

Supporting Information

Synthesis, structure and photochromic properties of hybrid molecules based on fullerene C₆₀ and spiropyrans

A.R. Tuktarov,¹ A.A. Khuzin,¹ A.R. Tulyabaev,¹ O.V. Venidictova,² T.M. Valova,² V.A. Barachevsky,² L.M. Khalilov,¹ U.M. Dzhemilev¹

¹ *Institute of Petrochemistry and Catalysis, Russian Academy of Sciences
141 Prospekt Oktyabrya, Ufa, 450075, Russia*

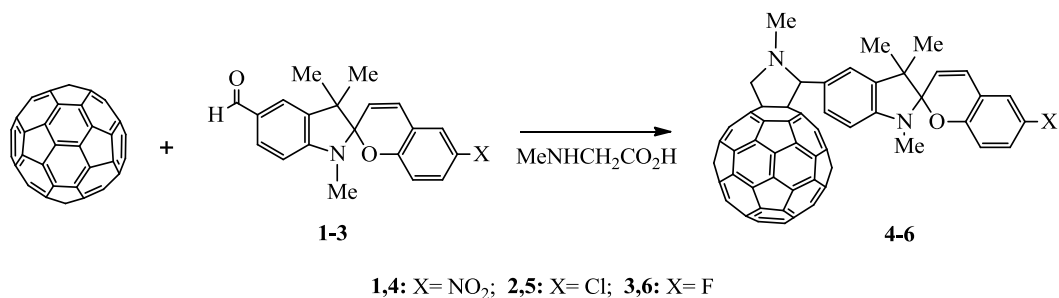
² *Photochemistry Center, Russian Academy of Science
7a, bld.1, Ul. Novatorov, Moscow, 119421, Russia*

TABLE OF CONTENTS

Contents	Page number
1) General considerations, and experimental procedures	2
2) ¹ H, ¹³ C, HSQC and HMBC spectra	4
3) Spectral-kinetic studies	13

General considerations. Commercially available [60]fullerene (99.5% pure, Sigma-Aldrich) was used. Spiropyrans were prepared by standard procedures. The reaction products were analyzed on a HPLC chromatograph HEWLETT PACKARD (model HP 1090 Liquid Chromatograph) at 340 nm. The mixtures were separated on a metal preparative column Cosmosil Buckyprep Waters (250×10 mm) at ~20 °C. Toluene was used as eluent, the flow rate was 3.0 mL·min⁻¹. The ¹H and ¹³C NMR spectra were run on a Bruker Avance-500 spectrometer at 500.17 and 125.78 MHz, respectively. The mixture of CDCl₃ and CS₂ (1:5) was used as a solvent. The mass spectra were obtained on UltraFlex III TOF/TOF (Bruker Daltonik GmbH, Germany) operating in a linear mode. S₈ was used as a matrix. For the application on a metal target, the toluene solutions of the samples were used.

General synthetic procedure of the preparation of pyrrolidinofullerenes 4-6. To a solution of 0.1 g (0.139 mmol) of C₆₀ in 15 ml of chlorobenzene 0.025 g (0.278 mmol) of sarcosine and 0.695 mmol of corresponding spiropyran aldehyde **1-3** were added. The resulting mixture was heated for two hours at 100-110 °C. The reaction products **4-6**, and the starting fullerene C₆₀ were separated by the semi-preparative HPLC, eluent was toluene.



Spectral-kinetic studies. Spectrophotometric measurements for solutions were carried out on a CARY 50bio spectrophotometer (Varian) in a quartz cell (KU-1 quartz) with optical path length of 2 mm. The photochromic properties of **1-4** were studied at room temperature for solutions with the molar concentration $c = 2 \cdot 10^{-4}$ M. For photochemical studies, solutions were irradiated with a L8253 xenon lamp included in an LC-4 radiation unit (Hamamatsu) at a medium radiation power through color glass filter UFS-1. The UFS -1 optical filter transmits UV irradiation into the spectral range of 235-400 nm. UV light powers through UFS -1 optical filter and without it were 49 and 66,5 W/m². To study the photodegradation using unfiltered light in the presence of air oxygen. A series of experiments was carried out at a lower temperature. The solution was cooled in a freezer until the solution temperature -1 ÷ + 5° C and irradiated «NORMA» light flash lamp in a quartz cuvette 0.2 cm thick. Absorption spectra and kinetics of photochromic

transformations were recorded at intervals of 1 ms, using fiber optic USB-2000 spectrometer with a multichannel detector company Ocean Optics.

Also studied samples of amorphous films photochromic monomer and hybrid molecules. Amorphous films were prepared by single-watering the concentrated solutions of the compounds in chloroform onto quartz glass. After drying at room temperature, samples finally dried in an oven at 50 ° C for 30 min.

Pyrrolidinofullerene 4. IR: 526, 710, 953, 1061, 1089, 1123, 1271, 1379, 1464, 1479, 1492, 1518, 1578 cm^{-1} . UV (CHCl_3), λ_{max} , nm: 256, 326, 427. ^1H NMR (500 MHz, CDCl_3): δ 1.26 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 2.92 (s, 3H, CH_3 , N-Me pyrrolidine), 4.30 (d, H, CH_2 , pyrrolidine, $J = 9.0$), 4.94 (s, 1H, CH, pyrrolidine), 5.00 (d, H, CH_2 , pyrrolidine, $J = 9.0$), 5.83 (d, 1H, CH, pyran, $J = 10.0$), 6.79 (d, 1H, CH, $J = 10.0$), 6.96 (d, 1H, CH, pyran, $J = 10.0$), 7.99 (d, 1H, CH, indole, $J = 8.0$), 8.03 (s, 1H, CH, indole), 8.04 (d, 1H, CH, indole, $J = 8.0$), 8.05 (s, 1H, CH). ^{13}C NMR (125 MHz, CDCl_3): δ 19.99, 25.47, 25.76, 28.87, 28.96, 40.15, 52.19, 68.82, 70.11, 77.83, 77.95, 83.73, 106.29, 106.44, 115.39, 115.45, 118.62, 121.44, 122.82, 125.91, 128.39, 128.52, 135.96, 136.41, 136.52, 136.57, 136.62, 139.34, 139.42, 139.95, 140.21, 140.29, 141.09, 141.13, 141.68, 141.75, 141.89, 142.03, 142.10, 142.18, 142.24, 142.34, 142.68, 142.78, 143.09, 143.29, 144.43, 144.48, 144.72, 144.78, 145.19, 145.29, 145.36, 145.48, 145.52, 145.55, 145.58, 145.69, 145.83, 145.85, 145.99, 146.18, 146.24, 146.28, 146.37, 146.59, 146.99, 147.33, 147.36, 147.77, 153.62, 153.68, 154.06, 154.23, 156.45, 156.50, 159.44, 159.47. MALDI TOF: m/z found 1096.1 $[\text{M-H}]^-$.

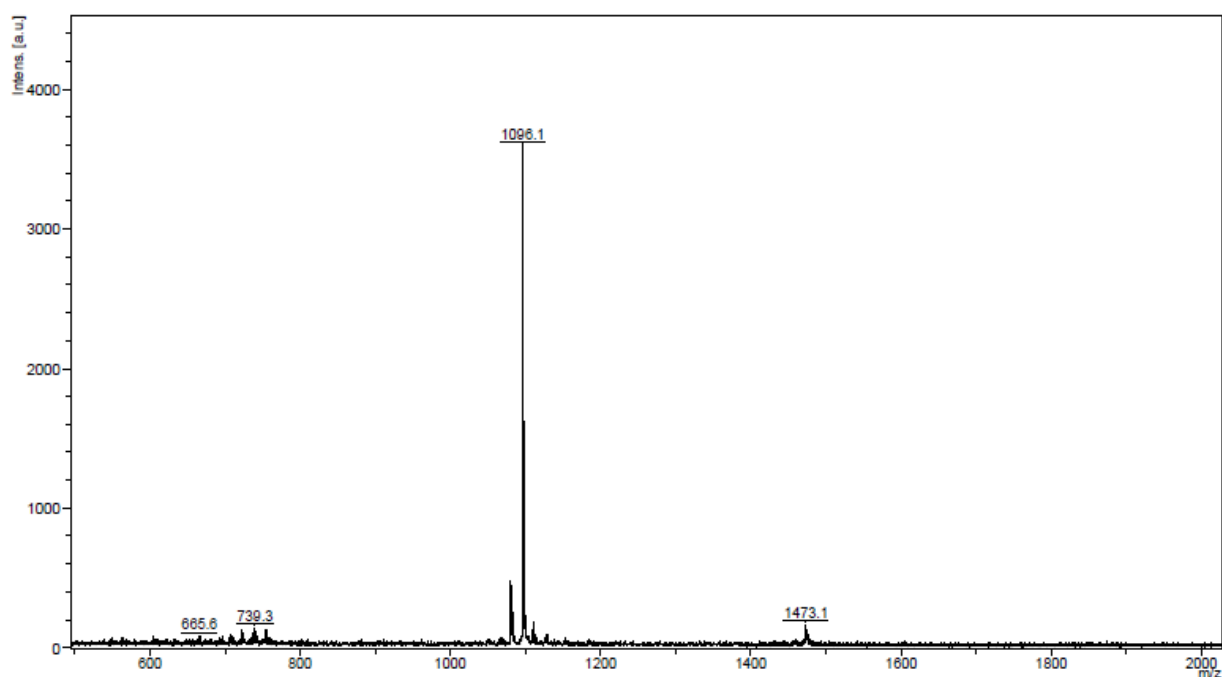


Figure 1. Mass spectra MALDI TOF of compound **4** (matrix – S_8).

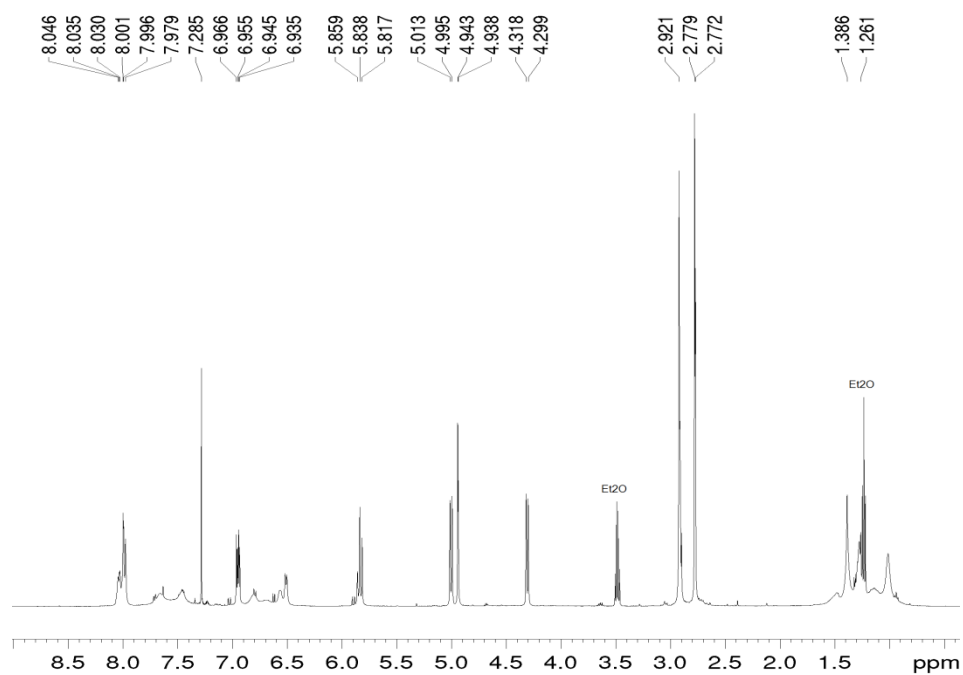


Figure 2. The ^1H NMR spectrum of compound **4** (500.17 MHz, solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

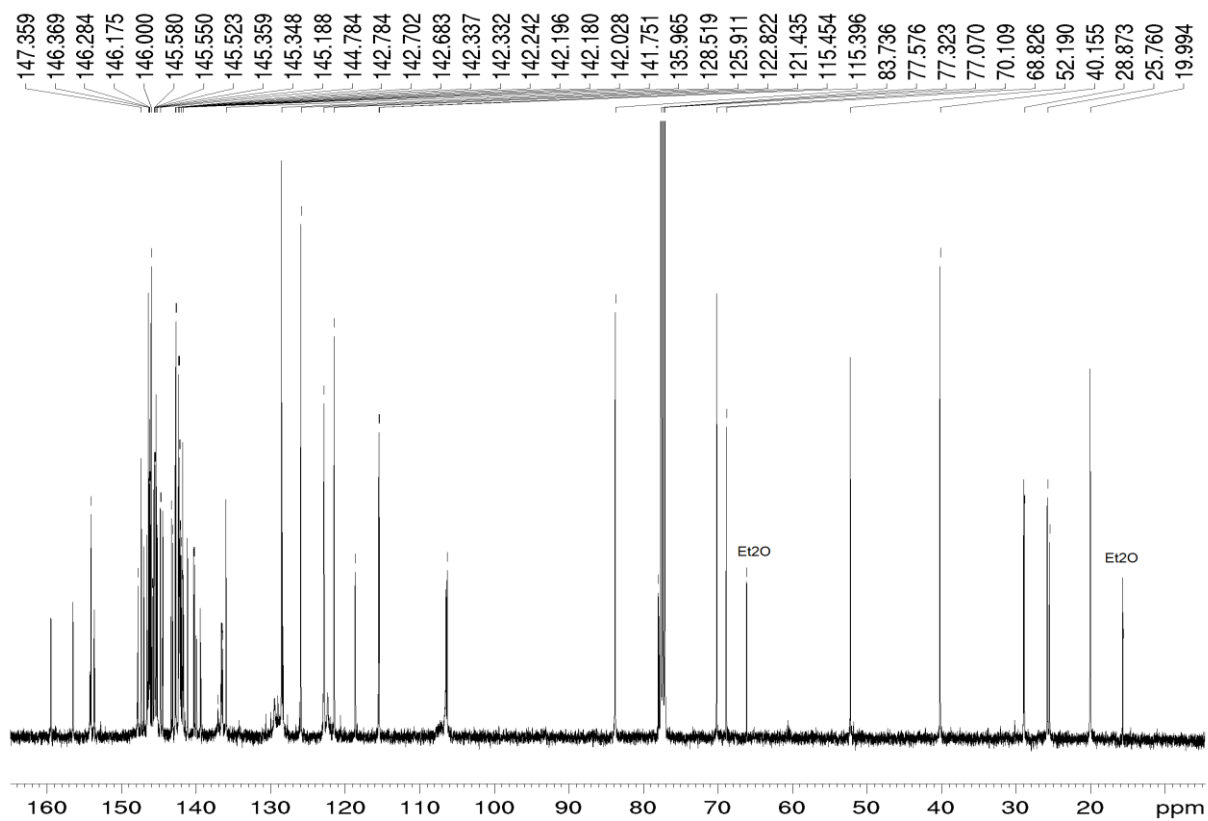


Figure 3. The ^{13}C NMR spectrum of compound **4** (125.78 MHz, solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

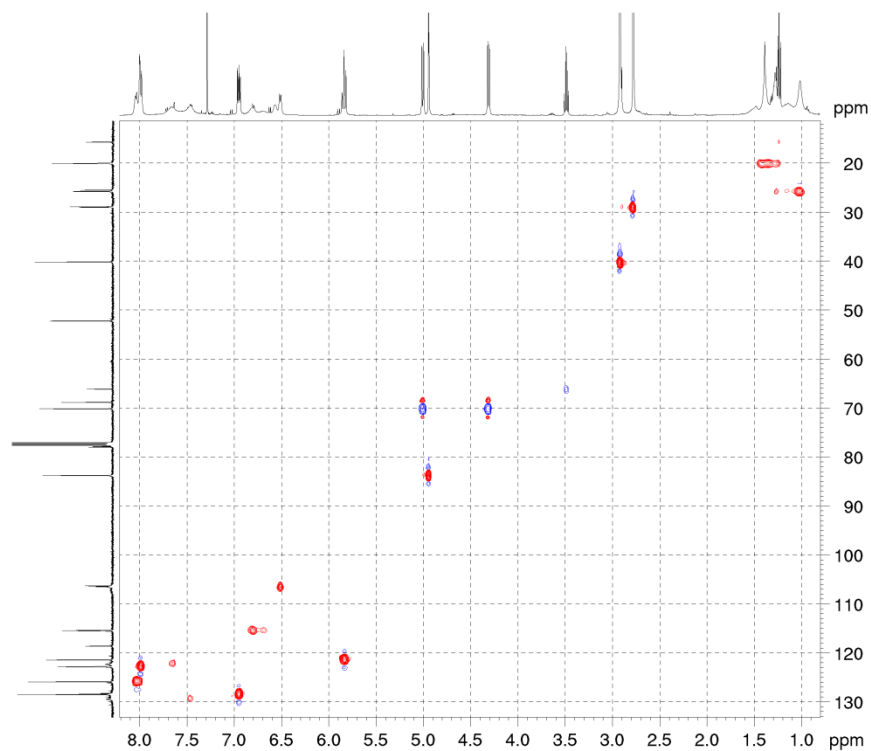


Figure 4. The HSQC spectrum of compound **4** (500.17 MHz for ^1H , 125.78 MHz for ^{13}C , solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

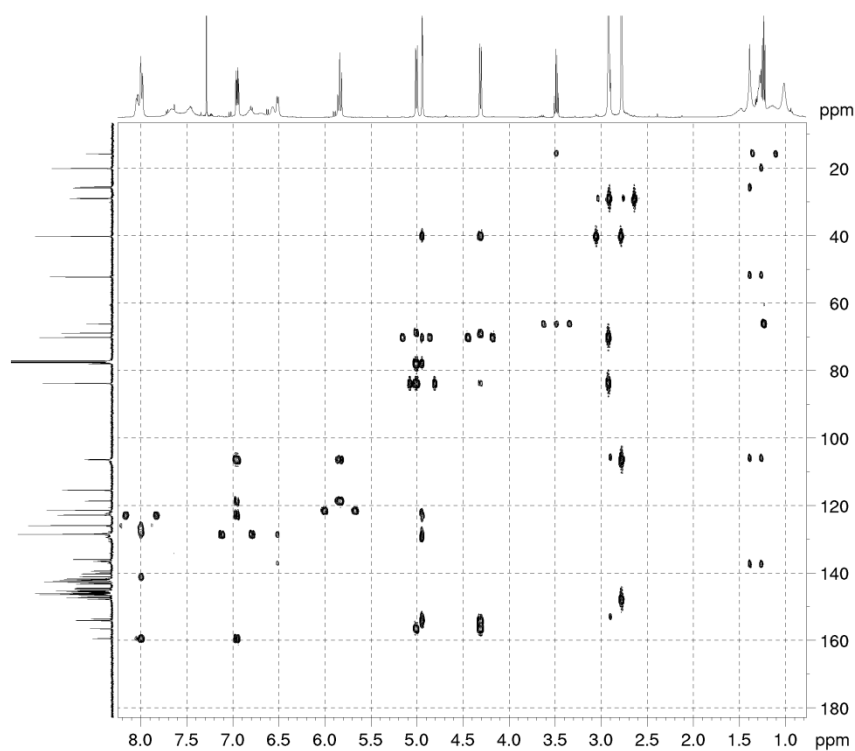


Figure 5. The HMBC spectrum of compound **4** (500.17 MHz for ^1H , 125.78 MHz for ^{13}C , solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

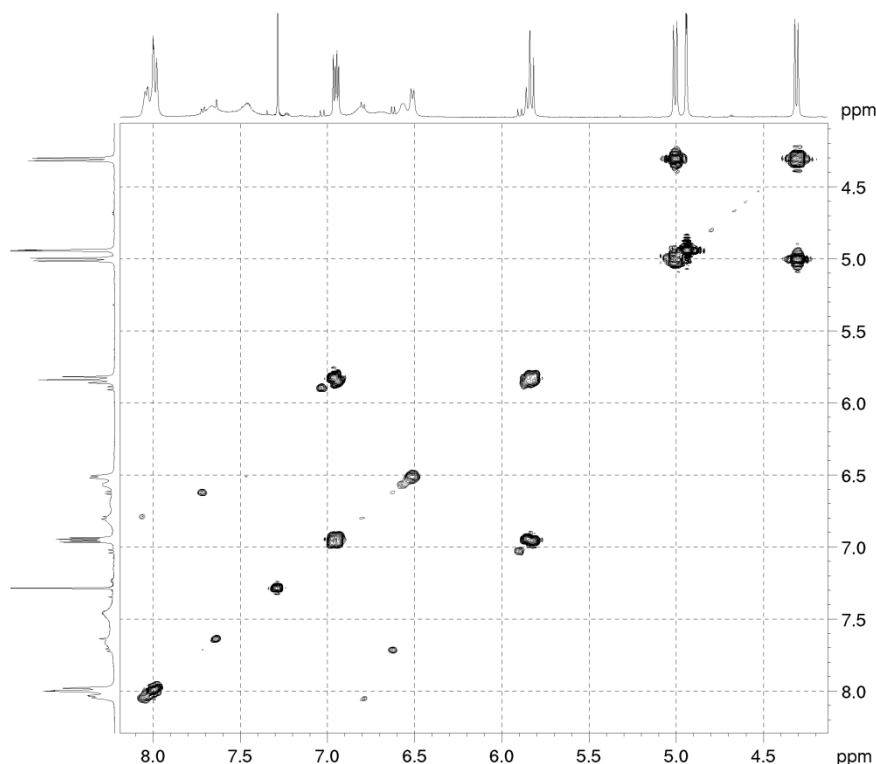


Figure 6. The H-H COSY spectrum of compound **4** (500.17 MHz for ^1H , solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

Pyrrolidinofullerene 5. IR: 526, 731, 962, 1122, 1179, 1260, 1464, 1476, 1491 cm^{-1} . UV (CHCl_3), λ_{max} , nm: 255, 327, 430. ^1H NMR (500 MHz, CDCl_3): δ 1.26 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 2.91 (s, 3H, CH_3 , N-Me pyrrolidine), 4.29 (d, H, CH_2 , pyrrolidine, $J = 9.0$), 4.92 (s, 1H, CH, pyrrolidine), 4.99 (d, H, CH_2 , pyrrolidine, $J = 9.0$), 5.70 (d, 1H, CH, pyran, $J = 10.0$), 6.79 (d, 1H, CH, $J = 10.0$), 6.98 (d, 1H, CH, pyran, $J = 10.0$), 7.22 (d, 1H, CH, indole, $J = 8.0$), 7.29 (s, 1H, CH, indole), 7.44 (s, 1H, CH), 7.45 (d, 1H, CH, indole, $J = 8.0$). ^{13}C NMR (125 MHz, CDCl_3): δ 20.16, 25.46, 25.74, 28.89, 28.98, 40.12, 51.75, 68.83, 70.11, 77.89, 78.02, 83.83, 104.45, 104.61, 116.33, 116.37, 119.99, 120.51, 125.19, 126.39, 126.43, 127.69, 127.75, 128.73, 129.56, 130.61, 135.91, 135.95, 136.00, 136.37, 136.49, 136.64, 136.70, 139.41, 139.46, 139.96, 140.16, 140.18, 140.27, 141.68, 141.77, 141.78, 141.92, 142.04, 142.07, 142.09, 142.11, 142.19, 142.23, 142.34, 142.36, 142.66, 142.76, 143.07, 143.27, 144.45, 144.77, 145.17, 145.29, 145.32, 145.46, 145.49, 145.52, 145.54, 145.58, 145.68, 145.84, 145.87, 145.98, 146.15, 146.22, 146.28, 146.35, 146.47, 146.62, 147.05, 147.33, 148.12, 152.82, 152.87, 153.75, 153.82, 154.12, 154.37, 156.50, 156.56. MALDI TOF: m/z found 1085.1 $[\text{M}-\text{H}]^-$.

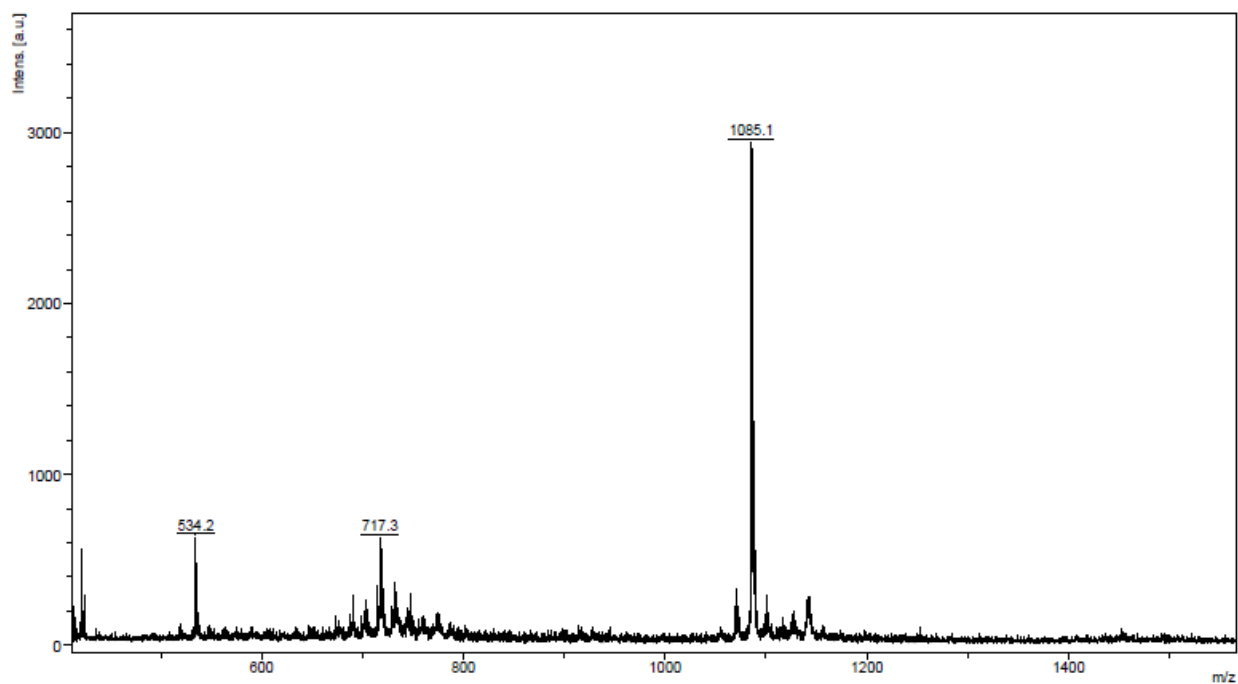


Figure 7. Mass spectra MALDI TOF of compound **5** (matrix – S_8).

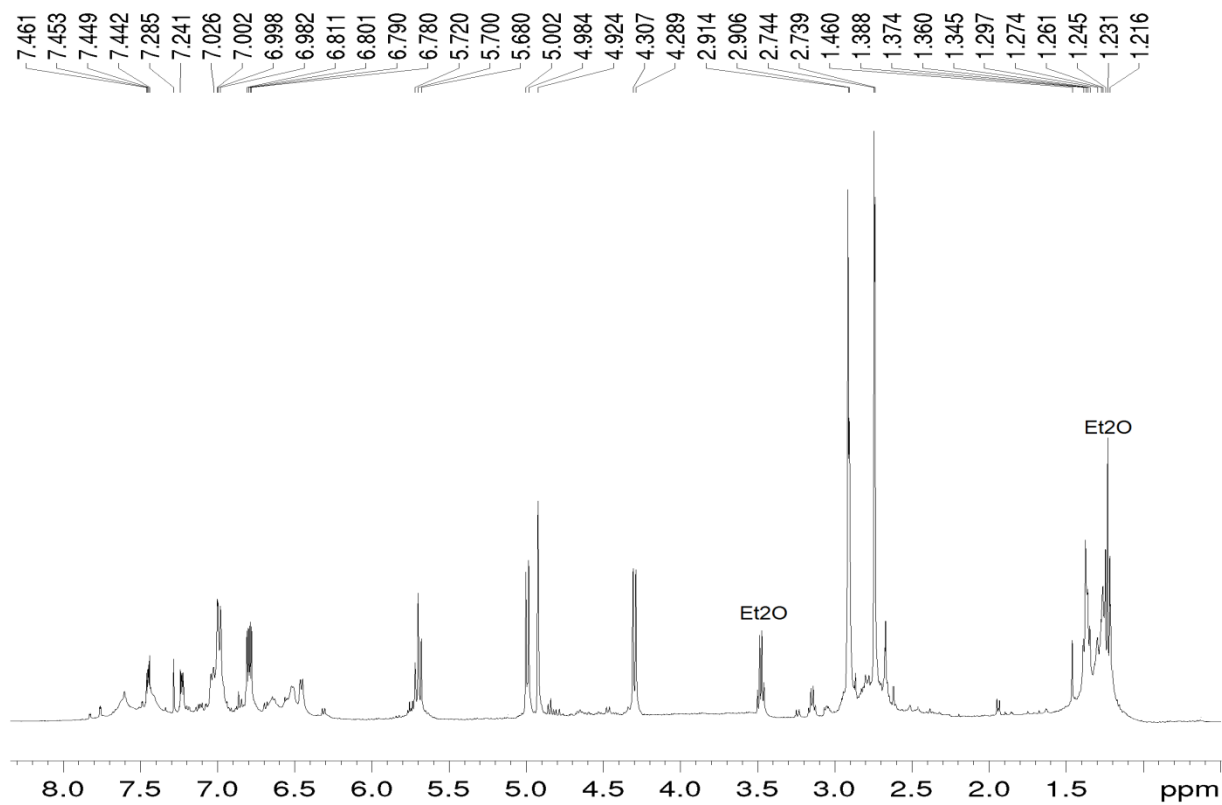


Figure 8. The ^1H NMR spectrum of compound **5** (500.17 MHz, solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

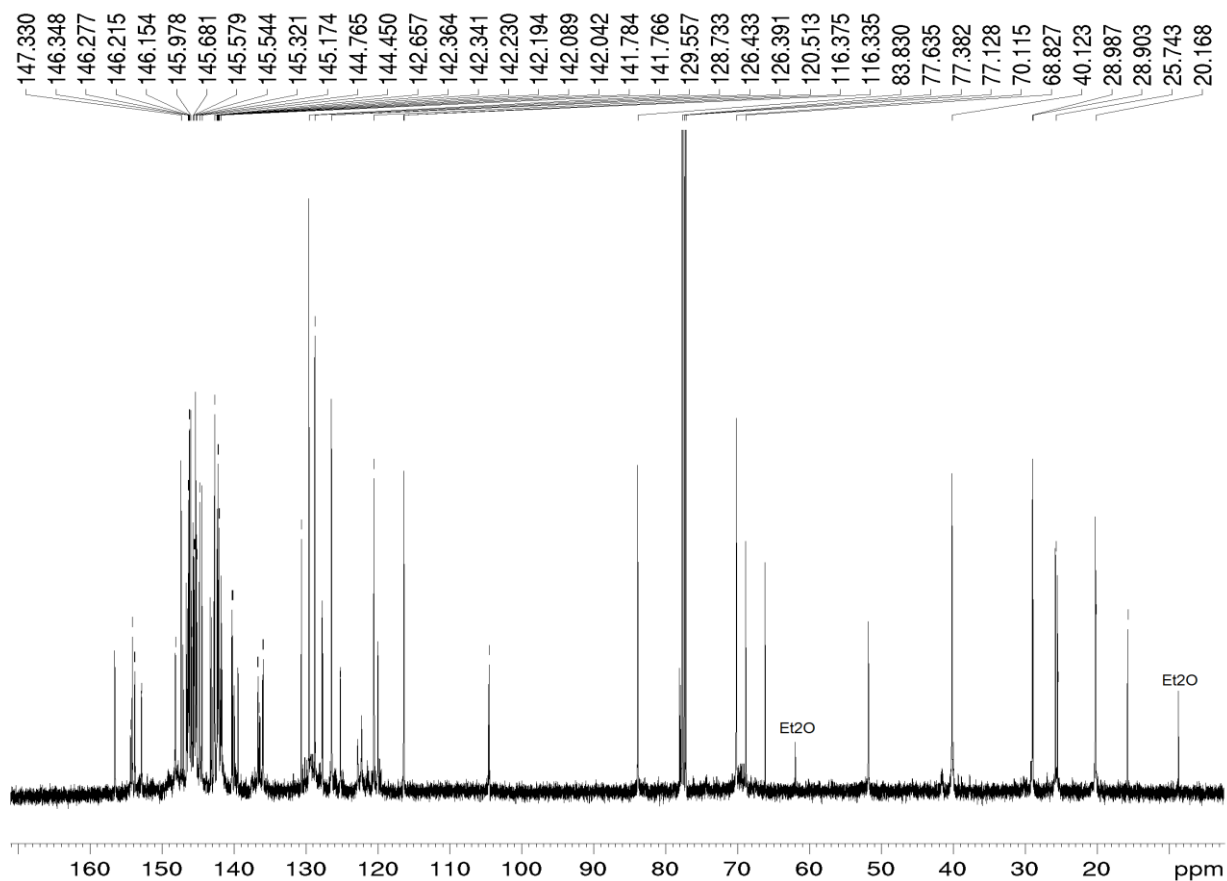


Figure 9. The ^{13}C NMR spectrum of compound **5** (125.78 MHz, solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

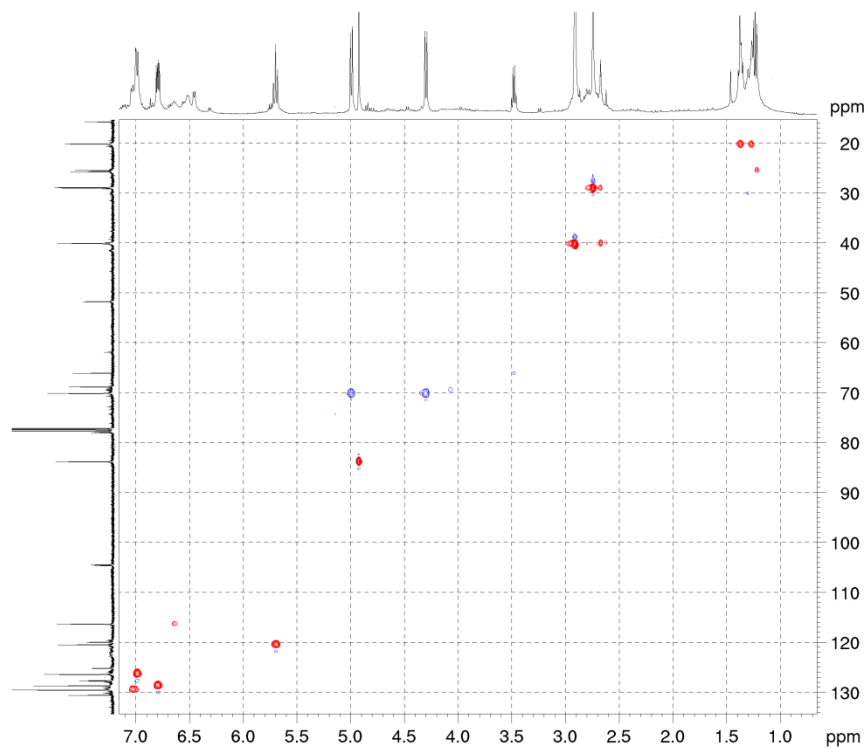


Figure 10. The HSQC spectrum of compound **5** (500.17 MHz for ^1H , 125.78 MHz for ^{13}C , solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

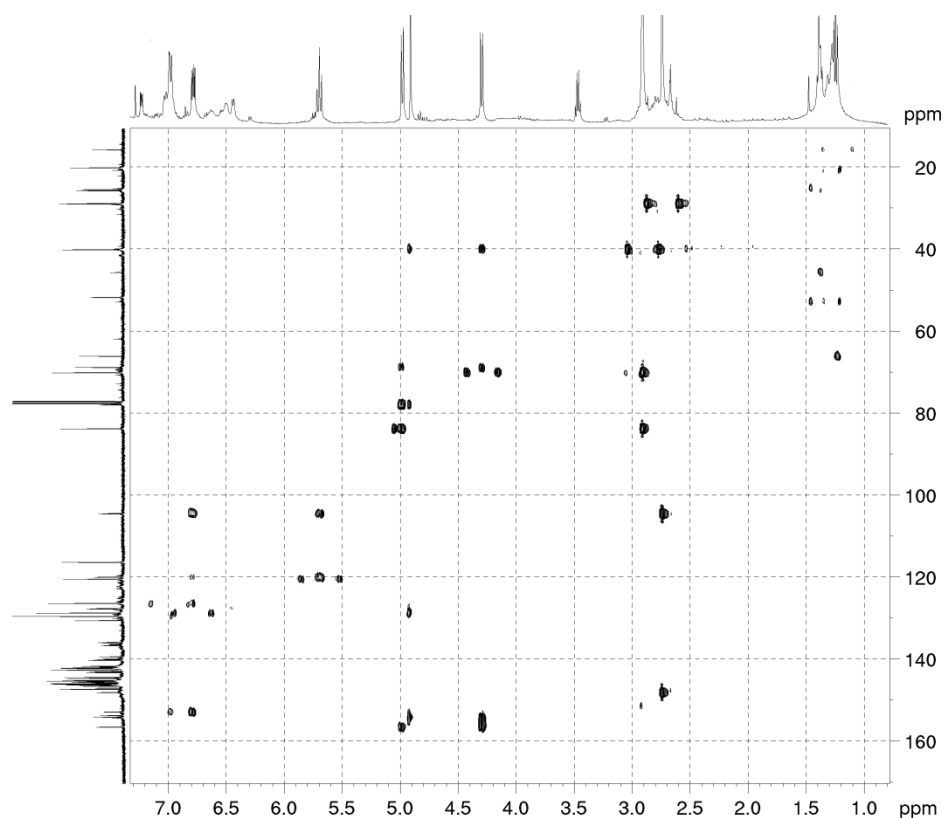


Figure 11. The HMBC spectrum of compound **5** (500.17 MHz for ^1H , 125.78 MHz for ^{13}C , solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

Pyrrolidinofullerene 6. IR: 526, 729, 935, 1179, 1251, 1463, 1485 cm^{-1} . UV (CHCl_3), λ_{max} , nm: 254, 326, 430. ^1H NMR (500 MHz, CDCl_3): δ 1.26 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 2.74 (s, 3H, CH_3), 2.92 (s, 3H, CH_3 , N-Me pyrrolidine), 4.30 (d, H, CH_2 , pyrrolidine, $J = 9.0$), 4.92 (s, 1H, CH, pyrrolidine), 4.99 (d, H, CH_2 , pyrrolidine, $J = 9.0$), 5.69 (d, 1H, CH, pyran, $J = 10.0$), 6.44 (d, 1H, CH, $J = 10.0$), 6.50 (d, 1H, CH, pyran, $J = 10.0$), 6.72 (d, 1H, CH, indole, $J = 8.0$), 6.79 (s, 1H, CH, indole), 6.80 (d, 1H, CH, indole, $J = 8.0$), 6.81 (s, 1H, CH). ^{13}C NMR (125 MHz, CDCl_3): δ 20.23, 25.46, 25.74, 28.91, 28.99, 40.12, 51.67, 68.83, 70.13, 77.89, 78.02, 83.86, 104.17, 104.29, 112.69, 112.88, 115.86, 116.04, 116.23, 119.26, 119.31, 120.65, 127.63, 128.89, 135.91, 136.35, 136.49, 136.66, 139.42, 139.94, 139.96, 140.18, 140.29, 141.69, 141.78, 142.08, 142.22, 142.36, 142.66, 142.76, 143.07, 143.26, 143.28, 144.46, 144.77, 145.19, 145.33, 145.56, 145.69, 145.87, 145.98, 146.17, 146.35, 146.62, 147.06, 147.33, 148.18, 150.25, 153.76, 153.80, 154.13, 154.38, 155.64, 156.58, 157.55. MALDI TOF: m/z found 1069.1 [M-H].

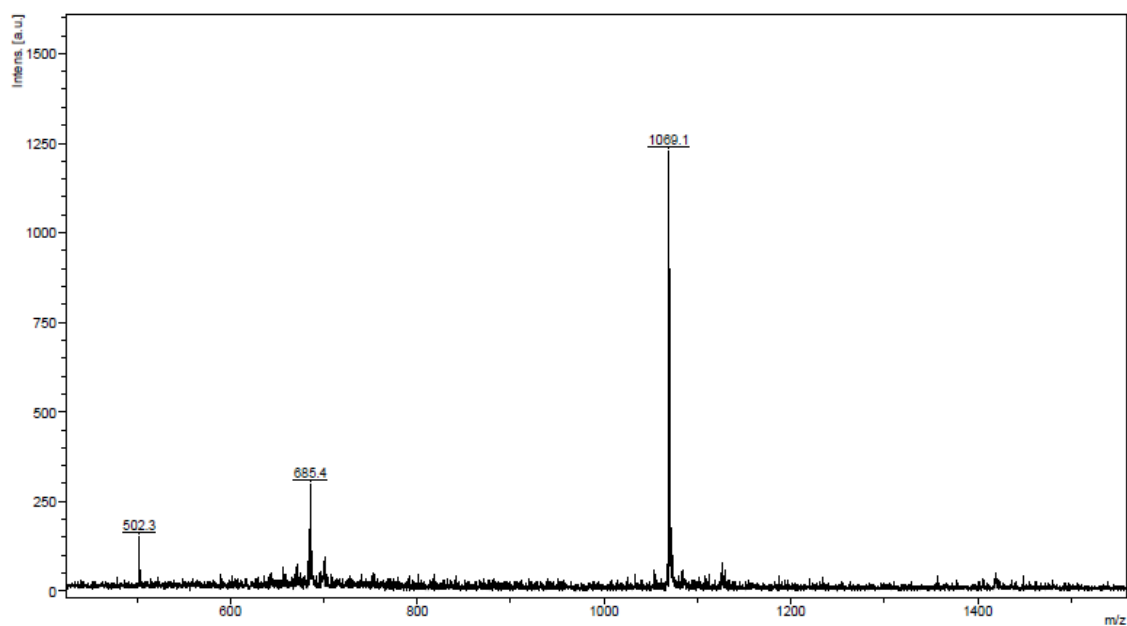


Figure 12. Mass spectra MALDI TOF of compound **6** (matrix – S₈).

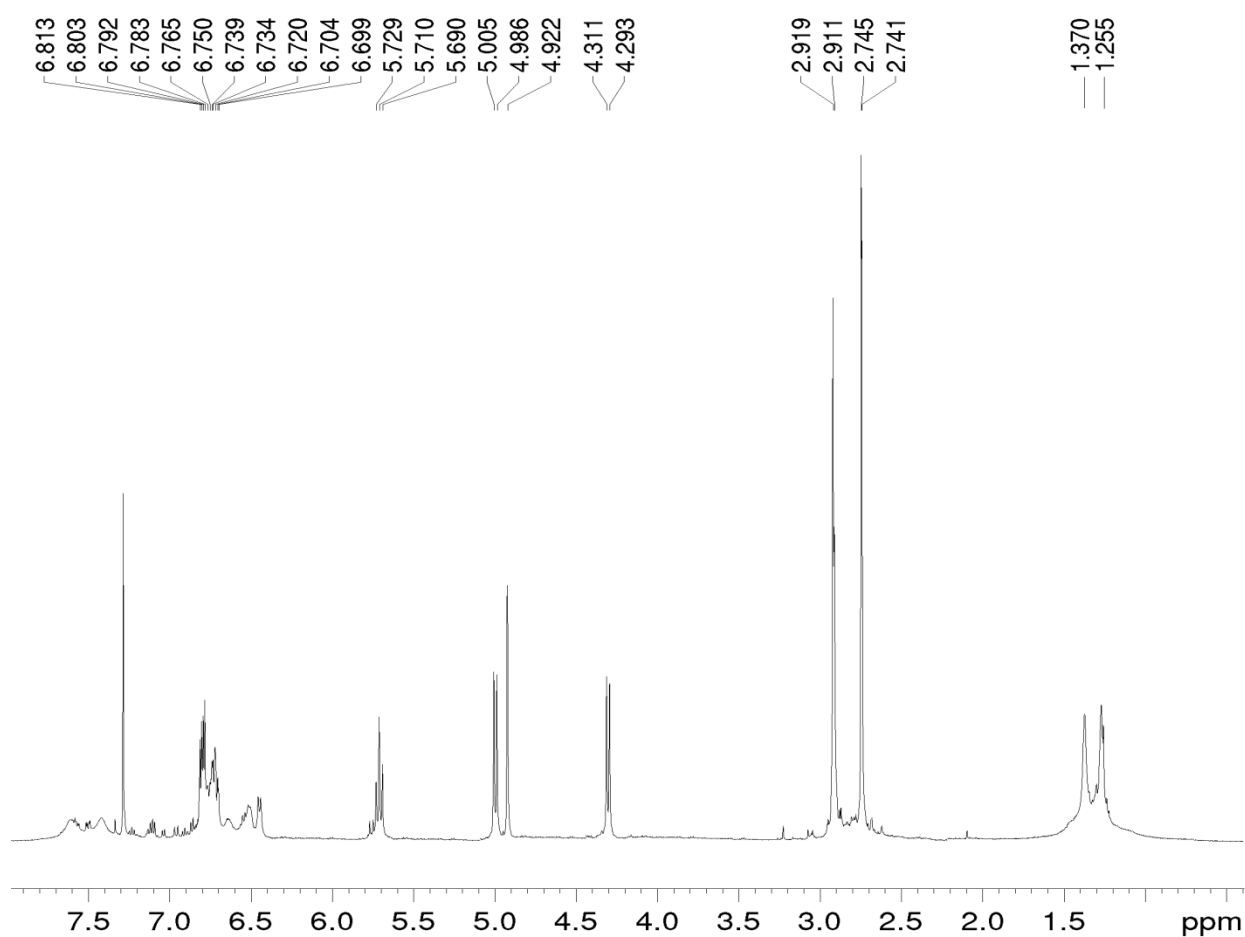


Figure 13. The ¹H NMR spectrum of compound **6** (500.17 MHz, solvent CS₂ : CDCl₃ = 5:1)

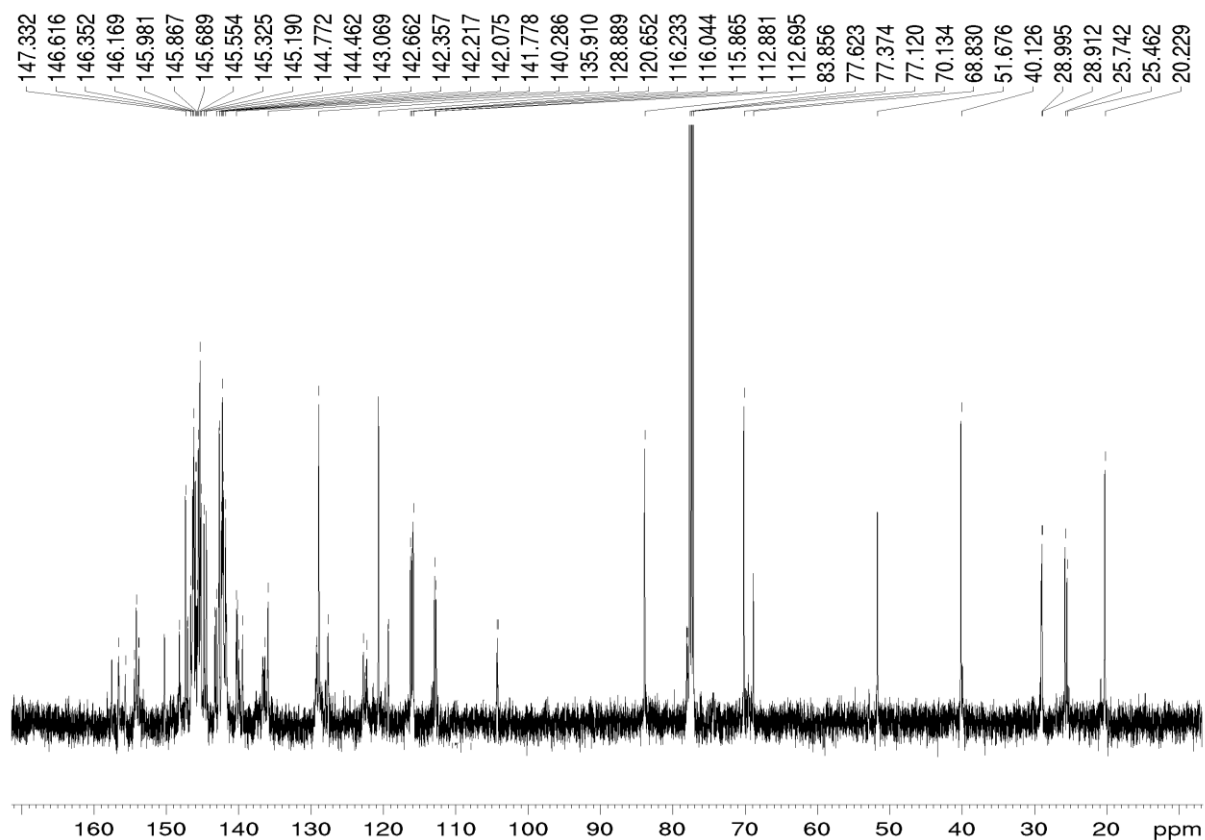


Figure 14. The ^{13}C NMR spectrum of compound **6** (125.78 MHz, solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

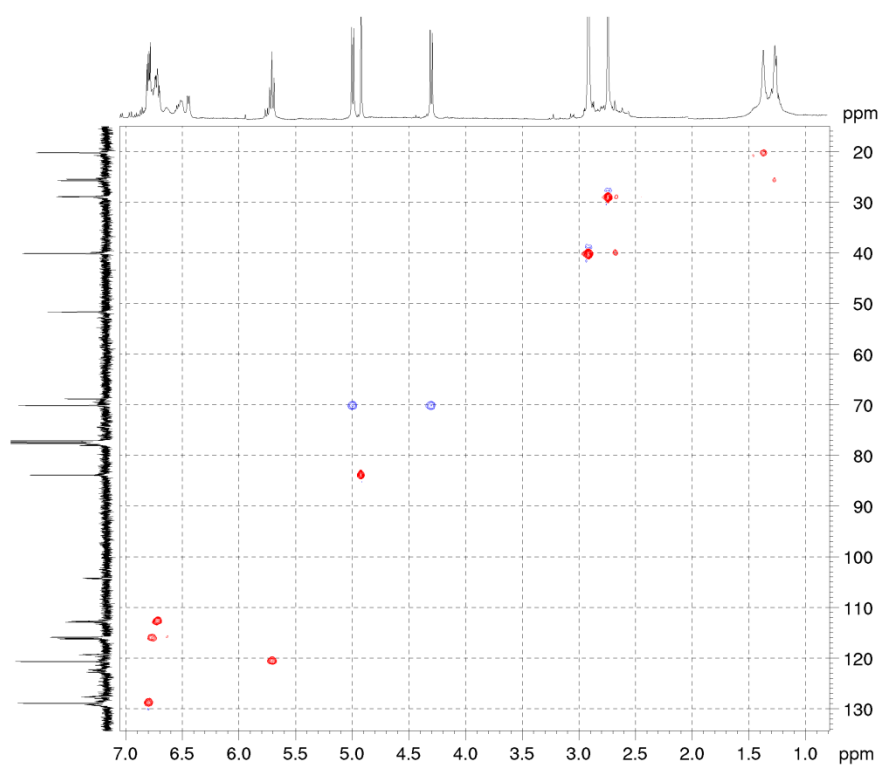


Figure 15. The HSQC spectrum of compound **6** (500.17 MHz for ^1H , 125.78 MHz for ^{13}C , solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$)

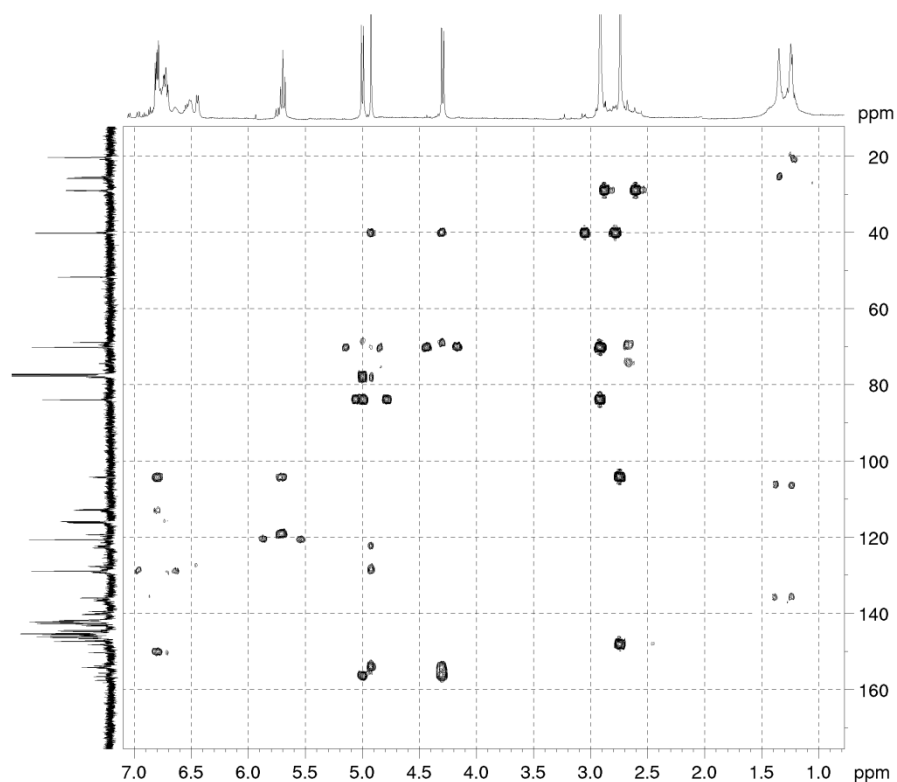


Figure 16. The HMBC spectrum of compound **6** (500.17 MHz for ^1H , 125.78 MHz for ^{13}C , solvent $\text{CS}_2 : \text{CDCl}_3 = 5:1$).

Spectral-kinetic studies.

Table 1. Spectral-kinetic characteristic of **1-6** in toluene and chloroform.

Compound	Solvent	$\lambda_{\text{A}}^{\text{max}}$, nm	ϵ , $\text{M}^{-1}\cdot\text{sm}^{-1}$	$\lambda_{\text{B}}^{\text{max}}$, nm	$\Delta D_{\text{B}}^{\text{phot}}/D_{\text{A}}^{\text{max}}$	k_{To}^* , s^{-1}	$\tau_{1/2}^{\text{phtdgr}}$, s
1	toluene	315	-	580 620	0.6	0.10	52
4	toluene	325	56250	610	0.4	0,04	143
1	chloroform	320	7750	595	0.3	0.07	21
4	chloroform	325	47500	590	0.2	0.03	57
1	amorphous films	330	-	560	0.2	-	-

4	amorphous films	213 257 325	-	615	0.02	-	-
3	toluene	315 390 580	-	490	0.1	0.70	75
6	toluene	320	50000	-	-	-	-
3	chloroform	330 390 575	9000	540	0.2	0,27	120
6	chloroform	320	46500	-	-	-	-
2	toluene	320	-	600	0.03	2,15	40
5	toluene	320	43500	-	-	-	-
2	chloroform	325 382	12750	505	0.4	0,002	325
5	chloroform	320	21000	-	-	-	-

Note: λ_A^{\max} и λ_B^{\max} – maxima of absorption bands of initial spirane and photoinduced merocyanine forms spiropyrane of a fragment of a hybrid compound, respectively; ϵ - a coefficient of molar extinction; $\Delta OD_B^{\text{phot}}/OD_A^{\max}$ – a ratio of values of optical density at a maximum of the absorption band of the photoinduced merocyanine form of spiropyrane at a photoequilibrium state to the value of optical density in the maximum of the absorption band of the initial compounds; k_{db} – a rate constant of spontaneous bleaching the photoinduced merocyanine form at room temperature; $\tau_{1/2}^{\text{pdegr}}$ – time of halving decreasing of the value of optical density at the maximum of the absorption band of the merocyanine form at constant irradiation by nonfiltered light. *It was measured with precision up to 2,2 %.

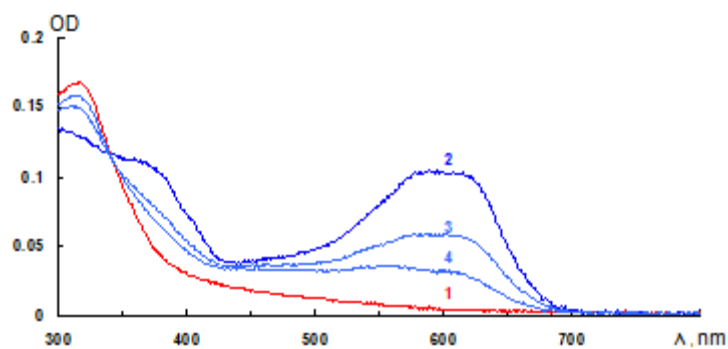


Figure 17. Absorption spectra of spiropyran **1** in toluene before exposure to radiation (1), during the irradiation through a UFS-1 optical filter (2), and after the subsequent bleaching in the dark (3,4,5).

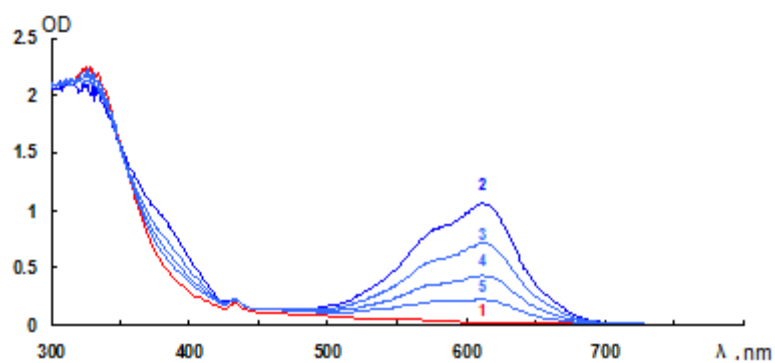


Figure 18. Absorption spectra of fulleropyrrolidine **4** in toluene before exposure to radiation (1), during the irradiation through a UFS-1 optical filter (2), and after the subsequent bleaching in the dark (3,4,5).

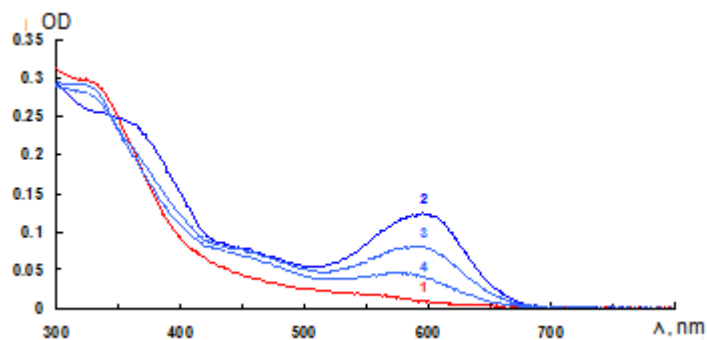


Figure 19. Absorption spectra of spiropyran **1** in chloroform before (1), during (2) the irradiation through a UFS-1 optical filter (2), and after the subsequent bleaching in the dark (3,4).

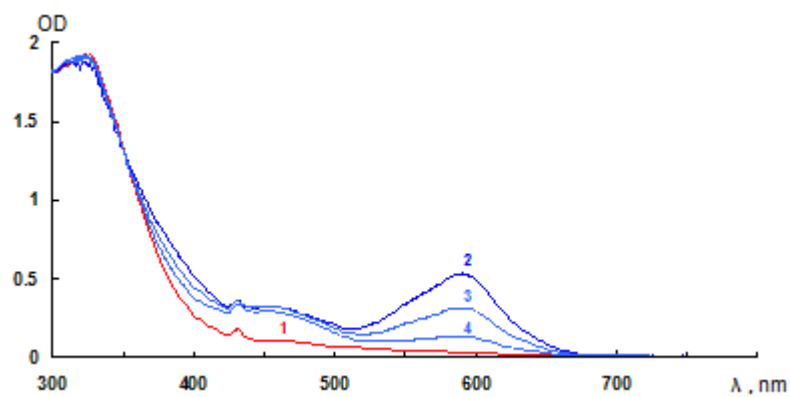


Figure 20. Absorption spectra of fulleropyrrolidine **4** in chloroform before (1), during (2) the irradiation through a UFS-1 optical filter (2), and after the subsequent bleaching in the dark (3,4).

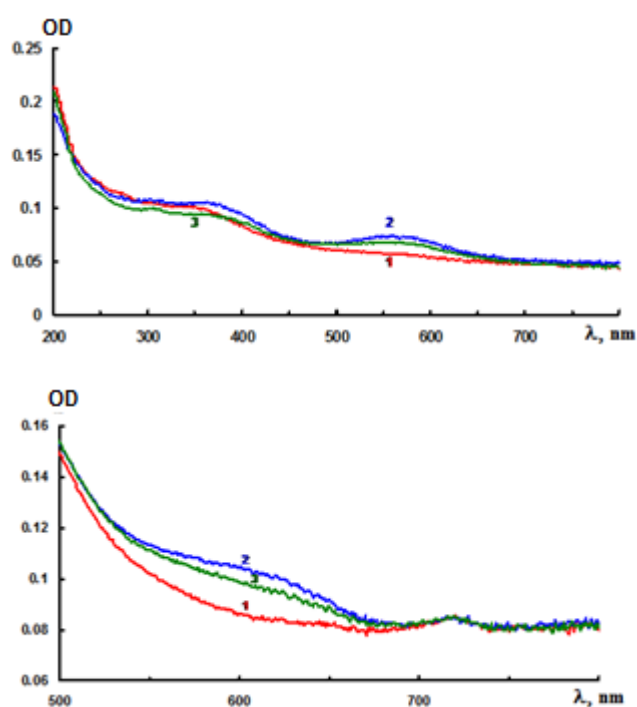


Figure 21. Absorption spectra of spiropyran **1** (above) and its hybrid compound with fullerene **4** (below) in amorphous films before (1) and after the exposure to unfiltered light (2), followed by dark relaxation for 1 hour (3).

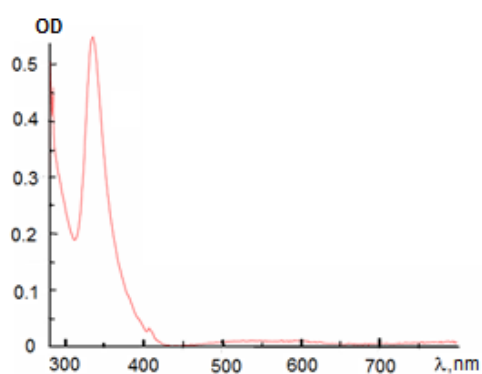


Figure 22. Absorption spectra of [60]fullerene in toluene

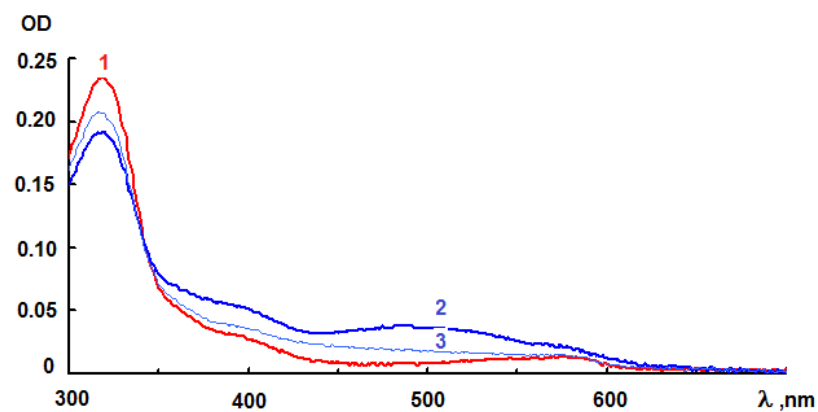


Figure 23. Absorption spectra of the compound **3** in toluene before (1), after UV irradiation through the UFS-1 optical filter (2) and after subsequent dark bleaching (3).

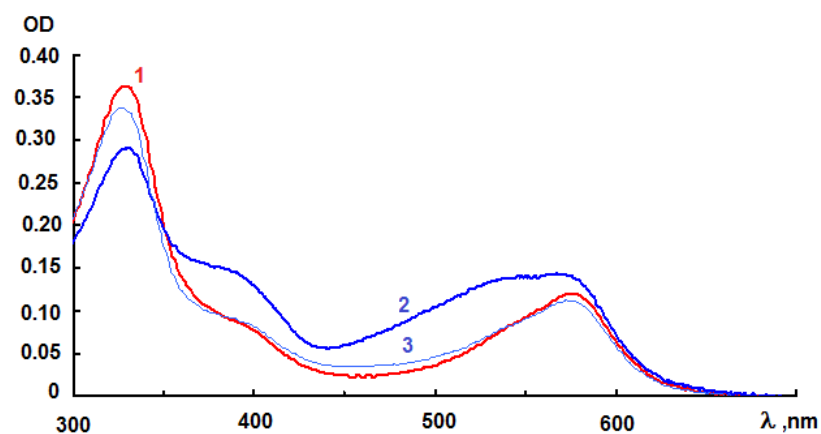


Figure 24. Absorption spectra of the compound **3** in chloroform before (1), after UV irradiation through the UFS-1 optical filter (2) and after subsequent dark bleaching (3).

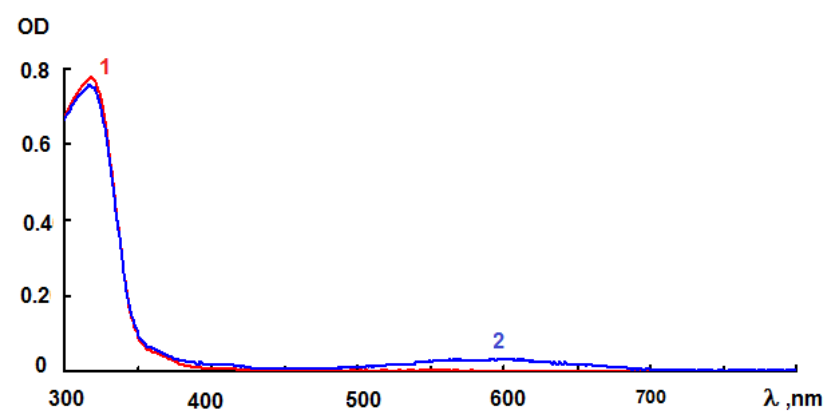


Figure 25. Absorption spectra of the compound **2** in toluene before (1), after UV irradiation through the UFS-1 optical filter (2).

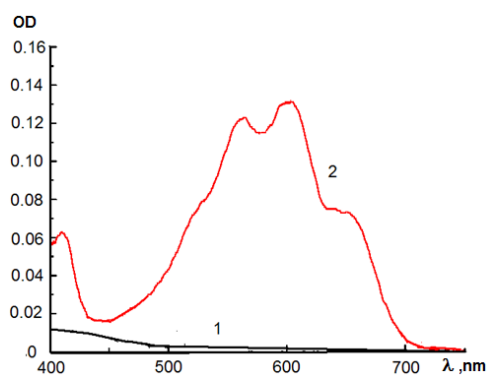


Figure 26. Absorption spectra the initial (1) and photoinduced (2) forms of compound **2** in toluene under pulse UV irradiation through the UFS – 1 optical filter.

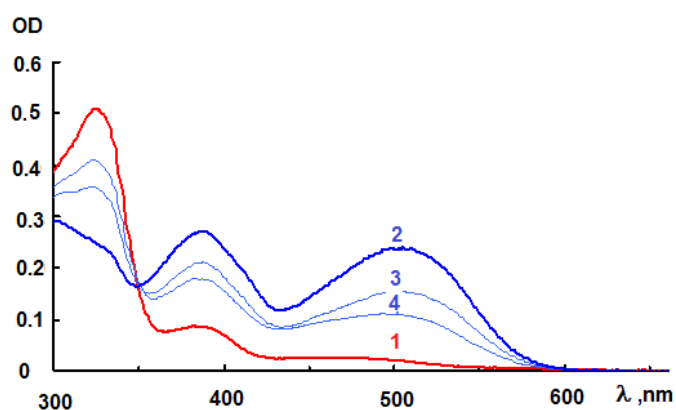


Figure 27. Absorption spectra of the compound **2** in chloroform before (1), after UV irradiation through the UFS-1 optical filter (2) and after subsequent dark bleaching (3,4).