Supporting Information

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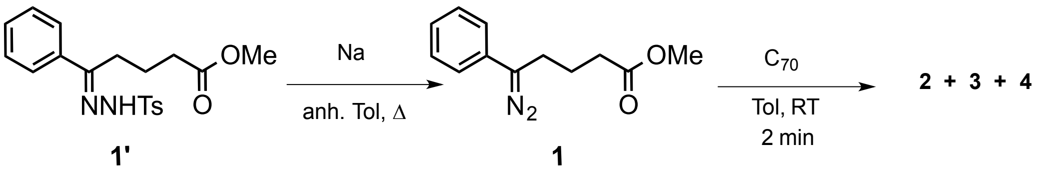
Reaction of Diazocompounds with C_{70}: Unprecedented Synthesis and Characterization of Isomeric [5,6]-Fulleroids

General Methods.

The commercially available reagents and solvents were used without further purification. All solvents were dried according to standard procedures. All air-sensitive reactions were carried out under argon atmosphere. NMR experiments were recorded on a BRUKER AVANCE-300 in $CDCl_3$ or $CS_2/CDCl_3$, or a BRUKER AVANCE AMX-700 in $CDCl_3$ or $CS_2/CDCl_3$ at 23°C, and referenced to $CDCl_3$; coupling constants (*J*) are reported in Hz and the chemical shifts (δ) in ppm. Cyclic voltammograms were recorded with a potentiostat/galvanostat AUTOLAB with PGSTAT30 equipped with GPES software for Windows version 4.9 in a conventional three-compartment cell by using a GCE (glassy carbon electrode) as the working electrode, $Ag/AgNO_3$ as the reference electrode, $Bu_4N{\cdot}PF_6$ as the supporting electrolyte, *o*-dichlorobenzene/acetonitrile as the solvent (4:1 v/v), and a scan rate of 100 mVs^{-1}. Mass spectra were recorded on a $HP_{1100}EMD$ (ESI), and BRUKER-REFLEX (MALDI-TOF). Reactions were monitored by thin-layer chromatography carried out on 0.2 mm TLC-aluminum sheets of silica gel (Merck, TLC Silica gel 60 F_{254}). Flash column chromatographies were performed using silica gel (230-400 mesh). The relative yields and the isolation of some products was carried out in HPLC, columns: 5PYE (4,6 ID x 250mm; toluene/hexane/acetonitrile (60:36:4); 0.5 ml/min; 320 nm; 25ºC), Buckyprep Waters (4,6 ID x 250mm; toluene/hexane/acetonitrile (60:36:4); 0.5 ml/min; 320 nm; 25ºC), and 5PYE semipreparative (10 ID x 250mm; toluene/hexane/acetonitrile (60:36:4); 1 ml/min; 320 nm; 25ºC). All the HPLC chromatograms were monitored in a 320 nm spectrophotometer detector. UV-vis spectra were recorded with a Shimadzu Spectrophotometer UV-3600 or directly in the HPLC UV diodes detector at 320nm.

Synthesis of compounds 2, 3 and 4:



To a solution of tosylhydrazone **1’** (previously described) (9 mg, 0.03 mmol, 2.5eq) in anhydrous toluene (4 ml) was added sodium (50-fold) and was refluxed until the color turned red indicating the formation of the diazocompound **1**. Then, the crude was filtered to remove the solid residues. To the solution of the diazocompound was added C_{70} (10 mg, 0.012 mmol, 1 eq) and the mixture was stirred for 2 minutes at room temperature. The solvent was removed under vacuum, and the crude was purified by silica-gel column chromatography using CS_2 as eluent to recover the unreacted C_{70}, and then, a mixture of solvents (toluene/hexane 8:2) to collect compounds **2**, **3** and **4** with 86% yield (based on recovered C_{70}). They were purified and isolated by HPLC. HPLC conditions: column: 5PYE; solvents: toluene/hexane/acetonitrile (60:36:4); flow: 0.5 ml/min; λ= 320 nm; temperature: 25ºC.

NMR experiments of mixture of compounds 2, 3 and 4:

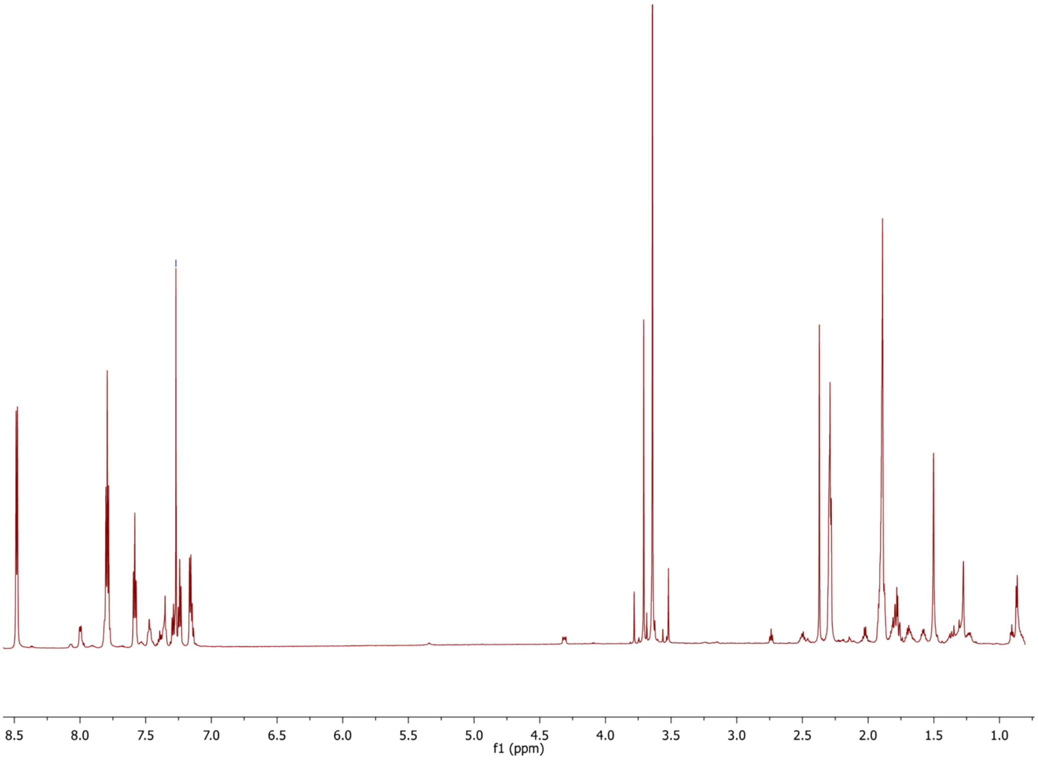


Figure S1. ^{1}H NMR (700 MHz, 298K, $CDCl_3$) of the mixture of compounds **2**, **3** and **4**.

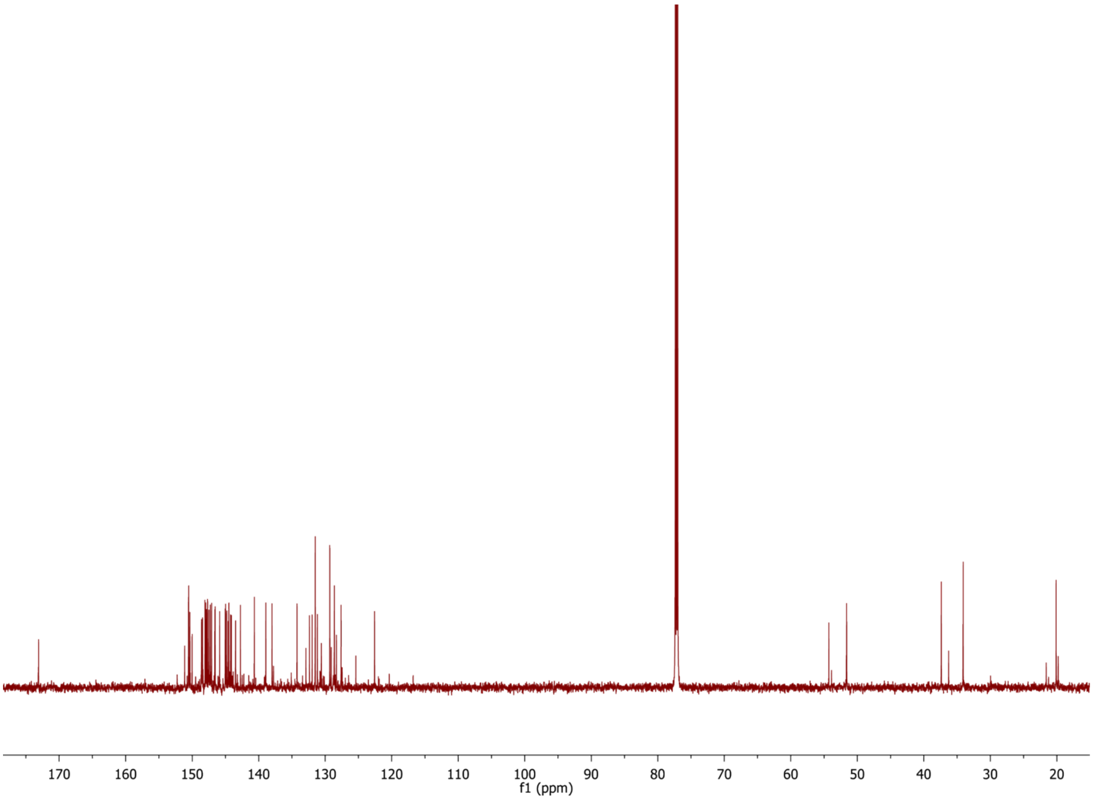
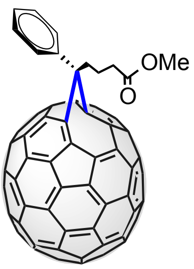


Figure S2. ^{13}C NMR (175 MHz, 298 K, $CDCl_3$) of the mixture of compounds **2**, **3** and **4**.

Compound 2: *a*-[5,6]PC$_{71}$BM:



2

***a*-[5,6]-fulleroid**

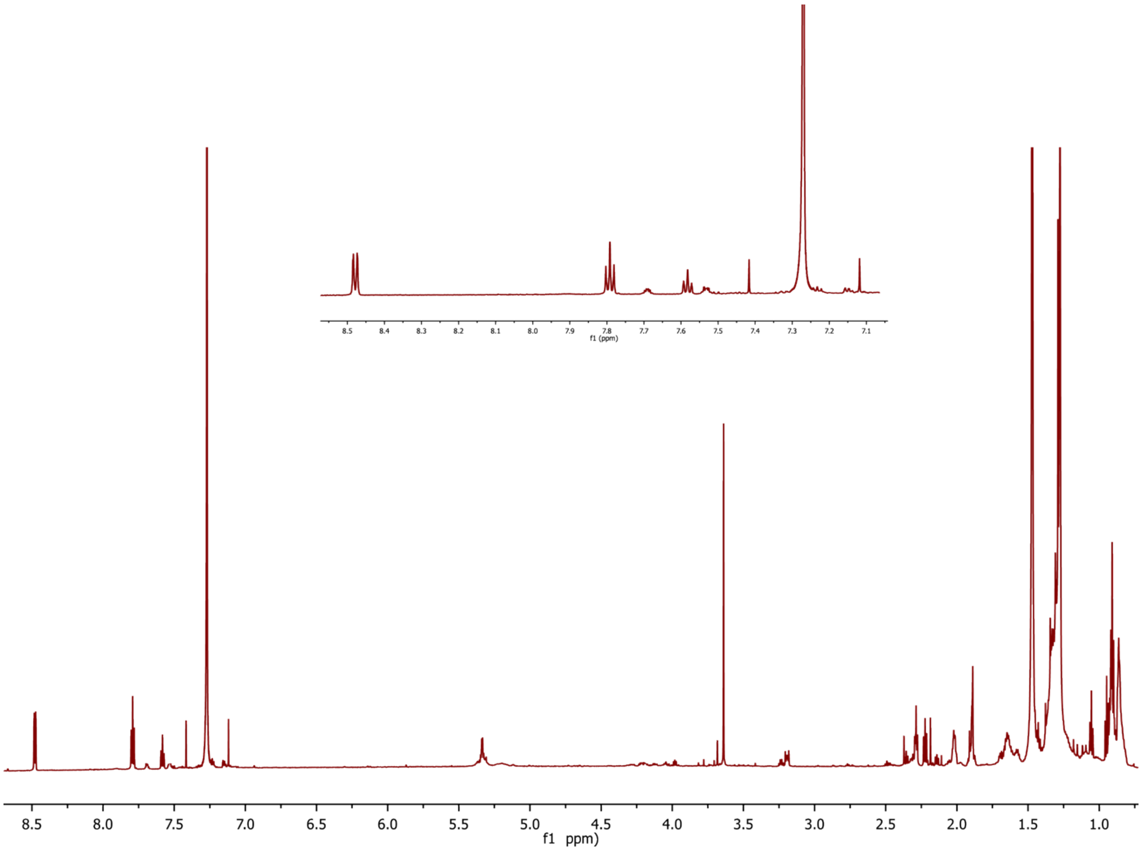


Figure S3. ^{1}H NMR (700 MHz, 298K, CDCl$_3$) of compound **2**.

^{1}H NMR of compound 2: (700 MHz, 298K, CDCl$_3$) δ 1.43 (m, 2H), 1.65 (m, 2H), 2.22 (m, 2H), 3.64 (s, 3H), 7.61 – 7.56 (m, 1H), 7.82 – 7.77 (m, 2H), 8.48 (d, *J* = 7.1 Hz, 2H) ppm.

^{13}C NMR of compound 2: δ 20.1, 34.0, 37.3, 51.6, 54.2, 122.5, 127.6, 128.3, 128.6, 129.3, 131.1, 131.5, 132.3, 131.9, 134.2, 138.0, 138.9, 140.6, 142.7, 144.1, 143.4, 144.2, 144.4, 144.5, 144.7, 144.9, 145.0, 145.8, 146.5, 146.6, 147.0, 147.2, 147.4, 147.6, 147.7, 147.8, 147.9, 148.0, 148.4, 148.5, 150.0, 150.3, 150.5, 150.6, 151.1, 151.4, 173.1 ppm.

UV-vis of compound 2:

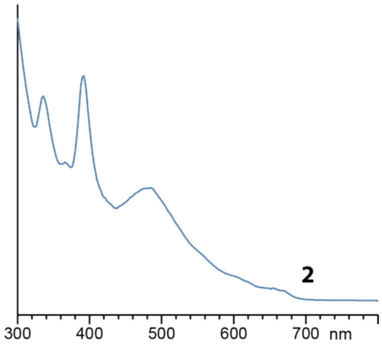
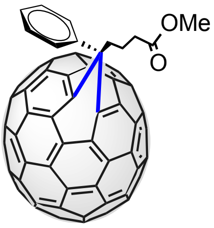


Figure S4. UV-vis spectrum of compound **2** in toluene.

MS (MALDI TOF) of compound 2: m/z 1030.099 calculated for $C_{82}H_{14}O_2$; found m/z 1030.053.

Compound 3: *b*-[5,6]PC$_{71}$BM:



3

b-[5,6]-fulleroid

^{1}**H NMR of compound 3**: (700 MHz, 298K, $CDCl_3$) δ 1.44 – 1.40 (m, 2H), 1.58 (m, 2H), 2.22 (m, 2H), 3.71 (s, 3H), 7.47 (m, 1H), 7.58 (m, 2H), 7.99 (m, 2H) ppm.

The yield of compound **3** is too low to obtain a good quality ^{13}C NMR spectrum.

MS (MALDI TOF) of compound 3: m/z 1030.099 calculated for $C_{82}H_{14}O_2$; found m/z 1030.167.

UV-vis of compound 3:

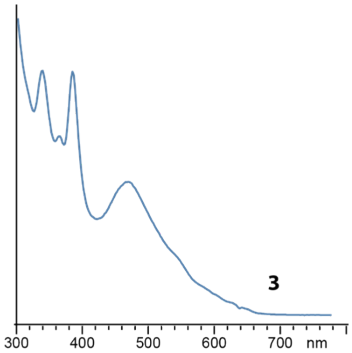
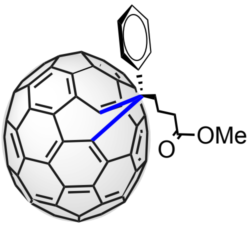


Figure S5. UV-vis spectrum of compound **3** in toluene.

Compound 4: *c*-[5,6]PC$_{71}$BM:



4

***c*-[5,6]-fulleroid**

Due to the small amount of compound **4**, the NMR characterization is not accurate enough for a proper assignation.

MS (MALDI TOF) of compound 4: m/z 1030.099 calculated for $C_{82}H_{14}O_2$; found m/z 1030.120

UV-vis compound 4:

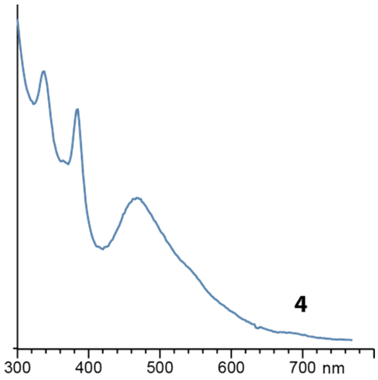
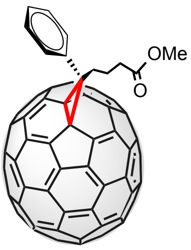


Figure S6. UV-vis spectrum of compound **4** in toluene.

Synthesis of Compounds 5, 6 and 7:

A solution of fulleroids **2**, **3** and **4** in toluene was degassed with argon for 10 min. Then, it was irradiated at 360 nm for 4h to achieve a complete isomerization to compounds **5**, **6** and **7**.

Compound 5 : α-[6,6]PC$_{71}$BM:



5

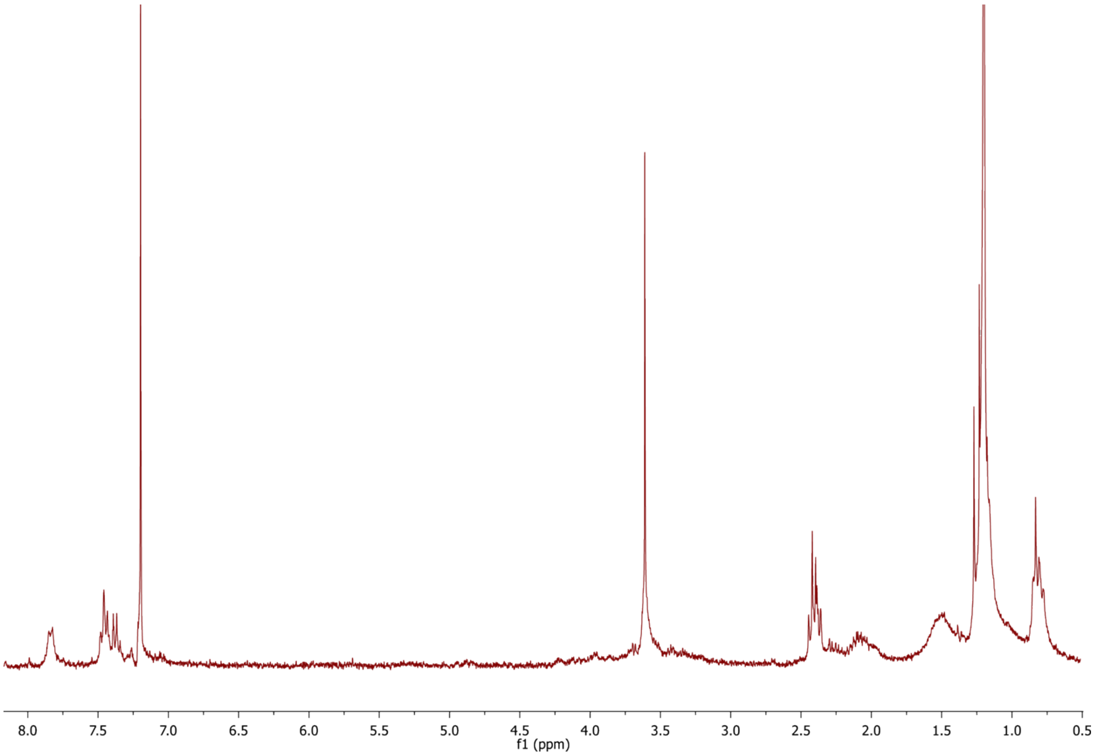


Figure S7. ^{1}H NMR (700 MHz, 298 K, CDCl$_3$) of compound **5**.

^{1}H NMR of compound 5: (700 MHz, 298K, CDCl$_3$) δ 2.10 (m, 2H), 2.17 (m, 2H), 2.49 (t, 2H, J = 7.6 Hz), 3.68 (s, 3H), 7.43 (m, 1H), 7.52 (m, 2H), 7.91 (m, 2H, J = 7.5 Hz) ppm.

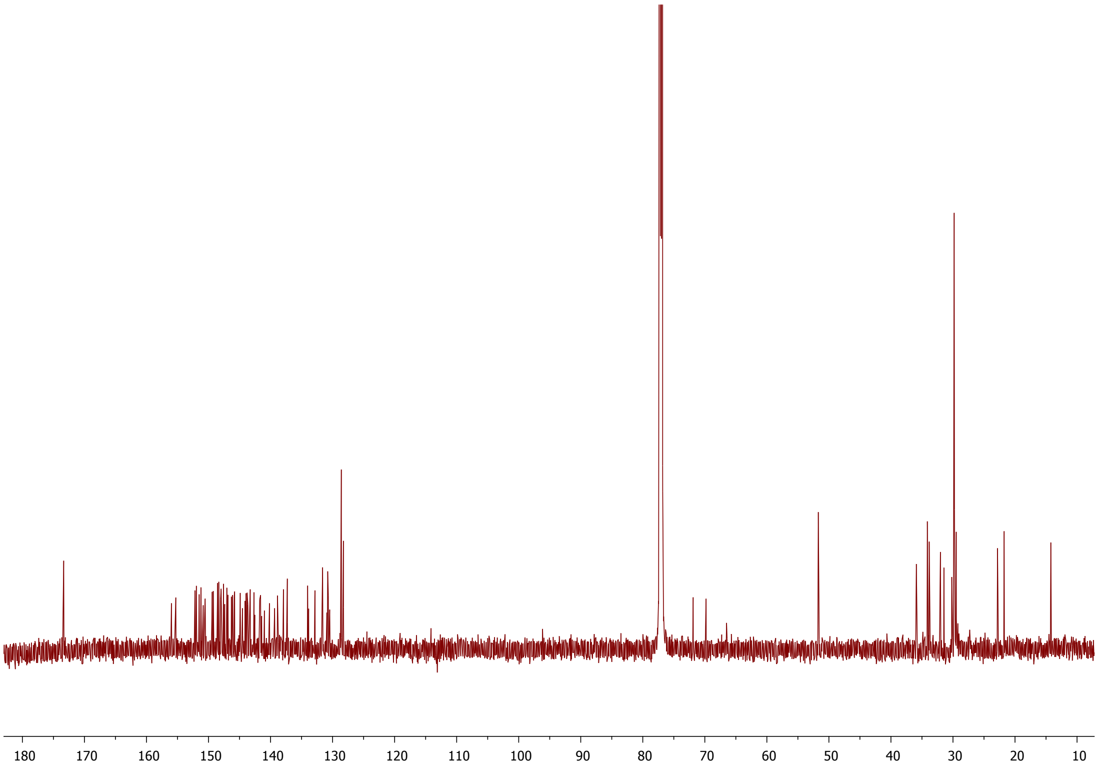


Figure S8. ^{13}C NMR (175 MHz, 298K, $CDCl_3$) of compound **5**.

^{13}C NMR of compound 5: (175 MHz, 298K, $CDCl_3$) δ 14.2, 21.7, 29.5, 35.9, 51.7, 69.8, 71.9, 128.2, 128.6, 130.7, 130.8, 131.6, 132.8, 134.0, 137.3, 137.9, 138.9, 139.3, 140.2, 141.6, 141.7, 142.7, 143.3, 143.4, 143.8, 143.9, 144.1, 144.5, 144.9, 145.7, 145.8, 145.8, 146.1, 146.3, 146.9, 147.0, 147.4, 147.5, 147.6, 147.9, 148.1, 148.3, 148.4, 148.5, 149.1, 149.2, 149.4, 150.5, 150.8, 151.1, 151.2, 151.5, 151.9, 152.2, 155.3, 155.9, 173.3 ppm.

MS (MALDI TOF) of compound 5: m/z 1030.099 calculated for $C_{82}H_{14}O_2$; found: m/z 1030.090.

UV-vis of compound 5:

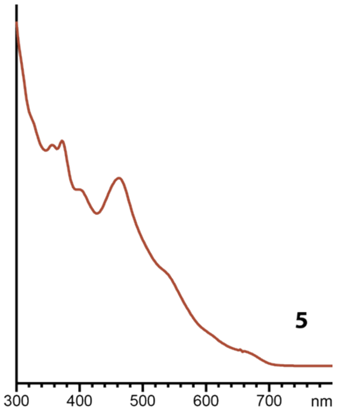


Figure S9. UV-vis spectrum of compound **5** in toluene.

Compounds 6 and 7: β-[6,6]PC$_{71}$BM:

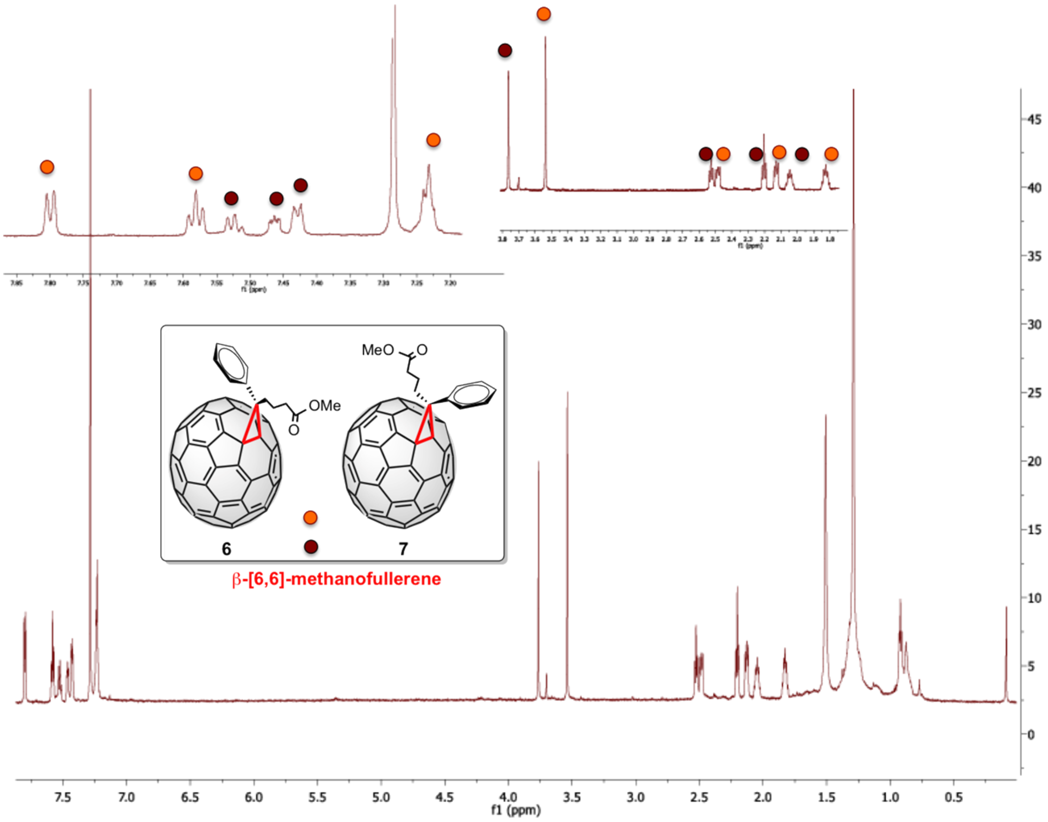


Figure S10. ^{1}H NMR (700 MHz, 298 K, CDCl$_3$) of compounds **6** and **7**.

Mayor β-**[6,6]PC$_{71}$BM:** ^{1}H NMR (700 MHz, 298K, CDCl$_3$) δ 2.08 – 1.99 (m, 2H), 2.20 (t, *J* = 7.4 Hz, 2H), 2.57 – 2.51 (m, 2H), 3.54 (d, *J* = 1.3 Hz, 3H), 7.24 (d, *J* = 5.7 Hz, 1H), 7.58 (t, *J* = 6.8 Hz, 2H), 7.80 (d, *J* = 7.4 Hz, 2H), ppm.

Minor β-**[6,6]PC$_{71}$BM:** ^{1}H NMR (700 MHz, 298K, CDCl$_3$) δ 1.88 – 1.79 (m, 2H), 2.15 – 2.09 (m, 2H), 2.51 – 2.46 (m, 2H), 3.54 (d, *J* = 1.3 Hz, 3H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.54 – 7.50 (m, 2H), ppm.

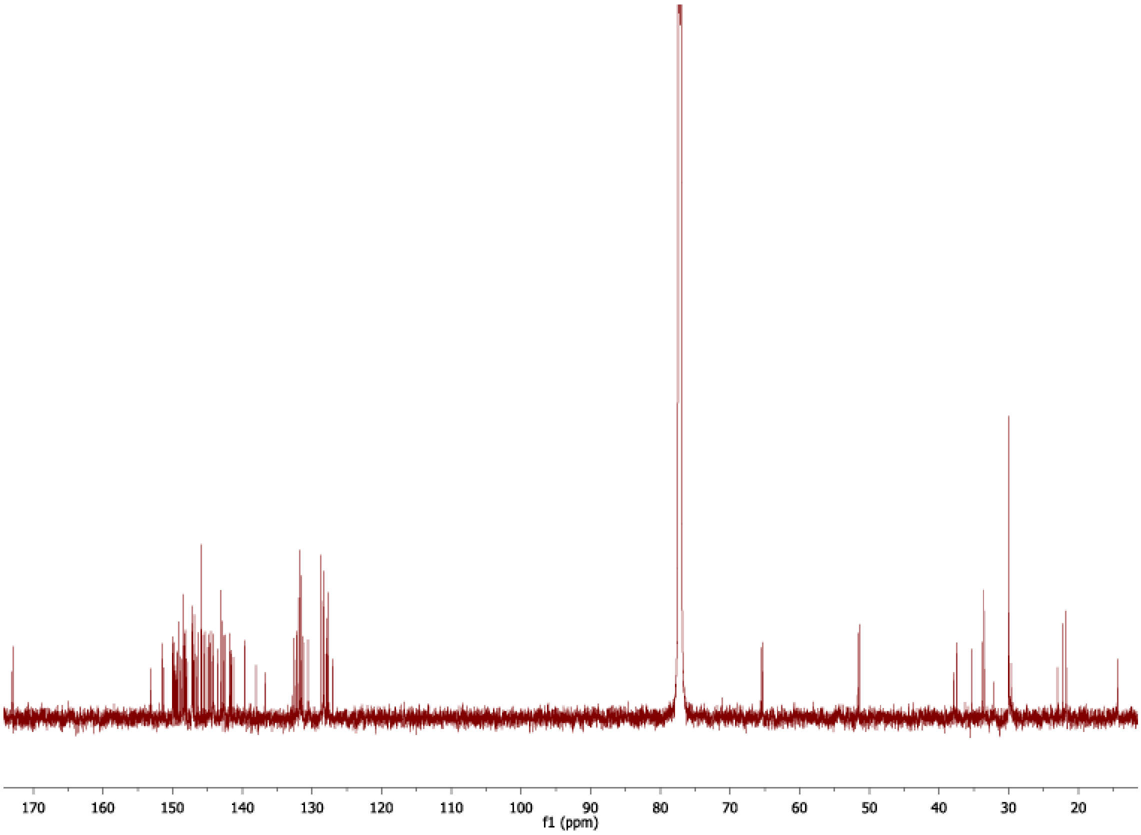


Figure S11. ^{13}C NMR (175 MHz, 298K, $CDCl_3$) of compounds **6** and **7.**

^{13}C NMR (175 MHz, 298K, $CDCl_3$) of the mixture of 6 and 7: 14.3, 21.7, 22.2, 33.5, 33.6, 33.8, 35.3, 37.4, 51.4, 51.6, 65.3, 65.6, 127.0, 127.7, 127.8, 127.9, 128.3, 128.3, 128.6, 130.5, 131.2, 131.2, 131.5, 131.6, 131.8, 132.2, 132.2, 132.5, 136.6, 138.0, 139.7, 140.0, 141.2, 141.5, 141.7, 141.8, 142.5, 142.6, 142.7, 142.8, 143.1, 143.5, 144.1, 144.2, 144.3, 144.5, 144.6, 144.8, 144.9, 145.3, 145.5, 145.6, 145.8, 145.9, 146.3, 146.5, 146.8, 147.1, 147.2, 147.9, 148.1, 148.2, 148.2, 148.3, 148.6, 148.8, 149.1, 149.2, 149.3, 149.4, 149.4, 148.5, 149.5, 149.6, 149.7, 149.8, 149.9, 150.0, 151.2, 151.4, 153.2, 172.8, 173.1 ppm.

MS (MALDI TOF) of compound 6+7: m/z 1030.099 calculated for $C_{82}H_{14}O_2$; found: m/z 1030.093.

UV-vis of the mixture of compounds 6+7:

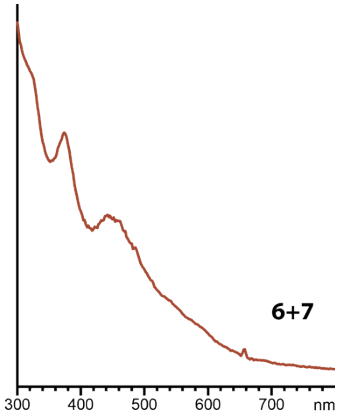
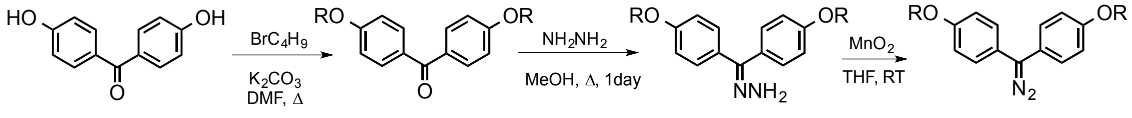


Figure S12. UV-vis spectrum of compounds **6** and **7** in toluene.

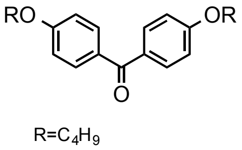
Synthesis of compound 8:

The diazocompound **8** was synthesized using the procedure described somewhere else.[1]



8' **8**

4,4’-bis(butylphenyl)benzophenone:

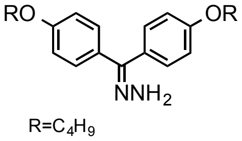


^{1}H NMR of 4,4’-bis(butylphenyl)benzophenone: (300 MHz, 298K, $CDCl_3$) δ 0.89 (t, 3H, *J*= 7.40Hz, CH_3-R); 1.20-1.53 (m, 2H, R-CH_2-R); 1.82 (m, 2H, R-CH_2-R); 4.00 (t, 2H, *J*= 6.40 Hz, R-CH_2O); 6.94 (d, 2H, *J*= 8.52Hz, Ar); 7.35 (d, 2H, *J*= 8.52Hz, Ar) ppm.

^{13}C NMR of **4,4’-bis(butylphenyl)benzophenone:** (75 MHz, 298K, $CDCl_3$) δ 14.0, 20.3, 31.8, 68.1, 113.9, 130.5, 132.2, 162.4, 193.0 ppm.

MS (ESI): Chemical Formula: $C_{21}H_{26}O_3$: m/z 326, found: m/z 327 [M+]

4,4’-bis(butylphenyl)benzohydrazine (8’):

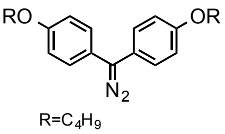


^{1}H NMR of 8': (300 MHz, 298K, $CDCl_3$) δ= 0.99 (t, 3H, *J* = 7.50 Hz, CH_3-R), 1.49-1.54 (m, 2H, R-CH_2-R), 1.78 (m, 2H, R-CH_2-R), 3.97 (t, 2H, *J* = 6.25 Hz, R-CH_2O), 6.92 (d, 2H, J = 8.75 Hz, Ar), 7.92 (d, 2H, *J* = 8.75 Hz, Ar) ppm.

^{13}C NMR of 8': (75MHz, 298 K, $CDCl_3$) δ 14.1, 20.0, 31.2, 67.5, 123.5, 129.5, 131.2, 144.2, 154.8 ppm.

MS (ESI): Chemical Formula: $C_{21}H_{28}N_2O_2$: m/z 340, found: m/z 341 [M+]

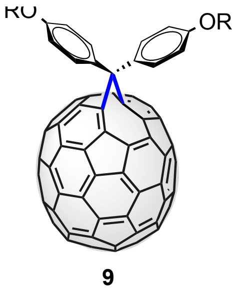
Diazocompound 8:



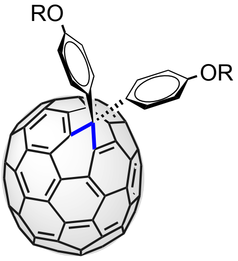
To a solution of compound **8'** (0.4 g, 1.14 mmol, 1 equiv.) in THF (15 mL) was added manganese dioxide (539 mg, 6.2 mmol, 5.4eq). The mixture was stirred at room temperature for 30 minutes in the dark and then was filtered on celite. The solvent was removed under vacuum obtaining the diazocompound **8** as a purple solid that was used without further purification (85 % yield). This compound is highly unstable to light and must be immediately used for the next step of synthesis.

Synthesis of Compounds 9,10, 11:

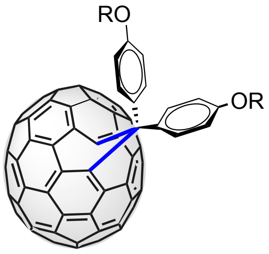
Diazocompound **8** (4mg, 0.012 mmol, 1 eq) was added to a solution of [70]fullerene (10 mg, 0.012 mmol, 1 eq) in toluene (4 ml). The mixture was stirred at room temperature for 2 min. Then, the solvent was removed under vacuum, and the crude product was purified by silica-gel column chromatography using CS_2 as eluent to recover the unreacted C_{70}, and a mixture of solvents (hexane/toluene 8:2) to collect compounds **9**, **10** and **11** (72% yield, based on recovered C_{70}) with a small fraction of the [6,6]closed derivatives **12** and **13**, (15% yield, based on recovered C_{70}). HPLC conditions: column: Buckyprep; solvents: toluene/hexane/acetonitrile (60:36:4); flow: 0.5 ml/min; λ= 320 nm; temperature: 25°C.



9



10



11

R= C_4H_9

Compound 9: *a*-[5,6]-[70]DPM:

^{1}H NMR of compound 9: (700 MHz, 298 K, $CDCl_3$) δ 0.99 (t, *J* = 7.4 Hz, 3H), 1.10 – 1.06 (t, *J* = 7.4 Hz, 3H), 1.49 – 1.46 (m, 2H), 1.74 (dd, *J* = 14.7, 6.9 Hz, 2H), 1.82 – 1.78 (m, 2H), 1.91 – 1.85 (m, 2H), 3.91 (dd, *J* = 11.8, 5.3 Hz, 2H), 4.12 (t, *J* = 6.4 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 7.19 (dd, *J* = 23.1, 8.1 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 2H), 8.47 (d, *J* = 8.6 Hz, 2H) ppm.

^{13}C NMR of compound 9: (175 MHz, 298 K, $CDCl_3$) δ 14.1, 19.5, 31.5, 67.8, 114.2, 114.7, 115.4, 123.8, 128.4, 130.3, 131.2, 131.3, 132.0, 132.4, 133.5, 134.0, 137.4, 140.8, 140.9, 142.8, 143.3, 144.0, 144.1, 144.4, 144.5, 144.8, 145.8, 146.3, 146.4, 146.5, 147.0, 147.3, 147.5, 147.8, 147.9, 148.0, 148.4, 148.5, 150.4, 150.6, 151.0, 152.0, 157.8 ppm.

Compound 10: *b*-[5,6]-[70]DPM:

^{1}H NMR of compound 10: (700 MHz, 298 K, $CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 1.60 (m, 2H), 1.75-1.71 (m, 2H), 1.83 – 1.80 (m, 2H), 1.90- 1.87 (m, 2H), 3.81 (t, *J* = 6.4 Hz, 2H), 4.04 (t, d, *J* = 6.4 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 2H) ppm.

The yield of compound **10** is too low to obtain a good quality ^{13}C NMR spectrum.

Compound 11: *c*-[5,6]-[70]DPM: The yield of compound **11** is too low to obtain a good quality ^{1}H and ^{13}C NMR spectra.

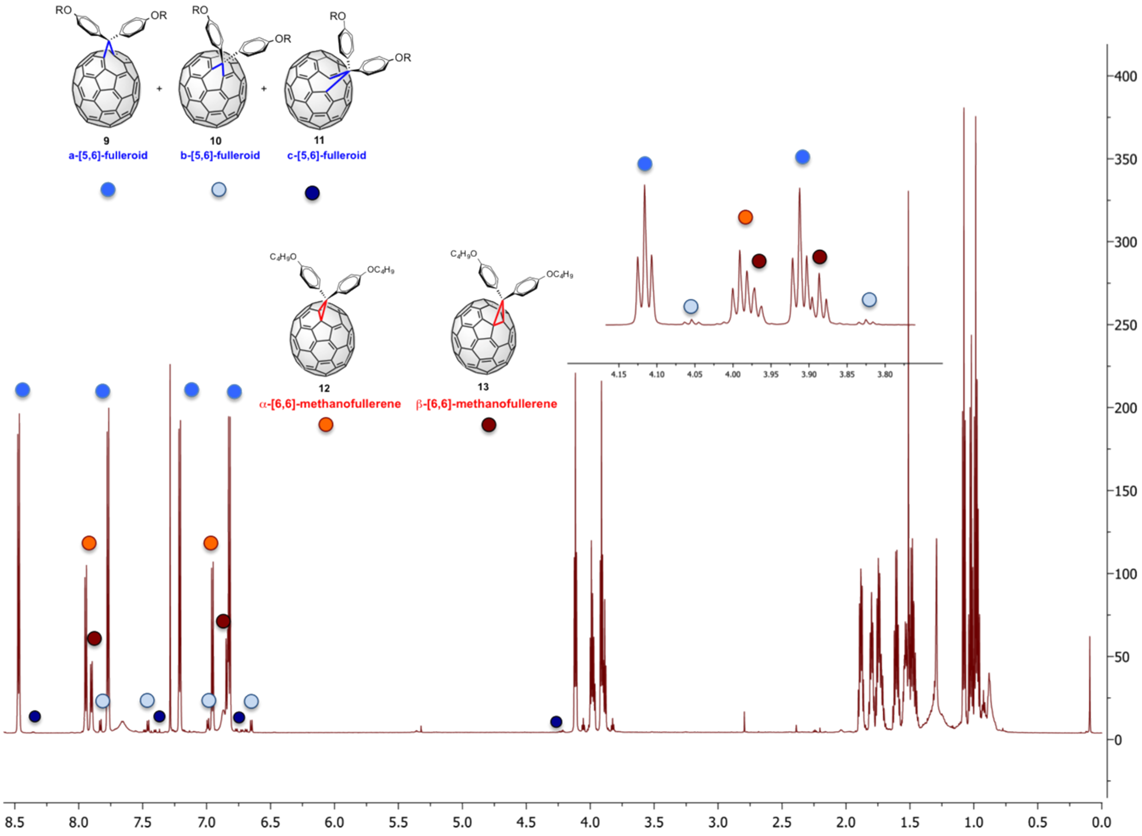


Figure S13. ^{1}H NMR (700MHz, 298K, $CDCl_3$) of the fraction of monoadducts containing fulleroids **9-11** and methanofullerenes **12-13**. Unfortunately, the yield of compound **11** is too low therefore the signals in the spectrum are too small to be assigned with accuracy.

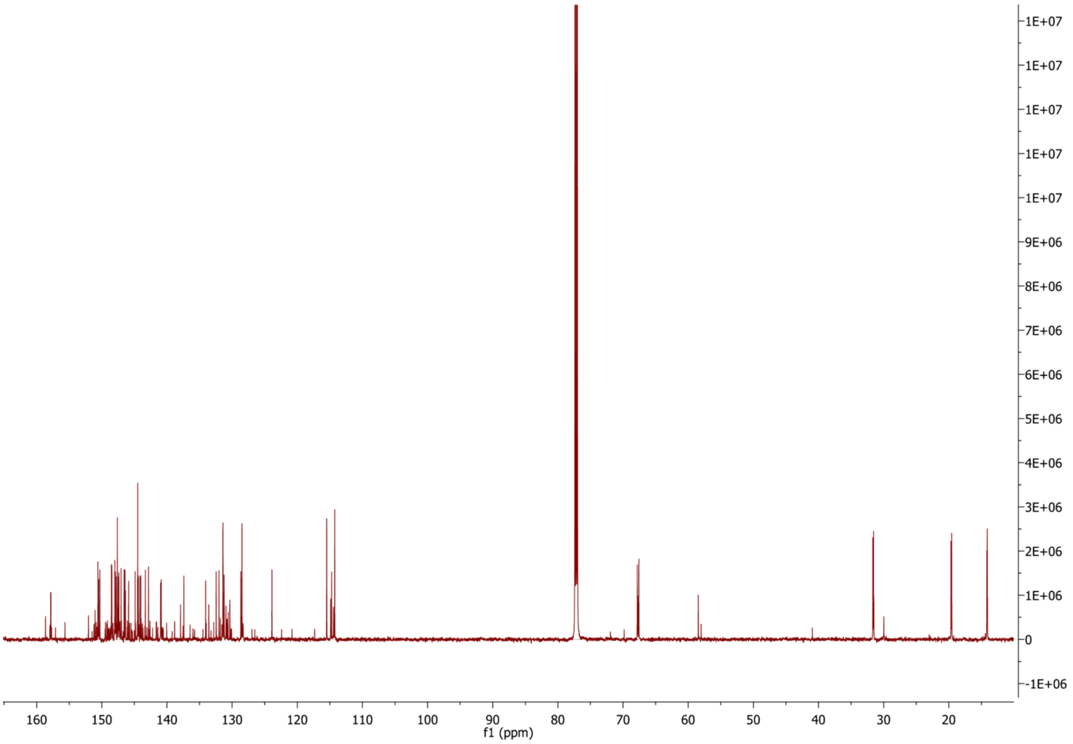


Figure S14. **^{13}C NMR** (175 MHz, 298K, $CDCl_3$) of compounds **9**, **10** and **11**.

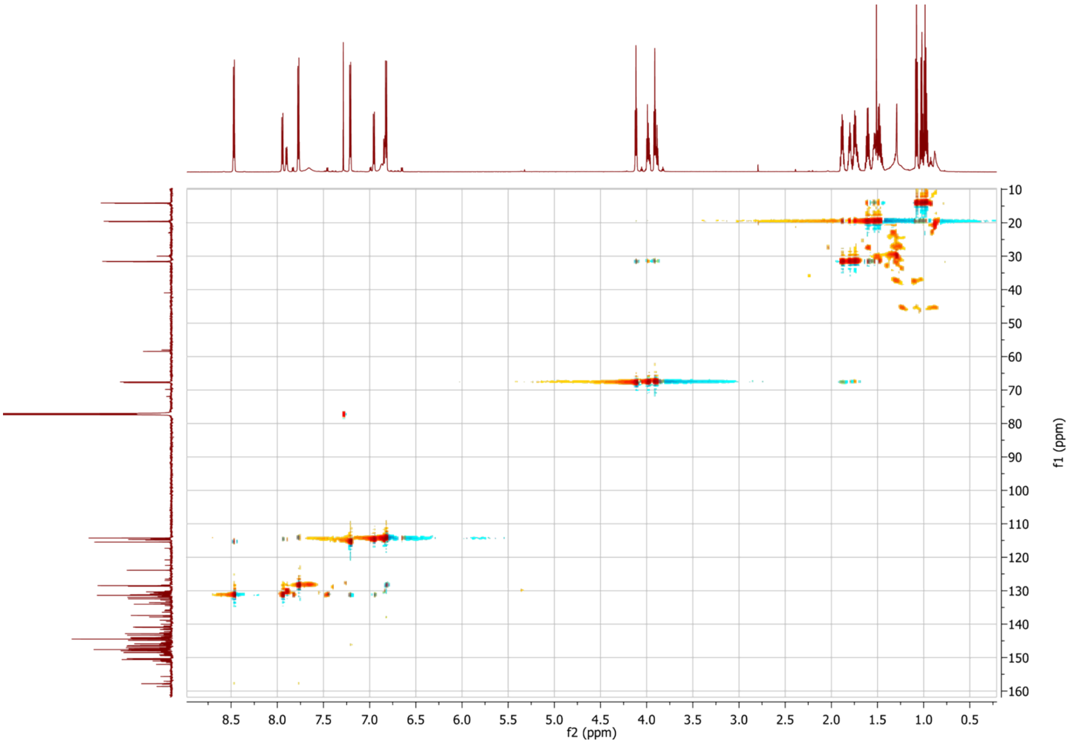


Figure S15. HSQC-NMR (700MHz, 298K, $CDCl_3$) of the fraction of monoadducts containing fulleroids **9-11** and methanofullerenes **12-13**. Unfortunately, the yield of compound **13** is too low therefore the signals in the spectrum are too small to be assigned with accuracy.

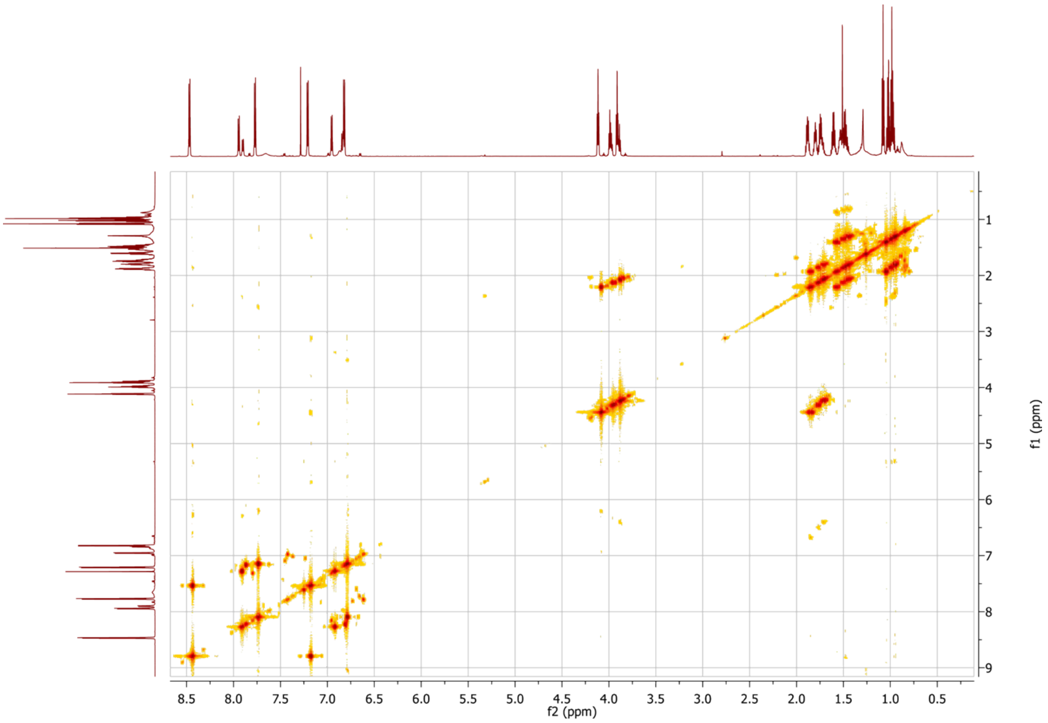


Figure S16. Cosy-NMR (700MHz, 298K, $CDCl_3$) of the fraction of monoadducts containing fulleroids **9-11** and methanofullerenes **12-13**. Unfortunately, the yield of compound **13** is too low therefore the signals in the spectrum are too small to be accurately assigned.

UV-vis of compound 9:

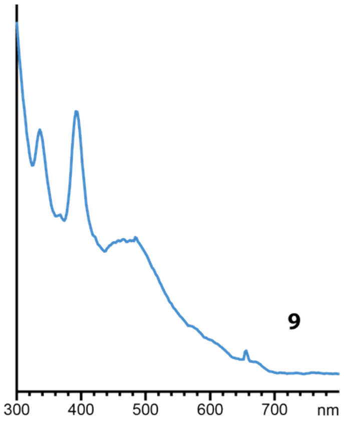


Figure S17. UV-vis spectrum of compound **9** in toluene.

UV-vis of compound 10:

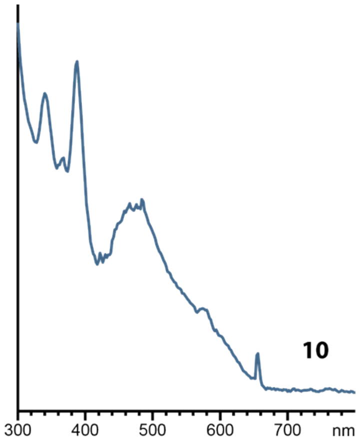


Figure S18. UV-vis spectrum of compound **10** in toluene.

UV-vis of compound 11:

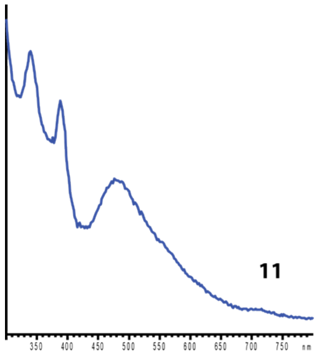


Figure S19. UV-vis spectrum of compound **11** in toluene.

MS (MALDI TOF) of compounds 9+10+11: m/z 1150.193 calculated for $C_{91}H_{26}O_2$; found: m/z 1150.201.

Synthesis of compounds 12 and 13:

The fulleroids fraction containing compounds **9**, **10** and **11** was irradiated at 360nm for 4h at room temperature giving rise to compounds **12** and **13** in a quantitative manner.

Compounds 12 and 13: [6,6]-[70]DPM:

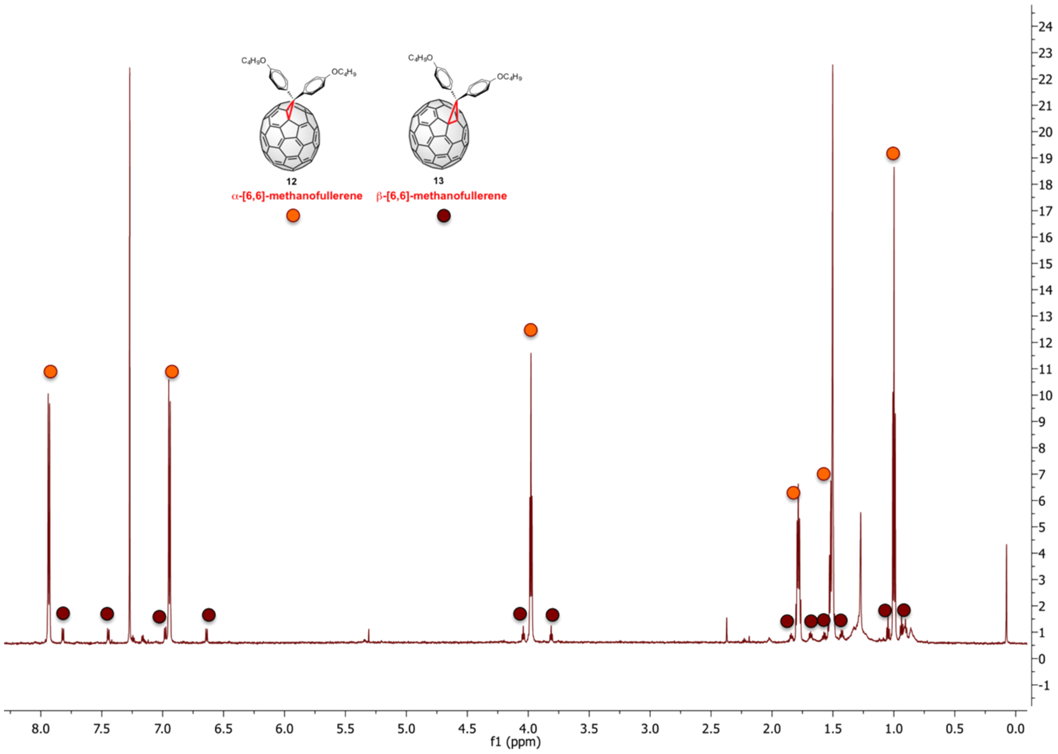


Figure S20. ^{1}H NMR (700 MHz, 298K, $CDCl_3$) of compounds **12** and **13**.

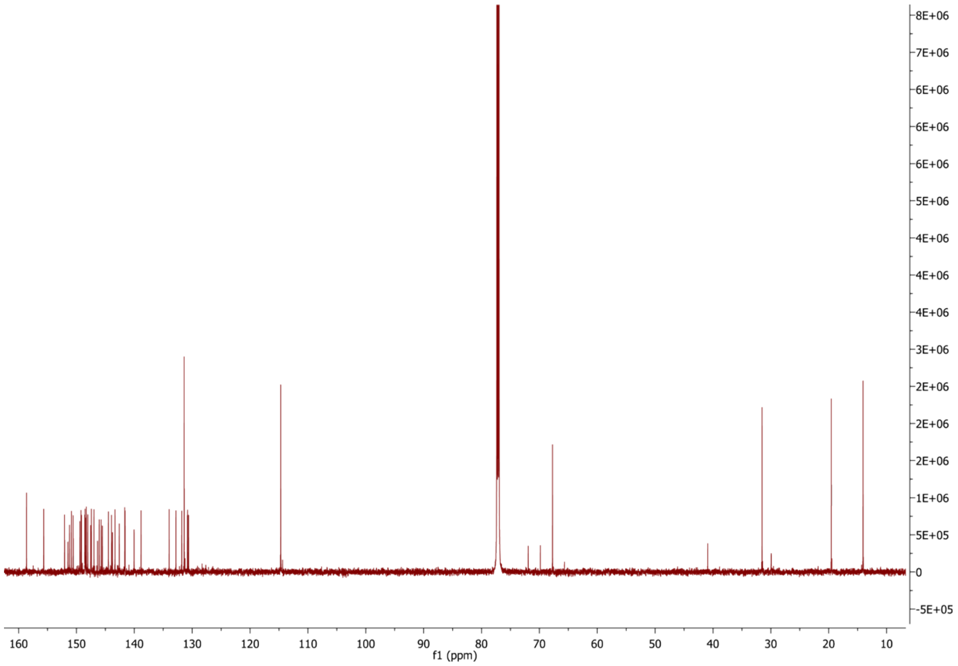


Figure S21. ^{13}C NMR (175 MHz, 298K, $CDCl_3$) of compounds **12** and **13.**

α-[6,6]-[70]DPM (12):

^{1}H NMR (700 MHz, 298K, CDCl$_3$) δ 1.00 (t, *J* = 7.4 Hz, 6H), 1.52 (m, 4H), 1.81 – 1.75 (m, 4H), 3.98 (t, *J* = 6.5 Hz, 4H), 6.94 (d, *J* = 8.4 Hz, 4H), 7.93 (d, *J* = 8.4 Hz, 4H) ppm.

^{13}C NMR (175 MHz, 298K, CDCl$_3$) δ 14.0 19.5, 31.5, 67,7 69.8, 71.9, 114.7, 130.6, 130.7, 130.8, 131.3, 131.8, 132.8, 133.9, 138.8, 140.0, 141.6, 141.6, 142.6, 143.3, 143.7, 143.9, 144.4, 145.5, 145.7, 146.0, 146.3, 146.9, 147.4, 147.5, 148.0, 148.2, 148.4, 148.5, 148.5, 149.1, 149.2, 149.4, 150.5, 150.8, 151.2, 151.4, 152.1, 155.6, 158.6 ppm.

MS (MALDI TOF) of compound 12: m/z 1150.193 calculated for $C_{91}H_{26}O_2$; found: m/z 1150.143.

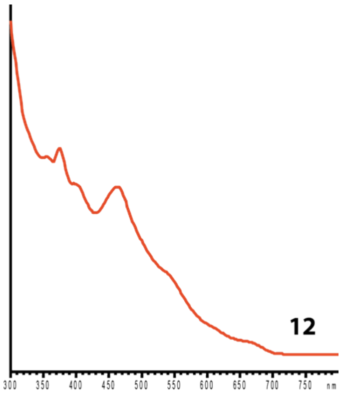


Figure S22. UV-vis spectrum of compound **12** in toluene.

β-[6,6]-[70]DPM (13):

^{1}H NMR (700 MHz, 298K, CDCl$_3$) δ 0.99 – 0.94 (m, 6H) 1.10 – 1.04 (m, 6H), 1.44 (m, *J* = 7.5 Hz, 4H), 1.58 (m, *J* = 8.0 Hz, 4H), 1.86 (m, 4H), 1.70 (m, 4H), 3.82 (t, *J* = 6.4 Hz, 4H), 4.04 (t, *J* = 6.4 Hz, 4H), 6.65 (d, *J* = 8.3 Hz, 4H), 6.99 (d, *J* = 7.5 Hz, 4H), 7.46 (d, *J* = 8.4 Hz, 4H), 7.83 (d, *J* = 8.4 Hz, 4H), ppm.

The yield is too low to obtain a good quality ^{13}C NMR spectrum.

MS (MALDI TOF) of compound 13: m/z 1150.193 calculated for $C_{91}H_{26}O_2$; found: m/z 1150.212.

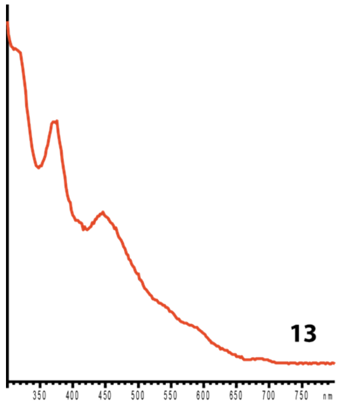


Figure S23. UV-vis spectrum of compound **13** in toluene.

Cyclic voltammetry of compounds 2, 3 and 4 (fulleroids) vs compounds 5, 6 and 7 (methanofullerenes):

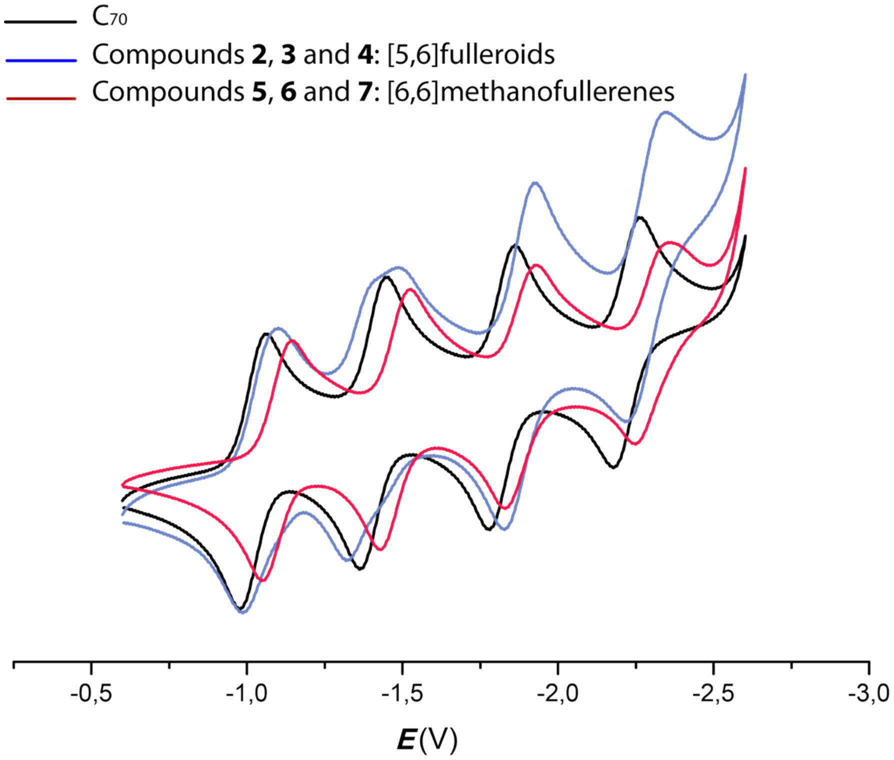


Figure S24. Cyclic voltammogram of C_{70} (black), fulleroids fraction (blue) and methanofullerenes fraction (red) in o-DCB/ACN 4:1 using a GCE (glassy carbon electrode) as the working electrode, $Ag/AgNO_3$ as the reference electrode, $Bu_4N{\cdot}PF_6$ as the supporting electrolyte.

Cyclic voltammetry of compounds 9, 10 and 11 (fulleroids) vs compounds 12 and 13 (methanofullerenes).

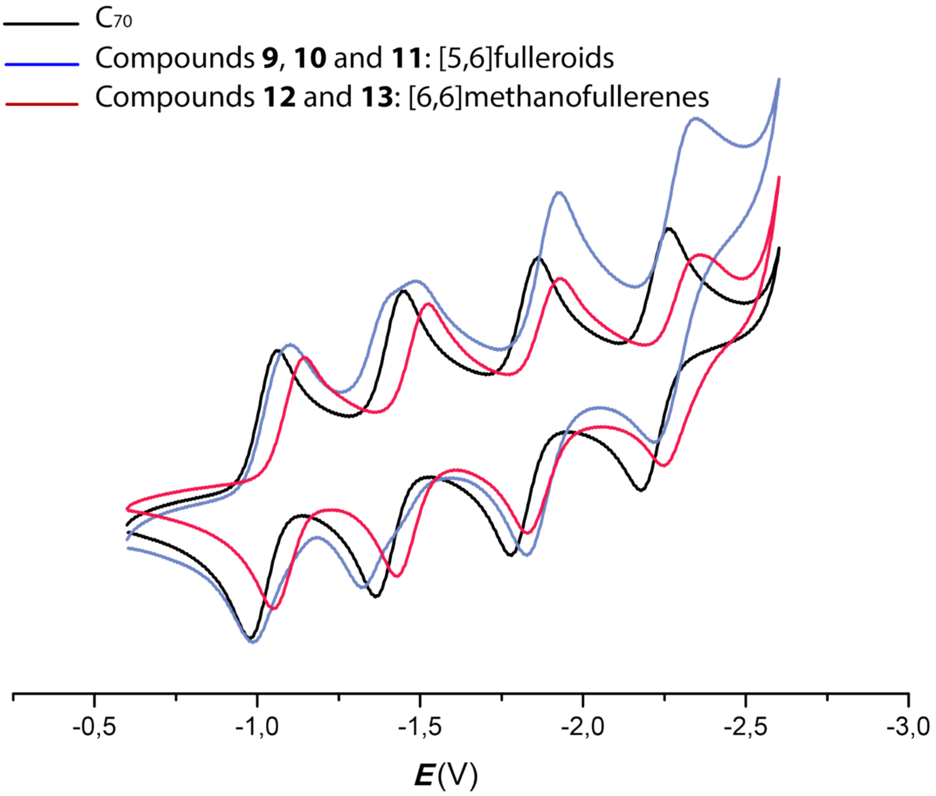


Figure S25. Cyclic voltammogram of C_{70} (black), fulleroids fraction (blue) and methanofullerenes fraction (red) in o-DCB/ACN 4:1 using a GCE (glassy carbon electrode) as the working electrode, Ag/AgNO$_3$ as the reference electrode, $Bu_4N{\cdot}PF_6$ as the supporting electrolyte.

Table S1. Reduction potentials of compounds **2-7**, **9-13** and C_{70} in V *vs* Fc/Fc+ couple. (GCE (glassy carbon electrode) as the working electrode, Ag/AgNO$_3$ as the reference electrode and $Bu_4N{\cdot}PF_6$ as the supporting electrolyte).

Compounds	$E_1^{1/2}$ **(V)**	$E_2^{1/2}$ **(V)**	$E_3^{1/2}$ **(V)**
C_{70}	-1,02	-1,40	-1,82
2-4	-1,03	-1,37	-1,83
5-7	-1,13	-1,52	-1,92
9-11	-1,04	-1,40	-1,87
12 and **13**	-1,10	-1,49	-1,89

HPLC profiles of compounds 2-4 before and after irradiation (5-7):

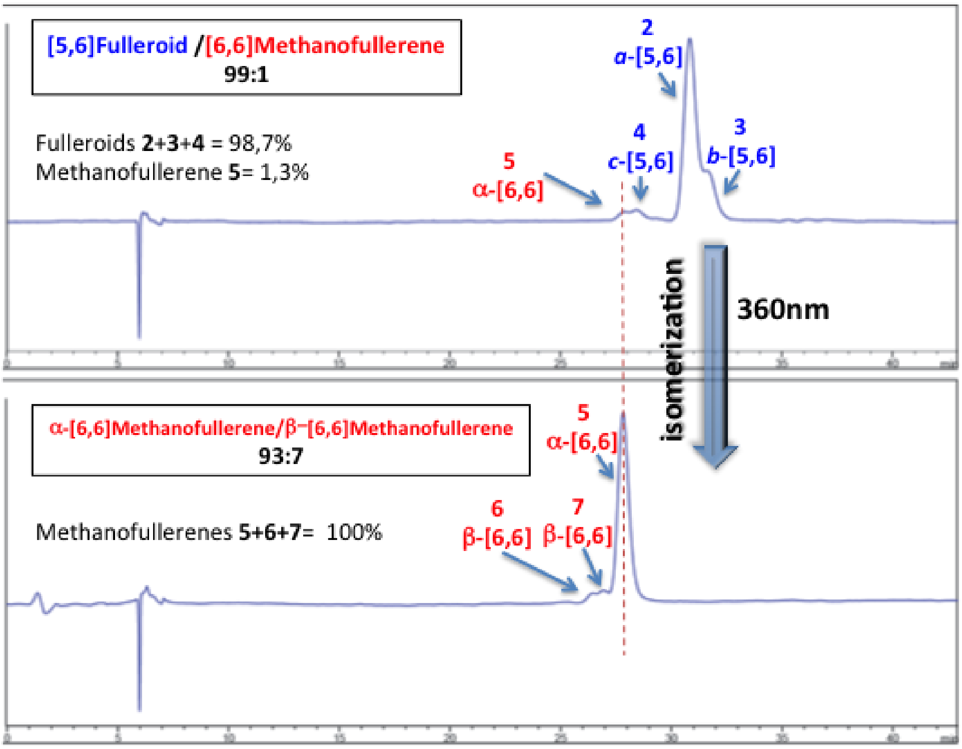


Figure S26. HPLC profiles of the fraction of fulleroids **2-4** after the reaction of **1** and C_{70} in the dark (top), and after the irradiation at 360nm (bottom) (**5**, **6** and **7**). HPLC column: 5PYE (4,6 ID x 250mm; toluene/hexane/acetonitrile (60:36:4); 0.5 ml/min; 320 nm; 25^0C).

HPLC analysis of compounds 9-13:

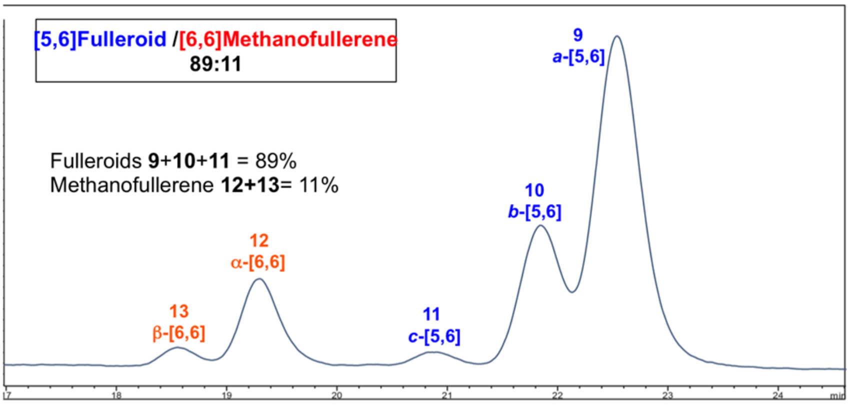


Figure S27. HPLC profile of [70]DPM-fulleroids (**9-11**) in a 89% together with the methanofullerenes **12** and **13**. HPLC column: Buckyprep waters (4,6 ID x 250mm; toluene/hexane/acetonitrile (60:36:4); 0.5 ml/min; 320 nm; 25^0C).

HPLC profiles of compounds 9-11 before and after irradiation (12 and 13):

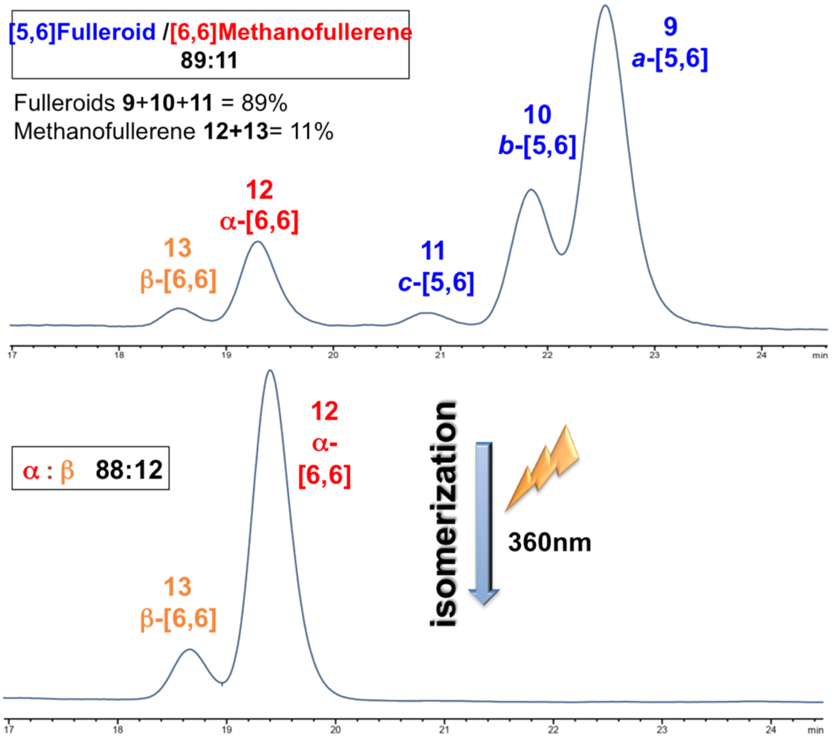


Figure S28. HPLC profile of [70]DPM-fulleroids (**9-11**) after the reaction of **8** and C_{70} in the dark (top), and after the irradiation at 360nm (bottom) (**12** and **13**). HPLC column: Buckyprep waters (4,6 ID x 250mm; toluene/hexane/acetonitrile (60:36:4); 0.5 ml/min; 320 nm; 25^{0}C).

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[1] M. Izquierdo, M. R. Cerón, M. M. Olmstead, A. L. Balch and L. Echegoyen, *Angew. Chem., Int. Ed.* 2013, **52**, 11826.