Supporting Information

Subphthalocyanine capsules: Molecular reactors for photoredox transformations of fullerenes

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1) Materials and methods

1.1 Synthesis and structural characterization

Chemical reagents were purchased from Merck-Sigma Aldrich and were used without further purification. Solvents were purchased from Carlo Erba Reagents. All reactions were performed in standard glasswares, except for the cyclotetramerization reactions that were carried out in high pressure sealed tubes. Monitoring of the reactions has been carried out by thin layer chromatography (TLC), employing aluminum sheets coated with silica gel type 60 F254 (0.2 mm thick, E. Merck). Purification and separation of the synthesized products was performed by column chromatography, using silica gel (230–400 mesh, 0.040-0.063 mm, Merck). Mass Spectrometry (MS) and High Resolution Mass Spectrometry (HRMS) spectra were recorded employing Electrospray Ionization (ESI Positive TOF_MS) mass spectra using a MAXIS II spectrometer, or Matrix Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) using a Bruker Ultraflex III TOF/TOF spectrometer, with a nitrogen laser operating at 337 nm, or with a NdYAG laser operating at 335 nm. The different matrixes employed are indicated for each spectrum. Mass spectrometry data are expressed in *m/z* units. All MS experiments were carried out at the Servicio Interdepartmental de Investigación (SIdI) of the Universidad Autónoma de Madrid. ^{1}H NMR and ^{13}C NMR were recorded on Bruker XRD-500 (500 MHz) instruments. Deuterated solvents employed are indicated in each spectrum. Photochemical reactions were carried out under visible light by 15 W monochromatic Green LED (λ= 520-550 nm) at room temperature. The sample was placed at an approximate distance of 5 cm from the lamp.

1.2 Spectroscopic and photophysical characterization

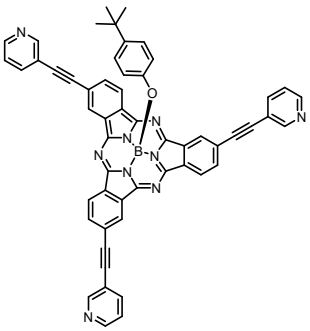
UV-vis spectra were recorded on a JASCO-V660 UV-vis spectrophotometer using spectroscopic grade solvents and 10x10mm quartz cuvettes with a Jasco Peltier ETCS-761 temperature controller incorporated, or in a double beam UV-Vis-NIR Varian Cary 6000i spectrophotometer (Varian, Palo Alto, CA, USA). Absorption coefficients were derived from the slopes of Lambert-Beer plots.

Fluorescence spectra were recorded with a JACSO FP-8600 spectrophotometer using spectroscopic grade solvents and quartz cuvettes (1cm) with a Jasco Peltier ETCS-761 temperature controller incorporated, or in a Spex Fluoromax-4 spectrofluorometer (Horiba Jobin-Yvon, Edison, NJ, USA). The samples were excited at 576 nm.

CV spectra: was measured with an Autolab equipment, using carbon electrode (work electrode), Ag/Ag+ electrode (Reference electrode) and Pt electrode (Counterelectrode). Ferrocene was employed as internal reference. E is given in volts, vs Fc/Fc+.

2) Synthesis of Photosensitizers

Synthesis of SubPc (1) [1]

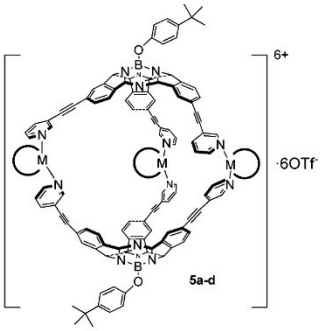


In a two-neck round bottom flask were placed triodo-SubPc (50 mg, 0.054 mmol, 1.0 equiv.), 3-ethynylpyridine (23 mg, 0.22 mmol, 4 equiv.) $Pd(PPh_3)Cl_2$ (16 mg, 0.022 mmol, 0.4 equiv) and CuI (2.05 mg, 0.012 mmol, 0.2 equiv) under Ar. The mixture was dissolved in 2 ml of previously degassed trimethylamine and stirred 3h at 40 ºC. Subsequently, 10 mL of water are added, and the product extracted with CH_2C_{l2} (3x10mL), then the organic layer was dried with Na_2SO_4 and solvent was evaporated under vacum. Product was purified through column

chromatography on silica gel using AcOEt:Heptane as eluent (9:1) obtaining a purple solid (40 mg, 0.047 mmol) Yield: 87%

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.01 (s, 3H), 8.79 (s, 3H), 8.76 (d, 3H, J = 8.17 Hz), 8.52 (d, 3H, J = 4.85 Hz), 8.01 (dt, 3H, Jo = 8.17 Hz, J =1.27 Hz), 7.87 (d, 3H, J = 7.9 Hz), 7.29 (dd, 3H, J = 7.79 Hz, J= 4.82 Hz), 6.72 (d, 2H, J = 8.14 Hz), 5.29 (d, 2H, J = 8.14 Hz), 1.09 (s, 9H) ppm.

Synthesis of Pd_2SubPc_3 (2) [1]

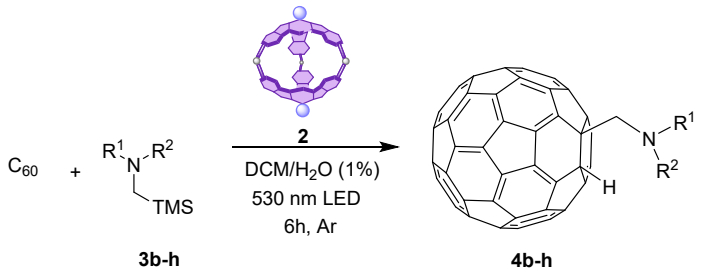


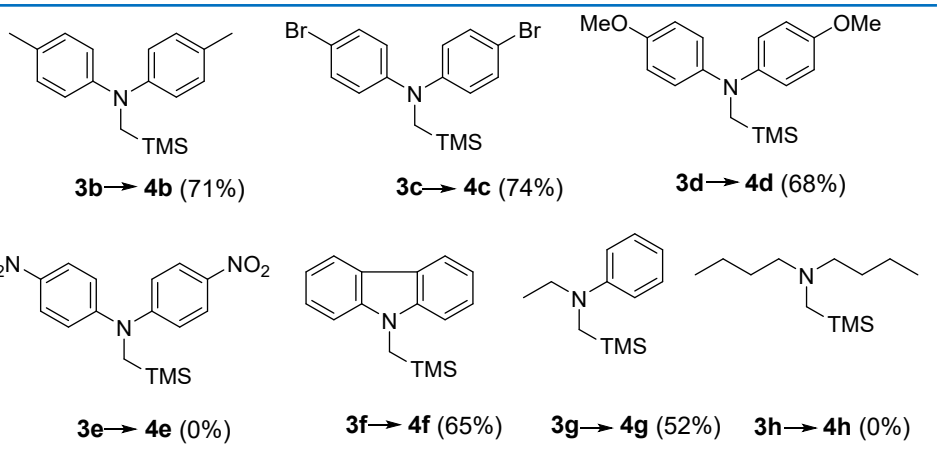
SubPc **1** (7.0 mg, 0.011 mmol, 1.0 equiv.) and Pd(dppp)]OTf_2 (13 mg, 0.016 mmol, 1.0 equiv.) were dissolved in dry dichoromethane (7ml). The resuting purple solution was stirred under argon atmosphere and warmed at reflux for 5 h and then left at room temperature overnight. After that, the solution was concentrated and diethylether was added. Finally, the resulting precipitate was filtered and washed sequentially with cold toluene, hexane and diethylether to obtain a purple powder (16 mg, yield 94%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.66 (s, 6H), 8.75 (s, 6H), 8.65 (d, 6H, J = 8 Hz), 8.58 (bs, 6H), 8.08 (m, 12H), 8.00 (d, 6H, J = 8 Hz), 7.65-7.14 (m, 60H), 6.70(d, 4H, J = 8 Hz), 5.23 (d, 4H, J = 8 Hz), 3.74 (m, 6H), 2.87 (m, 12H), 1.04 (s, 18H) ppm. (see Figure S1 in page 8)

3) Reactions of 2 with different α-silylamines

Table S1. Photoredox reaction of C_{60} with amines 3b-h in the SubPc cage.





Conditions: C_{60} (1 equiv.) 0.08 M, **3b-h** (1.5 equiv.), **2** (1 equiv.), at rt with irradiation by 530 nm LED under Ar.

3.1 Synthesis of α-silylamines

General procedure A (GP-A)[2]

A solution of the respective amine (1.0 equiv.) in THF (0.4 M) under Ar atmosphere, was cooled to 0 °C. Then n-BuLi (2.5M in hexanes, 1.2 equiv.) was added dropwise at 0 °C and the mixture was stirred for 30 min. and then stirred at room temperature for 1 h. (Iodomethyl)trimethylsilane (1.5 equiv.) was added slowly to the flask after the reaction was cooled back down to 0 °C, and the resulting solution was stirred at room temperature for 16 h. The reaction was then quenched with water and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (gradient elution with 0– 5% ethyl acetate-heptane)

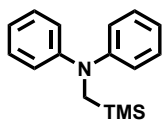
General Procedure B (GP-B)[3]

To a solution of diarylamine (1.0 equiv.) in THF (0.4 M) and HMPA (17% v/v,) was added n-BuLi (2.5 M in hexane, 1.5 equiv.) dropwise at -78 °C. The reaction mixture was stirred for 30 min, allowed to warm to room temperature, and then (iodomethyl)trimethylsilane (2.5 equiv.) was added slowly. The resulting solution was stirred overnight at room temperature. The reaction mixture was quenched with water (20 mL) and extracted with ethyl acetate (3 x 50 mL). The combined extract was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography (gradient elution with 0– 5% ethyl acetate-heptane).

General procedure C (GP-C)[4]

(Chloromethyl)trimethylsilane (1.0 equiv.) DMF (1.0 M) and the respective amine (2.0 equiv.) were added to a Schlenk tube. The reaction mixture was stirred at 90 °C for 16 h. The reaction was allowed to cool to room temperature and quenched with water and extracted by Et_2O (3 × 20 mL). The combined organics were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by column chromatography on silica gel to afford the title compounds.

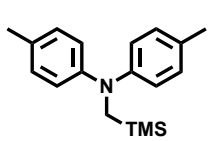
<u>*N*-Phenyl-*N*-((trimethylsilyl)methyl)aniline (**3a**)[2]</u>



Following the *GP-A*, diphenylamine (500 mg, 2.95 mmol) was converted to the title compound (530 mg, 2.07 mmol, yield 70%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.23 (m, 4H), 7.06–7.00 (m, 4H), 6.98–6.92 (m, 2H), 3.34 (s, 2H), –0.01 (s, 9H).

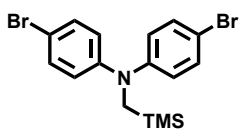
<u>4-Methoxy-*N*-(4-methoxyphenyl)-*N*-((trimethylsilyl)methyl)aniline (**3b**)[3]</u>



Following the *GP-B*, di-p-tolylamine (300 mg, 1.5 mmol) was converted to the respective silylamine (276 mg, 0.98 mmol, yield 65%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, J = 8.3 Hz, 4H), 6.86 (d, J = 8.4 Hz, 4H), 3.23 (s, 2H), 2.29 (s, 6H), –0.05 (s, 9H).

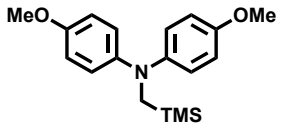
<u>4-Bromo-*N*-(4-bromophenyl)-*N*-((trimethylsilyl)methyl)aniline (**3c**)[3]</u>



Following the *GP-B,* 4,4'-dibromodiphenylamina (250 mg, 0.76 mmol) was converted to the respective silylamine (254 mg, 0.61 mmol, yield 81%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 4H), 6.85 – 6.82 (m, 4H), 3.24 (s, 2H), -0.03 (s, 9H)

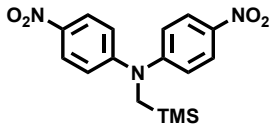
4-Methoxy-*N*-(4-methoxyphenyl)-*N*-((trimethylsilyl)methyl)aniline (**3d**)[3]



Following the *GP-B,* 4,4'-dimethoxydiphenylamina (175 mg, 0.76 mmol) was converted to the desired product (180 mg, 0.57 mmol, yield 75%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 – 6.85 (m, 4H), 6.82 – 6.79 (m, 4H), 3.77 (s, 6H), 3.14 (s, 2H), -0.08 (s, 9H)

4-Nitro-*N*-(4-nitrophenyl)-*N*-((trimethylsilyl)methyl)aniline (**3e**)



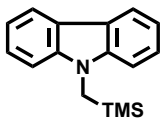
Following the *GP-A*, bis-*p*-tolylamine (500 mg, 1.92 mmol) was converted to the title compound (564 mg, 1.63 mmol, yield 85%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.2 Hz, 4H), 7.13 (d, *J* = 9.2 Hz, 4H), 3.54 (s, 2H), 0.04 (s, 9H).

^{13}C NMR (300 MHz, $CDCl_3$) δ 152.83, 129.89, 125.80, 120.61, 45.01, -0.96.

MS (GC-EI) Calc.: 345.1145, found: 345.1159.

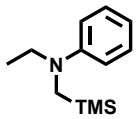
9-((Trimethylsilyl)methyl)-9H-carbazole (**3f**)[2]



Following the *GP-A*, 9H-carbazole (250 mg, 1.49 mmol) was converted to the desire compound (317 mg, 1.25 mmol, yield 84%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, J=7.8Hz, 2H), 7.46 (ddd, J=8.2, 7.2, 1.1Hz, 2H), 7.34 (d, J=8.2Hz, 2H), 7.21 (ddd, J=7.8, 7.2, 1.1Hz, 2H), 3.86 (s, 2H), 0.07 (s, 9H)

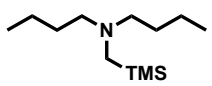
N-ethyl-*N*-((trimethylsilyl)methyl)aniline (**3g**)[2]



Following the *GP-A* ethylphenylamine (500 mg, 4.13 mmol) was converted to the title compound (599 mg, 2.89 mmol, yield 70%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (t, J = 8.0 Hz, 2H), 6.60 (m, 3H), 3.36 (q, J = 7.0 Hz, 2H), 2.79 (s, 2H), 1.11 (t, J = 7.0 Hz, 3H), 0.08 (s, 9H).

N-Butyl-*N*-((trimethylsilyl)methyl)butan-1-amine (**3h**)[4]



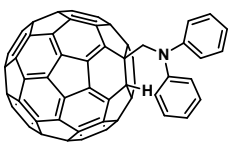
Following the *GP-C*, dibutylamine (3.4 mL, 20 mmol) was converted to the title compound (3.14 g, 14.6 mmol, yield 73%) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.36 – 2.28 (m, 4H), 1.90 (s, 2H), 1.44 – 1.34 (m, 4H), 1.34 - 1.23 (m, 4H), 0.90 (t, J = 7.2 Hz, 6H), 0.04 (s, 9H) ppm.

3.2 Photoredox Reactions of Fullerene with α-silylamines.

In a 5 mL sealed flask were placed [60] fullerene (C_{60}) (2.2 mg, 0.003 mmol, 1.0 equiv.), Pd_3SubPc_2 (10 mg, 0.003 mmol, 1.0 equiv.) and 2 mL of dry DCM under Ar. Then, a solution of the correspondent silylamine (0.0046 mmol, 1.5 equiv.) in distilled water (0.02 ml) was added and the mixture was photoirradiated with green LED for 6 h keeping the temperature at 30 °C. The solution was concentrated in vacuo and the resulting crude was purified by column chromatography on silica gel (gradient elution with 0– 95% DCM-heptane), rendering a brown solid.

1-[*N*,*N*-diphenylaminomethyl]-1,9-dihydro(C60-I_h)[5,6]fullerene (**4a**)[5]



Yield 86%.

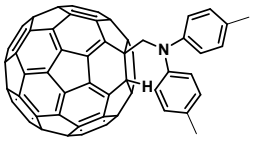
^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ (ppm): 7.38 (d, J = 8.0 Hz, 4H), 7.35 – 7.27 (m, 4H), 7.04 – 6.98 (m, 2H), 6.63 (s, 1H), 5.80 (s, 2H).

^{13}C NMR (126 MHz, CS_2/$CDCl_3$ (5%)) δ (ppm): 154.5, 153.8, 148.7, 147.6, 147.4, 147.4, 146.8, 146.7, 146.6, 146.5, 146.2, 146.1, 145.9, 145.8, 145.3, 145.2, 144.9, 144.8, 143.5, 143.0, 142.5, 142.4, 142.1, 142.1, 141.6, 141.5, 140.7, 140.4, 136.8, 136.1, 128.7, 122.7, 68.1, 66.5, 58.5

MS (MALDI, DCTB) m/z= 903.1 [M^-]

HR-MS: calc. for $C_{73}H_{13}N$: 903.1053. Found: 903.1080

1-[*N*,*N*-bis(4-methylphenyl)aminomethyl]-1,9-dihydro(C60-*I*$_h$)[5,6]fullerene (**4b**)[5]



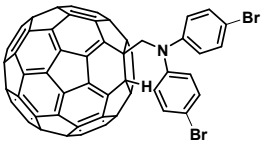
Yield 71%

^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ (ppm): 6.92 (d, J = 10.0 Hz, 4H), 6.75 (d, J = 7.6 Hz, 4H), 6.64 (s, 1H), 5.72 (s, 2H), 2.25 (s, 6H).

MS (MALDI, DCTB) m/z= 931.1 [M^-]

HR-MS: calc. for $C_{73}H_{11}NBr_2$: 931.1366. Found: 931.1366

1-[N,N-bis(4-bromolphenyl)aminomethyl]-1,9-dihydro(C60-*I*$_h$)[5,6]fullerene (**4c**)



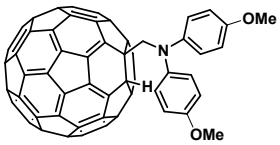
Yield 78%

^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ (ppm): 7.40 (d, J = 4.0 Hz, 4H), 7.28 (d, J = 2.6 Hz, 4H), 6.49 (s, 1H), 5.74 (s, 2H).

MS (MALDI, DCTB) m/z= 1060.9 [M^-]

HRMS: calc. for $C_{73}H_{11}NBr_2$: 1058.9264. Found: 1058.9230

1-[N,N-bis(4-methoxyphenyl)aminomethyl]-1,9-dihydro(C60-*I*$_h$)[5,6]fullerene (**4d**)



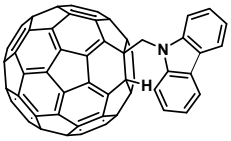
Yield 68%

^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ (ppm): 7.38 (d, J = 2.2 Hz, 4H), 7.34 (d, J = 1.5 Hz, 4H), 6.91 (s, 1H), 5.23 (s, 2H), 3.80 (s, 6H).

MS (MALDI, DCTB) m/z= 961.2 [M^+]

HR-MS: Calc. for $C_{75}H_{17}N$: 961.1097. Found: 961.1080

1-[carbazolylaminomethyl]-1,9-dihydro(C60-*I*$_h$)[5,6]fullerene (**4f**)



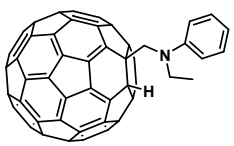
Yield 65%

^{1}H NMR (300 MHz, CS_2/$CDCl_3$) δ (ppm): 7.87 (d, J = 7.7 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.15 – 7.02 (m, 3H), 6.94 (s, 1H), 5.26 (s, 2H).

MS (MALDI, DCTB) m/z= 901.0 [M^-]

HR-MS: Calc. for $C_{73}H_{11}N$: 901.0987. Found: 901.0920

1-[*N*-ethyl-*N*-phenylaminomethyl]-1,9-dihydro(C60-*I*$_h$)[5,6]fullerene (**4g**)



Yield 52%

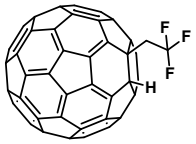
^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ (ppm): 7.59 (d, J = 7.7 Hz, 2H), 7.48 (m, 3H), 6.6 (s, 1H), 5.26 (s, 2H), 4.18 (q, J = 7.0 Hz, 2H), 2.71 (t, J = 7.0 Hz, 3H).

MS (MALDI, DCTB) m/z= 855.1 [M^+]

HR-MS: Calc. for $C_{69}H_{13}N$: 855.1043. Found: 855.1052

4) Photoredox Reactions of Fullerene with 1,1,1-trifluoro-2-iodoethane (5b)

1-[(2,2,2)-Trifluoroethyl]-1,9-dihydro(C_{60}-I_h)[5,6]fullerene



In a 5 mL sealed flask were placed, under Ar, [60] fullerene (C_{60}) (2.2 mg, 0.003 mmol, 1.0 equiv.), Pd_3SubPc_2 (10 mg, 0.003 mmol, 1.0 equiv.), PPh_3 (0.78 mg, 0.003 mmol, 1.0 equiv.), CF_3CH_2I (0.76 mg, 0.0036 mmol, 1.2 equiv), $(TMS)_3SiH$ (0.75 mg, 0.003 mmol, 1.0 equiv.) and 2 mL of dry DCM. Then the mixture was photoirradiated with green LED for 6 h keeping the temperature at 30 °C. The solution was concentrated in vacuo and the resulting crude was purified by column chromatography on silica gel (gradient elution with 0– 95% DCM-heptane obtaining the compound (1.65 mg, 0.0021 mmol, yield 69%) as a brown solid.

^{1}H NMR δ (300 MHz, $CDCl_3$) δ (ppm): 4.68 (s, 1H), 3.54 – 3.43 (m, 2H).

^{13}C NMR δ (126 MHz, $CDCl_3$) δ (ppm): 166.5, 163.5, 154.6, 154.0, 148.9, 146.9, 146.6, 145.9, 145.4, 145.0, 144.2, 143.6, 143.1, 142.5, 142.2, 140.5, 138.6, 136.9, 136.2, 133.2, 130.8, 130.2, 129.9, 129.2, 128.8, 123.6, 122.9, 68.3, 66.7, 58.6, 38.0 (q).

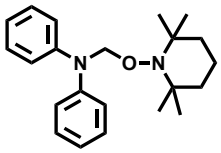
^{19}F NMR δ (500 MHz, $CDCl_3$) δ (ppm): -62.83.

MS (MALDI, DCTB) m/z= 804.1 [M^-]

HR-MS: Calc. for $C_{69}H_{13}N$: 804.0181. Found: 804.0188

5) Photoredox Reactions with TEMPO.

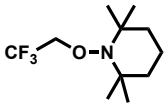
N-phenyl-N-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)aniline



In a 5 mL sealed flask were placed [60] fullerene (C_{60}) (2.2 mg, 0.003 mmol, 1.0 equiv.), Pd_3SubPc_2 (10 mg, 0.003 mmol, 1.0 equiv.) TEMPO (1.0 mg, 0.006 mmol, 2.0 equiv) 2 mL of dry DCM under Ar. Then, a solution of **3a** (1.2 mg, 0.0046 mmol, 1.5 equiv.) in distilled water (0.02 ml) was added and the mixture was photoirradiated with green LED for 6 h keeping the temperature at 30 °C. The solution was concentrated in vacuo and the resulting crude was characterized by HR-MS.

HR-MS: Calc. for $C_{22}H_{31}N_2O$: m/z 339.24 ([M+H]$^+$), found: m/z = 339.2541 ([M+H]$^+$). See Figure page 19.

2,2,6,6-tetramethyl-1-(2,2,2-trifluoroethoxy)piperidine



In a 5 mL sealed flask were placed, under Ar, [60] fullerene (C_{60}) (2.2 mg, 0.003 mmol, 1.0 equiv.), Pd_3SubPc_2 (10 mg, 0.003 mmol, 1.0 equiv.), PPh_3 (0.78 mg, 0.003 mmol, 1.0 equiv.), CF_3CH_2I (0.76 mg, 0.0036 mmol, 1.2 equiv), $(TMS)_3SiH$ (0.75 mg, 0.003 mmol, 1.0 equiv.) and 2 mL of dry DCM. Then the mixture was photoirradiated with green LED for 6 h keeping the temperature at 30 °C. The solution was concentrated in vacuo and the resulting crude was characterized by ^{19}F-NMR.

^{19}F NMR δ (500 MHz, $CDCl_3$) δ (ppm): -62.83. See Figure page 24.

6) Reciclability of cage 2

	2 recovered	Yield of **3a**
Reaction 1	80 %	70%
Reaction 2	65 %	68%
Reaction 3	40 %	67%

Table S1: Recyclability of cage **2** in subsequent photoredox reactions with **3a**.

7) NMR and Mass Spectra

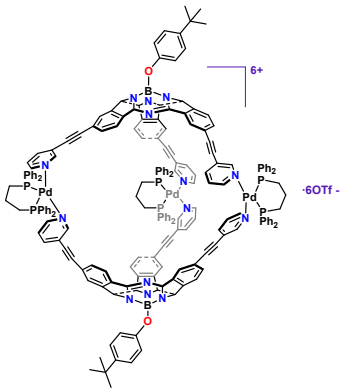


*Figure S1: ^{1}H-NMR of Pd_3SubPc_2 **2***

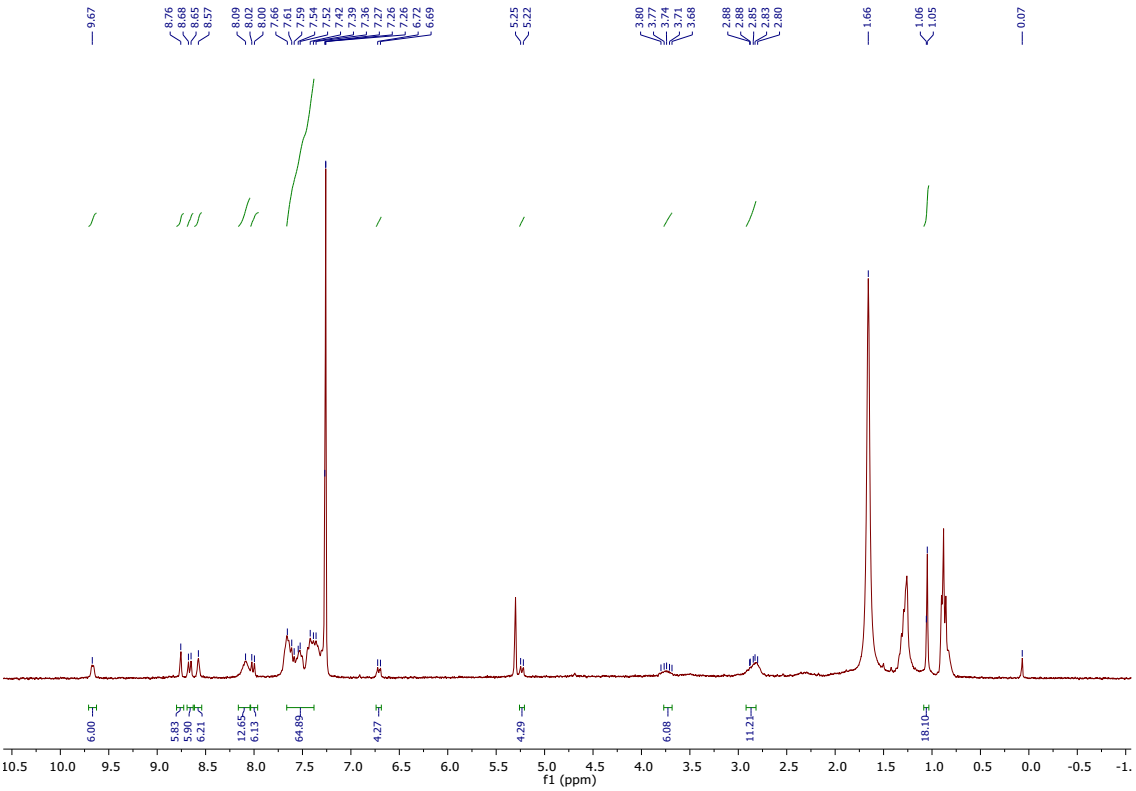
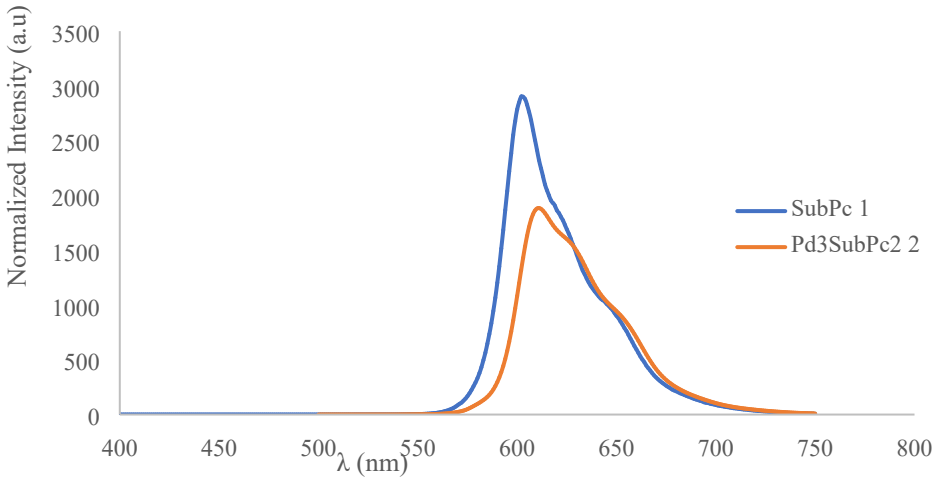
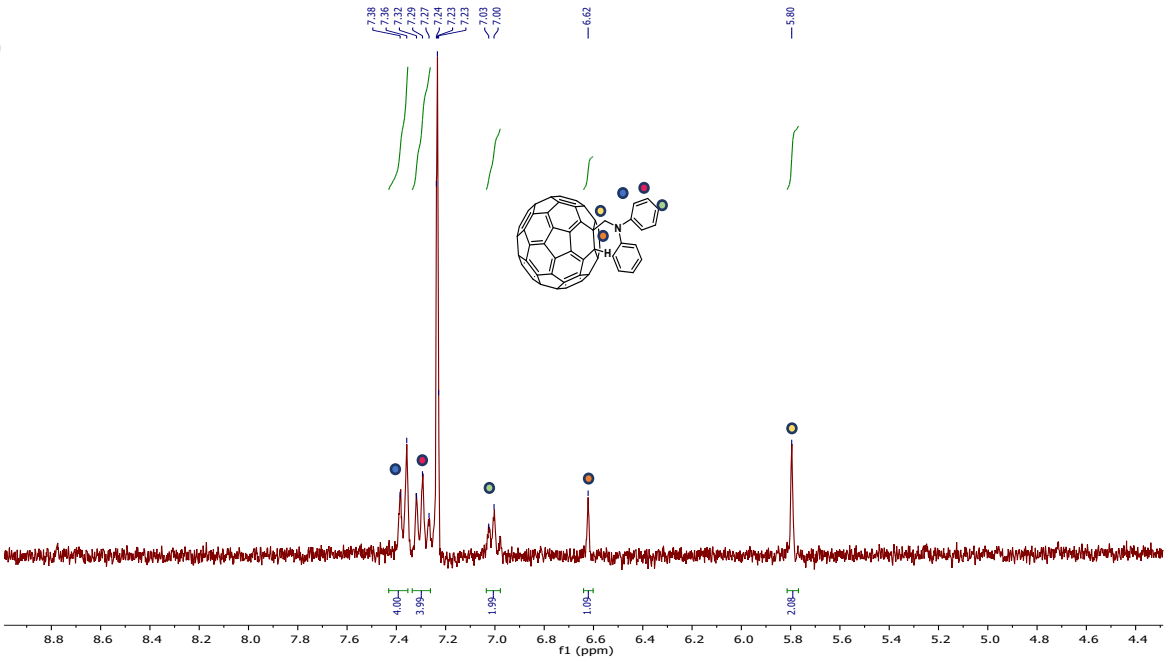


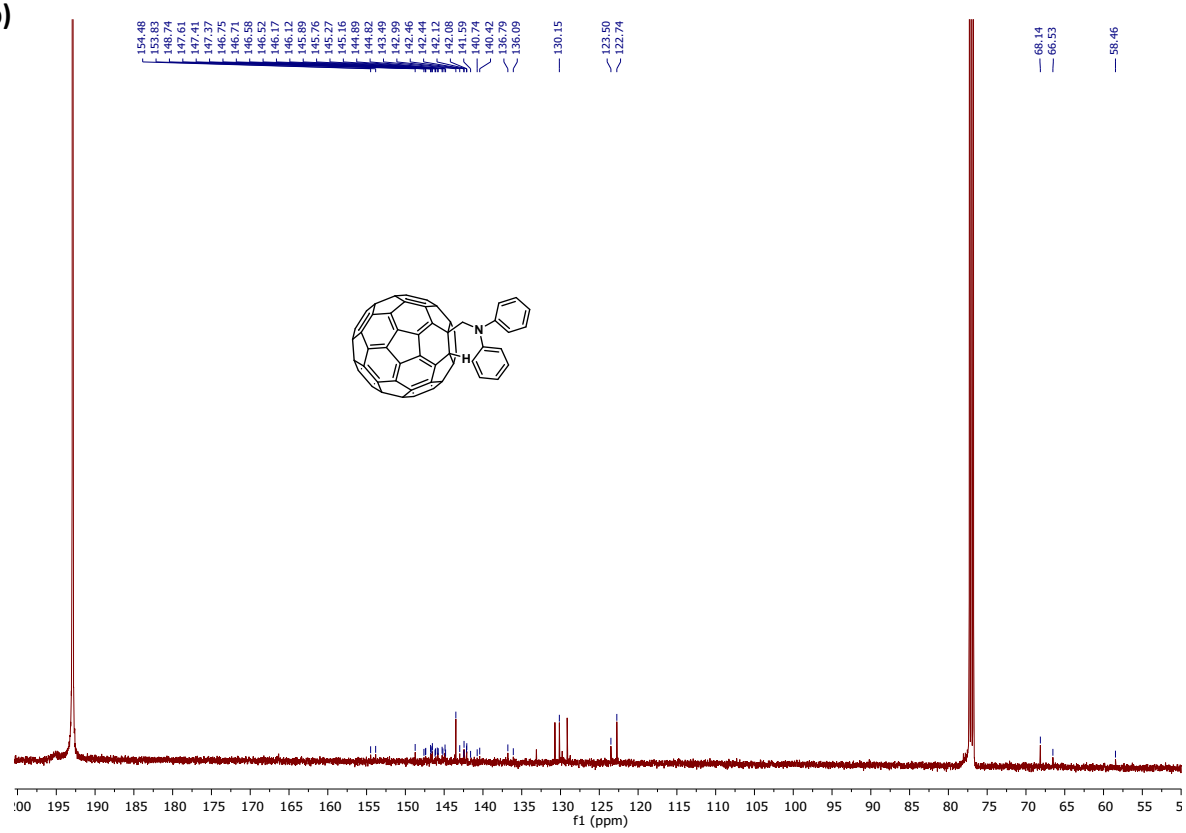
*Figure S2: Comparative Normalized fluorescence emission between SubPc **1** (2.14·10-5 M) y Pd_3SubPc_2 **2** (2.14·10-5)*

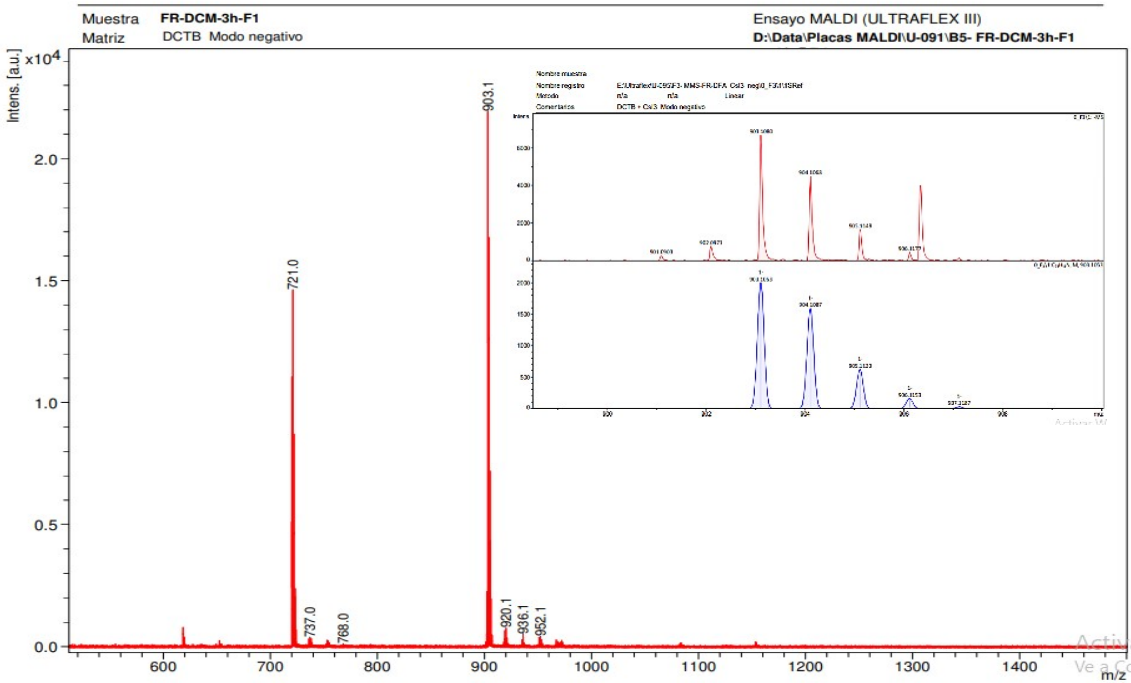


a)



b)


154.48
153.83
149.24
147.61
147.41
147.37
146.75
146.71
146.58
146.52
146.17
146.12
145.89
145.76
145.27
145.16
144.89
144.82
143.49
142.99
142.46
142.44
142.12
142.08
141.59
140.74
140.43
136.79
136.09
130.15
123.50
122.74
68.14
66.53
58.46
N
H
f1 (ppm)


Muestra FR-DCM-3h-F1
Matriz DCTB Modo negativo
Ensayo MALDI (ULTRAFLEX III)
D:\Data\Placas MALDI\U-091\B5- FR-DCM-3h-F1
Intens. [a.u.]
x10^4
2.0
1.5
1.0
0.5
0.0
721.0
737.0
768.0
903.1
920.1
936.1
952.1
600
700
800
900
1000
1100
1200
1300
1400
m/z

c)

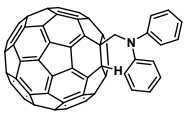

N
H

Figure S3: a) ^{1}H-NMR in $CS_2/CDCl_3$, and b) *^{13}C-NMR in CS_2/C_6D_6 y c) MALDI MS / HRMS of* ***4a***

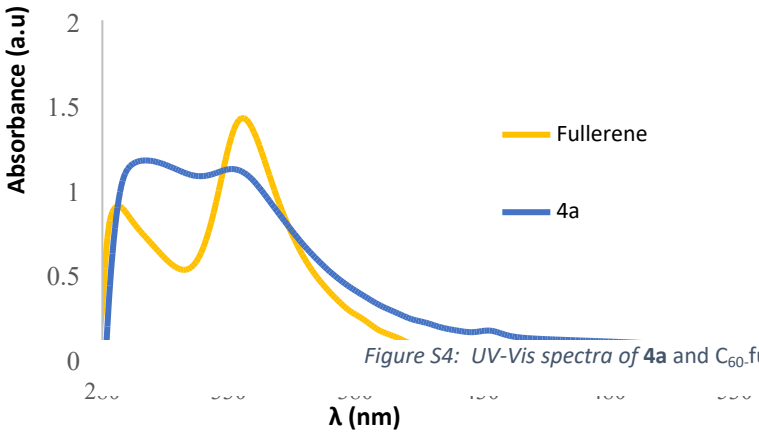


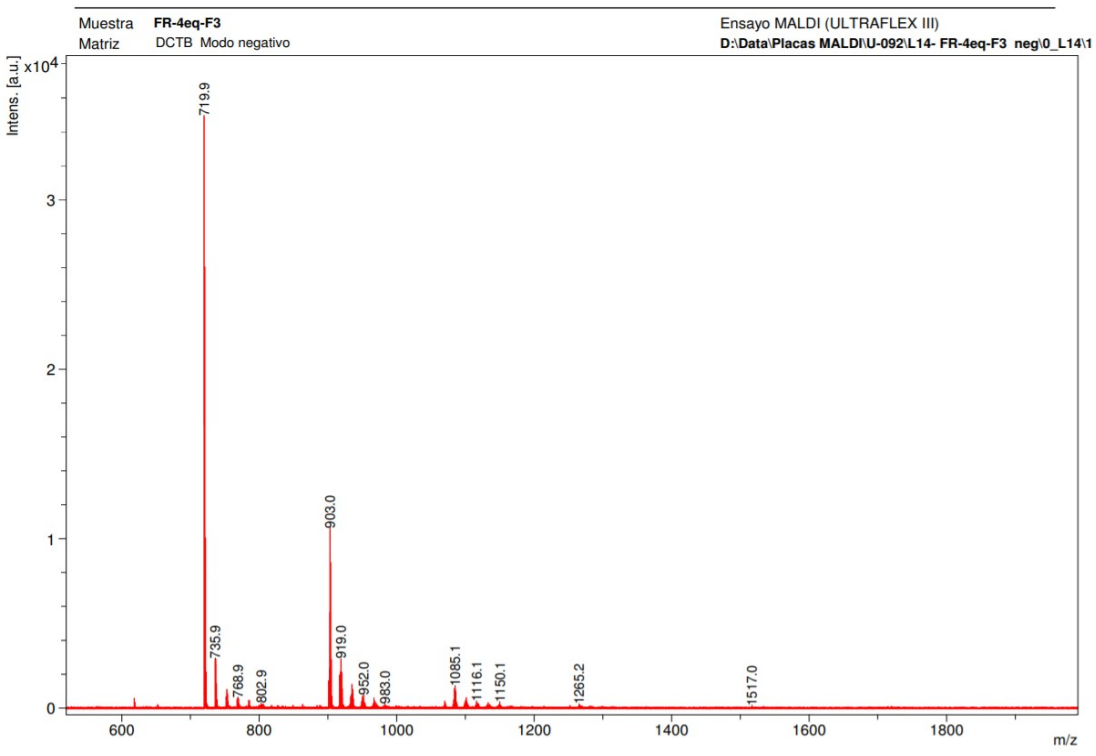
Figure S4: UV-Vis spectra of **4a** and C_{60} fullerene in toluene.

Mono addition

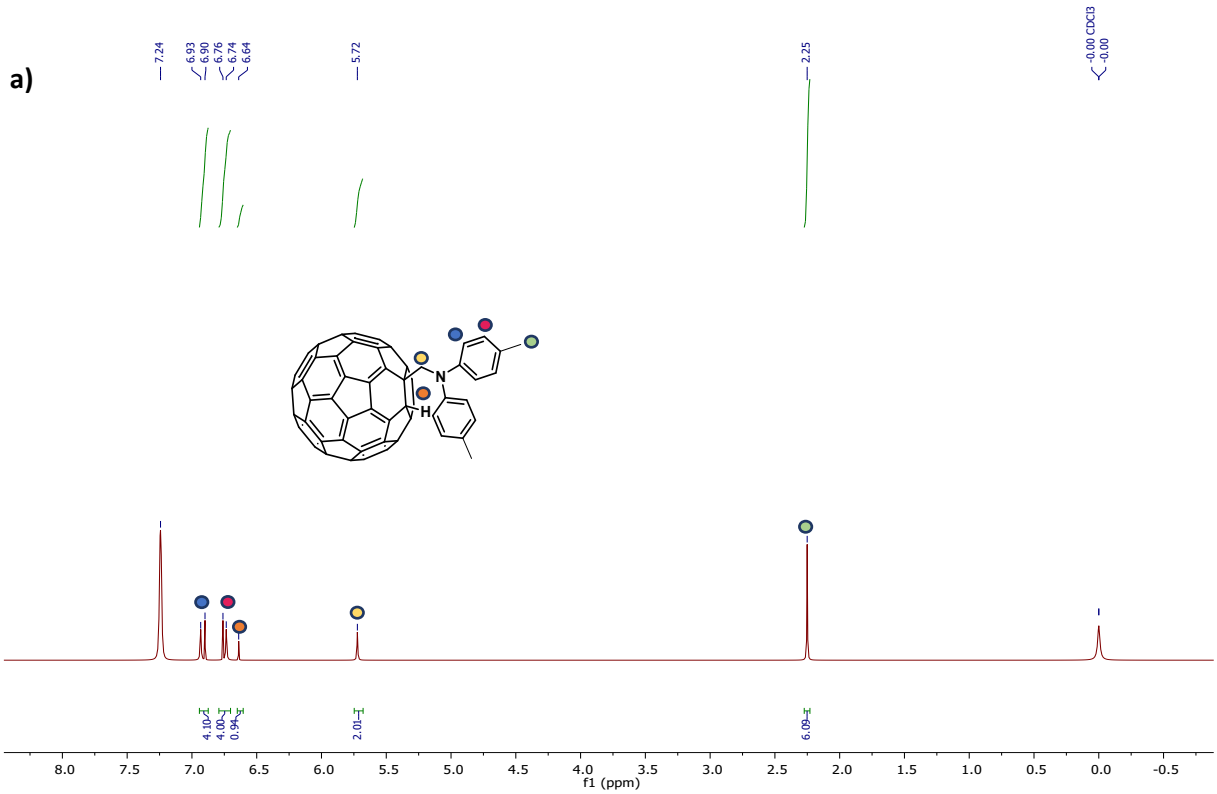
Double addition

Triple addition

Figure S5: MALDI MS corresponding with double and triple additions of the amine radical to the fullerene



a)


7.24
6.93
6.90
6.76
6.74
6.64
5.72
2.25
0.00 CDCl3
0.00
N
H
4.10
4.00
0.94
2.01
6.09
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

b)

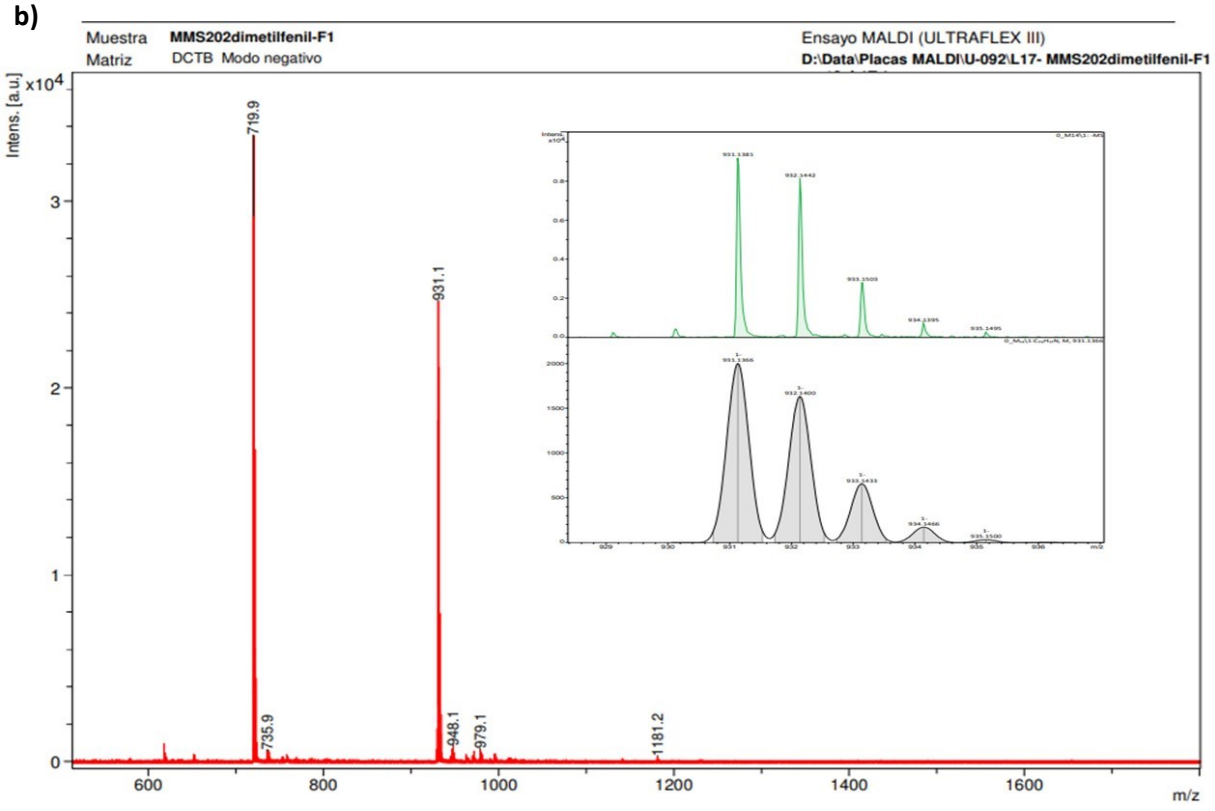
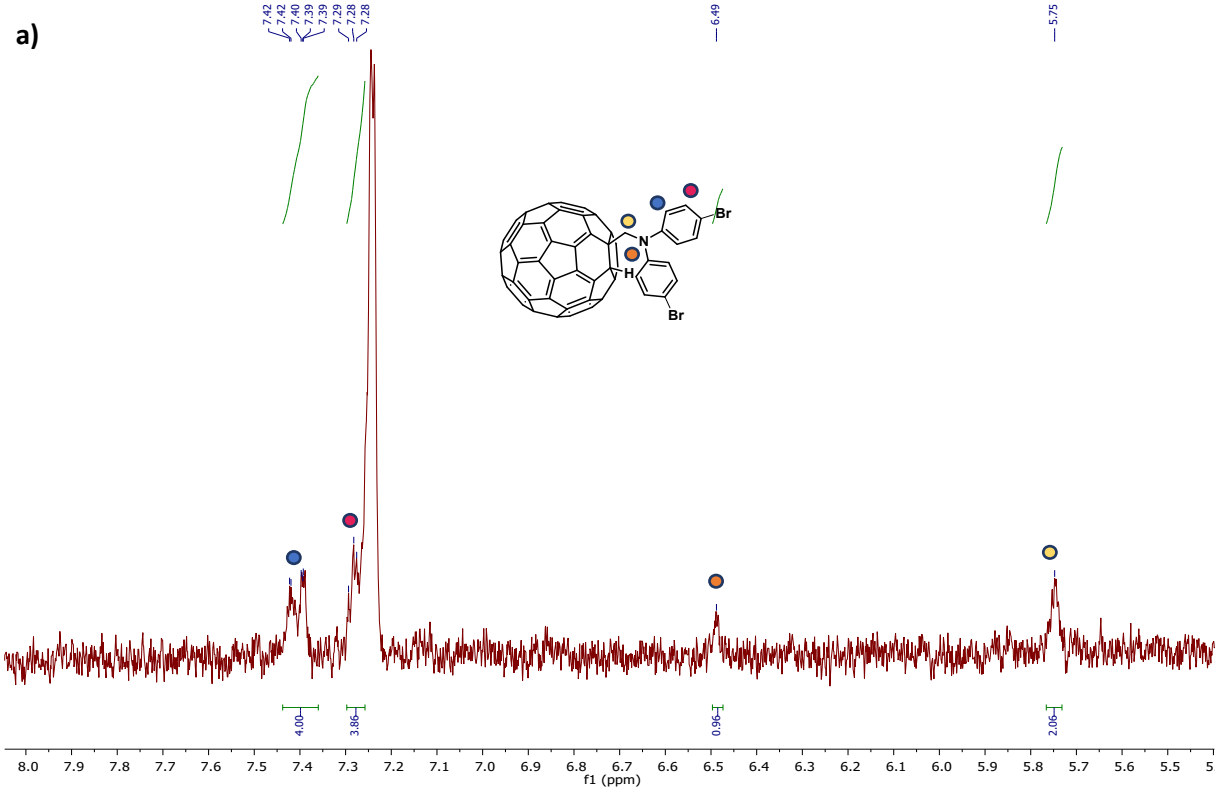
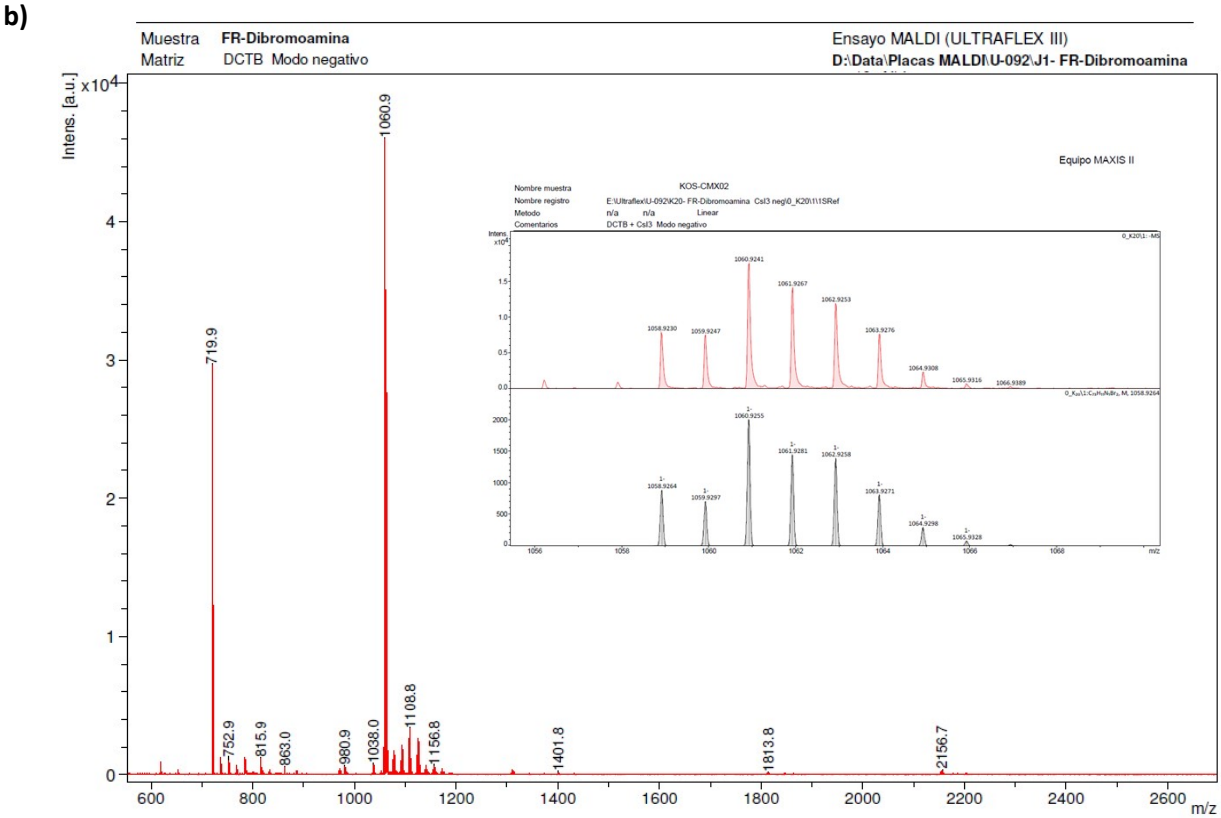

Muestra MMS202dimetilfenil-F1
Matriz DCTB Modo negativo
Ensayo MALDI (ULTRAFLEX III)
D:\Data\Placas MALDI\U-092\L17- MMS202dimetilfenil-F1
Intens. [a.u.]
x10^4
719.9
931.1
735.9
948.1
979.1
1181.2
600
800
1000
1200
1400
1600
m/z

Figure S6: a) ^{1}H-NMR in $CS_2/CDCl_3$ and b) *MALDI MS/ HRMS of* ***4b***

a)



b)



a)

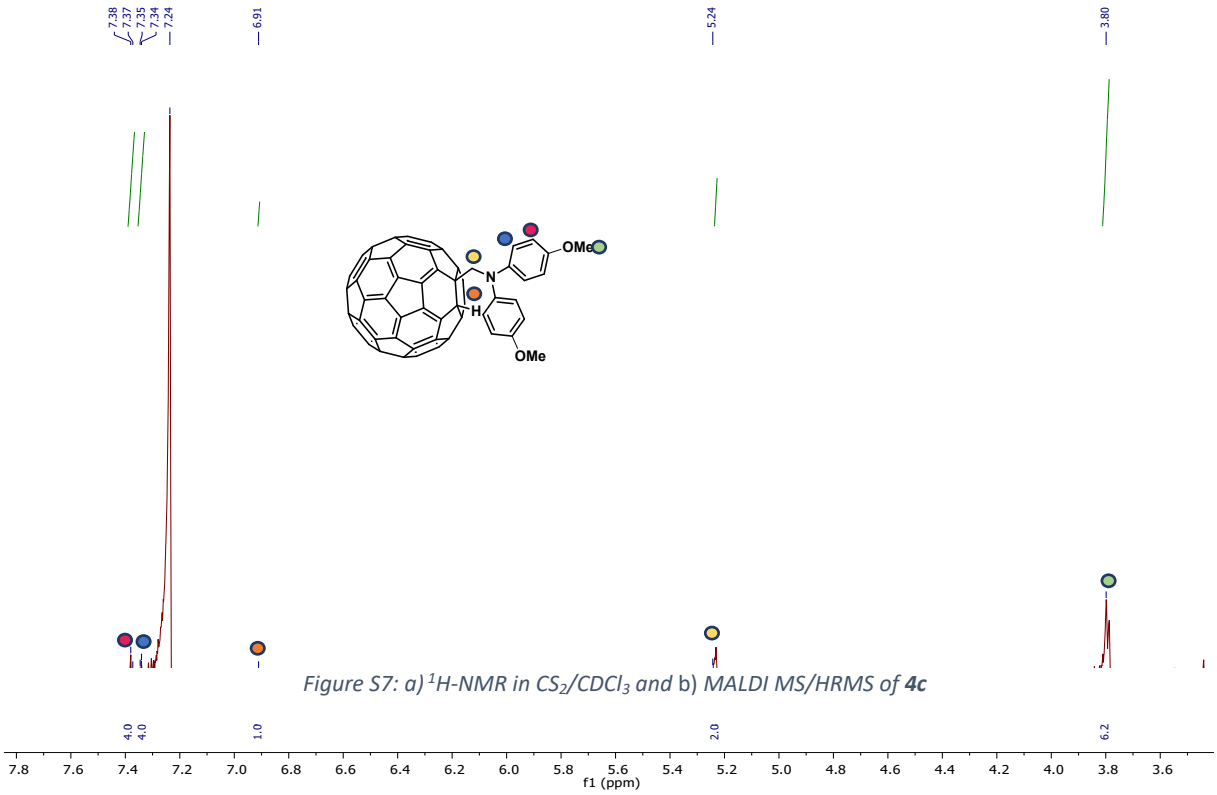


Figure S7: a) ^{1}H-NMR in $CS_2/CDCl_3$ and b) *MALDI MS/HRMS of* ***4c***

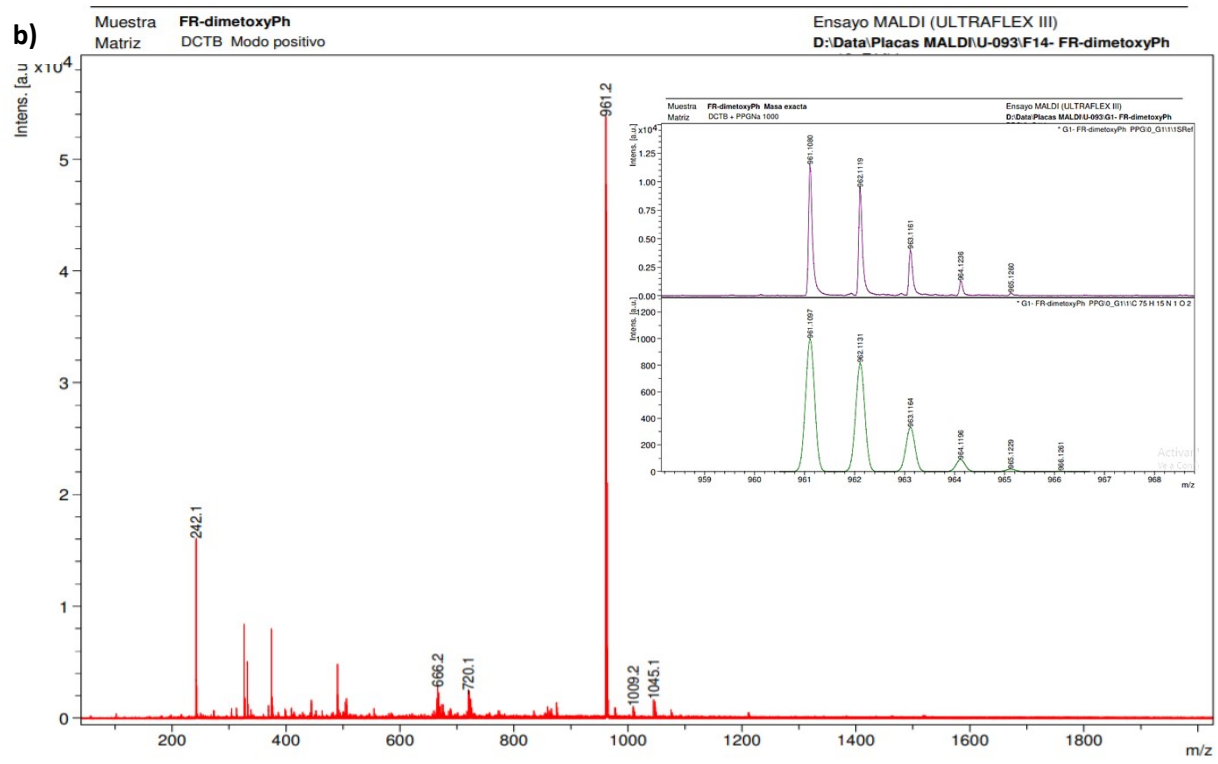
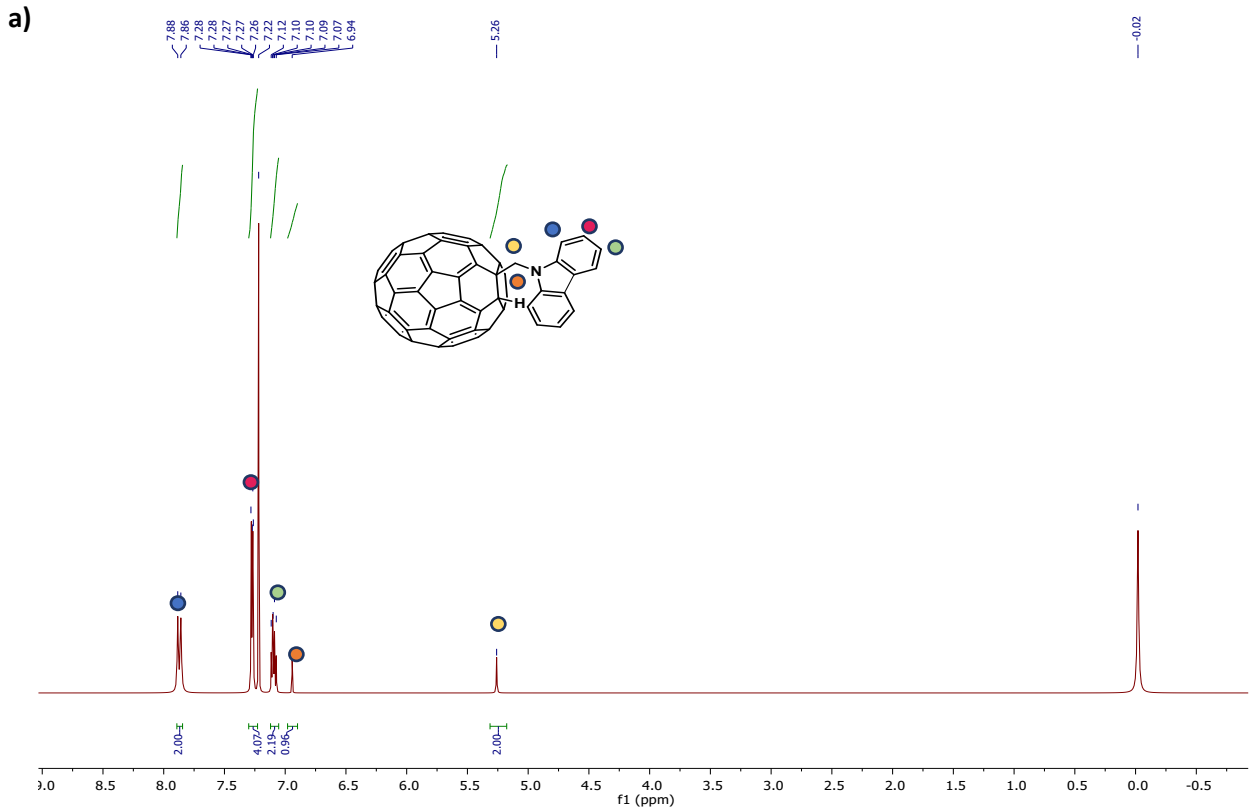


Figure S8: a) ^{1}H-NMR in $CS_2/CDCl_3$ and b) *MALDI MS/HRMS of* ***4d***



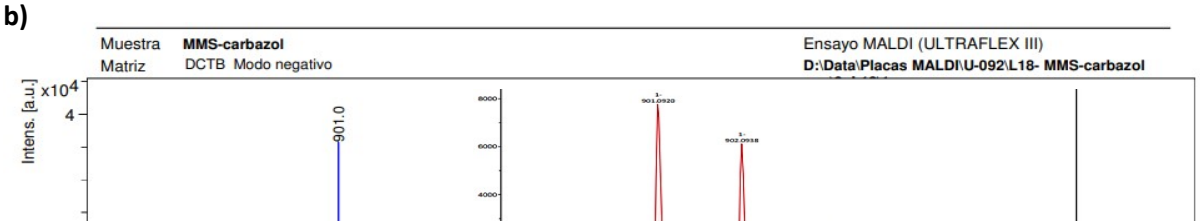
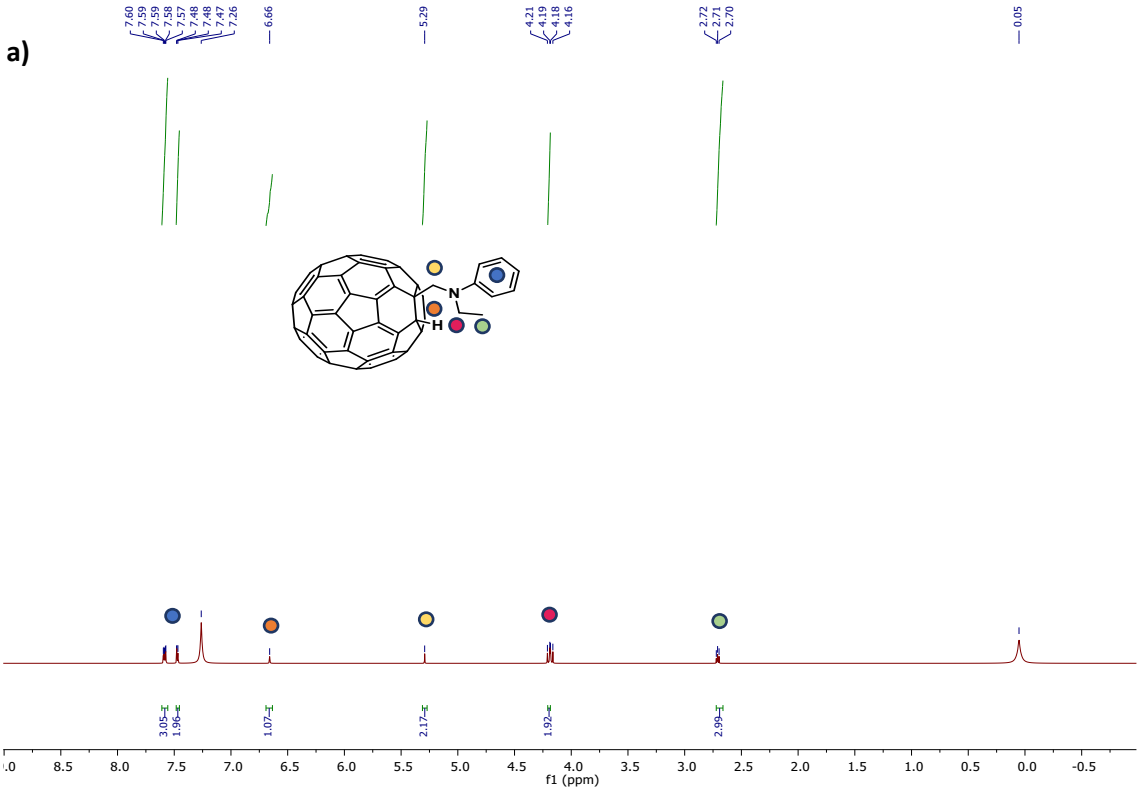


Figure S9: a) ^{1}H-NMR in $CS_2/CDCl_3$ and b) *MALDI MS/HRMS of* ***4f***



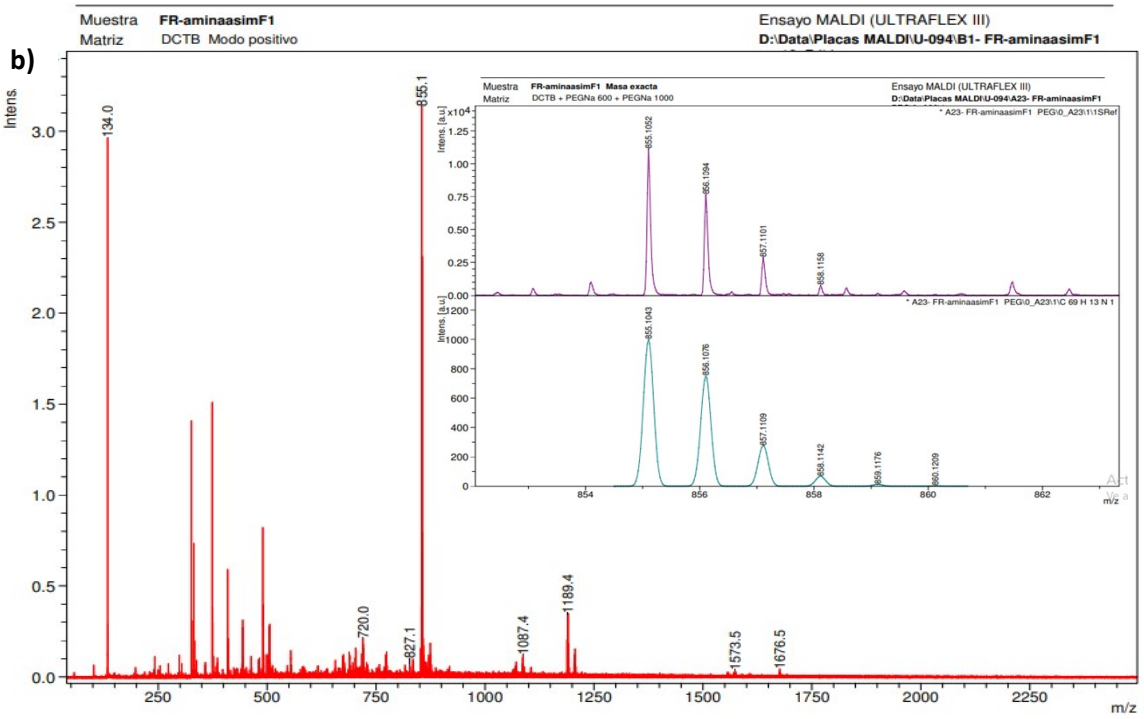


Figure S10: a) ^{1}H-NMR in CS_2/$CDCl_3$ and MALDI MS / HRMS of ***4g***

8) *Experiments for the elucidation of the mechanism for the addition of arylamines 3 to C_{60}.*

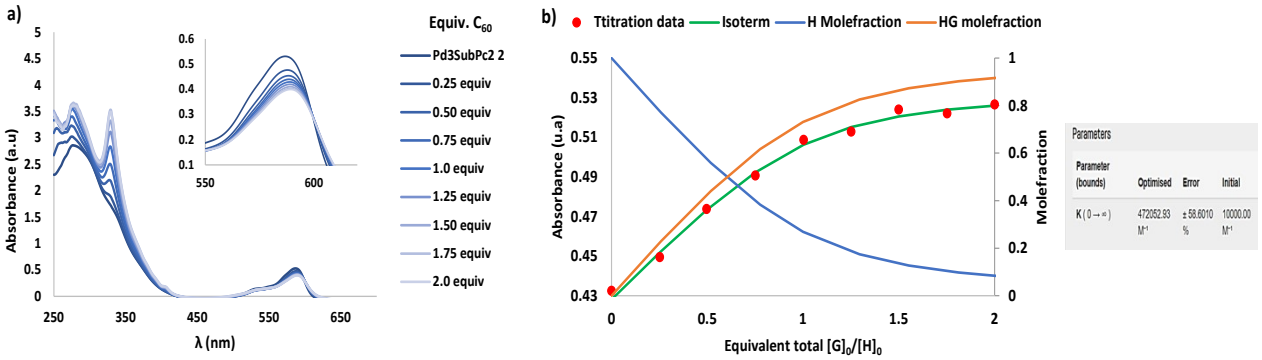


Figure S11: a) UV-vis titration experiments for the complexation of C_{60} by cage **2** (c= $2.14 \cdot 10^{-5}$ M^{-1} in DCM)**;** b) *Binding constants simulation performed with* http://app.supramolecular.org/bindfit

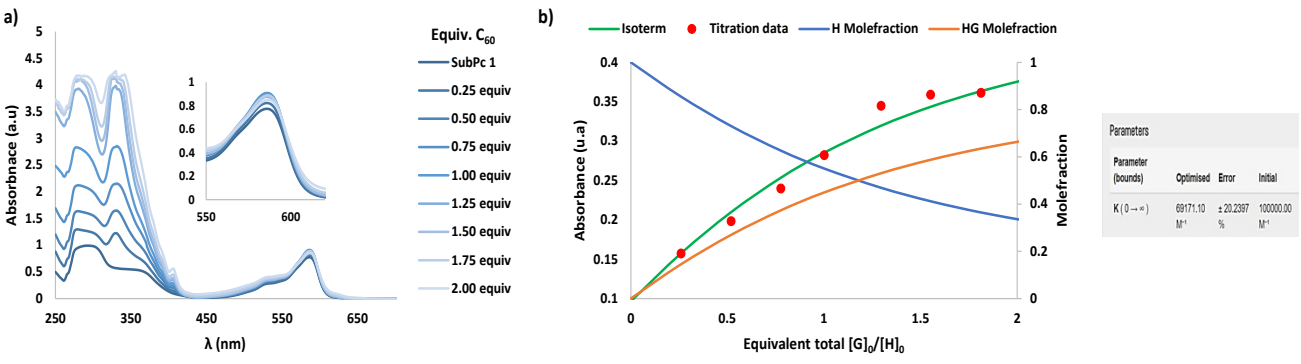


Figure S12: a) UV-vis titration experiments for the complexation of C_{60} by **1** (c= $2.14 \cdot 10^{-5}$ M^{-1} in DCM)**;** b) *Binding constants simulation for a 1:1 performed with* http://app.supramolecular.org/bindfit

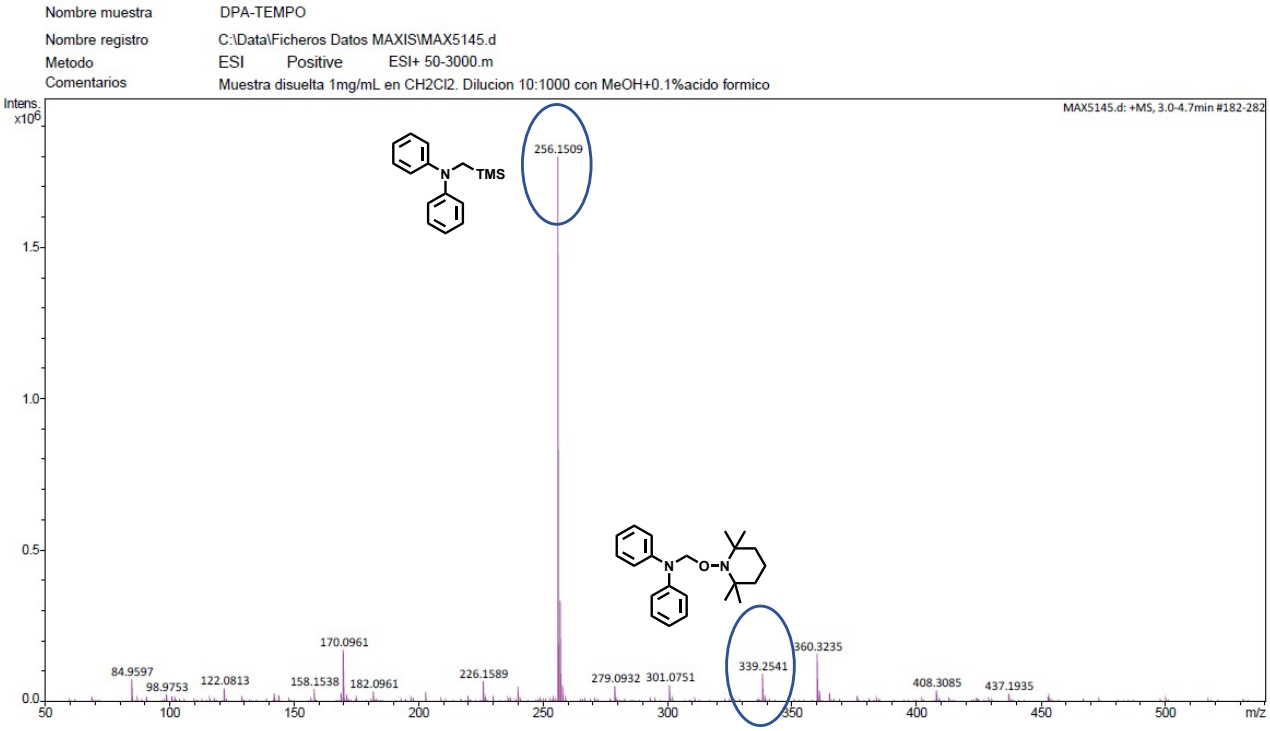


Figure S13: MS spectrum of the reaction of the photocatalyzed reaction with ***3a*** *in the presence of TEMPO*

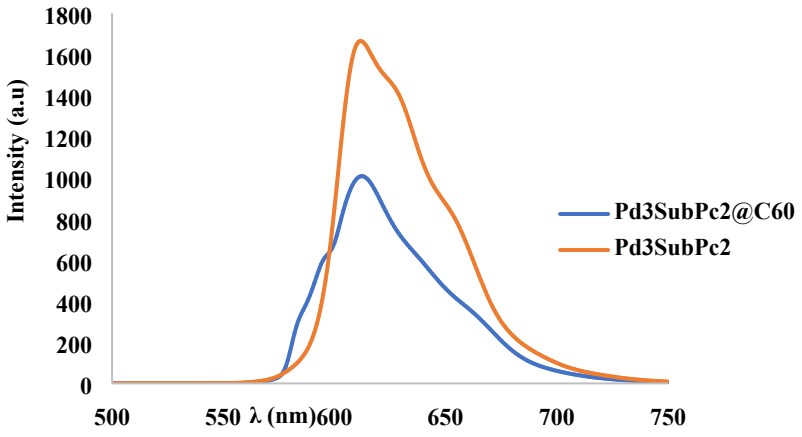
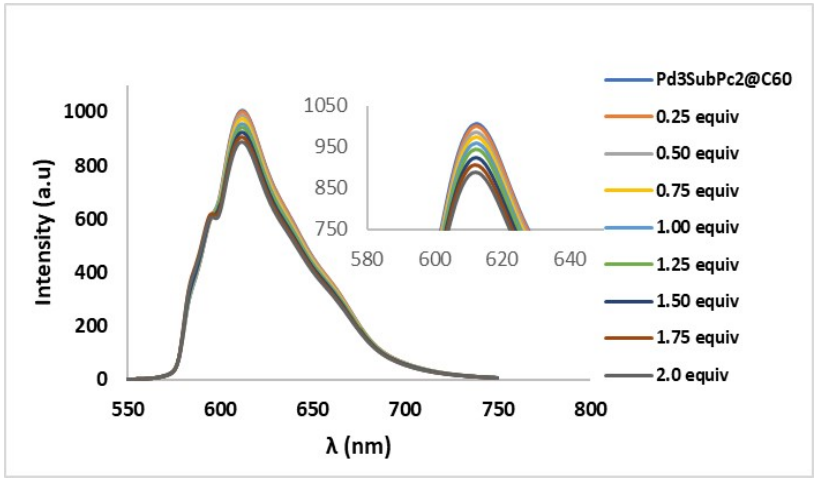
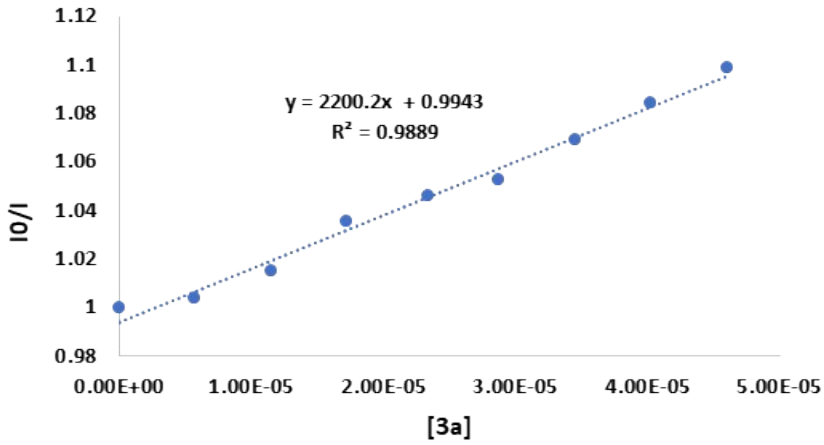


Figure S14: Compared emission spectra of ***2*** *(*CH_2Cl_2*, 2.14·10^-5 M) and the corresponding host guest complex (*$C_{60} \subset$ ***2****)* (toluene, *2.14·10^-5 M*)

a)





b)

*Figure S15: a) Fluorescence quenching of [C_{60} ⊂ **2**](2.14·10^{-5} M) by addition of **3a** (0 to 2.0 equiv) in toluene. b) Stern-Volmer plot*

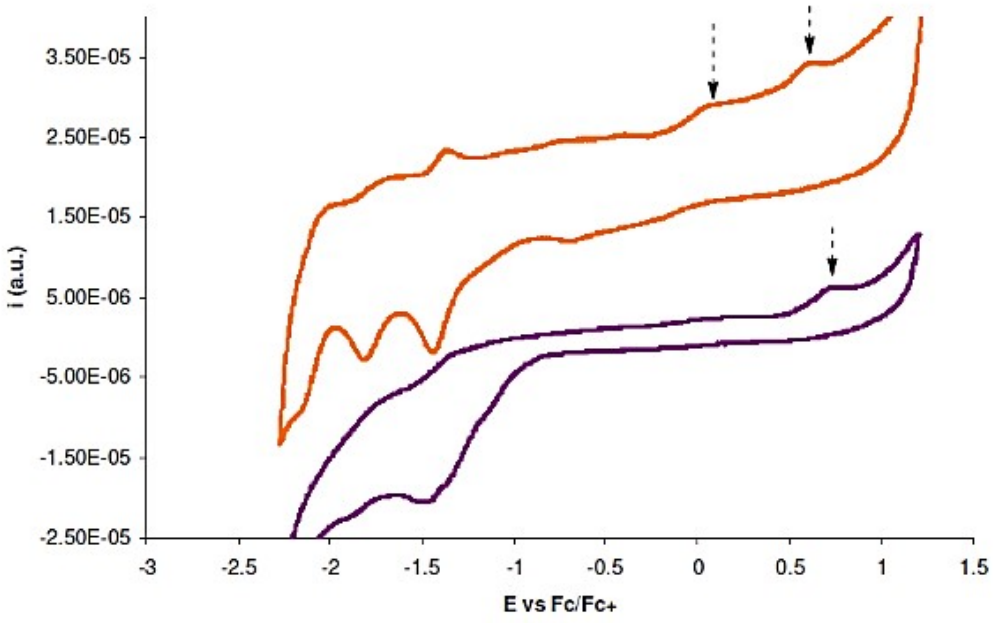


*Figure S16: a) Cyclic voltammetry of **1** (orange) and **2** (purple) in DCM* versus Ag/$AgNO_3$ as reference electrode with ferrocene as internal reference *with 0.1 M [TBA][PF_6] as supporting electrolyte*

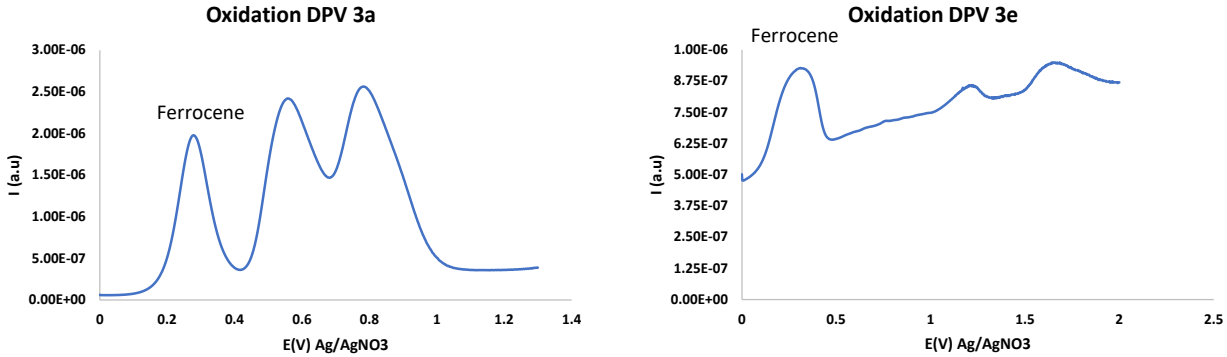


*Figure S17: Differential Pulse Voltammetry (DPV) of **3a** (left) and **3e** (right) in the oxidation regime,* versus $Ag/AgNO_3$ as reference electrode with ferrocene as internal reference, *in DCM with 0.1 M [TBA][PF_6] as supporting electrolyte*

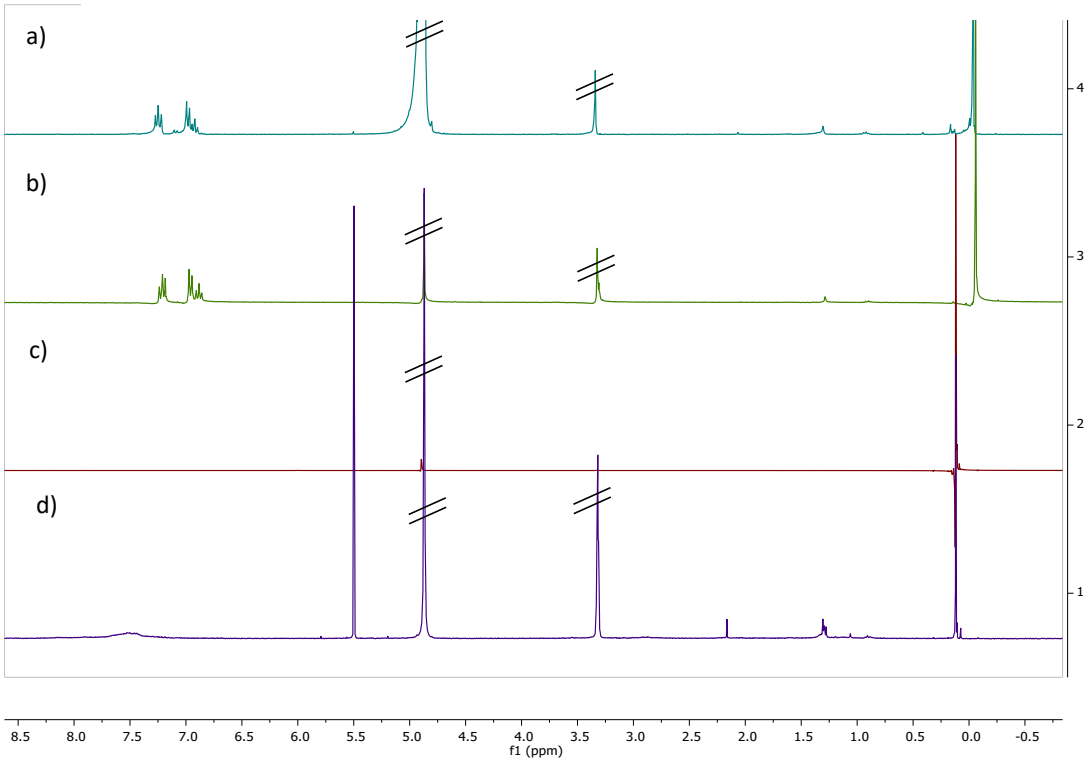


*Figure S18: Comparative ^{1}H-NMR in CD_3OD of a) crude of the photoredox reaction of **3a** and C_{60} in the absence of photocatalyst, after precipitation of the fullerene; b) **3a** (the spectrum fully matches with a); c) commercial trimethylsylanol; c) crude of the transformation of **3a** in the presence of the **2** (without C_{60}).*

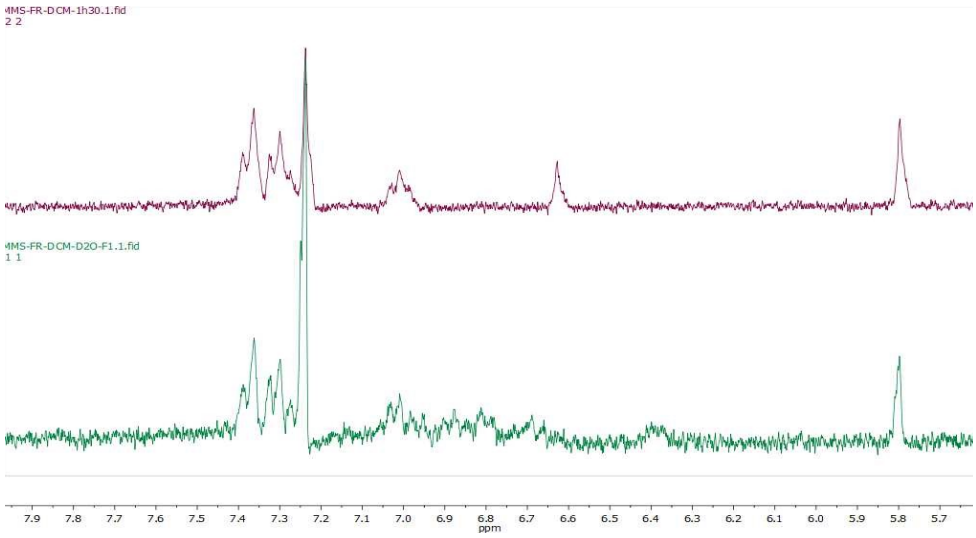
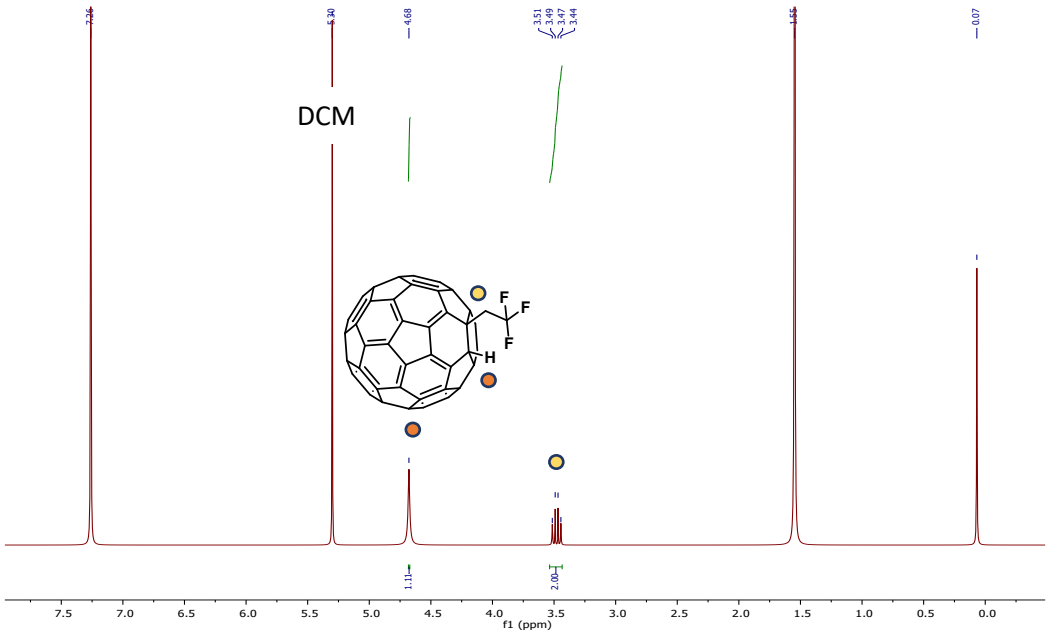


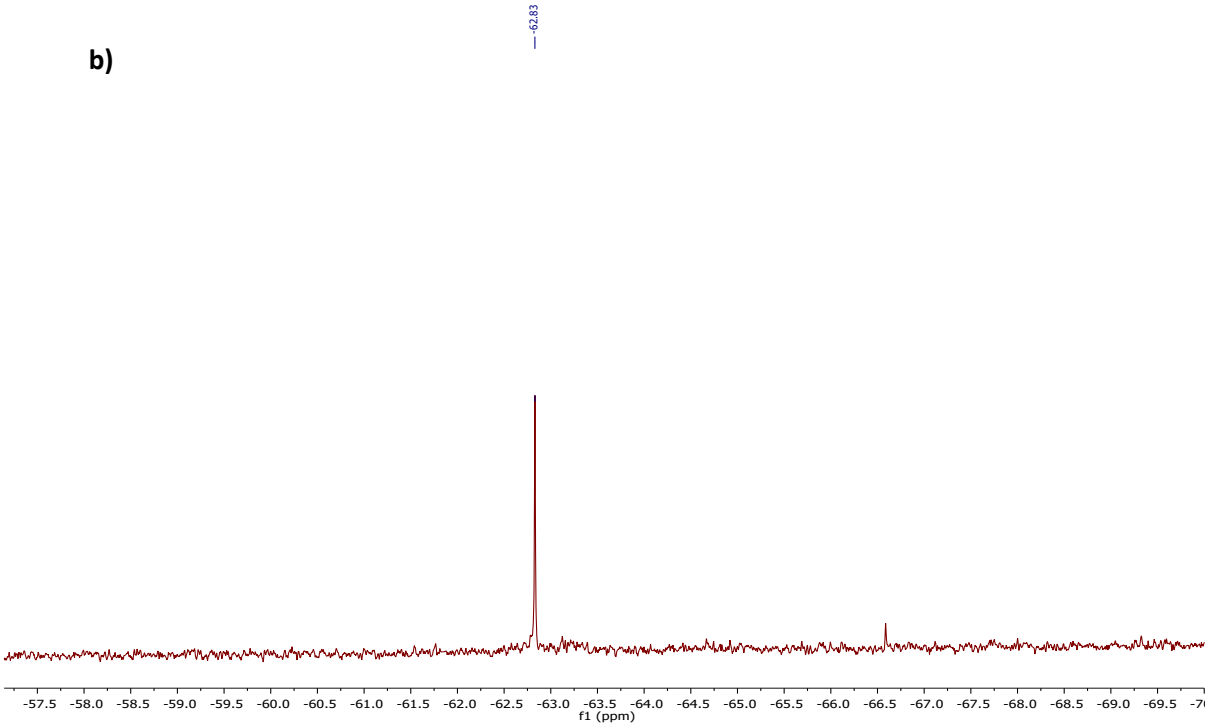
*Figure S19: Comparative ^{1}H-NMR of **4a** and the corresponding deuterated product in $CS_2/CDCl_3$*

9) NMR and mass spectra of 5b

a)

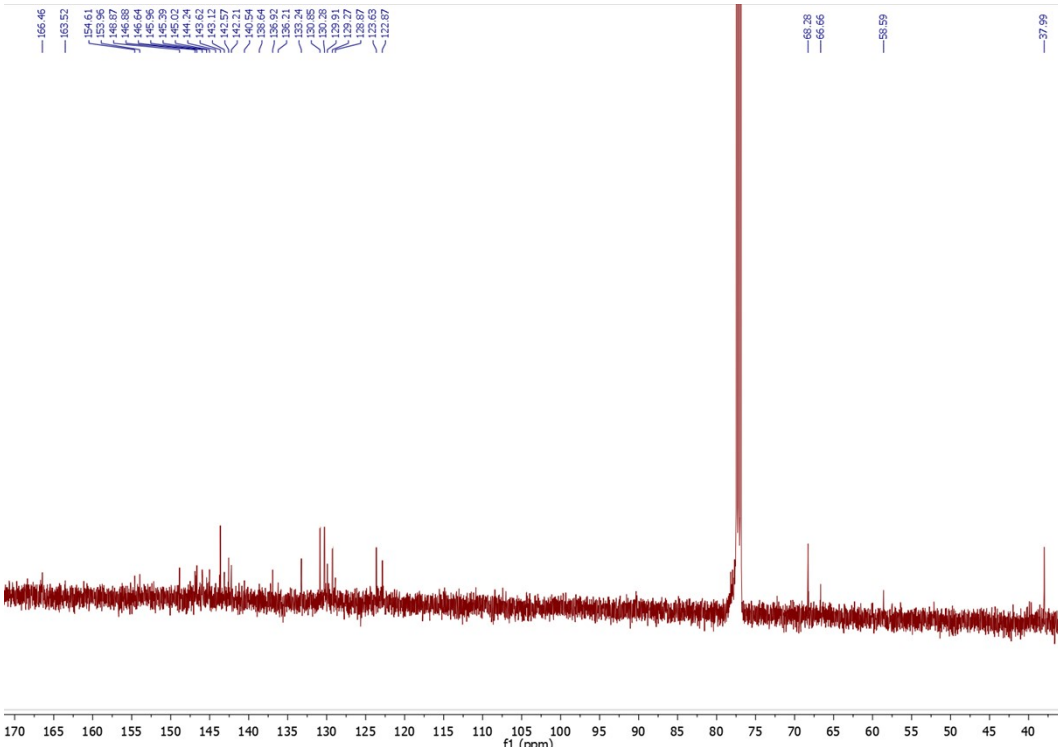


b)


-62.83
-57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5 -69.0 -69.5
f1 (ppm)

c)

*Figure S20: a) ^{1}H-NMR, b)^{19}F-NMR and c) ^{13}C-NMR of **5b** in $CDCl_3$.*



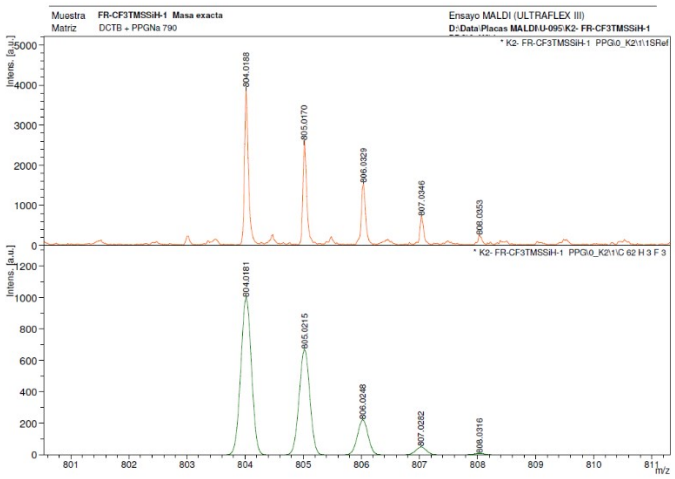
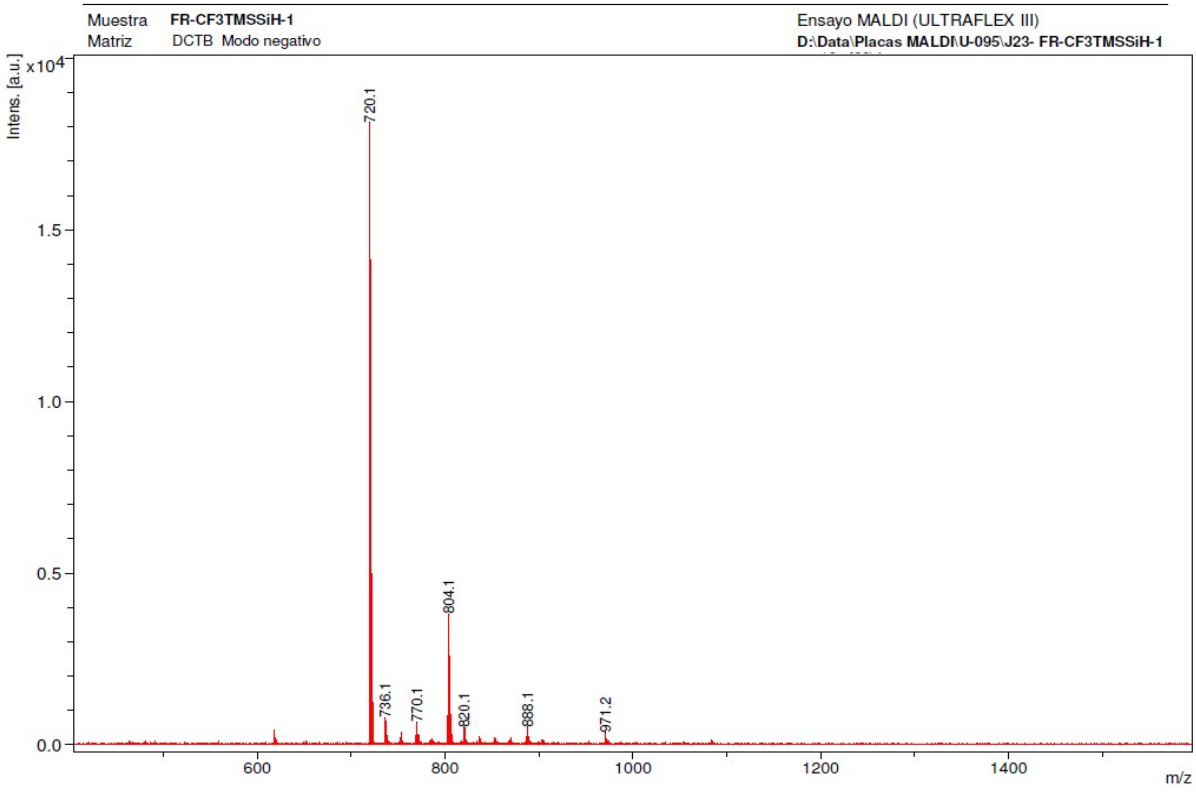


*Figure S21: MALDI MS / HRMS of **5b***



10) Experiments for the elucidation of the mechanism for the addition of CF_3CH_2I to C_{60}.

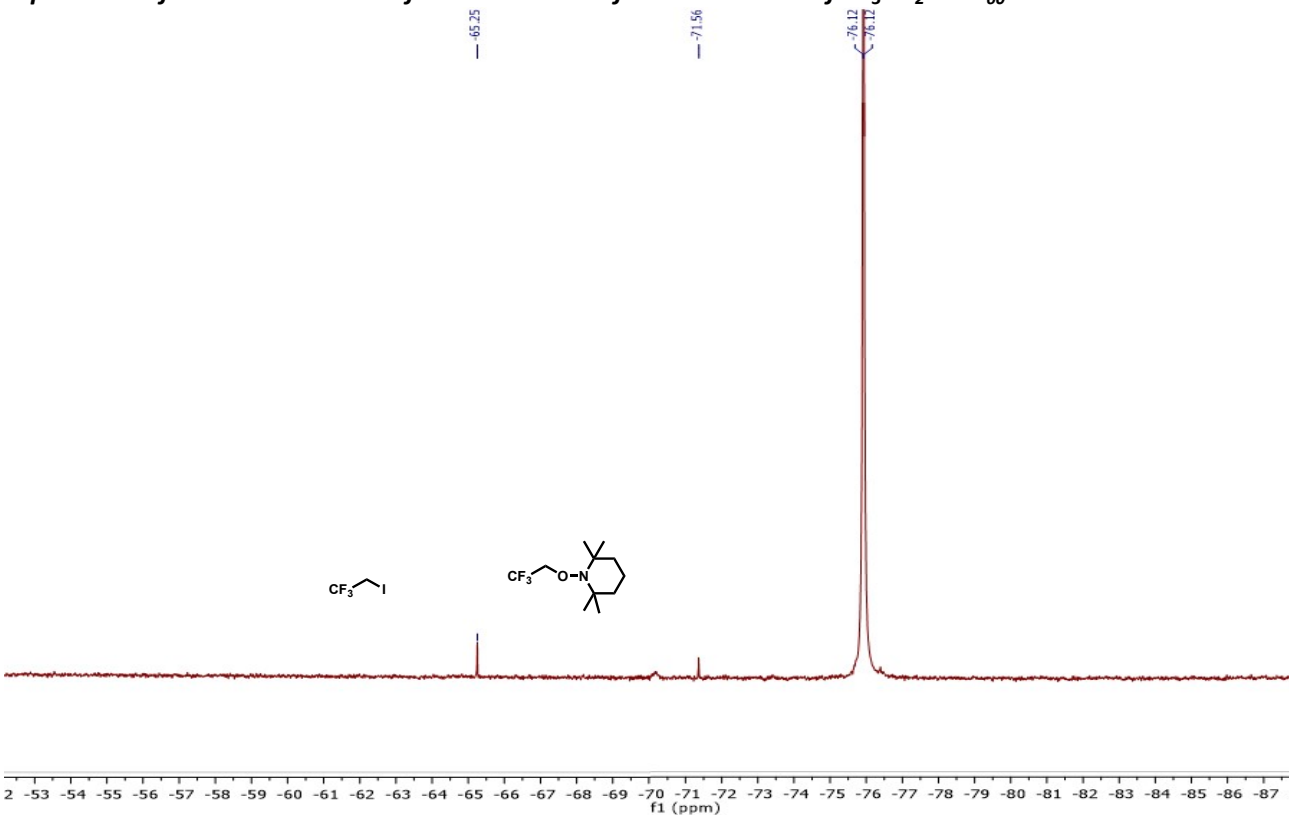
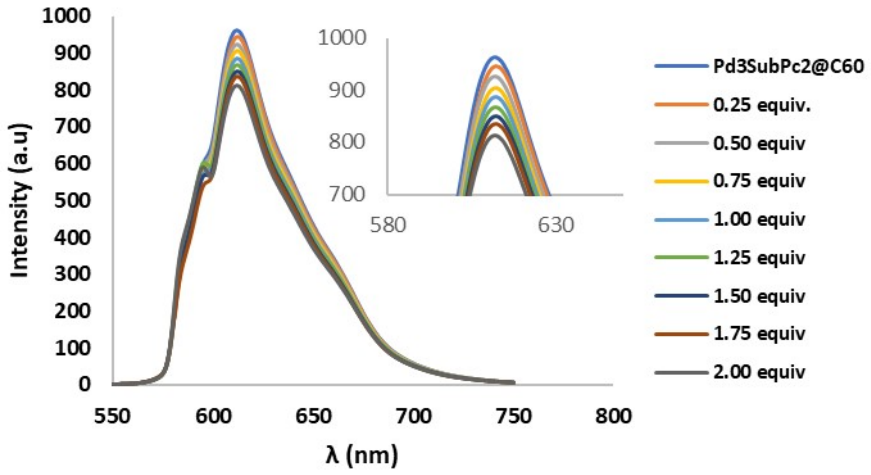


Figure S22: ^{19}F-NMR in $CDCl_3$ of the crude obtained after performing the hydrotrifluoroethylation reaction in the presence of TEMPO. Following literature precedents,[6] we have assigned the signal at -71.5 ppm to the product resulting from the coupling between the CF_3CH_2 radical and TEMPO.

a)



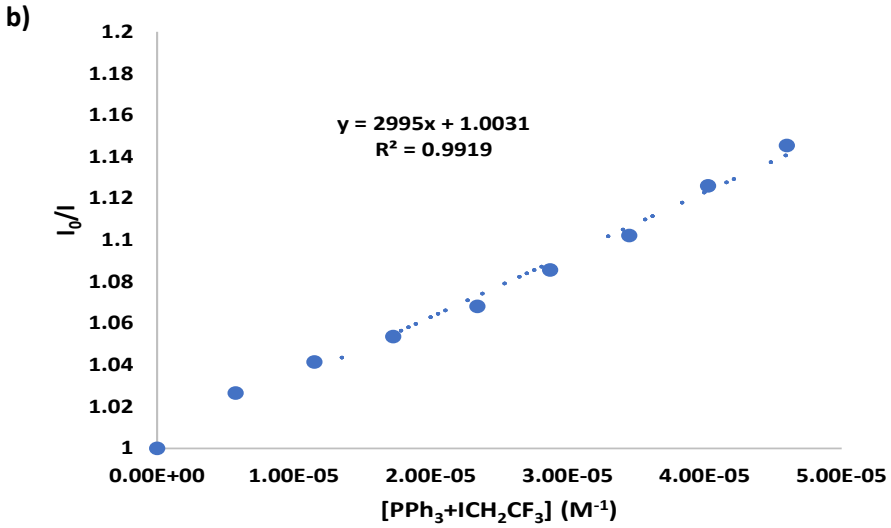
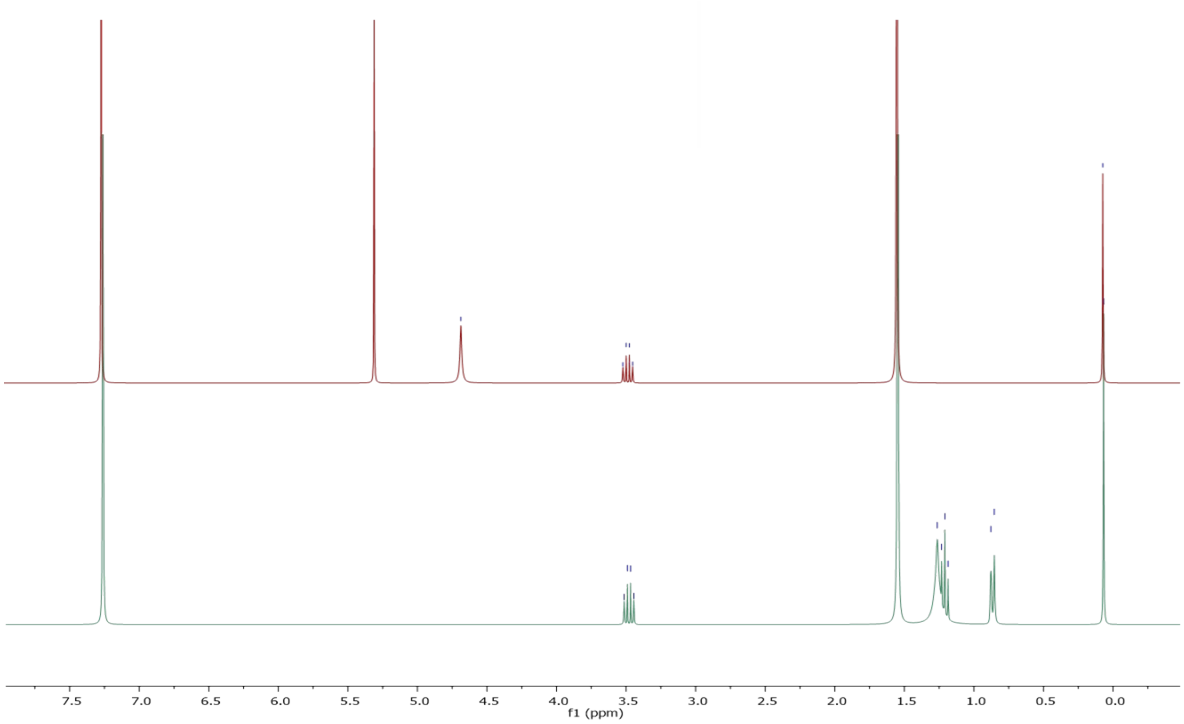


*Figure S23: a) Fluorescence quenching of [C_{60} ⊂ **2**](2.14·10^{-5} M) by addition of **PPh_3-ICH_2CF_3** (0 to 2.0 equiv) in toluene. b) Stern-Volmer plot.*

*Figure S24: Comparative ^{1}H-NMR of **5b** and the corresponding deuterated product in $CDCl_3$*



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