SUPPORTING INFORMATION FOR THE ARTICLE:

TANDEM DIELS-ALDER REACTION OVERRULE ENTROPY: THE GATE TO A THERMALLY STABLE, YET THERMALLY RECYCLABLE FURAN-BASED POLYMERS

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1. General information

Furfural (99.5%) was purchased from "Komponent reaktiv" and purified by vacuum distillation. Sodium borohydride (98%, Acros Organics), aniline (99.8%, Acros Organics), maleic anhydride (99%, Aldrich) was purchased from Aldrich and used as received. Progress of reactions was monitored by thin-layer chromatography using Merck 60 F254 precoated silica gel plate and visualized by short-wave ultraviolet light. Column and flash chromatography were performed with high-purity grade silica gel, pore size 60 Å, 40-63 μm particle size (230-400 mesh).

1) ^{1}H and ^{13}C NMR spectra of the synthesized compounds were recorded for DMSO-d_6 solutions with Bruker Avance 300, 400 and 600 FT-spectrometers (300.15, 400.13 and 600.22 MHz ^{1}H frequency, respectively). Residual signals of DMSO-d_6 (^{1}H 2.50 ppm, ^{13}C 39.5 ppm) were used as references; 2) ATR-FTIR was performed on Nicolet iS10 spectrometer in the range of 4000 to 650 cm^{-1} on germanium crystal; 3) FTIR spectra were recorded on a Bruker IR Fourier spectrometer Tensor 37 with a resolution of 2 cm^{-1} using KBr pellets and solution of the sample in dichloro-methane or carbon tetrachloride for solid compounds. Curve fitting procedure was performed using a Omnic 8 program package; 4) High resolution mass spectra (HRMS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180°C;(1) 5) Elemental analyses was performed using automatic C,H,N analyzer; 6) DSC experiments were performed with a NETZH DSC 204 F1 Phoenix calorimeter within a temperature range of 0 to 300°C with heating rate of 5K min^{-1} in argon atmosphere; 7) X-ray diffraction experiments were carried out at 120 K with a Bruker APEX2 DUO CCD diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å); 8) Thermomechanical analysis (TMA) was performed with a thermomechanical analyzer TMA/SDTA 2+ LN/600 (Mettler-Toledo, Switzerland) at a heating rate of 5°C/min from 0 to 250°C with load 0.01-0.1 N using a quartz stem with a ball point tip (diameter 3 mm); 9) LC-MS (liquid chromatography–mass spectrometry) analysis of the tandem Diels-Alder adducts were performed on Shimadzu LCMS-2020 High Performance Liquid Chromatograph Mass Spectrometer with electrospray ionization (ESI) method and single quadrupole detector (negative and positive ions). Desolvation line/heat block temperature were 250/400°C. Nitrogen (99.5%) was used like nebulizer and drying gas. Acetonitrile (99.9+% HPLC gradient grade, Chem-Lab) were used as mobile phase with flow rate 0.4 ml/min

without any pretreatment. DA adducts (3a-3e) were dissolved in acetonitrile, injection volume 5 µl. The mass range between 100 and 2000 was scanned; 10) Thermogravimetric analysis (TGA) was performed on NETZSCH TG 209 F1 Libra (Selb, Germany) within a temperature range of 30 to 550°C at a heating/cooling rate of 10 K min^{-1} in an argon atmosphere; 11) Gel permeation chromatography (GPC) analyses were performed using a Shimadzu Prominence LC-20 (Kyoto, Japan) apparatus equipped with a RID 20A refractive index detector and three PSS GRAM analytical columns 100 Å (8.0 × 300 mm^2) linked in series, at 65°C, and using N,N-Dimethylacetamide (DMA) containing 0.5 g/L LiBr as the mobile phase at a flow rate of 1.0 mL min^{-1}. Molecular weights reported against polymethylmethacrylate (PMMA) standards.

2. Computational details

The reaction pathways (Scheme 1, Figure 3) were calculated using universal functional PBE0(2) and Def2-TZVP basis set.(3) Temperature dependence of ΔG^{o} for the formation CA and TA adducts (Scheme 1) was calculated using ORCA program(4, 5) at a hybrid calculation level, in which the ΔE_{tot} values for PBE0 optimized geometry were estimated at the DLPNO-CCSD(T)/Def2-TZVP level with the tight PNOs(6), the thermal, vibration and other corrections were calculated at the PBE0/Def2-TZVP level. For acceleration, the RIJCOSX approximation(7-9) with Def2/j(10) fitting basis set was used.

Table S1. The energy values ΔH^{o}_{300} and ΔG^{o}_{300} for classical **(3a, 3b)** and tandem **(5a**, **5b)** DA adducts in the direct Diels-Alder reaction). The calculation was performed at the different calculation level.

Calculation conditions	**PBE0**			**DLPNO-CCSD(T)**		
kcal/mol	ΔE_{tot}	ΔH^{o}_{300}	ΔG^{o}_{300}	ΔE_{tot}	ΔH^{o}_{300}	ΔG^{o}_{300}
			5a (N-Ph)			
TS1	12.9	12.4	28.8	8.3	7.8	24.2
Intermediate	-12.0	-13.0	4.6	-20.0	-20.9	-3.4
TS2	10.3	8.4	28.2	2.8	1.0	20.7
Product	-25.4	-27.6	-7.2	-34.2	-36.5	-16.0
			5b (N-Et)			
TS1	13.0	12.4	28.5	8.8	8.2	24.3
Intermediate	-13.0	-14.1	3.2	-20.5	-21.6	-4.2
TS2	9.4	7.4	26.9	2.5	0.6	20.1
Product	-26.5	-28.8	-8.5	-34.8	-37.2	-16.9
			3a (N-Ph)			
TS1	14.3	13.7	30.0	10.2	9.7	25.9
Product	-9.6	-10.6	6.4	-17.0	-18.0	-1.0
			3b (N-Et)			
TS1	14.2	13.6	29.6	10.6	10.0	25.9
Product	-10.6	-11.6	5.1	-17.6	-18.6	-1.8

Table S2. Activation energy (ΔG‡, kcal/mol) of reverse DA reaction for tandem DA adducts 5a, 5b (DLPNO-CCSD(T)//PBE0).

ΔG, kcal/mol	**5a (N-Ph)**	**5b (N-Et)**
E_{act} (Product to Intermediate)	35.4	35.4
E_{act} (Intermediate to Initial reagents)	23.9	25.3

2.1. Stereochemical features of the tandem DA reaction

ΔE_{tot} of all 4 possible diastereomers of tDA adduct **5a** were calculated (Fig. S1, Table S3) and isomers **A** (*exo-exo*) and **D** (*exo-endo*) were found to be ~15 kcal/mol more stable compared to **B** (endo-endo) and **C** (endo-exo).

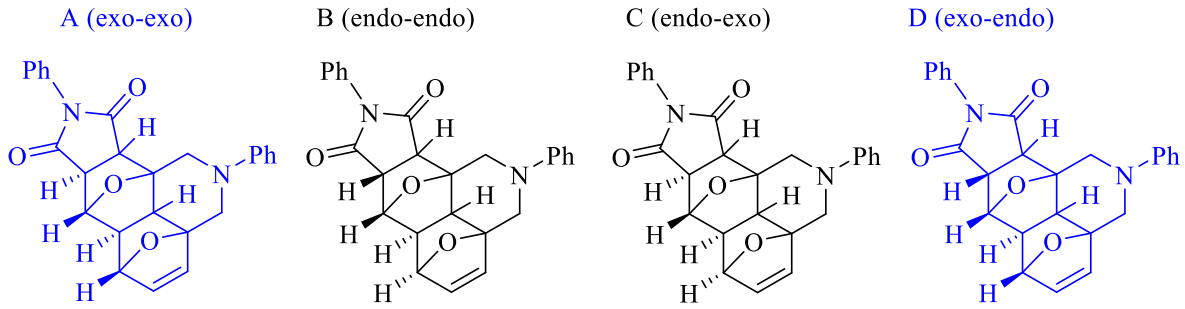


Figure S1. All stereoisomers of compound **5a**

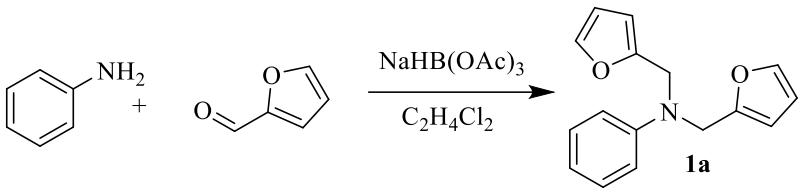
Table S3. ΔE_{tot} (kcal/mol) formation of compound **5a** isomers

Isomers	PBEO	DLPNO-CCSD(T)
exo-exo (A)	**-25.4**	**-40.1**
exo-endo (D)	**-22.2**	**-38.2**
endo-exo (C)	-10.4	-25.1
endo-endo (B)	-7.2	-23.7

The calculation results correlate well with experimental data. All tDA adducts (**5a-e**) were synthesized either as a mixture of *exo-exo* and *exo-endo* isomers or as pure *exo-exo* compounds.

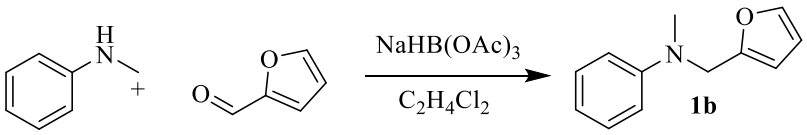
3. Synthesis of furfuryl derivatives

Synthesis of N,N-difurfuryl-aniline **1a**



Acetic acid (5.358 ml) was added dropwise to the solution of sodium borohydride (1.167 g, 30.71 mmol) in 1,2-dichloroethane (50 ml) maintaining the temperature between 0 and 5 °C. Then the reaction mixture was stirred for 3 h at 0 °C. Afterwards, aniline (0.979 ml, 10.75 mmol), furfural (2.065 ml, 21.51 mmol) and molecular sieves (4 Å) were added. The mixture was stirred at room temperature for 24 h. After the reaction completed (TLC monitoring: Rf=0.5, EtOAc - Petroleum ether (1:10)), 50 ml of 0.1 N aq. NaOH was added. The product was extracted with EtOAc (15 mL × 3), the organic layer was washed with water and then dried over sodium sulfate, volatiles were removed under reduced pressure. The product was purified by column chromatography on silica gel eluting with EtOAc - Petroleum ether (1:10) to give a colourless oil (0.650 g, 23%). δ_H(600 MHz; DMSO-d_6) 4.52 (4 H, s, 8-9-H), 6.26 (2 H, d, *J* = 2.6, 11-16-H), 6.38 (2 H, m, 12-17-H), 6.64 (1 H, t, *J* = 7.1, 2-H), 6.88 (2 H, d, *J* = 8.3, 1-3-H), 7.13-7.16 (2 H, t, *J* = 7.9, 4-6-H), 7.58 (2 H, s, 13-18-H). δ_C(151 MHz; DMSO-d_6) 46.72, 107.75, 110.43, 112.96, 116.79, 128.88, 142.33, 147.77, 152.14. Spectra are in agreement with the literature data.(11, 12)

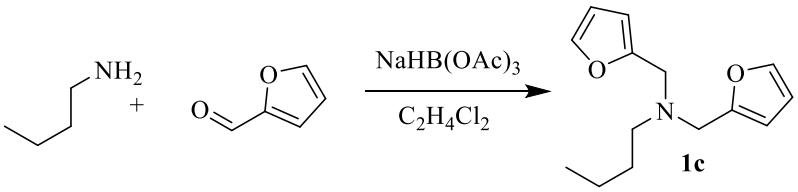
Synthesis of N-2-Furfuryl-N-methylaniline **1b**



Acetic acid (2.328 ml, 4.5 eq.) was added dropwise to the solution of sodium borohydride (0.507 g, 13.34 mmol, 1.5 eq.) in 1,2-dichloroethane (15 ml) maintaining the temperature between 0 and 5 °C. Then the reaction mixture was stirred for 3 h at 0 °C. Afterwards, N-methylaniline (1.010 ml, 9.35 mmol, 1 eq.), furfural (0.773 ml, 9.34 mmol, 1 eq.) and molecular sieves (4 Å) were added. The mixture was stirred at room temperature for 72 h. After the reaction completed (TLC monitoring), 30 ml of 0.1 N aq. NaOH was added. The product was extracted with EtOAc (15 mL × 3), the organic layer was washed with water and then dried over sodium sulfate, volatiles were removed under reduced pressure to give a light yellow oil (1.598 g, 92%). Compound **1b** was used in the next step without further purification. δ_H(600 MHz; $CDCl_3$-d_1) 2.90 (3 H, s, N-Me), 4.37 (2 H, s, 8-H), 6.05 (1 H,

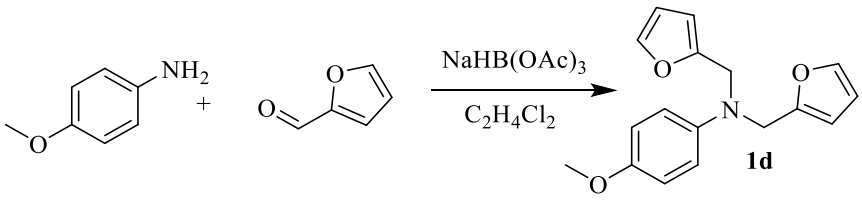
m, 11-H), 6.20 (1 H, m, 12-H), 6.64−6.67 (1 H, t, *J* = 7.2, 2-H), 6.74 (2 H, d, *J* = 8.2, 4-6-H), 7.15 (2 H, t, *J* = 7.6, 1-3-H), 7.26 (1 H, s, 13-H). **δ_C**(151 MHz; $CDCl_3$-*d_1*) 38.42, 49.95, 107.33, 110.26, 113.07, 117.18, 129.20, 141.91, 149.39, 152.38. Spectra are in agreement with the literature data.(13)

Synthesis of N,N-bis(furan-2-ylmethyl)butan-1-amine **1c**



Acetic acid (14.101 ml, 246.58 mmol, 18 eq.) was added dropwise to the solution of sodium borohydride (3.123 g, 82.19 mmol, 6 eq.) in dichloromethane (40 ml) maintaining the temperature between 0 and 5 °C. Then the reaction mixture was stirred for 3h at 0 °C. Afterwards, n-butylamine (1.351 ml, 13.70 mmol, 1 eq.), furfural (6.802 ml, 82.19 mmol, 6 eq.) and molecular sieves (4Å) were added. The mixture was stirred at room temperature for 72 h. After the reaction completed (TLC monitoring), 30 ml of 0.1 N aq. NaOH was added. The product was extracted with EtOAc (20 ml × 3), the organic extracts were washed with water and then dried over magnesium sulfate, volatiles were removed under reduced pressure, followed by flash chromatography on silica gel eluting with EtOAc - Petroleum ether (1:5). Product isolated as a yellow oil (2.150 g, 66%). **δ_H**(600 MHz; DMSO-*d_6*) 0.81 (3 H, t, *J* = 7.4, 16-Me), 1.20-1.26 (2 H, sextet, *J* = 7.4, 16-H), 1.38-1.43 (2 H, m, 15-H), 2.32 (2 H, t, *J* = 7.3, 8-H), 3.56 (4 H, s, 6-9-H), 6.28 (2 H, d, *J* = 3.2, 3-11-H), 6.40 (2 H, m, 2-12-H), 7.59 (2 H, m, 1-13-H). **δ_C**(151 MHz; DMSO-*d_6*) 13.77, 19.83, 28.76, 49.22, 51.83, 108.59, 110.26, 142.32, 152.25. Spectra are in agreement with the literature data.(11, 12, 14)

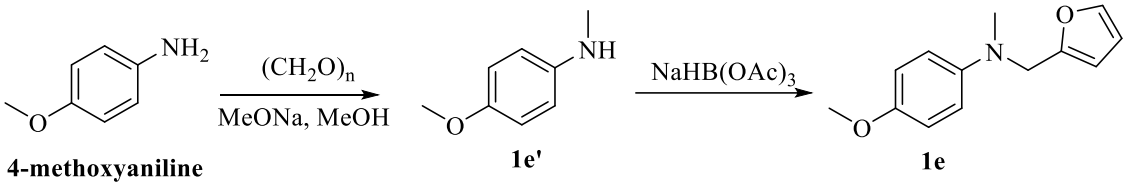
Synthesis of N,N-bis(furan-2-ylmethyl)-4-methoxyaniline **1d**



Acetic acid (5.358 ml) was added dropwise to the solution of sodium borohydride (1.167 g, 30.71 mmol) in 1,2-dichloroethane (50 ml) maintaining the temperature between 0 and 5 °C and the reaction mixture was stirred for 3 h at 0 °C. Afterwards, 4-methoxyaniline (1.353 g, 11.00 mmol), furfural (2.003 ml, 24.20 mmol) and molecular sieves (4 Å) were added. The mixture was stirred at room temperature for 24 h. After the reaction completed (TLC monitoring: Rf=0.6, EtOAc - Petroleum ether (1:5)), 50 ml of 0.1 N aq. NaOH was added. The product was extracted with EtOAc

(15 mL × 3), the organic layer was washed with water and then dried over sodium sulfate, volatiles were removed under reduced pressure. The product was purified by flash column chromatography on silica gel eluting with EtOAc - Petroleum ether (1:5) to give a colourless oil (2.222 g, 71%). δ_H(600 MHz; DMSO-d_6) 3.65 (3 H, s, O-Me), 4.40 (4 H, s, 8-16-H), 6.22 (2 H, d, *J* = 3.0, 10-18-H), 6.36 (2 H, m, 11-19-H), 6.77 (2 H, d, *J* = 9.0, 4-6-H), 6.85 (2 H, d, *J* = 9.0, 1-3-H), 7.56 (2 H, m, 12-20-H). δ_C(151 MHz; DMSO-d_6) 47.50, 55.18, 107.83, 110.36, 114.28, 115.49, 142.24, 142.30, 151.69, 152.27. Spectra are in agreement with the literature data.(15, 16)

N-(furan-2-ylmethyl)-4-methoxy-N-methylaniline **1e**

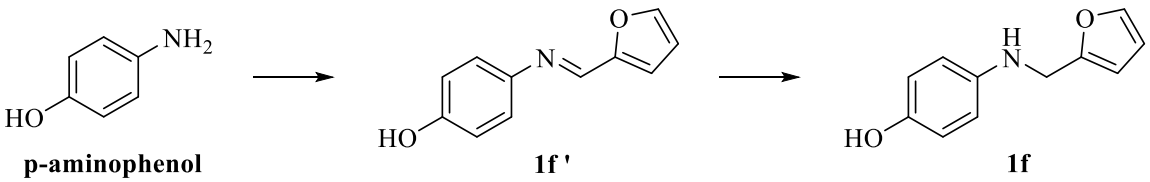


1. To a solution of 4-methoxyaniline (2.044 g, 16.62 mmol, 1 equiv.), paraformaldehyde (1.496 g, 49.85 mmol, 3 eq.) in MeOH (250 ml) was added sodium methoxide solution (3.590 g, 66.40 mmol, 4 eq.) and stirred at 50 °C for 5 hours. Then, sodium borohydride (1.894 g, 49.85 mmol, 3 eq.) was added under argon and the reaction was stirred at room temperature. The reaction mixture was monitored by TLC until 4-methoxyaniline was consumed, the solvent was removed under reduced pressure. The dried crude mixture was washed with aq. NH_4Cl and extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography. N-Methyl-p-anisidine **1e'** was obtained as yellow oil (1.340 g, 61%). δ_H(600 MHz; $CDCl_3$-d_1) 2.81 (3 H, s, N-Me), 3.34 (1 H, br.s, NH), 3.77 (3 H, s, O-Me), 6.59-6.62 (2 H, m, 4-6-H), 6.82 (2 H, m, 1-3-H). δ_C(151 MHz; $CDCl_3$-d_1) 31.67, 55.87, 113.71, 114.92, 143.72, 152.10. Spectra are in agreement with the literature data.(17)

2. Acetic acid (1.279 ml, 4.5 eq.) was added dropwise to the solution of sodium borohydride (0.239 g, 7.34 mmol, 1.5 eq.) in 1,2-dichloroethane (15 ml) maintaining the temperature between 0 and 5 °C. Then the reaction mixture was stirred for 3 h at 0 °C. Afterwards, 4-methoxy-N-methylaniline (0.670 ml, 4.89 mmol, 1 eq.) **1e'** and furfural (0.404 ml, 7.34 mmol, 1 eq.) were added. The mixture was stirred at room temperature for 48 h. After the reaction completed, 30 ml of 0.1 N aq. NaOH was added. The product was extracted with EtOAc (15 mL × 3), the combined organic layers were washed with water and then dried over sodium sulfate, volatiles were removed under reduced pressure to give a light yellow oil (0.860 g, 81%). Compound **1e** was used in the next step without further purification. δ_H(400 MHz; DMSO-d_6) 2.83 (3 H, m, N-Me), 3.65 (3 H, m, O-Me), 4.39 (2 H, s, 8-H), 6.19 (1 H, m, 12-H), 6.34 (1 H, m, 13-H), 6.77 (4 H, m, Ph), 7.53 (1 H, m, 10-H). δ_C(101 MHz;

DMSO-d_6) 38.70, 49.41, 55.23, 91.17, 107.70, 110.26, 114.38, 114.67, 142.17, 151.34, 152.32. Spectra are in agreement with literature data.(18)

N-Furfuryl-p-aminophenol **1f**



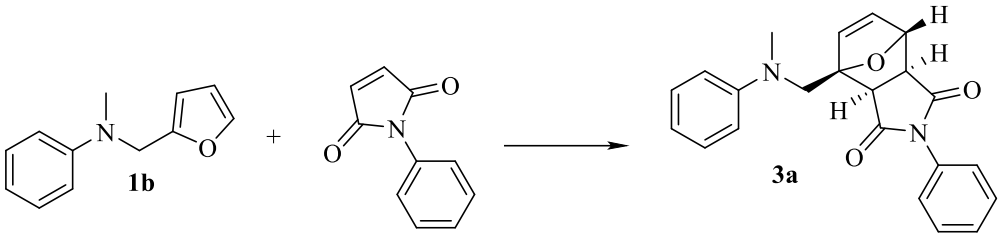
p-aminophenol **1f '** **1f**

1. To a solution of p-aminophenol (0.589 g, 5.40 mmol) in MeOH (30 ml) was added furfural (0.519 g, 5.40 mmol) and mixture stirred at room temperature for 24 h. The reaction was carried out in the presence of molecular sieves (4 Å) and p-toluenesulfonic acid. Afterwards, the molecular sieves were filtered, and then the volume of the solvent was halved under reduced pressure. The reaction mixture was cooled to 0 °C. The resulting precipitate was filtered, washed with cold diethyl ether and dried to obtain compounds **1f'** as a beige solid (0.575 g, 57%). δ_H(400 MHz; DMSO-d_6) 6.67 (1 H, m, 11-H), 6.78-6.82 (2 H, d, *J* = 8.8, 4-6-H), 7.06 (1 H, d, *J* = 3.5, 10-H), 7.16-7.20 (2 H, d, *J* = 8.7, 1-3-H), 7.89 (1 H, s, 12-H), 8.42 (1 H, s, OH), 9.56 (1 H, s, 8-H). δ_C(101 MHz; DMSO-d_6) 112.39, 115.49, 115.76, 122.44, 142.32, 145.14, 145.77, 152.37, 156.40. **HRMS (ESI)**: calculated for $C_{11}H_9NO_2$ (M+H) 188.0713, found: 188.0706.

2) To a solution of the compound **1f'** (0.300 g, 1.60 mmol) in 5 ml of 20% aq. NaOH zinc dust (3 eq., 0.313 g, 4.81 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. The excess of the zinc dust was decanted and the solution was neutralized with acetic acid. The resulting precipitate was filtered, washed with cold water and dried to obtain compound **1f** as a beige solid (0.300 g, 99%). δ_H(600 MHz; DMSO-d_6) 4.13 (2 H, d, *J* = 6.1, 8-H), 5.34-5.38 (1 H, t, *J* = 6.2, NH), 6.24 (1 H, dd, J_1 = 1.0, J_2 = 3.2, 11-H), 6.36 (1 H, m, 10-H), 6.47-6.56 (4 H, m, Ph), 7.54 (1 H, m, 12-H), 8.42 (1 H, s, OH). δ_C(151 MHz; DMSO-d_6) 41.01, 106.62, 110.30, 113.76, 115.56, 141.18, 141.69, 148.58, 153.91. **HRMS (ESI)**: calculated for $C_{11}H_{11}NO_2$ (M+H) 190.0863, found: 190.0863. The synthesis was reproduced from «Syntheses and reactions of furan substances»(19), but no spectroscopic data were found in the literature for comparison.

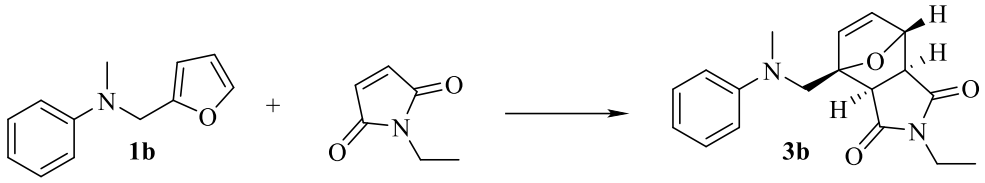
4. Synthesis of classic and tandem adducts of Diels-Alder reaction

Synthesis of **3a**



N-phenylmaleimide (0.278 g, 1.60 mmol) was added to the solution of N-2-Furfuryl-N-methylaniline **1b** (0.300 g, 1.60 mmol) in THF (5 ml). The reaction mixture was refluxed for 24 h, cooled to room temperature, and volatiles were removed under reduced pressure. The product **3a** was isolated by column chromatography on silica gel ($Rf_{(endo)}$ = 0.1, $Rf_{(exo)}$ = 0, eluent-1 – EtOAc - Petroleum ether (1:5); $Rf_{(endo)}$ = 0.6, $Rf_{(exo)}$ = 0.4, eluent-2 – EtOAc - Petroleum ether (1:1)). There were obtained two isomers (exo-, endo-) of the product **3a**. Product **3a-exo** was obtained as a white powder (0.107 g, 19%). **δ_H**(600 MHz; DMSO-*d_6*, ***exo-isomer***) 2.93 (3 H, s, N-Me), 3.21-3.24 (2 H, m, 10-11-H), 3.64-3.67 (1 H, d, J_1 = 16.4, 8'-H), 4.36-4.39 (1 H, d, J_1 = 16.3, 8''-H), 5.21 (1 H, d, *J* = 1.6, 12-H), 6.39 (1 H, d, *J* = 5.8, 14-H), 6.55 (1 H, m, 13-H), 6.61-6.64 (1 H, t, J_1 = 7.3, 2-H), 6.81 (2 H, d, J_1 = 8.1, 1-3-H), 7.15-7.18 (2 H, m, 4-6-H), 7.26 (2 H, m, 22-26-H), 7.44 (1 H, m, 24-H), 7.52 (2 H, m, 23-25-H). **δ_C**(151 MHz; DMSO-*d_6*) 38.84, 48.99, 50.33, 51.05, 80.47, 92.21, 112.00, 115.98, 126.96, 128.53, 128.94, 129.07, 132.15, 137.25, 137.94, 149.60, 174.54, 175.56. **HRMS (ESI):** calculated for $C_{22}H_{20}N_2O_3$ (M+H) 361.1557, found: 361.1547.

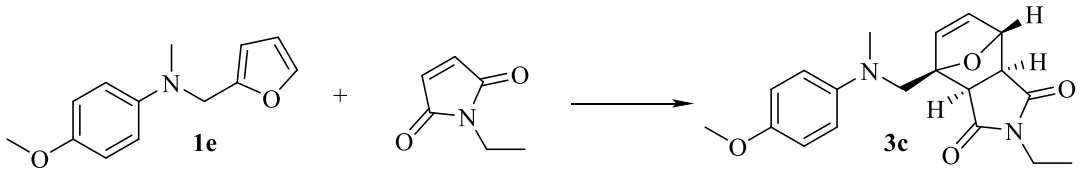
Synthesis of **3b**



N-Ethylmaleimide (0.204 g, 1.63 mmol) was added to the solution of N-2-Furfuryl-N-methylaniline **1b** (0.305 g, 1.63 mmol) in THF (1 ml). The reaction mixture was refluxed for 3 days, and volatiles were removed under reduced pressure. The obtained oil was left in an oven at 70 °C for 10 days. The product **3b** was isolated by column chromatography on silica gel (Rf(endo) = 0.1, Rf(exo) = 0, eluent-1 – EtOAc - Petroleum ether (1:5); Rf(endo) = 0.6, Rf(exo) = 0.4, eluent-2 – EtOAc - Petroleum ether (1:2)). Product **3b-exo** was obtained as white powder (0.319 g, 64%). **δ_H**(600 MHz; DMSO-*d_6*, ***exo-isomer***) 1.06 (3 H, t, *J* = 7.2, 21-Me), 2.89 (3 H, s, N-Me), 3.04 (2 H, m, 11-H), 3.40-3.43 (2 H, q, *J* = 6.4, 21-H), 3.55-3.58 (1 H, d, *J* = 16.1, 8''-H), 4.29-4.32 (1 H, d, *J* = 16.3, 8'-H), 5.10 (1 H, d, *J* = 1.8, 12-H), 6.34 (1 H, d, *J* = 5.7, 13-H), 6.50 (1 H, m, 14-H), 6.61 (1 H, t, *J* = 7.2, 2-H), 6.76 (2 H, d, *J* = 8.0, 4-6-H), 7.14 (2 H, m, 1-3-H). **δ_C**(151 MHz; DMSO-*d_6*) 12.82, 32.96, 38.78, 48.67, 49.99, 50.98, 80.18,

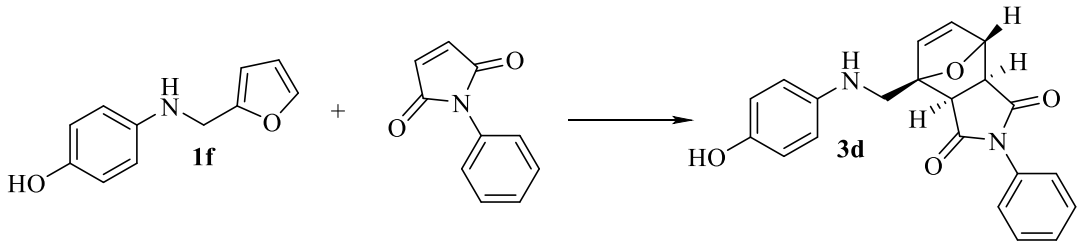
91.87, 111.94, 115.94, 128.88, 137.07, 137.77, 149.58, 175.10, 176.13. **HRMS (ESI):** calculated for $C_{18}H_{20}N_2O_3$ (M+H) 313.1543, found: 313.1547.

Synthesis of **3c**



N-Ethylmaleimide (0.174 g, 1.39 mmol) and N-(furan-2-ylmethyl)-4-methoxy-N-methylaniline **1e** (0.302 g, 1.39 mmol) were added to the flask. The reaction was carried out in an oven at 70 °C for 7 days. Then the reaction mixture was cooled to room temperature. The product **3c** was isolated by column chromatography on silica gel ($Rf_{(endo)}$ = 0.5, $Rf_{(exo)}$ = 0.3, eluent – EtOAc - Petroleum ether (1:2)). Product **3c-exo** was obtained as yellowish oil (0.164 g, 35%). **δ_H**(600 MHz; DMSO-*d_6*, ***exo-isomer***) 1.03-1.07 (3 H, t, *J* = 7.1, 21-Me), 2.83 (3 H, s, N-Me), 2.99-3.04 (2 H, q, J_1 = 6.4, J_2 = 4.6, 10-11-H), 3.37-3.47 (3 H, m, 8''-21-H), 3.65 (3 H, m, O-Me), 4.19-4.23 (1 H, d, J_1 = 16.2, 8'-H), 5.09 (1 H, m, 12-H), 6.33-6.35 (1 H, m, 14-H), 6.49 (1 H, m, 13-H), 6.72-6.79 (4 H, m, Ph). **δ_C**(151 MHz; DMSO-*d_6*) 12.84, 32.96, 39.31, 48.73, 49.98, 52.33, 55.27, 80.18, 91.94, 113.73, 114.41, 136.81, 137.95, 144.55, 151.03, 175.11, 176.17. **HRMS (ESI):** calculated for $C_{19}H_{22}N_2O_4$ (M+H) 343.1652, found: 343.1654.

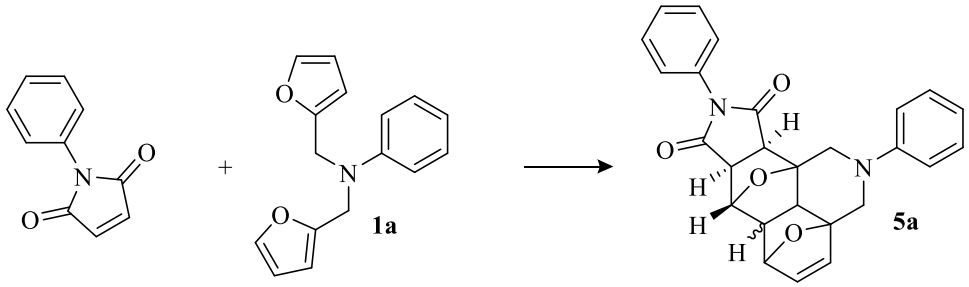
Synthesis of **3d**



N-phenylmaleimide (0.326 g, 1.89 mmol) was added to the solution of **1f** (0.357 g, 1.89 mmol) in THF (5 ml). The reaction mixture was refluxed for 7 days and cooled to room temperature. The precipitate was filtered, washed with a small amount of cold THF and dried overnight in a desiccator. Product **3d** was obtained as a white powder (0.260 g, 38%). **δ_H**(600 MHz; DMSO-*d_6*, ***exo-isomer***) 3.16 (1 H, d, *J* = 6.4, 10-H), 3.26 (1 H, d, *J* = 6.4, 11-H), 3.40-3.43 (1 H, dd, J_1 = 5.2, J_2 = 13.8, 8''-H), 3.75-3.78 (1 H, dd, J_1 = 6.9, J_2 = 13.7, 8'-H), 4.82 (1 H, t, *J* = 5.9, NH), 5.23 (1 H, s, 12-H), 6.54-6.61 (6 H, m, 1-2-4-5-13-14-H), 7.23 (2 H, d, *J* = 7.6, 19-23-H), 7.41-7.44 (1 H, t, *J* = 7.4, 21-H), 7.48-7,51 (2 H, t, *J* = 7.5, 20-22-H), 8.47 (1 H, s, OH). **δ_C**(151 MHz; DMSO-*d_6*) 43.90, 48.60, 50.46, 80.64, 91.30, 114.05,

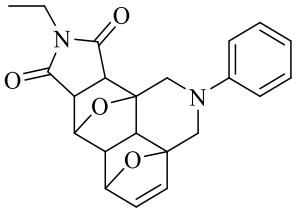
115.58, 126.87, 128.45, 128.99, 132.12, 136.89, 138.49, 141.54, 148.77, 174.36, 175.58. **HRMS (ESI):** $C_{17}H_{18}N_2O_3$ (M+H) 363.1333, calculated: 363.1339.

Synthesis of **5a**



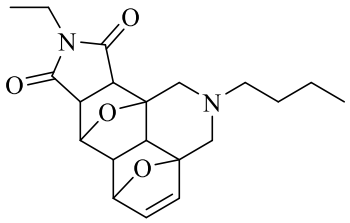
N-phenylmaleimide (0.431 g, 2.49 mmol) was added to the solution of N,N-difurfuryl-aniline **1a** (0.630 g, 1.60 mmol) in THF (5 ml). The reaction mixture was stirred at room temperature for 3 days. The precipitate was filtered, washed with a small amount of cold THF and dried overnight in a desiccator to give product **5a** as a white powder (0.495 g, 47%). δ_H(600 MHz; DMSO-*d*$_6$, ***exo-exo-isomer***) 2.00 (1 H, d, *J* = 6.3, 15-H), 2.23 (1 H, d, *J* = 6.4, 14-H), 3.22 (1 H, d, *J* = 6.2, 11-H), 3.32 (1 H, d, *J* = 7.1, 10-H), 3.49-3.55 (2 H, m, 34-H, 36-H), 3.96-3.99 (1 H, d, *J* = 15.2, 33-H), 4.14 (1 H, d, *J* = 14.0, 35-H), 4.73 (1 H, s, 13-H), 4.93 (1 H, s, 22-H), 6.41 (1 H, d, *J*=5.2, 24-H), 6.48 (1 H, d, *J*=6.1, 23-H), 6.71 (1 H, t, *J* = 7.2, 5-H), 6.89 (2 H, d, *J* = 7.2, 1-3-H), 7.17 (2 H, t, *J* = 7.2, 4-6-H), 7.23 (2 H, d, *J* = 8.3, 28-32-H), 7.43 (1 H, t, *J* = 8.3, 30-H), 7.51 (2 H, t, *J* = 8.3, 29-31-H). δ_C(151 MHz; DMSO-*d*$_6$) 47.27, 47.60, 48.06, 49.03, 51.34, 51.50, 80.36, 80.81, 82.74, 84.51, 115.85, 118.22, 126.90, 128.47, 128.94, 129.03, 132.22, 137.99, 150.99, 174.64, 176.45. To clarify the relative configuration of protons 33-36 the NOESY-experiment was carried out. According to ^{1}H-NMR spectra, there was 20% of the *endo-exo* isomer in the investigated sample. The full identification of the minor isomer was impossible due to signal overlap. **IR** vmax/cm^{-1} (tablet KBr) 2970, 2823, 1776, 1714, 1600, 1497, 1447, 1393, 1243, 1141, 979, 947, 693. **Elemental analysis.** Found: C, 73.06; H, 5.16; N, 6.50. Calc. for $C_{26}H_{22}N_2O_4$: C, 73.23; H, 5.20; N, 6.57%. **X-ray:** it was received X-ray crystallography data for the exo-exo isomer.

Synthesis of **5b**



N-Ethylmaleimide (0.087 g, 0.70 mmol) was added to the compound **1a** (0.177 g, 0.70 mmol). The reaction mixture was heated for 30 hours at 100 °C. The reaction was carried out until the complete crystallization of the reaction mixture. The reaction mixture was shown to be pure product (3c). Product **5b** was obtained as a white solid (0.264 g, 99%). δ_H(600 MHz; DMSO-d_6, ***exo-exo-isomer***) 1.02 (3 H, t, *J* = 7.3, 27-Me), 1.91 (1 H, d, *J* = 6.5, 10-H), 2.13 (1 H, d, *J* = 6.5, 13-H), 3.02 (1 H, d, *J* = 6.7, 17-H), 3.14 (1 H, d, *J* = 6.7, 18-H), 3.37-3.40 (2 H, m, 27-H), 3.47-3.50 (2 H, dd, J_1 = 5.9, J_2 = 13.6, 8'-12'-H), 3.89-3.92 (1 H, d, *J* = 14.6, 8''-H), 4.12 (1 H, d, *J* = 14.3, 12'-H), 4.60 (1 H, s, 19-H), 4.88 (1 H, d, *J*=1.8, 14-H), 6.38 (1 H, d, *J*=5.7, 16-H), 6.45 (1 H, dd, J_1 = 1.6, J_2 = 5.5, 15-H), 6.70 (1 H, t, *J* = 7.1, 2-H), 6.84 (2 H, d, *J* = 8.2, 4-6-H), 7.15-7.18 (2 H, t, *J* = 7.5, 1-3-H). δ_C(151 MHz; DMSO-d_6) 12.76. 33.03, 47.28, 47.43, 47.97, 48.94, 50.96, 51.08, 80.28, 80.36, 82.33, 84.41, 115.50, 115.66, 118.08, 128.87, 137.91, 150.92, 175.13, 176.87. **ATI-FTIR:** 2978, 1767, 1692, 1596, 1496, 1405, 1246, 1141, 983, 949, 695. **HRMS (ESI):** found for $C_{22}H_{22}N_2O_4$ (M+Na) 401.1486, calculated: 401.1472.

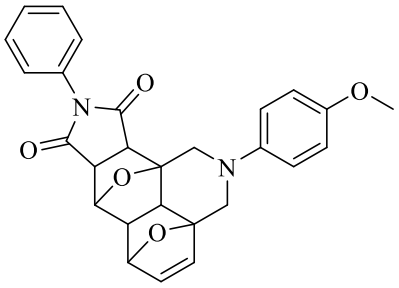
Synthesis of **5c**



N-Ethylmaleimide (0.268 g, 2.15 mmol) was added to the compound **1c** (0.500 g, 2.15 mmol). The reaction mixture was heated for 30 hours at 60 °C. The reaction was carried out until the complete crystallization of the reaction mixture. The reaction mixture was shown to be pure product **5c**. Product **5c** was obtained as a white solid (0.768 g, 100%). δ_H(600 MHz; DMSO-d_6, ***exo-exo-(maj.)- and exo-endo-(min.)-isomer***) 0.85-0.89 (3 H, m, 2-$Me_{maj+min}$), 0.94 (3 H, t, *J*=7.1, 25-Me_{min}), 0.97-1.03 (3 H, t, *J*=6.9, 25-Me_{maj}), 1.22-1.30 (2 H, m, $2_{maj+min}$-H), 1.35-1.45 (2 H, m, $3_{maj+min}$-H), 1.70 (1 H, d, *J* = 6.6, 8_{maj}-H), 1.74 (1 H, d, *J* = 6.6, 8_{min}-H), 2.07 (1 H, d, *J* = 6.6, 11_{maj}-H), 2.42-2.49 (2 H, m, $4_{maj+min}$-H), 2.56-2.66 (2 H, m, 6_{maj}'-10_{maj}'-H), 2.91 (1 H, d, *J* = 6.5, 15_{maj}-H), 3.05-3.08 (1 H, m, $16_{maj+min}$-H), 3.19 (2 H, d, *J* = 13.2, 6_{maj}''-10_{maj}''-H), 3.29-3.35 (2 H, m, $25_{maj+min}$-H), 4.56 (1 H, s, 17_{maj}-H), 4.75 (1 H, d, *J*=6.5, 17_{min}-H), 4.85 (1 H, s, 12_{maj}-H), 4.88 (1 H, s, 12_{min}-H), 6.24 (1 H, d, *J* = 5.6, 14_{min}-H), 6.28 (1 H, d, *J* = 5.6, 14_{maj}-H), 6.34 (1 H, dd, J_1 = 1.7, J_2 = 5.7, 13_{min}-H), 6.39 (1 H, dd, J_1 = 1.6, J_2 = 5.6, 13_{maj}-H). δ_C(151 MHz; DMSO-d_6) 12.46, 12.83, 13.99, 20.00, 28.48, 28.52, 32.66, 32.99, 40.06, 43.46, 45.78, 47.35, 49.00, 50.91, 51.28, 51.68, 51.77, 51.87, 52.02, 52.81, 53.43, 56.86, 57.10, 78.63, 80.21, 80.47, 82.78, 83.33, 84.62, 84.71, 137.37, 137.59, 138.38, 174.90, 175.10, 175.22, 177.03. **ATI-FTIR:**

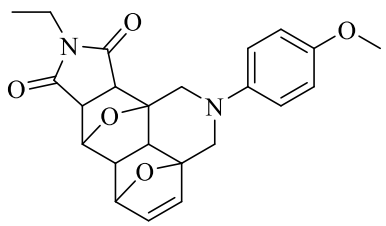
2962, 2762, 1769, 1692, 1412, 1142, 984, 691. **HRMS (ESI):** found for $C_{20}H_{26}N_2O_4$ (M+H) 459.1977, calculated: 459.1965.

Synthesis of **5d**



N-phenylmaleimide (0.305 g, 1.77 mmol) was added to the solution of N,N-bis(furan-2-ylmethyl)-4-methoxyaniline **1d** (0.500 g, 1.77 mmol) in THF (3 ml). The reaction mixture was refluxed for 48 hours. The precipitate was filtered, washed with a small amount of cold THF and dried overnight in a desiccator. Product **5d** was obtained as a white powder (0.331 g, 40%). δ_H(600 MHz; DMSO-d_6, ***exo-exo-isomer***) 1.94 (1 H, d, *J* = 6.5, 19-H), 2.22 (1 H, d, *J* = 6.5, 20-H), 3.20 (1 H, d, *J* = 6.9, 23-H), 3.32 (1 H, d, *J* = 6.9, 22-H), 3.38-3.42 (2 H, m, 25'-28'-H), 3.74-3.77 (1 H, d, *J* = 14.1, 25''-H), 3.90 (1 H, d, *J* = 13.4, 28''-H), 4.73 (1 H, s, 21-H), 4.93 (1 H, m, 32-H), 6.39 (1 H, d, *J*=5.6, 30-H), 6.47 (1 H, d, J_1 = 1.8, J_2 = 5.5, 31-H), 6.82 (2 H, d, *J* = 9.1, 3-5-H), 6.88 (2 H, d, *J* = 9.1, 2-6-H), 7.22 (2 H, m, *J* = 7.2, 10-14-H), 7.42 (1 H, t, *J* = 7.7, 12-H), 7.49 (2 H, t, *J* = 7.9, 11-13-H). δ_C(151 MHz; DMSO-d_6) 46.96, 49.08, 49.29, 49.65, 51.33, 51.52, 55.19, 80.37, 80.78, 82.87, 84.61, 114.31, 118.32, 126.90, 128.46, 129.01, 132.22, 137.92, 138.08, 145.34, 152.77, 174.61, 176.48. To clarify the relative configuration of protons 25-28 the NOESY-experiment was carried out. **IR** vmax/cm^{-1} (tablet KBr): 2990, 2939, 2832, 1772, 1713, 1514, 1497, 1373, 1249, 1144, 978, 951, 694. **X-ray:** it was received X-ray crystallography data for the exo-exo isomer.

Synthesis of **5e**

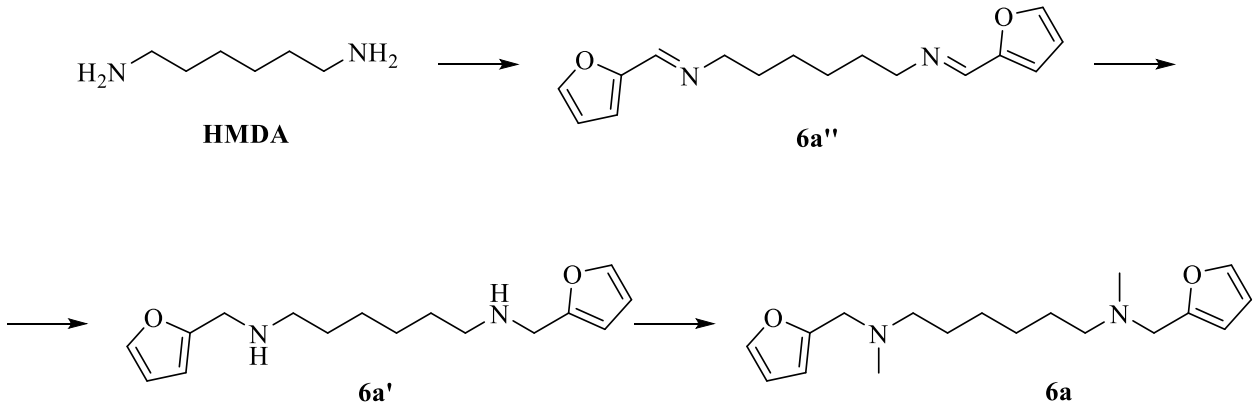


N-Ethylmaleimide (0.159 g, 1.27 mmol) was added to the N,N-bis(furan-2-ylmethyl)-4-methoxyaniline **1d** (0.360 g, 1.27 mmol). The reaction mixture was heated for 48 hours at 60 °C. The obtained precipitate was washed with a small amount of cold THF on the glass filter and dried overnight in a desiccator. Product **5e** was obtained as a white powder (0.183 g, 35%). δ_H(600 MHz;

DMSO-d_6, ***exo-exo-isomer***) 0.99-1.02 (3 H, t, *J* = 7.3, 8-Me), 1.85 (1 H, d, *J* = 6.5, 14-H), 2.14 (1 H, d, *J* = 6.5, 15-H), 3.01 (1 H, d, *J* = 6.6, 18-H), 3.13 (1 H, d, *J* = 6.9, 17-H), 3.32-3.38 (4 H, m, 8-20'-21'-H), 3.66-3.68 (4 H, m, 21''-H, O-Me), 3.87 (1 H, d, *J* = 13.4, 20''-H), 4.61 (1 H, s, 16-H), 4.90 (1 H, d, *J* = 1.5, 7-H), 6.36 (1 H, d, *J* = 5.6, 5-H), 6.45 (1 H, d, J_1 = 1.6, J_2 = 5.7, 6-H). **δ_C**(151 MHz; DMSO-d_6) 12.83, 33.05, 46.98, 49.04, 49.22, 49.60, 50.98, 51.17, 55.20, 80.31, 80.35, 82.49, 84.55, 114.30, 118.24, 137.88, 138.05, 145.33, 152.74, 175.16, 176.97. **ATI-FTIR:** 2980, 2829, 1774, 1698, 1512, 1408, 1250, 1144, 989, 949, 695. **HRMS (ESI):** found for $C_{23}H_{24}N_2O_5$ (M+Na) 431.1598, calculated: 431.1577.

5. Synthesis of tetra- and difurfuryl monomer derivatives

Synthesis of N,N-difurfuryl-N,N-dimethylhexamethylenediamine **6a**



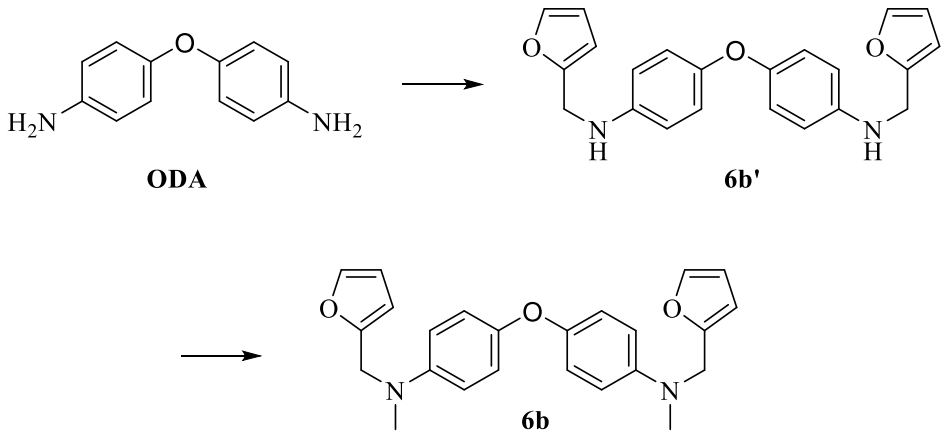
1. Furfural (6.784 ml, 81.98 mmol, 2 eq.) was added to the solution of hexamethylenediamine (4.755 g, 40.99 mmol, 1 eq.) **HMDA** in absolute dichloromethane (30 ml). The mixture was stirred at room temperature over 4Å molecular sieves for 24 h. Afterwards, the molecular sieves were filtered under vacuum and filtrate was evaporated at reduced pressure. The product was obtained as an orange oil (9.477 g, 85%). The resulting dimine **6a''** was used in the next step without further purification. **δ_H**(600 MHz; DMSO-d_6) 1.31 (4 H, m, 10-11-H), 1.57 (4 H, m, 9-12-H), 3.48 (4 H, t, *J* = 6.7, 8-13-H), 3.59 (2 H, m, 3-17-H), 6.87 (2 H, d, *J* = 3.4, 2-18-H), 7.80 (2 H, m, 1-19-H), 8.13 (2 H, s, 6-15H).

2. Diimine **6a''** (9.477 ml, 34.84 mmol, 1 eq.) was dissolved in absolute methanol (50 ml) and $NaBH_4$ (5.296 g, 139.36 mmol, 4 eq.) was added to the reaction mixture portionwise maintaining the temperature between 0 and 5 °C. Then the reaction mixture was stirred for 24 h at room temperature. The reaction mixture was monitored by TLC until diimine **6a''** was consumed, and 30 ml of 0.1 N aq NaOH was added. The product was extracted with EtOAc (30 mL × 3), the organic layer was washed with water and then dried under anhydrous magnesium sulfate, the solvent was removed under reduced pressure. The product **6a'** was obtained as a yellow oil (5.172 g, 54%). The resulting diamine **6a'** was used in the next step without further purification. **δ_H**(600 MHz; DMSO-d_6)

1.23 (4 H, m, 10-11-H), 1.37 (4 H, m, 9-12-H), 2.44 (4 H, t, *J* = 6.9, 8-13-H), 2.81 (2 H, br.s., NH), 3.63 (4 H, s, 6-15-H), 6.20 (2 H, d, *J* = 3.1, 3-17-H), 6.36 (2 H, dd, J_1 = 2.0, J_2 = 3.3, 2-18-H), 7.53 (2 H, m, 1-19-H). **δ_C**(151 MHz; DMSO-*d_6*) 26.84, 29.37, 45.59, 48.53, 106.50, 110.25, 141.66, 154.62. **HRMS (ESI):** found for $C_{16}H_{24}N_2O_2$ (M+H) 277.1908, calculated: 277.1911.

3. To a solution of N,N-difurfurylhexamethylenediamine **6a'** (2.400 g, 8.70 mmol, 1 eq.), paraformaldehyde (1.565 g, 52.17 mmol, 6 eq.) in MeOH (150 ml) was added sodium methoxide solution (2.817 g, 52.17 mmol, 6 eq.) and stirred at 50 °C for 5 hours. Then, sodium borohydride (1.983 g, 52.17 mmol, 6 eq.) was added under argon and the reaction was stirred for 24 h at room temperature. The reaction mixture was monitored by TLC until N,N-difurfurylhexamethylenediamine was consumed, the solvent was removed under reduced pressure. The dried crude mixture was washed with NH_4Cl and extracted with ethyl acetate. The combined organic layer was dried over $NaSO_4$, filtered and concentrated. The crude material was purified by flash chromatography. The product **6a** was obtained as yellow oil (1.990 g, 75%). **δ_H**(600 MHz; DMSO-*d_6*) 1.22 (4 H, m, 10-11-H), 1.39 (4 H, m, 9-12-H), 2.10 (6 H, s, N-Me), 2.25 (4 H, t, *J* = 7.2, 8-13-H), 3.46 (4 H, s, 6-15-H), 6.24 (2 H, d, *J* = 3.1, 3-17-H), 6.37-6.40 (2 H, dd, J_1 = 1.8, J_2 = 3.2, 2-18-H), 7.56 (2 H, m, 1-19-H). **δ_C**(151 MHz; DMSO-*d_6*) 26.70, 26.81, 41.62, 53.13, 56.04, 108.29, 110.19, 142.12, 152.40. **HRMS (ESI):** found for $C_{18}H_{28}N_2O_2$ (M+H) 305.2228, calculated: 305.2224.

Synthesis of 4,4'-oxybis(N-(furan-2-ylmethyl)-N-methylaniline) **6b**

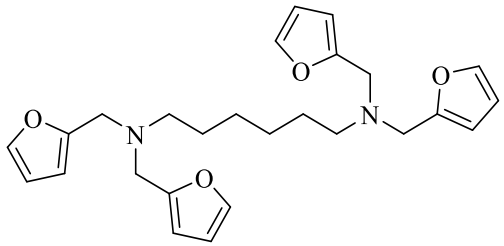


1. Furfural (0.828 ml, 10.00 mmol, 2 eq.) was added to the solution of 4,4'-oxydianiline (1.000 g, 5.00 mmol, 1 eq.) **ODA** in methanol (50 ml). The mixture was stirred at room temperature over 4Å molecular sieves for 24 h. Afterwards, the molecular sieves were filtered under vacuum and 0.760 g (20.00 mmol, 4 eq.) of $NaBH_4$ was added to the reaction mixture. After the reaction completed (TLC monitoring: Rf=0.3, EtOAc - Petroleum ether (1:5)), 50 ml of 0.1 N aq NaOH was added. The yellow pearlescent precipitate was filtered and dried in the air. The product **6b'** was obtained as a

yellow pearlescent powder (1.490 g, 83%). **δ_H**(600 MHz; DMSO-d_6) 4.19 (4 H, d, *J* = 6.0, 6-9-H), 5.87-5.90 (2 H, t, *J* = 6.1, NH), 6.28 (2 H, m, 3-11-H), 6.38 (2 H, m, 2-12-H), 6.61 (4 H, d, *J* = 8.9, 17-21-22-26-H), 6.70 (4 H, d, *J* = 8.7, 18-20-23-25-H), 7.56 (2 H, s, 1-13-H). **δ_C**(151 MHz; DMSO-d_6) 40.43, 106.88, 110.40, 113.25, 118.99, 141.91, 144.15, 148.61, 153.50. **Elemental analysis.** Found: C, 72.98; H, 5.78; N, 7.85. Calc. for $C_{22}H_{22}N_2O_3$: C, 73.32; H, 5.59; N, 7.77%

2. 0.210 g of the diamine **6b'** (0.58 mmol, 1 eq.), 0.880 ml of the HCOOH (99 %, 23.33 mmol, 40 eq.), 3.237 ml of the triethylamine (23.33 mmol, 40 eq.) and DMSO (3 mL) were placed in a pressure tube. The mixture was bubbled with argon for 15 min and then stirred at 150 °C for 9 h. Then the reaction mixture was cooled to room temperature and aqueous NaOH solution was added. The product was extracted with CH_2Cl_2 (10 ml x 3). The organic layers were washed with brine, and dried under anhydrous sodium sulfate. The solvent was evaporated under reduced pressure. Product **6b** was isolated by flash chromatography on silica gel eluting with EtOAc - Petroleum ether (1:5, Rf=0.4) as a light yellow oil (0.137 g, 61%). **δ_H**(600 MHz; DMSO-d_6) 2.88 (6 H, s, N-Me), 4.44 (4 H, s, 6-9-H), 6.27 (4 H, d, *J* = 3.2, 3-11-H), 6.36-6.39 (4 H, dd, J_1 = 1.9, J_2 = 3.2, 2-12-H), 6.78 (8 H, m, Ph), 7.56 (2 H, m, 1-13-H). **δ_C**(151 MHz; DMSO-d_6) 38.48, 49.00, 107.65, 110.26, 114.11, 118.90, 142.20, 144.99, 148.80, 152.18. **HRMS (ESI):** found for $C_{24}H_{24}N_2O_3$ (M+H) 388.1791, calculated: 388.1781.

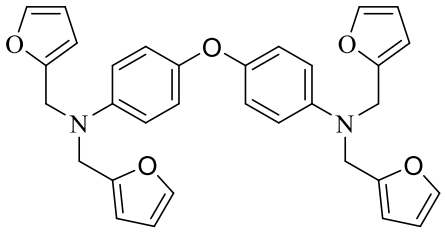
Synthesis of N,N,N,N-tetrafurfurylhexamethylenediamine **9a**



To obtain sodium triacetoxyborohydride acetic acid (12.222 ml, 213.72 mmol, 24 eq.) was added dropwise to the solution of sodium borohydride (2.707 g, 71.24 mmol, 8 eq.) in dichloromethane (40 ml) maintaining the temperature between 0 and 5 °C. Then the reaction mixture was stirred for 3 h at 0 °C. Afterwards, hexamethylenediamine (1.033 g, 8.91 mmol, 1 eq.) **HMDA**, furfural (5.896 ml, 71.24 mmol, 8 eq.) and molecular sieves (4 Å) were added. The mixture was stirred at room temperature for 72 h. After the reaction was completed (TLC monitoring), 30 ml of 0.1 N aq NaOH was added. The product was extracted with EtOAc (20 mL × 3), the organic layer was washed with water and then dried under anhydrous magnesium sulfate, the solvent was removed under reduced pressure. Product **9a** was isolated by flash chromatography on silica gel eluting with EtOAc - Petroleum ether (1:5) as a yellow oil (2.095 g, 54%). **δ_H**(600 MHz; DMSO-d_6) 1.14 (4 H, m, 16-17-H), 1.38 (4 H, m, 15-18-H), 2.27-2.30 (4 H, t, *J* = 7.3, 8-19-H), 3.56 (8 H, s, 6-9-21-22-H), 6.28 (4 H, dd, *J* =

3.1, 3-11-25-29-H), 6.39 (4 H, dd, J_1 = 2.0, J_2 = 3.2, 2-12-26-30-H), 7.58 (4 H, dd, J_1 = 0.9, J_2 = 1.8, 1-13-27-31-H). **δ_C**(151 MHz; DMSO-*d_6*) 26.43, 26.55, 49.25, 52.13, 108.58, 110.27, 142.30, 152.27. **HRMS (ESI):** found for $C_{26}H_{32}N_2O_4$ (M+H) 437.2456, calculated: 437.2435.

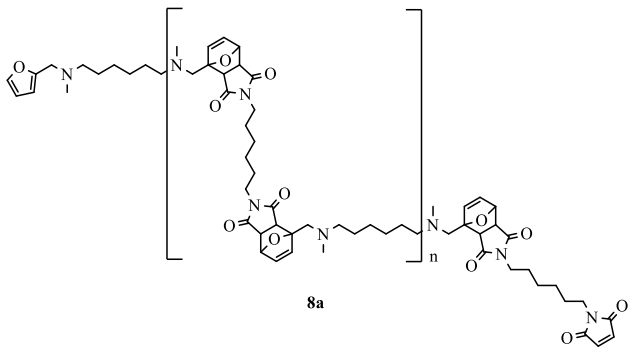
Synthesis of 4,4'-oxybis(N,N-bis(furan-2-ylmethyl)aniline) **9b**



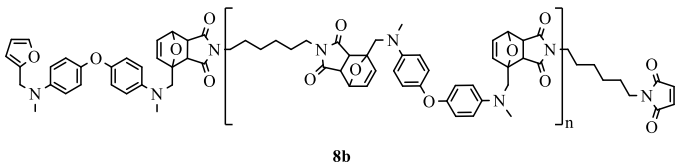
To obtain sodium triacetoxyborohydride acetic acid (2.188 g, 3.65 mmol, 12 eq.) was added dropwise to the solution of sodium borohydride (0.462 g, 1.22 mmol, 4 eq.) in dichloromethane (25 ml) maintaining the temperature between 0 and 5 °C. Then the reaction mixture was stirred for 3 h at 0 °C. Afterwards, 4,4'-oxybis(N-(furan-2-ylmethyl)aniline) **6b'** (1.094 g, 3.04 mmol, 1 eq.), furfural (1.167 g, 1.22 mmol, 4 eq.) and molecular sieves (4 Å) were added. The mixture was stirred at room temperature for 72 h. After the reaction was completed (TLC monitoring), 50 ml of 0.1 N aq NaOH was added. The product was extracted with EtOAc (10 ml x 3), the organic layer was washed with water and then dried under anhydrous magnesium sulfate, the solvent was removed under reduced pressure. The product **9b** was isolated by flash chromatography on silica gel eluting with EtOAc - Petroleum ether (1:5, Rf=0.4) as a yellow powder (1.014 g, 51%). **δ_H**(600 MHz; DMSO-*d_6*) 4.46 (8 H, s, 15-16-20-21-H), 6.27 (4 H, d, *J* = 3.2, 24-28-32-36-H), 6.36-6.39 (4 H, dd, J_1 = 1.9, J_2 = 3.2, 25-29-33-37-H), 6.78 (4 H, m, 1-3-10-12-H), 6.86-6.89 (4 H, m, 4-6-9-13-H), 7.58 (4 H, m, 26-30-34-38-H). **δ_C**(151 MHz; DMSO-*d_6*) 47.16, 107.85, 110.40, 114.65, 118.89, 142.32, 143.88, 149.04, 152.12. **Elemental analysis.** Found: C, 73.31; H, 5.50; N, 5.18. Calc. for $C_{32}H_{28}N_2O_5$: C, 73.83; H, 5.52; N, 5.38%

6. Synthesis of polymer compound 8a/b, 10a/b via Diels-Alder reaction

Synthesis of polymer **8a/b** *based on classic Diels-Alder adducts*



8a

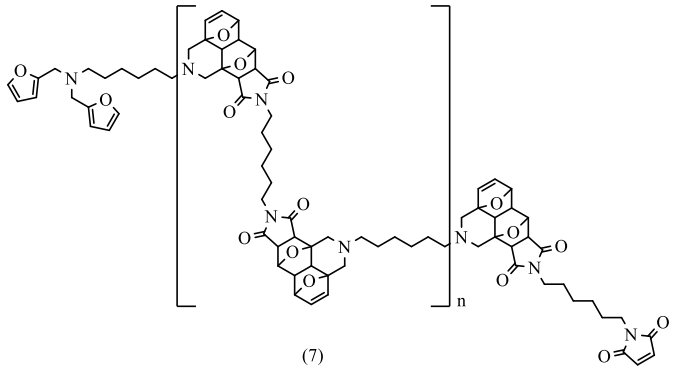


8b

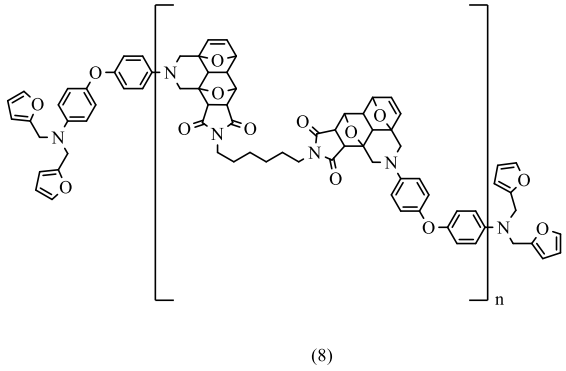
HMBMI (1 eq.) was added to the solution of compound **6a** or **6b** in absolute dimethylacetamide

under an argon atmosphere. 2,6-Di-tert-butyl-4-methylphenol (0.01 eq.) was added. Then the reaction mixture was stirred for 24 h at 100 °C. After cooling the reaction mixture to room temperature, DCM or Et_2O was added in a tenfold excess by volume. The precipitate formed was centrifuged (5 min, 6000 rpm) and the centrifugation-decantation procedure was repeated three times. The product **8a/b** was dried in a vacuum for 72 h. The product **8a/b** was obtained as a milk-coloured or light brown powder in a **19-29%** yield.

Synthesis of polymer **10a/b** *based on tandem Diels-Alder adducts*



(7)



(8)

HMBMI (1/1.05/1.2 eq.) was added to the solution of compound **9a** or **9b** (1 eq.) in absolute dimethylacetamide under an argon atmosphere. 2,6-Di-tert-butyl-4-methylphenol (0.01 eq.) was added. Then the reaction mixture was stirred for 24 h at 80/100/120/135/140°C. After cooling the reaction mixture to room temperature, DCM or Et_2O was added in a tenfold excess by volume. The precipitate formed was centrifuged (5 min, 6000 rpm) and the centrifugation-decantation procedure was repeated three times. The product **10a/b** was dried in a vacuum for 72 h. The product **10a/b** was obtained as a milk-coloured or light brown powder in a **45-96%** yield.

7. NMR

7.1. Spectrum of the synthesized compounds

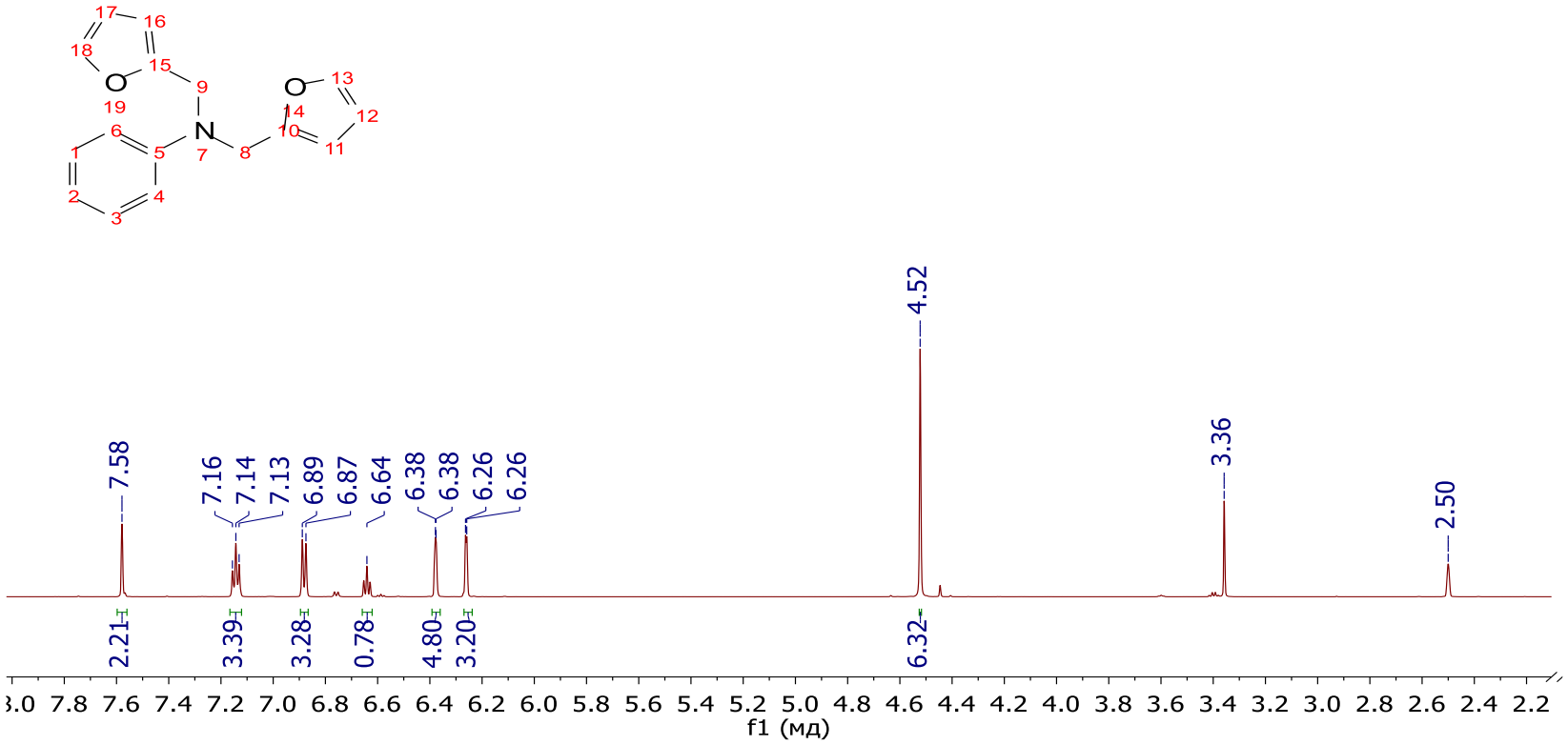


Figure S2. ^{1}H-NMR spectrum of N,N-difurfuryl-aniline **1a**, (600 MHz, DMSO-d_6).

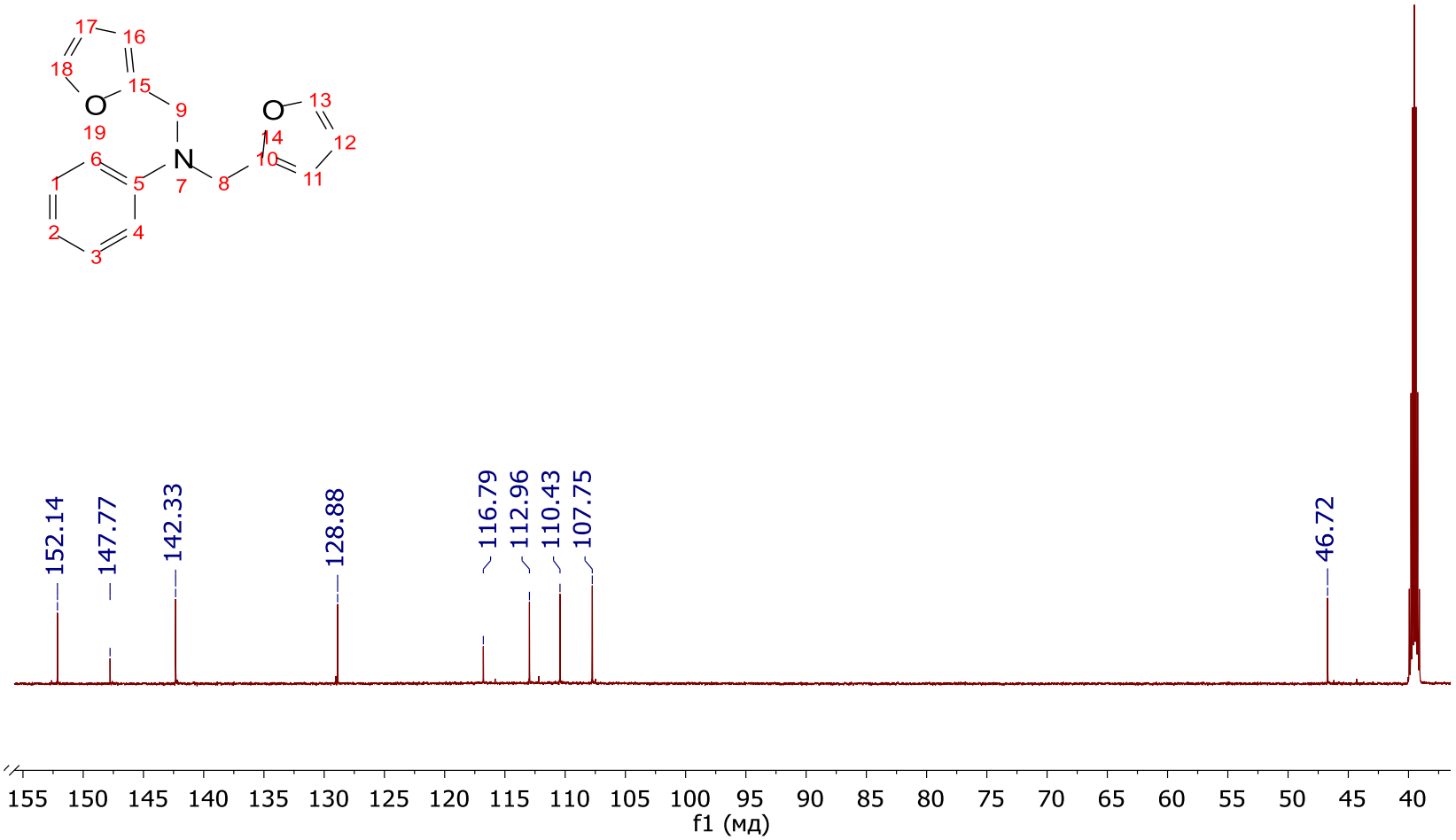


Figure S3. ^{13}C-NMR spectrum of N,N-difurfuryl-aniline **1a**, (151 MHz, DMSO-d_6).

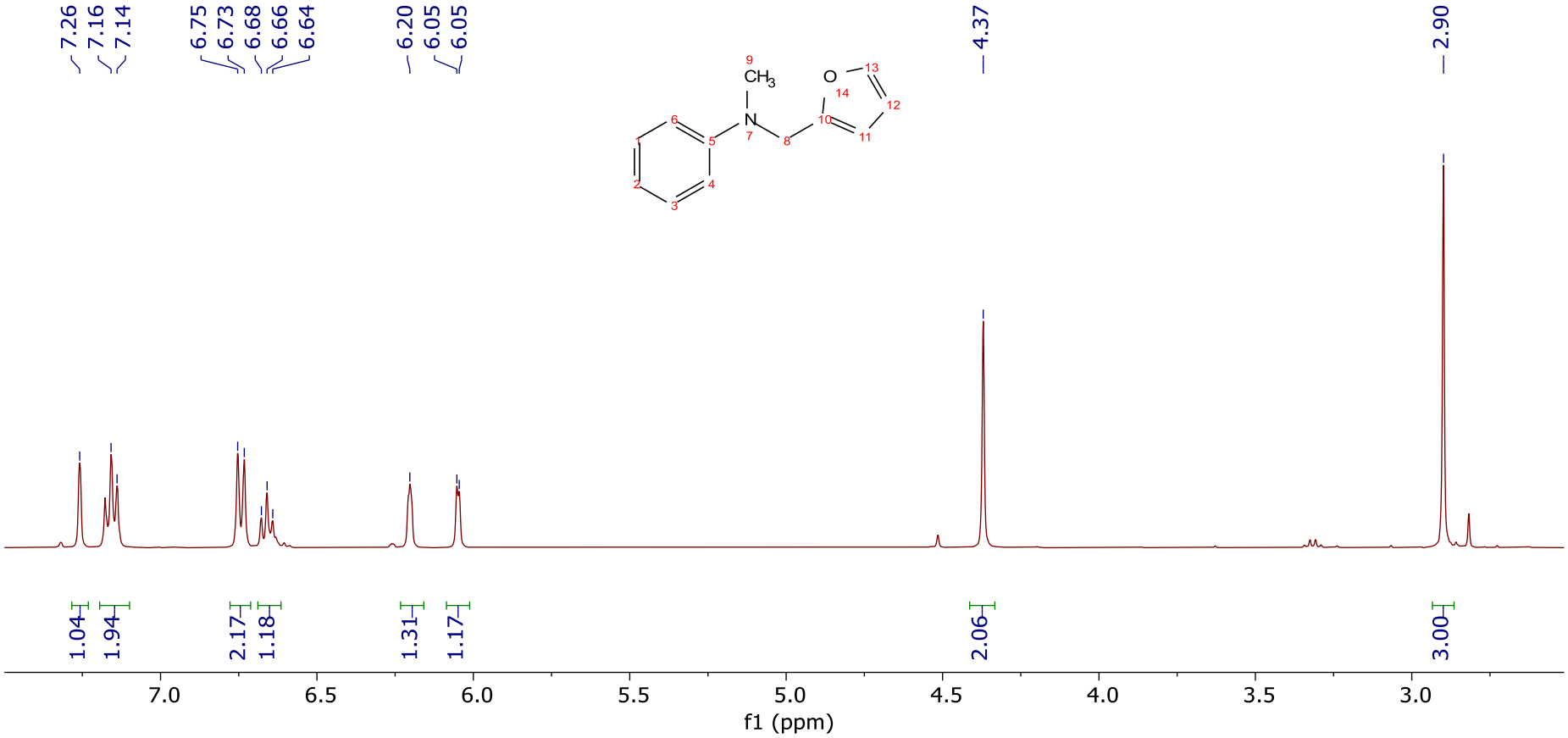


Figure S4. ^{1}H-NMR spectrum of N-2-Furfuryl-N-methylaniline **1b**, (400 MHz, $CDCl_3$-d_1).

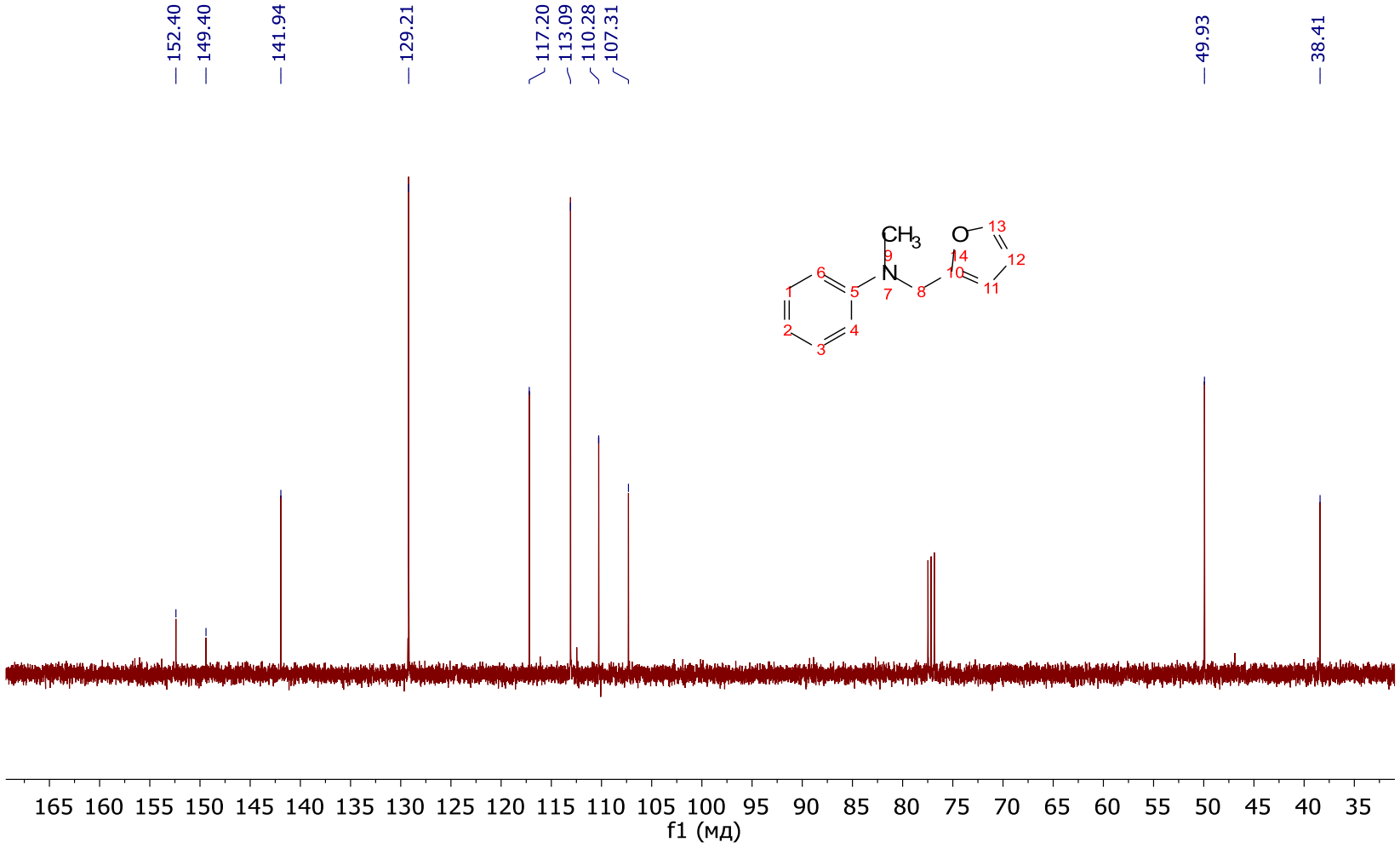


Figure S5. ^{13}C-NMR spectrum of N-2-Furfuryl-N-methylaniline **1b**, (101 MHz, $CDCl_3$-d_1).

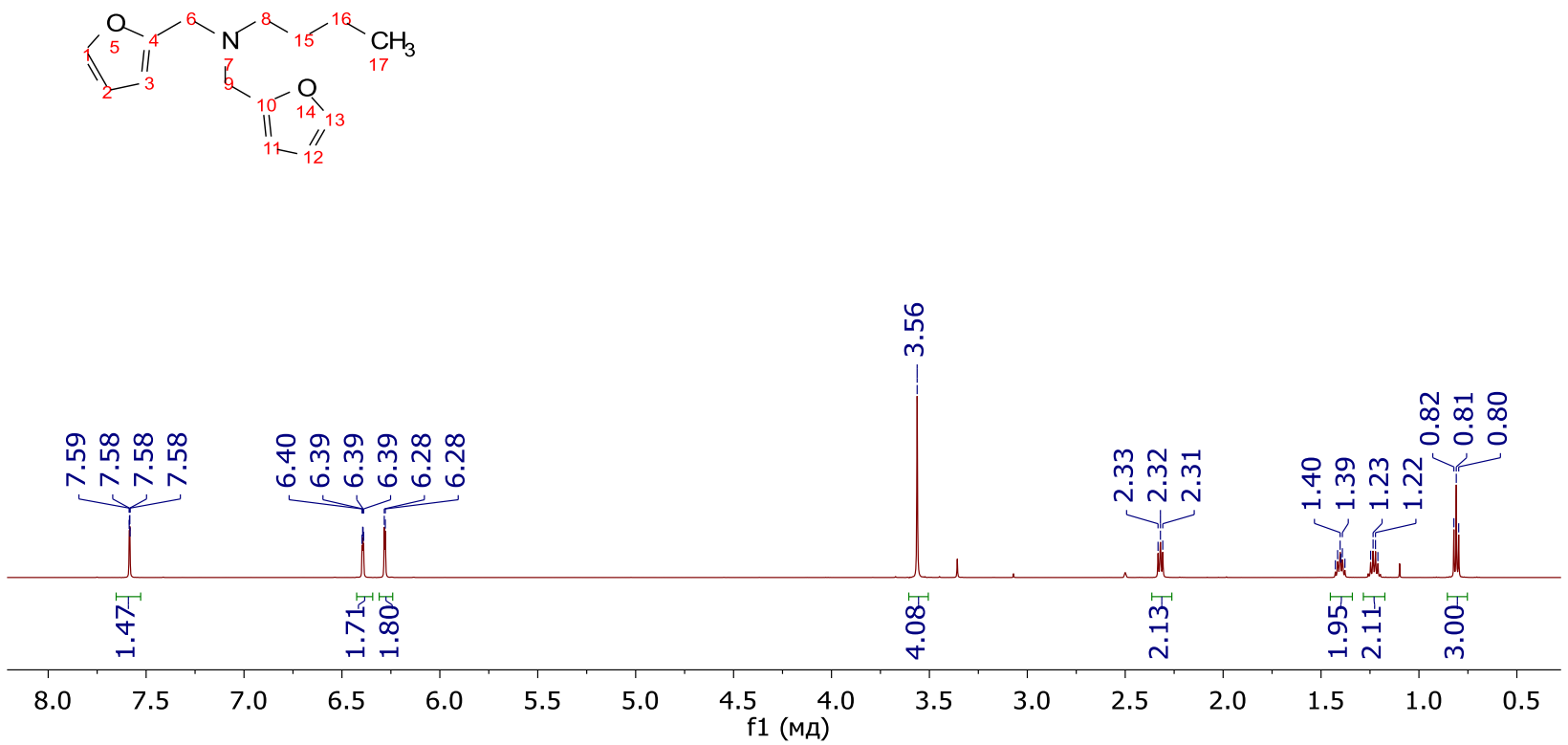


Figure S6. ^{1}H-NMR spectrum of N,N-bis(furan-2-ylmethyl)butan-1-amine **1c**, (600 MHz, DMSO-d_6).

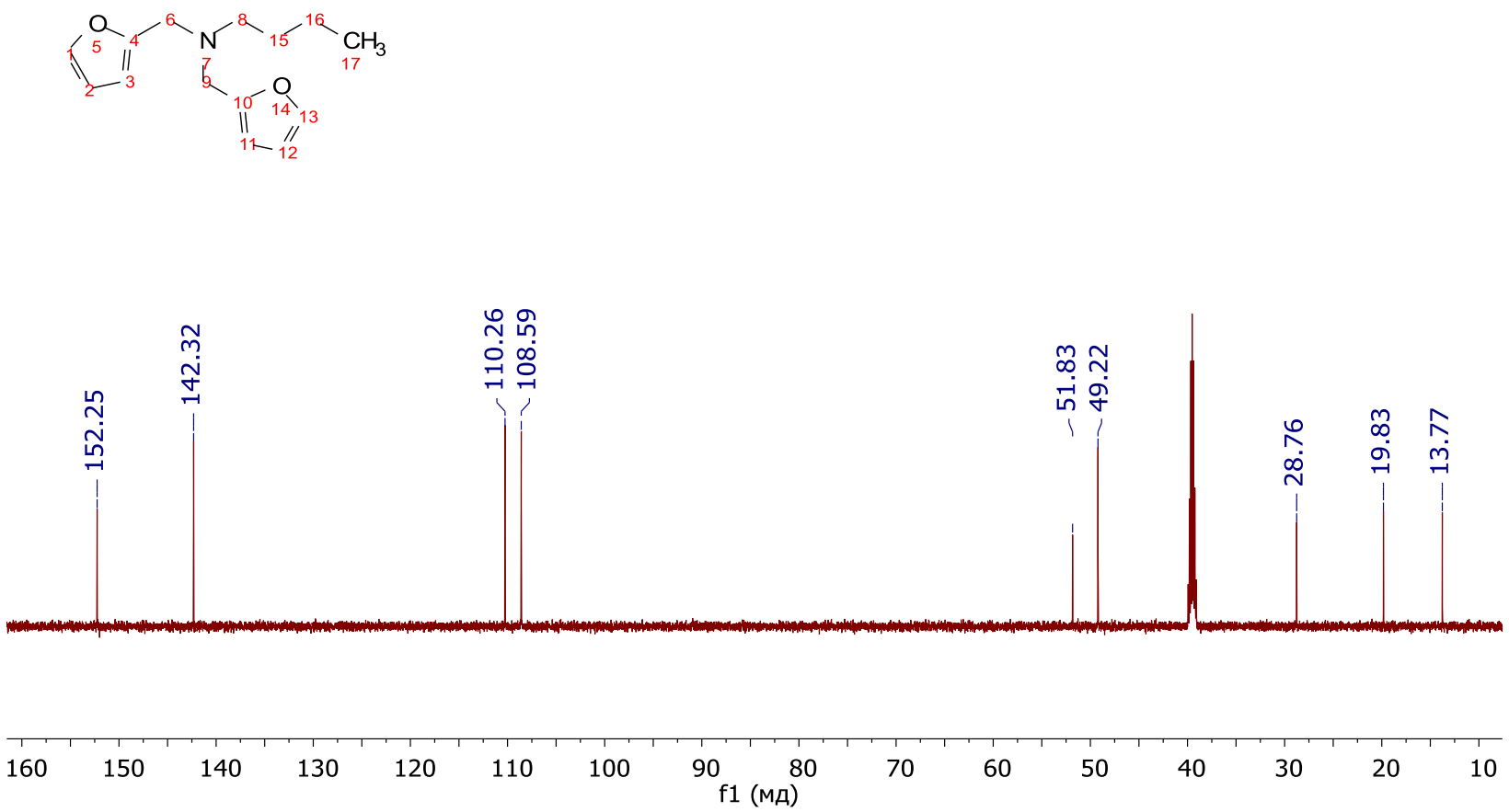


Figure S7. ^{13}C-NMR spectrum of N,N-bis(furan-2-ylmethyl)butan-1-amine **1c**, (151 MHz, DMSO-d_6).

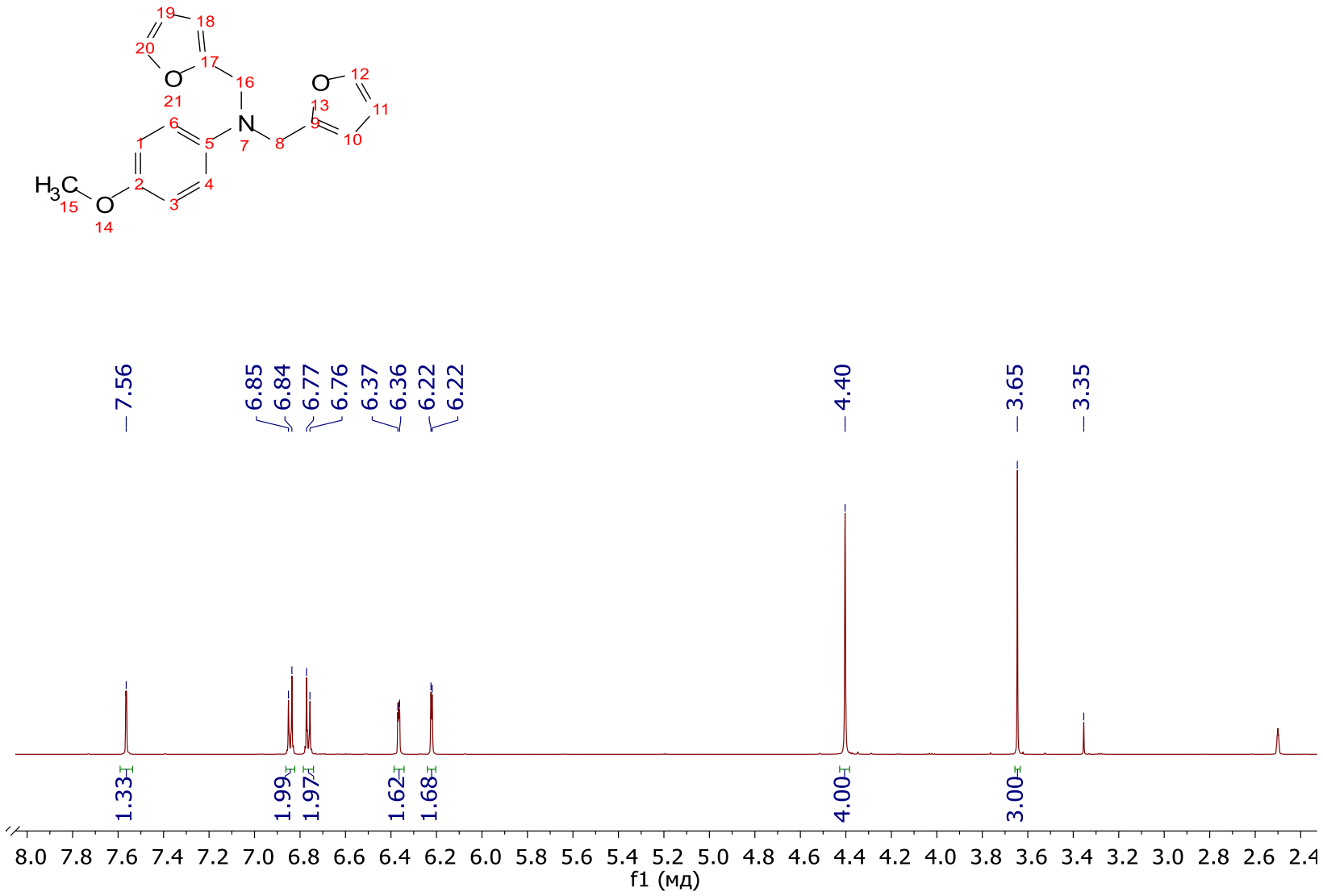


Figure S8. ^{1}H-NMR spectrum of N,N-bis(furan-2-ylmethyl)-4-methoxyaniline **1d**, (600 MHz, DMSO-d_6).

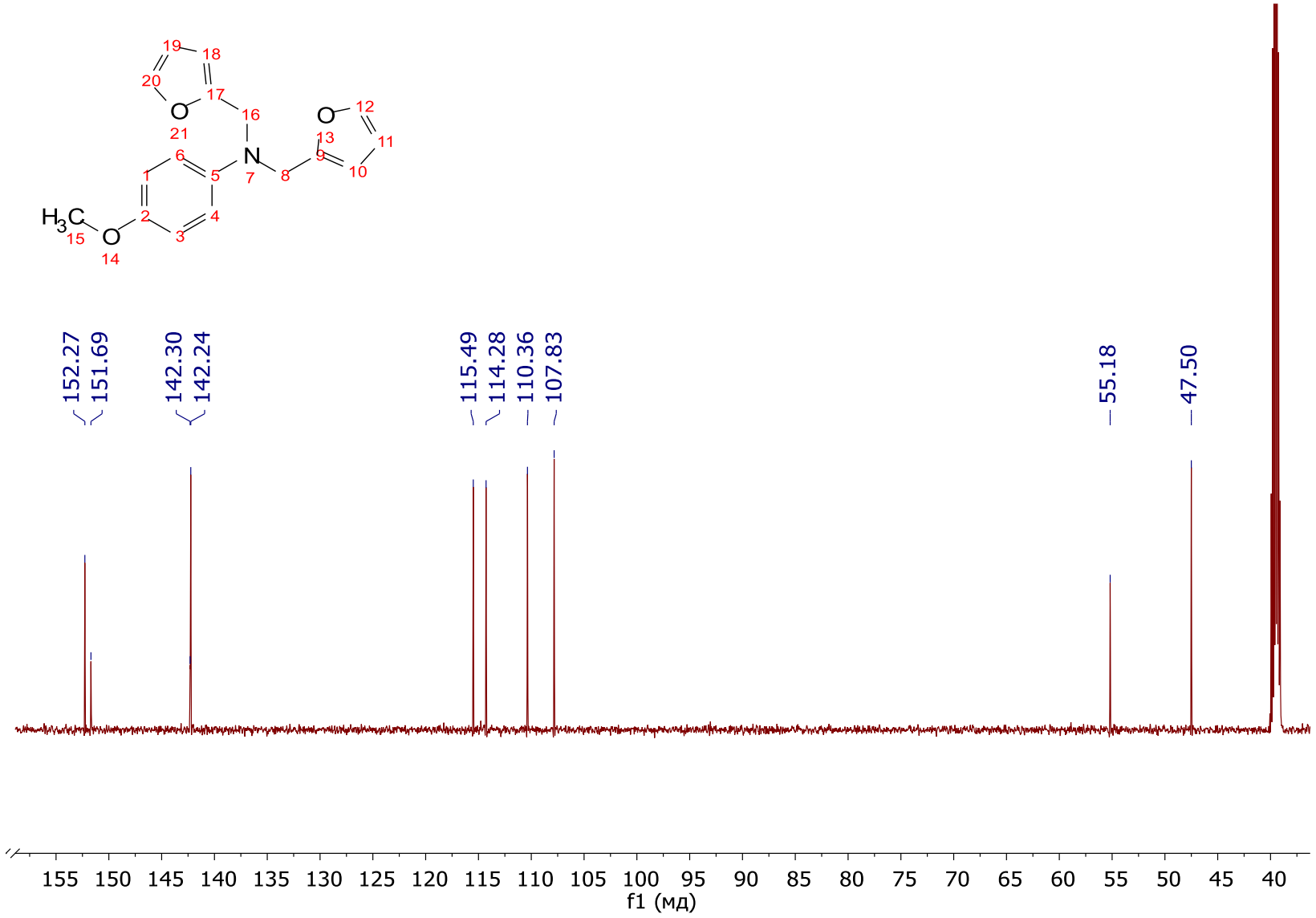


Figure S9. ^{13}C-NMR spectrum of N,N-bis(furan-2-ylmethyl)-4-methoxyaniline **1d**, (151 MHz, DMSO-d_6).

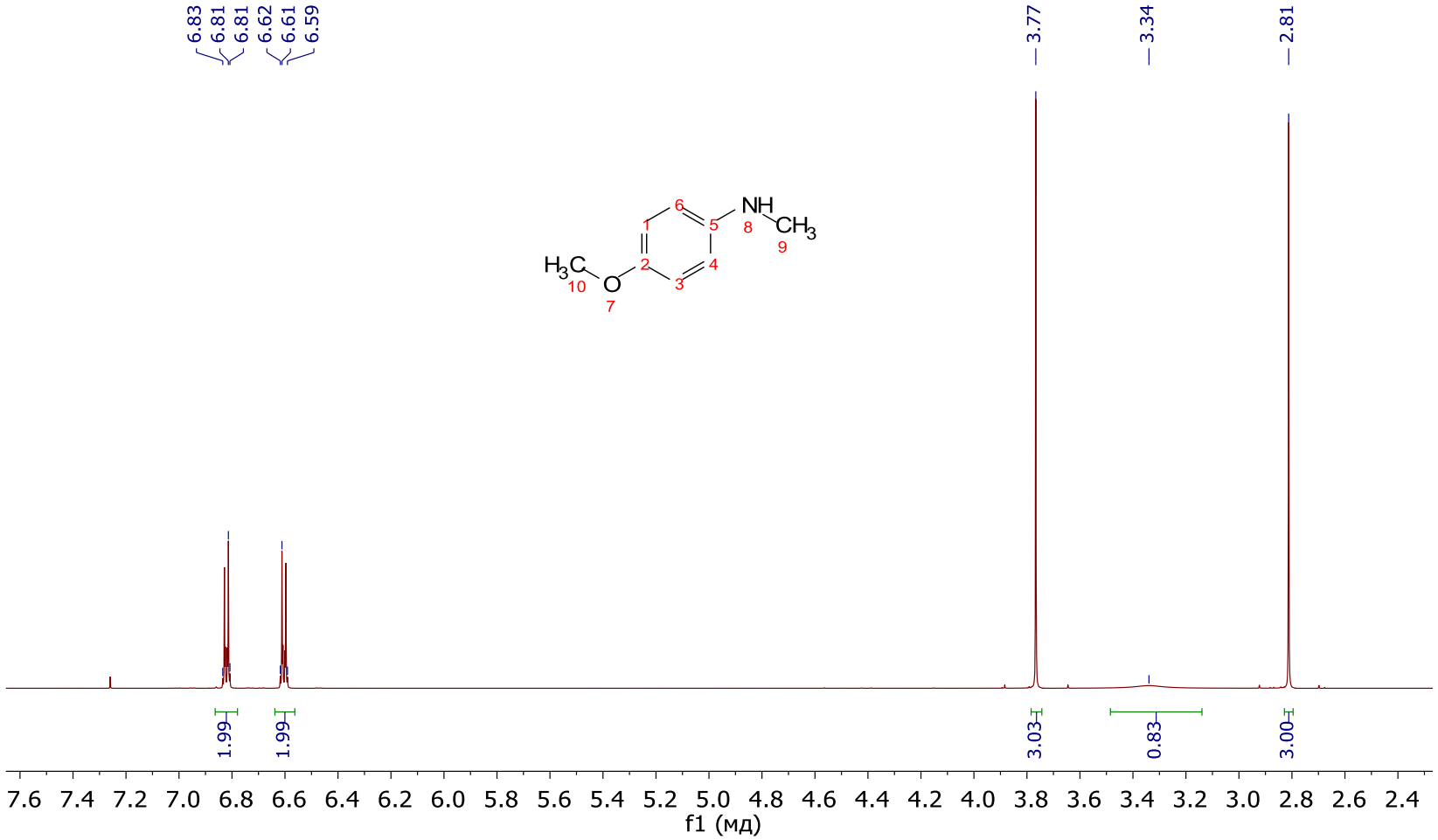


Figure S10. ^{1}H-NMR spectrum of 4-methoxy-N-methylaniline **1e'**, (600 MHz, $CDCl_3$-d_1).

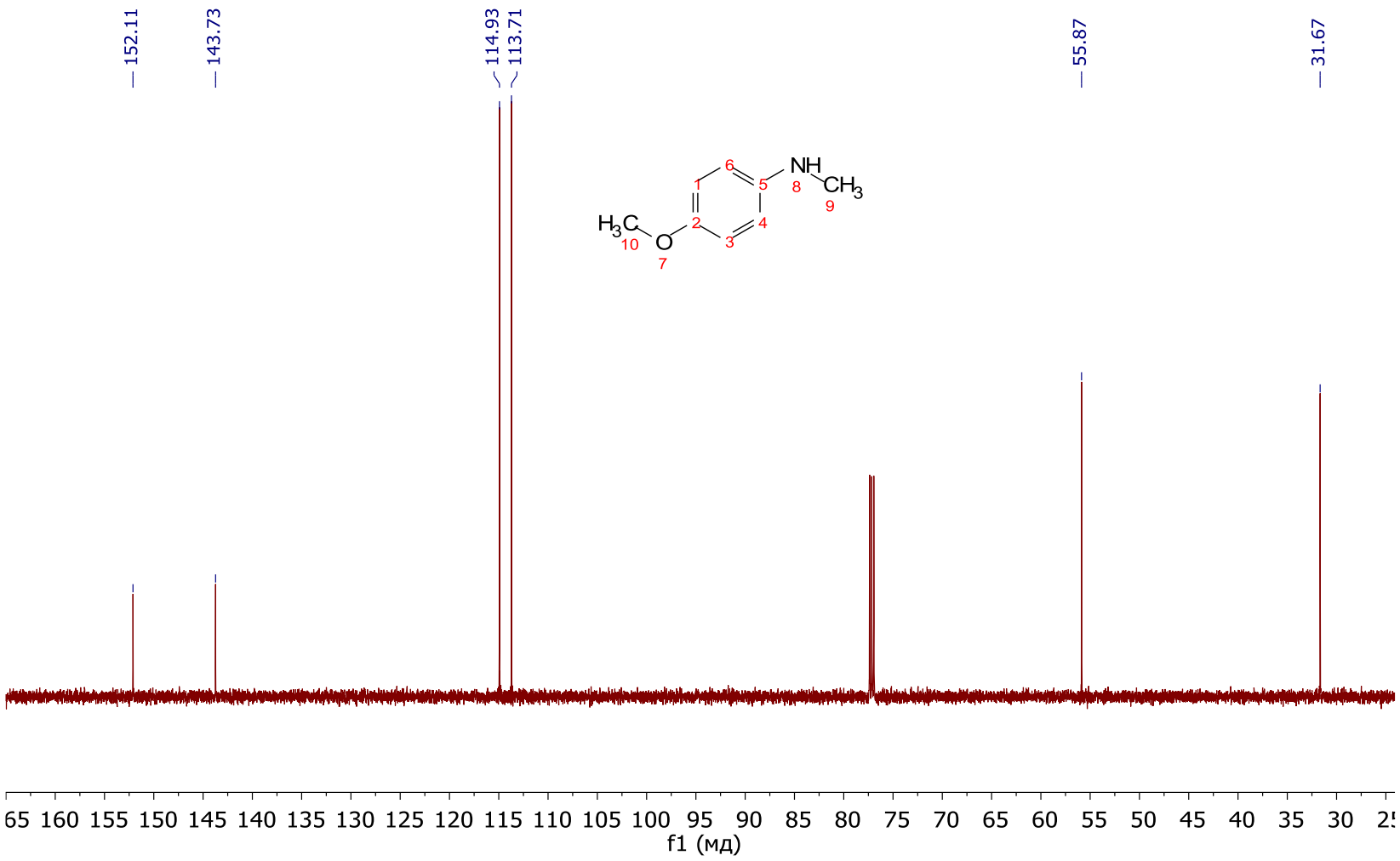


Figure S11. ^{13}C-NMR spectrum of 4-methoxy-N-methylaniline **1e'**, (151 MHz, $CDCl_3$-d_1).

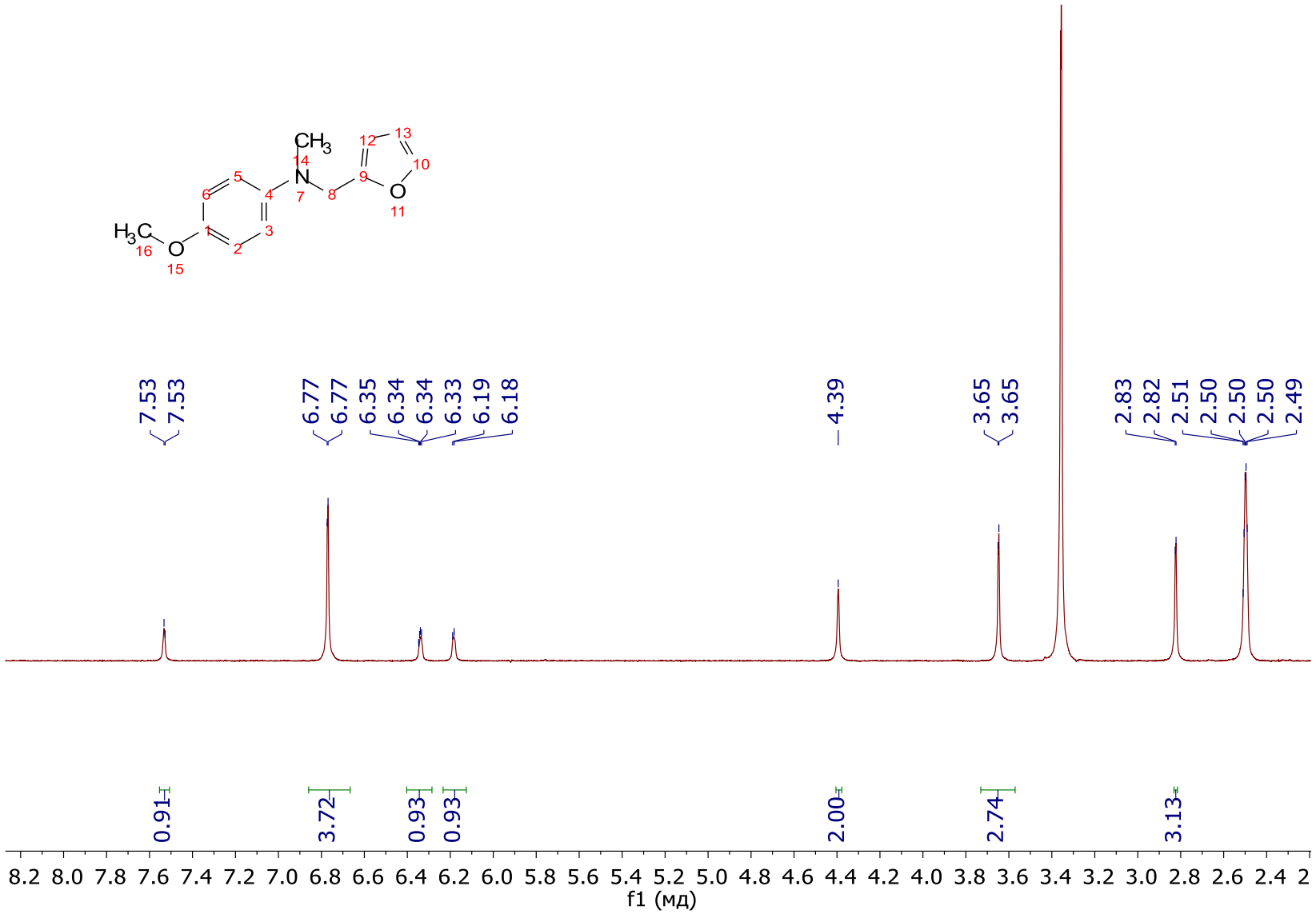


Figure S12. ^{1}H-NMR spectrum of N-(furan-2-ylmethyl)-4-methoxy-N-methylaniline **1e**, (400 MHz, DMSO-d_6).

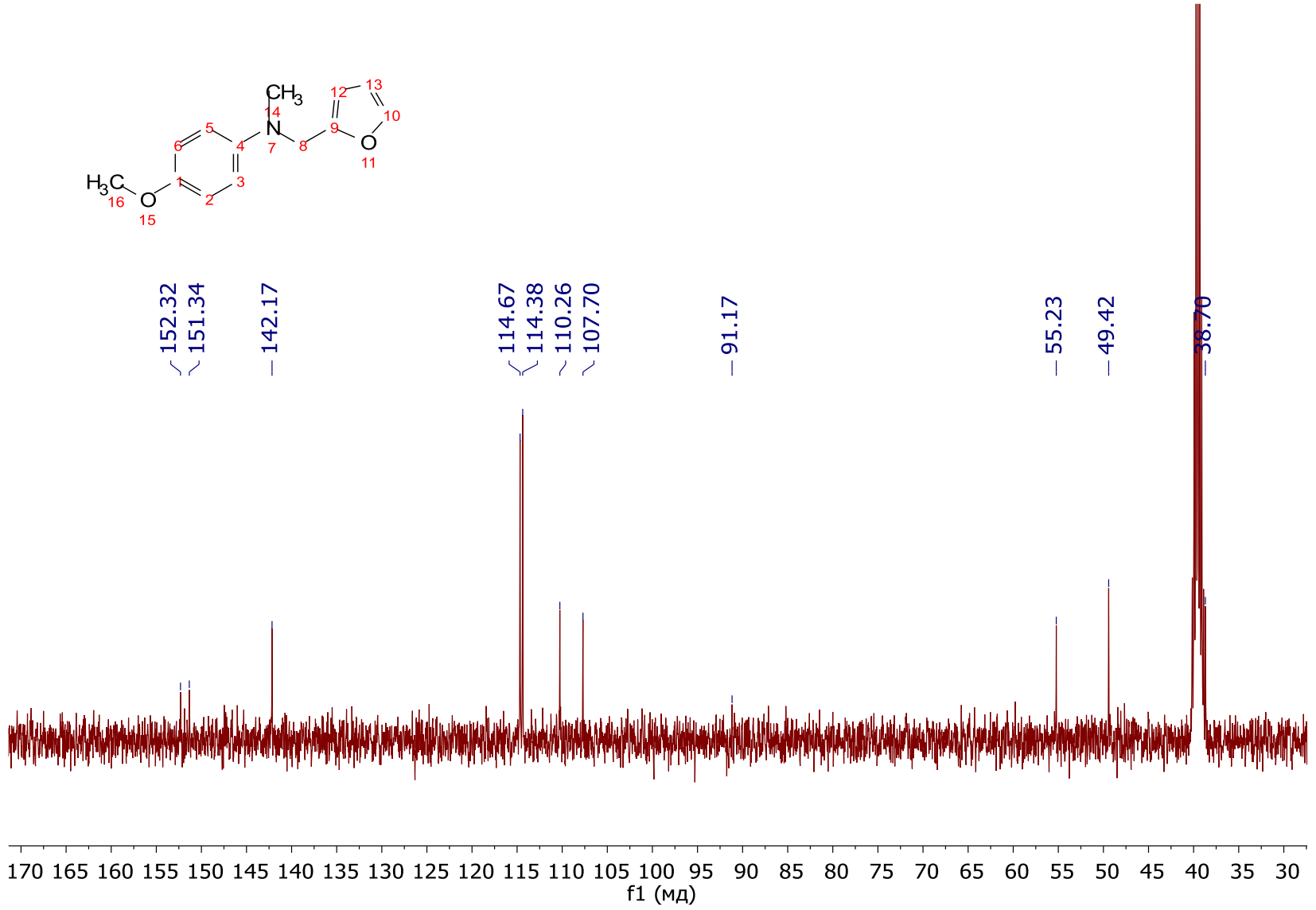


Figure S13. ^{13}C-NMR spectrum of N-(furan-2-ylmethyl)-4-methoxy-N-methylaniline **1e**, (101 MHz, DMSO-d_6).

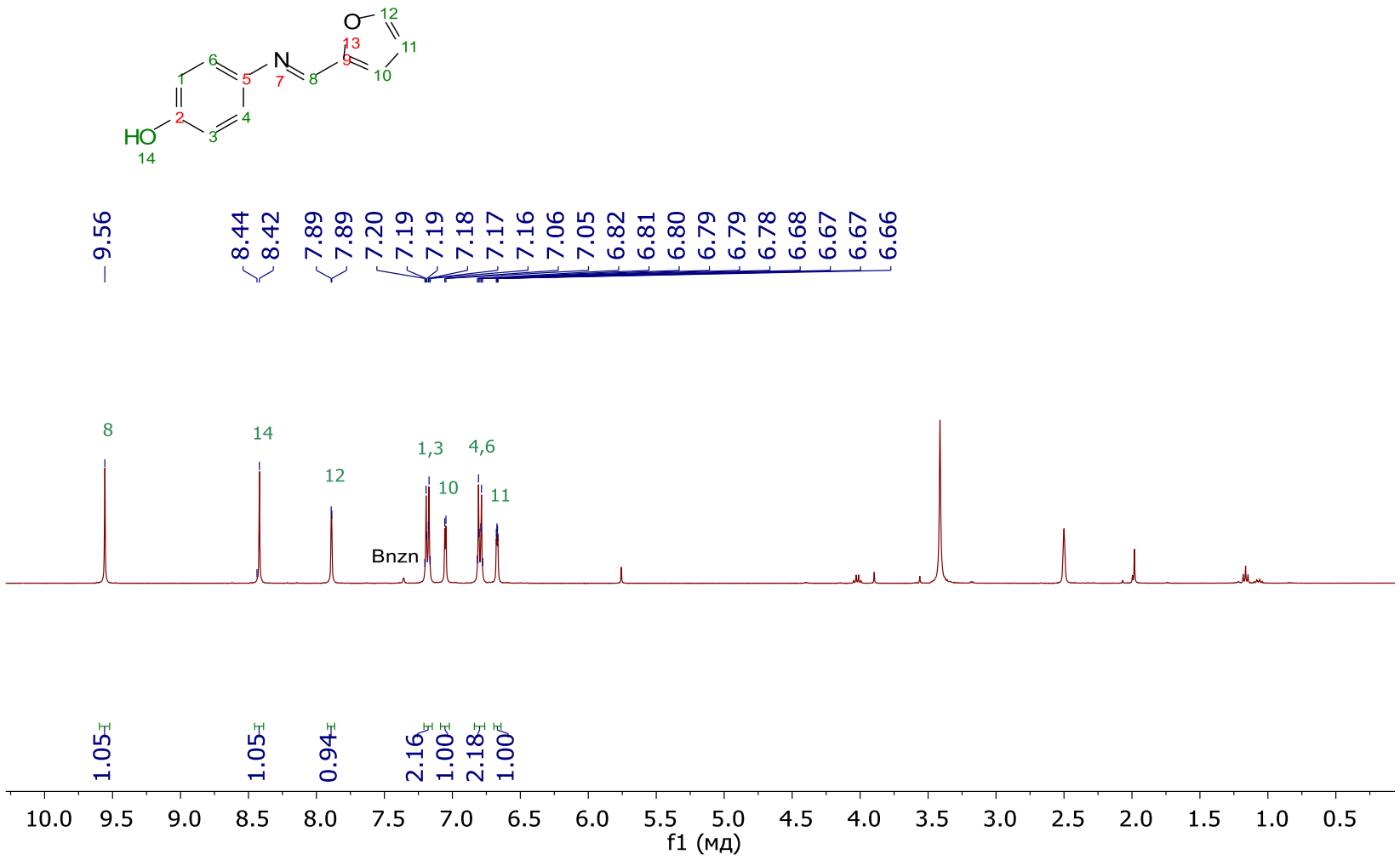


Figure S14. ^{1}H-NMR spectrum of **1f '**, (400 MHz, DMSO-d_6).

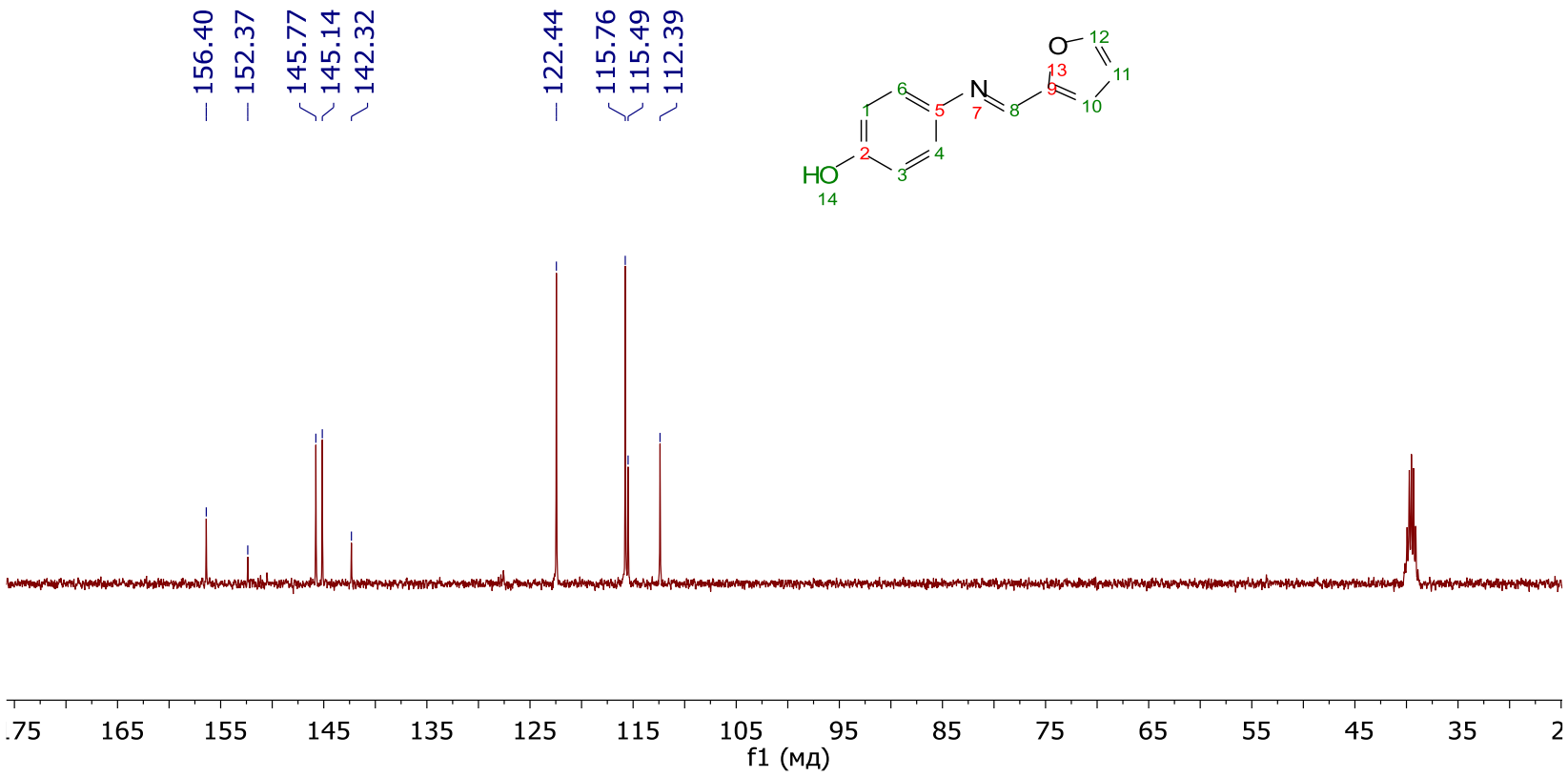


Figure S15. ^{13}C-NMR spectrum of **1f '**, (101 MHz, DMSO-d_6).

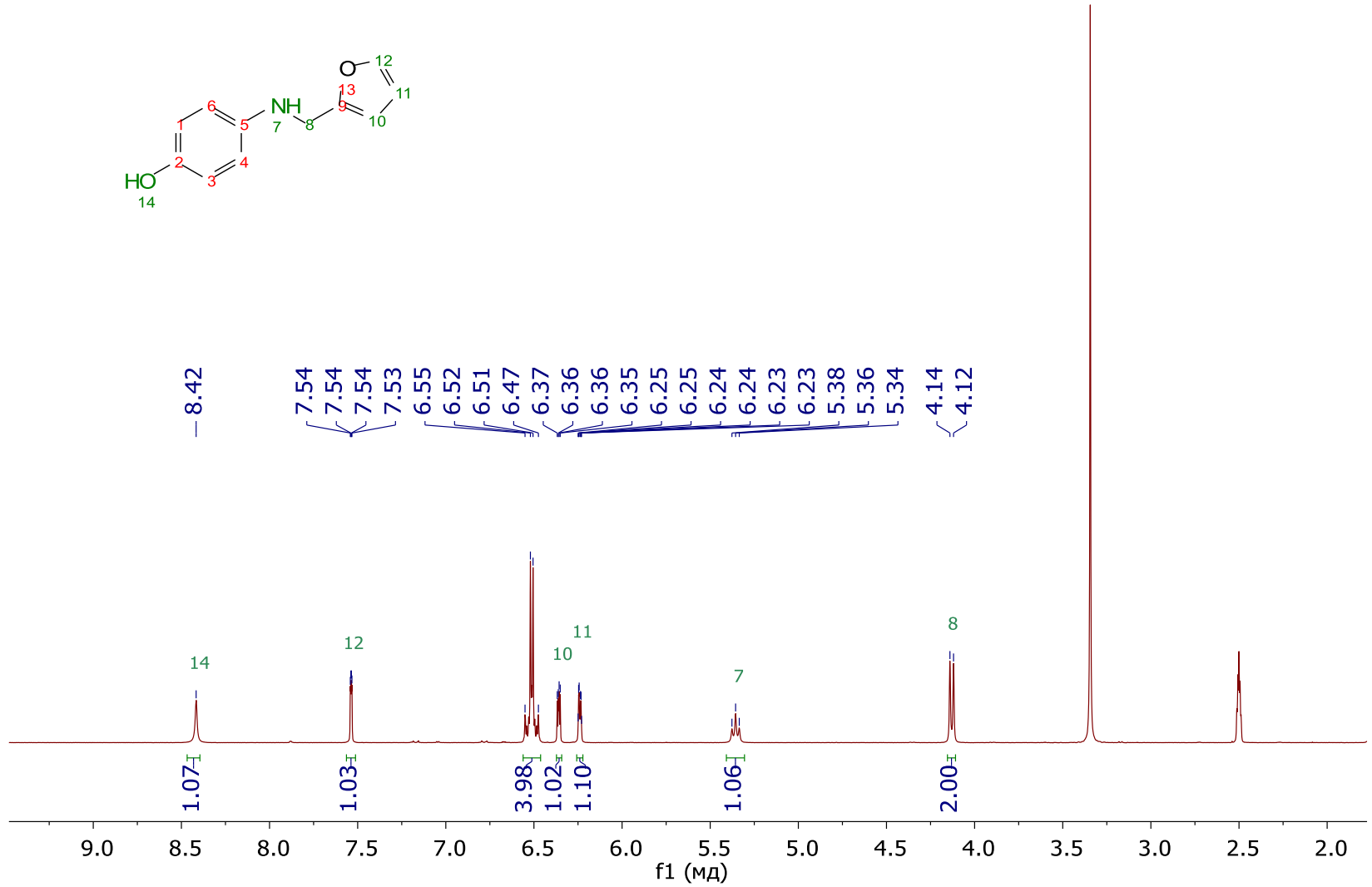


Figure S16. ^{1}H-NMR spectrum of N-Furfuryl-p-aminophenol **1f**, (600 MHz, DMSO-d_6).

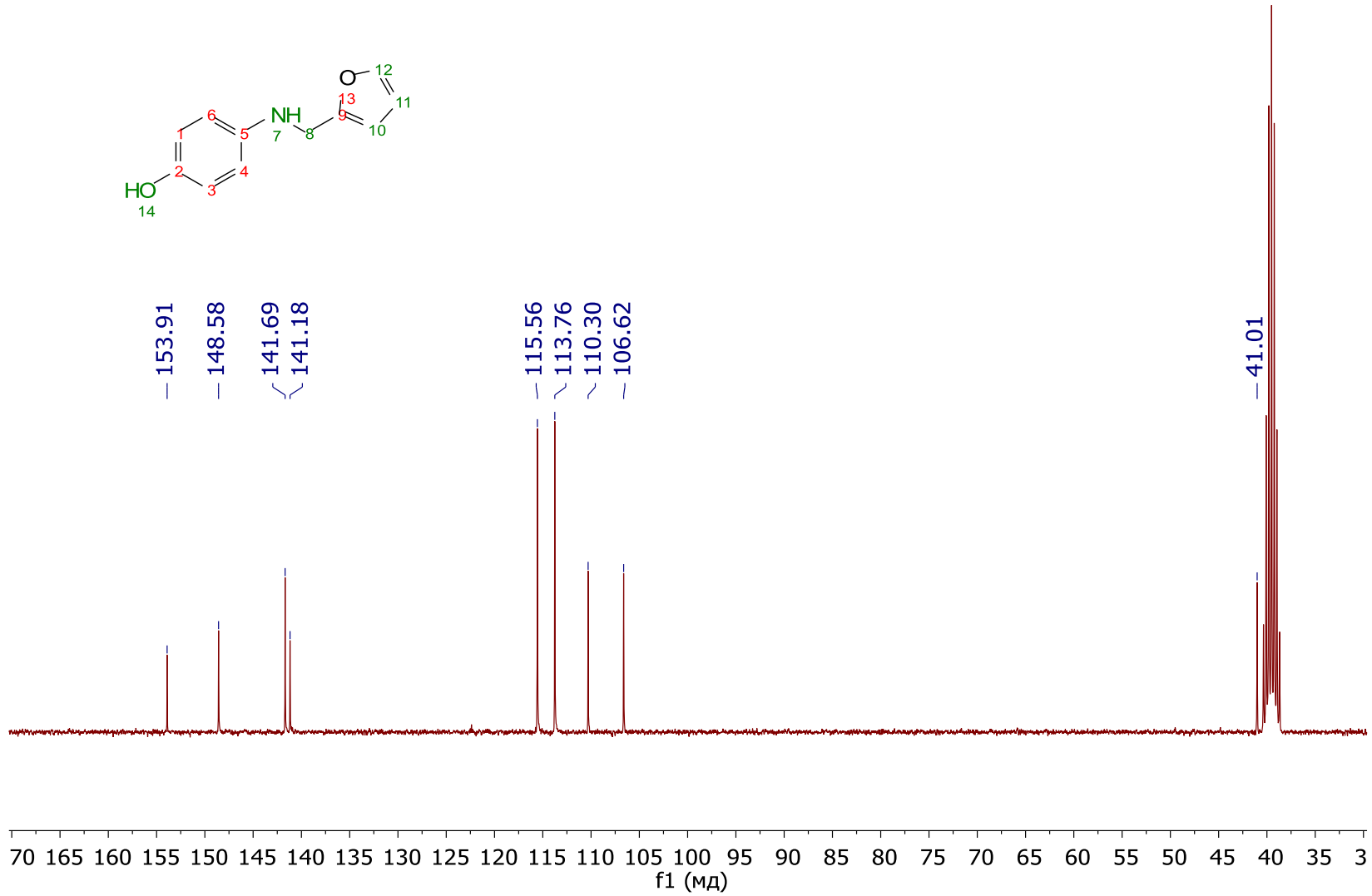


Figure S17. ^{13}C-NMR spectrum of N-Furfuryl-p-aminophenol **1f**, (151 MHz, DMSO-d_6).

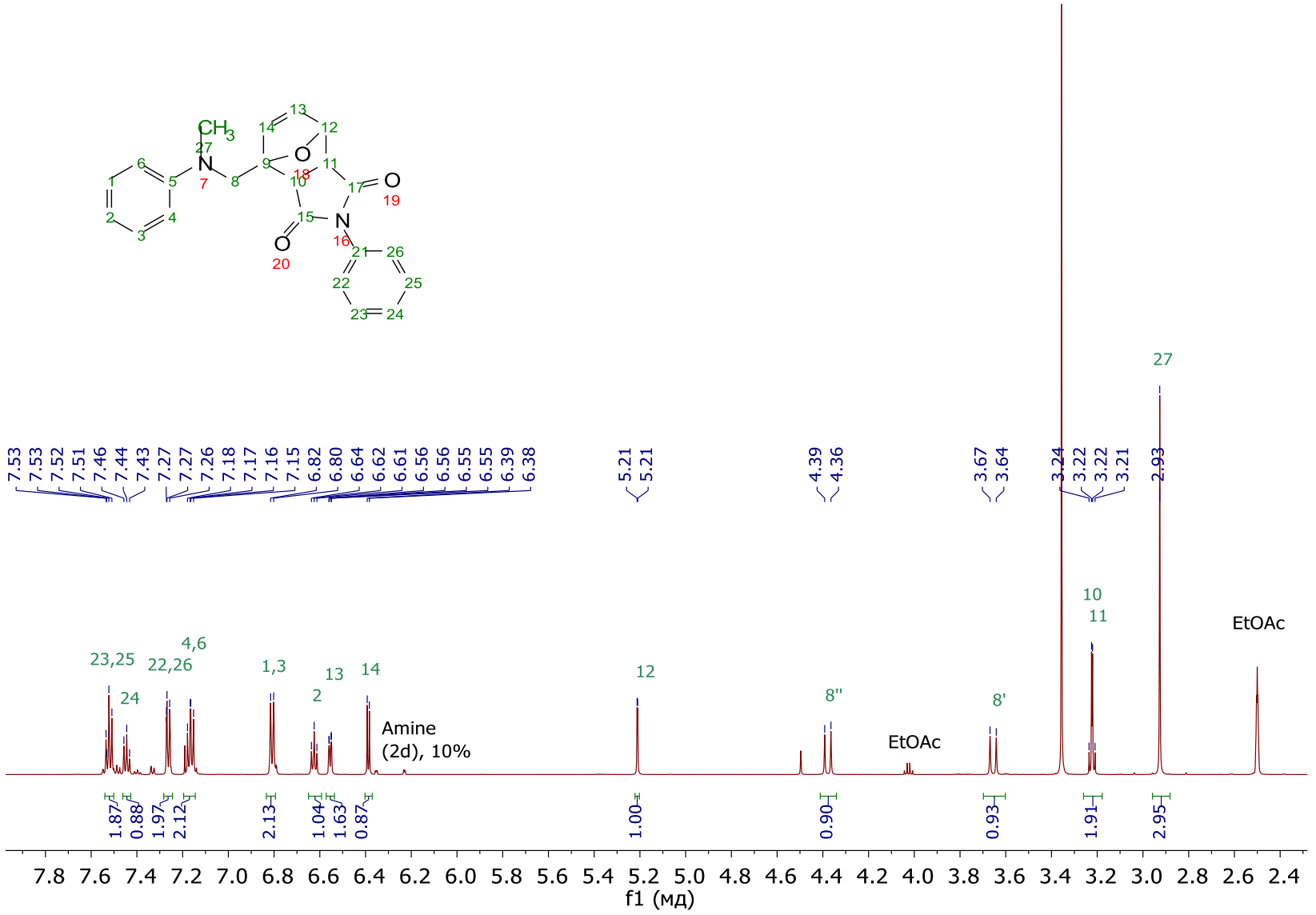


Figure S18. ^{1}H-NMR spectrum of **3a**, (600 MHz, DMSO-d_6).

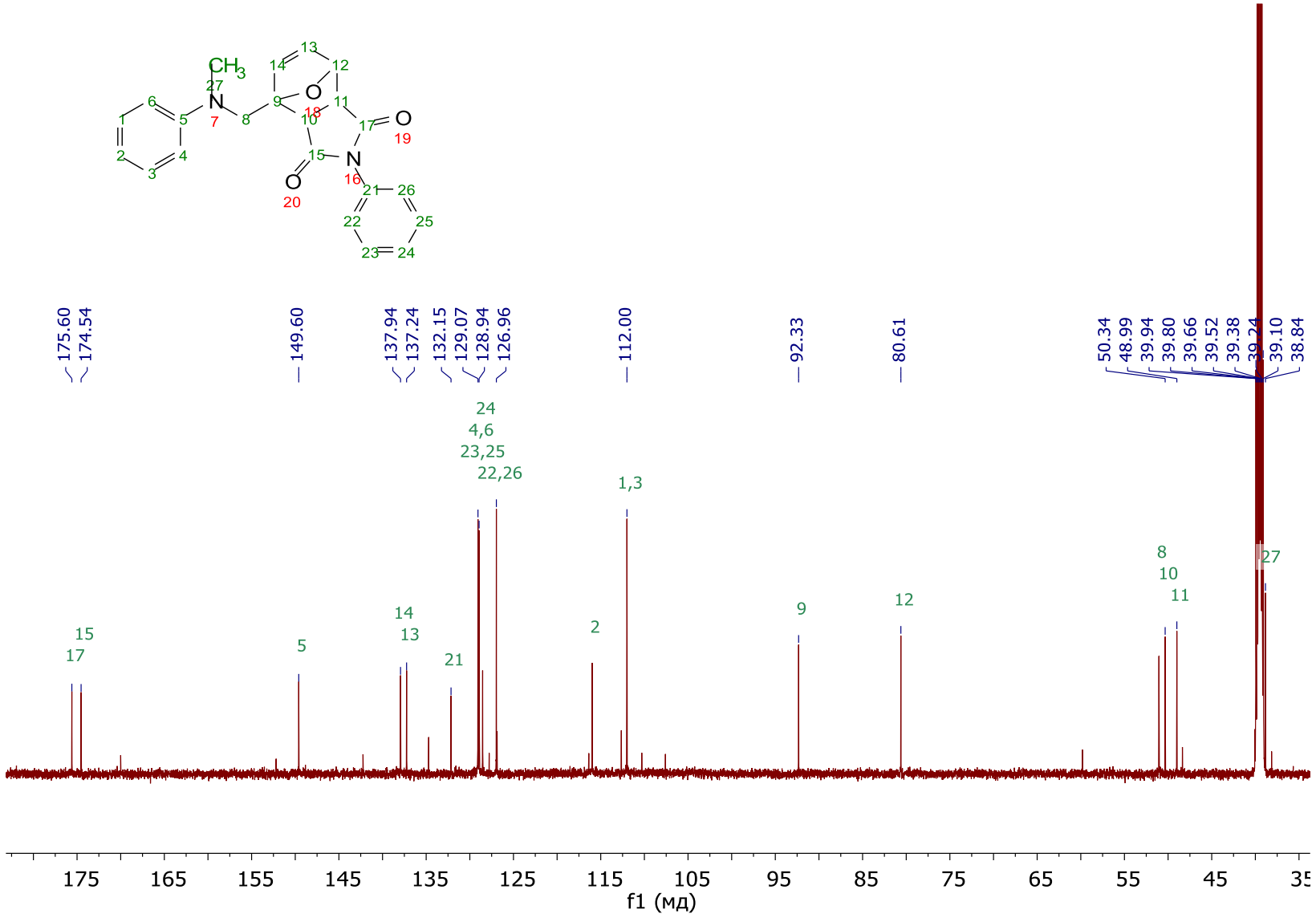


Figure S19. ^{13}C-NMR spectrum of **3a**, (151 MHz, DMSO-d_6).

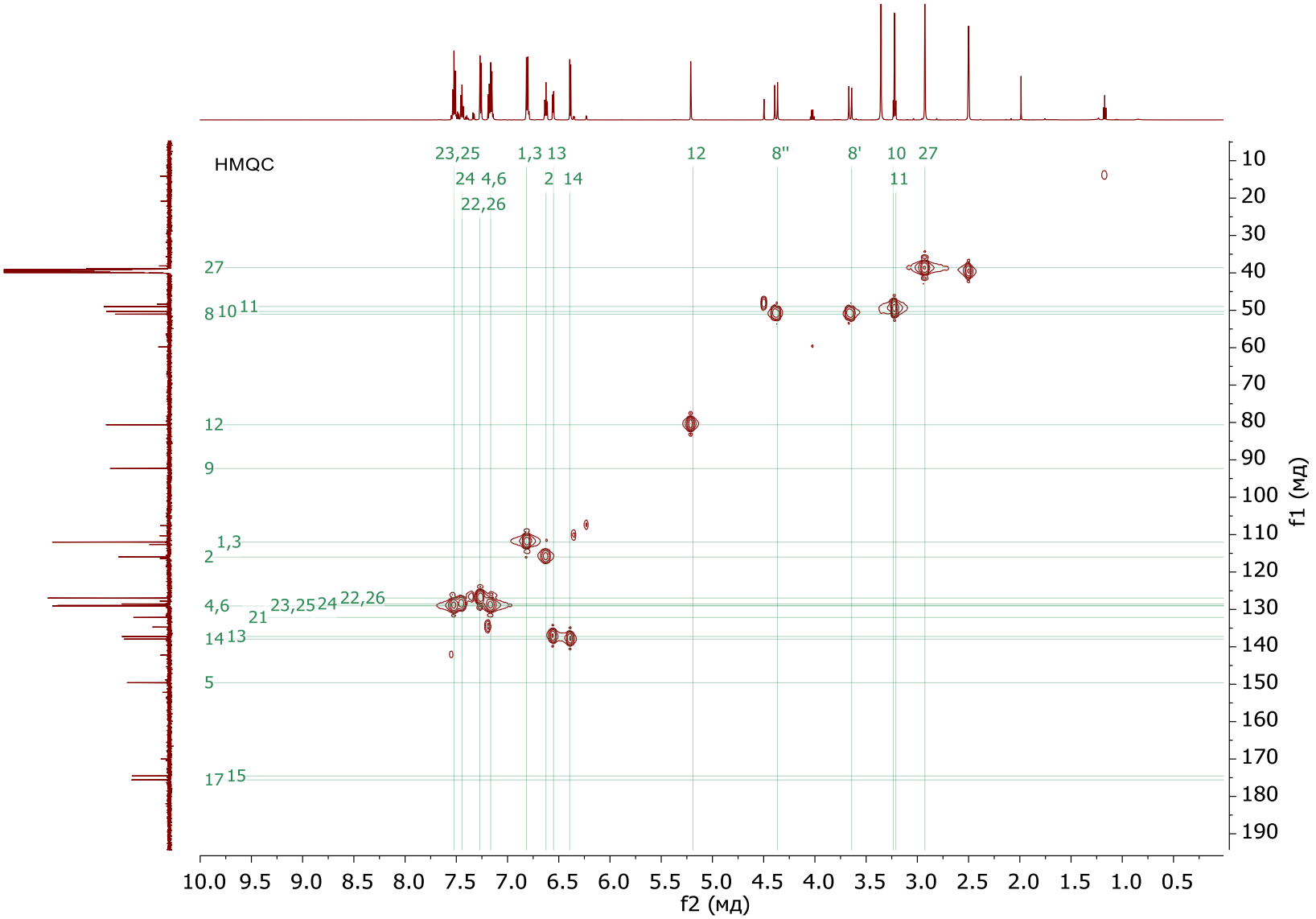


Figure S20. HMQC spectrum of **3a**, (600 MHz, DMSO-d_6).

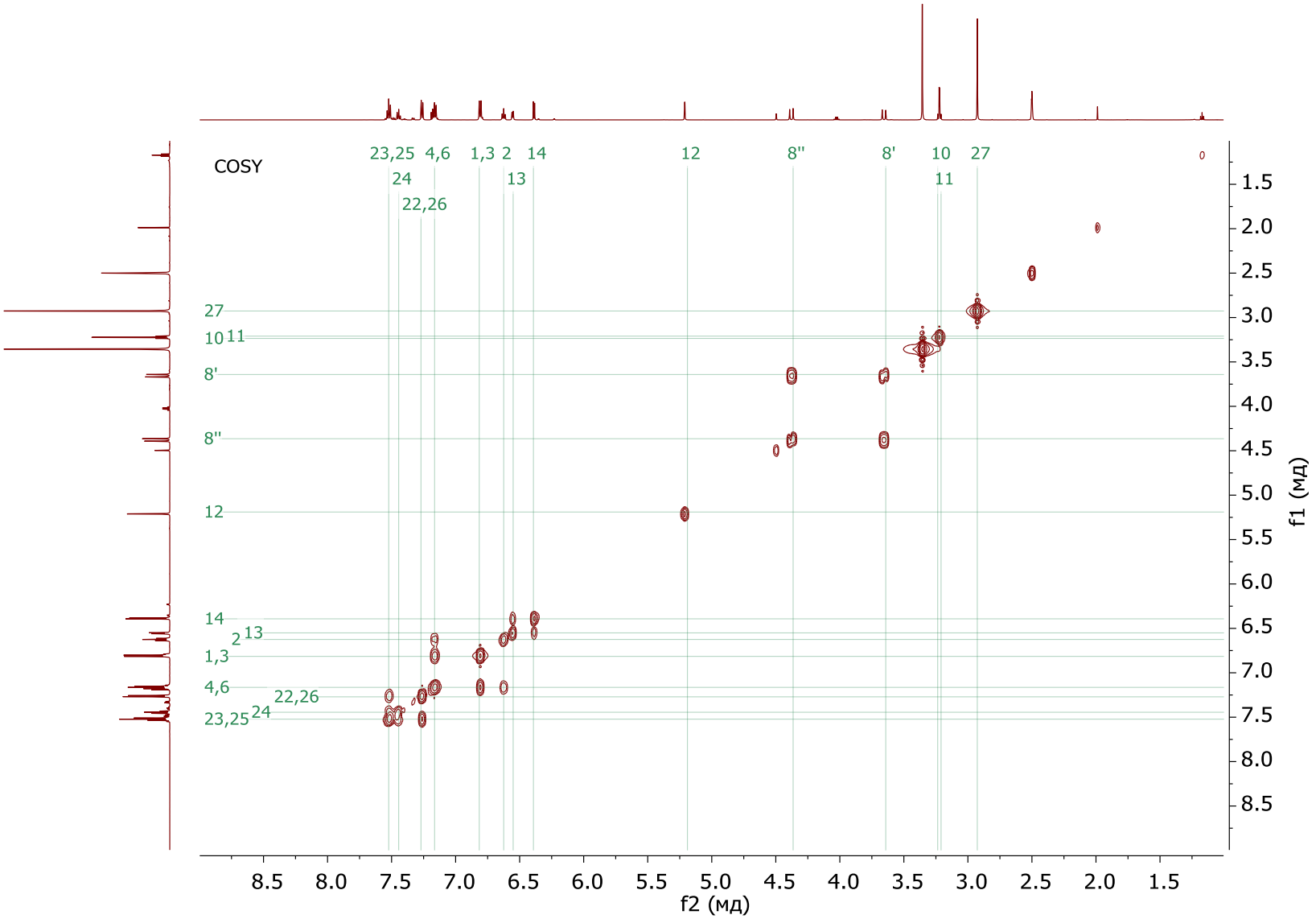


Figure S21. COSY spectrum of **3a**, (600 MHz, DMSO-d_6).

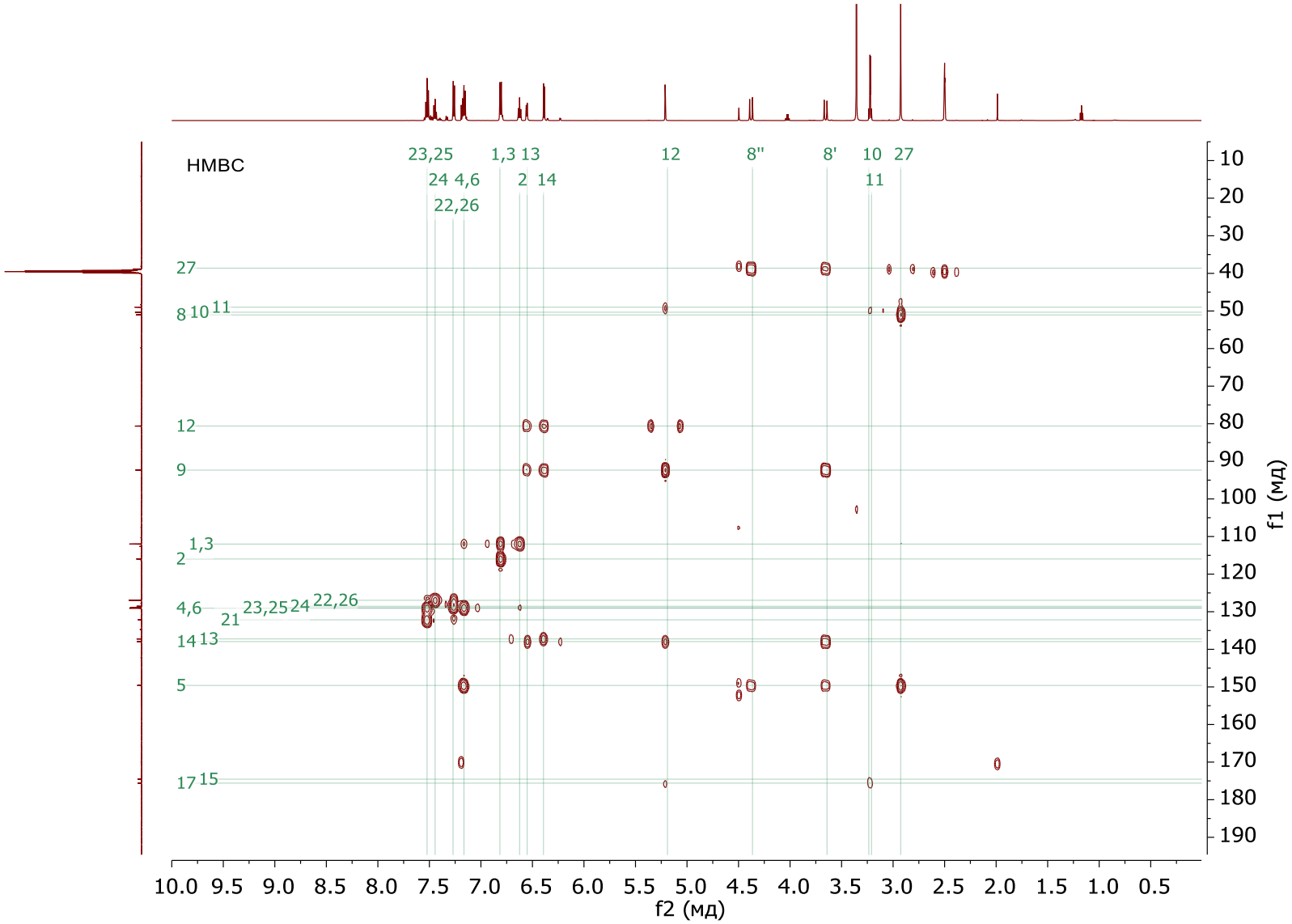


Figure S22. HMBC spectrum of **3a**, (600 MHz, DMSO-d_6).

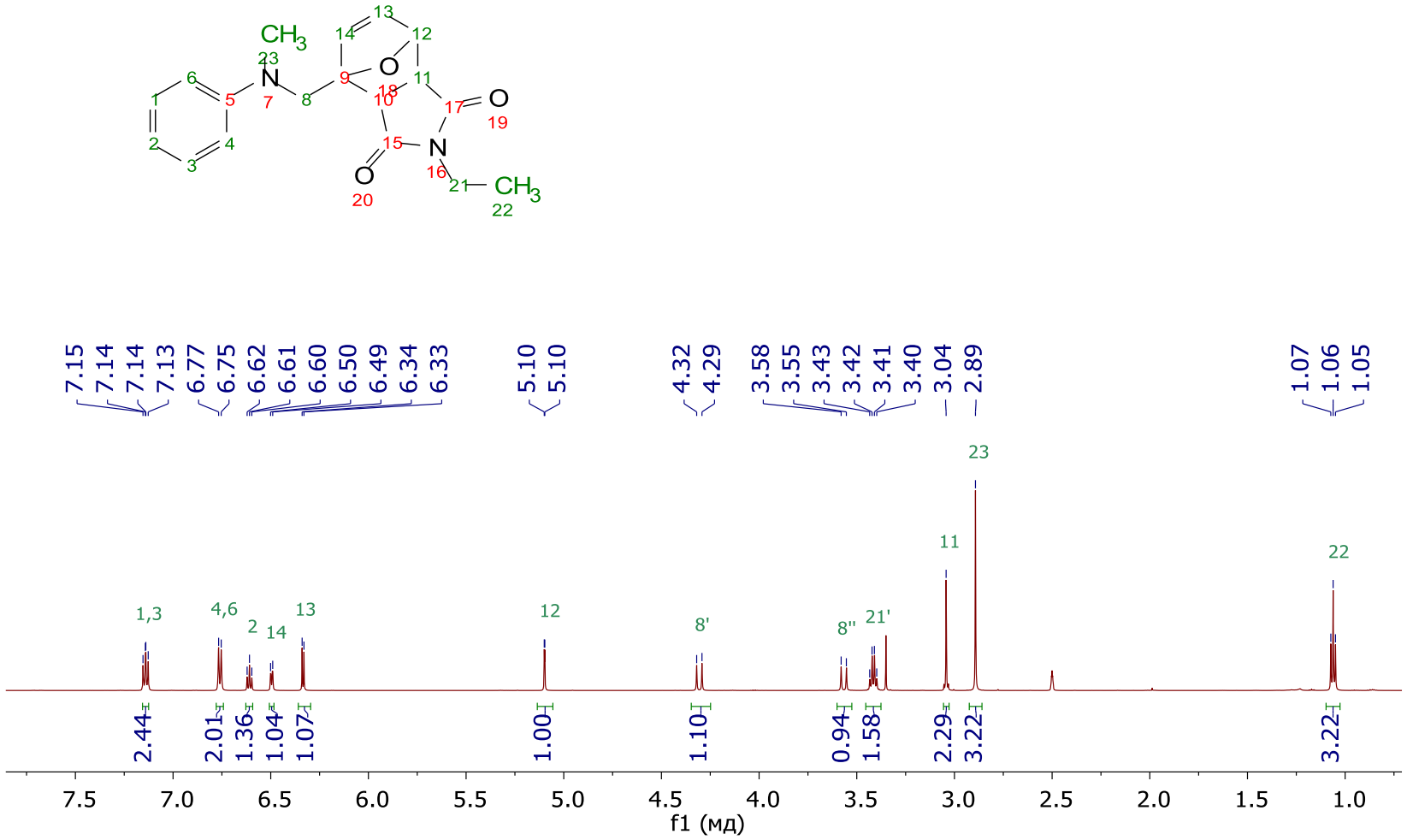


Figure S23. ^{1}H-NMR spectrum of **3b**, (600 MHz, DMSO-d_6).

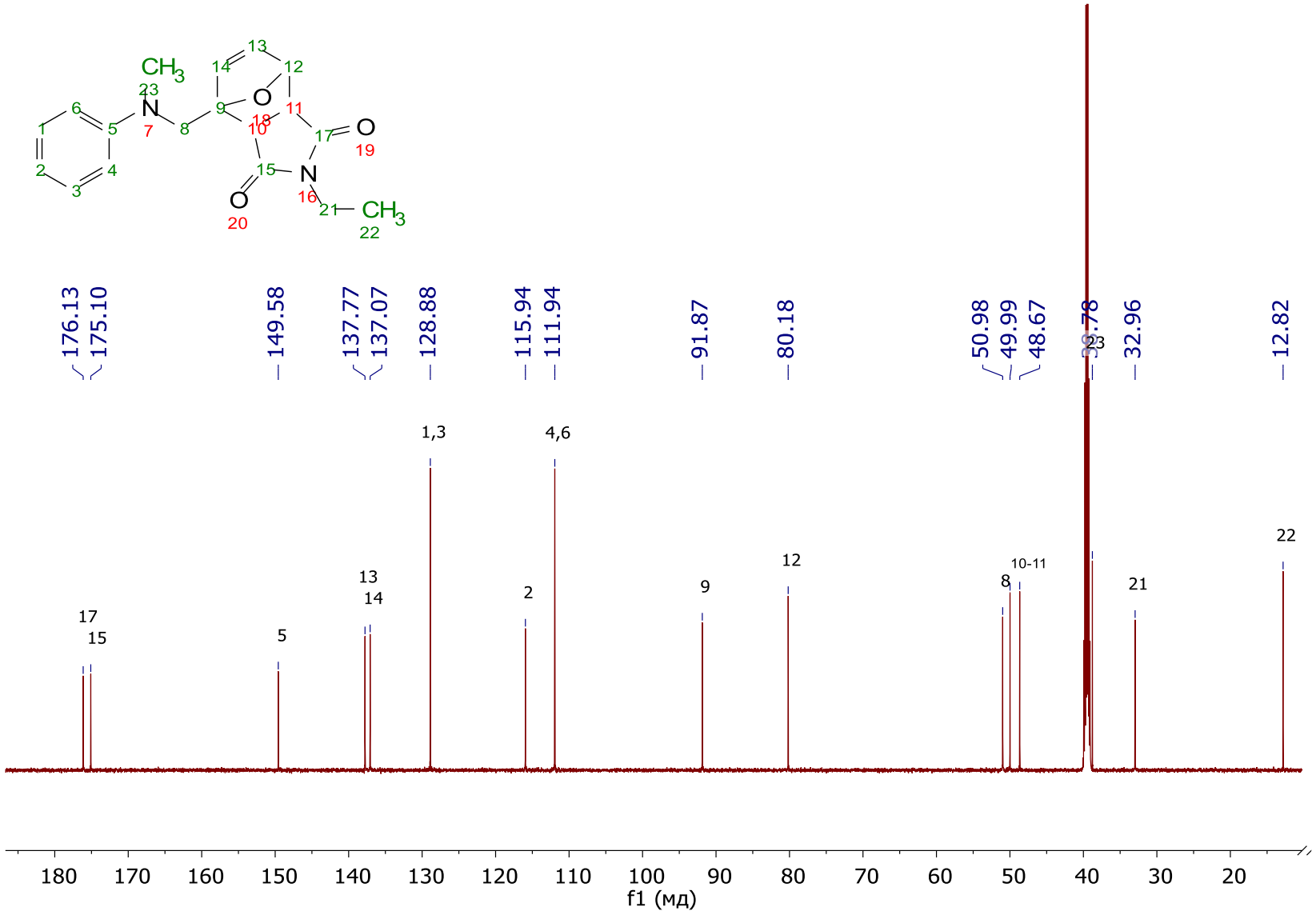


Figure S24. ^{13}C-NMR spectrum of **3b**, (151 MHz, DMSO-d_6).

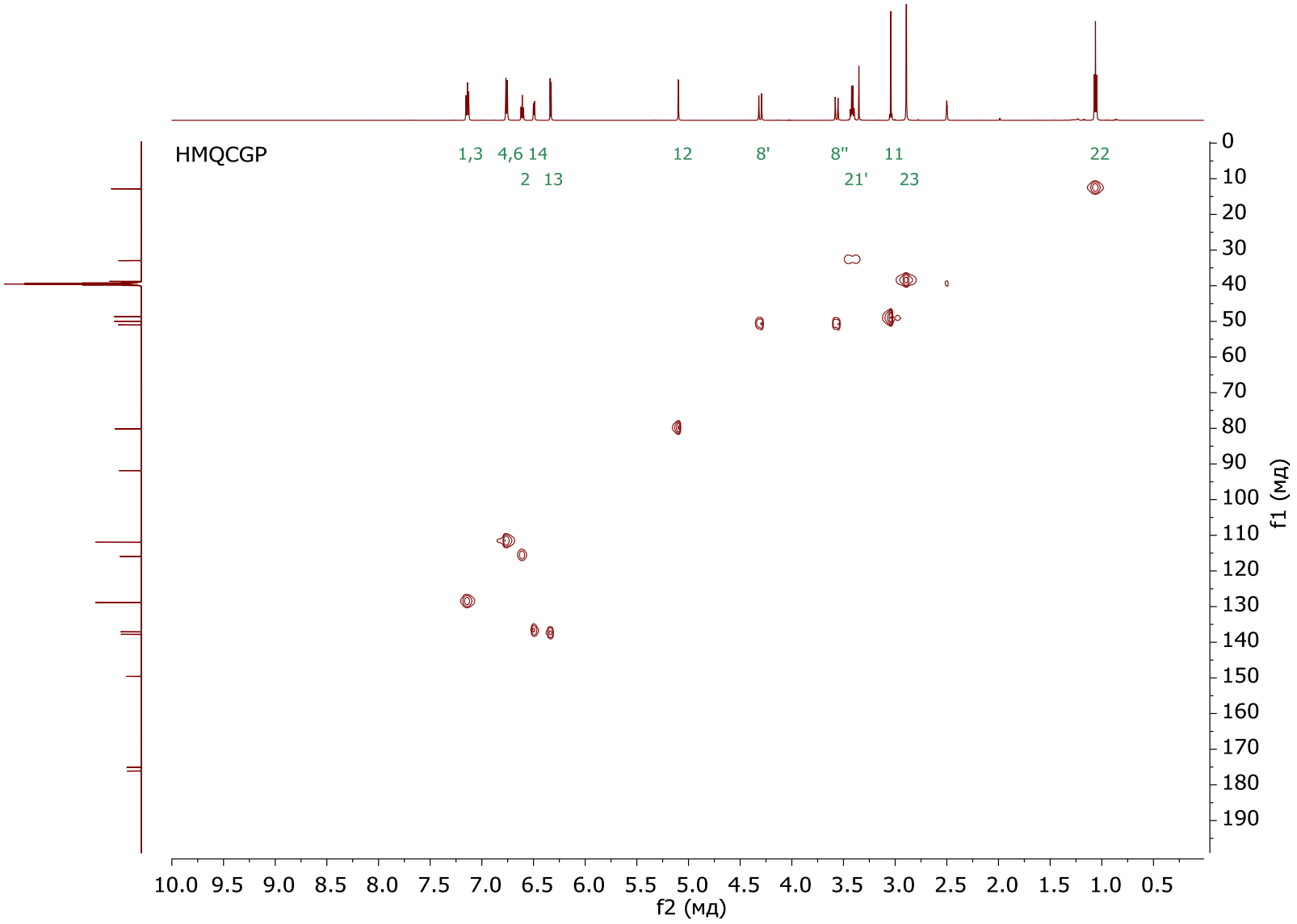


Figure S25. HMQC spectrum of **3b**, (600 MHz, DMSO-d_6).

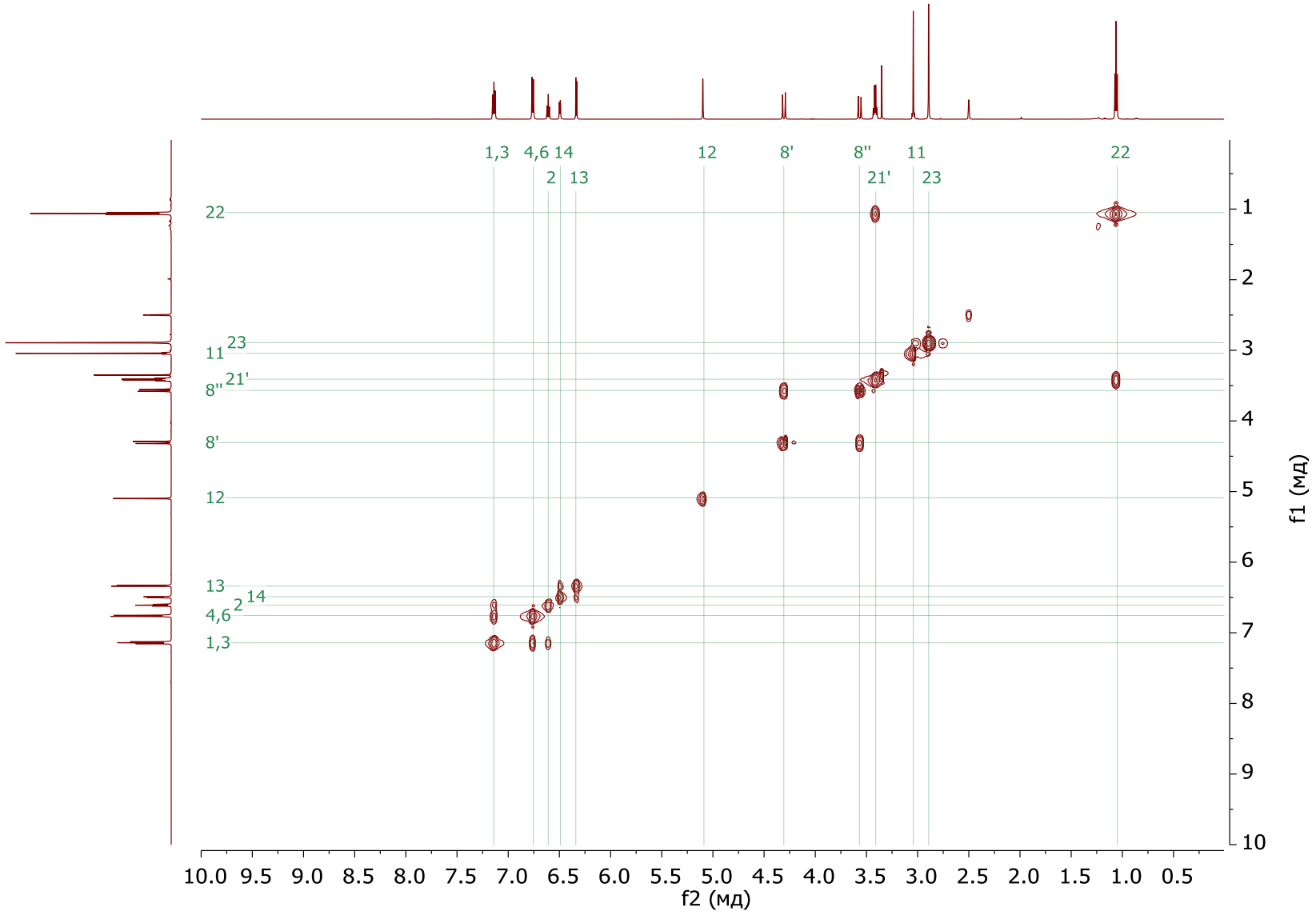


Figure S26. COSY spectrum of **3b**, (600 MHz, DMSO-d_6).

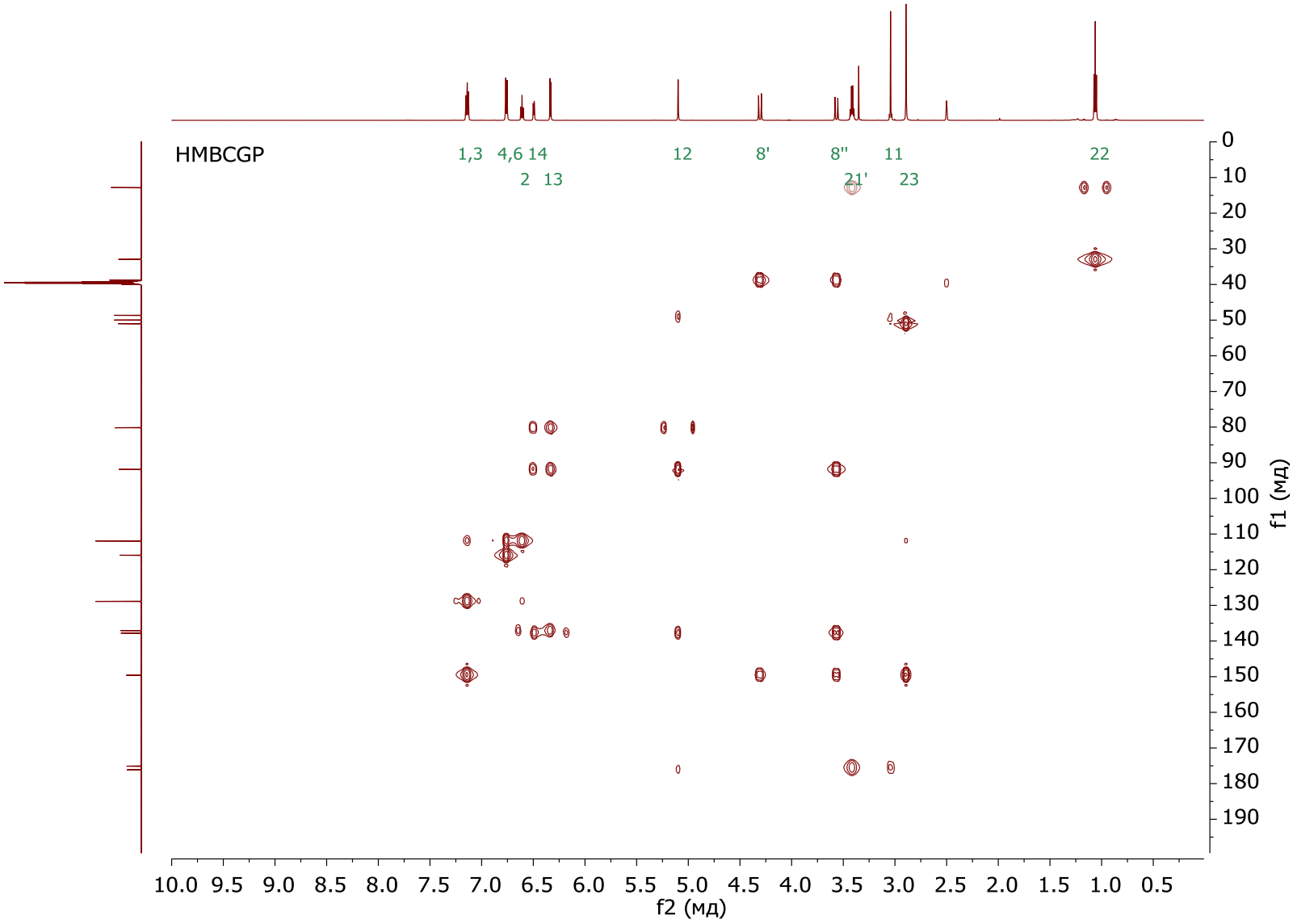


Figure S27. HMBC spectrum of **3b**, (600 MHz, DMSO-d_6).

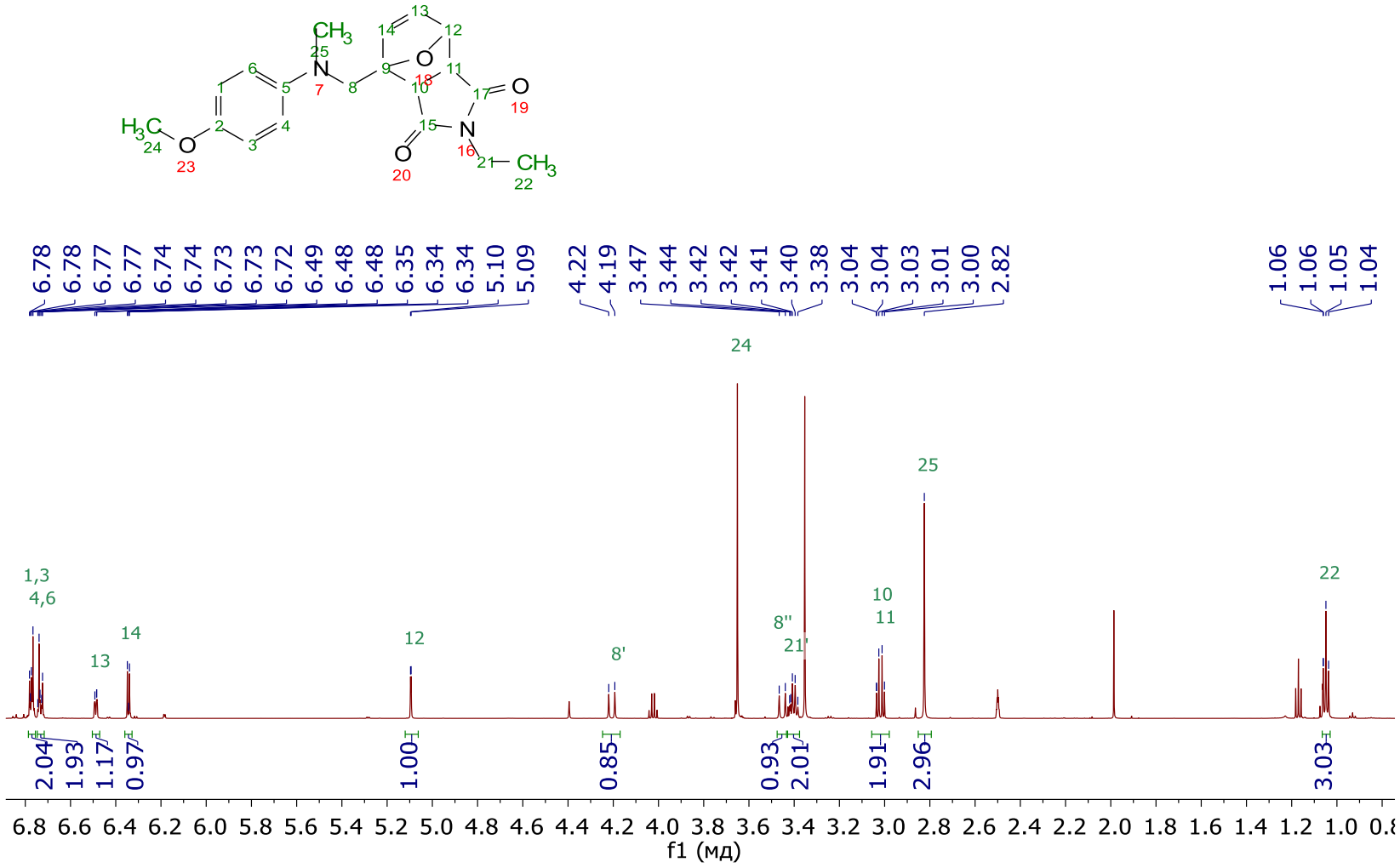


Figure S28. ^{1}H-NMR spectrum of **3c**, (600 MHz, DMSO-d_6).

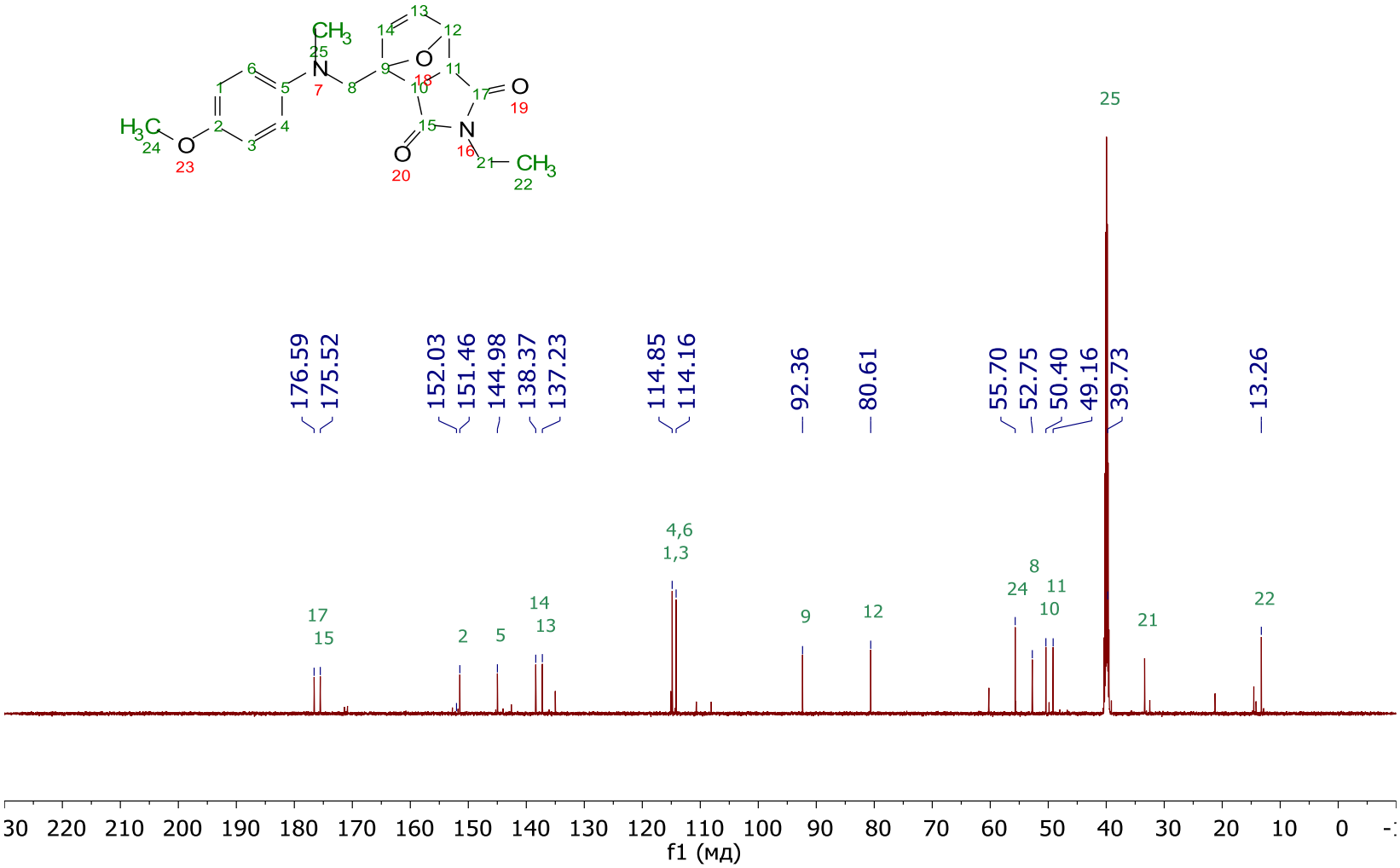


Figure S29. ^{13}C-NMR spectrum of **3c**, (151 MHz, DMSO-d_6).

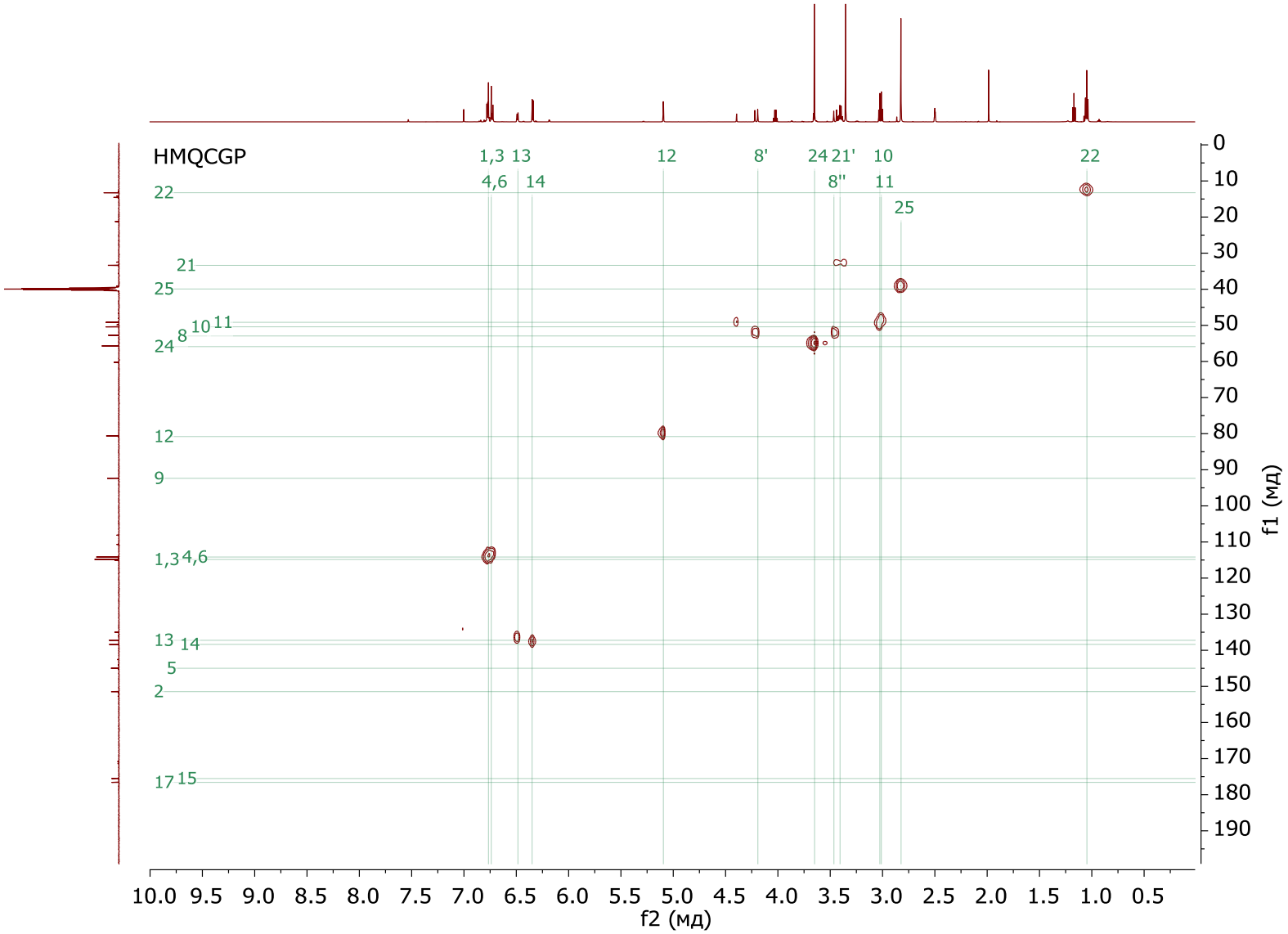


Figure S30. HMQC spectrum of **3c**, (600 MHz, DMSO-d_6).

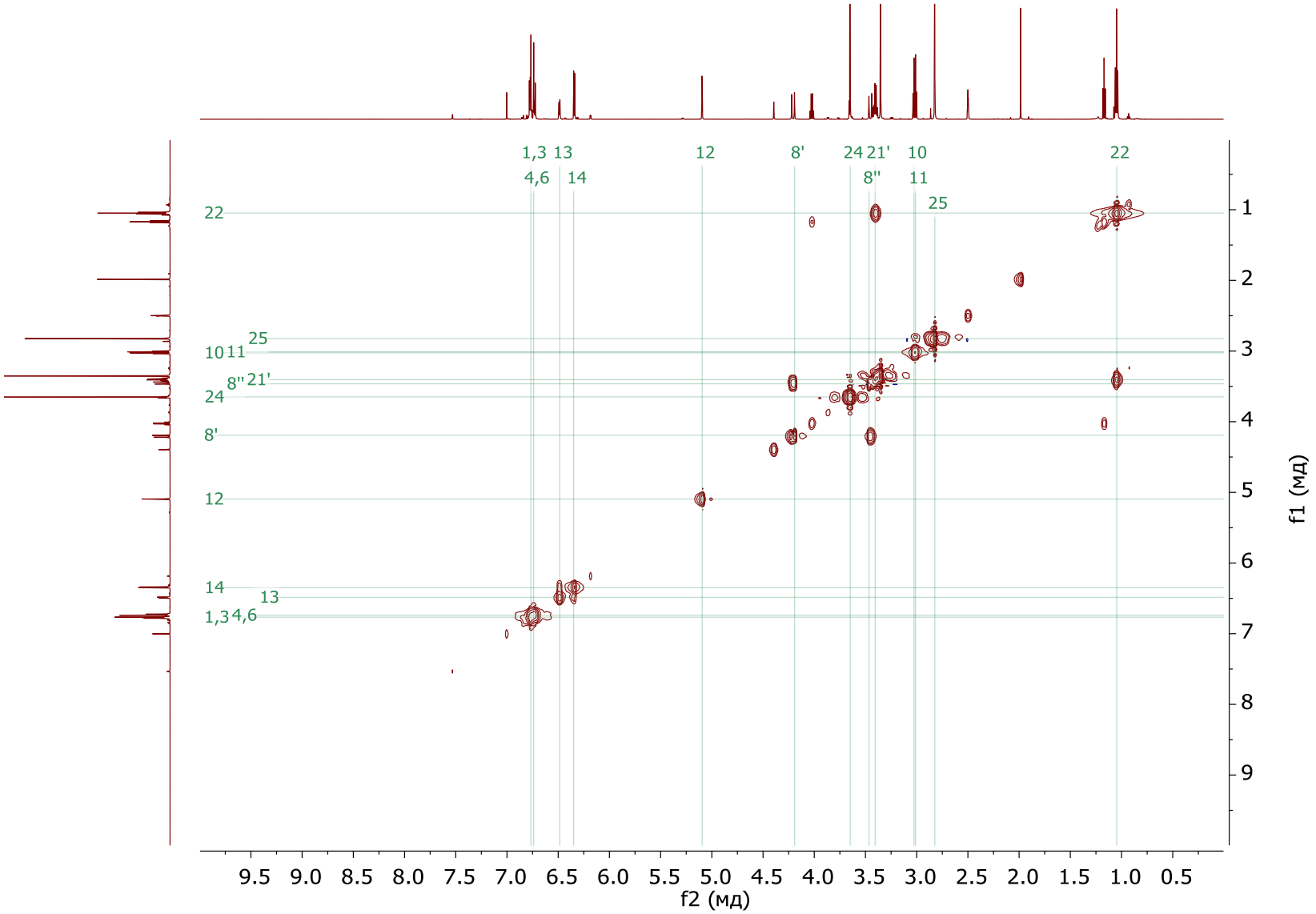


Figure S31. COSY spectrum of **3c**, (600 MHz, DMSO-d_6).

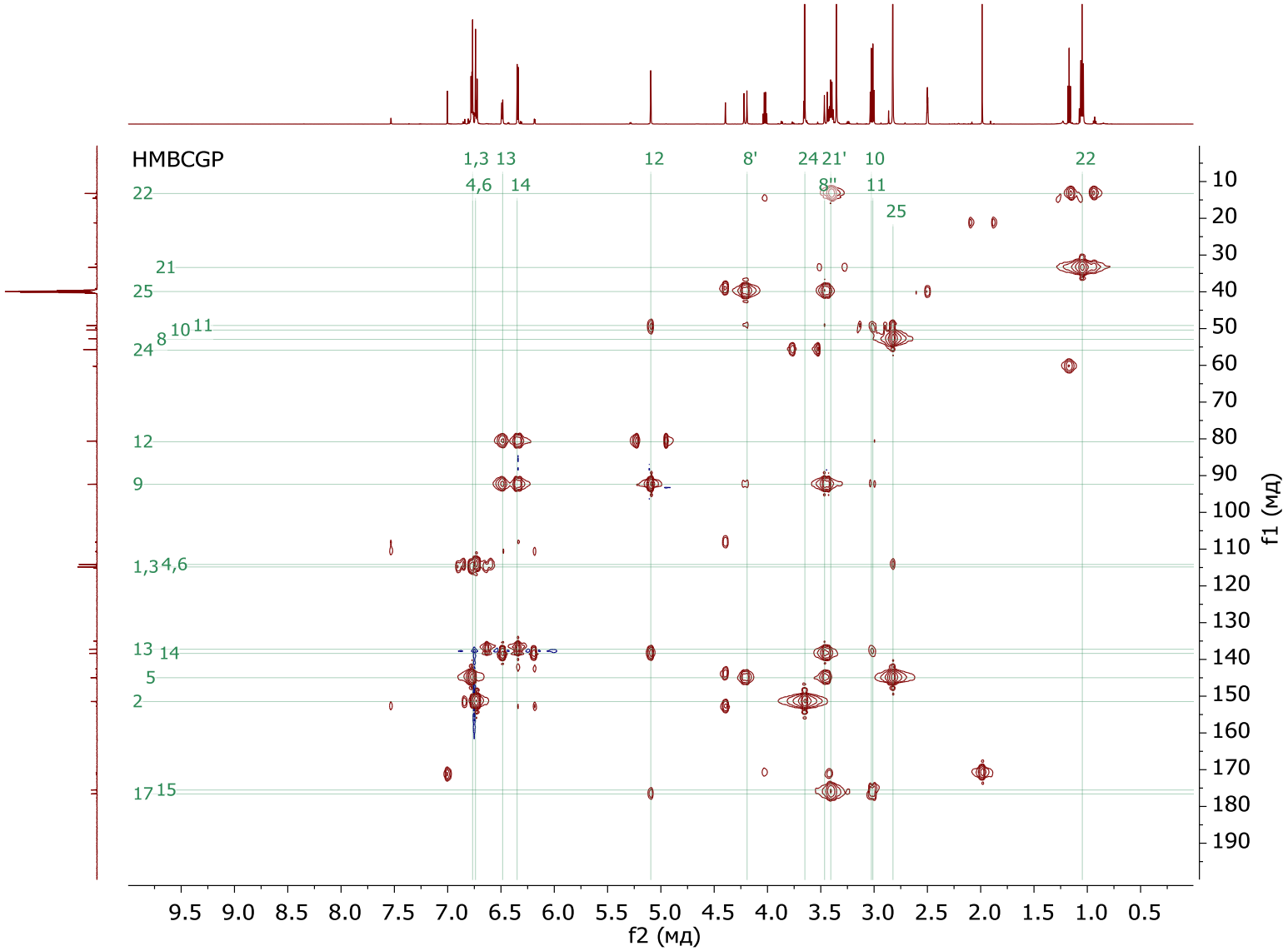


Figure S32. HMBC spectrum of **3c**, (600 MHz, DMSO-d_6).

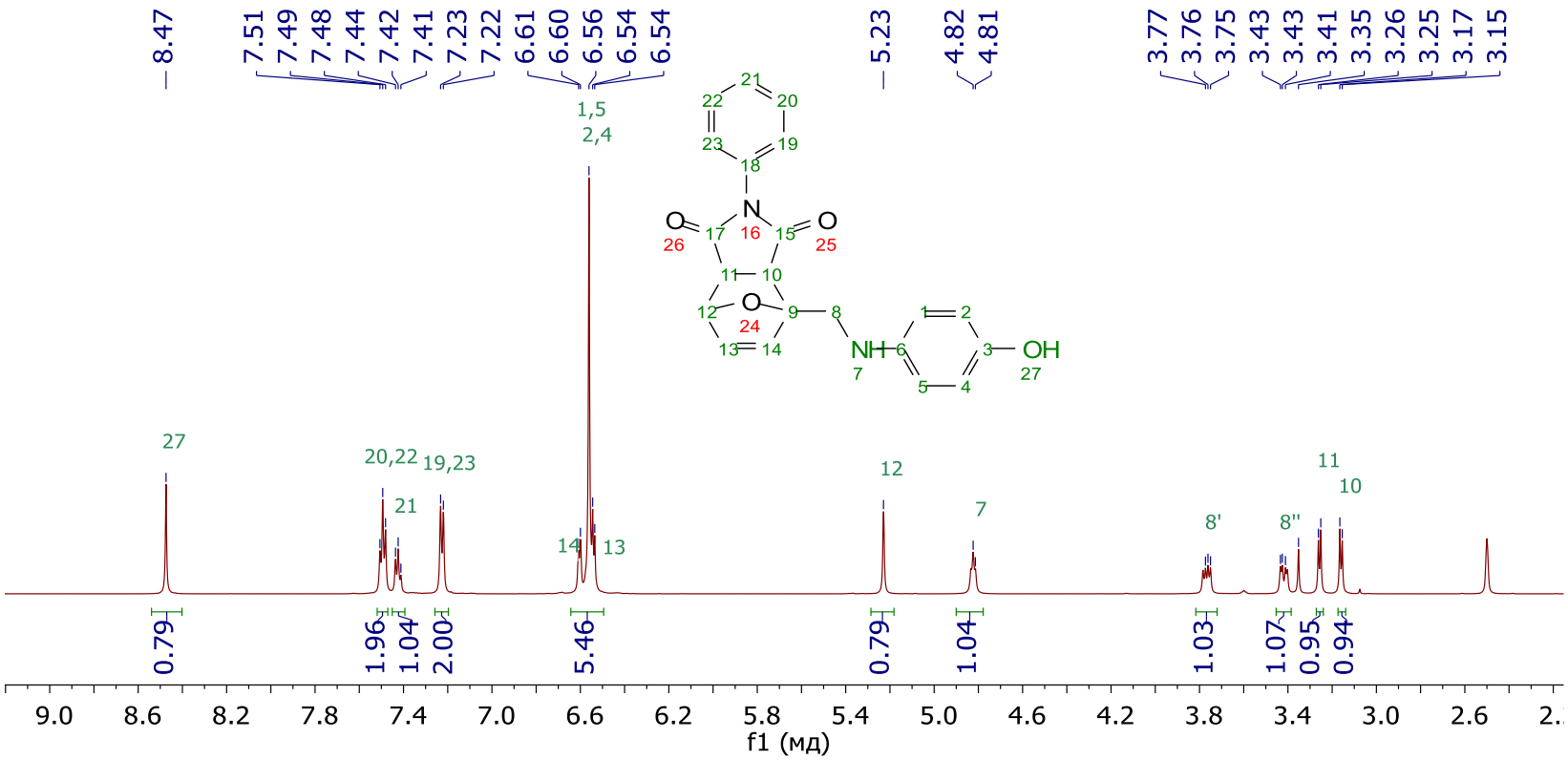


Figure S33. ^{1}H-NMR spectrum of **3d**, (600 MHz, DMSO-d_6).

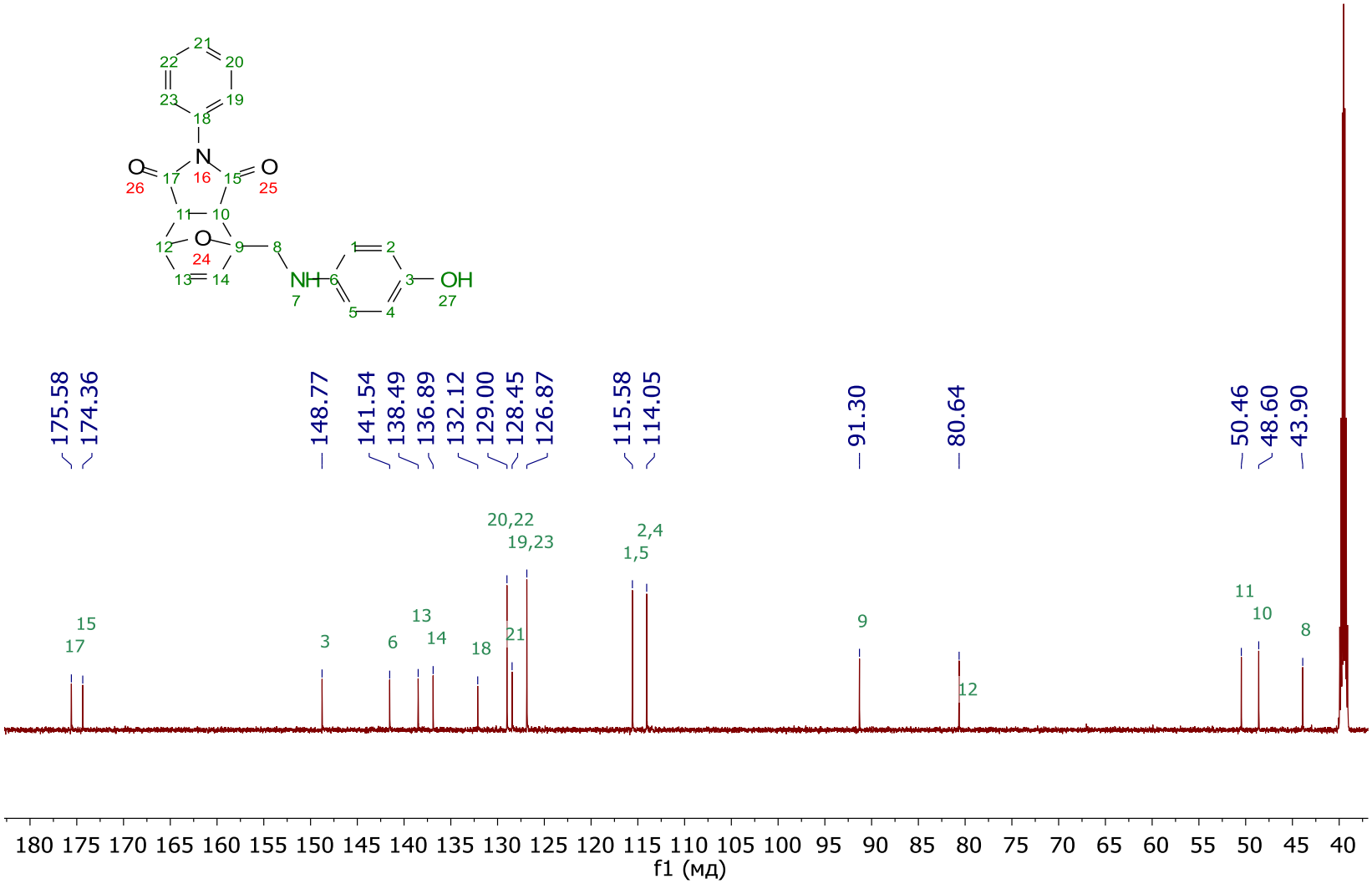


Figure S34. ^{13}C-NMR spectrum of **3d**, (151 MHz, DMSO-d_6).

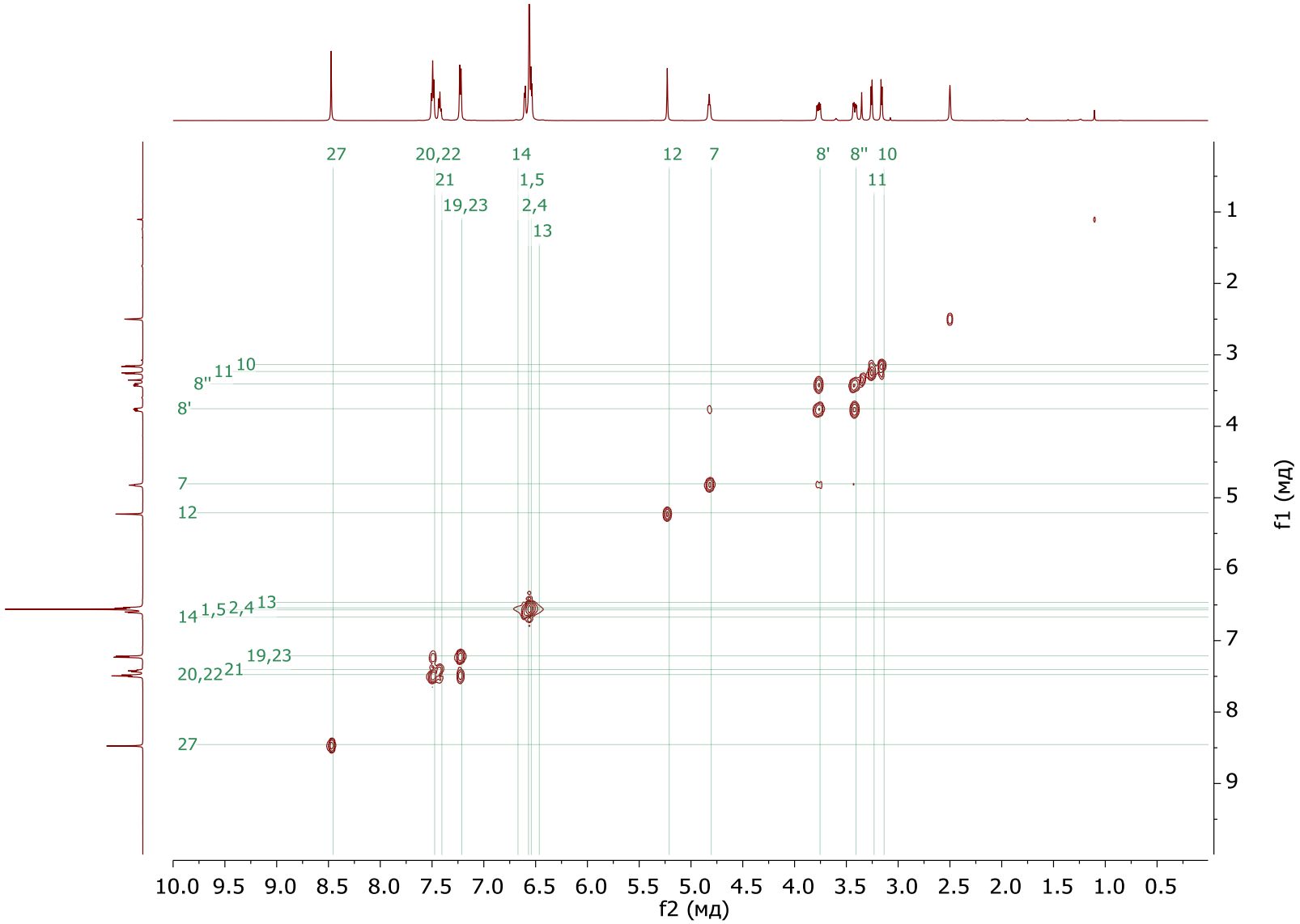


Figure S35. HMQC spectrum of **3d**, (600 MHz, DMSO-d_6).

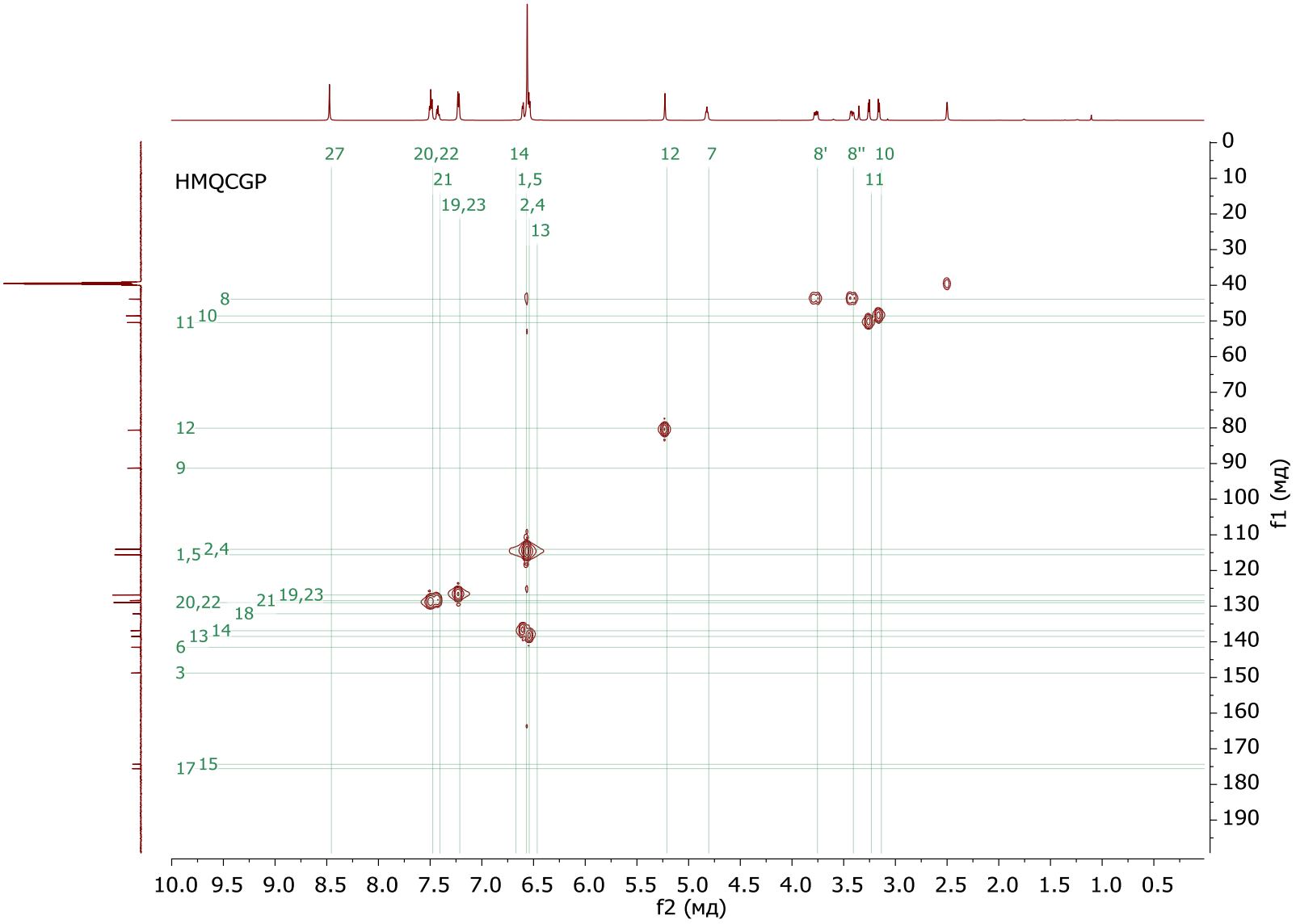


Figure S36. COSY spectrum of **3d**, (600 MHz, DMSO-d_6).

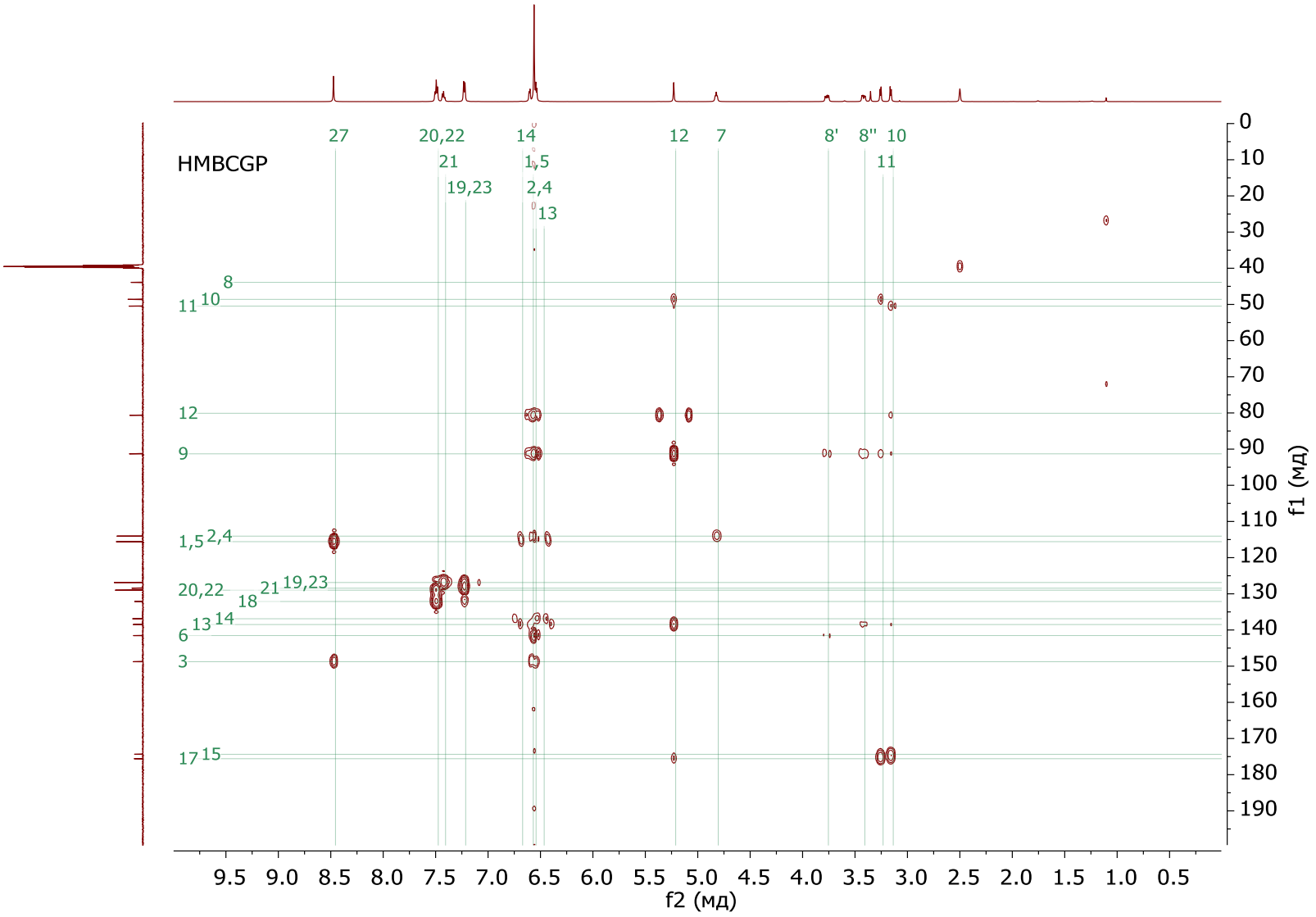


Figure S37. HMBC spectrum of **3d**, (600 MHz, DMSO-d_6).

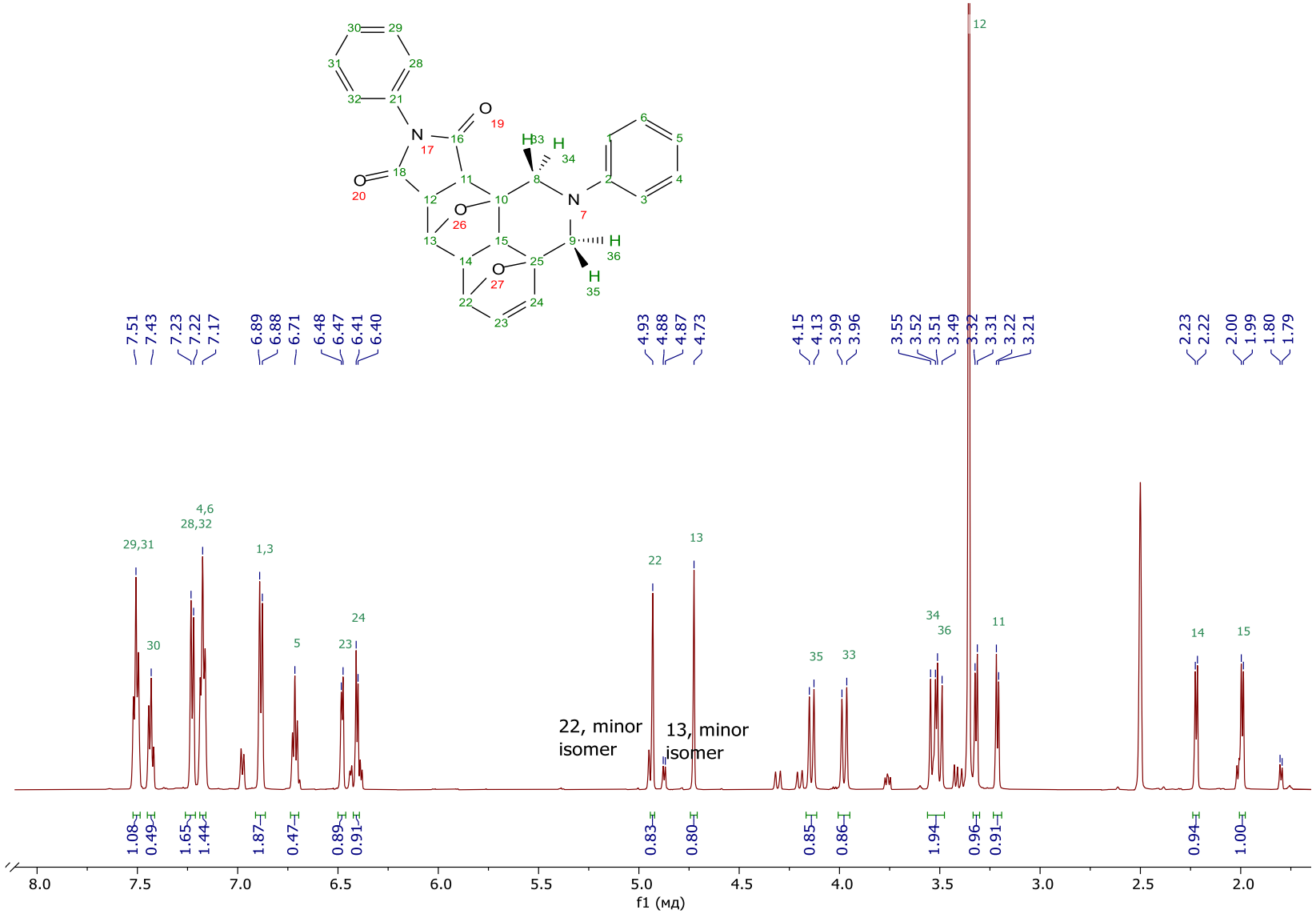


Figure S38. ^{1}H-NMR spectrum of **5a**, (600 MHz, DMSO-d_6).

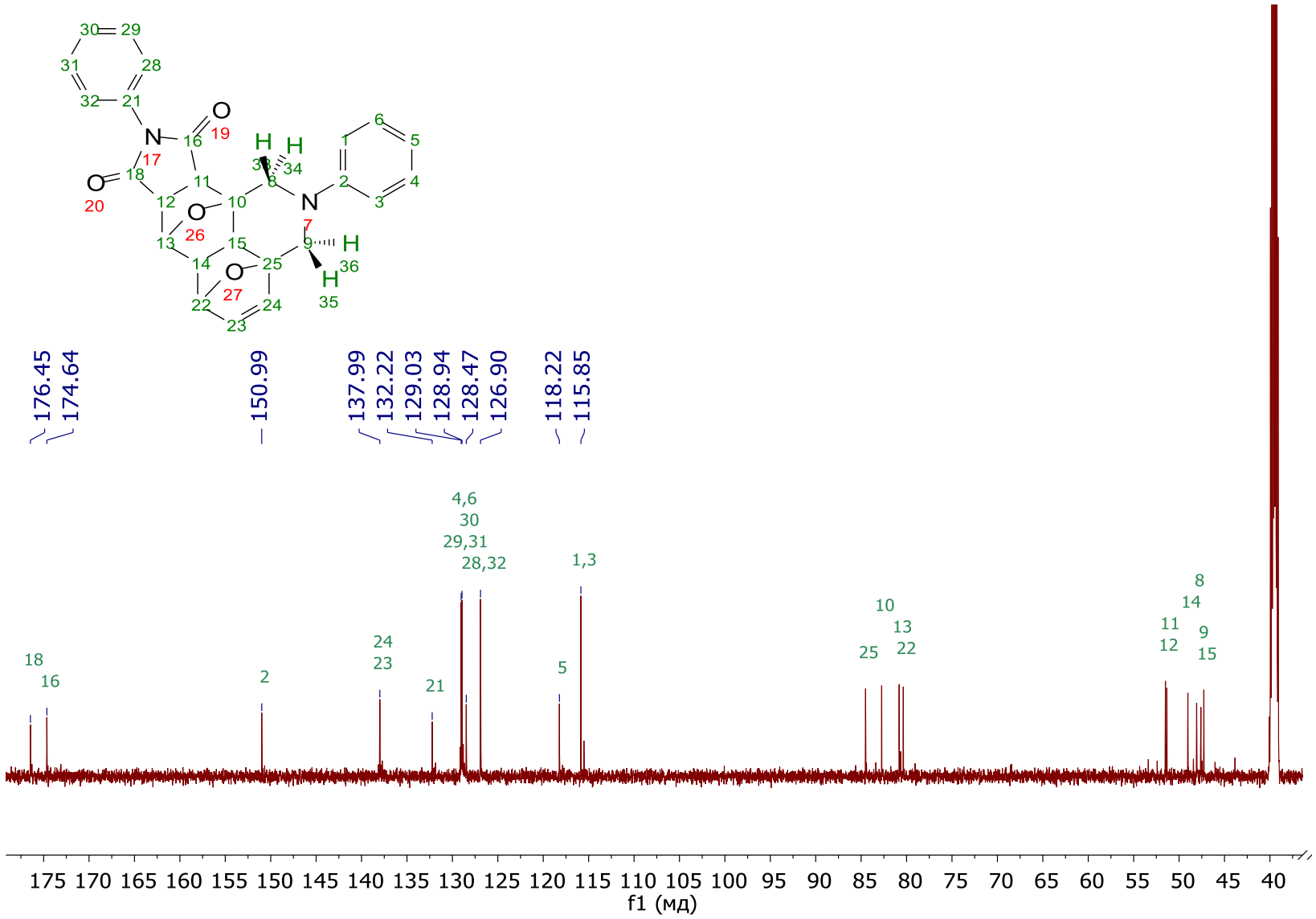


Figure S39. ^{13}C-NMR spectrum of **5a**, (151 MHz, DMSO-d_6).

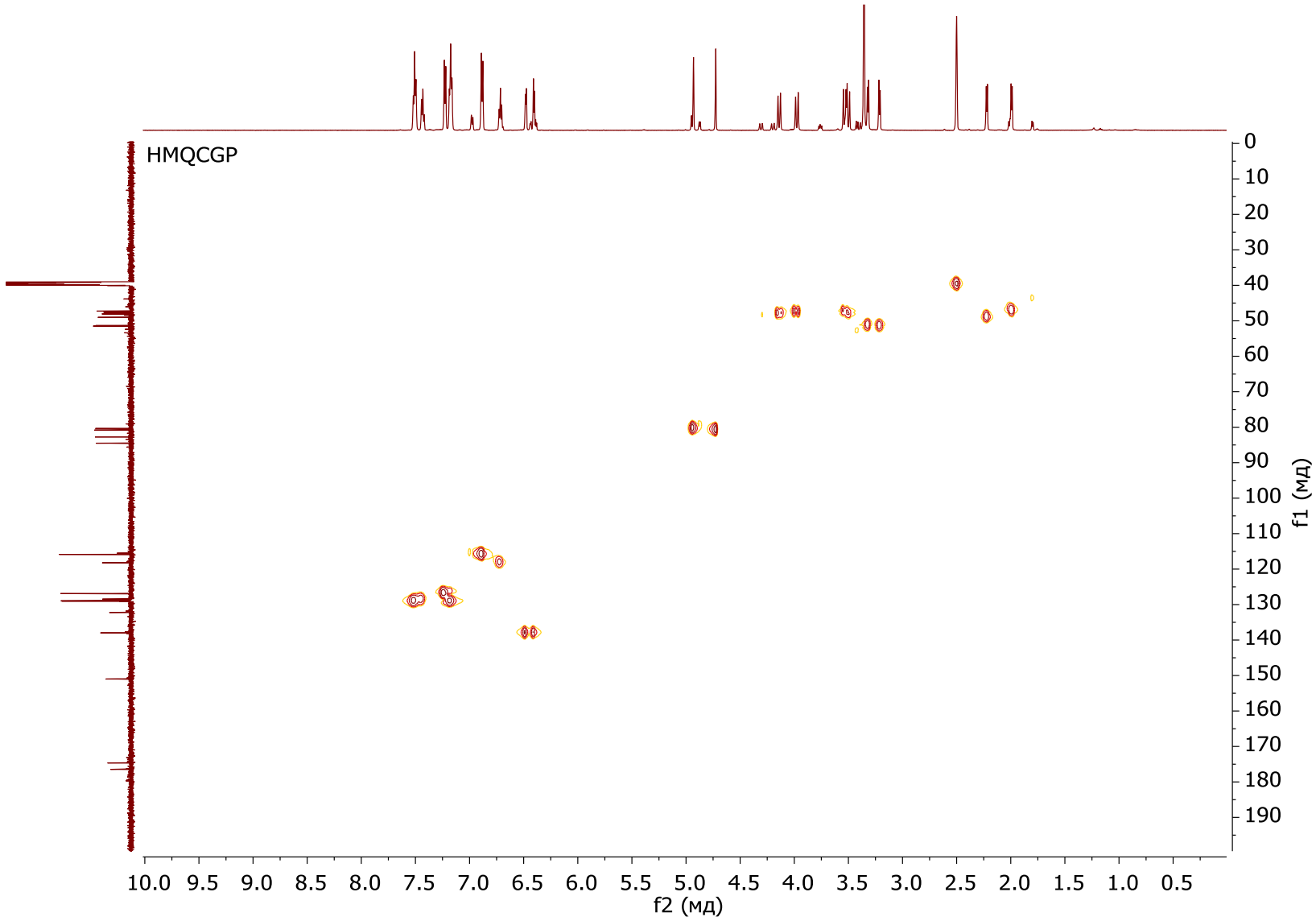


Figure S40. HMQC spectrum of **5a**, (600 MHz, DMSO-d_6).

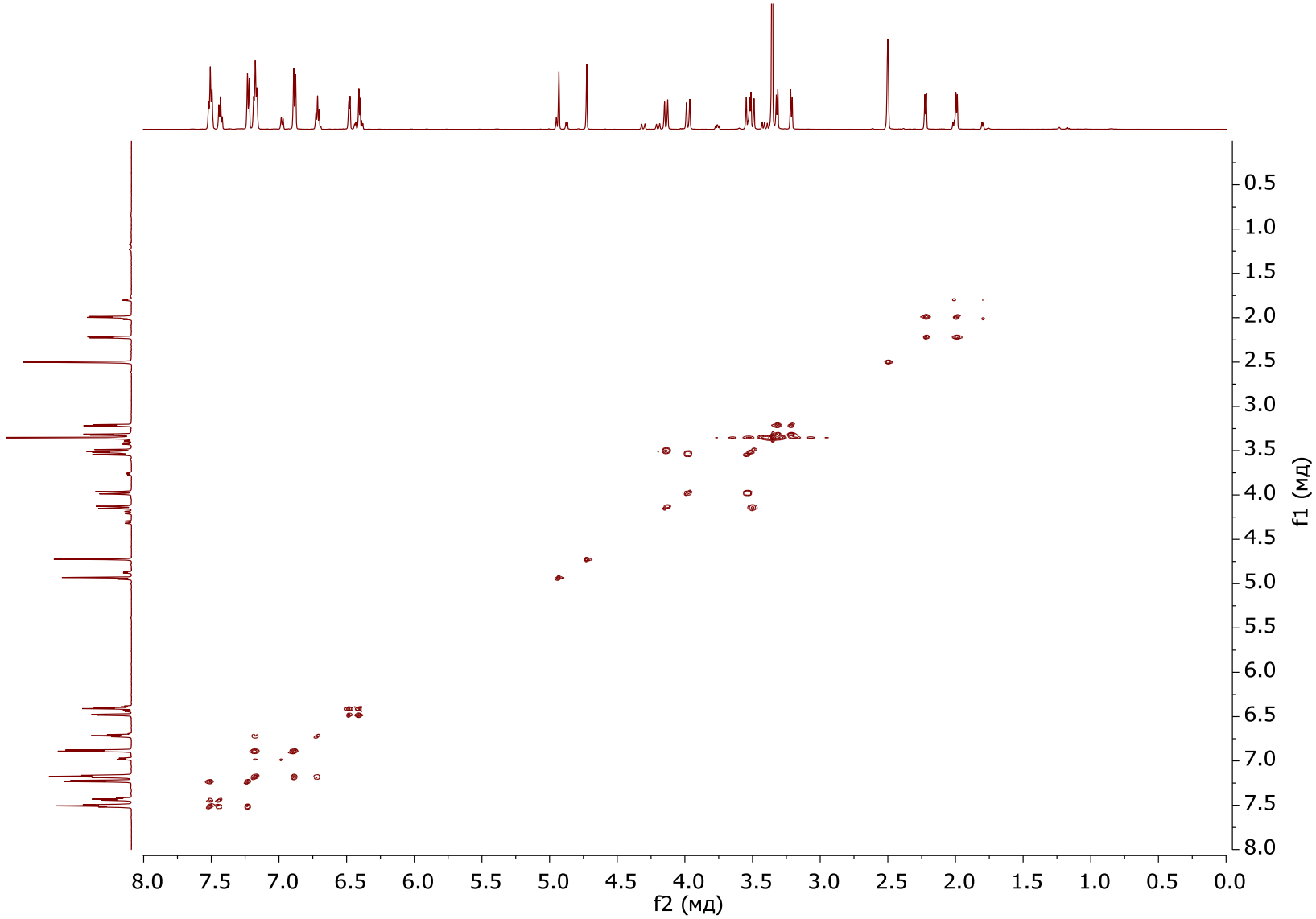


Figure S41. COSY spectrum of **5a**, (600 MHz, DMSO-d_6).

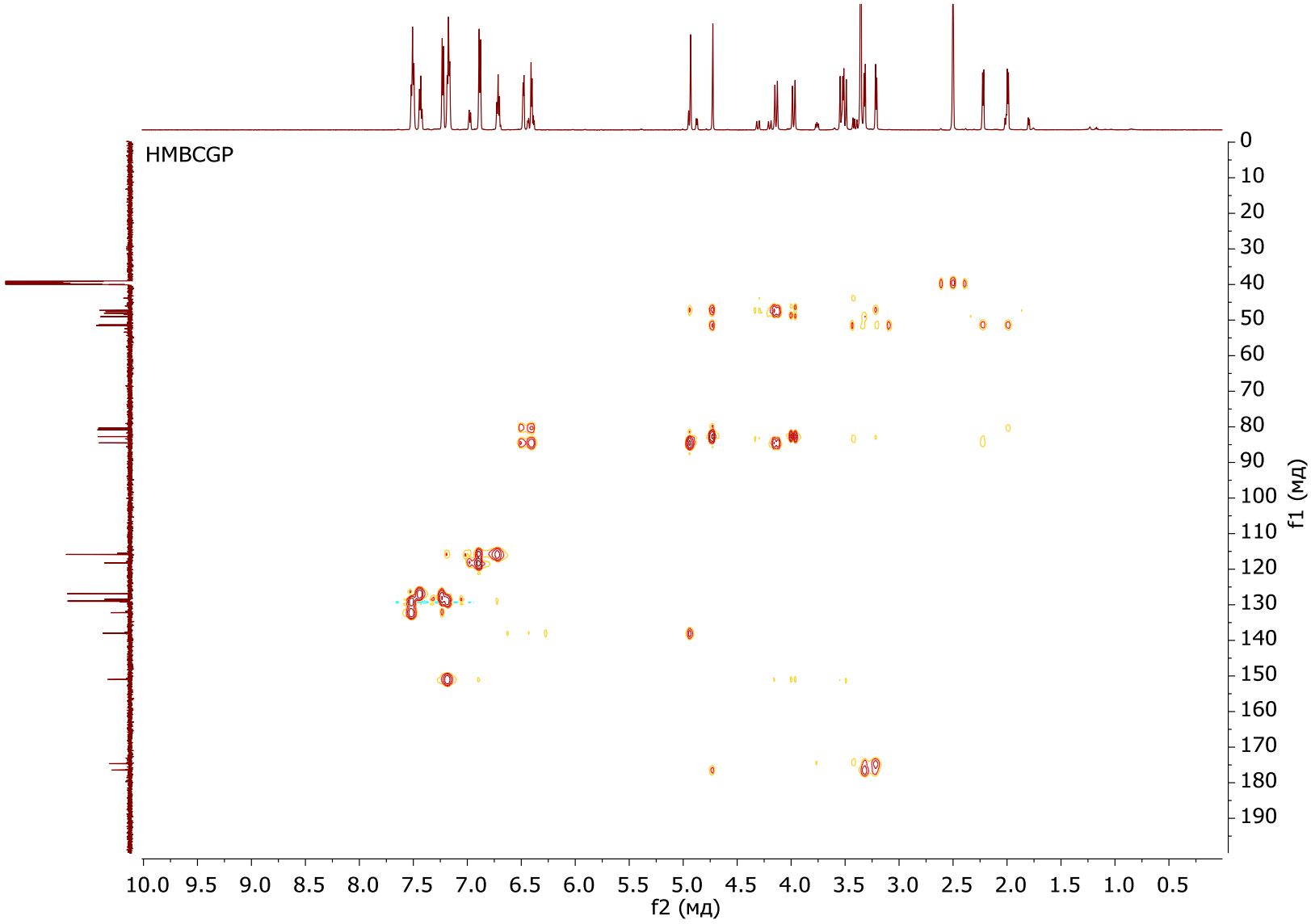


Figure S42. HMBC spectrum of **5a**, (600 MHz, DMSO-d_6).

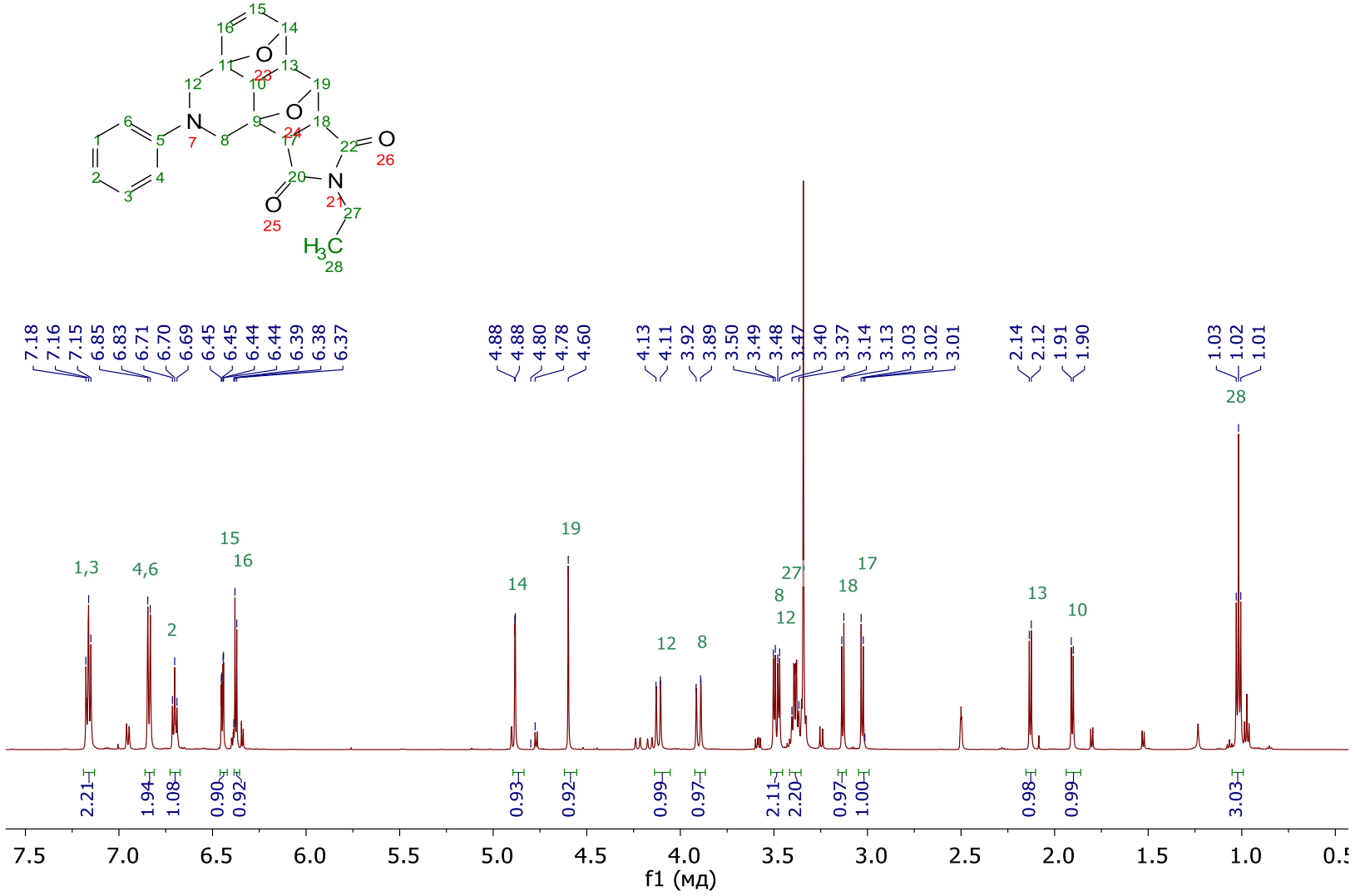


Figure S43. ^{1}H-NMR spectrum of **5b**, (600 MHz, DMSO-d_6).

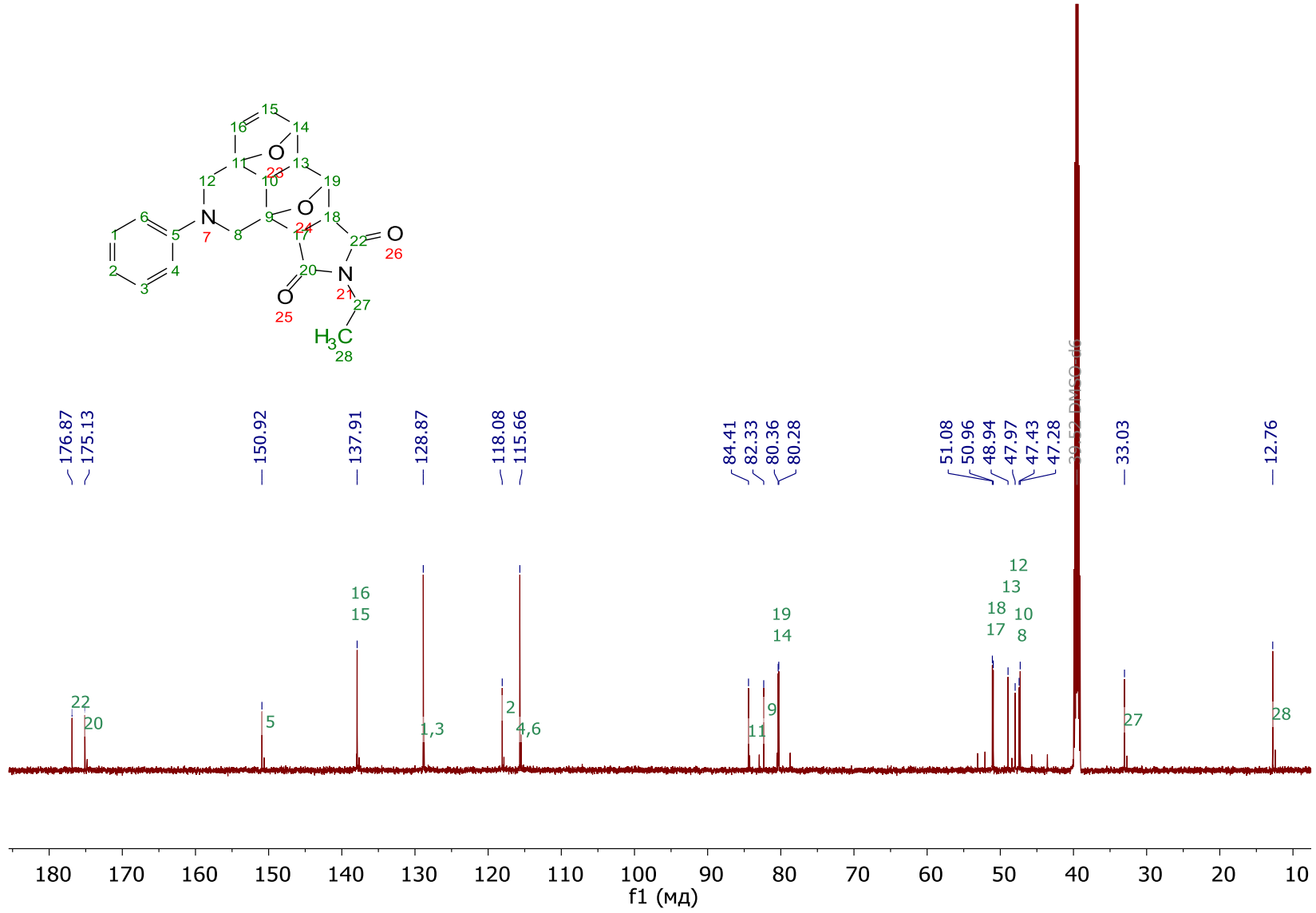


Figure S44. ^{13}C-NMR spectrum of **5b**, (151 MHz, DMSO-d_6).

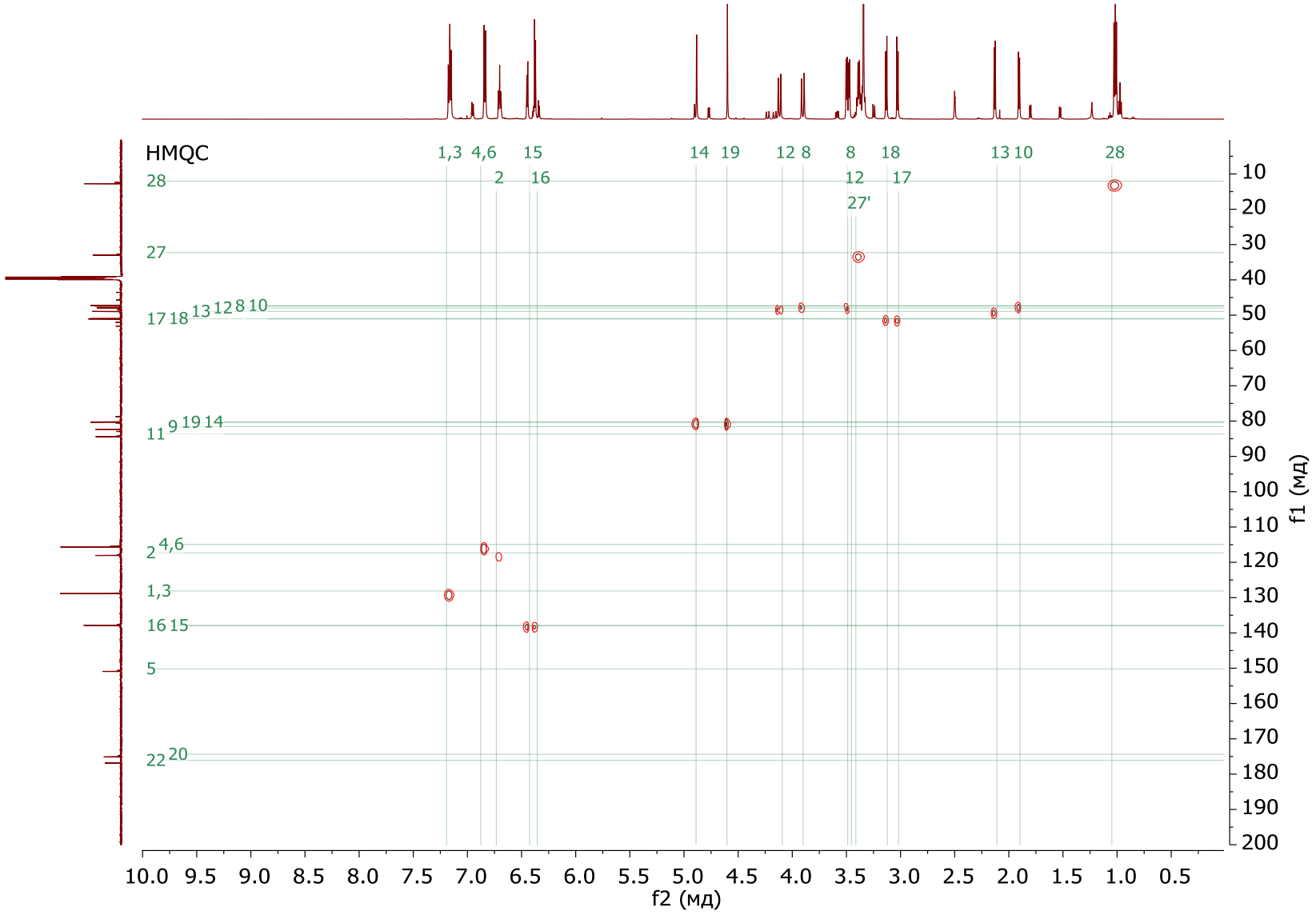


Figure S45. HMQC spectrum of **5b**, (600 MHz, DMSO-d_6).

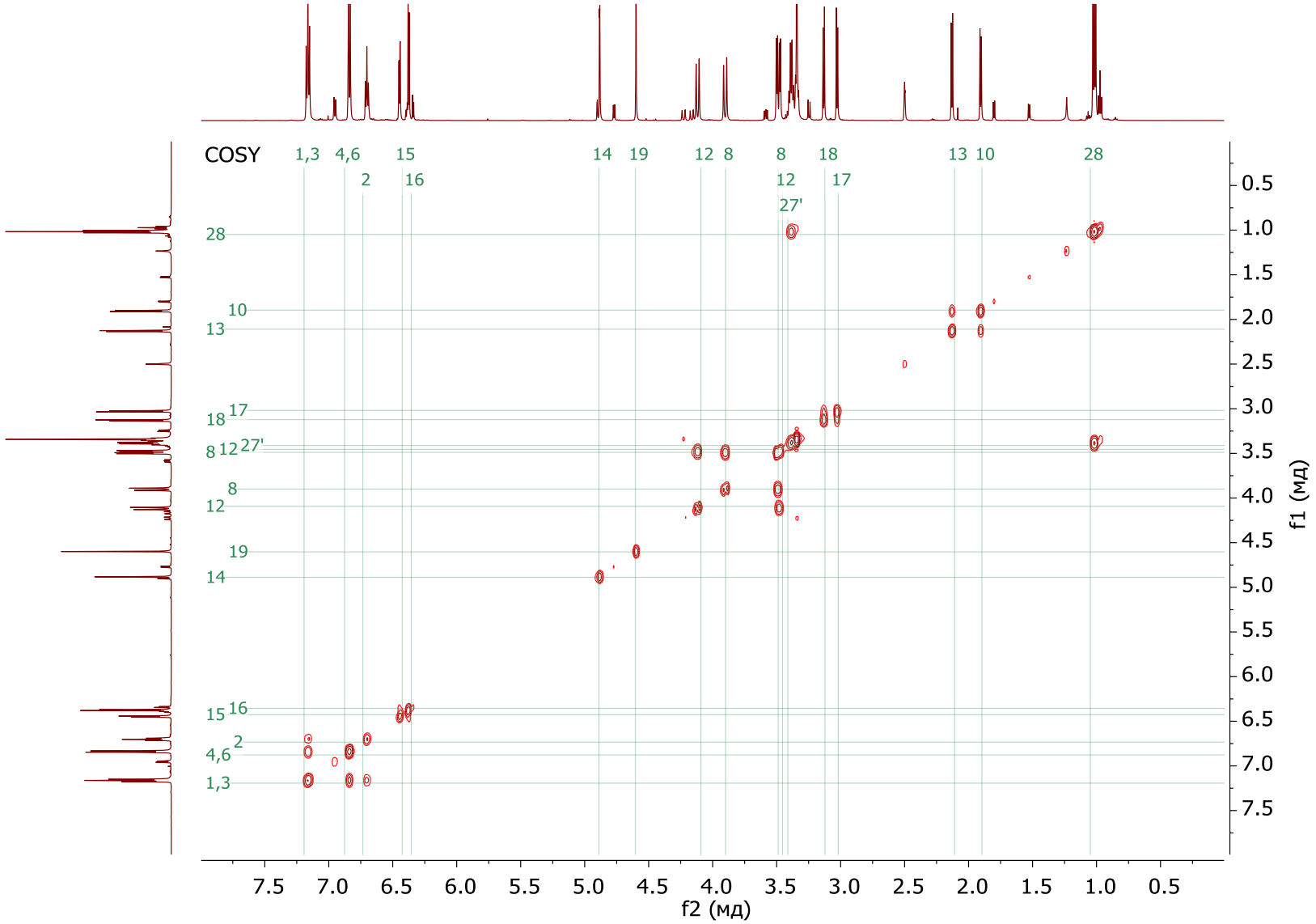


Figure S46. COSY spectrum of **5b**, (600 MHz, DMSO-d_6).

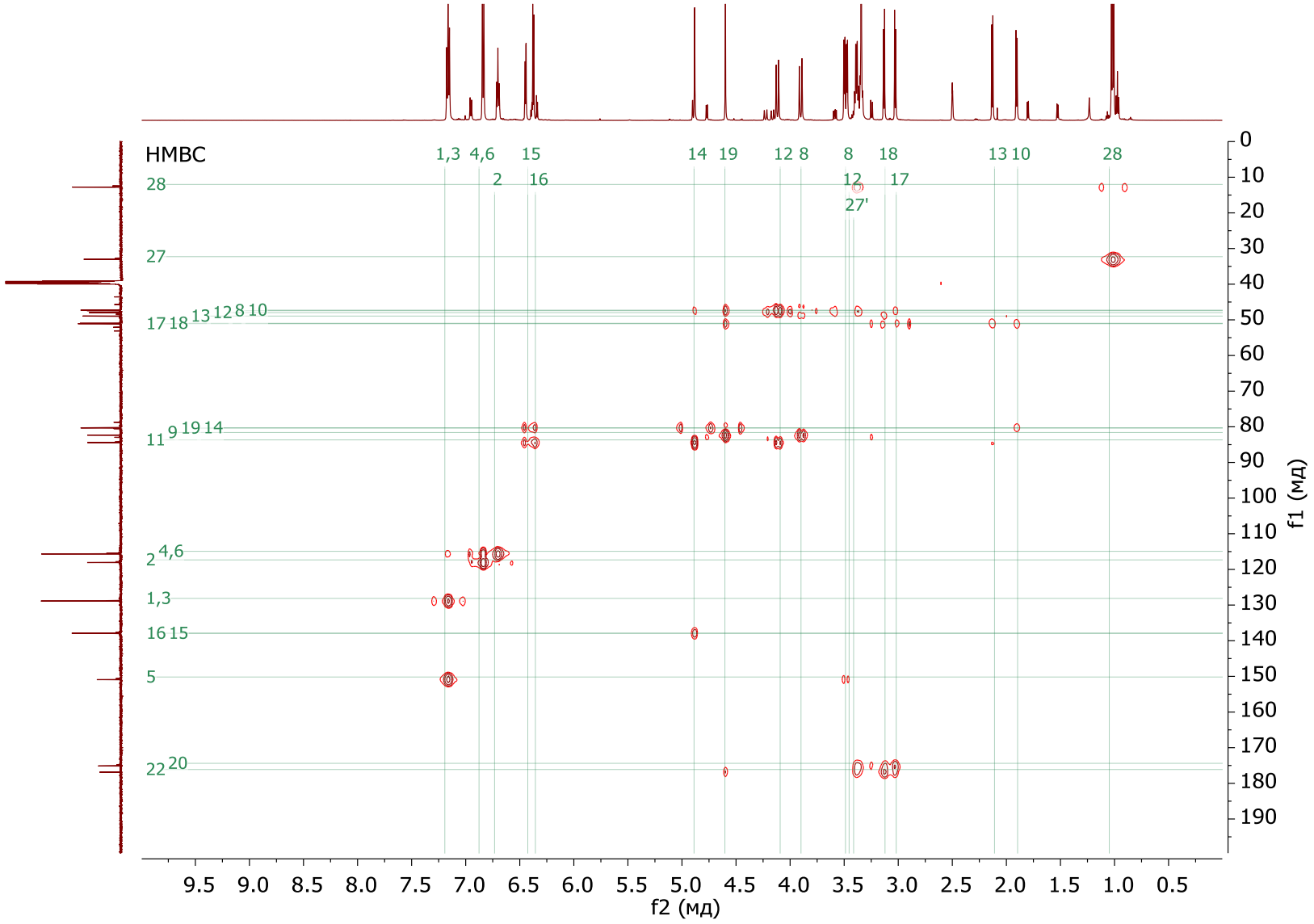


Figure S47. HMBC spectrum of **5b**, (600 MHz, DMSO-d_6).

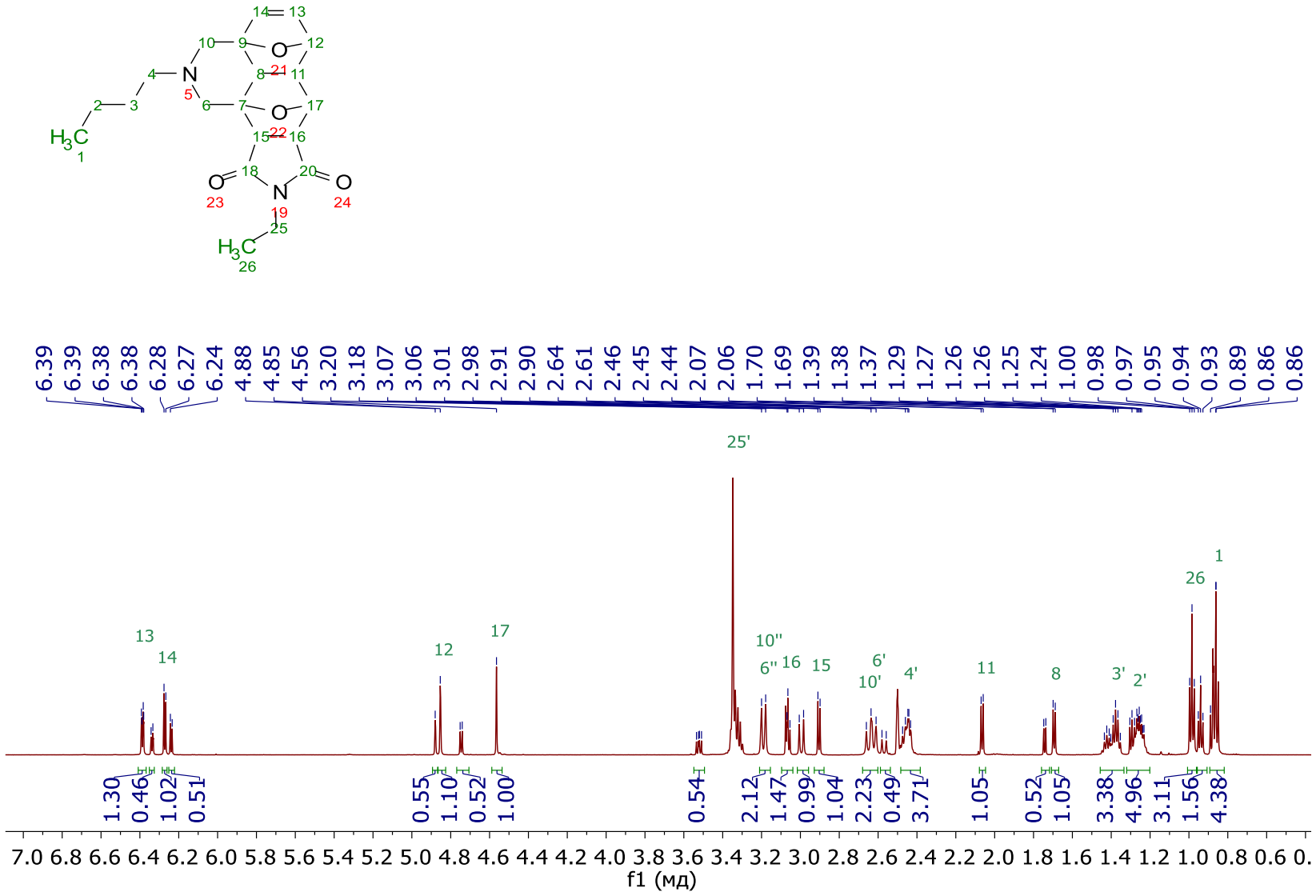


Figure S48. ^{1}H-NMR spectrum of **5c**, (600 MHz, DMSO-d_6).

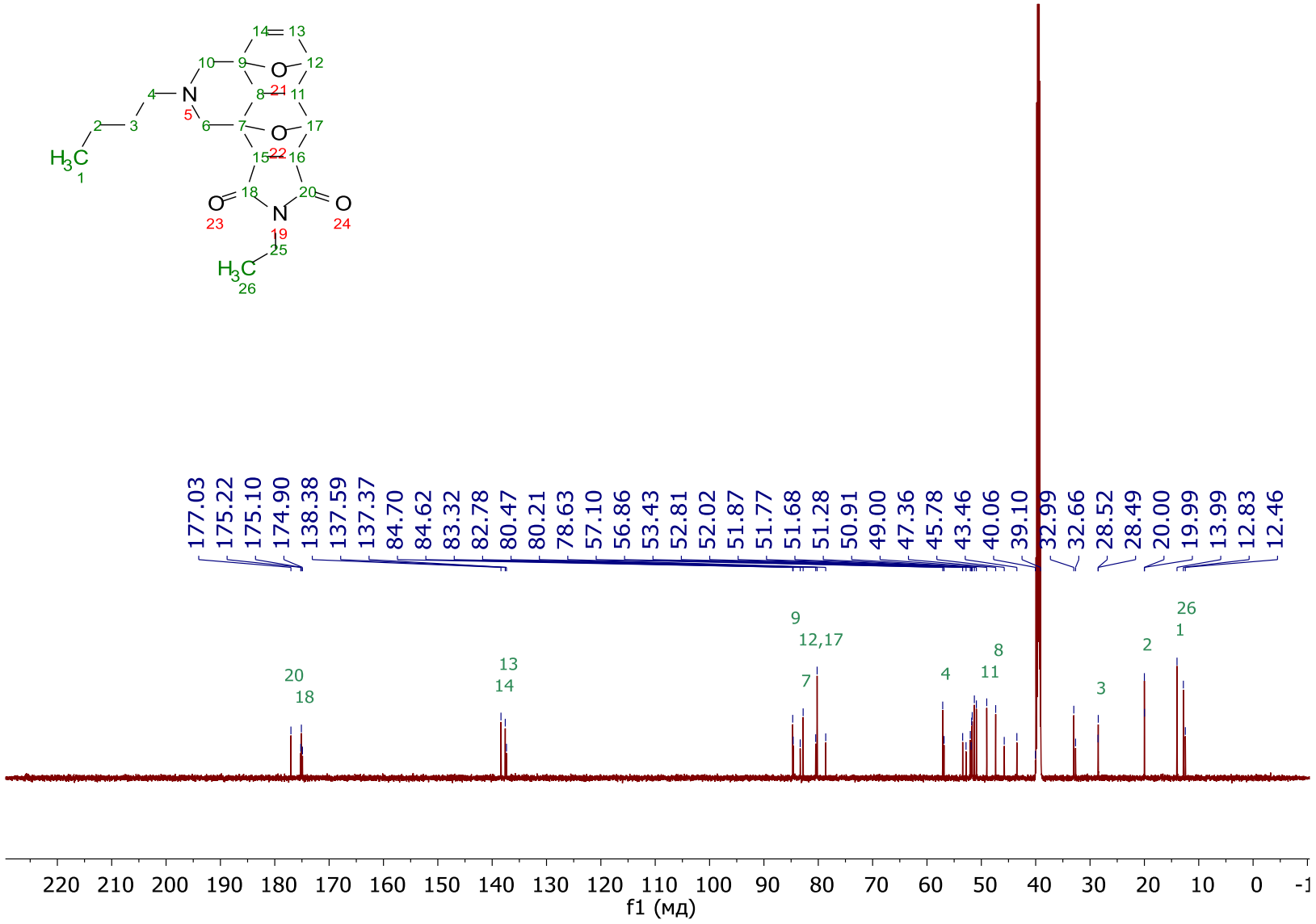


Figure S49. ^{13}C-NMR spectrum of **5c**, (151 MHz, DMSO-d_6).

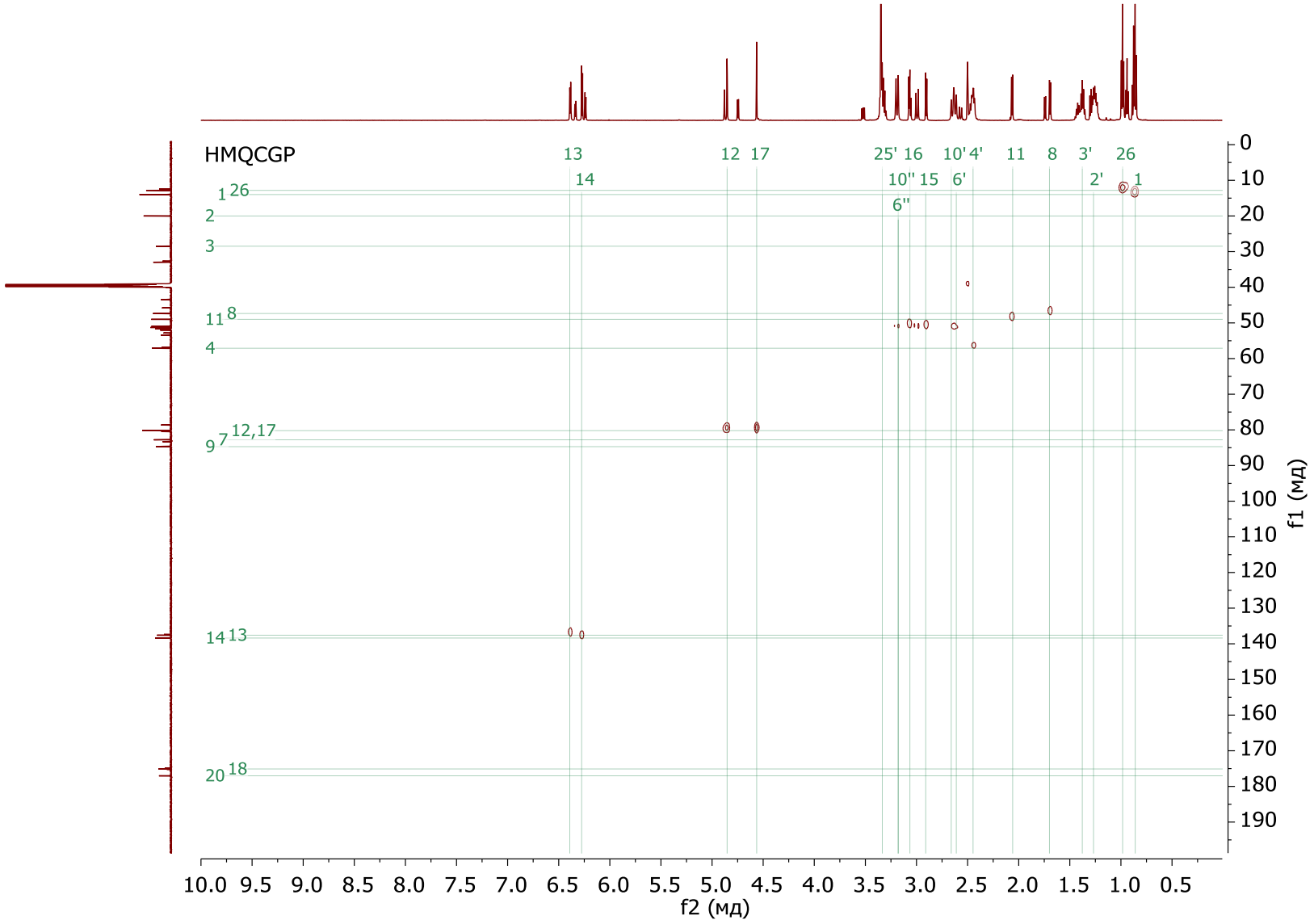


Figure S50. HMQC spectrum of **5c**, (600 MHz, DMSO-d_6).

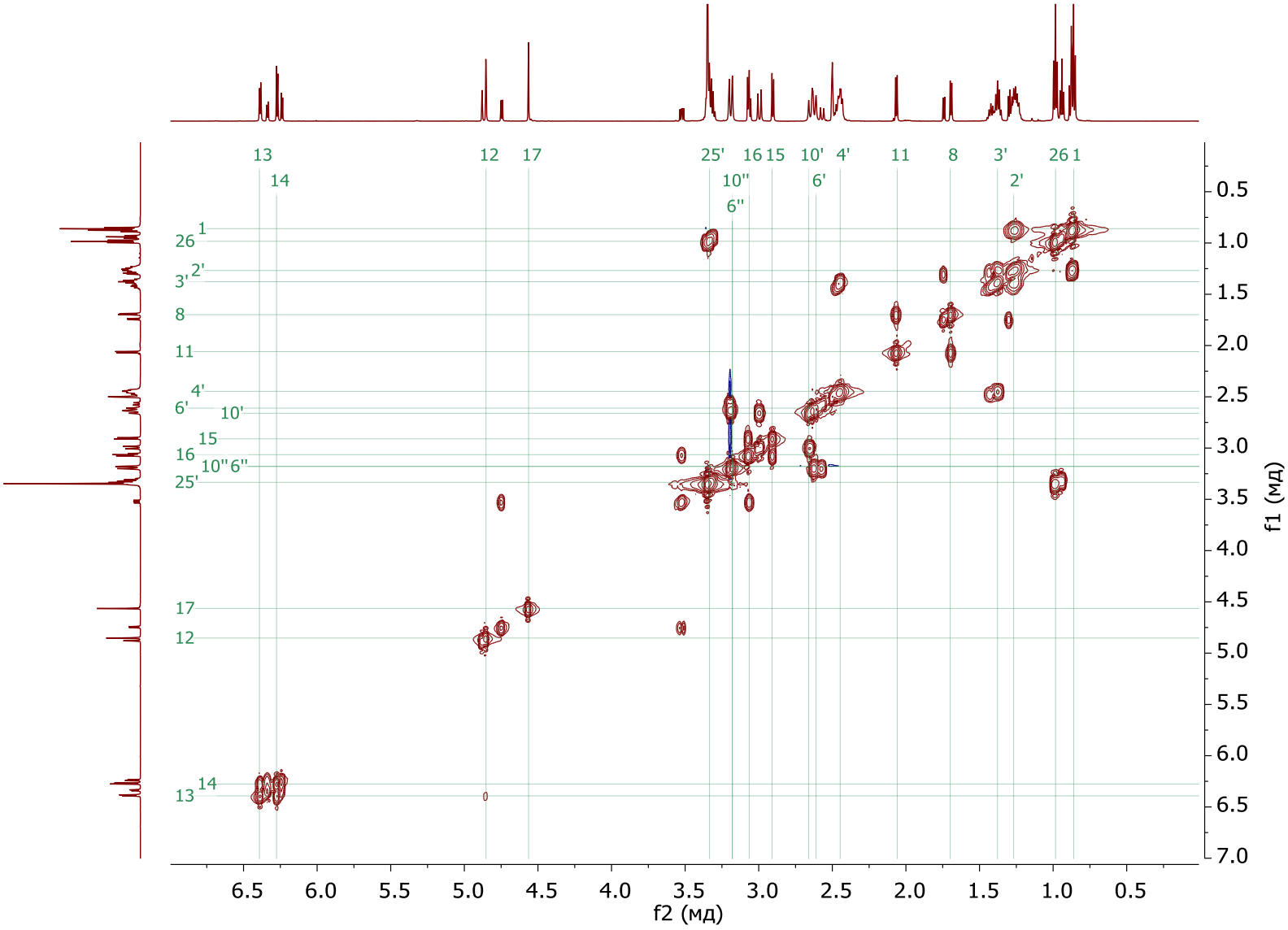


Figure S51. COSY spectrum of **5c**, (600 MHz, DMSO-d_6).

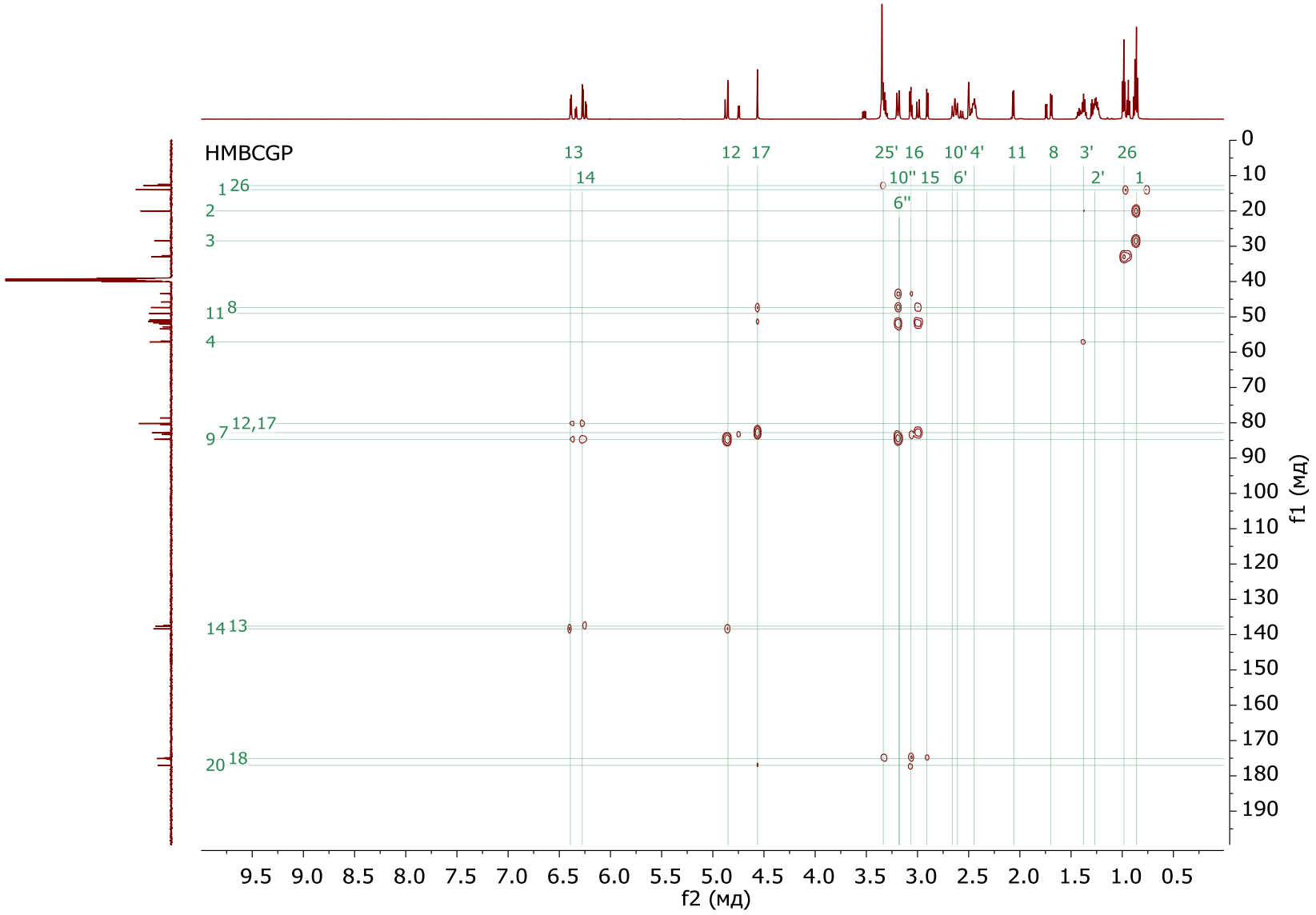


Figure S52. HMBC spectrum of **5c**, (600 MHz, DMSO-d_6).

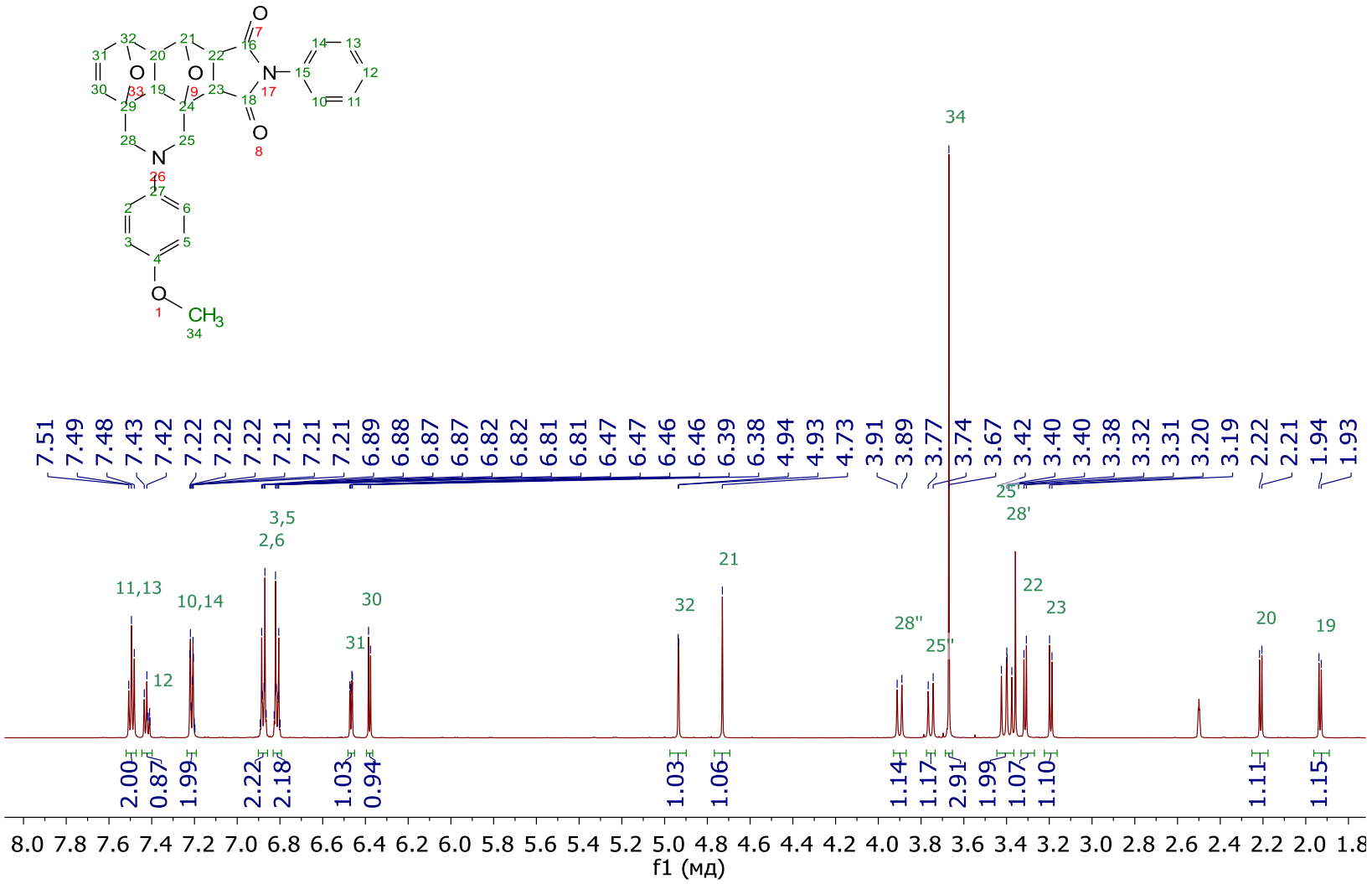


Figure S53. ^{1}H-NMR spectrum of **5d**, (600 MHz, DMSO-d_6).

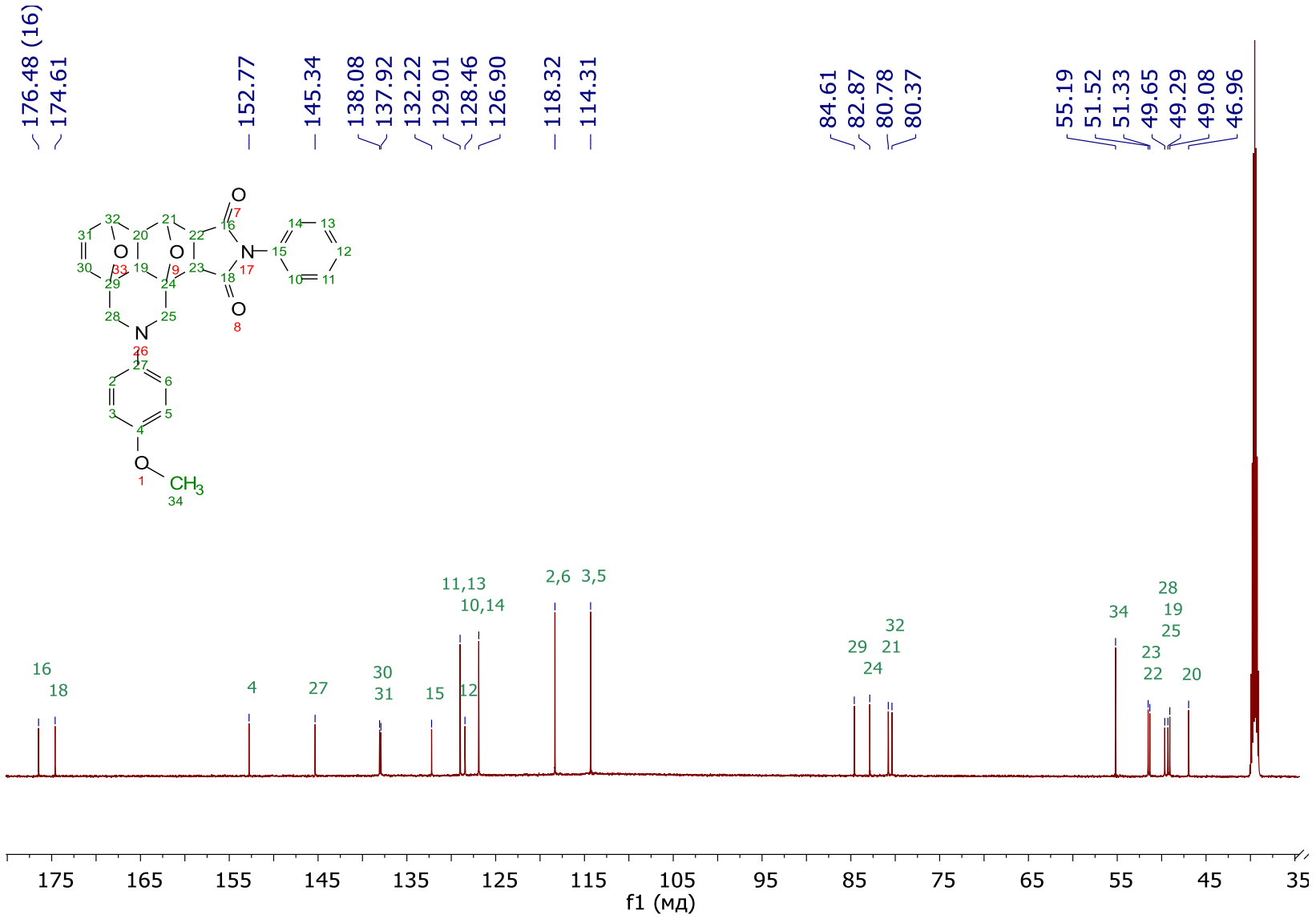


Figure S54. ^{13}C-NMR spectrum of **5d**, (151 MHz, DMSO-d_6).

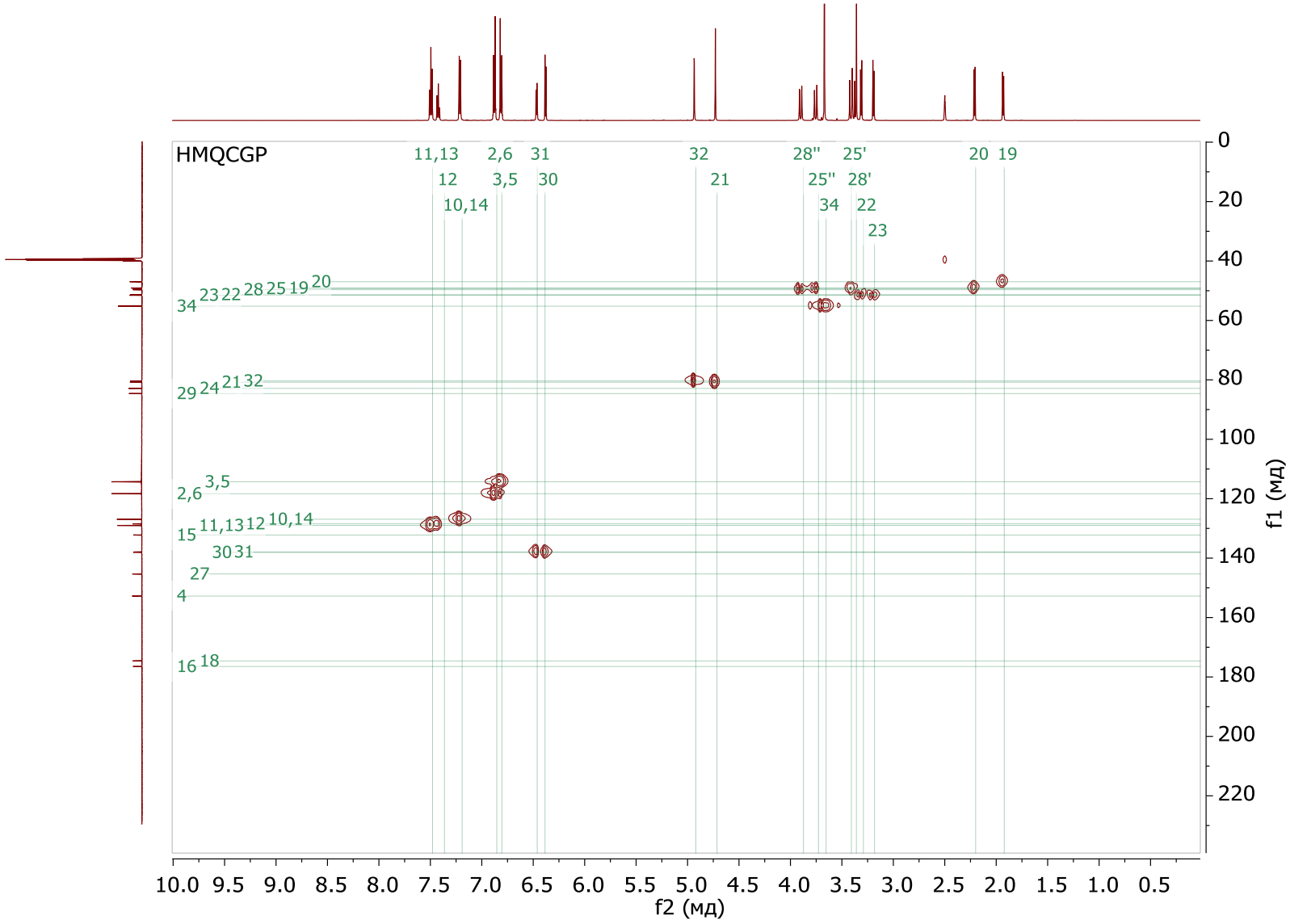


Figure S55. HMQC spectrum of **5d**, (600 MHz, DMSO-d_6).

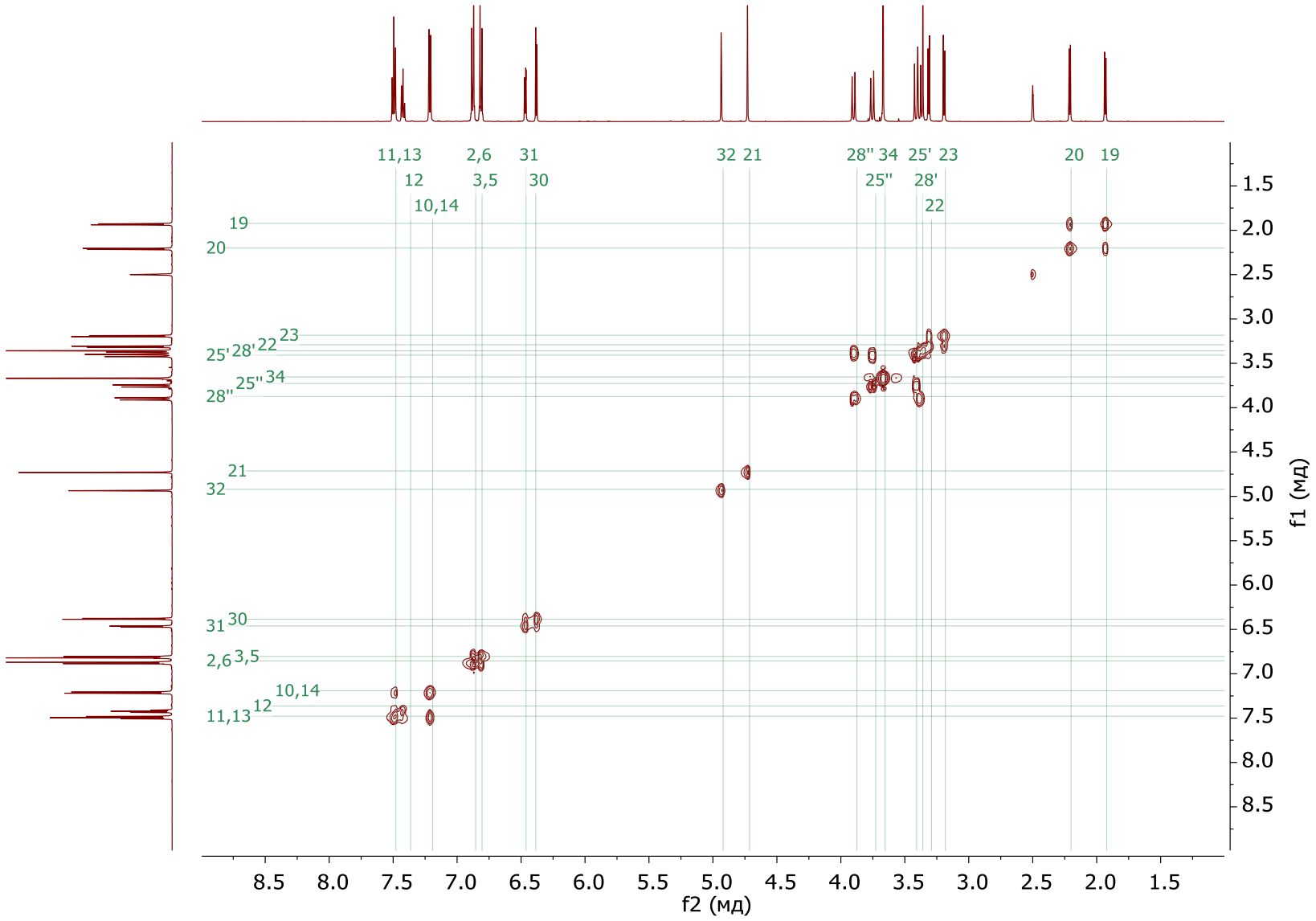


Figure S56. COSY spectrum of **5d**, (600 MHz, DMSO-d_6).

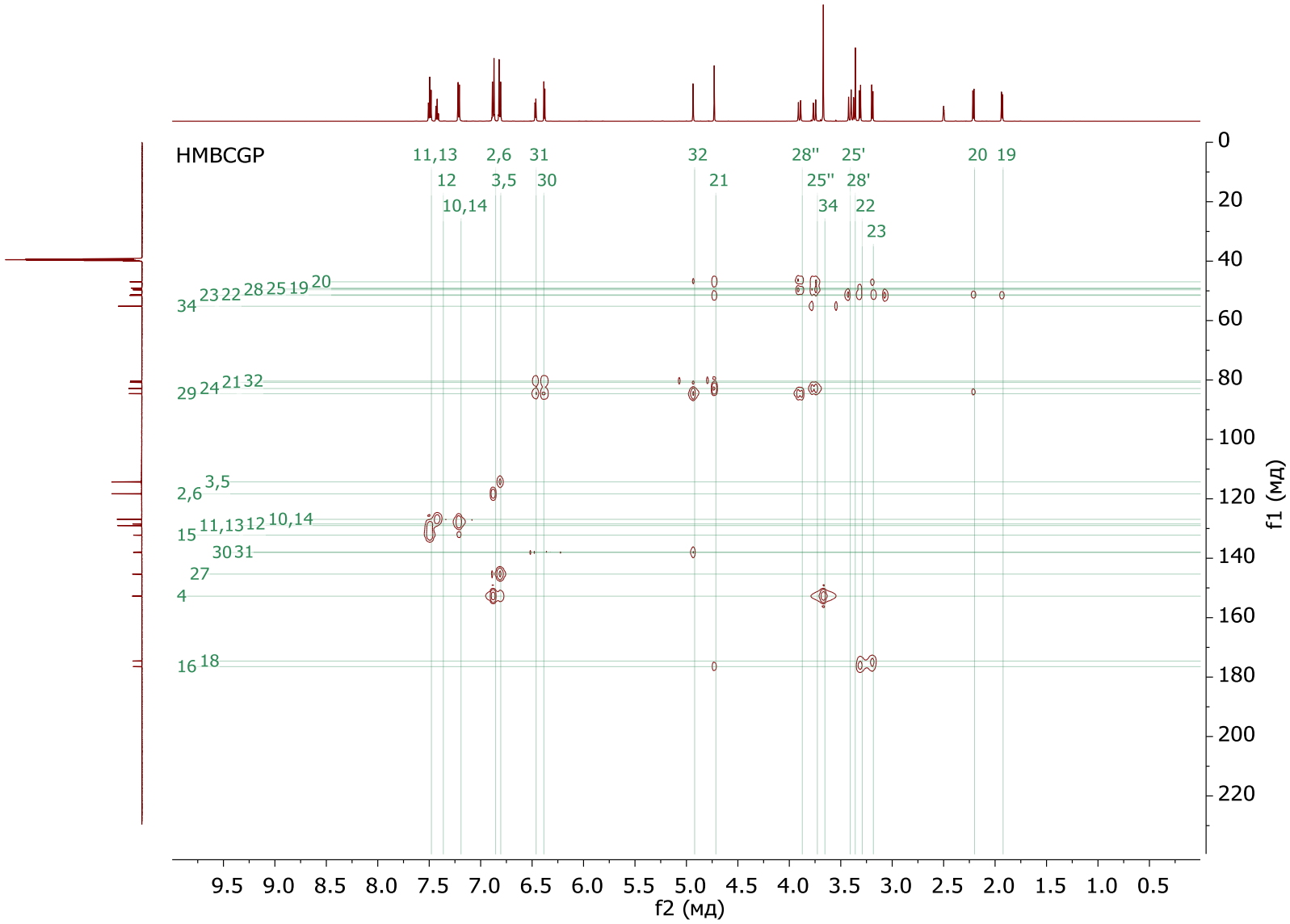


Figure S57. HMBC spectrum of **5d**, (600 MHz, DMSO-d_6).

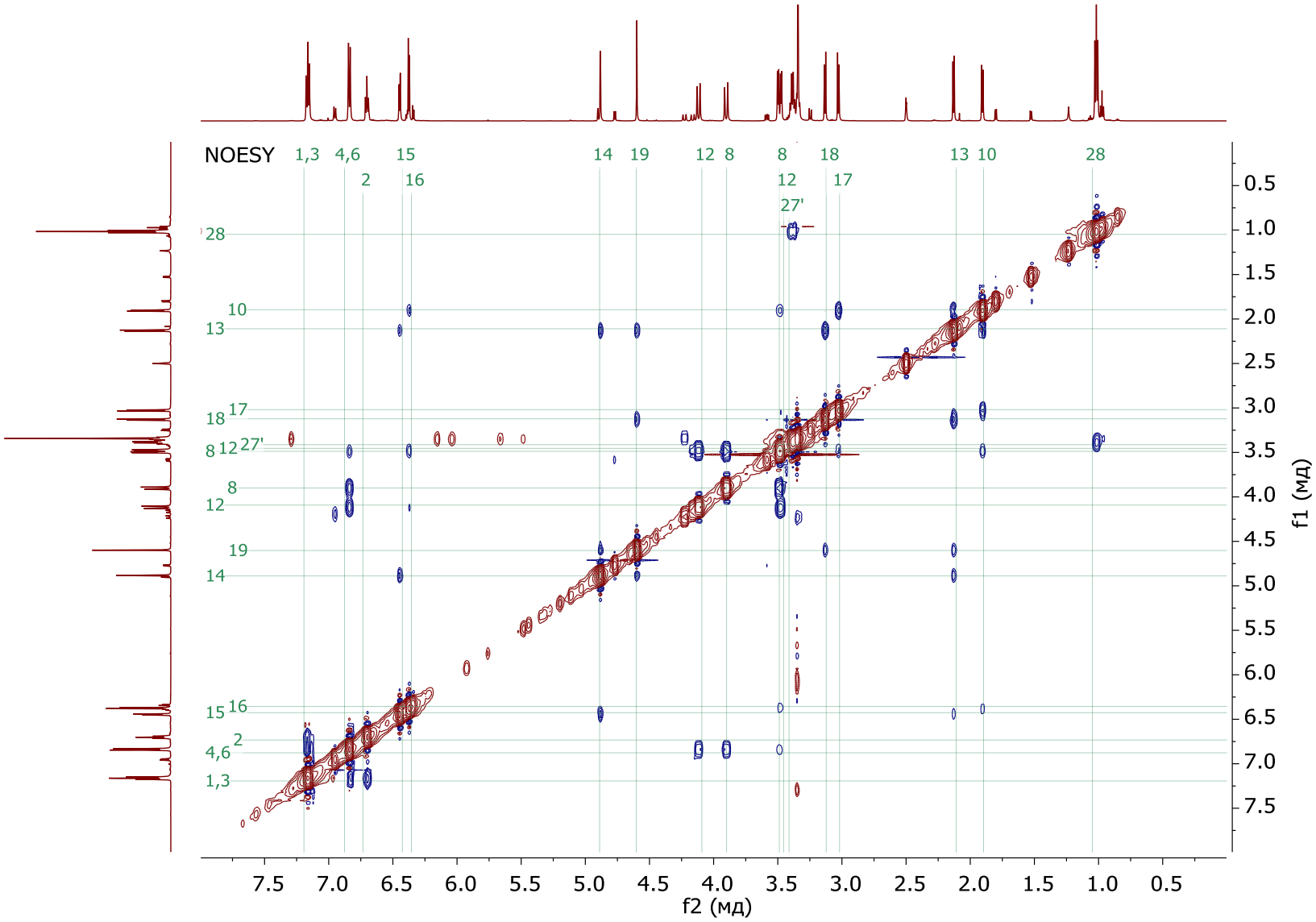


Figure S58. NOESY spectrum of **5d**, (600 MHz, DMSO-d_6).

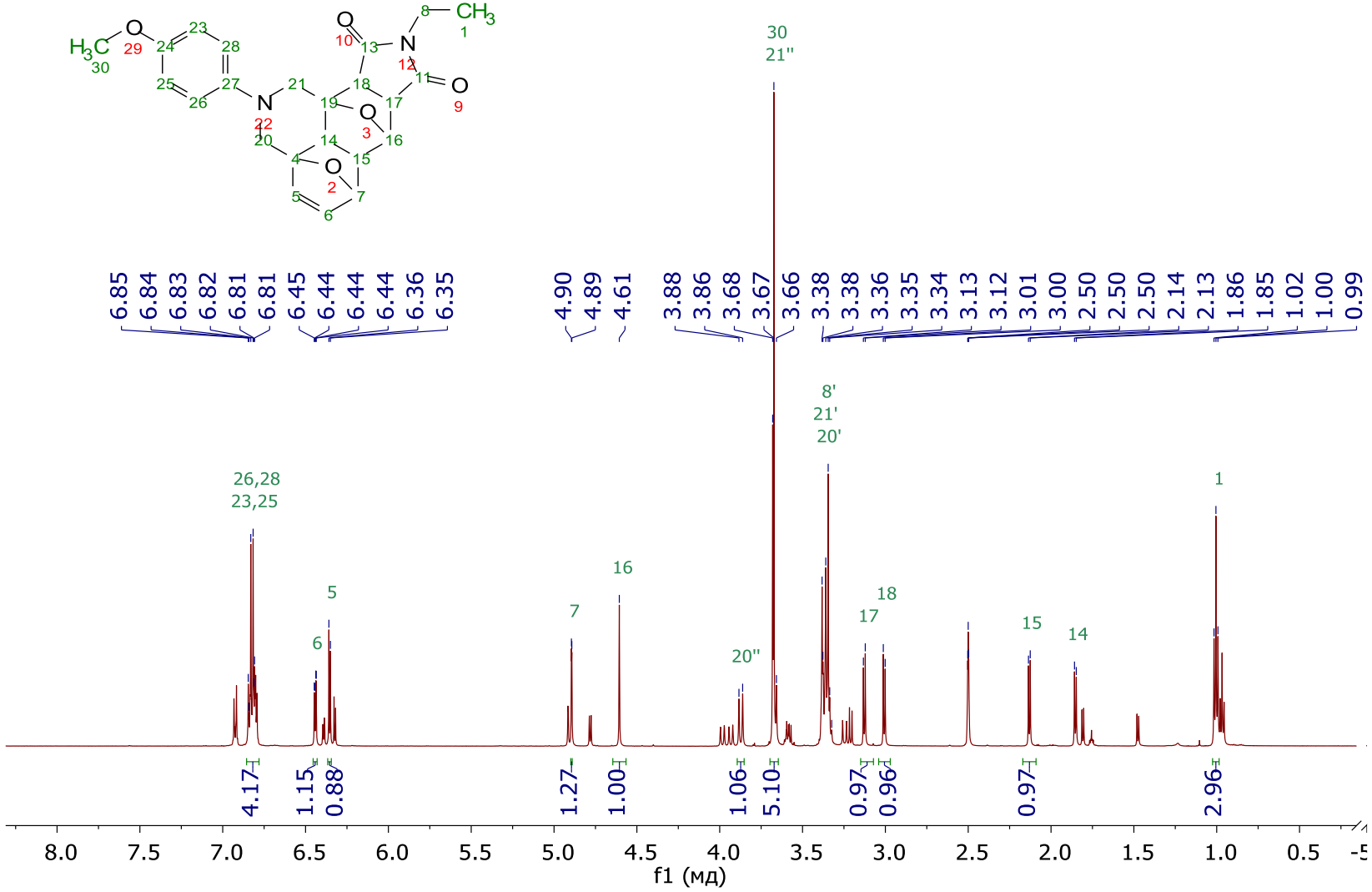


Figure S59. ^{1}H-NMR spectrum of **5e**, (600 MHz, DMSO-d_6).

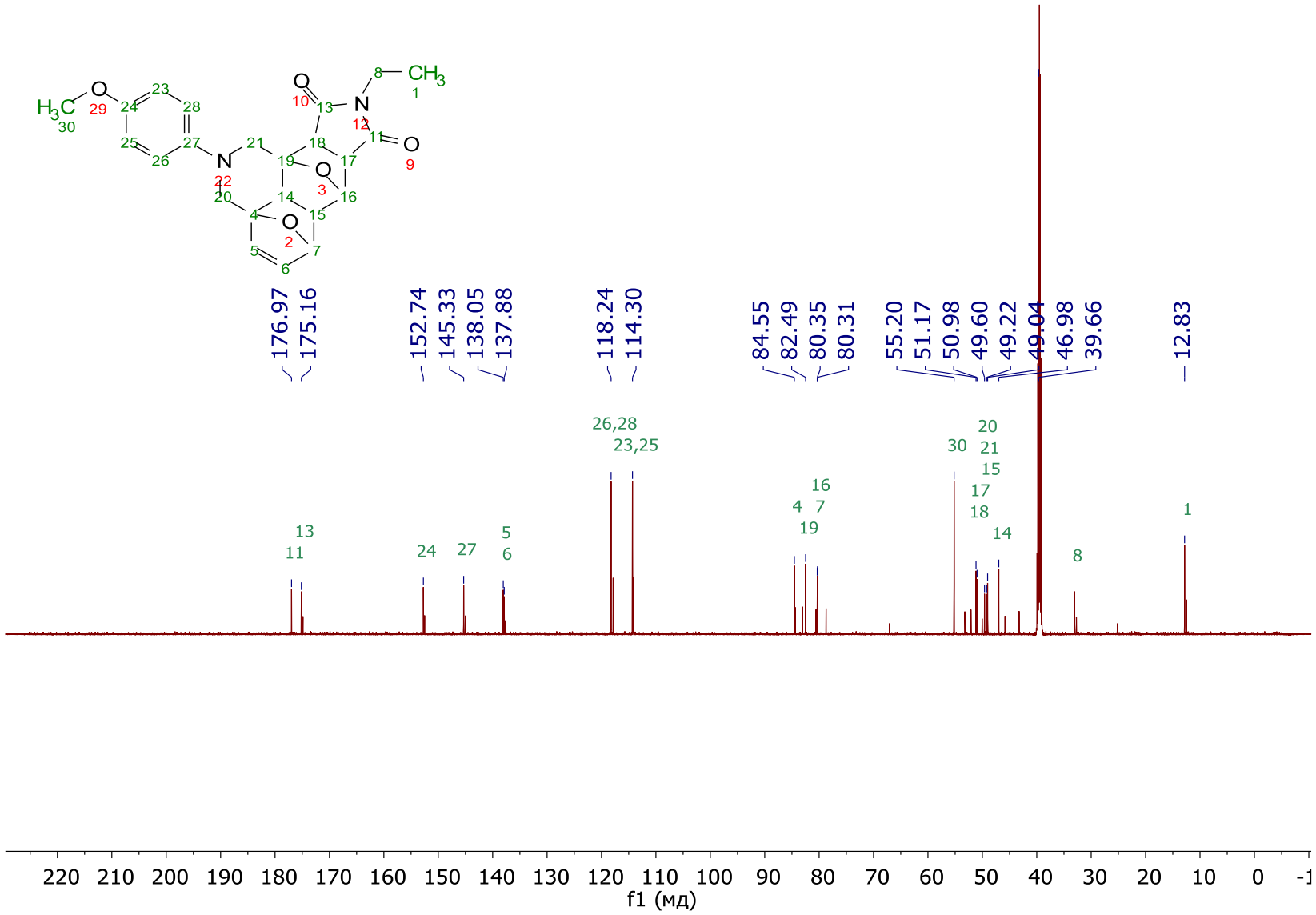


Figure S60. ^{13}C-NMR spectrum of **5e**, (151 MHz, DMSO-d_6).

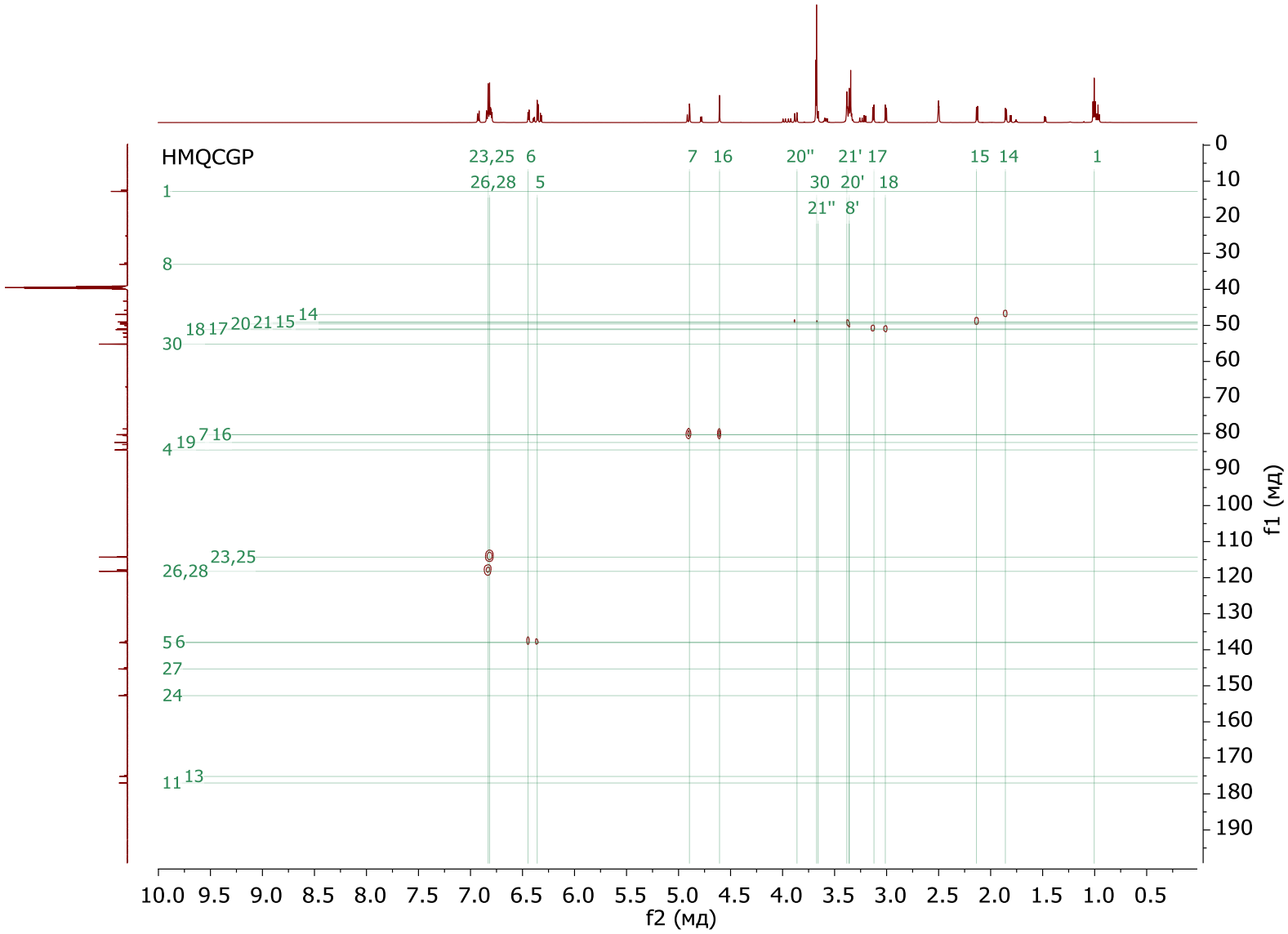


Figure S61. HMQC spectrum of **5e**, (600 MHz, DMSO-d_6).

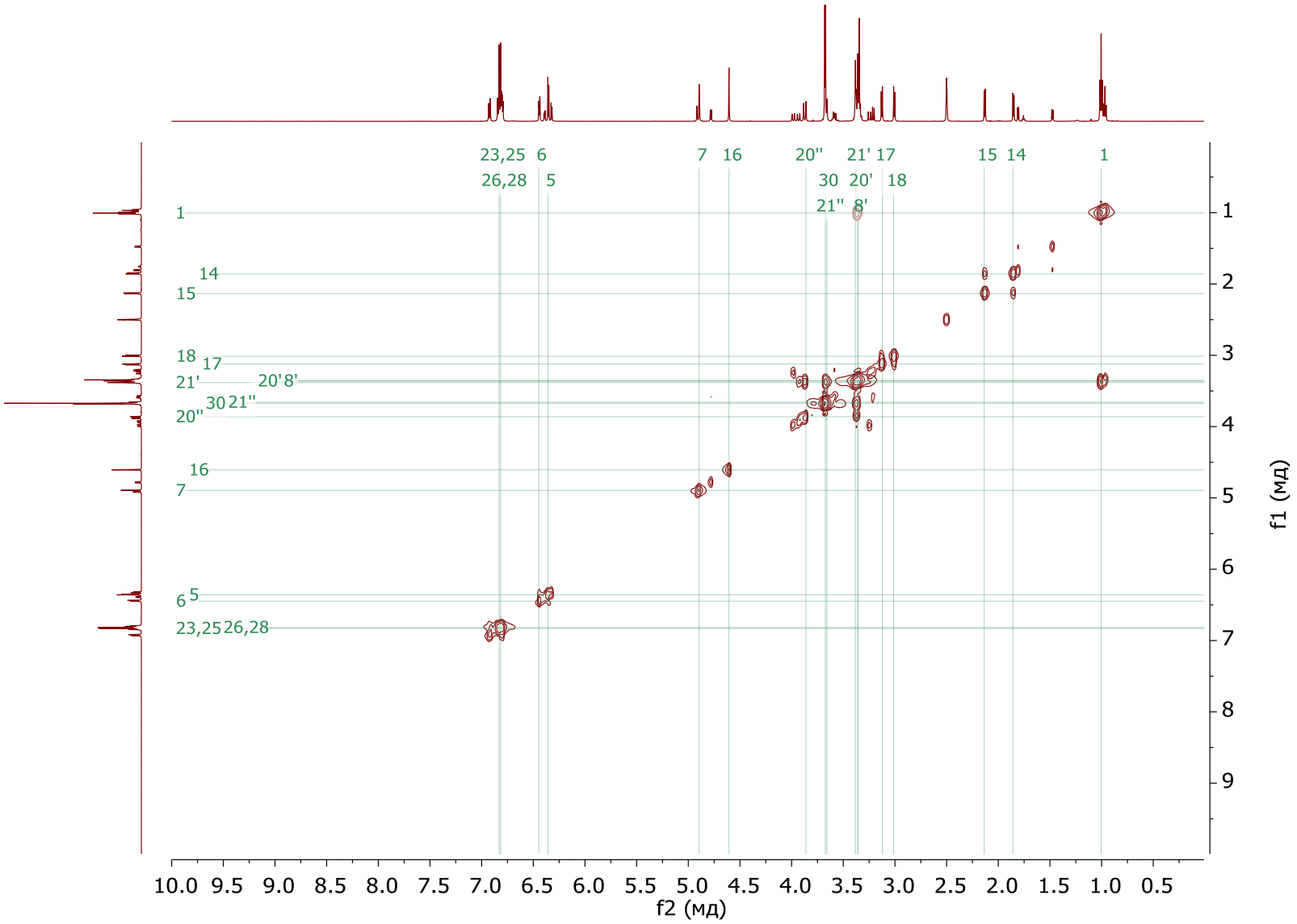


Figure S62. COSY spectrum of **5e**, (600 MHz, DMSO-d_6).

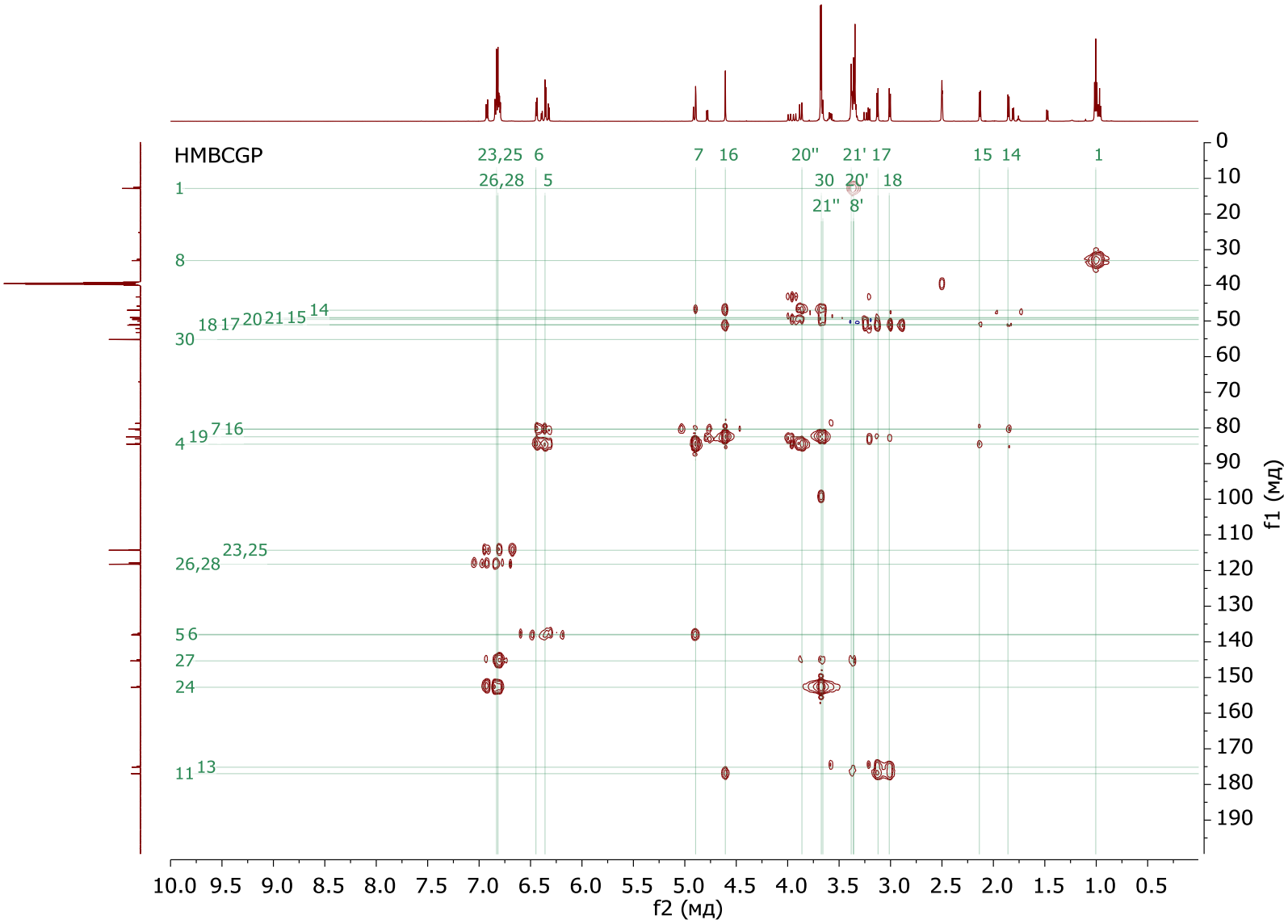


Figure S63. HMBC spectrum of **5e**, (600 MHz, DMSO-d_6).

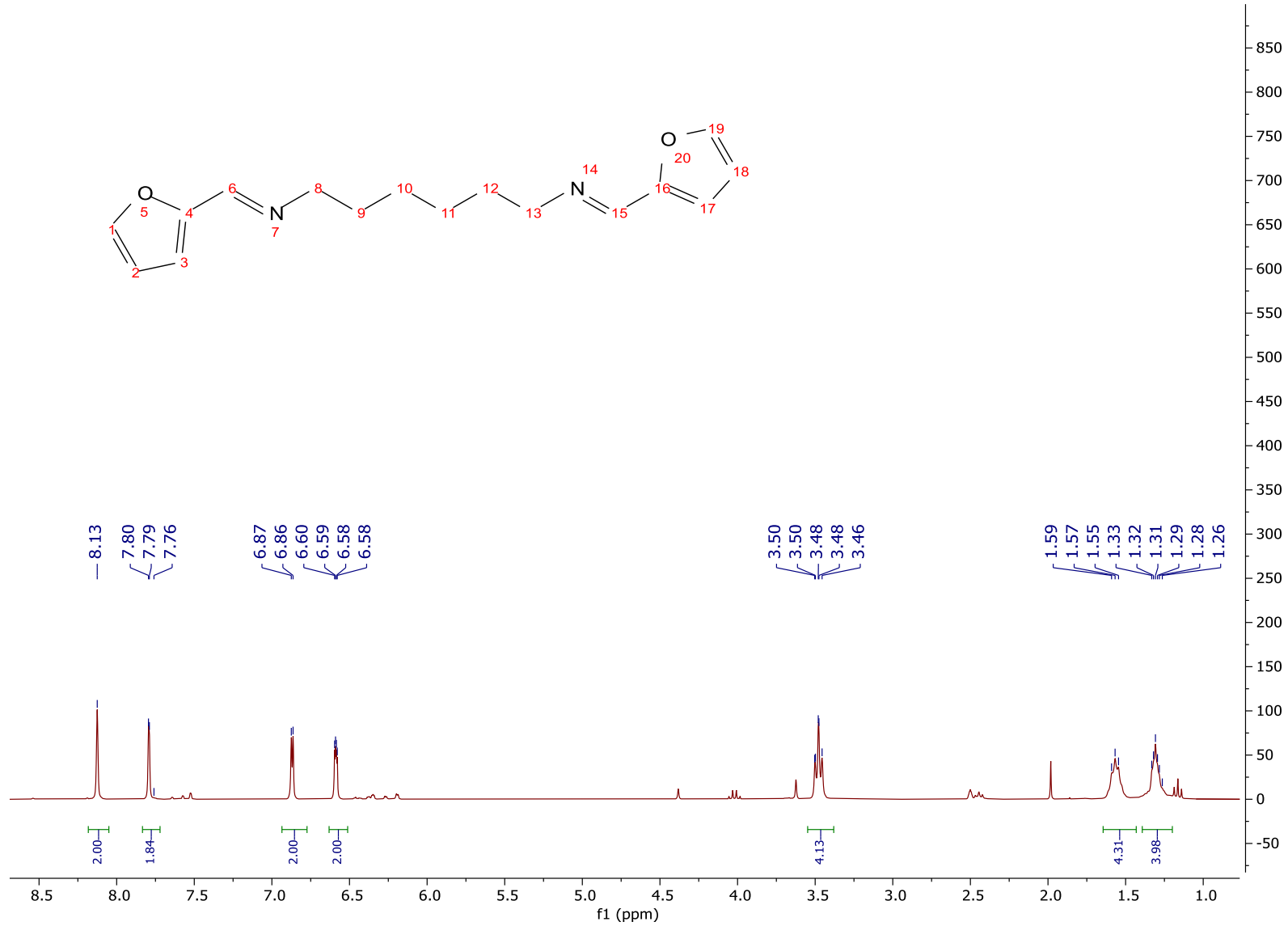


Figure S64. ^{1}H-NMR spectrum of **6a''**, (600 MHz, DMSO-d_6).

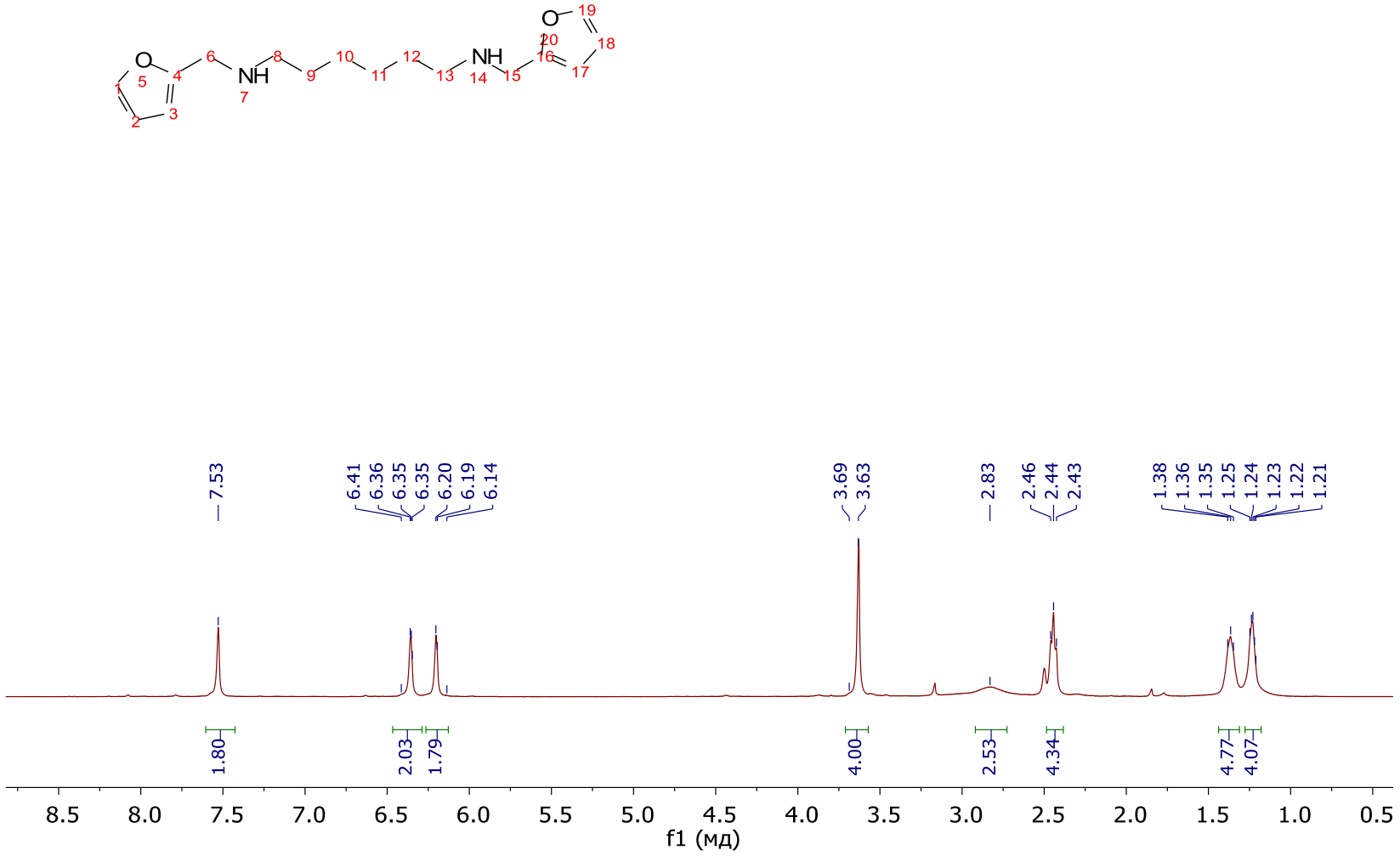


Figure S65. ^{1}H-NMR spectrum of **6a'**, (600 MHz, DMSO-d_6).

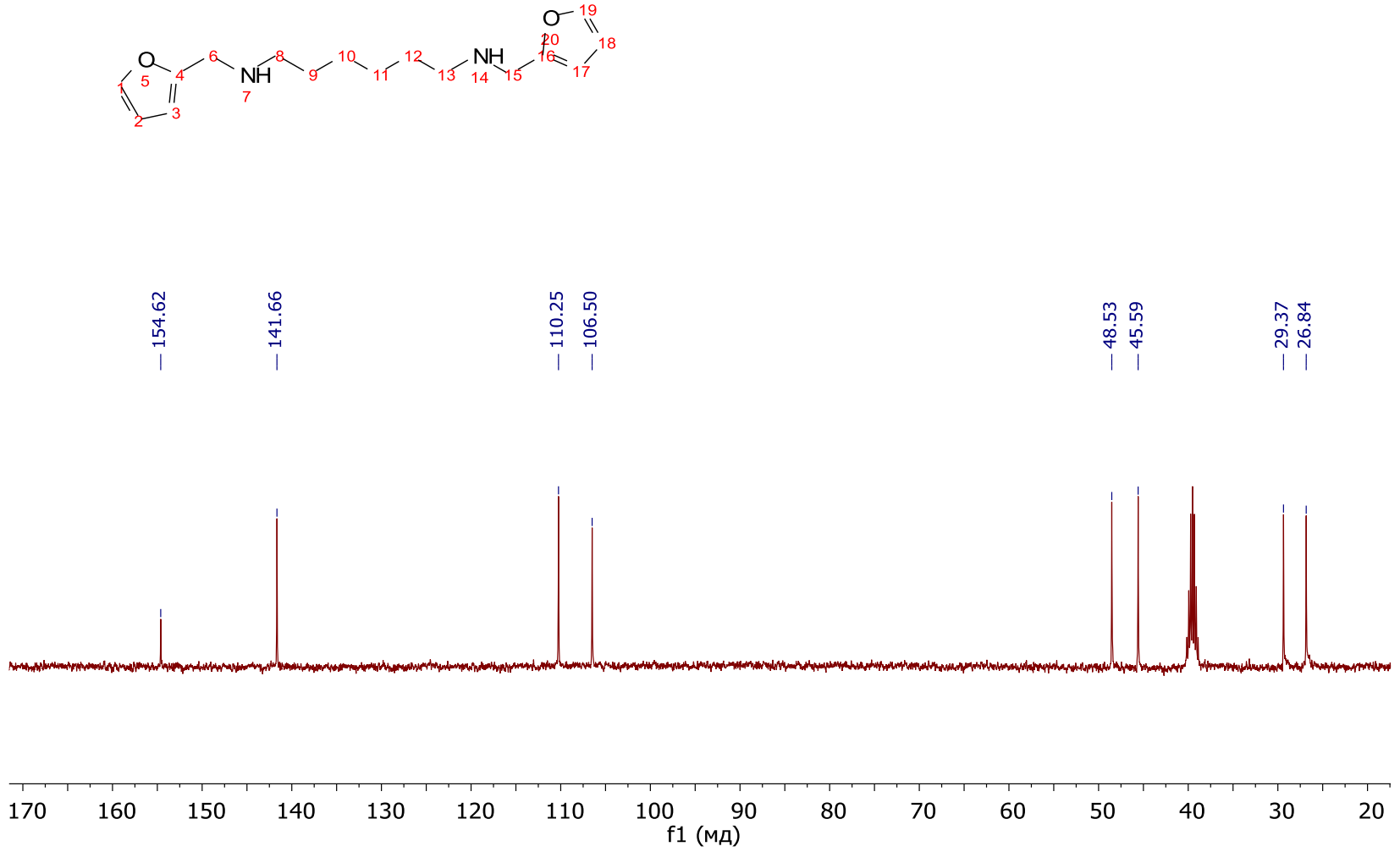


Figure S66. ^{13}C-NMR spectrum of **6a'**, (151 MHz, DMSO-d_6).

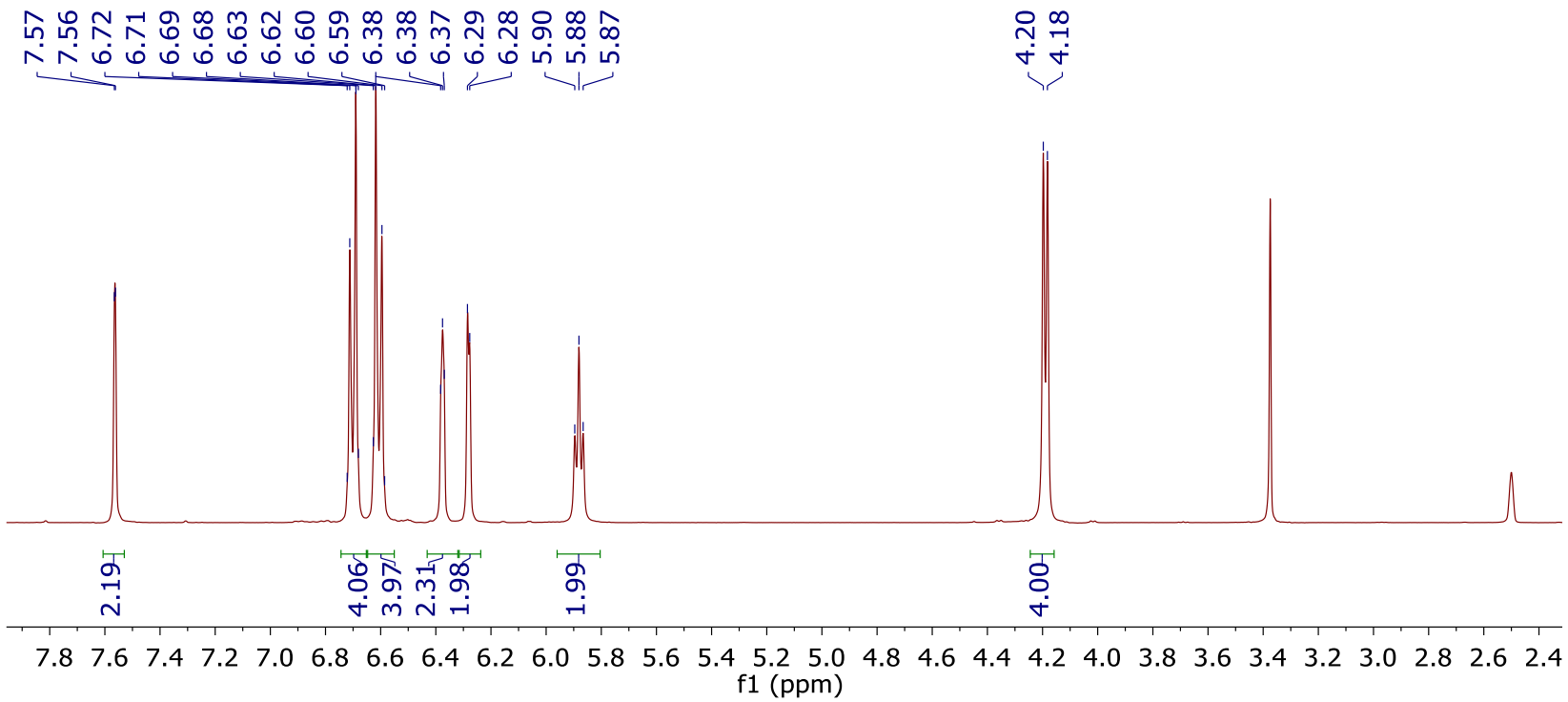


Figure S67. ^{1}H-NMR spectrum of 4,4'-oxybis(N-(furan-2-ylmethyl)aniline) **6b'**, (600 MHz, DMSO-d_6).

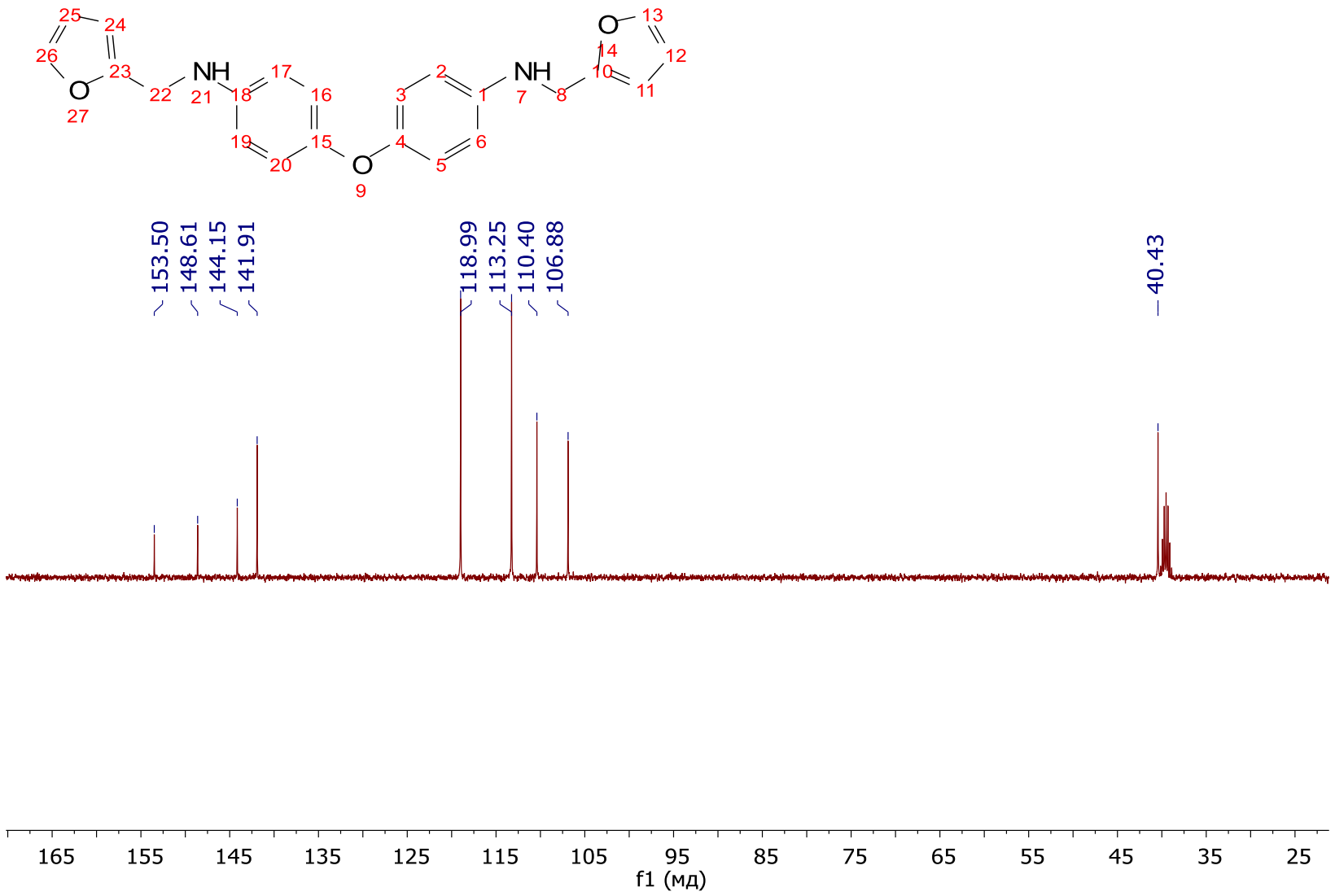


Figure S68. ^{13}C-NMR spectrum of 4,4'-oxybis(N-(furan-2-ylmethyl)aniline) **6b'**, (151 MHz, DMSO-d_6).

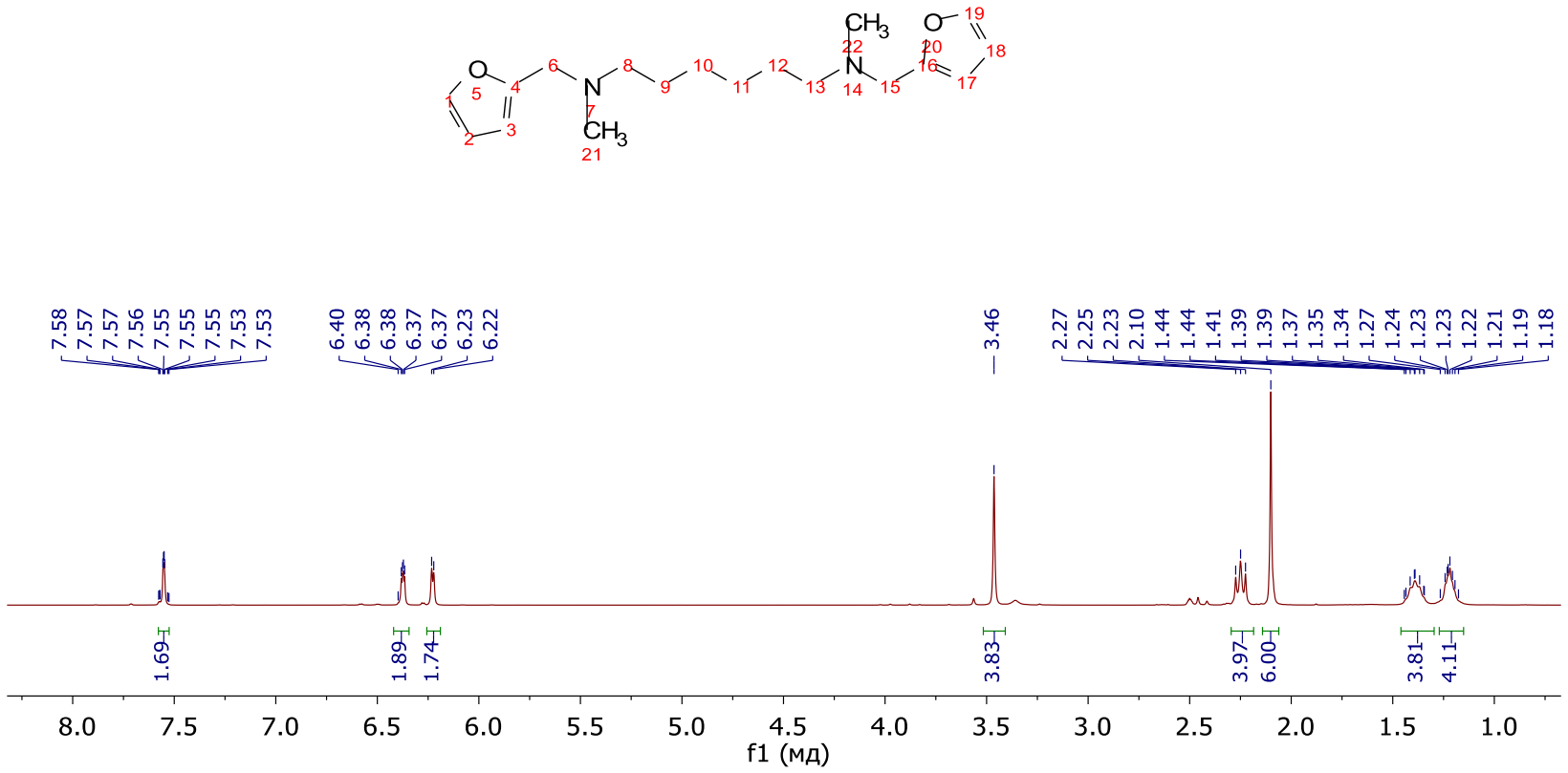


Figure S69. ^{1}H-NMR spectrum of **6a**, (600 MHz, DMSO-d_6).

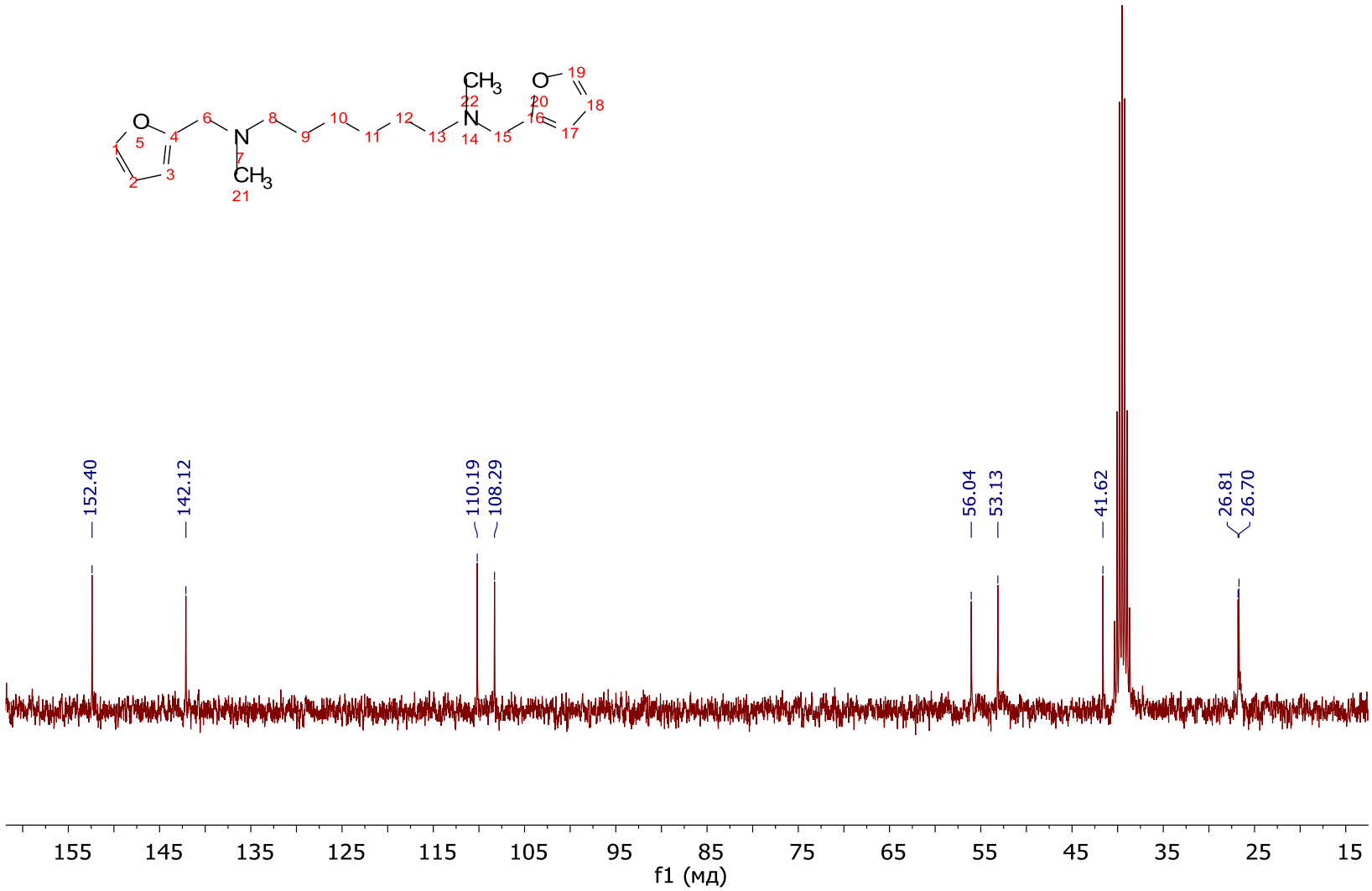


Figure S70. ^{13}C-NMR spectrum of **6a**, (151 MHz, DMSO-d_6).

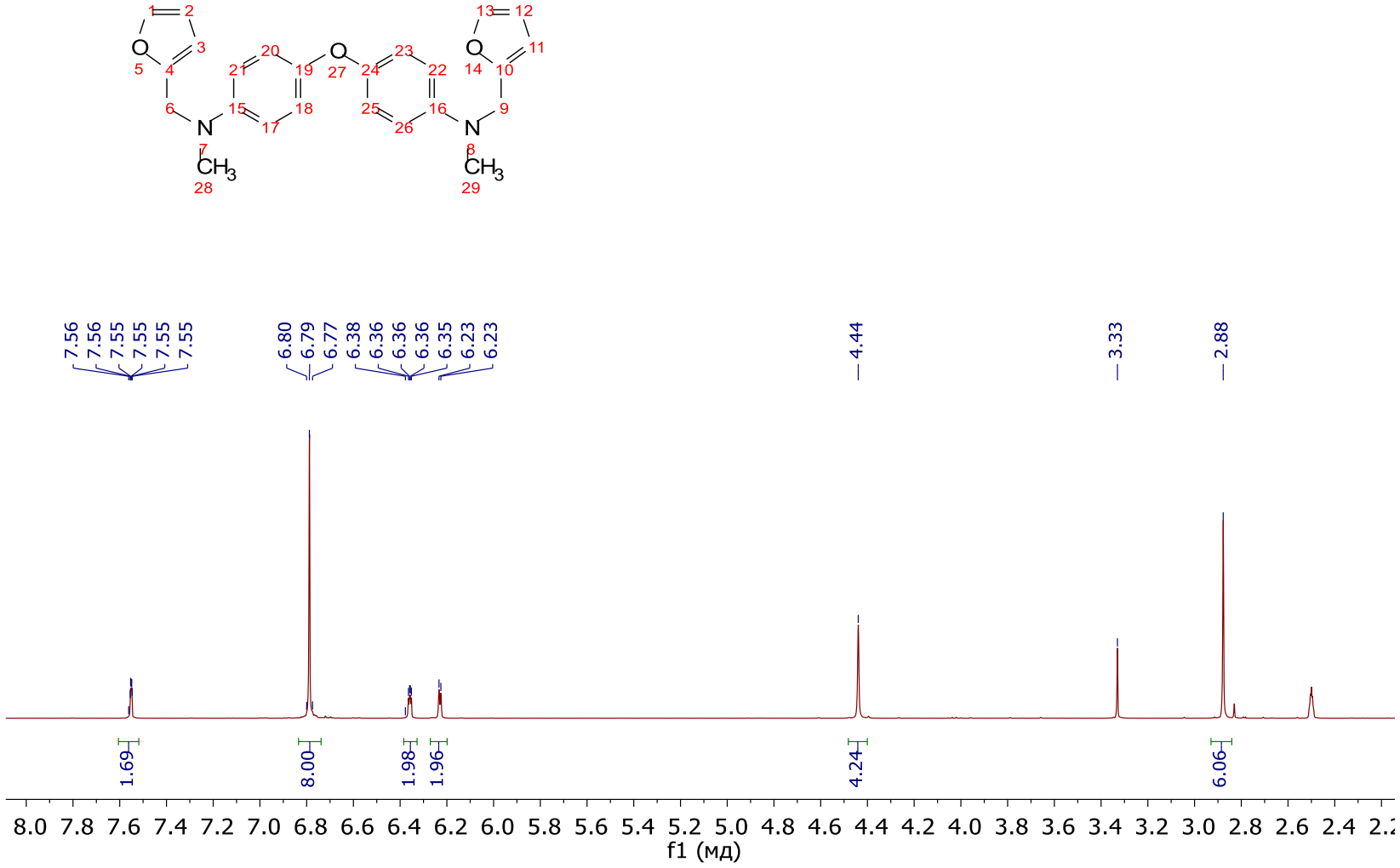


Figure S71. ^{1}H-NMR spectrum of **6b**, (400 MHz, DMSO-d_6).

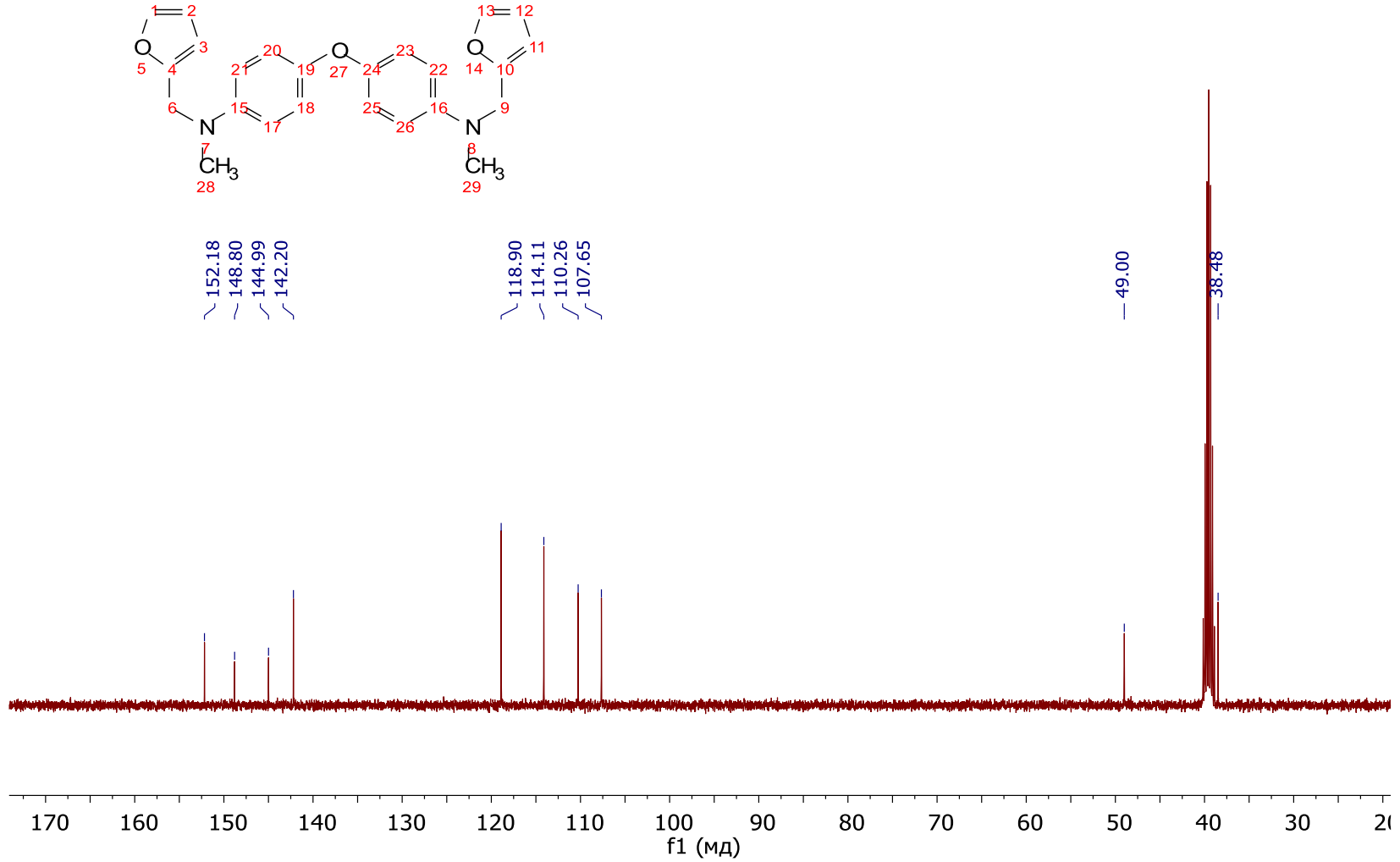


Figure S72. ^{13}C-NMR spectrum of **6b**, (101 MHz, DMSO-d_6).

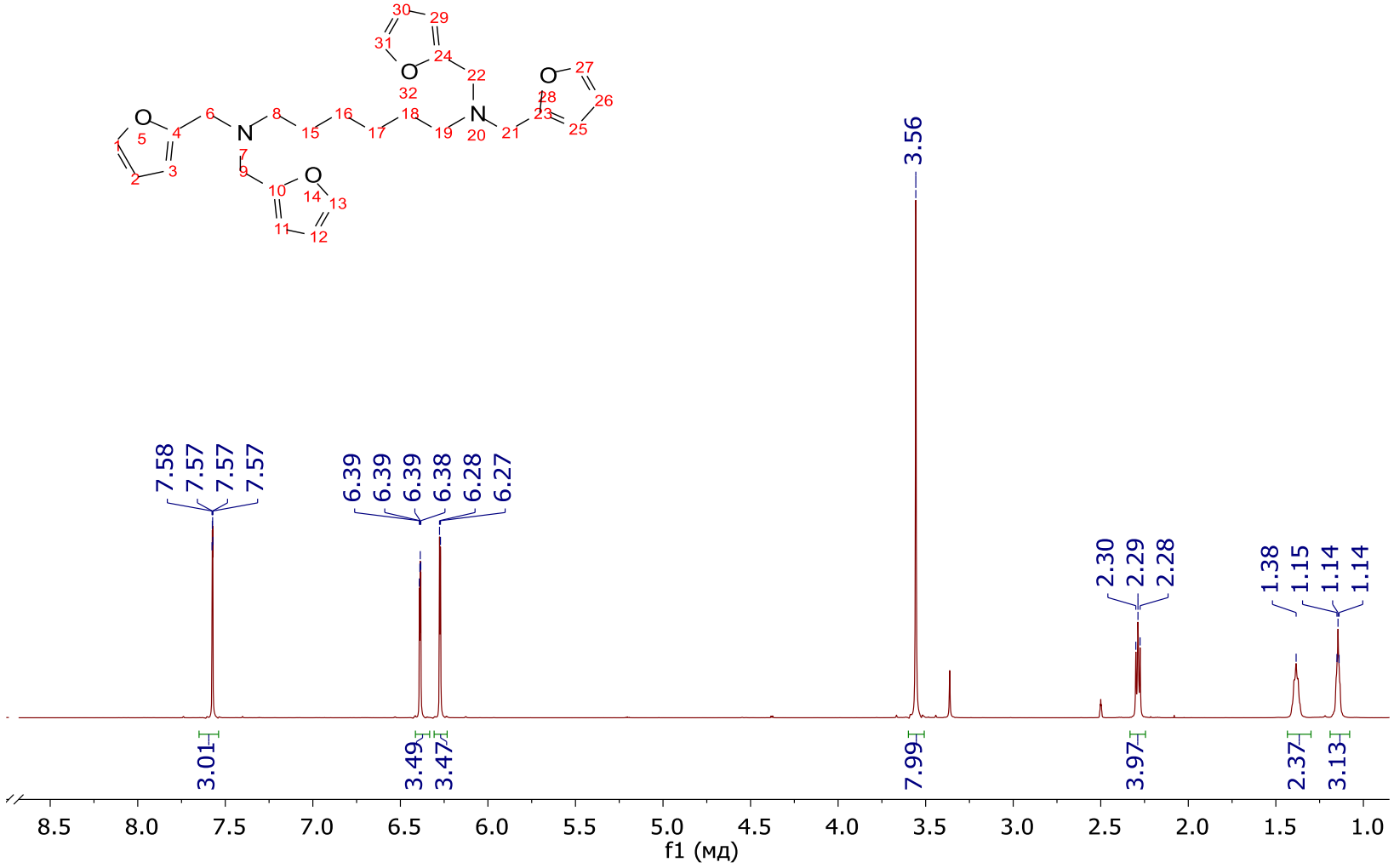


Figure S73. ^{1}H-NMR spectrum of **9a**, (600 MHz, DMSO-d_6).

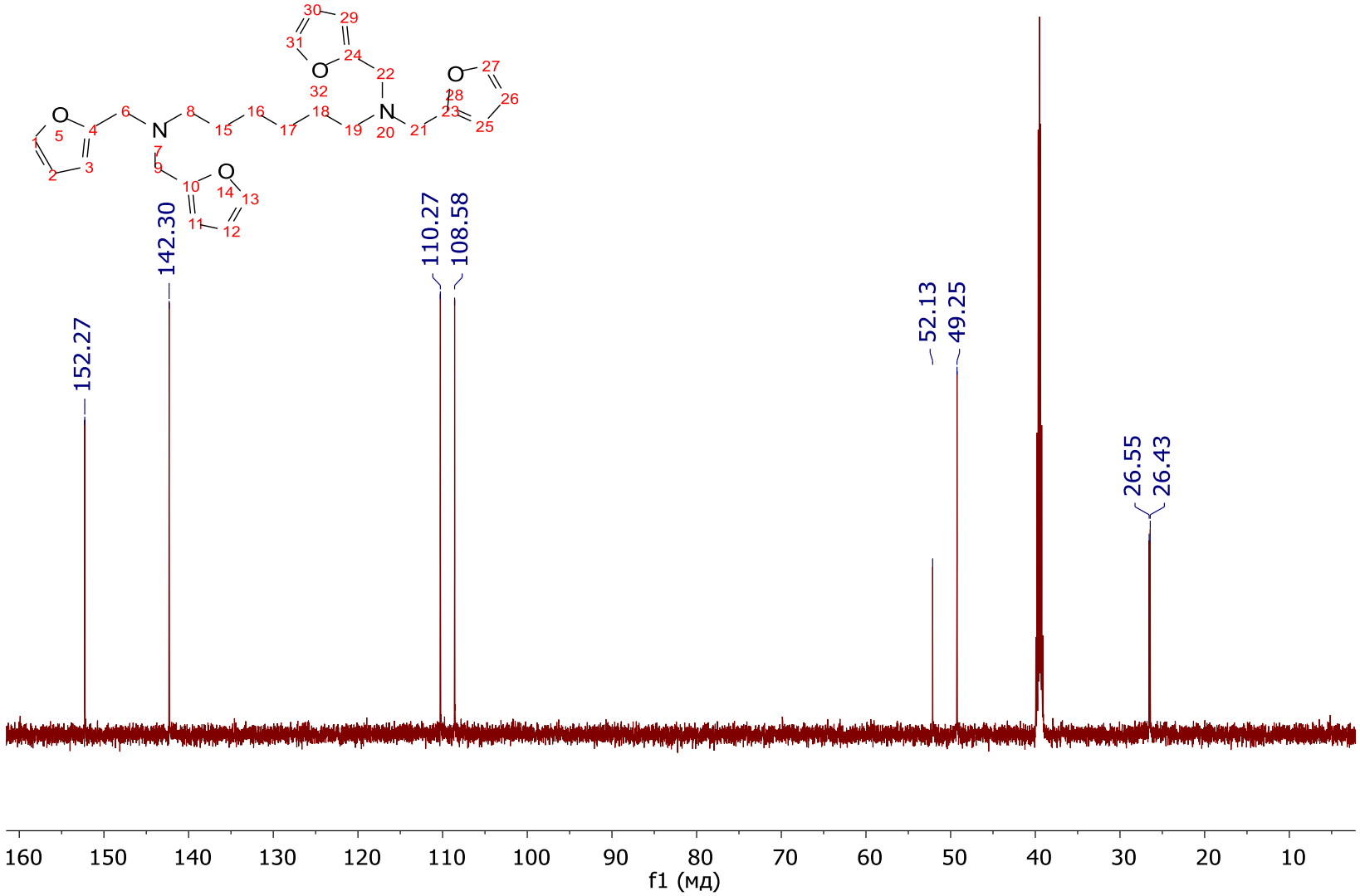


Figure S74. ^{13}C-NMR spectrum of **9a**, (151 MHz, DMSO-d_6).

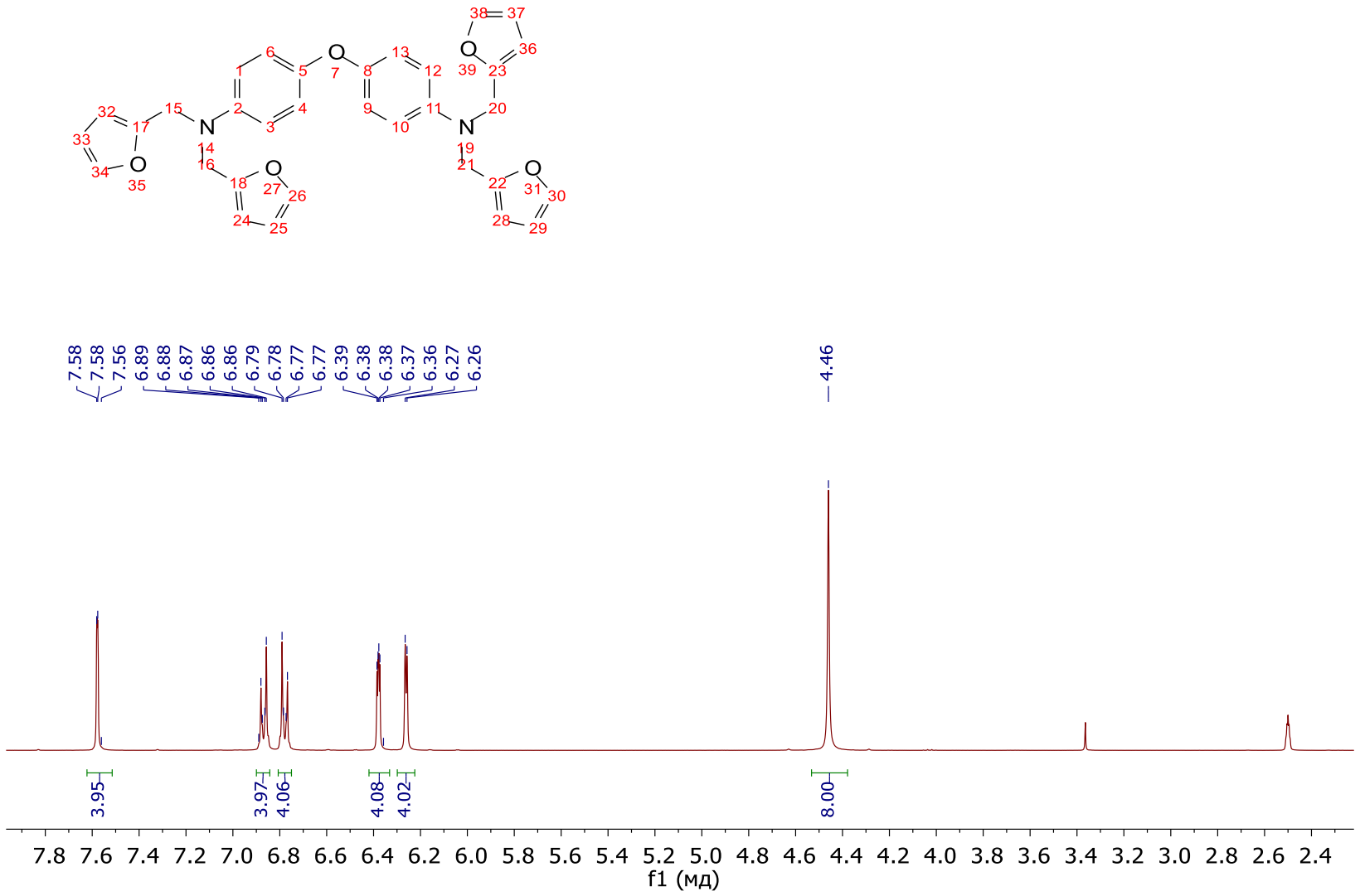


Figure S75. ^{1}H-NMR spectrum of **9b**, (600 MHz, DMSO-d_6).

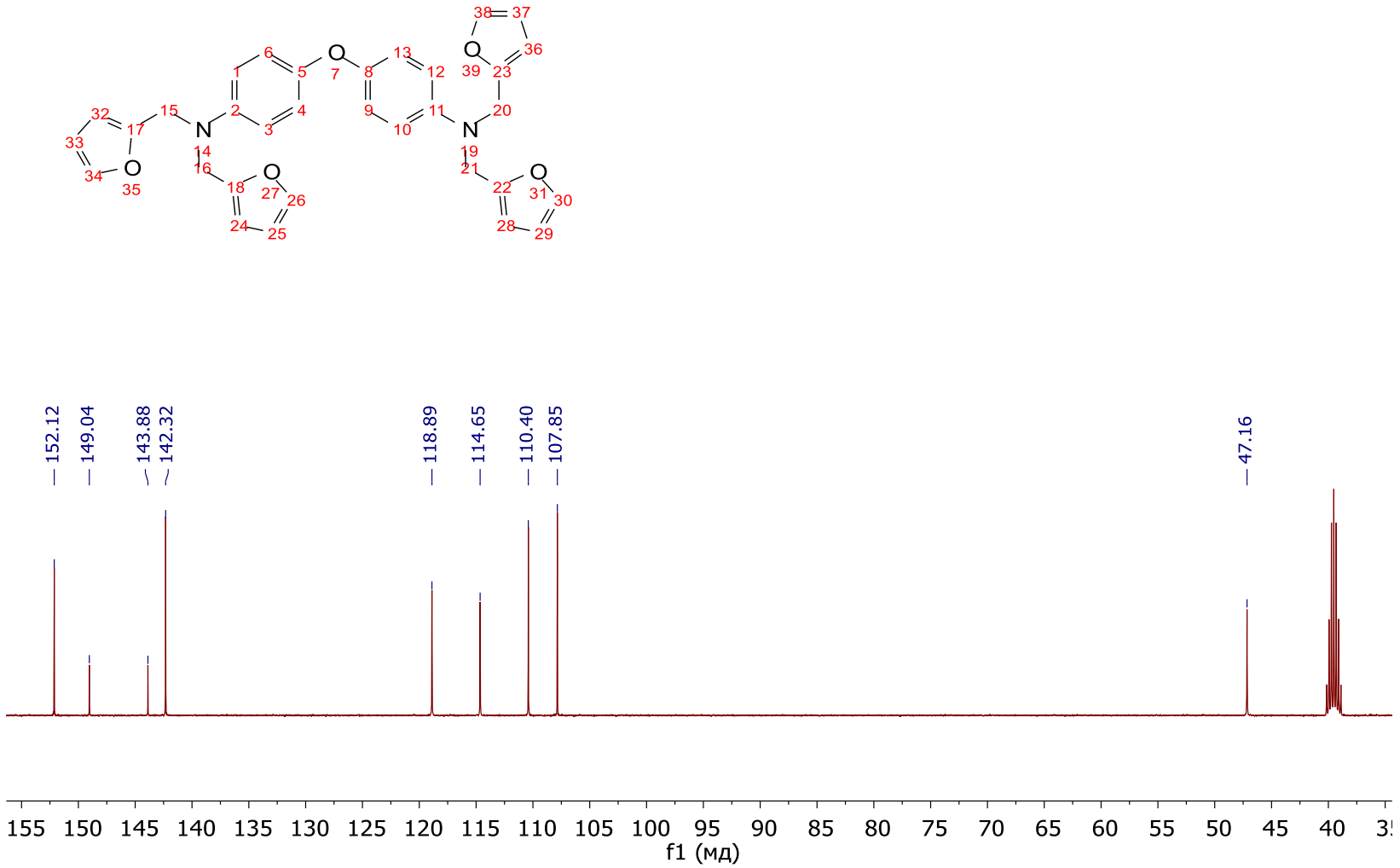


Figure S76. ^{13}C-NMR spectrum of **9b**, (151 MHz, DMSO-d_6).

7.2. Analysis of the polymer compounds by NMR spectroscopy

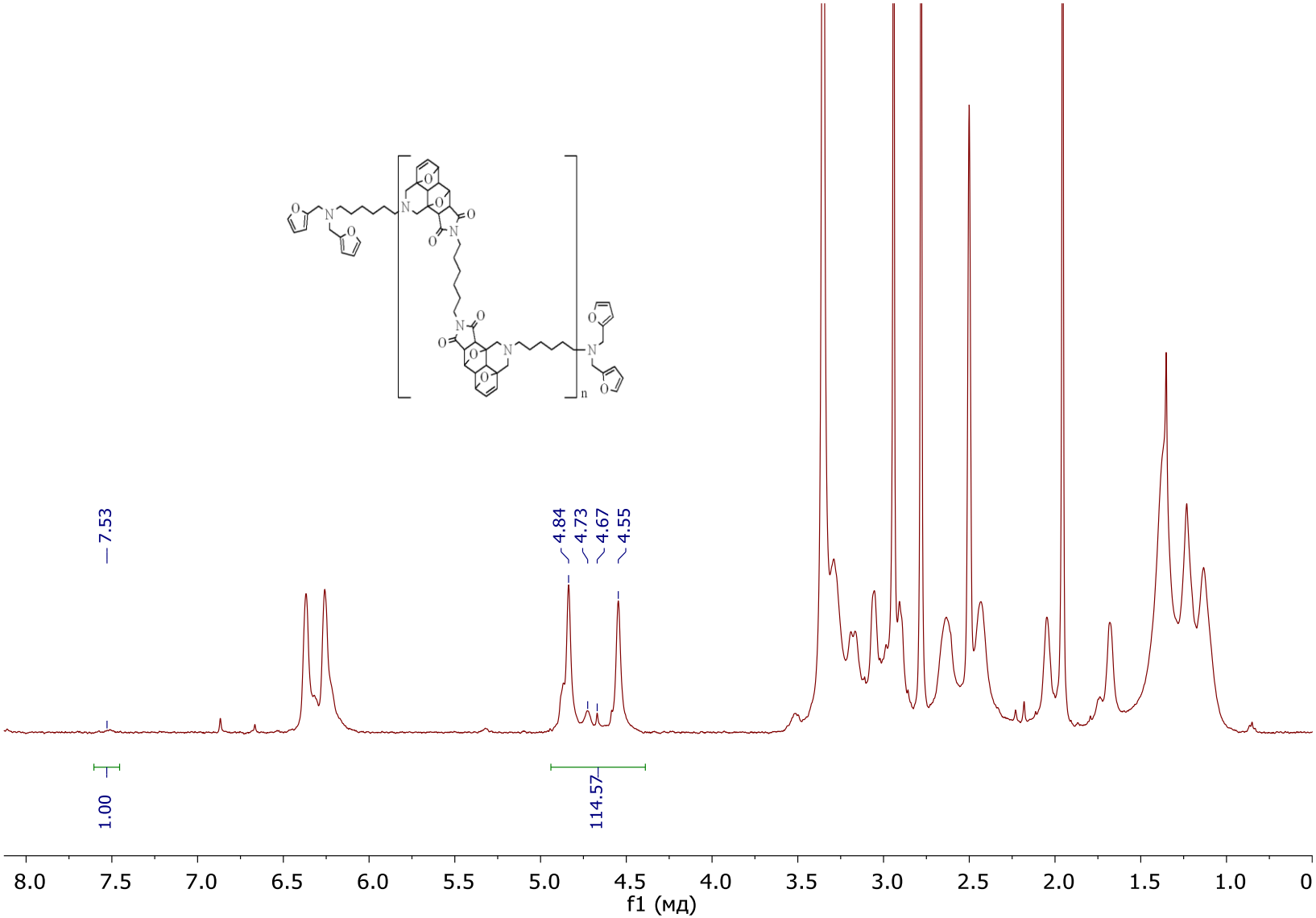
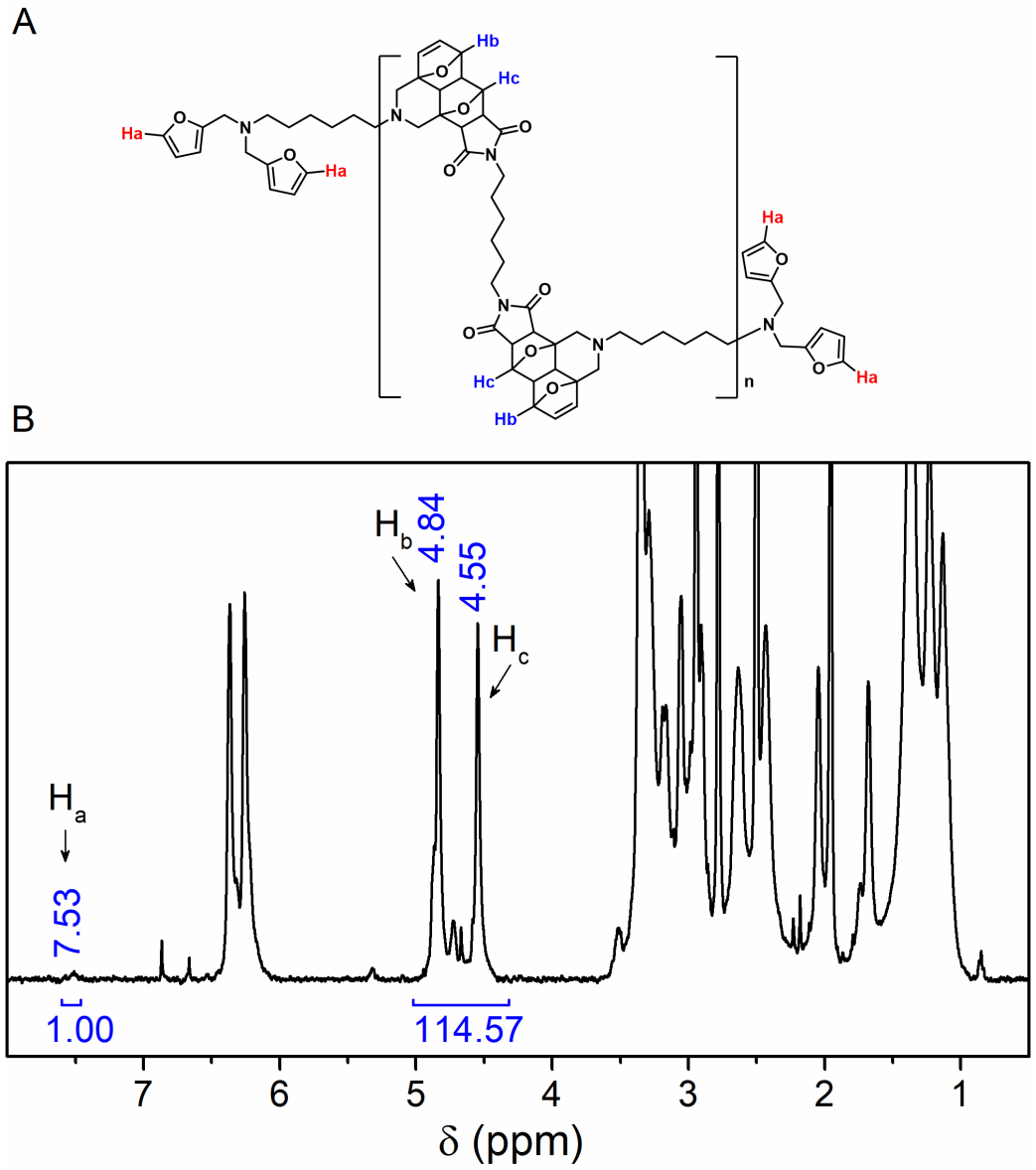


Figure S77. ^{1}H-NMR spectrum of **10a-7**, (400 MHz, DMSO-d_6).



We estimate the degree of polymerization (n_{cp}) for the obtained polymer samples based on ^{1}H NMR spectroscopy. The degree of polymerization (n_{cp}) of each sample was calculated from the ratio of the protons of the terminal furan groups (H_a, 7.53 ppm) to the bridging protons (H_b, H_c, 4.55-4.84 ppm) (see Table 3). Given the known molecular weight of the monomer unit ($M_{mu.}$), the average molecular weight of the resulting polymer sample (M_n) was calculated. The degree of polymerization (n_{cp}) is calculated in a similar way when the terminal groups are maleimide residues. In the latter case, the ratio of bridging protons (H_b, H_c, 4.55-4.84 ppm) to protons corresponding to the double bond of the maleimide ring (HMBMI, 7.00 ppm) was used.

$$n_{\text{cp}} = \frac{(H_b + H_c)}{H_a} \qquad (1)$$

$$n_{\text{cp}} \times M_{\text{зв.}} = Mn \qquad (2)$$

Figure S78. Quantitative analysis of the resulting polymer sample **10a-7** using ^{1}H NMR spectroscopy.

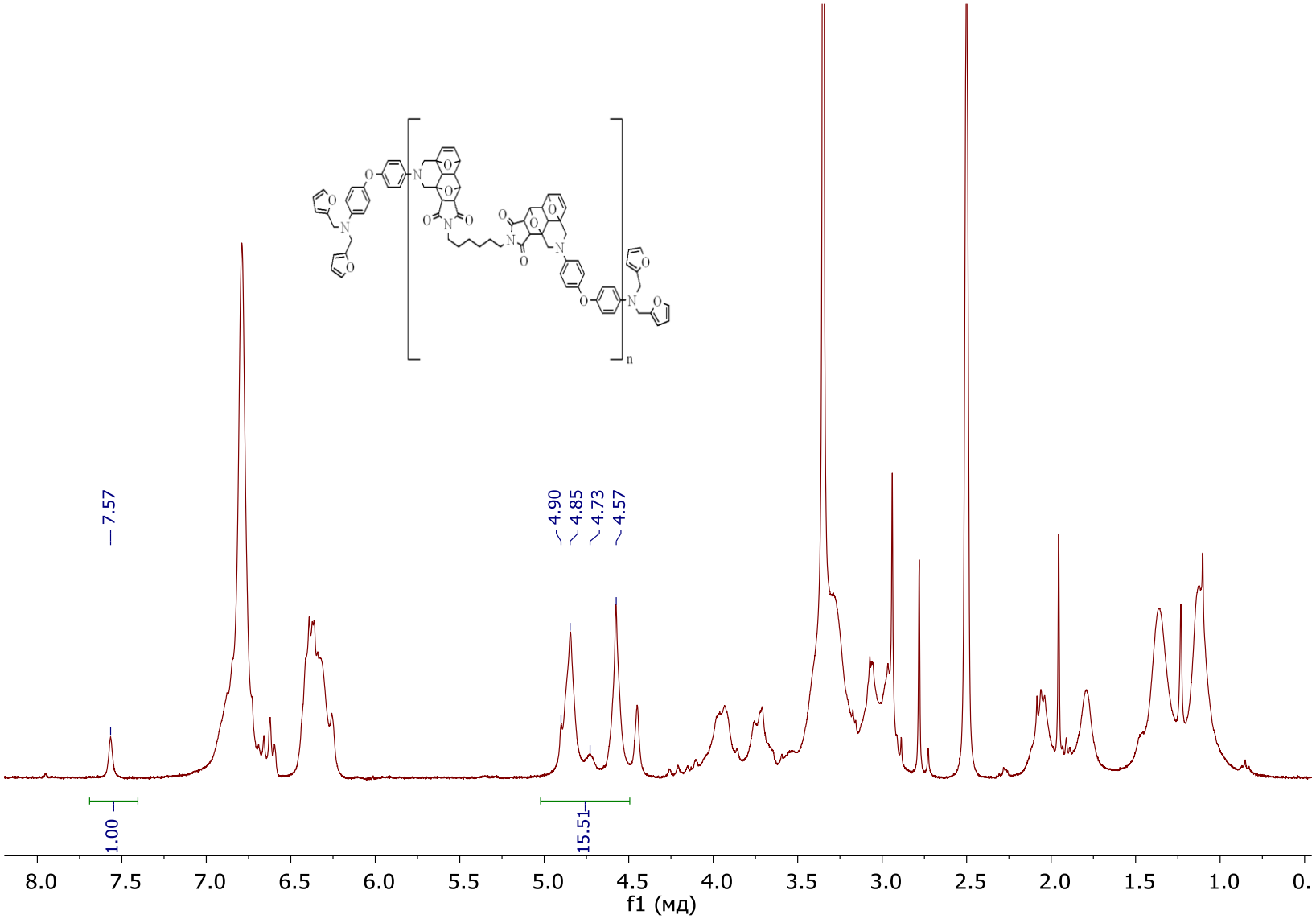


Figure S79. ^{1}H-NMR spectrum of **10b-1**, (400 MHz, DMSO-d_6).

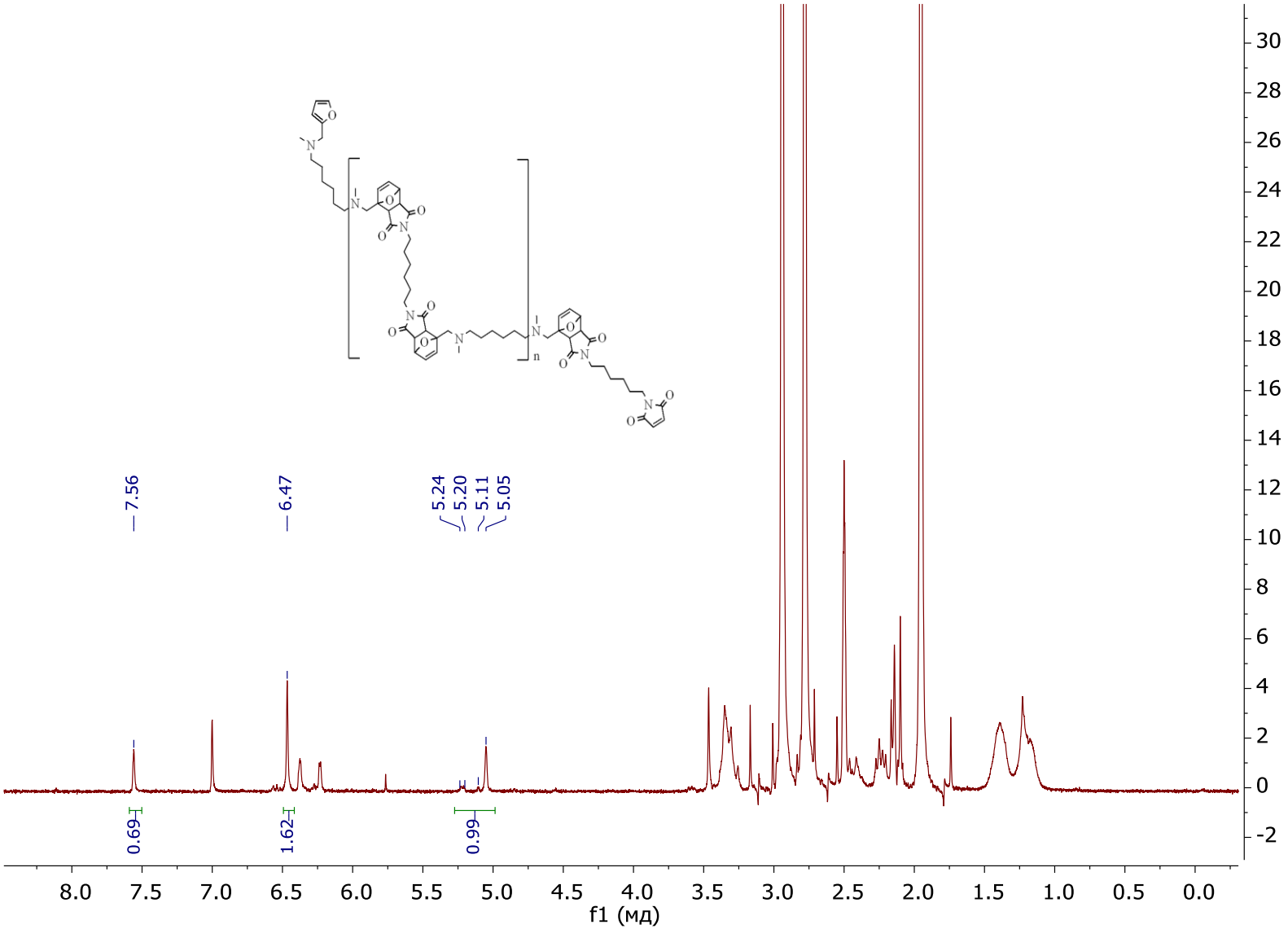


Figure S80. ^{1}H-NMR spectrum of **8a**, (400 MHz, DMSO-d_6).

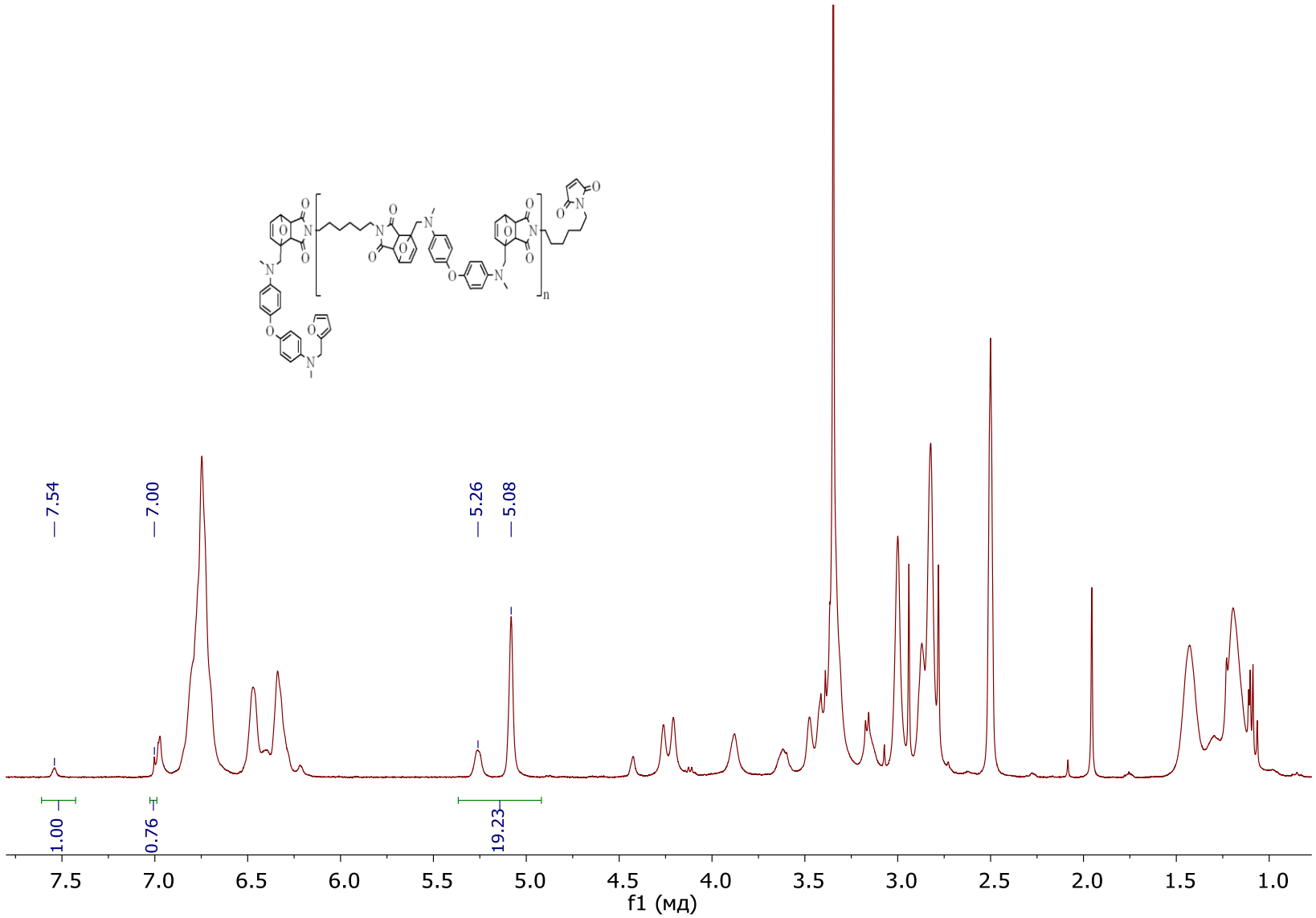


Figure S81. ^{1}H-NMR spectrum of **8b**, (400 MHz, DMSO-d_6).

7.3. NMR spectra after the DSC-experiment

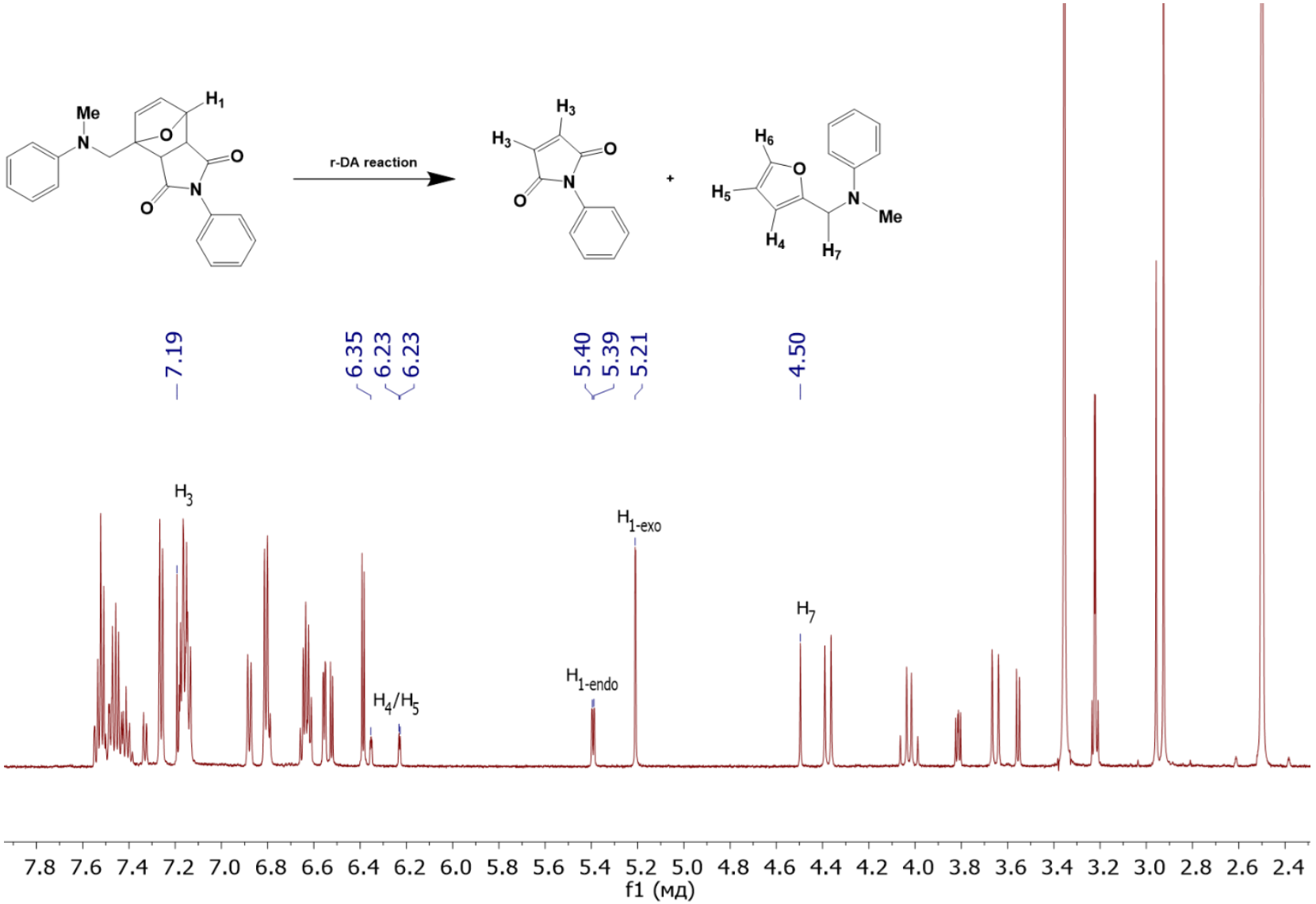


Figure S82. ^{1}H-NMR spectrum of **3a** after DSC analysis (400 MHz, DMSO-d_6). It was found that in sample **3a** heated up to 180°C the percentage of compound **1b** was increased to 15% and the ratio of endo/exo isomers after DSC analysis became 1:2.

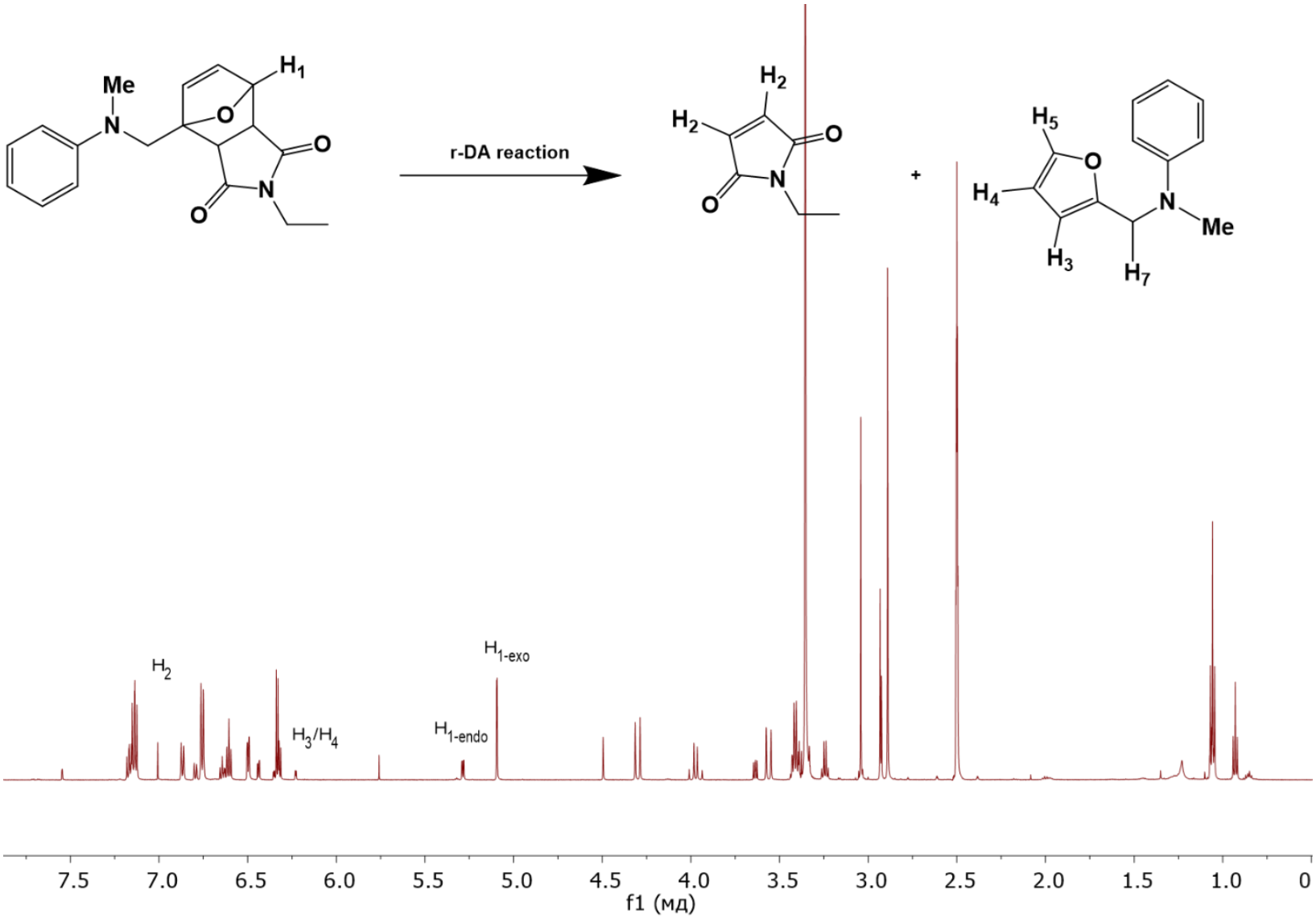


Figure S83. ^{1}H-NMR spectrum of **3b** after DSC analysis (400 MHz, DMSO-d_6).

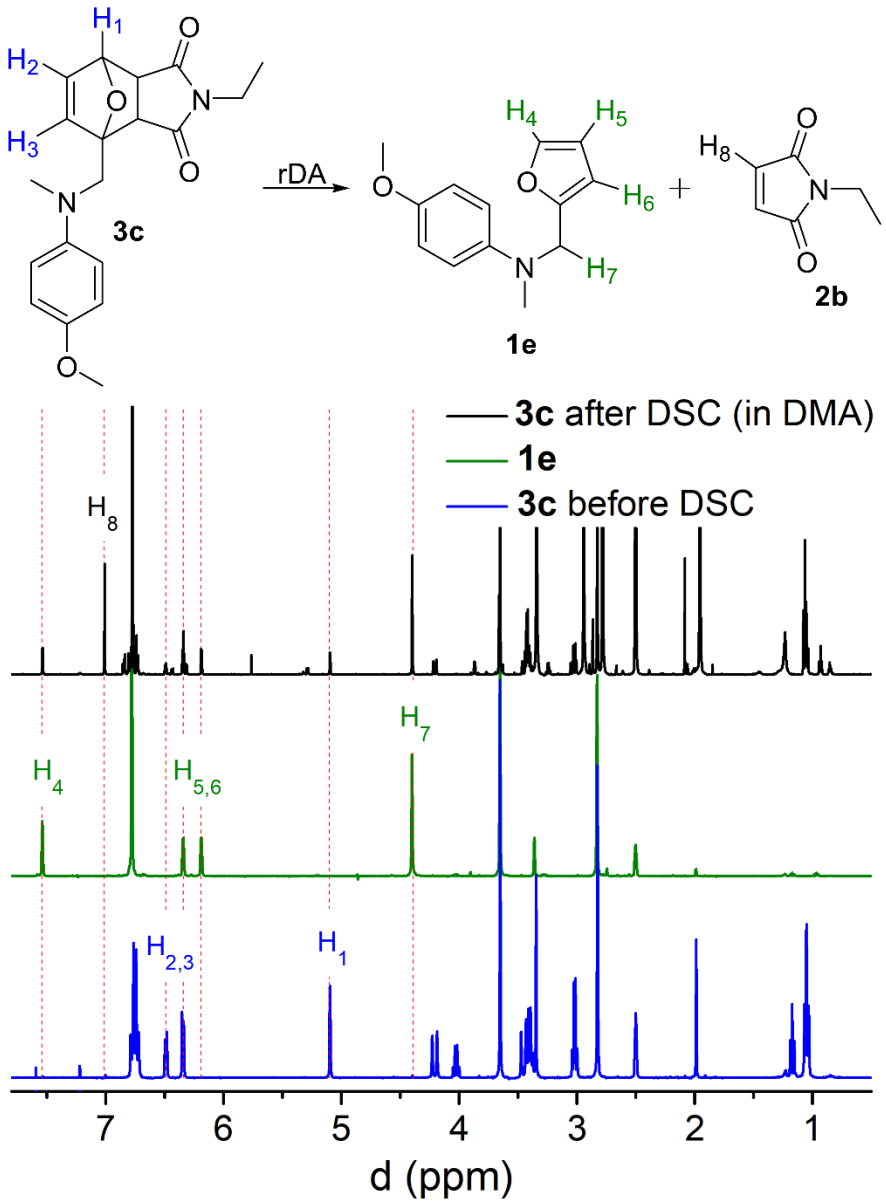


Figure S84. Comparison of ^{1}H-NMR spectrum (400 MHz, DMSO-d_6) 1) of **3c** after DSC analysis in DMA. The ratio of **1e** : **3c-endo** : **3c-exo** was determined as 4:1:2; 2) of compound **1e**; 3) of **3c** before DSC analysis.

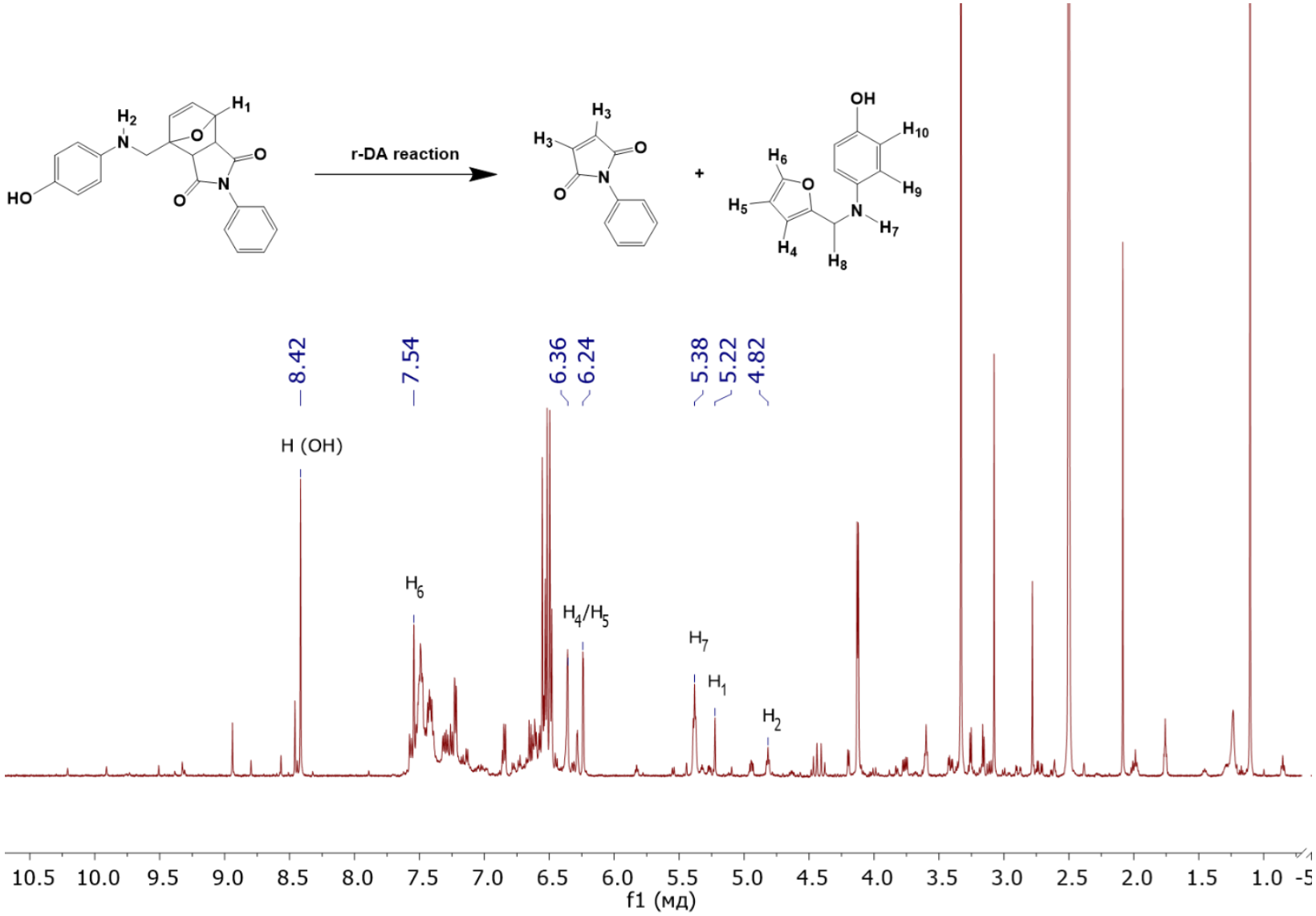


Figure S85. ^{1}H-NMR spectrum of **3d** after DSC analysis (400 MHz, DMSO-d_6). The accumulation of compound **1f** occurred. The ratio of **1f** : **3d-exo** was determined as 2:1.

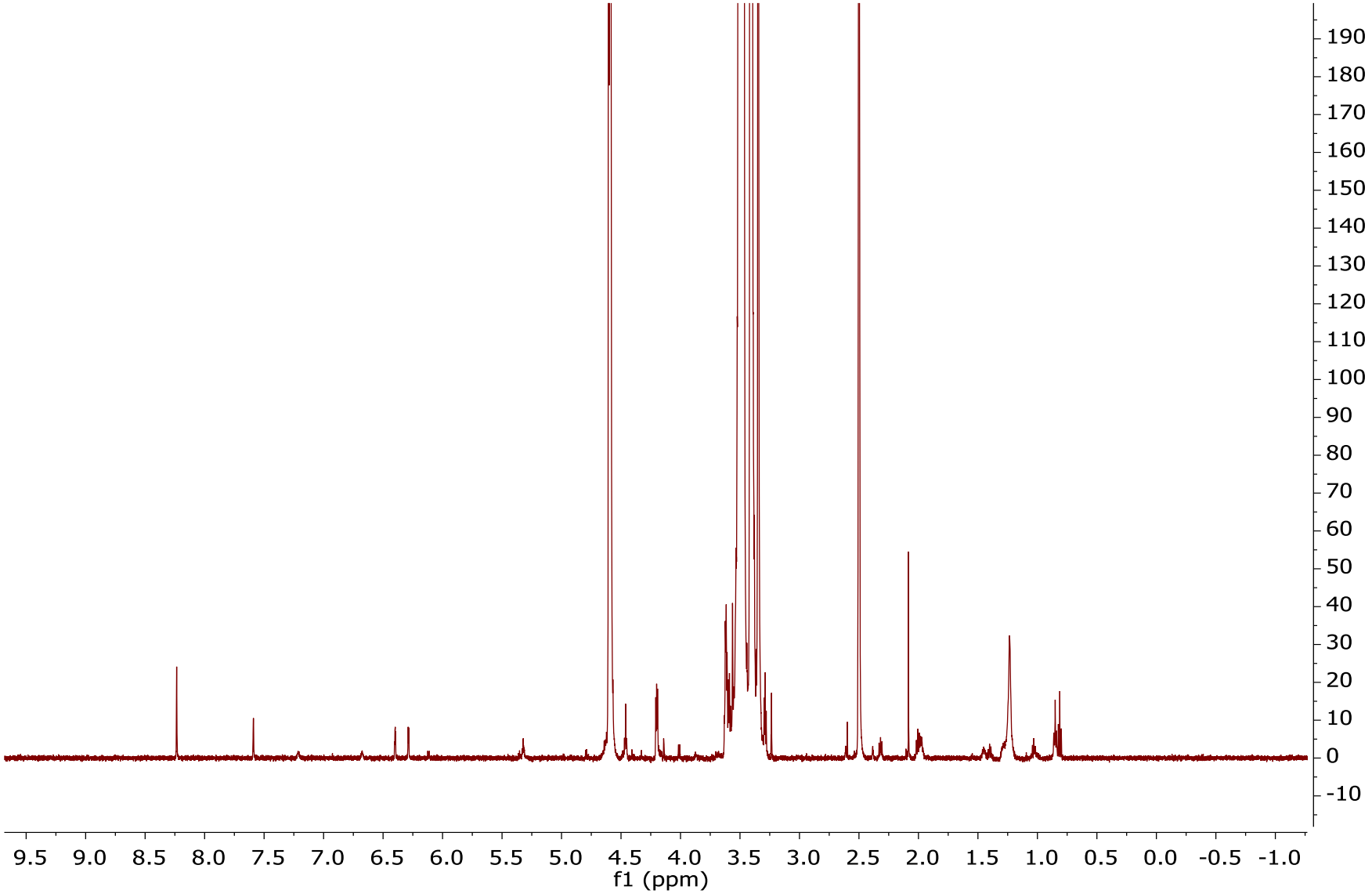


Figure S86. ^{1}H-NMR spectrum of **5c** after DSC analysis in TEG from 0 to 300°C (400 MHz, DMSO-d_6).

8. Thermoanalytical methods of analysis

8.1. DSC data

Conditions of experiment A: heating from 0 to 300°C, heating rate - 5K/min. For the experiments from 3.8 to 12.3 mg of the compounds **3a-3d**, and **5a-5e** were used. DSC analysis was carried out in pierced crucibles.

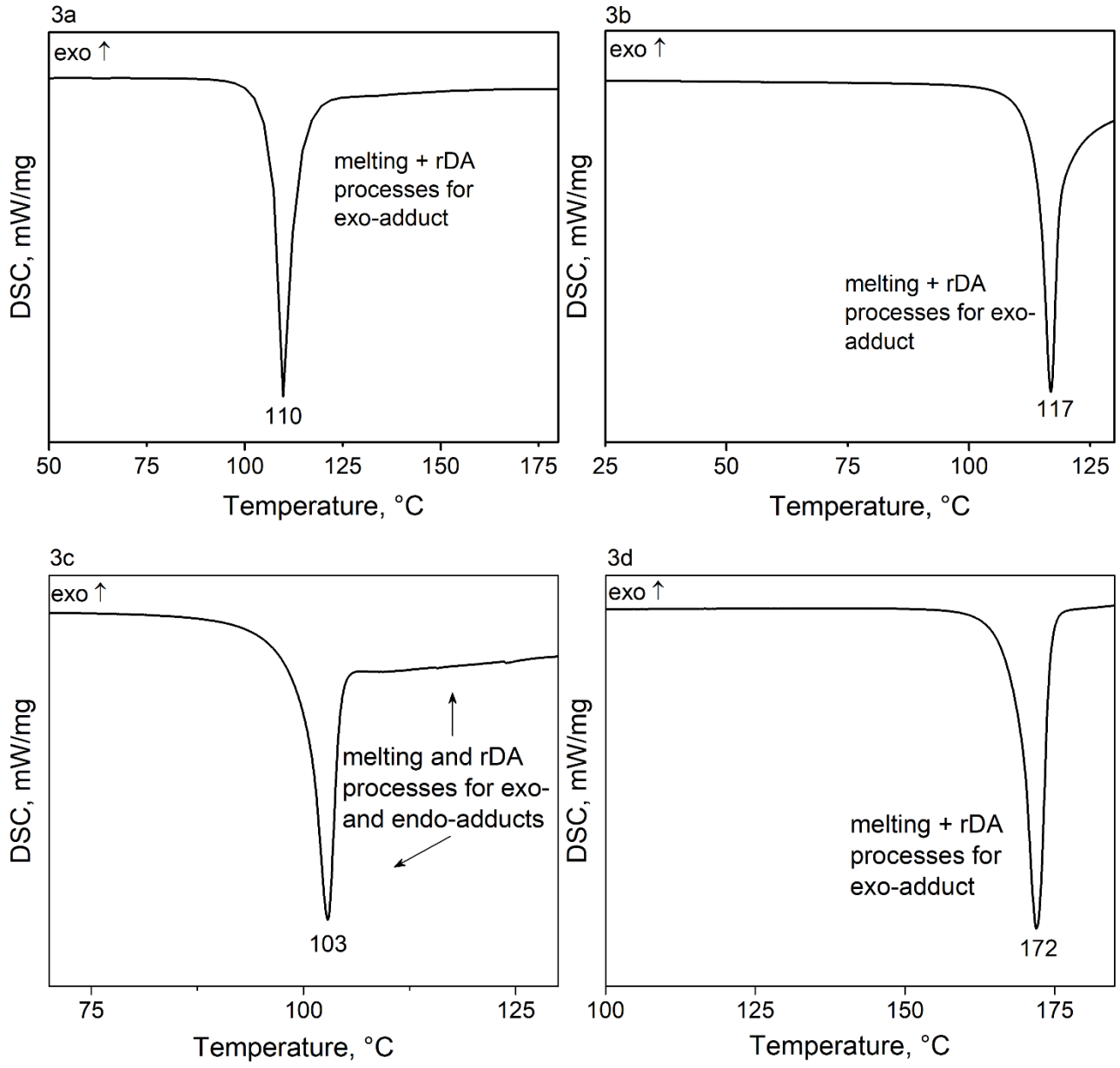


Figure S87. DSC thermograms for the CA **3a-d.**

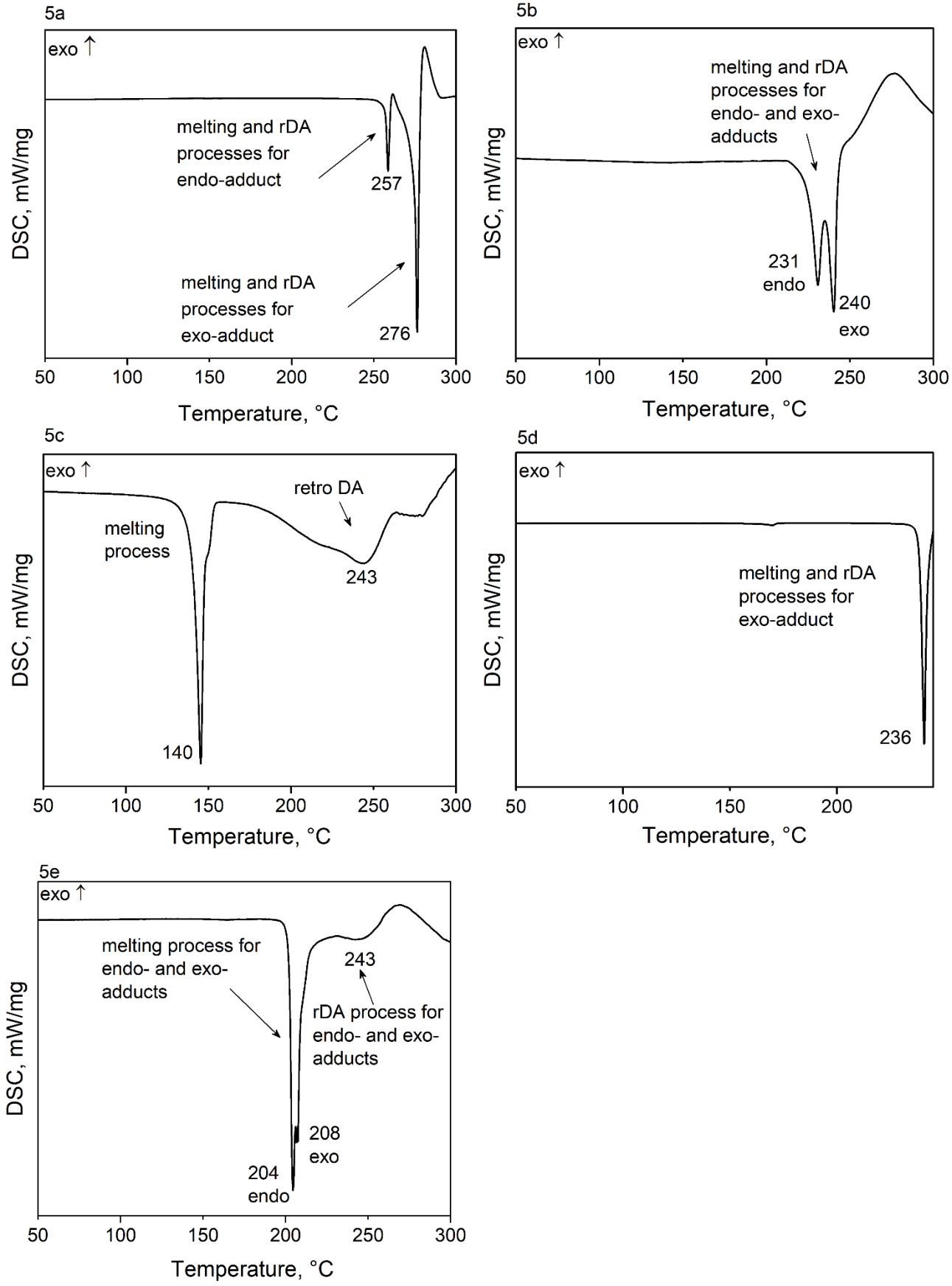


Figure S88. DSC thermograms for the TA **5a-e**.

8.2. Comparison of thermal stability of 5a-exo-endo, 5a-exo-exo by DSC

In the thermogram (Fig. S89A mixture of *exo-exo* and *exo-endo*-adducts), we recorded two endothermic peaks: at 257°C and 276°C, which corresponds to the melting temperatures and the reverse reaction process DA for the *exo-endo* isomer and *exo-exo* isomer, respectively. Under the experimental conditions, the sample is heated above the melting point and the reverse reaction DA for the *exo-endo* isomer (up to 262°C, Fig. S89, A-H1), as a result, the accumulation of the *exo-exo* isomer occurs on the second heating (Fig. S89, A-H2) the endothermic peak corresponding to the melting process and the reverse DA reaction of for the *exo-endo* isomer is no longer observed. The characteristic region of the NMR spectra of the samples under study is shown in (Fig. S89B): the spectrum of the original sample contains peaks belonging to the bridging protons H_1, H_2 of both the *exo-exo* isomer and the *exo-endo* isomer (Fig. S89, B-1). In a DSC experiment, the individual *exo-exo* isomer was obtained by melt isomerization, as demonstrated by a ^{1}H NMR spectrum (Fig. S89, B-2)

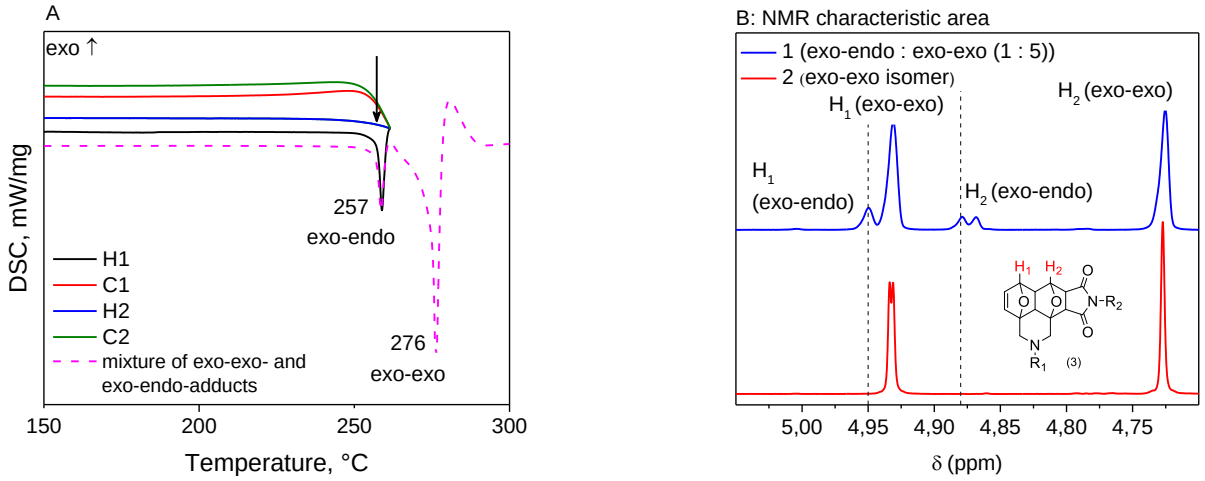


Figure S89. A) The DSC experiment was carried out by heating sample **5a** from 0 to 261.5°C, 5K/min. For the experiment 7.8 mg of compound **5a** was used. H1 and H2 are the first and second heating, stages C1 and C2 are the first and second cooling, respectively. The dotted line shows a DSC thermogram (0-300°C, 5 K/min) for the initial sample, which is a mixture of *exo-exo*- and *exo-endo*-adducts. B1) Characteristic area of the ^{1}H-NMR spectra for compound **5a** before DSC analysis. The ratio of exo-endo and exo-exo is 1:5; B2) Characteristic area of the ^{1}H-NMR spectra for the compound **5a** after DSC-analysis – ^{1}H-NMR spectra of the pure *exo-exo* isomer.

To confirm the purity of the received sample one more DSC experiment was carried out (conditions: heating from 0 to 300°C, 5K/min). It was shown that the temperature of the endothermic peak within an acceptable range of error corresponds to the temperature of the reverse Diels-Alder reaction for the *exo-exo* isomer.

8.3. DSC of polymer samples

Indirect confirmation of the occurrence of the reverse DA reaction is the exothermic peak at 200 and 247°C for classical and tandem polymer samples, respectively. This exothermic peak, according to literature data, is associated with the homopolymerization of bismaleimide released because of the reverse DA reaction.

The DSC curves strongly depend on the polymerization conditions under which the polymer sample was obtained (time and temperature of the reaction), in addition, to the conditions of sample preparation. Without the preheating procedure, the curves of polymer samples have a strong endothermic peak in the region of 60-90°C, which often does not allow identifying the glass transition temperature of the samples.

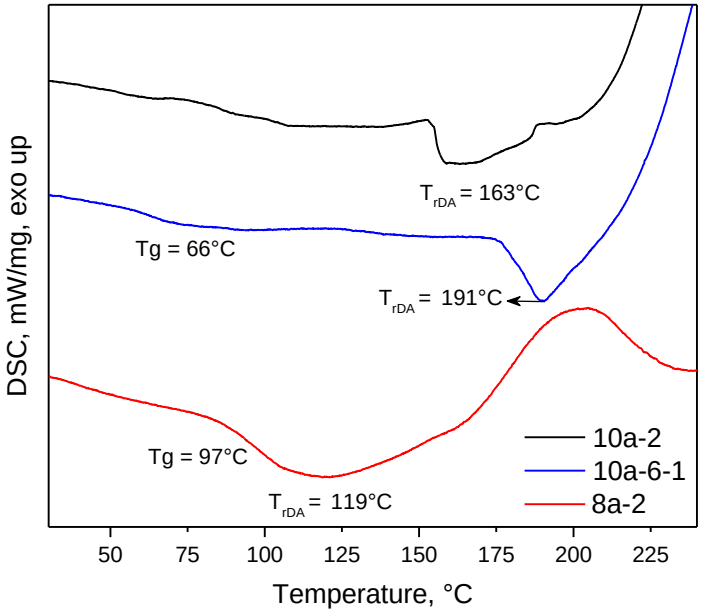


Figure S90. DSC thermogram for the samples **10a-2**, **10a-6-1**, **8a-2**.

Table S4. DSC analysis data of the polymer samples (**8a/b**, **10a/b**).

Sample	Preheating	Polymerization			$T_{max(rDA)}$, °C
		$T_{reaction}$, °C	t, hours	T_g, °C	
10a-2	3 days heating in oven at 60°C	100	24	-	163
10a-6-1	5 days heating in oven at 60°C	145	24	66	191
10a-6-2	20 days heating in oven at 60°C	145	24	96	203 (+ DSC preheating from 0 to 150°C)
10b-1-1	3 days heating in oven at 60°C	100	24	-	203

10b-1-2	3 days heating in oven at 60°C + DSC preheating from 0 to 110°C	100	24	91	175
10b-2	3 days heating in oven at 60°C	100	72	117	203
8a-1	3 days heating in oven at 60°C	100	24	-	120
8a-2	3 days heating in oven at 60°C + DSC preheating from 0 to 85°C	100	24	97	119
8b-1	3 days heating in oven at 60°C	100	24	-	130-140
8b-2	3 days heating in oven at 60°C + DSC preheating from 0 to 85°C	100	24	97	130-140

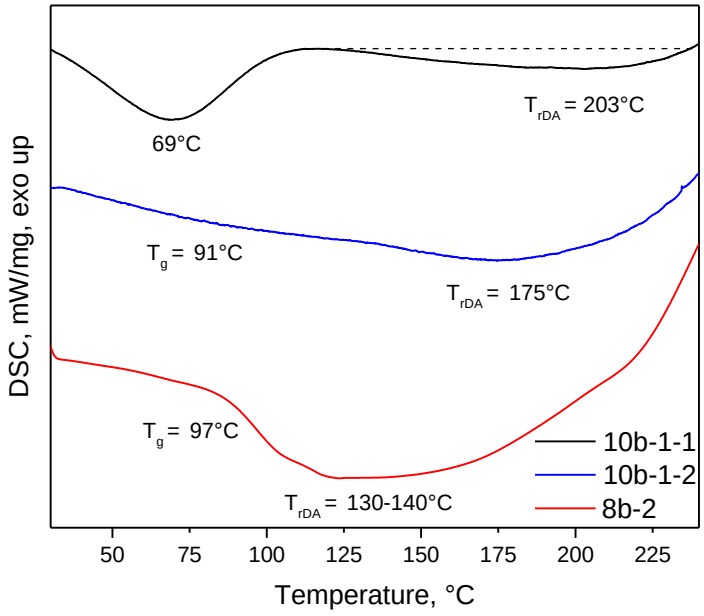


Figure S91. DSC thermogram for the samples **10b-1-1**, **10b-1-2**, **8b-2**.

The data of the DSC method correlate with the data obtained by the TGA (8.4.) and TMA (8.5.) methods

8.4. TGA

Table S5. Thermogravimetric analysis data of the polymer samples (**8a/b**, **10a/b**).

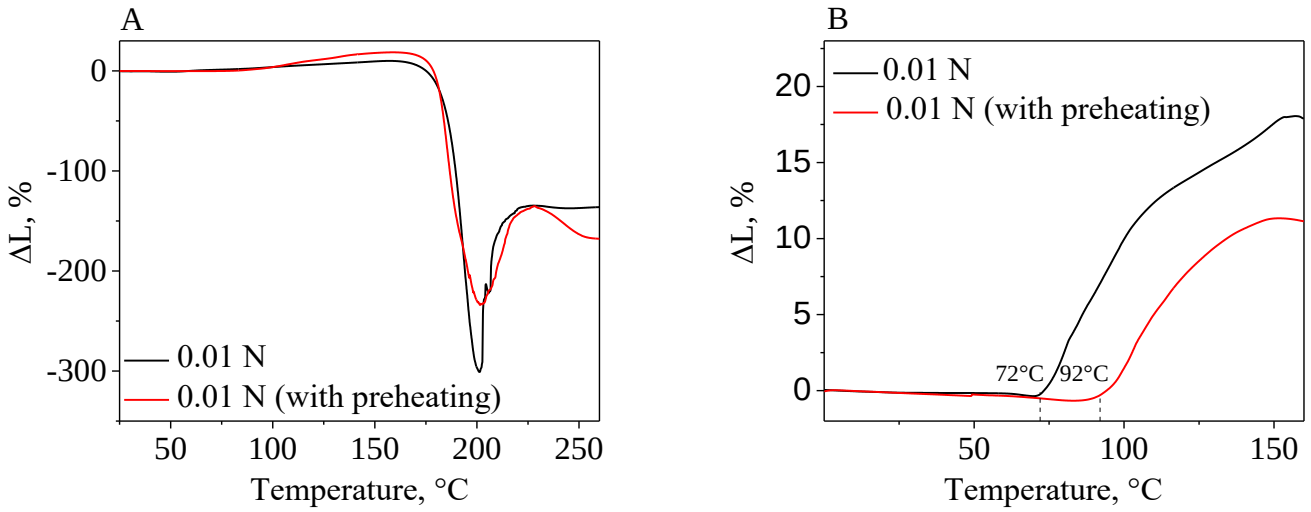
Sample	$T_{5\%}$, °C	$T_{10\%}$, °C	T_{max}, °C	Residual mass, %
10a-2	244.2	284.2	436.0	43.5

10a-6-2	205.6	243.9	447.4	41.8
10b-1	300.1	332.9	462.2	47.31
8a	186.4	252.3	454.3	31.1
8b	246.1	299.2	448.1	35.31

8.5. Mechanical properties of polymer materials (TMA)

The sample of the film **10a-6-2** was investigated using thermomechanical analysis (TMA). The graphs showing the change in sample thickness as a function of temperature under load and without load are presented in Fig. S92. Experiments were conducted on the polymer sample in dilatometric mode without load (Fig. S92A, B. 0.01 N - residual load required to bring the probe into contact with the sample surface), as well as with loads of 0.05 N and 0.1 N (Fig. S92C, D) in the temperature range of 0-300°C. Measurements were performed both with and without preheating from 0 to 160°C.

According to the experiment without load, four stages can be distinguished that the **10a-6-2** polymer sample undergoes in the temperature range of 0-300°C, according to the TMA thermogram. From 0 to 60°C, no change in sample thickness associated with temperature change is observed. From 60 to 170°C, a decrease in sample thickness of 10-19% is observed. From 170 to 200°C, an increase in sample thickness by 2.5-3 times is observed. This effect is likely due to the reverse Diels-Alder reaction, which leads to the release of the initial monomers that vaporize within the sample bulk. At 200°C, a change in the trend towards an increase in sample thickness is observed, and the sample begins to recover its initial thickness. At 225°C, the change in sample thickness reaches a constant value corresponding to a one-and-a-half to two-fold increase in thickness relative to the initial value.



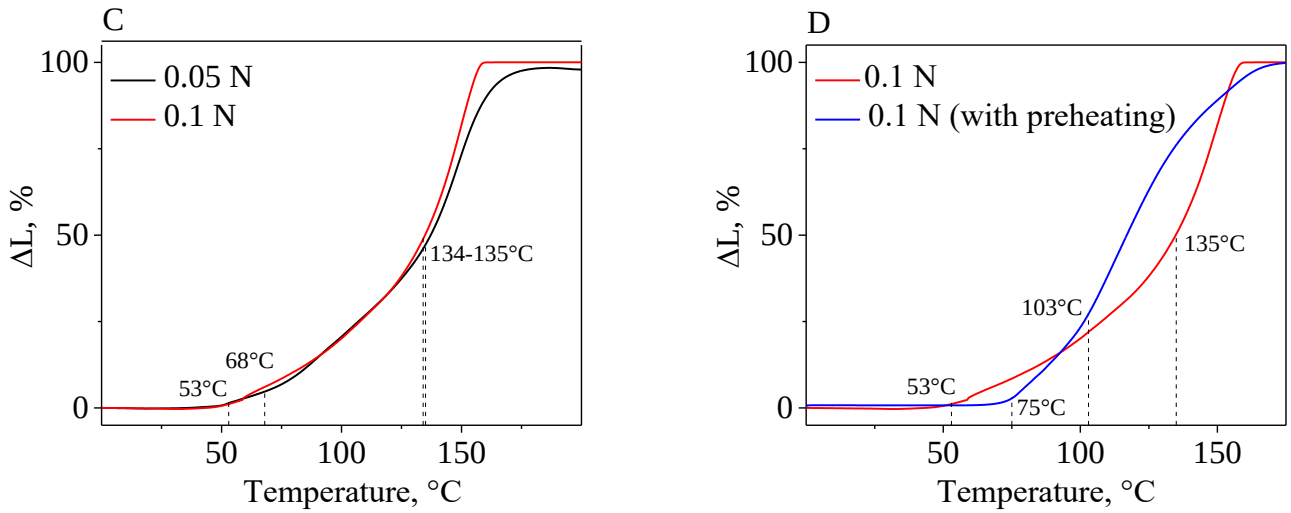


Figure S92. A: TMA curve in dilatometric mode without load (0.01 N) in the range of 0-300°C with and without preheating; B: TMA curve in dilatometric mode without load (0.01 N) in the range of 0-160°C with and without preheating; C: TMA curve with loads of 0.05 N and 0.1 N without preheating; D: TMA curve with a load of 0.1 N with and without preheating.

Additional experiments on the **10a-6-2** compound were conducted for the temperature range of 0-160°C, before the onset of the Diels-Alder reaction (Fig. S92B). It was shown that in the experiment without load and preheating, Tg=72°C, and the decrease in sample thickness reached 19%. However, after two stages of preheating from 0 to 160°C, Tg=92°C, and the decrease in sample thickness is less than 10%.

In the TMA experiments with load, it was shown that regardless of the applied load (0.05 N, 0.1 N), the sample failure corresponds to almost identical thermomechanical curves (Fig. S92C). Similar to the experiments without load (Fig. S92B), we demonstrated that with a load of 0.1 N, the glass transition temperature increases by approximately 20°C for the sample that underwent the preheating procedure (Fig. S92D).

9. X-ray diffraction

X-ray diffraction data for **5a** and **5d** (Figs 93, 94), the latter as a solvate with one DMSO molecule per two symmetry-independent molecules of the product, were collected at 120 K with a Bruker APEX2 DUO CCD diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Using Olex2(20), the structures were solved with the ShelXT(21) structure solution program using Intrinsic Phasing and refined with the XL(22) refinement package using Least-Squares minimization against F^2 in anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated, and they were refined in isotropic approximation within the riding model. Crystal data and structure refinement parameters are given in Table 1. CCDC 2007735 and 2007738 contain the supplementary crystallographic data for **5a** and **5d**, respectively.

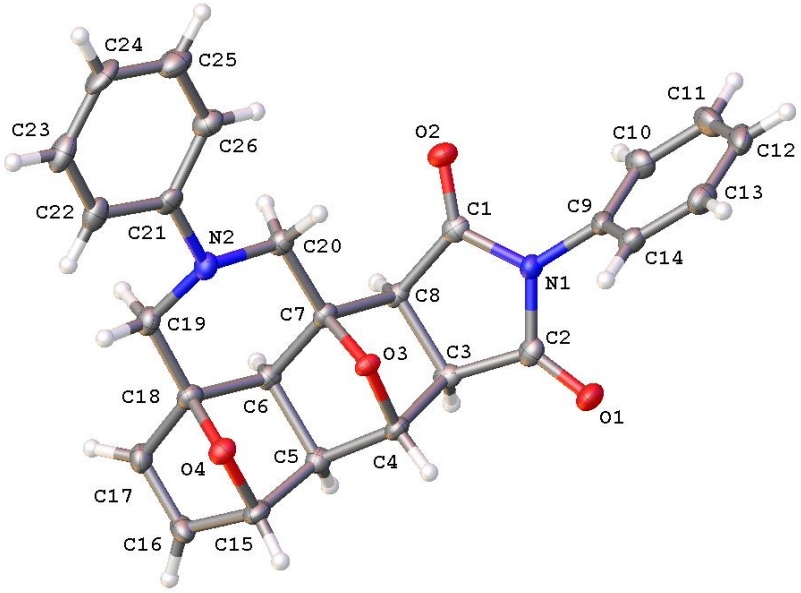


Figure S93. General view of the compound **5a**. Hereinafter, non-hydrogen atoms are shown as thermal ellipsoids at a 50% probability level.

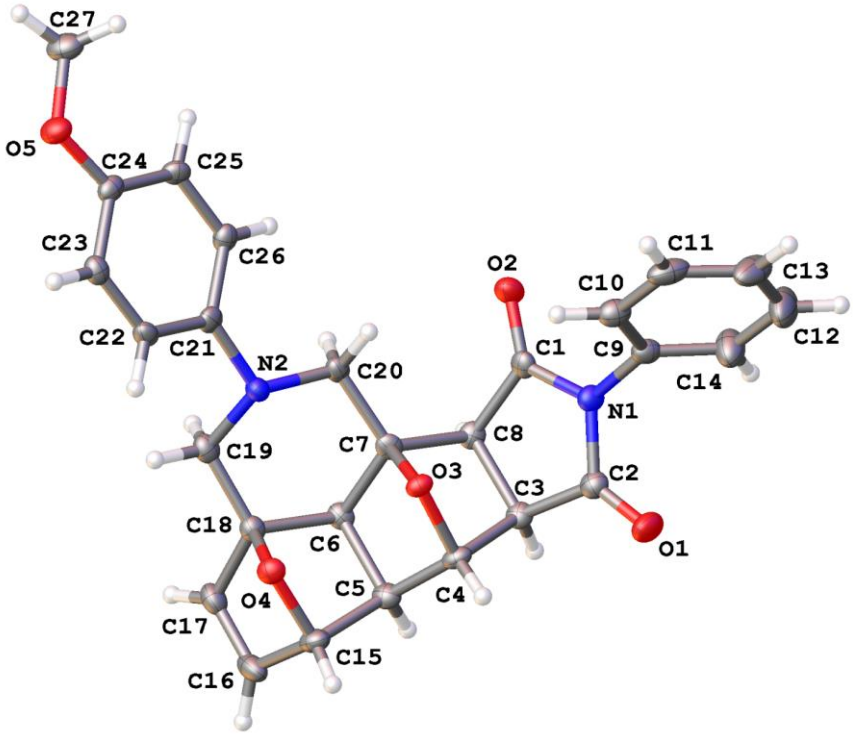


Figure S94. General view of the compound **5d**. The second symmetry-independent molecule and the solvate molecule of DMSO are not shown.

Table 6. Crystal data and structure refinement parameters for **5a** and **5d**.

	5a	**5d**
Empirical formula	$C_{24}H_{22}N_2O_4$	$C_{56}H_{54}N_4O_{11}S$
Formula weight	426.45	991.09
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
Z	4	4
a, Å	14.310(4)	9.8335(10)
b, Å	14.559(4)	18.2519(19)
c, Å	10.188(3)	26.581(3)
β, °	103.215(7)	90.016(3)
V, Å^3	2066.3(10)	4770.8(9)
D_{calc} (g cm^{-1})	1.371	1.380
Linear absorption, μ (cm^{-1})	0.93	1.38
F(000)	896	2088
$2\theta_{max}$, °	50	50
Reflections measured	18275	42274
Independent reflections	3632	8397
Observed reflections [I > 2σ(I)]	1879	5473
Parameters	290	653
R1	0.0552	0.0481
wR2	0.1145	0.1068
GOF	0.972	0.985
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	0.274/-0.233	0.363/-0.322

10. LC-MS

5a

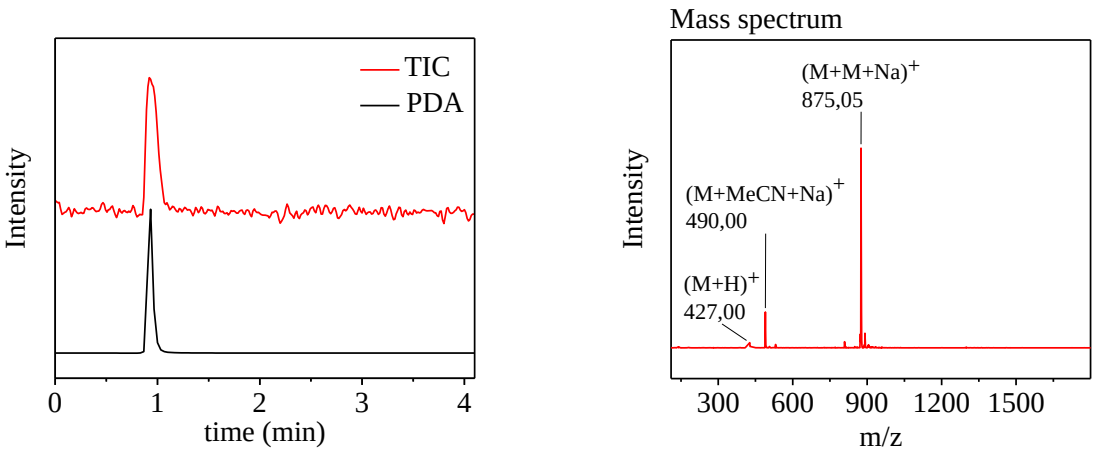


Figure S95. LC-MS: $(M+H)^+$ 427.000, $(M+ACN+Na)^+$ 490.000, $(M+M+Na)^+$ 875.000

5b

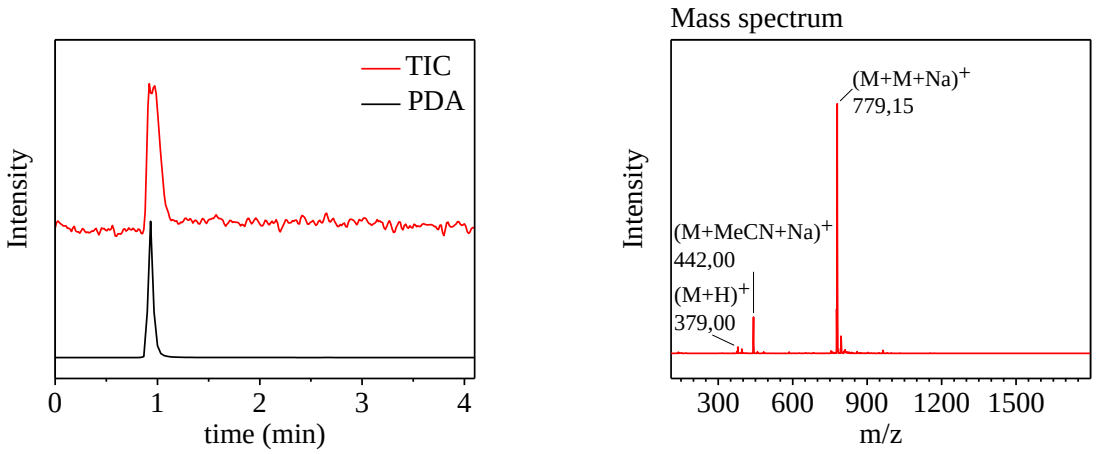


Figure S96. LC-MS: $(M+H)^+$ 379.000, $(M+ACN+Na)^+$ 442.000, $(M+M+Na)^+$ 779.150

5c

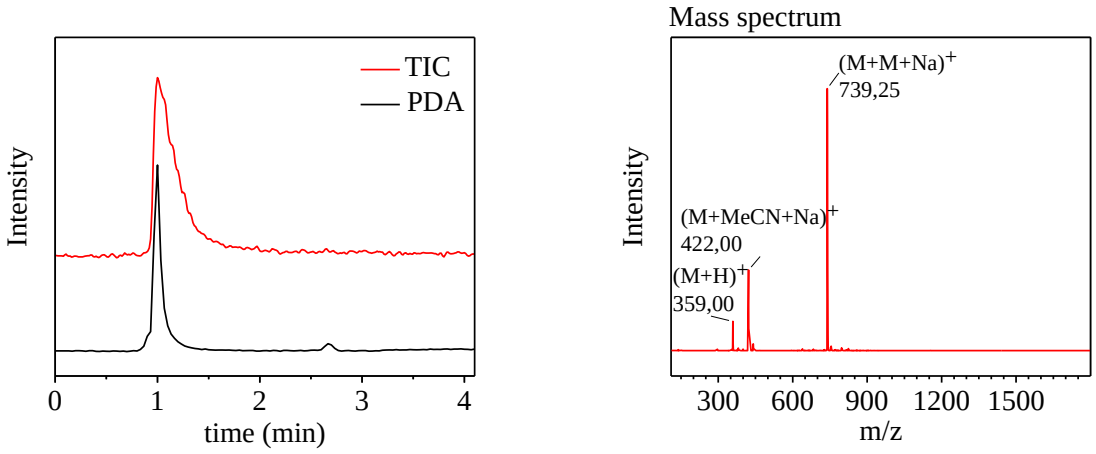


Figure S97. LC-MS: $(M+H)^+$ 359.000, $(M+ACN+Na)^+$ 422.000, $(M+M+Na)^+$ 739.000

5d

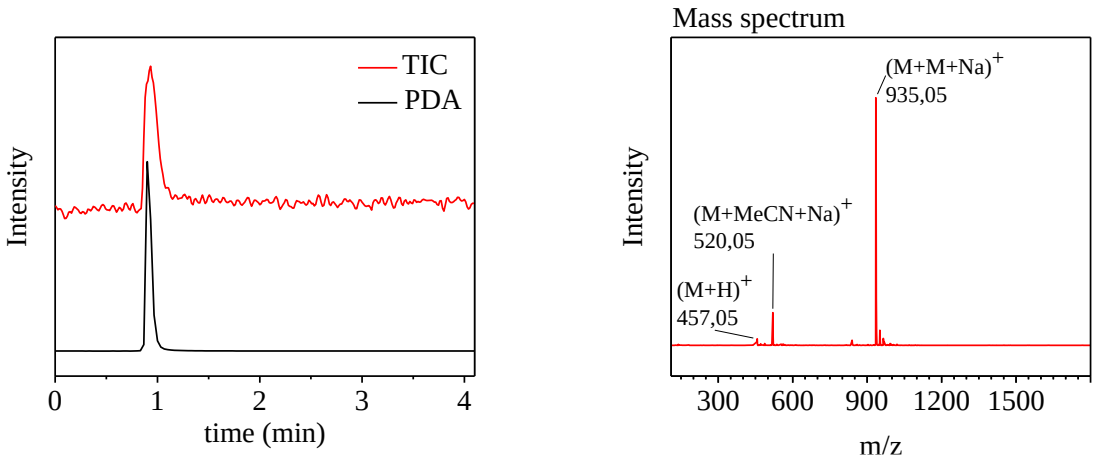


Figure S98. LC-MS: $(M+H)^+$ 457.050, $(M+ACN+Na)^+$ 520.050, $(M+M+Na)^+$ 935.000

5e

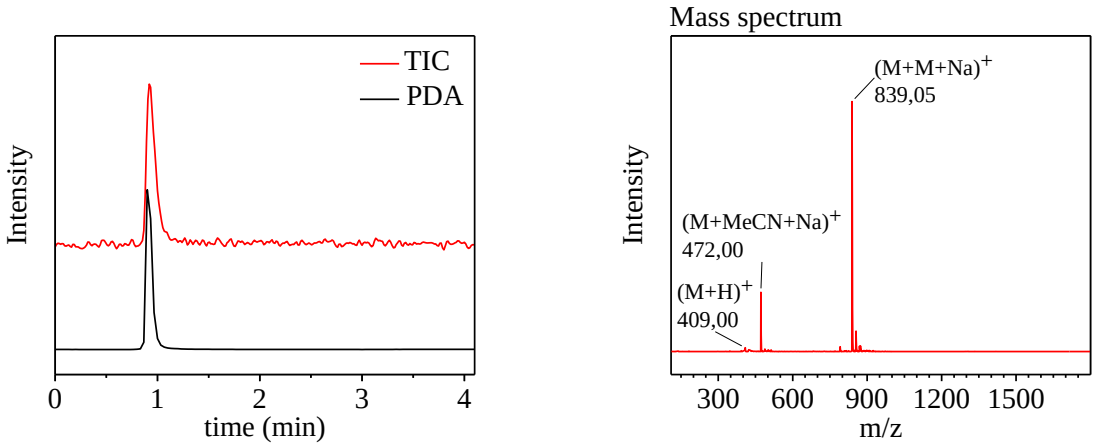


Figure S99. LC-MS: $(M+H)^+$ 409.000, $(M+ACN+Na)^+$ 472.000, $(M+M+Na)^+$ 839.050

11. NMR kinetic experiment

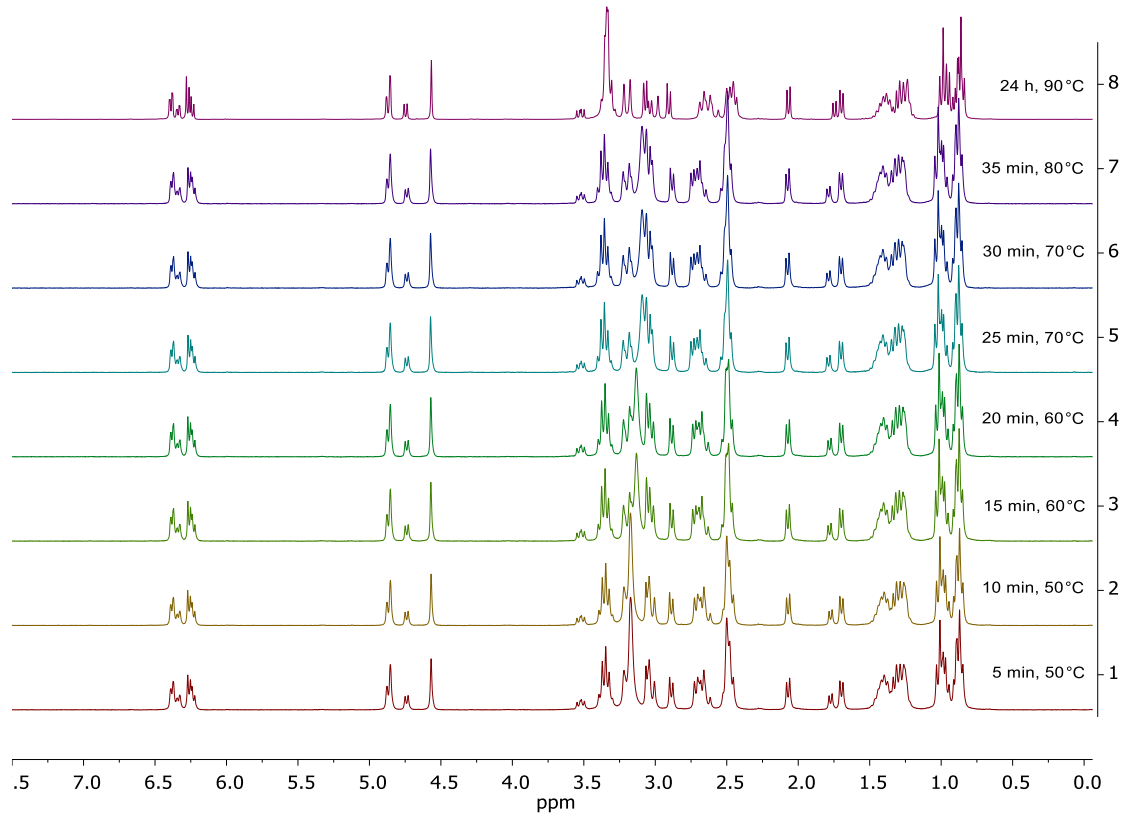


Figure S100. Investigation of the stability of the compound **5c** by ^{1}H-NMR spectroscopy.

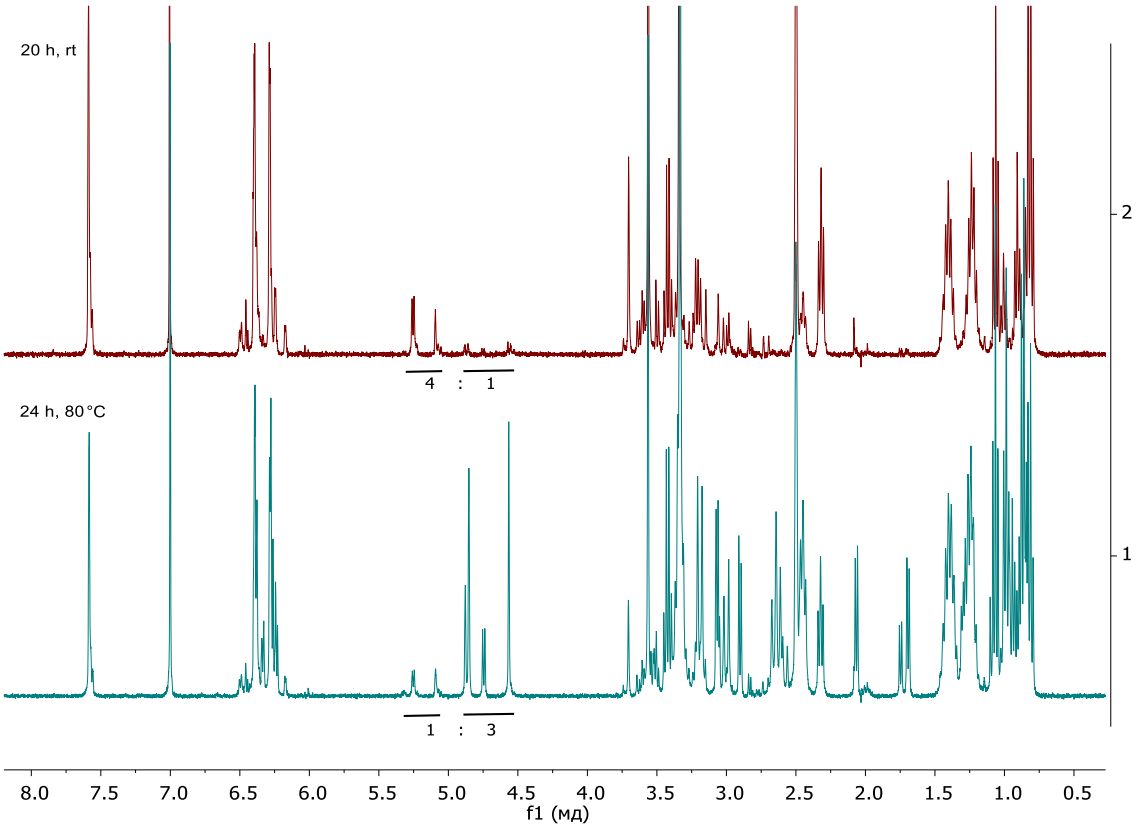


Figure S101. Monitoring of the direct DA reaction during the synthesis of the compound **5c** by ^{1}H-NMR spectroscopy. 1) ^{1}H-NMR spectrum of the reaction mixture after carrying out the reaction for 24 hours at 80°C

in DMSO-d_6. 2) ^{1}H-NMR spectrum of the reaction mixture after carrying out the reaction for 20 hours at room temperature in solvent-free conditions.

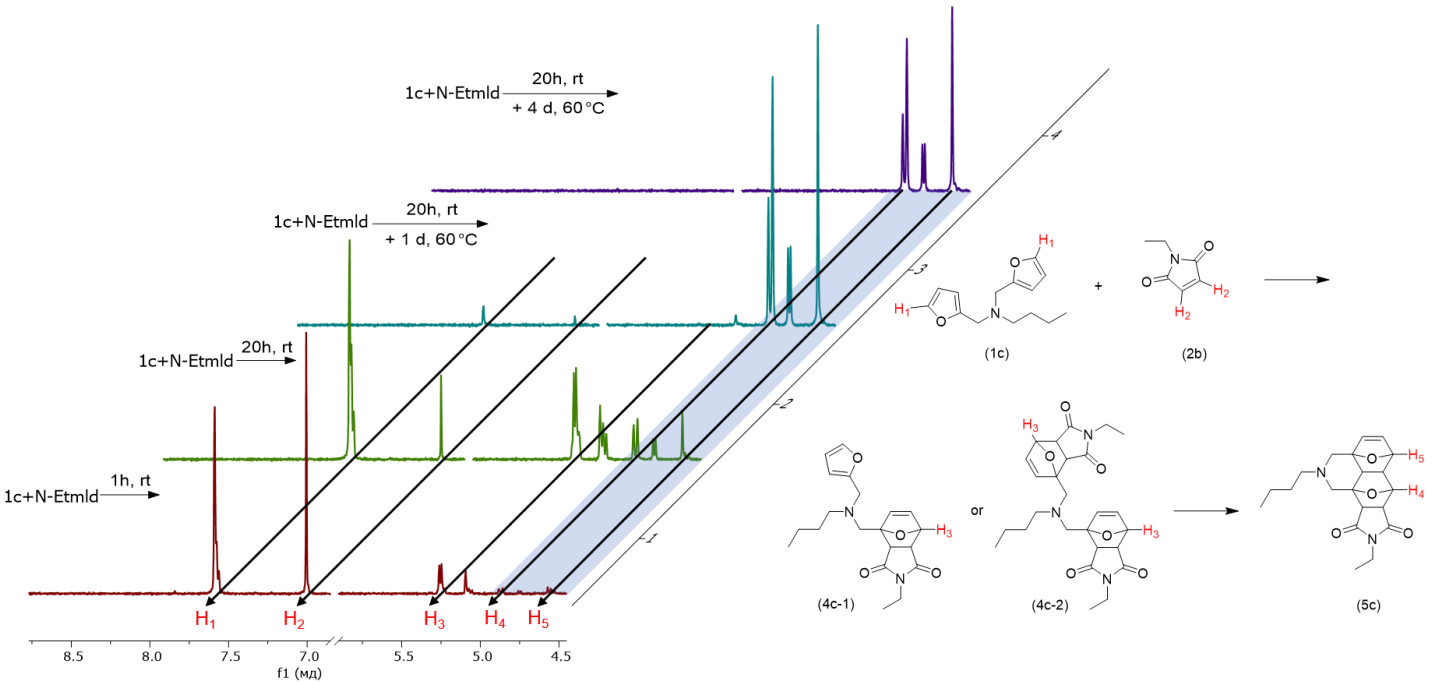


Figure S102. Monitoring of the direct DA reaction during the synthesis of the compound **5c** by ^{1}H-NMR spectroscopy. The initial compounds **1c** and N-ethylmaleimide were mixed in equivalent quantities, the reaction was carried out in the absence of a solvent. The reaction was carried out at room temperature and samples were taken to register ^{1}H-NMR spectrum after 1 and 20 hours. Then the reaction was carried out at 60°C for four days, samples were taken to register the ^{1}H-NMR spectrum 1 and 4 days after the start of the heating.

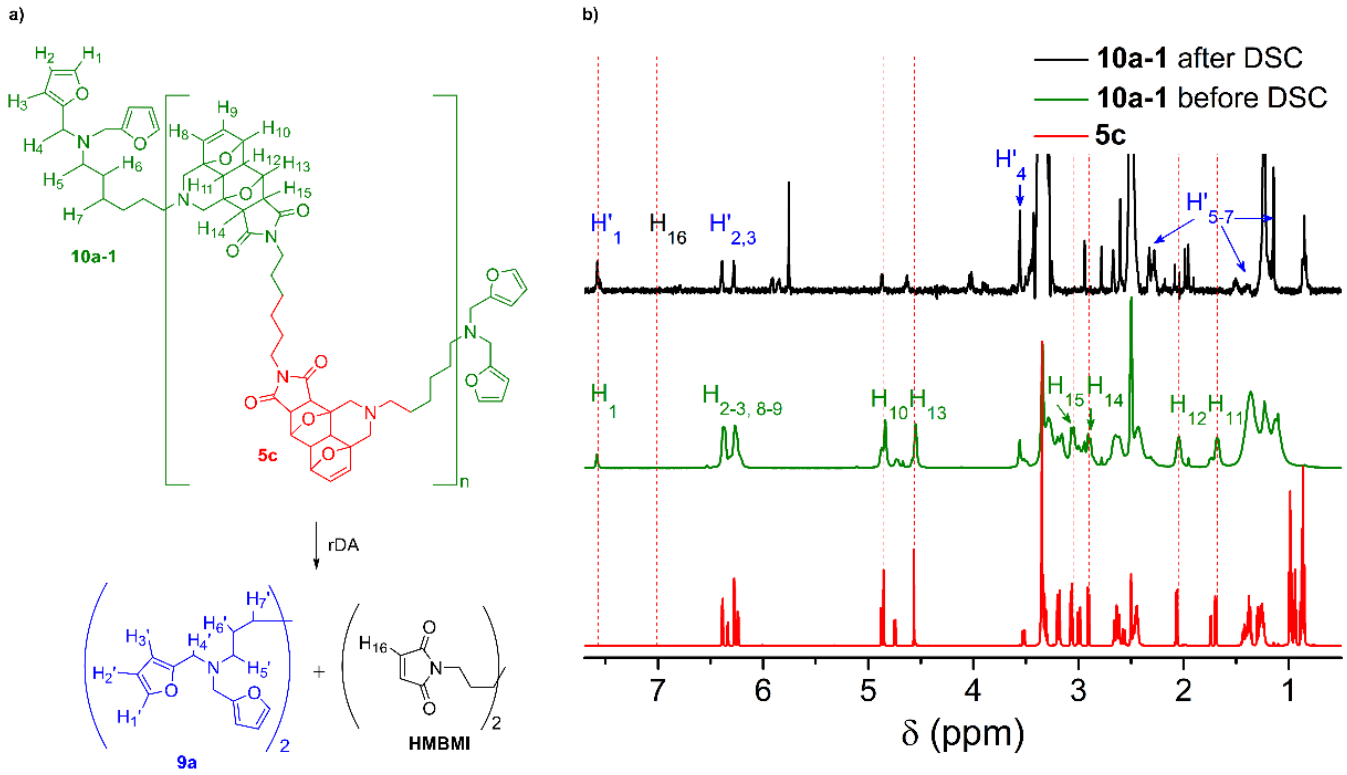


Figure S103. A) retro Diels-Alder reaction for the compound 10a-1; B) Comparison of ^{1}H-NMR spectrum of 10a-1 before and after DSC analysis and spectrum of the compound 5c.

12. GPC

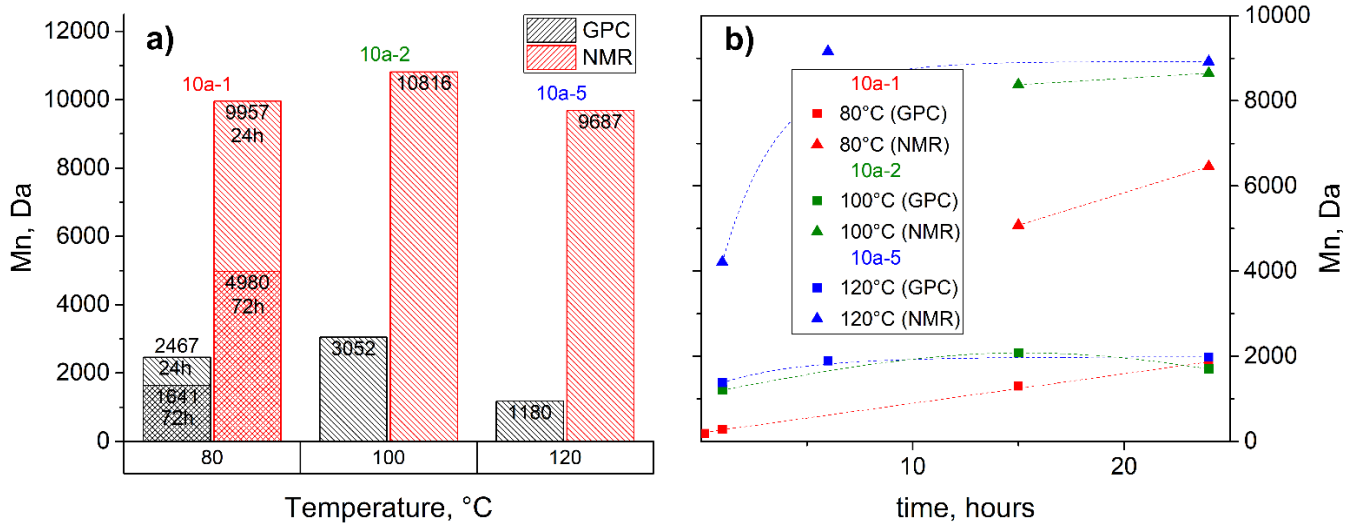


Figure S104. a): Comparison of GPC and NMR data for the powder samples **10a-1, 10a-2, 10a-5**; b) The kinetic data for the polymerization reaction of ptDA at different temperatures, obtained through GPC analysis and NMR spectroscopy, are presented in Table S7.

Table S7. The kinetic data for the polymerization reaction of ptDA at various temperatures, obtained through GPC analysis and NMR spectroscopy, provide information about the rate of reaction and the molecular weight distribution of the resulting polymer. These data are crucial for understanding the polymerization process and

optimizing reaction conditions. GPC analysis allows for the determination of the molecular weight distribution, while NMR spectroscopy provides insights into the chemical structure and composition of the polymer. By studying the kinetic data at different temperatures, researchers can gain valuable insights into the reaction mechanism and make informed decisions regarding reaction conditions and polymer properties.[a]

Sample	Reaction temperature, °C	Reaction time	GPC			M_n (^{1}H-NMR)[b]; CA : TA[c]	#
			M_n	M_w	M_w/M_n		
10a-1	80	10 min	183	286	1.6	ND	1
		1 h	283	685	2.4	**CA : TA** 1 : 1.8[b] **CA** 1 : 1.3 (endo : exo) **TA** 1 : 2.5 (exo-endo : exo-exo)	2
		15 h	1300	2805	2.2	5079 **TA** 1 : 4.4 (exo-endo : exo-exo)	3
		24 h	1833	4758	2.6	6457 **TA** 1 : 4.2 (exo-endo : exo-exo)	4
10a-2	100	10 min	ND	ND	ND	**CA : TA** 2 : 1[b] **CA** 1 : 1 (endo :exo)	5
		1 h	1209	2529	2.1	**CA : TA** 1 : 16[b] **TA** 1 : 5 (exo-endo : exo-exo)	6
		15 h	2080	4285	2.1	8381 **TA** 1 : 6.1 (exo-endo : exo-exo)	7
		24 h	1699	4601	2.7	8651	8
10a-5	120	1 h	1382	2978	2.2	4213	9
		6 h	1890	3977	2.1	9162	10
		24 h	1983	4310	2.2	8921 **TA** 1 : 6.8 (exo-endo : exo-exo)	11
10b-1	100	1 h	1759	2939	1.7	**CA : TA** 1 : 2.4[b] **CA** 1 : 1.7 (endo : exo) TA NC	12
		18 h	-	-	-	13560 **TA** 1 : 6.9 (exo-endo : exo-exo)	13
		24 h	2676	4486	1.7	13560 TA NC	14

[a] Kinetic studies were conducted on aliquots taken from the reaction mixture. b) Mn (number average molecular weight) was determined only for samples in which the reaction mixture consisted exclusively of tandem adducts of the DA reaction, based on 1H-NMR spectroscopy data. c) For samples in which the reaction mixture contained both classical and tandem adducts of the DA reaction, the ratio is provided in the table CA : TA.

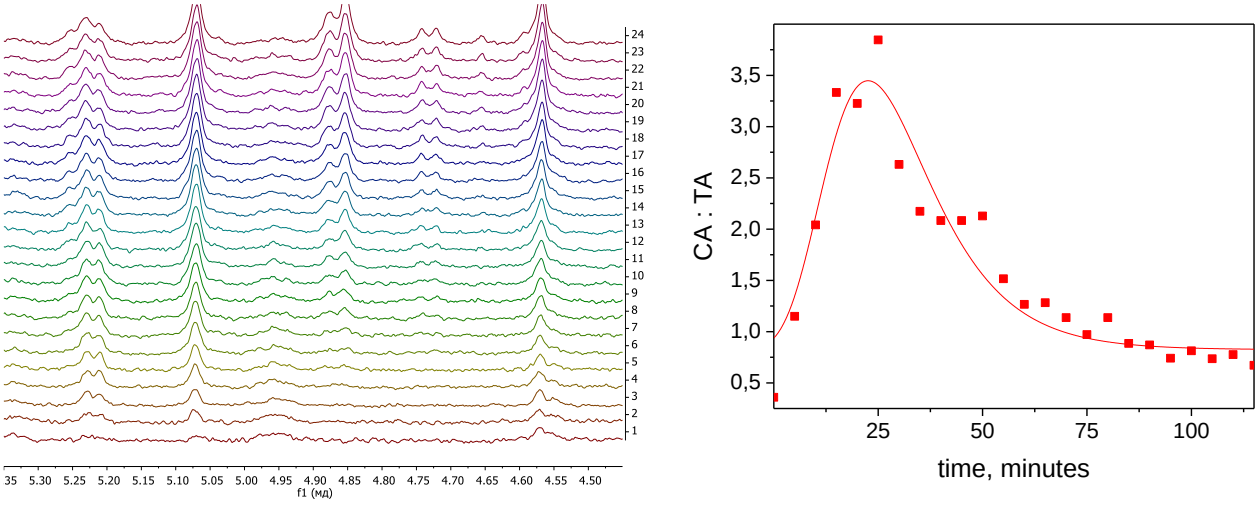


Figure S105. a) Kinetic data for the polymerization reaction of tDA **10a-1**. The characteristic region is 4.50-5.30 ppm, corresponding to classical and tandem adducts of DA. b) Distribution of the CA:TA ratio as a function of reaction time.

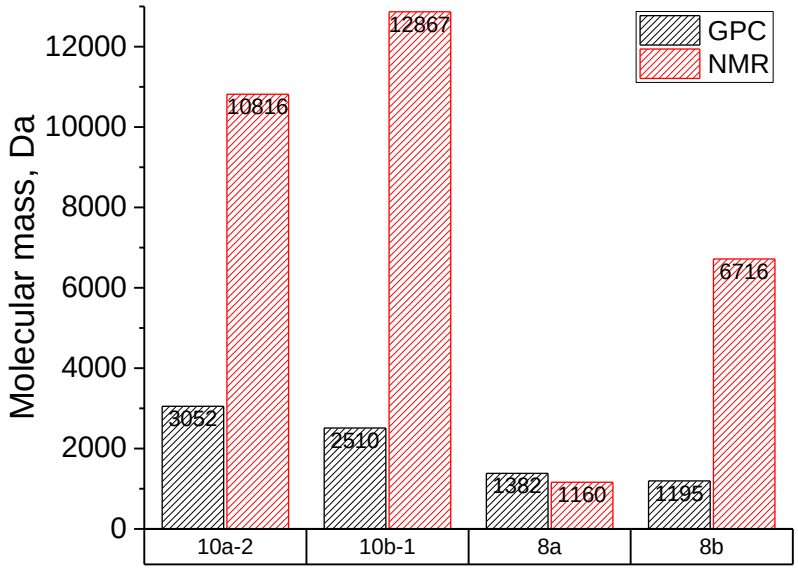
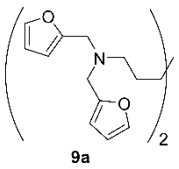
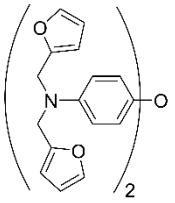
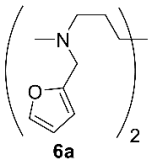
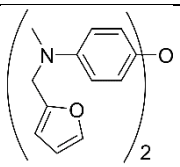


Figure S106. GPC and NMR analysis for the powder samples **10a-2, 10b-1, 8a, 8b**. For numerical data see Table S8.

Table S8. Numerical data from GPC and NMR spectroscopy were obtained for the samples **10a-2, 10b-1, 8a, 8b.**

Sample	Monomer	GPC			M_n (^{1}H-NMR)
		M_n	M_w	M_w/M_n	

10a-2	 9a	3052	8102	2.7	10816
10b-1	 9b	2510	3536	1.4	12867
8a	 6a	1382	2358	1.7	1160
8b	 6b	1995	4375	2.2	6716

13. References

1. Tsedilin AM, Fakhrutdinov AN, Eremin DB, Zalesskiy SS, Chizhov AO, Kolotyrkina NG, et al. How sensitive and accurate are routine NMR and MS measurements? Mendeleev Communications. 2015;25(6):454-6.
2. Adamo C, Barone V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. The Journal of chemical physics. 1999;110(13):6158-70.
3. Weigend F, Ahlrichs R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. Physical Chemistry Chemical Physics. 2005;7(18):3297-305.
4. Neese F. The ORCA program system. Wiley Interdisciplinary Reviews: Computational Molecular Science. 2012;2(1):73-8.
5. Neese F. Software update: the ORCA program system, version 4.0. Wiley Interdisciplinary Reviews: Computational Molecular Science. 2018;8(1):e1327.
6. Liakos DG, Sparta M, Kesharwani MK, Martin JML, Neese F. Exploring the accuracy limits of local pair natural orbital coupled-cluster theory. Journal of chemical theory and computation. 2015;11(4):1525-39.
7. Neese F. An improvement of the resolution of the identity approximation for the formation of the Coulomb matrix. Journal of computational chemistry. 2003;24(14):1740-7.
8. Neese F, Wennmohs F, Hansen A, Becker U. Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree–Fock exchange. Chemical Physics. 2009;356(1-3):98-109.
9. Dutta AK, Neese F, Izsák R. Speeding up equation of motion coupled cluster theory with the chain of spheres approximation. The Journal of chemical physics. 2016;144(3).
10. Weigend F. Accurate Coulomb-fitting basis sets for H to Rn. Physical chemistry chemical physics. 2006;8(9):1057-65.
11. Zanetti JE, Bashour JT. α-Furfurylpropylamine and Di-α-furfuryl Tertiary Amines. Journal of the American Chemical Society. 1940;62(4):742-3.
12. Lin C, Zhou J, Zheng Z, Chen J. An efficient approach to biomass-based tertiary amines by direct and consecutive reductive amination of furfural. Journal of Catalysis. 2022;410:164-79.

13. Bernardo JR, Sousa SCA, Florindo PR, Wolff M, Machura B, Fernandes AC. Efficient and chemoselective direct reductive amination of aromatic aldehydes catalyzed by oxo–rhenium complexes containing heterocyclic ligands. Tetrahedron. 2013;69(43):9145-54.
14. Sun R, Xiao L, Wu W. In-situ carbon-encapsulated Ni2P@ C catalysts for reductive amination of furfural. Molecular Catalysis. 2024;553:113710.
15. Hammami A, Rabti A, Raouafi N. A novel electrochemical and chromogenic guest-responsive anisidine-based chemosensor for transition metallic cations. Journal of Electroanalytical Chemistry. 2014;731:179-83.
16. Lautens M, Fillion E. An expedient route for the stereoselective construction of bridged polyheterocyclic ring systems using the tandem "pincer" Diels− Alder reaction. The Journal of Organic Chemistry. 1997;62(13):4418-27.
17. Le Pera A, Leggio A, Liguori A. Highly specific N-monomethylation of primary aromatic amines. Tetrahedron. 2006;62(25):6100-6.
18. Jia L, Wang X, Gao X, Makha M, Wang X-C, Li Y. Tunable synthesis of furfurylamines or β-amino alcohols via Ru-catalyzed N–H functionalization using biomass-derived polyols. Green Synthesis and Catalysis. 2022;3(3):259-64.
19. Ponomarev AA. Syntheses and reactions of furan derivatives, 1960.
20. Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H. _journal_name_full'American Mineralogist'_journal_year 2021 _journal_volume 106 _journal_page_first 1844 _journal_paper_doi 10.2138/am-2021-7785. J Appl Cryst. 2009;42:339-41.
21. Sheldrick GM. SHELXT–Integrated space-group and crystal-structure determination. Acta Crystallographica Section A: Foundations and Advances. 2015;71(1):3-8.
22. Sheldrick GM. A short history of SHELX. Acta Crystallographica Section A: Foundations of Crystallography. 2008;64(1):112-22.