Electronic supplementary materials *Mendeleev Commun.*, 2014, **24**, 105−107

Synthesis of new ring-fused thiocarbamates by condensation of 2-thioxo- and 2-oxo-1,3-dialkyl-4,5-dihydroxy-4,5-diphenylimidazolidines with KSCN

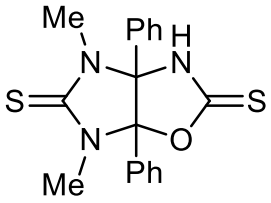
Vladimir V. Baranov, Angelina N. Kravchenko and Yulia V. Nelyubina

Contents

I. General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The product were purified by recrystallization. ^{1}H and ^{13}C NMR were recorded at 24 to 30 °C on a Bruker Avance II 300, and TMS as internal standard. MS and ESI were recorded using Kratos MS-30 and Bruker micrOTOF II mass spectrometers respectively. X-ray diffraction experiments were perfomed using Bruker Smart 1000 CCD difractometer. Elemental analyses were performed on a Perkin Elmer 2400 Elemental CHN analyzer and Euro EA elemental Analizer. 4,5-Dihydroxy-1,3-dimethyl-4,5-diphenylimidazolidine-2-thione **10a**, 1,3-diethyl-4,5-dihydroxy-4,5-diphenylimidazolidine-2-thione **10b** and 4,5-dihydroxy-1,3-dimethyl-4,5-diphenylimidazolidin-2-one **11** were prepeared by the similar method as previously reported papers[1-3].

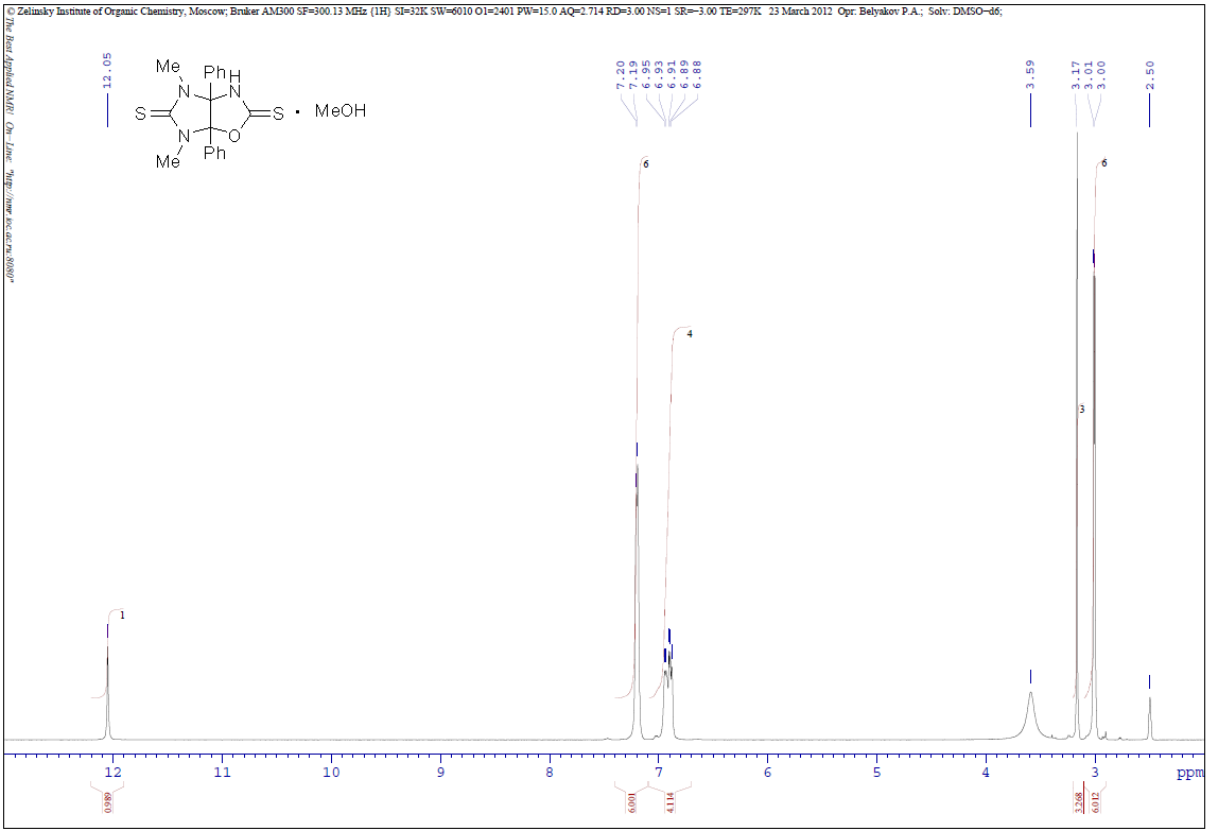
II. Reaction HNCS with compounds 10, 11 and analytical data of 8, 9.

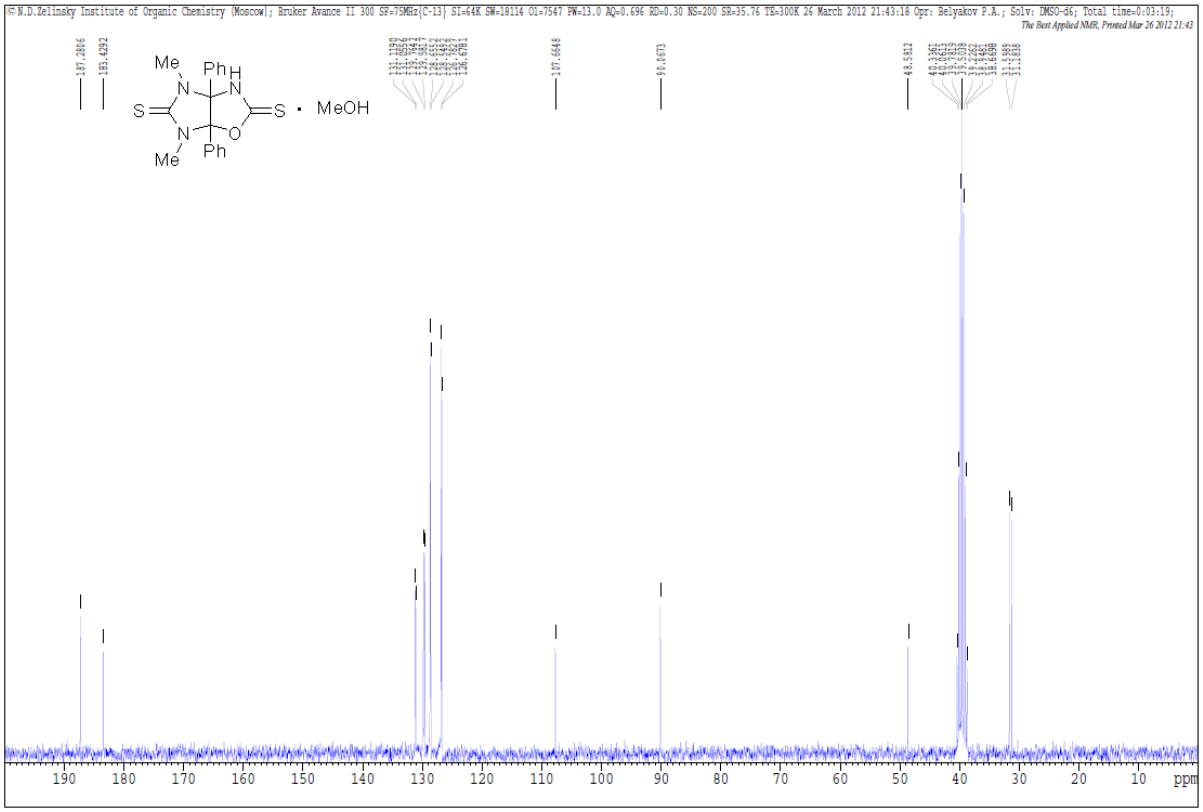


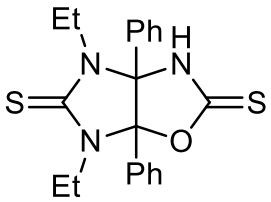
4,6-Dimethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione **8a**.

To the solution of 4,5-dihydroxy-1,3-dimethyl-4,5-diphenylimidazolidine-2-thione **10a** (1.07 g, 0.0034 mol) and KSCN (0.44 g, 0.0045 mol) in MeOH (20 ml) at r.t. was added AcOH (3.00 ml). Reaction mixture was refluxed for 1 h. The reaction mixture was concentrated and precipitate was filtered off and recrystallized from MeOH. The precipitate was filtered off and washed MeOH to give 1.12 g (86%) of the product **8a** as a solvate with MeOH.

Colorless prisms (**8a**•MeOH) unstable on air which on losing MeOH form white powder (**8a**) were obtained, mp 223–225 °C (decomp.) ^{1}H NMR, δ, ppm.; *J*/Hz (DMSO-d_6): 3.00 (s, 3 H, Me), 3.01 (s, 3 H, Me), 3.17 (s, 3 H, Me), 6.82 – 6.97 (m, 4 H, Ph), 7.13 – 7.28 (m, 6 H, Ph), 12.05 (s, 1 H, NH). ^{13}C NMR, δ, ppm.; (DMSO-d_6): 31.18, 31.60, 48.58 (Me), 90.07, 107.66 (C–C bridge), 126.68, 126.78, 128.55, 128.66, 129.58, 129.76, 131.06, 131.12 (Ph), 183.43, 187.28 (C=S). HRMS, m/z, found: 356.0885 $[M+H]^+$ (calcd for $C_{18}H_{18}N_3OS_2$ 356.0891).


© Zelinsky Institute of Organic Chemistry, Moscow; Bruker AM300 SF=300.13 MHz (1H) SI=32K SW=6010 O1=2401 PW=15.0 AQ=2.714 RD=3.00 NS=1 SR=-3.00 TE=297K 23 March 2012 Opr: Belyakov P.A.; Solv: DMSO-d6;
12.05
7.20
7.19
6.95
6.93
6.91
6.89
6.88
3.59
3.17
3.01
3.00
2.50
Me
Ph
H
N
S
S
N
O
Me
Ph
MeOH
1
6
4
3
6
12
11
10
9
8
7
6
5
4
3
ppm
0.989
6.001
4.114
3.268
6.012

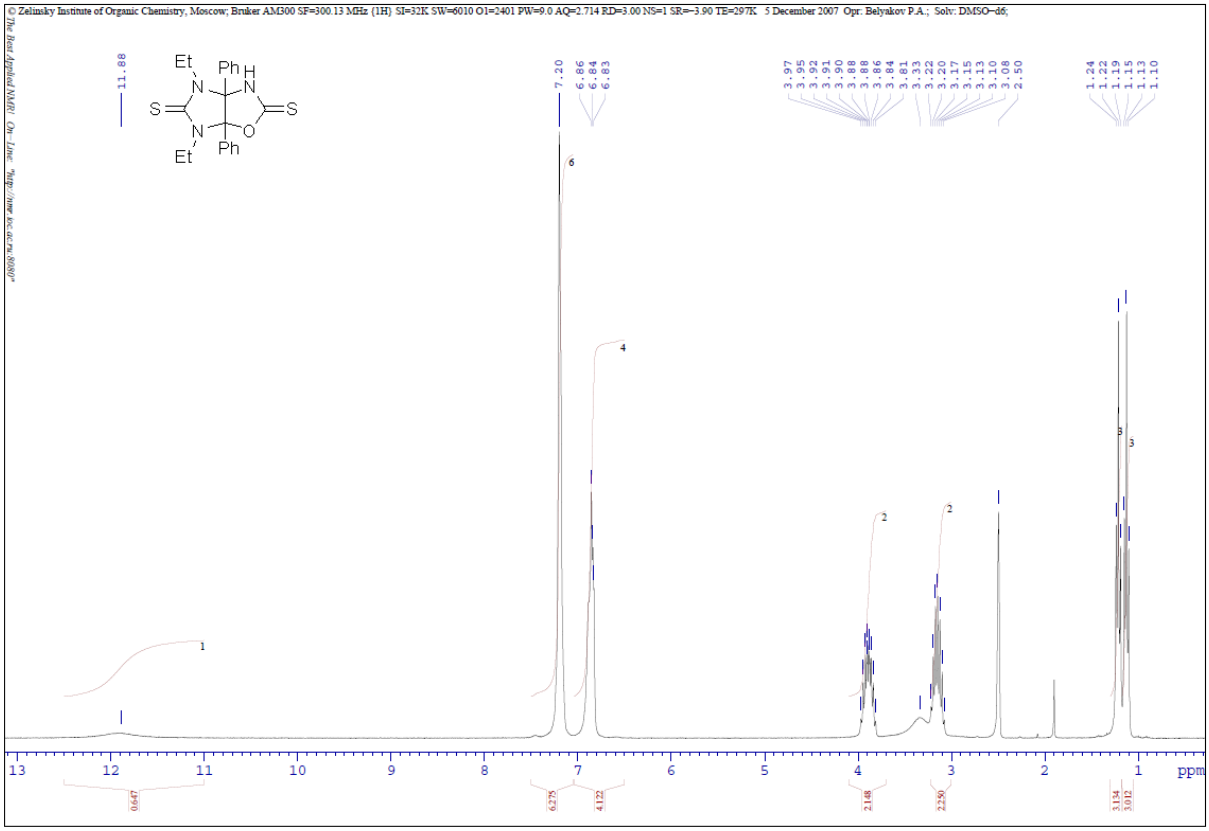

© N.D.Zelinsky Institute of Organic Chemistry (Moscow); Bruker Avance II 300 SF=75MHz[C-13] SI=64K SW=18114 O1=7547 PW=13.0 AQ=0.696 RD=0.30 NS=200 SR=35.76 TE=300K 26 March 2012 21:43:18 Opr: Belyakov P.A.; Solv: DMSO-d6; Total time=0:03:19;
The Best Applied NMR, Printed Mar 26 2012 21:43
187.2866
183.4292
Me
Ph
H
N
S
S
N
O
Me
Ph
MeOH
107.6648
90.6873
48.5812
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

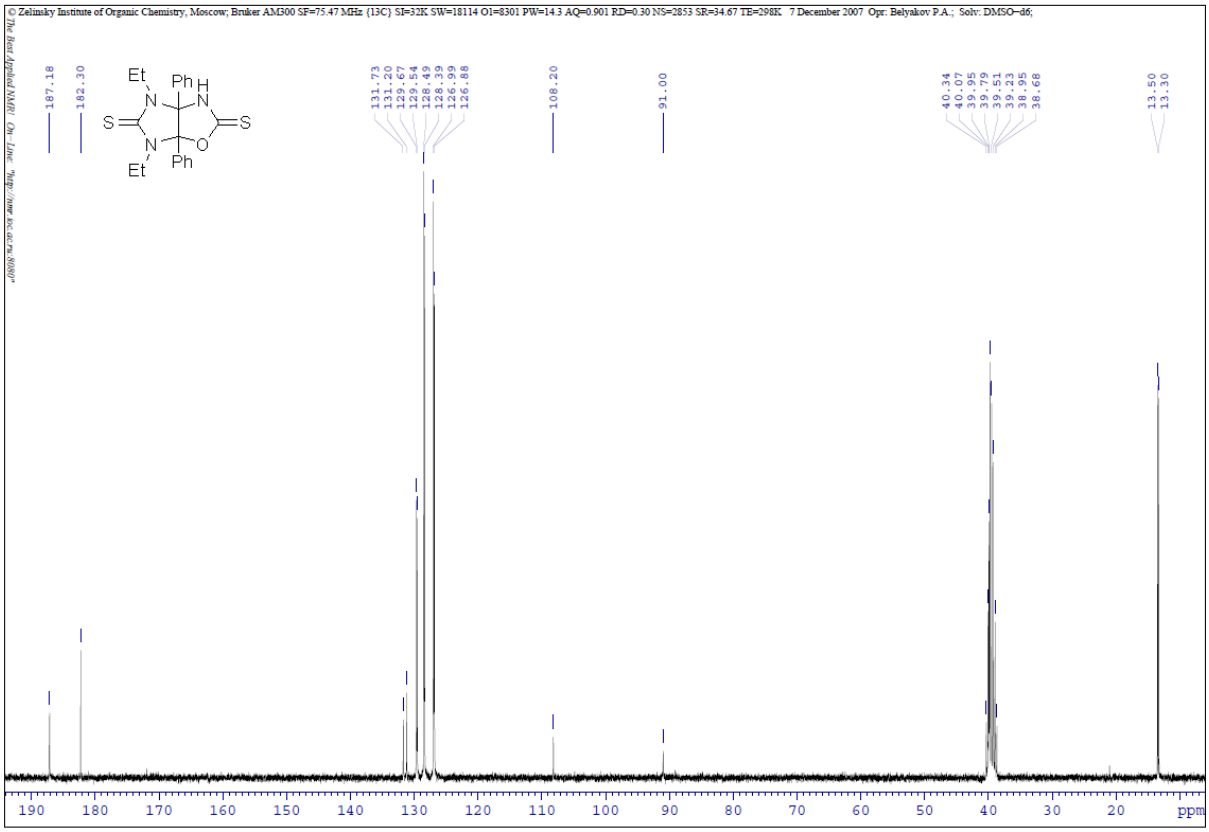


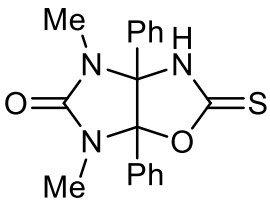
4,6-Diethyl-3a,6a-diphenyltetrahydro-2*H*-imidazo[4,5-*d*]oxazole-2,5(3*H*)-dithione **8b**.

To the solution of 1,3-diethyl-4,5-dihydroxy-4,5-diphenylimidazolidine-2-thione **10b** (1.16 g, 0.0034 mol) and KSCN (0.44 g, 0.0045 mol) in MeOH (20 ml) at r.t. was added AcOH (2.25 ml). Reaction mixture was refluxed for 1 h. The reaction mixture was concentrated and precipitate was filtered and recrystallized from MeOH. The precipitate was filtered and washed MeOH to obtain 1.04 g (80%) of the product.

Colorless prisms, mp 243–245 °C (decomp.). ^{1}H NMR, δ, ppm.; *J*/Hz (DMSO-d_6): 1.13 (t, 3 H, Me, *J* = 7.0 Hz), 1.22 (t, 3 H, Me, *J* = 7.0 Hz), 3.08 – 3.22 (m, 2 H, CH_2), 3.81 – 3.97 (m, 2 H, CH_2), 6.79 – 6.93 (m, 4 H, Ph), 7.12 – 7.28 (m, 6 H, Ph), 11.50 – 12.40 (br s, 1 H, NH). ^{13}C NMR, δ, ppm.; (DMSO-d_6): 13.30, 13.50 (Me), 39.79, 39.95 (CH_2) 91.00, 108.20 (C–C), 126.88, 126.99, 128.39, 128.49, 129.54, 129.67, 131.20, 131.73 (Ph), 182.30, 187.18 (C=S). Calcd for $C_{20}H_{21}N_3OS_2$: C 62.63%, H 5.52%, N 10.96%, S 16.72%. Found: C 62.59%, H 5.59%, N 10.91%, S 16.68%. MS, m/z, (*I* %): 383[M^+](39), 324(44), 308(56), 279(52), 253(100), 194(67), 166(78).



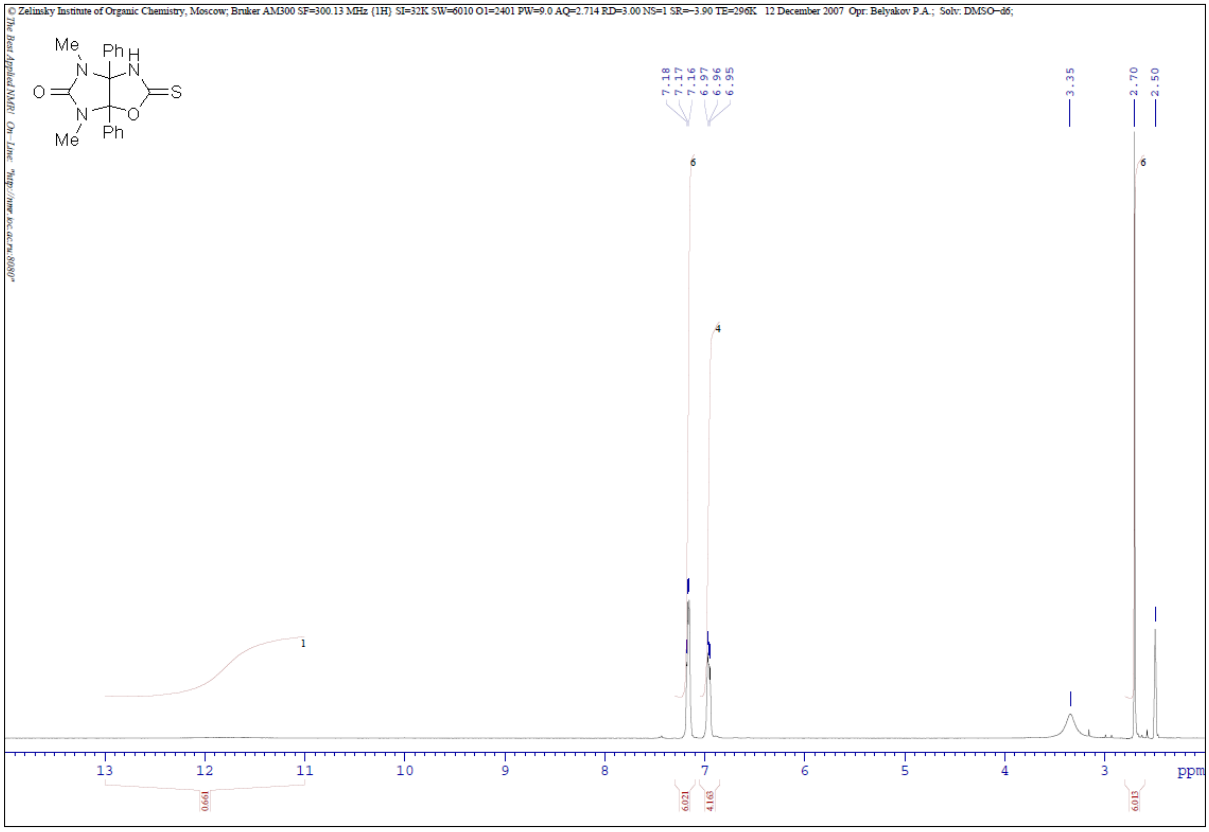


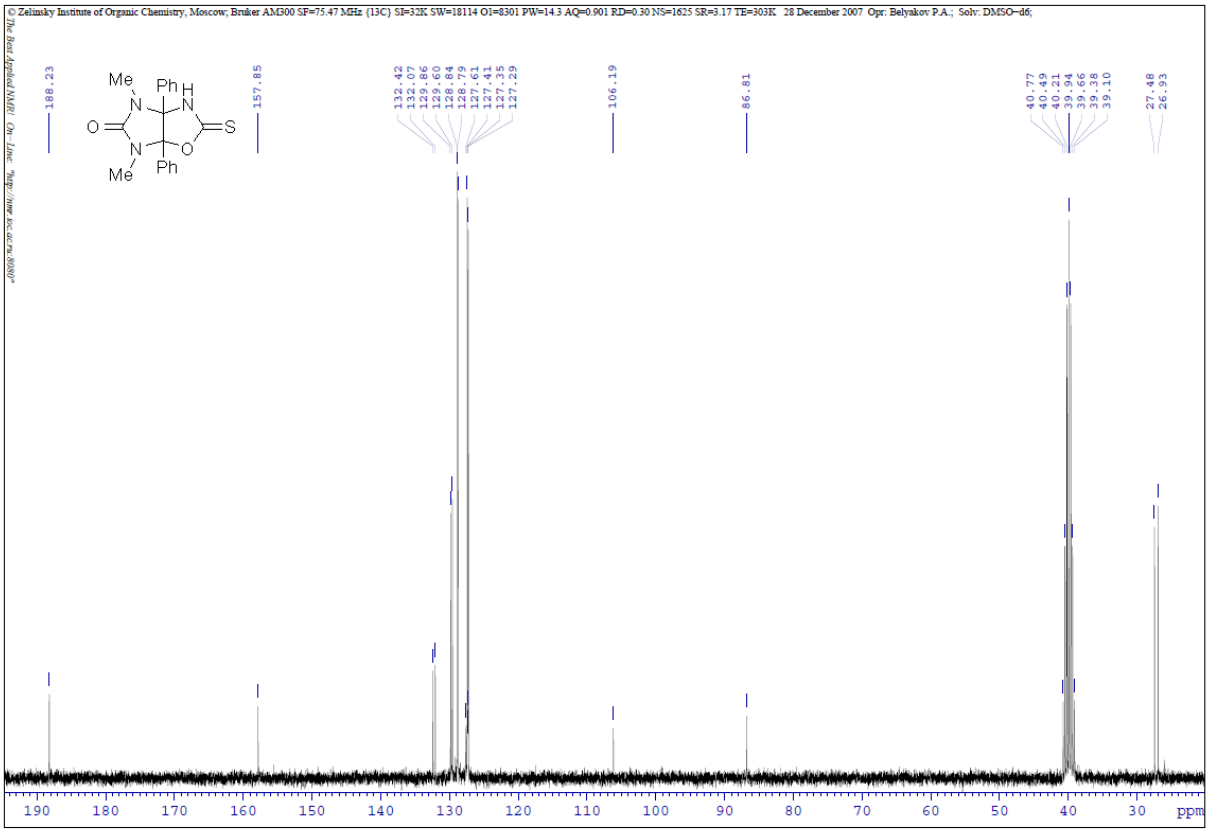


4,6-Dimethyl-3a,6a-diphenyl-2-thioxotetrahydro-2*H*-imidazo[4,5-d]oxazol-5(*3H*)-one **9**.

To the solution of 4,5-dihydroxy-1,3-dimethyl-4,5-diphenylimidazolidin-2-one **11** (1.01 g, 0.0034 mol) and KSCN (0.44 g, 0.0045 mol) in MeOH (40 ml) at r.t. was added AcOH (2.25ml). Reaction mixture was refluxed for 1 h. The reaction mixture was concentrated and precipitate was filtered off and recristallyzed from MeOH. The precipitate was filtered off and washed MeOH to furnish 0.97 g (84%) of the product.

Colorless hexahonal prisms, mp 227–230 °C. ^{1}H NMR, δ, ppm.; *J*/Hz (DMSO-d_6): 2.70 (s, 6 H, Me), 6.92 – 7.00 (m, 4 H, Ph), 7.12 – 7.22 (m, 6 H, Ph), 11.50 – 12.50 (br s, 1 H, NH). ^{13}C NMR, δ, ppm.; (DMSO-d_6): 26.93, 27.48 (Me), 86.81, 106.19 (C–C bridge), 127.29, 127.35, 127.41, 127.61, 128.79, 128.84, 129.60, 129.86, 132.07, 132.42 (Ph), 157.85 (C=O), 188.23 (C=S). Calcd for $C_{18}H_{17}N_3O_2S$: C 63.70%, H 5.05%, N 12.38%, S 9.45%. Found: C 63.68%, H 5.00%, N 12.34%, S 9.49%. MS, m/z, (*I* %): 339[M^+](32), 280(15), 264(21), 223(13), 203(31), 194(40), 165(18), 118(100).





1 V. V. Baranov, Yu. V. Nelyubina, A. A. Korlyukov and A. N. Kravchenko, *Mendeleev Commun.*, 2009, **19**, 211.

2 A. N. Kravchenko, V. V. Baranov, Yu. V. Nelyubina, G. A. Gazieva and I. V. Svitan`ko, *Russ. Chem. Bull., Int. Ed.*, 2012, **61**, 64.

3 R. G. Naville, *J. Org. Chem.*, 1958, **23**, 1588.

Crystal structure determination and data collection. X-ray diffraction experiments were carried out with a SMART 1000 CCD diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans) at 120K. The structures were solved by direct method. Note that the crystal **8b** was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell Now, and the two components were integrated using Apex2. The data were corrected for absorption using Twinabs, and the structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.413(2). All structures were then refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of NH groups in all cases and of OH group of a solvate metanole molecule in **8a** were found in difference Fourier synthesis; the H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model. Crystal data and structure refinement parameters are given in Table 1. All calculations were performed using the SHELXTL software [G.M. Sheldrick, A short history of SHELX, *Acta Cryst. A*, **2008**, *64*, 112-122].

Table 1. Crystal data and structure refinement parameters for **8a,b** and **9**.

	8a	**8b**	**9**
Empirical formula	$C_{19}H_{21}N_3O_2S_2$	$C_{20}H_{21}N_3OS_2$	$C_{18}H_{17}N_3O_2S$
Formula weight	387.51	383.52	339.41
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	P-1	$P2_1/n$
Z	4	2	4
a, Å	8.0624(4)	8.934(5)	9.6933(7)
b, Å	15.8738(7)	9.096(5)	11.9078(9)
c, Å	15.0658(7)	13.718(9)	14.7807(11)
α, °	90.00	73.824(11)	90.00
β, °	93.7220(10)	81.107(13)	96.327(2)
γ, °	90.00	65.090(8)	90.00
V, $Å^3$	1924.07(16)	970.1(10)	1695.7(2)
D_{calc} (g cm^{-1})	1.338	1.313	1.329
Linear absorption, μ (cm^{-1})	2.95	2.88	2.06
F(000)	816	404	712
$2\theta_{max}$, °	58	58	58
Reflections measured	20975	5382	18391
Independent reflections	5106	5382	4490
Observed reflections [$I > 2\sigma(I)$]	4047	4372	2943
Parameters	238	238	219

R1	0.0467	0.0353	0.0519
wR2	0.1228	0.0900	0.1247
GOF	1.004	1.004	0.999
$\Delta\rho_{max}$/ $\Delta\rho_{min}$ (e Å^{-3})	0.510/-0.385	0.354/-0.315	0.537/-0.259