Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supporting information

for

Photochemical deuterium exchange in phenyl-substituted pyrroles and indoles in CD_3CN-D_2O

By

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Table of contents:

1. Experimental procedure for the preparation of compounds

N-*tert*-Butoxycarbonyl-2-phenylpyrrole: To a stirred solution of iodobenzene (193 mg, 0.95 mmol), cesium carbonate (620 mg, 1.89 mmol) and *tetrakis*(triphenylphosphine)palladium (5 % mol) in toluene (20 mL) at reflux under nitrogen was added a solution of (1-tert-butyloxycarbonylpyrrol-2-yl)boronic acid[1] (200 mg, 0.95 mmol) in the mixture of toluene (10 mL) and methanol (3 mL) during 7 h. The mixture was stirred at reflux for 17 h, cooled and methanol was evaporated under reduced pressure. To a toluene suspension was added water (30 mL) and the layers were separated, the water layer was extracted with dichloromethane (3 × 25 mL). Combined organic extracts were washed with water (30 mL) and dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The resulting crude product was purified by chromatography on silica eluting with the mixture of dichloromethane and hexane (10 → 30%) to yield 185 mg (86 %) of *N-tert*-Butoxycarbonyl-2-phenylpyrrole as a clear oil. The ^{1}H NMR and ^{13}C NMR spectra were identical to the literature data.[2]

2-Phenylpyrrole (8): A suspension of sodium methoxide (freshly prepared by reacting 84 mg of sodium with 10 mL of methanol) was added to a stirred solution of *N-tert*-butoxycarbonyl-2-phenylpyrrole (280 mg, 1.22 mmol) in methanol (40 mL) and stirred at reflux for 3h, and at 25 °C for 15 h. The solvent was evaporated and the residue was portioned between dichloromethane and water. Water layer was extracted with dichloromethane (2 × 25 mL), and the combined organic extracts were washed with brine (30 ml). Organic extracts were dried over anhydrous $MgSO_4$, solvent was evaporated to give 158 mg (90 %) of the product as a white crystalline solid. The ^{1}H NMR and ^{13}C NMR spectra were identical to the literature data.[2]

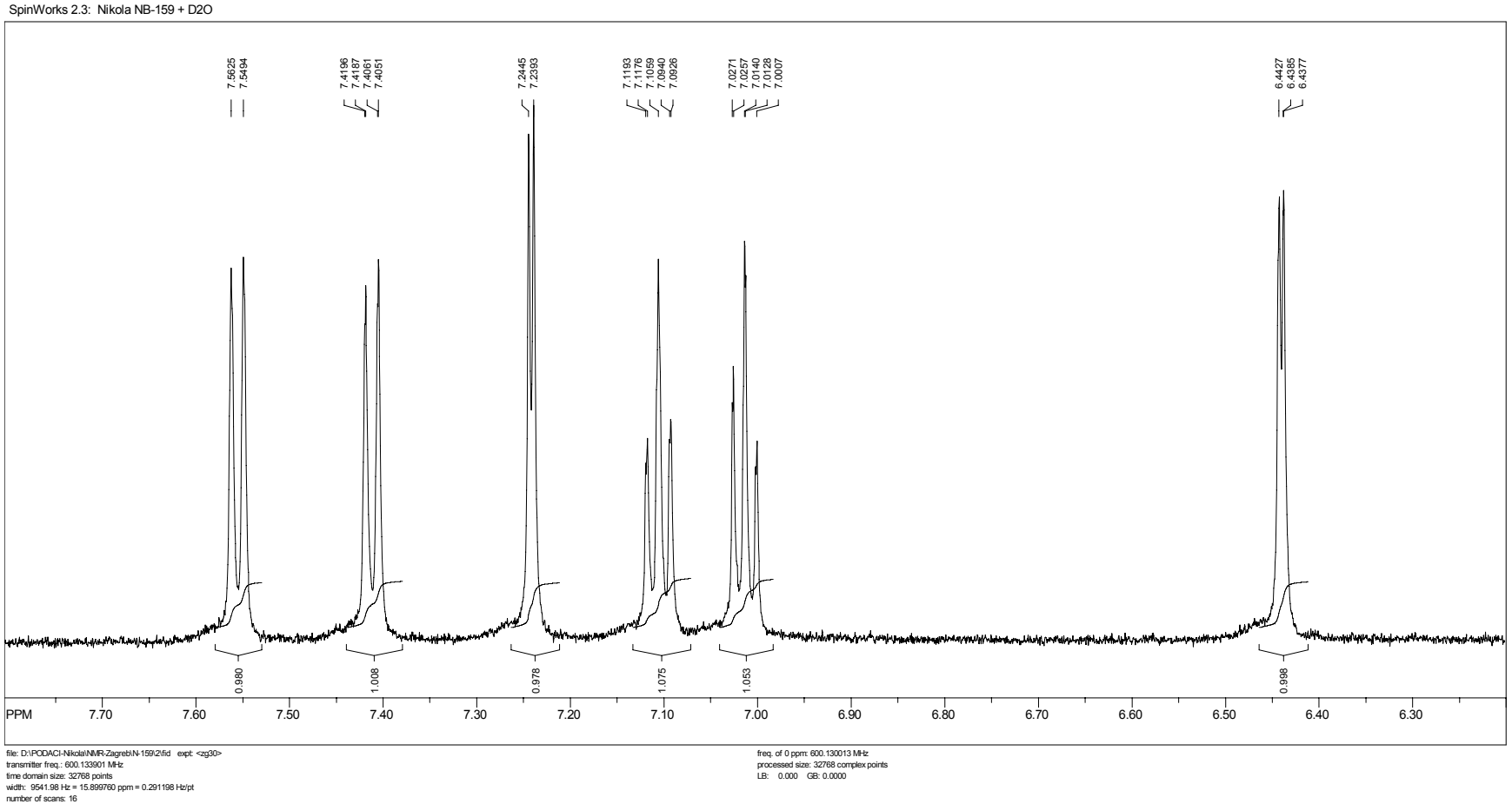
7-Phenylindole (12): A round bottom flask (50 mL) was charged with 7-bromoindole (255 mg, 1.3 mmol), phenylboronic acid (158 mg, 1.3 mmol), tetrakis(triphenylphsophine)palladium (40 mg), K_2CO_3 (300 mg), toluene (10 mL) and methanol (5 mL). The mixture was heated to reflux for 24 h under N_2. During this time, the orange solution turned to deep purple. After cooling to rt, 30 mL of HCl (1M) was added and the mixture was extracted with CH_2Cl_2 (4 × 15 mL). The resulting deep-red organic extracts were combined and dried over anhydrous $MgSO_4$. The solvent was evaporated on a rotary evaporator to yield the crude product in the form of dark oil that was purified by column

chromatography on silica gel eluting with a mixture of CH_2Cl_2 - Hexanes (1:3). The resulting clear oil crystallized spontaneously upon storage at 10 ºC.

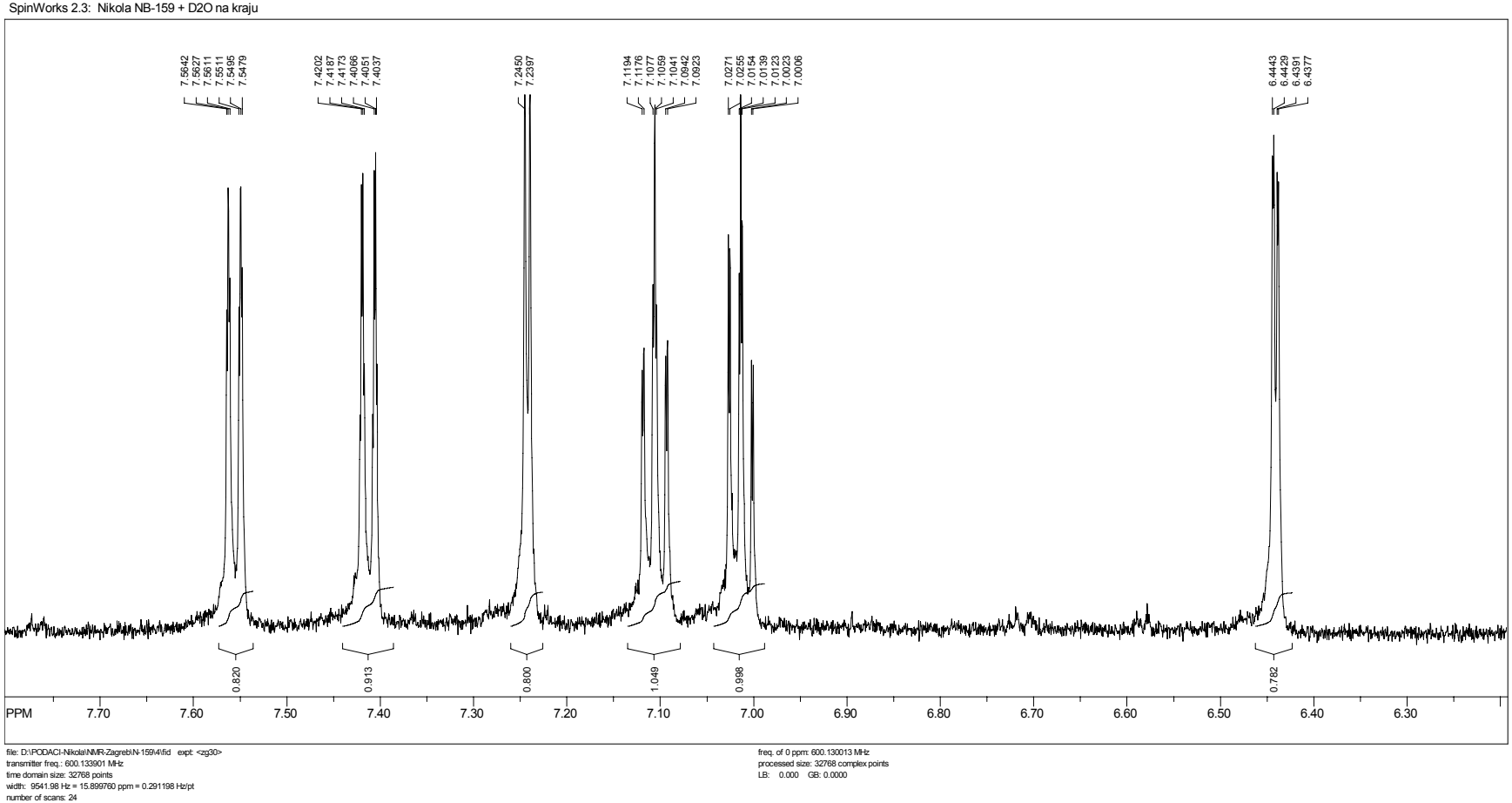
1. S. Martina, V. Enkelmann, G. Wegner, A.-D. Schlüter, *Synthesis* **1991** 613-615.
2. A. Burghart, H. Kim, M. B. Welch, L. H. Thorensen, J. Reibenspies, K. Burgess, *J. Org. Chem.* **1999**, *64*, 7813-7819.

[1]H NMR spectra after photolyses in deuterated solvents

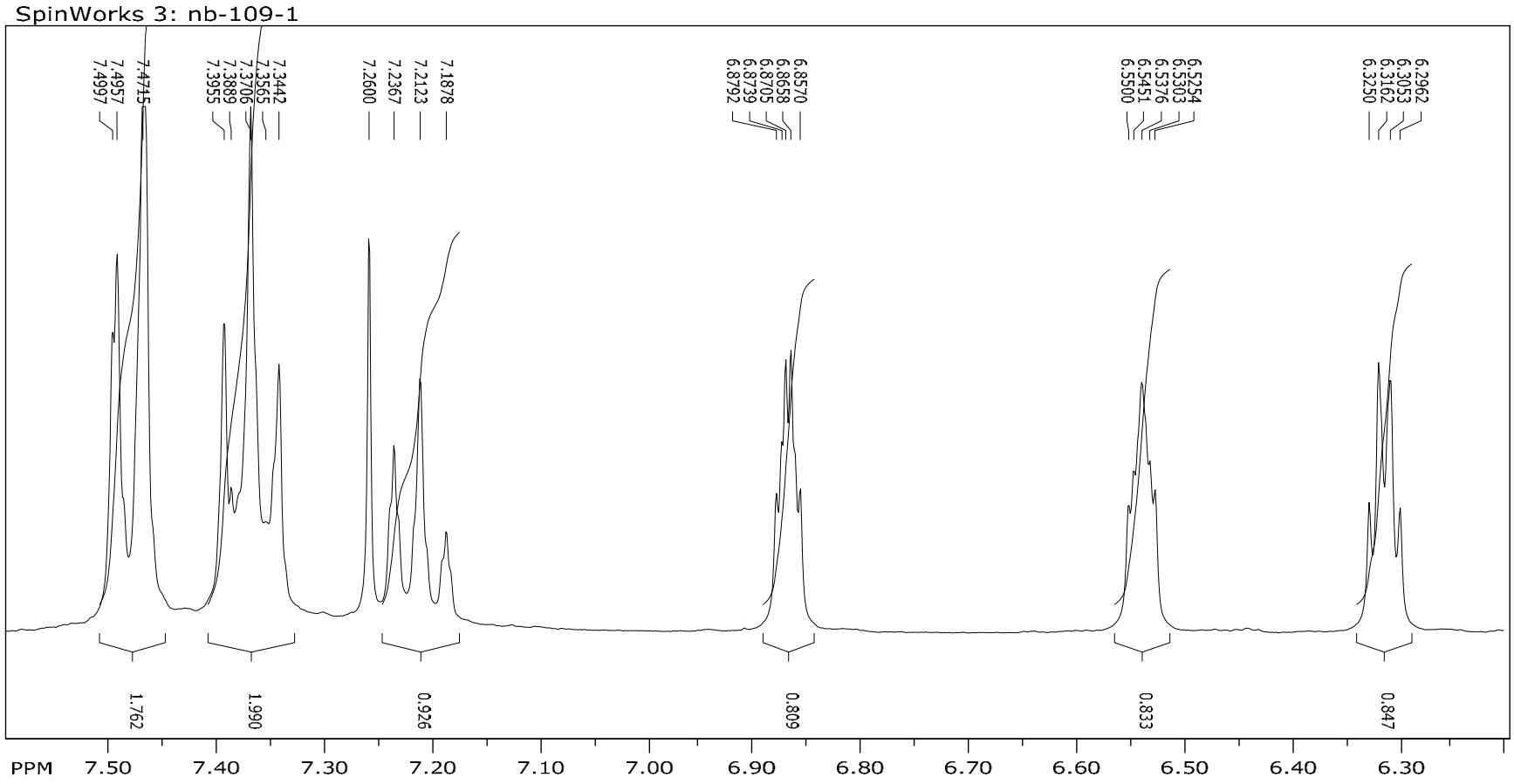
^{1}H NMR ($CD_3CN + D_2O$) after thermal ("dark") experiment for **7** in $CD_3CN – D_2O$



^{1}H NMR (CD_3CN + D_2O) after photolysis (45min) of **7** at 254 nm in a quartz NMR tube



^{1}H NMR ($CDCl_3$) after photolysis (2h) of **8** in CH_3CN – D_2O (1M)



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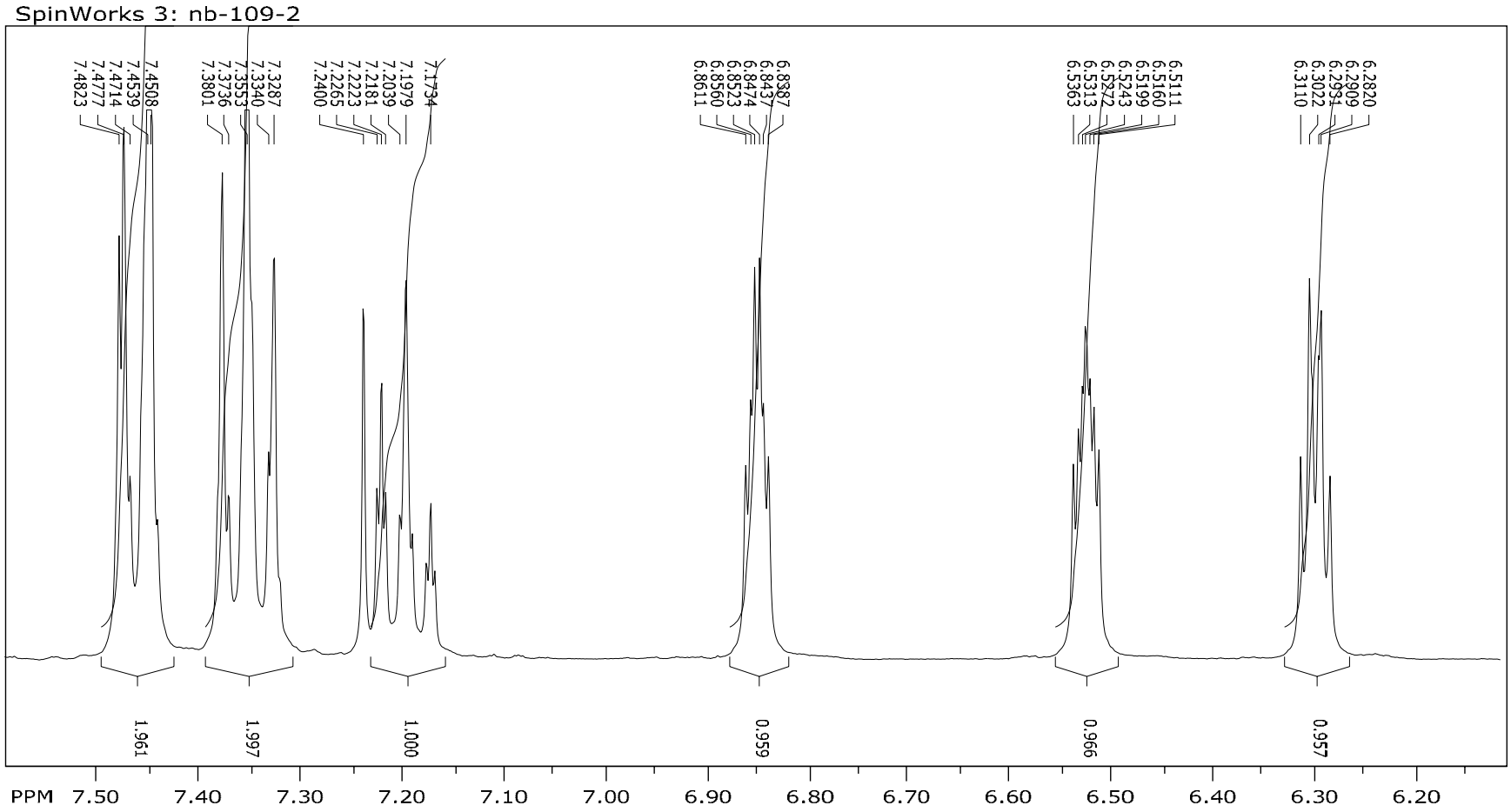
^{1}H NMR ($CDCl_3$) after thermal ("dark") experiment (2h) for **8** in CH_3CN – D_2O (1M)



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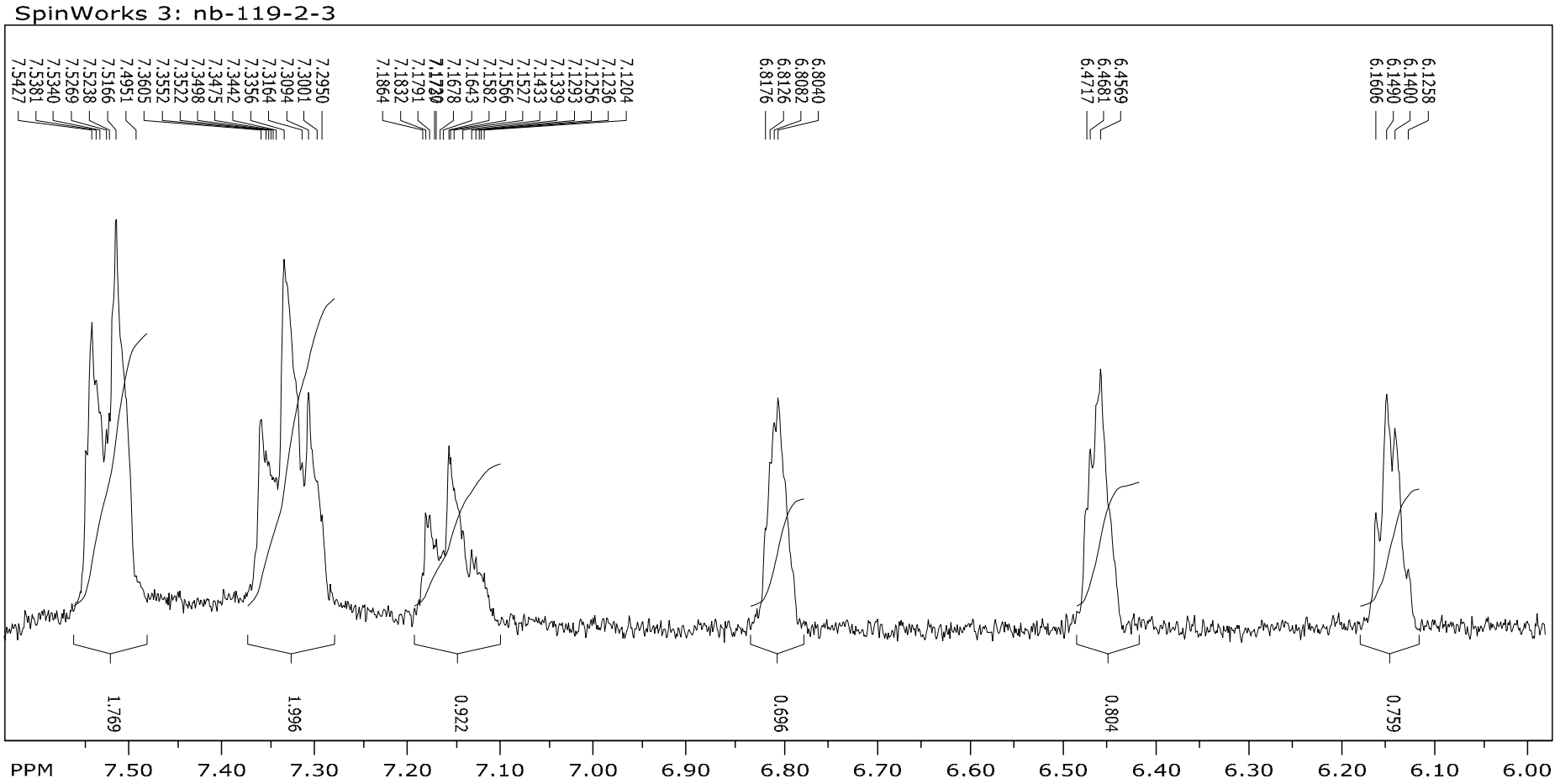
^{1}H NMR (CD_3CN) after photolysis (30 min) of **8** in CD_3CN – D_2O (1M)



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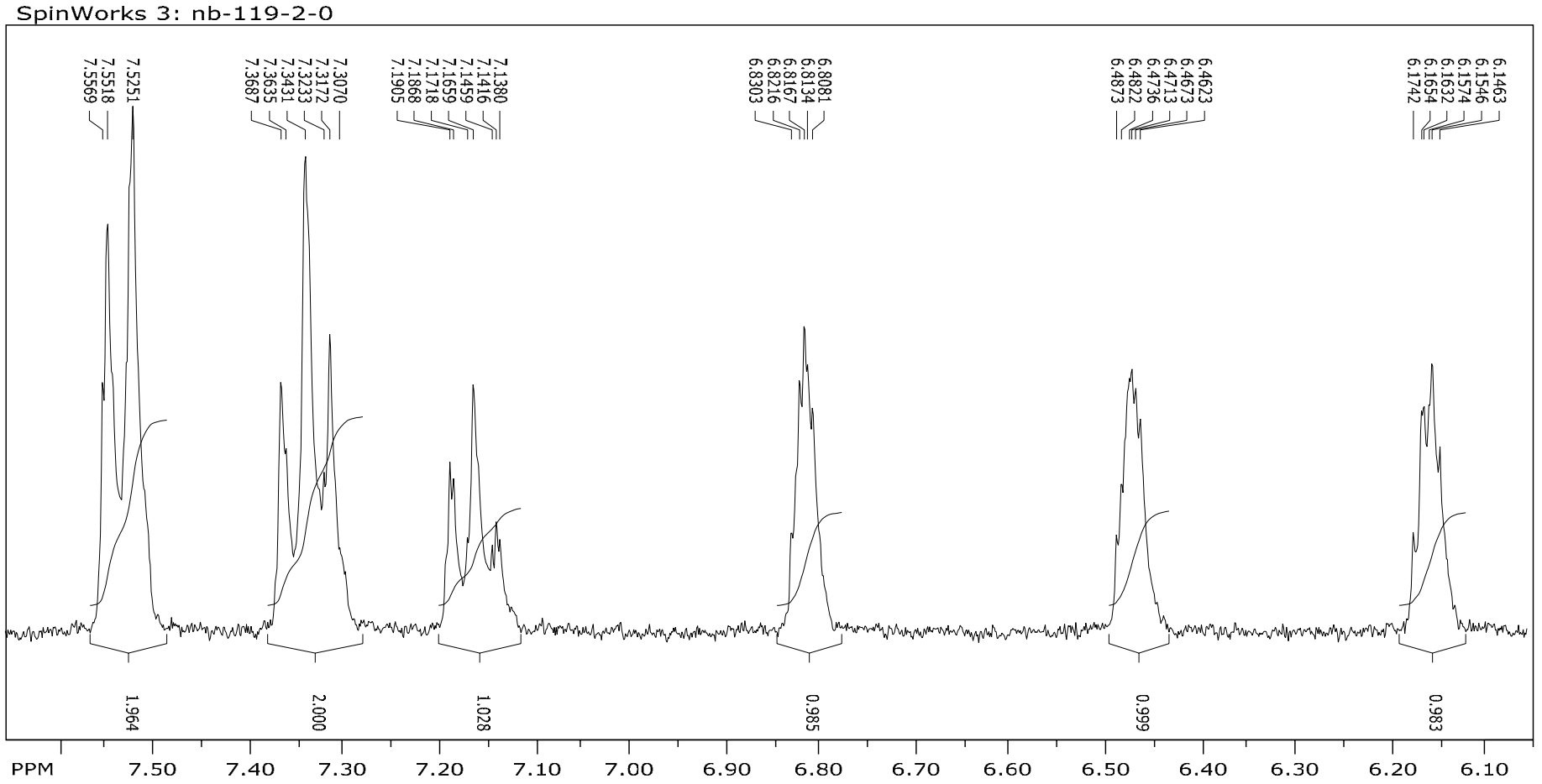
^{1}H NMR ($CDCl_3$) after thermal ("dark") experiment for **8** in CD_3CN – D_2O (1M)



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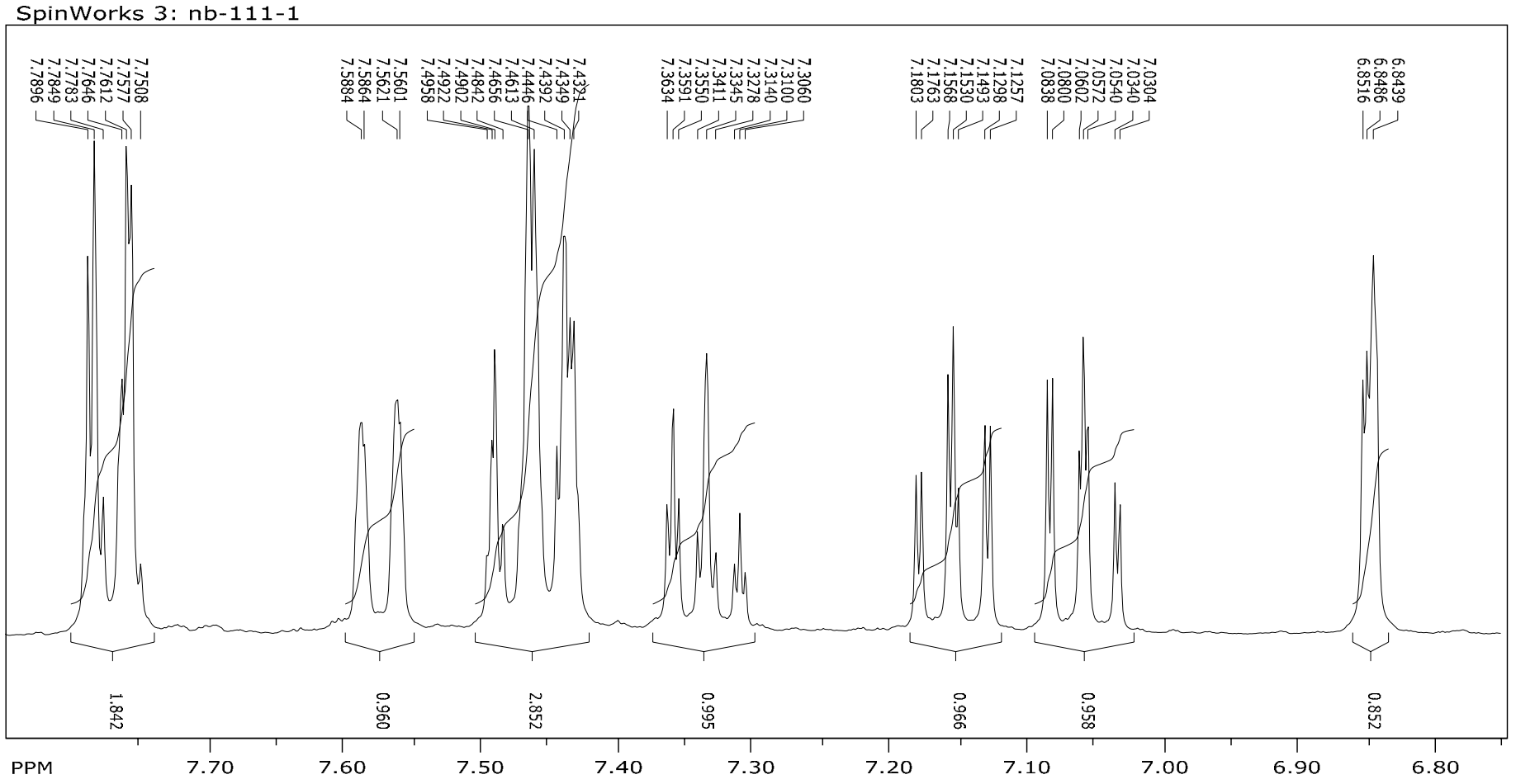
^{1}H NMR (CD_3CN) after photolysis (4h) of **9** in CH_3CN – D_2O (1M)



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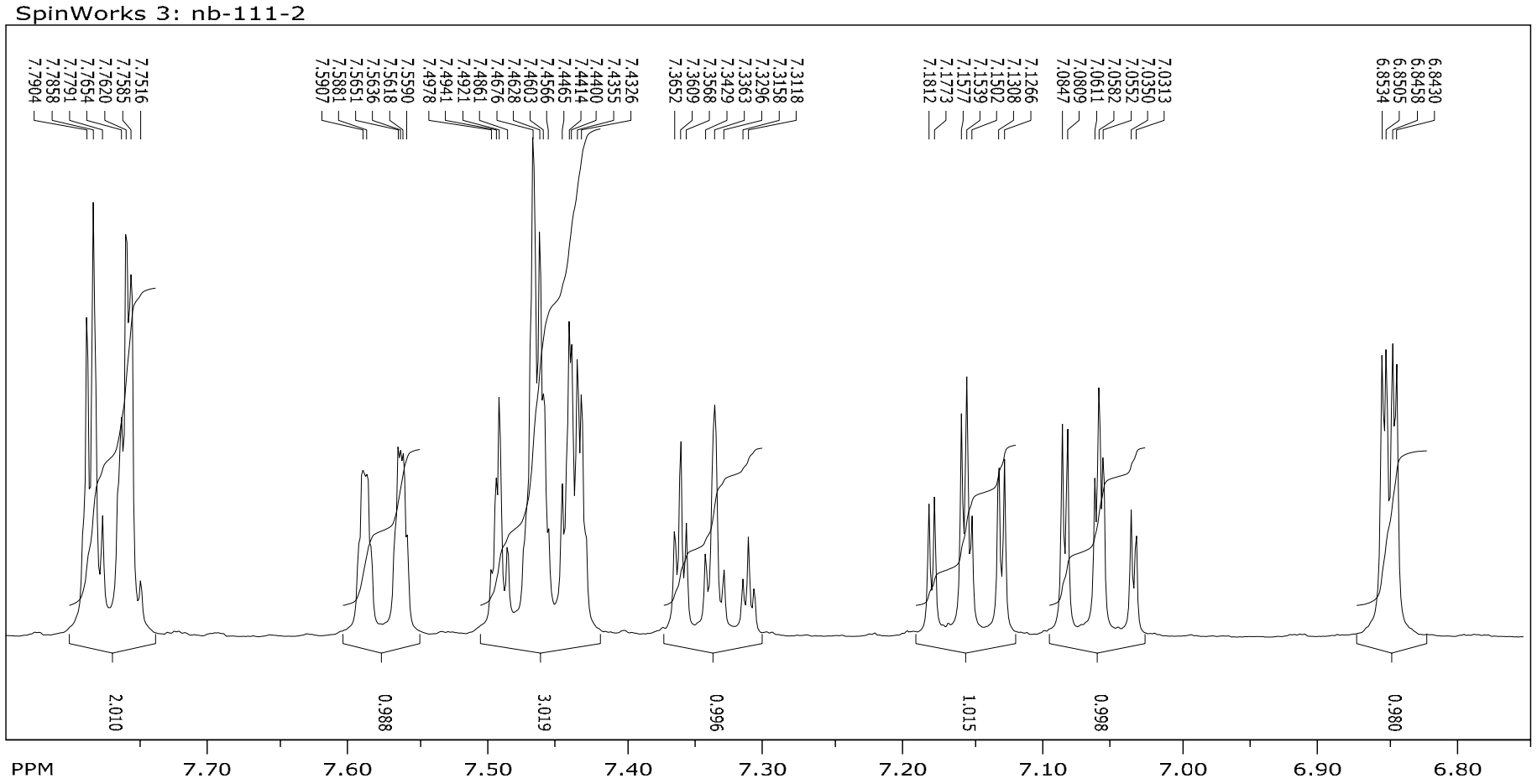
^{1}H NMR (CD_3CN) after thermal ("dark") experiment (4h) for **9** in CH_3CN – D_2O (1M)



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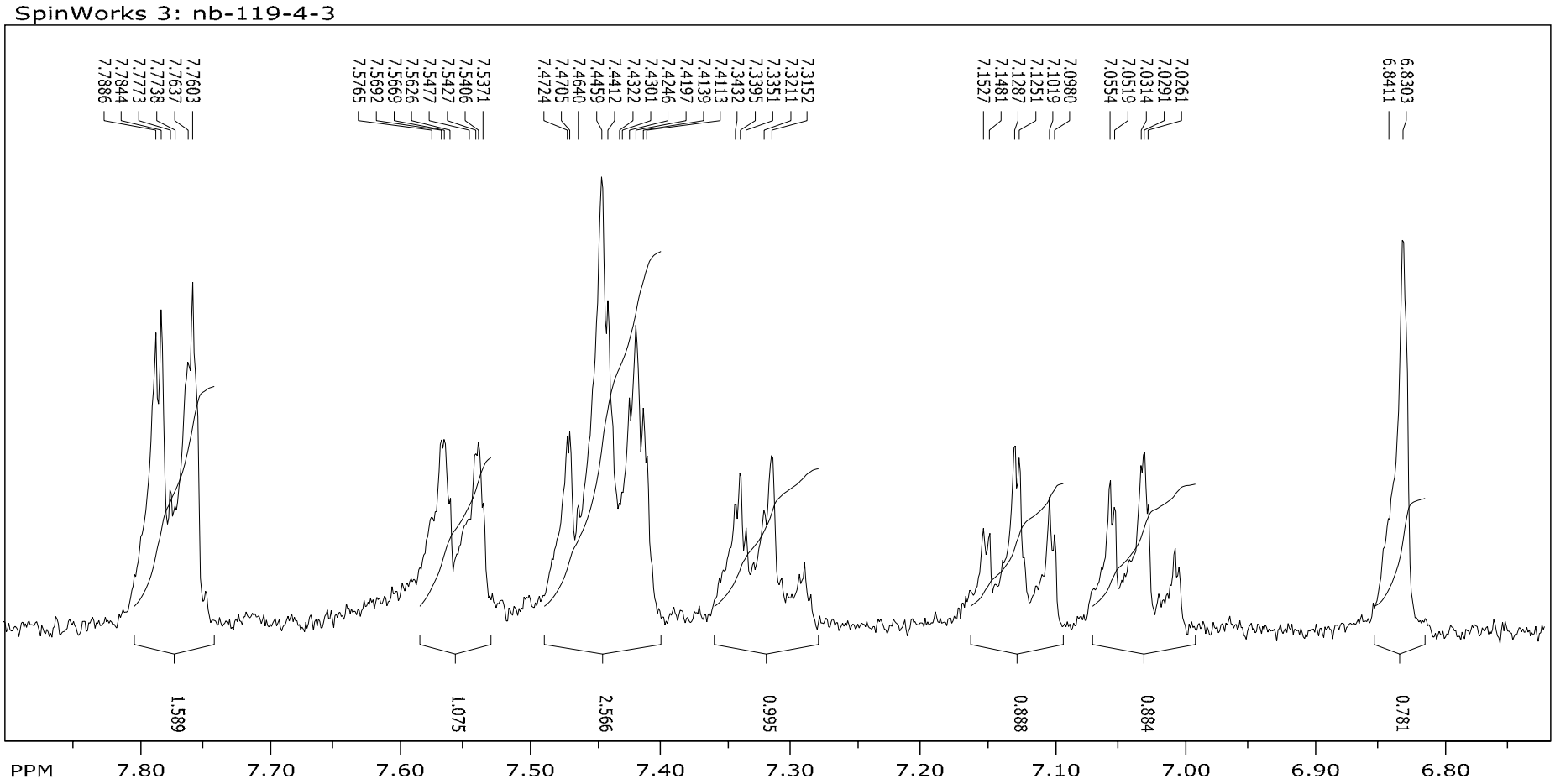
^{1}H NMR (CD_3CN) after photolysis (30 min) of **9** in CD_3CN – D_2O (1M)



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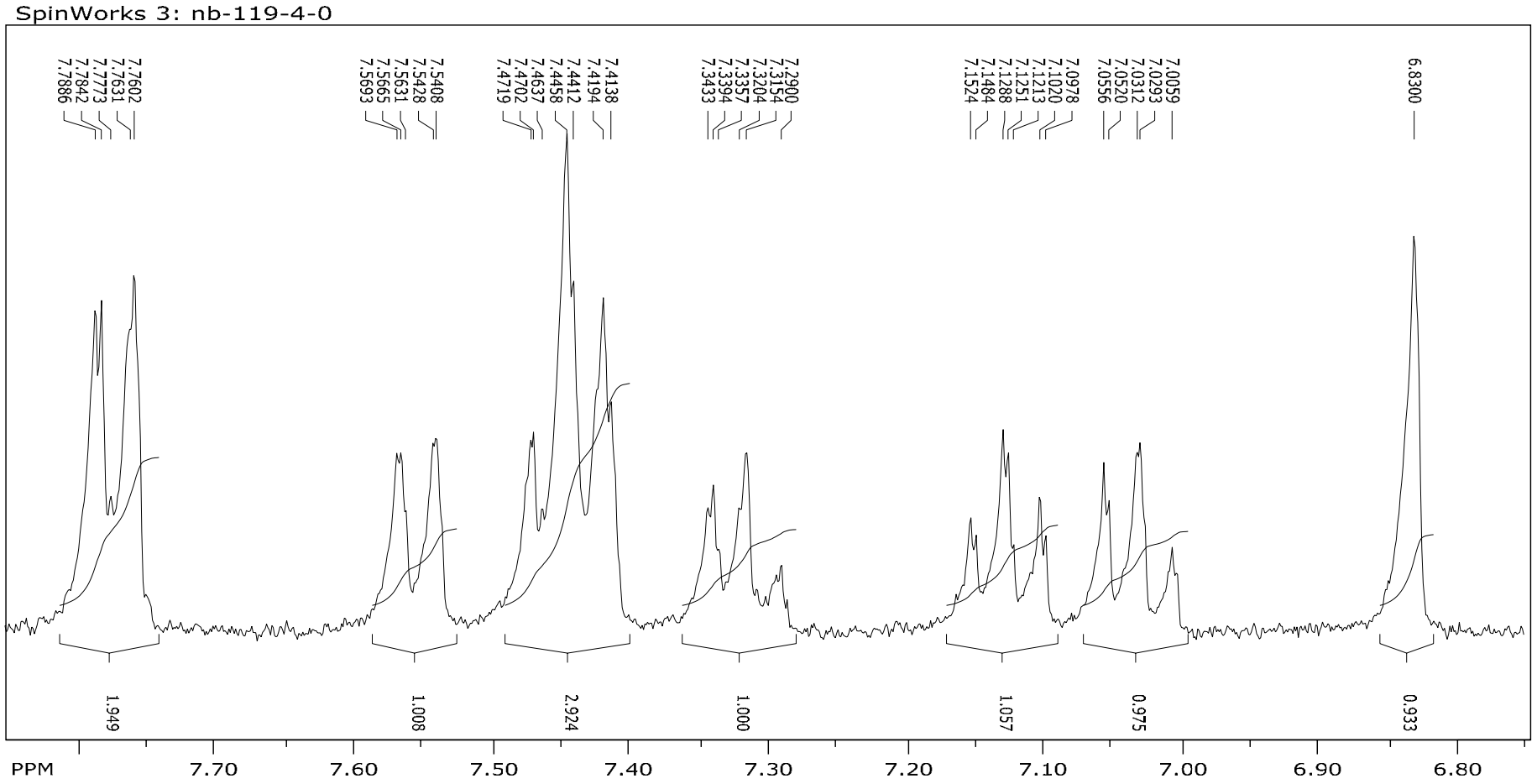
^{1}H NMR (CD_3CN) after thermal ("dark") experiment (30 min) for **9** in CD_3CN – D_2O (1M)



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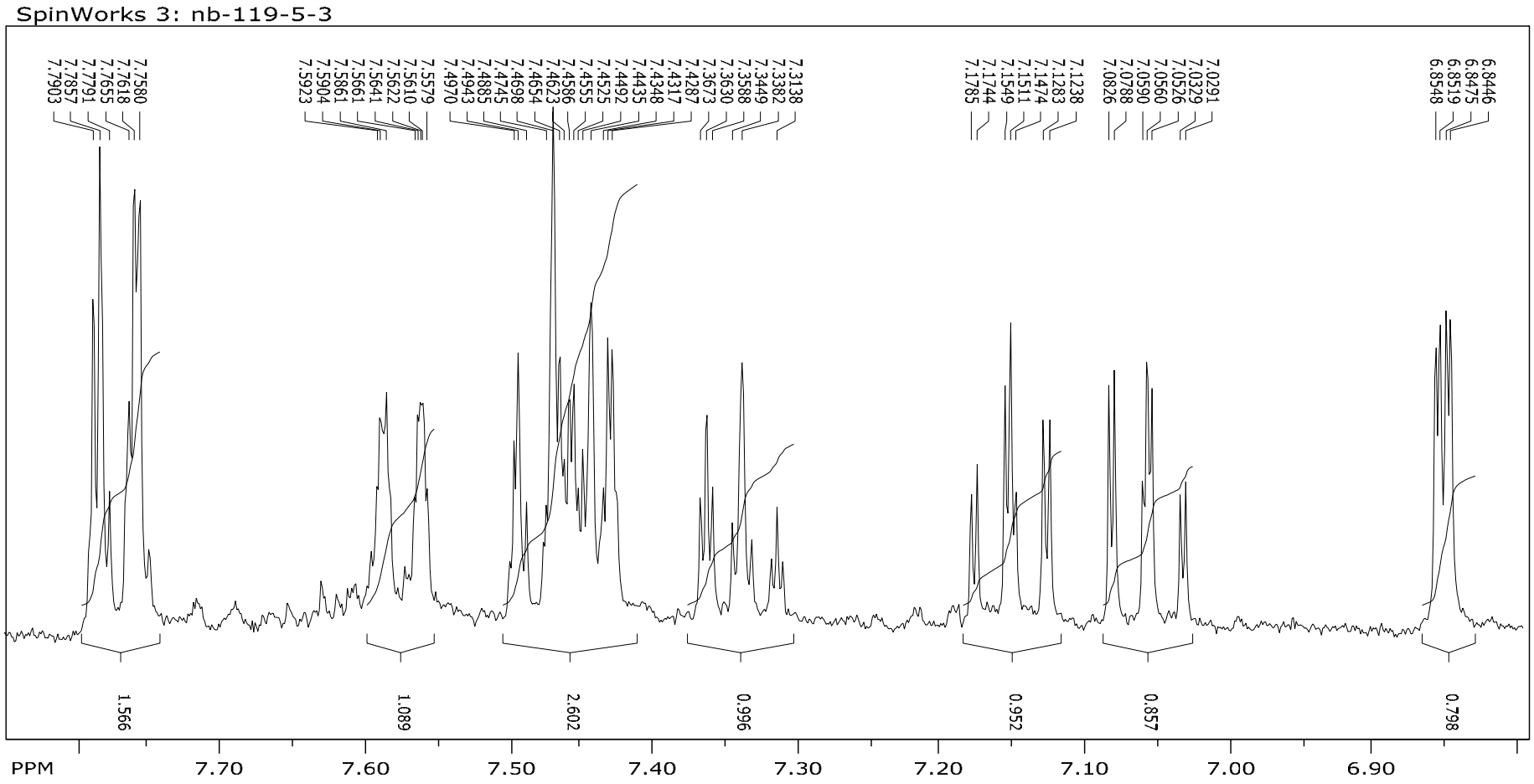
^{1}H NMR (CD_3CN) after photolysis (30 min) of **9** in CD_3CN



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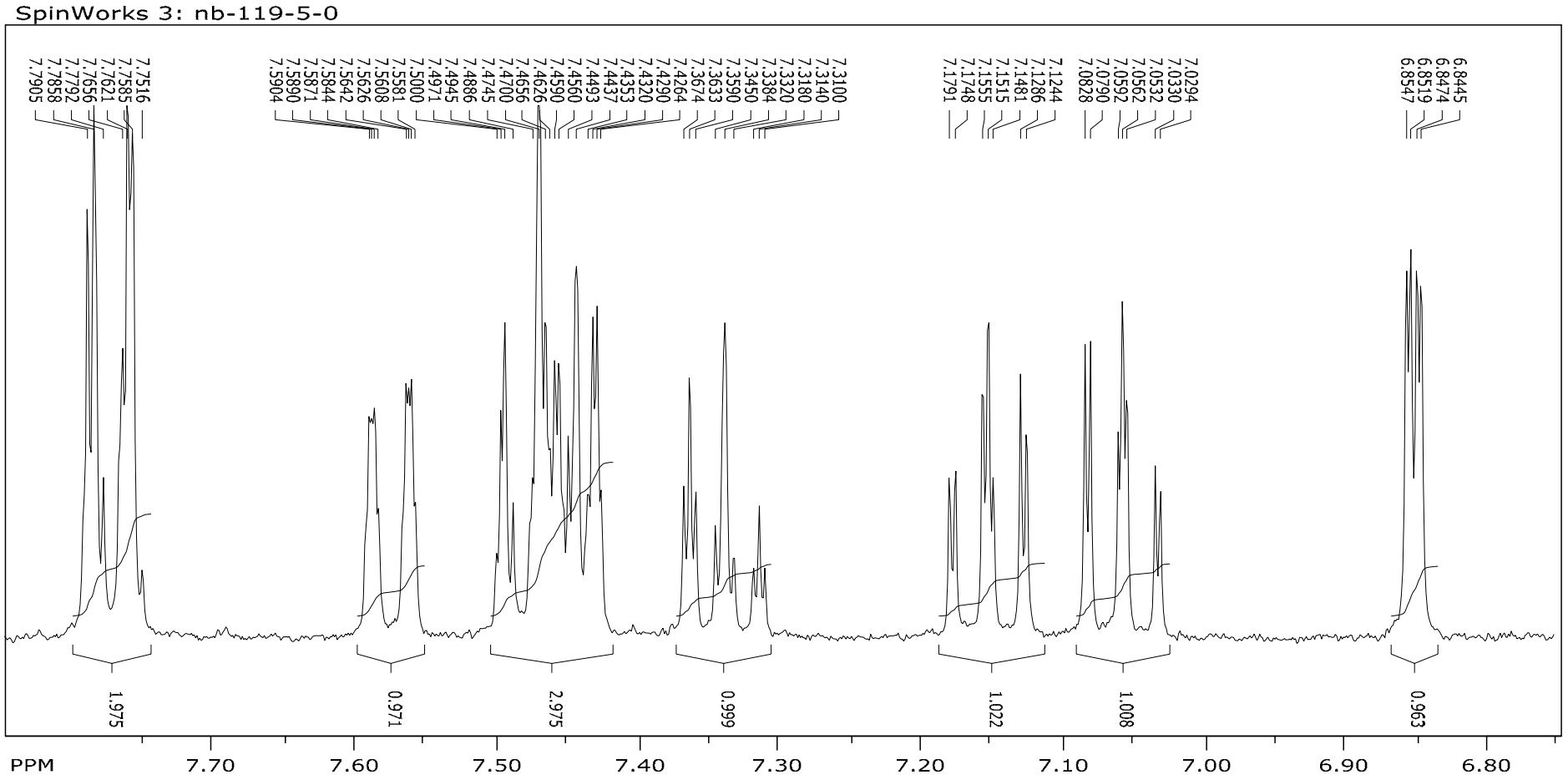

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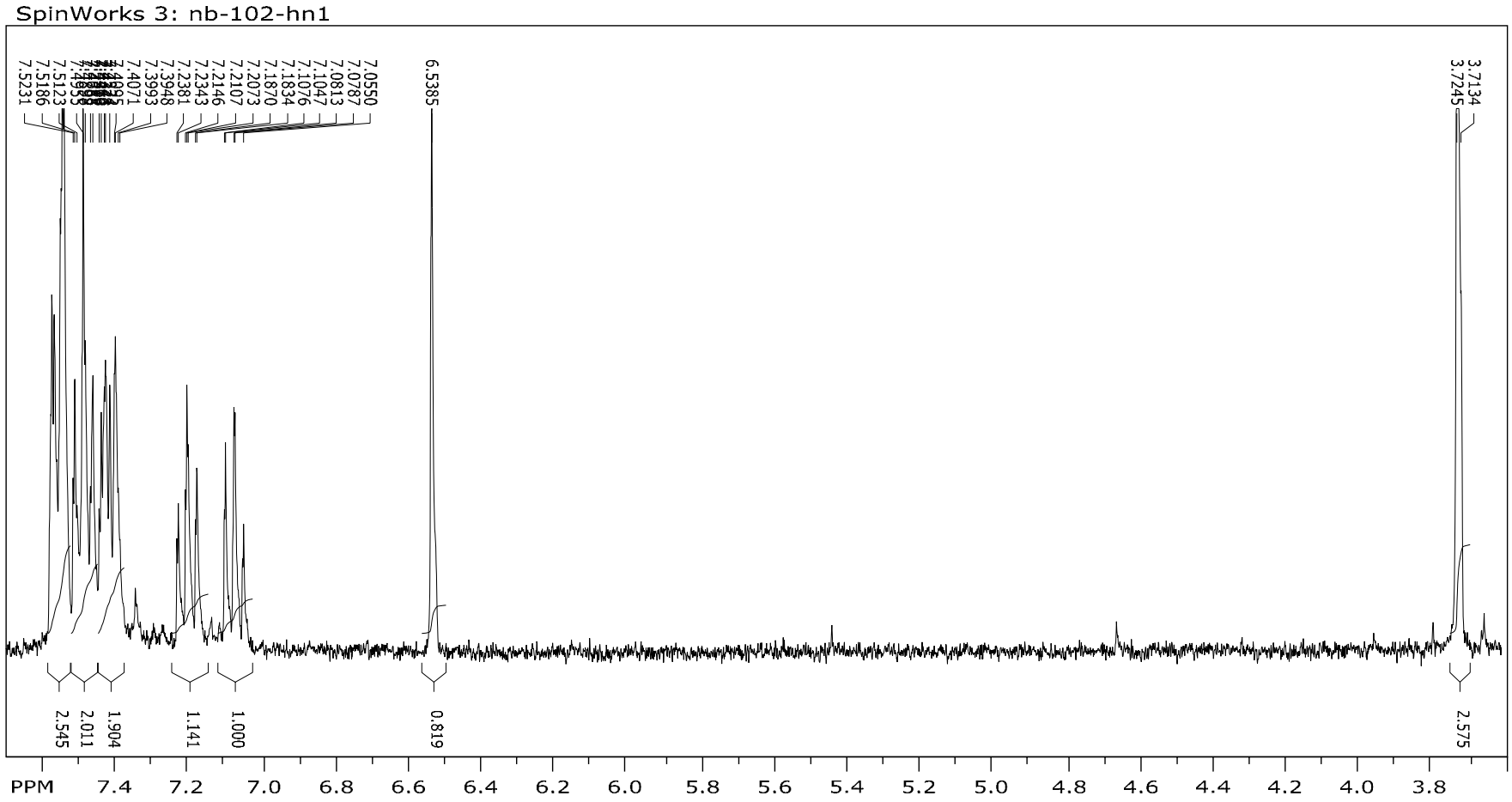
^{1}H NMR (CD_3CN) after photolysis (15 min) of **10** in CD_3CN – D_2O (1M)



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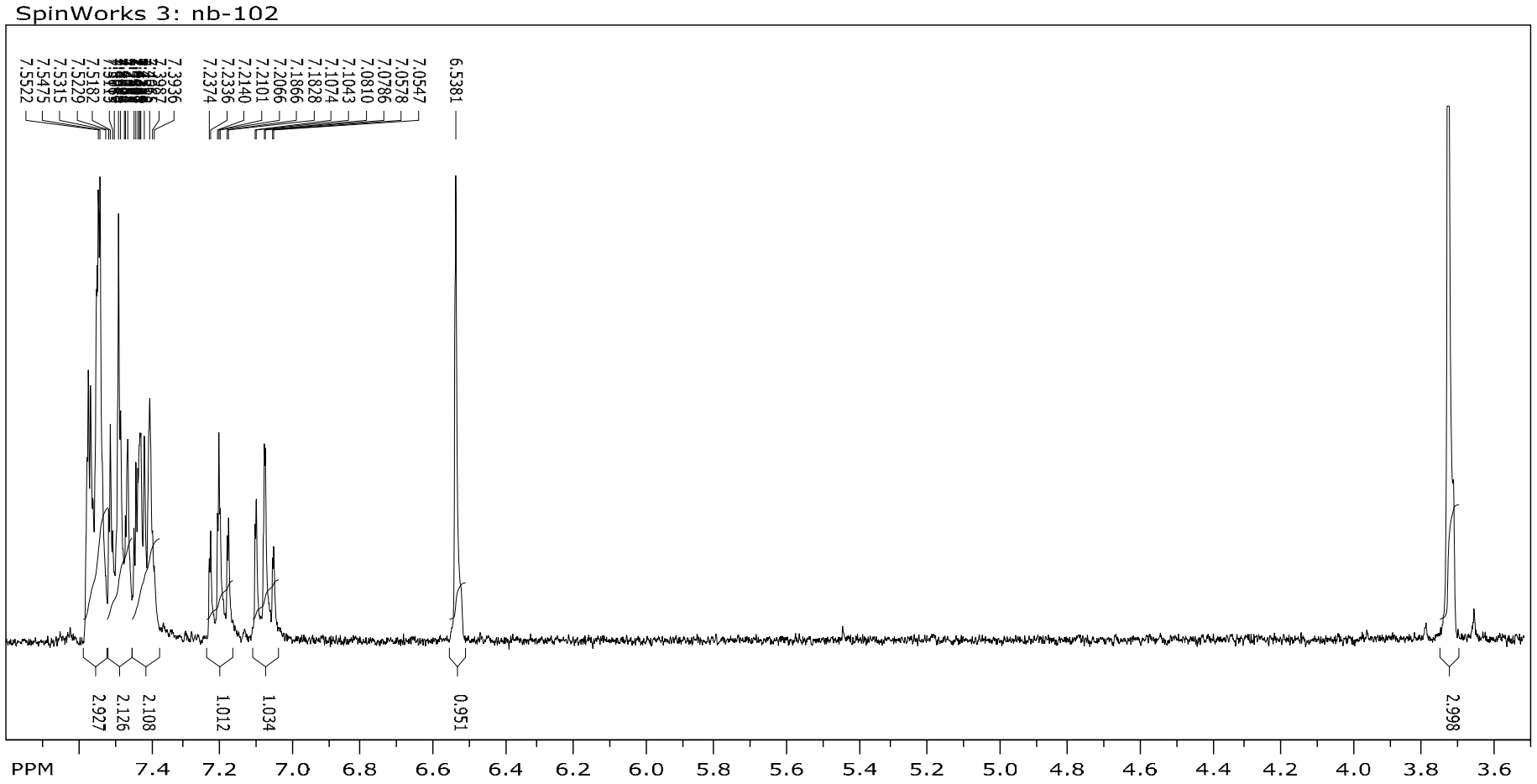

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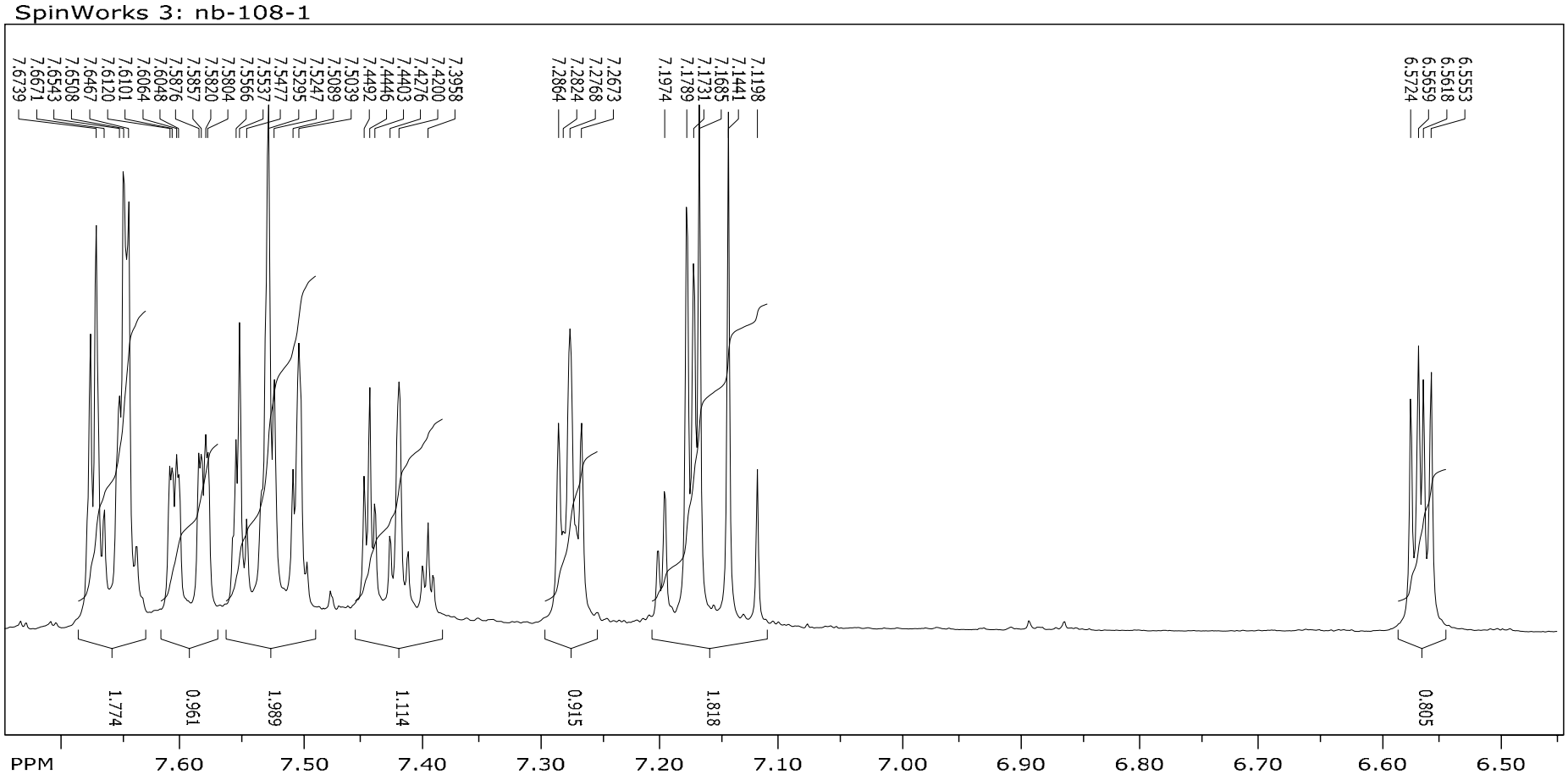
^{1}H NMR (CD_3CN) after photolysis (4 h) of **12** in CH_3CN – D_2O (1M)



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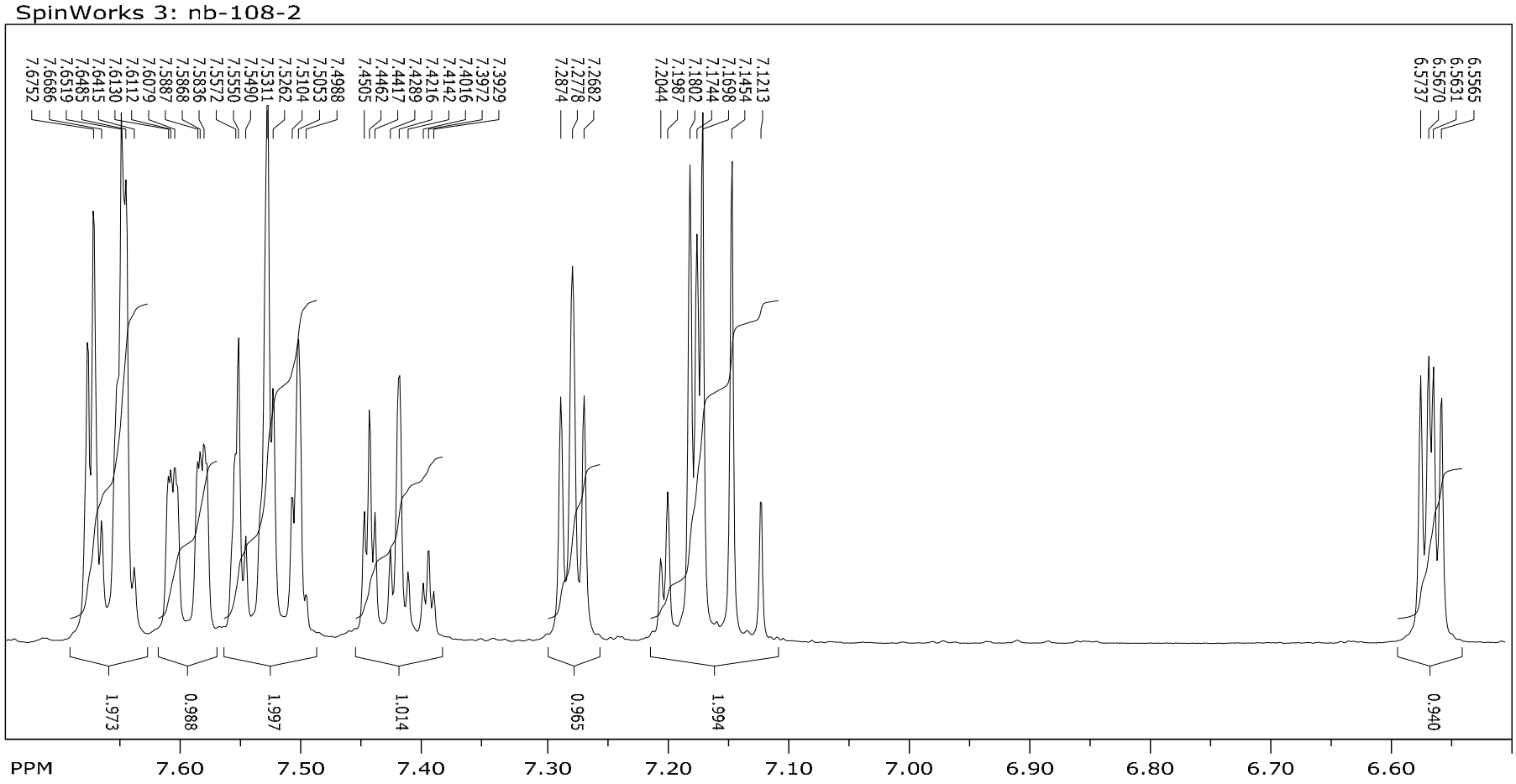
^{1}H NMR (CD_3CN) after thermal ("dark") experiment (4 h) for **12** in CH_3CN – D_2O (1M)



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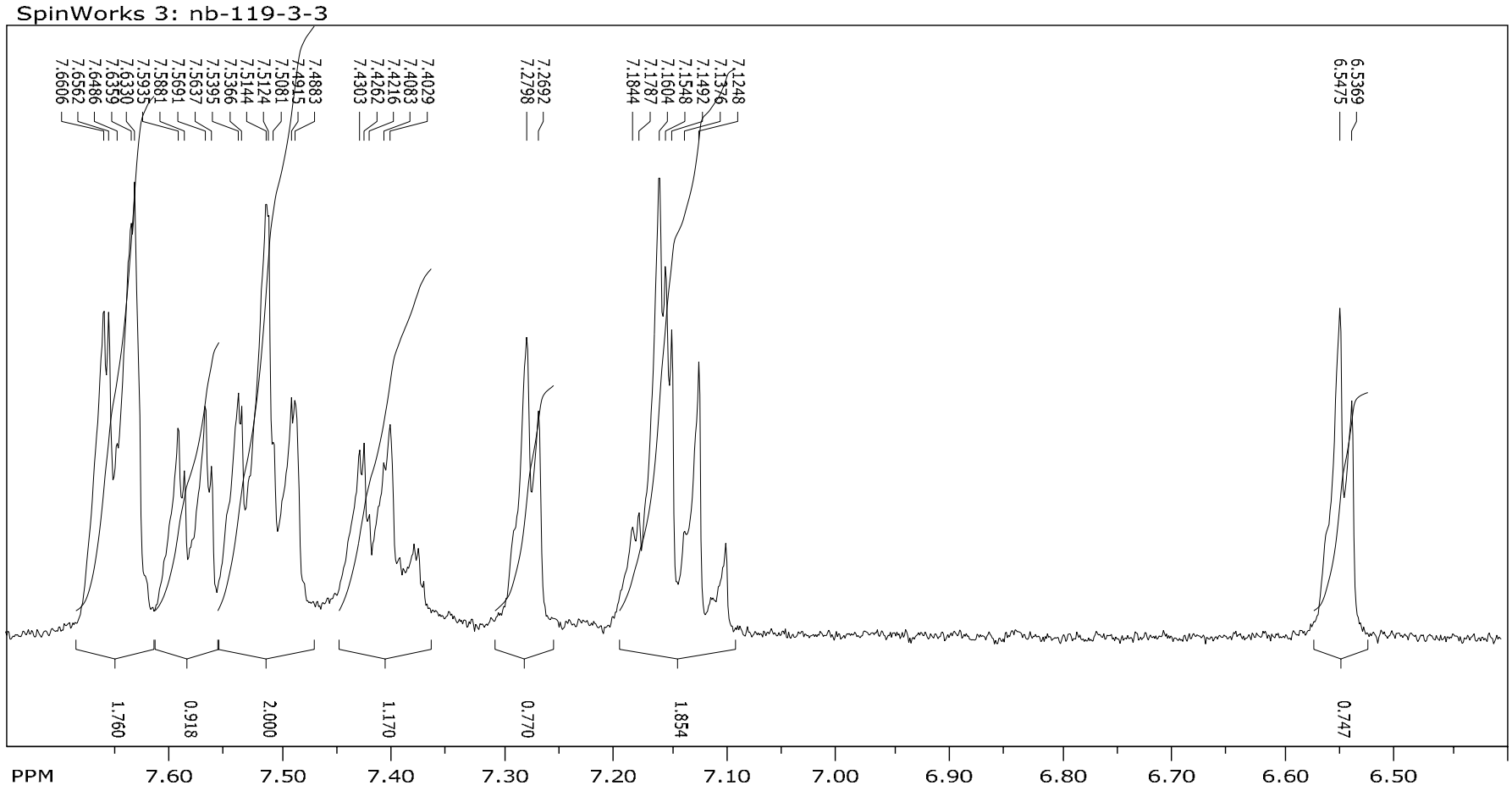
^{1}H NMR (CD_3CN) after photolysis (30 min) of **12** in CD_3CN – D_2O (1M)



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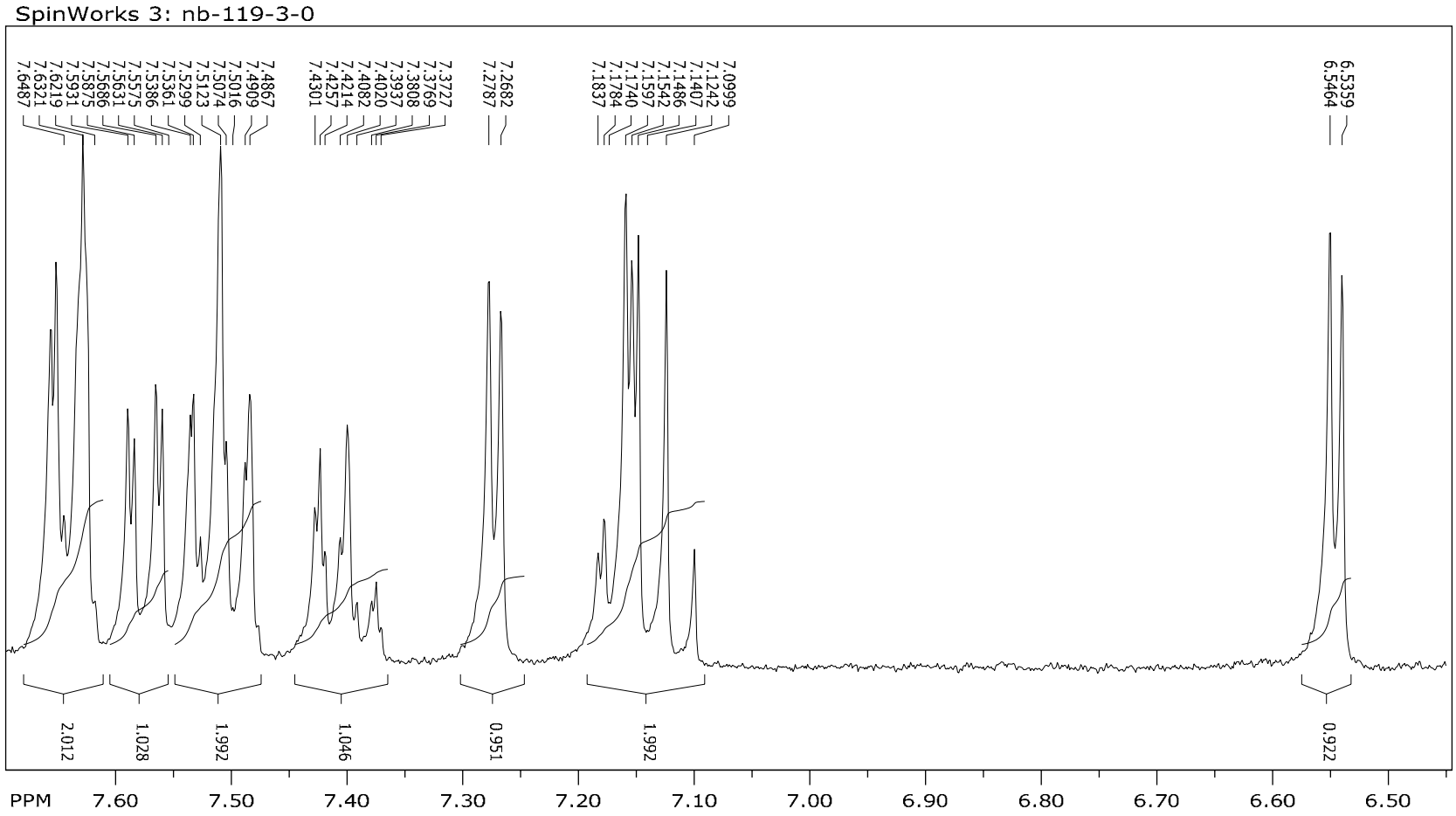
^{1}H NMR (CD_3CN) after thermal ("dark") experiment (30 min) for **12** in CD_3CN – D_2O (1M)



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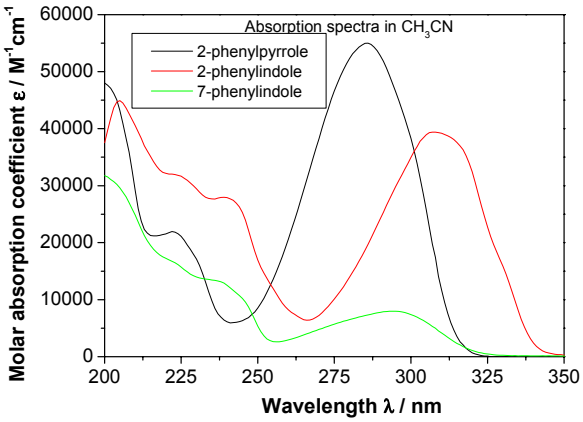
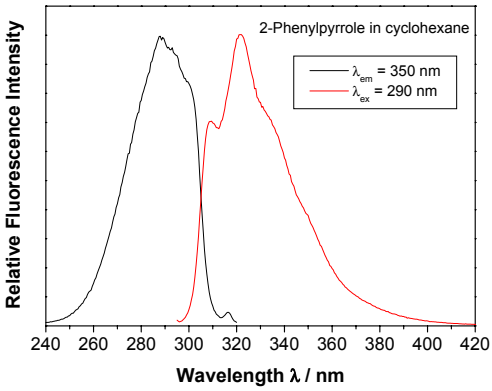
3. Fluorescence study

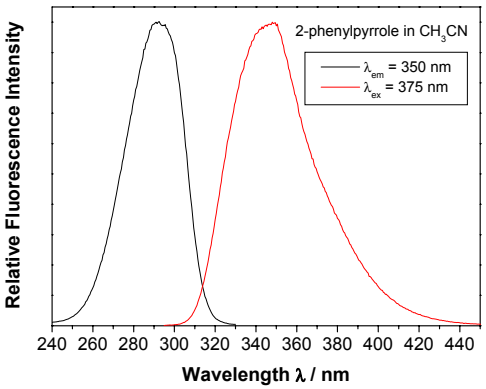
UV-vis spectra of 2-phenylpyrrole (**8**), 2-phenylindole (**9**) and 7-phenylindole (**12**) in CH_3CN.



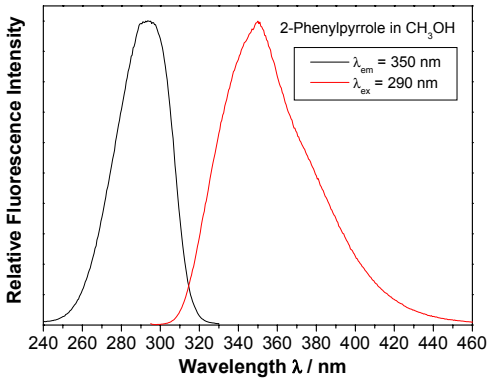
Excitation and emission spectrum of 2-phenylpyrrole (**8**) in cyclohexane.



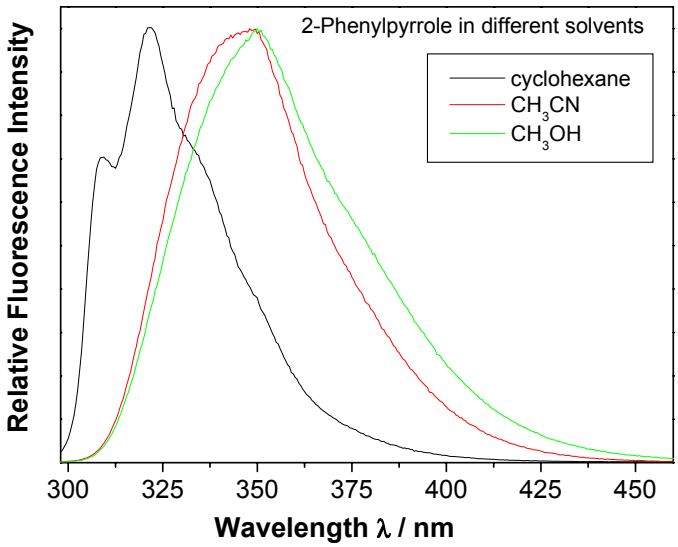
Excitation and emission spectrum of 2-phenylpyrrole (**8**) in CH_3CN.



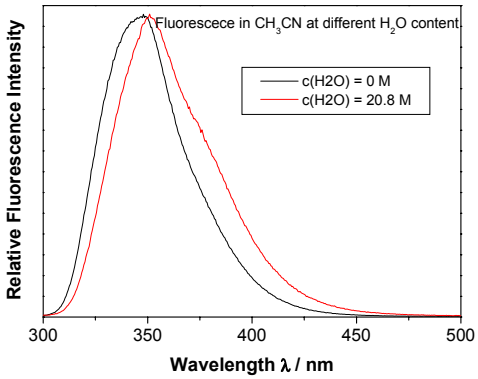
Excitation and emission spectrum of 2-phenylpyrrole (**8**) in CH_3OH.

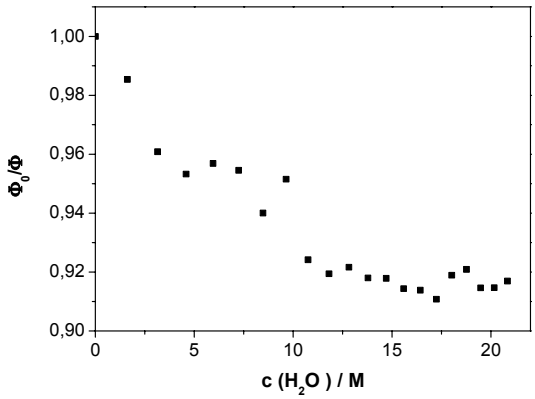


Emission spectra of 2-phenylpyrrole (**8**) in different solvents.

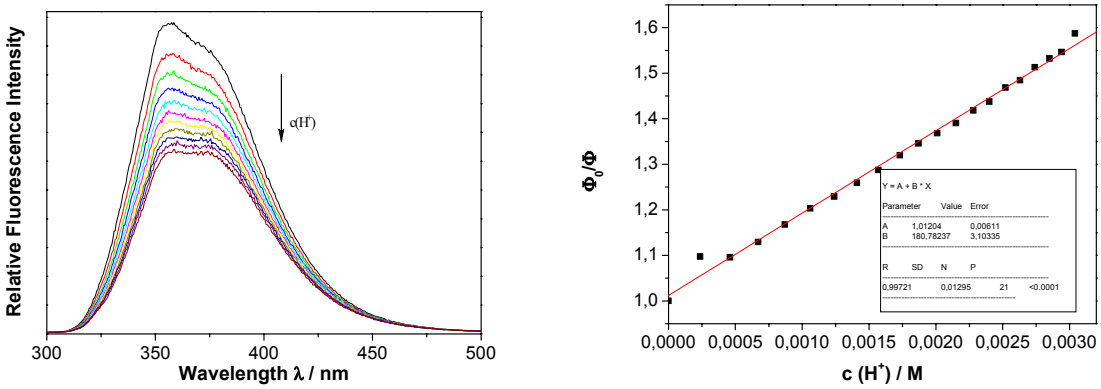


Fluorescence spectra of 2-phenylpyrrole (**8**) in CH_3CN at different H_2O content and Stern-Volmer plot of fluorescence quenching by H_2O.

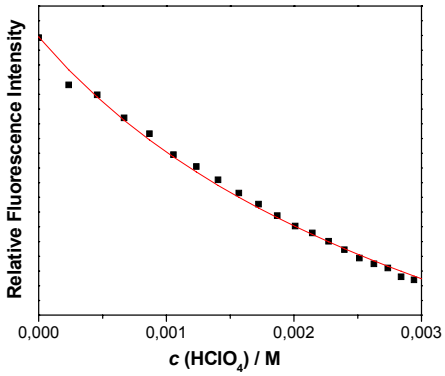




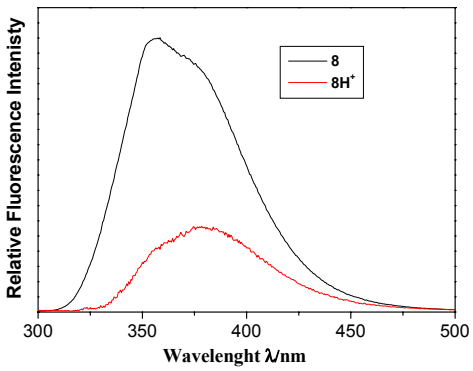
Fluorescence quenching of 2-phenylpyrrole (**8**) in CH_3CN-H_2O (1:4) by $HClO_4$, and Stern-Volmer plot of the fluorescence quenching by $HClO_4$.



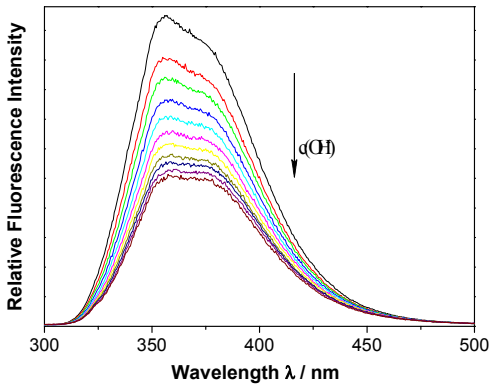
Relative fluorescence intensity of 2-phenylpyrrole (**8**) in CH_3CN-H_2O (4:1) at 358 nm as a function of $HClO_4$ concentration. Red line represents the fitting of the model to the experimental values (black dots) obtained by the factor analysis in the SPECFIT program.

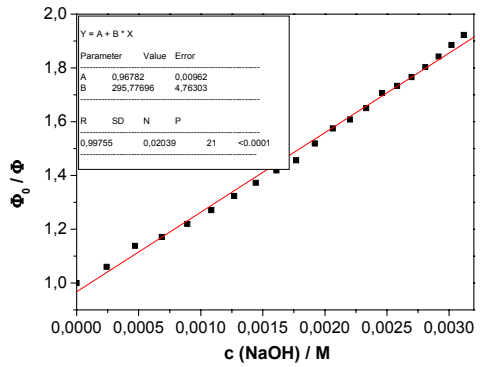


Relative fluorescence intensity of 2-phenylpyrrole (**8**) in CH_3CN-H_2O (4:1) in the protonated and non-protonated form, obtained by the factor analysis in the SPECFIT program.

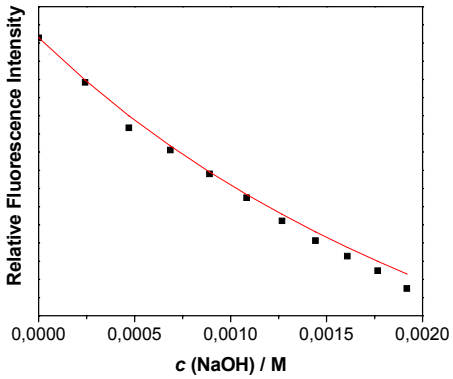


Fluorescence quenching of 2-phenylpyrrole (**8**) in CH_3CN-H_2O (1:4) by NaOH, and Stern-Volmer plot of the fluorescence quenching by NaOH.

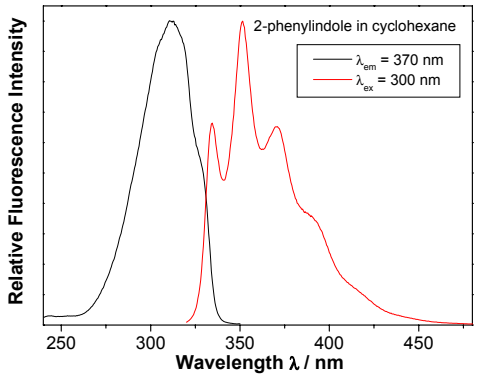




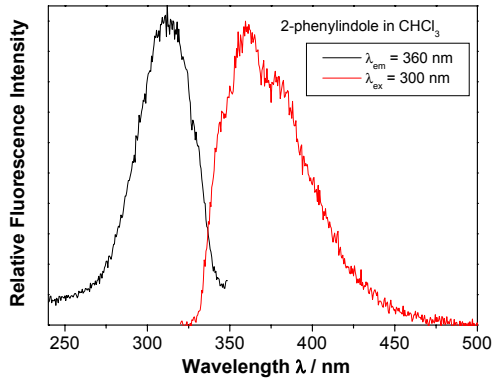
Relative fluorescence intensity of 2-phenylpyrrole (**8**) in CH_3CN-H_2O (4:1) at 356 nm as a function of NaOH concentration. Red line represents the fitting of the model to the experimental values (black dots), obtained by the factor analysis in the SPECFIT program.



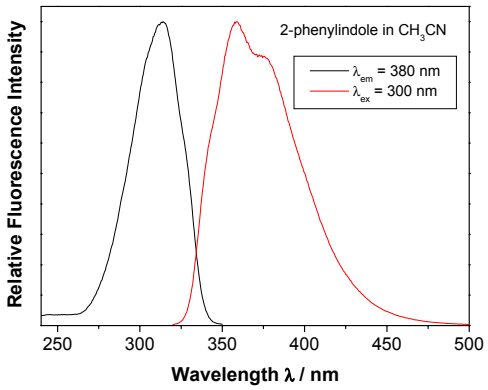
Excitation and emission spectrum of 2-phenylindole (**9**) in cyclohexane.



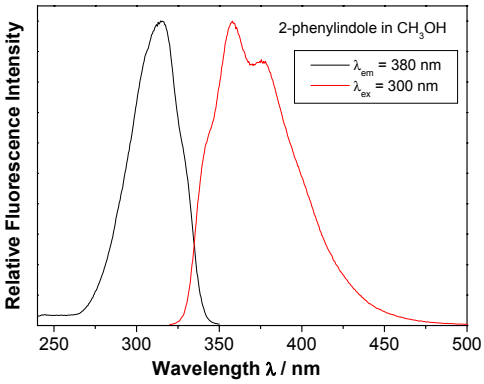
Excitation and emission spectrum of 2-phenylindole (**9**) in chloroform.



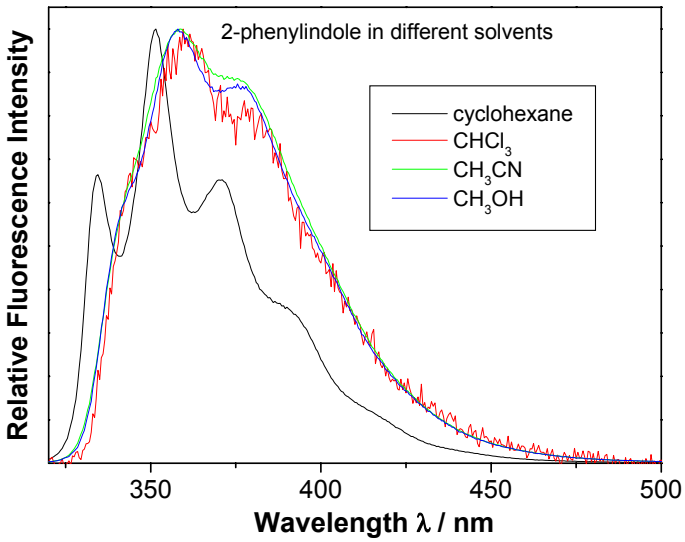
Excitation and emission spectrum of 2-phenylindole (**9**) in CH_3CN.



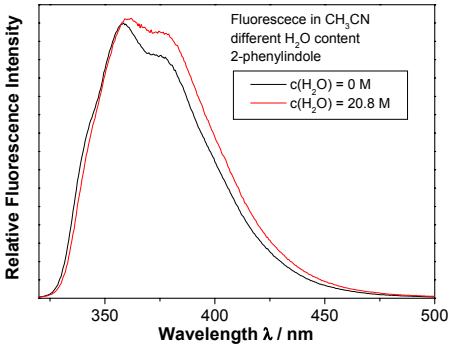
Excitation and emission spectrum of 2-phenylindole (**9**) in CH_3OH.

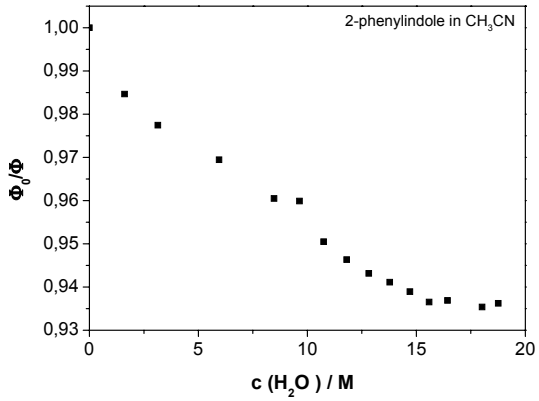


Emission spectra of 2-phenylindole (**9**) in different solvents.

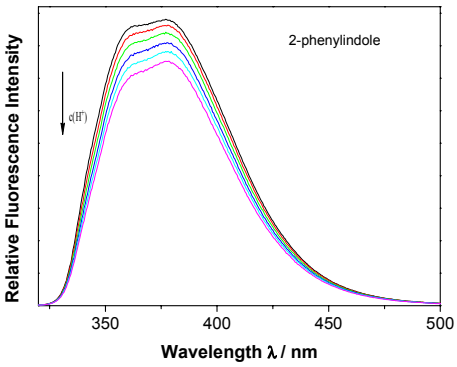


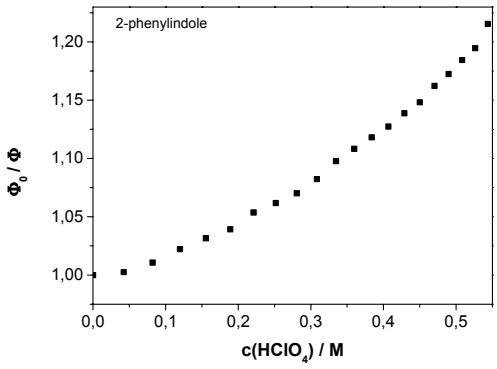
Fluorescence spectra of 2-phenylindole (**9**) in CH_3CN at different H_2O content and Stern-Volmer plot of fluorescence quenching by H_2O.



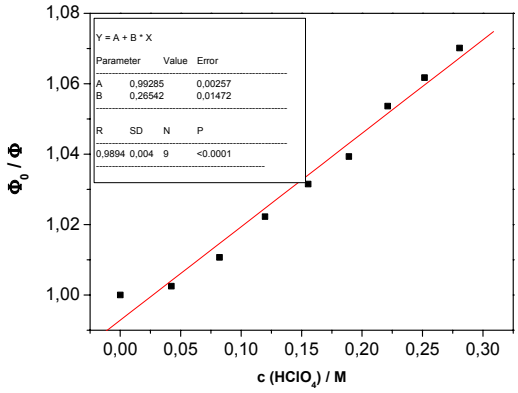


Fluorescence quenching of 2-phenylindole (**9**) in CH_3CN-H_2O (1:4) by $HClO_4$, and Stern-Volmer plot of the fluorescence quenching by $HClO_4$.

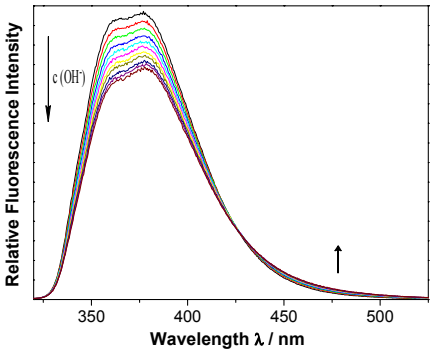


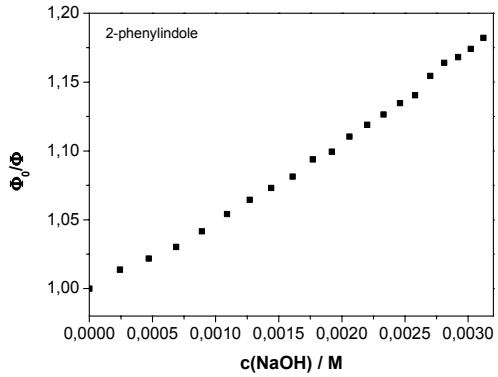


Stern-Volmer plot of the fluorescence quenching of 2-phenylindole (**9**) in CH_3CN-H_2O (1:4) by $HClO_4$.

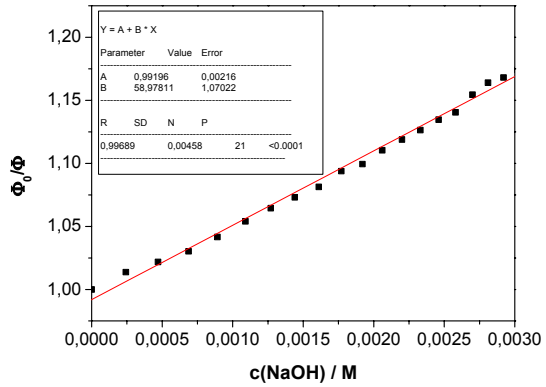


Fluorescence quenching of 2-phenylindole (**9**) in CH_3CN-H_2O (1:4) by NaOH, and Stern-Volmer plot of the fluorescence quenching by NaOH.

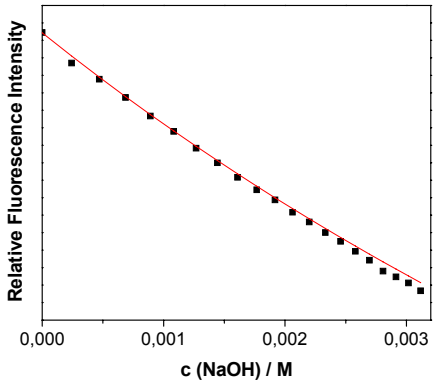




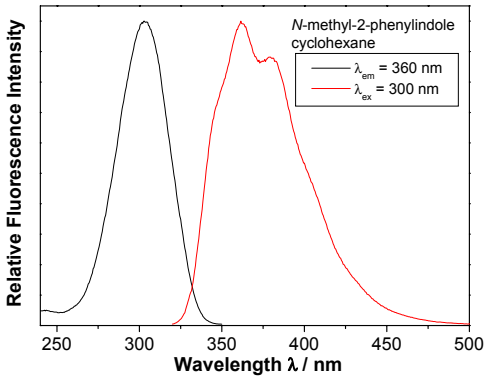
Stern-Volmer plot of the fluorescence quenching of 2-phenylindole (**9**) in CH_3CN-H_2O (1:4) by NaOH.



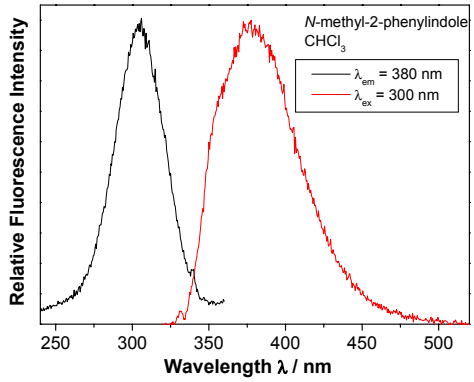
Relative fluorescence intensity of 2-phenylindole (**9**) in CH_3CN-H_2O (4:1) at 377 nm as a function of NaOH concentration. Red line represents the fitting of the model to the experimental values (black dots), obtained by the factor analysis in the SPECFIT program.



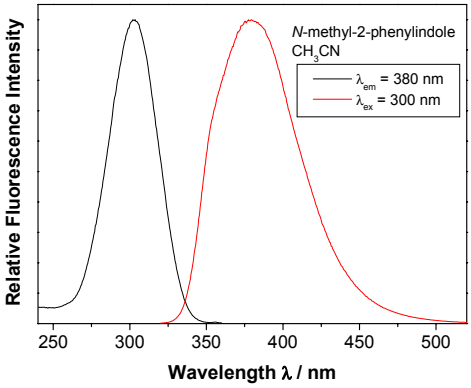
Excitation and emission spectrum of *N*-methyl-2-phenylindole (**10**) in cyclohexane.



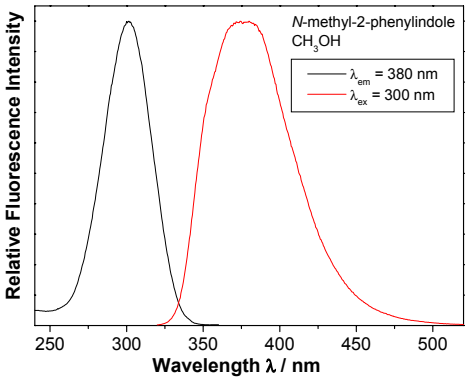
Excitation and emission spectrum of *N*-methyl-2-phenylindole (**10**) in $CHCl_3$.



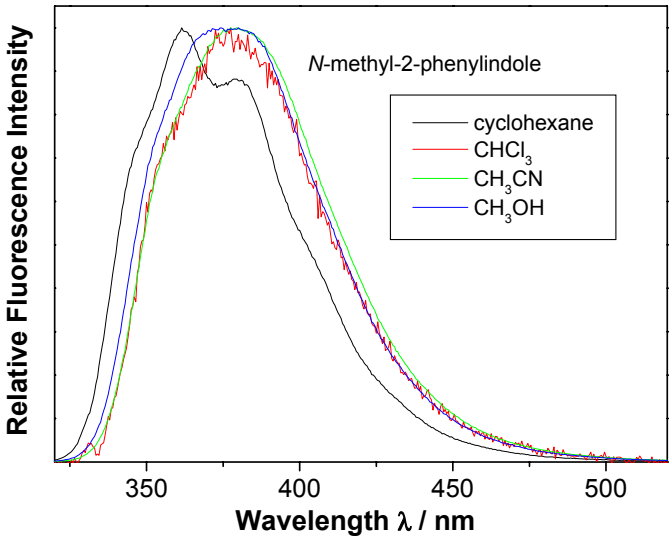
Excitation and emission spectrum of *N*-methyl-2-phenylindole (**10**) in CH_3CN.



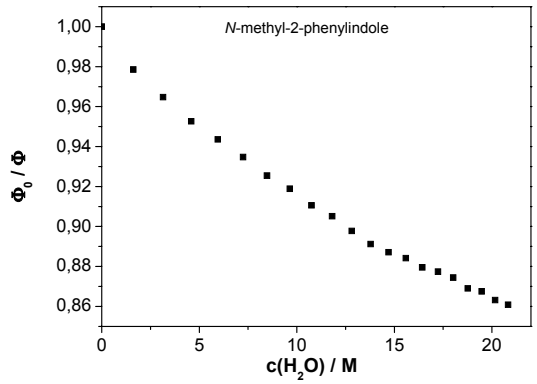
Excitation and emission spectrum of *N*-methyl-2-phenylindole (**10**) in CH_3OH.



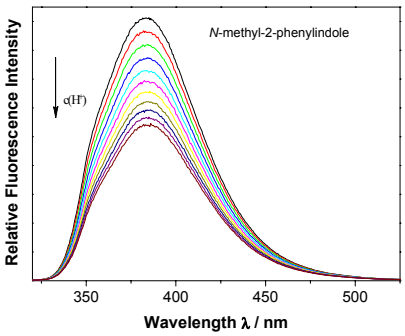
Emission spectra of *N*-methyl-2-phenylindole (**10**) in different solvents.

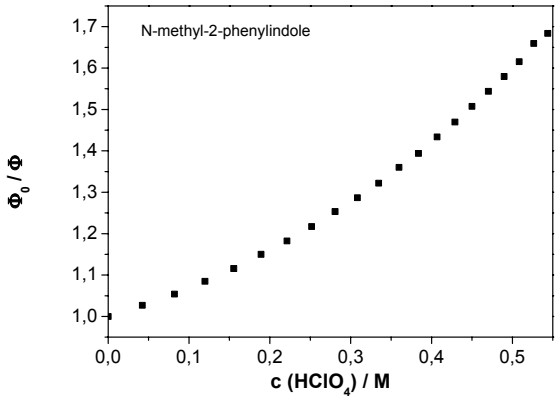


Stern-Volmer plot of the fluorescence quenching of *N*-methyl-2-phenylindole (**10**) in CH_3CN by H_2O.

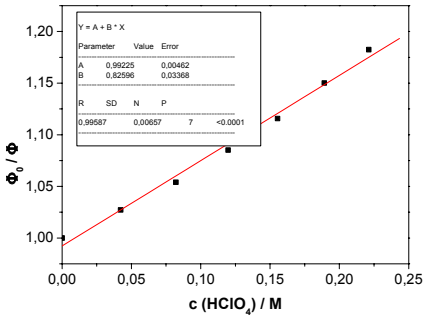


Fluorescence quenching of *N*-methyl-2-phenylindole (**10**) in CH_3CN-H_2O (1:4) by $HClO_4$, and Stern-Volmer plot of the fluorescence quenching by $HClO_4$.

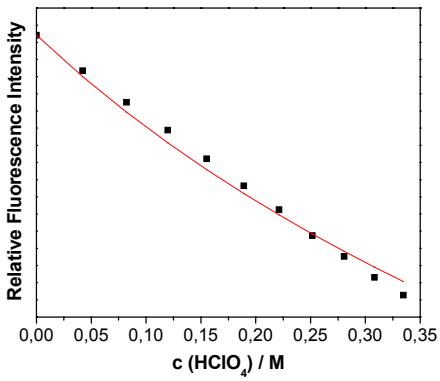




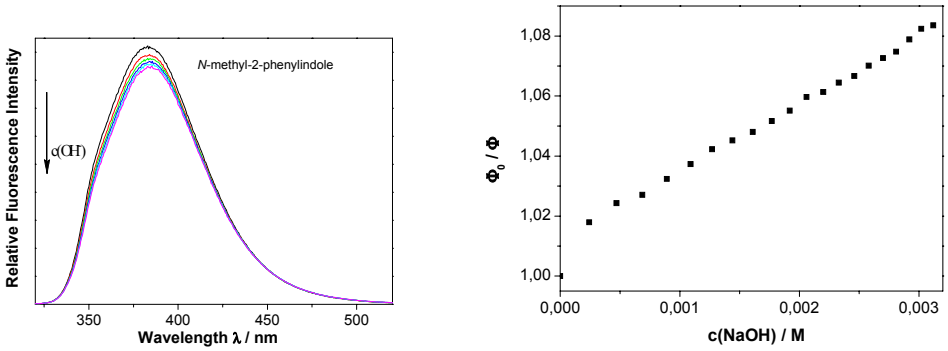
Stern-Volmer plot of the fluorescence quenching of *N*-methyl-2-phenylindole (**10**) in CH_3CN-H_2O (1:4) by $HClO_4$.



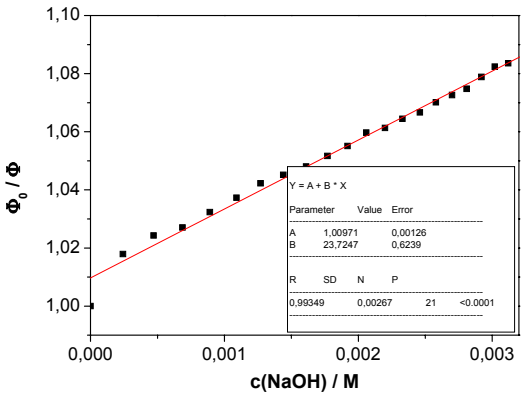
Relative fluorescence intensity of *N*-methyl-2-phenylindole (**10**) in CH_3CN-H_2O (4:1) at 384 nm as a function of $HClO_4$ concentration. Red line represents the fitting of the model to the experimental values (black dots), obtained by the factor analysis in the SPECFIT program.



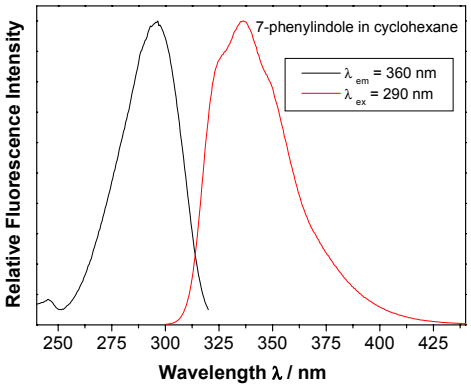
Fluorescence quenching of *N*-methyl-2-phenylindole (**10**) in CH_3CN-H_2O (1:4) by NaOH, and Stern-Volmer plot of the fluorescence quenching by NaOH.



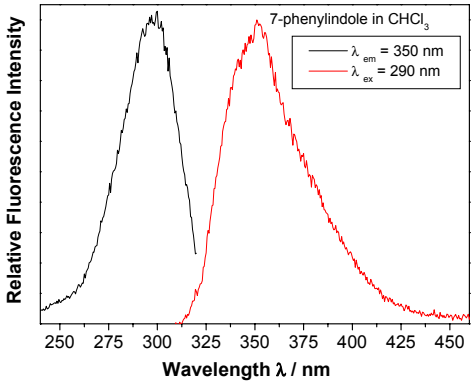
Stern-Volmer plot of the fluorescence quenching of *N*-methyl-2-phenylindole (**10**) in CH_3CN-H_2O (1:4) by NaOH.



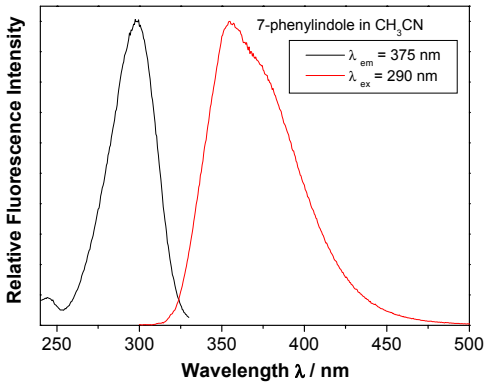
Excitation and emission spectrum of 7-phenylindole (**12**) in cyclohexane.



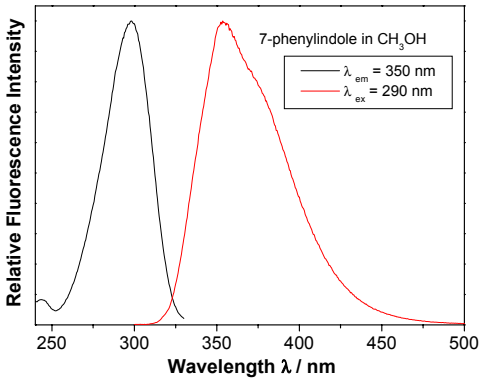
Excitation and emission spectrum of 7-phenylindole (**12**) in $CHCl_3$.



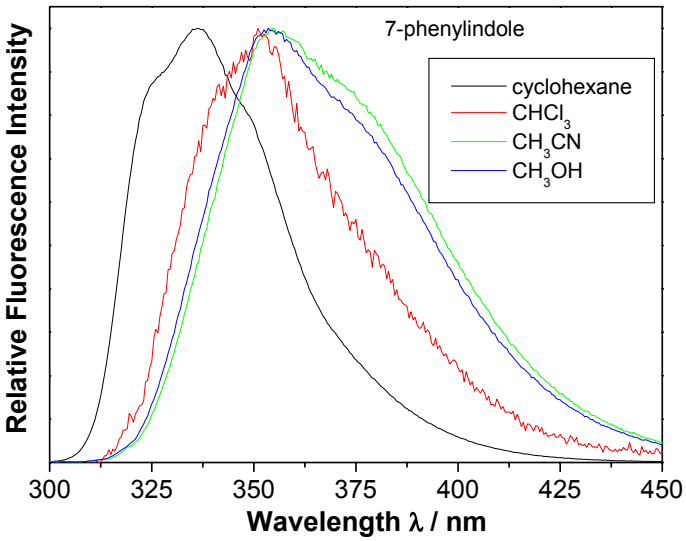
Excitation and emission spectrum of 7-phenylindole (**12**) in CH_3CN.



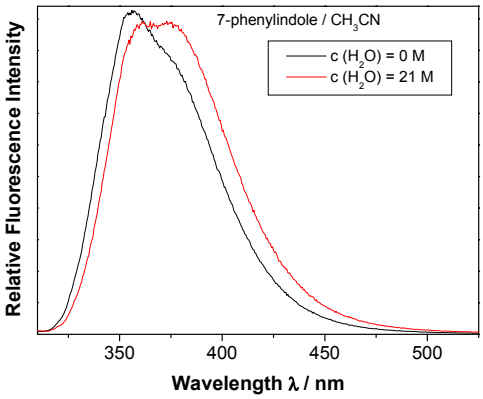
Excitation and emission spectrum of 7-phenylindole (**12**) in CH_3OH.

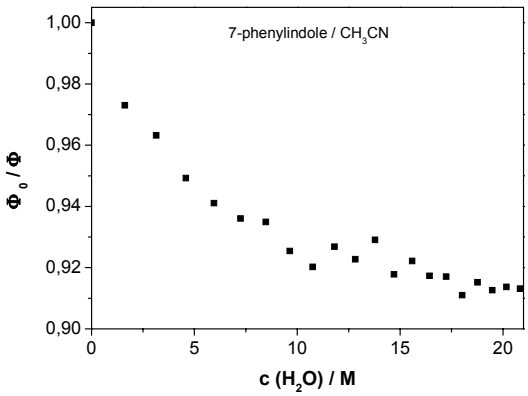


Emission spectra of 7-phenylindole (**12**) in different solvents.

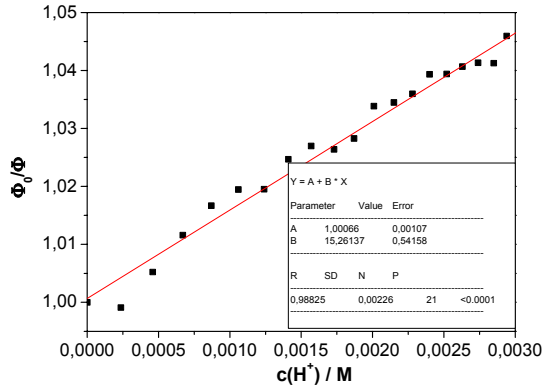


Fluorescence spectra of 7-phenylindole (**12**) in CH_3CN at different H_2O content and Stern-Volmer plot of fluorescence quenching by H_2O.

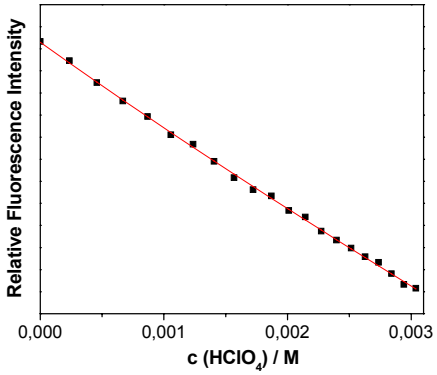




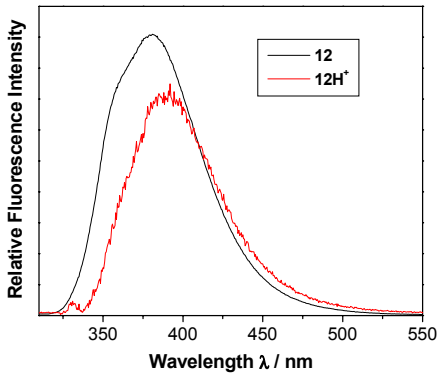
Stern-Volmer plot of the fluorescence quenching of 7-phenylindole (**12**) in CH_3CN-H_2O (1:4) by $HClO_4$.



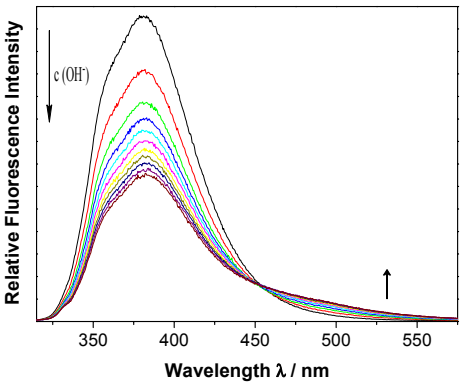
Relative fluorescence intensity of 7-phenylindole (**12**) in CH_3CN-H_2O (4:1) at 381 nm as a function of $HClO_4$ concentration. Red line represents the fitting of the model to the experimental values (black dots), obtained by the factor analysis in the SPECFIT program.

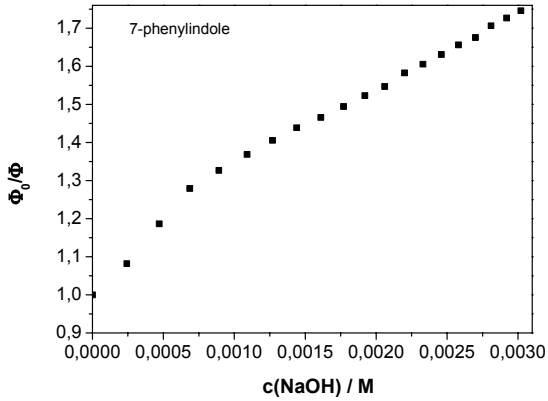


Relative fluorescence intensity of 7-phenylindole (**12**) in CH_3CN-H_2O (4:1) in the protonated and non-protonated form, obtained by the factor analysis in the SPECFIT program.

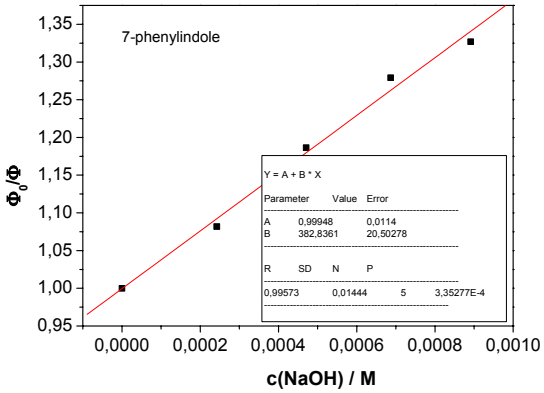


Fluorescence quenching of 7-phenylindole (**12**) in CH_3CN-H_2O (1:4) by NaOH, and Stern-Volmer plot of the fluorescence quenching by NaOH.

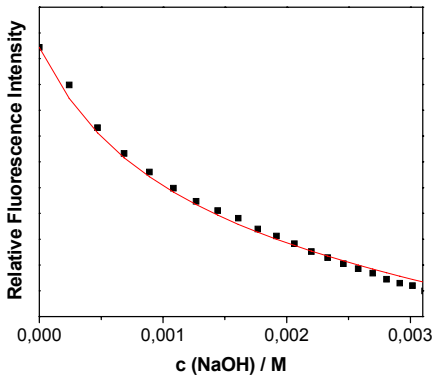




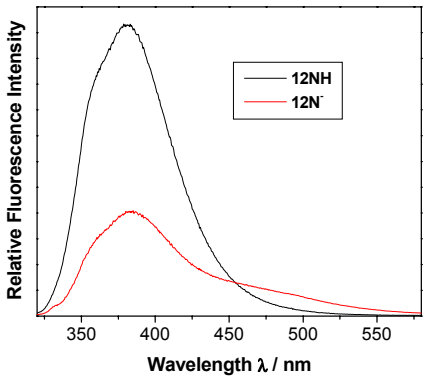
Stern-Volmer plot of the fluorescence quenching of *7*-phenylindole (**12**) in CH_3CN-H_2O (1:4) by NaOH.



Relative fluorescence intensity of 7-phenylindole (**12**) in CH_3CN-H_2O (4:1) at 378 nm as a function of NaOH concentration. Red line represents the fitting of the model to the experimental values (black dots), obtained by the factor analysis in the SPECFIT program.

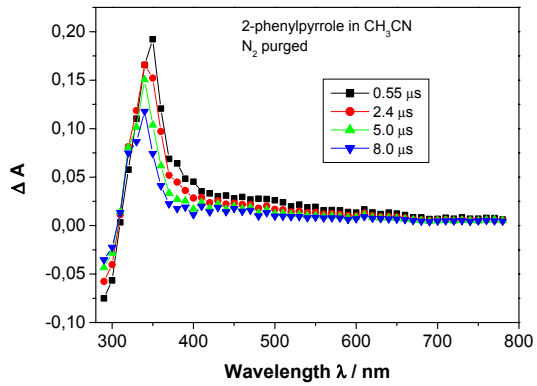


Relative fluorescence intensity of 7-phenylindole (**12**) in CH_3CN-H_2O (4:1) in the neutral and deprotonated form, obtained by the factor analysis in the SPECFIT program.

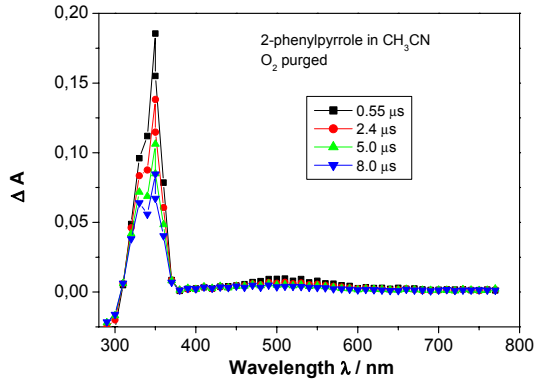


4. Laser flash photolysis

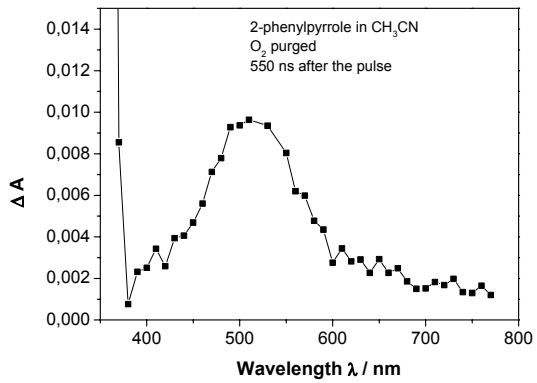
Transient absorption spectra of 2-phenylpyrrole (**8**) in N_2-purged CH_3CN solution.

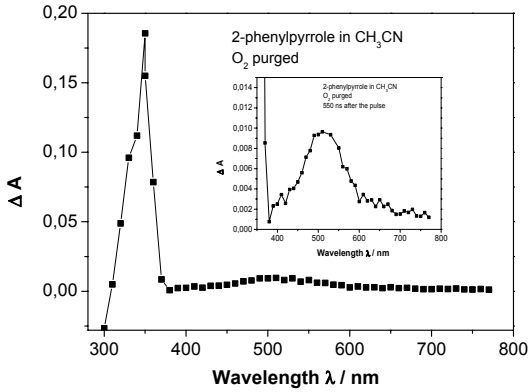


Transient absorption spectra of 2-phenylpyrrole (**8**) in O_2-purged CH_3CN solution.

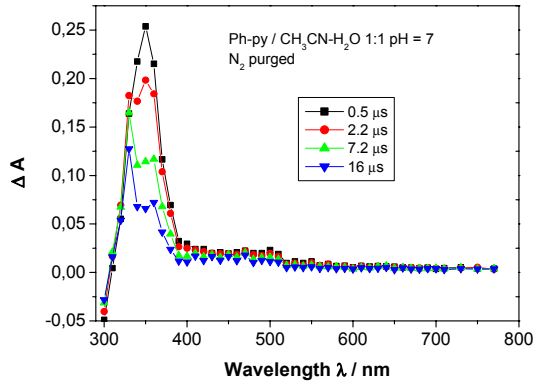


Transient absorption spectrum of 2-phenylpyrrole (**8**) in O_2-purged CH_3CN solution 550 ns after the laser pulse.

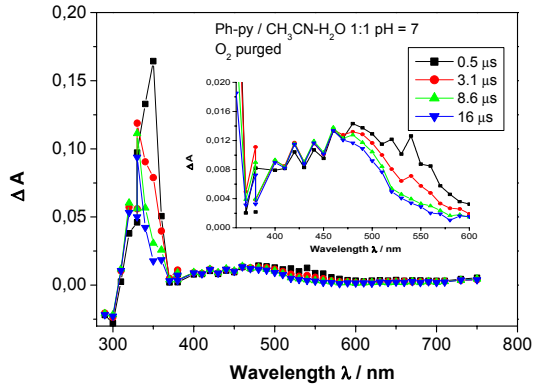




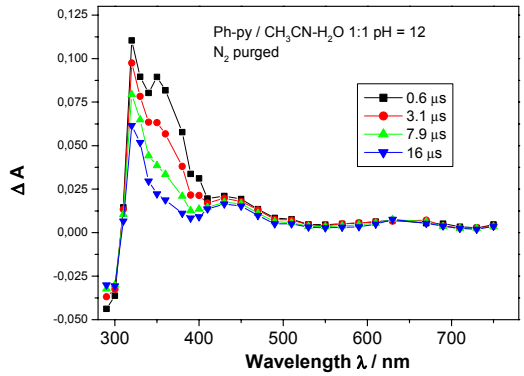
Transient absorption spectra of 2-phenylpyrrole (**8**) in N_2-purged CH_3CN-H_2O (1:1) solution, pH = 7.



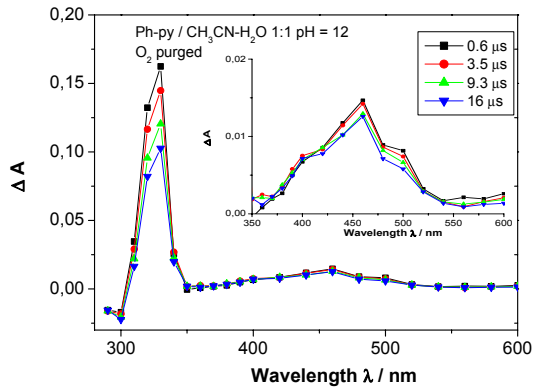
Transient absorption spectra of 2-phenylpyrrole (**8**) in O_2-purged CH_3CN-H_2O (1:1) solution, pH = 7.



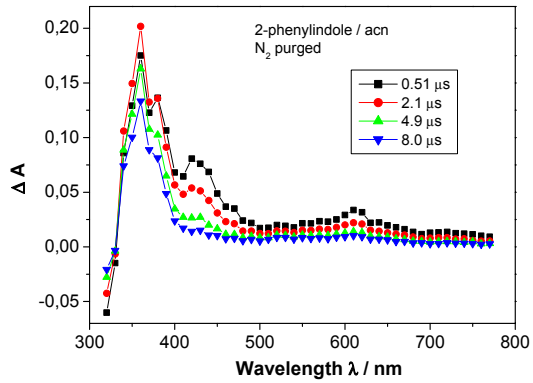
Transient absorption spectra of 2-phenylpyrrole (**8**) in N_2-purged CH_3CN-H_2O (1:1) solution, pH = 12.



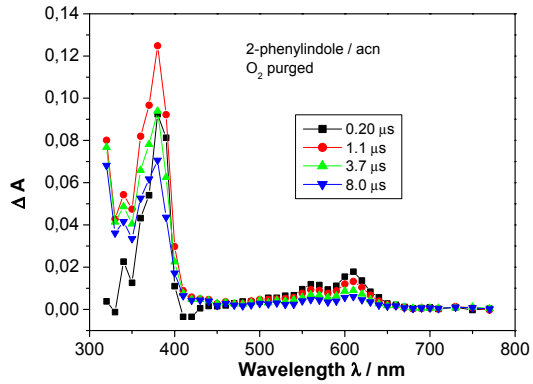
Transient absorption spectra of 2-phenylpyrrole (**8**) in O_2-purged CH_3CN-H_2O (1:1) solution, pH = 12.



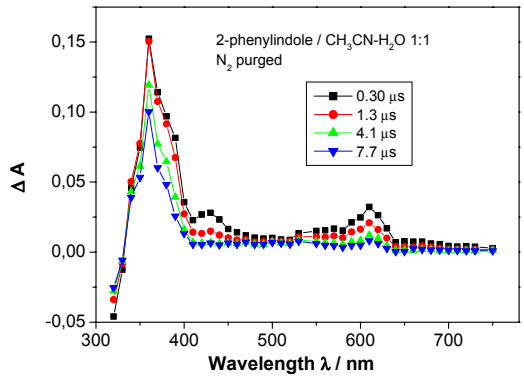
Transient absorption spectra of 2-phenylindole (**9**) in N_2-purged CH_3CN solution.



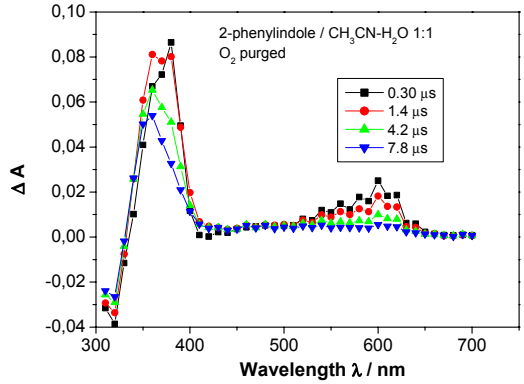
Transient absorption spectra of 2-phenylindole (**9**) in O_2-purged CH_3CN solution.



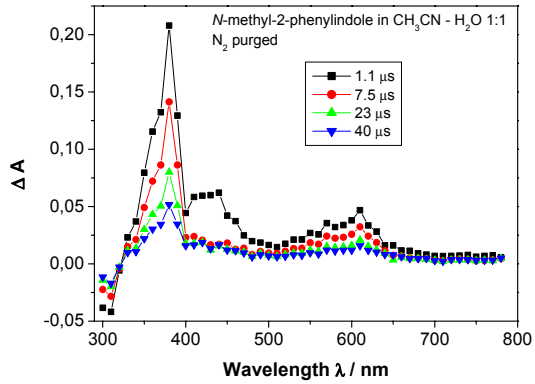
Transient absorption spectra of 2-phenylindole (**9**) in N_2-purged CH_3CN-H_2O (1:1) solution.



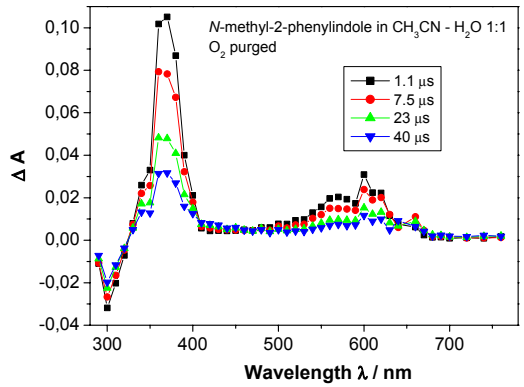
Transient absorption spectra of 2-phenylindole (**9**) in O_2-purged CH_3CN-H_2O (1:1) solution.



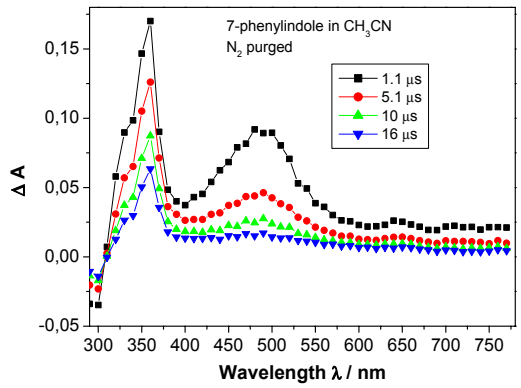
Transient absorption spectra of *N*-methyl-2-phenylindole (**10**) in N_2-purged CH_3CN-H_2O (1:1) solution.



Transient absorption spectra of *N*-methyl-2-phenylindole (**10**) in O_2-purged CH_3CN-H_2O (1:1) solution.



Transient absorption spectra of 7-phenylindole (**12**) in N_2-purged CH_3CN solution.



Transient absorption spectra of 7-phenylindole (**12**) in O_2-purged CH_3CN solution.