

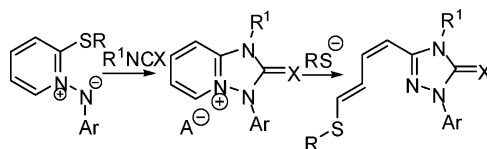
New Facile Tandem Route to Oxo- and Thioxo[1,2,4]triazolo[1,5-*a*]pyridinium Salts

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2-Arylsulfanyl- and benzylsulfanylpyridinium *N*-arylimides (**2**), easily available from tetrazolo[1,5-*b*]pyridinium salts (**1**), participate in 1,3-dipolar cycloaddition with aryl isothiocyanates and aryl isocyanates to result in formation of fused thioxo- and oxo[1,2,4]triazolium salts (**5** and **12**), respectively. This transformation is interpreted as a regular 1,3-cycloaddition followed by spontaneous elimination of the aryl- or benzylsulfanyl group. Formation of these triazolium salts can be followed—under appropriate reaction conditions—by ring-opening reactions to afford some new triazolylidienes (**6**). Recognition of the intermediate participation of the thiolate anion along the pathway **1** → **5** allowed elaboration of a simple procedure to **5** implying a tandem reaction sequence.

Introduction

In our recent papers^{1,2} we described that tetrazolopyridinium salts (**1**), available from 2-aminopyridines in two simple reaction steps in high yields,³ can conveniently be transformed to 2-arylsulfanylpyridinium arylimides (**2**) of zwitterionic structure (mesomeric betaines) by reaction with aryl- or benzylthiolates. These strongly dipolar derivatives (**2**) proved to be suitable starting compounds for various cyclizations and subsequent ring transformations. Thus, these compounds undergo 1,3-dipolar cycloaddition (e.g., with *N*-phenylmaleimide) to give tetrahydropyrazolo[1,5-*a*]pyridines (**3**) as cycloaddition products, and this transformation was followed by a facile ring transformation to tetrahydropyrrolo[3,2-*b*]pyridines (**4**) in good yields. In these reactions the 1,3-dipolar cycloadditions proceeded in a regioselective manner with the exclusive participation of C-6 and the exo nitrogen atom of the sulfanylpyridinium arylimide compound (**2**) (Scheme 1).

Results and Discussion

In this paper the continuation of these studies will be discussed, and reaction of the mesomeric betaines (**2**) with

isothiocyanates and isocyanates as 1,3-dipolarophiles will be described. These reagents, containing cumulated double bonds, proved to be suitable dipolarophiles in several cases.^{4,5,6,7}

Experiments with reactions of several derivatives of **2** with aryl or benzyl isothiocyanates in dichloromethane led to unexpected results. In most cases a mixture was obtained containing two components: a fused thioxotriazolium salt (**5**, A = Cl) and a triazolylidene (**6**, Schemes 2 and 3). To the best of our knowledge, few examples for oxo or thioxo derivatives of this ring system have been published.⁸ To rationalize the surprising formation of a salt containing a chloride anion it had to be assumed that isothiocyanates react with **2** in a 1,3-dipolar cycloaddition but, in contrast to the above-mentioned earlier cases, with a different regioselectivity. If it is C-2 besides the exo nitrogen atom in **2** that participates in the cycloaddition, a cycloadduct (**7**) can be formed from which a spontaneous elimination of the arylthiolate anion can occur to yield the fused thioxo[1,2,4]triazolium arylthiolate salt **8** as a second intermediate. As the isolated salt (**5**, A = Cl) contained a chloride anion,⁹

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(1) Riedl, Zs.; Kövér, P.; Soós, T.; Hajós, Gy.; Egyed, O.; Fábián, L.; Messmer, A. *J. Org. Chem.* **2003**, *68*, 5652.

(2) Messmer, A.; Kövér, P.; Riedl, Zs.; Gömöry, Á.; Hajós, Gy. *Tetrahedron* **2002**, *58*, 3613.

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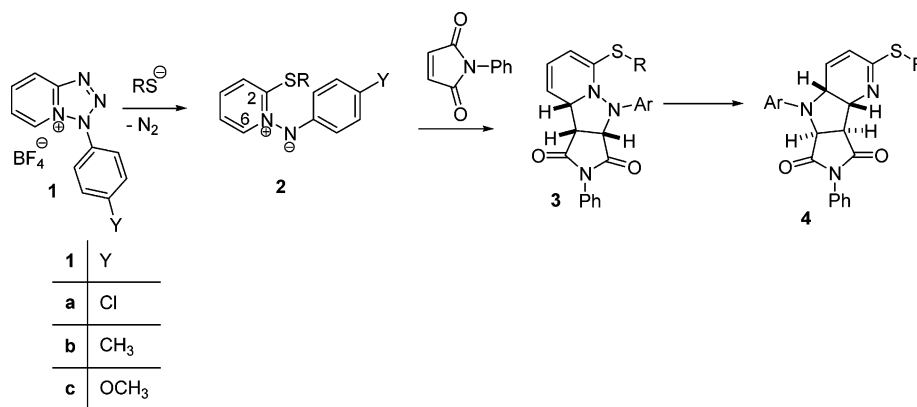
(5) Valenciano, J.; Sanches-Pavon, E.; Cuadro, A. M.; Vaquero, J. J.; Alvarez-Builla, J. *J. Org. Chem.* **2001**, *66*, 8528.

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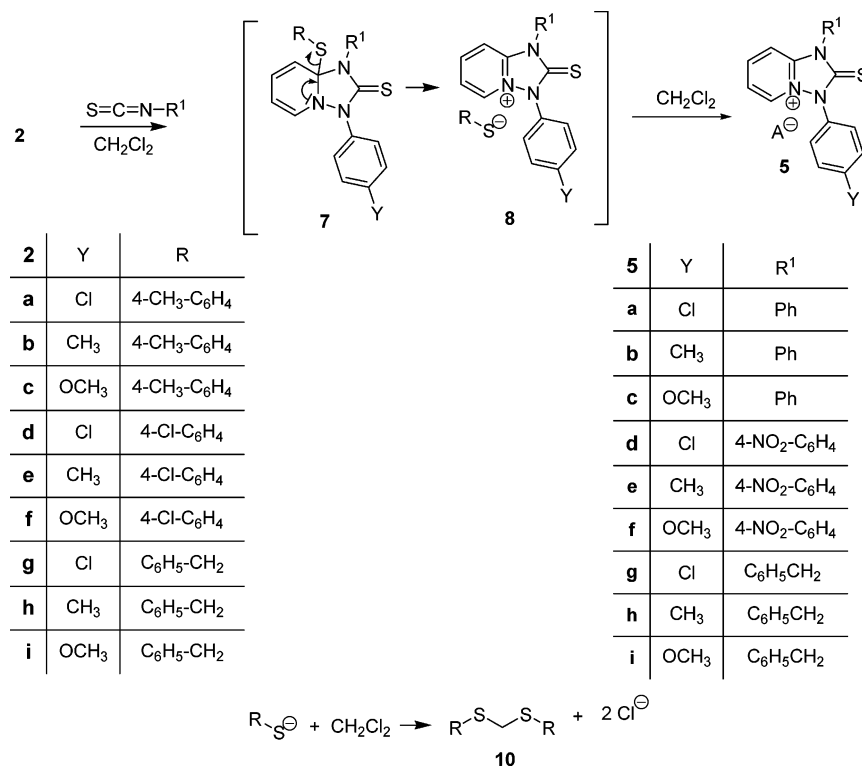
(7) Ritter, T.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 936.

(8) (a) Molina, P.; Alajarin, M.; Arques, A.; Hernandez, H. *J. Chem. Soc. Perkin Trans. I* **1984**, 1891. (b) Palazzo, G.; Baiocchi, L. *Gazz. Chim. Ital.* **1966**, *96*, 1020.

SCHEME 1



SCHEME 2



its origin can exclusively be the dichloromethane solvent. Thus, it had to be anticipated that the liberated arylthiolate anion reacted with dichloromethane to yield formaldehyde diarylthioacetal (**10**) and chloride anion.¹⁰ In accordance with these considerations, a thorough chromatographic analysis of the mother liquor obtained after work up of the reaction mixture allowed detection and identification (by mass spectrometry) of acetal **10** (Scheme 2). For analytical purposes the chloride salts

(9) Direct evidence of the presence of chloride anion in derivative **5b** (A = Cl) and **12e** (A = Cl) was provided by both elemental analysis and observation of HCl fragment in EI mass spectra.

(10) Similar reactions of thiolates and dichloromethane or dibromomethane in the presence of strong base or acid have been reported earlier, see: (a) Bertaina, B.; Rouvier, E.; Cambon, A. *J. Fluorine Chem.* **1994**, *66*, 287. (b) Weissflog, E. *Phosphorus Sulfur* **1981**, *12*, 89. (c) Ono, N.; Miyake, H.; Saito, T.; Kaji, A. *Synthesis* **1980**, *11*, 952. (d) Patney, H. K. *Org. Prepr. Proc. Int.* **1994**, *26*, 377. Quite recently such transformation in the presence of weak base and rhodium catalyst has also been observed, see: Tanaka, K.; Kaori, A. *Org. Lett.* **2005**, *7*, 1537. It should be noted that the present case represents a third experimental condition as neither base nor acid is present in the reaction mixture.

5 (A = Cl) were transformed to the more stable tetrafluoroborate salts **5** (A = BF₄).

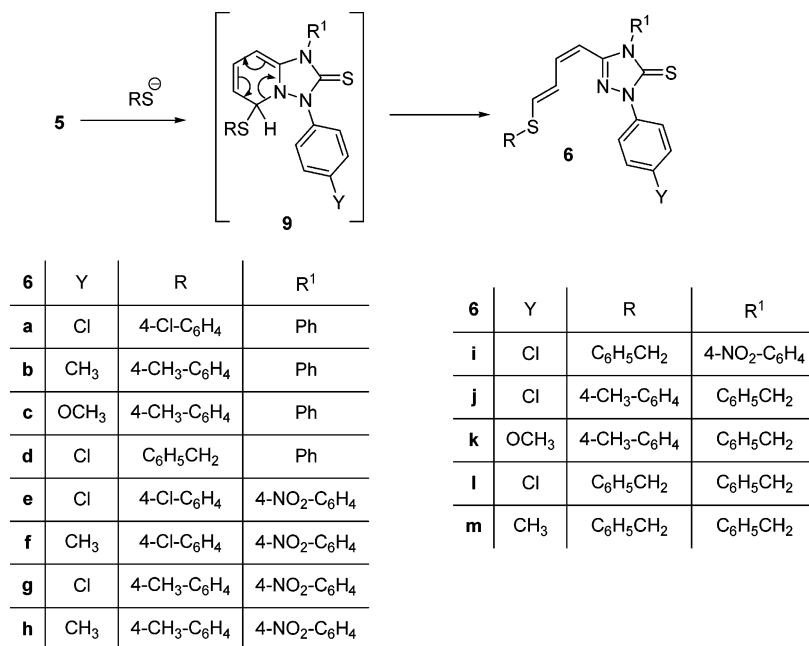
Formation of dienes **6** can easily be rationalized based upon some earlier observations:^{11–13} azolopyridinium salts containing bridgehead nitrogen atom can react with nucleophiles so that first an addition product (**9**) is formed which undergoes retro-electrocyclization to yield dienes. As arylthiolates are formed in the above transformations (Scheme 2), these fairly nucleophilic species are capable of such additions and can easily lead to arylsulfanyldienes (**6**). Ring opening of triazolium salt **5** to diene **6** has also been supported experimentally: the isolated salt **5b** was reacted with *p*-tolylthiophenolate and pyrrolidine to give the appropriate 1-arylsulfanyl-4-triazolyldiene (**6b**) and 1-pyrrolidinyl-4-triazolyldiene (**11**), respectively (Scheme 4).

Comparison of the relative yields for **5** and **6** in various experiments indicates that these ratios can vary to a considerable

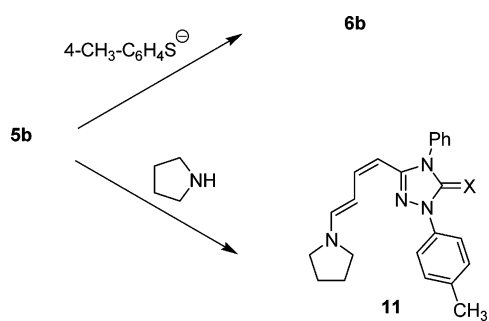
(11) Messmer, A.; Hajós, Gy.; Timári, G. *Tetrahedron* **1992**, *48*, 8451.

(12) Hajós, Gy.; Kotschy, A. *Acta Chim. Slovenica* **1998**, *45*, 285.

SCHEME 3



SCHEME 4

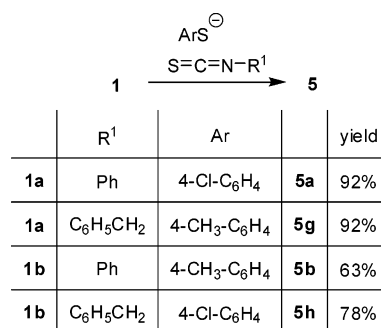


extent, and these differences could not be correlated to any properties of the starting compounds (Table 1). Thus, the question arose whether the reaction could be directed to either the triazolium or the diene product; thus, elaboration of a practical procedure to selectively obtain either of these compounds was desirable.

As triazolium salt (**5**) seemed to be an intermediate in the pathway leading to the arylsulfanyldiene (**6**), a possible reason for a relatively high ratio of the triazolium salt in some cases (e.g., entries 8 and 10 in Table 1) could be its poor solubility which hinders its participation in the subsequent ring opening. This idea led to the recognition that the yield of the triazolium salt might be increased by changing the chloride anion to another anion, causing even lower solubility. In line with this consideration, reactions of **2** with aryl isothiocyanates were carried out in dibromomethane (method C), and the resulting bromide products (**5**, A = Br) were obtained in high yield without formation of a detectable amount of the diene **6** (Entry 3, Table 1). Similar improvement of the yield of triazolium salt **5** was achieved when the reaction was carried out in dichloromethane containing tetrabutylammonium bromide (Entry 2, Table 1).

This also solved the problem of the selective preparation of the dienes. The above-mentioned experiments showed that the

SCHEME 5

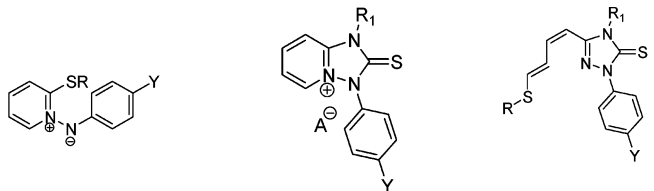


highly crystalline triazolium salts could be isolated in high yields. If these triazolium salts were treated in a separate experiment with arylthiolates, dienes **6** could be obtained only as products. This was demonstrated for the case of **5b** (A = Cl): when this compound was first transformed to the soluble tetrafluoroborate salt **5b** (A = BF₄) and then this salt was reacted with 4-tolylthiolate, diene **6b** was obtained in good yield (Scheme 4).

The fact that in the above-discussed procedure the triazolium salts (**5**) are obtained from tetrazolium salts (**1**) in two synthetic steps (i.e., via formation of **2**) with intermediate participation of the arylsulfanyl group has an interesting consequence. As the arylthiolate anion enters the tetrazolium salt in the first step to give the zwitterions **2** and then is eliminated in the second step to give the triazolium salt, the question arises whether these two consecutive transformations could be carried out with much lower amount of arylthiolate. In other words, the question arose whether triazolium salt (**5**) could be prepared by a one-pot tandem procedure by reacting tetrazolium salt **1** with an aryl isothiocyanate reagent in the presence of a small amount of arylthiolate.

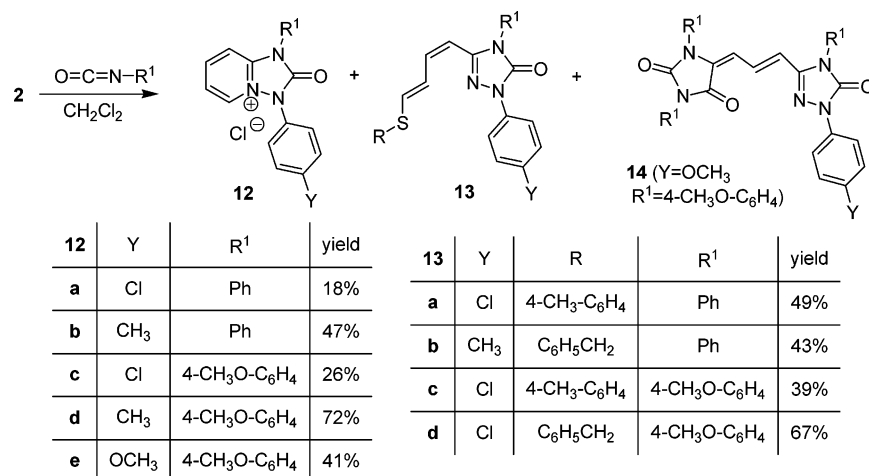
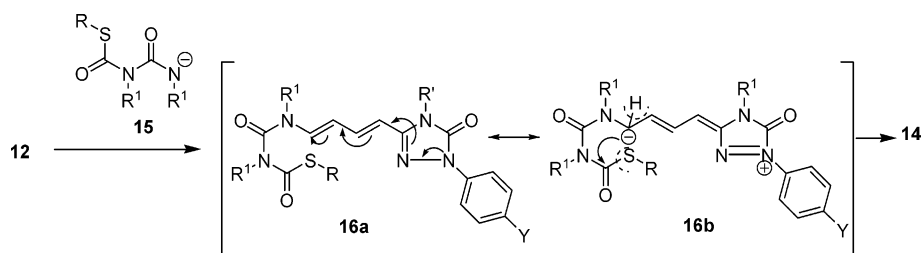
Experiments in this respect proved to be successful. Two selected tetrazolium salts (**1a** and **1b**) were treated with phenyl and benzyl isothiocyanate in the presence of 0.1 equiv of 4-chlorophenyl and 4-tolylthiolate. The data shown in Scheme

(13) Nagy, I.; Kónya, D.; Riedl, Zs.; Kotschy, A.; Timári, G.; Messmer, A.; Hajós, Gy. *Tetrahedron* **2003**, *59*, 7485–7489.

TABLE 1. Yields of Selected Derivatives of 2-Thioxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Salts **5** and Aryl- or Aralkylsulfanylbutadienyl]-2,4-dihydro-3*H*-[1,2,4]triazole-3-thiones (**6**)^a


entry	method	2a–e,g	R1	5a–e,h,i	yield	A	6a,c,e,f,g,h,i,k	yield
1	A	2b	4-NO ₂ -C ₆ H ₄	5e	5%	Cl	6h	82%
2	B	2b	4-NO ₂ -C ₆ H ₄	5e	73%	Br		
3	C	2b	Ph	5b	88%	Br		
4	A	2c	Ph	5c	60%	Cl	6c	11%
5	A	2c	C ₆ H ₅ CH ₂	5i	44%	Cl	6k	18%
6	A	2a	4-NO ₂ -C ₆ H ₄	5d	6%	Cl	6g	58%
7	A	2d	Ph	5a	52%	Cl	6a	41%
8	A	2e	C ₆ H ₅ CH ₂	5h	80%	Cl	-	
9	A	2d	4-NO ₂ -C ₆ H ₄	5d	13%	Cl	6e	77%
10	A	2e	4-NO ₂ -C ₆ H ₄	5e	60%	Cl	6f	15%
11	A	2g	4-NO ₂ -C ₆ H ₄	5d			6i	92%

^a Method A: reaction of **2** and isothiocyanate in dichloromethane. Method B: reaction of **2** and isothiocyanate in dichloromethane in the presence of tetrabutylammonium bromide. Method C: reaction of **2** and isothiocyanate in dibromomethane.

SCHEME 6**SCHEME 7**

5 reveal that the expected thioxotriazolium salts **5a**, **5b**, **5g**, and **5h** were obtained in good to excellent yields.

Reaction of pyridinium arylimidates **2** with aryl isocyanates led to further interesting findings. Similar to the transformations with aryl isothiocyanates, in these cases formation of two main products has been observed also: the oxo-substituted dihydrotriazolo[1,5-*a*]pyridinium salts (**12**) and oxotriazolylidene (**13**), obviously formed by the same reaction mechanism as discussed above (Scheme 6).

Analysis of the mother liquor obtained from reaction of **2c** with 4-methoxyphenyl isocyanate, however, also indicated the

presence of a third component in a small (max. 11%) amount which was separated by column chromatography. X-ray analysis of this isolated and strongly fluorescent yellow solid^{14,15}

(14) Compound **14**: C₃₆H₃₁N₅O₇, *M*_r = 654.66, yellow needle, size 0.50 × 0.17 × 0.13 mm, triclinic, space group *P*-1, *a* = 10.5170(1) Å, *b* = 12.589(1) Å, *c* = 13.541(1) Å, α = 72.45(1)°, β = 70.51(1)°, γ = 70.07(1)°, *V* = 1588.7(3) Å³, *Z* = 2, ρ_{calc} = 1.350 g/cm³, μ = 0.787 mm⁻¹, *T* = 293(2) K. The final model (437 parameters) was refined to *w*R₂ = 0.1802 for all data (6603 reflections), *R*₁ = 0.0575 for reflections with *I* > 2σ(*I*) (4966), and GOF = 1.105.

(15) ORTEP representation of the dienylium salt **14** is given in the Supporting Information. Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

showed—and NMR spectral data supported—that a new oxotriazolylidene was formed bearing a ring-closed dioximidazolone substituent at the end of the diene chain (**14**). Because of the fact that this imidazolone ring contained two R¹ substituents on the ring nitrogen atoms deriving from the aryl isocyanate reagent, the reaction mechanism for formation of **14** shown in Scheme 7 had to be anticipated.

The presence of the diene moiety in this product clearly indicated that in the course of the reaction to **14** a nucleophilic attack on the oxotriazolium salt (**12**) took place. If some amount of unreacted aryl isocyanate is present at that stage of the reaction when arylthiolate anion has already been formed, reaction of these two species—in accordance with literature sources¹⁶—can occur to yield anion **15**. Reaction of this anion with **12** results in formation of a diene (**16a**), which can also be represented by valence-bond structure **16b**. This dipolar structure convincingly shows the possibility of the ring closure to the dioximidazolone moiety to yield the final product **14**. This mechanism seemed to be supported by the finding that the protonated species of **15** was isolated from the reaction mixture.

Conclusion

The present findings show that reaction of the easily accessible arylthio- and benzylthiopyridinium arylimidates (**2**) with isocyanates and isothiocyanates can open a way to hitherto unknown group of heterocyclic derivatives and, furthermore, a convenient procedure to the new oxo- and thioxo dihydro[1,2,4]-triazolo[1,5-*a*]pyridinium salts implying a tandem reaction sequence has been elaborated. Investigation of the possible generalization of ring openings to dienes related to **14** as well as elaboration of feasible experimental procedures to these compounds are in progress. Detailed further investigations are planned for rationalization of the regioselectivity of these cycloadditions with cumulenes which proved to be in contrast to reactions with other dipolarophiles. It should be noted that this difference might be due to the concerted or stepwise course of these cycloadditions.¹⁷

Experimental Section

X-ray Crystallography. Crystals of **14** were mounted on glass fibers. The data set was collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu K α radiation at room temperature. Lattice parameters were determined by a least-squares fit for 25 reflections. The intensities of three standard reflections were monitored every hour, and no decay was indicated. All reflections were corrected for Lorentz and polarization effects.¹⁸ Absorption correction was applied using ψ -scan data.¹⁹ The space groups were determined from the unit cell parameters and intensity statistics. The structures were solved by direct methods (SHELXS-97²⁰). All non-hydrogen atoms were modeled anisotropically in the

structure refinement (SHELXL-97²¹). Hydrogen atoms were placed in ideal positions and refined isotropically in the riding mode.

Syntheses of tetrazolo[1,5-*b*]pyridinium salts (**1**)³ and 2-arylsulfanyl- and 2-benzylsulfanylpyridinium-*N*-arylimides^{1,2} (**2**) have been published earlier. Novel derivatives (i.e., **1b**, **2b**, **c**, **e**, **f**, **h**, **i**) have been prepared according to these literature procedures.

3-(4-Tolyl)-3*H*-tetrazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (1b**).** Yield 53% (1.6 g); colorless crystals; mp >300 °C. Anal. Calcd for C₁₂H₁₁BF₄N₄ (298.05): C, 48.36; H, 3.72; N, 18.80. Found: C, 48.42; H, 3.62; N, 18.76.

2-(4-Tolylsulfanyl)pyridinium-*N*-(4-tolyl)imide (2b**).** This compound was obtained from 3-(4-methylphenyl)-3*H*-tetrazolo[1,5-*a*]pyridin-4-ium tetrafluoroborate (**1b**, 1.5 g, 5 mmol) and sodium 4-tolylthiolate generated from 4-tolylthiophenol (0.7 g, 5.8 mmol) and sodium hydride (0.26 g, 108 mmol). Yield 1.39 g, (90%); red crystals; mp 116–120 °C. ¹H (CDCl₃) δ (ppm): 8.54 (1H, dd, *J* = 6 + 1.5 Hz, H2), 7.54 (2H, m, H2' + H6''), 7.30 (2H, m, H3'' + H5''), 6.96–7.14 (4H, m, H2' + H3' + H5' + H6'), 6.85 (2H, m, H3 + H4), 6.54 (1H, dd *J* = 8.5 + 1.5 Hz, H5), 2.44 (3H, s, CH₃), 2.29 (3H, s, CH₃). ¹³C (CDCl₃) δ (ppm): 20.8 (CH₃), 21.3 (CH₃), 118.4 (C2' + C6'), 120.4 (C3), 122.7 (C5), 123.8 (C4), 126.4 (C4'), 130.2 (C3'' + C5''), 130.3 (C4''), 131.0 (C3' + C5'), 132.2 (C2), 136.0 (C2'' + C6''), 140.6 (C1''), 148.6 (C6), 149.4 (C1'). Anal. Calcd for C₁₉H₁₈N₂S (306.42): N, 9.14; S, 10.46. Found: N, 8.96; S, 10.36.

2-(4-Tolylsulfanyl)pyridinium-*N*-(4-methoxyphenyl)imide (2c**).** Red crystals (1.39 g, 85%); mp 96–99 °C.

2-(4-Chlorophenylsulfanyl)pyridinium-*N*-(4-tolyl)imide (2e**).** Red crystals (1.25 g, 74%); mp 135–138 °C.

2-(4-Chlorophenylsulfanyl)pyridinium-*N*-(4-methoxyphenyl)imide (2f**).** Orange crystals (1.41 g, 81%); mp 95–115 °C.

2-(4-Benzylsulfanyl)pyridinium-*N*-(4-tolyl)imide (2h**).** Red crystals (1.3 g, 85%); mp 127–134 °C.

2-(4-Benzylsulfanyl)pyridinium-*N*-(4-methoxyphenyl)imide (2i**).** Red crystals (1.58 g, 97%); mp 100–114 °C.

General Procedure for Reaction of Aryl- and Benzylsulfanylpyridinium Arylimides (2**) with Aryl Isothiocyanates.** A solution of the appropriate pyridinium arylimide (**2**, 2 mmol) and aryl isothiocyanate (2.4 mmol) in abs. dichloromethane (22 mL) was stirred at room temperature, and the progress of the reaction was monitored by TLC. After disappearance of the starting material (5–20 h) the deposited colorless crystals were filtered off and washed with dichloromethane to give the corresponding 1,3-diaryl-2-thio-2,3-dihydro[1,2,4]triazolo[1,5-*a*]pyridinium chloride (**5**, A = Cl). This salt was converted to the appropriate tetrafluoroborate salt using tetrafluoroboric acid. The filtrate was then evaporated and subjected to column chromatography on alumina by a hexane–ethyl acetate mixture 4:1 as an eluent. Separation of the main fraction around *R*_f = 0.6 gave the appropriate 1-arylsulfanyldienyl-4-(1,4-diaryl[1,2,4]triazol-5(1*H*))thione (**6**).

3-(4-Methoxyphenyl)-1-(4-nitrophenyl)-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5f**, A = BF₄).** This compound was prepared from **2f** (0.684 g, 2 mmol) and 4-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol) to give 0.31 g of product (37%); colorless crystals; mp 256–257 °C. ¹H (DMSO-*d*₆) δ (ppm): 8.71 (1H, dd, *J* = 7.1 + 1.2 Hz, H5), 8.61 (2H, m, H3' + H5'), 8.39 (1H, ddd, *J* = 9 + 8.2 + 1.2 Hz, H7), 7.98 (2H, m, H2' + H6'), 7.90 (1H, dd, *J* = 9 + 1 Hz, H8), 7.77 (1H, ddd, *J* = 8.2 + 7.1 + 1 Hz, H6), 7.69 (2H, m, H2'' + H6''), 7.37 (2H, m, H3'' + H5''), 3.90 (3H, s, OCH₃). ¹³C (DMSO-*d*₆) δ (ppm): 56.6 (OCH₃), 111.0 (C8), 117.2 (C3'' + C5''), 121.4 (C6), 122.2 (C1''), 126.5 (C3' + C5'), 127.0 (C5), 130.6 (C2' + C6'), 132.0 (C2'' + C6''), 137.2 (C1'), 141.4 (C4'), 142.4 (C7), 149.4 (C2), 163.0 (C8a), 166.8 (C4''). Anal. Calcd for C₁₉H₁₅BF₄N₄O₃S (466.22): C, 48.95; H, 3.24; N, 12.02; S, 6.88. Found: C, 49.11; H, 3.20; N, 11.92; S, 6.91.

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(17) Matsouka, T.; Harano, K. *Tetrahedron* **1995**, *51*, 6451.

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(20) Sheldrick, G. M. *SHELXS-97 Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

3-(4-Chlorophenyl)-1-phenyl-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]-triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5a, A = BF₄). This compound was prepared from **2d** (0.694 g, 2 mmol) and phenyl isothiocyanate (0.324 g, 2.4 mmol) to give 0.39 g of product (52%); colorless crystals; mp >300 °C.

3-(4-Tolyl)-1-phenyl-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5b, A = BF₄). This compound was prepared from **2e** (0.652 g, 2 mmol) and phenyl isothiocyanate (0.324 g, 2.4 mmol) to give 0.59 g of product (83%); colorless crystals; mp > 300 °C.

3-(4-Methoxyphenyl)-1-phenyl-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]-triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5c, A = BF₄). This compound was prepared from **2c** (0.644 g, 2 mmol) and phenyl isothiocyanate (0.324 g, 2.4 mmol) to give 0.44 g of product (60%); colorless crystals; mp 264–265 °C.

3-(4-Chlorophenyl)-1-(4-nitrophenyl)-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5d, A = BF₄). This compound was prepared from **2a** (0.652 g, 2 mmol) and 4-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol) to give 0.06 g of product (6%); colorless crystals; mp 294–298 °C.

3-(4-Tolyl)-1-(4-nitrophenyl)-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]-triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5e, A = BF₄). This compound was prepared from **2a** (0.612 g, 2 mmol) and 4-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol) to give 0.03 g of product (4%); colorless crystals; mp 298–300 °C.

1-Benzyl-3-(4-chlorophenyl)-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]-triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5g, A = BF₄). This compound was prepared from **2a** (0.612 g, 2 mmol) and benzyl isothiocyanate (0.357 g, 2.4 mmol) to give 0.02 g of product (2%); colorless crystals; mp 219–222 °C.

1-Benzyl-3-(4-tolyl)-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5h, A = BF₄). This compound was prepared from **2e** (0.652 g, 2 mmol) and benzyl isothiocyanate (0.357 g, 2.4 mmol) to give 0.59 g of product (80%); colorless crystals; mp 198–199 °C.

1-Benzyl-3-(4-methoxyphenyl)-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]-triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5i, A = BF₄). This compound was prepared from **2c** (0.644 g, 2 mmol) and benzyl isothiocyanate (0.358 g, 2.4 mmol) to give 0.34 g of product (44%); colorless crystals; mp 217–220 °C.

4-Benzyl-2-(4-chlorophenyl)-5-[(1*Z*,3*E*)-4-[(4-tolyl)thio]buta-1,3-dien-1-yl]-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6j). This compound was prepared from **2a** (0.652 g, 2 mmol) and benzyl isothiocyanate (0.357 g, 2.4 mmol) to give 0.35 g of product (37%); yellow crystals; mp 112–114 °C. ¹H (CDCl₃) δ (ppm): 8.0 (2H, m, H^{2''} + H^{6''}), 7.44 (2H, m, H^{3''} + H^{5''}), 7.34 (2H, m, H^{2^{IV}} + H^{6^{IV}}), 7.29 (5H, m, H^{2'''} + H^{3'''} + H^{4'''} + H^{5'''} + H^{6'''}), 7.20 (1H, ddd, *J* = 14.5 + 11.5 + 1 Hz, H^{3'}), 7.11 (2H, m, H^{3^{IV}} + H^{5^{IV}}), 6.83 (1H, d, *J* = 14.5 Hz, H^{4'}), 6.46 (1H, dd, *J* = 11.5 + 11.5 Hz, H^{2'}), 5.63 (1H, dd, *J* = 11.5 + 1 Hz, H^{1'}), 5.38 (2H, s, CH₂), 2.28 (3H, s, CH₃). ¹³C (CDCl₃) δ (ppm): 21.4 (CH₃), 47.9 (CH₂), 105.1 (C^{1'}), 123.9 (C^{4'}), 125.2 (C^{3'''} + C^{5'''}), 127.3 (C^{2''} + C^{6''}), 128.1 (C^{1^{IV}}), 128.4 (C^{4'''}), 128.9 (C^{3'''} + C^{5'''}), 129.2 (C^{2'''} + C^{6'''}), 130.4 (C^{3^{IV}} + C^{5^{IV}}), 132.9 (C^{2^{IV}} + C^{6^{IV}}), 133.4 (C^{4^{IV}}), 135.0 (C^{1'''}), 137.2 (C^{4''}), 137.7 (C^{2'}), 139.1 (C^{1''}), 140.6 (C^{3'}), 148.5 (C⁵), 166.5 (C³). Anal. Calcd for C₂₆H₂₂ClN₃S (476.06): C, 65.60; H, 4.66; N, 8.83; S, 13.47. Found: C, 65.53; H, 4.83; N, 8.70; S, 13.59.

2-(4-Chlorophenyl)-5-[(1*Z*,3*E*)-4-[(4-chlorophenyl)thio]buta-1,3-dien-1-yl]-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6a). This compound was prepared from **2d** (0.694 g, 2 mmol) and phenyl isothiocyanate (0.324 g, 2.4 mmol) to give 0.4 g of product (41%); yellow crystals; mp 162–163 °C.

2-(4-Tolyl)-5-[(1*Z*,3*E*)-4-[(4-tolyl)thio]buta-1,3-dien-1-yl]-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6b). This compound was prepared from **2b** (0.612 g, 2 mmol) and phenyl isothiocyanate (0.324 g, 2.4 mmol) to give 0.05 g of product (6%); yellow crystals; mp 168–174 °C.

2-(4-Methoxyphenyl)-5-[(1*Z*,3*E*)-4-[(4-tolyl)thio]buta-1,3-dien-1-yl]-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6c). This compound was prepared from **2c** (0.644 g, 2 mmol) and phenyl isothiocyanate (0.324 g, 2.4 mmol) to give 0.1 g of product (11%); mp 122–124 °C.

5-[(1*Z*,3*E*)-4-(benzylthio)buta-1,3-dien-1-yl]-2-(4-chlorophenyl)-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6d). This compound was prepared from **2g** (0.652 g, 2 mmol) and phenyl isothiocyanate (0.324 g, 2.4 mmol) to give 0.54 g of product (58%); yellow crystals; mp 102–105 °C.

2-(4-Chlorophenyl)-5-[(1*Z*,3*E*)-4-[(4-chlorophenyl)thio]buta-1,3-dien-1-yl]-4-(4-nitrophenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6e). This compound was prepared from **2d** (0.694 g, 2 mmol) and *p*-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol) to give 0.82 g of product (77%); yellow crystals; mp 189–191 °C.

5-[(1*Z*,3*E*)-4-[(4-Chlorophenyl)thio]buta-1,3-dien-1-yl]-2-(4-tolyl)-4-(4-nitrophenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6f). This compound was prepared from **2e** (0.652 g, 2 mmol) and 4-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol) to give 0.15 g of product (15%); yellow crystals; mp 170–179 °C.

2-(4-Chlorophenyl)-5-[(1*Z*,3*E*)-4-[(4-tolyl)thio]buta-1,3-dien-1-yl]-4-(4-nitrophenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6g). This compound was prepared from **2a** (0.652 g, 2 mmol) and 4-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol) to give 0.77 g of product (58%); yellow crystals; mp 136–142 °C.

2-(4-Tolyl)-5-[(1*Z*,3*E*)-4-[(4-tolyl)thio]buta-1,3-dien-1-yl]-4-(4-nitrophenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6h). This compound was prepared from **2a** (0.612 g, 2 mmol) and 4-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol) to give 0.8 g of product (82%); yellow crystals; mp 158–164 °C.

5-[(1*Z*,3*E*)-4-(Benzylthio)buta-1,3-dien-1-yl]-2-(4-chlorophenyl)-4-(4-nitrophenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6i). This compound was prepared from **2g** (0.652 g, 2 mmol) and 4-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol) to give 0.93 g of product (92%); yellow crystals; mp 170–180 °C.

4-Benzyl-2-(4-methoxyphenyl)-5-[(1*Z*,3*E*)-4-[(4-tolyl)thio]buta-1,3-dien-1-yl]-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6k). This compound was prepared from **2c** (0.644 g, 2 mmol) and benzyl isothiocyanate (0.358 g, 2.4 mmol) to give 0.17 g of product (18%); yellow crystals; mp 100–112 °C.

4-Benzyl-5-[(1*Z*,3*E*)-4-(benzylthio)buta-1,3-dien-1-yl]-2-(4-chlorophenyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6l). This compound was prepared from **2g** (0.652 g, 2 mmol) and benzyl isothiocyanate (0.358 g, 2.4 mmol) to give 0.45 g of product (48%); yellow crystals; mp 122–124 °C.

4-Benzyl-5-[(1*Z*,3*E*)-4-[(4-benzylthio)buta-1,3-dien-1-yl]-2-(4-tolyl)-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6m). This compound was prepared from **2h** (0.612 g, 2 mmol) and benzyl isothiocyanate (0.358 g, 2.4 mmol) to give 0.24 g of product (26%); yellow crystals; mp 109–111 °C.

Reaction of 2b with 4-Nitrophenyl Isothiocyanate in the Presence of Tetrabutylammonium Bromide: 3-(4-Tolyl)-1-(4-nitrophenyl)-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Bromide (5e, A = Br). This compound was prepared from **2b** (0.612 g, 2 mmol), 4-nitrophenyl isothiocyanate (0.432 g, 2.4 mmol), and tetrabutylammonium bromide (0.966 g, 3 mmol) to give 0.65 g of product (73%); colorless crystals; mp >300 °C. The signals of this product in the NMR spectra were identical with those of **5e** (A = BF₄). Anal. Calcd for C₁₉H₁₅BrN₄O₂S (443.32): C, 51.48; H, 3.41; N, 12.64. Found: C 51.32; H, 3.41; N, 12.31.

Reaction of 2b with Phenyl Isothiocyanate in Dibromomethane: 3-(4-Tolyl)-1-phenyl-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Bromide (5b, A = Br). This compound was prepared from **2b** (0.306 g, 1 mmol) and phenyl isothiocyanate (0.162 g, 1.2 mmol) in dibromomethane (11 mL) to give 0.35 g of product (88%); colorless crystals; mp > 300 °C. The signals of this product in the NMR spectra were identical with those of **5b** (A = BF₄). Anal. Calcd for C₁₉H₁₆BrN₃S (398.32): C,

57.29; H, 4.05; N, 10.55; S, 8.05. Found: C 57.12; H, 4.01; N, 10.40; S, 8.09.

Formation of Dienes (6b and 11) by Reaction of Triazolium Salt (5b) with 4-Tolylthiophenole and Pyrrolidine. 2-(4-Tolyl)-5-[(1*Z*,3*E*)-4-[(4-tolylthio]buta-1,3-dien-1-yl]-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (6b). To a mixture of sodium hydride (0.041 g, 17 mmol), *p*-thiocresol (0.112 g, 0.9 mmol), and abs. THF (2 mL), a solution of 5b (A = BF₄) (0.2 g, 0.6 mmol) in abs. acetonitrile (4 mL) was added, and the reaction mixture was stirred for 6 h at room temperature. The product was isolated by column chromatography to give 6b, 0.126 g (46%). All physical and spectroscopic data of this product were identical with earlier isolated compound obtained from 2b and phenyl isothiocyanate.

2-(4-Tolyl)-4-phenyl-5-[(1*Z*,3*E*)-4-pyrrolidin-1-ylbuta-1,3-dien-1-yl]-2,4-dihydro-3*H*-1,2,4-triazole-3-thione (11). To a suspension of 5b (A = BF₄) (0.12 g, 0.3 mmol) in abs. acetonitrile (1 mL), pyrrolidine (0.042 g, 0.6 mmol) was added at room temperature. A brown solution was formed, and the product was precipitated. The solid was filtered off to give 0.04 g of product (64%); yellow crystals; mp 143–152 °C.

Direct Formation of 3-(4-Chlorophenyl)-1-phenyl-2-thiooxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (5a, A = BF₄) from 3-(4-chlorophenyl)-3*H*-tetrazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (1a). Tandem Route. After generation of sodium 4-chlorothiophenolate (sodium hydride (0.0086 g, 0.36 mmol), 4-chlorothiophenol (0.025 g, 0.18 mmol), in abs. THF (1 mL)) the solution was cooled to –40 °C, and a mixture of 1a (0.51 g, 1.6 mmol) and phenyl isothiocyanate (0.256 g, 1.9 mmol) in abs. acetonitrile (8 mL) was added gradually. The reaction mixture was allowed warm to room temperature and stirred for 28 h, and after evaporation of solvent the residue was treated with Et₂O to give white precipitate, which was recrystallized from acetonitrile to give 0.63 g (92%) of 5a (A = BF₄).

The same procedure was applied for the following conversions. 1a (0.51 g, 1.6 mmol), benzyl isothiocyanate (0.283 g, 1.9 mmol), *p*-thiocresolate prepared from sodium hydride (0.0086 g, 0.36 mmol) and *p*-thiocresol (0.023 g, 0.18 mmol) gave 0.64 g (92%) of 5g (A = BF₄). 1b (0.50 g, 1.6 mmol), phenyl isothiocyanate (0.256 g, 1.9 mmol), *p*-thiocresolate prepared from sodium hydride (0.0086 g, 0.36 mmol) and *p*-thiocresol (0.023 g, 0.18 mmol) gave 0.43 g (63%) of 5b (A = BF₄). 1b (0.50 g, 1.6 mmol), benzyl isothiocyanate (0.283 g, 1.9 mmol), 4-chlorothiophenolate prepared from sodium hydride (0.0086 g, 0.36 mmol) and 4-chlorothiophenol (0.025 g, 0.18 mmol) gave 0.55 g (78%) of 5h (A = BF₄).

General Procedure for Reaction of Aryl- and Benzylsulfanylpriidinium Arylimides (2) with Aryl Isocyanates. A solution of the appropriate pyridinium arylimide (2, 2 mmol) and aryl isocyanate (2.4 mmol) in abs. dichloromethane (22 mL) was stirred at room temperature, and the progress of the reaction was monitored by TLC. After disappearance of the starting material (5–20 h) the deposited colorless crystals were filtered off and washed with dichloromethane to give the corresponding 1,3-diaryl-2-oxo-2,3-dihydro[1,2,4]triazolo[1,5-*a*]pyridinium salts (12). The filtrate was then evaporated and subjected to column chromatography on alumina by a hexane–ethyl acetate mixture 4:1 as eluent. Separation of the main fraction around *R*_f = 0.6 gave the appropriate 1-arylsulfanyldienyl-4-(1,4-diaryl[1,2,4]triazol-5(1*H*)) one (13)

1,3-Bis(4-methoxyphenyl)-2-oxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Chloride (12e, A = Cl). This compound was prepared from 2c (0.644 g, 2 mmol) and 4-methoxyphenyl isocyanate (0.348 g, 2.4 mmol) to give 0.33 g of product (41%); colorless crystals; mp 294–295 °C. ¹H (DMSO-*d*₆) δ (ppm): 8.62 (1H, dd, *J* = 6.5 + 1 Hz, H5), 8.27 (1H, ddd, *J* = 8.5 + 7.5 + 1 Hz, H7), 7.74 (2H, m, H2' + H6'), 7.70 (1H, dd, *J* = 8.5 + 1.5 Hz, H6), 7.63 (1H, ddd, *J* = 7.5 + 6.5 + 1.5 Hz, H6), 7.60 (2H, m, H2'' + H6''), 7.32 (2H, m, H3' + H5'), 7.25 (2H, m, H3'' + H5''), 3.90 (3H, s, OCH₃), 3.85 (3H, s, OCH₃). ¹³C (DMSO-*d*₆) δ (ppm): 56.4 (OCH₃), 56.6 (OCH₃), 110.3 (C8), 116.2 (C3'' + C5''), 116.9 (C3' + C5'), 119.9 (C6), 121.1 (C1'), 122.8 (C1'), 126.7

(C5), 129.2 (C2' + C6'), 132.0 (C2'' + C6''), 140.2 (C8a), 141.2 (C7), 148.1 (C2), 161.3 (C4'), 162.8 (C4''). Anal. Calcd for C₂₀H₁₈ClN₃O₃ (383.83): C, 62.58; H, 4.73; N, 10.95; Found: C 62.52; H, 4.71; N, 10.75.

3-(4-Chlorophenyl)-2-oxo-1-phenyl-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (12a, A = BF₄). This compound was prepared from 2a (0.652 g, 2 mmol) and phenyl isocyanate (0.285 g, 2.4 mmol) to give 0.13 g of product (18%); colorless crystals; mp > 300 °C.

3-(4-Tolyl)-2-oxo-1-phenyl-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (12b, A = BF₄). This compound was prepared from 2b (0.612 g, 2 mmol) and phenyl isocyanate (0.285 g, 2.4 mmol) to give 0.32 g of product (47%); colorless crystals; mp > 300 °C.

3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-2-oxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (12c, A = BF₄). This compound was prepared from 2c (0.652 g, 2 mmol) and 4-methoxyphenyl isocyanate (0.357 g, 2.4 mmol) to give 0.2 g of product (26%); colorless crystals; mp > 300 °C.

1-(4-Methoxyphenyl)-3-(4-tolyl)-2-oxo-2,3-dihydro-1*H*-[1,2,4]triazolo[1,5-*a*]pyridin-4-ium Tetrafluoroborate (12d, A = BF₄). This compound was prepared from 2e (0.652 g, 2 mmol) and 4-methoxyphenyl isocyanate (0.348 g, 2.4 mmol) to give 0.53 g of product (72%); colorless crystals; mp > 300 °C.

5-[(1*Z*,3*E*)-4-(Benzylthio)buta-1,3-dien-1-yl]-2-(4-tolyl)-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (13b). This compound was prepared from 2h (0.612 g, 2 mmol) and phenyl isocyanate (0.285 g, 2.4 mmol) to give 0.3 g of product (43%); yellow crystals; mp 163–166 °C. ¹H (CDCl₃) δ (ppm): 7.91(2H, m, H2'' + H6''), 7.61 (1H, ddd, *J* = 14.5 + 11.5 + 1 Hz, H3'), 7.18–7.58 (12H, m), 6.69 (1H, d, *J* = 14.5 Hz, H4'), 6.34 (1H, dd, *J* = 11.5 + 11.5 Hz, H2'), 5.44 (1H, dd, *J* = 11.5 + 1 Hz, H1'), 4.10 (2H, CH₂), 2.35 (3H, CH₃). ¹³C (CDCl₃) δ (ppm): 21.0, 36.8, 106.3, 118.7–(2C), 123.7, 127.5(2C), 128.5, 128.7(2C), 128.8(2C), 128.9, 129.5–(2C), 129.6(2C), 132.7, 135.0, 135.2, 135.5, 136.3, 137.4, 143.4, 144.0. Anal. Calcd for C₂₆H₂₃N₃O (425.55): C, 73.38; H, 5.45; N, 9.87; S, 7.54. Found: C, 73.22; H, 5.38; N, 9.87; S, 7.75.

2-(4-Chlorophenyl)-5-[(1*Z*,3*E*)-4-[(4-tolylthio]buta-1,3-dien-1-yl]-4-phenyl-2,4-dihydro-3*H*-1,2,4-triazol-3-one (13a). This compound was prepared from 2a (0.652 g, 2 mmol) and phenyl isocyanate (0.285 g, 2.4 mmol) to give 0.44 g of product (49%); yellow crystals; mp 112–119 °C.

2-(4-Chlorophenyl)-4-(4-methoxyphenyl)-5-[(1*Z*,3*E*)-4-[(4-tolylthio]buta-1,3-dien-1-yl]-2,4-dihydro-3*H*-1,2,4-triazol-3-one (13c). This compound was prepared from 2e (0.652 g, 2 mmol) and 4-methoxyphenyl isocyanate (0.348 g, 2.4 mmol) to give 0.37 g of product (39%); yellow crystals; mp 119–123 °C.

5-[(1*Z*,3*E*)-4-(Benzylthio)buta-1,3-dien-1-yl]-2-(4-chlorophenyl)-4-(4-methoxyphenyl)-2,4-dihydro-3*H*-1,2,4-triazol-3-one (13d). This compound was prepared from 2g (0.652 g, 2 mmol) and *p*-methoxyphenyl isocyanate (0.348 g, 2.4 mmol) to give 0.54 g of product (67%); colorless crystals; 156–166 °C.

Isolation of Compound 14. (E)-5-(E)-3-(1,4-Bis(4-methoxyphenyl)-5-oxo-4,5-dihydro-1*H*-1,2,4-triazol-3-yl)allylidene)-1,3-bis(4-methoxyphenyl)imidazolidine-2,4-dione (14). This compound was isolated by column chromatography (alumina, hexane: EtOAc as eluent) from the reaction mixture of 2c (0.644 g, 2 mmol) and 4-methoxyphenyl isocyanate (0.348 g, 2.4 mmol) to give 0.07 g of product (11%); yellow crystals; mp 215–227 °C. ¹H (CDCl₃) δ (ppm): 8.45 (1H, dd, *J* = 15.5 + 12 Hz, H2'), 7.96 (2H, m), 7.39 (2H, m), 7.24 (2H, m), 7.21 (2H, m), 7.04 (2H, m), 7.02 (2H, m), 7.0 (2H, m), 6.94 (2H, m), 6.05 (1H, dd, *J* = 15.5 + 1 Hz, H3'), 5.90 (1H, dd, *J* = 12 + 1 Hz, H1'), 3.8–3.9 (12H, s, OCH₃). Anal. Calcd for C₃₆H₃₁N₅O₇ (645.66): C, 66.97; H, 4.84; N, 10.85. Found: C, 66.97; H, 4.84; N, 10.55.

Isolation of Compound 15. S-(4-Tolyl)(4-methoxyphenyl){[(4-methoxyphenyl)amino]carbonyl}thiocarbamate (15). This compound was isolated by column chromatography (alumina, hexane: EtOAc as eluent) from the reaction mixture 2c (0.644 g, 2 mmol)

and 4-methoxyphenyl isocyanate (0.348 g, 2.4 mmol) to give 0.06 g of product (7%); colorless crystals; mp 175–176 °C. Anal. Calcd for $C_{23}H_{22}N_2O_4S$ (422.50): C, 65.38; H, 5.25; N, 6.63; S, 7.59. Found: C, 65.47; H, 5.36; N, 6.50; S, 7.43.

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Supporting Information Available: More detailed information, NMR spectra of all compounds, 1H NMR data (Tables 2–4), elemental analysis (Table 5), crystallographic information file (CIF), and ORTEP diagram of compound **14**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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