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Synthesis, Transformations of Pyrrole- and 1,2,4-Triazole-Containing Ensembles, and Generation of Pyrrole-Substituted Triazole NHC

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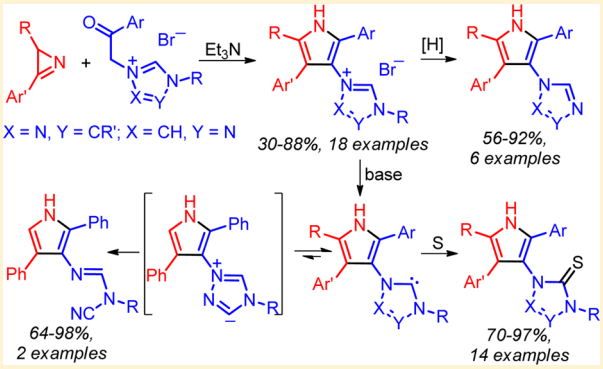
Supporting Information

ABSTRACT: Unprecedented pyrrole- and 1,2,4-triazole-containing ensembles, substituted 1-(1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazol-1-ium bromides and 4-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazol-4-ium bromides, were prepared from 2*H*-azirines and triazolium phenacyl bromides using a simple procedure. *N*-(1*H*-Pyrrol-3-yl)-*N*′-benzyltriazolium bromides undergo reductive debenzylation on Pd/C to give substituted 1-(1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazoles and 4-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazoles in high yields. Betaines (triazoliumylpyrrolides) and pyrrolyltriazole NHCs, which are possible products of dehydrobromination of pyrrolyltriazolium salts, have comparable thermodynamic stabilities in nonpolar solvents according to calculations at the DFT B3LYP/6-31G(d) level. The carbene forms can be easily trapped by the reaction of salts with base in the presence of sulfur. The corresponding 1- and 4-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazole-5(4*H*)-thiones are formed in high yields. In the absence of sulfur as a trap, the opening of the triazole ring occurs with the formation of derivatives of *N*-cyanoformimidamide. According to the DFT calculations the latter is most probably formed via a pyrrolyltriazoliumide intermediate, which is the minor component of the equilibrium triazoliumylpyrrolide−pyrrolyltriazole NHC−pyrrolyltriazoliumide. Blocking of the pyrrolyltriazoliumide intermediate formation, by introduction of a substituent at the 3-position of the triazole ring, made it possible to generate the first pyrrole-substituted triazole NHC.



INTRODUCTION

The pyrrole moiety is present in the most important natural molecular systems (chlorophyll, hemoglobin, hormones, pigments, pheromones, and antibiotics), as well as in synthetic drugs, fluorophores, and numerous advanced materials.[1] In contrast, the 1,2,4-triazole ring is very rare in natural product scaffolds.[2] At the same time, it is a component of a wide range of synthetic biologically active compounds[3] and has a wide variety of uses in materials science.[4] Despite the diverse pharmacological activities that are inherent to pyrrole and 1,2,4-triazole-containing compounds alone, only a few structural combinations of derivatives of these heterocycles have been reported.[5−8] Thus, 1-[4-(pyrrol-1-yl)phenylmethyl]-l*H*-1,2,4-triazoles can be used in the treatment of circulatory disorders; they are particularly useful in the treatment or control of hypertension and congestive heart failure.[6] Derivatives of 4-triazolylpyrrole-2-carboxylic acid were patented as inhibitors of c-Met protein kinase,[7] and l*H*-1,2,4-triazoles with substituents containing pyrrole derivatives are useful in the treatment of a disorder mediated by kinesin spindle protein.[8] It was also found that the combination of the plant microbicides 4-(2,3-dichlorophenyl)-1*H*-pyrrole-3-carbonitrile and 1-[2-[2-chloro-4-(4-chlorophenoxy)phenyl]-2-methoxybutyl]-1*H*-1,2,4-triazole results in a synergistically enhanced activity in the control of plant diseases.[9] All of this demonstrates the potential utility of compounds containing both pyrrole and 1,2,4-triazole fragments for medicinal chemistry and agriculture. To extend the use of such compounds, there is a need to develop simple and effective methods for their preparation.

Another important point is that derivatives of 1-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazole and 4-(1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazole can serve as sources of new heterocyclic betaines and/or carbenes. Interchange of N-heterocyclic carbenes (NHCs) and heterocyclic betaines has been intensively investigated now as an important tool for generating and modifying NHCs. The achievements in this field were recently reviewed.[10] Furthermore, many papers studying various types of such tautomeric equilibria have been published in the past few years.[10,11] 1,2,4-Triazole-containing structures were studied from this point of view in only three works.[11c,e,g] Meanwhile, NHCs from 1,2,4-triazolium salts have been widely used in metal-free organocatalysis.[12,13]

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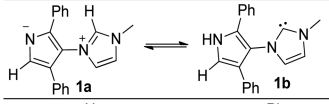
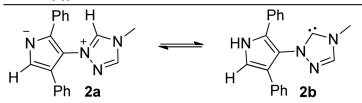
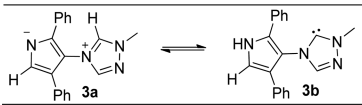
Table 1. Gibbs Free Energy of Betaine−Carbene Tautomerization for Betaines 1a−3a[a]

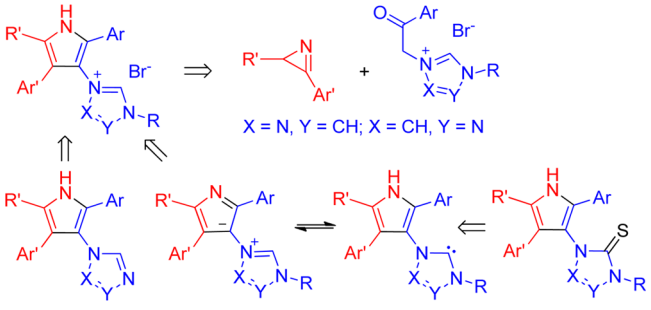
Equilibrium	Gas phase	DCM	THF	MeOH
	0.2	8.7	8.2	9.7
	-9.1	0.0	-0.5	2.0
	-6.4	0.5	0.1	1.6

[a] $\Delta G_{\text{carbene-betaine}}$ values are given in units of kcal mol^{-1}; calculations were carried out at the DFT B3LYP/6-31G(d) level in the gas phase or with the PCM model for the solvents at 298 K.

In the framework of our research concerning the synthesis of aza heterocycles by ring expansion of strained azirines,[14,15] we have recently presented an effective approach to pyrrolyl-substituted heterocycles based on annulation of azirines with nitrogen ylides.[15h] Reaction of azirines with imidazolium phenacylides as nucleophiles led to derivatives of 1-(1*H*-pyrrol-3-yl)imidazole.[11d,f] It was found that synthesized 3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides under the action of a base easily give a new type of stable betaine, 3-(1*H*-imidazol-3-ium-3-yl)pyrrol-1-ides, which could be in principle in tautomeric equilibrium with the corresponding NHC. According to calculations at the DFT B3LYP/6-31G(d) level, the carbene and the betaine have a close thermodynamic stability in the gas phase; however, in solution the betaine is much more stable (Table 1). Indeed it was found that 3-(1*H*-imidazol-3-ium-3-yl)pyrrol-1-ides exist in solution and in the solid state in the betaine form.[11d,f] Preliminary DFT calculations of the relative stability of the carbene and betaine forms of pyrrolylimidazole (**1a**/**1b**) and pyrrolyltriazoles (**2a**/**2b**, **3a**/**3b**) (Table 1) showed that the introduction of an additional nitrogen, i.e. replacement of the imidazole moiety with the 1,2,4-triazole moiety, will increase the stability of the carbene form, even in solution. This will change the chemical properties of 1,2,4-triazole-containing ensembles in comparison with imidazole analogues.

Taking all this into account, we decided to apply the mentioned approach[15h] for the synthesis of pyrrolyltriazoles of the two types by the reaction of azirines with the corresponding triazolium phenacylides (Scheme 1) in order to study their chemical properties and to generate pyrrolyl-substituted triazole NHC. For a start, the triazolium phenacylides should be at least nucleophilic enough to react with the C=N bond of azirines.

Scheme 1. Retrosynthetic Scheme for the Preparation of Pyrrolyltriazole Derivatives

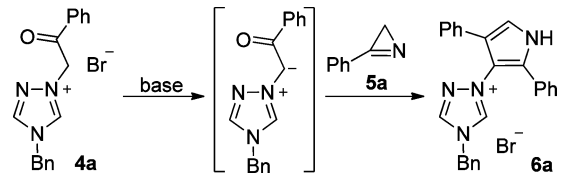


However, not as much is known so far about the nucleophilic reactivity of these species. It was only shown that triazolium phenacylides, generated in situ from the corresponding triazolium salts, are able to substitute chlorine in very electrophilic 1-chloro-2,4,6-trinitro- or tricyanobenzenes.[16] However, to the best of our knowledge nobody has yet studied nucleophilic reactions of triazolium phenacylides toward multiple bonds.

RESULTS AND DISCUSSION

We reacted 4-benzyl-1-(2-oxo-2-phenylethyl)-4*H*-1,2,4-triazol-1-ium bromide (**4a**) with 3-phenyl-2*H*-azirine (**5a**) under the optimal conditions, which were used for preparation of pyrrolylimidazoles (3 equiv of Et_3N, DCM, reflux),[11f] but we could detect only traces of the target product **6a**. We therefore studied the reaction in different solvents, using various bases and different temperatures and reaction times in order to find the optimal conditions for the preparation of pyrrolyltriazoles (Table 2). The reaction in acetonitrile occurred faster than in DCM probably due to better solubility of triazolium bromides

Table 2. Optimization of the Reaction Conditions for the Synthesis of Pyrrolyltriazolium Bromides 6



entry	conditions	time, h	base; amt, equiv	**6a**:**4a**[a]	yield,[b] %
1	MeCN, room temp	24	Et_3N; 0.1	50:50	
2	DCM, room temp	24	Et_3N; 0.1	30:70	
3	MeCN, room temp	312	Et_3N; 0.15	100:0	24
4	MeCN, reflux	35	Et_3N; 0.1	40:60	
5	MeCN, reflux	57	Et_3N; 0.15	50:50	
6	MeCN, room temp	48	DIPEA; 0.2	22:78	
7	MeCN, room temp	48	DIPEA; 0.5	100:0	60
8	MeCN, room temp	48	Et_3N; 0.5	100:0	47
9	MeCN, room temp	48	DIPEA; 0.6	94:6	64
10	MeCN, room temp	24	Et_3N; 0.6	93:7	75
11	MeCN, room temp	48	DBU; 0.6−3		
12	MeCN, room temp	36	DIPEA; 1.0	99:1	62
13	MeCN, room temp	36	Et_3N; 1.0	98:2	70

[a] Ratio of **6a** to **4a** according to ^{1}H NMR spectra of the reaction mixture after 24 h. [b] Isolated yield.

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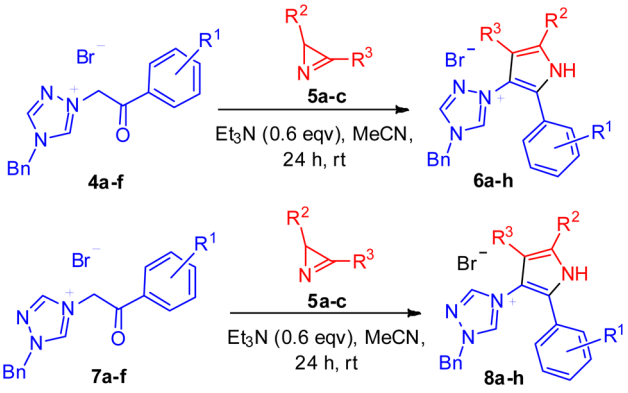
Table 3. Synthesis of Pyrrolyltriazolium Bromides 6a–h and 8a–h



R^1	R^2	R^3	4	5	6; yield, %	7	5	8; yield, %
H	H	Ph	**a**	**a**	**a**; 75	**a**	**a**	**a**; 70
2-Br	H	Ph	**b**	**a**	**b**; 71	**b**	**a**	**b**; 73
3-NO_2	H	Ph	**c**	**a**	**c**; 67	**c**	**a**	**c**; 83
4-NO_2	H	Ph	**d**	**a**	**d**; 75	**d**	**a**	**d**; 58
4-Cl	H	Ph	**e**	**a**	**e**; 78	**d**	**a**	**e**; 82
4-MeO	H	Ph	**f**	**a**	**f**; 75	**f**	**a**	**f**; 88
H	CO_2Me	4-BrC_6H_4	**a**	**b**	**g**; 30	**a**	**b**	**g**; 54
H	Ph	Ph	**a**	**c**	**h**; 57	**a**	**c**	**h**; 54

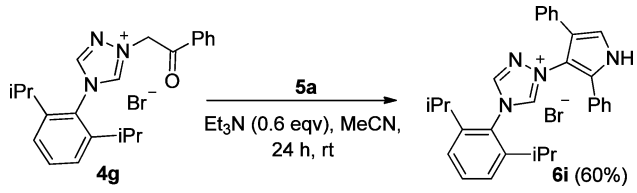
in this solvent. It was also found that both triethylamine and ethyldiisopropylamine (DIPEA) promoted the reaction, unlike DBU, which led to a tarring of the reaction mixture. Previously, when azinium[15h] and azolium[11d,f] salts were reacted with 2*H*-azirines, an excess of triethylamine was necessary to sufficiently shift the equilibrium steps of the process, despite the fact that the reaction is a catalytic one. The reaction of triazolium salts with less than 1 equiv of base gave higher product yields. It was also shown that the reaction at ambient temperature gives better results than refluxing of the reaction mixture. As a result, the conditions of entry 10 (Table 2) were chosen as optimum for further experiments (MeCN, room temperature, 24 h, Et_3N 0.6 equiv).

The found reaction conditions were used for the synthesis of two series of compounds: 1-(1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazol-1-ium bromides **6** and 4-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazol-4-ium bromides **8** (Table 3). The benzyl group was chosen as the protective group to allow the possibility of transforming the salts to the corresponding pyrrolyltriazoles (vide infra). The reactions tolerate nitro, methoxy, and halogen substituents in the aryl group and a methoxycarbonyl group in the azirine. Compounds **6** and **8** were obtained with 50–90% yields, with the exception of compound **6g** (30%), where the yield decrease is apparently due to the relatively low stability of the starting azirine **5b**. The isolation of the products does not require the use of chromatographic purification. All new compounds were characterized by ^1H and ^{13}C NMR and IR spectroscopy and mass spectrometry. The structure of the crystalline compound **8a** was also analyzed by single-crystal X-ray diffraction (see the Supporting Information).

Compound **6i** was additionally obtained by the reaction of triazolium bromide **4g** with azirine **5a** (Scheme 2) in the hope of using it for the preparation of a stable triazolium carbene (vide infra).

It should be noted that the developed experimental procedure is very simple and allows the preparation of analytically pure target compounds without any special purification. 1*H*-Pyrrole-3-yltriazolium salts **6a,b,e–i** and

Scheme 2. Synthesis of Pyrrolyltriazolium Bromide 6i



8a,b,e–h are high-melting white crystalline solids, while the salts **6c,d** and **8c,d** with a nitrophenyl substituent are bright yellow. All of these salts are nonhygroscopic compounds that are both stable at room temperature and on heating up to their melting point. They are soluble in methanol and dimethyl sulfoxide, less soluble in aliphatic alcohols, poorly soluble in acetonitrile and dichloromethane, and insoluble in ethyl acetate, hexane, and diethyl ether.

A proposed mechanism of the formation of (1*H*-pyrrol-3-yl)triazolium bromides **6** and **8** (Scheme 3) involves the generation of triazolium ylide **9** from salt **4** under the action of triethylamine, activation of the C=N bond of azirine by protonation (**5-H**$^+$), nucleophilic attack of the triazolium ylide **9** on the C=N bond of intermediate **5-H**$^+$ to afford the adduct **10** which then undergoes dehydrobromination with the formation of ylide **11**; opening of the strained aziridine ring and cyclization onto the carbonyl group (**12**), and dehydration of intermediate **13** to complete the domino sequence leading to pyrroles **6** and **8**. The need for the activation of the azirine C=N bond, via protonation or complexation of the nitrogen atom for effective attack of a nucleophile, has been shown in recently published works.[15c,d,17]

Salts **6** and **8** were debenzylated on Pd/C with hydrogen (method B) or by the use of ammonium formate as the source of hydrogen (method A). The reactions led to the formation of the corresponding 1-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazoles **14** and 4-(1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazoles **15** in high yields (Table 4). It should be noted that debenzylation of salts **6** proceeded smoothly, and reaction products **14** crystallized in pure form

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Scheme 3. Proposed Mechanism of Formation of Pyrrolyltriazolium Salts 6 and 8

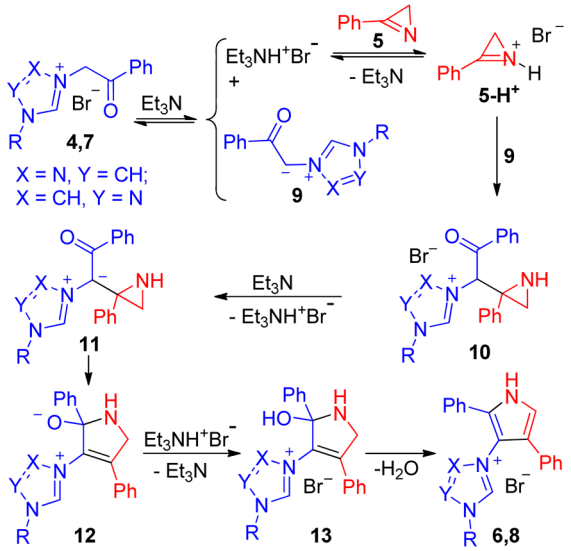
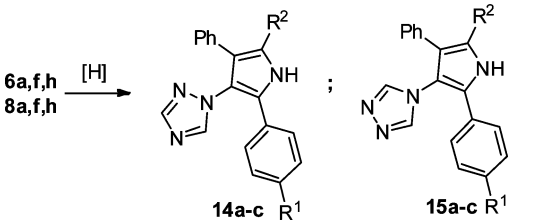


Table 4. Debenzylation of Pyrrolyltriazolium Bromides 6 and 8

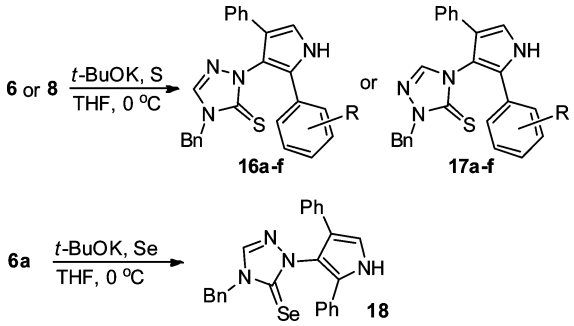


R^1	R^2	6	method	14; yield, %	8	method	15; yield, %
H	H	**a**	A	**a**; 91	**a**	A	**a**; 84
MeO	H	**f**	B	**b**; 92	**f**	B	**b**; 68
H	Ph	**h**	B	**c**; 86	**h**	B	**c**; 56

from the reaction mixture and did not need additional purification. Meanwhile, the debenzylations of compounds **8** were accompanied by some side reactions and products **15** were purified by column chromatography or recrystallization. It was found that, under the conditions used, the debenzylation of salts with a nitrophenyl substituent (**6c,d** and **8c,d**) is accompanied by the reduction of the nitro group into an amino group. Amino-substituted pyrrolyltriazoles formed were, however, not sufficiently stable for their isolation in pure form. Halogenated salts **6** and **8b,e** also undergo hydrodehalogenation along with debenzylation under the reaction conditions used to give the corresponding pyrrolyltriazoles. Compounds **14** and **15** are high-melting (mp >190 °C) colorless crystalline solids that are stable at room temperature. These compounds are slightly soluble in methanol and dimethyl sulfoxide and insoluble in aliphatic alcohols, chloroform, ethyl acetate, dichloromethane, diethyl ether, and toluene.

Dehydrobromination of salts **6** and **8** may lead to the formation of betaines, which can be in tautomeric equilibrium with the corresponding NHC (Table 1). According to DFT calculations, the relative thermodynamic stabilities of the NHCs derived from pyrrolyltriazolium salts are higher than in the case of NHCs derived from pyrrolylimidazolium salts (Table 1). Thus, although stable betaines, 3-(1*H*-imidazol-3-ium-3-yl)-pyrrol-1-ides, were obtained by treatment of the corresponding 3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides with a base,[11d,f] the higher stability of the NHCs derived from pyrrolyltriazolium salts in comparison with the corresponding betaines (and therefore higher concentration of these reactive species in the equilibrium) could make the reaction path of the dehydrobromination of pyrrolyltriazolium bromides **6** and **8** more complicated. Indeed, complex mixtures of unidentified products were formed in reactions of salts **6** and **8** with aqueous potassium hydroxide under the same reaction conditions as those used for the high-yield preparation of stable betaines from pyrrolylimidazolium salts. We decided, therefore, to trap the carbene form by a fast reaction with sulfur or selenium. A suspension of salt **6a** or **8a** and sulfur in anhydrous THF was treated with potassium *tert*-butoxide at 0 °C under an inert atmosphere. The reactions were completed almost immediately, and the resulting compounds were isolated by column chromatography. Under these conditions a series of pyrrolyltriazolethiones **16** and **17** were obtained in high yields (Table 5). Pyrrolyltriazoleselenone **18** was prepared in 70% yield by

Table 5. Synthesis of Pyrrolyltriazolethiones 16 and 17 and Pyrrolyltriazoleselenone 18



R	6	16; yield, %	8	17; yield, %
H	**a**	**a**; 85	**a**	**a**; 95
2-Br	**b**	**b**; 82	**b**	**b**; 75
3-NO_2	**c**	**c**; 70	**c**	**c**; 93
4-NO_2	**d**	**d**; 87	**d**	**d**; 97
4-Cl	**e**	**e**; 90	**e**	**e**; 90
4-MeO	**f**	**f**; 87	**f**	**f**; 93

the reaction of salt **6a** with selenium and potassium *tert*-butoxide under the same conditions. The structure of pyrrolyltriazoleselene **18** was verified by single-crystal X-ray diffraction measurement (see the Supporting Information).

Assuming that the replacement of the 4-benzyl group in compound **6a** with a sterically hindered 2,6-diisopropylphenyl group is likely to be able to stabilize carbene **19a** kinetically, salt **6i** was treated with KOH, whereupon a compound with the exact mass corresponding to the mass of the carbene **19a** was isolated in 94% yield. The same compound was obtained in quantitative yield by the reaction of salt **6i** with potassium *tert*-butoxide (anhydrous THF, 0 °C). However, no signal was found having a chemical shift in the region δ 200−250 ppm in the ^{13}C NMR spectrum, which is characteristic of triazole-based NHC.[13,18] The structure of the isolated compound, *N*-cyanoformimidamide **20** (Scheme 4), was established by analysis of ^{1}H and ^{13}C, HSQC $^{1}H-^{13}C$, HSQC $^{1}H-^{15}N$ and HMBC $^{1}H-^{13}C$ NMR (Supporting Information), and IR spectroscopy data. Meanwhile the reaction of salt **6i** with sulfur in the presence of potassium *tert*-butoxide (anhydrous THF, 0 °C) immediately gave thione **21** in quantitative yield.

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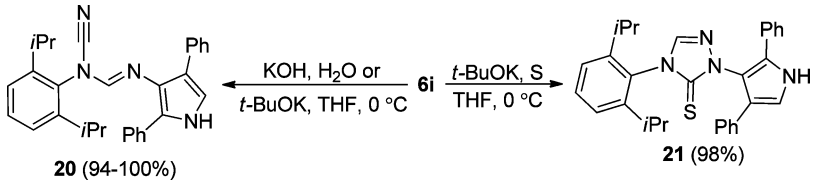
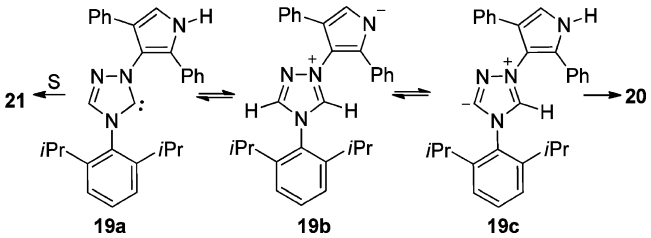
Scheme 4. Reactions of Pyrrolyltriazolium Salt 6i under Basic Conditions in the Presence and Absence of Sulfur



To explain the observed phenomenon, we propose that in the equilibrium carbene **19a**–betaine **19b** the pyrrolyltriazoliumide **19c** can possibly participate as well. The latter is thought to easily undergo triazole ring opening with the formation of *N*-cyanoformimidamide **20** (Scheme 5).

Scheme 5. Plausible Precursors of Compounds 20 and 21



To test this hypothesis, quantum chemical calculations of the relative energies of intermediates **19a–c** were performed, as well as the barrier for conversion of pyrrolyltriazoliumide **19c** into compound **20** in THF, water, and DMSO (Figure 1).

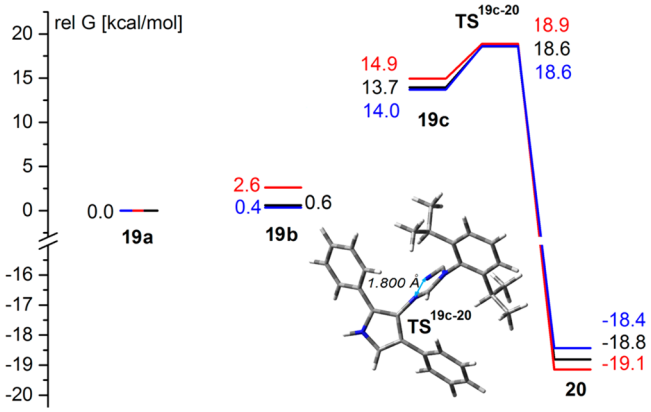
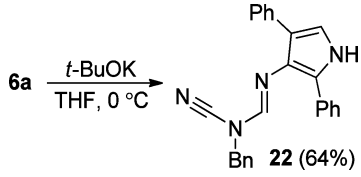


Figure 1. Relative Gibbs free energies (in kcal mol^{-1}, 298 K, PCM model for the solvents (black) DMSO, (red) THF, and (blue) H_2O) of molecules **19a–c** and the transition state **TS**$^{19c\rightarrow20}$ computed at the B3LYP/6-31g(d) level.

From the data obtained it follows that betaine **19b** is only slightly less stable than carbene **19a** in polar solvents (water and DMSO), although carbene **19a** is much more stable than betaine **19b** in less polar THF. The stability of intermediate **19c** is much less than that of betaine **19b** and carbene **19a** in any solvent used in the calculations. This means that the concentration of intermediate **19c** in the equilibrium is so negligible that the use of an effective carbene trap such as sulfur should result in the formation of triazolethione **21** as the only product. However, even an extremely low concentration of intermediate **19c** ensures the formation of nitrile **20** as the main reaction product in the absence of carbene traps, since the barrier for transformation of intermediate **19c** to nitrile **20** is only 5 kcal/mol.

Looking back, we performed a dehydrobromination of salt **6a** with potassium *tert*-butoxide (anhydrous THF, 0 °C) and obtained nitrile **22** in 64% yield (Scheme 6), while in the presence of sulfur under the same reaction conditions the only product was triazolethione **16a** (Table 4).

Scheme 6. Synthesis of *N*-Cyanoformimidamide 22



We can conclude that our inability to obtain the corresponding betaines or carbenes under dehydrobromination of the salts **6** and **8** with aqueous KOH is due to triazole ring opening with the formation of derivatives of *N*-cyanoformimidamide, which then can undergo further reactions in aqueous KOH to give a complex mixture of products. The impossibility of such a transformation in the case of 3-(1*H*-pyrrol-3-yl)-1*H*-imidazol-3-ium bromides, containing an imidazole ring instead of a triazole ring, previously allowed receiving appropriate stable betaines.[11d,f] Meanwhile, when it is taken into account that the transformation of triazolium salt **6i** into *N*-cyanoformimidamide **20** proceeds through pyrrolyltriazoliumide intermediate **19c**, it is possible to block this reaction of the triazolium salt by introducing a substituent at the 3-position of the triazole ring of compound **6i**, since this will make the formation of intermediate **19c** impossible. To check this hypothesis and to generate carbene **23a**, compound **6j** was synthesized from 4-(2,6-diisopropylphenyl)-3-phenyl-4*H*-1,2,4-triazole (**24**) with a phenyl substituent at the 3-position of the triazole ring, phenacyl bromide, and azirine **5a** according to the developed procedure (Scheme 7).

Salt **6j** was reacted with potassium *tert*-butoxide (anhydrous THF, 0 °C) to give compound **23** as a white solid. This compound reacts with sulfur, affording the corresponding triazolethione **25** in 93% yield. According to calculations at the DFT B3LYP/6-31G(d) level, carbene **23a** is more stable in benzene solution than betaine **23b** (ΔG = 1.0 kcal mol^{-1} at 298 K). In good agreement with this prediction, we were fortunate to confirm the presence of the first pyrrolyl-substituted triazole NHC **23a** in benzene-d_6 by ^{13}C NMR (see the Supporting Information). The ^{13}C NMR spectrum contains a signal at 210.2 ppm which is characteristic of the carbenic carbon of triazole-based NHCs.[13,18]

In conclusion, unprecedented pyrrole- and 1,2,4-triazole-containing ensembles of two types, (1) substituted 1-(1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazol-1-ium bromides **6** and (2) substituted 4-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazol-4-ium bromides **8**,

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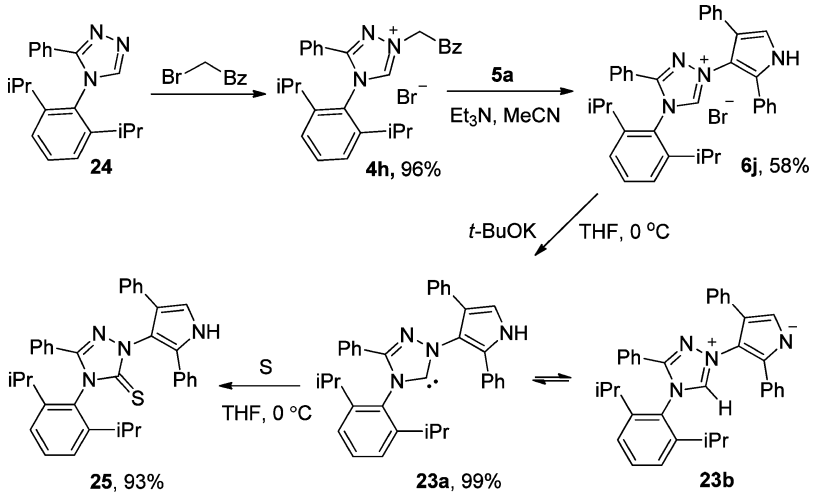
Scheme 7. Synthesis and Reaction of Triazole NHC 23a



were prepared from 2*H*-azirines and triazolium phenacyl bromides under mild conditions using a very simple procedure without any special purification. *N*-(1*H*-Pyrrol-3-yl)-*N*′-benzyltriazolium bromides under reductive debenzylation on Pd/C gave substituted 1-(1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazoles **14** and 4-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazoles **15** in high yields; however, halo-substituted aryl groups simultaneously lose halogen. According to calculations at the DFT B3LYP/6-31G(d) level the first two components of the tautomeric mixture triazoliumylpyrrolide−pyrrolyltriazole NHC−pyrrolyltriazoliumide, resulting from salts **6** and **8** under dehydrobromination conditions, have comparable Gibbs free energies in nonpolar solvents. The thermodynamically less stable tautomer (pyrrolyltriazoliumide) was able to undergo low-barrier triazole ring opening to the corresponding *N*-cyanoformimidamide. The carbene forms could be easily trapped by the reaction of the salt **6** and **8** with base in the presence of sulfur, giving the corresponding derivatives of 1- and 4-(1*H*-pyrrol-3-yl)-1*H*-1,2,4-triazole-5(4*H*)-thiones **16** and **17** in high yields. In the absence of a carbene trap, the opening of the triazole ring occurred with formation of derivatives of *N*-cyanoformimidamide. By blocking the formation of the pyrrolyltriazoliumide by introducing a phenyl substituent at the 3-position of the triazole ring of compound **6**, it was possible to generate the first pyrrole-substituted triazole NHC.

EXPERIMENTAL SECTION

General Information and Methods. Melting points were determined on a capillary melting point apparatus. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were determined in $CDCl_3$, DMSO-d_6, and C_6D_6. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane (TMS; δ 0.00). ^{1}H NMR spectra were calibrated according to the residual peak of $CDCl_3$ (7.26 ppm) or DMSO-d_6 (2.50 ppm). For all new compounds, ^{13}C {^{1}H} and ^{13}C DEPT135 spectra were recorded and calibrated according to the peak of $CDCl_3$ (77.00 ppm) or DMSO-d_6 (39.51 ppm). Mass spectra were recorded on an HRMS-ESI-QTOF instrument (electrospray ionization, positive mode). IR spectra were recorded for tablets in KBr. Single-crystal X-ray diffraction experiments were performed on a diffractometer at 100 K using monochromated Cu Kα radiation. Thin-layer chromatography (TLC) was conducted on aluminum sheets with 0.2 mm silica gel with a fluorescent indicator.

Typical Procedure for the Synthesis of Phenacyltriazolium Bromides 4a−h and 7a−f. A solution of 2-bromoacetophenone (1.89 g, 9.5 mmol) and 4-benzyl-4*H*-1,2,4-triazole (1.5 g, 9.5 mmol) in acetone (20 mL) was stirred under reflux for 10−15 h. The mixture was cooled, and the product was filtered, washed with acetone (3 × 10 mL), and dried.

*4-Benzyl-1-(2-oxo-2-phenylethyl)-4H-1,2,4-triazol-1-ium Bromide (**4a**).* Compound **4a** (2.99 g, 88%) was obtained from 4-benzyl-4*H*-1,2,4-triazole (1.50 g, 9.5 mmol) and 2-bromoacetophenone (1.89 g, 9.5 mmol) according to the typical procedure. Colorless solid, mp 197−198 °C. ^{1}H NMR (DMSO-d_6): δ 5.66 (s, 2H), 6.32 (s, 2H), 7.42−7.56 (m, 5H), 7.60−7.68 (t, J = 7.7 Hz, 2H), 7.74−7.81 (t, J = 7.4 Hz, 1H), 8.03−8.01 (m, 2H), 9.46 (s, 1H), 10.20 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.6, 58.3, 128.3, 128.6, 129.06, 129.08, 129.13, 133.4, 133.7, 134.7, 144.3, 144.7, 190.4. ESI/MS (m/z): 278.1288 calcd for $C_{17}H_{16}N_3O^+$ [M − Br]$^+$, found 278.1296. IR (KBr, cm^{-1}): ν 3001 (br), 1681, 1231, 1154, 1007, 752, 686.

*4-Benzyl-1-(2-(2-bromophenyl)-2-oxoethyl)-4H-1,2,4-triazol-1-ium Bromide (**4b**).* Compound **4b** (1.02 g, 74%) was obtained from 4-benzyl-4*H*-1,2,4-triazole (490 mg, 3.1 mmol) and 2-bromo-2′-bromoacetophenone (870 mg, 3.1 mmol) according to the typical procedure. Colorless solid, mp 180−181 °C. ^{1}H NMR (DMSO-d_6): δ 5.67 (s, 2H), 6.22 (s, 2H), 7.42−7.55 (m, 5H), 7.56−7.67 (m, 2H), 7.80−7.88 (m, 1H), 7.96−8.03 (m, 1H), 9.48 (s, 1H), 10.25 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.7, 59.6, 119.4, 128.0, 128.7, 129.11, 129.13, 130.6, 133.7, 134.1, 134.5, 135.1, 144.2, 144.9, 192.0. ESI/MS (m/z): 356.0393 calcd for $C_{17}H_{15}BrN_3O^+$ [M − Br]$^+$, found 356.0393. IR (KBr, cm^{-1}): ν 3001 (br), 1691, 1566, 1221, 1157, 1003, 752, 718, 660.

*4-Benzyl-1-(2-(3-nitrophenyl)-2-oxoethyl)-4H-1,2,4-triazol-1-ium Bromide (**4c**).* Compound **4c** (313 mg, 82%) was obtained from 4-benzyl-4*H*-1,2,4-triazole (150 mg, 0.9 mmol) and 2-bromo-3′-nitroacetophenone (230 mg, 0.9 mmol) according to the typical procedure. Colorless solid, mp 202−204 °C. ^{1}H NMR (DMSO-d_6): δ 5.69 (s, 2H), 6.44 (s, 2H), 7.42−7.61 (m, 5H), 7.95 (t, J = 8.0 Hz, 1H), 8.46−8.53 (m, 1H), 8.56−8.65 (m, 1H), 8.73−8.81 (m, 1H), 9.50 (s, 1H), 10.22 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.7, 58.6, 122.7, 128.66, 128.66, 129.10, 129.14, 130.9, 133.7, 134.5, 134.7, 144.3, 144.8, 148.1, 189.5. ESI/MS (m/z): 323.1139 calcd for $C_{17}H_{15}N_4O_3^+$ [M − Br]$^+$, found 323.1140. IR (KBr, cm^{-1}): ν 3014 (br), 1690, 1531, 1357, 1230, 1153, 1008, 716.

*4-Benzyl-1-(2-(4-nitrophenyl)-2-oxoethyl)-4H-1,2,4-triazol-1-ium Bromide (**4d**).* Compound **4d** (789 mg, 89%) was obtained from 4-benzyl-4*H*-1,2,4-triazole (350 mg, 2.2 mmol) and 2-bromo-4′-nitroacetophenone (537 mg, 2.20 mmol) according to the typical procedure. Slightly yellow solid, mp 224−226 °C. ^{1}H NMR (DMSO-d_6): δ 5.68 (s, 2H), 6.40 (s, 2H), 7.42−7.56 (m, 5H), 8.26−8.33 (m, 2H), 8.41−8.48 (m, 2H), 9.49 (s, 1H), 10.21 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.7, 58.7, 124.1, 128.7, 129.15, 129.18, 129.9, 133.7, 138.0, 144.4, 144.9, 150.7, 189.9. ESI/MS (m/z): 323.1139 calcd for $C_{17}H_{15}N_4O_3^+$ [M − Br]$^+$, found 323.1140. IR (KBr, cm^{-1}): ν 3011 (br), 1693, 1523, 1349, 1153, 1007, 856, 714.

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*4-Benzyl-1-(2-(4-chlorophenyl)-2-oxoethyl)-4H-1,2,4-triazol-1-ium Bromide (**4e**).* Compound **4e** (480 mg, 82%) was obtained from 4-benzyl-4*H*-1,2,4-triazole (350 mg, 1.5 mmol) and 2-bromo-4′-chloroacetophenone (237 mg, 1.5 mmol) according to the typical procedure. Colorless solid, mp 210−212 °C. ^{1}H NMR (DMSO-d_6): δ 5.67 (s, 2H), 6.33 (s, 2H), 7.42−7.57 (m, 5H), 7.69−7.77 (m, 2H), 8.05−8.13 (m, 2H), 9.48 (s, 1H), 10.22 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.6, 58.3, 128.6, 129.09, 129.13, 129.2, 130.3, 132.1, 133.7, 139.6, 144.3, 144.7, 189.6. ESI/MS (m/z): 312.0898 calcd for $C_{17}H_{15}ClN_3O^+$ [M − Br]$^+$, found 312.0901. IR (KBr, cm^{-1}): ν 3004 (br), 1682, 1592, 1402, 1238, 1155, 1091, 1006, 824, 716.

*4-Benzyl-1-(2-(4-methoxyphenyl)-2-oxoethyl)-4H-1,2,4-triazol-1-ium Bromide (**4f**).* Compound **4f** (478 mg, 78%) was obtained from 4-benzyl-4*H*-1,2,4-triazole (250 mg, 1.6 mmol) and 2-bromo-4′-methoxyacetophenone (362 mg, 1.6 mmol) according to the typical procedure. Colorless solid, mp 185−186 °C. ^{1}H NMR (DMSO-d_6): δ 3.89 (s, 3H), 5.64 (s, 2H), 6.24 (s, 2H), 7.12−7.19 (m, 2H), 7.41−7.55 (m, 5H), 8.00−8.09 (m, 2H), 9.44 (s, 1H), 10.19 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.6, 55.8, 58.0, 114.4, 126.2, 128.6, 129.08, 129.13, 130.8, 133.8, 144.3, 144.7, 164.3, 188.6. ESI/MS (m/z): 308.1394 calcd for $C_{18}H_{18}N_3O_2^+$ [M − Br]$^+$, found 308.1401. IR (KBr, cm^{-1}): ν 2999 (br), 1669, 1605, 1578, 1242, 1185, 1006, 830, 698.

*4-(2,6-Diisopropylphenyl)-1-(2-oxo-2-phenylethyl)-4H-1,2,4-triazol-1-ium Bromide (**4g**).* Compound **4g** (627 mg, 70%) was obtained from 4-(2,6-diisopropylphenyl)-4*H*-1,2,4-triazole (478 mg, 2.1 mmol) and 2-bromoacetophenone (415 mg, 2.1 mmol) according to the typical procedure. Colorless solid, mp 272−274 °C. ^{1}H NMR (DMSO-d_6): δ 1.12−1.26 (m, 12H), 2.35−2.46 (m, 2H), 6.52 (s, 2H), 7.49−7.58 (m, 2H), 7.62−7.74 (m, 3H), 7.76−7.84 (m, 1H), 8.09−8.16 (m, 2H), 9.83 (s, 1H), 10.69 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 23.5, 23.6, 28.1, 58.9, 124.7, 127.3, 128.5, 129.1, 132.2, 133.2, 134.9, 145.1, 145.8, 146.0, 190.3. ESI/MS (m/z): 348.2070 calcd for $C_{22}H_{26}N_3O^+$ [M − Br]$^+$, found 348.2057. IR (KBr, cm^{-1}): ν 2969, 1700, 1598, 1561, 1451, 1297, 1233, 1091, 1010, 759, 692.

*4-(2,6-Diisopropylphenyl)-1-(2-oxo-2-phenylethyl)-3-phenyl-4H-1,2,4-triazol-1-ium Bromide (**4h**).* Compound **4h** (1.53 g, 96%) was obtained from 4-(2,6-diisopropylphenyl)-3-phenyl-4*H*-1,2,4-triazole (1.00 g, 3.28 mmol) and phenacyl bromide (652 mg, 3.28 mmol) by stirring the reaction mixture in toluene (10 mL) under reflux for 20 h. The compound was additionally purified by column chromatography using a mixture of dichloromethane and methanol as eluent (starting ratio of 100:1 with further increasing polarity to 10:1). Colorless hygroscopic solid, mp 113−115 °C. ^{1}H NMR ($CDCl_3$): δ 0.98 (d, J = 6.8 Hz, 6H), 1.32 (d, J = 6.8 Hz, 6H), 2.50 (septet, J = 6.8 Hz, 2H), 6.91 (s, 2H), 7.33−7.42 (m, 4H), 7.44 (d, J = 7.4 Hz, 2H), 7.49−7.60 (m, 3H), 7.62−7.72 (m, 2H), 8.09 (d, J = 7.4 Hz, 2H), 11.48 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 22.8, 25.0, 29.1, 59.6, 122.3, 125.6, 127.5, 128.0, 128.6, 129.2, 129.4, 132.9, 133.5, 134.9, 145.5, 147.1, 153.6, 189.5. HRMS (ESI) m/z: 424.2383 calcd for $C_{28}H_{30}N_3O^+$ [M − Br]$^+$, found 424.2366.

*1-Benzyl-4-(2-oxo-2-phenylethyl)-1H-1,2,4-triazol-4-ium Bromide (**7a**).* Compound **7a**[16b] (0.92 g, 68%) was obtained from 1-benzyl-1*H*-1,2,4-triazole (0.60 g, 3.8 mmol) and 2-bromoacetophenone (0.75 g, 3.8 mmol) according to the typical procedure. Colorless solid, mp 184−186 °C (lit.[16b] mp 175−176 °C). ^{1}H NMR (DMSO-d_6): δ 5.77 (s, 2H), 6.12 (s, 2H), 7.37−7.53 (m, 5H), 7.62−7.71 (m, 2H), 7.75−7.82 (m, 1H), 8.01−8.10 (m, 2H), 9.15 (s, 1H), 10.18 (s, 1H).

*1-Benzyl-4-(2-(2-bromophenyl)-2-oxoethyl)-1H-1,2,4-triazol-4-ium Bromide (**7b**).* Compound **7b** (479 mg, 58%) was obtained from 1-benzyl-1*H*-1,2,4-triazole (300 mg, 1.9 mmol) and 2-bromo-2′-bromoacetophenone (523 mg, 1.9 mmol) by stirring the reaction mixture in toluene (10 mL) under reflux for 20 h. Colorless solid, mp 145−146 °C. ^{1}H NMR (DMSO-d_6): δ 5.78 (s, 2H), 6.06 (s, 2H), 7.40−7.53 (m, 5H), 7.57−7.71 (m, 2H), 7.87 (dd, J = 7.8 Hz, 1.2 Hz, 1H), 8.03 (dd, J = 7.6 Hz, 1.8 Hz, 1H), 9.21 (s, 1H), 10.25 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 54.8, 55.3, 119.4, 128.1, 128.85, 128.94, 129.0, 131.0, 133.2, 134.3, 134.6, 134.8, 143.6, 146.0, 191.6. ESI/MS (m/z): 356.0393 calcd for $C_{17}H_{15}BrN_3O^+$ [M − Br]$^+$, found 356.0395. IR (KBr, cm^{-1}): ν 3060 (br), 1703, 1573, 1430, 1224, 1153, 998, 747, 714.

*1-Benzyl-4-(2-(3-nitrophenyl)-2-oxoethyl)-1H-1,2,4-triazol-4-ium Bromide (**7c**).* Compound **7c** (682 mg, 77%) was obtained from 1-benzyl-1*H*-1,2,4-triazole (350 mg, 2.2 mmol) and 2-bromo-3′-nitroacetophenone (537 mg, 2.2 mmol) according to the typical procedure. Colorless solid, mp 215−216 °C. ^{1}H NMR (DMSO-d_6): δ 5.79 (s, 2H), 6.21 (s, 2H), 7.40−7.53 (m, 5H), 7.96 (t, J = 8.0 Hz, 1H), 8.44−8.51 (m, 1H), 8.57−8.64 (m, 1H), 8.74 (t, J = 1.8 Hz, 1H), 9.17 (s, 1H), 10.21 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 54.2, 54.8, 122.6, 128.7, 128.8, 128.9, 129.0, 131.1, 133.3, 134.4, 134.7, 143.6, 146.1, 148.1, 189.5. ESI/MS (m/z): 323.1139 calcd for $C_{17}H_{15}N_4O_3^+$ [M − Br]$^+$, found 323.1145. IR (KBr, cm^{-1}): ν 3048 (br), 1698, 1535, 1350, 1236, 706, 670.

*1-Benzyl-4-(2-(4-nitrophenyl)-2-oxoethyl)-1H-1,2,4-triazol-4-ium Bromide (**7d**).* Compound **7d**[16c] (451 mg, 67%) was obtained from 1-benzyl-1*H*-1,2,4-triazole (265 mg, 1.7 mmol) and 2-bromo-4′-nitroacetophenone (407 mg, 1.7 mmol) according to the typical procedure. Colorless solid, mp 215−216 °C (lit.[16c] mp 211−212 °C). ^{1}H NMR (DMSO-d_6): δ 5.78 (s, 2H), 6.18 (s, 2H), 7.38−7.56 (m, 5H), 8.24−8.34 (m, 2H), 8.41−8.52 (m, 2H), 9.16 (s, 1H), 10.20 (s, 1H).

*1-Benzyl-4-(2-(4-chlorophenyl)-2-oxoethyl)-1H-1,2,4-triazol-4-ium Bromide (**7e**).* Compound **7e** (420 mg, 62%) was obtained from 1-benzyl-1*H*-1,2,4-triazole (273 mg, 1.7 mmol) and 2-bromo-4′-chloroacetophenone (403 mg, 1.7 mmol) according to the typical procedure. Colorless solid, mp 216−218 °C. ^{1}H NMR (DMSO-d_6): δ 5.77 (s, 2H), 6.11 (s, 2H), 7.39−7.53 (m, 5H), 7.70−7.79 (m, 2H), 8.04−8.13 (m, 2H), 9.15 (s, 1H), 10.19 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 54.0, 54.8, 128.8, 128.9, 129.0, 129.3, 130.1, 132.1, 133.2, 139.5, 143.6, 146.1, 189.6. ESI/MS (m/z): 312.0898 calcd for $C_{17}H_{15}ClN_3O^+$ [M − Br]$^+$, found 312.0909. IR (KBr, cm^{-1}): ν 2975 (br), 1703, 1587, 1342, 1228, 1150, 1078, 994, 829, 756.

*1-Benzyl-4-(2-(4-methoxyphenyl)-2-oxoethyl)-1H-1,2,4-triazol-4-ium Bromide (**7f**).* Compound **7f**[16c] (554 mg, 65%) was obtained from 1-benzyl-1*H*-1,2,4-triazole (346 mg, 2.2 mmol) and 2-bromo-4′-methoxyacetophenone (500 mg, 2.2 mmol) according to the typical procedure. Colorless solid, mp 186−187 °C (lit.[16c] mp 160−165 °C). ^{1}H NMR (DMSO-d_6): δ 3.89 (s, 3H), 5.76 (s, 2H), 6.07 (s, 2H), 7.13−7.21 (m, 2H), 7.39−7.52 (m, 5H), 7.99−8.08 (m, 2H), 9.16 (s, 1H), 10.19 (s, 1H).

Typical Procedure for the Synthesis of Pyrrolyltriazolium Bromides 6a−j and 8a−g. Triethylamine (169 mg, 1.68 mmol, 0.6 equiv) was added dropwise to a stirred suspension of 4-benzyl-1-(2-oxo-2-phenylethyl)-4*H*-1,2,4-triazol-1-ium bromide (**4a**; 2.79 mmol) and 2*H*-azirine (**5a**; 4.19 mmol, 1.5 equiv) in acetonitrile (5 mL), and then the reaction mixture was stirred for 24 h (monitored by ^{1}H NMR). In the case of 4*H*-1,2,4-triazole derivatives **6a−j**, the workout procedure was as follows: the mixture was concentrated in vacuo, and the residue was diluted with ethyl acetate. The precipitate was filtered, washed with ethyl acetate and water, and dried to give pure product **6a**.

In the case of 1*H*-1,2,4-triazole derivatives **8a−g**, the products were filtered directly from acetonitrile due to their lower solubility.

*4-Benzyl-1-(2,4-diphenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6a**).* Compound **6a** (934 mg, 73%) was obtained from bromide **4a** (1.00 g, 2.8 mmol), 3-phenyl-2*H*-azirine (**5a**; 490 mg, 4.2 mmol), and Et_3N (169 mg, 1.7 mmol) according to the general procedure. Colorless solid, mp 196−198 °C. ^{1}H NMR (DMSO-d_6): δ 5.59 (s, 2H), 7.05−7.16 (m, 2H), 7.18−7.32 (m, 7H), 7.33−7.39 (m, 3H), 7.40−7.51 (m, 4H), 9.62 (s, 1H), 10.67 (s, 1H), 12.32 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.9, 112.9, 117.1, 121.6, 126.2, 126.5, 126.7, 128.0, 128.1, 128.8, 128.86, 128.93, 129.06, 129.06, 129.4, 131.9, 133.9, 145.9, 146.1. ESI/MS (m/z): 377.1761 calcd for $C_{25}H_{21}N_4^+$ [M − Br]$^+$, found 377.1767. IR (KBr, cm^{-1}): ν 3166, 2946, 1610, 1489, 1215, 766, 694, 546.

*4-Benzyl-1-(2-(2-bromophenyl)-4-phenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6b**).* Compound **6b** (590 mg, 71%) was obtained from bromide **4b** (683 mg, 1.6 mmol), 3-phenyl-2*H*-azirine (**5a**; 274 mg, 2.3 mmol), and Et_3N (95 mg, 0.9 mmol) according to the general procedure. Colorless solid, mp 214−216 °C. ^{1}H NMR (DMSO-d_6): δ 5.53 (s, 2H), 7.13−7.23 (m, 4H), 7.24−7.34 (m, 3H),

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7.35−7.48 (m, 7H), 7.65−7.73 (m, 1H), 9.46 (s, 1H), 10.53 (s, 1H), 12.26 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.7, 114.4, 117.2, 119.8, 123.2, 126.7, 126.7, 127.8, 127.9, 128.1, 128.8, 128.9, 129.0, 129.8, 131.1, 131.9, 132.7, 133.0, 133.9, 144.8, 145.4. ESI/MS (m/z): 455.0866 calcd for $C_{25}H_{20}BrN_4^+$ [M − Br]$^+$, found 455.0881. IR (KBr, cm^{-1}): ν 3044, 1607, 1571, 1482, 1456, 1199, 755, 701, 649.

*4-Benzyl-1-(2-(3-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6c**).* Compound **6c** (125 mg, 67%) was obtained from bromide **4c** (150 mg, 0.4 mmol), 3-phenyl-2*H*-azirine (**5a**; 74 mg, 0.6 mmol), and Et_3N (25 mg, 0.3 mmol) according to the general procedure. Yellow solid, mp 155−156 °C. ^{1}H NMR (DMSO-d_6): δ 5.58 (s, 2H), 7.03−7.16 (m, 2H), 7.22−7.35 (m, 5H), 7.36−7.46 (m, 3H), 7.52−7.58 (m, 1H), 7.59−7.71 (m, 2H), 8.13 (s, 1H), 8.15−8.24 (m, 1H), 9.70 (s, 1H), 10.64 (s, 1H), 12.69 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 51.0, 114.0, 118.4, 120.7, 122.1, 122.5, 126.6, 127.0, 128.0, 128.95, 128.97, 129.03, 130.4, 130.8, 131.5, 132.5, 133.8, 146.1, 146.2, 148.2. ESI/MS (m/z): 422.1612 calcd for $C_{25}H_{20}N_5O_2^+$ [M − Br]$^+$, found 422.1628. IR (KBr, cm^{-1}): ν 3038, 1602, 1515, 1339, 1108, 852, 761, 697.

*4-Benzyl-1-(2-(4-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6d**).* Compound **6d** (234 mg, 75%) was obtained from bromide **4d** (250 mg, 0.6 mmol), 3-phenyl-2*H*-azirine (**5a**; 109 mg, 0.9 mmol), and Et_3N (38 mg, 0.4 mmol) according to the general procedure. Yellow solid, mp 222−224 °C. ^{1}H NMR (DMSO-d_6): δ 5.59 (s, 2H), 7.02−7.15 (m, 2H), 7.21−7.30 (m, 3H), 7.31−7.37 (m, 2H), 7.38−7.50 (m, 5H), 7.60 (s, 1H), 8.11−8.25 (m, 2H), 9.69 (s, 1H), 10.66 (s, 1H), 12.73 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 51.1, 114.8, 119.3, 122.5, 124.3, 126.7, 126.9, 127.1, 128.1, 128.91, 128.96, 129.00, 131.4, 133.8, 135.1, 146.2, 146.2, 146.2. ESI/MS (m/z): 422.1612 calcd for $C_{25}H_{20}N_5O_2^+$ [M − Br]$^+$, found 422.1618. IR (KBr, cm^{-1}): ν 3038, 1602, 1515, 1339, 1108, 852, 761, 697.

*4-Benzyl-1-(2-(4-chlorophenyl)-4-phenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6e**).* Compound **6e** (186 mg, 78%) was obtained from bromide **4e** (190 mg, 0.5 mmol), 3-phenyl-2*H*-azirine (**5a**; 85 mg, 0.7 mmol), and Et_3N (29 mg, 0.3 mmol) according to the general procedure. Colorless solid, mp 222−224 °C. ^{1}H NMR (DMSO-d_6): δ 5.59 (s, 2H), 7.04−7.15 (m, 2H), 7.20−7.34 (m, 7H), 7.38−7.51 (s, 6H), 9.63 (s, 1H), 10.62 (s, 1H), 12.41 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.9, 113.3, 117.5, 121.7, 126.6, 126.8, 127.7, 128.0, 128.1, 128.2, 128.8, 128.9, 129.0, 129.1, 131.8, 132.7, 133.9, 145.9, 146.1. ESI/MS (m/z): 411.1371 calcd for $C_{25}H_{20}ClN_4^+$ [M − Br]$^+$, found 411.1380. IR (KBr, cm^{-1}): ν 3173, 3065, 2944, 1487, 1457, 1214, 1093, 834, 718, 646.

*4-Benzyl-1-(2-(4-methoxyphenyl)-4-phenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6f**).* Compound **6f** (188 mg, 75%) was obtained from bromide **4f** (200 mg, 0.5 mmol), 3-phenyl-2*H*-azirine (**5a**; 90 mg, 0.8 mmol), and Et_3N (42 mg, 0.4 mmol) according to the general procedure. Colorless solid, mp 231−232 °C. ^{1}H NMR (DMSO-d_6): δ 3.78 (s, 3H), 5.59 (s, 2H), 6.87−6.97 (m, 2H), 7.07−7.13 (m, 2H), 7.14−7.20 (m, 2H), 7.22−7.35 (m, 5H), 7.36−7.40 (m, 1H), 7.41−7.50 (m, 3H), 9.63 (s, 1H), 10.66 (s, 1H), 12.19 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.9, 55.2, 112.2, 114.5, 116.4, 121.28, 121.34, 126.5, 126.6, 127.8, 128.0, 128.8, 128.9, 129.0, 129.6, 132.1, 133.9, 145.8, 146.0, 159.1. ESI/MS (m/z): 407.1866 calcd for $C_{26}H_{23}N_4O^+$ [M − Br]$^+$, found 407.1871. IR (KBr, cm^{-1}): ν 3101, 1605, 1571, 1517, 1498, 1248, 1185, 1077, 1025, 833, 754, 712.

*4-Benzyl-1-(4-(4-bromophenyl)-5-(methoxycarbonyl)-2-phenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6g**).* Compound **6g** (75 mg, 30%) was obtained from bromide **4a** (150 mg, 0.4 mmol), methyl 3-(4-bromophenyl)-2*H*-azirine-2-carboxylate (**5b**; 160 mg, 0.6 mmol), and Et_3N (25 mg, 0.3 mmol) according to the general procedure. Colorless solid, mp 204−206 °C. ^{1}H NMR (DMSO-d_6): δ 3.71 (s, 3H), 5.52 (s, 2H), 7.07−7.22 (m, 4H), 7.33−7.51 (m, 10H), 9.48 (s, 1H), 10.56 (s, 1H), 13.17 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.9, 51.6, 116.0, 118.1, 121.5, 126.8, 127.3, 127.7, 127.8, 128.8, 128.9, 129.0, 129.3, 129.4, 130.9, 131.8, 132.8, 133.7, 145.7, 146.1, 160.0. ESI/MS (m/z): 513.0921 calcd for $C_{27}H_{22}BrN_4O_2^+$ [M − Br]$^+$, found 513.0934. IR (KBr, cm^{-1}): ν 2952, 1701, 1452, 1297, 1216, 1156, 1091, 715.

*4-Benzyl-1-(2,4,5-triphenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6h**).* Compound **6h** (126 mg, 57%) was obtained from bromide **4a** (148 mg, 0.4 mmol), 2,3-diphenyl-2*H*-azirine (**2c**; 120 mg, 0.6 mmol), and Et_3N (25 mg, 0.3 mmol) according to the general procedure. Colorless solid, mp 225−227 °C. ^{1}H NMR (DMSO-d_6): δ 5.54 (s, 2H), 7.03−7.01 (m, 2H), 7.12−7.18 (m, 2H), 7.19−7.46 (m, 16H), 9.48 (s, 1H), 10.61 (s, 1H), 12.32 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 50.8, 115.6, 119.8, 126.9, 127.4, 127.5, 127.7, 127.8, 128.3, 128.5, 128.6, 128.71, 128.71, 128.86, 128.90, 128.93, 129.1, 129.5, 130.9, 131.5, 133.8, 145.5, 145.9. ESI/MS (m/z): 453.2074 calcd for $C_{31}H_{25}N_4^+$ [M − Br]$^+$, found 453.2087. IR (KBr, cm^{-1}): ν 3033, 1569, 1487, 1452, 1208, 1180, 1075, 766, 692.

*4-(2,6-Diisopropylphenyl)-1-(2,4-diphenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazol-1-ium Bromide (**6i**).* Compound **6i** (460 mg, 60%) was obtained from bromide **4g** (627 mg, 1.5 mmol), 3-phenyl-2*H*-azirine (**5a**; 257 mg, 2.2 mmol), and Et_3N (89 mg, 0.9 mmol) according to the general procedure. Colorless solid, mp 273−275 °C. ^{1}H NMR (DMSO-d_6): δ 0.95 (d, J = 6.7 Hz, 6H), 1.20 (d, J = 6.7 Hz, 6H), 2.10−2.22 (m, 2H), 7.16−7.25 (m, 2H), 7.26−7.41 (m, 5H), 7.42−7.56 (m, 6H), 7.65−7.73 (m, 1H), 10.08 (s, 1H), 11.21 (s, 1H), 12.51 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 23.0, 23.5, 28.5, 112.6, 117.2, 121.9, 124.8, 126.2, 126.6, 126.8, 127.1, 128.5, 128.7, 128.9, 129.2, 129.9, 131.8, 132.5, 144.6, 146.8, 147.3. ESI/MS (m/z): 447.2543 calcd for $C_{30}H_{31}N_4^+$ [M − Br]$^+$, found 447.2541. IR (KBr, cm^{-1}): ν 3096, 2968, 2869, 1609, 1536, 1490, 1462, 1301, 1101, 992, 939, 805, 758, 703, 645.

*4-(2,6-Diisopropylphenyl)-1-(2,4-diphenyl-1H-pyrrol-3-yl)-3-phenyl-4H-1,2,4-triazol-1-ium Bromide (**6j**).* Compound **6j** (348 mg, 58%) was obtained from bromide **4h** (500 mg, 0.991 mmol), 3-phenyl-2*H*-azirine (**5a**; 174 mg, 1.49 mmol, 1.5 equiv), and Et_3N (60 mg, 0.60 mmol, 0.6 equiv) according to the general procedure. Colorless solid, mp 311−313 °C. ^{1}H NMR (DMSO-d_6): δ 0.89 (d, J = 6.8 Hz, 6H), 0.95 (d, J = 6.7 Hz, 6H), 2.22 (septet, J = 6.7 Hz, 2H), 7.27−7.47 (m, 10H), 7.47−7.59 (m, 7H), 7.62−7.74 (m, 2H), 11.34 (s, 1H), 12.55 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 21.9, 24.1, 28.7, 112.6, 117.3, 121.4, 121.9, 125.6, 126.3, 126.5, 126.6, 127.2, 128.2, 128.5, 128.7, 129.0, 129.3, 129.7, 129.8, 131.8, 133.1, 133.2, 144.4, 147.9, 154.5. HRMS (ESI) m/z: 523.2856 calcd for $C_{36}H_{35}N_4^+$ [M − Br]$^+$, found 523.2866.

*1-Benzyl-4-(2,4-diphenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazol-4-ium Bromide (**8a**).* Compound **8a** (215 mg, 70%) was obtained from bromide **7a** (241 mg, 0.7 mmol), 3-phenyl-2*H*-azirine (**5a**; 118 mg, 1.0 mmol), and Et_3N (41 mg, 0.4 mmol) according to the general procedure. Colorless solid, mp 235−238 °C. ^{1}H NMR (DMSO-d_6): δ 5.71 (s, 2H), 7.08−7.20 (m, 2H), 7.20−7.35 (m, 7H), 7.36−7.50 (m, 7H), 9.53 (s, 1H), 10.75 (s, 1H), 12.35 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 55.2, 109.4, 117.3, 121.3, 126.6, 126.93, 126.94, 128.17, 128.18, 128.6, 128.8, 128.92, 128.93, 128.94, 129.1, 131.7, 133.4, 144.9, 146.8. ESI/MS (m/z): 377.1761 calcd for $C_{25}H_{21}N_4^+$ [M − Br]$^+$, found 377.1766. IR (KBr, cm^{-1}): ν 3106, 2902, 1607, 1485, 1455, 1201, 1149, 766, 714, 696, 652.

*1-Benzyl-4-(2-(2-bromophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazol-4-ium Bromide (**8b**).* Compound **8b** (316 mg, 73%) was obtained from bromide **7b** (355 mg, 0.8 mmol), 3-phenyl-2*H*-azirine (**5a**; 143 mg, 1.2 mmol), and Et_3N (49 mg, 0.5 mmol) according to the general procedure. Colorless solid, mp 255−258 °C. ^{1}H NMR (DMSO-d_6): δ 5.64 (s, 2H), 7.12−7.18 (m, 2H), 7.19−7.25 (m, 2H), 7.26−7.36 (m, 3H), 7.37−7.56 (m, 7H), 7.68−7.76 (m, 1H), 9.38 (s, 1H), 10.56 (s, 1H), 12.29 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 45.6, 110.9, 117.5, 119.5, 123.1, 126.87, 126.88, 127.4, 128.0, 128.1, 128.8, 128.9, 129.0, 129.5, 131.3, 131.6, 133.0, 133.3, 144.0, 146.4. ESI/MS (m/z): 455.0866 calcd for $C_{25}H_{20}BrN_4^+$ [M − Br]$^+$, found 455.0857. IR (KBr, cm^{-1}): ν 3416, 3004, 1605, 1562, 1477, 1455, 1152, 1105, 1024, 758, 718.

*1-Benzyl-4-(2-(3-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazol-4-ium Bromide (**8c**).* Compound **8c** (515 mg, 83%) was obtained from bromide **7c** (500 mg, 1.2 mmol), 3-phenyl-2*H*-azirine (**5a**; 218 mg, 1.9 mmol), and Et_3N (75 mg, 0.4 mmol) according to the general procedure. Yellow solid, mp 252−253 °C. ^{1}H NMR (DMSO-d_6): δ 5.70 (s, 2H), 7.11−7.18 (m, 2H), 7.25−7.36 (m, 5H),

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7.40−7.46 (m, 3H), 7.55 (s, 1H), 7.66−7.71 (m, 2H), 8.18−8.25 (m, 2H), 9.54 (s, 1H), 10.67 (s, 1H), 12.66 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 55.2, 110.7, 118.5, 121.2, 121.7, 122.6, 126.1, 127.07, 127.13, 128.2, 128.90, 128.91, 129.0, 130.4, 130.8, 131.4, 132.8, 133.2, 144.8, 146.6, 148.2. ESI/MS (*m*/*z*): 422.1612 calcd for $C_{25}H_{20}N_5O_2^+$ [M − Br]$^+$, found 422.1615. IR (KBr, cm^{-1}): ν 3427, 3084, 1566, 1525, 1341, 1161, 1102, 995, 748, 720, 698.

*1-Benzyl-4-(2-(4-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazol-4-ium Bromide (**8d**).* Compound **8d** (145 mg, 58%) was obtained from bromide **7d** (200 mg, 0.5 mmol), 3-phenyl-2*H*-azirine (**5a**; 87 mg, 0.7 mmol), and Et_3N (30 mg, 0.3 mmol) according to the general procedure. Yellow solid, mp 248−250 °C. ^{1}H NMR (DMSO-d_6): δ 5.70 (s, 2H), 7.09−7.18 (m, 2H), 7.27−7.36 (m, 5H), 7.41−7.48 (m, 3H), 7.51−7.57 (m, 2H), 7.68−7.63 (s, 1H), 8.18−8.27 (m, 2H), 9.53 (s, 1H), 10.68 (s, 1H), 12.70 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 55.3, 111.3, 119.4, 122.3, 124.3, 126.1, 127.1, 127.27, 127.28, 128.3, 128.93, 128.98, 129.0, 131.2, 133.3, 135.1, 144.4, 144.8, 146.6. ESI/MS (*m*/*z*): 422.1612 calcd for $C_{25}H_{20}N_5O_2^+$ [M − Br]$^+$, found 422.1619. IR (KBr, cm^{-1}): ν 3499, 3427, 3097, 1600, 1513, 1336, 1107, 853, 702.

*1-Benzyl-4-(2-(4-chlorophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazol-4-ium Bromide (**8e**).* Compound **8e** (205 mg, 82%) was obtained from bromide **7e** (200 mg, 0.5 mmol), 3-phenyl-2*H*-azirine (**5a**; 89 mg, 0.8 mmol), and Et_3N (31 mg, 0.3 mmol) according to the general procedure. Colorless solid, mp 231−232 °C. ^{1}H NMR (DMSO-d_6): δ 5.69 (s, 2H), 7.09−7.17 (m, 2H), 7.26−7.35 (m, 7H), 7.40−7.50 (m, 6H), 9.51 (s, 1H), 10.67 (s, 1H), 12.41 (s, H). ^{13}C NMR (DMSO-d_6): δ 55.2, 109.8, 117.7, 121.4, 126.98, 126.99, 127.4, 127.6, 128.2, 128.5, 128.91, 128.94, 129.1, 129.9, 131.6, 132.8, 133.4, 144.8, 146.7. ESI/MS (*m*/*z*): 411.1371 calcd for $C_{25}H_{20}ClN_4^+$ [M − Br]$^+$, found 411.1375. IR (KBr, cm^{-1}): ν 3496, 3138, 1603, 1564, 1493, 1299, 1100, 835, 766, 722, 656.

*1-Benzyl-4-(2-(4-methoxyphenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazol-4-ium Bromide (**8f**).* Compound **8f** (329 mg, 88%) was obtained from bromide **7f** (300 mg, 0.8 mmol), 3-phenyl-2*H*-azirine (**5a**; 135 mg, 1.2 mmol), and Et_3N (47 mg, 0.5 mmol) according to the general procedure. Colorless solid, mp 238−239 °C. ^{1}H NMR (DMSO-d_6): δ 3.79 (s, 3H), 5.70 (s, 2H), 6.92−6.99 (m, 2H), 7.10−7.16 (m, 2H), 7.18−7.24 (m, 2H), 7.26−7.34 (m, 5H), 7.35−7.40 (m, 1H), 7.41−7.49 (m, 3H), 9.50 (s, 1H), 10.69 (s, 1H), 12.20 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 55.2, 55.3, 108.9, 114.5, 116.6, 121.0, 121.1, 126.8, 126.9, 128.1, 128.2, 128.80, 128.89, 128.90, 128.91, 131.9, 133.4, 144.9, 146.9, 159.2. ESI/MS (*m*/*z*): 407.1866 calcd for $C_{26}H_{23}N_4O^+$ [M − Br]$^+$, found 407.1866. IR (KBr, cm^{-1}): ν 3628, 3473, 3170, 1604, 1503, 1442, 1253, 1183, 1024, 835, 726.

*1-Benzyl-4-(4-(4-bromophenyl)-5-(methoxycarbonyl)-2-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazol-4-ium Bromide (**8g**).* Compound **8g** (135 mg, 54%) was obtained from bromide **7a** (150 mg, 0.4 mmol), methyl 3-(4-bromophenyl)-2*H*-azirine-2-carboxylate (**2b**; 160 mg, 0.6 mmol), and Et_3N (25 mg, 0.3 mmol) according to the general procedure. Colorless solid, mp 228−230 °C. ^{1}H NMR (DMSO-d_6): δ 3.72 (s, 3H), 5.63 (s, 2H), 7.06−7.15 (m, 2H), 7.20−7.26 (m, 2H), 7.38−7.48 (m, 8H), 7.49−7.56 (m, 2H), 9.39 (s, 1H), 10.52 (s, 1H), 13.20 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 51.7, 55.1, 112.6, 118.3, 121.6, 126.5, 127.3, 128.0, 128.1, 128.87, 128.87, 129.0, 129.3, 129.4, 131.1, 132.0, 132.2, 133.2, 144.66, 144.68, 160.1. ESI/MS (*m*/*z*): 513.0921 calcd for $C_{27}H_{22}BrN_4O_2^+$ [M − Br]$^+$, found 513.0908. IR (KBr, cm^{-1}): ν 2984, 1720, 1565, 1497, 1455, 1294, 1223, 1111, 1006, 768, 709.

*1-Benzyl-4-(2,4,5-triphenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazol-4-ium Bromide (**8h**).* Compound **8h** (177 mg, 59%) was obtained from bromide **7a** (200 mg, 0.6 mmol), 2,3-diphenyl-2*H*-azirine (**2c**; 162 mg, 0.8 mmol), and Et_3N (34 mg, 0.3 mmol) according to the general procedure. Colorless solid, mp 281−282 °C. ^{1}H NMR (DMSO-d_6): δ 5.65 (s, 2H), 7.08−7.18 (m, 4H), 7.26−7.49 (m, 16H), 9.47 (s, 1H), 10.64 (s, 1H), 12.34 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 55.1, 112.1, 119.6, 127.1, 127.50, 127.57, 127.58, 127.9, 128.2, 128.35, 128.41, 128.5, 128.75, 128.81, 128.90, 128.90, 129.0, 129.8, 130.8, 131.3, 133.2, 144.8, 146.8. ESI/MS (*m*/*z*): 453.2074 calcd for $C_{31}H_{25}N_4^+$ [M − Br]$^+$, found 453.2056. IR (KBr, cm^{-1}): ν 3049, 1595, 1490, 1453, 1293, 1087, 768, 698.

Typical Procedure for the Debenzylation of Pyrrolyltriazolium Bromides. *Method A.* Pd/C (10 wt %) was added to a solution of 4-benzyl-1-(2,4-diphenyl-1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazol-1-ium bromide (**6a**; 0.22 mmol) and ammonium formate (2.2 mmol, 10 equiv) in MeOH (20 mL), and the resulting suspension was refluxed for 15 h (monitored by TLC). The reaction mixture was filtered off from Pd/C, evaporated to dryness, and suspended in water, and then the product was filtered, washed with water, and dried.

Method B. Pd/C (10 wt %) was added to a solution of 4-benzyl-1-(2-(4-methoxyphenyl)-4-phenyl-1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazol-1-ium bromide (**6f**; 0.16 mmol) in MeOH (10 mL), and the resulting suspension was stirred overnight under an atmosphere of hydrogen. After the completion of the reaction (monitored by TLC) the reaction mixture was filtered off from Pd/C and evaporated to dryness to give the pure product.

*1-(2,4-Diphenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole (**14a**).* Compound **14a** (57 mg, 91%) was obtained from **6a** (100 mg, 0.22 mmol), ammonium formate (0.138 mg, 2.2 mmol), and Pd/C (6 mg, 10 wt %) according to Method A. Colorless solid, mp 215−217 °C. ^{1}H NMR (DMSO-d_6): δ 7.01−7.07 (m, 2H), 7.08−7.17 (m, 3H), 7.18−7.26 (m, 3H), 7.27−7.40 (m, 3H), 8.29 (s, 1H), 8.60 (s, 1H), 11.89 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 115.5, 116.4, 122.1, 125.3, 125.9, 126.1, 127.2, 128.5, 128.54, 128.8, 130.2, 133.2, 147.2, 152.4. ESI/MS (*m*/*z*): 287.1291 calcd for $C_{18}H_{15}N_4^+$ [M + H]$^+$, found 287.1304. IR (KBr, cm^{-1}): ν 3177, 1608, 1488, 1279, 1135, 1007, 947, 766, 699, 661, 640.

*1-(2-(4-Methoxyphenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole (**14b**).* Compound **14b** (48 mg, 92%) was obtained from **6f** (80 mg, 0.2 mmol) and Pd/C (5 mg, 10 wt %) according to Method B. Gray solid, mp 190−192 °C. ^{1}H NMR (DMSO-d_6): δ 3.73 (s, 3H), 6.85−6.94 (m, 2H), 6.98−7.10 (m, 4H), 7.11−7.17 (m, 1H), 7.18−7.25 (m, 2H), 7.27−7.34 (m, 1H), 8.27 (s, 1H), 8.56 (s, 1H), 11.82 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 55.1, 114.2, 114.7, 115.6, 121.8, 122.7, 125.85, 125.93, 126.7, 128.5, 128.7, 133.3, 147.1, 152.3, 158.5. ESI/MS (*m*/*z*): 317.1397 calcd for $C_{19}H_{17}N_4O^+$ [M + H]$^+$, found 317.1392; 339.1216 calcd for $C_{19}H_{16}N_4NaO^+$ [M + Na]$^+$, found 339.1211. IR (KBr, cm^{-1}): ν 3115, 1603, 1520, 1502, 1253, 1182, 1136, 1031, 947, 835, 762, 699.

*1-(2,4,5-Triphenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole (**14c**).* Compound **14c** (53 mg, 86%) was obtained from **6h** (90 mg, 0.2 mmol) and Pd/C (9 mg, 10 wt %) according to Method B. Colorless solid, mp 209−211 °C. ^{1}H NMR (DMSO-d_6): δ 7.01−7.10 (m, 2H), 7.15−7.22 (m, 3H), 7.23−7.29 (m, 4H), 7.30−7.43 (m, 6H), 8.14 (s, 1H), 8.55 (s, 1H), 11.93 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 118.2, 120.3, 126.0, 126.6, 127.1, 127.3, 127.9, 128.19, 128.20, 128.23, 128.3, 128.6, 129.4, 129.9, 131.7, 132.8, 147.2, 152.0. ESI/MS (*m*/*z*): 363.1604 calcd for $C_{24}H_{19}N_4^+$ [M + H]$^+$, found 363.1596; 385.1424 calcd for $C_{24}H_{18}N_4Na^+$ [M + Na]$^+$, found 385.1414. IR (KBr, cm^{-1}): ν 3051, 1595, 1484, 1315, 766, 694.

*4-(2,4-Diphenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazole (**15a**).* Compound **15a** (53 mg, 84%) was obtained from **8a** (100 mg, 0.2 mmol), ammonium formate (0.138 mg, 2.2 mmol), and Pd/C (10 mg, 10 wt %) according to Method A. Colorless solid, mp 312−313 °C. ^{1}H NMR (DMSO-d_6): δ 7.01−7.07 (m, 2H), 7.08−7.14 (m, 2H), 7.15−7.21 (m, 1H), 7.22−7.29 (m, 3H), 7.30−7.39 (m, 3H), 8.69 (s, 2H), 11.97 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 112.1, 116.6, 121.7, 125.5, 126.21, 126.23, 127.3, 127.8, 128.6, 128.9, 130.1, 133.0, 145.1. ESI/MS (*m*/*z*): 309.1111 calcd for $C_{18}H_{14}N_4Na^+$ [M + Na]$^+$, found 309.1138. IR (KBr, cm^{-1}): ν 3112, 1610, 1486, 1413, 1292, 1158, 1101, 979, 766, 751, 695, 654.

*4-(2-(4-Methoxyphenyl)-4-phenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazole (**15b**).* Compound **15b** (35 mg, 68%) was obtained from **8f** (80 mg, 0.2 mmol) and Pd/C (8 mg, 10 wt %) according to Method B and was additionally purified by column chromatography using a mixture of dichloromethane and methanol (10:1) as eluent. Gray solid, mp 289−291 °C. ^{1}H NMR (DMSO-d_6): δ 3.75 (s, 3H), 6.89−6.95 (m, 2H), 6.99−7.09 (m, 4H), 7.14−7.20 (m, 1H), 7.22−7.31 (m, 3H), 8.67 (s, 2H), 11.83 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 55.1, 111.3, 114.3, 115.8, 121.4, 122.6, 126.10, 126.11, 127.0, 127.9, 128.6, 133.2, 145.1, 158.5. ESI/MS (*m*/*z*): 317.1397 calcd for $C_{19}H_{17}N_4O^+$ [M + H]$^+$, found 317.1399; 339.1216 calcd for $C_{19}H_{16}N_4NaO^+$ [M + Na]$^+$,

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found 339.1221. IR (KBr, cm^{-1}): ν 3113, 1604, 1521, 1503, 1463, 1284, 1251, 1181, 1109, 1029, 835, 752, 697.

*4-(2,4,5-Triphenyl-1H-pyrrol-3-yl)-4H-1,2,4-triazole (**15c**).* Compound **15c** (30 mg, 56%) was obtained from **8h** (80 mg, 0.2 mmol) and Pd/C (8 mg, 10 wt %) according to Method B and was additionally purified by recrystallization from methanol. Colorless solid, mp 346−347 °C. ^{1}H NMR (DMSO-d_6): δ 7.05−7.12 (m, 2H), 7.20−7.39 (m, 13H), 8.62 (s, 2H), 11.94 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 114.9, 120.2, 126.2, 126.9, 127.0, 127.44, 127.44, 127.6, 128.3, 128.35, 128.38, 128.7, 129.7, 131.6, 132.6, 145.06, 145.06. ESI/MS (m/z): 363.1604 calcd for $C_{24}H_{19}N_4^+$ [M + H]$^+$, found 363.1609; 385.1424 calcd for $C_{24}H_{18}N_4Na^+$ [M + Na]$^+$, found 385.1429. IR (KBr, cm^{-1}): ν 3113, 1604, 1521, 1503, 1463, 1284, 1251, 1181, 1109, 1029, 835, 752, 697.

Typical Procedure for the Synthesis of Pyrrolyltriazole-thiones 16a−f, 17a−f, 18, and 21. Sulfur (1.75 mmol, 2 equiv) and potassium *tert*-butoxide (0.97 mmol, 1.1 equiv) were added consecutively to a stirred suspension of 4-benzyl-1-(2,4-diphenyl-1*H*-pyrrol-3-yl)-4*H*-1,2,4-triazol-1-ium bromide (**6a**; 0.88 mmol, 1 equiv) in dry tetrahydrofuran (5 mL) under an argon atmosphere at 0 °C. The mixture was stirred at 0 °C for an additional 10 min and then for 20 min at room temperature. The solvent was evaporated, and the residue was purified by column chromatography using EtOAc/hexanes (2:1) as eluent to afford the product.

*4-Benzyl-1-(2,4-diphenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**16a**).* Compound **16a** (305 mg, 85%) was obtained from **6a** (400 mg, 0.9 mmol), sulfur (56 mg, 1.8 mmol), and potassium *tert*-butoxide (108 mg, 1.0 mmol) according to the typical procedure. Slightly yellow solid, mp 174−175 °C. ^{1}H NMR (DMSO-d_6): δ 5.20−5.41 (m, 2H), 7.12−7.45 (m, 16H), 8.76 (s, 1H), 11.85 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 49.8, 116.2, 116.8, 123.8, 126.3, 126.4, 127.4, 127.5, 127.9, 128.6, 128.8, 129.0, 129.3, 130.1, 130.6, 133.7, 135.0, 140.0, 170.3. ESI/MS (m/z): 409.1481 calcd for $C_{25}H_{21}N_4S^+$ [M + H]$^+$, found 409.1479; 431.1301 calcd for $C_{25}H_{21}N_4NaS^+$ [M + Na]$^+$, found 431.1300. IR (KBr, cm^{-1}): ν 3407, 3259, 3034, 1609, 1541, 1489, 1404, 767, 694.

*4-Benzyl-1-(2-(2-bromophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**16b**).* Compound **16b** (78 mg, 82%) was obtained from **6b** (105 mg, 0.2 mmol), sulfur (13 mg, 0.4 mmol), and potassium *tert*-butoxide (24 mg, 0.2 mmol) according to the typical procedure. Colorless solid, mp 219−221 °C. ^{1}H NMR (DMSO-d_6): δ 5.19−5.28 (m, 2H), 7.12−7.18 (m, 3H), 7.19−7.37 (m, 10H), 7.52−7.57 (m, 1H), 7.66−7.71 (m, 1H), 8.60 (s, 1H), 11.71 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 48.1, 115.9, 117.2, 121.0, 123.2, 125.7, 126.2, 127.0, 127.3, 127.7, 128.4, 128.5, 128.7, 130.0, 131.6, 132.1, 133.0, 133.8, 136.0, 141.6, 169.2. ESI/MS (m/z): 487.0587 calcd for $C_{25}H_{20}BrN_4S^+$ [M + H]$^+$, found 487.0576; 509.0406 calcd for $C_{25}H_{19}BrN_4NaS^+$ [M + Na]$^+$, found 509.0395. IR (KBr, cm^{-1}): ν 3232, 1603, 1547, 1417, 1367, 1220, 1080, 1009, 940, 757, 723, 695.

*4-Benzyl-1-(2-(3-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**16c**).* Compound **16c** (70 mg, 70%) was obtained from **6c** (111 mg, 0.2 mmol), sulfur (14 mg, 0.4 mmol), and potassium *tert*-butoxide (27 mg, 0.2 mmol) according to the typical procedure. Yellow solid, mp 202−203 °C (chloroform/hexane). ^{1}H NMR (DMSO-d_6): δ 5.26−5.37 (m, 2H), 7.15−7.30 (m, 7H), 7.32−7.40 (m, 3H), 7.41−7.45 (m, 1H), 7.58−7.65 (m, 1H), 7.67−7.74 (m, 1H), 8.05−8.13 (m, 1H), 8.16−8.24 (m, 1H), 8.85 (s, 1H), 12.24 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 48.4, 117.4, 117.7, 119.8, 121.4, 122.9, 126.1, 126.4, 126.8, 127.2, 127.9, 128.5, 128.6, 130.3, 131.5, 132.1, 133.3, 135.9, 142.4, 148.2, 169.1. ESI/MS (m/z): 454.1332 calcd for $C_{25}H_{20}N_5O_2S^+$ [M + H]$^+$, found 454.1333; 476.1152 calcd for $C_{25}H_{19}N_5NaO_2S^+$ [M + Na]$^+$, found 476.1152. IR (KBr, cm^{-1}): ν 3219, 3130, 1523, 1399, 1343, 1220, 1115, 929, 867, 758, 709.

*4-Benzyl-1-(2-(4-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**16d**).* Compound **16d** (118 mg, 87%) was obtained from **6d** (150 mg, 0.3 mmol), sulfur (19 mg, 0.6 mmol), and potassium *tert*-butoxide (37 mg, 0.3 mmol) according to the typical procedure. Orange solid, mp 267−268 °C. ^{1}H NMR (DMSO-d_6): δ 5.24−5.38 (m, 2H), 7.17−7.27 (m, 5H), 7.30−7.34 (m, 2H), 7.36−7.43 (m, 3H), 7.45−7.50 (m, 3H), 8.11−8.16 (m, 2H), 8.85 (s, 1H), 12.29 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 48.4, 118.4, 118.7, 123.4, 124.1, 125.7, 126.2, 126.5, 126.8, 127.4, 127.9, 128.5, 128.6, 133.1, 136.0, 136.8, 142.5, 145.4, 168.9. ESI/MS (m/z): 454.1332 calcd for $C_{25}H_{20}N_5O_2S^+$ [M + H]$^+$, found 454.1313; 476.1152 calcd for $C_{25}H_{19}N_5NaO_2S^+$ [M + Na]$^+$, found 476.1134. IR (KBr, cm^{-1}): ν 3350, 1595, 1508, 1401, 1327, 851, 762, 699.

*4-Benzyl-1-(2-(4-chlorophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**16e**).* Compound **16e** (99 mg, 90%) was obtained from **6e** (122 mg, 0.3 mmol), sulfur (16 mg, 0.5 mmol), and potassium *tert*-butoxide (31 mg, 0.3 mmol) according to the typical procedure. Colorless solid, mp 195−196 °C (chloroform/hexane). ^{1}H NMR (DMSO-d_6): δ 5.24−5.37 (m, 2H), 7.14−7.26 (m, 5H), 7.27−7.33 (m, 5H), 7.34−7.44 (m, 5H), 8.78 (s, 1H), 11.93 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 48.3, 116.5, 116.7, 122.6, 125.9, 126.4, 127.26, 127.29, 127.9, 128.0, 128.4, 128.6, 128.7, 129.5, 131.6, 133.6, 136.0, 142.1, 169.1. ESI/MS (m/z): 465.0911 calcd for $C_{25}H_{19}ClN_4NaS^+$ [M + Na]$^+$, found 465.0914. IR (KBr, cm^{-1}): ν 3357, 1604, 1541, 1487, 1403, 926, 720, 693.

*4-Benzyl-1-(2-(4-methoxyphenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**16f**).* Compound **16f** (71 mg, 87%) was obtained from **6f** (90 mg, 0.2 mmol), sulfur (12 mg, 0.4 mmol), and potassium *tert*-butoxide (23 mg, 0.2 mmol) according to the typical procedure. Yellow solid, mp 140−142 °C. ^{1}H NMR (DMSO-d_6): δ 3.75 (s, 3H), 5.25−5.39 (m, 2H), 6.82−6.91 (m, 2H), 7.11−7.17 (m, 1H), 7.17−7.32 (m, 9H), 7.34−7.44 (m, 3H), 8.75 (s, 1H), 11.70 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 48.3, 55.1, 114.1, 115.3, 115.5, 122.3, 123.3, 125.7, 126.3, 127.1, 127.3, 127.8, 128.4, 128.6, 129.3, 133.9, 136.1, 141.8, 158.3, 169.2. ESI/MS (m/z): 439.1587 calcd for $C_{26}H_{23}N_4OS^+$ [M + H]$^+$, found 439.1573; 461.1407 calcd for $C_{26}H_{22}N_4NaOS^+$ [M + Na]$^+$, found 461.1399. IR (KBr, cm^{-1}): ν 3233, 1603, 1538, 1512, 1456, 1405, 1365, 1251, 1179, 1027, 939, 831, 722, 694.

*1-Benzyl-4-(2,4-diphenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**17a**).* Compound **17a** (102 mg, 95%) was obtained from **8a** (120 mg, 0.3 mmol), sulfur (17 mg, 0.5 mmol), and potassium *tert*-butoxide (32 mg, 0.3 mmol) according to the typical procedure. Pale yellow solid, mp 211−213 °C. ^{1}H NMR (DMSO-d_6): δ 5.40−5.57 (m, 2H), 7.16−7.45 (m, 16H), 8.54 (s, 1H), 11.95 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 51.7, 112.3, 116.5, 122.5, 125.8, 126.1, 126.6, 127.2, 127.3, 127.7, 128.46, 128.51, 128.7, 129.0, 130.3, 133.3, 136.1, 142.8, 168.9. ESI/MS (m/z): 409.1481 calcd for $C_{25}H_{21}N_4S^+$ [M + H]$^+$, found 409.1494; 431.1301 calcd for $C_{25}H_{20}N_4NaS^+$ [M + Na]$^+$, found 431.1316. IR (KBr, cm^{-1}): ν 3235, 3149, 1606, 1536, 1485, 1442, 1412, 1329, 1258, 944, 771, 729, 695.

*1-Benzyl-4-(2-(2-bromophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**17b**).* Compound **17b** (55 mg, 75%) was obtained from **8b** (80 mg, 0.2 mmol), sulfur (10 mg, 0.3 mmol) and potassium *tert*-butoxide (18 mg, 0.2 mmol) according to the typical procedure. Colorless solid, mp 144−146 °C. ^{1}H NMR (DMSO-d_6): δ 5.28−5.41 (m, 2H), 7.08−7.13 (m, 2H), 7.15−7.21 (m, 1H), 7.23−7.28 (m, 4H), 7.29−7.39 (m, 6H), 7.58 (dd, J = 7.4, 1.9 Hz, 1H), 7.70 (dd, J = 7.7, 1.5 Hz, 1H), 8.49 (s, 1H), 11.81 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 51.5, 113.3, 116.2, 120.9, 123.5, 126.0, 126.4, 127.0, 127.4, 127.6, 128.4, 128.5, 128.6, 130.4, 131.4, 132.5, 132.8, 133.3, 136.0, 142.9, 169.7. ESI/MS (m/z): 487.0587 calcd for $C_{25}H_{20}BrN_4S$+ [M + H]$^+$, found 487.0592. IR (KBr, cm^{-1}): ν 3233, 1607, 1480, 1441, 1411, 1328, 944, 758, 726.

*1-Benzyl-4-(2-(3-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**17c**).* Compound **17c** (84 mg, 93%) was obtained from **8c** (100 mg, 0.2 mmol), sulfur (13 mg, 0.4 mmol), and potassium *tert*-butoxide (25 mg, 0.2 mmol) according to the typical procedure. Yellow solid, mp 213−215 °C. ^{1}H NMR (DMSO-d_6): δ 5.38−5.56 (m, 2H), 7.17−7.32 (m, 7H), 7.33−7.42 (m, 3H), 7.44−7.48 (m, 1H), 7.61−7.67 (m, 1H), 7.70−7.78 (m, 1H), 8.12 (dd, J = 8.1, 1.5 Hz, 1H), 8.27−8.36 (m, 1H), 8.59 (s, 1H), 12.31 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 51.8, 113.5, 117.9, 120.2, 121.7, 122.9, 126.4, 126.6, 126.7, 127.4, 127.8, 128.5, 128.6, 130.4, 131.7, 131.8, 132.8, 136.90, 142.6, 148.2, 168.6. ESI/MS (m/z): 476.1152 calcd for $C_{25}H_{19}N_5NaO_2S^+$ [M + Na]$^+$, found 476.1158. IR (KBr, cm^{-1}): ν 3209, 1606, 1527, 1406, 1347, 1260, 725.

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*1-Benzyl-4-(2-(4-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**17d**).* Compound **17d** (79 mg, 97%) was obtained from **8d** (90 mg, 0.2 mmol), sulfur (11 mg, 0.4 mmol), and potassium *tert*-butoxide (22 mg, 0.2 mmol) according to the typical procedure. Orange solid, mp 221−223 °C. ^{1}H NMR (DMSO-d_6): δ 5.35−5.59 (m, 2H), 7.20−7.45 (m, 10H), 7.49−7.58 (m, 3H), 8.13−8.23 (m, 2H), 8.60 (s, 1H), 12.37 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 52.1, 114.7, 119.2, 123.6, 124.3, 126.2, 126.7, 126.8, 127.0, 127.7, 128.0, 128.7, 128.8, 132.8, 136.2, 136.8, 142.7, 145.8, 168.6. ESI/MS (m/z): 476.1152 calcd for $C_{25}H_{19}N_5NaO_2S^+$ [M + Na]$^+$, found 476.1161. IR (KBr, cm^{-1}): ν 3247, 1599, 1519, 1439, 1404, 1334, 1100, 851, 713, 697.

*1-Benzyl-4-(2-(4-chlorophenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**17e**).* Compound **17e** (81 mg, 90%) was obtained from **8e** (100 mg, 0.2 mmol), sulfur (13 mg, 0.4 mmol), and potassium *tert*-butoxide (25 mg, 0.2 mmol) according to the typical procedure. Colorless solid, mp 246−249 °C. ^{1}H NMR (DMSO-d_6): δ 5.37−5.53 (m, 2H), 7.18−7.32 (m, 7H), 7.34−7.44 (m, 8H), 8.55 (s, 1H), 11.02 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 51.8, 112.6, 117.0, 122.6, 126.2, 126.7, 127.4, 127.5, 127.8, 127.9, 128.50, 128.51, 128.8, 129.2, 131.9, 133.1, 136.0, 142.7, 168.8. ESI/MS (m/z): 465.0911 calcd for $C_{25}H_{19}ClN_4NaS^+$ [M + Na]$^+$, found 465.0923. IR (KBr, cm^{-1}): ν 3262, 3114, 1608, 1537, 1495, 1437, 1405, 1326, 1260, 1181, 1010, 826, 759, 719, 697.

*1-Benzyl-4-(2-(4-methoxyphenyl)-4-phenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**17f**).* Compound **17f** (84 mg, 93%) was obtained from **8f** (100 mg, 0.2 mmol), sulfur (13 mg, 0.4 mmol), and potassium *tert*-butoxide (25 mg, 0.2 mmol) according to the typical procedure. Colorless solid, mp 242−244 °C. ^{1}H NMR (DMSO-d_6): δ 3.76 (s, 3H), 5.39−5.54 (m, 2H), 6.86−6.96 (m, 2H), 7.16−7.44 (m, 13H), 8.51 (s, 1H), 11.80 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 51.8, 55.1, 111.5, 114.2, 115.8, 122.1, 122.8, 126.0, 126.6, 127.35, 127.37, 127.7, 128.4, 128.5, 129.2, 133.4, 136.1, 142.9, 158.5, 169.0. ESI/MS (m/z): 461.1407 calcd for $C_{26}H_{22}N_4NaOS^+$ [M + Na]$^+$, found 461.1428. IR (KBr, cm^{-1}): ν 3257, 1602, 1534, 1511, 1409, 1325, 1252, 1184, 1008, 838, 764, 691, 613.

*4-Benzyl-1-(2,4-diphenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-selenone (**18**).* Compound **18** (56 mg, 70%) was obtained from **6a** (80 mg, 0.2 mmol), selenium (28 mg, 0.4 mmol), and potassium *tert*-butoxide (22 mg, 0.2 mmol) according to the typical procedure. Yellow solid, mp 170−172 °C. ^{1}H NMR (DMSO-d_6): δ 5.39−5.49 (m, 2H), 7.14−7.26 (m, 6H), 7.27−7.35 (m, 7H), 7.36−7.44 (m, 3H), 8.90 (s, 1H), 11.87 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 49.9, 116.3, 116.8, 122.3, 125.7, 125.9, 126.4, 127.0, 127.3, 127.9, 128.4, 128.60, 128.62, 128.9, 130.6, 133.7, 135.9, 143.5, 165.1. ESI/MS (m/z): 479.0745 calcd for $C_{25}H_{20}N_4NaSe^+$ [M + Na]$^+$, found 479.0744. IR (KBr, cm^{-1}): ν 3271, 1702, 1606, 1540, 1487, 1396, 1362, 1216, 965, 938, 765, 697.

*4-(2,6-Diisopropylphenyl)-1-(2,4-diphenyl-1H-pyrrol-3-yl)-1H-1,2,4-triazole-5(4H)-thione (**21**).* Compound **21** (53 mg, 98%) was obtained from **6i** (60 mg, 0.1 mmol), sulfur (7 mg, 0.2 mmol), and potassium *tert*-butoxide (14 mg, 0.1 mmol) according to the typical procedure. Colorless solid, mp 312−314 °C. ^{1}H NMR (DMSO-d_6): δ 1.11−1.18 (m, 6H), 1.22 (d, J = 6.8 Hz, 6H), 2.51−2.59 (m, 2H), 7.19−7.25 (m, 1H), 7.26−7.33 (m, 4H), 7.34−7.42 (m, 6H), 7.44−7.49 (m, 2H), 7.51−7.56 (m, 1H), 8.87 (s, 1H), 11.90 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 23.18, 23.19, 23.86, 23.91, 28.27, 28.34, 116.0, 116.3, 122.6, 124.07, 124.09, 125.7, 126.0, 126.5, 127.2, 128.2, 128.5, 129.2, 129.8, 130.6, 130.7, 133.8, 142.4, 145.9, 146.0, 170.1. ESI/MS (m/z): 479.2264 calcd for $C_{30}H_{31}N_4S^+$, [M + H]+, found 479.2274. IR (KBr, cm^{-1}): ν 3418, 2961, 1723, 1605, 1459, 1383, 1339, 936, 759, 694.

*4-(2,6-Diisopropylphenyl)-1-(2,4-diphenyl-1H-pyrrol-3-yl)-3-phenyl-1H-1,2,4-triazole-5(4H)-thione (**25**).* Compound **25** was obtained from carbene **23a** (70 mg, 0.13 mmol) and sulfur (9 mg, 0.3 mmol, 2 equiv) according to the typical procedure for the synthesis of pyrrolyltriazolethiones, but without the addition of the base. Yield: 69 mg, 93%. Colorless solid, mp 248−250 °C. ^{1}H NMR (DMSO-d_6): δ 0.89 (d, J = 6.8, 6H), 1.22 (d, J = 6.7 Hz, 6H), 2.57 (septet, J = 6.8 Hz, 2H), 7.13−7.24 (m, 3H), 7.25−7.33 (m, 5H), 7.34−7.48 (m, 8H), 7.53 (d, J = 7.3 Hz, 2H), 7.57−7.63 (m, 1H), 11.95 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 22.78, 22.82, 24.1, 28.5, 28.6, 115.8, 116.4, 122.6, 124.7, 124.88, 124.92, 125.8, 126.1, 126.5, 126.7, 127.2, 128.3, 128.5, 128.9, 129.2, 130.2, 130.7, 131.10, 131.12, 133.8, 145.6, 145.7, 149.1, 171.6. HRMS (ESI) m/z: 577.2396 calcd for $C_{36}H_{34}N_4NaS^+$ [M + Na]$^+$, found 577.2386.

(*E*)-*N*-Cyano-*N*-(2,6-diisopropylphenyl)-*N*′-(2,4-diphenyl-1*H*-pyrrol-3-yl)formimidamide (20). Potassium hydroxide (21 mg, 0.38 mmol, 2 equiv) was added to a stirred suspension of **6i** (100 mg, 0.19 mmol) in distilled water (5 mL), and the reaction mixture was vigorously stirred for 10 days. The precipitate was filtered off, washed with water, and dried to give pure **20**. Yield: 80 mg, 94%. Beige solid, mp 135−137 °C. ^{1}H NMR (DMSO-d_6): δ 1.01 (d, J = 6.8 Hz, 6H), 1.23 (d, J = 6.8 Hz, 6H), 2.96−3.09 (m, 1H), 7.01 (d, J = 3.0 Hz, 1H), 7.14−7.23 (m, 2H), 7.27−7.39 (m, 6H), 7.41−7.50 (m, 3H), 7.55−7.63 (m, 2H), 7.65 (s, 1H), 11.30 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 23.0, 23.7, 28.2, 110.6, 116.9, 117.8, 121.3, 124.6, 125.41, 125.43, 127.3, 127.4, 128.3, 128.4, 130.2, 130.9, 132.3, 134.9, 146.5, 148.6. ESI/MS (m/z): 447.2543 calcd for $C_{30}H_{30}N_4^+$ [M + H]$^+$, found 447.2560; 915.4833 calcd for $C_{60}H_{60}N_8Na^+$ [2M + Na]$^+$, found 915.4838. IR (KBr, cm^{-1}): ν 3361, 2965, 2224, 1651, 1603, 1458, 1252, 1201, 765, 697.

***N*-Benzyl-*N*-cyano-*N*′-(2,4-diphenyl-1*H*-pyrrol-3-yl)-formimidamide (22).** Potassium *tert*-butoxide (27 mg, 0.24 mmol, 1.1 equiv) was added to a stirred suspension of **6a** (100 mg, 0.22 mmol) in anhydrous THF (5 mL), and the reaction mixture was stirred for the next 10 min; then the solvent was evaporated and the residue was purified by column chromatography using dichloromethane as eluent. Yield: 52 mg, 64%. Colorless solid, mp 167−168 °C. ^{1}H NMR ($CDCl_3$): δ 4.86 (s, 2H), 6.86 (d, J = 3.0 Hz, 1H), 7.19−7.25 (m, 2H), 7.29−7.35 (m, 4H), 7.35−7.43 (m, 7H), 7.47 (d, J = 7.4 Hz, 2H), 7.57 (s, 1H), 8.16 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 50.2, 112.6, 116.2, 119.7, 122.6, 125.8, 126.1, 126.3, 127.5, 127.9, 128.4, 128.6, 128.7, 128.8, 128.9, 131.9, 134.4, 146.5. HRMS (ESI): m/z 399.1580 calcd for $C_{25}H_{20}N_4Na^+$ [M + Na]$^+$, found 399.1566.

4-(2,6-Diisopropylphenyl)-1-(2,4-diphenyl-1*H*-pyrrol-3-yl)-3-phenyl-1*H*-1,2,4-triazol-5-ylidene (23a). Compound **23a** was obtained from 4-(2,6-diisopropylphenyl)-1-(2,4-diphenyl-1*H*-pyrrol-3-yl)-3-phenyl-4*H*-1,2,4-triazol-1-ium bromide (**6j**; 150 mg, 0.249 mmol) and potassium *tert*-butoxide (29 mg, 0.26 mmol, 1.0 equiv). A mixture of bromide **6j** and KO*t*Bu in 10 mL of THF was stirred at room temperature for 30 min. It became almost homogeneous. Then it was filtered, evaporated, redissolved in benzene, and evaporated to dryness again. Yield: 129 mg, 99%. Colorless solid, mp 143−145 °C. ^{1}H NMR (DMSO-d_6, 80 °C): δ 0.94 (d, J = 6.9 Hz, 6H), 1.00 (d, J = 6.8 Hz, 6H), 2.55 (septet, J = 6.8 Hz, 2H), 7.13−7.19 (m, 1H), 7.20−7.36 (m, 14H), 7.37−7.43 (m, 1H), 7.46 (d, J = 7.3 Hz, 2H), 7.48−7.54 (m, 1H), 11.56 (s, 1H). ^{1}H NMR (C_6D_6, 60 °C): δ 0.93 (d, J = 6.9 Hz, 6H), 0.95 (d, J = 6.8 Hz, 6H), 2.88 (septet, J = 6.8 Hz, 2H), 6.33 (s, 1H), 6.80−6.90 (m, 3H), 6.91−6.97 (m, 2H), 6.98−7.02 (m, 3H), 7.09−7.14 (m, 2H), 7.22−7.28 (m, 2H), 7.43 (d, J = 7.2 Hz, 2H), 7.51 (dd, J = 8.1, 1.5 Hz, 2H), 7.56 (d, J = 7.2 Hz, 2H). ^{13}C NMR (C_6D_6, 60 °C): δ 22.7, 24.6, 28.9, 117.0, 120.4, 121.7, 124.3, 125.6, 126.0, 127.2, 127.2, 127.4, 128.4, 128.5, 128.6, 128.7, 128.8, 130.0, 130.0, 130.1, 132.7, 134.9, 136.0, 146.1, 153.1, 210.2 (C carbene). HRMS (ESI): m/z 523.2856 calcd for $C_{36}H_{35}N_4^+$ [M + H]$^+$, found 523.2858.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02200.

NMR spectra for all new compounds, computation details: energies of the reactants, transition states, their Cartesian coordinates. (PDF)

Crystallographic data for **8a** (CIF)

Crystallographic data for **18** (CIF)

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Notes

The authors declare no competing financial interest.

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