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**NOVEL INTRAMOLECULAR CYCLIZATION-SKELETAL  
REORGANIZATION OF 2-ARYLTHIAZOLES UNDER  
PHOTOIRRADIATION**

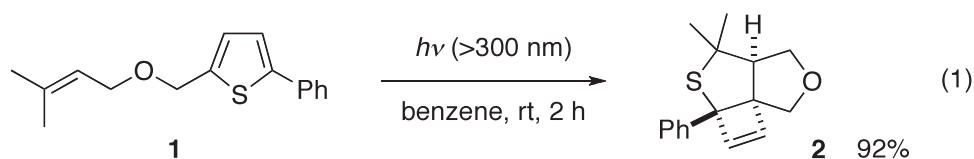
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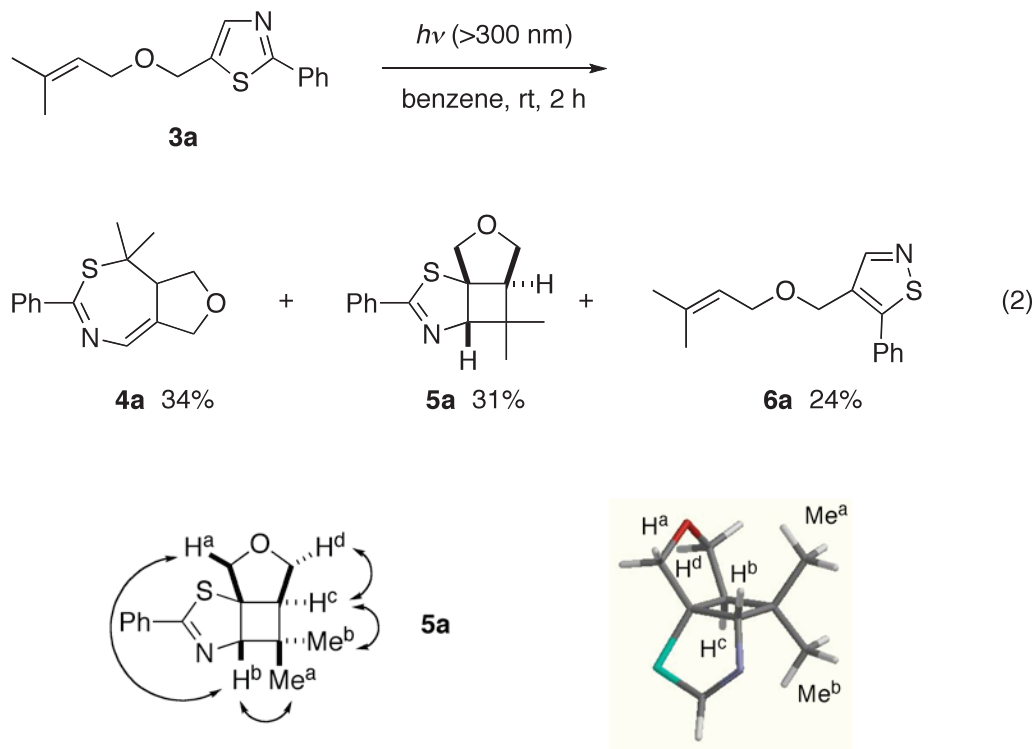
*This paper is dedicated to Professor Isao Kuwajima on the occasion of his 77th birthday.*

**Abstract** – Photoirradiation of 2-arylthiazoles derivatives linked with an alkene moiety through a three-atom spacer was investigated. The main products were unexpected tetrahydrofuran-fused thiazepine derivatives with concomitant formation of [2+2] cycloaddition products and regioisomeric thiazoles. The product distribution was little influenced by the reaction conditions and substituents of the substrates.

The photochemical behavior of 5-membered heteroaromatic compounds is one of the major research areas of organic photochemistry, and has already inspired numerous reports.<sup>1-4</sup> Among them, reactions involving carbon-carbon bond formation are of interest from a synthetic point of view. The [2+2] cycloaddition and electrocyclization are the typical examples;<sup>2-5</sup> however, the construction of complex molecular frameworks by irradiation of simple molecules has been less developed.<sup>6-9</sup> We have reported that photoirradiation of  $\alpha$ -arylthiophene derivatives linked with an alkene moiety through a three-atom spacer **1** gave unprecedented cyclobutene-fused perhydrothiapentalene-type compounds **2** in high yields (Eq. 1).<sup>10</sup> In the course of our study on the photoreaction of sulfur-containing 5-membered heteroaromatic compounds, we found that 2-arylthiazole derivatives under photoirradiation show interesting behavior that is completely different from the behavior of thiophenes.



Our study began with the photoirradiation of 2-phenylthiazole derivative **3a**. Irradiation of a 5 mM solution of **3a** in benzene at room temperature through Pyrex<sup>®</sup> glass gave the unexpected thiazepine **4a** in moderate yield, accompanied by the [2+2] addition product **5a** and isomerized isothiazole **6a**, with small recovery of **3a** (2%) (Eq. 2). The relative configuration of **5a** was determined by NOE experiment (Figure 1). When H<sup>b</sup> was irradiated, clear NOE enhancements were observed for the signals of H<sup>a</sup> and protons of Me<sup>a</sup>, and vice versa. Irradiation at H<sup>c</sup> also showed enhancements of the signals of H<sup>d</sup> and Me<sup>b</sup>. This observation indicates that compound **5a** has the relative configuration depicted in the figure.



**Figure 1.** NOE correlation of **5a**. The phenyl group at thiazole 2-position is omitted in the three-dimensional drawing.

It is well known that photo irradiation of thiazoles causes the isomerization to regioisomers,<sup>1,11,12</sup> whereas examples of carbon-carbon bond formation have rarely been reported.<sup>13</sup> As far as we know, there has been no report of thiazepine formation from thiazole under photoirradiation.<sup>14</sup> We were interested in this extraordinary photoreaction of thiazole derivatives, and decided to investigate the reaction in detail.

Setting **3a** as a standard substrate, we carried out the reaction in a range of solvents. The results are summarized in Table 1.



**Table 2.** Substituent effect on the photocyclization of 2-aryl thiazoles

Entry	R	Conversion [%]	Yield [%] <sup>a</sup>		
			4a-e	5a-e	6a-e
1	C <sub>6</sub> H <sub>5</sub> ( <b>3a</b> )	98	34	31	24
2	4-FC <sub>6</sub> H <sub>4</sub> ( <b>3b</b> )	>99	22	13	31
3	4-MeOC <sub>6</sub> H <sub>4</sub> ( <b>3c</b> )	>99	34	12	30
4	Me ( <b>3d</b> )	6	0	0	0
5	H ( <b>3e</b> )	2	0	0	0
6 <sup>b</sup>	H	14	0	0	0

<sup>a</sup> Estimated by <sup>1</sup>H NMR integrals using pyrazine as an internal standard.

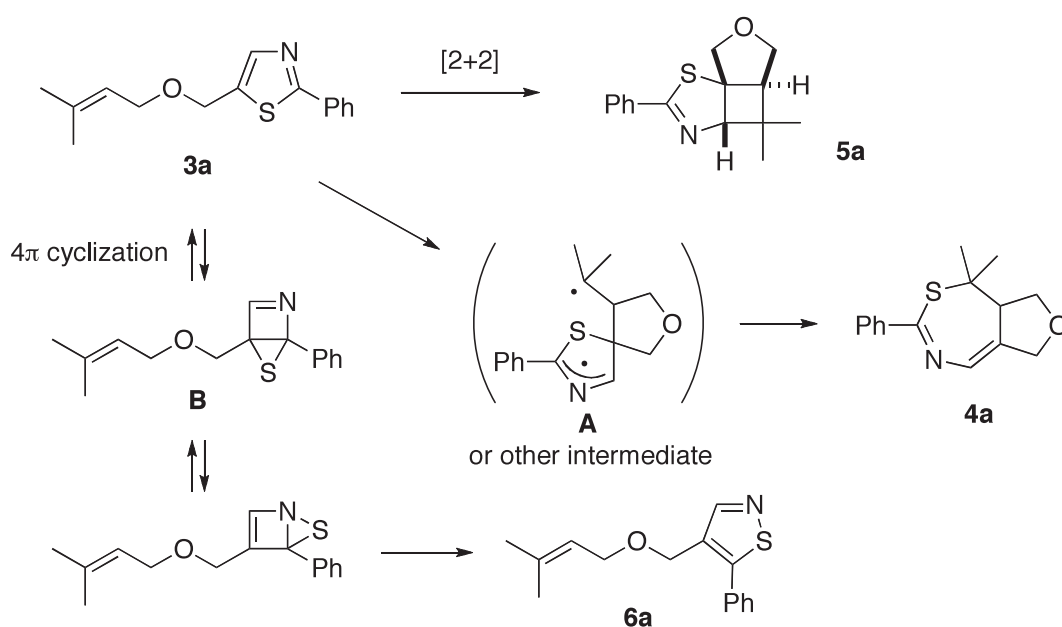
<sup>b</sup> The reaction was carried out in the presence of 10 mol% of 9,10-dicyanoanthracene.

Introduction of 4-fluorophenyl group at the 2-position of thiazole gave better selectivity in favor of thiazepine **4b** but the combined yield of **4b** and **5b** decreased (Entry 2). The substrate with a 4-methoxyphenyl group at the 2-position showed improved selectivity in favor of **4c** without a decrease of the yield compared to **3a** (Entry 3). However, the cyclized products in this case were unstable and decomposed during chromatographic purification on silica gel. The reactions with 2-methyl and 2-unsubstituted thiazoles hardly proceeded under the same conditions (Entries 4 and 5). This was attributed to the poor absorption of **3d** and **3e** in the range of >300 nm. Then we tried the reaction in the presence of 9,10-dicyanoanthracene (DCA) as a photosensitizer, which has previously been proven effective in several photocyclizations (Entry 6).<sup>16-18</sup> The conversion was somewhat increased in this case, but no identifiable product was obtained.

To obtain more insight into the reaction, the stability of the isolated reaction products (**4a**, **5a**, and **6a**) under photoirradiation (in benzene, for 1 h) was checked. Isothiazole **6a** was stable under the conditions employed, whereas partial decomposition was observed in the cases of **4a** and **5a**, to give a mixture of many compounds, including **6a**. The inertness of **6a** under the reaction conditions was attributed to the difference of photoabsorption between **6a** and **3a**. The absorption edge of **6a** was approximately 300

nm and this compound absorbed almost no light through Pyrex<sup>®</sup> glass (approximately >300 nm), while the absorption edge of **3a** was about 350 nm.

The mechanism of the reaction is not clear at present, and the details should be disclosed by further investigation. We surmise the reaction would proceed through the pathway depicted in Scheme 1. Thiazepine **4a** could be formed via biradical species **A**, which was produced by the addition of the excited thiazole to the olefinic moiety, followed by successive [1,3]-transposition of sulfur to give the thiazepine **4a**. A similar intermediate has been postulated in the photocyclization of furan.<sup>18</sup> The [2+2] cycloaddition between thiazole and alkene likely gives the tricyclic compound **5a**.<sup>13</sup> The isomerization to isothiazole **6a** would be caused by the formation of the Dewar thiazole **B**, which is involved as an intermediate in the photoisomerization of thiazole derivatives.<sup>1,11</sup>



**Scheme 1.** Plausible reaction pathway

In summary, we demonstrated a novel photochemical transformation of 2-aryltiazoles **3** that gave thiazepine derivatives **4** in moderate yield with concomitant formation of the [2+2] adduct **5** and isothiazole **6**. This is an unprecedented category of photoreaction of thiazoles, although there remains room for improvement in the product selectivity and yield. Though the mechanism of the reaction is unclear at this stage, the thiazepine might be formed via a biradical intermediate **A**, followed by skeletal rearrangement.

## EXPERIMENTAL

NMR spectra were obtained on a JEOL JNM-ECS400, and JNM-ECX400P spectrometer. Carbon multiplicity was assigned by a DEPT experiment. IR spectra were recorded on JASCO FT/IR-4100

spectrophotometer. Silica gel column chromatography was performed with Kanto Chemical Co., Inc. Silica Gel 60N (63–210  $\mu\text{m}$ ), or Fuji Silisia FL60D. Preparative thin layer chromatography was carried out with Wako Gel B-5F (Wako Pure Chemical Industries, Ltd.). Solvents and reagents were used as received, unless otherwise noted. Mass spectrometry and elemental analyses were carried out at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University.

### Starting materials

The starting materials were prepared from known compounds according to conventional transformations, including the Williamson etherification of known 2-aryl-5-hydroxymethylthiazoles.<sup>19,20</sup> A typical example is as follows:

#### 5-(3-Methyl-2-butenyloxy)methyl-2-phenylthiazole (3a)

To a flask containing a dispersion of NaH (95.8 mg, 60% oil dispersion, 2.4 mmol, washed with hexane before use) in DMF (1 mL) was added a solution of 5-hydroxymethyl-2-phenylthiazole (269.7 mg, 1.41 mmol) in DMF (2 mL) at 0 °C with stirring. After stirring at rt for 30 min, 1-chloro-3-methyl-2-butene (280  $\mu\text{L}$ , 2.5 mmol) was added at 0 °C, and the mixture was stirred for 2 h at rt. The reaction mixture was quenched by addition of cold water, followed by extraction with hexane–EtOAc (1:1, 20 mL x 3). The combined extracts were successively washed with water and brine, and dried with anhydrous sodium sulfate. Purification of the crude material by silica-gel column chromatography (hexane–EtOAc, 7:1 to 4:1) gave **3a** as pale yellow oil (350.5 mg, 96%).

IR (KBr) 2975, 2865, 1456, 1433, 1377, 1357, 1068, 974, 763, 689  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.68 (s, 3H), 1.77 (s, 3H), 4.04 (d,  $J = 6.8$  Hz, 2H), 4.71 (s, 2H), 5.36–5.40 (m, 1H), 7.41–7.47 (m, 3H), 7.71 (s, 1H), 7.92–7.95 (m, 2H). <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  18.0 ( $\text{CH}_3$ ), 25.7 ( $\text{CH}_3$ ), 63.7 ( $\text{CH}_2$ ), 66.2 ( $\text{CH}_2$ ), 120.3 (CH), 126.3 (CH), 128.8 (CH), 129.9 (CH), 133.6 (C), 135.8 (C), 137.9 (C), 142.1 (CH), 168.9 (C). HRMS (ESI<sup>+</sup>)  $m/z$  260.1106 ( $\text{M}+\text{H}^+$ ), calcd for  $\text{C}_{15}\text{H}_{18}\text{NOS}$ : 260.1104.

#### 2-(4-Fluorophenyl)-5-(3-methyl-2-butenyloxy)methylthiazole (3b)

Faintly yellow solid. Mp 39.5–41.0 °C ( $\text{CH}_2\text{Cl}_2$ ). IR (KBr) 2971, 2851, 1600, 1509, 1443, 1226, 1066, 999, 981, 856, 835  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.68 (s, 3H), 1.77 (s, 3H), 4.04 (d,  $J = 6.8$  Hz, 2H), 4.70 (s, 2H), 5.35–5.40 (m, 1H), 7.11–7.16 (m, 2H), 7.68 (s, 1H), 7.90–7.94 (m, 2H). <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  18.1 ( $\text{CH}_3$ ), 25.8 ( $\text{CH}_3$ ), 63.7 ( $\text{CH}_2$ ), 66.4 ( $\text{CH}_2$ ), 116.0 (d,  $J_{\text{C-F}} = 22.5$  Hz, CH), 120.3 (CH), 128.2 (d,  $J_{\text{C-F}} = 8.5$  Hz, CH), 130.0 (C), 136.0 (C), 138.1 (C), 142.2 (CH), 163.8 (d,  $J_{\text{C-F}} = 250$  Hz, C), 167.8 (C). HRMS (ESI<sup>+</sup>)  $m/z$  278.1006 ( $\text{M}+\text{H}^+$ ), calcd for  $\text{C}_{15}\text{H}_{17}\text{FNOS}$ : 278.1009.

#### 2-(4-Methoxyphenyl)-5-(3-methyl-2-butenyloxy)methylthiazole (3c)

Yellow oil. IR (KBr) 2933, 2853, 1607, 1515, 1450, 1254, 1173, 1069, 1034, 975, 834  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.67 (s, 3H), 1.77 (s, 3H), 3.86 (s, 3H), 4.03 (d,  $J = 7.3$  Hz, 2H), 4.68 (s, 2H),

5.36–5.39 (m, 1H), 6.95 (d,  $J = 8.6$  Hz, 2H), 7.64 (s, 1H), 7.86 (d,  $J = 8.6$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  18.0 ( $\text{CH}_3$ ), 25.8 ( $\text{CH}_3$ ), 55.3 ( $\text{CH}_3$ ), 63.8 ( $\text{CH}_2$ ), 66.2 ( $\text{CH}_2$ ), 114.2 (CH), 120.4 (CH), 126.6 (C), 126.6 (CH), 127.8 (CH), 134.8 (C), 138.0 (C), 142.0 (CH), 161.1 (C), 169.0 (C). HRMS (ESI<sup>+</sup>)  $m/z$  290.1209 (M+H<sup>+</sup>), calcd for  $\text{C}_{16}\text{H}_{20}\text{NO}_2\text{S}$ : 290.1209.

### **2-Methyl-5-(3-methyl-2-butenyloxy)methylthiazole (3d)**

Light yellow oil. IR (KBr) 2972, 2926, 2856, 1674, 1536, 1472, 1446, 1377, 1359, 1161, 1068, 967, 903  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.66 (s, 3H), 1.76 (s, 3H), 2.69 (s, 3H), 3.99 (d,  $J = 6.8$  Hz, 2H), 4.62 (s, 2H), 5.33–5.37 (m, 1H), 7.48 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  17.9 ( $\text{CH}_3$ ), 19.2 ( $\text{CH}_3$ ), 25.7 ( $\text{CH}_3$ ), 63.6 ( $\text{CH}_2$ ), 66.0 ( $\text{CH}_2$ ), 120.3 (CH), 135.2 (C), 137.8 (C), 140.8 (CH), 166.9 (C). HRMS (ESI<sup>+</sup>)  $m/z$  198.0950 (M+H<sup>+</sup>), calcd for  $\text{C}_{10}\text{H}_{16}\text{NOS}$ : 198.0947.

### **5-(3-Methyl-2-butenyloxy)methylthiazole (3e)**

Light yellow oil. IR (KBr) 2973, 2912, 2857, 1673, 1521, 1407, 1377, 1358, 1068, 873  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.67 (s, 3H), 1.76 (s, 3H), 4.01 (d,  $J = 7.1$  Hz, 2H), 4.71 (s, 2H), 5.34–5.38 (m, 1H), 7.79 (s, 1H), 8.79 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  17.8 ( $\text{CH}_3$ ), 25.6 ( $\text{CH}_3$ ), 63.2 ( $\text{CH}_2$ ), 66.2 ( $\text{CH}_2$ ), 120.1 (CH), 135.7 (C), 137.8 (C), 141.7 (CH), 153.5 (CH). HRMS (ESI<sup>+</sup>)  $m/z$  184.0793 (M+H<sup>+</sup>), calcd for  $\text{C}_9\text{H}_{14}\text{NOS}$ : 184.0791.

### **General procedure for the photocyclization and physical data of the products**

The reaction of **3a** is representative.

In a Pyrex<sup>®</sup> test tube (or reaction vessel (for preparative scale)) were charged **3a** (13.3 mg, 0.0513 mmol) and benzene (10 mL, degassed by  $\text{N}_2$  bubbling for 30 min), and air present in the tube was replaced with argon by several cycles of rapid evacuation/Ar introduction. The solution was irradiated by a 100 W high-pressure mercury lamp (UVL-100HA; Riko) externally for 2 h. After the solution was evaporated, pyrazine (30  $\mu\text{L}$  of 0.132 M solution in benzene, 4.0  $\mu\text{mol}$ ) was added to the mixture as an internal standard. The yields of **4a**, **5a**, and **6a** were estimated by  $^1\text{H}$  NMR integrals. The pure sample for analysis could be isolated by chromatographic purification with case-dependent loss due to decomposition.

### **1,3,3a,4-Tetrahydro-4,4-dimethyl-6-phenylfuro[3,4-*e*][1,3]thiazepine (4a)**

Light yellow oil. IR (KBr) 2965, 1750, 1727, 1671, 1602, 1551, 1447, 1368, 1222, 1096, 1056, 930, 767, 693  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.52 (s, 3H), 1.57 (s, 3H), 3.31 (br m, 1H), 3.81 (dd,  $J = 9.4, 5.1$  Hz, 1H), 3.93 (dd,  $J = 9.4, 7.6$  Hz, 1H), 4.47–4.51 (m, 1H), 4.60–4.64 (m, 1H), 6.98–7.00 (m, 1H), 7.24–7.28 (m, 1H), 7.36–7.43 (m, 3H), 7.94–7.97 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  26.3 ( $\text{CH}_3$ ), 31.7 ( $\text{CH}_3$ ), 54.0 (CH), 63.7 (C), 70.7 ( $\text{CH}_2$ ), 71.4 ( $\text{CH}_2$ ), 128.2 (CH), 128.3 (CH), 128.6 (CH), 130.6 (CH), 133.1 (C), 140.7 (C), 162.5 (C). HRMS (ESI<sup>+</sup>)  $m/z$  260.1106 (M+H<sup>+</sup>), calcd for  $\text{C}_{15}\text{H}_{18}\text{NOS}$ : 260.1109.

**3a,4,4a,5-Tetrahydro-4,4-dimethyl-2-phenyl-7H-furo[3',4':2,3]cyclobuta[1,2-d][1,3]thiazole (5a)**

Faintly yellow oil. IR (KBr) 2960, 2861, 1594, 1446, 1065, 957, 941, 912, 767, 702, 690  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.14 (s, 3H), 1.24 (s, 3H), 2.63 (d,  $J = 5.9$  Hz, 1H), 3.55 (d,  $J = 9.4$  Hz, 1H), 3.70 (dd,  $J = 10.4, 5.9$  Hz, 1H), 3.98 (d,  $J = 9.4$  Hz, 1H), 4.08 (d,  $J = 10.4$  Hz, 1H), 4.77 (d,  $J = 0.8$  Hz, 1H), 7.40–7.50 (m, 3H), 7.79–7.82 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  22.8 ( $\text{CH}_3$ ), 24.6 ( $\text{CH}_3$ ), 43.5 (C), 57.5 (CH), 61.9 (C), 69.7 ( $\text{CH}_2$ ), 72.8 ( $\text{CH}_2$ ), 90.6 (CH), 128.4 (CH), 128.5 (CH), 130.6 (CH), 133.3 (CH), 133.2 (C), 168.3 (C). HRMS (ESI<sup>+</sup>)  $m/z$  260.1105 ( $\text{M}+\text{H}^+$ ), calcd for  $\text{C}_{15}\text{H}_{18}\text{NOS}$ : 260.1109.

**4-(3-Methylbut-2-enyloxy)methyl-5-phenylisothiazole (6a)**

Light yellow oil. IR (KBr) 2971, 2914, 2855, 1486, 1444, 1062, 769, 700  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.66 (s, 3H), 1.75 (s, 3H), 4.07 (d,  $J = 7.2$  Hz, 2H), 4.74 (s, 2H), 5.38–5.41 (m, 1H), 7.37–7.48 (m, 3H), 7.69 (d,  $J = 7.2$  Hz, 2H), 8.80 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  18.0 ( $\text{CH}_3$ ), 25.8 ( $\text{CH}_3$ ), 63.7 ( $\text{CH}_2$ ), 66.8 ( $\text{CH}_2$ ), 120.3 (CH), 128.1 (CH), 128.5 (CH), 128.7 (CH), 130.4 (C), 134.4 (C), 138.3 (C), 151.7 (CH), 153.4 (C). HRMS (ESI<sup>+</sup>)  $m/z$  282.0924 ( $\text{M}+\text{Na}^+$ ), calcd for  $\text{C}_{15}\text{H}_{17}\text{NNaOS}$ : 282.0929.

**6-(4-Fluorophenyl)-1,3,3a,4-tetrahydro-4,4-dimethylfuro[3,4-e][1,3]thiazepine (4b)**

Yellow oil. IR (KBr) 2961, 2925, 2854, 1752, 1599, 1502, 1231, 1155, 1057, 1036, 842, 809  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.51 (s, 3H), 1.56 (s, 3H), 3.29 (br m, 1H), 3.80 (dd,  $J = 9.4, 5.0$  Hz, 1H), 3.93 (dd,  $J = 9.4, 7.2$  Hz, 1H), 4.48 (d,  $J = 13.5$  Hz, 1H), 4.62 (dt,  $J_d = 13.5, J_t = 1.8$  Hz, 1H), 6.96 (d,  $J = 1.8$  Hz, 1H), 7.03–7.08 (m, 2H), 7.96–7.99 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  26.2 ( $\text{CH}_3$ ), 31.7 ( $\text{CH}_3$ ), 53.9 (CH), 63.9 (C), 70.7 ( $\text{CH}_2$ ), 71.4 ( $\text{CH}_2$ ), 115.1 (d,  $J_{\text{C-F}} = 21.7$  Hz, CH), 128.6 (CH), 130.3 (d,  $J_{\text{C-F}} = 8.4$  Hz, CH), 133.3 (C), 136.9 (C), 161.1 (C), 164.4 (d,  $J_{\text{C-F}} = 251$  Hz, C). HRMS (ESI<sup>+</sup>)  $m/z$  278.1006 ( $\text{M}+\text{H}^+$ ), calcd for  $\text{C}_{15}\text{H}_{17}\text{FNOS}$ : 278.1009.

**2-(4-Fluorophenyl)-3a,4,4a,5-tetrahydro-4,4-dimethyl-7H-furo[3',4':2,3]cyclobuta[1,2-d][1,3]thiazole (5b)**

Yellow oil. IR (KBr) 2961, 2860, 1606, 1507, 1263, 1234, 1156, 1065, 957, 942, 912, 842  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.13 (s, 3H), 1.23 (s, 3H), 2.63 (d,  $J = 6.3$  Hz, 1H), 3.55 (d,  $J = 9.4$  Hz, 1H), 3.69 (dd,  $J = 10.3, 6.3$  Hz, 1H), 3.98 (d,  $J = 9.4$  Hz, 1H), 4.08 (d,  $J = 10.3$  Hz, 1H), 4.75 (s, 1H), 7.11 (t,  $J = 8.5$  Hz, 2H), 7.80 (dd,  $J = 8.5, 5.4$  Hz, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  22.8 ( $\text{CH}_3$ ), 24.6 ( $\text{CH}_3$ ), 43.5 (C), 57.5 (CH), 62.3 (C), 69.7 ( $\text{CH}_2$ ), 72.8 ( $\text{CH}_2$ ), 90.7 (CH), 115.6 (d,  $J_{\text{C-F}} = 22.6$  Hz, CH), 129.5 (C), 130.5 (d,  $J_{\text{C-F}} = 8.4$  Hz, CH), 164.5 (d,  $J_{\text{C-F}} = 253$  Hz, C), 166.9 (C). HRMS (ESI<sup>+</sup>)  $m/z$  278.1007 ( $\text{M}+\text{H}^+$ ), calcd for  $\text{C}_{15}\text{H}_{17}\text{FNOS}$ : 278.1009.

**5-(4-Fluorophenyl)-4-(3-methylbut-2-enyloxy)methylisothiazole (6b)**

Colorless oil. IR (KBr) 3065, 2914, 2861, 1672, 1605, 1497, 1224, 1159, 1064, 882, 844  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.67 (s, 3H), 1.76 (s, 3H), 4.07 (d,  $J = 6.8$  Hz, 2H), 4.70 (s, 2H), 5.37–5.41 (m, 1H), 7.12–7.18 (m, 2H), 7.66–7.71 (m, 2H), 8.79 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  18.0

(CH<sub>3</sub>), 25.8 (CH<sub>3</sub>), 63.4 (CH<sub>2</sub>), 66.8 (CH<sub>2</sub>), 115.4 (d,  $J_{C-F}$  = 20.6 Hz, CH), 120.2 (CH), 129.9 (C), 130.5 (d,  $J_{C-F}$  = 8.4 Hz, CH), 138.4 (C), 151.7 (CH), 152.6 (C), 162.7 (d,  $J_{C-F}$  = 248 Hz, C). HRMS (ESI<sup>+</sup>)  $m/z$  278.1008 (M+H<sup>+</sup>), calcd for C<sub>15</sub>H<sub>17</sub>FNOS: 278.1009.

**1,3,3a,4-Tetrahydro-6-(4-methoxyphenyl)-4,4-dimethylfuro[3,4-*e*][1,3]thiazepine (4c)**

**3a,4,4a,5-Tetrahydro-2-(4-methoxyphenyl)-4,4-dimethyl-7*H*-furo[3',4':2,3]cyclobuta[1,2-*d*][1,3]thiazole (5c)**

We could isolate neither **4c** nor **5c** due to the rapid decomposition of these compounds during chromatographic purification. The yields shown in Table 2 were estimated from <sup>1</sup>H NMR of the crude mixture by using pyrazine as an internal standard. The assignment of signals was based on the analogy of **4a** and **5a**.

**5-(4-Methoxyphenyl)-4-(3-methylbut-2-enyloxy)methylisothiazole (6c)**

Faintly yellow oil. IR (KBr) 2972, 2914, 2858, 1605, 1497, 1224, 1158, 1064, 844 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.67 (s, 3H), 1.76 (s, 3H), 3.86 (s, 3H), 4.07 (d,  $J$  = 6.7 Hz, 2H), 4.71 (s, 2H), 5.38–5.41 (m, 1H), 6.97–7.00 (m, 2H), 7.62–7.66 (m, 2H), 8.78 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 18.0 (CH<sub>3</sub>), 25.8 (CH<sub>3</sub>), 55.3 (CH<sub>3</sub>), 63.7 (CH<sub>2</sub>), 66.8 (CH<sub>2</sub>), 113.9 (CH), 120.3 (CH), 127.0 (C), 128.9 (C), 130.0 (CH), 138.2 (C), 151.5 (CH), 153.3 (C), 159.5 (C). HRMS (ESI<sup>+</sup>)  $m/z$  290.1208 (M+H<sup>+</sup>), calcd for C<sub>16</sub>H<sub>20</sub>NO<sub>2</sub>S: 290.1209.

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