Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information (ESI)

Experimental

All moisture sensitive reactions were carried out under an atmosphere of argon using dried glassware. 1,2-Dichlorobenzene was freshly distilled from P_2O_5 before use. Compounds **1a**, **3a**, and **5a** were purchased from Tokyo Chemical Industry CO., LTD. and were used without further purification.

^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-ECX-400P spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to tetramethylsilane (TMS) and are referenced to internal TMS or residual non-deuterated solvent. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured on a Bruker Daltonics autoflex III smartbeam with 1,1,4,4-tetraphenylbuta-1,3-diene (TPB) as the matrix. Absorption spectra were recorded on JASCO V-670 spectrophotometer. The electrolysis process was carried out with a BAS ALS 630DT potentiostat/galvanostat and performed in a divided glass cell (K-3) consisting of two platinum plate electrodes that was obtained from Techno Sigma Co.

Procedure for preparation and reaction of C_{60} radical anion

General procedure for preparation and reaction of C_{60} radical anion

C_{60} radical anion (18.0 mg, 0.025 mmol) was prepared by bulk electrolysis of C_{60} (18.0 mg, 0.025 mmol) in 1,2-dichlorobenzene (15 mL) containing tetrabutylammonium perchlorate (TBAP: 0.684 g, 2.0 mmol). The applied potential was chosen based on in situ CV measurements and was more negative than E_{red} for the C_{60}/C_{60} radical anion redox pair. The production and consumption of the C_{60} radical anion was confirmed by vis NIR absorption spectra. Alkyl halide was added to the generated C_{60} radical anion, and the solution was stirred at room temperature. After evaporation of the solvent, CS_2 was added and removed TBAP by filtration. Purification and isolation of recovered C_{60} and the corresponding C_{60} adducts were accomplished by FC or preparative HPLC (Buckyprep ϕ20 x 250 mm; Cosmsil; Nacalai Tesque Inc., toluene. Flow rate 9.9 mL min^{-1}).

Entry 1: **2a** was prepared in 40% yield (17.6 mg, 0.020 mmol) from C_{60} (36.0 mg, 0.05 mmol) and **1a** (119.1 mg, 0.50 mmol) in 1,2-dichlorobenzene (30 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **1a**. HPLC gave pure **2a** and C_{60} in 48% (17.4 mg, 0.024 mmol).

Entry 2: **2b** was prepared in 38% yield (8.1 mg, 0.0096 mmol) from C_{60} (18.1 mg, 0.025 mmol) and **1b** (52.4 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **1b**. Flash chromatography (SiO_2 toluene/hexane 1:1, toluene, then toluene/AcOEt 1:1) gave pure **2b** and C_{60} in 52% (9.5mg, 0.013 mmol).

Entry 3: **2c** was prepared in 42% yield (9.5 mg, 0.010 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **1c** (67.8 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **1c**. Flash chromatography (toluene/hexane 1:1, then toluene) gave pure **2c** and C_{60} in 55% (9.9 mg, 0.014 mmol).

Entry 4: **2d** was prepared in 34% yield (7.5 mg, 0.085 mmol) from C_{60} (18.1 mg, 0.025 mmol) and **1d** (60.3 mg, 0.25 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **1d**. Flash chromatography (toluene, then toluene/AcOEt 1:1) gave pure **2d** and C_{60} in 60% (10.8 mg, 0.015 mmol).

Entry 5: **2e** was prepared in 30% yield (7.1 mg, 0.0075 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **1e** (75.8 mg, 0.25 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **1e**. HPLC gave pure **2e** and C_{60} in 58% (10.5 mg, 0.015 mmol).

Entry 6: **2a** was prepared in 29% yield (6.3 mg, 0.0072 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **1f** (79.0 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **1f**. Flash chromatography (SiO_2 toluene/hexane1:1, toluene, then toluene/AcOEt 1:1) gave pure **2a** and C_{60} in 58% (10.4 mg, 0.014 mmol).

Entry 7: **2a** was prepared in 38% yield (8.3 mg, 0.0094 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **1f** (5.0 mg, 0.016 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **1f**. Flash chromatography (SiO_2 toluene/hexane1:1, toluene, then toluene/AcOEt 1:1) gave pure **2a** and C_{60} in 40% (7.2 mg, 0.010 mmol).

Entry 8: **4** was prepared in 11% yield (2.5 mg, 0.0028 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **3a** (42.8 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 20 h at room temperature after the addition of **3a**. HPLC gave pure **4** and C_{60} in 39% (7.1 mg, 0.0099 mmol).

Entry 9: **4** was prepared in 17% yield (3.8 mg, 0.0042 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **3a** (213 mg, 1.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 18 h at room temperature after the addition of **3a**. HPLC gave pure **4** and C_{60} in 61% (11.0 mg, 0.015 mmol).

Entry 10: **4** was prepared in 31% yield (6.9 mg, 0.0076 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **3b**

(54.8 mg, 0.25 mmol) in 1,2-dichlorobenzene (15 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **3b**. HPLC gave pure **4** and C_{60} in 44% (8.0 mg, 0.011 mmol).

Entry 11: **6** was prepared in 41% yield (8.5 mg, 0.010 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **5a** (66.1 mg, 0.25 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 72 h at room temperature after the addition of **5a**. HPLC gave pure **6** and C_{60} in 56% (10.1 mg, 0.014 mmol).

Entry 12: **6** was prepared in 33% yield (6.7 mg, 0.0081 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **5b** (89.3 mg, 0.25 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 30 min at room temperature after the addition of **5b**. HPLC gave pure **6** and C_{60} in 63% (11.3 mg, 0.016 mmol).

Entry 13: **6** was prepared in 39% yield (8.1 mg, 0.0098 mmol) from C_{60} (18.0 mg, 0.025 mmol) and **5b** (5.4 mg, 0.015 mmol) in 1,2-dichlorobenzene (16 mL) containing 0.13 M TBAP. The solution was stirred for 1 h at room temperature after the addition of **5b**. HPLC gave pure **6** and C_{60} in 44% (8.0 mg, 0.011 mmol).

Spectral data (**2d**)
^{1}H NMR (400 MHz, CS_2:$CDCl_3$=1:1)
δ 2.75 (s, 3H), 7.58-7.61 (m, 2H), 7.68-7.73 (m, 1H), 8.53-8.56 (m, 2H)
^{13}C NMR (100 MHz, CS_2:$CDCl_3$=1:1)
δ 27.75, 66.99, 73.36, 129.38, 130.07, 134.00, 134.97, 137.23, 138.44, 141.04, 141.87, 142.10, 142.85, 142.89, 143.00, 143.04, 143.65, 143.69, 144.40, 144.55, 144.61, 144.68, 145.07, 145.12, 145.44, 145.75, 186.31, 193.69
MALDI-TOF-MS (TPB) calcd for $C_{70}H_8O_2^-$ ($[M]^-$): *m/z* (%): 880.052; found 879.894.

Synthesis of **1b**, **1c**, **1d**, **1e**, **1f**, **3b**, and **5b** was conducted according to literature procedures.
1b, **1c**, **1d**, **1e**: *Synlett.*, 2006, **14**, 2287.
1f: *Tetrahedron Lett.*, 2005, **46**, 4749.
3b, **5b**: *J. Org. Chem.*, 2009, **74**, 4177.

Synthetic procedure:
1c. A mixture of ethyl benzoylacetate (1.29 mL, 7.5 mmol), KBr (4.46 g, 37.5 mmol), 1 M aq HCl (37.5 mL), and 30% H_2O_2 (17 mL) in toluene (37.5 mL) was stirred for 2 h at room temperature. The organic layer was washed with a saturated aqueous solution of sodium bicarbonate, a saturated aqueous solution of sodium thiosulfate, and brine. The organic layer was dried over $MgSO_4$ and

concentrated under reduced pressure. Flash chromatography afforded pure **1c** (1.83 g, 90%) as a pale-yellow oil.

1f. Bromine (0.9 mL, 17.5 mmol) was added to a solution of sodium hydroxide (2.2 g, 55 mmol) in water (25 mL) at -6 °C. The mixture was stirred for 30 min then added dropwise to a solution of diethyl malonate (0.92 mL, 6.1 mmol) in acetone (25 mL) and glacial acetic acid (10 mL) at -8 °C. The reaction mixture was stirred for 1 h at 0 °C, then extracted with CH_2Cl_2. The organic layer was washed with a saturated aqueous solution of sodium thiosulfate, a saturated aqueous solution of sodium bicarbonate, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. Flash chromatography afforded pure **1f** (1.74 g, 5.5 mmol) as a pale-yellow oil in 90% yield.

3b. Benzyl bromide (0.6 mL, 5 mmol) and NaI (1.5 g, 10 mmol) were dissolved in acetone (7 mL). The mixture was stirred for 24 h at room temperature in the dark. The reaction was quenched with water (20 mL) and extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford pure **3b** as a colorless oil in 93% yield (1.02 g, 4.7 mmol).

5b. 1,2-bis(bromomethyl)benzene (0.66 g, 2.5 mmol) and NaI (1.5 g, 10 mmol) were dissolved in acetone (7 mL). The mixture was stirred for 24 h at room temperature in the dark. The reaction was quenched with water (20 mL) and extracted with diethyl ether. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to afford pure **5b** as a pale-yellow solid in 96% yield (0.86 g, 2.4 mmol).

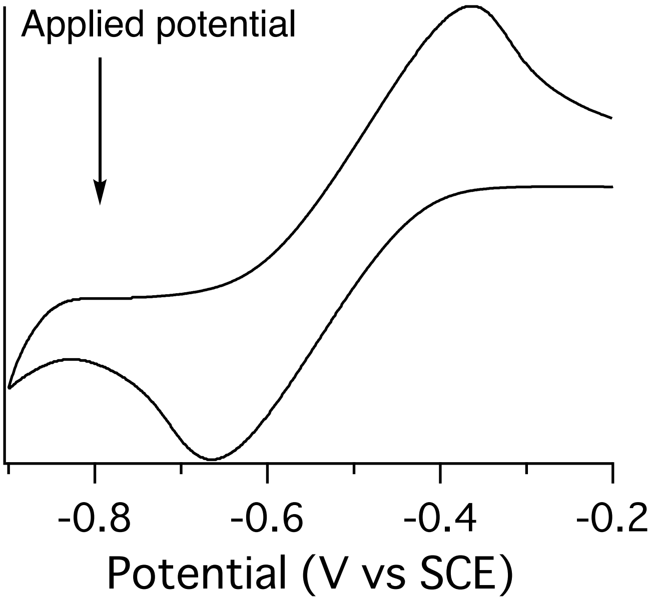

Figure S1. In situ cyclic voltammogram of C_{60} at 100 mV/s in 1,2-DCB containing 0.13 M TBAP before bulk electrolysis.

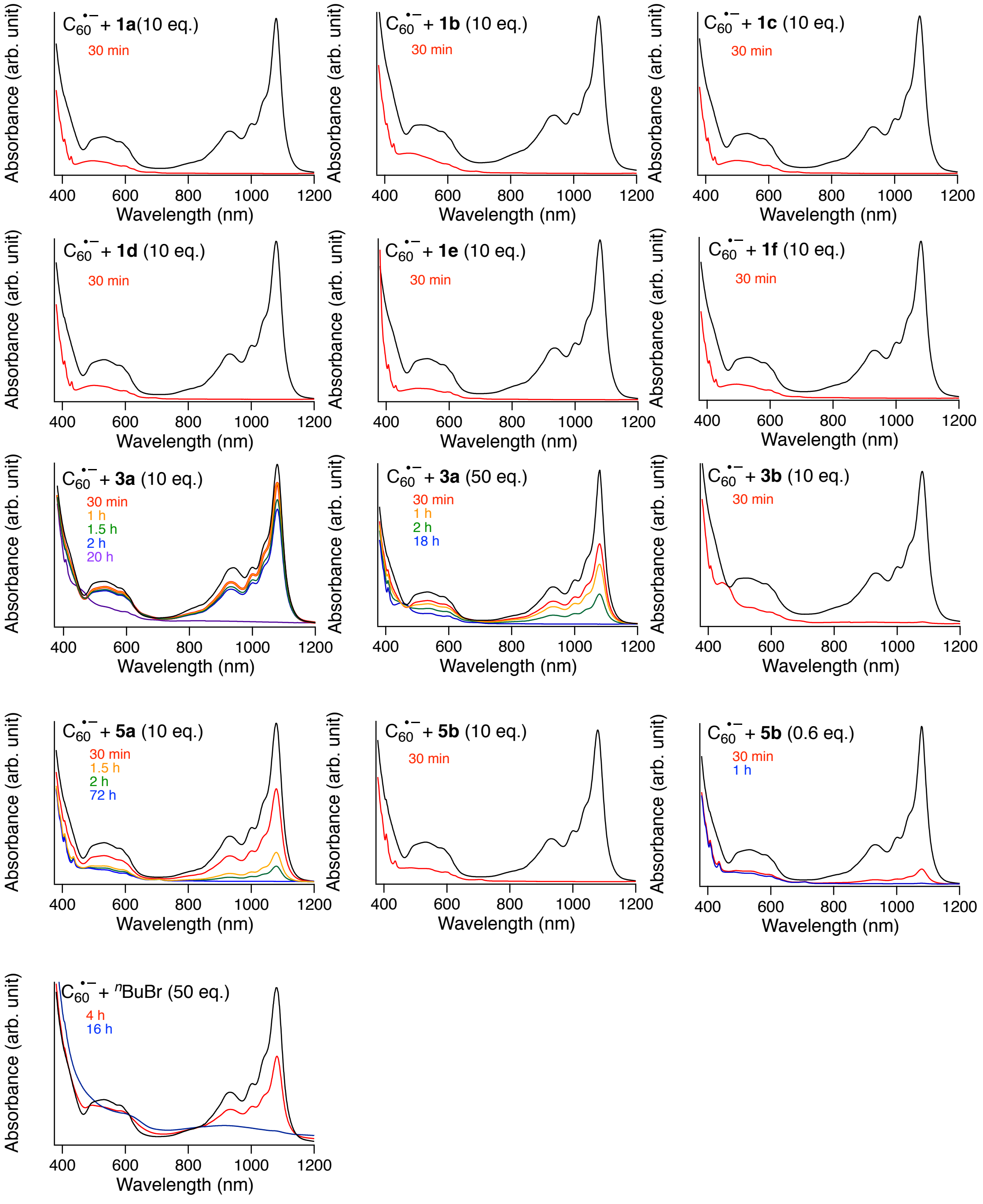

Figure S2. Absorption spectra of C_{60} radical anion before and after the addition of alkyl halides.

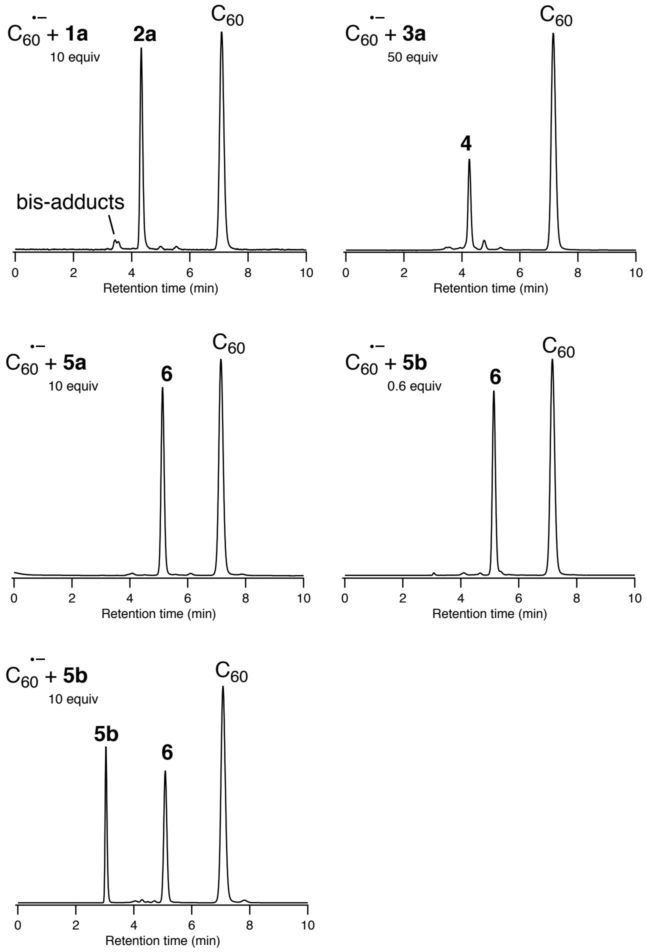

Figure S3. HPLC profiles of reaction mixtures. Conditions: Column, Buckyprep ϕ4.6 x 250 mm; temp., 40°C; flow rate, 1 mL min^{-1}; eluent, toluene; monitor, 330 nm detection.

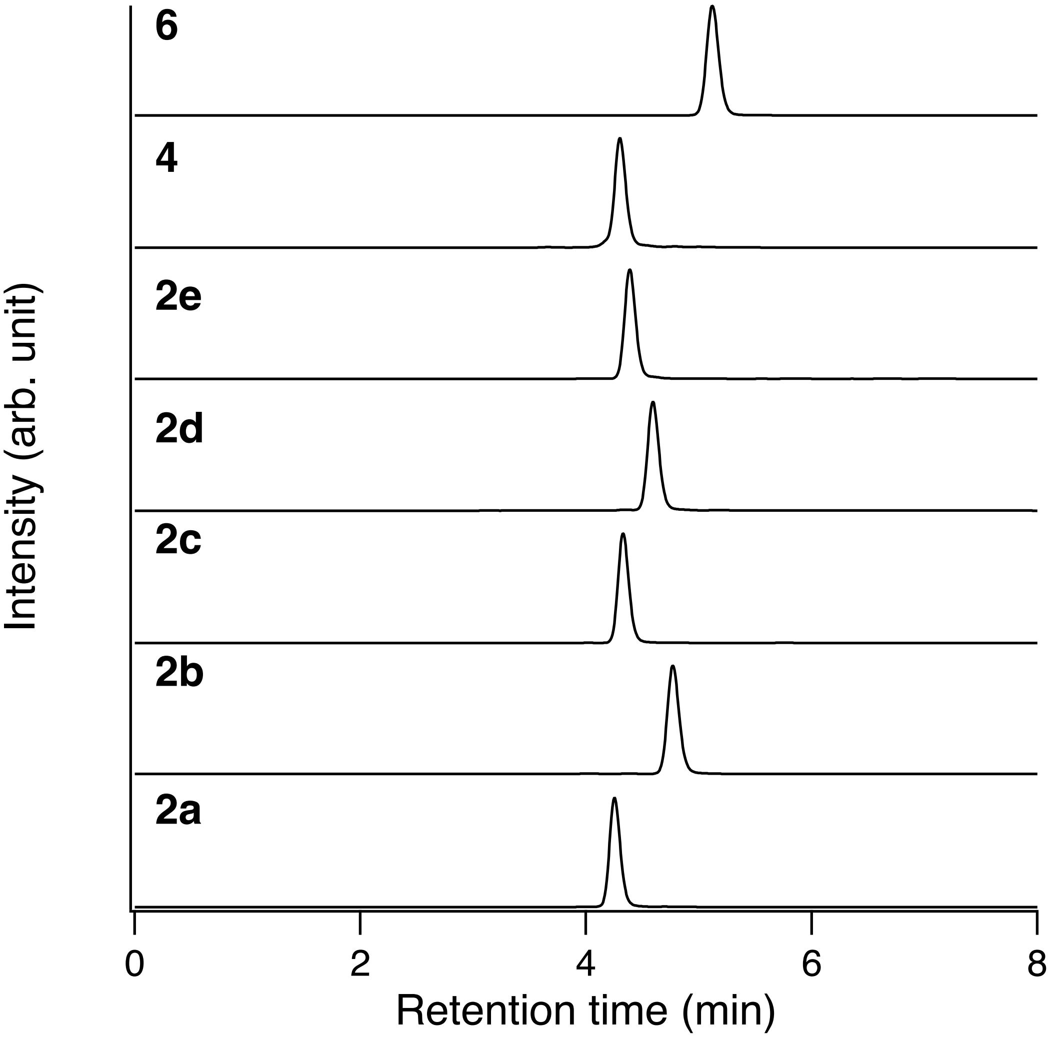

Figure S4. HPLC profiles of isolated fullerene derivatives. Conditions: Column, Buckyprep ϕ4.6 x 250 mm; temp., 40˚C; flow rate, 1 mL min^{-1}; eluent, toluene; monitor, 330 nm detection.

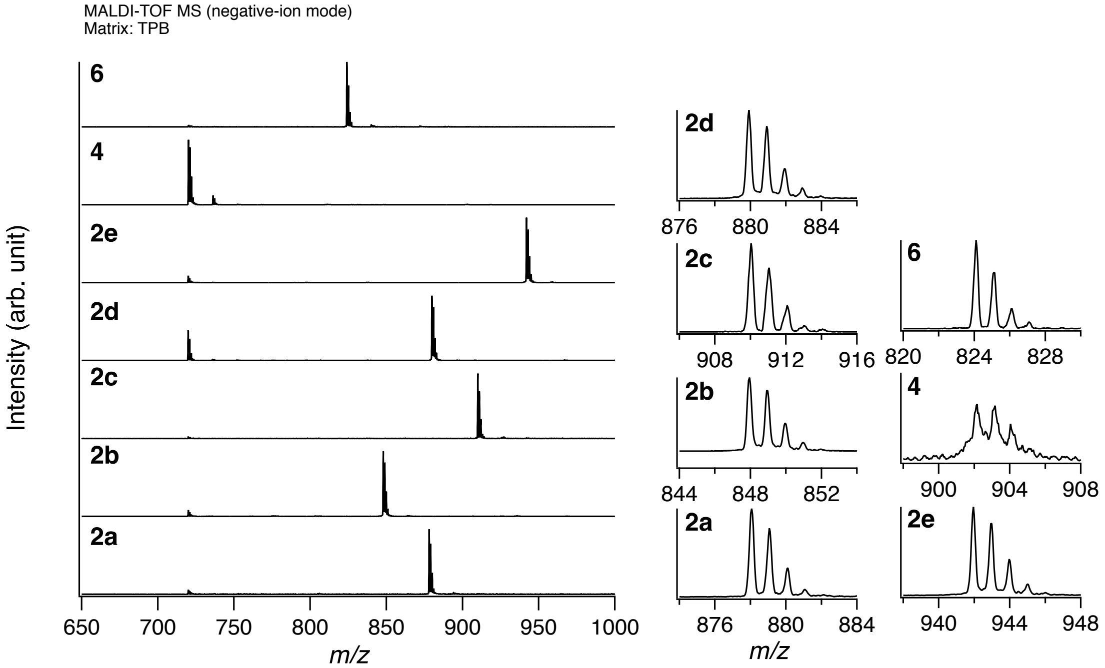

Figure S5. MALDI-TOF mass spectra of isolated fullerene derivatives in negative-ion mode.

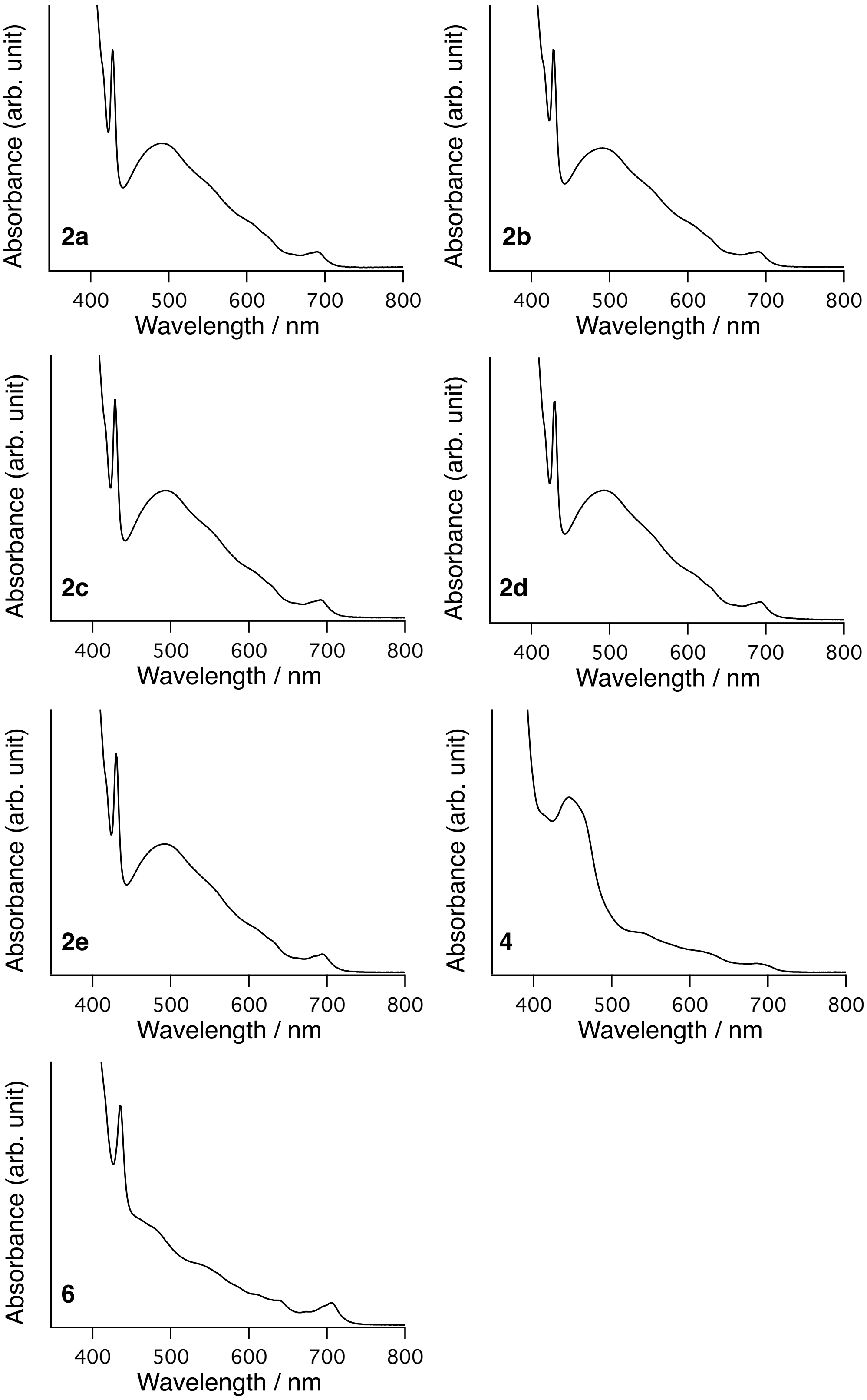

Figure S6. Absorption spectra of isolated fullerene derivatives in CS_2.

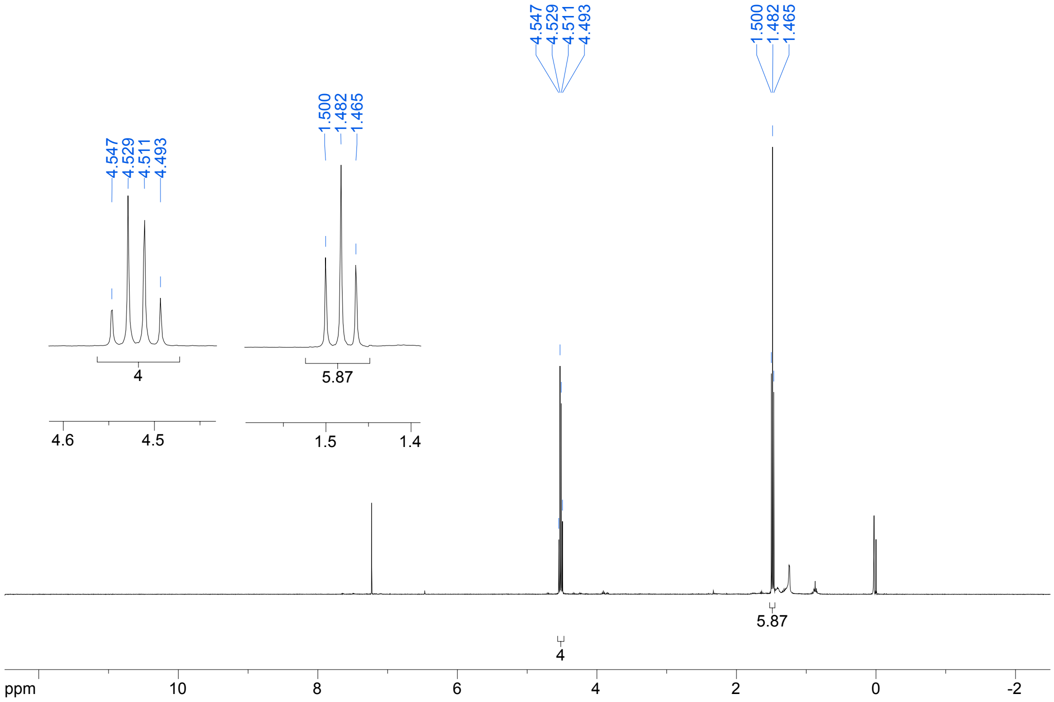

Figure S7. ^{1}H NMR spectrum of $C_{61}(CO_2Et)_2$ (**2a**) in $CDCl_3/CS_2$=1:1.

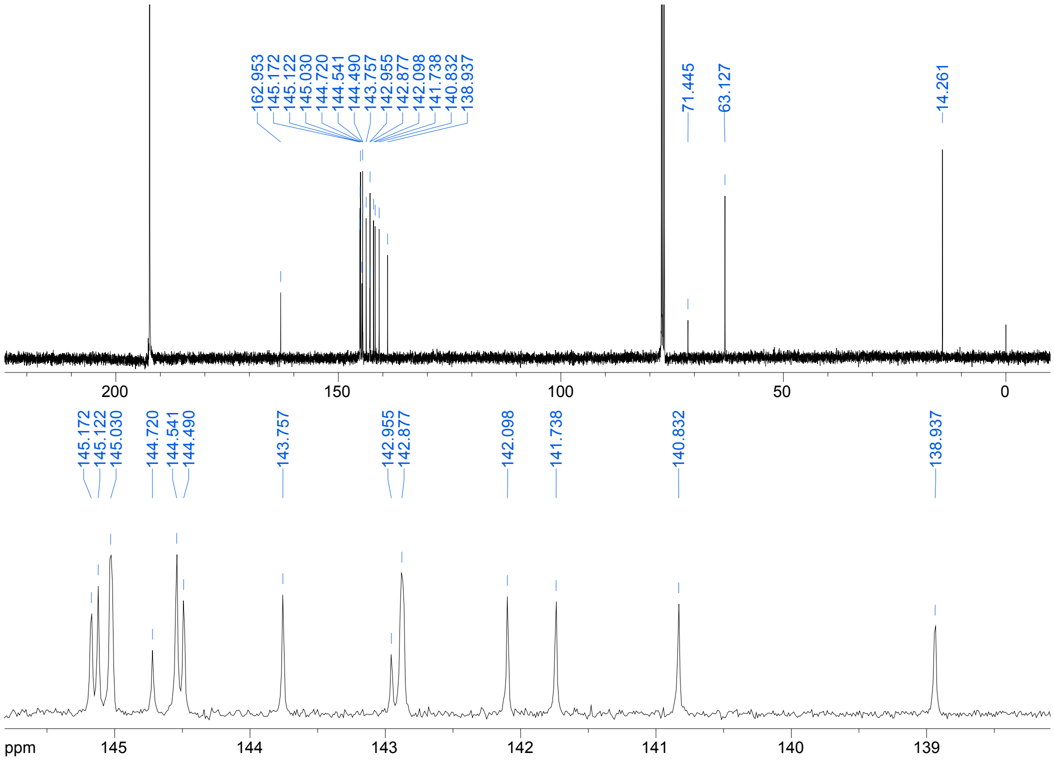

Figure S8. ^{13}C NMR spectrum of $C_{61}(CO_2Et)_2$ (**2a**) in $CDCl_3/CS_2$=1:1.

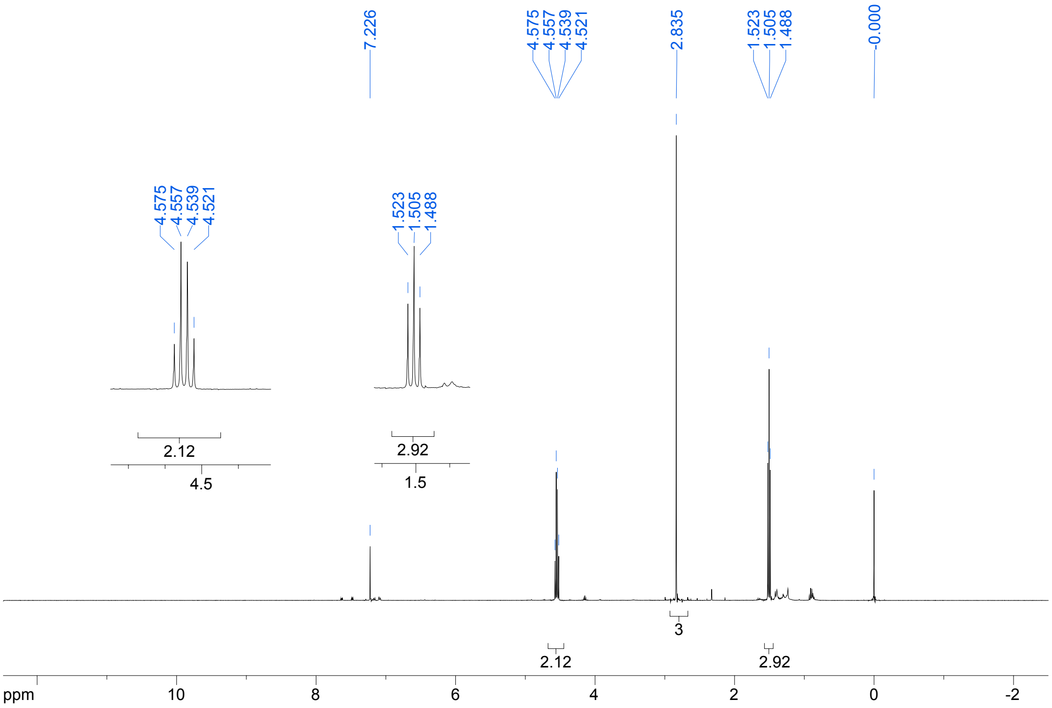

Figure S9. ^{1}H NMR spectrum of $C_{61}(COMe)(CO_2Et)$ (**2b**) in $CDCl_3/CS_2$=1:1.

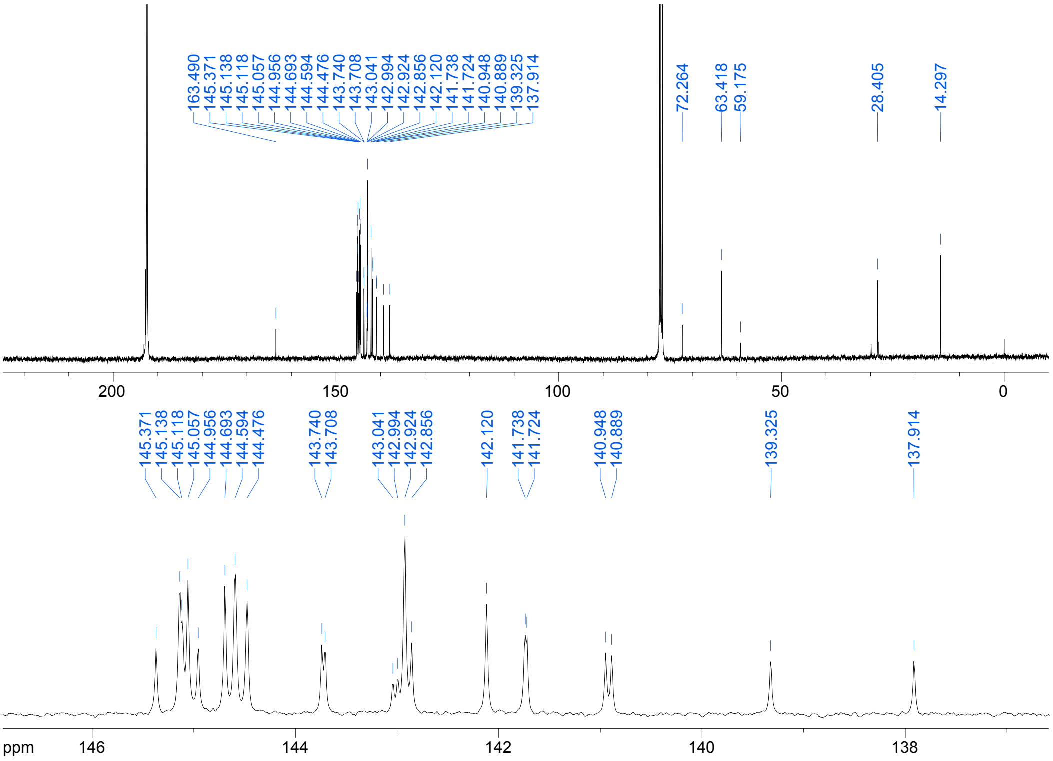

Figure S10. ^{13}C NMR spectrum of $C_{61}(COMe)(CO_2Et)$ (**2b**) in $CDCl_3/CS_2$=1:1.

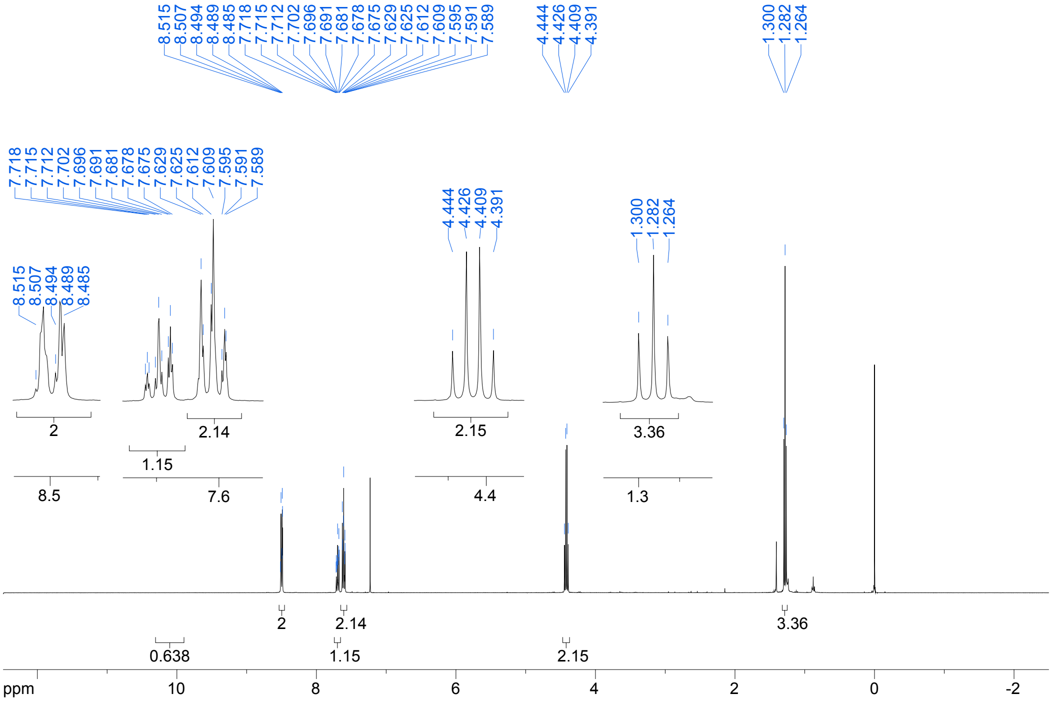

Figure S11. ^{1}H NMR spectrum of $C_{61}(COPh)(CO_2Et)$ (**2c**) in $CDCl_3/CS_2$=1:1.

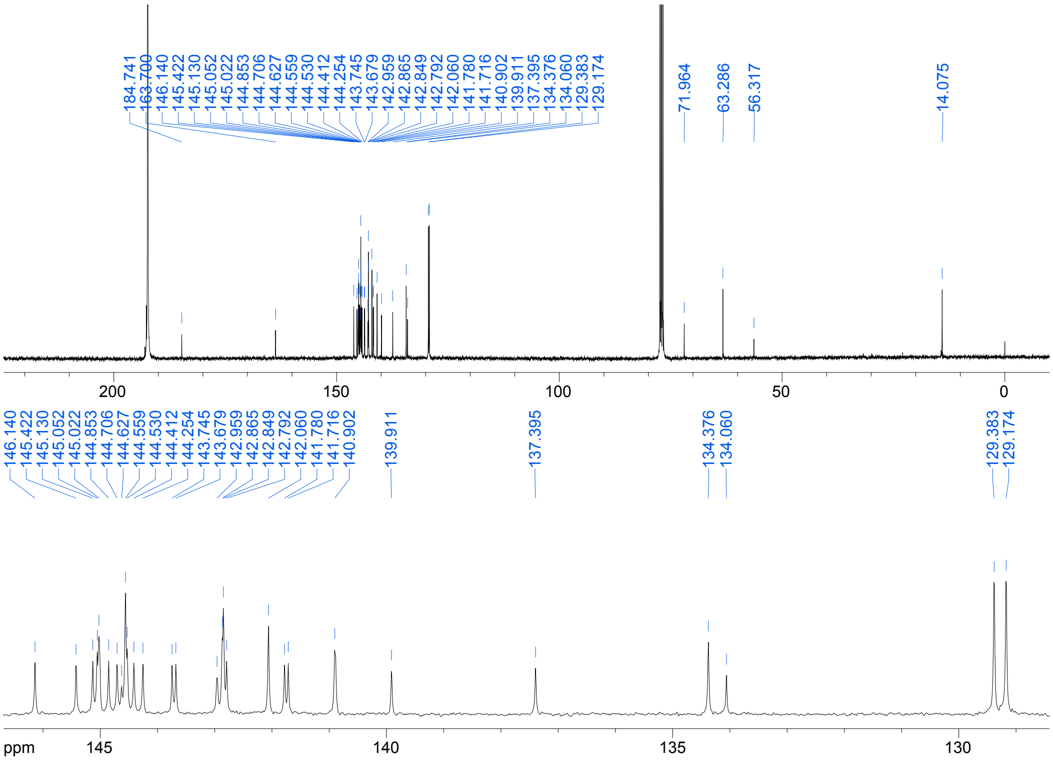

Figure S12. ^{13}C NMR spectrum of $C_{61}(COPh)(CO_2Et)$ (**2c**) in $CDCl_3/CS_2$=1:1.

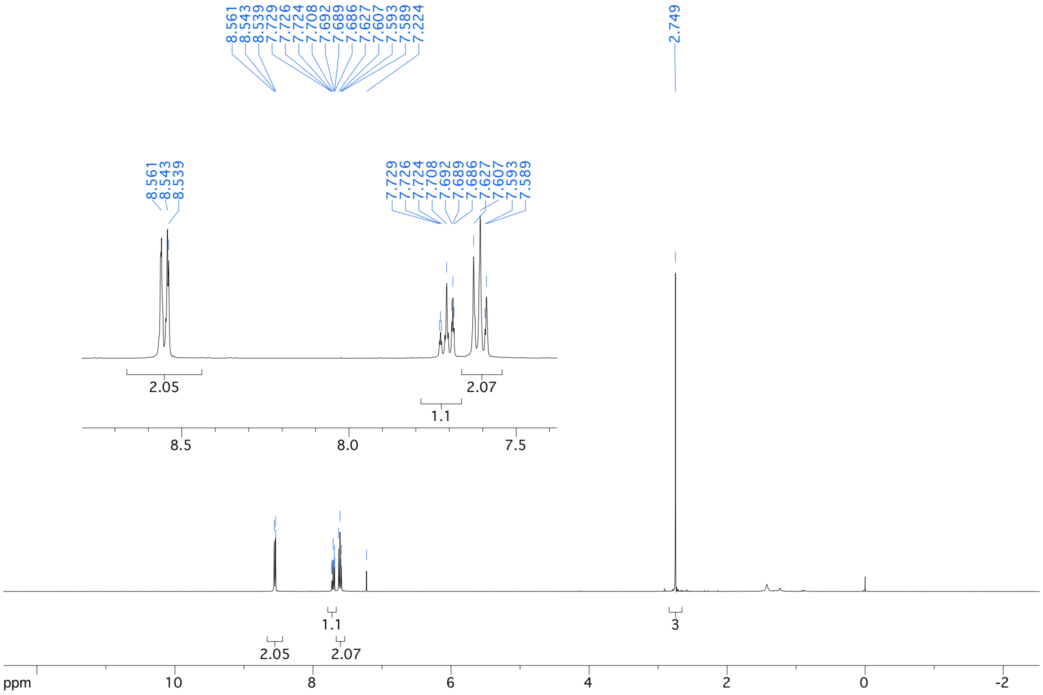

Figure S13. ^{1}H NMR spectrum of $C_{61}(COPh)(COCH_3)$ (**2d**) in $CDCl_3/CS_2$=1:1.

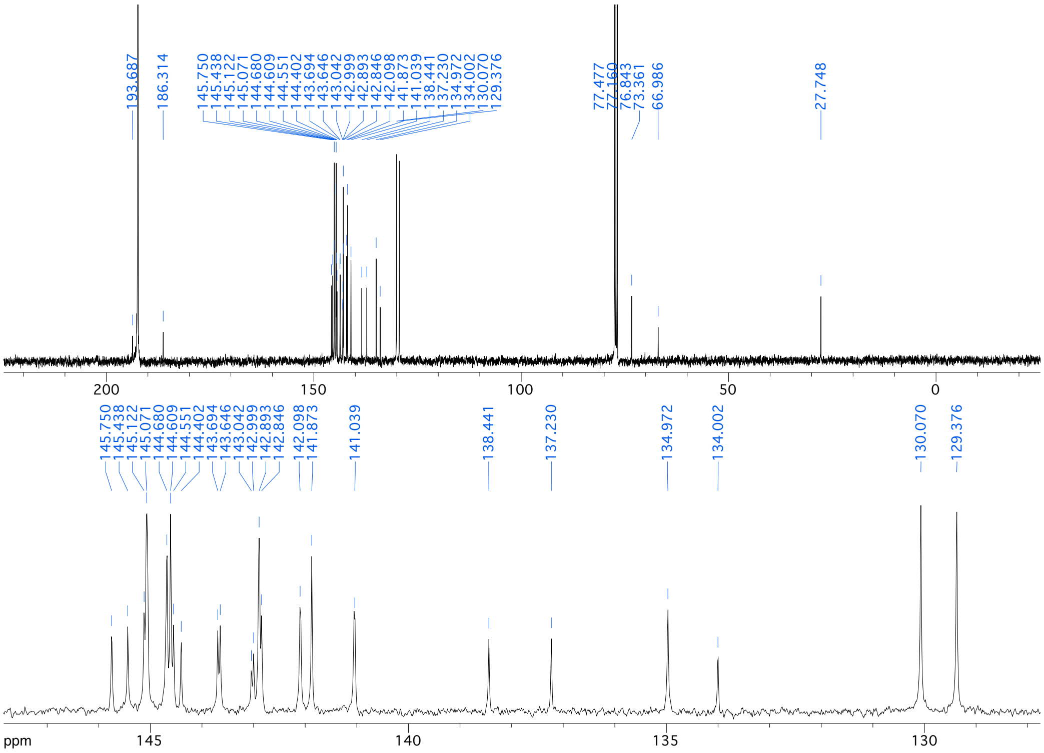

Figure S14. ^{13}C NMR spectrum of $C_{61}(COPh)(COCH_3)$ (**2d**) in $CDCl_3/CS_2$=1:1.

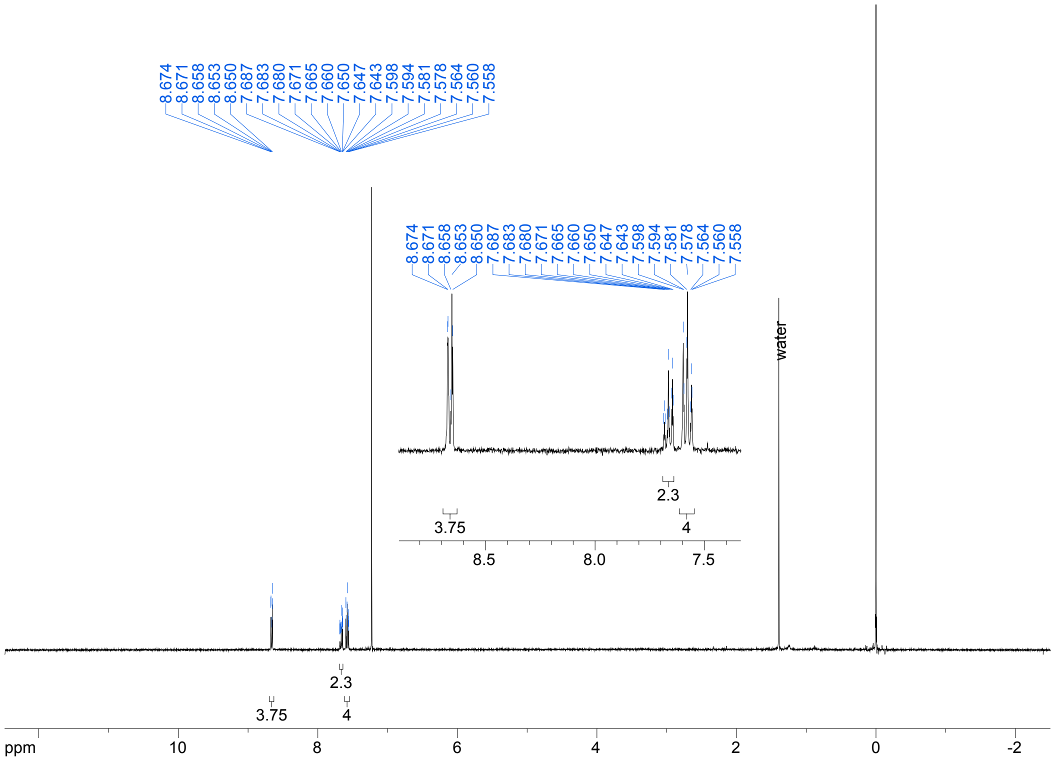

Figure S15. ^{1}H NMR spectrum of $C_{61}(COPh)_2$ (**2e**) in $CDCl_3/CS_2$=1:1.

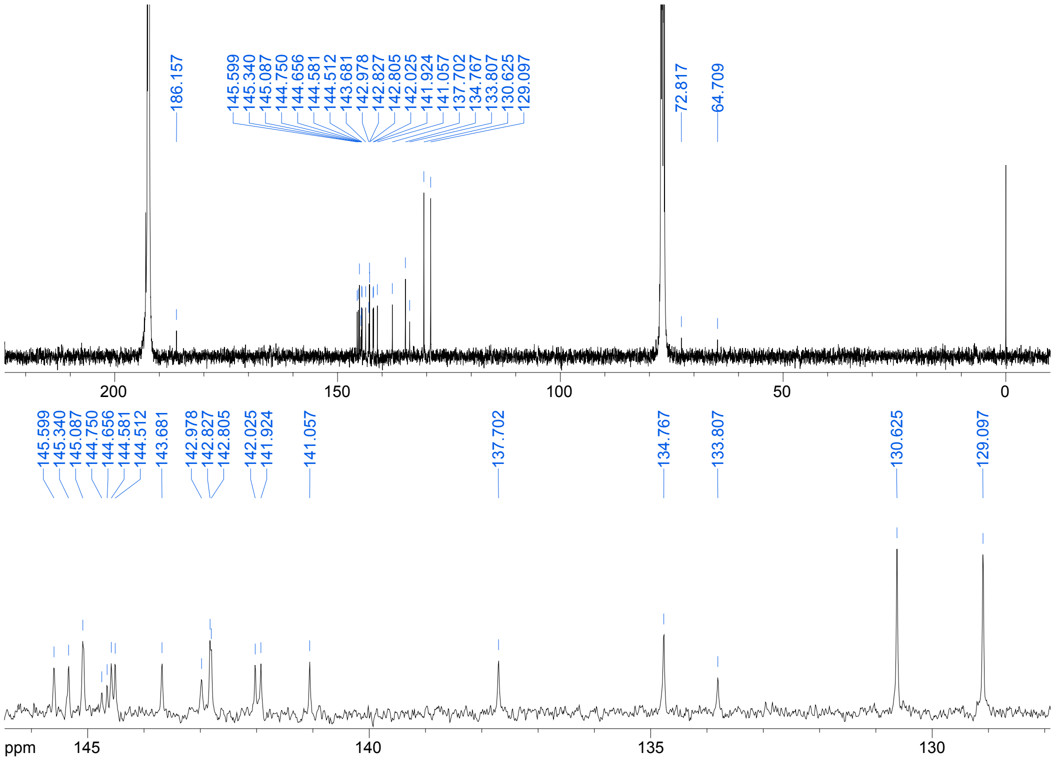

Figure S16. ^{13}C NMR spectrum of $C_{61}(COPh)_2$ (**2e**) in $CDCl_3/CS_2$=1:1.

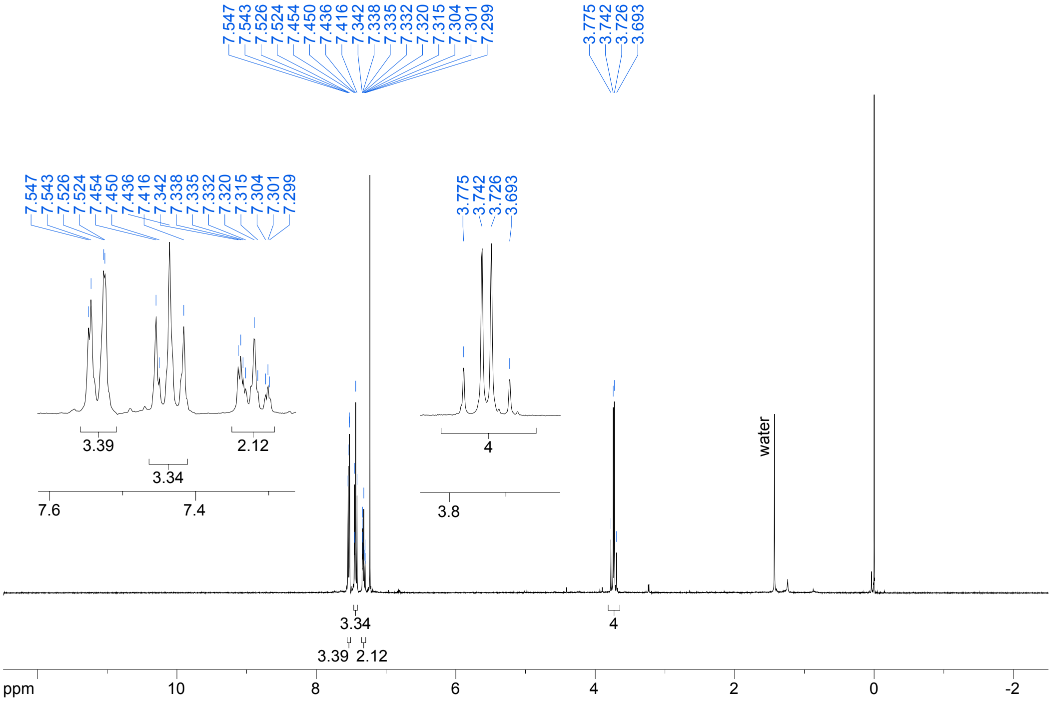

Figure S17. ^{1}H NMR spectrum of $C_{60}(CH_2Ph)_2$ (**4**) in $CDCl_3/CS_2$=1:1.

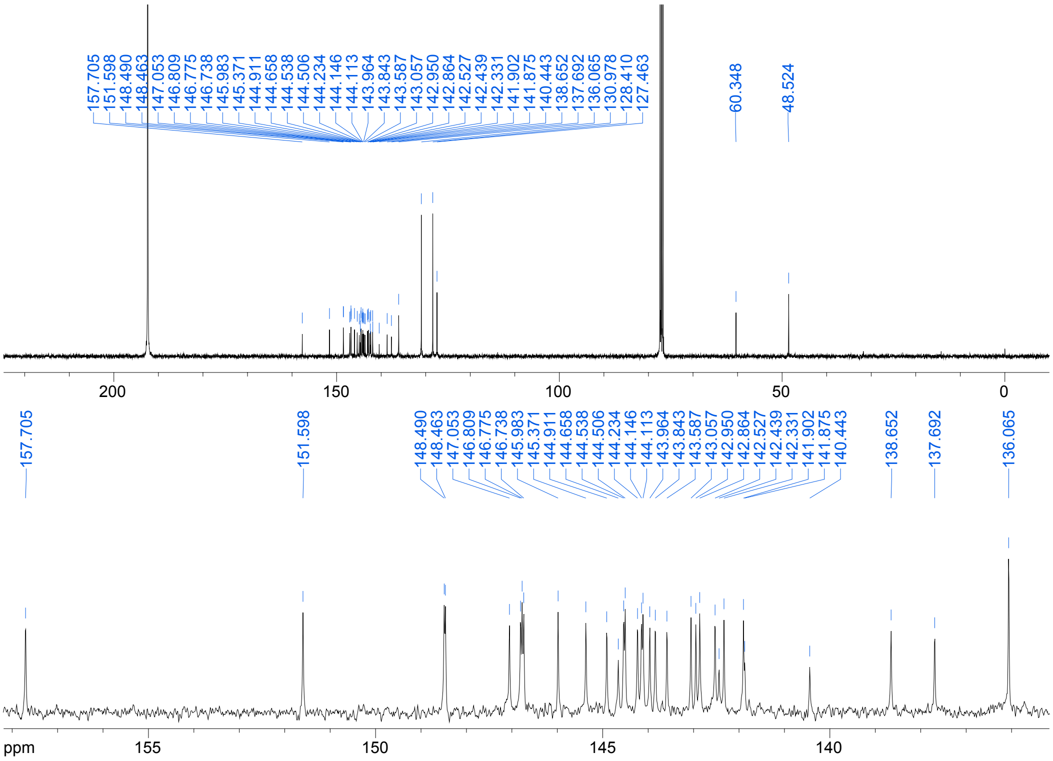

Figure S18. ^{13}C NMR spectrum of $C_{60}(CH_2Ph)_2$ (**4**) in $CDCl_3/CS_2$=1:1.

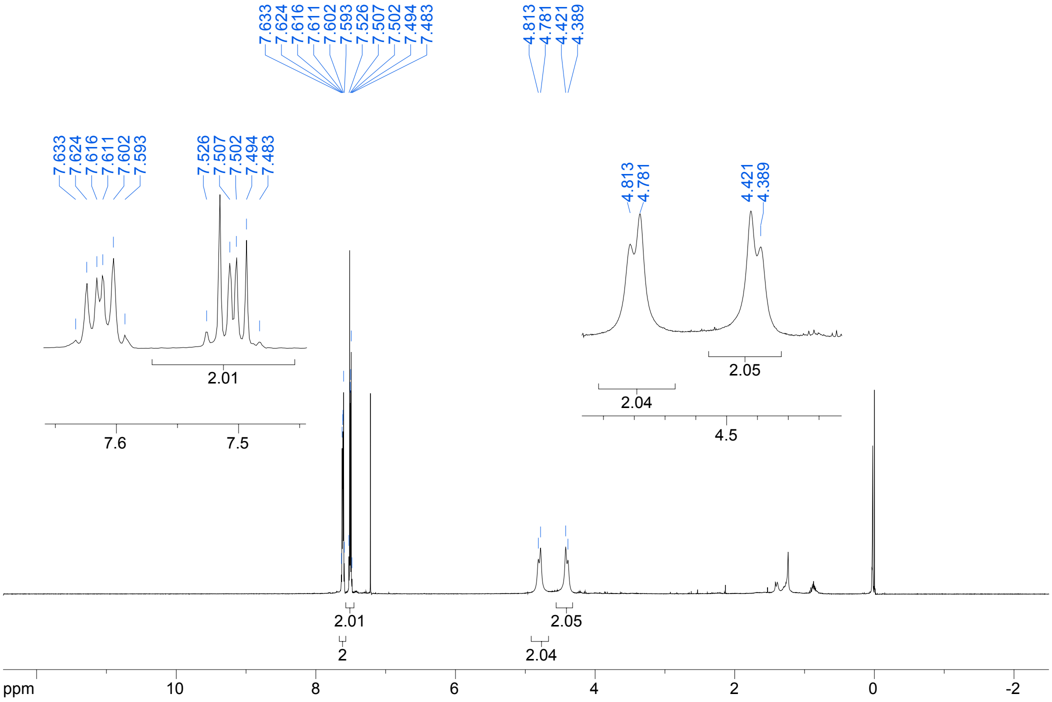

Figure S19. ^{1}H NMR spectrum of $C_{60}C_8H_8$ (**6**) in $CDCl_3/CS_2$=1:1.

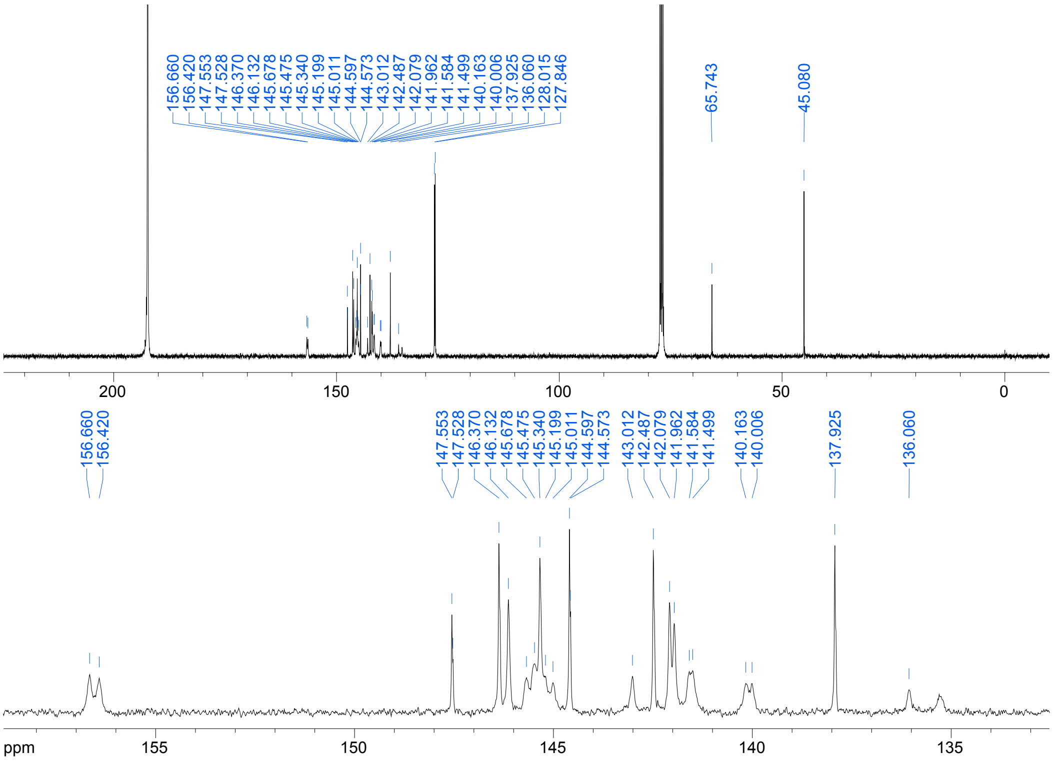

Figure S20. ^{13}C NMR spectrum of $C_{60}C_8H_8$ (**6**) in $CDCl_3/CS_2$=1:1.