Copper(I)-Catalyzed Amination of Halogenopyridines with Polyamines

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Cu^I-Catalyzed amination of 2-bromo-, and 2-, 3-, and 4-iodopyridines with tri- and tetraamines aimed at the synthesis of *N*,*N*′-diheteroaryl derivatives was studied. A strong dependence of the product yields on the nature of starting compounds and the ligand used was observed. The increase in the number of ethene-1,2-diamine fragments in the polyamine structure led to the increase in the yields of polyheteroarylated compounds, whereas propane-1,3-diamine fragments favored the formation of monopyridinyl derivatives and promoted the heteroarylation of the secondary amino groups. 2-Iodopyridine, as a more reactive compound, readily formed *N*,*N*-diarylated products. The best yields of the target *N*,*N*′-dipyridin-2-yl derivatives were 76% in the case of the triamine and 68% in the case of the tetraamine. A comparison of Cu^I- and Pd^0-mediated heteroarylation of polyamines was also presented.

Introduction. – Linear diamines and polyamines attracted substantial interest due to their versatile biological activities [1–4], *e.g.*, natural tri- and tetraamines and their synthetic analogs can act as anticancer agents [5]. Polyamines containing aromatic moieties are also interesting physiologically active compounds [6]; however, in the majority of the cases, the aromatic group is bound to the N-atoms *via* a CH_2 linker. The introduction of pyridine moieties in the polyamine structure is of great value due to extraordinarily high and versatile biological activities of aminopyridines [7]. However, only one example, documented in the literature concerning non-catalytic formation of *N*,*N*′-dipyridinyl derivatives of linear diamines [8], clearly demonstrates the unexplored character of this topic. Catalytic methods for the construction of $C(sp^2)$–N bonds have been successfully applied to the synthesis of various aminopyridines. In 1996, the first successful Pd^0-catalyzed amination of 2-bromopyridine with simple monoamines was reported by *Wagaw* and *Buchwald* [9], and various catalytic systems were investigated for 3-bromopyridine amination [10–13] and 2,6-dibromopyridine diamination [14][15]. The reactivity of the halogen atoms at C(2) and C(3) was found to be dramatically different [16][17], as well as the difference in the reactivity of Cl- and I-atoms [18–20], which were used for the selective monoamination of pyridine derivatives *via* I substitution. Our contribution to this field was the investigation of Pd^0-catalyzed arylation of linear polyamines with chloro- and bromopyridines, as well as the synthesis of macrocycles comprising 2,6- and 3,5-diaminopyridine moieties [21–24]. It was found out that 2-Br-substituted pyridines participated not only in *N*-heteroarylation of the primary NH_2 groups of polyamines, but also in *N*,*N*-diarylation of these

groups, and also the non-catalytic substitution of Br by a ^{t}BuO group was observed in the reactions catalyzed with a standard [Pd(dba)$_2$]/BINAP/^{t}BuONa system [24]. Ni-Mediated reactions, on the other hand, were widely employed for the amination of 3-chloropyridines [25–28], and several studies were focused on the application of the catalysis by Cu^I complexes. 2-Iodo- and 2-bromopyridines were shown to readily participate in the Cu^I-mediated amination with monoamines [29–32], less reactive 3-iodo- and 3-bromopyridines were also successfully used in the amination reactions [29][31–35]; however, all literature data cover only monoamines in the Cu^I-catalyzed reactions with halopyridines.

Recently, we have carried out an in-depth investigation of the Cu^I-catalyzed arylation of polyamines and oxadiamines using aryl bromides and iodides, and we encountered substantial difficulties concerning the reactivity of polyamines in the presence of Cu^I catalysts and found an appropriate catalytic system for polyamine arylation [36]. In the present study, we searched for the conditions of polyamine heteroarylation with halopyridines in view of the synthesis of valuable *N*,*N*′-dipyridinyl derivatives.

2. Results and Discussion. – The Cu^I-catalyzed heteroarylation of polyamines **1**–**6** (*Fig.*) was studied using 2- and 3-bromopyridines, and 2-, 3-, and 4-iodopyridines. In accordance with our previous investigations [36], we applied 2.2–2.5 equiv. of halogenopyridines and used the catalytic systems CuI/L-proline (CuI/**L1**) and CuI/*N*,*N*-dimethylglycine (CuI/**L2**); MeCN and EtCN were employed as solvents, and Cs_2CO_3 as a base. The reactions were conducted under Ar with different amounts of the catalytic systems (1–10 mol-% CuI/2–20 mol-% ligand) at concentrations in the range of 0.25–0.5M, in boiling MeCN or EtCN, with 2 equiv. of ligand always being taken for 1 equiv. of CuI. The compositions of the reaction mixtures were analyzed by ^{1}H-NMR, the main reaction products were isolated by column chromatography on silica gel, and the yields of isolated compounds are given throughout the present contribution.

The simplest diethylenetriamine (= bis(2-aminoethyl)amine; **1**) reacted with halopyridines mainly to give complex reaction mixtures due to low selectivity of the amination process (arylation of the primary and secondary amino groups, *N*,*N*-diarylation of the primary amino groups). It may be explained by a strong chelation of Cu^I, which severely affected its catalytic activity. Only in the reaction with 2-iodopyridine at low catalyst loading (1 mol-%), we managed to obtain the target *N*,*N*′-

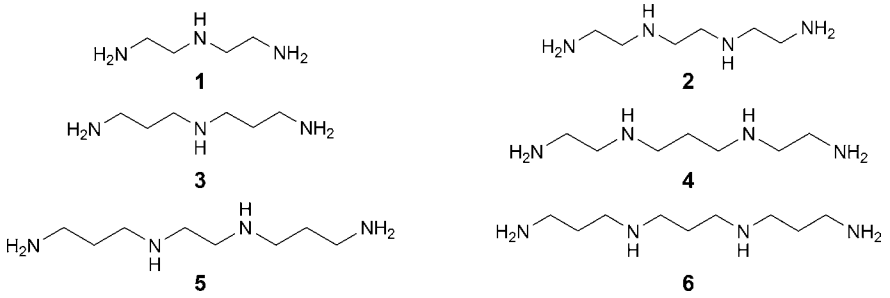
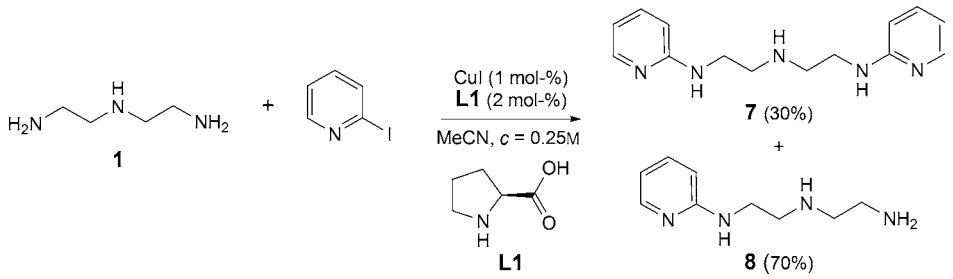


Figure. *Tri- and tetraamines used in the Cu^I-catalyzed heteroarylation*

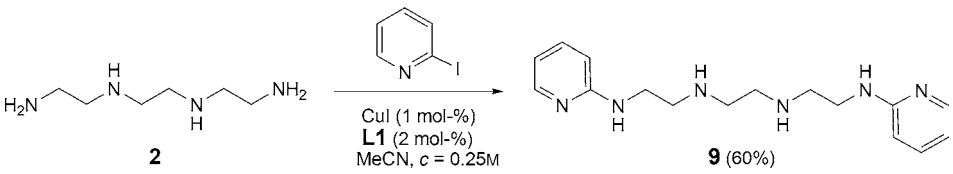
diarylation product **7** in 30% yield, together with the monoamination product **8** (*Scheme 1*). It should be noted that the reaction with less reactive 3-iodopyridine gave only a mixture of di- and polyarylated products.

Scheme 1



A similar result was observed in the reaction of triethylenetetraamine (= *N*,*N*′-Bis(2-aminoethyl)ethane-1,2-diamine; **2**) with 2-iodopyridine: under the same conditions, the *N*,*N*′-diheteroarylation product **9** was isolated in 60% yield (*Scheme 2*). Again, the attempts to realize selective disubstitution with 3-iodopyridine failed.

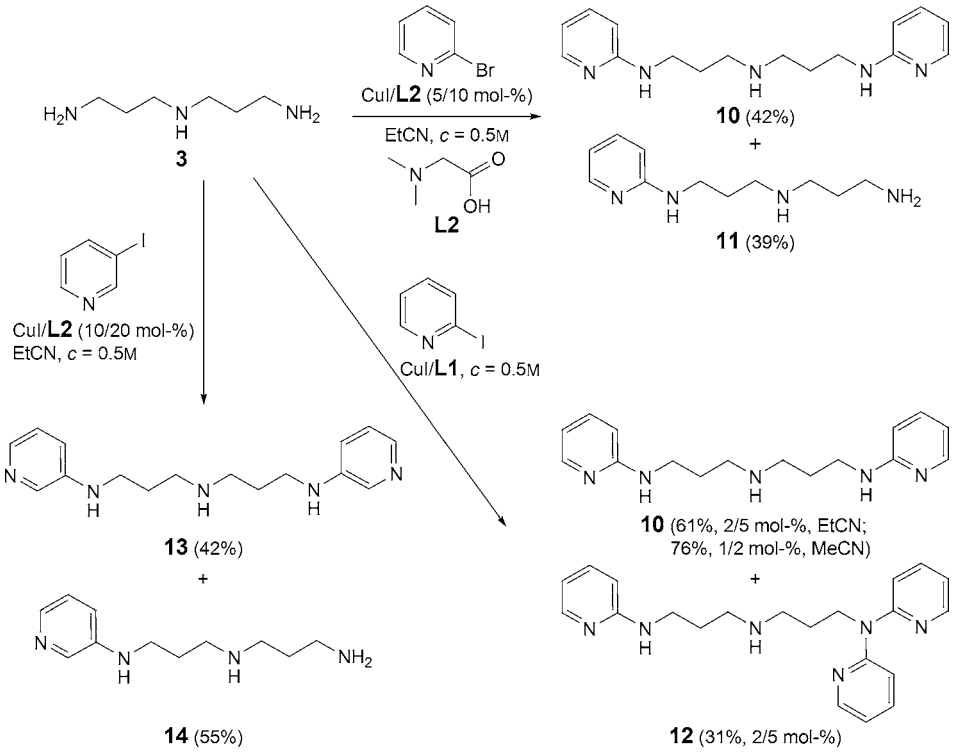
Scheme 2



The heteroarylation of the bis(3-aminopropyl)amine (**3**) proceeded more selectively, possibly due to its lower reactivity. 2-Bromopyridine was found to be suitable for the synthesis of *N*,*N*′-dipyridinyl derivative **10** using the CuI/**L2** system (5/10 mol-%) in EtCN (*Scheme 3*). The monopyridinyl triamine derivative **11** was isolated in a comparable yield. The reaction with a more active 2-iodopyridine required lower catalyst loadings, and the use of **L1** instead of **L2**. With 2 mol-% catalyst, the target derivative **10** was obtained in 61% yield together with the N^1,N^1,N^3-tripyridinyl triamine **12** (31%); with 1 mol-% catalyst in MeCN, the yield of compound **10** increased to 76%. Less reactive 3-iodopyridine required much more catalyst (CuI/**L2**, 10/20 mol-%); however, the monopyridinyl derivative **14** prevailed over N^1,N^3-dipyridinyl product **13** (55 and 42%, resp.).

The attempts using 4-iodopyridine were unsuccessful: at higher catalyst loadings, polyarylation products were obtained, and lowering the amount of catalyst led to partial conversion. Also 3-bromopyridine was completely inefficient in the reactions with polyamines due to its very poor reactivity. Therefore, we did not use it in further studies.

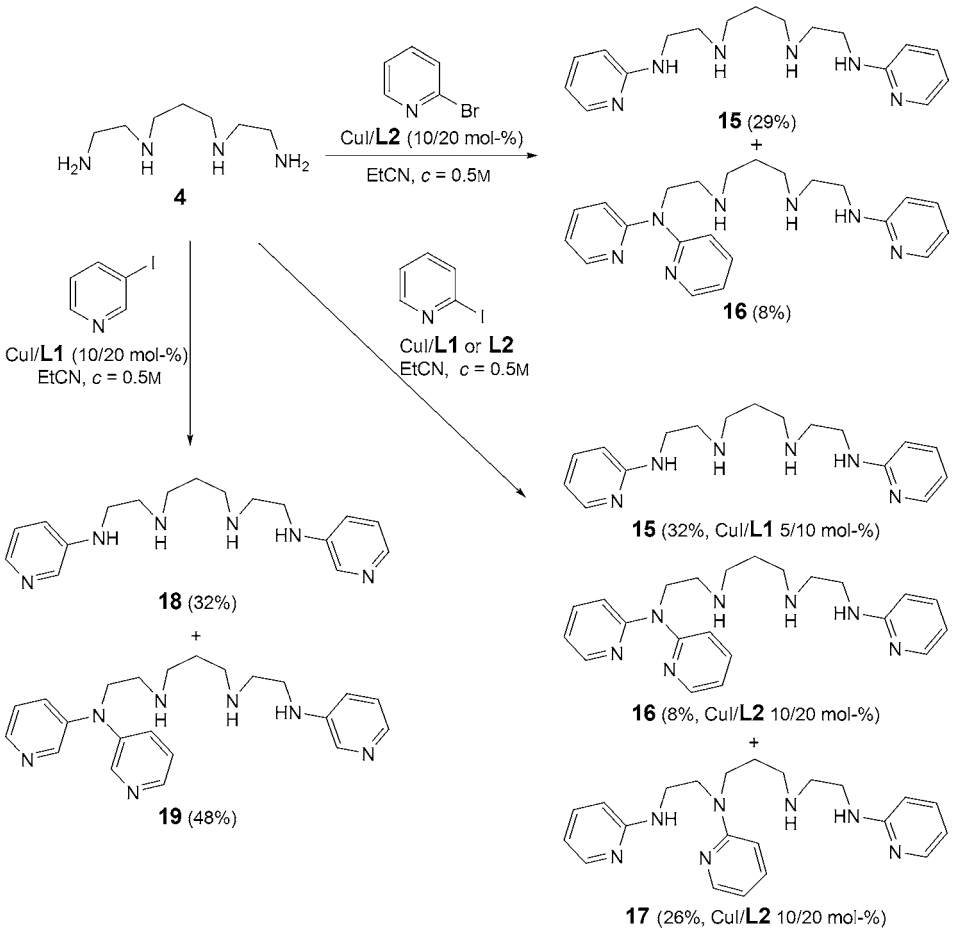
Scheme 3



The Cu-catalyzed heteroarylation of *N*,*N*′-bis(2-aminoethyl)propane-1,3-diamine (**4**), which possesses two ethylenediamine and one triethylendiamine moieties, was a challenge.

The reaction of **4** with 2-bromopyridine in the presence of CuI/**L2** (10/20 mol-%) led to the desired product **15** in 29% yield, and triarylated by-product **16** was also isolated (*Scheme 4*). The heteroarylation using a more reactive 2-iodopyridine gave a similar yield of the compound **15** (32%), while 3-iodopyridine also afforded the N^1,N^4-dipyridinyl derivative **18** in 32% yield. In the latter case, the second product, N^1,N^1,N^4-tripyridinyl substituted tetraamine **19**, was obtained even in a higher yield (48%). Numerous experiments with 2- and 3-iodopyridines were carried out in order to suppress *N*,*N*-diarylation of the primary amino group; we used lower catalyst loadings (2/5 and 1/2 mol-%), MeCN instead of EtCN as a solvent, lowered the concentration of the reagents (0.25 instead of 0.5M), and also used other ligands (**L2**, **L1** with Ph_3P or Ph_3PO); however, all these attempts did not increase the yields of the target N^1,N^4-dipyridinyl derivatives due to the formation of polyheteroarylated species. In the majority of cases, they could not be obtained as individual compounds, but, in the reaction with 2-iodopyridine catalyzed with CuI/**L2** (10/20 mol-%), we managed to isolate **16** in 8% yield and an isomeric N^1,N^2,N^4-tripyridinyl substituted tetraamine **17** in 26% yield (*Scheme 4*). The latter compound was also detected among other

Scheme 4



polyheteroarylated products in many other reactions of 2-iodopyridine with **4** carried out under different conditions. Compounds **16** and **17** can be easily distinguished by their ^{1}H-NMR spectra in mixtures: the first exhibits a typical *triplet* at δ(H) 4.28, which is the most upfield-shifted aliphatic H-signal corresponding to the CH_2 group in the (pyridin-2-yl)$_2$NCH_2 fragment, the second displays *a triplet* at δ(H) 3.68 which is also the most upfield-shifted aliphatic H-signal corresponding to the CH_2 group in the (pyridin-2-yl)NCH_2 fragment.

The heteroarylation of another tetraamine, *N*,*N*′-bis(3-aminopropyl)ethane-1,2-diamine (**5**), containing one ethylenediamine and two trimethylenediamine fragments, turned out to be more successful. The reaction with 2-bromopyridine catalyzed with CuI/**L1** (10/20 mol-%) provided the target N^1,N^4-dipyridinyl derivative **20** in 28% yield, and the application of CuI/**L2** system increased the yield to 52% (*Scheme 5*, and *Table 1*, *Entries 1* and *2*). The same yield of **20** was obtained using 2-iodopyridine in the

Scheme 5

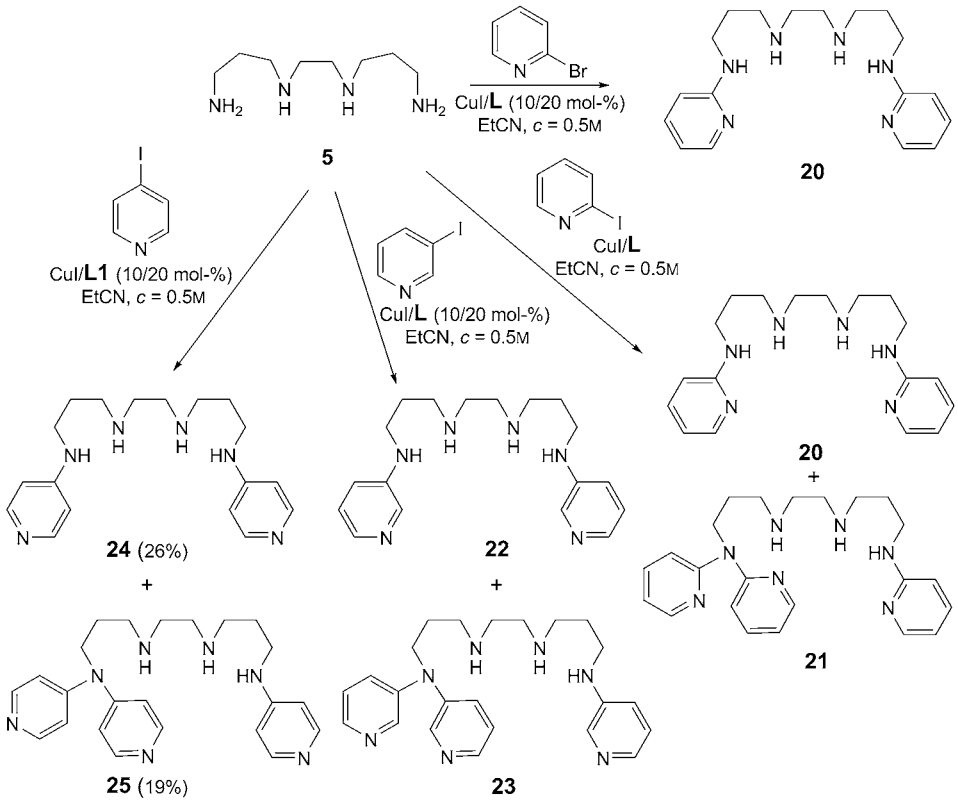


Table 1. *Heteroarylation of Tetraamine* **5** *with Halogenopyridines in EtCN*

Entry	Halogenopyridine	Ligand	CuI/**L** [mol-%]	Conc. [M]	Products (yield [%])
1	2-Bromopyridine	**L2**	10/20	0.5	**20** (28)
2	2-Bromopyridine	**L1**	10/20	0.5	**20** (52)
3	2-Iodopyridine	**L1**	10/20	0.5	**20** (52)
4	2-Iodopyridine	**L1**	2/5	0.5	**20** (49); **21** (6)
5	2-Iodopyridine	**L2**	10/20	0.5	**20** (32); **21** (12)
6	3-Iodopyridine	**L1**	10/20	0.5	**22** (43)
7	3-Iodopyridine	**L2**	10/20	0.5	**22** (16); **23** (9)
8	4-Iodopyridine	**L1**	10/20	0.5	**24** (26); **25** (19)

presence of CuI/**L1** (10/20 mol-%) catalyst (*Table 1*, *Entry 3*), it was still almost the same as obtained with 2 mol-% catalyst (*Table 1*, *Entry 4*), while with CuI/**L2** the reaction proceeded less efficiently and afforded the target product in 32% yield (*Table 1*, *Entry 5*). In all cases, polyarylation was observed as side process, and we isolated the individual N^1,N^1,N^4-tripyridinyl derivative **21** in some cases (*Table 1*, *Entries 4* and *5*). It should be noted that even with 0.5 mol-% catalyst, *N*,*N*-diarylation

was not suppressed, according to ^{1}H-NMR analysis of the reaction mixture. N^1,N^4-Dipyridinyl tetraamine **22** was usually synthesized by the reaction with 3-iodopyridine in the presence of CuI/**L1** (10/20 mol-%; *Table 1*, *Entry 6*). The same reaction, catalyzed with CuI/**L2** (10/20 mol-%), was less successful, since it provided the target product and N^1,N^1,N^4-tripyridinyl tetraamine **23** in 16 and 9% yields, respectively (*Table 1*, *Entry 7*). Tetraamine **5** was the only compound which furnished N^1,N^4-dipyridinyl derivative **24** in the reaction with 4-iodopyridine, though its yield was rather low (26%). N^1,N^1,N^4-Trisubstituted tetraamine **25** (19% yield) was also formed with this very active halogenopyridine, together with other polyheteroarylation products (*Table 1*, *Entry 8*).

The reactions of halogenopyridines with *N*,*N*′-bis(3-aminopropyl)propane-1,3-diamine (**6**), which possesses only trimethylenediamine moieties, proceeded sometimes in a different manner (*Scheme 6*). For example, the reaction with 2-bromopyridine led to only small amounts (9%) of the target diheteroaryl tetraamine **26**, and the second isolated product was N^1,N^2,N^4-tripyridinyl derivative **27** (*Table 2*, *Entry 1*). Better yields of compound **26** were obtained in the reaction with 2-iodopyridine, though in all cases comparable amounts of the tripyridinyl derivative **27** were also isolated (*Table 2*, *Entries 2–7*). Application of 10/20 mol-% catalyst favored polyarylation (*Table 2*,

Scheme 6

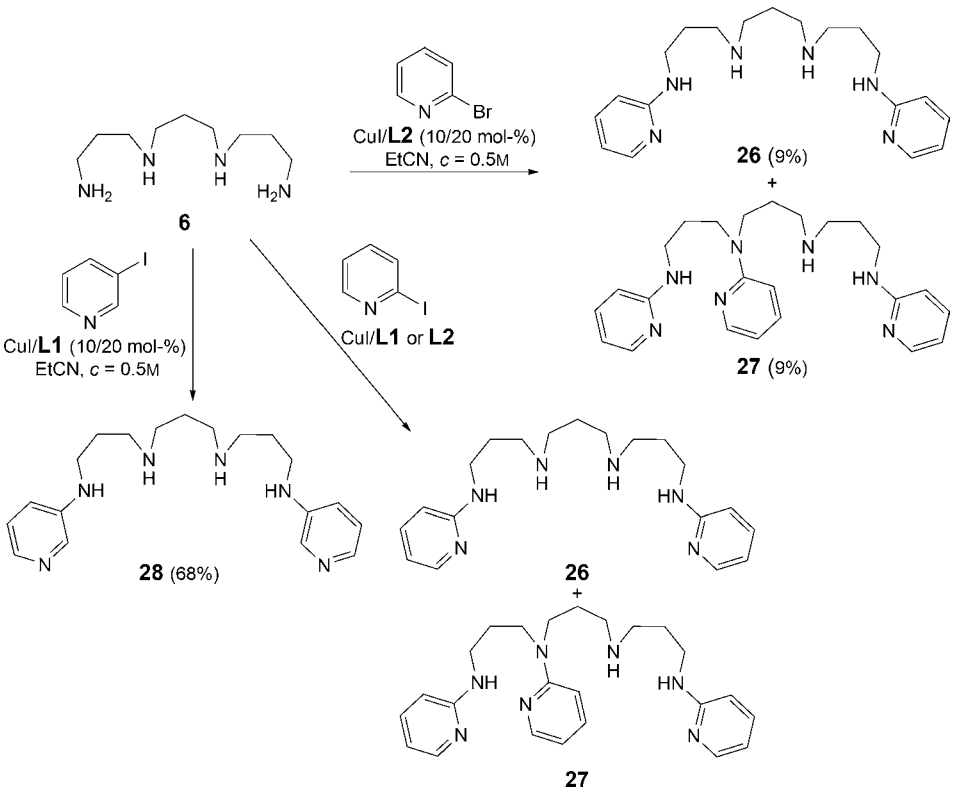


Table 2. *Heteroarylation of Tetraamine* **6** *with Halogenopyridines in EtCN*

Entry	Halogenopyridine	Ligand	CuI/**L** [mol-%]	Conc. [M]	Products ([yield [%]) **26**	**27**
1	2-Bromopyridine	**L2**	10 : 20	0.5	9	9
2	2-Iodopyridine	**L1**	10 : 20	0.5	19	44
3	2-Iodopyridine	**L1**	5 : 10	0.5	15	15
4	2-Iodopyridine	**L1**	2 : 5	0.5	30	20
5	2-Iodopyridine	**L1**	1 : 2	0.5	29	21
6	2-Iodopyridine[a])	**L1**	1 : 2	0.25	18	38
7	2-Iodopyridine	**L2**	10 : 20	0.5	37	29
8	3-Iodopyridine	**L1**	10 : 20	0.5	**28** (68)	–

[a]) In MeCN.

Entry 2), and 1–2 mol-% loadings were found to work better (*Table 2*, *Entries 4* and *5*), though lower concentrations of the reagents, and using MeCN instead of EtCN resulted in a poorer yield of **26** (*Table 2*, *Entry 6*).

The optimal result was achieved with the **L2** ligand (*Table 2*, *Entry 7*), however, tripyridinyl by-product **27** was also obtained. With tetraamine **6**, *N*,*N*-diarylation of the primary amino group was never observed. The reaction with 3-iodopyridine, using CuI/**L1** (10/20 mol-%), proceeded much better to afford the N^1,N^4-dipyridinyl derivative **28** in 68% yield (*Table 2*, *Entry 8*); no polyarylation of any type was observed in this case.

Comparing Cu- and Pd-catalyzed amination reactions, *N*,*N*-diarylation of the primary amino group is a common side-process with Pd^0 catalysts, and exhaustive polyarylation of diamines could be achieved [37]; however, we did not observe this side-reaction with common aryl iodides and aryl bromides in the Cu^I-mediated arylation of polyamines, and only with the most active 1-iodo-4-nitrobenzene, it took place [36]. On the other hand, competing amination of the secondary dialkylamino group does not take place with Pd^0 catalysts, but it often occurs in Cu^I-catalyzed arylation of polyamines with various aryl and heteroaryl halides. 2-Iodopyridine was found to be more active than the substituted iodoarenes we studied earlier, while 2-bromopyridine and 3-iodopyridine were of similar reactivity. 3-Bromopyridine was inactive in the reactions with polyamines, possibly due to unfavorable coordination with Cu^I. The difference in the reactivity of polyamines turned out to be pronounced and correlated with the presence of a different number of ethylenediamine and triethylenediamine moieties in their molecules. These moieties possess different abilities to coordinate Cu^I, thus affecting its activity. Ethylenediamine fragments increase the catalyst's activity in the case of mono- and diheteroarylation of primary diamino groups, while triethylenediamine fragments decrease the catalyst's activity and lower the heteroarylation selectivity towards primary and secondary amino groups. The result is either formation of substantial amounts of monopyridinyl-substituted products as in the reaction with triamines **1** and **3**, or *N*,*N*-and *N*,*N*′-polyheteroarylation processes as in the reactions with tetraamines.

3. Conclusions. – Cu^I-Catalyzed heteroarylation of tri- and tetraamines was found to be a challenging task. We demonstrated the possibility to use 2-bromopyridine for polyamine diheteroarylation, though it was not of general character. Substantial differences in the reactivity of polyamines were shown, mainly due to the presence and number of ethylenediamine and trimethylenediamine moieties. Besides the target *N*,*N*′-dipyridinyl polyamines, monopyridinyl triamines were also obtained, and *N*,*N*-diheteroarylation of primary amino groups and the heteroarylation of secondary dialkylamino groups in tetraamines took place. Considering the much lower cost of copper catalysts, the Cu^I-mediated synthesis can be recommended for *N*,*N*′-dipyridinyl polyamines **9**, **10**, **13**, **19**, **21**, and **26**, while Pd^0-catalyzed amination will be preferable for compounds **7**, **15**, **17**, and **24**.

This work was supported by the *RFBR*, grant No. 12-03-00796, and by the *Russian Academy of Sciences* program '*Elaboration of the methods for the synthesis of chemical compounds and construction of new materials*'.

Experimental Part

General. 2- and 3-bromopyridines, 2-, 3- and 4-iodopyridines, polyamines **1**–**6**, CuI, L-proline, *N*,*N*-dimethylglycine, and Cs_2CO_3 were obtained from *Sigma–Aldrich* and used without special purification. DMF and MeCN were distilled over CaH_2, and EtCN, CH_2Cl_2, MeOH were used after distillation. Column chromatography (CC): silica gel (SiO_2, 40–60 μm; *Fluka*). ^{1}H- and ^{13}C-NMR spectra: *Bruker Avance 400* spectrometer; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. MALDI-TOF-MS: *Bruker Autoflex II* spectrometer; in positive-ion mode; 1,8,9-trihydroxyanthracene as matrix and polyethylene glycol (PEG) as internal standard; in *m*/*z*.

General Procedure for the Synthesis of Pyridinyl-Substituted Polyamines **7**–**28**. A two-neck flask flushed with dry Ar, equipped with a magnetic stirrer and reflux condenser, was charged with the corresponding halogenopyridine (1.25 mmol), CuI (1–10 mol-%), ligand (2–20 mol-%), solvent (1 ml), polyamine (0.5 mmol), and Cs_2CO_3 (1.25 mmol, 408 mg). The mixture was stirred under reflux for 24 h, cooled to r.t., CH_2Cl_2 (5–10 ml) was added, and the residue was filtered off and washed with additional 5–10 ml of CH_2Cl_2. The org. phases were combined and evaporated *in vacuo*. The mixture was analyzed by ^{1}H-NMR spectrometry and subjected to CC (SiO_2; CH_2Cl_2, CH_2Cl_2/MeOH 50:1–3:1, CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:20:1–10:4:1).

N-*(Pyridin-2-yl)*-N′-*[2-(pyridin-2-ylamino)ethyl]ethane-1,2-diamine* (**7**). Obtained from *bis(2-aminoethyl)amine* (**1**; 52 mg), 2-iodopyridine (256 mg) in the presence of CuI (1 mg) and L-proline (1.2 mg) in 2 ml of MeCN. Eluent: CH_2Cl_2/MeOH 3:1. Yield: 38 mg (30%). Yellowish viscous oil. ^{1}H-NMR: 3.23 (br. *s*, 4 H); 3.69 (br. *s*, 4 H); 5.88 (br. *s*, 2 H); 6.47–6.53 (*m*, 2 H); 6.66 (*d*, *J* = 8.2, 2 H), 7.30–7.35 (*m*, 2 H); 7.82 (*d*, *J* = 4.8, 2 H) (H-atom of one NH group was not assigned). ^{13}C-NMR: 39.5 (2 C); 49.3 (2 C); 110.3 (2 C); 113.6 (2 C); 137.9 (2 C); 146.3 (2 C); 157.9 (2 C). MALDI-TOF-MS: 258.1682 ($[M+H]^+$, $C_{14}H_{20}N_5^+$; calc. 258.1719).

N-*(2-Aminoethyl)*-N′-*(pyridin-2-yl)ethane-1,2-diamine* (**8**). Obtained as the second product in the synthesis of **7**. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:25:5. Yield: 63 mg (70%). Yellowish viscous oil. ^{1}H-NMR: 2.72 (br. *s*, 2 H); 2.84 (br. *s*, 2 H); 3.37 (br. *s*, 2 H); 3.44 (br. *s*, 2 H); 5.33 (br. *s*, 1 H), 6.41 (*d*, *J* = 7.7, 1 H); 6.49 (br. *s*, 1 H); 7.30–7.36 (*m*, 1 H); 8.00 (br. *s*, 1 H) (H-atoms of one NH and NH_2 groups were not assigned). ^{13}C-NMR: 40.8 (1 C); 41.4 (1 C); 48.4 (1 C); 50.6 (1 C); 107.4 (1 C); 112.6 (1 C); 137.3 (1 C); 147.8 (1 C); 158.8 (1 C). MALDI-TOF-MS: 181.13 ($[M+H]^+$; $C_9H_{17}N_4^+$, calc. 181.1453).

N-*(Pyridin-2-yl)*-N′-*(2-{[2-(pyridin-2-ylamino)ethyl]amino}ethyl)ethane-1,2-diamine* (**9**). Obtained from N,N′-*bis(2-aminoethyl)ethane-1,2-diamine* **2** (72 mg), 2-iodopyridine (256 mg) in the presence of CuI (1 mg) and L-proline (1.2 mg) in 2 ml of MeCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:20:2. Yield: 90 mg (60%). Yellowish viscous oil. ^{1}H-NMR: 2.69 (br. *s*, 4 H); 2.80 (*t*, *J* = 5.9, 4 H); 3.11 (br. *s*, 2 H); 3.33 (br. *s*, 4 H); 5.39 (br. *s*, 2 H); 6.34 (*d*, *J* = 8.3, 2 H); 6.42–6.47 (*m*, 2 H); 7.25–7.31 (*m*, 2 H); 7.98 (*d*,

$J = 4.0$, 2 H). ^{13}C-NMR: 41.2 (2 C); 48.3 (4 C); 107.3 (2 C); 112.4 (2 C); 137.1 (2 C); 147.7 (2 C); 158.7 (2 C). MALDI-TOF-MS: 301.2177 ($[M+H]^+$, $C_{16}H_{25}N_6^+$; calc. 301.2141).

N-*(Pyridin-2-yl)*-N′-*[3-(pyridin-2-ylamino)propyl]propane-1,3-diamine* (**10**). Obtained from *bis(3-aminopropyl)amine* (**3**; 66 mg), 2-iodopyridine (256 mg) in the presence of CuI (1 mg) and L-proline (1.2 mg) in 1 ml of MeCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 2. Yield: 108 mg (76%). Yellowish viscous oil. ^{1}H-NMR: 1.72 (*quint.*, $J = 6.5$, 4 H); 2.29 (br. *s*, 2 H); 2.65 (*t*, $J = 6.5$, 4 H); 3.29 (br. *s*, 4 H); 5.36 (br. *s*, 2 H); 6.30 (*d*, $J = 8.5$, 2 H); 6.43 – 6.48 (*m*, 2 H); 7.27 – 7.32 (*m*, 2 H); 7.99 (*dd*, $J = 4.9$, $J = 1.0$, 2 H). ^{13}C-NMR: 29.2 (2 C); 40.4 (2 C); 47.7 (2 C); 106.7 (2 C); 112.2 (2 C); 137.1 (2 C); 147.8 (2 C); 158.8 (2 C). MALDI-TOF-MS: 286.1980 ($[M+H]^+$, $C_{16}H_{24}N_5^+$; calc. 286.2032).

N-*(3-Aminopropyl)*-N′-*(pyridin-2-yl)propane-1,3-diamine* (**11**). Obtained as the second product in the synthesis of **10** from **3** (66 mg), 2-bromopyridine (198 mg) in the presence of CuI (4.8 mg) and *N,N*-dimethylglycine (5.2 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 10 : 4 : 1. Yield: 40 mg (39%). Yellowish viscous oil. ^{1}H-NMR: 1.61 (*quint.*, $J = 6.9$, 2 H); 1.69 (br. *s*, 3 H); 1.77 (*quint.*, $J = 6.6$, 2 H); 2.64 (*t*, $J = 7.0$, 2 H); 2.71 (*t*, $J = 6.6$, 2 H); 2.74 (*t*, $J = 6.8$, 2 H); 3.33 (*q*, $J = 5.8$, 2 H); 5.04 (br. *s*, 1 H); 6.34 (*d*, $J = 8.5$, 1 H); 6.48 – 6.53 (*m*, 1 H); 7.34 – 7.38 (*m*, 1 H); 8.04 (*d*, $J = 4.9$, 1 H). ^{13}C-NMR: 29.5 (1 C); 33.7 (1 C); 40.4 (1 C); 40.8 (1 C); 47.8 (1 C); 48.0 (1 C); 106.8 (1 C); 112.5 (1 C); 137.3 (1 C); 148.1 (1 C); 158.9 (1 C). MALDI-TOF-MS: 209.17 ($[M+H]^+$, $C_{11}H_{21}N_4^+$; calc. 209.1766).

N,N-*Di(pyridin-2-yl)*-N′-*[3-(pyridin-2-ylamino)propyl]propane-1,3-diamine* (**12**). Obtained as the second product in the synthesis of **10** from **3** (66 mg), 2-iodopyridine (256 mg) in the presence of CuI (2 mg) and L-proline (3 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 3. Yield: 47 mg (31%). Yellowish viscous oil. ^{1}H-NMR: 1.74 (*quint.*, $J = 6.4$, 2 H); 1.85 (*quint.*, $J = 6.4$, 2 H); 2.48 (br. *s*, 1 H); 2.59 (*t*, $J = 6.2$, 2 H); 2.67 (*t*, $J = 6.3$, 2 H); 3.31 (br. *s*, 2 H); 4.25 (*t*, $J = 6.5$, 2 H); 5.30 (br. *s*, 1 H); 6.31 (*d*, $J = 8.3$, 1 H); 6.43 – 6.48 (*m*, 1 H); 6.75 – 6.80 (*m*, 2 H); 7.04 (*d*, $J = 8.3$, 2 H); 7.27 – 7.33 (*m*, 1 H); 7.40 – 7.46 (*m*, 2 H); 8.00 (br. *d*, $J_{obs} = 2.9$, 1 H); 8.25 (br. *d*, $J_{obs} = 2.8$, 2 H). ^{13}C-NMR: 27.7 (1 C); 29.2 (1 C); 40.5 (1 C); 45.3 (1 C); 46.5 (1 C); 47.6 (1 C); 107.0 (1 C); 112.3 (1 C); 114.6 (2 C); 116.9 (2 C); 137.1 (3 C); 147.9 (1 C); 148.1 (2 C); 157.2 (2 C); 158.9 (1 C). MALDI-TOF-MS: 363.2276 ($[M+H]^+$, $C_{21}H_{27}N_6^+$; calc. 363.2297).

N-*(Pyridin-3-yl)*-N′-*[3-(pyridin-3-ylamino)propyl]propane-1,3-diamine* (**13**). Obtained from **3** (66 mg), 3-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and *N,N*-dimethylglycine (10.3 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 2. Yield: 60 mg (42%). Yellowish viscous oil. ^{1}H-NMR: 1.76 (*quint.*, $J = 6.5$, 4 H); 2.71 (*t*, $J = 6.5$, 4 H); 3.15 (*t*, $J = 6.5$, 4 H); 4.47 (br. *s*, 2 H); 6.79 (*ddd*, $J = 8.2$, $J = 2.7$, $J = 1.1$, 2 H); 7.00 (*dd*, $J = 8.2$, $J = 4.6$, 2 H); 7.87 (*d*, $J = 4.6$, 2 H); 7.96 (*d*, $J = 2.7$, 2 H) (H-atom of one NH group was not assigned). ^{13}C-NMR: 29.1 (2 C); 42.2 (2 C); 48.0 (2 C); 118.2 (2 C); 123.6 (2 C); 135.8 (2 C); 138.2 (2 C); 144.4 (2 C). MALDI-TOF-MS: 286.2058 ($[M+H]^+$, $C_{16}H_{24}N_5^+$; calc. 286.2032).

N-*(3-Aminopropyl)*-N′-*(pyridin-3-yl)propane-1,3-diamine* (**14**). Obtained as the second product in the synthesis of **13**. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 10 : 4 : 1. Yield: 57 mg (55%). Yellowish viscous oil. ^{1}H-NMR: 1.63 (*quint.*, $J = 6.7$, 2 H); 1.78 (*quint.*, $J = 6.4$, 2 H); 2.62 (br. *s*, 3 H); 2.66 (*t*, $J = 6.8$, 2 H); 2.74 (*t*, $J = 6.4$, 2 H); 2.77 (*t*, $J = 6.7$, 2 H); 3.16 (*t*, $J = 6.4$, 2 H); 4.72 (br. *s*, 1 H); 6.81 (*dd*, $J = 8.2$, $J = 2.4$, 1 H); 7.03 (*dd*, $J = 8.2$, $J = 4.6$, 1 H); 7.97 (*d*, $J = 2.4$, 1 H); 7.98 (*d*, $J = 4.6$, 1 H). ^{13}C-NMR: 28.9 (1 C); 33.1 (1 C); 40.3 (1 C); 42.6 (1 C); 47.8 (1 C); 48.4 (1 C); 118.1 (1 C); 123.6 (1 C); 136.0 (1 C); 138.2 (1 C); 144.6 (1 C). MALDI-TOF-MS: 209.18 ($[M+H]^+$, $C_{11}H_{21}N_4^+$; calc. 209.1766).

N,N′-*Bis[2-(pyridin-2-ylamino)ethyl]propane-1,3-diamine* (**15**). Obtained from N,N′-*bis(2-aminoethyl)propane-1,3-diamine* (**4**; 80 mg), 2-iodopyridine (256 mg) in the presence of CuI (4.8 mg) and L-proline (6 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 3. Yield: 50 mg (32%). Yellowish viscous oil. ^{1}H-NMR: 1.62 (*quint.*, $J = 6.5$, 2 H); 2.48 (br. *s*, 2 H); 2.65 (*t*, $J = 6.6$, 4 H); 2.79 (*t*, $J = 5.6$, 4 H); 3.34 (*q*, $J = 5.4$, 4 H); 5.27 (br. *s*, 2 H); 6.35 (*d*, $J = 8.3$, 2 H); 6.45 – 6.49 (*m*, 2 H); 7.29 – 7.33 (*m*, 2 H); 8.00 (*d*, $J = 4.5$, 2 H). ^{13}C-NMR: 29.4 (1 C); 41.3 (2 C); 48.1 (2 C); 48.6 (2 C); 107.2 (2 C); 112.5 (2 C); 137.2 (2 C); 147.8 (2 C); 158.8 (2 C). MALDI-TOF-MS: 315.2275 ($[M+H]^+$, $C_{17}H_{27}N_6^+$; calc. 315.2297).

N-*{2-[Di(pyridin-2-yl)amino]ethyl}*-N′-*[2-(pyridin-2-ylamino)ethyl]propane-1,3-diamine* (**16**). Obtained as the second product in the synthesis of **15** from **4** (80 mg), 2-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and *N,N*-dimethylglycine (10.3 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/

$NH_3 \cdot H_2O$ 100:20:2. Yield: 13 mg (8%). Yellowish viscous oil. ^{1}H-NMR: 1.62 (*quint.*, $J = 6.8$, 2 H); 2.60–2.90 (*m*, 10 H); 3.33 (*t*, $J = 5.4$, 2 H); 4.28 (*t*, $J = 6.3$, 2 H); 5.13 (br. *s*, 1 H); 6.38 (*d*, $J = 8.3$, 1 H); 6.48–6.52 (*m*, 1 H); 6.83 (*ddd*, $J = 7.2$, 5.1, 0.6, 2 H); 7.04 (*d*, $J = 8.5$, 2 H); 7.32–7.37 (*m*, 1 H); 7.47 (*ddd*, $J = 8.3$, 7.2, 1.9, 2 H); 8.02 (*dd*, $J = 4.8$, 1.9, 1 H); 8.30 (*dd*, $J = 5.1$, 1.9, 2 H). ^{13}C-NMR: 29.6 (1 C); 41.3 (1 C); 47.7 (1 C); 47.9 (1 C); 48.0 (1 C); 51.9 (1 C); 53.5 (1 C); 107.4 (1 C); 112.5 (1 C); 114.7 (2 C); 117.2 (2 C); 137.2 (2 C); 137.3 (1 C); 147.8 (1 C); 148.3 (2 C); 157.2 (2 C); 158.7 (1 C). MALDI-TOF-MS: 392.2594 ($[M+H]^+$, $C_{22}H_{30}N_7^+$; calc. 392.2563).

N-*(Pyridin-2-yl)*-N,N′-*bis[2-(pyridin-2-ylamino)ethyl]propane-1,3-diamine* (**17**). Obtained as the third product in the synthesis of **15** from **4** (80 mg), 2-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and *N*,*N*-dimethylglycine (10.3 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:20:1. Yield: 43 mg (26%). Yellowish viscous oil. ^{1}H-NMR: 1.77 (br. *s*, 2 H), 2.58 (br. *s*, 2 H); 2.76 (br. *s*, 2 H); 3.34 (br. *s*, 2 H); 3.46 (br. *s*, 2 H); 3.47 (br. *s*, 2 H); 5.20 (br. *s*, 1 H); 5.49 (br. *s*, 1 H); 6.33 (*d*, $J = 8.3$, 1 H); 6.37 (*d*, $J = 8.3$, 1 H); 6.44–6.54 (*m*, 4 H); 7.28–7.38 (*m*, 3 H); 7.98–8.08 (*m*, 3 H) (H-atom of one NH group was not assigned). ^{13}C-NMR: 27.6 (1 C); 40.5 (1 C); 41.4 (1 C); 46.6 (2 C); 47.6 (1 C); 48.6 (1 C); 105.8 (1 C); 107.2 (1 C); 107.4 (1 C); 111.5 (1 C); 112.3 (1 C); 112.5 (1 C); 137.0 (1 C); 137.2 (2 C); 147.6 (1 C); 147.7 (1 C); 148.2 (1 C); 158.0 (1 C); 158.5 (1 C); 158.7 (1 C). MALDI-TOF-MS: 392.2529 ($[M+H]^+$, $C_{22}H_{30}N_7^+$; calc. 392.2563).

N,N′-*Bis[2-(pyridin-3-ylamino)ethyl]propane-1,3-diamine* (**18**). Obtained from **4** (80 mg), 3-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and L-proline (11.5 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:20:3. Yield: 49 mg (32%). Yellowish viscous oil. ^{1}H-NMR: 1.62 (*quint.*, $J = 6.5$, 2 H); 2.65 (*t*, $J = 6.4$, 4 H); 2.78 (*t*, $J = 5.6$, 4 H); 3.12 (*t*, $J = 5.6$, 4 H); 3.49 (br. *s*, 2 H); 4.77 (br. *s*, 2 H); 6.77 (*d*, $J = 8.1$, 2 H); 6.97 (*dd*, $J = 8.1$, 4.7, 2 H); 7.83 (*d*, $J = 4.7$, 2 H); 7.93 (br. *s*, 2 H). ^{13}C-NMR: 28.4 (1 C); 42.2 (2 C); 47.8 (2 C); 47.9 (2 C); 118.4 (2 C); 123.6 (2 C); 135.6 (2 C); 138.1 (2 C); 144.2 (2 C). MALDI-TOF-MS: 315.2330 ($[M+H]^+$, $C_{17}H_{27}N_6^+$; calc. 315.2297).

N-*{2-[Di(pyridin-3-yl)amino]ethyl}*-N′-*[2-(pyridin-3-ylamino)ethyl]propane-1,3-diamine* (**19**). Obtained as the second product in the synthesis of **18**. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:20:2. Yield: 79 mg (48%). Yellowish viscous oil. ^{1}H-NMR: 1.62 (*quint.*, $J = 6.6$, 2 H); 2.58 (br. *s*, 2 H); 2.60–2.68 (*m*, 4 H); 2.80–2.86 (*m*, 4 H); 3.16 (*t*, $J = 6.6$, 2 H); 3.81 (*t*, $J = 6.6$, 2 H); 4.53 (br. *s*, 1 H); 6.83 (*d*, $J = 8.1$, 1 H); 7.01 (*dd*, $J = 8.1$, 4.7, 1 H); 7.17 (*dd*, $J = 8.2$, 4.7, 2 H); 7.29 (*d*, $J = 8.2$, 2 H); 7.89 (*d*, $J = 4.7$, 1 H); 7.98 (*d*, $J = 2.2$, 1 H); 8.20 (*d*, $J = 4.7$, 2 H); 8.34 (*d*, $J = 2.1$, 2 H). ^{13}C-NMR: 29.7 (1 C); 42.7 (1 C); 46.8 (1 C); 48.0 (1 C); 48.2 (1 C); 48.4 (1 C); 52.0 (1 C); 118.6 (1 C); 123.7 (1 C); 123.9 (2 C); 127.7 (2 C); 135.9 (1 C); 138.5 (1 C); 142.9 (2 C); 143.1 (2 C); 143.3 (2 C); 144.4 (1 C). MALDI-TOF-MS: 392.2538 ($[M+H]^+$, $C_{22}H_{30}N_7^+$; calc. 392.2563).

N^{l},N$^{l\prime}$-*Ethane-1,2-diylbis[*N^{3}*-(pyridin-2-yl)propane-1,3-diamine]* (**20**). Obtained from N,N′-*bis(4-aminobutyl)ethane-1,2-diamine* (**5**; 87 mg), 2-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and L-proline (11.5 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:20:3. Yield: 85 mg (52%). Yellowish viscous oil. ^{1}H-NMR: 1.76 (*quint.*, $J = 6.5$, 4 H); 2.28 (br. *s*, 2 H); 2.69 (*s*, 4 H); 2.71 (*t*, $J = 6.7$, 4 H); 3.31 (*t*, $J = 6.3$, 4 H); 5.12 (br. *s*, 2 H); 6.32 (*d*, $J = 8.3$, 2 H); 6.46–6.51 (*m*, 2 H); 7.30–7.35 (*m*, 2 H); 8.02 (br. *d*, $J_{obs} = 3.8$, 2 H). ^{13}C-NMR: 29.4 (2 C); 40.6 (2 C); 47.7 (2 C); 49.2 (2 C); 106.7 (2 C); 112.4 (2 C); 137.2 (2 C); 148.0 (2 C); 158.9 (2 C). MALDI-TOF-MS: 329.2426 ($[M+H]^+$, $C_{18}H_{29}N_6^+$; calc. 329.2454).

N,N-*Di(pyridin-2-yl)*-N′-*(2-{[3-(pyridin-2-ylamino)propyl]amino}ethyl)propane-1,3-diamine* (**21**). Obtained as the second product in the synthesis of **20** in the presence of CuI (2 mg) and L-proline (3 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:20:2. Yield: 10 mg (6%). Yellowish viscous oil. ^{1}H-NMR: 1.74 (*quint.*, $J = 6.5$, 2 H); 1.83 (*quint.*, $J = 6.3$, 2 H); 2.59 (*t*, $J = 5.7$, 2 H); 2.67–2.81 (*m*, 6 H); 3.28 (*t*, $J = 6.3$, 2 H); 4.23 (*t*, $J = 6.7$, 2 H); 4.77 (br. *s*, 1 H); 6.31 (*d*, $J = 8.3$, 1 H); 6.43–6.49 (*m*, 1 H); 6.76–6.81 (*m*, 2 H); 7.04 (*d*, $J = 8.5$, 2 H); 7.28–7.34 (*m*, 1 H); 7.42–7.47 (*m*, 2 H); 8.00 (br. *d*, $J_{obs} = 3.0$, 1 H); 8.28 (br. *d*, $J_{obs} = 3.0$, 2 H) (H-atoms of two NH groups were not assigned). MALDI-TOF-MS: 406.2752 ($[M+H]^+$, $C_{23}H_{32}N_7^+$; calc. 406.2714).

N^{l},N$^{l\prime}$-*Ethane-1,2-diylbis[*N^{3}*-(pyridin-3-yl)propane-1,3-diamine]* (**22**). Obtained from **5** (87 mg), 3-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and L-proline (11.5 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100:20:2–100:20:3. Yield: 70 mg (43%). Yellowish viscous oil. ^{1}H-NMR: 1.76 (*quint.*, $J = 6.3$, 4 H); 2.15 (br. *s*, 2 H); 2.71 (*s*, 4 H); 2.73 (*t*, $J = 6.6$, 4 H); 3.16 (*t*, $J = 6.4$, 4 H); 4.58

(br. *s*, 2 H); 6.81 (*d*, *J* = 8.0, 2 H); 7.02 (*dd*, *J* = 8.0, *J* = 4.6, 2 H); 7.88 (*d*, *J* = 4.6, 2 H); 7.97 (*d*, *J* = 2.3, 2 H). ^{13}C-NMR: 29.1 (2 C); 42.4 (2 C); 48.1 (2 C); 49.4 (2 C); 118.2 (2 C); 123.7 (2 C); 135.9 (2 C); 138.2 (2 C); 144.5 (2 C). MALDI-TOF-MS: 329.2470 ($[M+H]^+$, $C_{18}H_{29}N_6^+$; calc. 329.2454).

N,N-*Di(pyridin-3-yl)*-N′-*(2-{[3-(pyridin-3-ylamino)propyl]amino}ethyl)propane-1,3-diamine* (**23**). Obtained as the second product in the synthesis of **22** in the presence of CuI (9.5 mg) and *N,N*-dimethylglycine (10.3 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 2. Yield: 15 mg (9%). Yellowish viscous oil. ^{1}H-NMR: 1.73 (*quint.*, *J* = 6.3, 2 H); 1.76 (*quint.*, *J* = 6.6, 2 H); 2.24 (br. *s*, 2 H); 2.62 (*t*, *J* = 6.6, 2 H); 2.66 (*s*, 4 H); 2.70 (*t*, *J* = 6.1, 2 H); 3.13 (*t*, *J* = 6.3, 2 H); 3.77 (*t*, *J* = 7.2, 2 H); 4.60 (br. *s*, 1 H); 6.79 (*d*, *J* = 8.3, 1 H); 7.01 (*dd*, *J* = 8.3, 4.4, 1 H); 7.15 (*dd*, *J* = 7.7, 4.7, 2 H); 7.26 (*d*, *J* = 7.7, 2 H); 7.85 (*d*, *J* = 4.4, 1 H); 7.94 (br. *s*, 1 H); 8.18 (*d*, *J* = 4.7, 2 H); 8.32 (br. *s*, 2 H). MALDI-TOF-MS: 406.2681 ($[M+H]^+$, $C_{23}H_{32}N_7^+$; calc. 406.2714).

N^{1},N$^{1'}$-*Ethane-1,2-diylbis[*N^{3}-*(pyridin-4-yl)propane-1,3-diamine]* (**24**). Obtained from **5** (87 mg), 4-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and L-proline (11.5 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 25 : 5. Yield: 43 mg (26%). Yellowish viscous oil. ^{1}H-NMR ((D$_6$)DMSO): 1.65 (*quint.*, *J* = 6.7, 4 H); 2.59 (*t*, *J* = 6.4, 4 H); 2.61 (*s*, 4 H); 3.06 (*q*, *J* = 5.2, 4 H); 6.44 (*d*, *J* = 5.1, 4 H); 6.58 (br. *s*, 2 H); 7.96 (br. *s*, 4 H) (H-atoms of two NH groups were not assigned). ^{13}C-NMR ((D$_6$)DMSO): 28.3 (2 C); 39.8 (2 C); 46.6 (2 C); 48.2 (2 C); 107.1 (4 C); 149.3 (4 C); 153.7 (2 C). MALDI-TOF-MS: 329.2483 ($[M+H]^+$, $C_{18}H_{29}N_6^+$; calc. 329.2454).

N,N-*Di(pyridin-4-yl)*-N′-*(2-{[3-(pyridin-4-ylamino)propyl]amino}ethyl)propane-1,3-diamine* (**25**). Obtained as the second product in the synthesis of **24**. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 3. Yield: 32 mg (19%). Yellowish viscous oil. ^{1}H-NMR: 1.73 (*quint.*, *J* = 6.3, 2 H); 1.76 (*quint.*, *J* = 6.7, 2 H); 2.07 (br. *s*, 2 H), 2.60 (*t*, *J* = 6.6, 2 H); 2.66 (*s*, 4 H); 2.70 (*t*, *J* = 6.3, 2 H); 3.17 (br. *q*, *J* = 4.4, 2 H); 3.84 (*t*, *J* = 7.3, 2 H); 5.34 (br. *s*, 1 H); 6.35 (*d*, *J* = 6.2, 2 H); 6.96 (*d*, *J* = 6.3, 4 H); 8.08 (*d*, *J* = 6.2, 2 H); 8.37 (*d*, *J* = 6.3, 4 H). ^{13}C-NMR: 27.7 (1 C); 28.7 (1 C); 41.4 (1 C); 46.7 (1 C); 47.9 (1 C); 48.7 (1 C); 49.4 (2 C); 107.3 (2 C); 114.9 (4 C); 149.6 (2 C); 150.8 (4 C); 151.9 (2 C); 153.5 (1 C). MALDI-TOF-MS: 406.2750 ($[M+H]^+$, $C_{23}H_{32}N_7^+$; calc. 406.2714).

N-*(Pyridin-2-yl)*-N′-*(3-{[3-(pyridin-2-ylamino)propyl]amino}propyl)propane-1,3-diamine* (**26**). Obtained from N,N′-*bis(3-aminopropyl)propane-1,3-diamine* (**6**; 94 mg), 2-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and *N,N*-dimethylglycine (10.3 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 3. Yield: 63 mg (37%). Yellowish viscous oil. ^{1}H-NMR: 1.66 (*quint.*, *J* = 6.5, 2 H); 1.75 (*quint.*, *J* = 6.4, 4 H); 2.12 (br. *s*, 2 H); 2.65 (*t*, *J* = 6.6, 4 H); 2.70 (*t*, *J* = 6.3, 4 H); 3.32 (br. *s*, 4 H); 5.09 (br. *s*, 2 H); 6.33 (*d*, *J* = 8.5, 2 H); 6.46 – 6.52 (*m*, 2 H); 7.31 – 7.37 (*m*, 2 H); 8.02 (br. *d*, J_{obs} = 3.5, 2 H). ^{13}C-NMR: 29.4 (2 C); 30.1 (1 C); 40.7 (2 C); 47.9 (2 C); 48.4 (2 C); 106.8 (2 C); 112.4 (2 C); 137.2 (2 C); 148.0 (2 C); 158.9 (2 C). MALDI-TOF-MS: 343.2586 ($[M+H]^+$, $C_{19}H_{31}N_6^+$; calc. 343.2610).

N,N′-*Di(pyridin-2-yl)*-N-*(3-{[3-(pyridin-2-ylamino)propyl]amino}propyl)propane-1,3-diamine* (**27**). Obtained as the second product in the synthesis of **26**. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 3. Yield: 51 mg (29%). Yellowish viscous oil. ^{1}H-NMR: 1.77 (*quint.*, *J* = 6.3, 2 H); 1.78 (*quint.*, *J* = 6.3, 2 H); 1.87 (*quint.*, *J* = 6.3, 2 H); 2.27 (br. *s*, 1 H); 2.61 (*t*, *J* = 6.3, 2 H); 2.70 (*t*, *J* = 6.3, 2 H); 3.29 (*q*, *J* = 5.6, 2 H); 3.34 (br. *s*, 2 H); 3.48 (*t*, *J* = 6.8, 2 H); 3.59 (*t*, *J* = 6.4, 2 H); 5.14 (br. *s*, 1 H); 5.34 (br. *s*, 1 H); 6.35 (*d*, *J* = 7.7, 1 H); 6.36 (*d*, *J* = 7.7, 1 H); 6.44 – 6.53 (*m*, 4 H); 7.33 – 7.38 (*m*, 3 H); 8.03 (*d*, *J* = 5.1, 1 H); 8.04 (br. *s*, 1 H); 8.10 (br. *d*, J_{obs} = 3.5, 1 H). ^{13}C-NMR: 27.3 (1 C); 27.7 (1 C); 29.4 (1 C); 39.1 (1 C); 40.7 (1 C); 45.5 (1 C); 46.2 (1 C); 47.1 (1 C); 47.9 (1 C); 105.6 (1 C); 106.8 (1 C); 107.2 (1 C); 111.3 (1 C); 112.4 (1 C); 112.5 (1 C); 137.2 (2 C); 137.3 (1 C); 147.8 (1 C); 148.0 (2 C); 157.9 (1 C); 158.9 (2 C). MALDI-TOF-MS: 420.2849 ($[M+H]^+$, $C_{24}H_{34}N_7^+$; calc. 420.2876).

N-*(Pyridin-3-yl)*-N′-*(3-{[3-(pyridin-3-ylamino)propyl]amino}propyl)propane-1,3-diamine* (**28**). Obtained from **6** (94 mg), 3-iodopyridine (256 mg) in the presence of CuI (9.5 mg) and L-proline (11.5 mg) in 1 ml of EtCN. Eluent: CH_2Cl_2/MeOH/$NH_3 \cdot H_2O$ 100 : 20 : 3 – 100 : 25 : 5. Yield: 116 mg (68%). Yellowish viscous oil. ^{1}H-NMR: 1.69 (*quint.*, *J* = 6.6, 2 H); 1.77 (*quint.*, *J* = 6.4, 4 H); 2.51 (br. *s*, 2 H); 2.69 (*t*, *J* = 6.7, 4 H); 2.74 (*t*, *J* = 6.4, 4 H); 3.15 (*t*, *J* = 6.4, 4 H); 4.81 (br. *s*, 2 H); 6.81 (*dd*, *J* = 8.2, *J* = 2.4, 2 H); 7.03 (*dd*, *J* = 8.2, 4.8, 2 H); 7.89 (*d*, *J* = 4.8, 2 H); 7.98 (*d*, *J* = 2.4, 2 H). ^{13}C-NMR: 28.8 (2 C); 29.7 (1 C); 42.5 (2 C); 48.3 (2 C); 48.4 (2 C); 118.1 (2 C); 123.7 (2 C); 135.9 (2 C); 138.1 (2 C); 144.5 (2 C). MALDI-TOF-MS: 343.2642 ($[M+H]^+$, $C_{19}H_{31}N_6^+$; calc. 343.2610).

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Received March 14, 2014