Electronic Supplementary Material (ESI) for ChemComm.

Pyrene-based mechanically interlocked SWNTs.

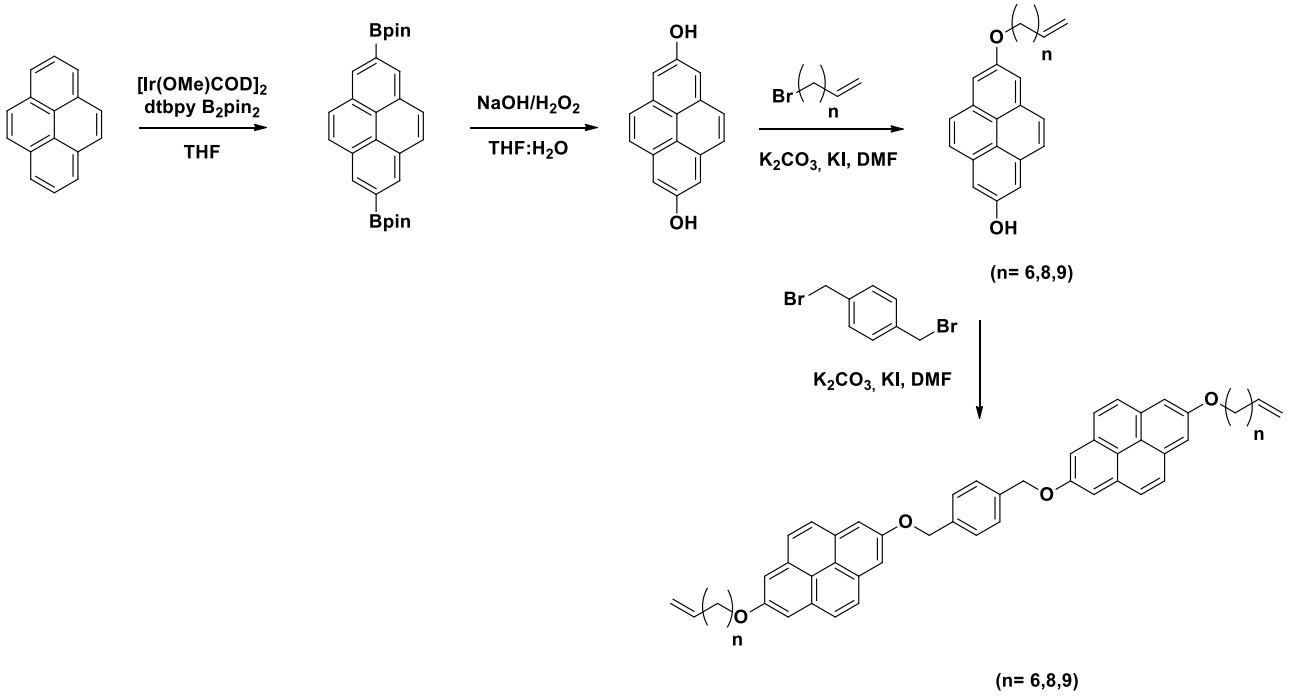
Alejandro López-Moreno and Emilio M. Pérez*

SUPPORTING INFORMATION

General. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh, or Scharlau 60, 230-240 mesh). Analytical thin layer chromatographies (TLC) were performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a BrukerAvance 300 (1H: 300 MHz; 13C: 75 MHz), a BrukerAvance 500 (1H: 500 MHz; 13C: 125 MHz) spectrometers at 298 K, unless otherwise stated, using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad.

Matrix-assisted Laser desorption ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a HP1100MSD spectrometer and a Bruker REFLEX spectrometer, respectively. Thermogravimetric analyses (TGA) were performed using a TA Instruments TGAQ500 with a ramp of 10 °C/min under air from 100 to 1000 °C. UV-vis-NIR spectrums were performed using a Shimadzu UV-VIS-NIR Spectrophotometer UV-3600. Photoluminescence excitation intensity maps (PLE) were obtained with NanoLog 4 HORIBA. Raman spectra were acquired with a Bruker Senterra confocal Raman microscopy instrument, equipped with 532, 633 and 785 nm lasers. Transmission electron microscopy (TEM) images were obtained with JEOL-JEM 2100F (2.5 Å resolution) instrument.

General Scheme of Synthesis of Compounds



2,7-dihydroxypyrene was synthetized as described in *Chem. Eur. J.* **2012**, *18*, 5022 – 5035.

General Procedure Of Synthesis Of Monoalkylated Compounds.

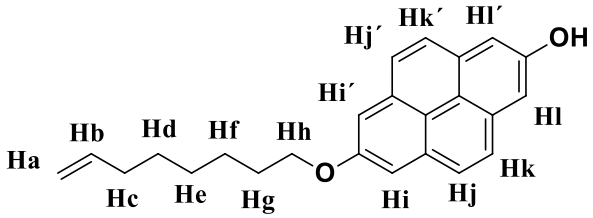
2,7-dihydroxypyrene 500 mg (2.14 mmol) was dissolved in 20 mL of dry DMF. Then, 300 mg (2.14 mmol) of dry K_2CO_3, 12.5 mmol) of bromo alkene , and a catalytic amount of KI were added and the mixture heated to reflux for 8 h. The crude reaction was poured into ice-cold 1 M aqueous HCl, and filtrated. The solid was redissolved in CH_2Cl_2 and washed with water (2x), the organic fraction was dried over $MgSO_4$, the solvent evaporated, and the resulting product subjected to column chromatography (CH_2Cl_2) to obtain the pure product as a light brown solid in 16-18% yield.

General Procedure Of Synthesis Of Lineal Receptors.

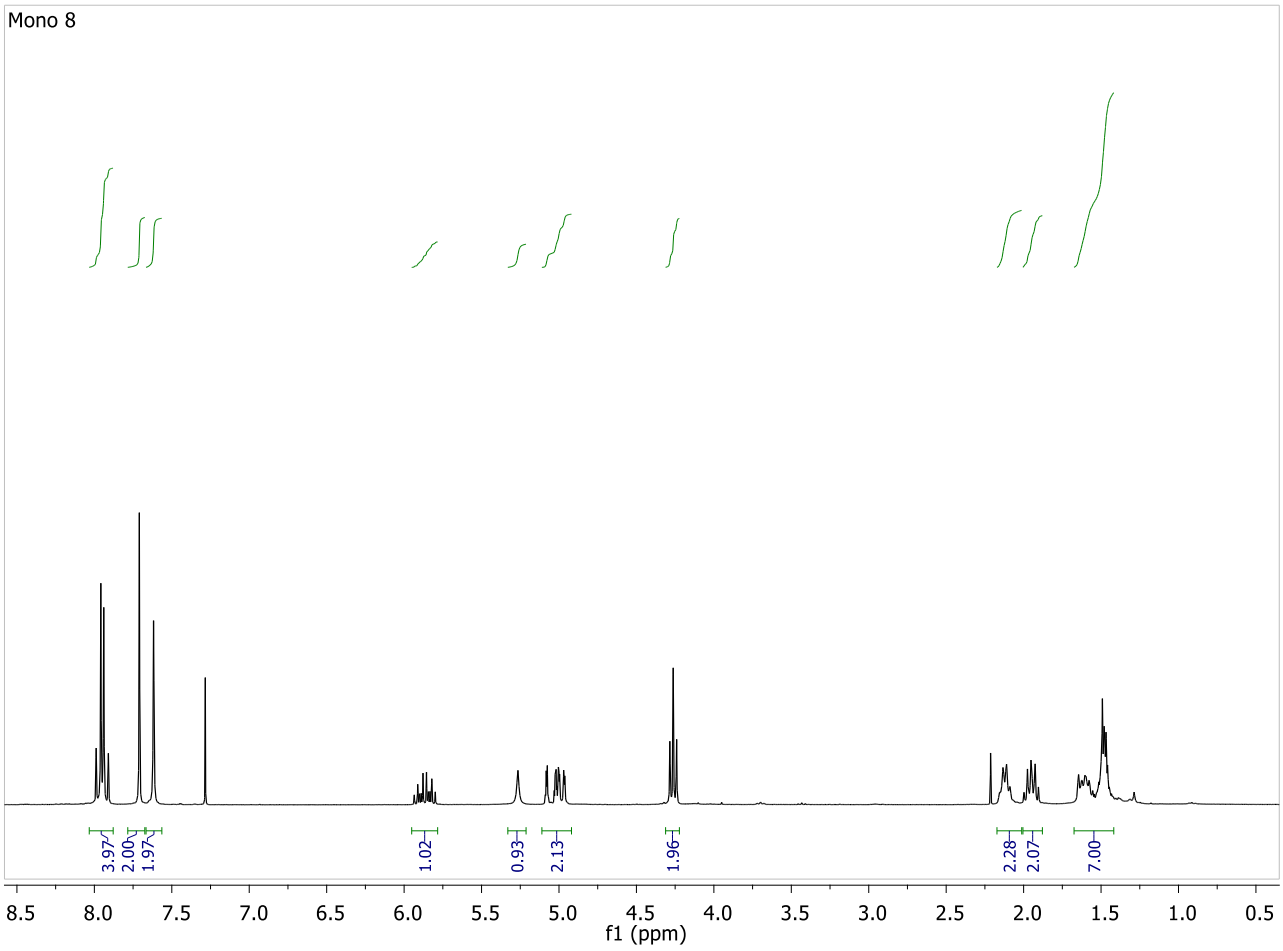
135 mg (1.04 mmol) of dry K_2CO_3, 56 mg (0.21 mmol) of α−α′ dibromo-p-xylene, and a catalytic amount of potassium iodide were added to a solution of 200 mg (0.52 mmol) of the monoalkylated dihydroxypyrene in 15 mL of dry N,N-dimethylformamide. The solution was heated to 80 ºC for 4 h.The crude reaction was poured into ice-cold 1 M aqueous HCl, and filtrated. The solid was redissolved in CH_2Cl_2 and washed with water (2x), the organic fraction was dried over $MgSO_4$, the

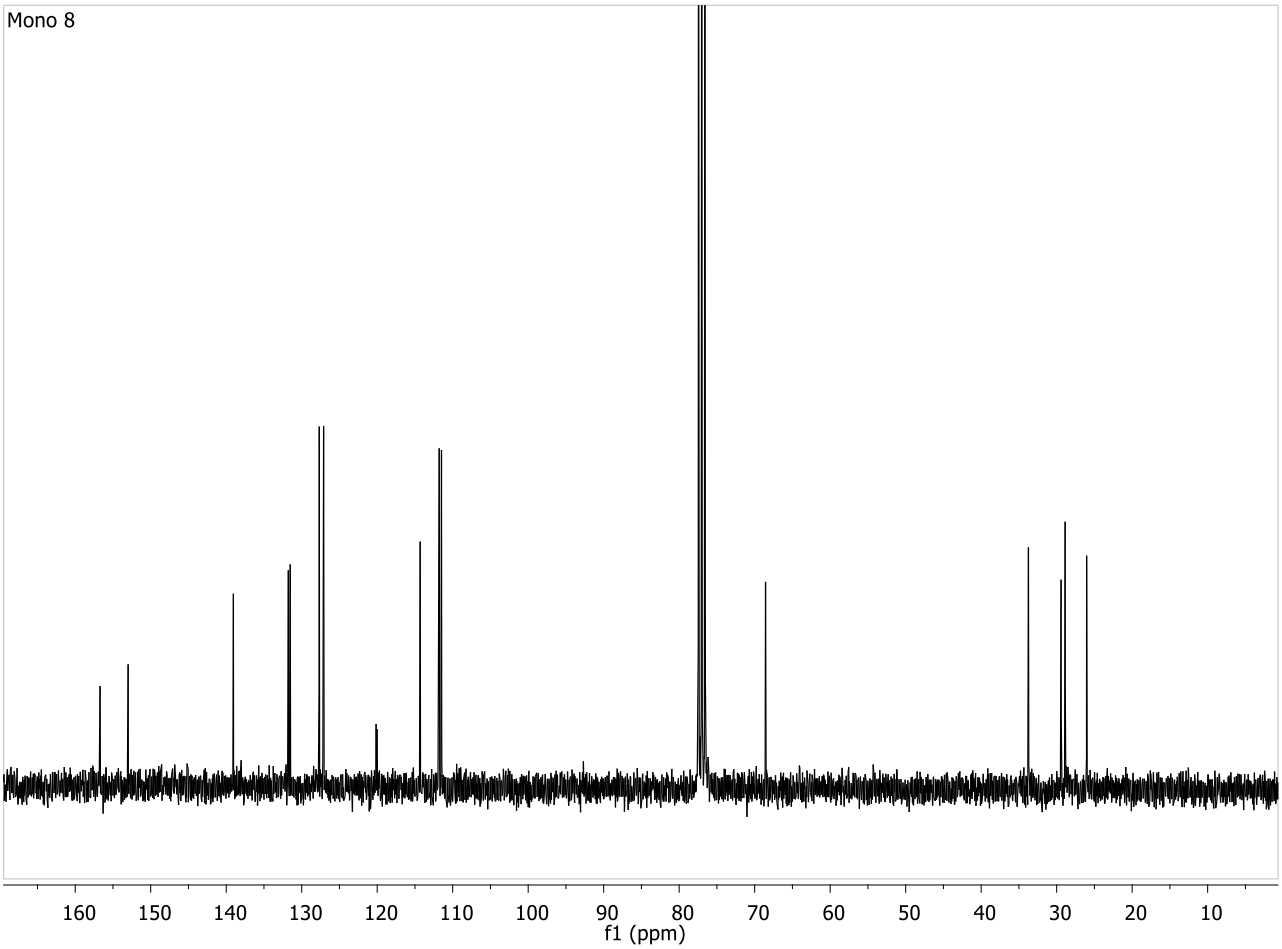
solvent evaporated, and the resulting product subjected to column chromatography (CH_2Cl_2) to obtain the pure product as a light brown solid in 58-61% yield.

7-(oct-7-en-1-yloxy)pyren-2-ol



^{1}H RMN ($CDCl_3$, 300 MHz) δ 7.95 (q, *J* = 9.0 Hz, 4H, Hj+j´+k+k´), 7.71 (s, 2H, Hi+i´), 7.62 (s, 2H, Hl+l´), 5.92 – 5.79 (m, 1H, Hb), 5.27 (s,1H, OH), 5.07 – 4.94 (m, 2H, Ha), 4.26 (t, J = 6.5 Hz, 2H, Hh), 2.12 – 2.05 (m, 2H, Hc), 1.99 – 1.90 (m, 2H, Hg), 1.61 – 1.29 (m, 6H, Hd+e+f). ^{13}C NMR (CDCl3, 75 MHz) δ 156.7, 153.0, 139.0, 131.8, 131.5, 127.7, 127.1, 120.1, 120.0, 114.3, 111.8, 111.5, 68.6, 33.7, 29.4, 28.9, 28.9, 26.0. MS m/z calculated for C24H24O2 344.1, found MALDI 344.2.


Mono 8
3.97
2.00
1.97
1.02
0.93
2.13
1.96
2.28
2.07
7.00
8.5
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
f1 (ppm)


Mono 8
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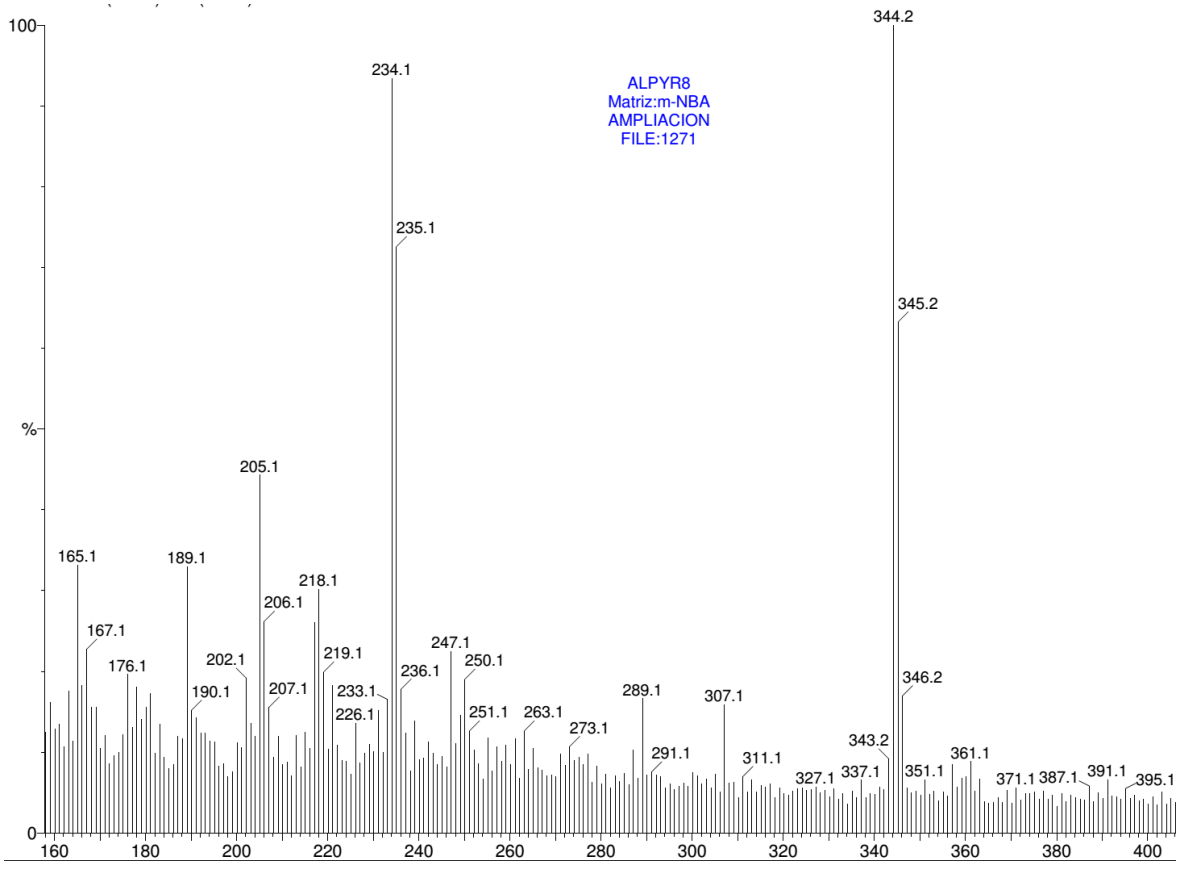
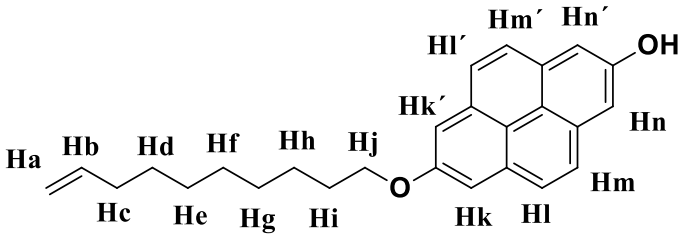
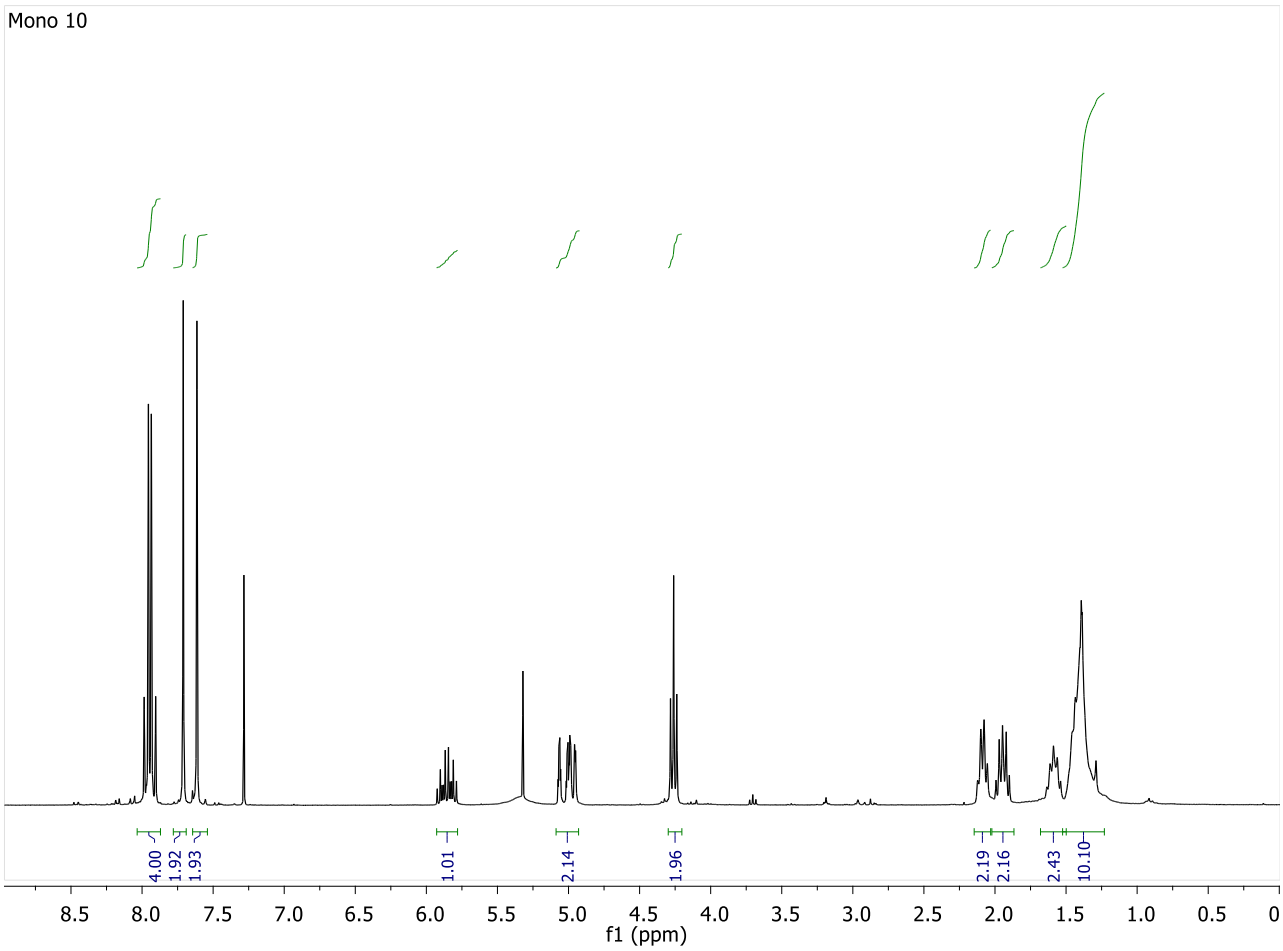
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

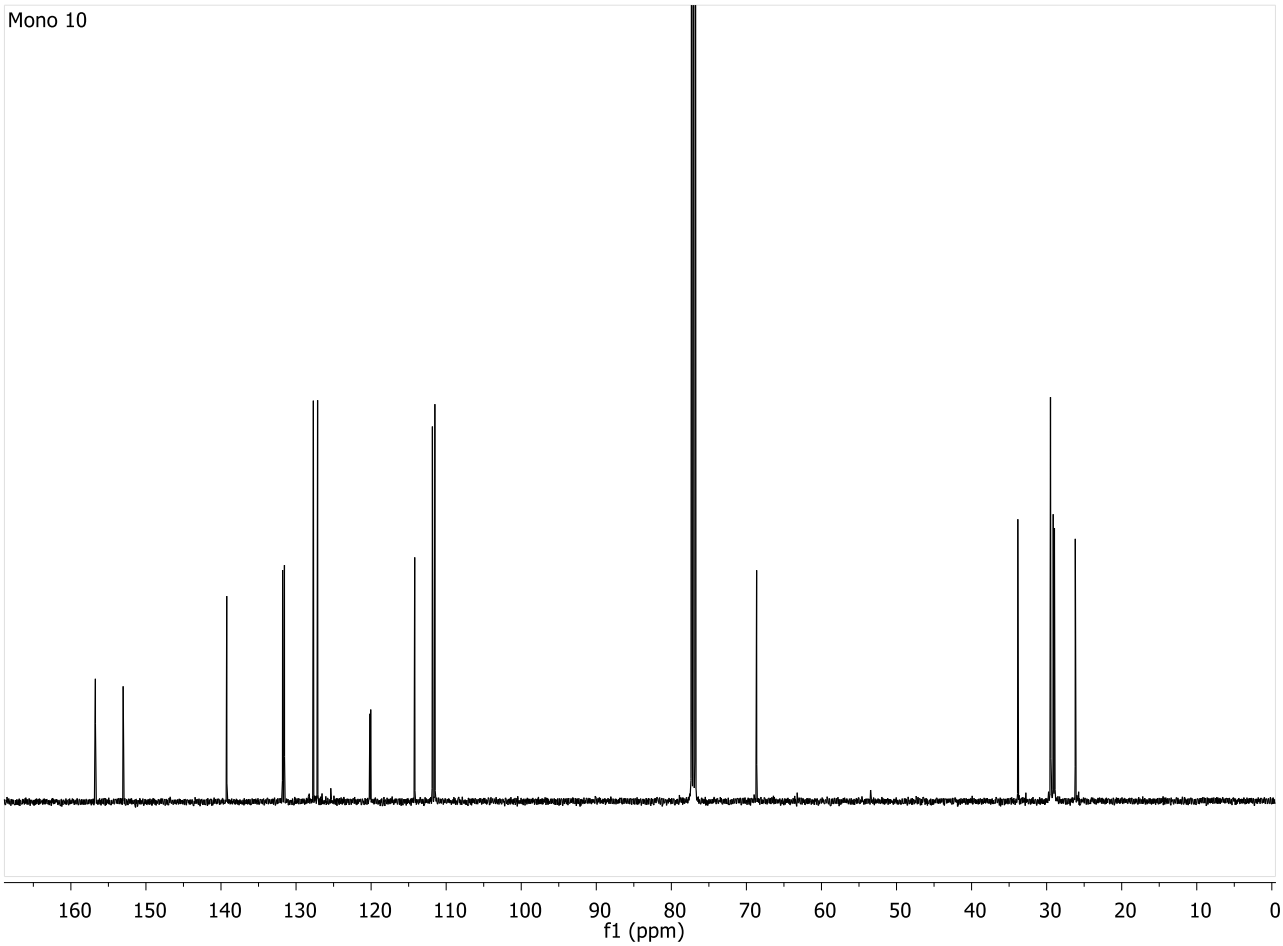

ALPYR8
Matriz:m-NBA
AMPLIACION
FILE:1271
100
%
0
344.2
234.1
235.1
345.2
205.1
165.1
189.1
218.1
206.1
167.1
247.1
250.1
202.1
219.1
176.1
236.1
190.1
207.1
233.1
251.1
263.1
289.1
307.1
226.1
273.1
291.1
311.1
343.2
361.1
327.1
337.1
351.1
371.1
387.1
391.1
395.1
346.2
160
180
200
220
240
260
280
300
320
340
360
380
400

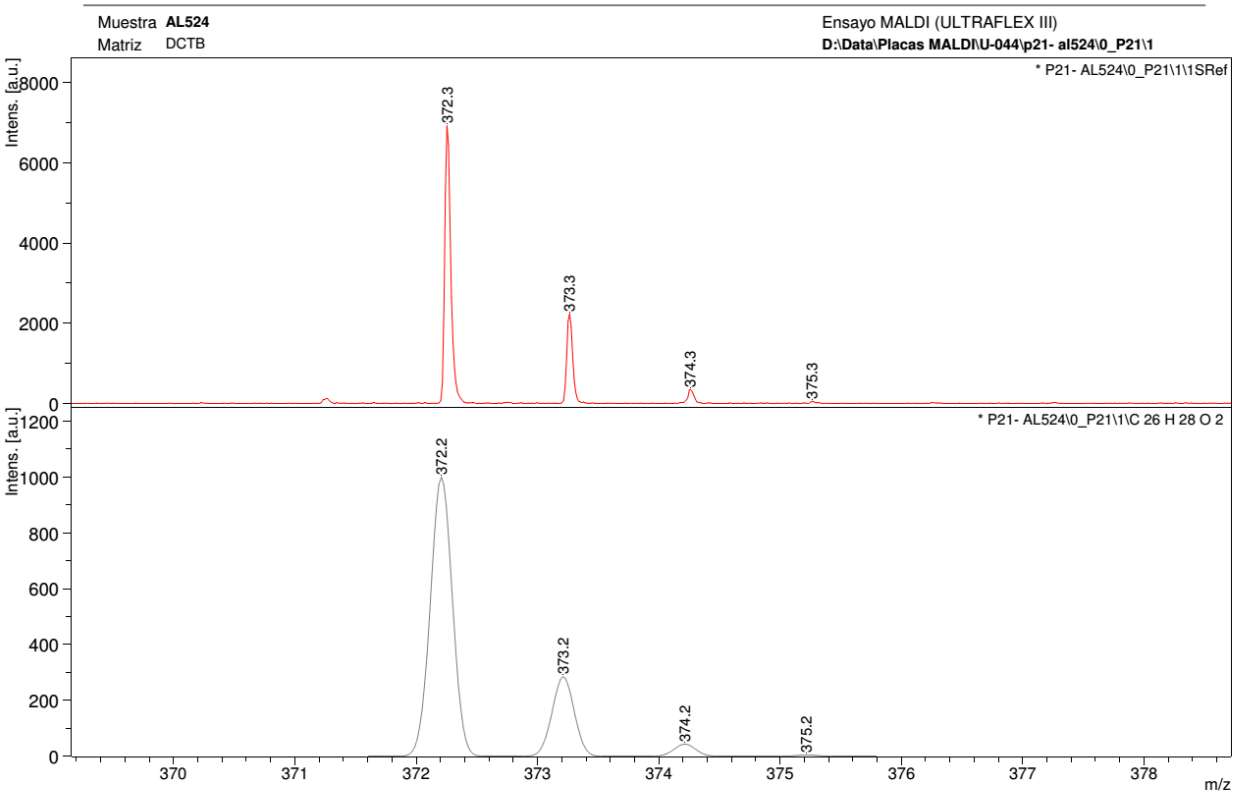
7-(dec-9-en-1-yloxy)pyren-2-ol



^{1}H RMN ($CDCl_3$, 300 MHz) δ 7.95 (q, *J* = 9.0 Hz, 4H, Hl+l´+m+m´), 7.71 (s, 2H, Hk+k´), 7.61 (s, 2H, Hn+n´), 5.92 – 5.78 (m, 1H, Hb), 5.32 (s,1H, OH), 5.06 – 4.95 (m, 2H, Ha), 4.26 (t, J = 6.5 Hz, 2H, Hj), 2.10 – 2.07 (m, 2H, Hc), 1.97 – 1.92 (m, 2H, Hi), 1.58 – 1.38 (m, 10H, Hd+e+f+g+h) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 156.7, 153.0, 139.2, 131.8, 131.5, 127.7, 127.1, 120.16, 120.0, 114.2, 111.8, 111.5, 68.6, 33.8, 29.5, 29.4, 29.1, 28.9, 26.2 ppm. MS m/z calculated for C26H28O2 372.1, found MALDI 372.3




Mono 10
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Muestra AL524
Matriz DCTB
Ensayo MALDI (ULTRAFLEX III)
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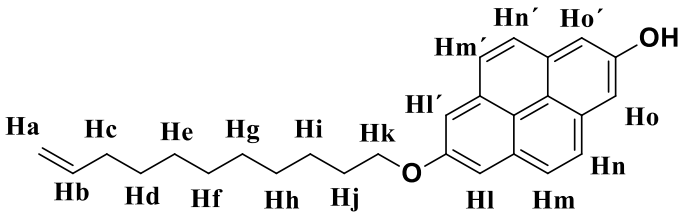
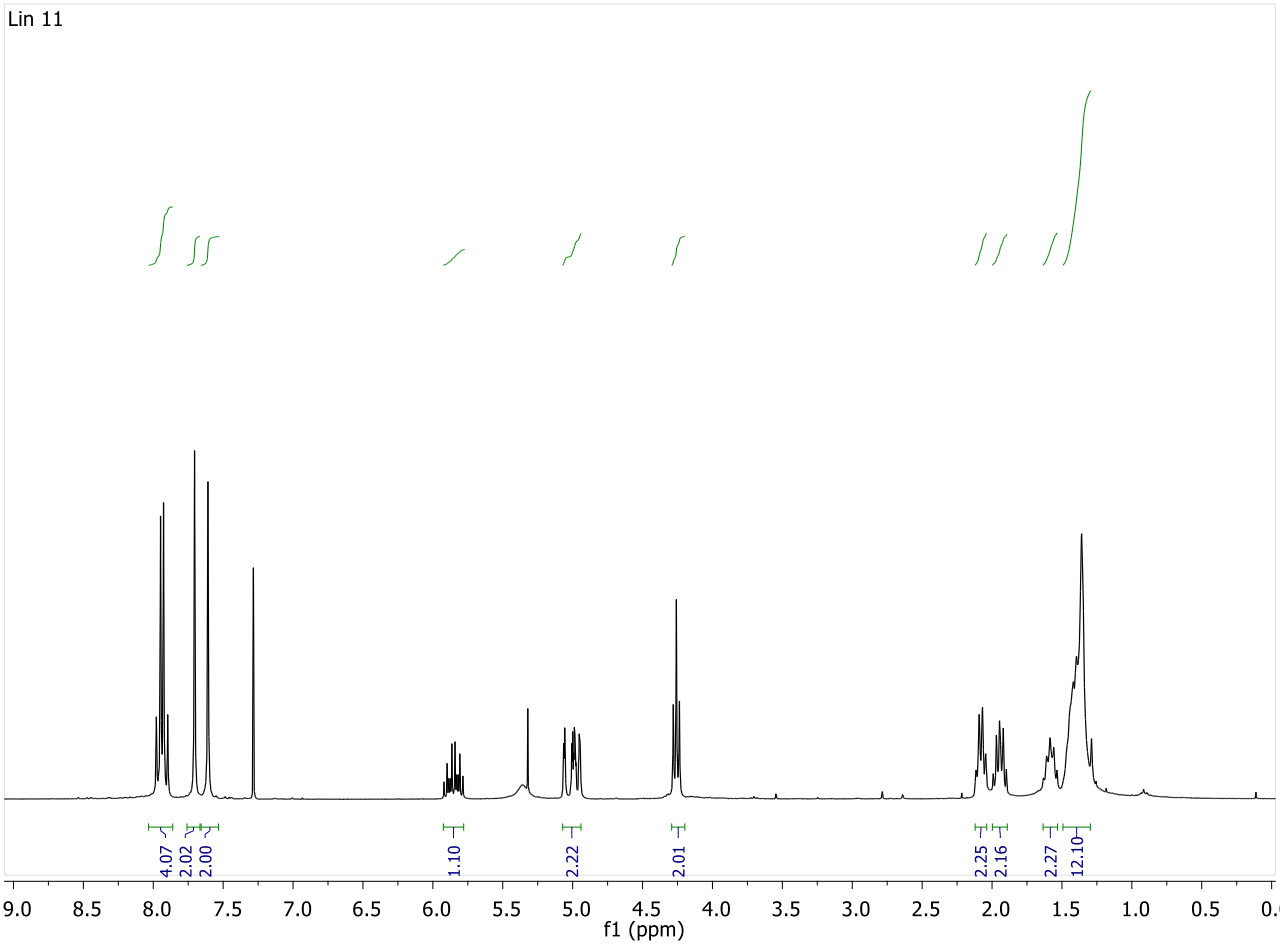
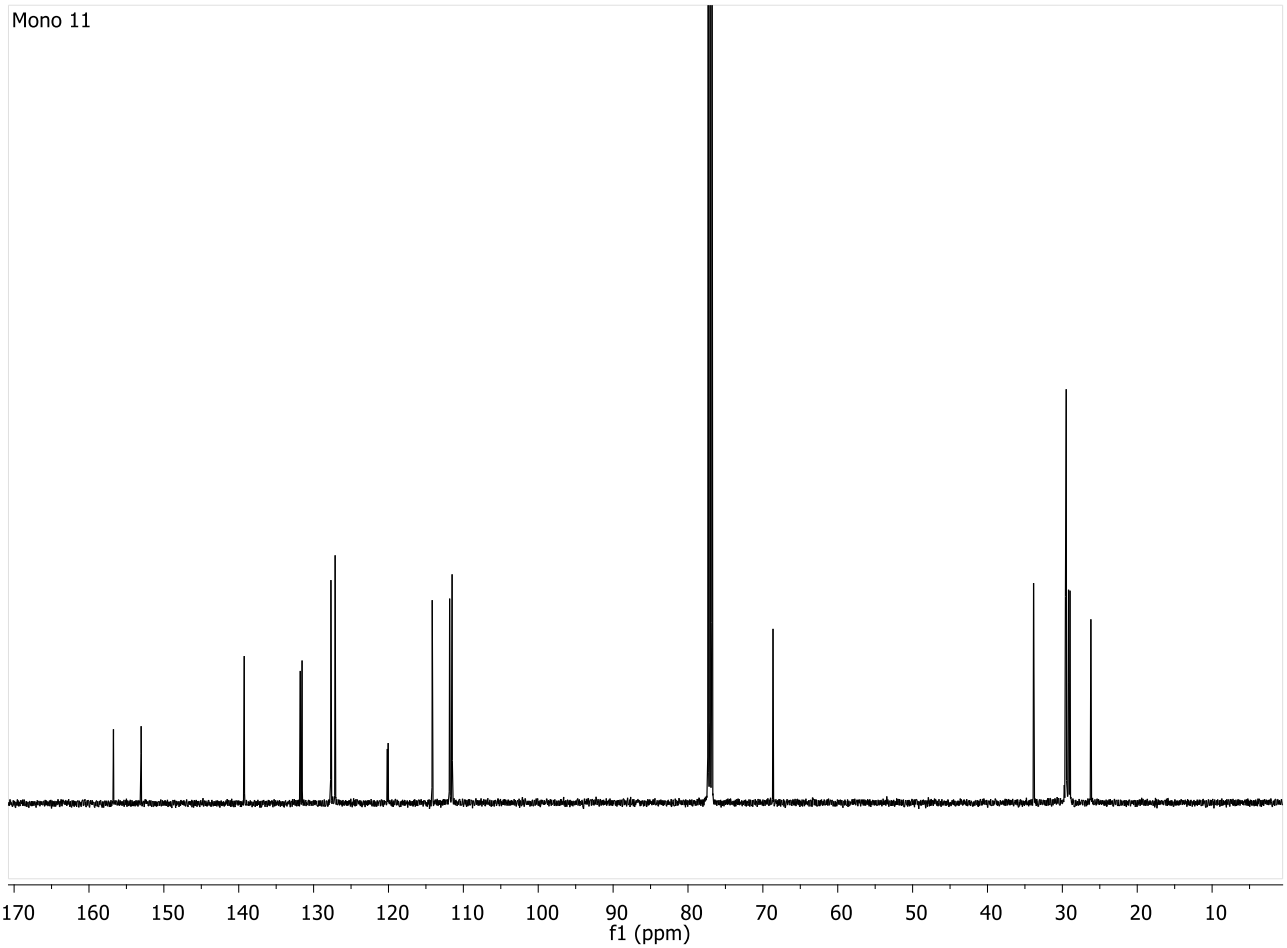
Intens. [a.u.]
8000
6000
4000
2000
0
372.3
373.3
374.3
375.3
* P21- AL524\0_P21\1\C 26 H 28 O 2
Intens. [a.u.]
1200
1000
800
600
400
200
0
372.2
373.2
374.2
375.2
370
371
372
373
374
375
376
377
378
m/z

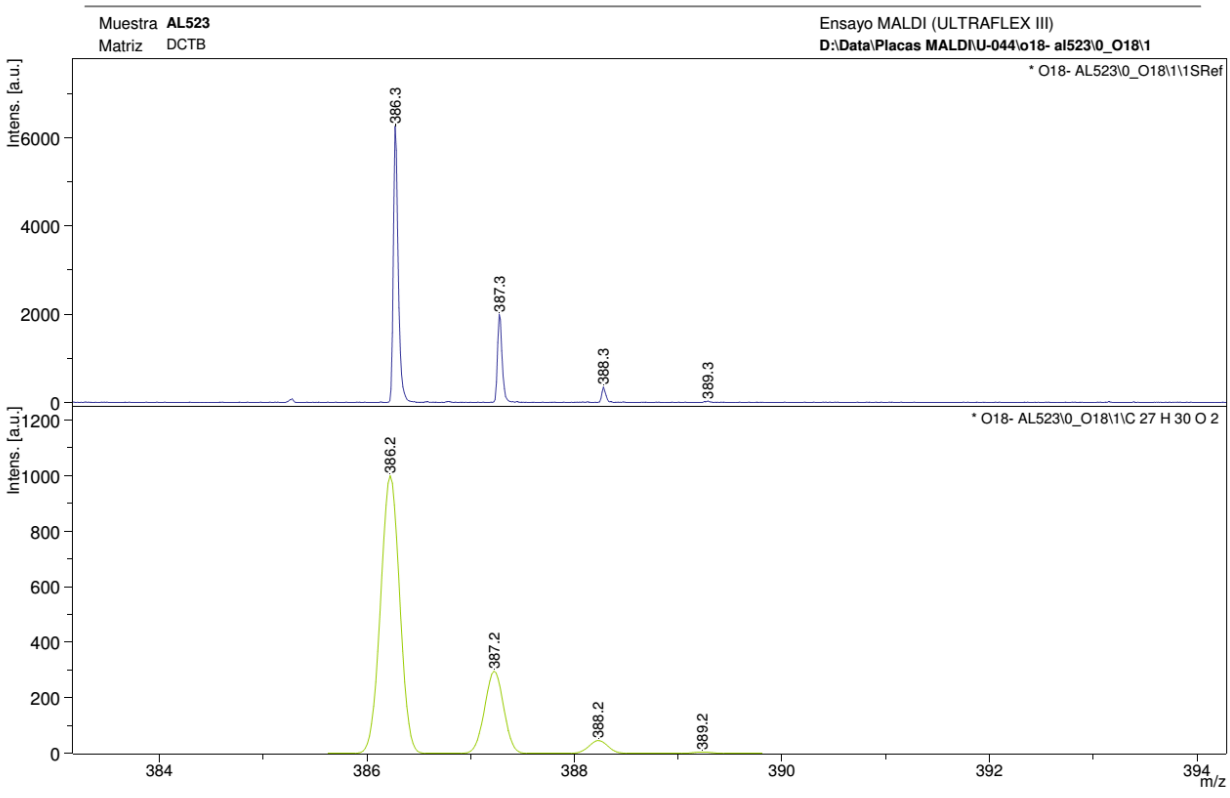
7-(undec-10-en-1-yloxy)pyren-2-ol



^{1}H RMN ($CDCl_3$, 300 MHz) δ 7.95 (q, *J* = 9.0 Hz, 4H, Hm+m´+n+n´), 7.70 (s, 2H, Hl+l´), 7.61 (s, 2H, Ho+o´), 5.92 – 5.79 (m, 1H, Hb), 5.32 (s,1H, OH), 5.06 – 4.95 (m, 2H, Ha), 4.26 (t, J = 6.5 Hz, 2H, Hk), 2.12 – 2.05 (m, 2H, Hc), 1.99 – 1.90 (m, 2H, Hj), 1.61 – 1.29 (m, 12H, Hd+e+f+g+h+i) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz) δ: 156.7, 153.0, 139.2, 131.8, 131.5, 127.7, 127.1, 120.1, 120.0, 114.2, 111.8, 111.5, 68.6, 33.8, 29.6, 29.5, 29.2, 28.9, 26.2 ppm. MS m/z calculated for C28H30O2 386.2, found MALDI 386.3




Mono 11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Muestra AL523
Matriz DCTB
Ensayo MALDI (ULTRAFLEX III)
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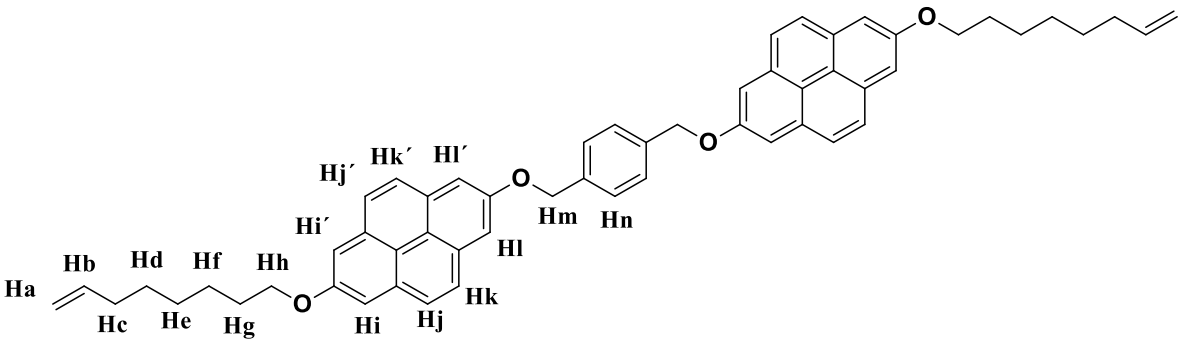
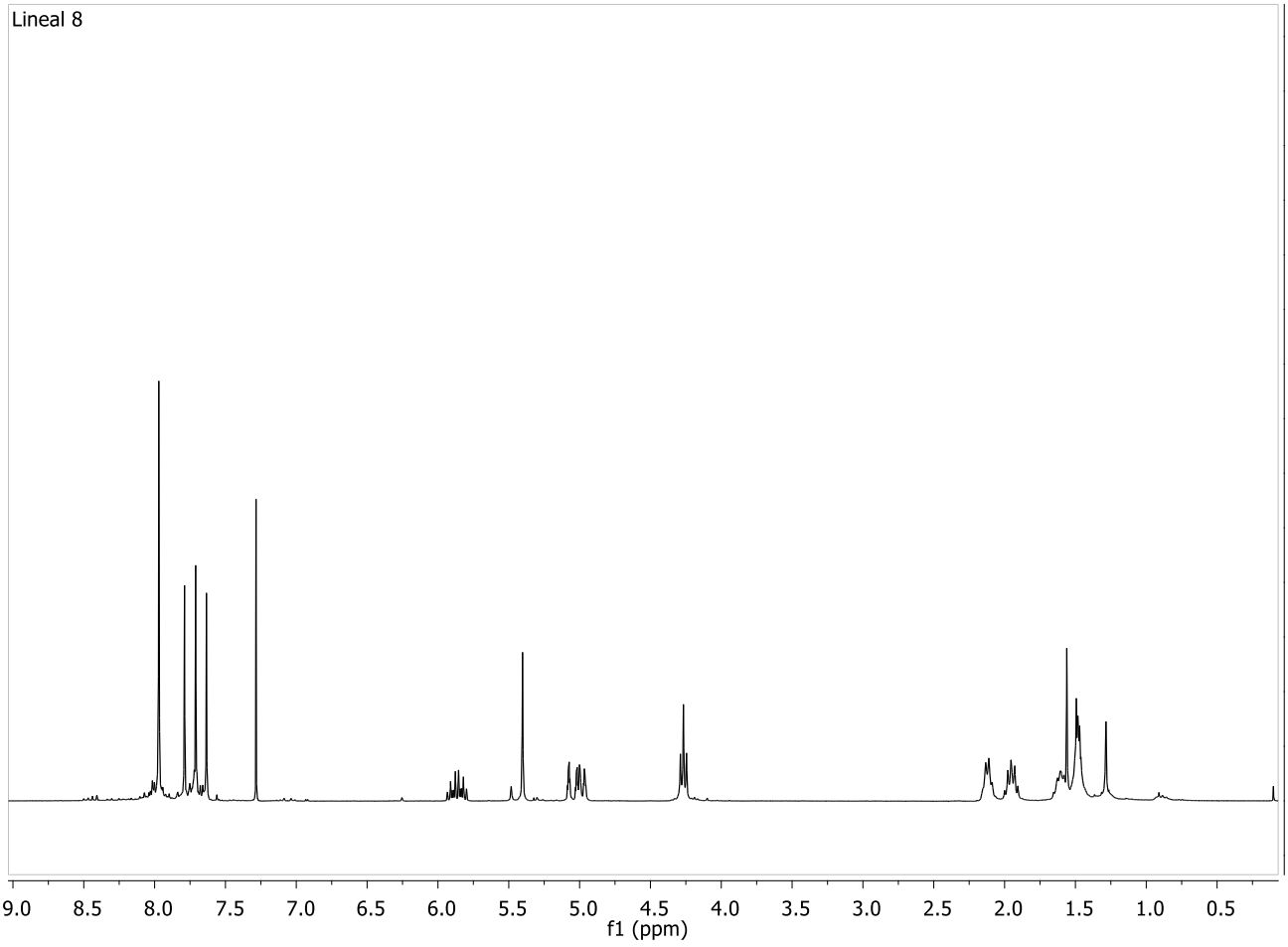
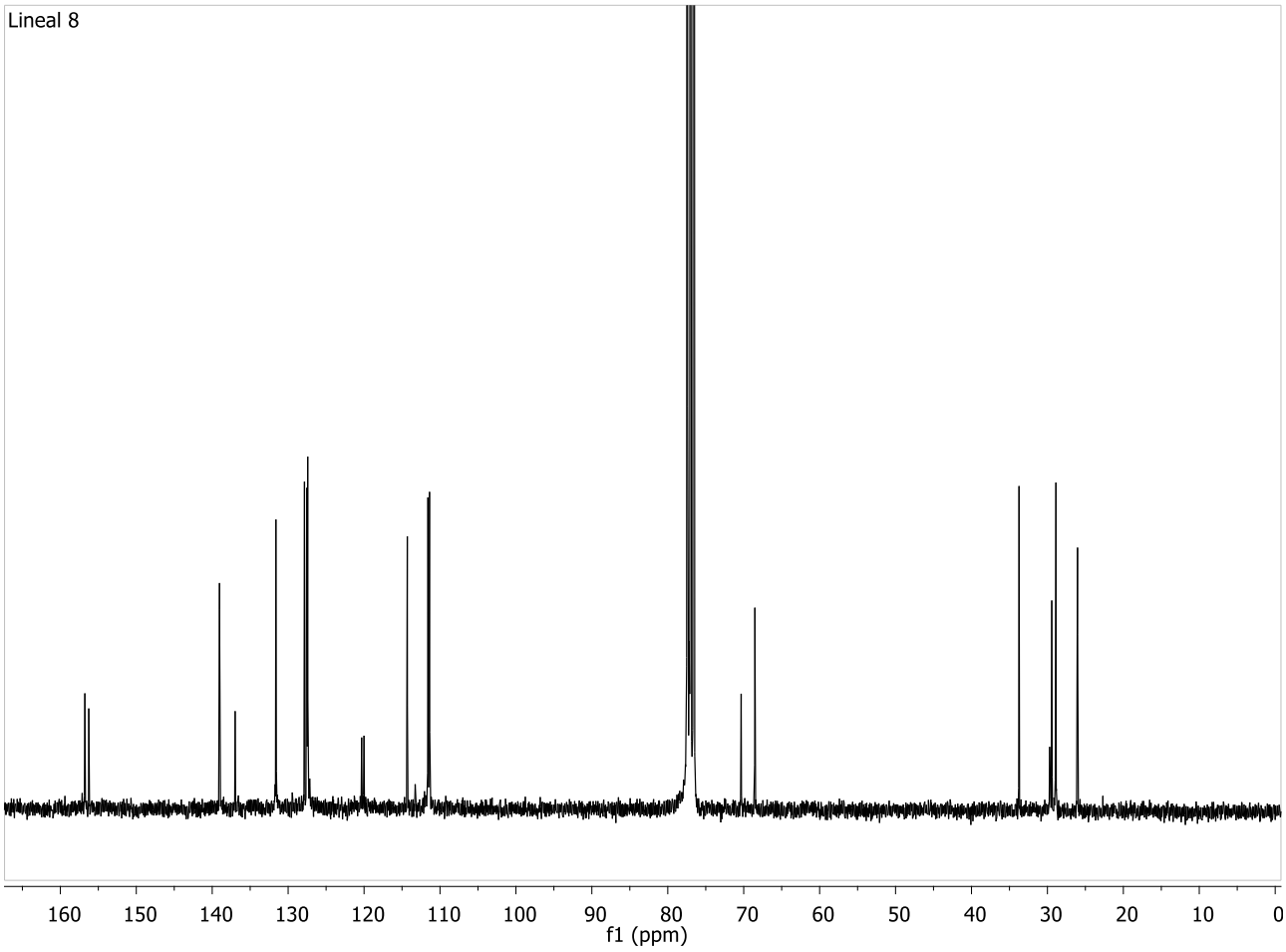
* O18- AL523\0_O18\1\1SRef
Intens. [a.u.]
6000
4000
2000
0
386.3
387.3
388.3
389.3
* O18- AL523\0_O18\1\C 27 H 30 O 2
Intens. [a.u.]
1200
1000
800
600
400
200
0
386.2
387.2
388.2
389.2
384
386
388
390
392
394
m/z

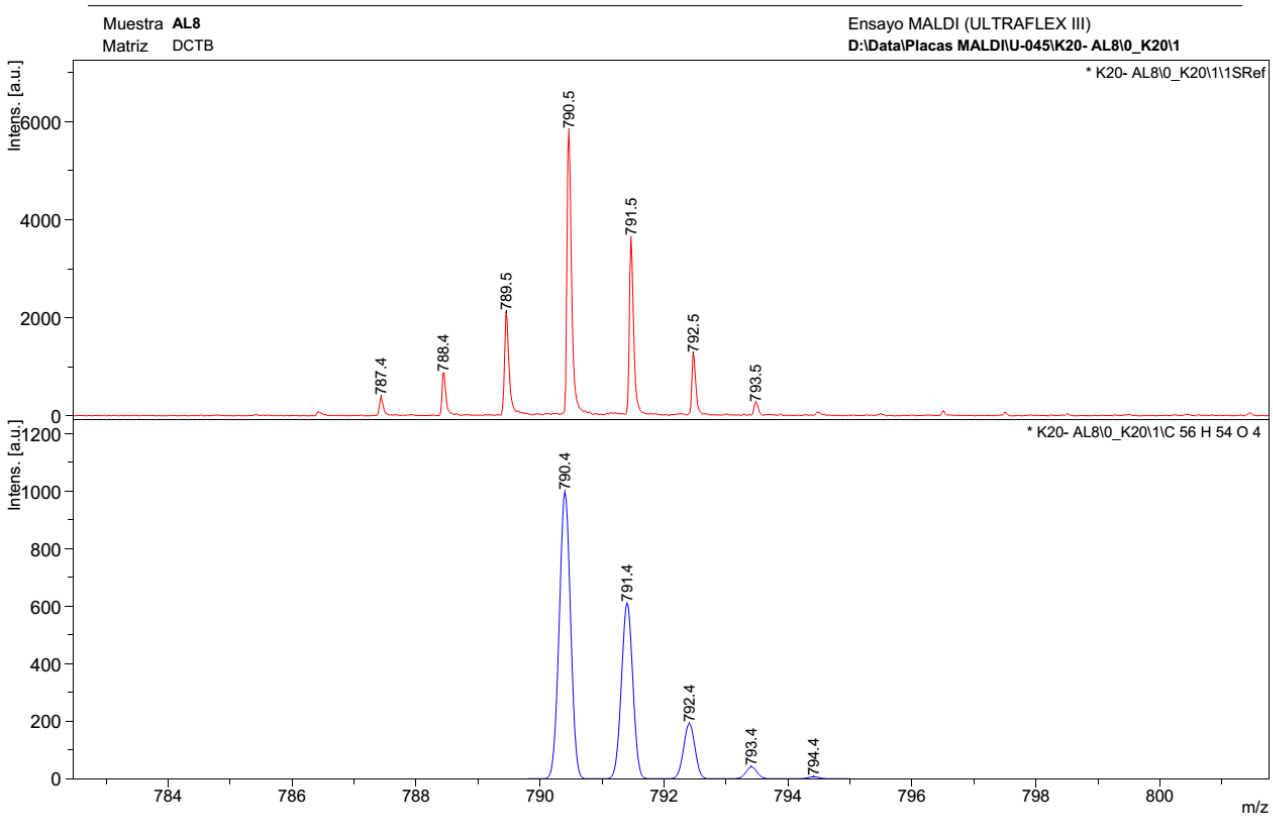
1,4-bis(((7-(oct-7-en-1-yloxy)pyren-2-yl)oxy)methyl)benzene



^{1}H RMN ($CDCl_3$, 300 MHz) δ: 7.97 (s, 8H, Hj+j´+k+k´), 7.79 (s, 4H, Hi+i´), 7.71 (s, 4H, Hl+l´), 7.63 (s, 4H, Hn), 5.93 – 5.80 (m, 2H, Ha), 5.40 (s, 4H, Hm), 5.08 – 4.96 (m, 4H, Hb), 4.27 (t, J = 6.5Hz, 4H, Hh), 2.13 – 2.09 (m, 4H, Hc), 2.00 – 1.91 (m, 4H, Hg), 1.63 – 1.58 (m, 4H, Hf), 1.49 – 1.46 (m, 8H, Hd+e) ppm.^{13}C NMR (CDCl3, 75 MHz) δ: 156.8, 156.3, 139.0, 136.9, 131.6, 131.6, 127.8, 127.5, 127.4, 120.3, 120.0, 114.3, 111.6, 111.4, 77.2, 70.3, 68.5, 33.7, 29.7, 29.4, 28.9, 28.9, 26.0 ppm. MS m/z calculated for C56H54O4 790.4, found MALDI 790.4.




Lineal 8
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Muestra AL8
Matriz DCTB
Ensayo MALDI (ULTRAFLEX III)
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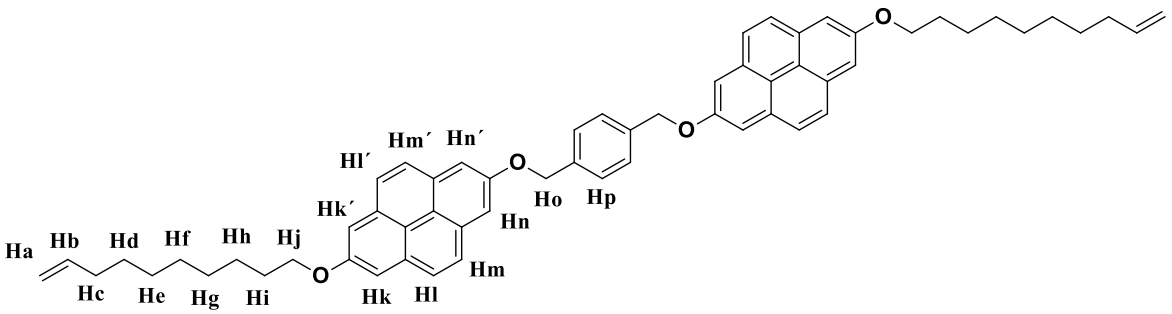
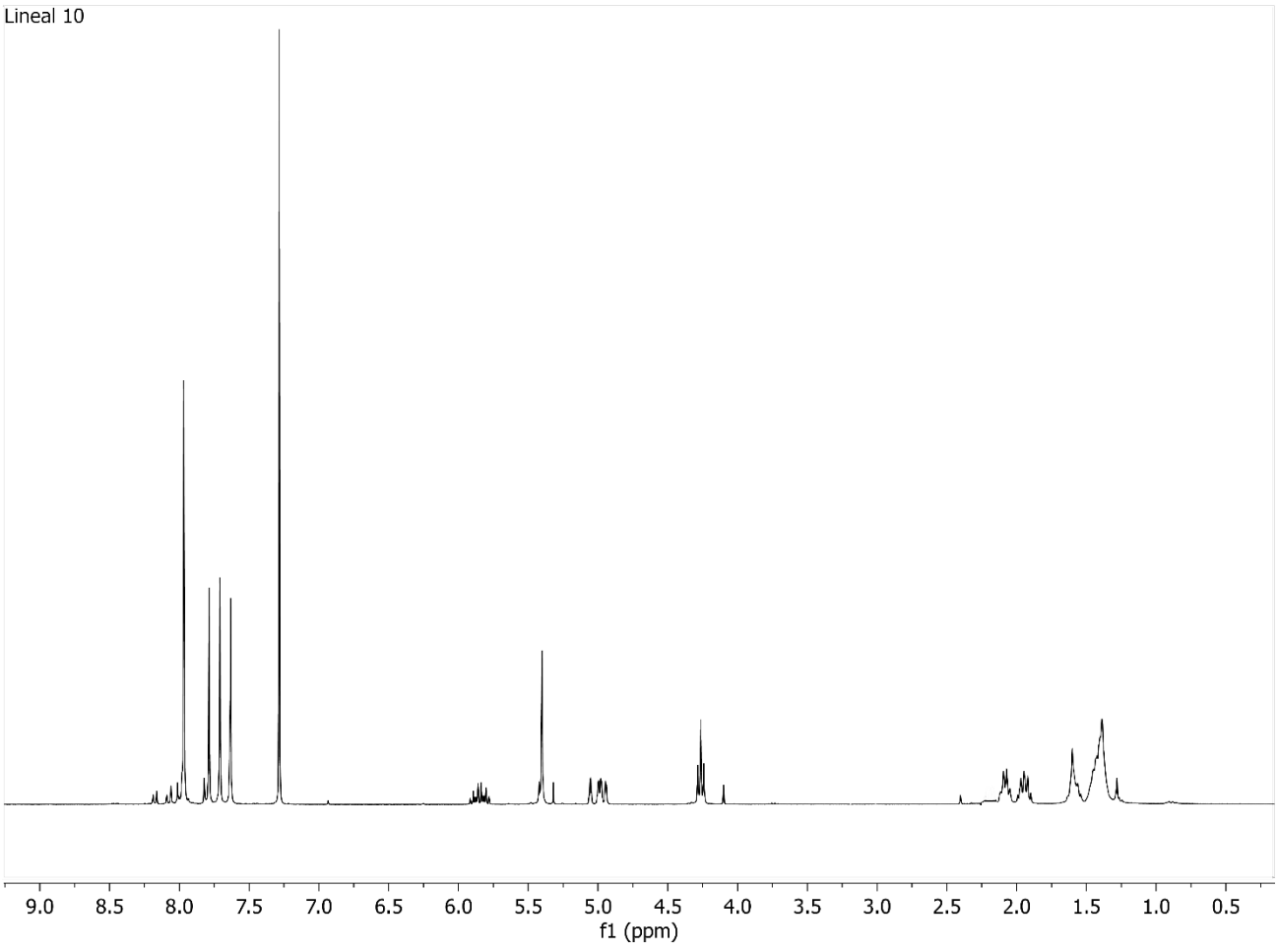
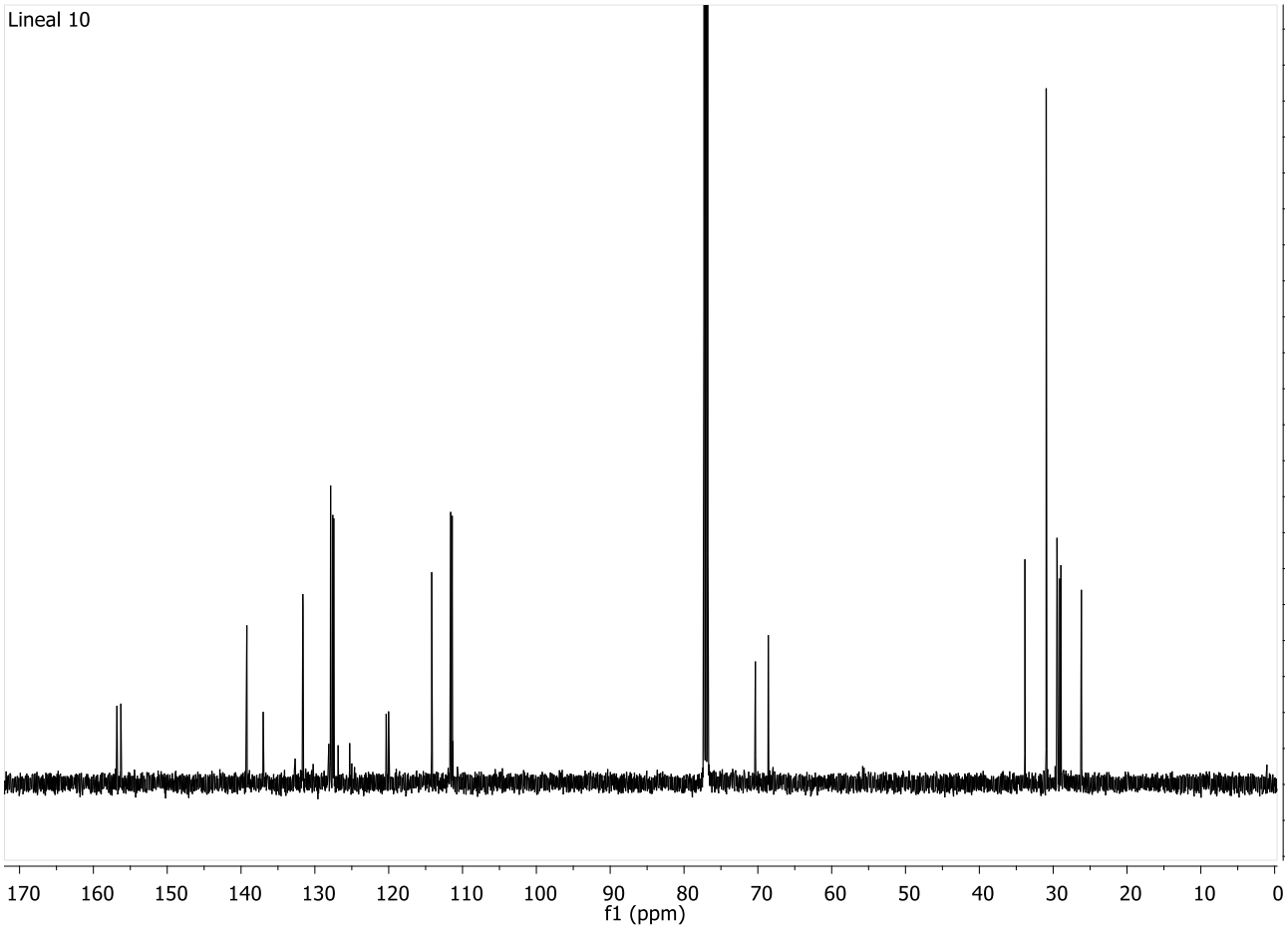
Intens. [a.u.]
6000
4000
2000
0
790.5
791.5
789.5
792.5
788.4
787.4
793.5
* K20- AL8\0_K20\1\C 56 H 54 O 4
1200
1000
800
600
400
200
0
790.4
791.4
792.4
793.4
794.4
784
786
788
790
792
794
796
798
800
m/z

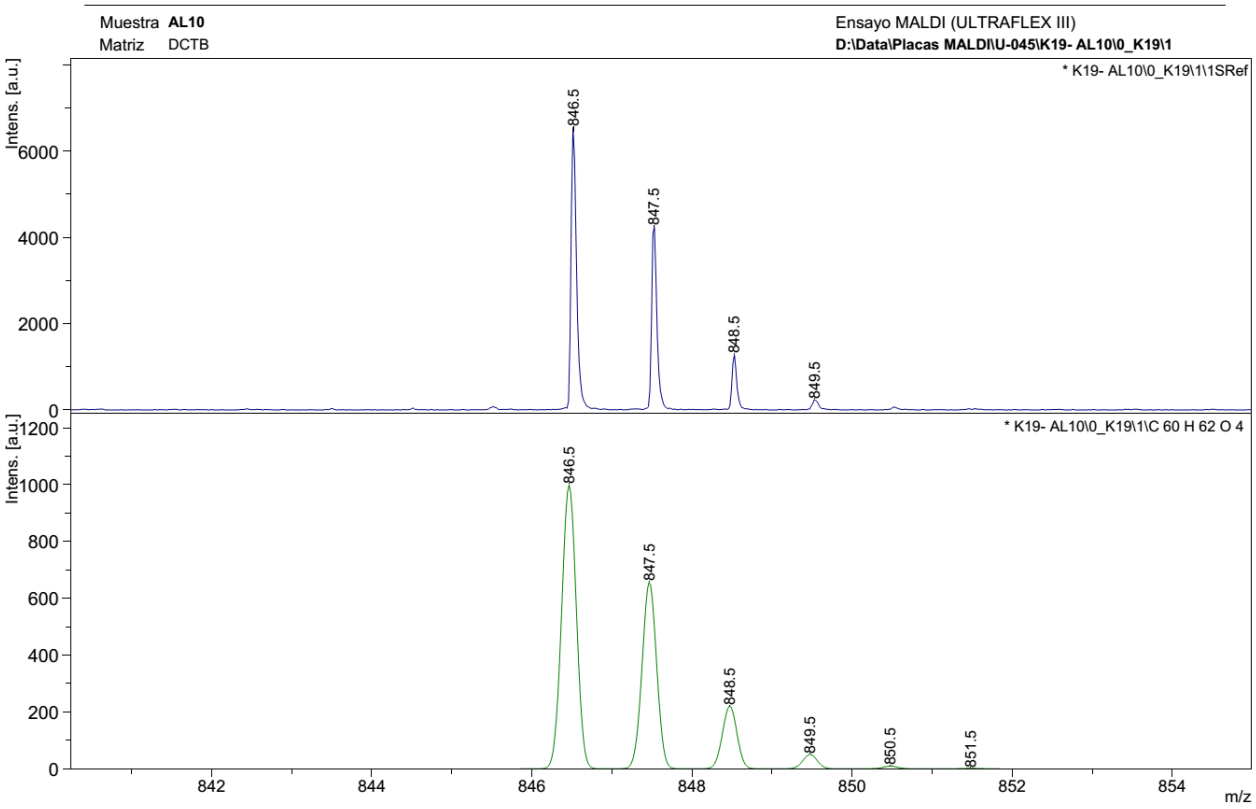
1,4-bis(((7-(dec-9-en-1-yloxy)pyren-2-yl)oxy)methyl)benzene



^{1}H RMN ($CDCl_3$, 300 MHz) δ 7.97 (s, 8H, Hl+l´+m+m´), 7.79 (s, 4H, Hk+k´), 7.71 (s, 4H, Hn+n´), 7.63 (s, 4H, Hp), 5.92 – 5.78 (m, 2H, Ha), 5.40 (s, 4H, Ho), 5.06 – 4.94 (m, 4H, Hb), 4.26 (t, J = 6.5Hz, 4H, Hj), 2.11 – 2.05 (m, 4H, Hc), 1.99 – 1.90 (m, 4H, Hi), 1.62 – 1.54 (m, 4H, Hh), 1.45 – 1.39 (m, 16H, Hd+e+f+g) ppm.^{13}C NMR (CDCl3, 126 MHz) δ: 156.8, 156.3, 139.2, 137.0, 131.6, 131.6, 127.9, 127.6, 127.4, 120.3, 120.0, 114.2, 111.6, 111.4, 77.2, 70.3, 68.6, 33.8, 30.9, 29.5, 29.4, 29.1, 28.9, 26.2 ppm. MS m/z calculated for C60H62O4 846.5, found MALDI 846.5.




Lineal 10
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Muestra AL10
Matriz DCTB
Ensayo MALDI (ULTRAFLEX III)
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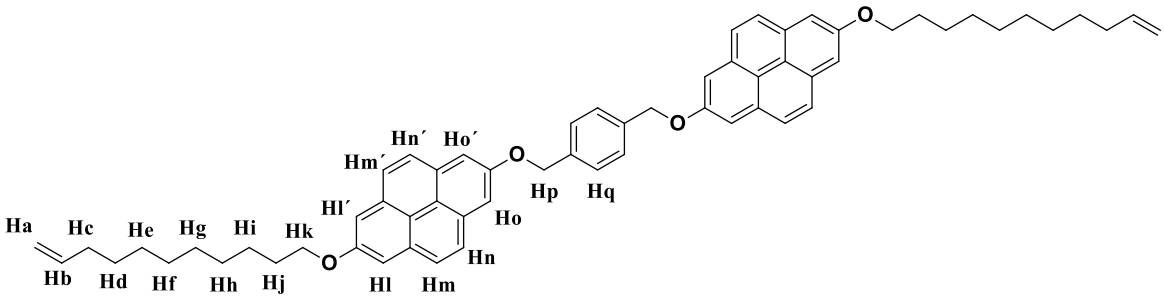
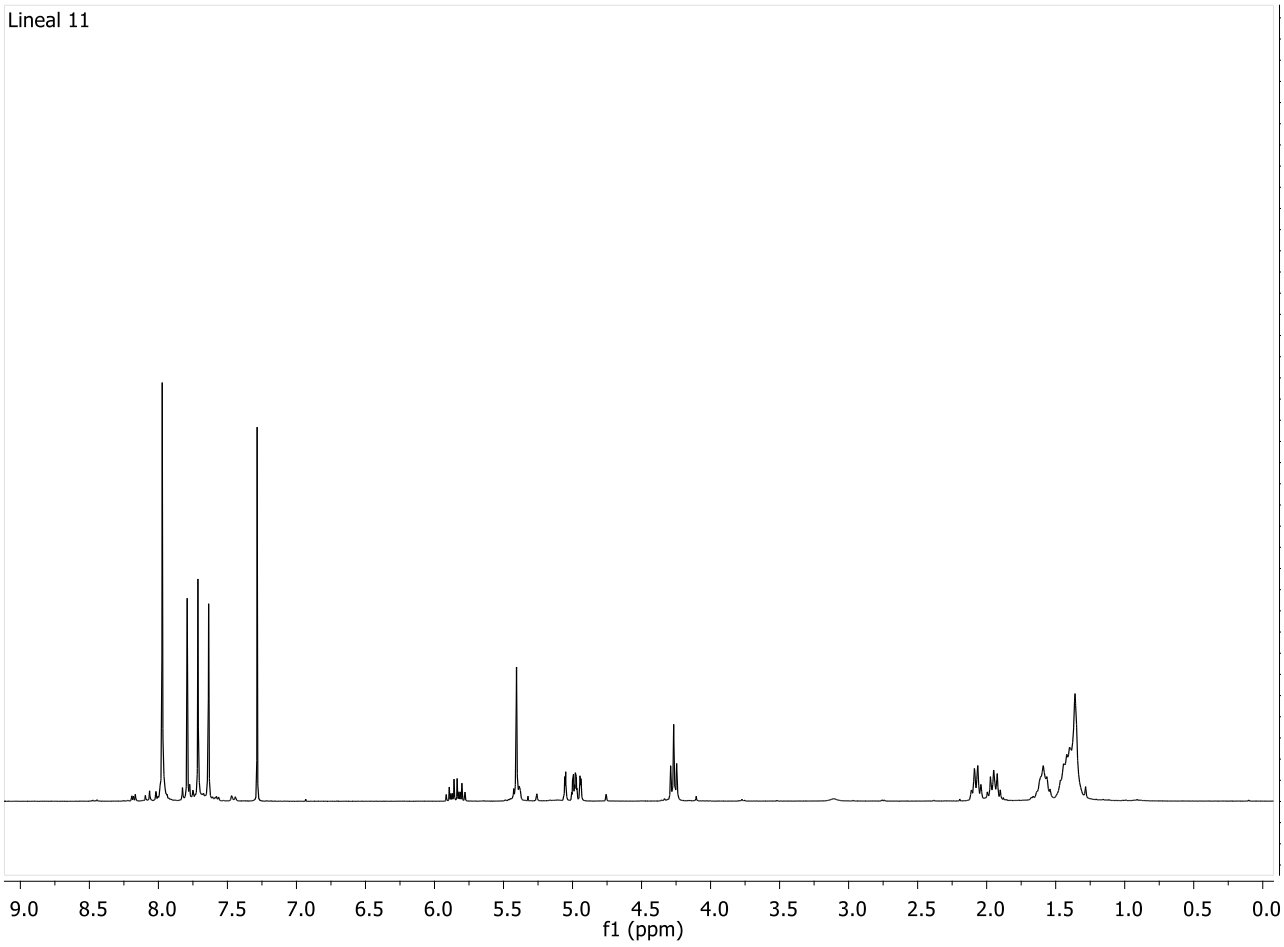
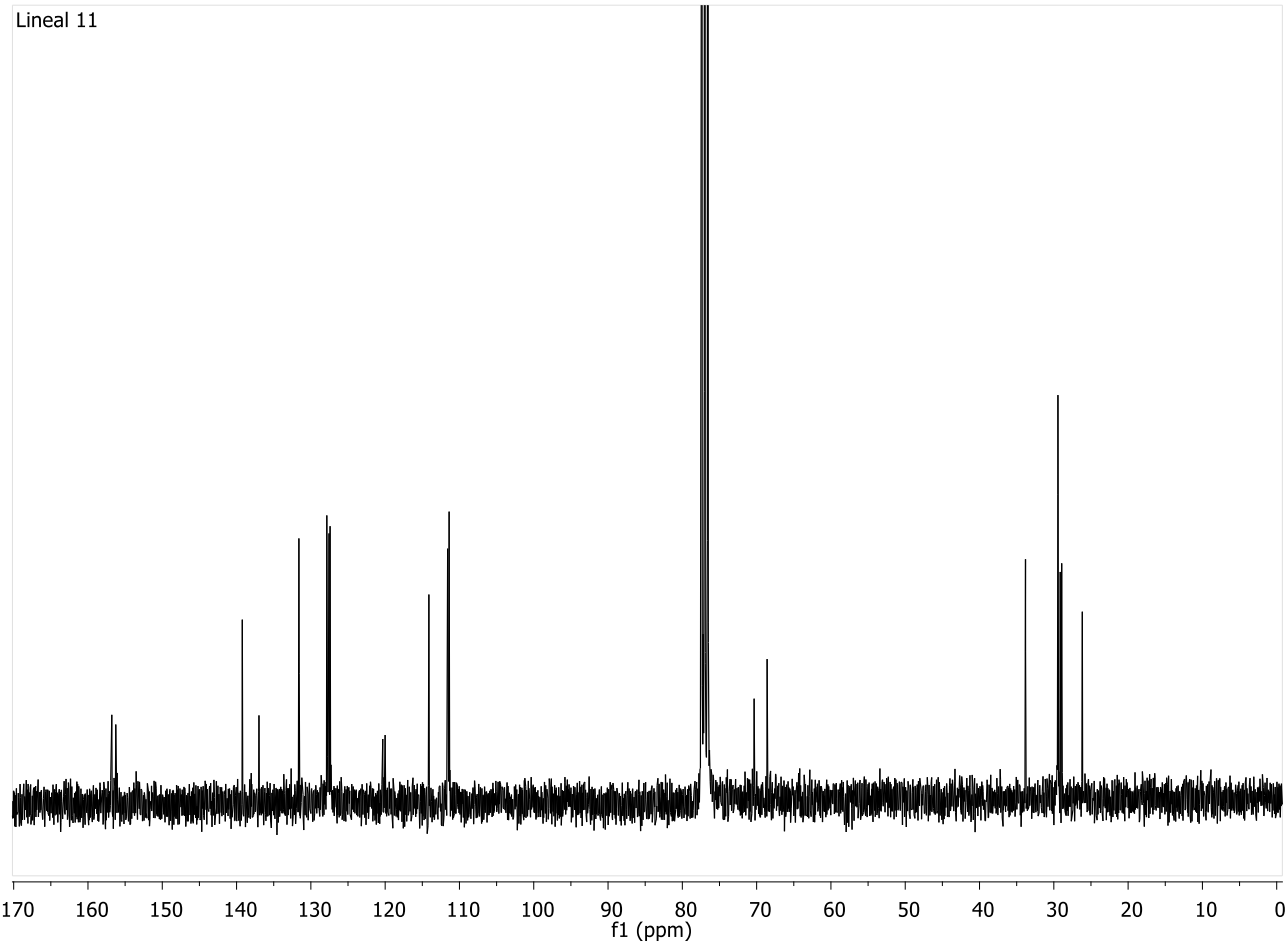
* K19- AL10\0_K19\1\1SRef
Intens. [a.u.]
6000
4000
2000
0
846.5
847.5
848.5
849.5
* K19- AL10\0_K19\1\C 60 H 62 O 4
Intens. [a.u.]
1200
1000
800
600
400
200
0
846.5
847.5
848.5
849.5
850.5
851.5
842
844
846
848
850
852
854
m/z

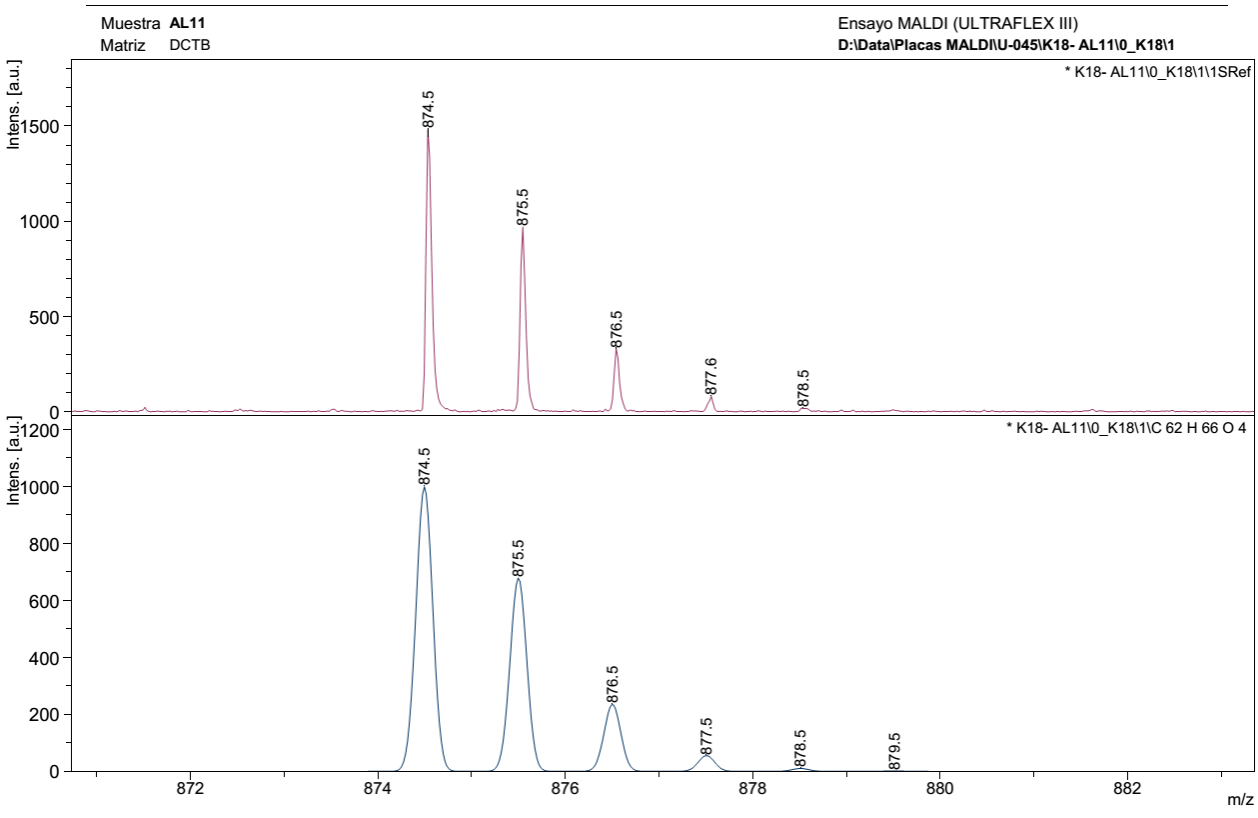
1,4-bis(((7-(undec-10-en-1-yloxy)pyren-2-yl)oxy)methyl)benzene



^{1}H RMN ($CDCl_3$, 300 MHz) δ: 7.97 (s, 8H, Hm+m´+n+n´), 7.79 (s, 4H, Hl+l´), 7.71 (s, 4H, Ho+o´), 7.64 (s, 4H, Hq), 5.91 – 5.78 (m, 2H, Ha), 5.41 (s, 4H, Hp), 5.06 – 4.93 (m, 4H, Hb), 4.27 (t, J = 6.5Hz, 4H, Hk), 2.09 – 2.04 (m, 4H, Hc), 1.97 – 1.92 (m, 4H, Hj), 1.59 – 1.54 (m, 4H, Hi), 1.50 – 1.30 (m, 20H, Hd+e+f+g+h) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 156.3, 139.2, 137.0, 131.6, 131.6, 127.8, 127.5, 127.4, 120.3, 120.0, 114.1, 111.6, 111.4, 77.2, 70.3, 68.6, 33.8, 29.6, 29.5, 29.1, 28.9, 26.2 ppm. MS m/z calculated for C62H66O4 874.5, found MALDI 874.5.




Lineal 11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Muestra AL11
Matriz DCTB
Ensayo MALDI (ULTRAFLEX III)
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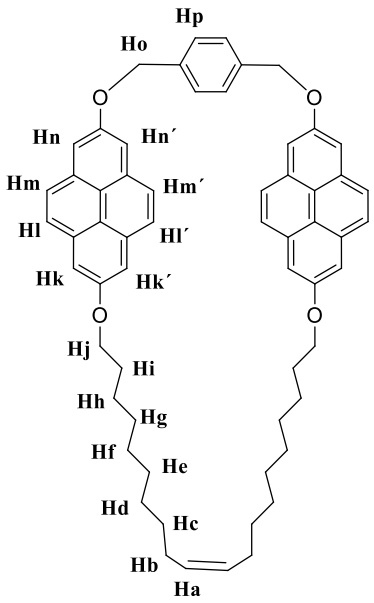
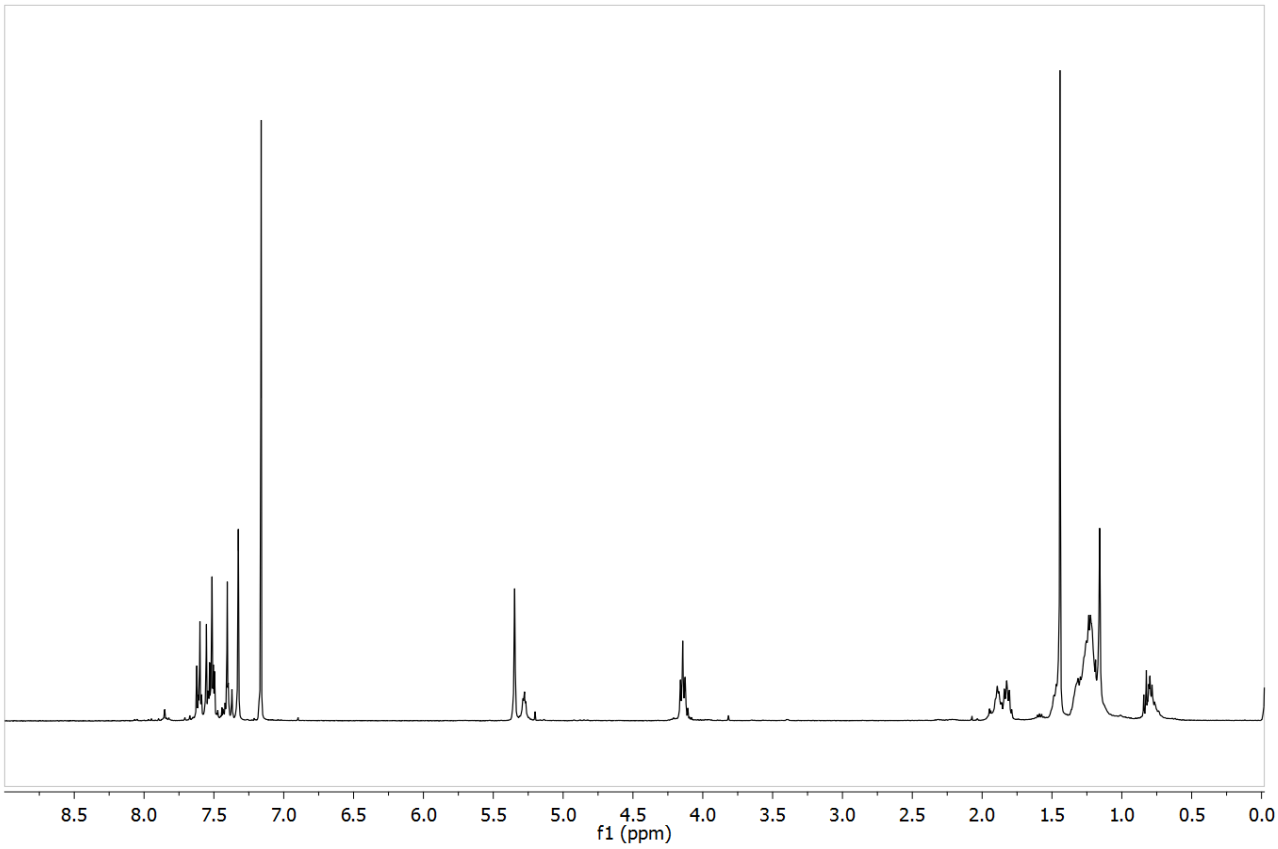
* K18- AL11\0_K18\1\1SRef
Intens. [a.u.]
874.5
875.5
876.5
877.6
878.5
* K18- AL11\0_K18\1\C 62 H 66 O 4
874.5
875.5
876.5
877.5
878.5
879.5
872 874 876 878 880 882
m/z

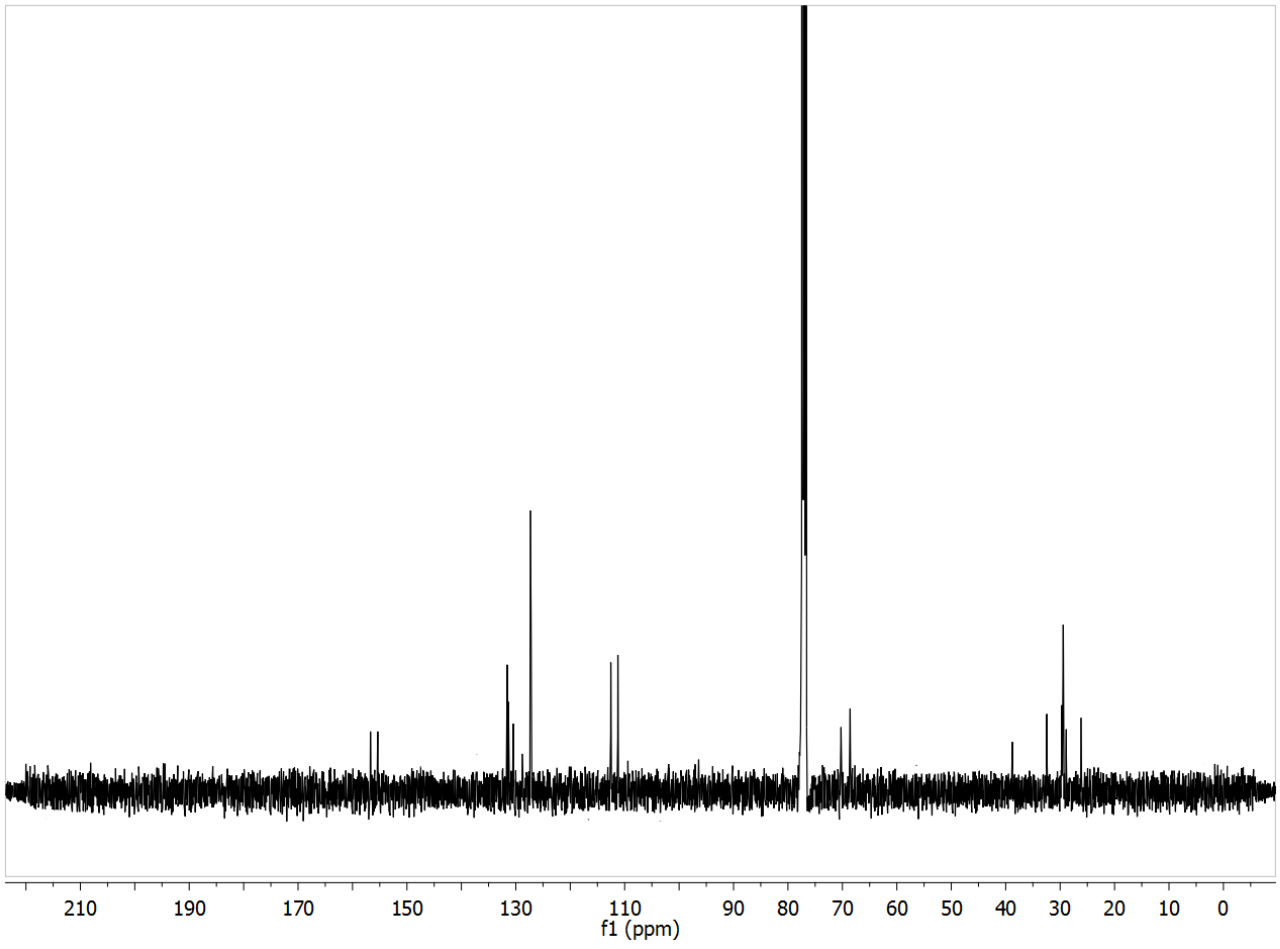
Procedure of Synthesis of Macrocycle

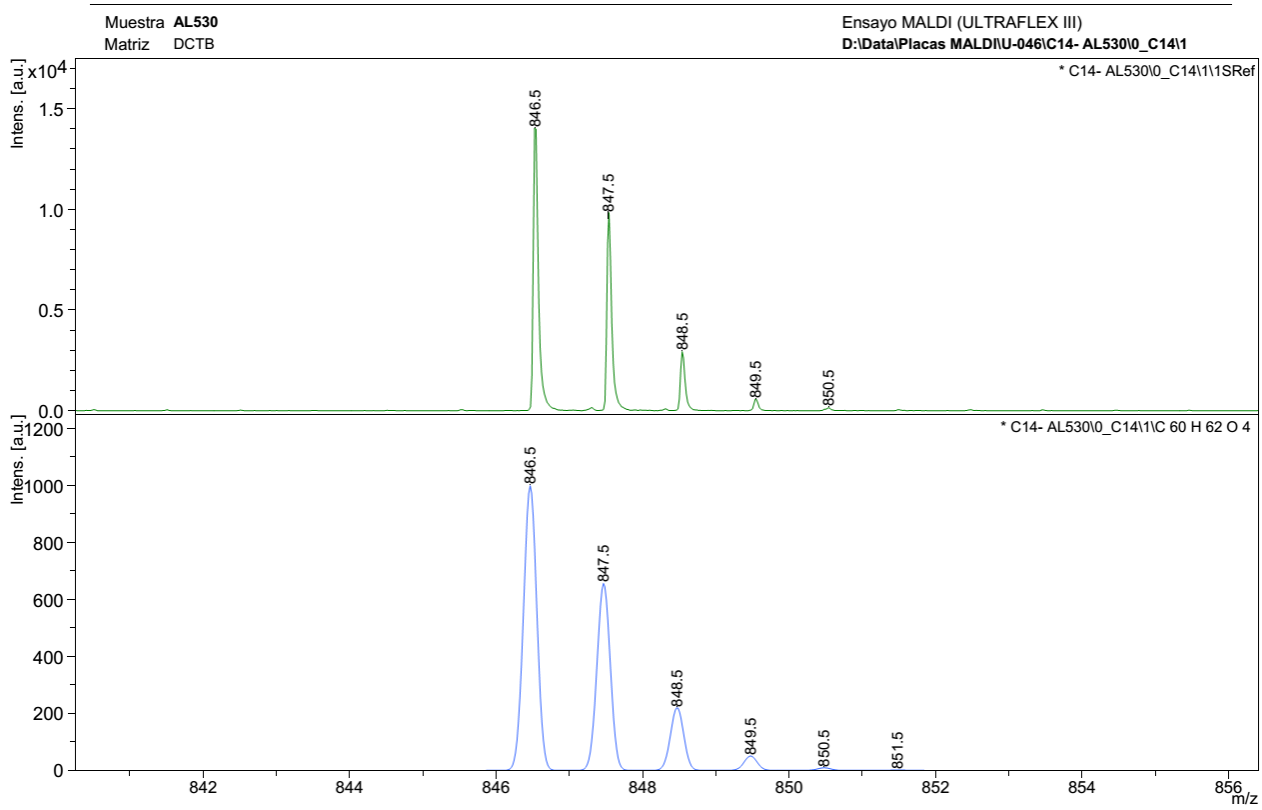


A catalytic amount of Grubb´s 1st generation catalyst was added to a solution of the linear precursor 1 in dry and degassed CH_2Cl_2. The solution was stirred at room temperature and its progress monitored by TLC (Hex:CH_2Cl_2 1:1). The reaction is then stopped, filtered through a pad of Celite, the solvent evaporated under reduced pressure, and the crude subjected to column chromatography silica gel (Hex:CH_2Cl_2 2:1) to obtain the product in 65% yield.

^{1}H RMN ($CDCl_3$, 400 MHz) δ 7.59-7.72 (m, 12H, Hk+k´+l+l´+m+m´), 7.50 (s, 4H, Hn+n´), 7.42 (s, 4H, Hp), 5.45 (s, 4H, Ho), 5.38 (m, 2H, Ha), 4.24 (t, J = 6.5 Hz, 4H, Hj), 1.99 – 1.90 (m, 2H, Hg), 1.35 – 1.26 (m, 24H, Hd+e+f). ^{13}C NMR (CDCl3, 101 MHz) δ 156.7, 155.4, 131.6, 131.3, 130.5, 127.3, 127.2, 112.5, 111.2, 77.3, 77.0, 76.7, 70.2, 68.6, 38.8, 32.4, 29.7, 29.4, 28.9, 26.2. MS m/z calculated for C60H62O4 846.5, found MALDI 846.5.


8.5
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
f1 (ppm)


210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



General Procedure for SWNTs Functionalization.

The (6,5)- and (7,6)-enriched SWNTs purchased from Sigma Aldrich Co were purified previously. 100 mg of SWNTs were suspended in 70 mL of 35% HCl, and sonicated for 10 min. The mixture was poured in 200 mL of miliQ water and filtered through a polycarbonate membrane of 0.2 µm pore size.

The solid was washed with water to neutral pH and then dried in an oven at 350^0C for 30 min. Pristine plasma-purified SWNTs were used without previous purification.

The nanotubes (5 mg) were suspended in 20 mL of tetrachloroethane (TCE) through sonication (10 min.) and mixed with linear precursors **1-3** (2.5 mg), and Grubb's 2nd generation catalyst at room temperature for 72 hours. After this time, the suspension was filtered through a PTFE membrane of 0.2 µm pore size, and the solid washed profusely with dichloromethane (DCM). The solid was re-suspended in 20 mL of DCM through sonication for 10 min. and filtered through a PTFE membrane of 0.2 µm pore size again. This washing procedure was repeated three times.

General Procedure for SWNTs Functionalization (varying the relative concentration of 3 with respect to SWNTs).

The nanotubes (1 mg/mL) were suspended in TCE through sonication (10 min.) and mixed with linear precursor (0.12 mM, 0.35 mM or 0.83 mM), and Grubb's 2nd generation catalyst at room temperature for 72 hours. After this time, the suspension was filtered through a PTFE membrane of 0.2 μm pore size, and the solid washed profusely with DCM. The solid was re-suspended in 20 mL of DCM through sonication for 10 min. and filtered through a PTFE membrane of 0.2 μm pore size again. This washing procedure was repeated three times.

General Procedure for SWNTs Functionalization (control experiments).

The nanotubes (5 mg) were suspended in 20 mL of TCE through sonication (10 min.) and mixed with either linear precursor or macrocycle (2.5 mg) at room temperature for 72 hours. After this time, the suspension was filtered through a PTFE membrane of 0.2 μm pore size, and the solid washed profusely with DCM. The solid was re-suspended in 20 mL of DCM through sonication for 10 min. and filtered through a PTFE membrane of 0.2 μm pore size again. This washing procedure was repeated three times.

General Procedure for Stability Test of Functionalized SWNTs.

The functionalized nanotubes (2 mg) were suspended in 5 mL of TCE by sonication for 5 min. and then heated to reflux (bp = 146^0C) for 30 min. The suspension was filtered through a PTFE membrane of 0.2 μm pore size, and the solid washed profusely with DCM. A small de-threading (<4%) was observed by TGA.

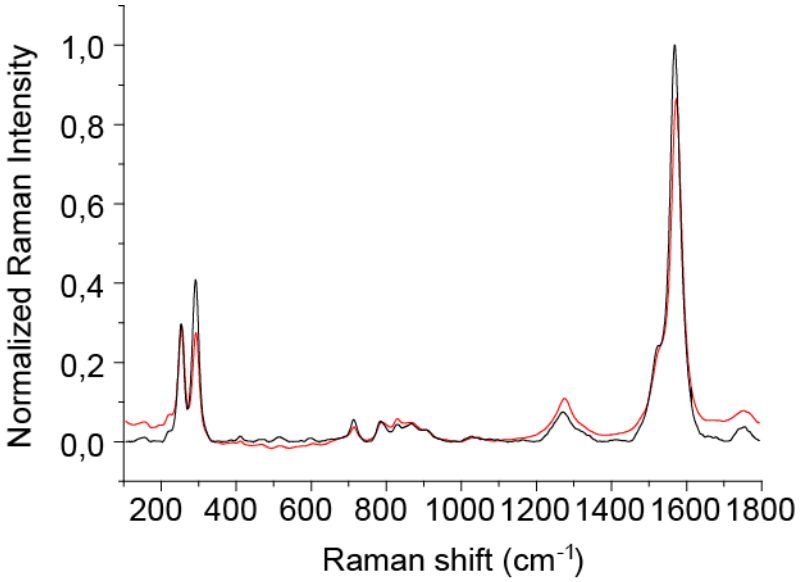


Figure S1. Raman spectra of (6,5)-enriched SWNTs (black) and the corresponding MINT(6,5) (red). The spectra is the average of three different measurements (λexc = 785 nm)

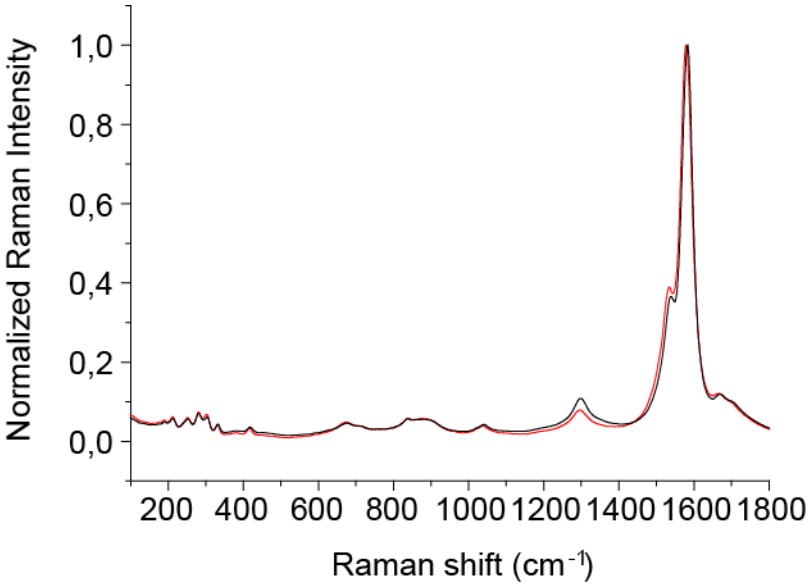


Figure S2. Raman spectra of (6,5)-enriched SWNTs (black) and the corresponding MINT(6,5) (red). The spectra is the average of three different measurements (λexc = 633 nm)

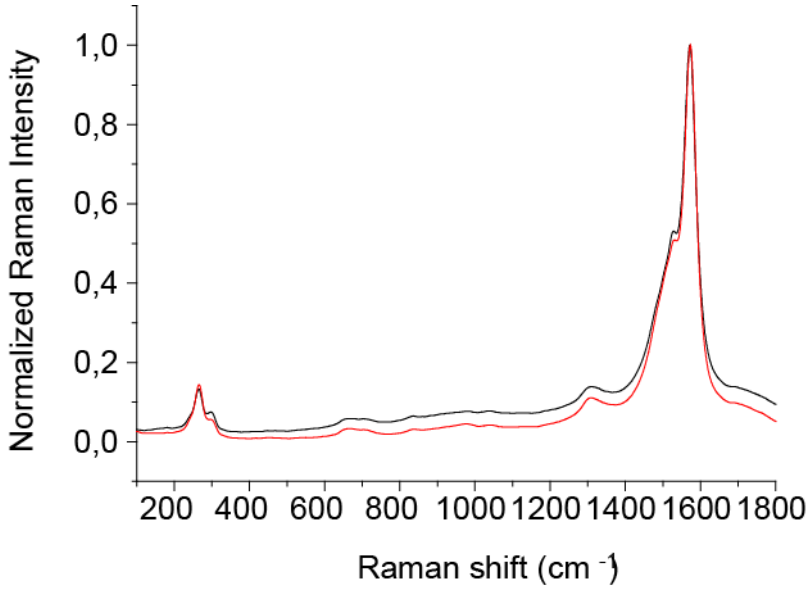


Figure S3. Raman spectra of (6,5)-enriched SWNTs (black) and the corresponding MINT(6,5) (red). The spectra is the average of three different measurements (λexc = 532 nm)

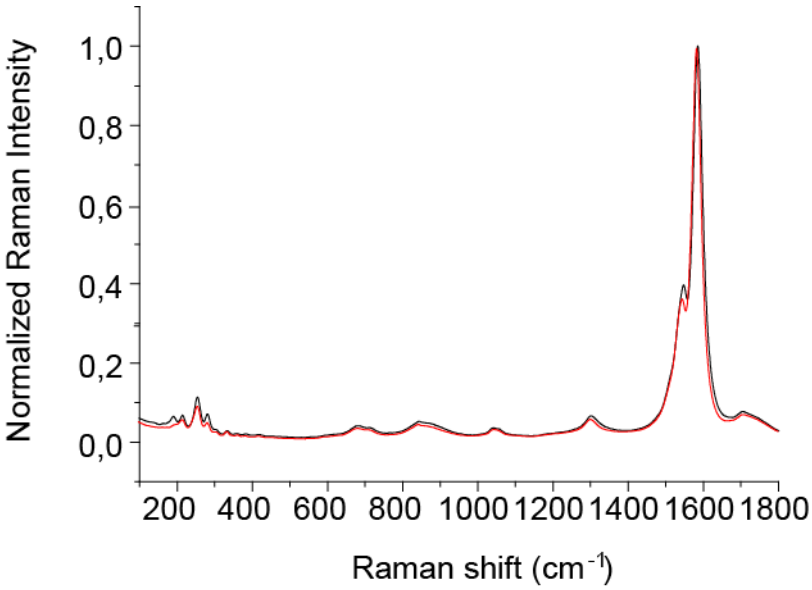


Figure S4. Raman spectra of (7,6)-enriched SWNTs (black) and the corresponding MINT(7,6) (red). The spectra is the average of three different measurements (λexc = 633 nm)

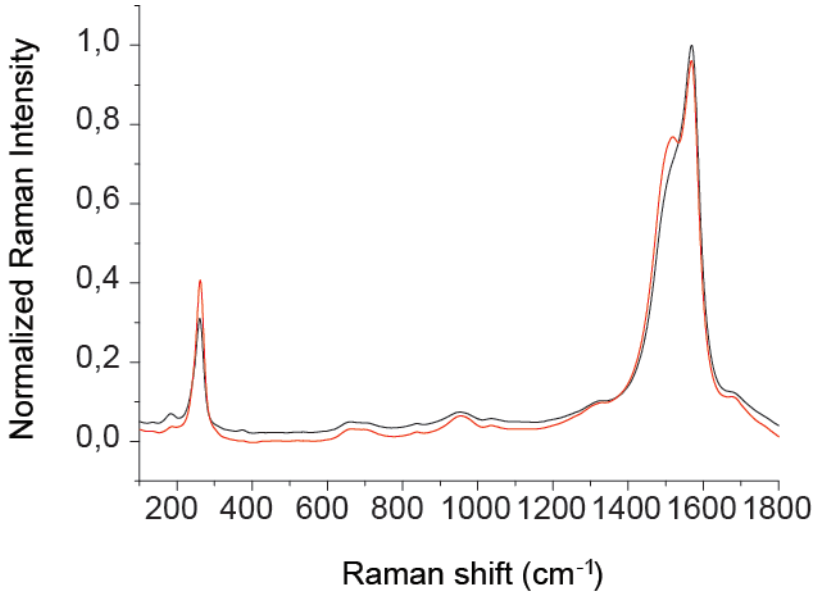


Figure S5. Raman spectra of (7,6)-enriched SWNTs (black) and the corresponding MINT(7,6) (red). The spectra is the average of three different measurements (λexc = 532 nm).

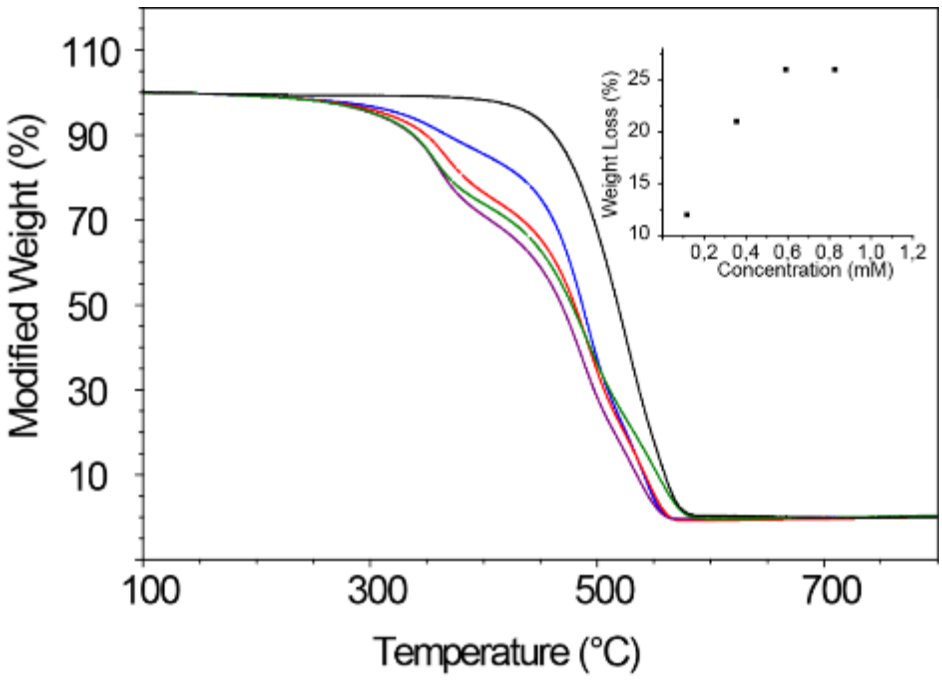


Figure S6. Variation in the degree of functionalization with the relative concentration of macrocycle **6** with respect to that of the SWNTs, as shown by TGA analysis (air, 10 ºCmin^{-1}): pristine (6,5)-enriched SWNTs (black), 0.12 mM (blue), 0.35 mM (red), 0.59 mM (green) and 0.83 mM (purple). Inset shows the relative weight loss versus the concentration.

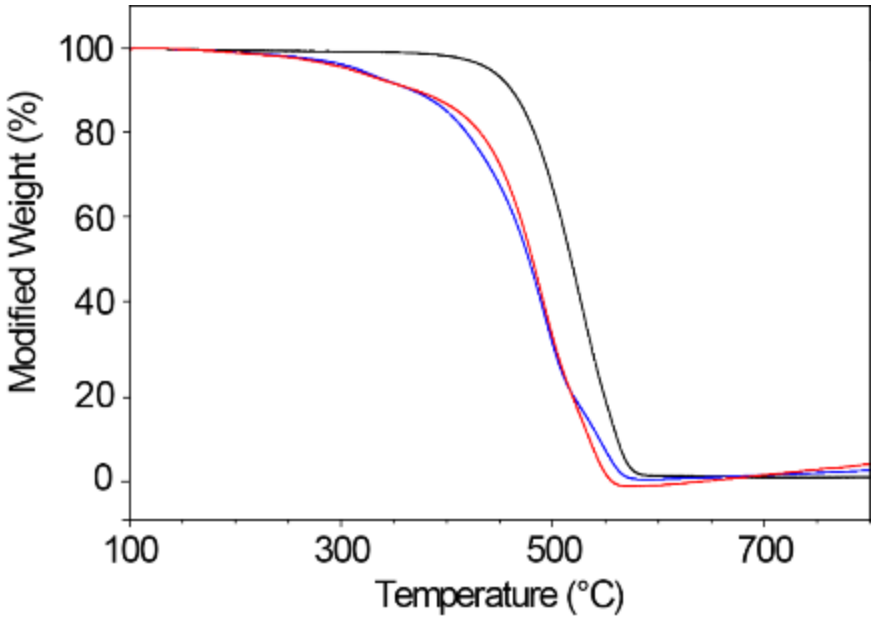


Figure S7. TGA analysis (air, 10 ºC / min) of: 1 (black), linear receptor control experiment (red) and preformed macrocycle **6** control experiment (blue).

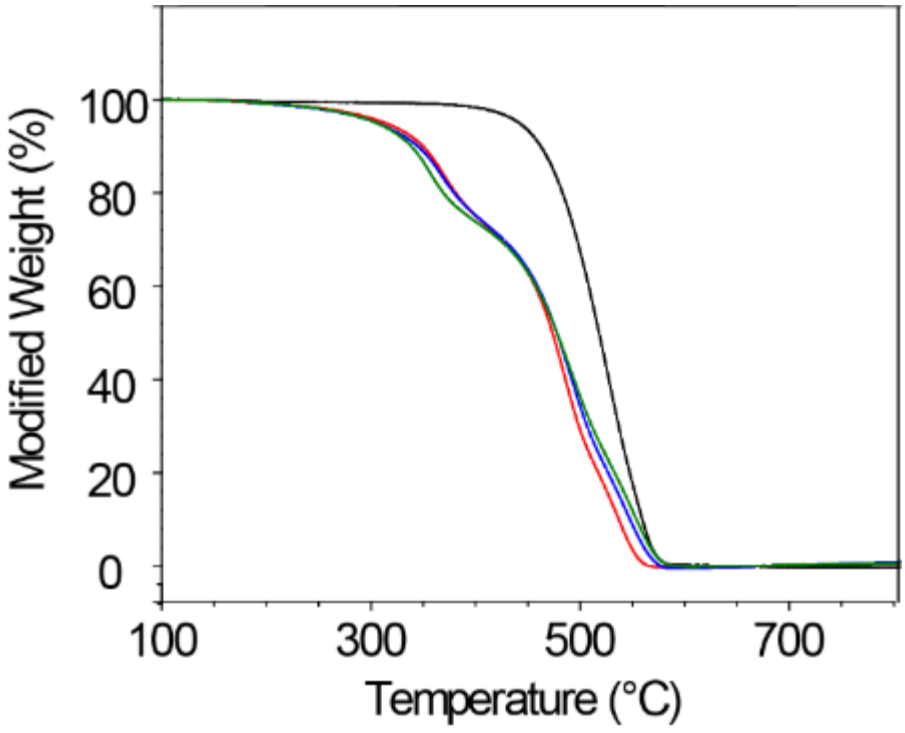


Figure S8. TGA analysis (air, 10ºCmin^{-1}) of pristine (7,6)-enriched SWNTs (black) and the product formed by treatment with **1**, **2** and **3** (blue)(red)(green) and the Grubbs second-generation catalyst in TCE at room temperature for 72 h.

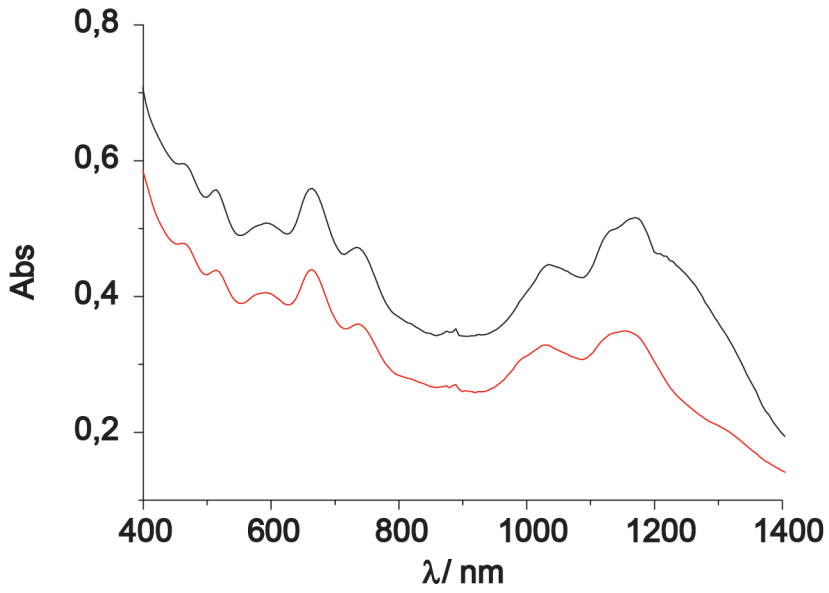


Figure S9. UV/Vis/NIR spectra (D_2O, 1 % sodium dodecyl sulfate (SDS), 298 K) of pristine (7,6)-enriched SWNTs (black) and MINT (7,6)-6(red)

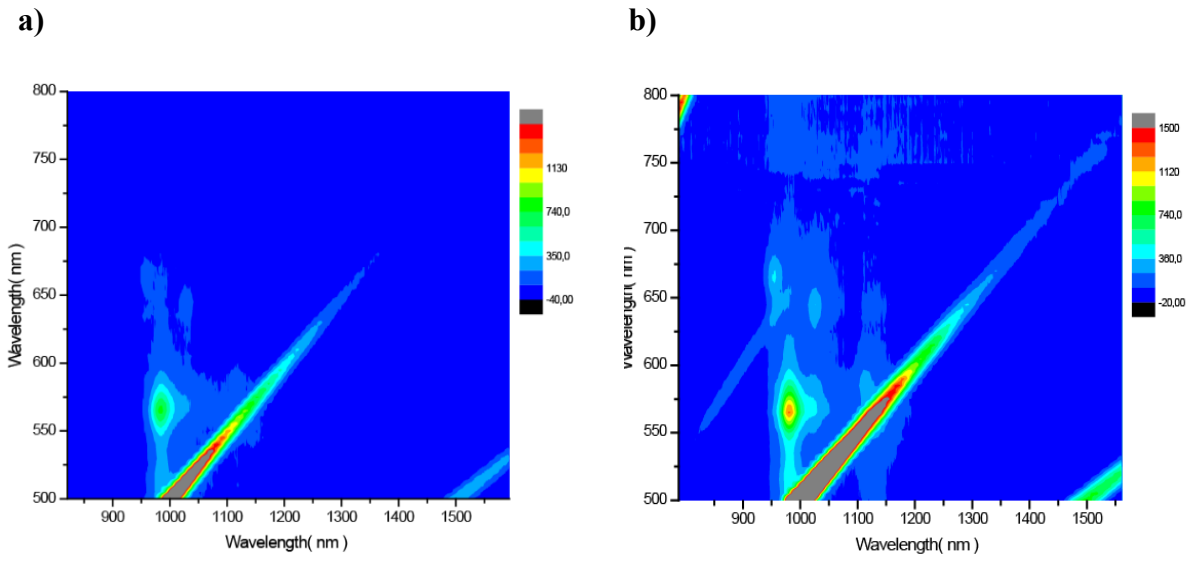


Figure S10. PLE intensity maps (D_2O, 1 % SDS, 298 K) of a) pristine (6,5)-enriched SWNTs and b) MINT(6,5)-6.