

## Inclusion of C<sub>60</sub> Fullerene in a M<sub>3</sub>L<sub>2</sub> Subphthalocyanine Cage

Christian G. Claessens<sup>\*a</sup> and Tomás Torres<sup>\*a</sup>

<sup>a</sup> Universidad Autónoma de Madrid, Departamento de Química Orgánica, Campus de Cantoblanco, Madrid, Spain. Fax: 34 91 497 3966; Tel: 34 91 497 4151; E-mail: [tomas.torres@uam.es](mailto:tomas.torres@uam.es) and [christian.claessens@uam.es](mailto:christian.claessens@uam.es)

---

## SUPPORTING INFORMATION

---

<b>S2</b> .....	General Remarks
<b>S3</b> .....	Compound <b>1</b>
<b>S8</b> .....	Compound <b>2</b> •6PF <sub>6</sub>
<b>S16</b> .....	Complex [C <sub>60</sub> ⊂ <b>2</b> ]•6PF <sub>6</sub>
<b>S21</b> .....	Kinetic study of the interconversion between the diastereoisomers

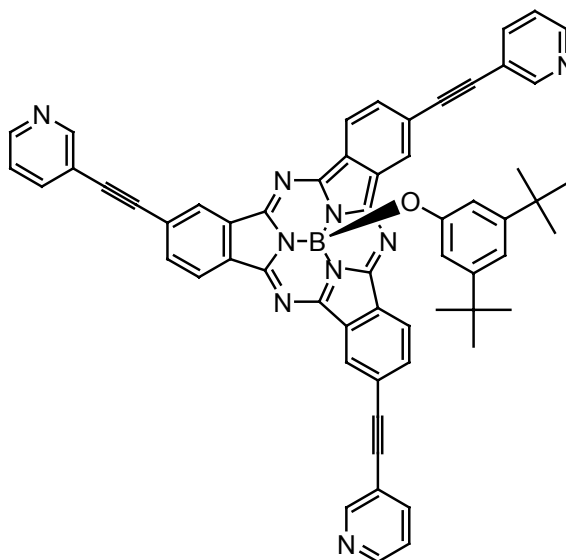
**General Remarks:**

UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. LSI-MS and HRMS spectra were determined on a VG AutoSpec instrument. MALDI-TOF MS were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with a BRUKER AC-300 instrument and a BRUKER DRX-500 instrument. Elemental analyses were performed with a Perkin-Elmer 2400 apparatus. Column chromatographies were carried out on silica gel Merck-60 (230-400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 F<sub>254</sub> (E. Merck). Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification.

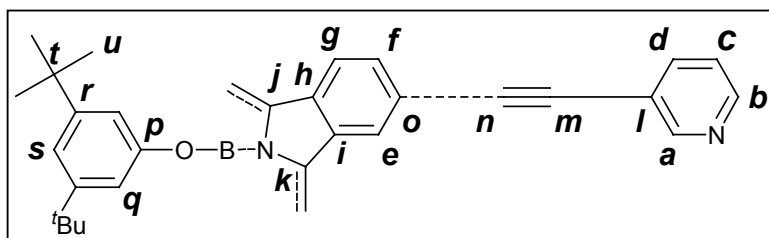
Supplementary data for:

---

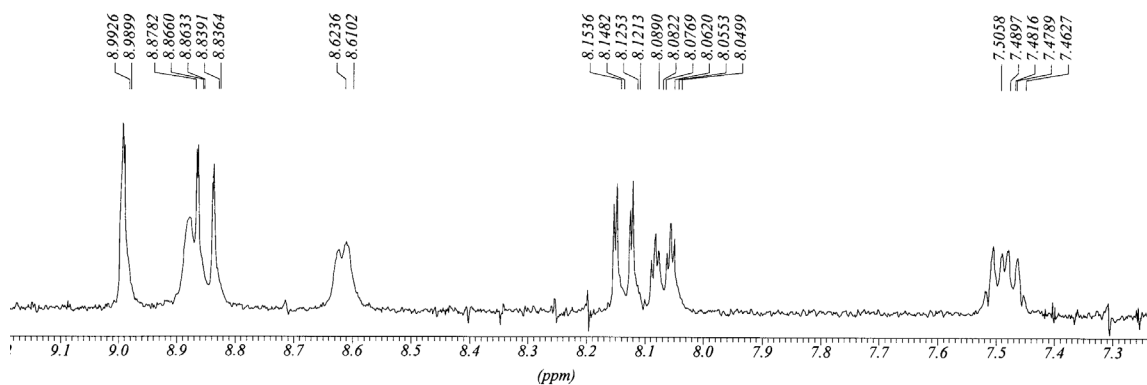
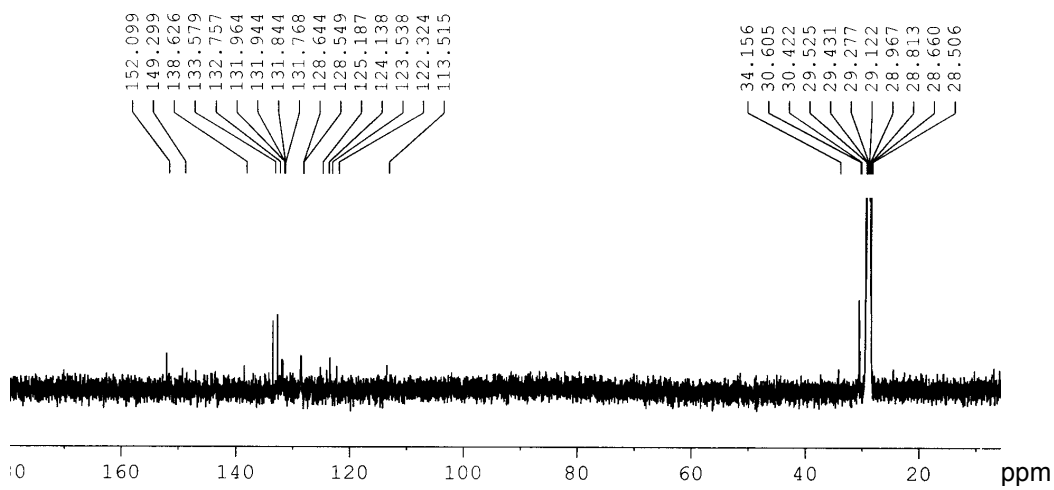
COMPOUND 1



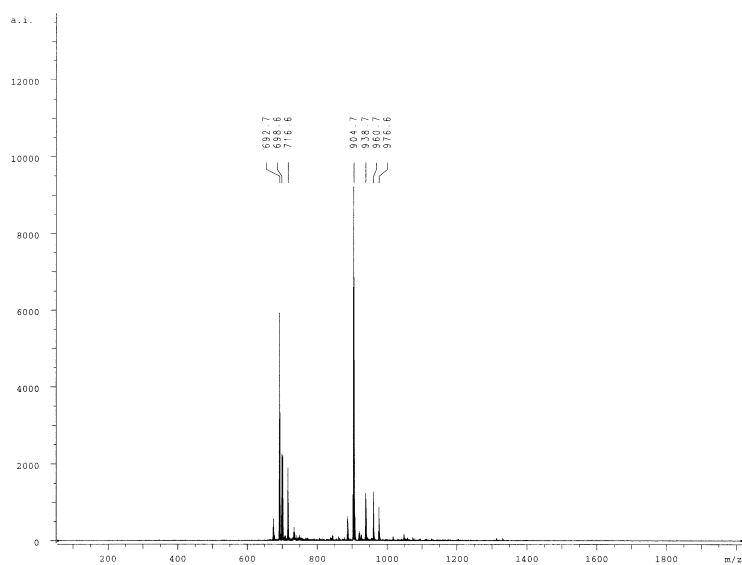
**Compound 1:** Under an argon atmosphere, 3-ethynylpyridine (19 mg, 0.184 mmol) was added to a mixture of triodo-3,5-di-*tert*-butyloxysubphthalocyanine (50 mg, 0.051 mmol), palladiumdiphenylphosphinedichloride (8 mg, 0.011 mmol) and copper iodide (2 mg, 0.011 mmol) in triethylamine (3 mL). The reaction was stirred under argon for 16 h and water (25 mL) was added. The resulting mixture was extracted with diethylether (3 x 10 mL) and the resulting organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the resulting solid was subjected to column chromatography on silica gel using acetone/hexane (3:2) as eluent. After evaporation of the eluent subphthalocyanine **1** was obtained as a purple solid, 32 mg (70%); m.p. > 250°C; <sup>1</sup>H NMR (CD<sub>3</sub>CN, 298 K, 500 MHz):  $\delta$  = 8.99 (br d, <sup>4</sup>J<sub>m</sub> = 1.2 Hz, 3H, **He**), 8.88 (br s, 3H, **Ha**), 8.85 (dd, <sup>3</sup>J<sub>o</sub> = 8.1 Hz, <sup>5</sup>J<sub>p</sub> = 0.8 Hz, 3H, **Hg**), 8.62 (br d, <sup>3</sup>J<sub>o</sub> = 4.8 Hz, 3H, **Hb**), 8.14 (dd, <sup>3</sup>J<sub>o</sub> = 8.1 Hz, <sup>4</sup>J<sub>m</sub> = 1.2 Hz, 3H, **Hf**), 8.07 (ddd, <sup>3</sup>J<sub>o</sub> = 8.1 Hz, <sup>4</sup>J<sub>m</sub> = 2.0 Hz, <sup>4</sup>J<sub>m</sub> = 1.6 Hz, 3H, **Hd**), 7.48 (dd, <sup>3</sup>J<sub>o</sub> = 8.1 Hz, <sup>3</sup>J<sub>o</sub> = 4.8 Hz, 3H, **He**), 6.76 (t, <sup>4</sup>J<sub>m</sub> = 1.6 Hz, 1H, **Hj**), 5.27 (d, <sup>4</sup>J<sub>m</sub> = 1.6 Hz, 2H, **Hk**), 1.04 (s, 18H, **Hw**);



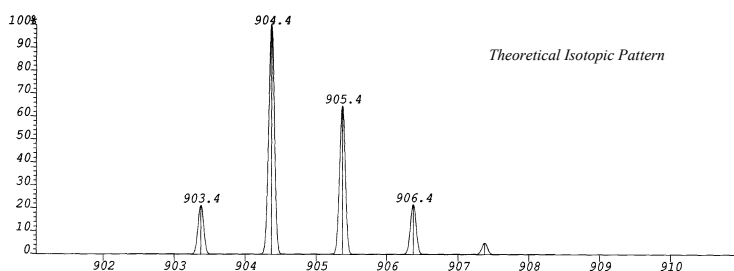
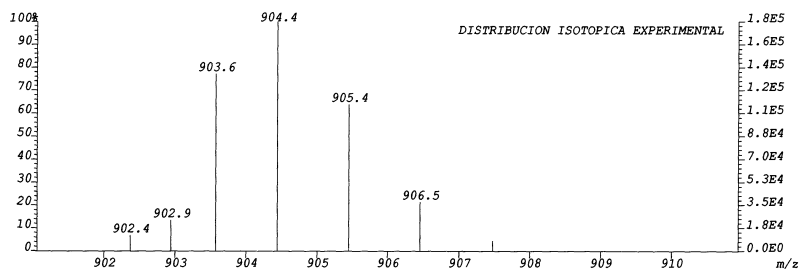
<sup>13</sup>C NMR (CD<sub>3</sub>COCD<sub>3</sub>, 298 K, 125 MHz): only primary carbon atoms  $\delta$  = 152.1 (**Ca**), 149.3 (**Cb**), 138.6 (**Cd**), 133.6 (**Cf**), 132.8 (**Cc**), 125.2 (**Ce**), 122.3 (**Cg**), 114.9 C(**s**), 113.5 (**Cq**), 34.2 (**Ct**), 30.6 (**Cu**) ppm; IR(KBr):  $\nu$  = 2365, 2206, 1618, 1456, 1304, 1263, 1223, 1180, 1065, 891, 837, 810, 756, 702, 635, 538, 444 cm<sup>-1</sup>; UV/Vis (MeCN):  $\lambda_{\max}(\log(\epsilon))$  = 584 (4.8), 570 (sh), 548 (sh), 537 (sh), 350 (4.5), 337 (sh) nm; LSI-MS:  $m/z$ : 904.4 [M+H]<sup>+</sup>, 903.4 [M]<sup>+</sup>, 698.3 [M-3,5-ditertbutylphenoxy]<sup>+</sup>; MALDI-TOF:  $m/z$ : 904.7 [M+H]<sup>+</sup>, 698.6 [M-3,5-ditertbutylphenoxy]<sup>+</sup>. HR-LSIMS calcd for C<sub>59</sub>H<sub>42</sub>N<sub>9</sub>OB: [M]<sup>+</sup>:  $m/z$ : 903.3605, found 903.3649; HR-LSIMS calcd for C<sub>59</sub>H<sub>43</sub>N<sub>9</sub>OB: [M+H]<sup>+</sup>:  $m/z$ : 904.3683, found 904.3694; elemental analysis calcd (%) for C<sub>59</sub>H<sub>42</sub>N<sub>9</sub>OB: C 78.40, H 4.68, N 13.95; found C 77.23, H 4.11, N 14.55.

$^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 300 MHz, 298 K) $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 125 MHz, 298 K)

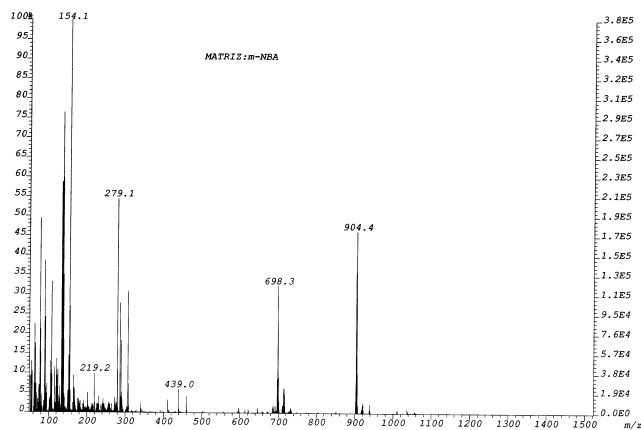
## MALDI-TOF (ditranol)



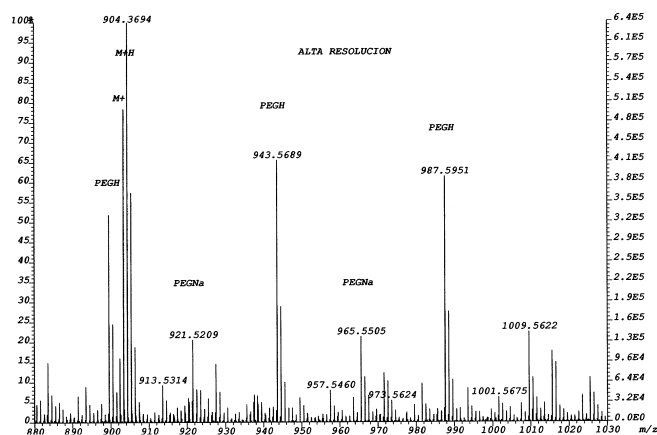
MALDI-TOF (ditranol), Isotopic Pattern



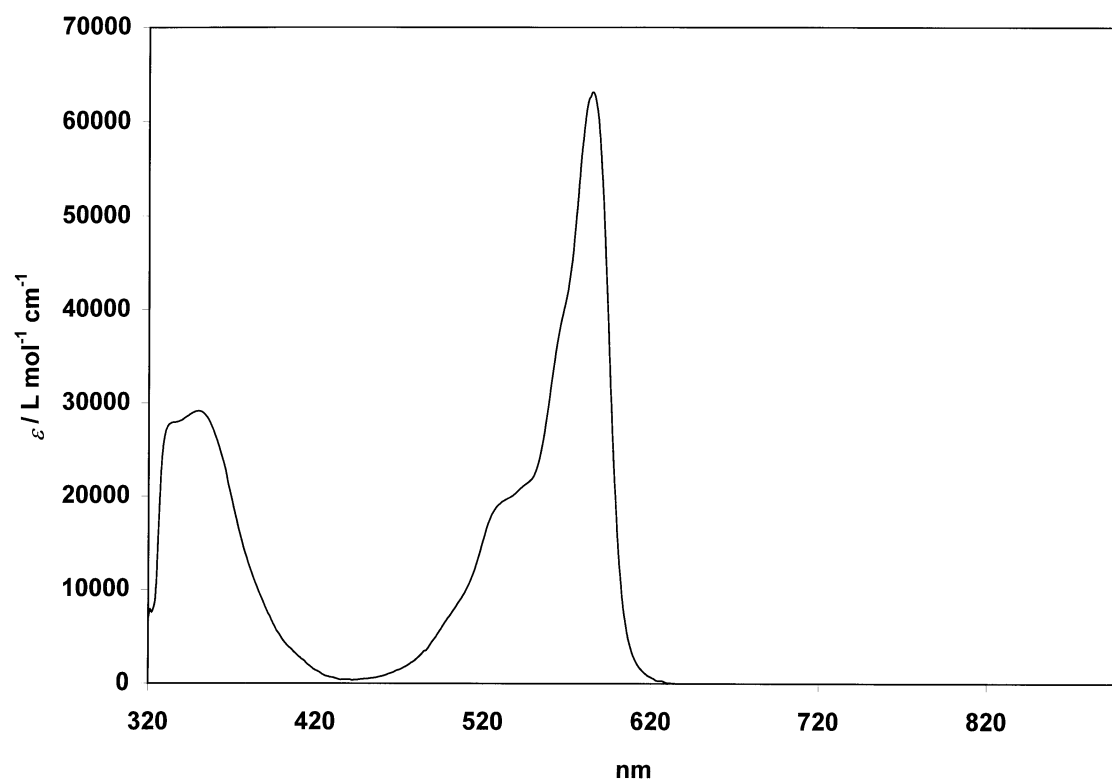
LSI-MS (m-NBA)



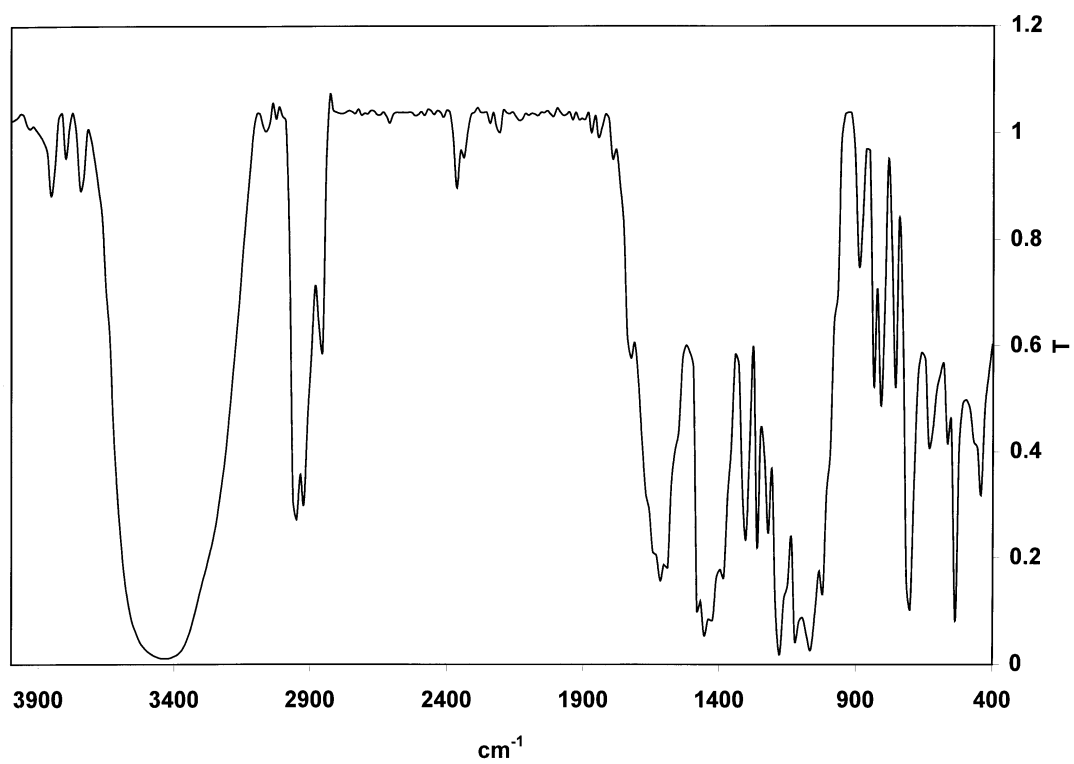
HR-LSI-MS (m-NBA)



UV-Vis (Acetone, 298 K)



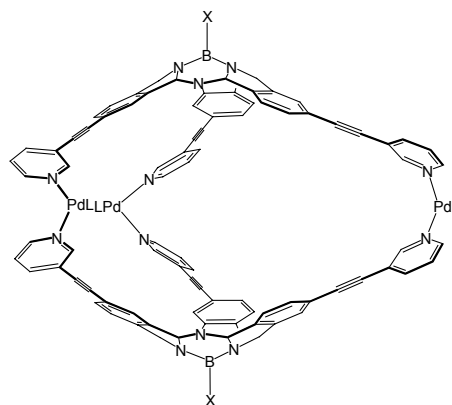
IR (KBr)



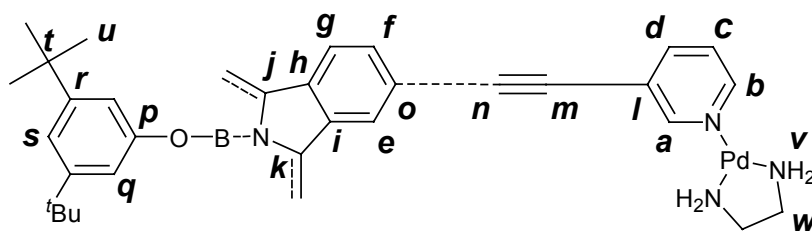
Supplementary data for:

---

**COMPOUND 2•6PF<sub>6</sub>**

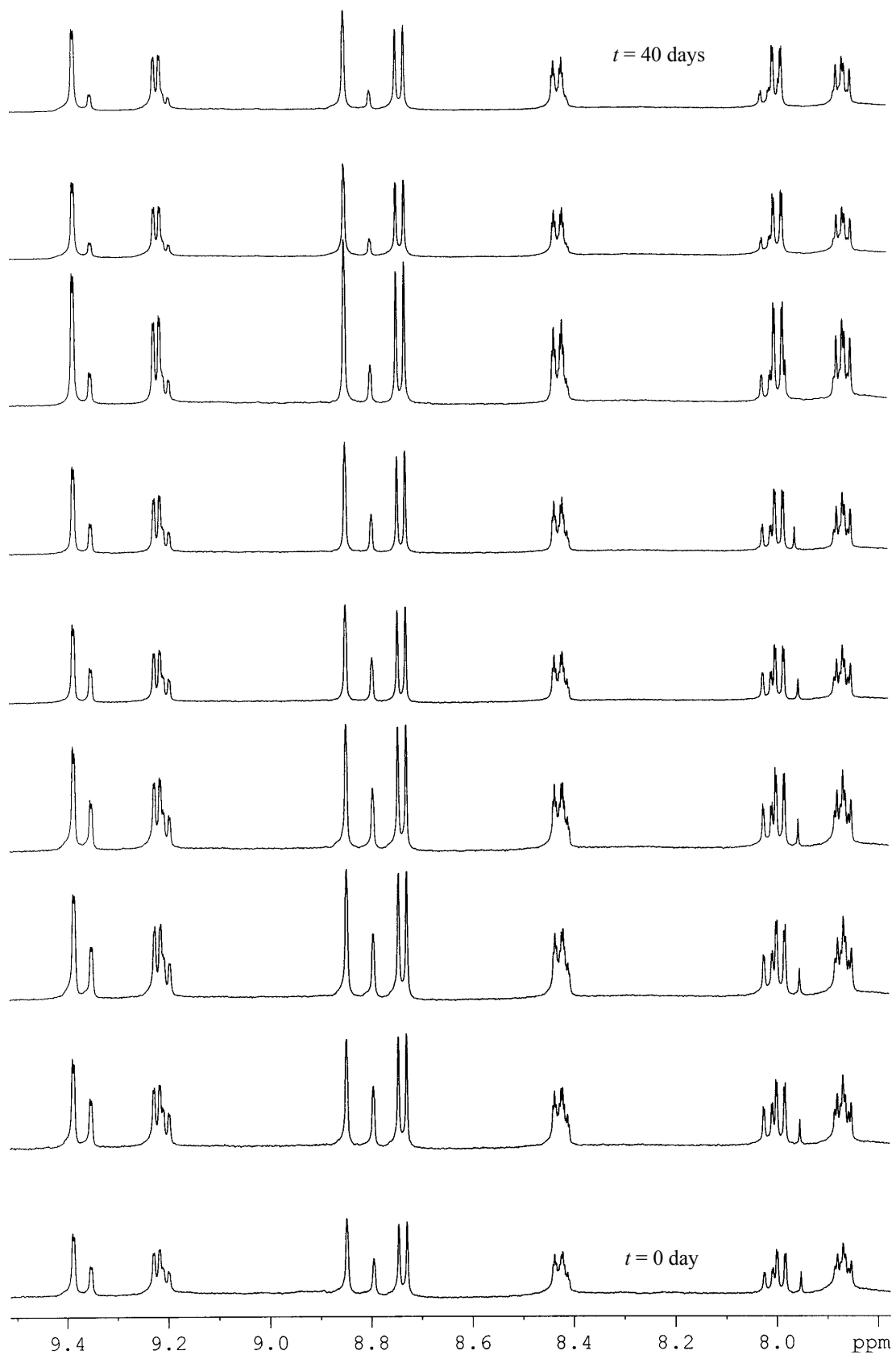


**Cage Compound 2•6PF<sub>6</sub>:** freshly prepared (en)Pd(NO<sub>3</sub>)<sub>2</sub> (10 mg, 0.041 mmol) was added in one portion to a solution of subphthalocyanine **1** (25 mg, 0.028 mmol) in a mixture of water (1 mL), methanol (1 mL) and acetonitrile (1 mL). The resulting solution was stirred at room temperature for 4 h. After evaporation of methanol and acetonitrile, NH<sub>4</sub>PF<sub>6</sub> (30 mg, 0.18 mmol) was added in one portion to the remaining water solution. The resulting **2•6PF<sub>6</sub>** precipitate was filtrated and washed with hexane and water before being collected as a purple powder, 42 mg (94%); m.p. > 250°C;

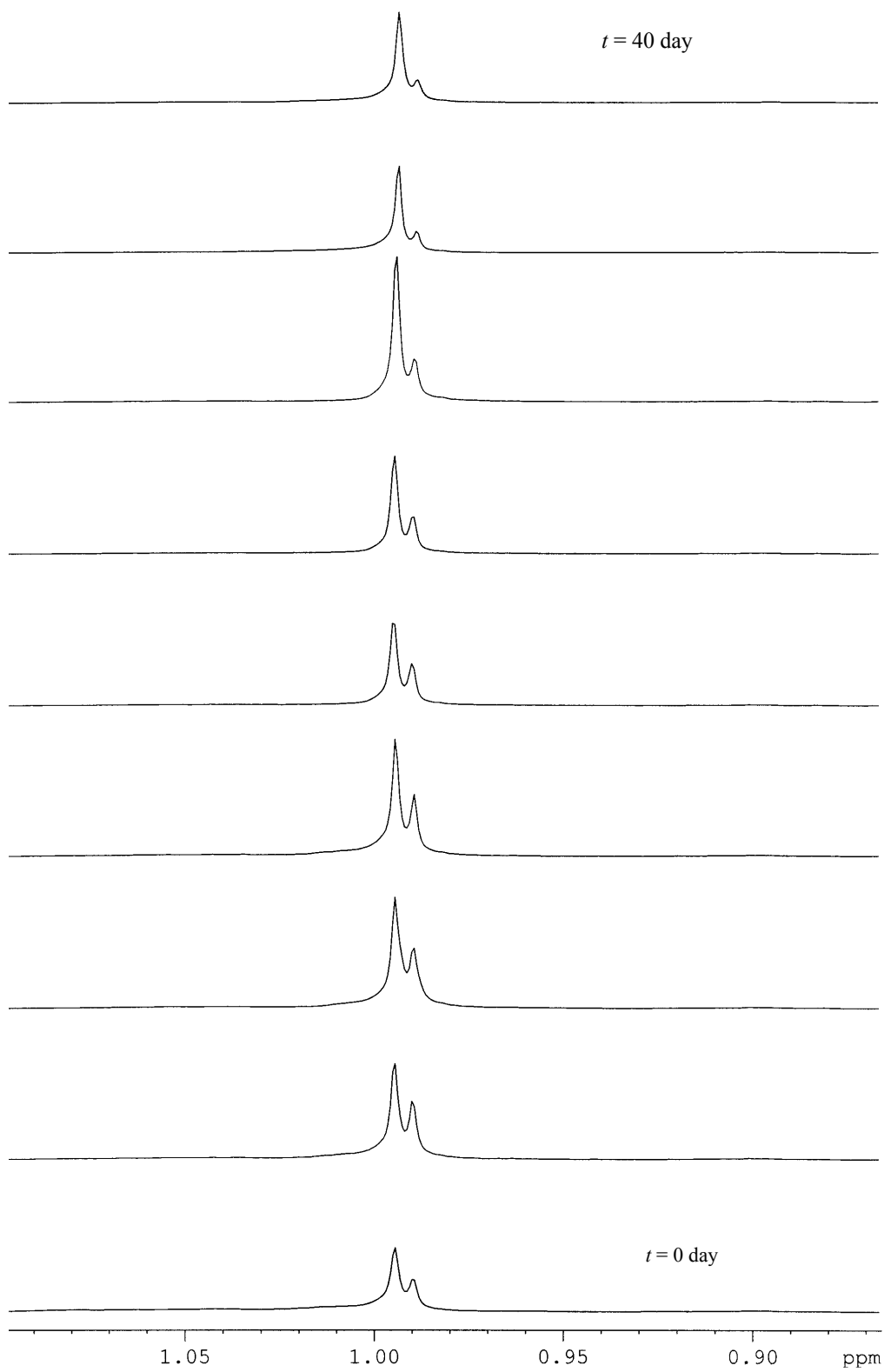


<sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 300 K):  $\delta$  = 9.37 (6H, d,  $J_m$  = 1.6 Hz, **Ha** Isomer 1), 9.33 (6H, d,  $J_m$  = 1.6 Hz, **Ha** Isomer 2), 9.20 (6H, dd,  $J_o$  = 5.7 Hz,  $J_m$  = 1.6 Hz, **Hb** Isomer 1), 9.18 (6H, dd,  $J_o$  = 5.7 Hz,  $J_m$  = 1.6 Hz, **Hb** Isomer 2), 8.83 (6H, dd,  $J_m$  = 1.4 Hz,  $J_p$  = 0.9 Hz, **He**, Isomer 1), 8.78 (6H, dd,  $J_m$  = 1.4 Hz,  $J_p$  = 0.9 Hz, **He**, Isomer 2), 8.72 (6H, dd,  $J_o$  = 8.3 Hz,  $J_p$  = 0.9 Hz, **Hg**, Isomers 1 and 2), 8.41 (6H, ddd,  $J_o$  = 8.0 Hz,  $J_m$  = 1.6 Hz, **Hd**, Isomer 1), 8.40 (6H, ddd,  $J_o$  = 8.0 Hz,  $J_m$  = 1.6 Hz, **Hd**, Isomer 2), 8.00 (6H, dd,  $J_o$  = 8.3 Hz,  $J_m$  = 1.4 Hz, **Hf**, Isomer 2), 7.98 (6H, dd,  $J_o$  = 8.3 Hz,  $J_m$  = 1.4 Hz, **Hf**, Isomer 1), 7.85 (6H, ddd,  $J_o(1)$  = 8.0 Hz,  $J_o(2)$  = 5.7 Hz,  $J_p$  = 0.6 Hz, **Hc**, Isomer 2), 7.84 (6H, ddd,  $J_o^1$  = 8.0 Hz,  $J_o^2$  = 5.7 Hz,  $J_p$  = 0.6 Hz, **Hc**, Isomer 1), 6.71 (2H, t,  $J_m$  = 1.6 Hz, **hs**, Isomers 1 and 2), 5.45-5.40 (12H, m, **Hv**, Isomers 1 and 2), 5.16 (4H, d,  $J_m$  = 1.6 Hz, **Hq**, Isomer 1), 5.15 (4H, d,  $J_m$  = 1.6 Hz, **Hq** Isomer 2), 3.26-3.21 (12H, m, **Hw** Isomers 1 and 2), 0.98 (36H, s, **Hu**, Isomer 1), 0.97 (36H, s, **Hu**, Isomer 2); <sup>13</sup>C NMR (CD<sub>3</sub>CN, 298 K, 125 MHz):  $\delta$  = 154.1 (**Ca**), 151.9, 151.8 (**Cj**, **Ck**, and **Cr** or **Cp**), 151.2 (**Cb**), 151.1 (**Cp** or **Cr**), 143.0 (**Cd**), 132.5 (**Cf**), 130.7, 130.5 (**Ch** and **ci**), 126.8 (**Cc**), 125.5 (**Ce**), 122.9, 122.7 (**Cl** and **Co**), 122.4 (**Cg**), 115.0 (**Cs**), 113.3 (**Cq**), 94.4, 85.7 (**Cn** and **Cm**), 47.5 (**Cw**), 34.1 (**Ct**), 30.9 (**Cu** Isomer 2), 30.5 (**Cu** Isomer 1); IR(KBr):  $\nu$  = 2355, 2222, 1722, 1614, 1479, 1452, 1385, 1304, 1263, 1223, 1182, 1155, 1115, 1074, 1061, 966, 845, 758, 717, 689, 635, 536, 444 cm<sup>-1</sup>; UV/Vis (MeCN):  $\lambda_{max}(\log(\epsilon))$  = 585 (4.8), 570 (sh), 548 (sh), 538 (sh), 349 (4.5), 336 (sh) nm; ESI-MS:  $m/z$ : 1443.0 [**M-2PF<sub>6</sub>**]<sup>2+</sup>, 913.7 [**M-3PF<sub>6</sub>**]<sup>3+</sup>, 649.4 [**M-4PF<sub>6</sub>**]<sup>4+</sup>, 490.2 [**M-5PF<sub>6</sub>**]<sup>5+</sup>, 384.7 [**M-6PF<sub>6</sub>**]<sup>6+</sup>; elemental analysis calcd (%) for C<sub>124</sub>H<sub>66</sub>N<sub>24</sub>O<sub>2</sub>B<sub>2</sub>Pd<sub>3</sub>P<sub>6</sub>F<sub>36</sub>: C 47.51, H 2.12, N 10.72; found C 47.04, H 2.69, N 11.22.

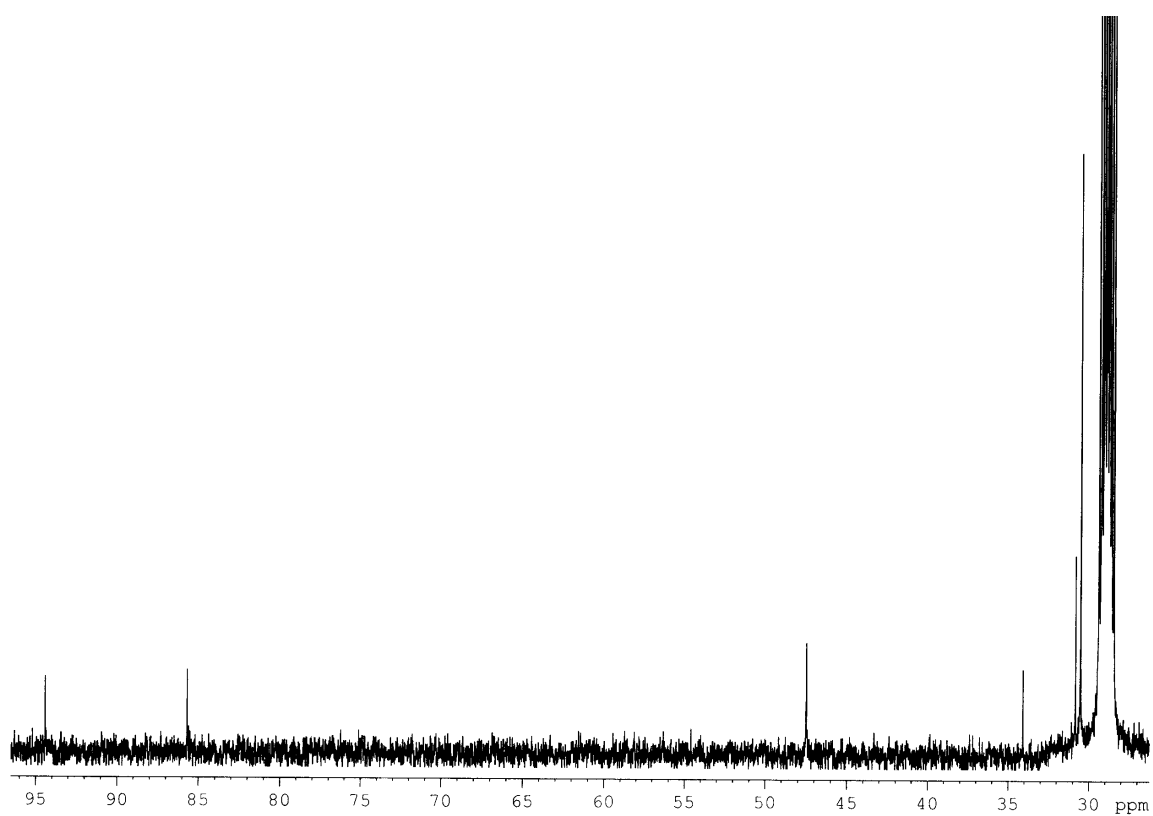
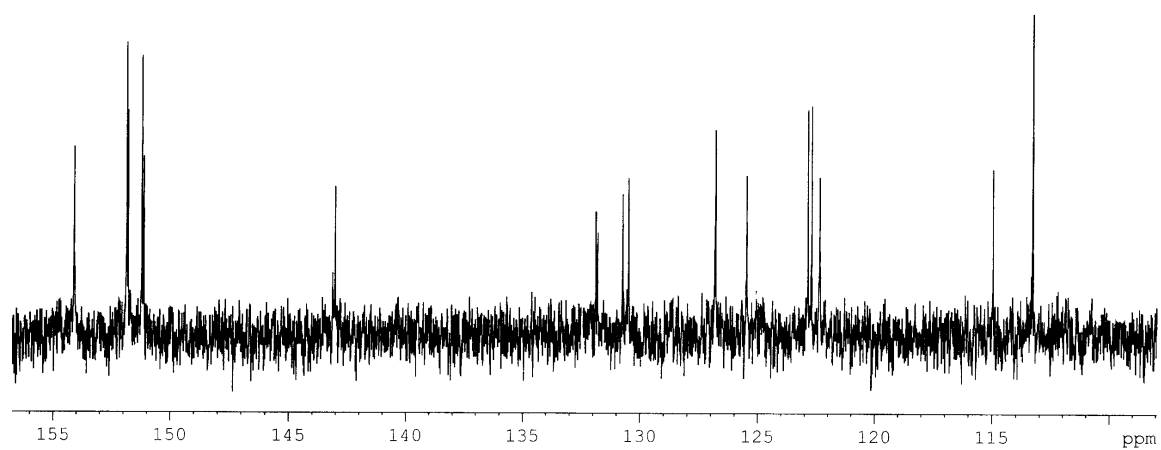
$^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 500 MHz, 298 K)



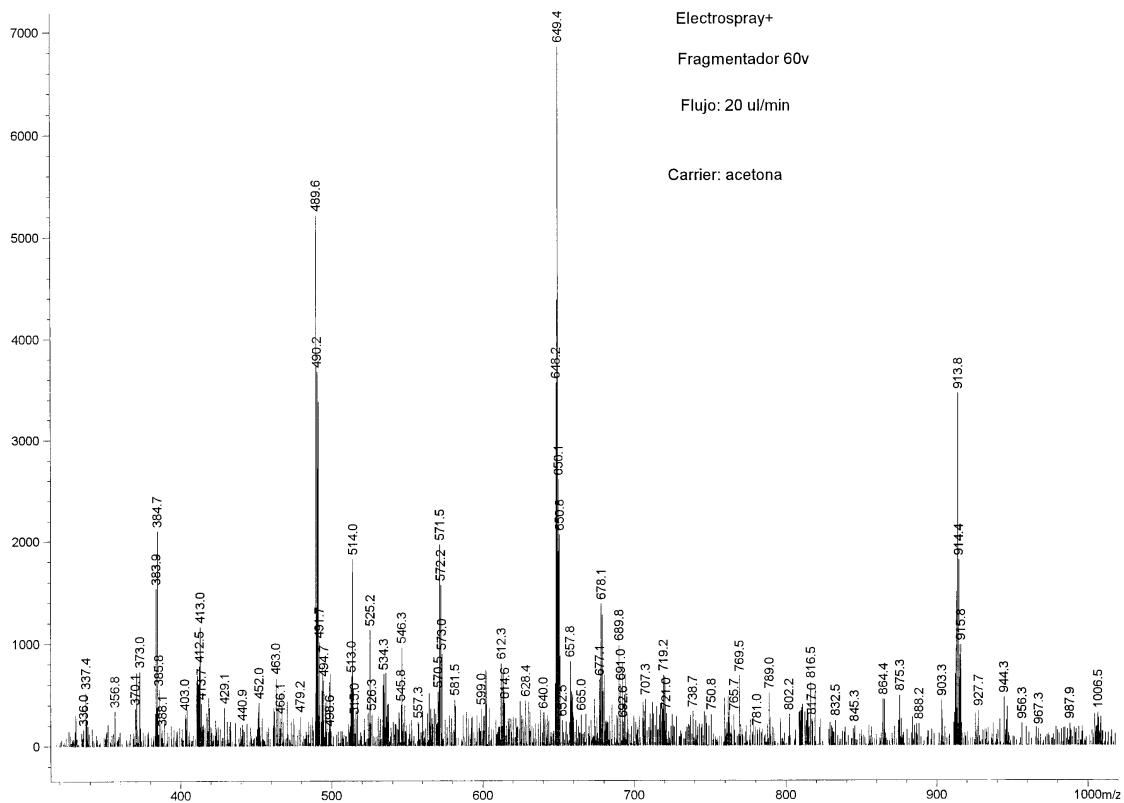




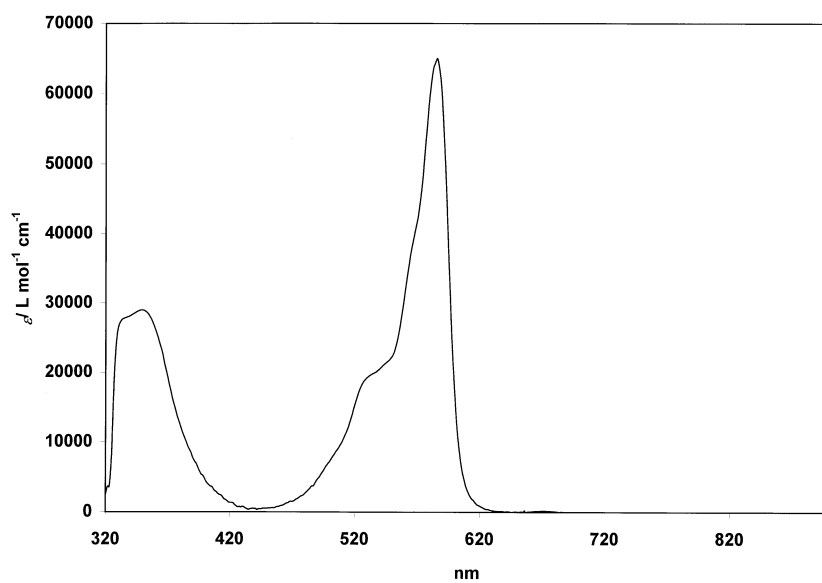
$^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 125 MHz, 298 K)



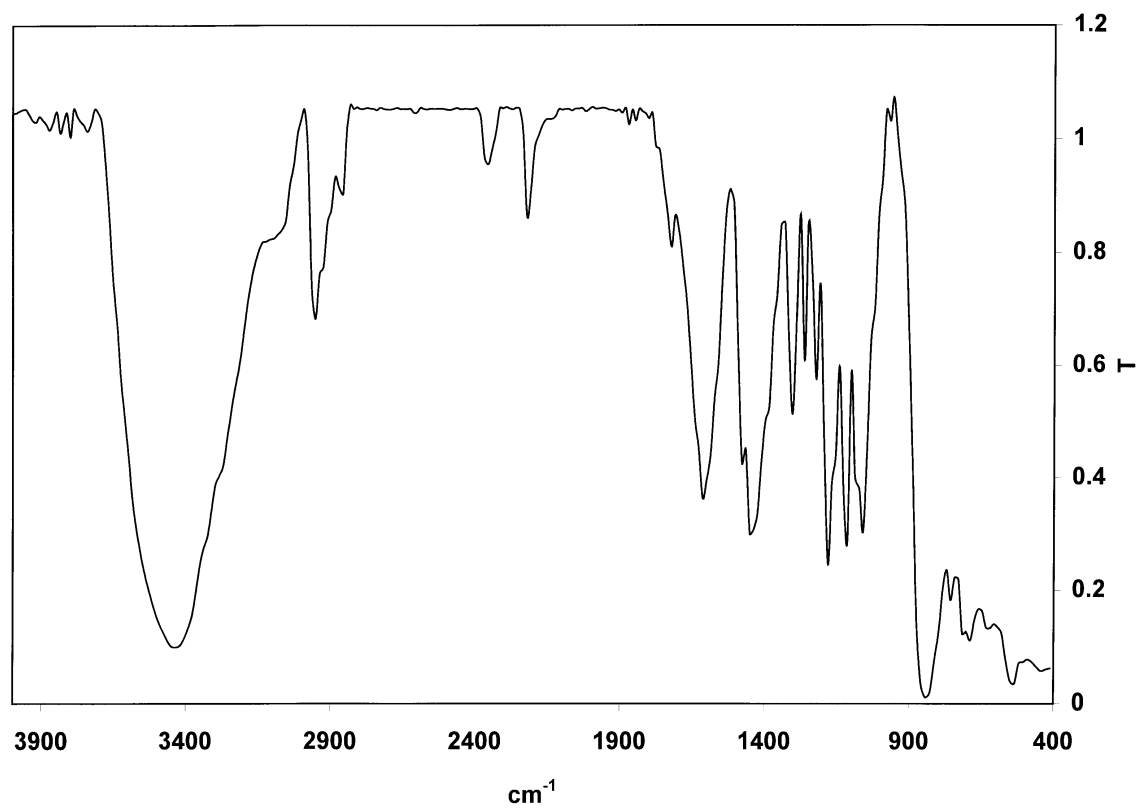
## ESI-MS



## UV-Vis (Acetone, 298 K)



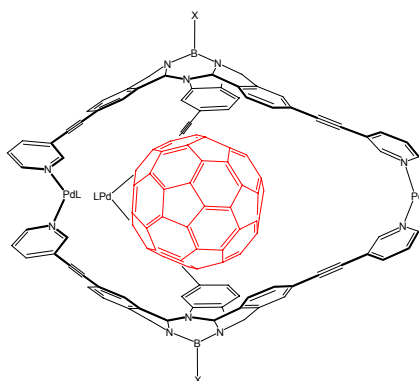
IR (KBr)



Supplementary data for:

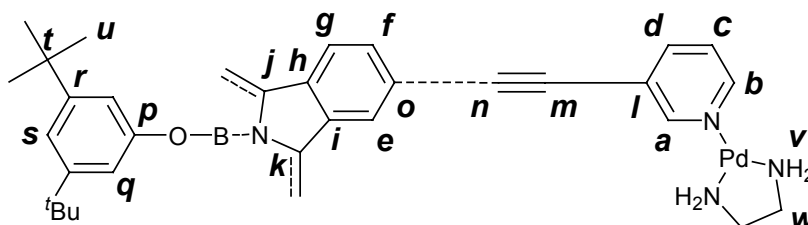
---

COMPOUND  $[C_{60}C_2] \cdot 6PF_6$



### Complex [C<sub>60</sub>⊂2]•6PF<sub>6</sub>:

[C<sub>60</sub>⊂2]•6PF<sub>6</sub> was obtained by mixing 2•6PF<sub>6</sub> and 5 equivalents C<sub>60</sub> in acetone for five minutes at room temperature. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 298 K, 500 MHz): δ = 9.45 (6H, br s, **Ha** Isomer 1), 9.39 (6H, br s, **Ha** Isomer 2), 9.21 (6H, br d, *J*<sub>o</sub> = 5.6 Hz, **Hb** Isomers 1 and 2), 8.85 (6H, br s, **He** Isomer 1), 8.79 (6H, br s, **He** Isomer 1), 8.74 (6H, br d, **Hg** Isomers 1 and 2), 8.42 (6H, br d, *J*<sub>o</sub> = 8.0 Hz, **Hd** Isomer 1), 8.41 (6H, br d, *J*<sub>o</sub> = 8.0 Hz, **Hd** Isomer 2), 8.02-7.97 (6H, m, **Hf** Isomers 1 and 2), 7.85 (6H, br dd, *J*<sub>o</sub><sup>1</sup> = 8.0 Hz, *J*<sub>o</sub><sup>2</sup> = 5.6 Hz, **Hc** isomers 1 and 2), 6.74-6.70 (2H, m, **Hs** Isomers 1 and 2), 5.52-5.42 (12H, m, **Hv** Isomers 1 and 2), 5.19-5.15 (4H, m, **Hq** Isomers 1 and 2), 3.28-3.20 (12H, m, **Hw** Isomers 1 and 2), 0.98 (36H, br s, **Hu** Isomers 1 and 2).



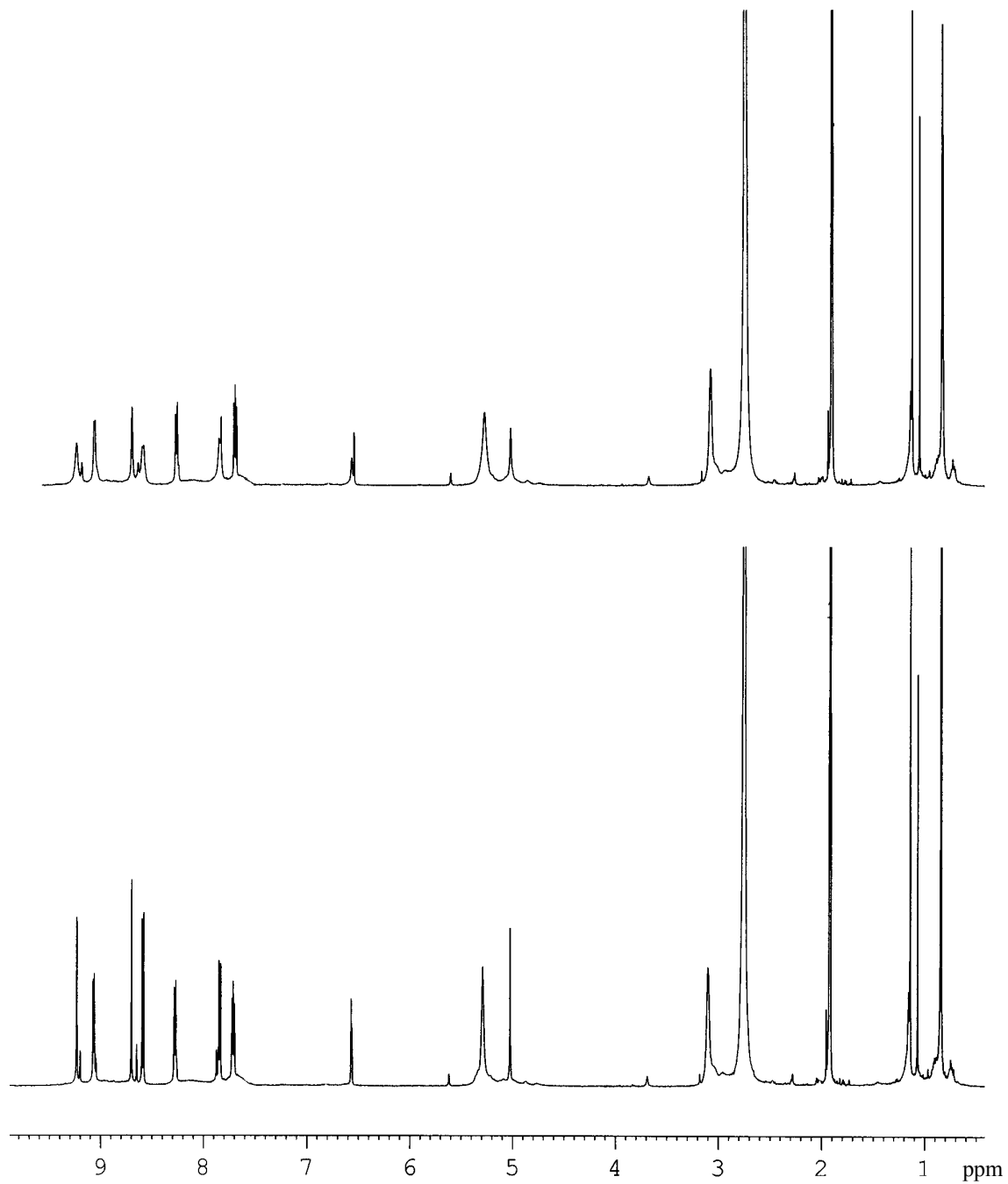
<sup>13</sup>C NMR (CD<sub>3</sub>CN, 298 K, 125 MHz): δ = 154.1 (**Ca**), 151.9 (**Cr** or **Cp**), 151.8-151.4 (br **Cj** and **Ck**), 151.3 (**Cb**), 151.2 (**Ct** or **Cu**), 143.1 (**Cd**), 140.1 (C<sub>60</sub>), 131.0-130.7 (br **Cp** and **Cq**), 126.9 (**Cc**), 122.7 (**Cl** and **Co**), 114.9 (**Cj**), 113.4 (**Ck**), 94.3, 85.9 (**Cm** or **Cn**), 47.5 (**Cl**), 34.1 (**Cv**), 30.8 (**Cw** Isomer 2), 30.5 (**Cw** Isomer 1). IR(KBr): ν = 2361, 2334, 2226, 1688, 1620, 1593, 1485, 1458, 1431, 1391, 1364, 1296, 1256, 1229, 1188, 1121, 1080, 1067, 974, 843, 758, 704, 690, 636, 555, 528, 434 cm<sup>-1</sup>; UV/Vis (MeCN): λ<sub>max</sub>(log(ε)) = 584 (4.8), 569 (sh), 548 (sh), 537 (sh), 349 (4.5), 336 (sh) nm; ESI-MS: *m/z*: 1154.8 [M-3PF<sub>6</sub>]<sup>3+</sup>, 829.7 [M-4PF<sub>6</sub>]<sup>4+</sup>, 634.5 [M-5PF<sub>6</sub>]<sup>5+</sup>, 634.5 [M-6PF<sub>6</sub>]<sup>6+</sup>, additional peaks: 649.8 [free cage-4PF<sub>6</sub>]<sup>4+</sup>.

### Blank experiment with pure C<sub>60</sub>:

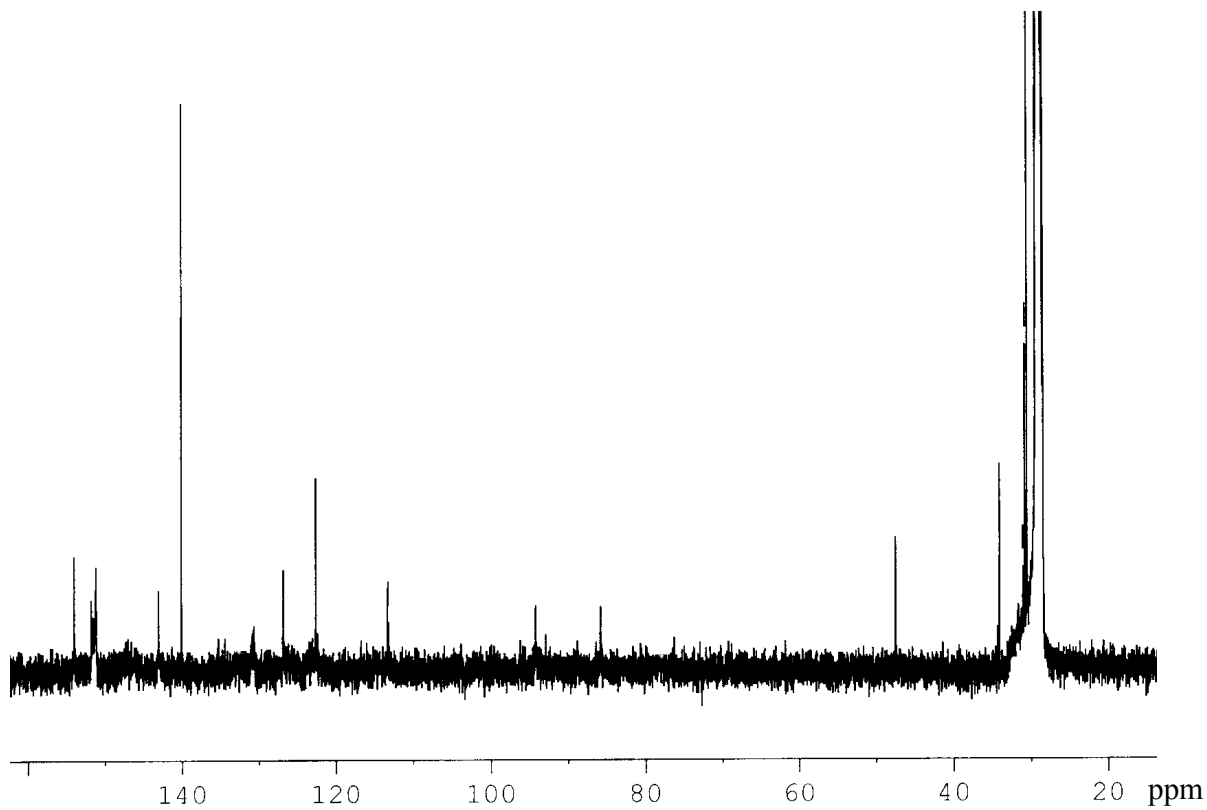
5 mg of pure C<sub>60</sub> were introduced in 0.5 ml of *d*<sub>6</sub>-acetone in an NMR tube, the <sup>13</sup>C NMR spectrum of this C<sub>60</sub> heterogeneous solution was run in the same conditions of acquisition time and relaxation time as the other experiments performed with the pure cage and with the complex and no C<sub>60</sub> signal could be observed: C<sub>60</sub> remained as a dark powder at the bottom of the NMR tube (C<sub>60</sub> is virtually not soluble in *d*<sub>6</sub>-acetone (1 μg/ml<sup>[1]</sup>)).

<sup>1</sup> R. S. Ruoff, D. S. Tse, R. Malhotra and D. C. Lorents, *J. Phys. Chem.*, 1993, **97**, 3379.

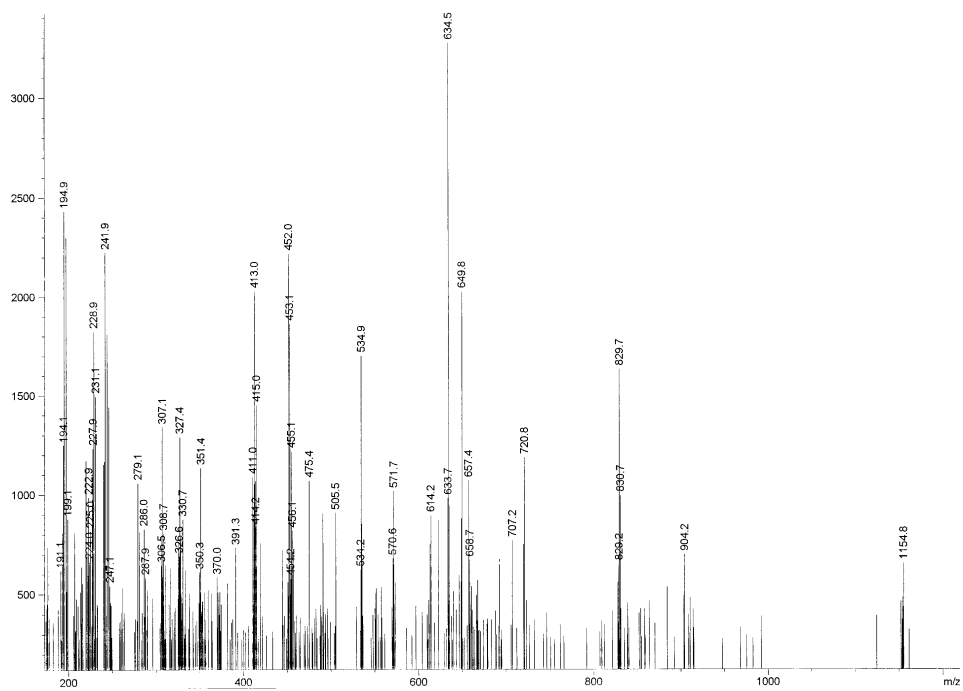
$^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 500 MHz, 298 K)



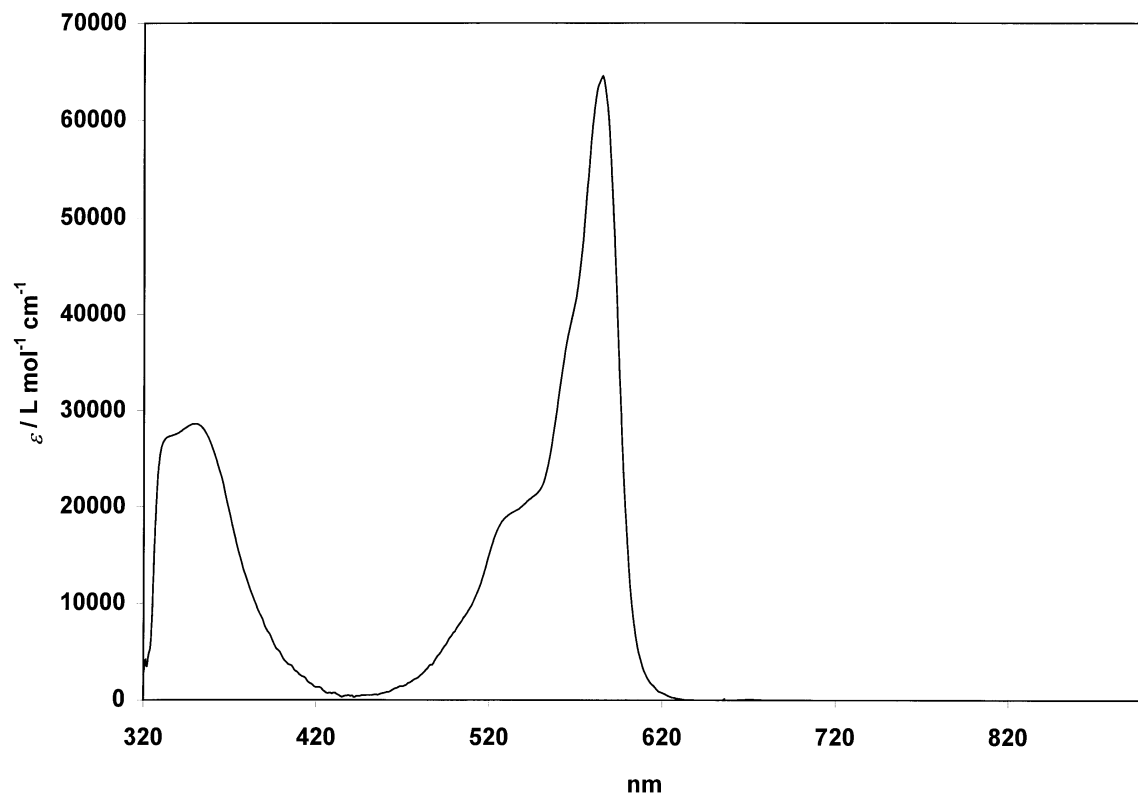
$^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 125 MHz, 298 K)



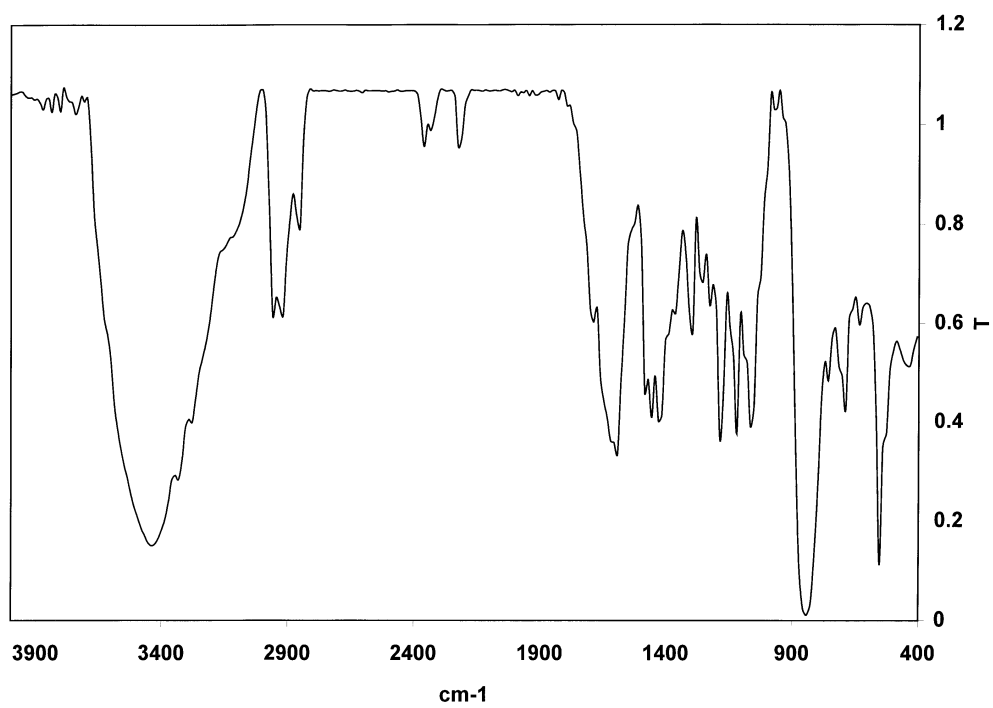
ESI-MS



UV-Vis (Acetone, 298 K)

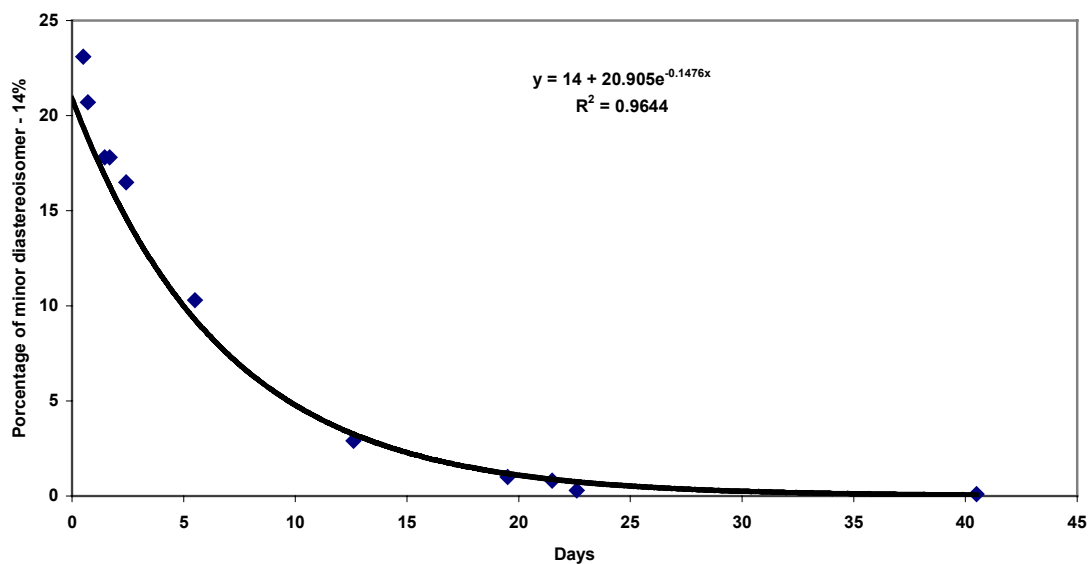


IR (KBr)

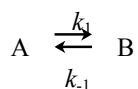


### Kinetic study of the interconversion between the diastereoisomers

Single points were obtained by integration of the relevant peaks in the  $^1\text{H}$  NMR spectra.



#### Basic Kinetic Equations:



$[A] + [B] = [C]_0$  at all times.

$$[A] = \frac{[C]_0}{\left(1 + \frac{k_1}{k_{-1}}\right)} - \left[ \frac{[C]_0}{\left(1 + \frac{k_1}{k_{-1}}\right)} - [A]_0 \right] e^{-(k_1 + k_{-1})t}$$

$$[A]_{eq} = \frac{[C]_0}{\left(1 + \frac{k_1}{k_{-1}}\right)}$$