Sulfur-Mediated Synthesis of Unsymmetrically Substituted *N*-Aryl Oxalamides by the Cascade Thioamidation/Cyclocondensation and Hydrolysis Reaction

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Table S1. X-ray crystallographic data and refinement details for studied molecules

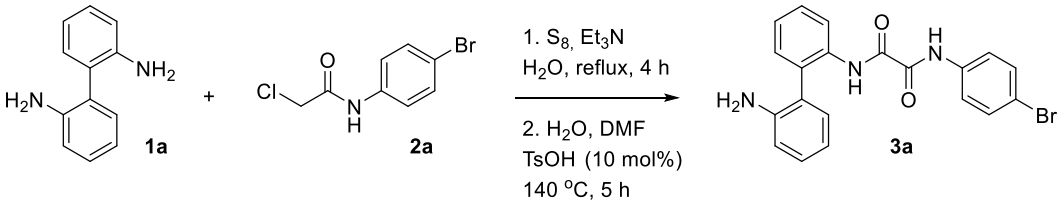
	3b	**3c**
CCDC number	1942001	1941999
Empirical formula	$C_{22}H_{19}ClN_3O_3S$	$C_{20}H_{16}ClN_3O_2$
Formula weight	440.91	365.81
T, K	120	120
Crystal system	Monoclinc	Monoclinc
Space group	C2/c	$P2_1/c$
Z (Z')	8 (1)	4(1)
a, Å	35.957(3)	12.174(2)
b, Å	6.1171(5)	12.709(3)
c, Å	19.5083(15)	12.335(3)
α, °	90	90
β, °	96.604(2)	117.06(3)
γ, °	90	90
V, $Å^3$	4262.5(6)	1699.6(7)
d_{calc},gcm^{-3}	1.374	1.430
μ, cm^{-1}	3.06	2.45
F(000)	1832	760
$2\theta_{max}$, °	58	58
Reflections collected	24783	14513
Reflections unique (R_{int})	5675 (0.0280)	4465 (0.0232)
Reflections with I > 2σ(I)	4770	3927
Variables/restraints	229/139	251/0
R1	0.0668	0.0353
wR2	0.2045	0.0943
GOF	1.059	1.034
Largest difference in peak / hole ($e/Å^3$)	1.034/-0.807	0.373/-0.401

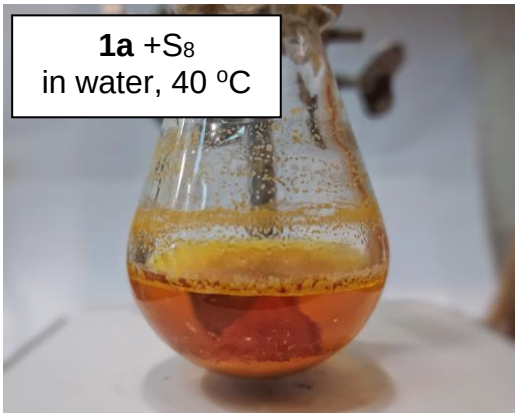
X-ray diffraction data for all studied compounds were collected using a SMART APEX II area-detector diffractometer (graphite monochromator, ω-scan technique) at the temperature of 120(2)K, using $Mo_{K\alpha}$radiation (0.71073 Å). The intensity data were integrated by the SAINT program and corrected for absorption and decay by the multi-scan method (semi-empirical from

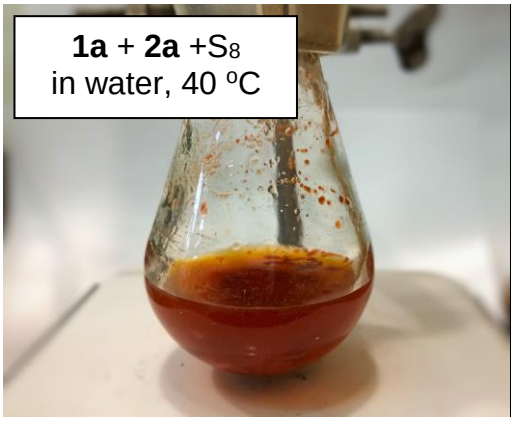
equivalents) implemented in SADABS.[1] All structures were solved by direct methods using SHELXS[2] and were refined against F^2 using SHELXL-2017.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-H hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters taken as $U_{iso}(H)=1.5U_{eq}(C)$ for methyl H atoms and $U_{iso}(H)=1.2U_{eq}(C)$ otherwise. Crystal data, data collection and structure refinement details are summarized in Table S1.

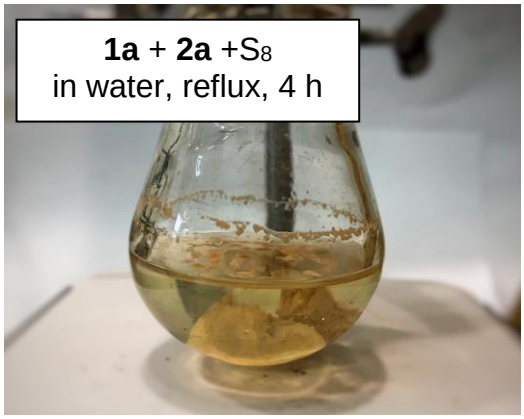
(1) *Bruker*. *APEXII*, Bruker AXS Inc.: Madison, Wisconsin, USA, 2008.
(2) Sheldrick, G. M. A short history of SHELX. *Acta Cryst., Sect. A* **2008**, *A64*, 112-122.
(3) Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3-8.

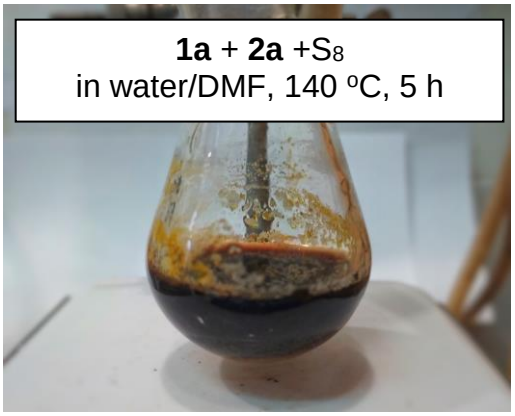
Pictures of experiments



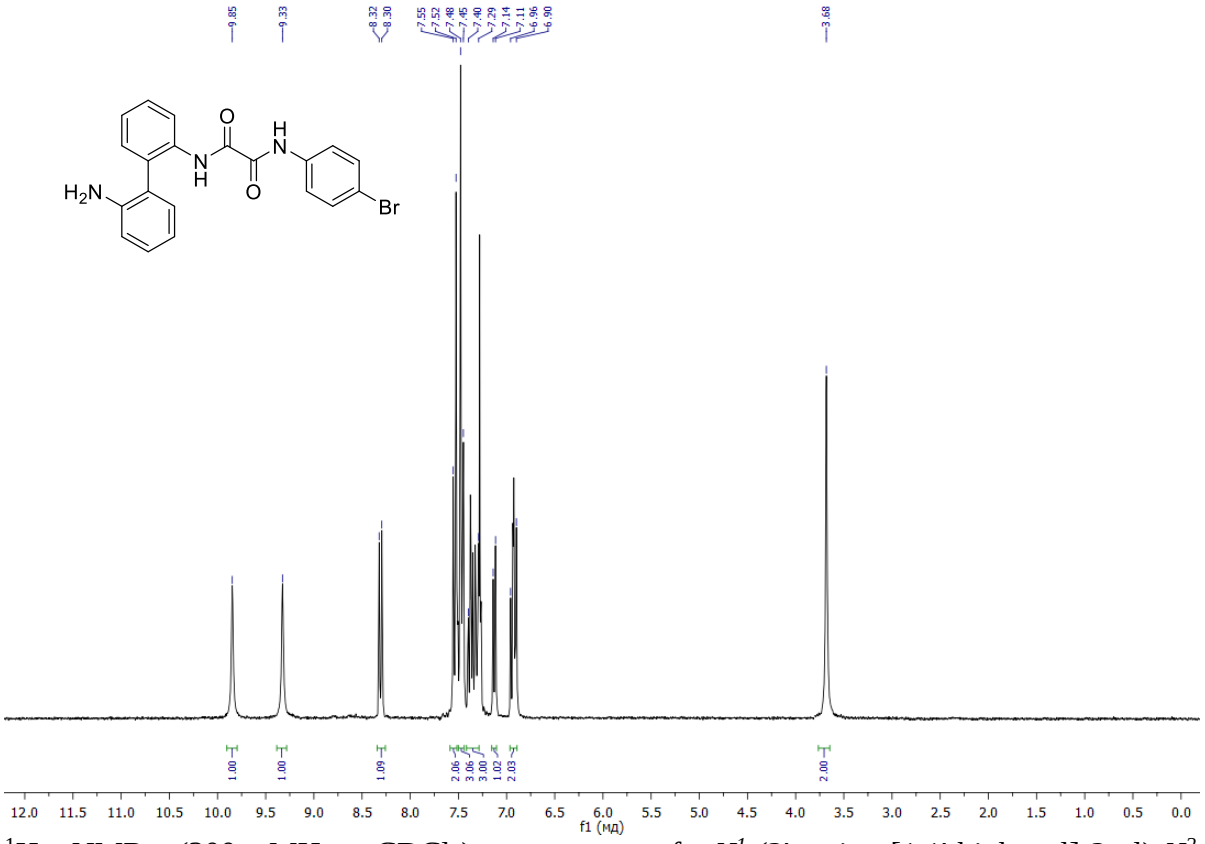




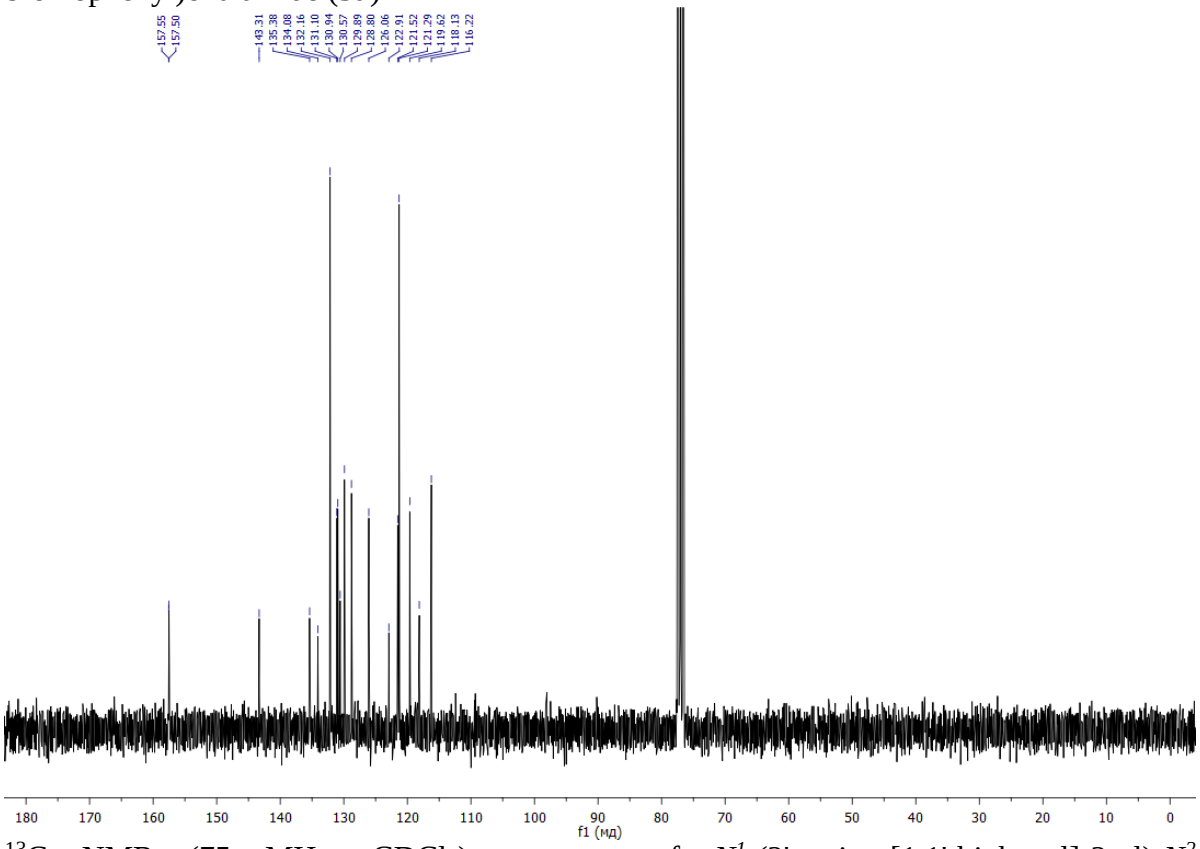




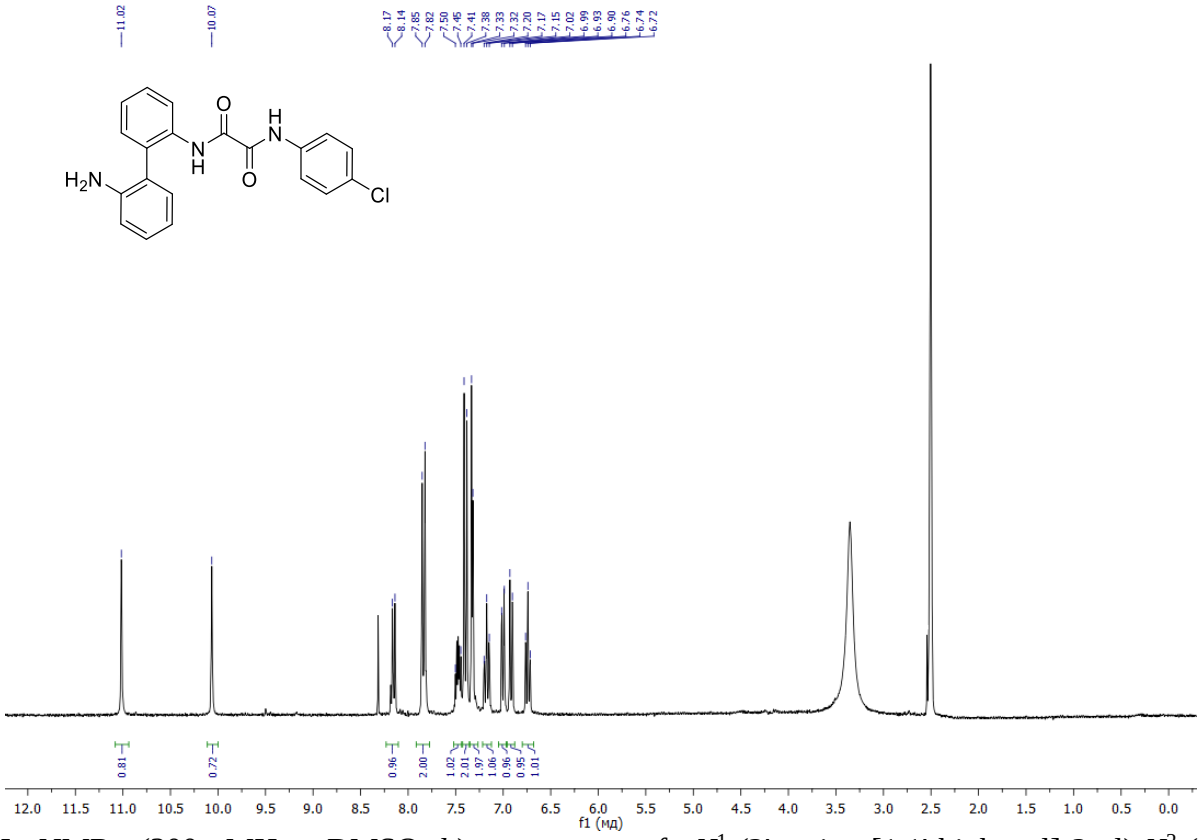
Copies of $^{1}H,^{13}C$ NMR Spectra



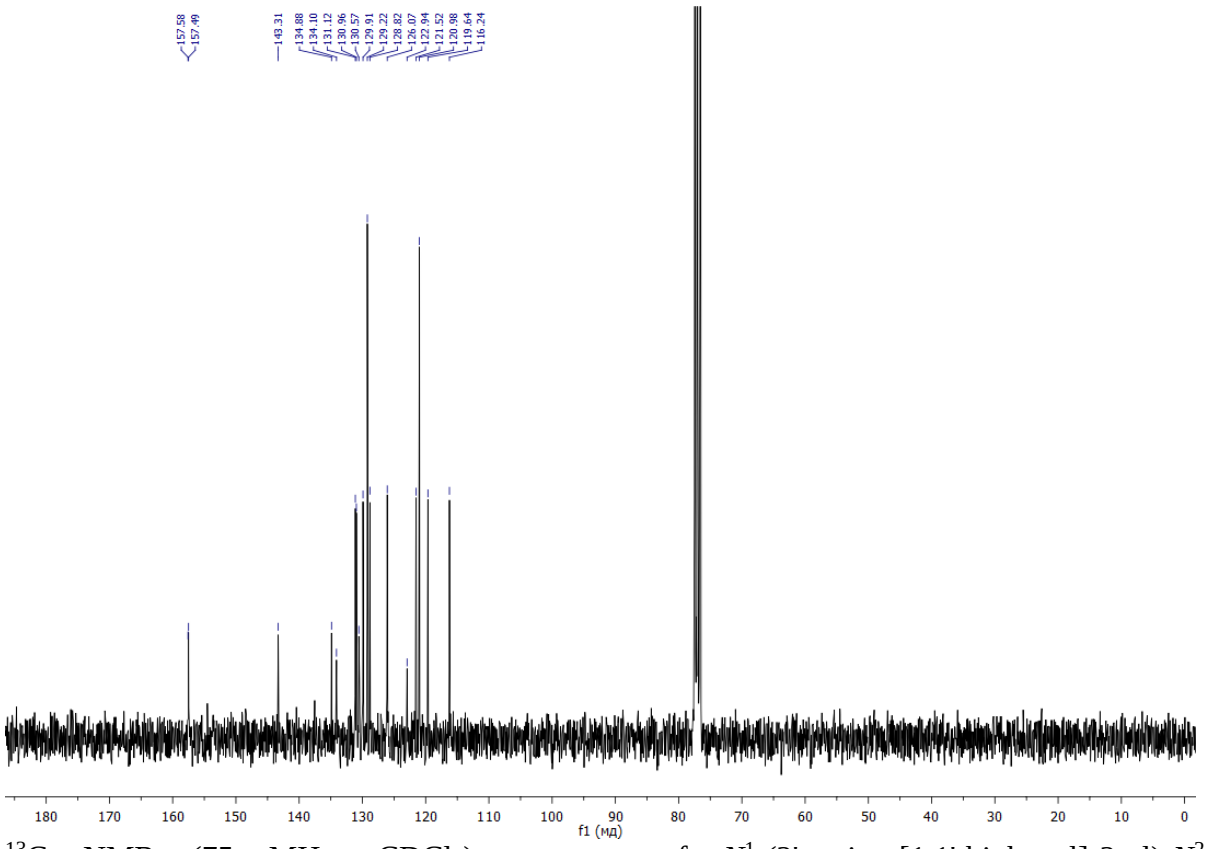
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(4-bromophenyl)oxalamide (**3a**)



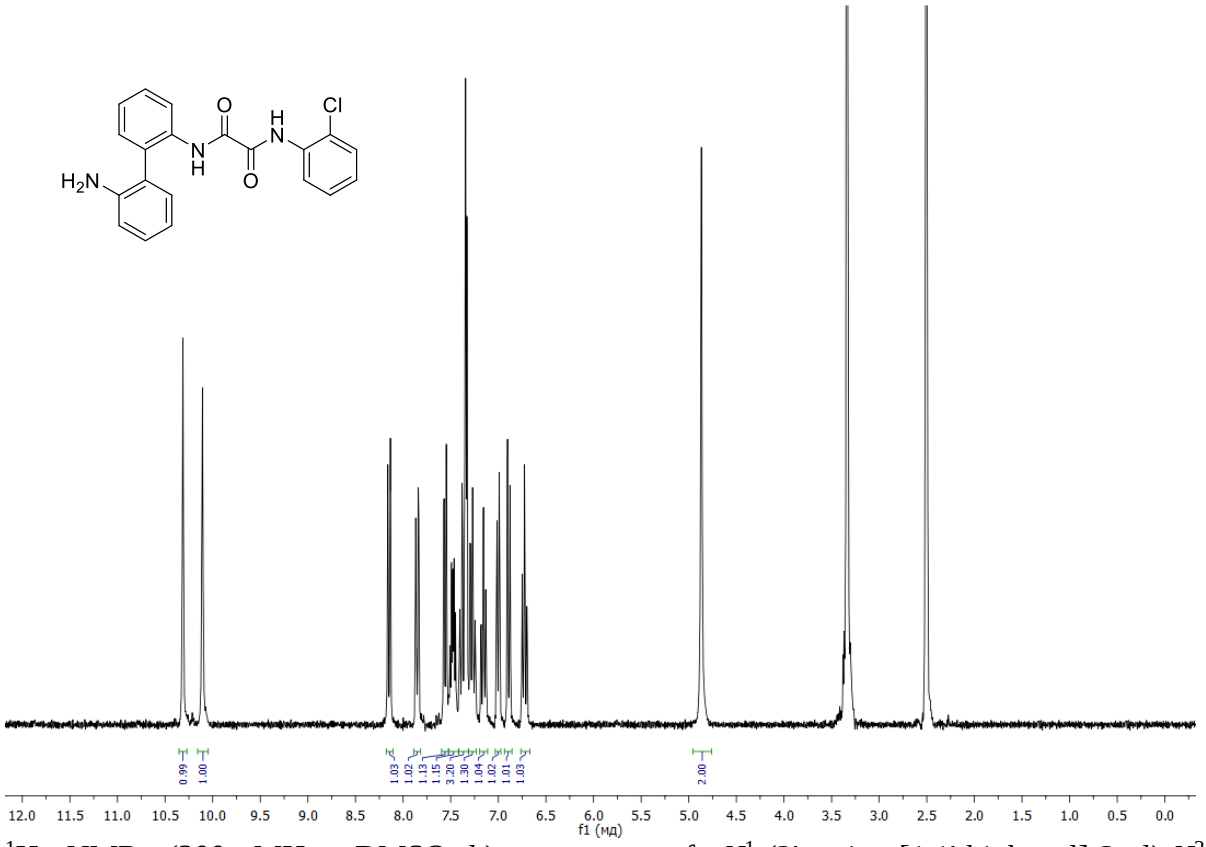
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(4-bromophenyl)oxalamide (**3a**)



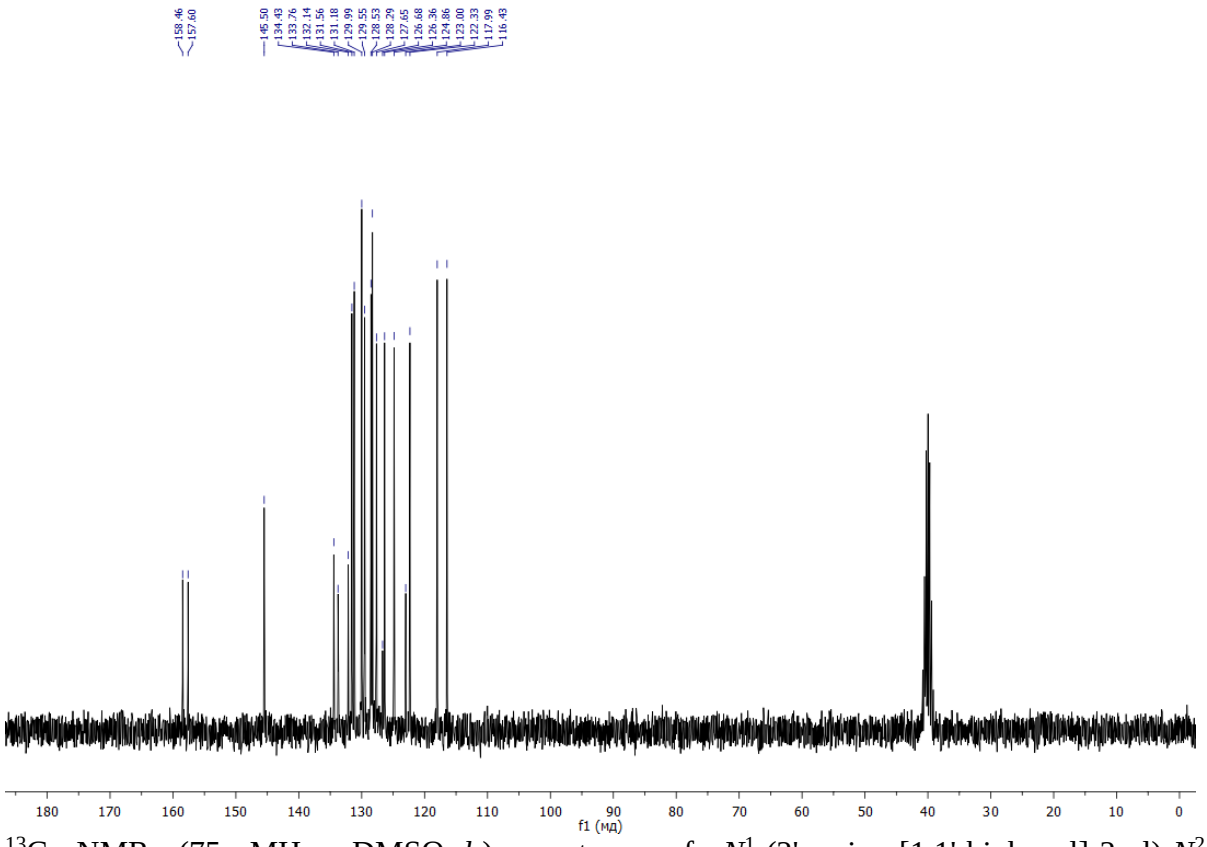
^{1}H NMR (300 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(4-chlorophenyl)oxalamide (**3b**)



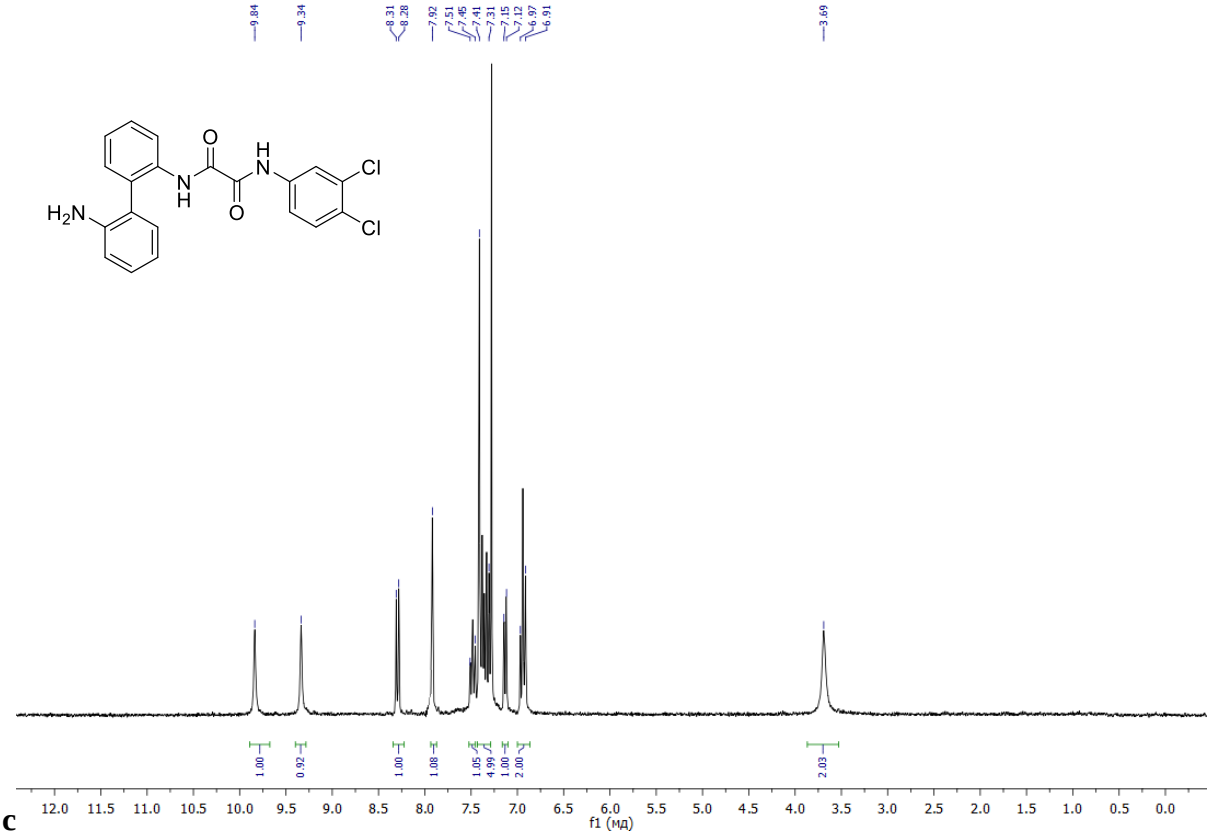
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(4-chlorophenyl)oxalamide (**3b**)



^{1}H NMR (300 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(2-chlorophenyl)oxalamide (**3c**)

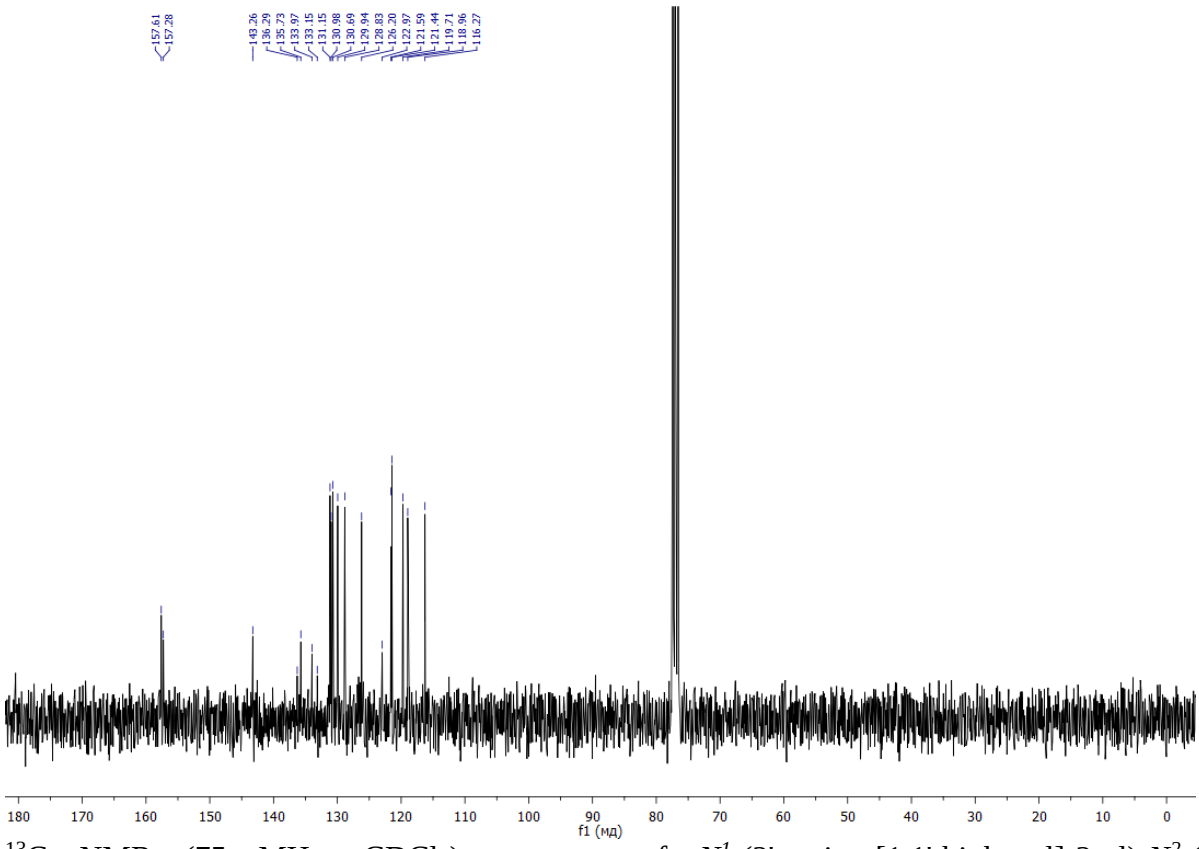


^{13}C NMR (75 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(2-chlorophenyl)oxalamide (**3c**)

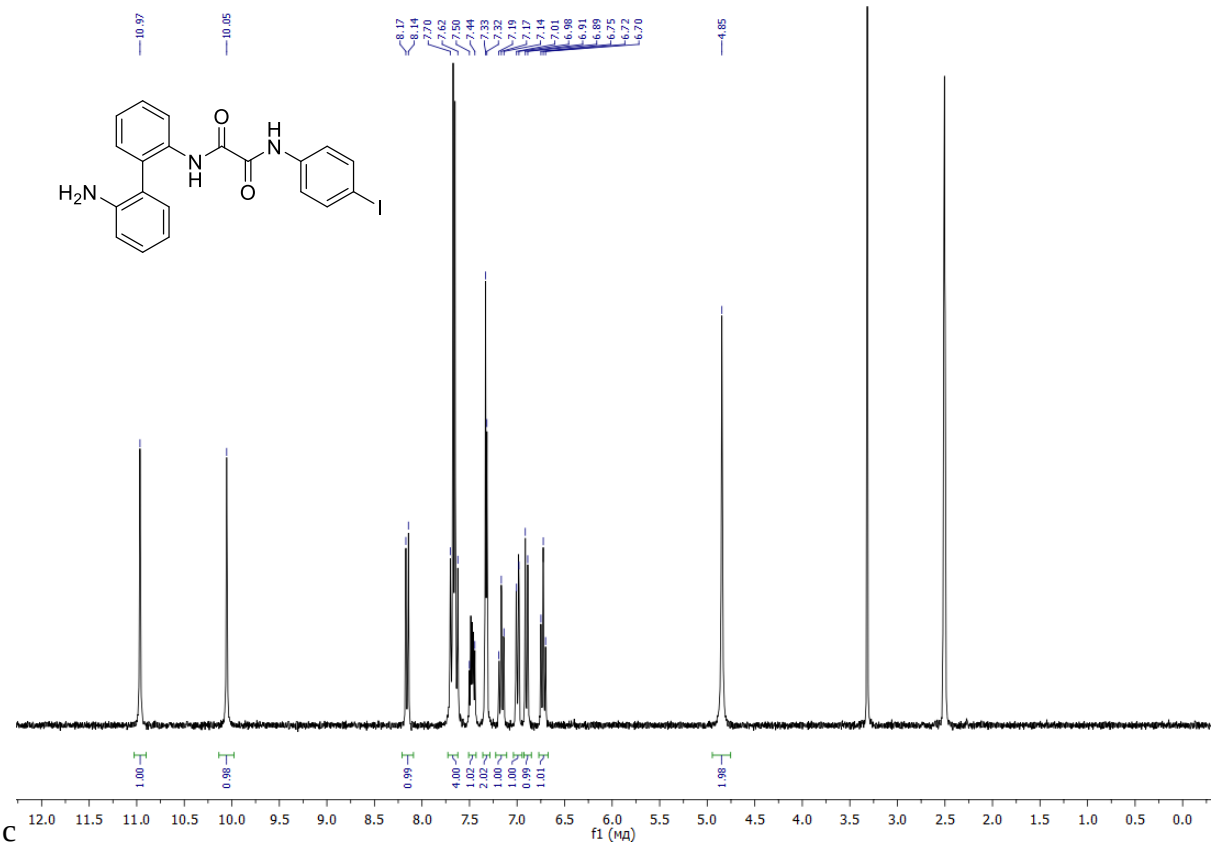


c

^{1}H NMR (300 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(3,4-dichlorophenyl)oxalamide (**3d**)

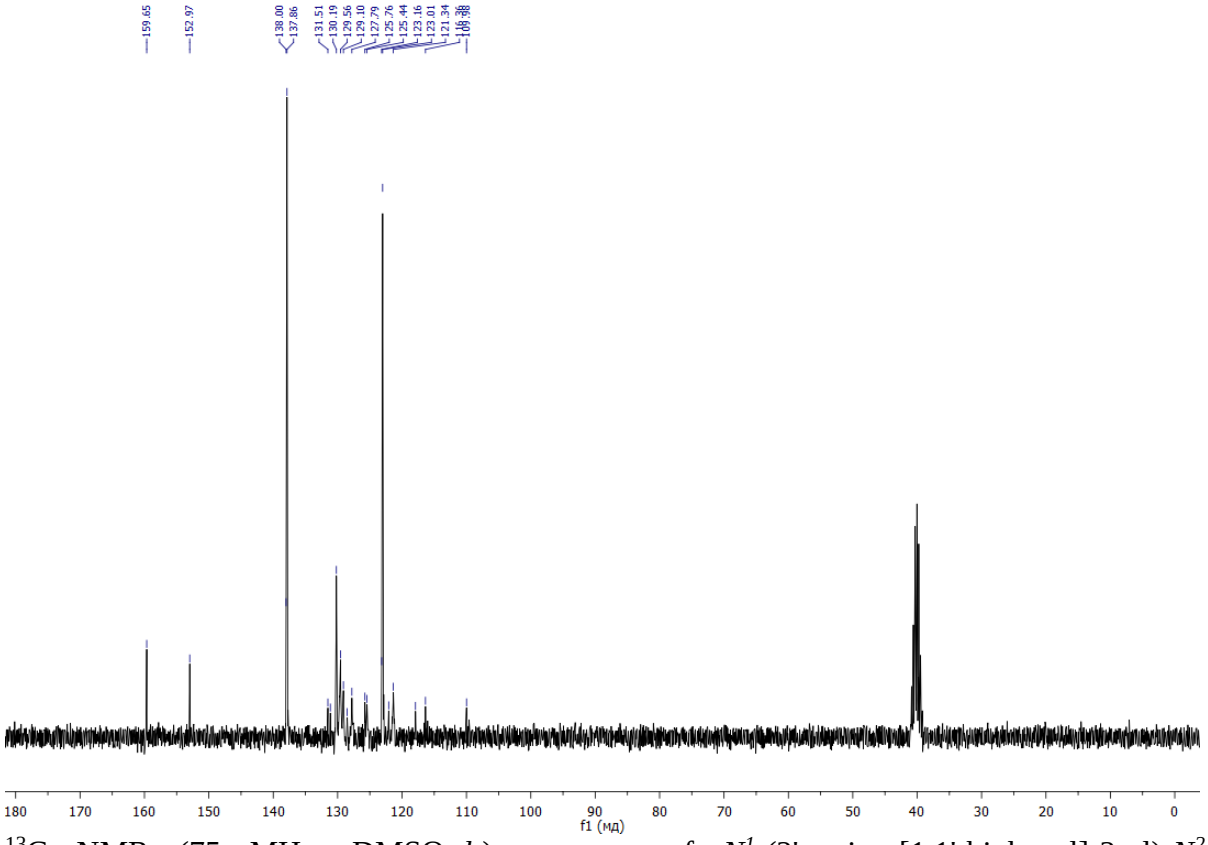


^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(3,4-dichlorophenyl)oxalamide (**3d**)

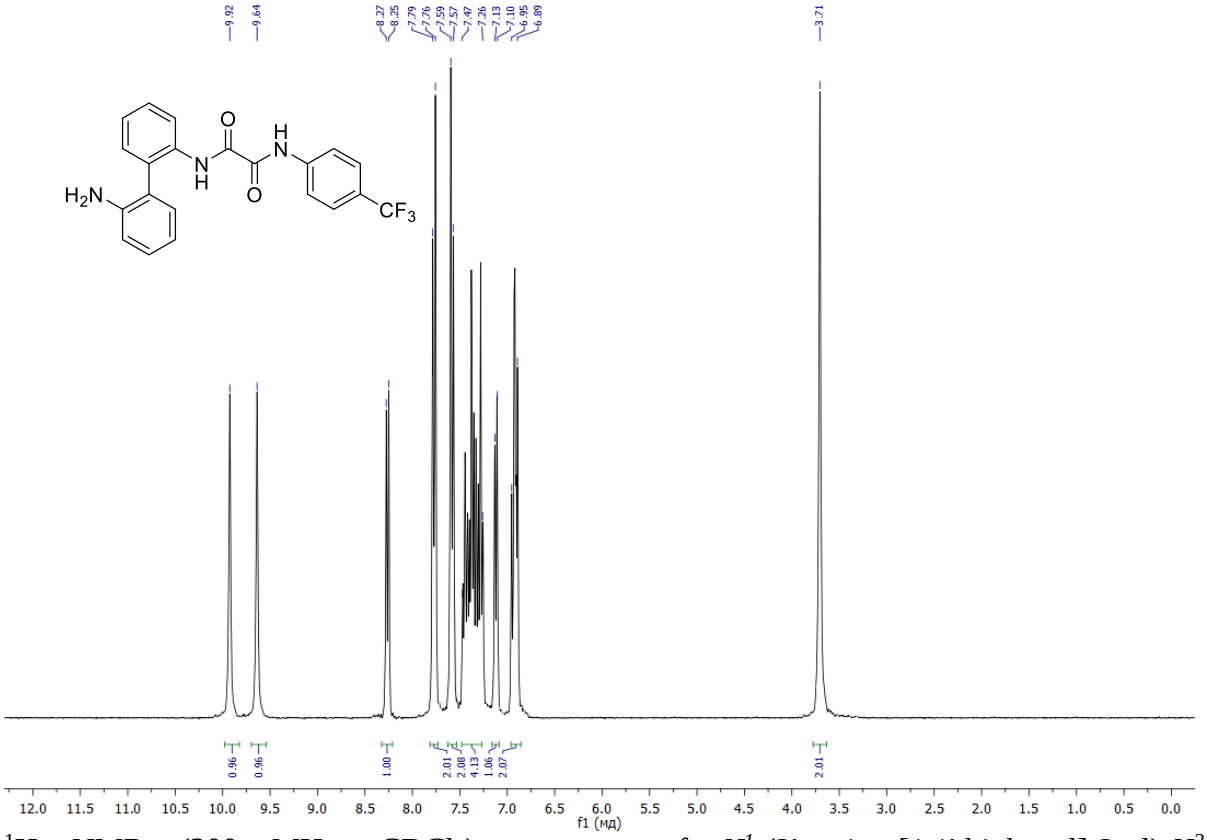


c

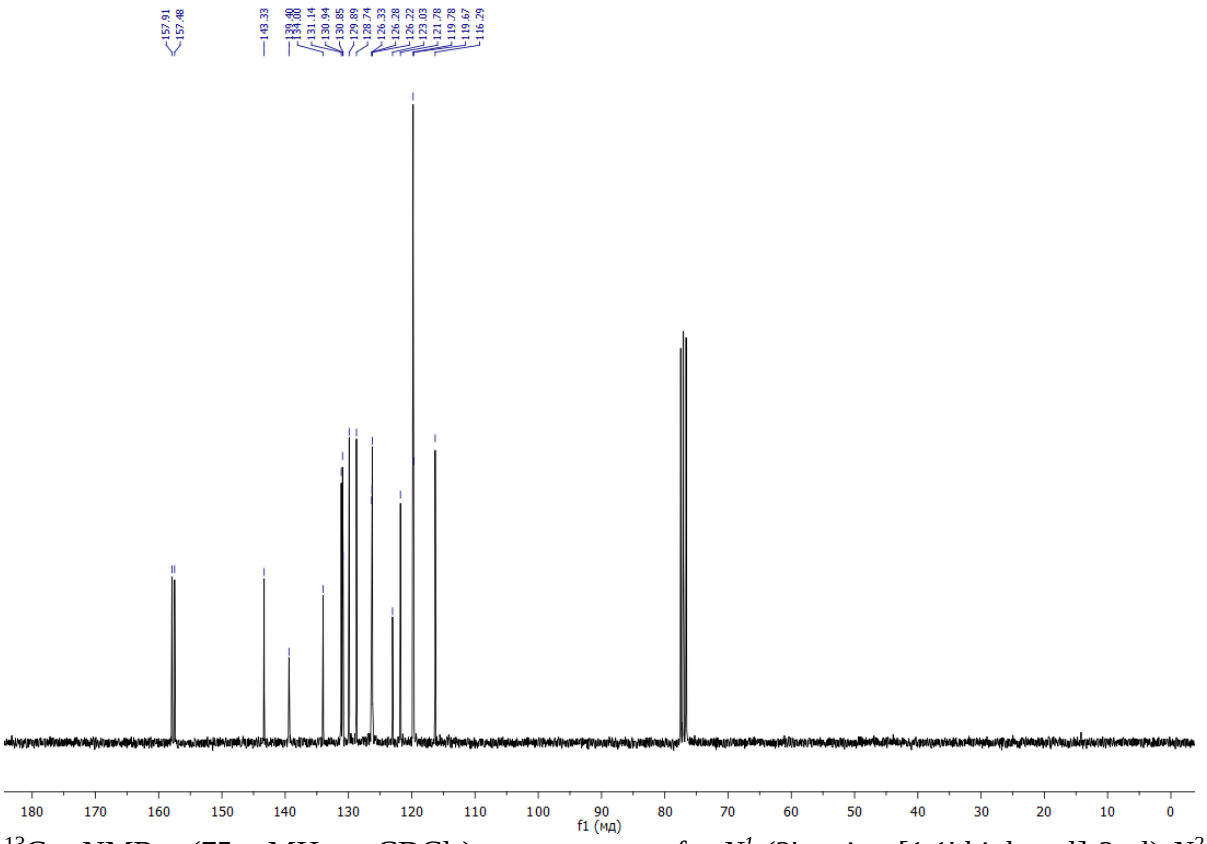
^{1}H NMR (300 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(4-iodophenyl)oxalamide (**3e**)



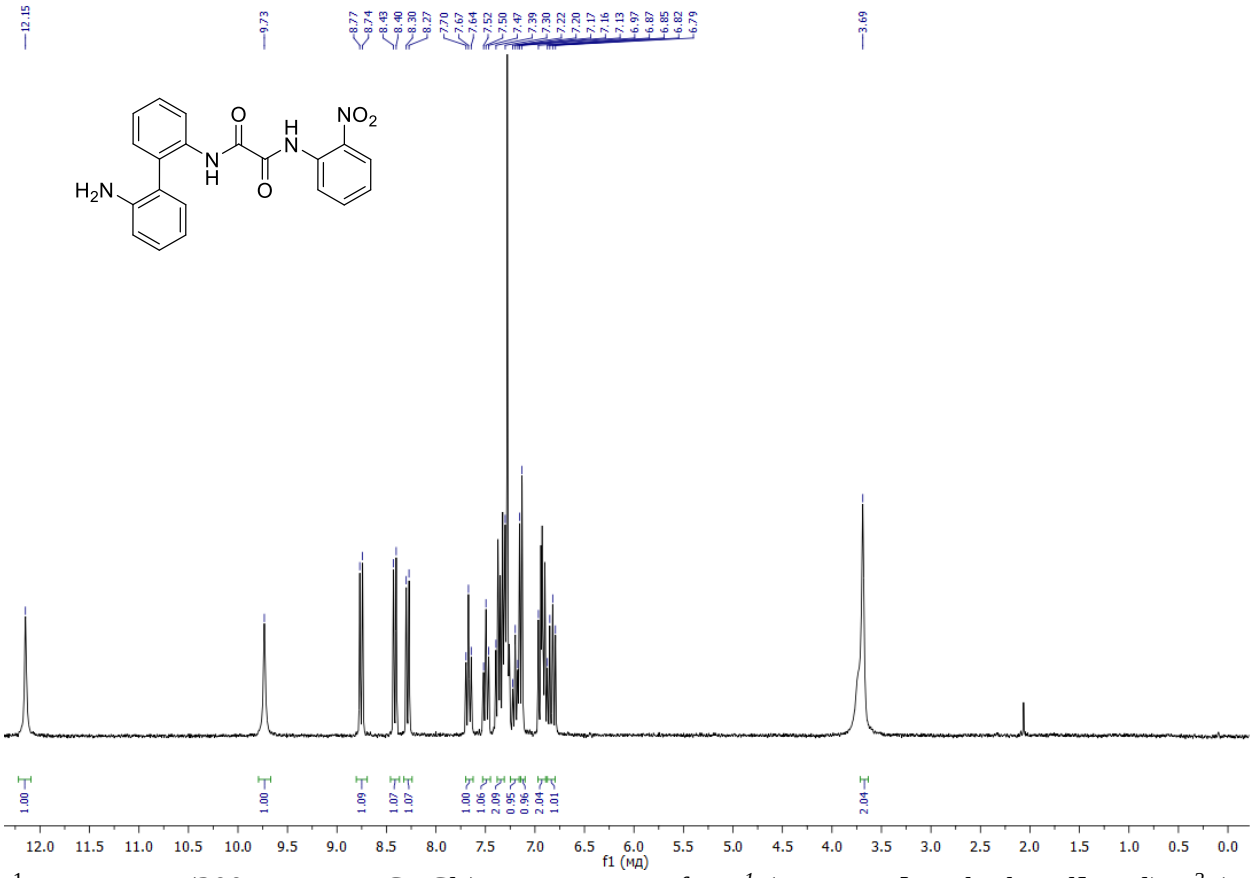
^{13}C NMR (75 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(4-iodophenyl)oxalamide (**3e**)



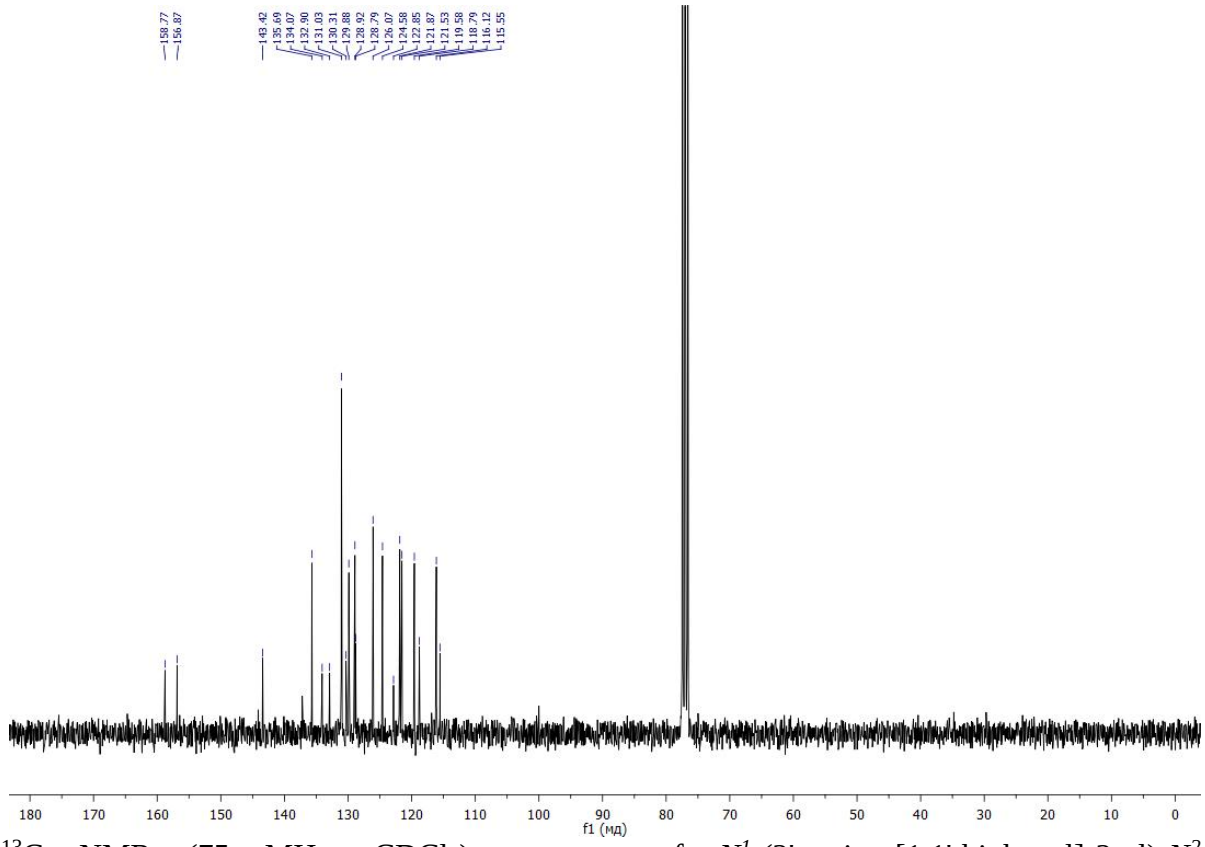
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(4-(trifluoromethyl)phenyl)oxalamide (**3f**)



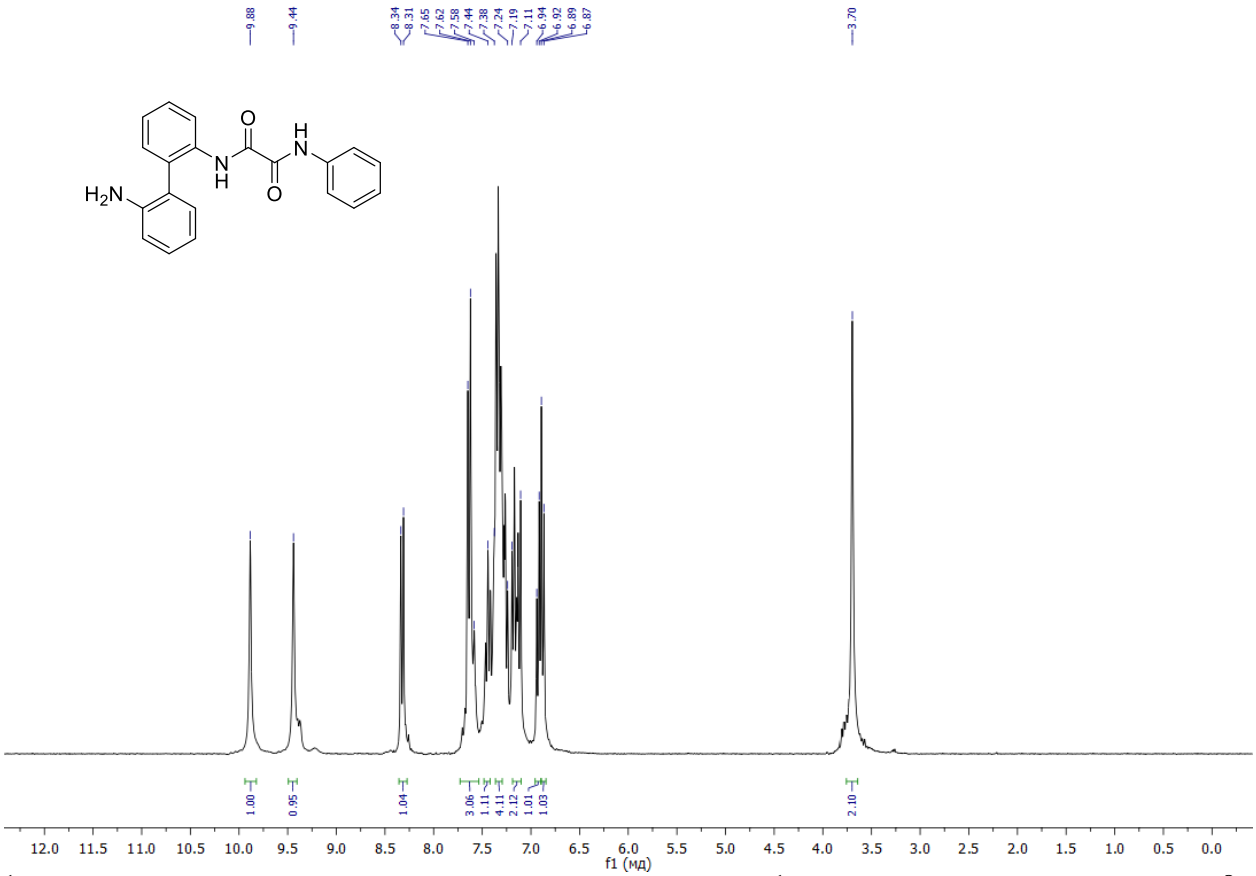
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(4-(trifluoromethyl)phenyl)oxalamide (**3f**)



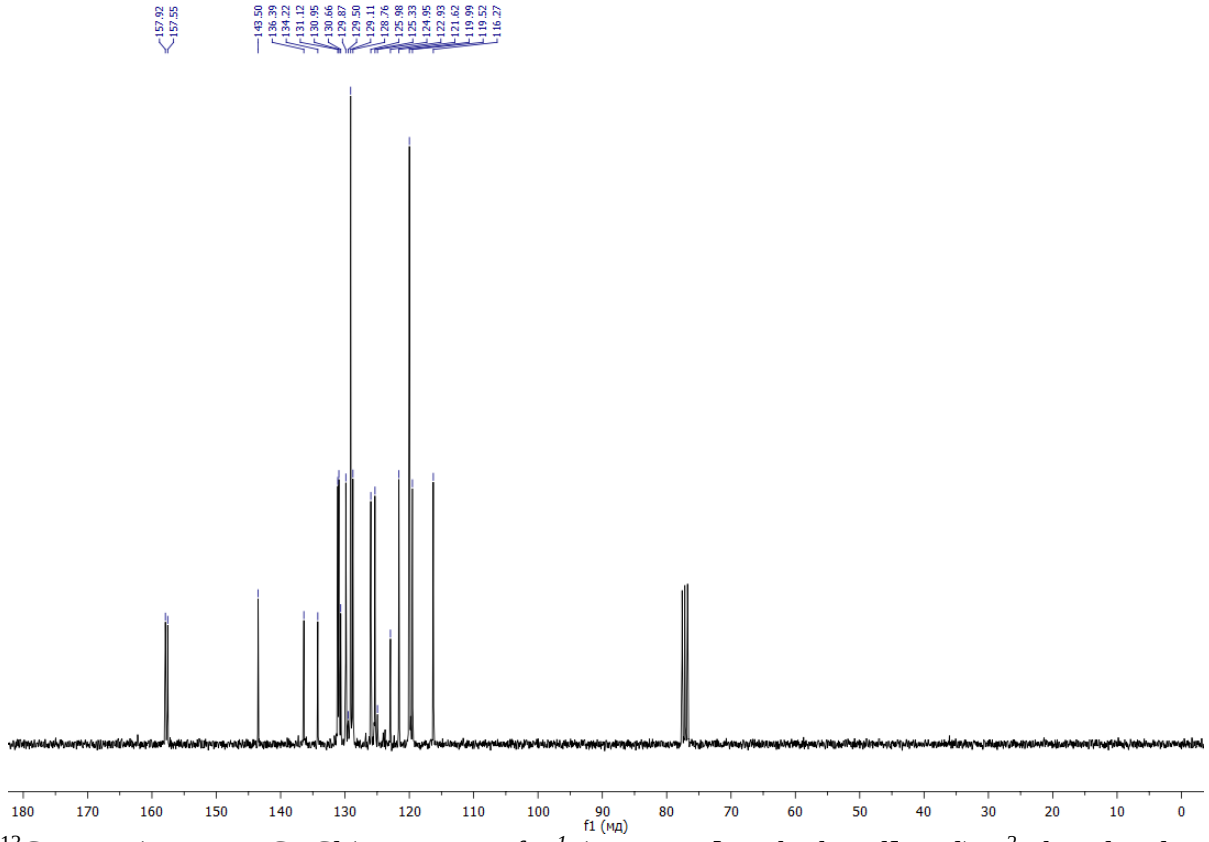
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(2-nitrophenyl)oxalamide (**3g**)



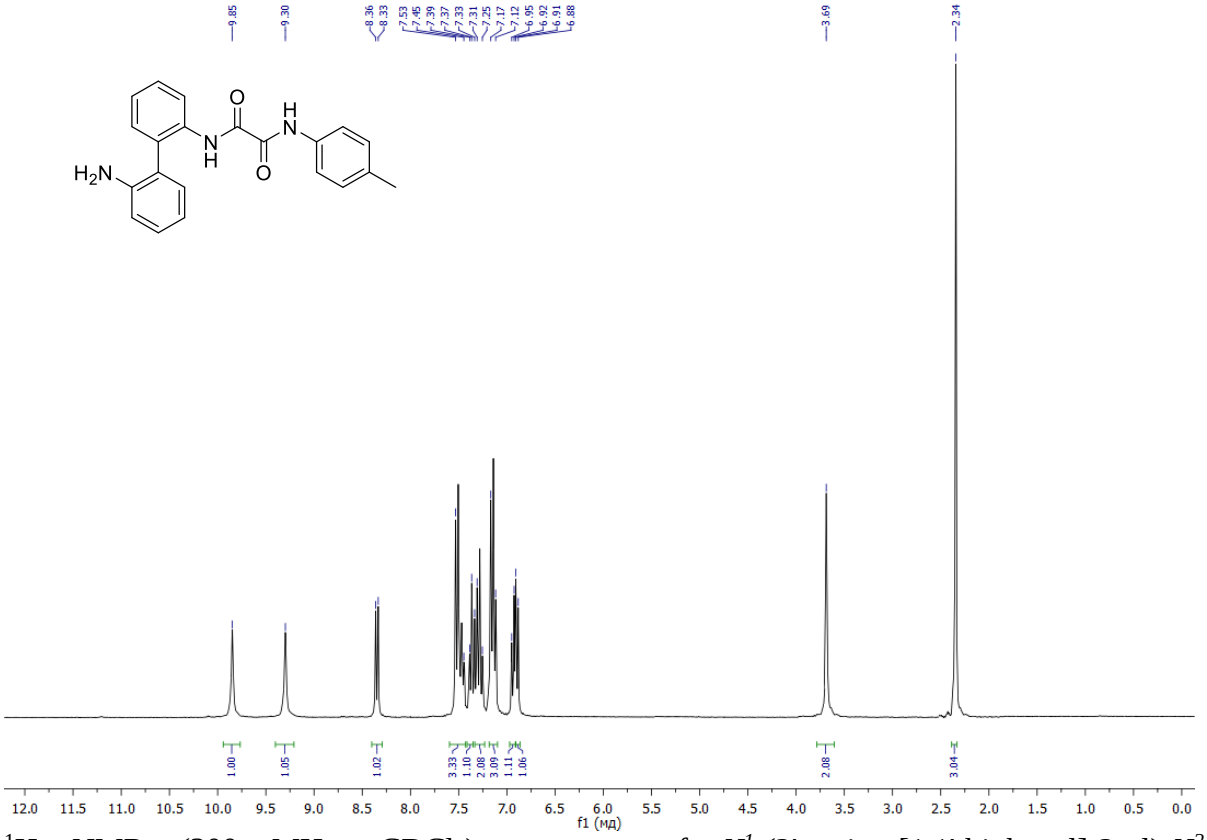
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(2-nitrophenyl)oxalamide (**3g**)



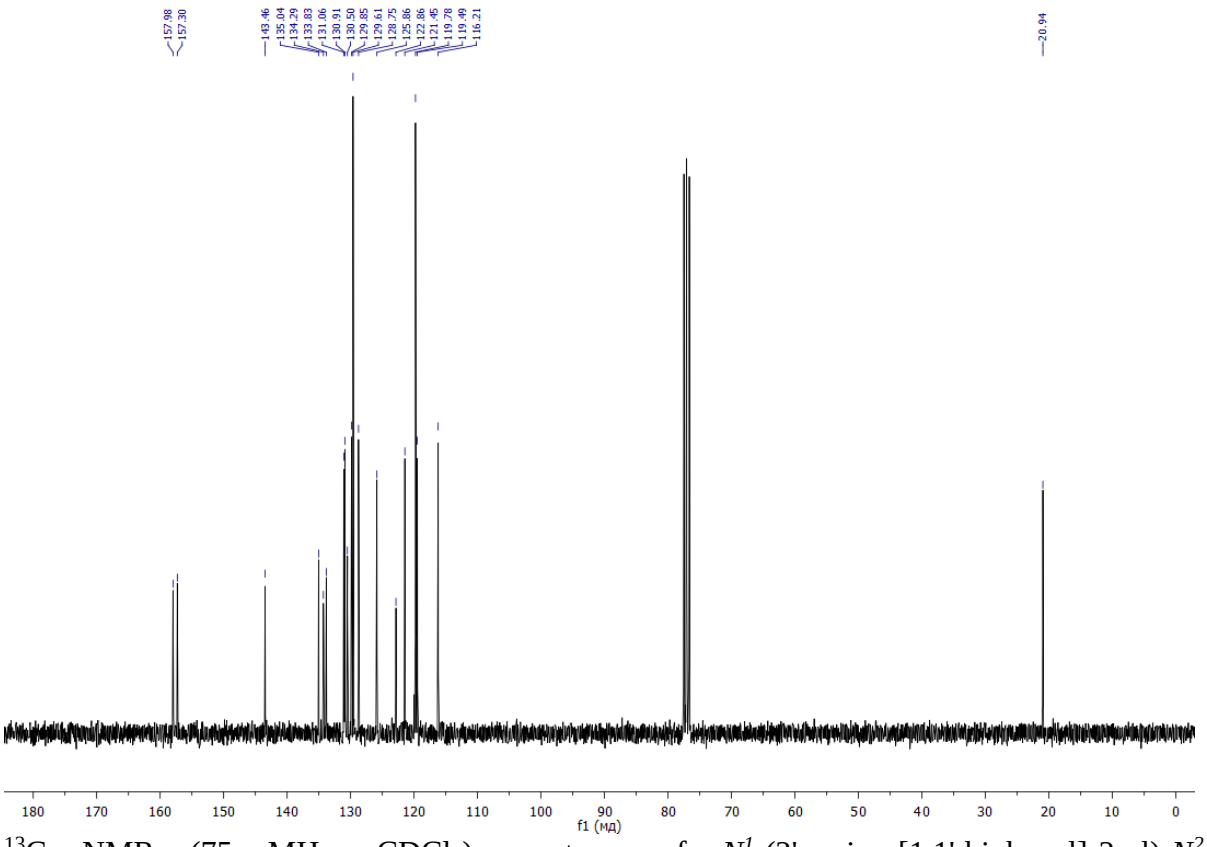
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of *N*^{1}-(2'-amino-[1,1'-biphenyl]-2-yl)-*N*^{2}-phenyloxalamide (**3h**)



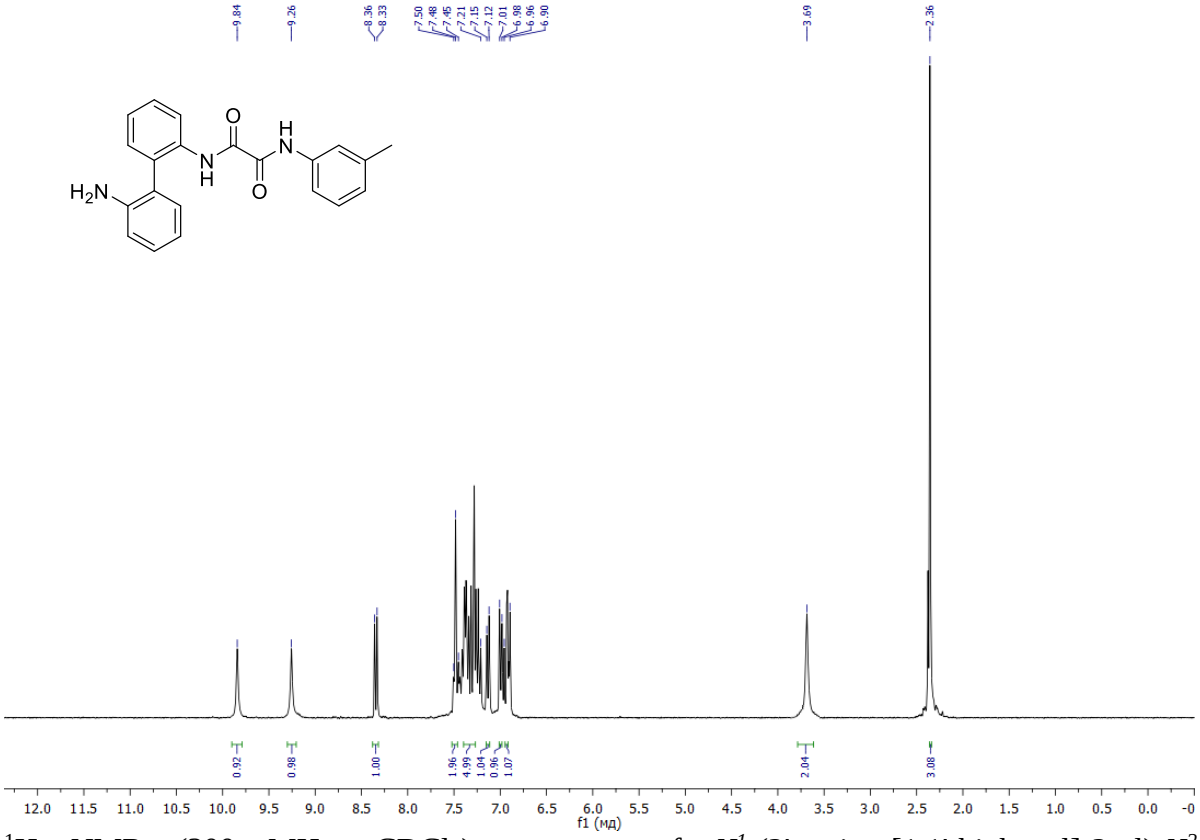
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of *N*^{1}-(2'-amino-[1,1'-biphenyl]-2-yl)-*N*^{2}-phenyloxalamide (**3h**)



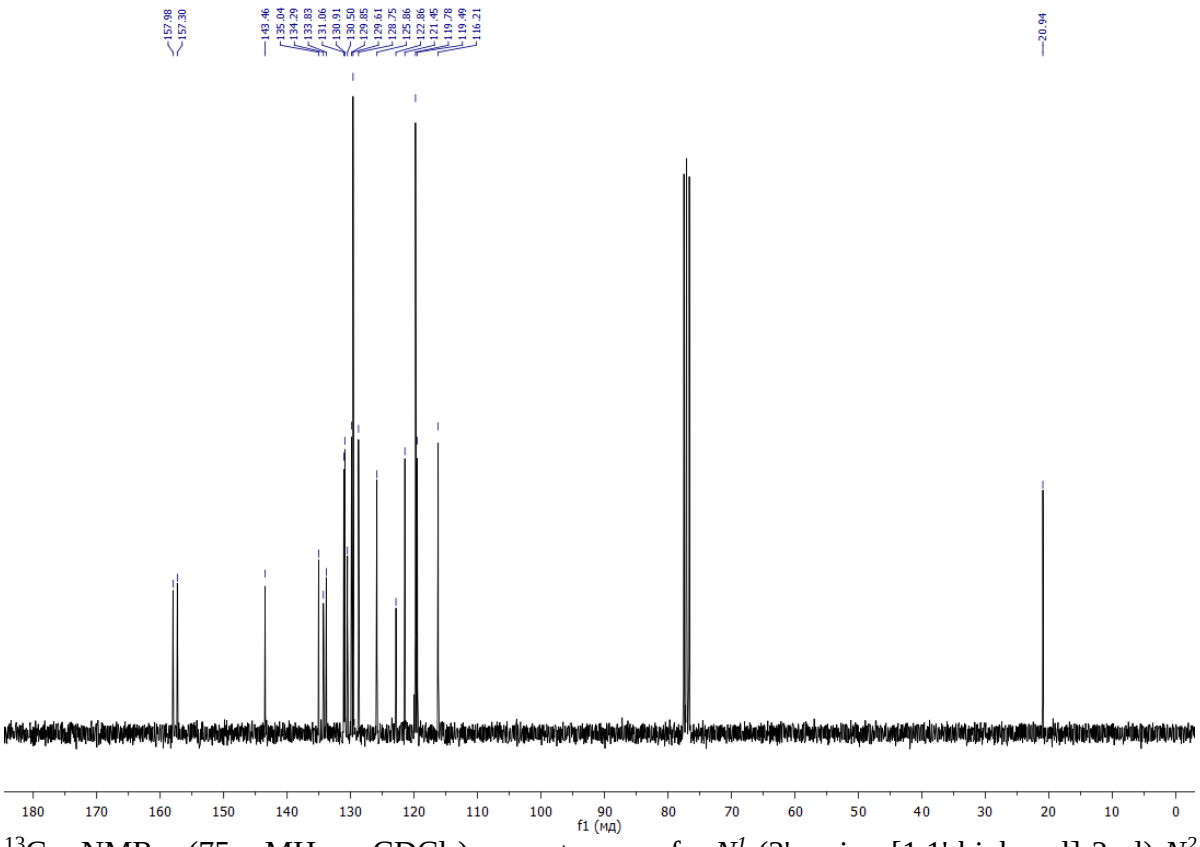
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(p-tolyl)oxalamide (**3i**)



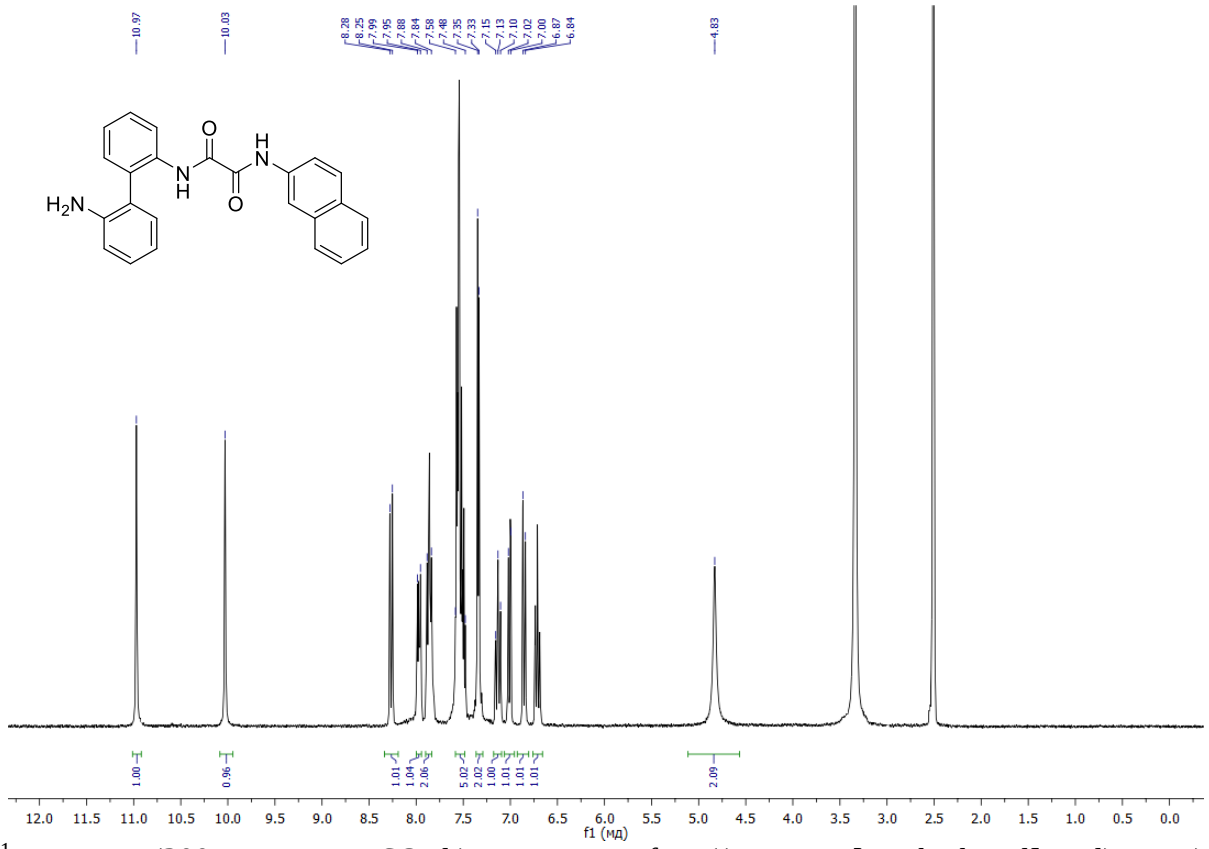
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(p-tolyl)oxalamide (**3i**)



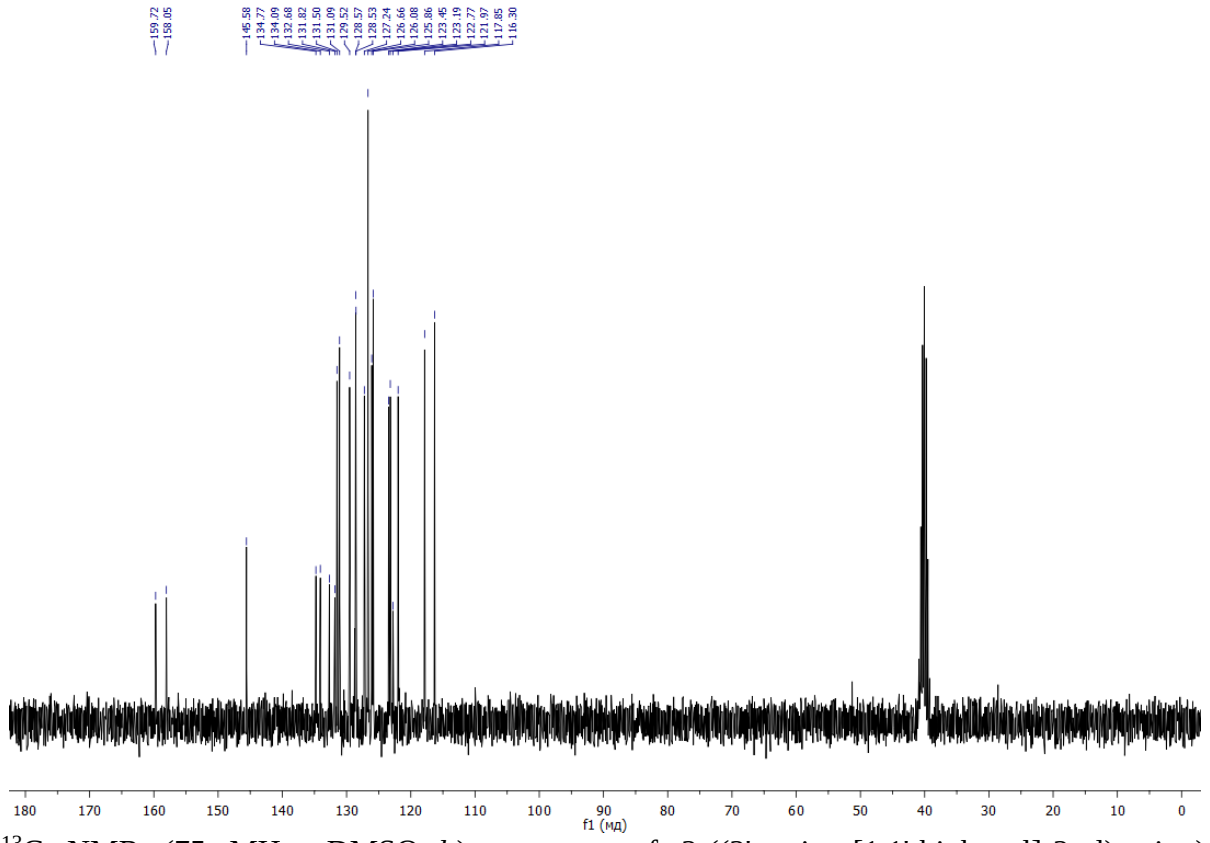
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(*m*-tolyl)oxalamide (**3j**)



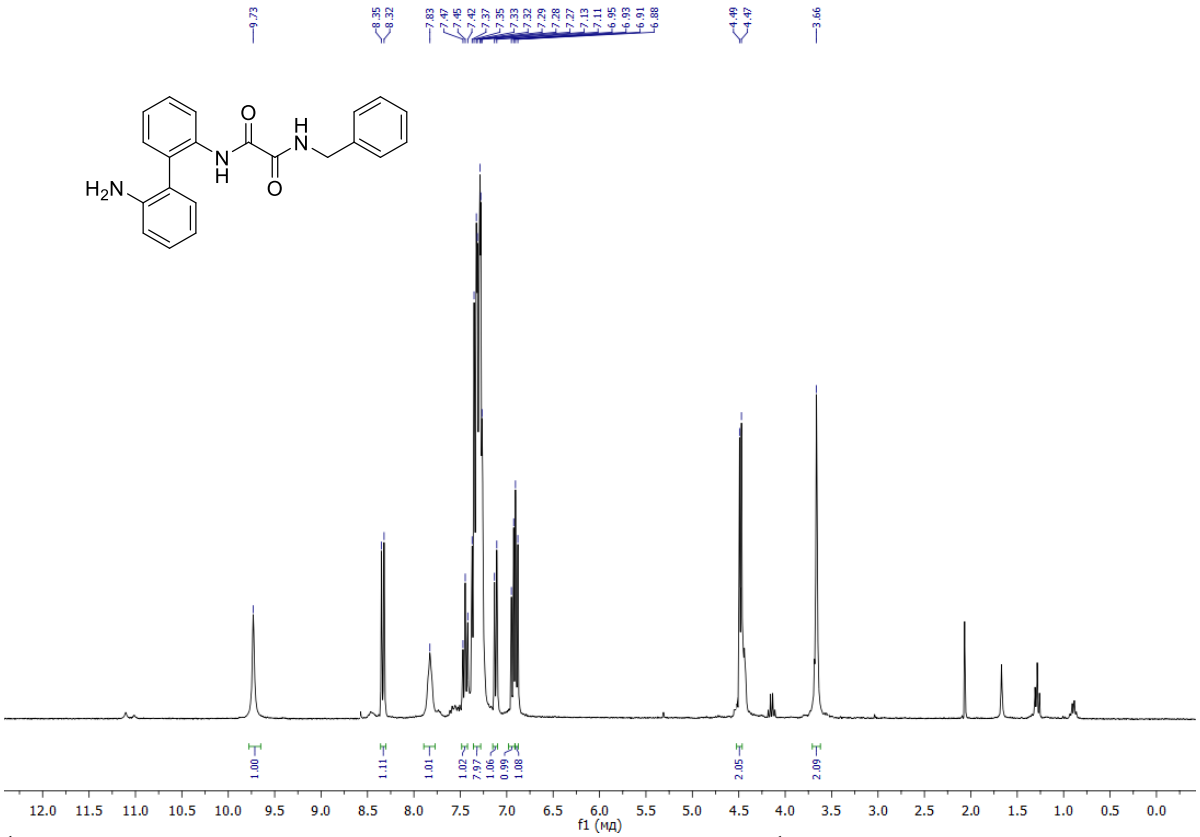
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-(*m*-tolyl)oxalamide (**3j**)



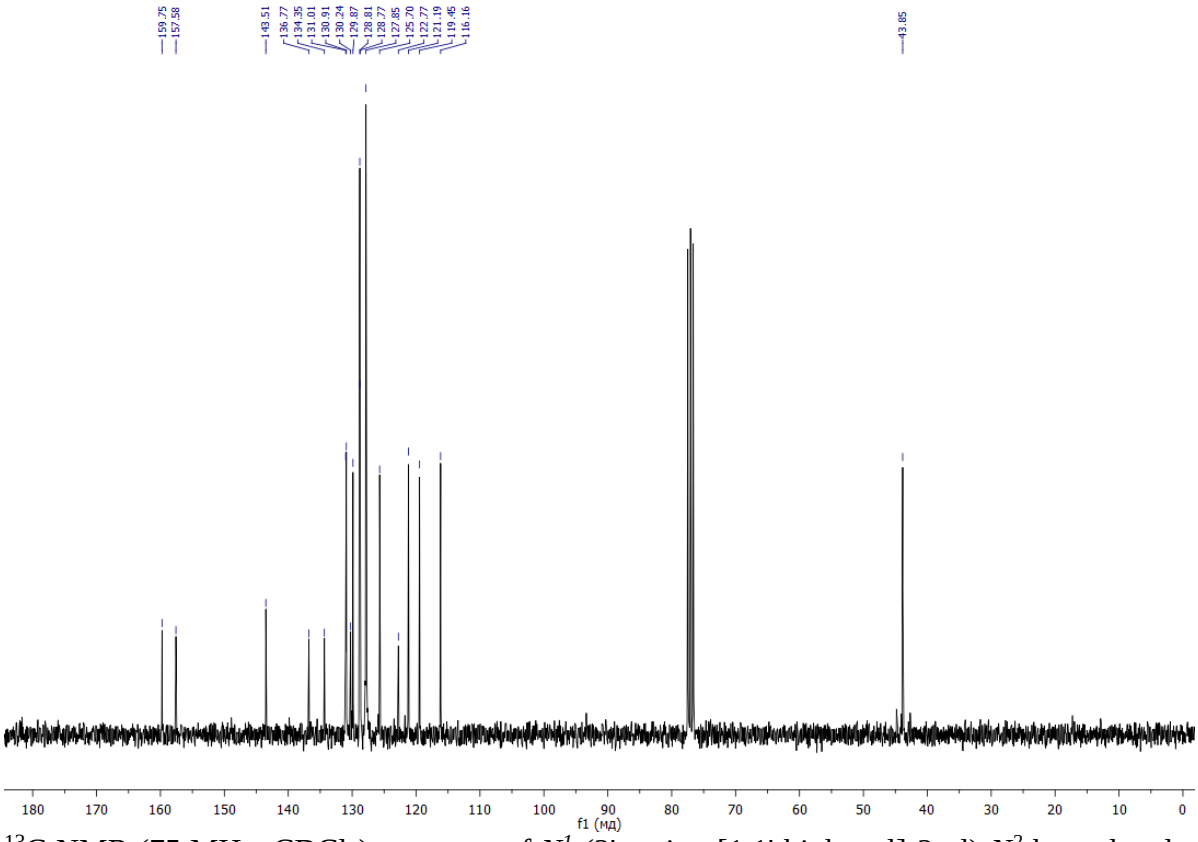
^{1}H NMR (300 MHz, DMSO-d_6) spectrum of 2-((2'-amino-[1,1'-biphenyl]-2-yl)amino)-*N*-(naphthalen-2-yl)acetamide (**3k**)



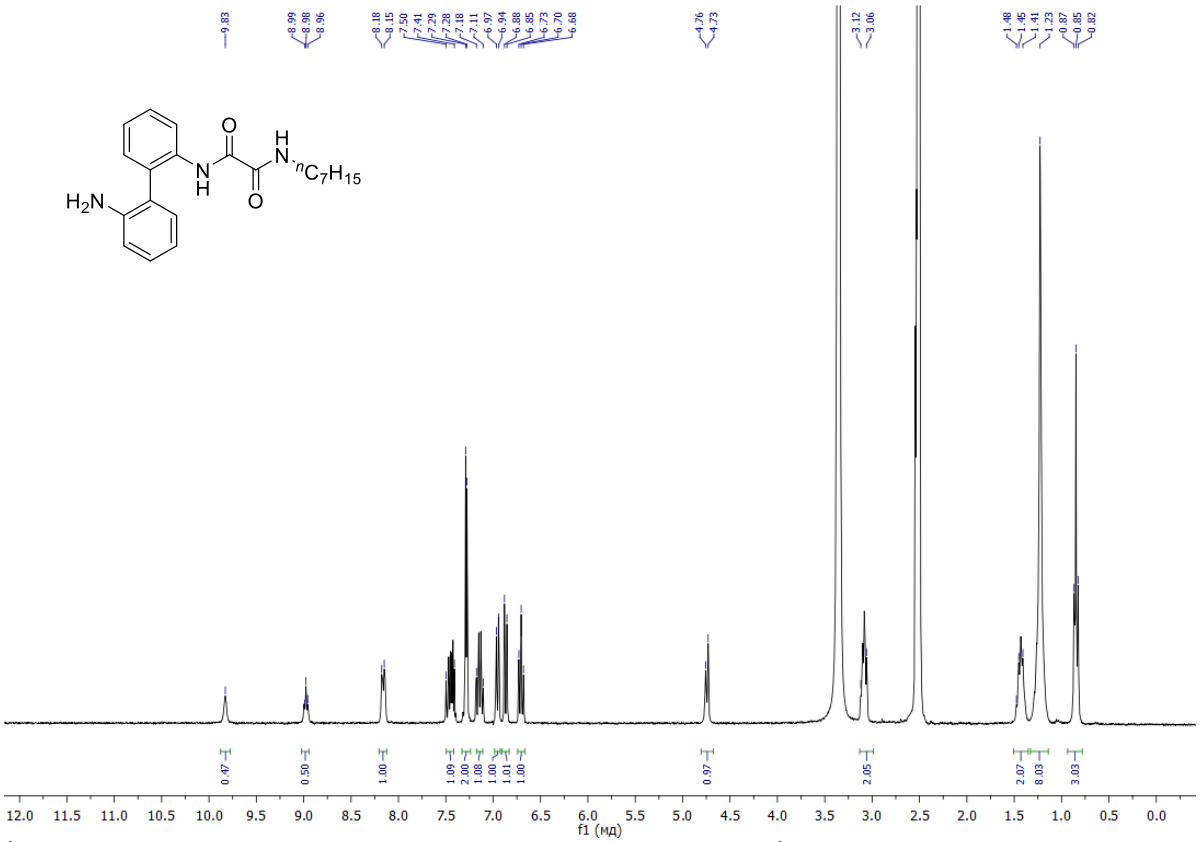
^{13}C NMR (75 MHz, DMSO-d_6) spectrum of 2-((2'-amino-[1,1'-biphenyl]-2-yl)amino)-*N*-(naphthalen-2-yl)acetamide (**3k**)



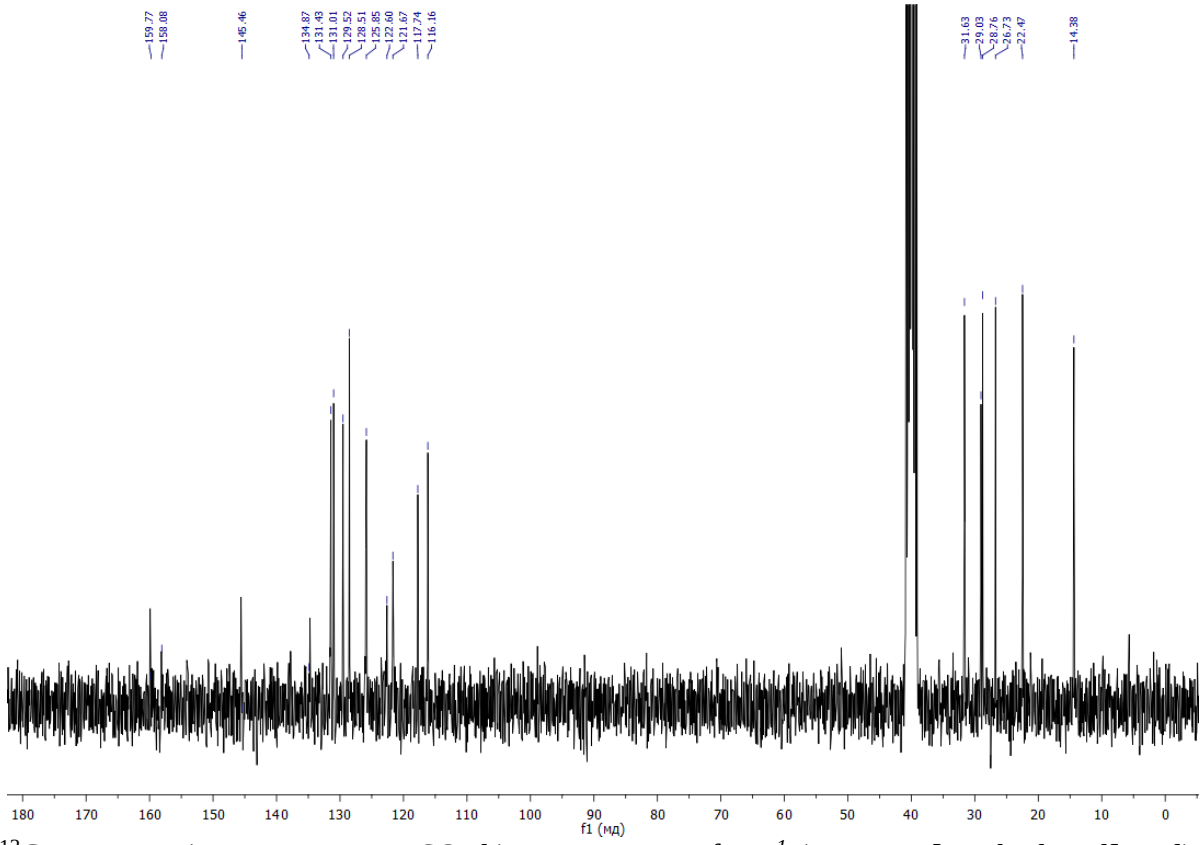
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-benzyloxalamide (**3l**)



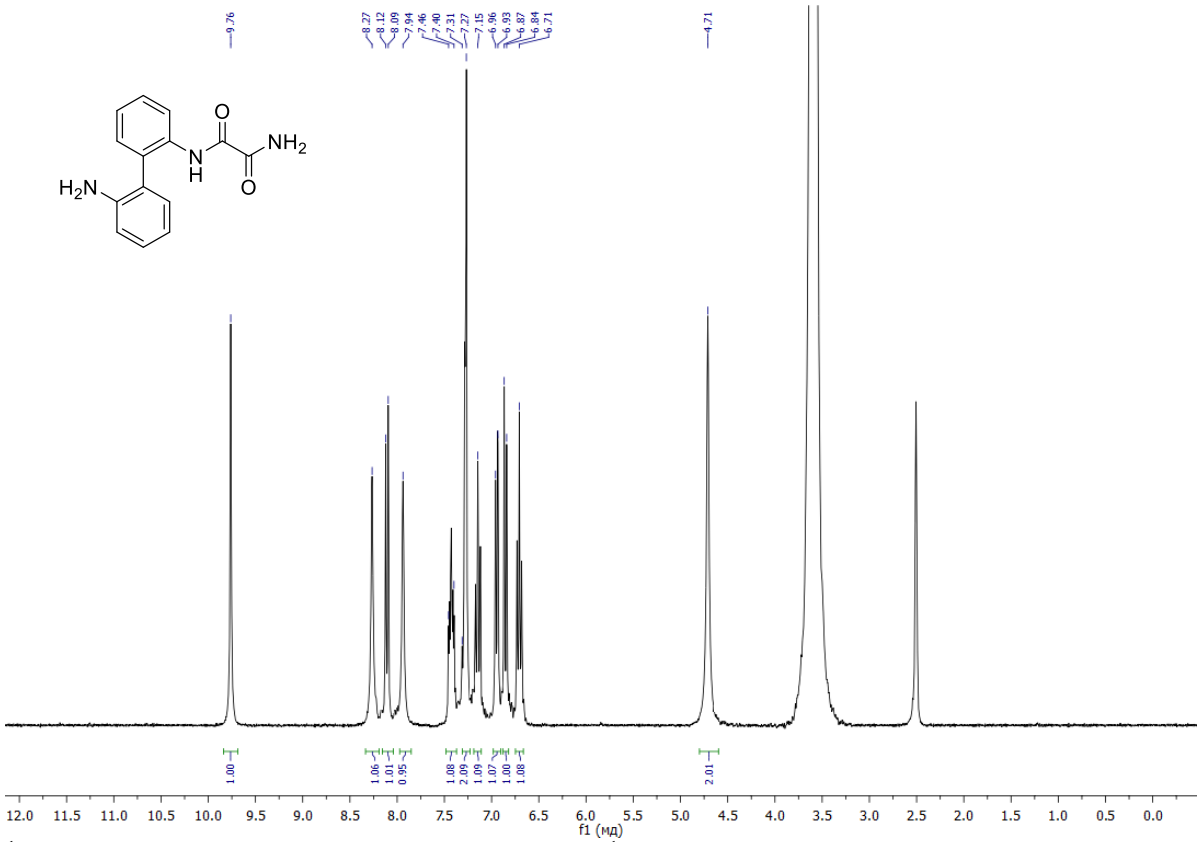
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-benzyloxalamide (**3l**)



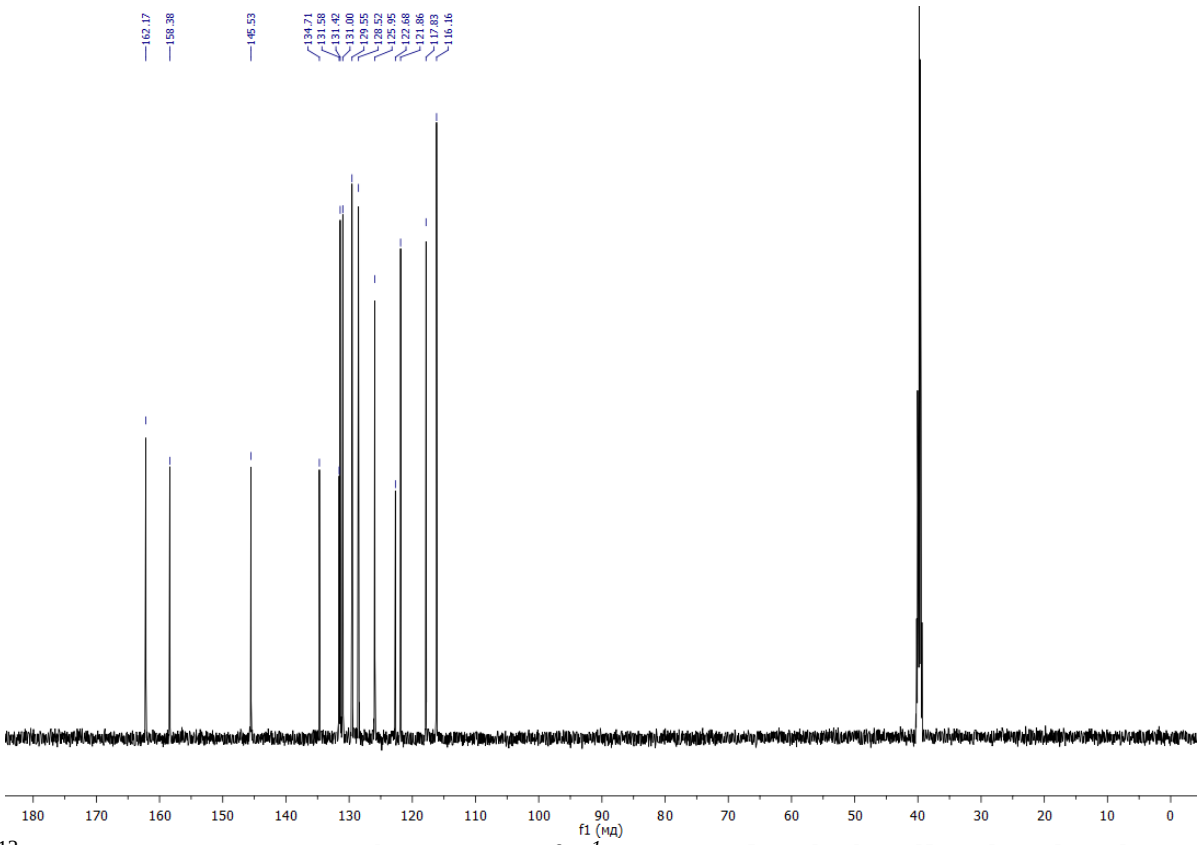
^{1}H NMR (300 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-heptyloxalamide (**3m**)



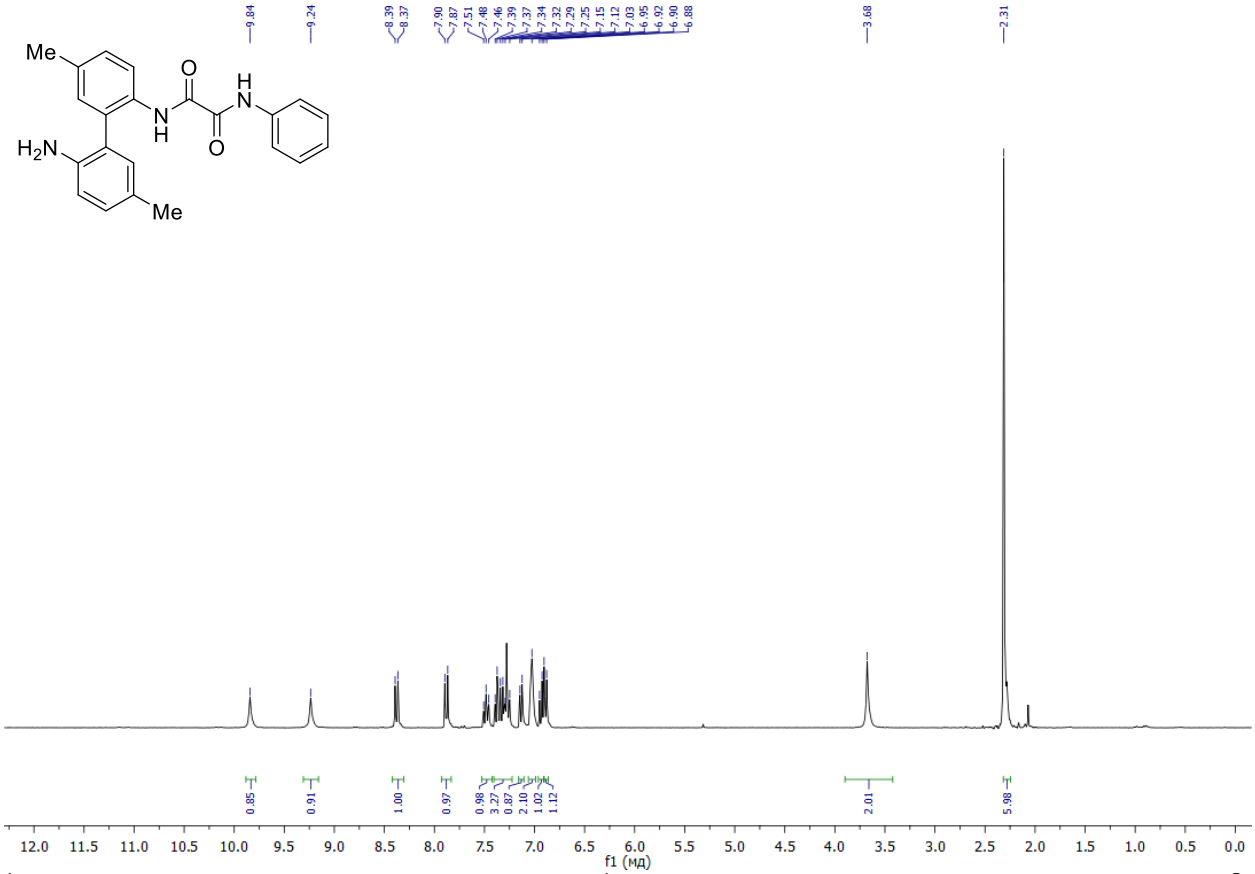
^{13}C NMR (75 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)-N^2-heptyloxalamide (**3m**)



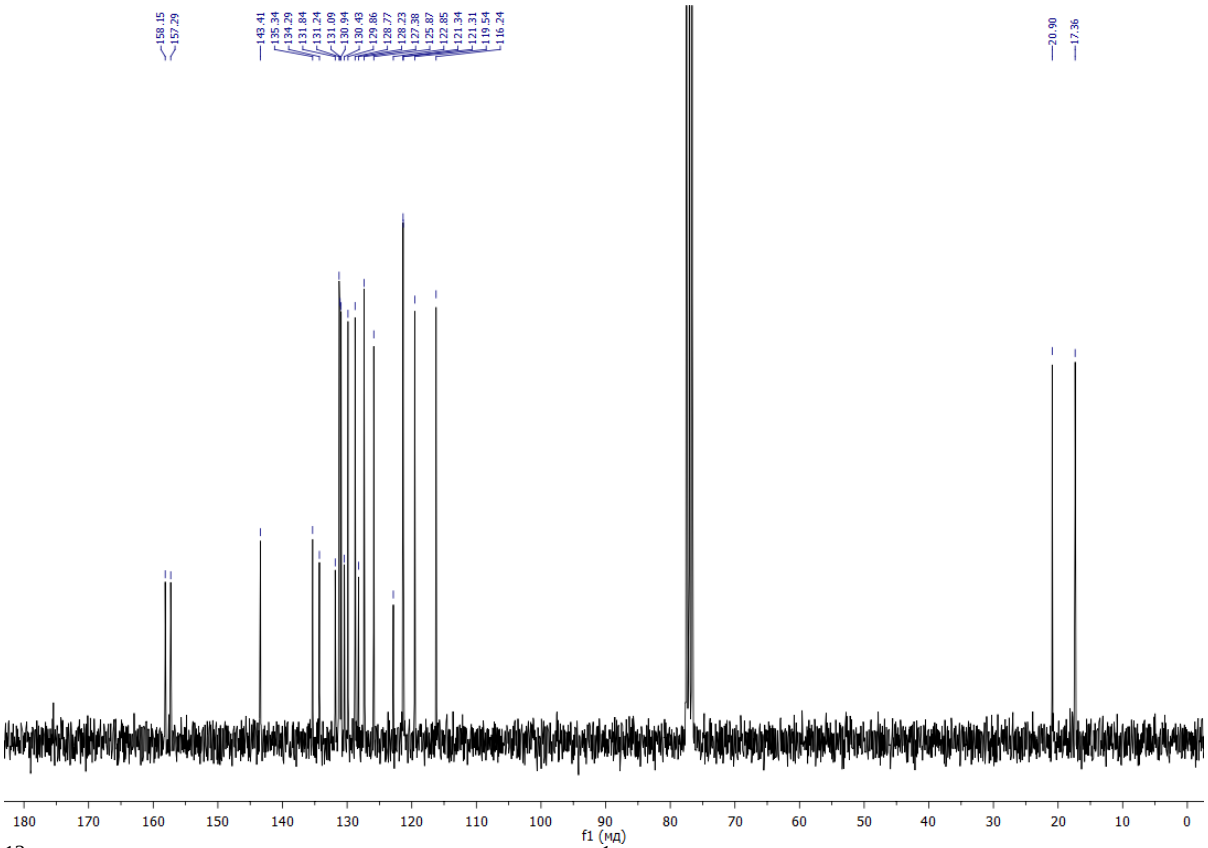
^{1}H NMR (300 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)oxalamide (**3n**)



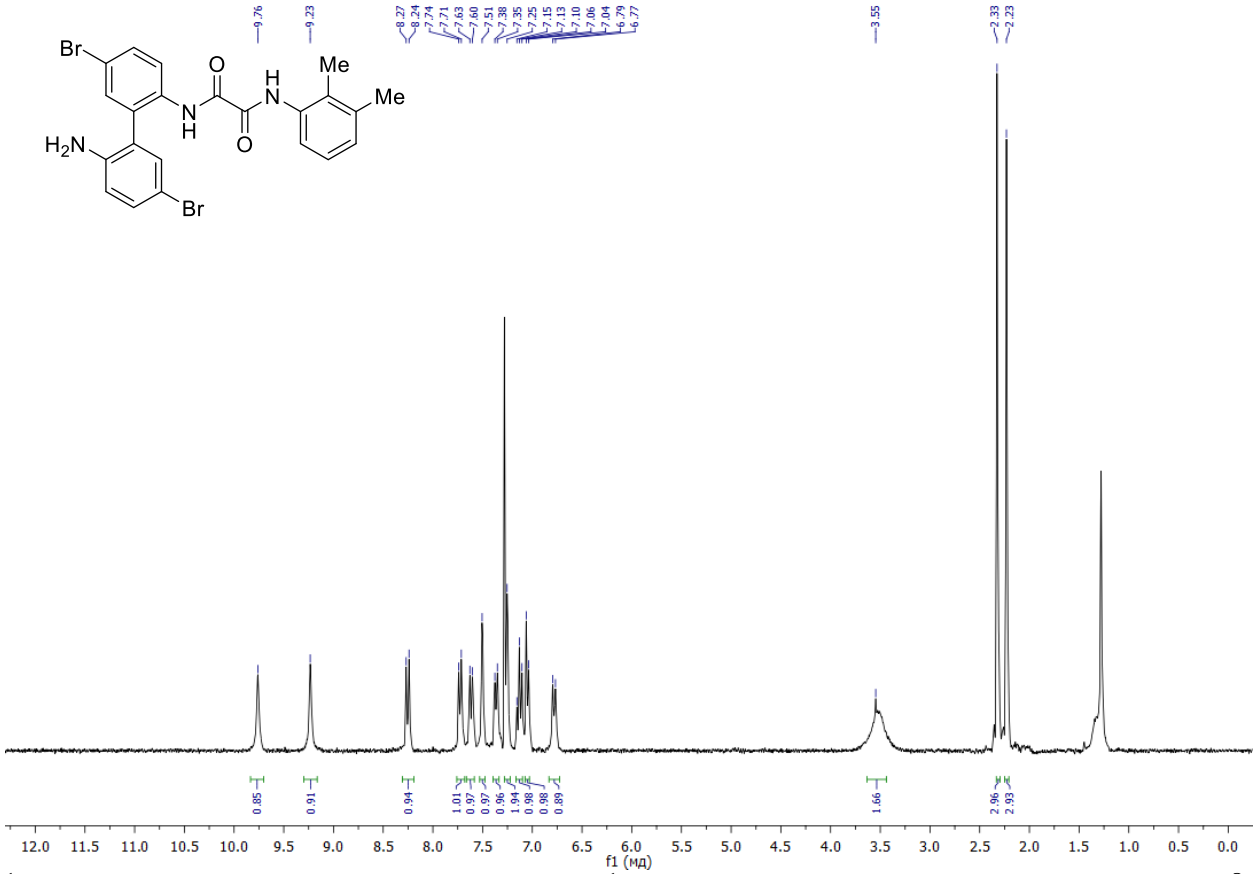
^{13}C NMR (75 MHz, DMSO-d_6) spectrum of N^1-(2'-amino-[1,1'-biphenyl]-2-yl)oxalamide (**3n**)



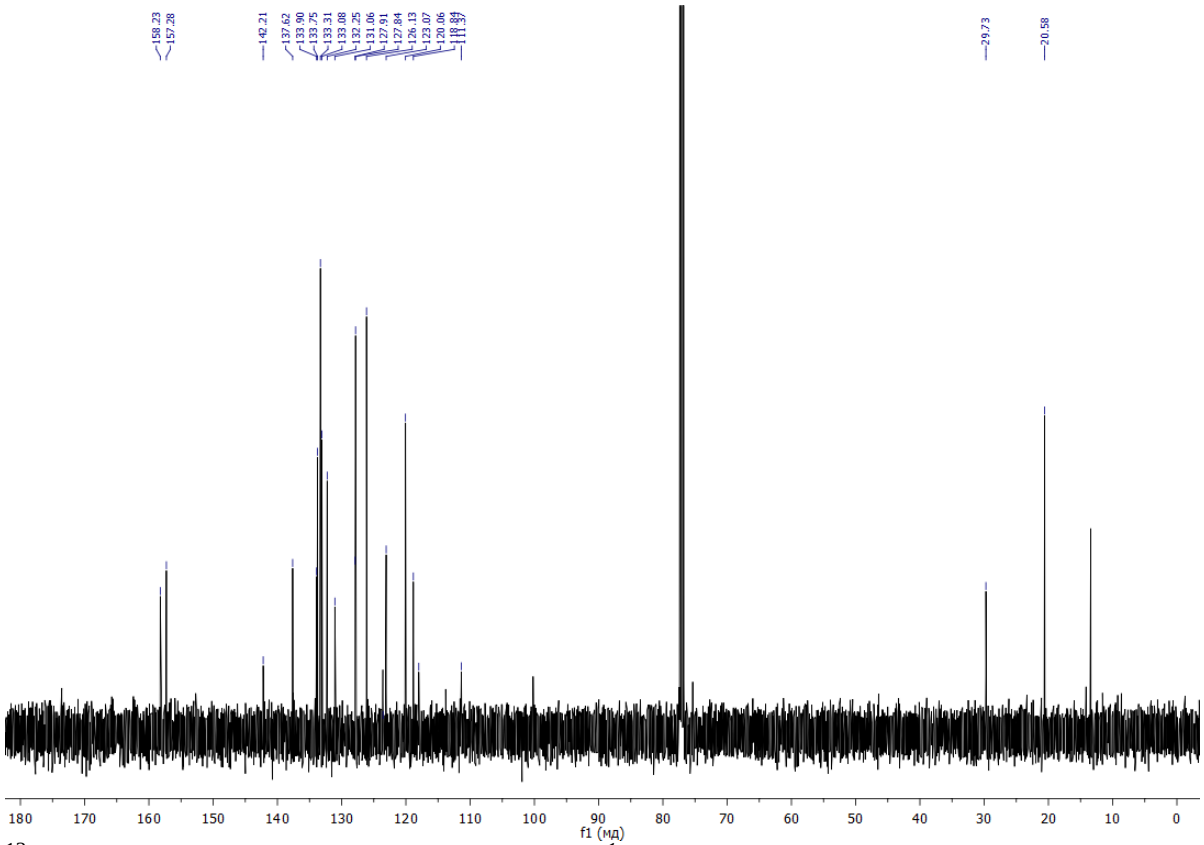
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of *N*^{1}-(2'-amino-5,5'-dimethyl-[1,1'-biphenyl]-2-yl)-*N*^{2}-phenyloxalamide (**3o**)



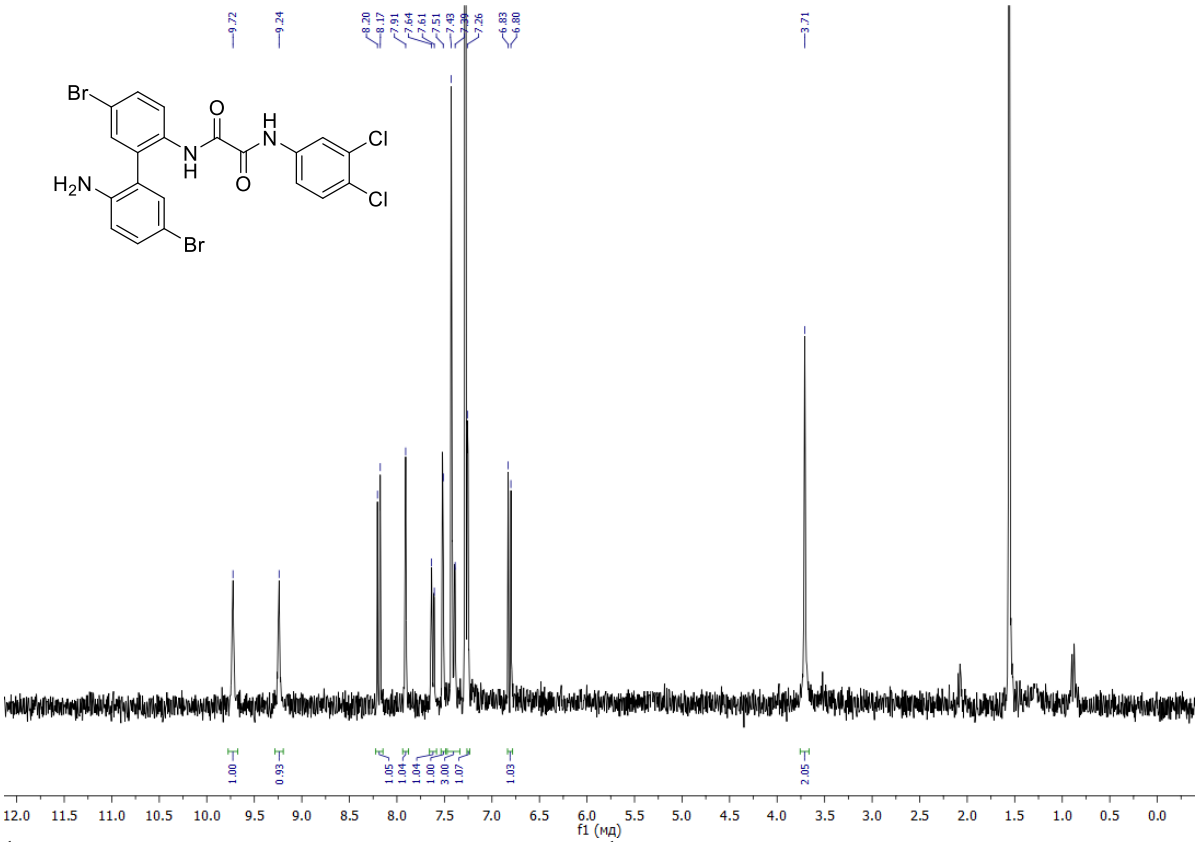
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of *N*^{1}-(2'-amino-5,5'-dimethyl-[1,1'-biphenyl]-2-yl)-*N*^{2}-phenyloxalamide (**3o**)



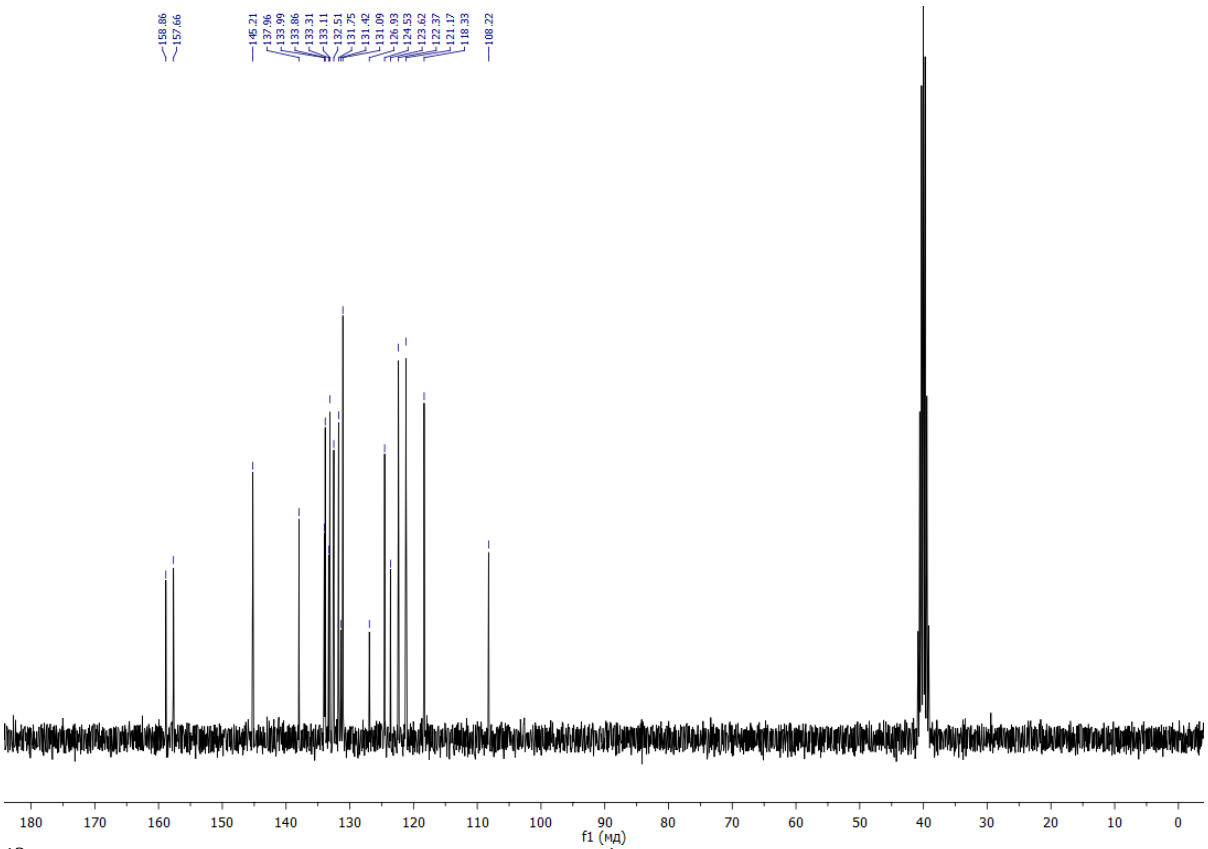
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of *N*^{1}-(2'-amino-5,5'-dibromo-[1,1'-biphenyl]-2-yl)-*N*^{2}-(2,3-dimethylphenyl)oxalamide (**3p**)



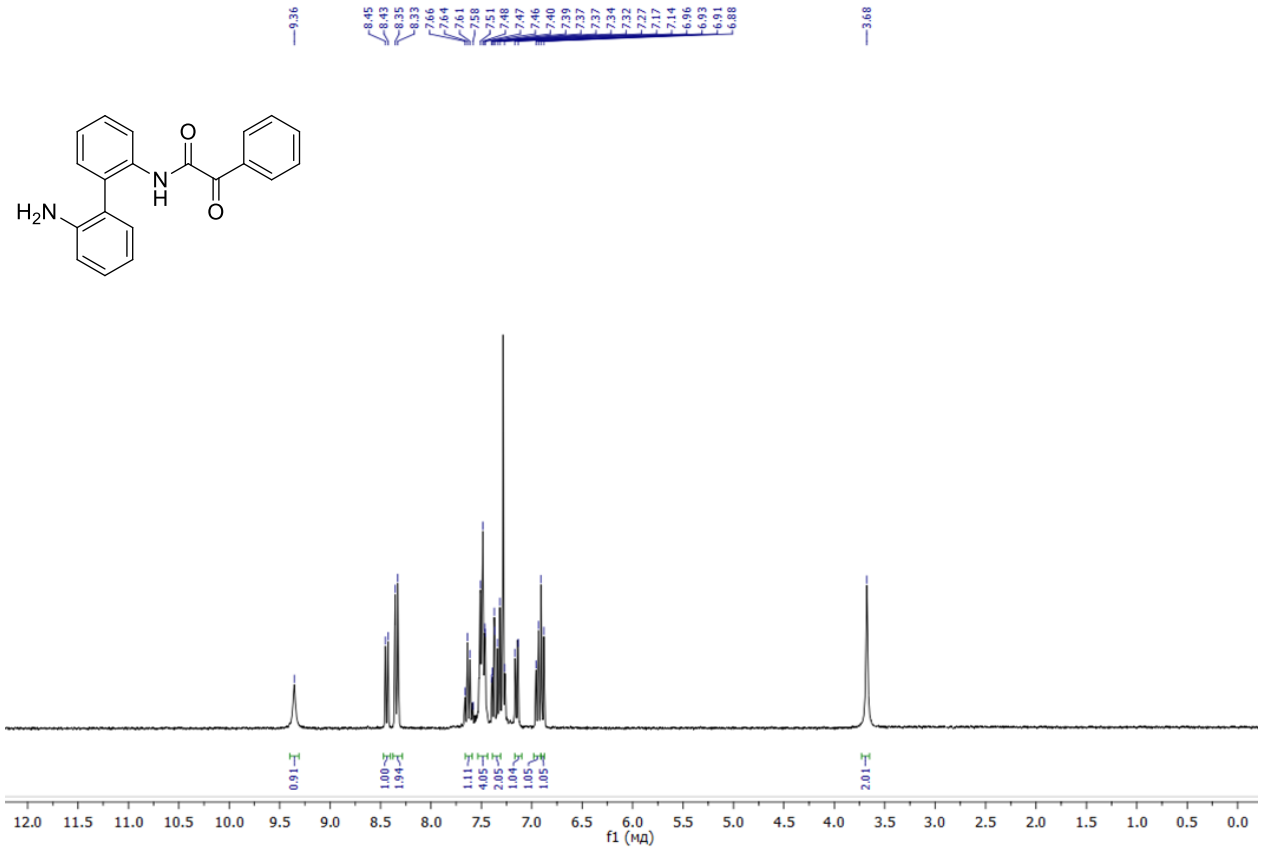
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of *N*^{1}-(2'-amino-5,5'-dibromo-[1,1'-biphenyl]-2-yl)-*N*^{2}-(2,3-dimethylphenyl)oxalamide (**3p**)



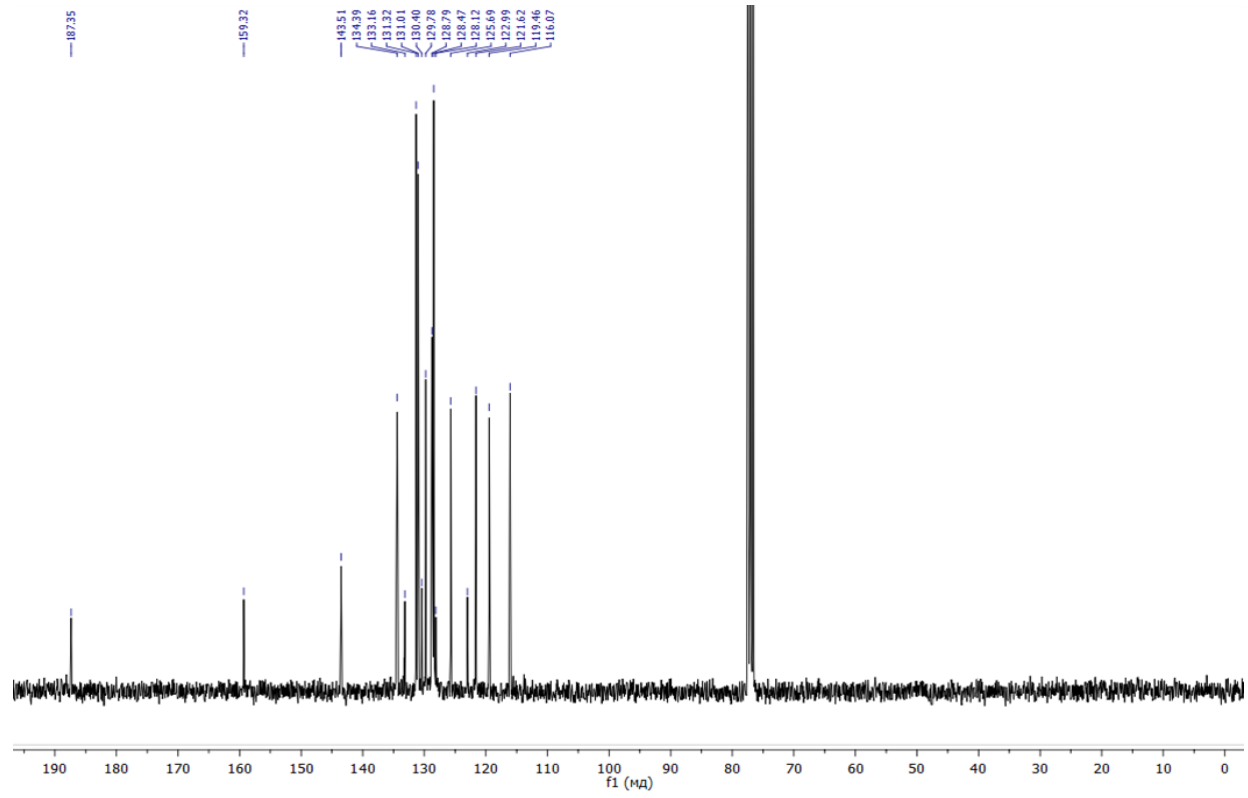
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of *N*^{1}-(2'-amino-5,5'-dibromo-[1,1'-biphenyl]-2-yl)-*N*^{2}-(3,4-dichlorophenyl)oxalamide (**3q**)



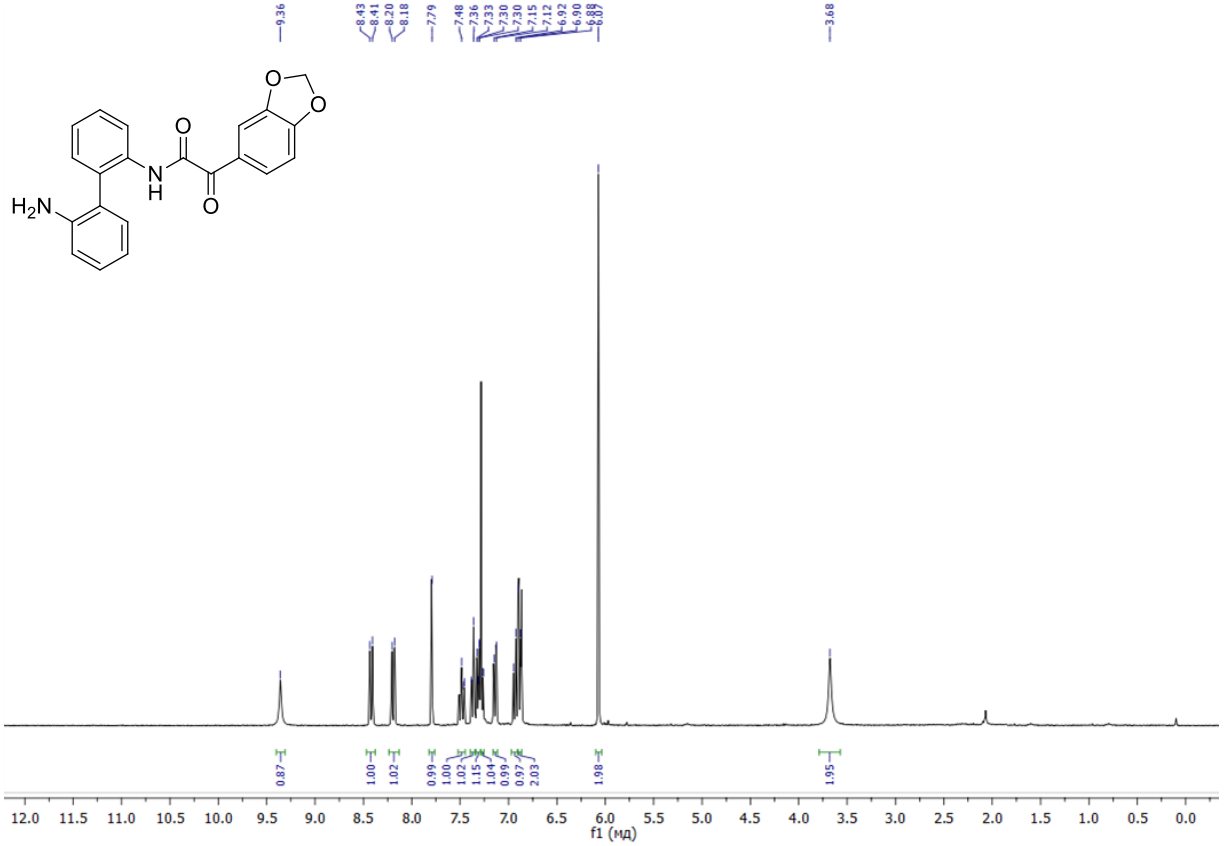
^{13}C NMR (75 MHz, DMSO-*d6*) spectrum of *N*^{1}-(2'-amino-5,5'-dibromo-[1,1'-biphenyl]-2-yl)-*N*^{2}-(3,4-dichlorophenyl)oxalamide (**3q**)



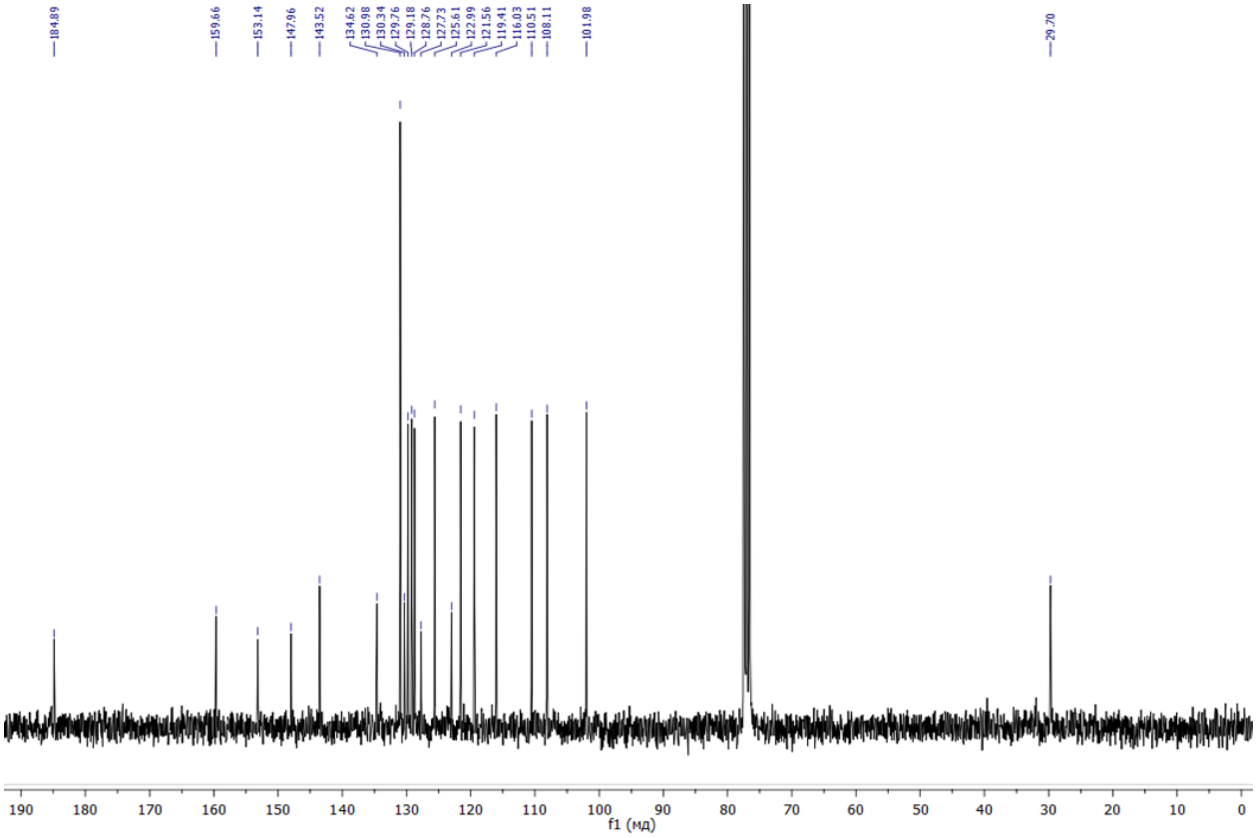
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of *N*-(2'-amino-[1,1'-biphenyl]-2-yl)-2-oxo-2-phenylacetamide (**6a**)



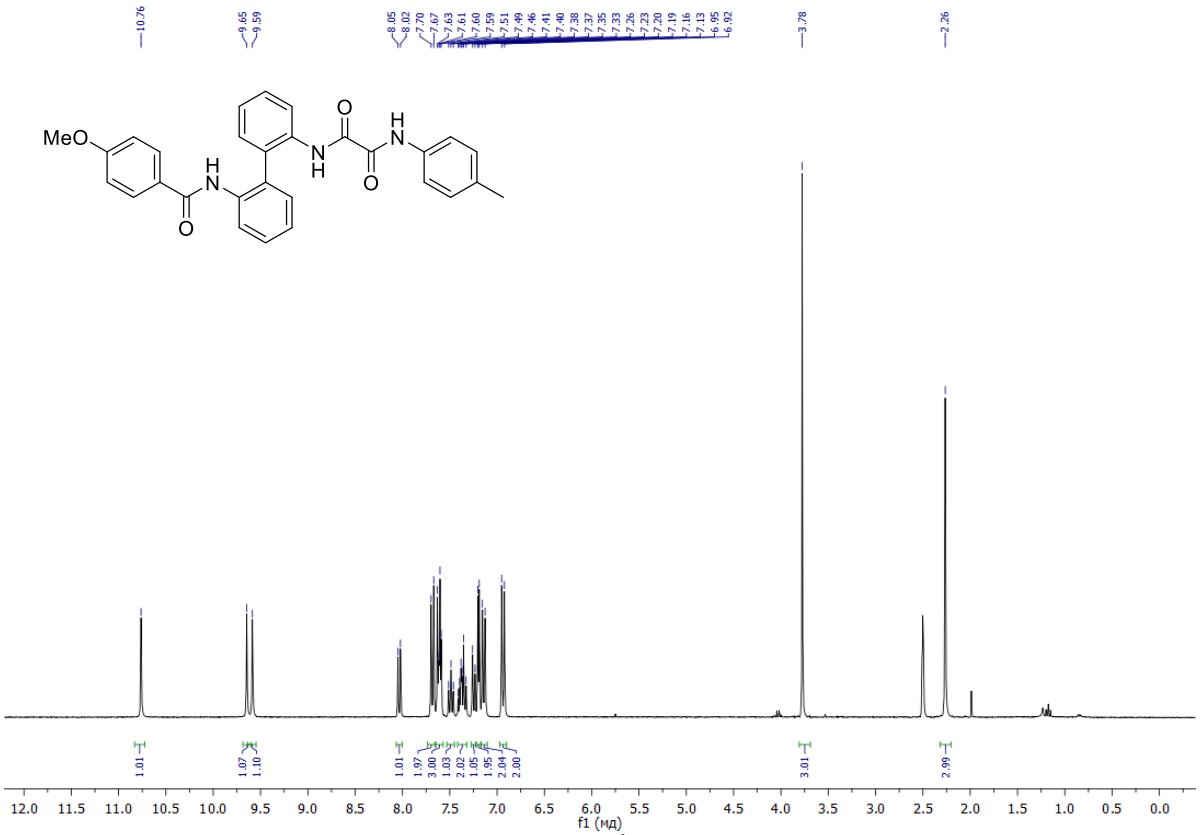
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of *N*-(2'-amino-[1,1'-biphenyl]-2-yl)-2-oxo-2-phenylacetamide (**6a**)



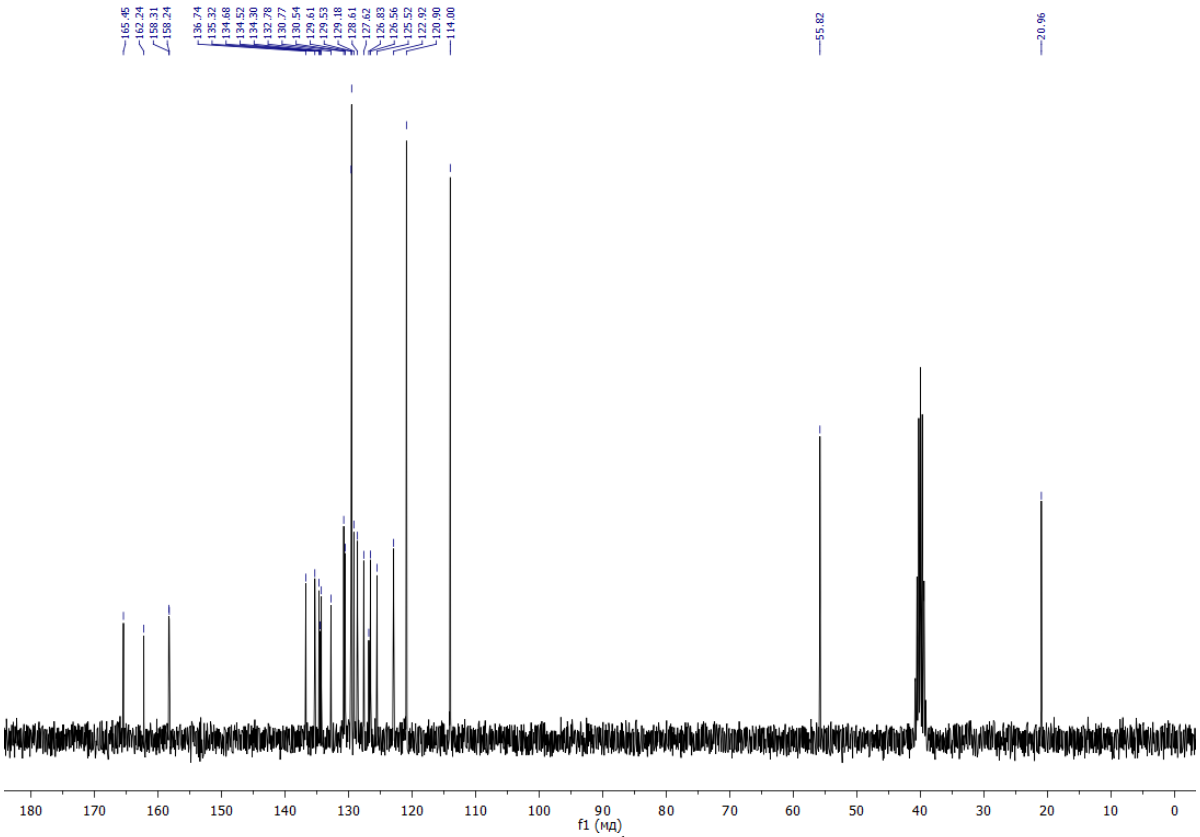
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of *N*-(2'-amino-[1,1'-biphenyl]-2-yl)-2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxoacetamide (**6b**)



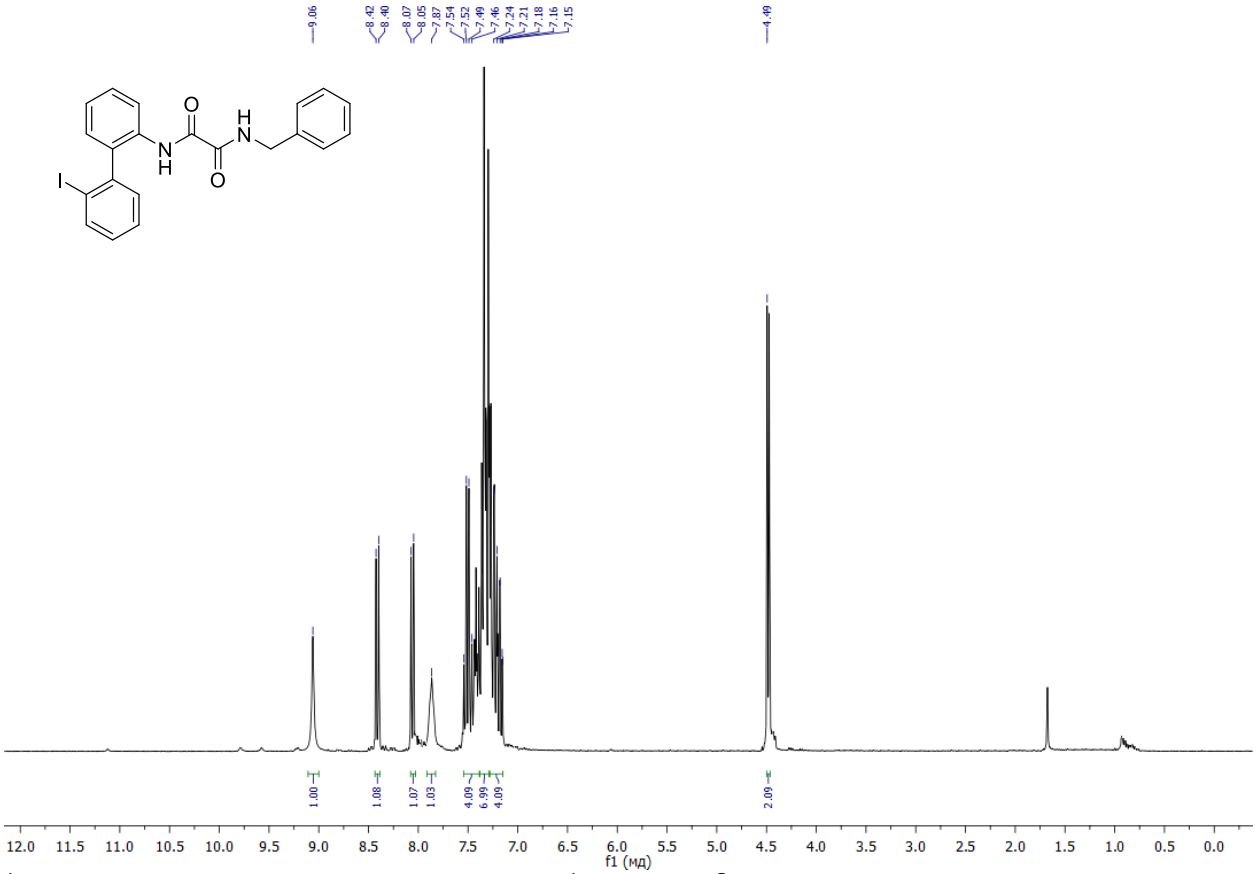
^{13}C NMR (75 MHz, $CDCl_3$) spectrum of *N*-(2'-amino-[1,1'-biphenyl]-2-yl)-2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxoacetamide (**6b**)



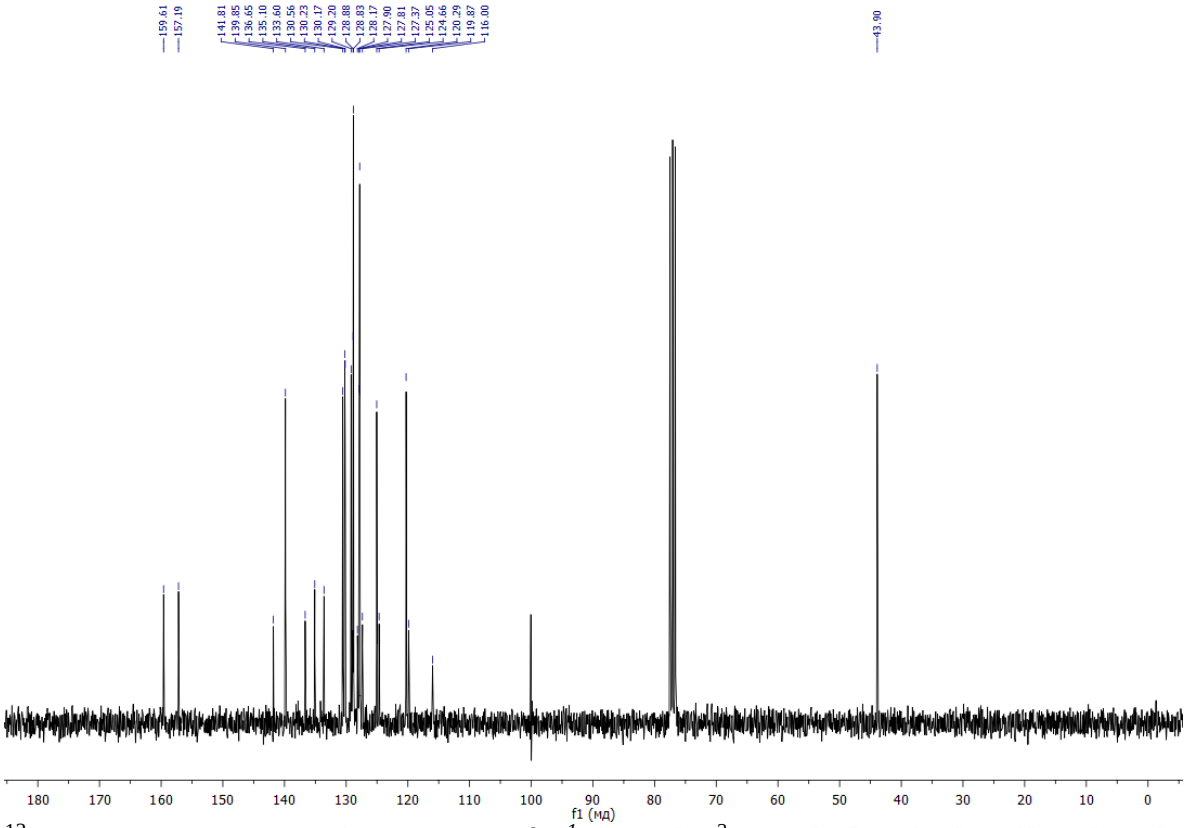
^{1}H NMR (300 MHz, DMSO-*d6*) spectrum of N^{1}-(2'-(4-methoxybenzamido)-[1,1'-biphenyl]-2-yl)-N^{2}-(*p*-tolyl)oxalamide (**7**)



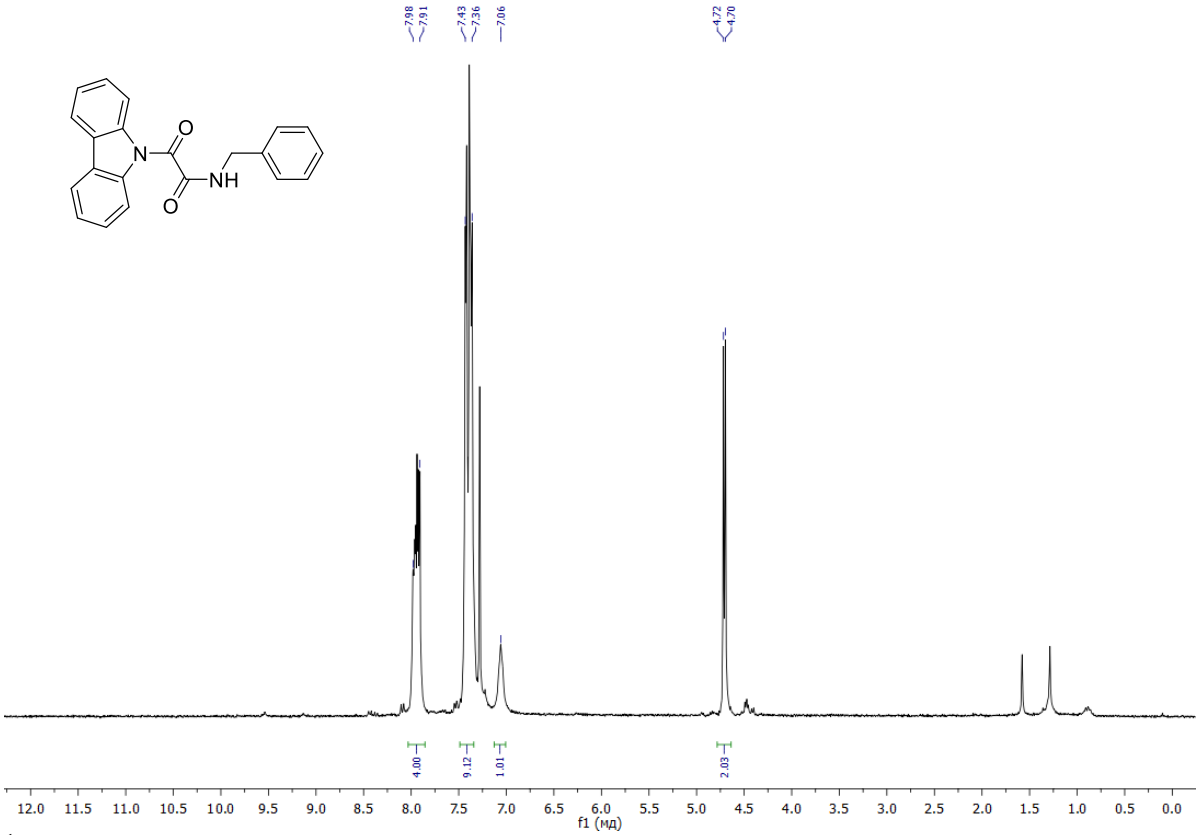
^{13}C NMR (75 MHz, DMSO-*d6*) spectrum of N^{1}-(2'-(4-methoxybenzamido)-[1,1'-biphenyl]-2-yl)-N^{2}-(*p*-tolyl)oxalamide (**7**)



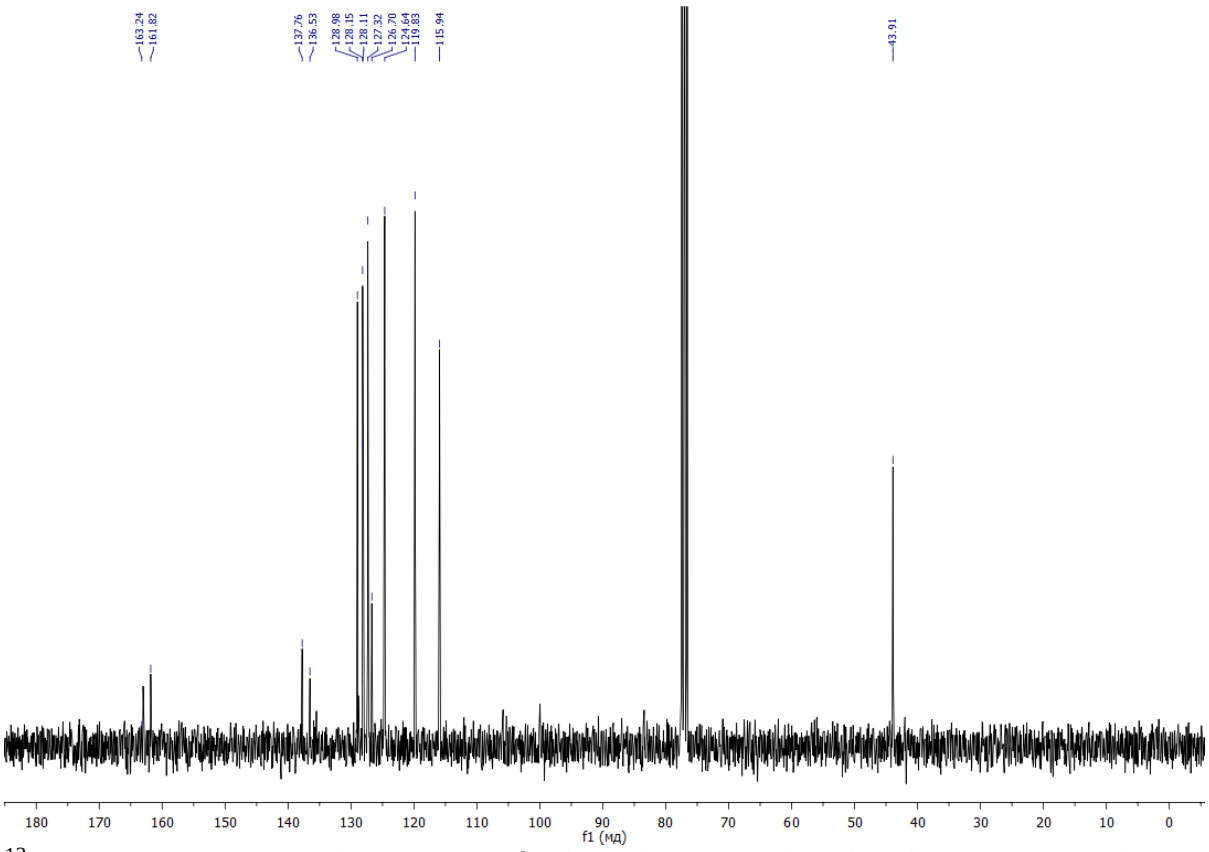
^{1}H NMR (300 MHz, $CDCl_3$) spectrum of N^1-(benzyl-N^2-(2'-iodo-[1,1'-biphenyl]-2-yl)oxalamide (**8**)



^{13}C NMR (75 MHz, $CDCl_3$) spectrum of N^1-(benzyl-N^2-(2'-iodo-[1,1'-biphenyl]-2-yl)oxalamide (**8**)



^{1}H NMR (300 MHz, $CDCl_3$) spectrum of *N*-benzyl-2-(*9H*-carbazol-9-yl)-2-oxoacetamide (**9**)



^{13}C NMR (75 MHz, $CDCl_3$) spectrum of *N*-benzyl-2-(*9H*-carbazol-9-yl)-2-oxoacetamide (**9**)