# Allylation of Azoles with Allyltributyltin *via* Unstable *N*-(Alkoxycarbonyl)azolium Salts

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The one-pot reactions of imidazoles with allyltributyltin in the presence of alkyl chloroformates gave 2-allyl-1,3-bis(alkoxycarbonyl)-4-imidazolines in good yields. The reactions of thiazoles and oxazoles also proceeded in a similar manner. The instability of the intermediary quaternary salts required the nucleophiles to be added simultaneously with the chloroformate. Therefore, the reaction was specific for allyltributyltin, since it doesn't react with the carbonyl group of chloroformates. The dihydro allyl adducts thus obtained were aromatized with potassium ferricyanide under basic conditions to afford the corresponding 2-allylazoles.

Imidazoles and their derivatives are ubiquitous, occurring in drugs,[1] ligands,[2] and natural products.[3] There has also been widespread interest in their chemistry,[4] although many simple imidazoles are not readily available. The 2-lithiated imidazoles have been used for the synthesis of 2-substituted imidazoles,[5] but carbon electrophiles have not been introduced. Nucleophilic reactions of imidazoles with no electron-withdrawing groups have been performed by the activation of imidazole rings by quaternization.[6] The activation by an acyl halide or alkyl chloroformate with base resulted in ring opening,[7] 1,2-diacylation,[8] or dimerization,[9] depending on the reaction conditions. Recently, a Reissert-type reaction of benzimidazole was used to introduce a cyano group at the C-2 position.[10] However, the attempted aromatization resulted in retro-Reissert reaction, which gave only starting material.[11] In the last few years, we have been studying the reactivities of heteroaromatic quaternary salts toward nucleophiles,[12] and we have focused on the lability of 1,3-bis(alkoxycarbonyl)imidazolium salts, which react with imidazoles to afford dimeric compounds. The difficulty of the isolation prompted us to trap them *in situ*. Tin reagents were thought to be logical candidates because they don't react with carbonyl groups in the absence of a Lewis acid.[13] The use of a tin reagent resulted in one-pot syntheses of 2-allyl-1,3-bis(alkoxycarbonyl)-4-imidazolines in good yields.[14] Moreover, the adducts thus obtained could be aromatized under basic conditions to afford 2-allylimidazoles, which are rarely synthesized by other methods. The above procedure was applied to thiazoles and oxazoles, and satisfactory results were obtained. This paper describes these results.

## Results and Discussion

**Reactions of Imidazoles with Allyltributyltin in the Presence of Alkyl Chloroformate.** Imidazole **1a** dimerized to triethyl 2,2′-bis-1*H*-imidazole-1,1′,3(2*H*)-tricarboxylate (**3a**) in the presence of ethyl chloroformate and triethylamine. When ethyl chloroformate was added dropwise to a mixture of imidazole, allyltributyltin, and triethylamine, 2-allyl-1,3-bis(ethoxycarbonyl)-4-imidazoline (**2a**) was obtained in 96% yield (Scheme 1). The application of the latter reaction conditions to imidazoles **1a–c** (Scheme 2) gave imidazolines **2a–2c′** (see Table 1, entries 1–8). Generally, the nature of the alkyl group of the chloroformate had little effect on the yield of **2**.[15]

Next, benzimidazoles **4a–g** were allowed to react under the same conditions, and the results are summarized in Scheme 3 and Table 2 (entries 1–12). The reaction rates for the benzimidazoles were slower than those of the imidazoles (Table 1), but the yields were good for substrates **4a–d**. Although electron-withdrawing substituents on the benzo ring lowered the yields (entries 7, 9, and 11), the use of a more electron-deficient chloroformate improved them (entries 8, 10, and 12).

**Reactions of Thiazoles and Oxazoles with Allyltributyltin.** Although the reactions of thiazoles with organometallic reagents have been widely investigated, the substrates have been limited to benzo-fused thiazoles.[16] Moreover, there are few papers that have reported the allylation of thiazole derivatives. It has been shown that allylmagnesium halide reacts with benzothiazole to afford

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(8) Bastiaansen, J. A. M. *Synthesis* **1978**, 633.

(9) Regel, E. *Liebigs Ann. Chem.* **1977**, 159.

(10) (a) Uff, B. C.; Burford, D. L. W.; Ho, Y.-P. *J. Chem. Res. (S)* **1989**, 386. (b) Jois, Y. H. R.; Gibson, H. W. *J. Org. Chem.* **1991**, *56*, 865. (c) Jois, Y. H. R.; Berg, M. A. G.; Merola, J. S.; Gibson, H. W. *Tetrahedron Lett.* **1991**, 2997.

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(15) In most cases, ethyl and 1-chloroethyl chloroformates were used because the former is the most inexpensive and general one and the latter afforded the best results for the aromatization process.

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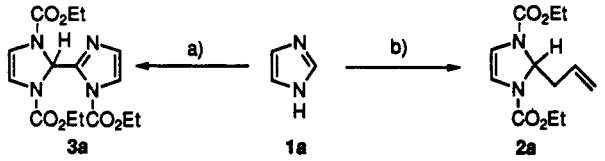
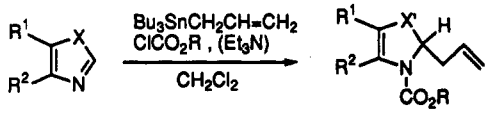
0022-3263/94/1959-1319$04.50/0 

**Scheme 1**[a]




[a] (a) $ClCO_2Et$ (2.4 equiv), $Et_3N$ (1.1 equiv), $CH_2Cl_2$, rt, 20 h; (b) $Bu_3SnCH_2CH{=}CH_2$ (1.2 equiv), $ClCO_2Et$ (2.4 equiv), $Et_3N$ (1.1 equiv), $CH_2Cl_2$, 0 °C, 1 h.

**Scheme 2**




1 X=NH, S, O 2 X'= $NCO_2R$, S, O

ring-opened products,[17] whereas 2-alkylbenzothiazole gives 2,2-diallylbenzothiazolines.[18] 2-Allyl derivatives are also obtained when 2-halobenzothiazoles are allowed to react with allyl Grignard reagents.[19] Thiazolium salts have attracted much attention because of the relationship to the reactivity of the thiamine active site.[20] They have highly acidic C-2 protons, and therefore, their reactions with carbanions have been limited to those of 2-methylbenzothiazolium salts with organometallics.[21]

Because thiazoles don't form stable quaternary salts with chloroformate,[22] we expected that our procedure would be successful for thiazoles. The reaction conditions described above were applied to thiazoles **1d–g** and oxazole **1h**. At first, thiazoles **1d–g** were allowed to react with allyltributyltin in the presence of alkyl chloroformate to afford 2-allyl-1-(alkoxycarbonyl)-4-thiazolines **2d–g′** (Table 1, entries 9–16). The reaction was also applied to oxazole **1h** to give 2-allyl-4-oxazoline **2h′**, although the weak basicity of **1h** required that 1-chloroethyl chloroformate be used to form the quaternary salt (Table 1, entries 17 and 18). Benzothiazoles **4h–j** and benzoxazole **4k** also underwent the reaction in the same manner to afford the corresponding products **5h–j** and **5k** (Table 2, entries 13–21).

**Aromatization of the Dihydro Adducts.** To the best of our knowledge, the synthesis of monocyclic 2-allylimidazole has been reported in only one paper.[23] Since the method involves the thermal rearrangement of 1-allylimidazole at 530 °C to give a mixture of 2- and 4-allylimidazole, it cannot be regarded as a general one. Our facile synthesis of imidazolines **2** prompted us to attempt the synthesis of allylimidazoles. We found that **2a′** was readily aromatized to 2-allylimidazole **6a** in 78% yield with basic aqueous potassium ferricyanide under reflux for 1 h. Under the same conditions, however, benzimidazoline **5a′** afforded 2-(1-propenyl)benzimidazole **8a**, probably through thermal isomerization of 2-allylbenzimidazole **7a**.[24] The conversion of **5a′** to **7a** was achieved in 74% yield with excess reagents at room temperature. Compound **7a** thus obtained was easily isomerized to **8a** on heating. The thermal instability of **7** suggests that this method is superior to others that have been reported.[22,23] The reaction was thought to proceed by the initial hydrolysis of the carbamate followed by oxidation of the unstable 2-allyl-4-imidazoline. Similar conditions caused aromatization to occur in the case of thiazoline derivatives but resulted in decomposition of oxazoline. When benzothiazoline **5h′** was a substrate, 2-allylbenzothiazoline **9h** was isolated as an intermediate. The results are summarized in Scheme 4 and Table 3.

The reaction scheme is shown with imidazole **1a** as an example (Scheme 5). First, imidazole **1** is transformed to bis(alkoxycarbonyl)imidazolium salt **10**, which, in the absence of tin reagent, reacts with a second imidazole to afford dimer **3**. In the presence of allyltributyltin, quaternary salt **10** is effectively trapped by allyltributyltin to form **2**. The aromatization is believed to proceed *via* initial hydrolysis of the ester to give an allylimidazoline, which is oxidized by potassium ferricyanide to allylimidazole. In the case of thiazoline **5h**, the assumption that the hydrolysis occurs first is supported by the fact that 2-allylbenzothiazoline **9h** was isolated.

In conclusion, allyltributyltin has been shown to trap unstable (alkoxycarbonyl)azolium salts to give allyl adducts, which can be aromatized to allylheteroazoles. The application of this process to other tin reagents and heteroaromatics is now in progress.

## Experimental Section

Melting points are uncorrected. $^1H$- and $^{13}C$-NMR spectra were recorded at 400 and 100 MHz, respectively, with TMS as an internal standard. Mass spectra and high-resolution mass spectra (HRMS) were measured at 70 eV.

**General Procedure for the Reaction of Imidazoles 1a–c, 4a–g with Allyltributyltin.** An imidazole (10 mmol), allyltributyltin (12 mmol), and triethylamine (11 mmol) were dissolved in 40 mL of $CH_2Cl_2$, and the mixture was cooled in an ice bath. 1-Chloroethyl chloroformate (24 mmol) was added dropwise to the mixture, and the solution was allowed to stir at 0 °C for 1 h to 3 d depending on the reaction rate. The reaction mixture was treated with 1 M KF (30 mL) and ether (100 mL), and the precipitate thus formed was removed by filtration. The filtrate was dried over $MgSO_4$ and evaporated to leave a residue, which was chromatographed on silica gel to afford a 2-allyl-1,3-bis[(1-chloroethoxy)carbonyl]-4-imidazoline.

**Reactions of Thiazoles and Oxazoles with Allyltributyltin.** The procedure was similar to that described above, except that triethylamine was omitted and only 12 mmol of alkyl chloroformate was required for complete reaction. All allyl adducts were obtained as mixtures of conformational isomers. Thus, the NMR spectra of the *N*-ethoxycarbonyl derivatives were measured in DMSO at 80 °C so that the conformers freely interconverted, and this procedure resulted in simplified data. *N*-[(1-Chloroethoxy)carbonyl]azolium salts, however, decomposed on heating to *N*-(1-methyl-3-butenyl) derivatives;[25] therefore, the spectra of these compounds were measured at rt as mixtures of conformational isomers.

**2-Allyl-1,3-bis(ethoxycarbonyl)-4-imidazoline (2a)**: colorless oil; $^1H$ NMR (DMSO-$d_6$, 80 °C) $\delta$ 1.23 (6H, t, $J$ = 7.0 Hz),

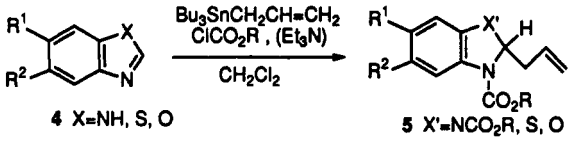
(17) Babudri, F.; Bartoli, G.; Ciminale, F.; Florio, S.; Ingrosso, G. *Tetrahedron Lett.* **1984**, 2047.
(18) Babudri, F.; Florio, S.; Inguscio, G. *Synthesis* **1985**, 522.
(19) Florio, S.; Epifani, E.; Ingrosso, G. *Tetrahedron* **1984**, *40*, 4527.
(20) Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1991**, *113*, 985, and references cited therein.
(21) Akiba, K.; Ohara, Y.; Hisaoka, M.; Inamoto, N. *Heterocycles* **1975**, *3*, 567.
(22) Dondoni, A.; Dall'Occo, T.; Fantin, G.; Fogagnolo, M.; Medici, A. *Tetrahedron Lett.* **1992**, 5399.
(23) Begg, C. G.; Grimmett, M. R.; Wethey, P. D. *Aust. J. Chem.* **1973**, *26*, 2435.

(24) It was reported that 2-allylbenzimidazole **7a** was obtained in 23% yield from the condensation of *o*-phenylenediamine and vinylacetic acid in refluxing 4 N HCl for 1 h. The authors claimed that **7a** isomerized to **8a** in refluxing benzene, but not under the above conditions. See, Raines, S.; Kovacs, C. A. *J. Heterocycl. Chem.* **1967**, *4*, 305.
(25) For example, compound **5h** was transformed quantiatively to 3-(1-methyl-3-butenyl)benzothiazolium salt in chloroform when heated at 70 °C for 1 h. Imidazoline **2a′** gave 1-(1-methyl-3-butenyl)imidazole in a quantative yield under the same conditions.

**Table 1. Reactions of Azoles with Allyltributyltin in the Presence of Alkyl Chloroformate**

| entry | substrate | X | X′ | $R^1$ | $R^2$ | R | conditions | product | yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1a | NH | $NCO_2R$ | H | H | Et | 0 °C, 1 h | 2a | 96 |
| 2 | 1a | NH | $NCO_2R$ | H | H | CHClMe | 0 °C, 2 h | 2a′ | 80 |
| 3 | 1a | NH | $NCO_2R$ | H | H | $CH_2CCl_3$ | 0 °C, 1 h | 2a″ | 78 |
| 4 | 1a | NH | $NCO_2R$ | H | H | Me | 0 °C, 1.5 h | 2a‴ | 63 |
| 5 | 1b | NH | $NCO_2R$ | Me | H | Et | 0 °C, 1.5 h | 2b | 90 |
| 6 | 1b | NH | $NCO_2R$ | Me | H | CHClMe | 0 °C, 2 h | 2b′ | 82 |
| 7 | 1c | NH | $NCO_2R$ | Me | Me | Et | 0 °C, 2 h | 2c | 69 |
| 8 | 1c | NH | $NCO_2R$ | Me | Me | CHClMe | 0 °C, 1.5 h | 2c′ | 77 |
| 9 | 1d | S | S | H | H | Et | 0 °C, 3 h to rt, 2 h | 2d | 61 |
| 10 | 1d | S | S | H | H | CHClMe | 0 °C, 2 h | 2d′ | 81 |
| 11 | 1e | S | S | H | Me | Et | rt, 6 h | 2e | 33 |
| 12 | 1e | S | S | H | Me | CHClMe | 0 °C, 2 h | 2e′ | 87 |
| 13 | 1f | S | S | Me | H | Et | rt, 3 h | 2f | 63 |
| 14 | 1f | S | S | Me | H | CHClMe | 0 °C, 2 h | 2f′ | 78 |
| 15 | 1g | S | S | Me | Me | Et | rt, 3 h | 2g | 54 |
| 16 | 1g | S | S | Me | Me | CHClMe | 0 °C, 2 h | 2g′ | 77 |
| 17 | 1h | O | O | H | H | Et | rt, 24 h | 2h | 0 |
| 18 | 1h | O | O | H | H | CHClMe | rt, 4 h | 2h′ | 75 |

**Scheme 3**




4 X=NH, S, O

5 X'=$NCO_2R$, S, O

2.62 (2H, dd, $J$ = 3.7 Hz, 7.0 Hz), 4.13 (4H, q, $J$ = 7.0 Hz), 5.03–5.05 (1H, m), 5.08 (1H, s), 5.67–5.78 (1H, m), 5.80 (1H, t, $J$ = 3.7 Hz), 6.24 (2H, s); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 14.3 ($2CH_3$), 36.6 ($CH_2$), 61.5 ($2CH_2$), 72.5 (CH), 113.2 (2CH), 119.0 ($CH_2$), 131.0 (CH), 150.3 (2CO); HRMS $m/z$ ($M^+$, 7%) calcd for $C_{12}H_{18}N_2O_4$ 254.1273, obsd 254.1270; ($M^+$ – allyl, 100%) calcd for $C_9H_{13}N_2O_4$ 213.0814, obsd 213.0844.

**2-Allyl-1,3-bis[(1-chloroethoxy)carbonyl]-4-imidazoline (2a′)**: colorless oil; $^1$H NMR ($CDCl_3$) δ 1.85 (6H, d, $J$ = 5.9 Hz), 2.70–2.86 (2H, m), 5.09–5.24 (2H, m), 5.56–6.07 (2H, m), 6.22–6.41 (2H, m), 6.62 (2H, q, $J$ = 5.9 Hz). The $^{13}$C NMR spectrum was recorded on a mixture of at least four conformers; $^{13}$C NMR ($CDCl_3$) δ 25.3 (2 peaks), 25.4 ($CH_3$), 35.1, 35.2, 36.7, 36.8 ($CH_2$), 73.1, 73.2, 73.3, 73.7 (CH), 82.8, 82.9 (2CH), 113.0, 113.6, 113.9 (2CH), 120.4, 120.9 ($CH_2$), 129.2, 129.5, 129.7 (CH), 147.5, 147.6, 147.8 (2CO); HRMS $m/z$ ($M^+$, 8%) calcd for $C_{12}H_{16}Cl_2N_2O_4$ 322.0487, obsd 322.0503; ($M^+$ – allyl, 100%) calcd for $C_9H_{11}Cl_2N_2O_4$ 281.0100, obsd 281.0124.

**2-Allyl-1,3-bis[(2,2,2-trichloroethoxy)carbonyl]-4-imidazoline (2a″)**: colorless needles from EtOH; mp 98–98.5 °C; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 2.77 (2H, dd, $J$ = 3.4 Hz, 7.3 Hz), 4.91 (4H, bs), 5.10 (1H, s), 5.14 (1H, d, $J$ = 5.4 Hz), 5.70–5.80 (1H, m), 5.98 (1H, bs), 6.41 (2H, s); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 35.9 ($CH_2$), 73.0 (CH), 74.5 ($2CH_2$), 95.5 ($2CCl_3$), 113.9 (2CH), 119.9 ($CH_2$), 130.0 (CH), 148.2 (2CO). Anal. Calcd for $C_{12}H_{12}Cl_6N_2O_4$: C, 31.26; H, 2.62; N, 6.07. Found: C, 31.21; H, 2.52; N, 6.09.

**2-Allyl-1,3-bis(methoxycarbonyl)-4-imidazoline (2a‴)**: colorless needles from hexane; mp 45.5–46 °C; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 2.61 (2H, dd, $J$ = 3.7 Hz, 7.0 Hz), 3.69 (6H, s), 5.04 (1H, d, $J$ = 4.4 Hz), 5.07 (1H, s), 5.66–5.77 (1H, m), 5.80 (1H, t, $J$ = 3.7 Hz), 6.24 (2H, s); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 36.5 ($CH_2$), 52.6 ($2CH_3$), 72.6 (CH), 113.2 (2CH), 119.0 ($CH_2$), 130.9 (CH), 150.8 (2CO). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.71; H, 6.19; N, 12.36.

**2-Allyl-1,3-bis(ethoxycarbonyl)-4-methyl-4-imidazoline (2b)**: colorless oil; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 1.21 (3H, t, $J$ = 6.8 Hz), 1.23 (3H, t, $J$ = 6.8 Hz), 2.01 (3H, d, $J$ = 1.5 Hz), 2.52–2.54 (2H, m), 4.12 (2H, q, $J$ = 6.8 Hz), 4.13 (2H, q, $J$ = 6.8 Hz), 5.02–5.04 (1H, m), 5.06 (1H, bs), 5.67–5.77 (1H, m), 5.80 (1H, t, $J$ = 3.9 Hz), 6.11 (1H, d, $J$ = 1.5 Hz); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 12.3 ($CH_3$), 14.2 ($CH_3$), 14.3 ($CH_3$), 37.1 ($CH_2$), 61.2 ($2CH_2$), 73.7 (CH), 111.0 (CH), 118.6 ($CH_2$), 123.3 (C), 131.3 (CH), 150.1 (CO), 151.3 (CO); HRMS $m/z$ ($M^+$, 8%) calcd for $C_{13}H_{20}N_2O_4$ 268.1415, obsd 268.1418; ($M^+$ – allyl, 100%) calcd for $C_{10}H_{15}N_2O_4$ 227.1029, obsd 227.1021.

**2-Allyl-1,3-bis[(1-chloroethoxy)carbonyl]-4-methyl-4-imidazoline (2b′)**: colorless viscous oil; $^1$H NMR ($CDCl_3$) δ 1.84 (6H, d, $J$ = 5.7 Hz), 2.10 (3H, s), 2.64 (2H, bs), 5.05–5.22 (2H, m), 5.51–6.03 (3H, m), 6.58 (2H, q, $J$ = 5.7 Hz). The $^{13}$C NMR spectrum was recorded on a mixture of four conformers: $^{13}$C NMR ($CDCl_3$) δ 12.3, 13.4 ($CH_3$), 25.2, 25.3 ($2CH_3$), 37.1, 38.3 ($CH_2$), 74.2 (CH), 82.6, 82.8, 82.9 (2CH), 111.1, 111.8 (CH), 119.8, 119.9, 120.1, 120.3 ($CH_2$), 125.2 (C), 129.6, 129.8, 130.1 (CH), 147.3, 147.4 (2CO). HRMS $m/z$ ($M^+$, 10%) calcd for $C_{13}H_{18}Cl_2N_2O_4$ 336.0641, obsd 336.0638; ($M^+$ – allyl, 100%) calcd for $C_{10}H_{13}Cl_2N_2O_4$ 295.0250, obsd 295.0232.

**2-Allyl-1,3-bis(ethoxycarbonyl)-4,5-dimethyl-4-imidazoline (2c)**: colorless oil; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 1.22 (6H, t, $J$ = 7.0 Hz), 1.96 (6H, s), 2.40 (2H, dd, $J$ = 4.4 Hz, 7.3 Hz), 4.11 (4H, q, $J$ = 7.0 Hz), 5.00 (1H, bs), 5.03–5.05 (1H, m), 5.62–5.73 (1H, m), 5.77 (1H, t, $J$ = 4.4 Hz); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 11.2 ($2CH_3$), 14.2 ($2CH_3$), 37.8 ($CH_2$), 61.1 ($2CH_2$), 73.5 (CH), 118.1 ($CH_2$), 119.5 (2C), 131.5 (CH), 151.5 (2CO); HRMS $m/z$ ($M^+$, 11%) calcd for $C_{14}H_{22}N_2O_4$ 282.1577, obsd 282.1577; ($M^+$ – allyl, 100%) calcd for $C_{11}H_{17}N_2O_4$ 241.1189, obsd 241.1192.

**2-Allyl-1,3-bis[(1-chloroethoxy)carbonyl]-4,5-dimethyl-4-imidazoline (2c′)**: colorless viscous oil; $^1$H NMR ($CDCl_3$) δ 1.84 (6H, d, $J$ = 5.9 Hz), 2.05 (6H, s), 2.56 (2H, bs), 5.02–5.23 (2H, m), 5.49–5.98 (2H, m), 6.60 (2H, q, $J$ = 5.9 Hz). The $^{13}$C NMR spectrum was recorded on a mixture of two conformers: $^{13}$C NMR ($CDCl_3$) δ 11.2, 12.1 ($2CH_3$), 25.3, 25.4 ($2CH_3$), 37.5, 38.0 ($CH_2$), 74.0 (CH), 82.6 (2CH), 119.3, 119.5 ($CH_2$), 121.2 (2C), 130.0, 130.2 (CH), 148.2, 149.1 (2CO); HRMS $m/z$ ($M^+$, 12%) calcd for $C_{14}H_{20}Cl_2N_2O_4$ 350.0779, obsd 350.0779; ($M^+$ – allyl, 100%) calcd for $C_{11}H_{15}Cl_2N_2O_4$ 309.0372, obsd 309.0389.

**2-Allyl-3-(ethoxycarbonyl)-4-thiazoline (2d)**: colorless oil; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 1.23 (3H, t, $J$ = 7.0 Hz), 2.46–2.56 (2H, m), 4.15 (2H, q, $J$ = 7.0 Hz), 5.07–5.10 (1H, m), 5.11–5.13 (1H, m), 5.59 (1H, dd, $J$ = 4.6 Hz, 7.0 Hz), 5.75 (1H, d, $J$ = 4.6 Hz), 5.73–5.84 (1H, m), 6.41 (1H, d, $J$ = 4.6 Hz); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 14.2 ($CH_3$), 40.8 ($CH_2$), 61.7 ($CH_2$), 63.8 (CH), 103.8 (CH), 118.6 ($CH_2$), 121.5 (CH), 132.4 (CH), 152.0 (CO). HRMS $m/z$ ($M^+$, 45%) calcd for $C_9H_{13}NO_2S$ 199.0665, obsd 199.0654; ($M^+$ – allyl, 100%) calcd for $C_6H_8NO_2S$ 158.0276, obsd 158.0284.

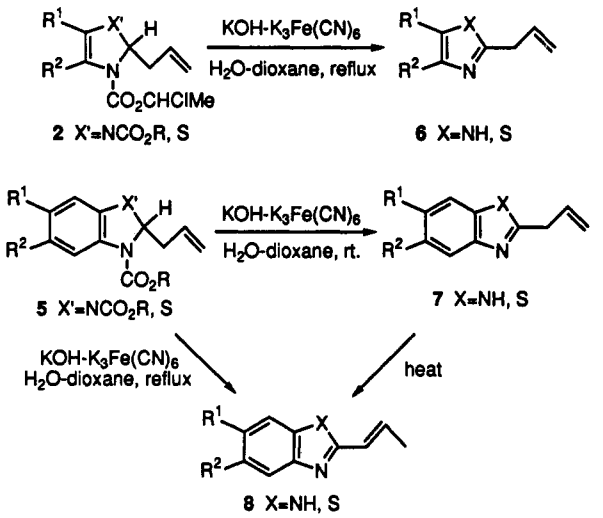
**2-Allyl-3-[(1-chloroethoxy)carbonyl]-4-thiazoline (2d′)**: colorless oil; $^1$H NMR ($CDCl_3$) δ 1.85 (3H, d, $J$ = 5.9 Hz), 2.62 (2H, t, $J$ = 6.6 Hz), 5.10–5.23 (2H, m), 5.44–6.02 (3H, m), 6.36–6.66 (2H, m). The $^{13}$C NMR spectrum was recorded on a mixture of four conformers: $^{13}$C NMR ($CDCl_3$) δ 25.3 (2 peaks), 25.4, 25.5 ($CH_3$), 40.5, 40.7, 41.8 ($CH_2$), 63.7 (2 peaks), 64.9, 65.0 (CH), 82.9 (2 peaks), 83.0 (CH), 105.5, 105.8 (CH), 119.5, 119.6, 119.7, 119.9 ($CH_2$), 120.2 (2 peaks), 121.3, 121.5 (CH), 131.4, 131.5, 131.6, 131.7 (CH), 149.6, 149.7, 149.9 (CO); HRMS $m/z$ ($M^+$, 40%) calcd for $C_9H_{12}ClNO_2S$ 233.0275, obsd 233.0269; ($M^+$ – allyl, 100%) calcd for $C_6H_7ClNO_2S$ 191.9887, obsd 191.9888.

**2-Allyl-3-(ethoxycarbonyl)-4-methyl-4-thiazoline (2e)**: colorless oil; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 1.23 (3H, t, $J$ = 7.3 Hz), 2.06 (3H, d, $J$ = 1.4 Hz), 2.46–2.49 (2H, m), 4.13 (2H, q, $J$ = 7.3 Hz), 5.06–5.11 (2H, m), 5.53 (1H, d, $J$ = 1.4 Hz), 5.60 (1H, t, $J$ = 5.6 Hz), 5.72–5.81 (1H, m); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 14.1 ($CH_3$), 16.2 ($CH_3$), 41.2 ($CH_2$), 61.4 ($CH_2$), 65.7 (CH), 102.9 (CH), 118.2 ($CH_2$), 131.4 (C), 132.6 (CH), 152.9 (CO). HRMS $m/z$ ($M^+$,

**Table 2. Reactions of Benzo-Fused Azoles with Allyltributyltin in the Presence of Alkyl Chloroformate**

| entry | substrate | X | X′ | $R^1$ | $R^2$ | R | conditions | product | yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **4a** | NH | $NCO_2R$ | H | H | Et | rt, 3 h | **5a** | 70 |
| 2 | **4a** | NH | $NCO_2R$ | H | H | CHClMe | 0 °C to rt, 2 h | **5a′** | 69 |
| 3 | **4b** | NH | $NCO_2R$ | Me | H | Et | rt, 3 h | **5b** | 83 |
| 4 | **4c** | NH | $NCO_2R$ | Me | Me | Et | rt, 15 h | **5c** | 84 |
| 5 | **4c** | NH | $NCO_2R$ | Me | Me | CHClMe | 0 °C to rt, 3 h | **5c′** | 96 |
| 6 | **4d** | NH | $NCO_2R$ | OMe | H | Et | rt, 15 h | **5d** | 81 |
| 7 | **4e** | NH | $NCO_2R$ | Cl | H | Et | rt, 3 days | **5e** | 39 |
| 8 | **4e** | NH | $NCO_2R$ | Cl | H | CHClMe | 0 °C to rt, 2 h | **5e′** | 94 |
| 9 | **4f** | NH | $NCO_2R$ | $CO_2Me$ | H | Et | rt, 3 days | **5f** | 0 |
| 10 | **4f** | NH | $NCO_2R$ | $CO_2Me$ | H | CHClMe | 0 °C to rt, 2 h | **5f′** | 73 |
| 11 | **4g** | NH | $NCO_2R$ | $NO_2$ | H | Et | rt, 3 days | **5g** | 0 |
| 12 | **4g** | NH | $NCO_2R$ | $NO_2$ | H | CHClMe | 0 °C to rt, 7 h | **5g′** | 87 |
| 13 | **4h** | S | S | H | H | Et | rt, 3.5 h | **5h** | 81 |
| 14 | **4h** | S | S | H | H | CHClMe | 0 °C, 1.5 h | **5h′** | 86 |
| 15 | **4i** | S | S | OMe | H | Et | rt, 20 h | **5i** | 88 |
| 16 | **4i** | S | S | OMe | H | CHClMe | 0 °C, 3 h | **5i′** | 91 |
| 17 | **4j** | S | S | $NO_2$ | H | Et | rt, 20 h | **5j** | 23 |
| 18 | **4j** | S | S | $NO_2$ | H | CHClMe | rt, 3 h | **5j′** | 85 |
| 19 | **4k** | O | O | H | H | Et | rt, 6 days | **5k** | 52 |
| 20 | **4k** | O | O | H | H | CHClMe | rt, 36 h | **5k′** | 92 |
| 21 | **4k** | O | O | H | H | $CH_2CCl_3$ | rt, 24 h | **5k″** | 82 |

**Scheme 4**




**Scheme 5**

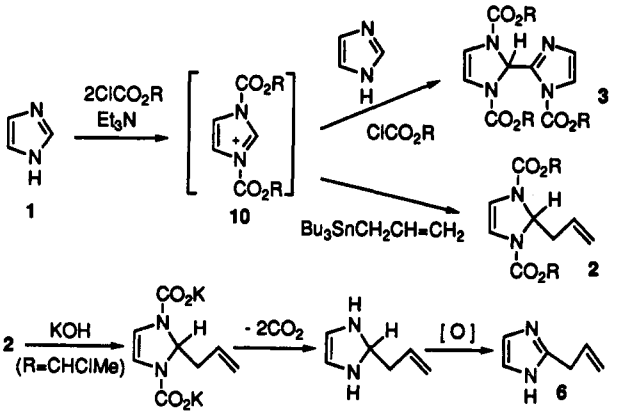



**Table 3. Aromatization of Allyl Adducts 2′ and 5′**

| entry | substrate | conditions | yield of 6 or 7 (%) |
|---|---|---|---|
| 1 | **2a′** | KOH (3 equiv), $K_3Fe(CN)_6$ (6 equiv), $H_2O$–dioxane, reflux, 1 h | 78 (**6a**) |
| 2 | **2b′** | *a* | 57 (**6b**) |
| 3 | **2c′** | *a* | 42 (**6c**) |
| 4 | **2f′** | KOH (1.5 equiv), $K_3Fe(CN)_6$ (3 equiv), $H_2O$–THF, reflux, 3 h | 60 (**6f**) |
| 5 | **5a′** | KOH (16 equiv), $K_3Fe(CN)_6$ (12 equiv), $H_2O$–dioxane, rt, 5 days | 74 (**7a**) |
| 6 | **5h′** | KOH (1.5 equiv), $K_3Fe(CN)_6$ (3 equiv), $H_2O$–dioxane, reflux, 3 h | 61 (**7h**) |

[a] Same as above.

35%) calcd for $C_{10}H_{15}NO_2S$ 213.0824, obsd 213.0832; ($M^+$ – allyl, 100%) calcd for $C_7H_{10}NO_2S$ 172.0433, obsd 172.0455.

**2-Allyl-3-[(1-chloroethoxy)carbonyl]-4-methyl-4-thiazoline (2e′)**: colorless oil; $^1H$ NMR ($CDCl_3$) $\delta$ 1.84 (3H, d, $J$ = 5.7 Hz), 2.15 (3H, d, $J$ = 0.9 Hz), 2.54 (2H, t, $J$ = 6.6 Hz), 5.06–5.33 (3H, m), 5.60–5.97 (2H, m), 6.58 (1H, q, $J$ = 5.7 Hz). The $^{13}C$ NMR spectrum was recorded on a mixture of three conformers: $^{13}C$ NMR ($CDCl_3$) $\delta$ 16.6 ($CH_3$), 25.3 (2 peaks), 25.40 ($CH_3$), 41.3, 41.4, 41.6 ($CH_2$), 65.6, 66.5 (CH), 82.7, 82.9 (CH), 103.4, 104.0, 104.6 (CH), 119.1, 119.2 ($CH_2$), 131.9 (2 peaks) (CH), 132.3, 132.4 (C), 150.3, 150.4 (CO); HRMS $m/z$ ($M^+$, 49%) calcd for $C_{10}H_{14}ClNO_2S$ 247.0431, obsd 247.0435; ($M^+$ – allyl, 100%) calcd for $C_7H_9ClNO_2S$ 206.0043, obsd 206.0068.

**2-Allyl-3-(ethoxycarbonyl)-5-methyl-4-thiazoline (2f)**: colorless oil; $^1H$ NMR (DMSO-$d_6$, 80 °C) $\delta$ 1.22 (3H, t, $J$ = 7.3 Hz), 1.86 (3H, d, $J$ = 1.5 Hz), 2.48–2.55 (2H, m), 4.13 (2H, q, $J$ = 7.3 Hz), 5.07–5.12 (2H, m), 5.55 (1H, dd, $J$ = 4.9 Hz, 6.8 Hz), 5.73–5.83 (1H, m), 6.21 (1H, d, $J$ = 1.5 Hz); $^{13}C$ NMR (DMSO-$d_6$, 80 °C) $\delta$ 13.0 ($CH_3$), 14.3 ($CH_3$), 41.1 ($CH_2$), 61.5 ($CH_2$), 64.8 (CH), 115.5 (C), 117.2 (CH), 118.5 ($CH_2$), 132.5 (CH), 151.9 (CO); HRMS $m/z$ ($M^+$, 23%) calcd for $C_{10}H_{15}NO_2S$ 213.0824, obsd 213.0833; ($M^+$ – allyl, 100%) calcd for $C_7H_{10}NO_2S$ 172.0433, obsd 172.0458.

**2-Allyl-3-[(1-chloroethoxy)carbonyl]-5-methyl-4-thiazoline (2f′)**: colorless oil; $^1H$ NMR ($CDCl_3$) $\delta$ 1.73 (3H, d, $J$ = 5.7 Hz), 1.91 (3H, d, $J$ = 1.3 Hz), 2.61 (2H, t, $J$ = 6.6 Hz), 5.07–5.29 (2H, m), 5.37–5.96 (2H, m), 6.13–6.20 (1H, m), 6.56 (1H, q, $J$ = 5.7 Hz). The $^{13}C$ NMR spectrum was recorded on a mixture of four conformers: $^{13}C$ NMR ($CDCl_3$) $\delta$ 13.6, 13.7 ($CH_3$), 25.3, 25.4 (2 peaks), 25.5 ($CH_3$), 40.8, 40.9, 42.0, 42.1 ($CH_2$), 64.5, 64.6, 65.7, 65.9 (CH), 82.8, 82.9, 83.0 (2 peaks) (CH), 115.6, 115.8, 116.7, 116.9 (CH), 118.1, 118.3 (C), 119.3, 119.4, 119.5, 119.7 ($CH_2$), 131.6, 131.7, 131.8, 131.9 (CH), 149.5 (2 peaks), 149.6 (CO); HRMS $m/z$ ($M^+$, 37%) calcd for $C_{10}H_{14}ClNO_2S$ 247.0431, obsd 247.0428; ($M^+$ – allyl, 100%) calcd for $C_7H_9ClNO_2S$ 206.0043, obsd 206.0071.

**2-Allyl-3-(ethoxycarbonyl)-4,5-dimethyl-4-thiazoline (2g)**: colorless oil; $^1H$ NMR (DMSO-$d_6$, 80 °C) $\delta$ 1.22 (3H, t, $J$ = 7.3 Hz), 1.82 (3H, s), 1.98 (3H, s), 2.40–2.43 (2H, m), 4.12 (2H, q, $J$ = 7.3 Hz), 5.05 (1H, bs), 5.07–5.09 (1H, m), 5.49 (1H, t, $J$ = 5.9 Hz), 5.67–5.78 (1H, m); $^{13}C$ NMR (DMSO-$d_6$, 80 °C) $\delta$ 12.8 ($CH_3$), 13.6 ($CH_3$), 14.2 ($CH_3$), 41.5 ($CH_2$), 61.3 ($CH_2$), 64.1 (CH), 113.1 (C), 118.0 (CH), 124.6 (C), 132.8 (CH), 153.2 (CO); HRMS $m/z$ ($M^+$, 28%) calcd for $C_{11}H_{17}NO_2S$ 227.0980, obsd 227.0987; ($M^+$ – allyl, 100%) calcd for $C_8H_{12}NO_2S$ 186.0588, obsd 186.0603.

**2-Allyl-3-[(1-chloroethoxy)carbonyl]-4,5-dimethyl-4-thiazoline (2g′)**: colorless oil; $^1H$ NMR ($CDCl_3$) $\delta$ 1.83 (3H, d, $J$ = 5.7 Hz), 1.83 (3H, s), 2.06 (3H, s), 2.49 (2H, t, $J$ = 6.6 Hz), 5.03–5.20 (2H, m), 5.38–5.93 (2H, m), 6.58 (1H, q, $J$ = 5.7 Hz). The $^{13}C$ NMR spectrum was recorded on a mixture of two conform-

ers: $^{13}C$ NMR ($CDCl_3$) δ 13.3 ($CH_3$), 13.8 ($CH_3$), 25.3, 25.4 ($CH_3$), 41.8 ($CH_2$), 63.7 (CH), 82.8 (CH), 114.1, 114.7 (C), 118.8, 118.9 ($CH_2$), 123.7, 124.7 (C), 132.1 (2 peaks) (CH), 150.3 (CO); HRMS *m/z* ($M^+$, 35%) calcd for $C_{11}H_{16}ClNO_2S$ 261.0591, obsd 261.0599; ($M^+$ – allyl, 100%) calcd for $C_8H_{11}ClNO_2S$ 220.0200, obsd 220.0203.

**2-Allyl-3-[(1-chloroethoxy)carbonyl]-4-oxazoline (2h')**: colorless oil; $^1H$ NMR ($CDCl_3$) δ 1.83 (3H, d, *J* = 5.9 Hz), 2.57–2.67 (2H, m), 5.11–5.27 (2H, m), 5.62–5.98 (2H, m), 6.16–6.23 (2H, m), 6.58 (1H, q, *J* = 5.9 Hz). The $^{13}C$ NMR spectrum was recorded on a mixture of four conformers: $^{13}C$ NMR ($CDCl_3$) δ 25.1, 25.2, 25.3, 25.4 ($CH_3$), 37.6, 37.7, 38.8 ($CH_2$), 82.7 (CH), 91.1 (2 peaks), 91.7, 91.9 (CH), 107.6, 108.0 (CH), 119.4, 119.6, 119.8 ($CH_2$), 130.4, 130.5 (2 peaks) (CH), 133.1, 133.7 (CH), 149.5 (CO); HRMS *m/z* ($M^+$, 38%) calcd for $C_9H_{12}ClNO_3$ 217.0505, obsd 217.0510; ($M^+$ – allyl, 100%) calcd for $C_6H_7ClNO_3$ 176.0113, obsd 176.0103.

**2-Allyl-1,3-bis(ethoxycarbonyl)benzimidazoline (5a)**: colorless plates from isopropyl ether-hexane; mp 73–73.5 °C. $^1H$ NMR (DMSO-$d_6$, 80 °C) δ 1.31 (6H, t, *J* = 7.3 Hz), 2.67 (2H, dd, *J* = 3.9 Hz, 7.3 Hz), 4.27 (4H, q, *J* = 7.3 Hz), 4.94–4.97 (1H, m), 5.01–5.06 (1H, m), 5.53–5.64 (1H, m), 6.10 (1H, t, *J* = 3.9 Hz), 6.95–6.99 (2H, m), 7.50–7.52 (2H, m). $^{13}C$ NMR (DMSO-$d_6$, 80 °C) δ 14.2 ($2CH_3$), 37.6 ($CH_2$), 61.9 ($2CH_2$), 74.5 (CH), 114.0 (2CH), 119.3 ($CH_2$), 123.2 (2CH), 130.7 (CH), 132.2 (2C), 150.8 (2CO). Anal. Calcd for $C_{16}H_{20}N_2O_4$: C, 63.14; H, 6.62; N, 9.21. Found: C, 63.29; H, 6.81; N, 9.27.

**2-Allyl-1,3-bis[(1-chloroethoxy)carbonyl]benzimidazoline (5a')**: colorless plates from isopropyl ether–ethyl acetate; mp 156–157 °C; $^1H$ NMR ($CDCl_3$) δ 1.93 (6H, d, *J* = 5.9 Hz), 2.68–2.81 (2H, m), 4.98–5.20 (2H, m), 5.40–5.80 (1H, m), 6.24 (1H, bs), 6.70 (2H, q, *J* = 5.9 Hz), 7.02–7.11 (2H, m), 7.35–7.77 (2H, m). The $^{13}C$ NMR spectrum was recorded on a mixture of three conformers: $^{13}C$ NMR ($CDCl_3$) δ 25.3, 25.5 ($2CH_3$), 37.7, 38.8 ($CH_2$), 74.5, 75.0 (CH), 82.8 (2CH), 114.6, 114.9, 115.1 (2CH), 121.0 ($CH_2$), 124.3, 124.5, 124.6 (2CH), 129.2 (CH), 131.8, 132.2 (2C), 147.8, 149.3 (2CO). Anal. Calcd for $C_{16}H_{18}Cl_2N_2O_4$: C, 51.49; H, 4.86; N, 7.51. Found: C, 51.49; H, 4.89; N, 7.52.

**2-Allyl-1,3-bis(ethoxycarbonyl)-5-methylbenzimidazoline (5b)**: colorless needles from isopropyl ether–hexane; mp 72.5–73 °C; $^1H$ NMR (DMSO-$d_6$, 80 °C) δ 1.30 (3H, t, *J* = 7.0 Hz), 1.31 (3H, t, *J* = 7.0 Hz), 2.26 (3H, s), 2.67 (2H, dd, *J* = 3.9 Hz, 7.3 Hz), 4.26 (2H, q, *J* = 7.0 Hz), 4.27 (2H, q, *J* = 7.0 Hz), 4.94–4.97 (1H, m), 5.00–5.05 (1H, m), 5.53–5.63 (1H, m), 6.08 (1H, t, *J* = 3.9 Hz), 6.78 (1H, d, *J* = 8.8 Hz), 7.36 (1H, s), 7.37 (1H, d, *J* = 8.8 Hz); $^{13}C$ NMR (DMSO-$d_6$, 80 °C) δ 14.3 ($2CH_3$), 20.9 ($CH_3$), 37.6 ($CH_2$), 61.8 ($CH_2$), 61.9 ($CH_2$), 74.6 (CH), 113.7 (CH), 114.8 (CH), 119.3 ($CH_2$), 123.4 (CH), 130.0 (C), 130.7 (CH), 132.3 (C), 132.4 (C), 150.8 (2CO). Anal. Calcd for $C_{17}H_{22}N_2O_4$: C, 64.13; H, 6.97; N, 8.80. Found: C, 64.41; H, 6.95; N, 8.80.

**2-Allyl-1,3-bis(ethoxycarbonyl)-5,6-dimethylbenzimidazoline (5c)**: colorless needles from ethanol; mp 72.5–73 °C; $^1H$ NMR (DMSO-$d_6$, 80 °C) δ 1.30 (6H, t, *J* = 7.0 Hz), 2.17 (6H, s), 2.66 (2H, dd, *J* = 3.9 Hz, 7.3 Hz), 4.25 (4H, q, *J* = 7.0 Hz), 4.94–4.97 (1H, m), 4.99–5.04 (1H, m), 5.52–5.62 (1H, m), 6.05 (1H, t, *J* = 3.9 Hz), 7.31 (2H, s); $^{13}C$ NMR (DMSO-$d_6$, 80 °C) δ 14.3 ($2CH_3$), 19.3 ($2CH_3$), 37.6 ($CH_2$), 61.7 ($2CH_2$), 74.5 (CH), 115.3 (2CH), 119.2 ($CH_2$), 130.1 (2C), 130.5 (2C), 130.8 (CH), 150.8 (2CO). Anal. Calcd for $C_{18}H_{24}N_2O_4$: C, 65.04; H, 7.28; N, 8.43. Found: C, 65.30; H, 7.33; N, 8.51.

**2-Allyl-1,3-bis[(1-chloroethoxy)carbonyl]-5,6-dimethylbenzimidazoline (5c')**: colorless needles from ethanol; mp 168–169 °C; $^1H$ NMR ($CDCl_3$) δ 1.92 (6H, d, *J* = 5.7 Hz), 2.23 (6H, s), 2.73 (2H, bs), 4.94–5.18 (2H, m), 5.38–5.76 (1H, m), 6.16 (1H, bs), 6.69 (2H, q, *J* = 5.7 Hz), 7.16–7.57 (2H, m). The $^{13}C$ NMR spectrum was recorded on a mixture of four conformers: $^{13}C$ NMR ($CDCl_3$) δ 19.9, 20.2 ($2CH_3$), 25.3, 25.5 ($2CH_3$), 37.7, 38.8 ($CH_2$), 74.4, 74.6, 74.8, 75.0 (CH), 82.6, 82.8, 83.2 (2CH), 115.8, 115.9, 116.2, 116.3 (2CH), 120.3, 120.8 ($CH_2$), 128.6, 129.0 (2C), 129.3, 129.6, 129.7 (CH), 132.3, 132.7, 132.8 (2C), 147.8, 149.1 (2CO). Anal. Calcd for $C_{18}H_{22}Cl_2N_2O_4$: C, 53.87; H, 5.53; N, 6.98. Found: C, 53.84; H, 5.55; N, 7.05.

**2-Allyl-1,3-bis(ethoxycarbonyl)-5-methoxybenzimidazoline (5d)**: colorless, viscous oil; $^1H$ NMR (DMSO-$d_6$, 80 °C) δ 1.30 (3H, t, *J* = 7.0 Hz), 1.31 (3H, t, *J* = 7.0 Hz), 2.67 (2H, dd, *J* = 3.7 Hz, 7.3 Hz), 3.72 (3H, s), 4.25 (2H, q, *J* = 7.0 Hz), 4.26 (2H, q, *J* = 7.0 Hz), 4.95–4.98 (1H, m), 5.01–5.06 (1H, m), 5.54–5.64 (1H, m), 6.08 (1H, t, *J* = 3.7 Hz), 6.54 (1H, dd, *J* = 2.4 Hz, 8.3 Hz), 7.15 (1H, bs), 7.38 (1H, d, *J* = 8.3 Hz); $^{13}C$ NMR (DMSO-$d_6$, 80 °C) δ 14.2 ($CH_3$), 14.3 ($CH_3$), 37.6 ($CH_2$), 55.6 ($CH_3$), 61.7 ($CH_2$), 62.0 ($CH_2$), 74.9 (CH), 101.9 (CH), 107.3 (CH), 114.3 (CH), 119.3 ($CH_2$), 125.9 (C), 130.7 (CH), 133.3 (C), 150.7 (CO), 150.8 (CO), 156.0 (C); HRMS *m/z* ($M^+$, 29%) calcd for $C_{17}H_{22}N_2O_5$ 334.1527, obsd 334.1527; ($M^+$ – allyl, 100%) calcd for $C_{14}H_{17}N_2O_5$ 293.1136, obsd 293.1136.

**2-Allyl-5-chloro-1,3-bis(ethoxycarbonyl)benzimidazoline (5e)**: colorless plates from hexane; mp 80.5–81 °C; $^1H$ NMR (DMSO-$d_6$, 80 °C) δ 1.31 (3H, t, *J* = 7.0 Hz), 1.32 (3H, t, *J* = 7.0 Hz), 2.70 (2H, dd, *J* = 3.4 Hz, 7.3 Hz), 4.27 (2H, q, *J* = 7.0 Hz), 4.30 (2H, q, *J* = 7.0 Hz), 4.97–5.01 (1H, m), 5.02–5.07 (1H, m), 5.54–5.64 (1H, m), 6.13 (1H, t, *J* = 3.4 Hz), 7.01 (1H, dd, *J* = 2.0 Hz, 8.3 Hz), 7.46 (1H, d, *J* = 8.3 Hz), 7.48 (1H, bs); $^{13}C$ NMR (DMSO-$d_6$, 80 °C) δ 14.2 ($2CH_3$), 37.5 ($CH_2$), 62.3 ($CH_2$), 75.3 (CH), 113.8 (CH), 114.7 (CH), 119.7 ($CH_2$), 122.7 (CH), 127.0 (C), 130.4 (CH), 131.5 (C), 133.7 (C), 150.6 (CO), 150.7 (CO). Anal. Calcd for $C_{16}H_{19}ClN_2O_4$: C, 56.72; H, 5.65; N, 8.27. Found: C, 56.77; H, 5.67; N, 8.32.

**2-Allyl-5-chloro-1,3-bis[(1-chloroethoxy)carbonyl]benzimidazoline (5e')**: colorless plates from ethanol; mp 123–123.5 °C; $^1H$ NMR ($CDCl_3$) δ 1.93 (6H, d, *J* = 5.7 Hz), 2.72–2.86 (2H, m), 4.97–5.20 (2H, m), 5.30–5.75 (1H, m), 6.17–6.30 (1H, m), 6.68 (2H, q, *J* = 5.7 Hz), 7.02 (1H, dd, *J* = 1.8 Hz, 8.4 Hz), 7.26–7.79 (2H, m). The $^{13}C$ NMR spectrum was recorded on a mixture of three conformers; $^{13}C$ NMR ($CDCl_3$) δ 25.2, 25.3, 25.4 ($2CH_3$), 37.6, 38.6 ($CH_2$), 75.2, 75.6 (CH), 82.9, 83.1, 83.2 (2CH), 115.0 (2 peaks) (CH), 115.4, 115.5, 115.7 (CH), 121.2 (2 peaks) ($CH_2$), 124.0, 124.2, 124.3 (CH), 128.4, 129.0 (CH), 129.5, 129.7, 129.8 (C), 130.6, 131.1, 131.8 (C), 133.0, 133.4 (C), 147.6, 148.9, 149.0 (2CO). Anal. Calcd for $C_{16}H_{17}Cl_3N_2O_4$: C, 47.14; H, 4.20; N, 6.87. Found: C, 46.88; H, 4.28; N, 6.88.

**2-Allyl-1,3-bis[(1-chloroethoxy)carbonyl]-5-(methoxycarbonyl)benzimidazoline (5f')**: colorless needles from isopropyl ether; mp 106–107 °C; $^1H$ NMR ($CDCl_3$) δ 1.95 (6H, d, *J* = 5.9 Hz), 2.72–2.86 (2H, m), 3.90 (3H, s), 4.98–5.20 (2H, m), 5.38–5.70 (1H, m), 6.26 (1H, bs), 6.70 (2H, q, *J* = 5.9 Hz), 7.82 (1H, bs), 7.84–8.36 (2H, m). The $^{13}C$ NMR spectrum was recorded on a mixture of four conformers: $^{13}C$ NMR ($CDCl_3$) δ 25.2, 25.3, 25.4 ($2CH_3$), 37.6, 38.6, 38.7 ($CH_2$), 52.2 ($CH_3$), 75.4, 75.7 (CH), 82.8, 82.9, 83.3 (2CH), 114.0, 114.1, 114.3 (2 peaks) (CH), 115.4, 116.0 (CH), 121.1, 121.6 ($CH_2$), 126.1, 126.2, 126.5 (C), 127.0, 127.3 (CH), 128.6, 129.0 (CH), 131.0, 132.1, 132.4 (C), 134.6, 135.8, 136.4 (C), 147.8, 149.0 (2CO), 166.3 (CO). Anal. Calcd for $C_{18}H_{20}Cl_2N_2O_6$: C, 50.22; H, 4.69; N, 6.51. Found: C, 50.23; H, 4.58; N, 6.40.

**2-Allyl-1,3-bis[(1-chloroethoxy)carbonyl]-5-nitrobenzimidazoline (5g')**: pale yellow granules from ethanol; mp 88–90 °C; $^1H$ NMR ($CDCl_3$) δ 1.96 (6H, d, *J* = 5.9 Hz), 2.78–2.92 (2H, m), 5.02–5.25 (2H, m), 5.38–5.72 (1H, m), 6.22–6.34 (1H, m), 6.72 (2H, q, *J* = 5.9 Hz), 8.03 (1H, dd, *J* = 2.0 Hz, 8.8 Hz), 7.90–8.59 (2H, m). The $^{13}C$ NMR spectrum was recorded on a mixture of three conformers: $^{13}C$ NMR ($CDCl_3$) δ 25.2, 25.4 ($2CH_3$), 37.5, 38.6 ($CH_2$), 76.0, 76.1 (CH), 82.9, 83.1, 83.5 (2CH), 109.8, 109.9, 110.2 (CH), 113.6, 113.8, 114.1 (CH), 121.0, 121.3 (CH), 121.7, 122.2, 122.6 ($CH_2$), 128.1, 128.5 (CH), 131.6, 132.8 (C), 137.3, 137.5 (C), 144.2, 144.4 (C), 147.8, 148.6 (2CO). Anal. Calcd for $C_{16}H_{17}Cl_2N_3O_6$: C, 45.94; H, 4.09; N, 10.04. Found: C, 45.56; H, 4.03; N, 9.93.

**2-Allyl-3-(ethoxycarbonyl)benzothiazoline (5h)**: colorless oil; $^1H$ NMR (DMSO-$d_6$, 80 °C) δ 1.30 (3H, t, *J* = 6.8 Hz), 2.55–2.57 (2H, m), 4.26 (2H, q, *J* = 6.8 Hz), 5.04–5.11 (2H, m), 5.69–5.78 (1H, m), 5.84 (1H, t, *J* = 6.1 Hz), 6.97–7.01 (1H, m), 7.06–7.10 (1H, m), 7.23 (1H, dd, *J* = 1.5 Hz, 7.5 Hz), 7.61 (1H, dd, *J* = 1.0 Hz, 7.3 Hz); $^{13}C$ NMR (DMSO-$d_6$, 80 °C) δ 14.2 ($CH_3$), 41.7 ($CH_2$), 62.0 ($CH_2$), 64.8 (CH), 117.2 (CH), 118.8 ($CH_2$), 122.4 (CH), 124.2 (CH), 125.1 (CH), 128.5 (C), 132.3 (CH), 137.5 (C), 152.1 (CO); HRMS *m/z* ($M^+$, 15%) calcd for $C_{13}H_{15}NO_2S$ 249.0821, obsd 249.0816; ($M^+$ – allyl, 100%) calcd for $C_{10}H_{10}NO_2S$ 208.0429, obsd 208.0406.

**2-Allyl-3-[(1-chloroethoxy)carbonyl]benzothiazoline (5h')**: colorless, viscous oil; $^1H$ NMR ($CDCl_3$) δ 1.90 (3H, d, *J* = 5.7 Hz), 2.50–2.69 (2H, m), 5.06–5.23 (2H, m), 5.54–5.94 (2H, m), 6.69 (1H, q, *J* = 5.7 Hz), 6.98–7.23 (3H, m), 7.74 (1H, bs). The $^{13}C$ NMR spectrum was recorded on a mixture of four conform-

ers: $^{13}$C NMR ($CDCl_3$) δ 25.3, 25.4 ($CH_3$), 4.15, 42.4 ($CH_2$), 65.0, 66.1 (CH), 82.9 (CH), 117.8 (CH), 119.6, 119.9 ($CH_2$), 122.5 (CH), 124.9, 125.0, 125.4 (2 peaks) (2CH), 128.5 (C), 131.6, 131.8 (CH), 136.9, 137.1 (C), 149.3, 149.6 (CO); HRMS *m/z* ($M^+$, 24%) calcd for $C_{13}H_{14}ClNO_2S$ 283.0431, obsd 283.0421; ($M^+$ – allyl, 100%) calcd for $C_{10}H_9ClNO_2S$ 242.0043, obsd 242.0070.

**2-Allyl-3-(ethoxycarbonyl)-6-methoxybenzothiazoline (5i)**: colorless, viscous oil; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 1.28 (3H, t, *J* = 6.8 Hz), 2.52–2.56 (2H, m), 3.72 (3H, s), 4.23 (2H, q, *J* = 6.8 Hz), 5.05–5.06 (1H, m), 5.07–5.11 (1H, m), 5.67–5.77 (1H, m), 5.82 (1H, t, *J* = 6.1 Hz), 6.64 (1H, dd, *J* = 2.5 Hz, 8.8 Hz), 6.86 (1H, d, *J* = 2.5 Hz), 7.49 (1H, d, *J* = 8.8 Hz). $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 14.2 ($CH_3$), 41.7 ($CH_2$), 55.6 ($CH_3$), 61.9 ($CH_2$), 65.3 (CH), 108.6 (CH), 110.6 (CH), 117.9 (CH), 118.7 ($CH_2$), 130.1 (C), 131.1 (C), 132.4 (CH), 152.1 (CO), 156.5 (C); HRMS *m/z* ($M^+$, 31%) calcd for $C_{14}H_{17}NO_3S$ 279.0926, obsd 279.0921; ($M^+$ – allyl, 100%) calcd for $C_{11}H_{12}NO_3S$ 238.0538, obsd 238.0553.

**2-Allyl-3-[(1-chloroethoxy)carbonyl]-6-methoxybenzothiazoline (5i′)**: colorless, viscous oil; $^1$H NMR ($CDCl_3$) δ 1.89 (3H, d, *J* = 5.7 Hz), 2.50–2.68 (2H, m), 3.77 (3H, s), 5.06–5.23 (2H, m), 5.56–5.93 (2H, m), 6.56–6.75 (3H, m), 7.70 (1H, bs). The $^{13}$C NMR spectrum was recorded on a mixture of three conformers: $^{13}$C NMR ($CDCl_3$) δ 25.4 ($CH_3$), 41.4, 42.4 ($CH_2$), 55.7 ($CH_3$), 65.3, 66.6 (CH), 82.7, 82.9, 83.5 (CH), 108.7 (CH), 110.3, 110.4 (CH), 118.3 (CH), 119.6, 119.9 ($CH_2$), 130.0 (C), 130.7 (C), 131.7, 131.8 (CH), 149.3, 150.6 (CO), 157.2 (2 peaks) (C); HRMS *m/z* ($M^+$, 36%) calcd for $C_{14}H_{16}ClNO_3S$ 313.0540, obsd 313.0545; ($M^+$ – allyl, 100%) calcd for $C_{11}H_{11}ClNO_3S$ 272.0148, obsd 272.0151.

**2-Allyl-3-(ethoxycarbonyl)-6-nitrobenzothiazoline (5j)**: pale yellow, viscous oil; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 1.33 (3H, t, *J* = 7.0 Hz), 2.60–2.64 (2H, m), 4.31 (2H, q, *J* = 7.0 Hz), 5.07–5.14 (2H, m), 5.68–5.79 (1H, m), 6.00 (1H, t, *J* = 4.9 Hz), 7.79 (1H, d, *J* = 9.3 Hz), 7.98 (1H, dd, *J* = 2.5 Hz, 9.3 Hz), 8.13 (1H, d, *J* = 2.4 Hz); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 14.0 ($CH_3$), 41.7 ($CH_2$), 62.8 ($CH_2$), 66.1 (CH), 116.0 (CH), 117.5 (CH), 119.5 ($CH_2$), 121.8 (CH), 131.0 (C), 131.6 (CH), 143.4 (C), 143.7 (C), 151.6 (CO); HRMS *m/z* ($M^+$, 13%) calcd for $C_{13}H_{14}N_2O_4S$ 294.0672, obsd 294.0670; ($M^+$ – allyl, 100%) calcd for $C_{10}H_9N_2O_4S$ 253.0264, obsd 253.0272.

**2-Allyl-3-[(1-chloroethoxy)carbonyl]-6-nitrobenzothiazoline (5j′)**: pale yellow needles from isopropyl ether; mp 130–131 °C; $^1$H NMR ($CDCl_3$) δ 1.93 (3H, d, *J* = 5.7 Hz), 2.54–2.73 (2H, m), 5.10–5.28 (2H, m), 5.62–5.95 (2H, m), 6.69 (1H, q, *J* = 5.7 Hz), 7.96–8.11 (3H, m). The $^{13}$C NMR spectrum was recorded on a mixture of two conformers: $^{13}$C NMR ($CDCl_3$) δ 25.2, 25.3 ($CH_3$), 42.4 ($CH_2$), 66.4 (CH), 83.2 (CH), 116.6, 116.9 (CH), 117.7, 117.8 (CH), 120.7, 120.9 ($CH_2$), 122.0 (2 peaks) (CH), 130.5, 130.6 (CH), 130.9 (C), 142.7 (C), 142.8 (C), 144.7 (2 peaks) (C), 149.3, 149.5 (CO). Anal. Calcd for $C_{13}H_{13}ClN_2O_2S$: C, 47.49; H, 3.98; N, 8.52. Found: C, 47.62; H, 3.83; N, 8.32.

**2-Allyl-3-(ethoxycarbonyl)benzoxazoline (5k)**: colorless, viscous oil; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 1.31 (3H, t, *J* = 7.0 Hz), 2.65–2.68 (2H, m), 4.26 (2H, q, *J* = 7.0 Hz), 5.09 (1H, dd, *J* = 2.0 Hz, 10.2 Hz), 5.15 (1H, dd, *J* = 2.0 Hz, 17.6 Hz), 5.69–5.80 (1H, m), 6.22 (1H, t, *J* = 4.2 Hz), 6.80–6.92 (3H, m), 7.37 (1H, d, *J* = 7.8 Hz); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 14.1 ($CH_3$), 38.4 ($CH_2$), 61.9 ($CH_2$), 93.2 (CH), 108.4 (CH), 113.6 (CH), 119.3 ($CH_2$), 121.0 (CH), 123.4 (CH), 129.4 (C), 130.7 (CH), 150.1 (C), 150.7 (CO); HRMS *m/z* ($M^+$, 26%) calcd for $C_{13}H_{15}NO_3$ 233.1049, obsd 233.1038; ($M^+$ – allyl, 100%) calcd for $C_{10}H_{10}NO_3$ 192.0658, obsd 192.0656.

**2-Allyl-3-[(1-chloroethoxy)carbonyl]benzoxazoline (5k′)**: colorless, viscous oil; $^1$H NMR ($CDCl_3$) δ 1.90 (3H, d, *J* = 5.9 Hz), 2.67–2.79 (2H, m), 5.06–5.29 (2H, m), 5.58–5.96 (1H, m), 6.21 (1H, t, *J* = 3.6 Hz), 6.58–6.88 (4H, m), 7.24–7.66 (1H, m). The $^{13}$C NMR spectrum was recorded on a mixture of four conformers: $^{13}$C NMR ($CDCl_3$) δ 25.2, 25.4 ($CH_3$), 38.3, 39.5 (2 peaks) ($CH_2$), 82.5, 82.7, 82.9 (2 peaks) (CH), 93.2, 93.3, 93.9 (2 peaks) (CH), 108.7, 109.3 (CH), 114.4, 114.5, 114.7 (CH), 120.0, 120.3 ($CH_2$), 121.2, 121.5 (CH), 124.5 (CH), 127.9, 128.8 (C), 129.8, 130.0 (CH), 147.7, 147.9, 148.9 (C), 150.3, 150.5 (CO); HRMS *m/z* ($M^+$, 40%) calcd for $C_{13}H_{14}ClNO_3$ 267.0661, obsd 267.0671; ($M^+$ – allyl, 100%) calcd for $C_{10}H_9ClNO_3$ 226.0270, obsd 226.0270.

**2-Allyl-3-[(2,2,2-trichloroethoxy)carbonyl]benzoxazoline (5k″)**: colorless, viscous oil; $^1$H NMR (DMSO-$d_6$, 80 °C) δ 2.73–2.76 (2H, m), 4.98–5.20 (4H, m), 5.71–5.81 (1H, m), 6.31 (1H, t, *J* = 4.1 Hz), 6.86–6.99 (3H, m), 7.47 (1H, dd, *J* = 1.0 Hz, 7.8 Hz); $^{13}$C NMR (DMSO-$d_6$, 80 °C) δ 38.2 ($CH_2$), 74.7 ($CH_2$), 93.4 (CH), 95.3 ($CCl_3$), 108.8 (CH), 113.9 (CH), 119.7 ($CH_2$), 121.2 (CH), 124.3 (CH), 128.6 (C), 130.3 (CH), 148.8 (C), 150.1 (CO); HRMS *m/z* ($M^+$, 40%) calcd for $C_{13}H_{12}Cl_3NO_3$ 334.9883, obsd 334.9900; ($M^+$ – allyl, 100%) calcd for $C_{10}H_7Cl_3NO_3$ 293.9489, obsd 293.9478.

**Typical Procedure for the Aromatization of 2.** Compound **2a′** (3 mmol), potassium ferricyanide (18 mmol), and KOH (9 mmol) were dissolved in dioxane (70 mL)–$H_2O$ (20 mL) solution, and the mixture was allowed to stand at 100 °C for 1 h. After the mixture cooled, an aqueous solution (100 mL) of 0.5 N KOH was added, and the mixture was extracted with $CH_2Cl_2$ (60 mL × 3). The aqueous layer was further extracted with $CH_2Cl_2$ (40 mL × 3) by salting-out. The salting-out was crucial for the isolation of the products in all the cases. The $CH_2Cl_2$ layers were combined, dried over $MgSO_4$, and evaporated. The residue was chromatographed on alumina to give **6a**.

**2-Allylimidazole (6a).** All the physical and spectral data were identical to literature values.[23]

**2-Allyl-4-methylimidazole (6b)**: colorless oil; $^1$H NMR ($CDCl_3$) δ 2.21 (3H, d, *J* = 1.0 Hz), 3.46 (2H, dt, *J* = 1.5 Hz, 6.8 Hz), 5.10 (1H, d, *J* = 1.5 Hz), 5.14 (1H, dd, *J* = 1.5 Hz, 8.8 Hz), 5.92–6.02 (1H, m), 6.63 (1H, s), 8.96 (1H, bs); $^{13}$C NMR ($CDCl_3$) δ 11.5 ($CH_3$), 33.1 ($CH_2$), 117.3 (CH), 117.6 ($CH_2$), 132.1 (C), 133.7 (CH), 145.5 (C); HRMS *m/z* ($M^+$) calcd for $C_7H_{10}N_2$ 122.0841, obsd 122.0840.

**2-Allyl-4,5-dimethylimidazole (6c)**: colorless needles from isopropyl ether; mp 128–130 °C; $^1$H NMR ($CDCl_3$) δ 2.12 (6H, s), 3.43 (2H, dd, *J* = 1.5 Hz, 6.8 Hz), 5.12–5.18 (2H, m), 5.90–6.00 (1H, m), 6.84 (1H, bs); $^{13}$C NMR ($CDCl_3$) δ 10.6 ($2CH_3$), 33.2 ($CH_2$), 117.8 ($CH_2$), 126.2 (2C), 133.7 (CH), 143.4 (C). Anal. Calcd for $C_8H_{12}N_2$: C, 70.55; H, 8.88; N, 20.57. Found: C, 70.48; H, 9.05; N, 20.54.

**2-Allyl-5-methylthiazole (6f)**: colorless oil; $^1$H NMR ($CDCl_3$) δ 2.43 (3H, d, *J* = 1.0 Hz), 3.72 (2H, d, *J* = 6.8 Hz), 5.20 (1H, dd, *J* = 1.5 Hz, 9.8 Hz), 5.25 (1H, dd, *J* = 1.5 Hz, 17.1 Hz), 5.98–6.08 (1H, m), 7.34 (1H, d, *J* = 1.0 Hz); $^{13}$C NMR ($CDCl_3$) δ 12.0 ($CH_3$), 37.8 ($CH_2$), 118.0 ($CH_2$), 133.4 (C), 134.1 (CH), 140.0 (CH), 167.6 (C); HRMS *m/z* ($M^+$) calcd for $C_7H_9NS$ 139.0456, obsd 139.0463.

**2-Allylbenzothiazole (7h).** The literature[19] reported only a low-resolution $^1$H NMR spectrum of **7h**, which was similar to our data; colorless oil; $^1$H NMR ($CDCl_3$) δ 3.89 (2H, dt, *J* = 1.5 Hz, 6.8 Hz), 5.28 (1H, dd, *J* = 1.5 Hz, 10.3 Hz), 5.34 (1H, dd, *J* = 1.5 Hz, 17.1 Hz), 6.07–6.17 (1H, m), 7.33–7.37 (1H, m), 7.43–7.48 (1H, m), 7.84 (1H, d, *J* = 8.3 Hz), 7.99 (1H, d, *J* = 8.3 Hz); $^{13}$C NMR ($CDCl_3$) δ 38.6 ($CH_2$), 119.0 ($CH_2$), 121.5 (CH), 122.6 (CH), 124.9 (CH), 126.0 (CH), 133.1 (CH), 135.3 (C), 153.1 (C), 170.2 (C); HRMS *m/z* ($M^+$) calcd for $C_{10}H_9NS$ 175.0454, obsd 175.0452. Compound **7h** was slowly isomerized at rt to 2-(1-propenyl)-benzothiazole (**8h**).

**2-(1-propenyl)benzothiazole (8h)**: colorless oil; $^1$H NMR ($CDCl_3$) δ 1.99 (3H, s), 6.72–6.75 (2H, m), 7.31–7.35 (1H, m), 7.41–7.45 (1H, m), 7.80 (1H, d, *J* = 7.8 Hz), 7.95 (1H, d, *J* = 8.3 Hz); $^{13}$C NMR ($CDCl_3$) δ 18.7 ($CH_3$), 121.4 (CH), 122.8 (CH), 125.1 (CH), 126.0 (CH), 126.1 (CH), 134.0 (C), 137.0 (CH), 153.6 (C), 167.4 (C); HRMS *m/z* ($M^+$) calcd for $C_{10}H_9NS$ 175.0454, obsd 175.0459.

**The Procedure for the Synthesis of 7a.** The application of the aromatization conditions described above to benzimidazoline **5a′** resulted in the formation of 2-(1-propenyl)benzimidazole (**8a**) as the sole product in 88% yield. The synthesis of **7a** was carried out at rt with excess reagents. Compound **5a′** (3 mmol), potassium ferricyanide (36 mmol), and KOH (48 mmol) were dissolved in dioxane (140 mL)–$H_2O$ (50 mL) solution, and the mixture was allowed to stand at rt for 5 days. An aqueous solution (100 mL) of 1 N NaOH was added, and the mixture was extracted with $CH_2Cl_2$ (200 mL × 3). The organic layer was dried over $MgSO_4$ and evaporated. The residue was chromatographed on alumina to give **7a**. All the physical and spectral data of **7a** and **8a** were identical to literature values.[24]

**Isolation of 2-Allylbenzothiazoline (9h)**: When **5h′** was treated with $K_2CO_3$ instead of KOH, intermediate **9h** was obtained. Thiazoline **5h′** (0.5 mmol), potassium ferricyanide (1.5 mmol), and $K_2CO_3$ (1.0 mmol) were dissolved in dioxane (6 mL)–$H_2O$ (2 mL) solution and the mixture was allowed to stand under

reflux for 3 h. After the mixture cooled, 2 mL of 1 N KOH solution was added, and the mixture was extracted with $CH_2Cl_2$ (20 mL × 3). The organic layer was dried over $MgSO_4$ and evaporated to leave a residue, which was chromatographed on silica gel to give **7h** (29%) and **9h** (45%).

**2-Allylbenzothiazoline (9h)**: colorless oil; $^1H$ NMR ($CDCl_3$) $\delta$ 2.56–2.66 (2H, m), 4.20 (1H, bs), 5.16–5.28 (3H, m), 5.76–5.87 (1H, m), 6.64 (1H, d, $J$ = 7.8 Hz), 6.71–6.75 (1H, m), 6.88–6.92 (1H, m), 7.06 (1H, dd, $J$ = 1.5 Hz, 7.3 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 42.9 ($CH_2$), 67.0 (CH), 110.6 (CH), 119.0 ($CH_2$), 120.7 (CH), 122.0 (CH), 125.2 (CH), 126.9 (C), 133.3 (CH), 146.2 (C); HRMS $m/z$ ($M^+$, 11%) calcd for $C_{10}H_{11}NS$ 177.0595, obsd 177.0602; ($M^+$ – allyl, 100%) calcd for $C_7H_6NS$ 136.0218, obsd 136.0206.

**Supplementary Material Available:** The $^1H$ and $^{13}C$ NMR spectra for all the oily compounds (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.