SYNTHESES OF 2,4-DIAMINOPYRIMIDINES AND 1-AMINOISOQUINOLINES IN THE REACTIONS OF ALKYL AND BENZYL KETONES WITH CYANAMIDE AND *N,N*-DIMETHYLCYANAMIDE

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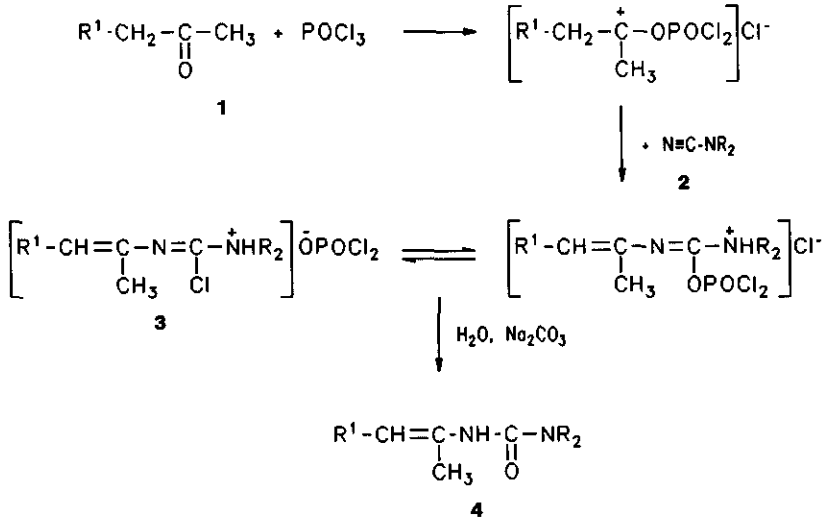
Abstract - The reaction of alkyl and benzyl ketones with cyanamide and *N,N*-dimethylcyanamide in the presence of $POCl_3$ was examined. At the first stage, chloroformamidine derivatives were formed. In the presence of $TiCl_4$, they underwent further reactions to the derivatives of 1-aminoisoquinoline and 2,4-diaminopyrimidine. The effect of a constitution of substrates on adequate ratios of heterocyclic compounds is discussed.

The earlier studies on reactions of benzyl and alkyl ketones in the presence of phosphoryl chloride[1,2] have proved a possiblility to synthesize *N*-vinylimidoyl compounds by the Ritter type reaction.[3] These compounds were then used in preparation of isoquinoline, pyrimidine or pyridine derivatives.[1,2,4] On the other hand, it is known that *N*-vinylimidoyl chlorides easily react with cyanamide[5] and *N,N*-dimethylcyanamide[6] yielding 4-aminopyrimidine derivatives.

In this work we have commenced to study the reactions of alkyl and benzyl ketones **(1)** with cyanamide or *N,N*-dimethylcyanamide **(2)** to *N*-vinyl- or *N*-styrylchloroformamidines **(3)** in order to their further use in synthesis of 2,4-diaminopyrimidines **(7)** and 1-aminoisoquinolines **(8)**.

A few examples for the reactions of ketones with cyanamide are only known yielding the corresponding cyanoimines,[7-9] compounds obtained from a reaction of the amino group in cyanamide with carbonyl carbon. The reaction of the nitryl nitrogen atom in cyanamide and its derivatives with ketones has not been hitherto known.

Examining the reaction of alkyl ketones with cyanamide and its *N,N*-dimethyl derivative in the presence of phosphoryl chloride we have found that adequate chloroformamidine derivatives can be prepared provided the nitryl nitrogen atom in cyanamide will attack the activated carbonyl carbon atom. It is possible to ensure such a course of reaction only when *O*-phosphorylation of the carbonyl oxygen will take place at the initial



stage in the reaction of ketone with $POCl_3$. Cyanamide or *N,N*-dimethylcyanamide were introduced in the second stage, when the whole $POCl_3$ reacted with ketone. These compounds reacted at a room temperature to afford the salts of corresponding chloroamidines **(3)**, practically in quantitative yields. The prepared salts were not purified, but used as crude in further reactions. *N*-(1-methyl-2-phenylvinyl)-*N'*,*N'*-dimethylchloroformamidine dichlorophosphate prepared from the reaction of benzyl methyl ketone with *N,N*-dimethylcyanamide was subjected to alkaline hydrolysis to 1,1-dimethyl-3-(1-methyl-2-phenylvinyl)urea **(4)** in order to prove constitution of the amidine.

In contrary to *N*-vinylimidoyl compounds,[5,6] the prepared salts of chloroformamidines as well as free chloroformamidines obtained after neutralization of salts did not react practically with excess of cyanamide and *N,N*-dimethylcyanamide.

To activate chloroformamidines, they were transformed to nitrilium salts **(5)** with $TiCl_4$. The prepared nitrilium salt is susceptible to the attack of the nucleophilic agents such as a nitryl nitrogen atom in *N,N*-dimethylcyanamide or cyanamide yielding a linear compound **(6)**. The latter easily undergoes cyclization to 2,4-diaminopyrimidines **(7)**. The nitrilium salt may undergo a von Braun fragmentation or cyclization to the 1-aminoisoquinolines **(8)** if the substituent R^1 is a phenyl group.

Aliphatic ketones **(1)** (R^1 = H, CH_3, C_2H_5, $(CH_3)_2CH$) and *N,N*-dimethylcyanamide used at a molar ratio 1 : 2 react to give 2,4-bis(dimethylamino)pyrimidines in yields of 60 ÷ 65 % (Table 1). The pyrimidine arrangement is formed also when chloroformamidine is heated without any excess of *N,N*-dimethylcyanamide in the presence of $TiCl_4$. It can be explained by fragmentation of the nitrylium salt yielding a *N,N*-dimethylcyanamide.

When benzyl ketones **(1)** (R^1 = $-C_6H_4-R^2$) are used to react with *N,N*-dimethylcyanamide, the corresponding 1-dimethylaminoisoquinolines and 2,4-bis(dimethylamino)-5-phenylpyrimidines are formed.

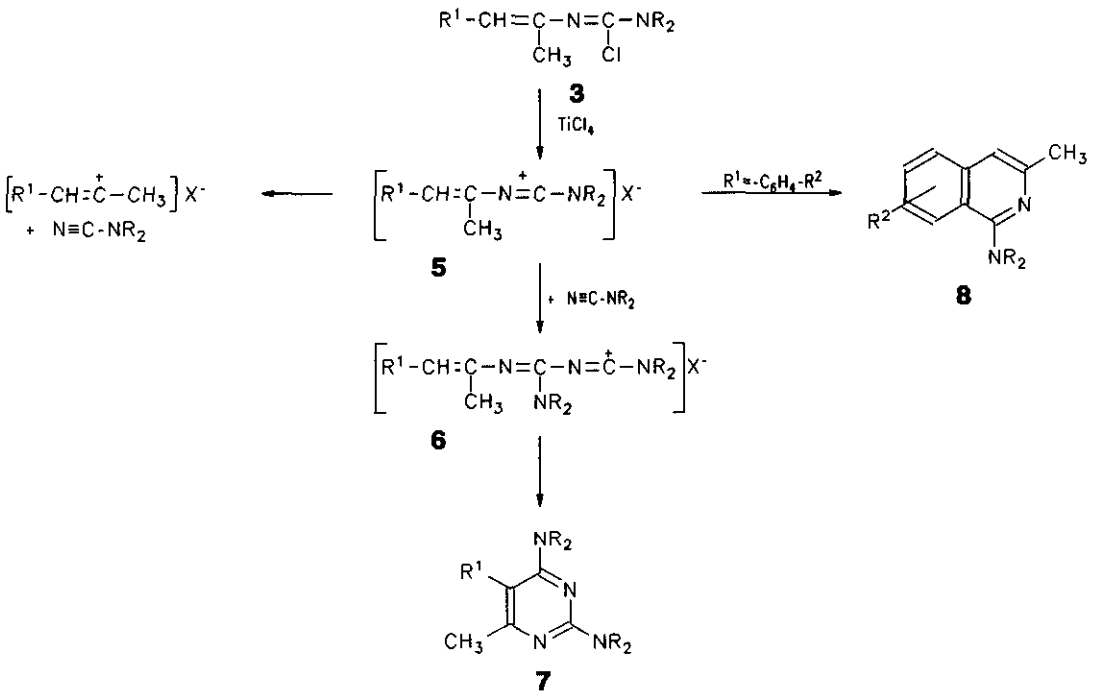
Table 1. Pyrimidines **(7)** and isoquinolines **(8)**.

	R^1	R	Mol. ratio	Pyrimidines **(7)**		Isoquinolines **(8)**		
			(1): (2)	Yield % mol	bp (°C/Torr) or mp (°C)	R^2	Yield % mol	bp (°C/Torr) or mp (°C)
a	H	CH_3	1:2	65	158/31[a]			
b	CH_3	CH_3	1:2	64	140/31			
c	C_2H_5	CH_3	1:2	61	160/28			
d	$(CH_3)_2CH$	CH_3	1:2	60	163/31			
e	C_6H_5	CH_3	1:2	65	86-87	H	-	124/1
			1:1	20			3	104-105
			1:0.7	8			11	
f	3-$CH_3C_6H_4$	CH_3	1:2	64	220/31	6-CH_3	10	154/4
			1:1	14			31	72-74
g	4-$CH_3C_6H_4$	CH_3	1:2	50	88-90	7-CH_3	6	160/13
			1:1	12			21	36-38
h	3-ClC_6H_4	CH_3	1:2	58	68-69	6-Cl	5	95-97
			1:1	25			25	
i	4-ClC_6H_4	CH_3	1:2	55	126-128	7-Cl	4	53-55
k	3-$CH_3OC_6H_4$	CH_3	1:1	-		6-CH_3O	48	160/4
l	4-$CH_3OC_6H_4$	CH_3	1:2	35	104-105	7-CH_3O	7	173/10
			1:1	9			33	51-52
m	3-$NO_2C_6H_4$	CH_3	1:2	71	134-135		-	
n	4-$NO_2C_6H_4$	CH_3	1:2	75	148-149		-	
o	C_6H_5	H	1:1	14	248-249[b]	H	14	129-130[c]

[a] lit.,[10] bp = 84-85/2

[b] lit.,[11] mp = 249-250

[c] lit.,[12] mp = 130-131



The yield and ratios of the resulting pyrimidines and isoquinolines are considerably influenced by electron effects on the substituents present in the benzene ring (R^2) and the ratio of the substrates (Table 1). Generally, the electron withdrawing substituents facilitate a formation of pyrimidines, while the electron donating substituents, increasing the electron density in the 2 position of the benzene ring make easily the intramolecular closure of the isoquinoline ring. When a ratio of *N,N*-dimethylcyanamide to benzyl ketones is smaller the reaction is shifted towards isoquinolines. Also, the transition from *N,N*-dimethylcyanamide (R = CH_3) to cyanamide (R = H) changes the ratio of the products towards isoquinolines, mainly due to steric hindrance effects.

Among the synthesized heterocyclic compounds, 2,4-bis(dimethylamino)-6-methylpyrimidine,[10] 2,4-diamino-6-methyl-5-phenylpyrimidine[11] and 1-amino-3-methylisoquinoline[12] were obtained by other methods.

EXPERIMENTAL

Mass spectral data were performed on a Shimadzu QP-2000 spectrometer. Microanalyses were performed with Perkin-Elmer 240 C analyzer. The physical and spectral data of the compounds are given in Table 1, Table 2 and Table 3.

1,1-Dimethyl-3-(1-methyl-2-phenylvinyl)urea (4e)

A solution of benzyl methyl ketone (13.4 g, 0.1 mol) and $POCl_3$ (7.6 g, 0.05 mol) in 50 ml of anhydrous benzene was heated under reflux for 10 min. Then, *N,N*-dimethylcyanamide (3.5 g, 0.05 mol) was added. The mixture was left at a room temperature for 2 h. Benzene was removed on a rotary evaporator and the residue was washed with anhydrous ether in order to separate an excess of benzyl methyl ketone. The resulting chloroformamidine salt in a form of oil was dissolved in a small amount of methanol and gradually poured into 5 % aqueous Na_2CO_3 solution, vigorously agitated. The solution was extracted with chloroform. Having the chloroform removed, the residue was washed with hexane to remove contaminants. A pure compound **(4e)** is obtained as yellowish oil in yield of 6.1 g (60 %). ^{1}H-Nmr ($CDCl_3$) δ 2.12 (d, J = 1.2 Hz, 3H, CH_3), 2.82 (s, 3H, NCH_3), 2.90 (s, 3H, NCH_3), 5.10 (wide s, 1H, NH), 6.87 (q, J = 1.2 Hz, 1H, CH), 7.00-7.40 (m, 5H, C_6H_5). Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.55; H, 7.89, N, 13.72. Found: C, 70.30; H, 7.70; N, 13.50.

Derivatives of 2,4-diaminopyrimidine (7) and 1-aminoisoquinoline (8)

A solution of alkyl or benzyl ketone (0.05 mol) and $POCl_3$ (7.6 g, 0.05 mol) in 50 ml of anhydrous benzene was heated under reflux for 10 to 15 min. Into the cooled solution *N,N*-dimethylcyanamide in quantity according to a molar ratio (Table 1) (7.0 g, 0.1 mol; 3.5 g, 0.05 mol or 2.45 g, 0.035 mol) or cyanamide (2.1 g, 0.05 mol) in 5 ml of anhydrous ether was added dropwise. The mixture was left at a room temperature for 1 h. Next, a solution of $TiCl_4$ (9.5 g, 0.05 mol) in 20 ml of anhydrous benzene was added dropwise into the reaction mixture with its simultaneous agitation and cooling. The mixture was heated for 1.5 h under reflux condenser, cooled and then 150 ml water was added. The obtained mixture was filtered off and the sediment was washed with ether. The filtrate was alkalized with 20 % NaOH solution and extracted with ether or chloroform. The prepared 2,4-bis(dimethylamino)-5-alkylpyrimidines were purified by distillation, whereas the mixtures of 2,4-diamino-5-phenylpyrimidines and 1-aminoisoquinolines were separated by distillation or fractional crystallization from methanol or hexane. Data of mass spectra and microanalysis of pyrimidines **(7)** and isoquinolines **(8)** were as follows: **(7b)** Ms (m/z): 194 (M^+, 56.3 %). Anal. Calcd for $C_{10}H_{18}N_4$: C, 61.82; H, 9.34; N, 28.84. Found: C, 61.71; H, 9.40; N, 28.89. **(7c)** Ms (m/z): 208 (M^+, 44.4 %). Anal. Calcd for $C_{11}H_{20}N_4$: C, 63.42; H, 9.68; N, 26.90. Found: C, 63.40; H, 9.72; N, 26.88. **(7d)** Ms (m/z): 222 (M^+, 27.7 %). Anal. Calcd for $C_{12}H_{22}N_4$:C, 64.82; H, 9.97; N, 25.21. Found: C, 65.00; H, 9.94; N. 25.06. **(7e)** Ms (m/z): 256 (M^+, 100 %). Anal. Calcd for $C_{15}H_{20}N_4$:C, 70.28; H, 7.86; N, 21.86. Found: C, 70.09; H, 7.94; N, 21.97. **(7f)** Ms (m/z): 270 (M^+, 100 %). Anal. Calcd for $C_{16}H_{22}N_4$:C, 71.07; H, 8.20; N, 20.73. Found: C, 70.98; H, 8.31; N, 20.71. **(7g)** Ms (m/z): 270 (M^+, 100 %). Anal. Calcd for $C_{16}H_{22}N_4$:C, 71.07; H, 8.20; N, 20.73. Found: C, 70.93; H, 8.27; N, 20.80. **(7h)** Ms (m/z): 290

Table 2. Spectral data of pyrimidines (**7**).

Product	uv (methanol/water)[a] medium	(λ_{max} nm) (ϵ*10^{-3})	^{1}H nmr (δ ppm, chloroform-d$_1$/TMS)[b]
7a	basic	228 (23.0); 298 (8.3)	2.20 (s, 3H, 6-CH_3); 2.98 (s, 6H, 4-$N(CH_3)_2$); 3.10 (s, 6H, 2-$N(CH_3)_2$); 5.57 (s, 1H, 5-H)
	acidic	229 (26.0); 255 (13.3)	
7b	basic	242 (18.8); 309 (7.5)	2.02 (s, 3H, 5-CH_3); 2.24 (s, 3H, 6-CH_3); 2.86 (s, 6H, 4-$N(CH_3)_2$); 3.09 (s, 6H, 2-$N(CH_3)_2$)
	acidic	230 (21.1); 264 (12.4)	
7c	basic	244 (18.6); 311 (7.0)	1.11 (t, J = 7.3 Hz, 3H, CH_2-$C\underline{H}_3$); 2.29 (s, 3H, 6-CH_3); 2.50 (q, J = 7.3 Hz, 2H, $C\underline{H}_2$-CH_3); 2.88 (s, 6H, 4-$N(CH_3)_2$); 3.09 (s, 6H, 2-$N(CH_3)_2$)
	acidic	231 (22.7); 266 (12.3)	
7d	basic	243 (18.8); 311 (6.1)	1.25 (d, J = 7 Hz, 6H, $(C\underline{H}_3)_2CH$); 2.36 (s, 3H, 6-CH_3); 2.78 (s, 6H, 4-$N(CH_3)_2$); 3.05 (m, J = 7 Hz, 1H, CH); 3.09 (s, 6H, 2-$N(CH_3)_2$)
	acidic	233 (22.5); 267 (11.6)	
7e	basic	236 (21.4); 308 (7.9)	2.04 (s, 3H, 6-CH_3); 2.33 (s, 3H, *m*-CH_3); 2.66 (s, 6H, 4-$N(CH_3)_2$); 3.15 (s, 6H, 2-$N(CH_3)_2$); 7.03-7.37 (m, 5H$_{Arom}$)
	acidic	234 (30.6)	
7f	basic	237 (25.6); 308 (10.5)	2.05 (s, 3H, 6-CH_3); 2.66 (s, 6H, 4-$N(CH_3)_2$); 3.15 (s, 6H, 2-$N(CH_3)_2$); 7.00-7.30 (m, 4H$_{Arom}$)
	acidic	235 (30.6)	
7g	basic	235 (19.9); 307 (6.9)	2.04 (s, 3H, 6-CH_3); 2.34 (s, 3H, *p*-CH_3); 2.66 (s, 6H, 4-$N(CH_3)_2$); 3.15 (s, 6H, 2-$N(CH_3)_2$); 6.93-7.44 (m, 4H$_{Arom}$)
	acidic	235 (28.6); 290 (8.0)	
7h	basic	239 (17.3); 305 (6.9)	2.04 (s, 3H, 6-CH_3); 2.66 (s, 6H, 4-$N(CH_3)_2$); 3.15 (s, 6H, 2-$N(CH_3)_2$); 7.08-7.28 (m, 4H$_{Arom}$)
	acidic	235 (27.8)	
7i	basic	243 (12.0); 307 (9.3)	2.04 (s, 3H, 6-CH_3); 2.66 (s, 6H, 4-$N(CH_3)_2$); 3.15 (s, 6H, 2-$N(CH_3)_2$); 7.01-7.33 (4H$_{Arom}$)
	acidic	235 (32.8)	
7l	basic	235 (28.6); 308 (12.1)	2.09 (s, 3H, 6-CH_3); 2.69 (s, 6H, 4-$N(CH_3)_2$); 3.18 (s, 6H, 2-$N(CH_3)_2$); 3.80 (s, 3H, *p*-OCH_3); 6.77-6.89 (2H$_{Arom}$); 6.98-7.10 (2H$_{Arom}$)
	acidic	234 (32.0)	
7m	basic	239 (17.8); 273 (11.6); 300 (8.9)	2.05 (s, 3H, 6-CH_3); 2.64 (s, 6H, 4-$N(CH_3)_2$); 3.15 (s, 6H, 2-$N(CH_3)_2$); 7.43-8.10 (4H$_{Arom}$)
	acidic	236 (26.1); 260 (22.0)	
7n	basic	236 (26.3); 256 (21.6); 304 (13.6)	2.07 (s, 3H, 6-CH_3); 2.67 (s, 6H, 4-$N(CH_3)_2$); 3.17 (s, 6H, 2-$N(CH_3)_2$); 7.24-7.41 (2H$_{Arom}$); 8.07-8.24 (2H$_{Arom}$)
	acidic	233 (30.6); 269 (22.7)	
7o	basic	234 (7.8); 286 (6.3); 335 (0.7)	2.02 (s, 3H, 6-CH_3); 4.47 (wide s, 2H, NH_2); 4.67 (wide s, 2H, NH_2); 7.13-7.45 (m, 5H$_{Arom}$)
	acidic	230 (13.5); 273 (5.5); 338 (0.5)	

Table 3. Spectral data of isoquinolines (**8**).

Product	uv (methanol/water)[a] medium	(λ_{max} nm) (ϵ*10^{-3})	^{1}H nmr (δ ppm, chloroform-d$_1$/TMS)[b]
8e	basic	235 (10.7); 290 (5.4); 337 (5.0)	2.50 (d, J = 0.8 Hz, 3H, 3-CH_3); 3.06 (s, 6H, $N(CH_3)_2$); 6.91 (q J = 0.8 Hz, 1H, 4-H,); 7.00-8.08 (m, 4H_{Arom})
	acidic	232 (10.0); 264 (9.5); 289 (7.3); 352 (8.1)	
8f	basic	240 (12.7); 297 (4.9); 334 (4.3)	2.45 (s, 3H, 6-CH_3); 2.49 (d, J = 0.8 Hz, 3H, 3-CH_3); 3.05 (s, 6H, $N(CH_3)_2$); 6.85 (q, J = 0.8 Hz, 1H, 4-H); 7.07-7.95 (m, 3H_{Arom}, 5, 7, 8-H)
	acidic	252 (19.3); 294 (5.8); 349 (7.3)	
8g	basic	233 (13.9); 290 (4.7); 342 (3.6)	2.47 (s, 3H, 7-CH_3); 2.50 (d, J =0.8 Hz, 3H, 3-CH_3); 3.05 (s, 6H, $N(CH_3)_2$); 6.91 (q, J = 0.8 Hz, 1H, 4-H); 7.18-7.81 (m, 3H_{Arom}, 5, 6, 8-H)
	acidic	235 (17.9); 270 (10.7); 280 (11.0); 359 (7.8)	
8h	basic	245 (10.7); 310 (4.2); 337 (3.9)	2.50 (d, J = 0.8 Hz, 3H, 3-CH_3); 3.06 (s, 6H, $N(CH_3)_2$); 6.85 (q, J = 0.8 Hz, 1H, 4-H); 7.13-8.00 (m, 3H_{Arom}, 5, 7, 8-H)
	acidic	219 (25.0); 255 (20.6); 298 (6.5); 354 (7.3)	
8i	basic	239 (12.1); 298 (4.9); 346 (3.5)	2.49 (d, J = 0.8 Hz, 3H, 3-CH_3); 3.05 (s, 6H, $N(CH_3)_2$); 6.90 (q, J = 0.8 Hz, 1H, 4-H); 7.11-8.00 (m, 3H_{Arom}, 5, 6, 8-H)
	acidic	237 (17.0); 288 (10.0); 363 (6.8)	
8k	basic	224 (27.5); 246 (12.2); 326 (3.6)	2.48 (d, J = 0.8 Hz, 3H, 3-CH_3); 3.04 (s, 6H, $N(CH_3)_2$); 3.87 (s, 3H, 6-OCH_3); 6.77 (q, J = 0.8 Hz, 1H, 4-H); 6.80-8.05 (m, 3H_{Arom}, 5, 7, 8-H)
	acidic	222 (15.2); 264 (18.9); 343 (3.8)	
8l	basic	235 (20.5); 274 (6.2); 351 (4.7)	2.50 (d, J = 0.8 Hz, 3H, 3-CH_3); 3.03 (s, 6H, $N(CH_3)_2$); 3.89 (s, 3H, 7-OCH_3); 6.92 (q, J = 0.8 Hz, 1H, 4-H); 7.07-7.55 (m, 3H_{Arom}, 5, 6, 8-H)
	acidic	220 (25.7); 243 (25.0); 282 (10.8); 371 (7.5)	
8o	basic	225 (15.8); 292 (6.5); 335 (4.1)	2.47 (d, J = 0.8 Hz, 3H, 3-CH_3); 5.15 (wide s, 2H, NH_2); 6.83 (q, J = 0.8 Hz, 1H, 4-H) 7.23-7.75 (m, 4H_{Arom})
	acidic	237 (23.0); 274 (7.2); 284 (7.3); 338 (6.3)	

[a] Measured using a SPECORD M-40 spectrophotometer, basic medium: 0.02 m NaOH in 1 % methanol; acidic medium: 0.02 m HCl in 1 % methanol

[b] Obtained on a TESLA BS 587 NMR Spectrometer (80 MHz)

(M^+, 100 %). Anal. Calcd for $C_{15}H_{19}N_4Cl$:C, 61.95; H, 6.59; N, 19.27; Cl, 12.19. Found: C, 62.10; H, 6.67; N, 19.09; Cl, 12.14. **(7i)** Ms (m/z): 290 (M^+, 100 %). Anal. Calcd for $C_{15}H_{19}N_4Cl$:C, 61.95; H, 6.59; N, 19.27; Cl, 12.19. Found: C, 62.00; H, 6.71; N, 19.24; Cl, 12.05. **(7l)** Ms (m/z): 286 (M^+, 100 %). Anal. Calcd for $C_{16}H_{22}N_4O$:C, 67.10; H, 7.74; N, 19.57. Found: C, 67.01; H, 7.83; N, 19.54. **(7m)** Ms (m/z): 301 (M^+, 100 %). Anal. Calcd for $C_{15}H_{19}N_5O_2$: C, 59.78; H, 6.36; N, 23.24. Found: C, 59.90; H, 6.41; N, 23.06. **(7n)** Ms (m/z): 301 (M^+, 100 %). Anal. Calcd for $C_{15}H_{19}N_5O_2$: C, 59.78; H, 6.36; N, 23.24. Found: C, 59.82; H, 6.47; N, 23.10. **(8e)** Ms (m/z): 186 (M^+, 37.7 %). Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.30; H, 7.64; N, 15.06. **(8f)** Ms (m/z): 200 (M^+, 29.5 %). Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.90; H, 8.00; N, 14.10. **(8g)** Ms (m/z): 200 (M^+, 36.8 %). Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.99; H, 7.97; N, 14.04. **(8h)** Ms (m/z): 220 (M^+, 28.4 %). Anal. Calcd for $C_{12}H_{13}N_2Cl$: C, 65.30; H, 5.94; N, 12.70; Cl, 16.06. Found: C, 65.25; H, 6.01; N, 12.75; Cl, 15.99. **(8i)** Ms (m/z): 220 (M^+, 39.4 %). Anal. Calcd for $C_{12}H_{13}N_2Cl$: C, 65.30; H, 5.94; N, 12.70; Cl, 16.06. Found: C, 65.38; H, 5.82; N, 12.77; Cl, 16.03. **(8k)** Ms (m/z): 216 (M^+, 37.5 %). Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.96. Found: C, 72.31; H, 7.30; N, 13.00. **(8l)** Ms (m/z): 216 (M^+, 58.8 %). Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.96. Found: C, 72.27; H, 7.42; N, 12.92.

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