Supporting information

Catalyzed ring transformation of cyclic *N*-aryl-azadiperoxides with participation of α,ω-dithiols

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A. General Information

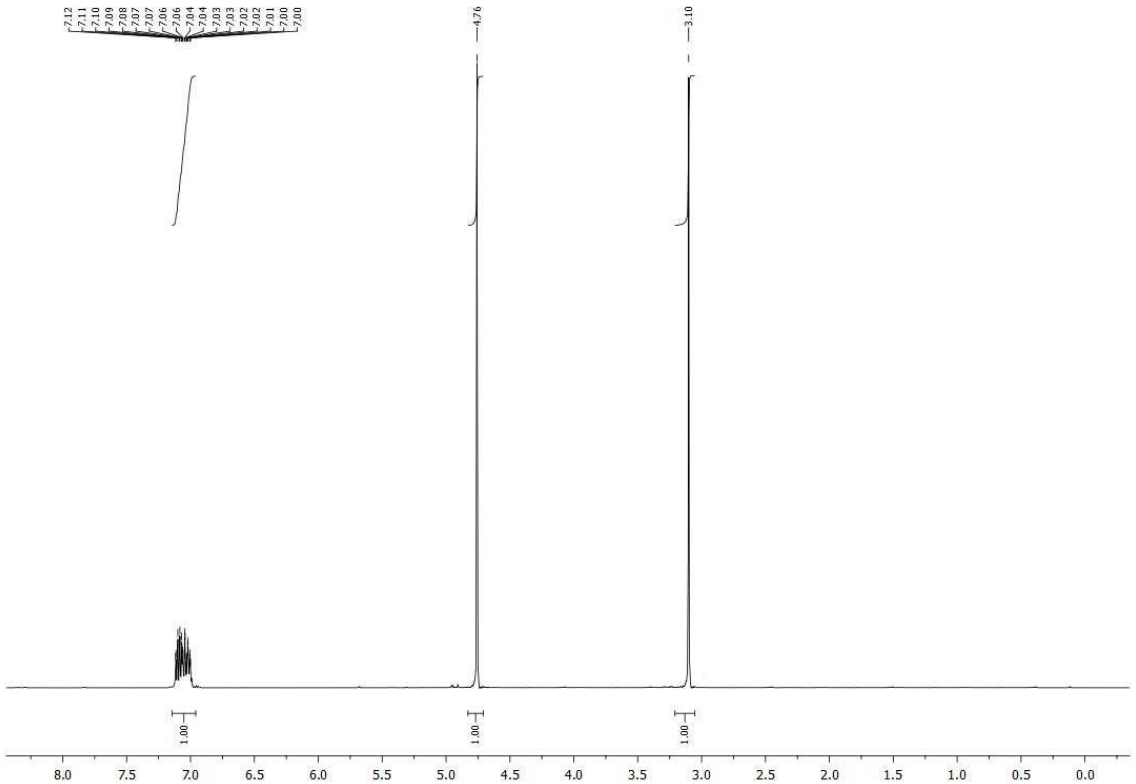
General Remarks. All reactions were performed at room temperature in air in round-bottom flasks equipped with a magnetic stir bar. The NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500.17 MHz for ^{1}H and 125.78 MHz for ^{13}C according to standard Bruker procedures. CDCl3 was used as the solvent, and tetramethylsilane, as the internal standard. The mixing time for the NOESY experiments was 0.3 sec. Mass spectra were recorded on a Bruker Autoflex III MALDI TOF/TOF instrument with α-cyano-4-hydroxycinnamic acid as a matrix. Samples were prepared by the dried droplet method. The C, H, and N were quantified by a Carlo Erba 1108 analyzer. The oxygen content was determined on a Carlo Erba 1108 analyzer. The progress of reactions was monitored by TLC on Sorbfil (PTSKh-AF-A) plates, with a 5:1 hexane : EtOAc mixture as the eluent and visualization with I_2 vapor. For column chromatography, silica gel MACHEREY-NAGEL (0.063-0.2 mm) was used.

The synthesis of the 10-aryl-7,8,12,13-tetraoxa-10-azaspiro[5.7]tridecanes **1, 14-24** was as reported in the literature.[1] Spectral data for compounds **8, 9, 25-35** completely coincide with those described in the literature.[2] Spectral data for compounds **10-13** completely coincide with those described in the literature.[3]

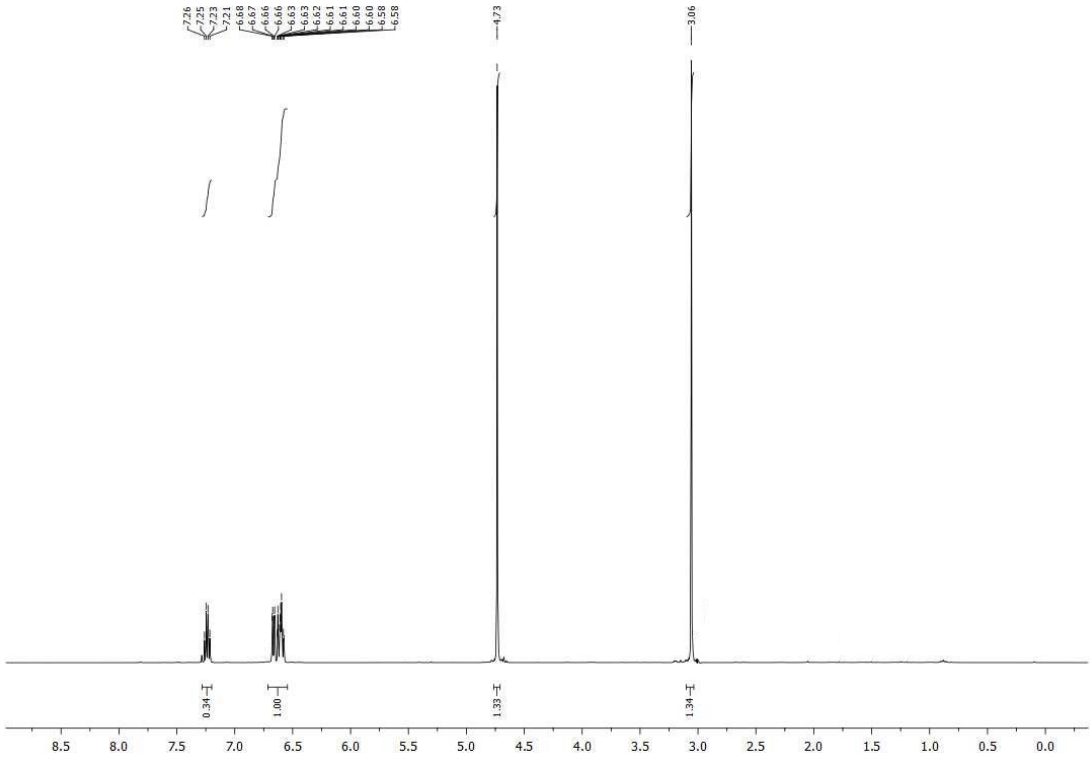
Catalyzed ring transformation reaction of 10-aryl-7,8,12,13-tetraoxa-10-azaspiro[5.7]tridecanes with α,ω-dithiols. General procedure. A Schlenk vessel mounted on a magnetic stirrer was charged under argon with THF (5 mL), $Co(OAc)_2$ (5 wt.%), alkan-α,ω-dithiols (1 mmol), and 10-aryl-7,8,12,13-tetraoxa-10-azaspiro[5.7]tridecanes[17] (1 mmol). The reaction mixture was stirred at ~20 °C for 20 h and THF was evaporated. Then CH_2Cl_2 (10 mL) was added and the mixture was washed with water (4×5 mL). The organic layer was separated and purified by column chromatography on SiO_2 using 10 : 1 PE : EtOAc as the eluent to isolate pure heterocyclic product (compounds **8-13, 25-35**). The progress of reactions was monitored by TLC, with a 5 : 1 hexane : EtOAc mixture as the eluent, visualization was performed with I_2 vapor.

B. Copy of NMR spectra

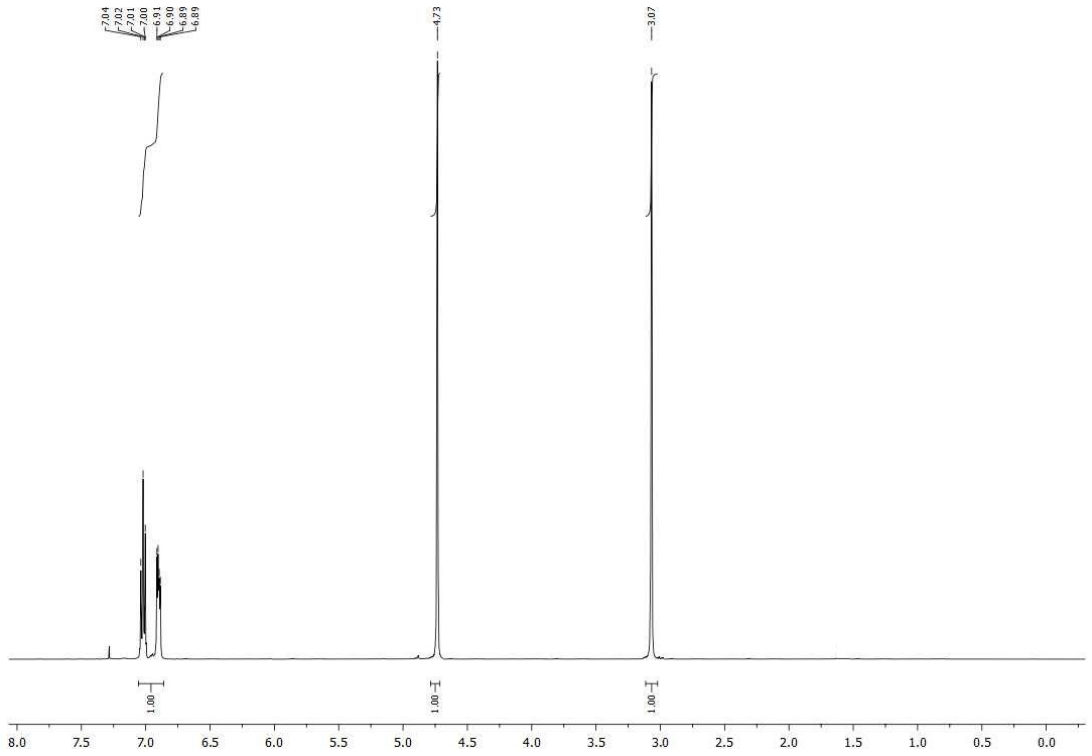
^{1}H-NMR spectrum of **3-(2-fluorophenyl)-1,5,3-dithiazepane 26**



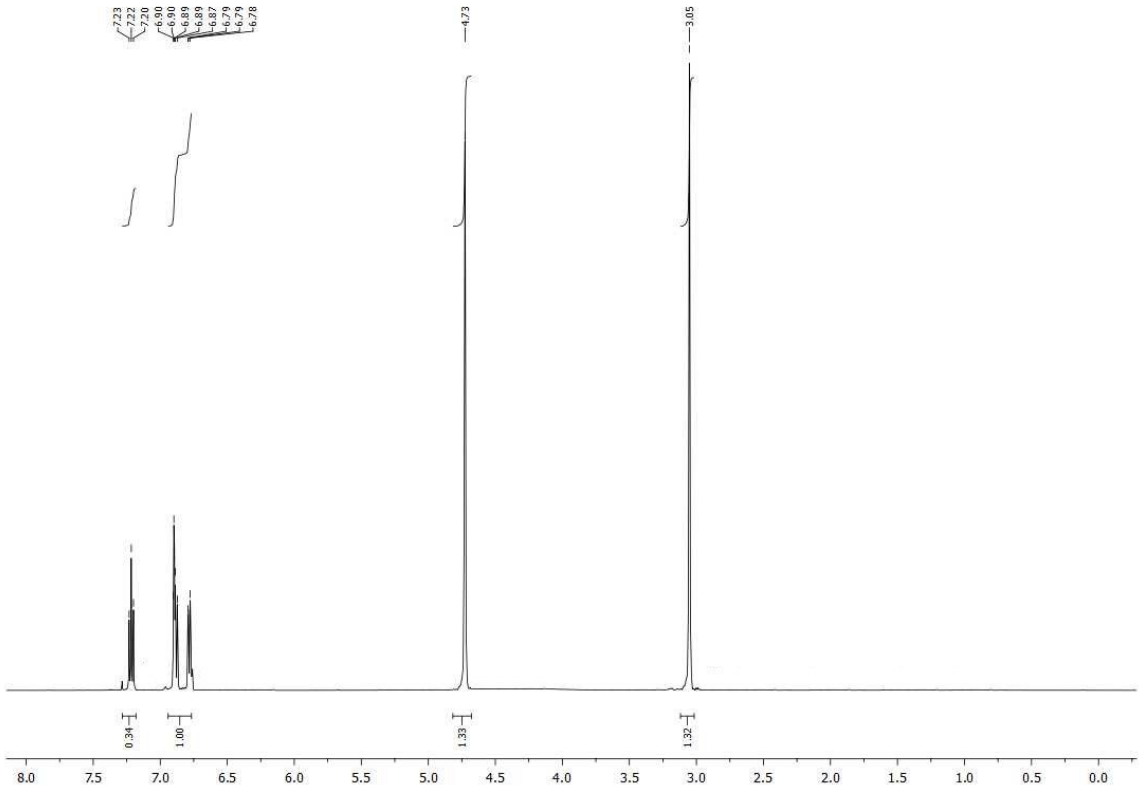
^{1}H-NMR spectrum of **3-(3-fluorophenyl)-1,5,3-dithiazepane 22**



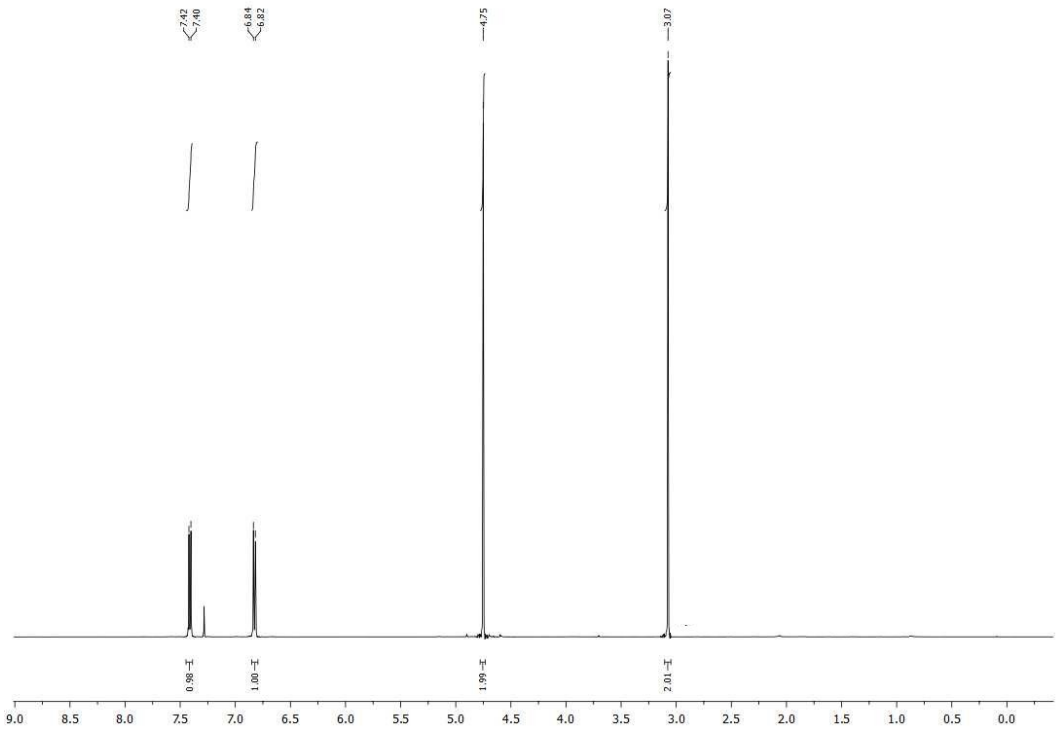
^{1}H-NMR spectrum of **3-(4-fluorophenyl)-1,5,3-dithiazepane 28**



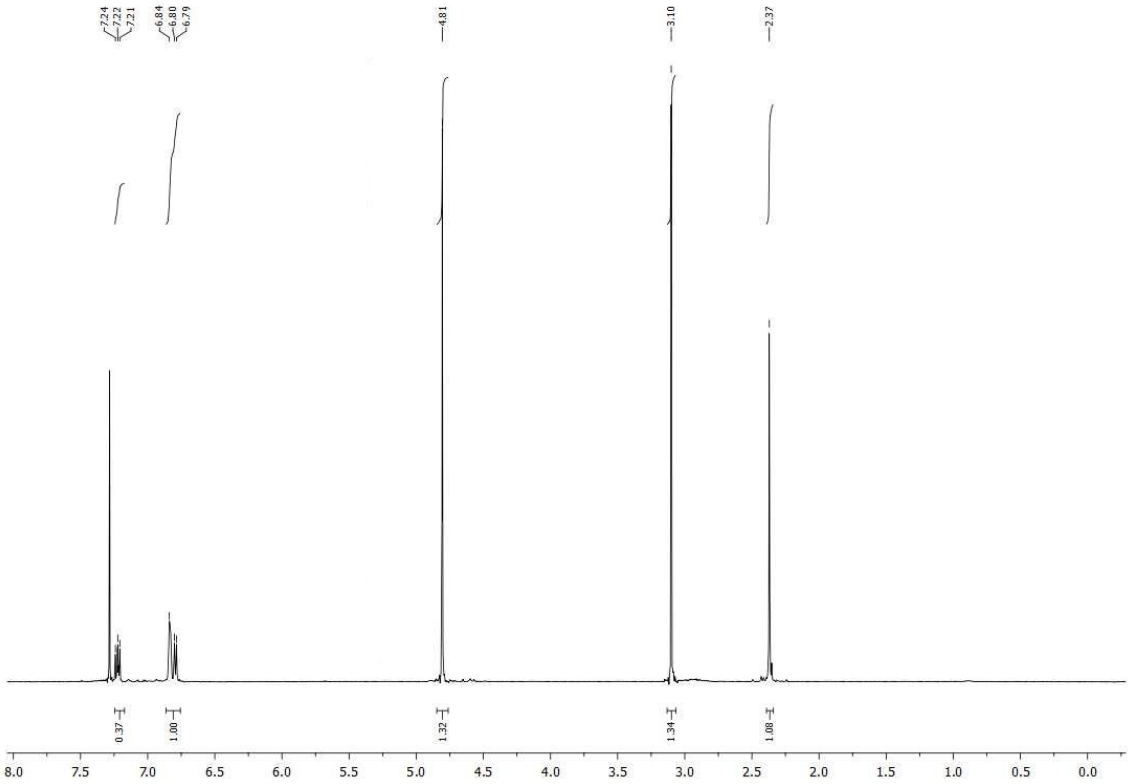
[1]H-NMR spectrum of **3-(3-chlorophenyl)-1,5,3-dithiazepane 30**



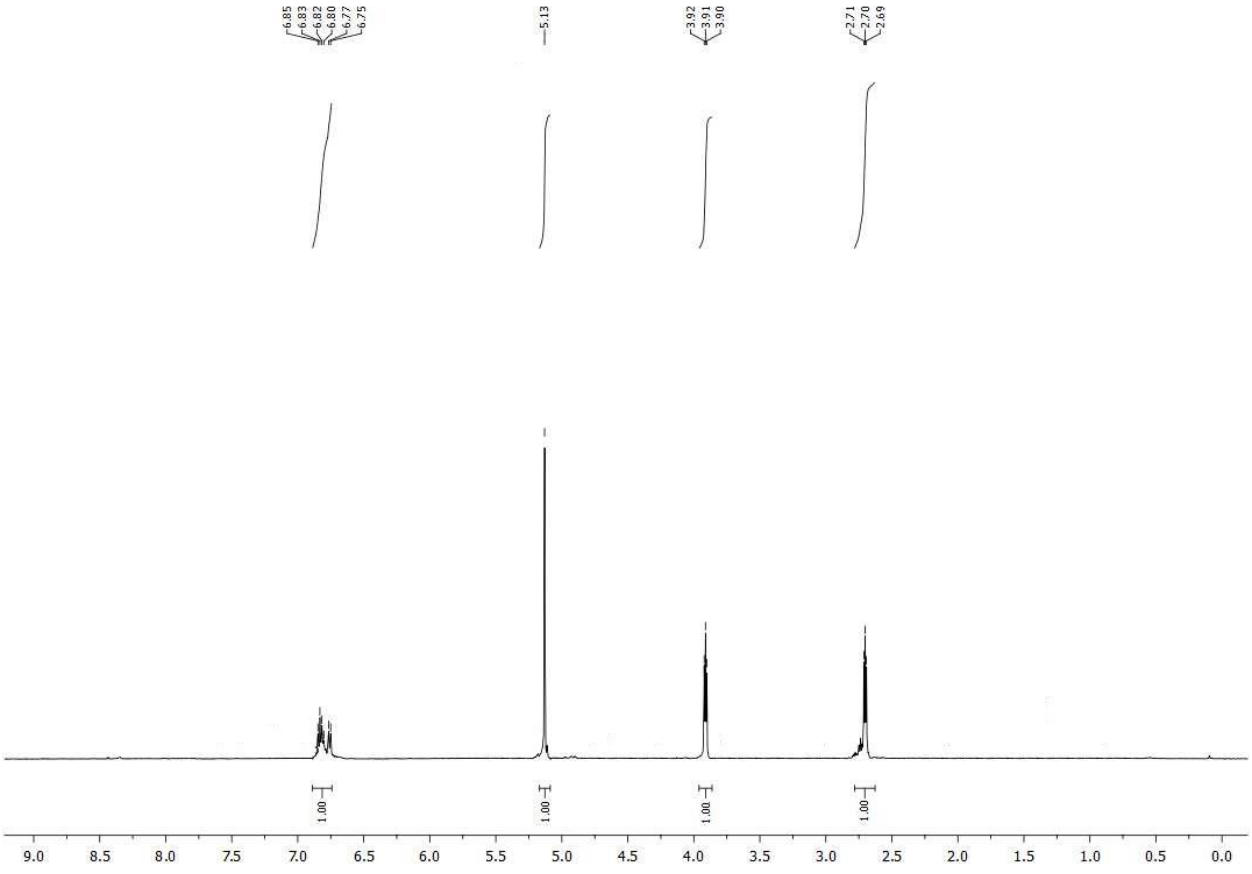
[1]H-NMR spectrum of **3-(4-bromophenyl)-1,5,3-dithiazepane 33**



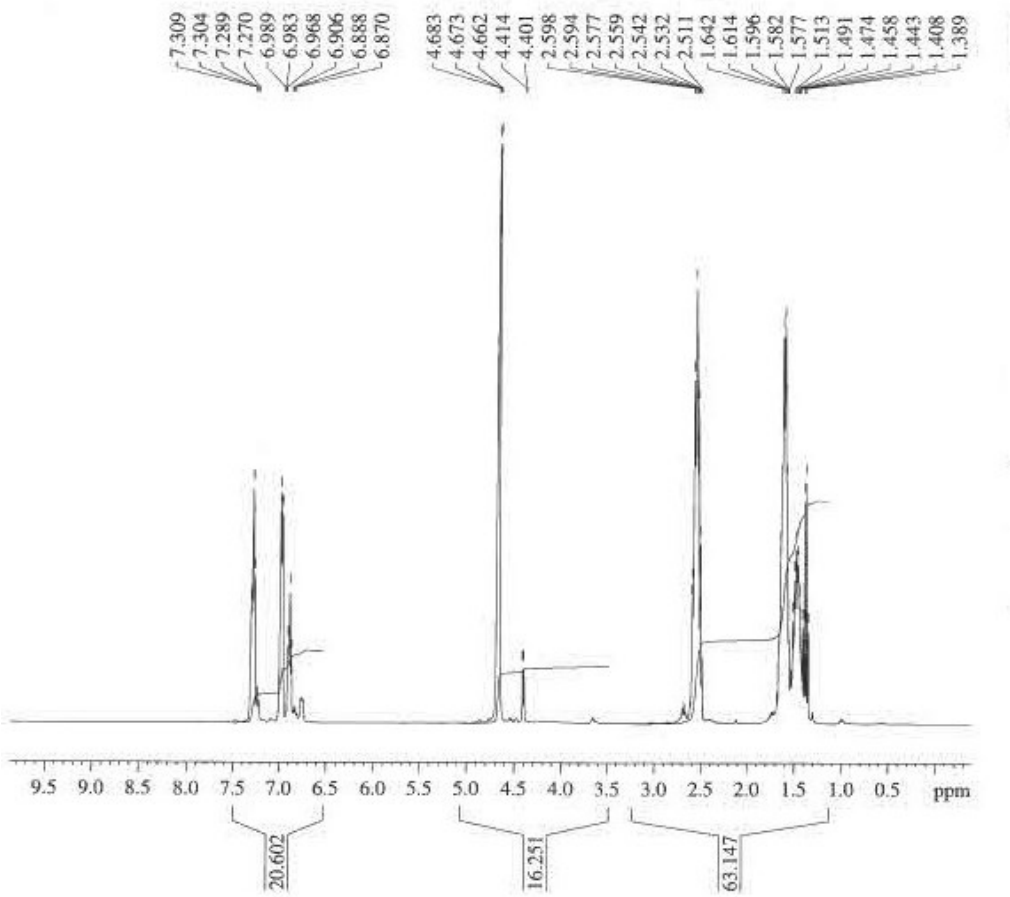
^{1}H-NMR spectrum of **3-(3-methylphenyl)-1,5,3-dithiazepane 35**



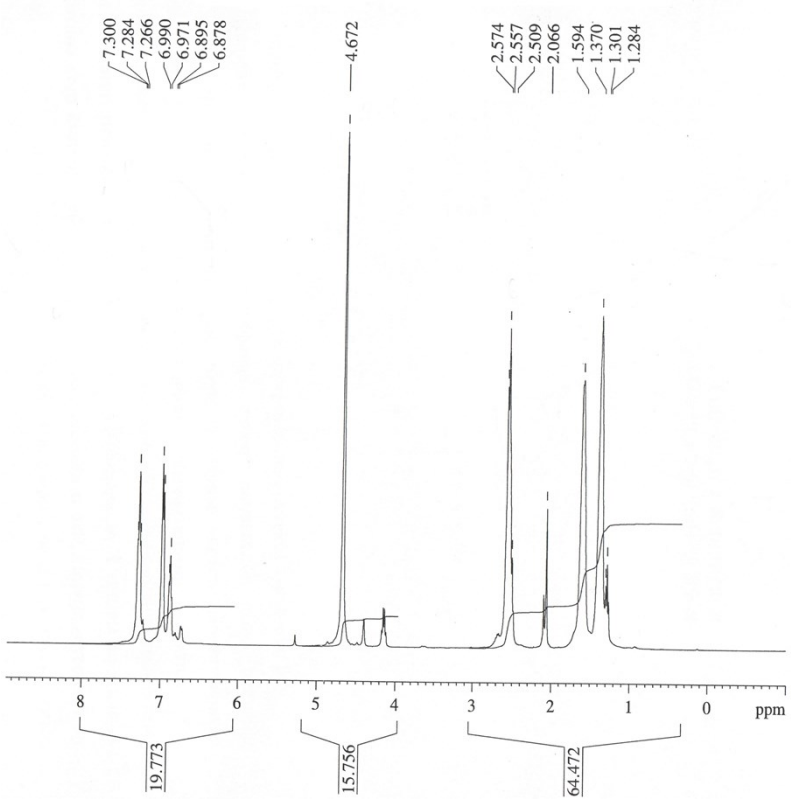
^{1}H-NMR spectrum of 9-phenyl-1,4-dioxa-7,11-dithia-9-azacyclotridecane 13



^{1}H-NMR spectrum of 3-phenyl-1,5,3-dithiazecane 11



^{1}H-NMR spectrum of 3-phenyl-1,5-dithia-3-azacycloundecane12



C. References

1. N. N. Makhmudiyarova, G. M. Khatmullina, R. Sh. Rakhimov, E. S. Meshcheryakova, A. G. Ibragimov, U. M. Dzhemilev, *Tetrahedron*, 2016, **72**, 3277.

2. N. N. Murzakova, , K. I. Prokof'ev, T. V. Tyumkina, A. G. Ibragimov, *Russ. J. Org. Chem*. 2012, **48**, 588.

3. N.N. Makhmudiyarova, L.V. Mudarisova, E.S. Meshcheryakova, A.G. Ibragimov, U.M. Dzhemilev, *Tetrahedron*, 2015, 71, 259.