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First examples of the synthesis of macroaluminahetero(N,S)cycles with the participation of metallo(Ti,Zr)cene catalysts

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Abstract: An efficient method is developed for the selective synthesis of 4-aryl-2,6,8,11-tetraethyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecanes via the reaction of 3-aryl-1,5,3-dithiazepanes with EtAlCl₂ involving the participation of a two-component catalyst based on Cp₂TiCl₂ and Cp₂ZrCl₂.

Keywords: catalysis, 3-aryl-1,5,3-dithiazepanes, magnesium, ethylaluminum dichloride, titanocene dichloride, zirconocene dichloride, substituted 1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecanes.

The discovery of the catalytic cycloalumination of olefins,¹ allenes,² and acetylenes³ provided a facile route to the selective synthesis of aluminacarbocycles. Aluminacarbocycles have attracted considerable interest due to their high reactivity in transformations without preliminary isolation to form cyclopropanes,⁴ cyclobutanes,⁵ thiophanes, selenophanes,⁶ phospholanes,⁷ cyclopropanols,⁸ cyclopentanols,⁹ and cyclopentanecarboxylic esters¹⁰ of of practical importance. Despite a diverse range of methods for the preparation of available,¹¹ reports aluminacarbocycles being on the selective synthesis of aluminahetero(N,S)cycles are lacking in the literature. Aluminaheterocycles are not formed upon catalytic cycloalumination of N,S,O-containing α -olefins¹² or by reactions of heterocycles with organoaluminum compounds,13

With the aim of developing an efficient method for the synthesis of new classes of N,Scontaining metallaheterocycles, and to examine the possibility of the synthesis of aluminaheterocycles by the insertion of Al atoms into the C-heteroatom bond in S,N-containing heterocycles, we studied the reaction of EtAlCl₂ with 3-aryl-1,5,3-dithiazepanes using catalysts based on metallocene dichlorides - Cp_2MCl_2 (M = Ti, Zr).

It is known that Cp_2Ti can insert into the C-S bond of substituted allylsulfanylbenzenes.¹⁴ We hypothesized that the *in situ* generation of titanocene by the reduction of Cp_2TiCl_2 with magnesium metal¹⁵ in a solution of an N,S-containing heterocycle would lead to the oxidative insertion of Cp_2Ti into the C-heteroatom bond of the starting heterocycle (by analogy with the reaction of Cp_2TiCl_2 with allylsulfanylbenzenes¹⁴), to form titanaheterocycles. We expected that the titanaheterocycles would react with $EtAlCl_2^{16}$ to afford the corresponding Al-containing heterocycles.

We studied the effect of the nature of the catalyst (Cp_2TiCl_2 , Cp_2ZrCl_2), the type of ethereal solvent (Et_2O , THF), the temperature (0-40 °C), and the reactant ratio on the yield of the resulting metallaheterocycles using the model reaction of 3-phenyl-1,5,3-dithiazepane with $EtAlCl_2$ in the presence of magnesium metal (powder) (Tables 1 and 2).

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We found that the reaction did not occur in the absence of catalysts or magnesium metal (powder). The Cp₂TiCl₂-catalyzed reaction of 3-phenyl-1,5,3-dithiazepane, EtAlCl₂, and Mg taken in a molar ratio of 0.05:1:5:5 afforded a mixture of aluminaheterocycles consisting of 2,6,8,11-tetraethyl-4-phenyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecane (1) and 2,4,7,9,12-pentaethyl-5-phenyl-1,8-dithia-5-aza-2,4,7,9,12-pentaeluminacyclododecane $(\mathbf{2})$ (Scheme 1) in a ratio of 45:55 and overall yield of 54% (Table 1). The overall yield of aluminaheterocycles 1 and 2 in the reaction catalyzed by Cp_2ZrCl_2 (5 mol%) was not higher than 8%. The reaction using a mixed catalyst composed of Cp_2TiCl_2 (5 mol%) and Cp_2ZrCl_2 (5 mol%) gave macroaluminaheterocycles 1 and 2 in a yield of 78% and ratio of \sim 15:1. It should be noted that the overall yield of 1 and 2 using γ -Al₂O₃-supported Cp₂TiCl₂ and Cp₂ZrCl₂ as the catalysts was not higher than 5%. The content of Cp_2TiCl_2 and Cp_2ZrCl_2 in the heterogeneous catalyst was 19.4 and 18.2 wt%, respectively (Table 2). The yields and the ratios of aluminaheterocycles 1 and 2 were determined based on hydrolysis products 3 and 4^{17}



Therefore, the reaction described above of 3-phenyl-1,5,3-dithiazepane, EtAlCl₂, Mg, Cp₂TiCl₂, and Cp₂ZrCl₂ in a molar ratio of 1:5:5:0.05:0.05 in a mixture of Et₂O–THF (1:1, v/v) at 40 °C afforded a mixture of 2,6,8,11-tetraethyl-4-phenyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecane (1)¹⁸ and 2,4,7,9,12-pentaethyl-5-phenyl-1,8-dithia-5-aza-2,4,7,9,12-pentaaluminacyclododecane (2) in a ratio of 94:6 in 78% yield.

Table 1. Effect of the nature of the catalyst and the reactant ratio on the yield of macroaluminaheterocycles 1 and 2. Reaction conditions: a mixture of THF and Et_2O as the solvent, 40 °C, 8 h

<i>N</i> -Phenyl-1,5,3- dithiazepane:EtAlCl ₂ :	[M]	Ratio of products		Overall yield of
Mg:[M], mmol		1	2	1+2 (%)
1:1:0:0	-	-	-	-
1:5:0:0	-	-	_	-
1:5:5:0	-	-	-	-
1:1:1:0.05	Cp ₂ TiCl ₂	-	-	-
1:2:2:0.05	Cp ₂ TiCl ₂	-	-	-
1:3:3:0.05	Cp ₂ TiCl ₂	-	-	-

1:4:4:0.05	Cp ₂ TiCl ₂	-	-	-	
1:5:0:0.05	Cp ₂ TiCl ₂	-	-	-	
1:5:5:0.05	Cp ₂ TiCl ₂	45	55	54	
1:5:5:0.05	Cp ₂ ZrCl ₂	61	39	8	
1:5:5:0.05:0.05	$Cp_2TiCl_2 + Cp_2ZrCl_2$	94	6	78	<
1:5:5:0.05:0.05	$Cp_2TiCl_2/Al_2O_3 + Cp_2ZrCl_2/Al_2O_3$	55	45	5	

Table 2. Effect of the nature of the ethereal solvent and the temperature on the yield ofN-phenylaluminaheterocycles1and2(3-phenyl-1,5,3-dithiazepane:EtAlCl_2:Mg:Cp_2TiCl_2:Cp_2ZrCl_2 = 1:5:5:0.05:0.05, 8 h)(3-phenyl-1,5,3-

Solvent	T (°C)	Ratio of J	Overall yield of $1+2$ (%)	
		1	2	
THF	0	46	54	50
THF	20	65	35	57
THF	50	71	29	68
Et ₂ O	0	48	52	32
Et ₂ O	20	55	45	41
Et ₂ O	35	86	14	55
THF-Et ₂ O	0	54	46	44
THF-Et ₂ O	20	59	41	59
THF-Et ₂ O	40	94	6	78

To examine the possibility of performing this reaction with other 3-aryl-1,5,3dithiazepanes, we studied the insertion of aluminum atoms into 3-[4-methyl(OCH₃, NO₂, Cl, Br)phenyl]-1,5,3-dithiazepanes **7a-d**¹⁹ via their reactions with EtAlCl₂ and Mg in the presence of the two-component catalyst, Cp₂TiCl₂–Cp₂ZrCl₂ (1:1) in the Et₂O–THF mixed solvent (1:1, v/v) at 40 °C. It was found that under the reaction conditions used, *p*-substituted 3-phenyl-1,5,3dithiazepanes reacted with EtAlCl₂ to give the corresponding 4-aryl-2,6,8,11-tetraethyl-1,7dithia-4-aza-2,6,8,11-tetraaluminacycloundecanes **9a-d**²⁰ in 73-88% yields (Scheme 2). The yields of **9a-d** were determined based on the hydrolysis products **10a-d**.²¹



Based on the experimental results and literature data, 15,16,22,23 the probable mechanism for the formation of the S,N-containing aluminaheterocycles is as follows. The first step involves reduction of the mixed catalyst (Cp₂TiCl₂ + Cp₂ZrCl₂) with magnesium metal¹⁵ to give Cp₂Ti and Cp₂Zr. Subsequent insertion of the *in situ* generated metallocene Cp₂M into the active C-S bonds of the 3-aryl-1,5,3-dithiazepane gives macroheterocycles **8**. The catalytic transmetallation^{16,22,23} of metallaheterocycles **8** with EtAlCl₂ produces 4-aryl-2,6,8,11-tetraethyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecanes **9**, accompanied by regeneration of the starting metallocene dichlorides (Scheme 3).



The structures of 4-aryl-2,6,8,11-tetraethyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecanes **9a-d** were determined by multinuclear NMR spectroscopy. The ²⁷Al NMR spectrum of macroheterocycles **9a-d** showed, in addition to the signal of the starting EtAlCl₂ ($\delta_{A1} = 106$), resonances at δ 50–55 characteristic of aluminum atoms bonded directly to a sulfur or nitrogen atom.²⁴ In the ¹H NMR spectra of aluminaheterocycles **9a-d**, the methylene protons of the ethyl substituents (CH₃CH₂Al) were responsible for the broadened high-field signals ($W_{1/2} = 3.5$ kHz) in the range δ –0.18 to 0.10, which is consistent with the literature data for trialkylalanes.²⁵ The signals of the methylene protons located between the aluminum atoms (Al-CH₂-CH₂-Al) of macrocycles **9a-d** were also observed in this δ range. The resonances due to the protons of the Al-CH₂-CH₂-Al and CH₃-CH₂-Al groups overlapped, whereas the chemical shifts of the corresponding carbon atoms of these moieties in the ¹³C NMR spectra were

substantially different. The carbon signals of the Al-<u>CH</u>₂-<u>C</u>H₂-Al group in macrocycles **9a-d** were shifted downfield to ~10 ppm with respect to the signals of the carbon atoms α to the Al atom in the ethyl substituent (CH₃-<u>C</u>H₂-Al). These results are illustrated in Figure 1 with product **9c** as an example. In the HSQC spectrum, the signals of the methylene protons bonded directly to the Al atom in the δ CH₂-Al range of -0.18 to 0.10 showed correlations to both the carbon signals at δ 0.0–0.2 and the carbon signals in the δ range 9.0–10.2. Apparently, the signals at δ 0.0–0.2 correspond to the carbon atoms bonded to aluminum (CH₃-<u>C</u>H₂-Al), and the signals at δ 9.0–10.2 can be assigned to the methylene carbon atoms located between the Al atoms (Al-<u>CH₂-CH₂-Al</u>) in macrocycles **9a-d**. The ¹³C NMR spectra of macrocycles **9a-d** showed signals at δ 28–30 which were assigned to the carbon atoms located between the nitrogen and aluminum atoms. The fact that these carbon atoms belong to the macroheterocycle was confirmed by their HMBC cross-peaks with the protons of the ethyl groups at the adjacent Al atom (Figure 1b). The presence of a series of cross-peaks between the narrow region of δ 9-10 for the carbon atoms and the whole broad region of the ¹H NMR spectrum from δ -0.3 also provided evidence in support of the heteronuclear couplings presented in Figure 2.





Figure 1. Heteronuclear correlation spectra of compound 9c, a) HSQC; b) HMBC



Figure 2. Key HMBC interactions for compound 9c

The above-described differences in the chemical shifts of the ethyl (CH₃-<u>C</u>H₂-Al) and ethane (Al-<u>C</u>H₂-<u>C</u>H₂-Al) α -carbon atoms bonded to the Al atoms observed in the ¹³C NMR spectra can be used additionally to establish the structure of macroaluminaheterocycle **2**, which we have proposed based on analysis of the hydrolysis and deuterolysis products. Since macrocycle **2** is non-symmetric, we envisaged that the HSQC spectrum of 2,4,7,9,12-pentaethyl-5-phenyl-1,8-dithia-5-aza-2,4,7,9,12-pentaaluminacyclododecane (**2**) would have a series of cross-peaks. Analysis of the HSQC spectrum of macroaluminaheterocycle **2** confirmed this fact (Figure 3). As can be seen from the spectrum, the signals at δ 9.5-10.5 belong to the Al<u>C</u>H₂CH₂Al group of macrocycle **2**, in which the carbon atoms are magnetically nonequivalent, and the signals at δ 4.0-6.5 were assigned to Al<u>C</u>H₂Al. The chemical shifts of this spacer appear, as expected, at higher field compared to the signals of Al<u>C</u>H₂CH₂Al due to the effect of geminal aluminum atoms.



Figure 3. Fragment of the HSQC spectrum of compound 2.

It should be noted that in the 1D 13 C NMR spectra of heterocycles **9a-d**, multiple splitting or broadening was observed for the signal of the methylene carbon atom located between the Al and N atoms (Al-<u>CH</u>₂-N); this signal does not coincide with other signals. This result can be attributed to the formation of diastereomeric complexes in solution. Actually, the coordination of Et₂O or THF solvent molecules to Al gives rise to stereogenic centers at each of the four aluminum atoms of macrocycles **9a-d** and, as a consequence, the number of diastereomeric complexes increases. Calculations of the thermodynamic parameters of complexation of macrocycles **9a-d** with four THF molecules showed that the formation of stereoisomeric complexes was energetically favorable. The Gibbs free energy of complexation of each THF molecule with the non-associated heterocycle is *ca*. 3.5 kcal/mol. Figure 4 presents the optimized structure of one of the stable diastereomers.



Figure 4. Optimized structure of the complex of macroaluminaheterocycle **1** with THF. In the calculated structure corresponding to the minimum in the potential energy surface of the complex (Figure 4), the bond lengths are as follows: d (Al-S) = 2.26 Å, d (Al-C_{cycle}) = d (Al-C_{acycle}) = 2.00 Å, d (Al-O) = 2.05 Å.

The structure of tetraaluminaheterocycle **1** was additionally confirmed by MALDI-TOF mass spectrometry using HCCA as the matrix. The spectrum showed a molecular ion peak at m/z 475.005 [M+K+H]⁺ (9%) and fragment ion peaks at m/z 461.327 [M-CH₂+K+H]⁺ (9%), m/z

356.347 [M-Ph-2H]⁺ (64%), and m/z 342.342 [M-Ph-N]⁺ (32%) indicative of the formation of aluminaheterocycle **1**.

In conclusion, we have developed a new method for the selective synthesis of 4-aryl-2,6,8,11-tetraethyl-1,7-dithia-4-aza-2,6,8,11-aluminacycloundecanes by the insertion of Al atoms into the C–S bonds in 3-aryl-1,5,3-dithiazepanes mediated by $EtAlCl_2$, with participation of a two-component catalyst based on Cp_2TiCl_2 and Cp_2ZrCl_2 .

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18. Synthesis of 2,6,8,11-tetraethyl-4-phenyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecane (1) and 2,4,7,9,12-pentaethyl-5-phenyl-1,8-dithia-5-aza-2,4,7,9,12-pentaaluminacyclododecane (2) (general procedure): Cp_2TiCl_2 (0.0125 g, 0.05 mmol), Cp_2ZrCl_2 (0.0146 g, 0.05 mmol), Mg powder (0.12 g, 5 mmol), N-phenyl-1,5,3-dithiazepane (1 mmol), THF (5 mL), and Et₂O (5 mL) were placed in a 50 mL glass reaction flask equipped with a

magnetic stir bar under dry Ar at 0 °C. The temperature was raised to 40 °C and the mixture was stirred for 8 h. The mixture was quenched by the addition of 25% aq. KOH. The organic layer was separated and the aqueous layer extracted with Et_2O (3 × 50 ml). The combined organic layer was dried over MgSO₄. Compounds **3** and **4** were identified by comparison with known samples.¹⁷

2,6,8,11-Tetraethyl-4-phenyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecane (1): colorless crystals (unstable in air). ¹H NMR (400.13 MHz, THF- d_8): δ -0.0 – 0.1 (br s, 4H, CH₂, H-9,10), - 0.2 – 1.2 (br s, 8H, CH₂, H-12,20,22,24), 0.9 – 1.1 (br s, 12H, CH₃, H-13,21,23,25), 1.5 – 1.7 (br s, 4H, CH₂, H-3,5), 6.4 - 6.5 (br s, 2H, CH, H-15,19), 6.6 – 6.7 (br s, 2H, CH, H-16,18), 7.0 – 7.2 (br s, 1H, CH, H-17). ¹³C NMR (100.62 MHz, THF- d_8): δ 0.0 – 3.0 (C-12,20,22,24), 8.8 – 10.6 (C-9,10,13,21,23,25), 28.6 and 30.6 (C-3 and C-5), 113.4 (C-16,18), 117.2 (C-15,19); 129.8 (C-17), 150.8 (C-14). ²⁷Al NMR (400.13 MHz, THF- d_8): δ 48.7 (W_{1/2} = 3.5 kHz).

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20. Synthesis of 2,6,8,11-tetraethyl-4-(aryl)-1,7-dithia-4-aza-2,6,8,11tetraaluminacycloundecanes **9a-d** (general procedure): Cp₂TiCl₂ (0.0125 g, 0.05 mmol), Cp₂ZrCl₂ (0.0146 g, 0.05 mmol), Mg powder (0.12 g, 5 mmol), *N*-aryl-1,5,3-dithiazepane (1 mmol), THF (5 mL), and Et₂O (5 mL) were placed in a 50 mL glass reaction flask equipped with a magnetic stir bar under dry Ar at 0 °C. The temperature was raised to 40 °C, and the mixture was stirred for 8 h. The mixture was quenched by the addition of 25% aq. KOH. The organic layer was separated and the aqueous layer was extracted with Et₂O (3 × 50 ml). The combined organic layer was dried over MgSO₄. Compound **10a** was identified by comparison with a known sample;¹⁷ compounds **10b-d** were identified by comparison with known samples.²¹

2,6,8,11-Tetraethyl-4-(4-methylphenyl)-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecane (**9a**): colorless crystals unstable (in air) . ¹H NMR (400.13 MHz, C₂D₅OC₂D₅, THF, C₂H₅OC₂H₅): δ -0.1 – 0.2 (br s, 12H, CH₂, H-9,10,12,20,22,24), 0.9 – 1.1 (br s, 12H, CH₃, H-13,21,23,25), 1.2 – 1.3 (br s, 4H, CH₂, H-3,5), 2.2 – 2.3 (br s, 3H, CH₃, H-26), 6.8 (d, *J* = 8.4 Hz, 2H, CH, H-16,18); 7.0 (d, 2H, *J* = 8.4 Hz, CH, H-15,19). ¹³C NMR (100.62 MHz, C₂D₅OC₂D₅, THF, C₂H₅OC₂H₅): δ 1.1 – 2.6 (C-12,20,22,24), 8.9 – 10.3 (C-9,10,13,21,23,25), 20.6 – 21.1 (C-26), 30.7 and 31.1 (C-3 and C-5), 117.0 (C-18), 117.1 (C-16), 128.0 (C-17), 130.1 – 130.5 (C-15,19), 144.9 – 145.5 (C-14). ²⁷Al NMR (400.13 MHz, C₂D₅OC₂D₅, THF, C₂H₅OC₂H₅): δ 54.3 (W_{1/2} = 3.5 kHz).

2,6,8,11-Tetraethyl-4-(4-methoxyphenyl)-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecane (**9b**): colorless crystals (unstable in air). ¹H NMR (400.13 MHz, C₂D₅OC₂D₅, THF, C₂H₅OC₂H₅): δ -0.1 – 0.3 (br s, 12H, CH₂, H-9,10,12,20,22,24), 1.0 – 1.1 (br s, 12H, CH₃, H-13,21,23,25), 1.4 – 1.6 (br s, 4H, CH₂, H-3,5), 2.2 – 2.3 (br s, 3H, CH₃, H-26), 6.7 (d, *J* = 8.1 Hz, 1H, CH, H-16); 6.8 (d, *J* = 8.1 Hz, 1H, CH, H-18), 7.0 (d, *J* = 8.1 Hz, 1H, CH, H-15); 7.1 (d, *J* = 8.1 Hz, 1H, CH, H-19). ¹³C NMR (100.62 MHz, C₂D₅OC₂D₅, THF, C₂H₅OC₂H₅): δ -0.1 – 1.1 (C-12,20,22,24), 8.0 – 9.7 (C-9,10,13,21,23,25), 19.3 – 20.1 (C-26), 28.4 and 28.6 (C-3 and C-5), 112.9 (C-18), 113.3 (C-16), 127.9 (C-19), 128.8 (C-15), 129.4 (C-17), 141.4 (C-14). ²⁷Al NMR (400.13 MHz, C₂D₅OC₂D₅, THF, C₂H₅OC₂H₅): δ 54.7 (W_{1/2} = 3.3 kHz).

4-(4-Chlorophenyl)-2,6,8,11-tetraethyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecane (**9c**): colorless crystal (unstable in air). ¹H NMR (400.13 MHz, THF- d_8): δ -0.1 – 0.1 (br s, 4H, CH₂, H-9,10), -0.2 – 1.2 (br s, 8H, CH₂, H-12,20,22,24), 0.9 – 1.0 (br s, 12H, CH₃, H-13,21,23,25), 1.3 – 1.4 (br s, 4H, CH₂, H-3,5), 6.5 – 6.9 (br s, 2H, CH, H-16,18), 6.9 – 7.0 (br s, 2H, CH, H-15,19). ¹³C NMR (100.62 MHz, THF- d_8 ,): δ = 1.0 – 3.1 (C-12,20,22,24), 8.9 – 10.4 (C-9,10,13,21,23,25), 28.5 and 30.0 (C-3 and C-5), 113.7 – 114.4 (C-16,18), 129.0 – 129.9 (C-15,19), 141.5 (C-14), 153.4 (C-17). ²⁷Al NMR (400.13 MHz, THF- d_8): δ = 53.1 (W_{1/2} = 3.1 kHz). 4-(4-Bromophenyl)-2,6,8,11-tetraethyl-1,7-dithia-4-aza-2,6,8,11-tetraaluminacycloundecane (**9d**): colorless crystal (unstable in air). ¹H NMR (400.13 MHz, THF- d_8): δ -0.0 (br s, 12H, CH₂,

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H-9,10,12,20,22,24), -0.6 – 2.8 (br s, 12H, CH₃, H-13,21,23,25), 1.2 – 1.4 (br s, 4H, CH₂, H-3,5), 6.5 (br s, 2H, CH, H-16,18), 7.0 (br s, 2H, CH, H-15,19). ¹³C NMR (100.62 MHz, THF-*d*₈): δ 0.6 – 2.9 (C-12,20,22,24), 9.1 – 10.0 (C-9,10,13,21,23,25), 28.6 and 29.7 (C-3 and C-5), 114.5 (C-16,18), 129.5 (C-15,19), 144.0 (C-14), 151.0 (C-17). ²⁷Al NMR (400.13 MHz, THF-*d*₈): δ = 41.6 (W_{1/2} = 3.1 kHz).

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Graphical Abstract

First examples of the synthesis of macroaluminahetero(N,S)cycles Et with the participation of metallo(Ti,Zr)cene catalysts +5Mg+5EtAlCl₂ Ar-Ar Ēt Natalia Ν. Makhmudiyarova, Liliya V. Mudarisova, Tatiyana V. Ar = C_6H_5 , p-Me C_6H_4 , p-MeO C_6H_4 , p-Cl C_6H_4 , p-Br C_6H_4 Tyumkina, Vasiliy M. Yanybin, Askhat G. Ibragimov, Usein M. Dzhemilev MAN