Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

Supplement

for

Zwitterionic biphenyl quinone methides in photodehydration reactions of 3-hydroxybiphenyl derivatives: laser flash photolysis and antiproliferation study

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1. Experimental procedures and characterization of compounds

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV- 300, 500 or 600 MHz. The NMR spectra were taken in $CDCl_3$ or DMSO-d_6 at rt using TMS as a reference and chemical shifts were reported in ppm. Melting points were determined using an original Köfler Mikroheiztisch apparatus (Reichter, Wien) and were not corrected. UV-VIS spectra were recorded on a Varian Cary 100 Bio spectrophotometer at rt. IR spectra were recorded on a FT-IR-ABB Bomem MB 102 spectrophotometer in KBr. Deuterium content was determined by MS recorded on an Agilent 6410 Triple Quadrupole Mass Spectrometer by use of the electrospray ionization technique. The spectra were obtained in the positive and negative mode in the presence of formic acid. HRMS were obtained on an Applied Biosystems 4800 Plus MALDI TOF/TOF instrument (AB, Foster City, CA). For the sample analysis a Shimadzu HPLC equipped with a Diode-Array detector and a Phenomenex Luna 3u C18(2) column was used. Mobile phase was CH_3OH-H_2O (20 %). For the chromatographic separations silica gel (Merck 0.05-0.2mm) was used. Analytical thin layer chromatography was performed on Polygram® SILG/UV_{254} (Machery-Nagel) plates. Irradiation experiments were performed in a Rayonet reactor equipped with 16 lamps with the output at 254 nm or a Luzchem reactor equipped with 8 lamps. During irradiations in the Rayonet, the irradiated solutions were continuously purged with Ar and cooled by a tap-water finger-condenser. Solvents for irradiation were of HPLC purity. Chemicals (dibromobenzenes, bromoanisoles, 2-adamantanone, solution of BBr_3) were purchased from the usual commercial sources and were used as received. Solvents for chromatographic separations were purified by distillation.

Suzuki reaction, general procedure

A two neck flask (100 mL) equipped with a condenser and a nitrogen inlet was charged with a methanol solution (15 mL) of 3-methoxyphenyl boronic acid (1.50 g, 10 mmol) and a toluene solution (35 mL) of dibromobenzene (2.33 g, 10 mmol). To the mixture was added anhydrous potassium carbonate (2.73 g, 19.72 mmol) and *tetrakis*-

triphenylphosphine palladium $Pd(PPh_3)_4$ (0.17 g, 0.148 mmol), and the mixture was heated at the temperature of reflux for 24 h. The next day, to the cooled mixture H_2O (50 mL) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL), the organic layers were combined and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator to afford crude product that was purified on a column of silica gel using hexane-CH_2Cl_2 (2:1) as an eluent.

2-bromo-3'-methoxybiphenyl

From 3-methoxyphenyl boronic acid (1.5 g, 10 mmol) and *o*-dibromobenzene (2.35 g, 10 mmol), in the presence of potassium carbonate (2.74 g, 20 mmol) and $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), the reaction furnished 1.03 g (40%) of the product in the form of yellowish oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.66 (d, 1H, J = 8.0 Hz), 7.30-7.38 (m, 3H), 7.20 (dd, 1H, J = 8.0 Hz, J = 3.1 Hz), 6.98 (dt, 1H, J = 7.7 Hz, J = 1.2 Hz), 6.90-6.96 (m, 2H), 3.84 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm 159.00 (s), 142.31 (s), 133.00 (d), 131.08 (d), 128.88 (d), 128.65 (d), 127.20 (d), 122.49 (s), 121.71 (d), 114.94 (d), 113.12 (d), 55.18 (q), one singlet was not observed.

3-bromo-3'-methoxybiphenyl

From 3-methoxyphenyl boronic acid (1.5 g, 10 mmol) and *m*-dibromobenzene (2.35 g, 10 mmol), in the presence of potassium carbonate (2.74 g, 20 mmol) and $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), the reaction furnished 1.64 g (62%) of the product in the form of yellowish oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm 7.72 (t, 1H, J = 1.7 Hz), 7.44-7.52 (m, 2H), 7.36 (t, 1H, J = 7.9 Hz), 7.29 (t, 1H, J = 7.9 Hz), 7.13 (d, 1H, J = 7.7 Hz), 7.07 (t, 1H, J = 2.0 Hz), 6.91 (dd, 1H, J = 0.7 Hz, J = 8.2 Hz), 3.86 (s, 3H, OCH_3); ^{13}C NMR (DMSO-d_6, 150 MHz) δ/ppm 159.75 (s), 142.49 (s), 140.04 (s), 130.91 (d), 130.27 (d), 130.04 (d), 129.33 (d), 125.89 (d), 122.27 (s), 119.10 (d), 113.85 (d), 112.18 (d), 55.17 (q).

4-bromo-3'-methoxybiphenyl

From 3-methoxyphenyl boronic acid (1.5 g, 10 mmol) and *p*-dibromobenzene (2.35 g, 10 mmol), in the presence of potassium carbonate (2.74 g, 20 mmol) and $Pd(PPh_3)_4$ (0.14 g, 0.12 mmol), the reaction furnished 1.35 g (51%) of the product in the form of yellowish oil.

^{1}H NMR ($CDCl_3$, 600 MHz) δ/ppm 7.54 (d, 2H, J = 8.5 Hz), 7.44 (d, 2H, J = 8.5 Hz), 7.34 (t, 1H, J = 7.9 Hz), 7.13 (d, 1H, J = 7.9 Hz), 7.07 (t, 1H, J = 2.0 Hz), 6.90 (d, 1H, J = 7.9 Hz), 3.85 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 150 MHz) δ/ppm 159.95 (s), 141.42 (s), 139.91 (s), 131.73 (d, 2C), 129.80 (d), 128.66 (d, 2C), 121.55 (s), 119.33 (d), 112.87 (d), 112.70 (d), 55.22 (q).

2. Irradiations of 4-8 in CH_3OH-H_2O under different conditions.

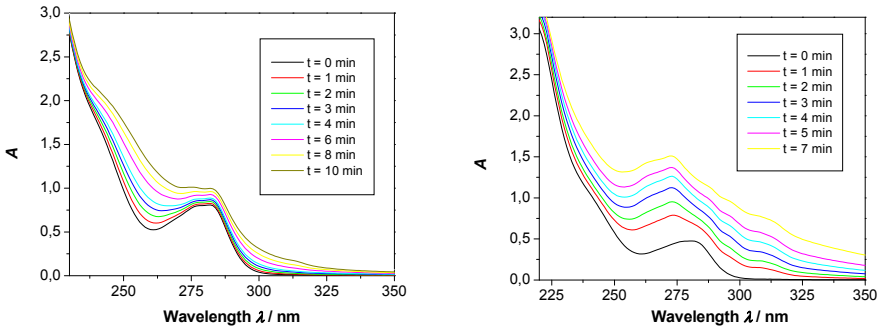


Fig 1. UV-Vis spectra after photolyses (16 lamps 254 nm) of **4** in a UV-vis cuvette in CH_3CN (left) and CH_3CN-H_2O (1:1) (right).

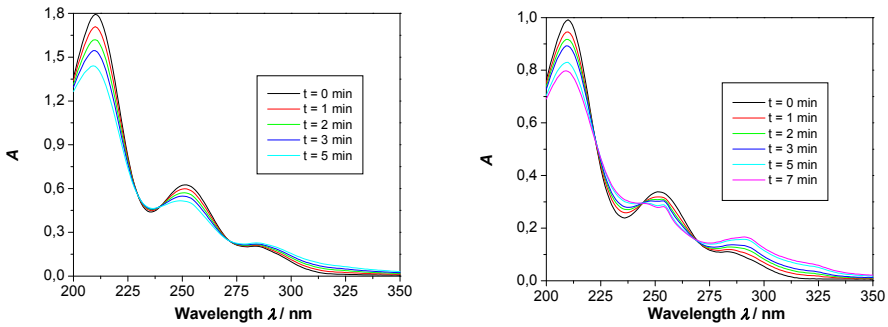


Fig 2. UV-Vis spectra after photolyses (16 lamps 254 nm) of **5** in a UV-vis cuvette in CH_3CN (left) and CH_3CN-H_2O (1:1) (right)

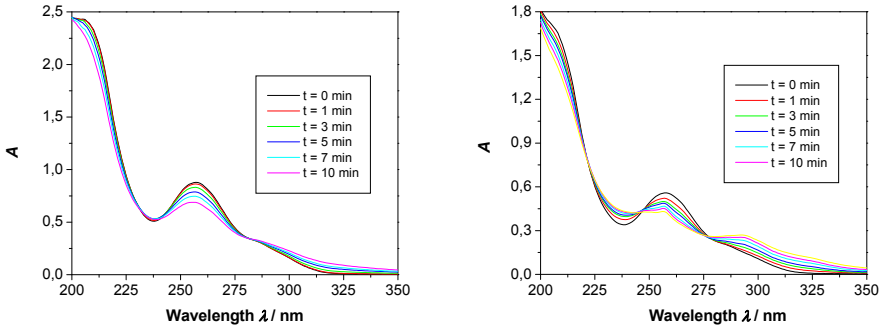


Fig 3. UV-Vis spectra after photolyses (16 lamps 254 nm) of **8** in a UV-vis cuvette in CH_3CN (left) and CH_3CN-H_2O (1:1) (right)

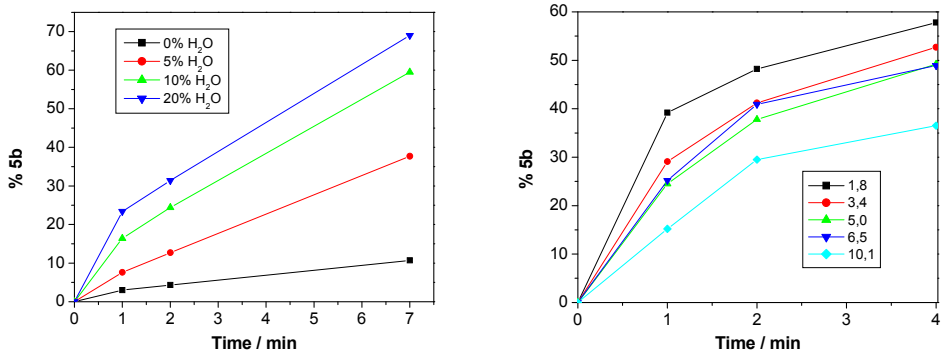


Fig. 4. Conversion of **5** to **5b** on photolysis (8 lamps, 254 nm) in CH_3OH-H_2O with different H_2O content (left) and in CH_3OH-H_2O (1:1) at different pH (right).

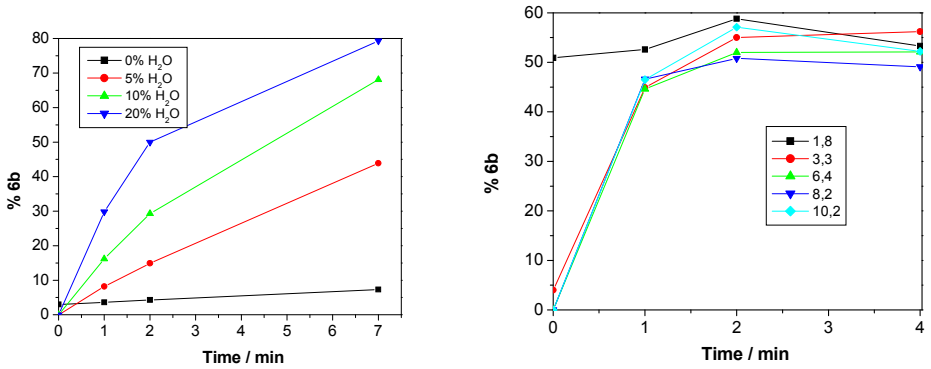


Fig. 5. Conversion of **6** to **6b** on photolysis (8 lamps, 254 nm) in CH_3OH-H_2O with different H_2O content (left) and in CH_3OH-H_2O (1:1) at different pH (right).

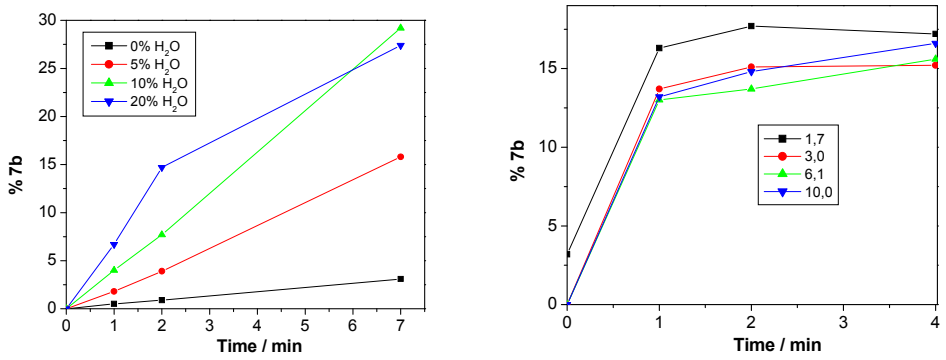


Fig. 6. Conversion of **7** to **7b** on photolysis (8 lamps, 254 nm) in CH_3OH-H_2O with different H_2O content (left) and in CH_3OH-H_2O (1:1) at different pH (right).

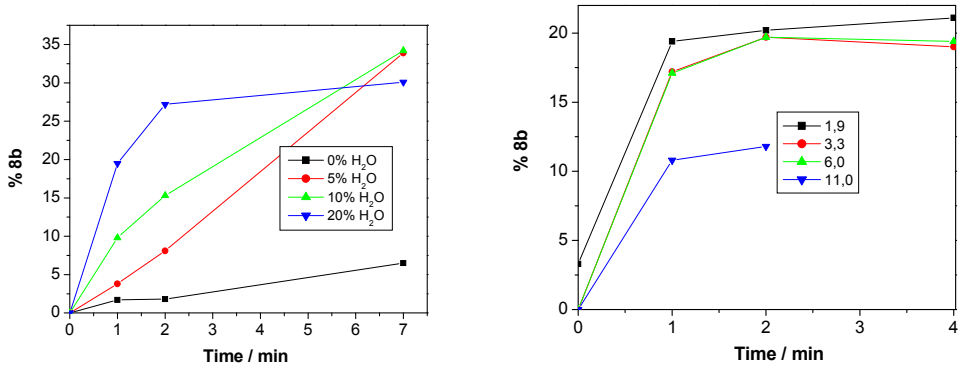


Fig. 7. Conversion of **8** to **8b** on photolysis (8 lamps, 254 nm) in CH_3OH-H_2O with different H_2O content (left) and in CH_3OH-H_2O (1:1) at different pH (right).

3. UV-vis and Fluorescence Spectra of 4-8.

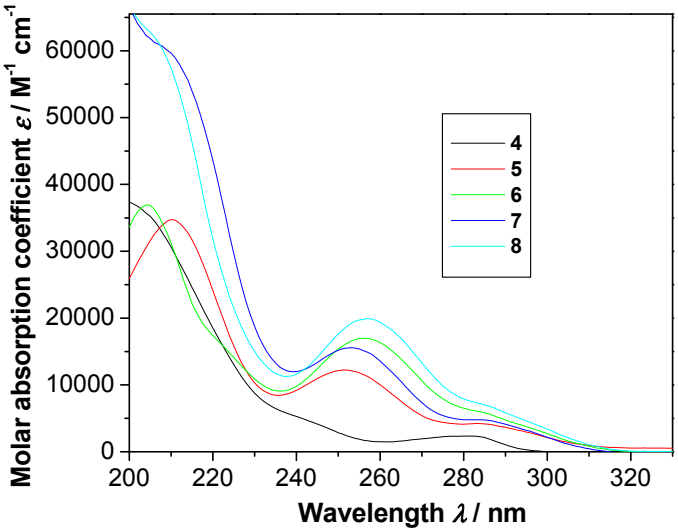


Fig. 8. Absorption spectra of **4**-**8**in CH_3CN.

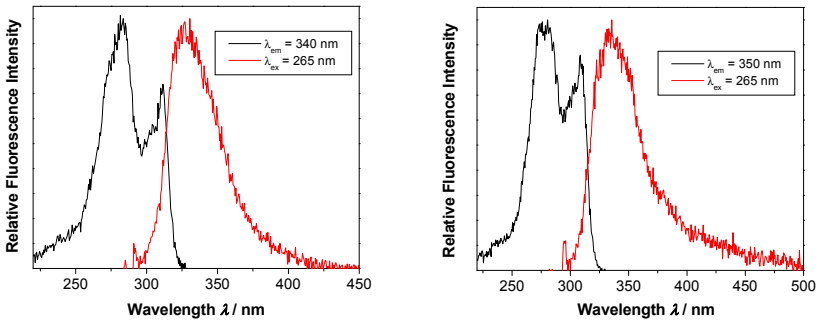


Fig. 9. Normalized excitation and emission spectra of **4** in CH_3CN (left) and CH_3CN-H_2O (1:4) (right).

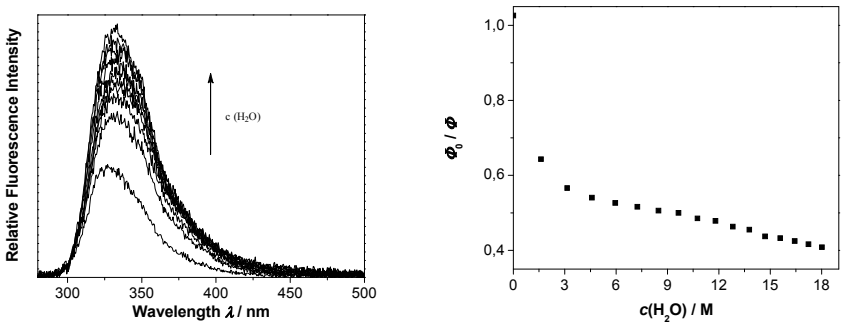


Fig. 10. Fluorescence spectra of **4** in CH_3CN on addition of H_2O (left) and Stern-Volmer quenching plot of fluorescence of **4** in CH_3CN by addition of H_2O (right).

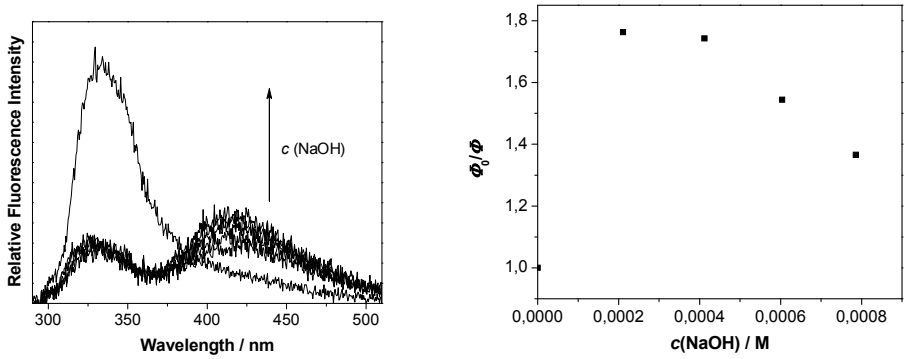


Fig. 11. Fluorescence spectra of **4** in CH_3CN-H_2O (1:4) on addition of NaOH (left), and Stern-Volmer quenching plot of fluorescence of **4** in CH_3CN-H_2O (1:4) by addition of NaOH (right).

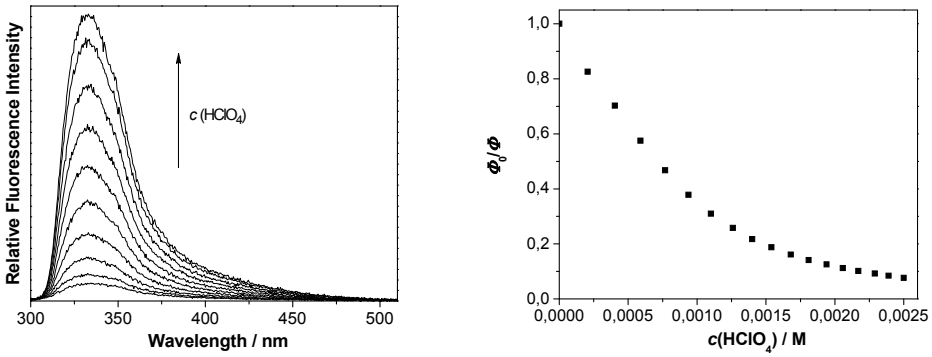


Fig. 12. Fluorescence spectra of **4** in CH_3CN-H_2O (1:4) on addition of $HClO_4$ (left), and Stern-Volmer quenching plot of fluorescence of **4** in CH_3CN-H_2O (1:4) by addition of $HClO_4$ (right).

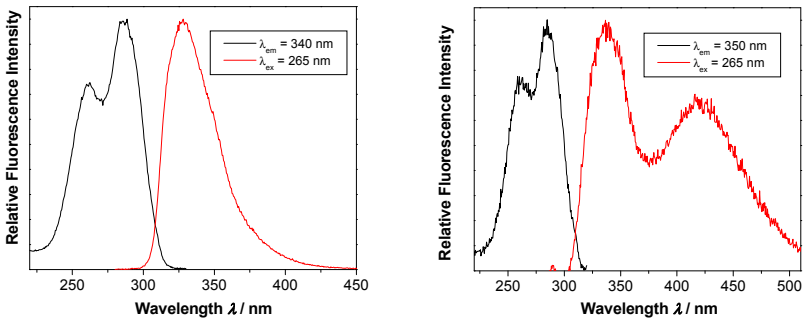


Fig. 13. Normalized excitation and emission spectra of **5** in CH_3CN (left) and CH_3CN-H_2O (1:4) (right).

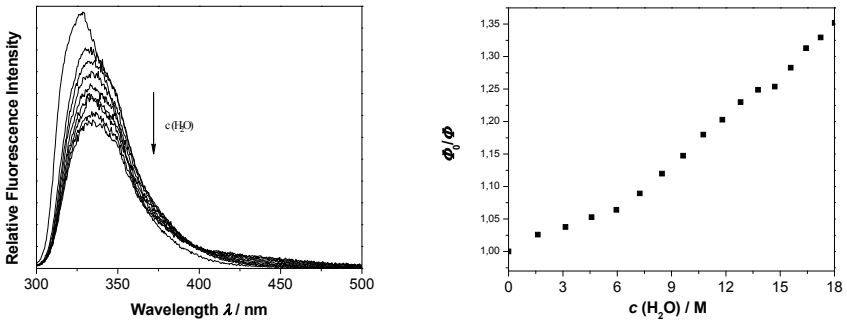


Fig. 14. Fluorescence spectra of **5** in CH_3CN on addition of H_2O (left) and Stern-Volmer quenching plot of fluorescence of **5** in CH_3CN by addition of H_2O (right).

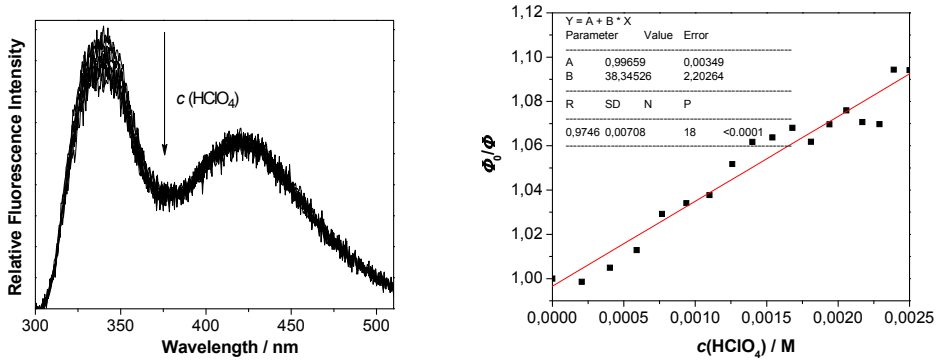


Fig. 15. Fluorescence spectra of **5** in CH_3CN-H_2O (1:4) on addition of $HClO_4$ (left), and Stern-Volmer quenching plot of fluorescence of **5** in CH_3CN-H_2O (1:4) by addition of $HClO_4$ (right).

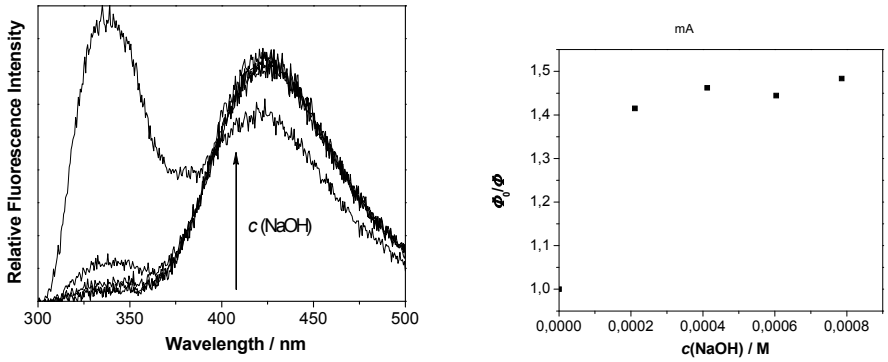


Fig. 16. Fluorescence spectra of **5** in CH_3CN-H_2O (1:4) on addition of NaOH (left), and Stern-Volmer quenching plot of fluorescence of **5** in CH_3CN-H_2O (1:4) by addition of NaOH (right).

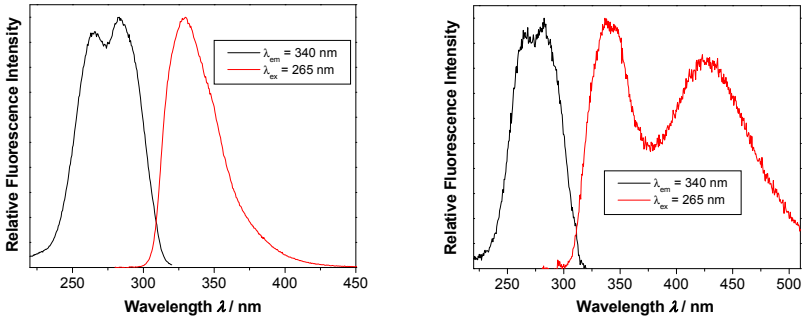


Fig. 17. Normalized excitation and emission spectra of **6** in CH_3CN (left) and CH_3CN-H_2O (1:4) (right).

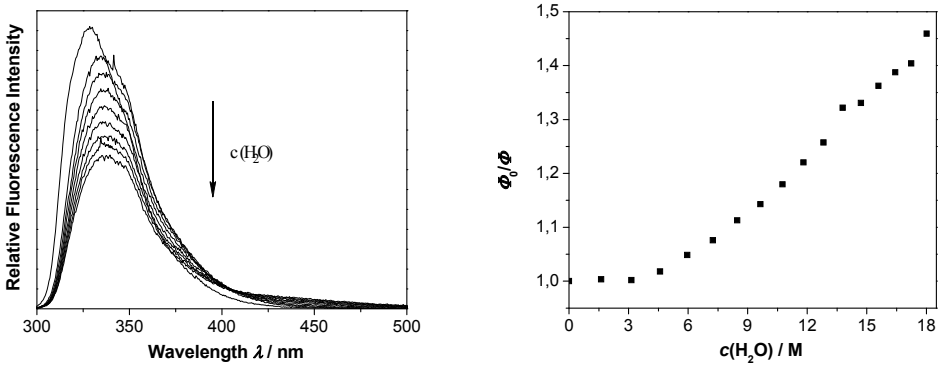


Fig. 18. Fluorescence spectra of **6** in CH_3CN on addition of H_2O (left) and Stern-Volmer quenching plot of fluorescence of **6** in CH_3CN by addition of H_2O (right).

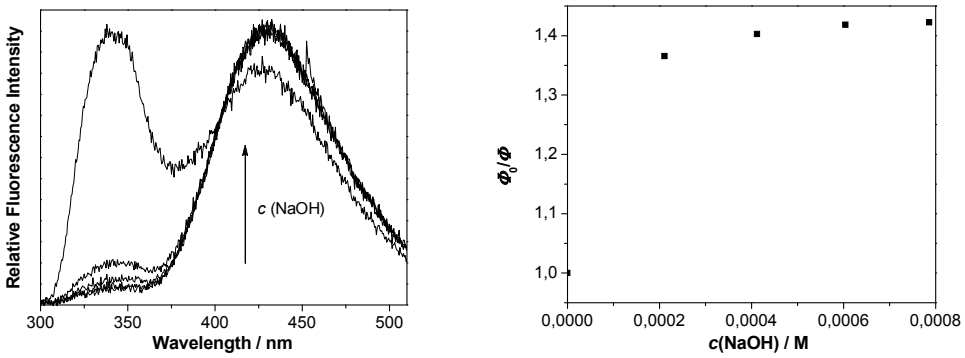


Fig. 19. Fluorescence spectra of **6** in CH_3CN-H_2O (1:4) on addition of NaOH (left), and Stern-Volmer quenching plot of fluorescence of **6** in CH_3CN-H_2O (1:4) by addition of NaOH (right).

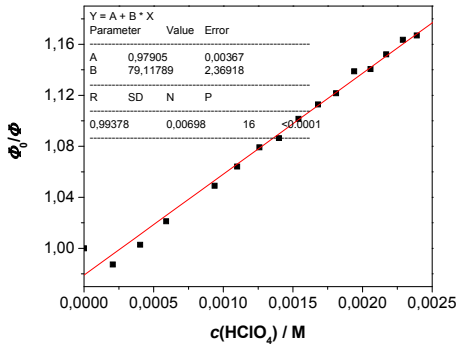


Fig. 20. Stern-Volmer quenching plot of fluorescence of **6** in CH_3CN-H_2O (1:4) by addition of $HClO_4$.

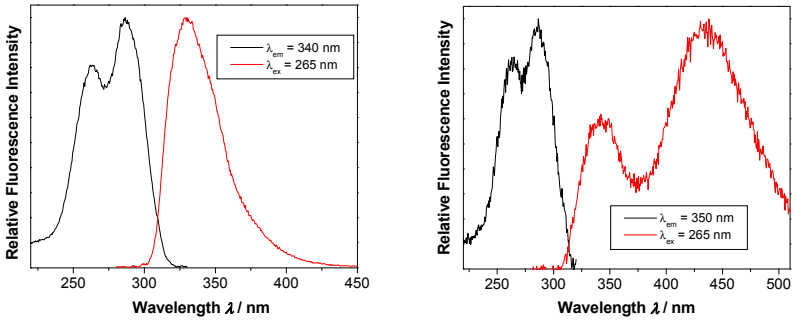


Fig. 21. Normalized excitation and emission spectra of **7** in CH_3CN (left) and CH_3CN-H_2O (1:4) (right).

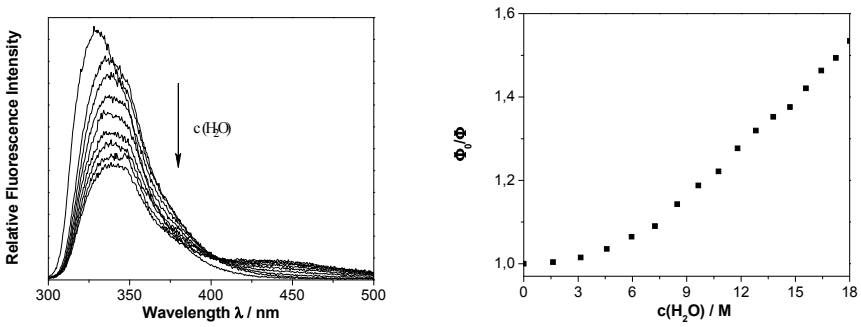


Fig. 22. Fluorescence spectra of **7** in CH_3CN on addition of H_2O (left) and Stern-Volmer quenching plot of fluorescence of **7** in CH_3CN by addition of H_2O (right).

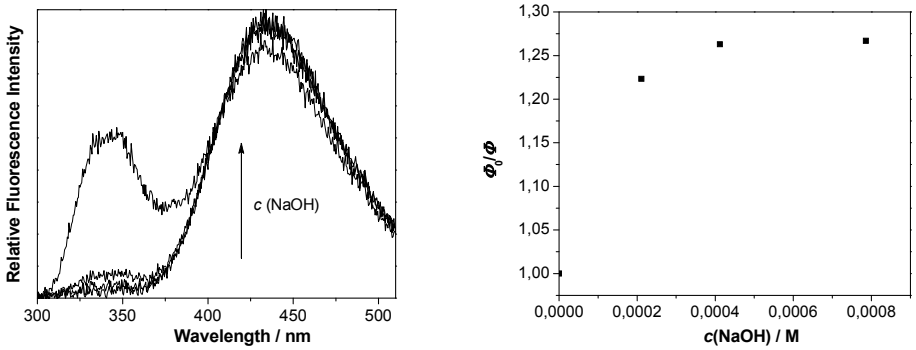


Fig. 23. Fluorescence spectra of **7** in CH_3CN-H_2O (1:4) on addition of NaOH (left), and Stern-Volmer quenching plot of fluorescence of **7** in CH_3CN-H_2O (1:4) by addition of NaOH (right).

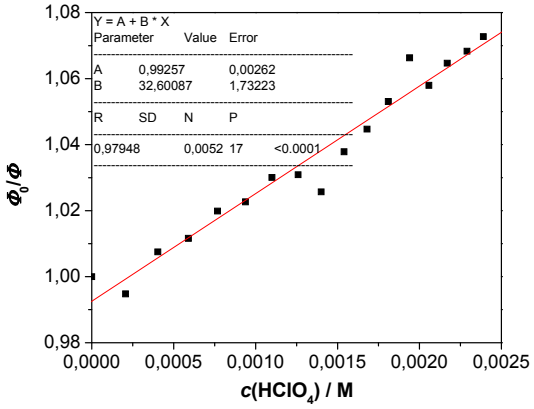


Fig. 24. Stern-Volmer quenching plot of fluorescence of **7** in CH_3CN-H_2O (1:4) by addition of $HClO_4$.

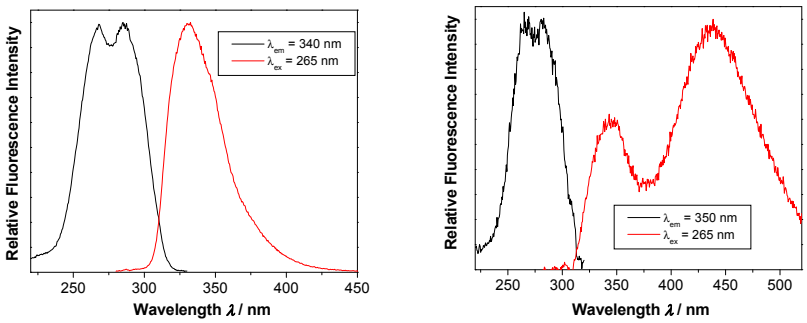


Fig. 25. Normalized excitation and emission spectra of **8** in CH_3CN (left) and CH_3CN-H_2O (1:4) (right).

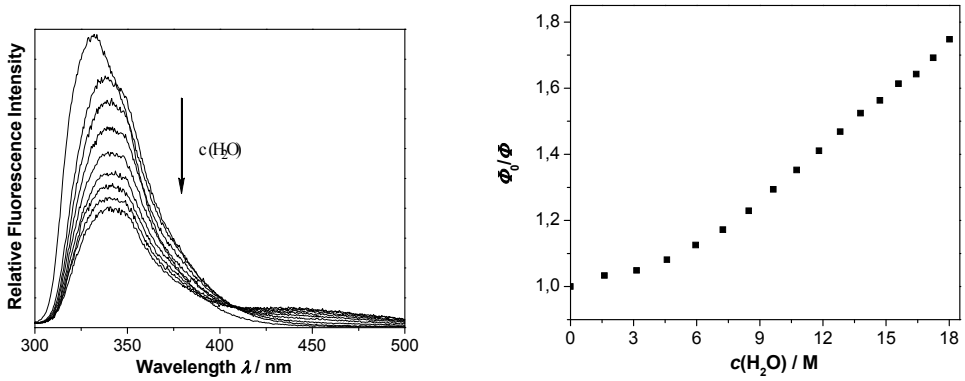


Fig. 26. Fluorescence spectra of **8** in CH_3CN on addition of H_2O (left) and Stern-Volmer quenching plot of fluorescence of **8** in CH_3CN by addition of H_2O (right).

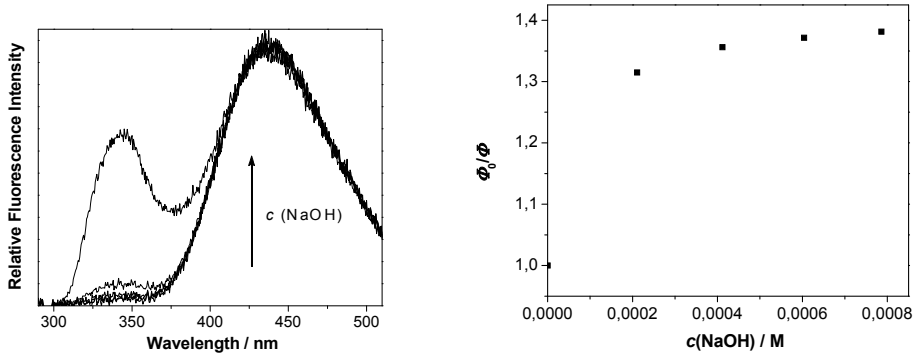


Fig. 27. Fluorescence spectra of **8** in CH_3CN-H_2O (1:4) on addition of NaOH (left), and Stern-Volmer quenching plot of fluorescence of **8** in CH_3CN-H_2O (1:4) by addition of NaOH (right).

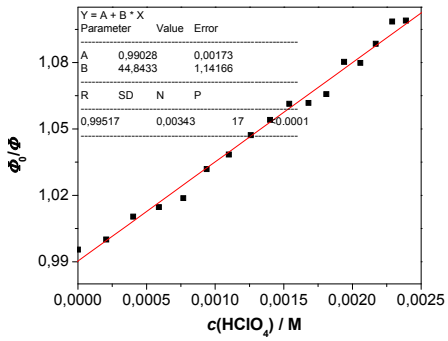


Fig. 28. Stern-Volmer quenching plot of fluorescence of **8** in CH_3CN-H_2O (1:4) by addition of $HClO_4$.

4. Laser Flash Photolysis

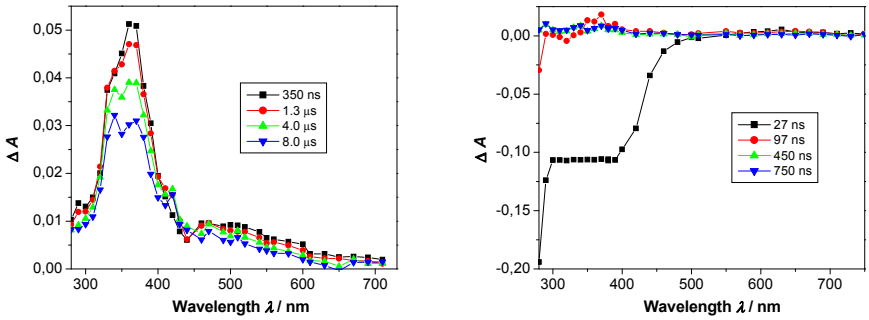


Fig. 29. Transient absorption spectra of N_2-purged TFE solution of **4** (left) and O_2-purged TFE solution of **4** (right).

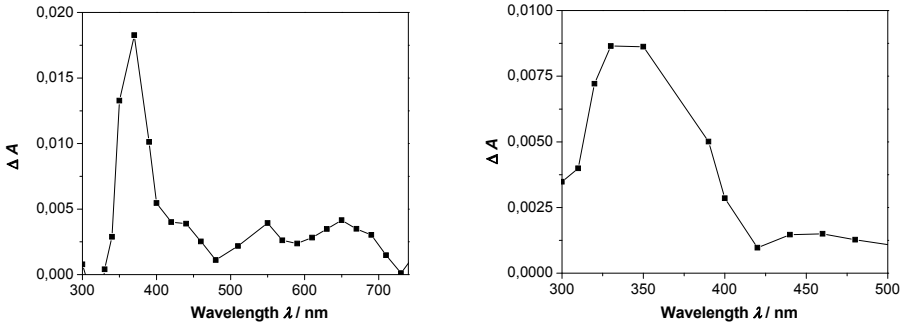


Fig. 30. Transient absorption spectra of O_2-purged TFE solution of **4**, 97 ns (left) and 450 ns (right) after the laser pulse.

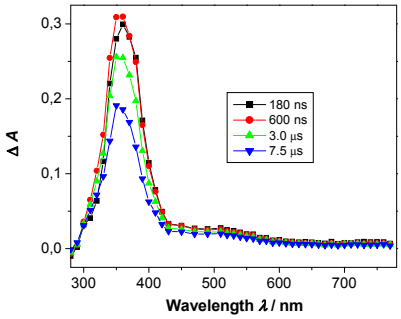


Fig. 31. Transient absorption spectra of N_2-purged TFE solution of **5**.

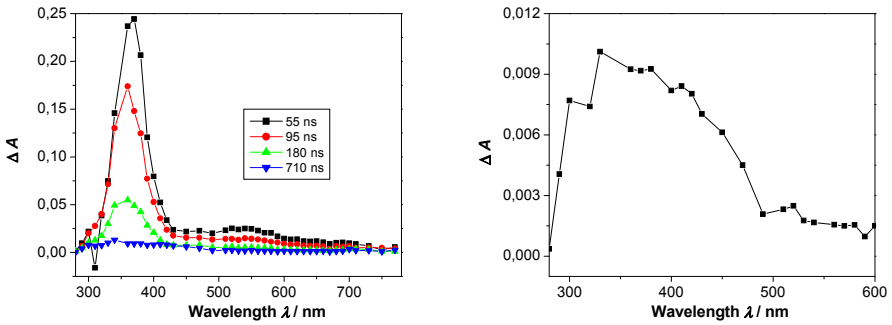


Fig. 32. Transient absorption spectra of O_2-purged TFE solution of **5** (left) and O_2-purged TFE solution of **5**, 710 ns after the laser pulse (right).

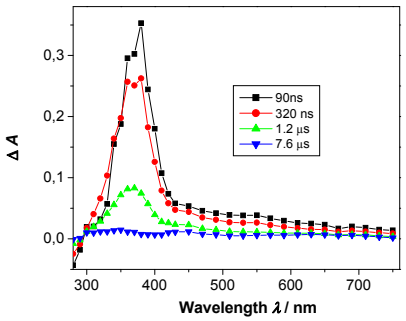


Fig. 33. Transient absorption spectra of N_2-purged TFE solution of **6**.

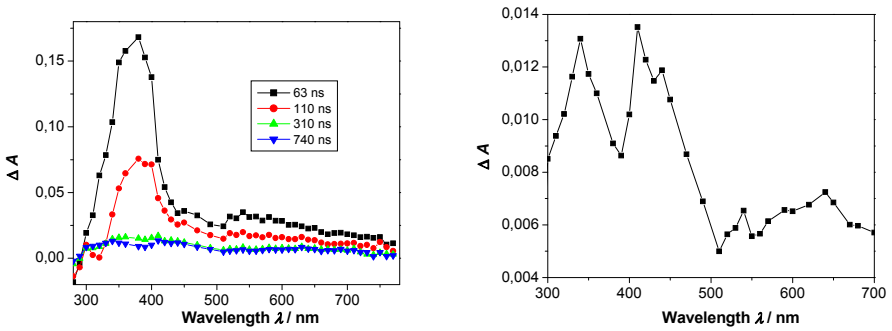


Fig. 34. Transient absorption spectra of O_2-purged TFE solution of **6** (left) and O_2-purged TFE solution of **6**, 740 ns after the laser pulse (right).

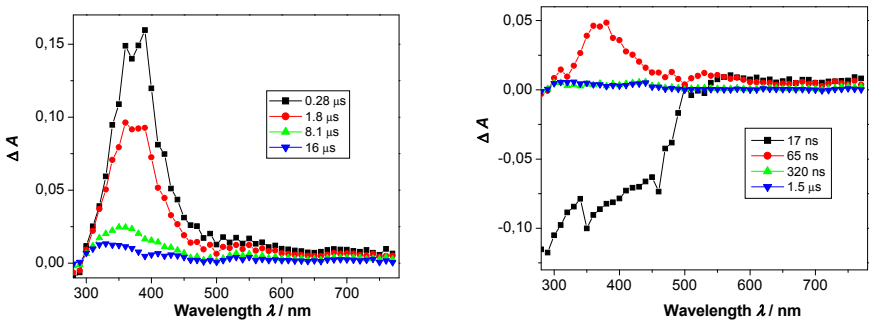


Fig. 35. Transient absorption spectra of N_2-purged (left) and O_2-purged (right) CH_3CN solution of **7**.

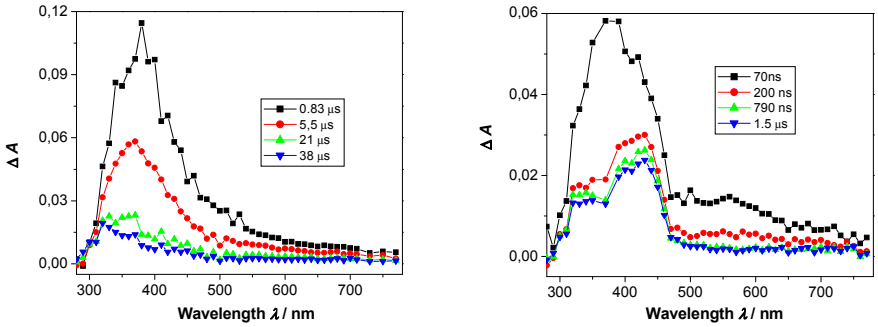


Fig. 36. Transient absorption spectra of N_2-purged and O_2-purged (right) CH_3CN-H_2O (1:1) solution of **7**.

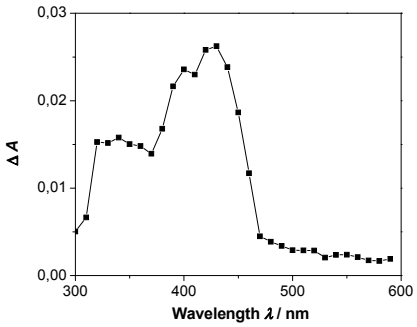


Fig. 37. Transient absorption spectrum of O_2-purged CH_3CN-H_2O (1:1) solution of **7**, 790 ns after the laser pulse.

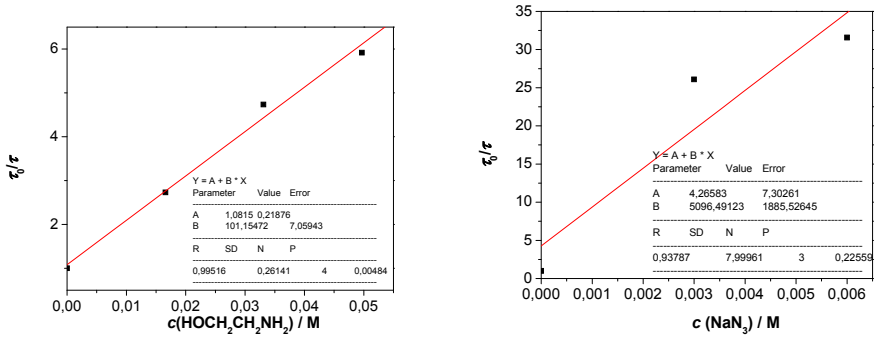


Fig. 38. Stern-Volmer plots for the quenching of the transient absorption of CH_3CN-H_2O (1:1) solution of **7** by ethanolamine (left) and NaN_3 (right).

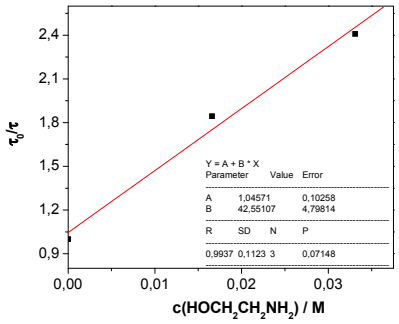


Fig. 39. Stern-Volmer plots for the quenching of the transient absorption at 600 nm of CH_3CN-H_2O (1:1) solution of **7** by ethanolamine.

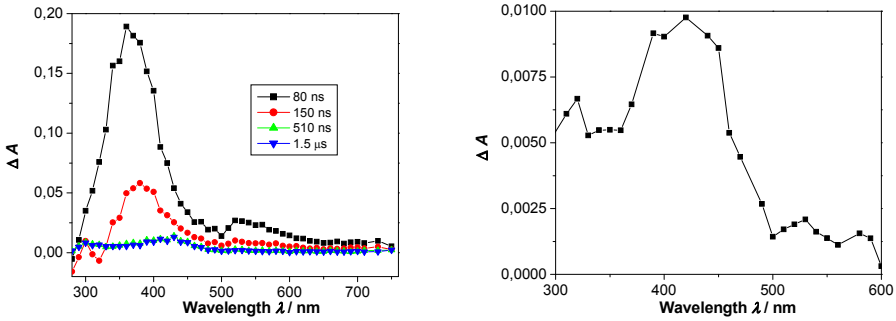


Fig. 40. Transient absorption spectra of O_2-purged TFE solution of **7** (left) and O_2-purged TFE solution of **7**, 1.5µs after the laser pulse (right).

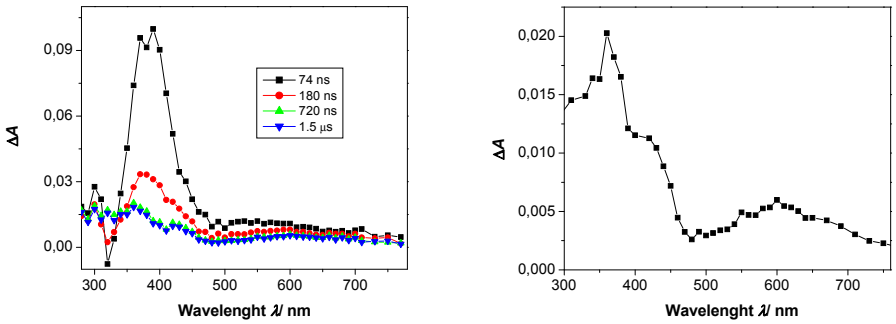


Fig. 41. Transient absorption spectra of O_2-purged CH_3CN-H_2O (1:1) solution of **7a** (left) and O_2-purged CH_3CN-H_2O (1:1) solution of **7a**, 720 ns after the laser pulse (right).

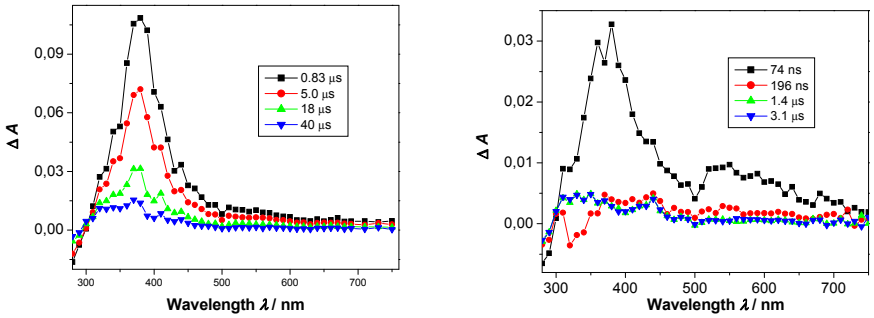


Fig. 42. Transient absorption spectra of N_2-purged (left) and O_2-purged (right) CH_3CN solution of **8**.

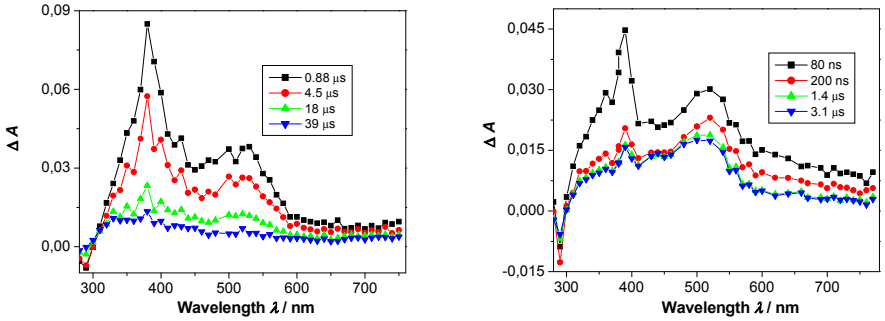


Fig. 43. Transient absorption spectra of N_2-purged (left) and O_2-purged (right) CH_3CN-H_2O (1:1) solution of **8**.

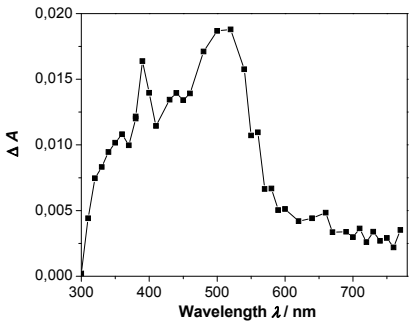


Fig. 44. Transient absorption spectrum of O_2-purged CH_3CN-H_2O (1:1) solution of **8**, 1.4 μs after the laser pulse.

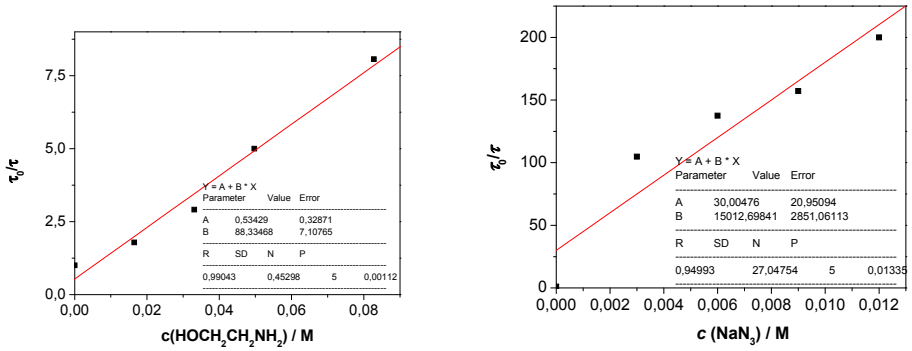


Fig. 45. Stern-Volmer plots for the quenching of the transient absorption of CH_3CN-H_2O (1:1) solution of **8** by ethanolamine (left) and NaN_3 (right).

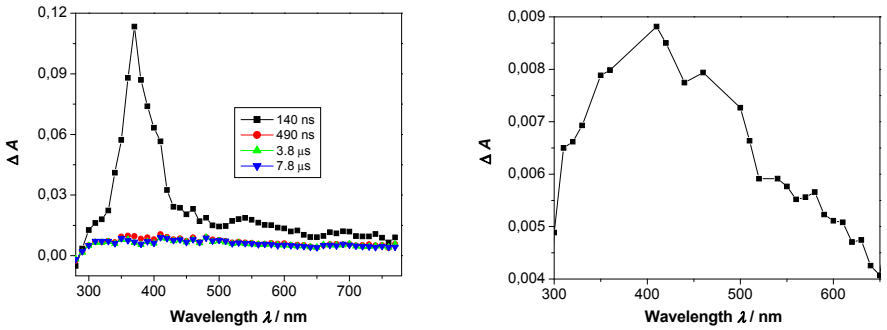


Fig. 46. Transient absorption spectra of O_2-purged TFE solution of **8** (left) and O_2-purged TFE solution of **8**, 4 μs after the laser pulse (right).

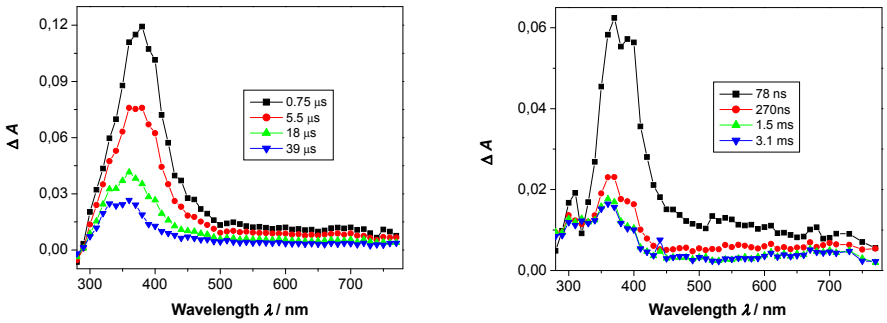


Fig. 47. Transient absorption spectra of N_2-purged (left) and O_2-purged (right) CH_3CN-H_2O (1:1) solution of **8a**.

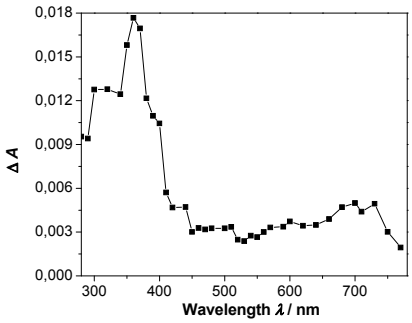
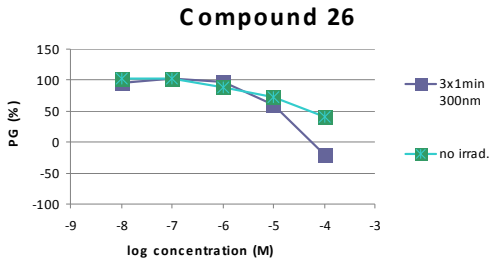


Fig. 48. Transient absorption spectrum of O_2-purged CH_3CN-H_2O (1:1) solution of **8a**, 1.5 µs after the laser pulse.
Radical cation at 600 nm 23 µs, quenched by ethanolamine, $k_q = 3 \times 10^8$ M^{-1} s^{-1}.

5. Antiproliferative investigation

A



B

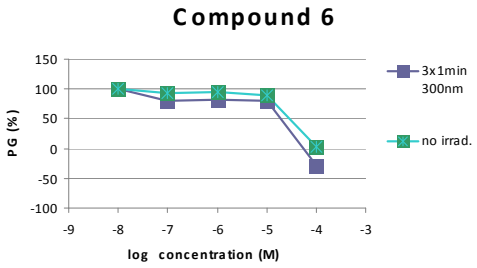


Fig 49. An example of dose-response profiles for compounds **26** and **6**, after irradiation 3×1 min at 300 nm and without irradiation, tested *in vitro* on MCF-7 cell line.

6. Cross-Linking and cleavage of Plasmid DNA

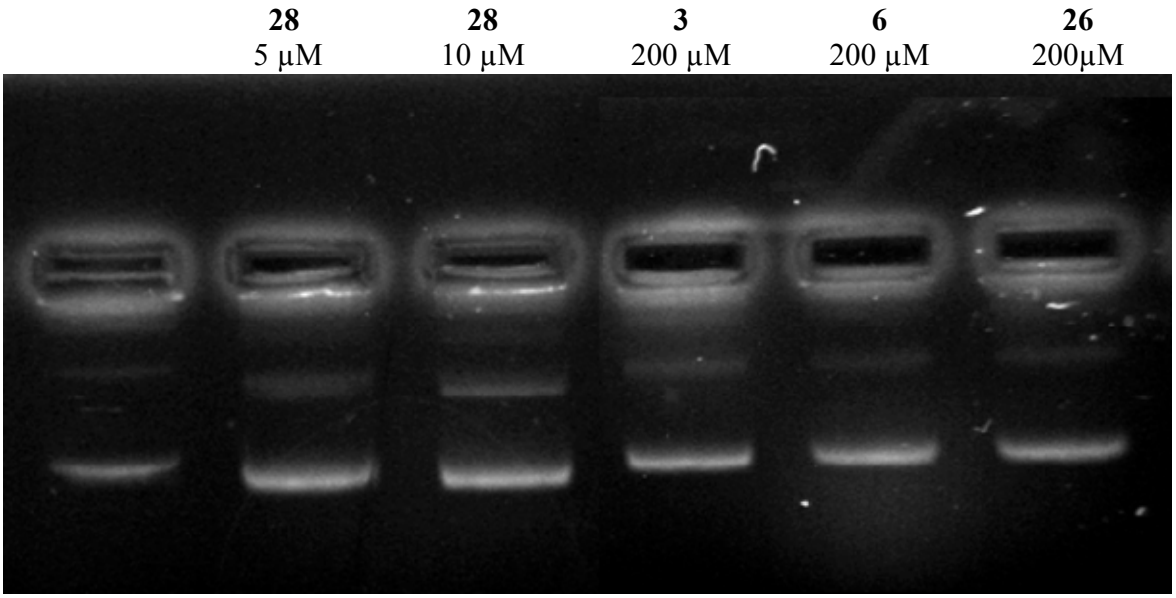


Fig. 50. Influence of selected test compounds on plasmid DNA cross-linking ability by compounds **3**, **6** and **26**, along with psoralen **28** as a positive control. Plasmid (pCI DNA (0.8 µg) lane 1) DNA was mixed with psoralen (5 µM), lane 2; (10 µM), lane 3, compoud **3** (200 µM), lane 4, **6** (200 µM), lane 5 and **26** (200 µM), lane 6. Reaction mixtures were irradiated at 300 nm for 3 minutes and loaded on 1% alkaline agarose gel. Gels were stained with ethidium bromide and the resulting products were visualized and documented with UV light at 254 nm (Image Master VDS, Pharmacia Biotech, Sweden).

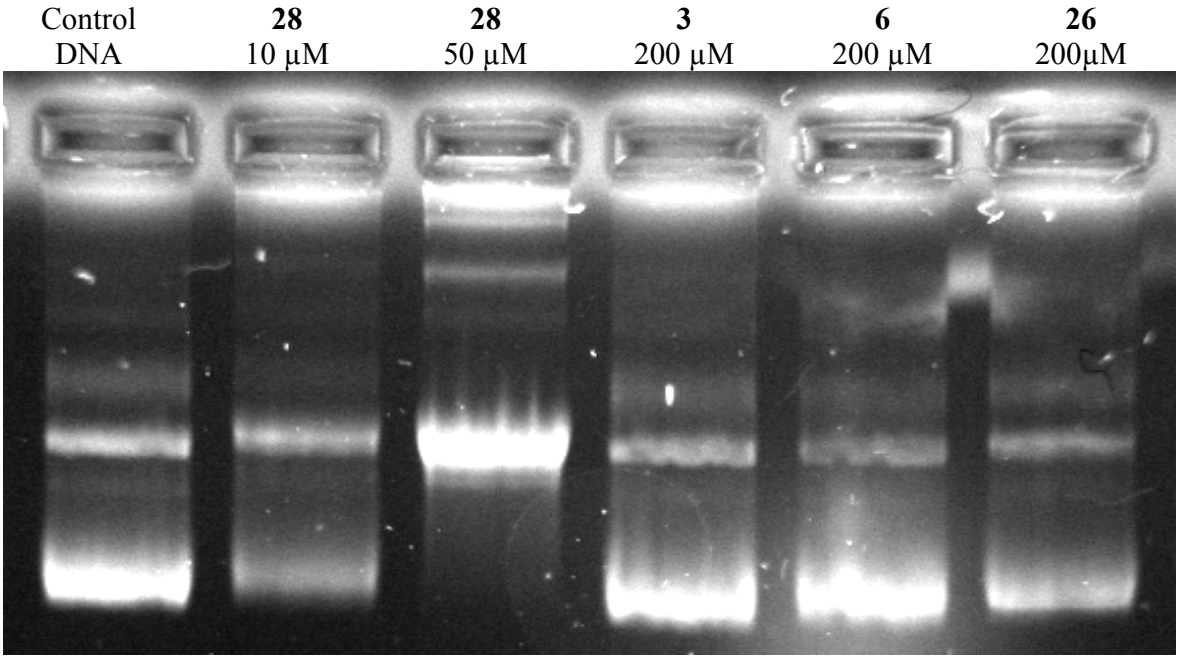


Fig. 51. Influence of selected test compounds on plasmid DNA cross-linking ability by compounds **3**, **6** and **26**, along with psoralen **28** as a positive control. Plasmid (pCI DNA (0.8 μg) lane 1) DNA was mixed with psoralen (10 μM), lane 2; (50 μM), lane 3, compoud **3** (200 μM), lane 4, **6** (200 μM), lane 5 and **26** (200 μM), lane 6. Reaction mixtures were irradiated at 300 nm for 3 minutes and loaded on 1% alkaline agarose gel. Gels were stained with ethidium bromide and the resulting products were visualized and documented with UV light at 254 nm (Image Master VDS, Pharmacia Biotech, Sweden).

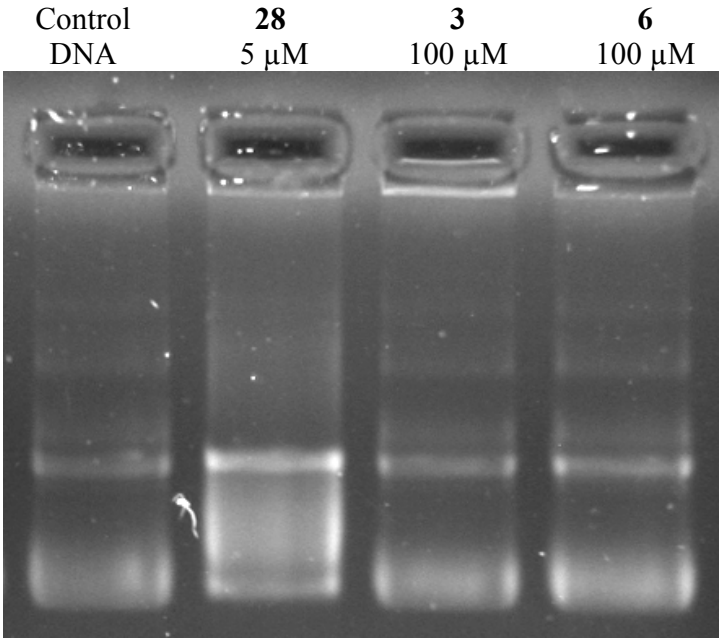
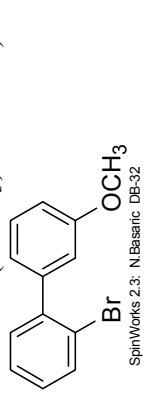
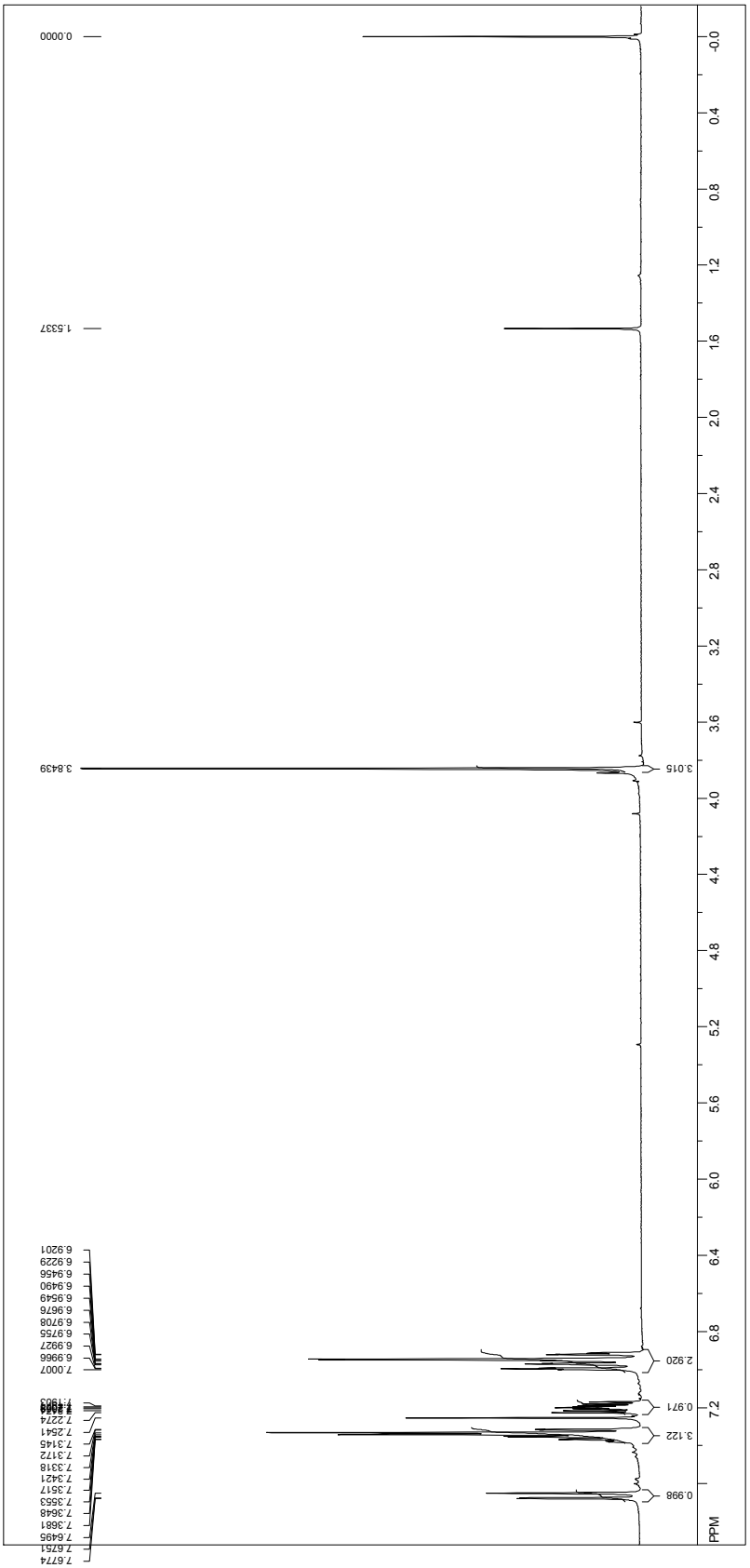


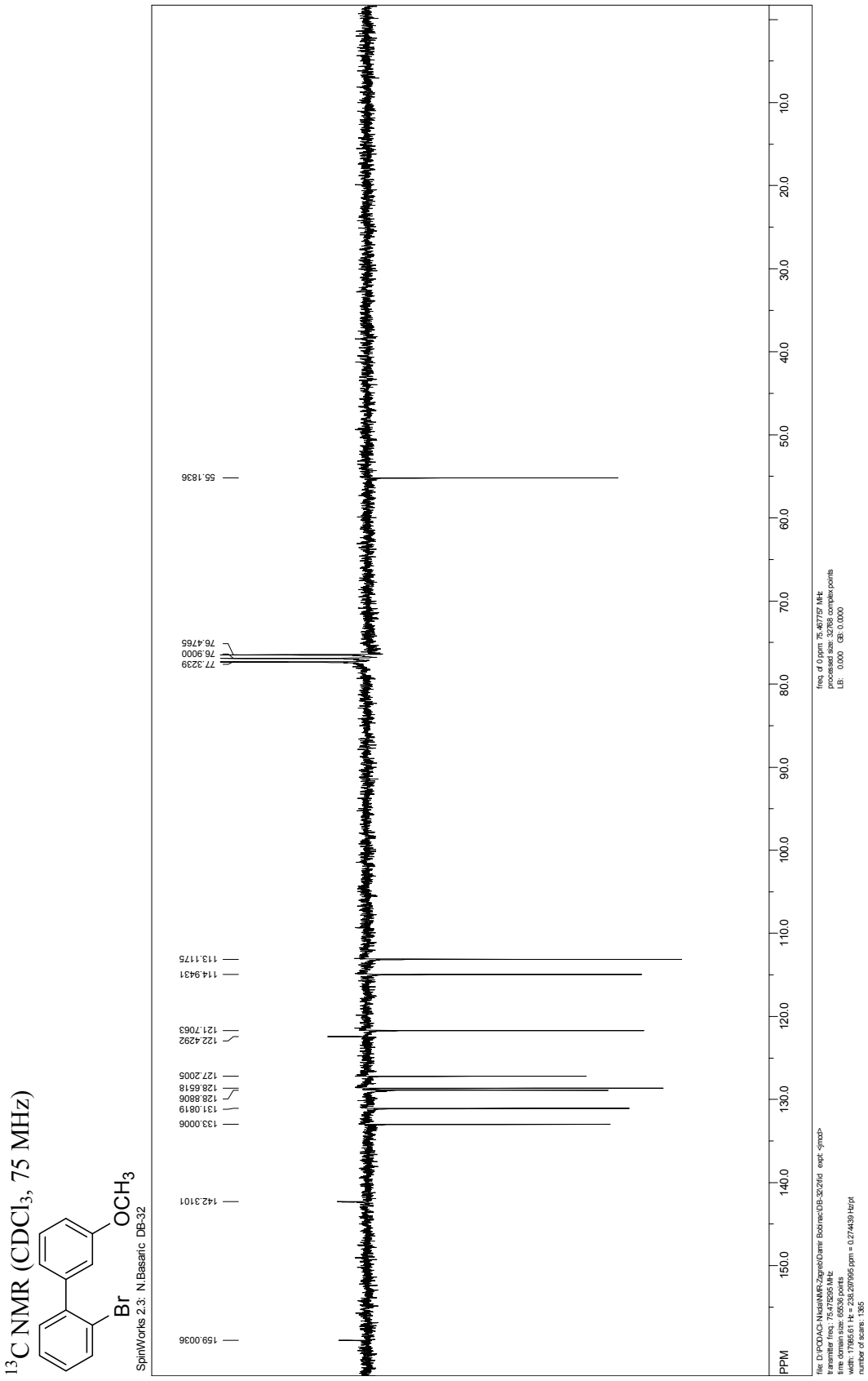
Fig. 52. Influence of selected test compounds on plasmid DNA unwinding/cleavage ability by compounds **3** and **6**, along with psoralen **28** as a positive control. Plasmid (pCI DNA (0.8 μg), lane 1) DNA was mixed with psoralen (5 μM), lane 2, compoud **3** (100 μM), lane 3, **6** (100 μM), lane 4. Reaction mixtures were irradiated at 300 nm for 3 minutes and loaded on 1% agarose gel. Gels were stained with ethidium bromide and the resulting products were visualized and documented with UV light at 254 nm (Image Master VDS, Pharmacia Biotech, Sweden).

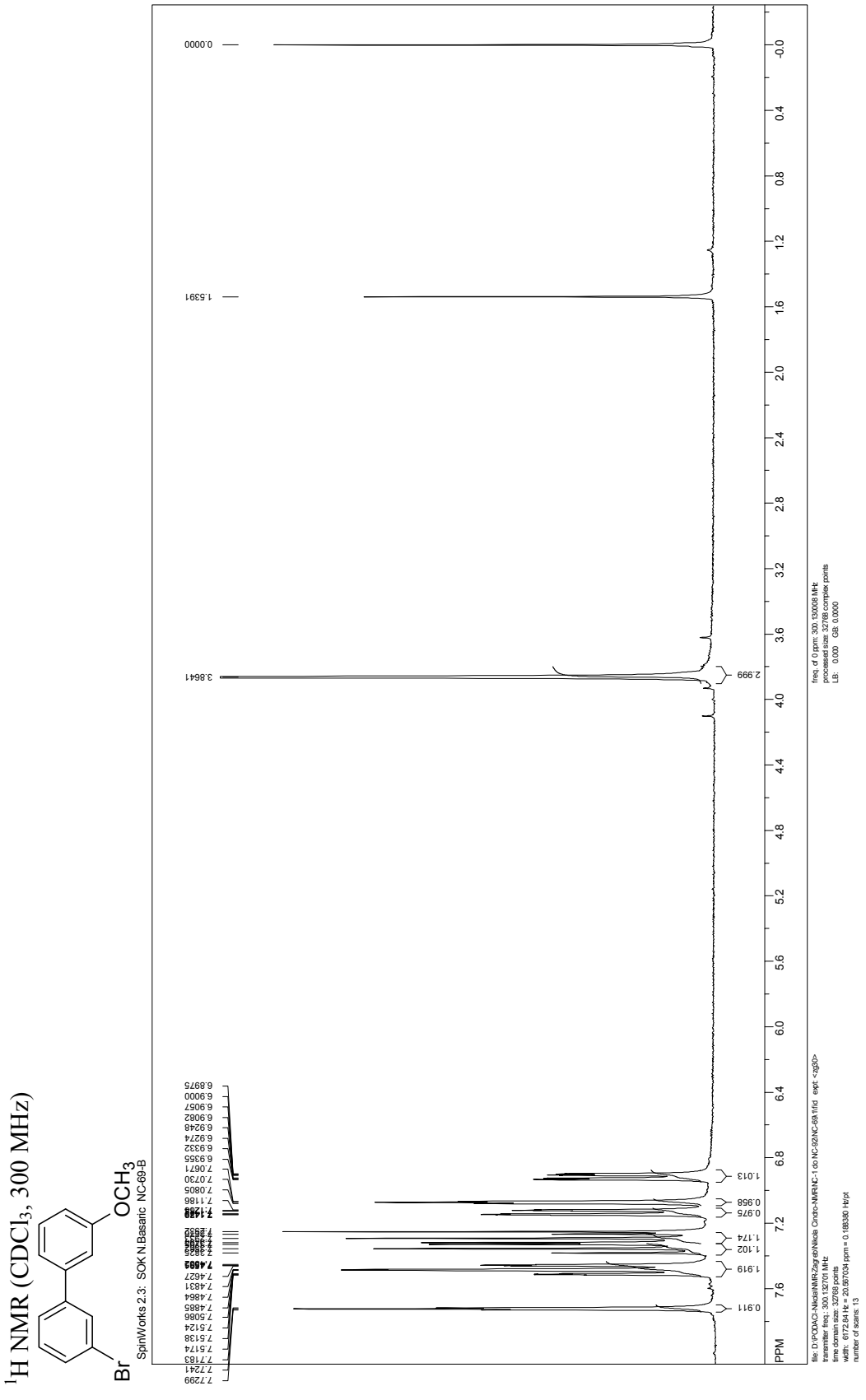
^{1}H NMR ($CDCl_3$, 300 MHz)



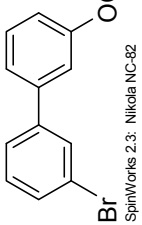
SpinWorks 2.3: N.Basaric DB-32



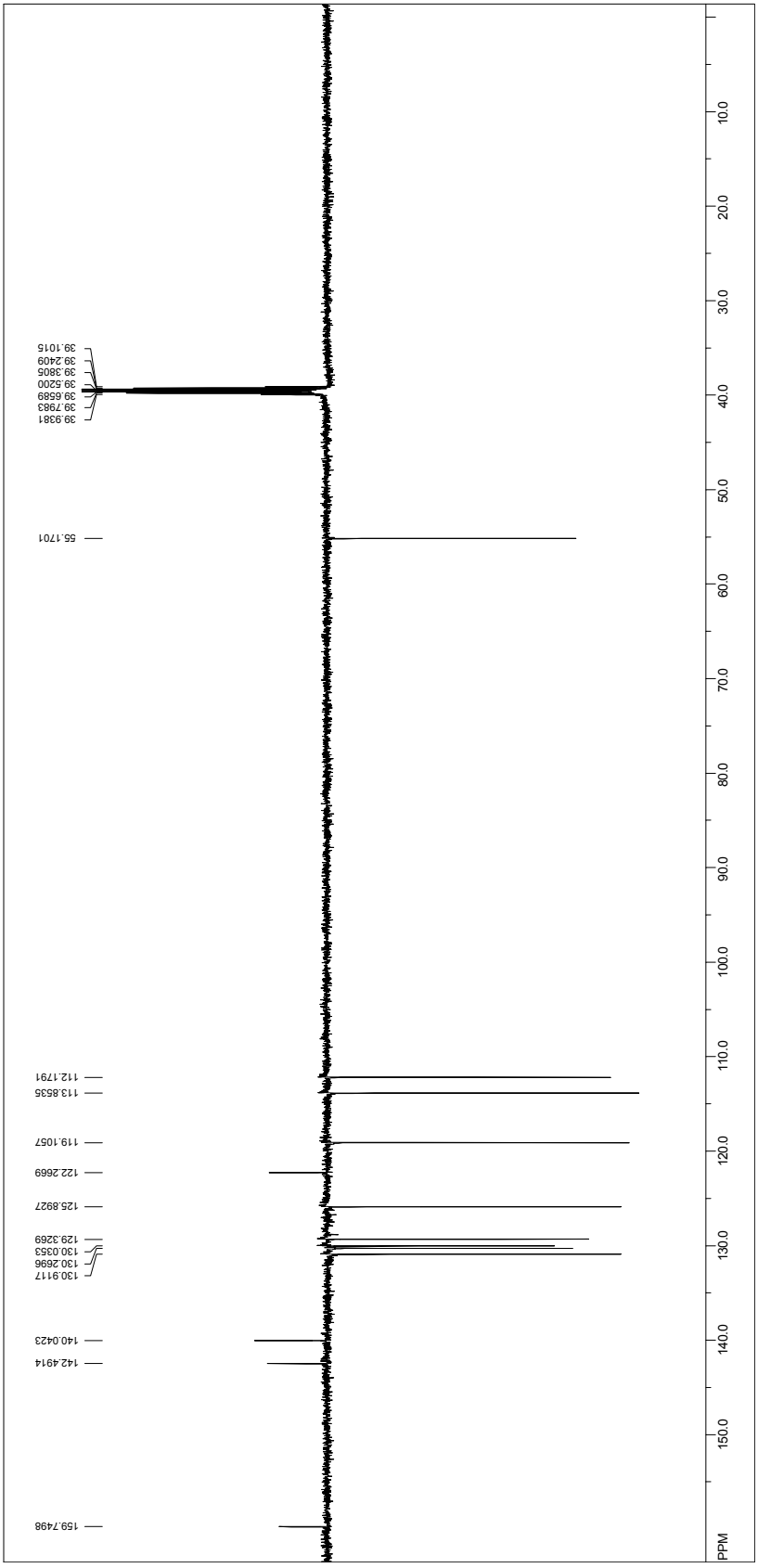

^{13}C NMR ($CDCl_3$, 75 MHz)
Br
OCH_3
SpinWorks 2.3: N.Basaric DB-32
159.0036
142.3101
133.0006
131.0819
128.8806
128.6518
127.2005
122.4292
121.7063
114.9431
113.1175
77.3239
76.9000
76.4765
55.1836
PPM
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
file: D:\HCDAC\-Nadal\NMR-Zagreb\Damir Babinec\DB-32-2.fid expt: <proton>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.297995 ppm = 0.274439 Hz/pt
number of scans: 1365
freq. of 0 ppm: 75.467757 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000


^{1}H NMR ($CDCl_3$, 300 MHz)
OCH3
Br
SpinWorks 2.3: SOK N.Basaric NC-69-B
0.0000
1.5391
3.8641
2.999
1.013
0.975
0.958
1.174
1.102
1.919
0.911
PPM

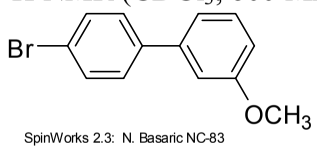
^{13}C NMR (DMSO-d_6, 150 MHz)

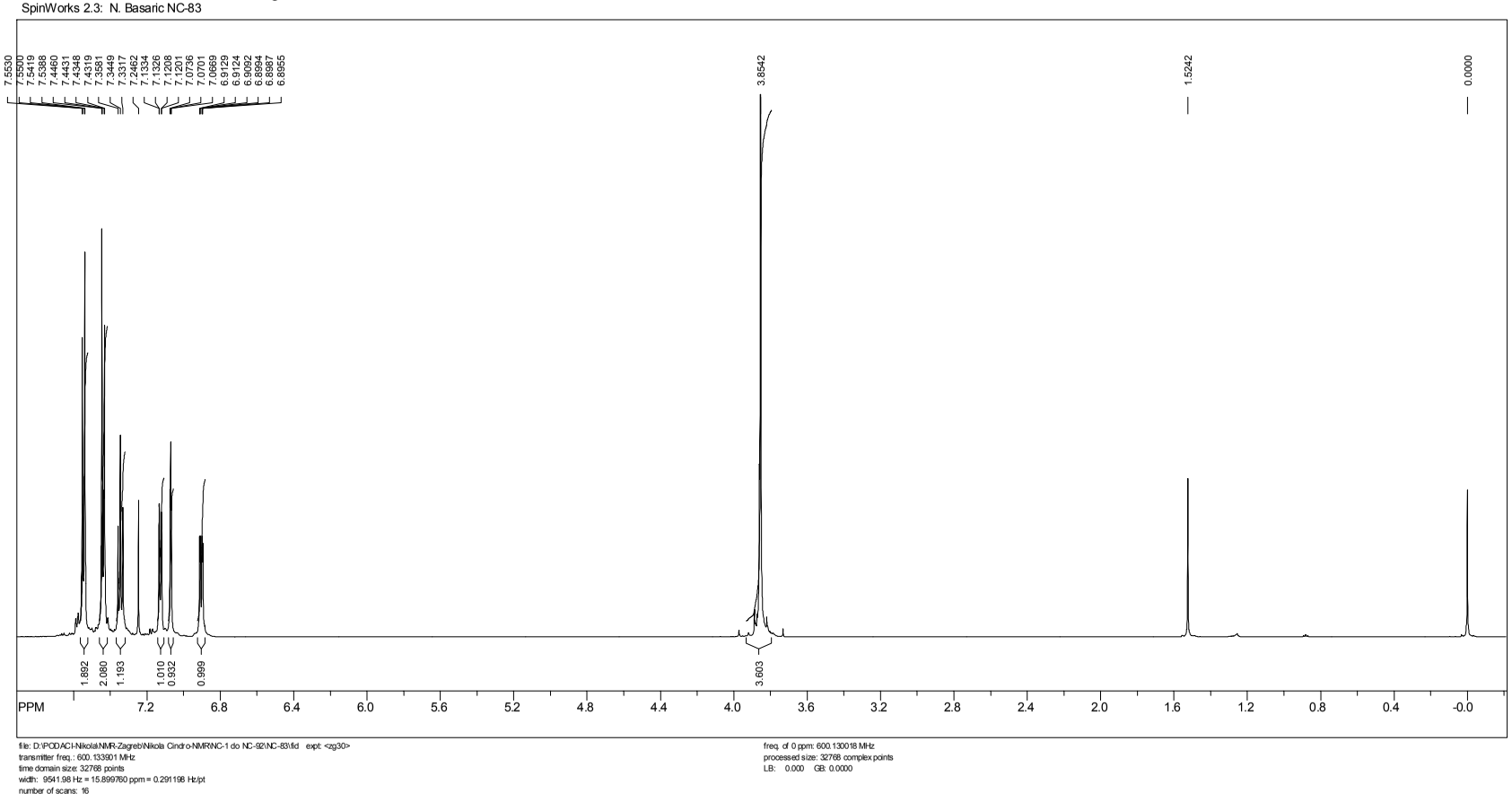


SpinWorks 2.3: Nikola NC-82

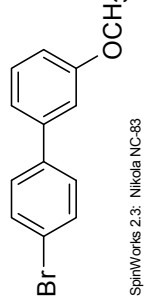


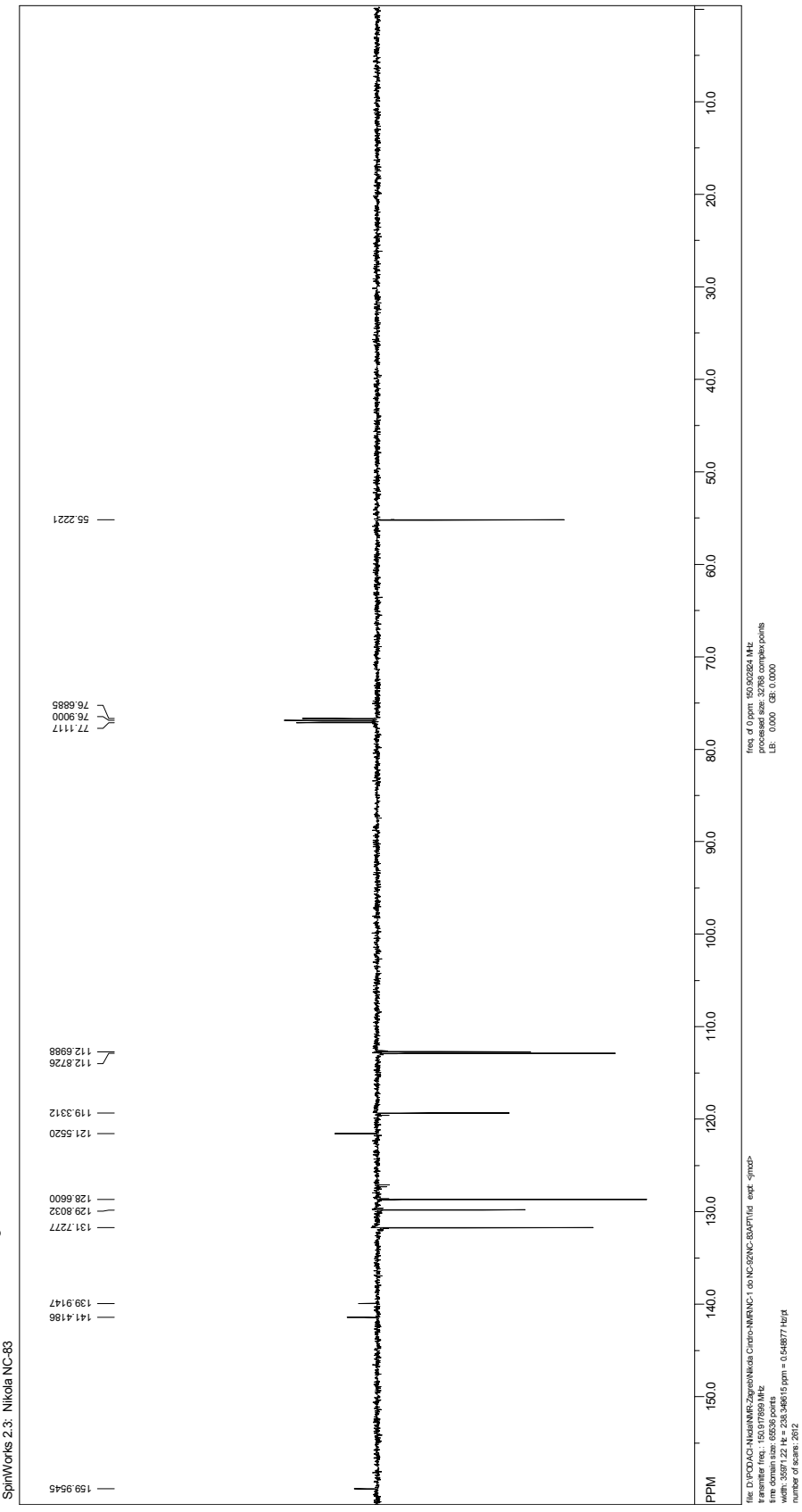
^{1}H NMR ($CDCl_3$, 600 MHz)



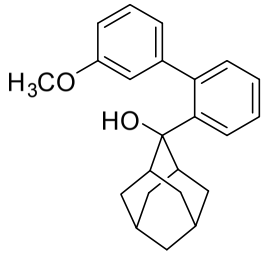


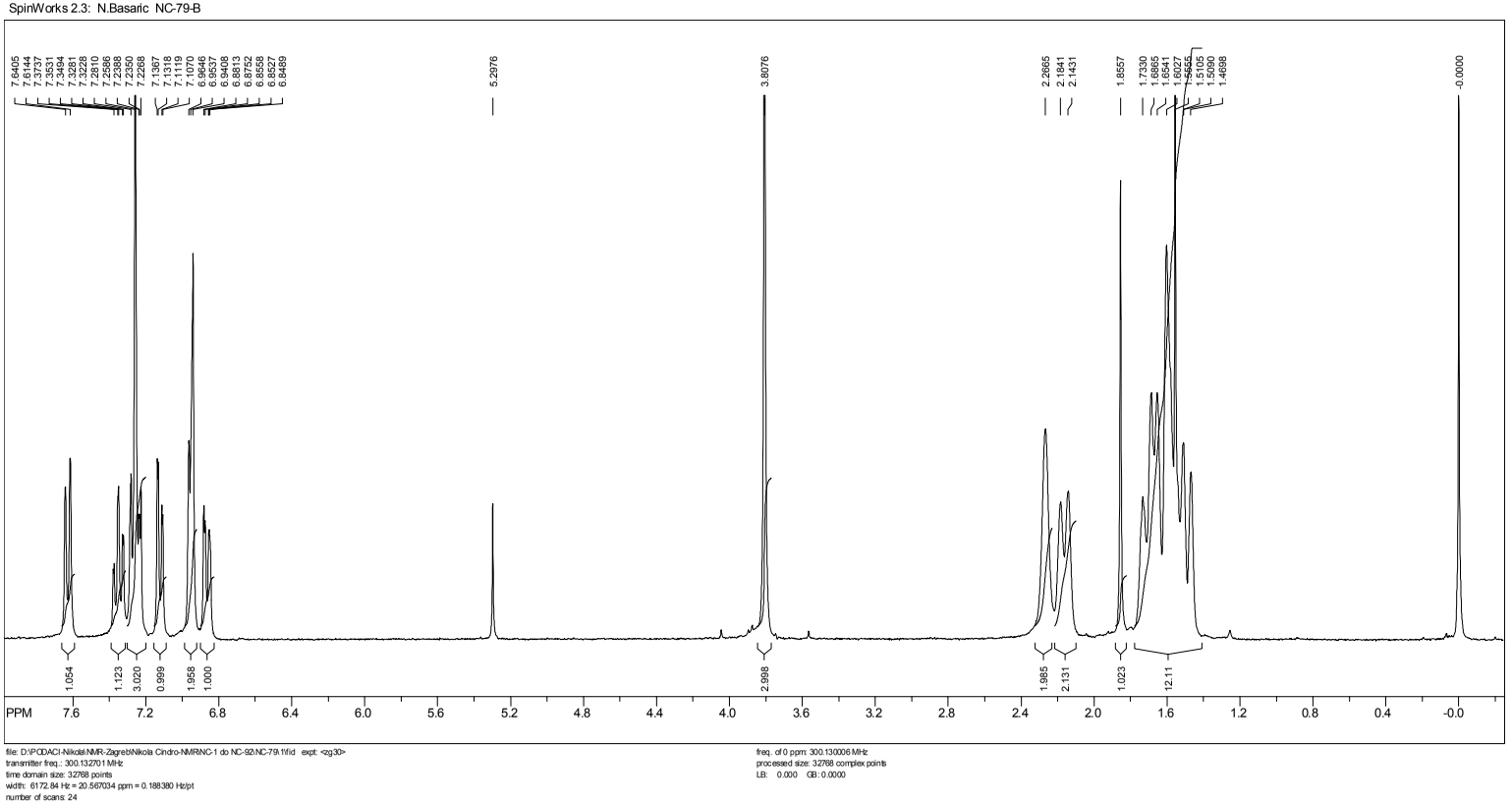
^{13}C NMR ($CDCl_3$, 150 MHz)



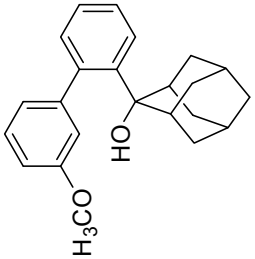


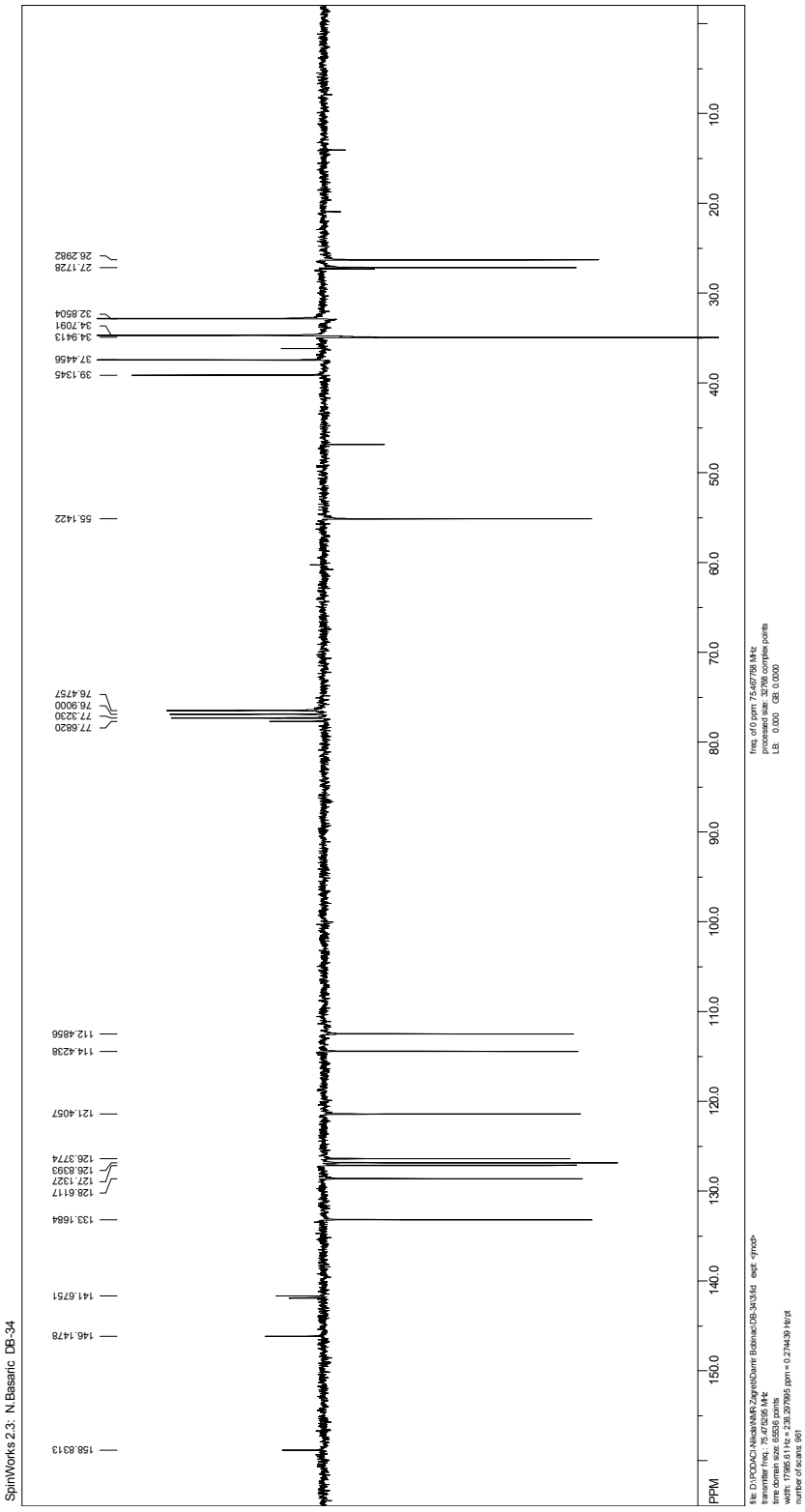
^{1}H NMR ($CDCl_3$, 300 MHz) of **4a**



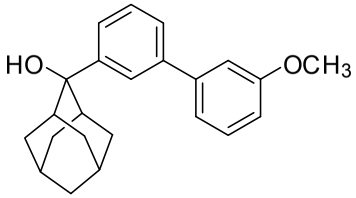


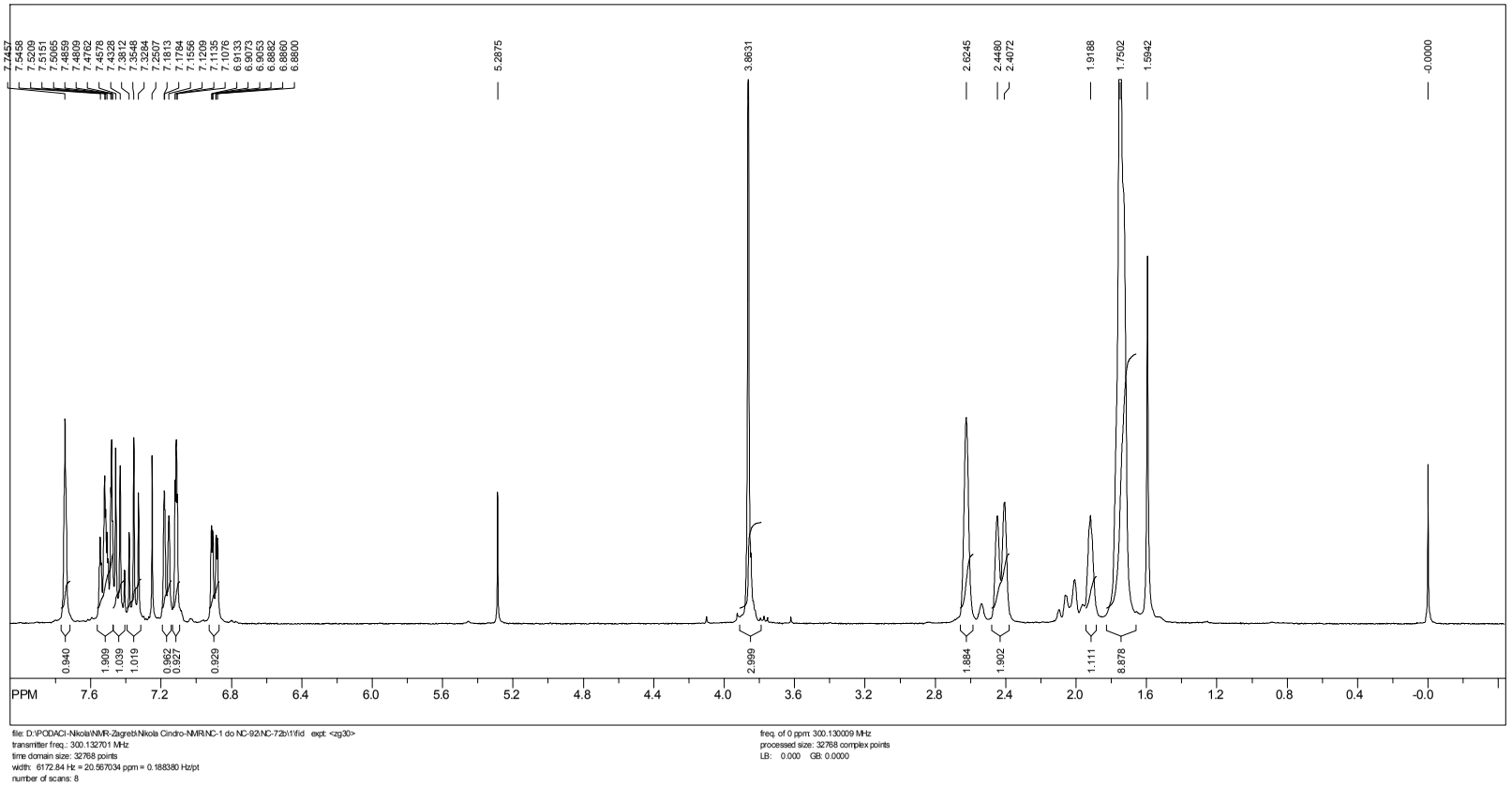
^{13}C NMR ($CDCl_3$, 75 MHz) of **4a**



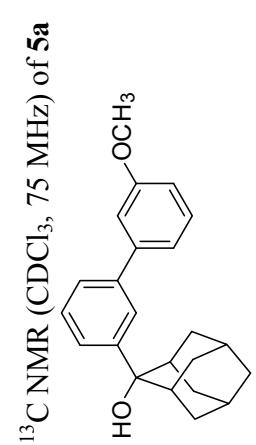


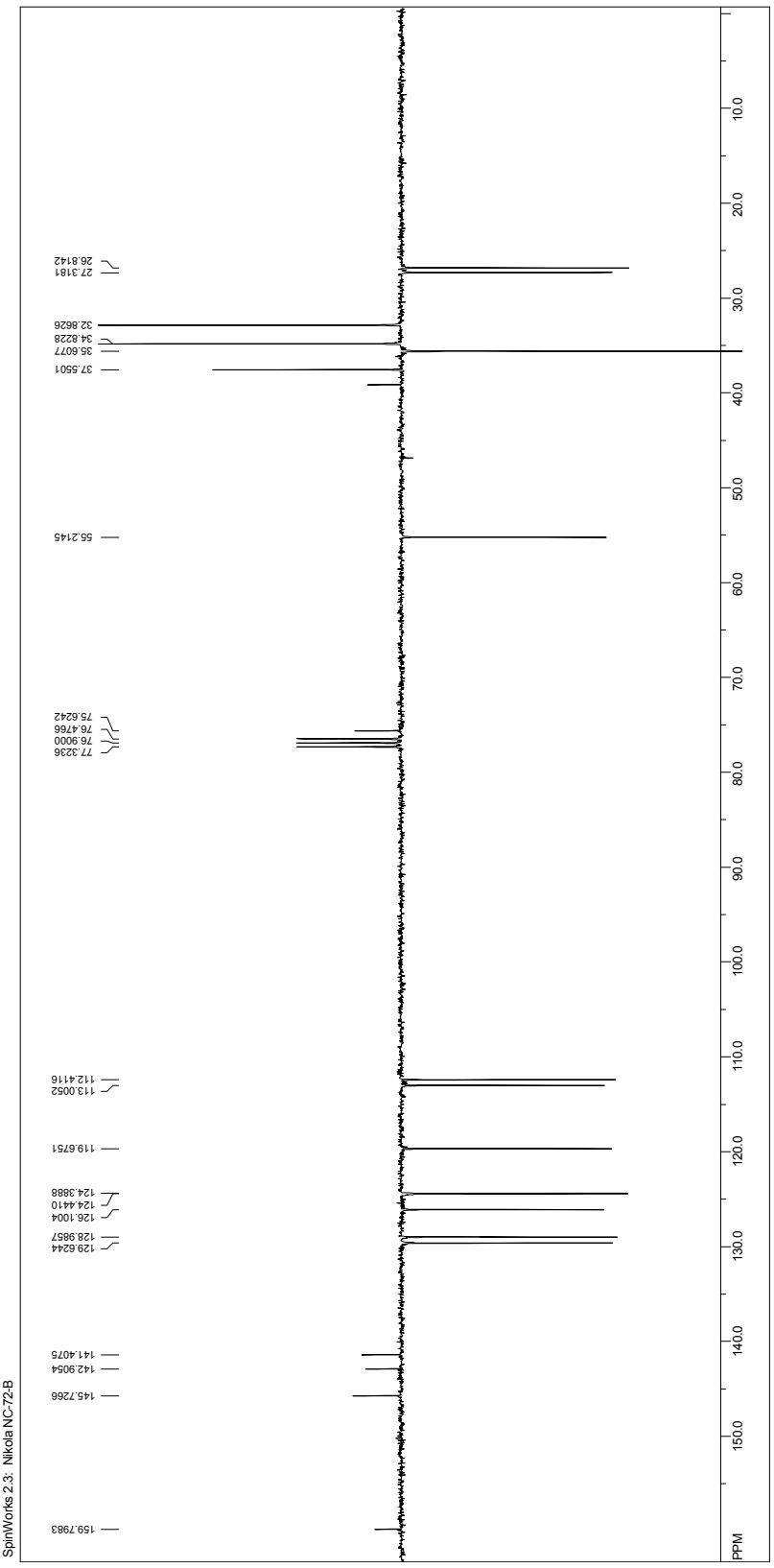
^{1}H NMR ($CDCl_3$, 300 MHz) of **5a**



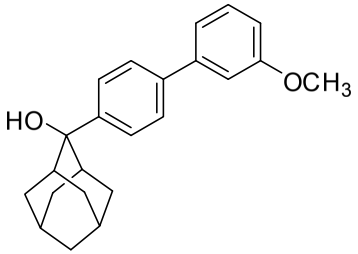


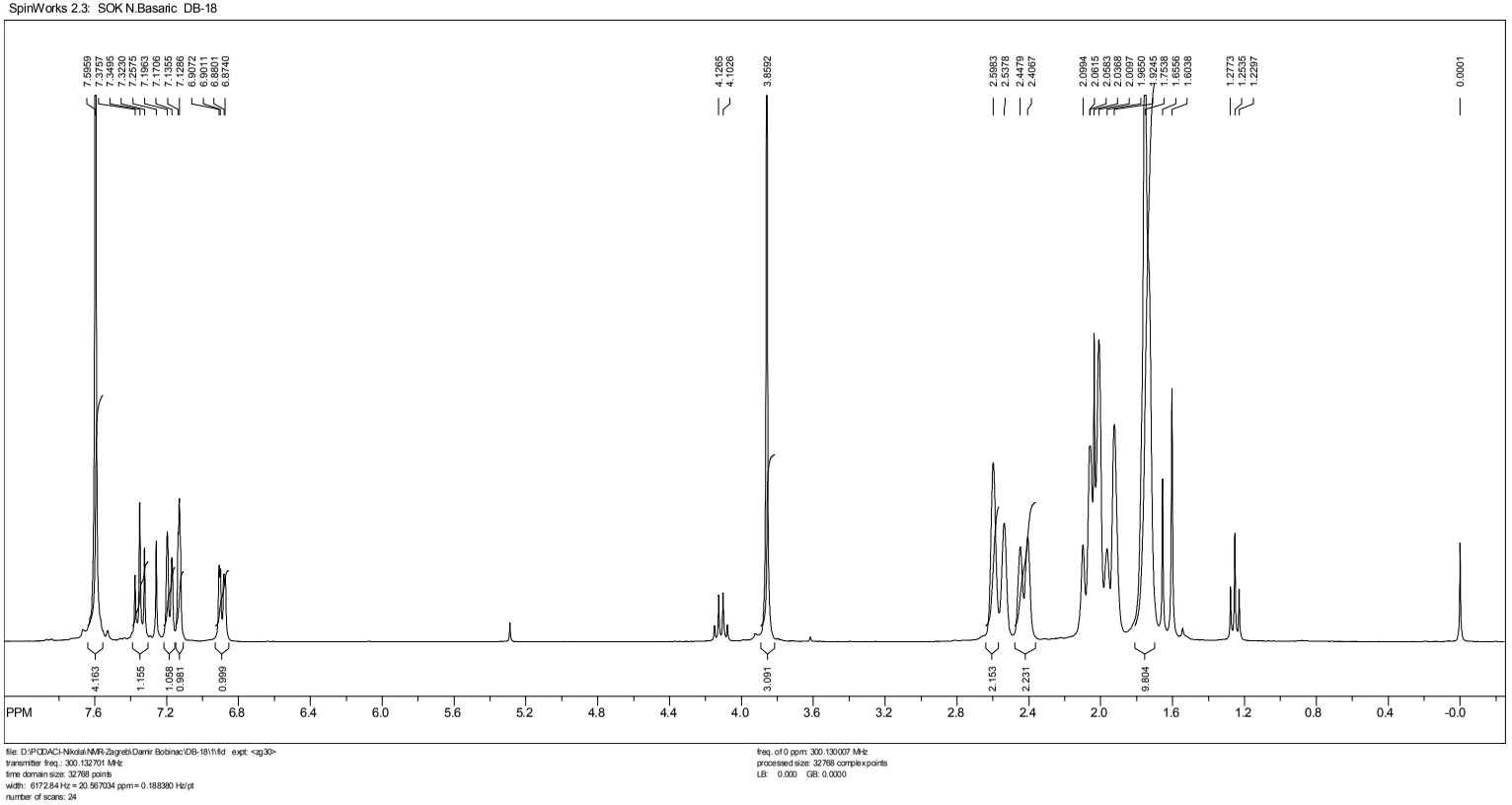
^{13}C NMR ($CDCl_3$, 75 MHz) of **5a**



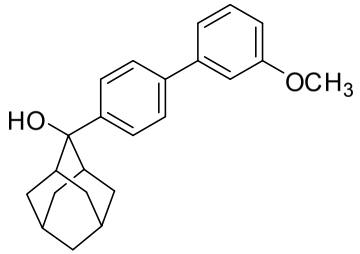


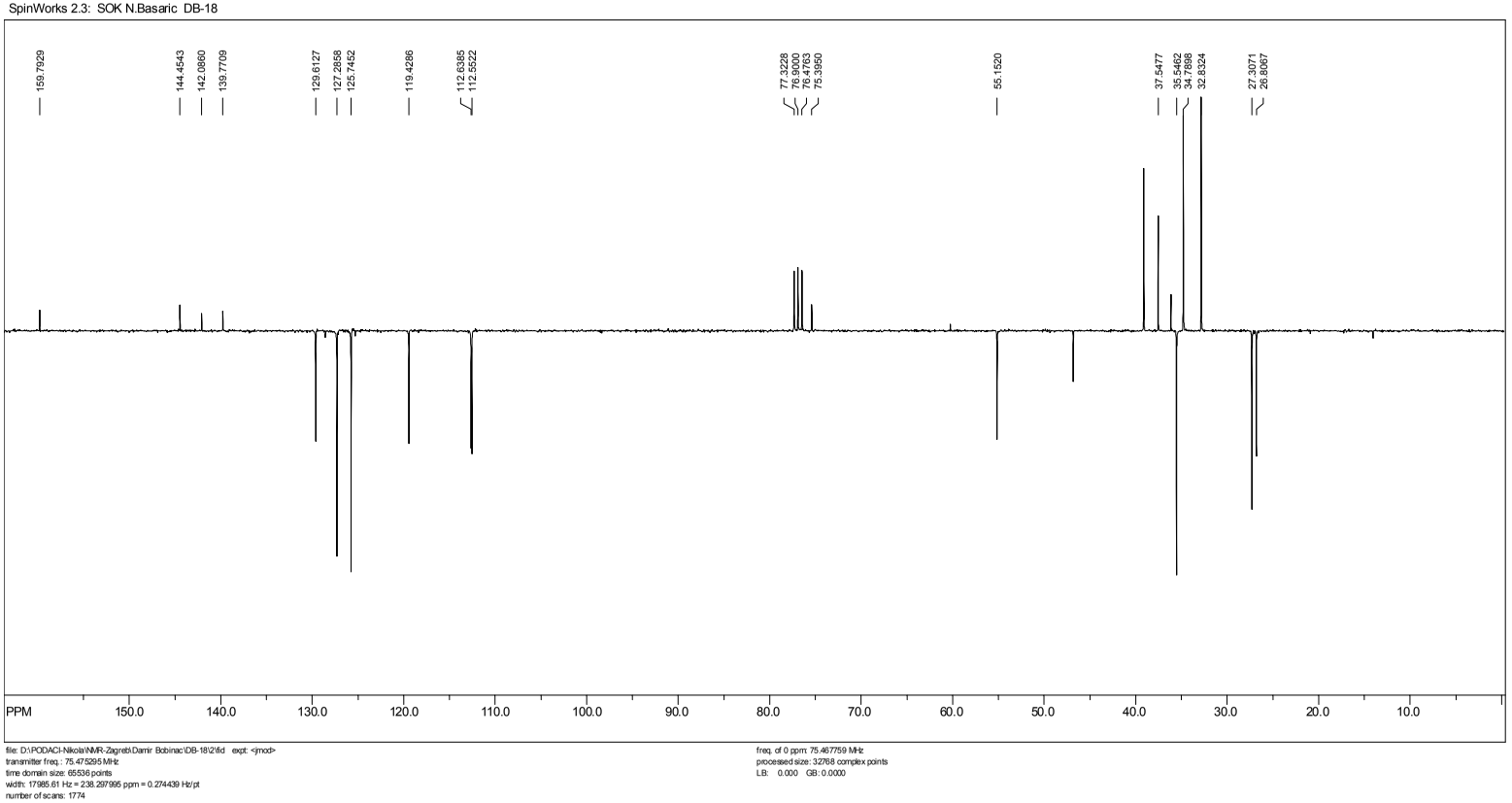
^{1}H NMR ($CDCl_3$, 300 MHz) of **6a**



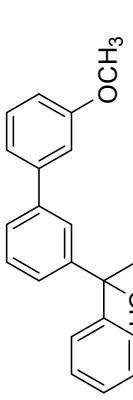


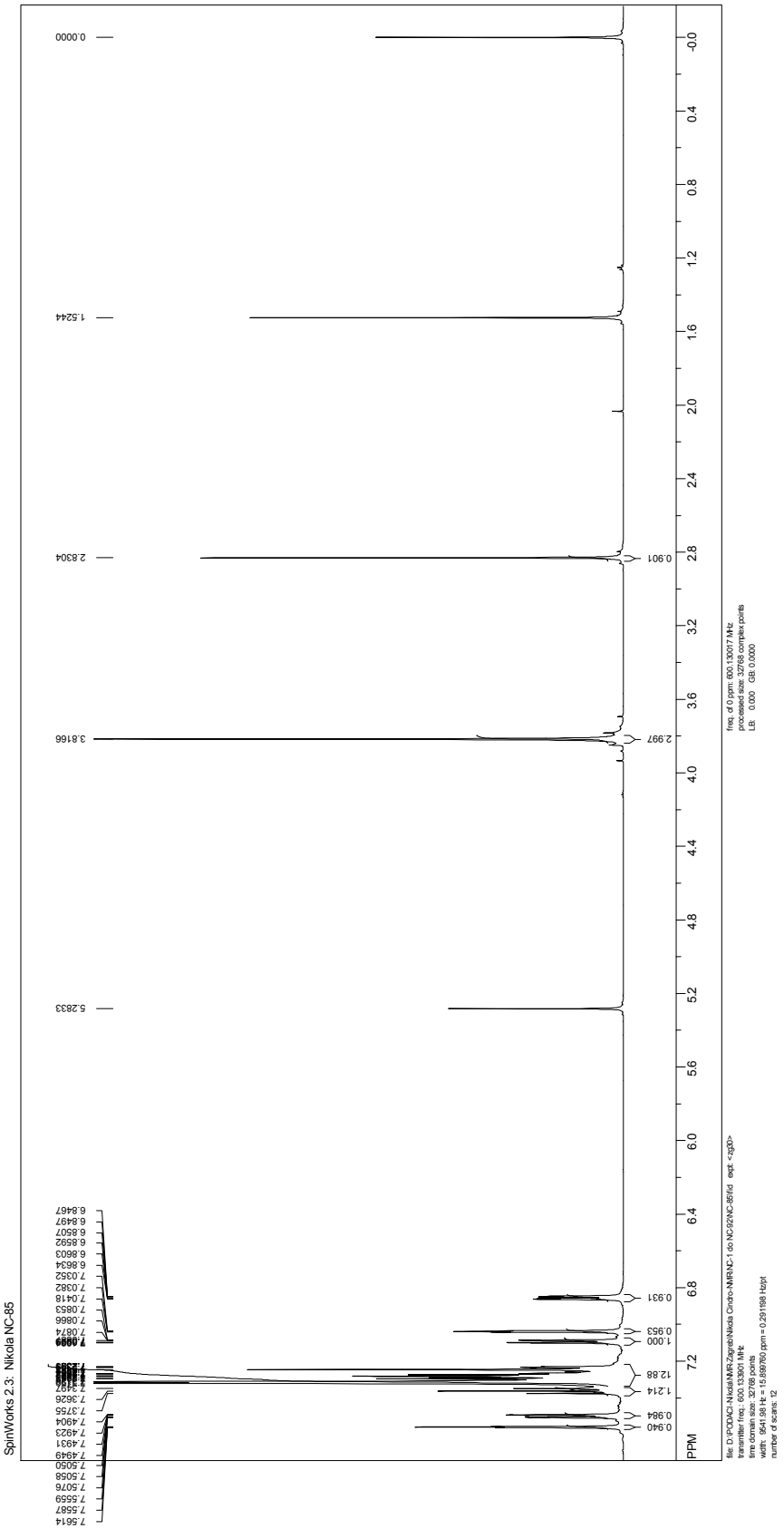
^{13}C NMR ($CDCl_3$, 75 MHz) of **6a**



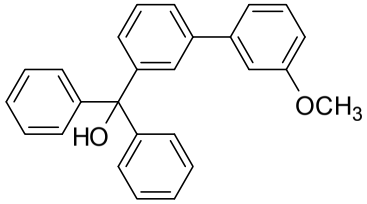


^{1}H NMR ($CDCl_3$, 600 MHz) of **7a**

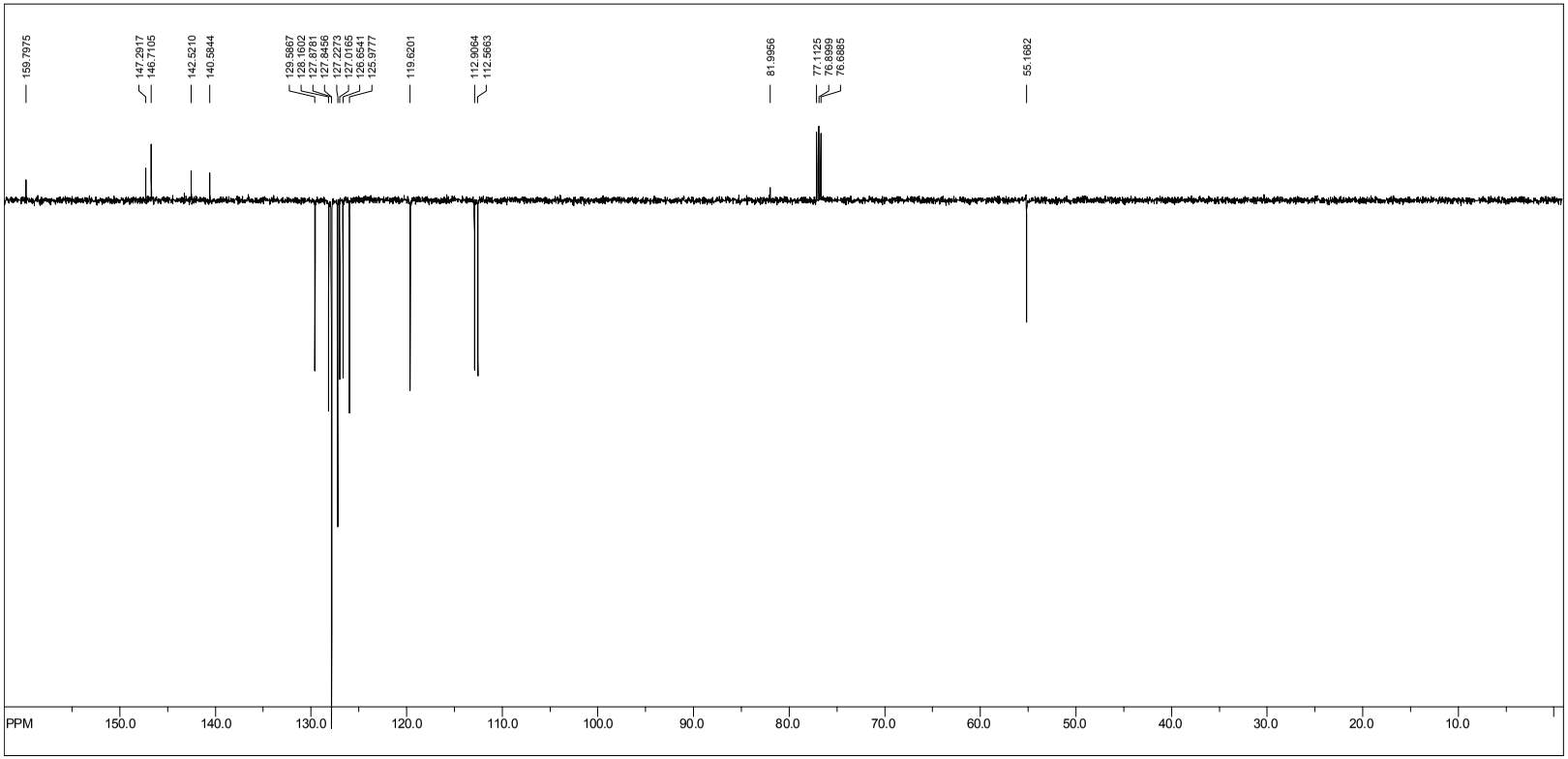




^{13}C NMR ($CDCl_3$, 150 MHz) of **7a**



SpinWorks 2.3: Nikola NC-85



file: D:\PODACI-Nikola\NMR-Zagreb\Nikola Cindro-NMR\NC-1 do NC-92\NC-85APT.fid expt: <jmod>
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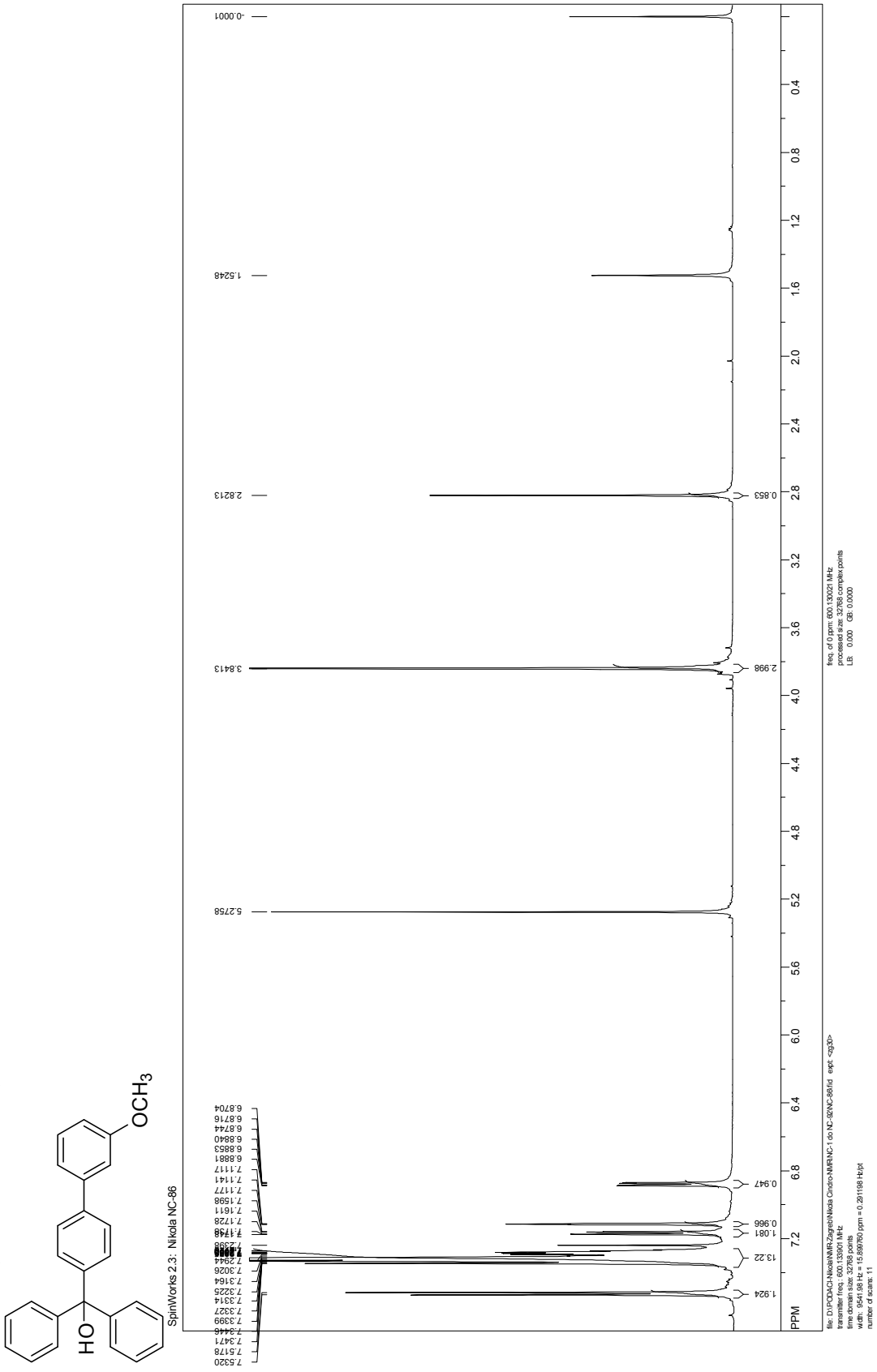
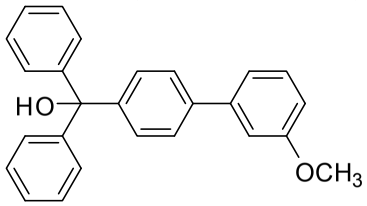
time domain size: 65536 points
width: 35971.22 Hz = 238.349615 ppm = 0.548877 Hz/pt
number of scans: 1425

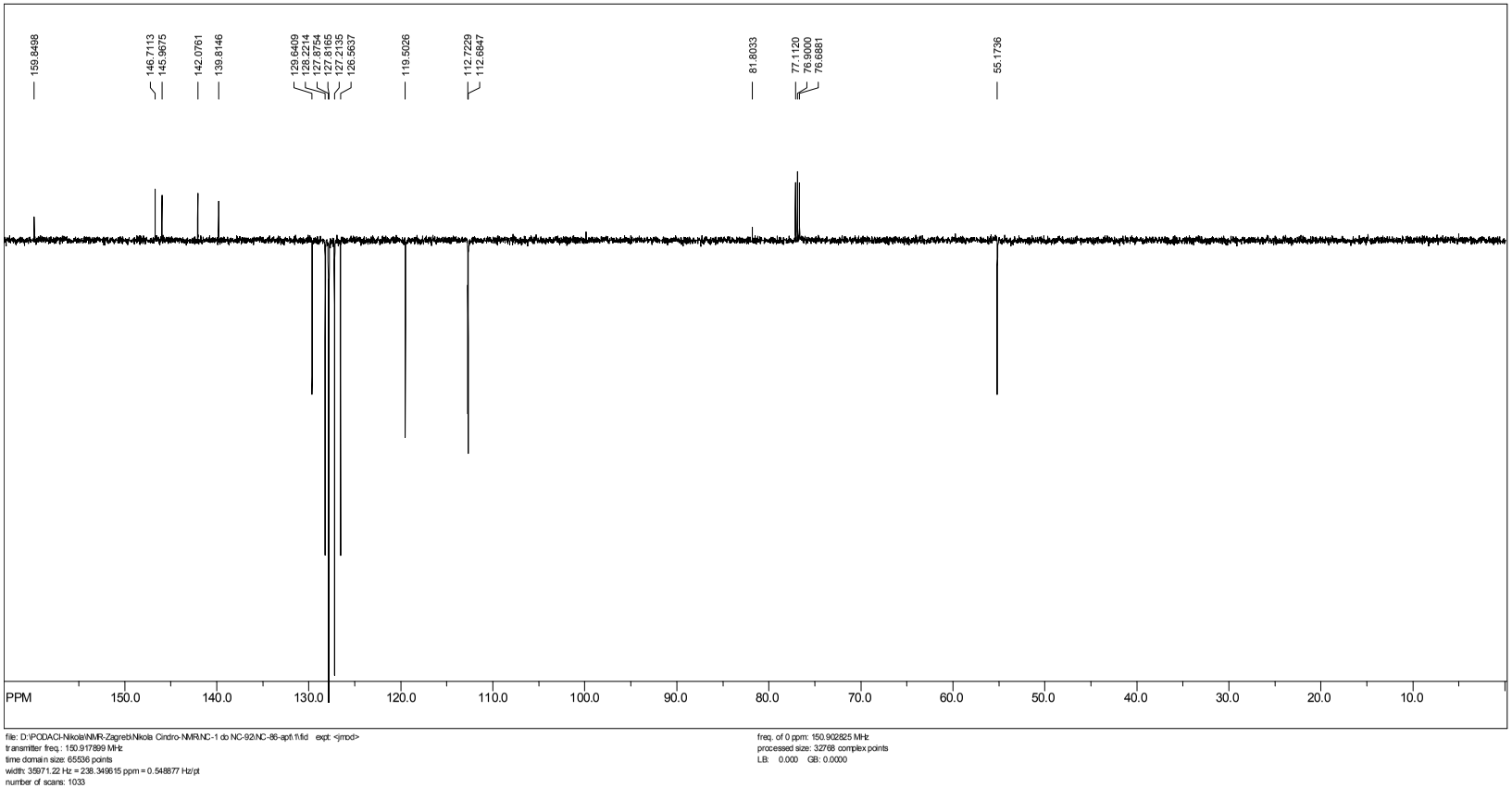
freq. of 0 ppm: 150.902824 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

^{1}H NMR ($CDCl_3$, 600 MHz) of **8a**



^{13}C NMR ($CDCl_3$, 150 MHz) of **8a**





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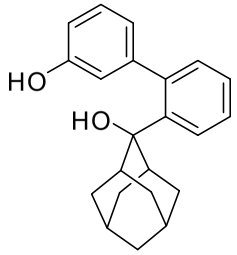
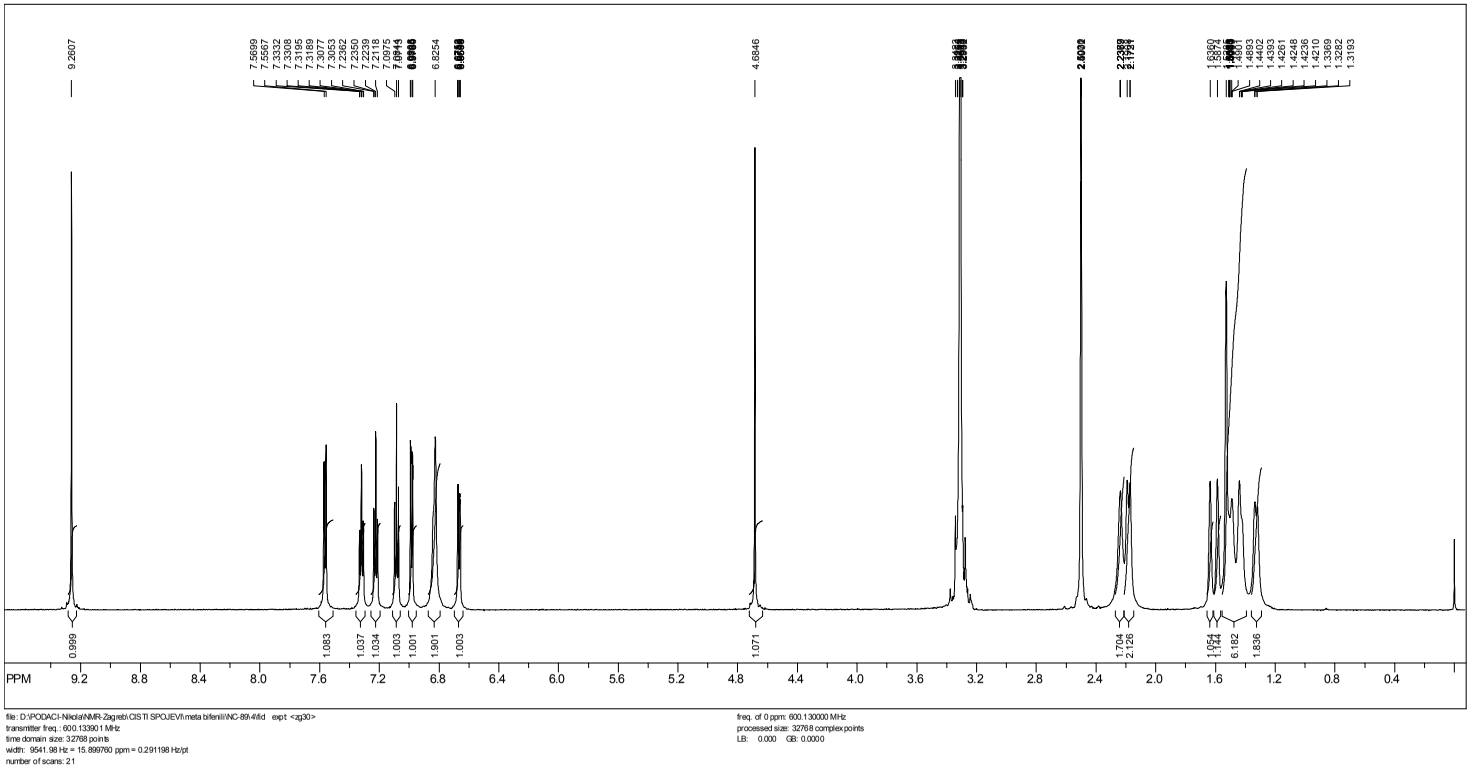
number of scans: 1033

freq. of 0 ppm: 150.902825 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

^{1}H NMR (DMSO-d_6, 600 MHz) of **4**





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time domain size: 32768 points
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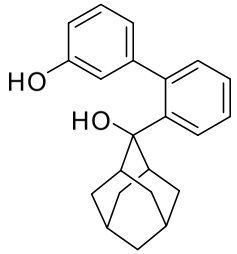
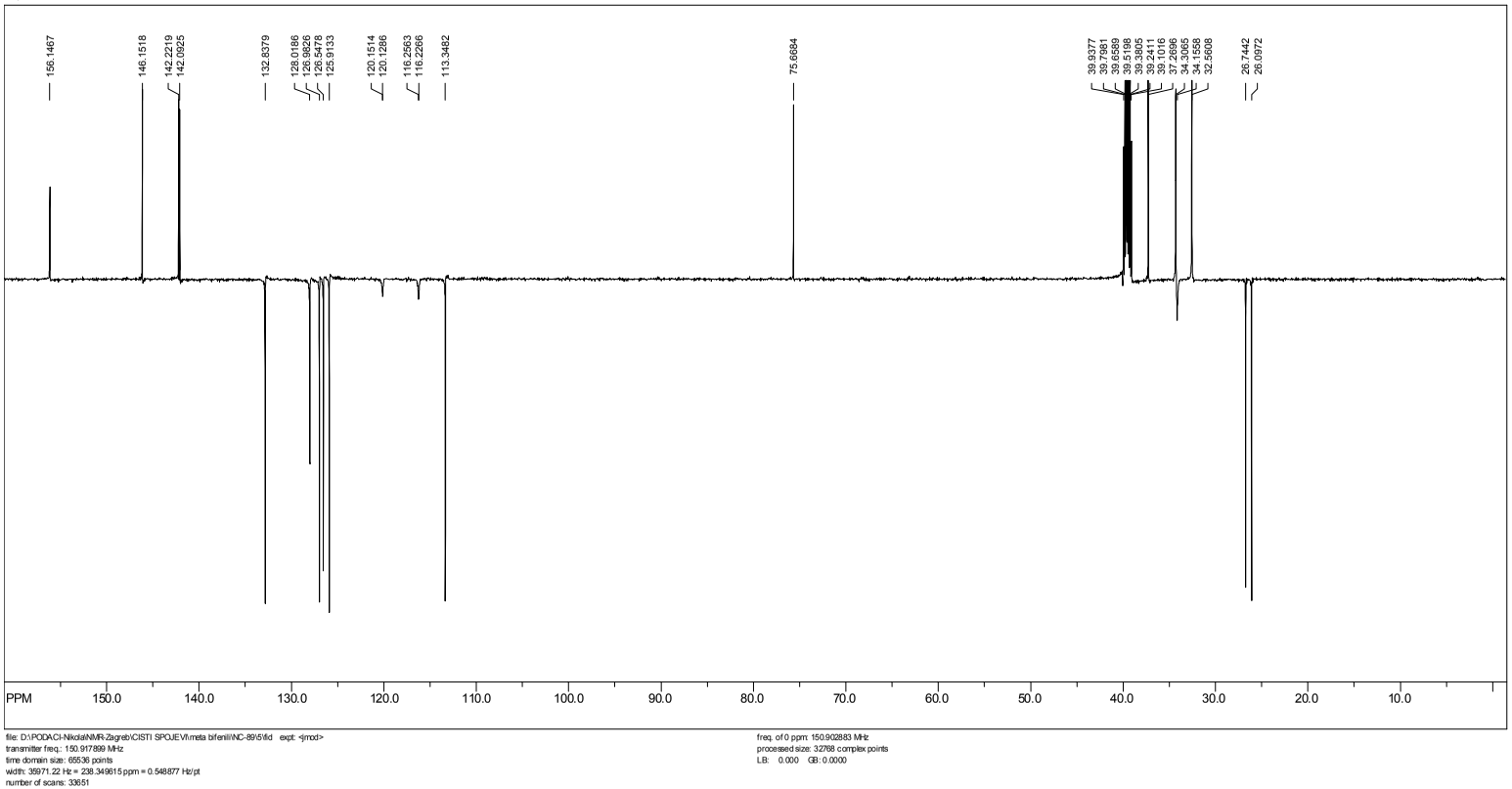
number of scans: 21

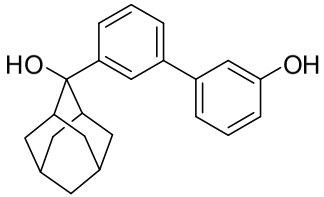
freq. of 0 ppm: 600.130000 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

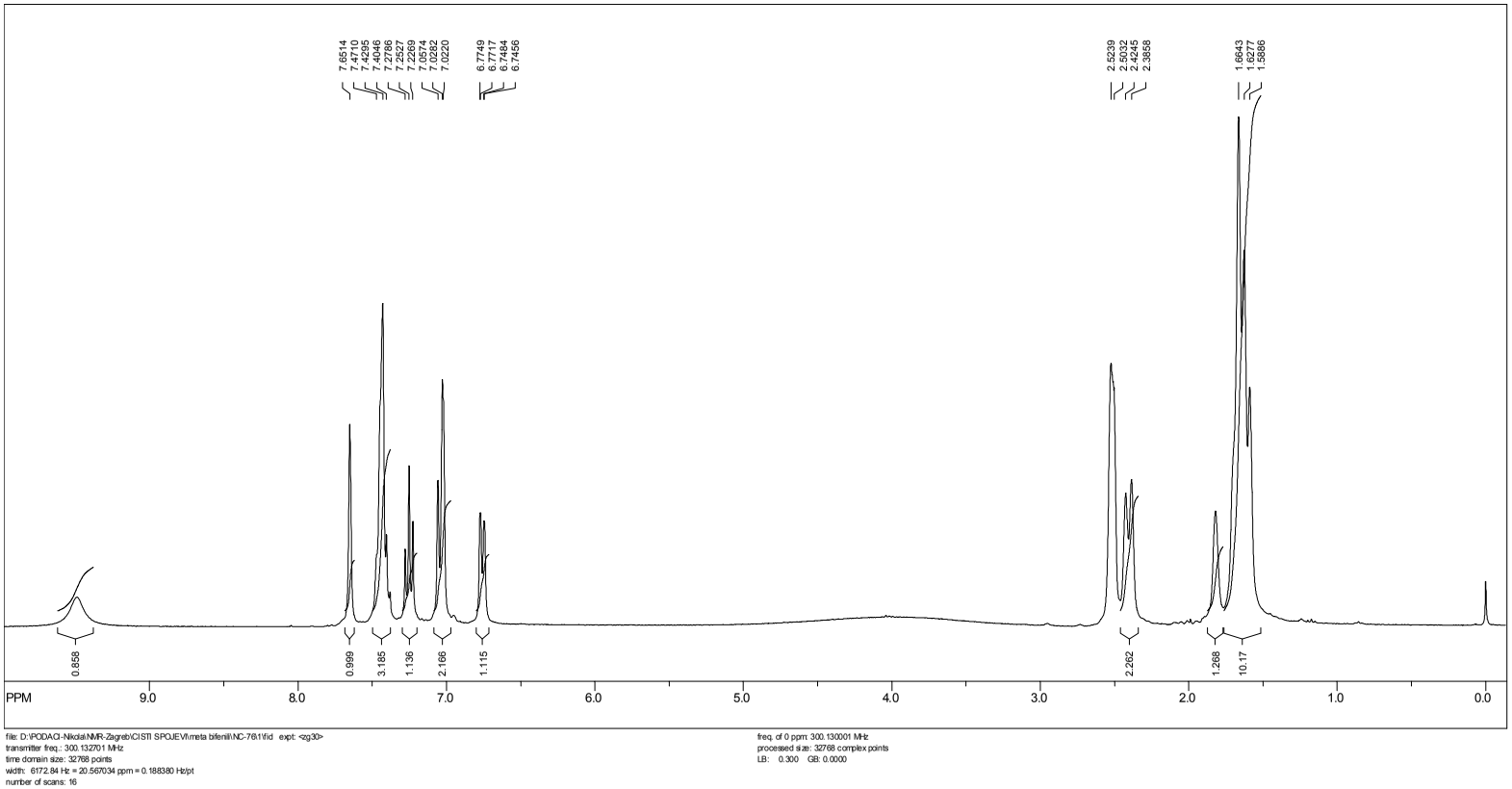
^{13}C NMR (DMSO-d_6, 150 MHz) of **4**



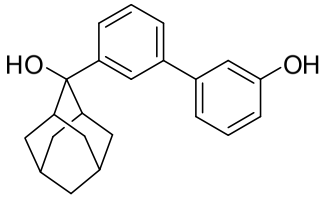


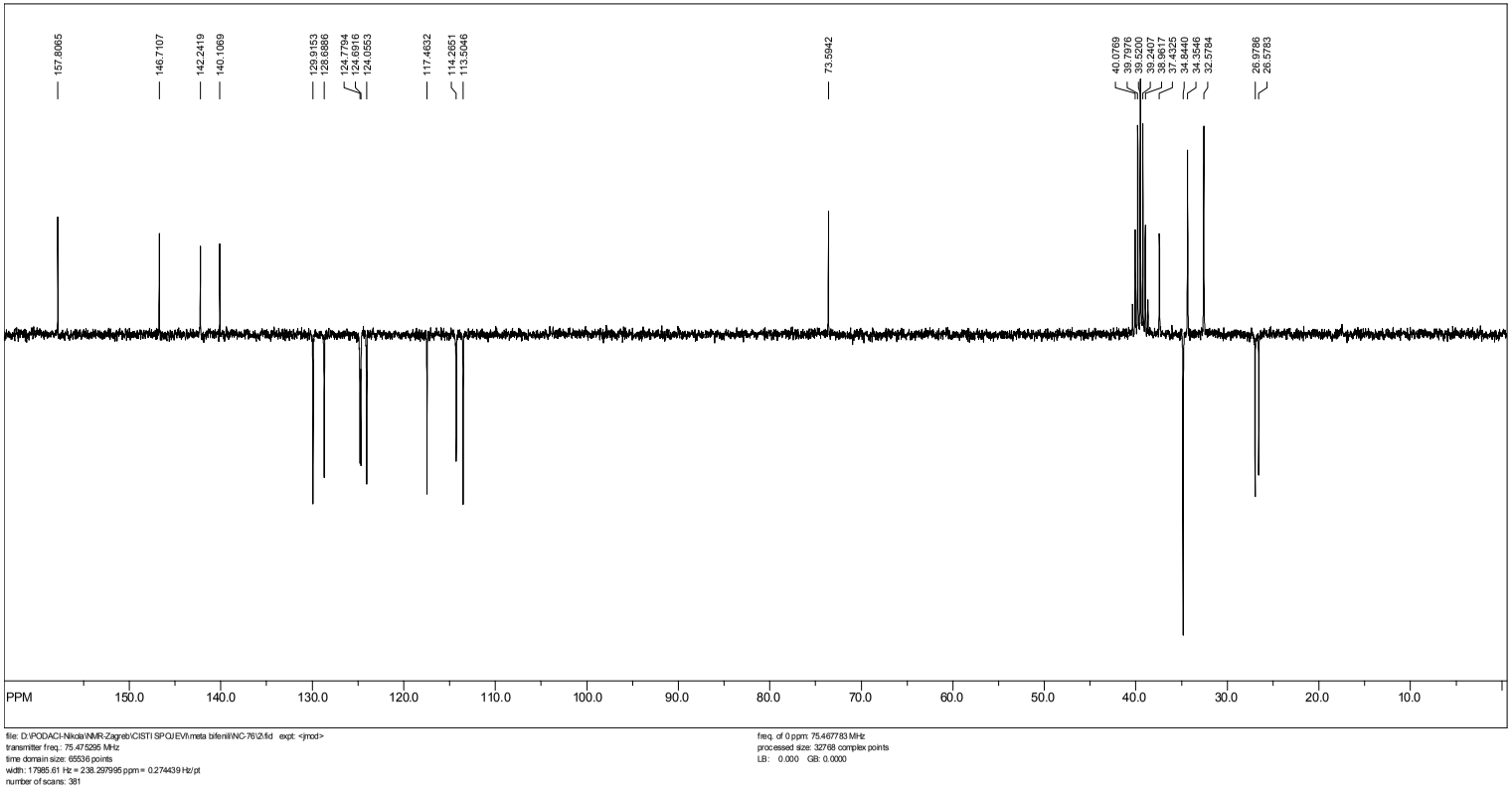
^{1}H NMR (DMSO-d_6, 300 MHz) of **5**



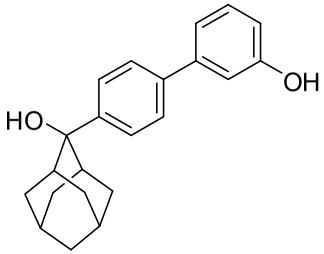


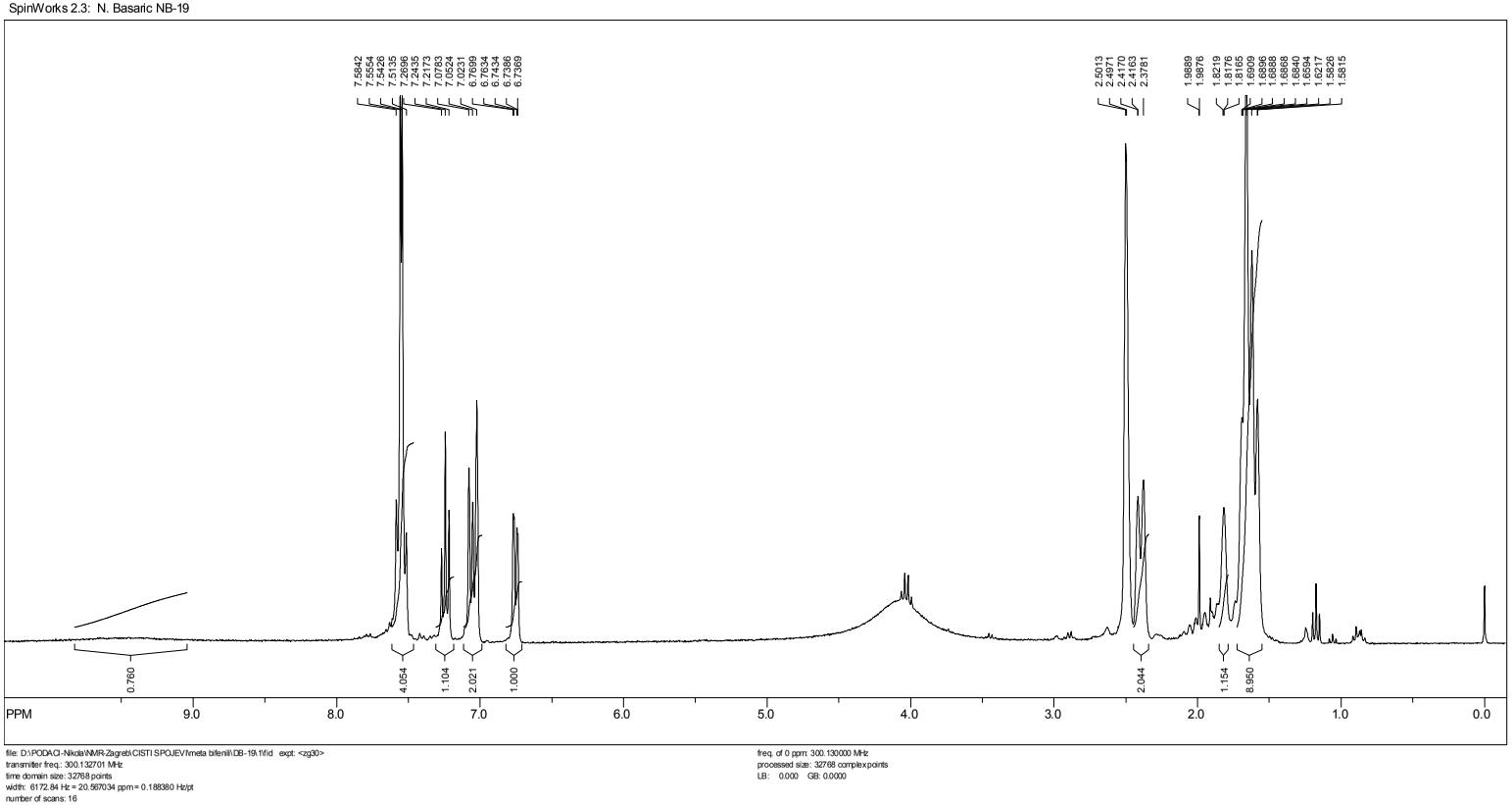
^{13}C NMR (DMSO-d_6, 75 MHz) of **5**



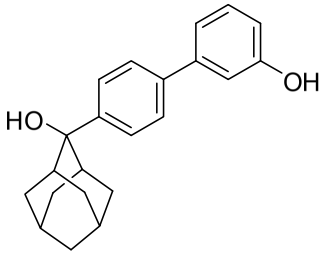


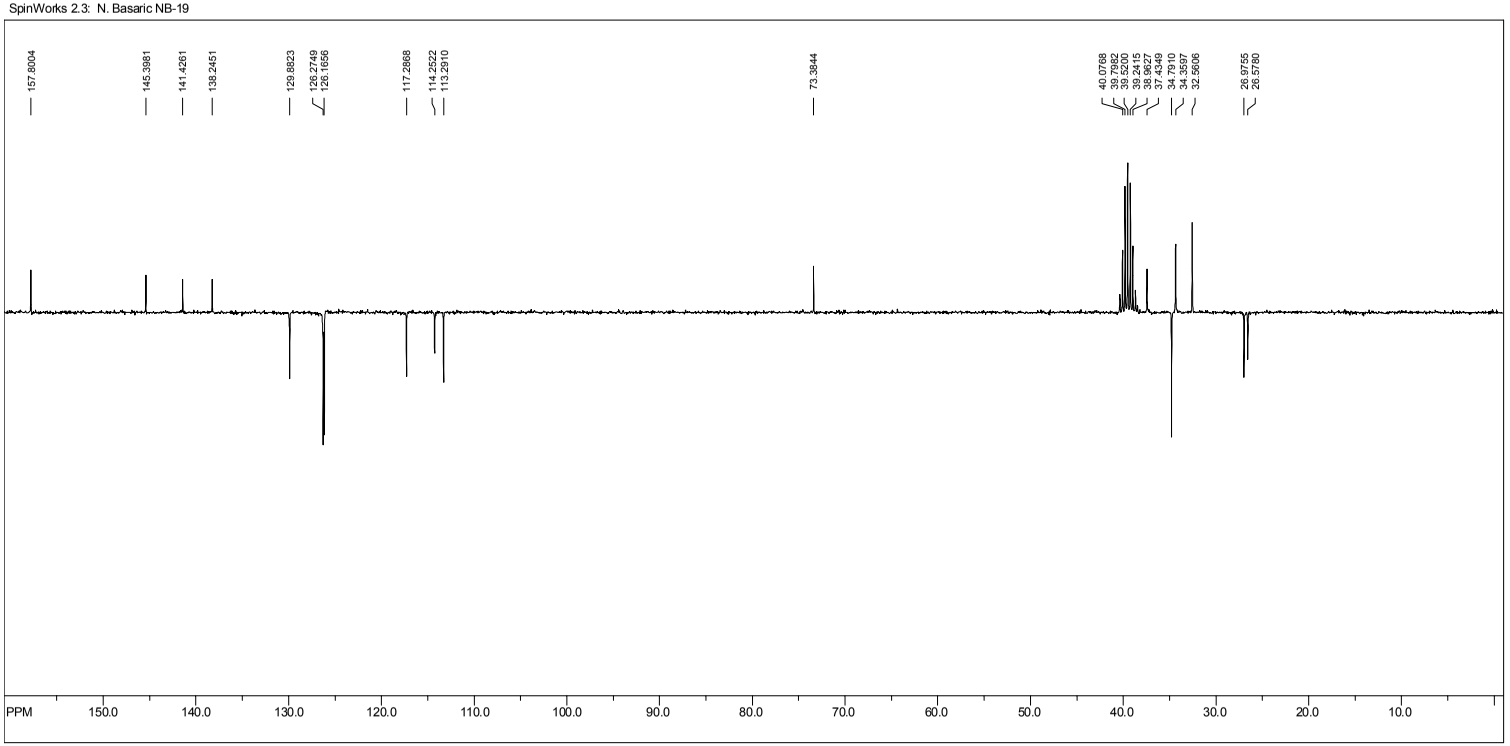
^{1}H NMR (DMSO-d_6, 300 MHz) of **6**





^{13}C NMR (DMSO-d_6, 75 MHz) of **6**





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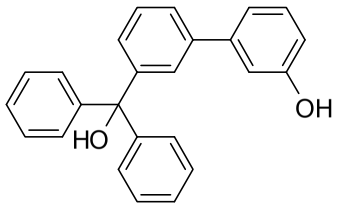
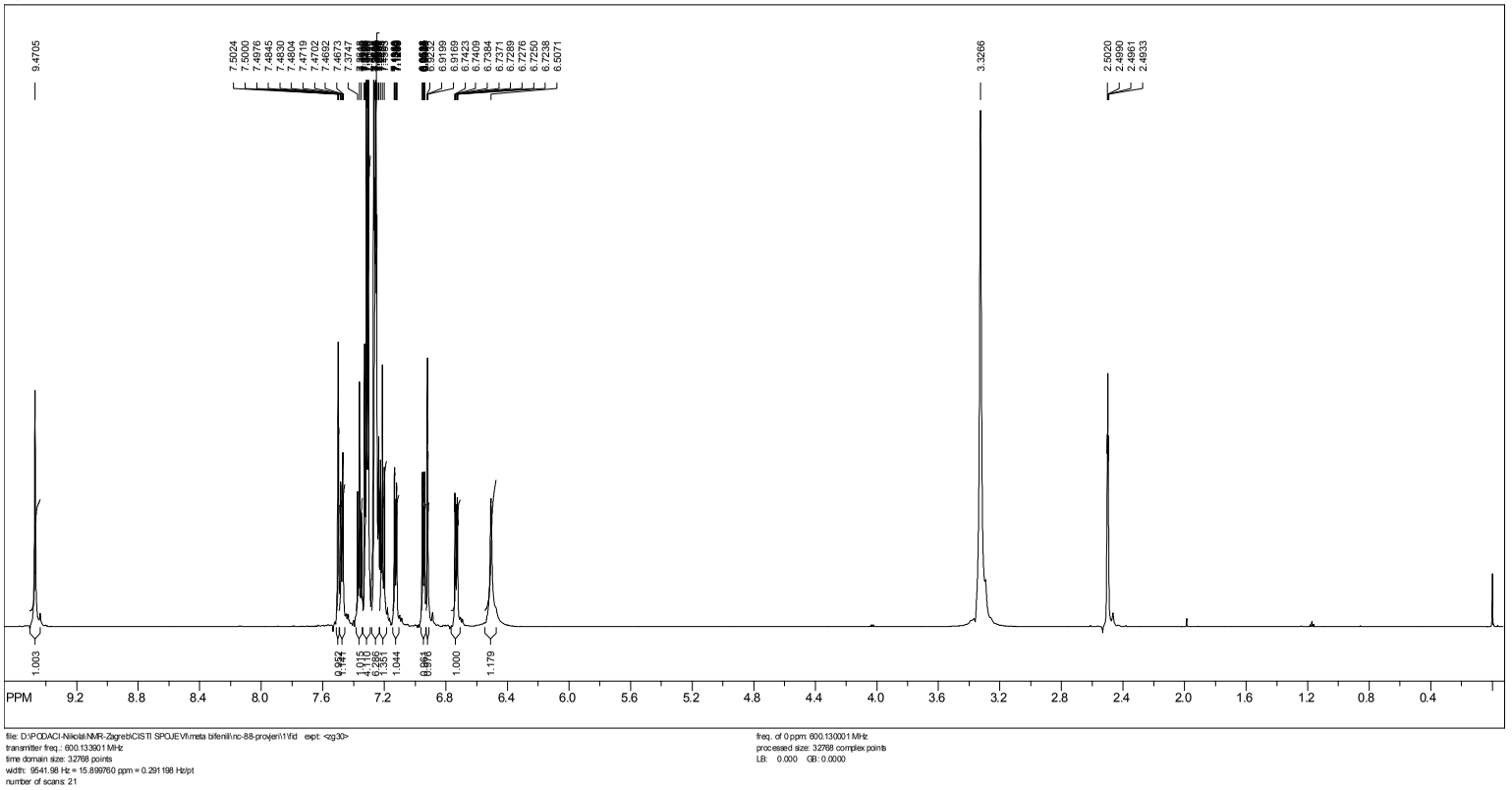
number of scans: 806

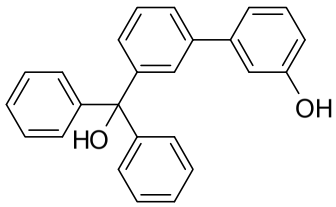
freq. of 0 ppm: 75.467783 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

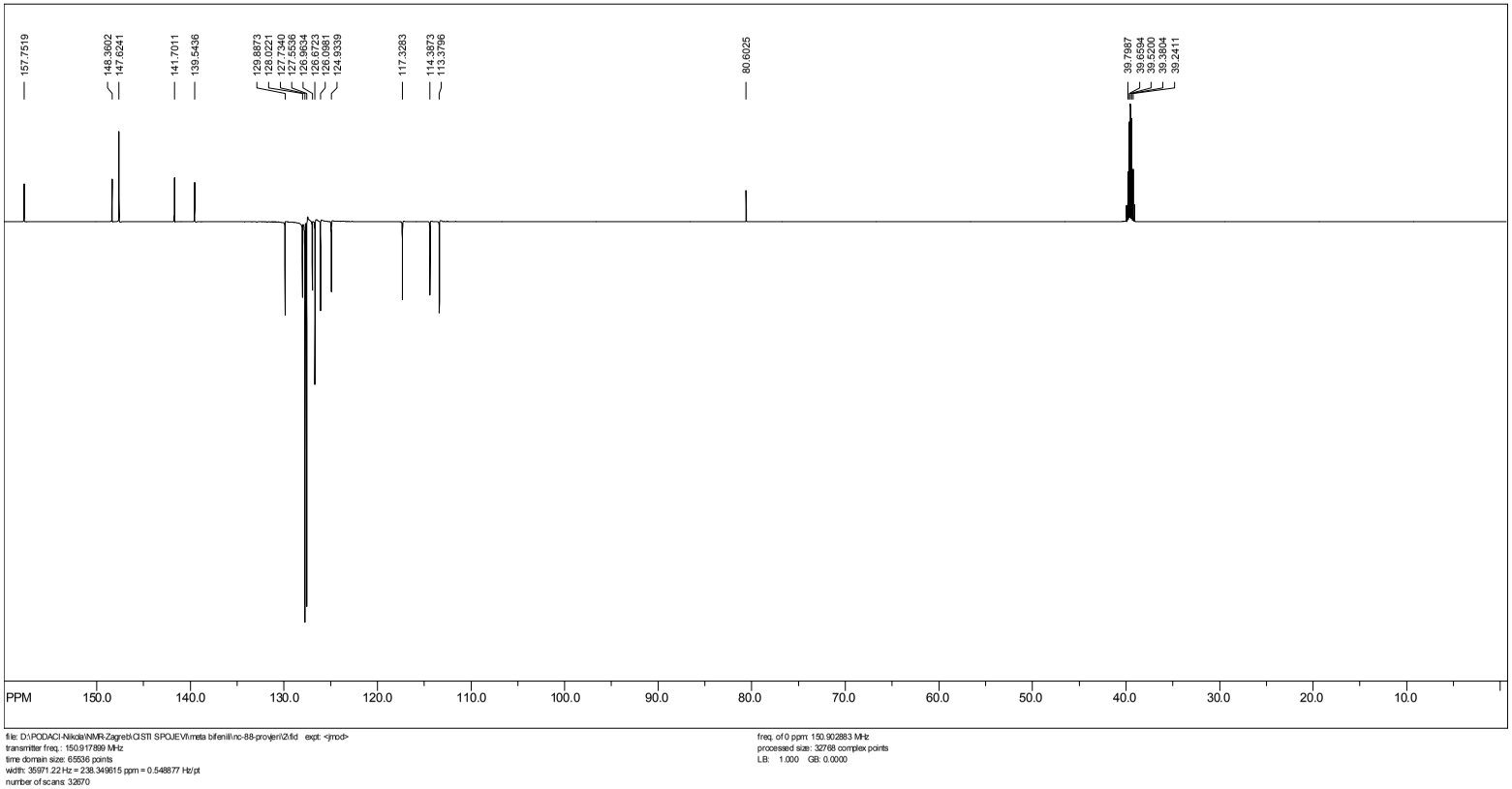
^{1}H NMR (DMSO-d_6, 600 MHz) of **7**



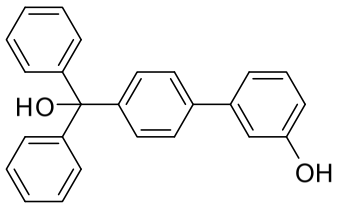


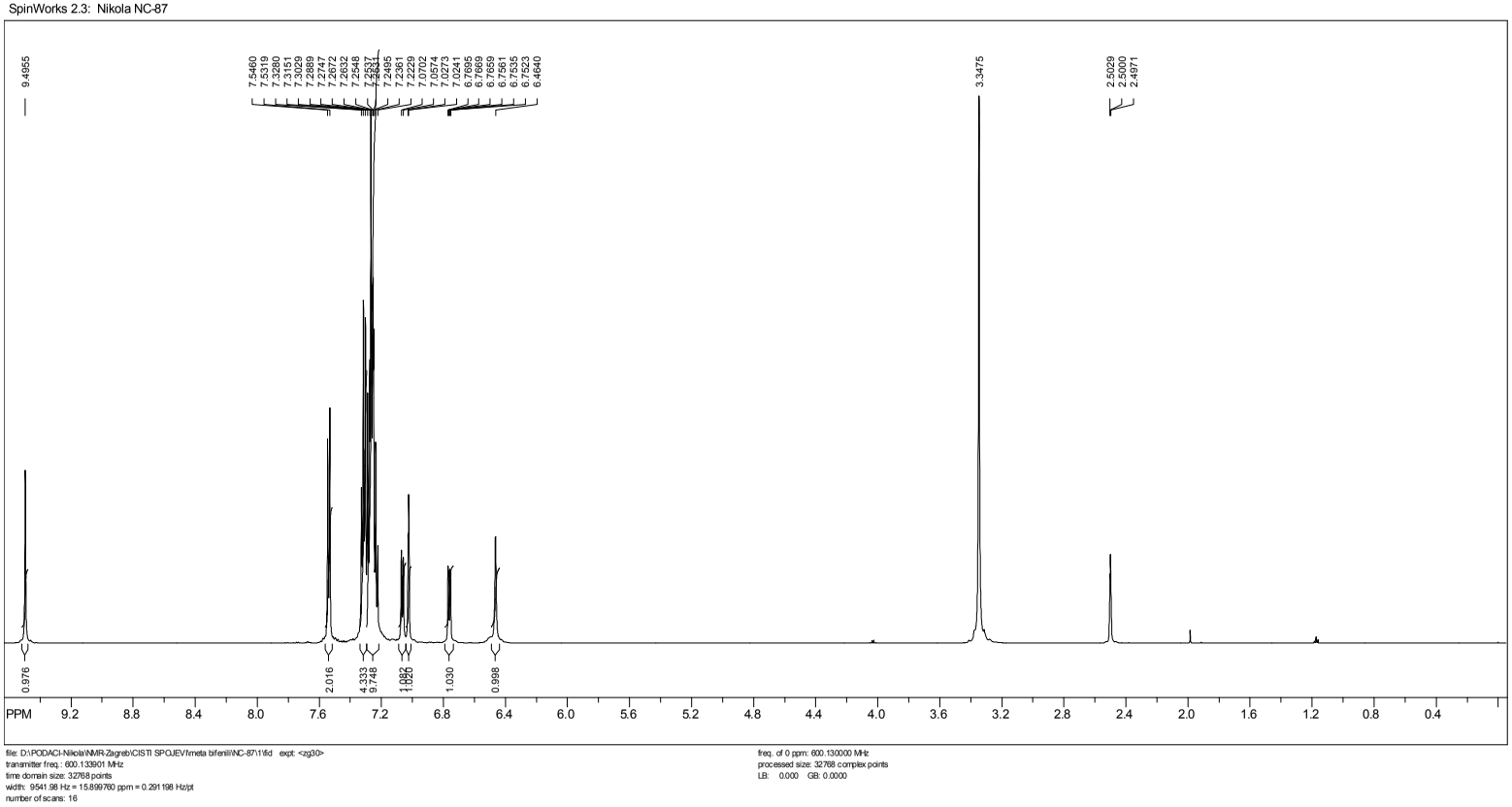
^{13}C NMR (DMSO-d_6, 150 MHz) of **7**



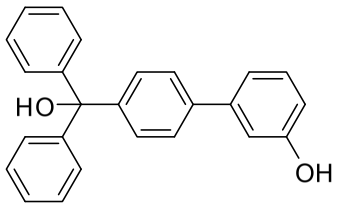


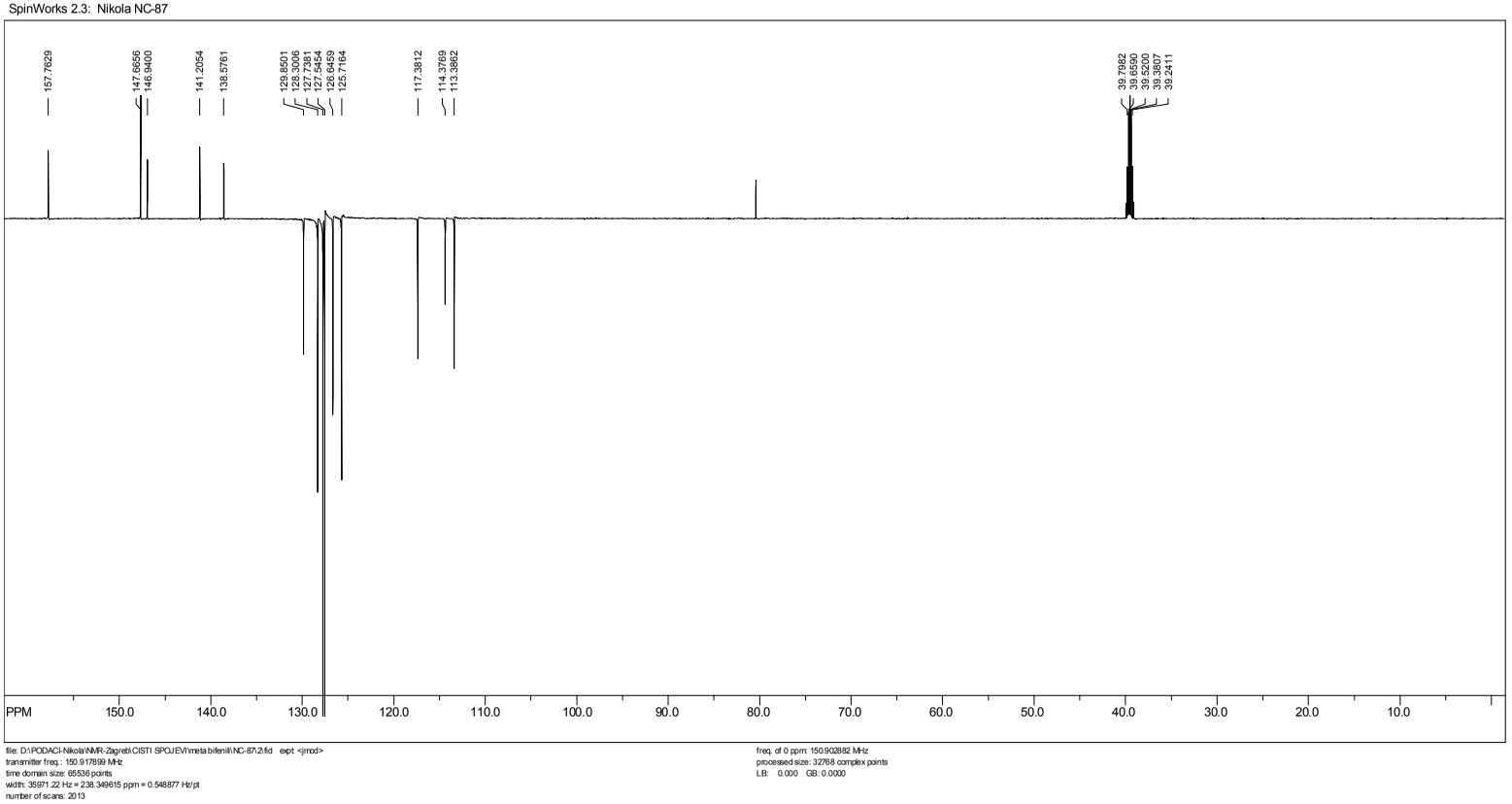
^{1}H NMR (DMSO-d_6, 600 MHz) of **8**



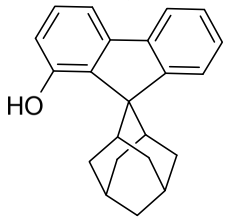


^{13}C NMR (DMSO-d_6, 150 MHz) of **8**

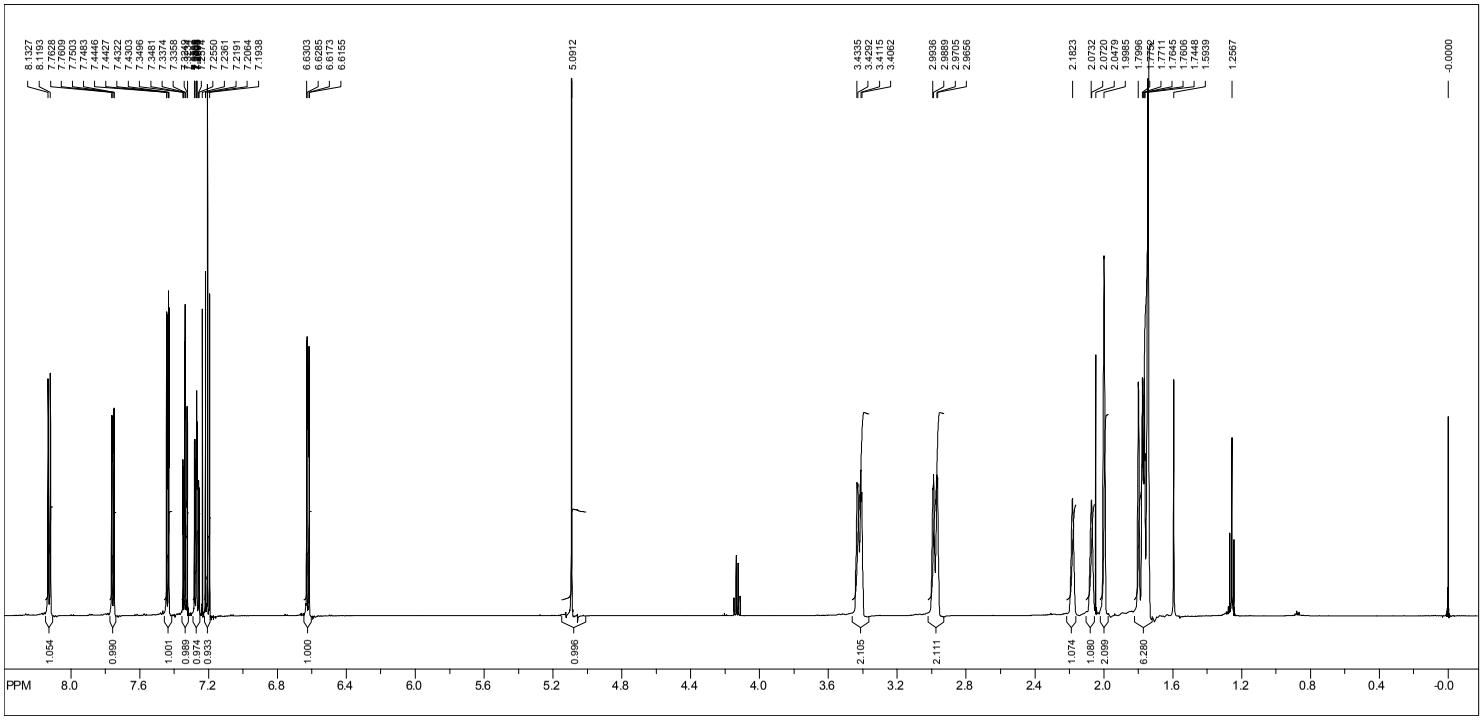




^{1}H NMR ($CDCl_3$, 600 MHz) of **9**



SpinWorks 2.3: N. Basaric DB-40/B



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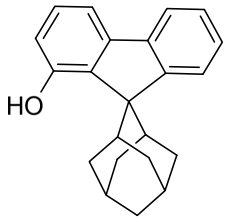
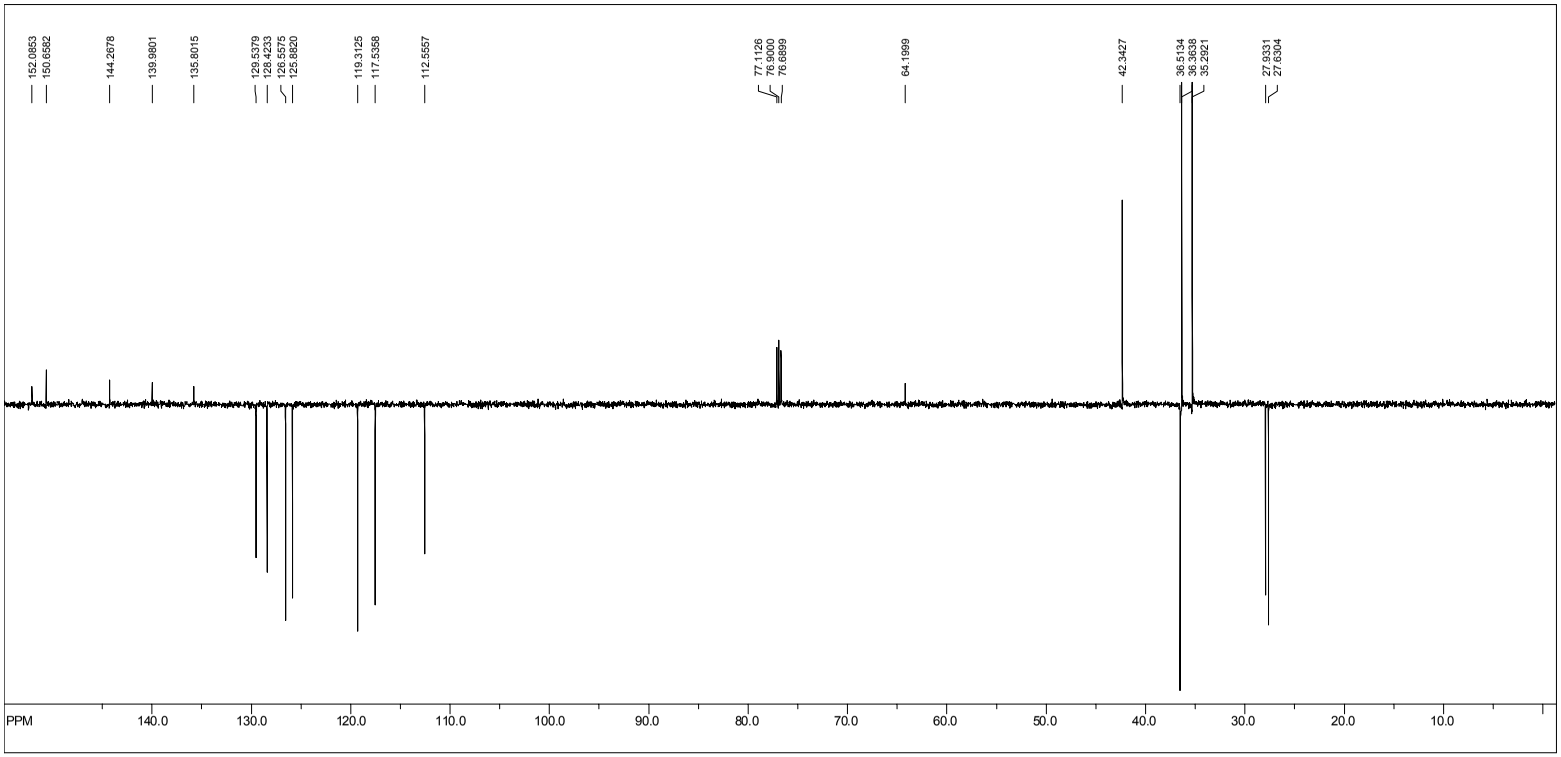
width: 9541.98 Hz = 15.899760 ppm = 0.291198 Hz/pt
number of scans: 24

freq. of 0 ppm: 600.130024 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

^{13}C NMR ($CDCl_3$, 150 MHz) of **9**



SpinWorks 2.3: N. Basaric DB-40/B



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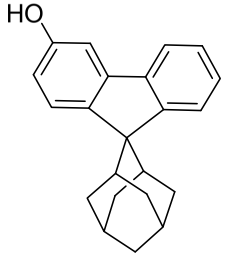
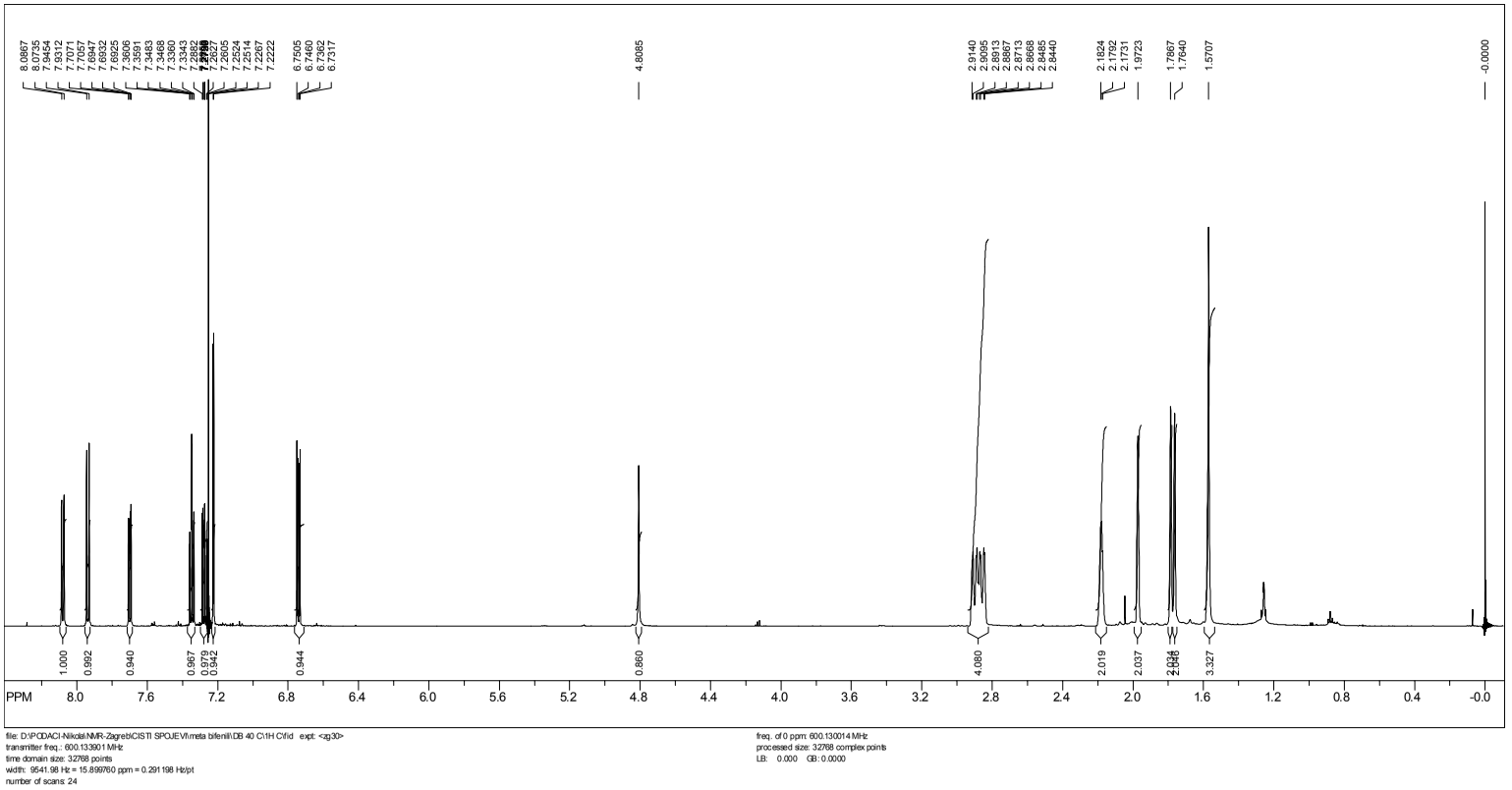
time domain size: 65536 points
width: 39370.08 Hz = 260.870838 ppm = 0.600740 Hz/pt
number of scans: 944

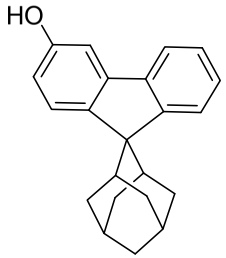
freq. of 0 ppm: 150.902825 MHz
processed size: 32768 complex points
LB: 0.000 GB: 0.0000

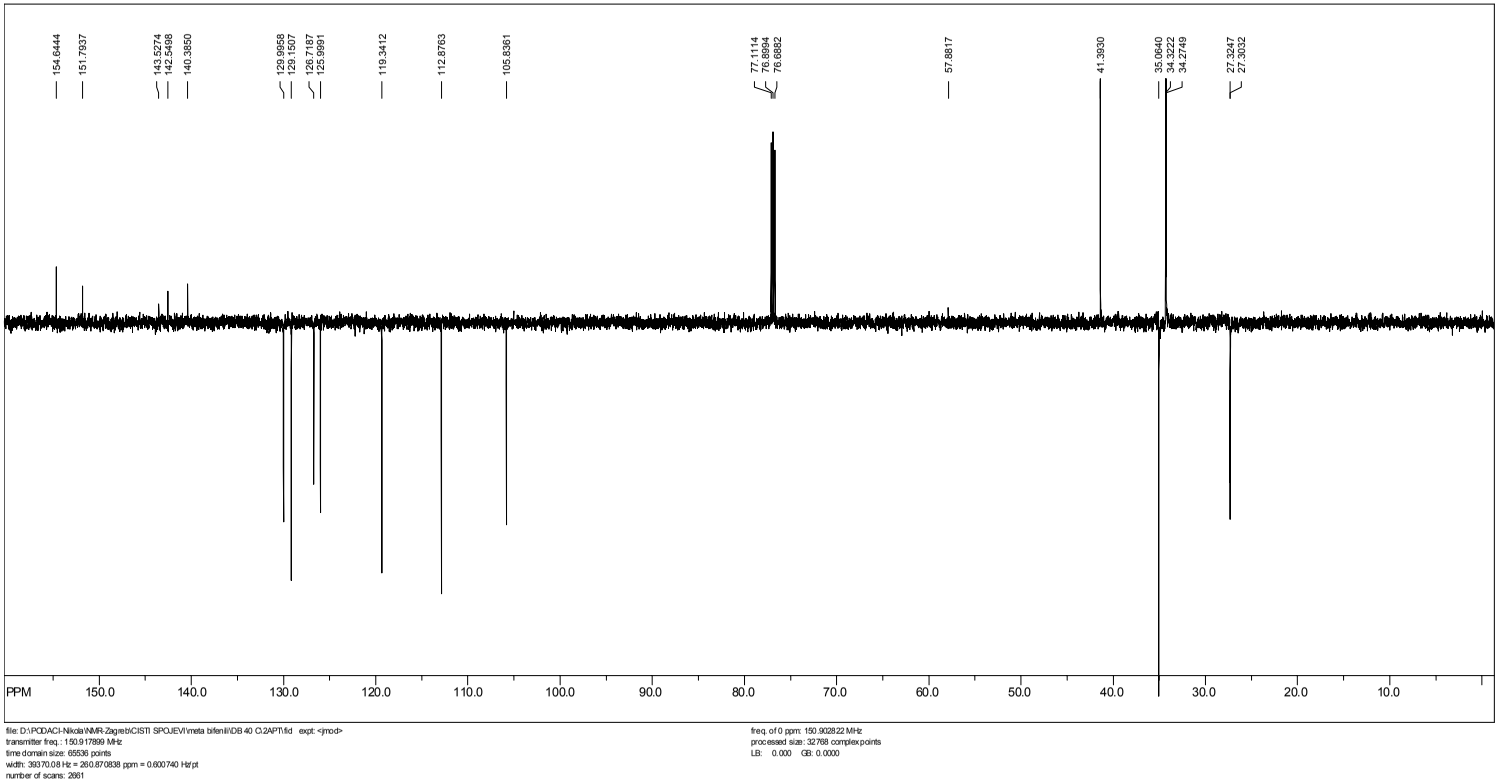
^{1}H NMR ($CDCl_3$, 600 MHz) of **10**



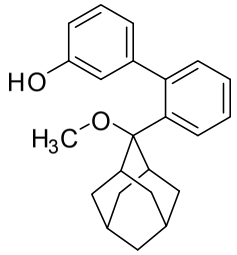


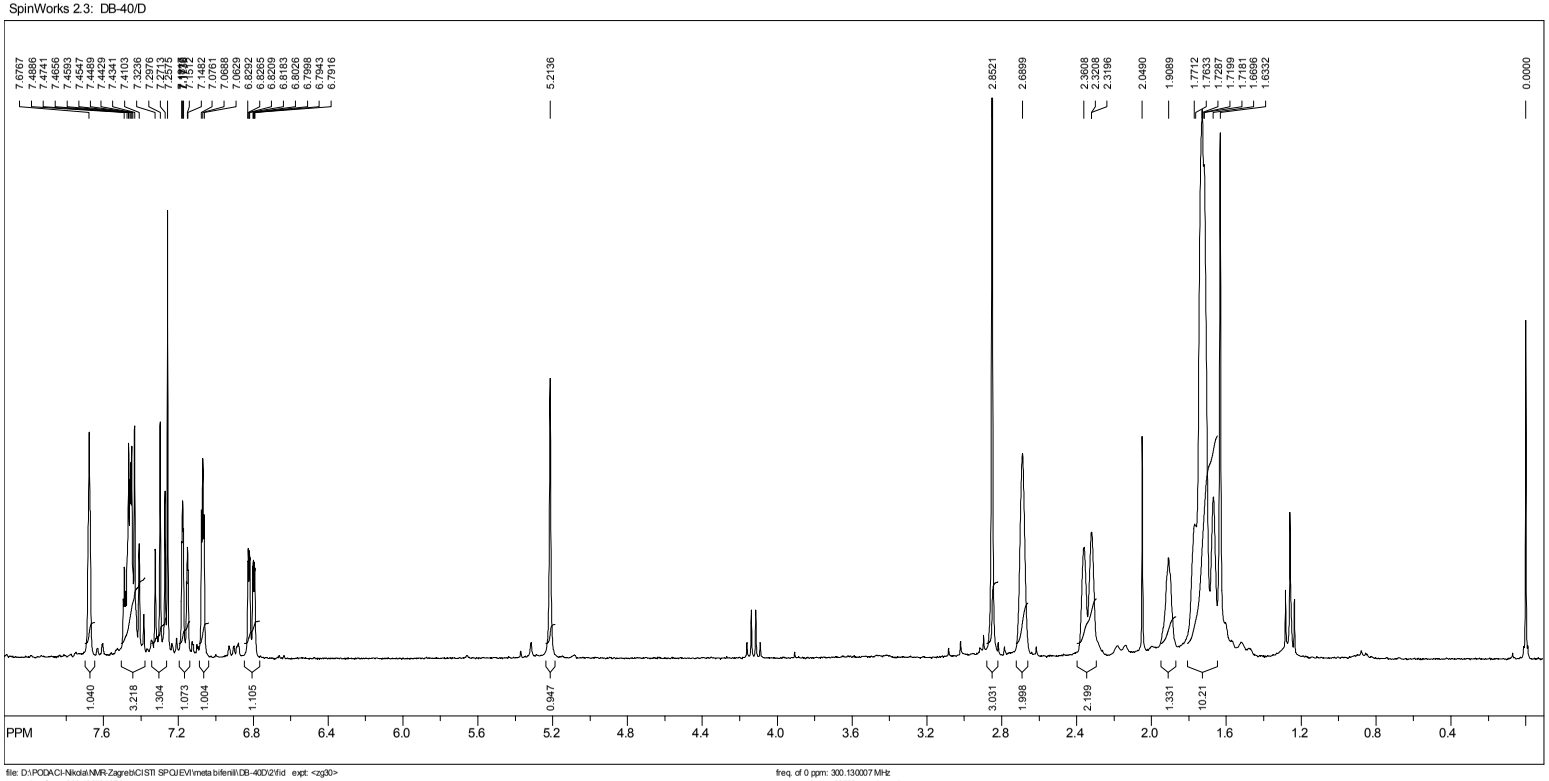
^{13}C NMR ($CDCl_3$, 150 MHz) of **10**



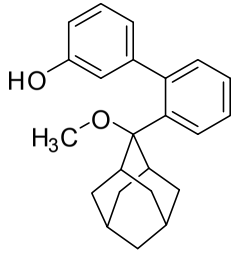


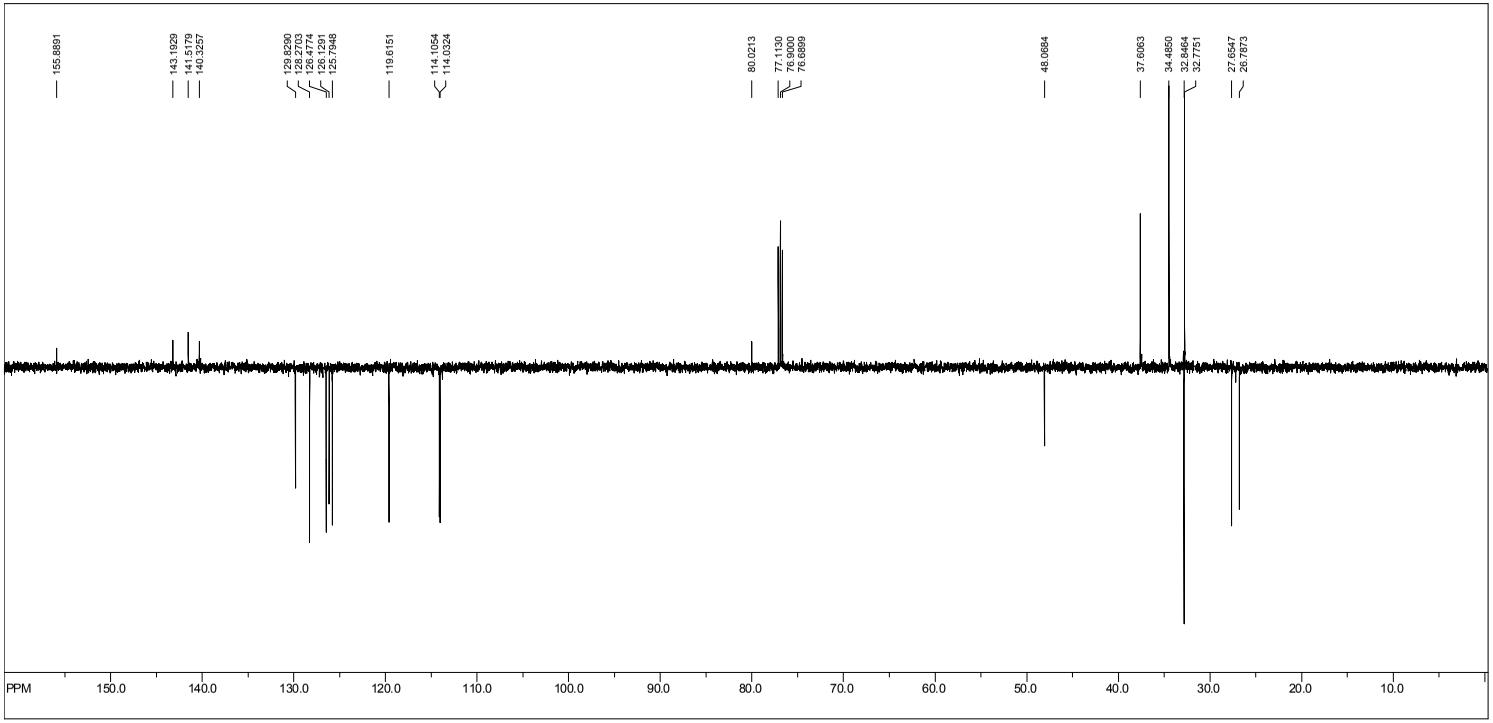
^{1}H NMR (DMSO-d_6, 300 MHz) of **4b**



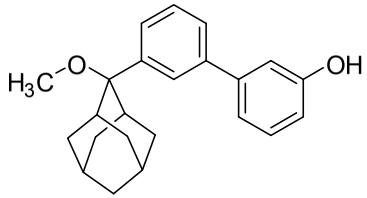


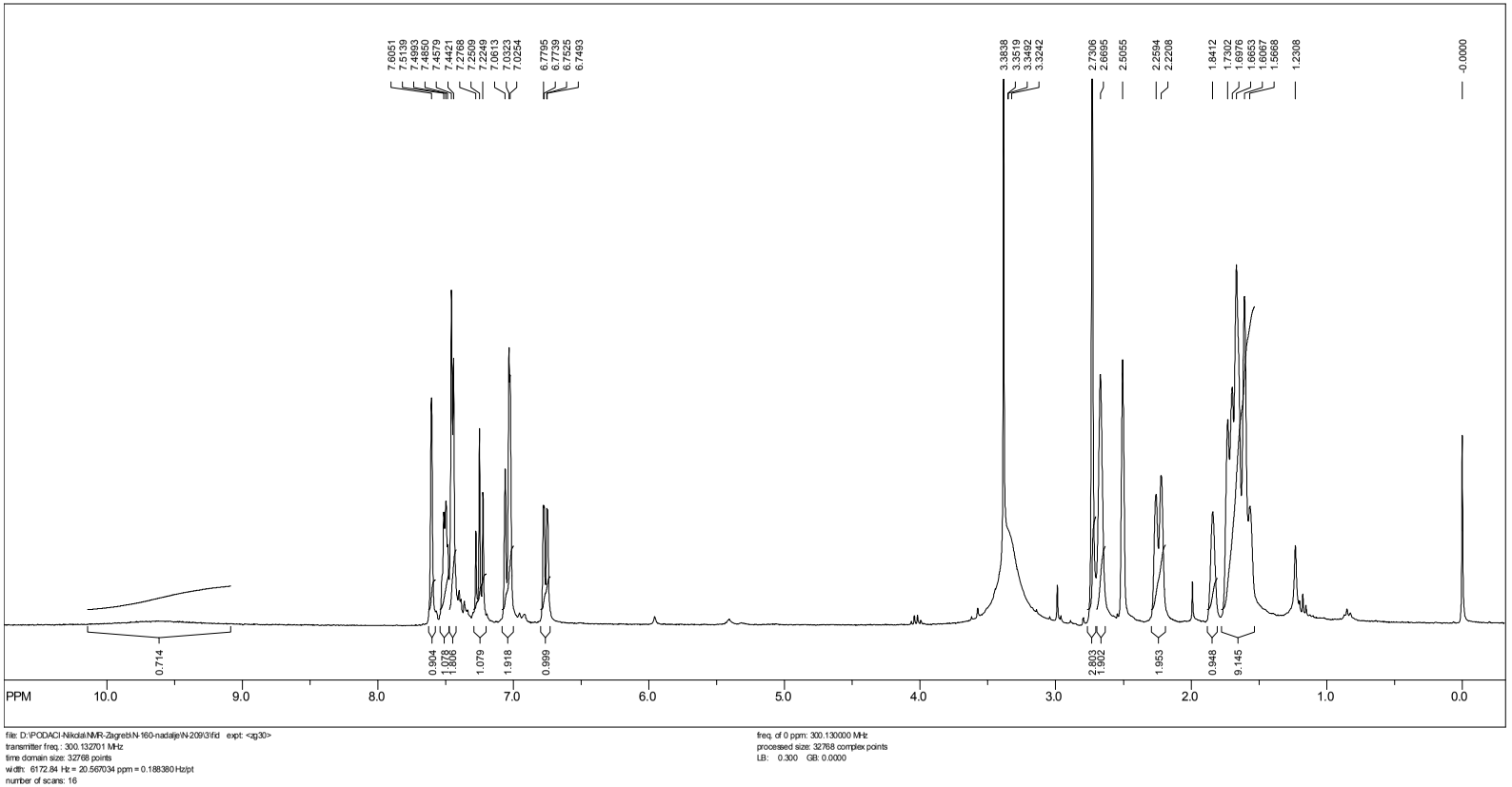
^{13}C NMR (DMSO-d_6, 150 MHz) of **4b**



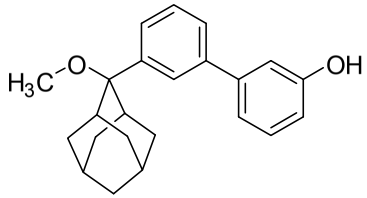


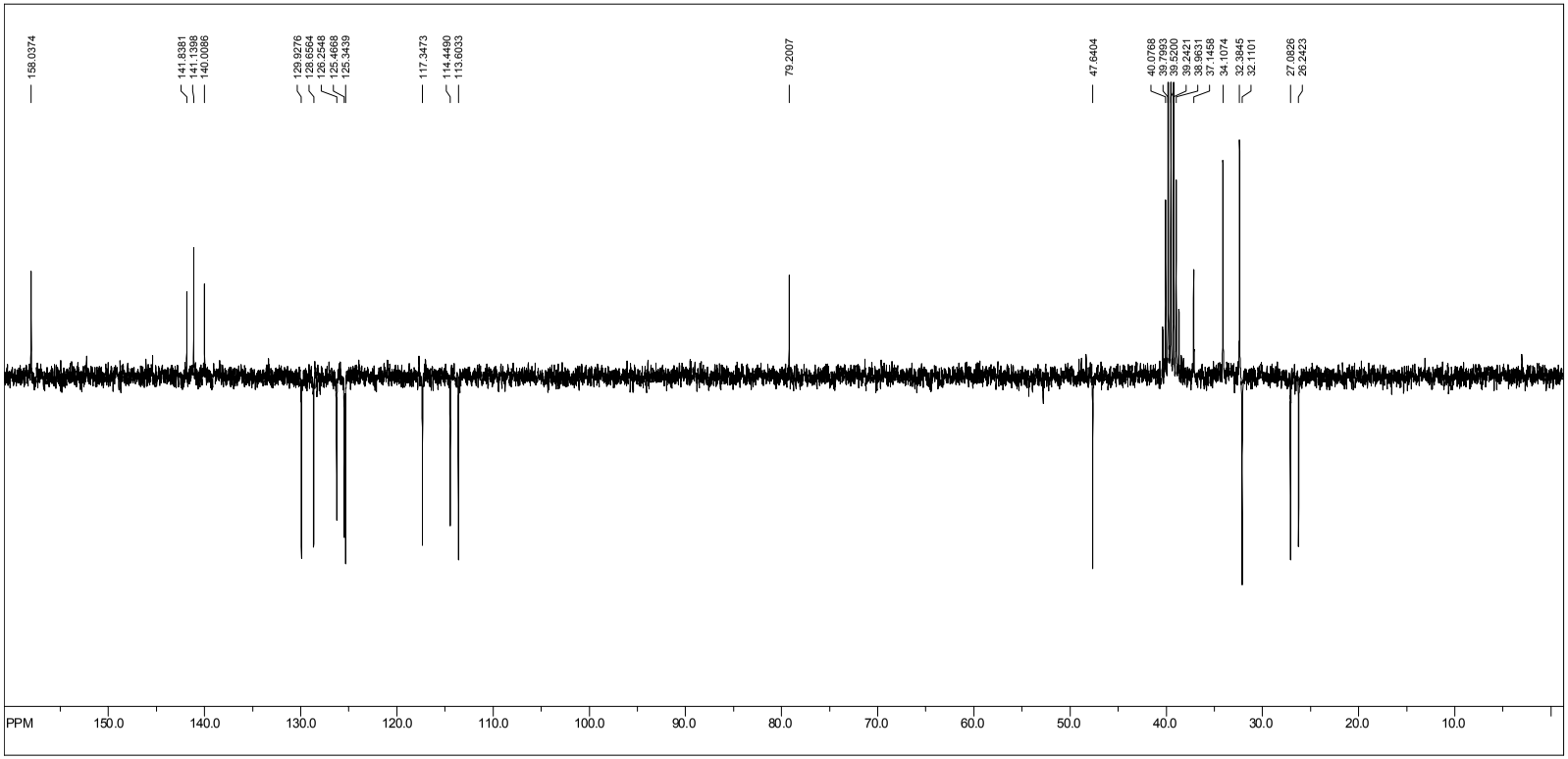
^{1}H NMR (DMSO-d_6, 300 MHz) of **5b**



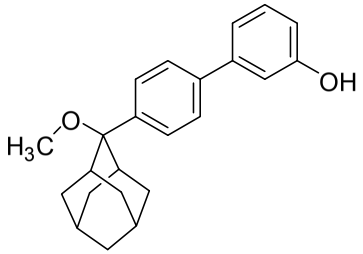


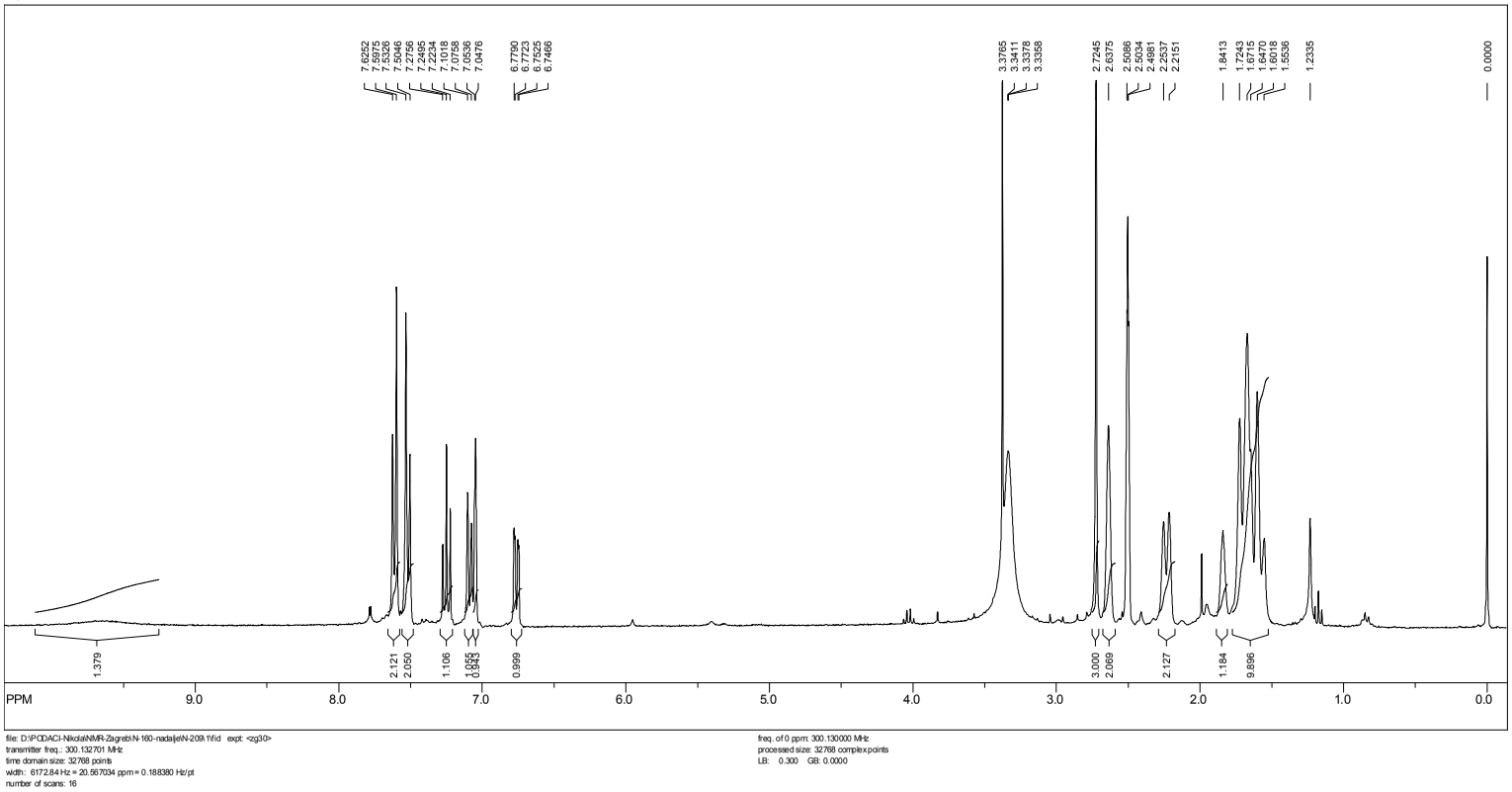
^{13}C NMR (DMSO-d_6, 75 MHz) of **5b**



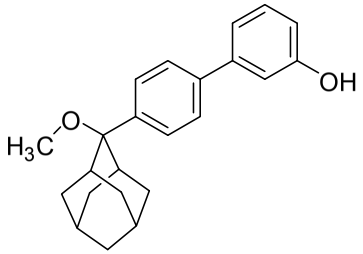


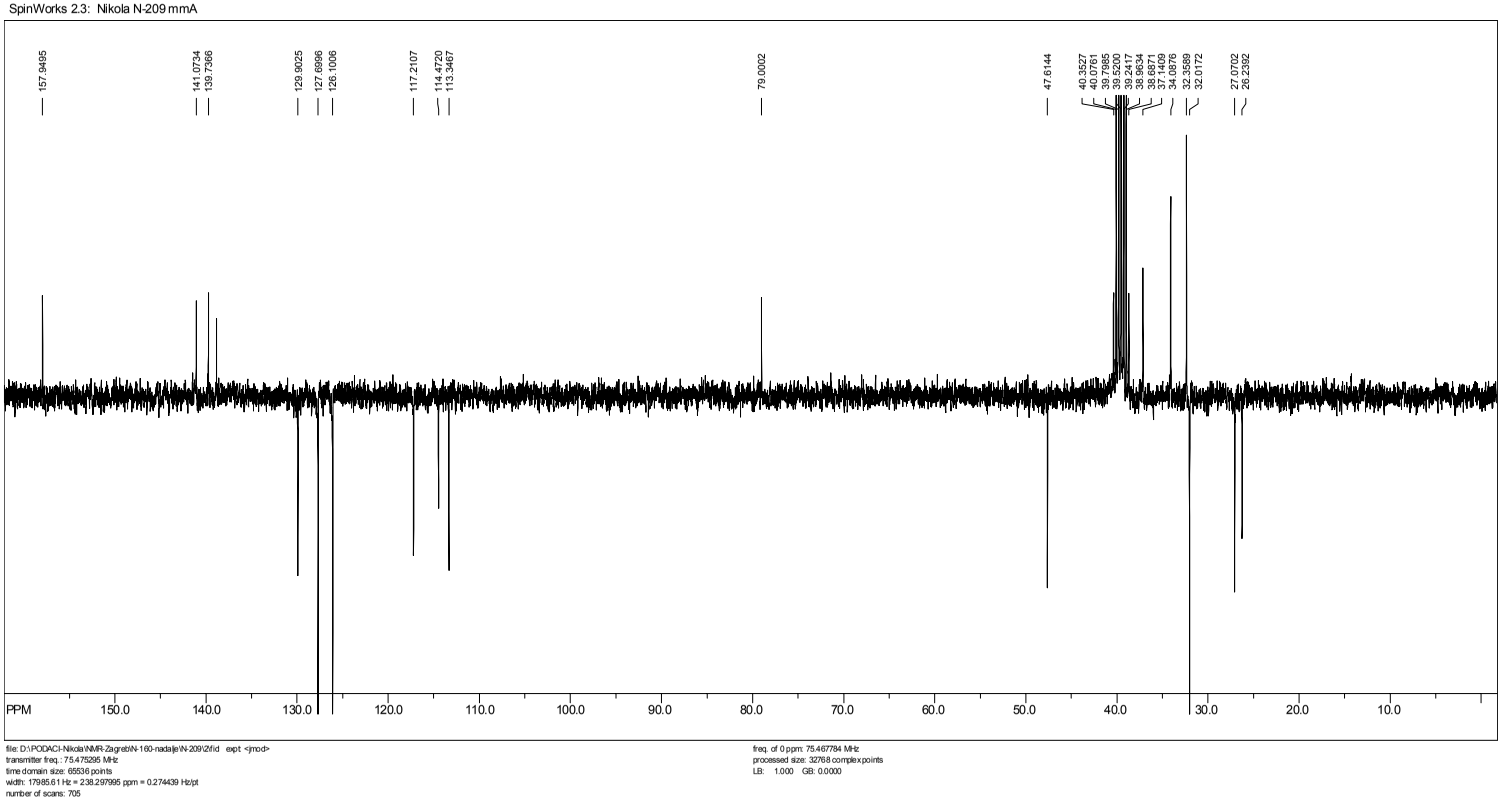
^{1}H NMR (DMSO-d_6, 300 MHz) of **6b**



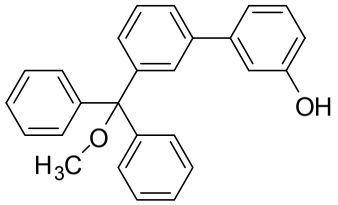


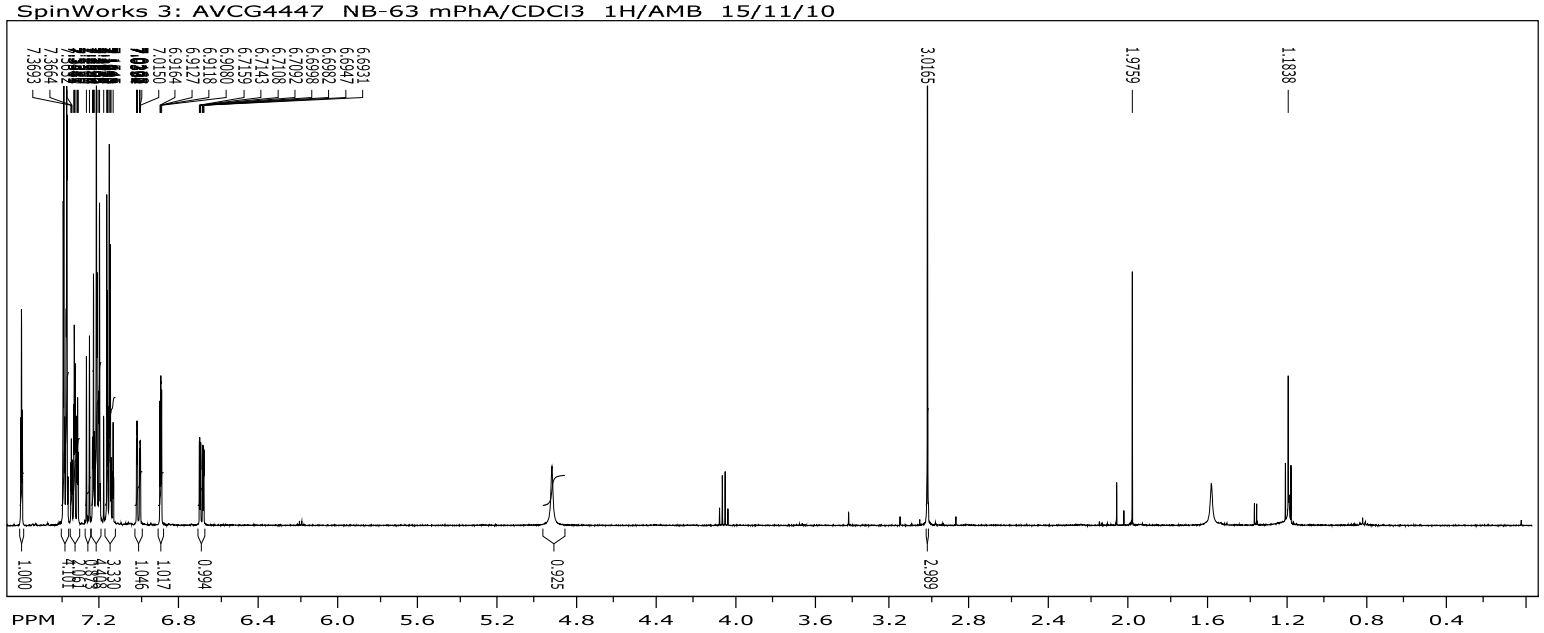
^{13}C NMR (DMSO-d_6, 75 MHz) of **6b**





^{1}H NMR ($CDCl_3$, 500 MHz) of **7b**





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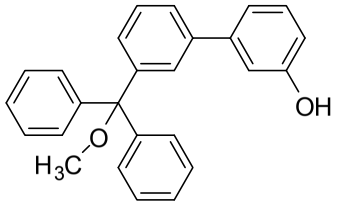
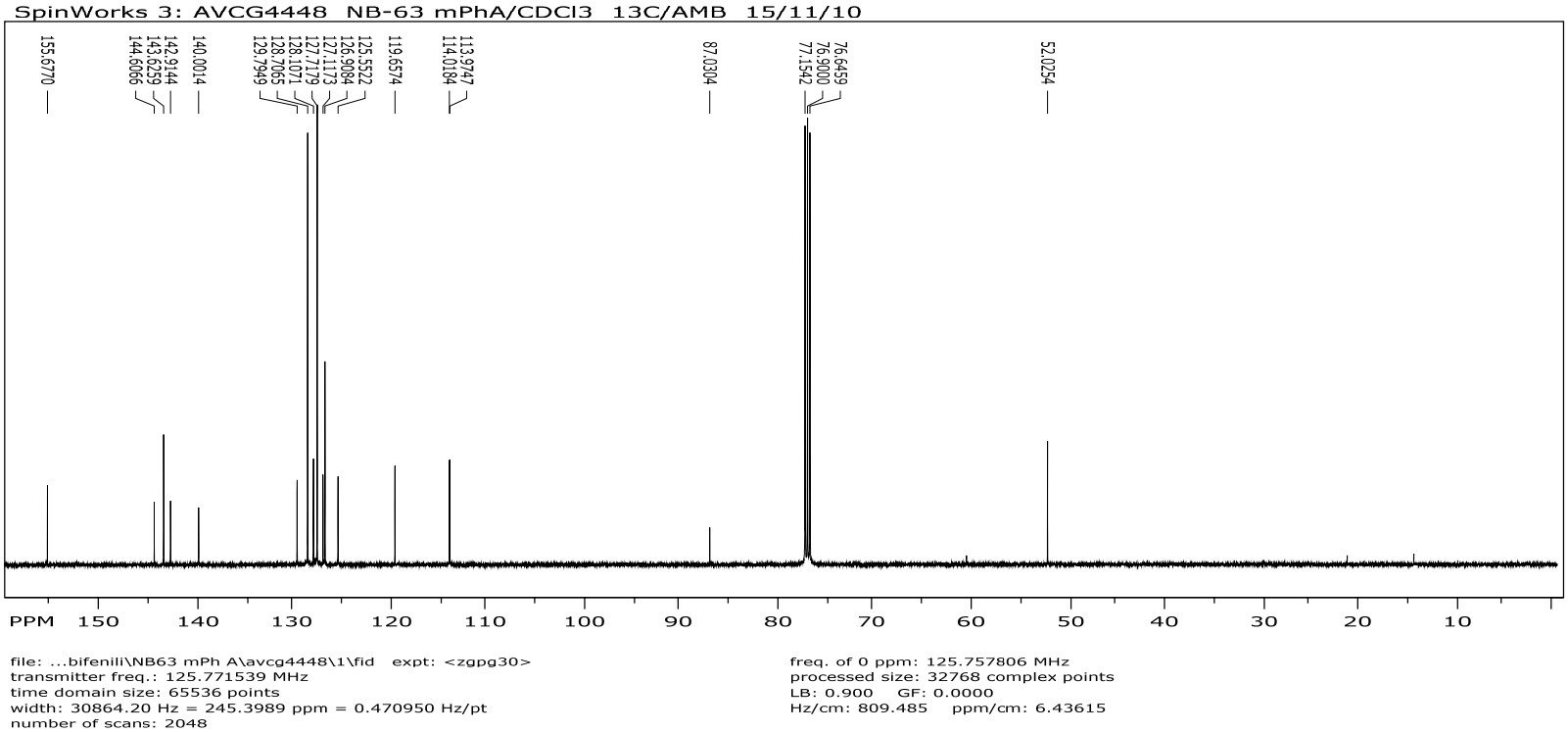
number of scans: 16

freq. of 0 ppm: 500.130056 MHz
processed size: 16384 complex points
LB: -0.200 GF: 0.5000
Hz/cm: 155.029 ppm/cm: 0.30998

^{13}C NMR ($CDCl_3$, 125 MHz) of **7b**





file: ...bifenili\NB63 mPh A\avcg4448\1\fid expt: <zgpg30>
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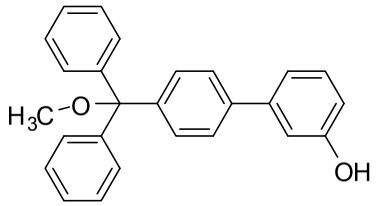
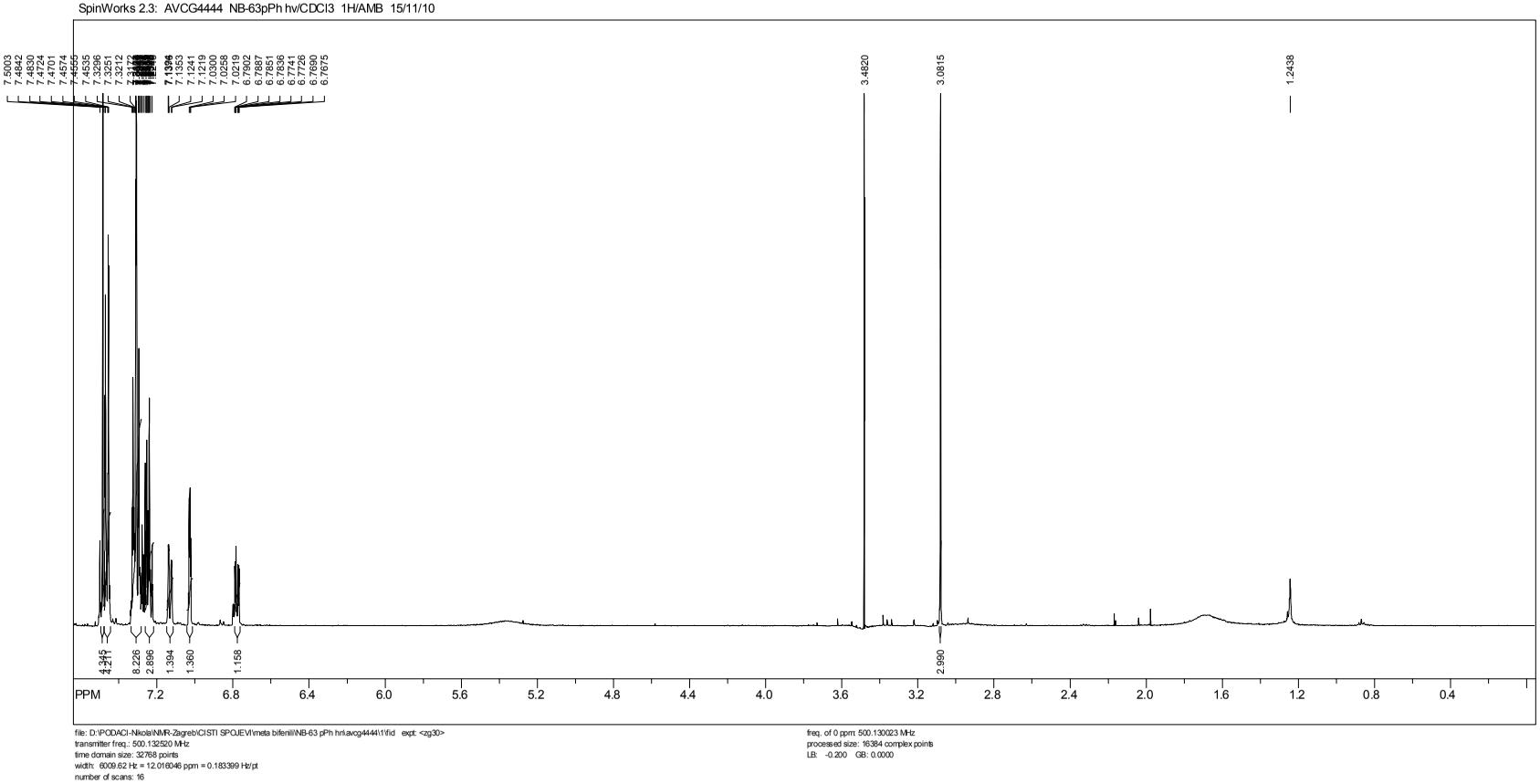
time domain size: 65536 points
width: 30864.20 Hz = 245.3989 ppm = 0.470950 Hz/pt
number of scans: 2048

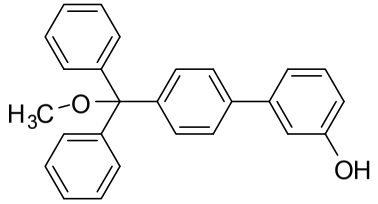
freq. of 0 ppm: 125.757806 MHz
processed size: 32768 complex points
LB: 0.900 GF: 0.0000
Hz/cm: 809.485 ppm/cm: 6.43615

^{1}H NMR ($CDCl_3$, 500 MHz) of **8b**

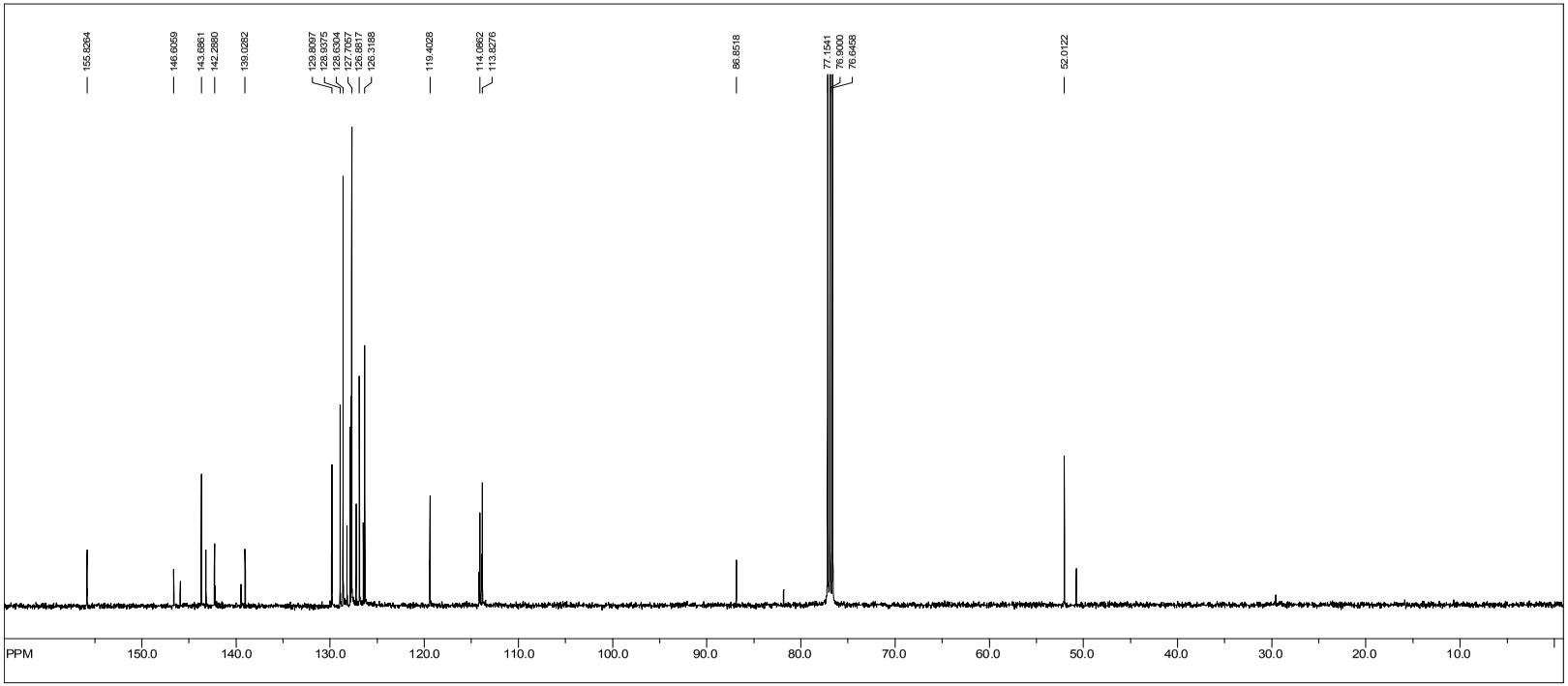




^{13}C NMR ($CDCl_3$, 125 MHz) of **8b**



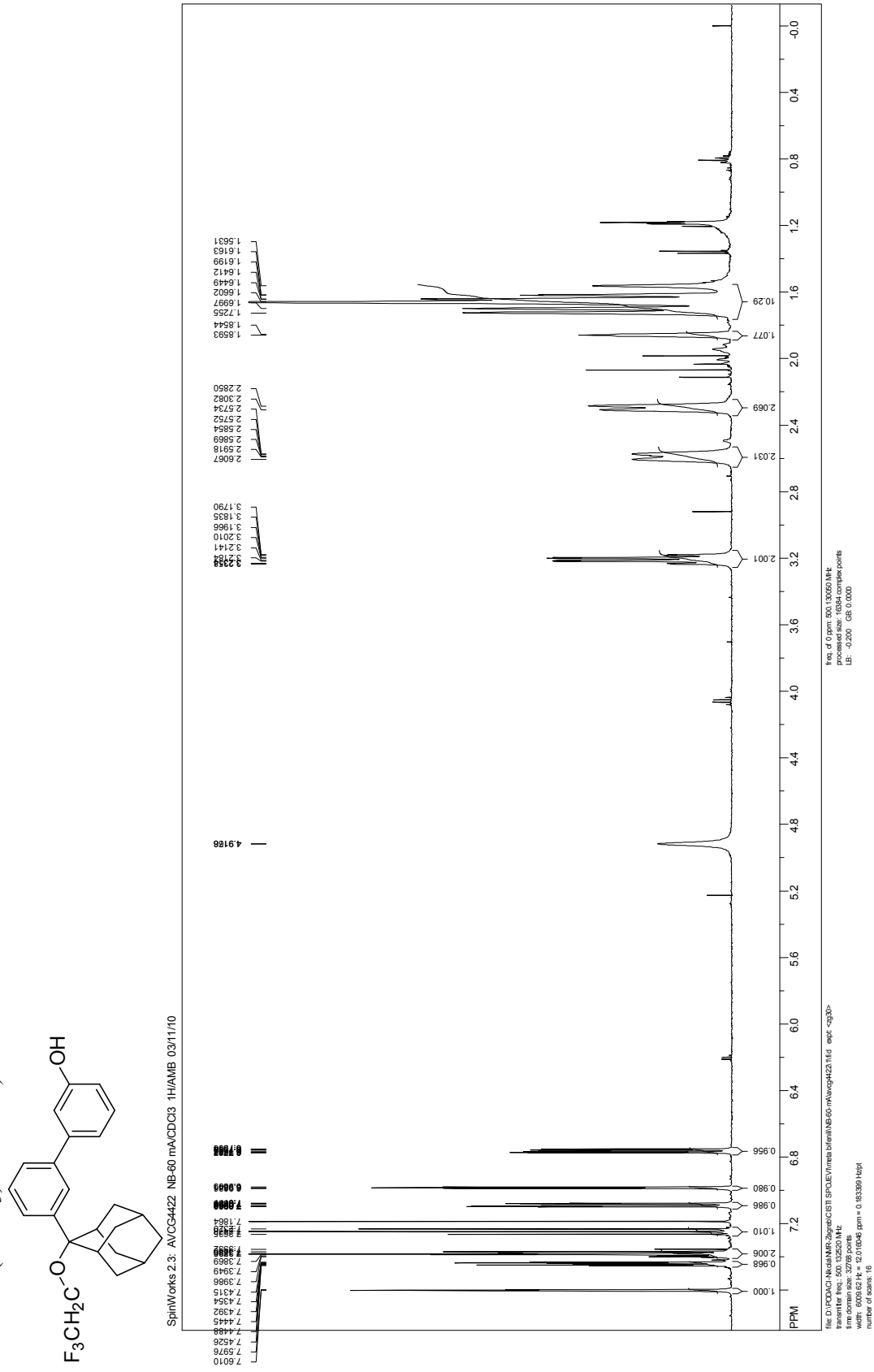
SpinWorks 2.3: AVCG4445 NB-63pPh hv\CDCl3 13C/AMB 15/11/10



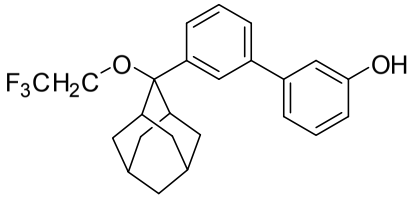
file: D:\PODACI-Nikola\NMR-Zagreb\CIST\ SPOJEVI\meta bifenili\NB-63 pPh hv\avcg4445.1\fid expt: <zgpg30>
transmitter freq.: 125.771539 MHz
time domain size: 65536 points
width: 30864.20 Hz = 245.398902 ppm = 0.470950 Hz/pt
number of scans: 2048

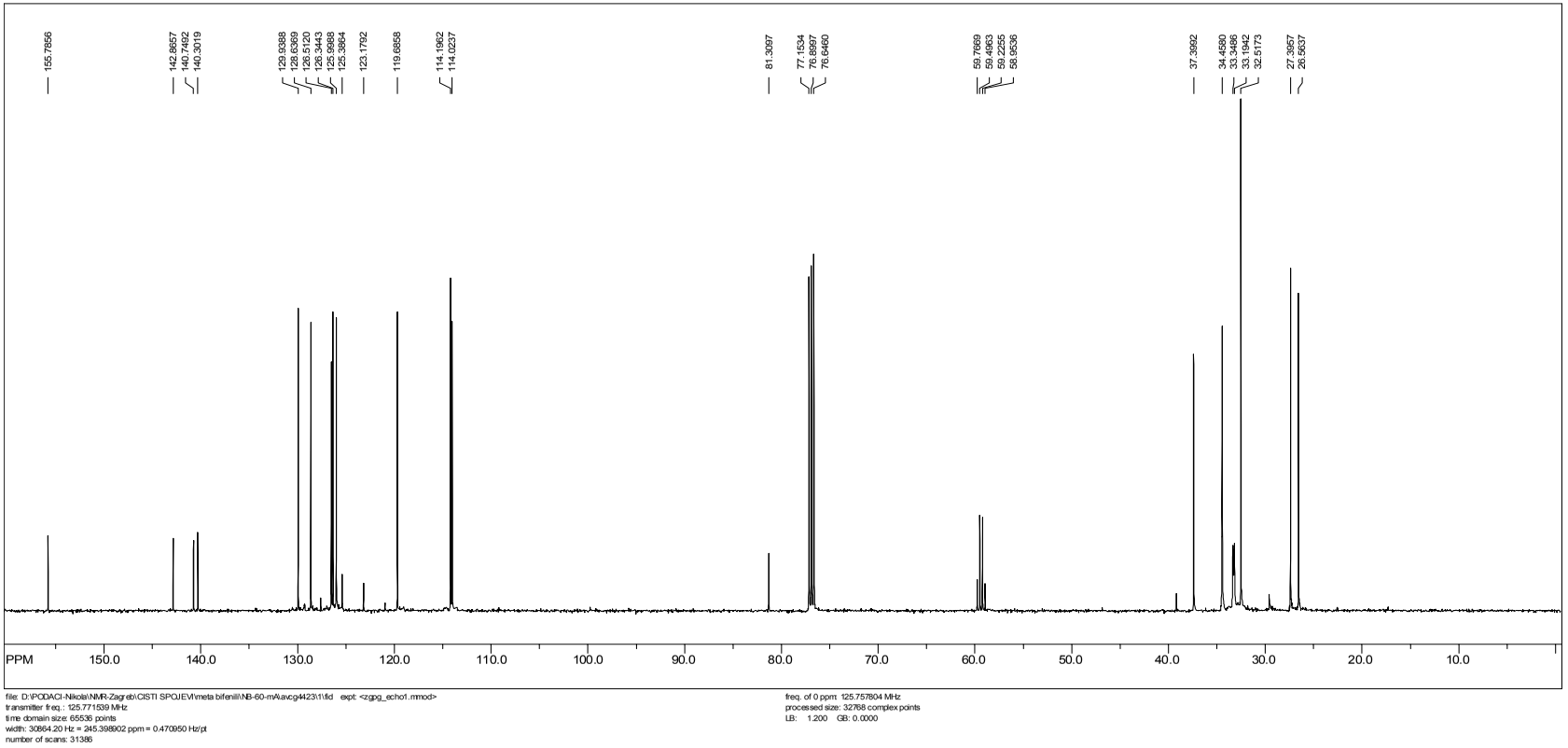
freq. of 0 ppm: 125.757807 MHz
processed size: 32768 complex points
LB: 0.900 GB: 0.0000

^{1}H NMR ($CDCl_3$, 500 MHz) of **11**

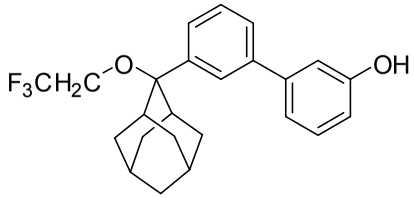


^{13}C NMR ($CDCl_3$, 125 MHz) of **11**

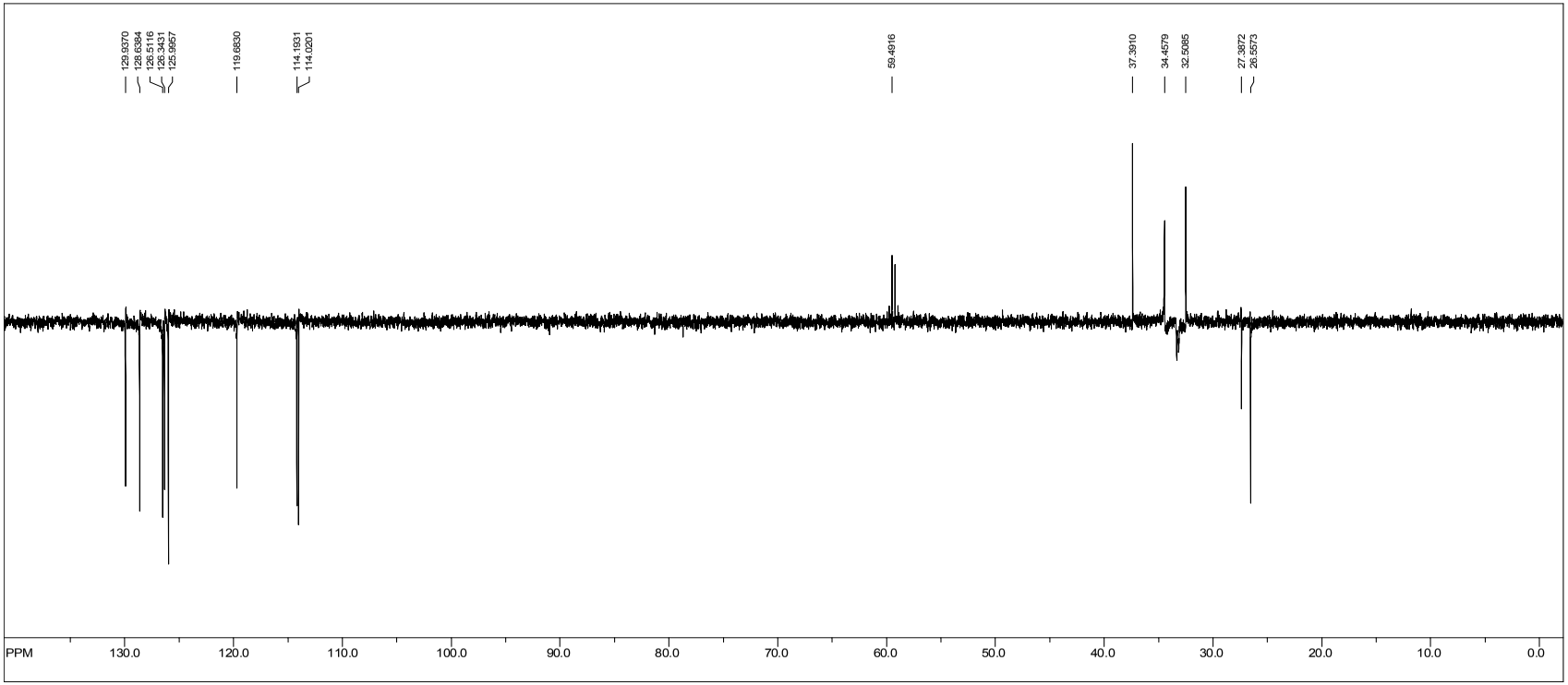




^{13}C NMR ($CDCl_3$, 125 MHz, DEPT) of **11**



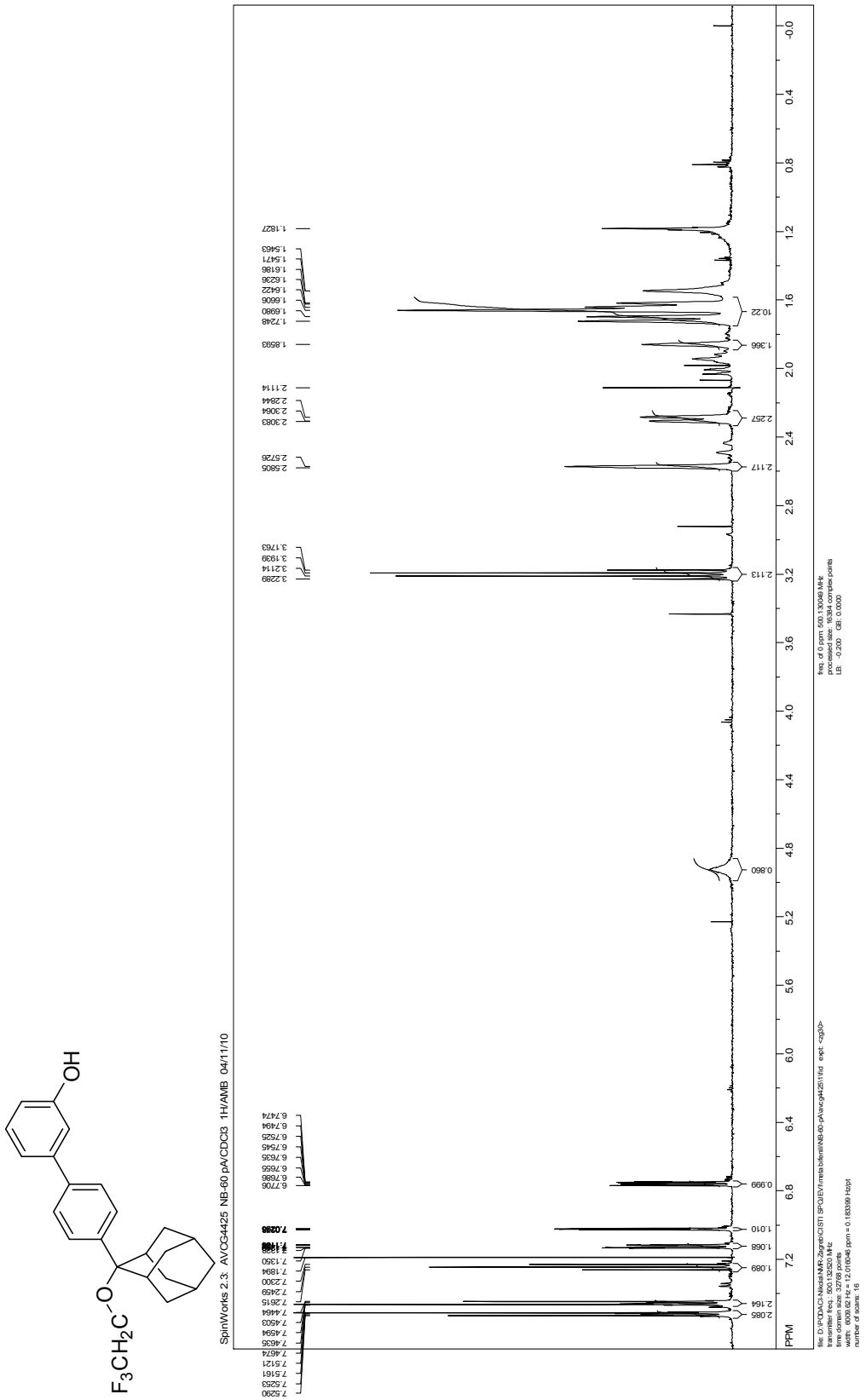
SpinWorks 2.3: AVCG4424 NB-60 mA/CDCl3 13C DEPT135/AMB 04/11/10



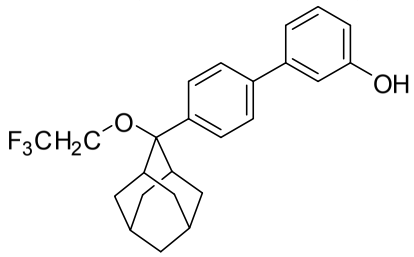
file: D:\PODACI-Nikola\NMR-Zagreb\CISTI SPOJEVI\meta bifenili\NB-60-mA\avcg4424i.11\fid expt: <dept135>
transmitter freq.: 125.771539 MHz
time domain size: 65536 points
width: 30864.20 Hz = 245.398902 ppm = 0.470950 Hz/pt
number of scans: 512

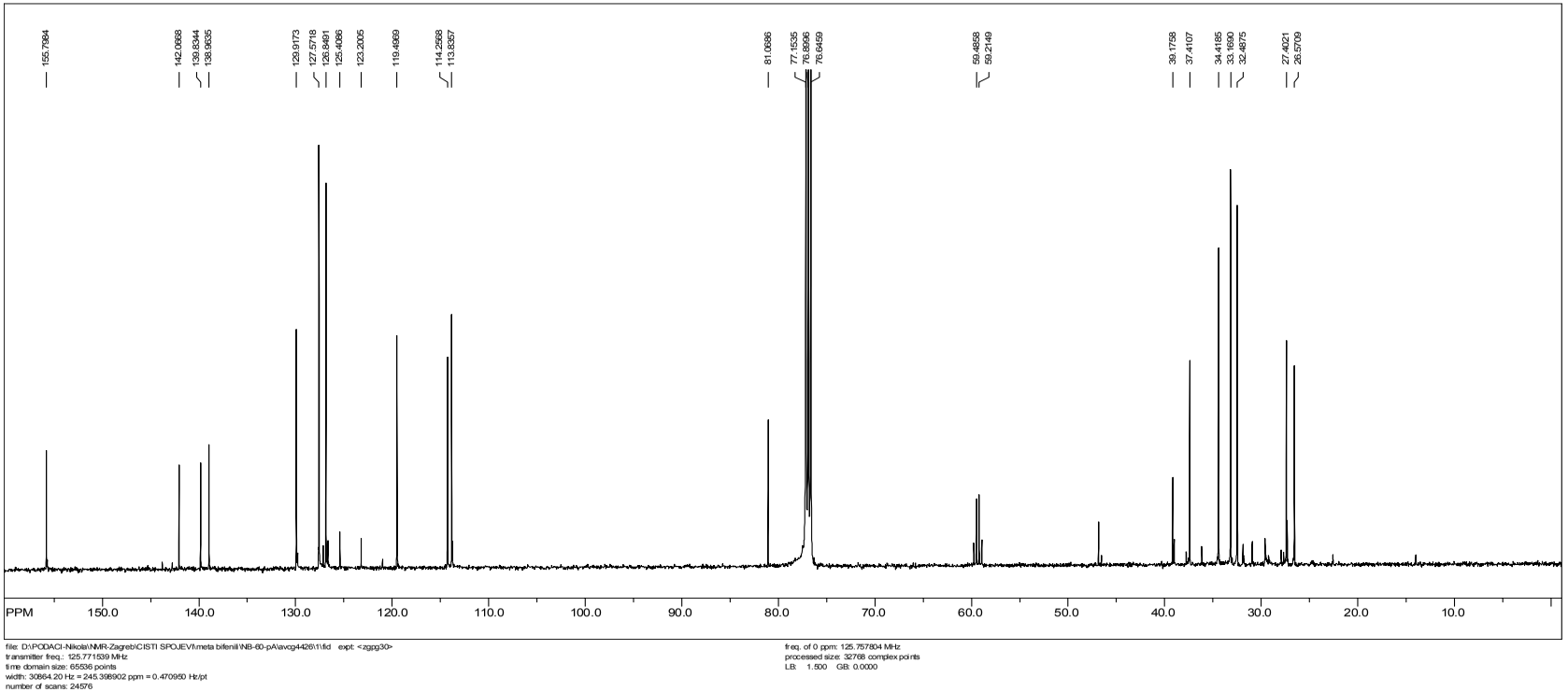
freq. of 0 ppm: 125.757804 MHz
processed size: 32768 complex points
LB: 0.900 GB: 0.0000

^{1}H NMR ($CDCl_3$, 500 MHz) of **12**

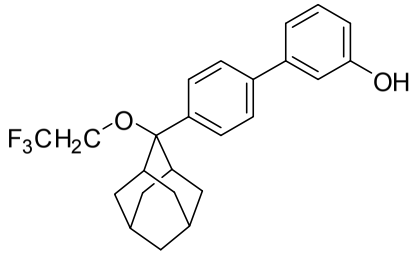


^{13}C NMR ($CDCl_3$, 125 MHz) of **12**

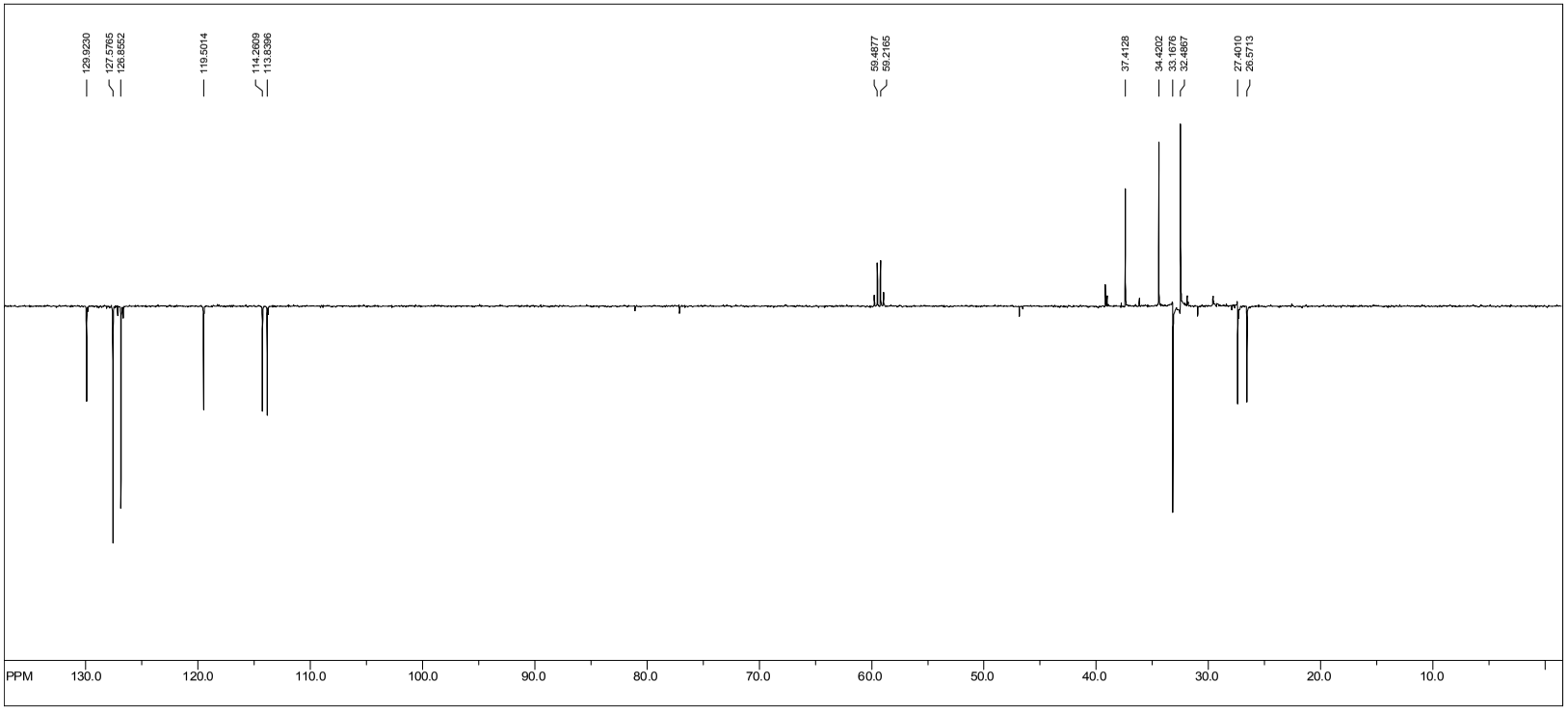




^{13}C NMR ($CDCl_3$, 125 MHz) of **12**



SpinWorks 2.3: AVCG4429 NB-60 pA/CDCl3 13C DEPT135/AMB 05/11/10



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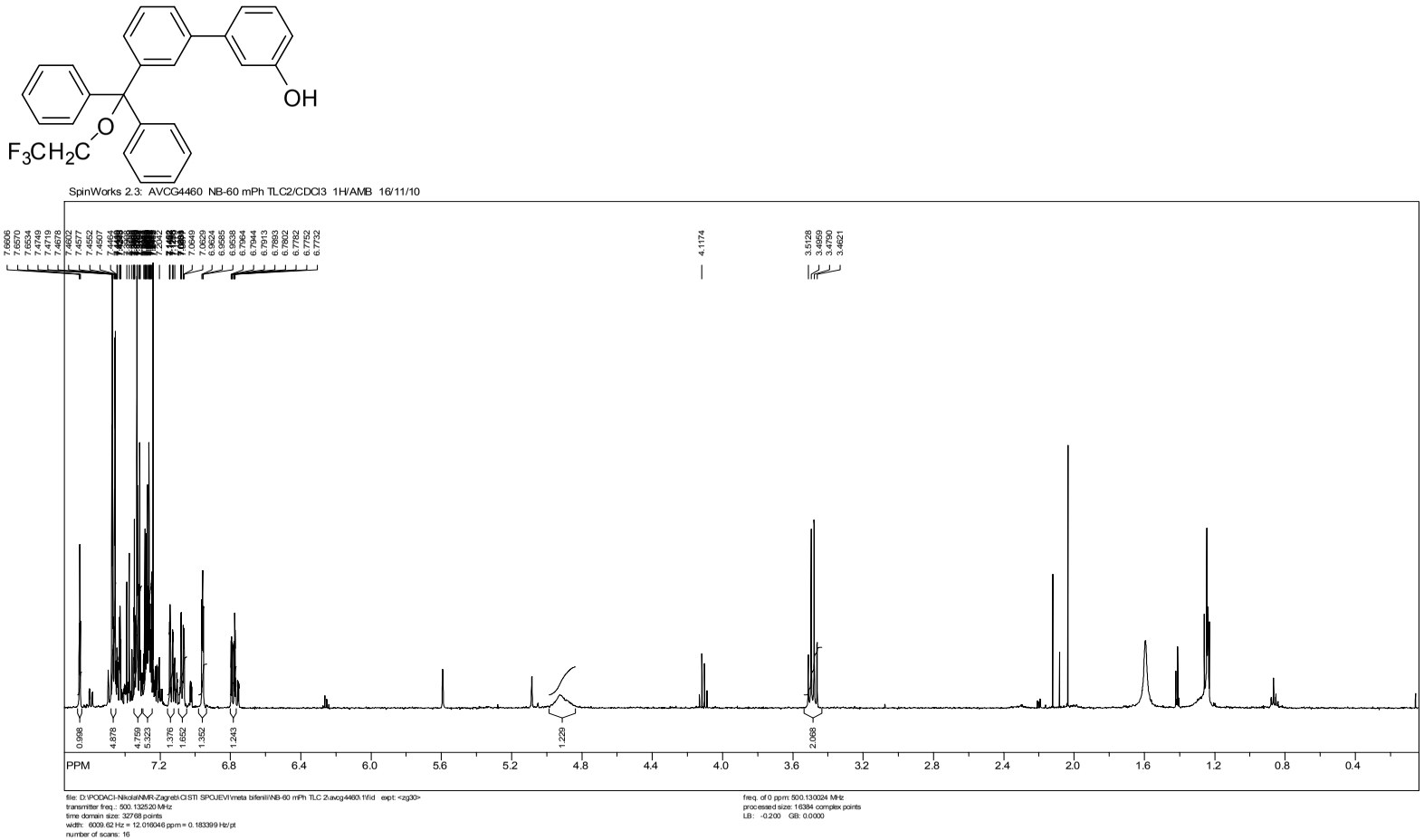
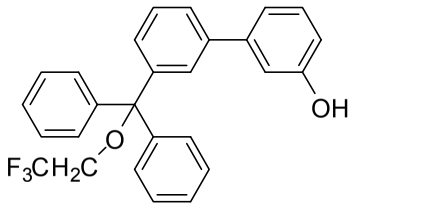
transmitter freq.: 125.771539 MHz
time domain size: 65536 points
width: 30864.20 Hz = 245.398902 ppm = 0.470950 Hz/pt
number of scans: 4096

freq. of 0 ppm: 125.757803 MHz
processed size: 32768 complex points
LB: 1.500 GB: 0.0000

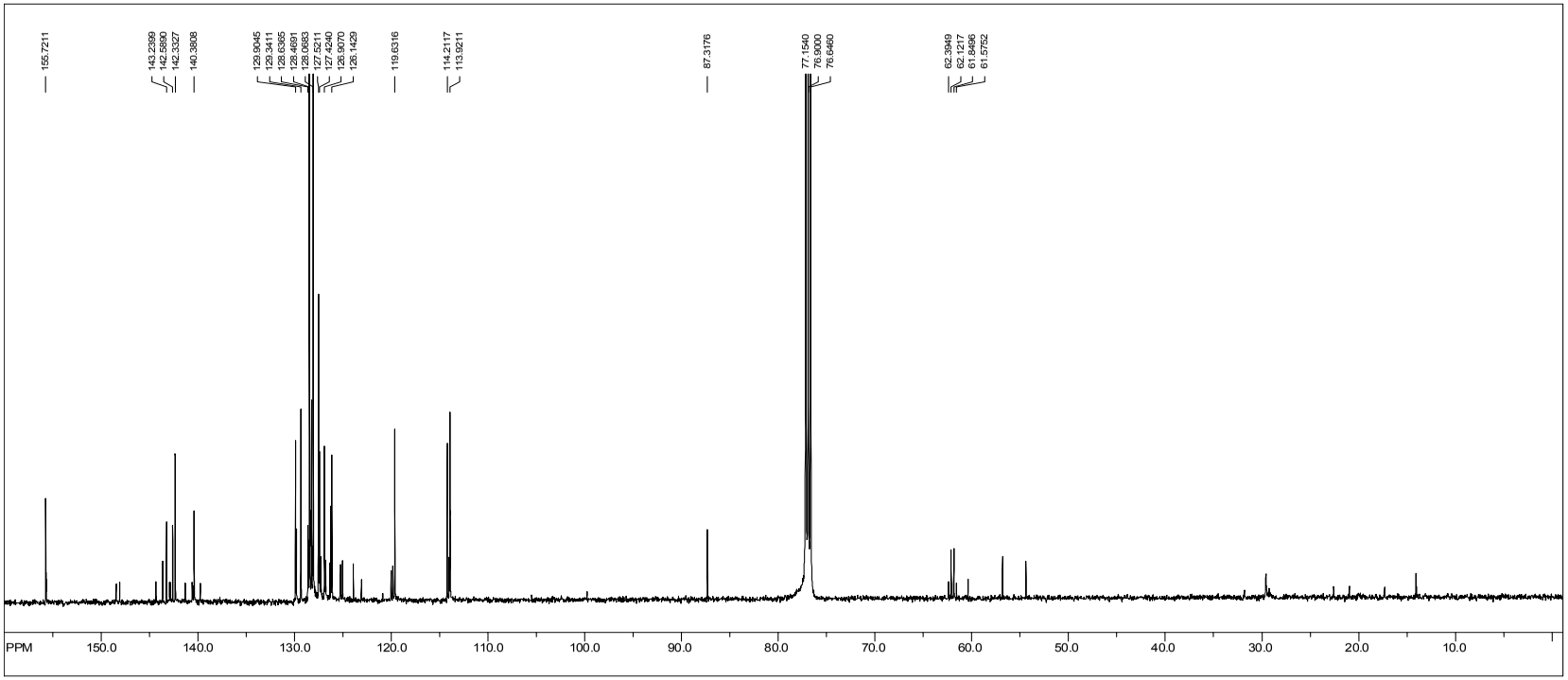
^{1}H NMR ($CDCl_3$, 500 MHz) of **12**



^{13}C NMR ($CDCl_3$, 125 MHz) of **12**



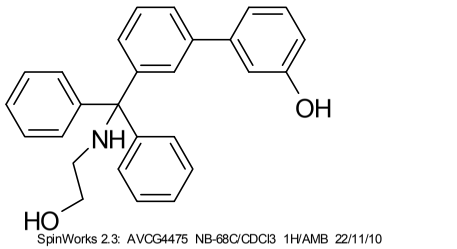
SpinWorks 2.3: AVCG4461 NB-60 mPh TLC2/CDCl3 13C/AMB 16/11/10

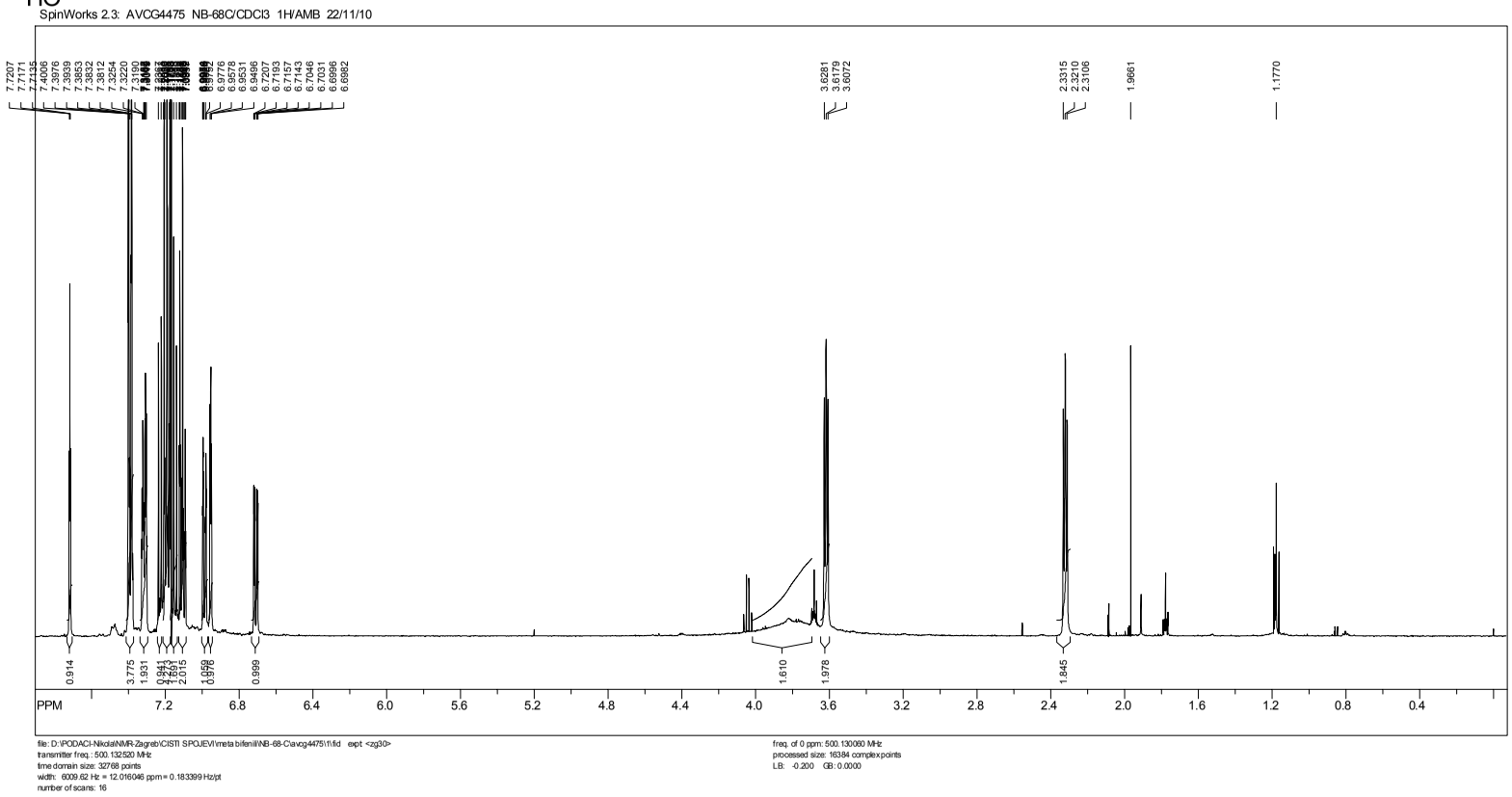


file: D:\PODACI-Nikola\NMR-Zagreb\CISTI SPOJEVI\meta bifenil\NB-60 mPh TLC 2\avcg4461\1\1\fid expt: <zgpg30>
transmitter freq.: 125.771539 MHz
time domain size: 65536 points
width: 30864.20 Hz = 245.398902 ppm = 0.470950 Hz/pt
number of scans: 14799

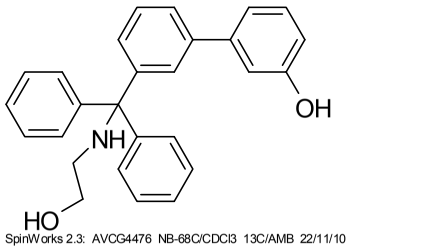
freq. of 0 ppm: 125.757804 MHz
processed size: 32768 complex points
LB: 1.500 GB: 0.0000

^{1}H NMR ($CDCl_3$, 500 MHz) of **14**

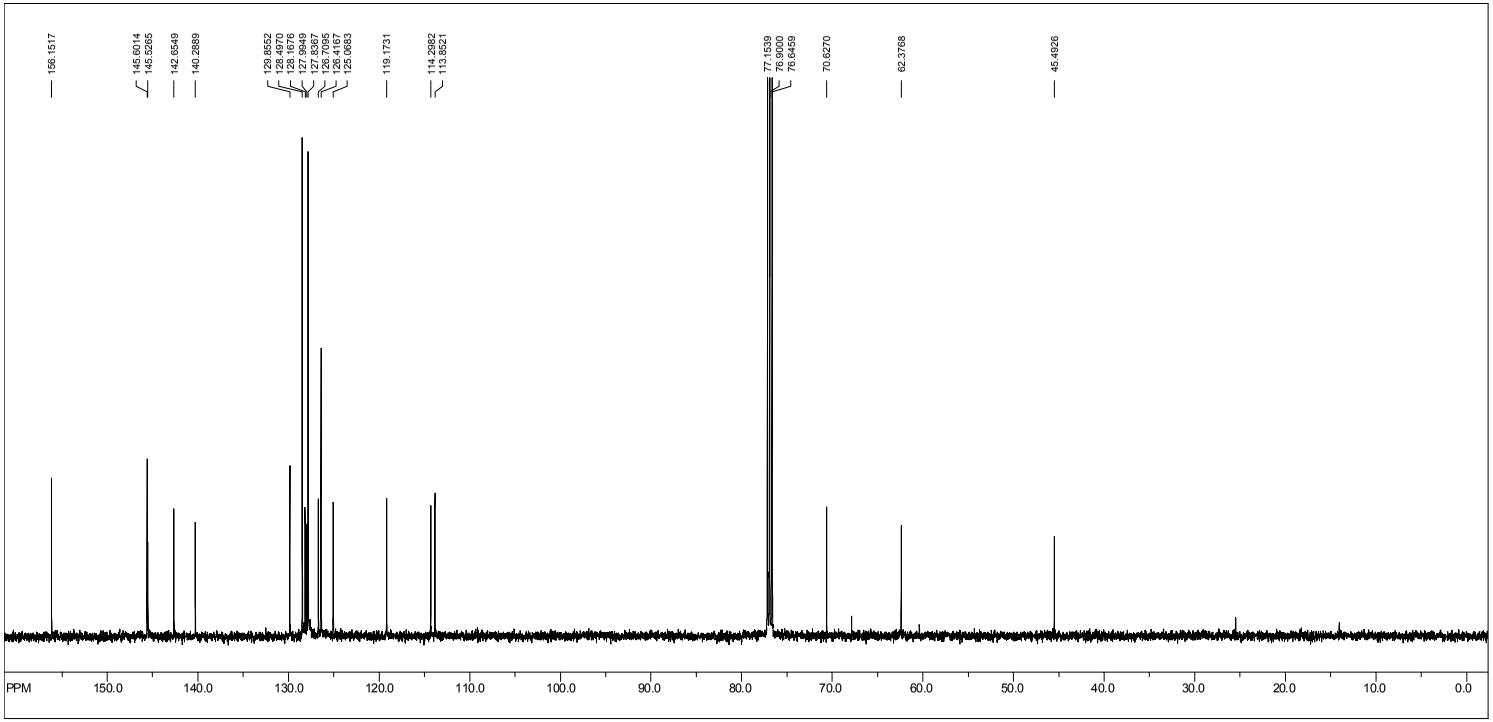




^{13}C NMR ($CDCl_3$, 125 MHz) of **14**



SpinWorks 2.3: AVCG4476 NB-68C/CDCl3 13C/AMB 22/11/10



file: D:\PODACI-Nikola\NMR-Zagreb\CISTI SPOJEVI\meta bifenili\NB-68-C\avcg4476\1\fid expt: <zgpg30>
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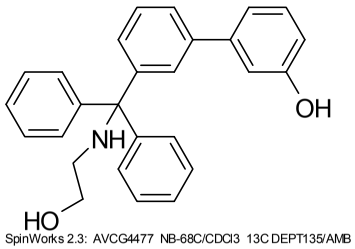
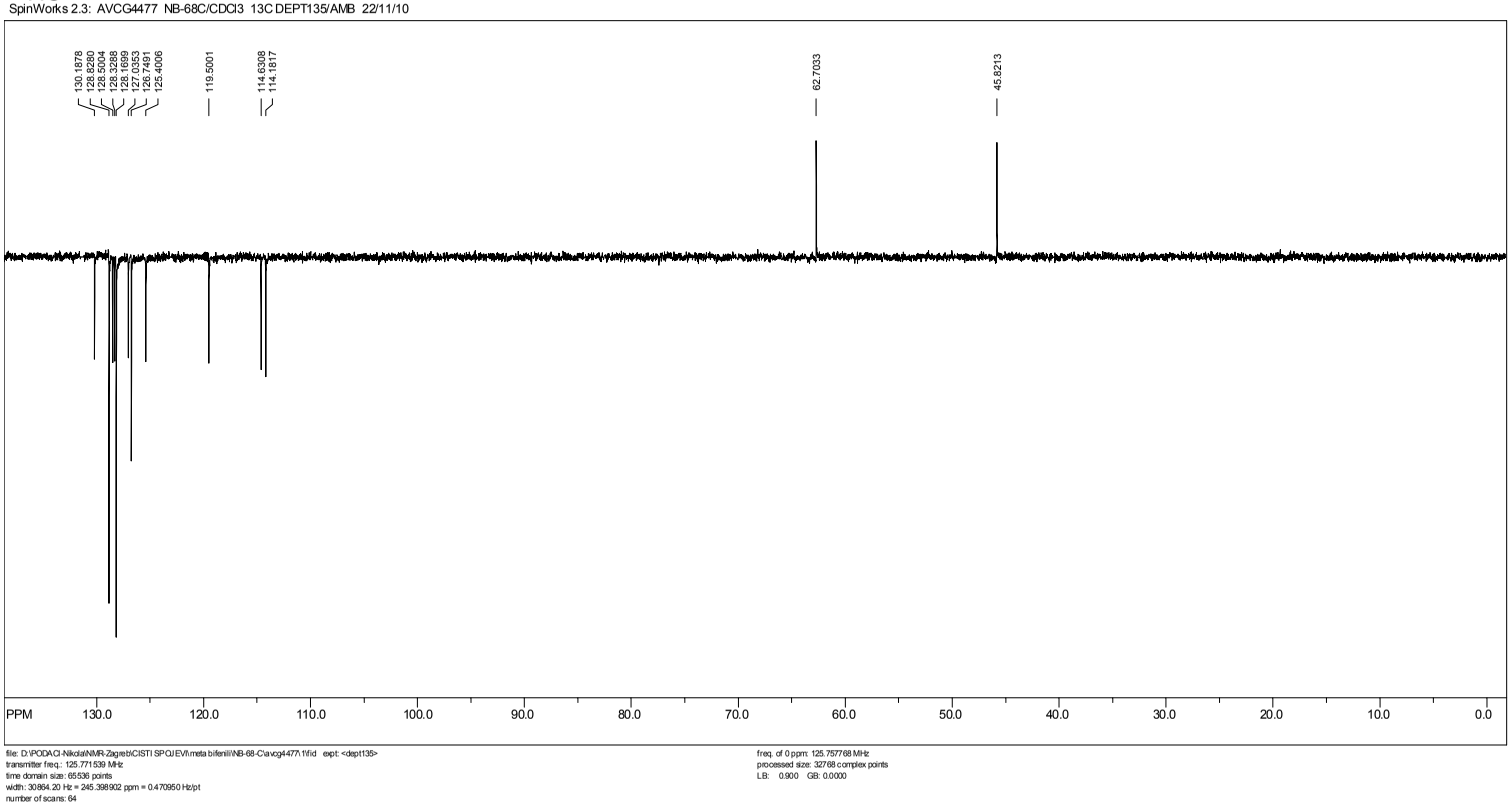
time domain size: 65536 points
width: 30864.20 Hz = 245.398902 ppm = 0.470950 Hz/pt
number of scans: 512

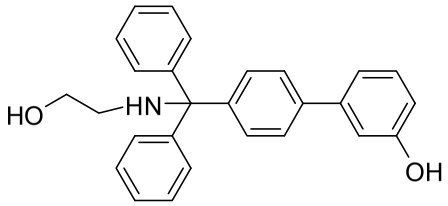
freq. of 0 ppm: 125.757808 MHz
processed size: 32768 complex points
LB: 0.900 GB: 0.0000

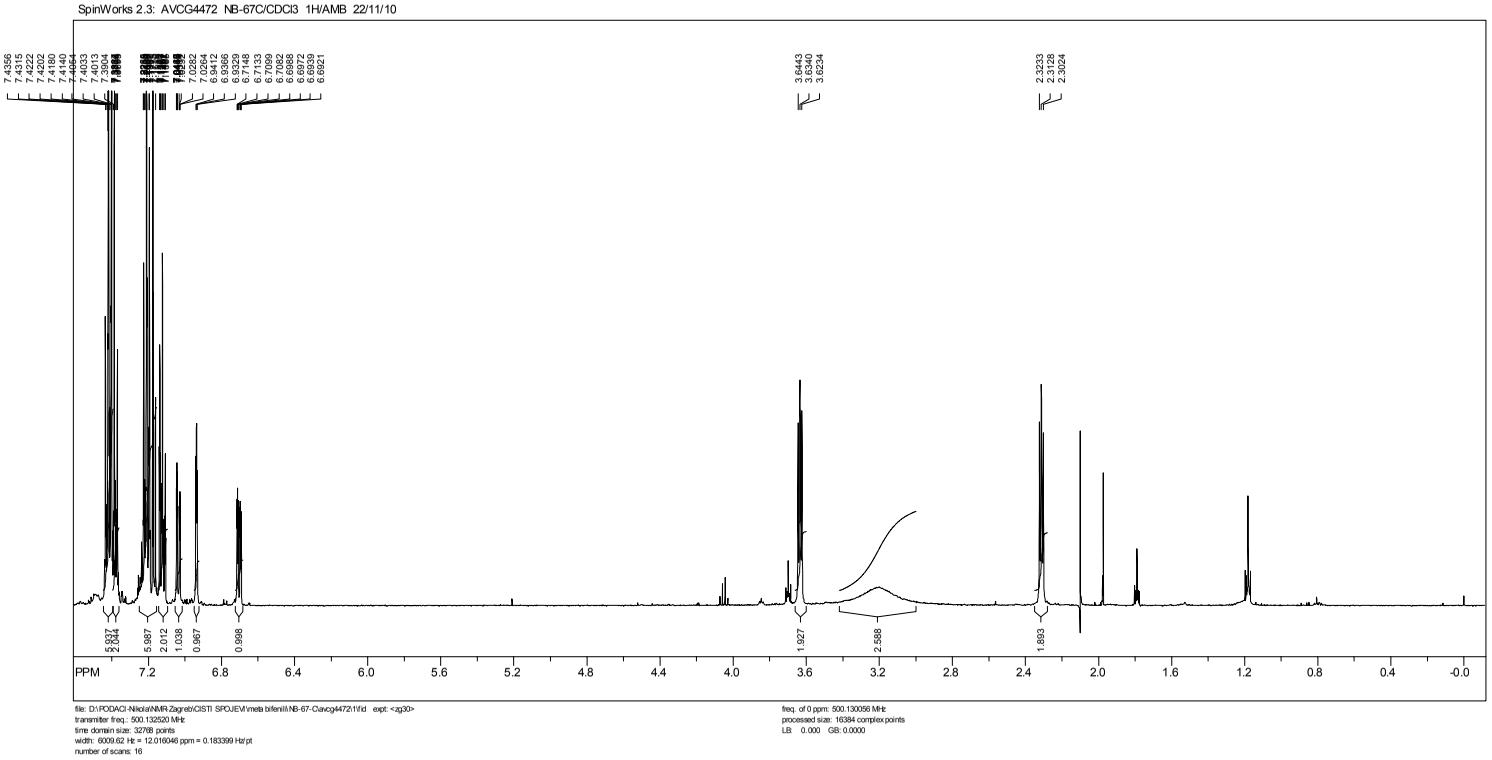
^{13}C NMR ($CDCl_3$, 125 MHz, DEPT) of **14**



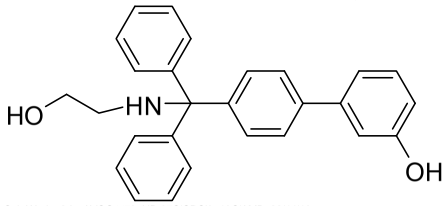


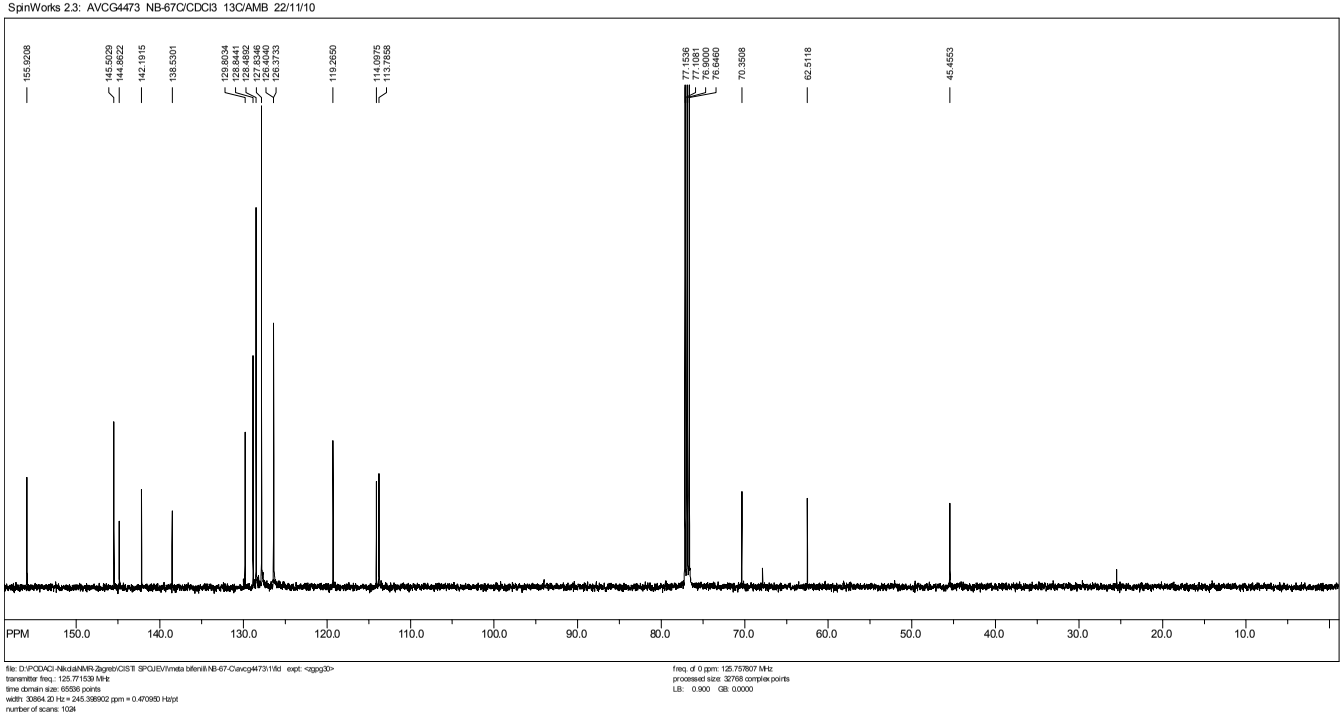
^{1}H NMR ($CDCl_3$, 500 MHz) of **15**



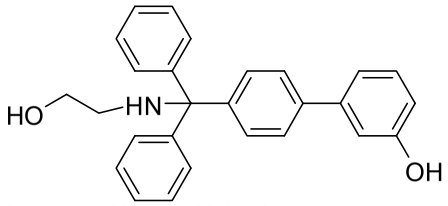


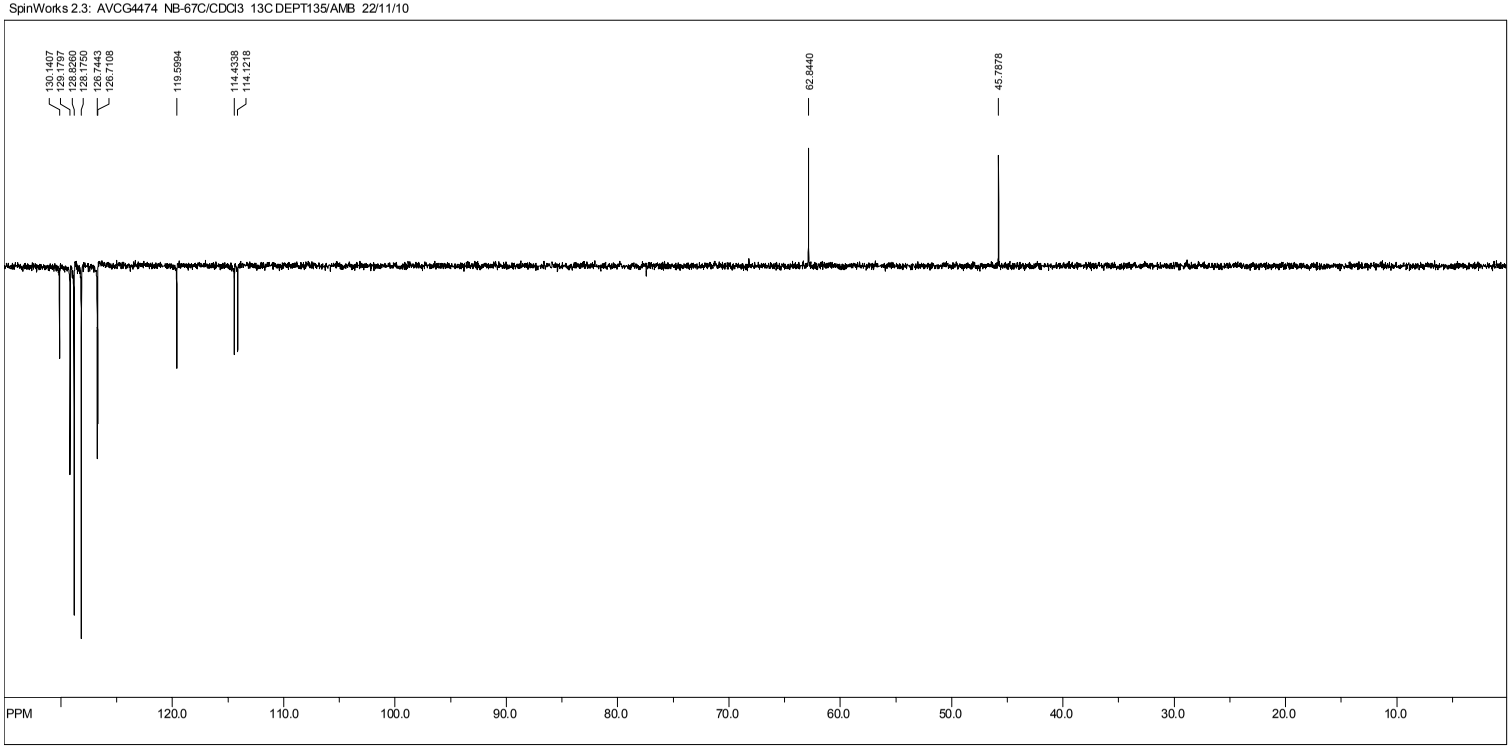
^{13}C NMR ($CDCl_3$, 125 MHz) of **15**





^{13}C NMR ($CDCl_3$, 125 MHz, DEPT) of **15**





file: D:\PODACI-Nikola\NMR-Zagreb\CISTI SPOJEVI\meta bifenil\NB-67-C\avcg4474.1\fid expt: <dept135>
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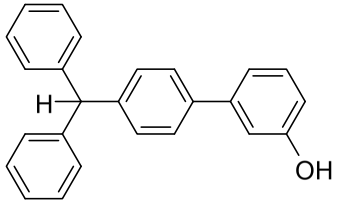
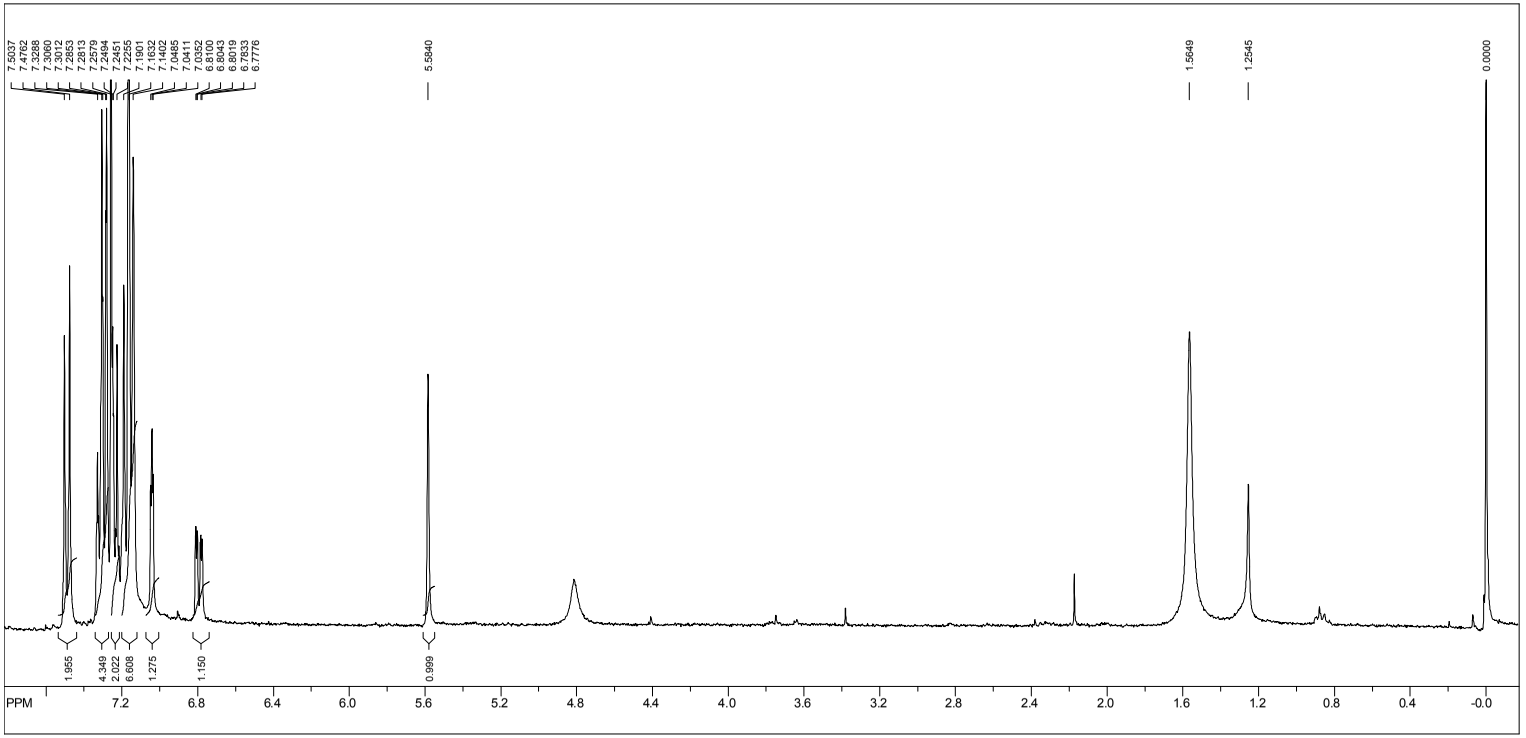
time domain size: 65536 points
width: 30864.20 Hz = 245.398902 ppm = 0.470950 Hz/pt
number of scans: 128

freq. of 0 ppm: 125.757766 MHz
processed size: 32768 complex points
LB: 0.900 GB: 0.0000

^{1}H NMR ($CDCl_3$, 300 MHz) of **16**



SpinWorks 2.3:



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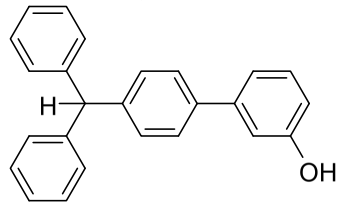
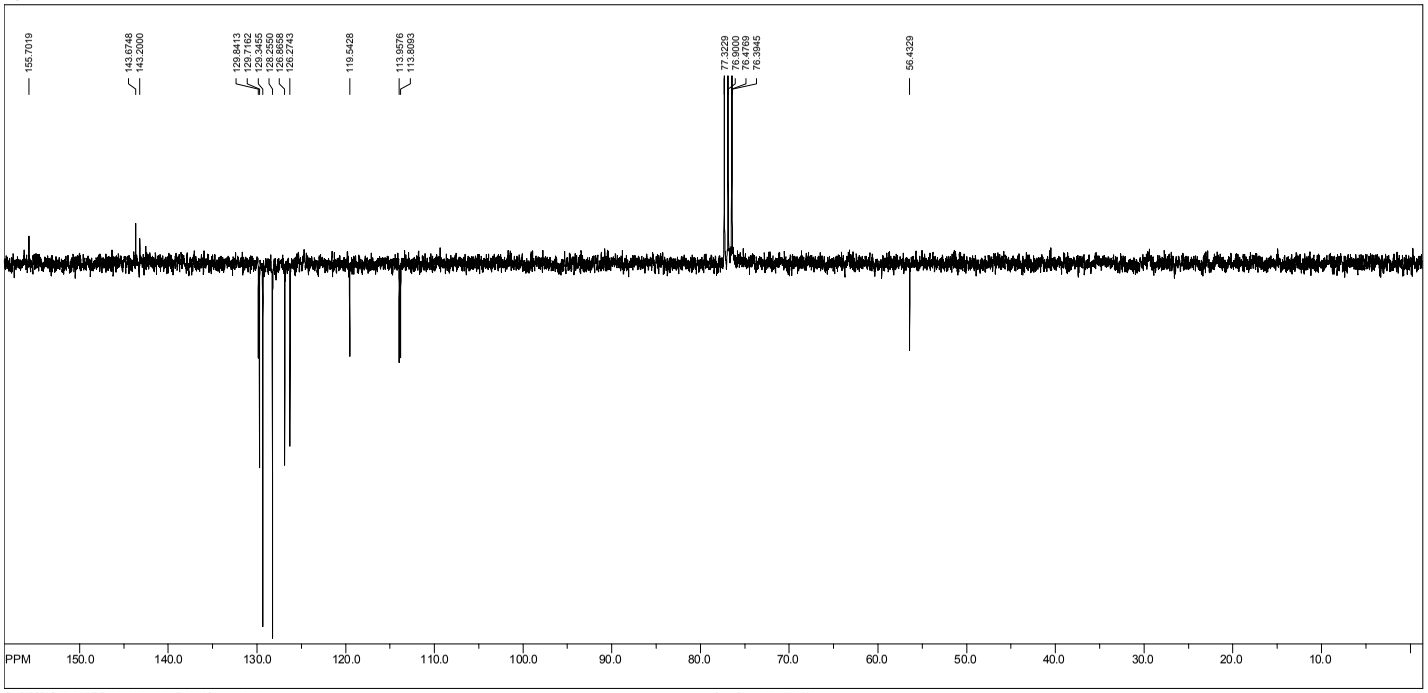
transmitter freq.: 300.132701 MHz
time domain size: 32768 points
width: 6172.84 Hz = 20.567034 ppm = 0.188380 Hz/pt
number of scans: 24

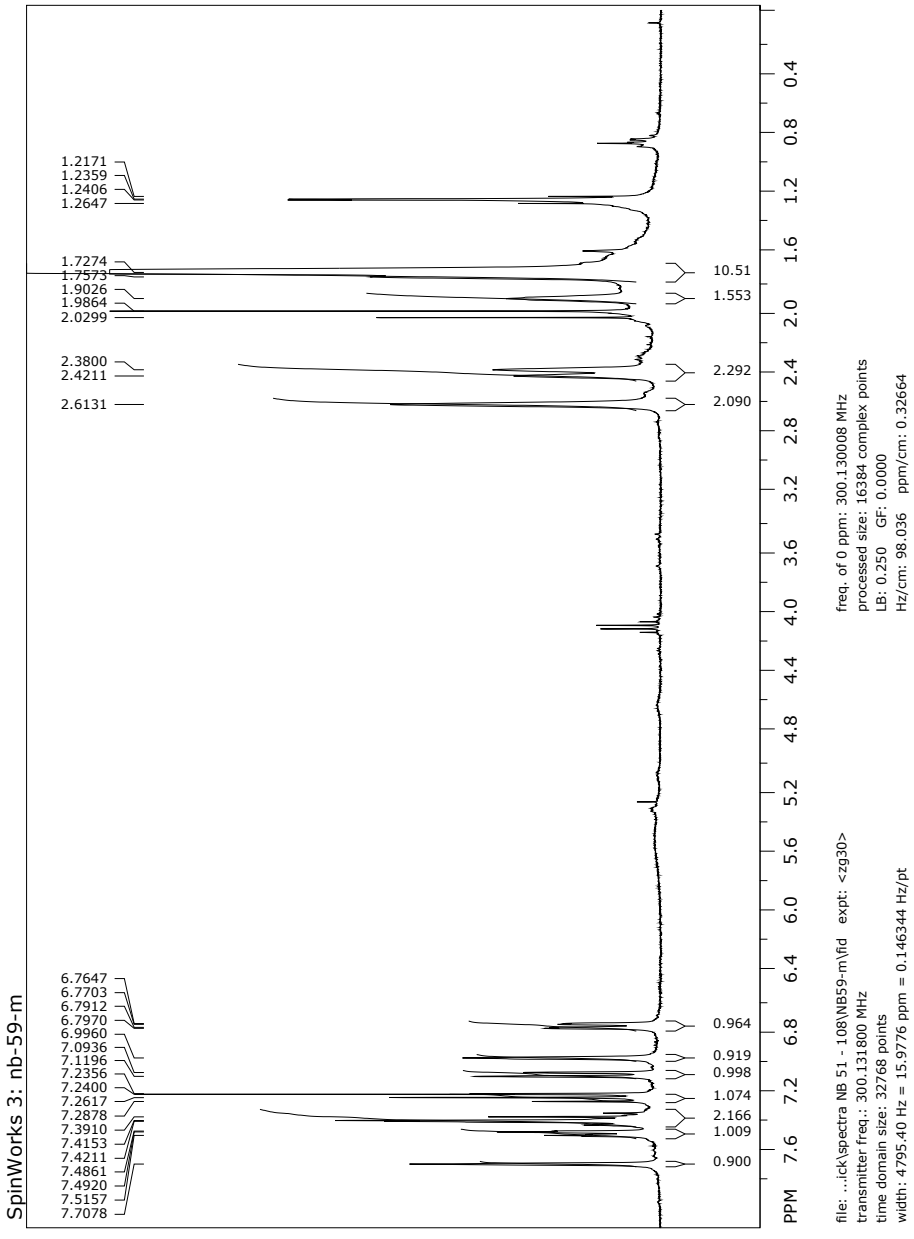
freq. of 0 ppm: 300.130007 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000

^{13}C NMR ($CDCl_3$, 75 MHz) of **16**





^{1}H NMR ($CDCl_3$, 300 MHz) after photolysis of **5** in CH_3CN-D_2O



^{1}H NMR ($CDCl_3$, 300 MHz) after photolysis of **6** in CH_3CN-D_2O