

# Supporting information

## Acyl Radical Reactions in Fullerene Chemistry: Direct Acylation of [60]Fullerene through an Efficient Decatungstate-Photomediated Approach.

*Manolis D. Tzirakis and Michael Orfanopoulos\**

Department of Chemistry, University of Crete, 71003 Voutes, Heraklion, Crete, Greece

E-mail: orfanop@chemistry.uoc.gr

### Table of Contents

1.	General Considerations.....	S2
2.	General Procedure for the TBADT-Catalyzed Photochemical Reactions of Aldehydes <b>1–14</b> with C <sub>60</sub> .....	S3
3.	Synthetic Procedure of <i>trans</i> -2-Phenylcyclopropanecarboxaldehyde ( <b>14</b> ) .....	S4
4.	Synthetic Procedure and Spectral Data of 4-Methoxybenzaldehyde- <i>d</i> <sub>4</sub> ( <b>3-d</b> <sub>4</sub> ) .....	S4
5.	Synthetic Procedure and Spectral Data of Benzene-1,4-dicarboxaldehyde- <i>d</i> <sub>1</sub> ( <b>4-d</b> <sub>1</sub> ) .....	S5
6.	Spectral Data of Functionalized Fullerenes <b>1a–11a, 13a–14a, 9b–12b</b> .....	S7
7.	<sup>1</sup> H, <sup>13</sup> C NMR, FT-IR, UV-vis Spectra of Functionalized Fullerenes <b>1a–11a, 13a–14a, 9b–12b</b> ....	S22
8.	<sup>1</sup> H and <sup>13</sup> C NMR Spectra of Methyl 4-methoxybenzoate- <i>d</i> <sub>3</sub> .....	S57
9.	<sup>1</sup> H and <sup>13</sup> C NMR Spectra of 4-Methoxybenzyl alcohol- <i>d</i> <sub>5</sub> .....	S58
10.	<sup>1</sup> H and <sup>13</sup> C NMR Spectra of 4-Methoxybenzaldehyde- <i>d</i> <sub>4</sub> ( <b>3-d</b> <sub>4</sub> ).....	S59
11.	<sup>1</sup> H and <sup>13</sup> C NMR Spectra of 1,4-Benzenedimethanol- <i>d</i> <sub>2</sub> .....	S60
12.	<sup>1</sup> H and <sup>13</sup> C NMR Spectra of Benzene-1,4-dicarboxaldehyde- <i>d</i> <sub>1</sub> ( <b>4-d</b> <sub>1</sub> ).....	S61
13.	<sup>1</sup> H NMR Spectrum and GC Chromatogram of Equimolar Mixture of <b>3-d</b> <sub>0</sub> / <b>3-d</b> <sub>4</sub> .....	S62
14.	Procedure and <sup>1</sup> H NMR Spectrum of the Reaction of C <sub>60</sub> with Valeraldehyde <b>6</b> in the Presence of D <sub>2</sub> O .....	S63
15.	<sup>1</sup> H NMR Spectrum of the Reaction of C <sub>60</sub> with <b>3-d</b> <sub>0</sub> / <b>3-d</b> <sub>4</sub> .....	S64
16.	<sup>1</sup> H NMR Spectrum of the Reaction of C <sub>60</sub> with <b>4-d</b> <sub>1</sub> .....	S65

## **1. General Considerations**

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. Tetrabutylammonium Decatungstate (TBADT) was prepared according to procedure reported in the literature.<sup>1</sup>

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker AMX-500 MHz (125 MHz for <sup>13</sup>C) and DPX-300 MHz (75 MHz for <sup>13</sup>C) spectrometers, in CDCl<sub>3</sub>, CDCl<sub>3</sub>/CS<sub>2</sub> or ODCB-d<sub>4</sub> solutions. Chemical shifts are reported in ppm downfield from Me<sub>4</sub>Si, by using the residual solvent peak as internal standard. FT-IR spectra were recorded on a PerkinElmer Fourier transform infrared spectrometer, using KBr pellets. UV-vis spectra were performed on a Shimadzu MultiSpec-1501 UV/Visible spectrometer. HPLC analysis was conducted on a Marathon III instrument equipped with a 5C18-MS (4.6 × 250 mm, Nacalai Tesque) reversed phase column with detection at 310 nm. A mixture of toluene/acetonitrile (1:1 v/v) was used as eluent at 1 mL/min flow rate. Semi-preparative HPLC was performed with a Marathon III instrument equipped with a Cosmosil 5PBB column (10 × 250 mm, Nacalai Tesque) with detection at 310 nm. A mixture of toluene/acetonitrile (4:1 v/v) was used as eluent (unless otherwise noted) at 5 mL/min flow rate. Flash column chromatography was carried out on SiO<sub>2</sub> (silica gel 60, SDS, 230-400 mesh ASTM). Evaporation of the solvents was accomplished with a rotary evaporator or by high vacuum distillation. Negative-ion MALDI spectra were recorded for all the new compounds using DCTB as the matrix. GC-MS analysis was performed on a Shimadzu GC MS-QP5050A apparatus equipped with a Supelco capillary column (MDN-5, 30m × 0.25mm, 0.25μm film thickness) and a 5971A MS detector. Photochemical reactions were carried out by using a 300-W xenon lamp as the light source.

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<sup>1</sup> See reference 7b.

## 2. General Procedure for the TBADT-Catalyzed Photochemical Reactions of Aldehydes 1–14 with C<sub>60</sub>

Unless otherwise noted in the individual procedures below, a solution of C<sub>60</sub> (20 mg, 0.028 mmol) in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL) was added in a 150-mL glass flask containing a magnetic stirring bar. This solution was degassed by performing three freeze-pump-thaw cycles under argon, and then TBADT (18.5 mg, 0.0056 mmol) and the aldehyde substrate (2.7 mmol) were added. The resulting solution was serum capped and purged for 20 min with argon. This solution was subsequently irradiated at 5–10 °C using an ice water bath, while a constant, slow argon stream was maintained over the solution (the progress of all reactions was monitored by HPLC). Then, the solvent and the aldehyde **1–14** were distilled from the reaction mixture under reduced pressure, and the remaining crude product was centrifuged three times with acetonitrile HPLC grade. The isolated product was further purified by flash column chromatography (eluent: hexane/toluene 4:1 v/v) and/or semi-preparative HPLC (eluent: toluene/acetonitrile 4:1 v/v, 5 mL/min flow rate, detection at 310 nm) to afford the fullerene adducts **1a–11a, 13a–14a** and **9b–12b**, along with a small amount of a complex mixture of several unidentified byproducts.

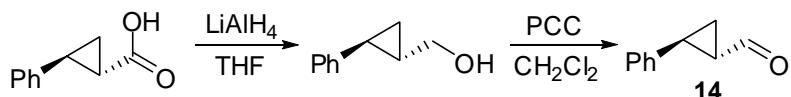
During the purification procedure, we noticed that adducts **1–5** were almost quantitatively converted into the hydrogenated fullerene adduct C<sub>60</sub>H<sub>2</sub> when treated with silica or alumina gel.<sup>2</sup> Thus, adducts **1a–5a** were purified with semi-preparative HPLC (eluent: toluene/acetonitrile 4:1 v/v, 5 mL/min flow rate, detection at 310 nm).

Blank experiments in the absence of TBADT showed that a small but considerable amount of the corresponding fullerene adducts could be formed, in the reaction of aromatic aldehydes **1–4** with C<sub>60</sub>. This result should be rationalized on the H-atom abstraction ability of the excited triplet state (n-π\*) of the carbonyl group in benzaldehydes.

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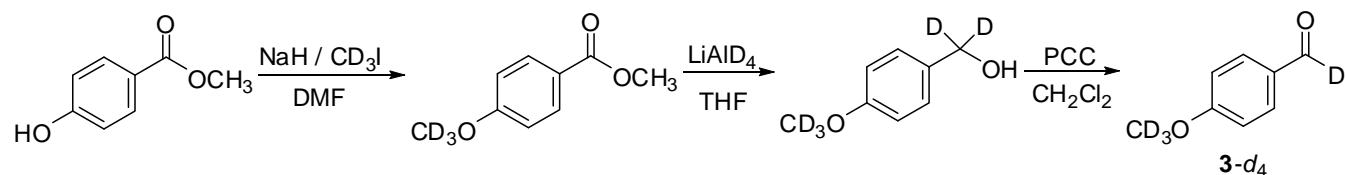
<sup>2</sup> C<sub>60</sub>H<sub>2</sub>: IR (KBr): ν (cm<sup>-1</sup>) = 2954, 1427, 1263, 1183, 1041, 577, 566, 550, 527; UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub> (nm) = 257, 328, 405, 433; MS (MALDI, negative, DCTB): m/z 722; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>): δ 7.00 (s, 1H); See also reference 15.

### 3. Synthetic Procedure of *trans*-2-Phenylcyclopropanecarboxaldehyde (**14**)



*trans*-2-Phenylcyclopropanecarboxaldehyde (**14**) was prepared following the reported procedure.<sup>3</sup> *trans*-2-Phenylcyclopropanecarboxylic acid was reduced with lithium aluminum hydride in THF to give the corresponding alcohol which was subsequently oxidized using PCC to afford *trans*-2-phenylcyclopropanecarboxaldehyde.

### 4. Synthetic Procedure and Spectral Data of 4-Methoxybenzaldehyde-*d*<sub>4</sub> (**3-d**<sub>4</sub>)



**Methyl 4-methoxybenzoate-*d*<sub>3</sub>.** Methyl 4-hydroxybenzoate (1.00 g, 6.57 mmol) was dissolved in 12 mL of dry DMF, under an Ar atmosphere. The solution was cooled to 0 °C and 315 mg (7.88 mmol) of NaH (60% in mineral oil) was added. The mixture was stirred at room temperature for 30 min and 0.9 mL of CD<sub>3</sub>I was added at 0 °C. Stirring was continued at room temperature for 30 min and then Et<sub>2</sub>O (30 mL) was added to the reaction mixture. The mixture was washed three times with brine, dried over MgSO<sub>4</sub> and concentrated *in vacuo* to afford the desired methyl 4-methoxybenzoate-*d*<sub>3</sub> (1.00 gr, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.99 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 3.88 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 166.60, 163.23, 131.43, 122.44, 113.44, 54.36 (Heptaplet, *J*<sub>C-D</sub> = 22 Hz), 51.59; MS: m/z = 169 (M-31, 138).

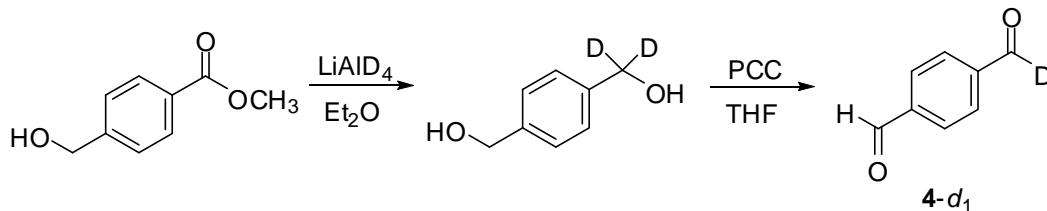
**4-Methoxybenzyl alcohol-*d*<sub>5</sub>.** To a solution of methyl 4-methoxybenzoate-*d*<sub>3</sub> (1.00 g, 5.91 mmol) in anhydrous THF (60 mL) under an Ar atmosphere at 0 °C, was added lithium aluminum deuteride LiAlD<sub>4</sub> (126 mg, 3 mmol). The reaction was then warmed to room temperature and stirred for 90 min. The mixture

<sup>3</sup> Baldwin, J. E.; Patapoff, T. W.; Barden, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1421–1426.

was treated with H<sub>2</sub>O and 10% NaOH, and extracted twice with Et<sub>2</sub>O. The layers were separated and the organic phase dried (MgSO<sub>4</sub>) and concentrated *in vacuo* to afford the desired 4-methoxybenzyl alcohol-*d*<sub>5</sub> (762 mg, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 158.64, 132.94, 128.33, 113.49, 63.27 (pentaplet, *J*<sub>C-D</sub> = 21.5 Hz), 54.04 (heptaplet, *J*<sub>C-D</sub> = 21.75 Hz); MS: m/z = 143 (M–30, 113).

**4-Methoxybenzaldehyde-*d*<sub>4</sub> (3-*d*<sub>4</sub>).** 4-Methoxybenzyl alcohol-*d*<sub>5</sub> (600 mg, 4.2 mmol) was oxidized to 4-methoxybenzaldehyde-*d*<sub>4</sub> (3-*d*<sub>4</sub>) with PCC (1.08 g, 5.0 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at room temperature (3–4 hours), under an Ar atmosphere. The reaction mixture was filtered through a plug of Celite - Silica gel to afford 4-methoxybenzaldehyde-*d*<sub>4</sub> (3-*d*<sub>4</sub>) (530 mg, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 189.92 (t, *J*<sub>C-D</sub> = 26.25 Hz), 164.20, 131.45, 129.47 (t, *J*<sub>C-D</sub> = 3.37 Hz), 113.90, 54.30 (Heptaplet, *J*<sub>C-D</sub> = 22 Hz); MS: m/z = 138 (M–60, 78).

## 5. Synthetic Procedure and Spectral Data of Benzene-1,4-dicarboxaldehyde-*d*<sub>1</sub> (4-*d*<sub>1</sub>)

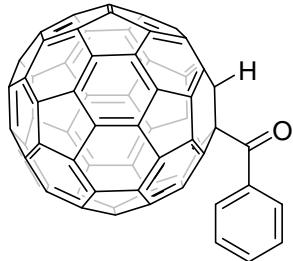


**1,4-Benzenedimethanol-*d*<sub>2</sub>.** To a solution of methyl 4-(hydroxymethyl)benzoate (1.0 g, 5.9 mmol) in anhydrous Et<sub>2</sub>O (40 mL) under an Ar atmosphere at 0 °C, was added lithium aluminum deuteride LiAlD<sub>4</sub> (252 mg, 6 mmol). The reaction mixture was refluxed for 24 h. The mixture was then treated with H<sub>2</sub>O and 10% NaOH, and extracted twice with Et<sub>2</sub>O. The layers were separated and the organic phase dried (MgSO<sub>4</sub>) and concentrated *in vacuo* to afford the desired 1,4-benzenedimethanol-*d*<sub>2</sub> (703 mg, 85%). <sup>1</sup>H NMR (500 MHz, Acetone-*d*<sub>6</sub>): δ 7.30 (s, 4H), 4.60 (d, *J* = 5.5 Hz, 2H), 4.17 (t, *J* = 5.5 Hz, 1H), 4.13 (s, 1H); <sup>13</sup>C NMR (125 MHz, Acetone-*d*<sub>6</sub>): δ 141.45, 141.33, 126.88, 126.82, 64.10, 63.41 (pentaplet, *J*<sub>C-D</sub> = 21.37 Hz); MS: m/z = 140 (M–61, 79).

**Benzene-1,4-dicarboxaldehyde-*d*<sub>1</sub> (**4-d**<sub>1</sub>).** 1,4-Benzenedimethanol-*d*<sub>2</sub> (600 mg, 4.28 mmol) was oxidized to benzene-1,4-dicarboxaldehyde-*d*<sub>1</sub> (**4-d**<sub>1</sub>) with PCC (1.85 g, 8.6 mmol) in dry THF (50 mL) at room temperature (4 hours), under an Ar atmosphere. The reaction mixture was filtered through a plug of Celite - Silica gel to afford benzene-1,4-dicarboxaldehyde-*d*<sub>1</sub> (**4-d**<sub>1</sub>) (520 mg, 90%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 10.14 (s, 1H), 8.06 (s, 4H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 191.54, 191.23 (t, J<sub>C-D</sub> = 27 Hz), 140.05, 139.97 (t, J<sub>C-D</sub> = 3.62 Hz), 130.14; MS: m/z = 135 (M–84, 51).

## 6. Spectral Data of Functionalized Fullerenes **1a–11a, 13a–14a, 9b–12b**

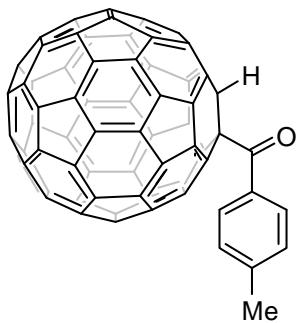
### ➤ Functionalized Fullerene **1a**



Compound **1a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 295 mg (2.78 mmol) of benzaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 30 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate by semi-preparative HPLC (5PBB, 10 × 250 mm, 5 mL/min, toluene/acetonitrile 8:2, 310 nm) afforded ca. 8.0 mg of **1a** (0.01 mmol, 35%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2915, 1672, 1426, 1224, 1180, 1008, 869, 691, 578, 526; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 255, 323, 433; MS (MALDI, negative, DCTB): *m/z* 826.157; <sup>1</sup>H NMR (300 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  7.36 (s, 1H), 7.68-7.80 (m, 3H), 8.70-8.73 (m, 2H); <sup>13</sup>C NMR (75 MHz, ODCB-*d*<sub>4</sub>):  $\delta$  196.92, 151.23, 150.31, 146.70, 146.53, 146.25, 145.69, 145.67, 145.51, 145.50, 145.01, 144.96, 144.76, 144.71, 144.68, 143.97, 143.65, 142.52, 142.26, 142.00, 141.89, 141.41, 141.39, 141.36, 141.03, 140.93, 140.88, 139.87, 139.37, 135.84, 135.35, 135.22, 132.89, 128.50, 76.76, 57.21.

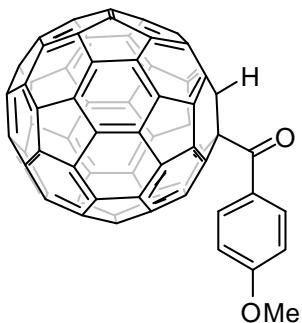
➤ Functionalized Fullerene **2a**



Compound **2a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 334 mg (2.78 mmol) of *p*-tolualdehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 50 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate by semi-preparative HPLC (5PBB, 10 × 250 mm, 5 mL/min, toluene/acetonitrile 8:2, 310 nm) afforded ca. 8.2 mg of **2a** (0.01 mmol, 35%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2915, 1671, 1604, 1511, 1426, 1233, 1180, 1008, 872, 801, 578, 526; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 257, 325, 433, 485; MS (MALDI, negative, DCTB): *m/z* 840.015; <sup>1</sup>H NMR (300 MHz, ODCB-*d*<sub>4</sub>):  $\delta$  8.74 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.13 (s, 1H), 2.39 (s, 3H); <sup>13</sup>C NMR (75 MHz, ODCB-*d*<sub>4</sub>): 195.51, 150.44, 149.94, 145.93, 145.78, 145.51, 145.47, 144.90, 144.89, 144.72, 144.23, 144.18, 143.96, 143.91, 143.31, 143.19, 142.93, 141.76, 141.22, 141.12, 140.65, 140.59, 140.55, 140.25, 140.21, 140.11, 139.10, 138.62, 134.58, 134.51, 132.13, 128.62, 128.52, 75.88, 56.74, 20.40.

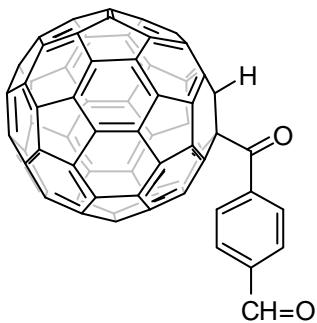
➤ Functionalized Fullerene **3a**



Compound **3a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 378 mg (2.78 mmol) of 4-methoxybenzaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 80 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate by semi-preparative HPLC (5PBB, 10 × 250 mm, 5 mL/min, toluene/acetonitrile 8:2, 310 nm) afforded ca. 8.4 mg of **3a** (0.01 mmol, 35%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2916, 1664, 1597, 1571, 1508, 1460, 1420, 1261, 1238, 1170, 1015, 872, 845, 729, 526; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 257, 325, 432; MS (MALDI, negative, DCTB): *m/z* 856.033; <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  8.86 (d, *J* = 9.0 Hz, 2H), 7.23 (s, 1H), 7.19 (d, *J* = 9.0 Hz, 2H), 4.02 (s, 3H); <sup>13</sup>C NMR (75 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  195.96, 164.13, 151.77, 151.36, 147.01, 146.83, 146.48, 146.42, 146.30, 146.29, 145.76, 145.74, 145.54, 145.50, 144.71, 144.55, 143.34, 142.79, 142.73, 142.71, 142.25, 142.13, 142.03, 141.81, 141.75, 141.71, 140.67, 140.20, 136.21, 135.81, 132.45, 128.40, 114.50, 77.36, 58.37, 55.66.

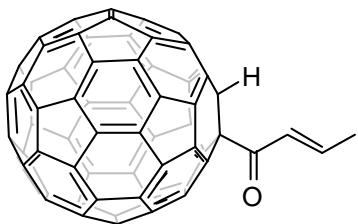
➤ Functionalized Fullerene **4a**



Compound **4a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 373 mg (2.78 mmol) of terephthalaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 25 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate by semi-preparative HPLC (5PBB, 10 x 250 mm, 5 mL/min, toluene/acetonitrile 8:2, 310 nm) afforded ca. 9.5 mg of **4a** (0.011 mmol, 40%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2964, 1698, 1503, 1422, 1262, 1094, 1020, 802, 699, 572, 522; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 258, 329, 433; MS (MALDI, negative, DCTB): *m/z* 854.041; <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  10.20 (s, 1H), 8.66 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.49 (s, 1H); <sup>13</sup>C NMR (125 MHz, ODCB-d<sub>4</sub>/CS<sub>2</sub>):  $\delta$  197.16, 189.60, 152.00, 149.87, 147.44, 147.24, 146.94, 146.54, 146.43, 146.29, 145.82, 145.76, 145.60, 145.51, 145.44, 144.76, 144.33, 143.34, 143.07, 142.83, 142.70, 142.20, 141.99, 141.84, 141.67, 141.56, 141.27, 140.76, 140.47, 140.16, 139.15, 136.31, 135.67, 129.67, 77.58, 57.17.

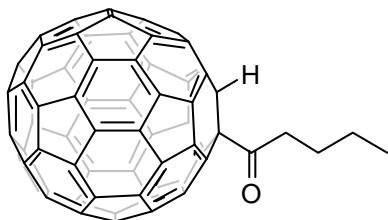
➤ Functionalized Fullerene **5a**



Compound **5a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 195 mg (2.78 mmol) of crotonaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 80 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate by semi-preparative HPLC (5PBB, 10 × 250 mm, 5 mL/min, toluene/acetonitrile 8:2, 310 nm) afforded ca. 8.7 mg of **5a** (0.011 mmol, 40%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2849, 1687, 1620, 1431, 1288, 1259, 1094, 1054, 957, 898, 806, 768, 574, 553, 526; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 256, 329, 433; MS (MALDI, negative, DCTB): *m/z* 790.025; <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  7.80 (s, 1H), 7.77–7.80 (m, 1H) 7.67–7.74 (m, 1H), 2.21 (dd,  $J_1$  = 7.0 Hz,  $J_2$  = 1.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  190.83, 153.46, 150.16, 148.59, 148.58, 147.68, 147.24, 147.15, 146.96, 146.49, 146.23, 146.14, 145.83, 145.57, 145.54, 145.29, 145.23, 144.73, 144.16, 143.28, 142.70, 142.59, 142.40, 142.16, 142.03, 141.70, 141.55, 141.54, 140.63, 140.07, 136.61, 135.17, 126.10, 77.53, 55.45, 19.08.

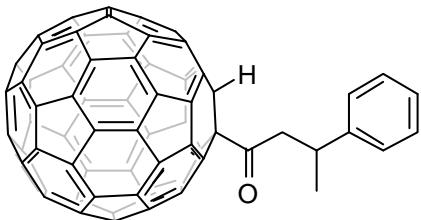
➤ Functionalized Fullerene **6a**



Compound **6a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 239 mg (2.78 mmol) of valeraldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 90 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 11.2 mg of **6a** (0.014 mmol, 50%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2919, 2852, 1720, 1460, 1429, 1185, 1121, 1052, 766, 574, 554, 528; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 257, 325, 405, 433; MS (MALDI, negative, DCTB): *m/z* 806.230; <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  7.72 (s, 1H), 3.73 (t, *J* = 7 Hz, 2H), 2.07 (m, 2H), 1.61 (m, 2H), 1.09 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  203.49, 153.48, 150.23, 147.56, 147.27, 147.15, 147.00, 146.53, 146.25, 146.19, 146.18, 145.86, 145.58, 145.56, 145.34, 145.26, 144.76, 144.17, 143.32, 142.76, 142.65, 142.41, 142.22, 142.07, 141.77, 141.61, 141.52, 140.68, 140.18, 136.42, 135.13, 78.70, 55.80, 39.92, 26.98, 22.76, 14.30.

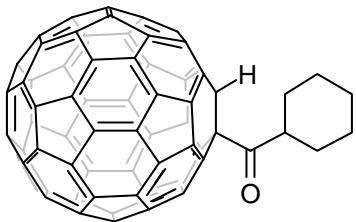
➤ Functionalized Fullerene **7a**



Compound **7a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 411 mg (2.78 mmol) of 3-phenylbutyraldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 60 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 10.8 mg of **7a** (0.012 mmol, 45%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2915, 1712, 1510, 1427, 1182, 754, 696, 575, 526; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 258, 328, 433; MS (MALDI, negative, DCTB): *m/z* 868.103; <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  7.59 (s, 1H), 7.30–7.36 (m, 4H), 7.20–7.23 (m, 1H), 4.06–4.14 (m, 1H), 3.81–3.90 (m, 2H), 1.58(d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  202.46, 153.44, 153.30, 149.75, 149.55, 147.56, 147.52, 147.33, 147.12, 147.06, 146.58, 146.55, 146.30, 146.24, 146.22, 146.21, 145.88, 145.86, 145.84, 145.64, 145.63, 145.54, 145.39, 145.34, 145.28, 145.24, 144.79, 144.21, 144.19, 143.34, 143.32, 143.12, 142.78, 142.68, 142.66, 142.42, 142.38, 142.24, 142.11, 141.80, 141.78, 141.66, 141.59, 141.53, 140.69, 140.66, 140.19, 140.08, 136.68, 136.50, 135.18, 135.11, 128.83, 127.11, 126.87, 78.95, 55.49, 48.25, 36.63, 22.02.

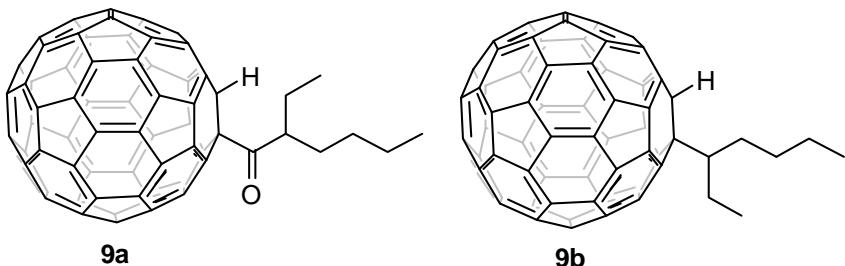
➤ Functionalized Fullerene **8a**



Compound **8a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 311 mg (2.78 mmol) of cyclohexanecarboxaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 60 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 10.4 mg of **8a** (0.012 mmol, 45%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2917, 1711, 1447, 1428, 1141, 1094, 998, 766, 730, 574, 554, 527; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 260, 325, 434; MS (MALDI, negative, DCTB): *m/z* 832.069; <sup>1</sup>H NMR (500 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  7.77 (s, 1H), 4.19–4.25 (m, 1H), 2.23–2.25 (m, 2H), 1.94–2.00 (m, 4H), 1.84–1.87 (m, 1H), 1.42–1.54 (m, 3H); <sup>13</sup>C NMR (125 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  206.16, 153.73, 149.77, 147.69, 147.29, 147.17, 147.04, 146.59, 146.31, 146.24, 146.22, 145.93, 145.64, 145.60, 145.39, 145.28, 144.83, 144.21, 143.38, 142.80, 142.69, 142.45, 142.28, 142.10, 141.81, 141.61, 140.68, 140.16, 136.58, 135.10, 78.79, 55.72, 47.05, 30.88, 25.87.

➤ Functionalized Fullerenes **9a** and **9b**



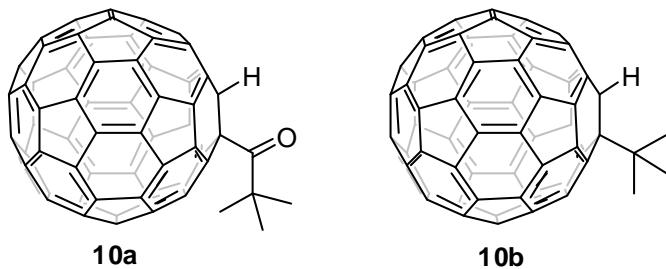
Compounds **9a** and **9b** have been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 37 mg (0.011 mmol) of TBADT and 356 mg (2.78 mmol) of 2-ethylhexanal, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 80 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 9.4 mg of **9a** (0.011 mmol, 40%) and ca. 0.5 mg of **9b** (0.6 µmol, 2%).

When the same reaction was carried out at T = -40 °C for 80 min, only the adduct **9a** was isolated in 35% yield (8.2 mg, 0.01 mmol).

**9a:** IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2917, 1712, 1460, 1427, 1028, 754, 574, 527; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\max}$  (nm) = 257, 328, 433; MS (MALDI, negative, DCTB): *m/z* 848.131; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  7.79 (s, 1H), 4.24 (m, 1H), 2.15 (m, 2H), 1.90 (m, 1H), 1.80 (m, 1H), 1.50 (m, 2H), 1.40 (m, 2H), 1.14 (t, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  207.11, 153.94, 153.93, 149.96, 149.93, 147.76, 147.69, 147.39, 147.27, 147.13, 146.67, 146.40, 146.32, 146.31, 146.01, 146.00, 145.72, 145.66, 145.64, 145.48, 145.36, 144.91, 144.29, 143.47, 143.19, 142.87, 142.76, 142.56, 142.36, 142.19, 141.88, 141.70, 141.69, 141.67, 140.74, 140.15, 140.09, 136.54, 135.18, 79.53, 56.03, 49.46, 32.59, 30.12, 26.38, 23.07, 14.10, 12.55.

**9b:** UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 256, 324, 433; MS (MALDI, negative, DCTB): *m/z* 820.135; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  6.48 (s, 1H), 3.05 (m, 1H), 2.94 (m, 2H), 2.40 (m, 2H), 1.95 (m, 1H), 1.86 (m, 1H), 1.67 (m, 2H), 1.53 (t, *J* = 7.5 Hz, 3H), 1.13 (t, *J* = 7.5 Hz, 3H).

➤ Functionalized Fullerenes **10a** and **10b**



Compounds **10a** and **10b** have been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 239 mg (2.78 mmol) of pivalaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 50 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 2.2 mg of **10a** (0.003 mmol, 10%) and ca. 3.9 mg of **10b** (0.005 mmol, 18%).

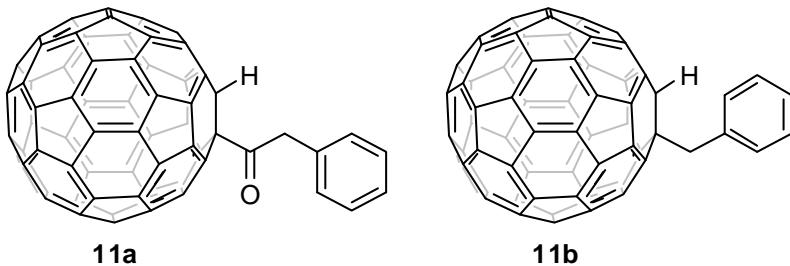
The same reaction was also carried out by using 5 mg (7 µmol) of C<sub>60</sub>, 11.6 mg (3.5 µmol) of TBADT and 120 mg (1.4 mmol) of pivalaldehyde, at T = -40 °C. After 25 min, the reaction was concentrated and purified by flash column chromatography on silica (hexane/toluene 8:2) to afford ca. 1.9 mg of **10a** (2.4 µmol, 35%) and ca. 0.2 mg of **10b** (0.2 µmol, 3%).

**10a:** IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2946, 1697, 1474, 1460, 1426, 1360, 1183, 1056, 1006, 880, 578, 526; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 255, 325, 433, 485; MS (MALDI, negative, DCTB): *m/z* 806.180; <sup>1</sup>H NMR (500 MHz, ODCB-*d*<sub>4</sub>):  $\delta$  6.56 (s, 1H), 1.89 (s, 9H); <sup>13</sup>C NMR (125 MHz, ODCB-*d*<sub>4</sub>):  $\delta$  210.28, 152.19, 150.94,

147,31, 147,17, 147,10, 146,34, 146,27, 146,18, 145,92, 145,71, 145,44, 145,40, 145,35, 144,66, 144,36, 143,23, 142,65, 142,59, 142,05, 142,00, 141,96, 141,74, 141,68, 141,56, 140,51, 139,76, 136,56, 136,37, 75,84, 60,53, 49,00, 27,87.

**10b:** (Mixture of 1,2 and 1,4-isomers, 5:1 molar ratio) IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) = 2959, 2866, 1512, 1462, 1427, 1397, 1370, 1200, 1189, 1094, 904, 764, 730, 583, 573, 554, 527; UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  (nm) = 256, 328, 433; MS (MALDI, negative, DCTB):  $m/z$  778.075;  $^1\text{H}$  NMR (500 MHz,  $\text{CS}_2/\text{CDCl}_3$ ):  $\delta$  6.69 (s, 1H, 1,2-isomer), 6.33 (s, 1H, 1,4-isomer), 2.10 (s, 9H, 1,2-isomer), 1.90 (s, 9H, 1,4-isomer);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CS}_2/\text{CDCl}_3$ ):  $\delta$  154.52, 153.92, 147.59, 147.31, 147.08, 146.96, 146.83, 146.30, 146.29, 146.14, 146.05, 145.76, 145.28, 145.26, 144.62, 144.42, 143.17, 142.58, 142.56, 142.13, 142.11, 142.00, 141.62, 141.53, 141.38, 140.31, 139.02, 136.43, 136.37, 73.44, 56.96, 48.81, 41.32, 41.13, 27.53, 26.79.

➤ Functionalized Fullerene **11a** and **11b**



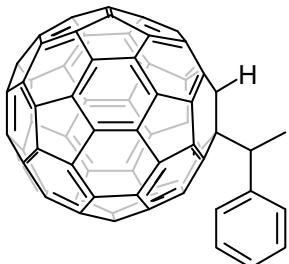
Compounds **11a** and **11b** have been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 334 mg (2.78 mmol) of phenylacetaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 60 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 2.3 mg of **11a** (0.003 mmol, 10%) and ca. 4.5 mg of **11b** (0.0055 mmol, 20%).

The same reaction was also carried out by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 46 mg (0.014 mmol) of TBADT and 667 mg (5.56 mmol) of phenylacetaldehyde, at T = -50 °C. After 70 min, the reaction was concentrated and purified by flash column chromatography on silica (hexane/toluene 8:2) to afford ca. 8.1 mg of **11a** (0.01 mmol, 35%).

**11a:** IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2916, 1720, 1493, 1426, 1088, 1037, 752, 703, 575, 527; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 259, 329, 433; MS (MALDI, negative, DCTB): *m/z* 840.067; <sup>1</sup>H NMR (500 MHz, ODCB-*d*<sub>4</sub>/CS<sub>2</sub>):  $\delta$  7.60 (s, 1H), 7.20–7.34 (m, 5H), 4.88 (s, 2H); <sup>13</sup>C NMR (125 MHz, ODCB-*d*<sub>4</sub>/CS<sub>2</sub>):  $\delta$  200.90, 153.56, 150.07, 147.78, 147.55, 147.35, 147.28, 146.82, 146.54, 146.47, 146.45, 146.11, 145.94, 145.87, 145.61, 145.52, 145.04, 144.44, 143.57, 143.31, 143.03, 142.92, 142.66, 142.50, 142.36, 142.04, 141.95, 141.77, 140.92, 140.53, 137.02, 135.40, 133.87, 132.72, 129.26, 79.14, 56.24, 46.37.

**11b:** IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 1493, 1460, 1452, 1427, 1259, 1215, 1181, 1064, 1024, 807, 760, 744, 722, 697, 662, 575, 546, 525, 512, 475; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 257, 326, 433, 485; MS (MALDI, negative, DCTB): *m/z* 812.015; <sup>1</sup>H NMR (500 MHz, ODCB-*d*<sub>4</sub>):  $\delta$  7.77 (d, *J* = 7.5 Hz, 2H), 7.45 (dd, *J*<sub>1</sub> = *J*<sub>2</sub> = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.52 (s, 1H), 4.65 (s, 2H); <sup>13</sup>C NMR (75 MHz, CS<sub>2</sub>/CDCl<sub>3</sub>):  $\delta$  155.22, 153.75, 147.45, 147.29, 146.92, 146.41, 146.37, 146.27, 146.24, 146.17, 145.77, 145.49, 145.43, 145.38, 144.70, 144.56, 143.22, 142.56, 142.19, 142.03, 141.97, 141.90, 141.65, 141.58, 140.21, 139.96, 136.33, 136.06, 135.74, 131.39, 128.81, 127.82, 65.85, 59.13, 53.20.

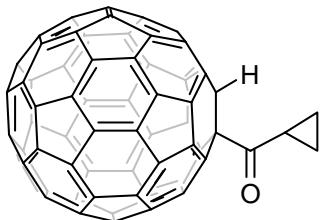
➤ Functionalized Fullerene **12b**



Compound **12b** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 18.5 mg (0.0056 mmol) of TBADT and 373 mg (2.78 mmol) of 2-phenylpropionaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 2 h, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 6.9 mg of **12b** (0.008 mmol, 30%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2978, 2921, 1600, 1451, 1427, 1359, 1183, 1024, 762, 700, 580, 552, 527; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 258, 327, 434; MS (MALDI, negative, DCTB): *m/z* 826.059; <sup>1</sup>H NMR (500 MHz, OBCB-*d*<sub>4</sub>/CDCl<sub>3</sub>):  $\delta$  7.75 (d, *J* = 7.0 Hz, 2H), 7.43 (m, 2H), 7.32 (m, 1H), 6.58 (s, 1H), 4.63 (q, *J* = 7.0 Hz, 1H), 2.37 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, ODCB-*d*<sub>4</sub>/CS<sub>2</sub>):  $\delta$  154.95, 154.70, 154.43, 154.12, 147.48, 147.29, 147.11, 147.01, 146.94, 146.83, 146.46, 146.45, 146.41, 146.26, 146.20, 145.86, 145.83, 145.51, 145.50, 145.42, 145.40, 144.79, 144.75, 144.60, 144.57, 143.27, 143.24, 143.06, 142.61, 142.59, 142.30, 142.10, 141.86, 141.83, 141.67, 141.57, 141.33, 140.24, 140.22, 139.74, 139.60, 136.65, 136.63, 136.53, 136.48, 128.85, 128.01, 70.33, 58.10, 53.83, 18.46.

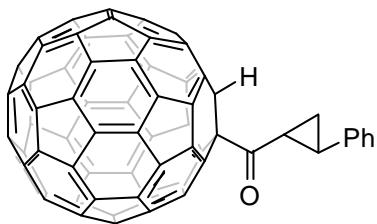
➤ Functionalized Fullerene **13a**



Compound **13a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 46 mg (0.014 mmol) of TBADT and 175 mg (2.5 mmol) of cyclopropanecarboxaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 35 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 8.8 mg of **13a** (0.011 mmol, 40%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 1702, 1429, 1374, 1183, 1054, 753, 577, 527; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 259, 329, 433; MS (MALDI, negative, DCTB): *m/z* 790.049; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  7.80 (s, 1H), 3.56 (m, 1H), 1.72 (m, 2H), 1.42 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  192.51, 153.41, 150.35, 147.82, 147.32, 147.17, 147.04, 146.56, 146.29, 146.21, 146.20, 145.91, 145.62, 145.59, 145.36, 145.29, 144.79, 144.23, 143.34, 143.09, 142.77, 142.66, 142.44, 142.23, 142.10, 141.78, 141.60, 140.69, 140.17, 136.52, 135.20, 78.72, 55.49, 19.27, 14.61.

➤ Functionalized Fullerene **14a**



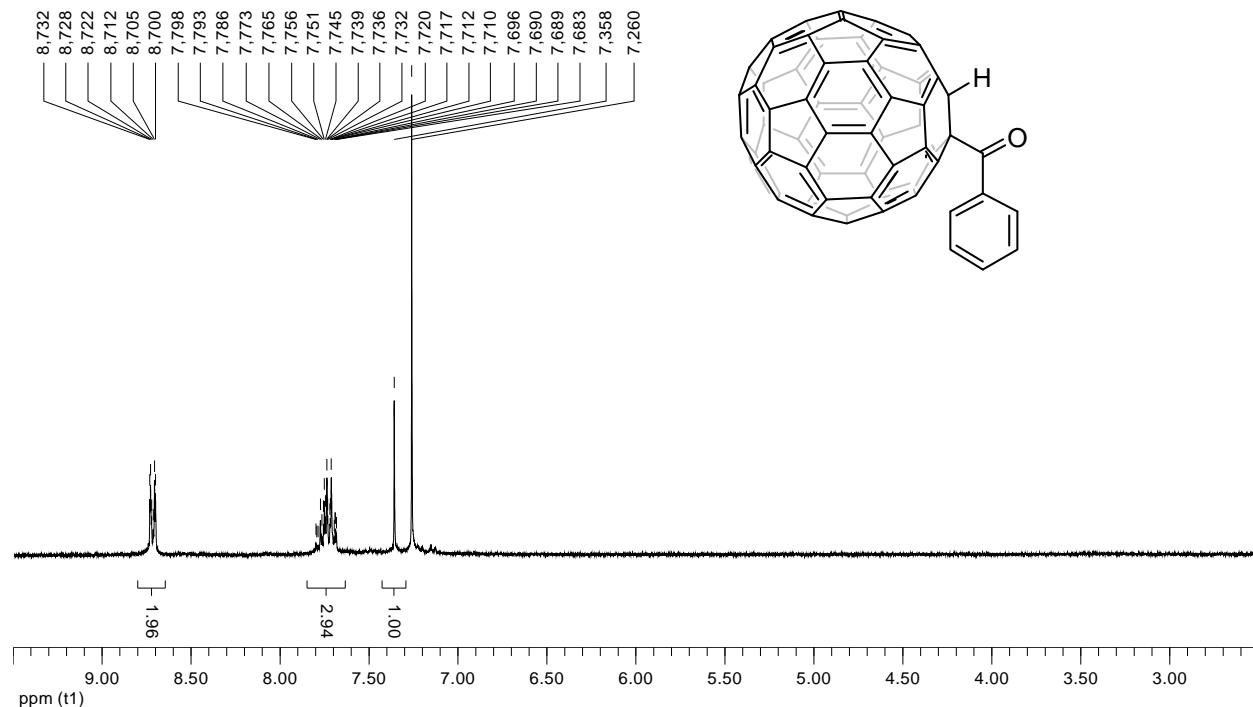
Compound **14a** has been prepared following the general procedure described in Section 2, by using 20 mg (0.0278 mmol) of C<sub>60</sub>, 46 mg (0.014 mmol) of TBADT and 365 mg (2.5 mmol) of 2-phenylcyclopropanecarboxaldehyde, in a mixture of chlorobenzene/acetonitrile 85:15 (80 mL). The progress of the reaction was monitored by analytical HPLC (5C18-MS, 4.6 x 250 mm, 1 mL/min, toluene/acetonitrile 1:1, 310 nm). The reaction mixture was irradiated at 5–10 °C for 40 min, after which time the solvent was evaporated under reduced pressure. Acetonitrile was then added and the resulting suspension was centrifuged at 4100 rpm for 10min (3 times). Further purification of the resulting precipitate *via* flash column chromatography on silica (hexane/toluene 8:2) afforded ca. 9.2 mg of **14a** (0.011 mmol, 40%).

IR (KBr):  $\nu$  (cm<sup>-1</sup>) = 2848, 1698, 1427, 1391, 1181, 1101, 1058, 904, 731, 694, 580, 526; UV-vis (CHCl<sub>3</sub>):  $\lambda_{\text{max}}$  (nm) = 258, 326, 433; MS (MALDI, negative, DCTB): *m/z* 866.057; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  7.80 (s, 1H), 7.29 (m, 2H), 7.22 (m, 3H), 3.74 (m, 1H), 3.17 (m, 1H), 2.32 (m, 1H), 1.89 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>/CS<sub>2</sub>):  $\delta$  201.90, 153.39, 153.34, 150.17, 150.07, 147.76, 147.67, 147.44, 147.25, 147.24, 147.18, 146.65, 146.64, 146.40, 146.31, 145.99, 145.72, 145.47, 145.39, 144.88, 144.33, 144.32, 143.41, 143.18, 142.86, 142.73, 142.53, 142.52, 142.32, 142.18, 141.86, 141.70, 141.67, 141.66, 140.77, 140.31, 140.29, 139.27, 136.70, 136.56, 135.33, 128.84, 127.20, 126.74, 78.65, 55.59, 32.61, 30.45, 21.67.

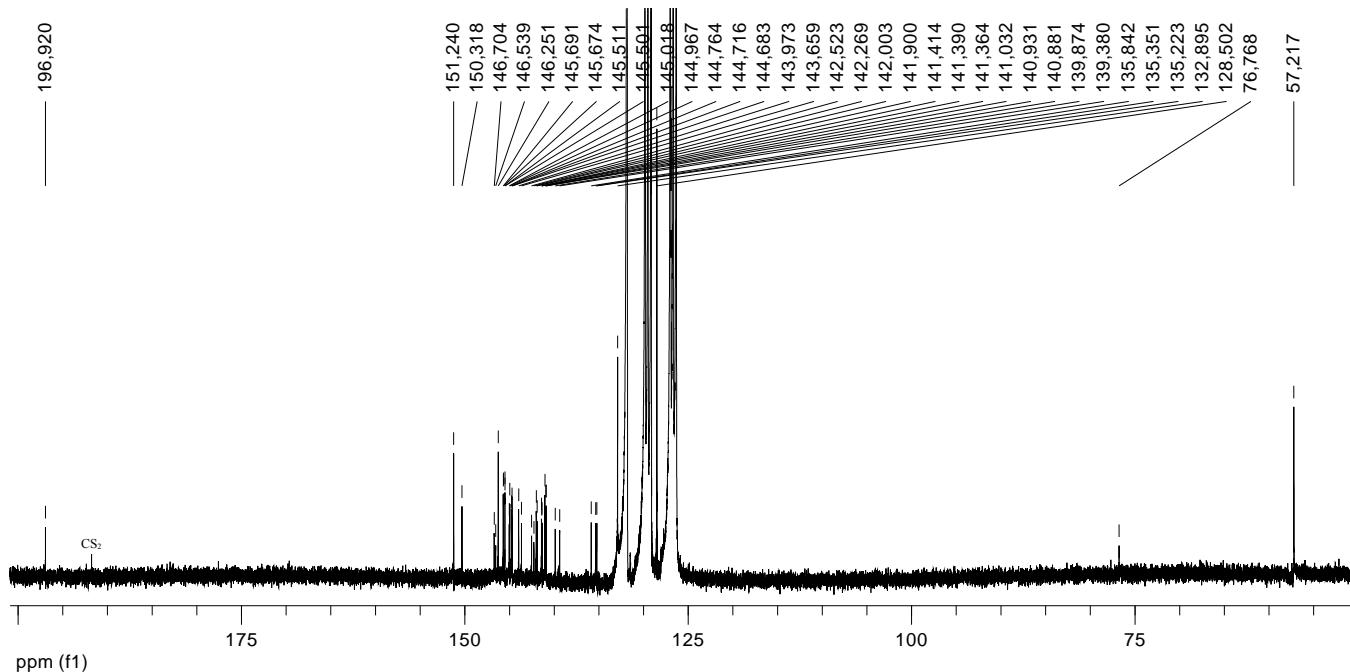
**7.  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, FT-IR, UV-vis Spectra of Functionalized Fullerenes 1a–11a, 13a–14a, 9b–12b**

➤ Compound **1a**

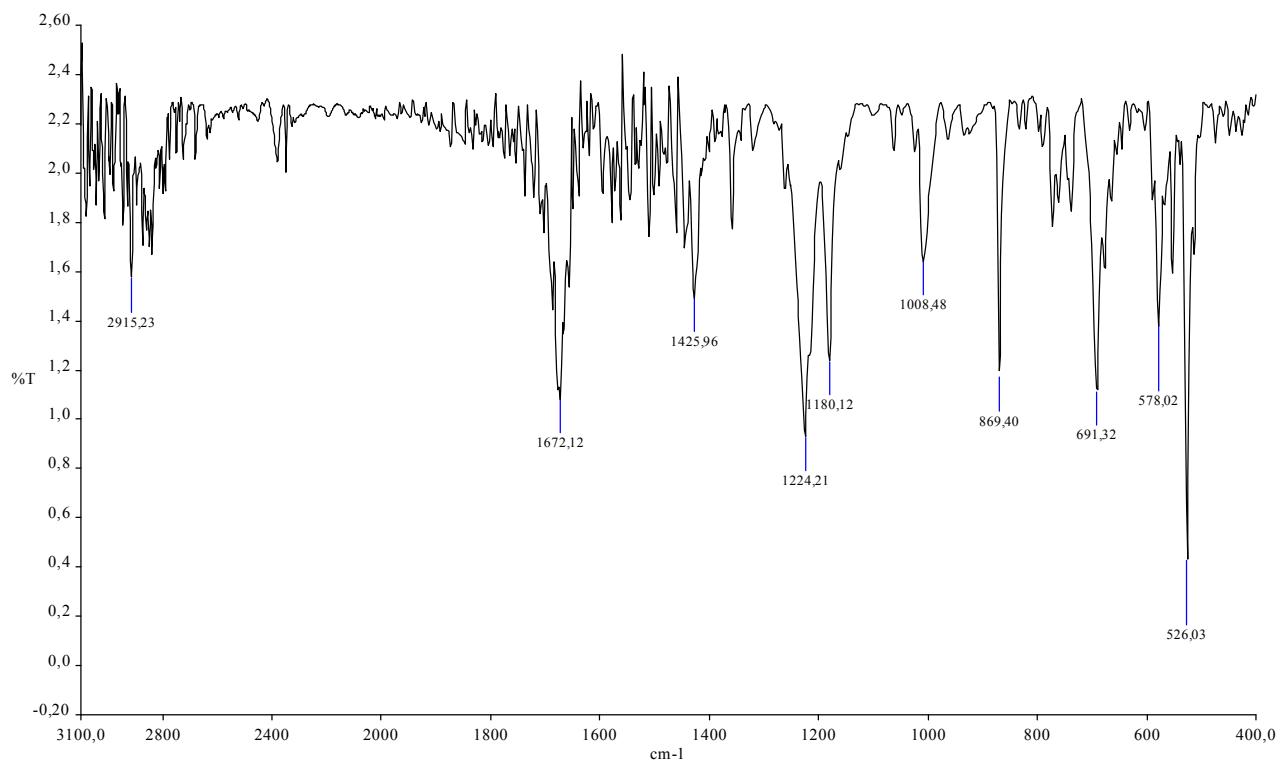
a)  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



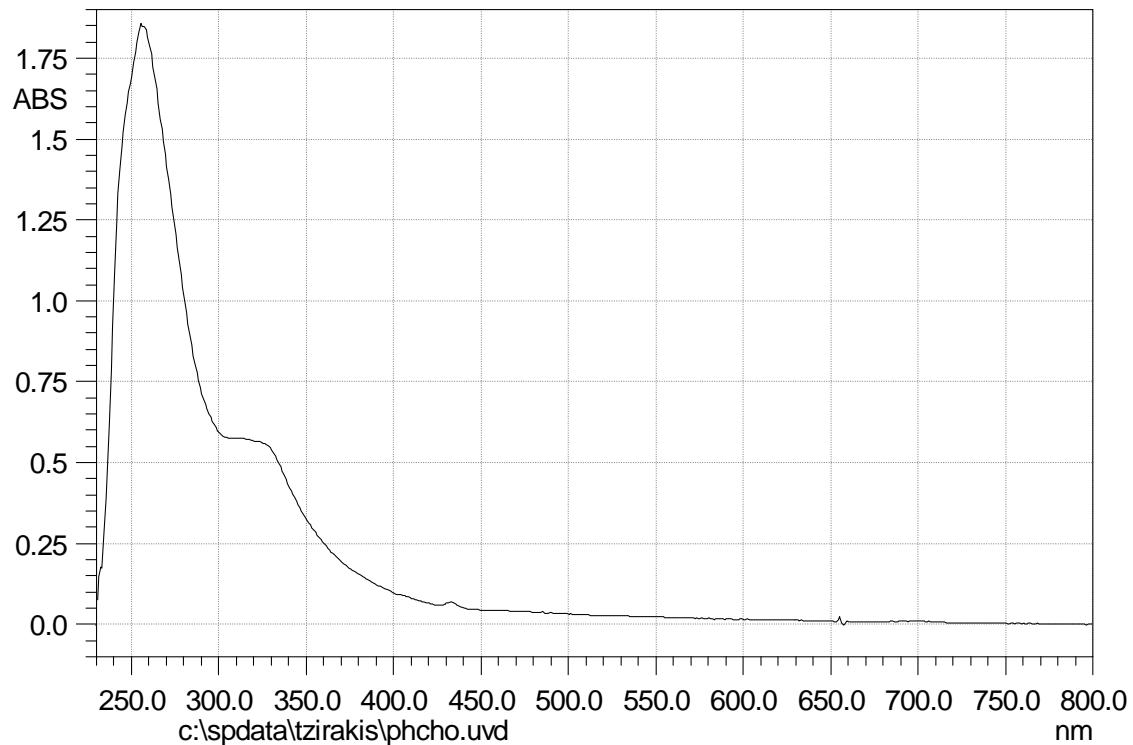
b)  $^{13}\text{C}$  NMR (75 MHz, ODCB- $d_4$ )



c) FT-IR (KBr)

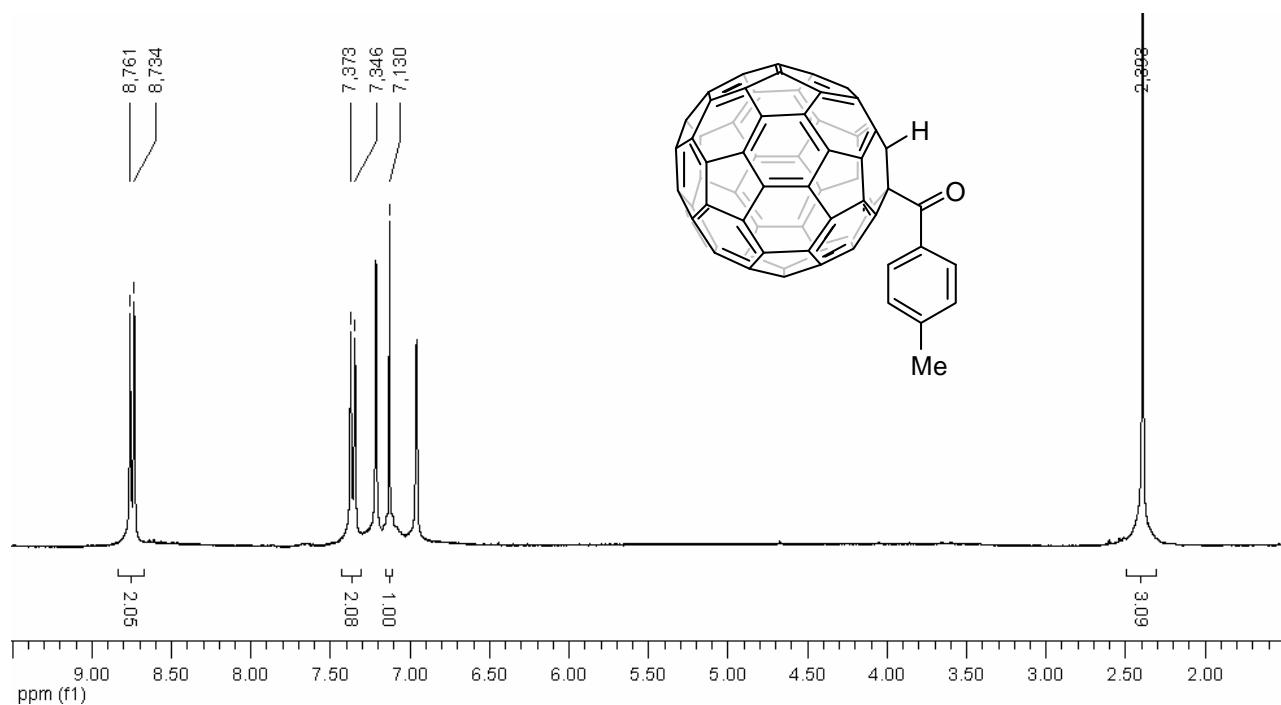


d) UV-vis ( $\text{CHCl}_3$ )

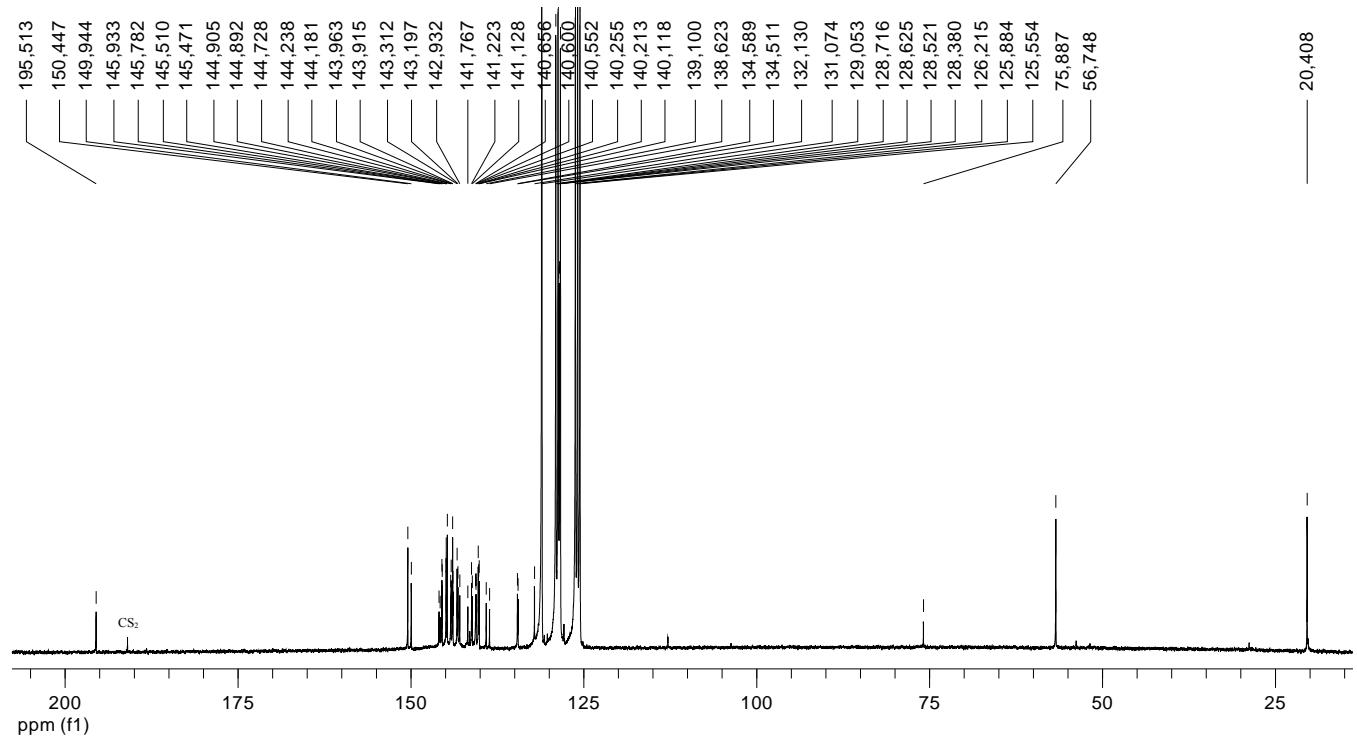


➤ Compound **2a**

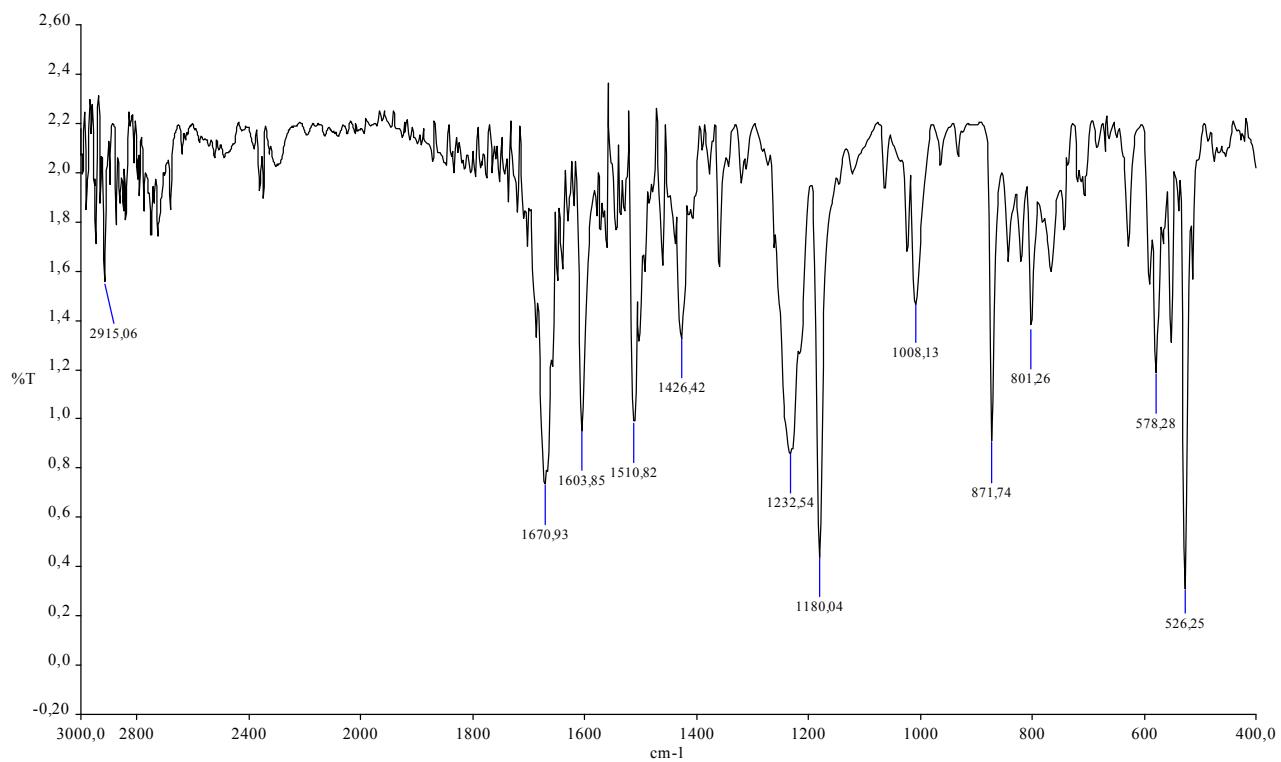
a)  $^1\text{H}$  NMR (300 MHz, ODCB- $d_4$ )



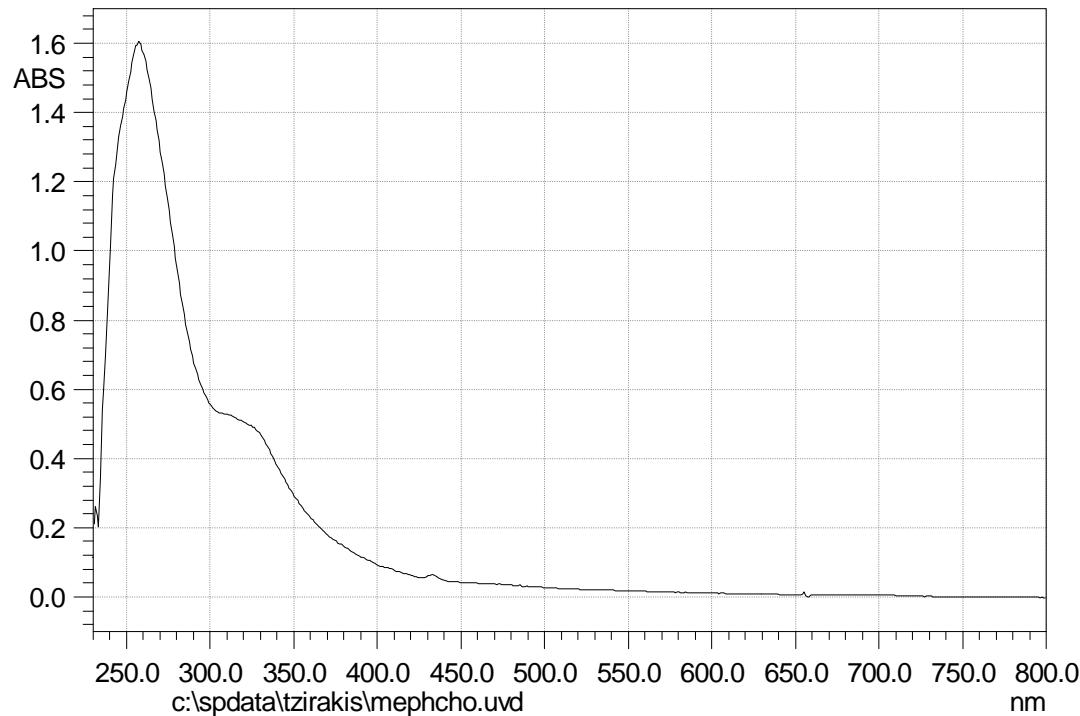
b)  $^{13}\text{C}$  NMR (75 MHz, ODCB- $d_4$ )



c) FT-IR (KBr)

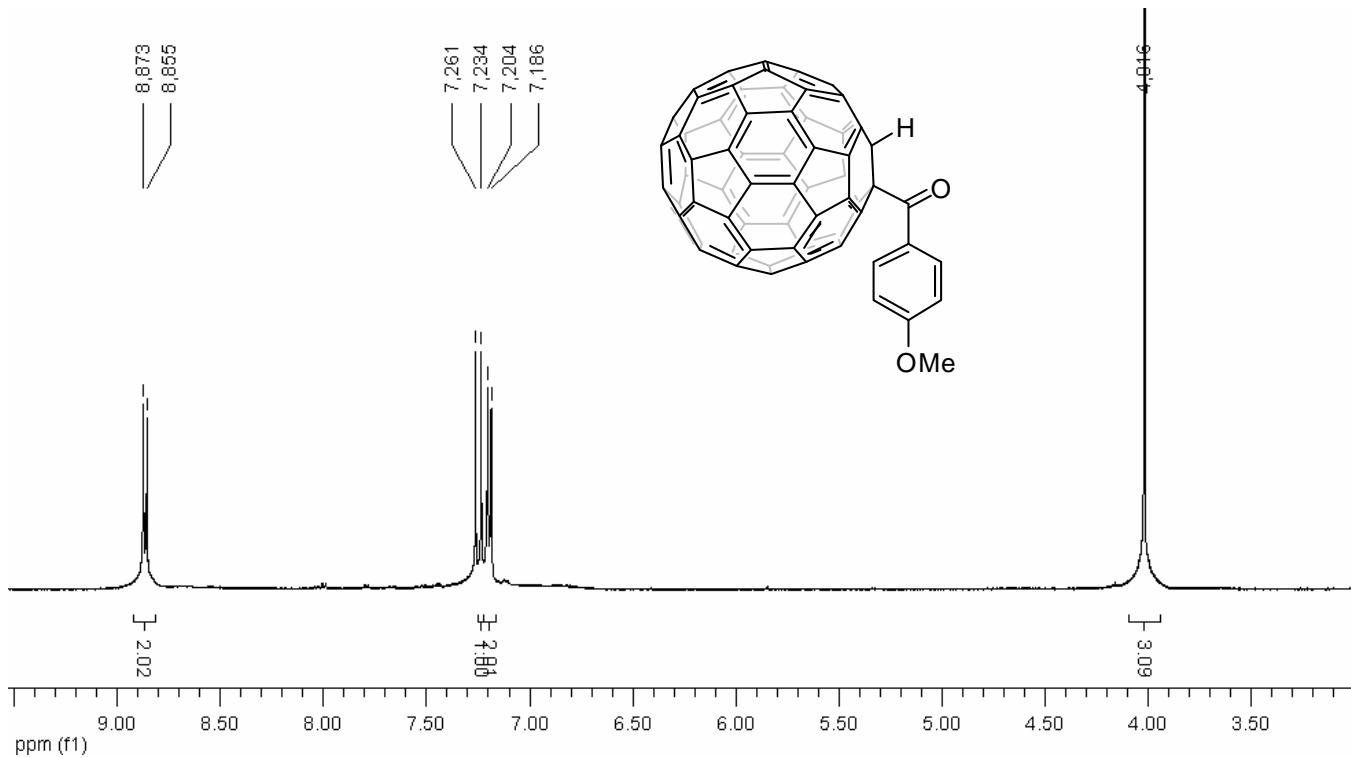


d) UV-vis (CHCl<sub>3</sub>)

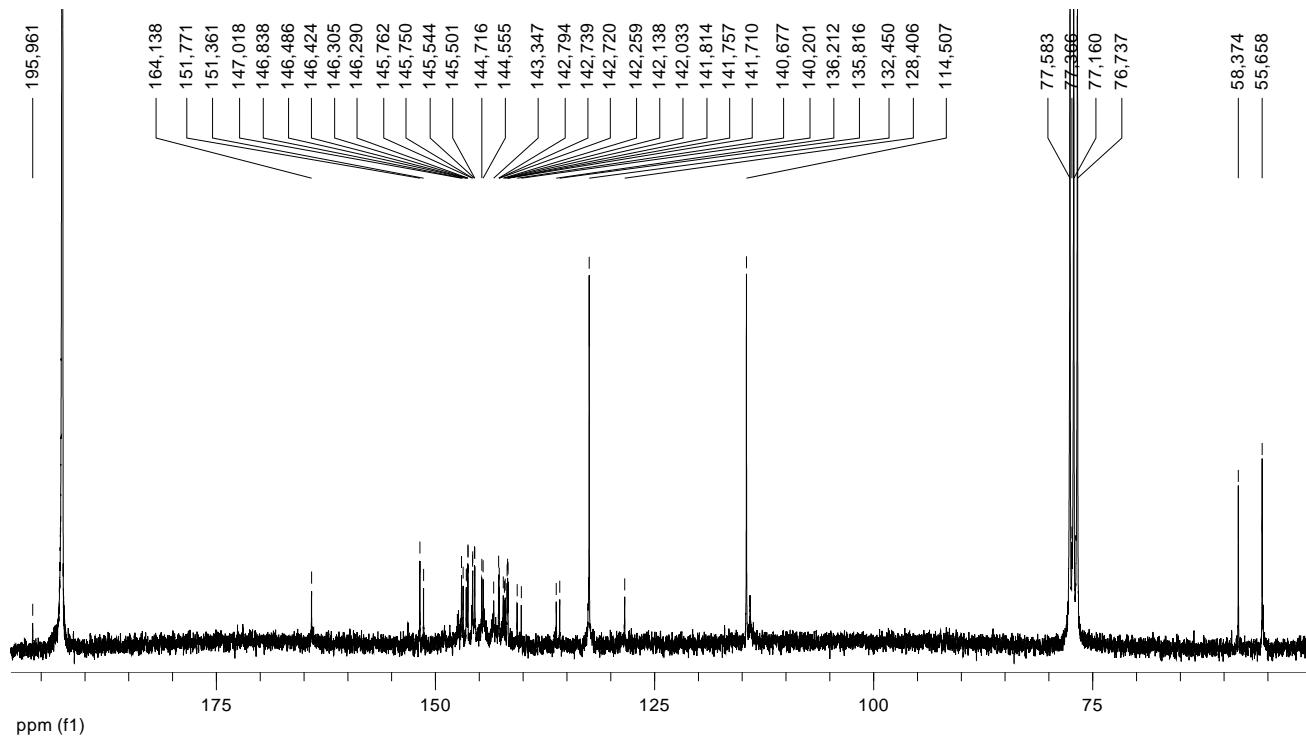


➤ Compound 3a

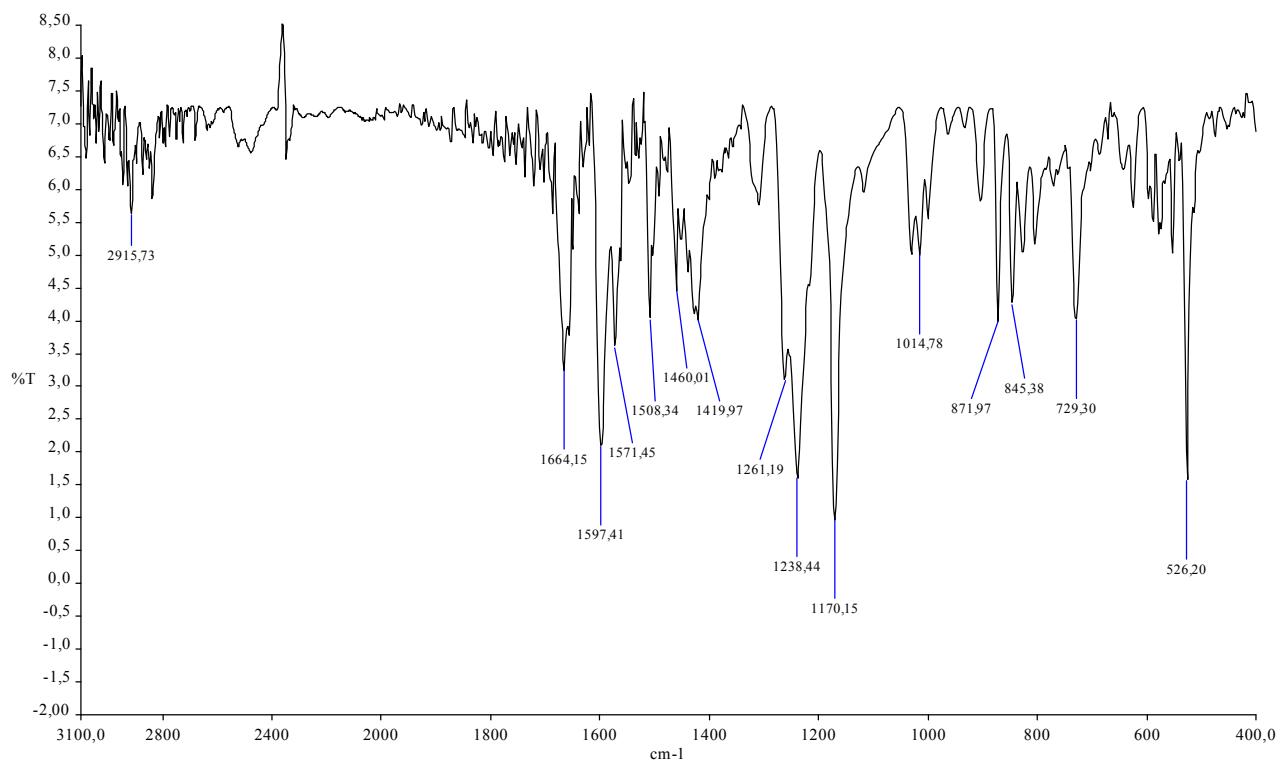
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



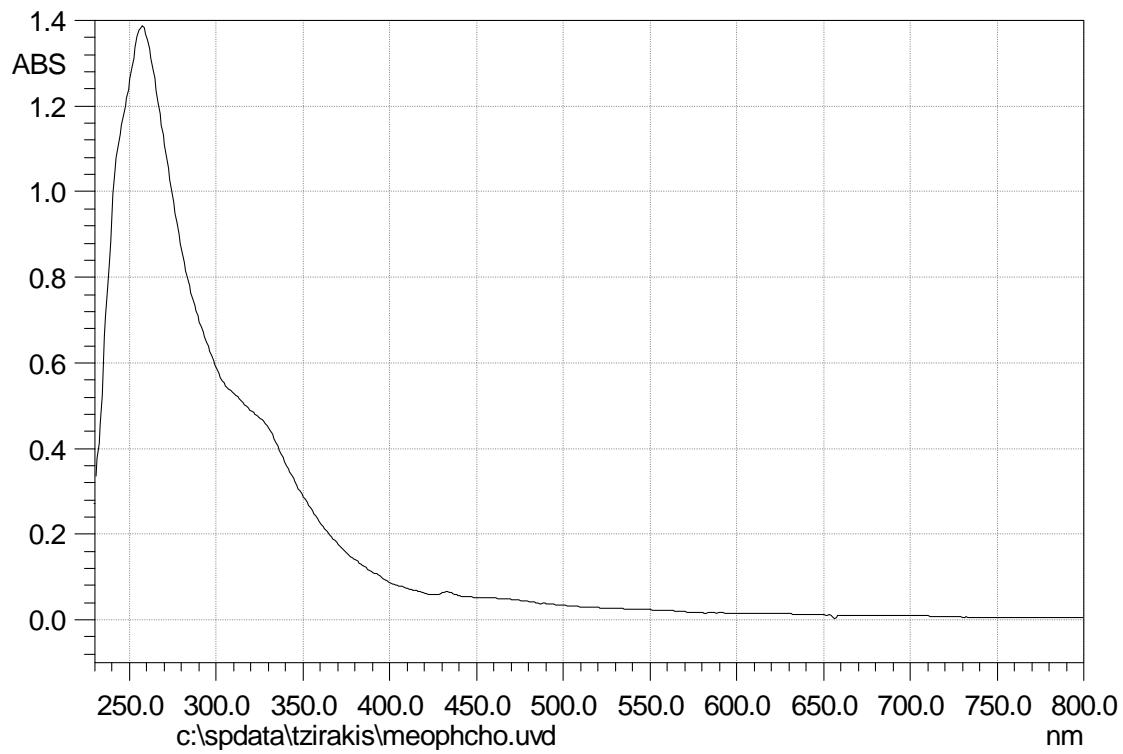
b)  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



c) FT-IR (KBr)

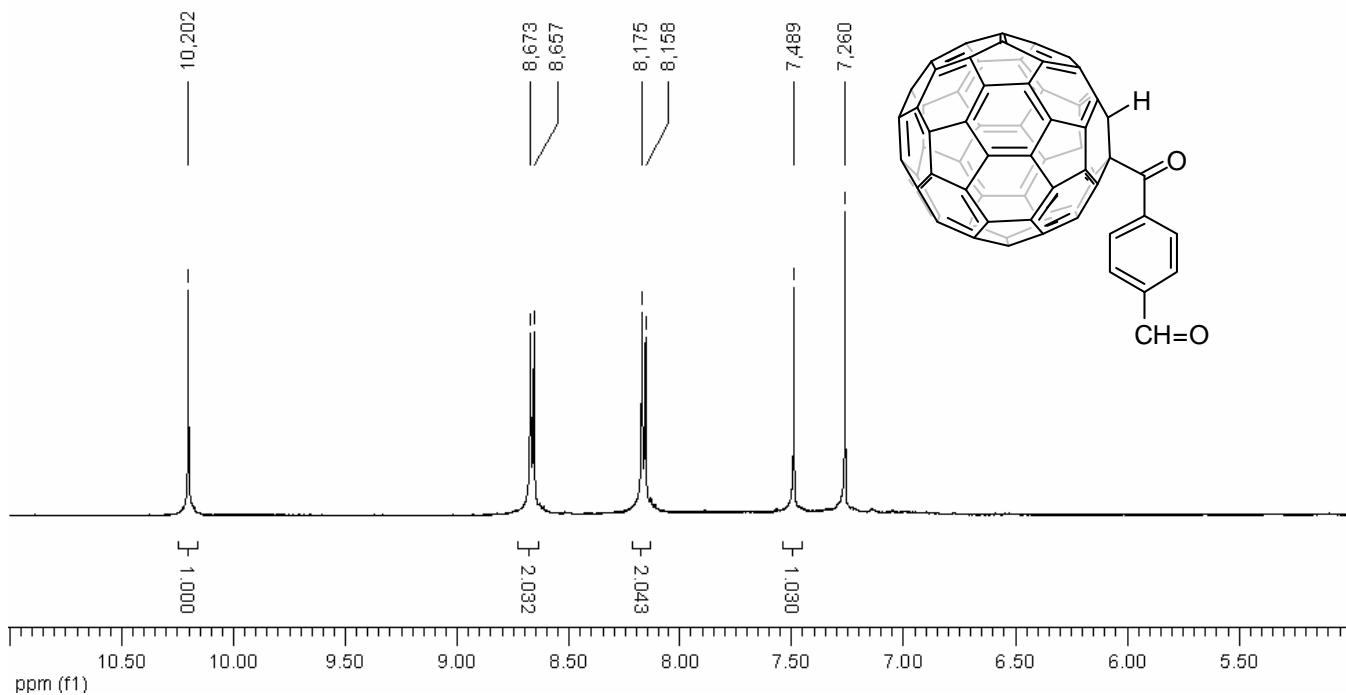


d) UV-vis (CHCl<sub>3</sub>)

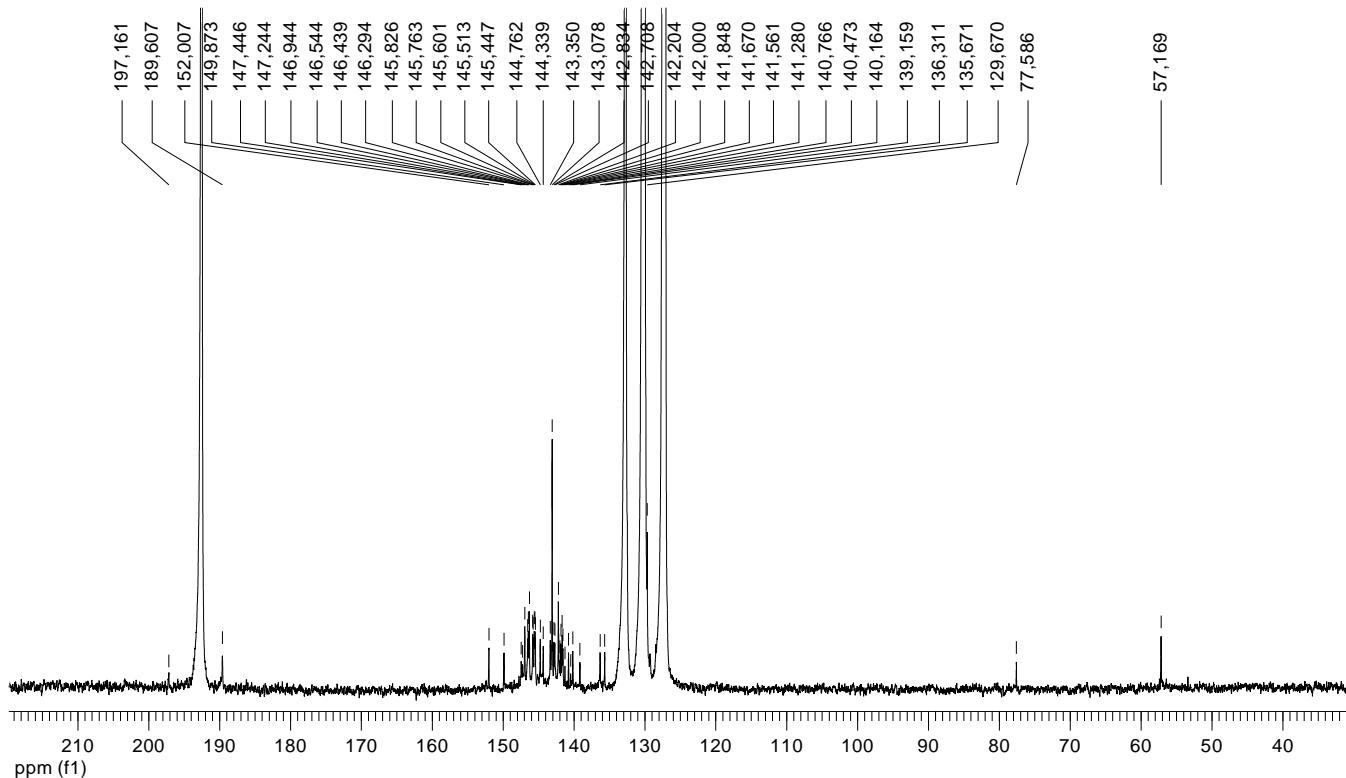


► Compound 4a

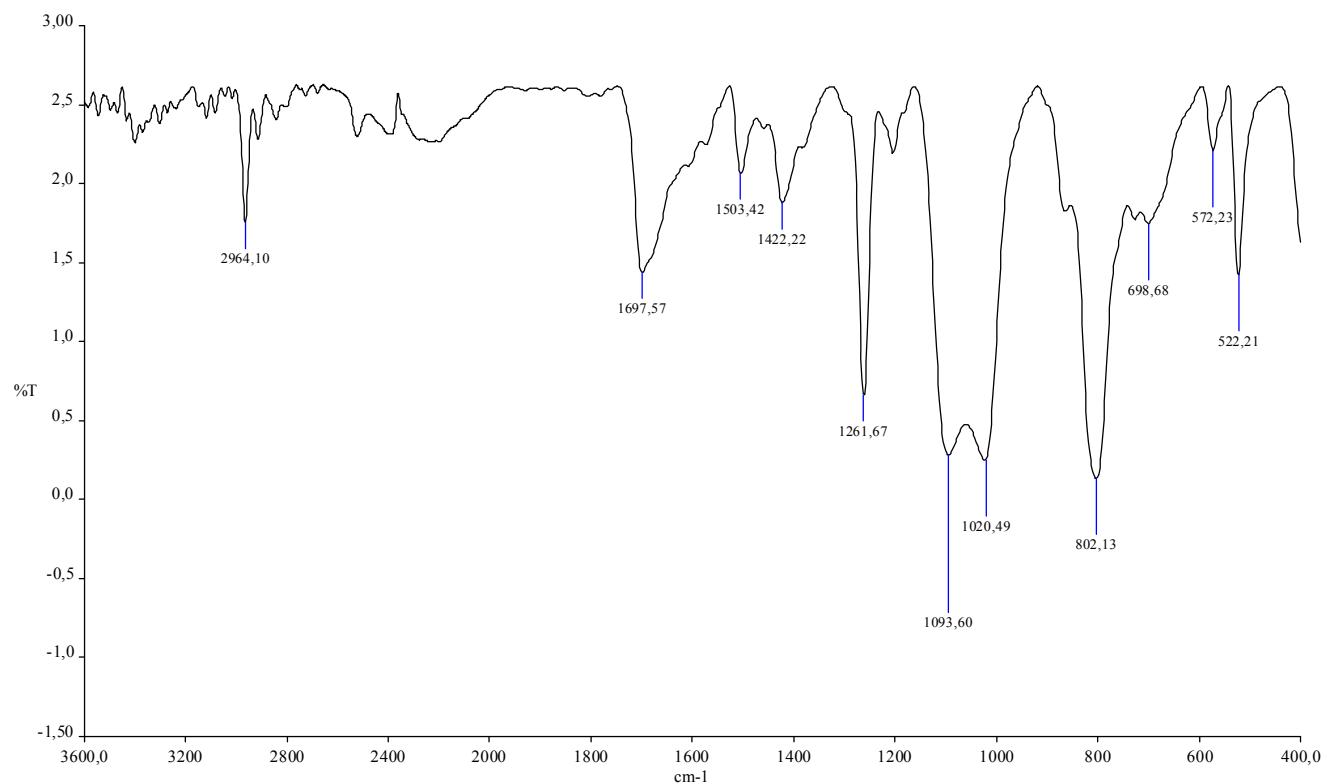
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



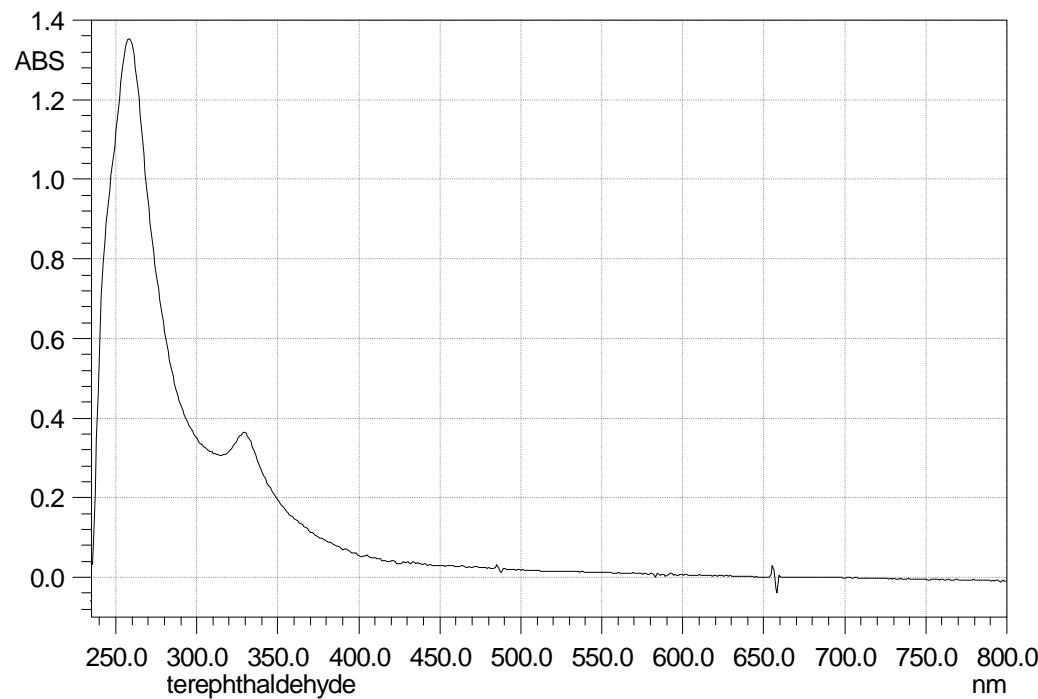
b)  $^{13}\text{C}$  NMR (125 MHz,  $\text{ODCB}-d_4/\text{CS}_2$ )



c) FT-IR (KBr)

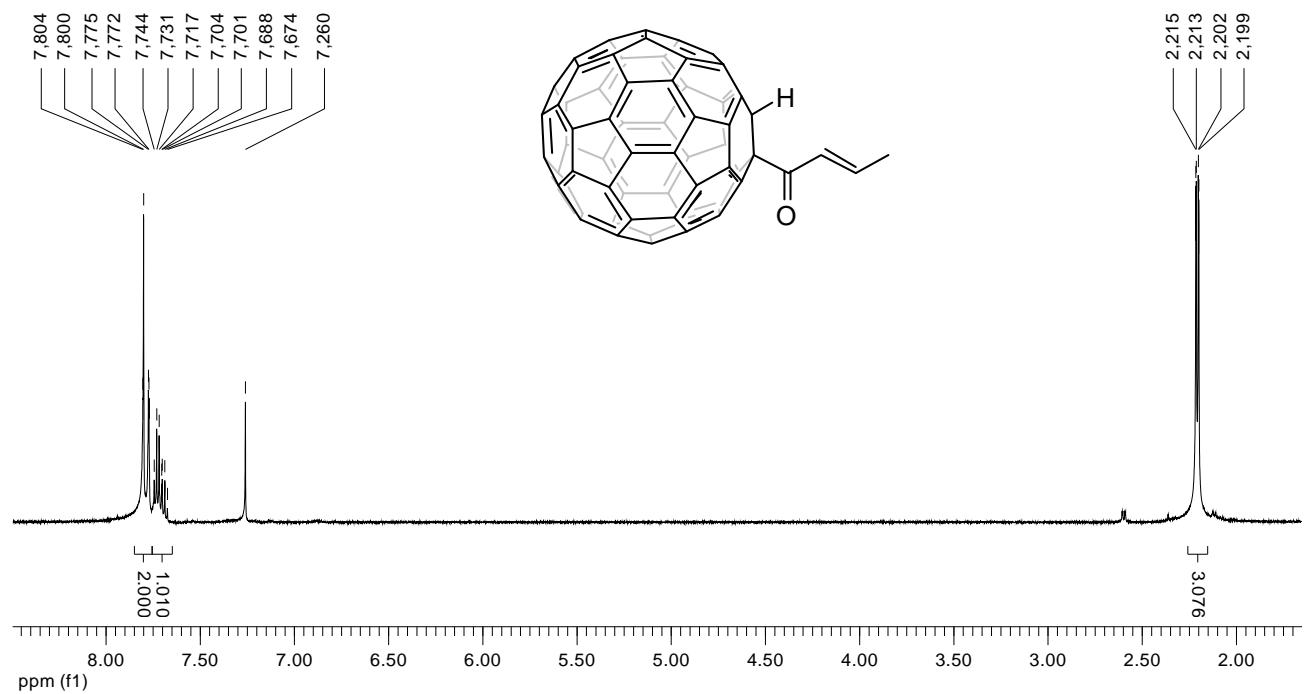


d) UV-vis ( $\text{CHCl}_3$ )

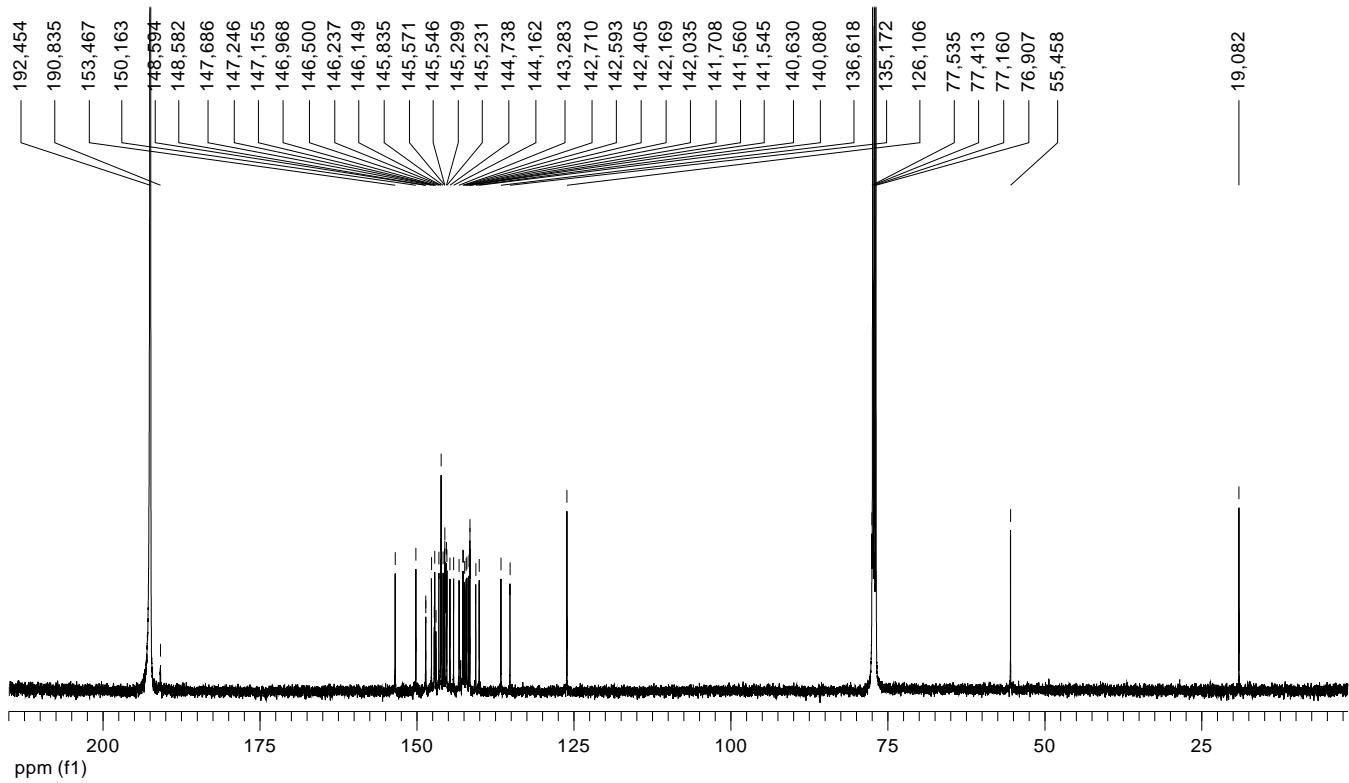


► Compound **5a**

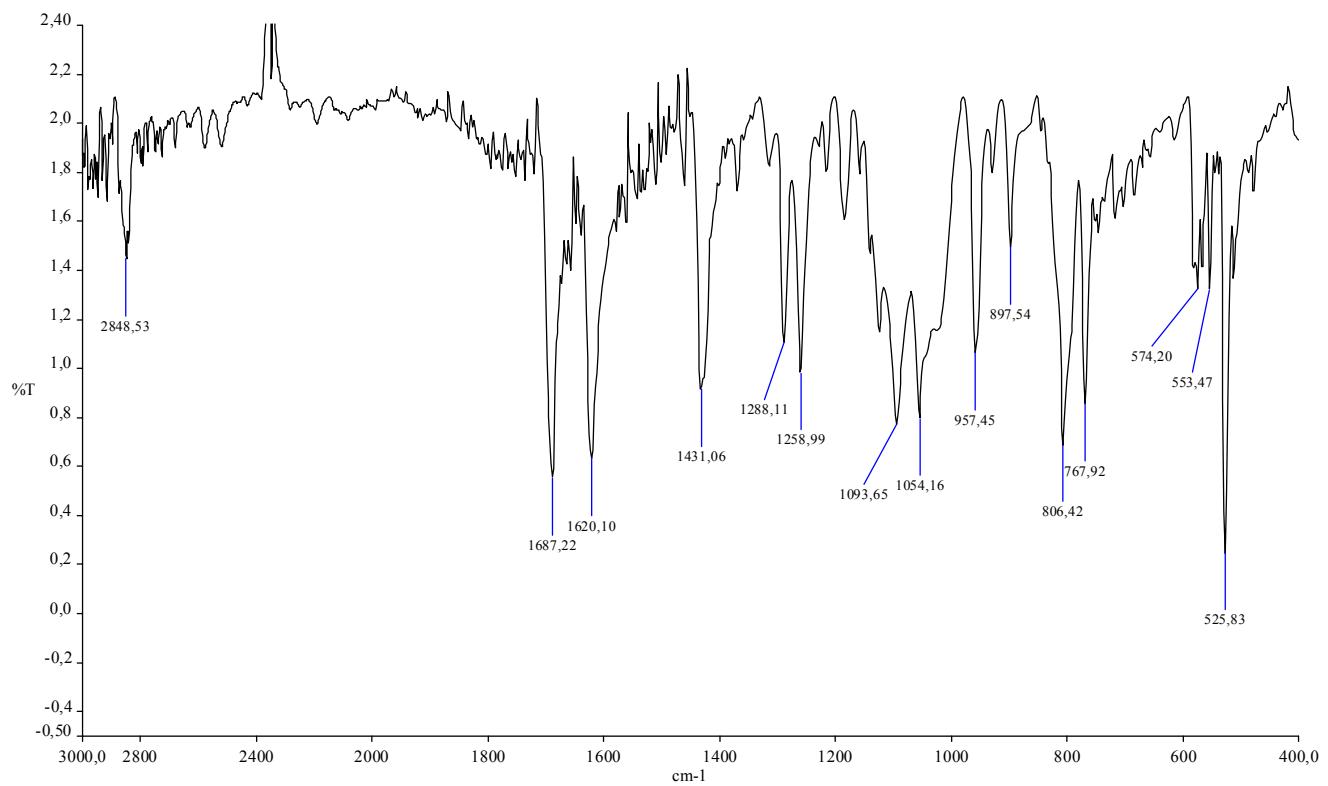
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



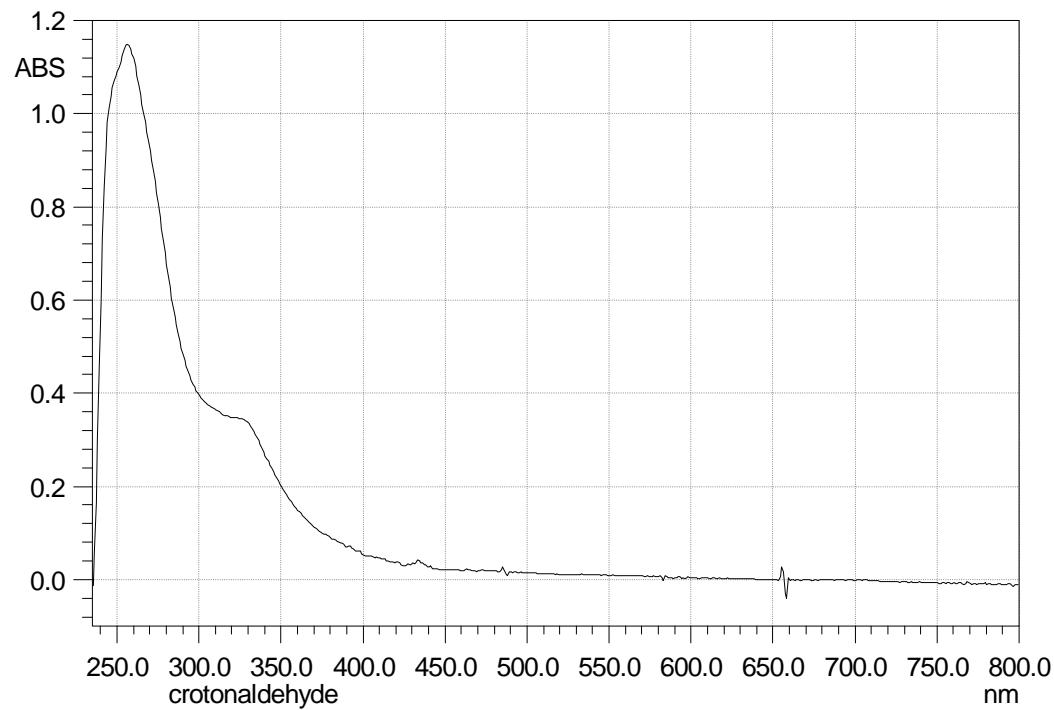
b)  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



c) FT-IR (KBr)

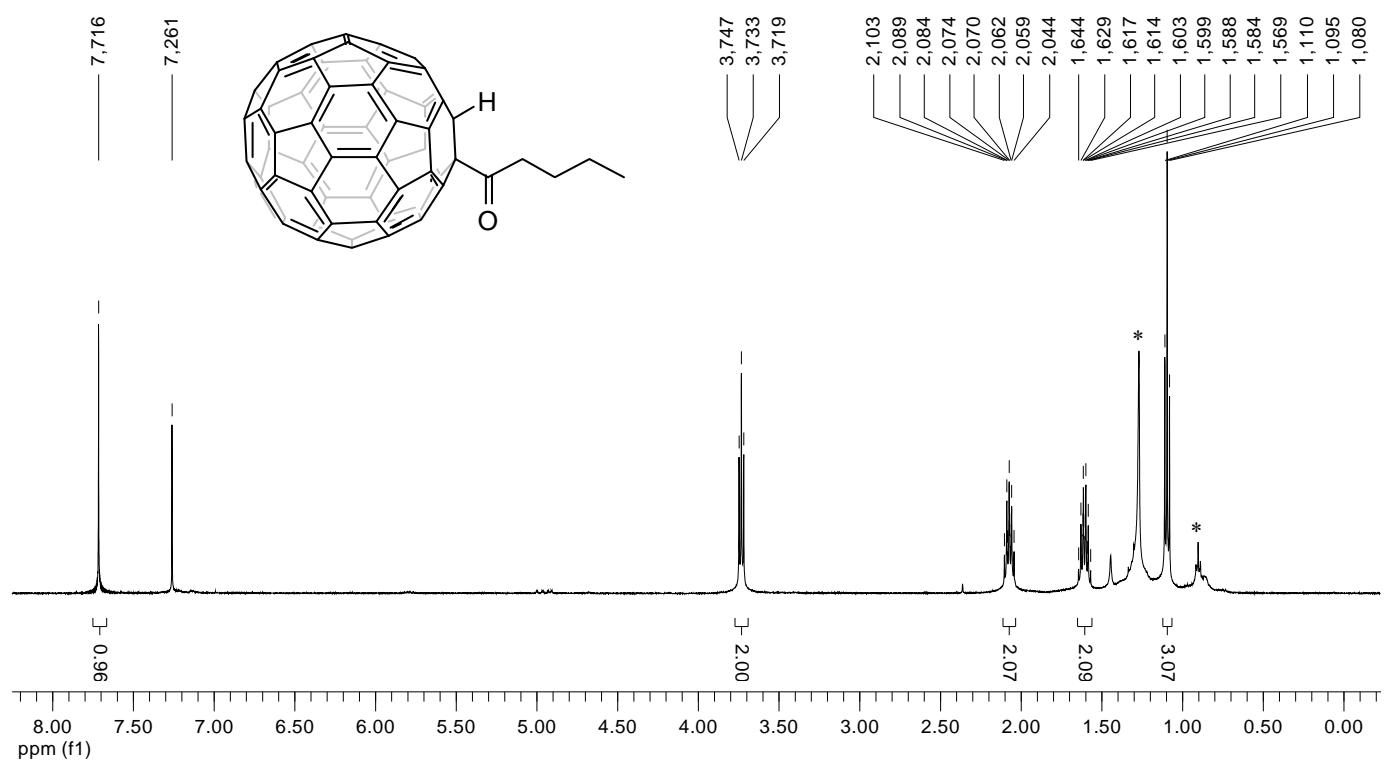


d) UV-vis ( $\text{CHCl}_3$ )

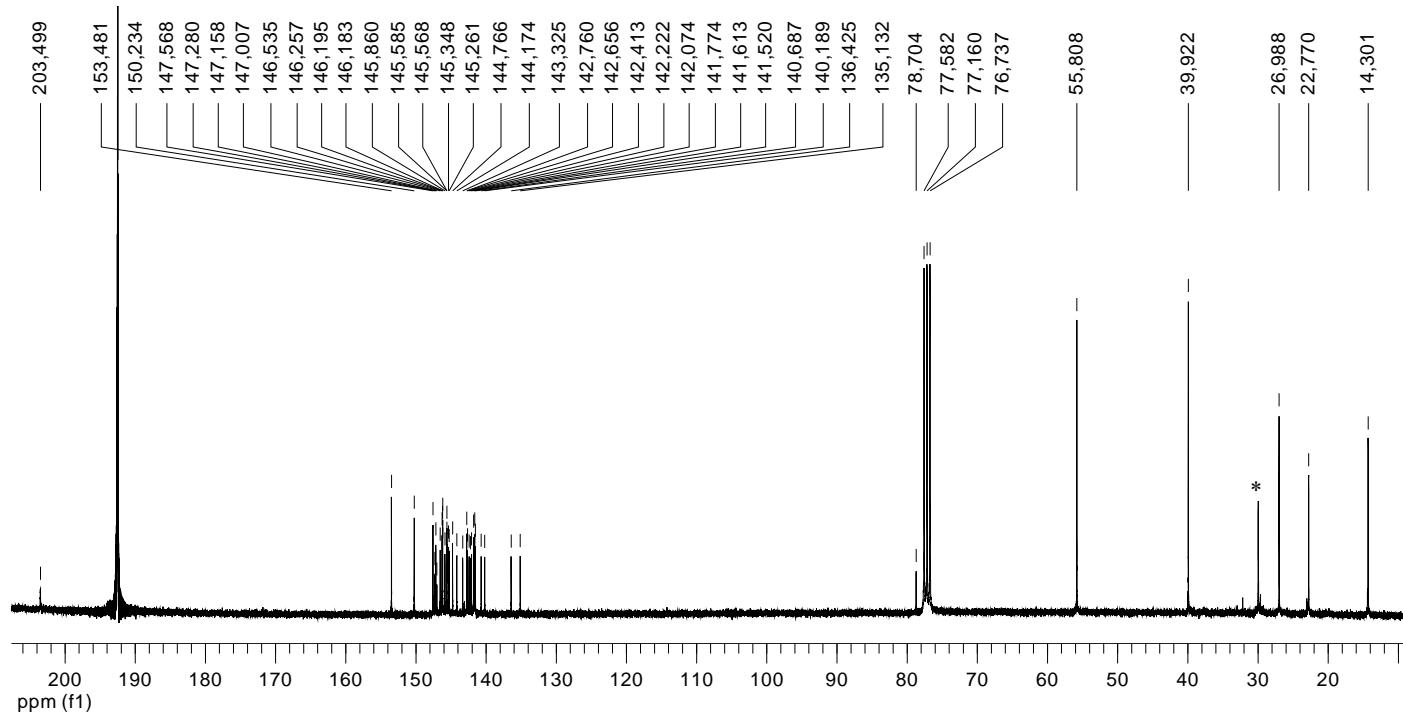


➤ Compound **6a**

a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )

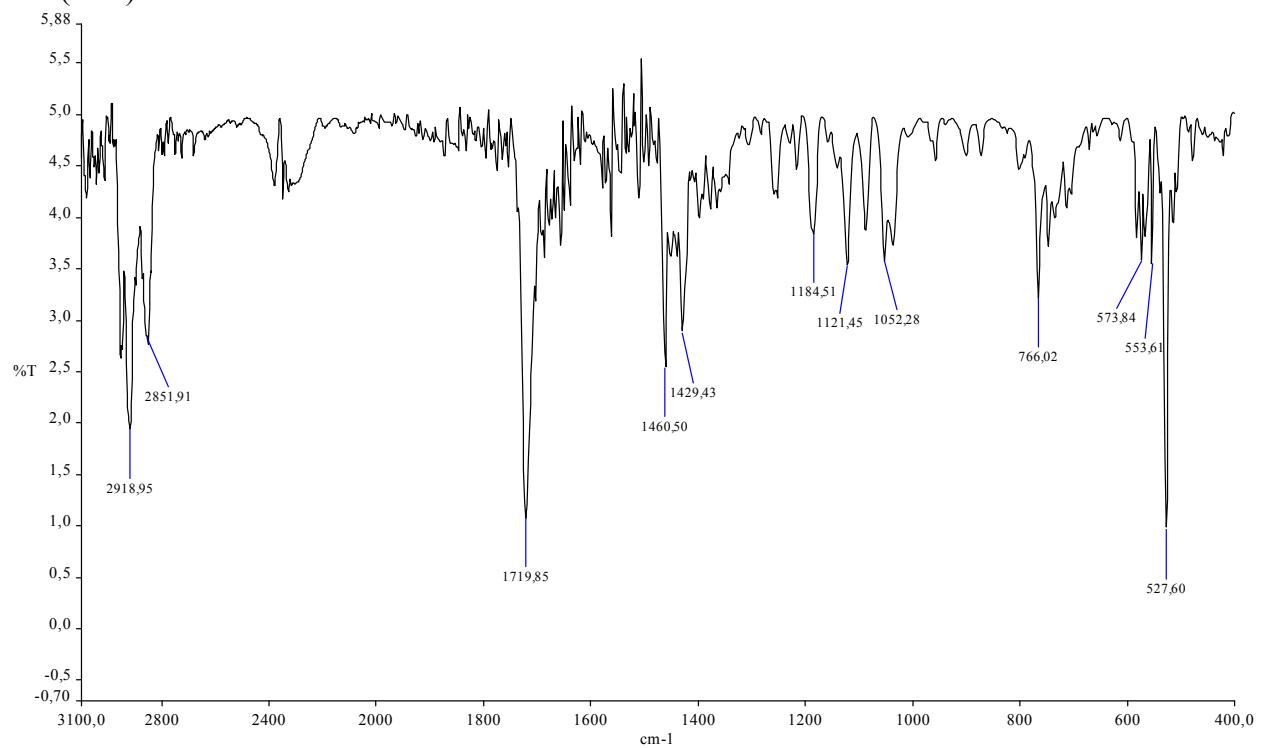


b)  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3/\text{CS}_2$ )

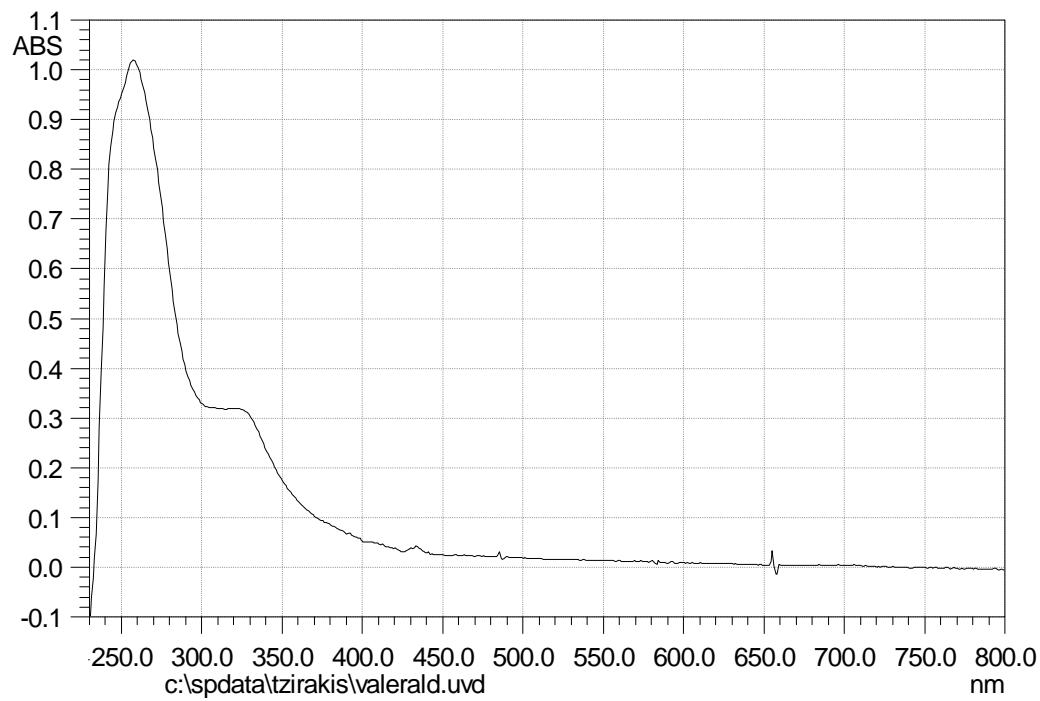


\*grease

c) FT-IR (KBr)

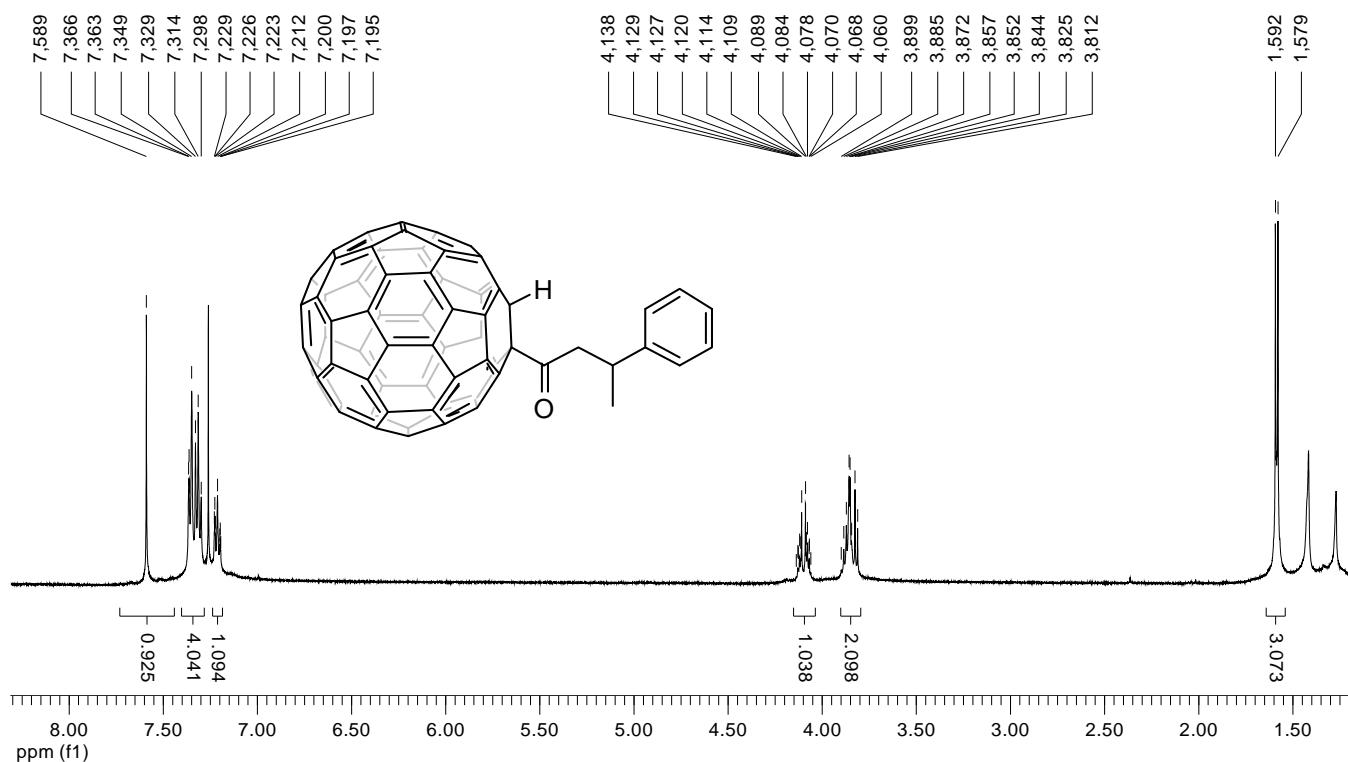


d) UV-vis (CHCl<sub>3</sub>)

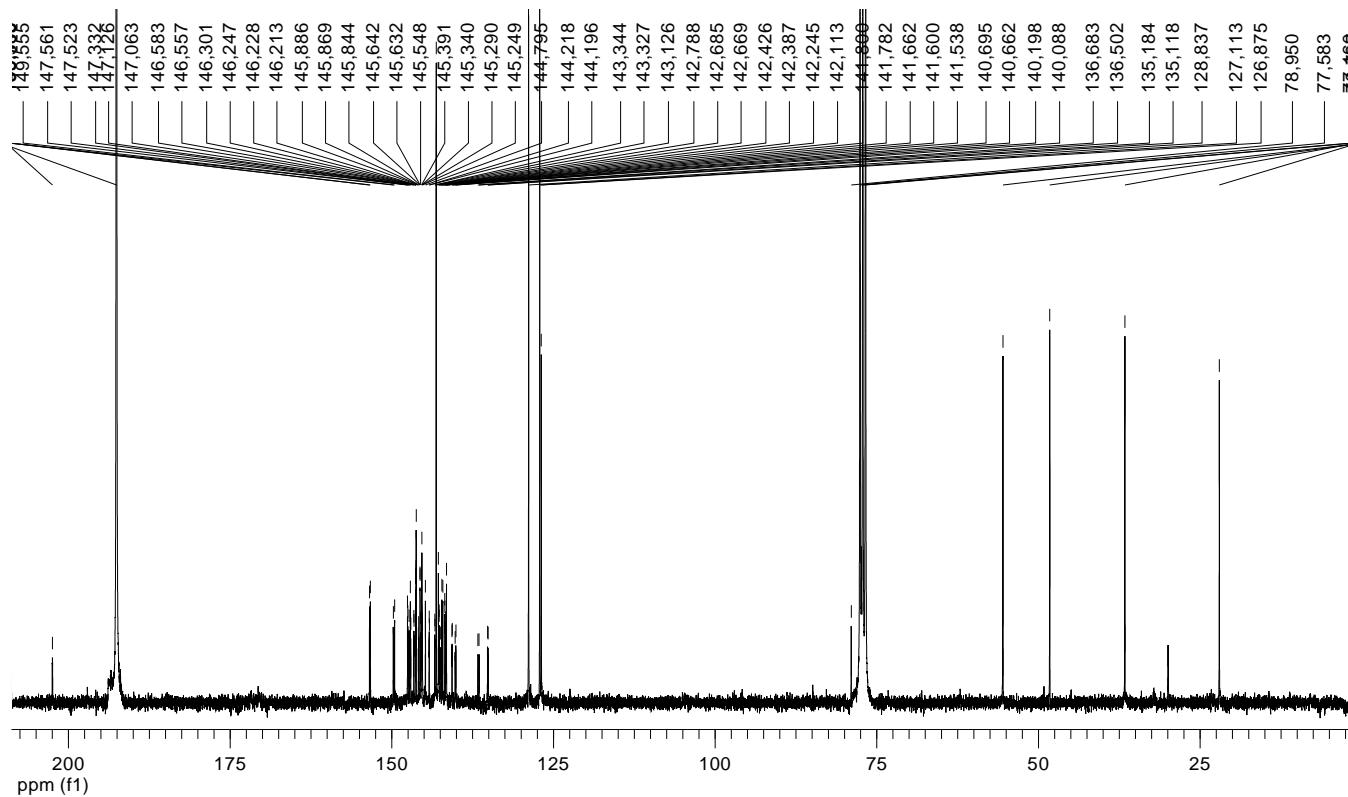


➤ Compound 7a

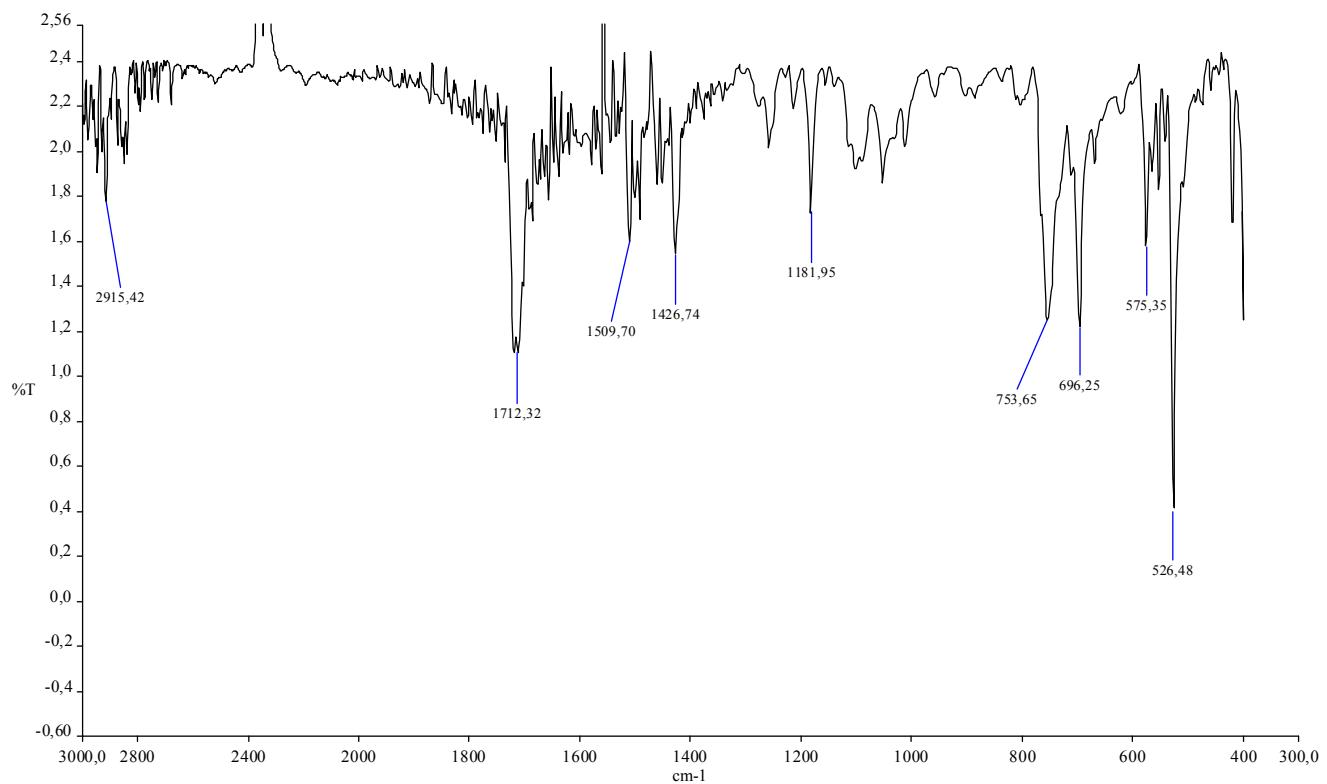
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



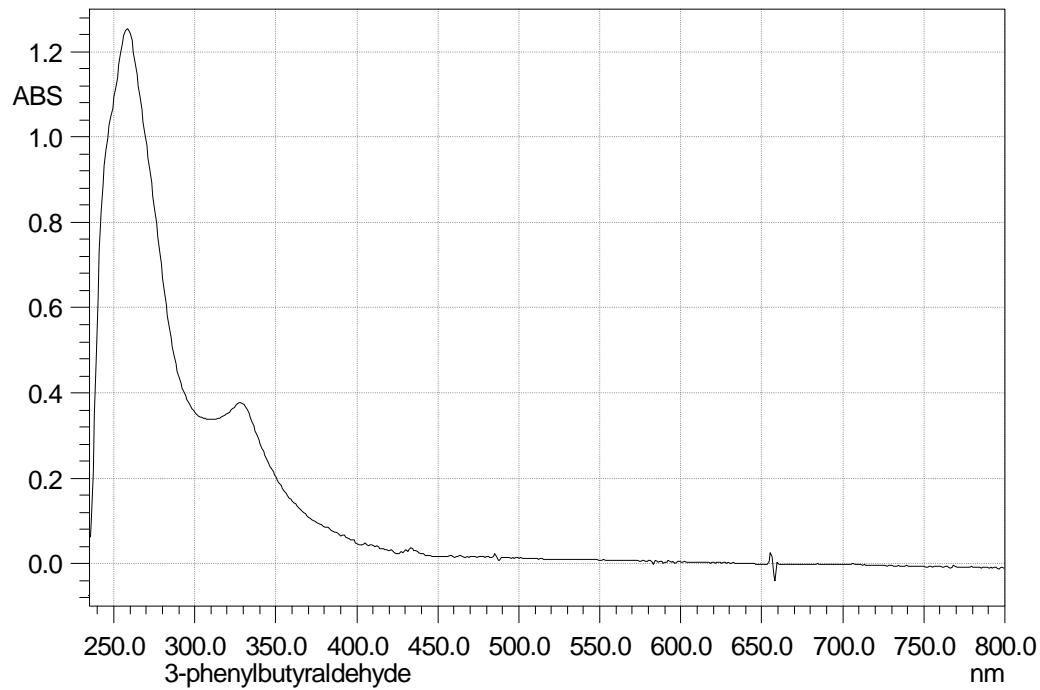
b)  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



c) FT-IR (KBr)

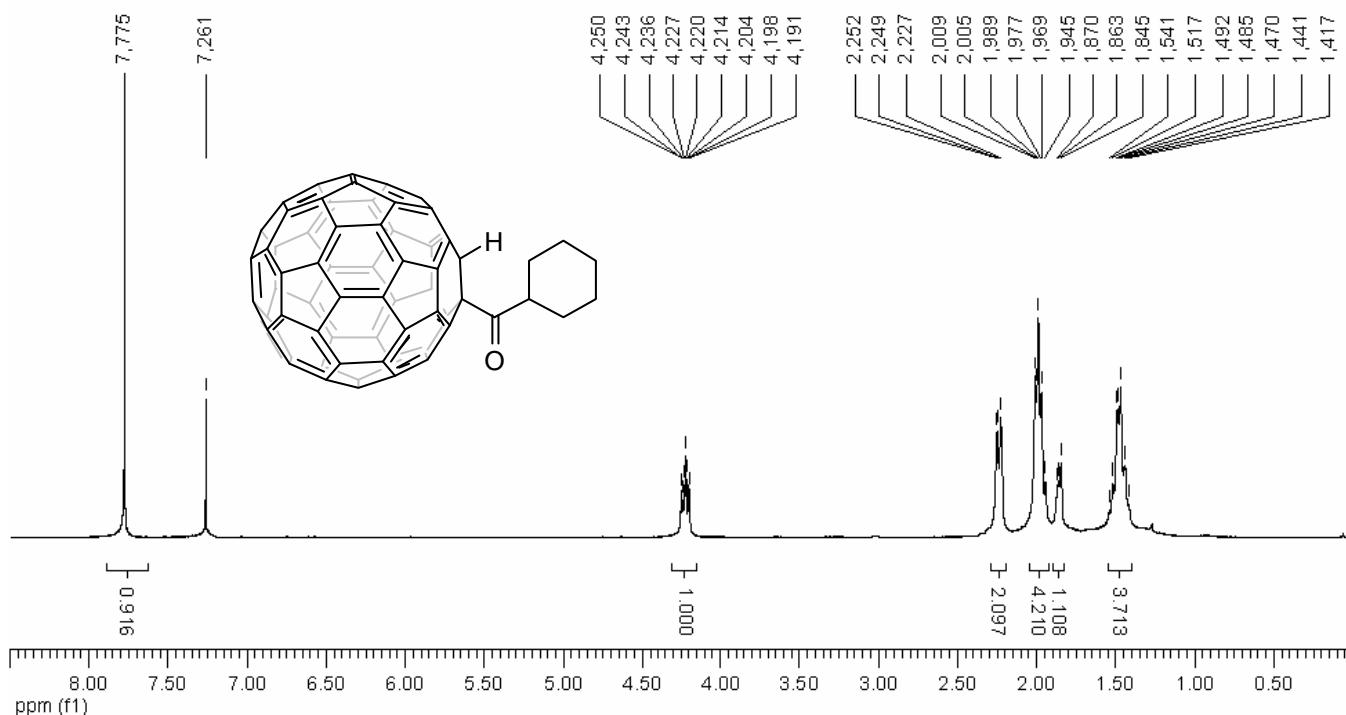


d) UV-vis (CHCl<sub>3</sub>)

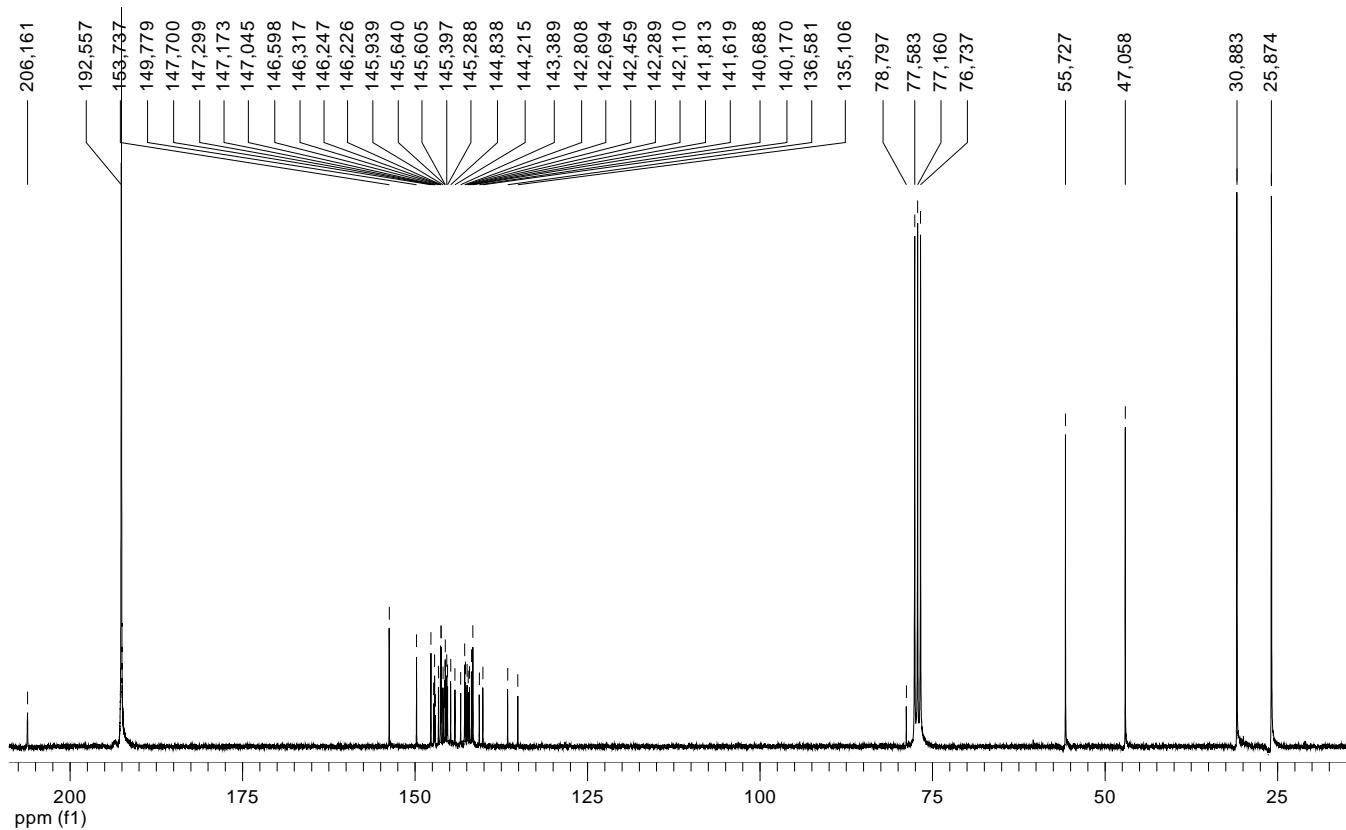


➤ Compound **8a**

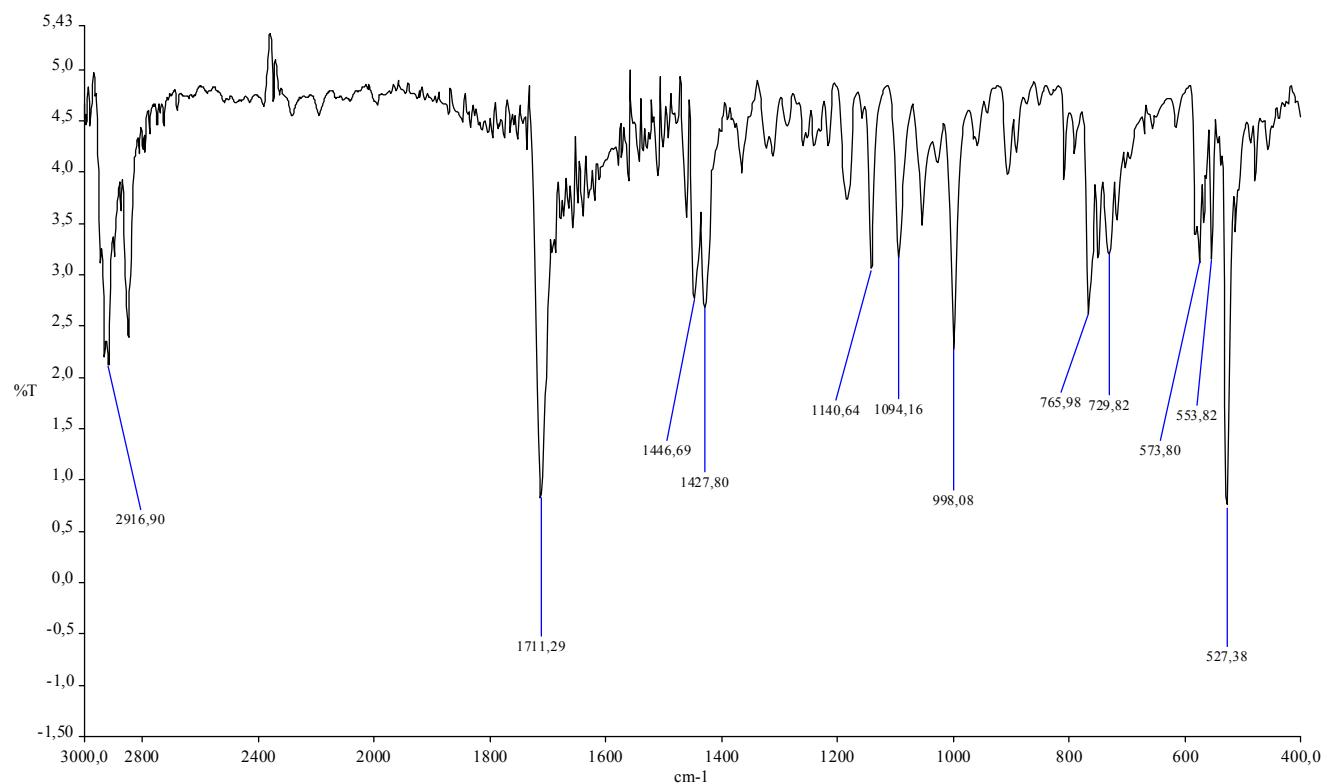
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



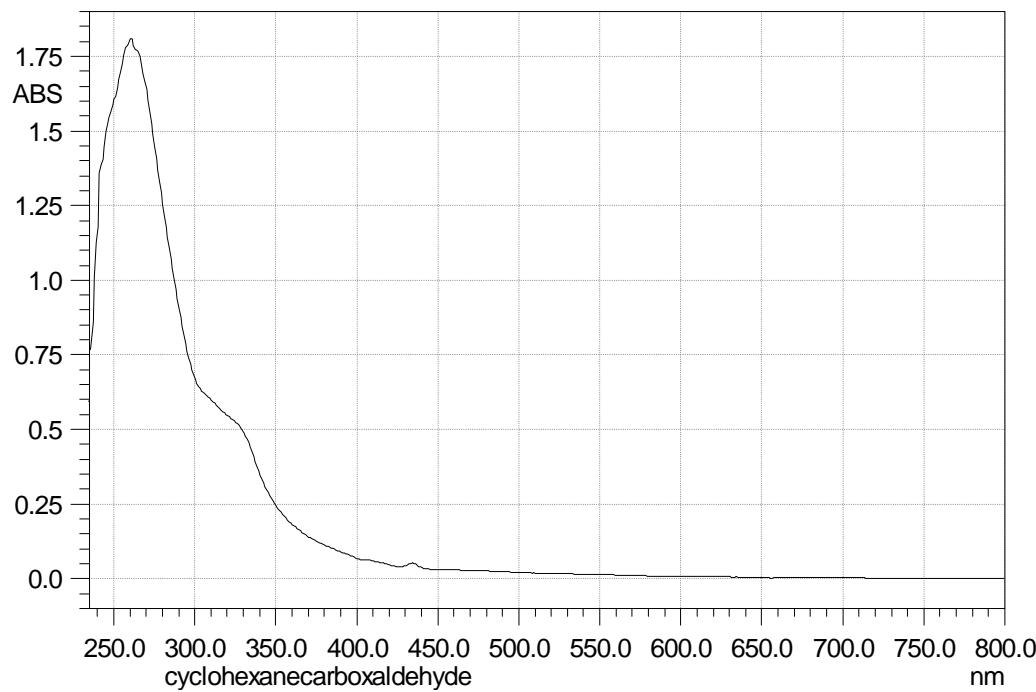
b)  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



c) FT-IR (KBr)

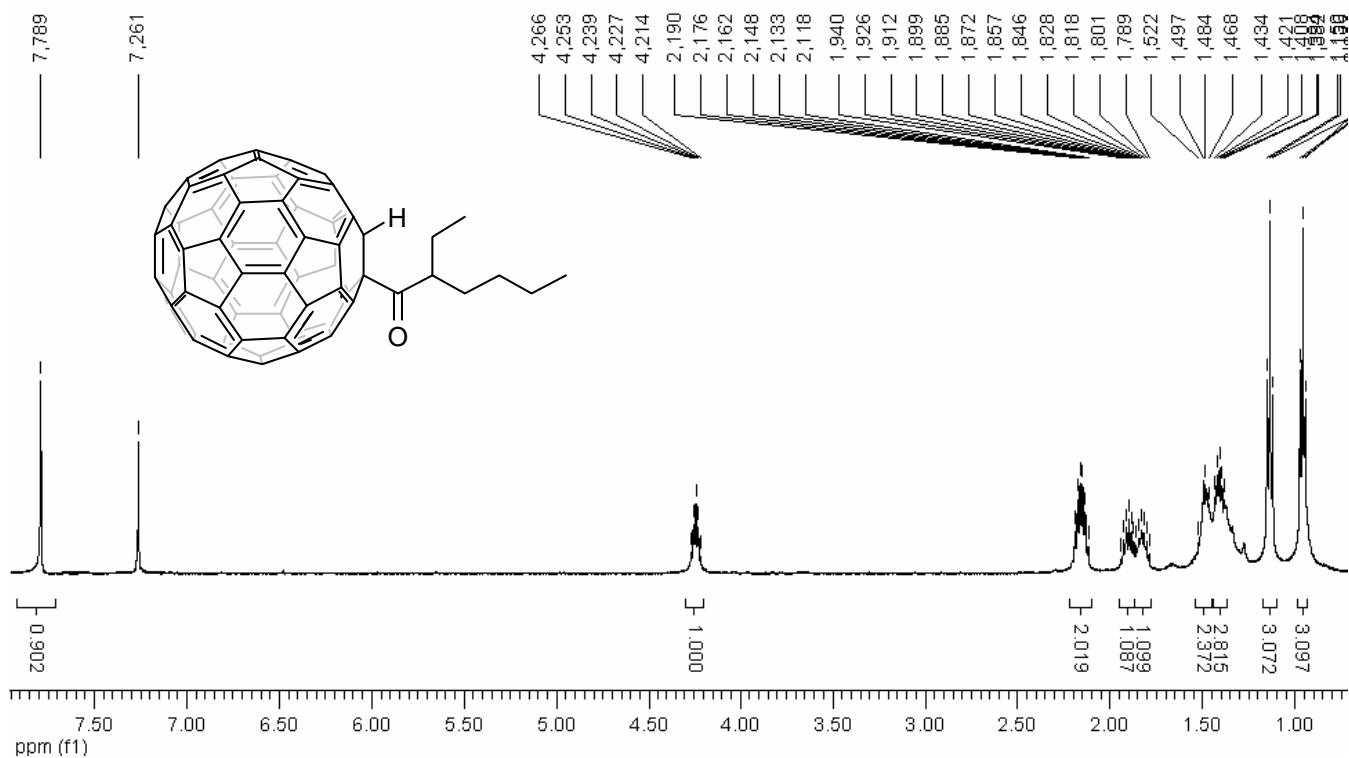


d) UV-vis (CHCl<sub>3</sub>)

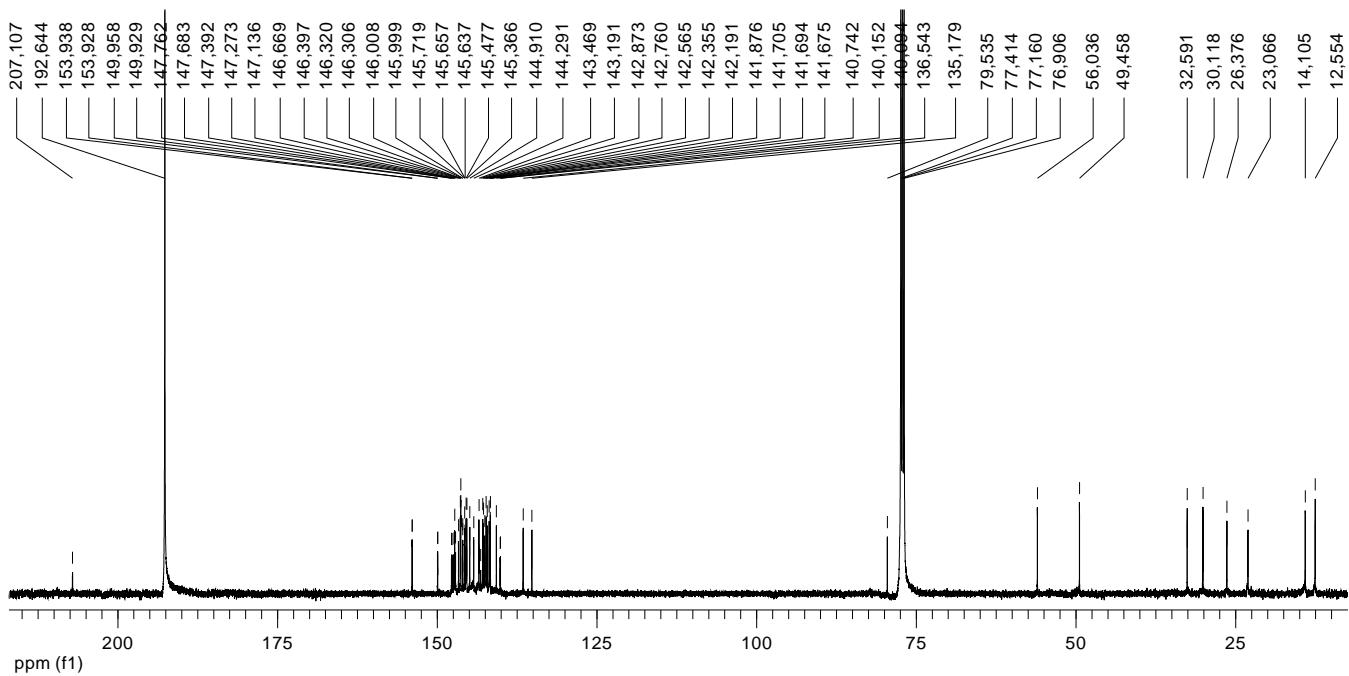


➤ Compound **9a**

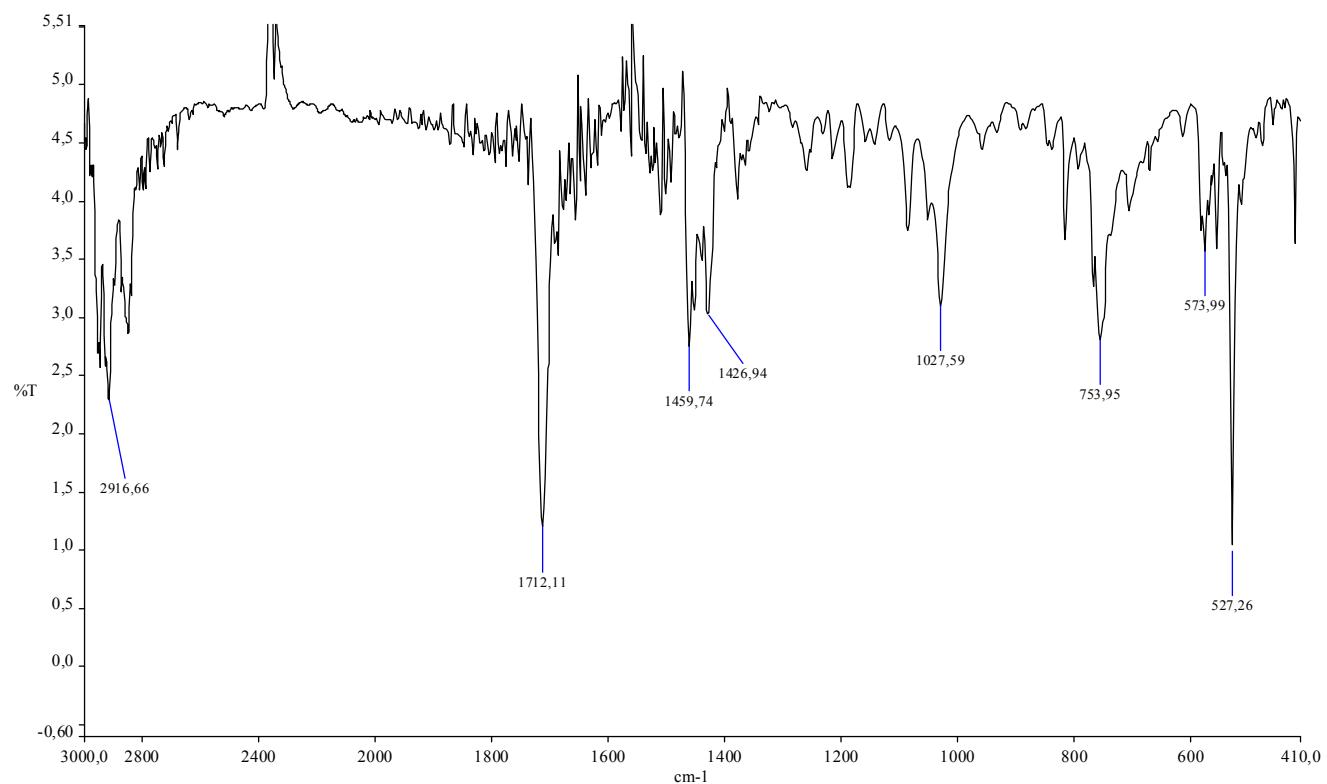
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



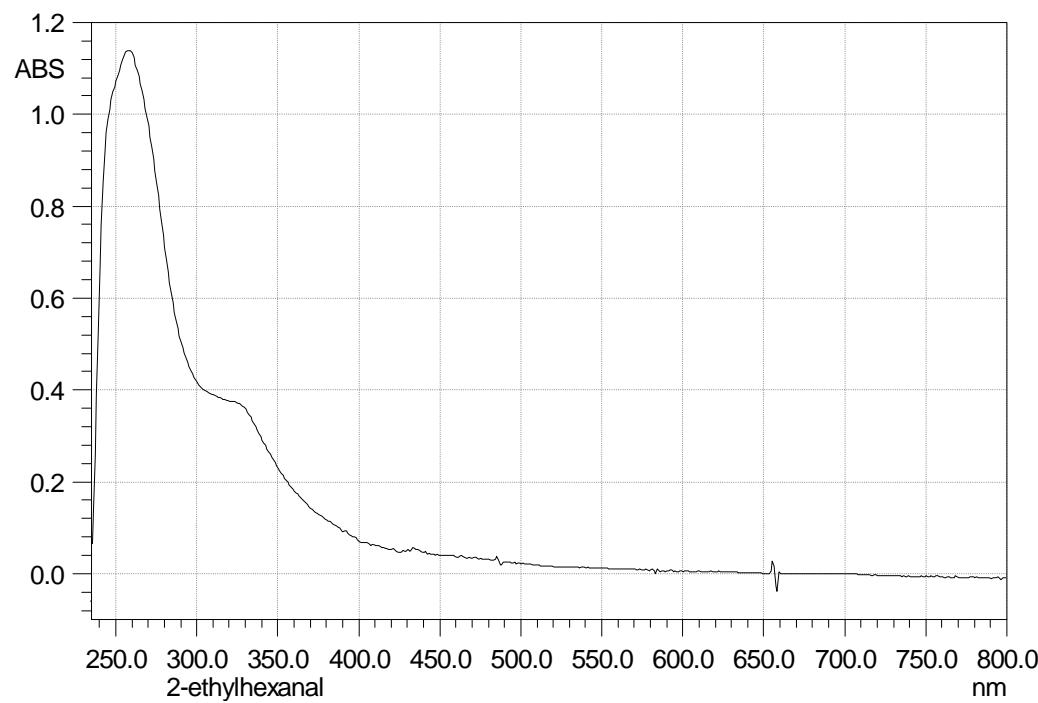
b)  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



c) FT-IR (KBr)

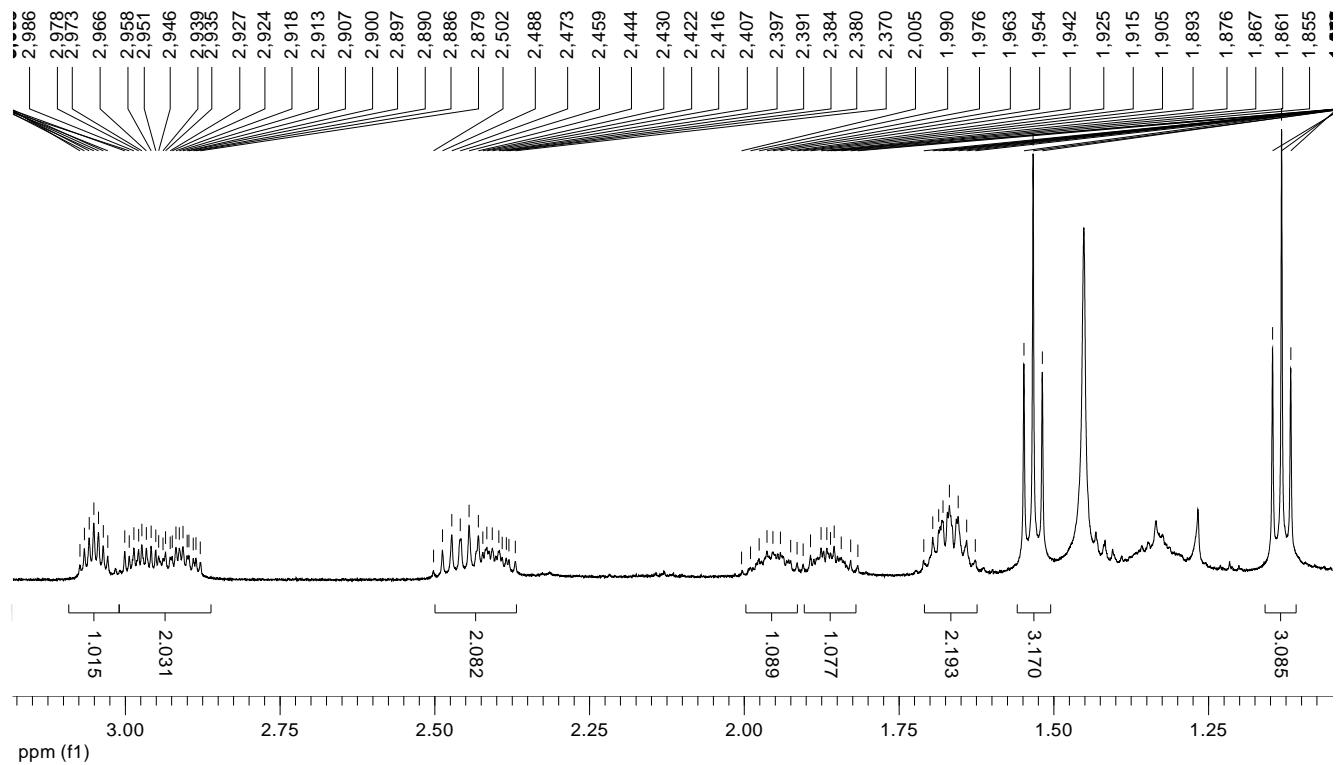
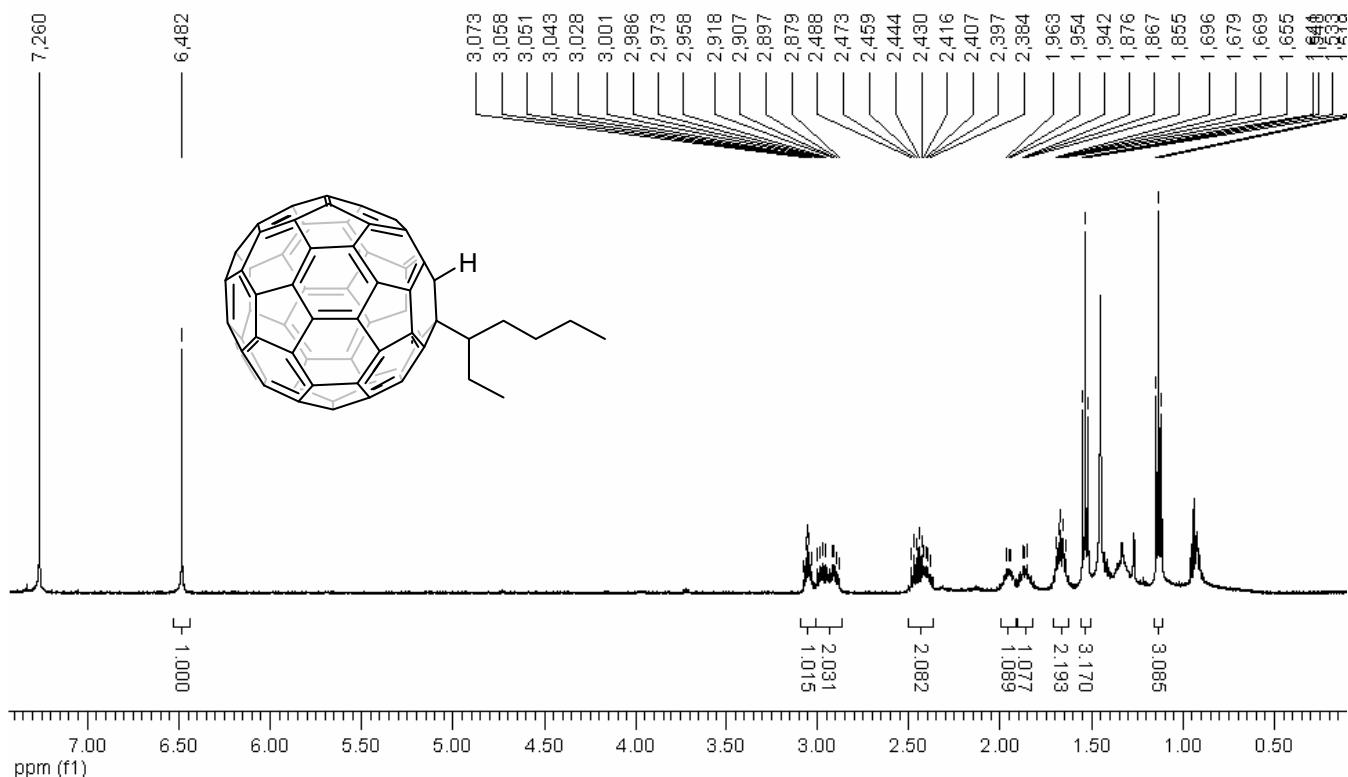


d) UV-vis (CHCl<sub>3</sub>)

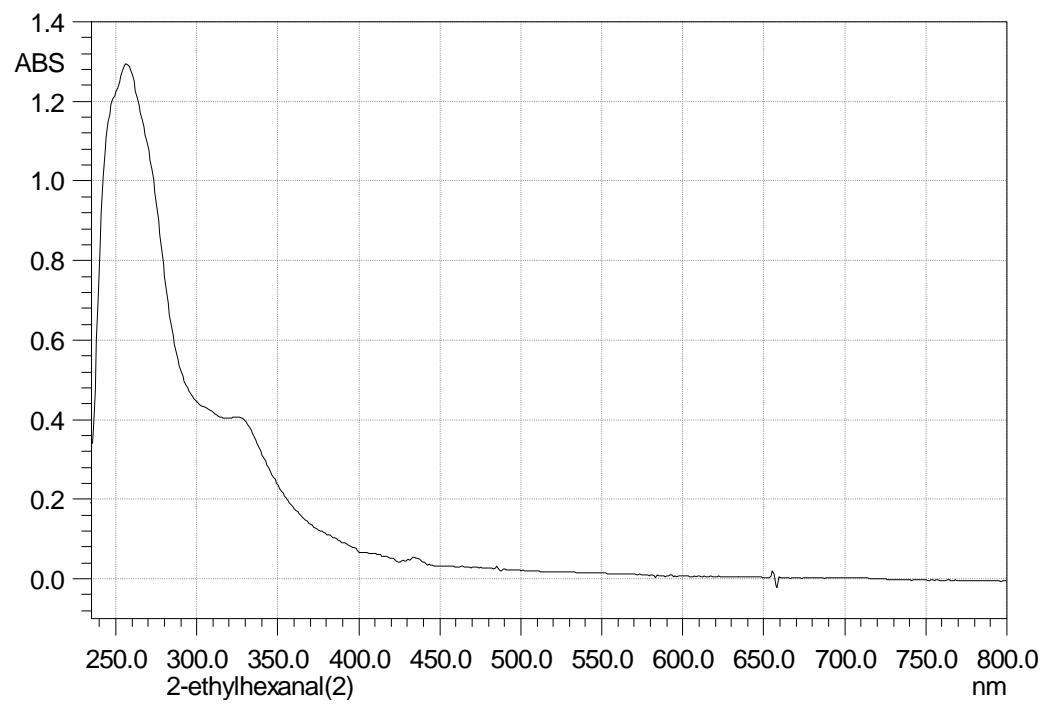


## ➤ Compound 9b

a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )

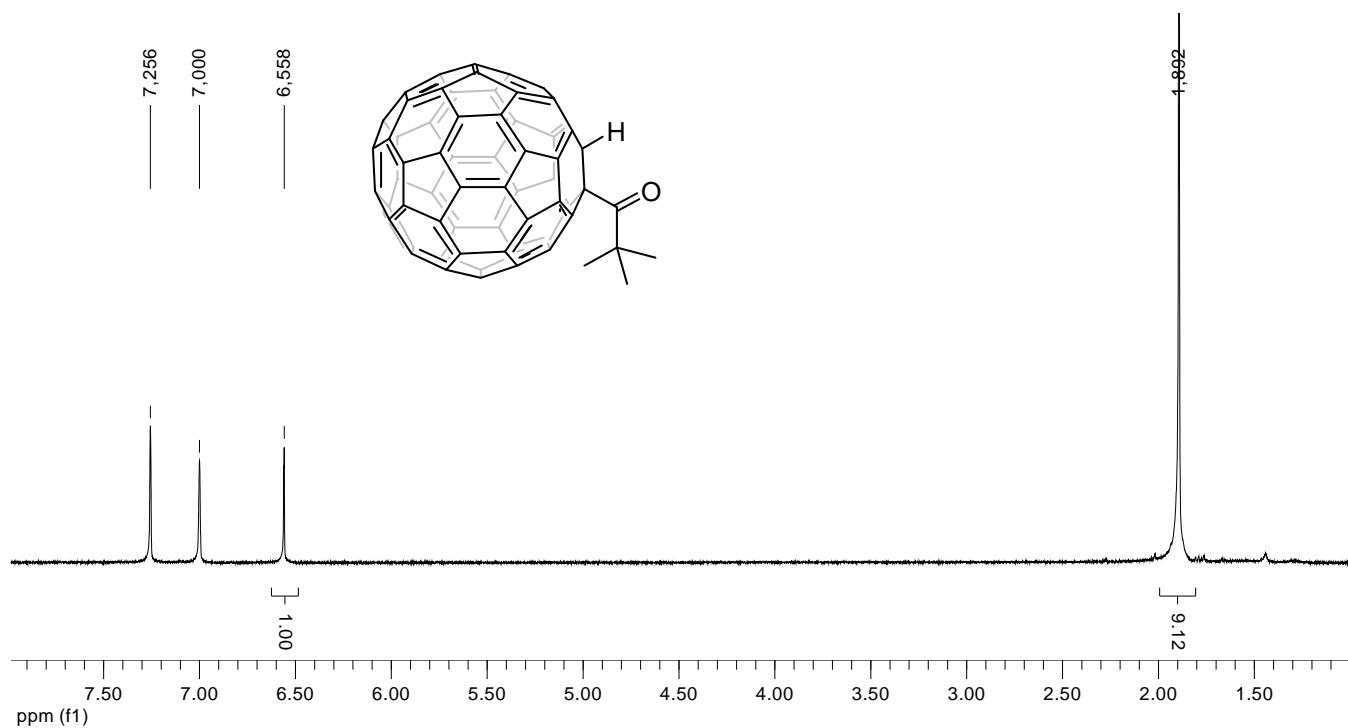


b) UV-vis ( $\text{CHCl}_3$ )

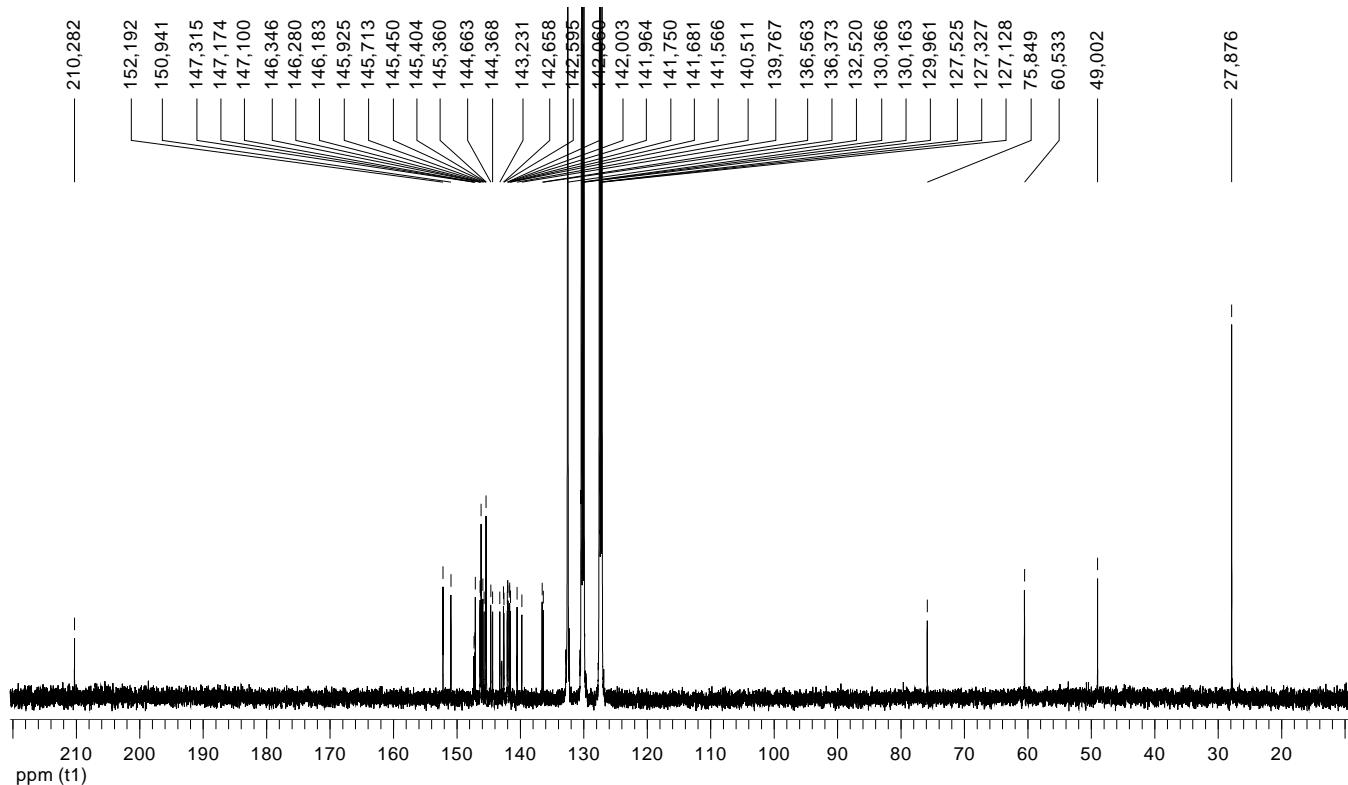


➤ Compound **10a**

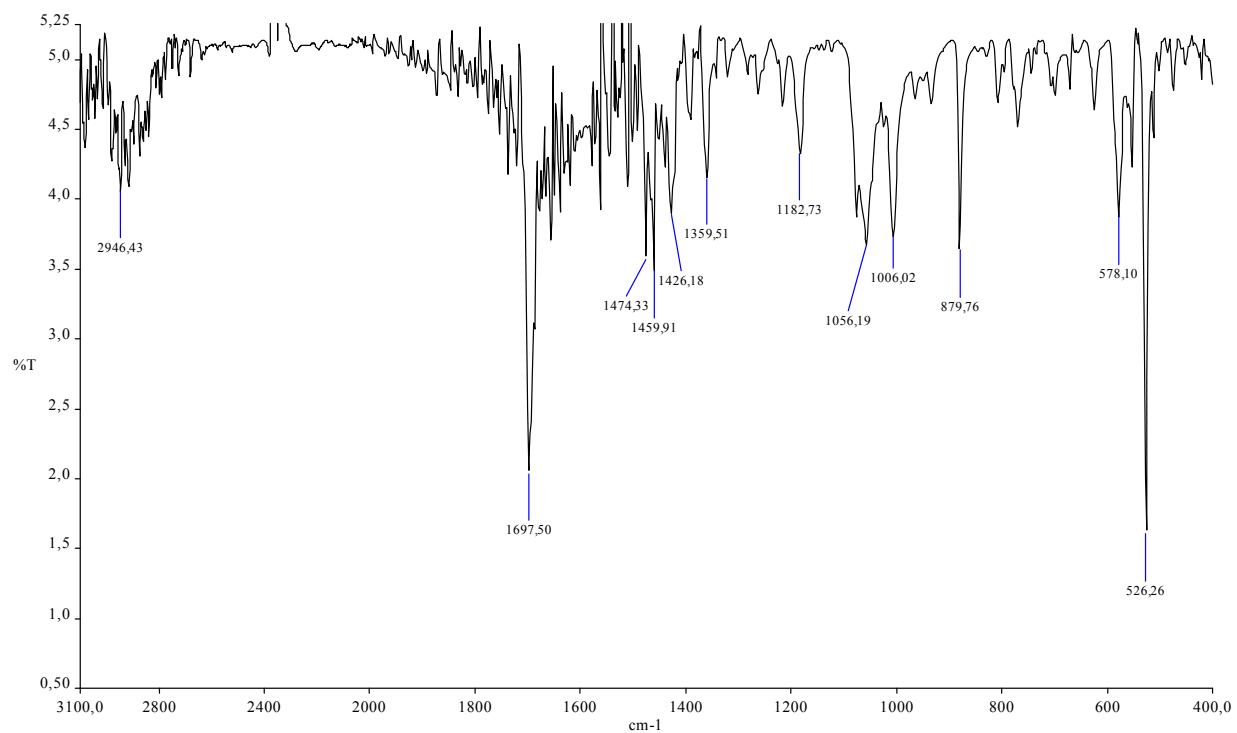
a)  $^1\text{H}$  NMR (500 MHz, ODCB- $d_4$ )



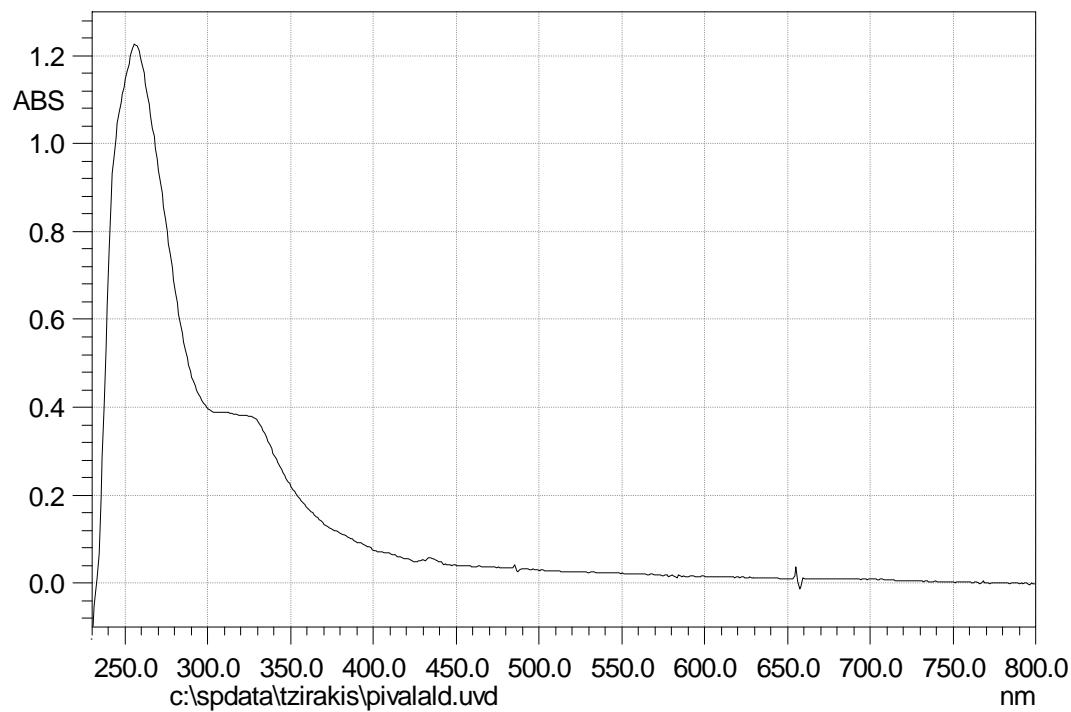
b)  $^{13}\text{C}$  NMR (125 MHz, ODCB- $d_4$ )



c) FT-IR (KBr)

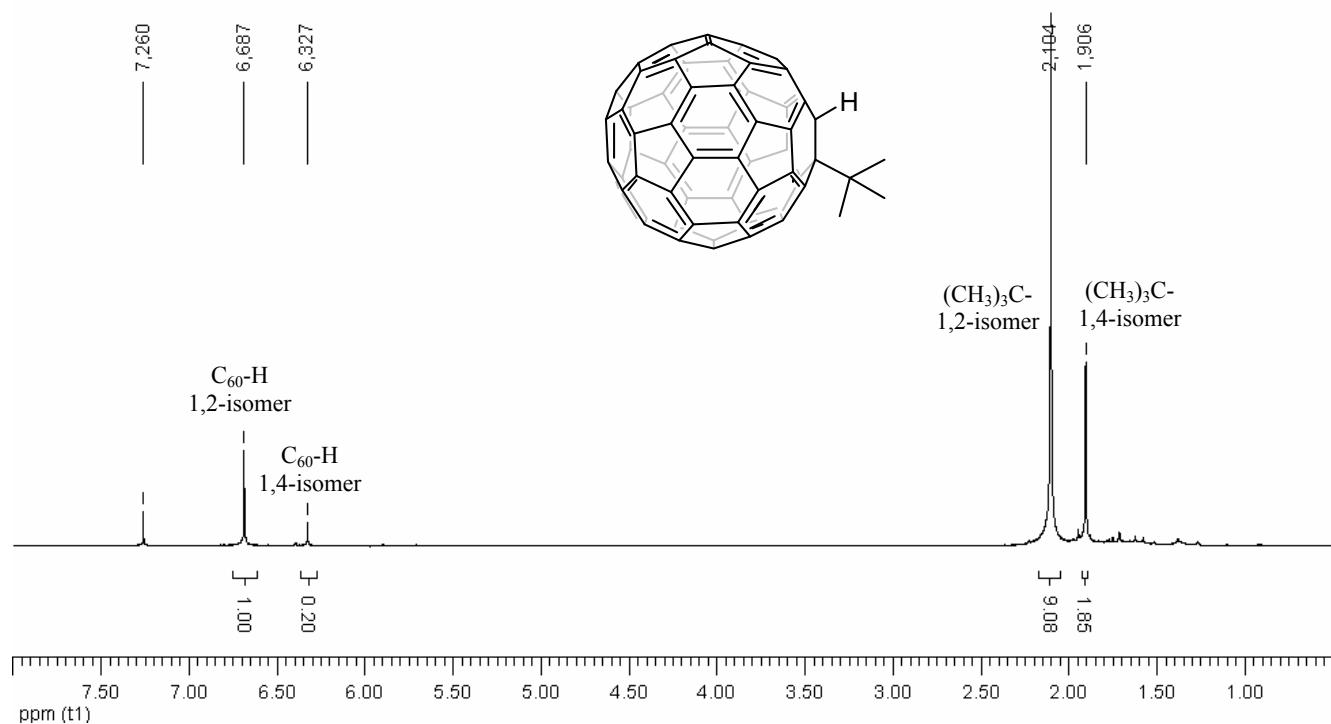


d) UV-vis (CHCl<sub>3</sub>)

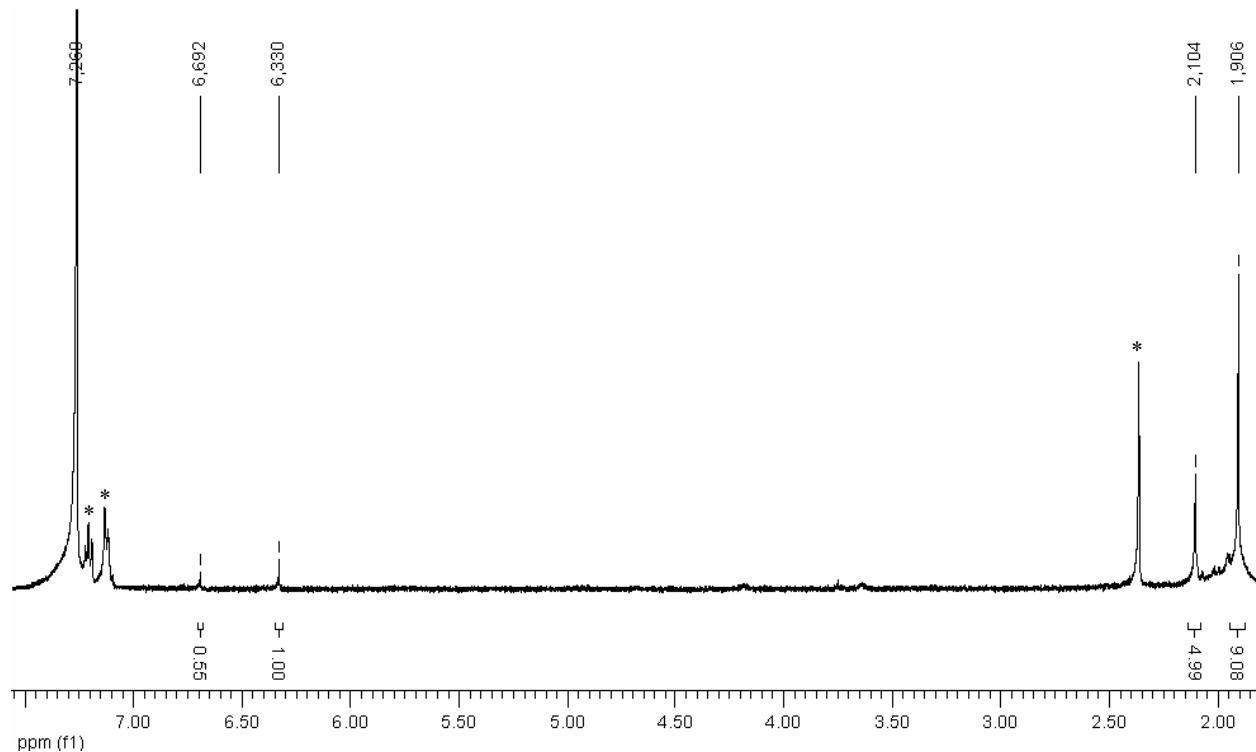


➤ Compound **10b**

a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ ) when the reaction of  $\text{C}_{60}$  with **10** was performed at  $T = 5\text{--}10\text{ }^\circ\text{C}$ .



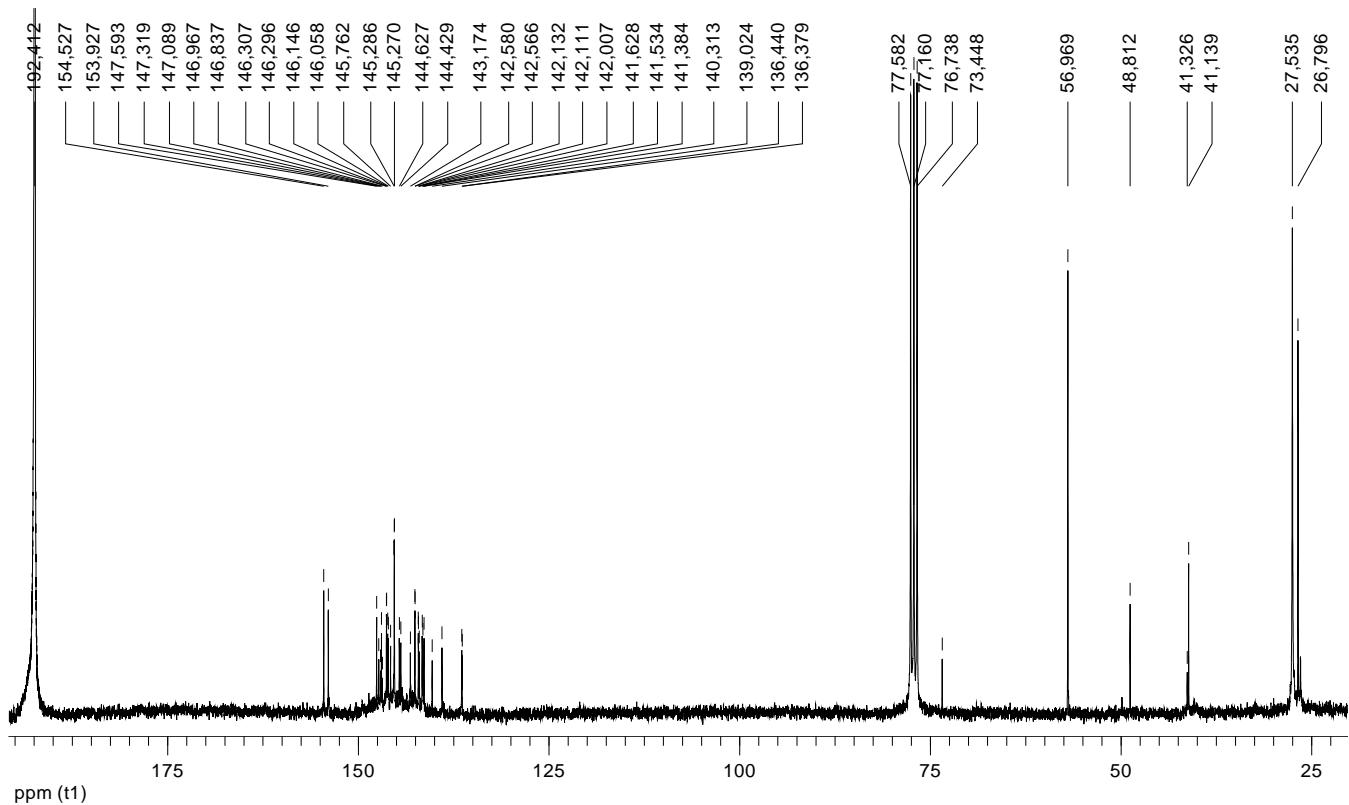
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ ) when the reaction of  $\text{C}_{60}$  with **10** was performed at  $-40\text{ }^\circ\text{C}$ .



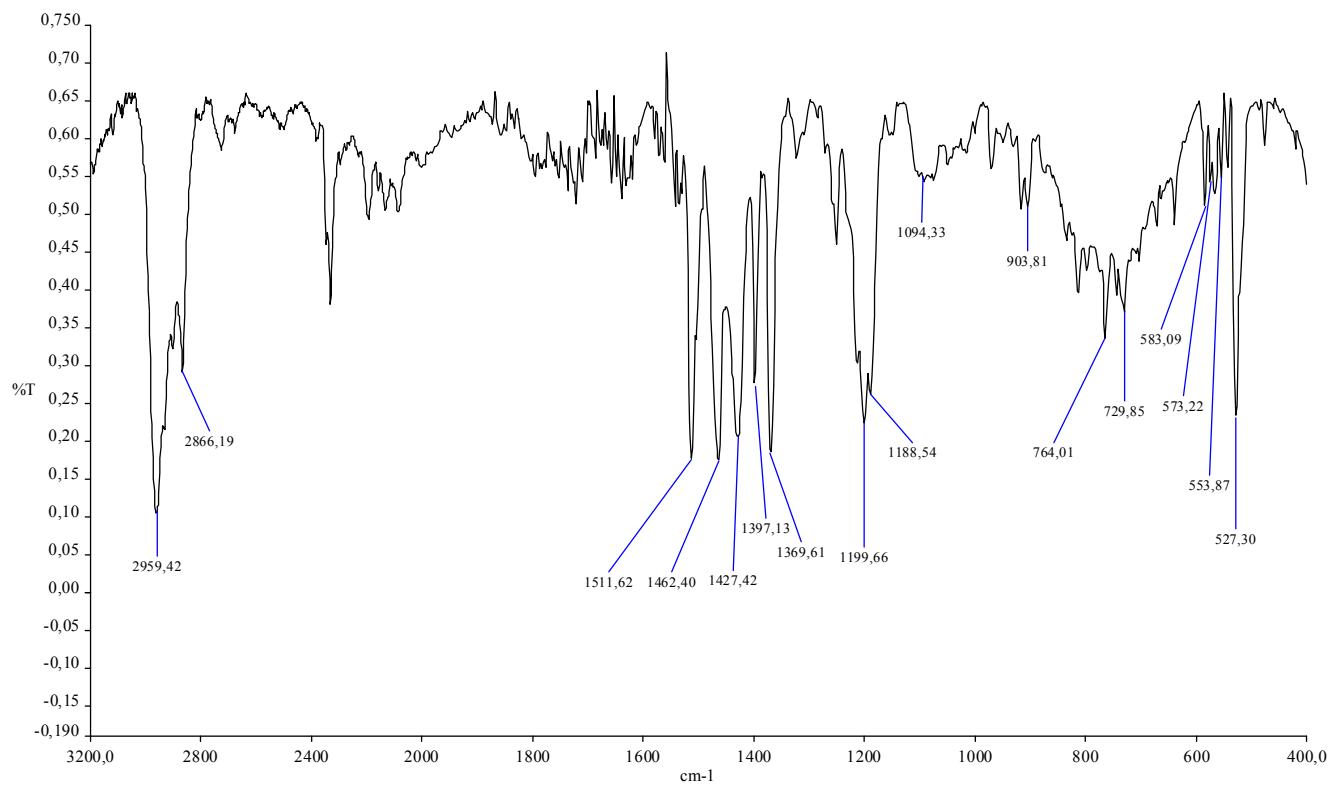
\* toluene

b)  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2$ )

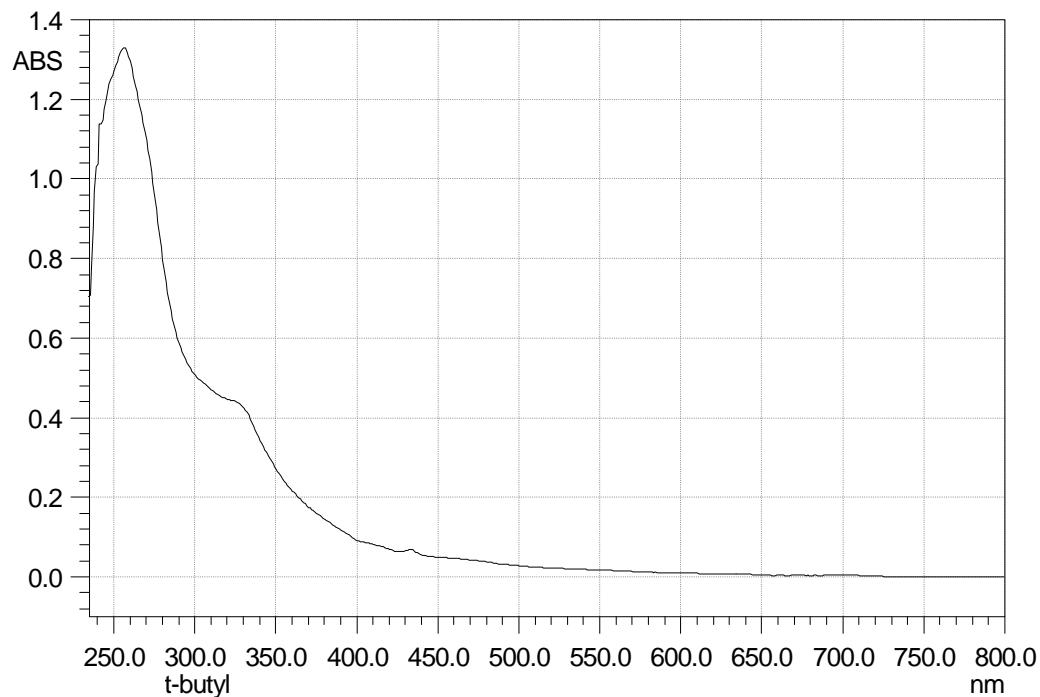
(Mixture of 1,2 and 1,4-isomers, 5:1 molar ratio)



c) FT-IR (KBr)

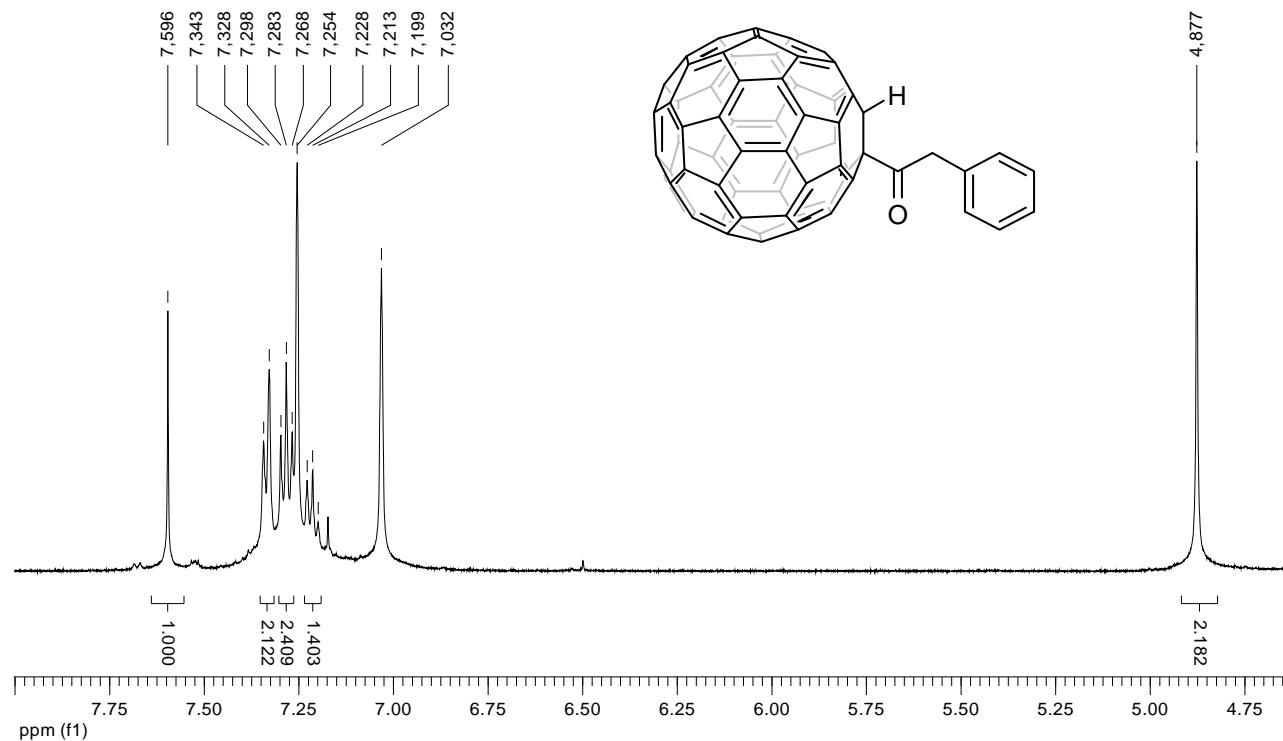


d) UV-vis (CHCl<sub>3</sub>)

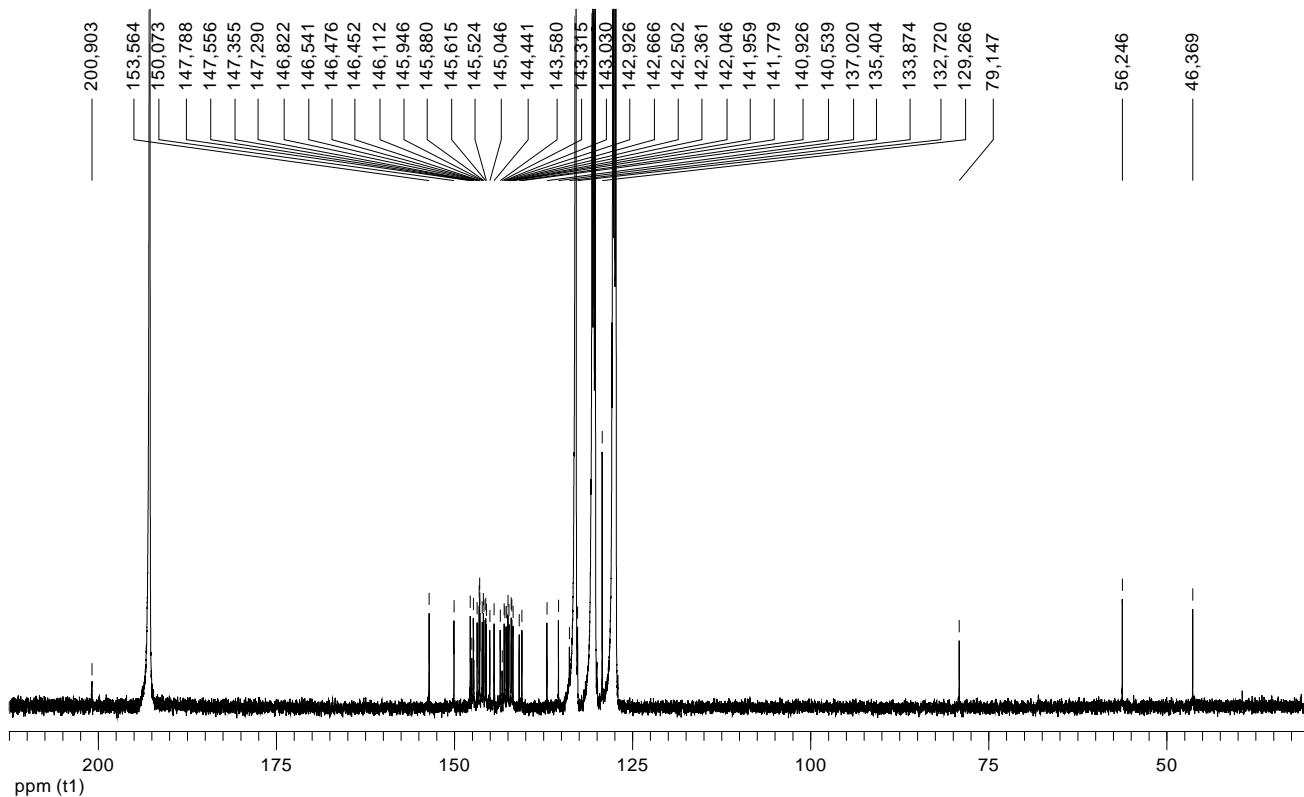


➤ Compound **11a**

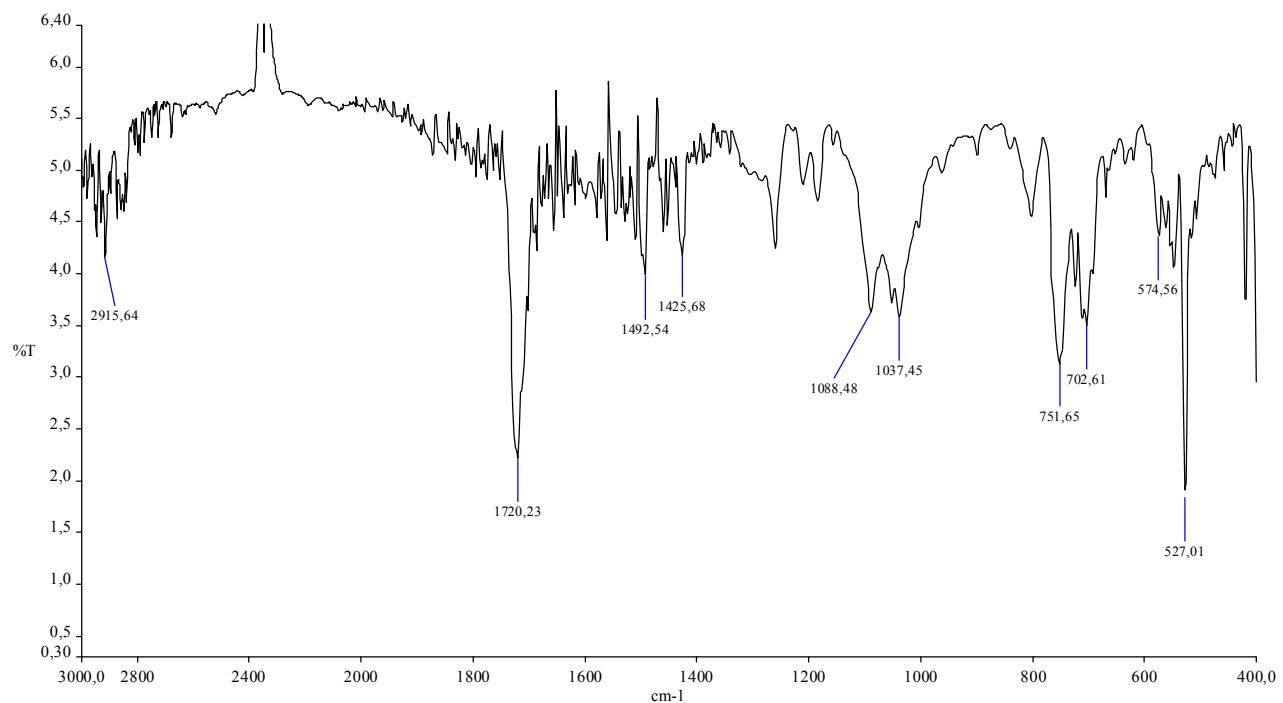
a)  $^1\text{H}$  NMR (500 MHz, ODCB- $d_4$ /CS<sub>2</sub>)



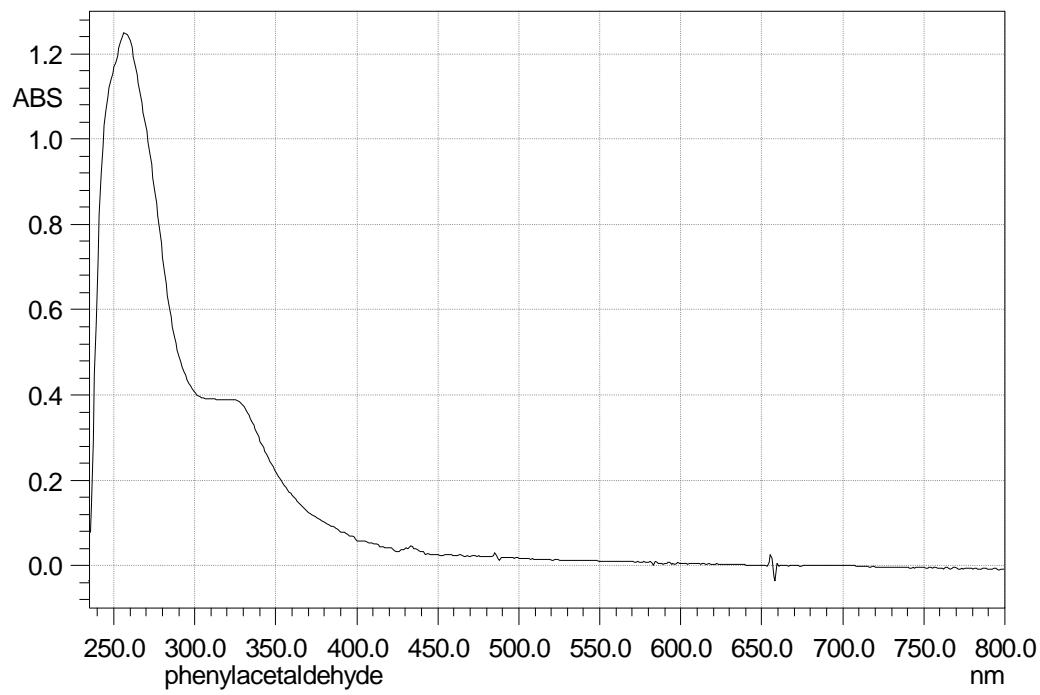
b)  $^{13}\text{C}$  NMR (125 MHz, ODCB- $d_4$ /CS<sub>2</sub>)



c) FT-IR (KBr)

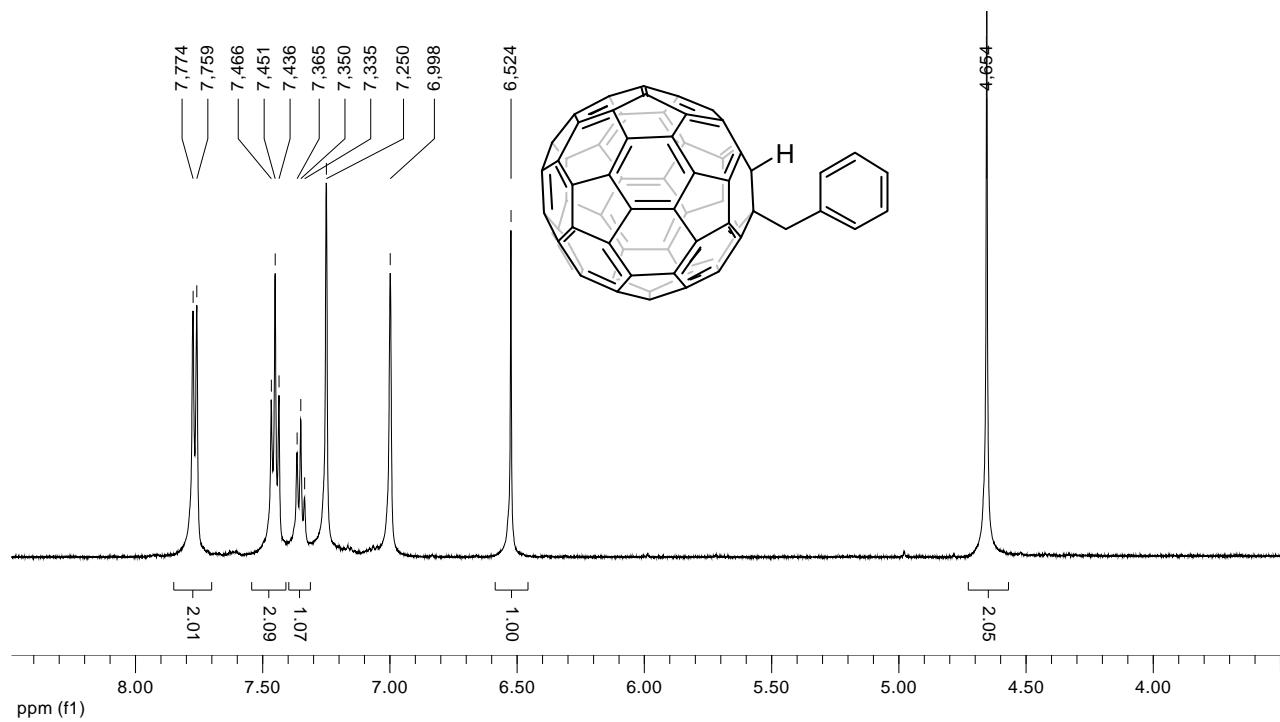


d) UV-vis (CHCl<sub>3</sub>)

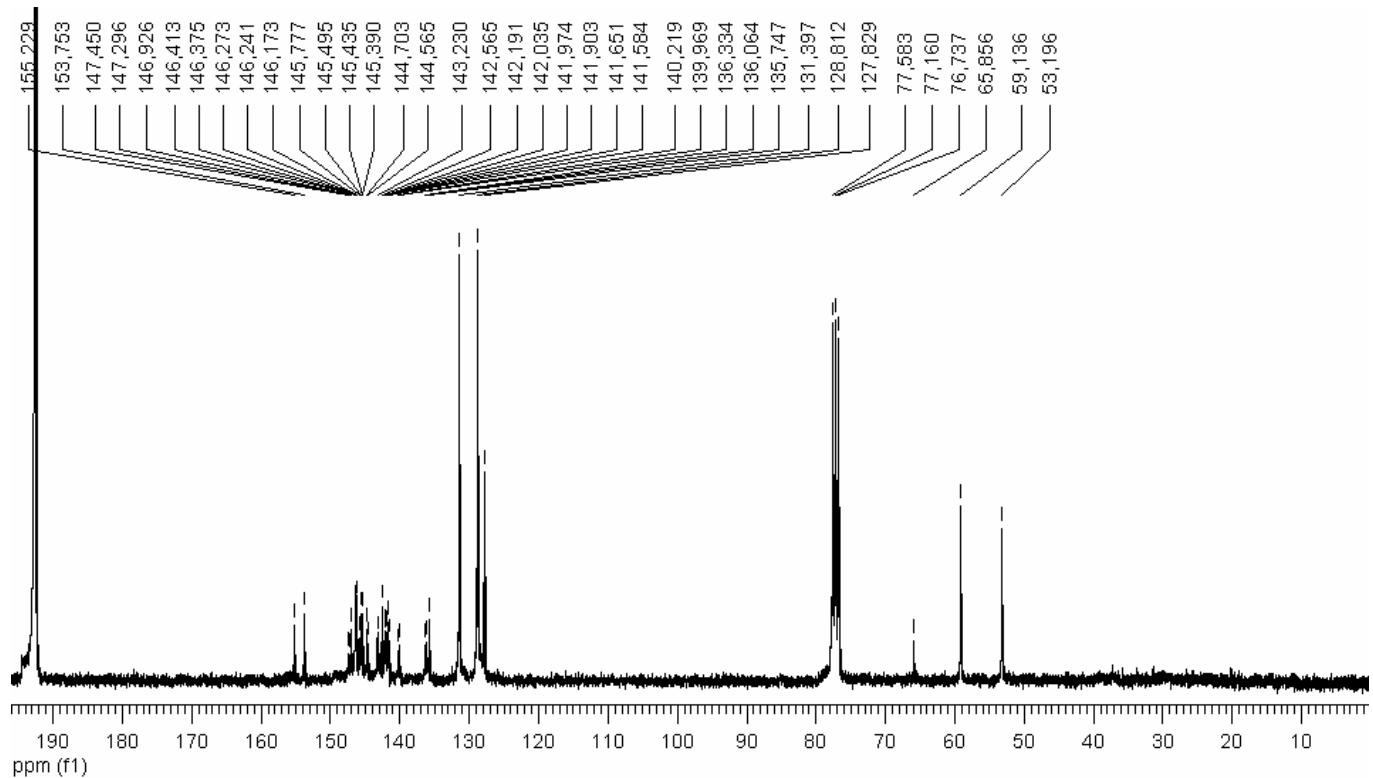


➤ Compound **11b**

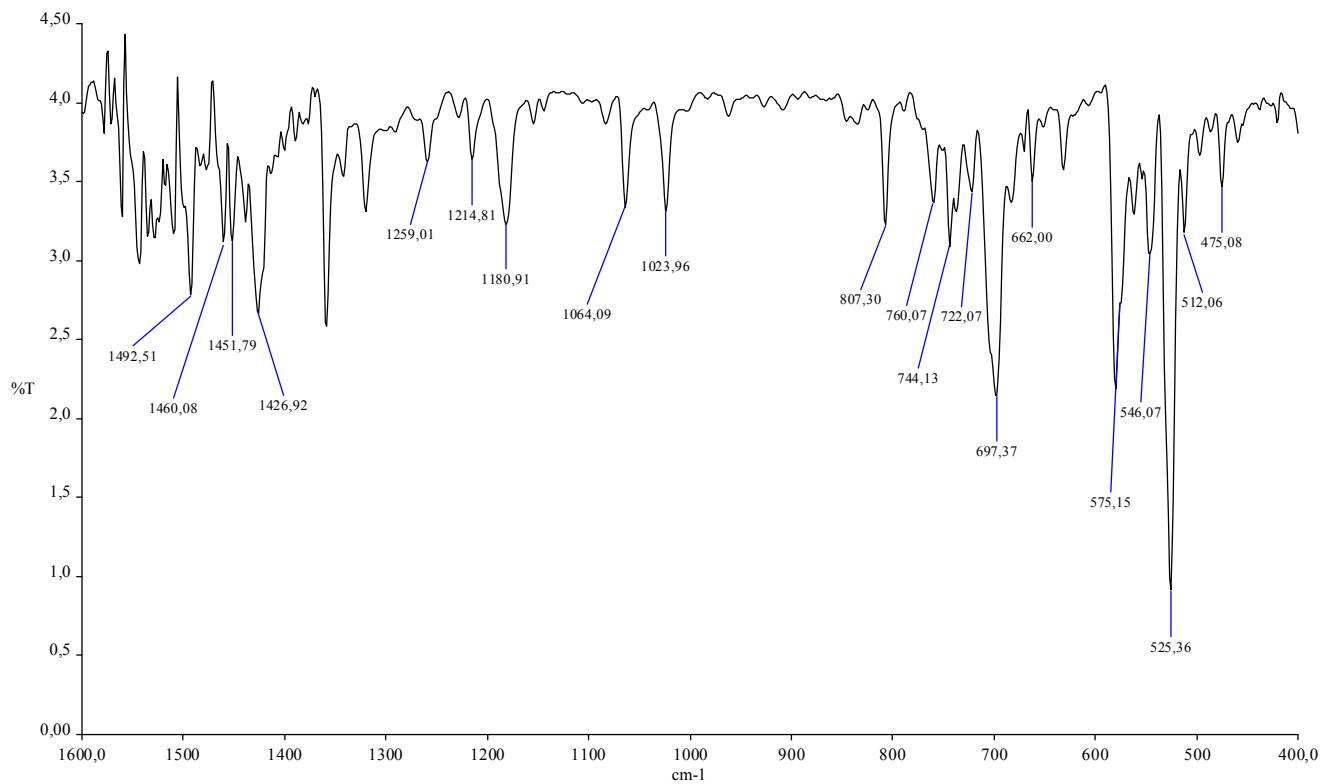
a)  $^1\text{H}$  NMR (500 MHz, ODCB- $d_4$ )



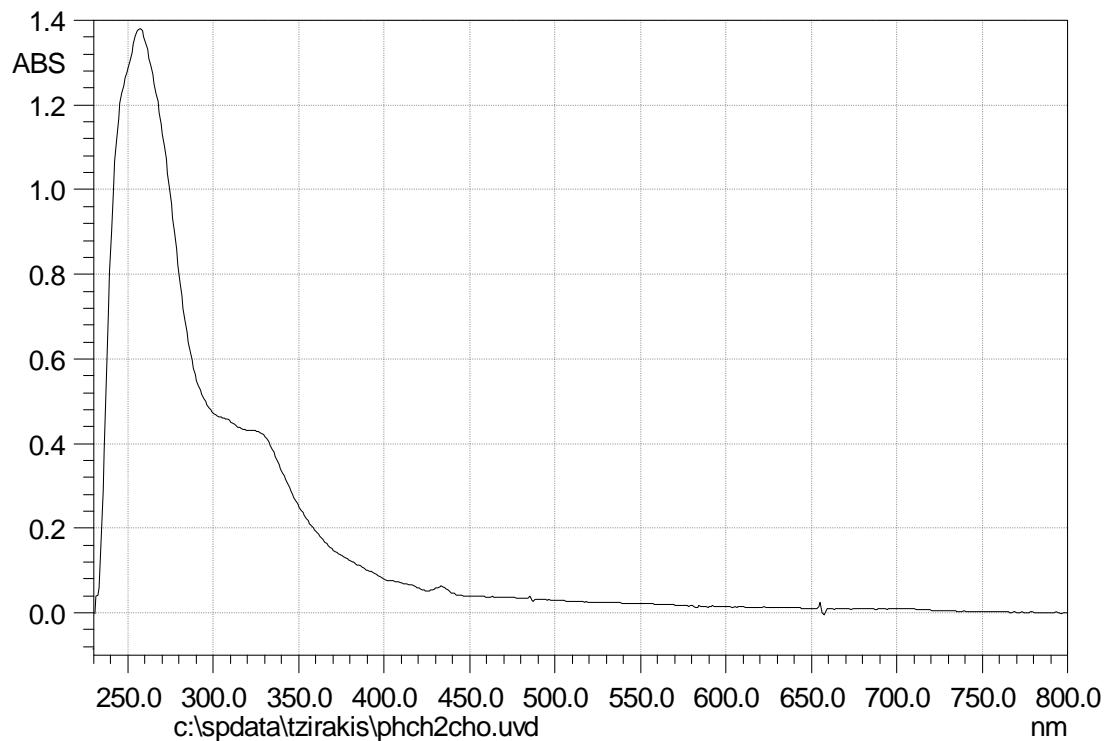
b)  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



c) FT-IR (KBr)

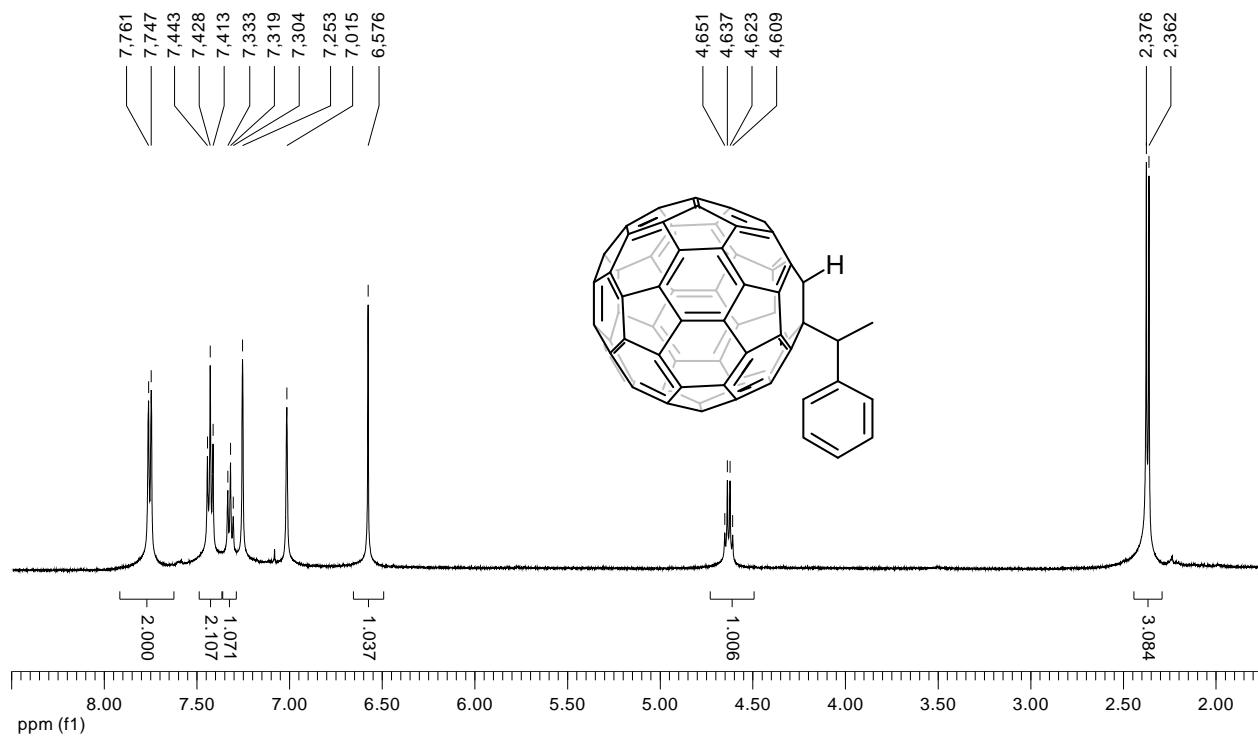


d) UV-vis ( $\text{CHCl}_3$ )

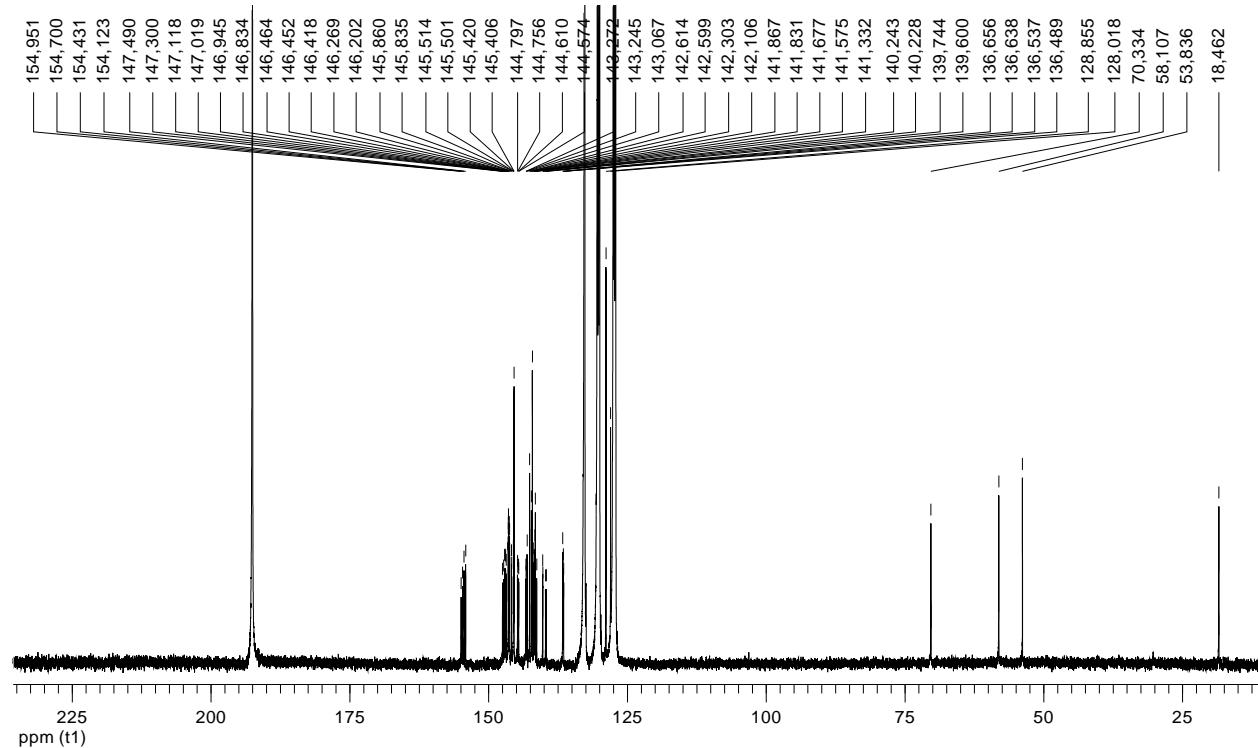


➤ Compound **12b**

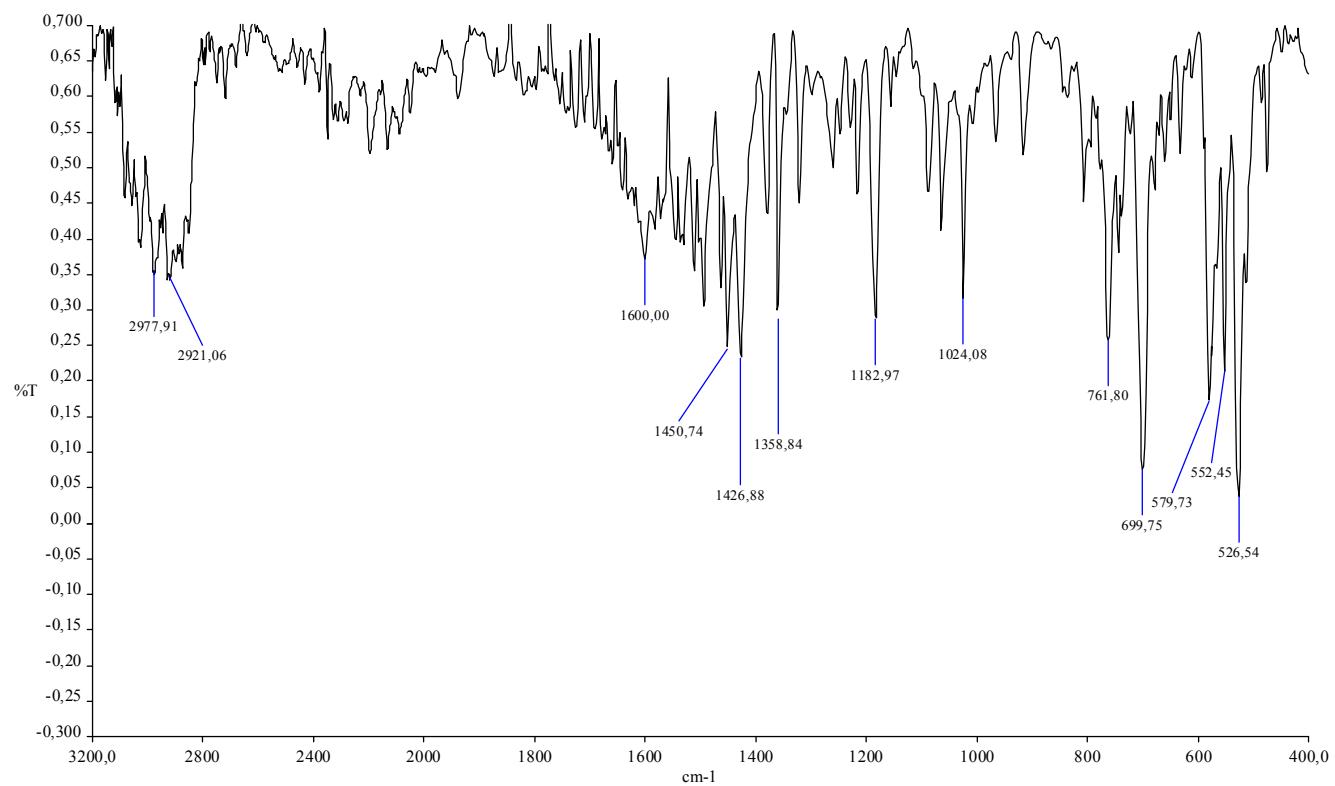
a)  $^1\text{H}$  NMR (500 MHz, ODCB- $d_4$ /CS<sub>2</sub>)



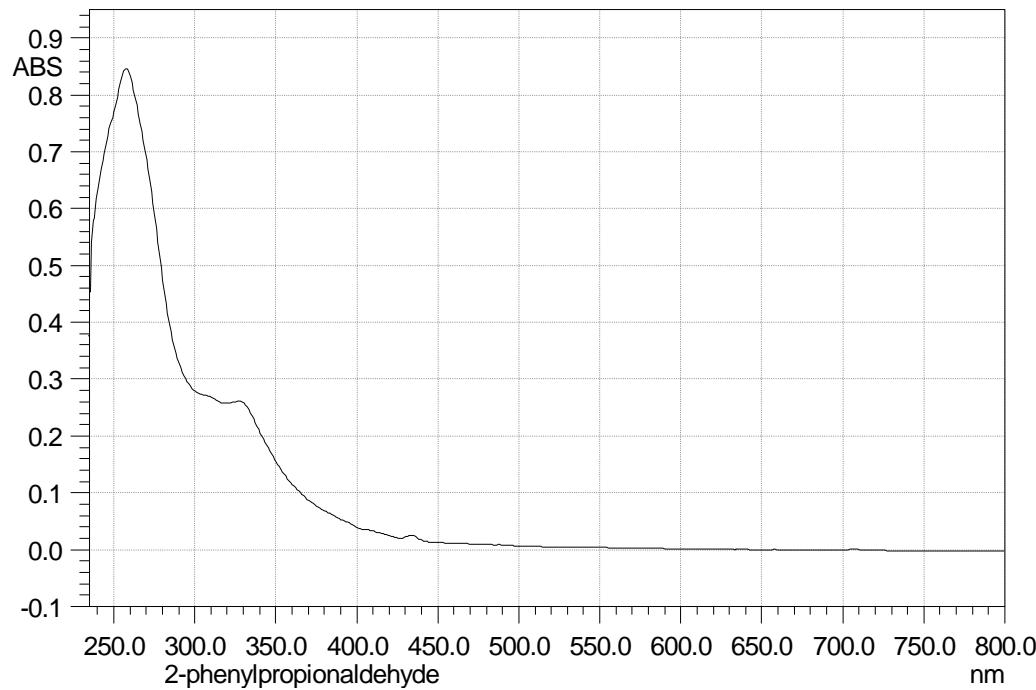
b)  $^{13}\text{C}$  NMR (125 MHz, ODCB- $d_4$ /CS<sub>2</sub>)



c) FT-IR (KBr)

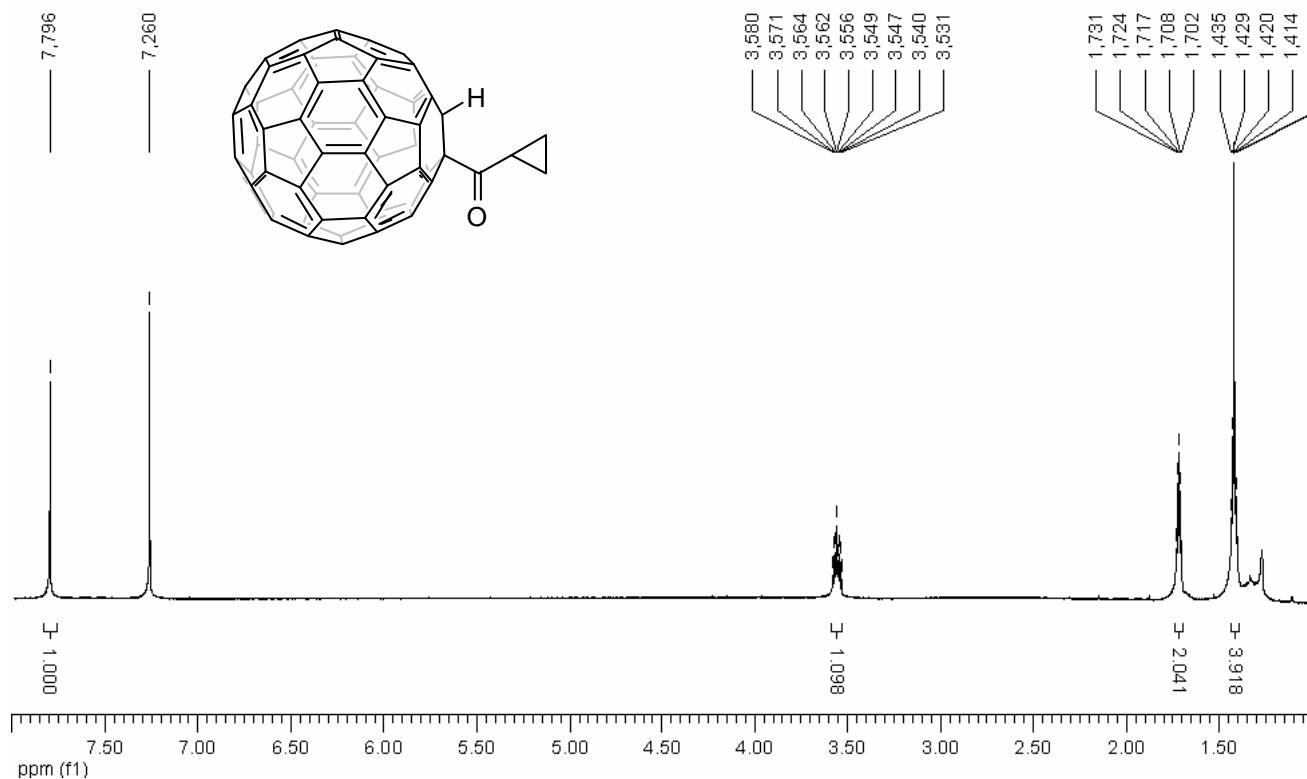


d) UV-vis (CHCl<sub>3</sub>)

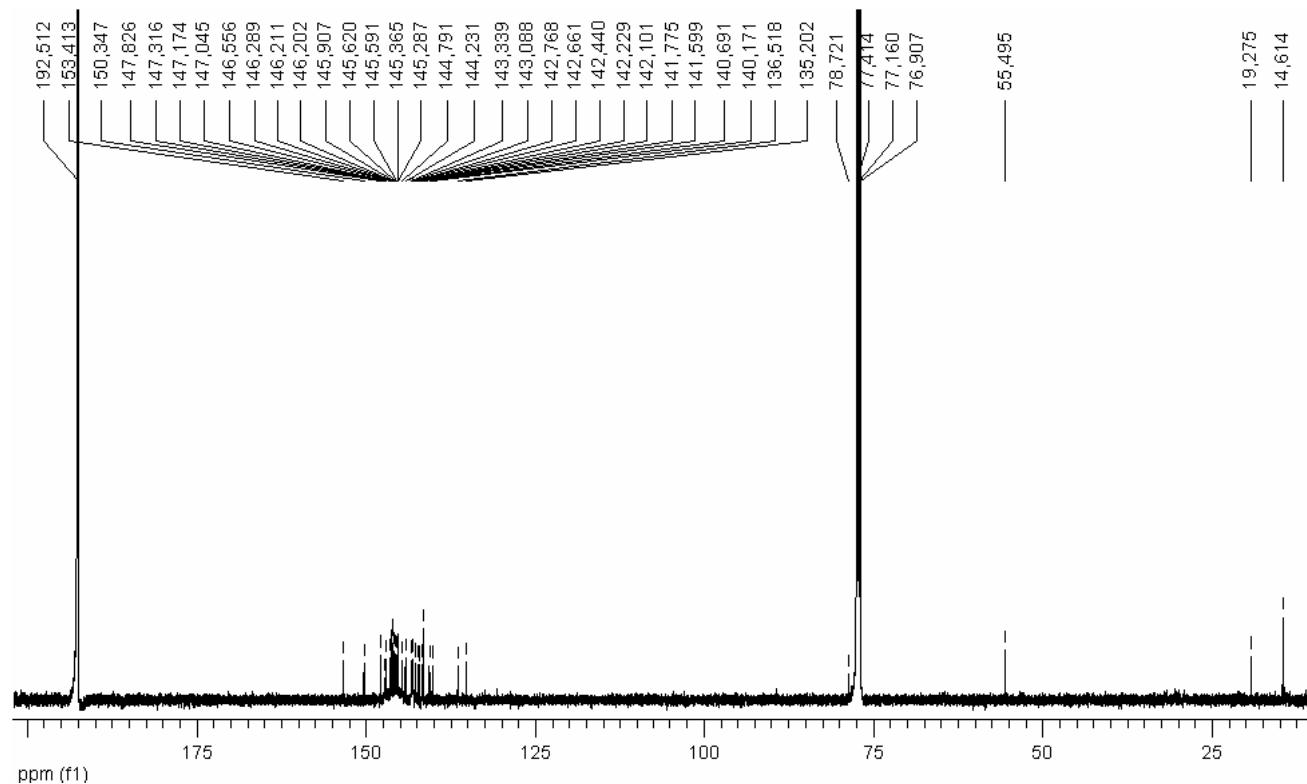


➤ Compound 13a

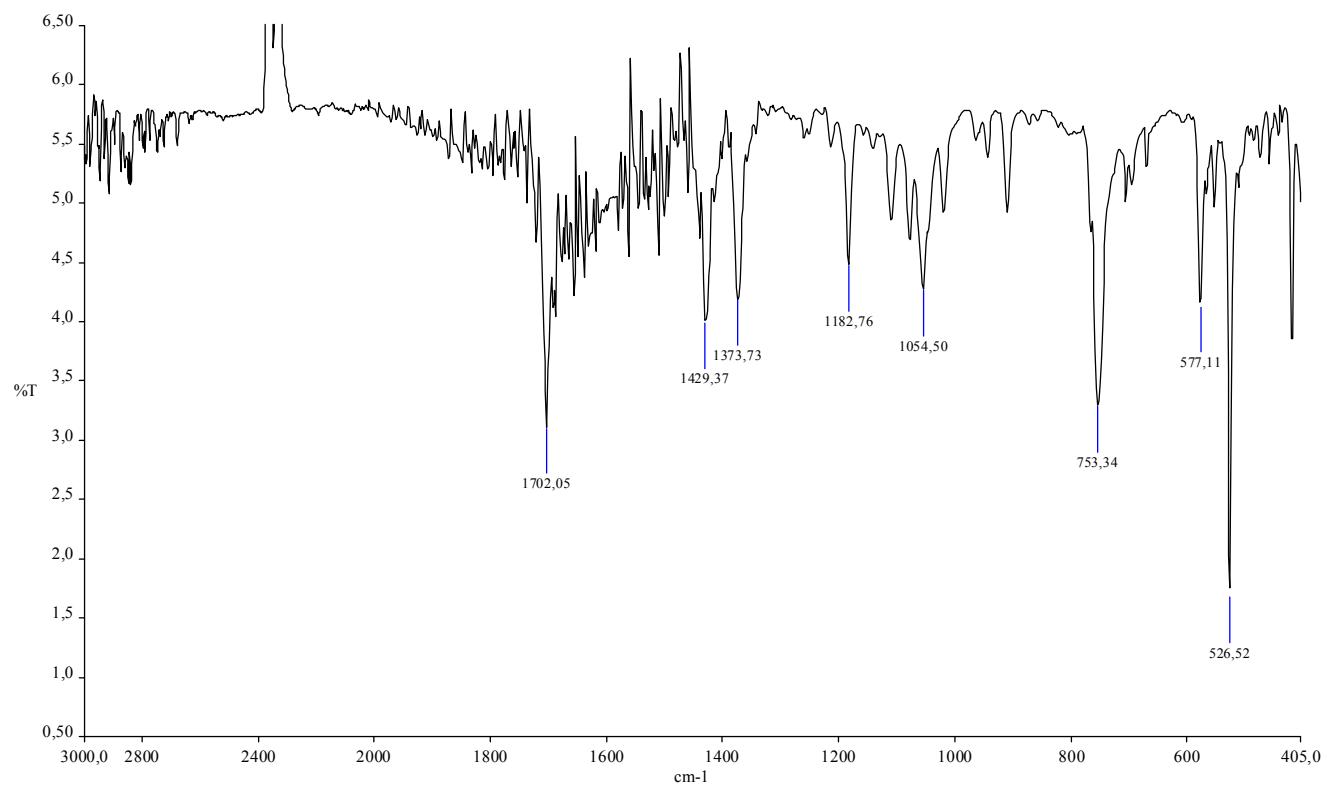
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



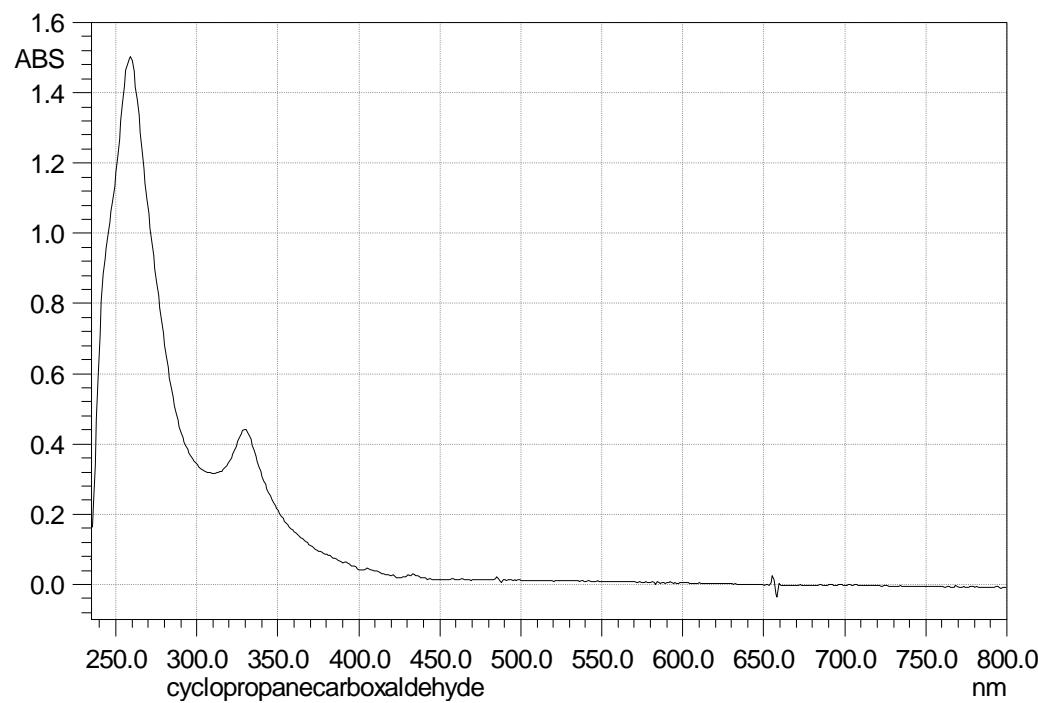
b)  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



c) FT-IR (KBr)

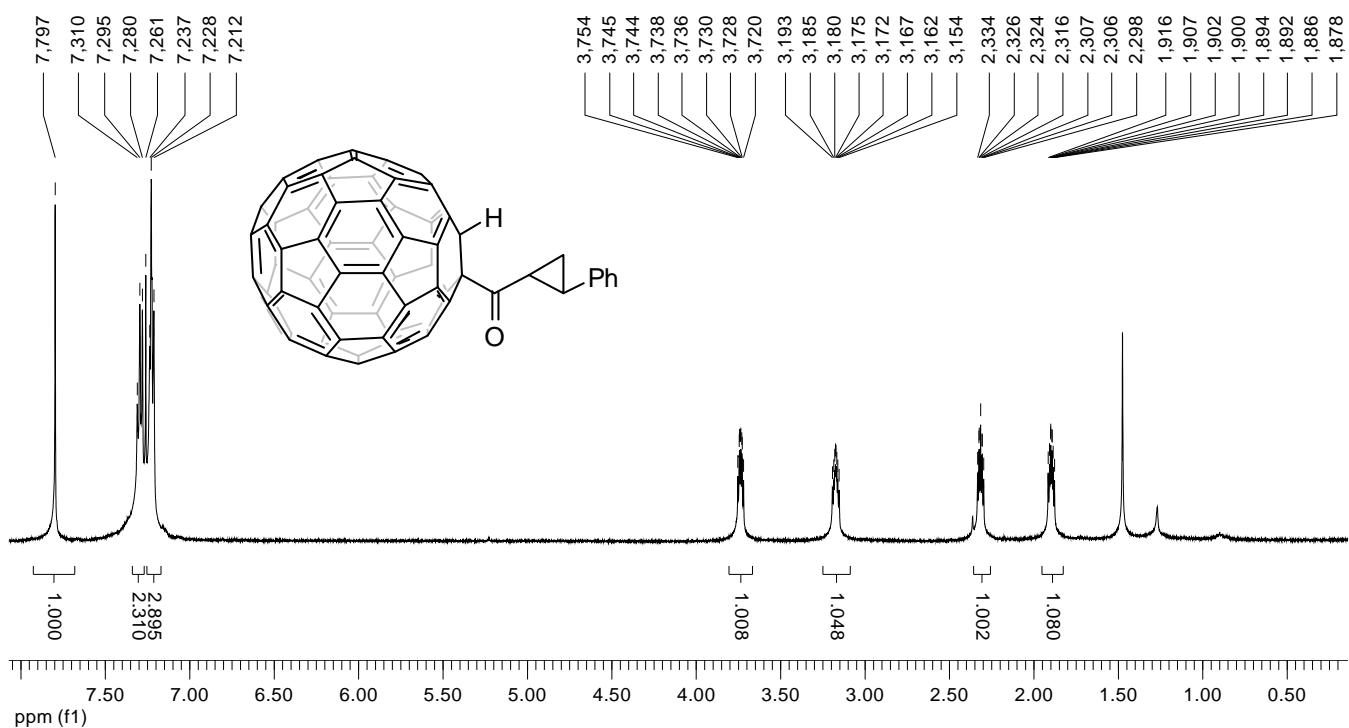


d) UV-vis (CHCl<sub>3</sub>)

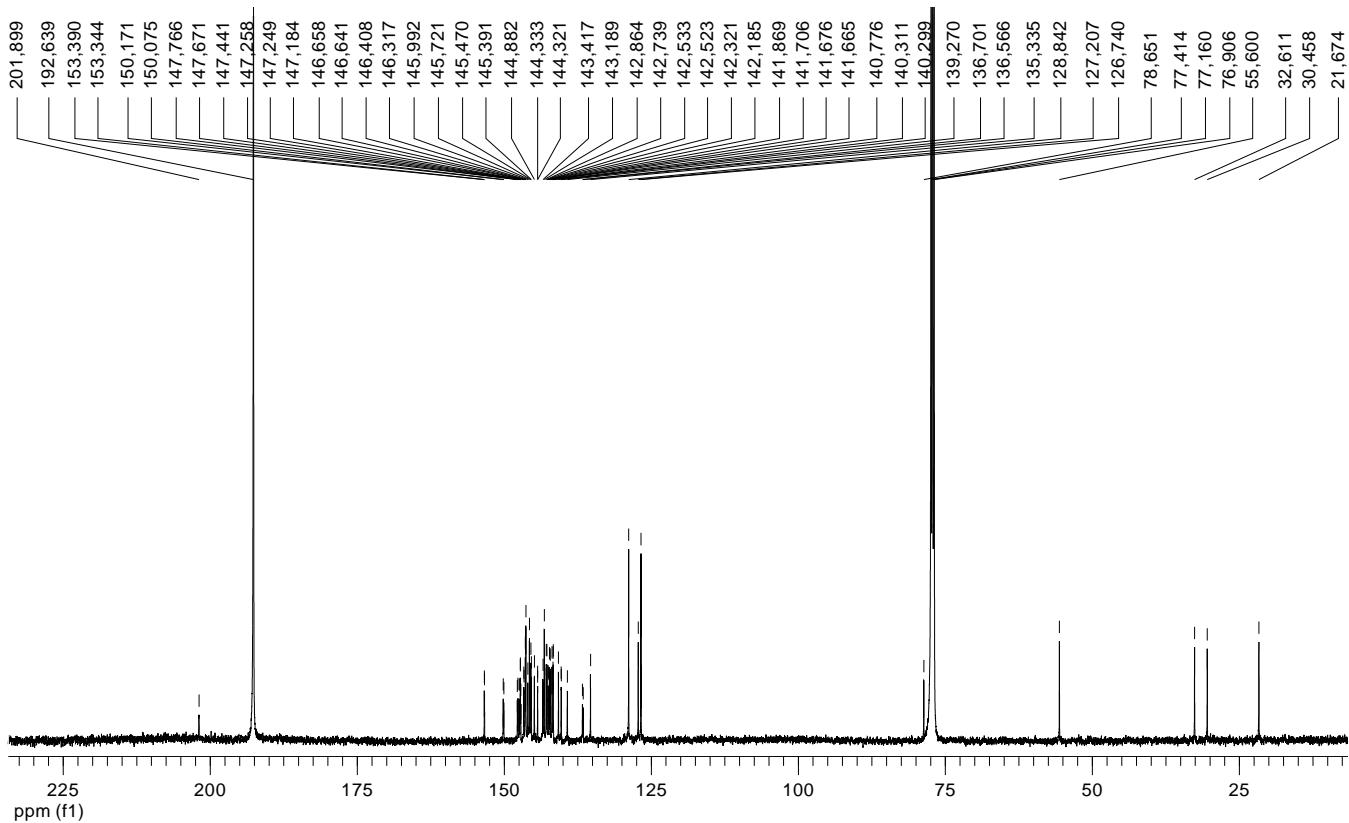


➤ Compound 14a

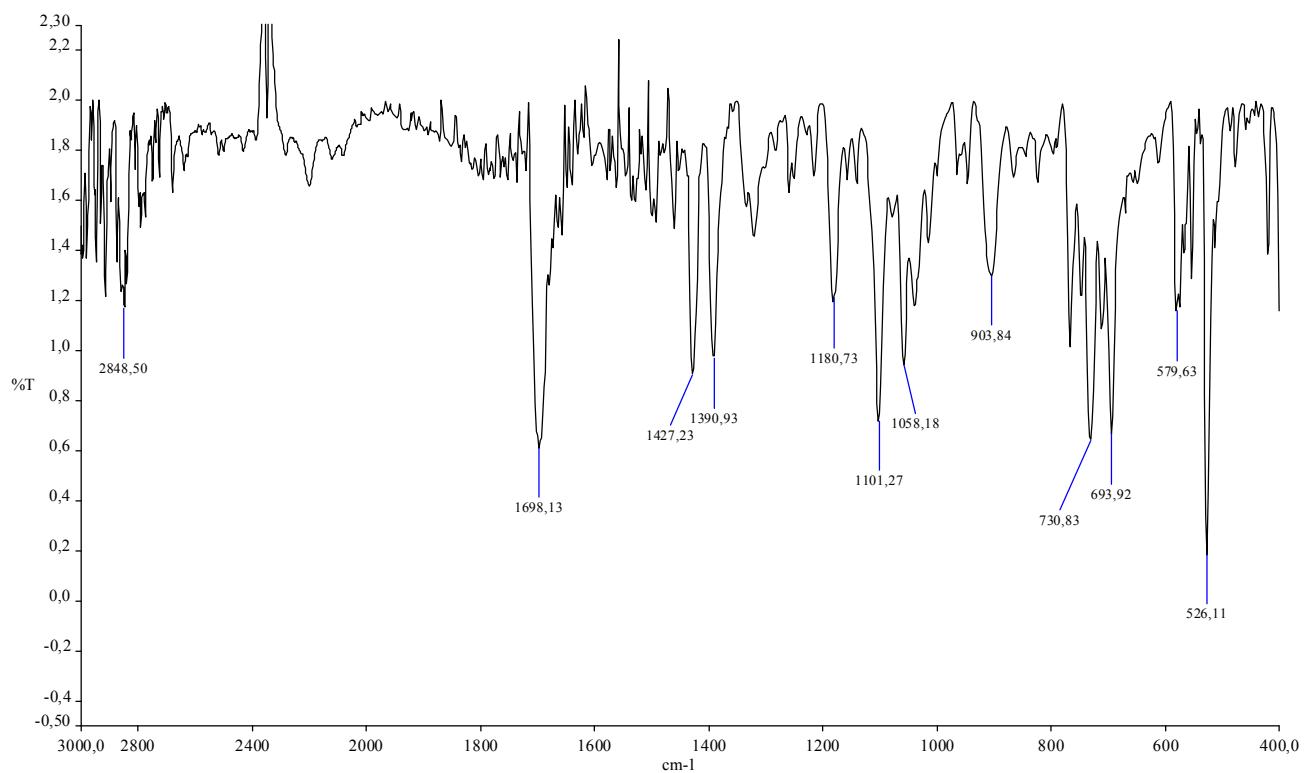
a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



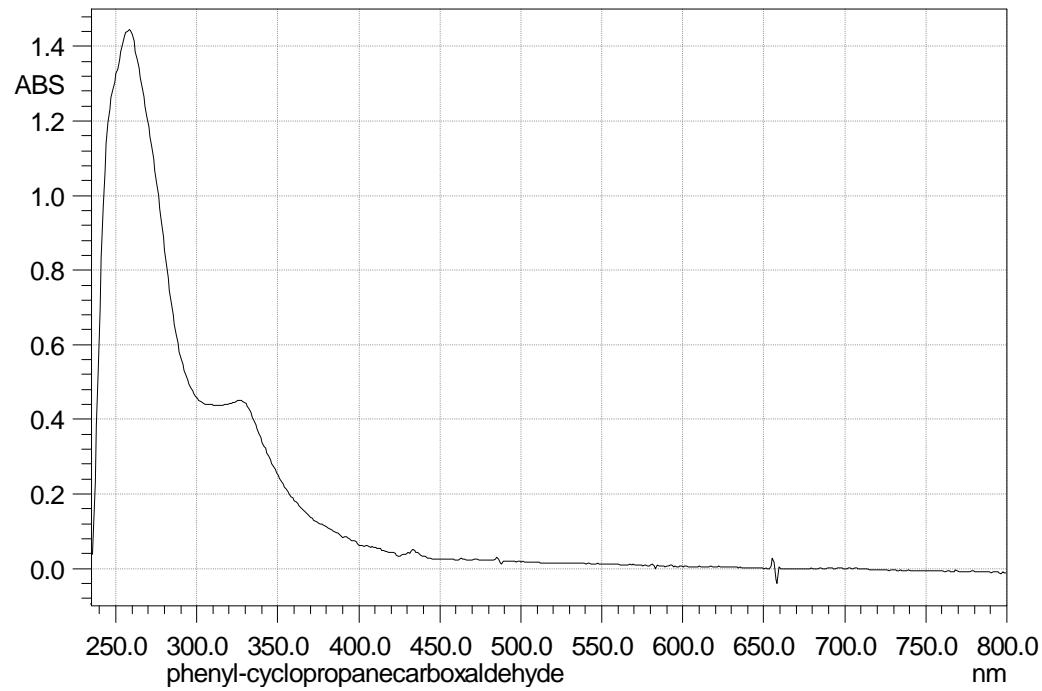
b)  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3/\text{CS}_2$ )



c) FT-IR (KBr)

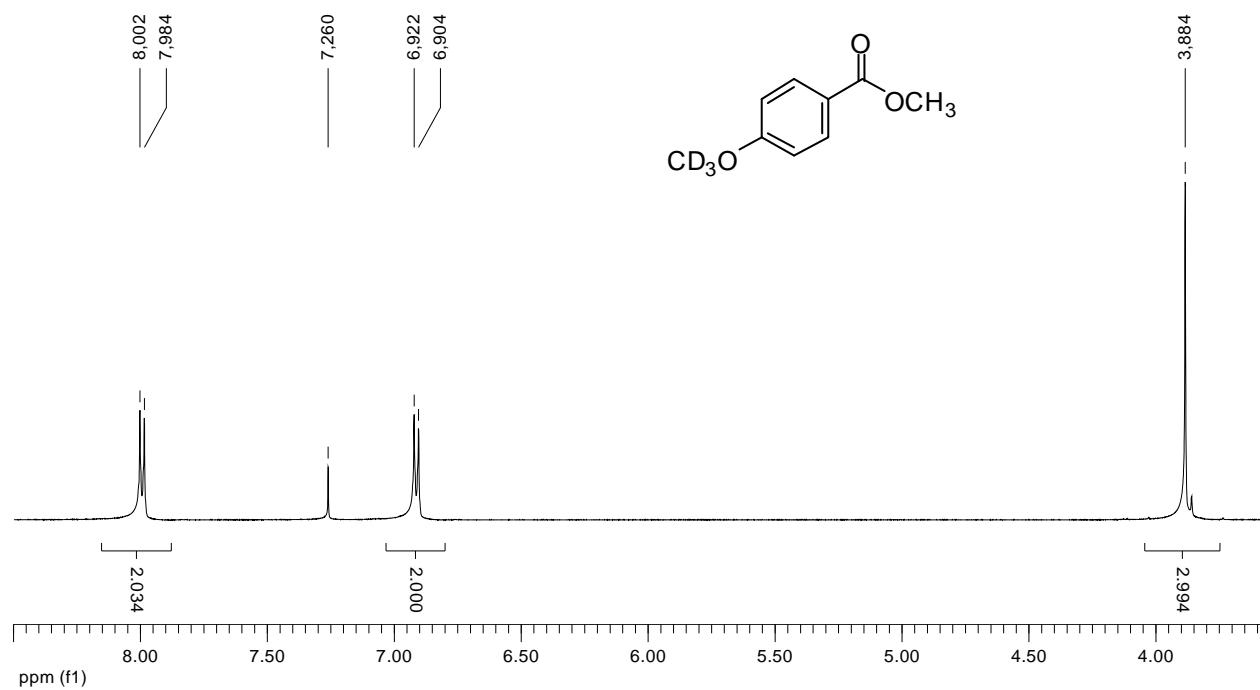


d) UV-vis (CHCl<sub>3</sub>)

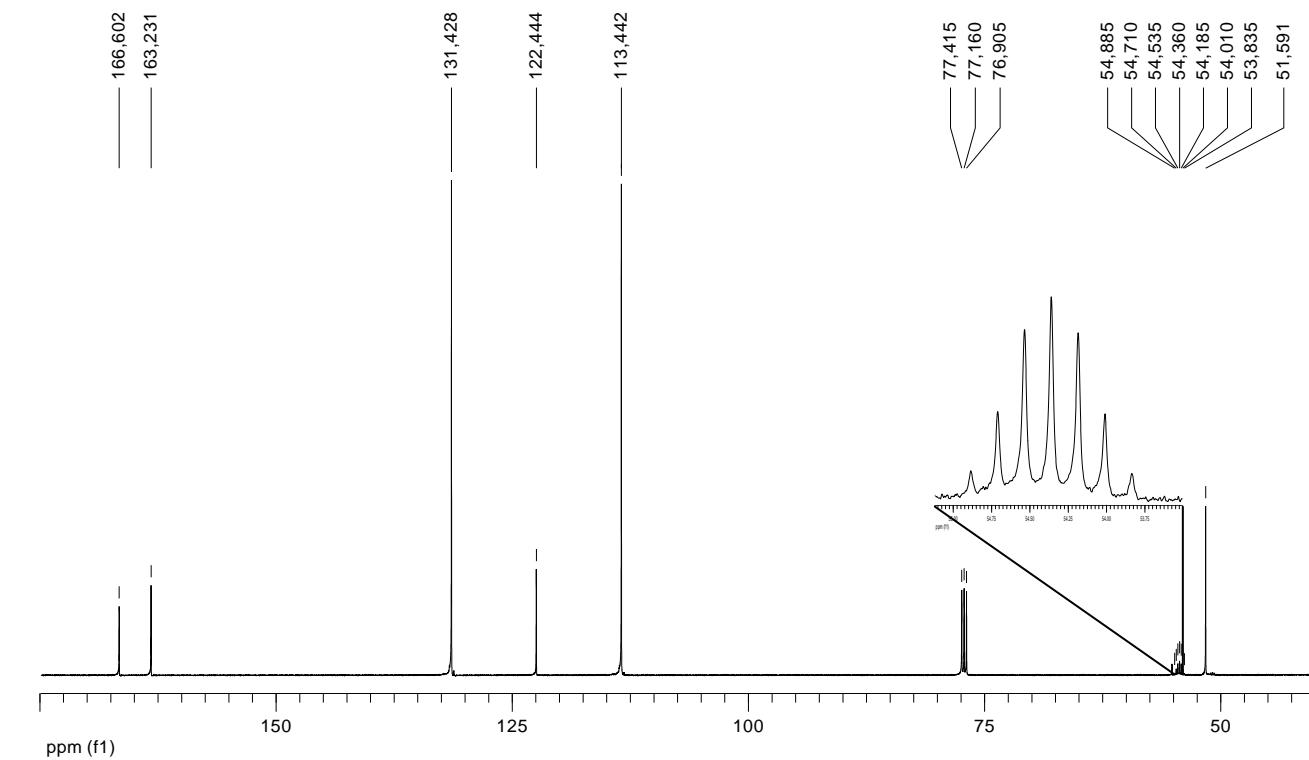


## 8. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Methyl 4-Methoxybenzoate- $d_3$

a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

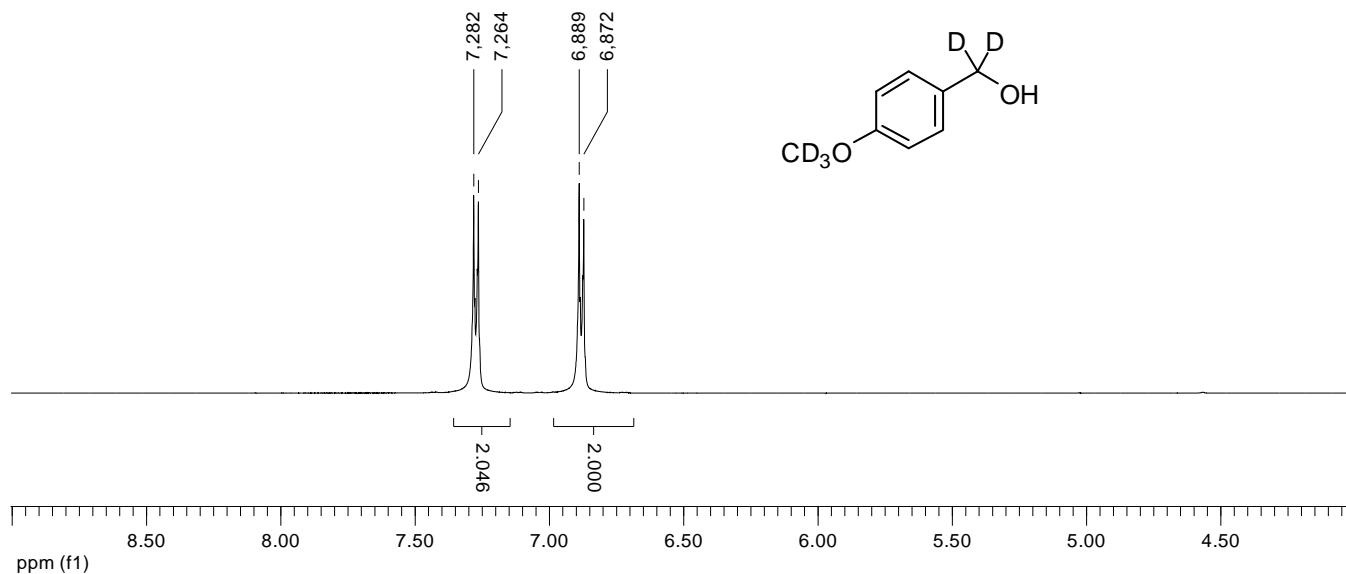


b)  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )

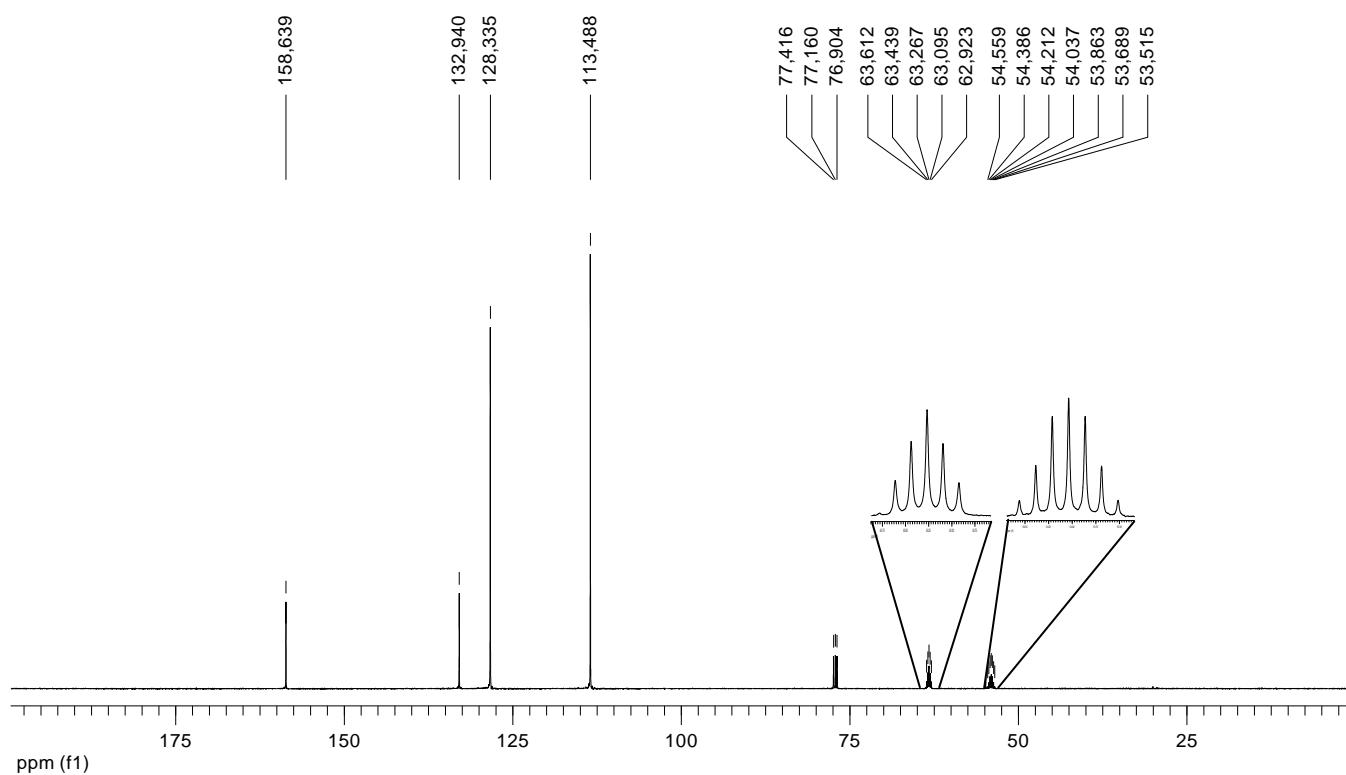


**9.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 4-Methoxybenzyl Alcohol- $d_5$**

a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

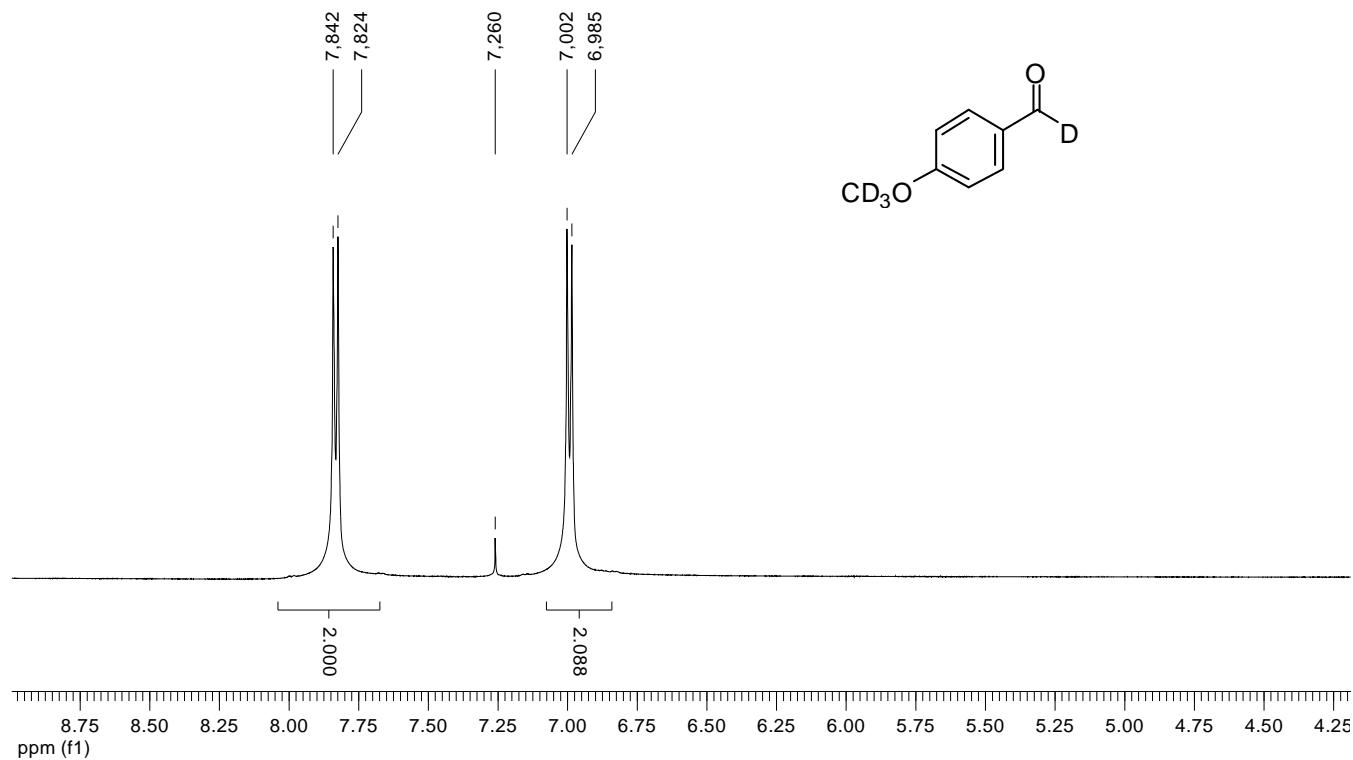


b)  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )

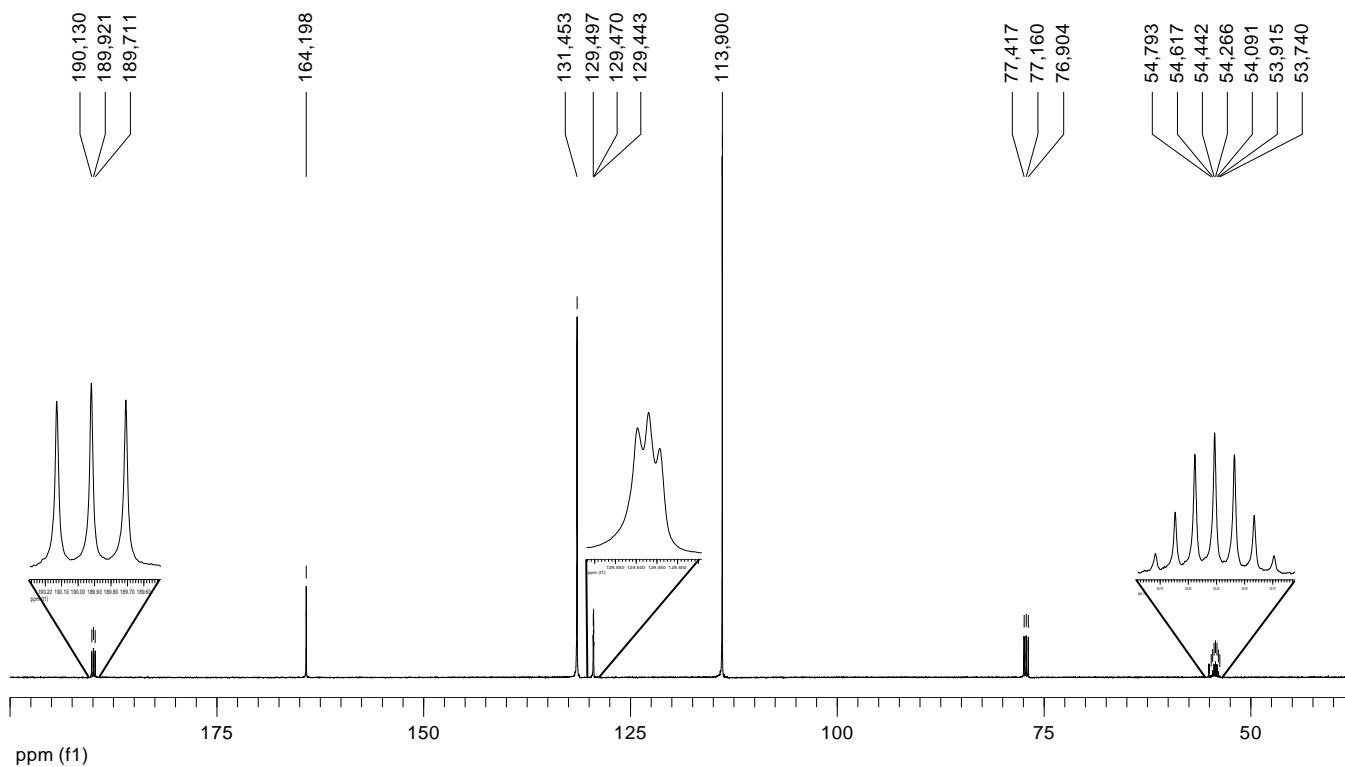


**10.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of 4-Methoxybenzaldehyde- $d_4$  (3- $d_4$ )**

a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

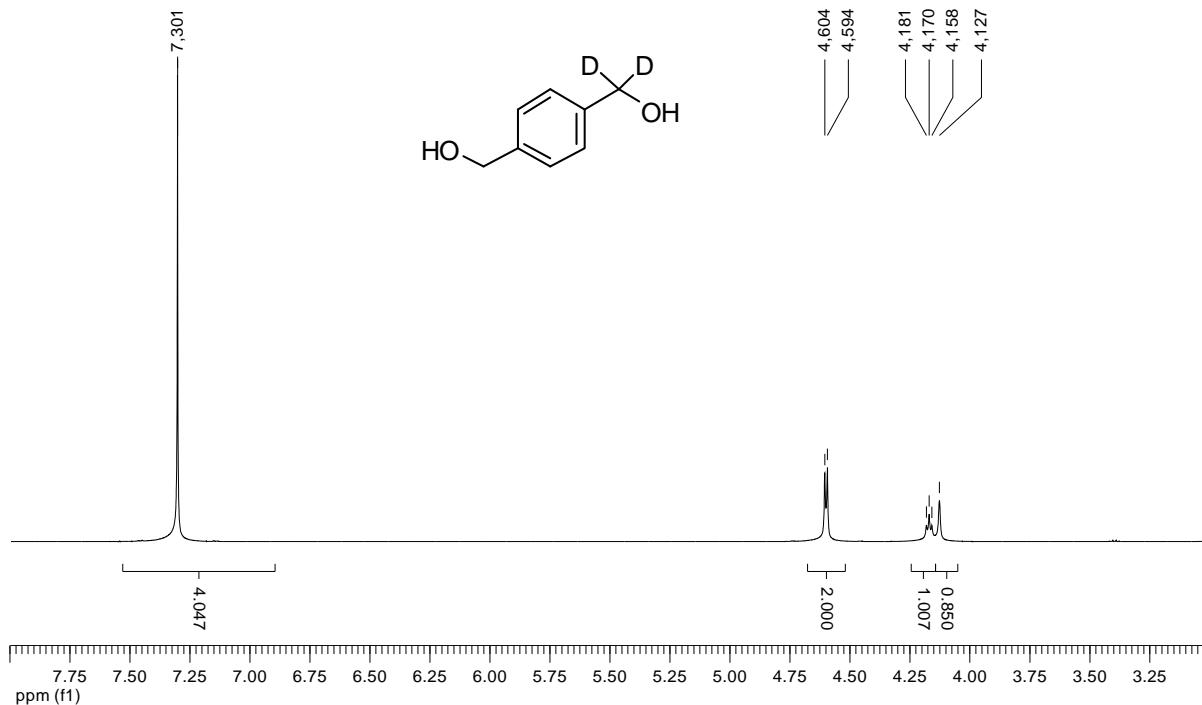


b)  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )

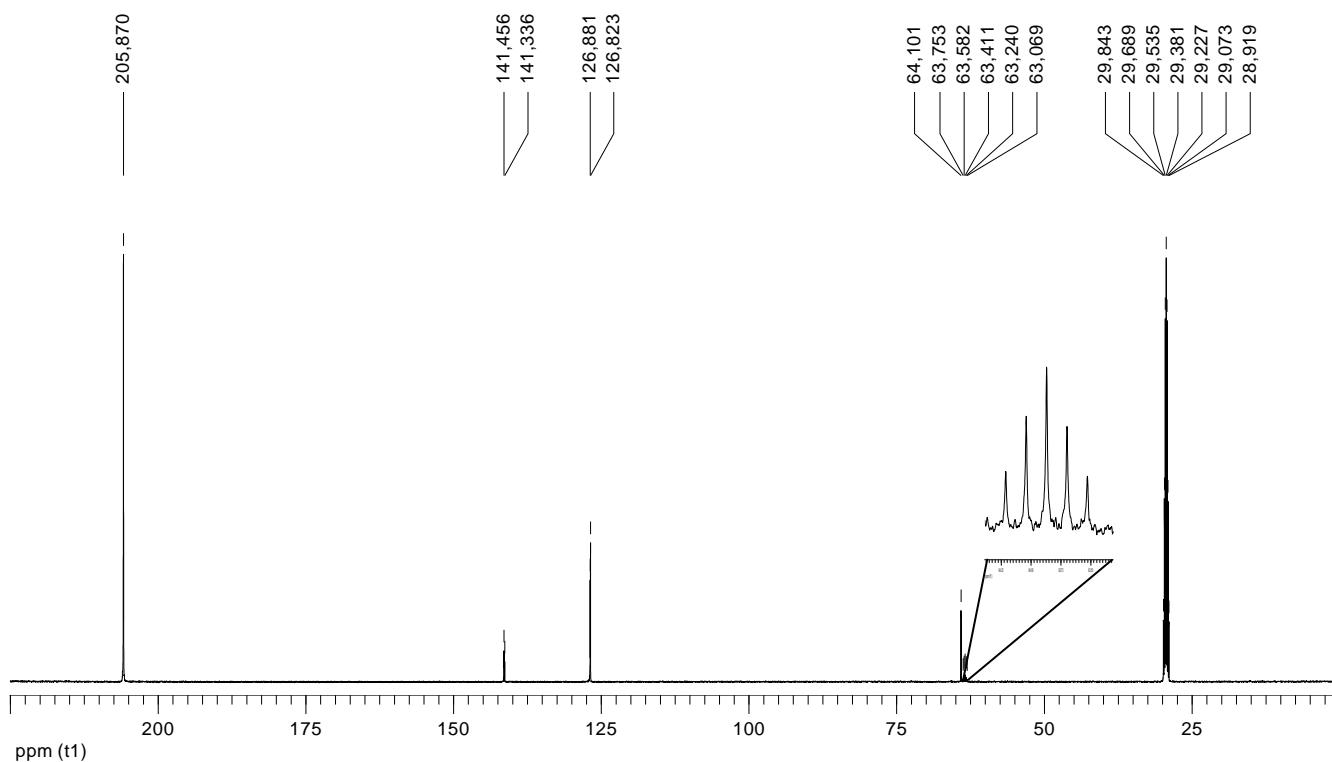


## 11. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of 1,4-Benzenedimethanol- $d_2$

a)  $^1\text{H}$  NMR (500 MHz, Acetone- $d_6$ )

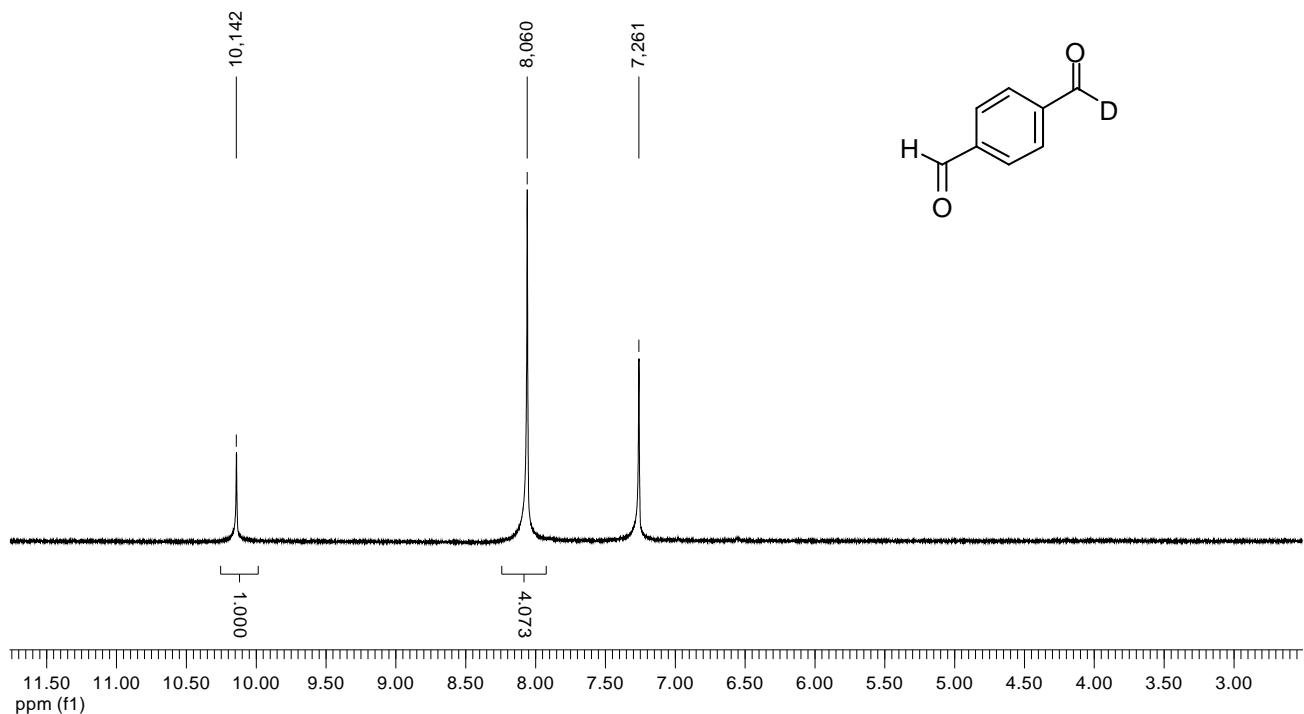


b)  $^{13}\text{C}$  NMR (500 MHz, Acetone- $d_6$ )

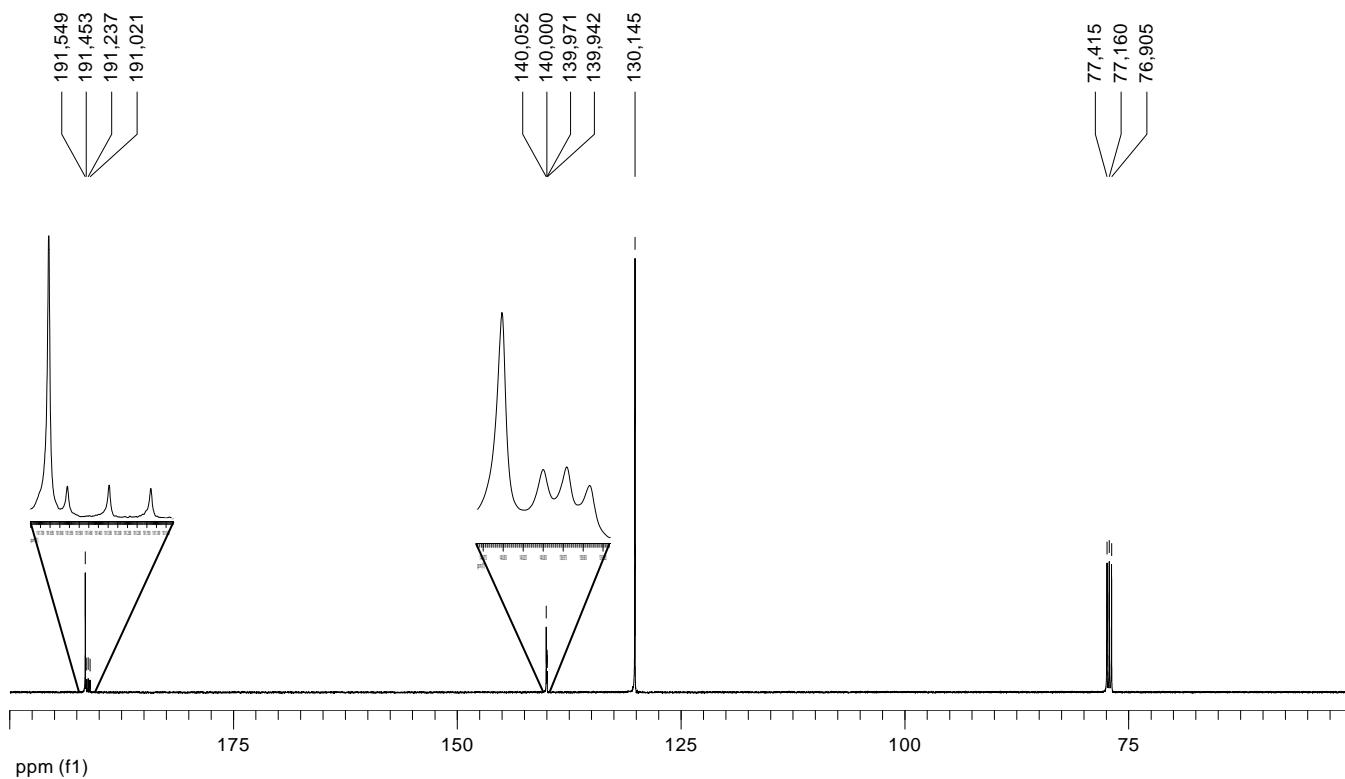


**12.  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectra of Benzene-1,4-dicarboxaldehyde- $d_1$  (4- $d_1$ )**

a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

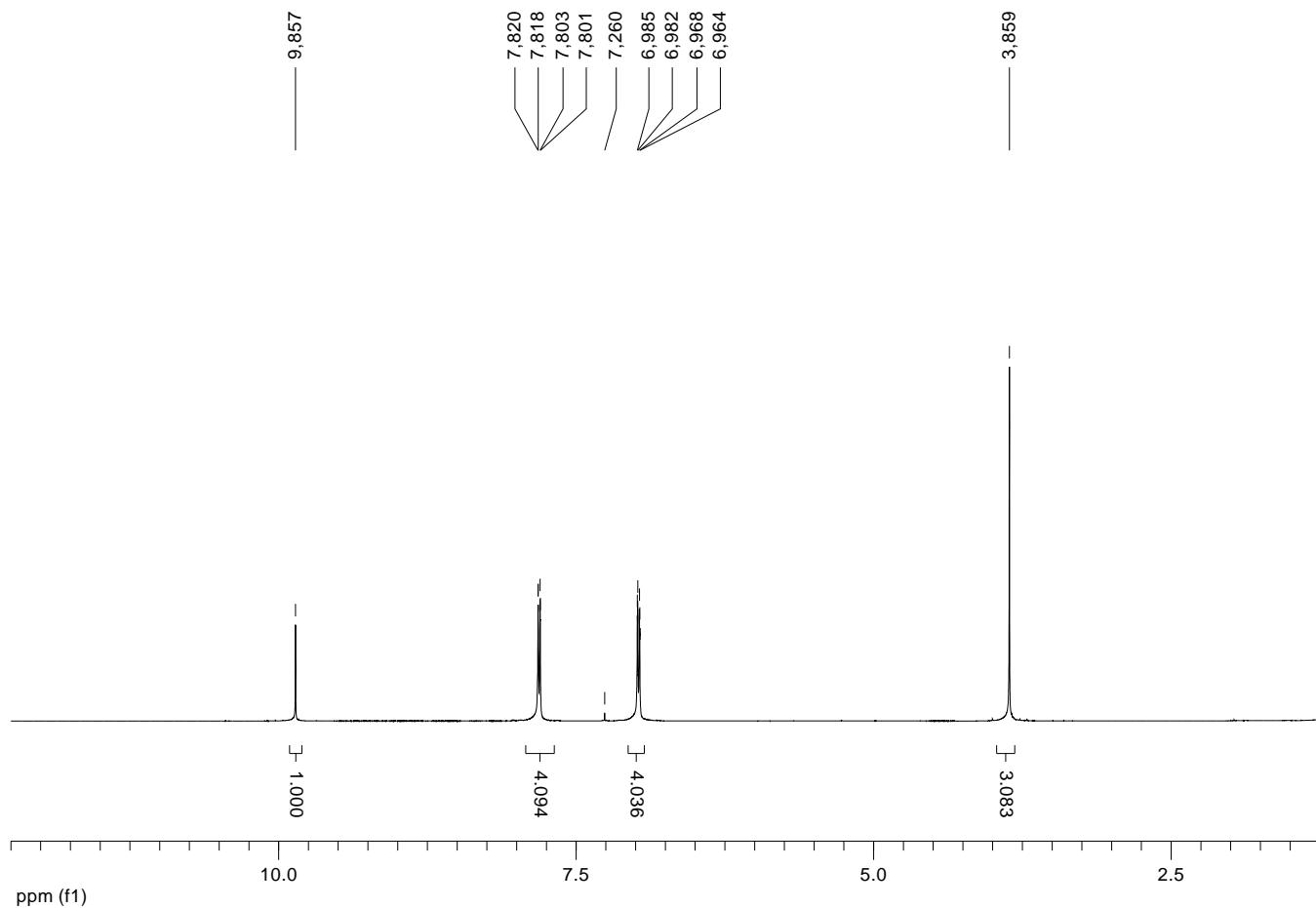


b)  $^{13}\text{C}$  NMR (500 MHz,  $\text{CDCl}_3$ )

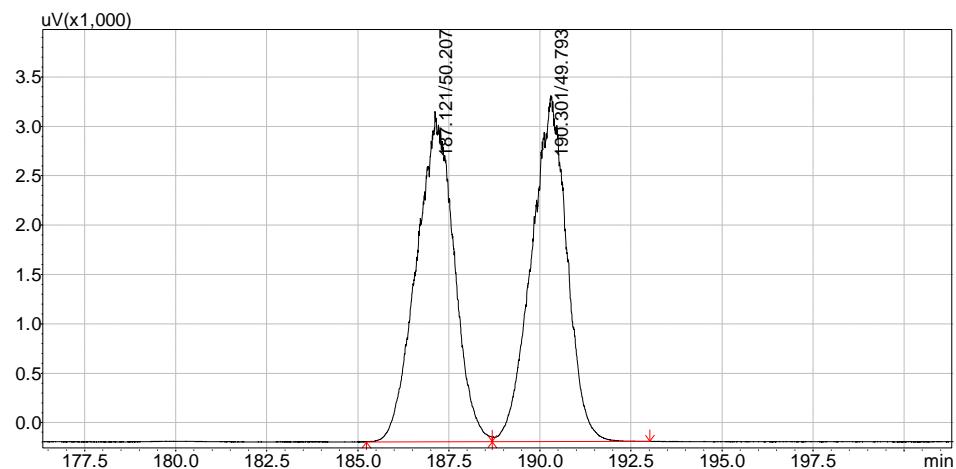


**13.  $^1\text{H}$  NMR Spectrum and GC Chromatogram of Equimolar Mixture of 3- $d_0$  / 3- $d_4$**

a)  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

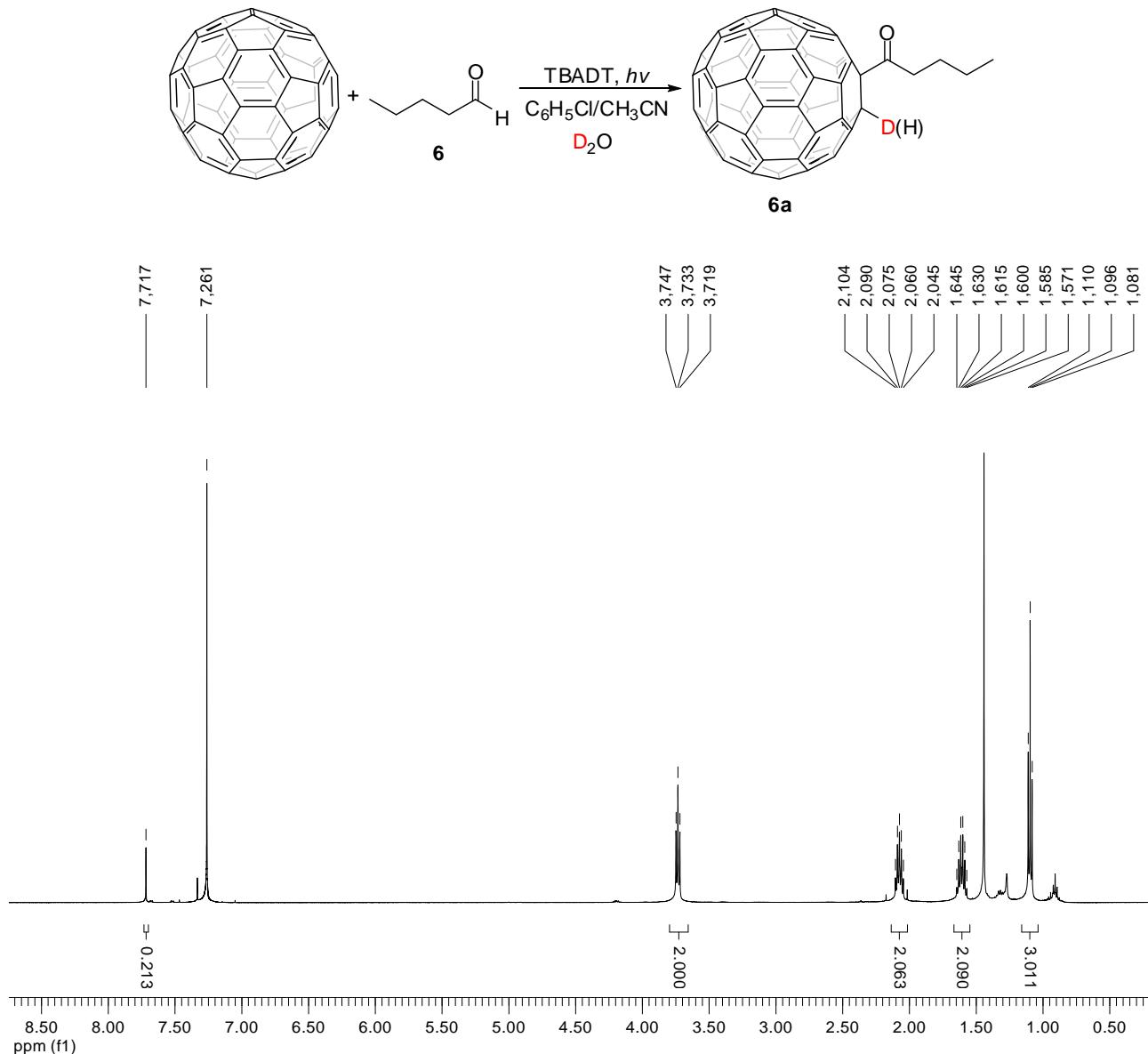


b) GC



**14. Procedure and  $^1\text{H}$  NMR Spectrum of the Reaction of  $\text{C}_{60}$  with Valeraldehyde **6** in the Presence of  $\text{D}_2\text{O}$**

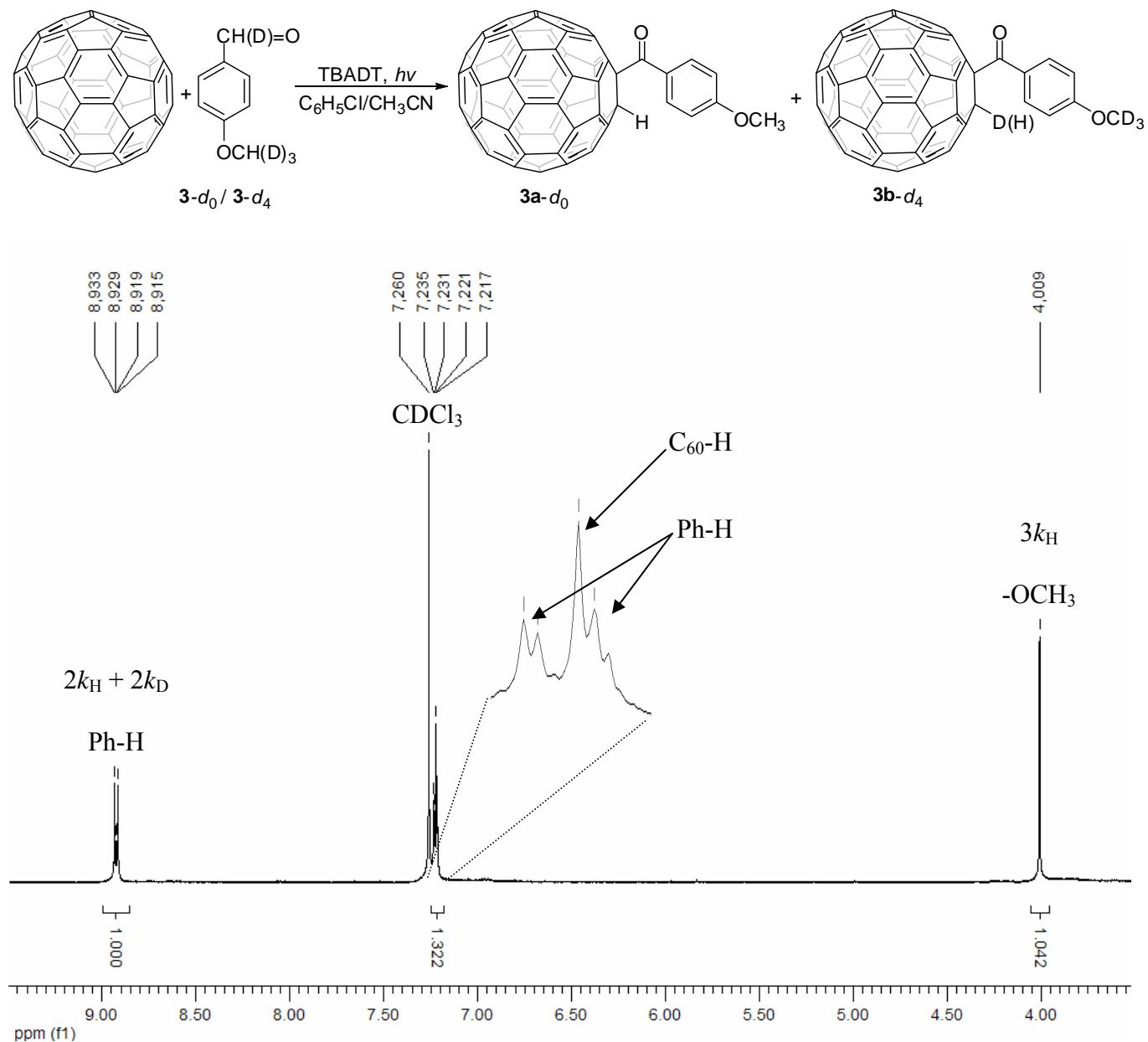
The reaction was performed following the general procedure described in Section 2, using 20 mg ( $0.028 \text{ mmol}$ ) of  $\text{C}_{60}$ , 465 mg (5.4 mmol) of valeraldehyde **6** and 46 mg (0.014 mmol) of TBADT in 75 mL of a 85:15 mixture of chlorobenzene/ $\text{CH}_3\text{CN}$  containing 0.75 mL  $\text{D}_2\text{O}$  ( $T \approx 10^\circ\text{C}$ ,  $t = 15 \text{ min}$ ).



**Control experiment:**

No considerable H-D exchange observed ( $^1\text{H}$  NMR) when a deaerated solution of **6a** (5.5 mg, 6.8  $\mu\text{mol}$ ) in 35 mL of a 85:15 mixture of chlorobenzene/ $\text{CH}_3\text{CN}$  was irradiated in the presence of TBADT (12 mg, 3.6  $\mu\text{mol}$ ) and 1%  $\text{D}_2\text{O}$  (0.35 mL) for 15 min, ruling out the possibility of the TBADT-catalyzed H-D exchange.

**15.  $^1\text{H}$  NMR Spectrum of the Reaction of  $\text{C}_{60}$  with  $3-d_0$  /  $3-d_4$**



**16.  $^1\text{H}$  NMR Spectrum of the Reaction of  $\text{C}_{60}$  with  $4-d_1$**

