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# PREPARATION OF NEW HEPTAFULVENES AND THE RELATED COMPOUNDS DERIVED FROM 2*H*-CYCLOHEPTA[*d*]THIAZOL-2-ONE AND -2-THIONE

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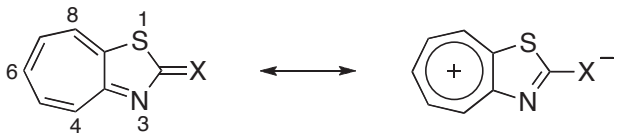
**Abstract** – 2*H*-Cyclohepta[*d*]thiazol-2-one reacted with dimethyl malonate in the presence of sodium hydride to generate the 6- and 4-adducts, which were oxidized by DDQ to afford a 2-thiazolone-fuzed heptafulvene and a tricyclic compound, respectively. The reaction of 2*H*-cyclohepta[*d*]thiazol-2-thione under the same addition conditions gave the similar 6- and 4-adducts. Oxidation of each separated adducts afforded the corresponding regioisomeric heptafulvene disulfides with thiazole rings, respectively.

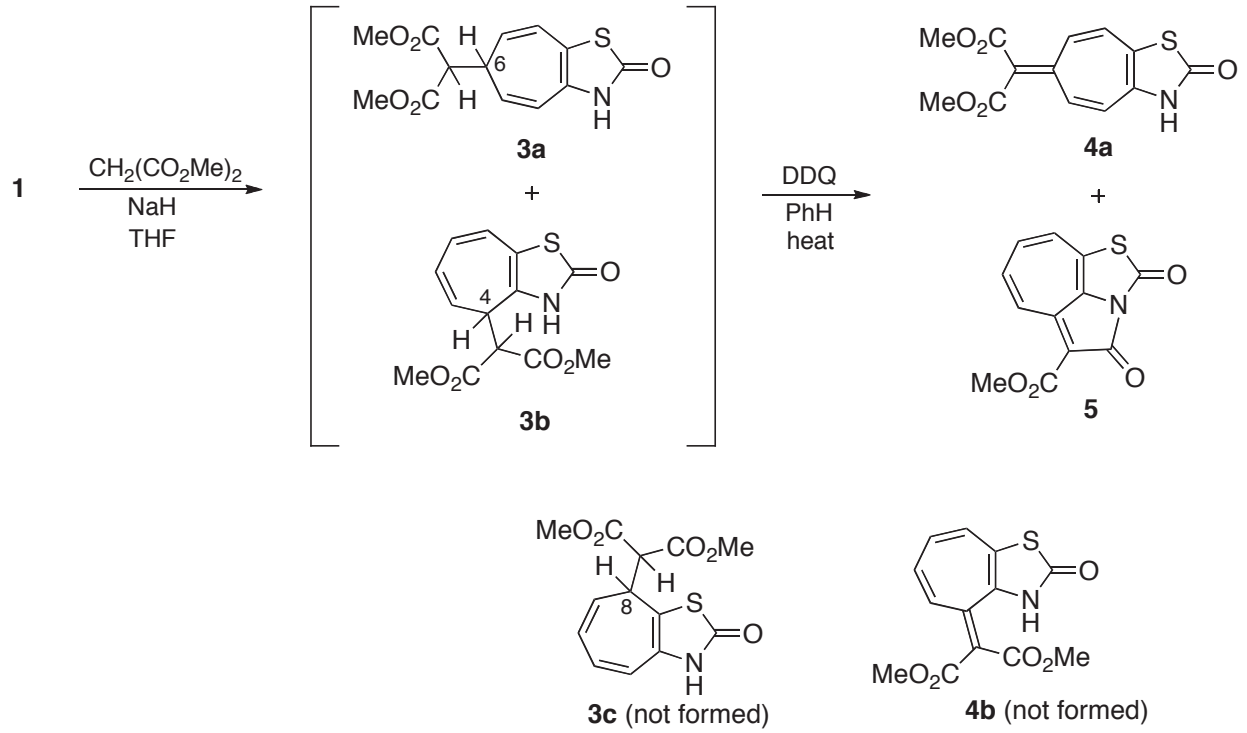
2*H*-Cyclohepta[*d*]thiazol-2-one (**1**) and the sulfur analogue, -2-thione (**2**) are classified as non-benzenoid aromatics, and their chemical and physical properties are of interest because of their polarized structure similar to that of azulenes. Although some preparation methods[1,2] and cycloaddition reactions[3,4] of **1** were reported, no attempt for the reaction with nucleophiles is known so far as we are aware. In this manuscript, we report the reactions of **1** and **2** with dimethyl malonate in the presence of sodium hydride and the successive oxidation that furnish new thiazolone/thiazole-fused heptafulvene systems. Heptafulvenes with electron-deficient substituents are stable compounds and their highly polarized properties have attracted attention for chemists, however, their synthetic methods have not been much investigated.[5-9]




**1**: X = O
**2**: X = S

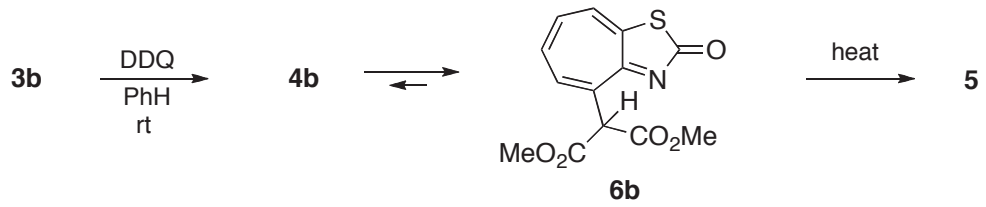
This paper is dedicated to Prof. Victor Snieckus on the occasion of the 77th birthday.

A reaction of **1** and dimethyl malonate with sodium hydride generated a mixture of **3a** and **3b**, adducts at the 6- and 4-positions, respectively. In this reaction, the 8-adduct (**3c**) was not formed. The calculated heats of formation using DFT method (B3LYP/6-31G*)[10] supported these results to a certain extent (**3a**: 0 kcal/mol, **3b**: +2.6 kcal/mol, **3c**: +52.6 kcal/mol). When the mixture was oxidized by DDQ, **3a** afforded a thiazolone-fuzed heptafulvene, 6-[di(methoxycarbonyl)methylene]-3*H*-cyclohepta[*d*]thiazol-2-one (**4a**, 33% from **1**), whereas **3b** produced not a heptafulvene (**4b**) but a tricyclic compound, methyl 2,3-dioxo-1-thia-2a-azacyclopent[*cd*]azulene-4-carboxylate (**5**, 41% from **1**).




Scheme 1

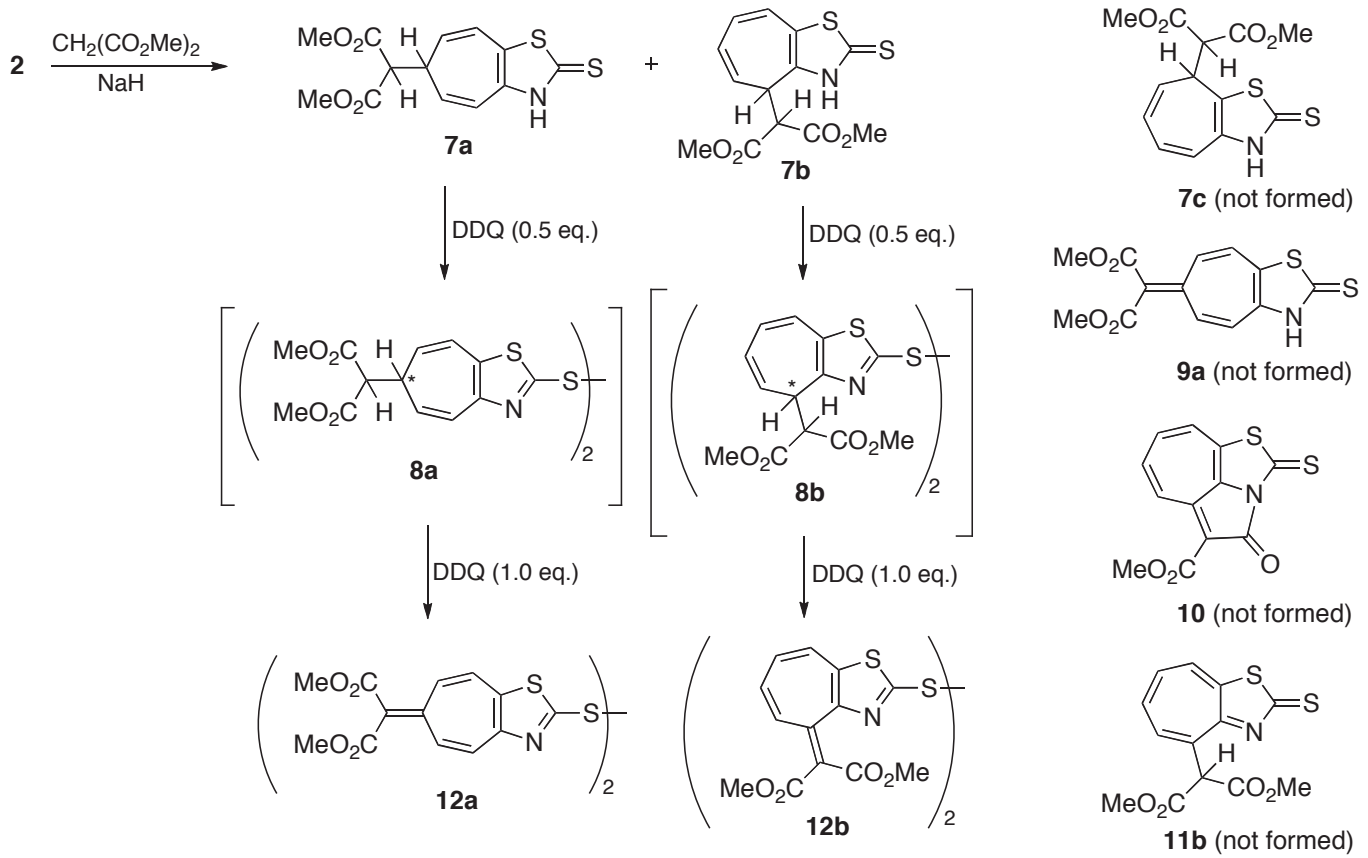
The mixture of **3a** and **3b** were able to separate by recrystallization (hexane-$CH_2Cl_2$). Treatment of separated **3b** with DDQ at room temperature formed 4-substituted cycloheptathiazol-2-one (**6b**, 67%), which was a tautomer of unstable **4b** (**6b**: 0 kcal/mol, **4b**: +71 kcal/mol by B3LYP/6-31G*). The intramolecular cyclization of isolated **6b** was accomplished under thermal conditions to give **5** (75%).




Scheme 2

The synthetic heptafulvene (**4a**) was an orange solid [155-156 °C (dec.)]. The $^1$H NMR spectrum showed four protons at $\delta$ 6.70, 6.90, 7.08 and 7.31 as a seven-membered ring moiety and a singlet peak at $\delta$ 3.68 as $CO_2Me$ moieties (chemically equivalent six protons). A NH proton was also observed at $\delta$ 11.23. The $^{13}$C NMR spectrum showed thirteen carbons involving three kinds of carbonyl ones ($\delta$ 166.3, 166.4 and 169.7). IR and MS spectra gave N-H and C=O stretching peaks ($\nu$ 3025, 1748, 1740, 1690) and a molecular ion peak [*m/z* 294 ($MH^+$)]. The tricyclic compound (**5**) was a yellow solid [284-285 °C (dec.)]. The $^1$H NMR spectrum showed four protons at $\delta$ 7.63, 7.86, 8.08 and 8.66 with appropriate coupling constants ($J$ = 11.2 and/or 9.4 Hz) as a seven-membered ring moiety and a singlet peak at $\delta$ 3.79 ($CO_2Me$, 3H). The $^{13}$C NMR spectrum showed three kinds of carbonyl carbons ($\delta$ 158.8, 162.8 and 163.7) within the twelve ones. IR and MS spectra gave three kinds of C=O stretching peaks ($\nu$ 1755, 1736 and 1705) and a molecular ion peak [*m/z* 262 ($MH^+$)]. Together with elemental analysis results of **4** and **5**, those spectral data supported their structures. Physical data of the intermediates **3a, 3b** and **6b** were also consistent with their proposed structures, respectively.

We next focused on the chemical properties of 2*H*-cyclohepta[*d*]thiazol-2-thione (**2**), the sulfur analogue of **1**. Preparation of **2** (75%) was carried out by the thermal reaction of **1** with Lawesson's reagent.[11,12] **2** was a reddish black solid [mp 141-142 °C (dec.)] and the structure was confirmed by the measurement of instrumental analysis data.




Scheme 3

The reaction of **2** under same addition conditions in the case of **1** afforded the 4- and 6-adducts **7a** (35%) and **7b** (48%), which were separated by recrystallization. The 8-adduct (**7c**) was not formed in a similar manner as described above. Oxidation of isolated **7a** with 0.5 mol *eq*. of DDQ at room temperature might produce not a heptafulvene monomer (**9a**) but a disulfide (**8a**) as a mixture of diastereoisomers. In the case of **7b**, the product might be a disulfide (**8b**), which was neither a tricyclic compound (**10**) nor 4-substituted cycloheptathiazol-2-thione (**11b**). The crude **8a** or **8b** was oxidized by further 1.0 mol *eq*. of DDQ to afford a heptafulvene disulfide, bis{[6-di(methoxycarbonyl)methylene]cyclohepta[*d*]thiazol-2-yl} disulfide [**12a**, a reddish orange solid; 173-174 °C (dec.), 63% from **7a**] or a 4-regioisomer (**12b**, red needles; mp 86-87 °C, 84% from **7b**), respectively. The structures of **7a**, **7b**, **12a** and **12b** were confirmed by the measurement of instrumental analysis data.

In conclusion, we have succeeded in the preparation of new thiazolone/thiazole-fuzed heptafulvenes derived from 2*H*-cyclohepta[*d*]thiazol-2-one (**1**) and -2-thione (**2**). Further work, aimed at the electrochemical properties arising from the contribution of their polarized structures and their chemical transformations toward the construction of functional compounds, is in progress.

## EXPERIMENTAL

Mps were determined with a Laboratory Devices MEL-TEMP apparatus and are uncorrected. $^{1}H$ and $^{13}C$ NMR spectra ($SiMe_4$ as the internal standard) were obtained with Bruker AV500, AM400, AV300, AC300 and/or AC200 spectrometers. IR spectra were obtained with a Perkin Elmer System 2000 FT instrument. MS spectra were obtained with a JEOL JMS700AM spectrometer. Unless otherwise stated the spectra were taken in the following solvents/media: IR, KBr; $^{1}H$ and $^{13}C$ NMR, $CDCl_3$; MS spectra were taken at 70 eV by electron impact (EI) and/or fast atom bombardment (FAB) method. The progress of reactions was followed by TLC method using Merck Silica gel $60F_{254}$.

**Preparation of a heptafulvene (4a) and a tricyclic compound (5):** To a solution of **1**[1] (130 mg, 8.0 x $10^{-1}$ mmol) in dry THF (5.0 mL), a mixture of dimethyl malonate (1.2 mol *eq*.) and sodium hydride (1.2 mol *eq*.) in dry THF (1.0 mL) was added at 0 °C under $N_2$. The solution was stirred for 4 h at rt. The reaction mixture was quenched with sat. *aq*. $NH_4Cl$ and the aqueous layer was extracted with $CH_2Cl_2$. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a mixture of crude **3a** and **3b**. To a solution of the mixture in benzene (6.0 mL), DDQ (1.0 mol *eq*.) was added and the reaction mixture was refluxed for 1 h. The solvent was removed and the residue was purified by $SiO_2$ column chromatography and/or recrystallization (hexane-$CH_2Cl_2$) to give **4a** (77 mg, 33%) and **5** (96 mg, 41%). The mixture of **3a** and **3b** was able to separate by recrystallization (hexane-$CH_2Cl_2$). A benzene (1.0 mL) solution of separated **3a** (10 mg, 3.4 x $10^{-2}$ mmol) and DDQ (1.0 mol *eq*.) was stirred for 2 h at rt under Ar. After removal of the solvent *in vacuo*, the residue was purified

by $SiO_2$ column chromatography to give **4a** (6.8 mg, 68%). A benzene (2.0 mL) solution of separated **3b** (30 mg, 1.0 x $10^{-1}$ mmol) and DDQ (1.0 mol *eq*.) was stirred for 2 h at rt under Ar and the solvent was removed. The resulting crude materials were recrystallized with benzene-hexane to give **6b** (20 mg, 67%). A benzene (1.0 mL) solution of **6b** (10 mg, 3.4 x $10^{-2}$ mmol) was refluxed for 2 h under Ar and the resulting solid was purified by recrystallization (hexane-$CH_2Cl_2$) to give **5** (6.7 mg, 75%).

**6-Adduct (3a):** colorless crystals; mp 160 °C (dec.); $^1$H NMR $\delta$ 2.79 (dt, $J$ = 11.2, 6.0 Hz, 1H), 3.77 (s, 6H), 3.80 (d, $J$ = 11.2 Hz, 1H), 5.24 (dd, $J$ = 9.6, 6.0 Hz, 1H), 5.44 (dd, $J$ = 9.6, 6.0 Hz, 1H), 6.34 (d, $J$ = 9.6 Hz, 1H), 6.37 (d, $J$ = 9.6 Hz, 1H), 9.61 (br.s, 1H); $^{13}$C NMR $\delta$ 38.3, 52.8 (2C), 53.2, 116.6, 119.3, 119.8, 120.6, 123.6, 132.6, 168.3 (2C), 172.2; IR (KBr) $\nu$ 3130, 1738, 1644 cm$^{-1}$; MS (FAB, NBA) *m/z* 296 ($MH^+$). Anal. Calcd for $C_{13}H_{13}NO_5S$: C, 52.87; H, 4.44; N, 4.74. Found: C, 52.71; H, 4.29; N, 4.78.

**4-Adduct (3b):** colorless needles; mp 110 °C (dec.); $^1$H NMR $\delta$ 3.49 (d, $J$ = 11.2 Hz, 1H), 3.68 (s, 3H), 3.72 (s, 3H), 4.25 (dd, $J$ = 11.2, 8.5 Hz, 1H), 5.54 (t like, $J$ = 10.4 Hz, 1H), 6.26 (m, 1H), 6.40-6.50 (m, 2H), 9.21 (br.s, 1H); $^{13}$C NMR $\delta$ 37.2, 49.7, 52.9, 53.1, 113.3, 121.4, 123.1, 124.8, 127.0, 128.3, 167.3, 168.0, 174.0; IR (KBr) $\nu$ 3152, 1759, 1733, 1675 cm$^{-1}$; MS (FAB, NBA) *m/z* 296 ($MH^+$). Anal. Calcd for $C_{13}H_{13}NO_5S$: C, 52.87; H, 4.44; N, 4.74. Found: C, 52.91; H, 4.26; N, 4.83.

**Heptafulvene (4a):** an orange solid; mp 155-156 °C (dec.); $^1$H NMR (DMSO-$d_6$) $\delta$ 3.68 (s, 6H), 6.70 (d, $J$ = 12.5 Hz, 1H), 6.90 (d, $J$ = 12.5 Hz, 1H), 7.08 (dd, $J$ = 12.5, 2.2 Hz, 1H), 7.31 (dd, $J$ = 12.5, 2.2 Hz, 1H), 11.23 (br.s, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 52.19, 52.21, 113.9, 122.9, 124.1, 126.1, 129.5, 131.9, 137.8, 148.0, 166.3, 166.4, 169.7; IR (KBr) $\nu$ 3025, 1748, 1740, 1690 cm$^{-1}$; MS (FAB, NBA) *m/z* 294 ($MH^+$). Anal. Calcd for $C_{13}H_{11}NO_5S$: C, 53.24; H, 3.78; N, 4.78. Found: C, 53.06; H, 3.75; N, 4.84.

**Tricyclic compound (5):** a yellow solid; mp 284-285 °C (dec.); $^1$H NMR (DMSO-$d_6$) $\delta$ 3.79 (s, 3H), 7.63 (dd, $J$ = 11.2, 9.4 Hz, 1H), 7.86 (dd, $J$ = 11.2, 9.4 Hz, 1H), 8.08 (d, $J$ = 11.2 Hz, 1H), 8.66 (d, $J$ = 11.2 Hz, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 51.0, 102.0, 130.0, 131.6, 132.5, 133.9, 138.4, 139.8, 145.5, 158.8, 162.8, 163.7; IR (KBr) $\nu$ 1755, 1736, 1705 cm$^{-1}$; MS (FAB, Thiogly.) *m/z* 262 ($MH^+$). Anal. Calcd for $C_{12}H_7NO_4S$: C, 55.17; H, 2.70; N, 5.36. Found: C, 55.16; H, 2.59; N, 5.43.

**4-Substituted cycloheptathiazol-2-one (6b):** yellow crystals; mp 135 °C (dec.); $^1$H NMR $\delta$ 3.80 (s, 6H), 6.17 (s, 1H), 7.49-7.59 (m, 2H), 8.01-8.04 (m, 1H), 8.06-8.10 (m, 1H); $^1$H NMR (benzene-$d_6$) $\delta$ 3.27 (s, 6H), 6.09 (t like, $J$ = 10 Hz, 1H), 6.35 (s, 1H), 6.37 (t like, $J$ = 10 Hz, 1H), 6.52 (d lile, $J$ = 10 Hz, 1H), 7.78 (d like, $J$ = 10 Hz, 1H); $^{13}$C NMR $\delta$ 53.3 (2C), 56.7, 128.4, 131.5 (2C), 135.1, 137.2, 141.3, 168.1, 171.7 (2C), 177.7; IR (KBr) $\nu$ 1742, 1677 cm$^{-1}$; MS (FAB, NBA) *m/z* 294 ($MH^+$). Anal. Calcd for $C_{13}H_{11}NO_5S$: C, 53.24; H, 3.78; N, 4.78. Found: C, 53.18; H, 3.62; N, 4.84.

**Preparation of cycloheptathiazol-2-thione (2):** A mixture of **1** (326 mg, 2.0 mmol) and Lawesson's reagent (0.5 mol *eq*.) in benzene (20 mL) was refluxed for 4 h under Ar. After removal of the solvent *in*

*vacuo*, the resulting crude material was purified by $SiO_2$ column chromatography to give **2** (270 mg, 75%). The purification should be carried out rapidly because of some lability of **2** in solution.

**Cycloheptathiazol-2-thione (2):** a reddish black solid; mp 141-142 °C (dec.); $^1$H NMR $\delta$ 7.50-7.56 (m, 2H), 7.76-7.83 (m, 1H), 7.95-7.98 (m, 1H), 8.07 (d like, $J$ = 11 Hz, 1H); $^{13}$C NMR $\delta$ 128.7, 132.8, 137.6, 138.2, 141.3, 165.5, 172.9, 206.3; IR (KBr) $\nu$ 1218 cm$^{-1}$; MS (EI) $m/z$ 179 ($M^+$); HRMS (EI) Calcd for $C_8H_5NS_2$: 178.9863. Found: 178.9860.

**Preparation of heptafulvene disulfides (12a and 12b):** To a solution of **2** (90 mg, 5.0 x 10$^{-1}$ mmol) in dry THF (3.0 mL), a mixture of dimethyl malonate (1.2 mol *eq*.) and sodium hydride (1.2 mol *eq*.) in dry THF (3.0 mL) was added at 0 °C under Ar. The solution was stirred for 4 h at rt. The reaction mixture was quenched with sat. *aq*. $NH_4Cl$ and the aqueous layer was extracted with $CH_2Cl_2$. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a mixture of crude **7a** and **7b**. The mixture was separated and purified by recrystallization (hexane-$CH_2Cl_2$) to give **7a** (54 mg, 35%) and **7b** (75 mg, 48%). A benzene (1.0 mL) solution of isolated **7a** (15 mg, 4.8 x 10$^{-2}$ mmol) and DDQ (0.5 mol *eq*.) was stirred for 2 h at rt under Ar and the solvent was removed. $^1$H NMR spectrum of the resulting residue suggested a formation of **8a** as a mixture of diastereoisomers [$\delta$ 2.92-2.98 (m, 2H), 3.73 (d like, $J$ = 11 Hz, 2H), 3.75 (s, 12H), 5.51 (m, 2H), 5.58 (m, 2H), 6.69 (d like, $J$ = 10 Hz, 2H), 6.89 (d like, $J$ = 10 Hz, 2H)]. DDQ (further 1.0 mol *eq*.) was added to a benzene (1.0 mL) solution of the residue and the reaction mixture was stirred for 14 h at rt under Ar. After removal of the solvent *in vacuo*, the resulting crude material was purified by $SiO_2$ column chromatography to give **12a** (9.3 mg, 63% from **7a**). A benzene solution (1.0 mL) of isolated **7b** (30 mg, 9.6 x 10$^{-2}$ mmol) and DDQ (total 1.5 mol *eq*.) was stirred for 14 h at rt under Ar. After removal of the solvent *in vacuo*, the residue was purified by $SiO_2$ column chromatography to give **12b** (25 mg, 84% from **7b**). The reaction of **7b** with DDQ (0.5 mol *eq*.) at rt for 2 h in benzene gave the similar results in the case of **7a**, which suggested a formation of **8b** as a mixture of diastereoisomers by the $^1$H NMR measurement [$\delta$ 3.59 (s, 6H), 3.74 (s, 6H), 3.92 (d, $J$ = 11.0 Hz, 1H), 3.94 (d, $J$ = 11.0 Hz, 1H), 4.07 (dd, $J$ = 11.0, 6.6 Hz, 1H), 4.11 (dd, $J$ = 11.0, 6.6 Hz, 1H), 5.71 (dd like, $J$ = 10, 7 Hz, 2H), 6.17-6.23 (m, 2H), 6.49-6.60 (m, 2H), 6.81 (d like, $J$ = 11 Hz, 2H)].

**6-Adduct (7a):** brown crystals; mp 106 °C (dec.); $^1$H NMR $\delta$ 2.82 (dt, $J$ = 11.2, 6.3 Hz, 1H), 3.77 (s, 6H), 3.79 (d, $J$ = 11.2 Hz, 1H), 5.36 (dd, $J$ = 9.6, 6.3 Hz, 1H), 5.54 (dd, $J$ = 9.6, 6.3 Hz, 1H), 6.40 (d like, $J$ = 9.6 Hz, 2H), 10.08 (br.s, 1H); $^{13}$C NMR (DMSO-$d_6$) $\delta$ 38.5, 53.1 (3C), 116.8, 119.3, 121.5, 125.3, 127.4, 140.2, 168.6 (2C), 187.5; IR (KBr) $\nu$ 3050, 1737, 1058 cm$^{-1}$; MS (FAB, NBA) $m/z$ 312 ($MH^+$). Anal. Calcd for $C_{13}H_{13}NO_4S_2$: C, 50.14; H, 4.21; N, 4.50. Found: C, 50.32; H, 4.18; N, 4.71.

**4-Adduct (7b):** a brown solid; mp 94 °C (dec.); $^1$H NMR $\delta$ 3.52 (d, $J$ = 11.4 Hz, 1H), 3.69 (s, 3H), 3.74 (s, 3H), 4.37 (dd, $J$ = 11.4, 8.5 Hz, 1H), 5.59 (t like, $J$ = 10 Hz, 1H), 6.26-6.31 (m, 1H), 6.41-6.56 (m, 2H), 11.17 (br.s, 1H); $^{13}$C NMR $\delta$ 36.8, 49.9, 53.2, 53.4, 120.8, 123.1, 123.2, 128.2, 128.5, 131.3, 167.2, 167.7,

189.7; IR (KBr) $\nu$ 2995, 1750, 1725, 1063 $cm^{-1}$; MS (FAB, NBA) *m/z* 312 ($MH^+$). Anal. Calcd for $C_{13}H_{13}NO_4S_2$: C, 50.14; H, 4.21; N, 4.50. Found: C, 49.86; H, 4.05; N, 4.43.

**Heptafulvene disulfide (12a):** a reddish orange solid; 173-174 °C (dec.); $^1H$ NMR $\delta$ 3.79 (s, 3H), 3.81 (s, 3H), 6.83 (d, *J* = 12.3 Hz, 1H), 7.08 (d, *J* = 12.3 Hz, 1H), 7.21 (dd, *J* = 12.3, 2.0 Hz, 1H), 7.29 (dd, *J* = 12.3, 2.1 Hz, 1H); $^{13}C$ NMR $\delta$ 52.4, 52.5, 118.7, 124.9, 128.9, 130.0, 130.7, 140.4, 147.4, 155.7, 166.0, 166.4, 166.7; IR (KBr) $\nu$ 1722, 1682 $cm^{-1}$; MS (FAB, NBA) *m/z* 617 ($MH^+$). Anal. Calcd for $C_{26}H_{20}N_2O_8S_4$: C, 50.64; H, 3.27; N, 4.54. Found: C, 50.49; H, 3.20; N, 4.58.

**Heptafulvene disulfide (12b):** red needles; mp 86-87 °C; $^1H$ NMR $\delta$ 3.78 (s, 3H), 3.80 (s, 3H), 6.48-6.59 (m, 2H), 6.86 (d like, *J* = 10 Hz, 1H), 8.05 (d like, *J* = 10 Hz, 1H); $^{13}C$ NMR $\delta$ 52.1, 52.3, 119.0, 122.9, 129.8, 130.6, 131.0, 141.1, 143.3, 149.3, 164.6, 165.9, 168.4; IR (KBr) $\nu$ 1716, 1695 $cm^{-1}$; MS (FAB, NBA) *m/z* 617 ($MH^+$). Anal. Calcd for $C_{26}H_{20}N_2O_8S_4 \cdot CH_2Cl_2$: C, 46.22; H, 3.16; N, 3.99. Found: C, 46.45; H, 3.04; N, 4.11.

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