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ARTICLE TYPE

Simple Approach to Pyrrolylimidazole Derivatives by Azirine Ring Expansion with Imidazolium Ylides

Alexander F. Khlebnikov,* Olesya A. Tomashenko, Liya D. Funt, and Mikhail S. Novikov

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Domino reaction of 2*H*-azirines with 1-alkyl-3-phenacyl-1*H*-imidazolium bromides in the presence of Et_3N provides a facile route to 1-alkyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides. 1-Benzyl derivatives can be reduced to 1-(1*H*-pyrrol-3-yl)-1*H*-imidazoles with HCO_2NH_4 on Pd/C. Action of KOH on pyrrolylimidazolium salts leads to a new type of stable ylide, 3-(1*H*-imidazol-3-ium-3-yl)-pyrrol-1-ides, which can, in principle, be in tautomeric equilibrium with the corresponding N-heterocyclic carbene. Although, according to the DFT B3LYP/6-31G(d) calculations *in vacuo,* electron-donating substituents in the 2-aryl-group cause the tautomeric equilibrium to shift to the carbene side, the investigated compounds exist in the ylide form in solution and in the solid state, which is in agreement with the relative stabilities of the species calculated with PCM solvent model.

Introduction

Pyrrole and imidazole are two of the most important nitrogen heterocycles, whose structural units are widely present in natural products, medical and material molecules.[1] There is even a particular class of bioactive alkaloids, the pyrrole-imidazole alkaloids, where both these heterocyclic units are present.[2] Another group of compounds containing both heterocyclic fragments under discussion is imidazole and pyrrole-containing polyamides which show good anticancer[1e,h,3] and antiviral[1e,4] activities. Here the pyrrole and imidazole rings are not bonded directly. Pyrrolylimidazoles are much less known, though some substituted 1-(1*H*-pyrrol-3-yl)-1*H*-imidazoles are among compounds, which are inhibitors of c-Met protein kinase[5] and protein tyrosine phosphatase activity.[6] The probable explanation for the low number of known pyrrolylimidazoles is that no efficient synthetic route has been developed.

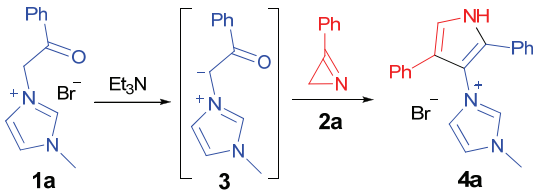
The synthesis of pyrrole derivatives by reactions of azirines with nucleophiles, such as enolates of carbonyl compounds or their synthetic equivalents, is well known.[7,8] At the same time, only one precedent of the use of carbonyl-substituted phosphorus ylides as nucleophiles in the reaction with azirines has been reported.[9] In the framework of our research concerning the synthesis of heterocycles by ring expansion of strained azirines, we have recently presented an effective approach to derivatives of 1-(1*H*-pyrrol-3-yl)pyridine by the reaction of carbonyl-substituted pyridinium ylides with 2*H*-azirines.[10] Pyridinium ylides have been widely used in organic synthesis,[11] and their reactivity as nucleophiles have been intensively studied.[11a,d,12] By contrast, carbonyl-substituted N-imidazolium ylides have scarcely been studied,[13] and their use as nucleophiles was mentioned only in two articles.[13a,b] In this study we have applied carbonyl-substituted imidazolium ylides as nucleophiles in the reaction with 2*H*-azirines to synthesize derivatives of 1-(1*H*-pyrrol-3-yl)-1*H*-imidazoles, including unknown pyrrolylimidazolium salts, and their corresponding ylides, 3-(1*H*-imidazol-3-ium-3-yl)pyrrolides, via azirine ring expansion. Imidazolium salts are widely used as ionic liquids,[14] bioactive molecules,[15] precursors to stable carbenes and their complexes,[16] as well as in sustainable chemistry.[17] Unknown 3-(1*H*-imidazol-3-ium-3-yl)pyrrolides like some other heterocyclic mesomeric betaines[18] can, in principle, tautomerize to N-heterocyclic carbenes. They can, therefore, potentially be used as precursors for new NHC-ligands with a pyrrole-substituent.

Results and discussion

To start with we reacted *N*-methylimidazolium bromide **1a** with azirine **2a** under the conditions used for pyridinium analogs,[10] but it was revealed that reaction **1a** proceeded much slower. Probably the imidazolium ylide **3** formed *in situ* under deprotonation of the salt **1a** is less reactive than its pyridinium analogue (Table 1). There was still a lot of starting material **1a** along with product **4a** after performing the reaction in dichloromethane (DCM) at room temperature for 17 h (Table 1, entry 1). In refluxing DCM the full conversion was achieved after 18 h (Table 1, entries 2-4) and the yield in this case was 68%. Acetonitrile could be the solvent of choice as the yield of **4a** is only slightly less than that in DCM (Table 1, entry 5). The product purification procedure is, however, not as convenient as with DCM because salt **4a** is quite soluble in acetonitrile while insoluble in DCM. THF failed to be a suitable solvent where only traces of **4a** were detected (Table 1, entry 6). In DCE, due to its higher boiling point, conversion was complete already after 5 h yet the yield of product was only 52% (Table 1, entry 7). The role of Et_3N seems to be crucial in the two stages of the domino reaction (Scheme 1), so in order to optimize its influence on the outcome of the reaction its ratio was varied

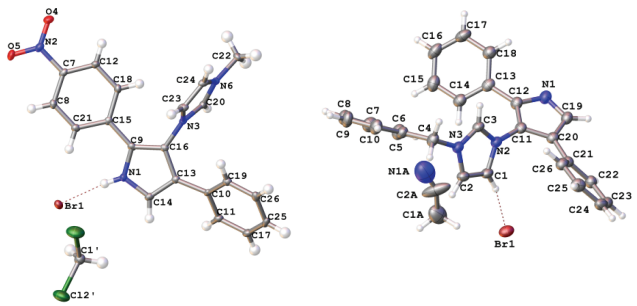
from 0.5 to 3 equiv. Subequimolar or an equimolar ratio of Et_3N was insufficient (Table 1, entries 8-10). At least two or rather three equiv. of base were required to accomplish the full conversion and obtain **4a** in good yield (Table 1, entries 11-12). An attempt to use DBU, which is a considerably stronger base, was not successful apparently due to side reactions. After performing the reaction with this base for 18 h in refluxing DCM only 40% of **1a** with traces of product **4a** were isolated.

Table 1 Optimization of reaction conditions

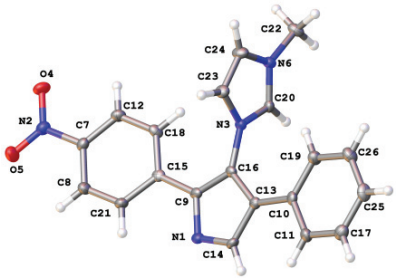


entry	conditions	time, h	Et_3N[a]	ratio, **4a**:**1a**[b]	**4a**, yield, %
1	DCM, rt	17	1.3	37:63	30
2	DCM, reflux	5	1.3	59:41	47
3	DCM, reflux	10	1.3	97:3	-
4	DCM, reflux	18	1.3	100:0	68
5	MeCN, rt	48	1.3	100:0	64
6	THF, reflux	5	1.3	2:98	-
7	DCE, reflux	5	1.3	100:0	52
8	DCM, reflux	15	0.5	67:33	50
9	DCM, reflux	15	1	92:8	63
10	DCM, reflux	15	1.5	98:2	64
11	DCM, reflux	18	2	100:0	70
12	DCM, reflux	18	3	100:0	73

[a] equiv. calcd on **1a**. [b] ratio of **4a**:**1a** in the isolated mixture according to ^{1}H NMR.



4b **4n**

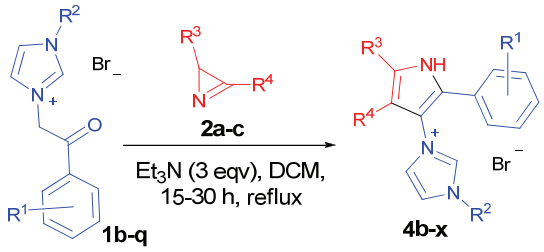


6b

Fig. 1 Molecular structure of salt **4b**,**n** and ylide **6b**.

To explore the scope and limitations of the approach to pyrrolylimidazolium salts a number of *N*-methyl- and *N*-benzylimidazolium bromides **1b-q** bearing both electron-donating and -withdrawing substituents were introduced into the reaction with azirines containing Ph, Me, and CO_2Et groups: 2-phenyl- and 2,3-diphenyl-2*H*-azirines (**2a**,**b**), and ethyl 3-methyl-2*H*-azirine-2-carboxylate (**2c**) (Table 2). The procedure is simple and convenient. Due to the low solubility of products **4a-x** in DCM it is enough just to filter a product and wash it with DCM to obtain an analytically pure sample. Furthermore the reaction can be scaled-up for multi gram quantities without yield decrease. Thus 3 g of salt **4a** were obtained with 74% yield. All compounds **4a-x** were characterized by ^{1}H, ^{13}C NMR, IR and HRMS. The structures of **4b** and **4n** were additionally confirmed by X-ray analysis (Figure 1). Crystals of **4b**, **n** were obtained as a solvate with one molecule of DCM and MeCN, respectively.

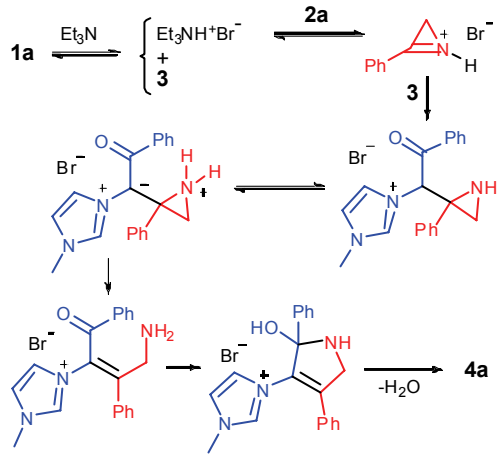
Table 2 Synthesis of 1-alkyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides **4b-x**



entry	R^1	R^2	R^3	R^4	**1**	**2**	time, h	**4**, yield, (%)
1	*p*-NO_2	Me	H	Ph	**b**	**a**	18	**b** (56)
2	*m*-NO_2	Me	H	Ph	**c**	**a**	18	**c** (57)
3	*p*-Br	Me	H	Ph	**d**	**a**	18	**d** (62)
4	*m*-Br	Me	H	Ph	**e**	**a**	30	**e** (54)
5	*p*-Cl	Me	H	Ph	**f**	**a**	18	**f** (73)
6	*p*-OMe	Me	H	Ph	**g**	**a**	30	**g** (64)
7	*o*,*p*-$(OMe)_2$	Me	H	Ph	**h**	**a**	30	**h** (40)
8	*p*-F	Me	H	Ph	**i**	**a**	21	**i** (67)
9	H	Me	Ph	Ph	**a**	**b**	21	**j** (71)
10	*p*-NO_2	Me	Ph	Ph	**b**	**b**	21	**k** (60)
11	*p*-Cl	Me	Ph	Ph	**f**	**b**	18	**l** (64)
12	*p*-NO_2	Me	CO_2Et	Me	**b**	**c**	19	**m** (51)
13	H	Bn	H	Ph	**j**	**a**	24	**n** (42)
14	*p*-NO_2	Bn	H	Ph	**k**	**a**	15	**o** (54)
15	*m*-NO_2	Bn	H	Ph	**l**	**a**	15	**p** (75)
16	*p*-Br	Bn	H	Ph	**m**	**a**	22	**q** (65)
17	*m*-Br	Bn	H	Ph	**n**	**a**	22	**r** (45)
18	*p*-Cl	Bn	H	Ph	**o**	**a**	24	**s** (75)
19	*p*-OMe	Bn	H	Ph	**p**	**a**	24	**t** (76)
20	*p*-F	Bn	H	Ph	**q**	**a**	18	**u** (78)
21	*m*-NO_2	Bn	Ph	Ph	**l**	**b**	15	**v** (63)
22	*p*-Br	Bn	Ph	Ph	**m**	**b**	24	**w** (55)
23	*p*-Cl	Bn	Ph	Ph	**o**	**b**	24	**x** (55)

The formation of pyrrolylimidazolium salts **4** can be rationalized by the reaction sequence involving the generation of imidazolium ylide **3**, its nucleophilic addition to protonated azirine **2** with formation of aziridine intermediate, followed by three-membered ring-opening, cyclization and dehydration (Scheme 1). Recently, the need for activation of the C=N bond by protonation for a

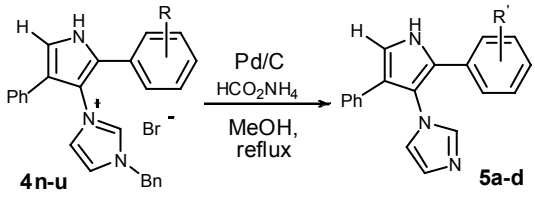
nucleophilic attack on azirine was clearly demonstrated.[19]



Scheme 1 Mechanistic scheme for salts **4** formation.

1-Benzyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides **4n-u** can be easily debenzylated in good yields on Pd/C, with ammonium formate as a source of hydrogen, to give corresponding 1-(1*H*-pyrrol-3-yl)-1*H*-imidazoles (Table 3). Still there are some limitations of this procedure. Thus nitro-substituted salt **4o** during debenzylation was reduced to the amino-derivative **5b**, and bromo- and chlorosubstituted salts **4q-s** underwent reductive dehalogenation with the formation of **5a**. On the other hand, the procedure allows obtaining the amino derivatives which can't be synthesized directly.

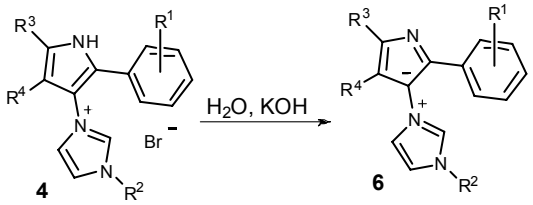
Table 3 Debenzylation of 1-benzyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides **4n-u**



entry	R	**4**	R'	time, h	**5**, yield, (%)
1	H	**n**	H	2	**a** (88)
2	*p*-NO_2	**o**	*p*-NH_2	1.5	**b** (80)
3	*p*-Br	**q**	H	1.5	**a** (91)
4	*m*-Br	**r**	H	2.5	**a** (90)
5	*p*-Cl	**s**	H	2	**a** (96)
6	*p*-OMe	**t**	*p*-OMe	1	**c** (88)
7	*p*-F	**u**	*p*-F	3	**d** (90)

Pyrrolylimidazolium bromides **4** readily produced the corresponding 3-(1*H*-imidazol-3-ium-3-yl)-pyrrol-1-ides **6** in almost quantitive yields by treating the salts with a water solution of KOH under ultrasonication (Table 4). Ylides **6** are stable non hygroscopic solids with high melting points. Structures of ylides **6**, that in principle can be in tautomeric equilibrium with carbenes **7** (Scheme 2), were verified by NMR spectroscopy. There is no signal for the N-H proton, which is observed for salts **4** at 12.1–12.6 ppm, in the ^{1}H NMR spectra of **6**. In the ^{13}C NMR spectra of **6** the carbon signals of the pyrrolide fragment are considerably shifted in comparison with those for the corresponding salts **4**, and there are no signals in the low field region around 200 ppm, which could correspond to carbene carbon.

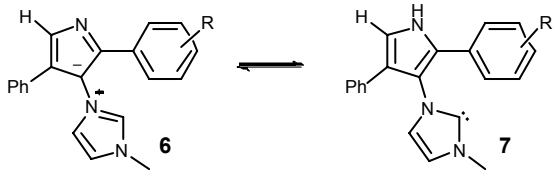
Table 4 Synthesis of 3-(1*H*-imidazol-3-ium-3-yl)-pyrrol-1-ides **6a-n**



entry	R^1	R^2	R^3	R^4	**4**	**6**, yield, (%)
1	H	Me	H	Ph	**a**	**a** (98)
2	*p*-NO_2	Me	H	Ph	**b**	**b** (99)
3	*m*-NO_2	Me	H	Ph	**c**	**c** (98)
4	*p*-Br	Me	H	Ph	**d**	**d** (98)
5	*m*-Br	Me	H	Ph	**e**	**e** (99)
6	*p*-Cl	Me	H	Ph	**f**	**f** (99)
7	*p*-OMe	Me	H	Ph	**g**	**g** (85)
8	*p*-F	Me	H	Ph	**i**	**h** (99)
9	H	Me	Ph	Ph	**j**	**i** (88)
10	*p*-NO_2	Me	Ph	Ph	**k**	**j** (91)
11	*p*-Cl	Me	Ph	Ph	**l**	**k** (98)
12	*p*-NO_2	Me	CO_2Et	Me	**m**	**l** (94)
13	H	Bn	H	Ph	**n**	**m** (90)
14	*p*-NO_2	Bn	H	Ph	**o**	**n** (99)

The structure of crystalline ylide **6b** was also analysed by X-ray (Figure 1). X-ray analysis cannot undoubtedly give preference to one of two possible structures with the same positions of heavy atoms: ylide **6** and NHC **7** (Scheme 2, R = *p*-NO_2). But comparison of CC and CN bond lengths obtained from X-ray analysis with bond lengths calculated at the DFT B3LYP/6-31G(d) and 6-311++G(dp) level of theory for both ylide **6b** and carbene **7a** (R = *p*-NO_2) shows that ylide **6b** is much more the plausible structure (For calculated geometries of **6b** and **7a** see Supporting information). Therefore it can be concluded that ylide **6** is thermodynamically more stable than the corresponding carbene **7** both in solution and in the solid state. Action of KOH on salt **4h**, containing the *o,p*-$(MeO)_2$-substituted phenyl group, lead to a complex mixture of unidentified products. Probably this is a consequence of the increase of relative stability of the corresponding NHC **7e** (*vide infra)*.

According to calculations at the DFT B3LYP/6-31G(d) level (Scheme 2, Table 5) a substituent in the benzene ring strongly influences the equilibrium between ylide **6** and carbene **7**.



Scheme 2 Possible tautomeric equilibrium ylide **6** – carbene **7**.

Thus, introduction of electron-donating substituents causes the tautomeric equilibrium to shift to the carbene side, while electron-withdrawing substituents shifts the equilibrium to the

opposite side. *In vacuo* carbenes **7** with electron-donating substituents are more thermodynamically stable than corresponding ylides **6**. However, as one can expect, solvent stabilizes much more the zwitterion species than the uncharged ones, and in solution the equilibrium shifts to the ylide side for all calculated structures. Probably reaction of carbene **7** with a metallic center can induce a shift of the tautomeric equilibrium ylide **6** - carbene **7** by conversion of **7** to corresponding N-heterocyclic carbene complex.[18] Work in this direction is now in progress.

Table 5 Relative Free Energies, carbene **7**– ylide **6**, computed at the DFT B3LYP/6-31G(d) level *in vacuo* or with PCM model for DCM and MeOH at 298K

R (Scheme 2)	6	7	$\Delta G_{7\text{-}6}$, kcal·mol^{-1}		
			vacuo	DCM	MeOH
p-NO_2	**b**	**a**	3.5	12.4	14.0
p-F	**h**	**b**	0.3	8.8	10.0
H	**a**	**c**	0.2	8.7	9.7
p-MeO	**g**	**d**	-0.5	8.0	9.2
o,*p*-$(MeO)_2$	**o**	**e**	-4.4	4.4	6.0

Conclusions

Domino reaction of substituted 2*H*-azirines with 1-alkyl-3-phenacyl-1*H*-imidazolium bromides, bearing both electron-donating and -withdrawing substituents, in the presence of Et_3N leads to the corresponding 1-alkyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides. The latter, having benzyl as alkyl group, were reduced to 1-(1*H*-pyrrol-3-yl)-1*H*-imidazoles with high yields. Action of KOH under ultrasonication on 3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides gives a new type of stable ylides, 3-(1*H*-imidazol-3-ium-3-yl)-pyrrol-1-ides in nearly quantitative yields. Very simple procedures used for isolation of products do not involve chromatography. The ylides, which can in principle be in tautomeric equilibrium with their corresponding N-heterocyclic carbenes, exist as ylides in solution and in solid state, though according to DFT B3LYP/6-31G(d) calculations *in vacuo* electron-donating substituents in the 2-aryl-group influence the equilibrium and shift it to the carbene side. Calculations with the PCM solvent model are in accordance with the experimental results.

Experimental

General

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker 400 MHz Avance, chemical shift values are reported in ppm on the δ scale relative to TMS (δ = 0.00). ^1H NMR spectra were calibrated according to the residual peak of DMSO-d_6 (2.50 ppm), *J* values are given in Hz. For all new compounds $^{13}C\{^1H\}$ and ^{13}C DEPT135 were recorded and calibrated according to the peak of DMSO-d_6 (39.51 ppm). Mass spectra were recorded on a Bruker maXis HRMS-ESI-QTOF, electrospray ionization, positive mode. Melting points were determined on a hot stage microscope and are uncorrected. IR-spectra were recorded on a Bruker FT-IR spectrometer Tensor 27. Thin-layer chromatography (TLC) was conducted on aluminium sheets with 0.2 mm silica gel (fluorescent indicator, Macherey-Nagel).

Characterization data of the compounds

General procedure for the synthesis of 1-methyl- and 1-benzyl-3-(2-oxo-2-phenylethyl)-1*H*-imidazol-3-ium bromides. A solution of 2-bromoacetophenone (6.09 mmol) and 1-methyl-1*H*-imidazole or 1-benzyl-1*H*-imidazole (6.09 mmol) in Et_2O (30 mL) was stirred at rt for 12 h. Colorless solid started to precipitate immediately. After 12 h the product was filtered, washed with Et_2O (3×20 mL) and dried.

1-Methyl-3-(2-(3-nitrophenyl)-2-oxoethyl)-1*H*-imidazol-3-ium bromide (1c): colorless solid, mp 225–226 °C, yield 1.78 g, 89%, obtained from 2-bromo-3'-nitroacetophenone (1.49 g, 6.09 mmol) and 1-methyl-1*H*-imidazole (500 mg, 6.09 mmol). ^1H NMR (DMSO-d_6): δ 3.96 (3H, s), 6.14 (2H, s), 7.70 (1H, t, *J* = 1.7), 7.79 (1H, t, *J* = 1.7), 7.93–7.98 m (1H), 8.47 (1H, d, *J* = 7.9), 8.59 (1H, ddd, *J* = 8.0, *J* = 2.3, *J* = 0.9), 8.74 (1H, t, *J* = 1.9), 9.06 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.0 (CH_3), 55.6 (CH_2), 122.5 (CH), 123.4 (CH), 123.9 (CH), 128.5 (CH), 131.0 (CH), 134.3 (CH), 135.0 (C), 137.7 (CH), 148.1 (C), 190.4 (C). HRMS (ESI) m/z: 246.0873 calcd for $C_{12}H_{12}N_3O_3$ $[M - Br]^+$, found 246.0877. IR (KBr, cm^{-1}): ν 3044, 1702, 1216, 1177.

3-(2-(3-Bromophenyl)-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium bromide (1e): colorless solid, mp 231–232 °C, yield 2.10 g, 96%, obtained from 2-bromo-3'-bromoacetophenone (1.69 g, 6.09 mmol) and 1-methyl-1*H*-imidazole (500 mg, 6.09 mmol). ^1H NMR (DMSO-d_6): δ 3.95 (3H, s), 6.06 (2H, s), 7.59–7.63 (1H, m), 7.68 (1H, s), 7.78 (1H, s), 7.98 (1H, d, *J* = 8.0), 8.05 (1H, d, *J* = 8.0), 8.21 (1H, t, *J* = 1.7), 9.05 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.0 (CH_3), 55.5 (CH_2), 122.3 (C), 123.4 (CH), 123.8 (CH), 127.2 (CH), 130.7 (CH), 131.3 (CH), 135.8 (C), 137.0 (CH), 137.6 (CH), 190.6 (C). HRMS (ESI) m/z: 279.0128 calcd for $C_{12}H_{12}BrN_2O$ $[M - Br]^+$, found 279.0119. IR (KBr, cm^{-1}): ν 3028, 1714, 1536, 1348.

3-(2-(4-Fluorophenyl)-2-oxoethyl)-1-methyl-1*H*-imidazol-3-ium bromide (1i): yellowish solid, mp 155–156 °C, yield 827 mg, 92%, obtained from 2-bromo-4'-fluoroacetophenone (661 mg, 3.05 mmol) and 1-methyl-1*H*-imidazole (250 mg, 3.05 mmol). ^1H NMR (DMSO-d_6): δ 3.96 (3H, s), 6.11 (2H, s), 7.45–7.52 (2H, m), 7.74 (1H, s), 7.81 (1H, s), 8.15 (2H, dd, J_{HH} = 8.2, J_{HF} = 4.0), 9.05 (1H, s). ^{13}C NMR (DMSO-d_6): δ 35.8 (CH_3), 55.08 (CH_2), 116.3 d (CH, $^2J_{CF}$ = 22.0), 123.3 (CH), 123.9 (CH), 130.5 d (C, $^4J_{CF}$ = 3.0), 131.3 d (CH, $^3J_{CF}$ = 9.1), 137.7 (CH), 165.7 d (C, $^1J_{CF}$ = 253.5), 190.1 (C). HRMS (ESI) m/z: 219.0928 calcd for $C_{12}H_{12}FN_2O$ $[M - Br]^+$, found 219.0922. IR (KBr, cm^{-1}): ν 3067, 1699, 1593 1220.

1-Benzyl-3-(2-(4-nitrophenyl)-2-oxoethyl)-1*H*-imidazol-3-ium bromide (1k): colorless solid, mp 158–160 °C, yield 1.14 g, 87%, obtained from 2-bromo-4'-nitroacetophenone (775 mg, 3.2 mmol) and 1-benzyl-1*H*-imidazole (500 mg, 3.2 mmol). ^1H NMR (DMSO-d_6): δ 5.59 (2H, s), 6.16 (2H, s), 7.37–7.52 (5H, m), 7.77 (1H, s), 7.93 (1H, s), 8.28 (2H, d, *J* = 8.8), 8.44 (2H, d, *J* = 8.8), 9.28 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.0 (CH_2), 56.0 (CH_2), 122.3 (CH), 124.1 (CH), 124.4 (CH), 128.3 (CH), 128.8 (C), 129.1 (CH), 129.7 (CH), 134.8 (CH), 137.4 (C), 138.4 (CH), 150.6 (C), 190.8 (C). HRMS (ESI) m/z: 322.1186 calcd for $C_{18}H_{16}N_3O_3$ $[M - Br]^+$, found 322.1191. IR (KBr, cm^{-1}): ν 3068, 1707, 1529, 1346, 1221, 715.

1-Benzyl-3-(2-(3-nitrophenyl)-2-oxoethyl)-1*H*-imidazol-3-ium bromide (1l): colorless solid, mp 157–158 °C, yield 1.1 g, 87%,

obtained from 2-bromo-3'-nitroacetophenone (775 mg, 3.2 mmol) and 1-benzyl-1*H*-imidazole (500 mg, 3.2 mmol). ^{1}H NMR (DMSO-d_6): δ 5.59 (2H, s), 6.20 (2H, s), 7.37–7.51 (5H, m), 7.77 (1H, s), 7.94 (1H, s), 7.91–7.98 (1H, m), 8.47 (1H, d, J = 7.8), 8.59 (1H, dd, J = 8.0 Hz, J = 2.3), 8.72 (1H, t, J = 2.0), 9.30 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.0 (CH_2), 55.8 (CH_2), 122.3 (CH), 122.5 (CH), 124.4 (CH), 128.3 (CH), 128.5 (CH), 128.8 (CH), 129.1 (CH), 131.0 (CH), 134.3 (CH), 134.8 (C), 135.0 (C), 137.4 (CH), 148.1 (C), 190.4 (C). HRMS (ESI) m/z: 322.1186 calcd for $C_{18}H_{16}N_3O_3$ $[M - Br]^+$, found 322.1181. IR (KBr, cm^{-1}): ν 3069, 1710, 1562, 1531, 1354, 1229, 1165, 808, 736, 712.

1-Benzyl-3-(2-(4-bromophenyl)-2-oxoethyl)-1*H*-imidazol-3-ium bromide (1m): colorless solid, mp 175–176 °C, yield 1.21 g, 87%, obtained from 2-bromo-4'-bromoacetophenone (880 mg, 3.2 mmol) and 1-benzyl-1*H*-imidazole (500 mg, 3.2 mmol). ^{1}H NMR (DMSO-d_6): δ 5.58 (2H, s), 6.09 (2H, s), 7.36–7.52 (5H, m), 7.76 (1H, s), 7.86 (2H, d, J = 8.5), 7.92 (1H, s), 7.98 (2H, d, J = 8.5), 9.29 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.0 (CH_2), 55.5 (CH_2), 122.2 (CH), 124.4 (CH), 128.3 (CH), 128.6 (C), 128.8 (CH), 129.1 (CH), 130.1 (CH), 132.2 (CH), 132.7 (C), 134.8 (C), 137.4 (CH), 190.7 (C). HRMS (ESI) m/z: 355.0441 calcd for $C_{18}H_{16}BrN_2O$ $[M - Br]^+$, found 355.0440. IR (KBr, cm^{-1}): ν 3044, 2949, 1698, 1586, 1165, 1072, 990, 708.

1-Benzyl-3-(2-(3-bromophenyl)-2-oxoethyl)-1*H*-imidazol-3-ium bromide (1n): colorless solid, mp 182–184 °C, yield 1.21 g, 88%, obtained from 2-bromo-3'-bromoacetophenone (880 mg, 3.2 mmol) and 1-benzyl-1*H*-imidazole (500 mg, 3.2 mmol). ^{1}H NMR (DMSO-d_6): δ 5.57 (2H, s), 6.09 (2H, s), 7.36–7.50 (5H, m), 7.58–7.63 (1H, m), 7.74 (1H, t, J = 1.5), 7.92 (1H, t, J = 1.6), 7.97 (1H, dd, J = 8.0, J = 1.0), 8.03 (1H, d, J = 7.9), 8.19 (1H, t, J = 1.7), 9.27 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.0 (CH_2), 55.6 (CH_2), 122.3 (CH), 122.32 (C), 124.4 (CH), 127.1 (CH), 128.3 (CH), 128.8 (CH), 129.1 (CH), 130.7 (CH), 131.4 (CH), 134.8 (C), 135.7 (C), 137.0 (CH), 137.4 (CH), 190.5 (C). HRMS (ESI) m/z: 355.0441 calcd for $C_{18}H_{16}BrN_2O$ $[M - Br]^+$, found 355.0437. IR (KBr, cm^{-1}): ν 3056, 3010, 1692, 1560, 1228, 1164, 702.

1-Benzyl-3-(2-(4-chlorophenyl)-2-oxoethyl)-1*H*-imidazol-3-ium bromide (1o): colorless solid, mp 154–155 °C, yield 1.01 g, 81%, obtained from 2-bromo-4'-chloroacetophenone (742 mg, 3.2 mmol) and 1-benzyl-1*H*-imidazole (500 mg, 3.2 mmol). ^{1}H NMR (DMSO-d_6): δ 5.55 (2H, s), 6.03 (2H, s), 7.38–7.49 (5H, m), 7.72 (2H, d, J = 8.5), 7.71 (1H, s), 7.89 (1H, s), 8.06 (2H, d, J = 8.5), 9.27 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.0 (CH_2), 55.5 (CH_2), 122.2 (CH), 124.4 (CH), 128.3 (CH), 128.8 (CH), 129.1 (CH), 129.3 (CH), 130.1 (CH), 132.4 (C), 134.8 (C), 137.4 (CH), 139.3 (C), 190.5 (C). HRMS (ESI) m/z: 311.0946 calcd for $C_{18}H_{16}ClN_2O$ $[M - Br]^+$, found 311.0941. IR (KBr, cm^{-1}): ν 3067, 2909, 2834, 1696, 1590, 1558, 1237, 1159, 1092, 993, 820, 720.

1-Benzyl-3-(2-(4-methoxyphenyl)-2-oxoethyl)-1*H*-imidazol-3-ium bromide (1p): colorless solid, mp 152–153 °C, yield 1.0 g, 82%, obtained from 2-bromo-4'-methoxyacetophenone (725 mg, 3.2 mmol) and 1-benzyl-1*H*-imidazole (500 mg, 3.2 mmol). ^{1}H NMR (DMSO-d_6): δ 3.88 (3H, s), 5.56 (2H, s), 6.03 (2H, s), 7.15 (2H, d, J = 8.7), 7.36–7.52 (5H, m), 7.75 (1H, s), 7.90 (1H, s), 8.02 (2H, d, J = 8.7), 9.28 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.0 (CH_2), 55.2 (CH_2), 55.8 (CH_3), 114.4 (CH), 122.2 (CH), 124.5 (CH), 126.5 (C), 128.3 (CH), 128.8 (CH), 129.1 (CH), 130.6 (CH), 134.9 (C), 137.5 (CH), 164.1 (C), 189.6 (C). HRMS (ESI) m/z: 307.1441 calcd for $C_{19}H_{19}N_2O_2$ $[M - Br]^+$, found 307.1449. IR (KBr, cm^{-1}): ν 3065, 1686, 1603, 1575, 1243, 1187, 1152, 729.

1-Benzyl-3-(2-(4-fluorophenyl)-2-oxoethyl)-1*H*-imidazol-3-ium bromide (1q): colorless hygroscopic solid, mp 116–118 °C, yield 930 mg, 82%, obtained from 2-bromo-4'-fluoroacetophenone (654 mg, 3.0 mmol) and 1-benzyl-1*H*-imidazole (476 mg, 3.0 mmol). ^{1}H NMR (DMSO-d_6): δ 5.57 (2H, s), 6.09 (2H, s), 7.37–7.55 m (7H), 7.76 (1H, s), 7.92 (1H, s), 8.14 (2H, d, J_{HH} = 8.7, J_{HF} = 5.5), 9.29 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.0 (CH_2), 55.5 (CH_2), 116.3 d (CH, $^2J_{CF}$ = 22.2), 122.2 (CH), 124.4 (CH), 128.3 (CH), 128.8 (CH), 129.1 (CH), 130.5 d (C, $^4J_{CF}$ = 3.0), 131.3 d (CH, $^3J_{CF}$ = 9.7), 134.8 (C), 137.5 (CH), 165.7 d (C, $^1J_{CF}$ = 253.7), 190.1 (C). HRMS (ESI) m/z: 295.1241 calcd for $C_{18}H_{16}FN_2O$ $[M - Br]^+$, found 295.1245. IR (KBr, cm^{-1}): ν 3067, 1699, 1600, 1234, 1158, 837, 708.

General procedure for the synthesis of 1-alkyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides 4a-x. To a stirred suspension of 1-alkyl-3-(2-oxo-2-phenylethyl)-1*H*-imidazol-3-ium bromide **1** (0.89 mmol) and 2*H*-azirine **2** (1.34 mmol, 1.5 equiv.) in dichloromethane (DCM) (5 mL) Et_3N (270 mg, 2.67 mmol, 3 equiv.) was added dropwise, and then the reaction mixture was refluxed for 15–30 h. In the case of methyl-substituted bromides **1a-i** the reaction was monitored by ^{1}H NMR. In the case of benzyl-substituted bromides **1j-w** it was possible to monitor the reaction by TLC (MeOH/DCM 1:10). After the reaction was completed the precipitate was collected, washed with DCM (3×3 mL) and dried to obtain an analytically pure product **4**.

3-(2,4-Diphenyl-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4a): colorless solid, mp 203–205 °C, yield 246 mg, 73%, obtained from bromide **1a** (250 mg, 0.89 mmol), 3-phenyl-2*H*-azirine **(2a)** (157 mg, 1.34 mmol, 1.5 equiv.) and Et_3N (270 mg, 2.67 mmol, 3 equiv.) (18 h, here and bellow the duration of reflux). ^{1}H NMR (DMSO-d_6): δ 3.92 (3H, s), 7.13 (2H, d, J = 8.0), 7.20–7.26 (3H, m), 7.29–7.35 (3H, m), 7.37–7.43 (3H, m), 7.96 (1H, t, J = 1.6), 7.99 (1H, t, J = 1.7), 9.44 (1H, s), 12.19 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.3 (CH_3), 113.1 (C), 117.0 (CH), 121.3 (C), 124.7 (CH), 125.8 (CH), 126.0 (CH), 126.4 (CH), 126.6 (CH), 127.8 (CH), 128.2 (C), 128.9 (CH), 129.1 (CH), 129.3 (C), 132.3 (C), 138.8 (CH). HRMS (ESI) m/z: 300.1495 calcd for $C_{20}H_{18}N_3$ $[M - Br]^+$, found 300.1496. IR (KBr, cm^{-1}): ν 3421, 3111, 1605, 741.

1-Methyl-3-(2-(4-nitrophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4b): dark yellow solid, mp > 250 °C, yield 212 mg, 56%, obtained from bromide **1b** (290 mg, 0.89 mmol), 3-phenyl-2*H*-azirine **(2a)** (157 mg, 1.34 mmol, 1.5 equiv.) and Et_3N (270 mg, 2.67 mmol, 3 equiv.) (18 h). ^{1}H NMR (DMSO-d_6): δ 3.94 (3H, s), 7.14 (2H, d, J = 7.1), 7.23–7.30 (1H, m), 7.30–7.36 (2H, m), 7.42 (2H, d, J = 8.9), 7.58 (1H, s), 7.97–8.03 (2H, m), 8.24 (2H, d, J = 8.9), 9.48 (1H, s), 12.60 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.5 (CH_3), 115.0 (C), 119.3 (CH), 122.3 (C), 124.4 (CH), 125.1 (CH), 125.3 (CH), 125.8 (C), 126.4 (CH), 126.6 (CH), 127.0 (CH), 129.0 (CH), 131.8 (C), 135.6 (C), 138.7 (CH), 145.9 (C). HRMS (ESI) m/z: 345.1346 calcd for $C_{20}H_{17}N_4O_2$ $[M - Br]^+$, found 345.1352. IR (KBr, cm^{-1}): ν 3422, 3144, 1598, 1511, 1330.

1-Methyl-3-(2-(3-nitrophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-

imidazol-3-ium bromide (4c): bright yellow solid, mp > 250 °C, yield 446 mg, 57%, obtained from bromide **1c** (600 mg, 1.84 mmol), 3-phenyl-2*H*-azirine **(2a)** (323 mg, 2.76 mmol, 1.5 equiv.) and Et_3N (557 mg, 5.52 mmol, 3 equiv.) (18 h). ^1H NMR (DMSO-d_6): δ 3.94 (3H, s), 7.15 (2H, d, *J* = 7.3), 7.22–7.29 (1H, m), 7.30–7.37 (2H, m), 7.53 (1H, s), 7.58 (1H, d, *J* = 7.7), 7.65–7.72 (1H, m), 8.04 (3H, s), 8.16 (1H, d, *J* = 8.1), 9.48 (1H, s), 12.58 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.4 (CH_3), 114.3 (C), 118.3 (CH), 120.2 (CH), 121.7 (C), 122.1 (CH), 125.0 (CH), 125.5 (CH), 125.8 (C), 126.5 (CH), 126.9 (CH), 128.9 (CH), 130.8 (C), 130.85 (CH), 131.9 (CH), 138.9 (CH), 138.9 (C), 148.2 (C). HRMS (ESI) m/z: 345.1346 calcd for $C_{20}H_{17}N_4O_2$ [M – Br]$^+$, found 345.1346. IR (KBr, cm^{-1}): ν 3019, 2899, 1533, 1346.

3-(2-(4-Bromophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4d): colorless solid, mp > 250 °C, yield 253 mg, 62%, obtained from bromide **1d** (320 mg, 0.89 mmol), 3-phenyl-2*H*-azirine **(2a)** (157 mg, 1.34 mmol, 1.5 equiv.) and Et_3N (270 mg, 2.67 mmol, 3 equiv.) (18 h). ^1H NMR (DMSO-d_6): δ 3.92 (3H, s), 7.12 (2H, d, *J* = 8.0), 7.16 (2H, d, *J* = 8.0), 7.21–7.26 (1H, m), 7.28–7.34 (2H, m), 7.42 (1H, s), 7.59 (2H, d, *J* = 8.5), 7.97 (2H, s), 9.43 (1H, s), 12.29 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.4 (CH_3), 113.4 (C), 117.4 (CH), 121.0 (C), 121.5 (C), 124.8 (CH), 125.5 (CH), 126.5 (CH), 126.7(CH), 127.0 (C), 128.0 (CH), 128.5 (C), 128.9 (CH), 132.0 (CH), 132.1 (C), 138.7 (CH). HRMS (ESI) m/z: 378.0600 calcd for $C_{20}H_{17}BrN_3$ [M – Br]$^+$, found 378.0605. IR (KBr, cm^{-1}): ν 3096, 3022, 1485, 826, 748.

3-(2-(3-Bromophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4e): colorless solid, mp > 250 °C, yield 343 mg, 54%, obtained from bromide **1e** (500 mg, 1.39 mmol), 3-phenyl-2*H*-azirine **(2a)** (244 mg, 2.09 mmol, 1.5 equiv.) and Et_3N (421 mg, 4.17 mmol, 3 equiv.) (30 h). ^1H NMR (DMSO-d_6): δ 3.93 (3H, s), 7.08 (1H, d, *J* = 7.6), 7.12 (2H, d, *J* = 10), 7.21–7.27 (1H, m), 7.28–7.35 (3H, m), 7.44 (1H, s), 7.50–7.55 (2H, m), 7.98–8.03 (2H, m), 9.44 (1H, s), 12.36 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.3 (CH_3), 113.7 (C), 117.7 (CH), 121.5 (C), 122.3 (C), 124.7 (CH), 124.8 (CH), 125.6 (CH), 126.5 (CH), 126.7 (CH), 128.6 (CH), 128.9 (CH), 130.4 (CH), 131.2 (CH), 131.5 (C), 132.1 (C), 138.9 (C), 138.9 (CH). HRMS (ESI) m/z: 378.0600 calcd for $C_{20}H_{17}BrN_3$ [M – Br]$^+$, found 378.0608. IR (KBr, cm^{-1}): ν 3421, 3105, 3008, 1606, 745.

3-(2-(4-Chlorophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4f): colorless solid, mp > 250 °C, yield 268 mg, 73%, obtained from bromide **1f** (281 mg, 0.89 mmol), 3-phenyl-2*H*-azirine **(2a)** (157 mg, 1.34 mmol, 1.5 equiv.) and Et_3N (270 mg, 2.67 mmol, 3 equiv.) (18 h). ^1H NMR (DMSO-d_6): δ 3.94 (3H, s), 7.13 (2H, d, *J* = 7.3), 7.20–7.28 (3H, m), 7.28–7.35 (2H, m), 7.42 (1H, s), 7.46 (2H, d, *J* = 8.5), 7.97 (1H, s), 8.01 (1H, s), 9.48 (1H, s), 12.34 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.4 (CH_3), 113.4 (C), 117.4 (CH), 121.4 (C), 124.8 (CH), 125.5 (CH), 126.5 (CH), 126.7 (CH), 127.0 (C), 127.7 (CH), 128.2 (C), 128.9 (CH), 129.1 (CH), 132.2 (C), 132.4 (C), 138.8 (CH). HRMS (ESI) m/z: 334.1106 calcd for $C_{20}H_{17}ClN_3$ [M – Br]$^+$, found 334.1103. IR (KBr, cm^{-1}): ν 3423, 3086, 3022, 1493, 827, 752.

3-(2-(4-Methoxyphenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4g): colorless solid, mp > 250 °C, yield 251 mg, 64%, obtained from bromide **1g** (300 mg, 0.96 mmol), 3-phenyl-2*H*-azirine **(2a)** (170 mg, 1.45 mmol, 1.5 equiv.) and Et_3N (292 mg, 2.89 mmol, 3 equiv.) (30 h). ^1H NMR (DMSO-d_6): δ 3.76 (3H, s), 3.92 (3H, s), 6.96 (2H, d, *J* = 8.8), 7.11 (2H, d, *J* = 7.2), 7.17 (2H, d, *J* = 8.6), 7.20–7.25 (1H, m), 7.29 (1H, s), 7.31 (2H, d, *J* = 8.0), 7.97 (2H, s), 9.44 (1H, s), 12.10 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.3 (CH_3), 55.2 (CH_3), 112.3 (C), 114.5 (CH), 116.3 (CH), 121.0 (C), 121.8 (C), 124.6 (CH), 125.8 (CH), 126.4 (CH), 126.5 (CH), 127.5 (CH), 128.3 (C), 128.9 (CH), 132.5 (C), 138.8 (CH), 158.9 (C). HRMS (ESI) m/z: 330.1601 calcd for $C_{21}H_{20}N_3O$ [M – Br]$^+$, found 330.1607. IR (KBr, cm^{-1}): ν 3432, 3120, 1532, 1253.

3-(2-(2,4-Dimethoxyphenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4h): colorless solid, mp > 250 °C, yield 45 mg, 40%, obtained from bromide **1h** (88 mg, 0.26 mmol), 3-phenyl-2*H*-azirine **(2a)** (46 mg, 0.39 mmol, 1.5 equiv.) and Et_3N (78 mg, 0.77 mmol, 3 equiv.). ^1H NMR (DMSO-d_6): δ 3.60 (3H, s), 3.79 (3H, s), 3.90 (3H, s), 6.55–6.63 (2H, m), 7.13 (2H, d, *J* = 7.2), 7.20 (1H, d, *J* = 8.4), 7.24 (1H, d, *J* = 7.3), 7.26–7.55 (3H, m), 7.72 (1H, s), 7.83 (1H, s), 9.29 (1H, s), 11.82 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.0 (CH_3), 55.1 (CH_3), 55.4 (CH_3), 98.5 (CH), 105.4 (CH), 110.4 (C), 113.8 (C), 116.2 (CH), 119.8 (C), 123.7 (CH), 125.5 (C), 125.5 (CH), 126.4 (CH), 126.5 (CH), 128.9 (CH), 131.1 (CH), 132.7 (C), 138.3 (CH), 157.3 (C), 160.9 (C). HRMS (ESI) m/z: 360.1707 calcd for $C_{22}H_{22}N_3O_2$ [M – Br]$^+$, found 360.1711. IR (KBr, cm^{-1}): ν 3122, 2965, 1604, 1576, 1504, 1203, 1027.

3-(2-(4-Fluorophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4i): colorless solid, mp > 250 °C, yield 239 mg, 67%, obtained from bromide **1i** (266 mg, 0.89 mmol), 3-phenyl-2*H*-azirine **(2a)** (157 mg, 1.34 mmol, 1.5 equiv.) and Et_3N (270 mg, 2.67 mmol, 3 equiv.) (21 h). ^1H NMR (DMSO-d_6): δ 3.92 (3H, s), 7.12 (2H, d, *J* = 7.2), 7.20–7.34 m (7H), 7.39 (1H, s), 7.96 (2H, s), 9.43 (1H, s), 12.22 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.4 (CH_3), 113.1 (C), 116.1 d (CH, $^2J_{CF}$ = 22.0), 117.0 (CH), 121.2 (C), 124.7 (CH), 125.7 (CH), 125.9 (C), 126.5 (CH), 126.7 (CH), 127.4 (C), 128.4 d (CH, $^3J_{CF}$ = 13), 128.9 (CH), 132.3 (C), 138.8 (CH), 161.6 d (C, $^1J_{CF}$ = 245.5). HRMS (ESI) m/z: 318.1401 calcd for $C_{20}H_{17}FN_3$ [M – Br]$^+$, found 318.1403. IR (KBr, cm^{-1}): ν 3421, 3112, 1504, 738.

1-Methyl-3-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4j): colorless solid, mp > 250 °C, yield 263 mg, 71%, obtained from bromide **1a** (229 mg, 0.81 mmol), 2,3-diphenyl-2*H*-azirine **(2b)** (189 mg, 0.98 mmol, 1.2 equiv.) and Et_3N (247 mg, 2.44 mmol, 3 equiv.) (21 h). ^1H NMR (DMSO-d_6): δ 3.86 (3H, s), 7.12–7.15 (2H, m), 7.24–7.45 (13H, m), 7.83 (1H, s), 7.94 (1H, s), 9.42 (1H, s), 12.18 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.2 (CH_3), 115.8 (C), 119.8 (C), 124.1 (CH), 125.9 (CH), 126.6 (CH), 127.35(CH), 127.4 (CH), 127.7 (CH), 127.9 (C), 128.0 (CH), 128.5 (CH), 128.6 (C), 128.7 (CH), 129.0 (CH), 129.7 (CH), 131.1 (C), 131.9 (C), 138.7 (CH), 138.7 (C). HRMS (ESI) m/z: 376.1808 calcd for $C_{26}H_{22}N_3$ [M – Br]$^+$, found 376.1804. IR (KBr, cm^{-1}): ν 3423, 3146, 3094, 3064, 3024, 702.

1-Methyl-3-(2-(4-nitrophenyl)-4,5-diphenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4k): orange-yellow solid, mp > 250 °C, yield 245 mg, 60%, obtained from bromide **1b** (265 mg, 0.81 mmol), 2,3-diphenyl-2*H*-azirine **(2b)** (189 mg, 0.98 mmol, 1.2 equiv.) and Et_3N (247 mg, 2.44 mmol, 3 equiv.) (21 h). ^1H

NMR (DMSO-d_6): δ 3.88 (3H, s), 7.10–7.20 (2H, m), 7.25–7.41 (8H, m), 7.57 (2H, d, J = 8.8), 7.88 (1H, s), 7.94 (1H, s), 8.25 (2H, d, J = 8.8), 9.46 (1H, s), 12.52 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.4 (CH_3), 117.7 (C), 120.8 (C), 124.3 (CH), 124.6 (CH), 125.4 (CH), 125.45 (C), 127.0 (CH), 127.7 (CH), 127.88 (CH), 127.9 (CH), 128.6 (CH), 128.8 (CH), 129.7 (CH), 130.7 (C), 130.73 (C), 131.3 (C), 135.2 (C), 138.7 (CH), 146.1 (C). HRMS (ESI) m/z: 421.1659 calcd for $C_{26}H_{21}N_4O_2$ [M – Br]$^+$, found 421.1645. IR (KBr, cm^{-1}): ν 3059, 1597, 1511, 1340.

3-(2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4l): colorless solid, mp > 250 °C, yield 256 mg, 64%, obtained from bromide **1f** (257 mg, 0.81 mmol), 2,3-diphenyl-2*H*-azirine **(2b)** (189 mg, 0.98 mmol, 1.2 equiv.) and Et_3N (247 mg, 2.44 mmol, 3 equiv.) (18 h). ^{1}H NMR (DMSO-d_6): δ 3.87 (3H, s), 7.12–7.18 (2H, m), 7.24–7.41 (10H, m), 7.49 (2H, d, J = 8.6), 7.86 (1H, t, J = 1.4), 7.92 (1H, t, J = 1.6), 9.45 (1H, s), 12.28 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.2 (CH_3), 116.1 (C), 119.9 (C), 124.3 (CH), 125.7 (CH), 126.6 (C), 127.5 (CH), 127.5 (CH), 127.7 (CH), 127.8 (C), 128.3 (CH), 128.5 (CH), 128.7 (CH), 128.9 (C), 129.0 (CH), 129.7 (CH), 131.0 (C), 131.8 (C), 132.6 (C), 138.7 (CH). HRMS (ESI) m/z: 410.1419 calcd for $C_{26}H_{21}ClN_3$ [M – Br]$^+$, found 410.1422. IR (KBr, cm^{-1}): ν 3418, 3056, 1490, 700.

3-(5-Ethoxycarbonyl-4-methyl-2-(4-nitrophenyl)-1*H*-pyrrol-3-yl)-1-methyl-1*H*-imidazol-3-ium bromide (4m): yellow solid, mp > 250 °C, yield 200 mg, 51%, obtained from bromide **1b** (293 mg, 0.9 mmol), ethyl 3-methyl-2*H*-azirine-2-carboxylate **(2c)** (171 mg, 1.35 mmol, 1.5 equiv.) and Et_3N (273 mg, 2.7 mmol, 3 equiv.) (19 h). ^{1}H NMR (DMSO-d_6): δ 1.34 t (3H, J = 7.1), 2.17 (3H, s), 3.95 (3H, s), 4.36 q (2H, J = 7.1), 7.55 (2H, d, J = 8.9), 7.86 (1H, t, J = 1.6), 7.99 (1H, s), 8.22 (2H, d, J = 8.9), 9.45 (1H, s), 12.89 (1H, s). ^{13}C NMR (DMSO-d_6): δ 8.9 (CH_3), 14.3 (CH_3), 36.4 (CH_3), 60.4 (CH_2), 118.6 (C), 119.8 (C), 123.86 (CH), 123.9 (C), 124.5 (CH), 124.8 (CH), 128.5 (CH), 128.7 (C), 134.2 (C), 138.6 (CH), 146.8 (C), 160.4 (C). HRMS (ESI) m/z: 355.1401 calcd for $C_{18}H_{19}N_4O_4$ [M – Br]$^+$, found 355.1409. IR (KBr, cm^{-1}): ν 3035, 1699, 1510, 1386, 1282.

1-Benzyl-3-(2,4-diphenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4n): colorless solid, mp 245–246 °C, yield 385 mg, 42%, obtained from bromide **1j** (714 mg, 2 mmol), 3-phenyl-2*H*-azirine **(2a)** (328 mg, 2.8 mmol, 1.5 equiv.) and Et_3N (606 mg, 6 mmol, 3 equiv.) (24 h). ^{1}H NMR (DMSO-d_6): δ 5.54 (2H, s), 7.10 (2H, d, J = 7.1), 7.16–7.48 m (14H), 8.00 (1H, s), 8.10 (1H, s), 9.80 (1H, s), 12.29 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.2 (CH_2), 113.1 (C), 116.9 (CH), 121.2 (C), 123.7 (CH), 125.9 (CH), 126.2 (CH), 126.4 (CH), 126.6 (CH), 127.6 (CH), 127.8 (CH), 128.1 (C), 128.7 (CH), 128.8 (CH), 128.96 (CH), 129.0 (CH), 129.2 (C), 132.2 (C), 135.0 (C), 138.8 (CH). HRMS (ESI) m/z: 376.1808 calcd for $C_{26}H_{22}N_3$ [M – Br]$^+$, found 376.1810. IR (KBr, cm^{-1}): ν 3474, 3133, 3035, 2950, 1562, 1495, 774, 709, 650.

1-Benzyl-3-(2-(4-nitrophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4o): yellow solid, mp 245–246 °C, yield 244 mg, 54%, obtained from bromide **1k** (363 mg, 0.9 mmol), 3-phenyl-2*H*-azirine **(2a)** (152 mg, 1.30 mmol, 1.5 equiv.) and Et_3N (274 mg, 2.71 mmol, 3 equiv.) (15 h). ^{1}H NMR (DMSO-d_6): δ 5.52 (2H, s), 7.0–7.14 (2H, m), 7.23–7.35 (5H, m), 7.38–7.46 (5H, m), 7.58 (1H, s), 8.03 (1H, s), 8.13 (1H, s), 8.18 (2H, d, J = 8.7), 9.75 (1H, s), 12.64 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.4 (CH_2), 115.1 (C), 119.2 (CH), 122.2 (C), 124.1 (CH), 124.3 (CH), 125.75 (C), 125.8 (CH), 126.5 (CH), 126.6 (CH), 127.0 (CH), 127.8 (CH), 128.7 (CH), 128.9 (CH), 129.0 (CH), 131.7 (C), 135.0 (C), 135.6 (C), 138.8 (CH), 146.0 (C). HRMS (ESI) m/z: 421.1659 calcd for $C_{26}H_{21}N_4O_2$ [M – Br]$^+$, found 421.1663. IR (KBr, cm^{-1}): ν 3420, 3002, 1600, 1518, 1338, 853, 762.

1-Benzyl-3-(2-(3-nitrophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4p): yellow solid, mp 247–248 °C, yield 343 mg, 75%, obtained from bromide **1l** (365 mg, 0.9 mmol), 3-phenyl-2*H*-azirine **(2a)** (149 mg, 1.27 mmol, 1.5 equiv.) and Et_3N (275 mg, 2.72 mmol, 3 equiv.) (15 h). ^{1}H NMR (DMSO-d_6): δ 5.52 (2H, s), 7.08–7.15 (2H, m), 7.23–7.32 (5H, m), 7.38–7.43 (3H, m), 7.53 (1H, s), 7.60–7.68 (2H, m), 8.06 (1H, s), 8.08 (1H, s), 8.13 (1H, s), 8.17 (1H, d, J = 7.9), 9.75 (1H, s), 12.61 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.3 (CH_2), 114.3 (C), 118.2 (CH), 120.3 (CH), 121.7 (C), 122.2 (CH), 124.0 (CH), 125.7 (C), 126.0 (CH), 126.5 (CH), 126.9 (CH), 127.7 (CH), 128.7 (CH), 128.9 (CH), 128.94 (CH), 130.75 (CH), 130.8 (C), 131.9 (C), 132.0 (CH), 134.8 (C), 138.8 (CH), 148.2 (C). HRMS (ESI) m/z: 421.1659 calcd for $C_{26}H_{21}N_4O_2$ [M – Br]$^+$, found 421.1667. IR (KBr, cm^{-1}): ν 3426, 3022, 1524, 1348, 743.

1-Benzyl-3-(2-(4-bromophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4q): colorless solid, mp 249–250 °C, yield 277 mg, 65%, obtained from bromide **1m** (350 mg, 0.8 mmol), 3-phenyl-2*H*-azirine **(2a)** (132 mg, 1.12 mmol, 1.5 equiv.) and Et_3N (243 mg, 2.41 mmol, 3 equiv.) (22 h). ^{1}H NMR (DMSO-d_6): δ 5.48 (2H, s), 7.07–7.10 (2H, m), 7.13 (2H, d, J = 8.5), 7.22–7.31 (5H, m), 7.39–7.46 (4H, m), 7.54 (2H, d, J = 8.5),7.98 (1H, s), 8.05 (1H, s), 9.65 (1H, s), 12.30 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.3 (CH_2), 113.5 (C), 117.4 (CH), 121.0 (C), 121.4 (C), 123.8 (CH), 126.0 (CH), 126.5 (CH), 126.8 (CH), 127.0 (C), 127.7 (CH), 128.1 (CH), 128.5 (C), 128.7 (CH), 128.9 (CH), 129.0 (CH), 132.0 (CH), 132.1 (C), 135.0 (C), 138.8 (CH). HRMS (ESI) m/z: 456.0913 calcd for $C_{26}H_{21}BrN_3$ [M – Br]$^+$, found 456.0914. IR (KBr, cm^{-1}): ν 3418, 3164, 2988, 1488, 828, 751, 708.

1-Benzyl-3-(2-(3-bromophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4r): colorless solid, mp 221–222 °C, yield 193 mg, 45%, obtained from bromide **1n** (350 mg, 0.8 mmol), 3-phenyl-2*H*-azirine **(2a)** (132 mg, 1.12 mmol, 1.5 equiv.) and Et_3N (243 mg, 2.41 mmol, 3 equiv.) (22 h). ^{1}H NMR (DMSO-d_6): δ 5.50 (2H, s), 7.05–7.13 (3H, m), 7.21–7.32 (6H, m), 7.37–7.43 (4H, m), 7.49 (1H, s), 7.53 (1H, d, J = 8.0), 8.02 (1H, s), 8.05 (1H, s), 9.66 (1H, s), 12.31 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.3 (CH_2), 113.8 (C), 117.7 (CH), 121.5 (C), 122.4 (C), 123.8 (CH), 124.8 (CH), 126.2 (CH), 126.46 (C), 126.5 (CH), 126.8 (CH), 127.6 (CH), 128.6 (CH), 128.7 (CH), 128.9 (CH), 129.1 (CH), 130.6 (CH), 131.2 (CH), 131.5 (C), 132.0 (C), 134.9 (C), 138.8 (CH). HRMS (ESI) m/z: 454.0913 calcd for $C_{26}H_{21}BrN_3$ [M – Br]$^+$, found 454.0909. IR (KBr, cm^{-1}): ν 3419, 3089, 1607, 1562, 1482, 757, 711, 698.

1-Benzyl-3-(2-(4-chlorophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4s): colorless solid, mp 244–245 °C, yield 329 mg, 75%, obtained from bromide **1o** (350 mg, 0.89 mmol), 3-phenyl-2*H*-azirine **(2a)** (146 mg, 1.25 mmol, 1.5 equiv.) and Et_3N (270 mg, 2.68 mmol, 3 equiv.) (24 h). ^{1}H NMR

(DMSO-d_6): δ 5.48 (2H, s), 7.06–7.12 (2H, m), 7.21 (2H, d, J = 8.4), 7.23–7.30 (5H, m), 7.37–7.47 (6H, m), 7.99 (1H, s), 8.06 (1H, s), 9.67 (1H, s), 12.33 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.3 (CH_2), 113.5 (C), 117.3 (CH), 121.3 (C), 123.8 (CH), 126.0 (CH), 126.5 (CH), 126.7 (CH), 126.9 (C), 127.7 (CH), 127.8 (CH), 128.1 (C), 128.7 (CH), 128.8 (CH), 129.0 (CH), 129.1 (CH), 132.1 (C), 132.4 (C), 135.1 (C), 138.8 (CH). HRMS (ESI) m/z: 410.1419 calcd for $C_{26}H_{21}ClN_3$ $[M - Br]^+$, found 410.1411. IR (KBr, cm^{-1}): ν 3422, 3091, 1491, 753, 708.

1-Benzyl-3-(2-(4-methoxyphenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4t): colorless solid, mp 234–235 °C, yield 355 mg, 76%, obtained from bromide **1p** (350 mg, 0.9 mmol), 3-phenyl-2*H*-azirine **(2a)** (148 mg, 1.27 mmol, 1.5 equiv.) and Et_3N (274 mg, 2.71 mmol, 3 equiv.) (24 h). ^{1}H NMR (DMSO-d_6): δ 3.77 (3H, s), 5.49 (2H, s), 6.91 (2H, d, J = 8.8), 7.08 (2H, d, J = 6.6), 7.14 (2H, d, J = 8.7), 7.20–7.31 (5H, m), 7.33 (1H, d, J = 1.8), 7.38–7.47 (3H, m), 7.97 (1H, s), 8.05 (1H, s), 9.71 (1H, s), 12.11 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.3 (CH_2), 55.3 (CH_3), 112.4 (C), 114.5 (CH), 116.2 (CH), 120.9 (C), 121.7 (C), 123.6 (CH), 126.3 (CH), 126.4 (CH), 126.6 (CH), 127.6 (CH), 127.7 (CH), 128.3 (C), 128.7 (CH), 128.8 (CH), 129.0 (CH), 132.4 (C), 135.1 (C), 138.9 (CH), 158.9 (C). HRMS (ESI) m/z: 406.1914 calcd for $C_{27}H_{24}ON_3$ $[M - Br]^+$, found 406.1913. IR (KBr, cm^{-1}): ν 3406, 3084, 2996, 1507, 1251, 748, 708.

1-Benzyl-3-(2-(4-fluorophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4u): colorless solid, mp 224–225 °C, yield 365 mg, 78%, obtained from bromide **1q** (350 mg, 0.93 mmol), 3-phenyl-2*H*-azirine **(2a)** (153 mg, 1.31 mmol, 1.5 equiv.) and Et_3N (283 mg, 2.8 mmol, 3 equiv.) (18 h). ^{1}H NMR (DMSO-d_6): δ 5.49 (2H, s), 7.02–7.12 (2H, m), 7.14–7.33 (9H, m), 7.36 (1H, s), 7.38–7.48 (3H, m), 7.93 (1H, s), 8.02 (1H, s), 9.68 (1H, s), 12.25 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.5 (CH_2), 113.3 (C), 116.2 d (CH, $^2J_{CF}$ = 21.6), 117.0 (CH), 121.3 (C), 123.8 (CH), 125.9 (C), 126.0 (CH), 126.3 (CH), 126.6 (CH), 126.9 (CH), 127.6 (C), 127.8 (CH), 128.6 d (CH, $^3J_{CF}$ = 8.4), 129.0 (CH), 129.1 (CH), 129.2 (CH), 132.3 (C), 135.1 (C), 138.9 (CH), 161.8 d (C, $^1J_{CF}$ = 245.7). HRMS (ESI) m/z: 394.1714 calcd for $C_{26}H_{21}FN_3$ $[M - Br]^+$, found 394.1735. IR (KBr, cm^{-1}): ν 3416, 3098, 1503, 1238, 838, 755, 709.

1-Benzyl-3-(2-(3-nitrophenyl)-4,5-diphenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4v): yellow solid, mp 248–249 °C, yield 226 mg, 63%, obtained from bromide **1l** (250 mg, 0.62 mmol), 2,3-diphenyl-2*H*-azirine **(2b)** (168 mg, 0.88 mmol, 1.5 equiv.) and Et_3N (188 mg, 1.87 mmol, 3 equiv.) (15 h). ^{1}H NMR (DMSO-d_6): δ 5.45 (2H, s), 7.07–7.11 (2H, m),7.14 (2H, d, J = 7.0), 7.24–7.45 (11H, m), 7.62–7.73 (2H, m), 7.96 (1H, s), 8.02 (1H, s), 8.20 (1H, d, J = 7.0), 8.3 (1H, s), 9.64 (1H, s), 12.52 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.1 (CH_2), 117.0 (C), 120.1 (C), 121.0 (CH), 122.4 (CH), 123.5 (CH), 125.2 (C), 126.1 (CH), 127.4 (CH), 127.6 (CH), 127.7 (CH), 127.7 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.9 (CH), 129.6 (CH), 130.5 (C), 130.6 (CH), 130.8 (C), 131.4 (C), 132.5 (CH), 134.7 (C), 138.7 (CH), 148.2 (C). HRMS (ESI) m/z: 497.1972 calcd for $C_{32}H_{25}N_4O_2$ $[M - Br]^+$, found 497.1969. IR (KBr, cm^{-1}): ν 3142, 3086, 1531, 1342.

1-Benzyl-3-(2-(4-bromophenyl)-4,5-diphenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4w): colorless solid, mp > 250 °C, yield 138 mg, 55%, obtained from bromide **1m** (180 mg, 0.41 mmol), 2,3-diphenyl-2*H*-azirine **(2b)** (112 mg, 0.58 mmol, 1.5 equiv.) and Et_3N (125 mg, 1.24 mmol, 3 equiv.) (24 h). ^{1}H NMR (DMSO-d_6): δ 5.43 (2H, s), 7.05–7.16 (4H, m), 7.22–7.43 (13H, m), 7.59 (2H, d, J = 10.8), 7.91 (1H, s), 7.94 (1H, s), 9.59 (1H, s), 12.27 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.1 (CH_2), 116.3 (C), 119.9 (C), 121.2 (C), 123.3 (CH), 126.1 (CH), 126.5 (C), 127.4 (CH), 127.4 (CH), 127.45 (CH), 127.6 (CH), 128.1 (C), 128.5 (CH), 128.55 (CH), 128.6 (CH), 128.7 (CH), 128.9 (C), 128.9 (CH), 129.7 (CH), 130.9 (C), 131.7 (C), 131.9 (CH), 134.9 (C), 138.7 (CH). HRMS (ESI) m/z: 530.1226 calcd for $C_{32}H_{25}BrN_3$ $[M - Br]^+$, found 530.1230. IR (KBr, cm^{-1}): ν 3057, 1489, 831, 706.

1-Benzyl-3-(2-(4-chlorophenyl)-4,5-diphenyl-1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromide (4x): colorless solid, mp > 250 °C, yield 150 mg, 55%, obtained from bromide **1o** (250 mg, 0.64 mmol), 2,3-diphenyl-2*H*-azirine **(2b)** (172 mg, 0.89 mmol, 1.5 equiv.) and Et_3N (193 mg, 1.91 mmol, 3 equiv.) (24 h). ^{1}H NMR (DMSO-d_6): δ 5.43 (2H, s), 7.05–7.15 (4H, m), 7.22–7.43 (13H, m), 7.46 (2H, d, J = 8.5), 7.91 (1H, s), 7.94 (1H, s), 9.60 (1H, s), 12.27 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.1 (CH_2), 116.3 (C), 119.8 (C), 123.3 (CH), 126.1 (CH), 126.5 (C), 127.4 (CH), 127.4 (CH), 127.45 (CH), 127.6 (CH), 127.7 (C), 128.4 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.8 (C), 128.9 (CH), 128.95 (CH), 129.6 (CH), 130.9 (C), 131.7 (C), 132.6 (C), 134.8 (C), 138.7 (CH). HRMS (ESI) m/z: 486.1732 calcd for $C_{32}H_{25}ClN_3$ $[M - Br]^+$, found 486.1734. IR (KBr, cm^{-1}): ν 3038, 1558, 1491, 1080, 754, 710.

General procedure for the debenzylation of 1-benzyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides 4n-u. Pd/C (10 wt%) was added to solution of 1-benzyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides **4** (0.3 mmol) and ammonium formate (189 mg, 3 mmol, 10 equiv.) in MeOH (15 mL). The resulting suspension was refluxed for 1.5–3 h. The conversion was monitored by TLC (MeOH/DCM 1:10). After the completion of the reaction the reaction mixture was evaporated to dryness and suspended in water and then the product was filtered, washed with water and dried.

1-(2,4-Diphenyl-1*H*-pyrrol-3-yl)-1*H*-imidazole (5a): colorless solid, mp > 250 °C, yield 82 mg, 88%, obtained from salt **4n** (150 mg, 0.33 mmol), ammonium formate (207 mg, 3.29 mmol, 10 equiv.) and Pd/C (15 mg, 10 wt%) (2 h, here and below the duration of reflux). ^{1}H NMR (DMSO-d_6): δ 6.95–7.40 (13H, m), 7.64 (1H, s), 11.84 (1H, s). ^{13}C NMR (DMSO-d_6): δ 116.0 (C), 116.5 (CH), 121.7 (C), 122.5 (CH), 125.1 (CH), 125.9 (CH), 126.2 (CH), 127.1 (CH), 127.5 (C), 128.7 (CH), 128.9 (CH), 129.5 (CH), 130.6 (C), 133.6 (C), 139.2 (CH). HRMS (ESI) m/z: 286.1339 calcd for $C_{19}H_{16}N_3$ $[M + H]^+$, found 286.1344. IR (KBr, cm^{-1}): ν 3470, 3115, 3059, 2901, 1609, 1493, 1069, 741, 696.

4-(3-(1*H*-Imidazol-1-yl)-4-phenyl-1*H*-pyrrol-2-yl)aniline (5b): colorless solid, mp >250 °C, yield 72 mg, 80%, obtained from salt **4o** (150 mg, 0.30 mmol), ammonium formate (189 mg, 3.0 mmol, 10 equiv.) and Pd/C (15 mg, 10 wt%) (1.5 h). ^{1}H NMR (DMSO-d_6): δ 5.17 (2H, s), 6.45 (2H, d, J = 8.5), 6.79 (2H, d, J = 8.5), 7.00 (2H, d, J = 7.3), 7.06–7.13 (2H, m), 7.14–7.22 (4H, m), 7.59 (1H, s), 11.45 (1H, s). ^{13}C NMR (DMSO-d_6): δ 113.8 (CH), 114.5 (CH), 118.2 (C), 120.9 (C), 122.5 (CH), 125.6 (CH), 125.6 (CH), 126.1 (CH), 128.4 (CH), 128.7 (C), 129.1 (CH), 133.9 (C),

139.1 (CH), 147.8 (C). HRMS (ESI) m/z: 301.1448 calcd for $C_{19}H_{17}N_4$ [M + H]$^+$, found 301.1451. IR (KBr, cm^{-1}): ν 3460, 3367, 3117, 3061, 1603, 1504, 833, 748.

1-(2-(4-Methoxyphenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazole (5c): colorless solid, mp 216–217 °C, yield 86 mg, 88%, obtained from salt **4t** (150 mg, 0.29 mmol), ammonium formate (183 mg, 2.9 mmol, 10 equiv.) and Pd/C (15 mg, 10 wt%) (1 h). ^{1}H NMR (DMSO-d$_6$): δ 3.73 (3H, s), 6.87 (2H, d, *J* = 8.8), 6.99–7.07 (4H, m), 7.08–7.15 (2H, m), 7.16–7.28 (4H, m), 7.62 (1H, s), 11.68 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 55.1 (CH_3), 114.2 (CH), 115.0 (C), 115.5 (CH), 121.2 (C), 122.4 (CH), 123.1 (C), 125.7 (CH), 125.8 (CH), 126.4 (CH), 127.4 (C), 128.5 (CH), 129.3 (CH), 133.6 (C), 139.1 (CH), 158.2 (C). HRMS (ESI) m/z: 316.1444 calcd for $C_{20}H_{18}N_3O$ [M + H]$^+$, found 316.1447. IR (KBr, cm^{-1}): ν 3111, 1600, 1503, 1254, 831.

1-(2-(4-Fluorophenyl)-4-phenyl-1*H*-pyrrol-3-yl)-1*H*-imidazole (5d): colorless solid, mp > 250 °C, yield 86 mg, 90%, obtained from salt **4u** (150 mg, 0.32 mmol), ammonium formate (200 mg, 3.2 mmol, 10 equiv.) and Pd/C (15 mg, 10 wt%) (3 h). ^{1}H NMR (DMSO-d$_6$): δ 7.03 (2H, d, *J* = 7.6), 7.09–7.28 (9H, m), 7.33 (1H, s), 7.65 (1H, s), 11.84 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 115.7 d (CH, $^2J_{CF}$ = 21.7), 115.8 (C), 116.3 (CH), 121.4 (C), 122.2 (CH), 125.7 (CH), 125.9 (CH), 126.5 (C), 127.0 d (CH, $^3J_{CF}$ = 8.1), 127.1 (C), 128.5 (CH), 129.5 (CH), 133.4 (C), 139.0 (CH), 161.0 d (C, $^1J_{CF}$ = 244.7). HRMS (ESI) m/z: 304.1245 calcd for $C_{19}H_{15}FN_3$ [M + H]$^+$, found 304.1246. IR (KBr, cm^{-1}): ν 3140, 3117, 3047, 2878, 1518, 1504, 1229, 1067, 841, 743, 694.

General procedure for the synthesis of 3-(1-alkyl-1*H*-imidazol-3-ium-3-yl)-pyrrol-1-ides 6a-n. A suspension of 1-alkyl-3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides **4a-o** (0.24–0.94 mmol) in aq solution of KOH (2 equiv., 15–50 mL H_2O, approx. 0.036 M) was sonicated in ultrasonic bath for 30 min and then vigorously stirred for 12 h. The precipitate was filtered, washed with water, and thoroughly dried to obtain analytically pure pyrrolide **6**.

3-(1-Methyl-1*H*-imidazol-3-ium-3-yl)-2,4-diphenylpyrrol-1-ide (6a): colorless solid, mp 182–185 °C, yield 154 mg, 98%, obtained from salt **4a** (200 mg, 0.53 mmol) and aq KOH (59 mg, 1.05 mmol, 2 equiv., 30 mL H_2O). ^{1}H NMR (DMSO-d$_6$): δ 3.92 (3H, s), 7.02 (2H, d, *J* = 7.4), 7.05–7.30 (9H, m), 7.91 (2H, s), 9.32 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 36.1 (CH_3), 112.3 (C), 120.5 (C), 122.1 (CH), 124.3 (CH), 125.0 (CH), 125.2 (CH), 125.5 (CH), 125.7 (CH), 126.1 (CH), 128.6 (CH), 128.7 (CH), 131.3 (C), 133.6 (C), 134.5 (C), 138.4 (CH). HRMS (ESI) m/z: 300.1495 calcd for $C_{20}H_{18}N_3$ [M + H]$^+$, found 300.1498. IR (KBr, cm^{-1}): ν 3138, 3107, 1594, 772, 702.

3-(1-Methyl-1*H*-imidazol-3-ium-3-yl)-2-(4-nitrophenyl)-4-phenylpyrrol-1-ide (6b): cherry red solid, mp 234–236 °C, yield 80 mg, 99%, obtained from salt **4b** (100 mg, 0.24 mmol) and aq KOH (26 mg, 0.48 mmol, 2 equiv., 15 mL H_2O). ^{1}H NMR (DMSO-d$_6$): δ 3.95 (3H, s), 6.99 (2H, d, *J* = 7.5), 7.02–7.10 (1H, m), 7.16–7.31 (3H, m), 7.26 (2H, d, *J* = 8.7), 7.90 (1H, s), 7.95 (1H, s), 7.98 (2H, d, *J* = 8.7), 9.32 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 36.2 (CH_3), 114.8 (C), 122.3 (C), 123.2 (CH), 124.1 (CH), 124.55 (CH), 124.6 (CH), 125.1 (CH), 125.8 (CH), 128.7 (CH), 130.2 (CH), 131.9 (C), 135.4 (C), 138.0 (CH), 142.4 (C), 143.8 (C). HRMS (ESI) m/z: 345.1346 calcd for $C_{20}H_{17}N_4O_2$ [M + H]$^+$, found 345.1348. IR (KBr, cm^{-1}): ν 3130, 3071, 1590, 1322, 1295.

3-(1-Methyl-1*H*-imidazol-3-ium-3-yl)-2-(3-nitrophenyl)-4-phenylpyrrol-1-ide (6c): orange solid, mp 138–140 °C, yield 317 mg, 98%, obtained from salt **4c** (400 mg, 0.94 mmol) and aq KOH (105 mg, 1.88 mmol, 2 equiv., 50 mL H_2O). ^{1}H NMR (DMSO-d$_6$): δ 3.93 (3H, s), 6.92–7.09 (4H, m), 7.12–7.22 (2H, m), 7.34–7.51 (2H, m), 7.75 (1H, d, *J* = 7.3), 7.85 (1H, s), 7.87 (1H, s), 7.95 (1H, s), 9.23 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 36.1 (CH_3), 112.9 (C), 117.75 (CH), 117.8 (CH), 120.9 (C), 124.2 (CH), 124.5 (CH), 125.0 (CH), 126.2 (CH), 128.4 (CH), 128.8 (CH), 129.7 (CH), 129.75 (CH), 131.8 (C), 136.1 (C), 138.2 (CH), 139.2 (C), 148.3 (C). HRMS (ESI) m/z: 345.1346 calcd for $C_{20}H_{17}N_4O_2$ [M + H]$^+$, found 345.1351. IR (KBr, cm^{-1}): ν 3080, 1530, 1348.

2-(4-Bromophenyl)-3-(1-methyl-1*H*-imidazol-3-ium-3-yl)-4-phenylpyrrol-1-ide (6d): yellowish solid, mp 165–168 °C, yield 120 mg, 98%, obtained from salt **4d** (150 mg, 0.33 mmol) and aq KOH (37 mg, 0.66 mmol, 2 equiv., 20 mL H_2O). ^{1}H NMR (DMSO-d$_6$): δ 3.91 (3H, s), 6.90–7.10 (6H, m), 7.13–7.24 (2H, m), 7.33 (2H, d, *J* = 7.9), 7.80 (1H, s), 7.87 (1H, s), 9.21 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 36.1 (CH_3), 112.3 (C), 117.2 (C), 120.5 (C), 124.3 (CH), 124.5 (CH), 125.1 (CH), 125.7 (CH), 126.1 (CH), 126.6 (CH), 128.8 (CH), 131.3 (CH), 131.9 (C), 135.3 (C), 135.6 (C), 138.2 (CH). HRMS (ESI) m/z: 378.0600 calcd for $C_{20}H_{17}BrN_3$ [M + H]$^+$, found 378.0610. IR (KBr, cm^{-1}): ν 3054, 1600, 1526, 1488, 829, 758.

2-(3-Bromophenyl)-3-(1-methyl-1*H*-imidazol-3-ium-3-yl)-4-phenylpyrrol-1-ide (6e): yellowish solid, mp 128–130 °C, yield 204 mg, 99%, obtained from salt **4e** (250 mg, 0.54 mmol) and aq KOH (61 mg, 1.09 mmol, 2 equiv., 30 mL H_2O). ^{1}H NMR (DMSO-d$_6$): δ 3.92 (3H, s), 6.92 (1H, d, *J* = 7.6), 6.97 (2H, d, *J* = 7.4), 7.01–7.13 (3H, m), 7.14–7.24 (3H, m), 7.45 (1H, s), 7.86 (1H, s), 7.91 (1H, s), 9.24 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 36.1 (CH_3), 112.5 (C), 120.6 (C), 122.1 (C), 122.8 (CH), 124.3 (CH), 124.5 (CH), 125.2 (CH), 126.1 (CH), 126.2 (CH), 126.9 (CH), 127.3 (CH), 128.8 (CH), 130.6 (CH), 131.5 (C), 135.6 (C), 138.3 (CH), 138.5 (C). HRMS (ESI) m/z: 378.0600 calcd for $C_{20}H_{17}BrN_3$ [M + H]$^+$, found 378.0611. IR (KBr, cm^{-1}): ν 3063, 1590, 1521, 755.

2-(4-Chlorophenyl)-3-(1-methyl-1*H*-imidazol-3-ium-3-yl)-4-phenylpyrrol-1-ide (6f): colorless solid, mp 226–227 °C, yield 159 mg, 99%, obtained from salt **4f** (200 mg, 0.48 mmol) and aq KOH (54 mg, 0.97 mmol, 2 equiv., 30 mL H_2O). ^{1}H NMR (DMSO-d$_6$): δ 3.91 (3H, s), 6.93 (2H, d, *J* = 7.5), 6.96–7.01 (2H, m), 7.08–7.20 (6H, m), 7.83 (1H, s), 7.89 (1H, s), 9.20 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 35.9 (CH_3), 111.8 (C), 120.1 (C), 123.6 (CH), 124.1 (CH), 124.6 (CH), 125.6 (CH), 126.2 (CH), 127.5 (CH), 127.7 (C), 128.0 (CH), 128.5 (CH), 132.9 (C), 136.4 (C), 136.5 (C), 138.0 (CH). HRMS (ESI) m/z: 334.1106 calcd for $C_{20}H_{17}ClN_3$ [M + H]$^+$, found 334.1107. IR (KBr, cm^{-1}): ν 3131, 3022, 1596, 1526, 928, 834, 721.

2-(4-Methoxyphenyl)-3-(1-methyl-1*H*-imidazol-3-ium-3-yl)-4-phenylpyrrol-1-ide (6g): colorless solid, mp 133–135 °C, yield 102 mg, 85%, obtained from salt **4g** (150 mg, 0.37 mmol) and aq KOH (41 mg, 0.73 mmol, 2 equiv., 20 mL H_2O). ^{1}H NMR (DMSO-d$_6$): δ 3.68 (3H, s), 3.90 (3H, s), 6.72 (2H, d, *J* = 8.8), 6.87–6.98 (4H, m), 7.07 (2H, d, *J* = 8.7), 7.10–7.18 (2H, m), 7.74 (1H, s), 7.82 (1H, s), 9.10 (1H, s). ^{13}C NMR (DMSO-d$_6$): δ 36.0 (CH_3), 55.0 (CH_3), 110.8 (C), 113.8 (CH), 119.3 (C), 123.5 (CH),

123.9 (CH), 124.6 (CH), 125.7 (CH), 126.5 (CH), 126.6 (CH), 128.7 (CH), 130.6 (C), 134.4 (C), 136.9 (C), 138.1 (CH), 156.3 (C). HRMS (ESI) m/z: 330.1601 calcd for $C_{21}H_{20}N_3O$ $[M + H]^+$, found 330.1611. IR (KBr, cm^{-1}): ν 3058, 2834, 1601, 1530, 1244, 830, 760.

2-(4-Fluorophenyl)-3-(1-methyl-1*H*-imidazol-3-ium-3-yl)-4-phenylpyrrol-1-ide (6h): colorless solid, mp 208–210 °C, yield 118 mg, 99%, obtained from salt **4i** (150 mg, 0.38 mmol) and aq KOH (42 mg, 0.76 mmol, 2 equiv., 20 mL H_2O). ^1H NMR (DMSO-d_6): δ 3.92 (3H, s), 7.03 (2H, d, J = 7.5), 7.06–7.15 (3H, m), 7.18 (1H, s), 7.19–7.29 (4H, m), 7.88 (1H, s), 7.92 (1H, s), 9.33 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.2 (CH_3), 112.3 (C), 115.6 d (CH, $^2J_{CF}$ = 21.3), 120.6 (C), 121.4 (CH), 124.4 (CH), 125.4 (CH), 125.7 (CH), 126.0 (CH), 127.4 d (CH, $^3J_{CF}$ = 7.9), 128.8 (CH), 129.7 (C), 130.1 (C), 134.2 (C), 138.5 (CH), 160.7 d (C, $^1J_{CF}$ = 243.2). HRMS (ESI) m/z: 378.1401, calcd for $C_{20}H_{17}FN_3$ $[M + H]^+$, found 318.1411. IR (KBr, cm^{-1}): ν 3107, 1533, 1505, 839, 761.

3-(1-Methyl-1*H*-imidazol-3-ium-3-yl)-2,4,5-triphenylpyrrol-1-ide (6i): colorless solid, mp 192–195 °C, yield 146 mg, 88%, obtained from salt **4j** (200 mg, 0.44 mmol) and aq KOH (49 mg, 0.88 mmol, 2 equiv., 25 mL H_2O). ^1H NMR (DMSO-d_6): δ 3.83 (3H, s), 7.00–7.06 (1H, m), 7.07–7.12 (3H, m), 7.12–7.18 (3H, m), 7.19–7.31 (6H, m), 7.40 (2H, d, J = 7.2), 7.76 (1H, s), 7.79 (1H, s), 9.20 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.7 (CH_3), 114.6 (C), 119.6 (C), 123.1 (CH), 123.2 (CH), 123.4 (CH), 124.2 (CH), 124.9 (CH), 126.1 (CH), 126.5 (CH), 127.3 (CH), 128.0 (CH), 128.0 (CH), 129.4 (CH), 133.0 (C), 135.7 (C), 137.4 (C), 137.9 (CH), 138.0 (C), 140.0 (C). HRMS (ESI) m/z: 376.1808 calcd for $C_{26}H_{22}N_3$ $[M + H]^+$, found 376.1817. IR (KBr, cm^{-1}): ν 3060, 1597, 699.

3-(1-Methyl-1*H*-imidazol-3-ium-3-yl)-2-(4-nitrophenyl)-4,5-diphenylpyrrol-1-ide (6j): cherry red solid, mp 158–160 °C, yield 142 mg, 91%, obtained from salt **4k** (190 mg, 0.38 mmol) and aq KOH (42 mg, 0.76 mmol, 2 equiv., 20 mL H_2O). ^1H NMR (DMSO-d_6): δ 3.85 (3H, s), 6.96–7.02 (1H, m), 7.03–7.16 (5H, m), 7.17–7.24 (2H, m), 7.33 (2H, d, J = 8.9), 7.40 (2H, d, J = 7.6), 7.76 (2H, d, J = 7.1), 7.98 (2H, d, J = 8.9), 9.19 (1H, s). ^{13}C NMR (DMSO-d_6): δ 36.1 (CH_3), 118.2 (C), 122.5 (C), 123.3 (CH), 124.0 (CH), 124.2 (CH), 124.5 (CH), 125.9 (CH), 126.1 (CH), 126.7 (CH), 127.7 (CH), 128.3 (CH), 129.6 (CH), 131.1 (C), 136.3 (C), 138.0 (CH), 139.0 (C), 139.5 (C), 142.2 (C), 144.3 (C). HRMS (ESI) m/z: 421.1659 calcd for $C_{26}H_{21}N_4O_2$ $[M + H]^+$, found 421.1655. IR (KBr, cm^{-1}): ν 3152, 1589, 1330.

2-(4-Chlorophenyl)-3-(1-methyl-1*H*-imidazol-3-ium-3-yl)-4,5-diphenylpyrrol-1-ide (6k): colorless solid, mp 175–178 °C, yield 117 mg, 98%, obtained from salt **4l** (143 mg, 0.29 mmol) and aq KOH (33 mg, 0.58 mmol, 2 equiv., 15 mL H_2O). ^1H NMR (DMSO-d_6): δ 3.81 (3H, s), 6.90–6.96 (1H, m), 7.00–7.12 (5H, m), 7.13–7.22 (6H, m), 7.38 (2H, d, J = 7.5), 7.68 (2H, s), 9.06 (1H, s). ^{13}C NMR (DMSO-d_6): δ 35.9 (CH_3), 115.2 (C), 120.0 (C), 123.5 (CH), 123.7 (CH), 125.3 (CH), 126.0 (CH), 126.4 (CH), 126.6 (CH), 127.6 (CH), 127.9 (C), 128.1 (CH), 128.2 (CH), 129.6 (CH), 132.0 (C), 136.3 (C), 136.6 (C), 137.1 (C), 138.0 (CH), 139.7 (C). HRMS (ESI) m/z: 410.1419 calcd for $C_{26}H_{21}ClN_3$ $[M + H]^+$, found 410.1428. IR (KBr, cm^{-1}): ν 3062, 1594, 1520, 828, 698.

2-(Ethoxycarbonyl)-3-methyl-4-(1-methyl-1*H*-imidazol-3-ium-3-yl)-5-(4-nitrophenyl)pyrrol-1-ide (6l): orange-red solid, mp > 250 °C, yield 108 mg, 94%, obtained from salt **4m** (141 mg, 0.32 mmol) and aq KOH (36 mg, 0.65 mmol, 2 equiv., 15 mL H_2O). ^1H NMR (DMSO-d_6): δ 1.26 (3H, t, J = 7.0), 2.02 (3H, s), 3.96 (3H, s), 4.16 (2H, q, J = 7.0), 7.30 (2H, d, J = 8.8), 7.77 (1H, s), 7.93 (1H, s), 7.99 (2H, d, J = 8.9), 9.28 (1H, s). ^{13}C NMR (DMSO-d_6): δ 10.2 (CH_3), 14.8 (CH_3), 36.0 (CH_3), 57.8 (CH_2), 118.3 (C), 123.78 (CH), 123.8 (C), 123.9 (CH), 124.2 (CH), 125.0 (CH), 129.0 (C), 132.3 (C), 137.8 (CH), 143.0 (C), 143.9 (C), 164.8 (C). HRMS (ESI) m/z: 355.1401 calcd for $C_{18}H_{19}N_4O_4$ $[M + H]^+$, found 355.1412. IR (KBr, cm^{-1}): ν 2946, 1670, 1657, 1589, 1297.

3-(1-Benzyl-1*H*-imidazol-3-ium-3-yl)-2,4-diphenylpyrrol-1-ide (6m): colorless solid, mp 165–170 °C, yield 186 mg, 90%, obtained from salt **4n** (250 mg, 0.55 mmol) and aq KOH (61 mg, 1.1 mmol, 2 equiv., 30 ml H_2O). ^1H NMR (DMSO-d_6): δ 5.48 (2H, s), 6.93 (2H, d, J = 7.3), 6.97–7.04 (2H, m), 7.05 (1H, s), 7.09–7.17 (6H, m), 7.32 (2H, d, J = 6.5), 7.38–7.48 (3H, m), 7.86 (1H, s), 7.98 (1H, s), 9.53 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.1 (CH_2), 111.8 (C), 120.0 (C), 123.1 (CH), 124.1 (CH), 124.5 (CH), 124.6 (CH), 124.9 (CH), 124.95 (CH), 126.7 (CH), 127.6 (CH), 128.2 (CH), 128.5 (CH), 128.6 (CH), 129.0 (CH), 132.9 (C), 135.4 (C), 135.7 (C), 135.9 (C), 138.1 (CH). HRMS (ESI) m/z: 376.1808 calcd for $C_{26}H_{22}N_3$ $[M + H]^+$, found 376.1802. IR (KBr, cm^{-1}): ν 3134, 1606, 771, 696.

3-(1-Benzyl-1*H*-imidazol-3-ium-3-yl)-2-(4-nitrophenyl)-4-phenylpyrrol-1-ide (6n): red solid, mp 237–238 °C, yield 245 mg, 99%, obtained from salt **4o** (300 mg, 0.6 mmol) and aq KOH (67 mg, 1.2 mmol, 2 equiv., 35 mL H_2O). ^1H NMR (DMSO-d_6): δ 5.50 (2H, s), 6.93 (2H, d, J = 7.5), 6.99–7.08 (1H, m), 7.09–7.26 (5H, m), 7.33–7.49 (5H, m), 7.87 (2H, d, J = 8.8), 7.91 (1H, s), 8.06 (1H, s), 9.55 (1H, s). ^{13}C NMR (DMSO-d_6): δ 52.3 (CH_2), 114.7 (C), 122.2 (C), 122.8 (CH), 123.6 (CH), 123.9 (CH), 124.3 (CH), 124.9 (CH), 126.3 (CH), 127.8 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 131.2 (CH), 132.3 (C), 135.4 (C), 135.6 (C), 137.9 (CH). 142.0 (C), 144.5 (C). HRMS (ESI) m/z: 421.1659 calcd for $C_{26}H_{21}N_4O_2$ $[M + H]^+$, found 421.1665. IR (KBr, cm^{-1}): ν 3124, 1587, 1531, 1489, 1298, 1103.

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Notes and references

Institute of Chemistry, Saint Petersburg State University, Universitetskii pr. 26, 198504 St. Petersburg, Russia. Fax: +7 812 4286939; Tel: +7 812 4284021; E-mail: alexander.khlebnikov@pobox.spbu.ru

† Electronic Supplementary Information (ESI) available: [^1H and ^{13}C NMR spectra for all new compounds. X-ray crystallographic data for compounds **4b**, **4n**, and **6b**. CCDC **4b** 992831, **4n** 992996, **6b** 991739. Computational details: energies of molecules **6**, **7**, and their Cartesian coordinates of atoms.]. See DOI: 10.1039/b000000x/

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