Diaziridine ring expansion in 6-aryl-1,5-diazabicyclo[3.1.0]hexanes upon reactions with activated olefins in ionic liquids

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Reactions of 1,3-diphenylpropen-2-one and β-nitrostyrenes with azomethine imines, generated from 6-aryl-1,5-diazabicyclo[3.1.0]hexanes on catalysis with $Et_2O \cdot BF_3$ in ionic liquids, were found to proceed with high regio- and stereoselectivity to afford the products of the diaziridine ring expansion, *viz.*, [3-aryl-2-phenyltetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazol-1-yl](phenyl)methanones, 1,3-diaryl-2-nitrotetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazoles and 5-aryl-6-(3-nitrophenyl)-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]pyrazolium tetrafluoroborates (hexafluorophosphates). The reactions discovered are new, more simple methods for the synthesis of bicyclic structures.

Key words: 6-aryl-1,5-diazabicyclo[3.1.0]hexanes, azomethine imines, β-nitrostyrenes, 1,3-diphenylpropen-2-one, ionic liquids, $Et_2O \cdot BF_3$, 1,3-diaryl-2-nitrotetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazoles, 5-aryl-6-(3-nitrophenyl)-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]pyrazolium tetrafluoroborate (hexafluorophosphate), (3-aryl-2-phenyltetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]-pyrazol-1-yl)(phenyl)methanones.

In the last years, our research group has developed new approaches to the synthesis of various nitrogen-containing heterocycles, which are based on the transformation of diaziridine derivatives, including 1,2-di- and 1,2,3-trialkyldiaziridines **1** and 1,5-diazabicyclo[3.1.0]-hexanes **2**, upon the action of electrophilic reagents, in particular, dipolarophiles. In these reactions, the diaziridine ring is opened at the N—N or C—N bond to form reactive dipolar intermediates, which have tendency to cycloaddition reactions.[1—9] Aryl ketenes,[1—4] aroylisocyanates and -isothiocyanates,[5,6] carbon disulfide,[7] activated nitriles,[8] diethyl acetylenedicarboxylate[9] were studied as the dipolarophiles. It was found that in common organic solvents, new heterocycles are formed only upon the action of aryl ketenes and aroylisocyanates. Other, less active reagents react with diaziridines **1** and **2** only in ionic liquids (IL), and in a number of cases the reactions proceed unpredictably. For instance, the reaction of aroylisothiocyanates and diethyl acetylenedicarboxylate with 1,2-dialkyldiaziridines **1** (R^2 = H) in IL leads in one preparative step to the earlier unknown derivatives of unfused 1,2,4,6-tetrazepane-5-thiones **3** (see Ref. 6) and 1,2,3,6-tetrahydropyrimidine **4** (see Ref. 9), respectively. The reactions of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2** with carbon disulfide and activated nitriles in 1-butyl-3-methylimidazolium tetrafluoroborate or hexafluorophosphate ([bmim][BF_4] or [bmim]-[PF_6]) in the presence of a $BF_3 \cdot Et_2O$ catalyst (Scheme 1) proceed through the formation of azomethine imine intermediates **7** with their subsequent cycloaddition to dipolarophiles, leading to 3-(aryl)dihydro-5*H*-pyrazolo-[1,2-*c*][1,3,4]thiadiazole-1-thiones **5** and 1-aryl-6,7-dihydro-1*H*,5*H*-pyrazolo[1,2-*a*][1,2,4]triazoles **6**.[7,8,10]

Earlier,[11] azomethine imines **7**, generated similarly from 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2** in MeCN in the presence of Lewis acids ($Et_2O \cdot BF_3$ or $In(OTf)_3$) at 20 °C, were shown to undergo cycloaddition to *N*-arylmaleimides, which are active dipolarophiles with the *cis*-orientation of substituents at the double bond. Azomethine imines **7** can be generated thermally (110—140 °C)[12—15] and involved into reactions with other activated olefins. However, not all the dipolarophiles can be used at high temperature.

In the present work, we for the first time studied reactions of azomethine imines **7**, generated catalytically from 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2**, under mild conditions with such activated *trans*-olefins as 1,3-diphenylpropen-2-one (chalcone) **8** and β-nitrostyrenes **9**.

It turned out that 6-aryl-1,5-diazabicyclo[3.1.0]-hexanes **2** do not react with chalcone **8** in the presence of $BF_3 \cdot Et_2O$ in MeCN without heating. The same result was obtained in the attempted analogous reaction of

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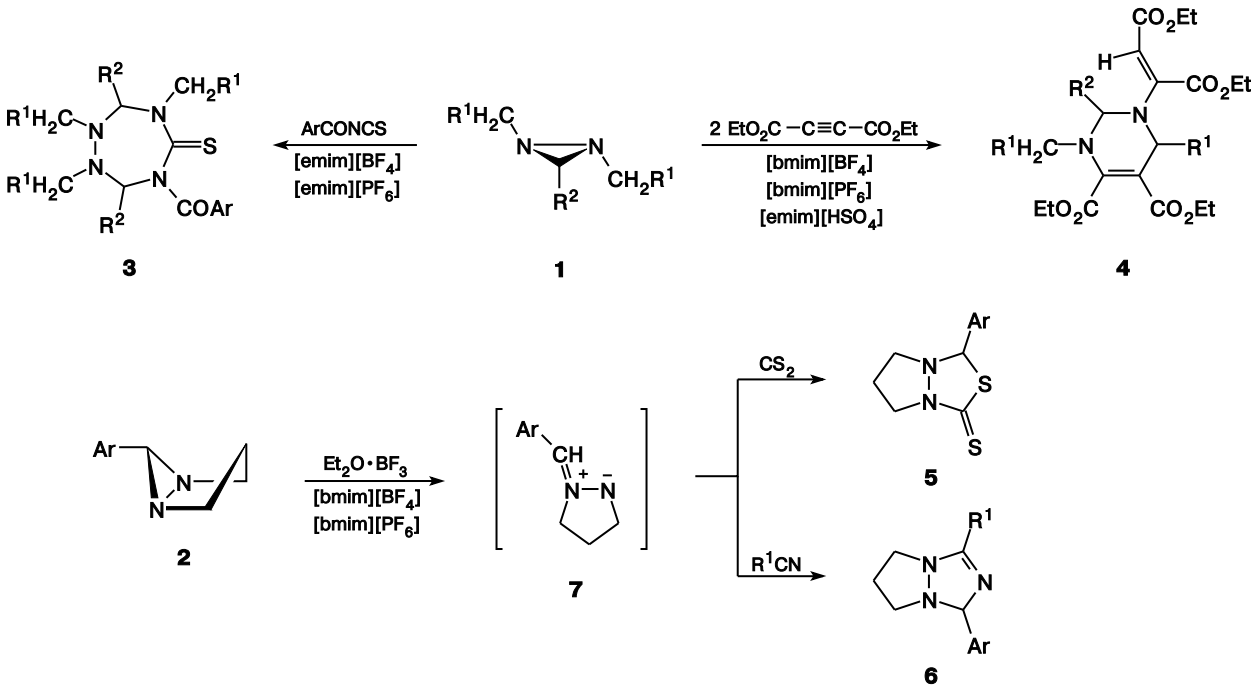
Scheme 1

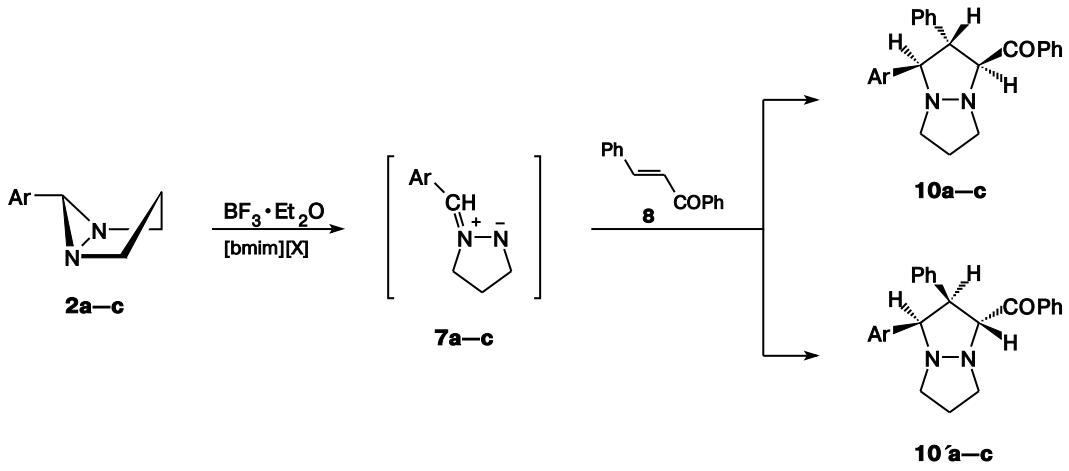


emim stands for 1-ethyl-3-methylimidazolium

β-nitrostyrenes **9**. Taking into account the data published earlier,[7,8,10] it could have been expected that the indicated reactions can be carried out changing MeCN for IL.

As the IL, [bmim][BF_4] and [bmim][PF_6] were used. It was found that 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2** do not give the reaction with chalcone **8** in the IL indicated in the presence of $Et_2O \cdot BF_3$ at 20—40 °C. However, when the temperature was elevated to 50 °C the reaction mixture turned its color from bright yellow to yellowish orange and formation of two products was observed (TLC monitoring, R_f ~0.2 and 0.4, with *n*-hexane—ethyl acetate (2 : 1) as an eluent). The rate of the reaction decreased in the order of compounds **2a** > **2b** > **2c**. The products isolated by column chromatography have proved diastereomers (3-aryl-2-phenyltetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazol-1-yl)(phenyl)methanones **10** and

Scheme 2



X = BF_4^-, PF_6^-; Ar = 4-$MeOC_6H_4$ (**a**), 4-$EtOC_6H_4$ (**b**), 4-$Pr^iOC_6H_4$ (**c**)

10´ with predominance of diastereomer **10**. Therefore, the reaction is diastereoselective and regiospecific to form products of the anti-Michael type (Scheme 2). As it is known,[16] regioselectivity of the reactions of electron-deficient alkenes with N-nucleophiles can either correspond to the regioselectivity of the Michael reaction[17,18], or differ from it depending on the structure of reacting compounds.

The structures of diastereomers **10** and **10´** were established by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy using the COSY, NOESY, {^{1}H—^{13}C} HMBC, {^{1}H—^{13}C} HSQC, and {^{1}H—^{15}N} HMBC procedures. It turned out that in diastereomers **10** (R_f ~0.2) substituents in the ring have the *trans-trans* orientation, whereas in diastereomers **10´** (R_f ~0.4), the *cis-trans*. The ratios of diastereomers **10** and **10´** and the time needed for the starting compounds **2a—c** to be completely converted are given in Table 1.

It is known[13—15] that activated *trans*-olefins react stereoselectively with azomethine imines **7** generated in common organic solvents at 110—140 °C to predominantly form the *trans-trans* adducts. In this case, a concerted cycloaddition is assumed. We think that the reaction of chalcone **8** with azomethine imines **7** in our case also occurs as a concerted process through the intermediate states **11** and **11´**, leading to the formation of diastereomers **10** and **10´** (Scheme 3). The regio- and stereoselectivity of the process observed can be apparently explained by the lower energies of the intermediate states **11** and **11´** (especially **11**), in which the anti-bonding spatial interactions are minimized.

Table 1. The ratio of diastereomers **10** and **10´** and the reaction time

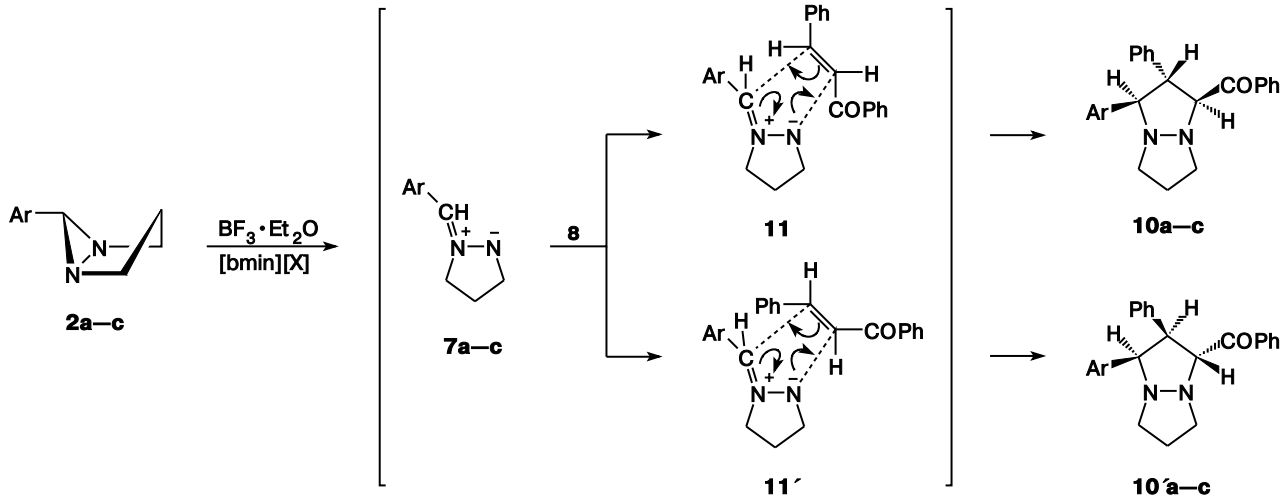
Starting compound **2**	Ratio **10** : **10´**	Reaction time/h
a	2.3 : 1	2
b	6.4 : 1	8
c	1.6 : 1	12

The method suggested for the generation of azomethine imine intermediates **7a—d** in IL was also used in the reactions of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **2a—d** with *trans*-β-nitrostyrenes **9a—c**. β-Nitrostyrene **9b** (Ar^2 = 3-$NO_2C_6H_4$) was studied first. In this case as well, the reaction between the reagents begins only at elevated temperature of 60 °C, and the reaction led to the formation of two cycloaddition products, one of which was soluble in IL, whereas another insoluble.

Compounds soluble in IL are the Michael cycloaddition products of β-nitrostyrene **9b** to azomethine imines **7a—d**, *viz.*, 1-aryl-2-nitro-3-(3-nitrophenyl)tetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazoles **12a—d**, in which substituents in the pyrazolidine ring have the *trans-trans* orientation. Compounds insoluble in IL unexpectedly have proved 5-aryl-6-(3-nitrophenyl)-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]pyrazolium salts **13a,b,d** containing BF_4^- or PF_6^- anions from the ionic liquids used (Scheme 4). The ratios of compounds obtained and the reaction times are given in Table 2.

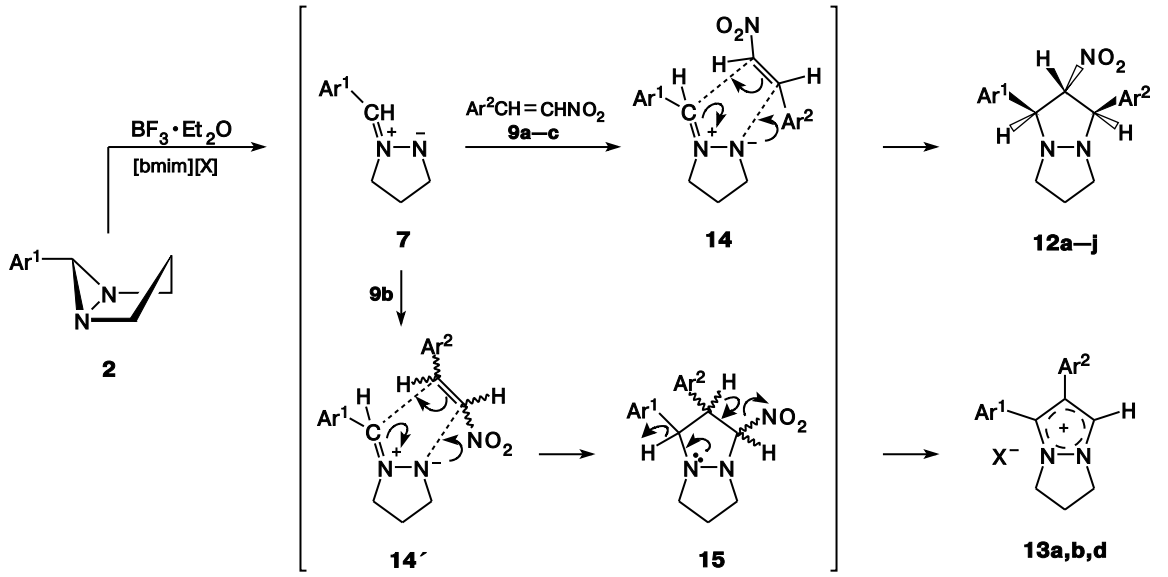
Unlike compound **9b**, β-nitrostyrenes **9a,c** containing no electron-withdrawing substituents in the aromatic ring react with azomethine imines **7a,b,d**, generated under the same conditions from bicyclic diaziridines **2a,b,d**, completely regio- and stereoselectively to form compounds **12e—j** alone. The structures of compounds **12** and **13**

Scheme 3



Ar = 4-$MeOC_6H_4$ (**a**), 4-$EtOC_6H_4$ (**b**), 4-$Pr^iOC_6H_4$ (**c**); X = BF_4^-, PF_6^-

Scheme 4



X = BF_4, PF_6; **9:** Ar^2 = Ph (**a**), 3-$NO_2C_6H_4$ (**b**), 3-MeC_6H_4 (**c**)

Compound	Ar^1	Ar^2	Compound	Ar^1	Ar^2	Compound	Ar^1	Ar^2	X
12a	4-$MeOC_6H_4$	3-$NO_2C_6H_4$	**12f**	4-$EtOC_6H_4$	Ph	**13a**	4-$MeOC_6H_4$	3-$NO_2C_6H_4$	BF_4
12b	4-$EtOC_6H_4$	3-$NO_2C_6H_4$	**12g**	4-MeC_6H_4	Ph	**13a´**	4-$MeOC_6H_4$	3-$NO_2C_6H_4$	PF_6
12c	4-$Pr^iOC_6H_4$	3-$NO_2C_6H_4$	**12h**	4-$MeOC_6H_4$	3-MeC_6H_4	**13b**	4-$EtOC_6H_4$	3-$NO_2C_6H_4$	BF_4
12d	4-MeC_6H_4	3-$NO_2C_6H_4$	**12i**	4-$EtOC_6H_4$	3-MeC_6H_4	**13d**	4-MeC_6H_4	3-$NO_2C_6H_4$	BF_4
12e	4-$MeOC_6H_4$	Ph	**12j**	4-MeC_6H_4	3-MeC_6H_4				

Table 2. The ratio of compounds **12** and **13** obtained by the reaction of β-nitrostyrene **9b** with azomethine imines **7a—d**

Starting compound **7**	Ratio **12** : **13**	Reaction time/h
a	0.3 : 1	3 (7*)
b	2.8 : 1	5
c	1.0 : 0	3
d	1.6 : 1	4**

* The reaction was carried out in [bmim][PF_6].

** The reaction takes place similarly either in the presence or in the absence of a $Et_2O \cdot BF_3$ catalyst.

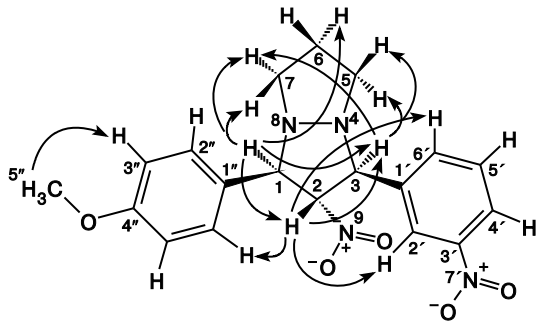


Fig. 1. Principal interactions of protons in the molecule of **12a** found using the NOESY method.

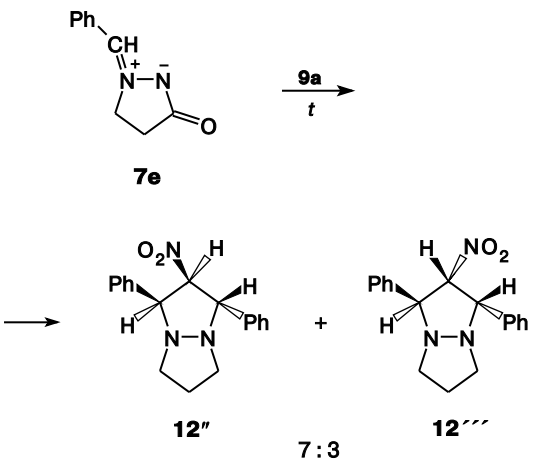
obtained were confirmed by a combination of the IR, mass, and ^1H, ^{13}C, and ^{15}N NMR spectroscopic (using the COSY, NOESY (Fig. 1), $^1H—^{13}C$ HMBC, $^1H—^{13}C$ HSQC, and $^1H—^{15}N$ HMBC procedures) data, and the structure of compound **13a** was additionally confirmed by X-ray diffraction.[19]

The stereospecificity of formation of compounds **12** allows us to suggest a concerted mechanism through the intermediate state **14**. Compounds **13** were apparently formed by the anti-Michael addition of the intermediates **7a,b,d** to β-nitrostyrene **9b** through the intermediate state **14´** with subsequent aromatization of adducts **15** through the elimination of HNO_2 and a hydride ion. By all accounts, the air oxygen was an oxidant (see Scheme 4).

Interestingly that according to the data in the work,[20] addition of β-nitrostyrene **9a** to azomethine imine **7e** in organic solvent has different stereochemistry. In this case, stereoisomers with *cis-trans* and *trans-cis* orientation of substituents in the pyrazolidine ring **12″** and **12´´´** in the ratio 7 : 3 are the reaction products (Scheme 5).

In conclusion, an approach suggested by us includes the use of IL as the reaction medium in the study of the diaziridine ring expansion reaction in 6-aryl-1,5-diazabicyclo[3.1.0]hexanes during their reactions with activated

Scheme 5



olefins and considerably complements already known[21–23] methods for the synthesis of tetrahydro-1*H*,5*H*-pyrazolo-[1,2-*a*]pyrazole derivatives, whose structural analogs exhibit various physiological activity. Compounds of the type **12** are potential inhibitors of NO-synthase[24] and can be efficient in the malfunction of immunity.[25] Compounds of the type **13** are of interest as highly conducting organic plastic crystals[23], they are also patented as active herbicides, fungicides, and antibacterial agents.[26,27]

Experimental

IR spectra were recorded on a UR-20 spectrometer in KBr pellets or for neat samples. ^{1}H, ^{13}C, and ^{15}N NMR spectra were recorded on a Bruker AV-600 spectrometer (600.13, 150.90, and 60.81 MHz, respectively) for compounds **10, 10´**, and **12**

Table 3. The yields and some physico-chemical characteristics of compounds isolated

Compound	Yield (%)	M.p./°C	R_f*	Found / Calculated (%)			Molecular formula
				C	H	N	
10a	58	—	0.18	78.35 78.36	6.60 6.58	7.03 7.03	$C_{26}H_{26}N_2O_2$
10´a	25	144.0—144.5	0.36	78.32 78.36	6.61 6.58	7.02 7.03	$C_{26}H_{26}N_2O_2$
10b	64	89.0—98.0 (decomp.)	0.16	78.64 78.61	6.81 6.84	6.77 6.79	$C_{27}H_{28}N_2O_2$
10c	47	74.0—86.5 (decomp.)	0.17	78.85 78.84	7.14 7.09	6.56 6.57	$C_{28}H_{30}N_2O_2$
10´c	29	—	0.42	78.83 78.84	7.11 7.09	6.54 6.57	$C_{28}H_{30}N_2O_2$
12a	75	Oil	0.56	67.25 67.24	6.21 6.24	12.36 12.38	$C_{19}H_{21}N_3O_3$
12b	78	101.0—101.5	0.58	67.94 67.97	6.58 6.56	11.84 11.89	$C_{20}H_{23}N_3O_3$
12c	72	Oil	0.54	70.55 70.57	6.61 6.55	12.96 12.99	$C_{19}H_{21}N_3O_2$
12d	20	110.0—110.5 (decomp.)	0.58	59.32 59.37	5.29 5.24	14.57 14.58	$C_{19}H_{20}N_4O_5$
12e	52	140.0—140.5 (decomp.)	0.60	60.24 60.29	5.59 5.57	14.05 14.06	$C_{20}H_{22}N_4O_5$
12f	76	90.0—90.5 (decomp.)	0.60	61.13 61.15	5.90 5.87	13.55 13.58	$C_{21}H_{24}N_4O_5$
12g	55	104.5—105.0 (decomp.)	0.57	61.92 61.95	5.50 5.47	15.24 15.21	$C_{19}H_{20}N_4O_4$
12h	73	—	0.46	65.03 65.03	6.31 6.28	11.34 11.37	$C_{20}H_{23}N_3O_4$
12i	76	—	0.47	65.75 65.78	6.59 6.57	10.98 10.96	$C_{21}H_{25}N_3O_4$
12j	65	84.0—84.5	0.46	67.92 67.97	6.60 6.56	11.92 11.89	$C_{20}H_{23}N_3O_3$
13a	65	195.5—196.0	—	53.90 53.93	4.32 4.29	9.90 9.93	$C_{19}H_{18}BF_4N_3O_3$
13a´	65	216.0—216.5	—	47.44 47.41	3.75 3.77	8.71 8.73	$C_{19}H_{18}PF_6N_3O_3$
13b	20	194.5—195.0	—	54.95 54.94	4.62 4.61	9.63 9.61	$C_{20}H_{20}BF_4N_3O_3$
13d	35	212.5—213.0	—	56.00 56.05	4.51 4.46	10.38 10.32	$C_{19}H_{18}BF_4N_3O_2$

* Hexane—ethyl acetate (2 : 1, v/v) was used as an eluent, visualization was made with diphenylamine and under the UV light.

Table 4. The IR and mass spectral data of compounds isolated

Compound	IR, ν/cm^{-1}	MS, m/z (I_{rel} (%))
10´a	640, 688, 708, 700, 736, 836, 1028, 1084, 1164, 1248, 1292, 1388, 1448, 1512, 1584, 1608, 1668, 2836, 2868, 2887, 3028, 3060	398 [M] (5), 207 [chalcone] (24), 189 [diaziridine] (32), 159 [diaziridine — MeO] (29), 121 [$MeOC_6H_4CH$ + H] (93), 105 [PhCO] (52), 91 [C_6H_4O] (17), 77 [Ph] (100), 70 [pyrazolidine] (4)
10c	620, 660, 700, 840, 952, 1020, 1108, 1120, 1256, 1300, 1332, 1376, 1448, 1464, 1488, 1508, 1576, 1600, 1668, 1732, 2856, 2928, 2980, 3012, 3032, 3064	—
10´c	616, 660, 696, 840, 952, 1000, 1036, 1020, 1036, 1108, 1120, 1256, 1300, 1332, 1376, 1384, 1448, 1508, 1576, 1600, 1664, 2856, 2928, 2980, 3012, 3032, 3064	—
12b	668, 772, 1044, 1188, 1248, 1264, 1300, 1396, 1496, 1612, 1652, 1684, 2884, 2932, 2980, 3132	—
12c	668, 700, 812, 840, 1044, 1160, 1232, 1288, 1356, 1456, 1552, 1616, 1684, 1740, 2852, 2924, 2960, 3028	174 [$CH_3C_6H_4CHN_2(CH_2)_3$] (25), 160 [M − $CH_3C_6H_4CH$ − − NO_2CH] (6), 149 [$C_6H_5(CH)_2NO_2$] (5), 111 [M − $C_6H_4CH_3$ − − NO_2 − C_6H_5] (7), 105 [$CH_3C_6H_4CH$] (100), 91 [$CH_3C_6H_4$] (45), 77 [Ph] (40), 69 [$N_2(CH_2)_3$ + H] (45), 43 [$(CH_2)_3$ − H] (60)
12d	—	384 [M] (7), 308 [M − NO_2 − Me] (38), 277 [M − $MeOC_6H_4$] (12), 190 [$MeOC_6H_4CHN_2(CH_2)_3$] (40), 194 [$NO_2C_6H_4(CH)_2NO_2$] (24), 88 [C_6H_4C] (100), 76 [C_6H_4] (54)
12e	644, 688, 740, 808, 828, 916, 1036, 1180, 1252, 1344, 1456, 1488, 1524, 1608, 1652, 1684, 2856, 2924, 2980, 3080	398 [M] (4), 322 [M − C_6H_4, M − NO_2 − Et] (45), 264 [M − 2 NO_2 − EtO] (7), 231 [M − EtO − C_6H_4 − NO_2] (10), 204 [$EtOC_6H_4CHN_2(CH_2)_3$] (45), 194 [$NO_2C_6H_4(CH)_2NO_2$] (38), 89 [C_6H_4CH] (100), 76 [C_6H_4] (67)
12g	646, 688, 745, 830, 914, 1040, 1182, 1253, 1348, 1486, 1524, 1606, 1680, 2862, 2934, 2978, 3074	—
12i	624, 668, 696, 792, 832, 924, 1048, 1116, 1156, 1176, 1248, 1288, 1304, 1364, 1392, 1456, 1464, 1488, 1512, 1548, 1584, 1612, 1684, 2836, 2888, 2928, 2980, 3064	—
13a	688, 736, 1084, 1188, 1252, 1307, 1344, 1448, 1520, 1612, 2856, 2952, 3074, 3152	377 [M − NO_2] (10), 324 [M − BF_4 − CH_3] (12), 308 [M − BF_4 − − MeO] (23), 295 [M − BF_4 − NO_2] (7), 278 [M − BF_4 − NO_2 − CH_3] (8), 190 [$MeOC_6H_4CHN_2(CH_2)_3$] (17), 121 [$C_6H_4NO_2$] (7), 76 [C_6H_4] (35), 41 [$(CH_2)_3$ − H] (100)
13´a	688, 736, 820, 1188, 1256, 1300, 1344, 1448, 1520, 1612, 2888, 2952, 3088, 3136	—
13b	688, 738, 840, 1076, 1190, 1250, 1305, 1346, 1442, 1522, 1614, 2876, 2964, 3080, 3146	—
13d	688, 748, 834, 852, 1052, 1192, 1348, 1524, 1552, 1580, 1616, 2984, 3072, 3092, 3144	—

in $CDCl_3$ and for compounds **13** in DMSO-d_6. Nitromethane ($\delta_{^{15}N}$ = 0.0) was used as an external standard for recording ^{15}N NMR spectra. Assignment of signals in the NMR spectra was performed using {^{1}H—^{1}H}gNOESY, {^{1}H—^{13}C}HMBC, {^{1}H—^{15}N}HMBC, and {^{1}H—^{13}C}HSQC techniques. All the 2D-spectra were recorded using standard procedures (Bruker) with the *Z*-gradient at 30 °C. Melting points were determined on a Gallenkamp apparatus (Sanyo). Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument. Reaction progress was monitored by TLC on Silufol UV-254 plates. The R_f values were determined in the *n*-hexane—ethyl acetate (2 : 1, v/v) system. Yields and some physico-chemical characteristics of reaction products isolated are given in Table 3, the IR spectroscopic and mass spectrometric data, in Table 4, NMR spectroscopic data, in Table 5.

Synthesis of (3-aryl-2-phenyltetrahydro-1*H*,5*H*-pyrazolo-[1,2-*a*]pyrazol-1-yl)(phenyl)methanones 10 and 10´ (general procedure). Boron trifluoride diethyl etherate (2 drops, 0.1 mmol) was added to a mixture of 6-aryl-1,5-diazabicyclo[3.1.0]hexane **2a—c** (0.5 mmol) and 1,3-diphenylpropen-2-one (chalcone) **8** (0.1 g, 0.5 mmol) in IL ([bmim][BF_4] or [bmim][PF_6]) (0.4 g) with stirring, and the mixture was heated to 50 °C and stirred

Table 5. The NMR spectral data of compounds isolated

Compound	NMR ($CDCl_3$), δ (*J*/Hz)	
	^1H	^{13}C
10a	2.08, 2.37 (both m, 2 H, $NCH_2C\underline{H}_2$, ^3J = 9.60, Δν = 58 Hz); 2.63, 2.91 (both m, 2 H, 4-$MeOC_6H_4CHNC\underline{H}_2$, ^3J = 9.60, Δν = 56 Hz); 3.24 (m, 2 H, $PhCOCHNC\underline{H}_2$, ^3J = 7.41); 3.89 (s, 3 H, OCH_3); 4.34 (d, 1 H, 4-$MeOC_6H_4C\underline{H}$, ^3J = 5.92); 4.36 (t, 1 H, $PhC\underline{H}$, ^3J = 5.92, ^3J = 7.41); 4.51 (d, 1 H, $PhCOC\underline{H}$, ^3J = 7.41); 6.76, 7.32 (both d, 4 H, 4-$MeOC_6\underline{H}_4$, ^3J = 6.67); 6.79, 7.22, 7.42 (t, t, d, 5 H, Ph, ^3J = 7.50); 6.89, 7.22, 7.42 (t, t, d, 5 H, PhCO, ^3J = 9.00)	50.59 ($NCH_2\underline{C}H_2$); 50.95 (4-$MeOC_6H_4CHN\underline{C}H_2$); 55.03 ($C_6H_4O\underline{C}H_3$); 59.77 ($PhCOCHN\underline{C}H_2$); 68.91 ($Ph\underline{C}H$); 71.48 (4-$MeOC_6H_4\underline{C}H$); 71.57 ($PhCO\underline{C}H$); 113.82, 127.21, 128.16, 128.48, 128.66, 133.16, 133.83, 136.44, 142.36 (Ar); 158.83 (CO)
10´a	2.26, 2.29 (both m, 2 H, $NCH_2C\underline{H}_2$, ^3J = 5.25, Δν = 15 Hz); 2.53, 2.61 (q, m, 2 H, 4-$MeOC_6H_4CHNC\underline{H}_2$, ^3J = 9.25, Δν = 40 Hz); 2.92, 3.06 (both qd, 2 H, $PhCOCHNC\underline{H}_2$, ^3J = 7.00, ^2J = 3.50, Δν = 70 Hz); 3.65 (s, 3 H, OMe); 4.31 (d, 1 H, 4-$MeOC_6H_4C\underline{H}$, ^3J = 10.87); 4.77 (t, 1 H, $PhC\underline{H}$, ^3J = 10.87, ^3J = 9.54); 5.08 (d, 1 H, $PhCOC\underline{H}$, ^3J = 9.54); 6.56, 7.12 (both d, 4 H, 4-$MeOC_6\underline{H}_4$, ^3J = 8.50); 6.87, 7.31, 7.51 (t, t, d, 5 H, Ph, ^3J = 7.50); 7.22, 7.47, 7.96 (t, d, t, 5 H, PhCO, ^3J = 10.00)	47.39 ($NCH_2\underline{C}H_2$, 4-$MeOC_6H_4CHN\underline{C}H_2$); 48.39 ($PhCOCHN\underline{C}H_2$); 55.13 ($C_6H_4O\underline{C}H_3$); 67.27 (4-$MeOC_6H_4\underline{C}H$, $Ph\underline{C}H$); 69.20 ($PhCO\underline{C}H$); 113.24, 114.14, 127.51, 127.84, 128.09, 128.22, 128.57, 129.77, 130.35, 132.51, 138.04 (Ar); 159.00 (CO)
10b	1.31 (t, 3 H, $C\underline{H}_3CH_2O$, ^3J = 8.95); 1.94, 2.22 (both br.m, 2 H, $NCH_2C\underline{H}_2$, ^3J = 7.16, ^2J = 4.48, Δν = 166 Hz); 3.05, 3.12 (dt, 2 H, 4-$EtOC_6H_4CHNC\underline{H}_2$, ^3J = 8.95, Δν = 42 Hz); 3.17 (m, 2 H, $PhCOCHNC\underline{H}_2$, ^3J = 8.95, ^2J = 6.25); 3.92 (q, 2 H, $CH_3C\underline{H}_2O$, ^3J = 8.95); 4.23 (d, 1 H, 4-$EtOC_6H_4C\underline{H}$, ^3J = 8.95); 4.25 (t, 1 H, $PhC\underline{H}$, ^3J = 8.95); 4.37 (d, 1 H, $PhCOC\underline{H}$, ^3J = 8.95); 6.76, 7.26 (both d, 4 H, 4-$EtOC_6\underline{H}_4$, ^3J = 8.95); 7.11, 7.19, 7.37 (t, t, d, 5 H, Ph, ^3J = 8.95); 7.13, 7.19, 7.38 (t, t, d, 5 H, PhCO, ^3J = 8.95)	50.66 ($NCH_2\underline{C}H_2$); 51.02 (4-$EtOC_6H_4CHN\underline{C}H_2$); 59.86 ($PhCOCHN\underline{C}H_2$); 63.32 ($C_6H_4O\underline{C}H_2$); 68.91 ($Ph\underline{C}H$); 71.66 (4-$EtOC_6H_4\underline{C}H$, $PhCO\underline{C}H$); 114.54, 127.25, 128.20, 128.53, 128.72, 133.16, 133.72, 136.61, 142.41 (Ar); 158.28 (CO)
10c	1.28 (t, 6 H, $(C\underline{H}_3)_2CHO$, ^3J = 8.90); 2.02, 2.29 (both br.m, 2 H, $NCH_2C\underline{H}_2$, ^3J = 7.20, ^2J = 4.55, Δν = 162 Hz); 3.12, 3.17 (dt, 2 H, 4-$Pr^iOC_6H_4CHNC\underline{H}_2$, ^3J = 8.90, Δν = 30 Hz); 3.23 (m, 2 H, $PhCOCHNC\underline{H}_2$, ^3J = 8.90); 4.27 (d, 1 H, 4-$Pr^iOC_6H_4C\underline{H}$, ^3J = 8.90); 4.28 (t, 1 H, $PhC\underline{H}$, ^3J = 8.90); 4.44 (d, 1 H, $PhCOC\underline{H}$, ^3J = 8.90); 4.48 (m, 1 H, $(CH_3)_2C\underline{H}O$, ^3J = 8.90); 6.78, 7.28 (both d, 4 H, 4-$Pr^iOC_6\underline{H}_4$, ^3J = 8.90); 7.13, 7.22, 7.29 (t, t, d, 5 H, Ph, ^3J = 8.90); 7.13, 7.37, 7.45 (t, t, d, 5 H, PhCO, ^3J = 8.90)	22.05 ($(\underline{C}H_3)_2CHO$), 50.84 ($NCH_2\underline{C}H_2$, 4-$Pr^iOC_6H_4CHN\underline{C}H_2$); 51.15 ($PhCOCHN\underline{C}H_2$); 69.12 ($Ph\underline{C}H$, 4-$Pr^iOC_6H_4\underline{C}H$); 69.94 ($C_6H_4O\underline{C}H(CH_3)_2$); 71.71 ($PhCO\underline{C}H$); 116.14, 127.45, 128.36, 128.55, 128.72, 128.94, 133.37, 133.92, 136.82, 142.76 (Ar); 157.38 (CO)
10´c	1.32 (d, 6 H, $(C\underline{H}_3)_2CHO$, ^3J = 6.34); 2.28 (m, 2 H, $NCH_2C\underline{H}_2$, ^3J = 4.44); 2.69 (m, 2 H, 4-$Pr^iOC_6H_4CHNC\underline{H}_2$, ^3J = 7.62, ^2J = 2.54); 2.91, 3.07 (both qd, 2 H, $PhCOCHNC\underline{H}_2$, ^3J = 4.44, ^2J = 1.90, Δν = 32 Hz); 4.38 (d, 1 H, 4-$Pr^iOC_6H_4C\underline{H}$, ^3J = 7.62); 4.49 (m, 1 H, $OC\underline{H}(CH_3)_2$, ^3J = 6.34); 4.78 (t, 1 H, $PhC\underline{H}$, ^3J = 7.62, ^3J = 9.52); 5.06 (d, 1 H, $PhCOC\underline{H}$, ^3J = 9.52); 6.53, 7.09 (both d, 4 H, 4-$Pr^iOC_6\underline{H}_4$, ^3J = 7.62); 6.87, 7.31, 7.51 (t, t, d, 5 H, Ph, ^3J = 7.62); 7.25, 7.48, 7.95 (t, d, t, 5 H, PhCO, ^3J = 9.54)	21.96 ($(\underline{C}H_3)_2CHO$); 47.46 ($NCH_2\underline{C}H_2$, 4-$Pr^iOC_6H_4CHN\underline{C}H_2$); 48.42, ($PhCOCHN\underline{C}H_2$); 62.32 ($(CH_3)_2\underline{C}HO$); 67.12 (4-$Pr^iOC_6H_4\underline{C}H$, $Ph\underline{C}H$); 69.20 ($PhCO\underline{C}H$); 115.35, 127.47, 127.81, 127.99, 128.16, 128.36, 128.53, 129.72, 130.27, 132.40, 138.01 (Ar); 157.23 (CO)
12a	2.14, 2.40 (both m, 2 H, $CH_2C\underline{H}_2CH_2$, ^3J = 5.87, Δν = 77.03 Hz); 3.25 (m, 4 H, $NC\underline{H}_2$, ^3J = 5.87); 3.81 (s, 3 H, $C_6H_4OC\underline{H}_3$); 4.68 (d, 1 H, $MeOC_6H_4C\underline{H}$, ^3J = 5.87); 4.77 (d, 1 H, $ArC\underline{H}$, ^3J = 5.87); 5.06 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.87); 6.90, 7.38 (both d, 4 H, $MeOC_6\underline{H}_4$, ^3J = 8.80); 7.35, 7.50 (both m, 5 H, Ph, ^3J = 7.34)	23.99 ($NCH_2\underline{C}H_2$); 50.74 ($CH_3ArCN\underline{C}H_2$); 51.13 ($ArCHN\underline{C}H_2$); 55.32 ($\underline{C}H_3OC_6H_4$); 71.76 ($CH_3OC_6H_4\underline{C}$); 71.87 ($Ph\underline{C}H$); 103.51 ($NO_2\underline{C}H$); 114.36, 127.20, 131.15, 159.63 ($CH_3O\underline{C}_6H_4$); 128.20, 128.55, 128.96, 139.82 (Ph)
12b	1.42 (t, 3 H, $C\underline{H}_3CH_2O$, ^3J = 6.83); 2.13, 2.37 (both m, 2 H, $CH_2C\underline{H}_2CH_2$, Δν = 48.84 Hz); 3.27 (m, 4 H, $NC\underline{H}_2$); 4.35 (q, 2 H, $CH_3C\underline{H}_2O$, ^3J = 7.32); 4.68 (d, 1 H, $EtOC_6H_4C\underline{H}$, ^3J = 6.35); 4.77 (d, 1 H, $PhC\underline{H}$, ^3J = 5.37); 5.07 (t, 1 H, $NO_2C\underline{H}$, ^3J = 6.35); 6.90, 7.37 (both d, 4 H, $EtOC_6\underline{H}_4$, ^3J = 8.3); 7.37, 7.52 (both m, 5 H, Ph, ^3J = 6.35)	14.84 ($\underline{C}H_3CH_2OAr$); 23.97 ($NCH_2\underline{C}H_2$); 50.71 ($CH_3OC_6H_4CN\underline{C}H_2$); 51.13 ($PhCN\underline{C}H_2$); 63.50 ($CH_3\underline{C}H_2OC_6H_4$); 71.78 ($CH_3OC_6H_4\underline{C}H$); 71.86 ($Ar\underline{C}H$); 103.53 ($NO_2\underline{C}H$); 114.89, 127.22, 130.94, 158.92 ($EtO\underline{C}_6H_4$); 128.20, 128.55, 128.97, 139.87 (Ph)

(*to be continued*)

Table 5 (*continued*)

Compound	NMR ($CDCl_3$), δ (*J*/Hz)	
	^1H	^{13}C
12c	2.16, 2.38 (both m, 2 H, $CH_2C\underline{H}_2CH_2$, Δν = 41.42 Hz); 2.36 (s, 3 H, $C\underline{H}_3C_6H_4$); 3.24, 3.34 (both m, 4 H, $NC\underline{H}_2$, ^3J = 5.38, Δν = 20.02 Hz); 4.71 (d, 1 H, $MeC_6H_4C\underline{H}$, ^3J = 6.35); 4.77 (d, 1 H, $PhC\underline{H}$, ^3J = 5.86); 5.08 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.86); 7.19, 7.37 (both d, 4 H, $MeC_6\underline{H}_4$, ^3J = 7.81); 7.37, 7.50 (both m, 5 H, Ph)	21.19 ($\underline{C}H_3C_6H_4$); 23.97 ($NCH_2\underline{C}H_2$); 50.84 ($CH_3C_6H_4CHN\underline{C}H_2$); 51.10 ($PhCHN\underline{C}H_2$); 71.94 ($CH_3C_6H_4\underline{C}H$ и $Ph\underline{C}H$); 103.44 ($NO_2\underline{C}H$); 127.25, 129.64, 136.13, 138.14 ($CH_3\underline{C}_6H_4$); 127.25, 128.26, 128.97, 139.66 (Ph)
12d[a]	2.13, 2.41 (both m, 2 H, $CH_2C\underline{H}_2CH_2$); 3.08, 3.27 (both m, 2 H, $MeOC_6H_4CNC\underline{H}_2$, ^2J = 10.0, ^3J = 4.8); 3.28, 3.40 (m, td, 2 H, $NO_2ArCNC\underline{H}_2$, ^2J = 10.1, ^3J = 4.8); 3.78 (s, 3 H, $C\underline{H}_3OC_6H_4$); 4.67 (d, 1 H, $MeOC_6H_4C\underline{H}$, ^3J = 6.8); 4.92 (d, 1 H, $NO_2C_6H_4C\underline{H}$, ^3J = 5.2); 4.98 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.8); 6.87, 7.33 (both d, 4 H, $MeOC_6\underline{H}_4$, ^3J = 8.4); 7.55 (t, 1 H, C(5)H in $NO_2C_6\underline{H}_4$, ^3J = 8.0); 7.83 (d, 1 H, C(4)H in $NO_2C_6H_4$, ^3J = 8.0); 8.16 (d, 1 H, C(6)H in $NO_2C_6H_4$, ^3J = 8.0); 8.45 (s, 1 H, C(2)H in $NO_2C_6H_4$)	23.90 ($NCH_2\underline{C}H_2$); 50.23 ($CH_3OC_6H_4CHN\underline{C}H_2$); 51.26 ($NO_2C_6H_4CHN\underline{C}H_2$); 55.22 ($\underline{C}H_3OC_6H_4$); 70.43 ($NO_2C_6H_4\underline{C}H$); 71.53 ($CH_3OAr\underline{C}H$); 102.79 ($NO_2\underline{C}H$); 114.36, 128.57, 129.70, 159.82 ($CH_3O\underline{C}_6H_4$), 122.21, 122.95, 129.84, 133.10, 142.72, 148.65 ($NO_2\underline{C}_6H_4$)
12e[b]	1.40 (t, 3 H, $C\underline{H}_3CH_2O$); 2.17, 2.41 (both m, 2 H, $CH_2C\underline{H}_2CH_2$); 3.07, 3.28 (td, m, 2 H, $EtOC_6H_4CNC\underline{H}_2$, ^2J = 9.6, ^3J = 4.6); 3.28, 3.40 (m, td, 2 H, $NO_2C_6H_4CNC\underline{H}_2$, ^2J = 9.8, ^3J = 4.7); 4.02 (q, 2 H, $CH_3C\underline{H}_2O$); 4.66 (d, 1 H, $EtOC_6H_4C\underline{H}$, ^3J = 6.8); 4.91 (d, 1 H, $NO_2C_6H_4C\underline{H}$, ^3J = 5.0); 4.98 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.7); 6.87, 7.31 (both d, 4 H, $EtOC_6\underline{H}_4$, ^3J = 8.5); 7.56 (t, 1 H, C(5)H in $NO_2C_6H_4$, ^3J = 8.0); 7.84 (d, 1 H, C(4)H in $NO_2C_6H_4$, ^3J = 8.0); 8.17 (d, 1 H, C(6)H in $NO_2C_6H_4$, ^3J = 8.0); 8.45 (s, 1 H, C(2)H in $NO_2C_6H_4$)	22.10 ($\underline{C}H_3CH_2OC_6H_4$); 23.93 ($NCH_2\underline{C}H_2$); 50.23 ($EtOC_6H_4CHN\underline{C}H_2$); 51.28 ($NO_2C_6H_4CHN\underline{C}H_2$); 63.47 ($CH_3\underline{C}H_2OC_6H_4$); 70.48 ($NO_2C_6H_4\underline{C}H$); 71.58 ($EtOC_6H_4\underline{C}H$); 102.85 ($NO_2\underline{C}H$); 114.70, 128.36, 129.53, 159.21 ($EtO\underline{C}_6H_4$); 122.23, 122.95, 129.84, 133.09, 142.78, 148.69 ($NO_2\underline{C}_6H_4$)
12f[c]	1.30 (d, 6 H, $(C\underline{H}_3)_2CHO$); 2.15, 2.40 (both m, 2 H, $CH_2C\underline{H}_2CH_2$); 3.08, 3.28 (td, m, 2 H, $Pr^iOC_6H_4CNC\underline{H}_2$, ^2J = 9.8, ^3J = 5.6); 3.28, 3.39 (m, td, 2 H, $NO_2C_6H_4CNC\underline{H}_2$, ^2J = 9.8, ^3J = 4.8); 4.51 (m, 1 H, $(CH_3)_2C\underline{H}O$, ^3J = 6.1); 4.66 (d, 1 H, $Pr^iOC_6H_4C\underline{H}$, ^3J = 6.8); 4.90 (d, 1 H, $NO_2C_6H_4C\underline{H}$, ^3J = 5.2); 4.98 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.0); 6.84, 7.28 (both d, 4 H in $Pr^iOC_6\underline{H}_4$, ^3J = 8.5); 7.55 (t, 1 H, C(5)H in $NO_2C_6H_4$, ^3J = 8.0); 7.84 (d, 1 H, C(4)H in $NO_2C_6H_4$, ^3J = 8.0); 8.15 (d, 1 H, C(6)H in $NO_2C_6H_4$, ^3J = 8.0); 8.44 (s, 1 H, C(2)H in $NO_2C_6H_4$)	21.90 ($(\underline{C}H_3)_2CHOC_6H_4$); 23.89 ($NCH_2\underline{C}H_2$); 50.23 ($Pr^iOC_6H_4CHN\underline{C}H_2$); 51.23 ($NO_2C_6H_4CHN\underline{C}H_2$); 69.86 ($(CH_3)_2\underline{C}HOC_6H_4$); 70.44 ($NO_2Ar\underline{C}H$); 71.53 ($Pr^iOAr\underline{C}H$); 102.79 ($NO_2\underline{C}H$); 116.14, 128.56, 129.40, 158.16 ($Pr^iO\underline{C}_6H_4$); 122.20, 122.92, 129.82, 133.11, 142.76, 148.63 ($NO_2\underline{C}_6H_4$)
12g[d]	2.18, 2.42 (both m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.34 (s, 3 H, $ArC\underline{H}_3$), 3.10, 3.28 (td, m, 2 H, $MeC_6H_4CNC\underline{H}_2$, ^2J = 9.8, ^3J = 4.7); 3.29, 3.41 (m, td, 2 H, $NO_2C_6H_4CNC\underline{H}_2$, ^2J = 9.9, ^3J = 4.8); 4.70 (d, 1 H, $MeC_6H_4C\underline{H}$, ^3J = 6.7); 4.91 (d, 1 H, $NO_2C_6H_4C\underline{H}$, ^3J = 5.0); 5.00 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.8); 7.17, 7.29 (both d, 4 H, H in $MeC_6\underline{H}_4$, ^3J = 7.8); 7.55 (t, 1 H, C(5)H in $NO_2C_6H_4$, ^3J = 8.0); 7.84 (d, 1 H, C(4)H in $NO_2C_6H_4$, ^3J = 8.0); 8.18 (d, 1 H, C(6)H in $NO_2C_6H_4$, ^3J = 8.0); 8.46 (s, 1 H, C(2)H in $NO_2C_6H_4$)	20.95 ($CH_3C_6H_4$); 23.96 ($NCH_2\underline{C}H_2$); 50.36 ($CH_3C_6H_4CHN\underline{C}H_2$); 51.27 ($NO_2C_6H_4CHN\underline{C}H_2$); 70.60 ($NO_2C_6H_4\underline{C}H$); 71.75 ($CH_3C_6H_4\underline{C}H$); 102.86 ($NO_2\underline{C}H$); 127.27, 129.68, 134.78, 138.42 ($CH_3\underline{C}_6H_4$); 122.28, 123.02, 129.86, 133.12, 142.56, 148.63 ($NO_2\underline{C}_6H_4$)
12h	2.12, 2.39 (both m, 2 H, $NCH_2C\underline{H}_2$, ^2J = 8.81, ^3J = 3.67, Δν = 76 Hz); 3.15, 3.27 (both m, 2 H, 4-$MeOC_6H_4CHNC\underline{H}_2$, ^2J = 10.43, ^3J = 4.91, Δν = 36 Hz); 3.33 (both m, 2 H, 3-$MeOC_6H_4CHNC\underline{H}_2$, ^2J = 9.89 Hz, ^3J = 6.14); 3.80 (s, 3 H, 4-$C\underline{H}_3OC_6H_4$); 3.81 (s, 3 H, 3-$C\underline{H}_3OC_6H_4$); 4.66 (d, 1 H, 4-$MeOC_6H_4C\underline{H}$, ^3J = 5.52); 4.74 (d, 1 H, 3-$MeOC_6H_4C\underline{H}$, ^3J = 6.75); 5.05 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.52, ^3J = 6.75); 6.90, 7.39 (both d, 4 H, 4-$MeOC_6\underline{H}_4$, ^3J = 8.14); 6.85, 7.05, 7.09, 7.28 (d, d, s, t, 4 H, 3-$MeOC_6\underline{H}_4$, ^3J = 7.32)	23.98 ($NCH_2\underline{C}H_2$); 50.72 (4-$MeOC_6H_4CHN\underline{C}H_2$); 51.16 (3-$MeOC_6H_4CHN\underline{C}H_2$); 55.25 (4-$\underline{C}H_3OC_6H_4$); 55.30 (3-$\underline{C}H_3OC_6H_4$); 71.74 (4-$MeOC_6H_4\underline{C}H$, 3-$MeOC_6H_4\underline{C}H$); 103.40 ($NO_2\underline{C}H$); 112.72, 113.66, 119.44, 129.97, 141.44, 159.67 (3-$MeO\underline{C}_6H_4$); 114.33, 128.54, 131.09, 160.11 (4-$MeO\underline{C}_6H_4$)
12i	1.38 (t, 3 H, $C\underline{H}_3CH_2O$, ^3J = 6.16); 2.12, 2.36 (both m, 2 H, $NCH_2C\underline{H}_2$, ^3J = 6.25, Δν = 48 Hz); 3.24 (m, 4 H, NCH_2); 3.78 (s, 3 H, $C\underline{H}_3O$); 4.01 (q, 2 H, $CH_3C\underline{H}_2O$, ^3J = 6.16); 4.63 (d, 1 H, 4-$EtOC_6H_4C\underline{H}$, ^3J = 5.62); 4.71 (d, 1 H, 3-$MeOC_6H_4C\underline{H}$, ^3J = 6.25); 5.05 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.62, ^3J = 6.25); 6.86, 7.36 (both d, 4 H, 4-$EtOC_6\underline{H}_4$, ^3J = 7.15); 6.83, 7.07, 7.09, 7.28 (d, d, s, t, 4 H, 3-$MeOC_6\underline{H}_4$, ^3J = 6.28)	14.75 (CH_3CH_2O); 23.89 ($NCH_2\underline{C}H_2$); 50.65 (4-$EtOC_6H_4CHN\underline{C}H_2$); 51.10 (3-$MeOC_6H_4CHN\underline{C}H_2$); 55.19 ($\underline{C}H_3O$); 63.43 ($CH_3\underline{C}H_2O$); 71.67 (4-$EtOC_6H_4\underline{C}H$, 3-$MeOC_6H_4\underline{C}H$); 103.34 ($NO_2\underline{C}H$); 112.63, 113.58, 119.38, 129.93, 141.40, 158.96 (3-$MeO\underline{C}_6H_4$); 114.79, 128.47, 130.81, 160.02 (4-$EtO\underline{C}_6H_4$)

(*to be continued*)

Table 5 (*continued*)

Compound	NMR ($CDCl_3$), δ (*J*/Hz)	
	^1H	^{13}C
12j	2.16, 2.39 (both m, 2 H, $NCH_2C\underline{H}_2$, ^2J = 10.25, ^3J = 5.79, Δν = 46 Hz); 2.35 (s, 3 H, 4-$C\underline{H}_3C_6H_4$); 3.19, 3.32 (both m, 2 H, 4-$MeC_6H_4CHNC\underline{H}_2$, ^2J = 9.80, ^3J = 4.46, Δν = 25 Hz); 3.32 (m, 2 H, 3-$MeOC_6H_4CHNC\underline{H}_2$, ^2J = 9.80, ^3J = 5.35); 3.82 (s, 3 H, 3-$C\underline{H}_3OC_6H_4$); 4.68 (d, 1 H, 4-$MeC_6H_4C\underline{H}$, ^3J = 5.78); 4.73 (d, 1 H, 3-$MeOC_6H_4C\underline{H}$, ^3J = 6.39); 5.06 (t, 1 H, $NO_2C\underline{H}$, ^3J = 5.78, ^3J = 6.36); 7.18, 7.36 (both d, 4 H, 4-$MeC_6\underline{H}_4$, ^3J = 7.63); 6.86, 7.05, 7.08, 7.27 (d, d, s, t, 4 H, 3-$MeOC_6\underline{H}_4$, ^3J = 8.02)	21.16 (4-$\underline{C}H_3C_6H_4$); 23.99 ($NCH_2\underline{C}H_2$); 50.83 (4-$MeC_6H_4CHN\underline{C}H_2$); 51.14 (3-$MeOC_6H_4CHN\underline{C}H_2$); 55.27 ($\underline{C}H_3O$); 71.84 (4-$MeC_6H_4\underline{C}H$); 71.94 (3-$MeOC_6H_4\underline{C}H$); 103.36 ($NO_2\underline{C}H$); 112.72, 113.71, 119.49, 129.98, 141.35, 160.12 (3-$MeO\underline{C}_6H_4$); 127.24, 129.62, 136.15, 138.17 (4-$Me\underline{C}_6H_4$)
13a[e]	2.90 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 3.84 (s, 3 H, $C_6H_4OC\underline{H}_3$); 4.54 (t, 2 H, $MeC_6H_4CNC\underline{H}_2$, ^3J = 6.9); 4.68 (t, 2 H, $NO_2C_6H_4CNC\underline{H}_2$, ^3J = 7.1); 7.15, 7.48 (both d, 4 H, H in $MeOC_6H_4$, ^3J = 7.9); 7.70 (m, 2 H, C(5)H, C(6)H in $NO_2C_6H_4$, ^3J = 8.0); 8.14 (s, 1 H, C(2)H in $NO_2C_6H_4$); 8.23 (d, 1 H, C(4)H in $NO_2C_6H_4$, ^3J = 8.0); 8.99 (s, 1 H, $NO_2C_6H_4C\underline{H}$)	26.21 ($NCH_2\underline{C}H_2$); 48.19 ($CH_3OC_6H_4CN\underline{C}H_2$); 49.22 ($CHN\underline{C}H_2$); 55.46 ($\underline{C}H_3OC_6H_4$); 122.39 ($NO_2C_6H_4\underline{C}$); 130.04 ($CH_2N\underline{C}H$); 139.58 ($CH_3OC_6H_4\underline{C}$); 115.09, 116.64, 130.80, 161.25 ($CH_3O\underline{C}_6H_4$); 122.48, 123.04, 130.68, 130.96, 134.31, 148.09 ($NO_2\underline{C}_6H_4$)
13a´	2.90 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 3.84 (s, 3 H, $C_6H_4OC\underline{H}_3$); 4.54 (t, 2 H, $MeC_6H_4CNC\underline{H}_2$, ^3J = 6.9); 4.68 (t, 2 H, $NO_2C_6H_4CNC\underline{H}_2$, ^3J = 7.1); 7.15, 7.48 (both d, 4 H, H in $MeOC_6H_4$, ^3J = 7.9); 7.70 (m, 2 H, C(5)H, C(6)H in $NO_2C_6H_4$, ^3J = 8.0); 8.14 (s, 1 H, C(2)H in $NO_2C_6H_4$); 8.23 (d, 1 H, C(4)H in $NO_2C_6H_4$, ^3J = 8.0); 8.99 (s, 1 H, $NO_2C_6H_4C\underline{H}$)	26.21 ($NCH_2\underline{C}H_2$); 48.19 ($CH_3OC_6H_4CN\underline{C}H_2$); 49.22 ($CHN\underline{C}H_2$); 55.46 ($\underline{C}H_3OC_6H_4$); 122.39 ($NO_2C_6H_4\underline{C}$); 130.04 (N$\underline{C}$H); 139.58 ($CH_3OAr\underline{C}$); 115.09, 116.64, 130.80, 161.25 ($CH_3O\underline{C}_6H_4$); 122.48, 123.04, 130.68, 130.96, 134.31, 148.09 ($NO_2\underline{C}_6H_4$)
13b[f]	1.46 (t, 3 H, $C_6H_4OCH_2C\underline{H}_3$); 2.90 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 4.11 (q, 2 H, $C_6H_4OC\underline{H}_2CH_3$); 4.53 (t, 2 H, $MeC_6H_4CNC\underline{H}_2$, ^3J = 7.2); 4.67 (t, 2 H, $NO_2C_6H_4CNC\underline{H}_2$, ^3J = 7.2); 7.12, 7.45 (both d, 4 H, H in $EtOC_6H_4$, ^3J = 8.6); 7.69 (m, 2 H, C(5)H, C(6)H in $NO_2C_6H_4$); 8.13 (s, 1 H, C(2)H in $NO_2C_6H_4$); 8.22 (d, 1 H, C(4)H in $NO_2C_6H_4$, ^3J = 7.1); 9.00 (s, 1 H, $NO_2C_6H_4C\underline{H}$)	14.41 ($\underline{C}H_3CH_2OC_6H_4$); 26.20 ($NCH_2\underline{C}H_2$); 48.18 ($CH_3OC_6H_4CN\underline{C}H_2$); 49.19 ($CHN\underline{C}H_2$); 63.46 ($CH_3\underline{C}H_2OC_6H_4$); 122.29 ($NO_2C_6H_4\underline{C}H$); 130.05 (N$\underline{C}$H); 139.54 ($CH_3OC_6H_4\underline{C}$); 115.44, 116.40, 130.75, 160.50 ($EtO\underline{C}_6H_4$); 122.42, 123.01, 130.65, 130.91, 134.24, 148.06 ($NO_2\underline{C}_6H_4$)
13d[g]	2.40 (s, 3 H, $C_6H_4C\underline{H}_3$); 2.92 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 4.54 (t, 2 H, $MeC_6H_4CNC\underline{H}_2$, ^3J = 7.2); 4.68 (t, 2 H, $NO_2ArCNC\underline{H}_2$, ^3J = 7.2); 7.41, 7.44 (both m, 4 H, H in MeC_6H_4, ^3J = 8.0); 7.68 (d, 1 H, C(6)H in $NO_2C_6H_4$, ^3J = 8.0); 7.70 (t, 1 H, C(5)H in $NO_2C_6H_4$, ^3J = 8.0); 8.14 (s, 1 H, C(2)H in $NO_2C_6H_4$); 8.22 (d, 1 H, C(4)H in $NO_2C_6H_4$, ^3J = 8.0); 9.01 (s, 1 H, $NO_2C_6H_4C\underline{H}$)	20.99 ($\underline{C}H_3C_6H_4$); 26.25 ($NCH_2\underline{C}H_2$); 48.33 ($CH_3C_6H_4CN\underline{C}H_2$); 49.31 ($CHN\underline{C}H_2$); 122.56 ($NO_2C_6H_4\underline{C}$); 130.11 (N$\underline{C}$H); 139.64 ($CH_3C_6H_4\underline{C}$); 121.88, 129.04, 130.14, 141.26 ($CH_3\underline{C}_6H_4$); 122.52, 123.09, 130.67, 130.84, 134.31, 148.09 ($NO_2\underline{C}_6H_4$)

[a] ^{15}N NMR spectrum, δ: +5.6 (NO_2CH); −10.4 ($NO_2C_6H_4$); −247.3 ($CH_3OC_6H_4CN$); −250.1 ($NO_2C_6H_4C\underline{N}$).
[b] ^{15}N NMR spectrum, δ: +6.8 (NO_2CH), −9.7 ($NO_2C_6H_4$), −249.29 ($CH_3OC_6H_4CHN$), −251.55 ($NO_2C_6H_4CH\underline{N}$).
[c] ^{15}N NMR spectrum, δ: +6.8 (NO_2CH); −9.7 ($NO_2C_6H_4$); −247.1 ($CH_3OC_6H_4CHN$); −249.6 ($NO_2C_6H_4CH\underline{N}$).
[d] ^{15}N NMR spectrum, δ: +6.1 (NO_2CH); −10.6 ($NO_2C_6H_4$); −247.9 ($CH_3C_6H_4CHN$); −249.7 ($NO_2C_6H_4CH\underline{N}$).
[e] ^{15}N NMR spectrum, δ: −10.3 (NO_2Ar); −167.7 (CH_3ArCN); −168.6 (CHN).
[f] ^{15}N NMR spectrum, δ: −8.7 ($NO_2C_6H_4$); −166.5 ($CH_3C_6H_4CN$); −168.6 (CHN).
[g] ^{15}N NMR spectrum, δ: −11.3 ($NO_2C_6H_4$); −167.3 ($CH_3C_6H_4CN$); −168.3 (CHN).

until the reaction was completed (TLC monitoring, hexane—ethyl acetate (2 : 1)). To extract the products obtained from the reaction mixture, CH_2Cl_2 (0.5 mL) was added first, followed by stirring (a homogeneous solution was obtained), then, diethyl ether (2.5 mL) was added and stirred, the IL precipitated, the upper organic layer was decanted; repeating the procedure 2—3 times (TLC monitoring) until the extraction was completed. The solvent was evaporated on a rotary evaporator without heating, the final products were isolated by column chromatography on SiO_2 using the same eluting system.

Reaction of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes 2 with β-nitrostyrenes 9a—c (general procedure). Boron trifluoride diethyl etherate (2 drops, 0.1 mmol) was added to a mixture of 6-aryl-1,5-diazabicyclo[3.1.0]hexane **2a—d** (0.5 mmol) and β-nitrostyrene **9a—c** (0.5 mmol) in IL ([bmim][BF_4] or [bmim][PF_6]) (0.4 g) with stirring, and the mixture was heated to 60 °C and stirred until complete conversion of compound **2** (TLC-monitoring, hexane—ethyl acetate (3 : 1)). To isolate the products obtained, CH_2Cl_2 (0.5 mL) was added first to the reaction mixture and it was stirred (to obtain a homogeneous

solution), then, diethyl ether (2.5 mL) was added and stirred, the IL precipitated, the upper organic layer was decanted, repeating the procedure 4 times (TLC monitoring until the extraction was completed). The solvent was evaporated on a rotary evaporator without heating, the final products **12** were purified by flash-chromatography on SiO_2 using the same eluting system. In the reaction with β-nitrostyrene **9b**, the IL obtained after extraction of compounds **12** was dissolved in the ethyl acetate—dichloromethane—diethyl ether (2 : 4 : 0.5, v/v) solvent mixture. The dissolved IL was separated by decantation, a precipitate of compounds **13** was washed with ethyl acetate (3×3 mL), dried in air for 1 day and analyzed. The solvent mixture was evaporated on a rotary evaporator, and the residual IL was used repeatedly in the same reactions.

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