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HYDROSILYLATION OF (HETERO)-AROMATIC ALDIMINES IN THE PRESENCE OF A Pd(I) COMPLEX

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The reaction of triethylsilane with heterocyclic and aromatic azomethines, catalyzed by the [Pd(allyl)Cl]$_2$ complex, was studied. It was found that the reaction is affected by the nature of the functional groups in the aza and methine parts of the aldimine molecules, which were produced by the condensation of furan, thiophene, and benzene aldehydes with aniline and its derivatives. The reactivity of a series of imines is compared with their electronic and structural characteristics, determined by quantum-chemical methods. The corresponding furan, thiophene, and aromatic amines and also certain silylamines were synthesized.

Keywords: transition metal complexes, Schiff bases, hydrosilylation, catalysis.

Investigations into catalytic hydrosilylation of the C=N bond are of both practical significance (for the production of useful items) and theoretical interest (to determine the relationships governing the processes). As known (see the reviews [1-3] and also the papers [4-6]), hydrosilylation of the CH=N double bond leads mainly to the formation of products silylated at the nitrogen atom. Recently, we found for the first time [7] in the reaction of alkylhydrosilanes with furan, thiophene, and pyridine aldimines containing a trifluoromethyl group at the *ortho* position of the aza part of the molecules that addition of the silyl group at the carbon atom of the imine CH=N bond takes place alongside N-silylation. It is possible that the last process takes place by a carbene mechanism [8]. In this connection it seemed of interest to determine the dependence of the direction of hydrosilylation on the structure of the initial amines and also the effect of electron-donating and accepting functional groups in the aza and methine parts of the molecules on this process.

In the present work the method that we developed previously [9-14] with molecular sieves as effective agents for the condensation of aromatic and heterocyclic aldehydes with various amines was used for the production of the aldimines. A series of syntheses were realized, and the corresponding N-(hetarylmethylidene)- and N-(arylmethylidene)anilines were obtained.

As we discovered earlier [5, 7], one of the most active catalysts for the hydrosilylation of imines is the dimeric complex of monovalent palladium bis{[μ-chloroallyl]palladium} – [Pd(allyl)Cl]$_2$. In the present work we studied the reaction of the above-mentioned previously synthesized aldimines with trimethylsilane in the presence of this complex. The reactions were conducted in benzene at 65°C with the substrate and silane in a molar ratio of 1:1.2 and a catalyst concentration of 2 mol %. The reactions were monitored by TLC and GLC-MS. At the end of silylation (the reaction times are given in Table 2) the reaction mixture was treated (as indicated in the experimental section) and was analyzed by ^{1}H NMR. The spectra of the reaction mixture

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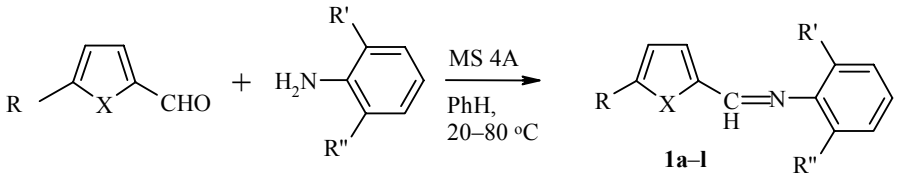
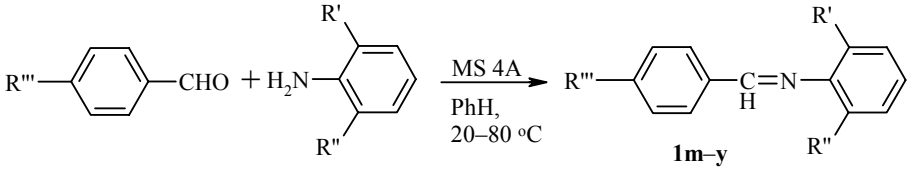
Scheme 1



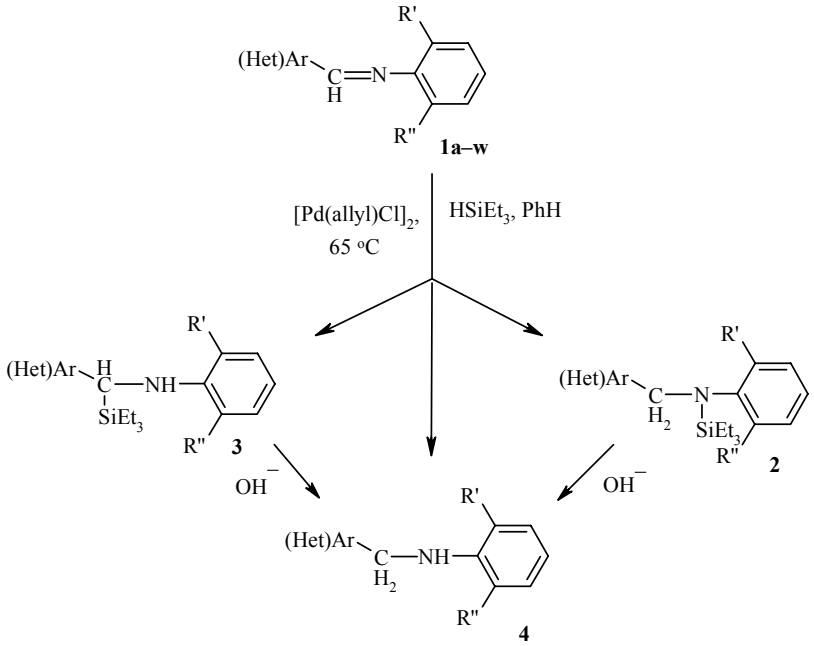
X = O, S; R = H, Me; R' = Me, Br; R" = H, Me



R' = H, Me, CF_3, Br, F, NO_2; R" = H, Me; R''' = H, Me, OMe, Br, NO_2

contain three sets of signals, indicating the formation of three types of products – structures **2**, **3**, and **4** (Scheme 2) containing Et_3SiCH–NH, CH_2–$NSiEt_3$, and CH_2–NH groups. These compounds are characterized respectively by two doublets for the protons of the CH–NH group (1H–1H), a singlet for CH_2 (2H), and for the amines **4** by a signal for CH_2 and a broad singlet for NH (2H and 1H) (Table 2). The mass spectra of the obtained compounds (Table 3) also correspond to the three indicated types of products.

Scheme 2



By preparative column chromatography it was possible to isolate nearly all the synthesized amines with structure **4** and also certain other silyl derivatives with structures **2** and **3** (Table 2). The signals of the ring protons in all the obtained compounds were in the characteristic regions of the spectrum. In the ^1H NMR spectra of the synthesized silyl compounds the $SiEt_3$ group appears in the form of two groups of signals for the CH_2 (6H, q) and CH_3 (9H, m) in the region of δ 0.5-1.6 ppm.

TABLE 1. The Characteristics of the Synthesized Aldimines

Imine*	X	R	R'	R''	R'''	T, °C	Time, h	Empirical formula	Found, % / Calculated, %				mp, °C*[2]	Yield, %
									C	H	N	S		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1a	O	H	Me	H	—	20	22	$C_{12}H_{11}NO$						76
1b	O	Me	Me	H	—	20	24	$C_{13}H_{13}NO$						76
1c	O	H	Br	H	—	20	21	$C_{11}H_8BrNO$						64
1d	O	Me	Br	H	—	20	26	$C_{12}H_{10}BrNO$						64
1e	O	H	Me	Me	—	20 80	24 1	$C_{13}H_{13}NO$						60
1f	O	Me	Me	Me	—	20 80	24 1	$C_{14}H_{15}NO$						66
1g	S	H	Me	H	—	20	24	$C_{12}H_{11}NS$						76
1h	S	Me	Me	H	—	20	24	$C_{13}H_{13}NS$	72.23 72.52	5.98 6.09	6.41 6.50	14.75 14.89	46-47	56
1i	S	H	Br	H	—	20 80	24 2	$C_{11}H_8BrNS$	49.70 49.64	2.84 3.03	4.98 5.26	12.02 12.05	49-50	52
1j	S	Me	Br	H	—	20 80	24 2	$C_{12}H_{10}BrNS$	51.14 51.44	3.43 3.60	4.82 4.99	11.55 11.44	45-46	50
1k	S	H	Me	Me	—	20	24	$C_{13}H_{13}NS$						74
1l	S	Me	Me	Me	—	20 80	24 8	$C_{14}H_{15}NS$						77

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1m	—	—	Me	H	H	20	23	$C_{14}H_{13}N$						76
1n	—	—	CF_3	H	H	20	22	$C_{14}H_{10}F_3N$						56
1o	—	—	Br	H	H	20	23	$C_{13}H_{10}BrN$						74
1p	—	—	F	H	H	20	22	$C_{13}H_{10}FN$	77.68 78.37	4.81 5.06	6.77 7.03		28-29	64
1q	—	—	NO_2	H	H	20 80	19 8	$C_{13}H_{10}N_2O_2$	68.36 69.02	4.36 4.46	12.69 12.38		71-72	72
1r	—	—	Me	Me	H	20 80	20 2	$C_{15}H_{15}N$						83
1s	—	—	H	H	Me	20	24	$C_{14}H_{13}N$						65
1t	—	—	H	H	OMe	20	21	$C_{14}H_{13}NO$	79.47 79.59	6.16 6.20	6.61 6.63		49-50	66
1u	—	—	H	H	Br	20	21	$C_{13}H_{10}BrN$	60.06 60.02	3.82 3.87	5.28 5.38		71-72	69
1v	—	—	H	H	NO_2	20	24	$C_{13}H_{10}N_2O_2$	69.03 69.02	4.44 4.46	12.28 12.38		86-87	74
1w	—	—	CF_3	H	OMe	20 80	22 3	$C_{15}H_{12}F_3NO$						64
1x	—	—	CF_3	H	Br	20	20	$C_{14}H_9BrF_3N$	51.40 51.25	2.72 2.76	4.17 4.27		59-60	87
1y	—	—	NO_2	H	Br	20 80	24 6	$C_{13}H_9BrN_2O_2$	51.21 51.17	2.85 2.97	9.08 9.18		96-97	64

* The imines **1a-g**,**k-o**,**r**,**s**,**w** were oily substances, **1p** was not recrystallized.

*[2] Solvent for recrystallization: hexane (**1h**,**i**,**t**,**u**,**x**) or 1:1 hexane–ethyl acetate (**1j**,**q**,**v**,**y**).

TABLE 2. The Characteristics of the Hydrosilylation Reactions and Their Products

Initial imine	Reaction time, h (T 65°C)	Conversion of imine, % (GLC)	Product		^{1}H NMR (in $CDCl_3$), δ, ppm, (*J*, Hz)					
			in reaction mixture*	after isolation*[2]	CH_3 (3H, s)	CH_2–NSi (structure **2**) CH_2 (2H, s)	SiCH–NH (structure **3**)		CH_2–NH (structure **4**)	
							CH (d)	NH (d)	CH_2 (s)	NH br. s)
1	2	3	4	5	6	7	8	9	10	11
1a	6	68	**4a**	**4a**	2.09				4.29	3.8
1b	6	86	**4b**	**4b**	2.04, 2.20				4.22	3.8
1c	4	53	**3c**	**3c**			4.33	4.6		
							J = 5.0			
			4c	**4c**					4.29	4.0
			$C_4H_3OCH_2NHPh$ (9%)							
1d	4	68	**3d**	**3d**	2.20		4.27	4.6		
							J = 5.0			
			4d	**4d**	2.22				4.20	3.9
			$MeC_4H_2OCH_2NHPh$ (18%)							
1e	24	86	**2e**	**2e**	2.00 (6H)	4.07				
			4e		2.15 (6H)				4.07	4.0
1f	24	0								
1g	15	41	**4g**	**4g**	2.11				4.51	3.8
1h	20	100	**4h**	**4h**	2.07, 2.36				4.38	3.8
1i	4	51	**4i**	**4i**					4.51	4.0
1j	20	90	**3j**	**3j**	2.40		4.44	4.6		
							J = 5.0			
			4j	**4j**	2.40				4.40	3.9
			$MeC_4H_2SCH_2NHPh$ (21%)							
1k	35	42	**2k**	**2k**	2.11 (6H)	4.31				
				4k	2.9 (6H)				4.27	~3.0

TABLE 2 (continued)

1	2	3	4	5	6	7	8	9	10	11
1l	35	60	**2l**	**2l**	2.04 (6H), 2.33 (3H)	4.22				
			4l	**4l**	2.27 (6H), 2.38 (3H)				4.18	3.2
1m	4	100	**4m**	**4m***[3]	2.11				4.33	—
1n	20	59	**2n**							
			4n	**4n**					4.38	4.8
1o	11	72	**2o**	**2o**		4.36				
			4o						4.31	~ 4.8
			$PhCH_2NHPh$ (31%)							
1p	8	100	**4p**						4.24	4.1
1q	20	100	**4q**, **q***[4]	**4q**					4.55	—
1r	8	86	**2r**							
			4r	**4r**	2.18 (6H)				4.04	2.9
1s	7	100	**2s**		2.27	4.51				
			4s		2.33				4.27	3.9
1t	15	81	**2t**	**2t**	3.73 (OCH_3)	4.22				
			4t	**4t**	3.73 (OCH_3)				4.18	4.0
1u	8	100	**4u**, $PhCH_2NHPh$ (82%), **u***[4]							
1u*[5]	26	24	**4u**, PhCHNPh (12%)							
1v	17	25	$H_2NC_6H_4CHNPh$							
1w	21	63	**2w**	**2w**	3.47 (OCH_3)	4.31				
			4w							

* According to the data from the ^{1}H NMR spectra and GLC-MS of the mixture of products.

*[2] The products were isolated by column chromatography. Eluants: 10:0.05 benzene–ethyl acetate (**4a-d**,**g**,**h**,**j**,**t**, **3c**,**d**,**j**, **2t**), 3:1 hexane–ethyl acetate (**2e**, **4i**), 9:1 benzene–ethyl acetate (**2k**,**l**, **4k**,**l**,**q**,**r**), benzene (**4n**), 9:1 hexane–ethyl acetate (**2o**).

*[3] The product was isolated by recrystallization from hexane (mp 54°C).

*[4] Unidentified side products were formed.

*[5] Catalyst: $RhCl(PPh_3)_3$.

TABLE 3. The Mass Spectra of the Hydrosilylation Products

Compound*	*m/z* (I_{rel}, %)*[2]
1	2
4a	187 $[M]^+$ (34), 186 $[M - H]^+$ (25), 118 (7), 106 $[M - C_4H_3OCH_2]^+$ (6), 91 (11), 81 $[C_4H_3OCH_2]^+$ (100), 77 (15), 65 (11), 53 (37)
4b	201 $[M]^+$ (18), 216 (2), 118 (2), 107 (12), 95 $[H_3CC_4H_2OCH_2]^+$ (100), 91 (8), 77 (8), 65 (11), 57 (7), 43 (13)
3c	252/250 $[M - SiEt_3]^+$ (100/100), 184/182 (7/8), 171 (11), 170 $[M - HSiEt_3 - Br]^+$ (9), 157/155 $[C_6H_4Br]^+$ (5/9), 143 (8), 131 (6), 115 $[SiEt_3]^+$ (25), 103 (9), 91 (5), 87 (18), 75 (9), 59 (14), 39 (7)
4c	253/251 $[M]^+$ (100/100), 184 (2), 172 (4), 157/155 $[C_6H_4Br]^+$ (2/3), 143 (4), 117/115 (3/5), 104 (3), 91 (10), 81 $[C_4H_3OCH_2]^+$ (100), 63 (10), 53 (30), 39 (10), 32 (25)
A	173 $[M]^+$ (42), 172 $[M - H]^+$ (32), 144 $[M - HCO]^+$ (10), 115 (12), 106 $[M - C_4H_3OCH_2]^+$ (5), 91 (5), 81 $[C_4H_3OCH_2]^+$ (100), 77 $[Ph]^+$ (26), 65 (15), 53 (31), 51 (21), 39 (23), 32 (89)
4d	267/265 $[M]^+$ (8/8), 186 $[M - Br]^+$ (4), 173/171 (4/4), 157 $[C_6H_4Br]^+$ (2), 143 (2), 130 (1), 115 (2), 104 (2), 95 $[H_3CC_4H_2OCH_2]^+$ (100), 91 (7), 77 (6), 65 (7), 51 (7), 43 (14)
B	187 $[M]^+$ (16), 172 $[M - H]^+$ (2), 95 $[H_3CC_4H_2OCH_2]^+$ (100), 77 $[Ph]^+$ (10), 65 (12), 51 (11), 43 (15), 32 (39)
2e	315 $[M]^+$ (15), 287 (24), 286 $[M - Et]^+$ (100), 205 (22), 184 (18), 176 (17), 153 (35), 148 (35), 146 (29), 125 (13), 115 (5), 105 (13), 91 (8), 87 (14), 81 $[C_4H_3OCH_2]^+$ (38), 77 (7), 59 (29), 53 (24)
4e	201 $[M]^+$ (38), 200 $[M - H]^+$ (32), 184 (3), 172 (2), 158 (4), 144 (3), 132 (8), 120 (12), 103 (5), 91 (20), 81 $[C_4H_3OCH_2]^+$ (100), 77 (24), 65 (10), 53 (42), 39 (15)
4g	203 $[M]^+$ (28), 106 (3), 97 $[C_4H_3SCH_2]^+$ (100), 91 (10), 77 (11), 65 (11), 53 (37), 45 (13), 39 (15)
4h	217 $[M]^+$ (18), 182 (2), 118 (3), 111 $[H_3CC_4H_2SCH_2]^+$ (100), 91 (11), 77 (21), 65 (14), 51 (12), 45 (10), 39 (13)
4i	269/267 $[M]^+$ (13/12), 186 (3), 172 (1), 157/155 $[C_6H_4Br]^+$ (2/3),143 (2), 115 (2), 105 (2), 97 $[C_4H_3SCH_2]^+$ (100), 91 (11), 63 (10), 77 (8), 63 (10), 53 (11), 45 (15), 39 (11)
4j	283/281 $[M]^+$ (9/9), 200 (1), 184 (2), 168 (2), 155 $[C_6H_4Br]^+$ (2), 143 (2), 104 (2), 111 $[H_3CC_4H_2SCH_2]^+$ (100), 91 (12), 77 (18), 63 (9), 51 (11), 45 (11), 39 (10)
C	203 $[M]^+$ (21), 111 $[H_3CC_4H_2SCH_2]^+$ (100), 77 $[Ph]^+$ (31), 65 (15), 51 (20), 45 (9), 39 (19)
2k	331 $[M]^+$ (23), 300 (13), 301 (27), 302 $[M - Et]^+$ (100), 274 (2), 234 (4), 216 $[M - SiEt]^+$ (3), 205 (19), 184 (2), 176 (21), 169 (34), 148 (40), 146 (35), 141 (24), 132 (13), 119 (7), 115 (17), 97 $[C_4H_3SCH_2]^+$ (38), 87 (21), 77 (8), 59 (38), 53 (14), 45 (16)
2l	345 $[M]^+$ (22), 314 (6), 315 (14), 316 $[M - Et]^+$ (100), 288 (2), 234 (2), 205 (9), 183 (43), 176 (12), 159 (17), 148 (27), 146 (25), 132 (10), 115 (12), 111 $[H_3CC_4H_2SCH_2]^+$ (100), 105 (7), 87 (18), 77 (15), 59 (38), 45 (10)
4l	231 $[M]^+$ (14), 134 $[M - H_3CC_4H_2SCH_2]^+$ (2), 121 (8), 111 $[H_3CC_4H_2SCH_2]^+$ (100), 105 (7), 87 (18), 77 (15), 59 (38), 45 (10)
4m	197 $[M]^+$ (40), 196 $[M - H]^+$ (13), 120 $[M - Ph]^+$ (11), 118 (7), 106 $[PhCH_2NH]^+$ (13), 91 $[PhCH_2]^+$ (100), 77 $[Ph]^+$ (13), 65 (26), 51 (11), 39 (13)
2n	365 $[M]^+$ (2), 230 (3), 213 (15), 214 $[M - SiEt_3 - 2F]^+$ (100), 192 $[M - SiEt_3 - 2F - HF]^+$ (7), 165 (7), 145 $[C_6H_4CF_3]^+$ (2), 134 (6), 109 (11), 91 $[PhCH_2]^+$ (81), 77 $[Ph]^+$ (23), 65 (10), 59 (9), 49 (6)
4n	251 $[M]^+$ (27), 230 (4), 212 (3), 165 (1), 154 (3), 145 $[C_6H_4CF_3]^+$ (2), 91 $[PhCH_2]^+$ (100), 77 (4), 69 (12), 51 (5), 39 (4), 32 (7)
4o	263/261 $[M]^+$ (18/19), 180 $[M - Br]^+$ (9), 152 (3), 143 (1), 104 (4), 91 $[PhCH_2]^+$ (100), 77 $[Ph]^+$ (9), 65 (14), 51 (7), 39 (6)
D	183 $[M]^+$ (55), 182 $[M - H]^+$ (22), 106 $[PhCH_2NH]^+$ (20), 91 $[PhCH_2]^+$ (100), 77 $[Ph]^+$ (26), 65 (22), 51 (15), 39 (10)
4p	201 $[M]^+$ (35), 200 $[M - H]^+$ (8), 124 $[M - Ph^+]$ (8), 122 (7), 91 $[PhCH_2]^+$ (100), 77 $[Ph]^+$ (9), 65 (15), 51 (8), 39 (7)

TABLE 3 (continued)

1	2
4q	228 $[M]^+$ (11), 210 (3), 195 (5), 181 (13), 190 (17), 168 (3), 152 (4), 105 (61), 91 $[PhCH_2]^+$ (100), 77 $[Ph]^+$ (14), 65 (24), 51 (11), 39 (10)
2r	325 $[M]^+$ (10), 297 (25), 296 $[M - Et]^+$ (100), 281 (6), 266 (3), 234 (2), 207 (16), 205 (10), 176 (13), 163 (8), 148 (29), 146 (14), 135 (10), 115 (4), 105 (8), 91 $[PhCH_2]^+$ (30), 87 (14), 73 (6), 59 (21)
4r	211 $[M]^+$ (40), 210 $[M - H]^+$ (8), 196 $[M - Me]^+$ (2), 134 $[M - Ph]^+$ (6), 120 $[M - PhCH_2]^+$ (42), 103 (3), 91 $[PhCH_2]^+$ (100), 77 $[Ph]^+$ (14), 65 (15), 51 (6), 39 (8)
2s	311 $[M]^+$ (15), 283 (26), 282 $[M - Et]^+$ (100), 254 (4), 194 (6), 177 (34), 149 (63), 121 (41), 120 (40), 115 (5), 105 $[C_6H_4CH_3]^+$ (56), 87 (23), 77 $[Ph]^+$ (35), 59 (47)
4s	197 $[M]^+$ (26), 182 (2), 105 $[C_6H_4CH_3]^+$ (100), 91 (4), 79 (10), 77 $[Ph]^+$ (26), 65 (7), 51 (8)
2t	327 $[M]^+$ (23), 299 (11), 298 $[M - Et]^+$ (100), 254 (2), 193 (19), 165 (29), 149 (4), 137 (13), 121 $[M - SiEt_3 - PhN]^+$ (100), 120 (14), 104 (4), 87 (13), 78 (15), 77 $[Ph]^+$ (20), 59 (23)
4t	213 $[M]^+$ (15), 196 (2), 168 (2), 121 $[M - PhNH]^+$ (100), 91 (6), 78 (12), 77 $[Ph]^+$ (18), 65 (8), 51 (8)
4u	263/261 $[M]^+$ (40/41), 262/260 $[M - H]^+$ (15/9), 182 $[M - Br]^+$ (18), 171/169 $[CH_2C_6H_4Br]^+$ (98/100), 106 $[PhNHCH_2]^+$ (20), 104 (12), 90 $[M - Br - PhNH]^+$ (54), 91 (46), 77 $[Ph]^+$(41), 65 (15), 63 (21), 51 (24), 39 (15)
E	181 $[M]^+$ (82), 180 $[M - H]^+$ (100), 104 $[M - Ph]^+$ (17), 77 $[Ph]^+$ (85), 63 (7), 51 (37), 39 (8)
F	196 $[M]^+$ (52), 195 $[M - H]^+$ (63), 178 (3), 167 (2), 118 (3), 104 $[PhNCH]^+$ (4), 98 (5), 92 $[M - PhNCH]^+$ (9), 77 $[Ph]^+$ (29), 65 (9), 51 (13), 40 (9), 32 (100)
2w	395 $[M]^+$ (3), 280 $[M - SiEt_3]^+$ (2), 242 $[M - SiEt_3 - 2F]^+$ (100), 222 (7), 172 (2), 134 (5), 121 $[CH_3OC_6H_4CH_2]^+$ (56), 109 (3), 91 (9), 77 (23), 59 (9)
4w	281 $[M]^+$ (10), 242 (2), 145 $[C_6H_4CF_3]^+$ (2), 121 $[CH_3OC_6H_4CH_2]^+$ (100), 106 (1), 91 (6), 78 (9), 77 (10), 63 (4), 51 (5), 39 (3)

* **A**-$C_4H_3OCH_2NHPh$, **B**-$H_3CC_4H_2OCH_2NHPh$, **C**-$H_3CC_4H_2SCH_2NHPh$, **D**-$PhCH_2NHPh$, **E**-PhCHNPh, **F**-$H_2NC_6H_4CHNPh$

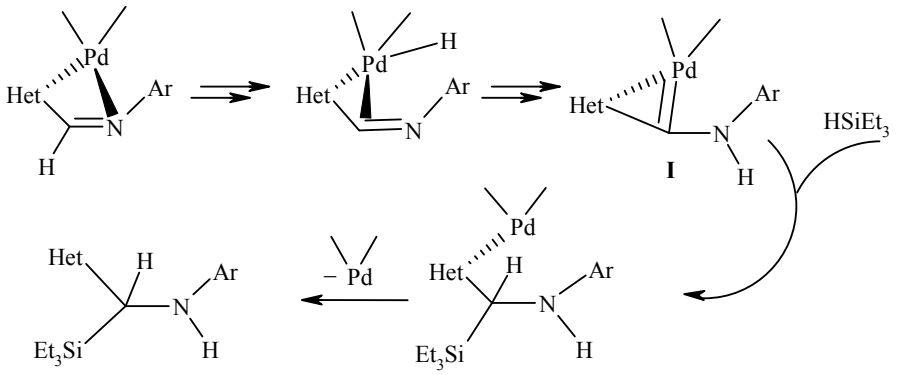
*[2] The signals of the characteristic ions are given.

The hydrosilylation of many of the investigated substrates (**1a-e**,**g-p**,**r-t**) mostly leads to the formation of the desired products having structures **2-4**. In most cases the respective amines were isolated. Of the initial heterocyclic compounds only the imine **1f** did not react with triethylsilane under the investigated conditions. Nearly all the bromine derivatives undergo debromination with the formation of the corresponding saturated compounds or the debromoimine (Tables 2 and 3). This applies particularly to the imine **1u**. An attempt to silylate the latter in the presence of the complex $RhCl(PPh_3)_3$ did not give positive results. N-Silylation products are hardly formed at all during the hydrosilylation of the two investigated nitro compounds **1q** and **1v**. Thus, the imine **1q** reacts with the formation mainly of unidentified side products, while in the reaction of the aldimine **1v** its nitro group is reduced to an NH_2 group. The last imine does not react with triethylsilane in the presence of $RhCl(PPh_3)_3$ (65°C, 26 h) or with dimethylphenylsilane in the presence of $[Pd(allyl)Cl]_2$ and $RhCl(PPh_3)_3$ (65°C, 13-14 h). Since the nitro- and bromine-containing aromatic imines **1q** and **1u** hardly gave the desired products at all, we did not investigate their analogs **1x**,**y**.

Of all the investigated compounds only the bromine-substituted heterocyclic imines are transformed into the C-silylation products **3c**,**d**,**j**, which were successfully isolated by column chromatography, demonstrating their adequate stability. The N-silylation products were recorded in the reactions of many imines: **1e**,**k**,**l**,**n**,**o**,**r-t**,**w**). Nearly all were isolated by chromatography (with the exception of the products **2n**,**r** that are probably hydrolyzed in the column to the corresponding amines **4n**,**r**, which were isolated (Table 2)).

Thus, the unusual direction of transformation leading to the formation of the C-silylated products is only observed in the reactions of the O- and S-heterocyclic imines. Here the presence of the bromine atom at the *ortho* position of the aza part of the molecules of the reacting imines promotes C-silylation. The obtained data agree with our previous results [7, 8]. Probably, the presence of the heterocycles in the molecules of the reacting imines leads to the appearance of intermediate carbene structures (type I, scheme 3), which are formed during complexation of the substrates with the catalyst (by analogy with the mechanism proposed in [15]) and lead to C-silylation. In addition, the bulky bromine atom at the *ortho* position to the carbon atom of the aromatic ring attached to the nitrogen atom of the reacting imine group N=C prevents N-silylation sterically (like the CF_3 group in [7]).

Scheme 3



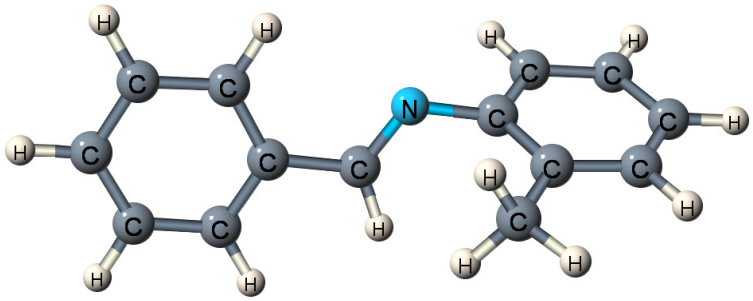
The structure and electronic characteristics of the aldimines **1m-r**, containing various substituents at the *ortho* position of the aza part of the molecule, were calculated by the quantum-chemical AM1 method in order to determine the effect of the functional groups on the characteristics of the molecules (Table 4 and Fig. 1).

By comparing the obtaining data it can be seen that the greatest differences in all the values of the parameters (Table 4) are, as expected, characteristic of the molecules **1q**,**r**, which contain the most electronegative NO_2 group and two donating CH_3 groups respectively. However, the molecules containing CF_3 and Br substituents, which have a special effect on hydrosilylation, are characterized by average values of all the calculated electronic parameters. It can, consequently, be supposed that steric and not electronic factors play the major role in the investigated reaction. In fact, as seen from the molecular structures of **1m** and **1n** (Fig. 1), the CF_3 group creates steric hindrances for the addition of the reagent to the nitrogen atom of the imine group, whereas the methyl substituent does not prevent such a reaction.

TABLE 4. The Characteristics of the Compounds, Obtained by the AM1 Quantum-chemical Method

Compound	q_N	q_C	HOMO, eV	LUMO, eV
1m	-0.148	-0.001	-8.91	-0.28
1n	-0.163	-0.020	-9.27	-0.85
1o	-0.158	-0.019	-9.09	-0.42
1p	-0.157	-0.004	-8.95	-0.61
1q	-0.194	-0.064	-9.51	-0.91
1r	-0.145	-0.004	-8.84	-0.26

a



b

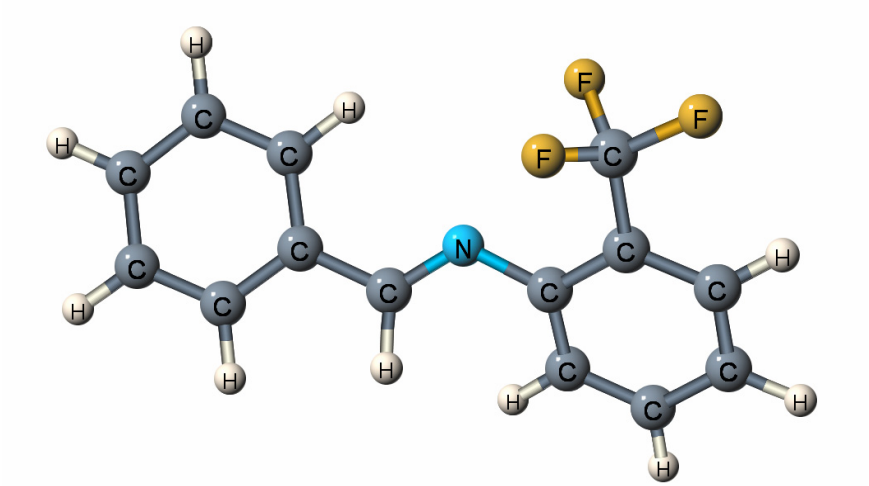


Fig. 1. The optimized structures of the molecules of the imines **1m** (a) and **1n** (b) obtained by the quantum-chemical AM1 method.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Varian Mercury-200 (200 MHz) and Bruker WH-90/DS (90 MHz) spectrometers for solutions in deuterochloroform with TMS as internal standard. The mass spectra were obtained on an HP6890 GC/MS chromato-mass spectrometer with an HP-5 MS capillary column (30.0 m × 250 μm × 0.25 μm) at programmed temperature from 70 to 260°C (10 deg/min). Before use the benzene was distilled over calcium hydride. Aldehydes, amines, hydrosilanes, and Pd complex produced by Acros, Aldrich, and Fluka were used. The molecular sieves were 4A (VEB Laborchemie Apolda).

General Procedure for the Synthesis of the Aldimines. In a round-bottom flask with a reflux condenser we placed 10 ml of dry benzene and 5 mmol each of the initial aldehyde and amine and then 5 g of the freshly baked molecular sieves. The reaction was conducted at room temperature or with heating on a water bath at 80°C in an atmosphere of argon. Samples were taken periodically and analyzed by TLC and GLC-MS. After a specific time interval, depending on the substrates (Table 1), they were almost completely converted into the respective products. At the end of the reaction the sieves were filtered off and washed with benzene. The filtrate was evaporated at reduced pressure (40°C/15 mm Hg), and the small residues of the initial substances

were removed under vacuum (45-50°C/0.1 mm Hg). The products were yellow oily or crystalline substances. The solid compounds were purified by recrystallization from hexane or its mixture with ethyl acetate, and the ^{1}H NMR spectra were recorded.

General Procedure for Hydrosilylation. A 5-cm^3 Pierce reaction tube was blown with argon, and 2 ml of dry benzene, 0.01 mmol of the catalyst, and 0.5 mmol of the initial imine were placed in it, after which the mixture was stirred at room temperature for 30 min. The solution was then cooled to 0°C with ice, and 0.6 mmol of hydrosilane was added with a syringe. The reaction was carried out at 65°C, and samples were taken periodically and analyzed by TLC and GLC-MS. At the end of silylation the reaction mixture was evaporated at reduced pressure (30°C/15 mm Hg), and the ^{1}H NMR spectra were recorded. The mixture was then separated by liquid chromatography on a column of silica gel (Kieselgel 60, 0.063-0.200 mesh, Merck) with various eluants. All the obtained products were yellow oily substances,

Quantum-chemical Calculations. All the calculations were carried out by the semiempirical AM1 method [16], included in the MOPAC 6 software package [17]. The equilibrium geometric structures of the molecules were calculated with full optimization of the parameters using the PRECISE enhanced accuracy criterion [18]. Analysis of the obtained frequencies of the molecular vibrations showed that all the optimized structures correspond to minima on the potential energy surface of the system. Computer design was realized by means of the JMol software [19].

N-(2-Furylmethylidene)-2-methylaniline (1a). Mass spectrum, *m/z* (I_{rel}, %): 186 $[M + H]^+$ (9), 185 $[M]^+$ (69), 184 $[M - H]^+$ (29), 168 (14), 157 (14), 156 $[M - HCO]^+$ (100), 154 (16), 130 (53), 129 (24), 128 (26), 117 (20), 91 $[C_6H_4CH_3]^+$ (35), 90 (9), 89 (20), 77 (18), 65 (54), 63 (24), 52 (29), 51 (45), 50 (21), 39 (53). ^{1}H NMR spectrum, δ, ppm: 2.33 (3H, s, CH_3); 6.3-7.8 (7H, m, Ar, Fur); 8.13 (1H, s, CH=N).

N-(5-Methyl-2-furylmethylidene)-2-methylaniline (1b). Mass spectrum, *m/z*, (I_{rel}, %): 200 $[M + H]^+$ (10), 199 $[M]^+$ (68), 198 $[M - H]^+$ (22), 184 $[M - Me]^+$ (25), 170 (8), 157 (14), 156 $[M - MeCO]^+$ (100), 154 (14), 130 (21), 129 (24), 128 (20), 117 (30), 91 $[C_6H_4CH_3]^+$ (32), 90 (8), 89 (15), 79 (13), 77 $[Ph]^+$ (12), 65 (52), 63 (17), 53 (19), 52 (16), 51 (34), 50 (14), 43 (30), 39 (32). ^{1}H NMR spectrum, δ, ppm: 2.27 (3H, s, CH_3); 2.33 (3H, s, CH_3); 6.0-7.3 (6H, m, Ar, Fur); 7.98 (1H, s, CH=N).

N-(2-Furylmethylidene)-2-bromoaniline (1c). Mass spectrum, *m/z* (I_{rel}, %): 251/249 $[M]^+$ (96/100), 250/248 $[M - H]^+$ (57/45), 222 $[M - HCO]^+$ (4), 195 (5), 184/182 (5/6), 171 (11), 170 $[M - Br]^+$ (91), 157/155 $[C_6H_4Br]^+$ (38/39), 142 (29), 141 (15), 140 (16), 115 (78), 102 (9), 89 (18), 77 (26), 76 (55), 75 (59), 74 (23), 64 (21), 63 (32), 52 (42), 51 (69), 50 (71), 39 (77). ^{1}H NMR spectrum, δ, ppm: 6.4-7.8 (7H, m, Ar, Fur); 8.09 (1H, s, CH=N).

N-(5-Methyl-2-furylmethylidene)-2-bromoaniline (1d). Mass spectrum, *m/z* (I_{rel}, %): 265/263 $[M]^+$ (99/100) , 264/262 $[M - H]^+$ (48/32), 222 $[M - MeCO]^+$ (7), 195 (3), 184 $[M - Br]^+$ (92), 169 (14), 157/155 $[C_6H_4Br]^+$ (29/34), 141 (9), 140 (8), 129 (12), 128 (15), 114 (6), 79 (14), 77 (14), 76 (24), 75 (25), 74 (8), 64 (7), 63 (9), 53 (21), 52 (12), 51 (25), 50 (23), 43 (19), 39 (14). ^{1}H NMR spectrum, δ, ppm: 2.38 (3H, s, CH_3); 6.0-7.7 (6H, m, Ar, Fur); 7.98 (1H, s, CH=N).

N-(2-Furylmethylidene)-2,6-dimethylaniline (1e). Mass spectrum, *m/z* (I_{rel}, %): 200 $[M + H]^+$ (10), 199 $[M]^+$ (71), 198 $[M - H]^+$ (33), 183 $[M - H- Me]^+$ (12), 171 (14), 170 $[M - HCO]^+$ (100), 168 (15), 156 (14), 155 (14), 154 (21), 144 (43), 143 (16), 142 (13), 130 (25), 129 (8), 128 (16), 117 (11), 115 (13), 103 (19), 91 (14), 89 (9), 79 (19), 78 (19), 77 (55), 65 (19), 63 (17), 52 (33), 51 (46), 50 (18), 39 (54). ^{1}H NMR spectrum, δ, ppm: 2.09 (6H, s, CH_3); 6.4-7.6 (6H, m, Ar, Fur); 7.91 (1H, s, CH=N).

N-(5-Methyl-2-furylmethylidene)-2,6-dimethylaniline (1f). Mass spectrum, *m/z* (I_{rel}, %): 214 $[M + H]^+$ (10), 213 $[M]^+$ (77), 212 $[M - H]^+$ (22), 198 $[M - Me]^+$ (8), 183 (6), 170 $[M - MeCO]^+$ (100), 168 (9), 155 (14), 154 (15), 144 (15), 143 (9), 142 (7), 130 (14), 128 (8), 117 (7), 115 (7), 103 (13), 91 (10), 79 (24), 78 (13), 77 (36), 65 (15), 53 (14), 51 (29), 50 (18), 43 (28), 39 (26). ^{1}H NMR spectrum, δ, ppm: 2.11 (6H, s, CH_3); 2.38 (3H, s, CH_3); 6.0-7.3 (6H, m, Ar, Fur); 7.82 (1H, s, CH=N).

N-(2-Thienylmethylidene)-2-methylaniline (1g). Mass spectrum, *m/z* (I_{rel}, %): 202 $[M + H]^+$ (15), 201 $[M]^+$ (100), 200 $[M - H]^+$ (64), 186 $[M - Me]^+$ (12), 169 (11), 168 $[M - HS]^+$ (78), 167 (41), 156 $[M - HCS]^+$ (12), 154 (6), 129 (7), 118 $[M - Th]^+$ (22), 117 $[M - H - Th]^+$ (28), 110 (6), 91 $[C_6H_4CH_3]^+$ (42), 90 (9), 89 (14), 77 (9), 70 (10), 65 (51), 63 (18), 58 (8), 52 (9), 51 (20), 50 (10), 45 (19), 39 (41). ^{1}H NMR spectrum, δ, ppm: 2.29 (3H, s, CH_3); 6.8-7.6 (7H, m, Ar, Th); 8.38 (1H, s, CH=N).

N-(5-Methyl-2-thienylmethylidene)-2-methylaniline (1h). Mass spectrum, *m/z* (I_{rel}, %): 216 $[M + H]^+$ (5), 215 $[M]^+$ (100), 214 $[M - H]^+$ (33), 200 $[M - Me]^+$ (28), 199 (22), 183 (11), 182 $[M - HS]^+$ (68), 181 (16), 180 (17), 167 (51), 156 $[M - MeCS]^+$ (15), 154 (11), 129 (8), 118 (19), 117 $[M - H - MeTh]^+$ (43), 109 (8), 97 $[MeTh]^+$ (29), 91 $[C_6H_4CH_3]^+$ (52), 90 (13), 89 (21), 77 (15), 69 (9), 65 (65), 63 (24), 59 (12), 53 (20), 52 (13), 51 (37), 50 (17), 45 (24), 39 (48). ^{1}H NMR spectrum, δ, ppm: 2.27 (3H, s, CH_3); 2.47 (3H, s, CH_3); 6.6-7.3 (6H, m, Ar, Th); 8.29 (1H, s, CH=N).

N-(2-Thienylmethylidene)-2-bromoaniline (1i). Mass spectrum, *m/z* (I_{rel}, %): 267/265 $[M]^+$ (76/78), 266/264 $[M - H]^+$ (57/45), 187 (14), 186 $[M - Br]^+$(100), 157/155 $[C_6H_4Br]^+$ (38/39), 140 (7), 115 (16), 93 (15), 84 (13), 77 (14), 76 (32), 75 (35), 74 (10), 63 (14), 52 (7), 51 (99), 50 (30), 45 (25), 39 (32). ^{1}H NMR spectrum, δ, ppm: 6.8-7.7 (7H, m, Ar, Th); 8.39 (1H, s, CH=N).

N-(5-Methyl-2-thienylmethylidene)-2-bromoaniline (1j). Mass spectrum, *m/z* (I_{rel}, %): 281/279 $[M]^+$ (62/63), 280/278 $[M - H]^+$ (51/43), 201 (14), 200 $[M - Br]^+$ (100), 157/155 $[C_6H_4Br]^+$ (23/24), 140 (3), 122 (12), 97 (29), 95 (12), 77 (19), 76 (33), 75 (33), 74 (11), 63 (14), 53 (15), 51 (24), 50 (29), 45 (25), 39 (21). ^{1}H NMR spectrum, δ, ppm: 2.51 (3H, s, CH_3); 6.6-7.7 (6H, m, Ar, Th); 8.29 (1H, s, CH=N).

N-(2-Thienylmethylidene)-2,6-dimethylaniline (1k). Mass spectrum, *m/z* (I_{rel}, %): 216 $[M + H]^+$ (18), 215 $[M]^+$ (100), 214 $[M - H]^+$ (59), 199 $[M - H - Me]^+$ (12), 182 $[M - HS]^+$ (55), 181 (16), 170 $[M - HCS]^+$ (13), 167 $[M - HS - Me]^+$ (39), 132 (24), 131 (24), 130 (32), 117 (13), 110 (5), 103 (22), 91 (13), 79 (23), 78 (19), 77 (60), 70 (6), 65 (18), 63 (19), 58 (9), 53 (13), 52 (15), 51 (30), 50 (12), 45 (25), 39 (36). ^{1}H NMR spectrum, δ, ppm: 2.04 (6H, s, CH_3); 6.8-7.6 (6H, m, Ar, Th); 8.20 (1H, s, CH=N).

N-(5-Methyl-2-thienylmethylidene)-2,6-dimethylaniline (1l). Mass spectrum, *m/z* (I_{rel}, %): 230 $[M + H]^+$ (18), 229 $[M]^+$ (100), 214 (17), 213 $[M - H - Me]^+$ (23), 196 $[M - HS]^+$ (51), 181 (37), 170 $[M - MeCS]^+$ (16), 132 (16), 131 (25), 130 (27), 117 (9), 105 (8), 103 (16), 97 (18), 79 (18), 78 (12), 77 (44), 65 (15), 63 (10), 53 (16), 52 (7), 51 (18), 50 (6), 45 (13), 39 (26). ^{1}H NMR spectrum, δ, ppm: 2.04 (6H, s, CH_3); 2.44 (3H, s, CH_3); 6.6-7.2 (5H, m, Ar, Th); 8.09 (1H, s, CH=N).

N-(Benzylidene)-2-methylaniline (1m). Mass spectrum, *m/z* (I_{rel}, %): 196 $[M + H]^+$ (10), 195 $[M]^+$ (73), 194 $[M - H]^+$ (66), 180 (4), 167 (6), 152 (5), 119 (9), 118 $[M - Ph]^+$ (100), 117 (24), 91 $[C_6H_4CH_3]^+$ (47), 90 (10), 89 (23), 77 $[Ph]^+$ (13), 65 (44), 63 (19), 51 (24), 50 (11). ^{1}H NMR spectrum, δ, ppm: 2.31 (3H, s, CH_3); 6.7-8.0 (9H, m, Ar); 8.33 (1H, s, CH=N).

N-(Benzylidene)-2-trifluoromethylaniline (1n). Mass spectrum, *m/z* (I_{rel}, %): 250 $[M + H]^+$ (11), 249 $[M]^+$ (79), 248 $[M - H]^+$ (100), 230 $[M - F]^+$ (6), 208 (4), 180 (5), 172 (10), 152 (6), 145 $[PhCF_3 - H]^+$ (53), 125 (11), 95 (16), 89 (7), 76 (14), 77 $[Ph]^+$ (16), 63 (9), 51 (18), 50 (11). ^{1}H NMR spectrum, δ, ppm: 6.9-8.0 (9H, m, Ar); 8.33 (1H, s, CH=N).

N-(Benzylidene)-2-bromoaniline (1o). Mass spectrum, *m/z* (I_{rel}, %): 261/259 $[M]^+$ (96/100), 260/258 $[M - H]^+$ (96/87), 180 $[M - Br]^+$ (60), 157/155 $[C_6H_4Br]^+$ (41/42), 152 (24), 102 (9), 90 (25), 89 (32), 76 (26), 77 $[Ph]^+$ (51), 76 (66), 75 (32), 74 (17), 64 (13), 63 (34), 52 (12), 51 (55) 50 (50). ^{1}H NMR spectrum, δ, ppm: 6.8-8.0 (9H, m, Ar); 8.31 (1H, s, CH=N).

N-(Benzylidene)-2-fluoroaniline (1p). Mass spectrum, *m/z* (I_{rel}, %): 200 $[M + H]^+$ (11), 199 $[M]^+$ (84), 198 $[M - H]^+$ (100), 122 $[M - Ph]^+$ (12), 95 (15), 78 (8), 77 $[Ph]^+$ (16), 74 (13), 51 (8). ^{1}H NMR spectrum, δ, ppm: 7.0-8.0 (9H, m, Ar); 8.49 (1H, s, CH=N).

N-(Benzylidene)-2-nitroaniline (1q). Mass spectrum, *m/z* (I_{rel}, %): 226 $[M]^+$ (13), 178 (7), 152 (12), 105 $[PhCHNH]^+$ (100), 89 (10), 78 (5), 77 $[Ph]^+$ (32), 76 (12), 63 (11), 51 (14). ^{1}H NMR spectrum, δ, ppm: 6.9-8.1 (9H, m, Ar); 8.38 (1H, s, CH=N).

N-(Benzylidene)-2,6-dimethylaniline (1r). Mass spectrum, *m/z* (I_{rel}, %): 210 $[M + H]^+$ (13), 209 $[M]^+$ (82), 208 $[M - H]^+$ (33), 193 $[M - H- Me]^+$ (23), 165 (6), 132 $[M - Ph]^+$ (100), 131 (14), 130 (15), 117 (21), 103 (18), 91 (9), 89 (15), 79 (17), 78 (13), 77 $[Ph]^+$ (39), 65 (10), 63 (12), 51 (19), 39 (15). ^{1}H NMR spectrum, δ, ppm: 2.09 (6H, s, CH_3); 6.9-8.0 (6H, m, Ar); 8.18 (1H, s, CH=N).

N-(4-Methylbenzylidene)aniline (1s). Mass spectrum, *m/z* (I_{rel}, %): 196 $[M + H]^+$ (11), 195 $[M]^+$ (81), 194 $[M - H]^+$ (100), 180 (5), 165 (3), 152 (3), 104 (7), 91 $[C_6H_4CH_3]^+$ (15), 77 $[Ph]^+$ (13), 65 (9), 51 (25). ^{1}H NMR spectrum, δ, ppm: 2.36 (3H, s, CH_3); 6.9-7.9 (9H, m, Ar); 8.39 (1H, s, CH=N).

N-(4-Methoxybenzylidene)aniline (1t). Mass spectrum, *m/z* (I_{rel}, %): 212 $[M + H]^+$ (13), 211 $[M]^+$ (88), 210 $[M - H]^+$ (100), 196 (6), 167 (22), 104 (6), 91 (5), 77 $[Ph]^+$ (69), 65 (13), 51 (38), 39 (12). ^{1}H NMR spectrum, δ, ppm: 3.76 (3H, s, OCH_3); 6.9-8.0 (9H, m, Ar); 8.36 (1H, s, CH=N).

N-(4-Bromobenzylidene)aniline (1u). Mass spectrum, *m/z* (I_{rel}, %): 261/259 $[M]^+$ (50/54), 260/258 $[M - H]^+$ (49/44), 179 $[M - Br]^+$ (13), 152 (8), 104 $[PhNCH]^+$ (19), 89 (11), 78 (9), 77 $[Ph]^+$ (100), 76 (20), 63 (14), 51 (47), 50 (24), 39 (13). ^{1}H NMR spectrum, δ, ppm: 7.1-7.9 (9H, m, Ar); 8.40 (1H, s, CH=N).

N-(4-Nitrobenzylidene)aniline (1v). Mass spectrum, *m/z* (I_{rel}, %): 227 $[M + H]^+$ (14), 226 $[M]^+$ (100), 225 $[M - H]^+$ (45), 179 (53), 167 (11), 152 (18),), 104 $[PhNCH]^+$ (30), 89 (3), 78 (9), 77 $[Ph]^+$ (96), 76 (16), 63 (13), 51 (45), 50 (20). ^{1}H NMR spectrum, δ, ppm: 7.1-8.4 (9H, m, Ar); 8.51 (1H, s, CH=N).

N-(4-Methoxybenzylidene)-2-trifluoromethylaniline (1w). Mass spectrum, *m/z* (I_{rel}, %): 280 $[M + H]^+$ (13), 279 $[M]^+$ (85), 278 $[M - H]^+$ (100), 260 $[M - F]^+$ (5), 235 (11), 145 $[PhCF_3 - H]^+$ (34), 134 (5), 125 (8), 108 (5), 95 (10), 77 (13), 65 (11), 51 (10), 39 (5). ^{1}H NMR spectrum, δ, ppm: 3.87 (3H, s, OCH_3); 6.9-8.0 (8H, m, Ar); 8.28 (1H, s, CH=N).

N-(4-Bromobenzylidene)-2-trifluoromethylaniline (1x). Mass spectrum, *m/z* (I_{rel}, %): 329/327 $[M]^+$ (79/85), 328/326 $[M - H]^+$ (89/78), 308 $[M - F]^+$ (5), 247 $[M - Br]^+$ (5), 227 (6), 201 (5), 179 (13), 172 (19), 145 $[PhCF_3 - H]^+$ (34), 125 (20), 102 (15), 95 (30), 89 (13), 77 (18), 76 (28), 75 (44), 63 (18), 51 (20), 50 (31), 39 (10). ^{1}H NMR spectrum, δ, ppm: 7.0-7.9 (8H, m, Ar); 8.32 (1H, s, CH=N).

N-(4-Bromobenzylidene)-2-nitroaniline (1y). Mass spectrum, *m/z* (I_{rel}, %): 306/304 $[M]^+$ (10/10), 259 $[M - NO_2]^+$ (2), 208 (7), 185/183 $[BrC_6H_4CHNH]^+$ (96/100), 178 (17), 167 (5), 157/155 $[C_6H_4Br]^+$ (15/16), 102 (10), 89 (26), 77 (23), 76 (30), 75 (19), 63 (31), 51 (26) 50 (30), 39 (20). ^{1}H NMR spectrum, δ, ppm: 7.0-8.1 (8H, m, Ar), 8.33 (1H, s, CH=N).

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