New growth regulators of corn based on *N*-mono- and *N*,*N*-bis-3-butenyldichloroacetamides

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Allylboration of imines, nitriles (including hydrocyanic acid), amides, lactams, aromatic azaheterocycles (pyridines, isoquinoline, and pyrrole) was used to synthesize a series of mono- and bis-3-butenylamines with different structures, which were converted to dichloroacetamides, new analogs of a known safener (herbicide antidote) Dichlormid successfully used in the cultivation of corn throughout the world. Biological tests for the germination of corn seeds showed that most of the dichloroacetamides obtained have growth-stimulating activity, which is mainly directed on the development of the root system. Compounds **2f**, *trans*- and *cis*-**2n**, *cis*-**2s**, and **2t** demonstrated outstanding activity, exceeding from two to three times the stimulating effect of Dichlormid on the developing root system of maize seedlings.

Key words: allylboranes, allylboration, plant growth regulators, Dichlormid, safeners.

Ensuring food security of the population is one of the priority tasks of Russia´s development.[1] The most important factor in solving this problem is increasing the soil fertility and yields of agricultural crops, which is largely determined by the level of weed population in the places of cultivation.[2] Balanced chemicalization of plant growing using growth regulators and herbicides allows one to achieve a significant increase in yields.[3] However, it must be understood that herbicides widely used in modern industrial agriculture adversely affect both weeds and cultivated plants.[4] Poorly controlled use of herbicides results in contamination of soil with their residues, which causes serious damage to crops in the following years, while underestimation of this effect leads to tangible losses in the yield of the main agricultural crops. Thus, when spraying fields with xenobiotics from 30 to 70% of them gets into the soil, contaminates it, and has a negative effect on the yield in subsequent years (sometimes, the yield losses reach 50%). This problem is especially acute when herbicides based on sulfonylureas are used, which, possessing unique biological activity (in doses of 10—25 g ha^{-1}), can persist in the soil for a long time.[5] Therefore, to efficiently use herbicides and other chemicals in modern agriculture, additives of the so-called safeners (antidotes, inductors of stability) are used in the pre-sowing treatment, which not only increase the selectivity of the action of herbicides, but also increase the stress resistance of plants.[4—7] Figure 1 shows the structures of a number of commercially available antidotes, while the types of herbicides used in combination with them are listed in Table 1. Cyprosulfamide is one of the newest antidotes (developed in 2005 by Bayer company) for the use in combination with sulfonylureas and chloro derivatives of benzoic acid (Dicamba) and triazine (Atrazine). These compounds are particularly efficient for the protection of maize.

There are also a number of successfully used antidotes, which are amide derivatives of dichloroacetic acid (see Fig. 1, Table 2). Dichlormid, the first representative of this class, was patented in 1972 by Pallos as the antidote of thiocarbamate herbicides for the use in maize.[6] Apart from that, Dichlormid is a more efficient safener than, for example, naphthalic anhydride (see Table 1), and is used in combination with a herbicide for soil application,[7] like other antidotes of this class, for example, benoxacor and AD 67.[4] Currently, the worldwide use of dichloroacetamide-based safeners exceeds 8,000 tonnes per year, while in the USA it reaches 2,000 tonnes per year, confirming their high efficiency.[8,9] The antidotes Dichlormid and DKA-24 are derivatives of di- and monoallylamine.

In different years, our team in the ZIOC and INEOS of RAS has developed efficient and simple single-step

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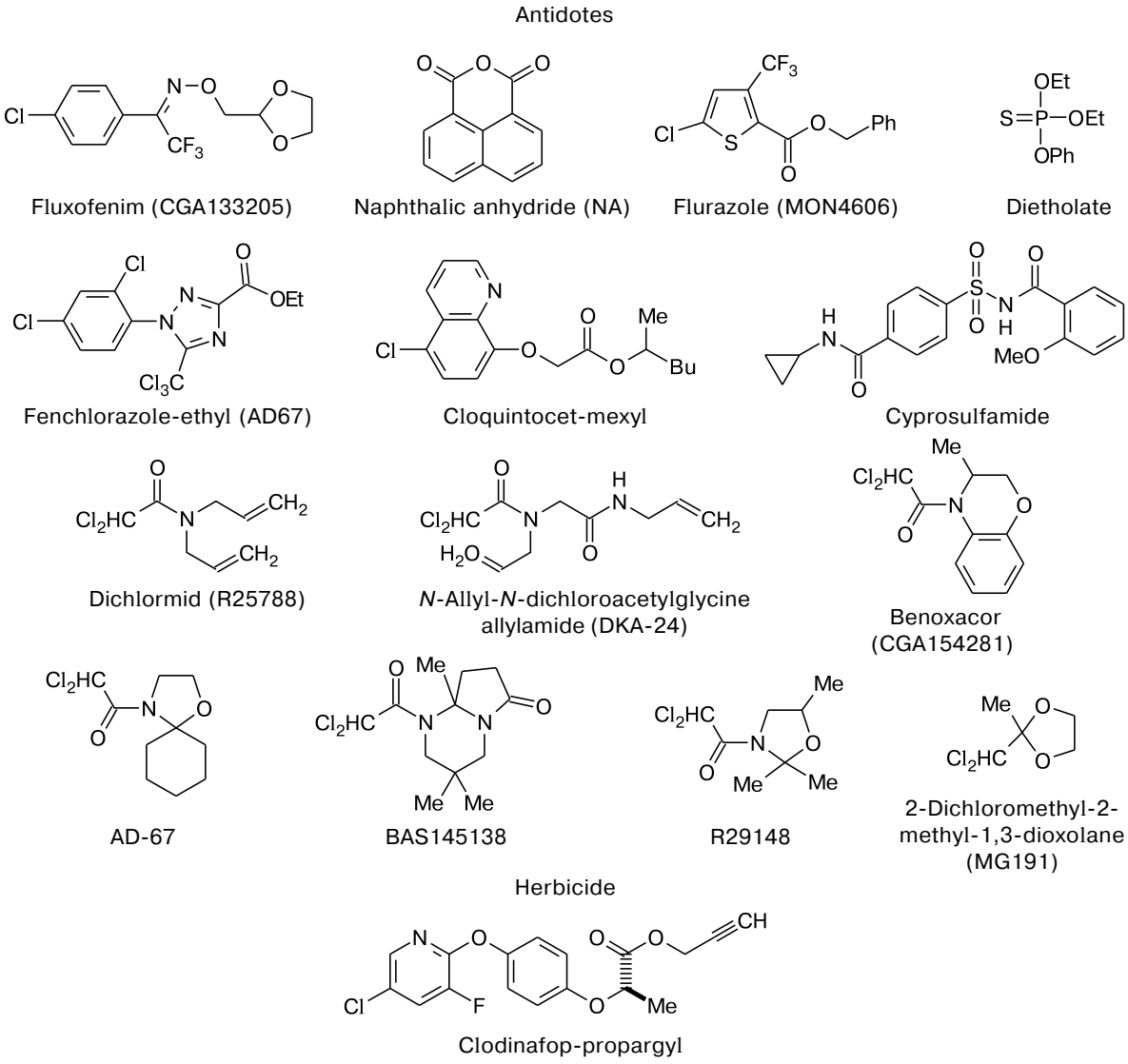


Fig. 1. Structures of commercially available antidotes and herbicides.

methods for the synthesis of various 3-butenylamines containing mainly two allylic fragments.

Since the amines we synthesized are homologs of allylamines, we anticipated that their dichloroacetyl derivatives would also exhibit antidotal activity. It is obvious that the preparation of new compounds with higher safener activity is of great practical importance in the development of new composite mixtures for the treatment of

Table 1. Antidotes of herbicides

Antidote	Herbicide	Cultures of cultivated plants for use
Fluxofenim (CGA133205)	Sulfonylureas, imidazolinones	Sorghum, rice, corn, cotton, soybeans, sugar beets
Naphthalic anhydride (NA)	Ureas, sulfonylureas, carbamates, and many other herbicides	Corn, cotton, sorghum
Flurazole (MON4606)	Acetanilides, imidazolinones	Corn, sorghum, rice
Fenchlorazole-ethyl (AD67)	Phenoxaprop-P-ethyl	Wheat, triticale
Diethолate	Thiocarbamates	Corn, cotton, wheat, rice
Cloquintocet-mexyl	Clodinafop-propargyl	Wheat, triticale, rye
Cyprosulfamide	Sulfonylureas, Dicamba, Atrazine	Wheat, corn, cotton

Table 2. Antidotes of herbicides based on dichloroacetic acid derivatives

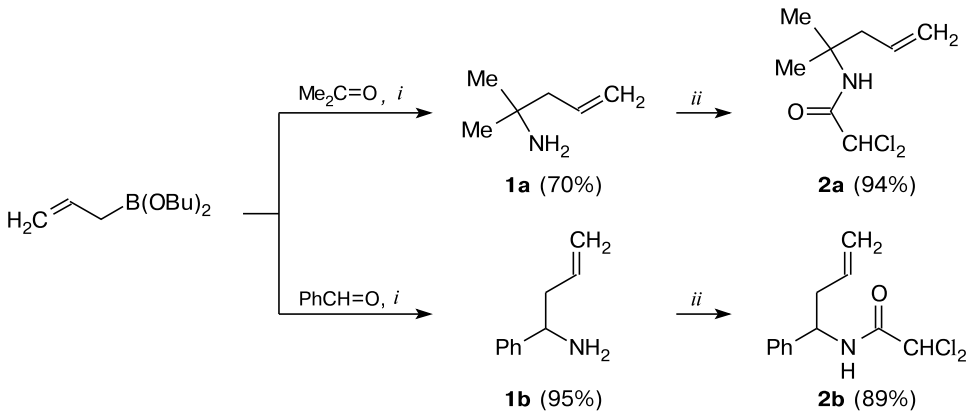
Antidote	Herbicide	Cultures of cultivated plants for use
Dichlormid (R25788)	Thiocarbamates, including S- ethyldipropyl-thiocarbamate (EPTC), butylate	Wheat, sorghum, rice, corn, oats
N-Allyl-*N*-dichloroacetyl glycine allylamide (DKA-24)	Thiocarbamates	Soybean, cotton, rapeseed
Benoxacor (CGA154281)	Chloroacetamides (metolachlor)	Corn
AD-67	EPTC	Corn
BAS145138	Sulfonylureas, thiocarbamates	Corn, sorghum, wheat, rice
R29148	Chloroacetamides	Wheat, corn, sunflower, rice, soybean, cotton, rapeseed, tobacco
2-Dichloromethyl-2-methyl-1,3-dioxolane (MG191)	Chloroacetamides, thiocarbamates	Corn, sorghum, rice

seeds and plants. The parent dichloroacetamide safener, Dichlormid, exhibits a complex biological activity when acting on seeds or seedlings. The comprehensive studies of the effect of Dichlormid, as well as of a number of its analogs, on plants (and especially corn) have shown that these compounds initiate an entire complex of biological processes related to both the enhancement of the metabolic activity responsible for the protective action and the biosynthesis of gibberellins responsible for the growth activity.[6,10,11] In particular, the level of glutathione grows, the activity of glutathione-bound enzymes (transferase and synthase), ATP-sulfurylase, acetohydroxyacid synthase, monooxygenase, and others increases.[10,11] It is assumed that the safener activity of dichloroacetamide derivatives correlates with their biological stimulating activity.

The purpose of the present work is the synthesis of dichloroacetamides from different homoallylamines (3-butenylamines) and the investigation of their biological effects on the germination of maize seeds. First, we synthesized a series of 3-butenylamines **1a**—**u** with various structures (Schemes 1—9). The amines **1a** and **1b** containing one allyl group were obtained by a three-component reaction of an aldehyde (ketone), ammonia (4—10 equiv.), and allyl dibutoxyborane (1.6 equiv.)[12] (Scheme 1).

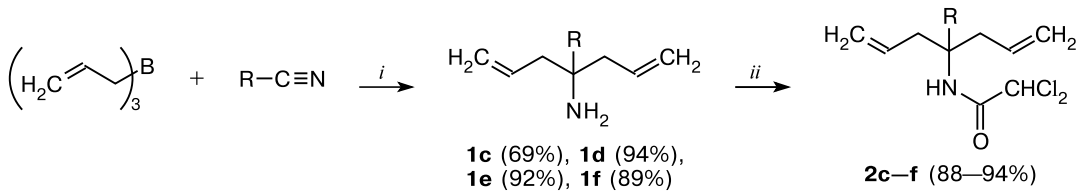
The most efficient approach to the synthesis of bis-3-butenylamines with linear structure, namely, 1-R-1-allyl-3-butenylamines **1c—f**, is the reaction of organic nitriles with triallylborane[13—15] (Scheme 2). The synthesis of amines **1d—f** was described earlier.[15] However, the first member of this series, 1-allyl-3-butenylamine (**1c**), was synthesized by the one-step allylboration of hydrocyanic acid for the first time. Earlier, amine **1c** was obtained from hepta-1,6-dien-4-ol in three steps.[16] As it turned out, the reaction of triallylborane with HCN proceeds slower (4.5 h) than with organic nitriles and requires a higher temperature (140 °C, instead of 110 °C for nitriles). Apparently, the absence of a substituent at the cyano group decreases steric interactions in the dimeric aminoboron intermediate and slows the transfer of the second allyl group during formation of the boretidine ring. After the reaction mixture was deborated with 20% NaOH, amine **1c** was isolated by distillation in 69% yield.

Scheme 1



Reagents and conditions: *i*. 7 *M* NH_3 (10 equiv.) in MeOH, 25 °C, 16 h; *ii*. $Cl_2CHC(O)Cl$ (DCAC), NaOH, CH_2Cl_2.

Scheme 2



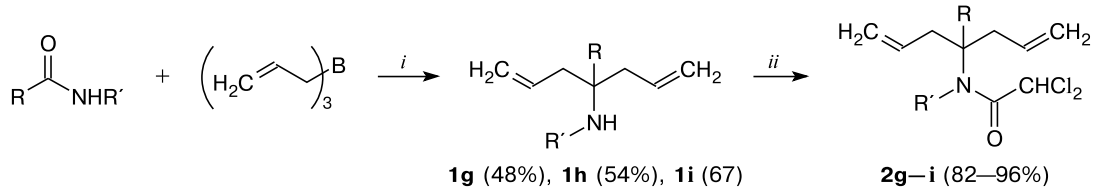
1, 2: R = H (**c**), Ph (**d**), $Bu^tOC(O)CH_2$ (**e**), $MeO(CH_2)_2$ (**f**)

Reagents and conditions: *i*. 1) −30—−20 °C, 2)100—140 °C, 1—5 h, 3) MeOH, 4) NaOH, 100 °C; *ii*. DCAC, NaOH, CH_2Cl_2.

Another method for preparation of bis-3-butenylamines is based on the reaction of triallylborane with amides containing at least one NH bond ($RCONH_2$ or RCONHR) (Scheme 3). These reactions require reflux in THF and reach completion within 1.5 h. This method was used to obtain primary amines **1g** (48%) and **1h** (54%).[15] A new substituted amine **1i** was synthesized by allylboration of *N*-methylbenzamide. Moderate yields of amines **1g—i** are explained by the side formation of diallylcarbinols $Allyl_2C(R)OH$, from which amines can be easily separated by acid-base extraction (treatment with HCl and then with an alkaline solution) (see Scheme 3).

2,2-Diallylated *N*-heterocycles **1j—m** were synthesized using two pathways: the allylboration of 3-chloropropionitrile with subsequent closure of the azetidine ring (**1j**) upon treatment with an alkali[17] or the allylboration of lactams with five- and six-membered ring (amines **1k,l**)[18] (Scheme 4). Derivative **1m** was obtained as described in the work,[17] but as a racemate.

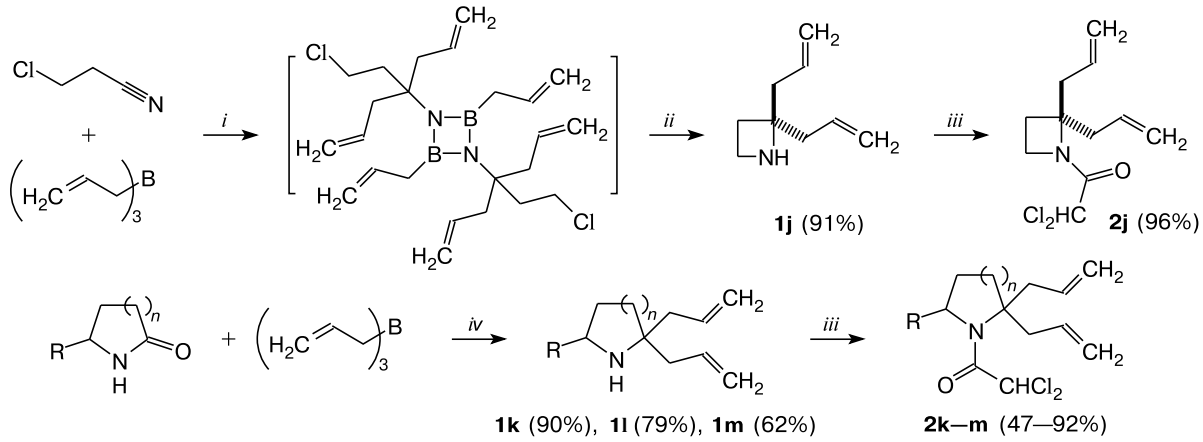
Scheme 3



1, 2: R = Bu^i, R′ = H (**g**), R = FCH_2, R′ = H (**h**), R = Ph, R′ = Me (**i**)

Reagents and conditions: *i*. 1) THF, 65 °C, 2) MeOH, 3) NaOH; *ii*. DCAC, NaOH, CH_2Cl_2.

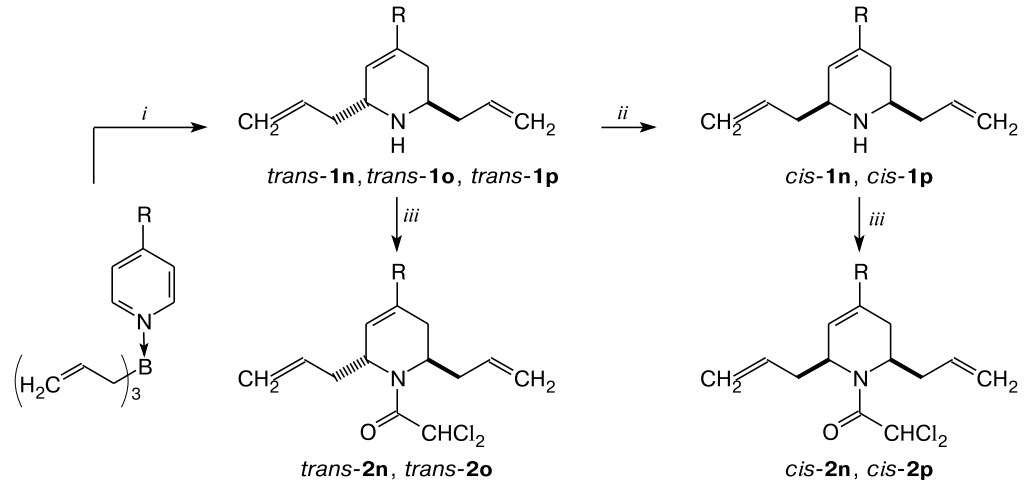
Scheme 4



1, 2: R = H, *n* = 1 (**k**), 2 (**l**); R = $HOCH_2$, *n* = 1 (**m**)

Reagents and conditions: *i*. 110 °C, 1 h; *ii*. NaOH, 70—100 °C; *iii*. DCAC, NaOH, CH_2Cl_2; *iv*. 1) THF, 65 °C, 2) MeOH, 3) NaOH, H_2O.

Scheme 5



1, 2: R = H (**n**), Me (**o**), OMe (**p**)

Compound	Yield (%)	Compound	Yield (%)
trans-**1n**	97	**1p**	59*
cis-**1n**	94	*cis*-**1p**	90
trans-**2n**	90	*cis*-**2p**	88
cis-**2n**	92		

* The ratio *trans*-**1p** : *cis*-**1p** = 2.2 : 1.

Reagents and conditions: *i*. 1) Pr^iOH (4 equiv.), 50 °C or 100 °C, 2 h, 2) MeOH, 3) NaOH, H_2O; *ii*. 1) $(H_2C{=}CHCH_2)_3B$, 130—135 °C, 5 h, 2) MeOH, 3) NaOH, H_2O; *iii*. DCAC, NaOH, CH_2Cl_2.

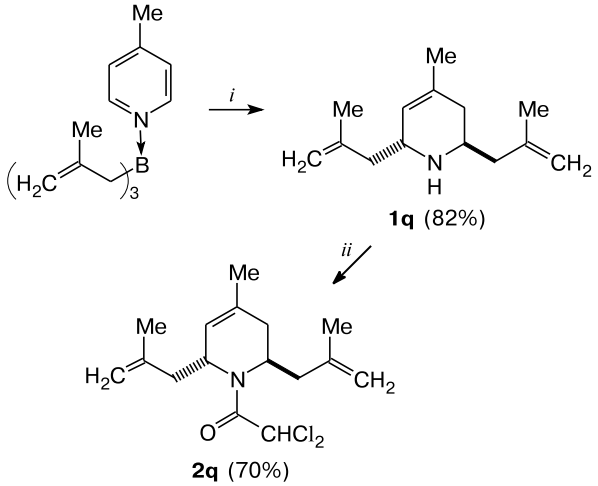
The most convenient (and the simplest) approach to *trans*- and *cis*-α,α′-diallylated derivatives of 3-piperideine and tetrahydroisoquinoline is a reductive diallylation of pyridines and isoquinolines with triallylborane in the presence of alcohols (methanol, ethanol, and, better, isopropyl alcohol).[19—21] It was found[19,20,22] that pyridine and many its derivatives (but not 2-picoline and its analogs) form 1 : 1 complexes with triallylborane, which do not decompose upon distillation *in vacuo*. The complex pyridine—triallylborane treated with propan-2-ol (20—100 °C, 2 h) undergoes a complete rearrangement with the formation of *trans*-2,6-diallyl-3-piperideine (*trans*-**1n**) in up to 80% yield. When the reaction was carried out in the presence of 0.5—1.0 moles of pyridine, the yield of *trans*-**1n** reached 97% (Scheme 5).

In the present work, we found that the reductive *trans*-2,6-diallylation of 4-picoline and 4-methoxypyridine should be carried out at 50 °C (4 equiv. of Pr^iOH, 2 h). Under these conditions, diallyl derivatives *trans*-**1o** and *trans/cis*-**1p** were obtained in 91% (*trans* : *cis* = 13 : 1) and 59% yields (*trans* : *cis* = 2.2 : 1), respectively. At 100 °C, the yield of compound **1o** varied from 37 to 76%, while no derivative **1p** was formed at all. The studies of this reaction by ^1H NMR spectroscopy showed that at the temperatures above 50 °C, the protolysis of the B—allyl bonds with the formation of propylene accompanied by the degradation of the complex of triallylborane with 4-substituted pyridine proceeds more actively instead of diallylation.

The thermodynamically more stable *cis*-derivatives *cis*-**1n** (94%)[22,23] and *cis*-**1p** (90%) were obtained by heating *trans*-isomer *trans*-**1n** and a mixture of isomers *trans/cis*-**1p** with triallylborane (130—135 °C, 5 h) (see Scheme 5). Attempted chromatographic isolation of individual *trans*-isomer *trans*-**1p** from the mixture of *trans/cis*-isomers *trans/cis*-**1p** (2.2 : 1) was unsuccessful.

trans-Dimethallyl-4-methyl-3-piperideine (*trans*-**1q**) (82%, *trans* : *cis* = 14 : 1) was synthesized by the reaction of trimethallylborane with 4-picoline (50 °C, 2 h) and isolated by chromatography (Scheme 6).

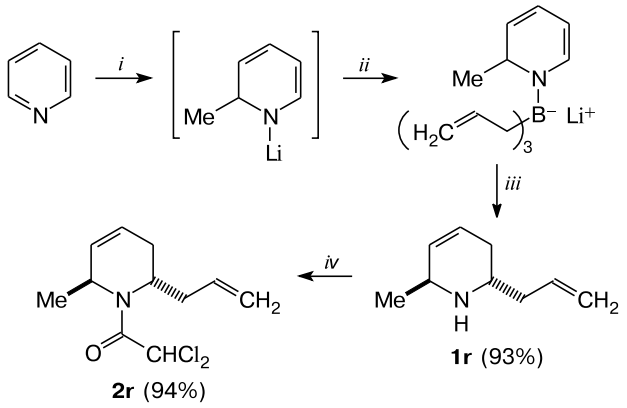
Scheme 6



Reagents and conditions: *i*. 1) Pr^iOH (4 equiv.), 50 °C, 2 h, 2) MeOH, 3) NaOH, H_2O; *ii*. DCAC, NaOH, CH_2Cl_2.

The method of allylboration of pyridines is so universal method that it allows synthesis of not only the diallyl-type derivatives **1n—q**, but also nonsymmetrically substituted compounds. Sequential treatment of pyridine with lithium derivatives RLi (R = Alk, Ar) and triallylborane can be used to obtain products containing alkyl (aryl) and allyl substituents.[24,25] Methyllithium smoothly adds to pyridine in diethyl ether with the formation of lithium 2-methyldienamide, which is captured by triallylborane (Scheme 7). Treatment of the intermediate triallylborane ate complex with methanol and subsequent deboration lead to *trans*-2-allyl-6-methyl-1,2,3,6-tetrahydropyridine (**1r**) in 93% yield.

Scheme 7



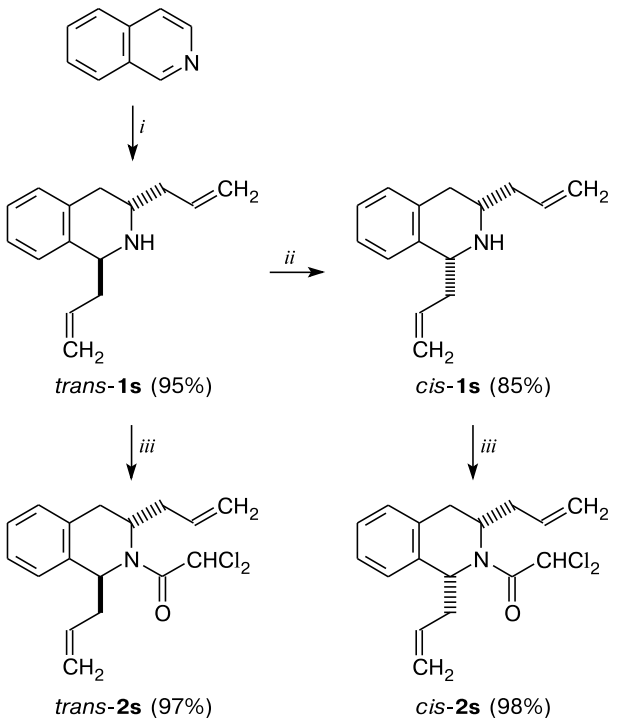
Reagents and conditions: *i*. MeLi, Et_2O, 0 °C, 1 h; *ii*. $(H_2C{=}CHCH_2)_3B$; *iii*. 1) MeOH, 2) NaOH, H_2O; *iv*. DCAC, NaOH, CH_2Cl_2.

Isoquinoline is more reactive toward triallylborane. The reaction in the presence of methanol (3 equiv.) proceeds at room temperature (2 h) and leads to *trans*-1,3-diallyl-1,2,3,4-tetrahydroisoquinoline (*trans*-**1s**) in up to 95% yield (Scheme 8).[23,26,27] Isomer *trans*-**1s** heated with triallylborane undergoes isomerization with the formation of the equilibrium mixture of *cis*- and *trans*-isomers (1 : 1), from which *cis*-isomer *cis*-**1s** is isolated by crystallization from hexane (*cis*-**1s**, m.p. 61 °C, *trans*-**1s** is an oil) or by chromatography.[23]

The reaction of triallylborane with pyrrole reached completion at room temperature within 2—3 h (at 70 °C, within 0.5 h) and led to two compounds: monoallylation product **1t** (15—30%) and *trans*-2,5-diallylpyrrolidine **1u** (60—63%) (Scheme 9).[23,28,29]

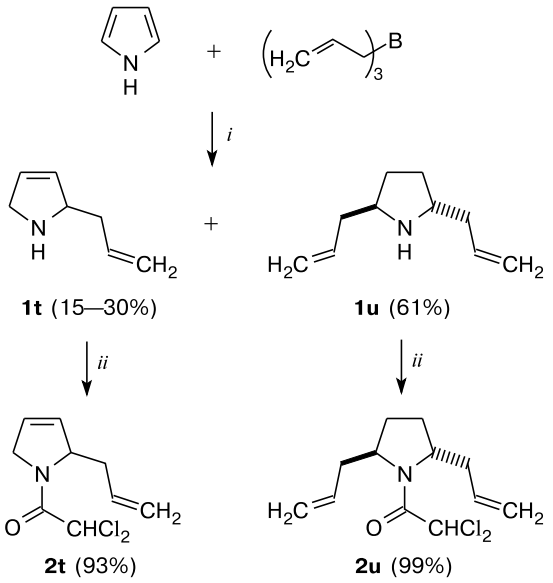
All the amines obtained (except a mixture of *trans/cis*-isomers *trans/cis*-**1p**) were converted to dichloroacetamides **2a—u** upon treatment with dichloroacetyl chloride (DCAC) (see Schemes 1—9). First, we tried an acylation procedure, which used Et_3N as a base at −30 °C, however, these conditions led to the formation of a large amount of resinification products of DCAC poorly separ-

Scheme 8



Reagents and conditions: *i*. 1) $(H_2C{=}CHCH_2)_3B$, MeOH (3 equiv.), 20 °C, 2 h, 2) MeOH, 3) NaOH, H_2O; *ii*. 1) $(H_2C{=}CHCH_2)_3B$, 130—135 °C, 2 h, 2) crystallization from hexane; *iii*. DCAC, NaOH,CH_2Cl_2.

Scheme 9



Reagents and conditions: *i*. 1) 20 °C, 2—3 h, 2) MeOH, 3) NaOH, H_2O; *ii*. DCAC, NaOH, CH_2Cl_2.

able from dichloroacetamides, while a conversion of the starting amine was not very high. The Schotten—Baumann acylation in a two-phase system CH_2Cl_2/20% aqueous NaOH at −15—−10 °C proceeds smoothly, but the rate of saponification of DCAC turns out to be higher and the conversion of the most hindered amines such as *trans*-**1n—q** lies within 20—40% even upon treatment with a 4—5-fold excess of DCAC. By reducing the rate of DCAC addition through a syringe pump, it became possible to completely and smoothly convert the amines to dichloroacetyl derivatives **2a—u** in high yields (up to 99%).

The library of synthesized dichloroacetamides of homoallylamines **2a—u** is representative for the primary screening of biological activity, since it presents the main structural variations of the starting butenyl amines. Amides **2a—u** were tested for stimulating activity. Dichlormid was used as a comparison reference (see Fig. 1 and Table 2). The stimulating activity was evaluated on germinating maize seeds (a hybrid Krasnodarsky 370 MV). The monitoring of seed germination was performed with photographic fixation. It was found that the most informative was the measurement of the length of seedlings and rootlets on the seventh day of the experiment. The regularities of the stimulating activity of Dichlormid were revealed, which made it possible to methodically correct study the new dichloroacetamide derivatives of homoallylamines. The test results are given in Table 3.

Dichlormid at the doses of 1 and 10 g (t of seeds)$^{-1}$ acts as a growth stimulant, increasing the length of seedlings and rootlets by 56 and 31.8%, respectively, however,

Table 3. The influence of dichloroacetamide derivatives **2a—u** on the germination of maize seeds (a simple midseason-ripening hybrid of maize Krasnodarsky 370 MV)

Entry	Variant of experiment[a]	Dose[b] of agent /g (t of seeds)$^{-1}$	Length of sprouts		Length of roots	
			average value /cm	in % to control	average value /cm	in % to control
1	Dichlormid	0.1	2.7	+8.0	4.0	−9.1
		1	2.8	+12.0	5.5	+25.0
		10	3.9	+56.0	5.8	+31.8
	Control	—[b]	2.5	0.0	4.4	0.0
2	**2a**	0.1	2.8	−3.4	3.9	−20.4
		1	3.1	+6.9	4.7	−4.1
		10	3.6	+24.1	4.8	−2.0
	Control	—[b]	2.9	0.0	4.9	0.0
3	**2b**	0.1	4.5	−6.3	4.1	+5.1
		1	5.1	+6.2	5.0	+28.2
		10	5.4	+12.5	4.6	+17.6
	Control	—[b]	4.8	0	3.9	0
4	**2c**	0.1	4.3	−15.7	3.5	−5.4
		1	5.3	+3.9	5.2	+40.5
		10	6.2	+21.6	5.6	+51.4
	Control	—[b]	5.1	0	3.7	0
5	**2d**	0.1	3.3	+13.8	4.4	−10.2
		1	3.3	+13.8	4.8	−2.0
		10	3.3	+13.8	6.1	+24.5
	Control	—[b]	2.9	0.0	4.9	0.0
6	**2e**	0.1	4.9	+2.1	4.1	+5.1
		1	4.7	−2.1	4.1	+5.1
		10	4.8	0	3.7	−5.1
	Control	—[b]	4.8	0	3.9	0
7	**2f**	1	6.7	+26.4	6.7	+48.9
		10	6.9	+30.2	8.3	+84.4
	Control	—[b]	5.3	0.0	4.5	0.0
8	**2g**	1	6.3	+18.9	4.5	0.0
		10	6.1	+15.1	5.4	+20.0
	Control	—[b]	5.3	0.0	4.5	0.0
9	**2h**	0.1	2.7	0.0	5.2	+4.0
		1	3.7	+37.0	6.0	+20.0
		10	3.5	+29.6	7.5	+50.0
	Control	—[b]	2.7	0.0	5.0	0.0

(*to be continued*)

Table 3 (*continued*)

Entry	Variant of experiment[a]	Dose[b] of agent /g (t of seeds)$^{-1}$	Length of sprouts		Length of roots	
			average value /cm	in % to control	average value /cm	in % to control
10	**2i**	1	5.7	+7.5	3.6	−20.0
		10	6.2	+17.0	4.0	−11.1
	Control	—[b]	5.3	0.0	4.5	0.0
11	**2j**	0.1	3.3	+22.2	5.3	+6.0
		1	3.1	+14.8	5.4	+8.0
		10	3.9	+44.4	6.5	+30.0
	Control	—[b]	2.7	0.0	5.0	0.0
12	**2k**	0.1	2.5	+4.2	5.3	+51.4
		1	2.6	+8.3	4.5	+28.6
		10	2.7	+12.5	5.3	+51.4
	Control	—[b]	2.4	0.0	3.5	0.0
13	**2l**	0.1	2.7	0.0	4.7	−6.0
		1	3.6	+33.3	5.8	+16.0
		10	3.0	+11.1	7.2	+44.0
	Control	—[b]	2.7	0.0	5.0	0.0
14	**2m**	1	6.8	+28.3	5.6	+24.4
		10	5.8	+9.4	4.4	−2.2
	Control	—[b]	5.3	0.0	4.5	0.0
15	*trans*-**2n**	0.1	3.2	+10.3	4.9	0.0
		1	3.5	+20.7	5.3	+8.2
		10	3.67	+24.1	9.8	+100.0
	Control	—[b]	2.9	0.0	4.9	0.0
16	*trans*-**2o**	1	5.4	+1.9	4.2	+6.7
		10	5.9	+11.3	5.6	+24.4
	Control	—[b]	5.3	0	4.5	0
17	**2q**	1	5.9	+11.3	4.7	+4.4
		10	7.0	+32.1	6.2	+37.8
	Control	—[b]	5.3	0	4.5	0
18	*cis*-**2n**	1	6.6	+24.5	8.2	+82.2
		10	6.5	+22.6	7.1	+57.8
	Control	—[b]	5.3	0	4.5	0
19	*cis*-**2p**	1	4.6	−19.3	3.1	−40.4
		10	6.0	+5.3	3.9	−25.0
	Control	—[b]	5.7	0	5.2	0
20	**2r**	0.1	3.2	+10.3	4.0	−18.4
		1	3.4	+17.2	4.6	−6.1
		10	3.3	+13.8	5.0	+2.0
	Control	—[b]	2.9	0.0	4.9	0.0
21	*trans*-**2s**	0.1	5.2	+8.3	4.5	+15.4
		1	5.6	+16.7	5.2	+33.3
		10	5.8	+20.8	5.1	+30.8
	Control	—[b]	4.8	0	3.9	0
22	*cis*-**2s**	1	6.8	+28.3	7.1	+57.8
		10	6.3	+18.9	8.3	+84.4
	Control	—[b]	5.3	0	4.5	0
23	**2t**	1	7.2	+35.8	9.2	+104.4
		10	6.7	+26.4	5.6	+24.4
	Control	—[b]	5.3	0	4.5	0
24	**2u**	1	6.0	+13.2	4.9	+8.9
		10	6.0	+13.2	6.6	+46.7
	Control	—[b]	5.3	0	4.5	0

[a] Control experiments were carried out using distilled water.
[b] Control was distilled water in a dose of 10 L (t of seeds)$^{-1}$.

at a minimum dose of 0.1 g (t of seeds)$^{-1}$ the root growth slows by 9.1%. Amide **2a** possesses a slightly higher toxicity and acts more as a growth retarder at the doses of 0.1 and 1 g (t of seeds)$^{-1}$, but at the dose of 10 g (t of seeds)$^{-1}$ manifested itself as a stimulant to sprouts with an activity of 24.1%, while retaining the toxic effect on rootlets (−2.0%). It is interesting to compare the effect of Dichlormid and its homolog, compound **2c**, which possesses a similar growth activity, but has the opposite distribution of activity, *i.e.*, sprouts are stimulated less actively (21.6%) and rootlets more actively (51.4%). The introduction of the phenyl group (compound **2d**) decreases the growth activity (13.8 and 24.5%) at the same dose of 10 g (t of seeds)$^{-1}$, while the methylation of the nitrogen atom (compound **2i**) leads to a general decrease in the growth activity on seedlings to 17% and exhibits a herbicidal effect on roots (−11%). The introduction of a substituent with the lipophilic bulky ester group (compound **2e**) gave an unusual effect, namely, the stimulating influence was almost completely lost and was observed only at a minimum dose of 0.1 g (t of seeds)$^{-1}$. In the case of compound **2f** (a reduced and *O*-methylated analog of **2e**), the growth activity was not only recovered, but even enhanced, which at the dose of 10 g (t of seeds)$^{-1}$ was 30.2% for sprouts and 84.4% for rootlets. The introduction of the bulky isobutyl group (compound **2g**) reduces the growth activity of sprouts and rootlets by 15.1 and 20.0% (at the dose of 10 g (t of seeds)$^{-1}$), respectively, indicating a general pattern associated with bulky substituents in the series of compounds **2c**—**g**.

The monofluoromethyl group in compound **2h** practically did not change the growth activity as compared to **2c**, which was found to be 29.6 and 50% for a 10 g (t of seeds)$^{-1}$ dose. It should be noted a stable tendency of a greater stimulating effect of our compounds on the root system growth as compared to Dichlormid.

Heterocyclic dichloroacetamides **2j**—**l** also possess a pronounced growth activity. The azetidine derivative **2j** exhibits a stimulating effect in all doses, giving a maximum value of 44.4% (for sprouts) and 30% (for rootlets) (obtained when used at the dose of 10 g (t of seeds)$^{-1}$). Pyrrolidine **2k** (at the dose of 10 g (t of seeds)$^{-1}$) has a similar effect, but it is directed more on the roots being 12.5% (for sprouts) and 51.4% (for rootlets). Further increase in the ring size does not lead to large changes; the growth activity of piperidine derivative **2l** (at the dose of 10 g (t of seeds)$^{-1}$) is 11.1 and 44.0%. The introduction of a hydroxymethyl group leads to the derivatives, which are more toxic for maize. Thus, for example, the activity of compound **2m** with respect to sprouts and rootlets at the dose of 1 g (t of seeds)$^{-1}$ is 28.3 and 24.4%, while at the dose of 10 g (t of seeds)$^{-1}$ it is 9.4 and −2.2%, respectively.

Heterocycles of tetrahydropyridine series, namely, *trans*-**2n**, *trans*-**2o**, *cis*-**2n**,**p**, **2q**, and **2r** have a dual structure, since, on the one hand, they are allylic amides and, on the other hand, homoallylic. Amide *trans*-**2n** with *trans*-arrangement of the allyl groups showed outstanding growth activity: an increase in the length of seedlings was 24.1% and that of rootlets was 100% (at the dose of 10 g (t of seeds)$^{-1}$). Its *cis*-isomer *cis*-**2n** possesses a smaller but also significant growth activity (24.5 and 82.2%), the maximum of which was achieved at the dose of 1 g (t of seeds)$^{-1}$. The introduction of a methyl group into the heterocycle of *trans*-**2o** sharply reduces the growth activity to 11.3 and 24.4% (at the dose of 10 g (t of seeds)$^{-1}$), thus demonstrating the importance of the steric environment at position 4 of the heterocycle. Some increase in the activity occurs when methallyl groups are introduced instead of allyl ones (compound **2q**). Note that compound **2q** has a balanced effect on the rootlets and seedlings: the growth activity was 32.1 and 37.8% (at the dose of 10 g (t of seeds)$^{-1}$). The influence of 4-methoxy derivative *cis*-**2p** has proved quite unexpected, which at the dose of 1 g (t of seeds)$^{-1}$ showed the herbicidal instead of growth activity −19.3% (for sprouts) and −44% (for rootlets); at the higher dose of 10 g (t of seeds)$^{-1}$, the herbicidal activity was slightly lower, +5.3 and -25%, respectively. The substitution of one of the allyl groups with the methyl one (compound **2r**) also leads to a decrease in the growth activity, which was 13.8 and 2.0% (10 g (t of seeds)$^{-1}$), while a herbicidal effect was observed at lower doses. In general, the presence of α-allyl or α-methallyl groups enhances the stimulating activity of the test compounds.

Tetrahydroisoquinoline derivatives *trans*- and *cis*-**2s** manifested good growth activity. For *trans*-isomer **2s**, it was (sprouts and rootlets) 16.7 and 33.3% (a 1 g (t of seeds)$^{-1}$ dose); 20.8 and 30.8% (a 10 g (t of seeds)$^{-1}$ dose), while for *cis*-isomer **2s** it was 28.3 and 57.8% (a 1 g (t of seeds)$^{-1}$ dose); 18.9 and 84.4% (a 10 g (t of seeds)$^{-1}$ dose). The activity of compound *cis*-**2s** was considerably higher, especially with respect to the root system development. The last compounds to be tested were derivatives of pyrroline **2t** and pyrrolidine **2u**. Compound **2t**, which, like compounds **2n**—**s**, is a hybrid of allyl- and homoallylamine, has proved the most potent growth stimulant (sprouts and rootlets): the growth activity was 35.8 and 104.4% (at the dose of 1 g (t of seeds)$^{-1}$), with an increase in the dose of the substance leading to a decrease in the stimulating effect, presumably, due to toxicity. Compound **2u** is an isomer of 2,2-diallylated derivative **2k** with a different arrangement of the allyl groups. The growth activity of **2u** was found to be close to the activity of compound **2k** and equal to (sprouts and rootlets) 13.2 and 46.7% (at the dose of 10 g (t of seeds)$^{-1}$).

From the examination of biological activity, it can be concluded that dichloroacetic acid 3-butenylamides have a high potential as plant growth stimulators. Unlike the stimulating activity of Dichlormid, the influence of 3-butenylamides has proved to be more potent and selective

with respect to the root system. The most active were aliphatic analogs of Dichlormid, especially that with 2-methoxyethyl group (compound **2f**). Heterocyclic 2,2-diallylated derivatives **2j—l** with different ring sizes also exhibited pronounced growth activity. The maximum activity was demonstrated by pyrrolidine derivative **2k**. The record-high activity on the root system growth was exhibited by 2,6-diallyl-1,2,3,6-tetrahydropyridine derivatives *trans*-**2n** (100%) and *cis*-**2n** (82%). A similar activity was also observed in the case of diallylated derivatives of tetrahydroisoquinoline *trans*- and *cis*-**2s**. Pyrroline amide **2t**, a unique hybrid of allyl- and homoallylamines, was also exceptionally active (104%). We plan to study further the effect of the structure of 3-butenylamines on the growth regulating activity, as well as its relationship with the potential antidotal activity of homoallylic compounds.

Experimental

Reactions were carried out under atmosphere of dry argon. All the solvents used were purified according to the standard procedures. NMR spectra were recorded on Bruker Avance-300 (compound *cis*-**1p**) and Bruker Avance-400 spectrometers (other compounds) in $CDCl_3$. Column chromatography was carried out using silica gel 60—230 mesh (Merck). Allylated amines **1a**,[12] **1b**,[16] **1c—h**,[15] **1j** and **1m**,[18] **1k** and **1l**[17], *trans*-**1n** and *cis*-**1n**[22], *trans*-**1o** and *cis*-**1s**,[23] **1r**,[24,25] *trans*-**1s**,[26] **1t** and **1u**[28,29] were obtained according to the described procedures.

1-Allylbut-3-enylamine (1c). Triallylborane (7.37 g, 9.51 mL, 55.0 mmol) was added dropwise to a solution of HCN (synthesized *in situ* from TMSCN (4.96 g, 6.25 mL, 50.0 mmol) in a mixture of CH_2Cl_2 (30 mL) and MeOH (1.60 g, 2.03 mL, 50.0 mmol) with stirring at 25 °C for 20 min)[30] cooled to −20 °C under argon atmosphere. The resulting solution was gradually heated to 140 °C, simultaneously distilling off CH_2Cl_2. The residual dense mass was heated at 140 °C for 4.5 h (until the mixture became homogeneous and liquid). Then, a 5 *M* solution of NaOH (33 mL, 165.0 mmol) was added slowly to the reaction mixture cooled down to 80 °C, so that the temperature did not exceed 110 °C. After the addition was completed, the mixture was refluxed for 1 h, followed by the addition of a saturated solution of KOH (50 mL) and, after cooling, by the extraction with a mixture of n-C_5H_{12}—Et_2O (1 : 1) (3×20 mL). The extracts were dried with KOH, concentrated, and distilled, collecting the fraction with b.p. 76 °C (90 Torr). The yield was 3.82 g (69%). ^{1}H NMR, δ: 5.83—5.73 (m, 2 H, 2 CH=); 5.10—5.06 (m, 4 H, CH_2=); 2.85 (tt, 1 H, CH, J = 4.7 Hz, J = 7.6 Hz); 2.25—2.19 (m, 2 H, 2 C$\underline{H}_A$H$_B$); 2.01 (dt, 2 H, 2 CH$_A\underline{H}_B$, J = 7.9 Hz, J = 13.7 Hz); 1.60 (br.s, 2 H, NH_2) (see Ref. 16). ^{13}C NMR, δ: 135.54 (2 C); 117.42 (2 C); 50.02; 41.89 (2 C).

***N*-(1-Allyl-1-phenylbut-3-enyl)-*N*-methylamine (1i).** Triallylborane (11.72 g, 15.14 mL, 87.5 mmol (a 1.6-fold excess)) was added to a solution of *N*-methylbenzamide (7.40 g, 54.7 mmol) in THF (20 mL). After the completion of the exothermic reaction, the mixture was refluxed for 1.5 h and cooled, after the careful addition of MeOH (10 mL) the mixture was refluxed for 30 min followed by the addition of 5 *M* NaOH (70 mL, 0.35 mol) and reflux for 1.5 h. After the complete deboration (test for green color of flame), the reaction mixture was diluted with hexane and cooled, the organic layer was separated and washed with water. Then, the organic phase was washed with 3 *M* HCl (20 mL), the aqueous layer was separated and twice extracted with a mixture of hexane—Et_2O (1 : 1). After that, the aqueous layer was alkalized by addition of solid NaOH (5 g) and extracted with hexane (3×10 mL), the combined extracts were dried with K_2CO_3, concentrated, and distilled *in vacuo*, collecting the fraction with b.p. 77—79 °C (0.5 Torr). Compound **1i** (7.37 g, 67%) was obtained as pale yellow liquid. ^{1}H NMR, δ: 7.42—7.39 (m, 2 H, Ph); 7.36—7.32 (m, 3 H, Ph); 5.58 (ddt, 2 H, 2 CH=, J = 7.2 Hz, J = 10.3 Hz, J = 16.5 Hz); 5.09—5.04 (m, 4 H, CH_2=); 2.57—2.52 (m, 4 H, 2 CH_2); 2.17 (s, 3 H, NMe); 1.73 (br.s, 1 H, NH). ^{13}C NMR, δ: 144.57; 133.85 (2 C); 128.00 (2 C); 126.62 (2 C); 126.28; 117.99 (2 C); 60.55; 41.49 (2 C); 28.54. Found (%): C, 83.66; H, 9.58; N, 7.01. $C_{14}H_{19}N$. Calculated (%): C, 83.53; H, 9.51; N, 6.96.

Reductive allylation of 4-substituted pyridines (general procedure). A 4-substituted pyridine (0.2 mol) was added dropwise to triallylborane (13.4 g, 16.8 mL, 0.1 mol) cooled to −30 °C under argon atmosphere. Then, the reaction mixture was allowed to stand to warm-up to 0 °C, followed by the addition of Pr^{i}OH (24.0 g, 30.6 mL, 0.4 mol) in one portion and heating the mixture at 50 °C for 2 h. Then, 5 *M* NaOH (40 mL, 0.2 mol) was added with stirring, the organic phase was diluted with hexane, the organic layer was separated, dried with K_2CO_3, and concentrated on a rotary evaporator. The residue was distilled *in vacuo*.

***trans*-2,6-Diallyl-4-methyl-1,2,3,6-tetrahydropyridine (*trans*-1o)** was synthesized according to the general procedure from 4-picoline (0.2 mol) and triallylborane (0.1 mol) in 32.04 g (91%) yield. According to the ^{1}H NMR spectrum, the ratio of *trans*/*cis*-isomers was 13 : 1. ^{1}H NMR, δ: 5.80—5.70 (m, 2 H, 2 CH=); 5.35 (m, 1 H, CH= of ring); 5.11—5.02 (m, 4 H, 2 CH_2=); 3.34 (br.s, 1 H, CHN); 2.96—2.89 (tt, 1 H, CHN, J = 4.1 Hz, J = 8.3 Hz); 2.23—2.05 (m, 4 H, 2 CH_2); 1.85 (br.dd, 2 H, C$\underline{H}_A$H$_B$ and NH, J = 4.1 Hz, J = 16.8 Hz); 1.70 (dd, 1 H, CH$_A\underline{H}_B$, J = 8.6 Hz, J = 16.8 Hz) 1.66 (s, 3 H, Me) (see Ref. 23).

***cis*/*trans*-2,6-Diallyl-4-methoxy-1,2,3,6-tetrahydropyridine (1p)** was synthesized according to the general procedure from 4-methoxypyridine (6.0 g, 5.6 mL, 0.055 mol) and triallylborane (3.69 g, 4.8 mL, 0.028 mol), the yield was 6.24 g (59%). According to the ^{1}H NMR spectrum, the ratio of *trans*/*cis*-isomers was 2.2 : 1. Found (%): C, 74.39; H, 10.12; N, 7.32. $C_{12}H_{19}NO$. Calculated (%): C, 74.57; H, 9.91; N, 7.25.

***trans*-2,6-Dimethallyl-4-methyl-1,2,3,6-tetrahydropyridine (1q)** was synthesized according to the general procedure from 4-picoline (0.05 mol) and trimethallylborane (0.025 mol), the yield was 4.20 g (82%), oil, b.p. 79—80 °C (0.5 Torr). According to the ^{1}H NMR spectrum, the ratio of *trans*/*cis*-isomers was 14 : 1. ^{1}H NMR, δ: 5.35—5.31 (m, 1 H, CH=); 4.81—4.78 (m, 2 H, CH_2=); 4.76—4.75 (m, 1 H, C$\underline{H}_A$H$_B$=); 4.67—4.66 (m, 1 H, CH$_A\underline{H}_B$=); 3.52—3.45 (m, 1 H, CHN); 3.00 (tt, 1 H, CHN, J = 4.5 Hz, J = 8.6 Hz); 2.12—2.07 (m, 3 H, 2C$\underline{H}_A$H$_B$ of methallyl and C$\underline{H}_A$H$_B$ of ring); 1.92 (dd, 1 H, CH$_A\underline{H}_B$ of methallyl, J = 0.5 Hz, J = 4.4 Hz); 1.92 (dd, 1 H, CH$_A\underline{H}_B$ of methallyl, J = 0.5 Hz, J = 4.4 Hz); 1.81—1.77 (m, 1 H, CH$_A\underline{H}_B$ of ring); 1.72—1.71 (m, 6 H, 2 CH_3); 1.68—1.67 (m, 3 H, CH_3). ^{13}C NMR, δ: 142.76; 142.17; 132.55; 123.05; 113.26; 113.17; 49.60; 44.34; 44.32; 43.08; 36.64; 23.32; 22.23; 22.06. Found (%): C, 81.82; H, 11.17; N, 6.84. $C_{14}H_{23}N$. Calculated (%): C, 81.89; H, 11.29; N, 6.82.

***cis*-2,6-Diallyl-4-methoxy-1,2,3,6-tetrahydropyridine (*cis*-1p).** Triallylborane (2.95 g, 3.8 mL, 22.0 mmol) was added dropwise to a mixture of *cis/trans*-isomers of compound **1p** (3.93 g, 20 mmol) with stirring and the resulting mixture was heated at 130—135 °C for 6 h. Then, it was treated with MeOH (1.8 mL) and 20% solution of NaOH (5.2 mL). After addition of hexane (10 mL), the organic layer was separated, dried with K_2CO_3, and concentrated on a rotary evaporator, the residue was distilled *in vacuo*, b.p. 88—90 °C (0.5 Torr). Compound *cis*-**1p** (3.36 g, 86%) was obtained as light yellow liquid. According to the ^{1}H NMR spectrum, the ratio of *cis/trans*-isomers was 15.2 : 1. ^{1}H NMR, δ: 5.96—5.73 (m, 2 H, 2 CH= of allyls); 5.22—5.12 (m, 4 H, 2 CH_2=); 4.58 (br.s, 1 H, CH= of ring); 3.57 (s, 3 H, OMe); 3.53—3.47 (m, 1 H, C(2)HN); 2.95—2.86 (m, 1 H, C(6)HN); 2.43—2.16 (m, 4 H, 2 CH_2 of allyls); 2.06—2.03 (m, 2 H, CH_2 of ring); 2.00 (br.s, 1 H, NH). ^{13}C NMR, δ: 154.79; 135.18; 134.78; 117.67; 117.51; 96.65; 53.97; 53.10; 52.47; 41.77; 40.68; 34.63. Found (%): C, 74.48; H, 10.02; N, 7.26. $C_{12}H_{19}NO$. Calculated (%): C, 74.57; H, 9.91; N, 7.25.

Synthesis of dichloroacetamides 2a—u (general procedure). A solution of dichloroacetyl chloride (DCAC) (4—8 mmol) in CH_2Cl_2 (2 mL) was added through a syringe pump over 2 h to a vigorously stirred mixture of amine **1a—u** (2.0 mmol), 20% solution of NaOH (10 mmol), and CH_2Cl_2 (5 mL) at −15 °C, so that the temperature did not exceed −10 °C. The reaction progress was monitored by TLC. After the disappearance of the starting amine **1a—u**, the reaction mixture was stirred for 15 min at 25 °C, the organic layer was separated, washed with 1 *M* HCl and water, dried with K_2CO_3, and concentrated on a rotary evaporator. The residue was subjected to chromatography or recrystallized from an appropriate solvent.

***N*-(1,1-Dimethylbut-3-enyl)dichloroacetamide (2a)** was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (6 : 1). The yield was 94%. R_f 0.56 (*n*-C_6H_{14}—EtOAc (6 : 1)), m.p. 39—40 °C (*n*-C_6H_{14}). ^{1}H NMR, δ: 6.33 (br.s, 1 H, NH); 5.79 (s, 1 H, $CHCl_2$); 5.77 (ddt, 1 H, CH=, J = 7.3 Hz, J = 10.2 Hz, J = 17.2 Hz); 5.16—5.11 (m, 2 H, CH_2=); 2.44 (d, 2 H, CH_2F, J = 7.6 Hz); 1.37 (s, 6 H, 2Me). ^{13}C NMR, δ: 162.97; 133.00; 119.42; 67.03; 53.98; 44.47; 26.15 (2 C). Found (%): C, 45.70; H, 6.28; N, 6.73. $C_8H_{13}Cl_2NO$. Calculated (%): C, 45.73; H, 6.24; N, 6.67.

***N*-(1-Phenylbut-3-enyl)dichloroacetamide (2b)** was recrystallized from a mixture of Et_2O—*n*-C_6H_{14}. The yield was 89%. R_f 0.31 (*n*-C_6H_{14}—EtOAc (6 : 1)), m.p. 91—92 °C. ^{1}H NMR, δ: 7.40—7.36 (m, 2 H, Ph); 7.33—7.28 (m, 3 H, Ph); 6.85 (br.s, 1 H, NH); 5.94 (s, 1 H, $CHCl_2$); 5.78—5.67 (m, 1 H, CH=); 5.22—5.16 (m, 2 H, CH_2=); 5.06 (q, 1 H, CHN, J = 7.0 Hz); 2.66 (dd, 2 H, CH_2, J = 6.7 Hz, J = 7.0 Hz). ^{13}C NMR, δ: 163.32; 140.17; 132.98; 128.76 (2 C); 127.72; 126.17 (2 C); 119.13; 66.50; 53.04; 40.21. Found (%): C, 55.94; H, 5.12; N, 5.50. $C_{12}H_{13}Cl_2NO$. Calculated (%): C, 55.83; H, 5.08; N, 5.43.

***N*-(1-Allylbut-3-enyl)dichloroacetamide (2c)** was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (6 : 1). The yield was 94%. R_f 0.41 (*n*-C_6H_{14}—EtOAc (6 : 1)), m.p. 43 °C. ^{1}H NMR, δ: 6.38 (br.s, 1 H, NH); 5.88 (s, 1 H, $CHCl_2$); 5.81—5.71 (m, 2 H, 2 CH=); 5.14—5.10 (m, 4 H, 2 CH_2=); 4.06—3.98 (m, 1 H, CHN); 2.37—2.24 (m, 4 H, 2 CH_2). ^{13}C NMR, δ: 163.55; 133.24 (2 C); 118.72 (2 C); 66.58; 48.92; 37.89 (2 C). Found (%): C, 48.58; H, 5.87; N, 6.40. $C_9H_{13}Cl_2NO$. Calculated (%): C, 48.67; H, 5.90; N, 6.31.

***N*-(1-Allyl-1-phenylbut-3-enyl)dichloroacetamide (2d)** was recrystallized from hot *n*-C_6H_{14}. The yield was 89%. R_f 0.52 (*n*-C_6H_{14}—EtOAc (6 : 1)), m.p. 121—122 °C. ^{1}H NMR, δ: 7.38—7.34 (m, 2 H, Ph); 7.29—7.25 (m, 3 H, Ph); 6.79 (br.s, 1 H, NH); 5.85 (s, 1 H, $CHCl_2$); 5.58 (dddd, 2 H, 2 CH=, J = 6.4 Hz, J = 8.3 Hz, J = 10.2 Hz, J = 16.5 Hz); 5.20—5.16 (m, 4 H, 2 CH_2=); 2.98 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 6.4 Hz, J = 14.0 Hz); 2.77 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 8.3 Hz, J = 14.0 Hz). ^{13}C NMR, δ: 162.73; 132.38 (2 C); 128.47 (2 C); 127.13; 125.19 (2 C); 119.98 (2 C); 67.10; 60.65; 42.58 (2 C). Found (%): C, 60.46; H, 5.83; N, 4.64. $C_{15}H_{17}Cl_2NO$. Calculated (%): C, 60.41; H, 5.75; N, 4.70.

***tert*-Butyl 3-allyl-3-[(dichloroacetyl)amino]-5-hexenoate (2e)** was recrystallized from cold *n*-C_6H_{14}. The yield was 88%. R_f 0.75 (*n*-C_6H_{14}—EtOAc (6 : 1)), m.p. 67—68 °C. ^{1}H NMR, δ: 7.49 (br.s, 1 H, NH); 5.81 (s, 1 H, $CHCl_2$); 5.78—5.70 (m, 2 H, 2 CH=); 5.17—5.12 (m, 4 H, 2 CH_2=); 2.77 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 7.0 Hz, J = 14.0 Hz); 2.54 (s, 2 H, CH_2COBu^t); 2.50 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 7.9 Hz, J = 14.0 Hz); 1.46 (s, 9 H, Bu^t). Some signals are split in the ^{13}C NMR spectrum, δ: 170.82; 163.22; (132.31; 132.24) (2 C); (119.92; 119.90; 119.85) (2 C); 81.79; 67.04; 57.67; 40.85; 40.31 (2 C); (28.27; 28.04; 28.01; 27.78) (3 C). Found (%): C, 53.47; H, 6.85; N, 4.16. $C_{15}H_{23}Cl_2NO_3$. Calculated (%): C, 53.58; H, 6.89; N, 4.17.

***N*-[1-Allyl-3-butenyl-1-(2-methoxyethyl)]dichloroacetamide (2f)** was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (20 : 1). The yield was 92%, light liquid. R_f 0.2 (*n*-C_6H_{14}—EtOAc (20 : 1)). ^{1}H NMR, δ: 7.81 (br.s, 1 H, NH); 5.77 (s, 1 H, $CHCl_2$); 5.76—5.66 (m, 2 H, 2 CH=); 5.10—5.06 (m, 4 H, 2 CH_2=); 3.56 (t, 2 H, CH_2O, J = 5.4 Hz); 3.31 (s, 3 H, MeO); 2.75 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 7.0 Hz, J = 14.0 Hz); 2.48 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 8.0 Hz, J = 14.0 Hz); 1.83 (t, 2 H, CH_2CN, J = 5.4 Hz). ^{13}C NMR, δ: 163.27; 132.88 (2 C); 118.93 (2 C); 68.76; 67.13; 58.66; 58.60; 40.13 (2 C); 34.55. Found (%): C, 51.38; H, 6.87; N, 4.92. $C_{12}H_{19}Cl_2NO_2$. Calculated (%): C, 51.44; H, 6.83; N, 5.00.

***N*-(1-Allyl-1-isobutylbut-3-enyl)dichloroacetamide (2g)** was recrystallized from cold *n*-C_6H_{14}. The yield was 90%. R_f 0.7 (*n*-C_6H_{14}—EtOAc (6 : 1)), m.p. 84—85 °C. The NMR spectrum showed the presence of rotamers in the ratio of 8 : 1. ^{1}H NMR, δ, major rotamer: 6.25 (br.s, 1 H, NH); 5.78 (s, 1 H, $CHCl_2$); 5.80—5.70 (m, 2 H, 2 CH=); 5.17—5.12 (m, 4 H, 2 CH_2=); 2.56 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 7.3 Hz, J = 14.0 Hz); 2.48 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 7.3 Hz, J = 14.0 Hz); 1.83—1.72 (m, 1 H, CH); 1.69 (d, 2 H, $C\underline{H}_2CH$, J = 5.7 Hz); 0.96 (d, 6 H, 2 CH_3, J = 6.7 Hz). ^{13}C NMR, δ: 162.63; 132.63 (2 C); 119.53 (2 C); 67.18; 59.13; 43.48; 39.99 (2 C); 24.46 (2 C); 23.79. The NMR spectra of the minor rotamer are not reported because of the low intensity and the overlap of the signals. Found (%): C, 56.16; H, 7.59; N, 4.99. $C_{13}H_{21}Cl_2NO$. Calculated (%): C, 56.12; H, 7.61; N, 5.03.

***N*-(1-Allyl-1-fluoromethylbut-3-enyl)dichloroacetamide (2h)** was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (10 : 1). The yield was 96%, oil. R_f 0.23 (*n*-C_6H_{14}—EtOAc (10 : 1)). ^{1}H NMR, δ, 6.42 (br.s, 1 H, NH); 5.82 (s, 1 H, $CHCl_2$); 5.77 (ddt, 2 H, 2 CH=, J = 7.3 Hz, J = 10.2 Hz, J = 17.2 Hz); 5.22—5.17 (m, 4 H, 2 CH_2=); 4.58 (d, 2 H, $C\underline{H}_2F$, J_{H-F} = 47.0 Hz); 2.59 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 7.3 Hz, J = 14.0 Hz); 2.49 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 7.6 Hz, J = = 14.0 Hz). ^{13}C NMR, δ: 163.43; 131.29 (2 C); 120.50 (2 C); (84.44, 82.69, $^{1,2}J_{CF}$ = 175 Hz); 66.73 (58.49, 58.32, $^{1,3}J_{CF}$ =

= 16.8 Hz); (37.05, 37.02, $^{1,4}J_{CF}$ = 3.6 Hz) (2 C). Found (%): C, 47.24; H, 5.47; N, 5.57. $C_{10}H_{14}Cl_2FNO$. Calculated (%): C, 47.26; H, 5.55; N, 5.51.

***N*-(1-Allyl-1-phenylbut-3-enyl)dichloro-*N*-methylacetamide (2i)** was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (15 : 1). The yield was 82%, oil. R_f 0.31 (*n*-C_6H_{14}—EtOAc (12 : 1)). ^{1}H NMR, δ: 7.33—7.30 (m, 2 H, Ph); 7.23—7.21 (m, 3 H, Ph); 6.13 (s, 1 H, $CHCl_2$); 5.55—5.45 (m, 2 H, 2 CH=); 5.13—5.08 (m, 4 H, 2 CH_2=); 3.26 (s, 3 H, NMe); 3.20 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 8.4 Hz, J = 12.6 Hz); 2.80 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 6.2 Hz, J = 13.1 Hz). ^{13}C NMR, δ: 163.00; 144.67; 132.84 (2 C); 128.15 (2 C); 126.67; 125.11 (2 C); 119.41 (2 C); 67.45; 39.75 (2 C); 34.60. Found (%): C, 61.48; H, 6.01; N, 4.54. $C_{16}H_{19}Cl_2NO$. Calculated (%): C, 61.55; H, 6.13; N, 4.49.

1-(2,2-Diallyl-1-azetidinyl)-2,2-dichloroethan-1-one (2j) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (10 : 1). The yield was 96%, oil. R_f 0.36 (*n*-C_6H_{14}—EtOAc (10 : 1)). ^{1}H NMR, δ: 5.86 (dddd, 2 H, 2 CH=, J = 7.0 Hz, J = 8.3 Hz, J = 10.5 Hz, J = 17.2 Hz); 5.78 (s, 1 H, $CHCl_2$); 5.20—5.15 (m, 4 H, 2 CH_2=); 4.11—4.07 (m, 2 H, CH_2N); 2.85 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 6.7 Hz, J = 14.0 Hz); 2.33 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 8.0 Hz, J = 14.0 Hz); 2.18—2.14 (m, 2 H, CH_2CN). ^{13}C NMR, δ: 161.79; 132.24 (2 C); 119.65 (2 C); 72.37; 65.22; 47.04; 41.11 (2 C); 23.48. Found (%): C, 53.28; H, 5.96; N, 5.57. $C_{11}H_{15}Cl_2NO$. Calculated (%): C, 53.24; H, 6.09; N, 5.64.

1-(2,2-Diallyl-1-pyrrolidino)-2,2-dichloroethan-1-one (2k) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (10 : 1). The yield was 92%, oil. R_f 0.42 (*n*-C_6H_{14}—EtOAc (8 : 1)). ^{1}H NMR, δ: 6.08 (s, 1 H, $CHCl_2$); 5.72—5.62 (m, 2 H, 2 CH=); 5.10—5.06 (m, 4 H, 2 CH_2=); 3.61 (t, 2 H, CH_2N, J = 6.6 Hz); 2.97 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 6.7 Hz, J = 13.4 Hz); 2.37 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 8.0 Hz, J = 13.7 Hz); 1.93—1.81 (m, 4 H, 2 CH_2). ^{13}C NMR, δ: 161.11; 133.39 (2 C); 118.88 (2 C); 68.94; 66.86; 49.37; 40.83 (2 C); 33.55; 23.13. Found (%): C, 55.02; H, 6.60; N, 5.31. $C_{12}H_{17}Cl_2NO$. Calculated (%): C, 54.97; H, 6.54; N, 5.34.

1-(2,2-Diallylpiperidino)-2,2-dichloroethan-1-one (2l) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (15 : 1). The yield was 90%, oil. R_f 0.49 (*n*-C_6H_{14}—EtOAc (10 : 1)). ^{1}H NMR, δ: 6.12 (s, 1 H, $CHCl_2$); 5.72 (ddt, 2 H, 2 CH=, J = 7.3 Hz, J = 10.2 Hz, J = 16.8 Hz); 5.11—5.06 (m, 4 H, 2 CH_2=); 3.54—3.51 (m, 2 H, CH_2N); 2.96 (dd, 2 H, 2 $C\underline{H}_AH_B$, J = 7.3 Hz, J = 13.6 Hz); 2.52 (dd, 2 H, 2 $CH_A\underline{H}_B$, J = 7.6 Hz, J = 13.6 Hz); 1.77—1.63 (m, 6 H, 3 CH_2). ^{13}C NMR, δ: 163.06; 133.54 (2 C); 118.61 (2 C); 67.63; 62.30; 43.33; 40.09 (2 C); 28.79; 21.69; 15.65. Found (%): C, 56.58; H, 6.89; N, 5.13. $C_{13}H_{19}Cl_2NO$. Calculated (%): C, 56.53; H, 6.93; N, 5.07.

1-[2,2-Diallyl-5-(hydroxymethyl)-1-pyrrolidino]-2,2-dichloroethan-1-one (2m), DCAC was used in an equivalent amount with respect to the aminoalcohol. The product was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (4 : 1). The yield was 47%, oil crystallizing on standing, m.p. 43—44 °C. R_f 0.28 (*n*-C_6H_{14}—EtOAc (4 : 1)). ^{1}H NMR, δ: 6.75 (s, 1 H, $CHCl_2$); 5.77—5.67 (m, 2 H, 2 CH=); 5.13—5.05 (m, 4 H, 2 CH_2=); 4.12—4.07 (m, 1 H, CHN); 3.58 (dd, 1 H, $C\underline{H}_AH_BOH$, J = 5.4 Hz, J = 10.8 Hz); 3.48 (dd, 1 H, $CH_A\underline{H}_BOH$, J = 9.9 Hz, J = 10.8 Hz); 3.04 (dd, 1 H, $C\underline{H}_AH_B$, J = 6.7 Hz, J = 13.7 Hz); 2.93 (dd, 1 H, $CH_A\underline{H}_B$, J = 7.0 Hz, J = 13.7 Hz); 2.58 (br.s, 1 H, OH); 2.41 (dd, 1 H, $C\underline{H}_{A'}H_{B'}$, J = 7.9 Hz, J = 13.6 Hz); 2.33 (dd, 1 H, $CH_{A'}\underline{H}_{B'}$, J = 8.3 Hz, J = 13.4 Hz); 2.09—1.91 (m, 2 H, $CHC\underline{H}_2$); 1.82 (ddd, 1 H, $C\underline{H}_AH_BCAll_2$, J = 1.6 Hz, J = 6.4 Hz, J = 11.4 Hz); 1.53 (ddd, 1 H, $CH_A\underline{H}_BCAll_2$, J = 2.2 Hz, J = 6.4 Hz, J = 12.1 Hz). ^{13}C NMR, δ: 163.39; 134.08; 133.60; 119.14; 118.70; 69.65; 67.03; 64.26; 60.34; 41.81; 40.41; 31.85; 25.31. Found (%): C, 53.36; H, 6.48; N, 4.81. $C_{13}H_{19}Cl_2NO_2$. Calculated (%): C, 53.44; H, 6.55; N, 4.79.

1-[*trans*-2,6-Diallyl-3,6-dihydro-(2*H*)-pyridino]-2,2-dichloroethan-1-one (*trans*-2n) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (15 : 1). The yield was 90%, oil. R_f 0.43 (*n*-C_6H_{14}—EtOAc (12 : 1)). The signals in the NMR spectra were broadened because of the hindered rotation around the amide bond. ^{1}H NMR, δ: 6.34 (br.s, 1 H, $CHCl_2$); 5.86 (br.s, 2 H, 2 CH= of ring); 5.74—5.63 (m, 2 H, 2 CH=); 5.08—5.04 (m, 4 H, 2 CH_2=); 4.31 (br.s, 1 H, CHN); 4.04 (br.s, 1 H, CHN); 2.74 (br.s, 1 H, $C\underline{H}_AH_B$); 2.41—2.35 (br.m, 3 H, $CH_A\underline{H}_B$, CH_2); 2.25—2.19 (br.m, 2 H, CH_2). ^{13}C NMR, δ: 164.09; 133.63 (br.); 133.04; 128.87 (br.); 122.62 (br.); 119.15 (br.); 118.29 (br.); 65.44 (br.); 52.72 (br.); 52.16 (br.); 39.34 (br.); 36.49 (br.); 27.06. Found (%): C, 56.83; H, 6.34; N, 5.07. $C_{13}H_{17}Cl_2NO$. Calculated (%): C, 56.95; H, 6.25; N, 5.11.

1-[*trans*-2,6-Diallyl-4-methyl-3,6-dihydro-(2*H*)-pyridino]-2,2-dichloroethan-1-one (*trans*-2o) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (10 : 1). The yield was 88%, oil. R_f 0.55 (*n*-C_6H_{14}—EtOAc (4 : 1)). The signals in the NMR spectra were broadened because of the hindered rotation around the amide bond. ^{1}H NMR, δ: 6.34 (br.s, 1 H, $CHCl_2$); 5.74—5.63 (m, 2 H, 2 CH=); 5.54—5.53 (br.s, 2 H, 2 CH= of ring); 5.17—4.98 (br.m, 4 H, 2 CH_2=); 4.28 (br.s, 1 H, CHN); 4.01 (br.s, 1 H, CHN); 2.66 (br.s, 1 H, $C\underline{H}_AH_B$); 2.44—2.15 (br.m, 4 H, $CH_A\underline{H}_B$, CH_2, $C\underline{H}_AH_B$ of ring); 2.01—1.92 (br.m, 1 H, $CH_A\underline{H}_B$ of ring); 1.76 (s, 3 H, Me). ^{13}C NMR, δ: 163.83; 133.82 (br.); 133.44 (br.); 131.19 (br.); 121.91 (br.); 119.13 (br.); 118.08 (br.); 65.42 (br.); 52.85; 52.29 (br.); 39.56 (br.); 36.98 (br.); 31.79; 23.39. Found (%): C, 58.37; H, 6.71; N, 4.76. $C_{14}H_{19}Cl_2NO$. Calculated (%): C, 58.34; H, 6.64; N, 4.86.

1-[4-Methyl-*trans*-2,6-bis(2-methyl-2-propenyl)-3,6-dihydro-(2*H*)-pyridino]-2,2-dichloroethan-1-one (2q) was recrystallized from cold *n*-C_6H_{14}. The yield was 70%. R_f 0.46 (*n*-C_6H_{14}—EtOAc (15 : 1)), m.p. 97—98 °C. The signals in the NMR spectra were broadened because of the hindered rotation around the amide bond. ^{1}H NMR, δ: 6.33 (br.s, 1 H, $CHCl_2$); 5.63 (br.s, 1 H, CH= of ring); 4.85—4.68 (br.m, 4 H, 2 CH_2=); 4.41 (br.s, 1 H, CHN); 4.16—4.12 (br.s, 1 H, CHN); 2.66—2.07 (br.m, 6 H, 3 CH_2); 1.78 (s, 3 H, Me); 1.76 (s, 6 H, 2 Me). ^{13}C NMR, δ: 163.66; 142.22 (br.); 141.19 (br.); 131.07 (br.); 122.55 (br.); 114.81 (br.); 113.29 (br.); 64.88; 53.01 (br.); 51.48; 43.46 (br.); 42.16 (br.); 30.94 (br.); 23.54; 22.71 (br.); 22.07 (br.). Found (%): C, 60.81; H, 7.28; N, 4.35. $C_{16}H_{23}Cl_2NO$. Calculated (%): C, 60.76; H, 7.33; N, 4.43.

1-[*cis*-2,6-Diallyl-3,6-dihydro-(2*H*)-pyridino]-2,2-dichloroethan-1-one (*cis*-2n) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (10 : 1). The yield was 92%, oil. R_f 0.47 (*n*-C_6H_{14}—EtOAc (6 : 1)). The NMR spectrum showed the presence of rotamers in the ratio of 4 : 1. ^{1}H NMR, δ, major rotamer: 6.25 (s, 1 H, $CHCl_2$); 5.91—5.69 (m, 4 H, 4 CH=); 5.14—5.08 (m, 4 H, 2 CH_2=); 4.61—4.56 (s, 1 H, CHN); 4.31 (dd, 1 H, CHN, J = 6.7 Hz, J = 13.6 Hz); 2.58—2.51 (m, 1 H, $C\underline{H}_AH_B$); 2.46—2.33 (m, 3 H, $CH_A\underline{H}_B$, CH_2); 2.25—2.14 (m, 2 H, CH_2). ^{13}C NMR, δ, major rotamer: 162.27;

134.44 (2 C); 125.92; 121.06; 118.59; 117.79; 66.29; 51.54; 51.31; 39.50; 38.07; 26.81. The NMR spectra of the minor rotamer are not reported because of the low intensity and the overlap of the signals. Found (%): C, 56.92; H, 6.17; N, 5.13. $C_{13}H_{17}Cl_2NO$. Calculated (%): C, 56.95; H, 6.25; N, 5.11.

1-[*cis*-2,6-Diallyl-4-methoxy-3,6-dihydro-(2*H*)-pyridino]-2,2-dichloroethan-1-one (*cis*-2p) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (12 : 1). The yield was 88%, oil. R_f 0.26 (*n*-C_6H_{14}—EtOAc (12 : 1)). The NMR spectrum showed the presence of rotamers in the ratio of 7.4 : 1. ^{1}H NMR, δ, major rotamer: 6.03 (s, 1 H, $CHCl_2$); 5.84 (dddd, 1 H, CH=, J = 6.2 Hz, J = 8.1 Hz, J = 10.2 Hz, J = = 17.0 Hz); 5.48 (dddd, 1 H, CH=, J = 6.0 Hz, J = 8.0 Hz, J = 10.4 Hz, J = 16.8 Hz); 5.08—5.01 (m, 2 H, CH_2=); 4.92—4.87 (m, 3 H, CH= of ring and CH_2=); 4.43 (t, 1 H, CHN, J = 2.6 Hz); 4.08—4.03 (m, 1 H, CHN); 3.11 (s, 3 H, OMe); 2.68—2.62 (m, 1 H, C$\underline{H}_A$H$_B$); 2.32—2.18 (m, 3 H, CH$_A\underline{H}_B$, CH_2); 2.08—2.00 (m, 2 H, CH_2). ^{13}C NMR, δ, major rotamer: 161.94; 151.07; 135.45; 134.78; 118.53; 117.56; 91.92; 67.04; 53.92; 51.90; 51.39; 41.33; 38.76; 30.34. The NMR spectra of the minor rotamer are not reported because of the low intensity and the overlap of the signals. Found (%): C, 55.22; H, 6.19; N, 4.57. $C_{14}H_{19}Cl_2NO_2$. Calculated (%): C, 55.27; H, 6.30; N, 4.60.

1-[*trans*-2-Allyl-6-methyl-3,6-dihydro-(2*H*)-pyridino]-2,2-dichloroethan-1-one (2r) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (10 : 1). The yield was 94%, oil. R_f 0.56 (*n*-C_6H_{14}—EtOAc (6 : 1)). The signals in the NMR spectra were broadened because of the hindered rotation around the amide bond. ^{1}H NMR, δ: 6.33 (br.s, 1 H, $CHCl_2$); 5.84—5.81 (br.m, 2 H, 2 CH= of ring); 5.75—5.65 (m, 1 H, CH=); 5.08—5.04 (m, 2 H, CH_2=); 4.33 (br.s, 1 H, CHN); 4.05 (br.s, 1 H, CHN); 2.39—2.23 (br.m, 4 H, 2 CH_2); 1.33 (br.d, 3 H, Me, J = 5.1 Hz). ^{13}C NMR, δ: 164.04 (br.); 133.81 (br.); 131.25 (br.); 121.19 (br.); 119.10 (br.); 52.73; 48.51 (br.); 39.02 (br.); 26.58; 19.46 (br.). Found (%): C, 53.30; H, 6.15; N, 5.61. $C_{11}H_{15}Cl_2NO_2$. Calculated (%): C, 53.24; H, 6.09; N, 5.64.

1-[*trans*-1,3-Diallyl-3,4-dihydro-(1*H*)-isoquinolino]-2,2-dichloroethan-1-one (*trans*-2s) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (10 : 1). The yield was 97%, a crystallizing oil, m.p. 69—70 °C. R_f 0.5 (*n*-C_6H_{14}—EtOAc (6 : 1)). The NMR spectrum showed the presence of rotamers in the ratio of 2.5 : 1. ^{1}H NMR, δ, a mixture of rotamers: 7.30—7.08 (m, 4 H, Ar); 6.47 (s, 0.28 H, $CHCl_2$); 6.43 (s, 0.72 H, $CHCl_2$); 5.69—5.53 (m, 2 H, 2 CH=); 5.16—5.03 (m, 2 H, CH_2=); 5.01—4.85 (m, 2.72 H, CH_2= and 0.72, CHN); 4.70—4.66 (m, 0.28 H, CHN); 4.56—4.54 (m, 0.28 H, CHN); 4.23—4.18 (m, 0.72 H, CHN); 3.20 (dd, 0.72 H, C$\underline{H}_A$H$_B$ of ring, J = 4.5 Hz, J = 15.3 Hz); 3.07 (dd, 0.28 H, C$\underline{H}_A$H$_B$ of ring, J = 4.8 Hz, J = 15.6 Hz); 2.93 (d, 0.28 H, CH$_A\underline{H}_B$ of ring, J = 15.6 Hz); 2.84 (dd, 0.72 H, CH$_A\underline{H}_B$ of ring, J = 1.9 Hz, J = 15.2 Hz); 2.66—2.61 (m, 0.72 H, C$\underline{H}_A$H$_B$); 2.53—2.50 (two m, 0.28 H, CH_2); 2.41 (dt, 0.72 H, CH$_A\underline{H}_B$, J = 8.3 Hz, J = 13.0 Hz); 2.36—2.33 (br.s, 0.28 H, C$\underline{H}_A$H$_B$); 2.02—1.89 (two m, 0.72 H, CH_2); 1.57 (dt, 0.28 H, CH$_A\underline{H}_B$, J = 9.8 Hz, J = 13.0 Hz). ^{13}C NMR, δ, major rotamer: 163.47; 135.60; 133.46; 132.80; 131.97; 128.66; 127.57; 127.48; 126.74; 119.42; 118.50; 65.06; 56.68; 53.02; 40.04; 39.74; 31.81. ^{13}C NMR, minor rotamer: 163.35; 134.93; 134.34; 133.10; 132.68; 129.23; 128.17; 127.11; 126.66; 119.65; 117.88; 64.70; 58.22; 52.51; 44.06; 35.78; 30.07. Found (%): C, 63.06; H, 5.88; N, 4.25. $C_{17}H_{19}Cl_2NO$. Calculated (%): C, 62.97; H, 5.91; N, 4.32.

1-[*cis*-1,3-Diallyl-3,4-dihydro-(1*H*)-isoquinolino]-2,2-dichloroethan-1-one (*cis*-2s) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (10 : 1). The yield was 98%, oil. R_f 0.75 (*n*-C_6H_{14}—EtOAc (6 : 1)). The NMR spectrum showed the presence of rotamers in the ratio of 1 : 1. ^{1}H NMR, δ, a mixture of rotamers: 7.33—7.31 (m, 0.5 H, Ar); 7.27—7.16 (m, 2.5 H, Ar); 7.12—7.10 (m, 1 H, Ar); 6.34 (s, 0.5 H, $CHCl_2$); 6.30 (s, 0.5 H, $CHCl_2$); 6.11—6.00 (m, 0.5 H, CH=); 5.92—5.69 (m, 1.5 H, CH=); 5.60—5.57 (m, 0.5 H, CHN); 5.20—5.05 (m, 4 H, 2 CH_2=); 5.03 (dd, 0.5 H, CHN, J = 7.3 Hz, J = 8.2 Hz); 4.58—4.53 (m, 0.5 H, CHN); 4.41—4.34 (m, 0.5 H, CHN); 3.11 (t, 0.5 H, C$\underline{H}_A$H$_B$ of ring, J = 5.7 Hz); 3.07 (t, 0.5 H, C$\underline{H}_A$H$_B$ of ring, J = 7.3 Hz); 2.95—2.88 (m, 1 H, 2 CH$_A\underline{H}_B$ of ring); 2.85—2.78 (m, 1 H, C$\underline{H}_A$H$_B$); 2.77—2.50 (m, 0.5 H, CH$_A\underline{H}_B$); 2.64—2.53 (m, 1.5 H, C$\underline{H}_A$H$_B$ and CH$_A\underline{H}_B$); 2.40—2.30 (m, 1 H, CH$_A\underline{H}_B$). ^{13}C NMR, δ, a mixture of rotamers: 162.78; 162.77; 136.07; 135.66; 135.43; 134.05 (2 C); 133.47; 133.14; 130.32; 129.22; 128.26; 127.99; 126.92; 126.63; 126.56; 126.48; 126.41; 119.16; 118.69; 118.09; 117.31; 66.43; 66.20; 58.75; 52.55; 52.13; 51.72; 43.34; 40.05; 40.01; 38.21; 32.04; 31.58. Found (%): C, 62.90; H, 5.98; N, 4.18. $C_{17}H_{19}Cl_2NO$. Calculated (%): C, 62.97; H, 5.91; N, 4.32.

1-(2-Allyl-2,5-dihydro-1*H*-pyrrol-1-yl)-2,2-dichloroethan-1-one (2t) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (6 : 1). The yield was 93%, oil. R_f 0.3 (*n*-C_6H_{14} — EtOAc (4 : 1)). The NMR spectrum showed the presence of rotamers in the ratio of 7.3 : 1. ^{1}H NMR, δ, a mixture of rotamers: 6.24 (s, 0.12 H, $CHCl_2$); 6.10 (s, 0.88 H, $CHCl_2$); 5.93—5.90 (m, 0.12 H, CH= of ring); 5.83—5.77 (m, 1.88 H, 2 CH= of ring); 5.71—5.61 (m, 1 H, CH= of allyl); 5.16—5.11 (m, 0.24 H, CH_2= of allyl); 5.08—5.03 (m, 1.76 H, CH_2= of allyl); 4.89—4.85 (m, 0.88 H, CHN); 4.74—4.71 (m, 0.12 H, CHN); 4.49—4.41 (m, 1 H, C$\underline{H}_A$H$_B$N); 4.35—4.30 (m, 0.88 H, CH$_A\underline{H}_B$N); 4.11—4.05 (m, 0.12 H, CH$_A\underline{H}_B$N); 2.63—2.49 (m, 1.76 H, CH_2 of allyl); 2.45—2.38 (m, 0.24 H, CH_2 of allyl). ^{13}C NMR, δ, major rotamer: 161.40; 132.40; 129.65; 124.05; 118.66; 65.79; 65.45; 53.64; 35.73. Found (%): C, 49.26; H, 4.98; N, 6.32. $C_9H_{11}Cl_2NO$. Calculated (%): C, 49.11; H, 5.04; N, 6.36.

1-(2,5-Diallyl-1-pyrrolidino)-2,2-dichloroethan-1-one (2u) was subjected to chromatography on SiO_2 in the system *n*-C_6H_{14}—EtOAc (4 : 1). The yield was 99%, a slowly crystallizing oil, m.p. 59—60 °C. R_f 0.37 (*n*-C_6H_{14}—EtOAc (4 : 1)). ^{1}H NMR, δ: 6.17 (s, 1 H, $CHCl_2$); 5.75—5.64 (m, 2 H, 2 CH=); 5.16—5.02 (m, 4 H, 2 CH_2=); 4.15 (td, 1 H, CHN, J = 2.9 Hz, J = 8.5 Hz); 3.93 (q, 1 H, CHN, J = 6.8 Hz); 2.61—2.55 (m, 1 H, C$\underline{H}_A$H$_B$ of allyl); 2.25—2.22 (m, 2 H, CH_2 of ring); 2.18—1.93 (m, 3 H, CH$_A\underline{H}_B$ of allyl, CH_2 of allyl); 1.83—1.75 (m, 2 H, CH_2 of ring). ^{13}C NMR, δ: 162.34; 134.26; 133.05; 119.04; 117.80; 65.07; 58.23; 58.11; 40.36; 35.41; 28.11; 25.42. Found (%): C, 54.87; H, 6.60; N, 5.28. $C_{12}H_{17}Cl_2NO$. Calculated (%): C, 54.97; H, 6.54; N, 5.34.

Study of biological activity of amides 2a—u was carried out using germinating maize seeds (a simple midseason-ripening hybrid of maize Krasnodarsky 370 MV). Before the experiment, a portion of test seeds (15 pieces) was treated with a solution of Dichlormid or amides **2a—u** (in doses 0.1, 1, and 10 g (t of seeds)$^{-1}$). For statistical reliability, each experiment

was carried out in three Petri dishes (in triplicate). Distilled water (4 mL) was added to the Petri dishes with test samples treated with dichloroacetamides and with an aqueous control sample. The Petri dishes with the treated seeds were incubated for 7 days at 25 °C. The seeds were ventilated every day by opening the dishes for 25—30 min, and distilled water (1—2 mL) was added if necessary to prevent the seeds from drying out. After 7 days, the lengths of sprouts and rootlets of germinating seeds were measured and their average values were found. The measurement data were mathematically processed using the following equation:

$$C = (L/D \cdot 100) - 100\%,$$

where C is the change in the length of a sprout or a rootlet relative to the water control; L is the average length of a sprout (or a rootlet) in the experimental, reference variants or in herbicide control, cm; D is the average length of a sprout (or a rootlet) in the control variant, cm.

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