73.59, 73.47, 73.14, 72.72, 72.42, 72.29, 72.18, 71.71, 71.55, 71.04, 58.39, 56.11, 55.67, 54.41, 54.05, 53.78, 52.65, 52.13, 52.07, 51.75, 51.32, 49.29, 47.36, 45.72, 39.64, 36.98, 33.64, 30.59, 29.83, 29.10, 29.04, 28.95, 28.84, 28.62. Since there are too many signals on  $^{13}\text{C}$  NMR spectrum due to regioisomers, only selected peaks are presented here. ESI-HRMS (+):  $\text{C}_{93}\text{H}_{55}\text{O}_{12}$   $[\text{M} + \text{H}^+]$  calc. 1363.3693, found 1363.3682.

**Compound 6.** A solution of compound **5** (810 mg, 0.59 mmol) in ODCB (45 mL) was heated to reflux for 16 h. The solution was cooled to room temperature and poured into hexane. The precipitate was collected and dried under vacuum overnight to give compound **6** (560 mg).  $^1\text{H}$  NMR (400 MHz,  $\text{ODCB-d}_4/\text{THF-d}_8$ ):  $\delta$  (ppm) 4.21-4.75 (m, *CH*). The acid protons underwent rapid exchange with protons of water in the solvent.  $^{13}\text{C}$  NMR (125 MHz,  $\text{ODCB-d}_4/\text{THF-d}_8$ ):  $\delta$  (ppm) 167.99, 167.70, 167.48, 167.38, 153.39, 151.38, 150.93, 150.38, 149.18, 149.09, 148.76, 148.61, 148.08, 147.78, 147.52, 147.21, 146.99, 146.72, 146.23, 146.10, 145.86, 145.64, 145.41, 145.00, 144.79, 144.49, 143.92, 143.73, 143.45, 143.25, 142.73, 142.51, 142.21, 142.11, 141.96, 141.43, 141.00, 140.60, 140.45, 139.84, 139.43, 137.36, 135.45, 72.36, 71.44, 42.33, 41.70, 41.51, 41.21, 40.85, 39.92, 38.94, 37.87, 37.40, 36.00, 34.75, 32.88. Since there are too many signals on  $^{13}\text{C}$  NMR spectrum due to regioisomers, only selected peaks are presented here.

**Tris-methano[60]fullerene ( $\text{C}_{60}(\text{CH}_2)_3$ ).** To a suspension of compound **6** (560 mg) in ODCB/PhCN (1:1, 225 mL) were added 1,10-phenanthroline (427 mg, 2.38 mmol) and  $\text{Ag}_2\text{CO}_3$  (328 mg, 1.19 mmol). The mixture was heated to reflux and irradiated by four lamps (13 W) for 36 h. The reaction mixture was cooled to room temperature and poured into methanol. The crude product was collected by filtration and purified

through a silica gel column with hexane/CS<sub>2</sub> (1:1) as the eluent. The first brown-red band was collected to give C<sub>60</sub>(CH<sub>2</sub>)<sub>3</sub> (66 mg, 15% yield from **5**). <sup>1</sup>H NMR (400 MHz, ODCB-d<sub>4</sub>/CS<sub>2</sub>): δ (ppm) 3.03-3.98 (m, 6H, CH<sub>2</sub>). <sup>13</sup>C NMR (150 MHz, ODCB-d<sub>4</sub>/CS<sub>2</sub>): δ (ppm) 152.73, 152.00, 151.17, 150.55, 150.00, 148.39, 147.94, 147.42, 147.22, 146.62, 146.07, 145.94, 145.28, 144.85, 144.15, 143.82, 143.54, 143.29, 142.60, 142.08, 141.86, 140.86, 140.27, 139.45, 138.45, 138.20, 137.98, 135.83, 133.91, 71.90, 70.94, 70.27, 69.65, 68.90, 27.87, 27.75, 26.26, 25.66, 25.27, 24.37, 23.96, 22.71. Since there are too many signals on <sup>13</sup>C NMR spectrum due to regioisomers, only selected peaks are presented here. MALDI-TOF-MS (+) for C<sub>63</sub>H<sub>6</sub> [M<sup>+</sup>]: 762.07.

**OQBMF.** To a solution of C<sub>60</sub>(CH<sub>2</sub>)<sub>2</sub> (350 mg, 0.47 mmol) in ODCB (70 mL) was added 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (157 mg, 0.93 mmol). The mixture was stirred at 100 °C for 4 h. Then the reaction solution was cooled to room temperature and poured into methanol. The crude product was collected by filtration and purified through a silica gel column with hexane/CS<sub>2</sub> (1:1) as the eluent. The first band was the unreacted C<sub>60</sub>(CH<sub>2</sub>)<sub>2</sub>. The second brown band was collected to give OQBMF (160 mg, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>): δ (ppm) 7.43-7.58 (m, 4H, Ar), 2.97-4.52 (m, 8H, CH<sub>2</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>): δ (ppm) 153.63, 153.13, 152.08, 151.89, 150.92, 150.32, 146.21, 145.93, 145.71, 145.41, 145.11, 144.80, 144.14, 143.83, 143.47, 142.97, 142.82, 142.41, 142.14, 141.72, 141.47, 141.11, 140.49, 140.03, 139.39, 138.97, 138.55, 137.37, 136.93, 136.55, 136.16, 135.37, 134.54, 134.32, 134.09, 132.79, 131.06, 128.89, 126.78, 126.51, 126.19, 70.55, 70.10, 69.73, 68.77, 68.03, 67.78, 66.87, 64.34, 63.63, 63.12, 62.88, 58.55, 56.25, 54.75, 45.08, 44.29, 43.52, 42.80, 28.25, 26.51, 24.60, 24.15, 24.02, 23.54, 22.94, 22.14, 21.87, 21.37. Since there are too many signals on <sup>13</sup>C NMR spectrum due to regioisomers, only selected peaks are presented here. ESI-HRMS (+): C<sub>70</sub>H<sub>13</sub> [M + H<sup>+</sup>] calc. 853.1017, found 853.0999.

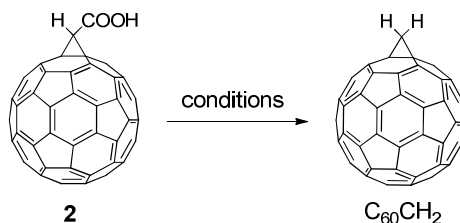
**OQTMF.** To a solution of C<sub>60</sub>(CH<sub>2</sub>)<sub>3</sub> (180 mg, 0.24 mmol) in ODCB (36 mL) was



added 1,4-dihydrobenzo[d][1,2]oxathiine 3-oxide (119 mg, 0.71 mmol). The mixture was stirred at 100 °C for 4 h. Then the reaction solution was cooled to room temperature and poured into methanol. The crude product was collected by filtration and purified through a silica gel column with hexane/CS<sub>2</sub> (1:1) as the eluent. The first band was the unreacted C<sub>60</sub>(CH<sub>2</sub>)<sub>3</sub>. The second brown-yellow band was collected to give OQTMF (95 mg, 46%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>): δ (ppm) 7.40-7.58 (m, 4H, Ar), 2.85-4.52 (m, 10H, CH<sub>2</sub>). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>): δ (ppm) 153.72, 151.96, 151.55, 150.78, 149.93, 149.52, 149.00, 148.35, 147.76, 147.40, 147.24, 146.95, 146.86, 146.77, 146.38, 146.25, 145.96, 145.79, 145.66, 145.49, 145.31, 145.16, 145.06, 144.77, 144.58, 144.30, 144.07, 143.87, 143.79, 143.37, 143.25, 143.15, 143.00, 142.75, 142.58, 142.31, 142.09, 141.75, 141.49, 141.18, 140.94, 140.80, 140.59, 140.38, 139.96, 139.48, 139.14, 138.92, 138.76, 138.51, 138.18, 137.87, 137.48, 137.11, 136.93, 136.79, 136.65, 136.33, 136.05, 135.62, 135.07, 134.83, 134.59, 134.25, 133.83, 133.28, 132.73, 131.91, 128.66, 126.52, 125.78, 71.60, 69.86, 68.83, 68.50, 68.26, 67.93, 67.47, 67.19, 66.79, 66.20, 65.72, 62.12, 61.76, 54.50, 49.54, 44.05, 43.61, 43.19, 42.96, 42.61, 42.31, 27.98, 26.72, 25.98, 24.67, 24.22, 23.77, 23.27, 22.10, 21.91, 21.33, 20.80, 19.91, 19.20, 18.84. Since there are too many signals on <sup>13</sup>C NMR spectrum due to regioisomers, only selected peaks are presented here. ESI-HRMS (+): C<sub>71</sub>H<sub>15</sub> [M + H<sup>+</sup>] calc. 867.1174, found 867.1152.

#### 4. Reaction condition screening for silver-mediated decarboxylation

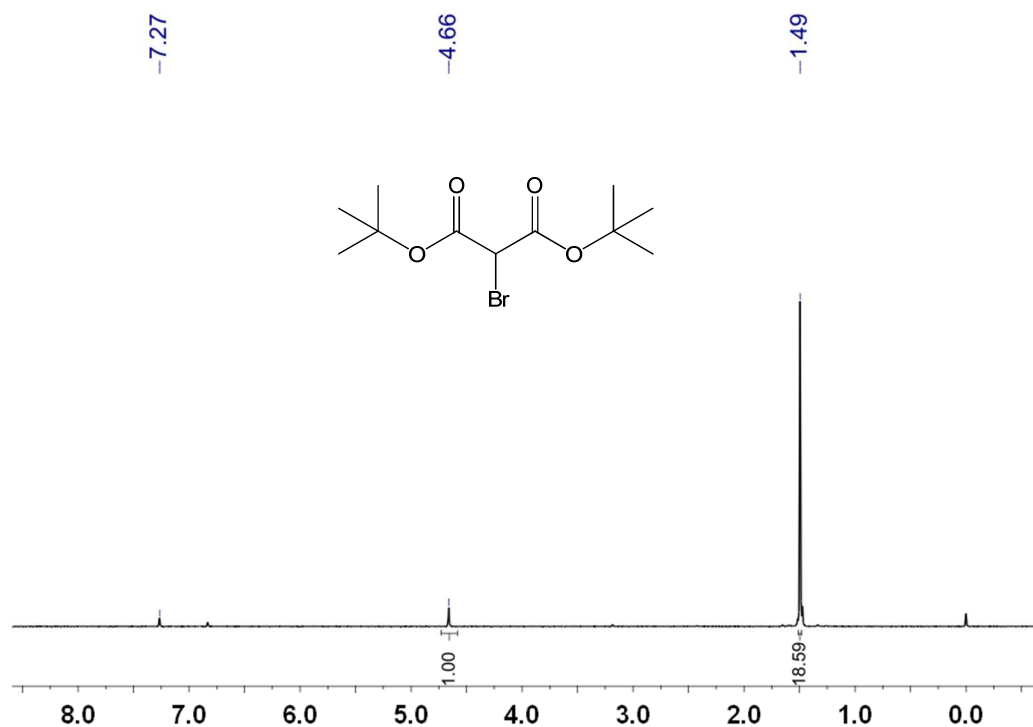
**Table S1** Optimization of the reaction conditions.<sup>a</sup>



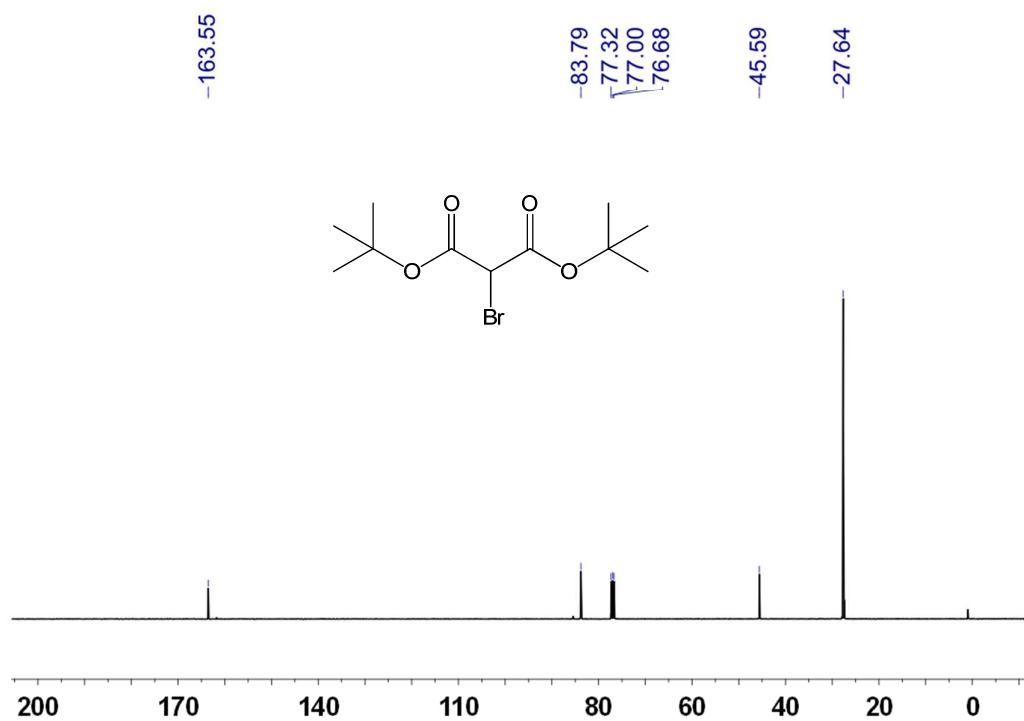
entry	metal compounds	ligand or additive	solvent	$T/^{\circ}\text{C}$ & $h\nu$	yield <sup>b</sup>
1	—	—	ODCB	150	0
2	$\text{Ag}_2\text{CO}_3$	—	ODCB	150	0
3	—	phen	ODCB	150	0
4	$\text{Ag}_2\text{CO}_3$	phen	ODCB	150	30%
5	$\text{AgOAc}$	phen	ODCB	150	29%
6	$\text{Ag}_2\text{O}$	phen	ODCB	150	trace
7	$\text{CF}_3\text{COOAg}$	phen	ODCB	150	trace
8	$\text{CuCl}$	phen	ODCB	150	0
9	$\text{Cu}_2\text{O}$	phen	ODCB	150	0
10	$\text{Pd}(\text{OAc})_2$	phen	ODCB	150	0
11	$\text{Ag}_2\text{CO}_3$	NMP	ODCB	150	0
12	$\text{Ag}_2\text{CO}_3$	DMSO	ODCB	150	0
13	$\text{Ag}_2\text{CO}_3$	$\text{PPh}_3$	ODCB	150	0
14	$\text{Ag}_2\text{CO}_3$	pyridine	ODCB	150	0
15	$\text{Ag}_2\text{CO}_3$	2,2'-dipyridine	ODCB	150	0
16	$\text{Ag}_2\text{CO}_3$	18-crown-6	ODCB	150	0
17	$\text{Ag}_2\text{CO}_3$	quinoline	ODCB	150	0
18	$\text{Ag}_2\text{CO}_3$	phen	ODCB	150, $h\nu$	37%
19	<b><math>\text{Ag}_2\text{CO}_3</math></b>	<b>phen</b>	<b>ODCB</b>	<b>180, <math>h\nu</math></b>	<b>51%</b>
20	$\text{AgOAc}$	phen	ODCB	180, $h\nu$	44%
21	$\text{Ag}_2\text{CO}_3$	phen, $\text{H}_2\text{O}$	ODCB	180, $h\nu$	31%
22	$\text{AgOAc}$	phen, $\text{K}_2\text{CO}_3$	ODCB	180, $h\nu$	trace
23	$\text{Ag}_2\text{CO}_3$	phen	PhCN	180, $h\nu$	26%
24	$\text{Ag}_2\text{CO}_3$	phen	ODCB/PhCN (5:1)	180, $h\nu$	44%
25	$\text{Ag}_2\text{CO}_3$	phen (2.0 eq)	ODCB	180, $h\nu$	42%
26	$\text{Ag}_2\text{CO}_3$ (0.25 eq)	phen (0.5 eq)	ODCB	180, $h\nu$	23%
27	$\text{Ag}_2\text{CO}_3$ (0.05 eq)	phen (0.1 eq)	ODCB	180, $h\nu$	trace

<sup>a</sup> Conditions: compound **2**, 30 mg, dispersed in 6 mL solvent; metal compounds, 0.5 eq for  $\text{Ag}_2\text{CO}_3$ ,  $\text{Ag}_2\text{O}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{Pd}(\text{OAc})_2$ ; 1.0 eq for others; ligand or additive, 1.0 eq; reaction time, 4 h. <sup>b</sup> Isolated yields. (phen=1,10-phenanthroline).

## 5. NMR spectra

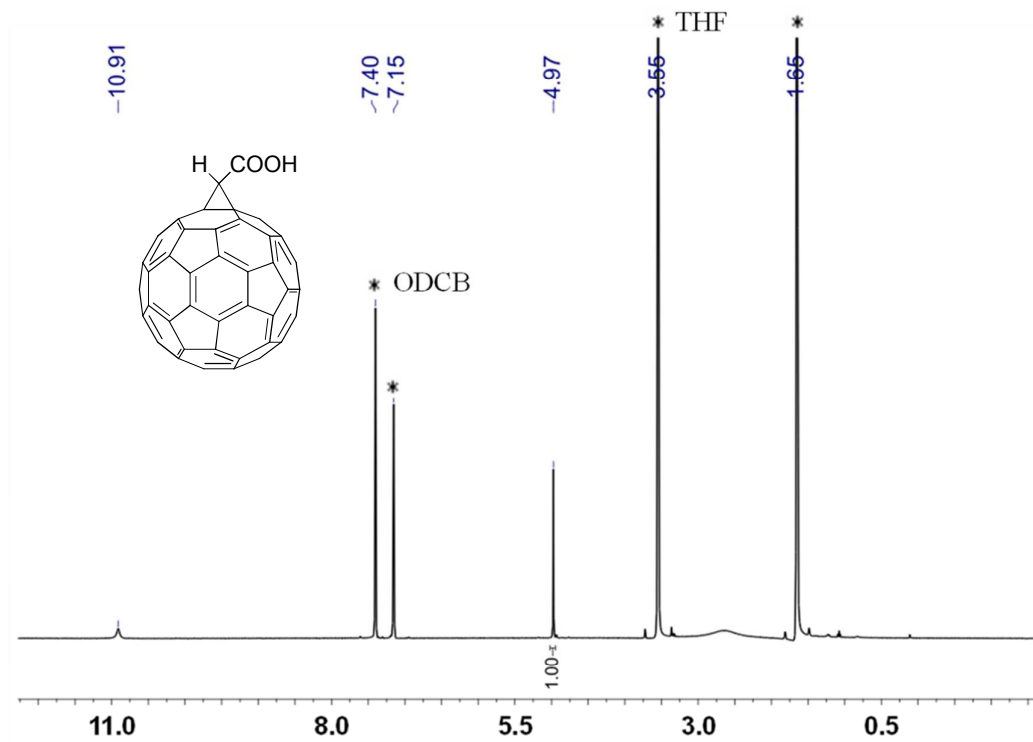


**Figure S1.** <sup>1</sup>H NMR spectrum of di-ter-butyl-2-bromomalonate (in CDCl<sub>3</sub>).

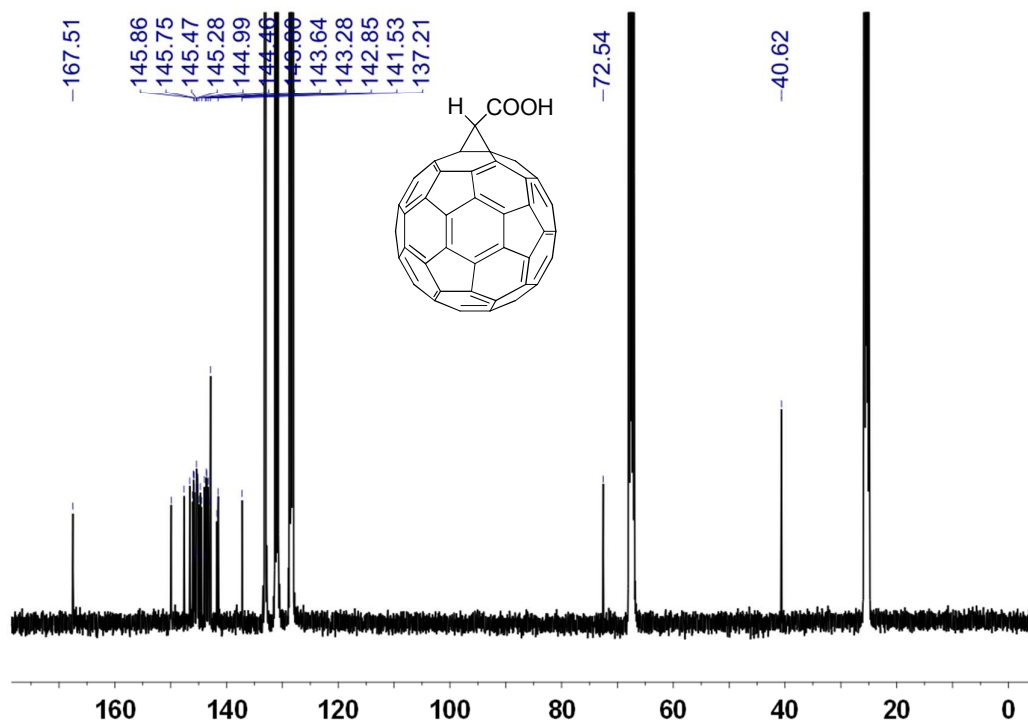


**Figure S2.** <sup>13</sup>C NMR spectrum of di-ter-butyl-2-bromomalonate (in CDCl<sub>3</sub>).

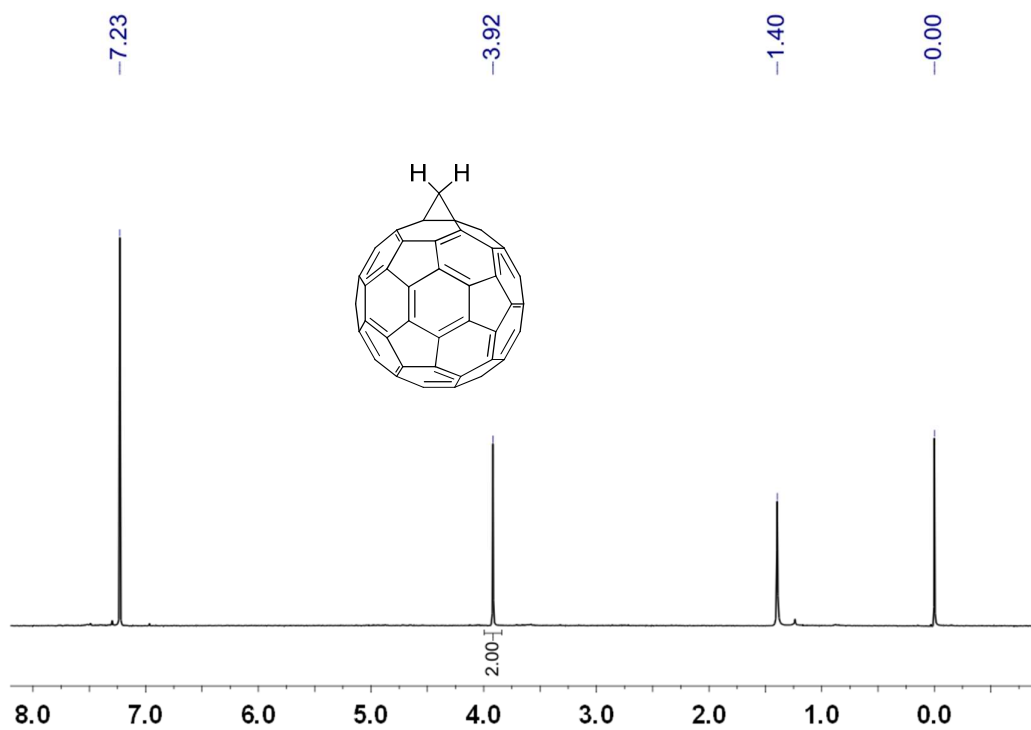




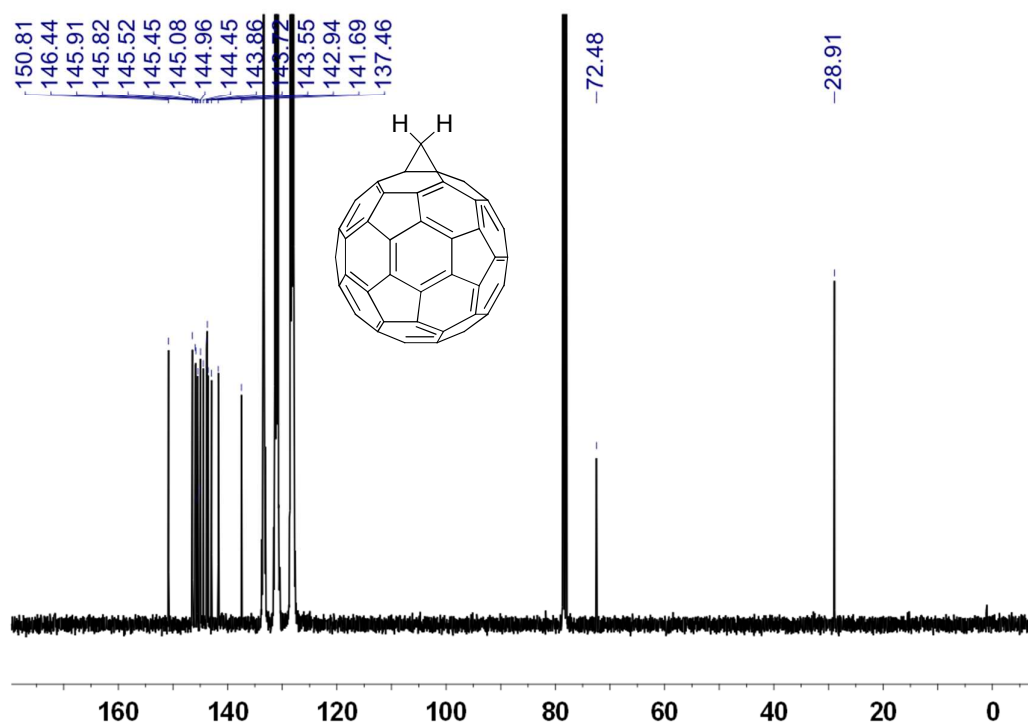
**Figure S5.** <sup>1</sup>H NMR spectrum of compound **2** (in ODCB-d<sub>4</sub>/THF-d<sub>8</sub>).



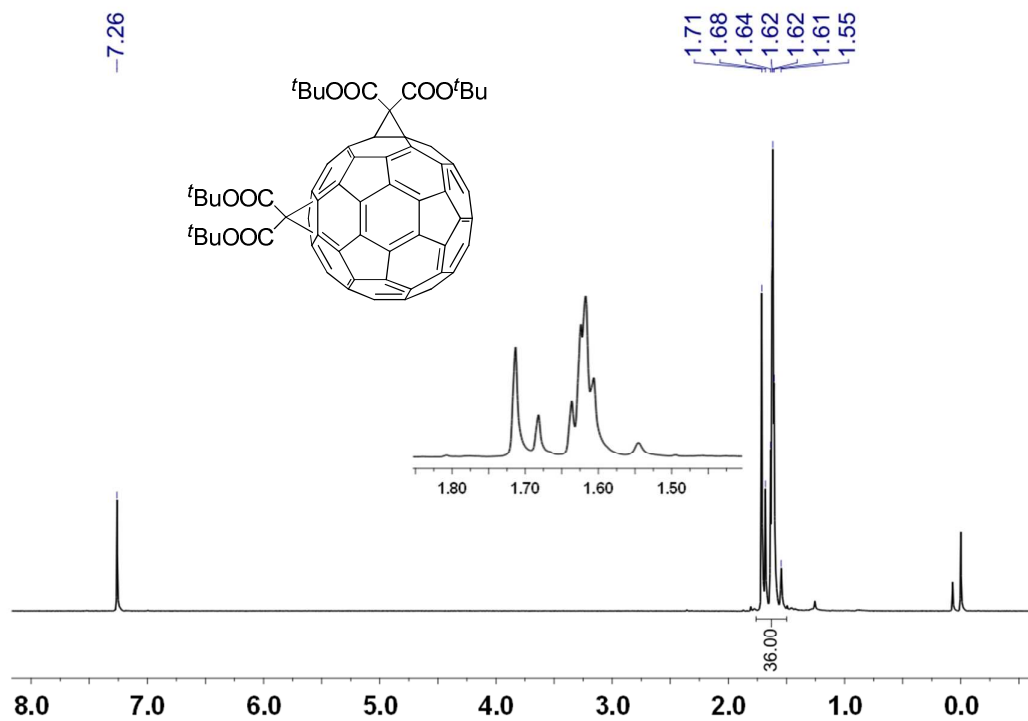
**Figure S6.** <sup>13</sup>C NMR spectrum of compound **2** (in ODCB-d<sub>4</sub>/THF-d<sub>8</sub>).



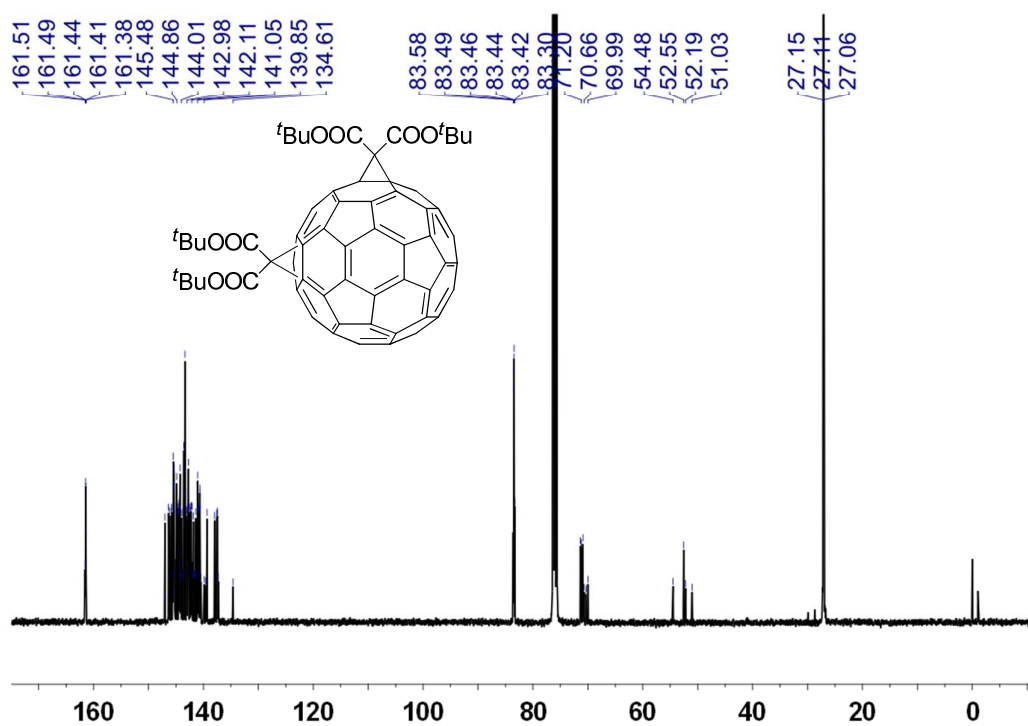
**Figure S7.** <sup>1</sup>H NMR spectrum of C<sub>60</sub>CH<sub>2</sub> (in CDCl<sub>3</sub>/CS<sub>2</sub>).



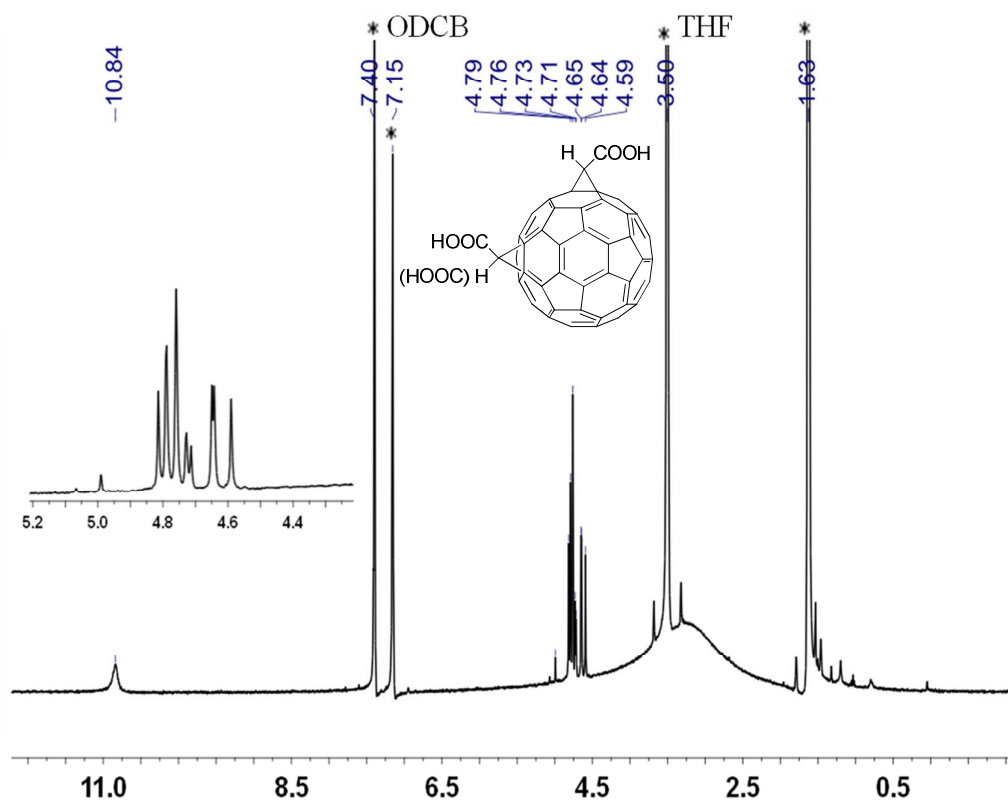
**Figure S8.** <sup>13</sup>C NMR spectrum of C<sub>60</sub>CH<sub>2</sub> (in ODCB-d<sub>4</sub>/CDCl<sub>3</sub>).



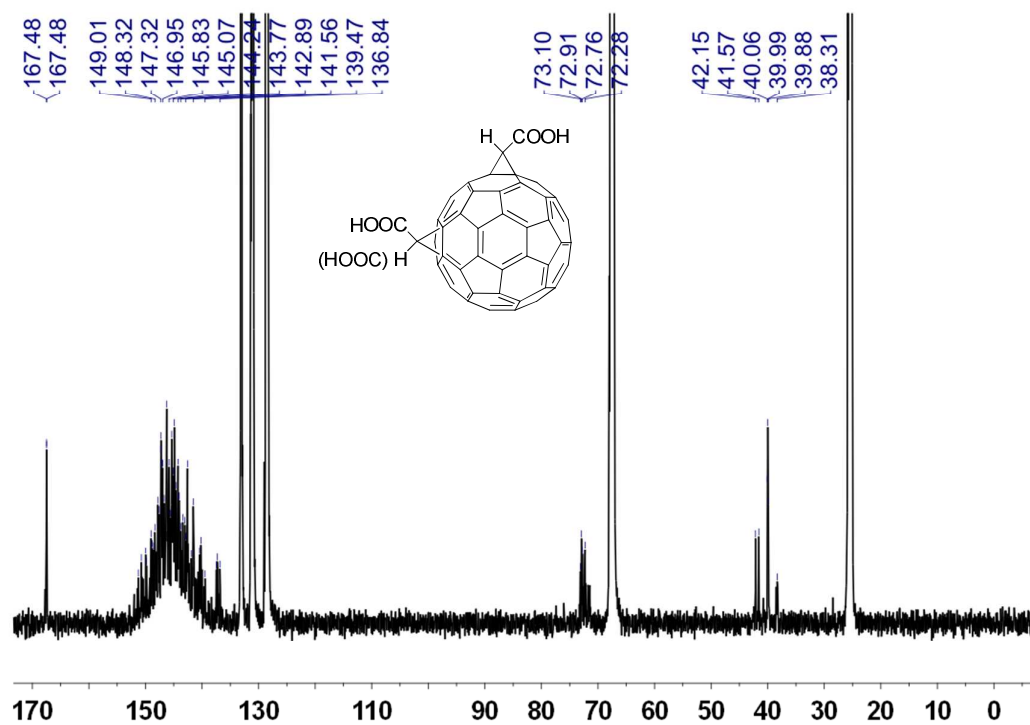
**Figure S9.** <sup>1</sup>H NMR spectrum of compound **3** (in CDCl<sub>3</sub>).



**Figure S10.** <sup>13</sup>C NMR spectrum of compound **3** (in CDCl<sub>3</sub>).

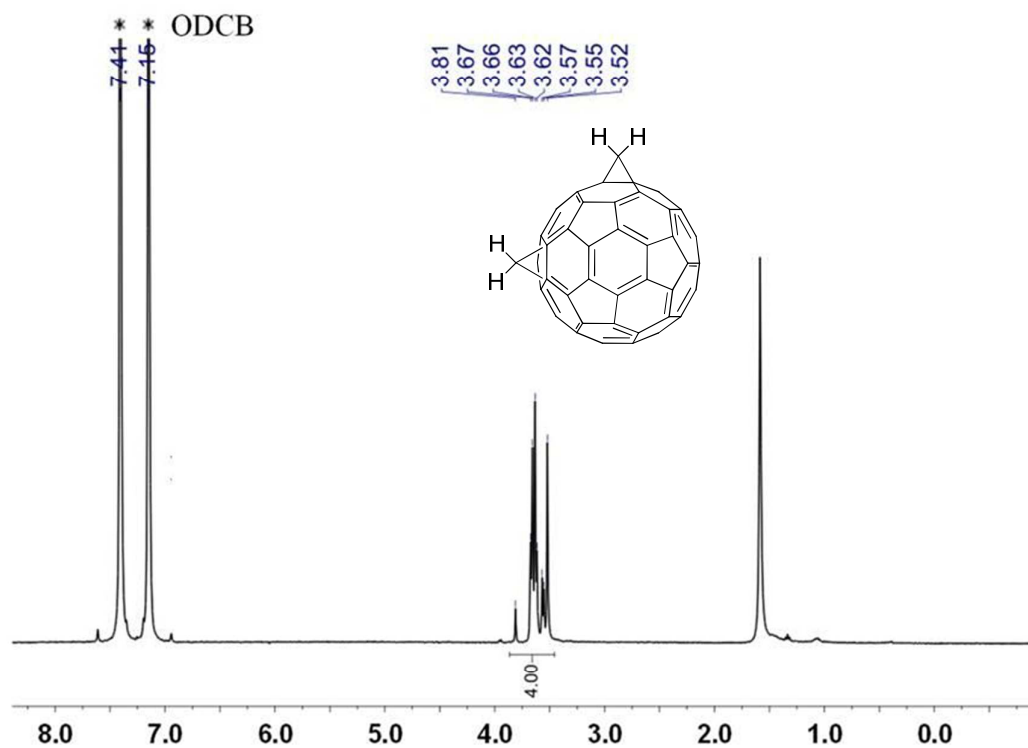


**Figure S11.** <sup>1</sup>H NMR spectrum of compound 4 (in ODCB-d<sub>4</sub>/THF-d<sub>8</sub>).

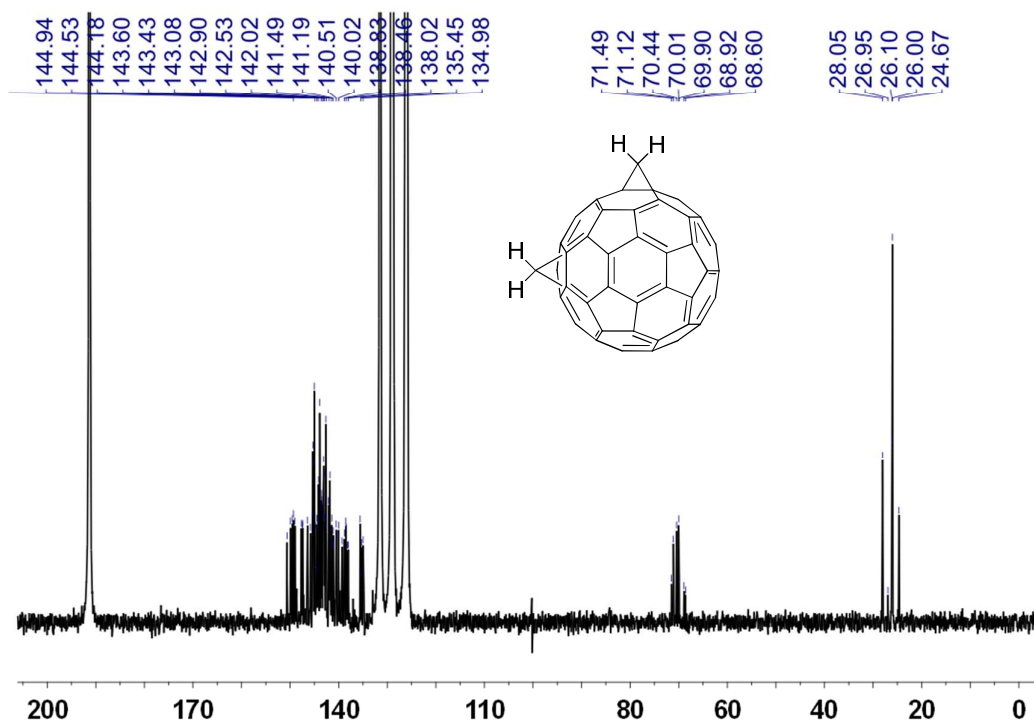


**Figure S12.** <sup>13</sup>C NMR spectrum of compound 4 (in ODCB-d<sub>4</sub>/THF-d<sub>8</sub>).

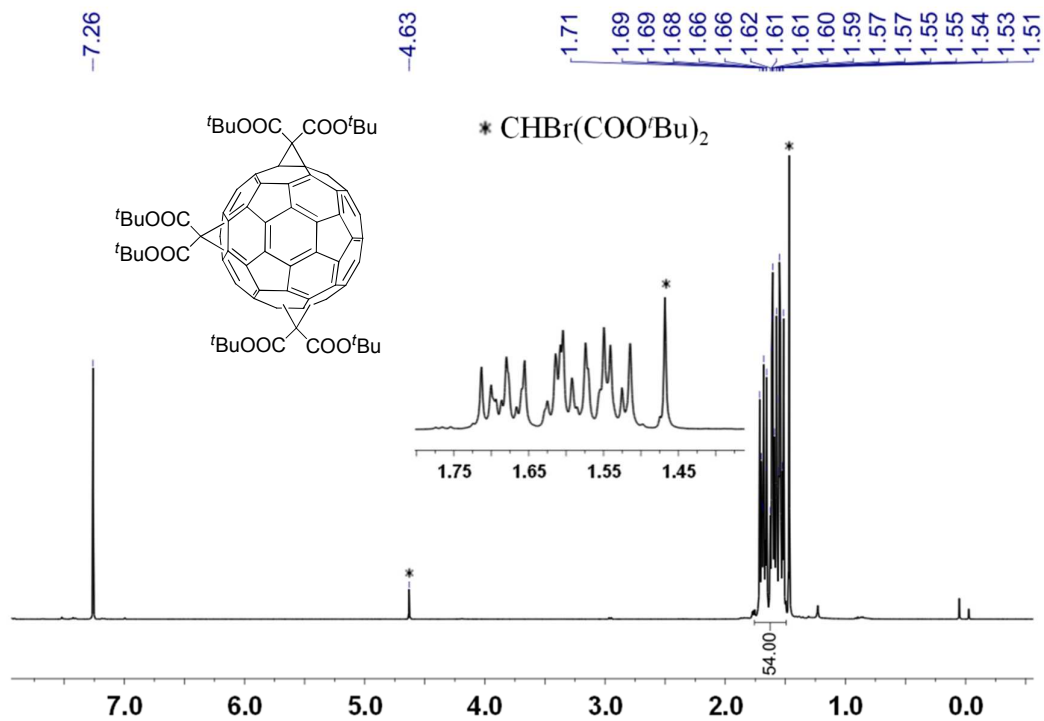




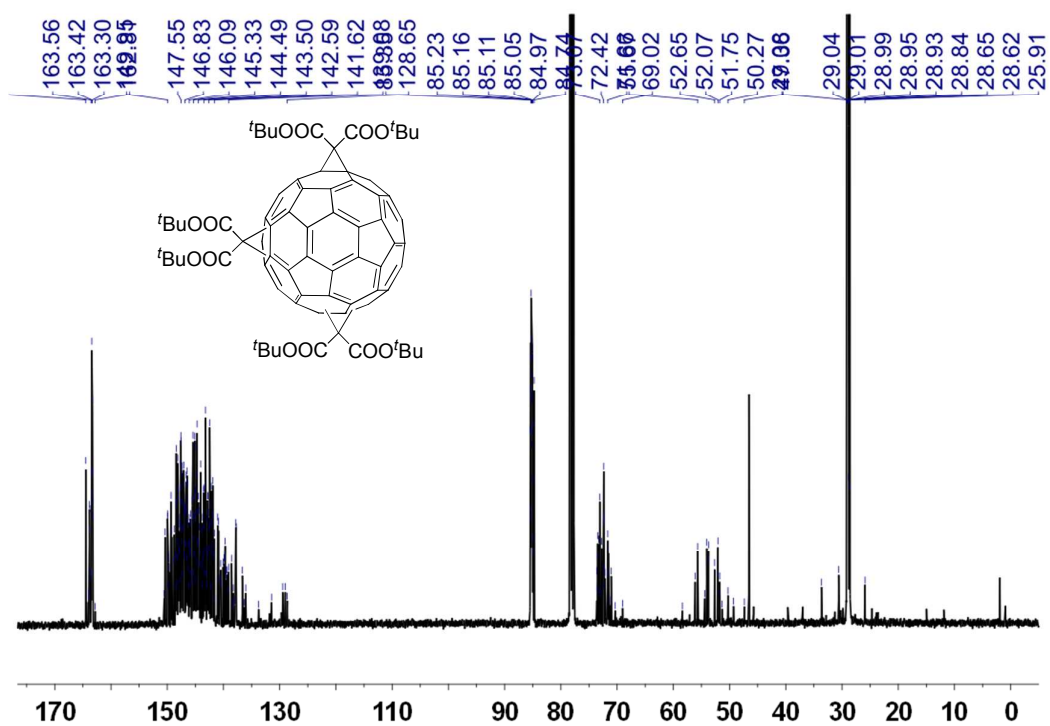
**Figure S13.** <sup>1</sup>H NMR spectrum of C<sub>60</sub>(CH<sub>2</sub>)<sub>2</sub> (in ODCB-d<sub>4</sub>/CS<sub>2</sub>).



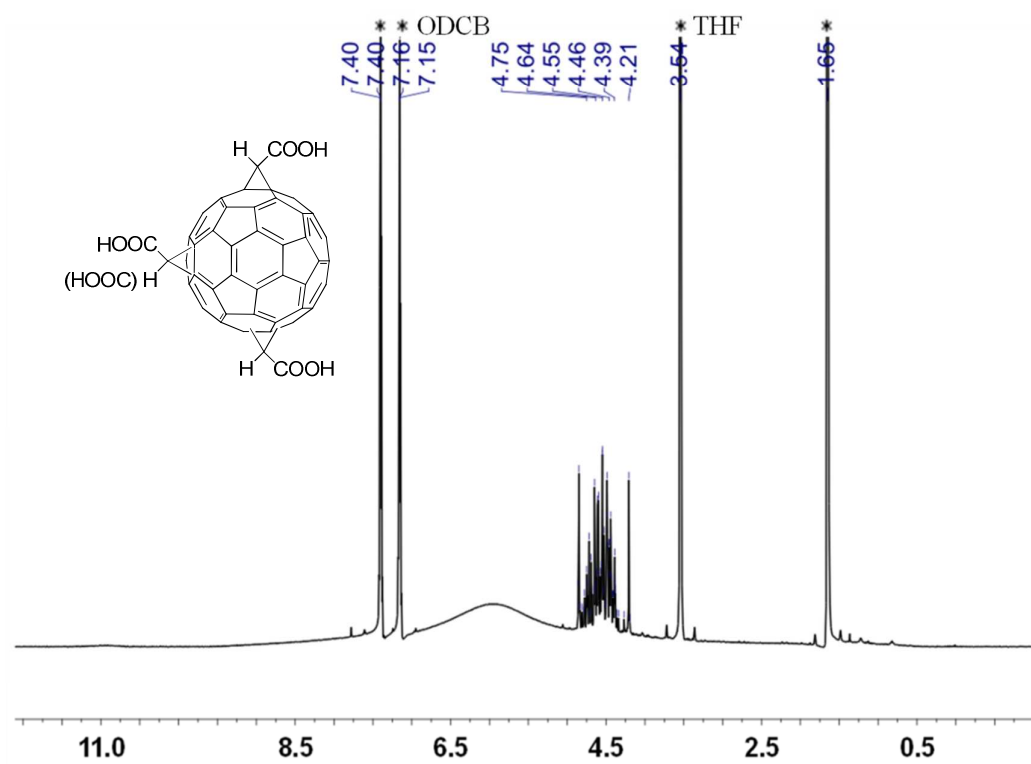
**Figure S14.** <sup>13</sup>C NMR spectrum of C<sub>60</sub>(CH<sub>2</sub>)<sub>2</sub> (in ODCB-d<sub>4</sub>/CS<sub>2</sub>).



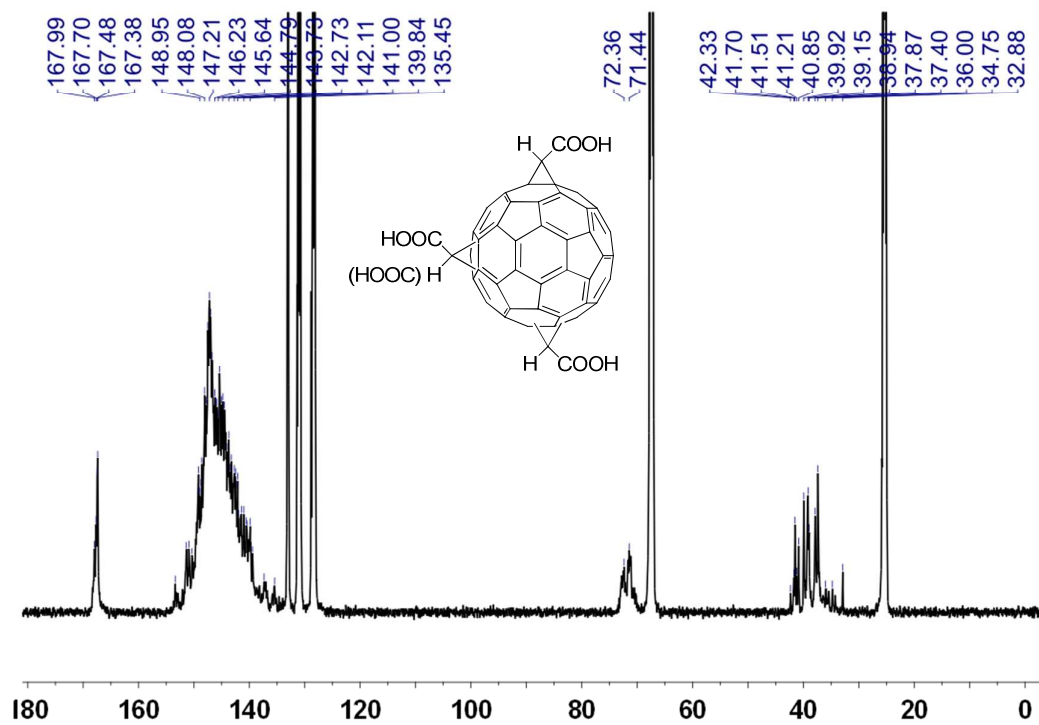
**Figure S15.** <sup>1</sup>H NMR spectrum of compound **5** (in CDCl<sub>3</sub>).



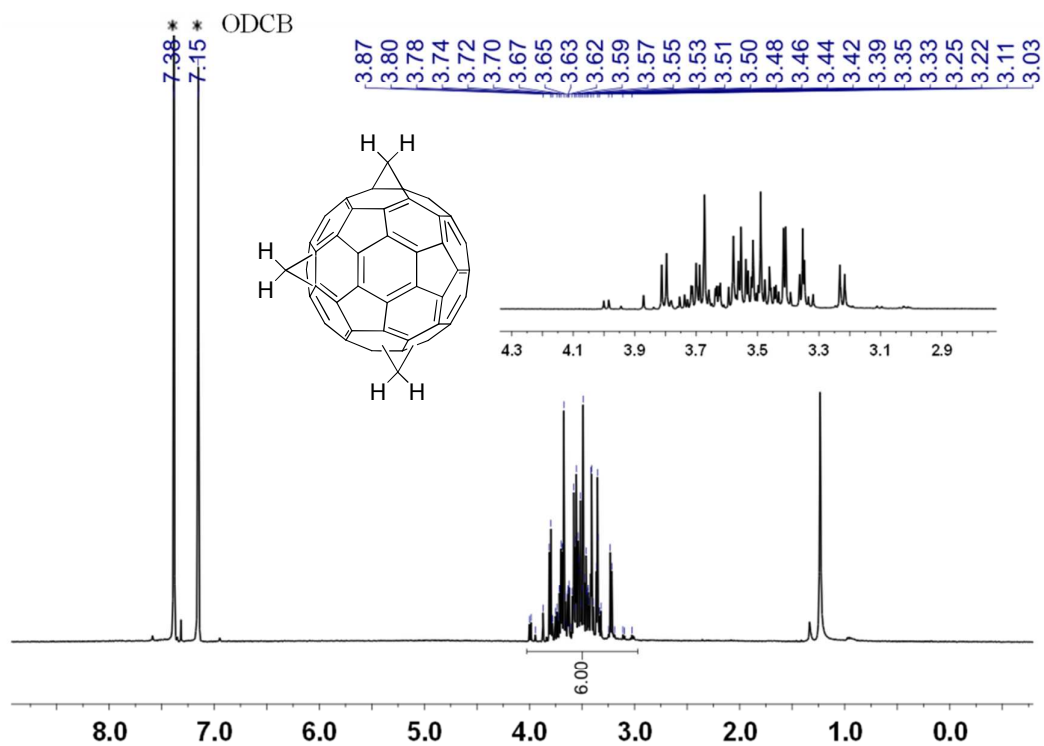
**Figure S16.** <sup>13</sup>C NMR spectrum of compound **5** (in CDCl<sub>3</sub>).



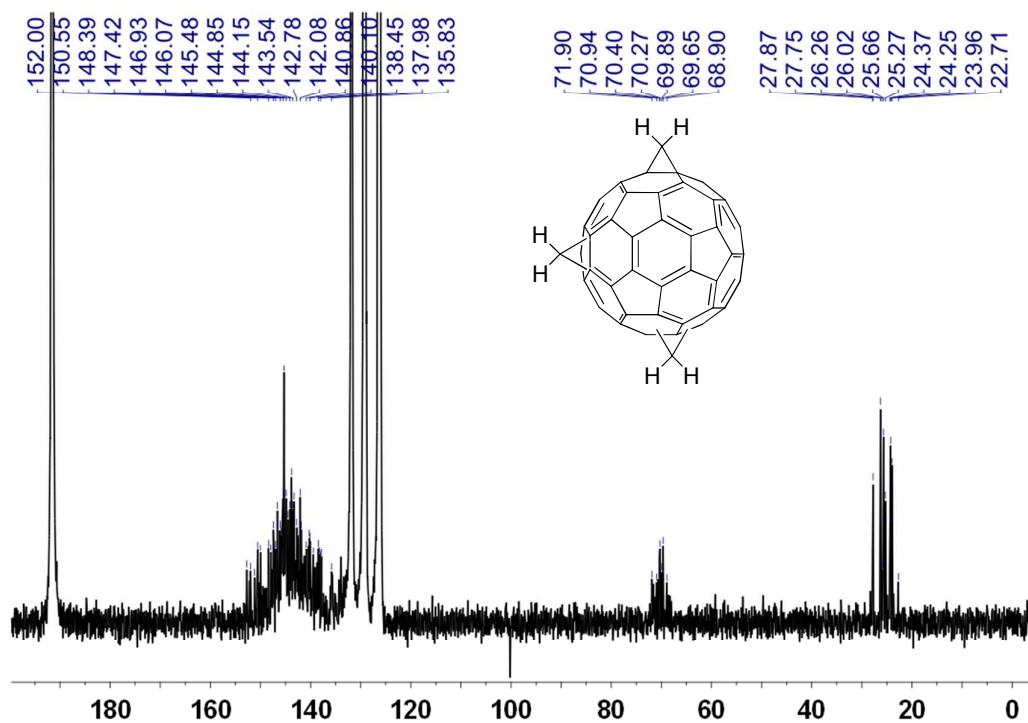
**Figure S17.** <sup>1</sup>H NMR spectrum of compound **6** (in ODCB-d<sub>4</sub>/THF-d<sub>8</sub>).



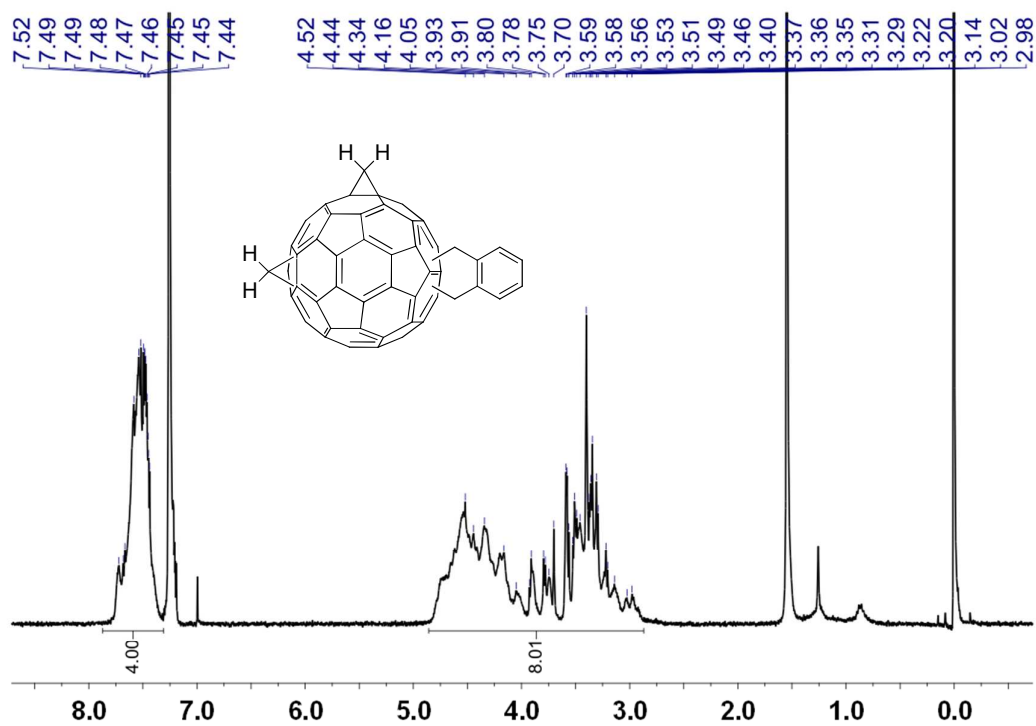
**Figure S18.** <sup>13</sup>C NMR spectrum of compound **6** (in ODCB-d<sub>4</sub>/THF-d<sub>8</sub>).



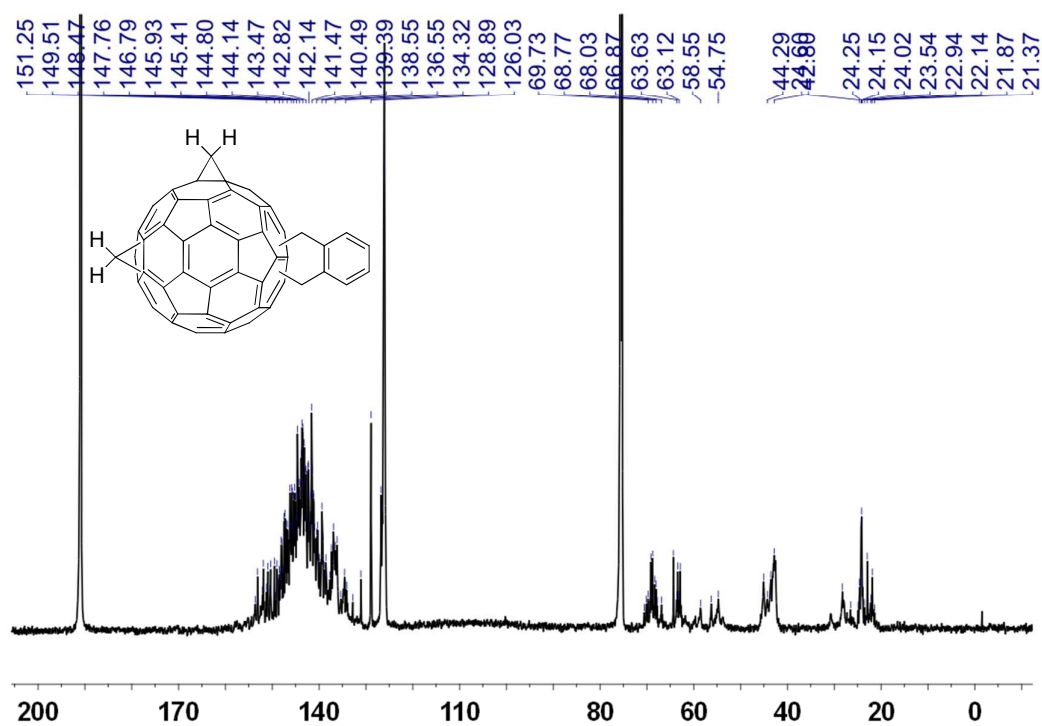
**Figure S19.** <sup>1</sup>H NMR spectrum of C<sub>60</sub>(CH<sub>2</sub>)<sub>3</sub> (in ODCB-d<sub>4</sub>/CS<sub>2</sub>).



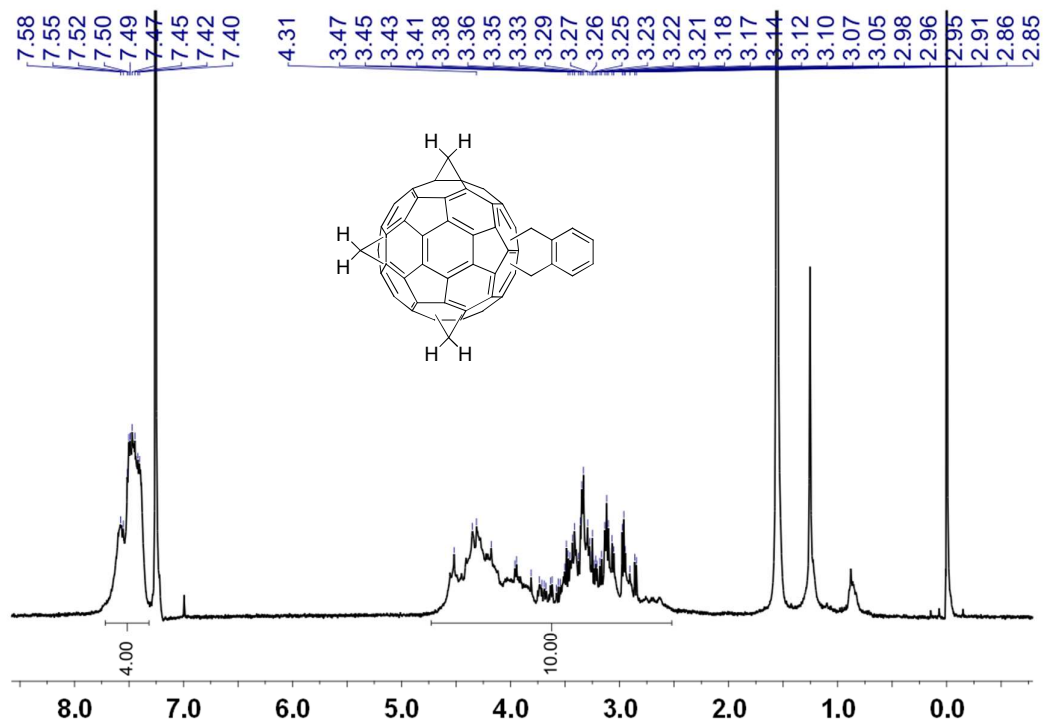
**Figure S20.** <sup>13</sup>C NMR spectrum of C<sub>60</sub>(CH<sub>2</sub>)<sub>3</sub> (in ODCB-d<sub>4</sub>/CS<sub>2</sub>).



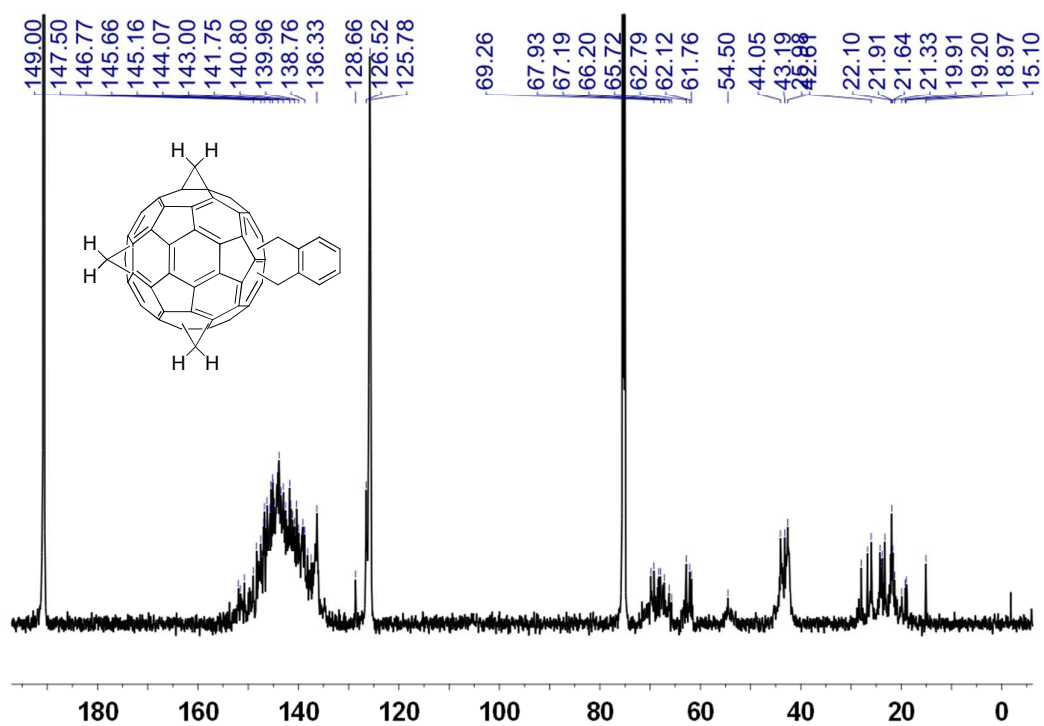
**Figure S21.** <sup>1</sup>H NMR spectrum of OQBMF (in CDCl<sub>3</sub>/CS<sub>2</sub>).



**Figure S22.** <sup>13</sup>C NMR spectrum of OQBMF (in CDCl<sub>3</sub>/CS<sub>2</sub>).



**Figure S23.** <sup>1</sup>H NMR spectrum of OQTMF (in CDCl<sub>3</sub>/CS<sub>2</sub>).



**Figure S24.** <sup>13</sup>C NMR spectrum of OQTMF (in CDCl<sub>3</sub>/CS<sub>2</sub>).

## 6. Mass spectra

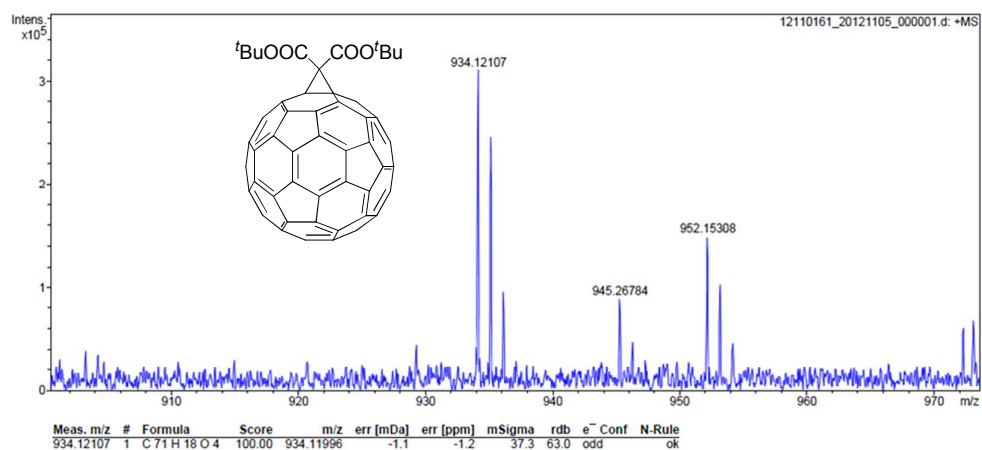


Figure S25. Mass spectrum of compound 1.

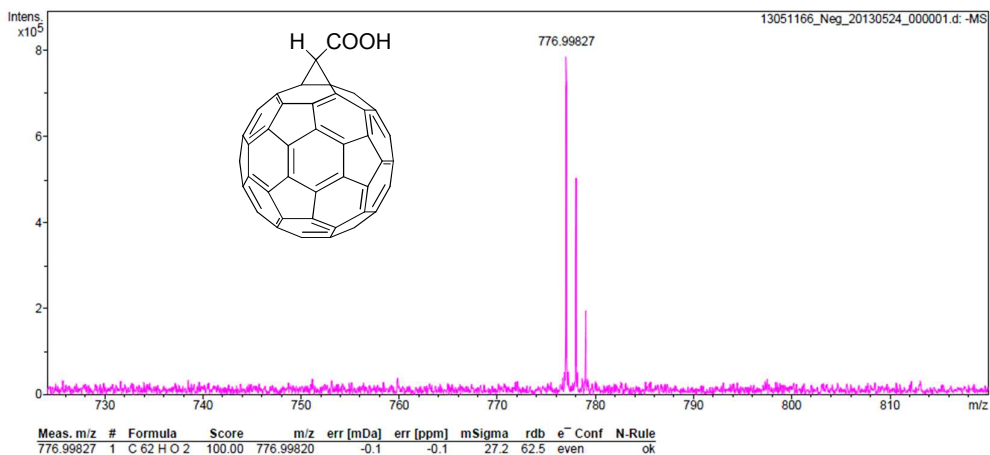


Figure S26. Mass spectrum of compound 2.

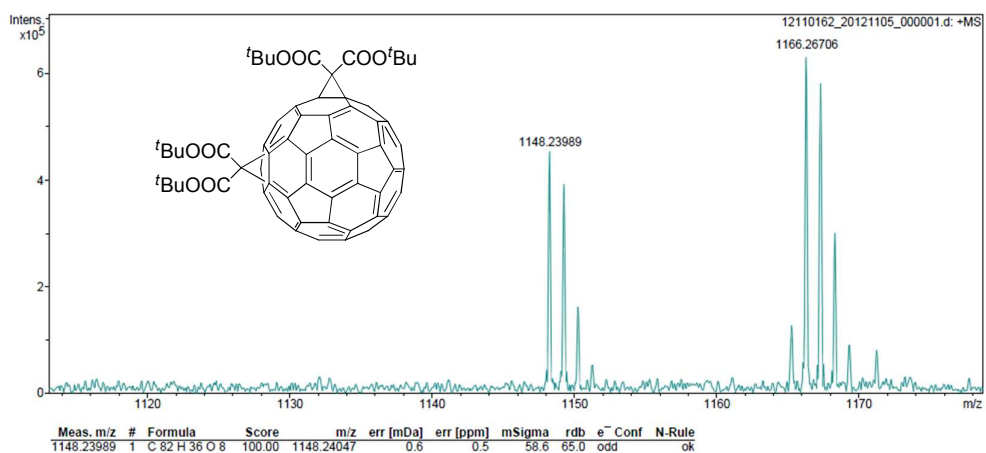


Figure S27. Mass spectrum of compound 3.

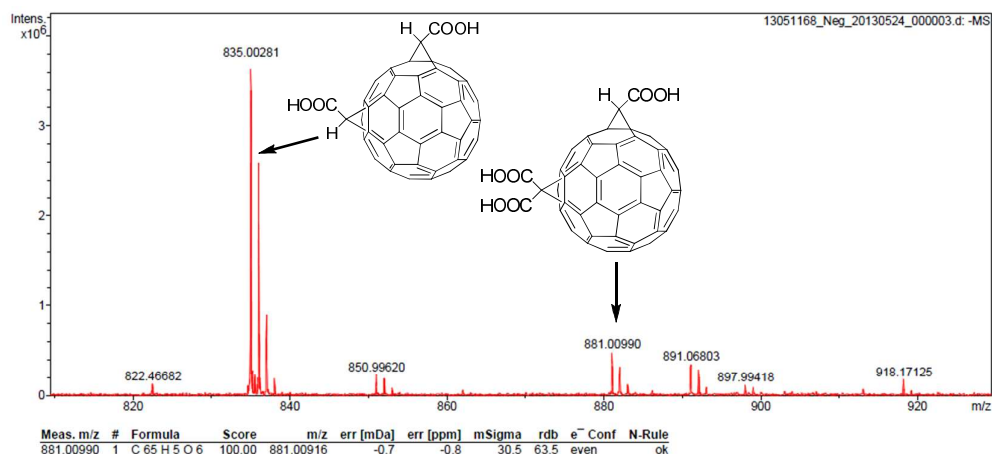


Figure S28. Mass spectrum of compound 4.

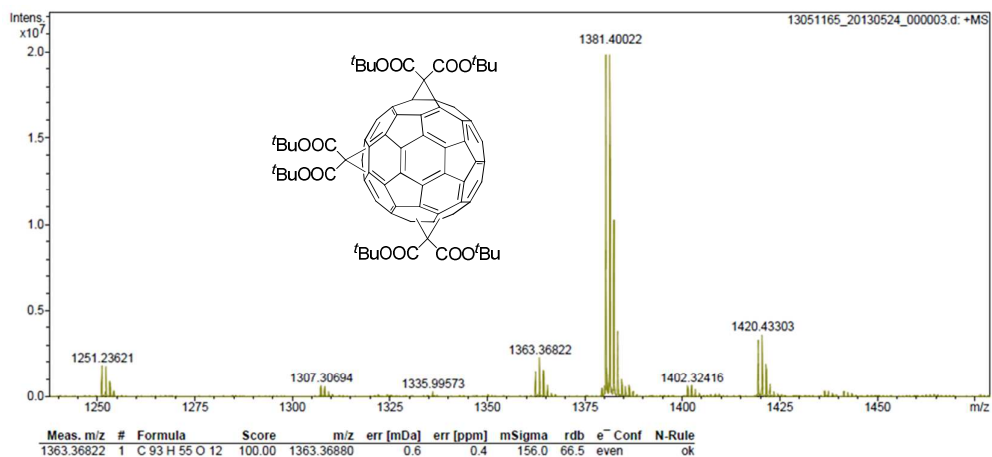


Figure S29. Mass spectrum of compound 5.

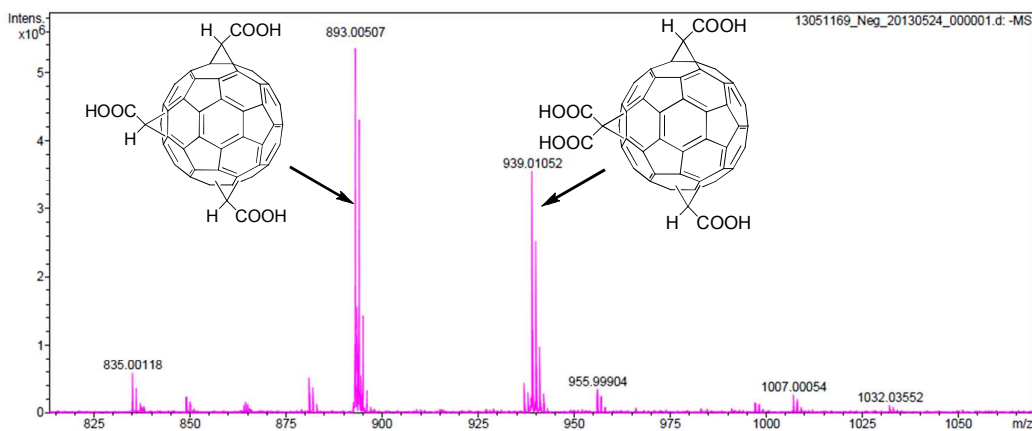
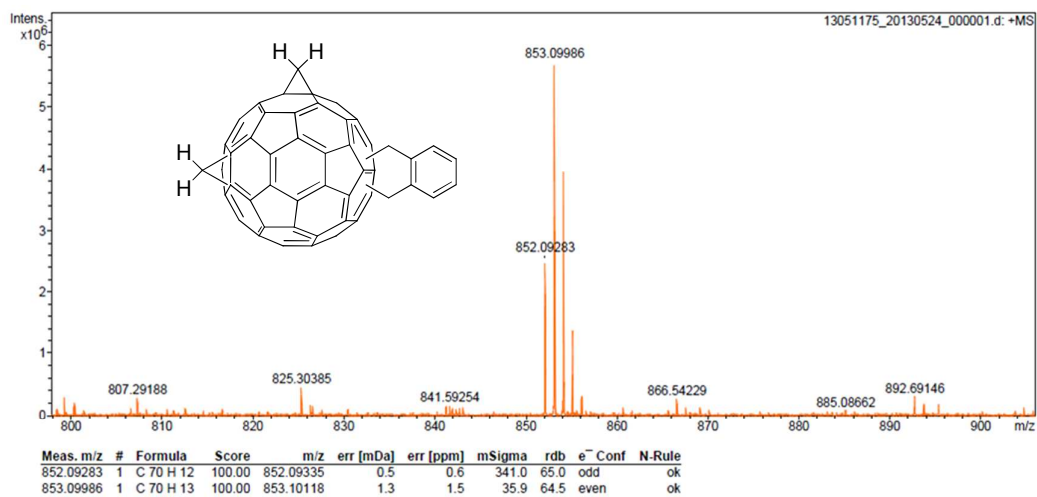
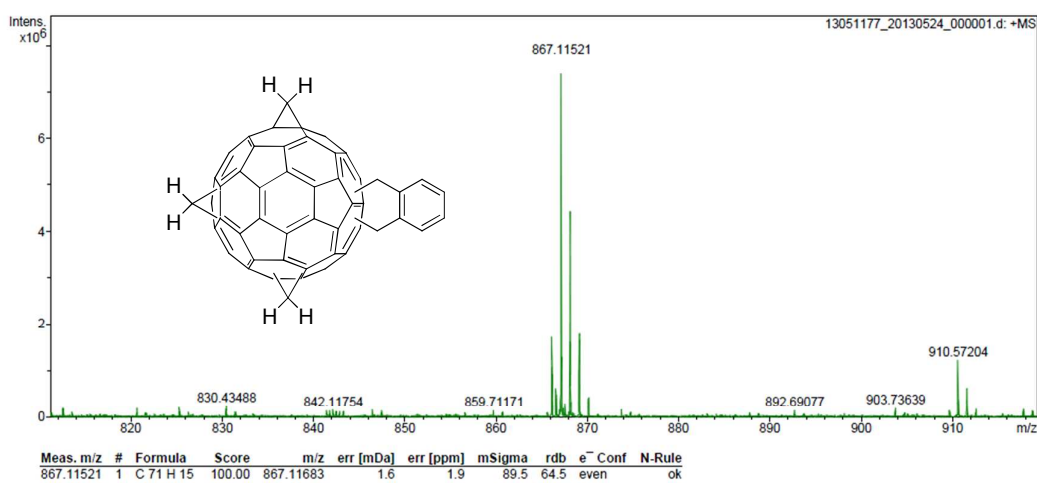


Figure S30. Mass spectrum of compound 6.



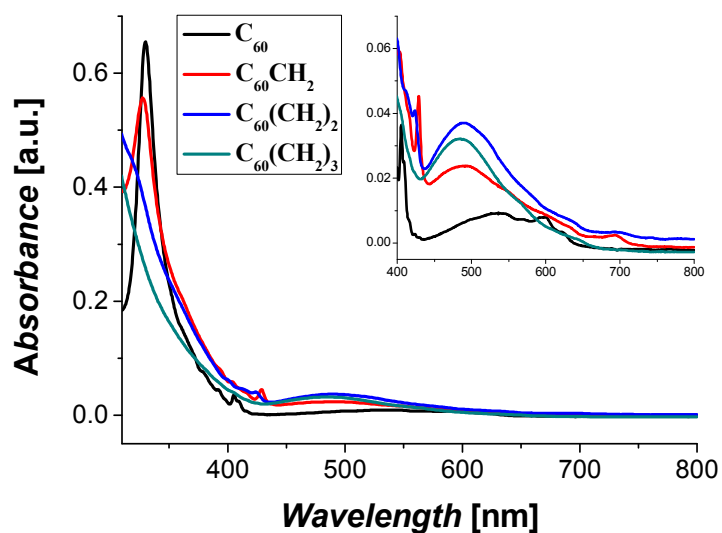


**Figure S31.** Mass spectrum of QBMF.

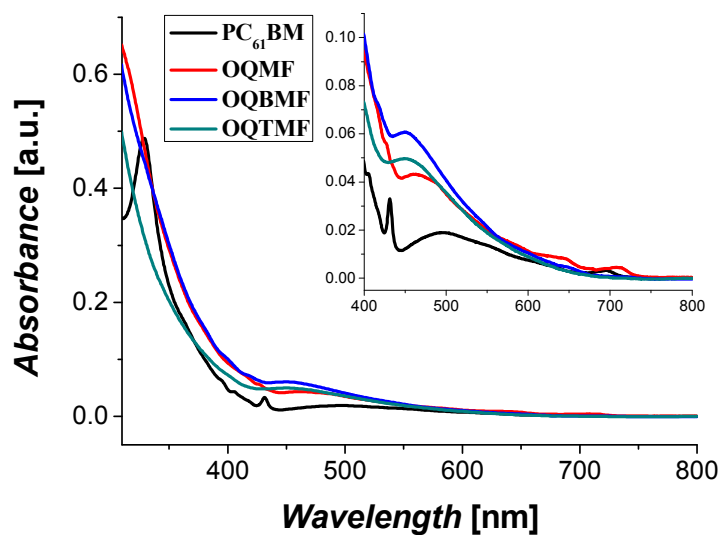


**Figure S32.** Mass spectrum of QTMF.

## 7. Absorption spectra

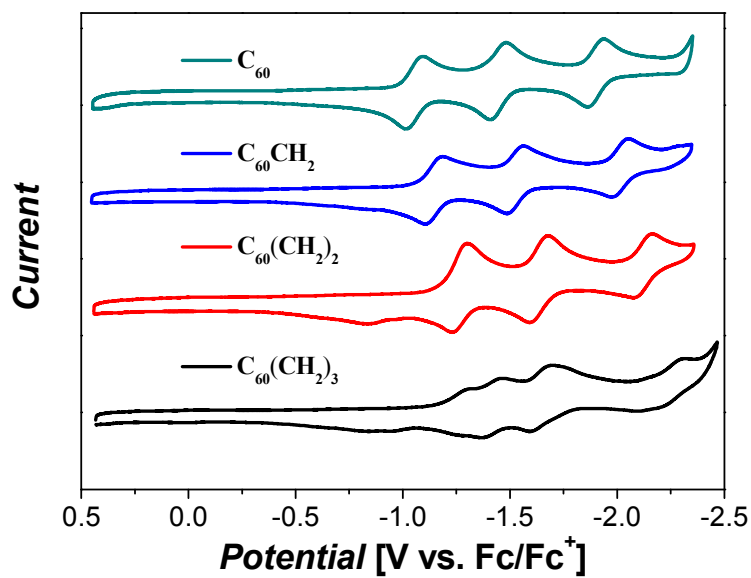


**Figure S33.** Absorption spectra of C<sub>60</sub>, C<sub>60</sub>CH<sub>2</sub>, C<sub>60</sub>(CH<sub>2</sub>)<sub>2</sub> and C<sub>60</sub>(CH<sub>2</sub>)<sub>3</sub> in CHCl<sub>3</sub> (10<sup>-5</sup> mol/L).

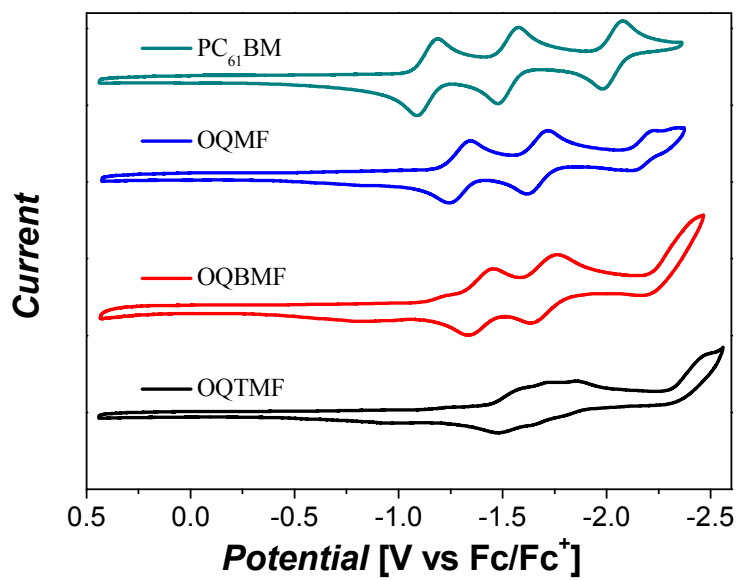


**Figure S34.** Absorption spectra of PC<sub>61</sub>BM, OQMF, OQBMF and OQTMF in CHCl<sub>3</sub> (10<sup>-5</sup> mol/L).

## 8. CV measurements



**Figure S35.** Cyclic voltammograms of C<sub>60</sub>, C<sub>60</sub>CH<sub>2</sub>, C<sub>60</sub>(CH<sub>2</sub>)<sub>2</sub> and C<sub>60</sub>(CH<sub>2</sub>)<sub>3</sub>.



**Figure S36.** Cyclic voltammograms of PC<sub>61</sub>BM, OQMF, OQBMF and OQTMF.

**Table S2.** Electrochemical and optical properties of fullerenes.

Compound	$E_{1/2}^{\text{red1}}$ [V]	$E_{1/2}^{\text{red2}}$ [V]	$E_{1/2}^{\text{red3}}$ [V]	LUMO <sup>a</sup> [eV]	$\lambda_{\text{onset}}$ [nm]	$E_g^{\text{opt } b}$ [eV]	HOMO <sup>c</sup> [eV]
C <sub>60</sub>	-1.05	-1.44	-1.90	-3.75	644	1.93	-5.68
C <sub>60</sub> CH <sub>2</sub>	-1.14	-1.52	-2.02	-3.66	724	1.71	-5.37
C <sub>60</sub> (CH <sub>2</sub> ) <sub>2</sub>	-1.27	-1.63	-2.12	-3.53	734	1.69	-5.22
C <sub>60</sub> (CH <sub>2</sub> ) <sub>3</sub>	-1.42	-1.64	-2.21	-3.38	698	1.78	-5.16
PC <sub>61</sub> BM	-1.14	-1.53	-2.03	-3.66	716	1.73	-5.39
OQMF	-1.29	-1.67	-2.17	-3.51	735	1.69	-5.20
OQBMF	-1.40	-1.70	N. D. <sup>d</sup>	-3.40	699	1.77	-5.17
OQTMF	-1.60	N. D.	N. D.	-3.20	688	1.80	-5.00

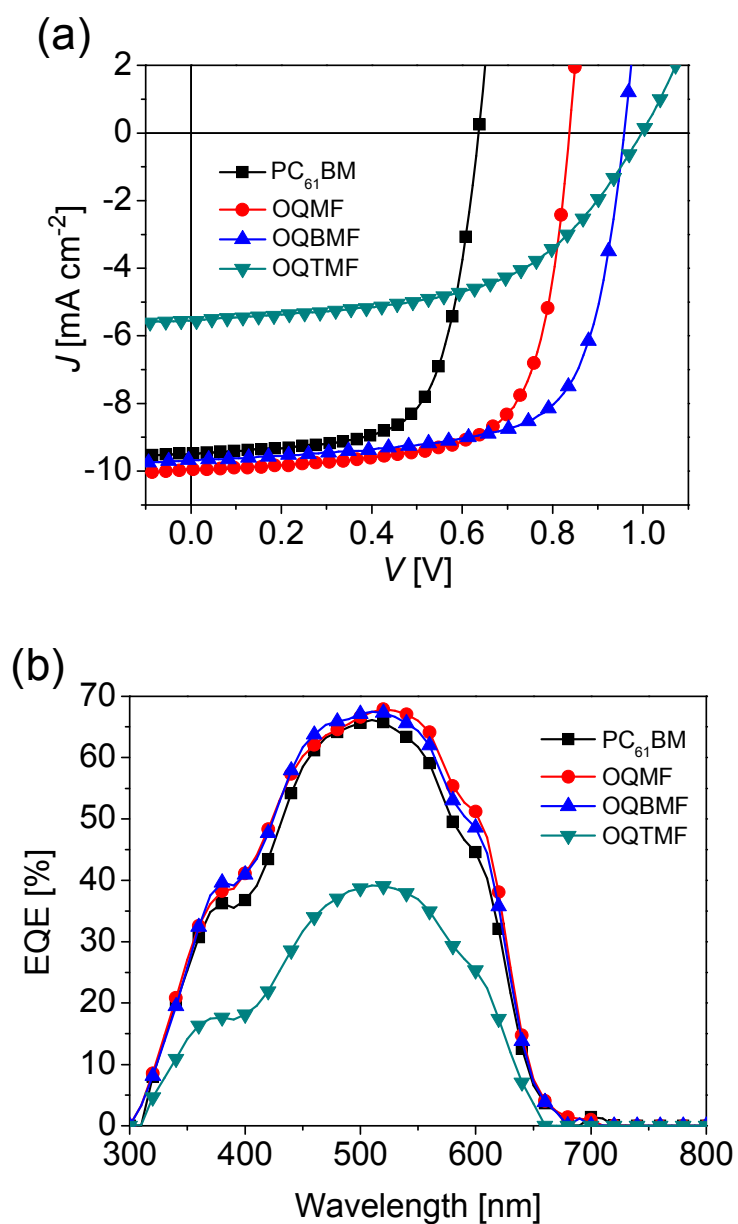
<sup>a</sup> LUMO =  $-(4.8 + E_{1/2}^{\text{red1}})$  eV

<sup>b</sup>  $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$

<sup>c</sup> HOMO = LUMO -  $E_g^{\text{opt}}$

<sup>d</sup> not detected

## 9. $J$ - $V$ curves and EQE spectra



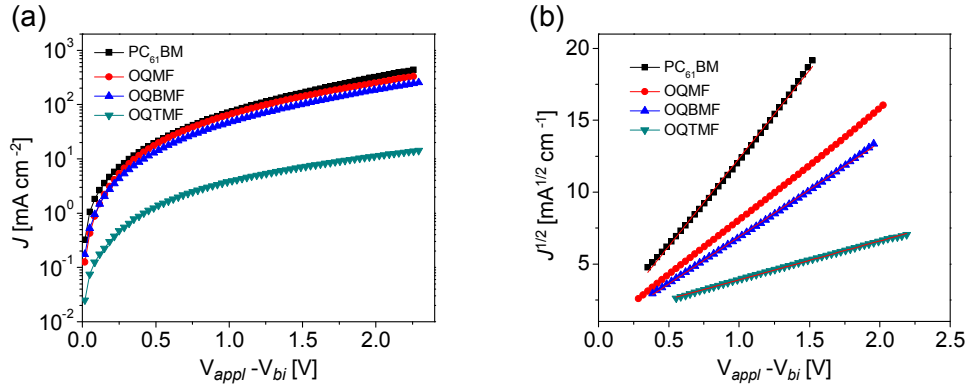
**Figure S37.**  $J$ - $V$  curves (a) and EQE spectra (b) for fullerene/P3HT solar cells.

## 10. Space charge limited current (SCLC) measurements

Charge carrier mobility was measured by SCLC method. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$$

where  $J$  is the current density,  $\mu$  is the zero-field mobility of electrons,  $\epsilon_0$  is the permittivity of the vacuum,  $\epsilon_r$  is the relative permittivity of the material,  $d$  is the thickness of the blend film, and  $V$  is the effective voltage,  $V = V_{\text{appl}} - V_{\text{bi}}$ , where  $V_{\text{appl}}$  is the applied voltage, and  $V_{\text{bi}}$  is the built-in potential determined by electrode workfunction difference. Figure S38 (a) shows  $J$ - $V$  curves for the electron-only devices. The mobility was calculated from the slope of  $J^{1/2}$ - $V$  curves.



**Figure S38.**  $J$ - $V$  curves (a) and the corresponding  $J^{1/2}$ - $V$  curves (b) for electron-only devices (in dark). The thicknesses of the blend films are 92 nm, 100 nm, 99 nm, and 105 nm, respectively.