# Supporting Information

**Sara Vidal, Marta Izquierdo, Wai Kit Law, Kui Jiang, Salvatore Filippone, Josefina Perles, He Yan,* and Nazario Martín***

## Photochemical Site-selective Synthesis of [70]Methanofullerenes

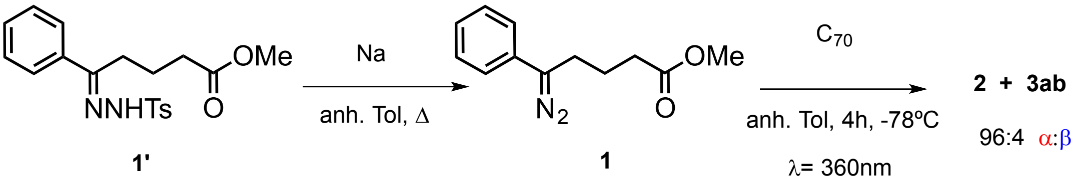
**General methods……………………………………………………………………... 2S**
**Synthesis of compounds 2, 3ab…..……………………………………………………….. 2S**
**Characterization of compound 2: $\alpha$-PC$_{71}$BM……….……………………………..…. 3S**
**Synthesis of compounds 4a,b…………………….……………………………………….. 7S**
**Synthesis of compounds 5a,b…………………….……………………………………….. 9S**
**Characterization of compound 5a: $\alpha$-[70]DPM4……………………………………….. 9S**
**Characterization of compound 5b: $\alpha$-[70]DPM6...……………………………………... 14S**
**HPLC profiles of compounds 2, 3 and 5...……...………………………………………… 18S**
**Cyclic voltammetry of compounds 2, 3 and 5…………………………………………..... 19S**
**Solar cell fabrication and testing…………………………..……………………………. 20S**
**Single crystal X-ray diffraction………………………………………………………...... 22S**

## 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 a BRUKER AVANCE AMX-700 in $CDCl_3$ at 23°C, and referenced to $CDCl_3$; coupling constants (*J*) are reported in Hz and the chemical shifts (δ) in ppm.  Mass spectra were reported on a $HP_{1100}$EMD (ESI), and BRUKER-REFLEX (MALDI-TOF). 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 $mVs^{-1}$. Reactions were monitored by thin-layer chromatography carried out on 0.2 mm TLC-aluminium 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/acetonitrile (1:1); 1 ml/min; 320 nm; 25ºC), Buckyprep Waters (4,6 ID x 250mm; toluene/acetonitrile (90:10); 1 ml/min; 320 nm; 25ºC). All these values 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. Melting points were determined using a Gallenkamp apparatus.

## Experimental Procedures and Characterizations.

### Synthesis of compounds 2 and 3ab.



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 bubbled with argon for 15 minutes in a _bath with dry ice and acetone (-78ºC). Finally was incident light wavelength 360 nm for four hours in the photoreactor. 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** and **3a,b** with 86% yield (based on recovered $C_{70}$). They were purified and isolated by HPLC. HPLC conditions: column: 5PYE; solvents: toluene/acetonitrile (1:1); flow: 1 ml/min; λ = 320 nm; temperature: 25ºC.

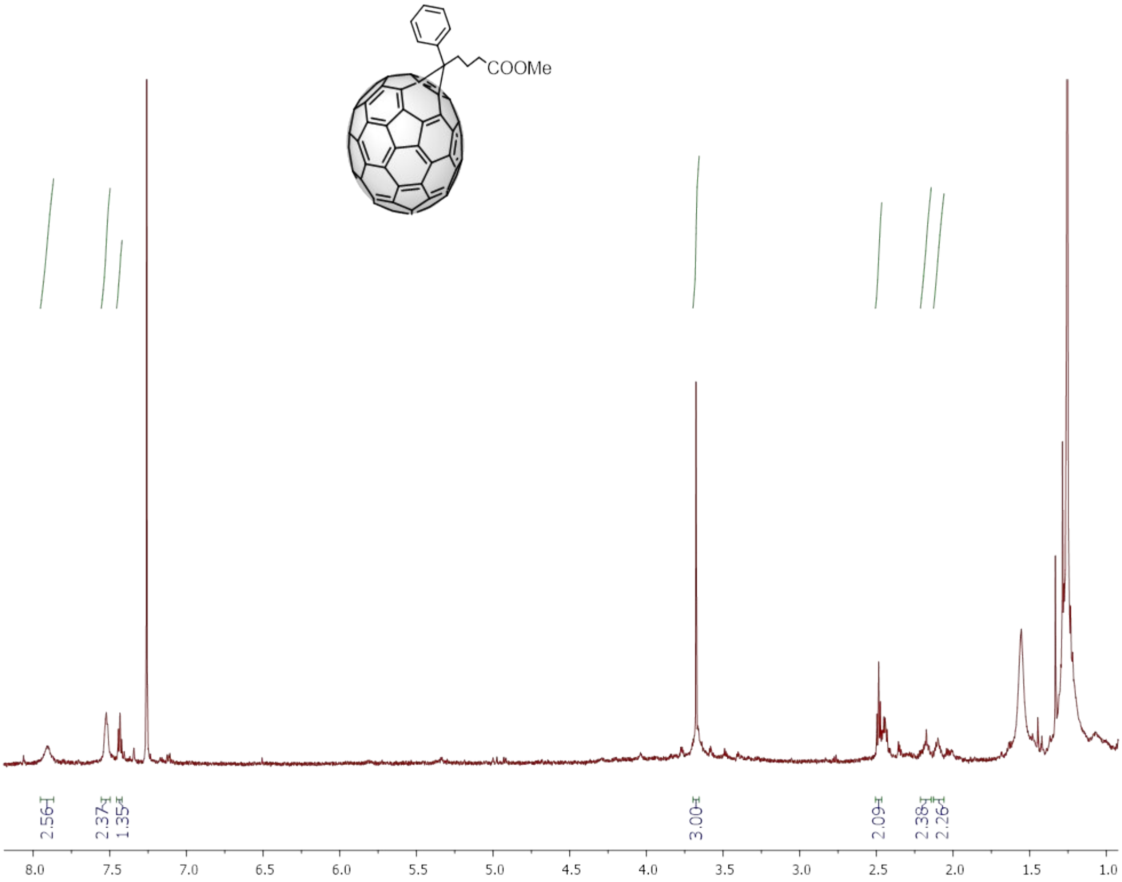


**Figure S1.** $^1$H NMR (700 MHz, 298 K, $CDCl_3$) of compound **2**.

**$^1$H NMR of compound 2** (700 MHz, 298 K, $CDCl_3$) δ 2.10 (m, 2H, -$CH_2$- $CH_2$-$CO_2$R), 2.17 (m, 2H, R-$CH_2$-R), 2.49 (t, 2H, *J*= 7.6 Hz, R-$CH_2$-$CO_2$R), 3.68 (s, 3H, -$OCH_3$), 7.43 (t, 1H, p-H Ar), 7.52 (m, 2H, m-H Ar), 7.91 (m, 2H, *J*= 7.5 Hz, o-H Ar) ppm.

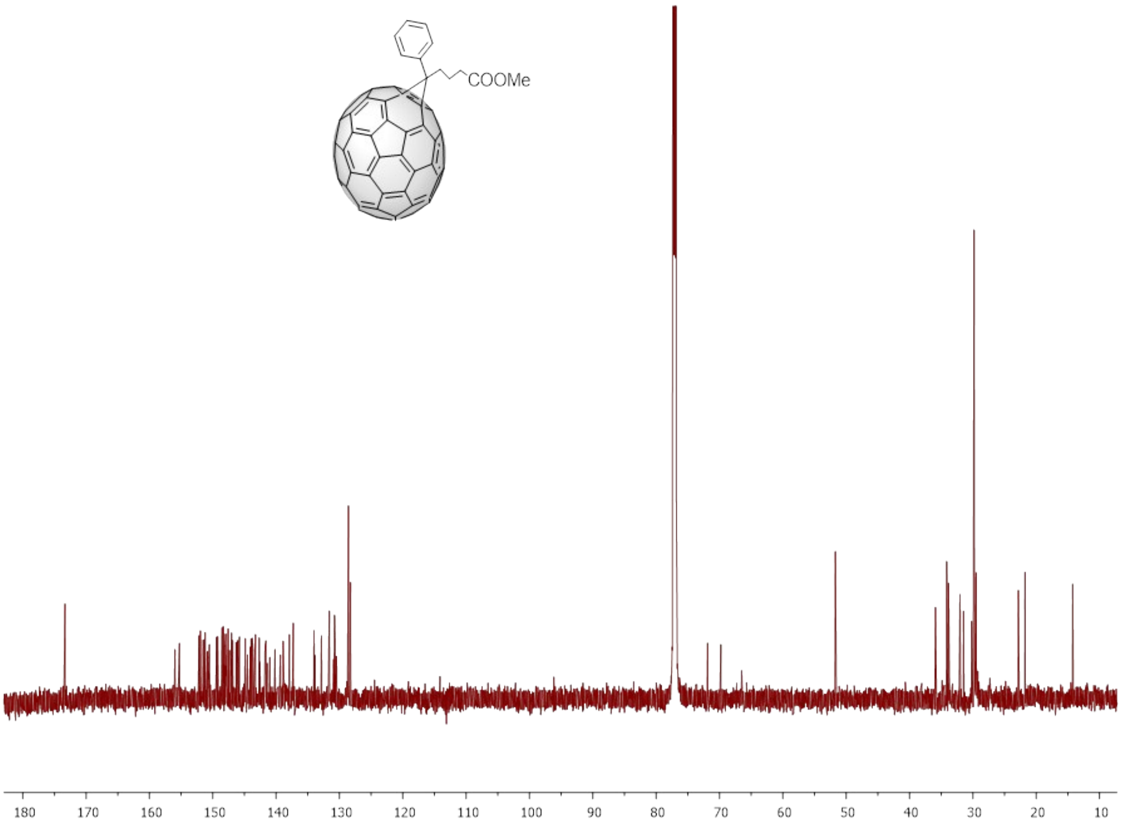
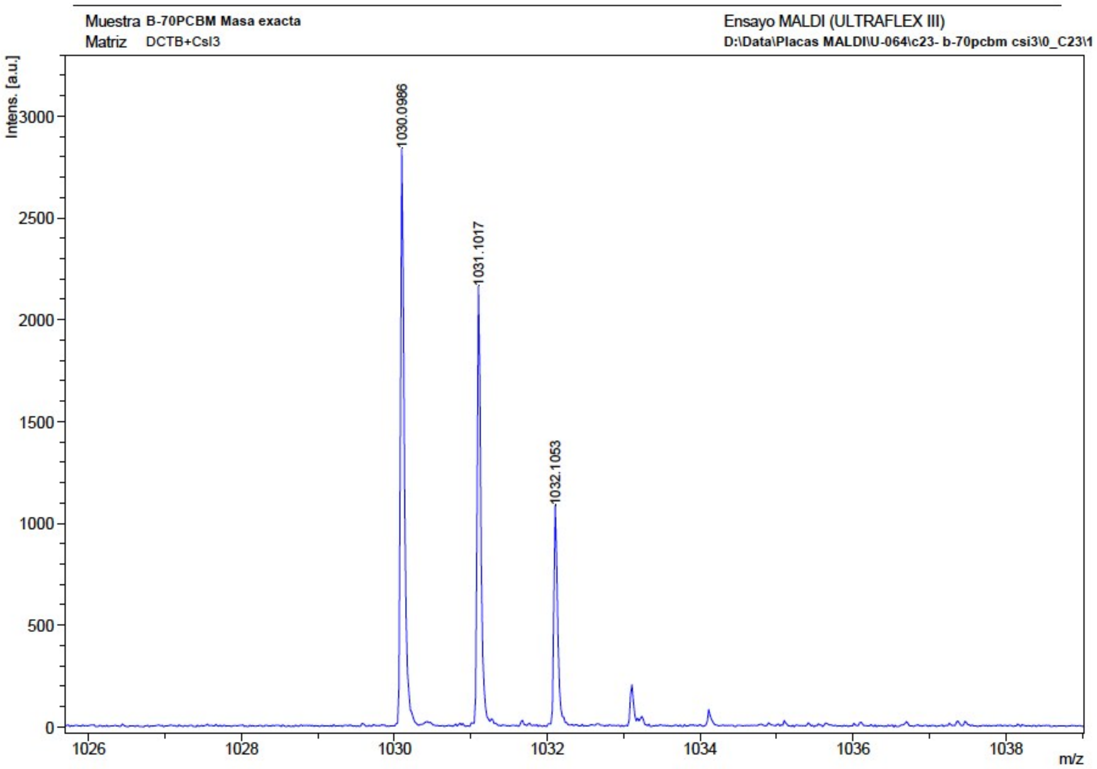


**Figure S2.** $^{13}$C NMR (175 MHz, 298 K, CDCl$_3$) of compound **2**.

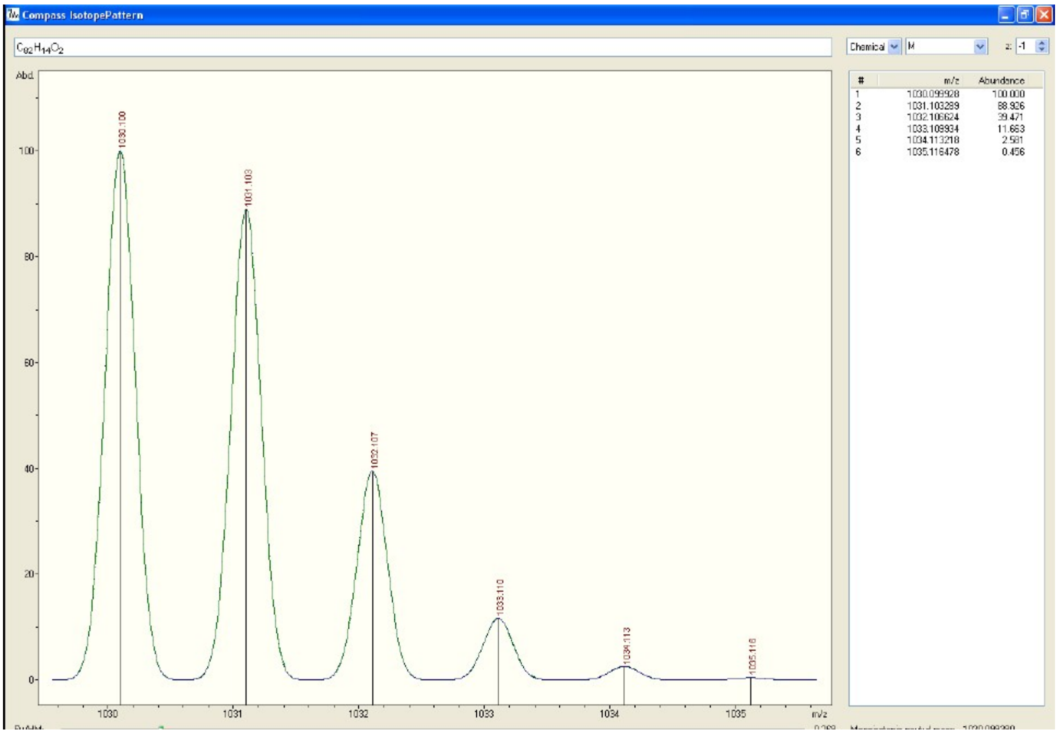
**$^{13}$C NMR of compound 2** (175 MHz, 298 K, CDCl$_3$) δ 14.2, 21.7, 22.8, 29.5, 29.8, 30.2, 31.5, 32.0, 33.8, 34.1, 35.9, 51.7, 69.8, 71.9, 128.2, 128.6, 130.7, 130.8, 131.6, 132.8, 134.0, 137.3, 137.9, 138.9, 139.3, 140.2, 141.6, 141.7, 142.7, 143.3, 143.4, 143.8, 143.9, 144.1, 144.5, 144.9, 145.7, 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.

**HRMS (MALDI TOF) of compound 2:** m/z 1030.0999 calculated for $C_{82}H_{14}O_2$; found: m/z 1030.0986.

a)



b)



$C_{82}H_{14}O_2$

| # | m/z | Abundance |
|---|---|---|
| 1 | 1030.099928 | 100.000 |
| 2 | 1031.103289 | 88.926 |
| 3 | 1032.106624 | 39.471 |
| 4 | 1033.109934 | 11.663 |
| 5 | 1034.113218 | 2.581 |
| 6 | 1035.116478 | 0.456 |

**Figure S3.** HRMS spectra of compound **2** (a) experimental spectrum; b) theoretical spectrum).

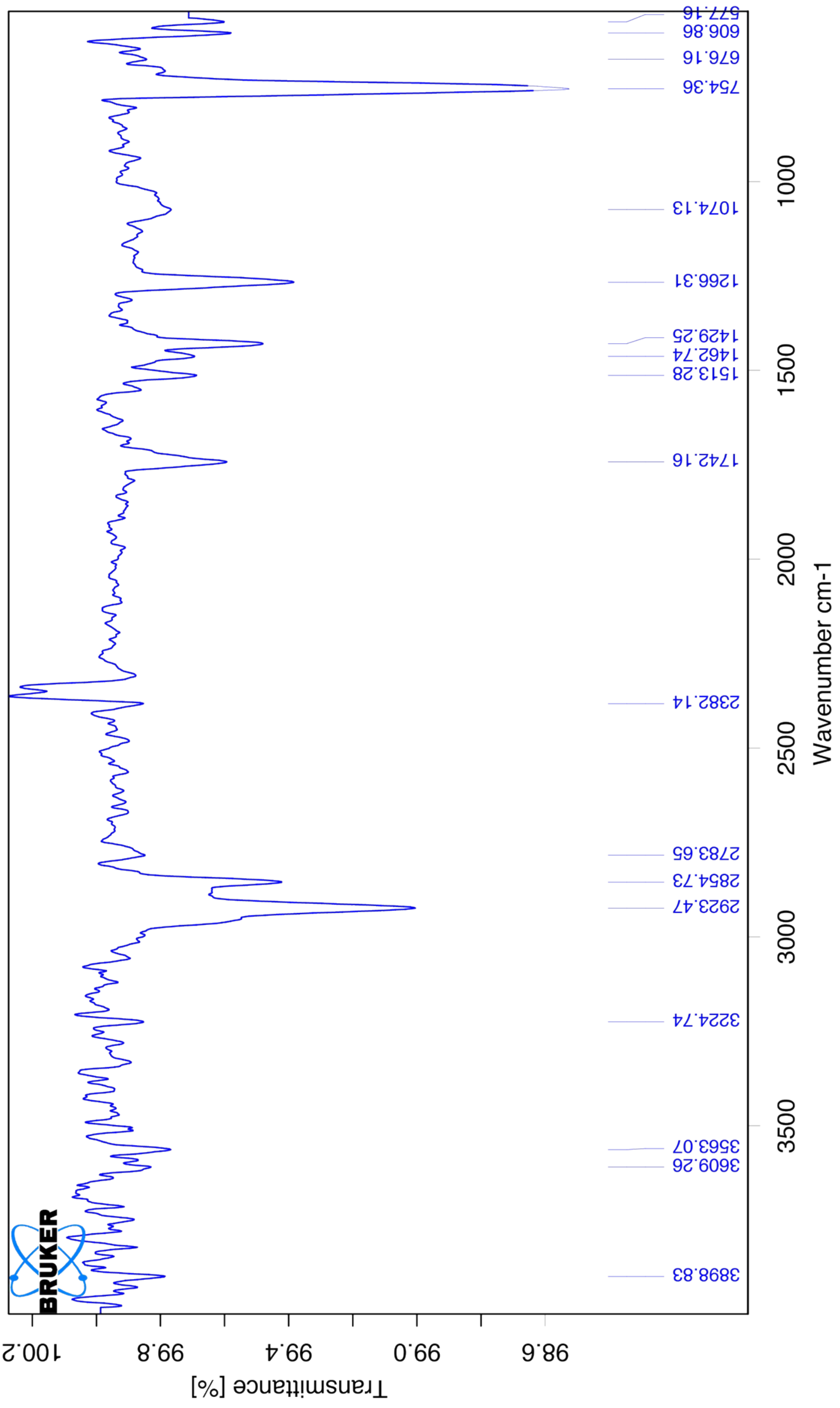
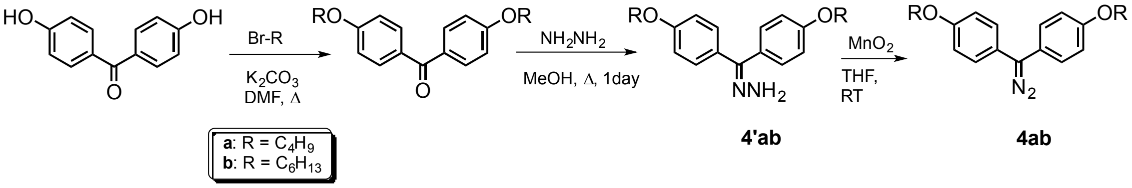


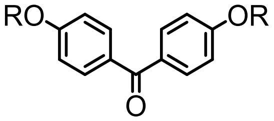
**Figure S4**. IR spectrum of compound **2** in $CHCl_3$.

**Synthesis of compound 4.**

The diazocompound **4a,b** was synthesized using the procedure described somewhere else.[i]



**4,4’-bis(butylphenyl)benzophenone:**



**a** : R=$C_4H_9$ ; **b** : R= $C_6H_{13}$

**$^1$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.

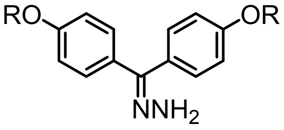
**MS (ESI):** Chemical Formula: $C_{21}H_{26}O_3$: m/z 326, found: m/z 327 [M+]

**$^1$H NMR of 4,4’-bis(hexylphenyl)benzophenone** (300 MHz, 298 K, $CDCl_3$) δ 0.93 (t, 3H, *J*= 7.55 $CH_3$-R), 1.26-1.50 (m, 6H, R-$CH_2$-R), 1.72-1.82 (m, 2H, R-$CH_2$-R), 4.03 (t, 2H, *J*= 6.42 Hz, R-$CH_2O$), 6.94 (d, 2H, *J*= 8.82Hz, Ar), 7.37 (d, 2H, *J*= 8.82Hz, Ar) ppm.

**$^{13}$C NMR of 4,4’-bis(hexylphenyl)benzophenone** (75 MHz, 298 K, $CDCl_3$) δ 14.0, 22.5, 25.6, 29.1, 31.5, 68.2, 113.9, 130.5, 132.2, 162.4, 195.4 ppm.

**MS (ESI):** Chemical Formula: $C_{25}H_{34}O_3$: m/z 382, found: m/z 383 [M+]

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



**a** : R=$C_4H_9$ ; **b** : R= $C_6H_{13}$

**$^1$H NMR of 4,4'-bis(butylphenyl)benzohydrazine** (300 MHz, 298 K, $CDCl_3$) δ 0.99 (t, 3H, *J*= 7.34Hz, $CH_3$-R); 1.03 (t, 3H, *J*= 7.34 Hz, $CH_3$-R); 1.53 (m, 4H, R-$CH_2$-R); 1.80 (q, 4H, *J*= 7.27 Hz, R-$CH_2$-R); 3.96 (t, 2H, *J*= 6.32 Hz, R-$CH_2$O); 4.02 (t, 2H, *J*= 6.32 Hz, R-$CH_2$O); 6.83 (d, 2H, *J*= 8.54 Hz, Ar); 7.04 (d, 2H, *J*= 8.54 Hz, Ar); 7.23(d, 2H, *J*= 8.54 Hz, Ar); 7.42 (d, 2H, *J*= 8.54 Hz, Ar) ppm.

**$^{13}$C NMR of 4,4'-bis(butylphenyl)benzohydrazine** (75 MHz, 298 K, $CDCl_3$) δ 14.1, 20.0, 31.2, 67.5, 123.5, 129.5, 131.2, 144.2, 154.8 ppm.

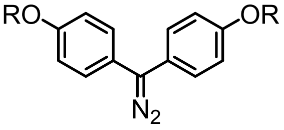
**MS (ESI):** Chemical Formula: $C_{21}H_{28}N_2O_2$: m/z 340, found: m/z 341 [M+]

**$^1$H NMR of 4,4'-bis(hexylphenyl)benzohydrazine** (300 MHz, 298 K, $CDCl_3$) δ 0.91 (t, 3H, *J*= 7.69 Hz, $CH_3$-R), 0.93 (t, 3H, *J*= 7.69 Hz, $CH_3$-R), 1.29-1.54 (m, 12H, R-$CH_2$-R), 1.71-1.89 (m, 4H, R-$CH_2$-R), 3.95 (t, 2H, *J*= 6.54 Hz, R-$CH_2$O), 4.02 (6.89 t, 2H, *J*= 6.54 Hz, R-$CH_2$O), 6.81 (d, 2H, *J*= 8.93 Hz, Ar), 7.03 (d, 2H, *J*= 8.93 Hz, Ar), 7.22(d, 2H, *J*= 8.93 Hz, Ar), 7.39 (d, 2H, *J*= 8.93 Hz, Ar) ppm.

**$^{13}$C NMR of 4,4'-bis(hexylphenyl)benzohydrazine** (75 MHz, 298 K, $CDCl_3$) δ 14.1, 21.7, 25.9, 29.2, 31.9, 68.7, 125.5, 128.3, 132.2, 143.2, 155.6 ppm.

**MS (ESI):** Chemical Formula: $C_{25}H_{36}N_2O_2$: m/z 396, found: m/z 397 [M+]

**Diazocompounds 4a,b.**



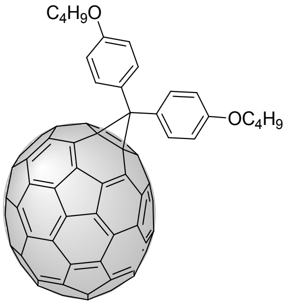
**a** : R=$C_4H_9$ ; **b** : R= $C_6H_{13}$

To a solution of compound **4'** (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 **4a,b** 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 5a,b.

Diazocompound **4a,b** (4 mg, 0.012 mmol, 1 eq) was added to a solution of [70]fullerene (10 mg, 0.012 mmol, 1 eq) in toluene anhydrous (4 ml). The mixture was bubbled with argon for 15 minutes in the dark in an ice-salt bath (-20ºC). Finally in the photoreactor was incident light wavelength 360 nm. 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 compound **5a,b** (72% yield, based on recovered $C_{70}$). HPLC conditions: column: Buckyprep; solvents: toluene/acetonitrile (90:10); flow: 1 ml/min; λ= 320 nm; temperature: 25ºC.

**Compound 5a: α-*site*-isomer**



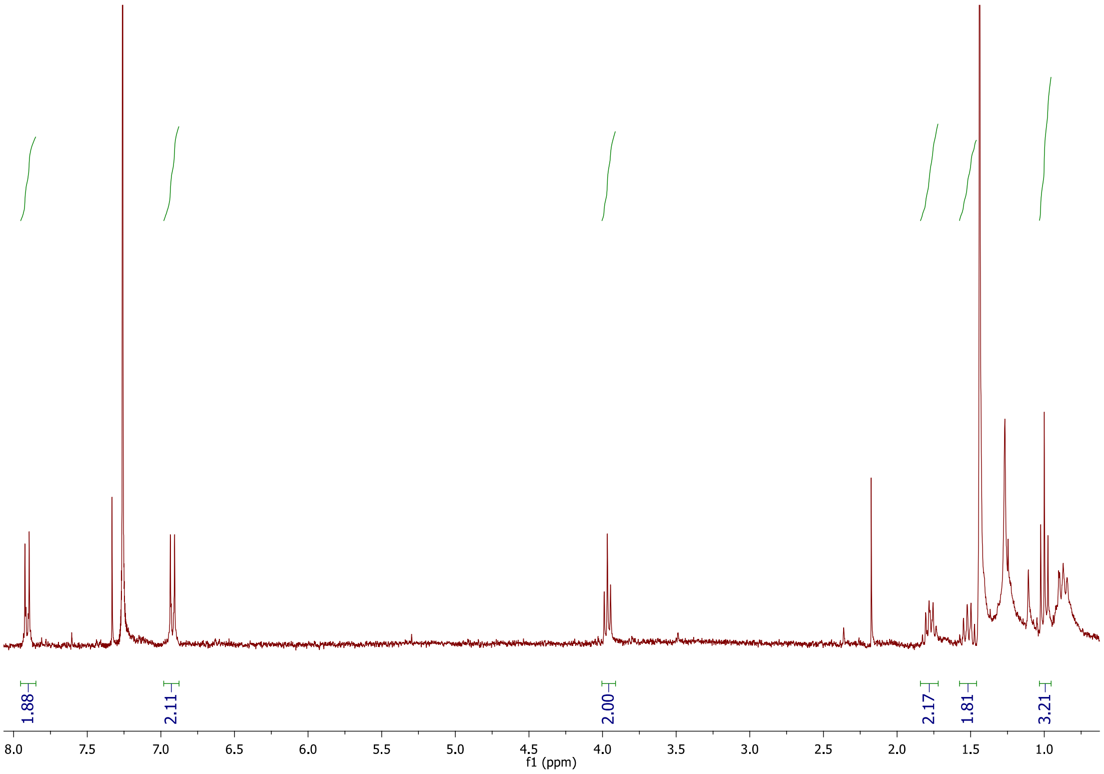


**Figure S5.** $^{1}H$ NMR (700 MHz, 298 K, $CDCl_3$) of compound **5a** (α-*site*-isomer).

**$^{1}$H NMR of compound 5a** (700 MHz, 298 K, $CDCl_3$) 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.

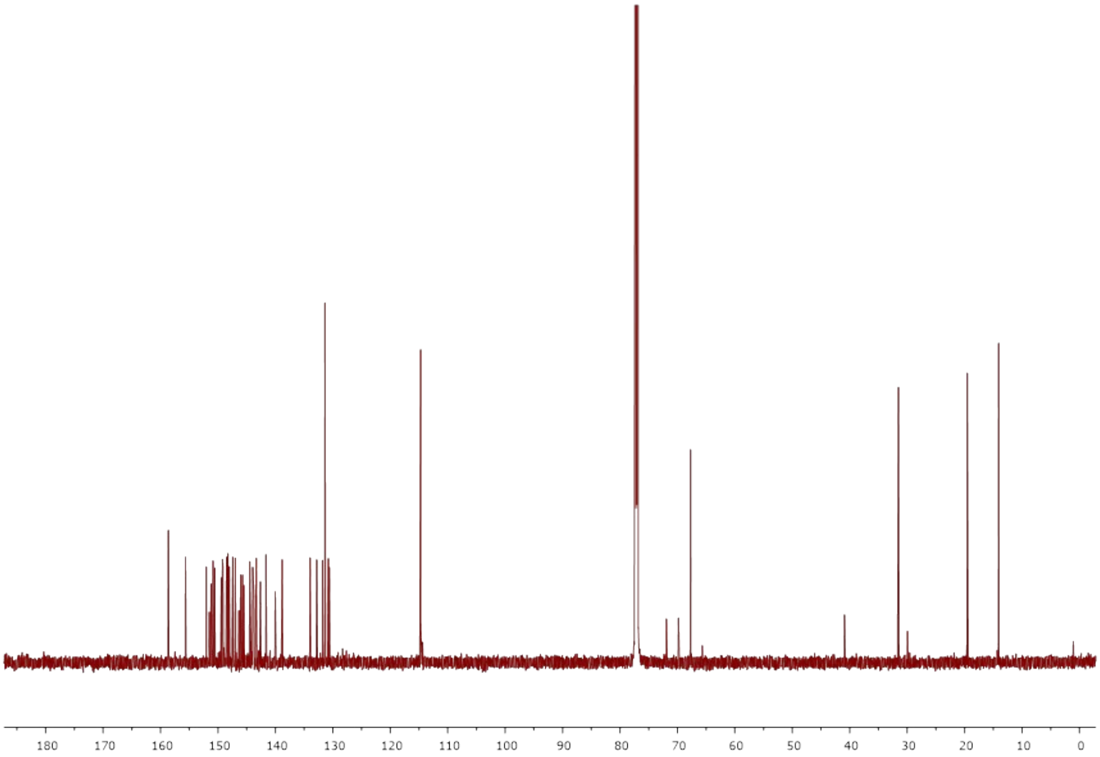
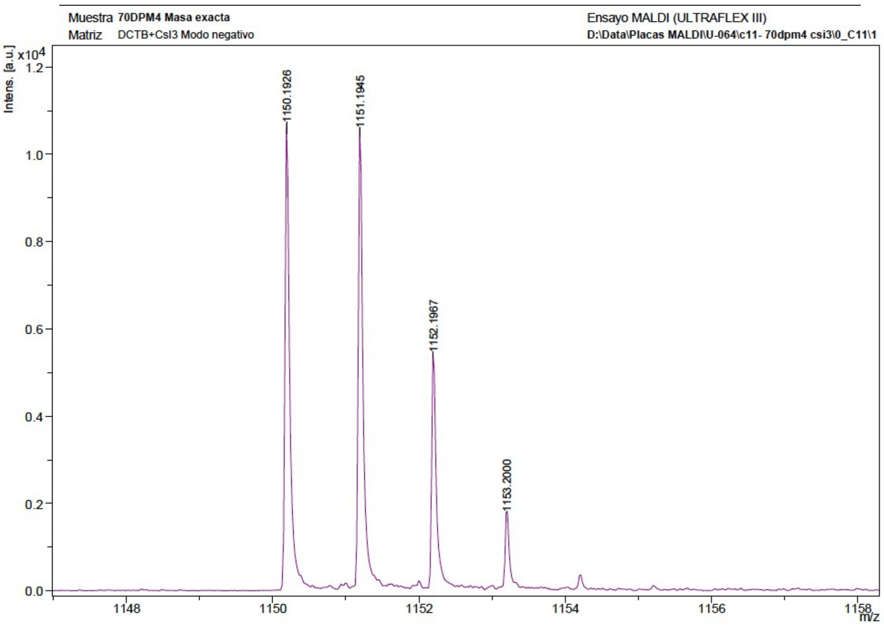


**Figure S6.** $^{13}$C NMR (175 MHz, 298K, $CDCl_3$) of compound **5a** (α-*site*-isomer).

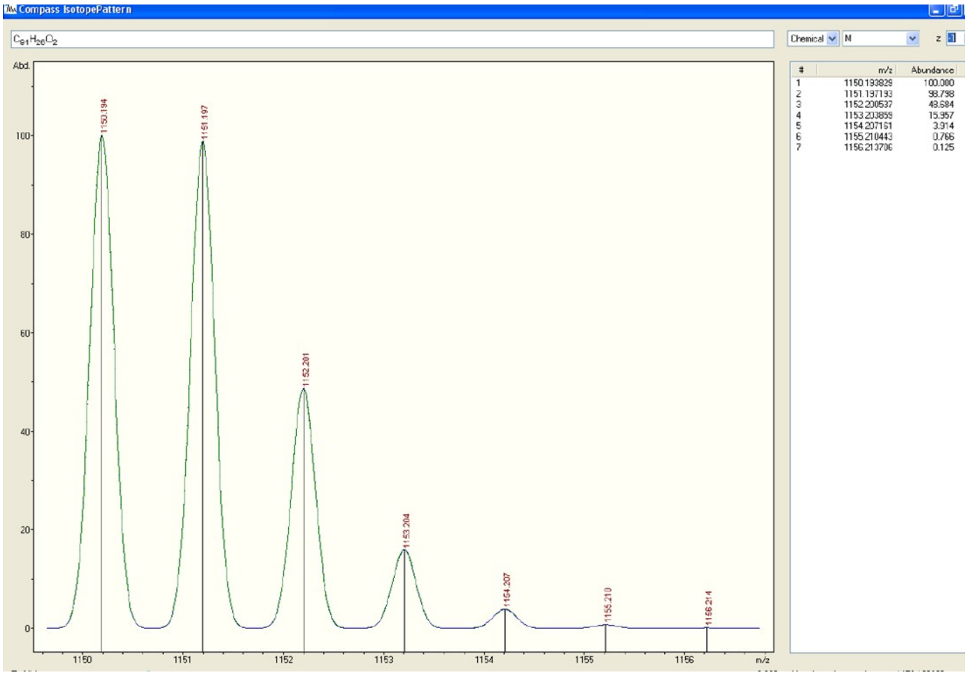
**$^{13}$C NMR of compound 5a** (175 MHz, 298 K, $CDCl_3$) δ 14.1, 19.5, 31.5, 40.9, 67.7, 69.8, 71.9, 114.7, 115.1, 130.6, 130.7, 130.8, 131.4, 131.8, 132.8, 133.9, 138.8, 140.0, 141.6, 141.7, 142.6, 143.3, 143.8, 143.9, 144.5, 145.5, 145.7, 146.1, 146.4, 146.9, 147.4, 147.5, 148.0, 148.3, 148.4, 148.5, 148.6, 149.1, 149.2, 149.4, 150.6, 150.9, 151.2, 151.5, 152.1, 155.7, 158.6 ppm.

**HRMS (MALDI TOF) of compound 5a:** m/z 1150.1938 calculated for $C_{91}H_{26}O_2$; found: m/z 1150.1926.

a)



b)



$C_{91}H_{26}O_2$

Chemical M z -1

| # | m/z | Abundance |
|---|---|---|
| 1 | 1150.193829 | 100.000 |
| 2 | 1151.197193 | 98.798 |
| 3 | 1152.200537 | 48.684 |
| 4 | 1153.203859 | 15.957 |
| 5 | 1154.207161 | 3.914 |
| 6 | 1155.210443 | 0.766 |
| 7 | 1156.213706 | 0.125 |

**Figure S7.** HRMS spectra of compound **5a** (a) experimental spectrum; b) theoretical spectrum).

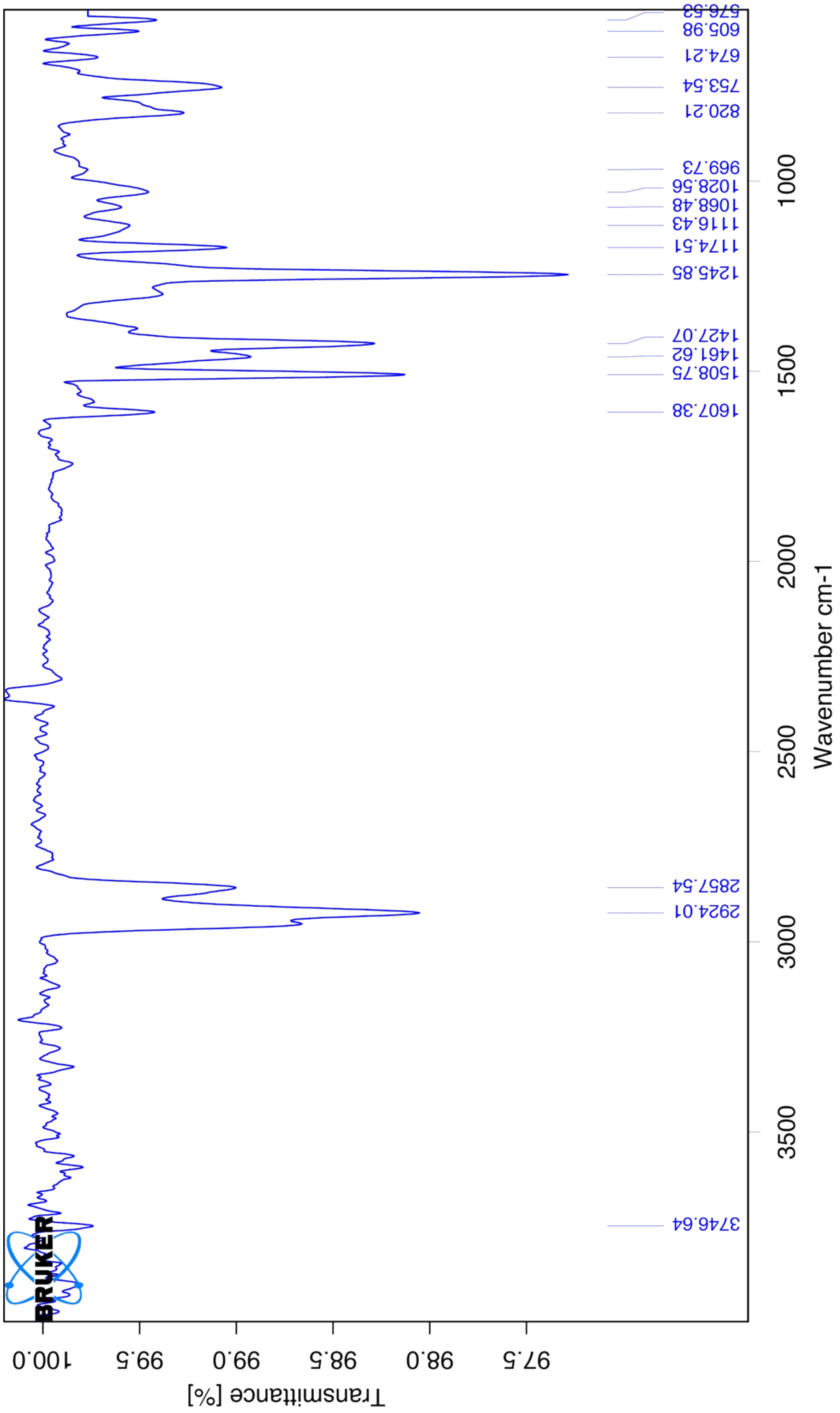
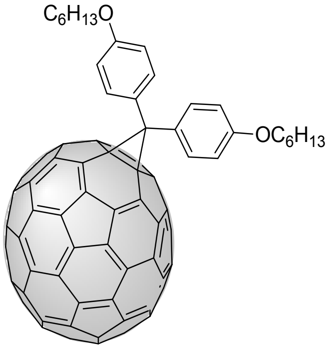


**Figure S8.** IR spectrum of compound **5a** in $CHCl_3$.

## Compound 5b: α-*site*-isomer



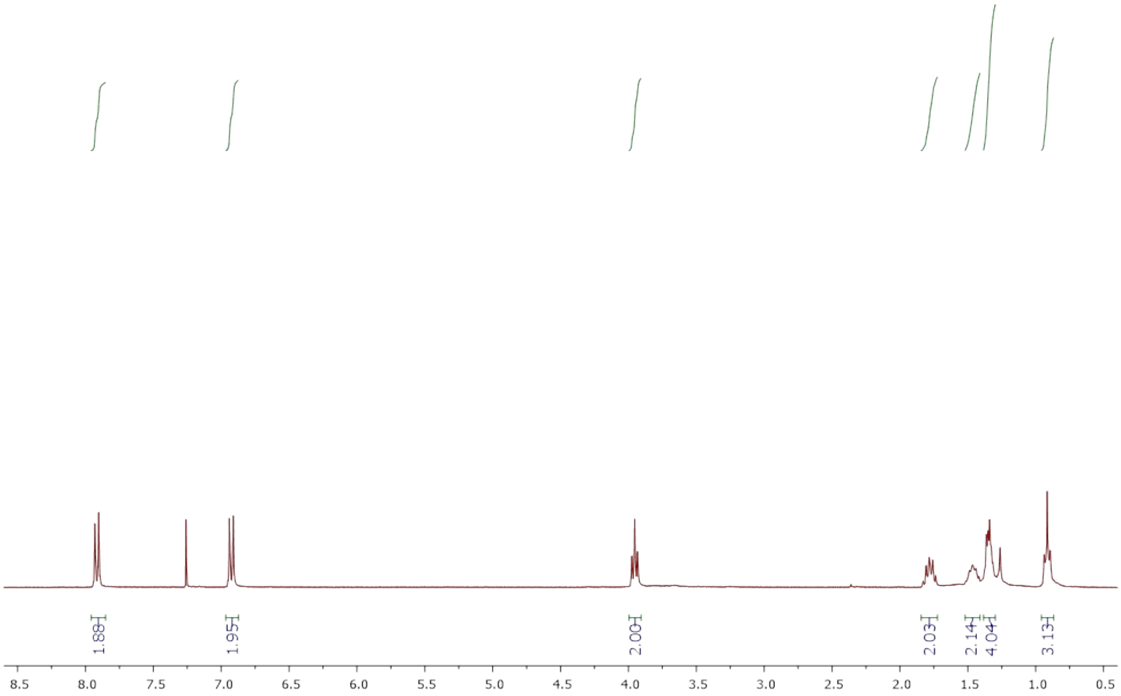


**Figure S9.** $^{1}$H NMR (700 MHz, 298 K, $CDCl_3$) of compound **5b** (α-*site*-isomer).

**$^{1}$H NMR of compound 5b** (700 MHz, 298 K, $CDCl_3$) δ 0.90 (t, 3H, *J*= 6.86 Hz, $CH_3$-R), 1.42-1.56 (m, 6H, R-$CH_2$-R), 1.78 (m, 2H, R-$CH_2$-R), 3.97 (t, 2H, *J*= 6.51 Hz, R-$CH_2O$), 6.96 ( d, 2H, *J*= 8.64 Hz, Ar), 7.80 (d, 2H, *J*= 8.64 Hz, Ar) ppm.

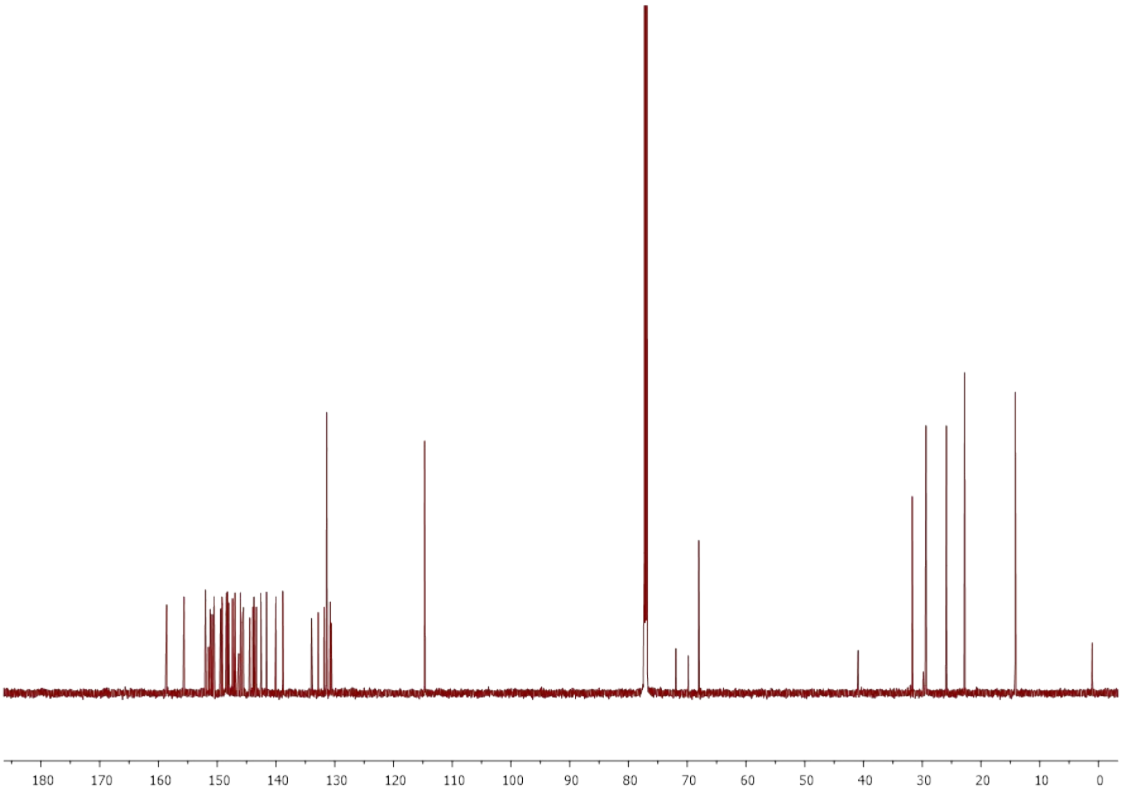
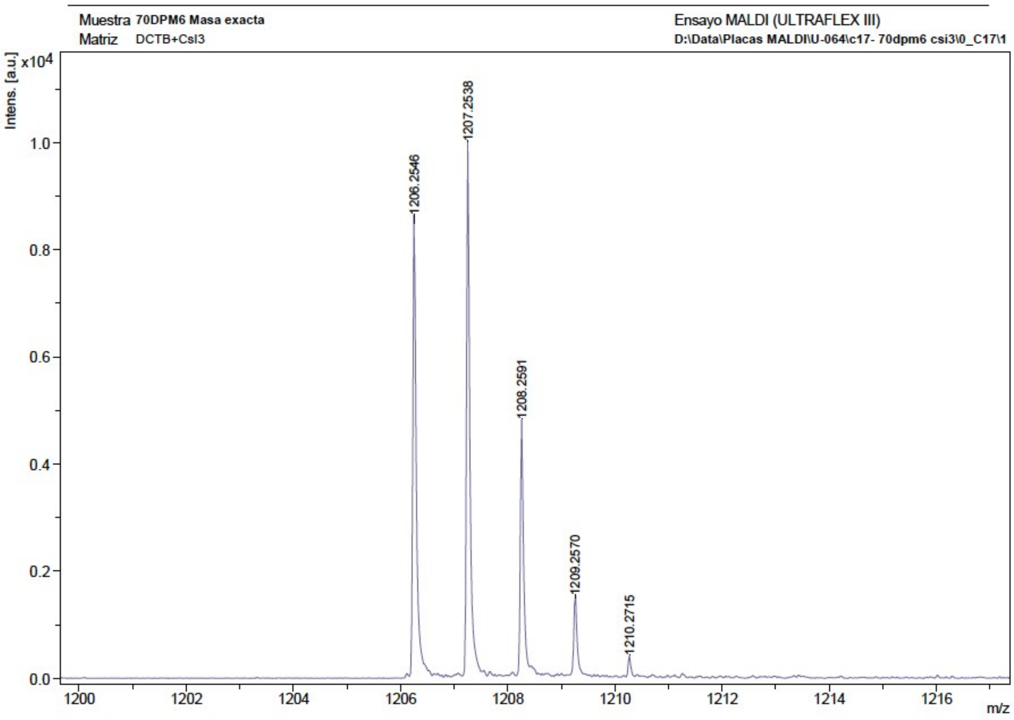


**Figure S10.** $^{13}C$ NMR (175 MHz, 298K, $CDCl_3$) of compound **5b.**

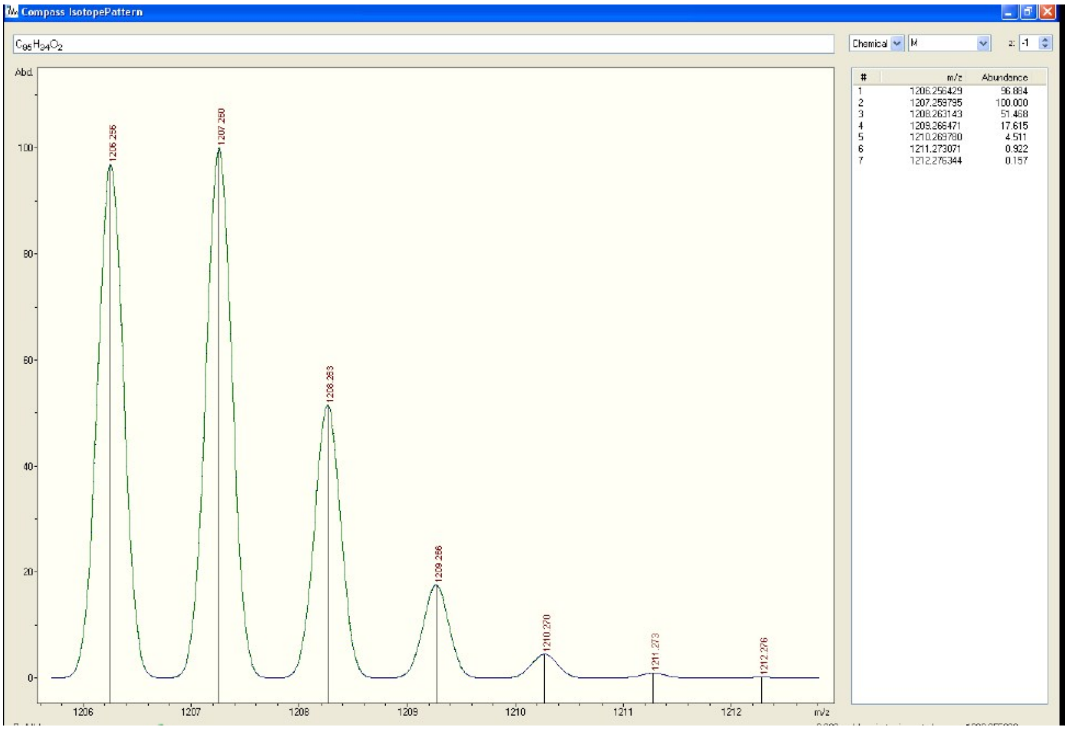
**$^{13}$C NMR of compound 5b** (175 MHz, 298 K, $CDCl_3$) δ 14.2, 22.8, 25.9, 29.4, 29.7, 31.7, 40.9, 68.0, 69.8, 71.9, 114.7, 130.6, 130.7, 130.8, 131.4, 131.8, 132.8, 133.9, 138.9, 140.0, 141.6, 142.6, 143.3, 143.8, 143.9, 144.5, 145.7, 146.0, 146.4, 146.9, 147.4, 147.5, 148.1, 148.3, 148.4, 148.5, 148.6, 149.1, 149.2, 149.4, 150.5, 150.9, 151.2, 151.5, 152.0, 155.7, 158.6 ppm.

**HRMS (MALDI TOF) of compound 5b:** m/z 1206.256 calculated for $C_{95}H_{34}O_2$; found: m/z 1207.2564.

a)



b)



$C_{95}H_{34}O_2$

Chemical M z: -1

| # | m/z | Abundance |
|---|---|---|
| 1 | 1206.256429 | 96.884 |
| 2 | 1207.259795 | 100.000 |
| 3 | 1208.263143 | 51.468 |
| 4 | 1209.266471 | 17.615 |
| 5 | 1210.269780 | 4.511 |
| 6 | 1211.273071 | 0.922 |
| 7 | 1212.276344 | 0.157 |

**Figure S11.** HRMS spectra of compound **5b** (a) experimental spectrum; b) theoretical spectrum).

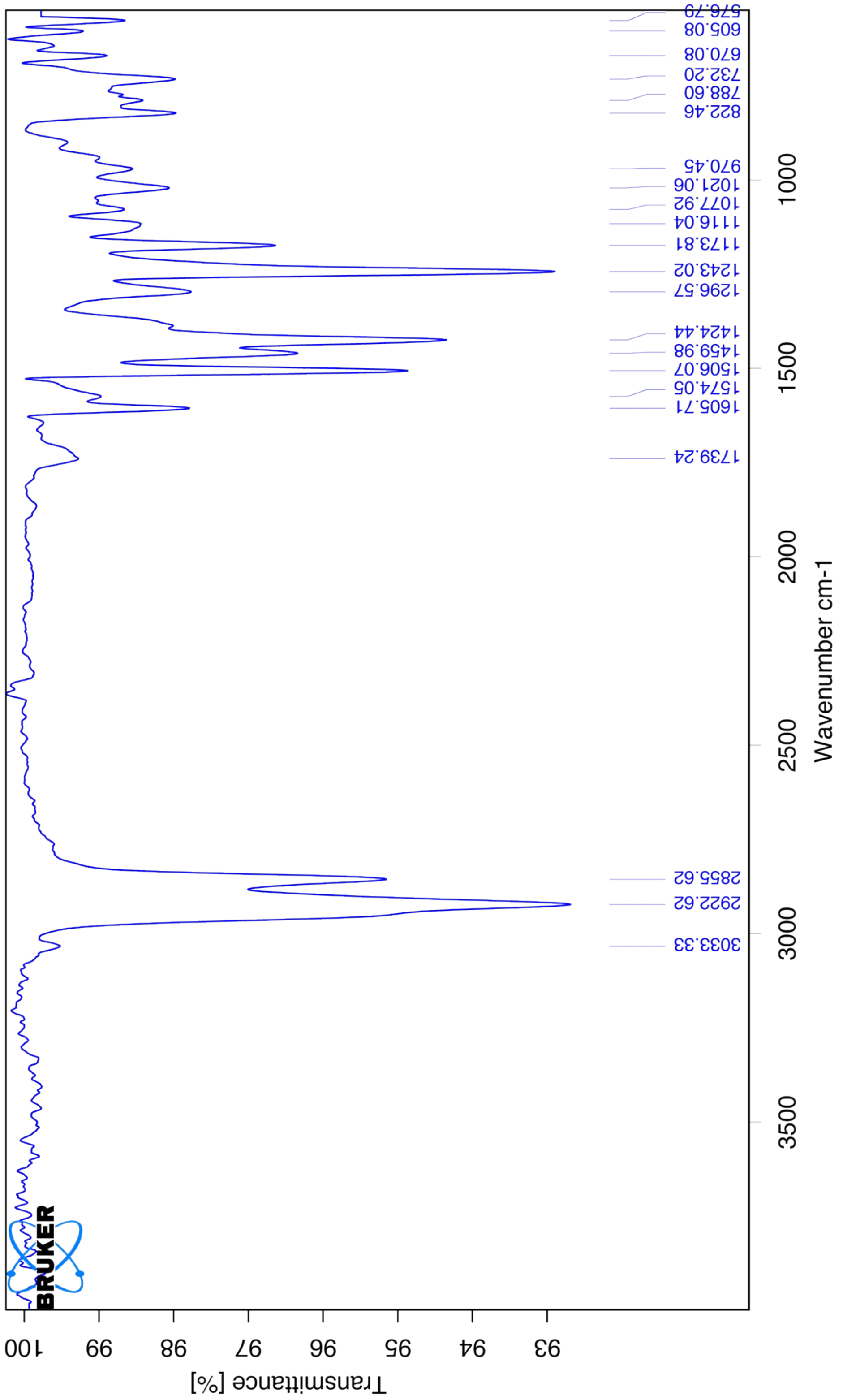


**Figure S12.** IR spectrum of compound **5b** in $CHCl_3$.

**HPLC profiles of compounds 2, 3a,b and 5ab.**

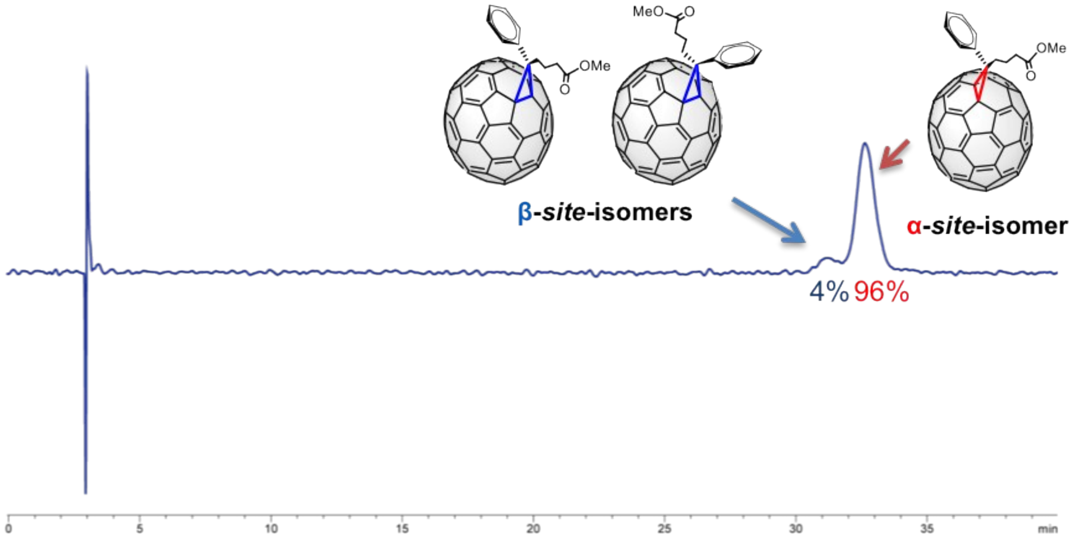


**Figure S13.** HPLC profile of α-[70]PCBM (**2**) that reveals the formation of α-*site*-isomer in a ratio (96:4 α:β). HPLC column: 5PYE (4,6 ID x 250mm; toluene/acetonitrile (1:1); 1 ml/min; 320 nm; 25ºC).

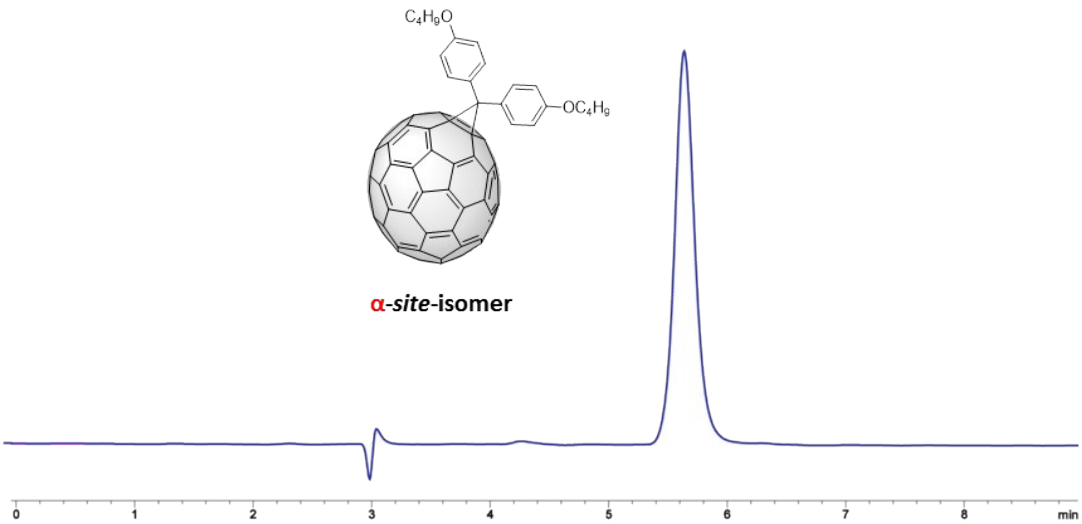


**Figure S14.** HPLC profile of α-[70]DPM-4 (**5a**) that reveals the exclusively formation of α-*site*-isomer. HPLC column: Buckyprep waters (4,6 ID x 250mm; toluene/acetonitrile (90:10); 1 ml/min; 320 nm; 25ºC).

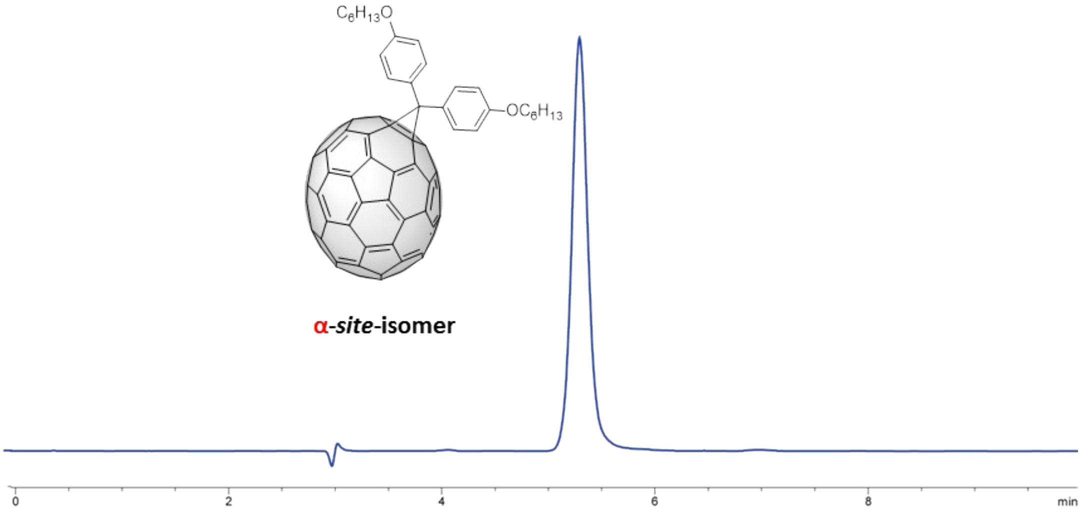


**Figure S15.** HPLC profile of α-[70]DPM-6 (**5b**) that reveals the exclusively formation of α-*site*-isomer. HPLC column: Buckyprep waters (4,6 ID x 250mm; toluene/acetonitrile (90:10); 1 ml/min; 320 nm; 25ºC).

## Cyclic voltammetry of compounds 2, 3, and 5.

**Table S1**. Reduction potential values of **$C_{70}$**, **2, 3, 5a, 5b** and the corresponding isomeric mixtures in V *vs* Fc/Fc+ couple.

| **Compound** | **$E_1^{1/2}$ (*V*)** | **$E_2^{1/2}$ (*V*)** | **$E_3^{1/2}$ (*V*)** |
|---|---|---|---|
| **$C_{70}$** | -1,02 | -1,40 | -1,82 |
| **2** (α-70PCBM) | -1,13 | -1,50 | -1,90 |
| **3** (β-70PCBM) | -1,14 | -1,51 | -1,95 |
| Mixture α+β 70PCBM | -1,13 | -1,52 | -1,92 |
| **5a** (α-70DPM4) | -1.13 | -1.49 | -1.90 |
| Mixture α+β 70DPM4 | -1.12 | -1.49 | -1.91 |
| **5b** (α-70DPM6) | -1.13 | -1.52 | -1.93 |
| Mixture α+β 70DPM6 | -1.12 | -1.49 | -1.91 |

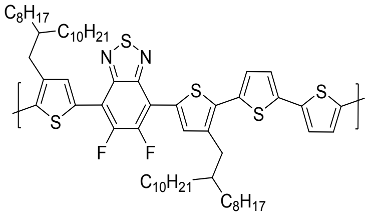
## Solar cell fabrication and testing

Pre-patterned ITO-coated glass with sheet resistance of 15Ω per square centimeter was used as the substrate. The glass substrate was cleaned by the sequential sonication in soap DI water, DI water, acetone and isopropanol for 30 min each step. After that, the glass substrate was treated by ultraviolet/ozone cleaner (Novascan, PSD Series digital UV ozone system) for 30 min. A ZnO (The diethylzinc solution 15wt% in toluene, diluted with tetrahydrofuran) electron transport layer was cast on the substrate by spin coating at spin rate of 5000 r.p.m. for 30s and then baked in air at 180℃ for 30 min in a dry box (relative humidity below 5%). Active layer solutions (polymer: fullerene weight ratio 1:1.2) were prepared in CB: DCB=6:4 with 2.5% DIO with polymer blend PffBT4T-2OD:$PC_{71}BM$. The polymer concentration was 10 mg/ml. To completely dissolve the polymer, the active layer solution was stirred on a hot plate at 100℃ for 2 hours. Before spin coating, both the polymer solution and ITO substrate were preheated on a hot plate at ~110℃. Active layers were spin coated from the warm polymer solution onto the preheated substrate in a $N_2$ glovebox at ~800 r.p.m. The active layer then treated with vacuum to remove the high boiling point additives. The blend films were annealed at 100℃ for 5 min. After that, the cast films were transferred to a thermal evaporator inside the same glovebox. At a vacuum level of $3 \times 10^{-6}$ Torr, a thin layer (20nm) of $V_2O_5$ was deposited as the anode interlayer, followed by deposition of 100 nm of Al as the top electrode. All cells were encapsulated using epoxy inside the glove box. Device *J-V* characteristics was measured under air mass 1.5 global (100 $mWcm^{-2}$) using a Newport Class a solar simulator (94021A, a Xenon lamp with an AM1.5G filter). A standard crystalline Si solar cell with a KG5 filter was purchased from PV measurements and calibrated by Newport Corporation. The light intensity was calibrated using the standard Si diode to bring spectral mismatch to unity. *J-V* characteristics were recorded using Keithley 236 or 2400 source meter unit. Typical cells have devices area of ~5.9 $mm^2$, which is defined by a metal mask with an aperture aligned with the device area.

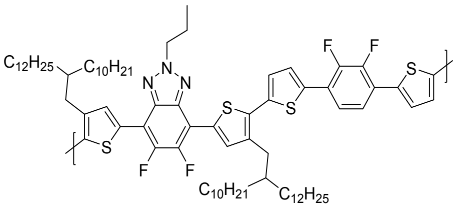
**Photovoltaic devices from pure α-[70]DPM6:**

**Table S2.** Average PCE% reached in a different polymer:fullerene BHJ solar cells using pure α-[70]PCBM isomer and a commercially available isomeric mixture. Polymer Y5: PffBT4T-2OD, polymer Z70:PFBT-O and polymer PBDB-T.

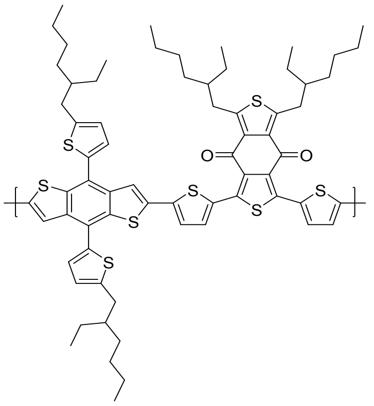
| Material Combinations | Condition Ratio: 1:1.2 | $V_{oc}$ [V] | $J_{sc}$ [mA/ cm$^2$] | FF [%] | PCE [%] | Best PCE [%] |
|---|---|---|---|---|---|---|
| **Y5:DPM[70]** | 10mg/Ml, CB/ DCB(6:4)+2.5%DIO | 0.852 | 8.39 | 0.437 | 3.13 | 3.39 |
| | | 0.856 | 8.57 | 0.442 | 3.25 | 3.46 |
| | | 0.854 | 8.50 | 0.454 | 3.29 | 3.35 |
| | | 0.855 | 8.34 | 0.436 | 3.11 | 3.20 |
| **Z70:DPM[70]** | 10mg/Ml, CB+2.5%DIO | 0.934 | 7.17 | 0.540 | 3.62 | 3.67 |
| | | 0.921 | 7.44 | 0.501 | 3.44 | 3.52 |
| **PBDB-T:DPM[70]** | 15mg/Ml, CB+2.5ULDIO | 0.911 | 9.32 | 0.452 | 3.84 | 3.84 |
| | | 0.893 | 8.89 | 0.409 | 3.25 | 3.32 |



**Y5**



**Z70**



**PBDB-T**

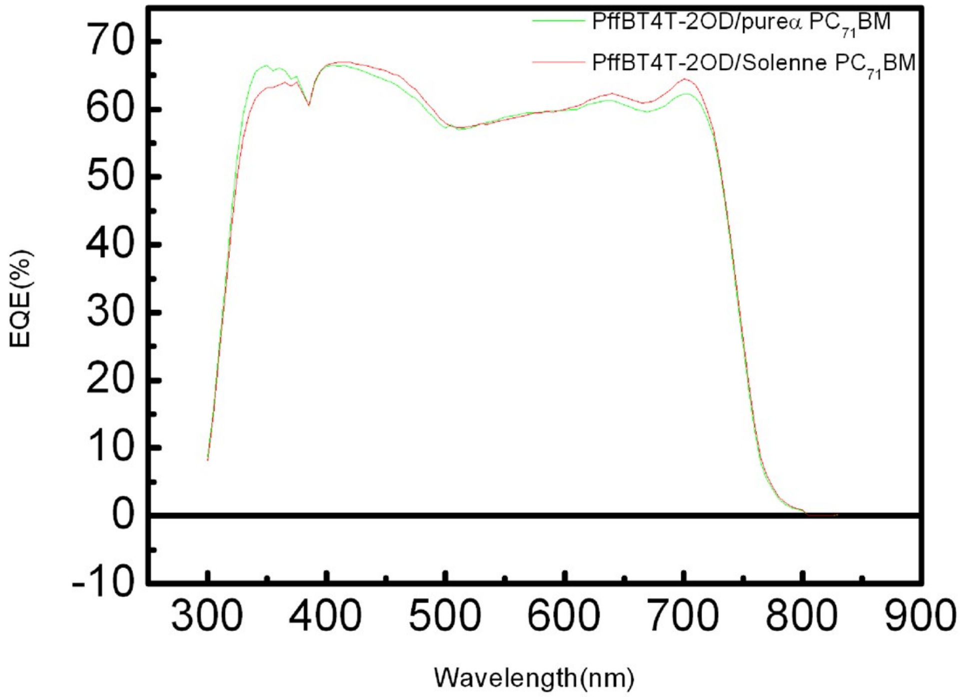


**Figure S16.** EQE for PffBT4T-2OD/α-[70]PCBM and Solenne mixture.

## Single crystal X-ray diffraction

### Experimental section

A suitable dark purple crystal of **5b** was coated with mineral oil and mounted on a Mitegen MicroMount. The sample was transferred to a Bruker Kappa Apex II diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). Full details of the data collection and refinement can be found in the supplementary material. Raw intensity data frames were integrated with the SAINT program,[ii] which also applied corrections for Lorentz and polarization effects. Empirical absorption corrections were subsequently applied (SADABS)[iii]. The Bruker SHELXTL Software Package was used for space group determination, structure solution, and refinement.[iv] The space group determination was based on a check of the Laue symmetry, and systematic absences were confirmed using the structure solution. The structures were solved by direct methods (SHELXS-97), completed with different Fourier syntheses, and refined with full-matrix least-squares using SHELXS-97 minimizing $\omega(F_o^2 - F_c^2)^2$. Weighted $R$ factors ($R_w$) and goodness of fit are based on $F^2$ while conventional $R$ factors ($R$) are based on $F$. Some non-hydrogen atoms were refined with anisotropic displacement parameters, but others were too disordered to allow this treatment and were refined isotropically (*i.e.* terminal atoms in the alkyl chains C12-C13 and C23-C25, and also many of the carbon atoms in the $C_{70}$ moiety). Hydrogen atoms were calculated geometrically and allowed to ride on their parent carbon atoms. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.10 program library.

The crystal structure of compound **5b** has been deposited at the Cambridge Crystallographic Data Centre with code CCDC 1493981.

***Single crystal X-ray diffraction structure determination of 5b***

A dark purple prismatic-like specimen of $C_{95}H_{34}O_2$, approximate dimensions 0.040 mm x 0.200 mm x 0.220 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured in a Bruker Kappa Apex II diffractometer.

***Data collection and integration***

The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 65373 reflections to a maximum θ angle of 25.40° (0.83 Å resolution), of which 10116 were independent (average redundancy 6.462, completeness = 99.5%, Rint = 12.11%, Rsig = 12.79%) and 4070 (40.23%) were greater than $2\sigma(F^2)$.

***Unit cell***

The final cell constants of $a$ = 10.8278(4) Å, $b$ = 30.7175(14) Å, $c$ = 16.9665(7) Å, β = 102.171(2)°, volume = 5516.3(4) Å$^3$, are based upon the refinement of the XYZ-centroids of 3862 reflections above 20 σ(I) with 4.675° < 2θ < 35.08°.

***Absorption correction***

Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.863. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9810 and 0.9970.

***Structure solution and refinement***

The final anisotropic full-matrix least-squares refinement on $F^2$ with 442 variables converged at $R_1$ = 26.09%, for the observed data and $wR_2$ = 76.16% for all data. The goodness-of-fit was 1.128. The largest peak in the final difference electron density synthesis was 1.222 e-/Å3 and the largest hole was -0.787 e-/Å3 with an RMS deviation of 0.191 e-/Å$^3$. On the basis of the final model, the calculated density was 1.454 g/cm3 and F(000), 2480 e-.

**Table S3. Sample and crystal data for 5b.**

| | | |
|---|---|---|
| **Chemical formula** | $C_{95}H_{34}O_2$ | |
| **Formula weight** | 1207.22 g/mol | |
| **Temperature** | 296(2) K | |
| **Wavelength** | 0.71073 Å | |
| **Crystal size** | 0.040 x 0.200 x 0.220 mm | |
| **Crystal habit** | intense green prismatic | |
| **Crystal system** | monoclinic | |
| **Space group** | $P2_1/c$ | |
| **Unit cell dimensions** | $a$ = 10.8278(4) Å | α = 90° |
| | $b$ = 30.7175(14) Å | β = 102.171(2)° |
| | $c$ = 16.9665(7) Å | γ = 90° |
| **Volume** | 5516.3(4) Å$^3$ | |
| **Z** | 4 | |
| **Density (calculated)** | 1.454 g/cm$^3$ | |
| **Absorption coefficient** | 0.085 mm$^{-1}$ | |
| **F(000)** | 2480 | |

**Table S4. Data collection and structure refinement for 5b.**

| | |
|---|---|
| **Theta range for data collection** | 1.33 to 25.40° |
| **Index ranges** | -13<=h<=12, -37<=k<=37, -20<=l<=20 |
| **Reflections collected** | 65373 |

| | |
|---|---|
| **Independent reflections** | 10116 [R(int) = 0.1211] |
| **Coverage of independent reflections** | 99.5% |
| **Absorption correction** | multi-scan |
| **Max. and min. transmission** | 0.9970 and 0.9810 |
| **Refinement method** | Full-matrix least-squares on $F^2$ |
| **Refinement program** | SHELXL-2014/7 (Sheldrick, 2014) |
| **Function minimized** | $\Sigma$ w($F_o^2$ - $F_c^2$)$^2$ |
| **Data / restraints / parameters** | 10116 / 14 / 442 |
| **Goodness-of-fit on $F^2$** | 1.128 |
| **$\Delta/\sigma_{max}$** | 0.002 |
| **Final R indices** | 4070 data; I>2σ(I) R1 = 0.2609, wR2 = 0.6744 |
| | all data R1 = 0.3909, wR2 = 0.7616 |
| **Weighting scheme** | $w=1/[\sigma^2(F_o^2)+(0.6130P)^2+3.3000P]$<br>where $P=(F_o^2+2F_c^2)/3$ |
| **Largest diff. peak and hole** | 1.222 and -0.787 eÅ$^{-3}$ |
| **R.M.S. deviation from mean** | 0.191 eÅ$^{-3}$ |

**Table S5. Hydrogen bond distances (Å) and angles (°) for 5b.**

| | **Donor-H** | **Acceptor-H** | **Donor-Acceptor** | **Angle** |
|---|---|---|---|---|
| **C16-H16···O1** | 0.93 | 2.66 | 3.536(16) | 157.4 |

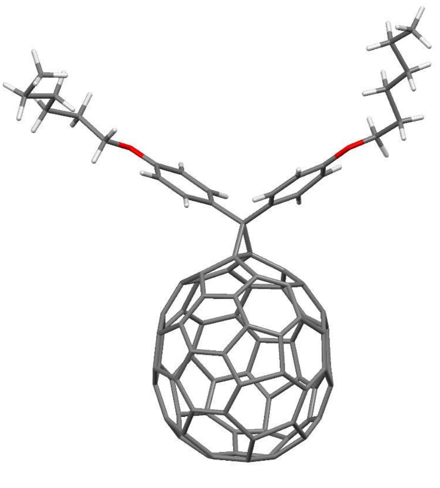


**Figure S17.** Molecular plot of compound **5b.**

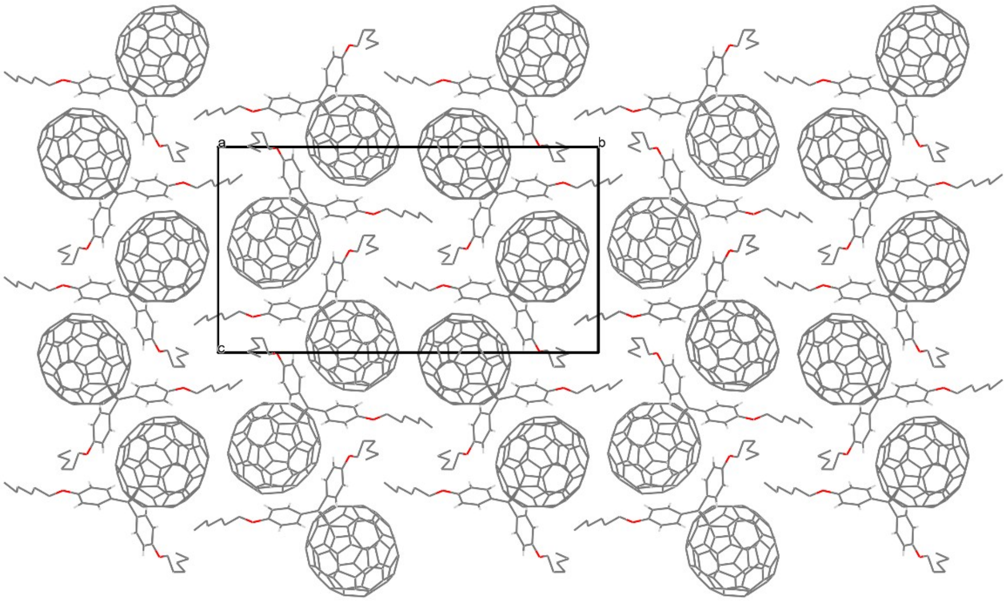


**Figure S18.** View of the packing of the molecules along the [100] direction.

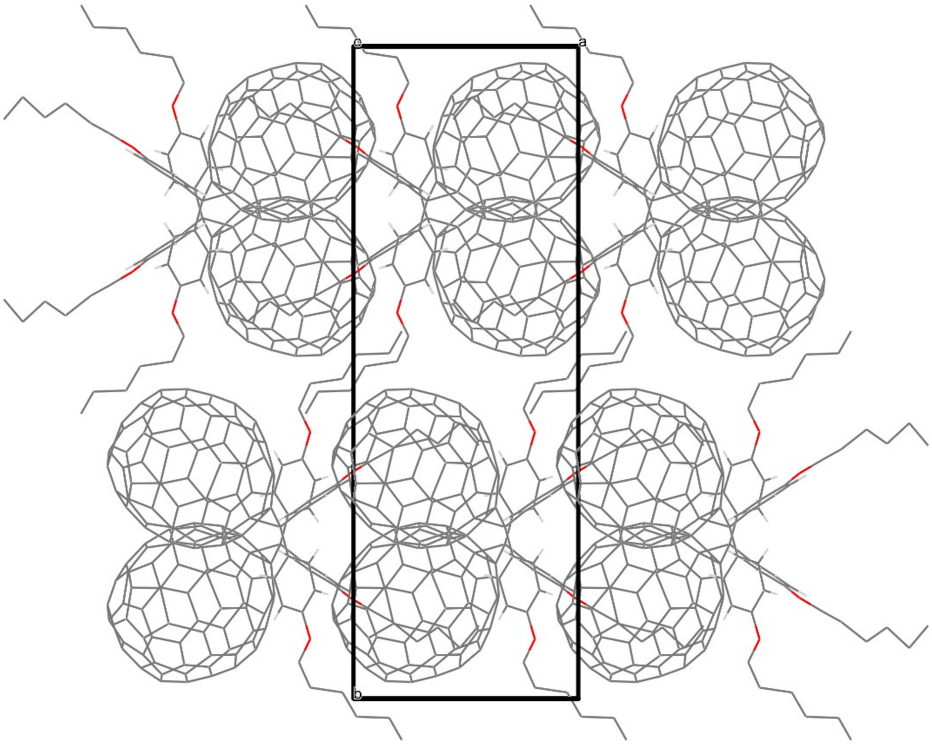


**Figure S19.** View of the packing of the molecules along the [001] direction.

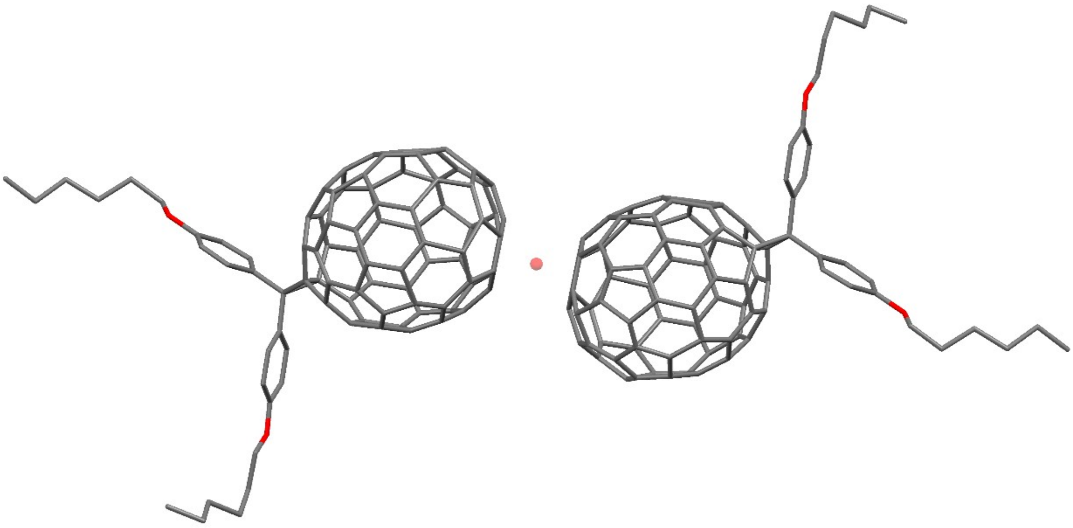


**Figure S20.** View of one of the pairs of molecules that display a π-π interaction between $C_6$ rings with the inversion centre depicted in translucent red. These inversion centres are the ones with coordinates 0, ½, 0 and 0, 0, ½; and their equivalents by translation.

---

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

[ii] SAINT+NT Version 6.04, SAX Area-Detector Integration Program; Bruker Analytical X-ray Instruments: Madison, WI, 1997−2001.

[iii] G. M. Sheldrick, SADABS Version 2.03, Program for Empirical 951 Absorption Correction; University of Göttingen: Germany, 1997−2001.

[iv] Bruker AXS SHELXTL Version 6.10, Structure Determination Package; Bruker Analytical X-ray Instruments: Madison, WI, 2000.