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Synthesis of Methyl 8-Cyanoheptafulvene-8-carboxylate Derivatives

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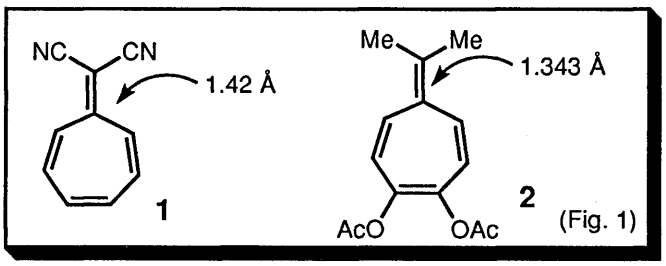
In order to provide a series of samples for measurement of thermodynamic parameters for the rotation of exocyclic C=C bond of heptafulvene derivatives, several fused-tropone derivatives were treated with methyl cyanoacetate in refluxing acetic anhydride to give methyl 8-cyanoheptafulvene-8-carboxylates fused by a heteroaromatic ring.

Heptafulvenes, fundamental members of non-alternant conjugated compounds, are known to be stabilized by introduction of electron-withdrawing substituents on the C-8 position, e.g., 8,8-dicyanoheptafulvene (**1**).[1] The bond lengths of the exocyclic C=C of the heptafulvenes have frequently been discussed as a measure of the contribution of a dipolar form.[1] For example, the exocyclic C=C bond length of **1** was 1.42 Å, which has a considerable single bond character.[1] On the other hand, that of 3,4-diacetoxy-8,8-dimethylheptafulvene (**2**),[2] carrying no electron-withdrawing substituents to assist the polarized 6π-contribution, was 1.343 Å, a typical length for the normal C=C bonds. These were explained in terms of the different dipolar contribution of molecules.



(Fig. 1)

Another measure of the dipolar contibutions should be the rates of rotation, which could be determined with variable-temperature NMR techniques. Indeed, the synthesized samples of heptafulvene derivatives frequently showed broadened ^{13}C NMR signals due to the facilitated rotation of the exocyclic C=C bond. Therefore, it will be interesting to investigate the quantitative measurement of the rotation of the "push-pull" heptafulvenes. However, there has been no systematic synthesis of "push-pull" heptafulvene derivatives carrying two different substituents on the C-8 positions.

In this paper, we describe the synthetic studies with such heptafulvenes together with monocyclic 3-substituted heptafulvenes.

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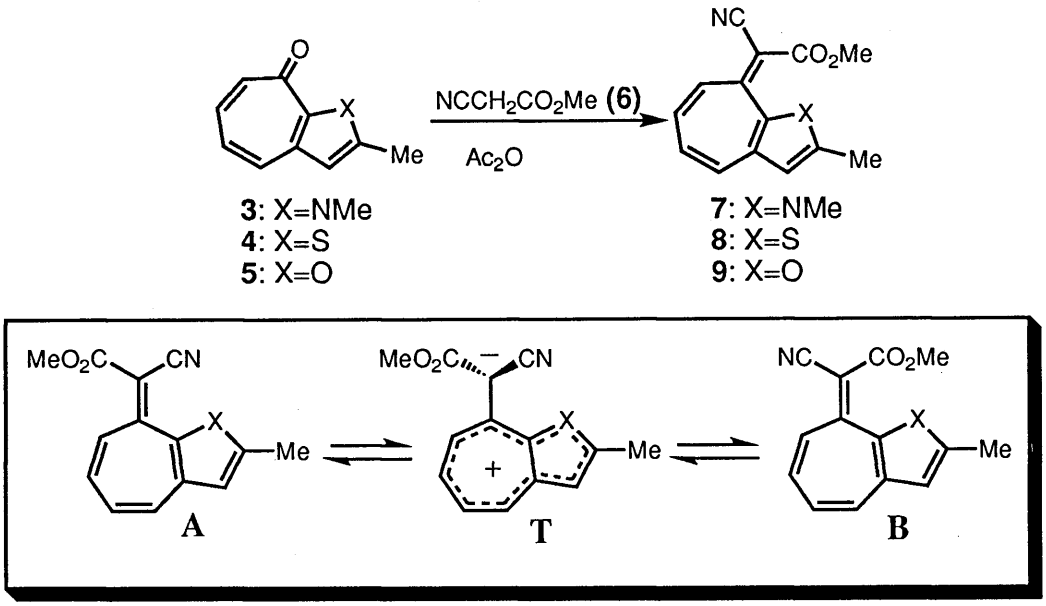
Results and Discussion

Previously, the heptafulvenes were synthesized conveniently from tropones and active methylene compounds by heating in acetic anhydride.[1] Particularly this was satisfactory for 8,8-dicyano derivatives. Since we needed different substitutents on C-8 position, 8-cyano-8-methoxycarbonyl derivatives were selected as the target molecules, although the yields were predicted to be inferior than the dicycano derivatives.[3]

Synthesis of Heptafulvene Derivatives from 1,2-Dimethylcyclohepta[*b*]pyrrol-8-one, 2-Methylcyclohepta[*b*]thiophen-8-one, and 2-Methylcyclohepta[*b*]furan-8-one. When 1,2-dimethylcyclohepta[*b*]pyrrol-8-one (**3**),[4] 2-methylcyclohepta[*b*]thiophen-8-ones (**4**),[5] and 2-methylcyclohepta[*b*]furan-8-one (**5**)[6] were respectively heated with methyl cyanoacetate (**6**) in acetic anhydride at 130-140 ℃, methyl 2-cyano-(1,2-dimethylcyclohepta[*b*]pyrrol-8-ylidene)acetate (**7**), methyl 2-cyano-(2-methylcyclohepta[*b*]thiophen-8-ylidene) acetate (**8**), and methyl 2-cyano-(1-methylcyclohepta[*b*]furan-8-ylidene) acetate (**9**) were obtained in reasonable yields. According to the NMR spectroscopic analysis, these derivatives revealed the presence of two rotamers throughout, and are suitable for kinetic analyses.

Synthesis of Heptafulvene Derivatives from 1,2-Dimethylcyclohepta[*b*]pyrrol-6-one, 2-Methylcyclohepta[*b*]thiophen-6-one, and 2-Methylcyclohepta[*b*]furan-6-one. For the rotation of the exocyclic C=C, these hetero atoms in **7**, **8**, and **9** contribute the stabilization of charge-transferred dipolar transition states, but in the same time, these hetero atoms are in the *peri*-position of the molecules, and their sterical environment varies



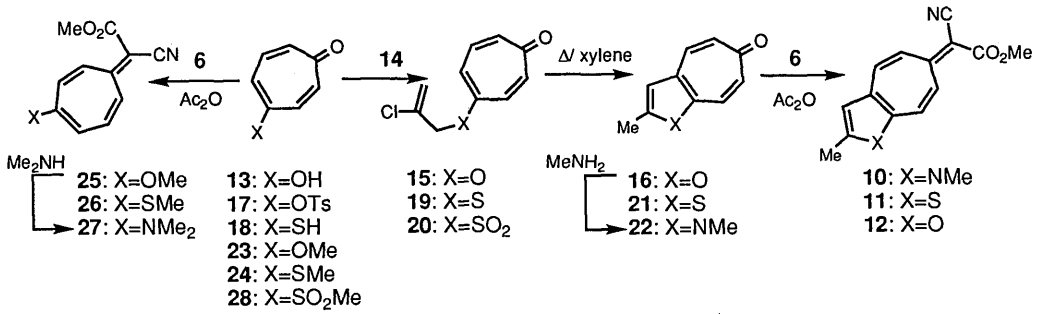
(Scheme 1)

in each case. Therefore, in a comparative point of view, it is desirable to prepare and analyze the rotation of exocyclic C=C of corresponding isomers, methyl 2-cyano-(1,2-dimethylcyclohepta[*b*]pyrrol-6-ylidene)acetate (**10**), methyl 2-cyano-(2-methylcyclohepta-[*b*]thiophen-6-ylidene) acetate (**11**), and methyl 2-cyano-(1-methylcyclohepta-[*b*]furan-6-ylidene) acetate (**12**).

Recently, we have found a new synthetic method for the precursor, 4-hydroxytropone (**13**).[7] In advantage of this development, easily-available **13** was treated with 2,3-dichloropropene (**14**) in hexamethylphosphoric triamide (HMPA) and sodium hydride, 4-(2-chloropropenyloxy)tropone (**15**) was obtained as a sole product. Then, the Claisen rearrangement by heating in xylene afforded 2-methylcyclohepta[*b*]furan-6-one (**16**).[8] Next, when 4-tosyloxytropone (**17**) was treated with sodium sulfide to give 4-mercaptotropone (**18**), which was immediately allowed to react with **14** to give 4-(2-chloropropenylthio)tropone (**19**). Due to a facile autooxidation, always accompanied by **19** was a small amount of 4-(2-chloropropenylsulfonyl)tropone (**20**). The Claisen rearrangement of **19** in *N*,*N*-dimethylformamide (DMF) gave the desired 2-methylcyclohepta[*b*]thiophen-6-one (**21**) in 53% yield. Since the *aza*-Claisen rearrangement of troponoids was not successful so far,[9] the cyclohepta[*b*]pyrrol-6-one derivative should be prepared from corresponding furan-6-one derivative. Thus, treatment of **16** with methylamine was carried out to afford 1,2-dimethylcyclohepta[*b*]pyrrol-6-one (**22**).

Treatment of these fused tropones (**16**, **21**, and **22**) with **6** in refluxing acetic anhydride smoothly afforded heptafulvene derivatives (**10**, **11**, and **12**).

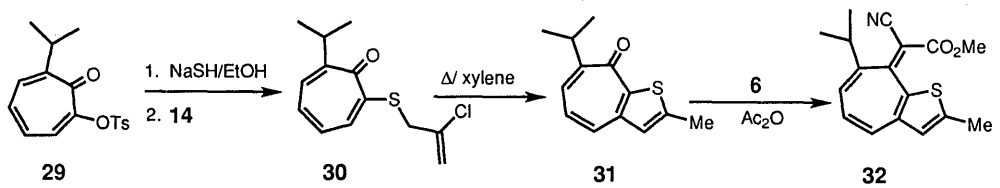
Subsequently, monocyclic heptafulvene derivatives were synthesized; by treatment with **6**, 4-methoxytropone (**23**) and 4-methylthiotropone (**24**) gave methyl 8-cyano-3-methoxyheptafulvene-8-carboxylate (**25**) and methyl 8-cyano-3-methylthioheptafulvene-8-carboxylate (**26**). A treatment of **25** with dimethylamine afforded methyl 8-cyano-3-(dimethylamino)-heptafulvene-8-carboxylate (**27**). In the series of the reactions with methylthio derivatives, always accompanied were sulfonyl derivatives; e.g., **24** was accompanied by 4-methylsulfonyltropone (**28**).



(Scheme 2)

Synthesis from 7-Isopropyl-2-methylcyclohepta[*b*]thiophen-8-one. Since the carbonyl group of 2-methylcyclohepta[*b*]thiophen-8-one derivative from 3-isopropyltropolone is sterically hindered, its reaction with **6** might suffer a considerable difficulty, and in that

case, the rotational behavior of the exocyclic C=C is of great interest. Thus, its *p*-toluenesulfonate (**29**), was at first converted into 7-isopropyl-2-mercaptotropone, which was, without purification, immediately condensed with **14** to give 2-(2-chloro-2-propynylthio)-tropones (**30**). Subsequent Claisen rearrangement smoothly afforded 7-isopropyl-2-methylcyclohepta[*b*]thiophen-8-one (**31**). Finally, the condensation with **6** furnished the corresponding heptafulvene (**32**) in 77% yield.



(Scheme 3)

As predicted, some of these heptafulvene derivatives showed the presence of two isomers, and the NMR spectroscopy firmly differentiated the geometrical isomerism. Namely, in the ^{1}H NMR spectrum of **8** in acetonitrile-d_3 at −39.8 ℃, signals ascribable to H-7 were appeared, as sharp doublet signals, at δ 8.46 (J=12.1 Hz) and at δ 7.42 (J=12.0 Hz) in a ratio of 91/9. From a consideration of the magnetic anisotropy of a methoxycarbonyl group, the major isomer with a signal at δ 8.46 is assigned to be **8A** and the other is **8B**. The smaller cyano group is located at an inner side of the major **8A**. In acetonitrile-d_3 at 60 ℃, **8** showed a broad and coalesced signal with a half-height width of 46 Hz. Assignments for others were based on the similar observations.

Since these heptafulvenes are good models for investigating the facilitated rotation of the polarized C=C, more detailed investigation will be carried out and the results will be a subject of an independent paper.

Experimental

Elemental analyses were performed by Mrs. M. Miyazawa of Institute of Advanced Material Study, Kyushu University. The mps were measured with a Yanagimoto Micro mp apparatus and are not corrected. The NMR spectra were measured by JEOL FX 100 and GSX 270H and 500 spectrometers in $CDCl_3$ at 27 ℃, unless otherwise specified, and the chemical shifts expressed were in δ units. Mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily materials using a JASCO IR-A 102 spectrometer. The UV spectra were measured with Hitachi U-3200 and U-3410 spectrophotometers. The stationary phase for the column chromatography was Wakogel C-300 and the elution solvents were mixtures of hexane and ethyl acetate.

Preparation of Heptafulvenes (General Procedure). An Ac_2O solution (2 cm^3) of tropones (1 mmol) and methyl cyanoacetate (**6**) (3 mmol) was heated at 130-140 ℃ for 2-6 h. Removal of the solvent in vacuo was followed by silica gel chromatography (EtOAc-hexane) to furnish the desired heptafulvenes.

7: Red prisms, mp 134-135 ℃ (EtOAc-hexane), 96%; ^{1}H NMR δ 2.46 (3H, s), 3.65

(3H, br s), 3.78 (3H, s), 6.48 (1H, br s), 6.73 (1H, ddm, J=10.6, 8.1 Hz), 6.96 (1H, dd, J=12.1, 8.1 Hz), 7.44 (1H, d, J=10.6 Hz), 7.7-8.7 (1H, br s); ^{1}H NMR (DMF-d_7 at −49.6 ℃) conformer **A** δ 2.55 (3H, s), 3.81 (3H, s), 3.91 (3H, s), 6.78 (1H, s), 6.93 (1H, dd, J=10.6, 7.7 Hz), 7.17 (1H, dd, J=12.5, 7.7 Hz), 7.71 (1H, d, J=10.6 Hz), 8.84 (1H, d, J=12.5 Hz); conformer **B** δ 2.55 (3H, s), 3.58 (3H, s), 3.73 (3H, s), 6.81 (1H, s), 6.96 (1H, dd, J=10.6, 7.7 Hz), 7.31 (1H, dd, J=12.5, 7.7 Hz), 7.70 (1H, d, J=12.5 Hz), 7.78 (1H, d, J=10.6 Hz); ^{13}C NMR δ 13.3, 33.3 (br), 51.9, 85.5, 109.4, 119.5, 125.7, 128.3 (br), 131.6, 131.7, 132.1, 133.8, 142.7, 151.7 (br), 164.6; IR (KBr) 2975, 2202, 1679, 1619, 1521, 1454, 1395, 1310, 1250, 1222, 1184, 1120, 1057, 838, 778, 702 cm^{-1}; UV (MeOH) 223 nm (ε 16900), 263 (12600), 278 (11500), 444 (16000); MS m/z (rel intensity) 254 (M^+, 100), 239 (21), 223 (41), 195 (61), 168 (24), 127 (11); Found: C, 70.68; H, 5.65; N, 10.96%. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02%.

8: Red needles, mp 129-130 ℃ (EtOAc-hexane), 62%; ^{1}H NMR δ 2.59 (3H, d, J=0.7 Hz), 3.85 (3H, s), 6.80 (1H, ddd, J=10.3, 8.0, 1.1 Hz), 6.91 (1H, ddd, J=12.1, 8.0, 1.2 Hz), 7.01 (1H, q, J=0.7 Hz), 7.36 (1H, dd, J=10.3, 1.1 Hz), 8.48 (1H, d, J=12.1 Hz); ^{1}H NMR (DMF-d_7 at −49.8 ℃) conformer **A** δ 2.71 (3H, d, J=0.7 Hz), 3.86 (3H, s), 7.15 (1H, dd, J=10.3, 7.3 Hz), 7.27 (1H, ddd, J=12.1, 7.3, 1.1 Hz), 7.50 (1H, m), 7.81 (1H, d, J=10.3 Hz), 8.58 (1H, d, J=12.1 Hz); conformer **B** δ 2.67 (3H, s), 3.86 (3H, s), 7.15 (1H, dd, J=10.3, 7.3 Hz), 7.35 (1H, dd, J=12.1, 7.3 Hz), 7.44 (1H, br s), 7.54 (1H, d, J=12.1 Hz), 7.81 (1H, d, J=10.3 Hz); ^{13}C NMR δ 15.6, 52.4, 89.0, 120.1, 127.9, 129.3, 129.6, 132.6, 133.1, 137.2, 145.9, 146.1, 156.6, 164.9; IR (KBr) 2940, 2184, 1695, 1564, 1501, 1428, 1401, 1318, 1241, 1222, 1192, 1115, 1066, 930, 871, 784, 659 cm^{-1}; UV (MeOH) 204 nm (ε 20400), 256 (14800), 268 (13900, sh), 331 (5300), 418 (15300); MS m/z (rel intensity) 257 (M^+, 100), 242 (15), 199 (16), 127 (6); Found: C, 65.35; H, 4.43; N, 5.43%. Calcd for $C_{14}H_{11}NO_2S$: C, 65.36; H, 4.31; N, 5.45%.

9: Deep red needles, mp 142-143 ℃ (EtOAc), 70%; ^{1}H NMR δ 2.57 (3H, d, J=0.7 Hz), 3.85 (3H, s), 6.48 (1H, q, J=0.7 Hz), 6.90 (1H, ddd, J=10.3, 8.4, 0.7 Hz), 7.07 (1H, ddd, J=12.5, 8.4, 1.5 Hz), 7.26 (1H, dd, J=10.3, 0.7 Hz), 9.01 (1H, dd, J=12.5, 1.5 Hz); ^{1}H NMR (DMF-d_7 at 19.9 ℃) conformer **A** δ 2.57 (3H, d, J=1.1 Hz), 3.81 (3H, s), 6.95 (1H, m), 7.16 (1H, ddd, J=10.3, 8.4, 0.7 Hz), 7.32 (1H, ddd, J=12.8, 8.4, 1.1 Hz), 7.64 (1H, br d, J=10.3 Hz), 8.97 (1H, dd, J=12.8, 0.7 Hz); conformer **B** δ 2.48 (3H, d, J=1.1 Hz), 3.82 (3H, s), 6.84 (1H, m), 7.00 (1H, ddd, J=10.3, 8.4, 1.1 Hz), 7.24 (1H, ddd, J=12.8, 8.4, 1.1 Hz), 7.47 (1H, dd, J=12.8, 1.1 Hz), 7.48 (1H, br d, J=10.3 Hz); ^{13}C NMR δ 13.9, 52.1, 81.7, 110.2, 120.0, 130.4, 131.1, 131.8, 135.0, 135.8, 148.4, 150.1, 158.5, 166.2; IR (KBr) 2190, 1686, 1630, 1602, 1531, 1471, 1318, 1254, 1220, 1120, 943, 843, 789, 702 cm^{-1}; UV (MeOH) 211 nm (ε 23400), 228 (15800, sh), 248 (10100, sh), 292 (8600, sh), 309 (9600), 416 (19600); MS m/z (rel intensity) 241 (M^+, 99), 210 (100), 183 (30), 158 (25), 127 (36); Found: C, 69.54; H, 4.70; N, 5.93%. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.59; N, 5.80%.

Reaction of 4-Hydroxytropone (13) with 2,3-Dichloro-1-propene (14). An EtOH solution (3 cm^3) of **13**[9] (105.3 mg, 0.86 mmol) and KOH (60 mg, 1.07 mmol) was agitated for 10 min with a sonicater. After removing the volatile material in vacuo, the residue was kept in vacuo for 30 min. To the resultant potassium salt of **13** was added a HMPA

solution (10 cm^3) of **14** (3.26 g, 2.17 mmol), After the mixture was heated at 70 ℃ for 8 h, the reaction was quenched by adding water. The aqueous layer was extracted with EtOAc and the organic layer was washed with 5% aqueous NaOH solution and a saturated NaCl solution. The organic layer was dried (Na_2CO_3) and concentrated in vacuo. The crude material was purified by silica gel chromatography (EtOAc:hexane = 1:1-1:2) to give **15** [a deep yellow oil, 105 mg, 62%; ^1H NMR δ 4.54 (2H, s), 5.51 (1H, dm, J = 1.8 Hz), 5.58 (1H, dm, J = 1.8 Hz), 6.23 (1H, dm, J = 8.4 Hz), 6.77 (1H, dd, J = 12.1, 2.2 Hz), 6.98-7.12 (3H, m); ^{13}C NMR δ 70.1, 110.0, 115.0, 133.8, 134.6, 135.0, 136.1, 141.4, 162.2, 186.7; IR (neat) 1641, 1572, 1527, 1223, 1200, 1173 cm^{-1}; UV (MeOH) 224.8 nm (ε 19100), 322.1 (12000); MS m/z (rel intensity) 198 (M^+ for ^{37}Cl, 4), 196 (M^+ for ^{35}Cl, 13), 161 (13), 133 (57), 105 (28), 75 (39), 65 (38), 39 (100); Found: m/z, 198.0259 (M^+ for ^{37}Cl), 196.0292 (M^+ for ^{35}Cl). Calcd for $C_{10}H_9O_2Cl$: 198.0261 (M, for ^{37}Cl), 196.0291 (M, for ^{35}Cl)].

Claisen Rearrangement of 15. A DMF solution (3 cm^3) of **15** (105 mg, 0.534 mmol) was refluxed for 5 h. The mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with a saturated NaCl solution and dried (Na_2CO_3). The solvent was removed in vacuo and the residue was chromatographed (EtOAc:hexane = 1:3-1:2) to give **16** [pale orange crystals, mp 72-74 ℃ (cyclohexane); 72 mg, 74%; ^1H NMR δ 2.44 (3H, d, J = 0.7 Hz), 6.40 (1H, t, J = 0.7 Hz), 6.88 (1H, dd, J = 12.5, 2.6 Hz), 6.96 (1H, dd, J = 11.7, 2.6 Hz), 7.36 (1H, d, J = 11.7 Hz), 7.48 (1H, dd, J = 12.5, 0.7 Hz); ^{13}C NMR δ 13.8, 108.8, 126.1, 130.5, 131.2, 133.5, 137.0, 154.2, 156.0, 187.3; IR (KBr) 1623, 1601, 1528, 1238, 1205 cm^{-1}; UV (MeOH) 230.9 nm (ε 17000), 244.6 (13100, sh), 259.7 (12000, sh), 267.7 (12700), 276.6 (10700, sh), 343.8 (17200); MS m/z (rel intensity) 160 (M^+, 57), 132 (71), 131 (100), 103 (12), 77 (16), 63 (10), 51 (14); Found: C, 75.02; H, 5.18%. Calcd for $C_{10}H_8O_2$: C, 74.98; H, 5.04%].

Condensation of 16 with Methylamine. Formation of 22. A 30%-aqueous NH_2Me solution (3 cm^3) of **16** (119.5 mg, 0.746 mmol) was heated at 90-100 ℃ in a sealed tube for 7h. The mixture was extracted with CH_2Cl_2 and the organic layer was washed with a saturated NaCl solution and dried (Na_2CO_3). The solvent was removed in vacuo and the residue was purified by chromatography (EtOAc:hexane = 1) to give **22** [pale yellow crystals, mp 154-155 ℃ (EtOAc-hexane); 57.4 mg, 44%; ^1H NMR δ 2.40 (3H, s), 3.72 (3H, s), 6.37 (1H, s), 6.84 (2H, dm, J = 12.1 Hz), 7.38 (1H, d, J = 12.1 Hz), 7.47 (1H, d, J = 12.1 Hz); ^{13}C NMR δ 12.8, 30.5, 109.4, 124.2, 128.8, 130.7, 132.3, 133.9, 134.7, 136.4, 187.6; IR (KBr) 1605, 1590, 1500, 861 cm^{-1}; UV (MeOH) 213.3 nm (ε 12300), 220.0 (11200, sh), 234.7 (6800, sh), 287.5 (30100), 362.1 (18100); MS m/z (rel intensity) 173 (M^+, 54), 145 (100), 144 (95), 77 (12); Found: C, 76.12; H, 6.41; N, 8.09%. Calcd for $C_{11}H_{11}ON$: C, 76.26; H, 6.41; N, 8.09%].

Preparation of 19 from 17 and 14. An EtOH solution (10 cm^3) of **17** (274 mg, 0.99 mmol) and 70%-NaSH (135 mg, 1.68 mmol) was sonicated for 10 min. To the resultant solution of **19** was added **14** (361 mg, 3.25 mmol) and K_2CO_3 (0.26 g) directly and the mixture was stirred for 4 h. After removing the solvent in vacuo, the residue was chromatographed on silica-gel column to give **19** [a brownish oil; 59.2 mg, 28%; ^1H NMR δ 3.79 (2H, br s), 5.39 (1H, dt, J = 1.8, 0.7 Hz), 5.50 (1H, dt, J = 1.8, 1.1 Hz), 6.7-6.95

(3H, m), 7.00 (1H, dd, J=12.1, 8.8 Hz), 7.06 (1H, dd, J=12.5, 1.8 Hz); ^{13}C NMR δ 40.8, 115.8, 129.7, 135.2, 135.7, 137.1, 138.6, 140.4, 145.5, 187.2; IR (NaCl) 1628, 1574, 1507, 1231, 895, 853 cm^{-1}; UV (MeOH) 228.3 nm (ε 16200), 289.8 (4650, sh), 289.4 (5200), 338.4 (9700); MS m/z (rel intensity) 214 (M^+ for ^{37}Cl, 4), 212 (M^+ for ^{35}Cl, 13), 184 (32), 149 (100), 109 (77); Found: C, 56.09; H, 4.46%. Calcd for $C_{10}H_9OSCl$: C, 56.46; H, 4.27%] and **20** [a yellow oil; 22.7 mg, 9%; ^{1}H NMR δ 3.58 (2H, d, J=0.7 Hz), 5.28 (1H, d, J=1.8 Hz), 5.34 (1H, dt, J=1.8, 0.7 Hz), 6.87-7.02 (2H, m), 7.05 (1H, dd, J=11.7, 8.8 Hz), 7.26 (1H, dd, J=12.1, 2.2 Hz), 7.30 (1H, m); ^{13}C NMR δ 47.3, 117.4, 129.1, 134.75, 134.83, 136.1, 139.6, 140.7, 145.4, 187.2; IR (NaCl) 1627, 1574, 1512, 1226, 893, 856 cm^{-1}; UV (MeOH) 228.6 nm (ε 16450), 280.2 (4700, sh), 284.6 (4720), 333.0 (9050); Found: C, 48.76; H, 3.91%. Calcd for $C_{10}H_9O_3SCl$: C, 49.08; H, 3.71%].

Claisen Rearrangement of 19. A DMF solution (3 cm^3) of **19** (21 mg, 0.1 mmol) was refluxed for 3 h. The mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with a saturated NaCl solution and dried (Na_2SO_4). The solvent was removed in vacuo and the residue was chromatographed (EtOAc:hexane = 1:3-1:2) to give **21** [pale orange crystals, mp 91.5-92 ℃ (EtOAc:hexane); 9 mg, 53%; ^{1}H NMR δ 2.58 (3H, d, J=1.1 Hz), 6.81 (1H, dd, J=12.1, 2.6 Hz), 6.90 (1H, dd, J=12.1, 2.6 Hz), 7.45 (1H, d, J=12.1 Hz), 7.46 (1H, d, J=12.1 Hz); ^{13}C NMR δ 15.6, 129.5, 131.9, 133.4, 136.1, 141.7, 142.1, 144.3, 187.8; IR (KBr) 1617, 1591, 1556, 1475, 1223, 859 cm^{-1}; UV (MeOH) 225.1 nm (ε 9850), 231.5 (9050, sh), 248.8 (8300), 287.7 (32450), 340.3 (12200); MS m/z (rel intensity) 176 (M^+, 16), 147 (100): Found: C, 67.91; H, 4.69%. Calcd for $C_{10}H_8OS$: C, 68.15; H, 4.58%].

Condensation of 16 with 6. An Ac_2O solution (5 cm^3) of **16** (67.6 mg, 0.422 mmol) and **6** (135 mg, 1.36 mmol) was heated at 130 ℃ for 4 h. After removing the volatile material in vacuo, the resultant crystalline mass was chromatographed (EtOAc:hexane=1:3) to give **12** [orange crystals, mp 187.5-189 ℃ (EtOH); 73.4 mg, 84%; ^{1}H NMR conformer **A** δ 2.46 (3H, s), 3.81 (3H, s), 6.39 (1H, s), 7.28 (1H, d, J=12.1 Hz), 7.35 (1H, d, J=12.1 Hz), 7.53 (1H, dd, J=12.1, 2.2 Hz), 8.85 (1H, dd, J=12.1, 2.2 Hz); conformer **B** δ 2.46 (3H, s), 3.81 (3H, s), 6.39 (1H, s), 7.25 (1H, d, J=12.1 Hz), 7.32 (1H, d, J=12.5 Hz) 7.47 (1H, dd, J=12.1, 2.2 Hz), 8.86 (1H, dd, J=12.5, 2.2 Hz); ^{1}H NMR (DMF-d_7 at 60.1 ℃) conformer **A** δ 2.49 (3H, d, J=0.7 Hz), 3.77 (3H, s), 6.76 (1H, m), 7.43 (1H, dd, J=12.1, 2.2 Hz), 7.68 (1H, d, J=12.1 Hz), 7.73 (1H, dd, J=12.1, 0.7 Hz), 8.80 (1H, dd, J=12.1, 2.2 Hz); conformer **B** δ 2.49 (3H, d, J=0.7 Hz), 3.78 (3H, s), 6.76 (1H, m), 7.48 (1H, dd, J=12.1, 0.7 Hz), 7.58 (1H, d, J=12.1 Hz), 7.63 (1H, dd, J=12.1, 0.7 Hz), 8.79 (1H, dd, J=12.1, 2.2 Hz); ^{13}C NMR conformer **A** δ 14.0, 51.9, 88.0, 109.0, 119.6, 126.6, 127.0, 131.9, 132.0, 133.5, 155.3, 158.6, 160.0, 165.4; conformer **B** δ 14.0, 51.9, 88.0, 109.1, 119.6, 127.1, 129.3, 129.4, 132.5, 132.7, 156.1, 158.6, 160.2, 165.5; IR (KBr) 2190, 1687, 1561, 1469, 1387, 1241, 1200 cm^{-1}; UV (MeOH) 210.7 (ε 16600), 240.2 (13300), 250.7 (11300, sh), 267.4 (9000, sh), 285.0 (8900, sh), 309.9 (6600, sh), 435.7 (33000), 452.3 (29100, sh); MS m/z (rel intensity) 241 (M^+, 79), 210 (99), 183 (47), 127 (76), 28 (100); Found: C, 69.42; H, 4.70; N, 5.65%. Calcd for $C_{14}H_{11}O_3N$: C, 69.69; H, 4.60; N, 5.81%].

Condensation of 22 with Methyl Cyanoacetate (6). An Ac_2O solution (5 cm^3) of

22 (41 mg, 0.237 mmol) and **8** (78 mg, 0.787 mmol) was heated at 120-130 ℃ for 5 h. After removing the volatile meterial in vacuo, the resultant crystalline mass was chromatographed (EtOAc:hexane = 2:1) to give **10** [orange crystals, mp 222-223.5 ℃ (EtOH); 52 mg, 86%; ^{1}H NMR conformer **A** δ 2.43 (3H, s), 3.73 (3H, s), 3.79 (3H, s), 6.40 (1H, br s), 7.33 (1H, d, J=12.1 Hz), 7.44 (1H, d, J=12.1 Hz), 7.48 (1H, dd, J=12.1, 2.2 Hz), 8.81 (1H, dd, J=12.1, 2.2 Hz); conformer **B** δ 2.43 (3H, s), 3.73 (3H, s), 3.79 (3H, s), 6.40 (1H, br s), 7.33 (1H, d, J=12.1 Hz), 7.44 (2H, d, J=1.1 Hz), 8.87 (1H, dm, J=12.5 Hz); ^{1}H NMR (DMF-d_7 at 40.0 ℃) conformer **A** δ 2.50 (3H, s), 3.73 (3H, s), 3.90 (3H, s), 6.65 (1H, br s), 7.45 (1H, dd, J=12.1, 2.3 Hz), 7.74 (1H, d, J=12.1 Hz), 7.94 (1H, dd, J=12.1, 0.7 Hz), 8.85 (1H, dd, J=12.1, 2.3 Hz); conformer **B** δ 2.50 (3H, s), 3.74 (3H, s), 3.90 (3H, s), 6.65 (1H, br s), 7.43 (1H, dd, J=11.7, 2.3 Hz), 7.81 (1H, d, J =11.7 Hz), 7.86 (1H, dd, J=12.3, 0.7 Hz), 8.90 (1H, dd, J=12.3, 2.3 Hz); ^{13}C NMR conformer **A** δ 13.1, 30.48, 51.4, 83.0, 110.0, 121.2, 124.4, 125.4, 126.9, 132.0, 134.8, 136.5, 140.1, 160.2, 166.4; conformer **B** δ 13.1, 30.51, 51.4, 82.9, 109.8, 121.1, 124.9, 125.3, 127.9, 131.3, 135.0, 137.2, 140.0, 160.3, 166.5; IR (KBr) 2180 1680, 1600, 1472, 1385, 1234 cm^{-1}; UV (MeOH) 215.2 nm (ε 18500), 231.5 (13500, sh), 261.9 (7950, sh), 274.4 (9400, sh), 301.0 (16100), 333.6 (4900, sh), 462.6 (47400, sh), 466.7 (47400); MS m/z (rel intensity) 254 (M^+, 100), 223 (99), 196 (61), 171 (51); Found: C, 71.06; H, 5.61; N, 10.83%. Calcd for $C_{15}H_{14}O_2N_2$: C, 70.84; H, 5.56; N, 11.02%].

Condensation of 21 with Methyl Cyanoacetate (6). An Ac_2O solution (3 cm^3) of **21** (9.2 mg, 0.036 mmol) and **6** (225 mg, 2.27 mmol) was heated at 110-125 ℃ for 4 h. After removing the volatile material in vacuo, the resultant crystalline mass was chromatographed (EtOAc:hexane=2:1) to give **11** [orange crystals, mp 216-217 ℃ (EtOH); 10 mg, 74%; ^{1}H NMR conformer **A** δ 2.58 (3H, d, J=1.1 Hz), 3.82 (3H, s), 6.97 (1H, br s), 7.29 (1H, d, J=12.1 Hz), 7.34 (2H, s), 8.72 (1H, dm, J=12.1 Hz); conformer **B** δ 2.58 (3H, d, J=1.1 Hz), 3.82 (3H, s), 6.97 (1H, br s), 7.31 (1H, d, J=12.1 Hz), 7.32 (1H, d, J =12.1 Hz), 7.44 (1H, dd, J=12.1, 2.2 Hz), 8.65 (1H, dd, J=12.1, 2.2 Hz); ^{1}H NMR (DMF-d_7 at 95.0 ℃) conformer **A** δ 2.62 (3H, d, J=1.1 Hz), 3.81 (3H, s), 7.27 (1H, m), 7.29 (1H, dd, J=12.1, 2.6 Hz), 7.56 (1H, d, J=12.5 Hz), 7.74 (1H, d, J=12.1 Hz), 8.61 (1H, dd, J=12.5, 2.6 Hz); conformer **B** δ 2.62 (3H, d, J=1.1 Hz), 3.81 (3H, s), 7.27 (1H, m), 7.38 (1H, dd, J=12.1, 2.6 Hz), 7.38 (1H, dd, J=12.1, 2.6 Hz), 7.64 (1H, d, J=12.6 Hz), 7.66 (1H, d, J=12.1 Hz), 8.54 (1H, dd, J=12.6, 2.6 Hz); ^{13}C NMR conformer **A** δ 15.8, 52.0, 89.5, 119.2, 128.3, 128.5, 129.5, 133.2, 134.1, 144.0, 144.8, 147.03, 160.2, 165.2; conformer **B** δ 15.8, 52.0, 89.5, 119.2, 125.9, 129.3, 131.2, 132.6, 134.7, 143.1, 144.8, 147.01, 160.1, 165.2; IR (KBr) 2192, 1691, 1604, 1455, 1399, 1237 cm^{-1}; UV (MeOH) 256.2 nm (ε 11050), 268.3 (8350, sh), 305.8 (16400), 317.9 (14700, sh), 427.0 (32900); Found: C, 65.40; H, 4.46; N, 5.43%. Calcd for $C_{14}H_{11}O_2NS$: C, 65.34; H, 4.32, N, 5.44%].

Preparation of 25. An Ac_2O solution (5 cm^3) of **23** (113 mg, 0.83 mmol) and **6** (281 mg, 2.83 mmol) was heated at 110-130 ℃ for 5 h. After removing the volatile material in vacuo, the resultant crystalline mass was chromatographed (EtOAc:hexane=2:1) to give **26** [orange crystals, mp 143-145 ℃ (EtOH); 83 mg, 47%; ^{1}H NMR conformer **A** δ 3.80 (6H, s), 6.21 (1H, dd, J=9.5, 2.9 Hz), 6.85 (1H, dd, J=13.2, 2.9 Hz), 6.96 (1H, dd, J = 12.1, 9.5 Hz), 7.55 (1H, dd, J = 13.2 2.6 Hz), 8.51 (1H, dd, J = 12.1, 2.6 Hz);

conformer **B** δ 3.80 (6H, s), 6.18 (1H, dd, J=9.5, 2.9 Hz), 6.83 (1H, dd, J=13.2, 2.9 Hz), 6.98 (1H, dd, J=12.1, 9.5 Hz), 7.24 (1H, dd, J=12.1, 2.6 Hz), 8.87 (1H, dd, J=13.2, 2.6 Hz); ^{1}H NMR (DMF-d_7 at 70.1 ℃) conformer **A** δ 3.77 (3H, s), 3.90 (3H, s), 6.62 (1H, dd, J=9.5, 3.3 Hz), 7.04 (1H, dd, J=12.8, 3.3 Hz), 7.21 (1H, dd, J=12.1, 9.5 Hz), 7.56 (1H, dd, J=12.8, 2.6 Hz), 8.46 (1H, dd, J=12.1, 2.6 Hz); conformer **B** δ 3.77 (3H, s), 3.90 (3H, s), 6.61 (1H, dd, J=9.2, 2.9 Hz), 7.04 (1H, dd, J=13.2, 2.9 Hz), 7.18 (1H, dd, J=11.7, 2.6 Hz), 7.30 (1H, dd, J=11.7, 9.2 Hz), 8.82 (1H, dd, J=13.2, 2.6 Hz); ^{13}C NMR conformer **A** δ 51.86, 56.0, 87.5, 111.2, 119.1, 127.2, 134.3, 137.0, 137.5, 159.8, 165.2, 165.6; conformer **B** δ 51.91, 56.0, 87.5, 110.4, 118.9, 129.2, 134.8, 135.5, 137.9, 160.0, 165.3, 166.3; IR (KBr) 2186, 1690, 1264, 1215 cm^{-1}; UV (MeOH) 238.2 nm (ε 11850, sh), 276.0 (7900), 417.4 (29200); MS m/z (rel intensity) 217 (M^+, 79), 186 (79), 115 (100); Found: C, 66.57; H, 5.22; N, 6.65%. Calcd for $C_{12}H_{11}O_3N$: C, 66.37; H, 5.07; N, 6.45%].

Condensation of 25 with Dimethylamine. Formation of 27. A 36%-aqueous Me_2NH solution (2.8 cm^3) of **25** (26 mg, 0.12 mmol) was heated at 60 ℃ in a sealed tube for 2 h. The mixture was cooled and the precipitates were collected. The precipitates were washed with EtOH to give red crystals. The filtrate was concentrated and chromatographed (EtOAc:hexane = 2:1-1:1) to give red crystals. The combined crystals were recrystallized to give **27** [red crystals; mp 198-199 ℃ (EtOH); 16 mg, 58%; ^{1}H NMR conformer **A** δ 3.19 (6H, s), 3.76 (3H, s), 6.0-7.15 (2H, m), 7.68 (1H, dd, J=13.2, 2.9 Hz), 8.38 (1H, dd, J=11.7, 2.9 Hz); conformer **B** δ 3.19 (6H, s), 3.76 (3H, s), 6.10 (1H, dd, J=10.6, 2.9 Hz), 6.9-7.15 (3H, m), 9.00 (1H, dd, J=13.2, 1.5 Hz); ^{1}H NMR (DMF-d_7 at −10.0 ℃) conformer **A** δ 3.34 (6H, s), 3.68 (3H, s), 6.48 (1H, dd, J=11.0, 3.3 Hz), 7.28 (1H, t, J=11.0 Hz), 7.54 (1H, dd, J=12.8, 3.3 Hz), 7.67 (1H, dd, J=12.8, 2.6 Hz), 8.40 (1H, dd, J=11.0, 2.6 Hz); conformer **B** δ 3.34 (6H, s), 3.68 (3H, s), 6.46 (1H, dd, J=11.0, 3.3 Hz), 6.95 (1H, dd, J=11.0, 2.6 Hz), 7.34 (1H, t, J=11.0 Hz), 7.44 (1H, dd, J=13.2, 3.3 Hz), 9.11 (1H, dd, J=13.2, 2.6 Hz); ^{13}C NMR conformer **A** δ 41.61 (2C), 51.25, 79.2, 112.4, 121.0, 123.2, 128.7, 138.8, 139.8, 157.4, 158.3, 166.7; conformer **B** δ 41.58 (2C), 51.30, 79.2, 111.6, 121.5, 124.3, 128.2, 136.1, 139.7, 158.0, 159.0, 166.8; IR (KBr) 2178, 1671, 1359, 1271, 1240 cm^{-1}; UV (MeOH) 225.1 nm (ε 18900), 244.3 (13550, sh), 311.8 (7500, sh), 326.9 (8300), 343.5 (7200, sh), 474.1 (39550); MS m/z (rel intensity) 230 (M^+, 100), 199 (7), 156 (10), 128 (22), 115 (26), 77 (32); Found: C, 67.77; H, 6.18; N, 12.46%. Calcd for $C_{13}H_{14}O_2N_2$: C, 67.80; H, 6.14; N, 12.17%].

Preparation of 24. An EtOH solution (30 cm^3) of **17** (826 mg, 3 mmol) and 70%-NaSH (350 mg, 4.37 mmol) was sonicated for 30 min. To the resultant solution were added MeI (1 cm^3) and K_2CO_3 (830 mg) and the mixture was stirred for 14 h. After the evaporation of the solvent, the residue was diluted with CH_2Cl_2 and the organic layer was washed with saturated NaCl solution and dried over Na_2SO_4. The solvent was removed in vacuo and the residue was chromatographed on a silica-gel column and on a PTLC plate to give **24** [yellow crystals: mp 31-33 ℃ (EtOAc-hexane); 88 mg, 19%; ^{1}H NMR δ 2.46 (3H, s), 6.53 (1H, dm, J=9.2 Hz), 6.80 (1H, ddd, J=12.1, 2.6, 0.7 Hz), 6.89 (1H, ddd, J=12.5, 2.6, 0.7 Hz), 6.94 (1H, dd, J=12.5, 2.2 Hz), 7.01 (1H, dd, J=12.1, 9.2 Hz); ^{13}C NMR δ 15.7, 124.6, 135.3, 136.35, 136.43, 140.0, 149.6, 187.4; IR (KBr) 1623, 1563, 1505 cm^{-1}; UV (MeOH) 245.8 nm (ε 12900), 290.7 (5700), 280.5 (5300, sh), 227.4 (16700); MS m/z

(rel intensity) 152 (M^+, 28), 124 (100), 109 (48); Found: C, 63.03; H, 5.27%. Calcd for C_8H_8OS: C, 63.12; H, 5.31%] and **28** [a brownish oil; 41 mg, 7%; ^1H NMR δ 2.46 (3H, s), 6.90 (1H, ddd, J=11.7, 2.9, 1.1 Hz), 6.99 (1H, ddd, J=12.1, 2.9, 1.1 Hz), 7.09 (1H, dd, J =11.7, 8.8 Hz), 7.21 (1H, dd, J=12.1, 1.8 Hz), 7.27 (1H, m); ^{13}C NMR δ 22.3, 128.0, 134.7, 134.9, 138.9, 140.7, 145.7, 187.1; IR (NaCl) 1626, 1574, 1512, 1226 cm^{-1}; UV (MeOH) 228.3 nm (ε 16300), 276.3 (5100), 333.3 (9400); MS m/z (rel intensity) 184 (M^+, 15), 156 (100), 141 (93); Found: C, 52.13; H, 4.54%. Calcd for $C_8H_8O_3S$: C, 52.16; H, 4.39%].

Condensation of 24 with 6. An Ac_2O solution (5 cm^3) of **24** (58 mg, 0.38 mmol) and **6** (112 mg, 1.13 mmol) was heated at 130-150 ℃ for 5 h. After the reaction, the mixture was poured into water and extracted with EtOAc. The organic layer was washed with sat. NaCl solution and dried over Na_2SO_4. After removing the volatile material in vacuo, the resultant crystalline mass was chromatographed to give **26** [orange crystals; mp 144.5-146.5 ℃ (EtOH); 13 mg, 14%; ^1H NMR conformer **A** δ 2.45 (3H, s), 3.80 (3H, s), 6.46 (1H, dd, J=8.1, 1.8, Hz), 6.76-6.92 (2H, m), 7.36 (1H, dd, J=12.5, 2.6 Hz), 8.50 (1H, dd, J=12.1, 2.6 Hz); conformer **B** δ 2.45 (3H, s), 3.80 (3H, s), 6.43 (1H, dd, J= 9.2, 1.8 Hz), 6.76-6.92 (2H, m), 7.24 (1H, dd, J=12.1, 2.9 Hz), 8.64 (1H, dd, J=12.8, 2.9 Hz); ^1H NMR (DMF-d_7 at 90.1 ℃) conformer **A** δ 2.58 (3H, s), 3.79 (3H, s), 6.84 (1H, ddd, J=8.8, 2.2, 0.7 Hz), 7.03 (1H, dd, J=12.1, 8.8 Hz), 7.17 (1H, dd, J=12.5, 2.2 Hz), 7.36 (1H, dd, J=12.5, 2.6 Hz), 8.40 (1H, ddd, J=12.1, 2.6, 0.7 Hz); conformer **B** δ 2.58 (3H, s), 3.79 (3H, s), 6.82 (1H, ddd, J=8.4, 2.2, 1.1 Hz), 7.06 (1H, dd, J=12.8, 2.2 Hz), 7.12 (1H, t, J=11.7 Hz), 7.20 (1H, ddd, J=11.7, 2.6, 1.1 Hz), 8.54 (1H, dd, J=12.8, 2.6 Hz); ^{13}C NMR conformer **A** δ 15.7, 52.01, 89.0, 118.7, 127.0, 129.4, 135.1, 136.2, 138.0, 152.2, 160.4, 164.9; conformer **B** δ 15.7, 52.04, 89.0, 118.6, 126.1, 131.5, 132.6, 136.7, 137.3, 153.1, 160.4, 164.9; IR (KBr) 2188, 1691, 1519, 1228 cm^{-1}; UV (MeOH) 227.0 nm (ε 10700, sh), 246.6 (9800), 321.4 (10800), 429.6 (26250); MS m/z (rel intensity): 233 (M^+, 100), 202 (83), 186 (75), 159 (62); Found: C, 61.55; H, 4.80; N, 5.92%. Calcd for $C_{12}H_{11}O_2NS$: C, 61.77; H, 4.76; N, 6.01%].

Preparation of 7-Isopropyl-2-(2-chloro-2-propenylthio)tropones (30). A pyridine solution (4 cm^3) of 3-isopropyltropolone (730 mg, 4.8 mmol) and *p*-toluenesulfonyl chloride (1.1 g, 5.8 mmol) was stirred at 0 ℃ for 8 h. The reaction mixture was then poured into cooled 2N HCl solution, and the aqueous layer was extracted with EtOAc. The organic layer was washed with water, dried, and concentrated. The product was recrystallized from EtOAc:hexane (1:3) to give **29** [colorless needles, mp 89-91 ℃; 1.35 g (92%); ^1H NMR δ 1.08 (3H, s), 1.11 (3H, s), 2.43 (3H, s), 3.41 (1H, sept, J=7.0 Hz), 6.88 (1H, t, J=9.5 Hz), 7.10 (1H, td, J=9.5, 1.1 Hz), 7.25 (1H, d, J=9.2 Hz), 7.33 (2H, d, J=8.4 Hz), 7.41 (1H, dd, J=9.2, 1.1 Hz), 7.90 (2H, d, J=8.4 Hz); ^{13}C NMR δ 21.7, 22.2 (2C), 30.6, 128.5, 128.6 (2C), 129.3, 129.6 (2C), 132.1, 133.4, 134.2, 145.3, 153.3, 160.8, 178.5; IR (KBr) 1597, 1359, 1194, 1178, 1083, 1064, 836, 758 cm^{-1}; UV (MeOH) 231 nm (ε 31300), 318 (7500); MS m/z (rel intensity) 318 (M^+, 6), 254 (31), 164 (12), 163 (100), 155 (9); Found: C, 64.23; H, 5.59%. Calcd for $C_{17}H_{18}O_4S$: C, 64.16; H, 5.66%].

Then, an EtOH solution (10 cm^3) of **29** (1.07 g, 3.38 mmol) and 70%-NaSH (325 mg, 4.06 mmol) was stirred at room temperature for 1 h, NaOMe (244 mg, 4.06 mmol) was

added to the mixture, and the resultant mixture was stirred for 1 h, to which, an EtOH solution (2 cm^3) of 2,3-dichloro-1-propene **14** (563 mg, 5.07 mmol) was added and stirred for another 3 h. The precipitates were filtered and the filtrate was concentrated. The residue was chromatographed (EtOAc:hexane=1:3) to give **30** [a yellow oil, 557 mg, 65%, ^{1}H NMR δ 1.18 (6H, d, J=7.0 Hz), 3.59 (1H, sept, J=7.0 Hz), 3.74 (2H, br s), 5.39 (1H, dt, J=1.8, 1.5 Hz), 5.59 (1H, dt, J=1.8, 0.7 Hz), 6.99 (1H, ddm, J=10.2, 1.5 Hz), 7.01 (1H, dm, J=11.7 Hz), 7.02-7.08 (1H, m), 7.30-7.34 (1H, m); ^{13}C NMR δ 22.6 (2C), 30.6, 39.4, 115.1, 127.9, 130.4, 130.5, 132.6, 135.9, 154.3, 154.7, 182.3; IR (neat) 2962, 1633, 1555, 1485, 1407, 1363, 1203, 1108, 1025, 893, 790, 747 cm^{-1}; UV (MeOH) 229 nm (ε 10500), 255 (11800), 276 (8300, sh), 345 (9500), 364 (8600, sh); MS m/z (rel intensity) 256 (M^+ for ^{37}Cl, 12), 254 (M^+ for ^{35}Cl, 34), 219 (100), 179 (67), 91 (24), 39 (18). Found: m/z 256.0507 (M^+ for ^{37}Cl), 254.0530 (M^+ for ^{35}Cl). Calcd for $C_{13}H_{15}OSCl$: 256.0502 (M, for ^{37}Cl), 254.0531 (M, for ^{35}Cl)].

Claisen Rearrangement of Isopropyl-2-(2-chloro-2-propenylthio)tropones (30). An anhydrous DMF solution (4 cm^3) of , **30** (490 mg, 1.92 mmol) in a sealed tube was heated at 180 ℃ for 30 min. The reaction mixture was diluted with water and extracted with benzene. The organic layer was washed with 2N NaOH solution and water, dried, and evaporated. The residue was chromatographed (EtOAc:hexane = 1:1) to give the rearrangement products, **31** [a pale yellow oil, 250 mg, 66%; ^{1}H NMR δ 1.23 (6H, d, J=7.0 Hz), 2.58 (3H, d, J=1.1 Hz), 3.67 (1H, sept, J=7.0 Hz), 6.94 (1H, dd, J=10.6, 9.6 Hz), 7.05 (1H, q, J=1.1 Hz), 7.31 (1H, d, J=9.6 Hz), 7.37 (1H, d, J=10.6 Hz); ^{13}C NMR δ 16.1, 22.6 (2C), 29.9, 127.6, 128.8, 130.4, 131.9, 141.1, 148.5, 150.4, 152.7, 179.3; IR (neat) 2960, 1622, 1554, 1521, 1490, 1462, 1402, 1348, 1085, 997, 900, 839, 789, 746, 658 cm^{-1}; UV (MeOH) 204 nm (ε 11200), 246 (21900), 291 (17800), 324 (7400, sh), 350 (4900, sh), 346 (3200); MS m/z (rel intensity) 218 (M^+, 100), 203 (79), 190 (20), 175 (30), 147 (15), 115 (8); Found: C, 71.22; H, 6.37%. Calcd for $C_{13}H_{14}OS$: C, 71.52; H, 6.46%].

Condensation of 31 with 6 to give 7-Isopropyl-2-methylcyclohepta[*b*]thiophen-8-one (32). Similar treatment of **31** (218 mg, 1.00 mmol) with **6** (300 mg, 3.0 mmol) gave **32** [yellow needles, mp 121-123 ℃ (cyclohexane-EtOAc), 231 mg, 77%; ^{1}H NMR δ 1.11 (6H, d, J=6.6 Hz), 2.53 (3H, d, J=1.1 Hz), 3.02 (1H, sept, J=6.6 Hz), 3.81 (3H, s), 6.37 (1H, dd, J=7.0, 1.1 Hz), 6.59 (1H, ddd, J=11.0, 7.0, 1.1 Hz), 6.84 (1H, q, J=1.1 Hz), 6.99 (1H, d, J=11.0 Hz); ^{13}C NMR δ 15.4, 22.9 (2C), 36.2, 52.8, 101.3, 116.6, 119.6, 126.0, 126.3, 127.2, 128.4, 139.9, 141.7, 141.8, 161.3, 162.0; IR (KBr) 2966, 2212, 1724, 1620, 1545, 1432, 1334, 1245, 1119, 1085, 843, 778 cm^{-1}; UV (MeOH) 240 nm (ε 12900, sh), 294 (6900), 396 (6900); MS m/z (rel intensity) 299 (M^+, 9), 257 (9), 231 (100); Found: C, 68.31; H, 5.78; N, 4.46%. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68%].

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