Preparation and *N*-Alkylation of 4-Aryl-1,2,4-triazoles

Stefanie C. Holm, Alexander F. Siegle, Christian Loos, Frank Rominger, Bernd F. Straub*

Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
E-mail: straub@oci.uni-heidelberg.de

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Dedicated to Professor Dr. Dr. h.c. mult. Rolf Huisgen on the occasion of his 90th birthday

Abstract: Heating of *N*,*N*-dimethylformamide azine dihydrochloride {*N*′-[(dimethylamino)methylene]-*N*,*N*-dimethylhydrazonoformamide dihydrochloride} with anilines in the absence of a solvent gave a range of 4-aryl-1,2,4-triazoles by direct transamination. *Ortho*-substituents were tolerated. Some triazoles were converted into symmetrically and nonsymmetrically substituted bistriazolium salts, one of which was converted into a dicopper complex.

Key words: aminations, cyclizations, heterocycles, alkylations, triazoles

Although the 1,2,4-triazole fragment is unknown in any natural product,[1] 4-substituted 1,2,4-triazoles show high levels of biological activity. Besides their use as anticonvulsants[2] and in cancer therapy,[3] their most important application is as biocides.[4] 1,2,4-Triazoles are highly efficient fungicides, and are therefore used as broad-spectrum fungicides in agriculture. 1,2,4-Triazole fungicides exert their biological effect through inhibition of the biosynthesis of ergosterol in fungi.[5]

Besides their agricultural and pharmaceutical applications, 1,2,4-triazoles are of interest as precursors in the synthesis of *N*-heterocyclic carbenes (NHCs).[6] The first NHC was isolated in 1991 by Arduengo et al.,[6b] and the first stable carbene with a 1,2,4-triazolylidene structure was reported four years later.[7] Nowadays, NHCs are well-established ligands in organometallic chemistry and catalysis. However, comparatively few complexes with triazolyl ligands have been synthesized. Gnanamgari et al.[8] report a triazolylidene-derived iridium(I) carbene complex that is catalytically active in transfer hydrogenation and reductive amination reactions. Complexes with chiral 1,2,4-triazole-derived NHC ligands have been used as catalysts in enantioselective azadiene Diels–Alder reactions,[9] Oxy-Cope rearrangements,[10] and Staudinger reactions of ketenes with imines.[11]

Many reactions have been established for the preparation of mono-, di-, and trisubstituted 1,2,4-triazoles. These syntheses are generally based on hydrazine or substituted hydrazines.[12] A patented procedure developed by Bayer et al.[4] is routinely used to synthesize 4-substituted 1,2,4-triazoles. In this procedure, formic hydrazide is treated with triethyl orthoformate to give *N*′-ethoxymethylene-*N*′-formylhydrazine, which undergoes subsequent addition of a primary amine. This one-pot approach affords 4-substituted 1,2,4-triazoles in moderate-to-good yields. However, this method has the disadvantage of requiring a tedious workup procedure that includes chromatographic separation. Bartlett and Humphrey[13] developed a method for synthesizing 4-substituted 1,2,4-triazoles by transamination of *N*,*N*-dimethylformamide azine {*N*′-[(dimethylamino)methylene]-*N*,*N*-dimethylhydrazonoformamide} with primary amines in the presence of a catalytic amount of 4-toluenesulfonic acid in refluxing toluene. *N*,*N*-Dimethylformamide azine is obtained as its dihydrochloride salt **1** (Scheme 1) by treating hydrazine or an *N*,*N*′-diacylhydrazine with thionyl chloride in *N*,*N*-dimethylformamide. The Bartlett and Humphrey reaction affords good yields of 1,2,4-triazoles, but *N*,*N*-dimethylformamide azine has to be liberated by treating the dihydrochloride **1** with sodium carbonate, followed by continuous extraction with diethyl ether for two days. The free base can be obtained more rapidly and in good yield by deprotonation of the dihydrochloride **1** with sodium ethoxide in ethanol.[14] Naik et al.[15] have shown that the transamination reaction also occurs when the dihydrochloride **1** is used directly, thereby avoiding the need to convert the compound into the corresponding free base. Moderate-to-good yields of 4-substituted 1,2,4-triazoles have been obtained by heating primary amines with the azine dihydrochloride **1** in benzene for 4–14 h. The authors report that the use of benzene is necessary because it permits azeotropic removal of the hydrochloric acid byproduct, thereby shifting the equilibrium towards the product. We propose a solvent-free protocol for the preparation of 4-aryl 1,2,4-triazoles that tolerates the presence of *ortho*-substituents and avoids the need to use carcinogenic benzene (Scheme 1).

The only other reported method for preparing 4-aryl-1,2,4-triazoles under solvent-free conditions involves microwave heating of *para*-substituted anilines with *N*,*N*′-diformyl hydrazide.[16] In our cost-efficient protocol, which involves a simple workup, anilines are heated with *N*,*N*-dimethylformamide azine dihydrochloride (**1**) in a ratio of 1:1 or 2:1 in the absence of solvent (Table 1).

Unlike the reaction in refluxing benzene, both *para*-substituted anilines and sterically shielded *ortho*-substituted anilines were successfully converted into the corresponding 1,2,4-triazoles (entries 2–5). An increase of the steric hindrance in the *ortho*-position resulted in a reduced yield or a longer reaction time. Nevertheless, even 2,6-diisopropylaniline was transformed into the respective triazole **2d** (entry 4) in a yield of up to 42%. Substitution of the sub-

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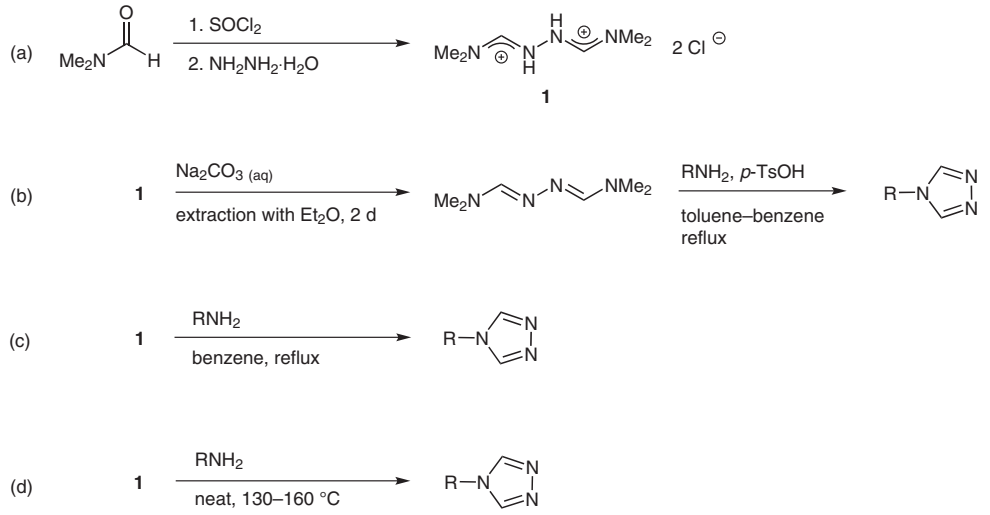


Scheme 1 (a) Preparation of *N*,*N*-dimethylformamide azine dihydrochloride; (b) Bartlett and Humphrey 1,2,4-triazole synthesis;[13] (c) Direct transamination with the *N*,*N*-dimethylformamide azine dihydrochloride **1** in refluxing benzene (Naik et al.[15]); (d) Direct transamination with the *N*,*N*-dimethylformamide azine dihydrochloride in the absence of a solvent, as reported in this work.

strate by thioether (entry 5) or trifluoromethyl (entry 6) groups was also tolerated. However, the presence of strongly electron-withdrawing nitro groups in the aniline precursor markedly reduced the yield of the reaction (entries 7 and 8).

The steric effect of an *ortho*-substituent is also manifested in the torsion angle between the planes of the triazole ring and the phenyl ring. A single-crystal X-ray structure analysis of triazole **2f** (Figure 1) showed that the two ring systems adopt a nearly coplanar orientation (torsion angle 17.9°).

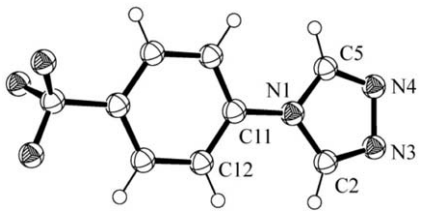


Figure 1 ORTEP plot of the molecular structure of 4-[4-(trifluoromethyl)phenyl]-4*H*-1,2,4-triazole (**2f**). Bond lengths [Å]: N1–C2, 1.350; C2–N3, 1.290; N3–N4, 1.383; N4–C5, 1.296; C5–N1, 1.360; N1–C11, 1.419. Angles [°]: C2–N1–C5, 102.7; N1–C2–N3, 112.5; C2–N3–N4, 106.5; C2–N1–C11, 128.7; C2–N1–C11–C12, 17.9.

In contrast, X-ray structure analysis of triazole **2b** (Figure 2) revealed a perpendicular orientation of the two rings (torsion angle 88.3°) as a result of steric interaction between the triazole system and the methyl groups in the *ortho*-positions of the phenyl ring.

Similarly, the X-ray structure analysis of triazole **2e** (Figure 3) showed the presence of twisting by 108.4° caused by the benzylthio substituent.

1,2,4-Triazoles are valuable precursors of *N*-heterocyclic carbenes. Electrophilic methylation of triazole **2e** with dimethyl sulfate gave the triazolium salt **3a** in good yield. To remove the reactive monomethyl sulfate anion, compound **3a** was subjected to a salt metathesis reaction by stirring a dichloromethane solution of the salt with aqueous 4-toluenesulfonic acid to replace the monomethyl sulfate counterion with a tosylate counterion (Scheme 2).

Table 1 Solvent-Free Direct Transamination Reactions of *N*,*N*-Dimethylformamide Azine Dihydrochloride

Entry	Aniline	Ratio aniline/**1**	Time (d)	Temp (°C)	Triazole	Isolated yield (%)
1	4-$MeC_6H_4NH_2$	2:1	1	140	**2a**	58
2	2,6-$Me_2C_6H_3NH_2$	1:1	1	130	**2b**	54
		2:1	3	150		68
3	2,4,6-$Me_3C_6H_2NH_2$	1:1	1	130	**2c**	56
4	2,6-*i*-$Pr_2C_6H_3NH_2$	1:1	1	150	**2d**	17
		2:1	6	150		42
5	2-$BnSC_6H_4NH_2$	1:1	3	150	**2e**	46
6	4-$F_3CC_6H_4NH_2$	1:1	1	130	**2f**	44
7	2-$O_2NC_6H_4NH_2$	2:1	1	130	**2g**	6
8	4-$O_2NC_6H_4NH_2$	2:1	7	160	**2h**	1

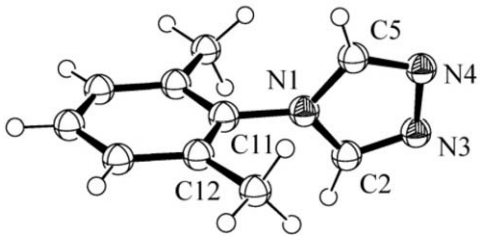


Figure 2 ORTEP plot of the molecular structure of 4-(2,6-dimethylphenyl)-4*H*-1,2,4-triazole (**2b**). Bond lengths [Å]: N1–C2, 1.357; C2–N3, 1.298; N3–N4, 1.389; N4–C5, 1.302; C5–N1, 1.356; N1–C11, 1.440. Angles [°]: C2–N1–C5, 102.9; N1–C2–N3, 111.6; C2–N3–N4, 106.5; C2–N1–C11, 126.9; C2–N1–C11–C12, 88.3.

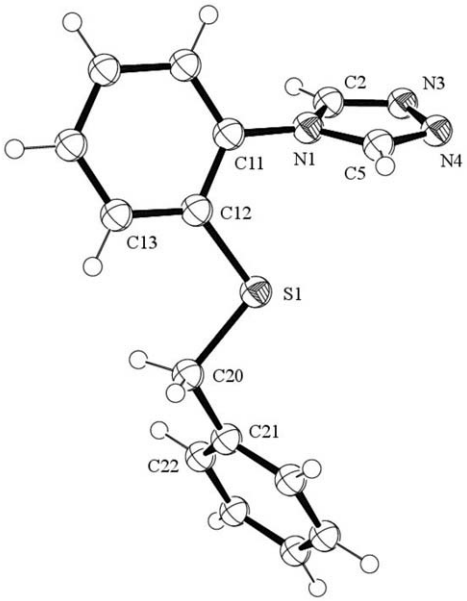
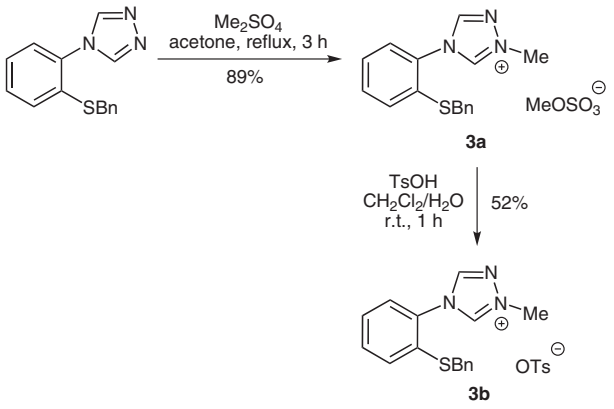
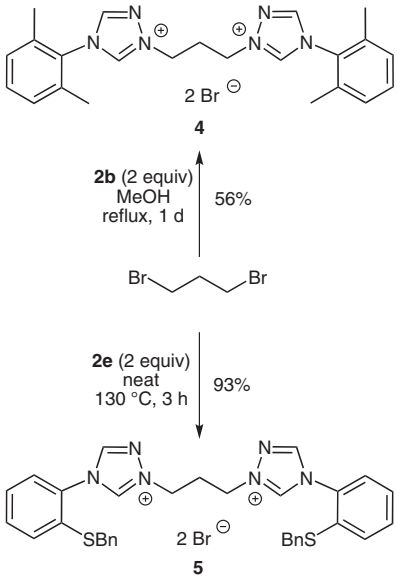


Figure 3 ORTEP plot of the molecular structure of 4-[2-(benzylthio)phenyl]-4*H*-1,2,4-triazole (**2e**). Bond lengths [Å]: N1–C2, 1.356; C2–N3, 1.304; N3–N4, 1.392; N4–C5, 1.303; C5–N1, 1.361; N1–C11, 1.439; C12–S1, 1.765; S1–C20, 1.819; C20–C21, 1.504. Angles [°]: C2–N1–C5, 103.8; N1–C2–N3, 111.5; C2–N3–N4, 106.6; C2–N1–C11, 127.5; C11–C12–S1, 117.5; C12–S1–C20, 103.7; S1–C20–C21, 107.4; C5–N1–C11–C12, 69.0; C13–C12–S1–C20, 7.0; S1–C20–C21–C22, 108.4.



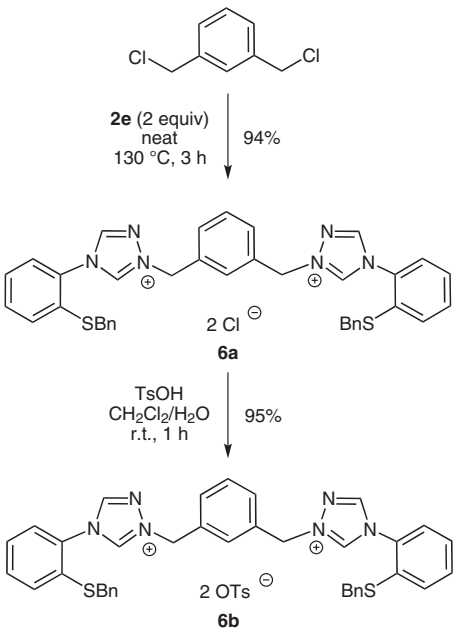
Scheme 2 Synthesis of 1-methyltriazolium salts **3a** and **3b**

Symmetrically or nonsymmetrically substituted alkyl or aryl bisimidazolinium salts and their transition metal complexes can be synthesized by well-established procedures developed by our group.[17] A similar methodology can be applied to the triazolium system.



Scheme 3 Synthesis of symmetrically substituted propylene-linked bistriazolium salts **4** and **5** from 1,2,4-triazoles **2b** and **2e**, respectively

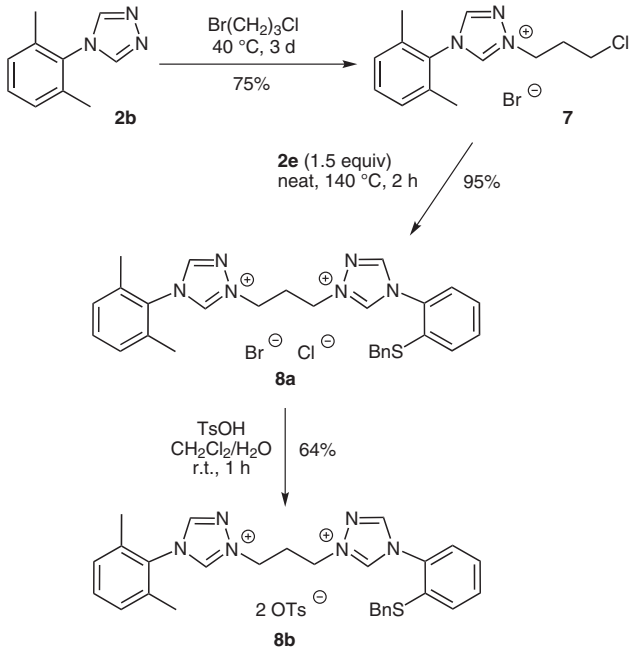
Reactions of 1,2,4-triazoles **2b** and **2e** with 1,3-dibromopropane gave the bistriazolium dibromides **4** and **5** in 56 and 93% yields, respectively (Scheme 3). The dications can also be linked through a more rigid α,α′-*meta*-xylylene group (Scheme 4).



Scheme 4 Synthesis of symmetrically substituted bistriazolium salts **6a** and **6b** from triazole **2e** with an α,α′-*meta*-xylylene linker

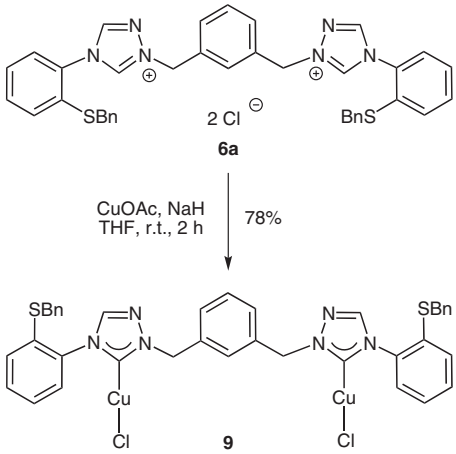
Because bistriazolium salts **4**–**6** with halides as counterions are barely soluble in organic solvents, it can be beneficial to exchange the halide counterions for tosylate ions, thereby increasing the solubility of the salts. The bistriazolium dichloride **6a** was converted into the corresponding ditosylate **6b** in good yield by salt metathesis, as described above (see Scheme 2).

A monotriazolium salt was synthesized for use as a building block for nonsymmetrical bistriazolium salts. Treatment of triazole **2b** with a twentyfold excess of 1-bromo-3-chloropropane gave the monotriazolium bromide **7**. The 3-chloropropyl substituent in cation **7** is receptive to a second nucleophilic attack by a 1,2,4-triazole (Scheme 5). Again, *N*-alkylation is favored over the formation of a sulfonium salt. The nonsymmetrical bistriazolium dication **8a** was thus obtained as a mixed bromide chloride salt. To avoid the presence of two halide counterions, this salt was converted into the corresponding ditosylate **8b**.



Scheme 5 Synthesis of monotriazolium salt **7** and the nonsymmetrically substituted bistriazolium salts **8a** and **8b**

The 1,2,4-triazolium salts that we prepared possess an acidic hydrogen atom in the 5-position that can be readily removed by a strong base to give a rather unstable transient carbene species that reacts immediately with a metal salt. We were able to attach a bistriazolyl ligand to two copper(I) atoms to form a dicopper(I) bis-NHC complex. Deprotonation of the symmetrically substituted ligand precursor **6a** with sodium hydride in absolute tetrahydrofuran containing copper(I) acetate gave complex **9** in good yield (Scheme 6). The ^{1}H and ^{13}C NMR chemical shifts of the SCH_2 unit in copper complex **9** are within the range of those of triazoles and triazolium salts. There is, therefore, no direct evidence of a thioether-to-copper coordination.



Scheme 6 Synthesis of dicopper(I) complex **9** by deprotonation of ligand precursor **6a** in the presence of copper(I) acetate

Currently, we are working on the syntheses of other dinuclear transition metal bis-NHC complexes with 1,4-disubstituted 1,2,4-triazolylidene ligands. Heterodinuclear complexes are of particular interest. After deprotection of thioethers by C–S-bond cleavage, free thiophenyl triazolium salts could serve as precursors of chelating NHC thiolate ligands. Such free ligands have not yet been described in the literature,[18] but could have a significant impact on both bioinorganic model chemistry and biomimetic catalysis.

Starting materials as supplied by Acros Organics, Aldrich Chemical Co., and TCI were used without further purification. Reactions involving air-sensitive reagents were carried out under N_2 or argon by using standard Schlenk techniques. Solvents were dried in an MBRAUN MB SCS-800 solvent-purification system. NMR spectra were recorded by using Bruker ARX-250, Bruker Avance 300, or Bruker Avance 500 spectrometers. Chemical shifts are reported in ppm relative to TMS, and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. Melting points were determined by using a Gallenkamp hot-stage microscope and are uncorrected.

4-(4-Methylphenyl)-4*H*-1,2,4-triazole (2a)[19]

4-$MeC_6H_4NH_2$ (30.0 mmol, 3.22 g) was added to the azine dihydrochloride **1** (15.0 mmol, 3.23 g) under argon, and the mixture was stirred at 140 °C for 24 h. The resulting melt was dissolved in toluene (150 mL) and the soln was basified with 1 M aq NaOH. The aqueous layer was extracted with toluene (3 × 25 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. Small amounts of Et_2O were added to the resulting oil. A crude product precipitated as a light brown solid; this was filtered off and sublimed (115 °C, 0.2 mbar) to give a colorless solid; yield: 1.39 g (58%); $C_9H_9N_3$ (M = 159.19 g/mol); mp 118 °C.

IR (KBr): 3117 (m), 2955 (w), 1636 (w), 1529 (s), 1446 (w), 1369 (w), 1297 (w), 1263 (w), 1244 (w), 1092 (m), 1000 (w), 822 (m), 653 (w), 623 (w), 530 (m) cm^{-1}.

^{1}H NMR (300.132 MHz, $CDCl_3$): δ= 2.35 (s, 3 H, CH_3), 7.21 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, $H_{Ph3/5}$), 7.26 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, $H_{Ph2/6}$), 8.40 (s, 2 H, N–C*H*–N).

^{13}C NMR (75.476 MHz, $CDCl_3$): δ = 20.9 (CH_3), 122.0 ($C_{Ph3/5}$), 130.6 ($C_{Ph2/6}$), 131.2 (C_{Ph1}), 139.1 (C_{Ph4}), 141.4 (N–*C*H–N).

MS (EI, 70 eV): *m/z* (%) = 159.07 (100) $[C_9H_9N_3]^+$, 131.05 (47) $[C_9H_9N_1]^+$.

Anal. Calcd for $C_9H_9N_3$: C, 67.90; H, 5.70; N, 26.40. Found: C, 67.79; H, 5.76; N, 26.45.

4-(2,6-Dimethylphenyl)-4*H*-1,2,4-triazole (2b)

2,6-$Me_2C_6H_3NH_2$ (10.0 mmol, 1.21 g) was added to the azine dihydrochloride **1** (10.0 mmol, 2.15 g) under argon, and the mixture was stirred at 130 °C for 24 h. The resulting melt was dissolved in toluene (50 mL) and the soln was basified with 1 M aq NaOH. The aqueous layer was extracted with toluene (3 × 15 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was washed with small amounts of Et_2O, and the resulting reddish crude product was sublimed (125 °C, 0.2 mbar) to give a colorless solid; yield: 0.94 g, (54%); $C_{10}H_{11}N_3$ (M = 173.21 g/mol); mp 173 °C. (The yield was increased to 68% by performing the reaction at 150 °C for 3 d with a 2:1 starting ratio of 2,6-$Me_2C_6H_3NH_2$ to dihydrochloride **1**.)

IR (KBr): 3111 (m), 2951 (w), 2921 (w), 1513 (s), 1471 (m), 1290 (m), 1213 (m), 1110 (m), 1083 (w), 1038 (w), 996 (m), 949 (w), 872 (w), 782 (s), 663 (s), 557 (w), 537 (w) cm^{-1}.

^1H NMR (300.132 MHz, $CDCl_3$): δ = 1.96 (s, 6 H, CH_3), 7.13 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, $H_{Ph3/5}$), 7.25 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, H_{Ph4}), 8.12 (s, 2 H, N–C*H*–N).

^{13}C NMR (75.476 MHz, $CDCl_3$): δ = 17.4 (*C*H_3), 128.7 ($C_{Ph3/5}$), 129.8 (C_{Ph4}), 131.9 (C_{Ph1}), 135.1 ($C_{Ph2/6}$), 142.7 (N–*C*H–N).

MS (ESI): *m/z* (%) = 369.30 (55) $[2M + Na]^+$, 212.13 (12) $[M + K]^+$, 195.96 (25) $[M + Na]^+$, 174.21 (10) $[M + H]^+$.

Anal. Calcd for $C_{10}H_{11}N_3$: C, 69.34; H, 6.40; N, 24.26. Found: C, 69.12; H, 6.46; N, 24.14.

4-Mesityl-4*H*-1,2,4-triazole (2c)[20]

2,4,6-$Me_3C_6H_2NH_2$ (10.0 mmol, 1.35 g) was added to the azine dihydrochloride **1** (10.0 mmol, 2.15 g) under argon, and the mixture was stirred at 130 °C for 24 h. The resulting melt was dissolved in toluene (50 mL), and the soln was basified with 1 M aq NaOH. The aqueous layer was extracted with toluene (3 × 15 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was washed with small amounts of Et_2O, and the resulting light yellow crude product was sublimed (125 °C, 0.2 mbar) to give a colorless solid; yield: 1.04 g (56%); $C_{11}H_{13}N_3$ (M = 187.24 g/mol); mp 233 °C.

IR (KBr): 3137 (w), 3116 (w), 3096 (w), 2958 (w), 2923 (w), 1631 (m), 1510 (s), 1447 (w), 1379 (w), 1286 (w), 1213 (m), 1171 (w), 1095 (s), 995 (m), 962 (w), 874 (m), 667 (m), 580 (m), 558 (w) cm^{-1}.

^1H NMR (300.132 MHz, $CDCl_3$): δ = 1.95 (s, 6 H, *o*-CH_3), 2.31 (s, 3 H, *p*-CH_3), 6.97 (s, 2 H, H_{Ph4}), 8.15 (s, 2 H, N–C*H*–N).

^{13}C NMR (75.476 MHz, $CDCl_3$): δ = 17.4 (*o*-*C*H_3), 20.9 (*p*-*C*H_3), 129.3 ($C_{Ph1/3/5}$), 134.8 ($C_{Ph2/6}$), 139.9 (C_{Ph4}), 142.9 (N–*C*H–N).

MS (EI, 70 eV): *m/z* (%) = 187.11 (100) $[C_{11}H_{13}N_3]^+$, 159.09 (27) $[C_{11}H_{13}N_1]^+$.

Anal. Calcd for $C_{11}H_{13}N_3$: C, 70.56; H, 7.00; N, 22.44. Found: C, 70.64; H, 7.01; N, 22.50.

4-(2,6-Diisopropylphenyl)-4*H*-1,2,4-triazole (2d)

2,6-*i*-$Pr_2C_6H_3NH_2$ (10.0 mmol, 1.77 g) was added to the azine dihydrochloride **1** (10.0 mmol, 2.15 g) under argon, and the mixture was stirred at 150 °C for 24 h. The resulting melt was dissolved in toluene (150 mL), and the soln was basified with 1 M aq NaOH. The aqueous layer was extracted with toluene (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was washed with Et_2O, and the resulting crude violet product was sublimed (135 °C, 0.2 mbar) to give a faintly violet solid; yield: 0.39 g (17%); $C_{14}H_{19}N_3$ (M = 229.32 g/mol); mp 228 °C. (The yield was increased to 42% by performing the reaction at 150 °C for 6 d with a 2:1 starting ratio of 2,6-*i*-$Pr_2C_6H_3NH_2$ to azine dihydrochloride **1**.)

IR (KBr): 3097 (s), 2963 (s), 2930 (w), 2870 (m), 1523 (s), 1508 (s), 1368 (m), 1286 (m), 1211 (m), 1117 (w), 1094 (s), 1061 (m), 996 (s), 810 (s), 766 (s), 668 (m) cm^{-1}.

^1H NMR (300.132 MHz, $CDCl_3$): δ = 1.06 [d, $^3J_{HH}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$], 2.26 [sept, $^3J_{HH}$ = 6.9 Hz, 2 H, C*H*$(CH_3)_2$], 7.22 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, $H_{Ph3/5}$), 7.42 (t, $^3J_{HH}$ = 7.8 Hz, 1 H, H_{Ph4}), 8.11 (s, 2 H, N–C*H*–N).

^{13}C NMR (75.476 MHz, $CDCl_3$): δ = 24.0 [$CH(CH_3)_2$], 28.1 [$CH(CH_3)_2$], 124.1 ($C_{Ph3/5}$), 128.8 (C_{Ph1}), 130.7 (C_{Ph4}), 143.8 (N–*C*H–N), 146.0 ($C_{Ph2/6}$).

MS (ESI): *m/z* (%) = 481.15 (100) $[2M + Na]^+$, 268.16 $[M + K]^+$, 252.20 $[M + Na]^+$, 230.25 $[M + H]^+$.

Anal. Calcd for $C_{14}H_{19}N_3$: C, 73.33; H, 8.35; N, 18.32. Found: C, 73.39; H, 8.32; N, 18.32.

4-(2-Benzylthiophenyl)-4*H*-1,2,4-triazole (2e)

2-$H_2NC_6H_4SBn$[21] (10.0 mmol, 2.15 g) and the azine dihydrochloride **1** (10.0 mmol, 2.15 g) were ground in a mortar and heated without solvent to 150 °C for 72 h under N_2. The resulting dark melt was dissolved in CH_2Cl_2 (100 mL), and the soln was basified with 1 M aq NaOH. The aqueous layer was extracted once with CH_2Cl_2 (50 mL). The combined organic layers were washed with H_2O (2 × 50 mL), dried ($MgSO_4$), and concentrated. The resulting dark oil was stirred in Et_2O (150 mL) to give a gray powder. The solid was filtered off and sublimed (170 °C, 0.5 mbar) to yield colorless crystals; yield: 2.47 g (46%); $C_{15}H_{13}N_3S$ (M = 267.35 g/mol); mp 126 °C.

IR (KBr): 3429 (br), 3114 (w), 1584 (w), 1520 (s), 1504 (s), 1470 (m), 1453 (m), 1434 (w), 1298 (w), 1218 (m), 1162 (w), 1095 (m), 1073 (m), 993 (m), 858 (w), 781 (w), 762 (s), 717 (s), 700 (m), 646 (s) cm^{-1}.

^1H NMR (300.132 MHz, $CDCl_3$): δ = 3.92 (s, 2 H, CH_2S), 7.01–7.04 (m, 2 H, H_{Bn}), 7.17 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{Ph}), 7.20–7.22 (m, 3 H, H_{Bn}), 7.34 (dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{Ph}), 7.44 (dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{Ph}), 7.59 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{Ph}), 8.03 (s, 2 H, N–C*H*–N).

^{13}C NMR (75.476 MHz, $CDCl_3$): δ = 39.3 (*C*H_2S), 126.6 (C_{Ph}), 127.5 (C_{Bn}), 128.0 (C_{Ph}), 128.5 (C_{Bn}), 128.6 (C_{Bn}), 130.2 (C_{Ph}), 132.6 (C_{Ph}), 132.8 (q-*C*), 134.1 (q-*C*), 136.0 (q-*C*), 142.8 (N–*C*H–N).

MS (EI, 70 eV): *m/z* (%) = 267.08 (100) $[C_{15}H_{13}N_3S]^+$, 91.05 (93) $[C_7H_7]^+$.

HRMS (EI): *m/z* calcd for $C_{15}H_{13}N_3S$: 267.0830; found: 267.0843.

Anal. Calcd for $C_{15}H_{13}N_3S$: C, 67.39; H, 4.90; N, 15.72; S, 11.99. Found: C, 67.22; H, 4.91; N, 15.78; S, 11.99.

4-[4-(Trifluoromethyl)phenyl]-4*H*-1,2,4-triazole (2f)

4-$F_3CC_6H_4NH_2$ (10.0 mmol, 1.61 g) was added to the azine dihydrochloride **1** (10.0 mmol, 2.15 g) under argon, and the mixture was stirred at 130 °C for 24 h. The resulting melt was dissolved in toluene (150 mL) and the soln was basified with 1 M aq NaOH. The aqueous layer was extracted with toluene (3 × 20 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was washed with small amounts of Et_2O, and the resulting light-yellow crude product was sublimed (140 °C, 0.2 mbar) to give a colorless solid; yield: 0.946 g (44%); $C_9H_6F_3N_3$ (M = 213.16 g/mol); mp 210 °C.

IR (KBr): 3120 (m), 1619 (s), 1533 (s), 1504 (m), 1432 (w), 1376 (m), 1328 (s), 1262 (w), 1243 (s), 1170 (m), 1130 (s), 1089 (w), 1067 (s), 997 (m), 843 (m), 595 (w), 471 (m) cm^{-1}.

^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 7.58 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, $H_{Ph2/6}$), 7.82 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, $H_{Ph3/5}$), 8.57 (s, 2 H, N–C*H*–N).

^{13}C NMR (75.476 MHz, $CDCl_3$): δ = 122.3 (s, $C_{Ph2/6}$), 123.3 (q, $^1J_{CF}$ = 272.5 Hz, *C*F_3), 127.6 (q, $^3J_{CF}$ = 3.7 Hz, $C_{Ph3/5}$), 131.2 (q, $^2J_{CF}$ = 33.4 Hz, C_{Ph4}), 136.5 (s, C_{Ph1}), 141.0 (s, N–*C*H–N).

MS (ESI): *m/z* (%) = 449.12 (100) [2M + Na]$^+$, 268.06 (61) [M + Na + MeOH]$^+$, 252.00 (55) [M + K]$^+$, 235.93 (87) [M + Na]$^+$, 213.79 (28) [M + H]$^+$.

Anal. Calcd for $C_9H_6F_3N_3$: C, 50.71; H, 2.84; N, 19.71. Found: C, 50.90; H, 2.78; N, 20.00.

4-(2-Nitrophenyl)-4*H*-1,2,4-triazole (2g)

2-$O_2NC_6H_4NH_2$ (20.0 mmol, 2.76 g) was added to the azine dihydrochloride **1** (10.0 mmol, 2.15 g) under argon, and the mixture was stirred at 130 °C for 24 h. The resulting melt was dissolved in toluene (200 mL), and the soln was basified with 1 M aq NaOH. The aqueous layer was extracted with toluene (3 × 25 mL), the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was washed with small amounts of Et_2O to give an ochre yellow solid; yield: 0.106 g (6%) (Further purification was abandoned because of the low yield.); $C_8H_6N_4O_2$ (M = 190.16 g/mol); mp 126 °C.

IR (KBr): 3117 (m), 1610 (m), 1586 (w), 1523 (s), 1347 (s), 1295 (w), 1256 (w), 1224 (m), 1105 (m), 1081 (w), 995 (m), 858 (w), 790 (m), 747 (m), 693 (w), 656 (m) cm^{-1}.

^{1}H NMR (300.132 MHz, $CDCl_3$): δ = 7.50 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, H_{Ph4}), 7.74 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, H_{Ph6}), 7.83 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, H_{Ph5}), 8.16 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, H_{Ph3}), 8.33 (s, 2 H, N–C*H*–N).

^{13}C NMR (75.476 MHz, $CDCl_3$): δ = 126.0 (C_{Ph3}), 127.1 (C_{Ph1}), 129.2 (C_{Ph4}), 131.2 (C_{Ph6}), 134.5 (C_{Ph5}), 142.8 (N–*C*H–N), 144.8 (C_{Ph2}).

MS (EI, 70 eV): *m/z* (%) = 190.07 (7) [$C_8H_6N_4O_2$]$^+$, 133.04 (46) [$C_7H_5N_2O$]$^+$, 105.04 (100) [$C_5H_3N_3$]$^+$, 90.03 (42) [C_6H_4N]$^+$.

Anal. Calcd for $C_8H_6N_4O_2$: C, 50.53; H, 3.18; N, 29.46. Found: C, 50.49; H, 3.27; N, 29.19.

4-(4-Nitrophenyl)-4*H*-1,2,4-triazole (2h)[19]

4-$O_2NC_6H_4NH_2$ (20.0 mmol, 2.76 g) was added to the azine dihydrochloride **1** (10.0 mmol, 2.15 g) under argon, and the mixture was stirred at 160 °C for 7 d. The resulting melt was dissolved in toluene (200 mL), and the soln was basified with 1 M aq NaOH. The aqueous layer was extracted with toluene (3 × 25 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was washed with Et_2O to give a yellow solid; yield: 0.02 g (1%) (Further purification was abandoned because of the low yield.); $C_8H_6N_4O_2$ (M = 190.16 g/mol).

^{1}H NMR (300.132 MHz, DMSO-d_6): δ = 8.04 (d, $^3J_{HH}$ = 9.0 Hz, 2 H, $H_{Ph2/6}$), 8.42 (d, $^3J_{HH}$ = 9.0 Hz, 2 H, $H_{Ph3/5}$), 9.32 (s, 2 H, N–C*H*–N).

^{13}C NMR (75.476 MHz, DMSO-d_6): δ = 121.5 ($C_{Ph2/6}$), 125.4 ($C_{Ph3/5}$), 138.7 (C_{Ph1}), 141.1 (N–*C*H–N), 146.1 (C_{Ph4}).

4-(2-Benzylthiophenyl)-1-methyl-4*H*-1,2,4-triazol-1-ium Methyl Sulfate (3a)

Me_2SO_4 (0.46 mL, 4.80 mmol) was added to a soln of triazole **2e** (4.00 mmol, 1.07 g) in acetone (30 mL), and the resulting yellow soln was refluxed for 3 h. On addition of Et_2O (30 mL), a product began to separate as a yellow oil that was washed with Et_2O (20 mL) and dried in vacuo; yield: 1.41 g (89%); $C_{17}H_{19}N_3O_4S_2$ (M = 393.48 g/mol).

^{1}H NMR (300.132 MHz, acetone-d_6): δ = 3.43 (s, 3 H, C$H_3OSO_3^-$), 4.14 (s, 2 H, CH_2S), 4.27 (s, 3 H, NCH_3), 7.11–7.15 (m, 2 H, H_{Bn}), 7.28–7.30 (m, 3 H, H_{Bn}), 7.57 (dt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, H_{Ph}), 7.67 (dt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H_{Ph}), 7.82–7.86 (m, 2 H, H_{Ph}), 9.02 (s, 1 H, N2–C*H*–N4), 10.25 (s, 1 H, N1–C*H*–N4).

^{13}C NMR (75.476 MHz, acetone-d_6): δ = 40.8 (N*C*H_3), 41.8 (*C*H_2S), 54.6 (*C*$H_3OSO_3^-$), 129.4 (C_{Ph}), 129.5 (C_{Bn}), 130.5 (C_{Bn}), 130.7 (C_{Bn}), 131.3 (C_{Ph}), 133.8 (C_{Ph}), 135.2 (q-*C*), 136.7 (C_{Ph}), 139.0 (q-*C*), 145.9 (N1–*C*H–N4), 146.4 (N2–*C*H–N4), 149.0 (q-*C*).

MS (ESI): *m/z* (%) = 282.11 (85) [M – $MeSO_4$]$^+$, 675.19 (100) [2M – $MeSO_4$]$^+$.

HRMS (ESI): *m/z* calcd for [$C_{16}H_{16}N_3S$]$^+$: 282.1059; found: 282.1058.

4-(2-Benzylthiophenyl)-1-methyl-4*H*-1,2,4-triazol-1-ium Tosylate (3b)

To exchange the anion, the methyl sulfate **3a** (1.19 g, 3.00 mmol) was dissolved in CH_2Cl_2 (20 mL) and a soln of TsOH·H_2O (1.71 g, 9.00 mmol) in H_2O (20 mL) was added. The two-layer system was thoroughly stirred for 1 h and then the layers were separated. The aqueous layer was extracted once with CH_2Cl_2 (20 mL). The combined organic layers were washed with H_2O (3 × 15 mL) to remove traces of TsOH and then dried ($MgSO_4$). On addition of Et_2O (40 mL) the crude product precipitated, which was washed with Et_2O (15 mL) to give a light-yellow solid; yield: 711 mg (52%); $C_{23}H_{23}N_3O_3S_2$ (M = 453.58 g/mol); mp 112 °C.

IR (KBr): 3445 (br), 3029 (br), 1633 (w), 1571 (w), 1535 (w), 1495 (w), 1479 (w), 1453 (w), 1198 (s), 1121 (m), 1073 (w), 1035 (m), 1073 (m), 1012 (m), 858 (w), 991 (w), 818 (w), 766 (w), 702 (w), 681 (m), 618 (w), 567 (m) cm^{-1}.

^{1}H NMR (300.132 MHz, acetone-d_6): δ = 2.28 (s, 3 H, OTs-CH_3), 4.08 (s, 2 H, CH_2S), 4.21 (s, 3 H, NCH_3), 7.05 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, OTs-C*H*), 7.09–7.12 (m, 2 H, H_{Bn}), 7.22–7.24 (m, 3 H, H_{Bn}), 7.44 (dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H_{Ph}), 7.55 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, OTs-C*H*), 7.60 (dt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H_{Ph}), 7.75–7.80 (m, 2 H, H_{Ph}), 9.15 (s, 1 H, N2–C*H*–N4), 10.59 (s, 1 H, N1–C*H*–N4).

^{13}C NMR (75.476 MHz, acetone-d_6): δ = 22.2 (OTs-*C*H_3), 40.7 (N*C*H_3), 41.7 (*C*H_2S), 127.6 (OTs-*C*H), 129.2 (C_{Ph}), 129.3 (OTs-*C*H), 129.9 (C_{Bn}), 130.4 (C_{Bn}), 130.7 (C_{Bn}), 131.0 (C_{Ph}), 133.6 (C_{Ph}), 135.0 (q-*C*), 136.5 (C_{Ph}), 138.8 (q-*C*), 139.8 (q-*C*), 146.1 (N1–*C*H–N4), 146.5 (N2–*C*H–N4), 147.5 (q-*C*).

MS (ESI): *m/z* (%) = 282.11 (100) [M – OTs]$^+$, 735.22 (23) [2M – OTs]$^+$.

HRMS (ESI): *m/z* calcd for [$C_{16}H_{16}N_3S$]$^+$: 282.1059; found: 282.1058.

Anal. Calcd for $C_{23}H_{23}N_3O_3S_2$: C, 60.90; H, 5.11; N, 9.26; S, 14.14. Found: C, 60.70; H, 5.08; N, 9.25; S, 14.19.

1,1′-Propane-1,3-diylbis[4-(2,6-dimethylphenyl)-4*H*-1,2,4-triazol-1-ium] Dibromide (4)

$Br(CH_2)_3Br$ (2.6 mmol, 0.52 g) was added to a soln of triazole **2b** (5.2 mmol, 0.90 g) in MeOH (1.5 mL), and the mixture was refluxed for 2 h until it became solid. More MeOH (10 mL) was added, and the mixture was refluxed for a further 24 h. On addition of Et_2O (20 mL), a colorless solid precipitated which was filtered off and dried in vacuo; yield: 0.79 g (56%); $C_{23}H_{28}Br_2N_6$ (M = 548.32 g/mol); mp 279 °C.

IR (KBr): 3080 (w), 2983 (br), 1628 (w), 1559 (s), 1520 (w), 1476 (s), 1451 (m), 1316 (m), 1231 (w), 1190 (m), 1108 (m), 984 (m), 788 (m), 671 (m), 641 (w), 558 (w), 537 (w) cm^{-1}.

^{1}H NMR (300.132 MHz, DMSO-d_6): δ = 2.20 (s, 12 H, CH_3), 2.83 (quin, $^3J_{HH}$ = 6.9 Hz, 2 H, $CH_2CH_2CH_2$), 4.77 (t, $^3J_{HH}$ = 6.9 Hz, 4 H, NCH_2CH_2), 7.38 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, $H_{Ph3/5}$), 7.50 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, H_{Ph4}), 9.69 (s, 2 H, N2–C*H*–N4), 10.93 (s, 2 H, N1–C*H*–N4).

^{13}C NMR (75.476 MHz, DMSO-d_6): δ = 17.5 (CH_3), 26.6 ($CH_2CH_2CH_2$), 49.2 (NCH_2CH_2), 129.0 ($C_{Ph3/5}$), 130.4 (C_{Ph1}), 131.1 ($C_{Ph2/6}$), 134.8 (C_{Ph4}), 143.8 (N1–*C*H–N4), 145.1 (N2–*C*H–N4).

MS (ESI): *m/z* (%) = 469.23 (26), 467.22 (28) [M – Br]$^+$, 387.20 (100) [M – Br – HBr]$^+$.

MS (ESI negative ion): *m/z* (%) = 80.94 (100), 78.94 (95) [Br]$^-$.

Anal. Calcd for $C_{23}H_{28}Br_2N_6$: C, 50.38; H, 5.15; N, 15.33. Found: C, 49.89; H, 5.18; N, 14.94.

1,1′-Propane-1,3-diylbis[4-(2-benzylthiophenyl)-4*H*-1,2,4-triazol-1-ium] Dibromide (5)

Triazole **2e** (18.0 mmol, 4.81 g) was melted at 130 °C. $Br(CH_2)_3Br$ (7.2 mmol, 0.73 mL) was added to the melt, and the mixture was heated at 130 °C for 3 h. The resulting yellow melt was dissolved in CH_2Cl_2 (150 mL). On addition of Et_2O (100 mL), a colorless solid precipitated which was filtered off, washed with Et_2O (50 mL), and dried in vacuo; yield: 4.90 g (93%), $C_{33}H_{32}Br_2N_6S_2$ (M = 736.59 g/mol); mp 235 °C.

IR (KBr): 3440 (br), 2996 (br), 1635 (w), 1601 (w), 1562 (s), 1495 (w), 1476 (w), 1453 (m), 1444 (m), 1319 (w), 1202 (w), 1099 (m), 1072 (w), 991 (w), 769 (s), 721 (w), 705 (m), 663 (w), 654 (w), 549 (w), 482 (w) cm^{-1}.

^{1}H NMR (300.132 MHz, DMSO-d_6): δ = 2.68 (quin, $^3J_{HH}$ = 6.6 Hz, 2 H, $CH_2CH_2CH_2$), 4.23 (s, 4 H, SCH_2), 4.72 (t, $^3J_{HH}$ = 6.6 Hz, 4 H, $CH_2CH_2CH_2$), 7.18–7.21 (m, 4 H, H_{Bn}), 7.24–7.28 (m, 6 H, H_{Bn}), 7.60 (dt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2 H, H_{Ph}), 7.69 (dt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2 H, H_{Ph}), 7.79–7.84 (m, 4 H, H_{Ph}), 9.52 (s, 2 H, N2–C*H*–N4), 10.70 (s, 2 H, N1–C*H*–N4).

^{13}C NMR (75.476 MHz, DMSO-d_6): δ = 27.0 ($CH_2CH_2CH_2$), 38.2 (SCH_2), 48.8 ($CH_2CH_2CH_2$), 127.4 (C_{Ph}), 127.4 (C_{Bn}), 128.4 (C_{Ph}), 128.5 (C_{Bn}), 128.7 (C_{Bn}), 131.6 (q-*C*), 131.9 (C_{Ph}), 132.1 (q-*C*), 132.7 (C_{Ph}), 136.3 (q-*C*), 143.5 (N1–*C*H–N4), 145.1 (N2–*C*H–N4).

MS (ESI): *m/z* (%) = 288.11 (24) [M-2Br]$^{2+}$, 575.20 (51) [M – HBr – Br]$^+$, 657.13 (100) [M – Br]$^+$.

HRMS (ESI): *m/z* calcd for $[C_{33}H_{32}BrN_6S_2]^+$: 655.1308; found: 655.1323.

1,1′-[1,3-Phenylenedi(methylene)]bis[4-(2-benzylthiophenyl)-4*H*-1,2,4-triazol-1-ium] Dichloride (6a)

Triazole **2e** (10.0 mmol, 2.67 g) and 1,3-$(ClCH_2)_2C_6H_4$ (4.0 mmol, 0.70 g) were ground together in a mortar and then heated without solvent to 130 °C for 2 h. The resulting yellow melt was dissolved in CH_2Cl_2 (150 mL). On addition of Et_2O (100 mL), a colorless solid precipitated which was filtered off, washed with Et_2O (50 mL), and dried in vacuo; yield: 2.67 g (94%); $C_{38}H_{34}Cl_2N_6S_2$ (M = 709.75 g/mol); mp 189 °C.

IR (KBr): 3450 (br), 3006 (br), 1562 (s), 1520 (w), 1494 (m), 1476 (m), 1453 (m), 1442 (m), 1317 (m), 1240 (w), 1202 (m), 1096 (m), 1071 (m), 1001 (w), 769 (s), 744 (m), 727 (m), 703 (s), 654 (m), 544 (w), 477 (w) cm^{-1}.

^{1}H NMR (500.133 MHz, DMSO-d_6): δ = 4.22 (s, 4 H, SCH_2), 5.86 (s, 4 H, NCH_2), 7.15–7.17 (m, 4 H, H_{Bn}), 7.22–7.23 (m, 6 H, H_{Bn}), 7.48–7.51 (m, 1 H, H_{Xyl}), 7.57 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, H_{Ph}), 7.60–7.62 (m, 2 H, H_{Xyl}), 7.67 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, H_{Ph}), 7.82 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, 2 H, H_{Ph}), 7.85–7.86 (m, 3 H, H_{Ph}, H_{Xyl}), 9.52 (s, 2 H, N2–C*H*–N4), 11.41 (s, 2 H, N1–C*H*–N4).

^{13}C NMR (125.758 MHz, DMSO-d_6): δ = 38.5 (SCH_2), 54.3 (NCH_2), 127.3 (C_{Bn}), 127.3 (C_{Ph}), 128.4 (C_{Bn}), 128.5 (C_{Ph}), 128.6 (C_{Bn}), 129.3 (C_{Xyl}), 129.3 (C_{Xyl}), 129.6 (C_{Xyl}), 131.8 (C_{Ph}), 132.0 (q-*C*), 133.1 (C_{Ph}), 133.7 (q-*C*), 136.3 (q-*C*), 143.7 (N1–*C*H–N4), 145.3 (N2–*C*H–N4). One quaternary carbon signal not detected.

MS (ESI): *m/z* (%) = 319.11 (6) [M – 2Cl]$^{2+}$, 637.22 (63) [M – Cl – HCl]$^+$, 673.20 (100) [M – Cl]$^+$.

HRMS (ESI): *m/z* calcd for $[C_{38}H_{34}ClN_6S_2]^+$: 673.1969; found: 673.1972.

1,1′-[1,3-Phenylenedi(methylene)]bis[4-(2-benzylthiophenyl)-4*H*-1,2,4-triazol-1-ium] Ditosylate (6b)

To exchange the anions, dichloride **6a** (1.07 g, 1.50 mmol) was dissolved in CH_2Cl_2 (50 mL) and a soln of TsOH·H_2O (1.71 g, 9.00 mmol) in H_2O (50 mL) was added. The two-layer system was thoroughly stirred for 1 h and then the layers were separated. The aqueous layer was extracted once with CH_2Cl_2 (50 mL). The combined organic layers were washed with H_2O (3 × 30 mL) to remove traces of TsOH, and then dried ($MgSO_4$). On addition of Et_2O (100 mL), a product precipitated. This was washed with Et_2O (50 mL) and dried in vacuo to give a colorless foam; yield: 1.40 g (95%); $C_{52}H_{48}N_6O_6S_4$ (M = 981.23 g/mol); mp 90 °C.

IR (KBr): 3433 (br), 3027 (br), 1925 (w), 1634 (w), 1562 (w), 1494 (w), 1476 (w), 1453 (w), 1193 (s), 1122 (m), 1101 (w), 1034 (m), 1011 (m), 817 (w), 768 (w), 702 (w), 682 (m), 617 (w), 568 (m), 477 (w) cm^{-1}.

^{1}H NMR (500.133 MHz, DMSO-d_6): δ = 2.28 (s, 6 H, OTs-CH_3), 4.18 (s, 4 H, SCH_2), 5.78 (s, 4 H, NCH_2), 7.09–7.12 (m, 8 H, H_{Bn}, OTs-C*H*), 7.21–7.23 (m, 6 H, H_{Bn}), 7.48 (d, $^3J_{HH}$ = 8.0 Hz, 4 H, OTs-C*H*), 7.52–7.58 (m, 5 H, H_{Xyl}, H_{Ph}), 7.69 (dt, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 2 H, H_{Ph}), 7.74 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 2 H, H_{Ph}), 7.76 (br s, 1 H, H_{Xyl}), 7.83 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 2 H, H_{Ph}), 9.41 (s, 2 H, N2–C*H*–N4), 10.68 (s, 2 H, N1–C*H*–N4).

^{13}C NMR (125.758 MHz, DMSO-d_6): δ = 20.7 (OTs-*C*H_3), 38.5 (SCH_2), 54.6 (NCH_2), 125.4 (OTs-*C*H), 127.2 (C_{Ph}), 127.3 (C_{Bn}), 128.0 (OTs-*C*H), 128.4 (C_{Bn}), 128.5 (C_{Ph}), 128.6 (C_{Bn}), 129.4 (2 C_{Xyl}), 129.7 (C_{Xyl}), 131.8 (C_{Ph}), 131.9 (q-*C*), 133.1 (C_{Ph}), 133.5 (q-*C*), 136.3 (q-*C*), 137.6 (q-*C*), 143.5 (N1–*C*H–N4), 145.3 (N2–*C*H–N4), 145.4 (q-*C*). One quarternary carbon signal not detected.

MS (ESI): *m/z* (%) = 319.11 (10) [M – 2OTs]$^{2+}$, 637.22 (3) [M – OTs – HOTs]$^+$, 809.24 (100) [M – OTs]$^+$.

HRMS (ESI): *m/z* calcd for $[C_{45}H_{41}N_6O_3S_3]^+$: 809.2397; found: 809.2405.

1-(3-Chloropropyl)-4-(2,6-dimethylphenyl)-4*H*-1,2,4-triazol-1-ium Bromide (7)

Triazole **2b** (11.5 mmol, 2.00 g) was dissolved in $Br(CH_2)_3Cl$ (230 mmol, 23 mL), and the mixture was stirred at 40 °C for 3 d. The colorless solid that precipitated was filtered off, washed with Et_2O (50 mL), and dried in vacuo; yield: 2.85 g (75%); $C_{13}H_{17}BrClN_3$ (M = 330.65 g/mol); mp 229 °C.

IR (KBr): 3077 (w), 3029 (s), 1559 (s), 1518 (w), 1478 (m), 1455 (w), 1436 (w), 1320 (w), 1221 (w), 1182 (m), 1103 (m), 1080 (w), 992 (w), 798 (s), 715 (w), 659 (w) cm^{-1}.

^{1}H NMR (500.133 MHz, DMSO-d_6): δ = 2.17 (s, 6 H, CH_3), 2.50 (m, 2 H, $CH_2CH_2CH_2$), 3.85 (t, $^3J_{HH}$ = 6.3 Hz, 2 H, $ClCH_2CH_2$), 4.68 (t, $^3J_{HH}$ = 6.8 Hz, 2 H, NCH_2CH_2), 7.39 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, $H_{Ph3/5}$), 7.50 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, H_{Ph4}), 9.63 (s, 1 H, N2–C*H*–N4), 10.78 (s, 1 H, N1–C*H*–N4).

^{13}C NMR (125.758 MHz, DMSO-d_6): δ = 17.2 (CH_3), 30.4 ($CH_2CH_2CH_2$), 42.0 ($ClCH_2CH_2$), 49.9 (NCH_2CH_2), 128.9 ($C_{Ph3/5}$), 130.3 (C_{Ph1}), 131.0 (C_{Ph4}), 134.7 ($C_{Ph2/6}$), 143.7 (N1–*C*H–N4), 145.1 (N2–*C*H–N4).

MS (ESI): *m/z* (%) = 581.13 (65), 579.13 (40) [2M – Br]$^+$, 250.09 (100) [M – Br]$^+$.

MS (ESI negative ion): *m/z* (%) = 412.07 (69), 409.98 (100) [M + Br]$^-$, 80.94 (9), 78.94 (8) [Br]$^-$.

Anal. Calcd for $C_{13}H_{17}BrClN_3$: C, 47.22; H, 5.18; N, 12.71. Found: C, 47.16; H, 5.18; N, 12.75.

4-(2-Benzylthiophenyl)-1-{3-[4-(2,6-dimethylphenyl)-4*H*-1,2,4-triazol-1-ium-1-yl]propyl}-4*H*-1,2,4-triazol-1-ium Bromide Chloride (8a)

Triazole **2e** (9.75 mmol, 2.61 g) and triazolium bromide **7** (6.50 mmol, 2.15 g) were ground together in a mortar and heated without solvent at 140 °C for 2 h. The resulting orange melt was dissolved in CH_2Cl_2 (150 mL). On addition of Et_2O (100 mL), a product precipitated from the soln as a yellow oil. The oil was separated by decantation, washed with Et_2O (50 mL), and dried in vacuo to give a light-yellow foam; yield: 3.67 g (95%); $C_{28}H_{30}BrClN_6S$ (M = 598.00 g/mol); mp 130 °C.

IR (KBr): 3440 (br), 2977 (br), 1635 (w), 1589 (w), 1561 (s), 1521 (w), 1495 (w), 1476 (m), 1453 (m), 1317 (w), 1190 (w), 1105 (m), 1011 (m), 998 (w), 772 (m), 728 (w), 704 (w), 670 (w), 650 (w), 556 (w) 536 (w), 479 (w) cm^{-1}.

^1H NMR (300.132 MHz, DMSO-d_6): δ = 2.19 (s, 6 H, CH_3), 2.76 (pseudo-quin, 2 H, $CH_2CH_2CH_2$), 4.23 (s, 2 H, SCH_2), 4.72–4.80 (m, 4 H, NCH_2CH$_2$CH_2N′), 7.20–7.22 (m, 2 H, H_{Bn}), 7.25–7.29 (m, 3 H, H_{Bn}), 7.38 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, H_{Xyl}), 7.47–7.52 (m, 1 H, H_{Xyl}), 7.59 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H_{Ph}), 7.68 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H_{Ph}), 7.81 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H_{Ph}), 7.87 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.4 Hz, 1 H, H_{Ph}), 9.54 (s, 1 H, N2–C*H*–N4), 9.69 (s, 1 H, N2′–C*H*–N4′), 10.94 (s, 1 H, N1–C*H*–N4), 11.11 (s, 1 H, N1′–C*H*–N4′).

^{13}C NMR (75.476 MHz, DMSO-d_6): δ = 17.4 (*C*H_3), 26.8 ($CH_2CH_2CH_2$), 38.3 (S*C*H_2), 48.8 (N*C*H_2CH$_2$CH$_2$N′), 48.9 (NCH$_2$CH$_2$*C*H_2N′), 127.3 (C_{Ph}), 127.4 (C_{Bn}), 128.3 (C_{Ph}), 128.4 (C_{Bn}), 128.7 (C_{Bn}), 129.0 (C_{Xyl}), 130.4 (q-*C*), 131.0 (q-*C*), 131.7 (C_{Xyl}), 131.8 (q-*C*), 132.1 (C_{Ph}), 132.7 (C_{Ph}), 134.7 (q-*C*), 136.4 (q-*C*), 143.6 (N1–*C*H–N4), 144.0 (N1′–*C*H–N4′), 145.0 (N2–*C*H–N4), 145.1 (N2′–*C*H–N4′).

MS (ESI): *m/z* (%) = 481.22 (100) [M – HCl – Br]$^+$, 563.14 (19) [M – Cl]$^+$, 1071.36 (2) [2M – 2Br + Cl]$^+$, 1115.31 (8) [2M – Br]$^+$, 1159.26 (9) [2M – Cl]$^+$, 1205.20 (3) [2M – 2Cl + Br]$^+$.

HRMS (ESI): *m/z* calcd for $[C_{28}H_{30}BrN_6S]^+$: 561.1431; found: 561.1440.

4-(2-Benzylthiophenyl)-1-{3-[4-(2,6-dimethylphenyl)-4*H*-1,2,4-triazol-1-ium-1-yl]propyl}-4*H*-1,2,4-triazol-1-ium Ditosylate (8b)

To exchange the anion, the bromide chloride **8a** (1.00 g, 1.67 mmol) was dissolved in CH_2Cl_2 (50 mL) and a soln of TsOH·H_2O (1.91 g, 10.00 mmol) in H_2O (50 mL) was added. The two-layer system was thoroughly stirred for 1 h and then the layers were separated. The aqueous layer was extracted once with CH_2Cl_2 (50 mL). The combined organic layers were washed with H_2O (3 × 30 mL) to remove traces of TsOH, then dried ($MgSO_4$). On addition of Et_2O (100 mL), the product precipitated from the mixture as a yellow oil. The oil was separated by decantation, washed with Et_2O (50 mL), and dried in vacuo give a light-yellow foam; yield: 769 mg (64%); $C_{42}H_{44}N_6O_6S_3$ (M = 825.03 g/mol); mp 73 °C.

IR (KBr): 3460 (br), 3027 (br), 1633 (w), 1601 (w), 1563 (m), 1495 (w), 1477 (w), 1453 (w), 1319 (w), 1192 (s), 1122 (m), 1106 (m), 1034 (s), 1012 (s), 989 (w), 817 (w), 770 (w), 703 (w), 682 (s), 618 (w), 569 (m) cm^{-1}.

^1H NMR (300.132 MHz, acetone-d_6): δ = 2.15 (s, 6 H, CH_3), 2.26 (s, 6 H, OTs-CH_3), 2.95 (pseudo-quin, 2 H, $CH_2CH_2CH_2$), 4.07 (s, 2 H, SCH_2), 4.97 (t, $^3J_{HH}$ = 6.6 Hz, 2 H, NCH_2CH$_2$CH$_2$N′), 5.06 (t, $^3J_{HH}$ = 6.9 Hz, 2 H, NCH$_2$CH$_2$CH_2N′), 7.00 (d, $^3J_{HH}$ = 7.9 Hz, 4 H, OTs-C*H*), 7.08–7.11 (m, 2 H, H_{Bn}), 7.22–7.25 (m, 5 H, H_{Bn}, H_{Xyl}), 7.35 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{Ph}), 7.38–7.44 (m, 1 H, H_{Xyl}), 7.47 (d, $^3J_{HH}$ = 7.9 Hz, 4 H, OTs-C*H*), 7.57 (dt, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{Ph}), 7.73 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{Ph}), 7.91 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, H_{Ph}), 9.06 (s, 1 H, N2–C*H*–N4), 9.45 (s, 1 H, N2′–C*H*–N4′), 10.86 (s, 1 H, N1–C*H*–N4), 11.05 (s, 1 H, N1′–C*H*–N4′).

^{13}C NMR (75.476 MHz, acetone-d_6): δ = 19.0 (*C*H_3), 22.2 (OTs-*C*H_3), 29.6 ($CH_2CH_2CH_2$), 41.9 (S*C*H_2), 51.4 (N*C*H_2CH$_2$CH$_2$N′), 51.5 (NCH$_2$CH$_2$*C*H_2N′), 127.7 (OTs-*C*H), 129.3 (C_{Bn}), 129.8 (C_{Ph}), 129.9 (OTs-*C*H), 130.5 (C_{Bn}), 130.7 (C_{Bn}), 131.0 (C_{Xyl}), 131.1 (C_{Ph}), 132.6 (q-*C*), 132.9 (C_{Xyl}), 133.5 (C_{Ph}), 133.6 (q-*C*), 135.3 (q-*C*), 136.6 (C_{Ph}), 137.2 (q-*C*), 139.0 (q-*C*), 139.9 (q-*C*), 146.3 (N1–*C*H–N4), 146.8 (N1′–*C*H–N4′), 147.0 (N2–*C*H–N4), 147.3 (N2′–*C*H–N4′), 147.4 (q-*C*).

MS (ESI): *m/z* (%) = 481.22 (5) [M – HOTs – OTs]$^+$, 653.24 (100) [M – OTs]$^+$.

HR-MS (ESI): *m/z* calculated for $[C_{35}H_{37}N_6O_3S_2]^+$: 653.2363; found: 653.2371.

1,1′-[1,3-Phenylenedi(methylene)]bis[4-(2-benzylthiophenyl)-4*H*-1,2,4-triazolylidene]dicopper(I) Dichloride (9)

The bistriazolium dichloride **6a** (0.838 mmol, 595 mg), CuOAc (1.84 mmol, 226 mg), and NaH (1.84 mmol, 44.2 mg) were dissolved in anhyd THF (15 mL) under argon, and the mixture was stirred at r.t. for 2 h. The gray precipitate was filtered off a light-blue soln. On addition of Et_2O (15 mL) to the soln, a product began to precipitate, and the mixture was stored overnight at 4 °C. The solid product was then filtered off, washed with Et_2O (10 mL), and dried in vacuo to give a colorless powder; yield: 548 mg (78%); $C_{38}H_{32}Cl_2Cu_2N_6S_2$ (M = 834.83 g/mol); mp 116 °C.

IR (KBr): 3442 (br), 3132 (w), 3105 (w), 3084 (w), 3060 (w), 3027 (w), 2926 (w), 1632 (w), 1613 (w), 1588 (w), 1531 (m), 1493 (m), 1479 (s), 1452 (s), 1421 (m), 1306 (w), 1241 (w), 1158 (w), 1071 (w), 985 (m), 763 (s), 723 (m), 701 (s), 665 (w) cm^{-1}.

^1H NMR (300.132 MHz, DMSO-d_6): δ = 4.14 (s, 4 H, SCH_2), 5.47 (s, 4 H, NCH_2), 7.22 (br s, 10 H, H_{Bn}), 7.31–7.33 (m, 3 H, H_{Xyl}), 7.36–7.38 (m, 2 H, H_{Ph}), 7.47 (br s, 1 H, H_{Xyl}), 7.50–7.55 (m, 4 H, H_{Ph}), 7.61–7.64 (m, 2 H, H_{Ph}), 9.69 (s, 2 H, N2–C*H*–N4).

^{13}C NMR (75.476 MHz, DMSO-d_6): δ = 37.9 (S*C*H_2), 55.5 (N*C*H_2), 127.3 (C_{Bn}, C_{Xyl}), 127.6 (C_{Ph}), 127.7 (C_{Ph}, C_{Xyl}), 128.4 (C_{Bn}), 128.8 (C_{Bn}), 129.1 (C_{Xyl}), 130.4 (C_{Ph}), 130.5 (C_{Ph}), 132.9 (q-*C*), 134.8 (q-*C*), 136.0 (q-*C*), 136.1 (q-*C*), 144.2 (N2–*C*H–N4), 178.4 (N1–*C*–N4).

MS (ESI): *m/z* (%) = 699.14 (100) [M – Cu – 2Cl]$^+$.

HRMS (ESI): *m/z* calcd for $[C_{38}H_{32}CuN_6S_2]^+$: 699.1420; found: 699.1429.

Anal. Calcd for $C_{38}H_{32}Cl_2Cu_2N_6S_2$: C, 54.67; H, 3.86; N, 10.07; S, 7.68. Found: C, 54.52; H, 4.11; N, 9.90; S, 7.46.

CCDC 775622 (**2b**), 775623 (**2e**), and 775624 (**2f**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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