Synthesis of 2*H*-Thiopyrans by Rhodium(II) Acetate-Catalyzed Reaction of 4-Amino-2,5-dihydro-3-thiophenecarbonitriles with α-Diazocarbonyl Compounds. Part 1

Kenji Yamagata*, Fumi Okabe, and **Motoyoshi Yamazaki**

Fukuoka (Japan), Faculty of Pharmaceutical Sciences, Fukuoka University

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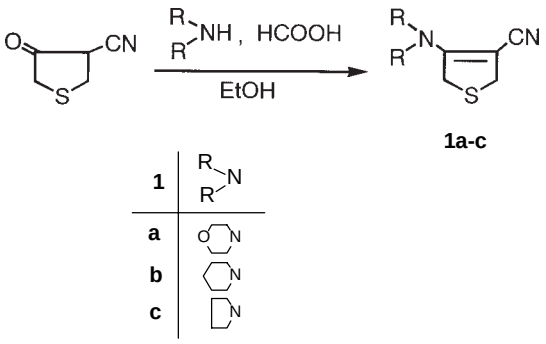
Abstract. 4-Amino-2,5-dihydro-3-thiophenecarbonitriles **1** reacted with dimethyl diazomalonate in the presence of rhodium(II) acetate to give regioselectively 4-cyano-2*H*-thiopyrans **2** (C_2–S insertion), and 5-cyano-2*H*-thiopyrans (C_5–S insertion) were not isolated. Similar insertion was also observed in the reaction of **1** with methyl diazoacetoacetate and ethyl diazobenzoylacetate. The starting compounds **1** were synthesized by the reaction of tetrahydro-4-oxo-3-thiophenecarbonitrile with morpholine, piperidine, and pyrrolidine in the presence of formic acid in ethanol.

The transition-metal-catalyzed reactions of diazo compounds with various types of compounds containing sulfur atom have been extensively studied [1–3]. These reactions have been proposed to proceed through ylide formation by reactions of carbenoids derived from diazo compounds [4–8].

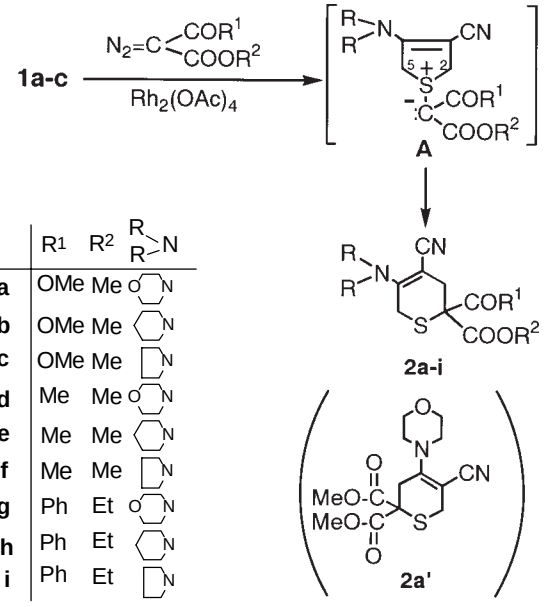
We have already reported that 4,5-dihydro-3-thiophenecarbonitriles react with diethyl diazomalonate in the presence of copper powder to form stable 4,5-dihydrothiophenium-1-bis(ethoxycarbonyl)methylides [9]. In recent study, we showed that 4,5-dihydro-3-thiophenecarbonitriles react with ethyl diazoacetoacetate in the presence of rhodium(II) acetate to yield 1,4-oxathiocines [10]. The formation of the 1,4-oxathiocines involves initial generation of unstable sulfonium ylides which subsequently undergo a thermal rearrangement to give the observed products. In continuation of these studies we investigated the reactions of 2,5-dihydro-3-thiophenecarbonitriles **1** with α-diazocarbonyl compounds in the presence of rhodium(II) acetate in order to prove whether or not stable sulfonium ylides are formed. α-Diazocarbonyl compounds used in this study include dimethyl diazomalonate [11], methyl diazoacetoacetate [12], and ethyl diazobenzoylacetate [13].

The starting compounds 2,5-dihydro-3-thiophenecarbonitriles **1a**–**c** were synthesized by reaction of tetrahydro-4-oxo-3-thiophenecarbonitrile with morpholine, piperidine, and pyrrolidine in the presence of formic acid in ethanol (Scheme 1).



Scheme 1 Preparation of 2,5-dihydro-3-thiophenecarbonitriles **1**

When a mixture of 2,5-dihydro-4-morpholino-3-thiophenecarbonitrile **1a**, dimethyl diazomalonate, and a catalytic amount of rhodium(II) acetate in toluene was refluxed for 2h, dimethyl 4-cyano-2*H*-thiopyran-2,2-dicarboxylate **2a** (C_2–S insertion) was obtained in 63% yield, and the corresponding sulfonium ylide was not isolated (Scheme 2). Ando *et al*. have reported that the photolysis of dimethyl diazomalonate in 2,5-dihydrothiophene give dimethyl 3,6-dihydro-2*H*-thiopyran-2,2-dicarboxylate [14]. The mass spectrum and the results of elemental analysis of **2a** indicate that **2a** has the molecular composition $C_{14}H_{18}N_2O_5S$. The IR spectrum of **2a** displays a band due to the non-conjugated ester carbonyl groups at 1740 cm^{-1}. The reaction was regioselective, and only one of the two possible regioisomers **2a** and dimethyl 5-cyano-2*H*-thiopyran-2,2-dicarboxylate **2a'** (C_5–S insertion) was isolated.



Scheme 2 Reaction of 2,5-dihydro-3-thiophenecarbonitriles **1** with α-diazocarbonyl compounds

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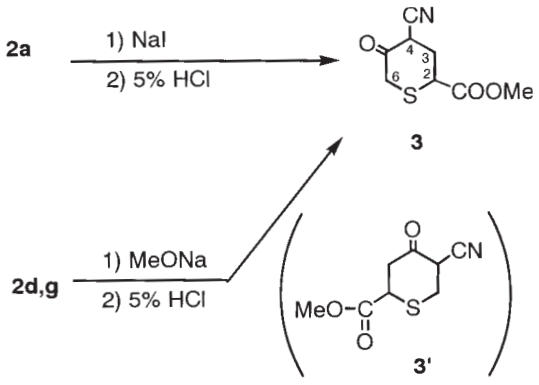
In order to confirm the structure of **2a**, successive treatment of **2a** with sodium iodide and hydrochloric acid resulted in the formation of methyl 4-cyanotetrahydro-5-oxo-2*H*-thiopyran-2-carboxylate **3** (Scheme 3). The ^{1}H NMR spectrum of **3** indicates a pair of one -proton doublets at δ = 3.14 and 3.77 ppm attributable to the two protons of the 6-H of the thiopyran ring and two one-proton double double doublets at δ = 2.84 and 3.07 ppm assignable to the two protons of the 3-H, in addition to the signals due to two methine protons (2-H and 4-H) and a methyl ester protons. In the NOESY spectrum of **3**, the absence of a NOE effect between 2-H and 4-H suggests a *trans* relationship of both protons. These results are consistent with the 4-cyano-5-oxothiopyran **3** rather than the 5-cyano-4-oxothiopyran **3'**. The formation of **3** confirms structure **2a** for the isolated insertion product, since the reaction of regioisomer **2a'** should lead to the formation of **3'**. The formation of the C_2–S insertion product **2a** can be deduced by the mechanism as shown in Scheme 2. Dimethoxycarbonylcarbenoid generated by the rhodium(II) acetate-catalyzed decomposition of dimethyl diazomalonate attacks the sulfur atom of **1a** to form the unstable sulfonium ylide **A**, which undergoes a Stevens rearrangement to form **2a**.

Subsequently, the rhodium(II) acetate-catalyzed reaction of **1a** with methyl diazoacetoacetate and ethyl diazobenzoylacetate in fluorobenzene afforded methyl 2-acetyl-4-cyano-2*H*-thiopyran-2-carboxylate **2d** and ethyl 2-benzoyl-4-cyano-2*H*-thiopyran-2-carboxylate **2g** in 69 and 70% yield, respectively. Successive treatment of **2d** with sodium methoxide and hydrochloric acid furnished **3**. Under the same conditions, compound **2g** was also converted into **3**. These findings indicate that both **2d** and **2g** have 4-cyano-5-morpholino-2*H*-thiopyran structure.



Scheme 3 Formation of 4-cyano-5-oxothiopyran **3**

Reactions of 2,5-dihydro-4-piperidino-(and -4-pyrrolidino)-3-thiophenecarbonitriles **1b**,**c** with α-diazocarbonyl compounds described above gave the corresponding 5-amino-4-cyano-2*H*-thiopyrans **2b**,**c**,**e**,**f**,**h**,**i** in 54 – 73% yields. The structural assignments of **2b**,**c**,**e**,**f**,**h**,**i** were based on the similarity of the ^{1}H NMR signals of 2*H*-thiopyran ring protons with those of **2a**,**d**,**g**.

Experimental

All melting points are uncorrected. IR spectra (KBr) were recorded with a Jasco A-302 instrument. ^{1}H NMR spectra were measured on a Jeol JNM-GX-400 (400 MHz) and Jeol JNM-A500 (500 MHz) in $CDCl_3$ with TMS as internal standard, δ scale; coupling constants in Hz. Mass spectra were recorded with a Jeol JMS-D300, 70eV.
Tetrahydro-4-oxo-3-thiophenecarbonitrile was obtained from commercial source (Tokyo Chemical Industry Co., Ltd.) and used without further purification.

Preparation of 4-Amino-2,5-dihydro-3-thiophenecarbonitriles 1 (General Procedure)

To an ice-cooled and stirred solution of tetrahydro-4-oxo-3-thiophenecarbonitrile (7.62 g, 60 mmol) and formic acid (8.28 g, 180 mmol) in EtOH (150 ml) morpholine (15.66 g, 180 mmol) [piperidine (15.30 g, 180 mmol) or pyrrolidine (12.78 g, 180 mmol)] was added. The mixture was refluxed for 3h. The solvent was removed and H_2O (150 ml) was added to the residue. The mixture was extracted with CH_2Cl_2. The extract was washed with 5% NaOH (50 ml), and then H_2O, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. Yields: **1a** (10.76 g, 91%), **1b** (8.31 g, 71%), and **1c** (10.11 g, 94%).

2,5-Dihydro-4-morpholino-3-thiophenecarbonitrile (**1a**)

Colorless needless; *m.p.* 88 – 89 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2 190 (C≡N). – ^{1}H NMR (400 MHz): δ/ppm = 3.51 – 3.56 [m, 4H, 2CH$_2$ (morpholine)], 3.71 – 3.75 [m, 4H, 2CH$_2$ (morpholine)], 3.79 – 3.83 (m, 4H, 2-H, 5-H). – MS (FAB) *m/z* (%): 197 (100)[M$^+$ + H].

$C_9H_{12}N_2OS$	Calcd.: C 55.08	H 6.16	N 14.27
(196.3)	Found: C 55.18	H 6.19	N 14.27.

2,5-Dihydro-4-piperidino-3-thiophenecarbonitrile (**1b**)

Colorless columns; *m.p.* 70 – 71 °C (Et$_2$O). – IR: ν/cm^{-1} = 2 170 (C≡N). – ^{1}H NMR (400 MHz): δ/ppm = 1.60 – 1.70 [m, 6H, 3CH$_2$ (piperidine)], 3.45 – 3.55 [m, 4H, 2CH$_2$ (piperidine)], 3.75 – 3.85 (m, 4H, 2-H, 5-H). – MS (FAB) *m/z* (%): 195 (86) [M$^+$ + H].

$C_{10}H_{14}N_2S$	Calcd.: C 61.82	H 7.26	N 14.42
(194.3)	Found: C 62.04	H 7.31	N 14.57.

2,5-Dihydro-4-pyrrolidino-3-thiophenecarbonitrile (**1c**)

Colorless needles; *m.p.* 91 – 92 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2 190 (C≡N). – ^{1}H NMR (400 MHz): δ/ppm = 1.90 – 2.00 [m, 4H, 2CH$_2$ (pyrrolidine)], 3.55 – 3.65 [m, 4H, 2CH$_2$(pyrrolidine)], 3.82 (s, 4H, 2-H, 5-H). – MS (FAB) *m/z* (%): 181(90) [M$^+$ + H].

$C_9H_{12}N_2S$	Calcd.: C 59.96	H 6.71	N 15.54
(180.3)	Found: C 60.13	H 6.73	N 15.57.

Reactions of 1 with α-Diazocarbonyl Compounds (General Procedure)

Procedure A: A mixture of **1** (5 mmol), dimethyl diazomalonate [11] (0.87 g, 5.5 mmol), and $Rh_2(OAc)_4$ (0.02 g) in toluene (10 ml) was refluxed for 2h. The solvent was removed and the residue was purified by column chromatography on

silica gel with CH_2Cl_2 as eluent. Yields: **2a** (1.02 g, 63%), **2b** (0.98 g, 60%), and **2c** (0.99 g, 64%).

Procedure B: A mixture of **1** (5 mmol), methyl diazoacetoacetate [12] (0.78 g, 5.5 mmol), and $Rh_2(OAc)_4$ (0.02 g) in C_6H_5F (10 ml) was refluxed for 2h. The solvent was removed and the residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent. Yields: **2d** (1.07 g, 69%), **2e** (1.07 g, 66%), and **2f** (0.79 g, 54%).

Procedure C: From **1** (5 mmol) and ethyl diazobenzoylacetate [13] (1.20 g, 5.5 mmol) as described for *Procedure B*. Yields: **2g** (1.36 g, 70%), **2h** (1.40 g, 73%), and **2i** (1.30 g, 70%).

Dimethyl 4-Cyano-3,6-dihydro-5-morpholino-2H-thiopyran-2,2-dicarboxylate (**2a**)

From **1a** (0.98 g, 5 mmol). Colorless prisms; *m.p*. 84–85 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2 180 (C≡N), 1 740 (C=O). – ^{1}H NMR (500 MHz): δ/ppm = 3.00 (s, 2H, 3-H), 3.24 (s, 2H, 6-H), 3.42–3.60 [m, 4H, $2CH_2$ (morpholine)], 3.72–3.76 [m, 4H, $2CH_2$(morpholine)], 3.81 (s, 6H, $2OCH_3$). – MS (FAB) *m/z* (%): 327 (100) [M$^+$ + H].

$C_{14}H_{18}N_2O_5S$	Calcd.: C 51.52	H 5.56	N 8.58
(326.4)	Found: C 51.59	H 5.47	N 8.59.

Dimethyl 4-Cyano-3,6-dihydro-5-piperidino-2H-thiopyran-2,2-dicarboxylate (**2b**)

From **1b** (0.97 g, 5 mmol). Colorless prisms; *m.p*. 74–75 °C (Et_2O/petroleum ether). – IR: ν/cm^{-1} = 2180 (C≡N), 1740 (C=O). – ^{1}H NMR (400 MHz): δ/ppm = 1.60–1.67 [m, 6H, $3CH_2$ (piperidine)], 2.99 (s, 2H, 3-H), 3.24 (s, 2H, 6-H), 3.37–3.43 [m, 4H, $2CH_2$ (piperidine)], 3.80 (s, 6H, $2OCH_3$). – MS (FAB) *m/z* (%): 325 (100) [M$^+$ + H].

$C_{15}H_{20}N_2O_4S$	Calcd.: C 55.54	H 6.21	N 8.64
(324.4)	Found: C 55.56	H 6.29	N 8.56.

Dimethyl 4-Cyano-3,6-dihydro-5-pyrrolidino-2H-thiopyran-2,2-dicarboxylate (**2c**)

From **1c** (0.90 g, 5 mmol). Colorless columns; *m.p*. 134–135 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2 180 (C≡N), 1 740 (C=O). – ^{1}H NMR (400 MHz): δ/ppm = 1.90–1.96 [m, 4H, $2CH_2$ (pyrrolidine)], 2.99 (s, 2H, 3-H), 3.30 (s, 2H, 6-H), 3.58–3.64 [m, 4H, $2CH_2$ (pyrrolidine)], 3.81(s, 6H, $2OCH_3$). – MS (FAB) *m/z* (%): 311 (100) [M$^+$ + H].

$C_{14}H_{18}N_2O_4S$	Calcd.: C 54.18	H 5.85	N 9.03
(310.4)	Found: C 54.25	H 5.88	N 9.04.

Methyl 2-Acetyl-4-cyano-3,6-dihydro-5-morpholino-2H-thiopyran-2-carboxylate (**2d**)

From **1a** (0.98 g, 5 mmol). Colorless scales; *m.p*. 123–124 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2 200 (C≡N), 1 730, 1 705 (C=O). – ^{1}H NMR (400 MHz): δ/ppm = 2.30 (s, 3H, CH_3), 2.92 (AB quartet, *J* = 15.6, 2H, 3-H), 3.18 (AB quartet, *J* = 15.6, 2H, 6-H), 3.38–3.42 [m, 4H, $2CH_2$ (morpholine)], 3.70–3.76 [m, 4H, $2CH_2$ (morpholine)], 3.83 (s, 3H, OCH_3). – MS (FAB) *m/z* (%): 311 (100) [M$^+$ + H].

$C_{14}H_{18}N_2O_4S$	Calcd.: C 54.18	H 5.85	N 9.03
(310.4)	Found: C 54.35	H 5.66	N 9.07.

Methyl 2-Acetyl-4-cyano-3,6-dihydro-5-piperidino-2H-thiopyran-2-carboxylate (**2e**)

From **1b** (0.97 g, 5 mmol). Colorless needles; *m.p*. 66–68 °C (Et_2O/petroleum ether). – IR: ν/cm^{-1} = 2 200 (C≡N), 1 740, 1 710 (C=O). – ^{1}H NMR (400 MHz): δ/ppm = 1.60–1.65 [m, 6H, $3CH_2$ (piperidine)], 2.30 (s, 3H, CH_3), 2.92 (AB quartet, *J* = 15.6, 2H, 3-H), 3.19 (AB quartet, *J* = 15.6, 2H, 6-H), 3.35–3.40 [m, 4H, $2CH_2$ (piperidine)], 3.81 (s, 3H, OCH_3). – MS (FAB) *m/z* (%): 309 (100) [M$^+$ + H].

$C_{15}H_{20}N_2O_3S$	Calcd.: C 58.42	H 6.54	N 9.08
(308.4)	Found: C 58.44	H 6.40	N 9.16.

Methyl 2-Acetyl-4-cyano-3,6-dihydro-5-pyrrolidino-2H-thiopyran-2-carboxylate (**2f**)

From **1c** (0.90 g, 5 mmol). Colorless prisms; *m.p*. 96–97 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2 180 (C≡N), 1 735, 1 700 (C=O). – ^{1}H NMR (400 MHz): δ/ppm = 1.90–1.96 [m, 4H, $2CH_2$ (pyrrolidine)], 2.30 (s, 3H, CH_3), 2.92 (AB quartet, *J* = 15.6, 2H, 3-H), 3.27 (AB quartet, *J* = 15.6, 2H, 6-H), 3.56–3.65 [m, 4H, $2CH_2$(pyrrolidine)], 3.82 (s, 3H, OCH_3). – MS (FAB) *m/z* (%): 295 (100) [M$^+$ + H].

$C_{14}H_{18}N_2O_3S$	Calcd.: C 57.12	H 6.16	N 9.52
(294.4)	Found: C 57.17	H 6.30	N 9.49.

Ethyl 2-Benzoyl-4-cyano-3,6-dihydro-5-morpholino-2H-thiopyran-2-carboxylate (**2g**)

From **1a** (0.98 g, 5 mmol). Pale yellow prisms; *m.p*. 115–116 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2 200 (C≡N), 1 740, 1 680 (C=O). – ^{1}H NMR (400 MHz): δ/ppm = 1.09 (t, *J* = 7.3, 3H, $OCH_2C\underline{H}_3$), 3.07 (AB quartet, *J* = 15.6, 2H, 3-H), 3.25 (AB quartet, *J* = 15.6, 2H, 6-H), 3.40–3.46 [m, 4H, $2CH_2$ (morpholine)], 3.72–3.77 [m, 4H, $2CH_2$ (morpholine)], 4.10–4.22 (m, 2H, $OC\underline{H}_2CH_3$), 7.40–7.45 (m, 2H, aryl), 7.52–7.57 (m, 1H, aryl), 7.85–7.88 (m, 2H, aryl). – MS (FAB) *m/z* (%): 387 (37)[M$^+$ + H].

$C_{20}H_{22}N_2O_4S$	Calcd.: C 62.16	H 5.74	N 7.25
(386.5)	Found: C 62.13	H 5.62	N 7.26.

Ethyl 2-Benzoyl-4-cyano-3,6-dihydro-5-piperidino-2H-thiopyran-2-carboxylate (**2h**)

From **1b** (0.97 g, 5 mmol). Colorless columns; *m.p*. 92–93 °C (Et_2O/petroleum ether). – IR: ν/cm^{-1} = 2 180 (C≡N), 1 745, 1 680 (C=O). – ^{1}H NMR (400 MHz): δ/ppm = 1.09 (t, *J* = 7.3, 3H, $OCH_2C\underline{H}_3$), 1.60–1.66 [m, 6H, $3CH_2$ (piperidine)], 3.08 (AB quartet, *J* = 15.6, 2H, 3-H), 3.27 (AB quartet, *J* = 15.6, 2H, 6-H), 3.35–3.45 [m, 4H, $2CH_2$ (piperidine)], 4.10–4.25 (m, 2H, $OC\underline{H}_2CH_3$), 7.40–7.44 (m, 2H, aryl), 7.52–7.56 (m, 1H, aryl), 7.84–7.87 (m, 2H, aryl). – MS (FAB) *m/z* (%): 385 (68) [M$^+$ + H].

$C_{21}H_{24}N_2O_3S$	Calcd.: C 65.60	H 6.29	N 7.29
(384.5)	Found: C 65.52	H 6.44	N 7.29.

Ethyl 2-Benzoyl-4-cyano-3,6-dihydro-5-pyrrolidino-2H-thiopyran-2-carboxylate (**2i**)

From **1c** (0.90 g, 5 mmol). Colorless plates; *m.p*. 146–148 °C (acetone/petroleum ether). – IR: ν/cm^{-1} = 2 180 (C≡N), 1 745, 1 680 (C=O). – ^{1}H NMR (400 MHz): δ/ppm = 1.09 (t, *J* = 7.3, 3H, $OCH_2C\underline{H}_3$), 1.92–1.96 [m, 4H, $2CH_2$ (pyrrolidine)], 3.08 (AB quartet, *J* = 15.2, 2H, 3-H), 3.32 (AB quartet, *J* = 14.7, 2H, 6-H), 3.56–3.68 [m, 4H, $2CH_2$ (pyrrolidine)], 4.10–4.23 (m, 2H, $OC\underline{H}_2CH_3$), 7.40–7.44 (m, 2H, aryl), 7.51–7.56 (m, 1H, aryl), 7.84–7.87 (m, 2H, aryl). – MS (FAB) *m/z* (%): 371 (77) [M$^+$ + H].

$C_{20}H_{22}N_2O_3S$	Calcd.: C 64.84	H 5.99	N 7.56
(370.5)	Found: C 64.78	H 5.75	N 7.62.

Methyl trans-4-Cyanotetrahydro-5-oxo-2H-thiopyran-2-carboxylate (**3**)

Procedure A: A mixture of **2a** (1.09 g, 3.3 mmol) and NaI (0.75 g, 5 mmol) in DMF (3 ml) was stirred at 130 °C for 1h. The DMF was removed *in vacuo* and 5%HCl (10 ml) was added to the residue. The resulting mixture was stirred at room temp. for 5 min. The mixture was extracted with CH_2Cl_2. The extract was washed with H_2O and dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent to give **3** (0.33 g, 50%).

Procedure B: A mixture of **2d** (1.03 g, 3.3 mmol) and sodium methoxide (0.27 g, 5 mmol) in MeOH (10 ml) was refluxed for 7h. The solvent was removed under reduced pressure and 5% HCl (15 ml) was added to the residue. The resulting mixture was stirred for 5min. The mixture was extracted with CH_2Cl_2. The extract was washed with H_2O and dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel with CH_2Cl_2 as eluent to afford **3** (0.07 g, 11%).

Procedure C: From **2g** (1.29 g, 3.3 mmol) as described for *Procedure B.* Yield **3** (0.05 g, 8%).
Colorless prisms; *m.p.* 89–90 °C (Et_2O). – IR: ν/cm^{-1} = 2 250 (C≡N), 1 720, 1 715 (C=O). – ^{1}H NMR (500 MHz): δ/ppm = 2.84 (ddd, *J* = 3.5/12.5/13.5, 1H, 3-H), 3.07 (ddd, *J* = 3.5/5.5/13.5, 1H, 3-H), 3.14 (d, *J* = 13.5, 1H, 6-H), 3.61 (t, *J* = 3.5, 1H, 2-H), 3.77 (d, *J* = 13.5, 1H, 6-H), 3.86 (s, 3H, OCH_3), 4.53 (dd, *J* = 5.5/12.5, 1H, 4-H). – MS (FAB) *m/z* (%): 200 (100) [M^+ + H].

$C_8H_9NO_3S$	Calcd.: C 48.23	H 4.55	N 7.03
(199.2)	Found: C 48.31	H 4.45	N 7.12.

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Address for correspondence:
Dr. K. Yamagata
Faculty of Pharmaceutical Sciences
Fukuoka University
8-19-1 Nanakuma, Jonanku
Fukuoka 814-0180, Japan
Fax: Internat. code 81-092-863-0389