

## Supporting Information

For

### A fullerene-distyrylbenzene photosensitizer for singlet oxygen production

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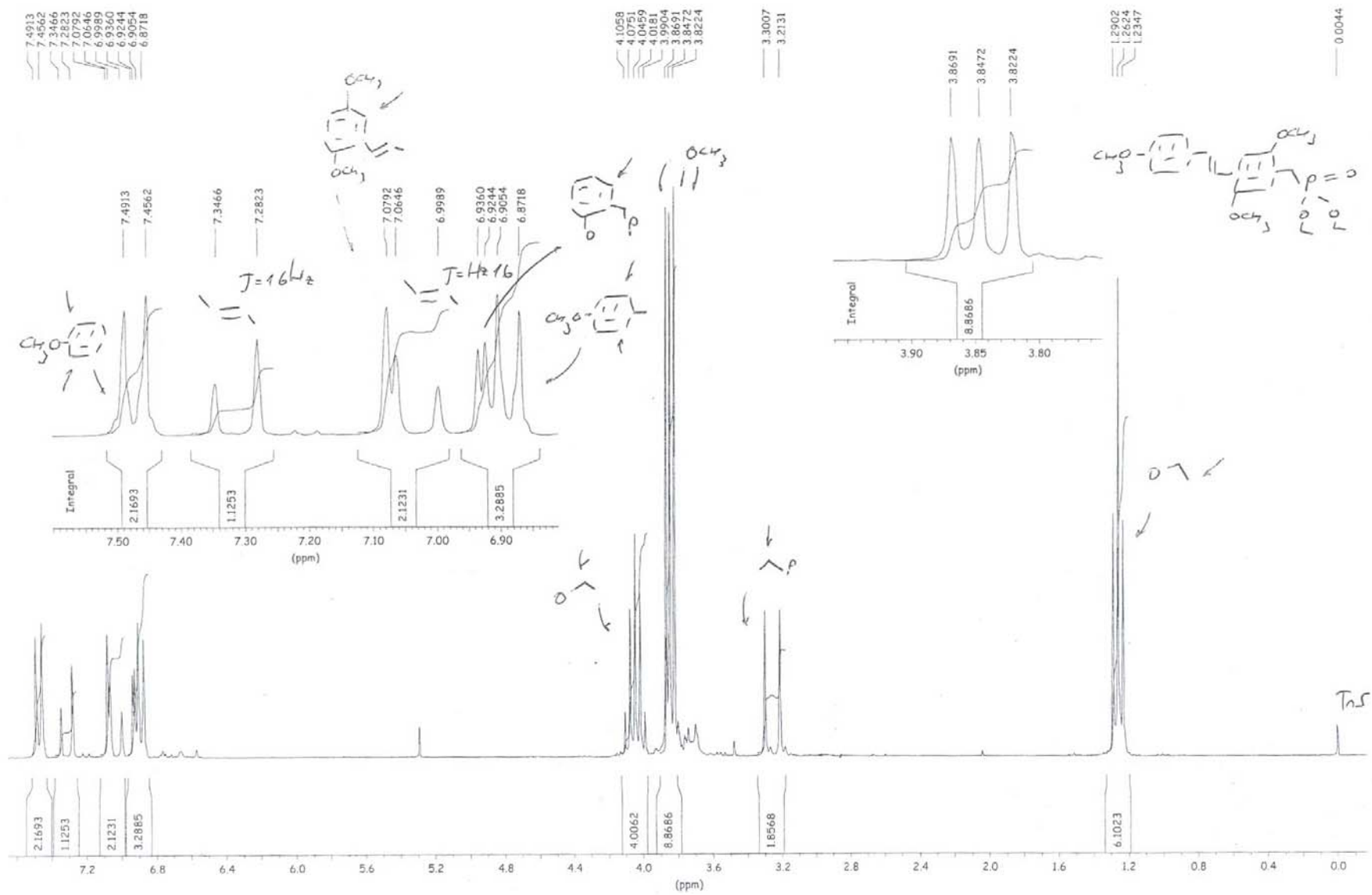
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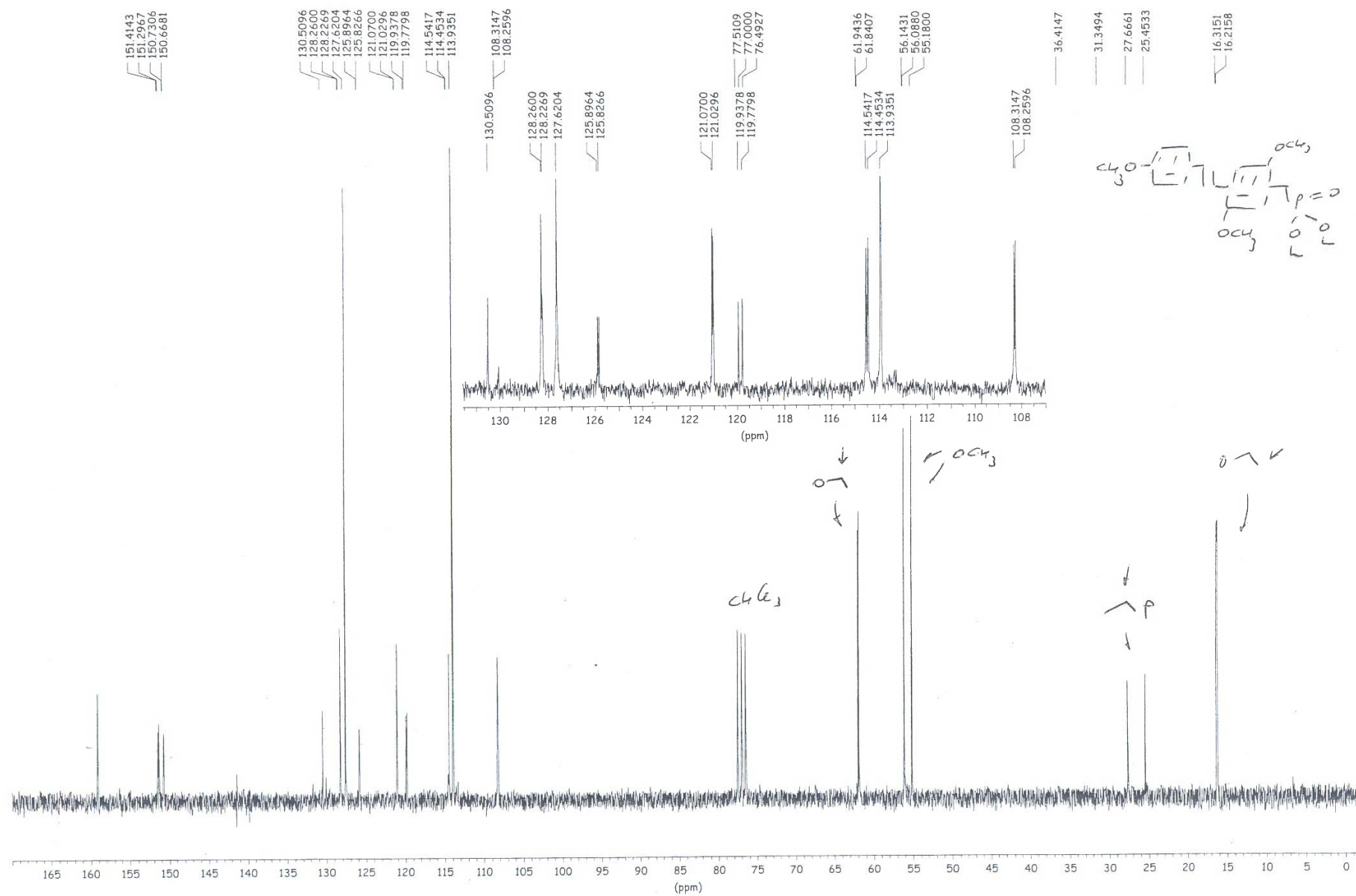
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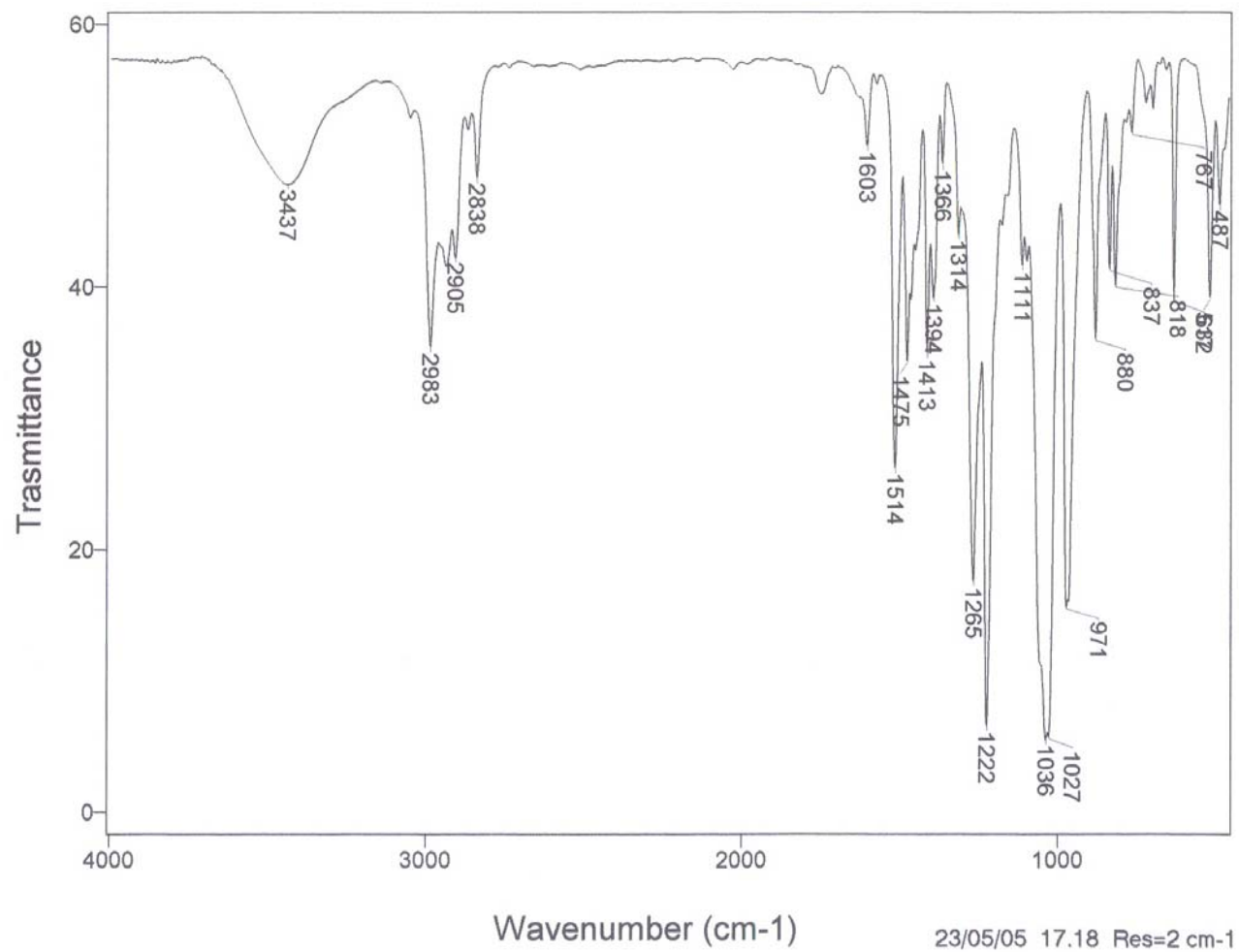
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**FIGURE S1** ( $^1\text{H}$  NMR of **2**,  $\text{CDCl}_3$ )



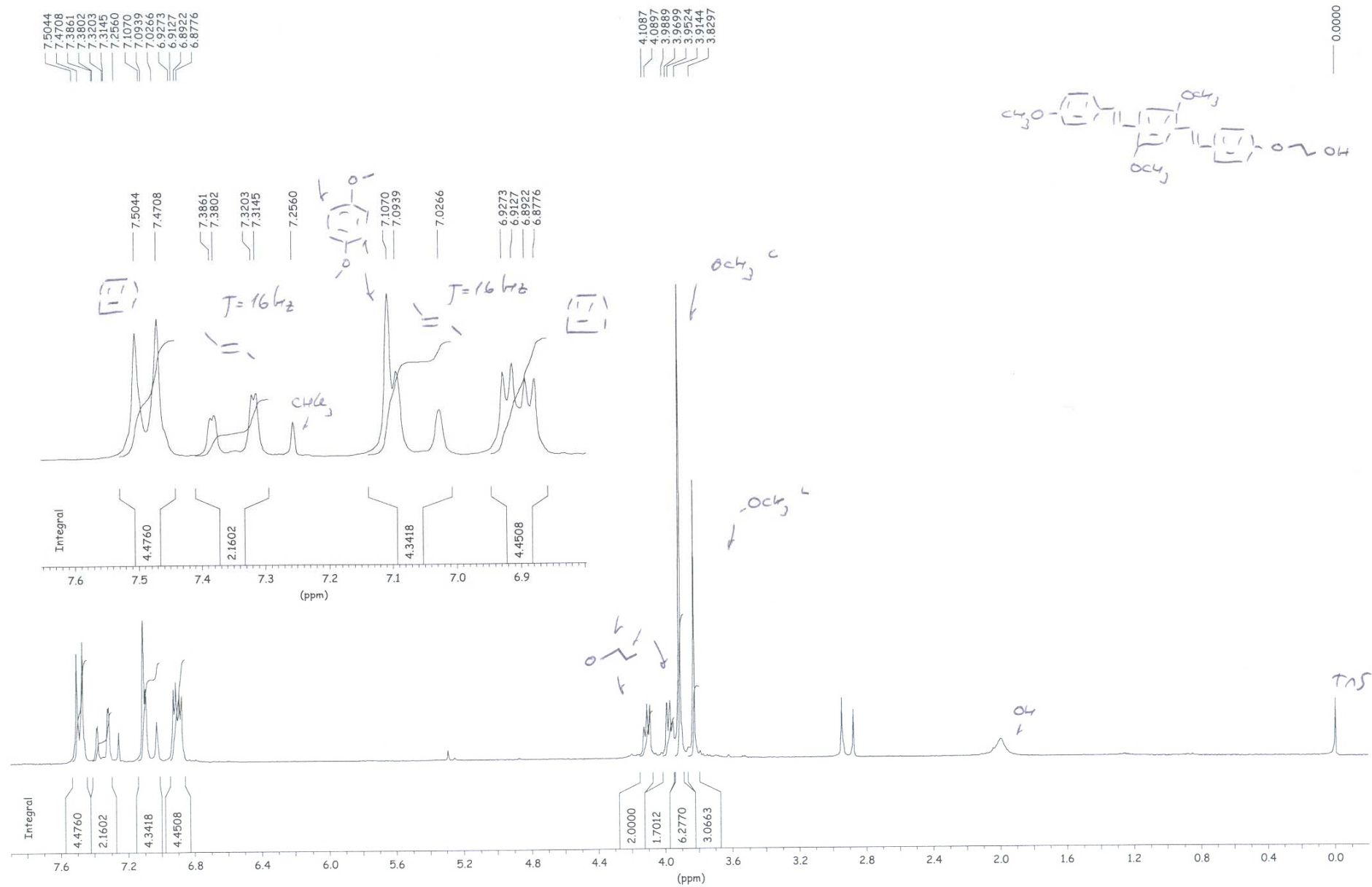
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**FIGURE S2** ( $^{13}\text{C}$  NMR of **2**,  $\text{CDCl}_3$ )



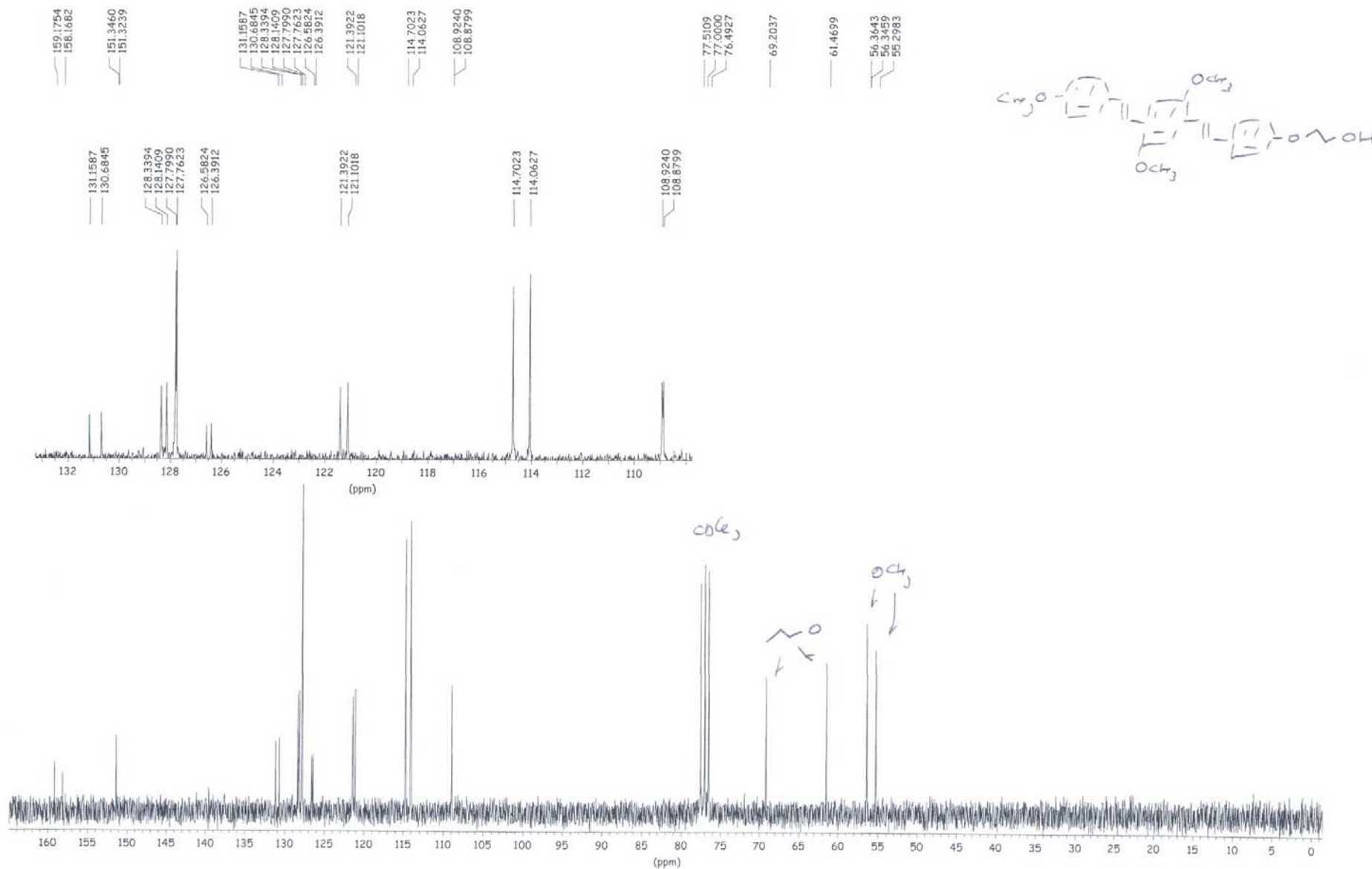
**FIGURE S3.** FT-IR spectrum of **2** (KBr).



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**FIGURE S4** ( $^1\text{H}$  NMR of **3**,  $\text{CDCl}_3$ )



**FIGURE S5** ( $^{13}\text{C}$  NMR of **3**,  $\text{CDCl}_3$ )



**FIGURE S6.** FT-IR spectrum of **3** (KBr).

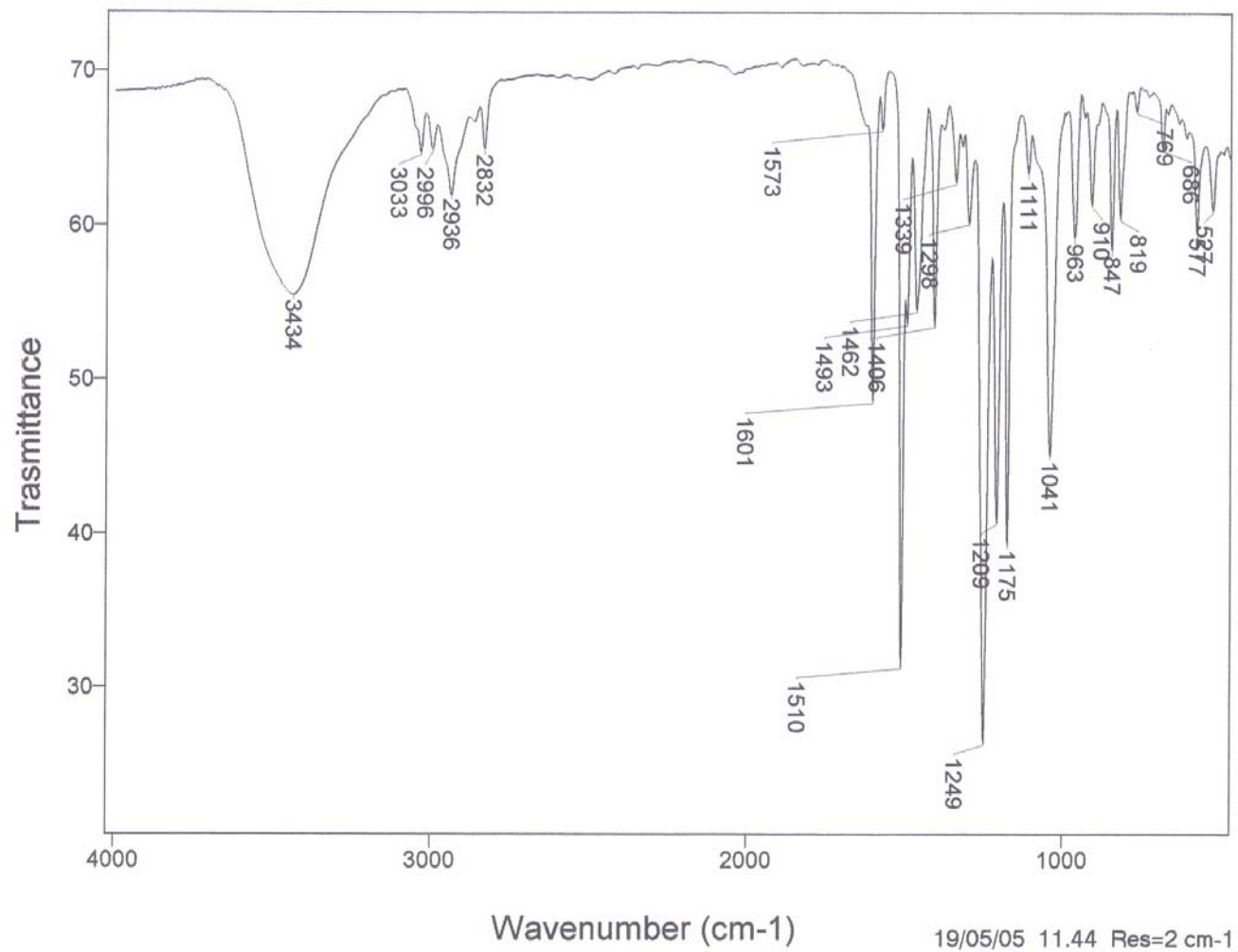
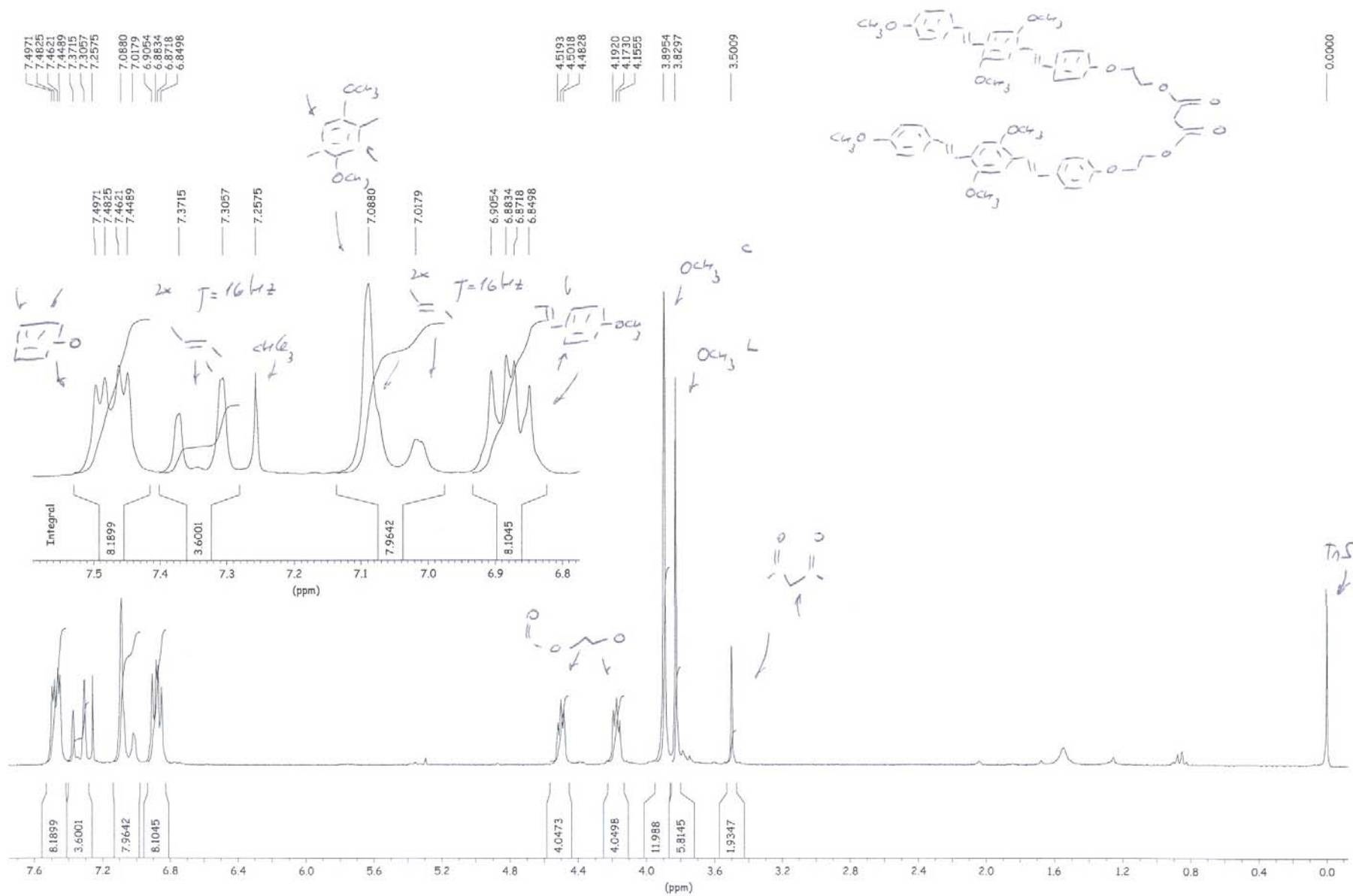
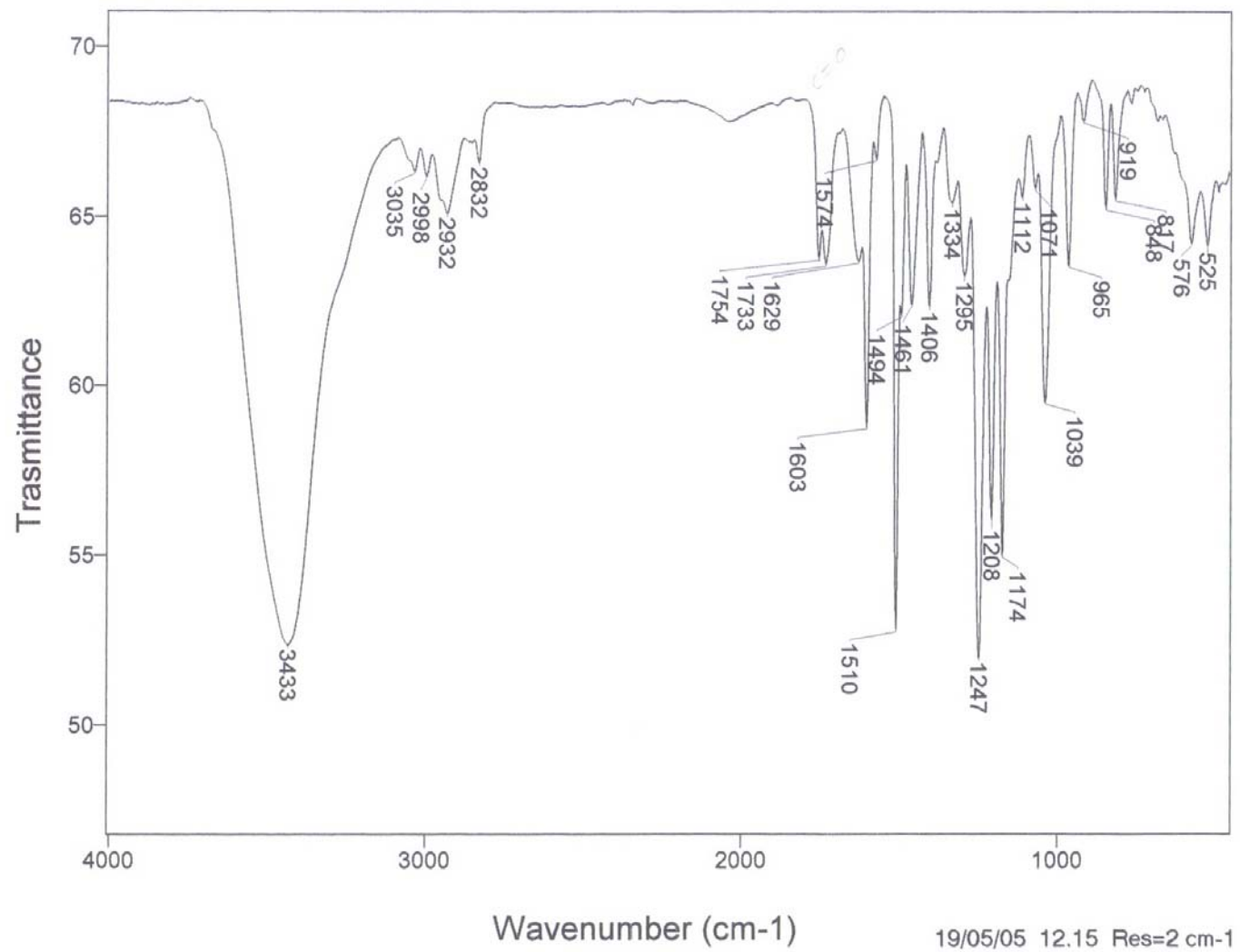


FIGURE S7 ( $^1\text{H}$  NMR of **4**,  $\text{CDCl}_3$ )

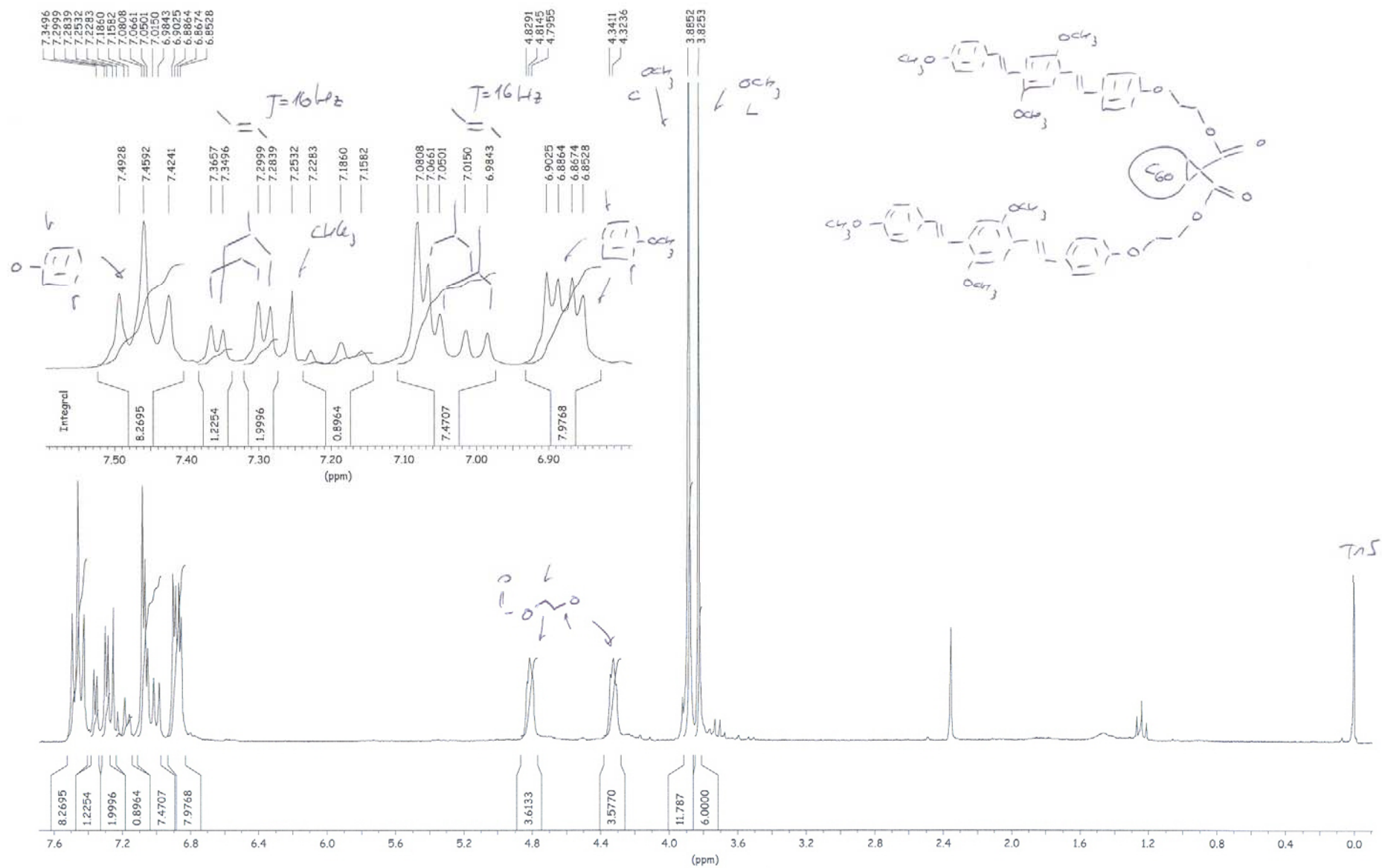




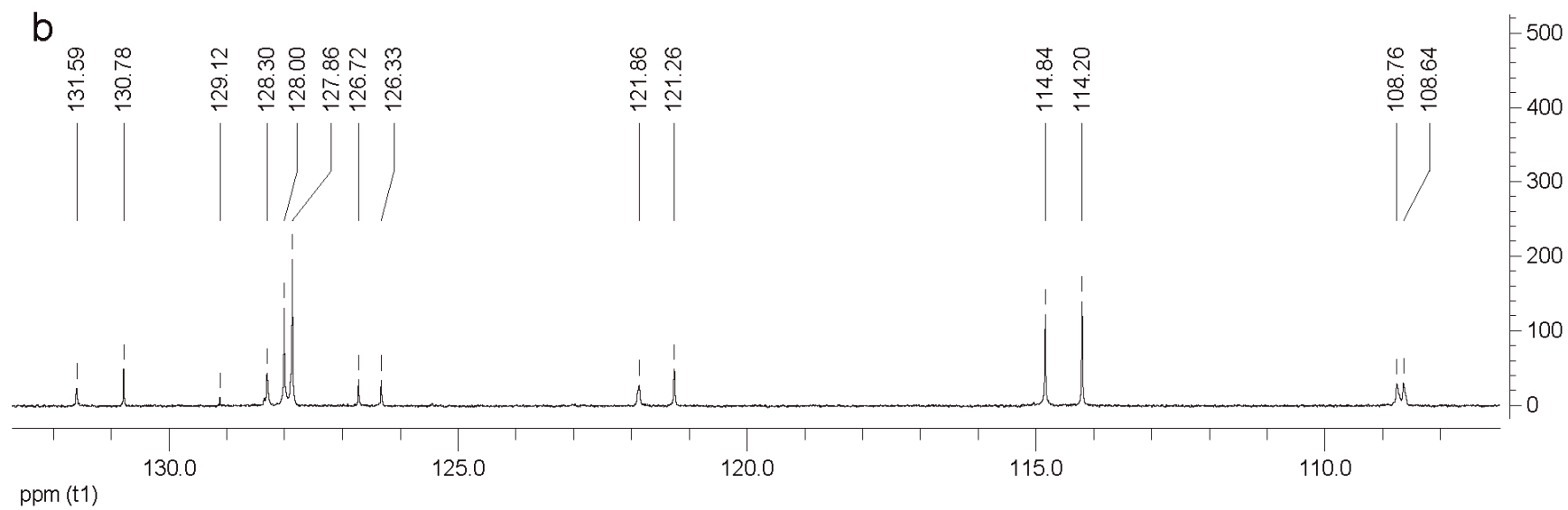
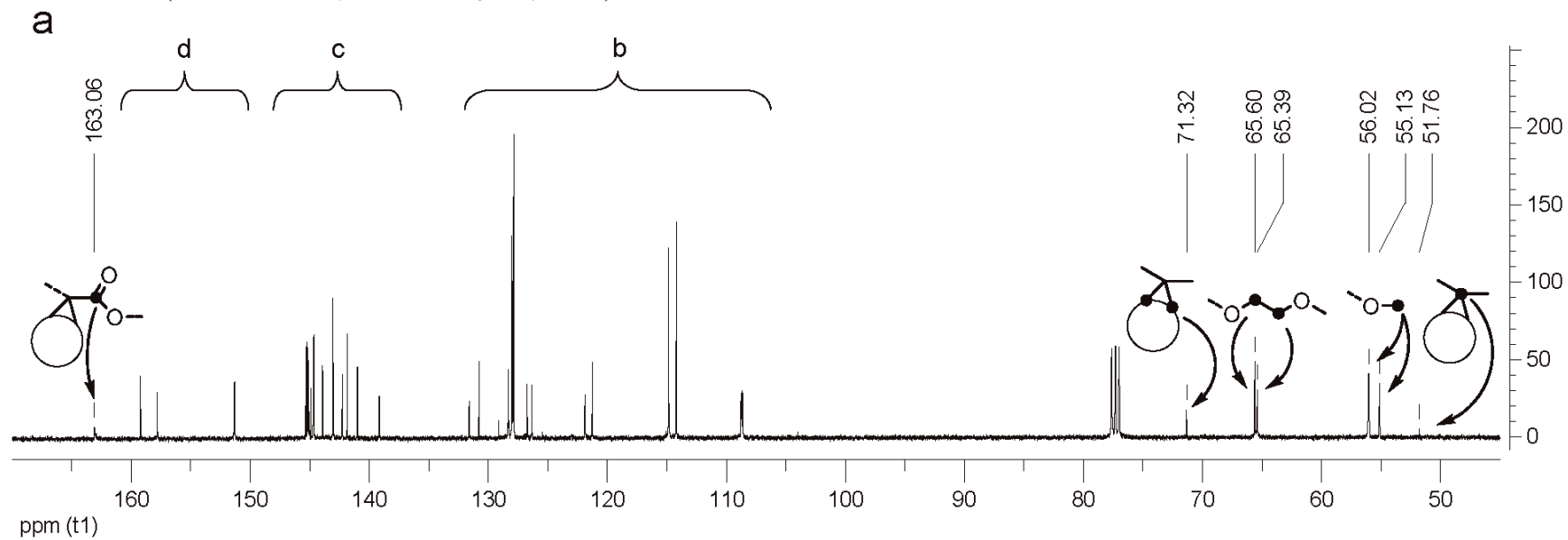
**FIGURE S8.** FT-IR spectrum of **4** (KBr).

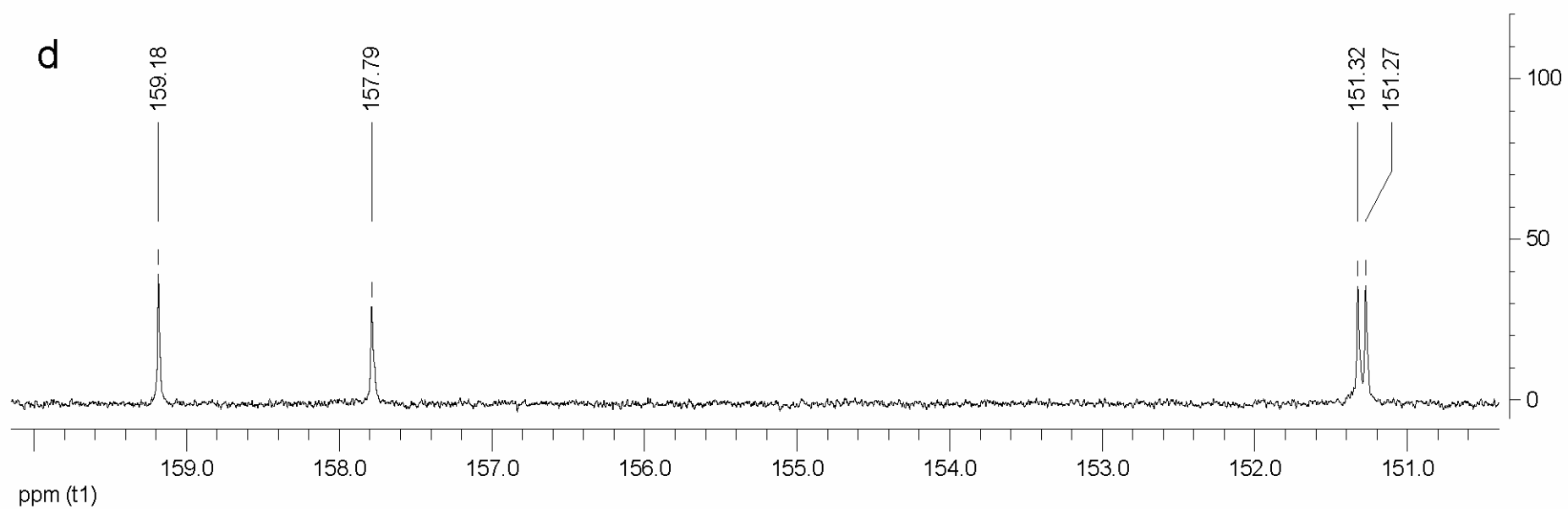
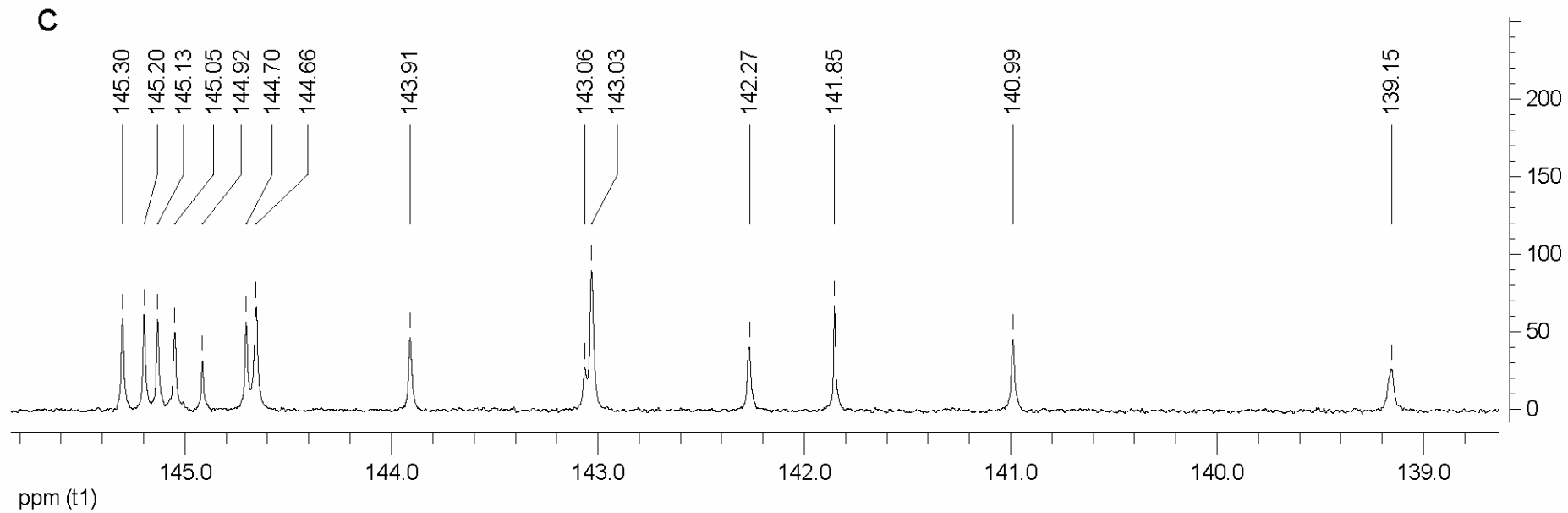


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**FIGURE S9** ( $^1\text{H}$  NMR of **1**,  $\text{CDCl}_3$ )



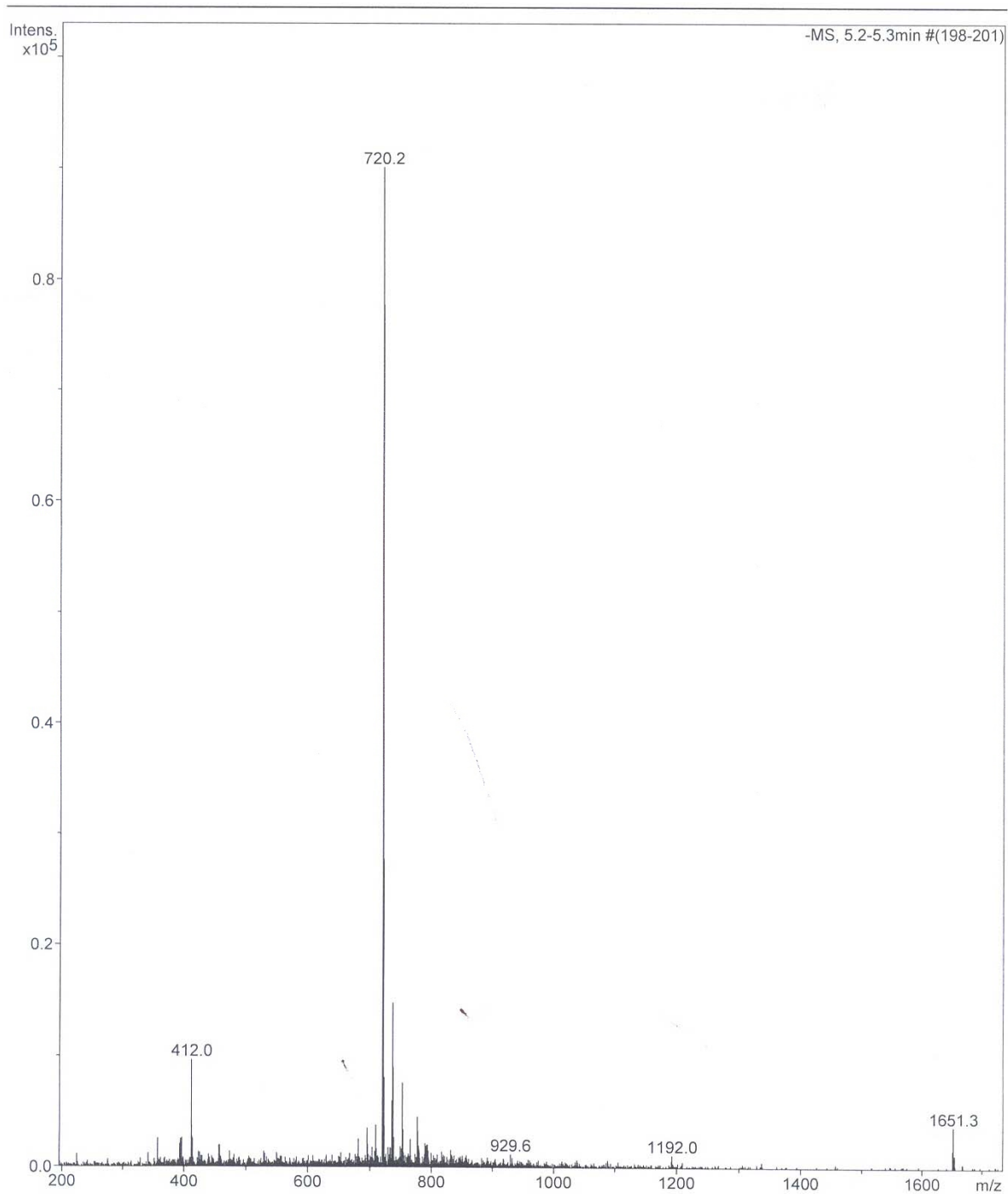
**FIGURE S10** ( $^{13}\text{C}$  NMR of **1**,  $\text{CS}_2/\text{CDCl}_3$  4:1, TMS)





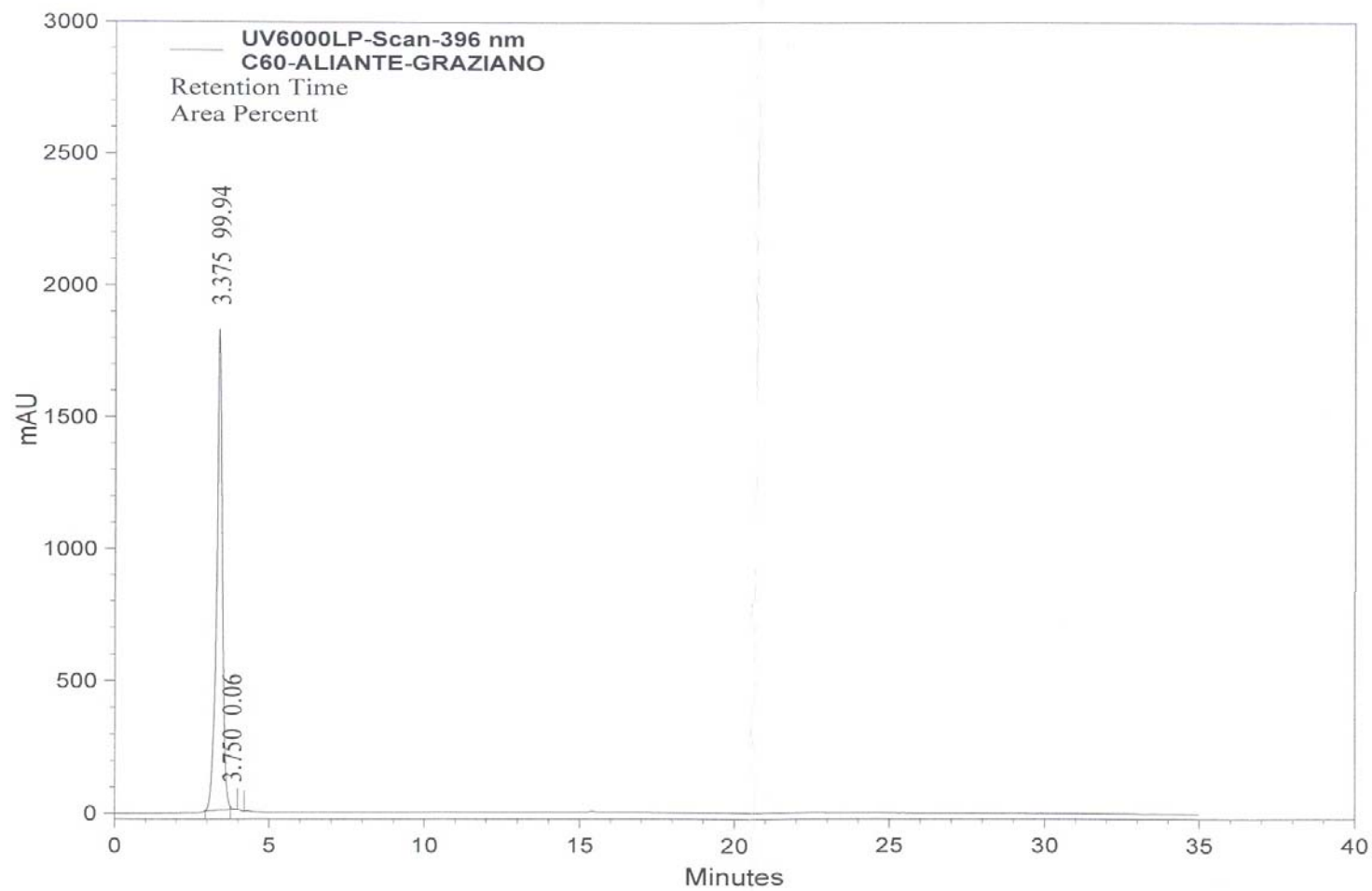
**FIGURE S11** (LC APPI-MS of **1**)

**Analysis Info:** ESI-, cicloesano, infusione, 10  
ml/h



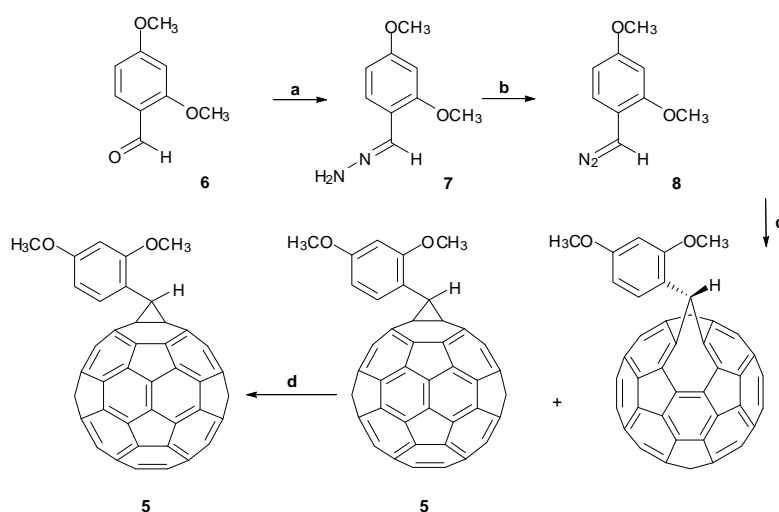
LC APPI (atmospheric pressure photoionization)-MS analysis of derivative **1** (m/z = 1651).

**FIGURE S12** (HPLC trace of **1**)



HPLC analysis of derivative **1** (SiO<sub>2</sub> Phenomenex Luna column (150 × 4.6 mm, 4 μm, eluent: toluene, flow rate: 2 ml/min)

**FIGURE S13.** Structure of methanofullerene **5**, lacking the distyrylbenzene moiety, used as a reference compound for photophysical characterizations.

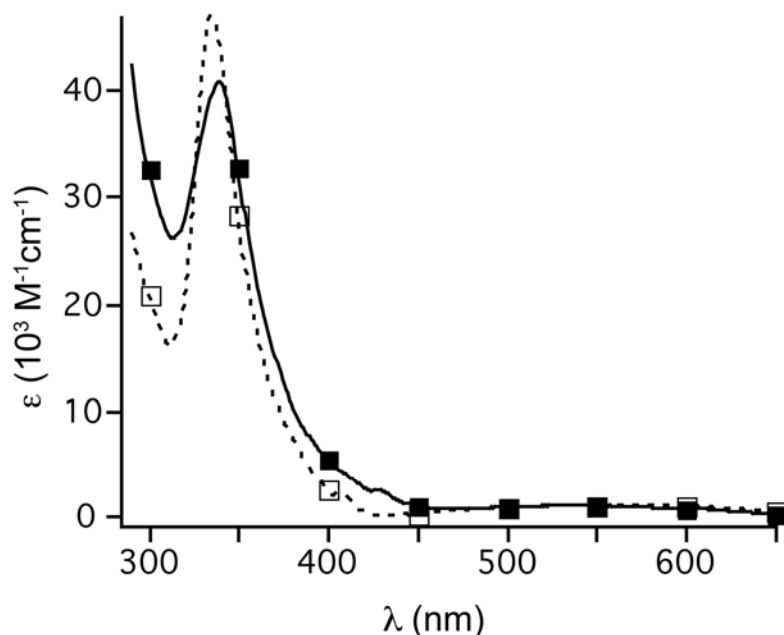


**Synthesis of methanofullerene 5.** Conditions: (a) excess hydrazine hydrate, EtOH, reflux temperature, 6 hours; (b) activated MnO<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, toluene, room temperature, 10 min.; (c) [60]fullerene, toluene, room temperature, 18 h, 14%; (d) thermal isomerization: toluene, reflux temperature 3 hours, >95%.

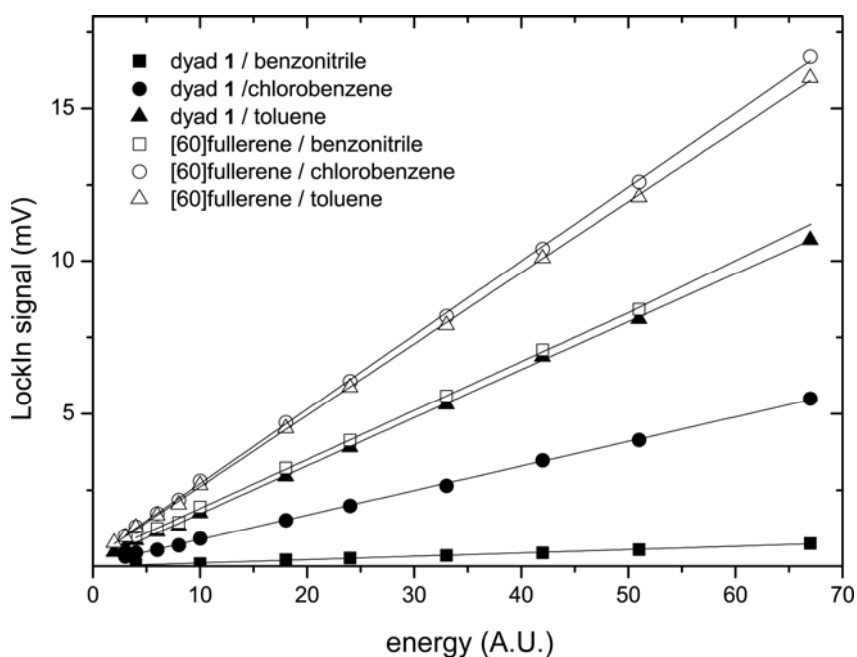
The hydrazone<sup>1</sup> of aldehyde **6** was prepared by dissolving **6** (1.0 g, 6.02 mmol) in absolute ethanol (15 ml). Excess commercial hydrazine hydrate (1.5 ml) was added and the mixture was stirred at reflux temperature for 6 hours. Then the solvents were removed at the rotary evaporator and excess hydrazine under high vacuum (0.1 torr) at 40 °C. The hydrazone **7**, that was used as a crude sample from the previous step without further purification, (116 mg, 0.64 mmol) was dissolved in toluene (10 ml) and dry MgSO<sub>4</sub> (100 mg) was added, followed by portionwise addition of 100 mg of activated MnO<sub>2</sub>. After stirring at room temperature for 10 minutes, the resulting purple solution containing diazoderivative **8** [IR (neat):  $\nu_{\text{N=N}} = 2100 \text{ cm}^{-1}$ ] was filtered through a pad of celite in order to remove all solids. Due to the instability to SiO<sub>2</sub> and concentration, the diazocompound was added directly to a solution of [60]fullerene (300 mg, 0.416 mmol) in toluene (150 ml). The solution was stirred at room temperature for 18 h. Then the solvents were removed in vacuo and the residue was purified by flash column chromatography (SiO<sub>2</sub>, eluent: toluene/petroleum ether 1:1): 51.5 mg (14% yield). The mixture of homofullerene and methanofullerene **5** was converted quantitatively to **5** by heating for 3 hours a solution of the crude mixture in toluene. <sup>1</sup>H NMR (250 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> 4:1, 25 °C, TMS):  $\delta = 7.18$  (d, 1H), 6.57 (s, 1H), 6.55 (d, 1H), 5.05 (s, 1H), 3.98 (s, 3H), 3.83 (s, 3H); <sup>13</sup>C NMR (100 MHz, CS<sub>2</sub>/CDCl<sub>3</sub> 4:1, 25 °C, TMS):  $\delta = 161.25, 159.93, 150.32, 148.60, 145.88, 145.83, 145.23, 145.17, 145.14, 145.01, 144.86, 144.73, 144.70, 144.68, 144.45, 144.41, 144.19, 143.82, 143.15, 143.11, 143.03, 143.01, 142.99, 142.96, 142.88, 142.52, 142.15, 141.13, 140.89, 138.16, 136.51, 133.15, 129.11, 128.34, 125.44, 113.38, 104.14, 99.21, 75.60, 55.81, 55.33, 39.63$ ; APPI-MS:  $m/z$  870 [M]<sup>+</sup>.

1. J. P. Lambooy, *J. Am. Chem. Soc.* **1956**, 78, 771.

**FIGURE S14.** Steady-state UV-Vis absorption spectra of pristine [60]fullerene (full line, filled squares) and model compounds **5** (dashed line, empty squares) in air-saturated toluene.



**FIGURE S15.** Comparison between efficiency of  $^1\text{O}_2$  sensitization of pristine [60]fullerene and dyad **1** in solvents with different dielectric constant; dots are experimental data, and the solid lines are linear fits. The slope ratio between linear fits relative to [60]fullerene and dyad **1** in the same solvent, suitable corrected by the number of absorbed photons (see  $\beta_i$  terms in Eq. 3), corresponds to the second term in the right side of Eq. 2. This term can be considered as an estimate of the relative efficiency of  $^1\text{O}_2$  generation for compound **1** with respect to [60]fullerene.

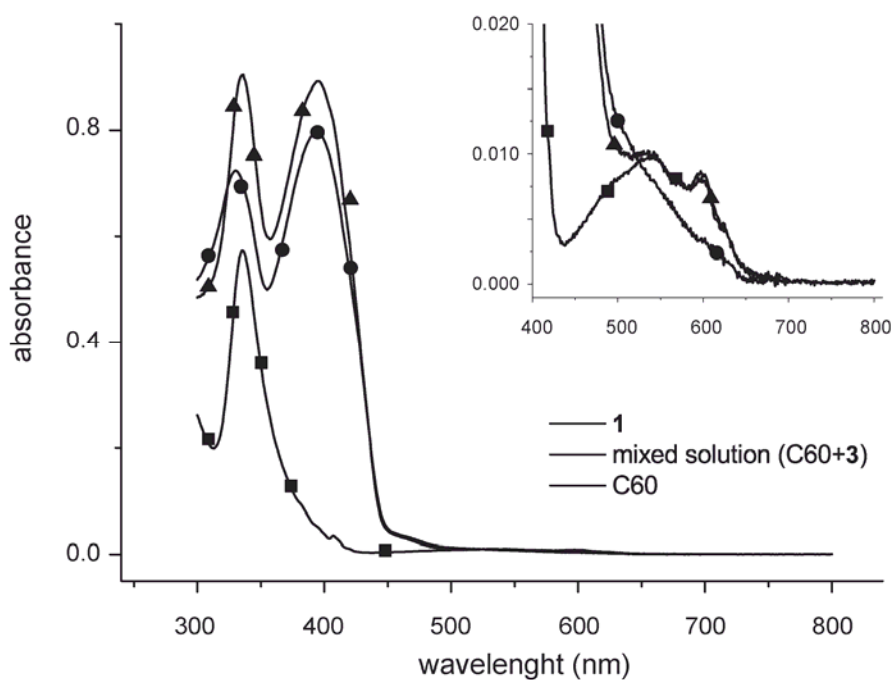




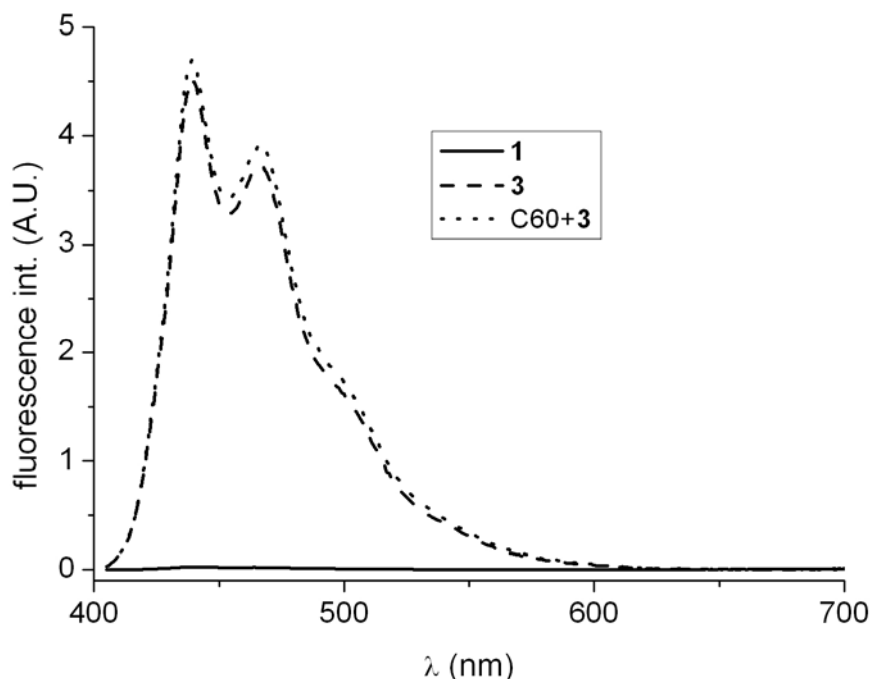
**TABLE S1.** Efficiency of Singlet Oxygen generation for compound **1** in solvents with increasing dielectric constant.

<i>solvent</i>	<i>dielectric constant</i> @ 20°C	$\beta_{C_{60}S_1} / \beta_{1S_{C_{60}}}$
toluene	2.4	0.33
chlorobenzene	5.7	0.2
benzonitrile	26.0	0.04

**FIGURE S16.** Steady-state UV-Vis absorption spectra of pristine [60]fullerene  $c=1 \times 10^{-5}$  M (squares), compound **1**  $c=1 \times 10^{-5}$  M (circles), and a mixed solution of [60]fullerene  $c=1 \times 10^{-5}$  M and compound **3**  $c=2 \times 10^{-5}$  M (triangles) in air-saturated toluene. Due to lack of material, it was not possible to prepare a mixed solution of [60]fullerene and **4**. The data shown in the main text demonstrated however that the photophysical properties of **4** are the sum of the properties of the two branches **3**.



**FIGURE S17.** Emission spectra of toluene solutions of **1** (solid line), **3** (dashed line) and a mixed solution of [60]fullerene and **3** (dotted line) excited at 595nm. The three solutions are approximately equimolar with respect to the amount of the single branch **3**. The fluorescence intensity of **3** is not perturbed by the presence of [60]fullerene, meaning that, in this range of concentrations, no interactions between the fullerene and the DSB moieties are active in absence of a covalent link (see quenched fluorescence of compound **1**).



**TABLE S2.** Comparison between the efficiency of singlet oxygen generation for a solution of compound **1** and an equimolar mixed solution of [60]fullerene and **3**. The  $\Phi_{\Delta}$  of the latter corresponds, within the experimental error, to the quantum yield of [60]fullerene, confirming the absence of detectable interactions between the fullerene and the DSB moieties in absence of a covalent link.

	<i>abs@400nm</i>	$\beta$	<i>slope</i>	$\Phi_{\Delta}$
<b>1</b>	0.39	0.592619722	1.15E-01	0.33
mixed solution	0.029*	0.064594326	0.03571	0.94

\* absorbance due to [60]fullerene