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Synthesis of [1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium and [1,2,4]triazolo[5,1-*b*][1,3]thiazin-4-ium salts via regioselective electrophilic cyclization of 3-[(2-alken-1-yl)sulfanyl]-4*H*-1,2,4-triazoles

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Abstract: A convenient procedure for the regioselective preparation of [1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium **10** and [1,2,4]triazolo[5,1-*b*][1,3]thiazin-4-ium salts **9** via regioselective electrophilic cyclization of 3-[(2-alken-1-yl) sulfanyl]-4*H*-1,2,4-triazoles **3** is reported. Direction of electrophilic heterocyclization strongly depends on nature of the alkenyl substitutent.

Keywords: electrophilic cyclization; halogen; regioselectivity; selenium tetrahalogenides; tellurium tetrahalogenides; [1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium; [1,2,4]triazolo[5,1-*b*][1,3]thiazin-4-ium.

Introduction

Among the large number of condensed derivatives of the symmetric triazoles many compounds show a wide range of biological activities: antimicrobial and antifungal [1–5], anti-inflammatory [6–8], and anti-convulsive properties [5, 9], among others [10]. Considering these observations, it was envisaged to search effective ways for synthesis of new condensed derivatives of symmetrical triazoles, which can possess valuable properties. In recent years, hetero-annelation processes based on electrophilic halocyclization have proved to be useful in producing various heterocycles including furan [11–14], pyrrole [11, 15], quinoline [16, 17], and a large number of complex heterocyclic compounds [18–30]. The regioselectivity of electrophilic halocyclization of 1,2,4-triazole derivatives was investigated as a function of the reaction conditions [25–27], nature of electrophilic agents [25, 27, 29, 30] and nature of the heterocyclic nucleophilic center in the molecule [26, 29]. On this basis, it was reasoned that introduction of various groups into an allyl substituent of 1,2,4-triazole system can also influence regioselectivity of the annelation reactions.

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Results and discussion

Synthesis of [1,3]thiazolo[2,3-*c*][1,2,4]triazoles upon halogenation of 3-allylsulfanyl-4,5-diphenyl-3*H*-1,2,4-triazole was discussed in our previous work [25]. In this work the regioselectivity of electrophilic cyclization of the alkenyl derivatives of 3-sulfanyl-1,2,4-triazole **3** was investigated. Compounds **3** were obtained by the reaction of an excess of the corresponding alkenyl chloride **2** with alkaline alcoholic solutions of triazoles **1.** Methylallyl chloride **2a** and cinnamyl chloride **2b** were used in the reaction conducted in boiling ethanol. Target sulfanyl ethers **3** precipitated after cooling the reaction mixture.

The structure of compounds **3a–d** was confirmed by using spectral methods.

Bromination of (methylallyl)sulfanyl compounds **3a,b** furnished condensed monobromides **4a,b**. The reactions were carried out at 15°C for 3 h with a ratio of Br_2/**3** of 2:1. It should be noted that the nature of solvent (chloroform, glacial acetic acid) did not influence the yields of salts **4a,b**. A similar pattern was observed in the reaction of iodine with (methylallyl)sulfanyl derivative **3a**. This treatment gave iodide **5a** as the cyclization product. On the other hand, condensed salts **7a–d** were obtained upon electrophilic cyclization of compound **3a** using selenium and tellurium tetrahalogenides **6a–d**. Solutions of the reagents **6a–d** in acetic acid were prepared from a chalcogen oxide in the presence of an excess amount of hydrochloric or hydrobromic acid.

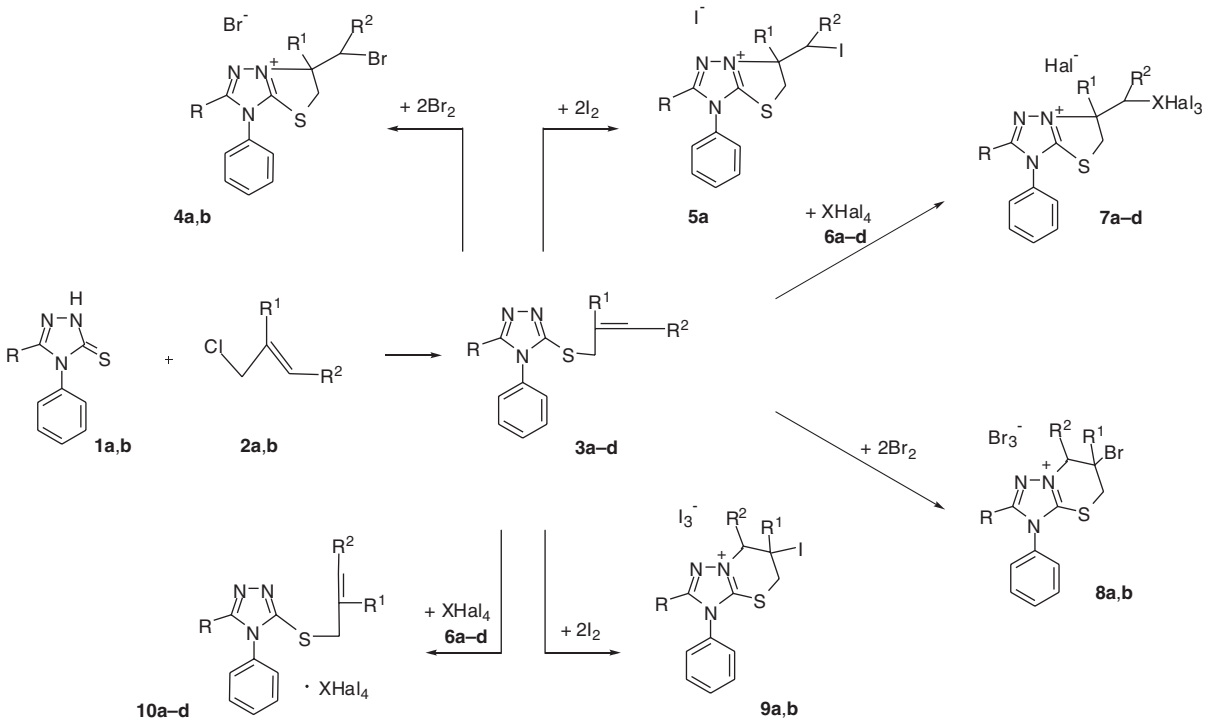
In comparison to the outcome of the reaction of methylallyl derivatives, the regioselectivity process of halocyclization of the cinnamyl analogs **3b,d** is different as the cyclization is accompanied by an annelation to a six-membered thiazine system to form [1,2,4]triazolo[5,1-*b*][1,3]thiazin-8-ium bromides **8a,b** and [1,2,4]triazolo[5,1-*b*][1,3]thiazin-8-ium iodides **9a,b**. The difference in halocyclization selectivity can be explained by a powerful steric effect of the aromatic substitutient in the cinnamyl fragment.

In contrast to the treatment with halogens, the reaction of tetrahalides of selenium and tellurium **6a–d** with cinnamyl derivatives does not cause annelation to form an additional heterocyclic system. This reaction yields stoichiometric yellowish adducts **10a–d**. The spectral characteristics of these adducts are almost identical to those of the substrates **3b,d**. This outcome can be explained in terms of the deactivating influence of steric factors of the cinnamyl substituent and selenium/tellurium tetrahalides. It should be noted that heating of compounds **10a–d** for 7 h did not lead to their cyclization, and the starting complexes **10a–d** were isolated in high yields.

All compounds **4–10** were characterized by means of NMR spectroscopy including ^{1}H, ^{13}C, ^{79}Se, NOE and COSY experiments, mass spectrometry and elemental analysis. The proposed structures are fully consistent with the experimental data.

Conclusions

Methylallylsulfanyl- and cinnamylsulfanyl-substituted 1,2,4-triazoles **3a–d** were synthesized and their diverse electrophilic transformations were studied. The nature of the alkenyl fragment exerts a strong influence on the product structure.



1a: R = Ph
1b: R = 4-O_2N-C_6H_4
2a: R^1 = Me; R^2 = H
2b: R^1 = H; R^2 = Ph
3a: R = Ph; R^1 = Me; R^2 = H
3b: R = Ph; R^1 = H; R^2 = Ph
3c: R = 4-O_2N-C_6H_4; R^1 = Me; R^2 = H
3d: R= 4-O_2N-C_6H_4; R^1 = H; R^2 = Ph

4a: R = Ph; R^1 = Me; R^2 = H
4b: R = 4-O_2N-C_6H_4; R^1 = Me; R^2 = H
5a: R = Ph; R^1 = Me; R^2 = H
6a: X = Se; Hal = Cl
6b: X = Te; Hal = Cl
6c: X = Se; Hal = Br
6d: X = Te; Hal = Br
7a: R = Ph; R^1 = Me; R^2 = H; X = Se; Hal = Cl
7b: R = Ph; R^1 = Me; R^2 = H; X = Te; Hal = Cl

7c: R = Ph; R^1 = Me; R^2 = H; X = Se; Hal = Br
7d: R = Ph; R^1 = Me; R^2 = H; X = Te; Hal = Br
8a: R = Ph; R^1 = H; R^2 = Ph
8b: R= 4-O_2N-C_6H_4; R^1 = H; R^2 = Ph
9a: R = Ph; R^1 = H; R^2 = Ph
9b: R = 4-O_2N-C_6H_4; R^1 = H; R^2 = Ph
10a: R = Ph; R^1 = H; R^2 = Ph; X = Se; Hal = Cl
10b: R = Ph; R^1 = H; R^2 = Ph; X = Te; Hal = Cl
10c: R = Ph; R^1 = H; R^2 = Ph; X = Se; Hal = Br
10d: R = Ph; R^1 = H; R^2 = Ph; X = Te; Hal = Br

Scheme 1

Experimental

^{1}H NMR (300 MHz or 400 MHz) and ^{13}C NMR (75 MHz or 100 MHz) spectra were recorded in DMSO-d_6 on a Varian VXR-300 or Bruker DPX-400 instruments; the ^{79}Se NMR spectrum of **7c** was recorded on a Bruker DPX-400 instrument. 2D-NOESY and COSY experiments were carried out for compounds **7d, 8b** in $CDCl_3$ on a Varian Mercury-400 instrument. Microanalyses were performed by the microanalytical unit of the Institute of Organic Chemistry of the National Academy of Sciences (Kyiv, Ukraine). The EI mass spectrum of compound **7d** was obtained using an Agilent 1100 LCMSD SL instrument. Melting points were determined on a Koefler block instrument and were not corrected.

General procedure for the preparation of substituted 4*H*-1,2,4-triazoles 3a–d

A substituted 2,4-dihydro-3*H*-1,2,4-triazole-3-thione **1a** or **1b** (10.0 mmol) was dissolved in ethanol (20 mL) with heating and the solution was cooled and treated with an alkenyl halogenide **2a** or **2b** (12.0 mmol) in ethanol (5 mL). The mixture was heated under reflux for 1 h. The precipitated product was filtered, washed with ether and dried.

3-[(2-Methylprop-2-en-1-yl)sulfanyl]-4,5-diphenyl-4*H*-1,2,4-triazole (3a) This compound was obtained from **1a** and **2a**; yield 80% of colorless crystals; mp 140°C; ^{1}H NMR (300 MHz): δ 1.70 (s, 3H), 3.76 (s, 2H), 4.83 (s, 1H), 4.91 (s, 1H), 7.35–7.55 (m, 10H). Anal. Calcd for $C_{18}H_{17}N_3S$: C, 70.33; H, 5.57; N, 13.67; S, 10.43. Found: C, 70.70; H, 5.61; N, 13.52; S, 10.29.

3,4-Diphenyl-5-[(3-phenylprop-2-en-1-yl)sulfanyl]-4*H*-1,2,4-triazole (3b) This compound was obtained from **1a** and **2b**; yield 52% of colorless crystals; mp 152–154°C; ^{1}H NMR (300 MHz): δ 3.97 (d, *J* = 4.2 Hz, 2H), 6.36 (m, 1H), 6.58 (d, *J* = 9.3 Hz, 1H), 7.23–7.52 (m, 15H). Anal. Calcd for $C_{23}H_{19}N_3S$: C, 74.77; H, 5.18; N, 11.37; S, 8.68. Found: C, 75.01; H, 5.11; N, 11.21; S, 8.50.

3-[(2-Methylprop-2-en-1-yl)sulfanyl]-5-(4-nitrophenyl)-4-phenyl-4*H*-1,2,4-triazole (3c) This compound was obtained from **1b** and **2a**; yield 57% of yellowish crystals; mp 168–170°C; ^{1}H NMR (300 MHz): δ 1.72 (s, 3H), 3.82 (s, 2H), 4.85 (s, 1H), 4.94 (s, 1H), 7.42–7.68 (m, 7H), 8.21 (d, *J* = 8.1 Hz, 2H). Anal. Calcd for $C_{18}H_{16}N_4O_2S$: C, 61.35; H, 4.58; N, 15.90; S, 9.10. Found: C, 61.48; H, 4.49; N, 15.72; S, 9.14.

3-(4-Nitrophenyl)-4-phenyl-5-[(3-phenylprop-2-en-1-yl)sulfanyl]-4*H*-1,2,4-triazole (3d) This compound was obtained from **1b** and **2b**; yield 64% of yellowish crystals; mp 170–172°C; ^{1}H NMR (300 MHz): δ 3.98 (d, *J* = 4.5 Hz, 2H), 6.32 (m, 1H), 6.58 (d, *J* = 9.9 Hz, 1H), 7.20–7.57 (m, 12H), 8.15 (d, *J* = 5.4 Hz, 2H); ^{13}C NMR (75 MHz): δ 153.2, 153.0, 148.1, 136.5, 133.9, 133.6, 133.0, 130.7, 130.5, 129.3, 129.0, 128.2, 128.0, 126.7, 124.8, 124.1, 35.2. Anal. Calcd for $C_{23}H_{18}N_4O_2S$: C, 66.65; H, 4.38; N, 13.52; S, 7.74. Found: C, 66.79; H, 4.16; N, 13.32; S, 7.70.

General procedure for the preparation of fused salts 4, 5, 7–9 and complexes 10

A solution of bromine or iodine (20.0 mmol) or a solution of a tetrahalogenide of selenium or tellurium **6a–d** (10.0 mmol) in acetic acid was added dropwise to the solution of a triazole **3a–d** (10.0 mmol) in acetic acid with constant stirring at room temperature. The resultant solid product was filtered, washed with acetone (**4, 5**, **8, 9**) or ether (**7, 10**) and dried.

6-(Bromomethyl)-6-methyl-2,3-diphenyl-5,6-dihydro-3*H*-[1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium bromide (4a) This compound was obtained by bromination of **3a**; yield 78% of a white powder; mp 285–287°C; ^{1}H NMR (300 MHz): δ 2.01 (s, 3H), 4.28–4.34 (m, 2H), 4.48 (dd, *J* = 31.5, 12.0 Hz, 2H), 7.46–7.75 (m, 10H); ^{13}C NMR (75 MHz): δ 160.1, 157.5, 132.6, 131.4, 129.6, 126.9, 123.9, 69.1, 48.2, 37.9, 23.3. Anal. Calcd for $C_{18}H_{17}Br_2N_3S$: C, 46.27; H, 3.67; Br, 34.20; N, 8.99; S, 6.86. Found: C, 45.98; H, 3.52; Br, 34.52; N, 8.84; S, 6.79.

6-(Bromomethyl)-6-methyl-2-(4-nitrophenyl)-3-phenyl-5,6-dihydro-3*H*-[1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium bromide (4b) This compound was obtained by bromination of **3c**; yield 56% of yellowish powder; mp 259–261°C; ^{1}H NMR (400 MHz): δ 1.96 (s, 3H), 4.21–4.25 (m, 2H), 4.45 (dd, *J* = 30.0, 11.6 Hz, 2H), 7.65–7.73 (m, 7H), 8.35 (d, *J* = 9.2 Hz, 2H). Anal. Calcd for $C_{18}H_{16}Br_2N_4O_2S$: C, 42.21; H, 3.15; Br, 31.20; N, 10.94; S, 6.26. Found: C, 42.02; H, 3.11; Br, 31.55; N, 10.78; S, 6.17.

6-(Iodomethyl)-6-methyl-2,3-diphenyl-5,6-dihydro-3*H*-[1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium iodide (5a) This compound was obtained by iodination of **3a**; yield 61% of a brown powder; mp 248–250°C; ^{1}H NMR (300 MHz): δ 1.98 (s, 3H), 3.95–4.04 (m, 2H), 4.41 (dd, *J* = 27.3, 12.0 Hz, 2H), 7.39–7.72 (m, 10H). Anal. Calcd for $C_{18}H_{17}I_2N_3S$: C, 38.52; H, 3.05; I, 45.22; N, 7.49; S, 5.71. Found: C, 38.79; H, 2.99; I, 45.56; N, 7.33; S, 5.68.

6-Methyl-2,3-diphenyl-6-[(trichloro-λ^4-selenanyl)methyl]-5,6-dihydro-3*H*-[1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium chloride (7a) This compound was obtained from **3a** and **6a**; yield 39% of a white powder; mp 220°C (dec); ^{1}H NMR (400 MHz): δ 2.01 (s, 3H), 3.96 (d, *J* = 9.0 Hz, 1H), 4.07 (d, *J* = 8.7 Hz, 1H), 4.41 (d, *J* = 11.1 Hz, 1H), 4.97 (d, *J* = 11.1 Hz, 1H), 7.22–7.41 (m, 10H). Anal. Calcd for $C_{18}H_{17}Cl_4N_3SSe$: C, 40.93; H, 3.24; Cl, 26.85; N, 7.96. Found: C, 41.20; H, 3.29; Cl, 26.68; N, 8.02.

6-Methyl-2,3-diphenyl-6-[(trichloro-λ^4-telluranyl)methyl]-5,6-dihydro-3*H*-[1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium chloride (7b) This compound was obtained from **3a** and **6b**; yield 45% of a white powder; mp 255°C (dec); ^{1}H NMR (400 MHz): δ 2.21 (s, 3H), 4.06 (d, *J* = 9.0 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 9.0 Hz, 1H), 5.17 (d, *J* = 12.0 Hz, 1H), 7.34–7.91 (m, 10H). Anal. Calcd for $C_{18}H_{17}N_3S$: C, 37.48; H, 2.97; Cl, 24.58; N, 7.28. Found: C, 37.72; H, 3.03; Cl, 24.28; N, 7.39.

6-Methyl-2,3-diphenyl-6-[(tribromo-λ^4-selenanyl)methyl]-5,6-dihydro-3*H*-[1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium bromide (7c) This compound was obtained from **3a** and **6c**; yield 44% of a yellowish powder; mp 210°C (dec); ^{1}H NMR (400 MHz): δ 2.02 (s, 3H), 4.35 (d, *J* = 11.1 Hz, 1H), 4.48 (d, *J* = 9.0 Hz, 1H), 4.59 (d, *J* = 9.0 Hz, 1H), 4.90 (d, *J* = 11.1 Hz, 1H), 7.24–7.50 (m, 10H); ^{13}C NMR (100 MHz): δ 159.5, 156.7, 132.4, 129.7, 126.5, 123.9, 70.9, 49.3, 45.4, 25.2; ^{79}Se NMR (DMSO-d_6): δ 660. Anal. Calcd for $C_{18}H_{17}Br_4N_3SSe$: C, 30.62; H, 2.43; Br, 45.27; N, 5.95. Found: C, 30.68; H, 2.42; Br, 45.36; N, 5.84.

6-Methyl-2,3-diphenyl-6-[(tribromo-λ^4-telluranyl)methyl]-5,6-dihydro-3*H*-[1,3]thiazolo[3,2-*b*][1,2,4]triazol-7-ium bromide (7d) This compound was obtained from **3a** and **6d**; yield 59% of an orange powder; mp 267°C (dec); ^{1}H NMR (400 MHz): δ 2.21 (s, 3H),

3.94 (d, *J* = 11.1 Hz, 1H), 4.14 (d, *J* = 9.0 Hz, 1H), 4.24 (d, *J* = 11.1 Hz, 1H), 4.91 (d, *J* = 9.0 Hz, 1H), 7.46–7.67 (m, 10H); ^{13}C NMR (100 MHz): δ 158.2, 157.6, 132.5, 123.3, 131.2, 129.8, 129.7, 126.7, 123.8, 67.8, 50.1, 40.0, 25.0; MS: *m/z* 354.0 (60), 326.0 (70), 309.8 (50), 308.0 (100), 253.8 (25), 238.2 (25). Anal. Calcd for $C_{18}H_{17}Br_4N_3STe$: C, 28.65; H, 2.27; Br, 42.35; N, 5.57. Found: C, 28.69; H, 2.25; Br, 42.22; N, 5.61.

6-Bromo-2,3,7-triphenyl-3,5,6,7-tetrahydro[1,2,4]triazolo[5,1-*b*][1,3]thiazin-8-ium tribromide (8a) This compound was obtained by bromination of **3b**; yield 44% of a white powder; mp 181–183°C; ^{1}H NMR (300 MHz): δ 3.72 (d, *J* = 12.0 Hz, 1H), 3.87 (dd, *J* = 13.6, 7.2 Hz, 1H), 5.45 (m, 1H), 6.33 (d, *J* = 4.0 Hz, 1H), 7.37–7.81 (m, 15H); ^{13}C NMR (75 MHz): δ 153.7, 153.6, 136.1, 133.0, 131.6, 130.3, 129.8, 129.6, 128.4, 128.2, 123.1, 69.0, 45.2, 32.1. Anal. Calcd for $C_{23}H_{19}Br_4N_3S$: C, 40.09; H, 2.78; Br, 46.38; N, 6.10; S, 4.65. Found: C, 40.21; H, 2.84; Br, 46.02; N, 6.18; S, 4.70.

6-Bromo-2-(4-nitrophenyl)-3,7-diphenyl-3,5,6,7-tetrahydro[1,2,4]triazolo[5,1-*b*][1,3]thiazin-8-ium tribromide (8b) This compound was obtained by bromination of **3d**; yield 90% of a yellowish powder; mp 115–120°C; ^{1}H NMR (400 MHz): δ 3.80 (d, *J* = 11.8 Hz, 1H), 3.97 (dd, *J* = 13.6, 7.1 Hz, 1H), 5.50 (m, 1H), 6.39 (d, *J* = 5.2 Hz, 1H), 7.42–7.98 (m, 12H), 8.29 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d6): δ 153.8, 151.6, 149.7, 135.4, 132.7, 131.2, 131.1, 130.9, 129.9, 129.3, 128.7, 128.3, 127.8, 124.4, 69.0, 45.0, 32.4. Anal. Calcd for $C_{23}H_{18}Br_4N_4O_2S$: C, 37.63; H, 2.47; Br, 43.54; N, 7.63; S, 4.37. Found: C, 37.72; H, 2.51; Br, 43.22; N, 7.69; S, 4.40.

6-Iodo-2,3,7-triphenyl-3,5,6,7-tetrahydro[1,2,4]triazolo[5,1-*b*][1,3]thiazin-8-ium triiodide (9a) This compound was obtained by iodination of **3b**; yield 57% of a brown powder; mp 190–192°C; ^{1}H NMR (300 MHz): δ 3.76 (d, *J* = 14.9 Hz, 1H), 3.92 (dd, *J* = 13.5, 6.9 Hz, 1H), 5.48 (m, 1H), 6.35 (d, *J* = 5.2 Hz, 1H), 7.33–7.91 (m, 15H). Anal. Calcd for $C_{23}H_{19}I_4N_3S$: C, 31.50; H, 2.18; I, 57.87; N, 4.79; S, 3.66. Found: C, 31.67; H, 2.21; I, 57.72; N, 4.84; S, 3.68.

6-Iodo-2-(4-nitrophenyl)-3,7-diphenyl-3,5,6,7-tetrahydro[1,2,4]triazolo[5,1-*b*][1,3]-thiazin-8-ium triiodide (9b) This compound was obtained by iodination of **3d**; yield 67% of a brown powder; mp 132–134°C; ^{1}H NMR (300 MHz): δ 3.79–3.90 (m, 1H), 3.97 (dd, *J* = 15.2, 7.0 Hz, 1H), 5.25 (m, 1H), 6.23 (d, *J* = 7.0 Hz, 1H), 7.46–7.67 (m, 7H), 7.77 (s, 5H), 8.28 (d, *J* = 8.9 Hz, 2H). Anal. Calcd for $C_{23}H_{18}I_4N_4O_2S$: C, 29.96; H, 1.97; I, 55.05; N, 6.08; S, 3.48. Found: C, 30.16; H, 2.01; I, 54.90; N, 6.12; S, 3.44.

Molecular complex 10a This compound was obtained from **3b** and **6a**; yield 32% of colorless crystals; mp 220°C (dec); ^{1}H NMR (300 MHz): δ 3.98 (d, *J* = 4.2 Hz, 2H), 6.38 (m, 1H), 6.61 (d, *J* = 9.3 Hz, 1H), 7.18–7.53 (m, 15H). Anal. Calcd for $C_{23}H_{19}Cl_4N_3SSe$: C, 46.80; H, 3.24; Cl, 24.03; N, 7.12. Found: C, 47.06; H, 3.20; Cl, 24.34; N, 7.26.

Molecular complex 10b This compound was obtained from **3b** and **6b**; yield 45% (colorless crystals); mp 255°C (dec); ^{1}H NMR (300 MHz): δ 3.98 (d, *J* = 4.2 Hz, 2H), 6.38 (m, 1H), 6.60 (d, *J* = 9.3 Hz, 1H), 7.22–7.56 (m, 15H). Anal. Calcd for $C_{23}H_{19}Cl_4N_3STe$: C, 43.24; H, 3.00; Cl, 22.20; N, 6.58. Found: C, 43.52; H, 3.08; Cl, 22.43; N, 6.50.

Molecular complex 10c This compound was obtained from **3b** and **6c**; yield 27% of a colorless crystals; mp 222°C (dec); ^{1}H NMR (300 MHz): δ 3.98 (d, *J* = 4.2 Hz, 2H), 6.36 (m, 1H), 6.61 (d, *J* = 9.3 Hz, 1H), 7.19–7.53 (m, 15H). Anal. Calcd for $C_{23}H_{19}Br_4N_3SSe$: C, 35.97; H, 2.49; Br, 41.61; N, 5.47. Found: C, 36.18; H, 2.45; Br, 41.94; N, 5.33.

Molecular complex 10d This compound was obtained from **3b** and **6d**; yield 39% of a colorless crystals; mp 267°C (dec); ^{1}H NMR (300 MHz): δ 3.98 (d, *J* = 4.2 Hz, 2H), 6.38 (m, 1H), 6.58 (d, *J* = 9.3 Hz, 1H), 7.26–7.58 (m, 15H). Anal. Calcd for $C_{23}H_{19}Br_4N_3STe$: C, 33.82; H, 2.34; Br, 39.14; N, 5.15. Found: C, 33.98; H, 2.29; Br, 39.46; N, 5.11.

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